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The Julia-Kocienski Olefination

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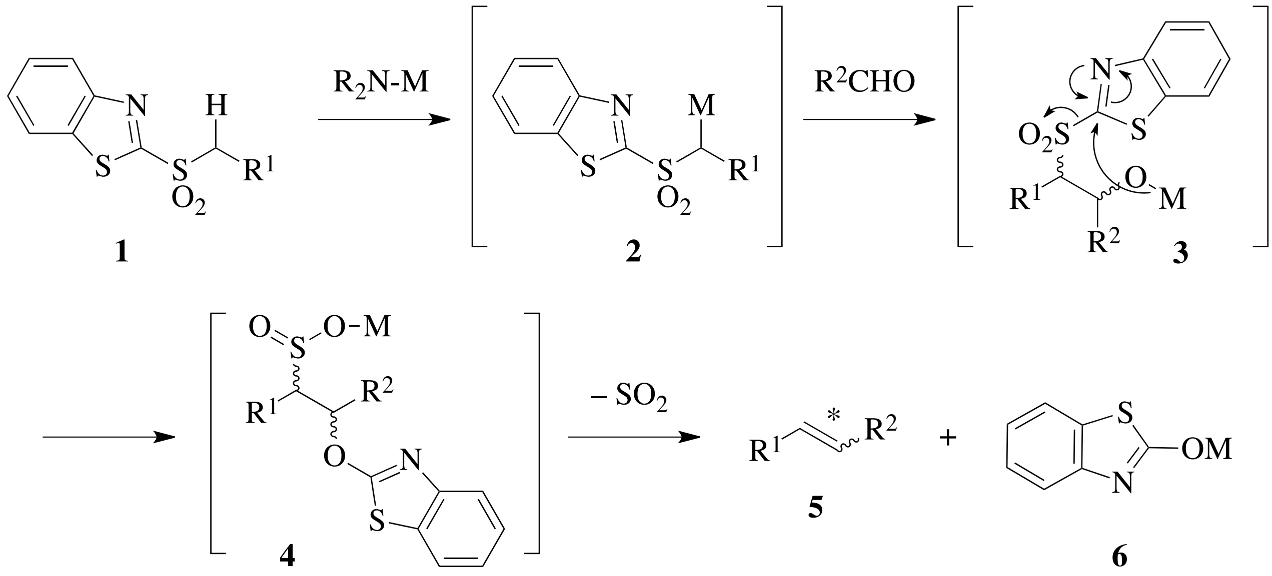
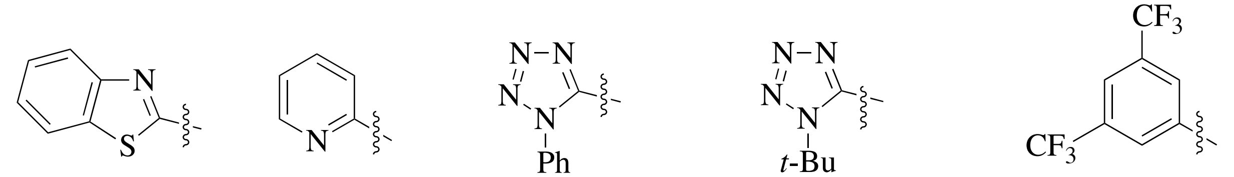
INTRODUCTION

The Julia-Kocienski olefination, also known as the modified Julia olefination, or the one-pot Julia olefination, is a connective synthesis of alkenes involving the reaction of an α-metalated aryl alkyl sulfone (sulfone anion) such as **2** with a carbonyl compound (Scheme 1).[1] The aryl group is chosen to allow for *ipso* substitution at the site associated with the sulfonyl moiety such that the initially generated addition adduct **3** may experience a spontaneous Smiles rearrangement (i.e., **3** to **4**).[2] Subsequent elimination of sulfur dioxide and an aryloxide anion from the Smiles rearrangement product **4** leads directly to the alkene. The reaction was first described using benzothiazol-2-yl (BT) sulfones (as illustrated in Scheme 1)[1] but it has since been extended to include a variety of alternate aromatic activating groups each with its own merits (Figure 1).[3-6] To avoid confusion, it is worth noting at the outset that the Julia-Kocienski olefination (discovered by S. A. Julia)[1] is distinct from the older Julia-Lythgoe olefination (discovered by M. Julia),[7] an indirect alkene synthesis that involves the addition of phenyl sulfone anions to carbonyl compounds followed by a separate reductive desulfonylation step (see Comparison with Other Methods).[8-12] Throughout this review an asterisk indicates the site of a newly introduced alkene.



Scheme 1



benzothiazol-2-yl (BT)	pyrid-2-yl (PYR)	1-phenyl-1*H*-tetrazol-5-yl (PT)	1-*tert*-butyl-1*H*-tetrazol-5-yl (TBT)	3,5-bis(trifluoromethyl) phenyl (BTFP)

Figure 1. Five aromatic activators (Act) commonly used in the Julia-Kocienski olefination.

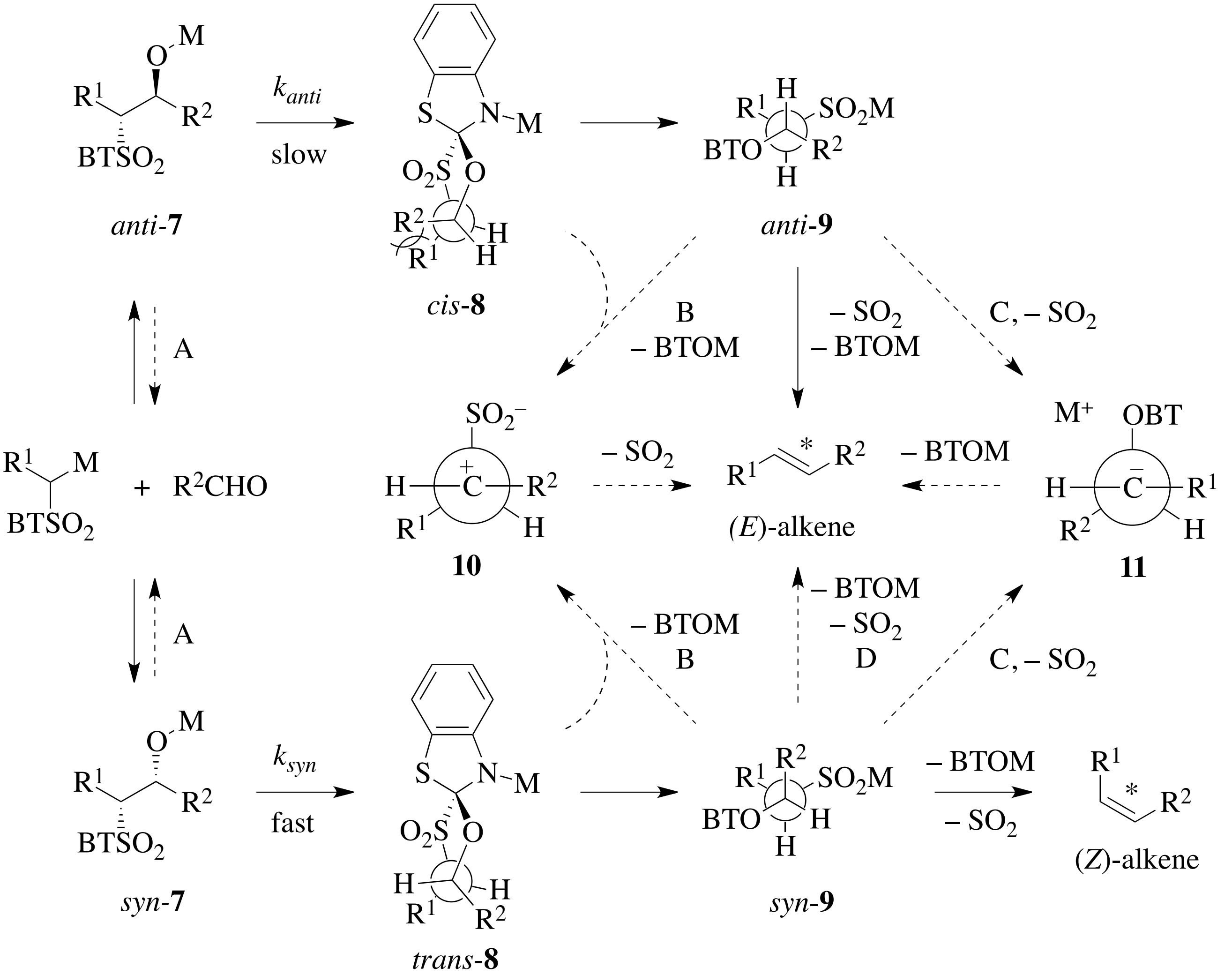
The outcome of the Julia-Kocienski olefination is sensitive to all variables and an informed selection of coupling partner types (sulfone and carbonyl component polarization, choice of bond disconnection in polyenes, type of activator) and reaction conditions (protocol for sulfone anion generation, type of base, base counter-cation, solvent, additives) is critical to obtain a high yielding alkene synthesis with the desired stereochemical bias. Providing that the coupling of interest is optimized and properly executed, the Julia-Kocienski olefination is capable of generating a wide variety of complex alkene targets, being especially well suited to the production of *trans*-1,2-disubstituted double bonds. The olefination process itself and the methods available for installing the activating sulfone moiety exhibit generally broad functional-group tolerance and consequently the Julia-Kocienski reaction has enjoyed widespread adoption as a reliable tool for the conjoinment of multifunctional sulfone and carbonyl compound coupling partners during the final stages of total synthesis efforts. This review focuses on how to achieve optimal results from the Julia-Kocienski olefination by a consideration of its theoretical and operational aspects, in what situations it is best applied, and when an alternative carbonyl olefination tactic is perhaps better suited. Notable variants of the process leading to non-alkene targets are also briefly surveyed. The Julia-Kocienski olefination has been previously reviewed and these accounts should be consulted for discourse on the historical development of the process.[2, 9, 11-14]

MECHANISM AND STEREOCHEMISTRY

The broader aspects of the mechanism for the Julia-Kocienski olefination are well understood; however, a rigorous framework to fully explain the influence of substituents and other parameters on the stereochemical outcome of the process is not yet available. Nonetheless, extensive experimental findings reveal substrate-dependent stereoselectivity traits, most of which can be rationalized on at least an empirical level.[3] A more complete understanding of the mechanistic origin of stereoselectivity in some special cases has been obtained by a combination of control experiments and computations.[13, 15-17]

Mechanism

The current mechanistic understanding of the Julia-Kocienski olefination is summarized below and illustrated for the synthesis of a 1,2-disubstituted alkene from a metalated BT-sulfone and an aldehyde (Scheme 2; solid arrows depict default pathway followed when R^1 and R^2 are non-conjugating substituents). Analogous pathways will be followed for alternative activators and for substrates leading to other classes of olefins. Addition of the metalated sulfone nucleophile to the carbonyl electrophile generates the expected pair of diastereomeric *syn*- and *anti-β*-alkoxy sulfone intermediates **7**; diastereoselectivity for this step is strongly dependent on reaction conditions and activator type. The initial addition adducts *syn*-**7** and *anti*-**7** are formed irreversibly if the sulfone anion is not stabilized (e.g., R^1 = alkyl) but are capable of equilibration via a retroaddition/re-addition mechanism (pathway A) if the sulfone anion is equipped with an anion-stabilizing group (e.g., R^1 = vinyl, aryl, carbonyl, etc.). Smiles rearrangement occurs by way of spirocyclic intermediates *trans*-**8** and *cis*-**8** (an example of which has been isolated)[18] which open to generate *syn*- and *anti-β*-aryloxy sulfinates **9**, respectively. Spirocyclization occurs more rapidly from *syn*-**7** than from *anti*-**7** because the spirocycle derived from the latter isomer (*cis*-**8**) exhibits higher strain.[15] This fact accounts for the observation of (*Z*)-selective Julia-Kocienski olefination in certain cases in which the initial addition reaction is reversible and the Curtin-Hammett principle operates (i.e., equilibration between *syn*-**7** and *anti*-**7** is faster than spirocyclization).



Scheme 2

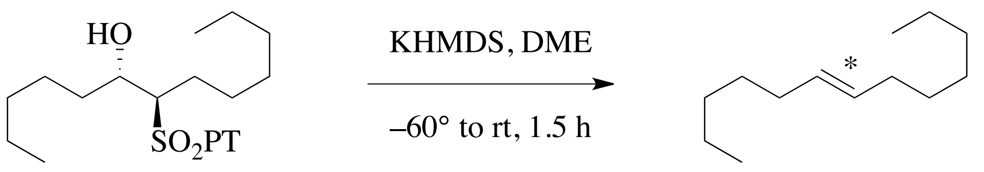
A variety of mechanistic pathways have been identified, or at least inferred by indirect evidence, for the production of alkenes from β-aryloxy sulfinates **9**. Loss of the aryloxide anion (BTOM) and sulfur dioxide from sulfinates **9** is wholly stereospecific only when R^1 and R^2 are non-conjugating substituents (e.g., simple alkyl); in such cases, elimination is a concerted E2-like process occurring from the illustrated conformers, wherein the β-C-OAct and α-C-SO_2^- bonds have an antiperiplanar alignment, and *anti*-**9** leads to the (*E*)-alkene whereas *syn*-**9** affords the (*Z*)-alkene. Unsaturation in either R^1 or R^2

potentially enables the non-stereospecific conversion of *β*-aryloxy sulfinate isomers **9** to alkene products: where R^2 is a cation-stabilizing substituent (aryl, vinyl, etc.) the suggestion of an E1-type elimination (from **9** or **8**) via zwitterion **10** was noted in Julia's original work (pathway B),[3] and when R^1 is a strongly electron-withdrawing group (e.g., carbonyl) an E1cB-type elimination via carbanion **11** (i.e., an enolate) is consistent with some relevant data (pathway C).[14, 16, 19] Conformational relaxation via rotation about the central C-C bond in intermediates **10** and **11** prior to respective electrofuge (SO_2) or nucleofuge (BTO^-) release leads preferentially to the (*E*)-alkene in both cases. More recent work casts doubt on the veracity of Julia's ad hoc zwitterion (**10**) hypothesis, at the very least for reactions involving R^2 = aryl, and a concerted *syn* E2-like elimination mechanism from *syn*-**9** (R^2 = aryl) via a conformation with synperiplanar *β*-C-OAct and *α*-C-SO_2^- bonds (not illustrated) is identified computationally and suggested by experiment (pathway D).[17] Related *syn*-elimination pathways from spirocycles **8** that bypass *β*-aryloxy sulfinate intermediates altogether and lead directly to alkene products have been located by computations for reactions involving BTFP sulfonyl acetates.[16] Results that support the various mechanistic pathways posited above and the relationship between substituent and other parameters on the stereochemical outcome of the Julia-Kocienski olefination are now considered.

Factors Influencing Stereoselectivity

Substituent effects play a major role in determining the stereochemical outcome of the Julia-Kocienski olefination and intrinsic selectivity trends can be accentuated or sometimes reversed by use of different activators. Selectivity is further strongly influenced in most cases by the base that forms the sulfone anion, the counter-cation, solvents, and any added cosolvents or cation complexing agents. The presence or absence of conjugation in each coupling partner has the most profound effect on stereoselectivity and reactions are usefully divided into four substrate pair classes according to this principle.[3] Examples within the same class share related stereochemical behaviors that can be rationalized within the mechanistic framework advanced above (Scheme 2). The four classes are: (I) reactions of sulfone anions that are not *β,γ*-unsaturated with carbonyl compounds that are not *α,β*-unsaturated, (II) reactions of sulfone anions that are *β,γ*-unsaturated with carbonyl compounds that are not *α,β*-unsaturated, (III) reactions of sulfone anions that are not *β,γ*-unsaturated with carbonyl compounds that are *α,β*-unsaturated, and (IV) reactions of sulfone anions that are *β,γ*-unsaturated with carbonyl compounds that are *α,β*-unsaturated. These broad reaction classes are now considered in turn within the context of 1,2-disubstituted alkene synthesis. Similar principles apply for tri- and tetrasubstituted alkene synthesis but these types of products cannot generally be obtained with high levels of stereoselectivity via the Julia-Kocienski olefination because steric interactions differentiating competing diastereomeric pathways are less energetically distinguished in higher-substituted cases (see Scope and Limitations).

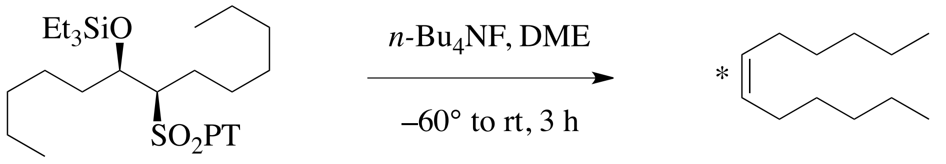
Stereoselectivity in Type I Reactions: Neither Component Conjugated. The stereochemical outcome of Type I reactions is determined by kinetic diastereoselectivity in the initial addition step because formation of β-alkoxy sulfone intermediates **7** is irreversible in such cases and their subsequent breakdown to alkene products is stereospecific. This fact was established experimentally for alkyl BT, PYR, and PT sulfones by studying the base-mediated elimination of alkyl-substituted stereodefined β-alkoxy sulfones.[15, 20] For example, treatment of *anti*-β-hydroxy sulfone **12** (generated from *trans*-7-tetradecene oxide by ring-opening with PTSH followed by oxidation of the resulting thioether) with KHMDS leads exclusively to (*E*)-7-tetradecene (Eq. 1). By contrast, in situ generation of the corresponding epimeric *syn*-β-alkoxy sulfone anion via desilylation of *syn*-β-silyloxy-PT-sulfone **13** with TBAF gives exclusively (*Z*)-7-tetradecene (Eq. 2).[20]



(Eq. 1)

12

(91%) (*E*)/(*Z*)* > 98:2

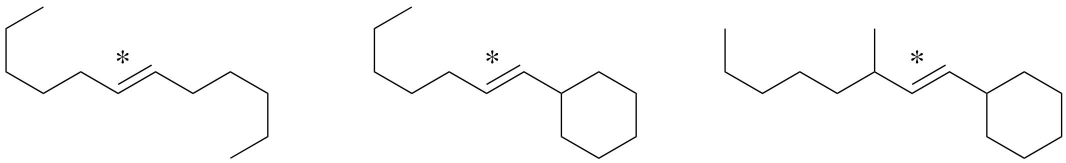


(Eq. 2)

13

(95%) (*E*)/(*Z*)* < 2:98

Type I reactions generally give poor stereoselectivity under the reaction conditions for olefination first described by Julia and coworkers (BT or PYR sulfones, LDA, THF, –78° to rt).[3] The inference of low diastereoselectivity in the sulfone anion addition step was confirmed in the case of lithiated alkyl PYR sulfones by isolation of β-hydroxy sulfones with dr ~ 50:50 directly from reactions with non-conjugated aldehydes.[15] Early efforts to apply the nascent Julia-Kocienski olefination to targetdirected syntheses revealed that variation in base counter-cation and solvent polarity markedly affects stereoselectivity.[21-23] Building on these findings, Kocienski and coworkers systematically investigated the role of base counter-cation, solvent polarity, and aromatic activator on the stereochemical outcome of simple Type I reactions.[4] Conditions that promote dissociation of the metal cation from the sulfone anion, e.g., K^+ counter-cation in a polar sovent, favor (*E*)-alkene products and the effect is pronounced for PT sulfones. As seen in Figure 2, an excellent level of *trans*-selectivity can be obtained from PT sulfones regardless of the degree of chain branching by using KHMDS as base in 1,2-dimethoxyethane (DME) solvent.[4] Other reaction conditions that likewise favor a 'naked' PT sulfone anion have the same effect, e.g., use of LiHMDS as base in DMF with an HMPA cosolvent,[24] or use of KHMDS base in THF with added 18-crown-6.[25]



Act = BT	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*
	Li	THF	60:40	Li	THF	66:34	Li	THF	72:28
	K	DME	75:25	K	DME	76:24	K	DME	36:64

Act = PT	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*
	Li	THF	75:25	Li	THF	69:31	Li	THF	53:47
	K	DME	94:6	K	DME	99:1	K	DME	99:1

Figure 2. Stereoselectivity of alkene formation via addition of R^1CHMSO_2Act to R^2CHO (–78° or –60° to rt); sulfone anions generated via premetallation with $(Me_3Si)_2NM$ bases; the group to the left of the double bond originated from sulfone (R^1).

A credible stereocontrol model to account for high *anti* diastereoselectivity, and ultimately (*E*)-selective olefination, in the addition of metalated sulfones to aldehydes under conditions favoring cation dissociation has been proposed.[14] An extension of the model to explain both high and low stereoselectivity scenarios is now elaborated. Sulfones do not stabilize adjacent negative charge density by 2p-3d π-bonding resonance but rather by a combination of inductive, polarization, and hyperconjugative effects.[26, 27] Solid-state and solution-phase studies of alkyl aryl sulfone metalates indicate the existence of species such as **14** or comparable dimers (Figure 3), wherein the metal cation is

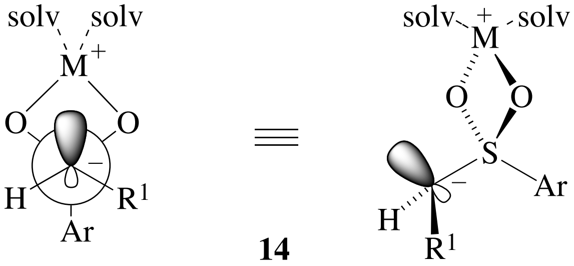


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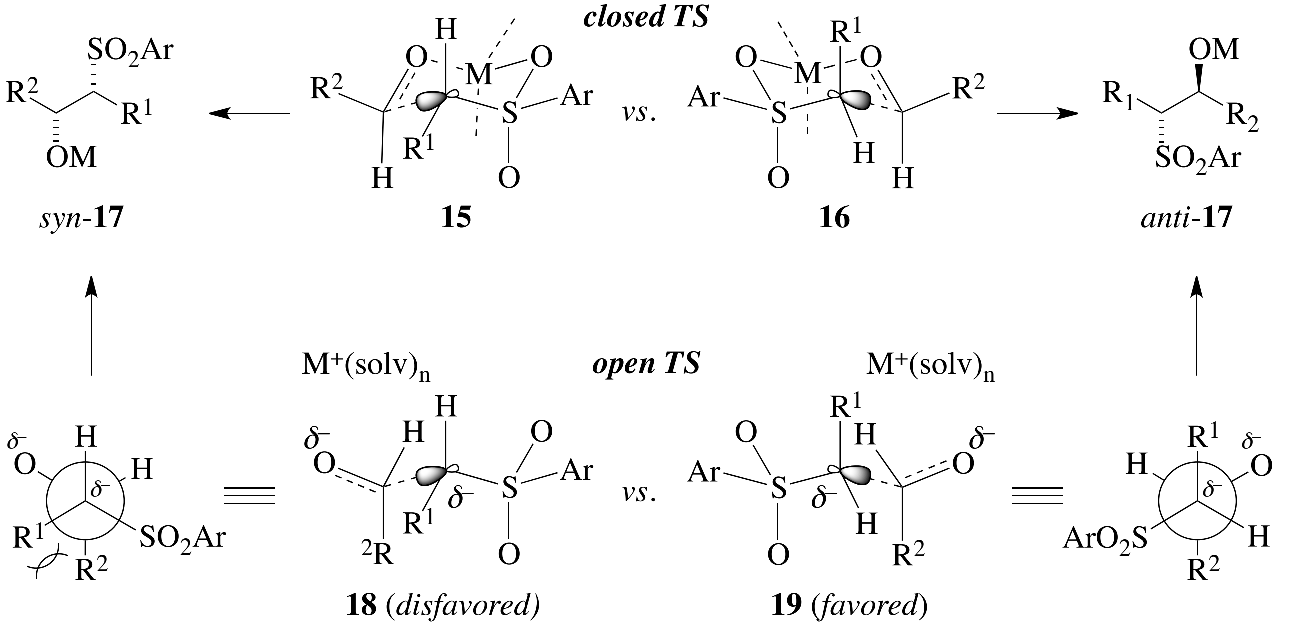
Figure 3. The structure of an alkyl aryl sulfone metalate.

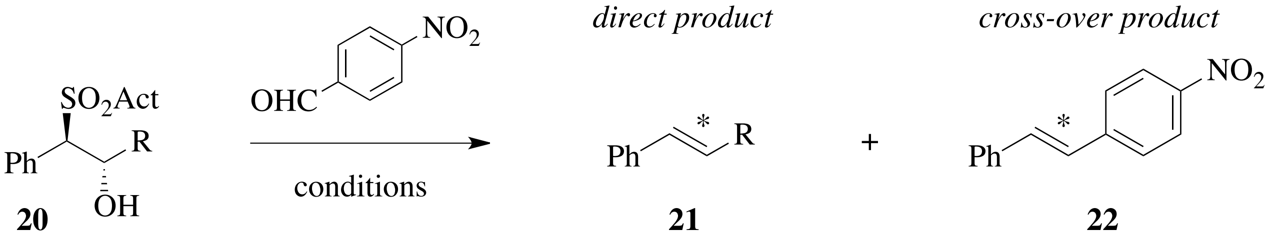
associated with the sulfone-oxygen atoms and a pyramidalized sp^3-hybridized carbanion is oriented to allow for $n_C \rightarrow \sigma^*_{S\text{-}Ar}$ orbital overlap.[28] For addition reactions wherein the cation is expected to be tightly bound to the metalated sulfone, e.g., M = Li and THF (or a less coordinating) solvent, closed chair-like transition states **15** and **16** are conceivable (Scheme 3).[29, 30] There is little to differentiate energetically between these two assemblies because significant 1,3-diaxial interactions do not exist to distinguish the axial disposition of R^1 in **16** from its equatorial placement in **15**. The observation of poor stereocontrol for Type I olefinations under Julia's original reaction conditions (LDA, THF, –78°) is understandable on this basis. By contrast, protocols that favor cation dissociation, e.g., M = K and DME solvent or M = Li and DMF-HMPA solvent, allow for open transition states such as **18** and **19**. The second transition state (**19**) is of lower energy because it lacks the gauche interaction between R^1 and R^2 that is present in the first transition state (**18**). Progression of the olefination process via the favored



Scheme 3

transition state **19** leads to the *anti*-*β*-alkoxy sulfone **17** and thence the (*E*)-alkene. Thus, a plausible hypothesis is at hand to account for the finding of high *trans*-selectivity under conditions involving 'naked' sulfone anions. Why PT sulfones offer intrinsically higher *anti*-selectivity than BT sulfones in this context has been the source of speculation,[14] but no definitive conclusion can yet be drawn. Taken as a whole, the mechanistic origin of diastereoselectivity in the addition of sulfone anions to carbonyl compounds warrants further study.

Stereoselectivity in Type II Reactions: Conjugated Sulfone Anion. The use of stabilized (e.g., R^1 = carbonyl) or semi-stabilized (e.g., R^1 = vinyl, alkynyl, aryl) conjugated sulfone anions enables the possibility of equilibration between intermediate *β*-alkoxy sulfones **7** via a retroaddition/re-addition mechanism (pathway A, Scheme 2). Conditions under which retroaddition operates in the case of metalated benzylic BT and PT sulfones have been identified experimentally in cross-over experiments involving 2-sulfonyl-2-phenylethanols **20** (Scheme 4).[13, 17, 20, 31] Treatment of *β*-hydroxy sulfones **20** with base in the presence of 4-nitrobenzaldehyde would generate solely the direct elimination product **21** if no fragmentation of the alkoxide anion occurs. However, if the intermediate alkoxide experiences retroaddition, a competition will exist between re-addition of the resulting sulfone anion $PhCHMSO_2Act$ to RCHO or 4-nitrobenzaldehyde. Observation of 'cross-over' product **22** therefore provides evidence



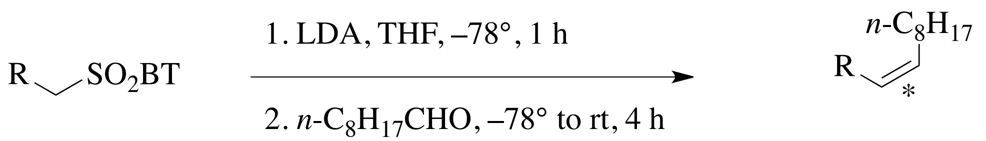
			Direct Product		Cross-Over Product	
R	Act	Conditions		$(E)/(Z)^*$		$(E)/(Z)^*$
Ph	BT	LDA, THF, –78° to rt	(40%)	≥ 98:02	(60%)	92:08
Ph	PT	LDA, THF, –78° to rt	(35%)	87:13	(60%)	69:31
H	BT	LiHMDS, DMF-HMPA (3:1), –60°	(>98%)[a]	na	(<2%)[a]	nd
H	BT	KHMDS, 18-crown-6, DMF, –55°	(34%)[a]	na	(66%)[a]	nd
H	BT	KHMDS, DMF-TDA (3:1), –60°	(22%)[a]	na	(72%)	nd
H	PT	KHMDS, DMF-TDA (3:1), –60°	(<2%)[a]	na	(93%)	nd

[a] Based on HPLC analysis.

Scheme 4

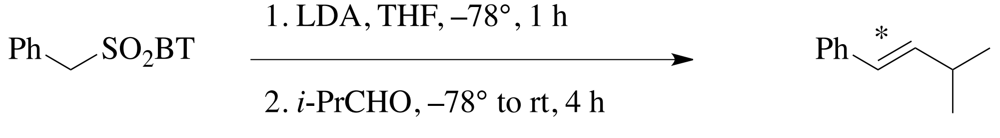
that some degree of retroaddition occurs. In the case of *anti-β*-hydroxy sulfones **20** (R = Ph), the Li-alkoxides of both BT and PT variants experience significant retroaddition between –78° to rt.[13, 20] In the case of the less substituted BT sulfone **20** (R = H), retroaddition from the derived Li-alkoxide does not occur to any measureable extent at –60° and the inducement of significant fragmentation requires generation of the K-alkoxide and the presence of K^+-selective complexing agents, 18-crown-6 or tris[2-(2-methoxyethoxy)ethyl]amine (TDA).[31] The K-alkoxide of the analogous PT sulfone **20** (R = H) exhibits a much higher propensity to fragment under the same reaction conditions.

In Type II reactions wherein a retroaddition mechanism operates, the ultimate stereochemical outcome of olefination is not a simple consequence of diastereoselectivity in the initial step. Furthermore, because *syn-β*-alkoxy sulfone intermediates **7** cyclize faster than their *anti* counterparts, the preferred formation of *cis*-alkenes is anticipated in cases where retroaddition is more facile than spirocyclization and where elimination from *β*-aryloxysulfinates **9** follows a stereospecific *anti* pathway (see Scheme 2). Indeed, potentially useful (*Z*)-selective olefination has been documented for many Type II reactions, and particularly for examples involving propargylic sulfones (Eq. 3); however, this outcome is by no means certain and the *cis* bias is generally found to be over-ridden when *α*-branched aldehydes are utilized (Eq. 4).[3] Less reactive aromatic activators such as PYR[3] and TBT[5] cause the energy barrier to Smiles rearrangement to be raised (by lower activator electrophilicity in the first case and by increased steric hindrance to *ipso* substitution in the second) and therefore promote (*Z*)-selectivity by enhancing equilibration between *syn-* and *anti-β*-alkoxy sulfone intermediates. As seen in Eq. 5, this kind of activator effect can be significant enough to result in a reversal in the sense of stereoselectivity.[5]



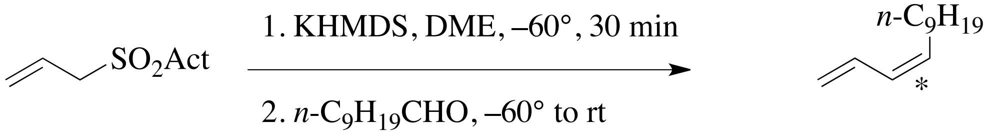
(Eq. 3)

R = Ph (81%) $(E)/(Z)^*$ = 37:63
R = CH_2=CH (66%) $(E)/(Z)^*$ = 40:60
R = n-$C_4H_9C{\equiv}C$ (26%) $(E)/(Z)^*$ < 1:99



(Eq. 4)

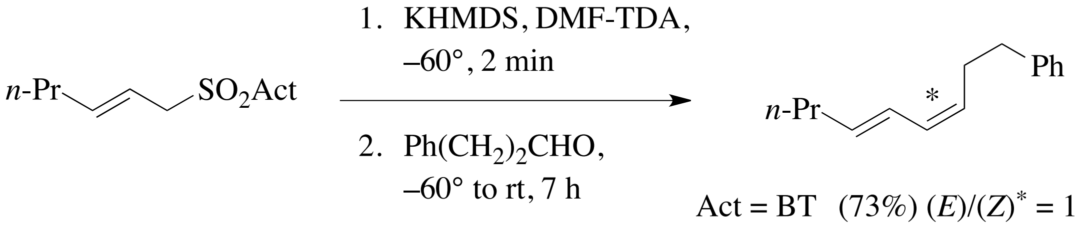
(51%) $(E)/(Z)^*$ = 90:10



(Eq. 5)

Act = PT (39%) $(E)/(Z)^* = 67:33$
Act = TBT (60%) $(E)/(Z)^* = 4:96$

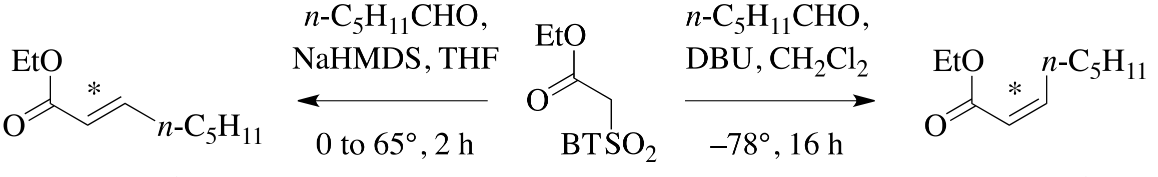
An alternative strategy to heighten (*Z*)-selectivity from semi-stabilized sulfone anions involves the use of the more common BT or PT activators under the reaction conditions noted above in Scheme 4 for optimal retroaddition (Eq. 6).[31] The presence of α-branching in the aldehyde again leads to (*E*)-olefins and it has been argued that this arises from the difficulty of generating *syn*-β-alkoxy sulfones via an open transition state (**18**, Scheme 3) where R^2 is bulky.[31] Steric effects are evidently not the only cause of *cis* selectivity being lost because non-branched α-oxygenated aldehydes also afford (*E*)-alkene products under these conditions.[31]



(Eq. 6)

Act = BT (73%) $(E)/(Z)^* = 17:83$
Act = PT (40%) $(E)/(Z)^* = 13:87$

Type II reactions involving highly stabilized sulfone anions (e.g., R^1 = carbonyl) follow the same trends highlighted above for semi-stabilized cases; thus, (*Z*)-α,β-unsaturated carbonyl compounds can be prepared from non-conjugated unbranched aldehydes but (*E*)-selectivity is observed in all other cases.[19] The sense of stereoselectivity is dependent on reaction temperature; any inherent (*Z*)-selectivity is accentuated at low temperature but (*E*)-selectivity is obtained upon heating (Eq. 7). [19] It has been suggested that at higher temperatures, loss of SO_2 and the aryloxide anion from β-aryloxy sulfinates **9** is non-concerted and follows an E1cB-type mechanism via **11** (pathway C, Scheme 2).[14] In this case (i.e.,

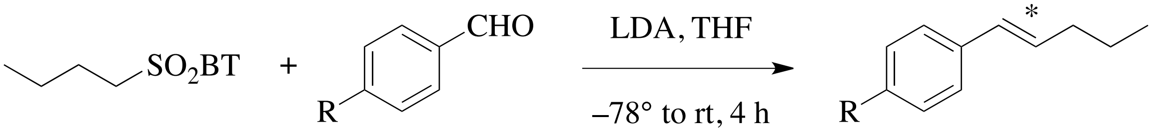


(Eq. 7)

(31%) $(E)/(Z)^* = 95:5$ (47%) $(E)/(Z)^* = 8:92$

R^1 = carbonyl or another strongly electron-withdrawing group), formation of the (*E*)-alkene would be anticipated if the stabilized carbanion (enolate) **11** eliminates ActO$^-$ from the lower-energy conformer. Synthesis of α,β-unsaturated carbonyl compounds and related alkenes, including fluorinated examples,[32] is discussed in more detail below (see Scope and Limitations).

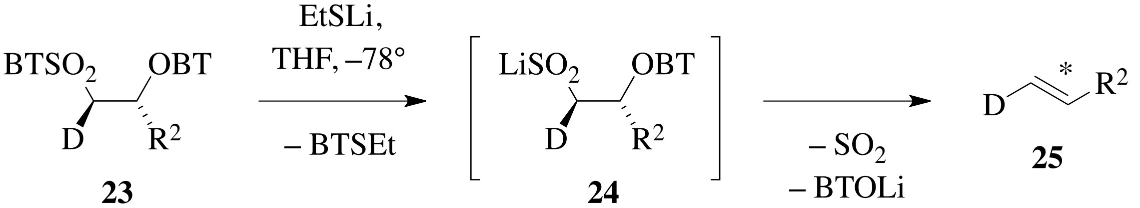
Stereoselectivity in Type III Reactions: Conjugated Carbonyl Compound. Julia-Kocienski olefinations involving non-conjugated primary BT or PT sulfone anions and α,β-unsaturated aldehydes (including aryl aldehydes) result in the preferential formation of (*E*)-configured 1,2-disubstituted alkenes in a vast majority of cases.[3] The level of stereoselectivity obtained is usually high, (*E*)/(*Z*) ratios well in excess of 4:1 are typical, and the stereochemical outcome is not particularly sensitive to solvent, cation, or additive effects, making these kinds of reactions reliable and easy to optimize. As for Type II reactions, kinetic diastereoselectivity in the initial addition step is not the determinant of alkene configuration;[15] however, in the case of Type III reactions this fact is attributed to the mechanistic complexity of the elimination stage from β-aryloxy sulfinate intermediates rather than issues of reversibility.[17] The observation of (*E*)-selectivity in Type III reactions and the correlation noted between product (*E*)/(*Z*) ratio and the electron richness of substituted benzaldehyde substrates (Eq. 8), prompted Julia and coworkers to propose the zwitterionic pathway hypothesis outlined above (pathway B, Scheme 2).[3] It was argued that zwitterionic intermediates **10** are potentially formed in cases where substituent R^2 is capable of stabilizing an adjacent carbocation; loss of SO_2 from the lower-energy conformer of **10** leads to the (*E*)-alkene regardless of the original *syn* or *anti* stereochemistry of the precursor β-aryloxy sulfinate **9** and substituents best able to stabilize the positive charge center are anticipated to promote the zwitterionic pathway and so accentuate stereoselectivity. The zwitterion hypothesis has predictive value; however, experimental proof is lacking and its validity is dubious given the poor nucleofugality of aryloxide anions such as BTO$^-$ and the expected high energy of zwitterions **10** in the comparatively non-polar ethereal solvent media within which olefination is conducted.



(Eq. 8)

R = Cl (51%) (*E*)/(*Z*)* = 77:23
R = H (68%) (*E*)/(*Z*)* = 94:6
R = OMe (95%) (*E*)/(*Z*)* = 99:1

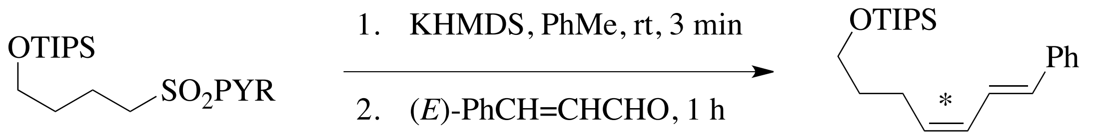
Recently performed calculations fail to locate zwitterions as credible intermediates in Type III (or Type IV) reactions and reveal stereoconvergence in the elimination of *β*-aryloxy sulfinates **9** (M = Li, R^1 = Me, R^2 = Ph) such that both possible diastereoisomers preferentially generate the (*E*)-alkene product but via distinct concerted mechanisms.[17] Thus, it was found that the lowest-energy pathway for loss of SO_2 and BTOLi from *anti*-**9** (M = Li, R^1 = Me, R^2 = Ph) is via antiperiplanar elimination but for *syn*-**9** (M = Li, R^1 = Me, R^2 = Ph) the synperiplanar elimination pathway is lower in energy (pathway D, Scheme 2). Lending credence to the major conclusions of this important computational study, generation of stereodefined isotopically labelled *β*-aryloxy sulfinates **24** from sulfones **23** leads predominantly to the (*E*)-alkene products **25** predicted by a *syn* elimination pathway (Eq. 9).[17] Given that the (*E*)- and (*Z*)-alkene products **25** in this case differ only by isotopic substitution, these findings are incompatible with the zwitterionic pathway hypothesis which would afford alkenes **25** with (*E*)/(*Z*) ~ 50:50. Significantly, the dependence of the (*E*)/(*Z*) ratio on the aryl moiety mirrors the trend found previously for Type III Julia-Kocienski olefinations involving aryl aldehydes (c.f., Eq. 8), indicating that electron-releasing R^2 substituents stabilize the transition state of the synperiplanar elimination pathway (which is precluded for *anti*-*β*-aryloxy sulfinates **7** with non-trivial substituents because of an eclipsing interaction between R^1 and R^2). It awaits to be seen whether or not stereoconvergence is also the cause of (*E*)-selectivity in Type III olefinations involving non-aromatic *α,β*-unsaturated aldehydes.



(Eq. 9)

R^2 = 4-ClC$_6$H$_4$ (89%) (*E*)/(*Z*)* = 81:19
R^2 = Ph (92%) (*E*)/(*Z*)* = 90:10
R^2 = 4-MeOC$_6$H$_4$ (87%) (*E*)/(*Z*)* = 94:6

Although most Type III reactions are (*E*)-selective, some exceptions are known. For example, in a limited focus study, it was found that the potassium metalate of a non-conjugated PYR sulfone reacts with (*E*)-configured *α,β*-unsaturated aldehydes to give the (*E,Z*)-diene products (Eq. 10).[33, 34] The mechanistic origin of selectivity for this reaction and its potential generality for the synthesis of conjugated (*Z*)-configured alkenes are unknown.



(Eq. 10)

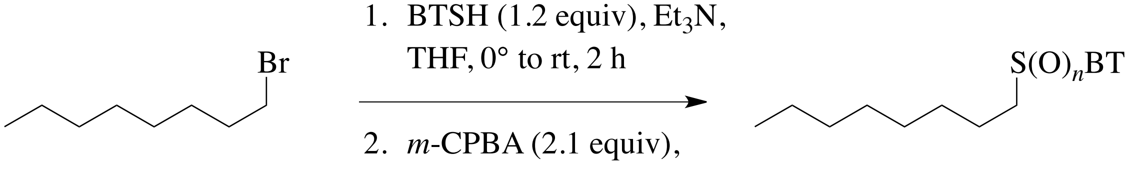
(70%) $(E)/(Z)^*$ = 8:92

Stereoselectivity in Type IV Reactions: Both Components Conjugated. For scenarios in which both R^1 and R^2 are conjugating substituents, all of the mechanistic possibilities discussed above for Type II and Type III reactions come into play. Prediction of the stereochemical outcome of Type IV olefination reactions is therefore fraught with difficulty unless one has knowledge of the behavior of closely related examples. Some specific examples are discussed below.

SCOPE AND LIMITATIONS

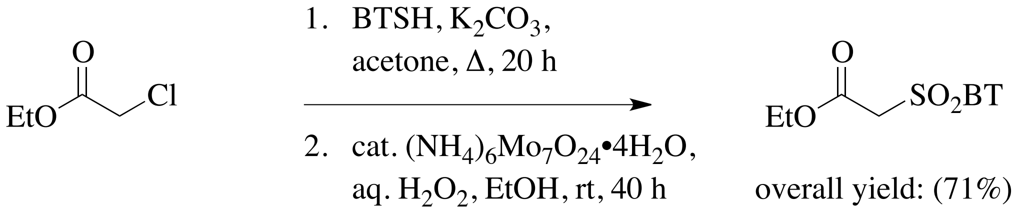
Methods for Introducing Sulfone Activators

Via Oxidation of Intermediate Thioethers. An attractive feature of the Julia-Kocienski olefination is the ease with which the activating sulfone moiety can be introduced into a fragment of interest. Sulfones are generally prepared via oxidation of the corresponding thioethers which are, in turn, typically produced by alkylation of the appropriate thiol ActSH (Act = BT, PT, PYR etc.) via an S_N2 substitution. It is worth noting from the standpoint of operational convenience that the heterocyclic thiols most commonly employed as starting materials are odorless solids. For simple R-groups (R = primary or secondary alkyl), thioether formation is most economically achieved by direct alkylation of the thiol by an alkyl halide or alkyl sulfonate ester in the presence of a base (e.g., step 1, Eqs. 11-13).[19, 33-35]

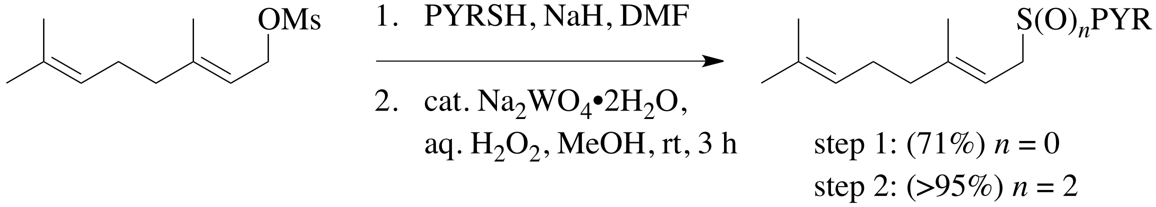


(Eq. 11)

step 1: (95%) $n = 0$
step 2: (90%) $n = 2$

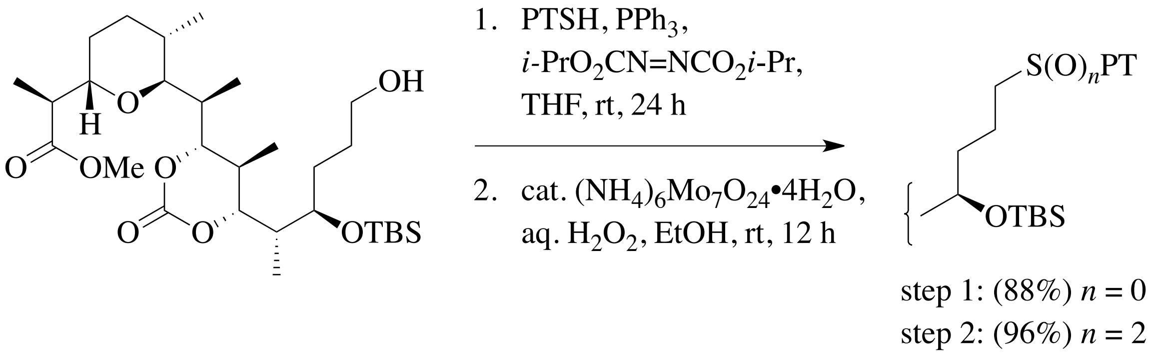


(Eq. 12)

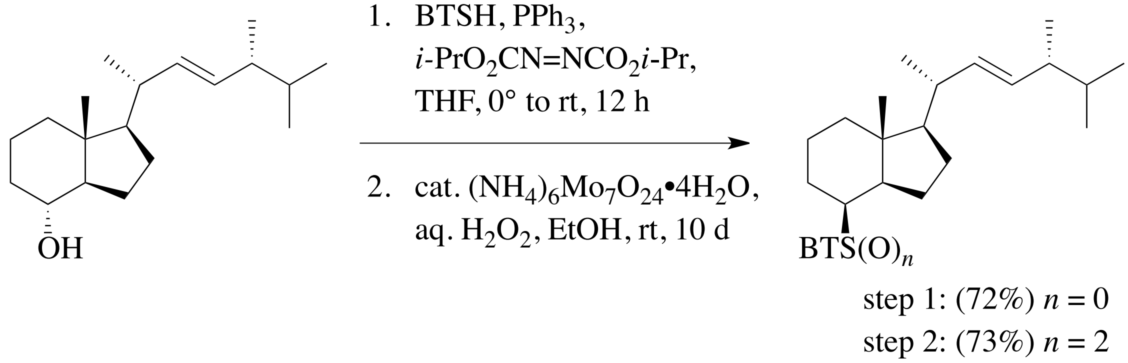


(Eq. 13)

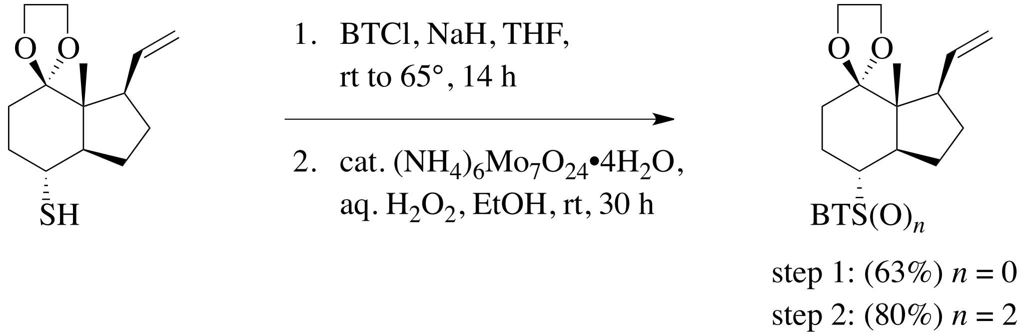
For more complex R-groups for which preparation of the alkyl halide or sulfonate would necessitate unwelcome additional operations, thioethers are conveniently produced from alcohol precursors and ActSH by the Mitsunobu reaction.[36] The Mitsunobu method is compatible with a wide range of aprotic functional groups (including common protecting groups) and it has been successfully applied to the synthesis of many late-stage polyfunctional intermediates en route to natural product targets (Eq. 14).[37] As expected, thioetherification of stereogenic secondary alcohols proceeds with inversion of configuration (Eq. 15).[38] An alternative and less-explored approach to thioethers en route to Julia-Kocienski reagents involves S_NAr reaction of a substrate thiol with an ActX type species (Eq. 16).[39]



(Eq. 14)



(Eq. 15)



(Eq. 16)

A wide variety of oxidants are capable of converting thioethers into the corresponding sulfones (e.g., *m*-CPBA, Oxone, transition-metal oxo complexes etc.); however, before implementing a particular method one must consider any relevant chemoselectivity issues. For example, peroxyacid reagents (e.g., *m*-CPBA) may result in competitive alkene epoxidation during the attempted conversion of an alkenyl thioether into a sulfone. Protocols based on the use of transition-metal oxo complexes are available that achieve chemoselective oxidation at sulfur while minimizing unwanted transformation at other sites. An ammonium molydate hydrate catalyst [$(NH_4)_6Mo_7O_{24}$•$4H_2O$] in the presence of 30 wt.% aqueous hydrogen peroxide as terminal oxidant has enjoyed widespread use for the synthesis of sulfones for the Julia-Kocienski olefination (e.g., step 2, Eqs. 14-16).[37-39] Catalysis of thioether oxidation by sodium tungstate hydrate is an alternative and has been reported to be superior to the use of Mo(VI) catalysts for sulfone production from particularly sensitive substrates (Eq. 13).[33, 34]

Regardless of the oxidation procedure employed, it should be noted that the conversion of thioethers to sulfones is an indirect process that proceeds via intermediate sulfoxides. Production of the sulfoxide from the thioether is rapid and further oxidation of the sulfoxide to the sulfone is considerably slower. Monitoring the extent of oxidation by TLC analysis is recommended: it is generally found that the sulfoxide is more polar than the thioether and that the sulfone has a polarity of intermediate range between that of the thioether and the sulfoxide (usually closer to the thioether than the sulfoxide). The NMR signature of the α-methylene unit in compounds ActS(O)$_n$CH$_2$CH$_2$R (where R is achiral) undergoes diagnostic changes as the oxidation state increases.[40] For the thioether (n = 0), a simple triplet (δ_H ~ 3.25 ppm) characteristic of a first order A_2X_2 spin system is observed. For the sulfoxide (n = 1), the stereogenic center at sulfur results in the emergence of an ABXY spin system with clearly differentiated chemical shift values for each individual diastereotopic α-H-atom. Further oxidation to the sulfone (n = 2) results in loss of stereogenicity at sulfur; however, the NMR signature of the α-methylene unit can be quite different in appearance to that seen in the symmetry-related thioether. Thus, in the case of the sulfone, the multiplet observed (δ_H ~ 3.50 ppm) is often not a simple triplet but instead a complex pattern characteristic of a second order AA'XX' spin system (Figure 4).[40, 41]

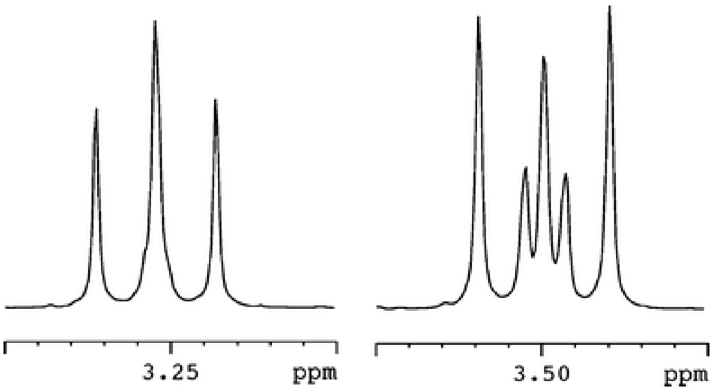
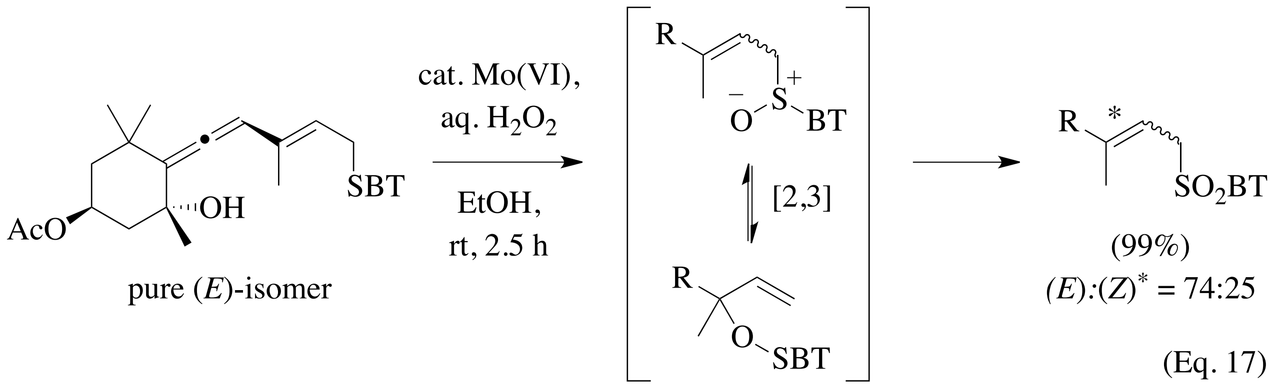
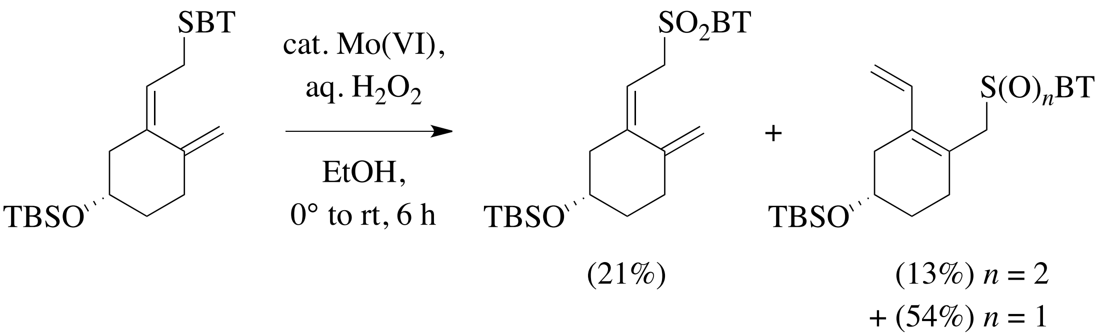


Figure 4. ^{1}H NMR spectral signature for the α-CH$_2$ group in BTSCH$_2$Et (left) and BTSO$_2$CH$_2$Et (right). Reproduced from ref. 40.

The synthesis of allylic sulfones via oxidation of allylic thioethers is potentially complicated by [2,3]-sigmatropic rearrangement[42]of the intermediate allylic sulfoxide. For example, synthesis of an allylic BT sulfone en route to the carotenoid peridinin from the corresponding isomerically pure (E)-configured thioether results in significant (E)/(Z)-isomerization as a consequence of [2,3]-sigmatropy of the intermediate sulfoxide (Eq. 17).[43] In a more dramatic example, a pair of consecutive [2,3]-sigmatropic rearrangements are responsible for relocation of the activating BT sulfone unit during an attempted synthesis of a vitamin D$_2$ A-ring precursor (Eq. 18).[38]

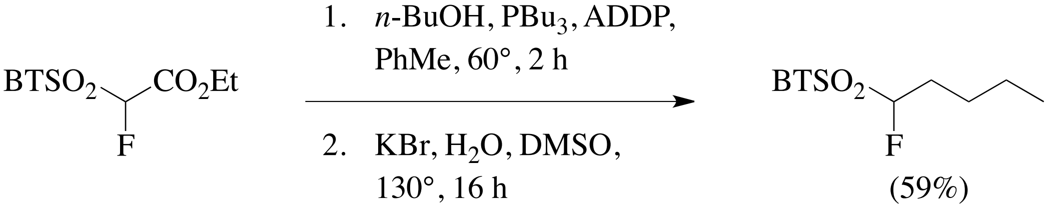


(Eq. 17)

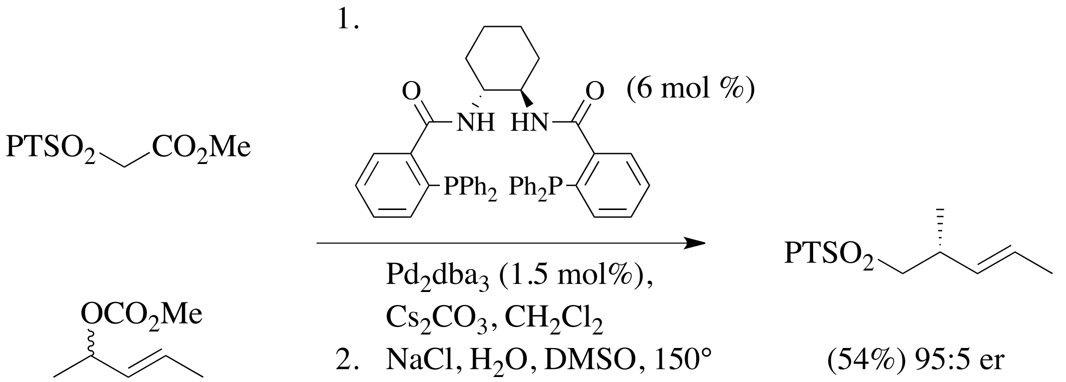


(Eq. 18)

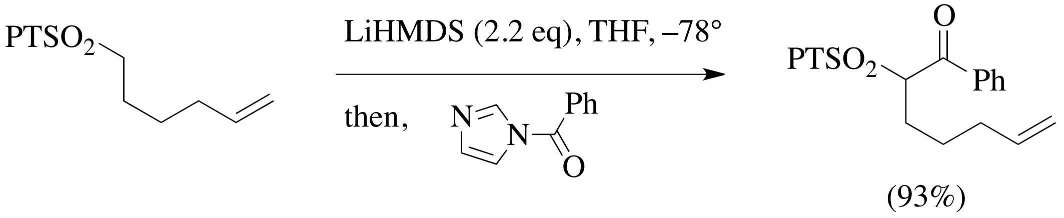
Via Sulfone Derivatization. Sulfones for Julia-Kocienski olefination are also potentially available by derivatization of simpler sulfone-containing precursors, providing that the chemistry involved does not induce any kind of unwanted sulfone degradation or premature olefination. *β*-Alkoxycarbonyl sulfones are versatile precursors in this regard since the *α*-position is readily derivatizatized (c.f., malonate chemistry) and the auxiliary ester group can be removed later if desired by Krapcho dealkoxycarbonylation[44] (Eqs. 19 and 20).[45, 46] The second example is notable in that sulfone synthesis is achieved in a catalytic enantioselective manner. Related asymmetric allylic alkylation of sulfonyl acetates using generic linear allylic carbonates and resulting in scalemic branched sulfone products has more recently been demonstrated with chiral Ir(I) catalysts.[47] In a reversal to the dealkoxycarbonylation strategy, it has proved possible to prepare *β*-alkoxycarbonyl sulfones and *β*-keto sulfones via a Claisen condensation type process involving acylation of sulfone metalates (Eq. 21).[48]



(Eq. 19)

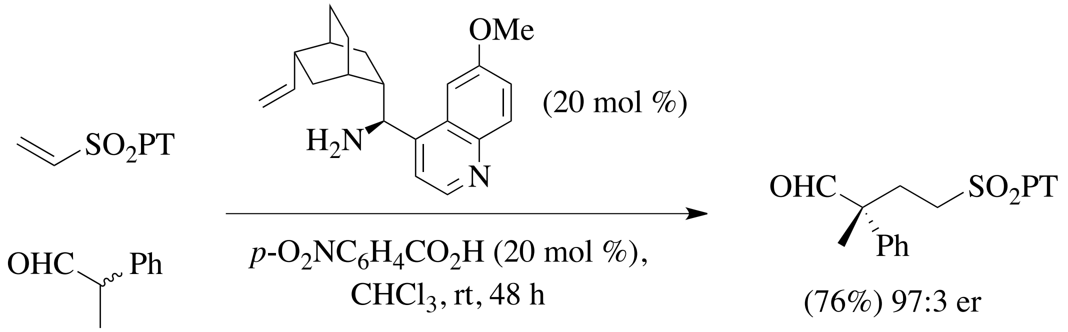


(Eq. 20)

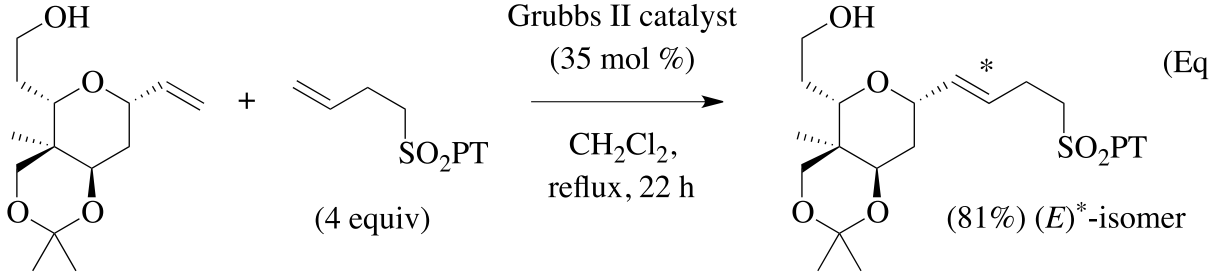


(Eq. 21)

Conjugate addition to vinyl sulfones has also been employed for the synthesis of Julia-Kocienski olefination reagents. For example, *β*-alkoxy[49] and *β*-amino[50] sulfones have been obtained by conjugate addition of heteroatom nucleophiles and enantioselective organocatalysis has been employed for the addition of carbon nucleophiles (Eq. 22).[51] Other types of reactions are likewise compatible with acceptor aryl sulfones and allow for efficient derivatization. Notable in this regard is the possibility of olefin cross-metathesis (Eq. 23).[52]



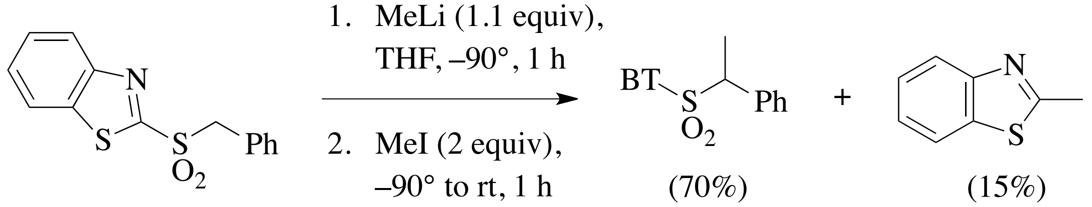
(Eq. 22)



(Eq. 23)

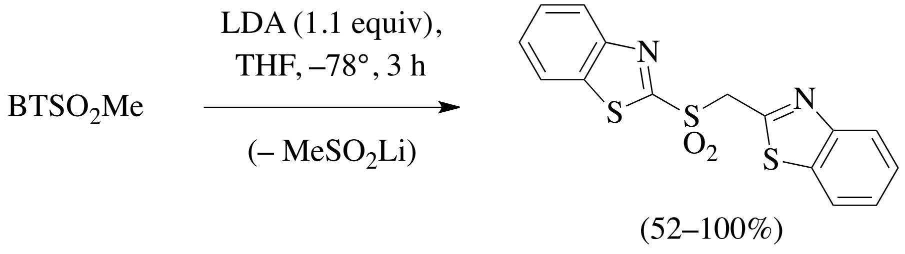
Generation of Sulfone Anions and Strategies to Avoid Self-Condensation

The electron-accepting nature of the aromatic activators found in Julia-Kocienski olefination reagents means that sulfone anion generation is best conducted with a non-nucleophilic base to avoid unwanted premature *ipso* substitution of the sulfinate nucleofuge. With the notable exception of PYR sulfones which can be cleanly metalated with *n*-BuLi,[3] the use of alkyllithiums for deprotonation is not recommended because some degree of nucleophilic attack will also occur (Eq. 24).[3] The pKa of the α-H-atoms in simple alkyl aryl sulfones is comparable to that found in esters (ca. 30 in DMSO);[53] accordingly, the hindered alkali-metal utility amides,[54] such as lithium diisopropylamide (LDA) and the commercially available hexamethyldisilazides (LiHMDS, NaHMDS, and KHMDS), are sufficiently strong to effect deprotonation and these types of reagents are used in a majority of Julia-Kocienski olefination reactions. Quantitative metalation within 15 minutes is generally observed at –78° in ethereal solvents. Curiously, metal-amide bases are ineffective for olefination reactions using BTFP sulfones and these compounds are instead treated with either KOH (in THF at room temperature) or a Schwesinger phosphazene base[55] such as P4-*t*-Bu (in THF at –78°).[56] When sulfone coupling partners are equipped with electron-withdrawing R^1 groups, weaker bases such as DBU or Cs_2CO_3 are sufficient to mediate successful olefination.



(Eq. 24)

The problem of premature *ipso* substitution is not necessarily confined to the metalation stage of the olefination process because the sulfone anions themselves are capable of pair-wise intermolecular self-condensation.[3, 5] The propensity for self-condensation is dependent on the net electrophilicity of the aromatic activator and the size of the substituent R^1 associated with the sulfone; BT and PT sulfones where R^1 is of low steric demand are particularly susceptible. For example, incubation of the lithiate of $BTSO_2Me$ in THF at –78° for a short time results in extensive self-condensation to afford the anticipated sulfone-linked bis(heterocyclic) adduct (Eq. 25).[3, 48] By contrast, PYR, TBT, and BTFP sulfone metalates are more resistant to self-condensation than comparable BT or PT derived species due to lower intrinsic electrophilicity of the aromatic activator (i.e., PYR and BTFP)[56] and/or steric protection of the electrophilic center (cf. TBT vs. PT).[5] Metalate stability in a series of benzylic sulfones has been quantified by exposure to varied basic reaction conditions followed by protonolysis and assessment of percent recovery of the non-decomposed starting material (Figure 5).[56] In addition to revealing the heightened stability of TBT and BTFP sulfone metalates, the data indicate that lithiated sulfones are more stable than other types of sulfone anion and that, despite earlier assertions to the contrary,[4] PT sulfone metalates are not necessarily any more stable that their BT congeners.[57]

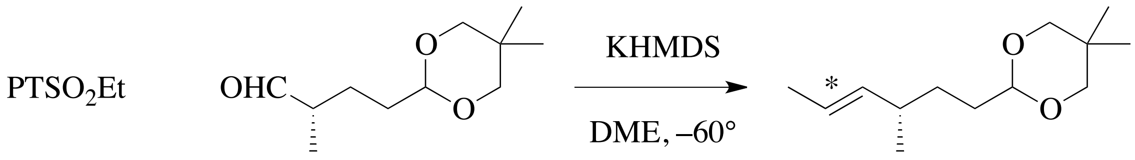


(Eq. 25)

Conditions	$\mathrm{Ph}\diagup\diagdown\mathrm{SO_2BT}$	$\mathrm{Ph}\diagup\diagdown\mathrm{SO_2PT}$	$\mathrm{Ph}\diagup\diagdown\mathrm{SO_2TBT}$	$\mathrm{Ph}\diagup\diagdown\mathrm{SO_2BTFP}$
LDA, THF, –78°, 24 h	(>95%)	(>95%)	(>95%)	(>95%)
KHMDS, DME, –60°, 24 h	(84%)	(50%)	(99%)	(75%)
P4-*t*-Bu, THF, –78°, 24 h	(73%)	(64%)	(78%)	(88%)
KOH, Bu_4NBr, THF, rt, 24 h	(5%)	(0%)	(0%)	(32%)

Figure 5. Percent recovery of benzylic sulfones following exposure to basic reaction conditions and then reprotonation with H_2O.

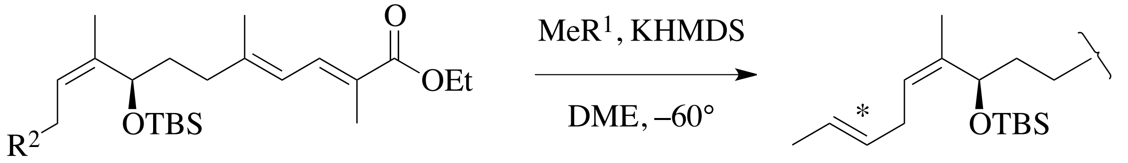
For sulfone metalates of low kinetic stability, the problem of self-condensation can often be ameliorated by adoption of a so-called 'Barbier' protocol wherein the base is added to a mixture of the sulfone and carbonyl compound rather than a more conventional 'premetalation' protocol involving addition of the latter only after complete sulfone deprotonation. Presumably, under Barbier conditions the sulfone anion is consumed by the carbonyl compound as soon as it is formed and thus self-condensation of the sulfone coupling partner is minimized. The possibility of an enolizable aldehyde or ketone being adversely affected by a Barbier protocol is a legitimate concern; however, a great many results attest to the effectiveness of the approach even in cases where chemical intuition suggests that it should fail. For example, the attempted synthesis of an (*E*)-configured 1,2-disubstituted alkene employing an enantioenriched α-substituted enolizable aldehyde and a sterically unencumbered PT sulfone gives an unacceptably low yield via a premetalation protocol because of sulfone metalate self-condensation (Eq. 26).[58] An otherwise identical experiment that involves premixing of the sulfone and aldehyde prior to the introduction of KHMDS results in a dramatically improved olefination yield without the intervention of detectable aldehyde racemization. In general, it is suggested that a premetalation protocol be evaluated initially and then Barbier conditions subsequently tested if a problem is encountered with the first approach. In some cases, a poor outcome due to sulfone metalate instability is best tackled by investigating alternative aryl activators and/or a strategic reversal in sulfone and carbonyl component selection (Eq. 27).[59]



(Eq. 26)

premetallation [sulfone + KHMDS, then aldehyde]: (15%) $(E)/(Z)^{*} > 90{:}10$

Barbier [sulfone + aldehyde, then KHMDS]: (93%) $(E)/(Z)^{*} = 93{:}07$



(Eq. 27)

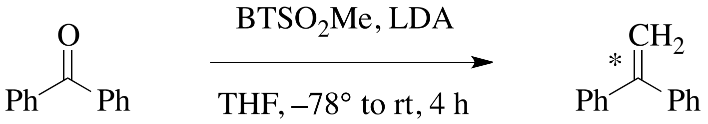
via Barbier $R^1 = CH_2SO_2PT$, $R^2 = CHO$: (26%) $(E)/(Z)^{*} =$ —

via premetallation $R^1 = CHO$, $R^2 = CH_2SO_2PT$: (90%) $(E)/(Z)^{*} = 86{:}14$

Optimal Targeting of Different Classes of Alkene

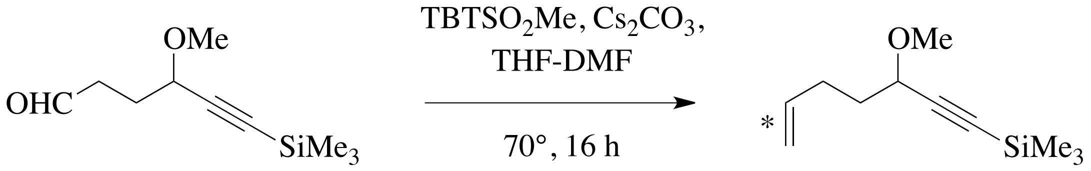
Monosubstituted and 1,1-Disubstituted Alkenes. The generation of these classes of alkenes by Julia-Kocienski olefination can be achieved via methylenation of an aldehyde or a ketone by a methyl sulfone reagent ($ActSO_2Me$) or alternatively by the use of formaldehyde as the carbonyl component. Both strategies have been successfully implemented although the former approach is far more common. Given the problem of self-condensation for sterically unencumbered sulfone metalates (see Eq. 25

above), the yield of methylenation is generally higher if the olefination reaction is performed under Barbier conditions (Eq. 28).[3] Although favorable outcomes have been described with BT and PT methyl sulfones, it has been discovered that the more robust TBT[60] and BTFP[56] methyl sulfones may offer superior results, particularly for the methylenation of hindered ketones. Methylenation with $TBTSO_2Me$ can be conveniently achieved by use of Cs_2CO_3 as base in a heated solvent blend of THF and DMF (Eq. 29). However, these reaction conditions result in partial racemization/epimerization of α-substituted carbonyl compounds and, in such cases, a more conventional protocol (NaHMDS, THF, –78°) should be employed (Eq. 30).[60] In one of the few examples of the Julia-Kocienski olefination using formaldehyde, it has been demonstrated that 4-nitrophenyl (NP) sulfonyl acetates engage with formalin in the presence of Cs_2CO_3 to afford methylidene esters directly via the usual mechanism (Eq. 31).[61]



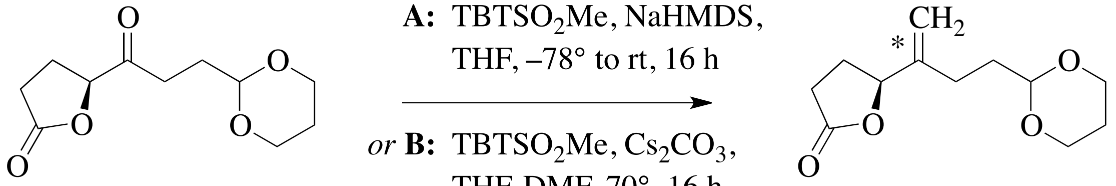
(Eq. 28)

via premetallation protocol: (11%)
via Barbier protocol: (55%)



(Eq. 29)

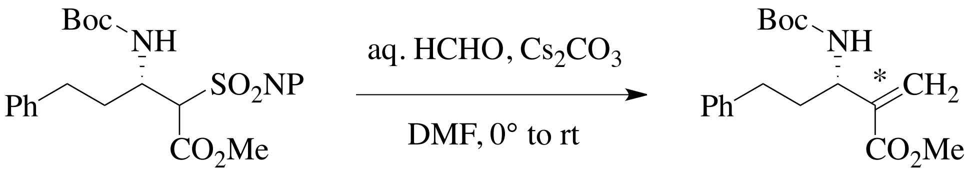
(96%)



(Eq. 30)

≥ 97:3 er

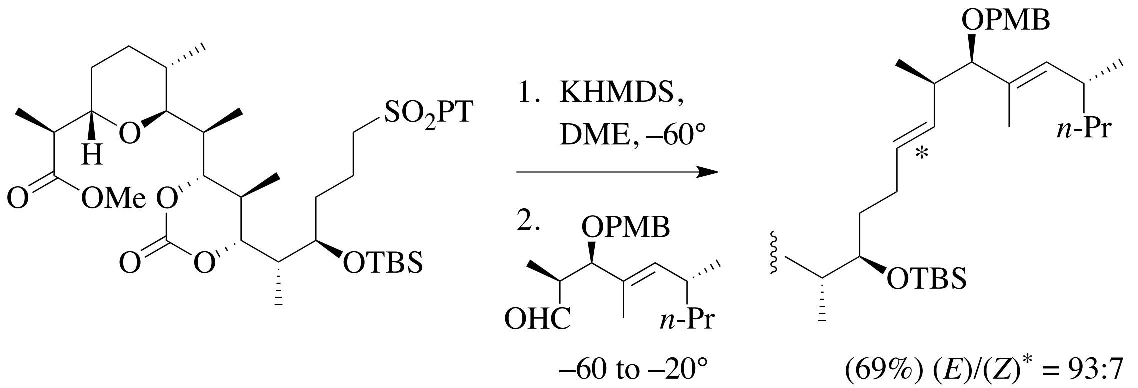
A: (59%) ≥ 97:3 er
B: (93%) 80.5:19.5 er



(85%) (Eq. 31)

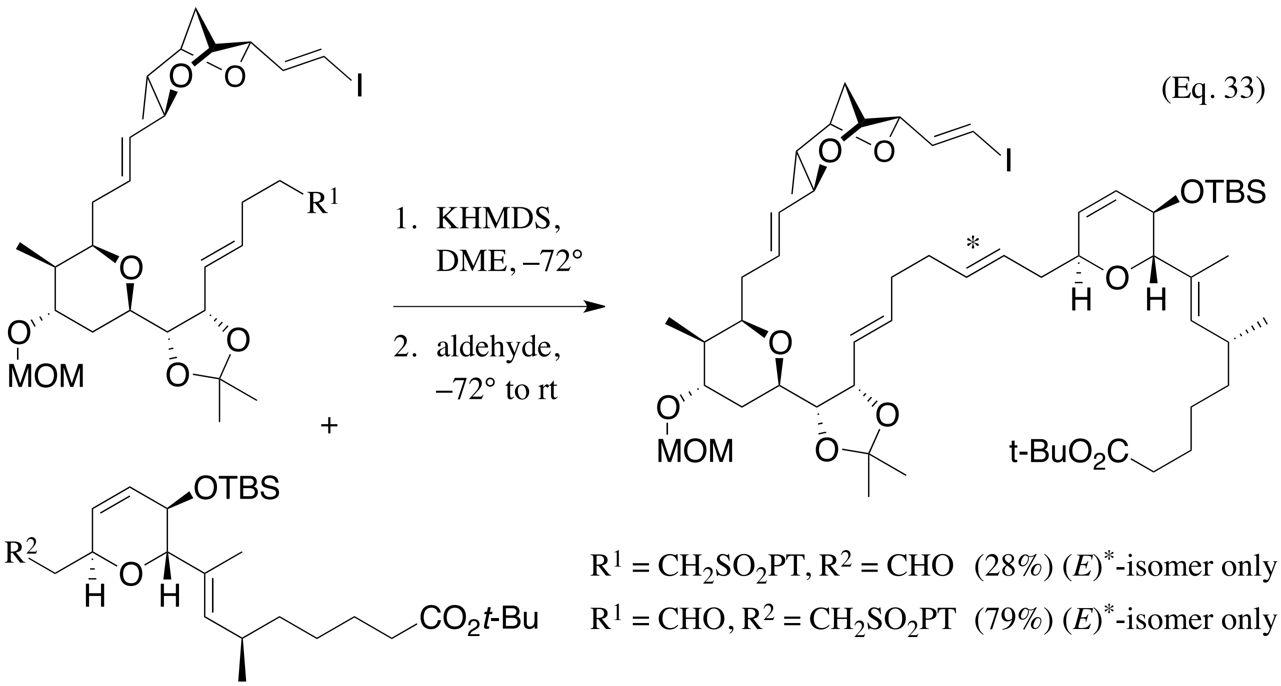
Non-Conjugated 1,2-Disubstituted Alkenes. The Julia-Kocienski olefination has enjoyed its most widespread application for the synthesis of non-conjugated 1,2-disubstituted alkenes. This popularity exists because the process is high yielding and that under appropriate reaction conditions, (*E*)-alkene isomers are formed preferentially with a synthetically useful level of stereoselectivity. The ability to prepare *trans*-alkenes in the absence of intrinsic steric or electronic biasing elements in either coupling partner stands in contrast to other common carbonyl olefination processes.[12] Significantly, the Julia-Kocienski olefination to form non-conjugated 1,2-disubstituted alkenes is stereocomplementary to the standard Wittig reaction which remains optimal for the synthesis of *cis* alkenes (see Comparison with Other Methods).

As detailed above (Factors Influencing Stereoselectivity), the use of PT sulfones under reaction conditions that favor a 'naked' sulfone anion species (i.e., polar/dipolar aprotic solvent, non-coordinating counter cations and/or cation complexation agents) generally leads to maximal (*E*)-selectivity for Type I reactions. Although not without exception, the use of BT sulfones is unlikely to result in the highest *trans* selectivity obtainable for this target class and certainly not if the original reaction conditions are employed (LDA, THF, –78°).[3] By contrast, Kocienski's reaction conditions as applied to PT sulfones (KHMDS, DME, –55°)[4] have proven effective in many different and complex scenarios (Eqs. 32 and 33).[37, 62] The urge to substitute the more common ether THF for the advocated solvent DME should be resisted when applying this protocol because stereoselectivity will be compromised to some degree; however, excellent (*E*)-selectivity can be restored if 18-crown-6 is added to the THF.[25] Replacing the KHMDS base with NaHMDS or LiHMDS in an ethereal solvent will also generally result in a lower (*E*)/(*Z*) ratio, although such a change is often accompanied by an increase in yield because potassiated sulfones are more prone to decomposition than their less reactive sodium or lithium counterparts.



(69%) $(E)/(Z)^* = 93:7$

(Eq. 32)

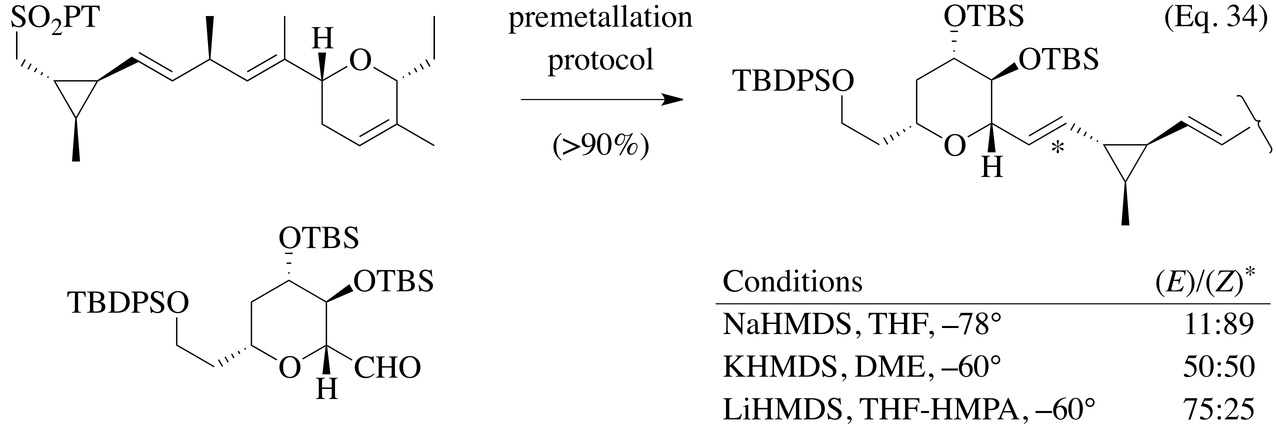


(Eq. 33)

$R^1 = CH_2SO_2PT$, R^2 = CHO (28%) (*E*)*-isomer only

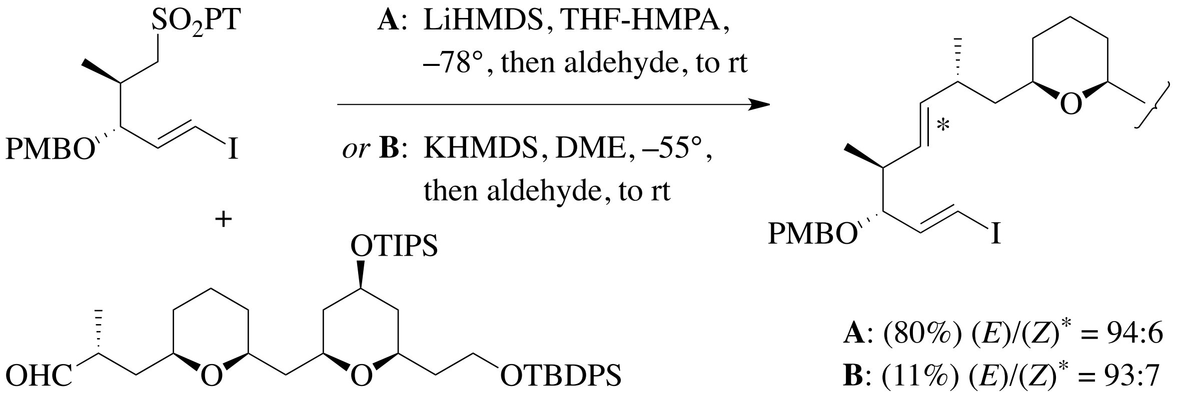
R^1 = CHO, $R^2 = CH_2SO_2PT$ (79%) (*E*)*-isomer only

High (*E*)-selectivity can be obtained when using lithiated PT sulfones if blended solvent media containing strong dipolar aprotic components such as THF-HMPA, DMF-HMPA, or DMF-DMPU are employed (Eq. 34).[24] Although cyclopropylmethyl sulfones give anomalous stereoselectivity in Julia-Kocienski olefination reactions (see below), the excellent *trans* stereoselectivity seen in Eq. 34 is quite general and extends to other types of PT sulfones. Indeed, because this protocol avoids potentially unstable potassiated sulfones it has proven superior in cases where Kocienski's conditions give unsatisfactorily low yields (Eq. 35).[63]



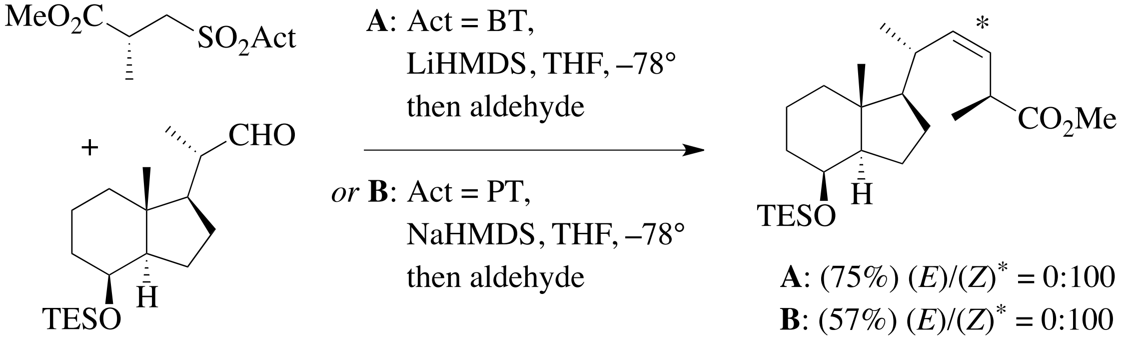
(Eq. 34)

Conditions	(*E*)/(*Z*)*
NaHMDS, THF, –78°	11:89
KHMDS, DME, –60°	50:50
LiHMDS, THF-HMPA, –60°	75:25
LiHMDS, DMF-HMPA, –35°	>97:3



(Eq. 35)

As alluded to above, anomalous outcomes have been noted for certain Type I olefination reactions wherein the expected stereoselectivity trend is not observed during the formation of a non-conjugated 1,2-disubstituted alkene. For example, the preferential formation of (*Z*)-configured alkenes from cyclopropylmethyl sulfones under certain reaction conditions was observed early on[23] and it has been encountered numerous times since including in the example cited above in Eq. 34 (note the high proportion of (Z)-alkene generated when NaHMDS or KHMDS in an ethereal solvent are employed).[24] In another notable exception, the exclusive formation of a (*Z*)-alkene product is found from a branched β-sulfonyl ester and an α-branched CD-ring steroidal aldehyde (Eq. 36).[64] This example is remarkable in that both BT and PT sulfones produce only the (*Z*)-product when using a variety of different bases and solvents (including KHMDS and DME). Other olefination reactions employing similar steroidal aldehydes and β-branched sulfones also favor formation of the (*Z*)-alkene.[65, 66]



(Eq. 36)

In summary, while occasional deviations from *trans* stereoselectivity in the synthesis of non-conjugated 1,2-disubstituted alkenes are encountered, the Julia-Kocienski olefination is typically (*E*)-selective in this context when properly tuned. As such, it should not be strategically applied to target non-conjugated 1,2-disubstituted (*Z*)-alkenes. When contemplating the synthesis of an (*E*)-configured non-conjugated 1,2-disubstituted alkene it is advocated that one first evaluate a PT sulfone and explore its reactivity with the aldehyde of choice utilizing either KHMDS in DME or LiHMDS in THF-HMPA (or DMF-HMPA) via a premetalation protocol. In the event of an unfavorable outcome, a Barbier protocol should be tested and then sulfone/aldehyde component reversal investigated before alternative reaction variations are considered. Equations 27 and 33 illustrate the dramatic difference that component reversal can make.[59, 62]

Conjugated 1,2-Disubstituted Alkenes. The Julia-Kocienski olefination has been broadly applied to the synthesis of conjugated 1,2-disubstituted alkenes. Component selection is particularly critical within this context because the manner in which the conjugated system is disconnected determines whether the olefination is of Type II or III (or IV in the case of extended conjugated systems) and this single factor has a dominant impact on whether (*E*)- or (*Z*)-stereoselectivity is likely to be encountered (see Factors Influencing Stereoselectivity). If the generation of an (*E*)-configured conjugated alkene is desired, it is logical to select coupling partners to make the olefination of Type III, i.e., an α,β-unsaturated aldehyde partnered with a non-conjugated sulfone anion (Figure 6). Conversely, a (*Z*)-configured conjugated alkene could potentially be targeted by making the olefination of Type II, i.e., a conjugated sulfone anion should be added to a non-conjugated aldehyde. In the second case, the attainment of *cis* selectivity is a credible prospect if the aldehyde in question is non-branched and the tactics highlighted above (in Eqs. 5 and 6)[5, 31] can be utilized to accentuate the natural stereoselectivity trait.

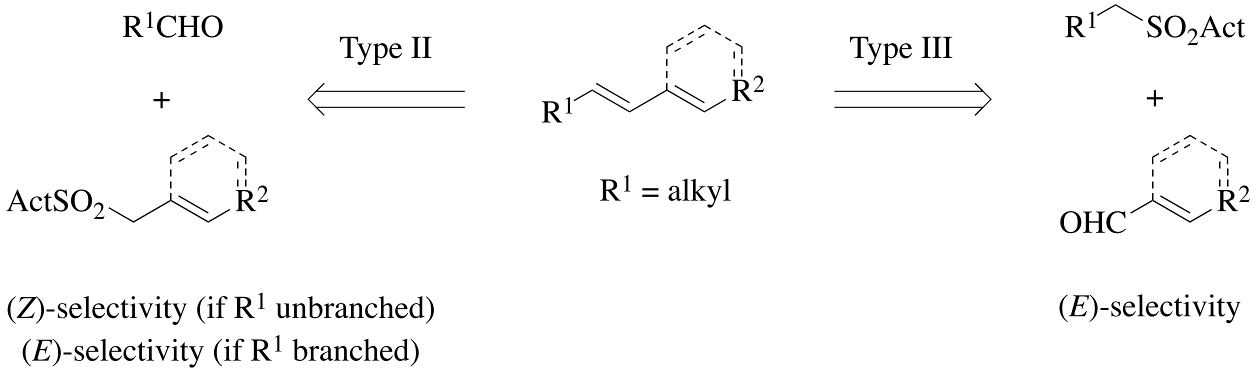
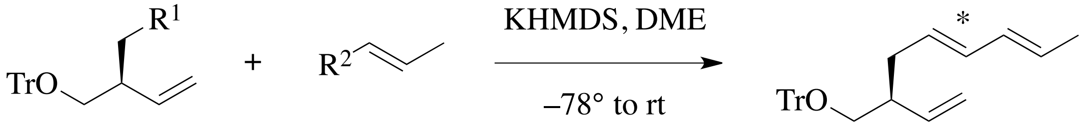


Figure 6. Disconnection strategies for a conjugated 1,2-disubstituted alkene and expected stereochemical bias.

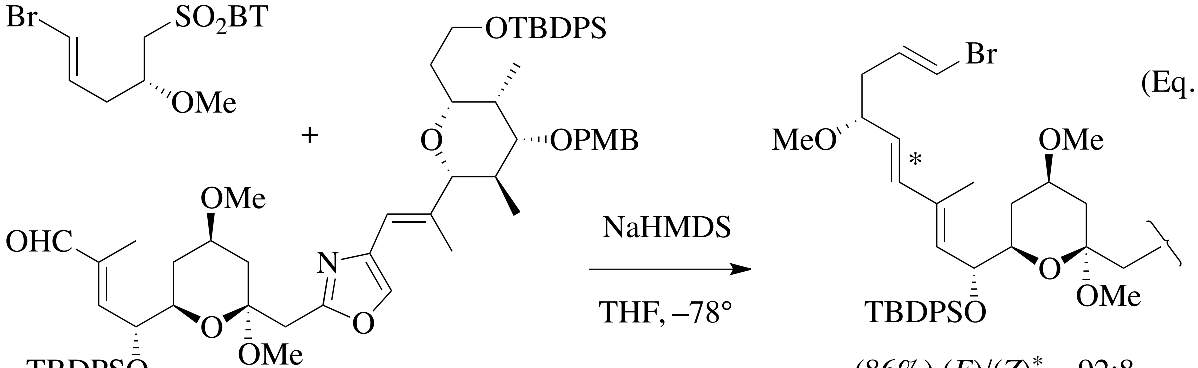
The synthesis of (*E*)-alkenes that comprise parts of conjugated diene systems has been extensively explored. Providing that the generally superior Type III component selection is made (Eq.

37 shows a direct comparison of Type II vs. Type III reactions),[67] high *trans* selectivity is readily achieved and the olefination outcome is not overly sensitive to reaction conditions. BT and PT sulfones are often equally efficacious in this regard and olefination using LiHMDS or NaHMDS base in THF solvent usually affords excellent results (Eqs. 38 and 39).[68, 69] The same behavior is observed during the synthesis of (*E*)-configured styryl systems which are likewise best obtained via the Type III disconnection from a non-conjugated sulfone anion and an aryl aldehyde (Eq. 40).[70] The large scale of the last example, a reaction used in the manufacture of a next-generation statin drug, is notable as is the fact that quenching of the reaction mixture at –80° rather than the indicated temperature (–10°) results in a significantly lower (*E*)/(*Z*) ratio (94:6 vs. >99:1, respectively). Eqs. 38 and 40 highlight that *β*-alkoxy sulfones are often largely resistant to *β*-elimination during Julia-Kocienski olefination.



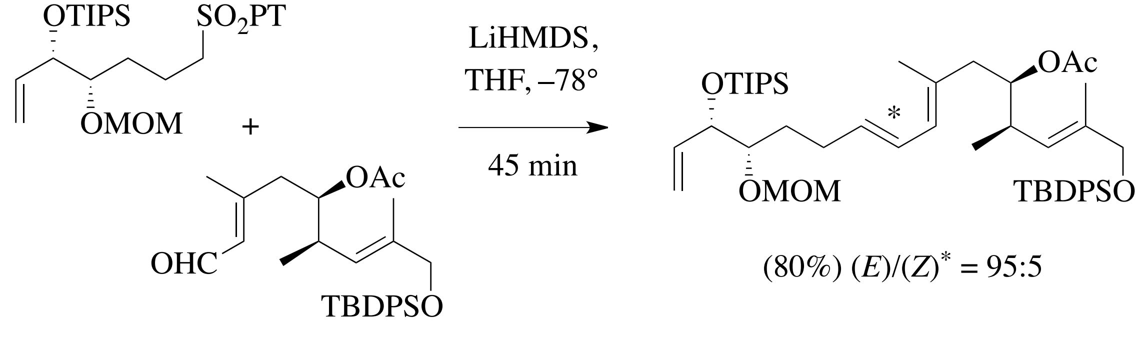
(Eq. 37)

Type II, R^1 = CHO, R^2 = CH_2SO_2PT: (81%) (*E*)/(*Z*)* = 63:37
Type III, R^1 = CH_2SO_2PT, R^2 = CHO: (69%) (*E*)/(*Z*)* = 94:06



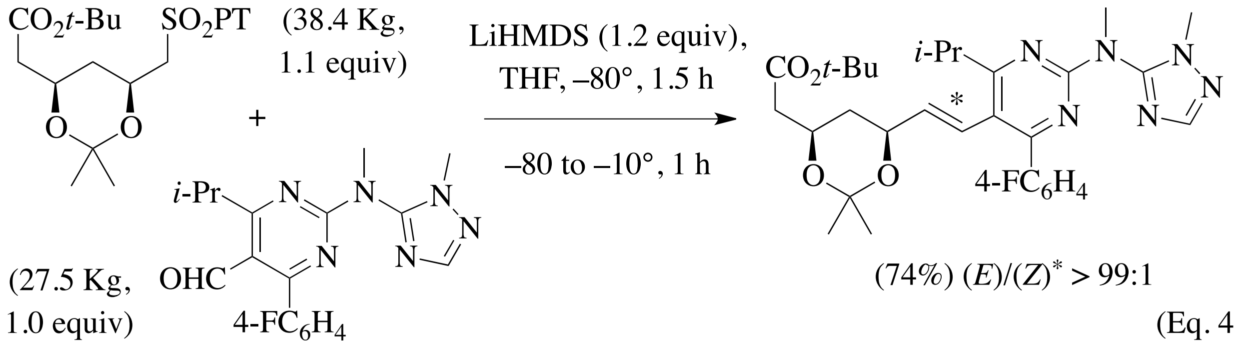
(Eq. 38)

(86%) (*E*)/(*Z*)* = 92:8



(Eq. 39)

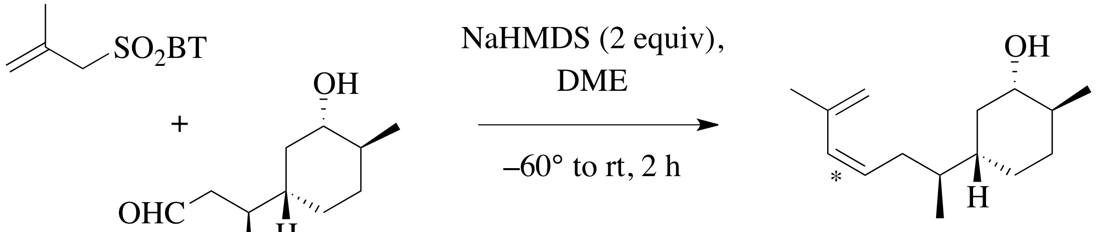
(80%) (*E*)/(*Z*)* = 95:5



(74%) $(E)/(Z)^* > 99{:}1$

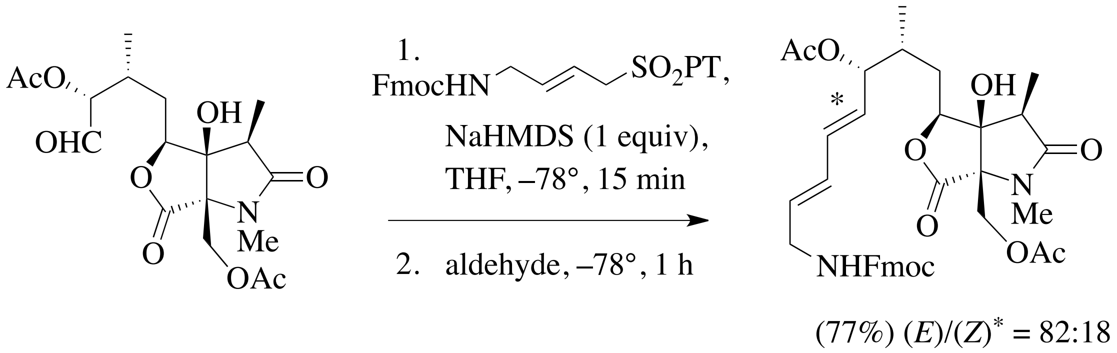
(Eq. 40)

Type II olefination reactions toward (*Z*)-alkenes within conjugated diene systems have rarely been deliberately exploited and the tactics described above to facilitate (*Z*)-selectivity through enhanced *β*-alkoxy sulfone diastereoisomer equilibration have yet to enter common usage. Nonetheless, providing that the aldehyde lacks significant chain branching about the carbonyl group, even quite standard reactions conditions will lead to (*Z*)-conjugated olefins with reasonable stereoselectivity (Eq. 41).[71] When the aldehyde is modestly branched, Type II reactions are less predictable and may give low stereoselectivity. By contrast, heavily branched aldehydes will lead to (*E*)-alkenes with good selectivity (Eq. 42),[72] albeit not as high as that routinely achieved via a Type III process. Certain types of conjugated sulfone anions give high levels of (*Z*)-selectivity regardless of the degree of branching within the aldehyde and without recourse to special activators or reaction conditions. Propagylic sulfones reliably generate (*Z*)-enynes in Julia-Kocienski olefination reactions (Eq. 43).[73] More recently, it has been discovered that Type II (and Type IV) reactions using *γ*-stannyl allylic sulfones[74, 75] also result in uniformly high *cis* selectivity (Eq. 44).[76]

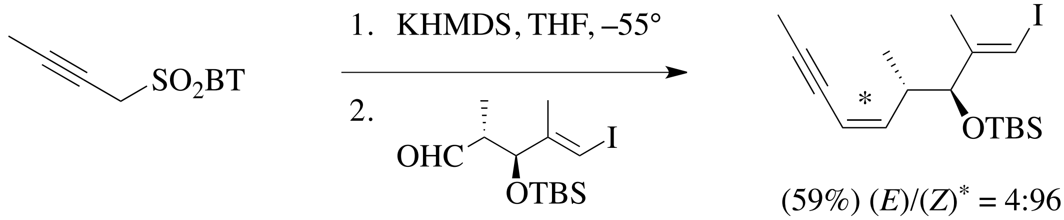


(Eq. 41)

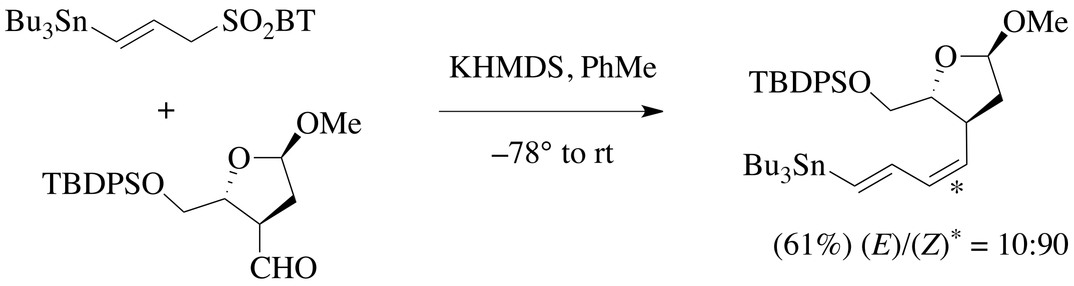
(79%) $(E)/(Z)^* = 25{:}75$



(Eq. 42)

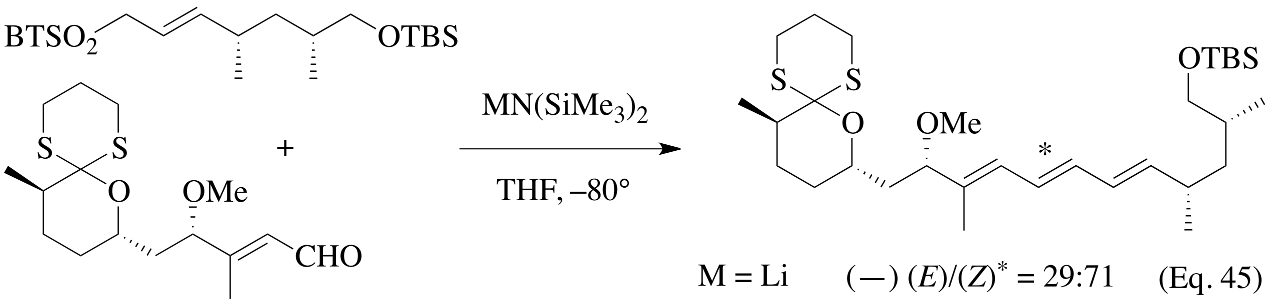


(Eq. 43)



(Eq. 44)

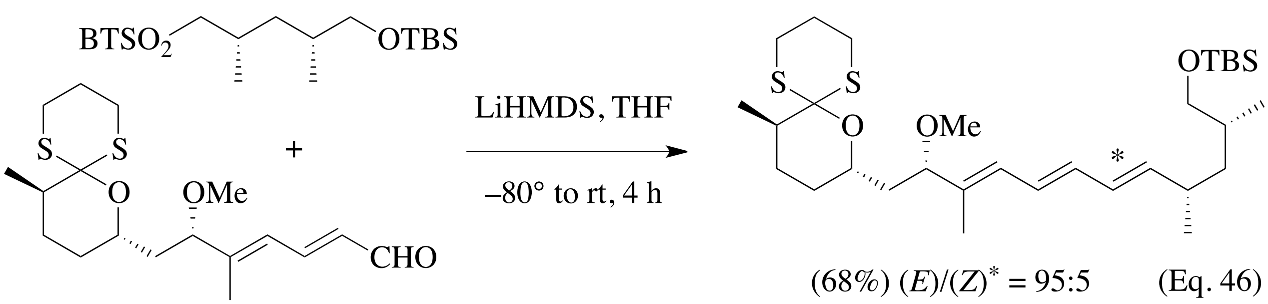
Conjugated trienes and higher-order systems of concatenated double bonds can be disconnected into components that reflect Type II, III, or IV olefinations. Electing to pursue the last option will offer the greatest degree of convergency because the system may then be disconnected down the middle; however, this strategic advantage will come at the expense of predictability since the stereochemical outcome of Type IV olefinations is variable. Selecting a Type II or III approach requires a sacrifice in convergency but prediction of stereochemical bias can then be made with a greater degree of confidence. An early application of the Julia-Kocienski olefination to the synthesis of the (*E,E,E*)-triene system of rapamycin is exemplary (Eqs. 45 and 46).[21] In this case, high stereoselectivity is not achievable via the Type IV olefination approach and the required (*E,E,E*)-triene system is never the major isomer produced (Eq. 45). The more reliable Type III olefination approach delivers the (*E,E,E*)-triene in a satisfactory manner (Eq. 46), albeit in this case the aldehyde coupling partner requires a more elaborate synthesis. Type IV olefinations have been most extensively studied during the convergent assembly of the polyolefinic regions of light-harvesting cartenoids such as peridinin.[43, 77-80] In constructing these massively extended conjugated π-systems, (*Z*)-stereoselectivity has generally been observed (Eq. 47).[78]



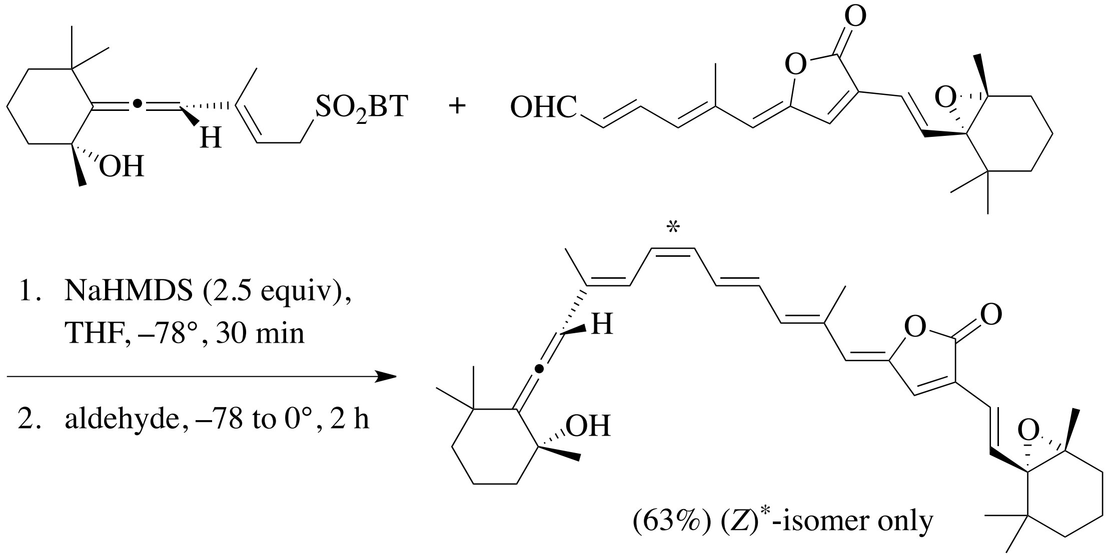
M = Li (—) $(E)/(Z)^*$ = 29:71 (Eq. 45)

M = Na (79%) $(E)/(Z)^*$ = 43:57

M= K (—) $(E)/(Z)^*$ = 18:82

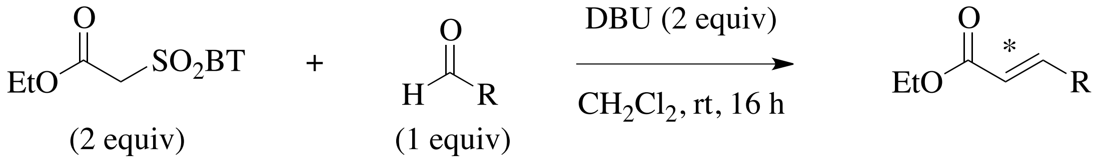


(68%) $(E)/(Z)^*$ = 95:5 (Eq. 46)



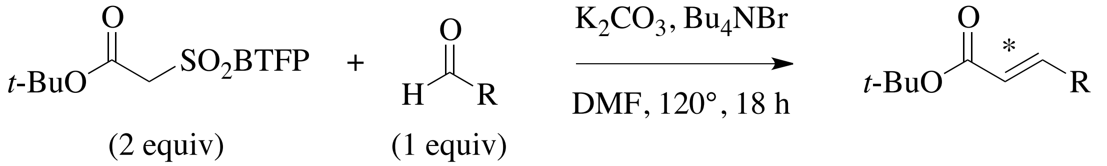
(Eq. 47)

The synthesis of *α,β*-unsaturated carbonyl compounds from *β*-oxosulfone species represents a special case of Type II (or IV) reactivity because an E1cB pathway is potentially involved in the generation of the olefin (see Factors Influencing Stereoselectivity). The relevant sulfone anions in this case are highly stabilized and, as a result, strong bases are not necessarily required for olefination to proceed. At the reaction temperatures usually employed (room temperature and above), alkene formation is typically (*E*)-selective, although non-branched aldehydes may yield (*Z*)-alkenes as observed for other Type II olefinations. Ethyl (benzothiazol-2-ylsulfonyl)acetate affords good yields of conjugated enoates when reacted with aryl aldehydes in the presence of DBU in CH_2Cl_2 solvent at room temperature; however, the olefination of enolizable aldehydes leads to variable results under the same conditions (Eqs. 7 and 48).[19] The comparable BTFP sulfone reagent gives low yields with enolizable aldehydes but again performs better with aryl aldehydes (Eq. 49).[16] Weinreb amides analogous to these BT and BTFP sulfonylacetate reagents react in the expected manner to give *trans* α,β-unsaturated enamides.[16, 81] (*E*)-Chalcones have likewise been generated by reaction of α-BT sulfonyl acetophenones with aldehydes.[82] In an extension of this chemistry, use of the indicated 2-hydroxyacetophenone sulfone derivative leads directly to flavanones via spontaneous intramolecular conjugate addition following the intermolecular Julia-Kocienski olefination reaction (Eq. 50).[82]



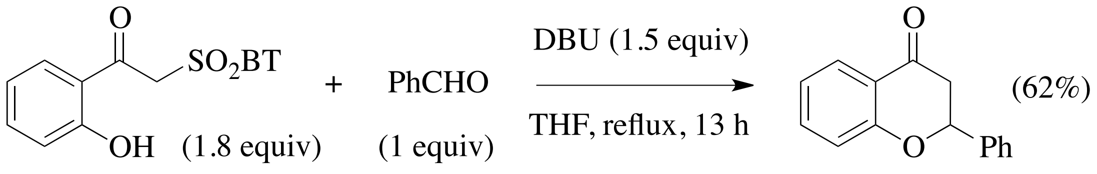
(Eq. 48)

R = 4-(MeO)C_6H_4: (93%) (*E*)/(*Z*)* = 92:08
R = *n*-C_5H_{11}: (41%) (*E*)/(*Z*)* = 19:81
R = $Me_2C{=}CH(CH_2)_2MeCHCH_2$: (64%) (*E*)/(*Z*)* = 30:70
R = *c*-C_6H_{11}: (80%) (*E*)/(*Z*)* = 80:20



(Eq. 49)

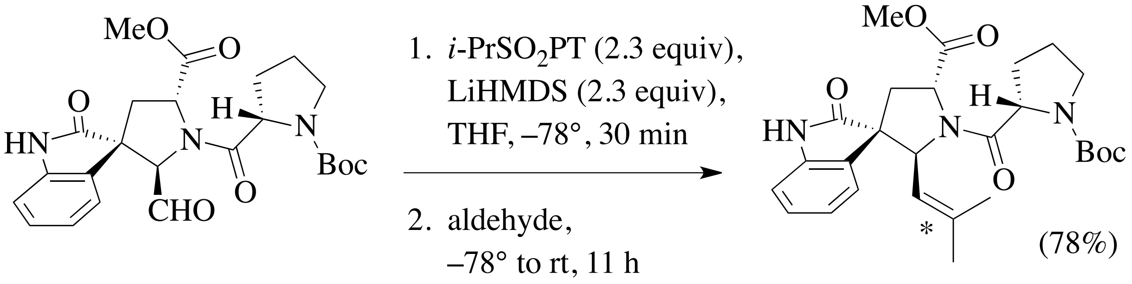
R = 4-MeOC_6H_4: (45%) (*E*)/(*Z*)* > 99:01
R = 4-$CF_3C_6H_4$: (74%) (*E*)/(*Z*)* > 99:01
R = *n*-C_9H_{19}: (14%) (*E*)/(*Z*)* = 68:32
R = *c*-C_6H_{11}: (15%) (*E*)/(*Z*)* = 75:25



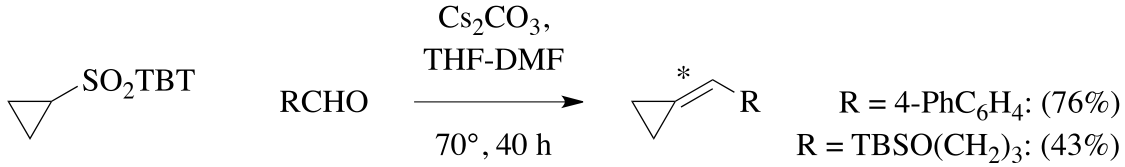
(Eq. 50)

Trisubstituted and Tetrasubstituted Alkenes. Comparatively few examples of the synthesis of (all-carbon) tri- and tetra-substituted alkenes have been reported using the Julia-Kocienski olefination. Although the method is reasonably effective at producing such olefins (and certainly the former class), stereoselectivity is modest at best with product isomeric ratios seldom exceeding 3:1 and the usual stereochemical traits for Type I-IV olefinations are only weakly followed.

Trisubstituted alkenes are successfully generated both from the union of secondary alkyl sulfone anions with aldehydes and the alternative coupling mode employing a primary alkyl sulfone anion and a ketone. When symmetric secondary alkyl sulfones are involved, stereoselectivity is not an issue and in this regard isopropyl PT sulfone has become a popular tool for the generation of prenyl groups from aldehyde substrates (Eq. 51).[83] Another symmetrical secondary alkyl sulfone, cyclopropyl TBT sulfone, is effective for the generation of methylene-cyclopropanes from aldehydes (Eq. 52).[84] Cyclopropyl pentachlorophenyl sulfones, formed in situ by base mediated cyclization of 3-halopropyl sulfones, are similarly employed.[85]

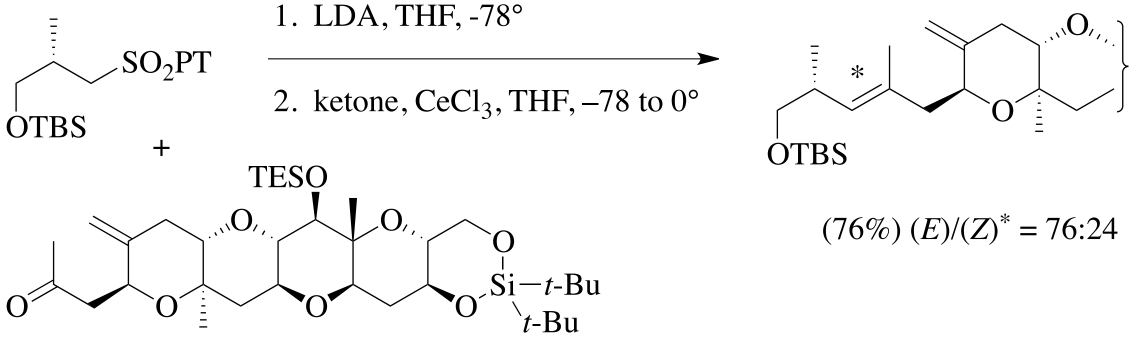


(Eq. 51)



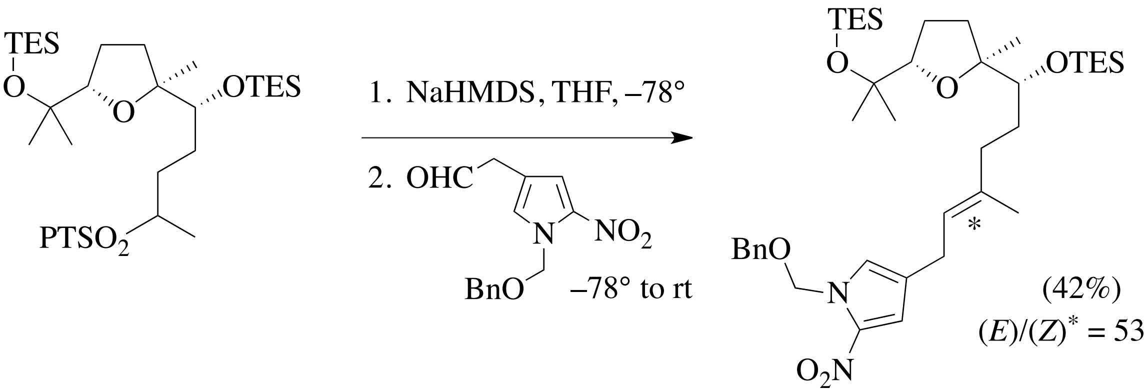
(Eq. 52)

In the case of Type I couplings toward non-symmetrical methyl group-bearing trisubstituted alkenes, addition of a primary alkyl sulfone anion to a methyl ketone generally results in higher (*E*)-selectivity than the reversed component selection (Eq. 53 vs. Eq. 54).[86, 87] The first of these examples is notable in that precomplexation of the ketone with anhydrous cerium(III) chloride significantly increases the yield of the coupling, conceivably by minimizing proton exchange between the lithiated sulfone and the enolizable ketone. The same approach has been applied to a more complex methyl ketone in the final stages of a total synthesis of gambieric acid A.[88]



(76%) $(E)/(Z)^{*}$ = 76:24

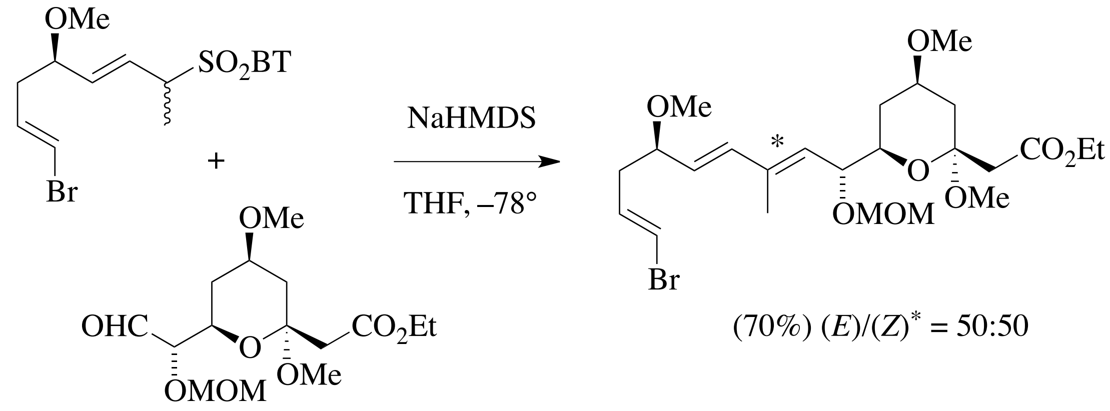
(Eq. 53)



(42%)
$(E)/(Z)^{*}$ = 53:47

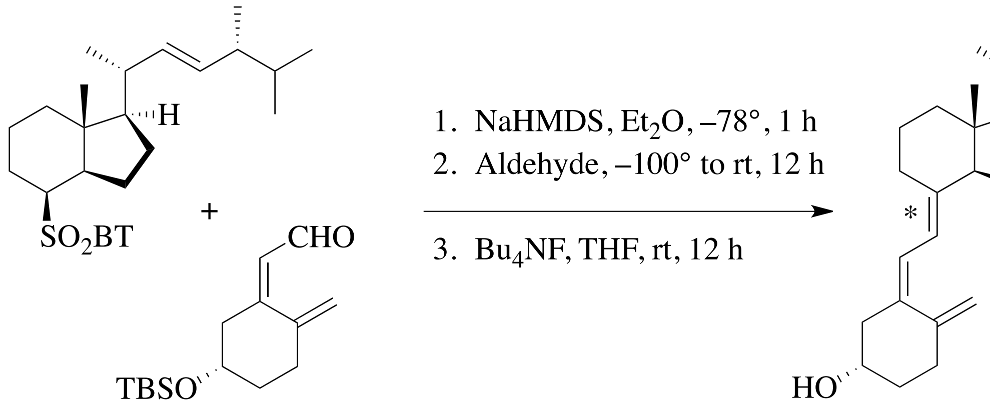
(Eq. 54)

The use of conjugated sulfone anions in Type II olefinations toward trisubstituted alkenes has yet to be thoroughly investigated; however, the limited data available suggest that such reactions do not offer generally useful levels of stereoselectivity (Eq. 55).[89] Better outcomes have been realized from Type III olefinations and modest (*E*)-selectivity is typically found when either conjugated aldehydes (Eq. 56)[38] or conjugated ketones (Eq. 57)[25] are employed as substrates. Of note, the highest stereoselectivities yet observed for the synthesis of trisubstituted alkenes via the Julia-Kocienski olefination involve a Type IV reaction toward simple (*Z*)-configured stilbene derivatives (Eq. 58).[90] The generality of this result as it may pertain to other Type IV olefinations en route to trisubstituted alkenes has not been established.



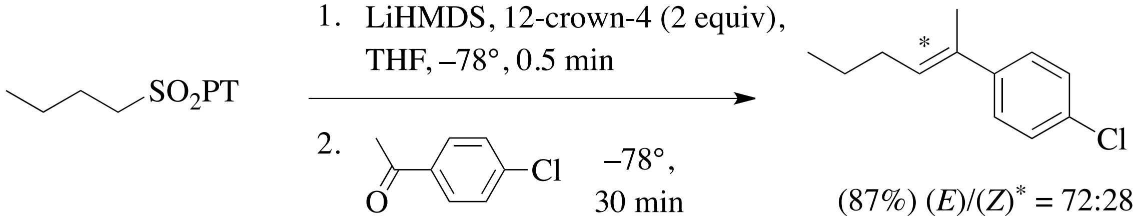
(70%) $(E)/(Z)^{*}$ = 50:50

(Eq. 55)



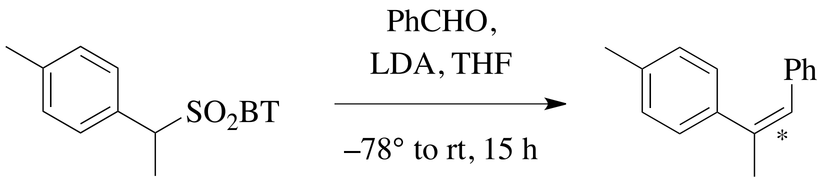
(Eq. 56)

(70%) $(E)/(Z)^*$ = 72:28



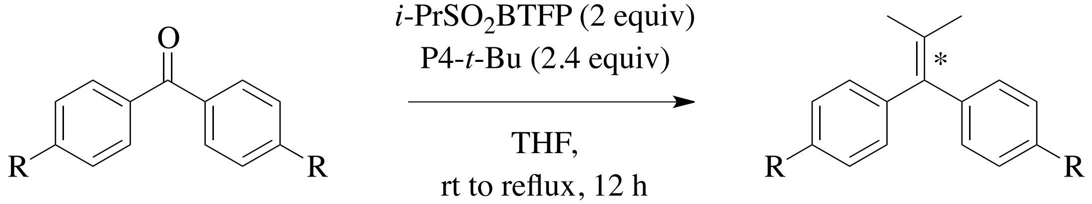
(Eq. 57)

(87%) $(E)/(Z)^*$ = 72:28



(75%) $(E)/(Z)^*$ = 5:95 (Eq. 58)

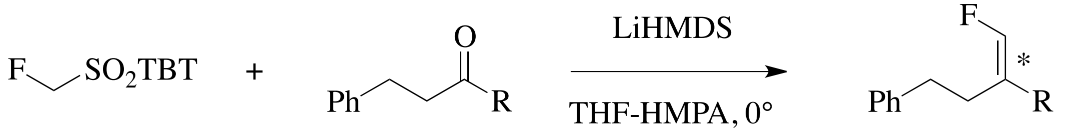
The synthesis of a tetrasubstituted alkene requires the addition of a secondary alkyl sulfone anion to a ketone. Given a comparative lack of reactivity in each coupling partner involved, the steric compression present in the initial addition adduct, and the high level of allylic strain found in the product alkene, this feat is not easy to accomplish;[91] nonetheless, some success has been reported using robust BTFP sulfone anions. Thus, isopropyl BTFP sulfone is modestly effective in the generation of symmetrical tetrasubstituted olefins from diaryl ketones (Eq. 59).[92] An attempt to apply this method to access a 1,1,2-triarylpropene from propylphen-1-yl BTFP sulfone failed.[92]



(Eq. 59)

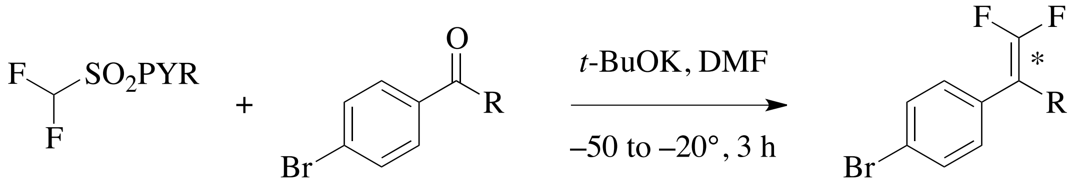
R = Cl: (71%)
R = H: (40%)
R = OMe: (10%)

Vinyl Halides. All types of haloalkenes have been successfully prepared via the Julia-Kocienski olefination but the process has found a particular niche for the synthesis of structurally varied vinyl fluorides.[32] Terminal fluoromethyl and difluoromethyl alkenes are accessed from aldehydes and ketones by base-mediated reactions with the illustrated TBT and PYR sulfones (Eqs. 60 and 61).[93, 94] Substituted α-fluoroalkyl sulfones are also effective for the synthesis of internal fluoroalkenes and in many cases the familiar stereoselectivity traits expected for Type I (Eq. 62),[95] Type II (Eq. 63),[96] and Type III (Eq. 64)[95] olefinations have been observed. Note that in these examples, the F-atom has the highest priority for the purposes of configurational assignment and so the (*Z*)-fluoroalkene is a *trans*-like system and the (*E*)-isomer is a *cis*-like system. In a related fashion, α-substituted fluoroethenes are prepared in good to excellent yields by the reaction of α-fluoroalkyl BT sulfone anions with paraformaldehyde[97] and reactions with ketones lead to fully substituted fluoroalkenes.[95]



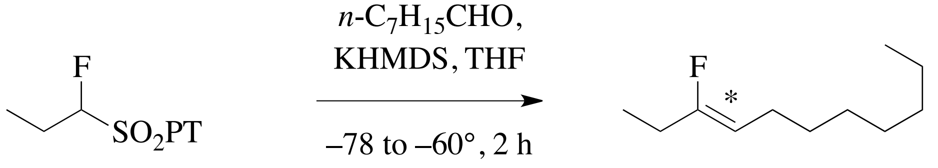
(Eq. 60)

R = H: (51%) (*E*)/(*Z*)* = 48:52
R= Me: (75%) (*E*)/(*Z*)* = 30:70



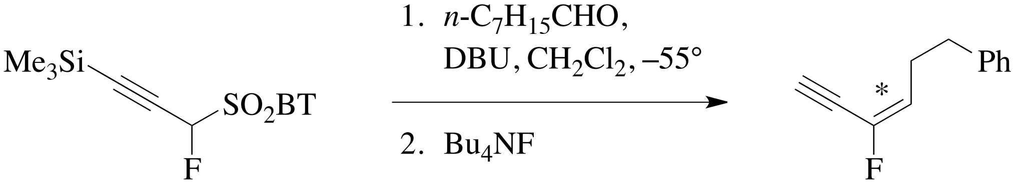
(Eq. 61)

R = H: (72%)
R= Me: (77%)



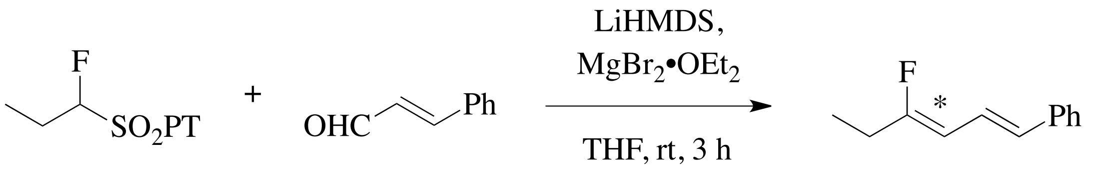
(Eq. 62)

(74%) (*E*)/(*Z*)* = 27:73



(Eq. 63)

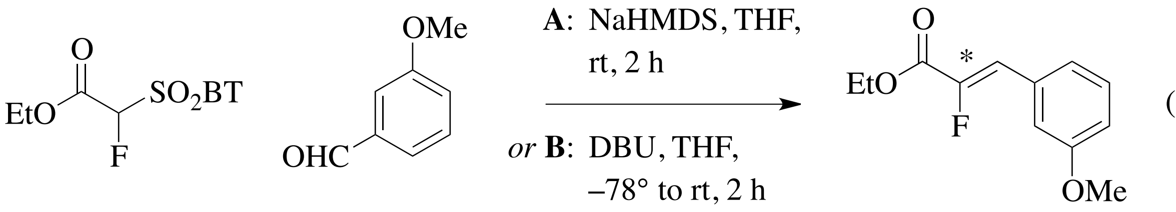
(79%) (*E*)/(*Z*)* = 85:15



(72%) $(E)/(Z)^{*}$ = 19:81

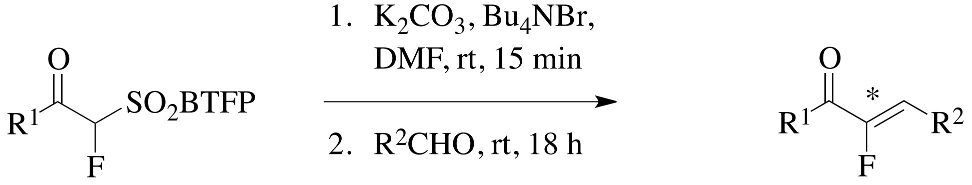
(Eq. 64)

α-Fluorosulfonyl acetates and acetamides and related activated (i.e., low pK_a) α-fluorosulfones are highly effective in the Julia-Kocienski olefination.[32, 98-100] Where examined, such reagents are more reactive than the corresponding non-fluorinated sulfones, possibly due to an α-effect.[98] As with non-fluorinated sulfonyl acetates,[19] variation in temperature and base mediator can be used to reverse the sense of stereoselectivity (Eq. 65).[99] Acetamido and acetonitrilo BT α-fluorosulfones give *trans*-like [(*Z*)-configured] products in common with the corresponding non-fluorinated starting materials.[100, 101] BTFP fluorosulfonyl acetates and acetamides are similarly used to good effect and universally favor the *trans*-like [(*Z*)-configured] product under the illustrated reaction conditions (Eq. 66).[102]



(Eq. 65)

A: (75%) $(E)/(Z)^{*}$ = 15:85
B: (74%) $(E)/(Z)^{*}$ = 85:15

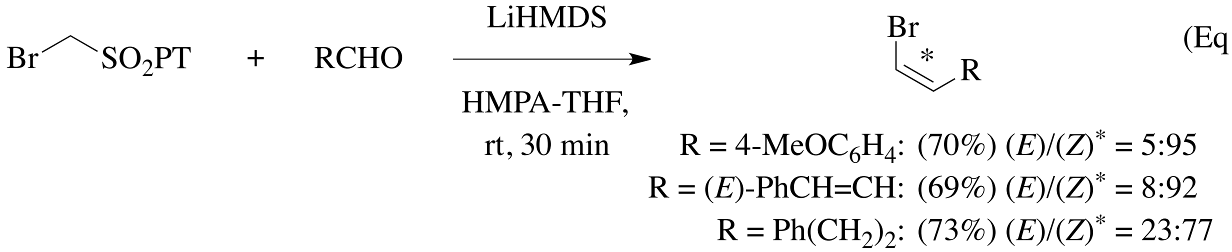


(Eq. 66)

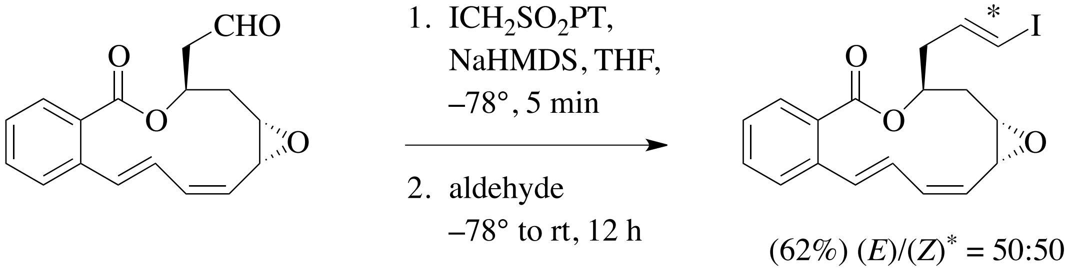
R^1	R^2		$(E)/(Z)^{*}$
MeO	Ph	(95%)	7:93
MeO	c-C_6H_{11}	(71%)	7:93
MeO(Me)N	Ph	(83%)	0:100
MeO(Me)N	c-C_6H_{11}	(65%)	0:100

Other types of vinyl halides (and particularly bromides and iodides) are valuable substrates in transition-metal-catalyzed cross-coupling reactions and a few useful protocols for their synthesis via the

Julia-Kocienski olefination have been developed. Chloro- and bromo-methyl PT sulfones give predominantly (*Z*)-haloalkenes upon reaction with aryl, alkenyl, and alkyl aldehydes (Eq. 67).[103] In some cases, replacing HMPA with $MgBr_2$•OEt_2 in an otherwise identical procedure results in the production of (*E*)-chloroalkenes from aryl aldehydes and the chloromethyl PT sulfone.[103] Iodomethyl PT sulfone has not been well investigated; in an isolated example, a non-stereoselective reaction is observed with a complex non-conjugated alkyl aldehyde (Eq. 68).[104]

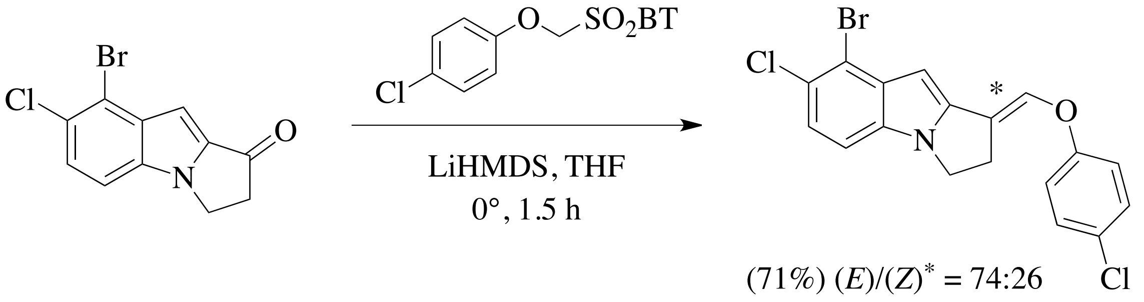


(Eq. 67)



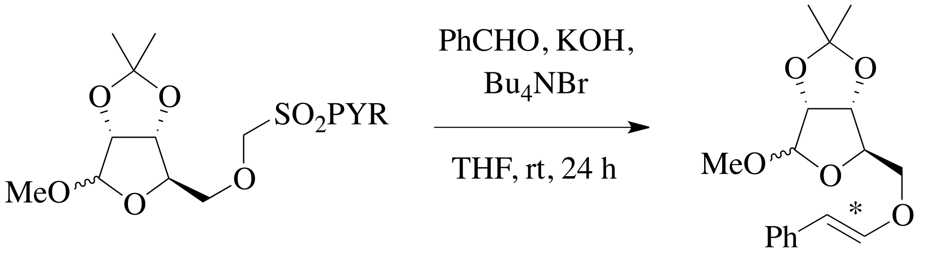
(Eq. 68)

Miscellaneous Alkene Classes. Beyond vinyl halides, various other types of heteroatom-substituted alkenes are prepared via the Julia-Kocienski olefination. Of these, the generation of enol ethers has received the greatest attention and two distinct approaches have been developed: first, via the addition of alkoxymethyl sulfone anions to aldehydes and ketones (Eqs. 69 and 70),[105, 106] and second, by a multi-step process involving addition of alkyl sulfone anions to lactones followed by DBU-mediated elimination (Eq. 71).[107, 108] In general, neither route is highly stereoselective, but each provides a potentially useful and non-conventional entry to enol ethers. The first approach has been extended to the synthesis of enamine-like compounds as illustrated in Eq. 72.[109] The benzotriazolylmethyl PT thioether precursor to the sulfone shown is prepared by a 1,3-dipolar cycloaddition of azidomethyl PT thioether to benzyne.



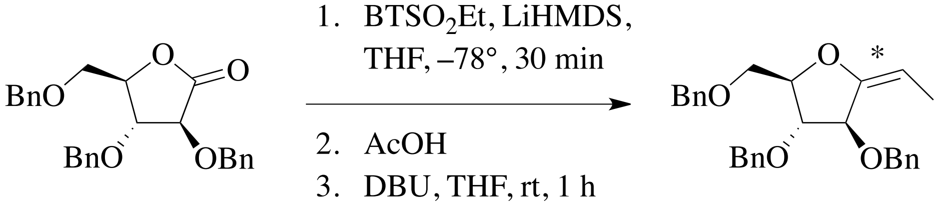
(71%) $(E)/(Z)^*$ = 74:26

(Eq. 69)



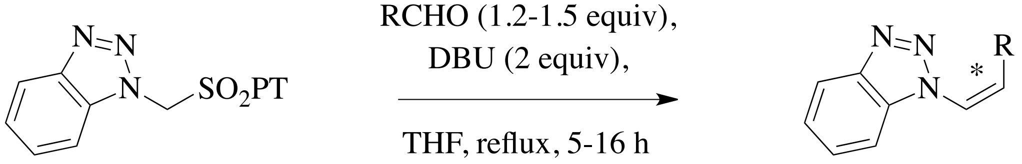
(72%) $(E)/(Z)^*$ = 94:6

(Eq. 70)



(77%) $(E)/(Z)^*$ = 80:20

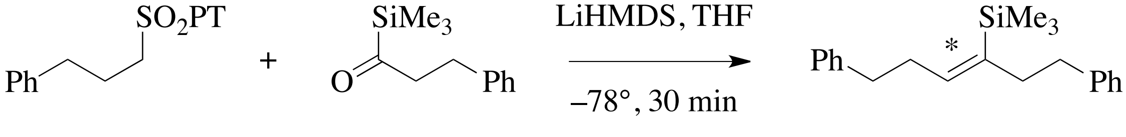
(Eq. 71)



(Eq. 72)

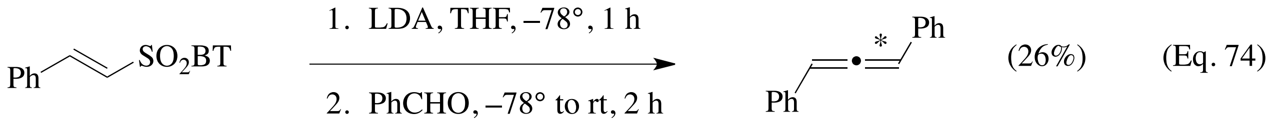
R = 2-MeOC$_6$H$_4$: (57%) $(E)/(Z)^*$ = 15:85
R = 2-FC$_6$H$_4$: (83%) $(E)/(Z)^*$ = 11:89
R = Et$_2$CH: (50%) $(E)/(Z)^*$ = 3:97

Acyl silanes are compatible with the Julia-Kocienski olefination process, providing an interesting, albeit not particularly stereoselective, synthesis of vinyl silanes (Eq. 73).[110] Lastly, in an approach to allenes that has yet to be further investigated, Julia uses an olefination reaction involving a vinyl BT sulfone anion (Eq. 74).[3]



(Eq. 73)

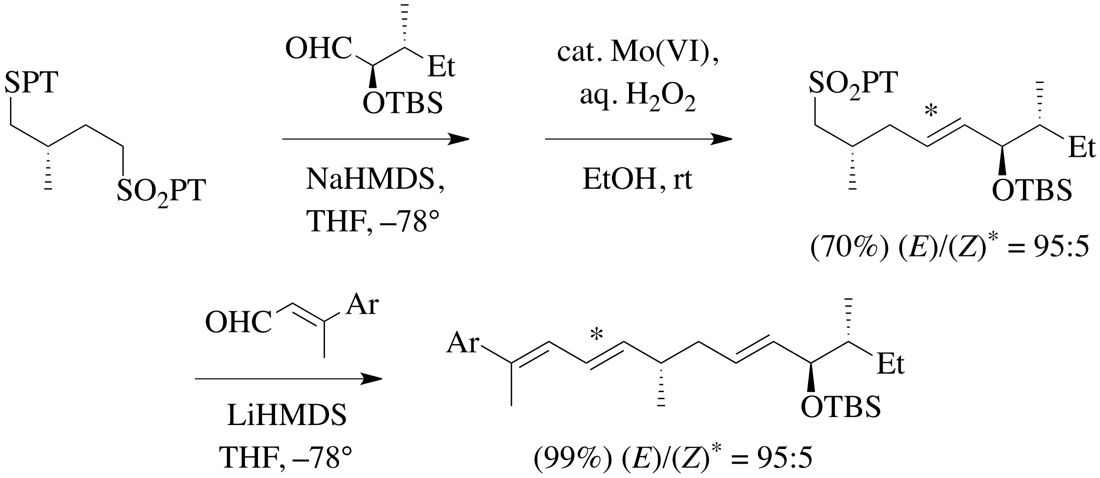
(93%) $(E)/(Z)^*$ = 64:36



(Eq. 74)

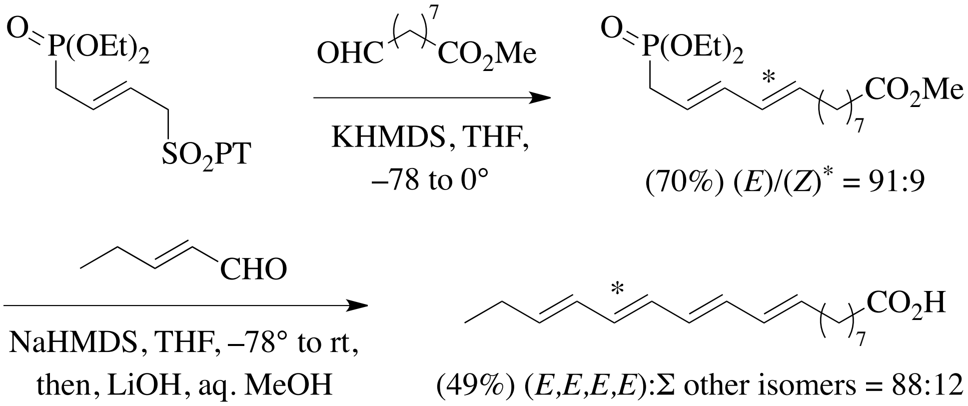
Functional-Group Tolerance of Olefination and Epimerization Possibilities

Even a cursory glance at the transformations shown above, and the many more found in the tabular surveys, reveals that the Julia-Kocienski olefination is broadly compatible with a wide variety of collateral functional-groups. For example, the process typically tolerates preexisting unsaturated carbon-carbon bonds (including vinyl halides and vinyl boronates), epoxides, esters, and common protecting groups for alcohols (such as silyl ethers) and amines (such as Boc and Fmoc carbamates). Furthermore, a small number of unprotected protic sites can be accommodated within the coupling partners providing that an additional equivalent of base is used to account for each available proton (Eqs. 41, 47, and 51). Despite the risk of *β*-elimination, sulfones containing *β*-oxygenated functionality often perform quite well, especially if Barbier conditions are adopted to minimize the lifetime of the sulfone anion (Eqs. 38, 40, and 75). Sulfones bearing functionality primed for multiple olefination events have also been successfully engaged and enable the rapid assembly of polyunsaturated materials (Schemes 5–7).[111-113] Scheme 5 exemplifies deployment of a sulfonyl thioether linch-pin reagent to achieve a pair of sequential Julia-Kocienski olefination reactions that are interspersed by an oxidation stage.[111] The same strategy can be applied with sulfonyl thioether reagents containing a mixture of different activators.[114] In the second example it is notable that Julia-Kocienski olefination is triggered before the Horner-

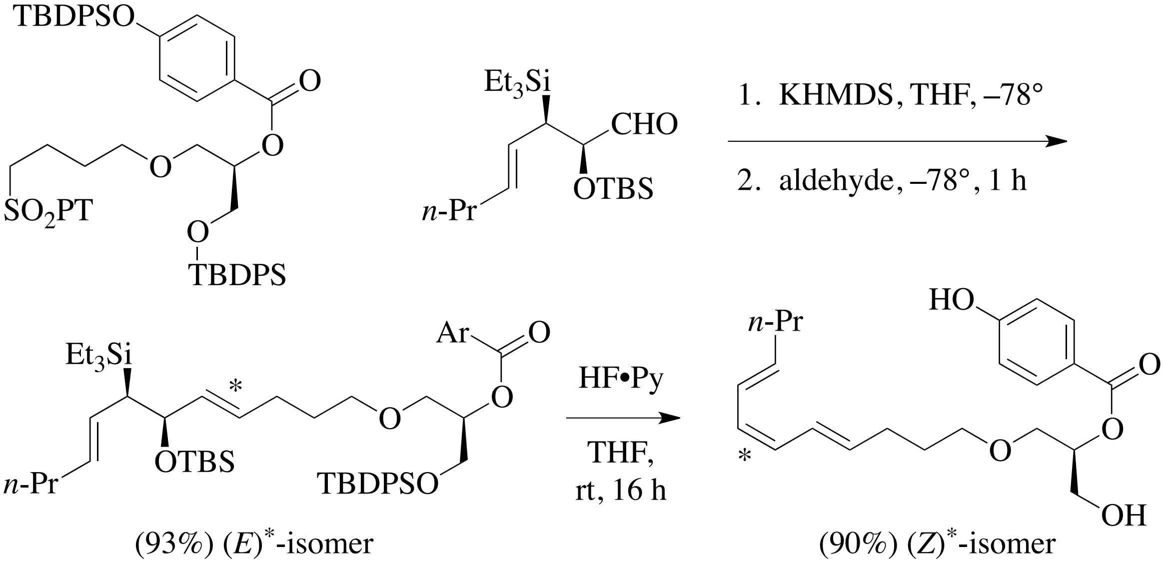


Scheme 5

Wadsworth-Emmons reaction (Scheme 6).[112] The third example shows a deft combination of Julia-Kocienski olefination and stereospecific Peterson elimination[115] for the generation of the (*E,Z,E*)-triene system found in bretonin B (Scheme 7).[113]

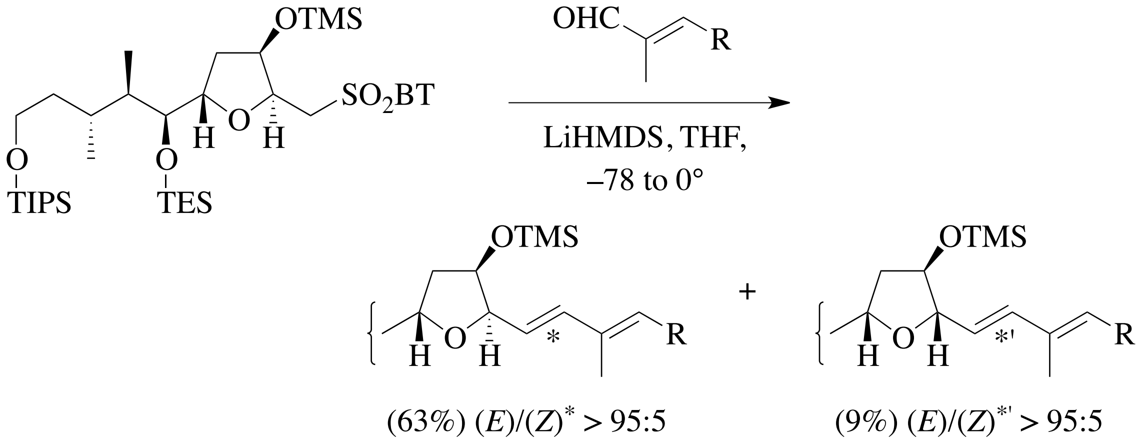


Scheme 6

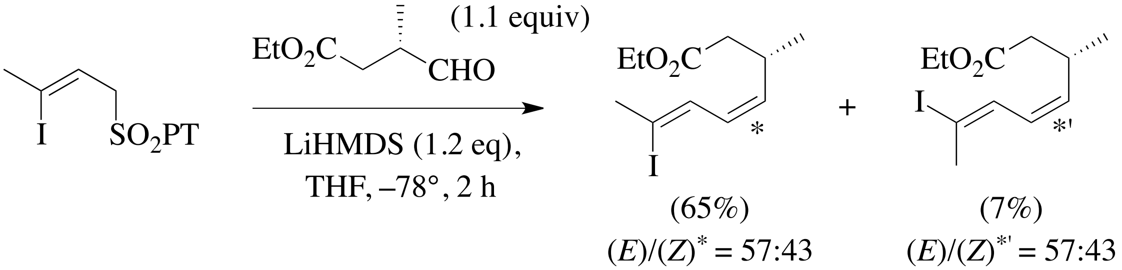


Scheme 7

Epimerization at preexisting stereogenic sites within either the sulfone or the carbonyl compound is rarely encountered, but some notable examples of unwanted isomerization have been documented. As commented above, although the possibility of epimerization of enolizable α-substituted aldehydes or ketones is an obvious concern, in reality, stereochemical integrity is typically well maintained at such positions even if Barbier conditions are employed. When such behavior is an issue, however, PT sulfones result in less epimerization than comparable BT sulfones.[116] Epimerization of a complex tetrahydrofurylmethyl sulfone is observed in the synthesis of the pectenotoxins (Eq. 75).[117] In this case, the mechanistic origin of epimerization is *β*-elimination from the sulfone anion followed by re-addition of the resulting alkoxide to the putative vinyl sulfone intermediate. The same epimerization phenomenon occurs in simpler tetrahydrofurylmethyl sulfones too.[118] Unwanted isomerization is also observed in Type II olefinations employing allylic sulfones (Eq. 76).[119]

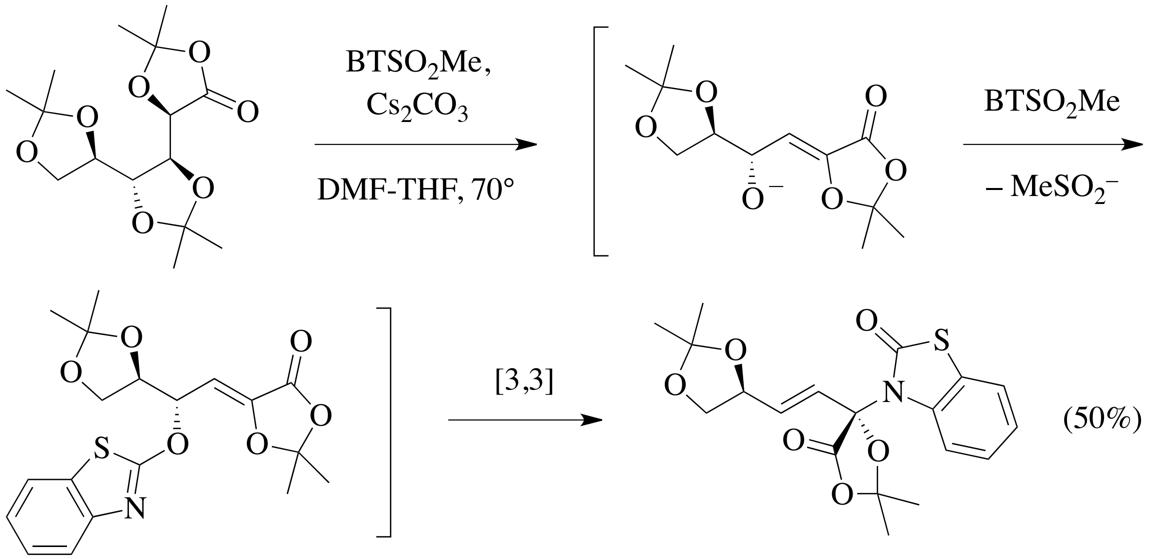


(Eq. 75)

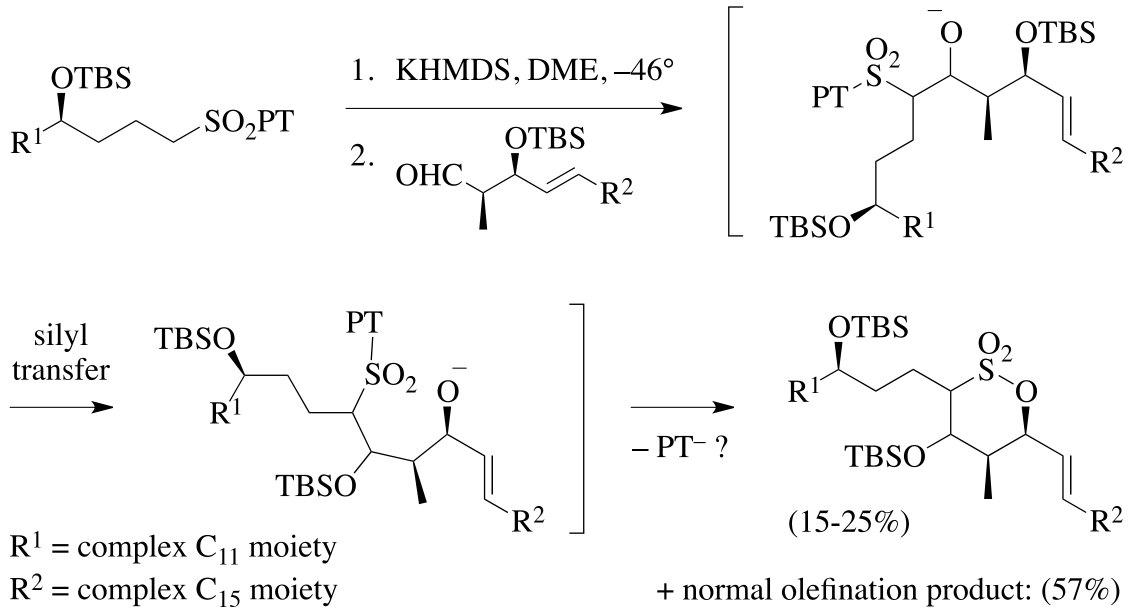


(Eq. 76)

On occasion, more exotic and unanticipated side-reactions are encountered. For instance, in an ill-fated attempt to methylenate a lactone carbonyl group using methyl BT sulfone, the basic reaction conditions cause E1cB elimination and then *ipso* attack by the revealed alkoxide anion on the sulfone reagent (Scheme 8).[120] The resulting allylic BT ether experiences a spontaneous Overman-type [3,3]-sigmatropic rearrangement to yield the illustrated final product. Another example of a side-reaction involving an unintentionally generated alkoxide anion is observed during the synthesis of the complex macrolide oasomycin A (Scheme 9).[121] In this case, transfer of a TBS silyl ether protecting group originating within the aldehyde to the alkoxide anion produced from the initial addition event, competed with spirocyclization. The resulting *δ*-alkoxy sulfone species leads to the generation of a sultone product via direct attack of the new alkoxide anion at sulfur with expulsion of a putative phenyltetrazolyl anion nucleofuge. No sultone formation is observed when LiHMDS is used as the base instead of KHMDS, but then (*E*)-selectivity is significantly reduced [(*E*)/(*Z*) = 88:12 with KHMDS vs. (*E*)/(*Z*) = 66:34 with LiHMDS].[121]



Scheme 8



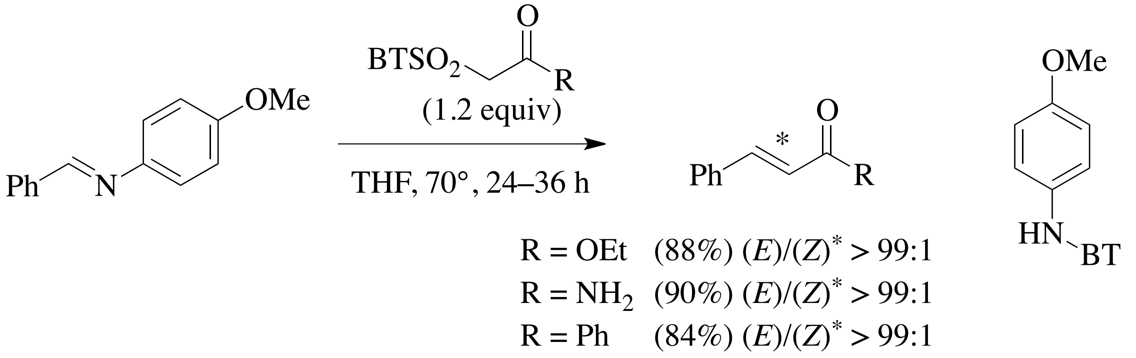
R^1 = complex C_{11} moiety
R^2 = complex C_{15} moiety

+ normal olefination product: (57%)

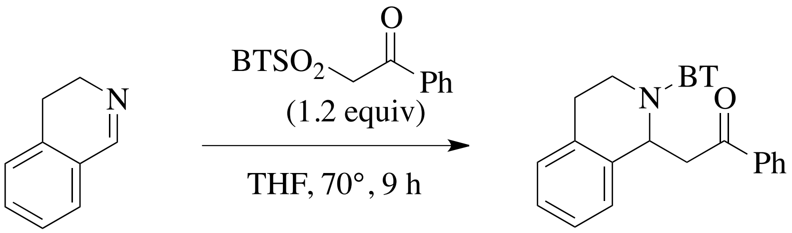
Scheme 9

Reaction Variants

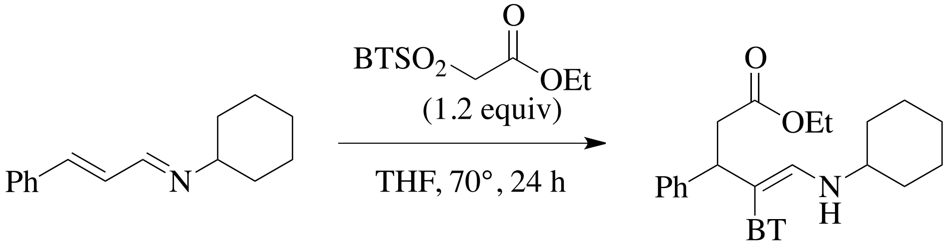
The pivotal Smiles rearrangement/elimination cascade that lies at the heart of the Julia-Kocienski olefination has been employed creatively in other types of useful transformations. In one of the more straightforward variants of the basic process that has been described, imines are substituted for the usual carbonyl compound electrophiles and react with *β*-oxo BT sulfones (Eqs. 77–79).[122] Reactions with simple acyclic imines lead to alkene products (Eq. 77), whereas in the case of cyclic imine substrates the now tethered 2-aminobenzothiazole moiety lost in the elimination stage engages in an intramolecular conjugate addition reaction with the incipient *α,β*-unsaturated carbonyl moiety to generate cyclic amine products (Eq. 78).[122] Along similar lines, *α,β*-unsaturated imine substrates are vicinally difunctionalized on either side of the electrophilic olefin moiety via a reaction cascade that begins with conjugate addition and proceeds via a Smiles rearrangement involving an intermediate enamine (Eq. 79).[122] In all of these reactions, the imine substrate itself serves to deprotonate the acidic *β*-oxosulfone and an exogenous base is not required.



(Eq. 77)

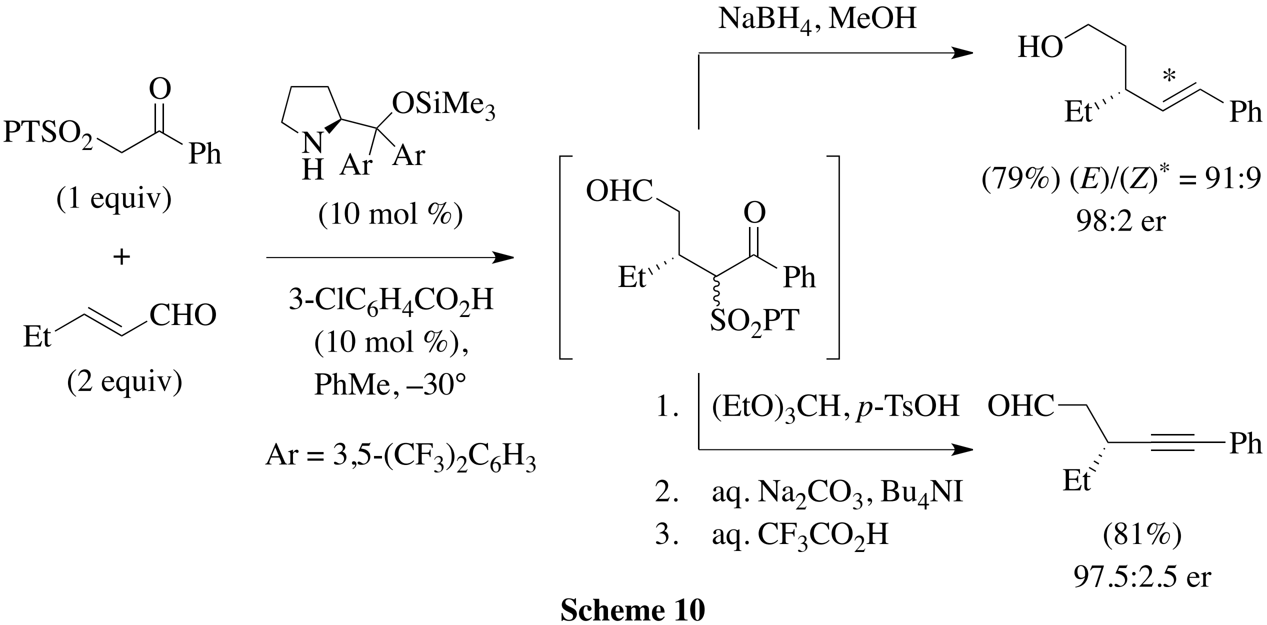


(94%) (Eq. 78)



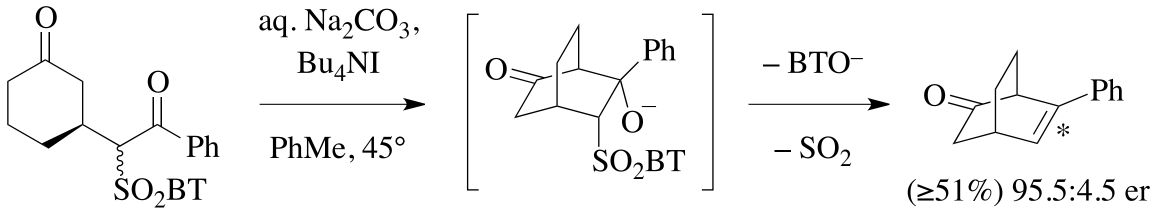
(63%) (Eq. 79)

A number of interesting reaction sequences have been reported that involve enantioselective organocatalytic Michael addition of β-oxosulfones to α,β-unsaturated carbonyl compounds and subsequent Smiles rearrangement from derived adducts.[123] For example, addition of the illustrated β-keto PT sulfone to 2-pentenal mediated by a proline-derived secondary amine catalyst affords the expected addition adduct in high enantioselectivity (Scheme 10).[124] In situ reduction of this intermediate results in the generation of a β-alkoxy sulfone moiety that forms an alkene via the usual elimination mechanism. Alternatively, following protection of the carbonyl group as an acetal, the same β-keto sulfone intermediate could be converted to an alkyne by treatment with sodium carbonate and TBAI.[124] The conversion of the enolates of such keto sulfones to alkynes is presumed to occur via the familiar Smiles rearrangement/elimination sequence;[123] whatever its mechanism, this kind of alkynylation process warrants further development. A related conjugate addition adduct formed from cyclohexenone evolves in a different manner when treated with Na_2CO_3/Bu_4NI (Eq. 80).[125] In this case, an intramolecular aldol reaction from the distal ketone enolate competes against alkyne formation from the thermodynamically favored β-keto sulfone enolate. The resulting aldol adduct (as shown) contains a β-alkoxy sulfone system which expels sulfur dioxide and the benzothiazolone anion to yield the observed bicyclo[2.2.2]octenone product. More recently, adducts such as that shown in Scheme 10 have been further processed in a similar fashion via *N*-heterocyclic carbene (NHC) catalyzed benzoin cyclization leading to cyclopentenones.[126] Along the same lines, addition of acetylides and enolates to non-

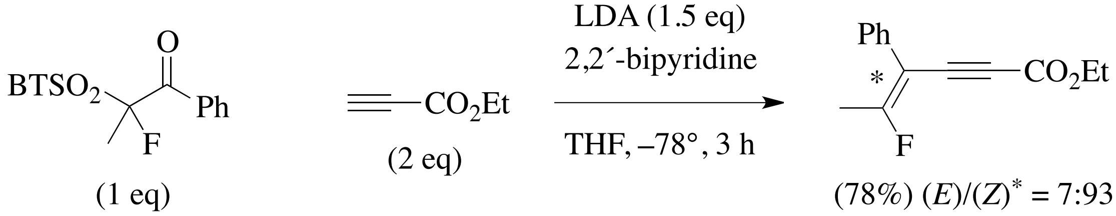


Scheme 10

enolizable α-fluoro-β-keto sulfones is highly effective for the stereoselective synthesis of tetrasubstituted fluoroalkenes (Eq. 81).[127] Taken together, the aforementioned results (Eqs. 80 and 81) indicate that, as a class, β-keto BT and PT sulfones can be regarded as vinyl cation equivalents providing that their enolization does not interfere with nucleophilic addition.

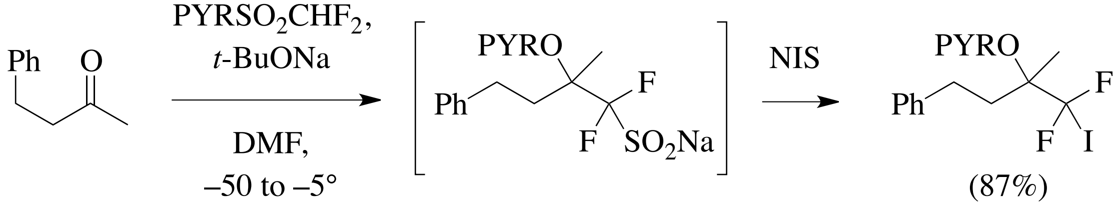


(Eq. 80)

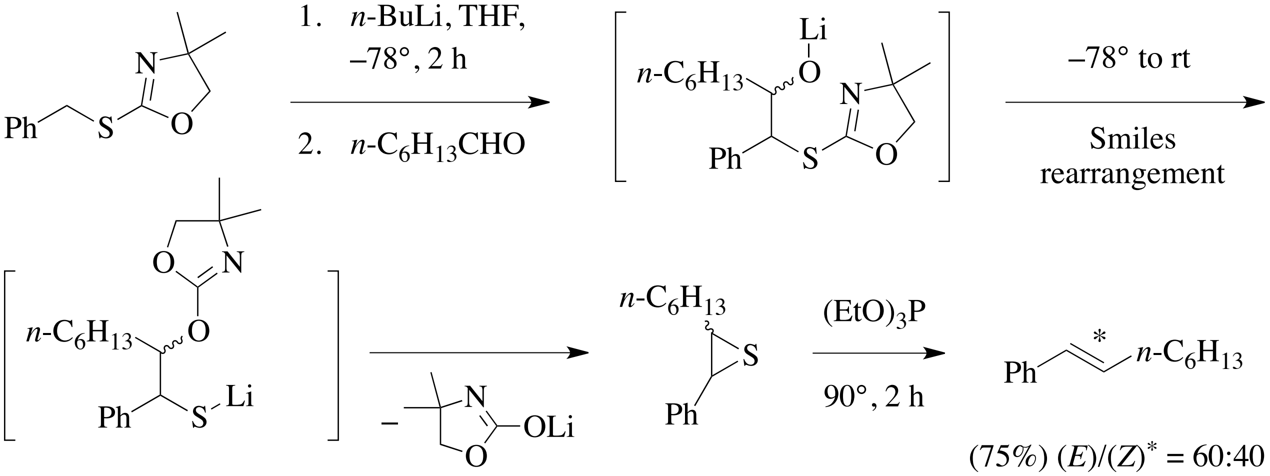


(Eq. 81)

Transformations in which Smiles rearrangement is not followed by the canonical elimination process have also found utility. For example, the reaction of difluoromethyl PYR sulfone anions with aldehydes or ketones proceeds as far as the Smiles rearrangement stage but then the intermediate sulfinate does not spontaneously eject PYRO⁻; interception of the sulfinate with electrophilic halogen sources results in a net halodifluoromethylation of the carbonyl compound (Eq. 82).[128] Finally, divergence from the familiar mechanism is also seen in an antecedent of the Julia-Kocienski which involves the addition of α-metalated 2-alkylthio-2-oxazolines to aldehydes and ketones (Scheme 11).[129] The primary products of this olefination are thiiranes which are generated by Smiles rearrangement of the initial adduct followed by a cyclization event rather than loss of elemental sulfur. Desulfurization of the thiiranes with triphenylphosphine or triethyl phosphite leads to the net product of carbonyl olefination.



(Eq. 82)



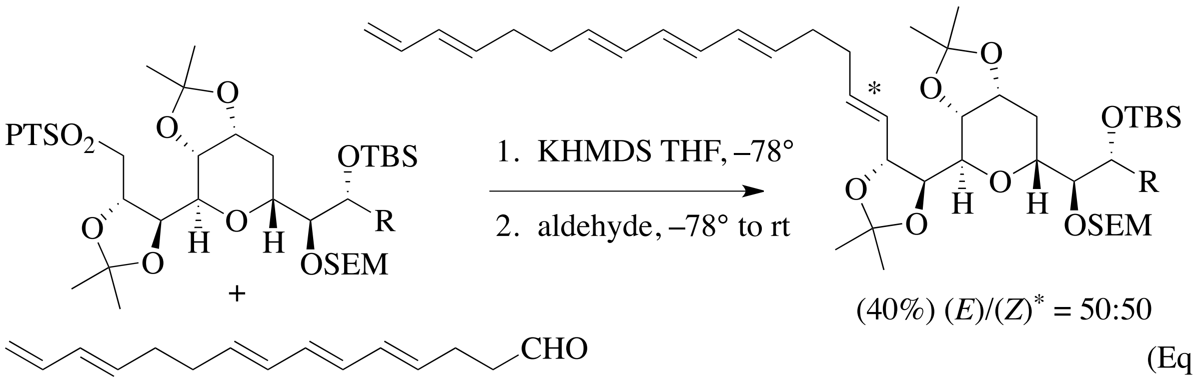
Scheme 11

COMPARISON WITH OTHER METHODS

The Julia-Kocienski olefination belongs to the broader class of connective alkene-forming reactions that involve the addition of a carbanion (or ylide) stabilized by an adjacent oxyphilic group to a carbonyl compound.[12] Typically, an ensuing cascade of fundamental steps then leads spontaneously to the formation of the olefin with the concomitant extrusion of an oxidized form of the activating group. Other well-known processes conforming to this general paradigm include the organophosphorus-based Wittig,[130-132] Horner-Wittig,[133] and Horner-Wadsworth-Emmons reactions,[130, 134] and the organosilicon-based Peterson olefination.[115, 135] The Julia-Lythgoe olefination[8, 10, 11] is a little different in that a separate reduction step is necessary to initiate elimination but like the other carbonyl olefination methods listed, it also provides the capability to splice together fragments with stereocontrol about a newly forged carbon-carbon double bond. In principle, all of the aforementioned processes offer the same strategic approach to alkene synthesis but one method may be favored over another in a given context for reasons of optimal yield, stereoselectivity, or general efficiency and convenience (including ease of precursor synthesis). Alternative approaches to access alkene-containing materials that are quite distinct from carbonyl olefination may also offer advantages to solve a particular synthesis problem. For example, transition metal-catalyzed processes involving the conversion of alkenes of one type into another type are of ever-increasing importance (e.g., cross-coupling, olefin metathesis); however, one should not lose sight of the fact that carbonyl olefination is often involved in the manufacture of the precursors for such transformations. A brief selection of cogent examples comparing the Julia-Kocienski olefination to other common carbonyl olefination tactics and to an assortment of different reactions for alkene synthesis, are now surveyed.

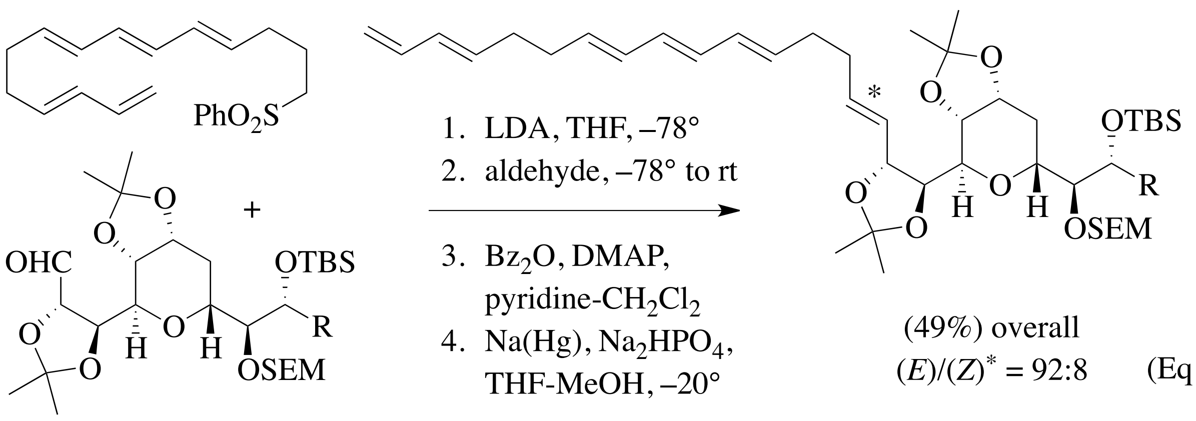
Julia-Lythgoe Olefination

The Julia-Lythgoe procedure for the olefination of carbonyl compounds using phenyl sulfone anions requires multiple synthetic operations to generate an alkene product.[7, 10] Nonetheless, it offers reliably high (*E*)-selectivity in various scenarios because of the radical nature of the reductive elimination stage[136, 137] and it continues to enjoy occasional application. For example, in a synthesis of a C31-C67 subunit of amphidinol 3, the Julia-Kocienski olefination fails to produce the target skipped polyene in a stereoselective manner (Eq. 83) whereas the Julia-Lythgoe method (albeit with a different component polarization) succeeds in generating the desired (*E*)-olefin with high stereoselectivity (Eq. 84).[138] Interestingly, other workers report the stereocontrolled synthesis of a closely related (*E*)-alkene [80%, (*E*)/(*Z*) > 95:5] using the same aldehyde depicted in Eq. 83 and a very similar PT sulfone under otherwise identical Julia-Kocienski reaction conditions.[139]



(40%) (*E*)/(*Z*)* = 50:50

(Eq. 83)

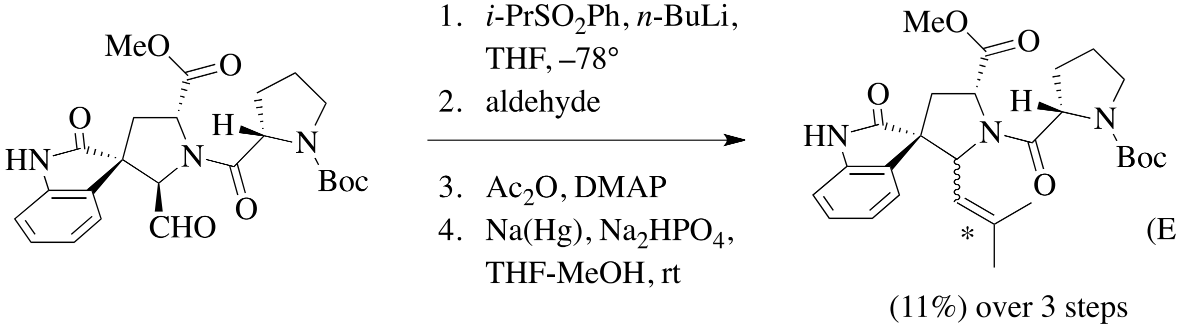


(49%) overall

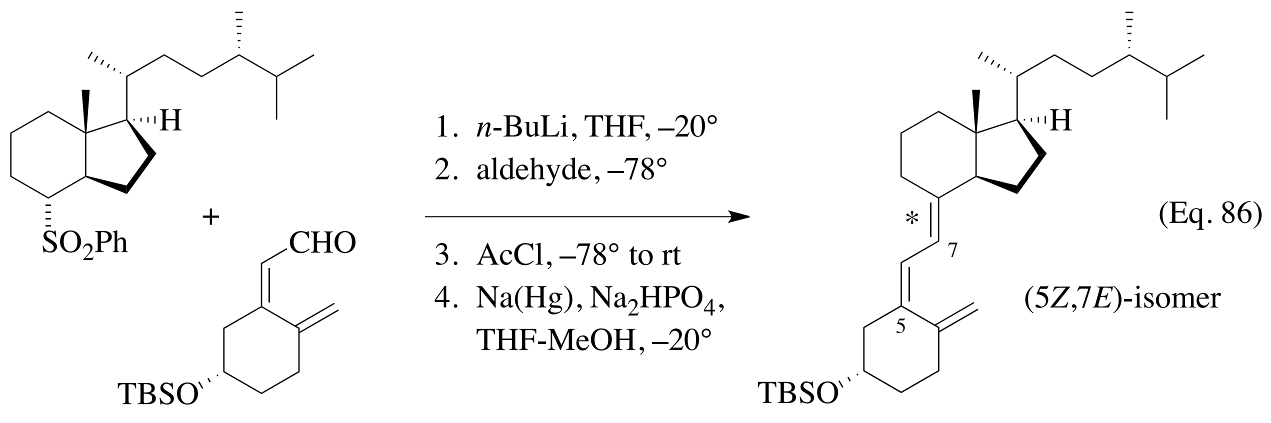
(*E*)/(*Z*)* = 92:8

(Eq. 84)

Although a few examples of the Julia-Lythgoe olefination out-performing the Julia-Kocienski olefination are documented, in a majority of cases in which the two processes have been directly compared, the latter method usually provides the superior outcome. For example, in a synthesis of spirotryprostatin B, conversion of a complex aldehyde to the corresponding isopropylidene derivative via the Julia-Lythgoe olefination results in a low yield and is accompanied by extensive epimerization of the aldehyde α-stereocenter (Eq. 85).[83] By contrast, the same product is accessed without detectable epimerization and in 78% yield by application of the Julia-Kocienski olefination using isopropyl PT sulfone (Eq. 51). The early development of the Julia-Lythgoe olefination was motivated by the need for new protocols capable of delivering the delicate conjugated triene system of the D vitamins with the natural (5*Z*,7*E*)-configuration.[140, 141] In this context, contemporary work also reveals that the Julia-Kocienski olefination offers generally better results than the older method. Thus, condensation of a CD-ring BT sulfone with an A-ring dienal, followed by silyl ether deprotection, affords vitamin D_2 in a 70% yield as a mixture of only two stereoisomers and favoring the desired (5*Z*,7*E*)-isomer over the (5*Z*,7*Z*)-isomer by 72:28 (Eq. 56).[38] A comparable synthesis of vitamin D_4 employing an analogous CD-ring phenyl sulfone via the Julia-Lythgoe protocol results in significant epimerization of the preexisting (*Z*)-alkene within the dienal and produces the target triene as a mixture of all four possible stereoisomers (Eq. 86).[142]



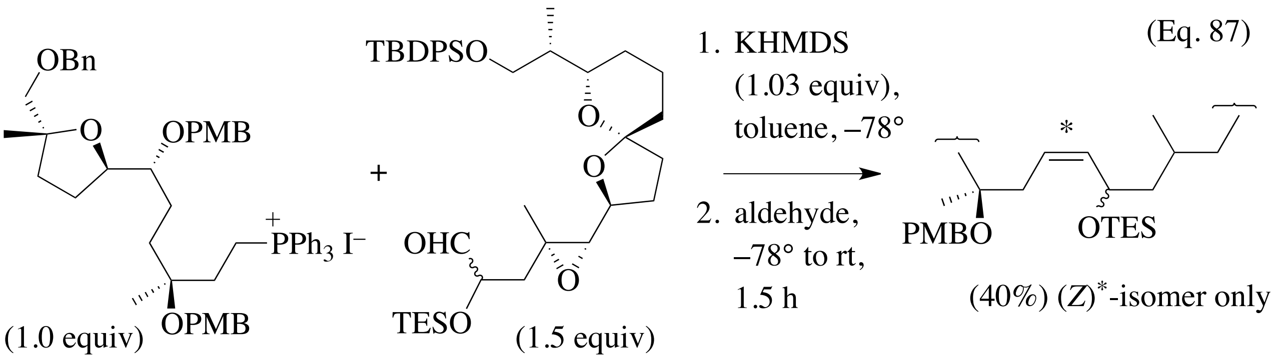
(Eq. 85)



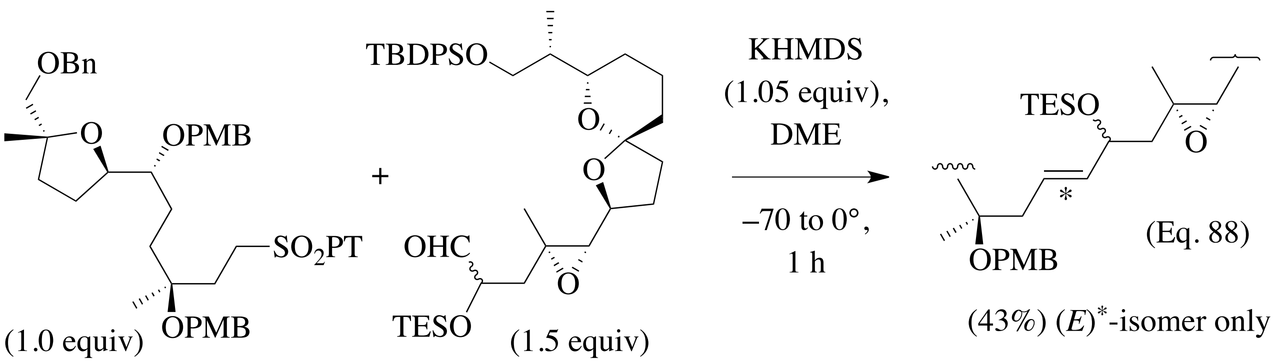
(68%) over 2 steps
(5*Z*,7*E*)/(5*Z*,7*Z*)/(5*E*,7*E*)/(5*E*,7*Z*)
= 75:10:10:5

Wittig Reaction and Other Phosphorus-Based Olefination Methods

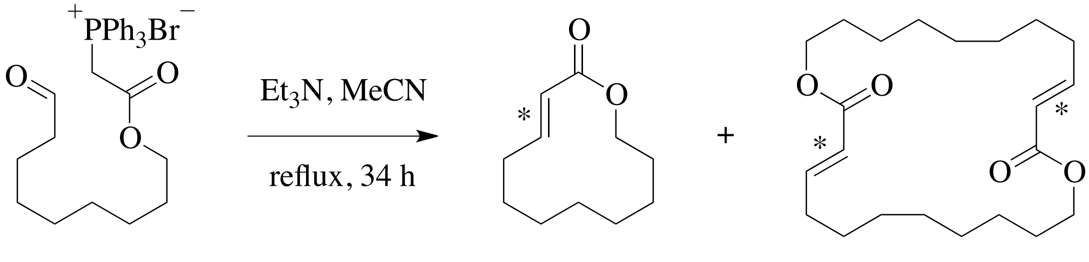
The venerable Wittig reaction[131] and the Julia-Kocienski olefination share a stereocomplementary relationship that can be confidently exploited. Thus, the well-known (albeit over-simplified) maxim for the Wittig reaction that non-stabilized phosphoranes preferentially yield (*Z*)-olefins whereas stabilized phosphoranes afford (*E*)-olefins,[143] can be approximately reversed when Julia-Kocienski reactions using comparable non-stabilized and stabilized sulfone anions are contemplated. For example, while evaluating different fragment linkage tactics en route to pectenotoxin-2, closely related Wittig (Eq. 87) and Julia-Kocienski (Eq. 88) olefinations employing non-stabilized nucleophilic components were observed to proceed with similar efficiencies but each favored formation of the opposite stereoisomer.[144] Also in line with expectation, it has been discovered that the synthesis of *α,β*-unsaturated macrolactones via intramolecular olefination using stabilized nucleophilic components leads preferentially to formation of (*E*)-macrolides and (*E*,*E*)-diolides via the Wittig reaction (Eq. 89)[145] but instead to (*Z*)-macrolides and (*Z*,*Z*)-diolides via the Julia-Kocienski olefination (Eq. 90).[146]



(40%) (*Z*)*-isomer only

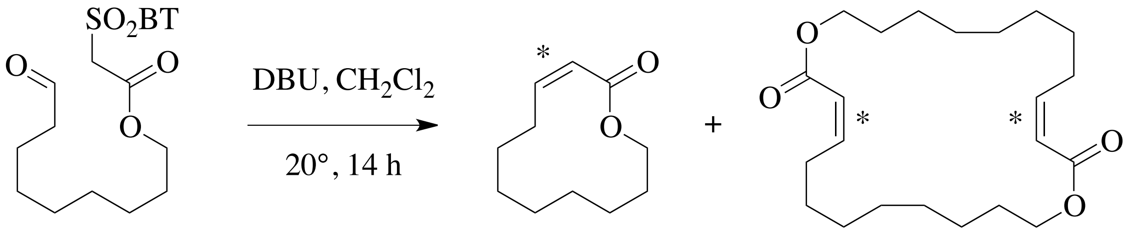


(43%) $(E)^*$-isomer only



(Eq. 89)

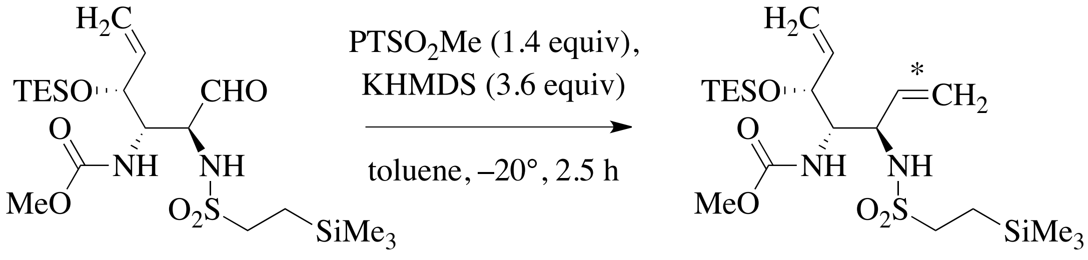
(55%) $(E)^*$-isomer (23%) $(E,E)^*$-isomer



(Eq. 90)

(44%) $(E)/(Z)^* = 13{:}87$ (21%) $(E,Z)/(Z,Z)^* = 23{:}77$

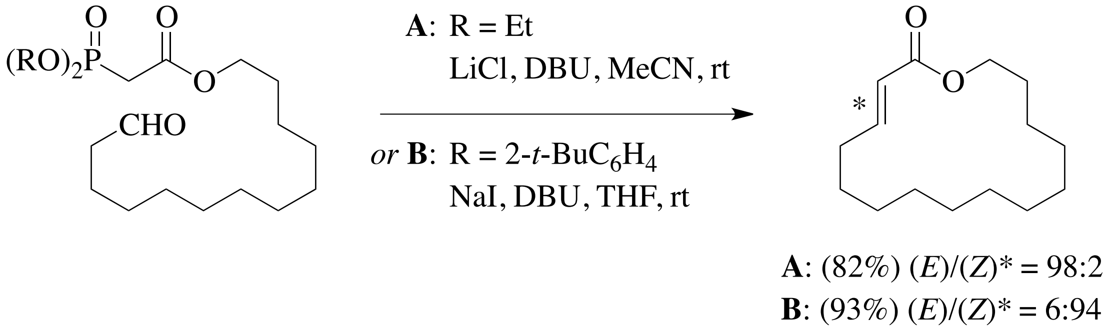
The Wittig reaction and the Julia-Kocienski olefination do not necessarily proceed with equal efficiency and in cases in which the stereochemical outcome is not a prime consideration, both methods are potentially worthy of consideration. Significantly, the sulfone-based method is competitive with the Wittig reaction for carbonyl methylenations. For example, in a synthesis of agelastatin A, methylenation of the illustrated aldehyde is unexpectedly difficult and the desired transformation was successfully achieved using methyl PT sulfone (Eq. 91) after the reaction failed with methylenetriphenylphosphorane and a number of other methylenation procedures (including Peterson and Tebbe methods).[147]



(Eq. 91)

(~61%)

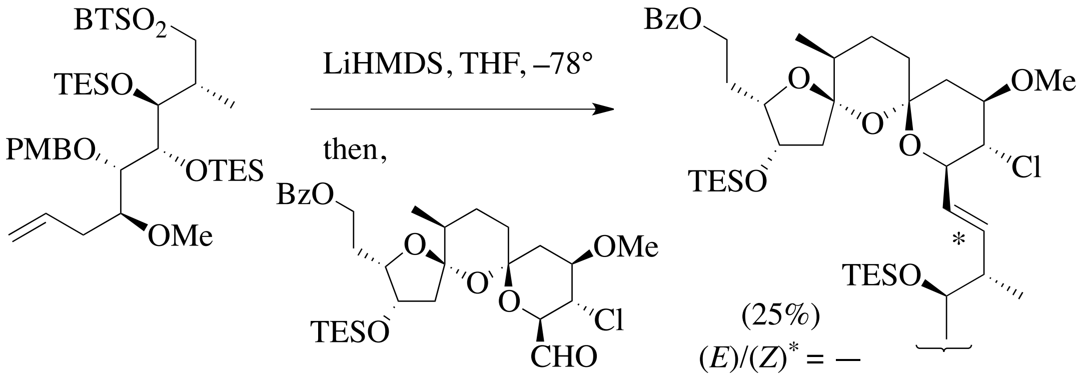
The Horner-Wadsworth-Emmons reaction[134] is narrower in scope than the Julia-Kocienski olefination, but it gives generally superior results for the synthesis of *α,β*-unsaturated carbonyl compounds. Furthermore, the Still-Gennari[148] or Ando[149] variants of this phosphonate-based method can be used if (*Z*)-configured products are desired rather than the more typically generated (*E*)-configured products. For example, the synthesis of *α,β*-unsaturated macrolactones using the Horner-Wadsworth-Emmons reaction is far more efficient and stereoselective than the Julia-Kocienski approach seen above (Eq. 90)[146] and (*E*)- or (*Z*)-enoates are available by selection of the appropriate reaction conditions and phosphonate type (Eq. 92).[150]



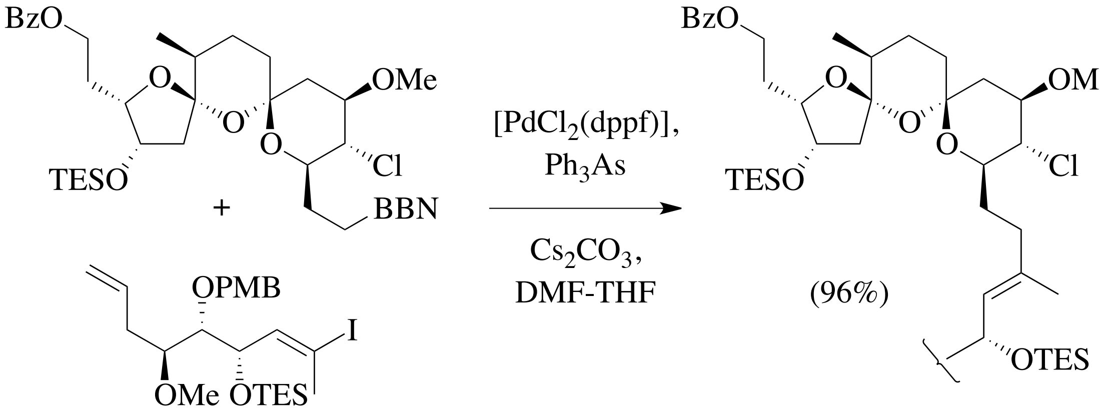
(Eq. 92)

Miscellaneous Methods for Alkene Synthesis

In relevant scenarios, palladium-catalyzed cross-coupling processes such as the Stille[151] and Suzuki-Miyaura[152] reactions may offer an alternative fragment linkage strategy to the Julia-Kocienski olefination or a comparable transformation. For example, a plan to access spirastrellolide A via the Julia-Kocienski olefination was abandoned when it was discovered that the requisite union between the illustrated BT sulfone and aldehyde could not be achieved in a high yield due to an extreme level of steric hindrance about the carbonyl group (Eq. 93).[153] Because olefination was being used purely to conjoin advanced fragments (i.e., the alkene formed was to be deleted by subsequent hydrogenation), a reworked plan involving *B*-alkyl Suzuki coupling targeting an adjacent bond disconnection was applicable and ultimately this strategy led to a vastly superior result (Eq. 94).[153]

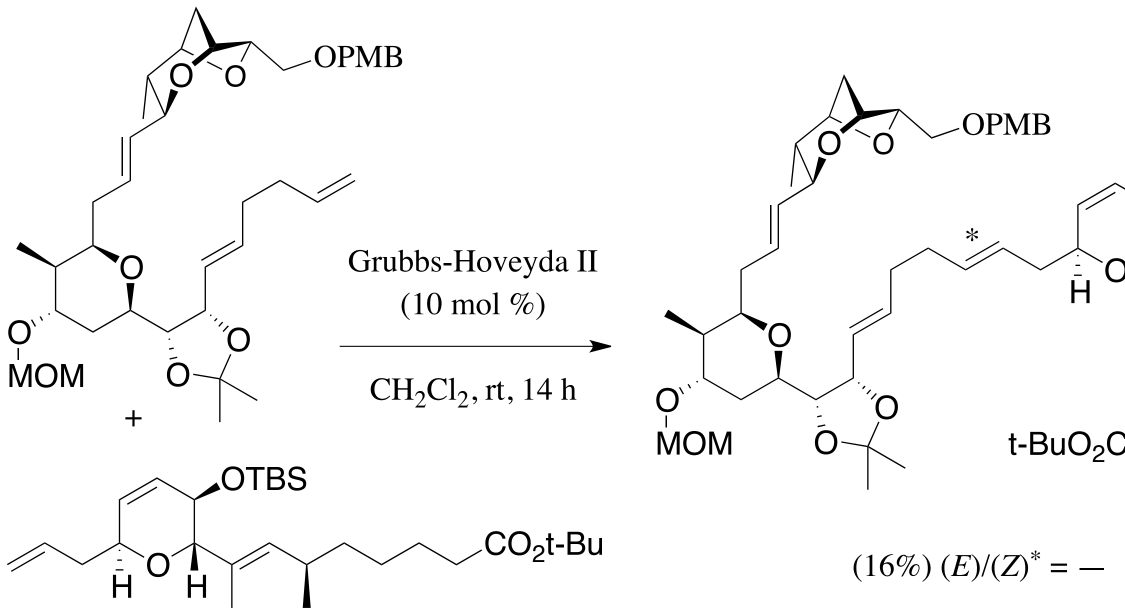


(Eq. 93)



(Eq. 94)

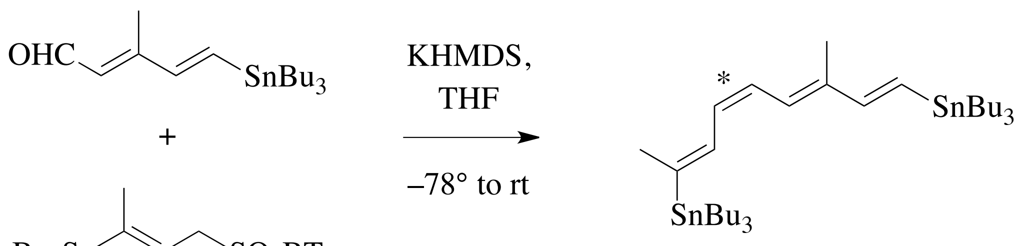
Olefin cross-metathesis has more recently emerged as a popular strategy to rival carbonyl olefination as an advanced fragment linkage tool.[154] Its advantage over a process like the Julia-Kocienski olefination is that precursor synthesis is trivial (i.e., the requisite terminal alkene addends can often be present from the outset of the synthesis). However, only certain pairs of olefinic reactants can be efficiently converted to the desired crossed adducts using this technique and one of the components must typically be used in a significant excess to bias the alkene shuffling toward the target.[155] A case in point is seen in a total synthesis of sorangicin A that incorporates a late-stage olefin cross-metathesis between two complex terminal alkenes (Eq. 95).[156] In this example, the desired 1,2-disubstituted (*E*)-configured alkene crossed adduct is obtained in low yield. By contrast, a closely related advanced fragment linkage of even greater complexity is successfully realized via the more controllable Julia-Kocienski olefination (Eq. 33).[62, 156]



(Eq. 95)

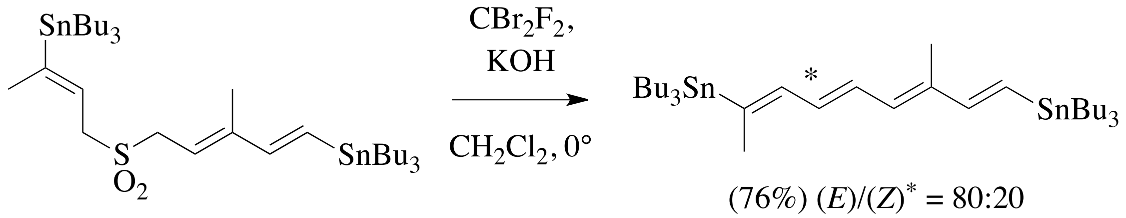
(16%) $(E)/(Z)^{*}$ = —

Finally, Julia-Kocienski olefinations offer a stereocomplementary outcome to the Ramberg-Bäcklund reaction[157] for the synthesis of α,ω-distannylated conjugated trienes, tetraenes, and pentaenes (Eqs. 96 and 97).[75] The high (*Z*)-selectivity realizable in this kind of Type IV Julia-Kocienski olefination is notable and it has been encountered in other scenarios (Eq. 47).[78]



(Eq. 96)

(73%) $(E)/(Z)^{*}$ = 5:95



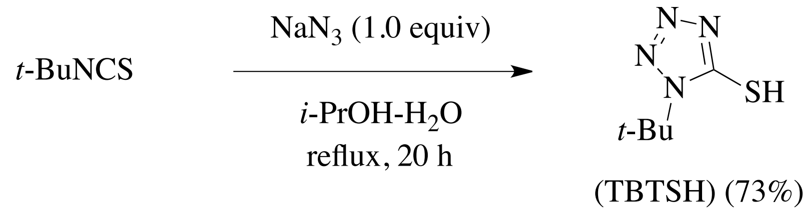
(Eq. 97)

(76%) $(E)/(Z)^{*}$ = 80:20

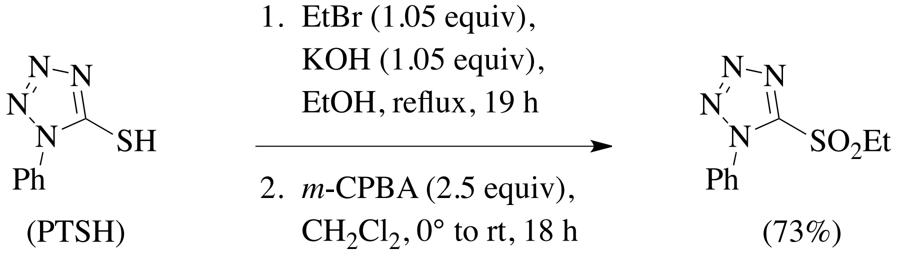
EXPERIMENTAL CONDITIONS

The Julia-Kocienski olefination typically calls for standard experimental techniques necessary to perform reactions under anaerobic, anhydrous, and low temperature conditions. In the most-commonly encountered scenario where a metal amide base is employed to deprotonate the sulfone, reactions should be conducted in anhydrous solvent under an inert atmosphere of N_2 or Ar at an initial temperature of –78° (dry-ice/acetone cold bath) or less cold for solvents that may freeze at this temperature (n.b., the melting point for pure DME is –58°). Dry and deoxygenated ethereal solvents (e.g., Et_2O, THF, and DME) are best obtained by traditional distillation from sodium benzophenone ketyl whereas solvents such as DMF or HMPA are dried by distillation from CaH_2 at reduced pressure and stored over 4Å molecular sieves.[158] Alternatively, anhydrous solvents collected from modern solvent purification systems that employ activated drying columns perform perfectly well, obviating the need for potentially dangerous distillation procedures.[159] Olefination reactions utilizing stabilized sulfone anions do not require any special precautions and can often be conducted without protection from air and in reagent-grade solvents used as received. Commercially available solutions of LiHMDS, NaHMDS, or KHMDS (all three bases are widely available at 1.0 M in toluene or THF) can be used directly as received, but the solvent the base is dispensed from should match, or have a similar polarity to, that called for in the olefination procedure since the net polarity of the overall reaction medium may affect stereoselectivity. Each of the aforementioned hexamethyldisilazide bases can also be purchased in solid form (the solids are flammable but non-pyrophoric) and thus custom stock solutions in any compatible solvent desired can be prepared, e.g., a solution of KHMDS in DME is preferable for the preparation of *trans* alkenes using the Kocienski procedure.[4, 160] LiHMDS and LDA are essentially interchangable; however, if the latter is used it is best freshly prepared by the addition of a solution of *n*-BuLi (1.5 to 2.5 M in hexanes, 1.0 equiv) to anhydrous diisopropylamine (distilled from CaH_2, 1.1 equiv) in the appropriate ethereal solvent (typically anhydrous THF) at ca. –20° under an inert atmosphere.[54] The olefination process does not necessarily reach completion at –78° (reaction mixtures are commonly allowed to warm somewhat before quenching with sat. aq. NH_4Cl) and so TLC analysis of a low-temperature reaction mixture can be misleading since the sampled aliquot will warm before it is spotted on the TLC plate.

EXPERIMENTAL PROCEDURES

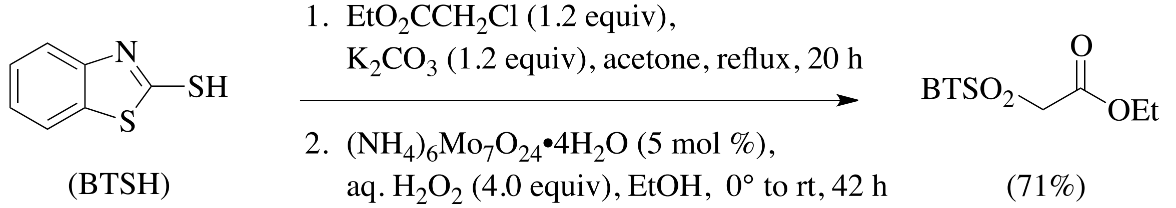


1-*tert*-Butyl-1*H*-tetrazole-5-thiol [Preparation of TBTSH].[5, 60, 161] *tert*-Butyl isothiocyanate (10.0 g, 86.8 mmol) in *i*-PrOH (25 mL) was added dropwise during 30 min via an additional funnel to a stirred solution of NaN_3 (CARE!! toxic and shock sensitive, 5.64 g, 86.8 mmol) in H_2O (25 mL) at rt. The resulting mixture was stirred at reflux for 20 h, then it was cooled in an ice bath and treated cautiously with conc. aq. HCl (15 mL). The acidified mixture was concentrated under vacuum and the residue stored at 0° overnight resulting in precipitation of a solid. The solid material was triturated with ice cold H_2O (20 mL), removed by filtration, and then dissolved in CH_2Cl_2 (50 mL). The organic phase was washed with brine (20 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was recrystallized from cyclohexane to afford the title compound (10.03 g, 63.4 mmol, 73%) as a colorless solid: mp 97-98° (cyclohexane); ^1H NMR (360 MHz, $CDCl_3$) δ 1.83 (s, 9H) ppm; ^{13}C NMR (90 MHz, $CDCl_3$) δ 162.8 (0), 63.6 (0), 27.6 (3C, 3) ppm.



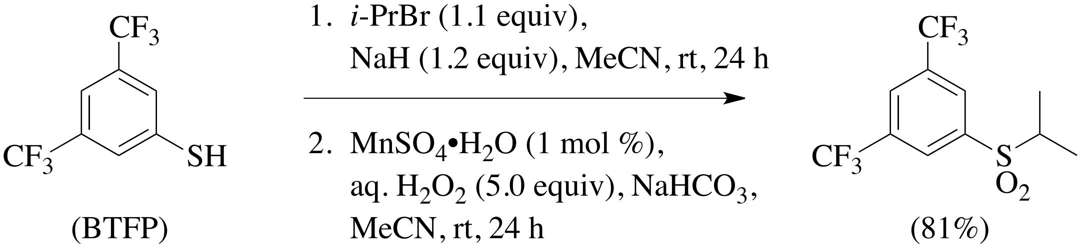
5-Ethylsulfonyl-1-phenyl-1*H*-tetrazole [Sulfone Preparation via Alkylation/Oxidation: PTSH, RBr, KOH/*m*-CPBA].[58] To a suspension of powdered KOH (3.3 g, 58.9 mmol) in EtOH (100 mL) was added 1-phenyl-1*H*-tetrazole-5-thiol (PTSH, 10.0 g, 56.2 mmol) and the resulting mixture was stirred at reflux for 1 h. After this time, ethyl bromide (4.4 mL, d = 1.47, 6.42 g, 58.9 mmol) was added dropwise and the reaction mixture was stirred at reflux for a further 18 h. The solvent was then removed under vacuum and the residue partitioned between H_2O (100 mL) and Et_2O (100 mL). The layers were then separated and the organic phase was washed with sat. aq. $NaHCO_3$ (2×75 mL) and brine (75 mL).

After drying ($MgSO_4$), the solvent was removed under vacuum to yield essentially pure 5-ethylthio-1-phenyl-1H-tetrazole (PTSEt, 9.86 g, 47.9 mmol, 86%) as a brown oil. A mechanically stirred suspension of the thioether (9.86 g, 47.9 mmol) and solid $NaHCO_3$ (20 g, 238 mmol) in CH_2Cl_2 (200 mL) was treated portionwise with 3-chloroperoxybenzoic acid (*m*-CPBA, 41.0 g, 50 wt.%, 119 mmol) and stirred vigorously for 18 h. After this time, the reaction mixture was poured into sat. $NaHCO_3$-$Na_2S_2O_3$ (200 mL) and was stirred vigorously for 3 h. The layers were then separated and the aqueous phase was extracted with CH_2Cl_2 (2×50 mL). The combined organic extracts were then washed with sat. aq. $NaHCO_3$ (3×75 ml), brine (75 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with a gradient of 40:60 to 55:45 Et_2O/hexanes) to yield the title compound (8.33 g, 35.0 mmol, 73% over two steps) as a colorless solid: mp 70-71° (10:90 EtOAc/hexanes); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.71–7.65 (m, 2H), 7.64–7.55 (m, 3H), 3.75 (q, *J* = 7.4 Hz, 2H), 1.52 (t, *J* = 7.4, 3H) ppm; ^{13}C NMR (90 MHz, $CDCl_3$) δ 153.2 (0), 133.1 (0), 131.6 (1), 129.8 (2C, 1), 125.2 (2C, 1), 50.9 (2), 7.0 (3) ppm.



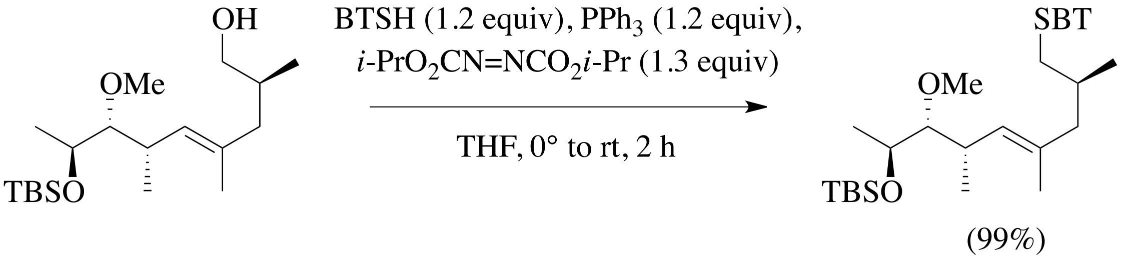
Ethyl (Benzothiazol-2-ylsulfonyl)acetate [Sulfone Preparation via Alkylation/Oxidation: BTSH, RCl, K_2CO_3/Mo(VI), H_2O_2].[19] A stirred suspension of 2-mercapto-1,3-benzothiazole (BTSH, 10.0 g, 59.8 mmol) and K_2CO_3 (9.9 g, 72 mmol) in acetone (100 mL) was treated with neat ethyl chloroacetate (7.6 mL, d = 1.16, 8.8 g, 72 mmol). The mixture was heated at reflux for 20 h, allowed to cool and filtered. Concentration of the filtrate under vacuum yielded 15.3 g of crude ethyl (benzothiazol-2-ylsulfanyl)acetate as a brown oil. A stirred solution of this material in EtOH (50 mL) at 0 ° was treated with $(NH_4)_6Mo_7O_{24}$•$4H_2O$ (3.7 g, 3.0 mmol) followed by aq. H_2O_2 (23.1 mL, d = 1.18, 27.2 g, 30 wt.%, 240 mmol). The resulting solution was allowed to warm slowly to rt and was stirred at rt for 42 h. After this time, the bulk of the EtOH solvent was removed *under vacuum* and the residue was partitioned between EtOAc (50 mL) and H_2O (50 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2x25 mL). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4), and concentrated under vacuum to yield 16.1 g of the title sulfone as an off-white solid

(>90% purity as judged by ^{1}H NMR analysis). Recrystallization from *tert*-butyl methyl ether (TBME) afforded analytically pure ethyl (benzothiazol-2-ylsulfonyl)acetate (12.1 g, 42.4 mmol, 71%) as colorless prisms: mp 58-59° (TBME); IR (neat) 3461, 2983, 1736, 1470, 1273, 1152, 1026, 910, 853, 770, 614 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (dd, J = 7.1, 1.8 Hz, 1H), 8.04 (dd, J = 7.0, 1.9 Hz, 1H), 7.67 (td, J = 7.2, 1.6 Hz, 1H), 7.62 (td, J = 7.3, 1.6 Hz, 1H), 4.58 (s, 2H), 4.18 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (0), 161.7 (0), 152.5 (0), 137.1 (0), 128.4 (1), 127.9 (1), 125.7 (1), 122.5 (1), 62.9 (2), 58.9 (2), 13.9 (3) ppm; MS (ES+) *m/z* 286 $(M+H)^+$. Anal. Calcd. for $C_{11}H_{11}NO_4S_2$: C, 46.30; H, 3.89; N, 4.91. Found: C, 46.40; H, 4.00; N, 4.95.

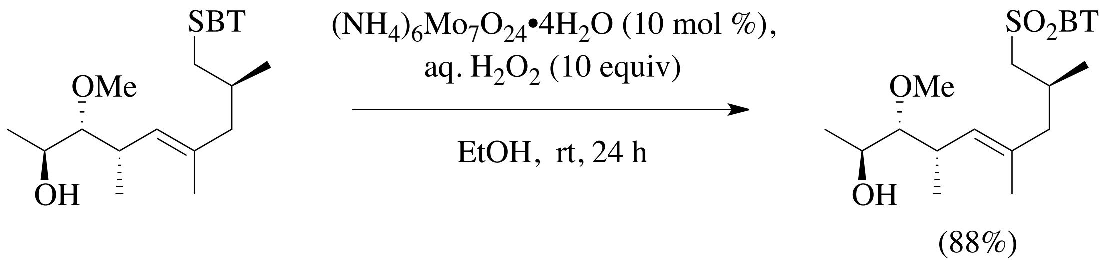


3,5-Bis(trifluoromethyl)phenyl Isopropyl Sulfone [Sulfone Preparation via Alkylation/Oxidation: BTFPSH, RBr, NaH/Mn(II), H_2O_2].[92] A mixture of 3,5-bis(trifluoromethyl)benzenethiol (BTFPSH, 1.23 g, 5.0 mmol) and NaH (150 mg, 95 wt. %, 6.0 mmol) in MeCN (15 mL) at rt under Ar was treated with isopropyl bromide (677 mg, 5.5 mmol) and stirred for 24 h. After this time, H_2O (20 mL) was added and the mixture was extracted with EtOAc (2x20 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under vacuum to afford the crude intermediate thioether (BTFPS*i*-Pr, 1.23 g, 4.27 mmol, 85%) as a yellow oil. A portion of the thioether (288 mg, 1.0 mmol) and $MnSO_4{\bullet}H_2O$ (2 mg, 0.012 mmol) were dissolved in MeCN (23 mL) and this solution was added dropwise to a stirred mixture of 30 wt.% aq. H_2O_2 (0.52 mL) and aq. $NaHCO_3$ (17 mL, 0.20 M) at 0°. Stirring was continued for 24 h and then the reaction mixture was treated with brine (30 mL) and was extracted with EtOAc (2x20 mL). The combined organic phases were dried (Na_2SO_4), concentrated under vacuum, and the residue was recrystallized from hexanes to afford the title compound (304 mg, 0.95 mmol, 95%) as a colorless solid: mp 80-83° (hexanes); IR 3091, 2989, 2937, 1621, 1363, 1286, 1136 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 2H), 8.17 (s, 1H), 3.28 (septet, J = 6.8 Hz, 1H), 1.35 (d, J = 6.9 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1 (0), 133.0 (q, $^2J_{CF}$ = 34.8

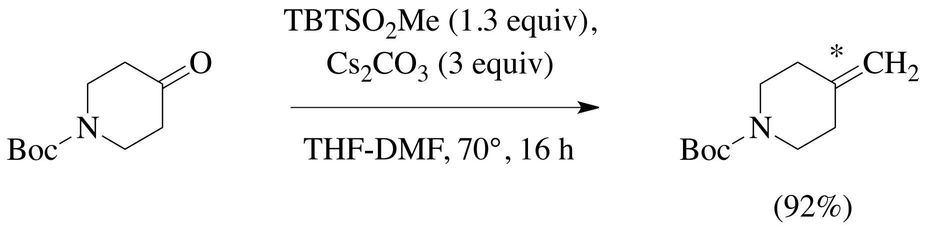
Hz, 2C), 129.3, 127.3 (1), 122.3 (q, $^1J_{CF}$ = 273.3 Hz, 2C), 55.8 (1), 15.4 (3, 2C) ppm; HRMS (EI) *m/z* 301.0325 (calcd. for $C_{11}H_{10}F_5O_2S$ (M–F)$^+$: 301.0322).



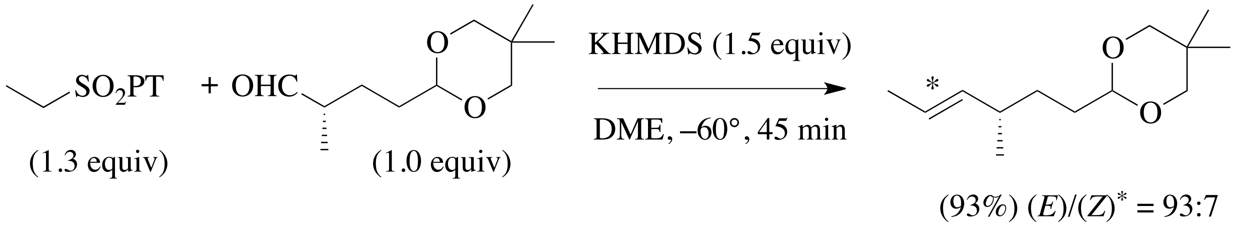
(*E*,2*S*,6*S*,7*R*,8*S*)-1-(1,3-Benzothiazol-2-ylsulfanyl)-8-(*tert*-butyldimethylsilyloxy)-7-methoxy-2,4,6-trimethylnon-4-ene [Mitsunobu Thioetherification].[58] To a stirred solution of the illustrated alcohol (1.47 g, 4.27 mmol) in anhydrous THF (25 mL) at rt under N_2 was added 2-mercaptobenzothiazole (BTSH, 0.86 g, 5.15 mmol) and triphenylphosphine (1.34 g, 5.11 mmol). The resulting solution was cooled to 0° and diisopropyl azodicarboxylate (DIAD, 1.10 ml, d = 1.03, 1.13 g, 5.59 mmol) was added dropwise. The cooling bath was then removed and the mixture was stirred at rt for 2 h. After this time, the solvent was removed under vacuum and the residue was further purified by column chromatography (SiO_2, eluting with 3:97 EtOAc/hexanes) to yield the title thioether (2.08 g, 4.21 mmol, 99%) as a colorless oil: $[\alpha]_D$ = +0.3 (c = 0.65, $CHCl_3$); IR (neat) 2956, 2928, 2894, 2856, 1461, 1428, 1255, 1103, 995, 836, 775, 755 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.86 (dm, *J* = 8.1 Hz, 1H), 7.75 (dm, *J* = 8.0 Hz, 1H), 7.41 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.29 (ddd, *J* = 8.1, 7.4, 1.2 Hz, 1H), 5.06 (dm, *J* = 9.9 Hz, 1H), 3.87 (dq, *J* = 6.2, 3.4 Hz, 1H), 3.54 (s, 3H), 3.45 (dd, *J* = 12.9, 5.3 Hz, 1H), 3.12 (dd, *J* = 12.9, 7.5 Hz, 1H), 2.88 (dd, *J* = 7.9, 3.4 Hz, 1H), 2.47 (ddq, *J* = 9.9, 7.8, 6.7 Hz, 1H), 2.27–2.10 (m, 2H), 1.93 (dd, *J* = 12.8, 8.0 Hz, 1H), 1.62 (d, *J* = 1.2 Hz, 3H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.03 (d, *J* = 6.5, 3H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.90 (s, 9H), 0.05 (s, 6H) ppm; ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.6 (0), 153.4 (0), 135.3 (0), 132.2 (0), 130.7 (1), 126.1 (1), 124.2 (1), 121.5 (1), 121.0 (1), 90.3 (1), 70.4 (1), 61.5 (3), 47.2 (2), 40.4 (2), 35.3 (1), 31.5 (1), 26.0 (3C, 3), 19.4 (3), 18.2 (0), 17.7 (3), 17.2 (3), 16.1 (3), –4.3 (3), –4.7 (3) ppm; MS (CI) *m/z* 493 (10%), 446 (6), 436 (4), 330 (47), 203 (97), 159 (33), 123 (63), 73 (100). Anal. Calcd. for $C_{26}H_{43}NO_2S_2Si$: C, 63.23; H, 8.78; N, 2.84. Found: C, 63.36; H, 8.84; N, 2.82.



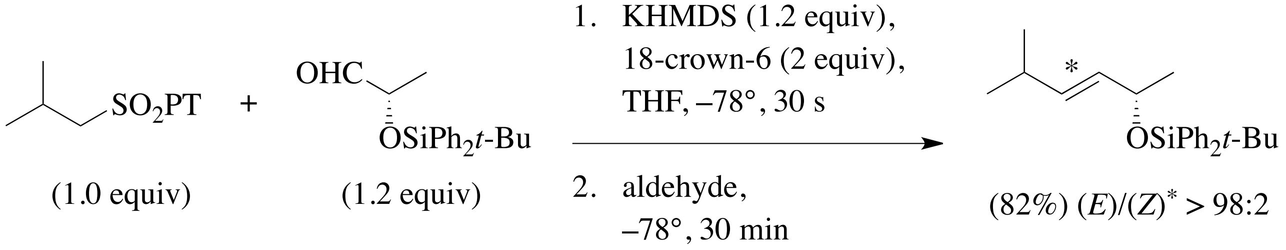
(*E*,2*S*,6*S*,7*R*,8*S*)-1-(1,3-Benzothiazol-2-ylsulfonyl)-7-methoxy-2,4,6-trimethylnon-4-en-8-ol [Thioether Oxidation: Cat. Mo(VI), H_2O_2].[58] To a stirred solution of the illustrated thioether (870 mg, 2.30 mmol) in EtOH (20 mL) at rt was added dropwise a yellow solution of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}$•$4H_2O$, 280 mg, 0.23 mmol] in aq. H_2O_2 (2.60 g, 30 wt. %, 22.9 mmol). The resultant mixture was stirred vigorously for 24 h and then was partitioned between Et_2O (30 mL) and H_2O (20 mL). The layers were shaken and then separated and the aqueous phase was extracted with Et_2O (3×10 mL). The combined organic extracts were washed with H_2O (2×20 mL), dried ($MgSO_4$), and then concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with 40:60 EtOAc/hexanes) to yield the title compound (835 mg, 2.03 mmol, 88%) as a colorless oil: $[\alpha]_D = -24.0$ (c = 1.09, $CHCl_3$); IR (neat) 3447, 2962, 2929, 1472, 1458, 1318, 1146, 1097, 763, 731, 632 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.19 (dm, J = 7.8 Hz, 1H), 8.01 (dm, J = 8.11 Hz, 1H), 7.63 (ddd, J = 8.1, 7.2, 1.4 Hz, 1H), 7.58 (ddd, J = 7.9, 7.2, 1.4 Hz, 1H), 5.02 (dm, J = 9.9 Hz, 1H), 3.79 (dq, J = 6.4, 3.8 Hz, 1H), 3.58 (dd, J = 14.4, 3.7 Hz, 1H), 3.50 (s, 3H), 3.23 (dd, J = 14.4, 8.7 Hz, 1H), 2.92 (dd, J = 8.0, 3.8 Hz, 1H), 2.50–2.39 (m, 2H), 2.07 (ddd, J = 13.4, 7.9, 1.1 Hz, 1H), 1.98 (dd, J = 13.6, 6.8 Hz, 1H), 2.0–1.80 (br, OH), 1.49 (d, J = 1.3, 3H), 1.10 (d, J = 6.4 Hz, 6H), 1.01 (d, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.7 (0), 152.8 (0), 136.8 (0), 131.6 (0), 131.3 (1), 128.2 (1), 127.8 (1), 125.5 (1), 122.5 (1), 89.4 (1), 69.2 (1), 61.4 (3), 60.0 (2), 47.4 (2), 35.5 (1), 26.6 (1), 20.2 (3), 17.6 (3), 17.5 (3), 15.9 (3) ppm; MS (CI) *m/z* 412 (100%), 380 (26), 362 (42), 322 (54). Anal. Calcd. for $C_{20}H_{29}NO_4S_2$: C, 58.36; H, 7.10; N, 3.40. Found: C, 58.17; H, 7.15; N, 3.42.



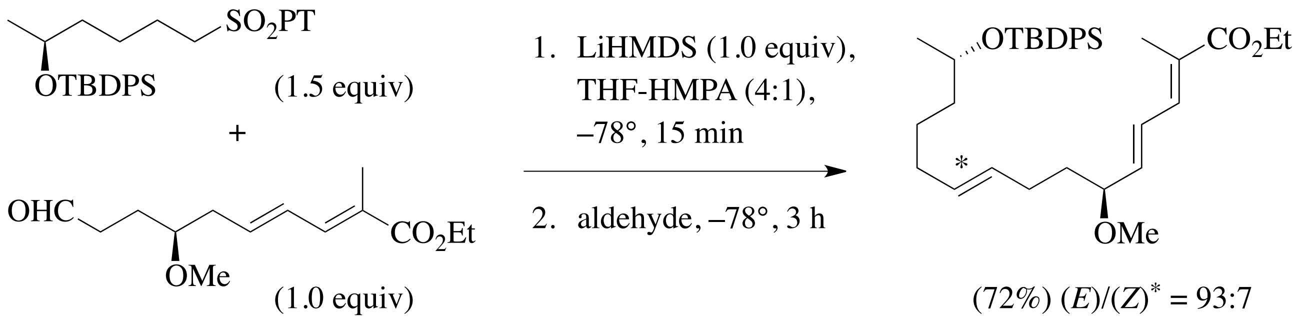
***N*-(*tert*-Butoxycarbonyl)-4-methylenepiperidine [Methylenation of a Ketone: $TBTSO_2Me$, Barbier, Cs_2CO_3, THF-DMF].**[60] A suspension of Cs_2CO_3 (248 mg, 0.760 mmol), *N*-Boc-4-piperidinone (50 mg, 0.251 mmol), and 1-*tert*-butyl-1*H*-tetrazol-5-yl methyl sulfone ($TBTSO_2Me$, 67 mg, 0.326 mmol, 1.3 eq) in anhydrous THF-DMF (3:1, 2.5 mL) was stirred at 70° under Ar for 16 h. After this time, the reaction mixture was cooled to rt, treated with sat. aq. NH_4Cl (10 mL), and extracted with TBME (20 mL). The combined organic extracts were washed with brine (10 M), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with 12.5:87.5 EtOAc/hexanes) to yield the title compound (46 mg, 0.233 mmol, 92%) as a colorless oil: IR (neat) 3074, 3006, 2978, 2941, 2909, 2864, 1699, 1652, 1365, 1238, 1171, 991, 892, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 2H), 3.42 (t, J = 6.0 Hz, 4H), 2.18 (t, J = 5.8 Hz, 4H), 1.47 (s, 9H) ppm; ^{13}C (100 MHz, $CDCl_3$) δ 154.9, 145.6, 109.2, 79.7, 45.6 (2C), 34.7 (2C), 28.6 (3C) ppm; MS (EI) *m/z* 197 ($M^{+\bullet}$, 10%), 141 (33), 124 (11), 96 (15), 82 (12), 57 (100). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71. Found: C, 66.84; H, 9.33.



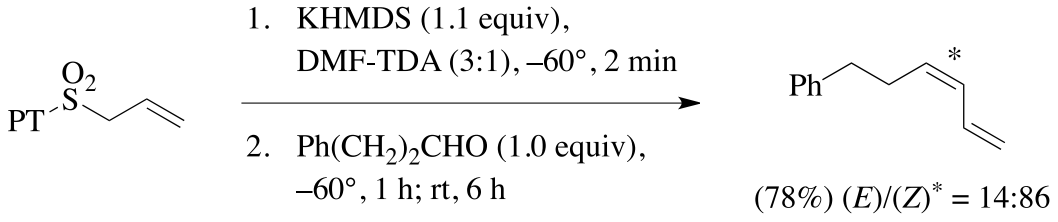
5,5-Dimethyl-2-[(*E*,*S*)-3-methylhex-4-enyl]-1,3-dioxane [Synthesis of a Non-conjugated 1,2-Disubstituted (*E*)-Alkene: PT Sulfone, Barbier, KHMDS, DME].[58] A stirred solution of ethyl (1-phenyl-1*H*-tetrazol-5-yl) sulfone (5.95 g, 25.0 mmol) and (*S*)-4-(5,5-dimethyl-1,3-dioxan-2-yl)-2-methylbutanal (3.82 g, 19.1 mmol) in anhydrous 1,2-dimethoxyethane (DME, 80 mL) at –60° (bath temperature) was treated dropwise via cannula with a solution of potassium hexamethyldisilazide (KHMDS, 7.00 g, 80 wt.%, 28.1 mmol) in anhydrous DME (40 mL) during 45 min. After this time, H_2O (10 mL) was added and the mixture was allowed to warm to rt. Et_2O (150 mL) and H_2O (80 mL) were added and the layers shaken and separated. The aqueous phase was extracted with Et_2O (3x50 mL) and the combined organic phases were washed with H_2O (3x50 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with a gradient of 0:100 to 10:90 Et_2O/hexanes) to yield the title compound (3.76 g, 17.7 mmol, 93%, (*E*)/(*Z*) = 93:7) as a colorless oil: $[\alpha]_D$ = +7.2 (c = 1.01, $CHCl_3$); IR (neat) 2956, 1454, 1394, 1122, 1044, 1020, 966 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 5.40 (ddq, *J* = 15.2, 6.2, 0.7 Hz, 1H), 5.26 (ddq, *J* = 15.2, 7.6, 1.3 Hz, 1H), 4.39 (t, *J* = 5.1 Hz, 1H), 3.60 (d, *J* = 9.9 Hz, 2H), 3.42 (d, *J* = 10.6 Hz, 2H), 2.04 (septet, *J* = 7.0 Hz, 1H), 1.63 (dm, *J* = 6.3 Hz, 3H), 1.70–1.52 (m, 2H), 1.44–1.27 (m, 2H), 1.19 (s, 3H), 0.72 (s, 3H), 0.96 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C (90 MHz, CDCl$_3$) δ 137.1 (1), 123.5 (1), 102.6 (1), 77.4 (2C, 2), 36.9 (1), 33.0 (2), 31.3 (2), 30.3 (0), 23.1 (3), 22.0 (3), 21.0 (3), 18.1 (3) ppm. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.36; H, 11.13.



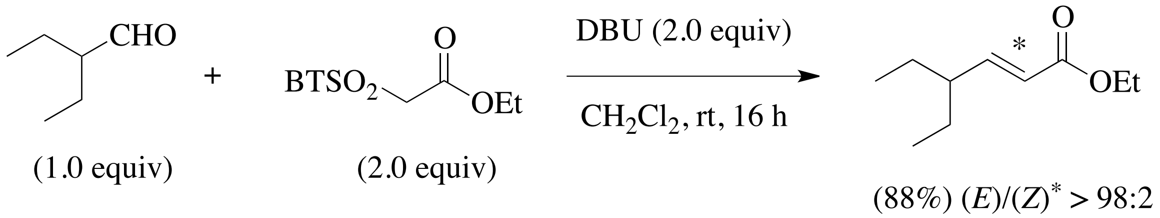
(*S,E*)-*tert*-Butyldiphenyl(5-methylhex-3-en-2-yloxy)silane [Synthesis of a Non-conjugated 1,2-Disubstituted (*E*)-Alkene: PT Sulfone, Premetalation, KHMDS, 18-crown-6, THF].[25] A stirred solution of isobutyl (1-phenyl-1*H*-tetrazol-5-yl) sulfone (50 mg, 0.188 mmol) and 18-crown-6 (99.4 mg, 0.376 mmol) in anhydrous THF (2 mL) at –78° was treated dropwise with potassium hexamethyldisilazide (KHMDS, 0.451 mL, 0.5 M in PhMe, 0.226 mmol) during 10 s. After 30 s, a solution of (*S*)-2-(*tert*-butyldiphenylsilyloxy)propanal (73 mg, 0.234 mmol) in anhydrous THF (0.5 mL) was added and stirring was continued for 30 min at –78°. Sat. aq. NH_4Cl (10 mL) was added and the mixture was extracted with EtOAc (2x10 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with a gradient of 0:100 to 5:95 EtOAc/hexanes) to yield the title compound (54.4 mg, 0.154 mmol, 82%, (*E*)/(*Z*) > 98:2) as a colorless oil: IR (neat) 3032, 2958, 2925, 2871, 2495, 2455, 967 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.72-7.33 (m, 10H), 5.42 (ddd, *J* = 15.6, 6.3, 0.5 Hz, 1H), 5.32 (dd, *J* = 15.5, 6.2 Hz, 1H), 4.26 (quintet, *J* = 6.2 Hz, 1H), 2.18 (m, 1H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.08 (s, 9H), 0.92 (d, *J* = 6.2 Hz , 3H), 0.90 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$) δ 137.0, 136.2, 136.1, 135.0, 131.5, 129.5, 127.6, 127.5, 70.8, 30.7, 27.2, 24.8, 22.5, 22.4, 19.4 ppm; MS (CI) *m/z* 353 (10%), 352 (28), 351 (100), 251 (24), 229 (22).



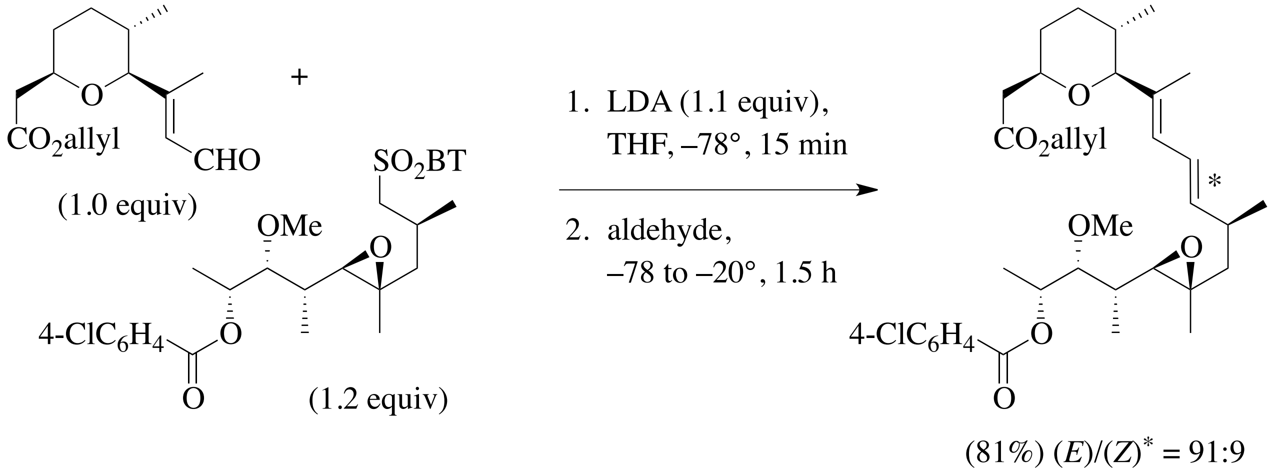
Ethyl (2*E*,4*E*,7*S*,10*E*,15*S*)-15-(*tert*-Butyldiphenylsilyloxy)-7-methoxy-2-methylhexadeca-2,4,10-trienoate [Synthesis of a Non-conjugated 1,2-Disubstituted (*E*)-Alkene: PT Sulfone, Premetalation, LiHMDS, THF-HMPA].[162] A solution of the sulfone (615 mg, 1.12 mmol) in anhydrous THF-HMPA (4:1, 4.0 mL) at –78° under Ar was treated with LiHMDS (0.75 mL, 1.0 M in THF, 0.75 mmol) and stirred for 15 min. After this time, a solution of the aldehyde (190 mg, 0.75 mmol) in THF-HMPA (4:1, 1.0 mL) was added dropwise and the resulting mixture was stirred at –78° for 3 h. Sat. aq. NH_4Cl (20 mL) was then added and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with a gradient of 4:96 to 6:94 EtOAc/hexanes) to afford the title compound (310 mg, 0.537 mmol, 72%, (*E*)/(*Z*)* = 93:7) as a colorless oil: $[\alpha]_D$ =–9.4 (c = 2.46, $CHCl_3$); IR (neat) 3620, 3404, 2929, 2360, 1704, 1365, 1219, 1105, 769, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76-7.57 (m, 4H), 7.46-7.31 (m, 6H), 7.19 (m, 1H), 6.41 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.08 (m, 1H), 5.42-5.25 (m, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.93-3.78 (m, 2H), 3.61 (m, 1H), 3.35 (s, 3H) 3.26 (m, 1H), 2.40 (t, *J* = 6.6 Hz, 2H), 2.12-1.77 (m, 8H), 1.94 (s, 3H), 1.58-1.21 (m, 9H), 1.06 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 138.6, 135.9, 134.8, 131.4, 129.7, 129.4, 127.6, 127.5, 127.4, 125.1, 79.8, 69.5, 68.9, 60.5, 56.8, 55.9, 39.0 (2C), 38.4, 37.3, 33.7, 32.5, 29.7, 28.4, 27.1, 25.2, 23.8, 23.2, 19.3, 14.3, 12.6 ppm; MS (ES) *m/z* 578 (100%); HRMS (ES) *m/z* 578.3767 (calcd. for $C_{36}H_{52}O_4Si$: 578.3791).



(*Z*)-6-Phenyl-1,3-hexadiene [Synthesis of a Conjugated 1,2-Disubstituted (*Z*)-Alkene via a Type II Olefination: PT Sulfone, Premetalation, KHMDS, DMF-TDA].[31] Potassium hexamethyldisilazide (KHMDS, 1.83 mL, 0.6 M in PhMe, 1.10 mmol) was added during 10 s to a stirred solution of allyl (1-phenyl-1*H*-tetrazol-5-yl) sulfone (250 mg, 1.00 mmol) in DMF-tris[2-(2-methoxyethoxy)ethyl]amine (10 mL, 3:1) at –60°. The resulting mixture was stirred for 2 min and then a solution of dihydrocinnamaldehyde (131 μL, d = 1.02, 134 mg, 1.00 mmol) in DMF (0.2 mL) was added dropwise. Stirring at –60° was continued for 1 h and then the mixture was allowed to warm to rt. After being stirred for 6 h at rt, sat. aq. NH_4Cl (10 mL) was added and the resulting mixture was extracted with EtOAc (3x10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with 2:98 EtOAc/hexanes) to afford the title compound (123 mg, 0.777 mmol, 78%, (*E*)/(*Z*) = 14:86) as a pale-yellow oil: IR (neat) 3031, 2956, 2887, 1524, 1487, 1334, 1001, 906, 800, 746, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.28 (m, 2H), 7.26-7.15 (m, 3H), 6.65 (dtd, *J* = 16.9, 10.6, 1.0 Hz, 1H), 6.06 (t, *J* = 10.9 Hz, 1H), 5.53 (dt, *J* = 10.5, 7.7 Hz, 1H), 5.22 (dd, *J* = 16.9, 1.7 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 2.67–2.80 (m, 2H), 2.55 (dd, J = 15.3, 7.6 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 137.4, 134.5, 132.3, 131.8, 129.9, 128.6, 128.5, 126.1, 117.5, 36.0, 29.8 ppm; HRMS (EI) *m/z* 158.1094 (calcd. for $C_{12}H_{14}$: 158.1096).

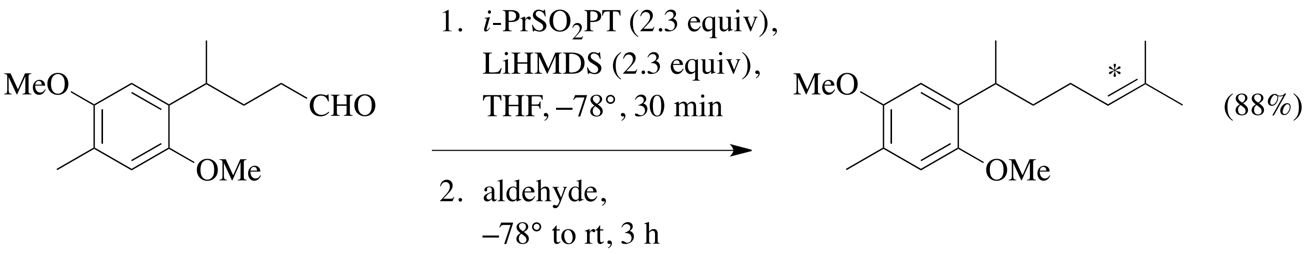


Ethyl (*E*)-4-Ethylhex-2-enoate [Synthesis of a Conjugated 1,2-Disubstituted (*E*)-Enoate via a Type II Olefination: BT Sulfone, Barbier, DBU, CH_2Cl_2].[19] A solution of ethyl (benzothiazol-2-ylsulfonyl)acetate (228 mg, 0.80 mmol) in CH_2Cl_2 (5 mL) was treated with DBU (0.12 mL, d = 1.02, 122 mg, 0.80 mmol) followed by 2-ethylbutanal (40 mg, 0.40 mmol) and was stirred at rt for 16 h. After this time, sat. aq. NH_4Cl (5 mL) was added and the layers shaken and separated. The aqueous phase was extracted with CH_2Cl_2 (2x10 mL) and the combined organic phases were washed with brine (10 mL), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with a gradient of 5:95 to 20:80 EtOAc/hexanes) to yield the title compound (60 mg, 0.353 mmol, 88%, (*E*)/(*Z*) > 98:2) as a colorless oil: IR (neat) 2930, 1731, 1461 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 15.7, 9.2 Hz, 1H), 5.79 (dm, *J* = 15.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.98 (dtt, *J* = 9.2, 8.3, 6.0 Hz, 1H), 1.57-1.41 (m, 2H), 1.39-1.24 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0 (0), 153.5 (1), 121.5 (1), 60.3 (2), 46.2 (1), 27.0 (2C, 2), 14.5 (3), 11.8 (2C, 3) ppm.

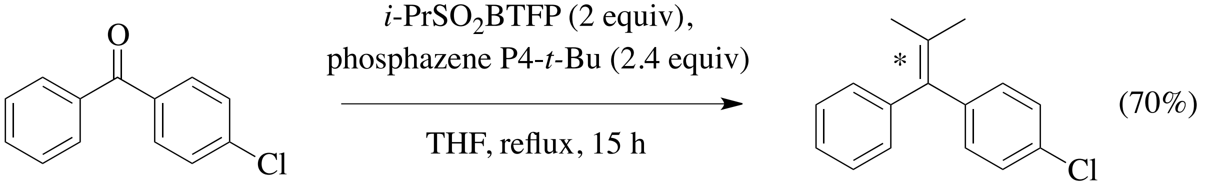


18-*O*-(4-Chlorobenzoyl)herboxidiene Allyl Ester [Synthesis of a Conjugated 1,2-Disubstituted (*E*)-Alkene via a Type III Olefination: BT Sulfone, Premetalation, LDA, THF].[58] To a stirred solution of the illustrated sulfone (331 mg, 0.58 mmol) in anhydrous THF (6 mL) at –78° under N_2 was added dropwise a solution of freshly prepared lithium diisopropylamide (LDA, 1.3 mL, 0.41 M in THF, 0.53 mmol) and the resulting deep-yellow solution was stirred for 15 min. A solution of the illustrated enal (131 mg, 0.49 mmol) in anhydrous THF (2 mL) was then added dropwise. The color of the reaction mixture lightened immediately. The mixture was stirred for 30 min at –78° and then was allowed to warm to –20° during 1 h. The resulting colorless solution was quenched by the addition of sat. aq. NH_4Cl (2 mL) and allowed to warm to rt with vigorous stirring. EtOAc (15 mL) and H_2O (15 mL) were added and the layers shaken and separated. The aqueous phase was extracted with EtOAc (3×5 mL) and the combined organic extracts were washed with brine (5 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with 15:85 EtOAc/hexanes) to yield the title compound (246 mg, 0.399 mmol, 81%, (*E*)/(*Z*)* = 91:9) as a colorless oil: $[\alpha]_D$ = –25 (c = 0.40, $CHCl_3$); IR (neat) 2927, 1720, 1091 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.22 (dd, *J* = 15.0, 10.9 Hz, 1H), 5.94–5.82 (m, 1H), 5.88 (dm, *J* = 10.4 Hz, 1H), 5.42 (dd, *J* = 15.0, 8.9 Hz, 1H), 5.30 (dm, *J* = 17.9 Hz, 1H), 5.27

(quintet, J = 6.9 Hz, 1H), 5.20 (dm, J = 10.5, 1H), 4.58 (d, J = 5.5 Hz, 2H), 3.83–3.74 (m, 1H), 3.52 (s, 3H), 3.37 (dd, J = 6.9, 3.9 Hz, 1H), 3.31 (d, J = 9.9 Hz, 1H), 2.62 (d, J = 9.7 Hz, 1H), 2.61 (dd, J = 15.1, 6.5 Hz, 1H), 2.43 (dd, J = 15.2, 6.5 Hz, 1H), 2.47–2.34 (m, 1H), 1.91 (dd, J = 13.5, 4.6 Hz, 1H), 1.88–1.80 (m, 1H), 1.72–1.65 (m, 1H), 1.69 (s, 3H), 1.57–1.46 (m, 2H), 1.40–1.15 (m, 3H), 1.29 (d, J = 6.5 Hz, 3H), 1.24 (s, 3H), 1.03 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H), 0.64 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (90 MHz, $CDCl_3$) δ 171.2 (0), 165.3 (0), 139.4 (1), 139.4 (0), 135.3 (0), 132.3 (1), 131.2 (2C, 1), 129.3 (0), 128.8 (2C, 1), 128.3 (1), 125.3 (1), 118.0 (2), 90.8 (1), 84.7 (1), 74.0 (1), 73.3 (1), 66.0 (1), 65.1 (2), 61.5 (3), 60.9 (0), 47.1 (2), 41.6 (2), 35.4 (1), 35.2 (1), 32.4 (2), 32.2 (1), 31.8 (2), 22.3 (3), 17.7 (3), 16.8 (3), 16.8 (3), 12.0 (3), 10.8 (3) ppm; HRMS (CI) m/z 616.3169 (calcd. for $C_{35}H_{49}ClO_7$: 616.3167).



1,4-Dimethoxy-2-methyl-5-(6-methylhept-5-en-2-yl)benzene [Synthesis of a Trisubstituted Alkene: PT Sulfone, LiHMDS, THF].[163] A solution of the sulfone (4.30 g, 17.0 mmol) in anhydrous THF (100 mL) at –78° under Ar was treated dropwise with LiHMDS (10.8 mL, 1.60 M in THF, 17.3 mmol) and stirred for 30 min. The resulting yellow solution of sulfone anion was added in one portion with a precooled syringe to a stirred solution of 4-(2,5-dimethoxy-4-methylphenyl)pentanal (1.77 g, 7.50 mmol) in anhydrous THF (100 mL). The reaction mixture was stirred at –78° for 3 h and then it was allowed to warm to rt during 10 min. After this time, H_2O (100 mL) was added and the mixture was extracted with Et_2O (2x200 mL) and the combined organic phases were washed with brine (50 mL) and then concentrated under vacuum. The residue was purified by column chromatography (SiO_2, eluting with 5:95 EtOAc/hexanes) to yield the title compound (1.73 g, 6.59 mmol, 88%) as a colorless oil: IR (neat) 2927, 2852, 1504, 1465, 1398, 1208, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 2H), 5.12 (t, J = 7.2 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.14 (sextet, J = 7.6 Hz, 1H), 2.20 (s, 3H), 2.00-1.85 (m, 2H), 1.67 (s, 3H), 1.67-1.48 (m, 2H), 1.54 (s, 3H), 1.18 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9 (0), 150.8 (0), 133.9 (0), 130.9 (0), 124.8 (1), 124.1 (0), 114.2 (1), 109.7 (1), 56.2 (3), 55.9 (3), 37.3 (2), 31.9 (1), 26.3 (2), 25.6 (3), 21.2 (3), 17.5 (3), 16.0 (3) ppm; HRMS (ES) *m/z* 285.1839 (calcd. for $C_{17}H_{26}NaO_2$: 285.1831).



1-(4-Chlorophenyl)-2-methyl-1-phenylpropene [Synthesis of a Tetrasubstituted Alkene: BTFP Sulfone, Barbier, P4-*t*-Bu, THF].[92] A stirred solution of 3,5-bis(trifluoromethyl)phenyl isopropyl sulfone (*i*-PrSO$_2$BTFP, 96 mg, 0.30 mmol) and 4-chlorobenzophenone (32 mg, 0.15 mmol) in anhydrous THF (6 mL) at rt under Ar was treated dropwise with phosphazene base P4-*t*-Bu (0.36 mL, 1.0 M in *n*-hexane, 0.36 mmol). The resulting mixture was heated to reflux overnight and was then cooled and concentrated under vacuum. H_2O (5 mL) was added and the mixture was extracted with pentane (2x10 mL). The combined organic phases were dried (Na_2SO_4), concentrated under vacuum, and the residue was purified by column chromatography (SiO_2, eluting with hexanes) to yield the title compound (25.5 mg, 0.105 mmol, 70%) as a colorless oil: IR (neat) 3083, 3064, 3026, 2983, 2918, 2848, 1649, 1600, 1568, 1482, 1450, 1401, 1369 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.03 (m, 9H), 1.79 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 141.6, 135.8, 131.7, 131.2, 129.8, 128.0, 127.9, 126.2, 22.5, 22.4 ppm; HRMS (EI) *m/z* 242.0871 (calcd. for $C_{16}H_{15}Cl$: 242.0862).

TABULAR SURVEY

Tables 1–6 are organized by the sulfone component of the olefination reaction according to the number of skeletal carbon atoms (carbon atoms found in the activators, heteroatom linked subdomains, and protecting-groups are excluded from the count) and in order of increasing oxidation state. Within clusters of otherwise identical sulfones, results are grouped according to the activating sulfone moiety in alphabetical order of their abbreviation. Unless otherwise stated, it should be assumed that the sulfone is the first component added to the reaction mixture. Use of a premetalation protocol is indicated by reaction conditions written as '(a) base; (b) add aldehyde/ketone'; otherwise, a Barbier protocol (i.e., sulfone and carbonyl compound premixed before addition of base) is involved. For each example an asterisk (*) clearly identifies the site of the newly introduced alkene in the product and the given (*E*)/(*Z*) ratios are about this double bond unless otherwise stated. Reaction stoichiometry is noted only when it differs significantly from the typical values seen in the experimental procedures given above. In general, the more valuable reaction coupling partner (sulfone or carbonyl compound) is used as the limiting reagent and a slight excess (1.1 to 1.5 equivalents) of the other component is employed. The quantity of base commonly used at least equals the amount of sulfone in the reaction mixture and when other protic sites are present (e.g., free hydroxyl groups, amide NH), an additional equivalent of base is used to accommodate each effective source of proton. The tables contain all examples published in the primary peer-reviewed literature by the end of 2013 as retrieved by SciFinder Scholar and Reaxys substructure, keyword, and citation searches.

The following abbreviations, excluding those found in "*The Journal of Organic Chemistry* Standard Abbreviations and Acronyms" are used in the text and the Tables.

ADDP = 1,1'-(azodicarbonyl)dipiperidide
BT = benzothiazol-2-yl
IM = 1-methylimidazol-2-yl
IQ = isoquinolin-1-yl
NAP = 2-naphthylmethyl
NP = 4-nitrophenyl
P4-*t*-Bu = 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene)
PT = 1-phenyl-1*H*-tetrazol-5-yl
PYM = pyrimidin-2-yl
PYR = pyrid-2-yl
SES = trimethylsilylethylsulfonyl
TBT = 1-*tert*-butyl-1*H*-tetrazol-5-yl
TDA = tris[2-(2-methoxyethoxy)ethyl]amine
TZ = 4-methyl-1,2,4-triazol-3-yl

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

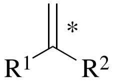
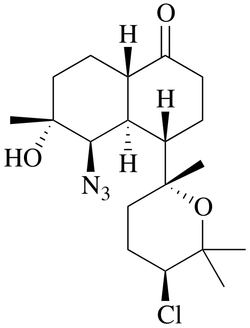
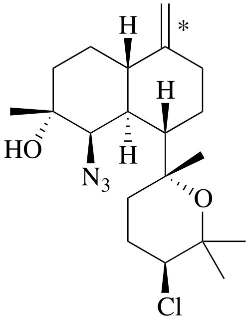
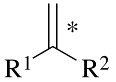
	Sulfone and Carbonyl Component		Conditions	Product(s) and Yield(s) (%)					Refs.
C_1	$BTSO_2Me$	R^1COR^2	**A**: LDA, THF, –78°, 3 h; rt, 1 h *or* **B**: 1. LDA, THF, –78° 2. Aldehyde, –78° to rt		R^1	R^2			3
					n-C_9H_{19}	H	**A**	(20)	
					4-$MeOC_6H_4$	H	**A**	(64)	
					4-$Me_2NC_6H_4$	H	**A**	(44)	
					–$(CH_2)_2$–CH(t-Bu)–$(CH_2)_2$–		**A**	(21)	
					4-$MeOC_6H_4$	Me	**A**	(50)	
					Ph	Ph	**A**	(55)	
					Ph	Ph	**B**	(11)	
	$BTSO_2Me$ (4 eq)		LiHMDS, THF, –78°, 3 h		(88)				164
	$BTFPSO_2Me$	R^1R^2CO	**A**: KOH, n-Bu_4NBr, THF, rt, 16 h *or* **B**: P4-t-Bu, THF-HMPA, 0° to rt, 16 h		R^1	R^2			56
					4-$MeOC_6H_4$	H	**A**	(60)	
					6-MeO-2-naphthyl	H	**A**	(80)	
					6-MeO-2-naphthyl	H	**B**	(82)	
					$Ph(CH_2)_2$	H	**B**	(30)	
					(E)-PhCH=CH	H	**A**	(50)	
					–$(CH_2)_2CH(t\text{-Bu})(CH_2)_2$–		**A**	(10)	
					–$(CH_2)_2CH(t\text{-Bu})(CH_2)_2$–		**B**	(74)	
					–$(CH_2)_2C(OCH_2CH_2O)(CH_2)_2$–		**B**	(41)	
					Ph	Ph	**B**	(36)	
					4-ClC_6H_4	4-ClC_6H_4	**B**	(50)	

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

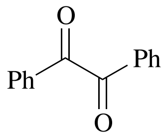
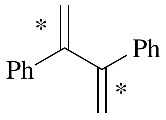
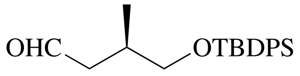
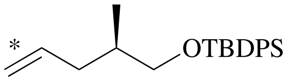
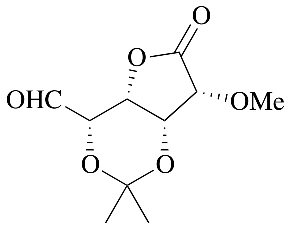
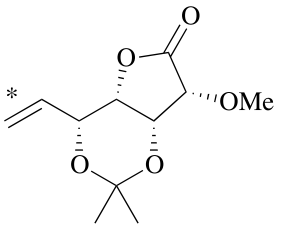
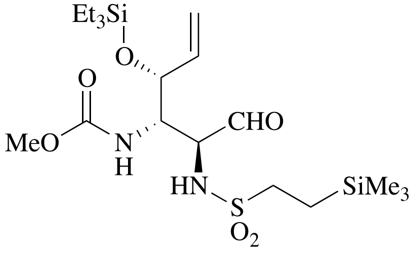
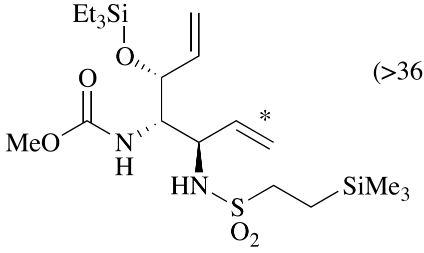
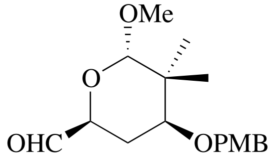
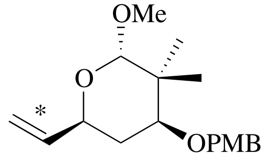
	Sulfone and Carbonyl Component		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1	$BTFPSO_2Me$		Sulfone (4 eq), diketone (1 eq) P4-*t*-Bu, THF-HMPA, 0° to rt, 16 h	 (45)	56
	$PTSO_2Me$		LiHMDS, THF, –78°, 3 h; rt	 (81)	165
	$PTSO_2Me$		LiHMDS, DMF-HMPA –35° to 35°, 12 h	 (6)	166
	$PTSO_2Me$		KHMDS, THF-PhMe, –20°	 (>36)	147
	$PTSO_2Me$		KHMDS, THF, PhMe –78°, 4 h; rt, 24 h	 (>44)	167

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

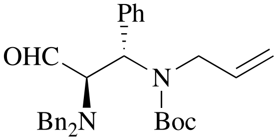
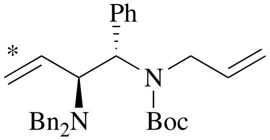
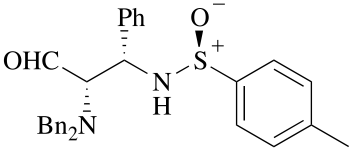
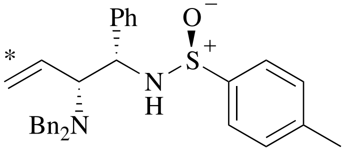
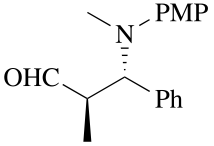
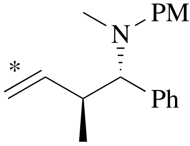
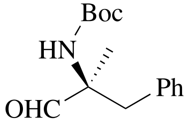
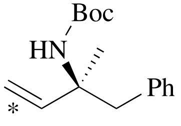
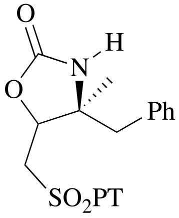
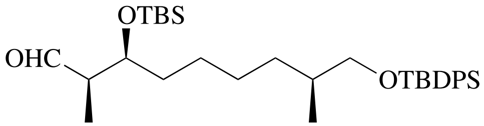
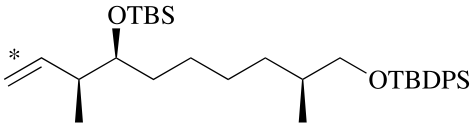
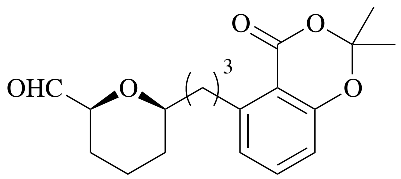
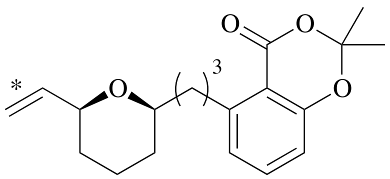
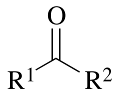
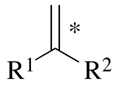
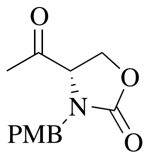
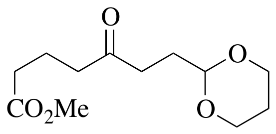
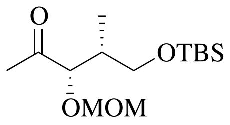
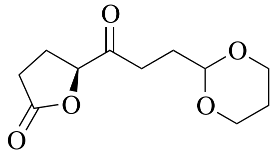
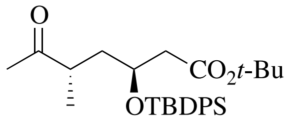
	Sulfone and Carbonyl Component		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1	$PTSO_2Me$		1. KHMDS, THF, –20° 2. Aldehyde	 (88)	168
	$PTSO_2Me$		1. KHMDS, THF, –20° 2. Aldehyde	 (≥70)	169
	$PTSO_2Me$		KHMDS, PhMe, –20°, 1.5 h	 (90)	170
	$PTSO_2Me$		1. $M(SiMe_3)_2$, THF, –20° 2. Aldehyde	 +  M Time Li 3 h (25) Na 24 h (52) K 19 h (40) "substantial amounts"	171
	$PTSO_2Me$		1. NaHMDS, THF, –78°, 30 min 2. Aldehyde; rt	 (74)	172

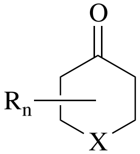
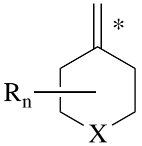
TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

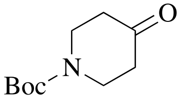
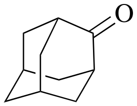
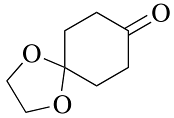
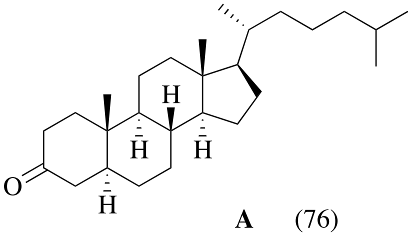
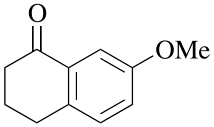
	Sulfone and Carbonyl Component		Conditions	Product(s) and Yield(s) (%)		Refs.
C_1						
	$PTSO_2Me$		1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 4 h		(93)	173 174
	$TBTSO_2Me$		**A**: NaHMDS, THF, –78° to rt, 16 h *or* **B**: Cs_2CO_3, THF-DMF, 70°, 16 h			60

Acyclic ketone R^1R^2CO			Acyclic ketone R^1R^2CO		
	**A**	(85)		**A**	(99)
	**A**	(77)		**A** **B**	(59) (93)[a]
	**A**	(90)			

[a] Partial racemization of ketone occurred (94% to 61% ee).

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

	Sulfone and Carbonyl Component	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1	$TBTSO_2Me$ 	**A**: NaHMDS, THF, –78° to rt, 16 h *or* **B**: Cs_2CO_3, THF-DMF, 70°, 16 h		60

Cyclic ketone			Cyclic ketone		
	**A**	(92)		**B**	(57)
	B	(93)			
	**A**	(90)			
	B	(84)			
	**B**	(45)		**A**	(76)

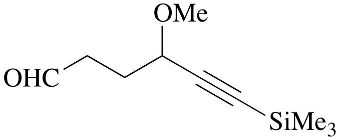
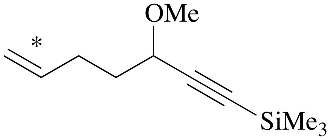
	Sulfone and Carbonyl Component	Conditions	Product(s) and Yield(s) (%)	Refs.
	$TBTSO_2Me$ 	Cs_2CO_3, THF-DMF, 70°, 16 h	 (96)	60

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

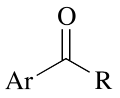
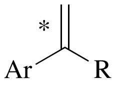
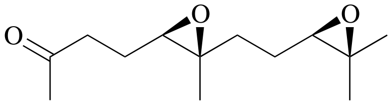
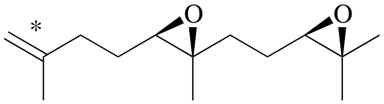
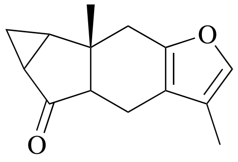
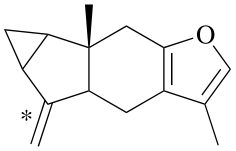
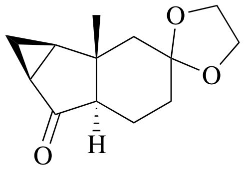
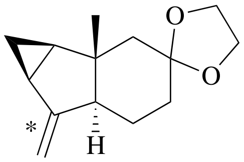
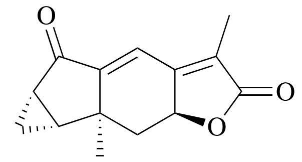
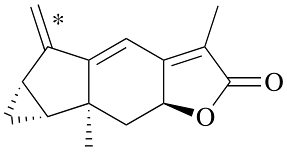
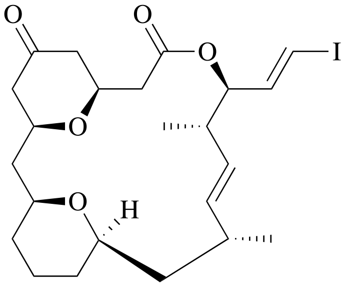
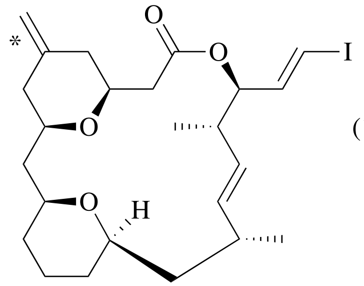
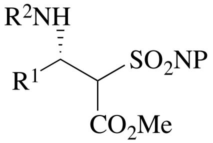
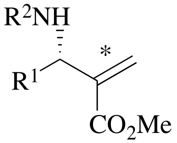
	Sulfone and Carbonyl Component	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1	$TBTSO_2Me$ 	**A**: NaHMDS, THF, –78° to rt, 16 h *or* **B**: Cs_2CO_3, THF-DMF, 70°, 16 h	 Ar — R $4\text{-}(MeO_2C)C_6H_4$ — H — **B** — (80) $4\text{-}PhC_6H_4$ — H — **B** — (93) $3,4\text{-}(MeO)_2\text{-}5\text{-}BrC_6H_2$ — H — **B** — (92) $2,6\text{-}(PMBO)_2C_6H_3$ — H — **A** — (93) $4\text{-}(MeO)C_6H_4$ — Me — **A** — (77) $4\text{-}(MeO)C_6H_4$ — Me — **B** — (63) $4\text{-}(EtO_2C)C_6H_4$ — Me — **B** — (71)	60
	$TBTSO_2Me$ 	NaHMDS, THF, –78° to rt	 (90)	175
	$TBTSO_2Me$ 	NaHMDS, THF, –78°	 (65)	176
	$TBTSO_2Me$ 	NaHMDS, THF, –78° to rt, 12 h	 (79)	177

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

	Sulfone and Carbonyl Component		Conditions	Product(s) and Yield(s) (%)		Refs.
C_1	TBTSO$_2$Me		NaHMDS, THF, –78°, 6 h		(47)	178
	TBTSO$_2$Me		NaHMDS, THF –78 to –17°, 1.5 h		(100)	63
$C_{4–13}$		aq. HCHO	Cs$_2$CO$_3$, DMF, 0° to rt			61

R^1	R^2		%*ee*
Ph(CH$_2$)$_2$	Boc	(85)	91
Ph(CH$_2$)$_2$	Cbz	(74)	78
Me	Boc	(88)	90
i-Bu	Cbz	(76)	84
n-C$_5$H$_{11}$	Cbz	(79)	88

R^1	R^2		%*ee*
n-C$_6$H$_{13}$	Boc	(91)	96
i-Pr	Boc	(74)	87
c-C$_6$H$_{11}$	Boc	(84)	92
Ph	Boc	(85)	91

R^1	R^2		%*ee*
2-naphthyl	Boc	(84)	84
4-MeOC$_6$H$_4$	Boc	(63)	89
4-ClC$_6$H$_4$	Boc	(70)	80
2-BrC$_6$H$_4$	Cbz	(75)	94

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED AND 1,1-DISUBSTITUTED ALKENES

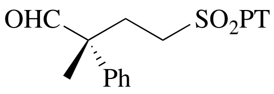
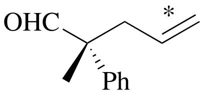
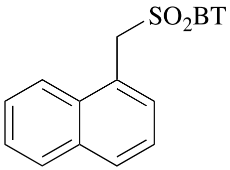
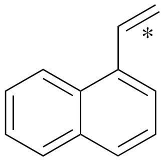
	Sulfone and Carbonyl Component	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
	 CH_2O (30 eq)	1. Ethylene glycol, *p*-TsOH, PhH 2. Aldehyde, KHMDS, DME, –78° 3. HCl, THF, 50°	 (30)	51
	 $[CH_2O]_n$	Cs_2CO_3, CH_2Cl_2, rt, 15 h	 (58)	97

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

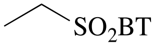
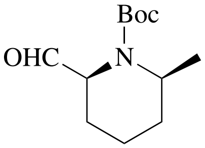
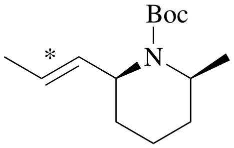
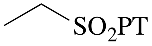
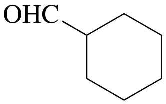
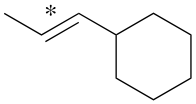
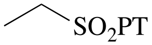
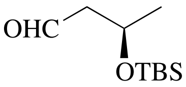
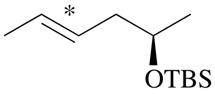
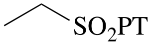
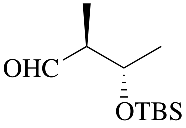
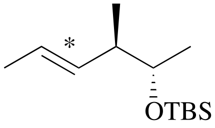
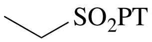
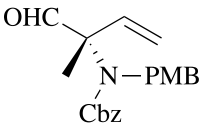
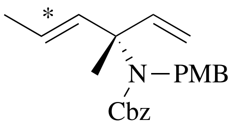
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_2						
			KHMDS, THF, –78°		(34) (*E*)/(*Z*)* = 86:14	179
			KHMDS, THF, –78°, 2 h		(54) (*E*)/(*Z*)* = 92:8	180
			1. KHMDS, THF, –78°, 25 min 2. Aldehyde; rt		(56) (*E*)*-isomer	181
			1. KHMDS, THF, –78°, 25 min 2. Aldehyde, rt		(65) (*E*)*-isomer	181
			KHMDS, DME, –60°		(75) (*E*)*-isomer only	182

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

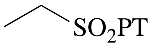
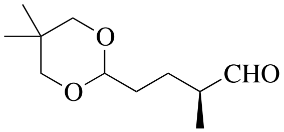
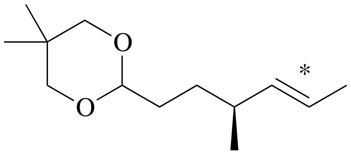
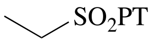
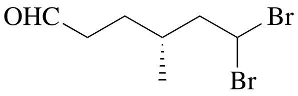
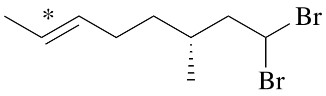
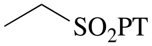
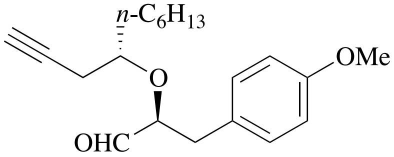
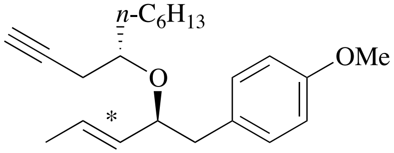
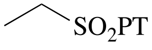
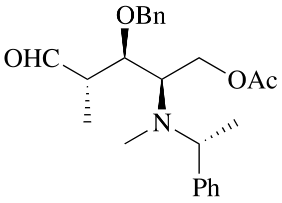
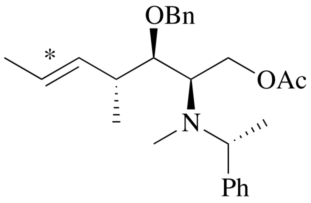
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	 	KHMDS, DME, –60°, 45 min	 (93) (*E*)/(*Z*)* = 93:7	58
	 	KHMDS, THF, –78°, 2 h; rt	 (80) (*E*)/(*Z*)* = 85:15	183
	 	KHMDS, DME, –60°, 12 h	 (>20) (*E*)/(*Z*)* = —	184
	 	KHMDS, THF, –78°, 40 min	 (89) (*E*)*-isomer only	185

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

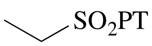
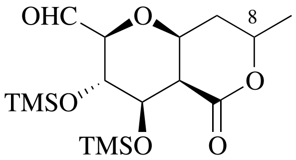
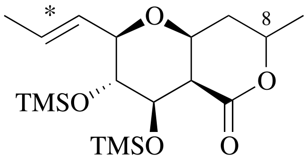
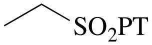
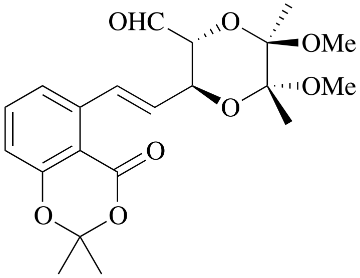
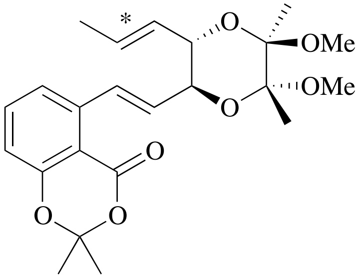
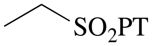
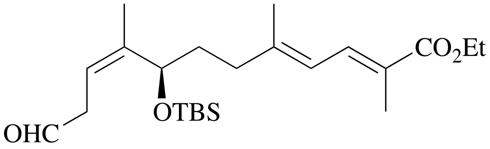
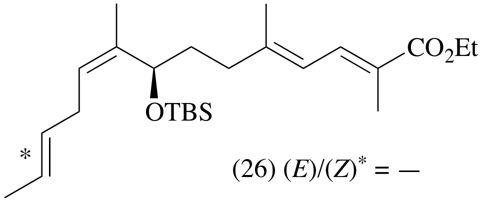
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			1. LiHMDS, solvent 2. Aldehyde	 C8 | Solvent | Temp. | | $(E)/(Z)^*$ (R) | THF | –78 | (76) | 55:45 (R) | DMF | –60 | (72) | 90:10 (R) | DMF | –35 | (73) | 94:6 (R) | DMF-HMPA | –35 | (70) | 83:17 (S) | DMF | –35 | (78) | 92:8	186
			KHMDS, DME, –60°	 (50) $(E)/(Z)^* = 80{:}20$	187
			KHMDS, DME, –60°	 (26) $(E)/(Z)^* = —$	59

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

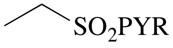
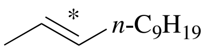
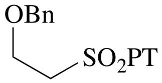
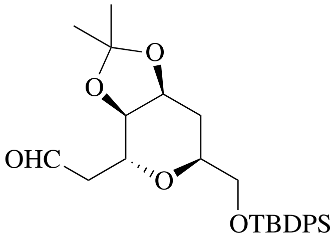
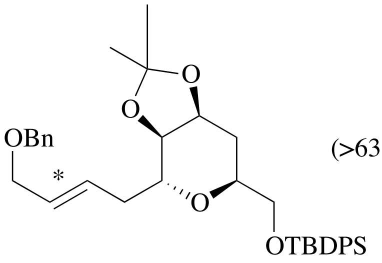
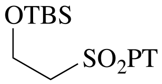
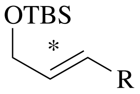
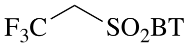
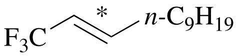
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2		n-$C_9H_{19}CHO$	1. n-BuLi, THF, –78°, 30 min 2. Aldehyde, –78°, 1.5 h; rt	 (47) $(E)/(Z)^* = 52:48$	3
			KHMDS	 (>63) $(E)/(Z)^* = 67:33$	188
		RCHO	KHMDS, –78°, 30 min; rt		189
				R — Solvent — — $(E)/(Z)^*$ $Ph(CH_2)_2$ — THF — (88) — 84:16 $Ph(CH_2)_2$ — DME — (83) — 91:9 n-Pr — THF — (89) — 88:12 c-C_6H_{11} — THF — (84) — 93:7 t-Bu — THF — (87) — >99:1 $BnOCH_2$ — THF — (91) — 92:8 $TBSO(CH_2)_2$ — THF — (88) — 98:2 $MeO_2C(CH_2)_3$ — THF — (89) — 96:4	
		n-$C_9H_{19}CHO$	TBAF, THF, –78° to rt, 16 h	 (76) $(E)/(Z)^* = 22:78$	190

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

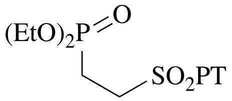
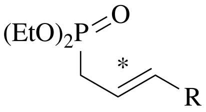
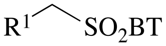
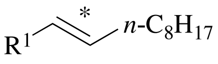
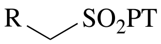
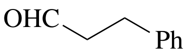
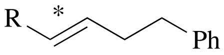
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2	 RCHO	1. THF, KHMDS, –78°, 5 min 2. Aldehyde, –78°, 20 min; 0°, 1 h	 R — (E)/(Z)* Et (77) 93:7 n-C_5H_{11} (82) >95:5 $Ph(CH_2)_2$ (85) >95:5 i-Pr (72) >95:5 c-C_5H_9 (80) >95:5 c-C_6H_{11} (79) >95:5 t-Bu (40) >95:5	112
C_{2-4}	 n-$C_8H_{17}CHO$	LDA, THF, –78°, 3 h; rt, 1h	 R^1 — (E)/(Z)* Me (26) 43:57 Et (48) 49:51 n-Pr (49) 50:50	3
C_{2-4}	 	**A**: 1. KHMDS, THF, –78° 2. Aldehyde **B**: 1. KHMDS (1.1 eq), 18-crown-6 (2.0 eq) THF, 0.5 min 2. Aldehyde, –78°, 30 min	 R — protocol A (E)/(Z)* — protocol B (E)/(Z)* Me (72) 89:11 (62) >98:2 n-Pr (74) 83:17 (86) >98:2	25

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

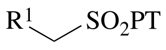
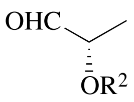
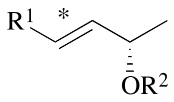
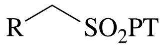
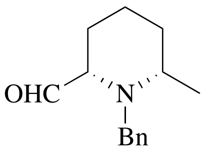
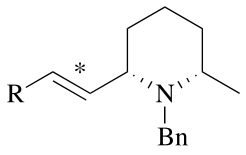
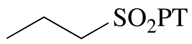
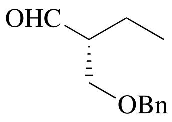
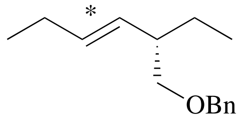
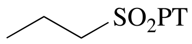
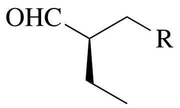
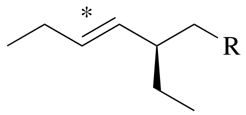
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-4}				
	 	**A**: 1. KHMDS, THF, –78° 2. Aldehyde **B**: 1. KHMDS (1.1 eq), 18-crown-6 (2.0 eq) THF, 0.5 min 2. Aldehyde, –78°, 30 min	 protocol A / protocol B R^1 — R^2 — (E)/(Z)* — (E)/(Z)* Me — Bn — (76) 80:20 — (75) 95:5 *n*-Pr — Bn — (68) 90:10 — (63) >98:2 *i*-Pr — Bn — (78) 95:5 — (75) >98:2 *i*-Pr — *t*-BuPh$_2$Si — (81) 95:5 — (82) >98:2	25
C_{2-8}				
	 	1. KHMDS, DME, –78°, 20 min 2. Aldehyde, rt	 R — (E)*-isomer Me — (72) *n*-C_7H_{15} — (78)	191
C_3				
	 	1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78° to rt, 18 h	 (64) (E)/(Z)* > 95:5	192
	 	1. KHMDS, DME, –78°, 3 h 2. Aldehyde, –78 to 23°	 R — (E)/(Z)* CH_2OBn — (80) 82:8 OTBS — (68) 95:5	193

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

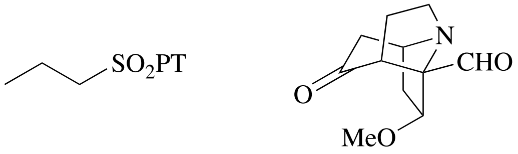
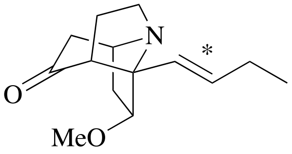
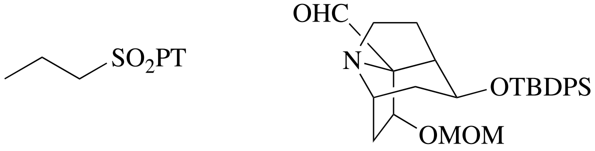
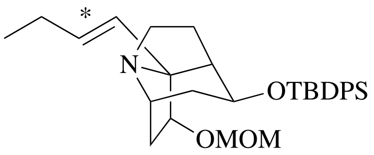
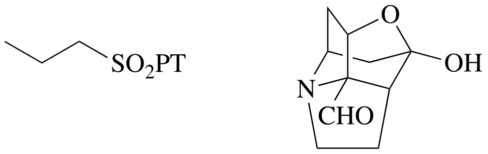
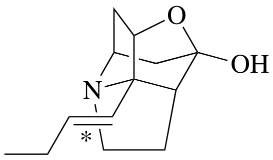
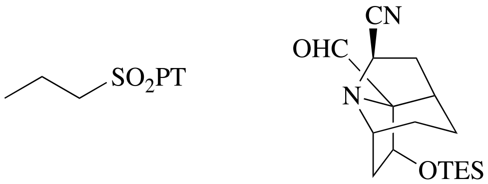
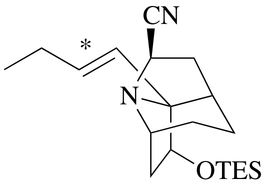
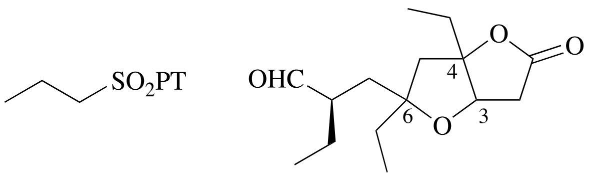
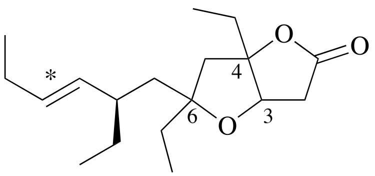
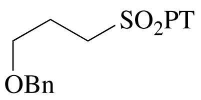
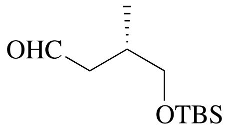
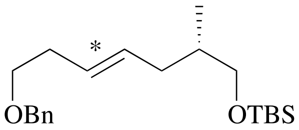
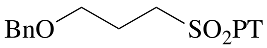
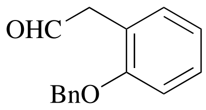
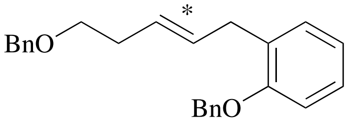
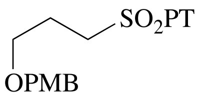
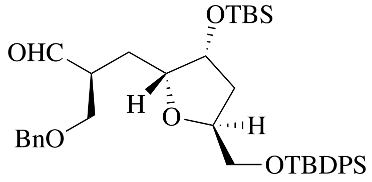
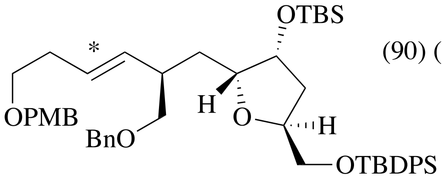
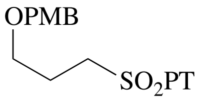
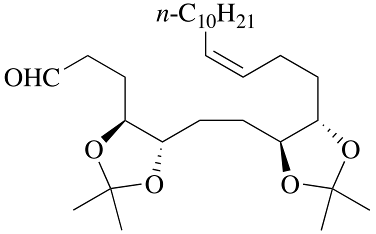
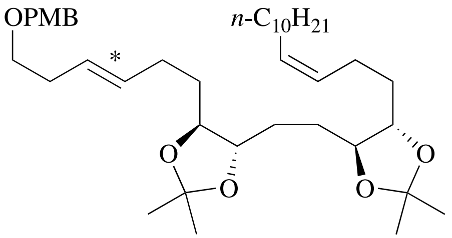
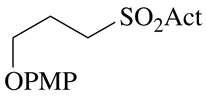
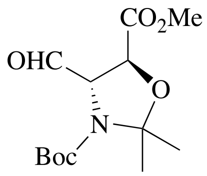
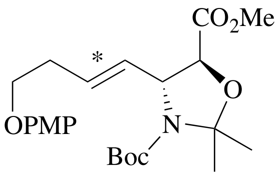
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		KHMDS, DME, –55°	 (>70) $(E)^*$-isomer only	194
		KHMDS, DME, –55°, 1 h; rt, 1 h	 (89) $(E)^*$-isomer	195
		KHMDS, DME, –55°	 (94) $(E)^*$-isomer	196
		KHMDS, DME, –55°	 (78) $(E)^*$-isomer	197
		KHMDS, THF, –78°; rt	 C3 C4 C6 $(E)/(Z)^*$ (*R*) (*R*) (*R*) (>60) 91:9 (*S*) (*S*) (*S*) (>69) —	198

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 	KHMDS, THF, –78°; rt	 (55) (*E*)/(*Z*)* = 95:5	199
	 	1. LiHMDS, THF, –78°; –65°, 1 h 2. Aldehyde, –65°, 1 h; rt, 15 h	 (77) (*E*)/(*Z*)* = 85:15	200
	 	LiHMDS, THF, –78°	 (90) (*E*)/(*Z*)* = —	201 202
	 	1. KHMDS, DME, –60°, 20 min 2. Aldehyde, –60° to rt, 16 h	 (93) (*E*)/(*Z*)* = 93:7	203
	 	Barbier conditions. See table.		204

Act	Base	Solvent	Temp	Time		(*E*)/(*Z*)*
BT	LDA	THF	–78°	17 h	(42)	55:45
PT	LDA	THF	–78°	17 h	(35)	62:38
PT	NaHMDS	DME	–60°	30 min	(58)	64:36
PT	KHMDS	DME	–60°	45 min	(67)	73:27

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

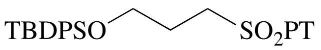
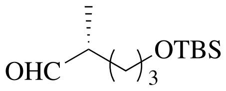
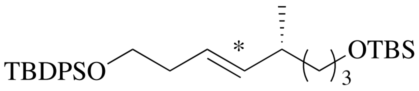
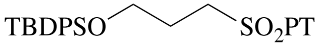
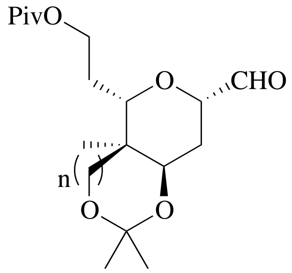
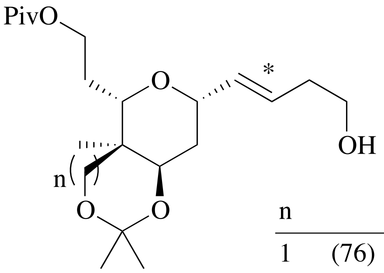
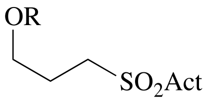
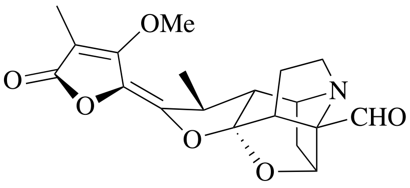
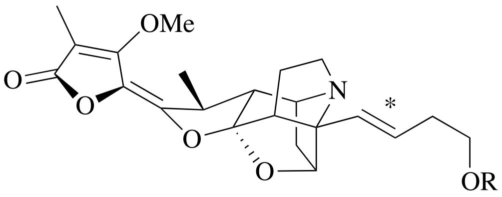
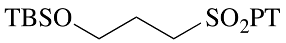
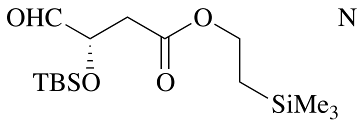
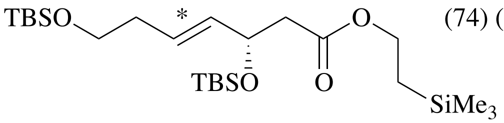
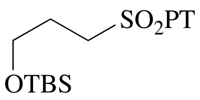
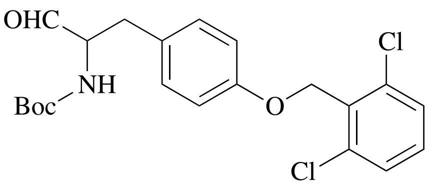
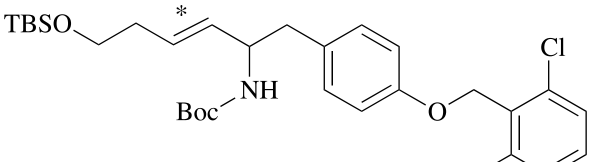
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 	1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78° to rt	 (78) $(E)^*$-isomer only	205
	 	1. LiHMDS, DMF-HMPA, –35° 2. Aldehyde, –35° to rt 3. TBAF, THF	 n — — $(E)/(Z)^*$ 1 (76) 95:5 2 (≥68) —	 206 207
	 	1. LiHMDS, DMF, –60°, 2 h 2. Aldehyde, –60°; rt, 20 h	 Act R — $(E)/(Z)^*$ BT TBS (33) 99:1 PT Me (15) 99:1	208
	 	NaHMDS, THF, –78°, 4 h; rt	 (74) $(E)/(Z)^*$ = 89:11	209
	 	KHMDS, DMF, –78° to rt, 2 h	 (40) $(E)^*$-isomer only	210

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

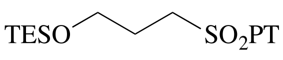
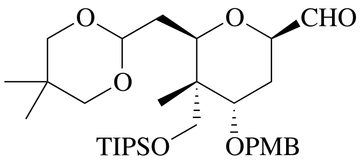
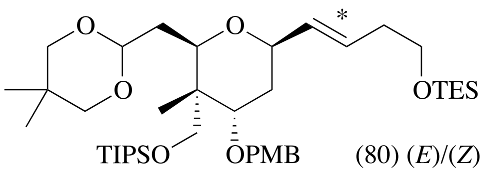
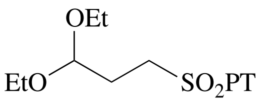
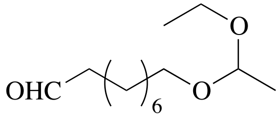
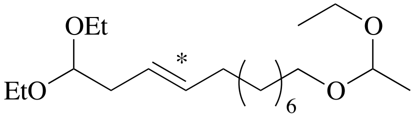
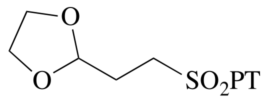
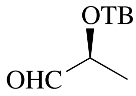
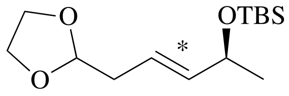
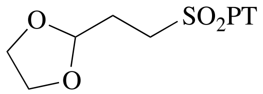
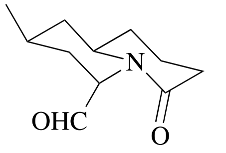
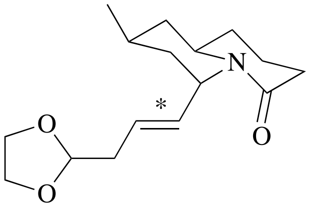
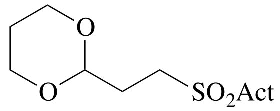
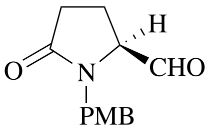
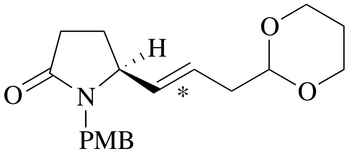
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 	KHMDS, DME, –60° to rt	 (80) (*E*)/(*Z*)* = 90:10	211
	 	1. KHMDS, DME, –55°, 1 h 2. Aldehyde, –55° to rt, 1.5 h	 (60) (*E*)/(*Z*)* = 97:3	212
	 	KHMDS, DME, –55° to 0°, 14 h	 (92) (*E*)/(*Z*)* = 95:5	213
	 	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 60; rt	 (70) (*E*)/(*Z*)* = 93:7	214
	 	KHMDS, DME	 Act | (*E*)/(*Z*)* PT (53) 100:0 BT (0) —	215

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

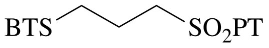
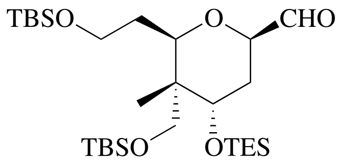
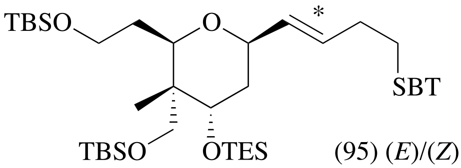
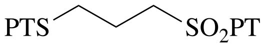
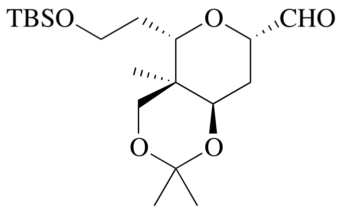
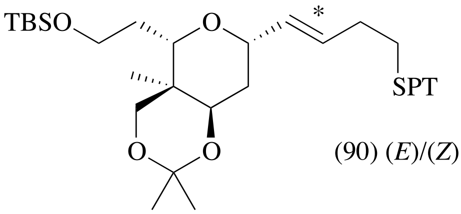
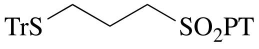
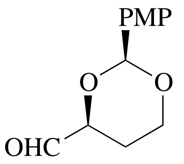
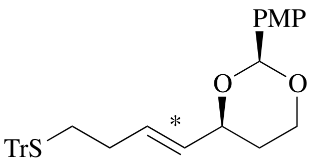
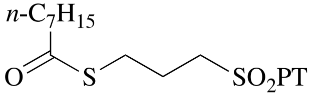
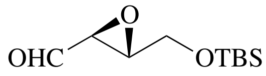
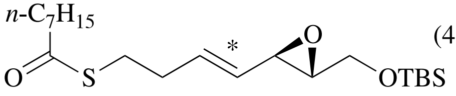
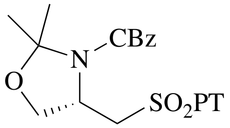
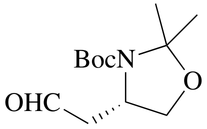
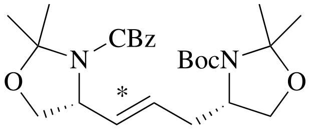
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 	KHMDS, DME, –70° to rt	 (95) (*E*)/(*Z*)* = 97:3	216
	 	1. KHMDS, DME-HMPA, –78°, 30 min 2. Aldehyde, –78°, 2 h	 (90) (*E*)/(*Z*)* = —	217
	 	LiHMDS, DMF, –60°, 2 h; 0°, 2 h	 (66) (*E*)/(*Z*)* = 83:17	218
	 	KHMDS, THF, –78°, 1 h; rt, 5 h	 (45) (*E*)/(*Z*)* = 77:23	219
	 	1. NaHMDS, THF, –70° 2. Aldehyde; rt, 2 h	 (71) (*E*)/(*Z*)* = —	220

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

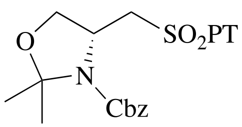
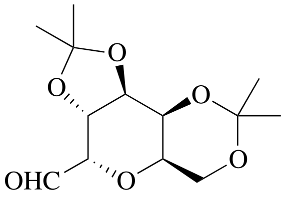
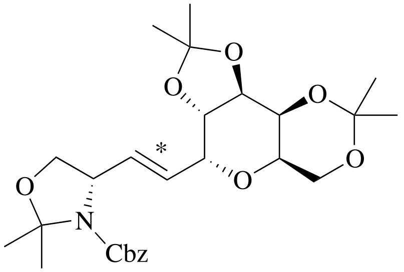
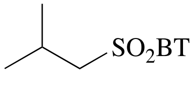
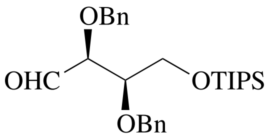
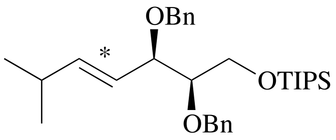
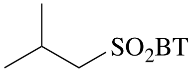
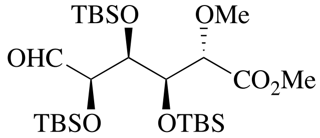
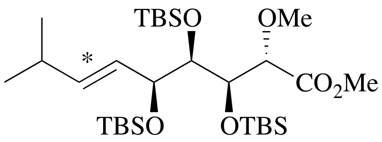
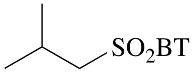
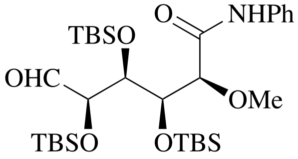
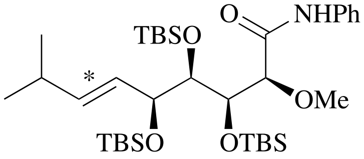
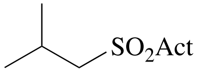
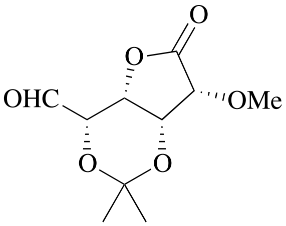
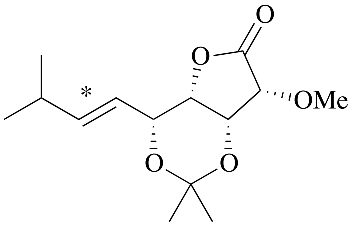
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_3			1. NaHMDS, THF, –78°, 5 min 2. Aldehyde, –78°, 1 h; rt, 2 h		(65) (*E*)*-isomer	221
C_4			1. LiHMDS, THF, –78° 2. Aldehyde, –78°, 1 h; rt		(>92) (*E*)/(*Z*)* > 95:5	222
			LiHMDS, DME, –78° to rt, 1.5 h		(62) (*E*)/(*Z*)* > 97:3	223
			LiHMDS, DME, –78° to rt		(>41) (*E*)/(*Z*)* = 95:5	224
			LiHMDS, DMF-HMPA –35° to 35°, 12 h		Act (*E*)/(*Z*)* BT (20-30) — PT (22) 95:5	166

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

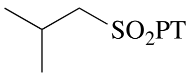
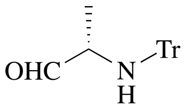
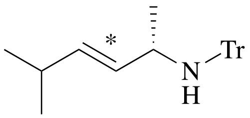
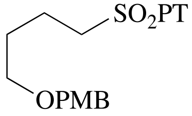
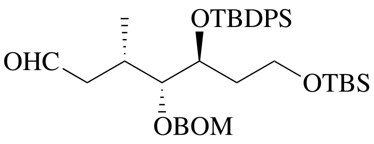
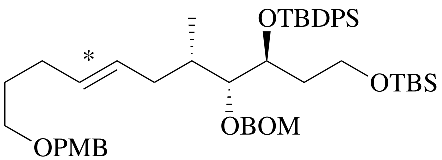
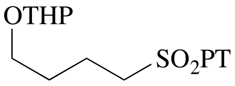
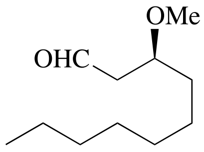
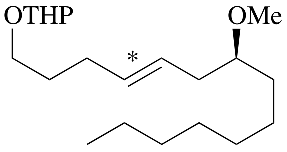
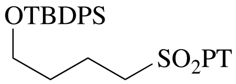
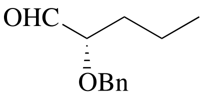
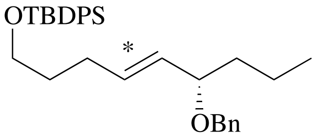
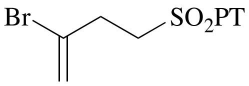
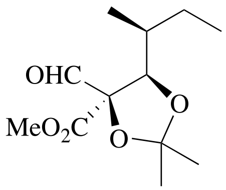
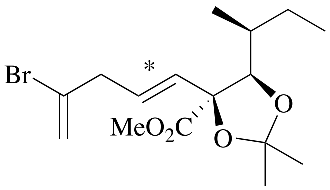
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 	NaHMDS (2 eq), DME, –55°, 3 h	 (70) (*E*)*-isomer only	225
	 	KHMDS, THF, –78°, 4 h; rt, 12 h	 (91) (*E*)*-isomer only	226
	 	1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 2 h; rt	 (80) (*E*)*-isomer	227
	 	KHMDS, DME, –78° to rt	 (>82) (*E*)/(*Z*)* = 88:12	228
	 	1. KHMDS, THF, –78°, 15 min 2. Aldehyde, –78°; rt, 12 h	 (79) (*E*)/(*Z*)* = 96:4	229

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

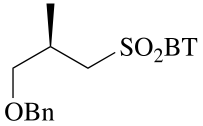
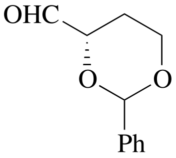
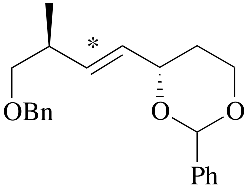
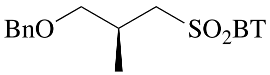
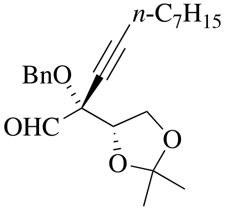
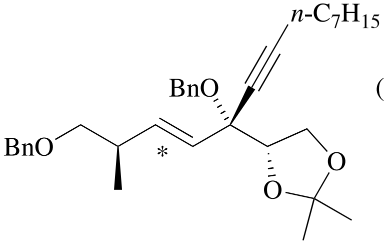
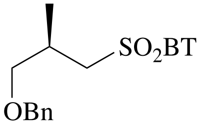
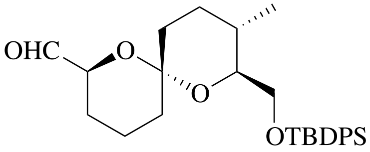
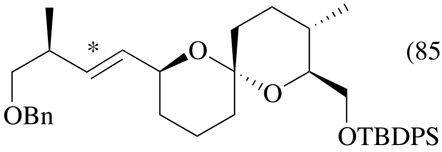
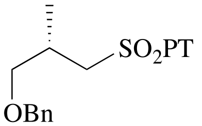
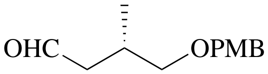
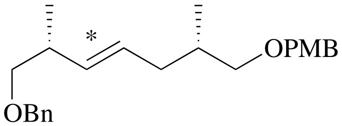
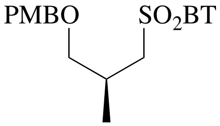
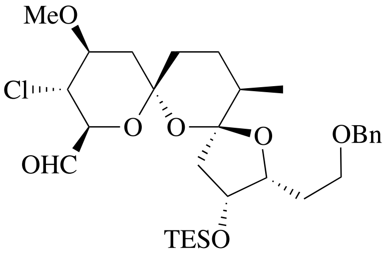
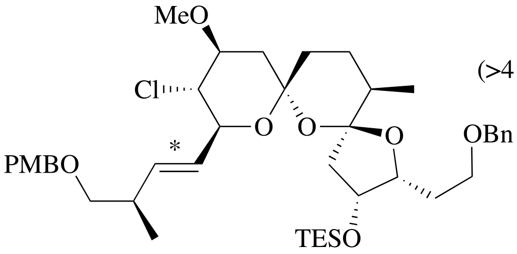
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 	1. LiHMDS, THF, –78° 2. Aldehyde, –78 to 50°	 (45) (*E*)/(*Z*)* = 72:28	230
	 	LiHMDS, THF	 (90) (*E*)/(*Z*)* = 97:3	231
	 	1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, –78 to 60°, 1.5 h	 (85) (*E*)/(*Z*)* = 70:30	232 233
	 	1. KHMDS, THF-DMPU, –78°, 40 min 2. Aldehyde, rt, 11.5 h	 (82) (*E*)/(*Z*)* = 86:14	234
	 	1. LiHMDS, THF, –78° 2. Aldehyde	 (>41) (*E*)/(*Z*)* —	235 153

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

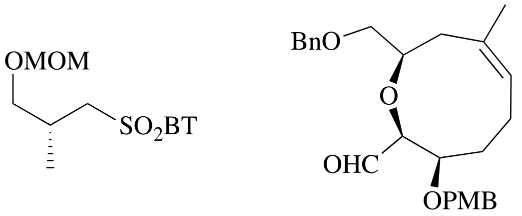
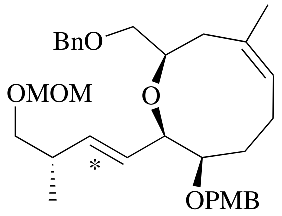
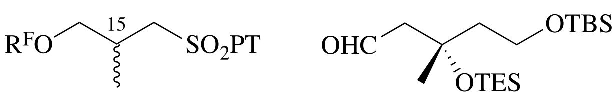
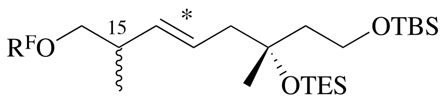
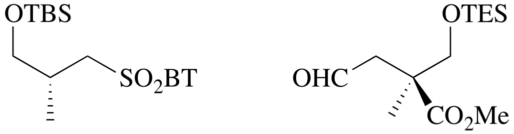
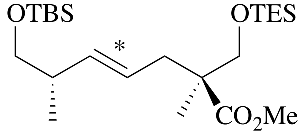
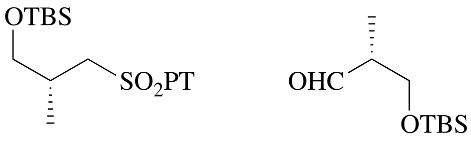
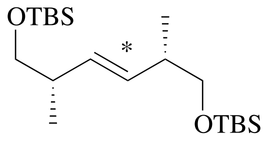
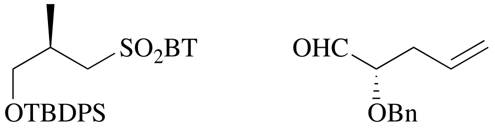
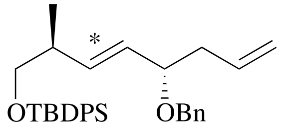
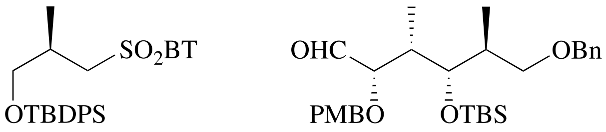
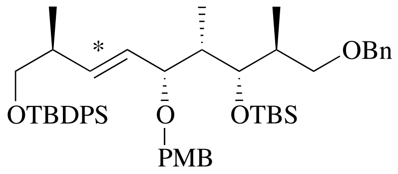
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4		KHMDS, THF, –78° to rt	 (69) (*E*)*-isomer	236
	 (15*R*), $R^F = 4\text{-}[F_9C_4(CH_2)_3O]C_6H_4CH_2$ + (15*S*), $R^F = 4\text{-}[F_{13}C_6(CH_2)_3O]C_6H_4CH_2$	1. LDA, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h	 (83) (*E*)/(*Z*)* = 80:20	237
		1. LiHMDS, THF, –78, 1 h 2. Aldehyde, –78°, 1 h; –30°, 4 h	 (96) (*E*)/(*Z*)* = 50:50	238 239
		1. KHMDS, DME, –55°, 1 h 2. Aldehyde, –55° to rt, 12 h	 (69) (*E*)*-isomer only	240
		1. LiHMDS, THF, 30 min 2. Aldehyde, –78 to –20°, 2.5 h	 (87) (*E*)/(*Z*)* = 60:40	241
		1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, THF, –78°, 12 h; rt, 10 h	 (90) (*E*)/(*Z*)* —	242

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

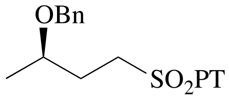
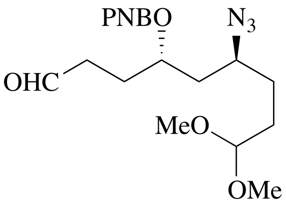
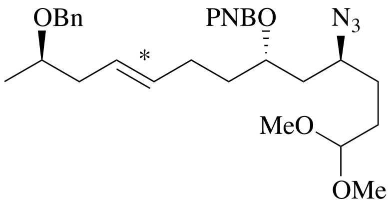
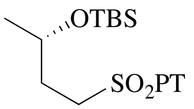
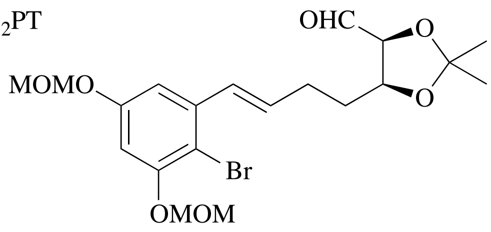
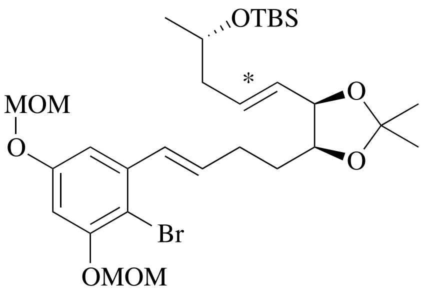
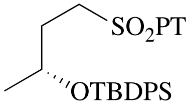
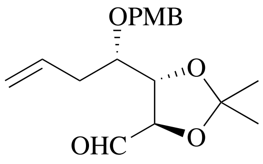
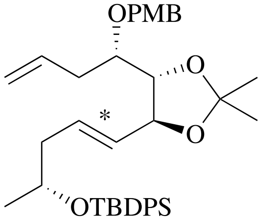
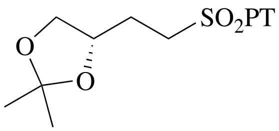
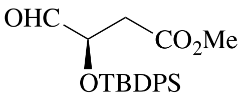
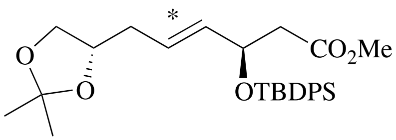
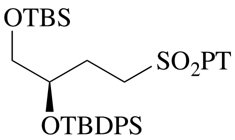
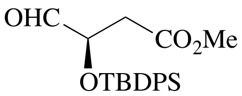
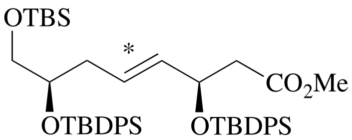
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 	1. LiHMDS, THF, –50°, 1 h 2. Aldehyde, –50°, 1 h; rt, 12 h	 (75) (*E*)/(*Z*)* = 60:40	243
	 	1. KHMDS, DME, –60°, 30 min 2. Aldehyde, –60°, 30 min; rt, 2 h	 (58) (*E*)/(*Z*)* = 83:17	244
	 	1. MN(Si(CH$_3$)$_3$)$_2$, additive THF, –98°, 30 min 2. Aldehyde; rt, 2 h	 M Additive (*E*)/(*Z*)* Li — (<5) — K — (—) 66:33 K HMPA (—) 80:20 K 18-c-6 (75) 95:5	245
	 	KHMDS, THF, –78°, 4 h; rt, 12 h	 (90) (*E*)/(*Z*)* = 75:25	226
	 	KHMDS, THF, –78°, 4 h; rt, 12 h	 (72) (*E*)/(*Z*)* = 80:20	226

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

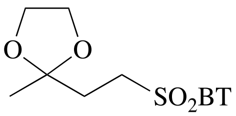
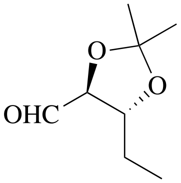
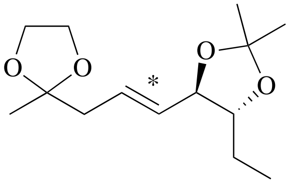
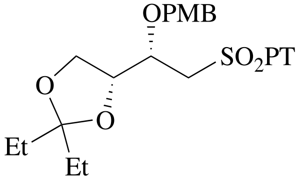
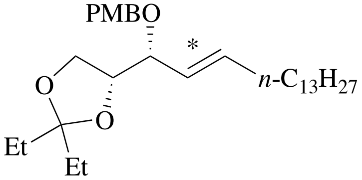
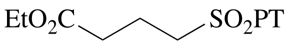
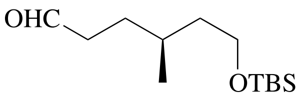
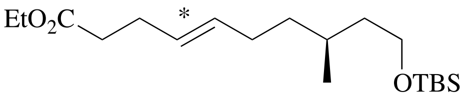
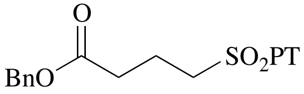
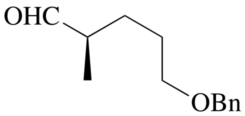
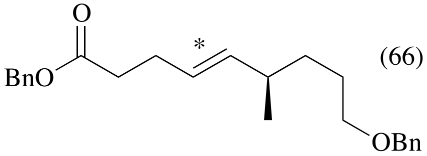
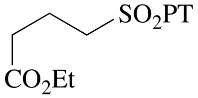
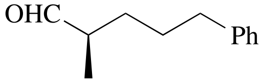
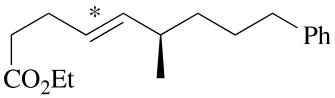
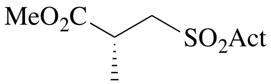
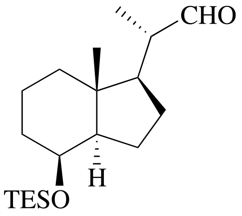
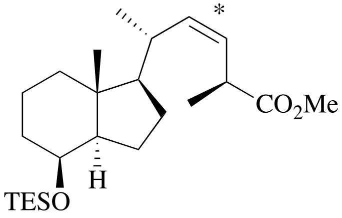
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 	LiHMDS, THF, –78° to rt, 3 h	 (68) (*E*)*-isomer only	246
	 n-$C_{13}H_{27}CHO$	1. KHMDS, DME, –55°, 30 min 2. Aldehyde, –55°, 15 min	 (53) (*E*)/(*Z*)* = 80:20	247
	 	1. KHMDS, THF, –78°, 20 min 2. Aldehyde, –78°, 15 min; –50°, 1 h	 (69) (*E*)/(*Z*)* = 96:4	248
	 	1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, –78°; rt, 21 h	 (66) (*E*)/(*Z*)* = 77:23	249
	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 14 h	 (81) (*E*)/(*Z*)* = —	250

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 	1. $MN(SiMe_3)_2$ (1.1 eq) solvent, temp. 2. Aldehyde (1.5 eq)		64

Act	M	Solvent	Temp.		$(E)/(Z)^*$
BT	Li	THF	–78°	(75)	0:100
PT	Li	THF	–78°	(35)	0:100
PT	Na	THF	–78°	(57)	0:100
PT	Na	DME	–55°	(0)	—
PT	K	THF	–55°	(0)	—
PT	K	DME	–55°	(4)	0:100

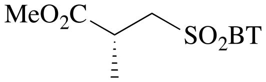
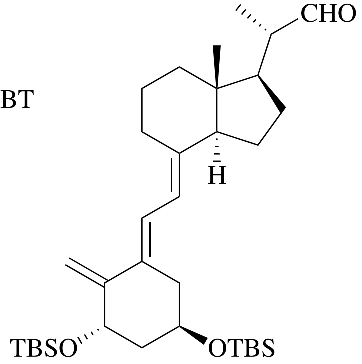
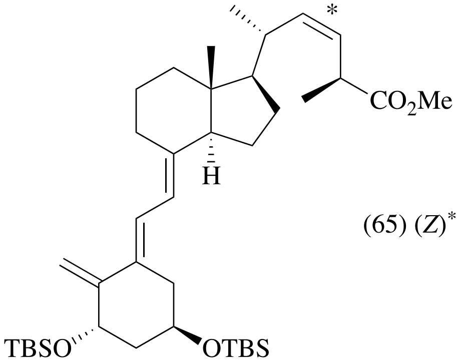
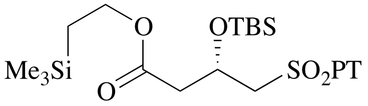
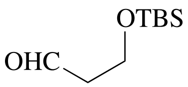
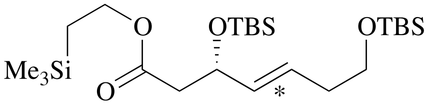
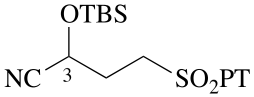
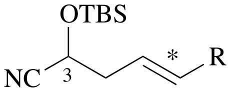
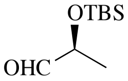
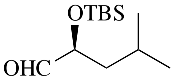
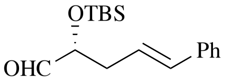
	 	1. LiHMDS, THF, –78° 2. Aldehyde	 (65) $(Z)^*$-isomer only	64 66
	 	NaHMDS, THF, –78°	 (35) $(E)/(Z)^*$ = 80:20	251

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 RCHO	1. $MN(SiMe_3)_2$, THF, –78°, 45 min 2. Aldehyde, –78°; rt, 3h		252

C3	RCHO	M		(E)/(Z)*
(*R*)	*i*-PrCHO	Na	(96)	95:5
(*R*)		K	(95)	98:2
(*S*)		K	(99)	95:5
(*R*)		K	(88)	95:5
(*S*)		K	(96)	95:5

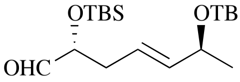
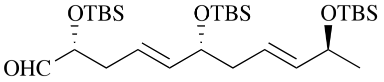
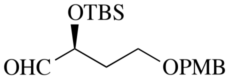
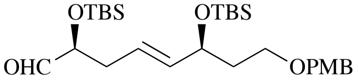
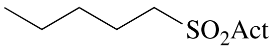
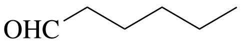
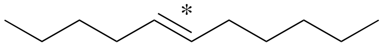
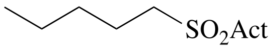
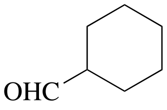
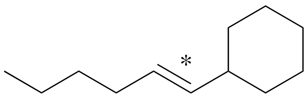
C3	RCHO	M		(E)/(Z)*
(*R*)		K	(83)	95:5
(*R*)		K	(85)	95:5
(*S*)		K	(85)	95:5
(*S*)		KK	(86)	95:5

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	1. $MN(SiMe_3)_2$, temp, 30 min 2. Aldehyde, temp, 3 h; to rt		4

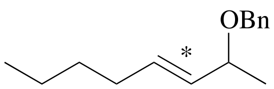
			Act = BT		Act = PT	
Solvent	Temp	M		$(E)/(Z)^*$		$(E)/(Z)^*$
PhMe	–78°	Li	(5)	40:60	(55)	57:43
PhMe	–78°	Na	(29)	51:49	(80)	59:41
PhMe	–78°	K	(15)	47:53	(13)	64:36
Et_2O	–78°	Li	(7)	43:57	(76)	73:27
Et_2O	–78°	Na	(17)	53:47	(90)	57:42
Et_2O	–78°	K	(68)	51:49	(30)	72:26
THF	–78°	Li	(42)	60:40	(97)	75:25
THF	–78°	Na	(0)	–:–	(89)	76:24
THF	–78°	K	(24)	55:45	(71)	86:14
DME	–60°	Li	(3)	55:45	(95)	77:23
DME	–60°	Na	(27)	77:23	(89)	86:14
DME	–60°	K	(6)	75:25	(71)	94:6

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

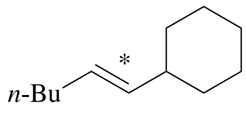
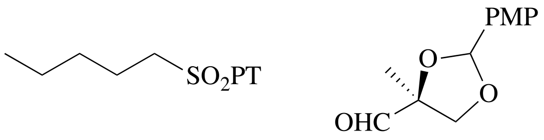
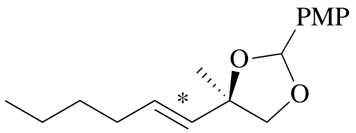
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	 	1. $MN(SiMe_3)_2$, temp, 30 min 2. Aldehyde, temp, 3 h; rt		4

			Act = BT		Act = PT	
Solvent	Temp	M		(*E*)/(*Z*)*		(*E*)/(*Z*)*
PhMe	–78°	Li	(1)	50:50	(90)	51:49
PhMe	–78°	Na	(20)	54:46	(51)	65:35
PhMe	–78°	K	(13)	54:46	(22)	77:23
Et_2O	–78°	Li	(2)	49:51	(66)	61:39
Et_2O	–78°	Na	(17)	50:50	(83)	65:35
Et_2O	–78°	K	(57)	51:49	(46)	89:11
THF	–78°	Li	(6)	66:34	(90)	69:31
THF	–78°	Na	(19)	62:38	(92)	73:27
THF	–78°	K	(27)	54:46	(71)	97:3
DME	–60°	Li	(2)	70:30	(94)	72:28
DME	–60°	Na	(32)	75:25	(95)	89:11
DME	–60°	K	(4)	76:24	(81)	99:1

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

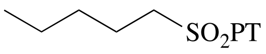
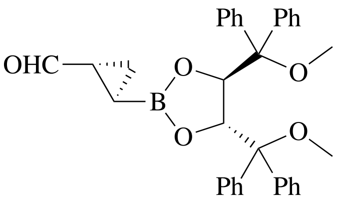
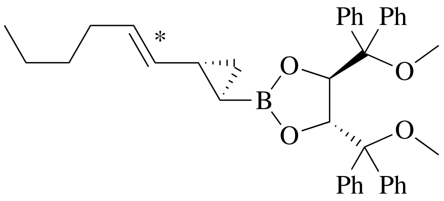
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. $MN(SiMe_3)_2$, temp, 30 min 2. Aldehyde, temp, 3 h; to rt		20

			Act = BT		Act = PT	
Solvent	Temp	M		$(E)/(Z)^*$		$(E)/(Z)^*$
PhMe	–78°	Li	(2)	50:50	(54)	31:69
PhMe	–78°	Na	(5)	52:48	(100)	49:51
PhMe	–78°	K	(8)	63:37	(47)	58:42
Et_2O	–78°	Li	(1)	55:45	(31)	35:65
Et_2O	–78°	Na	(5)	52:48	(82)	44:56
Et_2O	–78°	K	(10)	76:24	(78)	59:41
THF	–78°	Li	(23)	74:26	(91)	64:36
THF	–78°	Na	(32)	64:36	(100)	65:35
THF	–78°	K	(44)	61:39	(100)	72:38
DME	–60°	Li	(<1)	—	(88)	59:41
DME	–60°	Na	(25)	64:36	(96)	68:32
DME	–60°	K	(5)	58:42	(94)	79:21

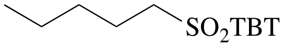
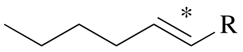
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Base, THF, rt 2. Aldehyde, 16 h		56
		1. KHMDS, –78° 2. Aldehyde, –78° to rt	 (79) $(E)^*$-isomer only	253

Base		$(E)/(Z)^*$
KOH, n-Bu_4NBr	(50)	75:25
P4-t-Bu	(60)	85:15
P2-Et	(70)	90:10

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	**A**: 1. $MN(SiMe_3)_2$, DME, Temp, 1 h 2. Aldehyde, DME, Time *or* **B**: $MN(SiMe_3)_2$, DME, Temp, Time		254 160

M	Eq base		Temp	Time		$(E)/(Z)^*$
Na	1.2	A	–78°	15 h	(43)	97:3
K	1.2	A	–60°	15 h	(46)	99:1
K	1.2	A	–78°	15 h	(20)	99:1
K	1.8	A	–60°	10 min	(93)	99:1
K	3.0	A	–78°	15 h	(36)	98:2
K	1.4	B	–60°	15 h	(54)	99:1
K	1.8	B	–60°	15 min	(73)	99:1
K	1.8	B	–78°	1 min	(71)	99:1

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 RCHO	**A**: 1. KHMDS, DME, –60°, 30 min 2. Aldehyde, –60° to rt *or* **B**: Cs_2CO_3, THF-DMF, 70°, 16 h		

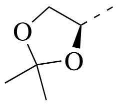
R		$(E)/(Z)^*$	Refs.
c-C_6H_{11}	(88)	89:11	5
2,5-$(PMBO)_2C_6H_3$	(98)	80:20	60
i-$Pr_3SiC{\equiv}C$	(72)	80:20	60
	(60)	70:30	60

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

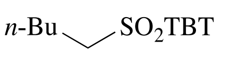
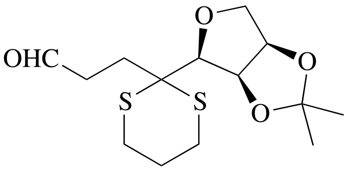
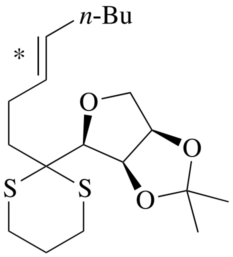
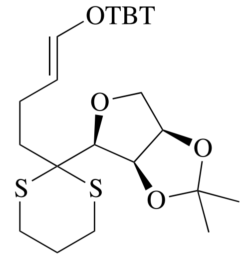
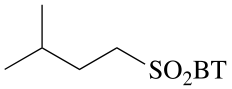
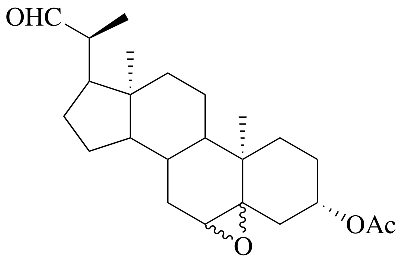
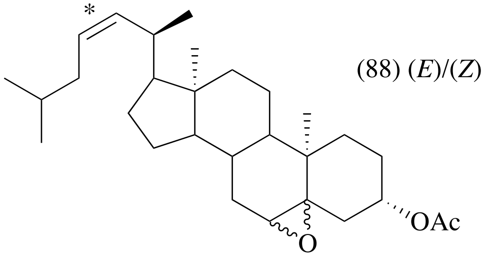
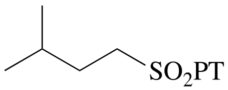
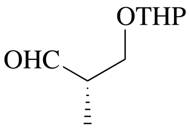
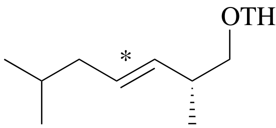
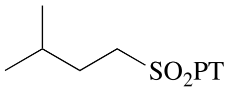
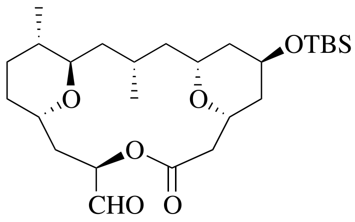
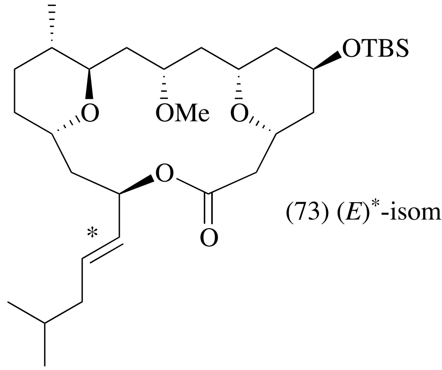
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	Cs_2CO_3, THF-DMF, 70°, 16 h	 +  (48) (*E*)/(*Z*)* = 75:25 (6) (*E*)/(*Z*)* = 33:67	60
	 	1. LiHMDS, THF, –78°, 1 h 2. Aldehyde, THF, –78°, 1 h; rt	 (88) (*E*)/(*Z*)* = 33:67	65
	 	1. KHMDS, DME, –55°, 1 h 2. Aldehyde, –50°, 1 h; rt, 12 h	 (>51) (*E*)/(*Z*)* ≥ 95:5	255
	 	1. KHMDS, DME, –78° 2. Aldehyde, –78° to rt	 (73) (*E*)*-isomer only	256 257

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

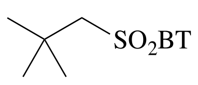
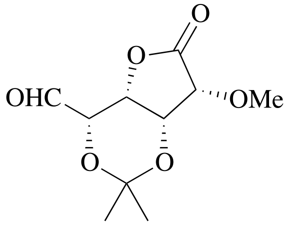
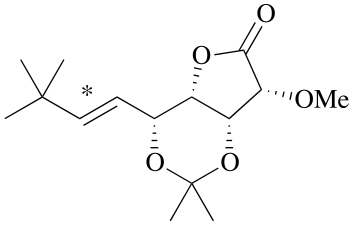
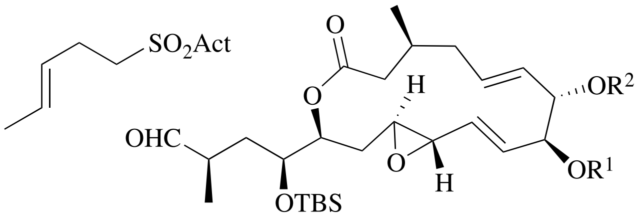
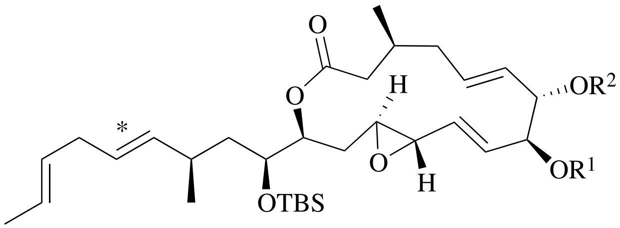
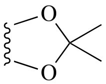
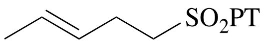
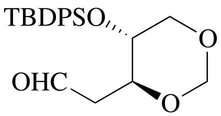
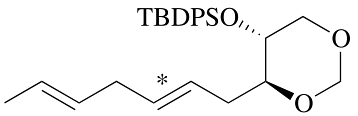
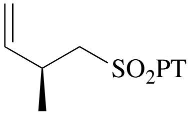
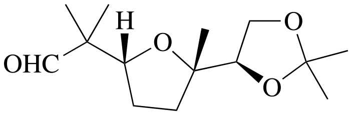
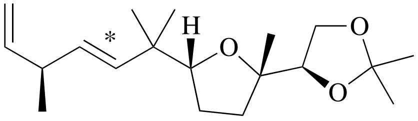
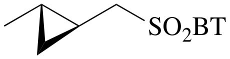
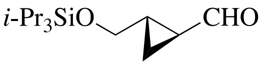
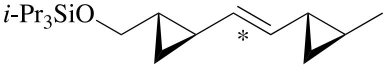
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	 	1. LiHMDS, THF, –55° to –75°, 1.5 h 2. Additive, –75° 3. Aldehyde, MeCN, –15° to 50°	 Additive — (E)/(Z)* TMSCl (50) 75:25 BF_3•OEt_2 (41) 91:9	18
		1. KHMDS, Solvent, –78°, 40 min 2. Aldehyde, –78°, 45 min; rt	 Act — R^1, R^2 — Solvent — (E)/(Z)* BT — TBS, TBS — THF-DMF — (>76) 93:7	258
			PT —  — DME — (>85) —	259
	 	1. KHMDS, DMPU, THF –78°, 1 h 2. Aldehyde; rt	 (61) (E)*-isomer	260
	 	1. LDA, THF, –78°, 20 min 2. Aldehyde, –78° to rt, 16 h; 4 h, reflux	 (91) (E)/(Z)* = 90:10	261 262

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_5			Barbier conditions. See table.		(>90)	23

Base	Solvent	Temp	$(E)/(Z)^*$
NaHMDS	PhMe	–78°	9:91
NaHMDS	CH_2Cl_2	–78°	9:91
NaHMDS	Et_2O	–78°	11:89
NaHMDS	THF	–78°	52:48
NaHMDS	DME	–60°	71:29
NaHMDS	DMF	–60°	78:22
KHMDS	PhMe	–78°	21:79
KHMDS	THF	–78°	55:45

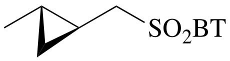
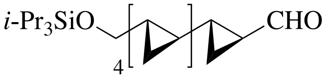
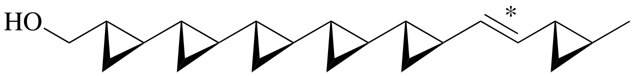
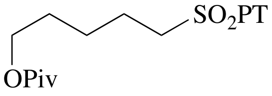
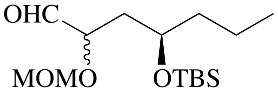
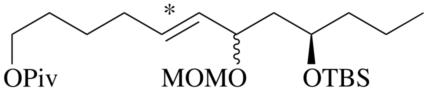
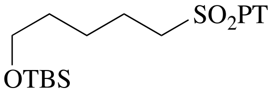
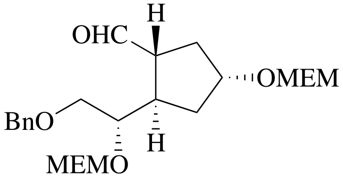
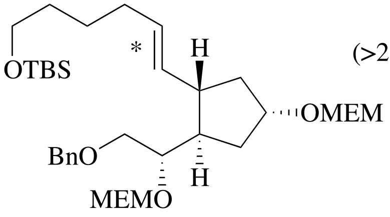
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. NaHMDS, THF-DMF, –60° 2. Bu_4NF, THF	 (92) $(E)/(Z)^* = 80{:}20$		23
			1. KHMDS, DME, –60° 2. Aldehyde, –60° to rt		(62) $(E)^*$-isomer	263
			1. KHMDS, DME, –78° 2. Aldehyde, –78°; rt		(>27) $(E)/(Z)^*$ —	264

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

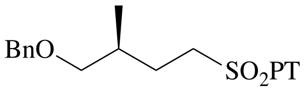
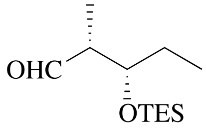
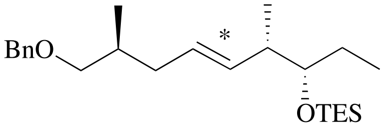
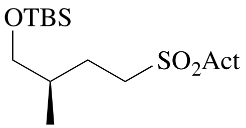
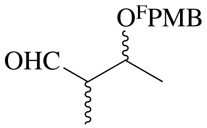
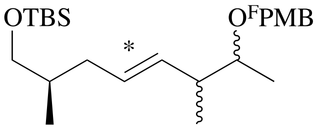
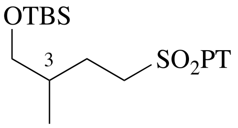
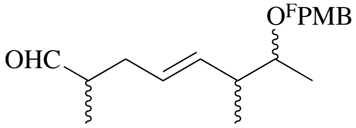
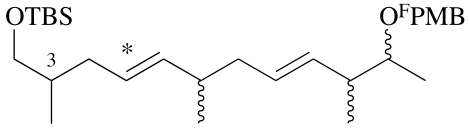
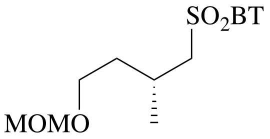
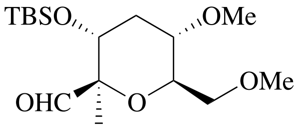
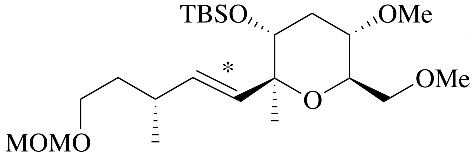
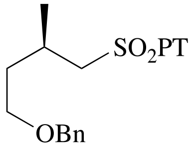
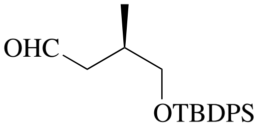
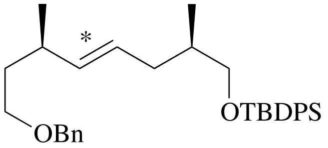
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	 	KHMDS, THF, –78°	 (68) (*E*)*-isomer only	265
	 	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 2 h	 Act (*E*)/(*Z*)* BT (81) — PT (93) —	266 116
	^{F}PMB = variable fluorine content p-methoxybenzyl groups			
	 	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 2 h	 (93) (*E*)/(*Z*)* = —	266 116
	^{F}PMB = variable fluorine content p-methoxybenzyl groups			
	 	LiHMDS, THF, –78° to rt	 (79) (*E*)/(*Z*)* = —	267
	 	LiHMDS, THF, –78°, 3 h; rt	 (78) (*E*)/(*Z*)* = 75:25	165

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

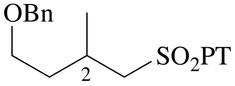
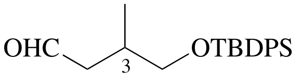
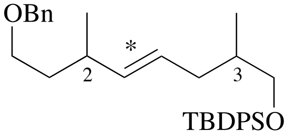
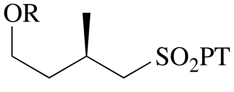
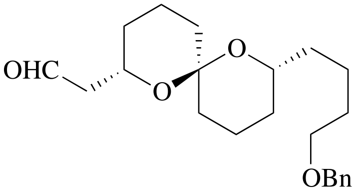
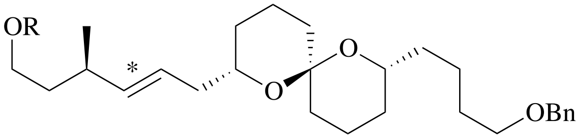
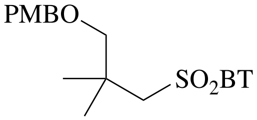
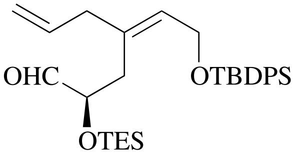
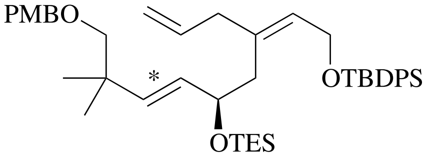
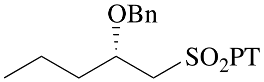
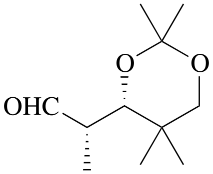
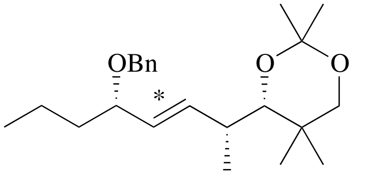
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	 	LiHMDS, THF, –78°; rt	 C2 C3 (*E*)/(*Z*)* (*R*) (*R*) (78) — (*R*) (*S*) (86) — (*S*) (*R*) (69) — (*S*) (*S*) (74) —	268
	 	1. Base, THF, –78°, 30 min 2. Aldehyde, –78°, 30 min	 R Base (*E*)/(*Z*)* TBDPS NaHMDS (77) 57:43 TBDPS KHMDS (27) 78:22 TBDPS LDA (98) 72:28 TBS LDA (86) 83:17	269
	 	1. LiHMDS, THF, –78°, 20 min 2. Aldehyde, –78° to rt	 (60) (*E*)/(*Z*)* = 75:25	270
	 	KHMDS, DME, –65 to 23°, 16 h	 (63) (*E*)/(*Z*)* = —	271

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

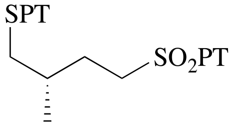
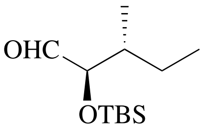
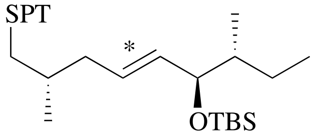
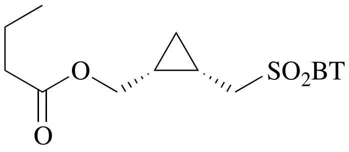
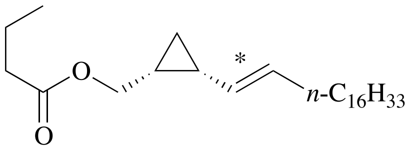
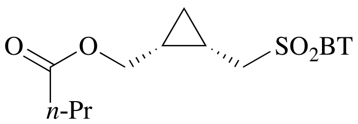
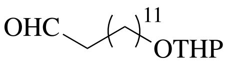
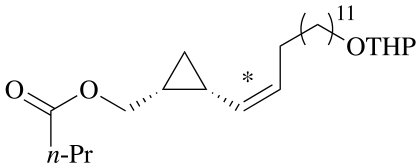
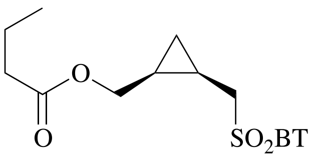
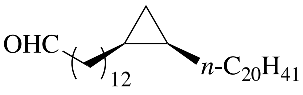
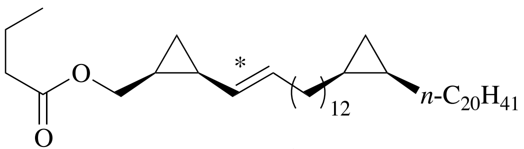
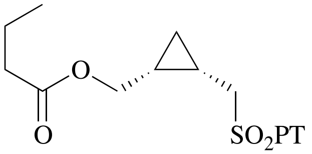
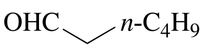
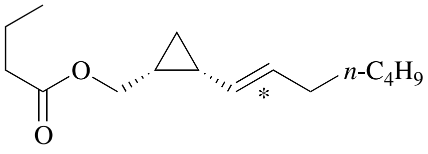
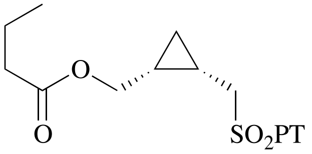
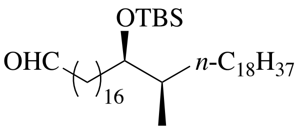
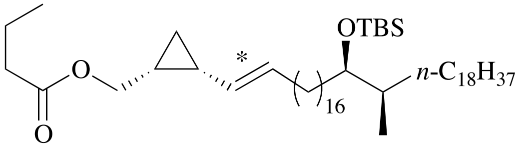
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	NaHMDS, THF, –78°; rt, 8 h	 (96) (*E*)/(Z)* = 95:5	111
	 n-$C_{16}H_{33}CHO$	NaHMDS, THF, –20°, 2 h; rt, 12 h	 (68) (*E*)/(Z)* = 57:43	272
	 	NaHMDS, THF	 (62) (*E*)/(Z)* = 43:57	273
	 	LiHMDS, THF, –15° to rt, 24 h	 (43) (*E*)/(Z)* = 50:50	274 275
	 	LiHMDS, THF, –20° to rt, 16 h	 (74) (*E*)/(Z)* = 67:33	276
	 	LiHMDS, THF, –10° to rt, 1.5 h	 (91) (*E*)/(Z)* = 62:38	277 278

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

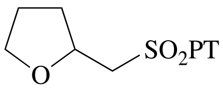
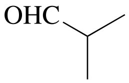
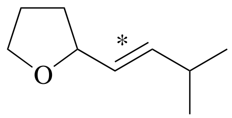
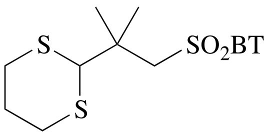
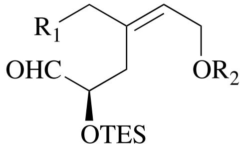
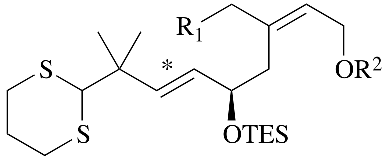
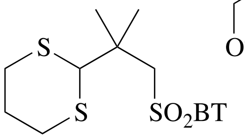
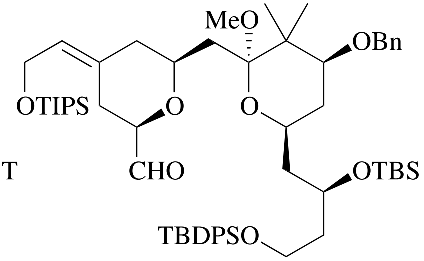
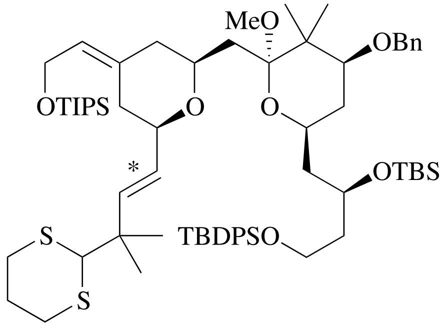
<table>
<tr><th></th><th>Sulfone and Aldehyde</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_5</td><td></td><td>1. $MN(SiMe_3)_2$, Solvent, Temp, 10 min
2. Aldehyde, Temp, 1 h; rt</td><td><table>
<tr><th>M</th><th>Solvent</th><th>Temp</th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>Na</td><td>THF</td><td>–78°</td><td>(—)</td><td>15:85</td></tr>
<tr><td>Na</td><td>DME</td><td>–78°</td><td>(—)</td><td>58:42</td></tr>
<tr><td>Na</td><td>DMF</td><td>–60°</td><td>(—)</td><td>85:15</td></tr>
<tr><td>K</td><td>THF</td><td>–78°</td><td>(—)</td><td>60:40</td></tr>
<tr><td>K</td><td>DME</td><td>–78°</td><td>(—)</td><td>85:15</td></tr>
<tr><td>K</td><td>DMF</td><td>–60°</td><td>(—)</td><td>90:10</td></tr>
<tr><td>K</td><td>DMF/HMPA</td><td>–78°</td><td>(—)</td><td>93:7</td></tr>
</table></td><td>118</td></tr>
<tr><td></td><td></td><td>1. LiHMDS, THF, –78°, 30 min
2. Aldehyde, –78° to rt, 1-1.5 h</td><td><table>
<tr><th>R_1</th><th>R_2</th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>$CH=CH_2$</td><td>$SiPh_2t$-Bu</td><td>(60)</td><td>—</td></tr>
<tr><td>CH_2OBOM</td><td>Si(<i>i</i>-Pr)$_3$</td><td>(95)</td><td>100:0</td></tr>
</table></td><td>270</td></tr>
<tr><td></td><td></td><td>A:
1. LiHMDS, THF, –78°, 30 min
2. Aldehyde, –78°, 20 min; rt, 2 h
<i>or</i> B:
1. LiHMDS, THF, –78°, 30 min
2. Aldehyde, –78° to rt, 16 h</td><td><table>
<tr><th></th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>A</td><td>(51)</td><td>100:0</td></tr>
<tr><td>B</td><td>(78)</td><td>67:33</td></tr>
</table></td><td>270</td></tr>
</table>

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

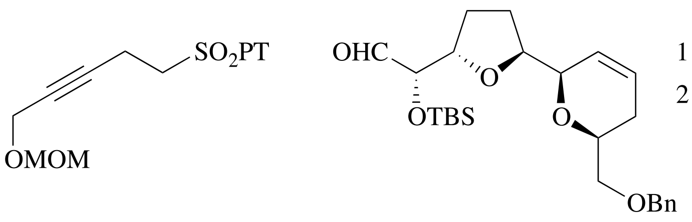
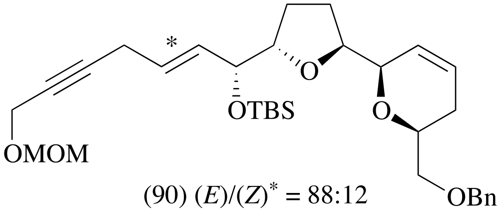
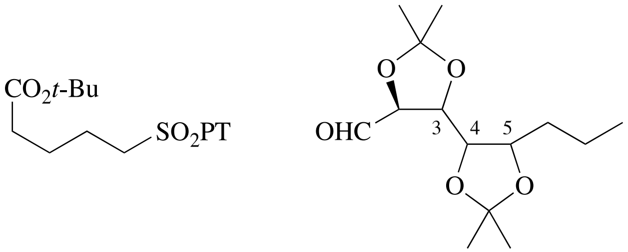
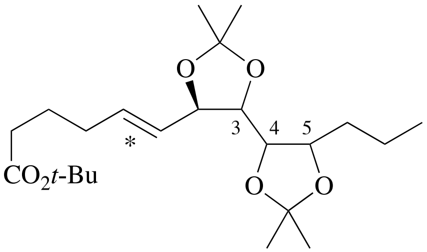
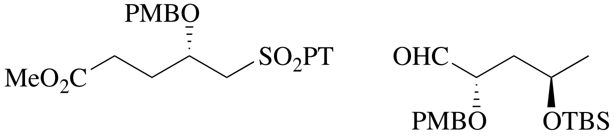
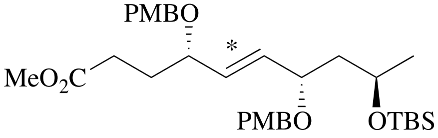
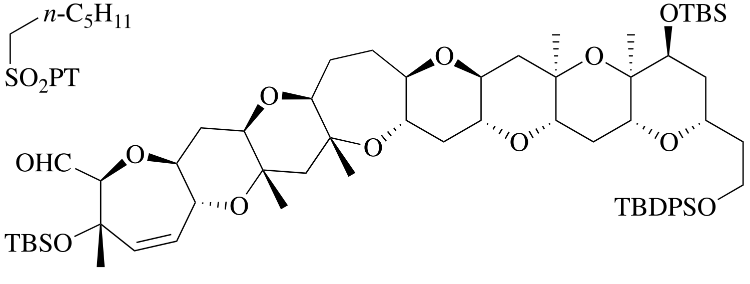
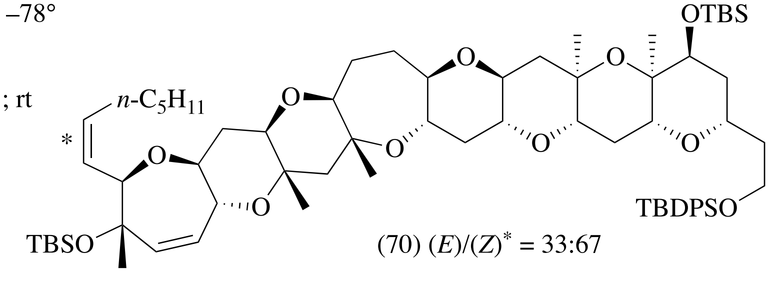
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		1. KHMDS, DME, –75°, 30 min 2. Aldehyde, 0°, 3 h	 (90) (*E*)/(*Z*)* = 88:12	279
		1. NaHMDS, DME, –78° 2. Aldehyde, –78° to rt, 12 h	 C3 C4 C5 (*E*)/(*Z*)* (*S*) (*S*) (*R*) (25) 75:25 (*R*) (*S*) (*R*) (46) 64:36 (*R*) (*S*) (*S*) (25) 62:38	280
		NaHMDS, THF-HMPA, –78°	 (60) (*E*)*-isomer	281
C_6		1. KHMDS, THF, –78° 40 min 2. Aldehyde, –78°; rt	 (70) (*E*)/(*Z*)* = 33:67	282

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

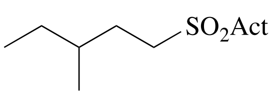
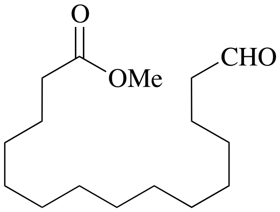
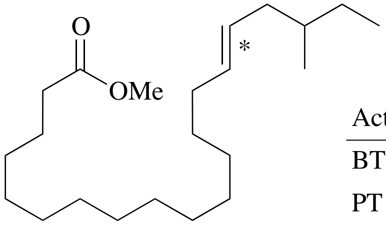
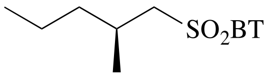
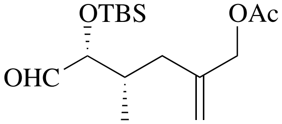
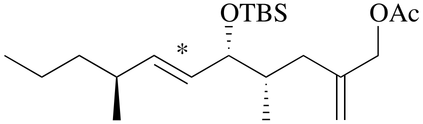
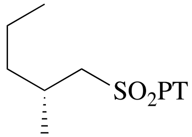
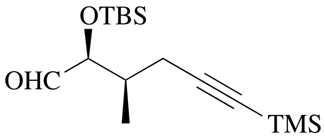
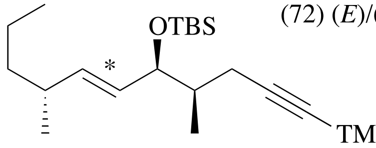
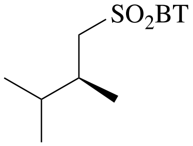
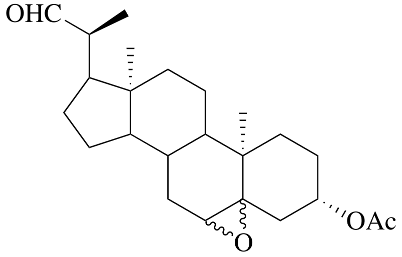
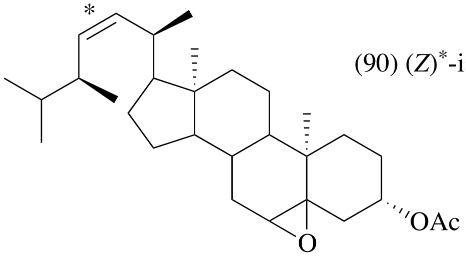
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	NaHMDS, THF, –78°	 Act (*E*)/(*Z*)* BT (30) — PT (58) —	283
	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 4 h	 (78) (*E*)/(*Z*)* = 80:20	284
	 	1. KHMDS, DME, –78°, 90 min 2. Aldehyde, to rt, 16 h	 (72) (*E*)/(*Z*)* > 95:5	285 46
	 	1. LiHMDS, THF, –78°, 1 h 2. Aldehyde, THF, –78°, 1 h; rt	 (90) (*Z*)*-isomer only	65

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

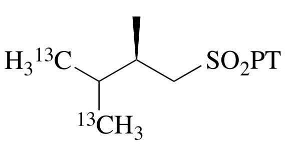
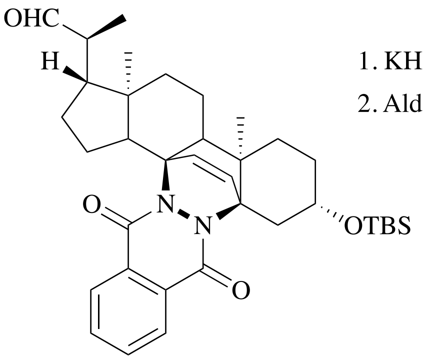
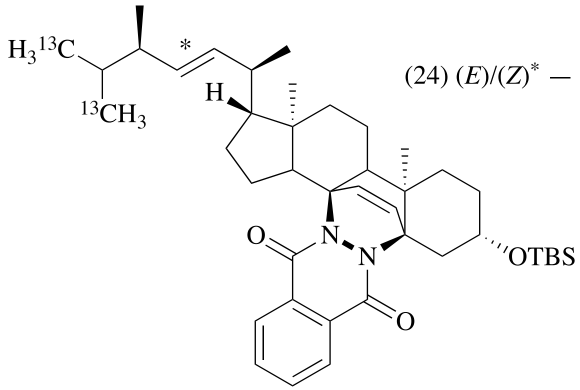
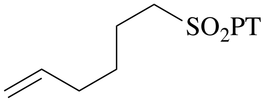
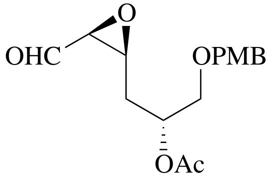
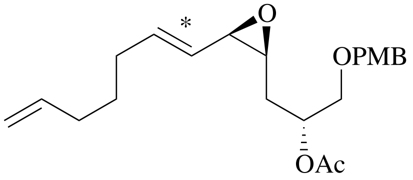
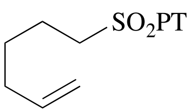
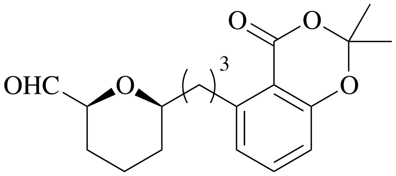
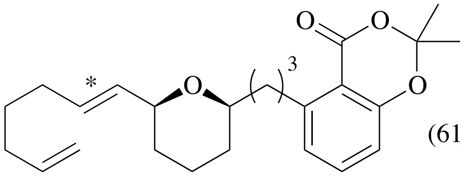
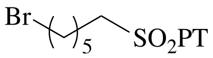
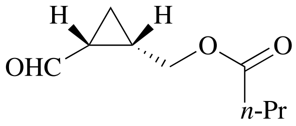
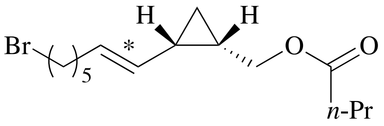
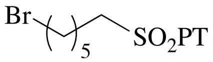
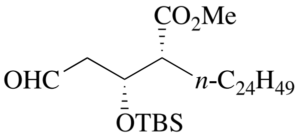
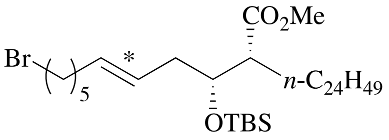
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	1. KHMDS, THF, –60 to –78°, 1 h 2. Aldehyde, –78°, 1 h; rt, 20 h	 (24) (*E*)/(*Z*)* —	286
	 	NaHMDS, –78 to 25°	 (74) (*E*)/(*Z*)* = 57:43	104
	 	1. NaHMDS, DMF-DMPU, –78°, 30 min 2. Aldehyde, –78° to rt, 4 h	 (61) (*E*)/(*Z*)* = 90:10	173
	 	LiHMDS, THF, –20° to rt, 16 h	 (78) (*E*)/(*Z*)* = 79:21	276
	 	LiHMDS, THF, –12°	 (94) (*E*)/(*Z*)* = 67:33	287

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

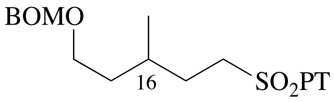
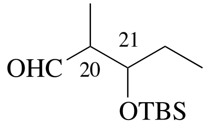
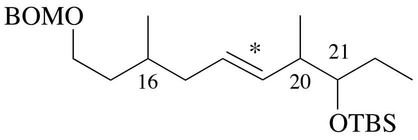
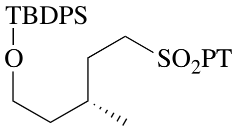
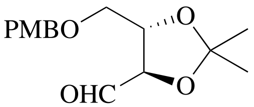
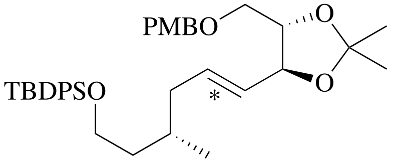
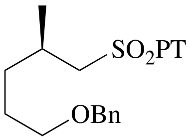
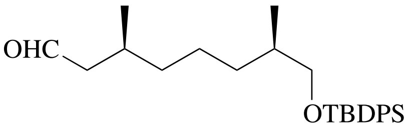
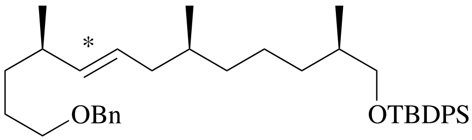
<table>
<tr><th></th><th>Sulfone and Aldehyde</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_6</td><td>
 </td><td>1. KHMDS, DME, –78°
2. Aldehyde, –78° to rt</td><td>
(<i>E</i>)/(<i>Z</i>)* = —
<table>
<tr><th>C16</th><th>C20</th><th>C21</th><th></th></tr>
<tr><td>(<i>R</i>)</td><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(68)</td></tr>
<tr><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(62)</td></tr>
<tr><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(66)</td></tr>
<tr><td>(<i>S</i>)</td><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(37)</td></tr>
</table></td><td>288</td></tr>
<tr><td></td><td>
 </td><td>1. $MN(SiMe_3)_2$, Solvent, –78°
2. Aldehyde, Time; rt</td><td>
<table>
<tr><th>M</th><th>Solvent</th><th>Time</th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>Li</td><td>DMF-DMPU</td><td>2 h</td><td>(58)</td><td>91:9</td></tr>
<tr><td>Li</td><td>DMF-DMPU</td><td>6 h</td><td>(68)</td><td>91:9</td></tr>
<tr><td>K</td><td>DME</td><td>2 h</td><td>(38)</td><td>84:16</td></tr>
<tr><td>K</td><td>DME</td><td>6 h</td><td>(40)</td><td>84:16</td></tr>
<tr><td>K</td><td>DME-HMPA</td><td>6 h</td><td>(42)</td><td>84:16</td></tr>
</table></td><td>259</td></tr>
<tr><td></td><td>
 </td><td>LiHMDS, THF, –78°, 3 h; rt</td><td>
(70) (<i>E</i>)/(<i>Z</i>)* = —</td><td>165</td></tr>
</table>

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

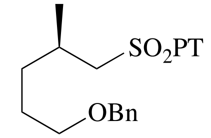
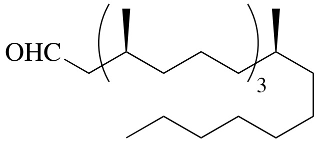
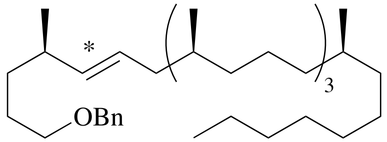
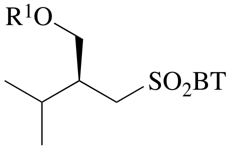
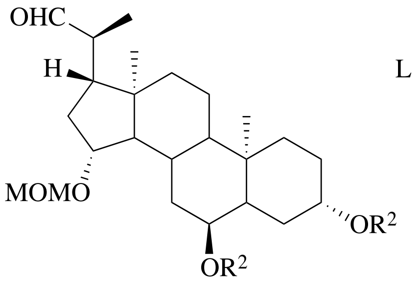
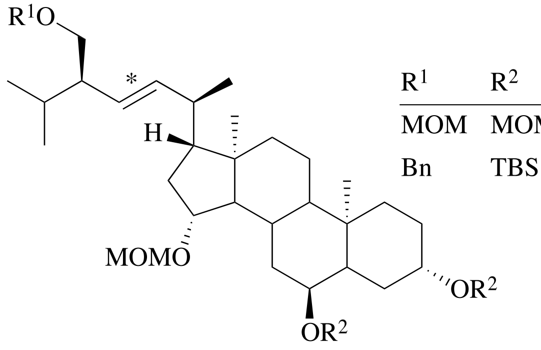
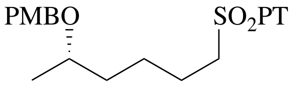
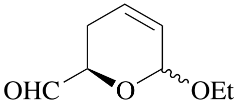
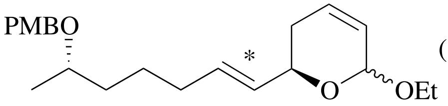
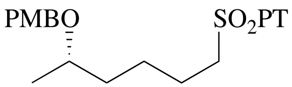
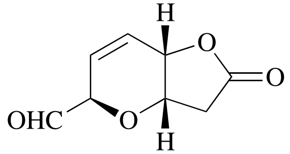
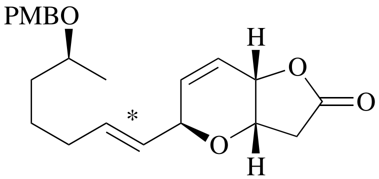
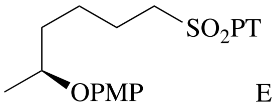
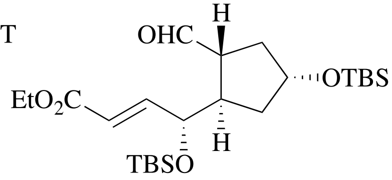
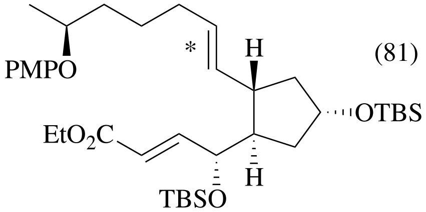
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	LiHMDS, THF, –78°, 3 h; rt	 (81) $(E)/(Z)^* = $ —	165
	 	LiHMDS, THF, –78°; rt	 R^1 / R^2 / Yield of $(E)^*$-isomer MOM / MOM / (57) Bn / TBS / (93)	289 290
	 	1. KHMDS, –78°, 20 min 2. Aldehyde, –78°, 1 h; –10°, 12 h	 (69) $(E)/(Z)^* = 91:9$	291
	 	1. $MN(SiMe_3)_2$, THF –78°, 15 min 2. Aldehyde, –78°, 1.5 h; rt	 M / / $(E)/(Z)^*$ Li / (>41) / 100:0 K / (—) / 67:33	292
	 	1. KHMDS, DME, –78°, 1 h 2. Aldehyde, –78°, 1 h; rt, 16 h	 (81) $(E)/(Z)^* = 92:8$	293

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

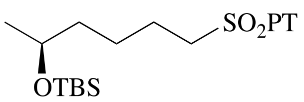
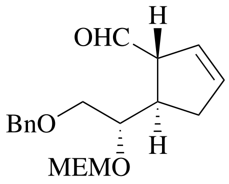
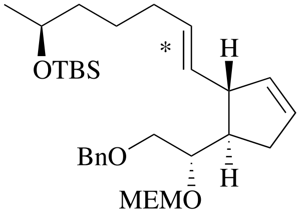
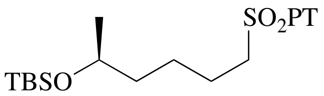
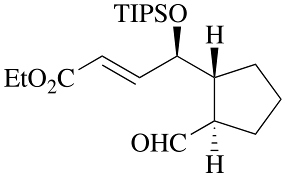
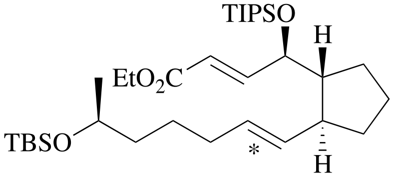
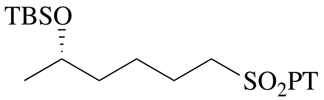
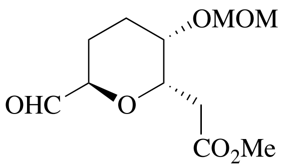
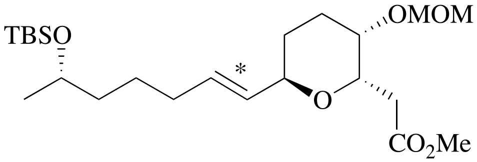
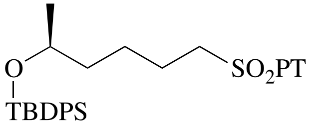
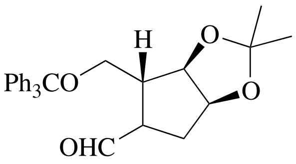
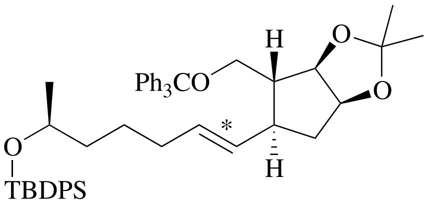
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_6			1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78°; rt		(88) (*E*)*-isomer	264
			KHMDS, DME, –78° to rt		(91) (*E*)*-isomer	294
			1. MN(SiMe$_3$)$_2$, –78°, 15 min 2. Aldehyde, –78°, 2 h; rt, 2 h	 M Solvent (*E*)/(*Z*)* Li THF/HMPA (57) 90:10 Na THF/HMPA (61) 88:12 K THF/HMPA (48) 67:33 K THF (54) 60:40 K DME (40) 50:50		295
			1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78°, 2 h; rt, 1 h		(81) (*E*)*-isomer	296

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

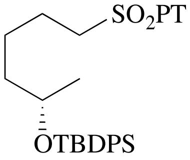
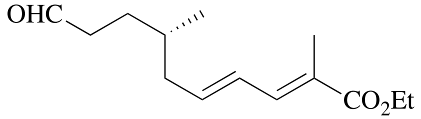
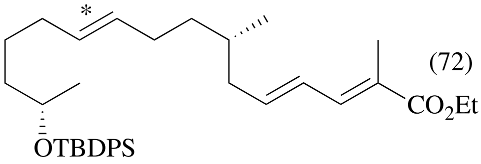
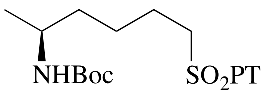
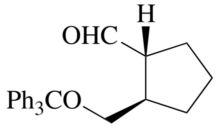
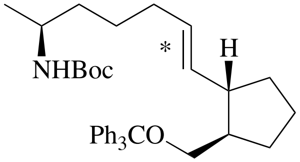
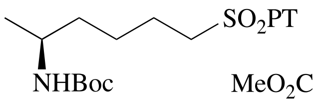
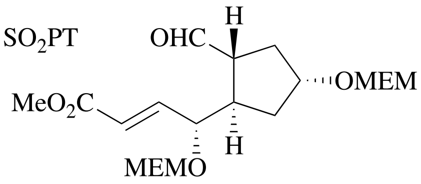
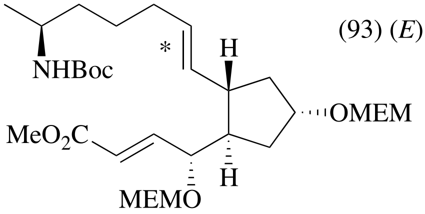
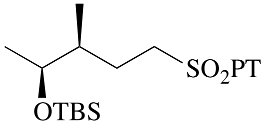
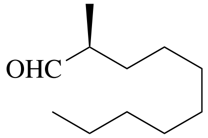
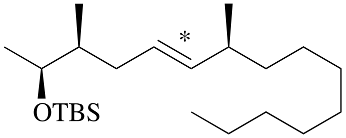
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	1. LiHMDS, THF-HMPA –78°, 15 min 2. Aldehyde, –78°, 3 h	 (72) (*E*)/(*Z*)* = 93:7	162
	 	1. KHMDS, DME, –78°, 35 min 2. Aldehyde, –78°, 3 h; rt, 1 h	 (83) (*E*)/(*Z*)* = 91:9	297
	 	1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78°, 2 h; rt, 1 h	 (93) (*E*)*-isomer	296
	 	1. LiHMDS, THF, –78°, 1 h 2. Aldehyde, 1 h; rt	 (83) (*E*)*-isomer	298

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

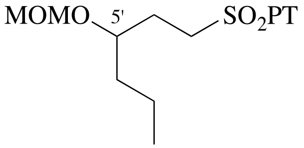
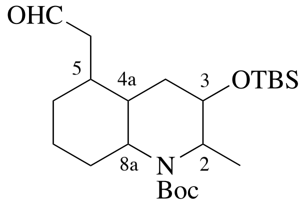
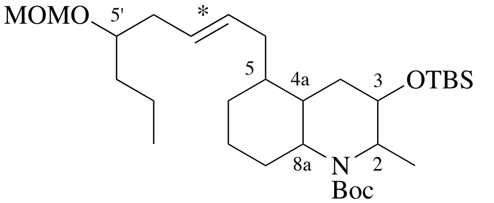
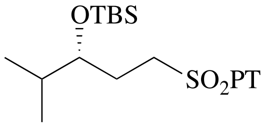
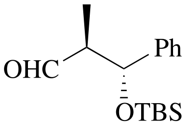
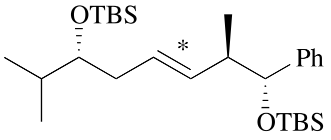
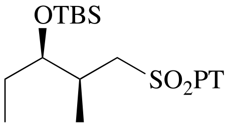
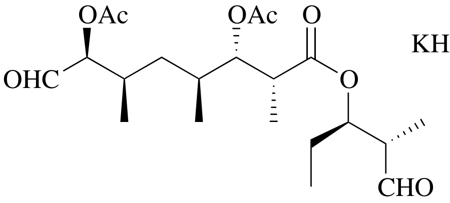
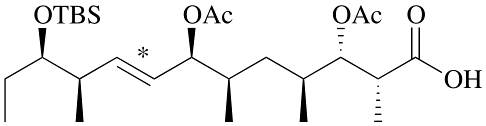
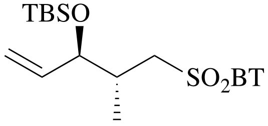
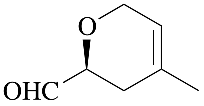
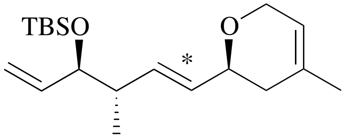
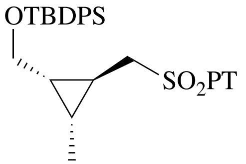
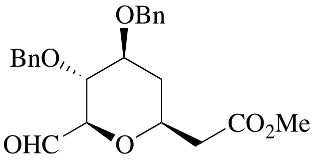
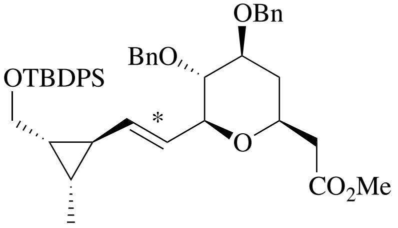
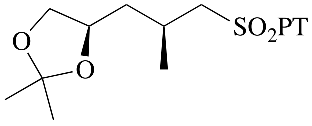
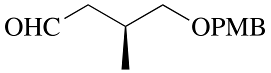
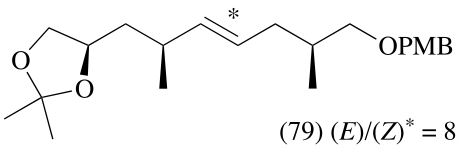
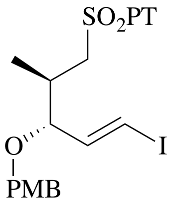
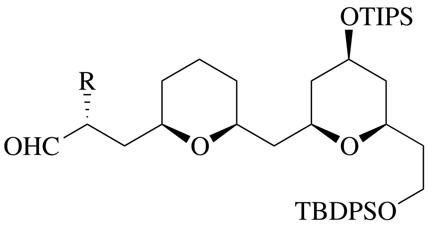
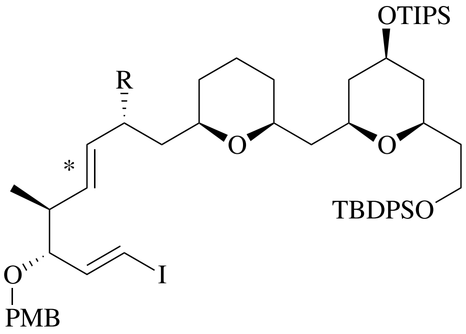
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt		
			C5' C5 C4a C8a C3 C2 Yield (*E*)*-isomer	
			(*R*) (*R*) (*S*) (*R*) (*R*) (*S*) (90)	299
			(*S*) (*R*) (*S*) (*R*) (*R*) (*S*) (90)	299
			(*R*) (*S*) (*R*) (*S*) (*S*) (*S*) (90)	300
			(*R*) (*R*) (*S*) (*R*) (*S*) (*R*) (>60)	301
			(*S*) (*R*) (*S*) (*R*) (*S*) (*R*) (>60)	301
	 	KHMDS	 (>56) (*E*)/(*Z*)* —	302
	 	KHMDS, THF, –78°; rt	 (50) (*E*)/(*Z*)* —	303
	 	1. KHMDS, THF, –78° 2. Aldehyde, –78°; rt	 (67) (*E*)/(*Z*)* = 88:12	153

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	 	1. $MN(SiMe_3)_2$ (2 eq), THF-HMPA, –78°, 5 min 2. Aldehyde (2 eq), –78° to rt, 3 h	 M (E)/(Z)* Li (63) 90:10 Na (78) 80:20 K (63) 50:50	304
	 	1. LiHMDS, THF/DMPU –78°, 45 min 2. Aldehyde, –78°; rt, 3 h	 (79) (*E*)/(*Z*)* = 83:17	305
	 	1. $MN(SiMe_3)_2$, see table 2. Aldehyde		306 63 307

R	M	Solvent	Temp/Time		(*E*)/(*Z*)*
H	Li	THF-HMPA	–78°, 20 min; rt, 3 h	(88)	93:7
Me	Li	THF-HMPA	–78°, 2.5 h; rt, 3.5 h	(63)	95:5
Me	Li	THF-HMPA	–78°, 0.5 h; rt, 2 h	(80)	94:6
Me	K	DME	–55°, 1 h; rt, 1.5 h	(11)	93:7
Me	K	THF	–78°, 1 h; rt, 21 h	(14)	88:12
Me	K	THF-HMPA	–78°, 2.5 h; rt, 3.5 h	(15)	95:5

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

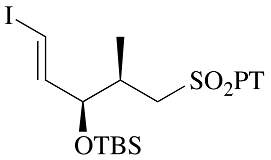
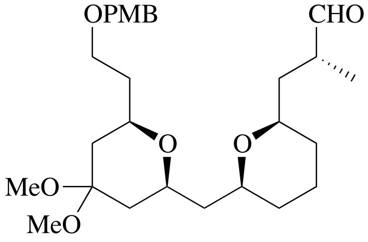
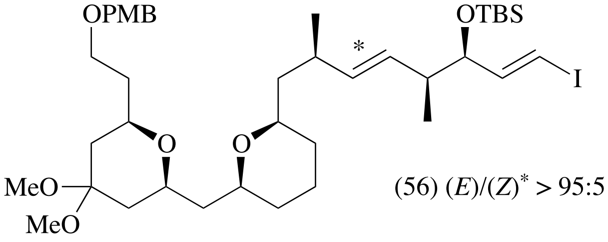
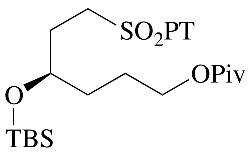
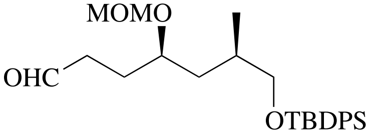
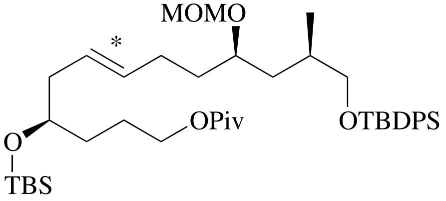
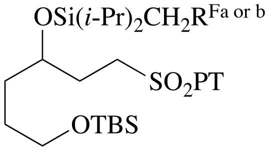
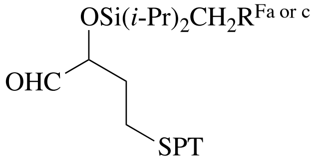
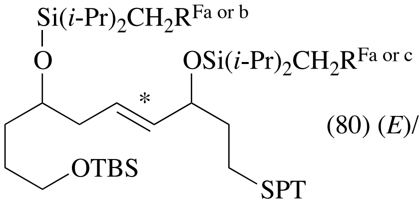
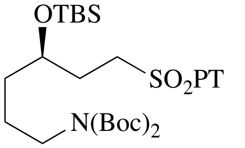
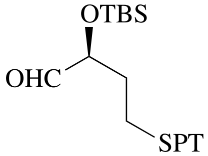
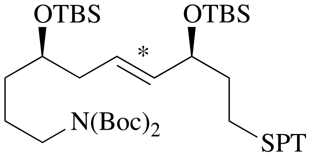
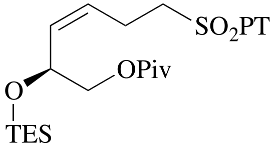
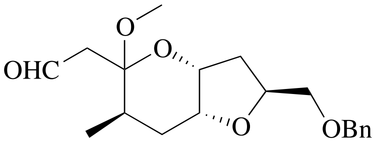
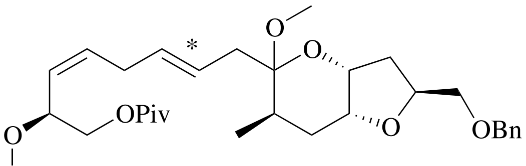
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			1. LiHMDS, THF-HMPA, –78°, 30 min 2. Aldehyde, –78°, 2 h; rt, 15 h	 (56) $(E)/(Z)^* > 95:5$	308
			1. KHMDS, THF, –78°, 40 min 2. Aldehyde, –78°, 1 h	 (60) $(E)^*$-isomer	309
	 $R^{Fa} = n\text{-}C_4F_9$; $R^{Fb} = n\text{-}C_3F_7$; $R^{Fc} = n\text{-}C_6F_{13}$		1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78°, 1.5 h; rt	 (80) $(E)/(Z)^* = 90:10$	310
			1. KHMDS 2. Aldehyde	 (86) $(E)^*$-isomer only	311
			1. KHMDS, DME, –60°, 40 min 2. Aldehyde; –50°, 1.5 h; 0°, 1.5 h; rt	 (88) $(E)/(Z)^* = 84:16$	312

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

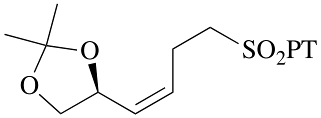
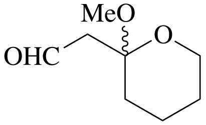
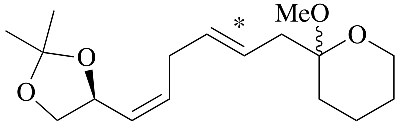
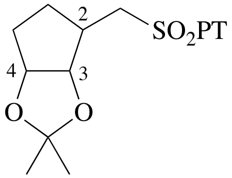
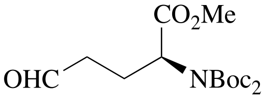
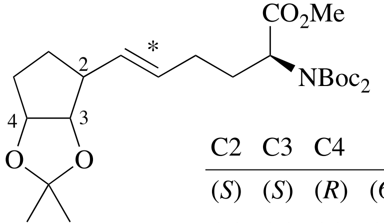
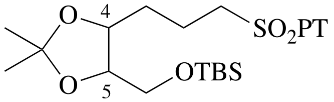
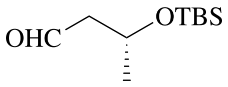
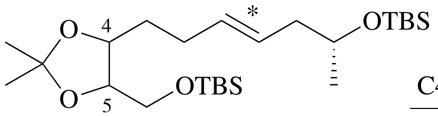
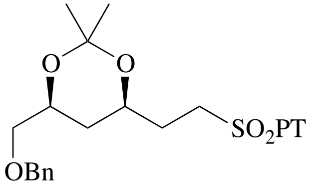
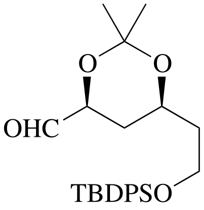
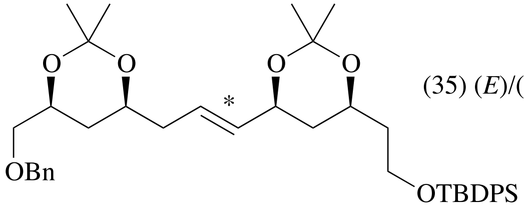
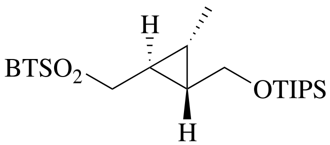
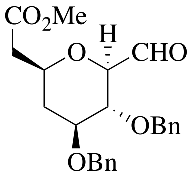
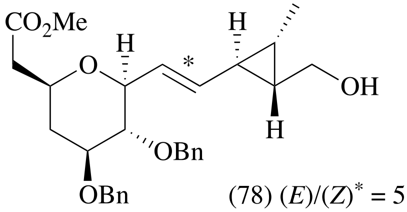
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	 	1. KHMDS, THF, –78°; rt, 1 h 2. Aldehyde, –78°, 2 h; rt, 1 h	 (90) (*E*)/(*Z*)* = 88:12	313
	 	1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1-3 h; rt, 20 h	 C2 C3 C4 (*E*)/(*Z*)* (*S*) (*S*) (*R*) (69) 90:10 (*R*) (*R*) (*S*) (71) 80:20	314
	 	LiHMDS, THF, –78°	 C4 C5 (*E*)/(*Z*)* (*S*) (*S*) (84) 73:27 (*R*) (*R*) (72) 71:29	315
	 	LiHMDS, 18-crown-6, DME, –78°, 24 h	 (35) (*E*)/(*Z*)* = 57:43	316
	 	1. NaHMDS, DMF, –45° to rt 2. p-TsOH, MeOH	 (78) (*E*)/(*Z*)* = 58:42	317

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

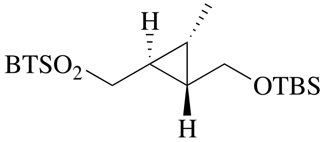
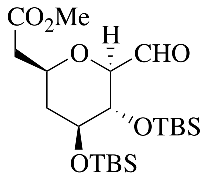
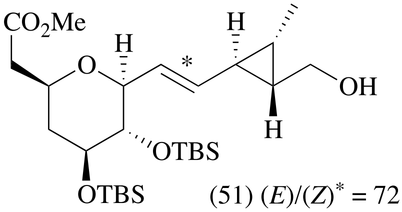
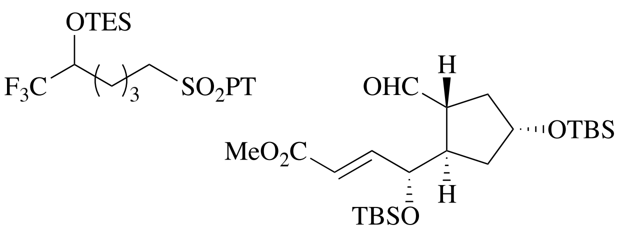
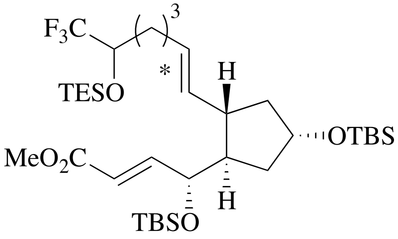
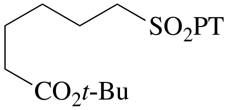
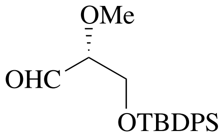
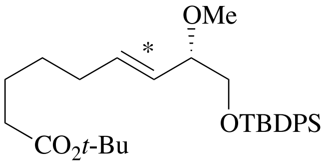
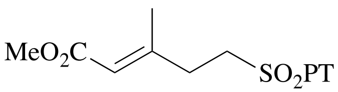
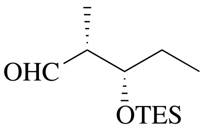
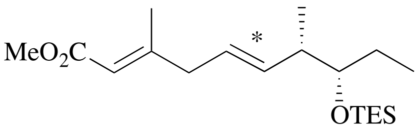
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	1. NaHMDS, DMF, –60°, 1 h; rt, 30 min 2. CF_3CO_2H, THF-H_2O, rt, 3h	 (51) (*E*)/(*Z*)* = 72:28	318 317
		KHMDS, DME, –78° to rt	 (90) (*E*)*-isomer	319
	 	1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78° to rt, 3 h	 (76) (*E*)/(*Z*)* = 50:50	320
	 	1. KHMDS, THF-DME, –60° 2. Aldehyde	 (97) (*E*)/(*Z*)* = 94:6	265

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

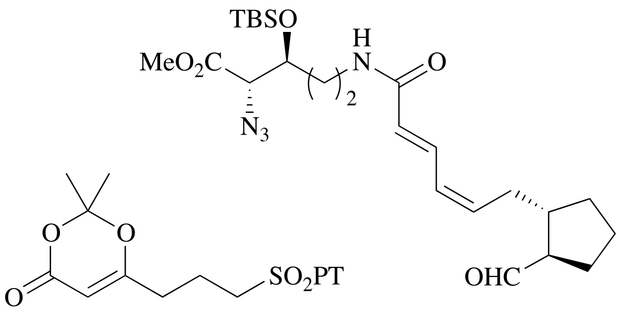
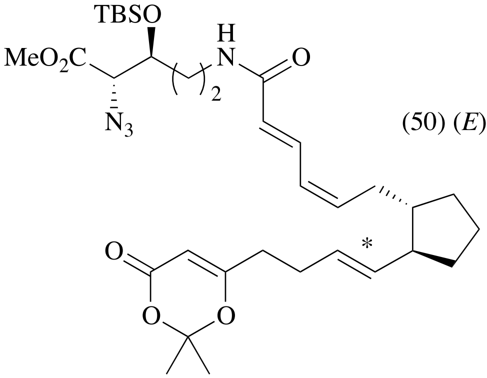
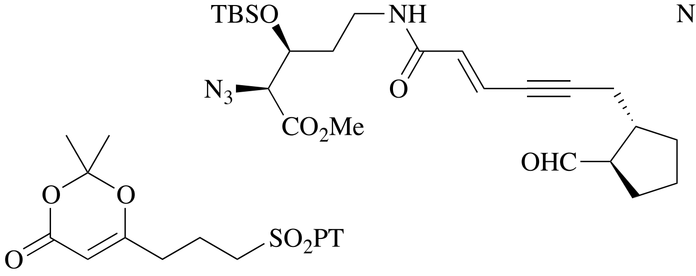
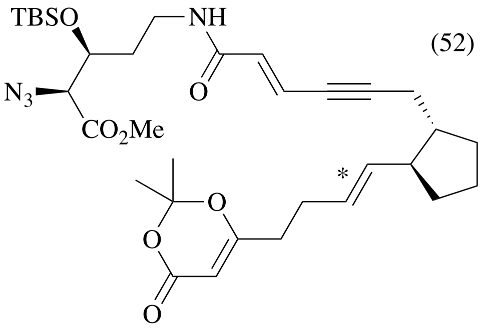
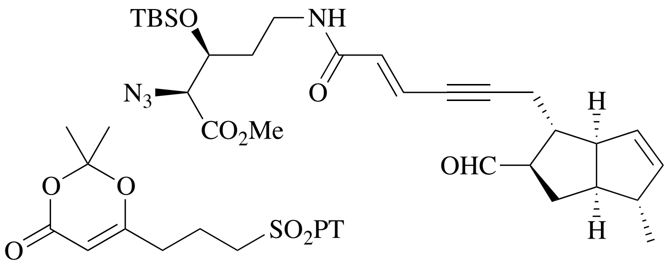
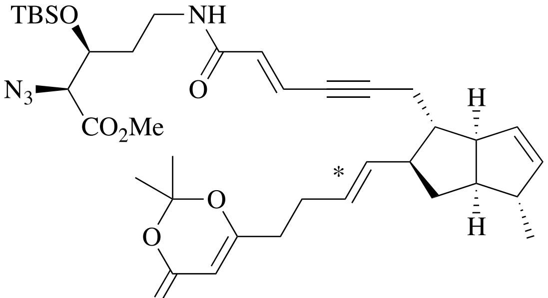
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		NaHMDS, DME, –78° to rt	 (50) (*E*)/(*Z*)* —	321
		NaHMDS, DME –55° to rt, 16 h	 (52) (*E*)/(*Z*)* —	321
		NaHMDS, DME, –55° to rt	 (52) (*E*)*-isomer only	322 323

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

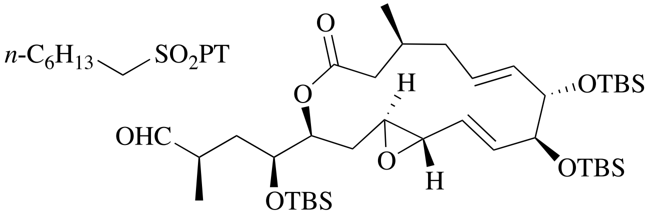
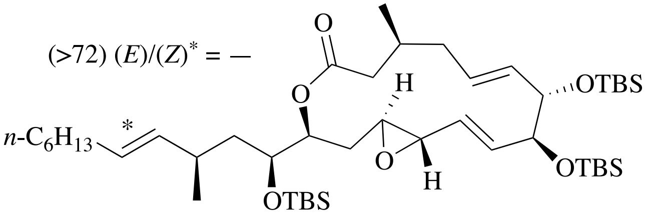
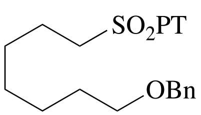
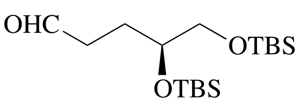
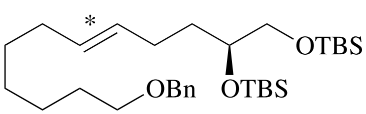
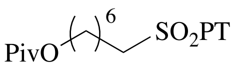
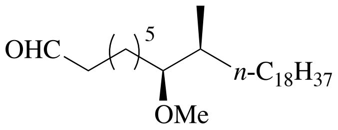
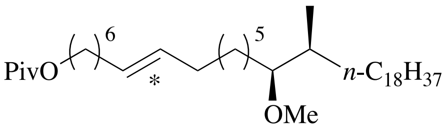
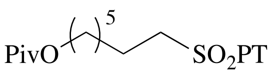
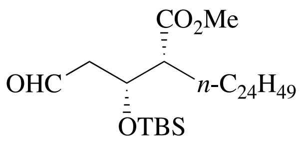
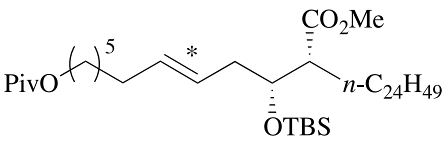
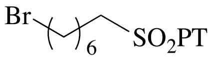
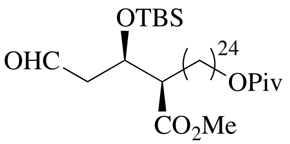
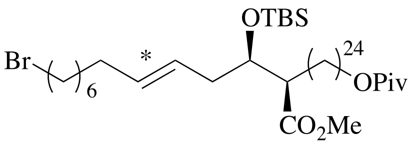
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. NaHMDS, THF-DMF, −78°, 40 min 2. Aldehyde, −78°, 45 min; rt	 (>72) (*E*)/(*Z*)* = —	258
	 	1. NaHMDS, DME, −78°, 5 min 2. Aldehyde, to −50°, 1 h	 (86) (*E*)/(*Z*)* = 97:3	324
	 	LiHMDS, THF, −12°	 (81) (*E*)/(*Z*)* —	287
	 	LiHMDS, THF, −15°	 (72) (*E*)/(*Z*)* = —	287
	 	LiHMDS, THF, −10° to rt	 (76) (*E*)/(*Z*)* = 67:33	325

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

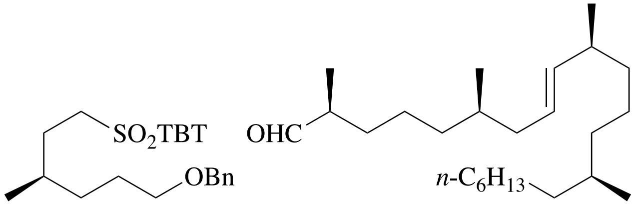
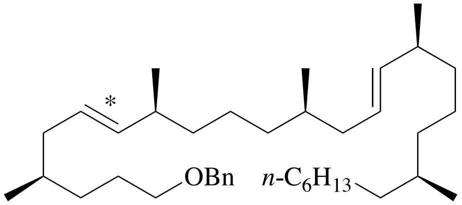
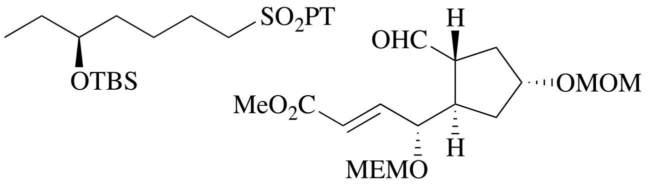
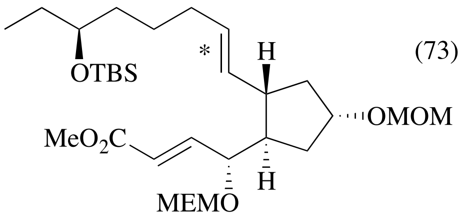
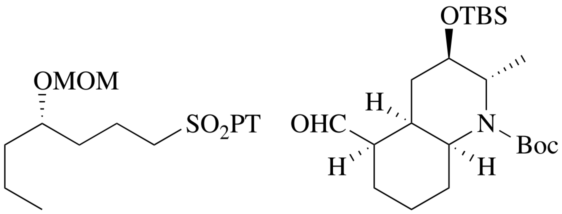
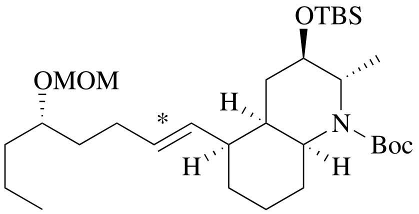
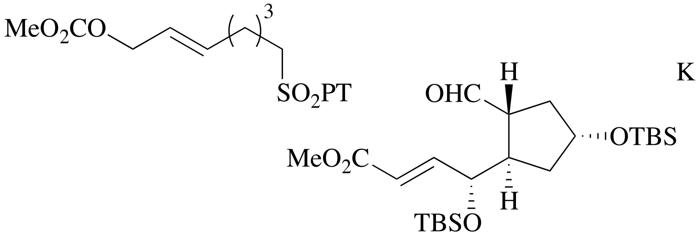
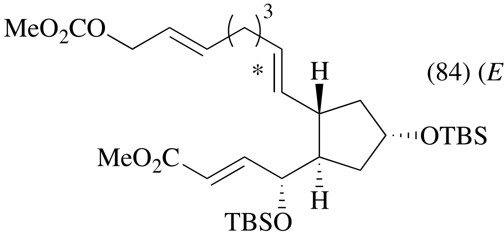
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		1. LiHMDS 2. Aldehyde, THF, –78° to rt	 (81) (*E*)/(*Z*)*= —	326 327
		1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78°; rt	 (73) (*E*)*-isomer	319
		1. KHMDS, THF, –78°, 45 min 2. Aldehyde, rt	 (68)	328
		KHMDS, DME, –78° to rt	 (84) (*E*)*-isomer	319

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

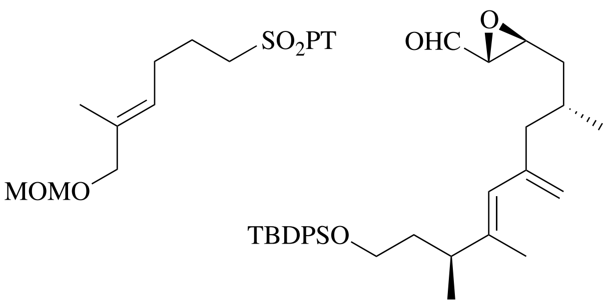
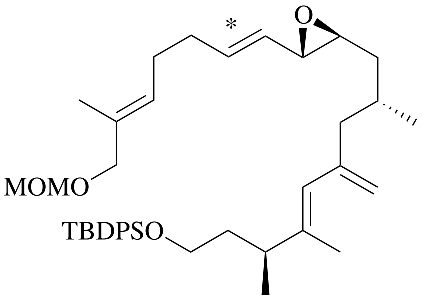
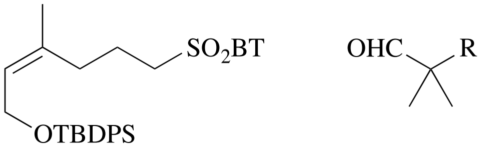
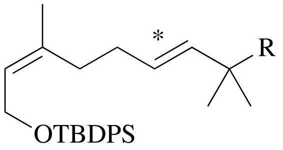
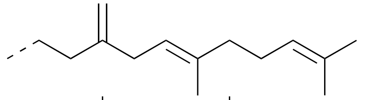
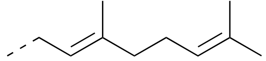
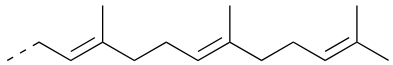
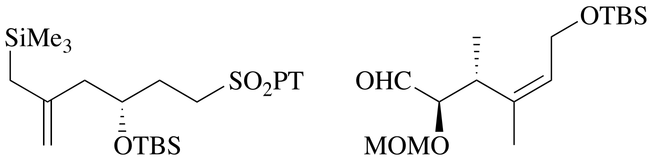
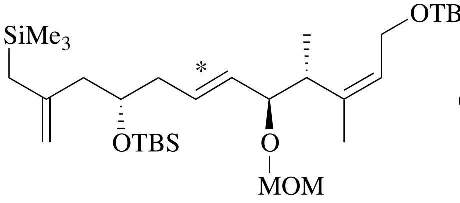
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		KHMDS, DMF, –78°, 16 h	 (75) (*E*)/(*Z*)* = 80:20	329
		NaHMDS, THF, –78°, 2 h	 (*E*)*-isomer only	330
			R	
			 (58)	
			 (55)	
			 (62)	
		1. KHMDS, THF 2. Aldehyde	 (71) (*E*)*-isomer	331

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

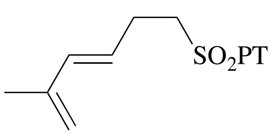
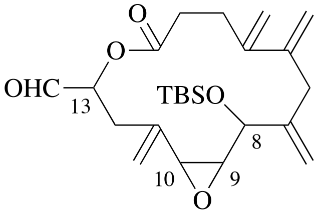
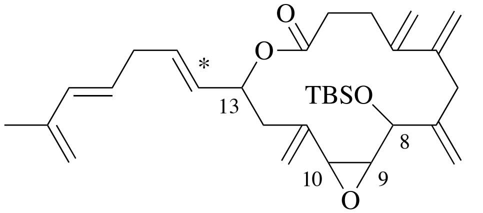
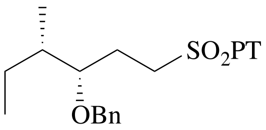
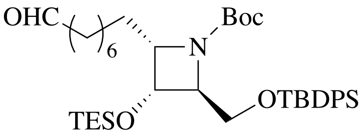
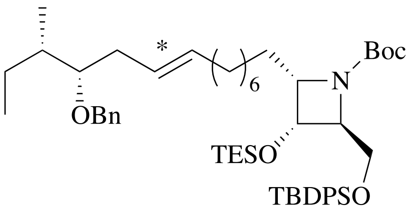
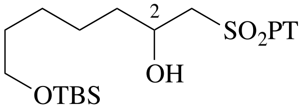
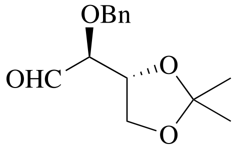
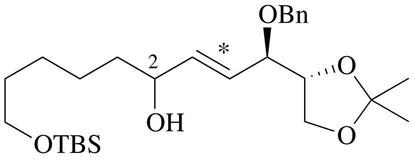
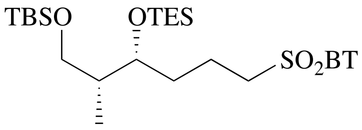
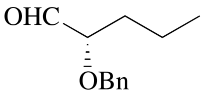
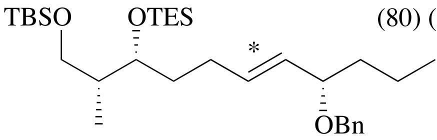
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7	 	1. KHMDS, solvent, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt, 30 min	 C8 C9 C10 C13 Solvent (*E*)/(*Z*)* (*R*) (*S*) (*S*) (*R*) THF (—) 75:25 (*R*) (*S*) (*S*) (*R*) DME-DMPU (70) 91:9 (*R*) (*S*) (*S*) (*S*) THF (66) 75:25 (*S*) (*S*) (*S*) (*S*) DME-DMPU (98) >91:9 (*R*) (*R*) (*R*) (*S*) THF (75) 75:25	332
	 	1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 15 min	 (93) 'predominantly' (*E*)*-isomer	333
	 	1. KHMDS, THF, 0° to rt, 20 min 2. Aldehyde, –78°, 3 h; rt 12 h	 C3 (*E*)/(*Z*)* (*R*) (66) 99:1 (*S*) (60) 99:1	334
	 	1. LiHMDS, THF, –78° 2. Aldehyde, –78° to rt	 (80) (*E*)/(*Z*)* = 55:45	228

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

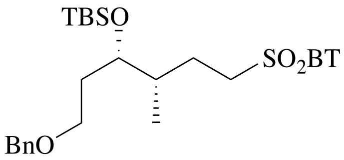
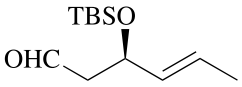
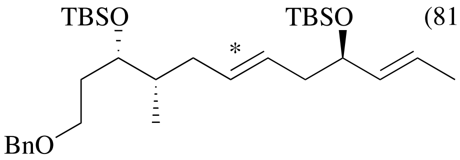
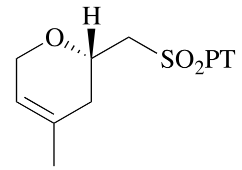
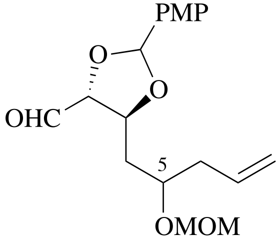
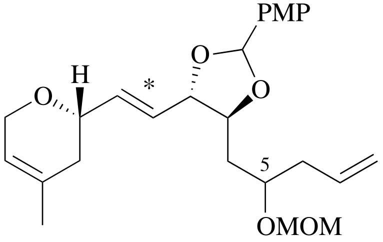
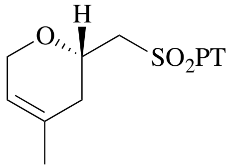
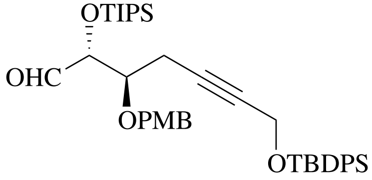
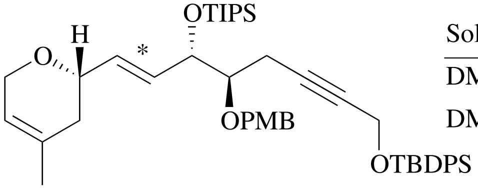
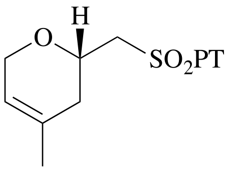
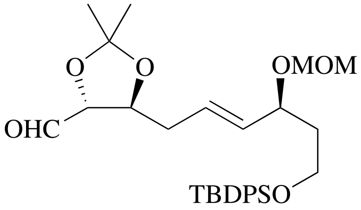
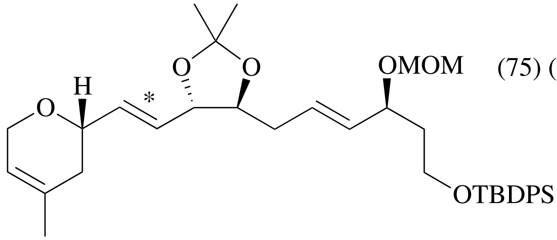
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 	LiHMDS, THF, –72 to –10°, 2 h	 (81) (*E*)/(*Z*)* = 50:50	335
	 	LiHMDS, DMF-HMPA –35° to rt	 C5 (*E*)*-isomer (*R*) (>64) (*S*) (>61)	336 337 338
	 	KHMDS, Solvent	 Solvent (*E*)/(*Z*)* DMF (80) 43:56 DME (81) 83:16	339
	 	1. KHMDS, DMF-HMPA –60°, 15 min 2. Aldehyde, –78°; rt, 12 h	 (75) (*E*)*-isomer	340

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

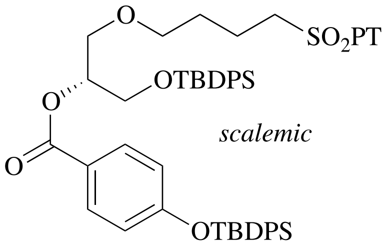
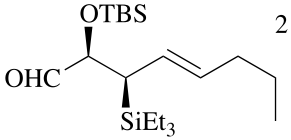
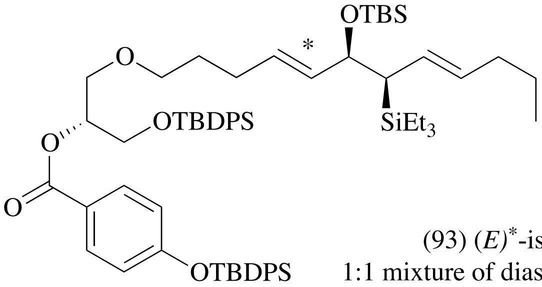
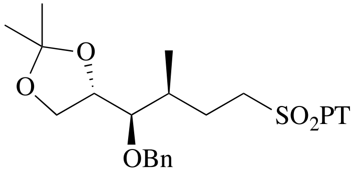
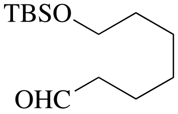
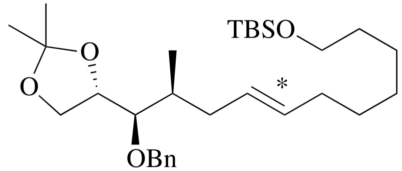
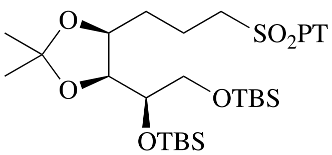
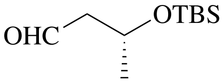
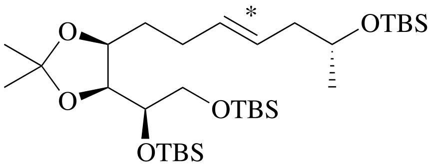
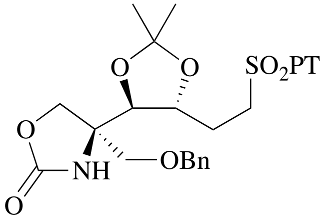
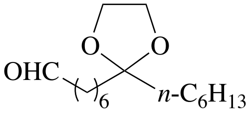
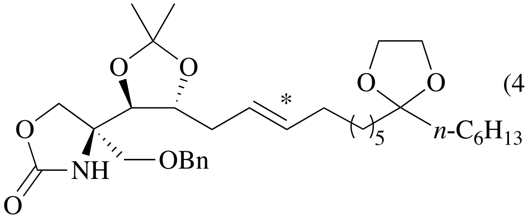
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 scalemic  racemic	1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1 h	 (93) (E)*-isomer 1:1 mixture of diastereoisomers	113
	 	KHMDS, DME, –56°, 3 h; rt, 2 h	 (76) (E)*-isomer only	341
	 	LiHMDS, THF, –78°	 (83) (E)*-isomer	315
	 	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt	 (46) (E)/(Z)* = 92:8	342

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

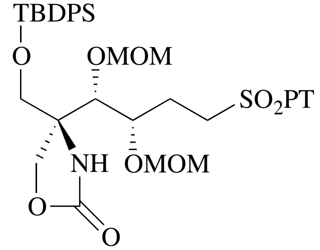
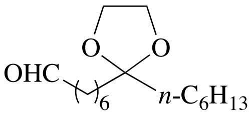
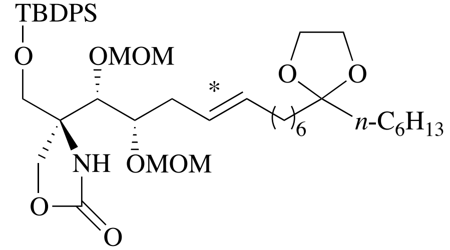
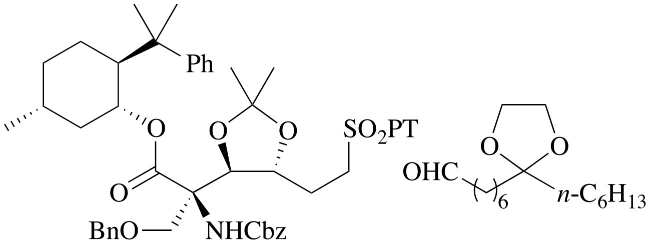
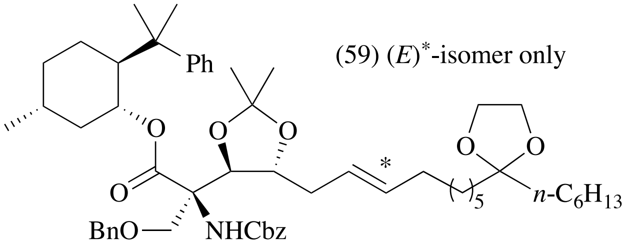
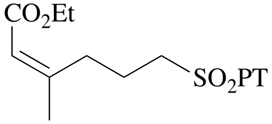
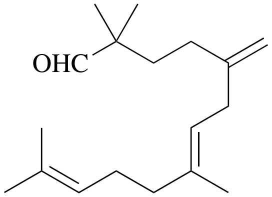
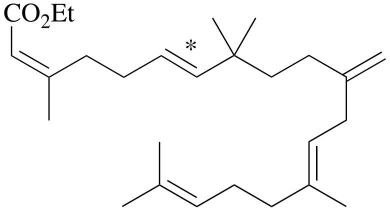
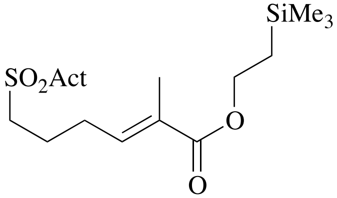
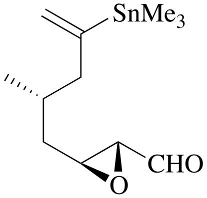
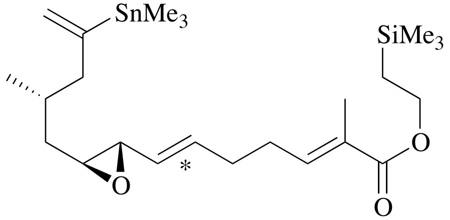
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 	KHMDS, DME	 (>61) 'predominantly $(E)^*$-alkene'	343
		1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3.5 h; rt, 1 h	 (59) $(E)^*$-isomer only	342
	 	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 12 h	 (80) $(E)/(Z)^*$ = 97:3	344
	 	KHMDS, DME, –78°	 Act (E)/(Z)* PT (65) 75:25 BT (—) 66:34	345

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

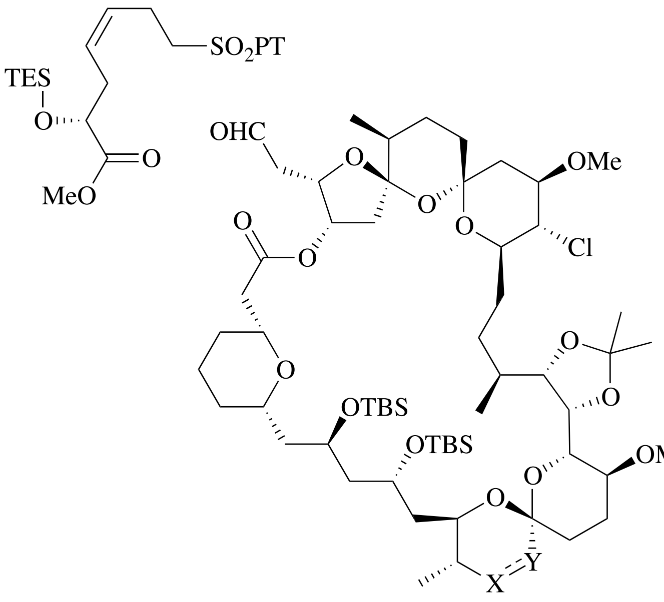
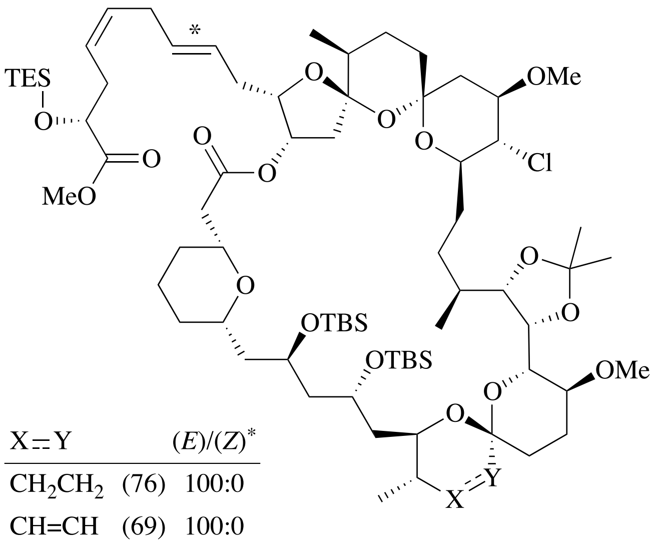
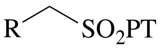
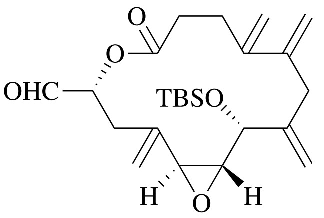
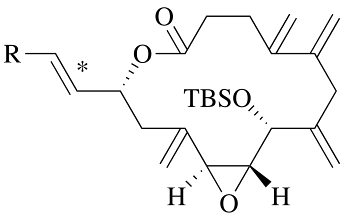
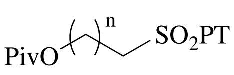
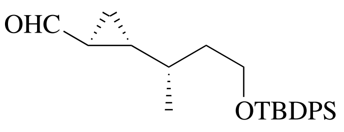
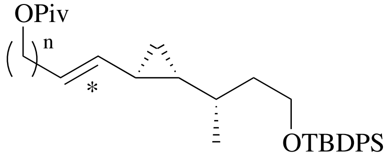
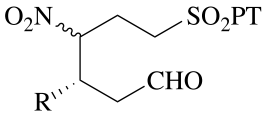
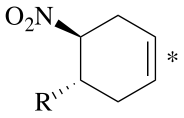
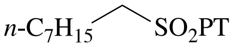
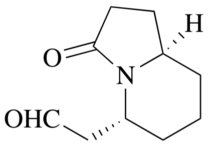
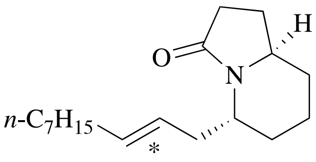
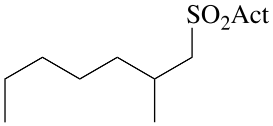
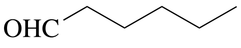
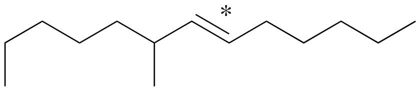
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		1. KHMDS, THF, –78°, 10 min to –60°, 2 h 2. Aldehyde, –78 to –65°, 1.5 h	 X⋯Y — $(E)/(Z)^*$ CH_2CH_2 (76) 100:0 CH=CH (69) 100:0	346 347
C_{7-8}	 	1. KHMDS, DME-DMPU, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt, 30 min	 R — $(E)/(Z)^*$ $Me_2C(CH_2)_3$ (46) >91:9 $PhCH_2$ (28) >91:9	332
C_{7-10}	 	LiHMDS, THF, –12°	 n — $(Z)/(E)^*$ 6 (69) 72:28 7 (75) — 9 (85) 78:22	287

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

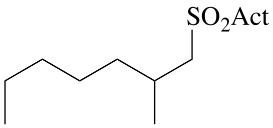
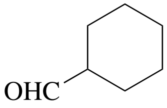
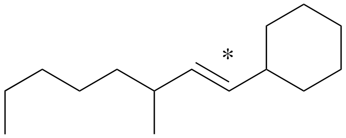
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-10}		**A**: 1. Cs_2CO_3, THF-DMF, 70°, 2 h 2. DBU, CH_3CN, –40°, 15 min *or* **B**: DBU, CH_3CN, 0 to –40°, 0.5 h		348
C_8	 	KHMDS, DME	 (62) (*E*)/(*Z*)* = 75:25	349

R			dr	R			dr
Me	**B**	(45)	79:21	$(MeO)_2CHCH_2$	**A**	(60)	90:10
Et	**A**	(51)	92:8	Ph	**B**	(52)	94:6
n-Pr	**A**	(57)	91:9	4-$NO_2C_6H_4$	**B**	(49)	91:9
n-Bu	**A**	(60)	85:15	4-ClC_6H_4	**B**	(50)	91:9
n-C_9H_{19}	**A**	(61)	76:24	4-$MeOC_6H_4$	**B**	(52)	85:15
(*Z*)-EtCH=CH$(CH_2)_2$	**A**	(63)	75:25				

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 	1. $MN(SiMe_3)_2$, temp, 30 min 2. Aldehyde, temp, 3 h; rt		4

			Act = BT		Act = PT	
Solvent	Temp	M		(*E*)/(*Z*)*		(*E*)/(*Z*)*
PhMe	–78°	Li	(86)	54:46	(96)	43:57
PhMe	–78°	Na	(78)	57:43	(65)	38:62
PhMe	–78°	K	(31)	26:74	(25)	62:38
Et_2O	–78°	Li	(74)	60:40	(61)	48:52
Et_2O	–78°	Na	(84)	58:42	(98)	32:68
Et_2O	–78°	K	(56)	36:64	(20)	37:63
THF	–78°	Li	(98)	57:43	(100)	67:33
THF	–78°	Na	(89)	39:61	(88)	32:68
THF	–78°	K	(68)	25:75	(23)	76:24
DME	–60°	Li	(100)	44:56	(100)	60:40
DME	–60°	Na	(87)	64:36	(100)	78:22
DME	–60°	K	(63)	46:54	(22)	96:4

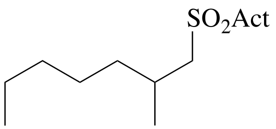
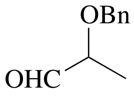
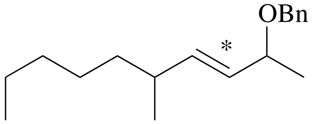
TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 	1. $MN(SiMe_3)_2$, temp, 30 min 2. Aldehyde, temp, 3 h; rt		4

			Act = BT		Act = PT	
Solvent	Temp	M		(*E*)/(*Z*)*		(*E*)/(*Z*)*
PhMe	–78°	Li	(88)	70:30	(85)	39:61
PhMe	–78°	Na	(66)	86:14	(83)	67:33
PhMe	–78°	K	(48)	76:24	(68)	98:2
Et_2O	–78°	Li	(70)	67:33	(74)	41:59
Et_2O	–78°	Na	(75)	87:13	(98)	53:47
Et_2O	–78°	K	(68)	78:22	(28)	92:8
THF	–78°	Li	(87)	72:28	(90)	53:47
THF	–78°	Na	(84)	67:33	(71)	48:52
THF	–78°	K	(85)	40:60	(58)	97:3
DME	–60°	Li	(83)	58:42	(100)	40:60
DME	–60°	Na	(96)	55:45	(100)	84:16
DME	–60°	K	(100)	36:64	(59)	99:1

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

C$_8$

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	1. MN(SiMe$_3$)$_2$, temp, 30 min 2. Aldehyde, temp, 3 h; rt		20

			Act = BT		Act = PT	
Solvent	Temp	M		(*E*)/(*Z*)*		(*E*)/(*Z*)*
PhMe	–78°	Li	(100)	47:53	(—)	43:57
PhMe	–78°	Na	(72)	61:39	(79)	30:70
PhMe	–78°	K	(98)	61:39	(71)	64:36
Et$_2$O	–78°	Li	(85)	48:52	(100)	42:58
Et$_2$O	–78°	Na	(34)	42:58	(100)	28:72
Et$_2$O	–78°	K	(88)	41:59	(48)	34:66
THF	–78°	Li	(89)	54:46	(87)	44:56
THF	–78°	Na	(84)	50:50	(99)	19:81
THF	–78°	K	(95)	34:66	(66)	45:55
DME	–60°	Li	(55)	68:32	(90)	45:55
DME	–60°	Na	(94)	57:43	(93)	50:50
DME	–60°	K	(86)	40:60	(37)	80:20

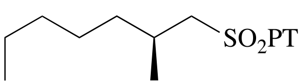
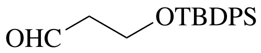
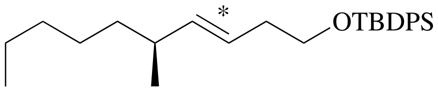
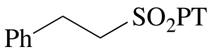
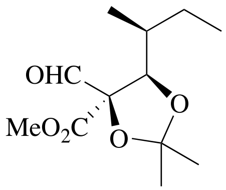
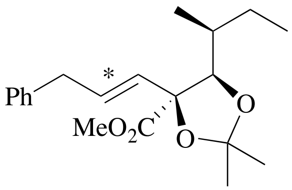
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	KHMDS, DME, –60° to rt, 12 h	 (35) (*E*)/(*Z*)* = 92:8	350
	 	1. KHMDS, THF, –78°, 15 min 2. Aldehyde, –78° to rt, 12 h	 (93) (*E*)/(*Z*)* > 96:4	229

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

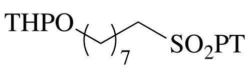
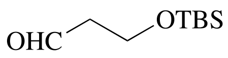
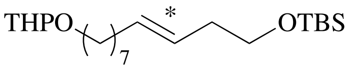
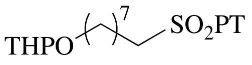
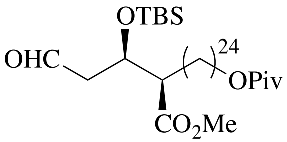
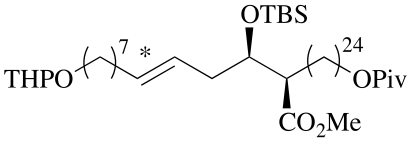
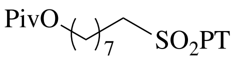
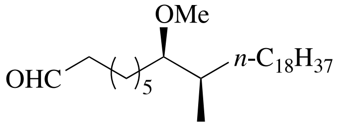
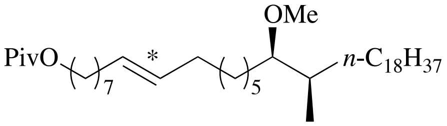
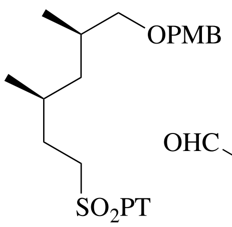
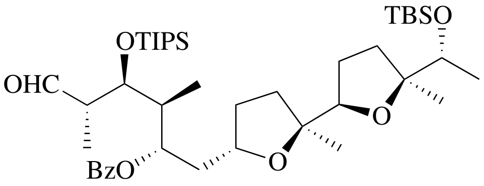
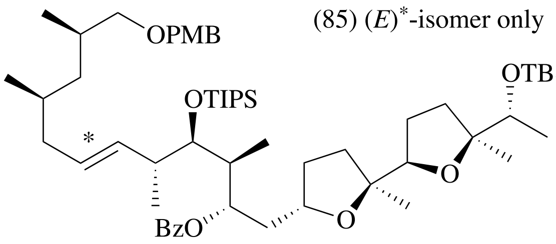
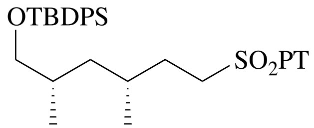
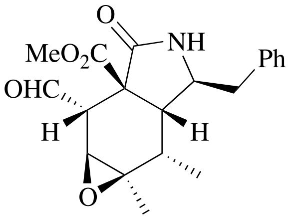
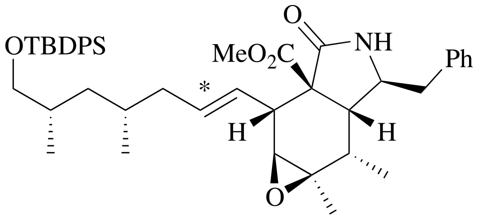
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	 	LiHMDS, THF, 0°	 (74) (*E*)/(*Z*)* = —	351
	 	LiHMDS, THF, –10° to rt	 (85) (*E*)/(*Z*)* = 72:28	325
	 	LiHMDS, THF, –2°; rt, 16 h	 (91) (*E*)/(*Z*)* = 72:28	276
	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt, 18 h	 (85) (*E*)*-isomer only	352
	 	1. KHMDS, THF, –78° 2. Aldehyde, –100 to –40°	 (86) (*E*)*-isomer only	353

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

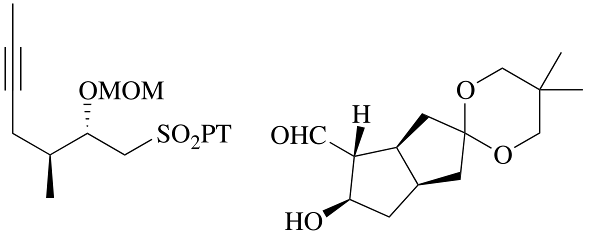
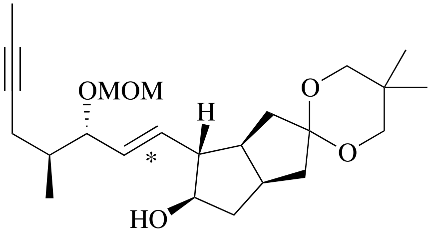
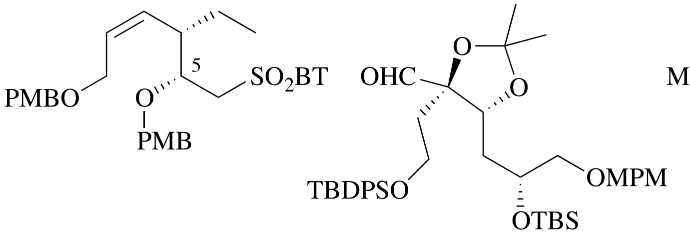
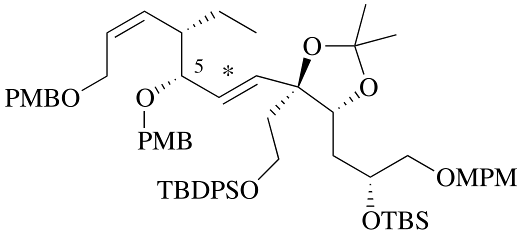
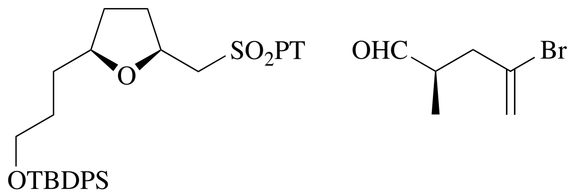
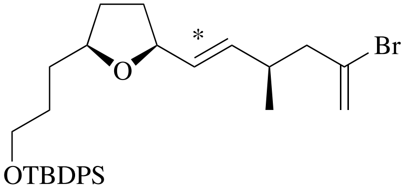
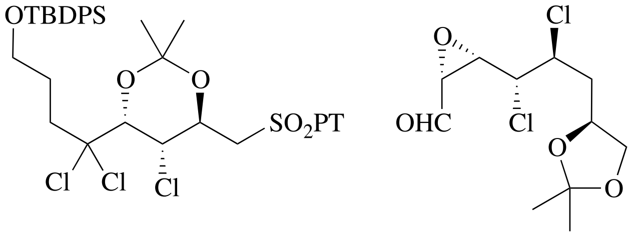
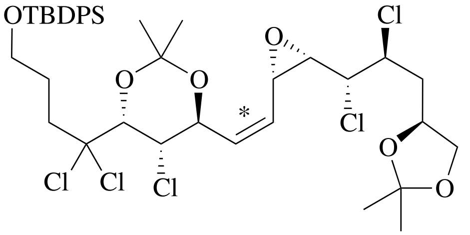
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		1. LiHMDS, THF, HMPA, –78°, 20 min 2. Aldehyde, –78° to rt, 6.5 h	 (57) (*E*)/(*Z*)* —	354
		$MN(SiMe_3)_2$	 M (*E*)/(*Z*)* dr (C5) Li (14) — 100:0 Na (49) — 60:40 K (5) — 25:75	355
		1. KHMDS, DMF-HMPA (4:1), –78°, 10 min 2. Aldehyde, –78°, 1 h; rt, 15 h	 (78) (*E*)/(*Z*)* > 95:5	118
		NaHMDS, PhMe, –78° to rt, 17 h	 (47) (*E*)/(*Z*)* = 17:83	356

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

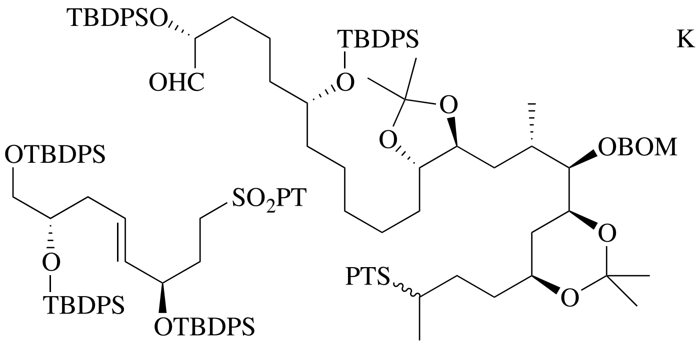
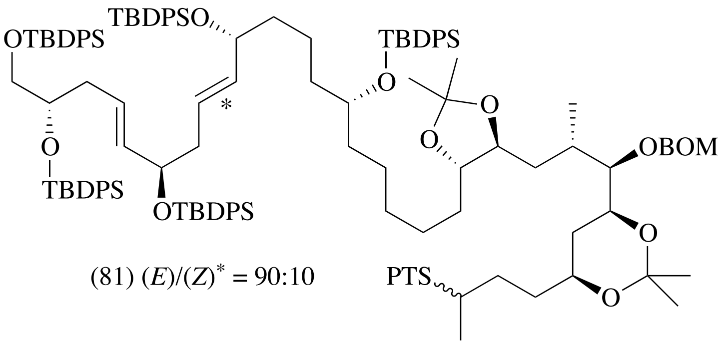
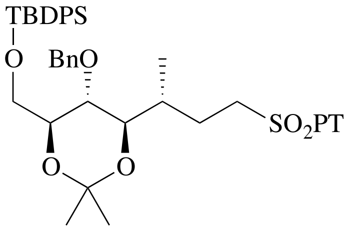
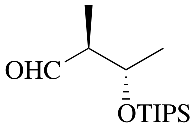
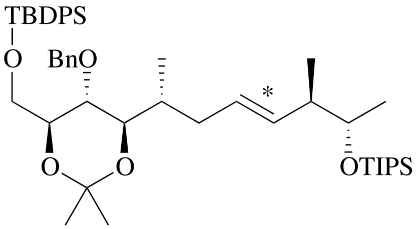
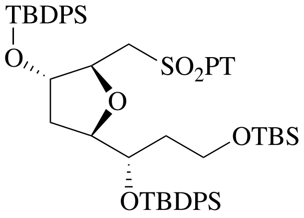
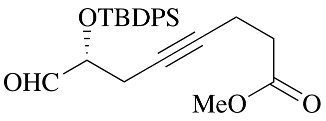
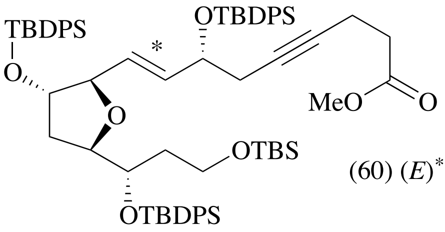
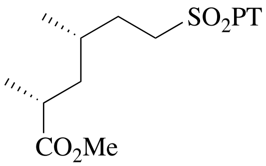
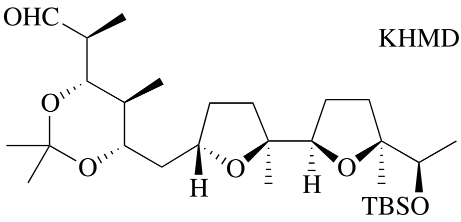
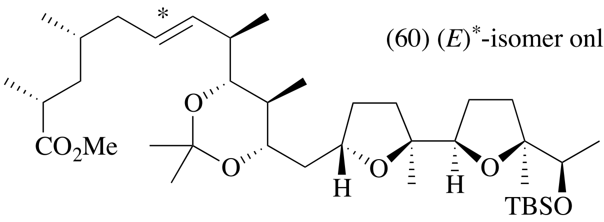
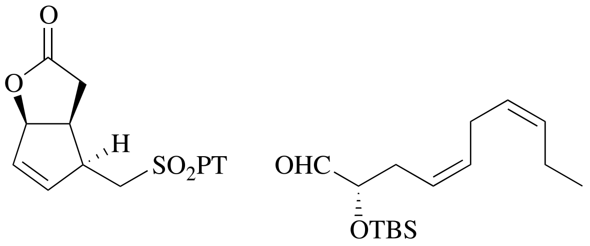
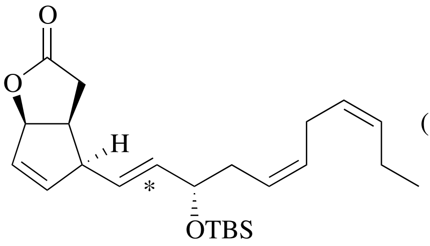
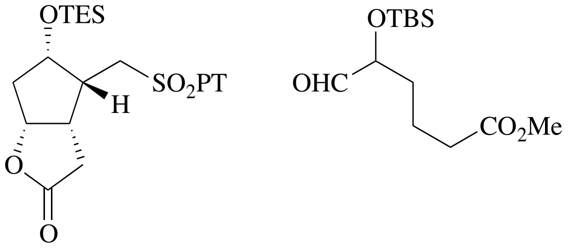
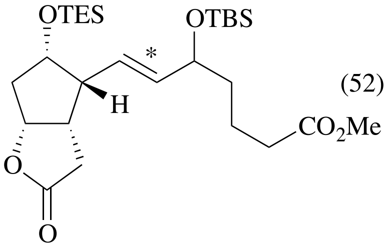
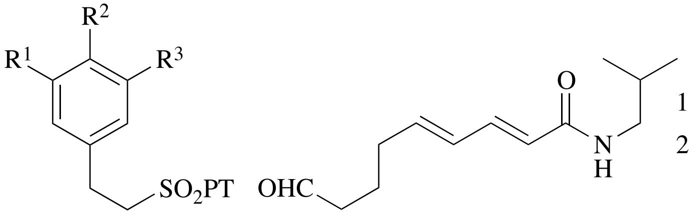
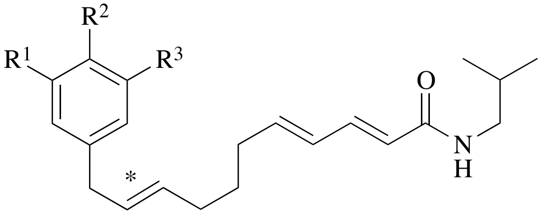
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		KHMDS, THF, –78°, 4 h; rt, 12 h	 (81) (*E*)/(*Z*)* = 90:10	226
	 	1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°; rt, 12 h	 (76) (*E*)*-isomer predominantly	357
	 	1. KHMDS, DME, –65°, 45 min 2. Aldehyde, –65°; rt, 1 h	 (60) (*E*)*-isomer only	358
	 	KHMDS, THF, –78°, 1 h; rt	 (60) (*E*)*-isomer only	359

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		1. KHMDS, DME, –78°, 1 h 2. Aldehyde, DME, –70°; rt, 4 h	 (60) (*E*)*-isomer only	360
		KHMDS, DME, –60°; rt, 8 h	 (52) (*E*)/(*Z*)* = 63:37	361 362
$C_{8–10}$		1. KHMDS, DME, –60°, 1 h 2. Aldehyde, –60°, 2 h; 30 min, rt		363

R^1	R^2	R^3		(*E*)/(*Z*)*
H	H	H	(51)	>93:7
H	F	H	(58)	—
H	Cl	H	(53)	—
H	MeO	H	(50)	—
MeO	MeO	H	(49)	—

R^1	R^2	R^3		(*E*)/(*Z*)*
MeO	MeO	MeO	(51)	—
$–OCH_2O–$		H	(58)	—
$–O(CH_2)_2O–$		H	(56)	—
$–O(CH_2)_2–$		H	(54)	—

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

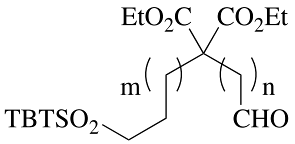
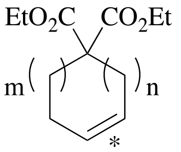
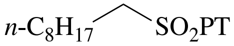
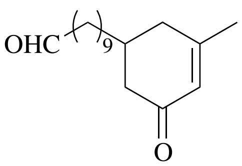
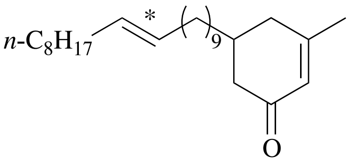
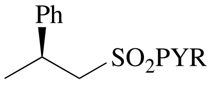
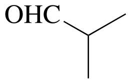
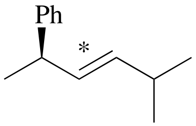
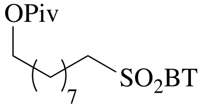
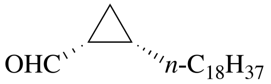
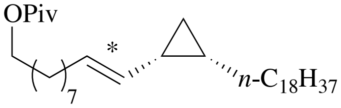
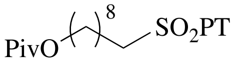
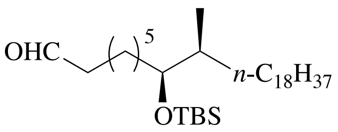
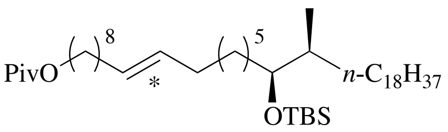
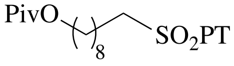
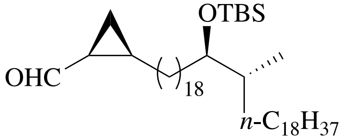
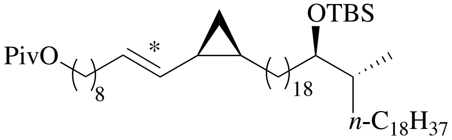
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-16}		Cs_2CO_3, THF-DMF, 70°, 16 h	 m n (E)/(Z)* 1 1 (91) 0:100 2 2 (32) 50:50 8 2 (56) 66:34	60
C_9	 	KHMDS	 (19) (*E*)/(*Z*)* = 83:17	364
	 	1. KHMDS, DME, –78°, 3 min 2. Aldehyde, –78°, 2 h	 (74) (*E*)/(*Z*)* = 65:35	365
	 	NaHMDS, THF, –10°, 1 h; rt, 12 h	 (75) (*E*)/(*Z*)* = 57:43	272
	 	LiHMDS, THF, –10°	 (91) (*E*)/(*Z*)* = 70:30	287
	 	LiHMDS, THF	 (87) (*E*)/(*Z*)* = —	277

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

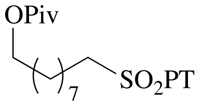
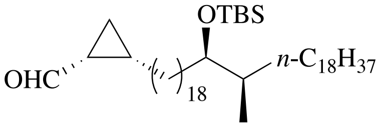
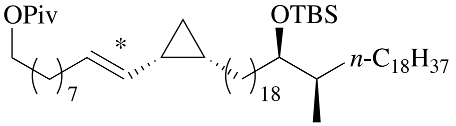
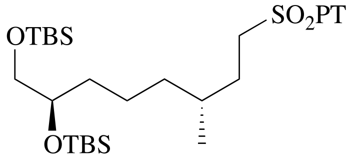
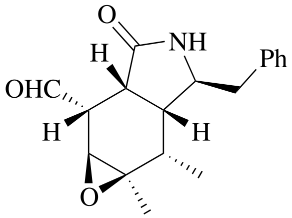
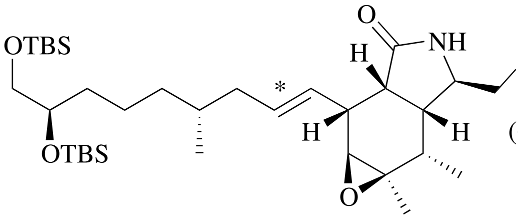
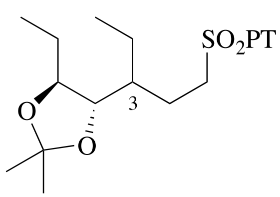
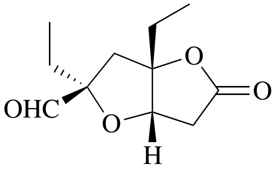
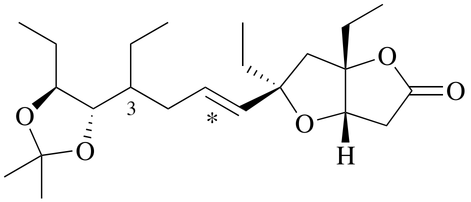
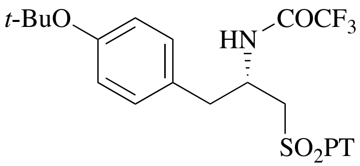
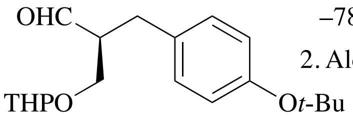
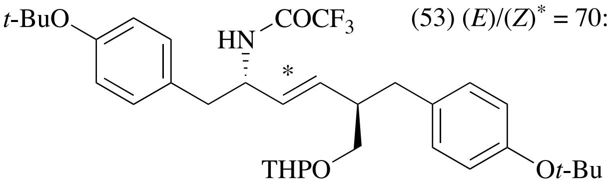
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9					
			LiHMDS, THF, –12° to rt, 2 h	 (87) isomeric ratio* = 86:14	278
			1. KHMDS, THF, –78° 2. Aldehyde, –100 to –40°	 (60) (*E*)*-isomer	353
			1. KHMDS, THF, –78°, 15 min 2. Aldehyde, –78°, 1 h; to rt	 C3 — Yield of (*E*)*-isomer (*R*) — (54) (*S*) — (40)	366 367
			1. NaHMDS (2 eq), DME, –78°, 30 min 2. Aldehyde, –78° to rt, 12 h	 (53) (*E*)/(*Z*)* = 70:30	368 369

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

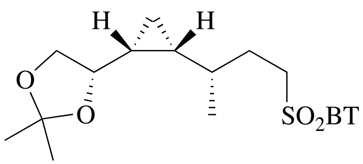
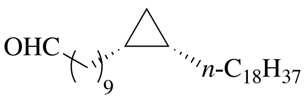
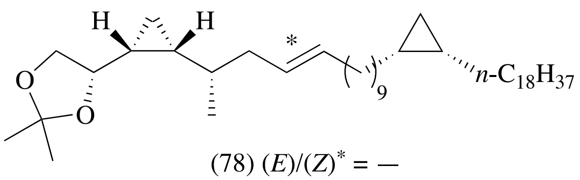
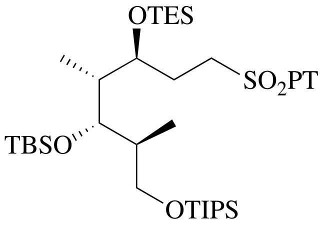
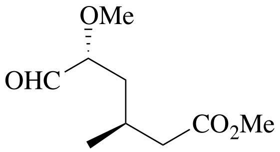
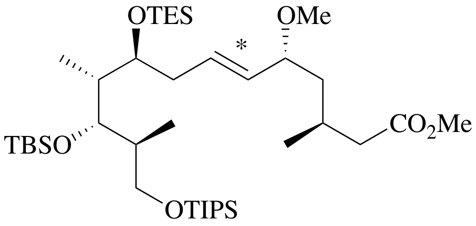
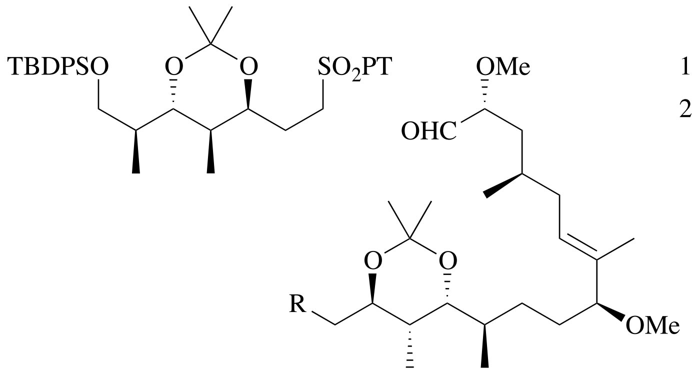
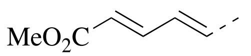
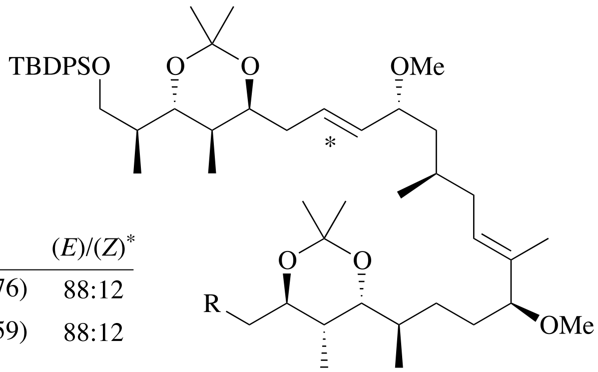
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	 	LiHMDS, THF, –5° to rt, 16 h	 (78) (*E*)/(*Z*)* = —	272
	 	1. M($SiMe_3$)$_2$, Solvent, –60°, 40 min 2. Aldehyde, –78°, 1 h; to rt	 M Solvent (*E*)/(*Z*)* Li THF — 67:33 Li DMF/HMPA (60) 92:8 K THF — 50:50 K DME (56) 85:15	370
		1. KHMDS, DME, –78° 2. Aldehyde R (*E*)/(*Z*)* $BnOCH_2$ (76) 88:12  (59) 88:12		371

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

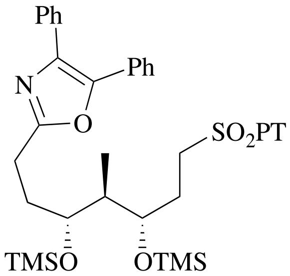
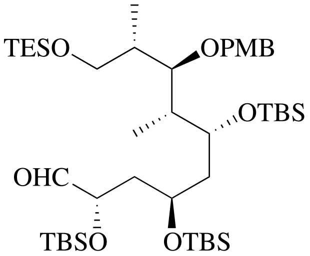
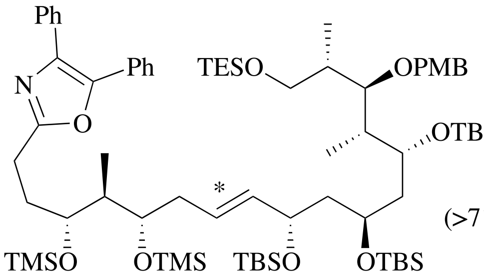
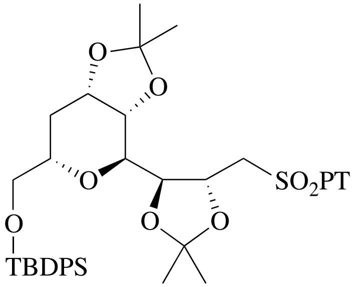
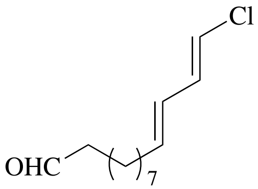
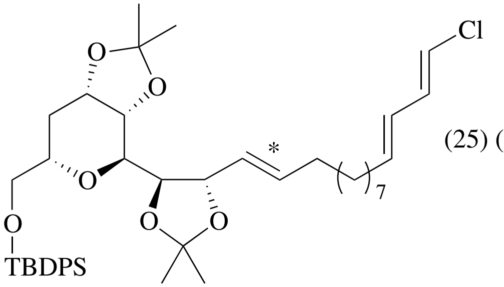
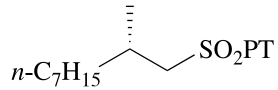
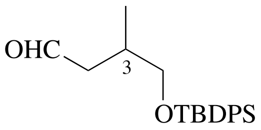
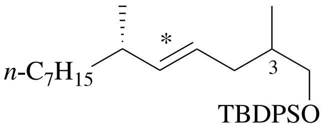
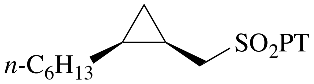
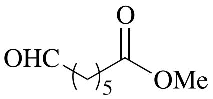
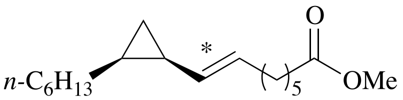
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9	 	KHMDS, DME, –48 to 20°	 (>71) (*E*)/(*Z*)* > 95:5	372
	 	1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1 h; rt, 2 h	 (25) (*E*)/(*Z*)* = 75:25	188
C_{10}	 	LiHMDS, THF, –78°; rt	 C3 (*E*)/(*Z*)* (*S*) (61) 70:30 (*R*) (65) —	268
	 	1. LiHMDS, THF, –78° 2. Aldehyde, –78°; rt	 (73) (*E*)/(*Z*)* = 70:30	373

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

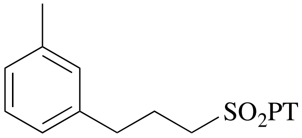
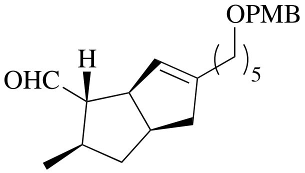
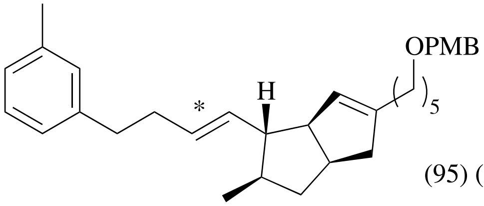
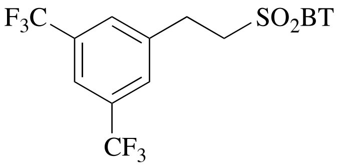
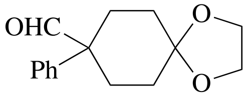
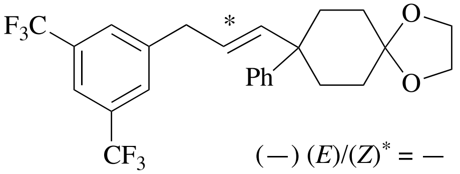
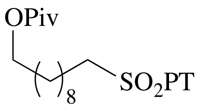
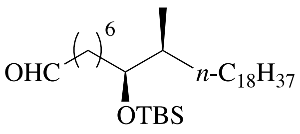
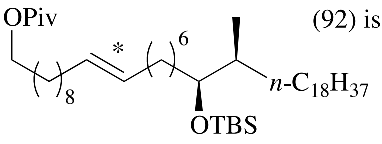
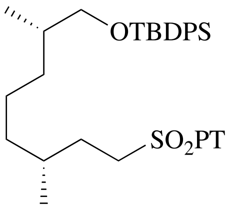
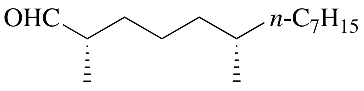
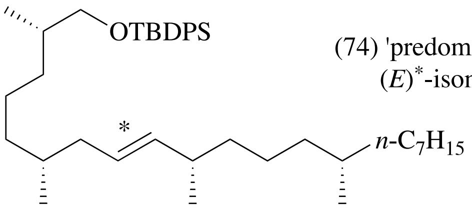
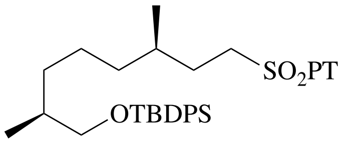
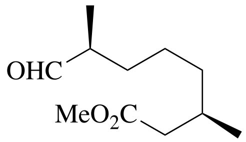
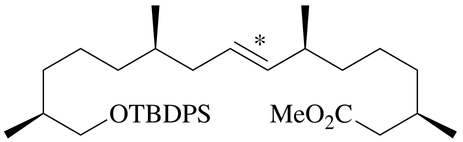
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	 	1. KHMDS, DME, –60°, 45 min 2. Aldehyde, –60°, 1.5 h; rt	 (95) $(E)^*$-isomer only	374
	 	LiHMDS, THF, –78° to rt	 (—) $(E)/(Z)^*$ = —	375
	 	LiHMDS, THF, –10° to rt, 1.5 h	 (92) isomeric ratio* = 70:30	278
	 	LiHMDS, THF, -78°, 3 h; rt	 (74) 'predominantly' $(E)^*$-isomer	327
	 	1. $MN(SiMe_3)_2$, THF, –78°, 30 min 2. Aldehyde, –78°; rt	 M (E)/(Z)* Li (84) 67:33 K (49) 100:0	 376 326

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

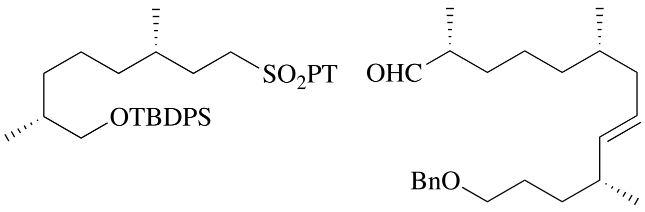
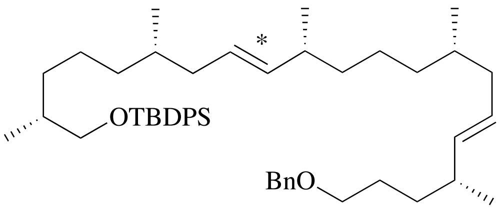
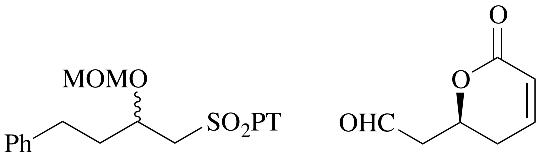
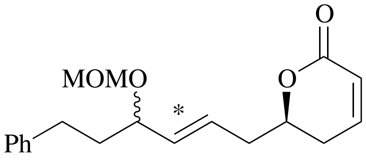
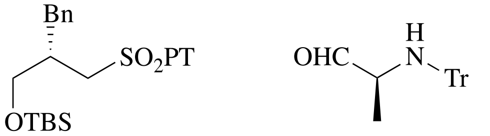
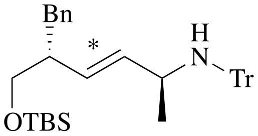
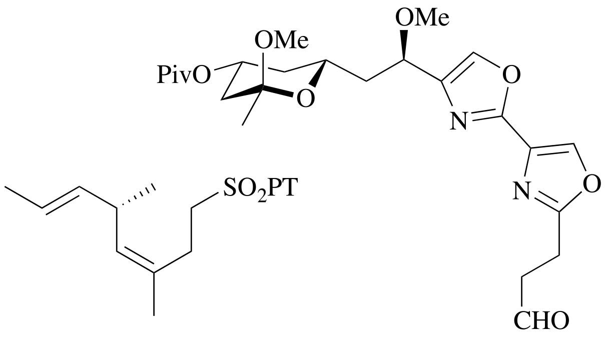
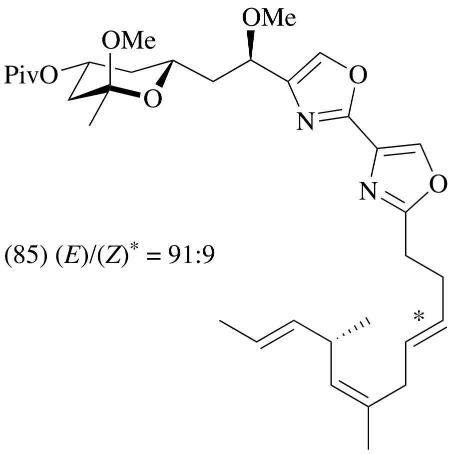
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		LiHMDS, THF, –78°, 3 h; rt	 (65) (*E*)/(*Z*)* = —	165
		1. KHMDS, THF, –78° 2. Aldehyde	 (65) (*E*)*-isomer	377
		1. LiHMDS, solvent –78°, 20 min 2. Aldehyde, –78 °, 3 h; rt, 15 h	 Solvent / (*E*)/(*Z*)* THF (68) 50:50 THF-HMPA (31) 100:0	378
		1. KHMDS, DME, –55° 2. Aldehyde, to rt	 (85) (*E*)/(*Z*)* = 91:9	379

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

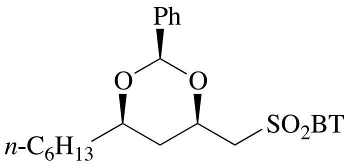
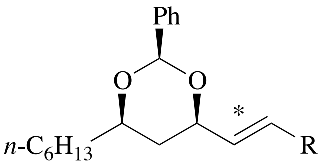
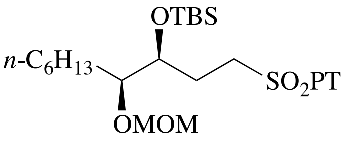
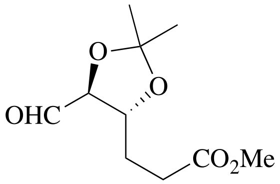
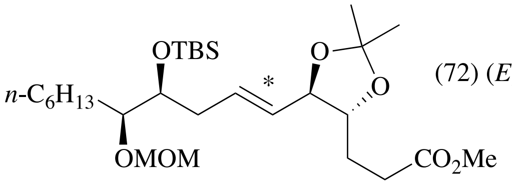
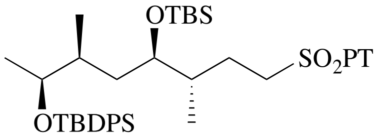
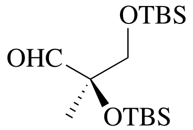
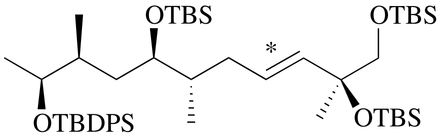
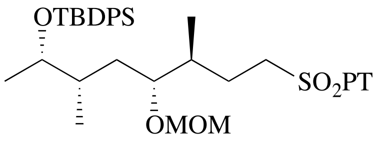
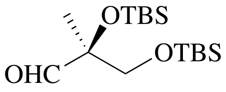
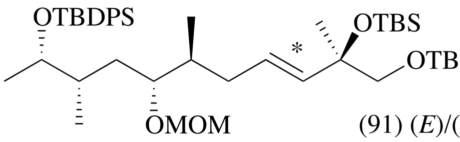
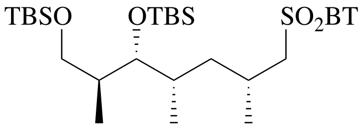
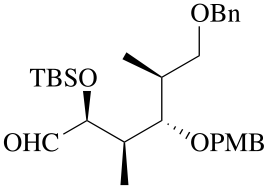
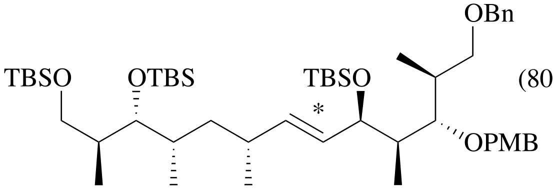
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		RCHO	NaH, THF, 20°	 R — (E)/(Z)* i-Pr (60) 25:75 $Ph(CH_2)_2$ (70) 25:75	49
			1. KHMDS, 18-crown-6, THF –100°, 30 min 2. Aldehyde, –100° to rt, 2 h	 (72) (E)/(Z)* = 91:9	380 381
			1. LiHMDS, DMF-HMPA, –40° 2. Aldehyde	 (50) (E)/(Z)* > 95:5	382
			1. LiHMDS, DMF-HMPA –40°, 10 min 2. Aldehyde, –40° to rt, 24 h	 (91) (E)/(Z)* = 95:5	383
			1. NaHMDS, DMF, –60°, 1.5 h 2. Aldehyde, –60°, 1 h; rt, 12 h	 (80) (E)/(Z)* = —	384

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

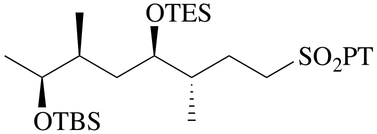
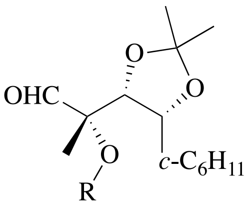
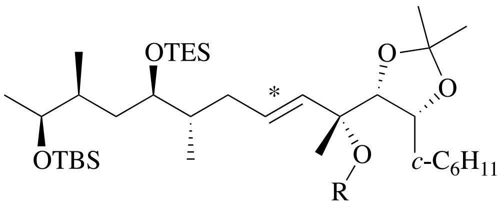
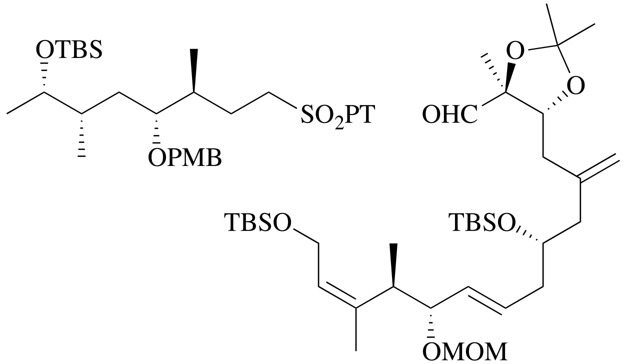
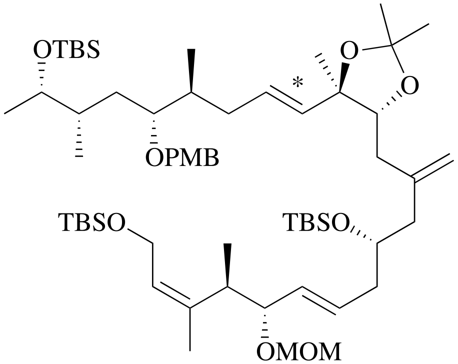
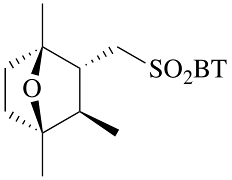
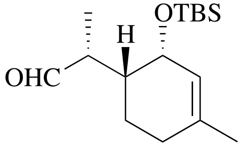
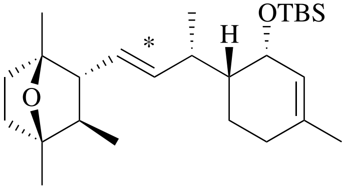
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, THF, –78°, 1 h; rt	 R · KHMDS solution · · $(E)/(Z)^*$ TES · PhMe · (29) · 60:40 TES · THF · (27) · 99:1 PMB · PhMe · (trace) · —	385
		KHMDS, DME, –78°, 1 h; rt	 (70) $(E)^*$-isomer	386
	 	LiHMDS, –78°, 2 h; rt, 1 h	 (88) $(E)/(Z)^* = 50:50$	387 388

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

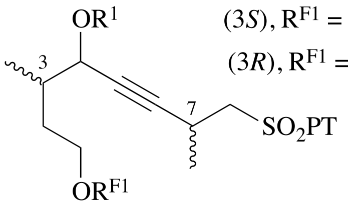
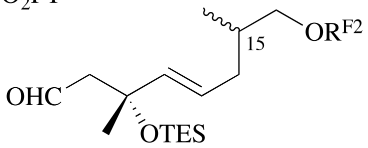
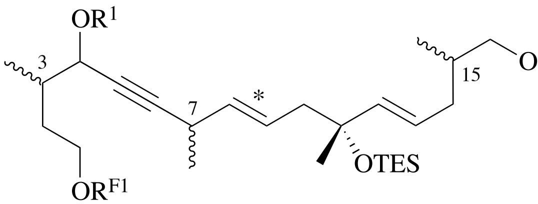
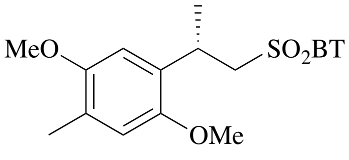
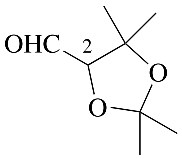
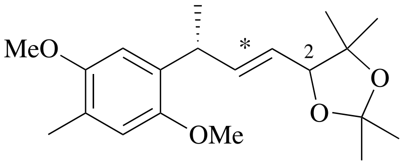
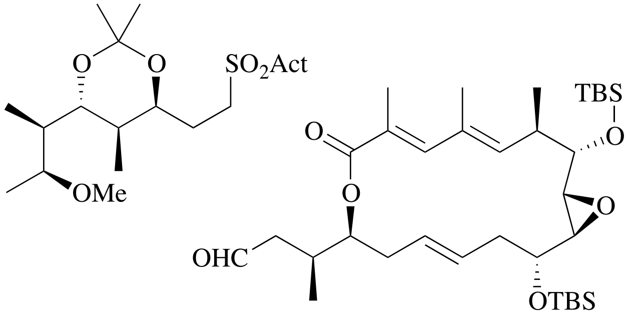
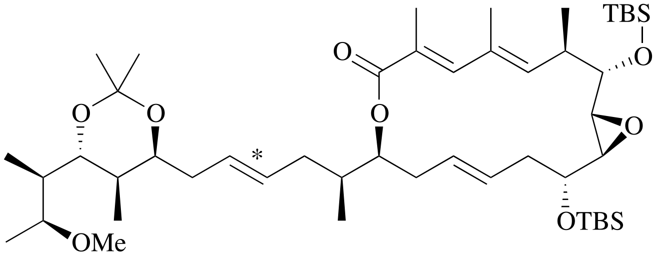
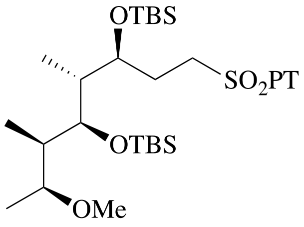
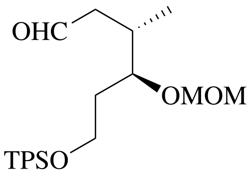
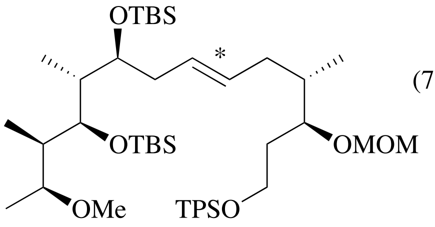
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}	 (3*S*), $R^{F1} = 4\text{-}[F_3C(CH_3)_2O]C_6H_4CH_2$ + (3*R*), $R^{F1} = 4\text{-}[F_9C_4(CH_2)_3O]C_6H_4CH_2$  (15*R*), $R^{F2} = 4\text{-}[F_9C_4(CH_2)_3O]C_6H_4CH_2$ + (15*S*), $R^{F2} = 4\text{-}[F_{13}C_6(CH_2)_3O]C_6H_4CH_2$	1. NaHMDS, THF, –78°, 30 min 2.Aldehyde, –78°, 2 h	 C7 R¹ (*E*)/(*Z*)* (*S*) H (35) — (*S*) TES (87) — (*R*) TES (89) —	237
	 	1. NaHMDS, THF, –78°, 15 min 2. Aldehyde, –78°, 1 h	 C2 (*E*)/(*Z*)* (*S*) (60) 75:25 (*R*) (61) 86:14	389
		1. KHMDS, THF, –78°, 5 min 2. Aldehyde, –78°, 45 min	 Act (*E*)/(*Z*)* BT (80) 100:0 PT (80) —	390 391
	 	1. NaHMDS, DME-HMPA, –78° 2. Aldehyde, –78°, 2 h	 (75) (*E*)/(*Z*)* > 95:5	392

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

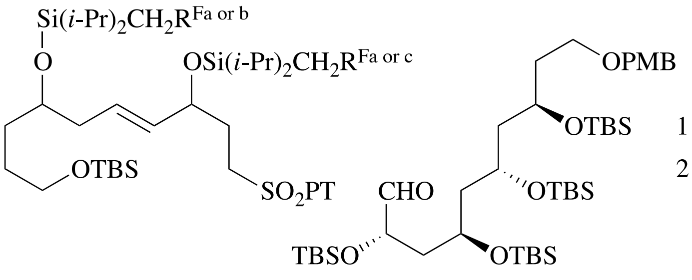
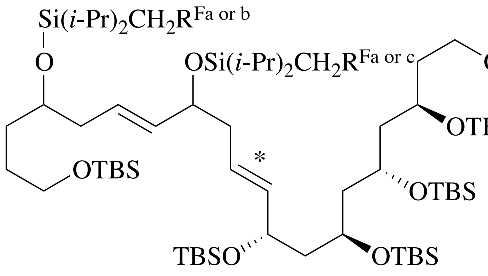
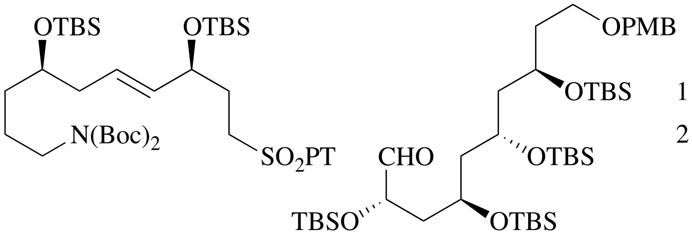
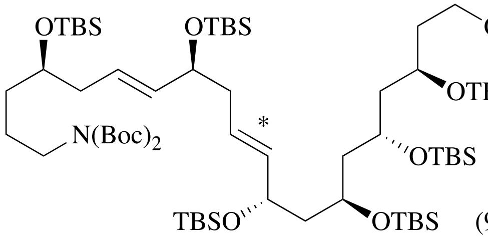
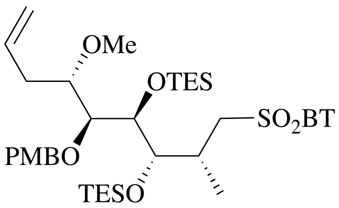
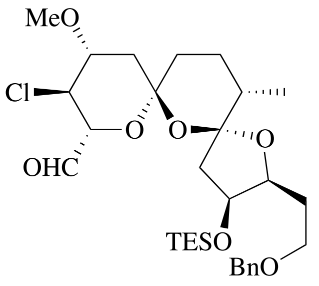
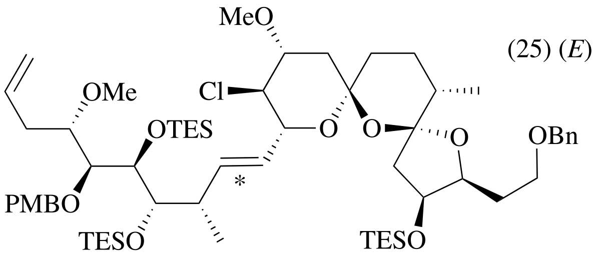
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}	 $R^{Fa} = n\text{-}C_4F_9$; $R^{Fb} = n\text{-}C_3F_7$; $R^{Fc} = n\text{-}C_6F_{13}$	1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78°, 1.5 h; rt	 (80) (*E*)/(*Z*)* = 90:10	310
		1. KHMDS 2. Aldehyde	 (94) (*E*)*-isomer only	311
	 	1. LiHMDS, THF, –78° 2. Aldehyde, –78° to rt	 (25) (*E*)*-isomer	393 153

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

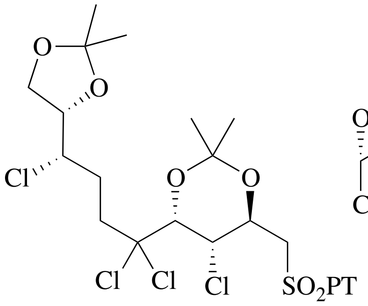
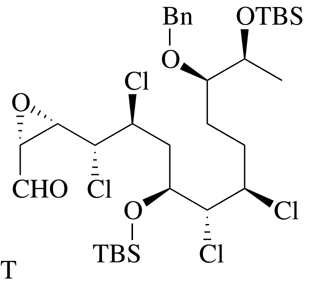
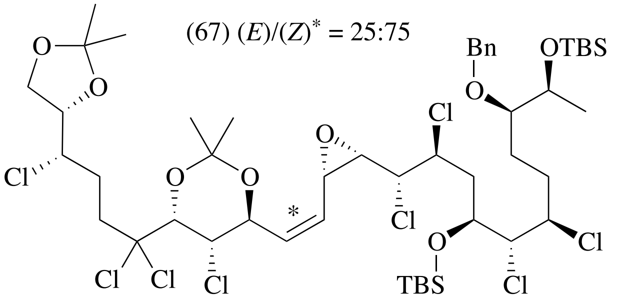
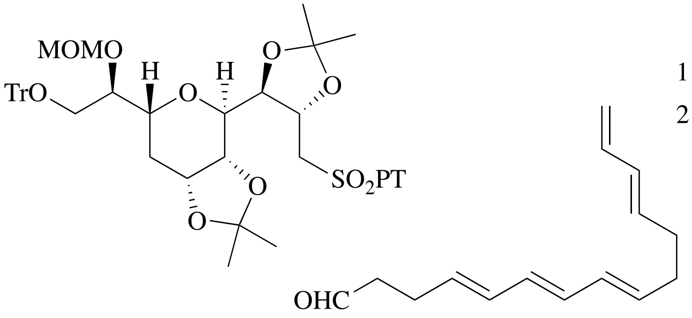
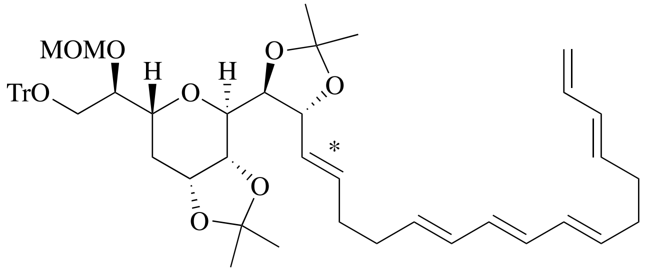
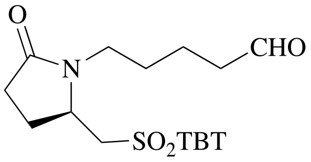
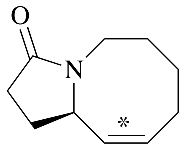
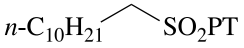
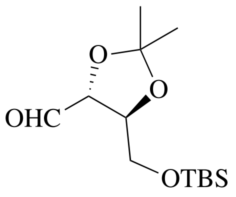
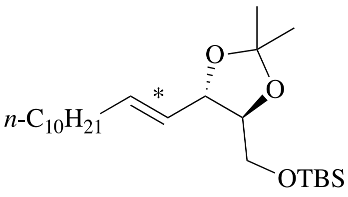
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	 	NaHMDS, PhMe, –78° to rt, 17 h	 (67) $(E)/(Z)^* = 25:75$	356
		1. KHMDS, THF 2. Aldehyde	 (80) $(E)/(Z)^* > 95:5$	139
		$CsCO_3$, DMF-THF, H_2O 70°, 10 h	 (56) $(Z)^*$ only	394
C_{11}				
	 	1. NaHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 2 h	 (65) $(E)/(Z)^*$ —	395

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

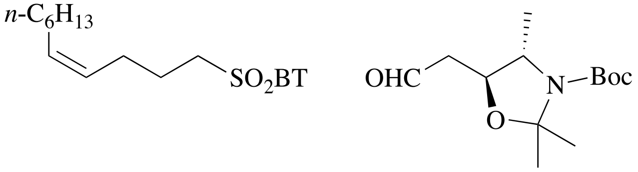
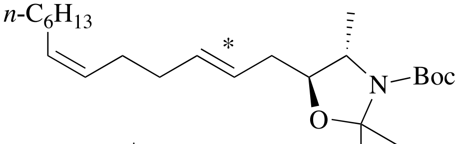
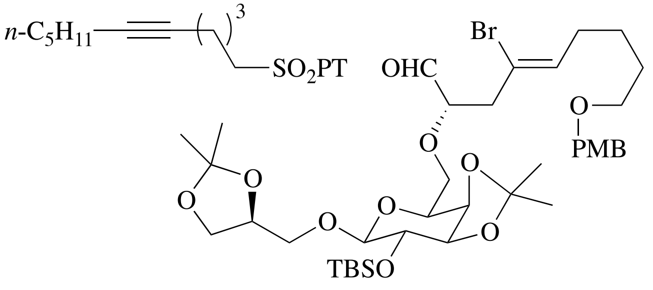
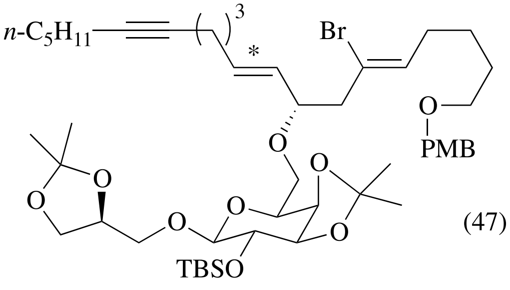
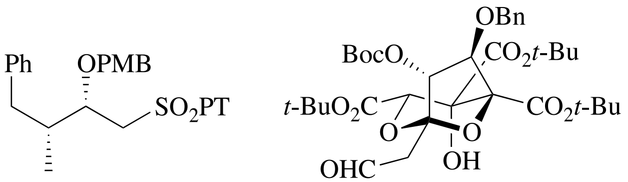
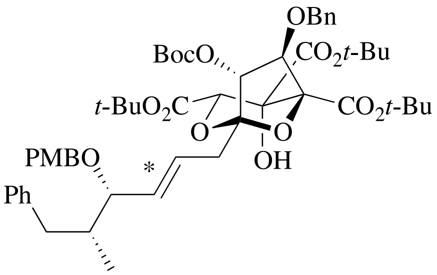
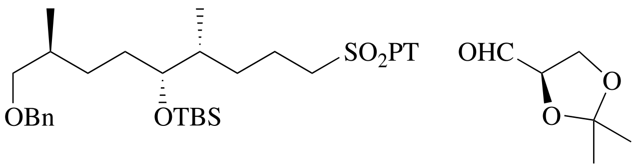
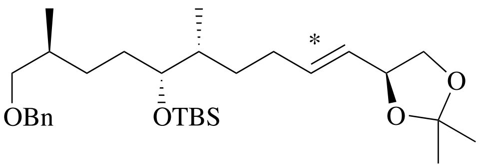
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		KHMDS, THF	 (70) (*E*)/(*Z*)* = 79:21	396
		1. KHMDS, THF, –78° 2. Aldehyde	 (47) (*E*)/(*Z*)* —	397
		LDA, THF, –78° to rt	 (0) (*E*)/(*Z*)* —	398
		1. KHMDS, DME, –60°, 30 min 2. Aldehyde, –60°, 2 h; 0°	 (82) (*E*)*-isomer only	399 400

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

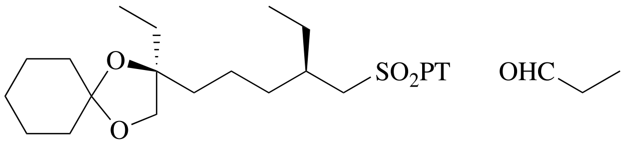
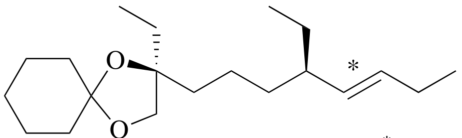
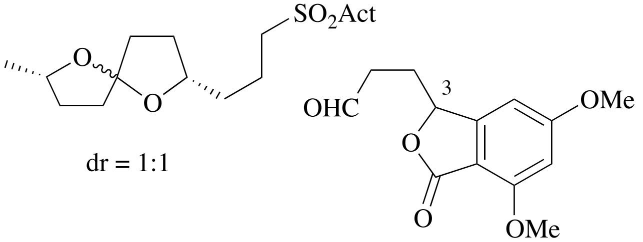
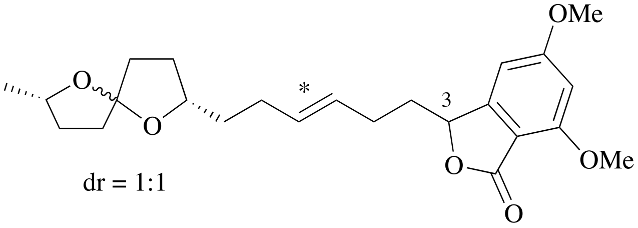
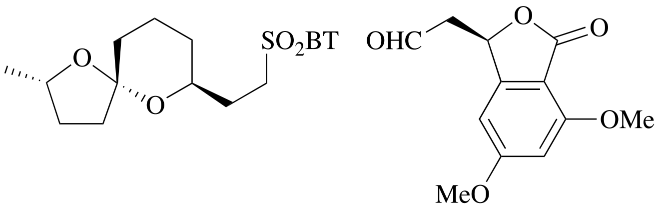
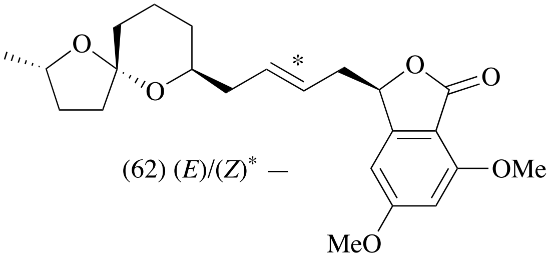
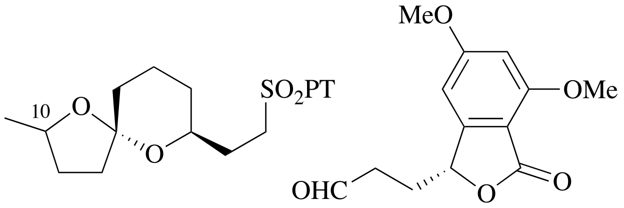
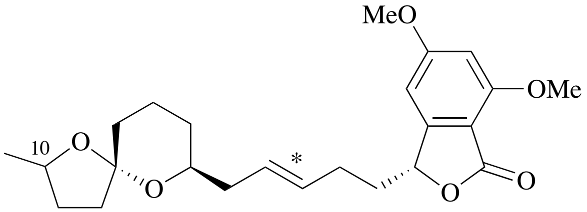
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		LiHMDS, DME	 (74) (*E*)/(*Z*)* = 60:40	401
	 dr = 1:1	1. KHMDS, THF, –78°, 20 min 2. Aldehyde, THF, –78°, 1.5 h; rt, 1 h	 dr = 1:1 Act C3 (*E*)/(*Z*)* PT (*S*) (84) — PT (*R*) (76) — BT (*S*) (19) —	402 403
		1. KHMDS, THF, –78°, 20 min 2. Aldehyde, –78°, 1.5 h; rt, 1 h	 (62) (*E*)/(*Z*)* —	404
		1. Base, THF, –78°, 45 min 2. Aldehyde, –78°, 4 h; rt, 45 min	 C10 Base (*E*)/(*Z*)* (*R*) KHMDS (75) >75:25 (*R*) LDA (40) — (*S*) LDA (37) —	405 406 406

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

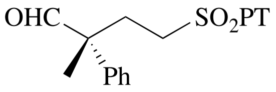
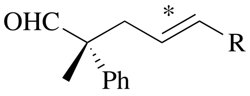
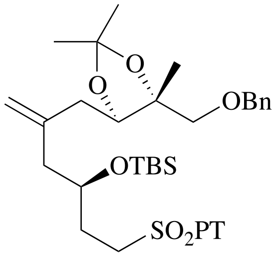
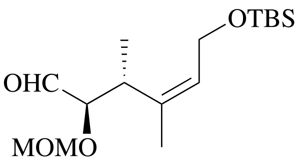
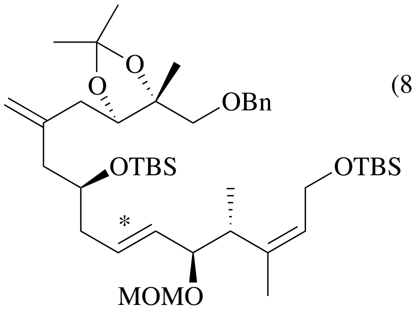
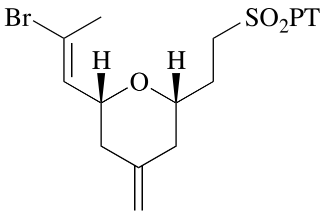
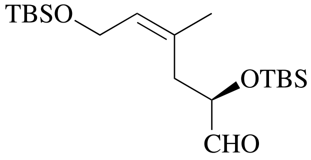
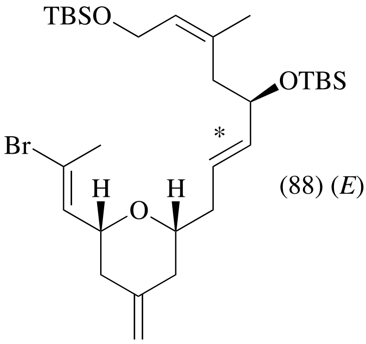
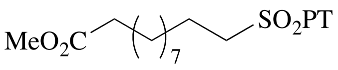
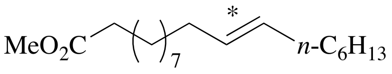
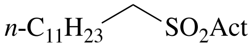
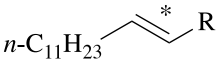
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{11}		RCHO	**A**: NaHMDS, DME, –78° *or* **B**: 1. Ethylene glycol, *p*-TsOH, PhH 2. Aldehyde, KHMDS, DME, –78° 3. HCl, THF, 50°		R — (*E*)/(*Z*)* Et **A** (15) 67:33 Et **B** (45) 89:11 *i*-Bu **B** (48) 87:13	51
			1. KHMDS, DME, –78°, 30 min 2. Aldehyde, –78°, 30 min; rt		(83) (*E*)*-isomer	386
			1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt		(88) (*E*)*-isomer only	407 408
		*n*-C_6H_{13}CHO	1. KHMDS, THF, –55°, 40 min 2. Aldehyde, –55°, 1 h		(50) (*E*)/(*Z*)* = 85:15	409

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}					
		RCHO	LDA, THF, –78°, 1 h; rt, 3 h		20

R	Act		$(E)/(Z)^*$
n-$C_{11}H_{23}$	BT	(47)	46:54
n-$C_{11}H_{23}$	PYR	(46)	35:65
n-$C_{11}H_{23}$	PYM	(5)	55:45
n-$C_{11}H_{23}$	IM	(12)	3:97
n-$C_{11}H_{23}$	TZ	(34)	43:57
n-$C_{11}H_{23}$	IQ	(54)	44:56
n-C_5H_{11}CHMe	BT	(58)	43:57
n-C_5H_{11}CHMe	IM	(17)	2:98
n-C_5H_{11}CHMe	TZ	(36)	28:72
n-C_5H_{11}CHMe	IQ	(44)	55:45

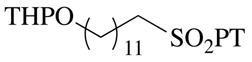
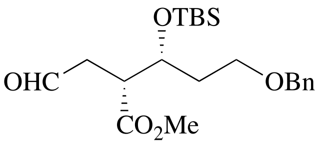
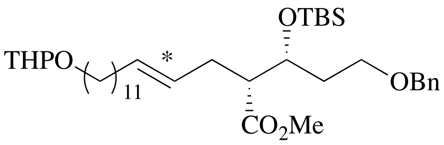
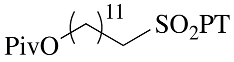
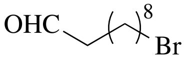
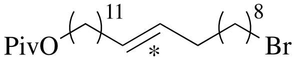
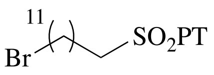
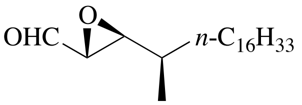
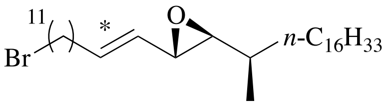
			LiHMDS, THF, –10° to rt	 (75) $(E)/(Z)^*$ = —	325
			LiHMDS, THF, 0°; rt	 (68) $(E)/(Z)^*$ = 67:33	325
			LiHMDS, THF, –10°	 (71) $(E)/(Z)^*$ = —	410

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

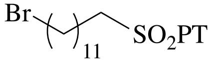
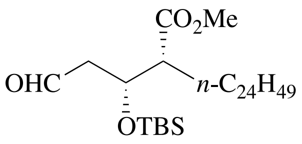
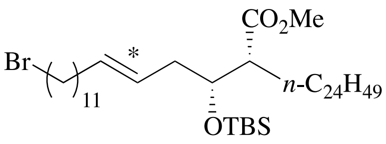
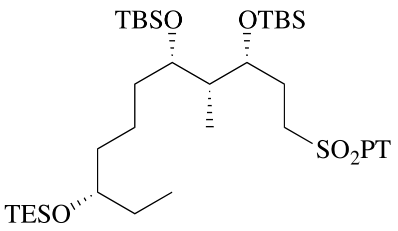
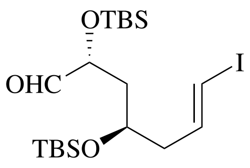
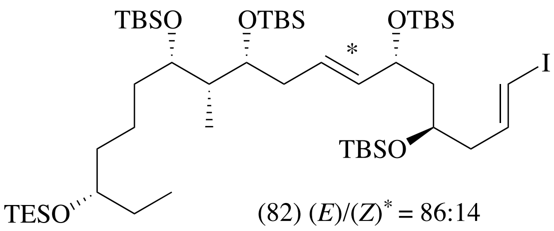
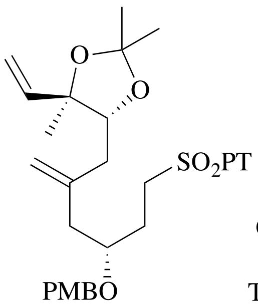
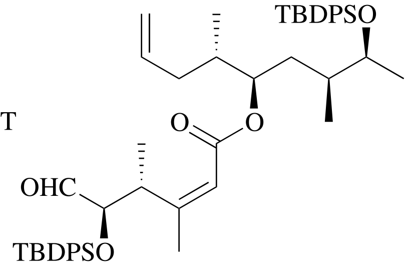
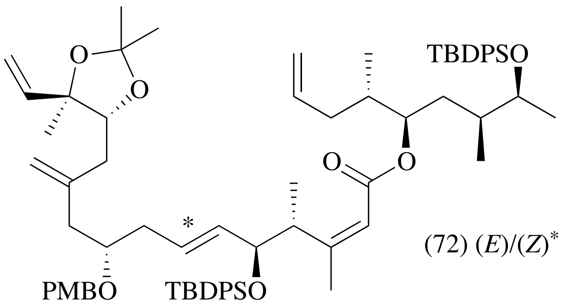
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
	 	LiHMDS, THF, –12° to rt, 3 h	 (82) (*E*)/(*Z*)* = 66:34	278
	 	KHMDS, THF, –78°	 (82) (*E*)/(*Z*)* = 86:14	411
	 	1. LiHMDS, DMF-HMPA, –50° 2. Aldehyde, –50° to rt, 16 h	 (72) (*E*)/(*Z*)* = 91:9	412

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

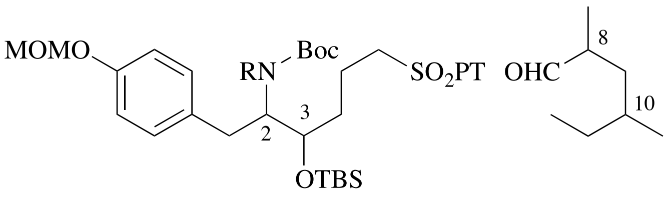
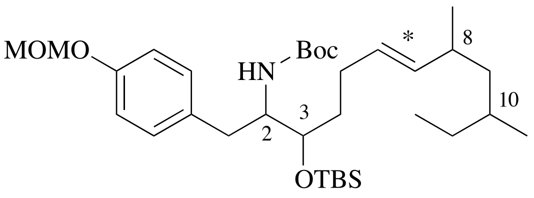
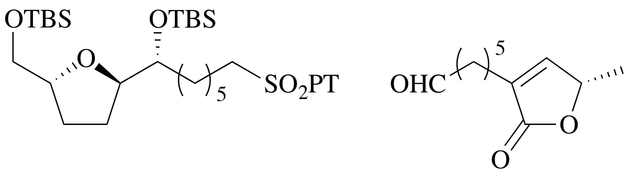
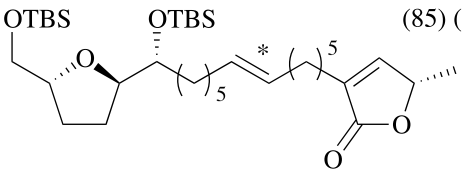
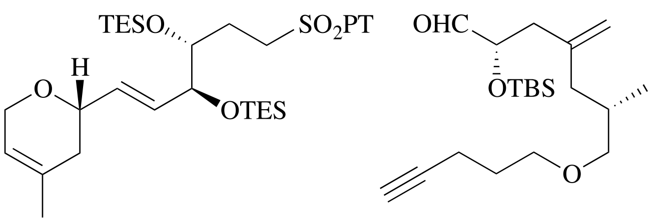
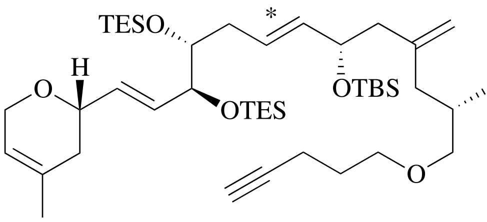
<table>
<tr><th></th><th>Sulfone and Aldehyde</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_{12}</td><td> </td><td>1. KHMDS, THF, –78°, 2 min
2. Aldehyde, –78°; rt</td><td>
<table>
<tr><th>R</th><th>C2</th><th>C3</th><th>C8</th><th>C10</th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>H</td><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(70)</td><td>100:0</td></tr>
<tr><td>Me</td><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(67)</td><td>100:0</td></tr>
<tr><td>Me</td><td>(<i>S</i>)</td><td>(<i>R</i>)</td><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(58)</td><td>100:0</td></tr>
<tr><td>Me</td><td>(<i>S</i>)</td><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(70)</td><td>100:0</td></tr>
<tr><td>Me</td><td>(<i>R</i>)</td><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(<i>S</i>)</td><td>(73)</td><td>100:0</td></tr>
<tr><td>Me</td><td>(<i>R</i>)</td><td>(<i>S</i>)</td><td>(<i>R</i>)</td><td>(<i>R</i>)</td><td>(56)</td><td>100:0</td></tr>
</table></td><td>413
414</td></tr>
<tr><td></td><td> </td><td>1. NaHMDS, THF, –78°
2. Aldehyde, THF; –20°</td><td> (85) (<i>E</i>)*-isomer only</td><td>415</td></tr>
<tr><td></td><td> </td><td>1. KHMDS, THF, –78°, 3 min
2. Aldehyde, –78°, 1.5 h</td><td> (78) (<i>E</i>)*-isomer only</td><td>416</td></tr>
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TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

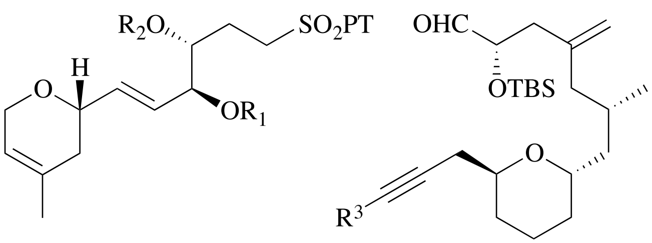
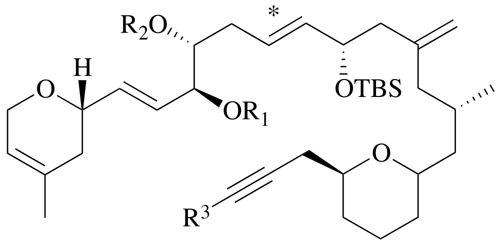
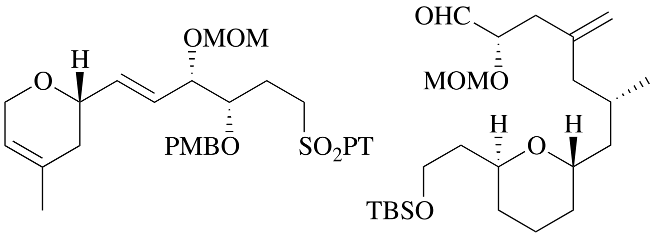
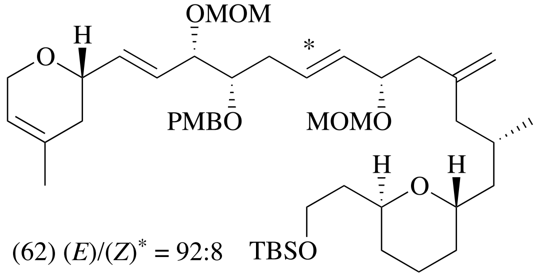
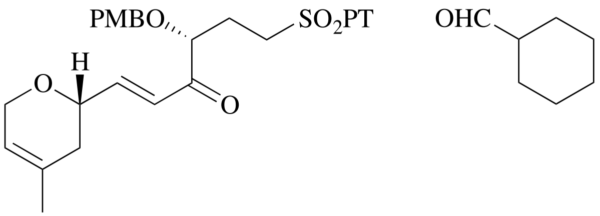
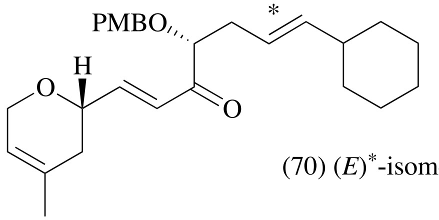
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1.5 h	 R^1 R^2 R^3 $(E)/(Z)^*$ TES PMB H (76) 100:0 MOM PMB H (86) 100:0 TBS PMB H (87) 100:0 TES TES H (80) 100:0 MOM PMB Me (74) 100:0	417 418
		1. KHMDS, DME, –60°, 25 min 2. Aldehyde, –60° to rt, 4 h	 (62) $(E)/(Z)^*$ = 92:8	419 420
		1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1.5 h	 (70) $(E)^*$-isomer only	418

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

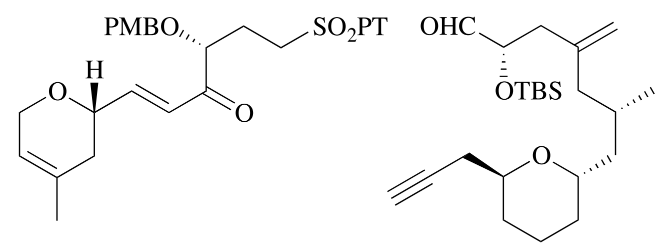
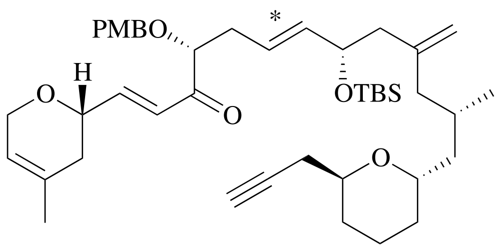
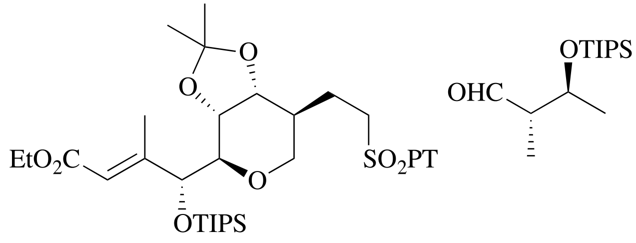
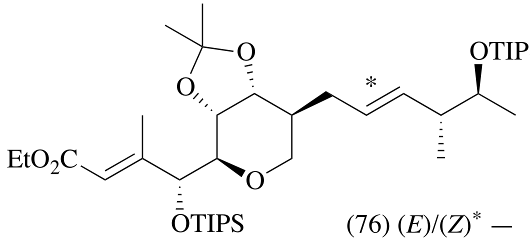
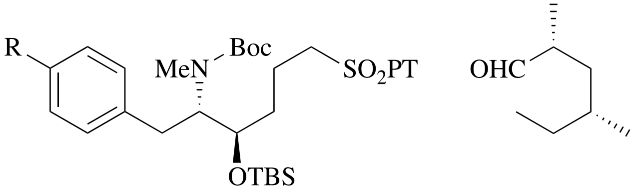
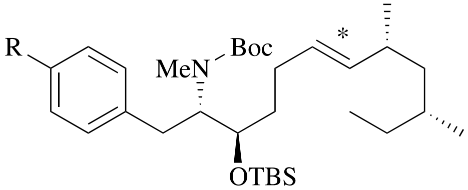
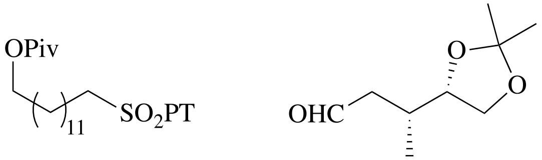
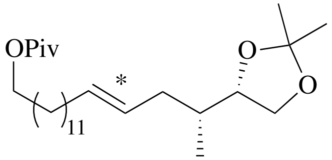
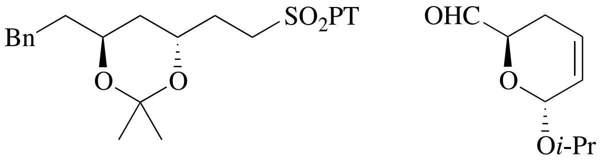
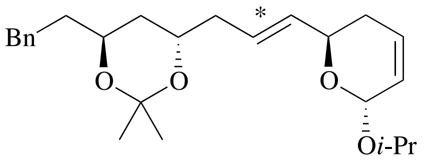
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1.5 h	 (24) $(E)^*$-isomer only	418
		1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 1.5 h; rt	 (76) $(E)/(Z)^*$ —	421
$C_{12\text{-}13}$		1. KHMDS, THF, –78°, 2 min 2. Aldehyde, EtOH, –78°; rt	 R — Yield of $(E)^*$-isomer H (82) Me (83) OMe (75) F (80)	422
C_{13}		LiHMDS, THF	 (86) $(E)/(Z)^*$ = —	423
		MN(SiMe$_3$)$_2$, DME, –55° to rt, 12 h	 M — $(E)/(Z)^*$ Na (77) 77:23 K (61) 89:11	424

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

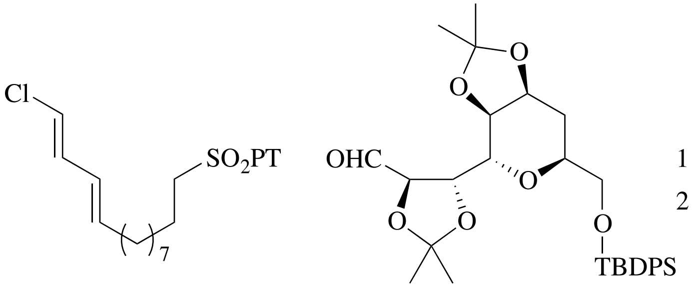
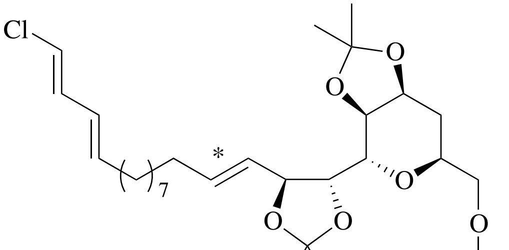
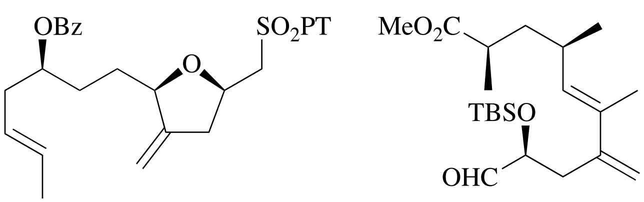
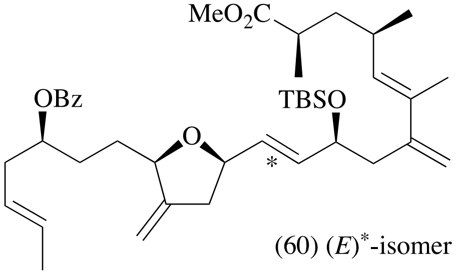
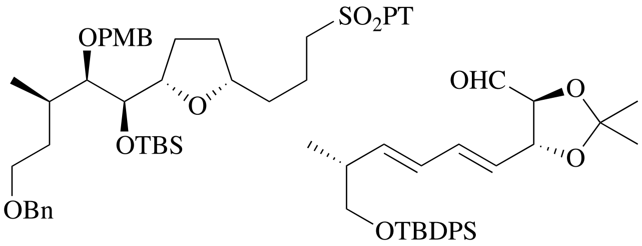
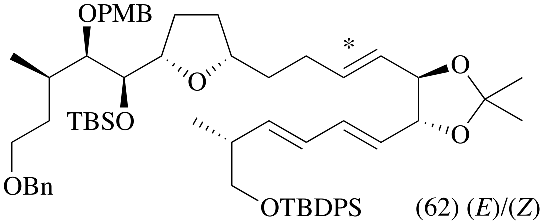
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1 h; rt, 2 h	 (>40) (*E*)/(*Z*)* = 60:40	188
		KHMDS, DMF, –78°, 30 min; rt, 1 h	 (60) (*E*)*-isomer only	425
		1. KHMDS, DME, –78 to –60° 2. Aldehyde, –78°; rt	 (62) (*E*)/(*Z*)* = 80:20	426

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

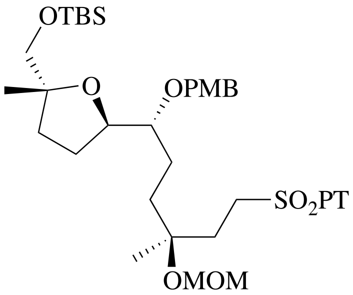
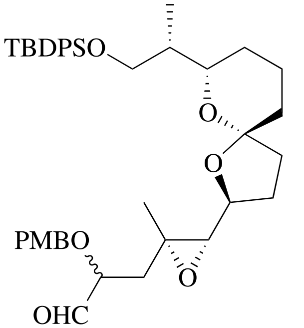
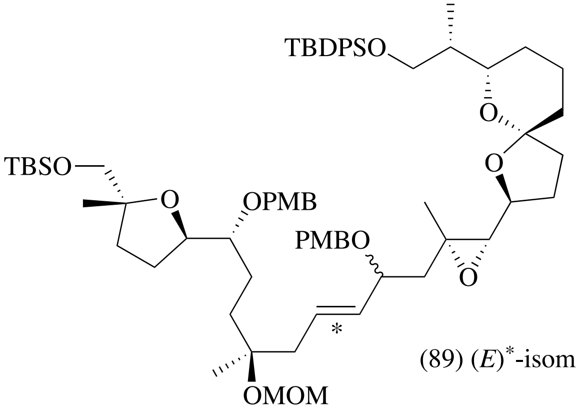
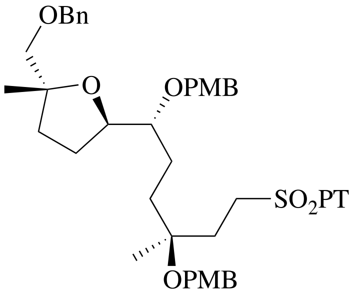
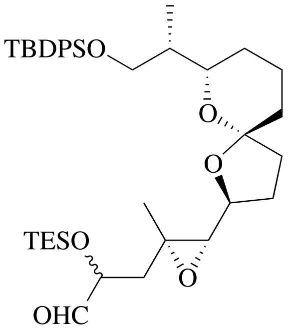
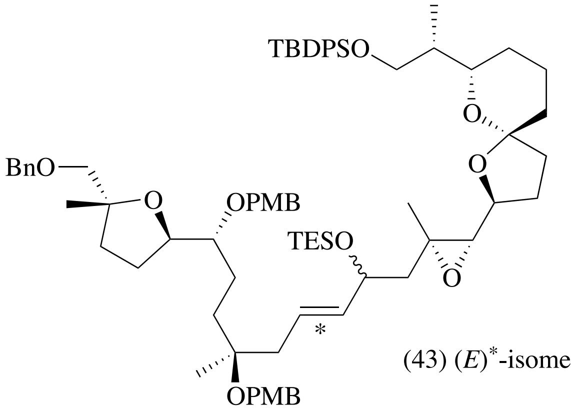
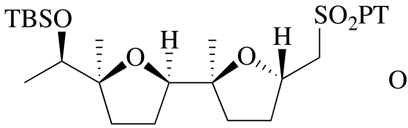
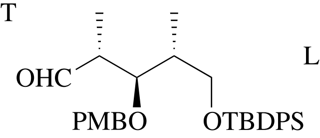
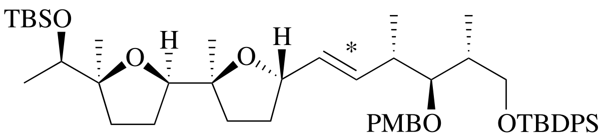
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
	 	KHMDS, DME, –75°, 30 min; 0°, 15 min	 (89) (*E*)*-isomer only	427
	 	KHMDS, DME, –70°, 30 min; 0°, 30 min	 (43) (*E*)*-isomer only	144
	 	LiHMDS, THF, –78°, 1 h; 0°	 (80) (*E*)/(*Z*)* = 70:30	359

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

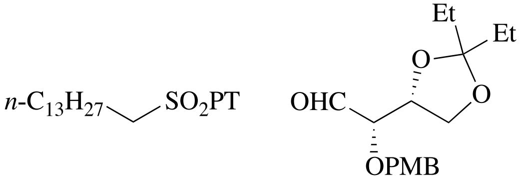
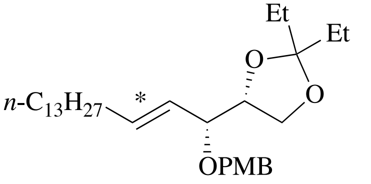
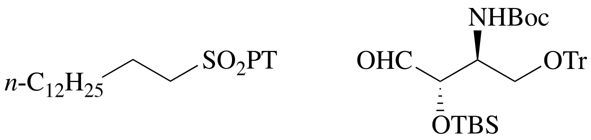
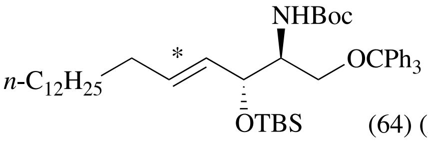
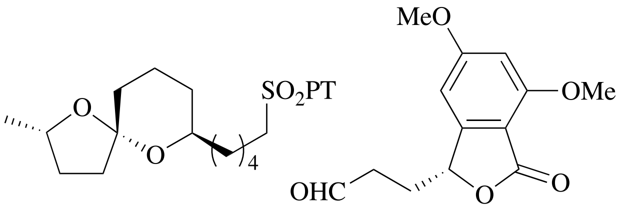
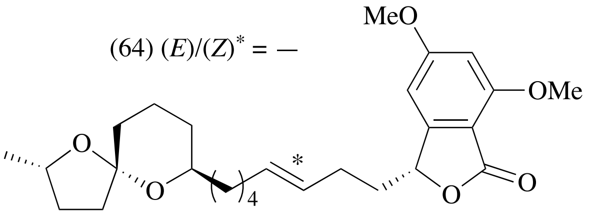
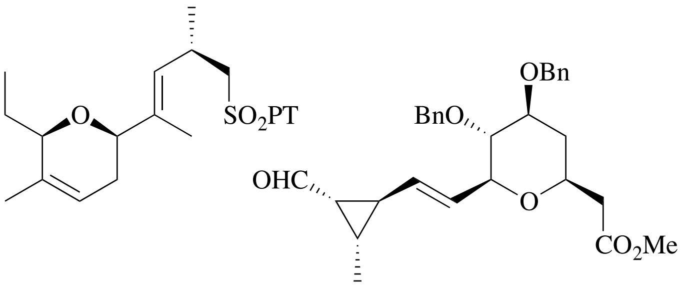
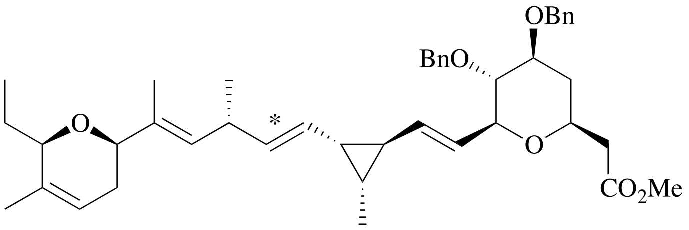
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}		KHMDS, DME, –55°, 30 min; rt	 (52) (*E*)/(*Z*)* = 80:20	247
		1. KHMDS, DME, –56°, 30 min 2. Aldehyde; –50°	 (64) (*E*)/(*Z*)* = 88:12	428
		1. KHMDS, THF, –78°, 20 min 2. Aldehyde, –78°, 1.5 h; rt, 1 h	(64) (*E*)/(*Z*)* = — 	404
		1. $MN(SiMe_3)_2$, THF-HMPA, –60°, 30 min 2. Aldehyde, –60 to 0°, 3 h	 M (*E*)/(*Z*)* Na (66) 68:32 K (15) 86:14	304

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

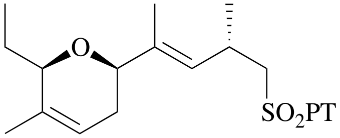
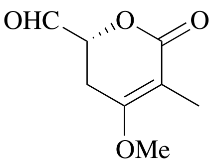
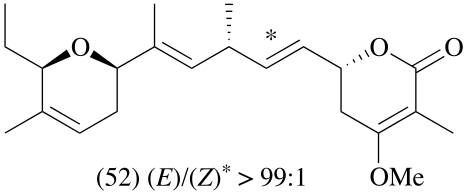
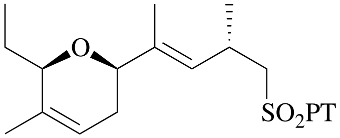
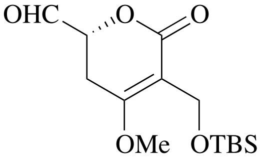
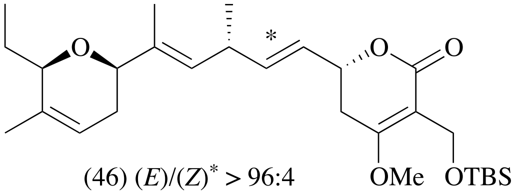
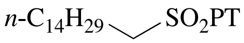
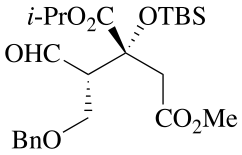
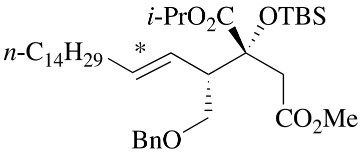
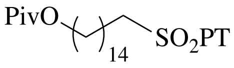
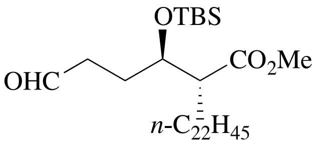
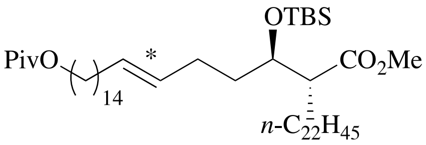
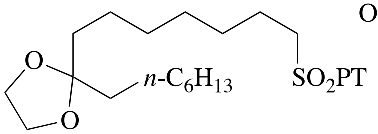
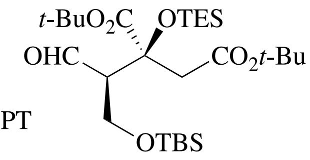
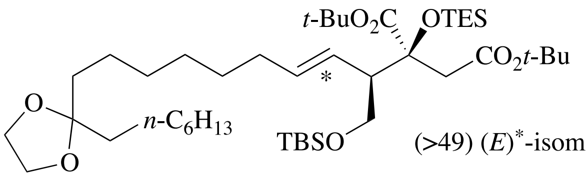
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			1. KHMDS, THF, –78°, 10 min 2. Aldehyde, –78° to rt	 (52) (*E*)/(*Z*)* > 99:1	429
			1. LiHMDS, DMF-HMPA –60°, 20 min 2. Aldehyde, 2 h, –60 to 0°	 (46) (*E*)/(*Z*)* > 96:4	430
C_{15}			1. KHMDS, –78°, 30 min 2. Aldehyde, –78° to rt, 12 h	 (70) (*E*)*-isomer only	431
			LiHMDS, THF, –10° to rt	 (95) (*E*)/(*Z*)* = 67:33	432
			1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 3 h	 (>49) (*E*)*-isomer only	433

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

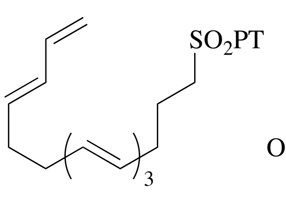
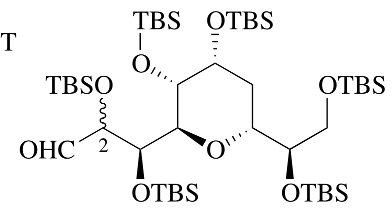
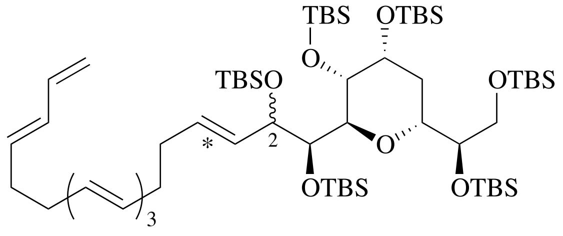
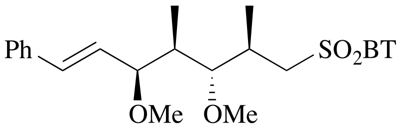
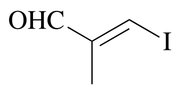
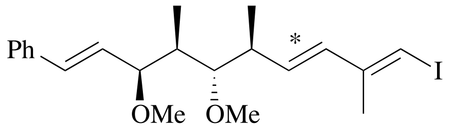
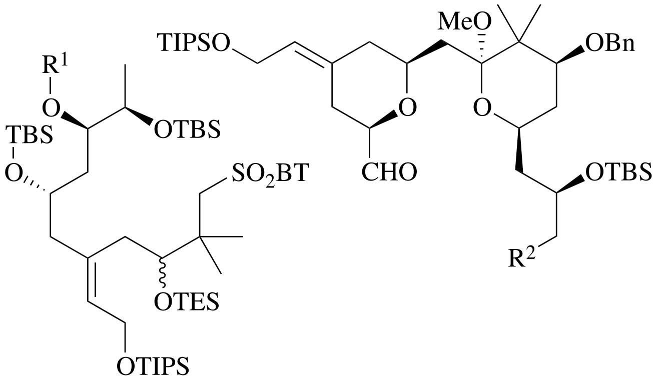
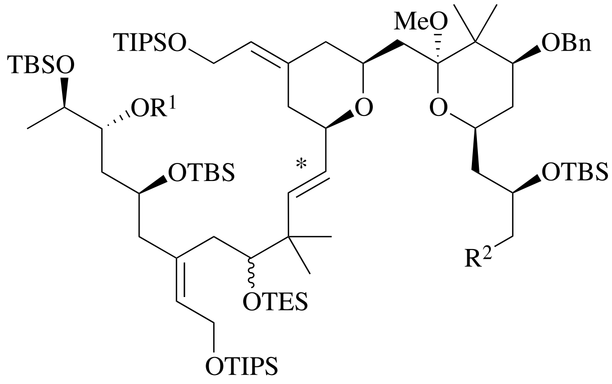
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}	 	1. KHMDS, THF, –78°, 10 min 2. Aldehyde, –78°, 30 min; rt, Time	 C2 — Time — — $(E)/(Z)^*$ (S) — 9 h — (92) — 92:8 (R) — 2 h — (65) — 100:0	434
	 	NaHMDS, THF, –78°, 30 min; rt, 30 min	 (43) $(E)/(Z)^*$ —	435
		1. LiHMDS, THF, –78 to –60°, 30 min 2. Aldehyde, THF, –78°, 20 min; rt, 30 min	 R^1 — R^2 — Yield of $(E)^*$-isomer SEM — $CH_2OTBDPS$ — (70) TMS — $C(O)OCH_2CH{=}CH_2$ — (>60)	270 436

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

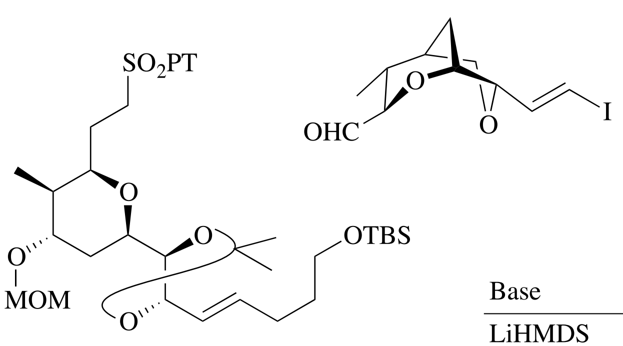
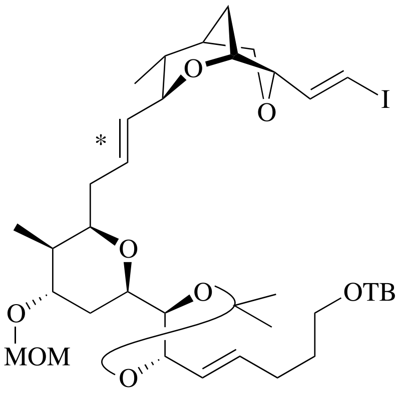
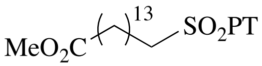
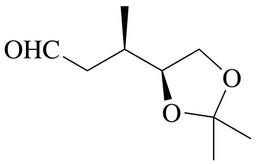
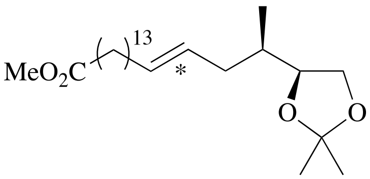
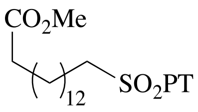
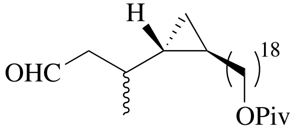
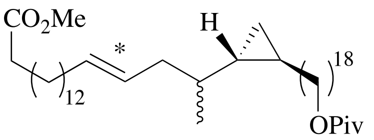
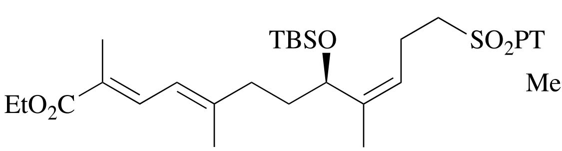
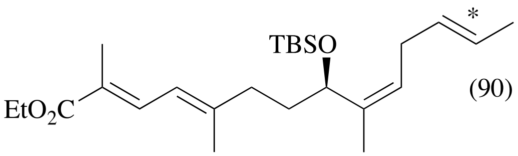
<table>
<tr><th></th><th>Sulfone and Aldehyde</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_{15}</td><td></td><td>1. Base, solvent, –72°
2. Aldehyde, –72° to rt
<table>
<tr><th>Base</th><th>Solvent</th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>LiHMDS</td><td>DMF-HMPA</td><td>(24)</td><td>100:0</td></tr>
<tr><td>NaHMDS</td><td>DMF-HMPA</td><td>(40)</td><td>78:22</td></tr>
<tr><td>KHMDS</td><td>DME</td><td>(54)</td><td>66:34</td></tr>
<tr><td>LDA</td><td>DMF-HMPA</td><td>(11)</td><td>100:0</td></tr>
<tr><td><i>t</i>-BuLi</td><td>DMF-HMPA</td><td>(39)</td><td>100:0</td></tr>
</table></td><td></td><td>437
62</td></tr>
<tr><td></td><td> </td><td>LiHMDS, THF, –10°</td><td> (61) (<i>E</i>)/(<i>Z</i>)* = —</td><td>410</td></tr>
<tr><td></td><td> </td><td>LiHMDS, THF, –15° to rt, 1 h</td><td>
<table>
<tr><th>Aldehyde epimer</th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>α</td><td>(65)</td><td>—</td></tr>
<tr><td>β</td><td>(70)</td><td>—</td></tr>
</table></td><td>438</td></tr>
<tr><td></td><td> MeCHO</td><td>1. KHMDS, DME, –60°, 20 min
2. Aldehyde, 30 min</td><td> (90) (<i>E</i>)/(<i>Z</i>)* = 86:14</td><td>59</td></tr>
</table>

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

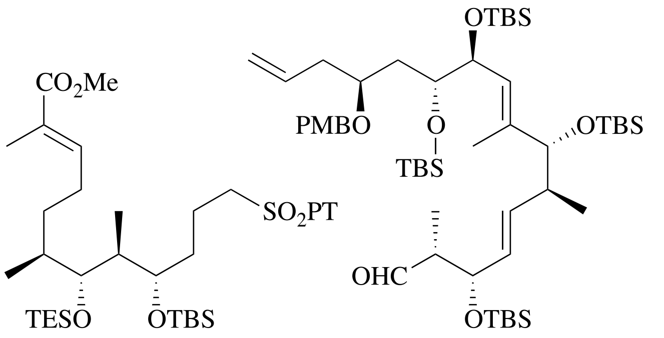
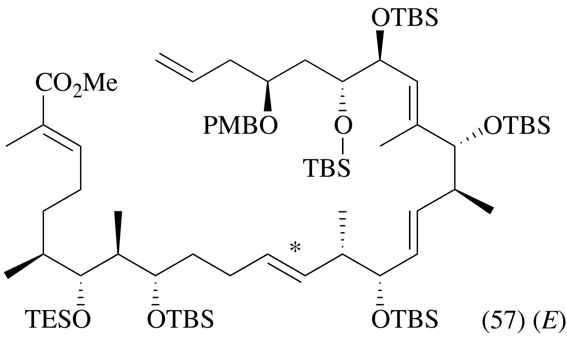
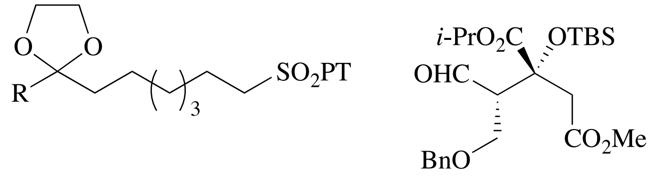
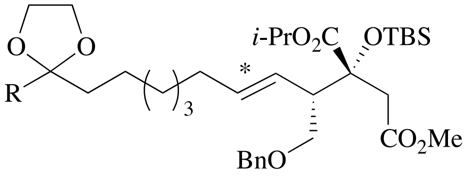
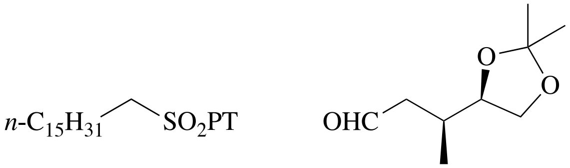
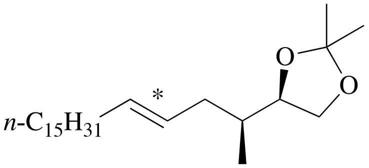
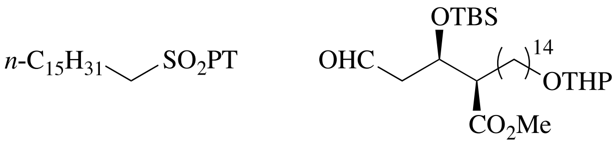
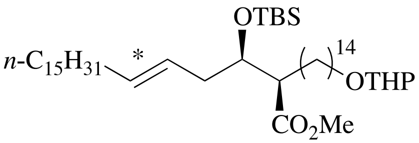
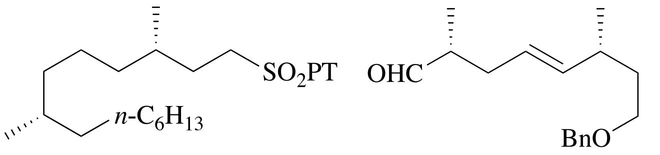
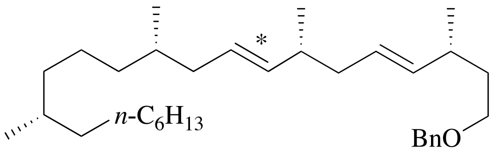
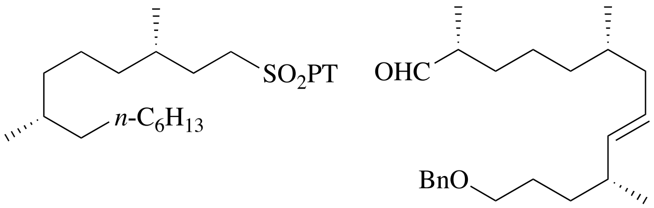
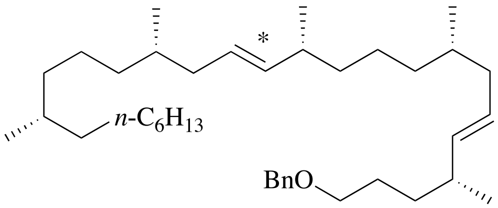
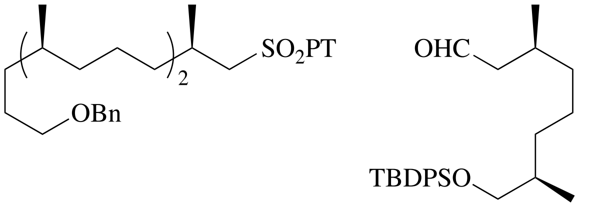
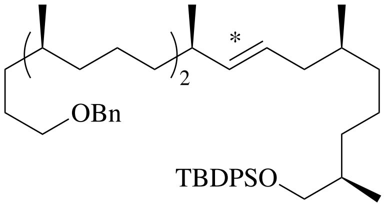
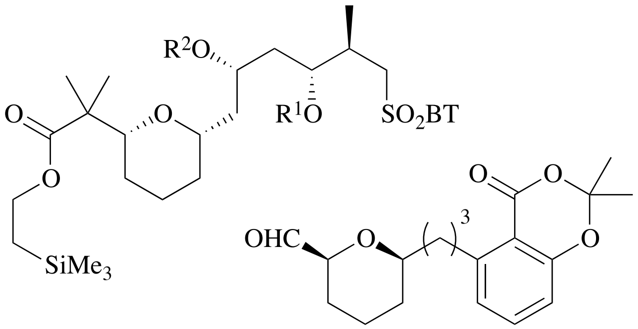
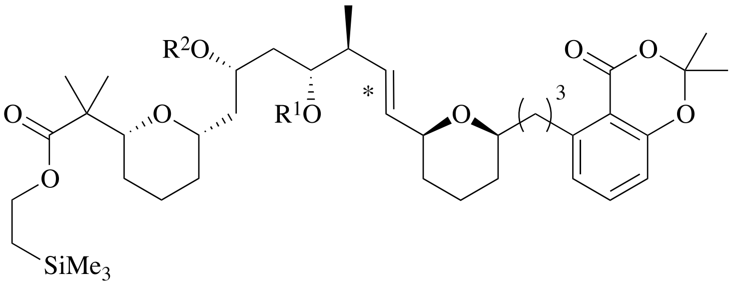
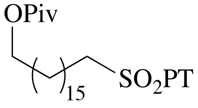
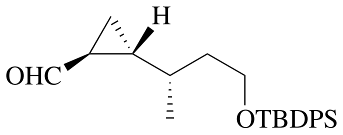
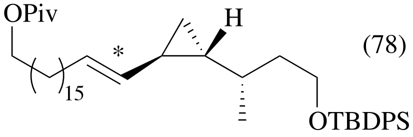
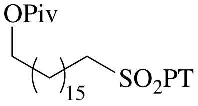
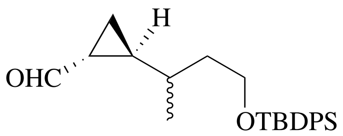
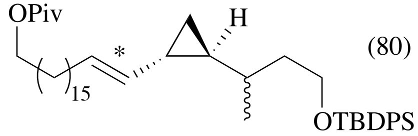
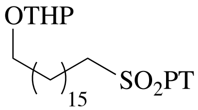
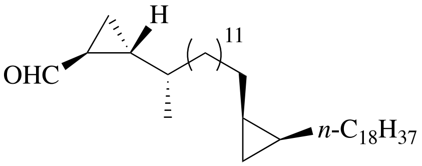
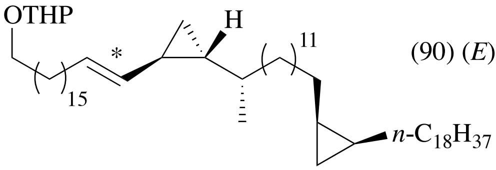
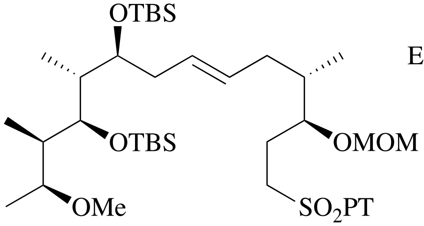
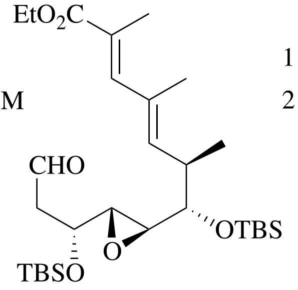
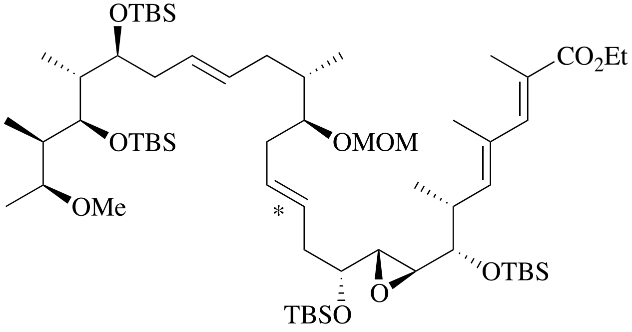
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		1. KHMDS, DME, –46° 2. Aldehyde, –46° to rt	 (57) $(E)/(Z)^{*} = 88{:}12$	121
C_{15-17}		1. KHMDS, –78°, 30 min 2. Aldehyde, –78° to rt, 12 h	 R — $(E)/(Z)^{*}$ n-C_7H_{15} (84) >98:2 n-C_9H_{19} (71) >98:2	439, 431
C_{16}		LiHMDS, THF, –20°; rt, 16 h	 (93) $(E)/(Z)^{*} = 71{:}29$	276
		LiHMDS, THF, –10° to rt	 (75) $(E)/(Z)^{*}$ = —	325

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}				
		LiHMDS, THF, –78°, 3 h; rt	 (78) $(E)/(Z)^* =$ —	165
		LiHMDS, THF, –78°, 3 h; rt	 (80) $(E)/(Z)^* =$ —	165
		LiHMDS, THF, –78°, 3 h; rt	 (56) $(E)/(Z)^* =$ —	165
		1. NaHMDS, Solvent, –78°, 15-30 min 2. Aldehyde, –78° to rt, 6-15 h		

R^1	R^2	Solvent		$(E)/(Z)^*$	
TBS	Bn	Et_2O	(83)	>95:5	440
Bn	SEM	THF	(79)	50:50	173

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{17}			LiHMDS, THF, –20° to rt, 2 h		(78) (*E*)/(*Z*)* = 73:27	438
		 dr = 1:1	LiHMDS, THF, –15° to rt, 2 h		(80) (*E*)/(*Z*)* = —	438
			LiHMDS, THF, –2° to rt, 2 h		(90) (*E*)/(*Z*)*mixture	272
			1. $MN(SiMe_3)_2$, –78° 2. Aldehyde, –78°, 3 h			392

M	Solvent		(E)/(Z)*
Na	DME-HMPA	(60)	50:50
K	THF	(23)	80:20

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

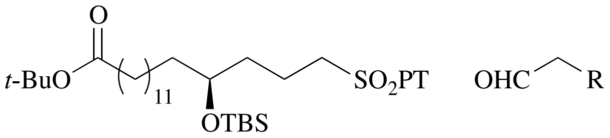
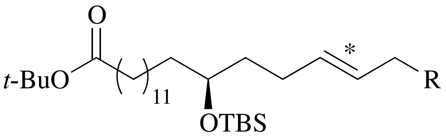
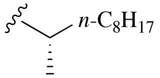
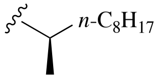
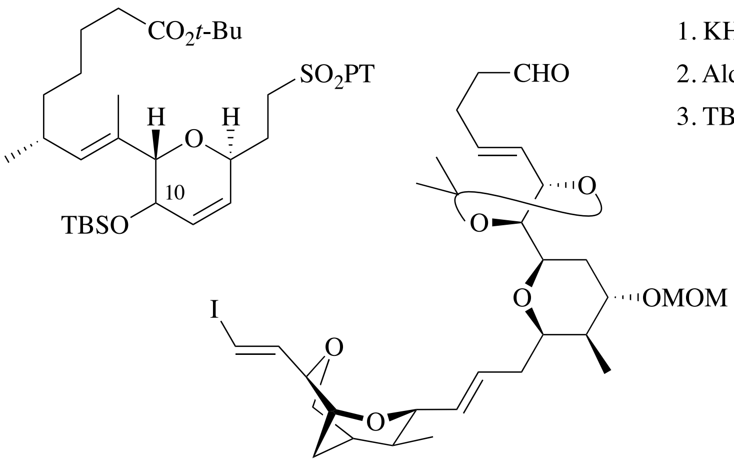
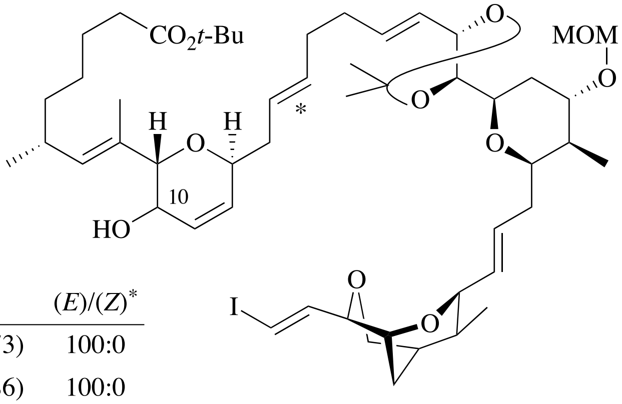
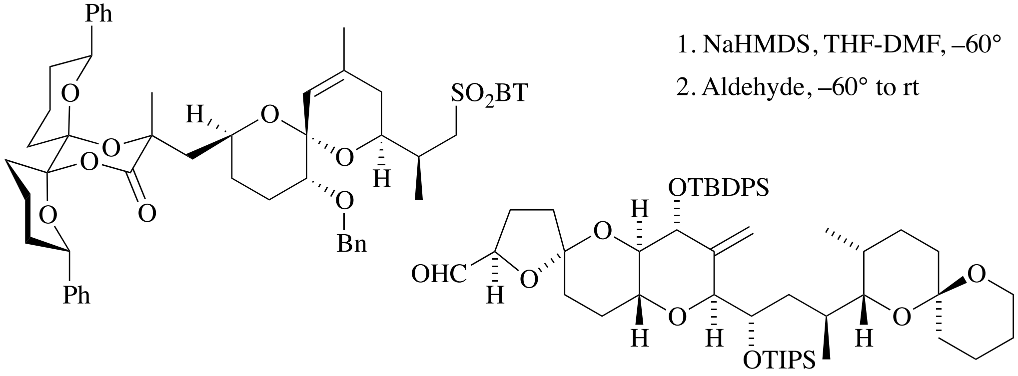
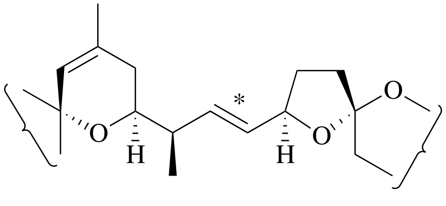
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		1. KHMDS, DME, –60°, 30 min 2. Aldehyde, –60°; rt, 16 h	 R — Yield of $(E)^*$-isomer  (45)  (75) n-C_9H_{19} (67)	441
		1. KHMDS, DME, –72° 2. Aldehyde, –72° to rt 3. TBAF, THF	 C10 — — $(E)/(Z)^*$ (R) (73) 100:0 (S) (86) 100:0	437 62 156
		1. NaHMDS, THF-DMF, –60° 2. Aldehyde, –60° to rt	 (66) of $(E)^*$-isomer; small quantity of (Z)-isomer detected by ^1H NMR spectroscopy	442

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

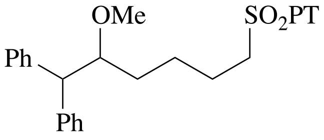
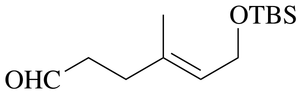
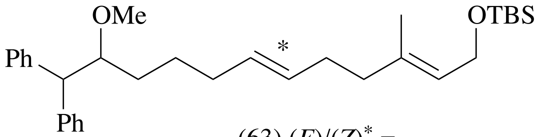
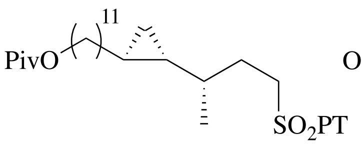
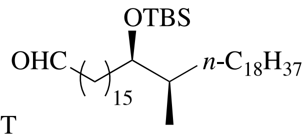
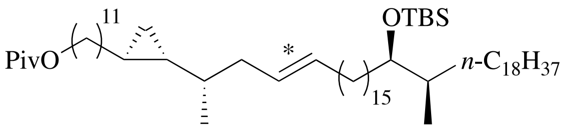
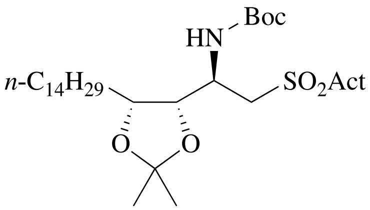
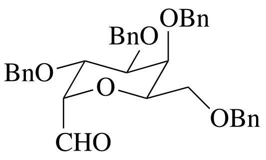
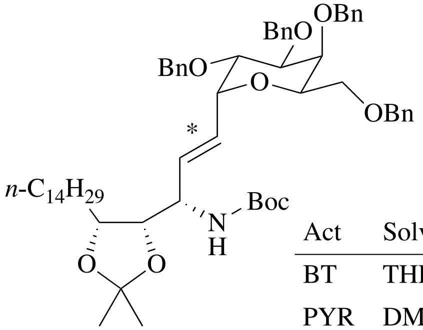
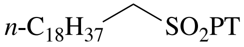
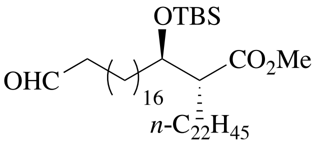
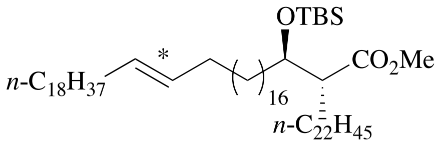
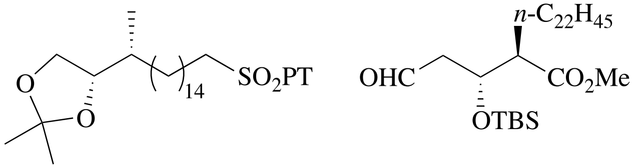
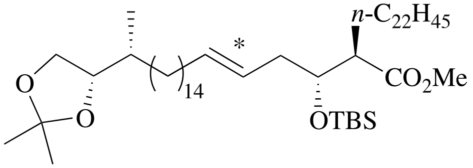
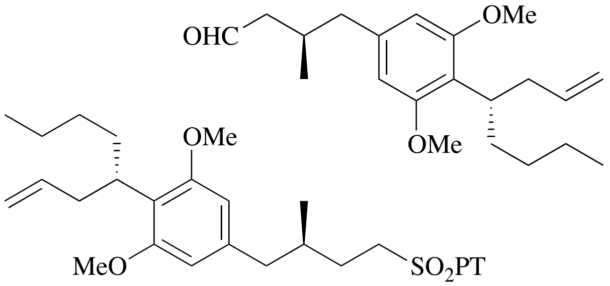
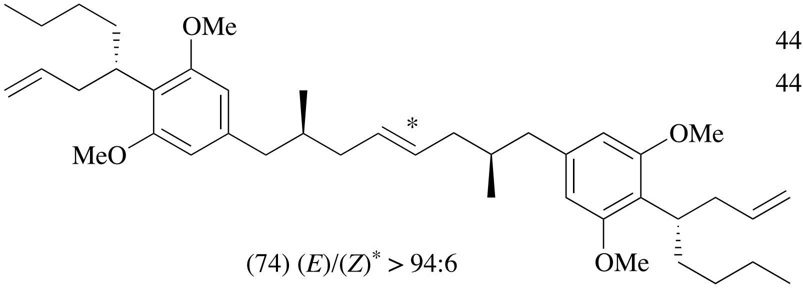
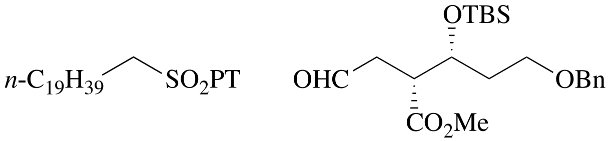
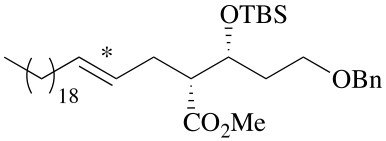
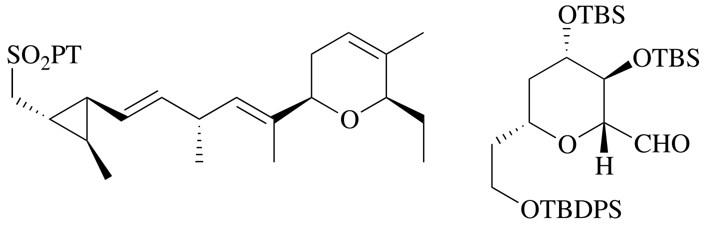
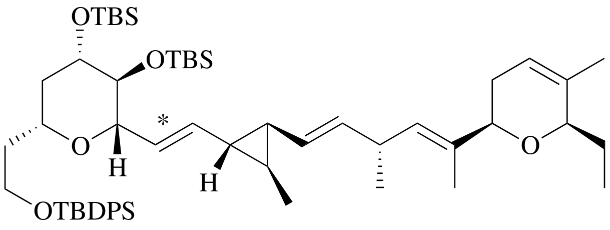
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}				
	 	1. KHMDS, DME, –78° 2. Aldehyde	 (63) (*E*)/(*Z*)* = —	443
	 	LiHMDS, THF, –12°	 (80) (*E*)/(*Z*)* = 75:25	287
	 	LiHMDS. See table.	 Act / Solvent / Temp / / (*E*)/(*Z*)* BT / THF / –78 to –10° / (71) / >98:2 PYR / DME / –20° to rt / (40) / 39:61	444
C_{19}				
	 	LiHMDS, THF, –10° to rt	 (70) (*E*)/(*Z*)* —	432

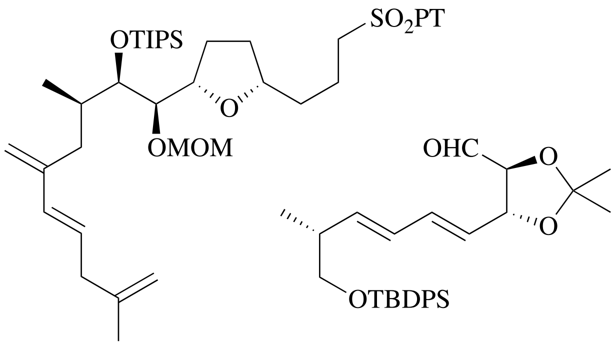
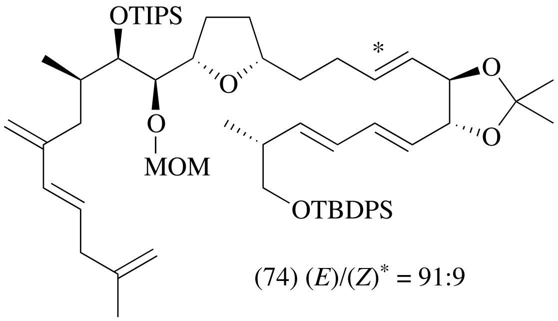
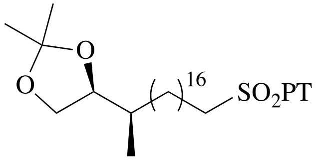
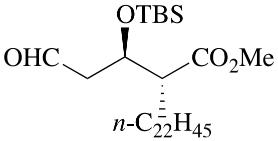
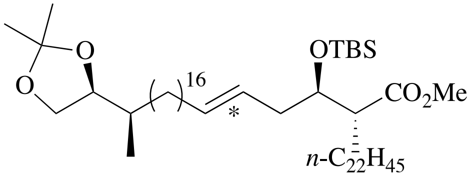
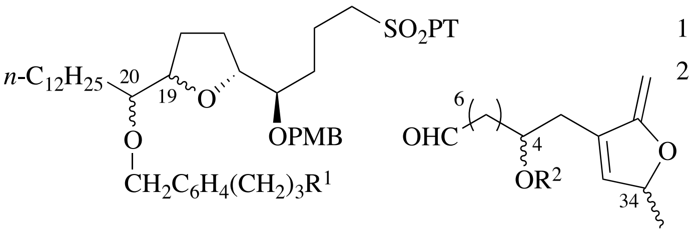
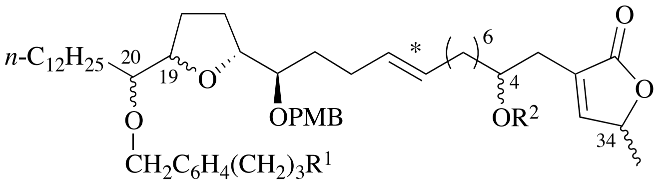
TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}		LiHMDS	 (86) $(E)/(Z)^* =$ —	423
		1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 2 h; rt, 19 h	 (74) $(E)/(Z)^* > 94:6$	445 446
C_{20}		LiHMDS, THF, –10° to rt	 (79) $(E)/(Z)^* = 67:33$	432
C_{20}		Barbier conditions. See table.	 (>90)	24

Base	Solvent	Temp	$(E)/(Z)^*$
NaHMDS	THF	–78°	11:89
NaHMDS	THF	–35°	14:86
KHMDS	DMF	–60°	50:50
KHMDS	DME, 18-crown-6	–60°	25:75

Base	Solvent	Temp	$(E)/(Z)^*$
LiHMDS	THF-HMPA	–60°	75:25
LiHMDS	DMF-HMPA	–35°	>97:3
LiHMDS	DMF-DMPU	–35°	>97:3

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}		1. LiHMDS, THF, –78 to –40°, 1 h 2. Aldehyde, DMF-DMPU, –78°; rt, 12 h	 (74) (*E*)/(*Z*)* = 91:9	447 426
C_{21}	 	LiHMDS, THF, –10°	 (89) (*E*)/(*Z*)* = —	410
		1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt *4x4 Component double mixture synthesis*	 x16 Compounds: (≥71) (*E*)/(*Z*)* = —	448

C19	C20	R^1
(*S*)	(*R*)	C_2F_5
(*S*)	(*S*)	n-C_4F_9
(*R*)	(*S*)	n-C_6F_{13}
(*R*)	(*R*)	n-C_8F_{17}

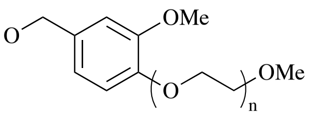
C4	C34	OR^2	n
(*R*)	(*S*)		1
(*R*)	(*R*)		2
(*S*)	(*S*)		3
(*S*)	(*R*)		4

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

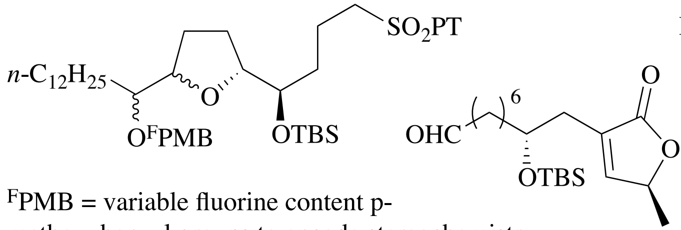
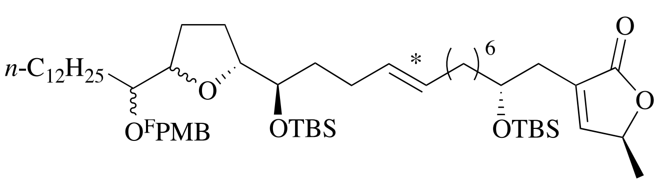
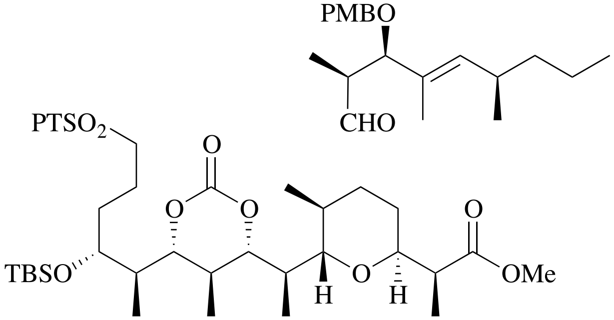
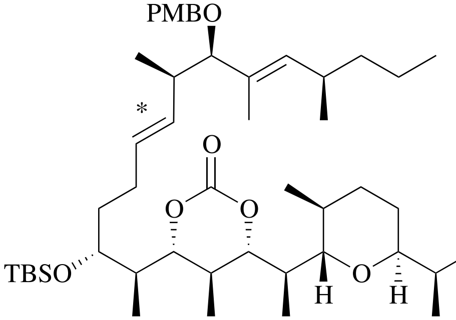
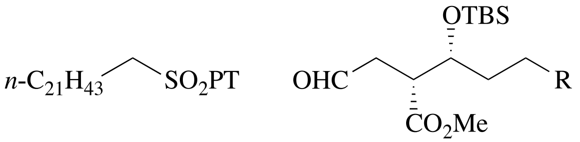
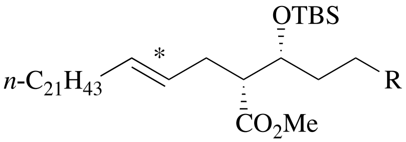
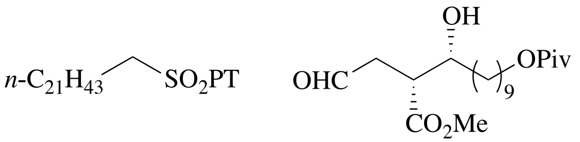
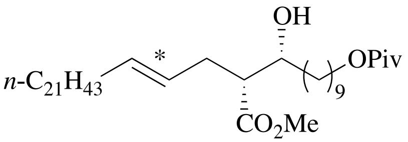
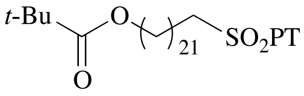
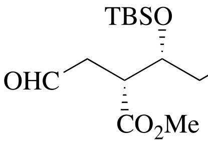
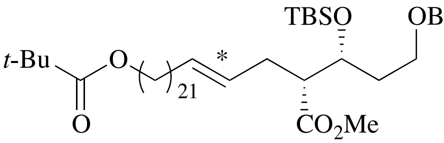
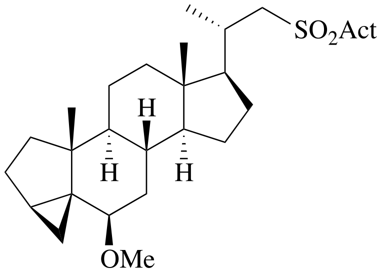
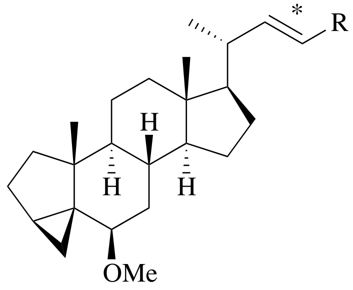
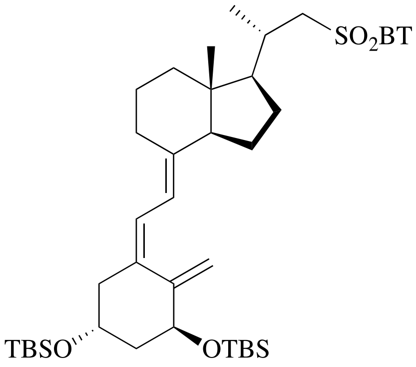
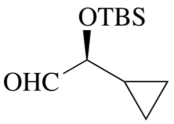
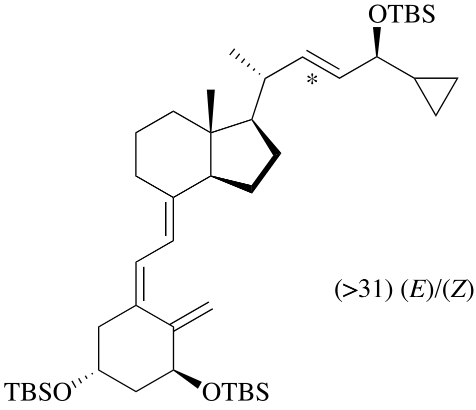
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}	 ^{F}PMB = variable fluorine content p-methoxybenzyl groups to encode stereochemistry	NaHMDS	 (79) $(E)/(Z)^*$ = —	449
		1. KHMDS, DME, –60° 2. Aldehyde, –60 to –20°, 1.5 h	 (69) $(E)/(Z)^*$ = 93:7	37
C_{22}		LiHMDS, THF	 R $(E)/(Z)^*$ BnO (83) — $PivO(CH_2)_3$ (83) —	278
		LiHMDS, THF, –10°; rt, 3 h	 (83) $(E)/(Z)^*$ = 72:27	276

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{22}			LiHMDS, THF, –10°; rt		(67) $(E)/(Z)^*$ = 67:33	325
		RCHO	1. NaHMDS, Solvent –78°, 15 min 2. Aldehyde, –78° to rt			57
			LiHMDS, DME, –70°, 30 min; rt, 3 h		(>31) $(E)/(Z)^*$ = —	450

Act	R	Solvent		$(E)/(Z)^*$
PT	*n*-Pr	THF	(39)	50:50
BT	*n*-Pr	THF	(61)	64:36
BT	*n*-Pr	THF/HMPA	(65)	80:20
BT	*i*-Pr	THF/HMPA	(90)	75:25

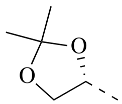
Act	R	Solvent		$(E)/(Z)^*$
BT	(*S*)-$Me_2CHCH(OBn)$	THF/HMPA	(82)	94:6
BT	(*R*)-$Me_2CHCH(OBn)$	THF/HMPA	(80)	82:18
BT	(*S*)-$TBSOCH_2CHMe$	THF/HMPA	(60)	85:15
BT		THF/HMPA	(81)	90:10

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

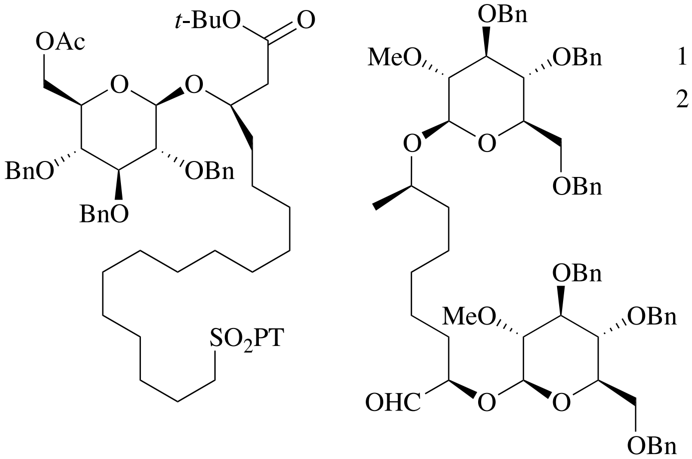
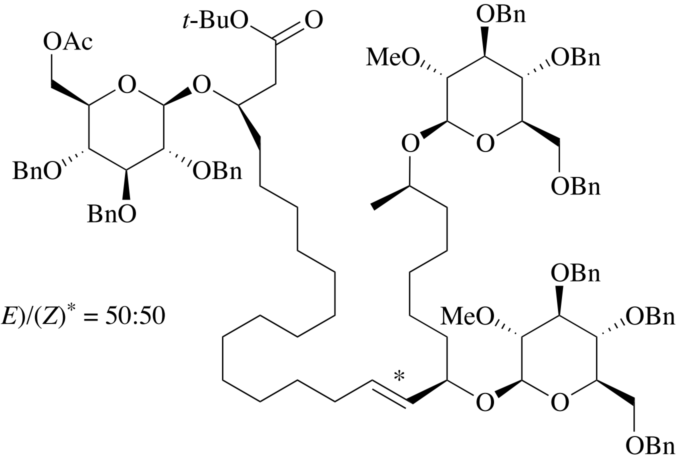
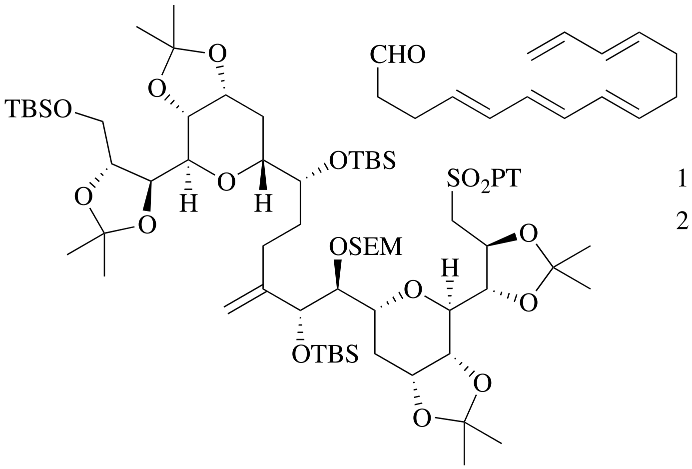
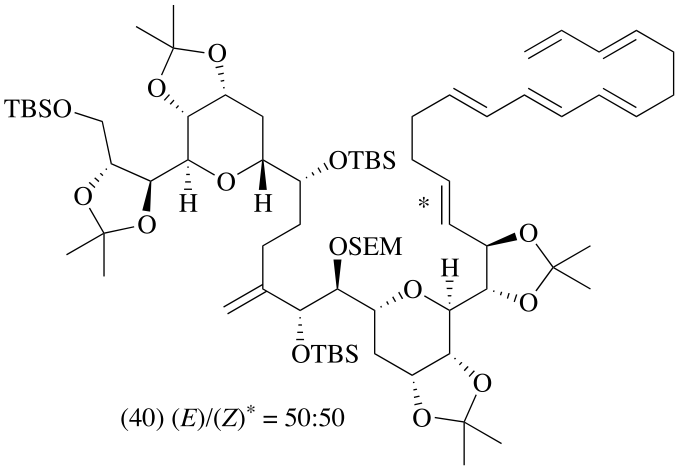
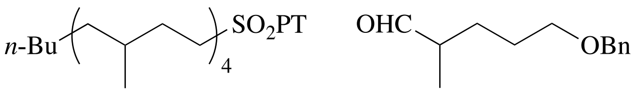
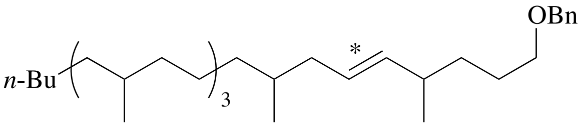
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}		1. LiHMDS, DME, –78° 2. Aldehyde, –78°	 (45) (*E*)/(*Z*)* = 50:50	451
C_{23}		1. KHMDS, THF, –78°, 15 min 2. Aldehyde, –78° to rt, 30 min	 (40) (*E*)/(*Z*)* = 50:50	138
C_{24}		1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt	 (90) (*E*)/(*Z*)* —	452

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

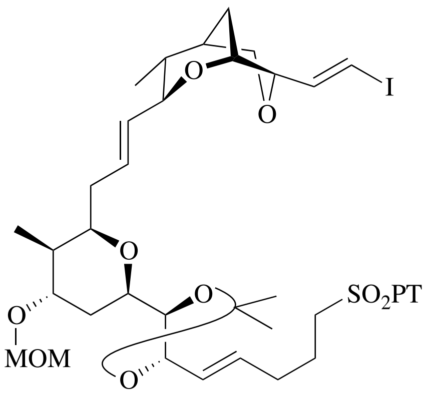
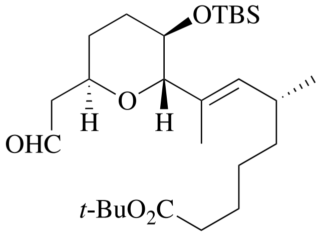
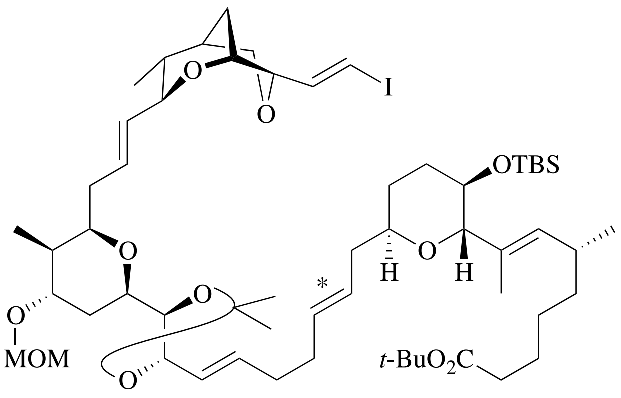
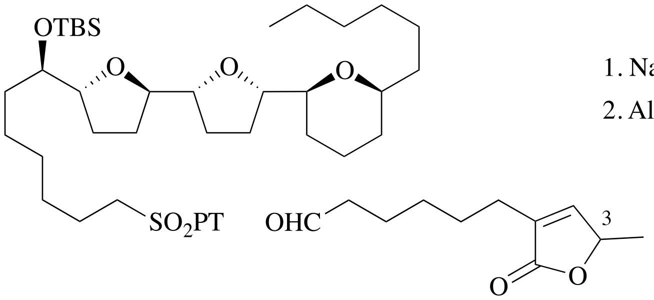
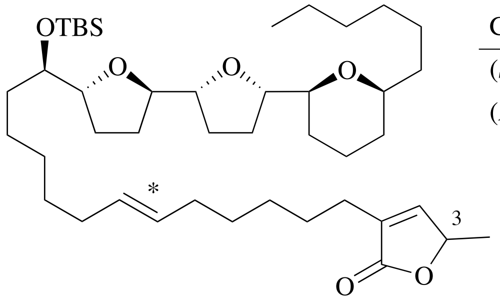
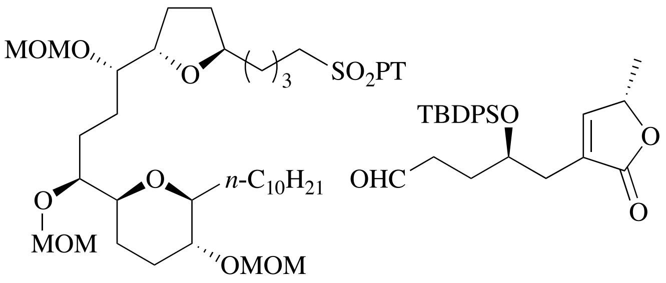
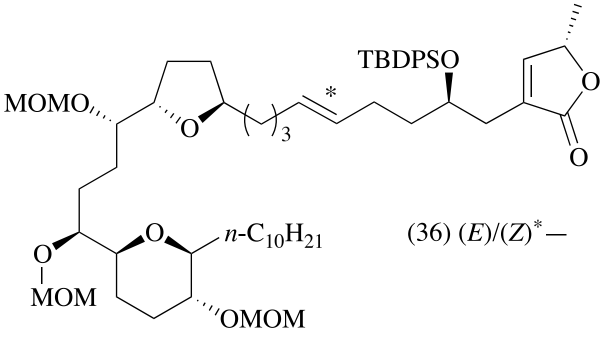
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{25}	 	1. Base, solvent, –72° 2. Aldehyde, –72° to rt		437 62
		Base / Solvent LiHMDS / DMF-HMPA KHMDS / DME	$(E)/(Z)^*$ (30) 50:50 (28) 100:0	
C_{26}		1. NaHMDS, THF, –78°, 10 min 2. Aldehyde, –78 to –20°, 4 h	 C3 / $(E)^*$-isomer (*S*) / (41) (*R*) / (71)	324 415
C_{27}		1. LiHMDS, PhMe, –78°, 1 h 2. Aldehyde; rt	 (36) $(E)/(Z)^*$—	453

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

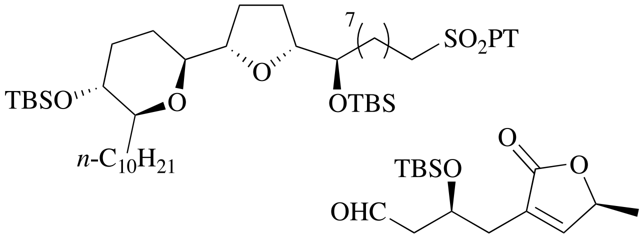
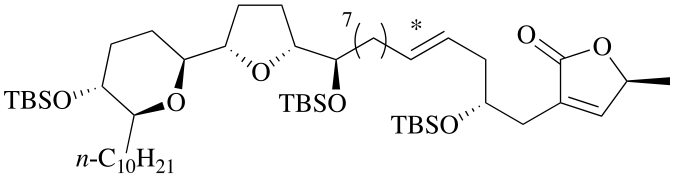
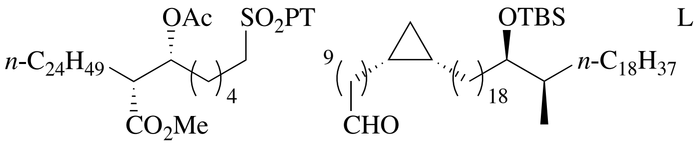
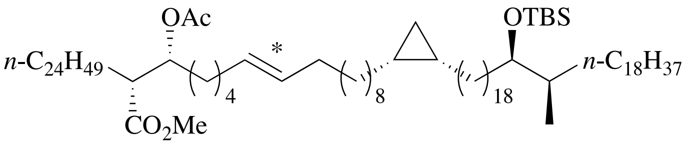
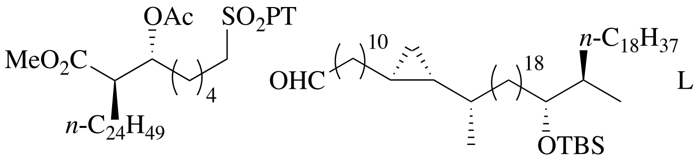
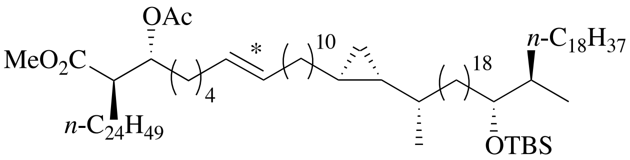
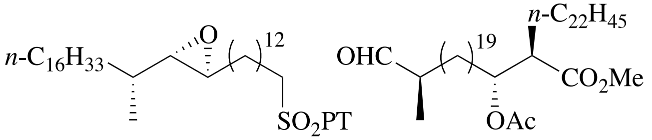
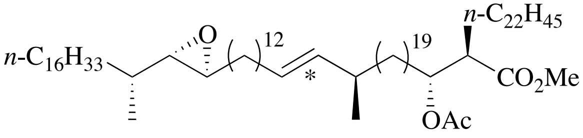
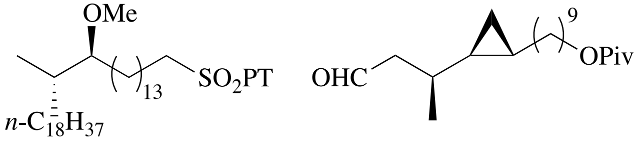
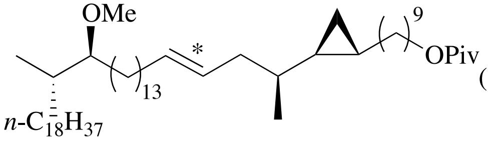
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}		1. LiHMDS, THF, –78°, 40 min 2. Aldehyde, –10°, 3 h	 (93) 'inseparable mixture' of (*E*)/(*Z*)*-isomers	454
C_{32}		LiHMDS, THF, –12° to rt, 2 h	 (56) isomeric ratio* = 66:34	277 278
		LiHMDS, THF, –5°	 (52) (*E*)/(*Z*)* = 67:33	287
C_{33}		KHMDS, DME, –5°	 (26) (*E*)/(*Z*)* = —	410
C_{35}		LiHMDS, THF, –20°	 (54) (*E*)/(*Z*)* = —	287

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

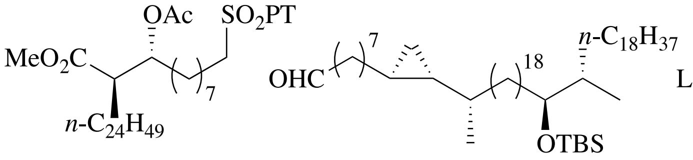
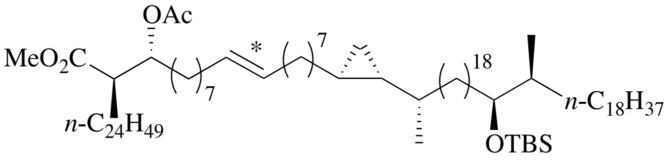
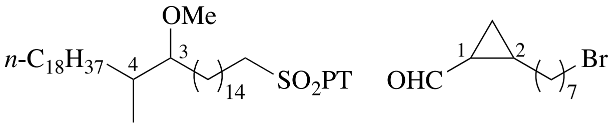
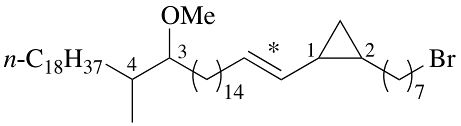
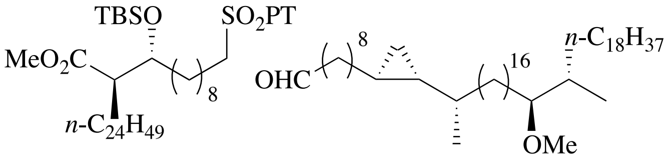
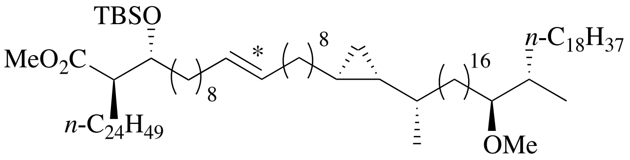
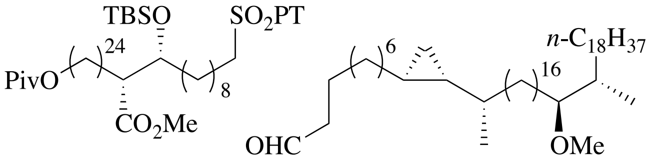
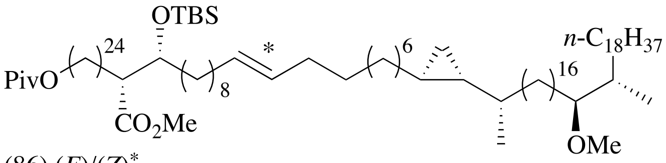
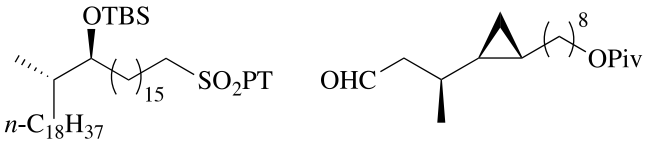
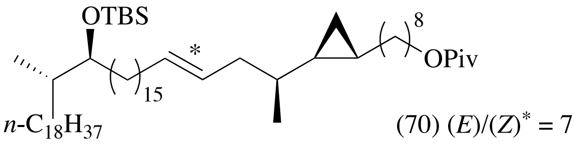
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{35}		LiHMDS, THF, –12°	 (47) (*E*)/(*Z*)* = 73:27	287
C_{36}		LiHMDS, THF, –15°; rt, 16 h	 C3 C4 C1 C2 (*E*)/(*Z*)* (*R*) (*R*) (*S*) (*S*) (92) — (*S*) (*S*) (*S*) (*S*) (87) —	276
		LiHMDS, THF	 (28) (*E*)/(*Z*)* = —	287
		LiHMDS, THF, 0 to 5°; rt	 (86) (*E*)/(*Z*)* = —	325
C_{37}		LiHMDS, THF, –12°	 (70) (*E*)/(*Z*)* = 75:25	287

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

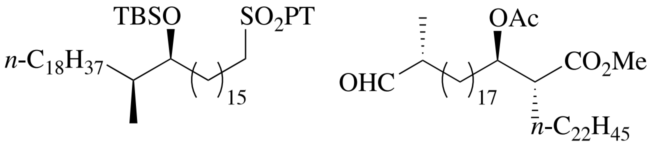
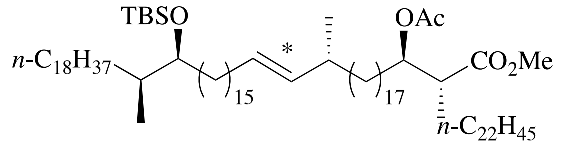
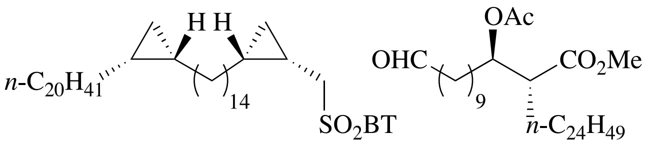
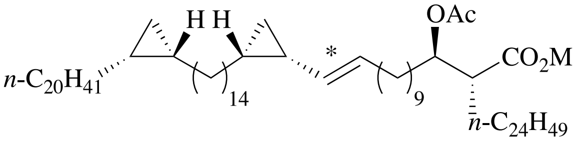
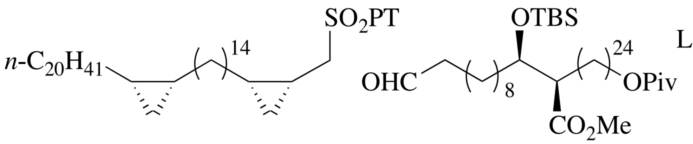
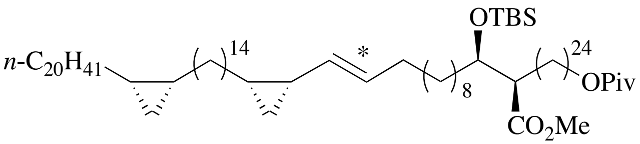
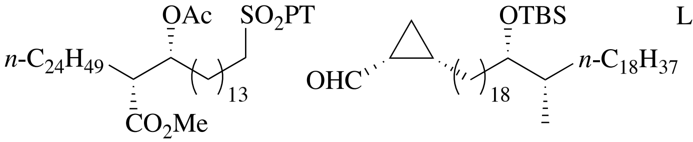
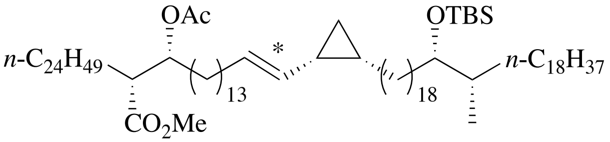
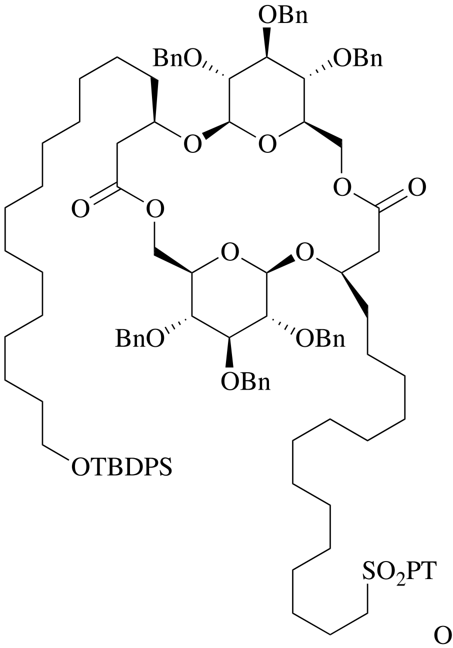
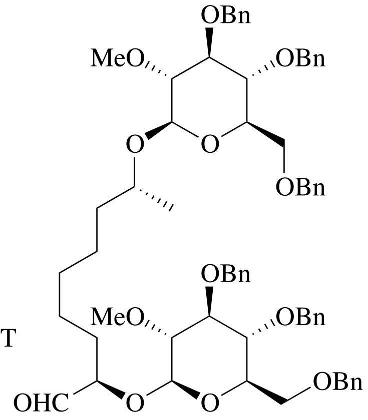
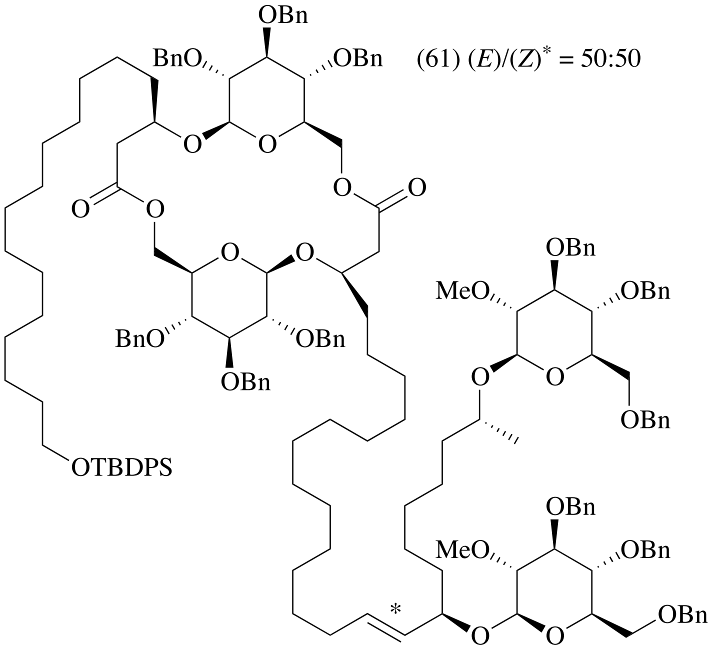
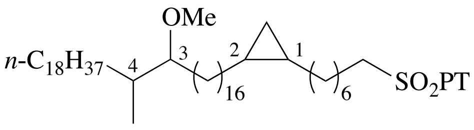
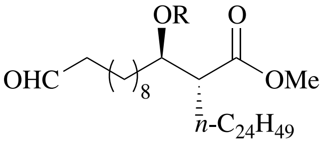
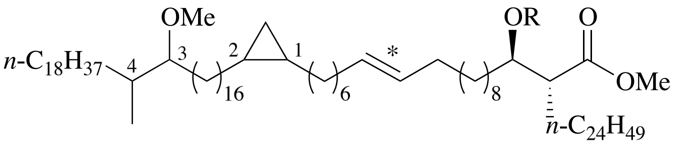
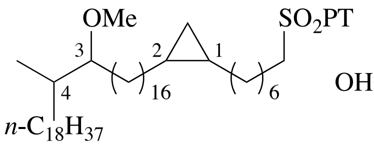
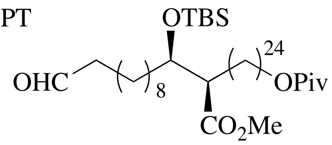
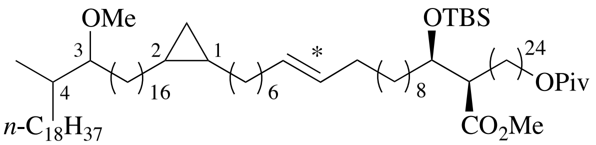
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{37}		KHMDS, DME	 (44) (E)*-isomer	423
C_{41}		LiHMDS, THF, –5° to rt, 24 h	 (37) (E)/(Z)* = 63:37	274 275
		LiHMDS, THF, –10° to rt	 (60) (E)/(Z)* = —	325
		LiHMDS, THF, –12° to rt, 2 h	 (72) isomeric ratio* = 80:20	278

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{46}	 	1. LiHMDS, DME, –78°, 10 min 2. Aldehyde, –78°, 1 h; rt, 30 min	 (61) (*E*)/(*Z*)* = 50:50	455 451
C_{47}	 	LiHMDS, THF, –12°; rt, 1-2 h		276

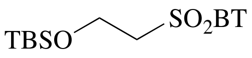
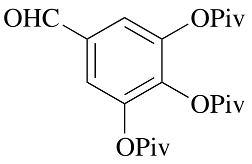
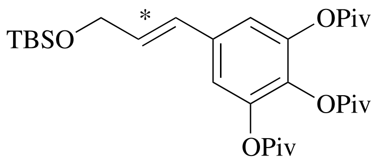
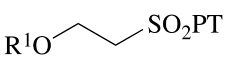
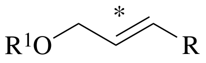
R	C1	C2	C3	C4		(*E*)/(*Z*)*
Ac	(*R*)	(*R*)	(*R*)	(*R*)	(68)	71:29
Ac	(*S*)	(*S*)	(*R*)	(*R*)	(60)	70:30
TBS	(*R*)	(*R*)	(*S*)	(*S*)	(80)	—
TBS	(*R*)	(*R*)	(*R*)	(*R*)	(77)	63:37

TABLE 2. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{47}				
	 	LiHMDS, THF, −10° to rt		325

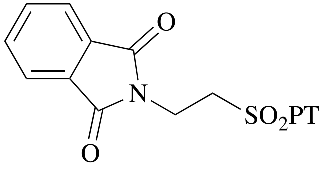
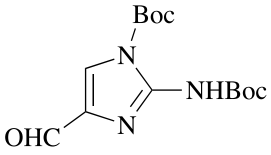
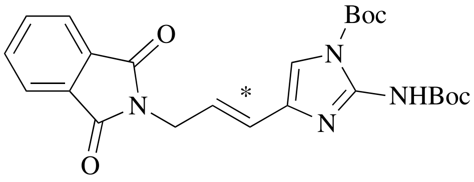
C1	C2	C3	C4		(*E*)/(*Z*)*
(*R*)	(*S*)	(*S*)	(*S*)	(71)	67:33
(*S*)	(*R*)	(*R*)	(*R*)	(89)	67:33

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	 	KHMDS, THF, –78°, 2 h; rt, 2 h	 (75) (*E*)/(*Z*)* = 75:25	456
	 R^2CHO	$MN(SiMe_3)$, –78°, 30 min; rt		189

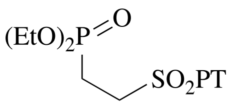
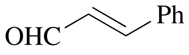
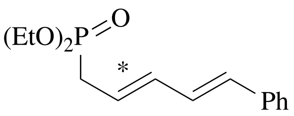
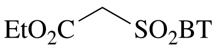
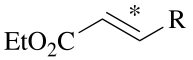
R^1	R^2	M	Solvent		(*E*)/(*Z*)*
TMS	Ph	Li	THF	(45)	62:38
TMS	Ph	Na	THF	(35)	72:28
TMS	Ph	K	THF	(28)	81:19
TBS	Ph	Li	THF	(81)	67:23
TBS	Ph	Na	THF	(79)	89:11

R^1	R^2	M	Solvent		(*E*)/(*Z*)*
TBS	Ph	K	THF	(83)	98:2
TBS	Ph	K	DME	(80)	>99:1
TBS	(*E*)-PhCH=CH	K	THF	(81)	97:3
TBS	(*E*)-PhCH=CH	K	DME	(69)	99:1
TBS	$H_2C{=}C(Me)$	K	THF	(91)	96:4

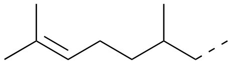
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	Barbier conditions using $M(SiMe_3)_2$ as base. See table.		457 458

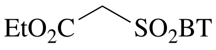
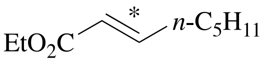
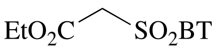
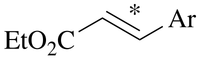
M	Eq aldehyde	Eq base	Solvent	Temp		(*E*)/(*Z*)*
Li	1.0	2.0	DME	–55°	(65)	75:25
Na	1.0	1.0	DME	–55°	(—)	~50:50
Na	1.0	2.0	DME	–55°	(60)	80:20
Na	1.0	3.0	DME	–78°	(31)	84:16
K	1.0	2.0	DME	–55°	(<43)	81:19
Na	1.0	2.0	THF	–55°	(61)	87:13
Na	1.0	2.0	THF	–55°	(63)	90:10
Na	1.5	2.5	THF	–78°	(79)	87:13

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_2						
			1. THF, KHMDS, –78°, 5 min 2. Aldehyde, –78°, 20 min; 0°, 1 h		(75) $(E)/(Z)^* = 86:14$	112
		RCHO	DBU, CH_2Cl_2, rt, 16 h			19

R		$(E)/(Z)^*$
n-C_5H_{11}	(41)	19:81
c-C_6H_{11}	(80)	80:20
Et_2CH	(88)	>98:2
t-Bu	(21)	>98:2

R		$(E)/(Z)^*$
Bn	(80)	>98:2
(E)-PhCH=CH	(0)	—
	(64)	30:70

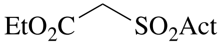
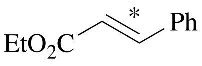
		n-$C_5H_{11}CHO$	**A**: DBU, CH_2Cl_2, –78°, 16 h *or* **B**: NaHMDS, THF, 0 to 65°, 2 h		$(E)/(Z)^*$ **A** (47) 8:92 **B** (31) 95:5	19
		ArCHO	DBU, CH_2Cl_2, rt, 16 h			19

Ar		$(E)/(Z)^*$
Ph	(78)	>95:5
4-$NO_2C_6H_4$	(89)	>98:2
4-$(HO_2C)C_6H_4$	(57)	96:4
4-ClC_6H_4	(77)	95:5

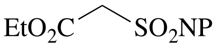
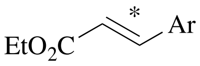
Ar		$(E)/(Z)^*$
4-$MeOC_6H_4$	(93)	92:8
2-ClC_6H_4	(72)	95:5
$2,6$-$Cl_2C_6H_3$	(83)	>98:2
$2,4,6$-$Me_3C_6H_2$	(70)	>98:2

Ar		$(E)/(Z)^*$
2-naphthyl	(65)	93:7
1-naphthyl	(86)	96:4
ferrocenyl	(82)	96:4

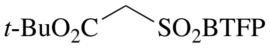
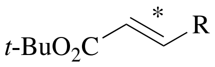
TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	 PhCHO	NaHMDS, THF, 65°, 2 h		19

Act		(*E*)/(*Z*)*
BT	(63)	>95:5
PT	(5)	>95:5
TBT	(0)	>95:5

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 ArCHO	1. Cs_2CO_3, DMF, temp 2. Aldehyde, time		459

Ar	Temp	Time		(*E*)/(*Z*)*
4-ClC_6H_4	60°	2 d	(50)	>99:1
4-BrC_6H_4	rt	4 d	(49)	>99:1
4-$NO_2C_6H_4$	rt	18 h	(41)	>99:1
4-$MeOC_6H_4$	60°	6 d	(40)	>99:1

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 RCHO	K_2CO_3, Bu_4NBr, DMF 120°, 18 h		16

R		(*E*)/(*Z*)*	R		(*E*)/(*Z*)*	R		(*E*)/(*Z*)*
n-C_9H_{19}	(14)	68:32	4-BrC_6H_4	(62)	>99:1	2-naphthyl	(48)	95:5
c-C_6H_{11}	(15)	75:25	4-$CF_3C_6H_4$	(74)	>99:1	6-MeO-2-naphthyl	(31)	95:5
Ph	(95)	96:4	4-$MeOC_6H_4$	(45)	>99:1	2-thienyl	(46)	85:15
4-ClC_6H_4	(56)	>99:1	2-ClC_6H_4	(52)	>99:1	4-pyridyl	(96)	96:4

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

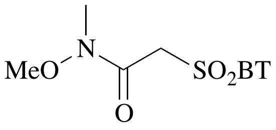
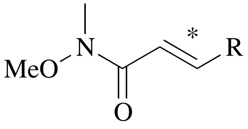
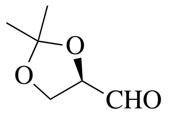
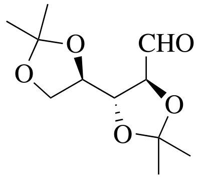
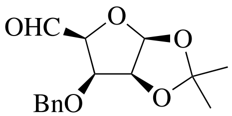
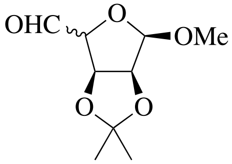
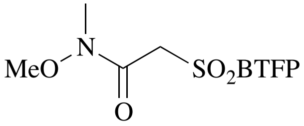
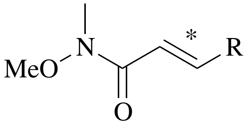
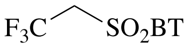
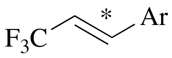
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	 RCHO	1. NaH, THF, rt, 2 min 2. Aldehyde, rt, 24 h	 $(E)^*$-isomers only	81
	R *n*-Pr (48) CH_2=CH(CH_2)$_2$ (57) Ph (67) 4-MeOC_6H_4 (44) 2-furyl (52) 5-(TBSOCH_2)-2-furyl (59) 2-thienyl (63)	**RCHO**  (50)  (72)	**RCHO**  (55)  (53)	
	 RCHO	K_2CO_3, Bu_4NBr, DMF 120°, 18 h	 $(E)/(Z)^* > 99:1$ **R** Ph (66) 4-ClC_6H_4 (47) 4-BrC_6H_4 (51) 4-$CF_3C_6H_4$ (82) 4-MeOC_6H_4 (20) 2-ClC_6H_4 (84) 2-naphthyl (30) 6-MeO-2-naphthyl (25) 2-thienyl (49) 2-furyl (50)	16

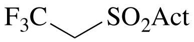
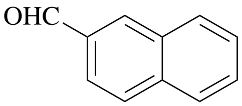
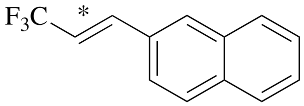
TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
		ArCHO	TBAF, THF, –78° to rt, 16 h		190

Ar		(*E*)/(*Z*)*
1-Naphthyl	(73)	58:42
2-Naphthyl	(80)	38:62
2-BrC_6H_4	(61)	76:24
2-(4-ClC_6H_4)SC_6H_4	(83)	65:35
2,6-$Cl_2C_6H_3$	(74)	100:0

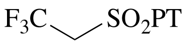
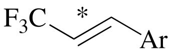
Ar		(*E*)/(*Z*)*
3-$PhOC_6H_4$	(73)	30:70
3-$NO_2C_6H_4$	(78)	23:77
4-PhC_6H_4	(83)	36:64
4-$NO_2C_6H_4$	(92)	100:0

Ar		(*E*)/(*Z*)*
4-*t*-BuC_6H_4	(75)	46:54
4-$MeCO_2C_6H_4$	(56)	27:73
4-$MeOC_6H_4$	(45)	44:56
4-BrC_6H_4	(61)	46:54

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
			See table.		460

Act	Base	Solvent	Temp		(*E*)/(*Z*)*
BT	TBAF	THF	rt	(27)	27:73
BT	TBAF	THF	0°	(29)	20:80
BT	TASF	CH_2Cl_2	rt	(23)	35:65
BT	CsF	DMSO	rt	(58)	44:56
PT	DBU	CH_2Cl_2	rt	(7)	28:72

Act	Base	Solvent	Temp		(*E*)/(*Z*)*
PT	TBAF	CH_3CN	rt	(34)	37:63
PT	TBAF	THF	rt	(47)	31:69
PT	CsF	DMSO	rt	(86)	41:59
PT	TBAF	DMSO	rt	(85)	40:60
TBT	CsF	DMSO	rt	(40)	30:70

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
		ArCHO	CsF, DMSO, rt		460

R		(*E*)/(*Z*)*
2-Naphthyl	(86)	41:59
1-Naphthyl	(65)	52:48
9-Phenanthrenyl	(42)	56:44
9-Anthracenyl	(50)	92:8
1-Pyrenyl	(62)	61:39
4-($MeCO_2$)C_6H_4	(50)	38:62

R		(*E*)/(*Z*)*
4-NCC_6H_4	(42)	39:61
4-$NO_2C_6H_4$	(52)	37:63
3-$MeOC_6H_4$	(37)	39:61
6-MeO-naphthen-2-yl	(51)	44:56
4-PhC_6H_4	(23)	40:60

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

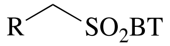
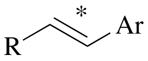
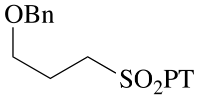
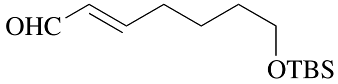
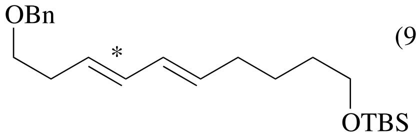
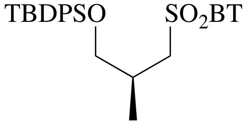
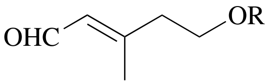
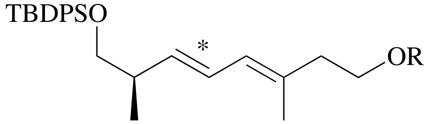
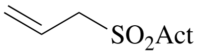
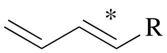
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-3}				
	 ArCHO	LDA, THF, –78°, 3 h; rt, 1 h	 R / Ar / / $(E)/(Z)^*$ Me / 4-MeOC_6H_4 / (54) / 98:2 Me / $3,4\text{-(MeO)}_2C_6H_3$ / (39) / 98:2 Et / 4-MeOC_6H_4 / (54) / 98:2 t-BuO$(CH_2)_2$ / Ph / (15) / 97:3	3
C_3	 	1. LiHMDS, THF, –78°; –65°, 1 h 2. Aldehyde, –65°, 1 h; rt, 18 h	 (90) $(E)/(Z)^* = 85:15$	461 462
	 	LiHMDS, THF, –78°	 R / / $(E)/(Z)^*$ $C(Me)_2OMe$ / (87) / >95:5 THP / (95) / >95:5	463

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3	 RCHO	**A**: KHMDS, THF, –78° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde *or* **B**: KHMDS, DMF, –55° *or* **D**: 1. KHMDS, DMF-TDA1, –60°, 2 min 2. Aldehyde		31

R		Act = PT		Act = BT	
			$(E)/(Z)^*$		$(E)/(Z)^*$
$Ph(CH_2)_2$	A	(72)	63:37	(68)	59:41
$Ph(CH_2)_2$	B	(65)	58:42	(53)	57:43
$Ph(CH_2)_2$	C	(74)	15:85	(39)	30:70
$Ph(CH_2)_2$	D	(78)	14:86	(42)	20:80
$BnO(CH_2)_2$	A	(68)	79:21	(69)	65:35
$BnO(CH_2)_2$	B	(47)	62:38	(65)	52:48
$BnO(CH_2)_2$	C	(36)	15:85	(73)	20:80
$BnO(CH_2)_2$	D	(48)	14:86	(74)	19:81

R		Act = PT		Act = BT	
			$(E)/(Z)^*$		$(E)/(Z)^*$
$BnOCH_2$	A	(82)	66:34	(72)	56:44
$BnOCH_2$	B	(67)	55:45	(66)	52:48
$BnOCH_2$	C	(63)	69:31	(70)	68:32
$BnOCH_2$	D	(72)	72:28	(71)	70:30

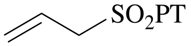
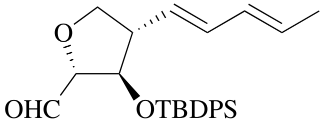
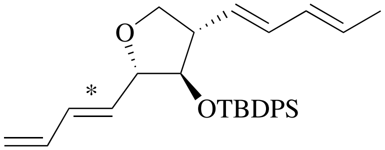
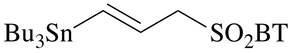
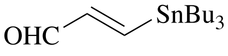
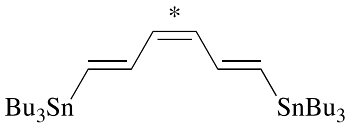
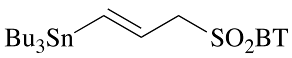
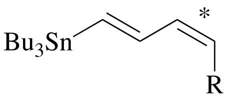
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 1 h	 (85) $(E)/(Z)^* = 67{:}33$	464
	 	KHMDS, THF, –78° to rt	 (69) $(E)/(Z)^* = 4{:}96$	465 466

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_3						
		RCHO	1. Base, solvent, –78° 2. Aldehyde, –78° to rt			74

R	Base	Solvent		$(E)/(Z)^*$
Et	LDA	THF	(60)	40:60
Et	KHMDS	PhMe	(61)	8:92
Et	KHMDS	THF	(50)	9:91
(*E*)-MeCH=CH	LDA	THF	(58)	22:78
(*E*)-MeCH=CH	KHMDS	PhMe	(55)	17:83
(*E*)-MeCH=CH	KHMDS	THF	(55)	7:93
(*E*)-Bu_3SnCH=CH	KHMDS	THF	(66)	4:96
Me_2C=CH	LDA	THF	(62)	62:38
Me_2C=CH	LiHMDS	THF	(43)	60:40
Me_2C=CH	KHMDS	PhMe	(59)	19:81
Me_2C=CH	KHMDS	THF	(56)	3:97
(*E*)-PhCH=CH	LDA	THF	(62)	60:40
(*E*)-PhCH=CH	KHMDS	PhMe	(60)	21:79
(*E*)-PhCH=CH	KHMDS	THF	(50)	6:94
Ph	LDA	THF	(61)	36:64
Ph	KHMDS	PhMe	(62)	54:46
Ph	KHMDS	THF	(58)	16:84

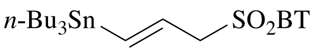
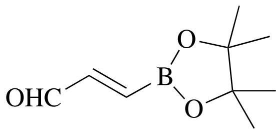
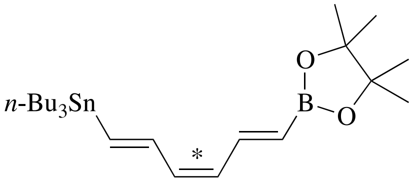
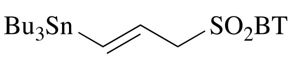
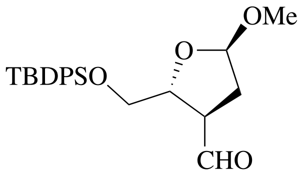
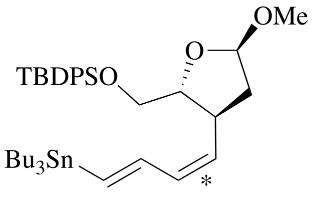
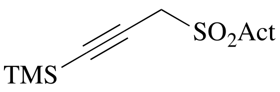
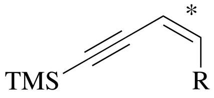
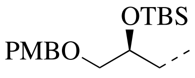
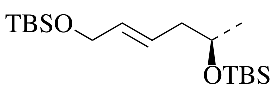
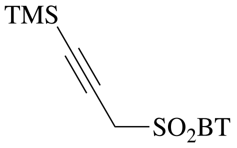
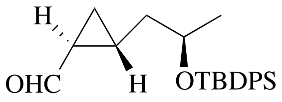
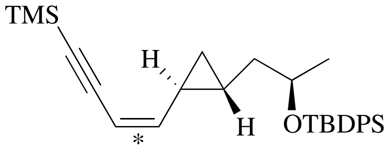
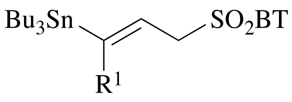
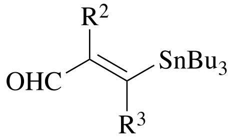
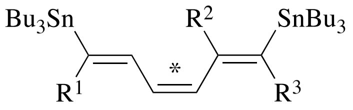
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
			KHMDS, THF, –78°, 16 h		(41) $(E)/(Z)^*$ = 4:96	467
			KHMDS, PhMe, –78°, 8 h; rt, 14 h		(61) $(E)/(Z)^*$ = 10:90	76

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3	 RCHO	**A**: 1. KHMDS, –65°, 30 min 2. Aldehyde, –65°, 3 h; 0°, 1 h *or* **B**: KHMDS, –65° to 0°		468 469

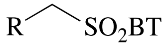
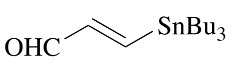
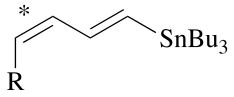
Act	Ar		Solvent		$(E)/(Z)^*$
BT	Ph	**A**	THF	(50)	13:87
BT	Ph	**B**	THF	(80)	4:96
BT	Ph	**A**	DME	(31)	2:98
PT	Ph	**B**	THF	(38)	2:98
BT	4-$MeOC_6H_4$	**A**	THF	(51)	22:78
BT	4-$MeOC_6H_4$	**B**	THF	(43)	3:97
BT	3-furyl	**A**	THF	(50)	5:95
BT	3-furyl	**B**	THF	(41)	<2:98

Act	Ar		Solvent		$(E)/(Z)^*$
BT	(*E*)-PhCH=CH	**A**	THF	(42)	43:66
BT	(*E*)-PhCH=CHh	**B**	THF	(46)	6:94
BT	$BnO(CH_2)_4$	**A**	THF	(44)	21:79
BT	$BnO(CH_2)_4$	**B**	THF	(23)	7:93
BT		**A**	THF	(56)	<2:98
BT		**A**	THF	(76)	14:86

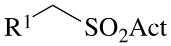
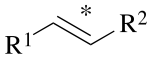
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	KHMDS, –78°, 1 h; –50°, 6 h	 (60) $(E)/(Z)^* = 5:95$	470
$C_{3\text{-}4}$	 	KHMDS, THF, –78° to rt		75

R^1	R^2	R_3		$(E)/(Z)^*$
H	H	H	(66)	4:96
Me	H	H	(56)	5:95
H	Me	H	(53)	18:82
Me	H	Me	(64)	5:95

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

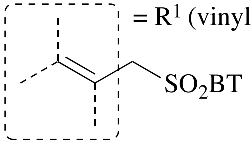
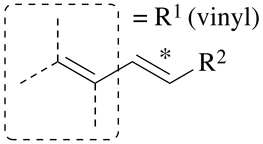
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{3–5}$			1. Base, THF, –78° 2. Aldehyde, –78° to rt		74

R	Base		$(E)/(Z)^*$
Et	LDA	(78)	53:47
Et	KHMDS	(78)	61:39
$CH_2{=}CH$	LDA	(59)	9:91
$CH_2{=}CH$	KHMDS	(60)	10:90
$MeC{\equiv}C$	LDA	(33)	5:95
$MeC{\equiv}C$	KHMDS	(38)	5:95
$Me_2C{=}CH$	LDA	(41)	29:71
$Me_2C{=}CH$	KHMDS	(43)	61:39

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{3–7}$		R^2CHO	1. KHMDS, DME, –60°, 30 min 2. Aldehyde, –60° to rt		5

		Act = PT		Act = TBT	
R^1	R^2		$(E)/(Z)^*$		$(E)/(Z)^*$
n-C_4H_9	Ph	(48)	>99:1	(80)	79:21
$H_2C{=}CH$	n-C_9H_{19}	(39)	67:33	(60)	4:96
Ph	n-C_9H_{19}	(70)	29:71	(95)	<1:99

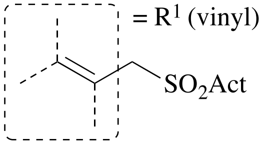
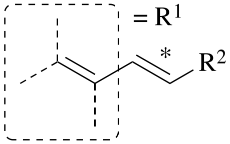
TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-7}	 R^2CHO	**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt *or* **B**: LDA, THF, –78° 3 h, to rt, 1h		3

R^1 (vinyl)	R^2 (α,β-unsat.)			(*E*)/(*Z*)*
CH_2=CH	Ph	**A**	(50)	31:69
CH_2=CH	4-MeOC_6H_4	**A**	(58)	95:5
CH_2=CMe	1-cyclohexenyl	**A**	(29)	99:1
CH_2=CMe	1-cyclohexenyl	**B**	(71)	>99:1
CH_2=CMe	Ph	**A**	(29)	99:1
CH_2=CMe	Ph	**B**	(88)	>99:1
Me_2C=CH	PhC≡C	**A**	(86)	58:42
Me_2C=CH	PhCH=CH	**A**	(77)	66:34
Me_2C=CH	PhCH=CH	**B**	(81)	65:35
Me_2C=CH	1-cyclohexenyl	**A**	(16)	67:33
Me_2C=CH	1-cyclohexenyl	**B**	(72)	80:20
Me_2C=CH	Ph	**A**	(80)	21:79

R^1 (vinyl)	R^2 (α,β-unsat.)			(*E*)/(*Z*)*
Me_2C=CH	Ph	**B**	(76)	62:38
Me_2C=CH	4-MeOC_6H_4	**A**	(85)	90:10
Me_2C=CH	4-MeOC_6H_4	**B**	(93)	60:40
Me_2C=CH	3,4-$(MeO)_2C_6H_3$	**A**	(64)	55:45
Me_2C=CH	4-ClC_6H_4	**B**	(79)	24:76
Me_2C=CH	4-$(CF_3)C_6H_4$	**A**	(52)	35:65
Me_2C=CH	1-furyl	**A**	(83)	77:23
1-cyclohexenyl	Me_2C=CH	**A**	(15)	78:22
1-cyclohexenyl	Me_2C=CH	**B**	(22)	93:7
1-cyclohexenyl	1-cyclohexenyl	**A**	(26)	>99:1
1-cyclohexenyl	1-cyclohexenyl	**B**	(20)	>99:1
1-cyclohexenyl	Ph	**A**	(50)	>99:1

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-11}	 R^2CHO	**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt *or* **B**: LDA, THF, –78° 3 h; rt, 1h *or* **C**: 1. *n*-BuLi, LiBr, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt		3

R^1 (vinyl)	Act	R^2 (alkyl)			(*E*)/(*Z*)*
CH_2=CH	BT	*n*-C_8H_{17}	**A**	(66)	40:60
CH_2=CH	BT	*n*-C_8H_{17}	$\mathbf{A}^a$	(85)	55:45
CH_2=CH	PYR	*n*-C_8H_{17}	$\mathbf{A}^b$	(25)	19:81
CH_2=CH	BT	*n*-C_9H_{19}	**A**	(78)	32:68
CH_2=CMe	BT	*n*-C_8H_{17}	**A**	(43)	42:58
CH_2=CMe	BT	*n*-C_8H_{17}	**B**	(46)	28:72
CH_2=CMe	PYR	*n*-C_8H_{17}	$\mathbf{A}^{a,b}$	(25)	>99:1

R^1 (vinyl)	Act	R^2 (alkyl)			(*E*)/(*Z*)*
Me_2C=CH	BT	*n*-C_6H_{13}	**A**	(75)	53:47
Me_2C=CH	BT	*n*-C_6H_{13}	**B**	(87)	45:55
Me_2C=CH	PYR	*n*-C_6H_{13}	**C**	(73)	7:93
(*E*)-PhCH=CH	BT	Et	**A**	(38)	33:67
(*E*)-PhCH=CH	BT	Et	**B**	(32)	40:60
n-C_8H_{17}CH=CH	BT	*n*-Bu	**A**	(51)	52:48

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

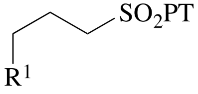
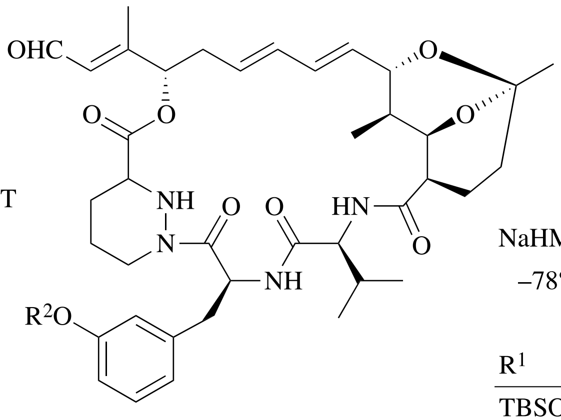
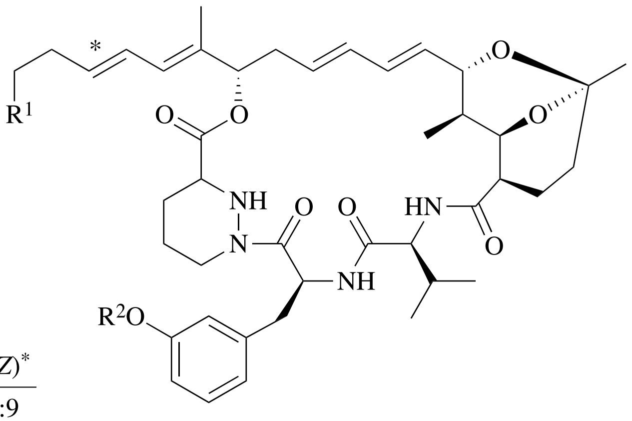
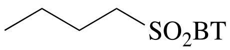
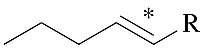
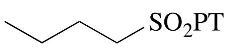
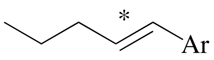
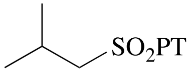
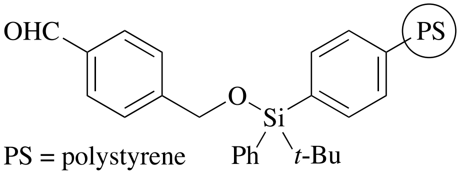
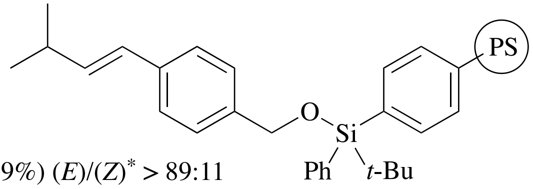
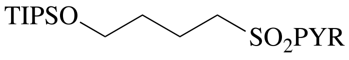
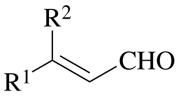
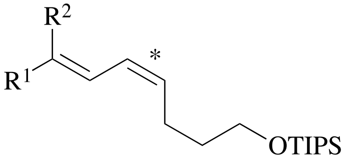
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-12}	 	NaHMDS, DME, –78° to rt R^1 / R^2 / / $(E)/(Z)^*$ TBSO / H / (49) / >91:9 Me / H / (74) / >91:9 $Ph(CH_2)_3$ / TBS / (64) / >91:9		 471 471 472
C_4	 RCHO	LDA, THF, –78°, 3 h; rt, 1h	 R / / $(E)/(Z)^*$ $4\text{-}MeOC_6H_4$ / (95) / 99:1 Ph / (68) / 94:6 $4\text{-}BrC_6H_4$ / (52) / 93:7 $4\text{-}ClC_6H_4$ / (51) / 77:23 $4\text{-}NCC_6H_4$ / (44) / 86:14 1-cyclohexenyl / (33) / 95:5 PhC≡C / (21) / 47:53	3

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 ArCHO	**A**: 1. KHMDS, THF, –78° 2. Aldehyde **B**: 1. KHMDS (1.1 eq), 18-crown-6 (2.0 eq) THF, 0.5 min 2. Aldehyde, –78°, 30 min		25

	protocol A		protocol B	
Ar		$(E)/(Z)^*$		$(E)/(Z)^*$
2-MeOC_6H_4	(59)	>98:2	(64)	>98:2
4-ClC_6H_4	(47)	98:2	(65)	96:4
$4\text{-NO}_2C_6H_4$	(54)	97:3	(54)	95:5
$3\text{-NO}_2C_6H_4$	(61)	95:5	(74)	91:9

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	  PS = polystyrene	1. KHMDS, THF, –78°, 40 min 2. Aldehyde, –35° to rt, 16 h	 (≥69%) $(E)/(Z)^* > 89:11$	473
	 	1. $MN(SiMe_3)_2$, PhMe, temp 2. Aldehyde		33 34

R^1	R^2	M	Temp		$(E)/(Z)^*$
Me	H	K	–78°	(35)	16:84
Me	H	K	0°	(53)	10:90
Me	H	K	rt	(67)	9:91
Me	H	Na	rt	(54)	9:91
Pr	H	K	rt	(64)	10:90
Ph	H	K	rt	(70)	8:92
$Me_2C{=}CH(CH_2)_2$	Me	K	rt	(64)	12:88
$Me_2C{=}CH(CH_2)_2$	Me	Na	rt	(73)	17:83

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

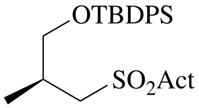
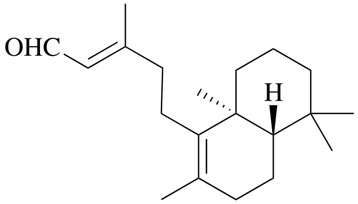
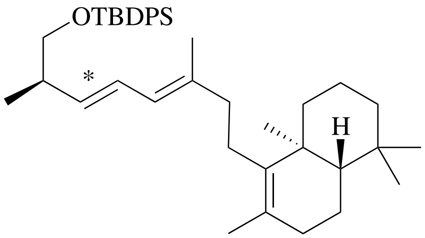
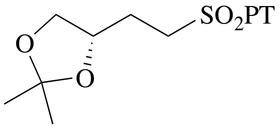
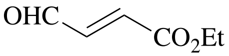
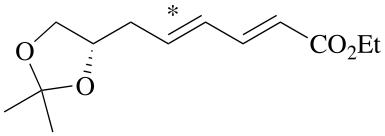
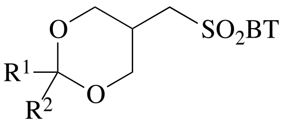
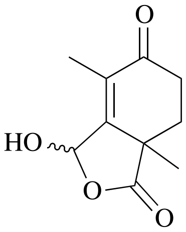
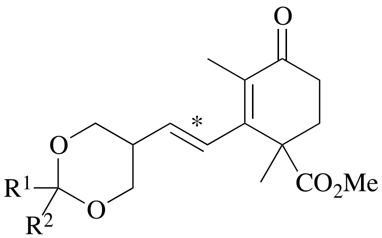
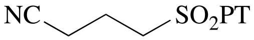
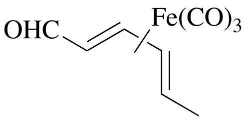
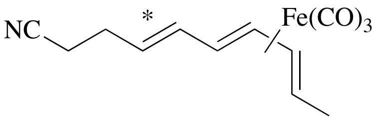
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 	LiHMDS, THF, –78°, time	 Act Time (*E*)/(*Z*)* BT 1 h (73) 86:14 PT 3 h (83) 92:8	474
	 	KHMDS, THF, –78°, 3 h; rt, 2 h	 (77) (*E*)/(*Z*)* = 74:26	356
	 	1. LDA, THF, –78° 2. Add sodium alkoxide of lactol (NaH + lactol) 3. CH_2N_2	 R^1 R^2 (*E*)/(*Z*)* Me Me (78) — *n*-Pr H (78) —	475 476
	 	KHMDS, THF, –78 °, 2 h; rt, 20 h	 (74) (*E*)/(*Z*)* = 96:4	477

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

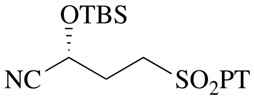
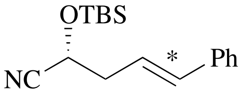
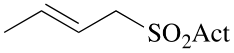
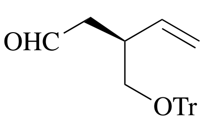
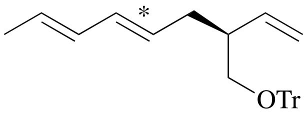
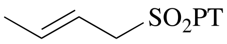
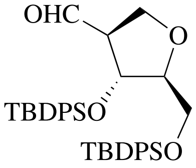
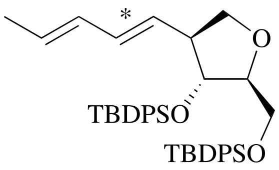
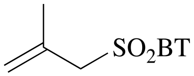
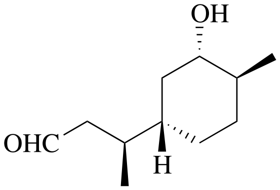
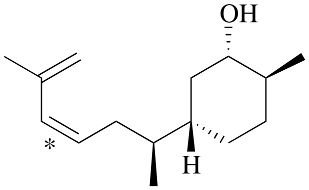
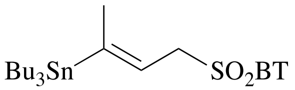
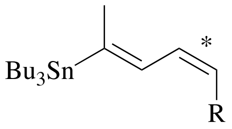
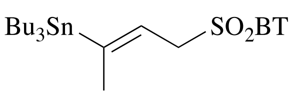
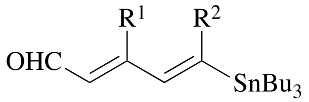
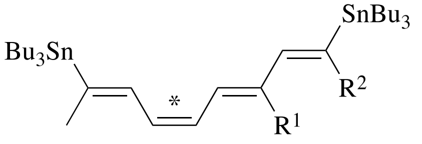
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 PhCHO	1. KHMDS, THF, –78°, 45 min 2. Aldehyde, –78° to rt, 3h	 (99) (*E*)/(*Z*)* = 98:2	252
	 	**A**: 1. MN(SiMe$_3$)$_2$, DME, –78° 2. Aldehyde, –78° to rt *or* **B**: MN(SiMe$_3$)$_2$, DME, –78° to rt	 Act M (*E*)/(*Z*)* BT Li **A** (100) 31:69 BT K **A** (90) 50:50 PT Li **A** (62) 60:40 PT K **B** (81) 63:37	67
	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 1 h	 (92) (*E*)/(*Z*)* = 72:28	464
	 	NaHMDS (2 eq), DME, –60° to rt, 2 h	 (79) (*E*)/(*Z*)* = 25:75	71

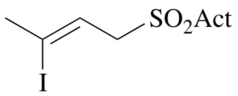
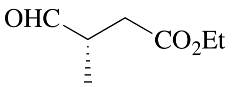
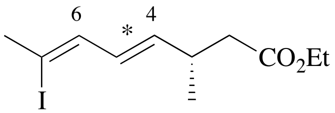
TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 RCHO	1. Base, THF, –78° 2. Aldehyde, –78° to rt		74

R	Base		$(E)/(Z)^*$
Et	LDA	(68)	37:63
Et	KHMDS	(54)	4:96
(*E*)-MeCH=CH	LDA	(58)	23:77
(*E*)-MeCH=CH	KHMDS	(58)	5:95
Me_2C=CH	LDA	(61)	32:68
Me_2C=CH	KHMDS	(56)	5:95
(*E*)-PhCH=CH	LDA	(57)	28:72
(*E*)-PhCH=CH	KHMDS	(52)	8:92
Ph	LDA	(60)	17:83
Ph	KHMDS	(55)	15:85

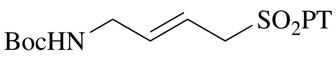
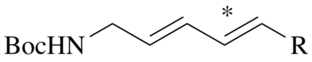
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	KHMDS, THF, –78° to rt		75

R^1	R^2		$(E)/(Z)^*$
H	Me	(64)	5:95
Me	H	(73)	5:95

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	**A**: 1. $M(SiMe_3)_2$, THF, –78° 2. Aldehyde, –78° to T *or* **B**: $M(SiMe_3)_2$, THF, –78° to T		119

Act			Additive	Temp		(4*E*,6*Z*):(4*Z*,6*Z*):(4*E*,6*E*):(4*Z*,6*E*)
BT	A	Li	none	–78°	(35)	36:58:00:06
BT	B	Li	none	25°	(45)	35:55:03:07
BT	A	Li	HMPA	–78°	(93)	33:54:02:11
BT	A	Na	none	–78°	(37)	27:68:00:05
BT	A	K	none	–78°	(60)	28:59:02:11
PT	A	Li	none	–78°	(72)	39:52:04:05
PT	B	Li	none	–78°	(42)	30:60:03:07
PT	A	K	none	–78°	(15)	44:56:00:00

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 RCHO	1. Base (2.1 eq), THF, –78°, 30 min 2. Sulfone metallate added to aldehyde, –78°; rt		478

R_1	Base = LiHMDS	$(E)/(Z)^*$	Base = KHMDS (+ 18-crown-6)	$(E)/(Z)^*$
Ph	(72)	13:87	(72)	72:28
4-$MeOC_6H_4$	(91)	13:87	(75)	70:30
4-ClC_6H_4	(86)	23:77	(75)	77:23
4-$CF_3C_6H_4$	(82)	16:84	(63)	80:20
4-CNC_6H_4	(95)	25:75	(86)	75:25
4-$NO_2C_6H_4$	(65)	65:35	(67)	80:20
(*E*)-PhCH=CH	(88)	23:77	(59)	95:5
2-furyl	(59)	34:66	(75)	84:16
n-C_5H_{11}	(80)	29:71	(78)	71:29
i-Pr	(76)	63:37	(73)	78:22
t-Bu	(88)	95:5	(23)	95:5

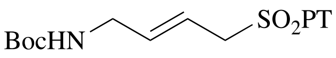
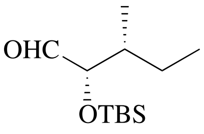
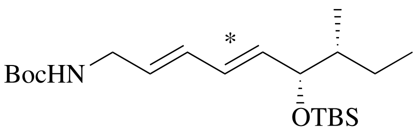
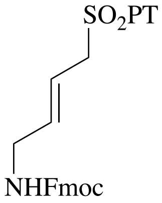
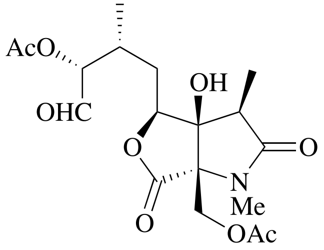
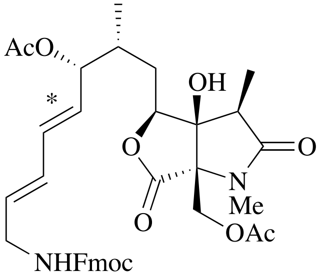
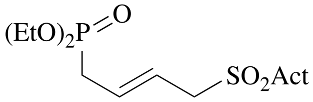
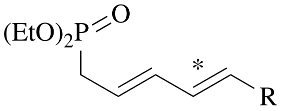
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	1. KHMDS (2.1 eq), 18-crown-6, THF, –78°, 30 min 2. Aldehyde, –78°; rt	 (93) $(E)/(Z)^* = 95:5$	478

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_4			1. NaHMDS, THF, –78°, 15 min 2. Aldehyde, –78°, 1 h		(77) (*E*)/(*Z*)* = 82:18	72
		RCHO	1. THF, KHMDS, –78°, 5 min 2. Aldehyde, –78°, 20 min; 0°, 1 h			112

	Act = PT		Act = BT	
R		(*E*)/(*Z*)*		(*E*)/(*Z*)*
Et	(75)	91:9	(81)	75:25
n-C_5H_{11}	(78)	>95:5		
$Ph(CH_2)_2$	(85)	90:10	(74)	78:22
i-Pr	(72)	89:11		
c-C_5H_9	(67)	95:5		
c-C_6H_{11}	(72)	91:9	(61)	86:14
t-Bu	(70)	>95:5		
(*E*)-PhCH=CH	(39)	62:38	(57)	68:32
$MeO_2C(CH_2)_7$	(70)	91:9		

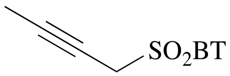
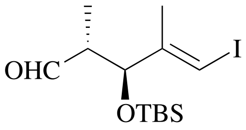
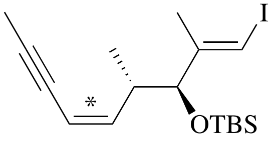
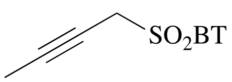
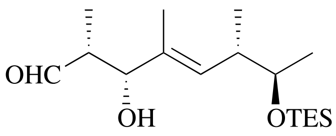
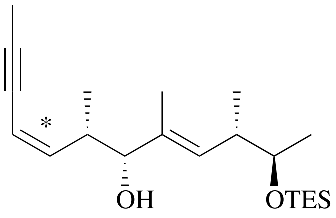
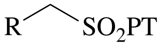
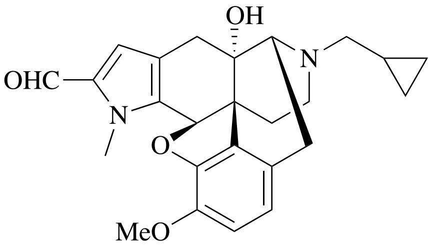
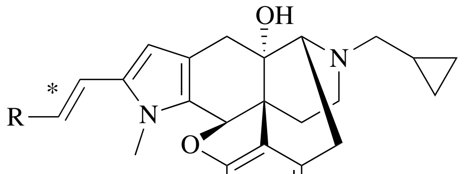
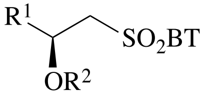
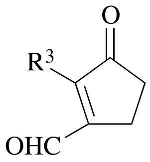
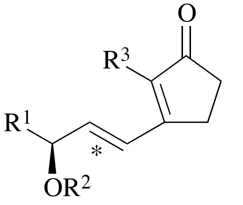
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. KHMDS, THF, –55°, 30 min 2. Aldehyde, –55°, 13 h		(56) (*E*)/(*Z*)* = 4:96	73

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

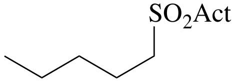
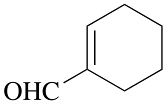
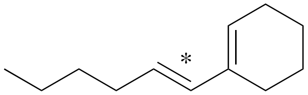
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4	 	KHMDS, THF, –55°	 (59) $(Z)^*$-isomer only	479
$C_{4\text{-}7}$	 	KHMDS, THF, –78° to rt		480
$C_{4\text{-}10}$	 	**A:** KHMDS, THF, –78°, 10 min; rt, 2 h *or* **B:** 1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78°; rt		481

R		$(E)/(Z)^*$
n-Pr	(86-91)	—
Ph	(86-91)	—

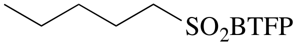
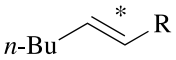
R^1	R^2	R^3			$(E)/(Z)^*$
Et	TBS	$MeO_2C(CH_2)_7$	A	(42)	86:14
n-C_5H_{11}	TBS	$MeO_2C(CH_2)_6$	A	(28)	86:14
$MeO_2C(CH_2)_7$	TBS	Et	A	(0)	—

R^1	R^2	R^3			$(E)/(Z)^*$
Et	*t*-Bu	$MeO_2C(CH_2)_7$	B	(61)	100:0
n-C_5H_{11}	*t*-Bu	$MeO_2C(CH_2)_6$	B	(52)	100:0
$MeO_2C(CH_2)_7$	*t*-Bu	Et	B	(65)	100:0

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	1. $MN(SiMe_3)_2$, temp, 30 min 2. Aldehyde, temp, 3 h; rt		20

			Act = BT		Act = PT	
Solvent	Temp	M		(*E*)/(*Z*)*		(*E*)/(*Z*)*
PhMe	–78°	Li	(15)	95:5	(74)	88:12
PhMe	–78°	Na	(43)	97:3	(81)	80:20
PhMe	–78°	K	(17)	>95:5	(41)	61:39
Et_2O	–78°	Li	(24)	99:1	(95)	89:11
Et_2O	–78°	Na	(48)	97:3	(82)	75:25
Et_2O	–78°	K	(60)	94:6	(69)	58:42
THF	–78°	Li	(35)	96:4	(91)	67:33
THF	–78°	Na	(13)	86:14	(99)	75:25
THF	–78°	K	(39)	79:21	(93)	66:34
DME	–60°	Li	(2)	—	(84)	84:16
DME	–60°	Na	(26)	77:23	(100)	88:12
DME	–60°	K	(35)	55:45	(64)	85:15

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 RCHO	1. Base, THF, temp 2. Aldehyde, 16 h		56

R	Base	Temp		(*E*)/(*Z*)*
Ph	KOH, *n*-Bu_4NBr	rt	(70)	67:33
Ph	P4-*t*-Bu	rt	(45)	75:25
(*E*)-PhCH=CH	KOH, *n*-Bu_4NBr	rt	(30)	12:88
(*E*)-PhCH=CH	P4-*t*-Bu	–78°	(28)	50:50

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

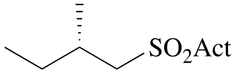
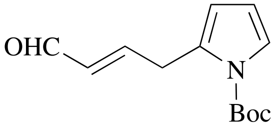
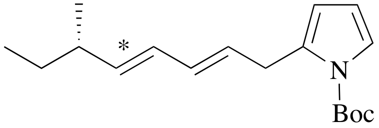
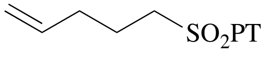
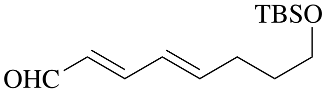
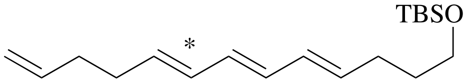
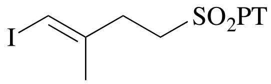
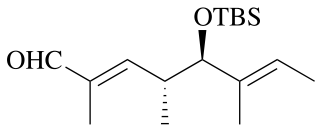
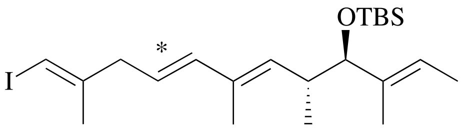
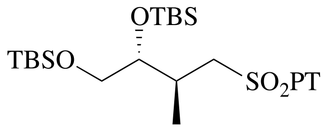
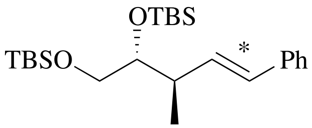
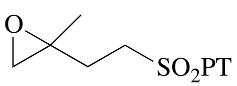
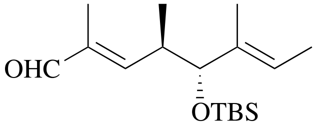
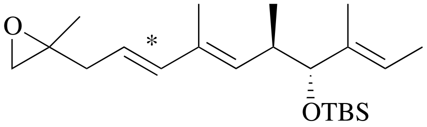
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	 	1. LDA, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 5 h	 Act (*E*)/(*Z*)* BT (—) 87:13 PT (58) 90:10	482
	 	KHMDS, THF, –78°	 (62) (*E*)/(*Z*)* = 90:10	483
	 	1. KHMDS, DME, –60°, 20 min 2. Aldehyde, –60°, 7 h; rt	 (60) (*E*)*-isomer only	484 485
	 PhCHO	1. KHMDS, DME, –55°, 40 min 2. Aldehyde, –55°, 1 h; rt, 1 h	 (70) (*E*)*-isomer only	486
	 	1. NaHMDS, DME, –78°; –60°, 30 min 2. Aldehyde, 0°, 18 h	 (83) (*E*)/(*Z*)* = 93:7	487 488

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

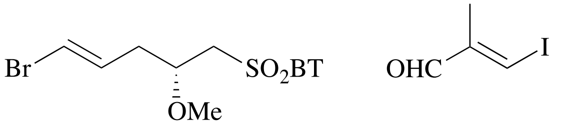
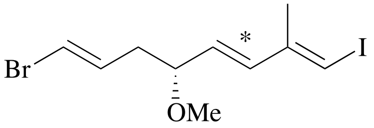
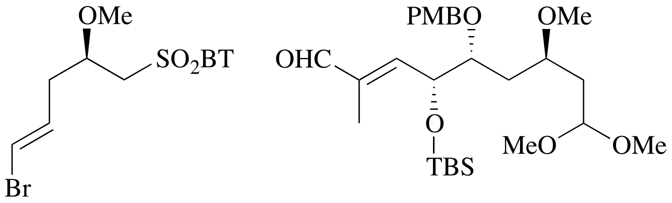
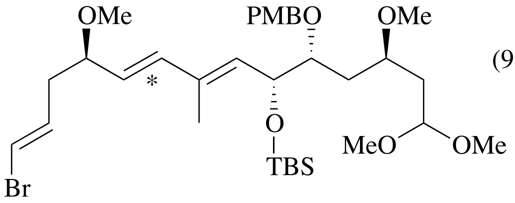
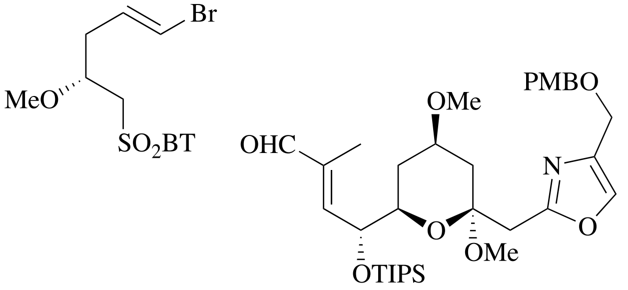
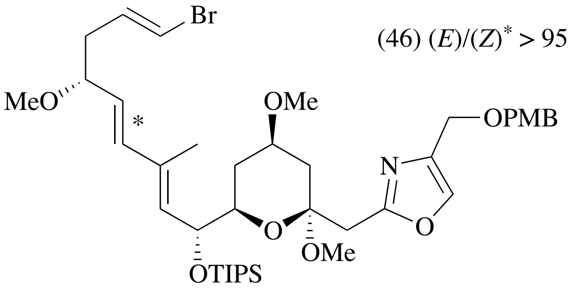
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		NaHMDS, THF, –78° to rt	 (75) (*E*)/(*Z*)* >95:5	489
		NaHMDS, THF, –78° to rt	 (93) (*E*)*-isomer only	490 491
		1. NaHMDS, THF, –78° 2. Aldehyde	 (46) (*E*)/(*Z*)* > 95:5	492

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

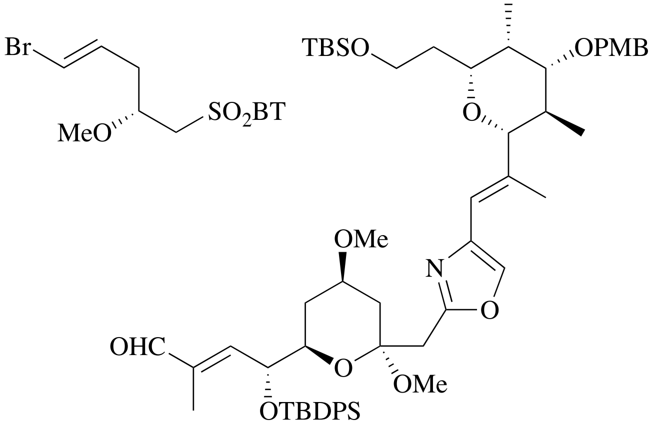
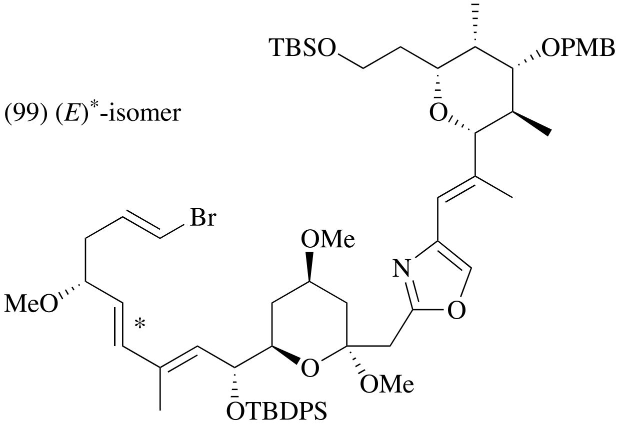
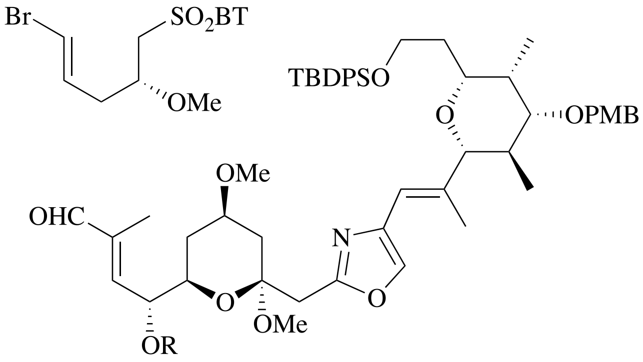
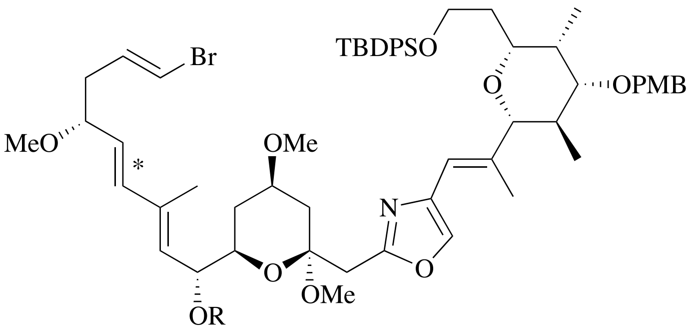
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		NaHMDS, THF, –78°, 30 min; 0°, 15 min; rt, 30 min	(99) $(E)^*$-isomer 	493 494
		NaHMDS, THF, –78°, 40 min	 R / / $(E)/(Z)^*$ TIPS (78) >95:5 TBDPS (86) 92:8	495 68

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

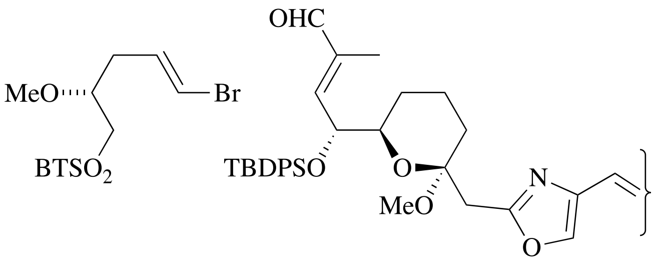
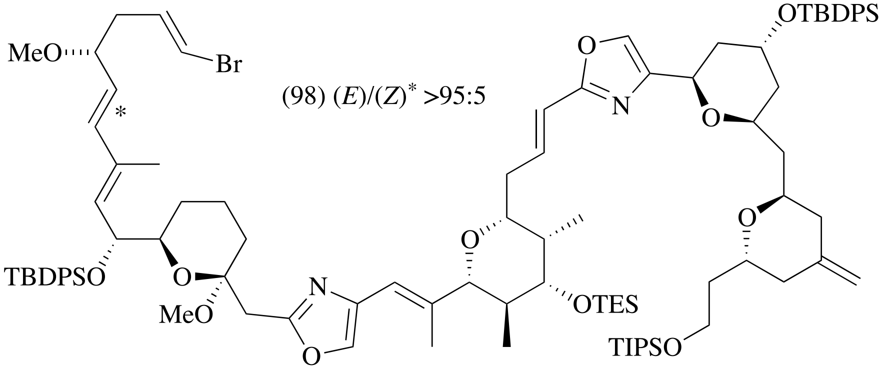
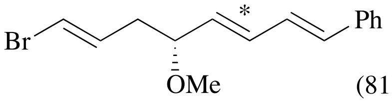
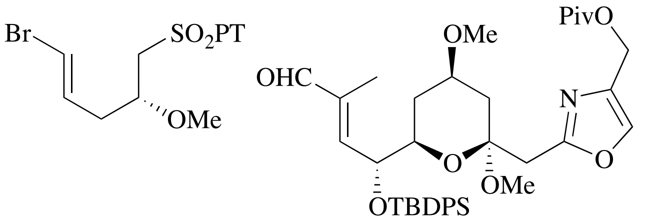
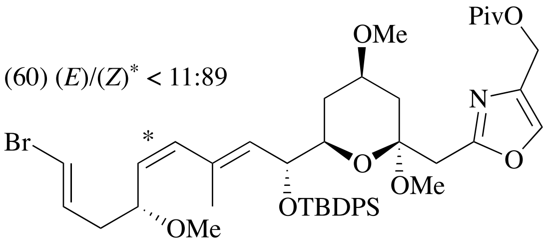
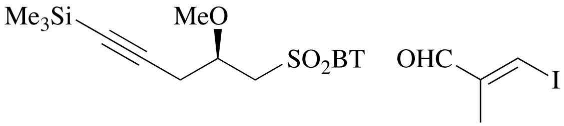
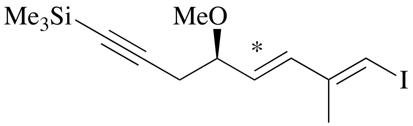
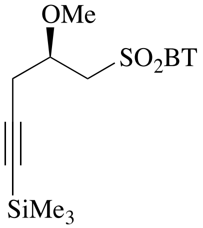
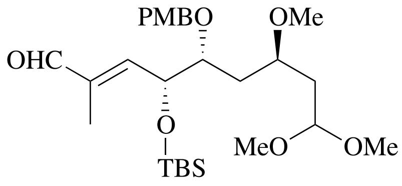
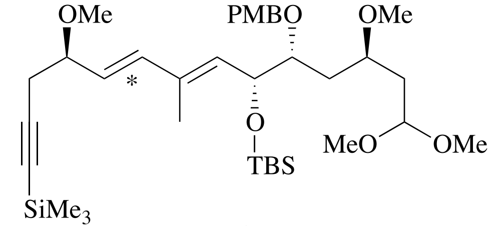
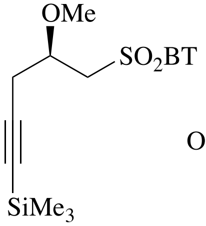
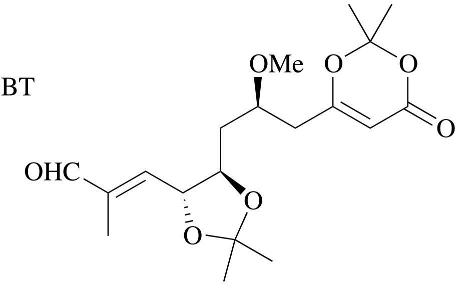
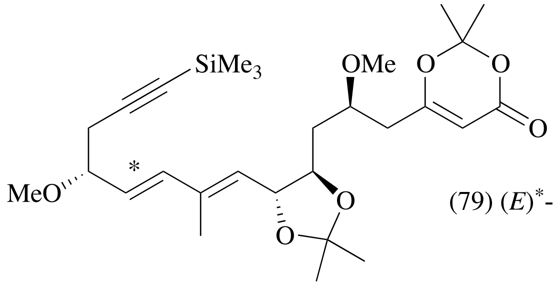
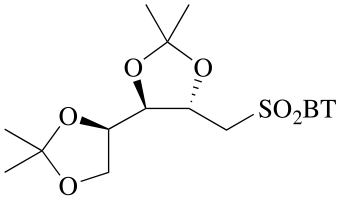
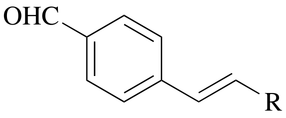
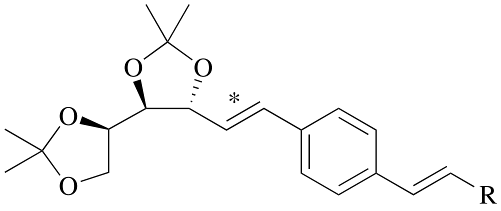
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		1. NaHMDS, THF, –78° 2. Aldehyde	 (98) $(E)/(Z)^*$ >95:5	496 497
		1. KHMDS, DME, –78° 2. Aldehyde	 (81) $(E)/(Z)^* = 89{:}11$	498
		1. KHMDS, DME, –78° 2. Aldehyde	(60) $(E)/(Z)^* < 11{:}89$ 	497
		NaHMDS, DMF, –60°, 1 h	 (90) $(E)/(Z) = 94{:}6$	499

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	 	NaHMDS, THF, –78°	 (74) $(E)^*$-isomer only	500 491
	 	1. NaHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 30 min; rt, 2 h	 (79) $(E)^*$-isomer	499
	 	1. NaH, DMF, 0°, 10 min 2. Aldehyde, 0°, 30 min; rt, 2 h		501

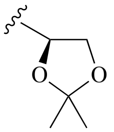
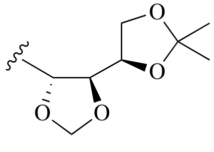
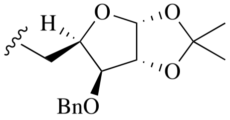
R		$(E)/(Z)^*$	R		$(E)/(Z)^*$	R		$(E)/(Z)^*$
	(62)	—		(65)	—		(82)	—

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

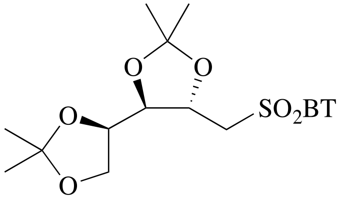
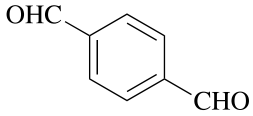
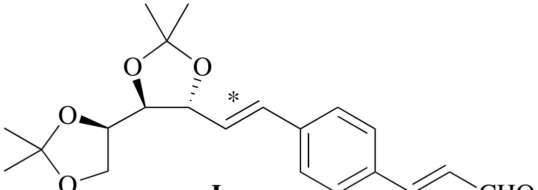
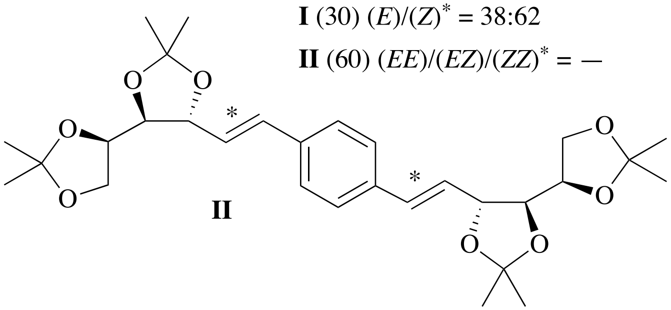
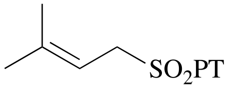
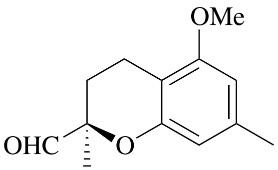
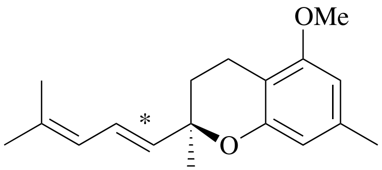
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	1. NaH, DMF, 0° 2. Aldehyde, 0°; rt, 24 h	 **I** **I** (30) $(E)/(Z)^*$ = 38:62 **II** (60) $(EE)/(EZ)/(ZZ)^*$ = —  **II**	501
	 	1. $MN(SiMe_3)_2$ 2. Aldehyde, –78°; rt	 M · Solvent · Temp · · $(E)/(Z)^*$ Li · DMF-HMPA · –35° · (88) · 83:17 Li · DMF-HMPA · –78° · (98) · 95:5 K · THF · –78° · (88) · 50:50	502

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

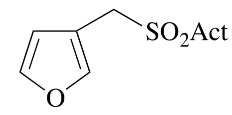
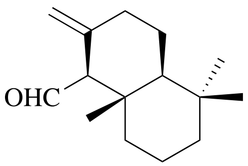
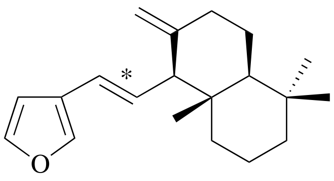
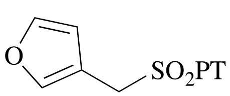
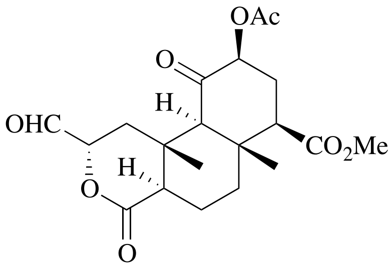
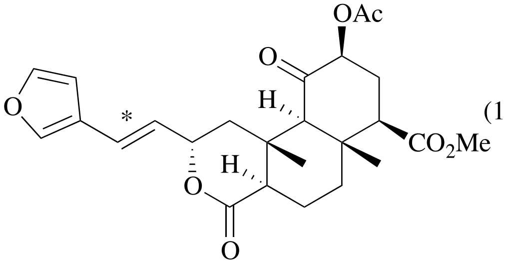
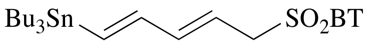
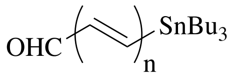
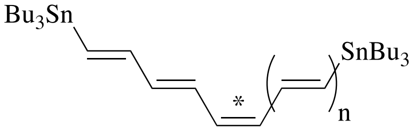
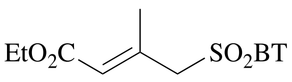
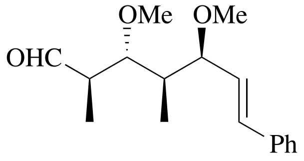
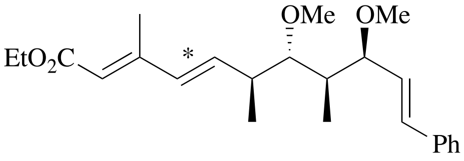
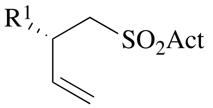
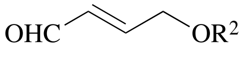
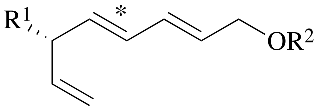
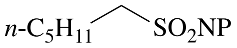
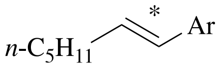
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	1. $MN(Si(CH_3)_3)_2$, –78°, 20 min 2. Aldehyde, –78°, 30 min	 Act M Solvent (E)/(Z)* BT Li THF (88) 87:13 BT Na THF (74) 88:12 BT K THF (75) 91:9 BT K DME (86) 97:3 PT K DME (73) 98:2	503
	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 2 h	 (12) (*E*)/(*Z*)* = 67:33	504
	 	KHMDS, THF, –78° to rt	 n (E)/(Z)* 1 (73) 5:95 2 (49) 5:95	75
	 	1. LiHMDS, THF, –78° 2. Aldehyde, –78°	 (56) (*E*)/(*Z*)* = —	505

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-6}				
	 	1. $MN(SiMe_3)_2$, solvent, –78° 2. Aldehyde; rt		47

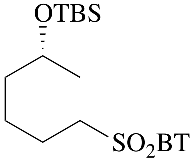
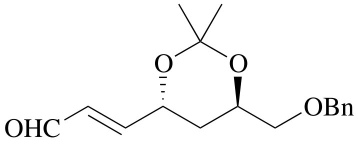
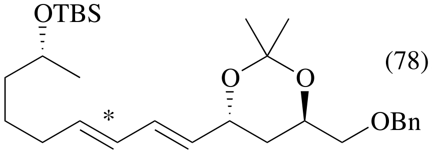
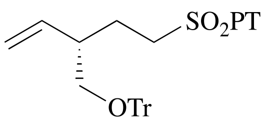
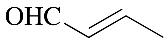
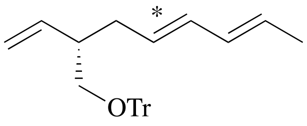
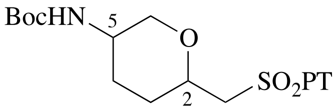
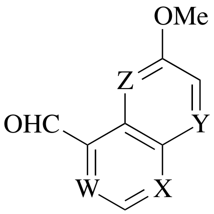
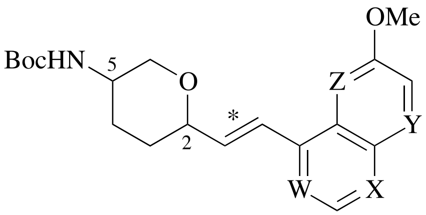
R^1	R^2	Act	M	Solvent	Eq. Aldehyde		$(E)/(Z)^*$
Me	TBDPS	PT	Li	DME	1.1	(82)	88:12
Et	TBDPS	PT	Li	DME	1.0	(97)	93:7
Me	PMB	PT	Li	DME	1.0	(71)	84:16
Me	PMB	PT	Li	DME	1.5	(88)	88:12
Et	PMB	PT	Li	DME	1.0	(93)	85:15
Et	PMB	BT	Li	DME	1.0	(83)	89:11
Me	TBDPS	PT	K	DME	1.0	(54)	90:10

R^1	R^2	Act	M	Solvent	Eq. Aldehyde		$(E)/(Z)^*$
Me	TBDPS	PT	K	THF	1.0	(55)	81:19
Me	TBDPS	BT	K	DME	1.1	(80)	—
Et	TBDPS	PT	K	DME	1.0	(54)	84:16
Me	PMB	PT	K	THF	1.1	(58)	69:31
Me	PMB	PT	K	DME	1.0	(47)	88:12
Me	PMB	BT	K	DME	1.1	(80)	—

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	 ArCHO	NaH, DMF, rt, 1 h		459

Ar		$(E)/(Z)^*$
Ph	(43)	94:6
4-ClC_6H_4	(68)	80:20
4-BrC_6H_4	(81)	82:18
4-$NO_2C_6H_4$	(64)	75:25
3-$NO_2C_6H_4$	(53)	77:23
2-$NO_2C_6H_4$	(64)	72:28
4-$MeOC_6H_4$	(78)	81:19
3,4-$(MeO)_2C_6H_3$	(82)	84:16
3,5-$(MeO)_2C_6H_3$	(89)	88:12
2,4,6-$(MeO)_3C_6H_2$	(54)	>99:1
3,4,5-$(MeO)_3C_6H_2$	(84)	85:15

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	 	NaHMDS, THF, –78°; rt, 30 min	 (78), (*E*)/(*Z*)* = 90:10	506
	 	**A**: 1. MN(SiMe$_3$)$_2$, DME, –78° 2. Aldehyde; rt *or* **B**: MN(SiMe$_3$)$_2$, DME, –78°; rt	 M (*E*)/(*Z*)* Li **A** (81) 80:20 K **B** (69) 94:6	67
	 	MN(SiMe$_3$)$_2$, DME, –60°, 30 min; rt, 45 min		507

C2	C5	M	W	X	Y	Z	Yield of (*E*)*-isomer
(*S*)	(*R*)	K	CH	N	CH	N	(68)
(*R*)	(*S*)	K	CH	N	CH	N	(75)
(*S*)	(*R*)	K	CH	CH	CH	N	(30)
(*S*)	(*R*)	Li	CH	CH	N	CH	(42)
(*S*)	(*R*)	Li	CF	N	CH	CH	(39)
(*S*)	(*R*)	Li	CF	CH	N	N	(52)
(*S*)	(*R*)	Li	CF	N	CH	N	(68)
(*S*)	(*R*)	—	CH	N	CF	CH	(74)
(*S*)	(*R*)	K	CH	N	CH	CH	(41)
(*S*)	(*R*)	Li	CH	CH	N	N	(57)

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

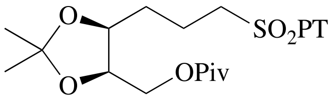
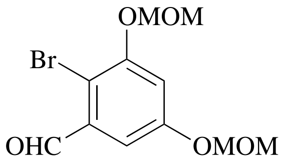
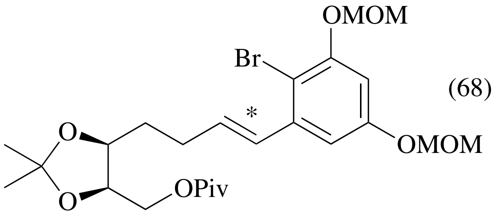
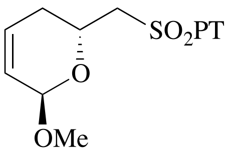
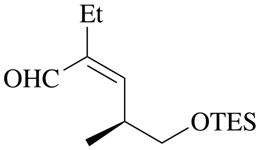
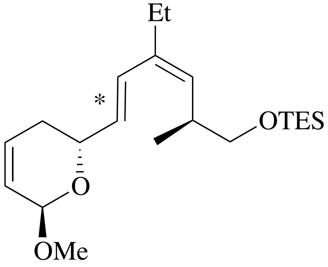
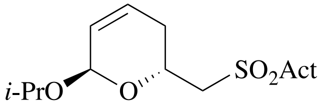
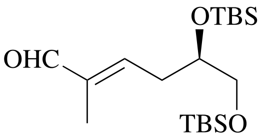
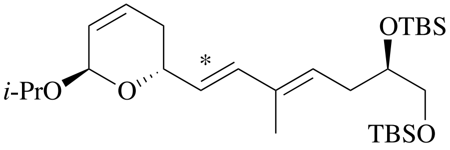
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	1. KHMDS, DME, –60°, 30 min 2. Aldehyde, –60°, 1 h; rt, 3 h	 (68) (*E*)/(*Z*)* = 96:4	244
	 	NaHMDS, DME-HMPA, –78°	 (35) (*E*)*-isomer only	508
	 	KHMDS, solvent, –78°, 4 h; rt	 Act / Solvent / / (*E*)/(*Z*)* BT / THF / (82) / 94:6 PT / DME / (76) / 88:12	509

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

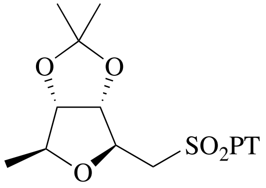
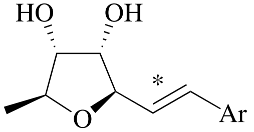
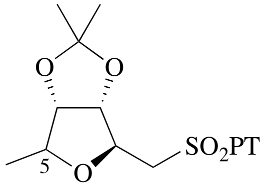
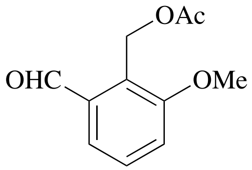
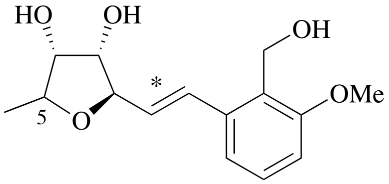
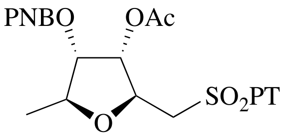
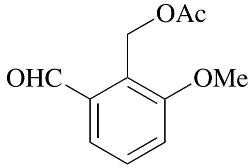
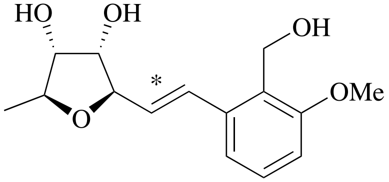
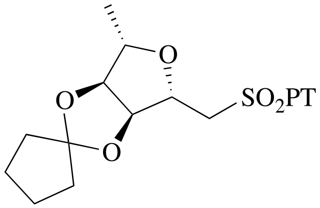
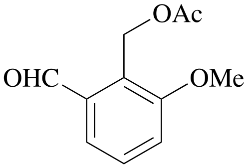
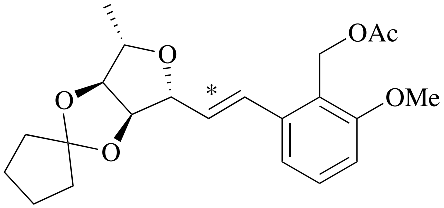
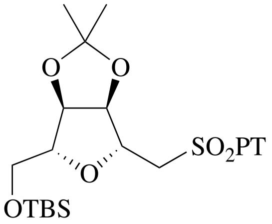
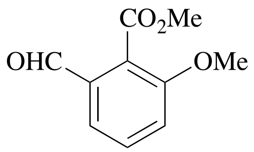
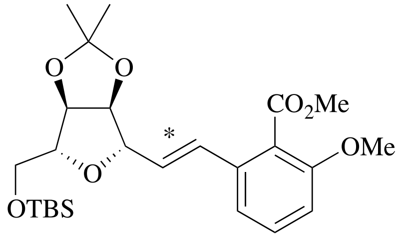
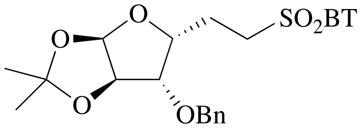
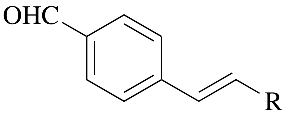
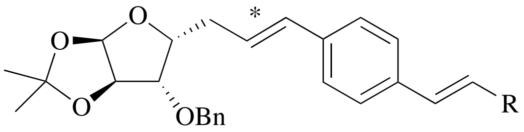
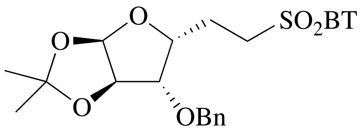
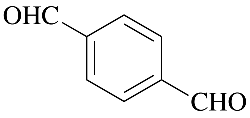
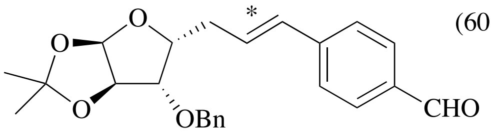
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_6		ArCHO	1. KHMDS, DME, –30° to rt, 12 h 2. aq. HCl, THF, rt		Ar (E)/(Z)* Ph (88) 60:40 4-$MeOC_6H_4$ (59) 69:31 2-$MeOC_6H_4$ (49) 61:39 2,4-$(MeO)_2C_6H_3$ (61) >99:1 2,5-$(MeO)_2C_6H_3$ (59) 90:10 2-$F_3CC_6H_4$ (41) >99:1 3-$F_3CC_6H_4$ (77) 48:52 4-BrC_6H_4 (98) 57:43 4-FC_6H_4 (42) 71:29 2-FC_6H_4 (43) 81:19	510
			1. KHMDS, DME, –30° to rt, 12 h 2. NaOMe, MeOH, rt, 4 h 3. aq. HCl, THF, rt, 5 h		C5 (E)/(Z)* (R) (78) 56:44 (S) (76) 74:26	511 510
			1. KHMDS, DME, –55° to rt, 10 h 2. NaOMe, MeOH, rt, 4 h		(63) (*E*)/(*Z*)* = —	512
			1. KHMDS, DMF-HMPA, –78°, 10 min 2. Aldehyde; rt, 12 h		(94) (*E*)*-isomer only	513

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	LiHMDS, DME, –78° to rt, 1 h	 (76) $(E)/(Z)^* = 65:35$	514
	 	1. NaH, DMF, 0°, 10 min 2. Aldehyde, 0°, 30 min; rt, 2 h		501
	 	1. NaH, DMF, 0° 2. Aldehyde, 0°; rt, 24 h	 (60) $(E)/(Z)^* = 25:75$	501

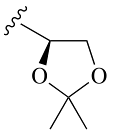
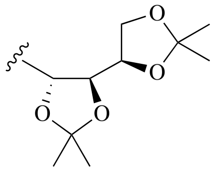
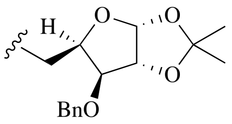
R		$(E)/(Z)^*$	R		$(E)/(Z)^*$	R		$(E)/(Z)^*$
	(62)	—		(65)	—		(80)	—

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

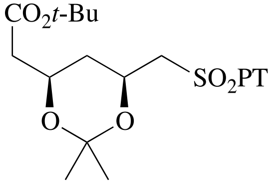
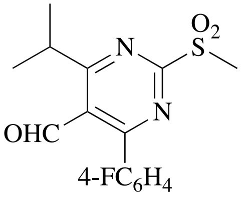
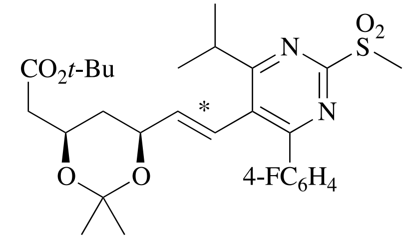
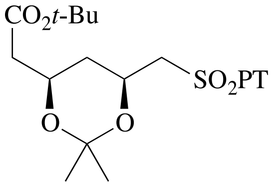
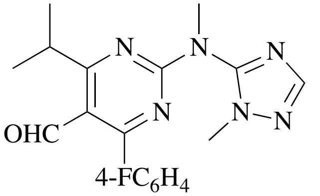
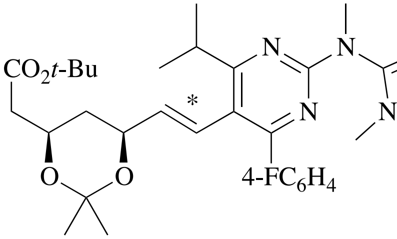
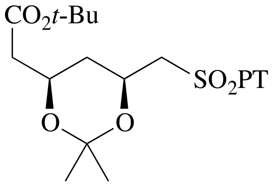
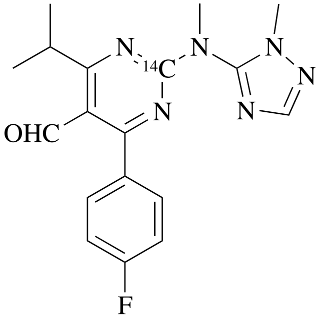
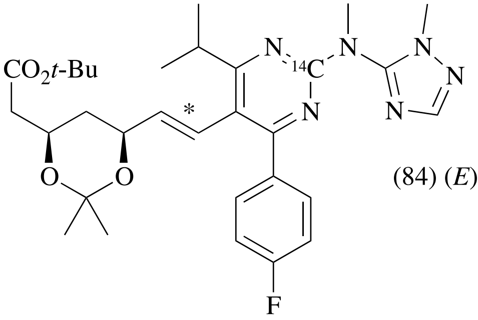
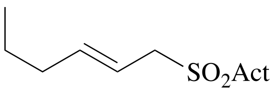
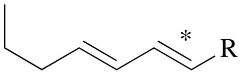
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			LiHMDS, THF, –60°, 15 min; rt	 (99) (*E*)/(*Z*)* = —	515
	 38.4 Kg (1.1 eq)	 27.5 Kg (1.0 eq)	LiHMDS (1.2 eq), THF, –80°, 1.3 h; –10°, 1 h	 (74) (*E*)/(*Z*)* = 99:1	70
			LiHMDS, THF, –78°, 30 min	 (84) (*E*)/(*Z*)* = 95:5	516

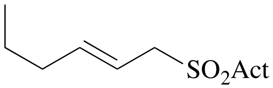
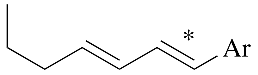
TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions		Product(s) and Yield(s) (%)	Refs.
C_6	 RCHO	**A**: KHMDS, THF, –78° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde	*or* **B**: KHMDS, DMF, –55° *or* **D**: 1. KHMDS, DMF-TDA1, –60°, 2 min 2. Aldehyde		31

		Act = PT		Act = BT	
R			(*E*)/(*Z*)*		(*E*)/(*Z*)*
$Ph(CH_2)_2$	A	(65)	71:29	(75)	58:42
$Ph(CH_2)_2$	B	(58)	40:60	(72)	55:45
$Ph(CH_2)_2$	C	(50)	16:84	(69)	20:80
$Ph(CH_2)_2$	D	(40)	13:87	(73)	17:83
$CH_3CH(OTBS)$	A	(59)	61:39	(68)	55:45
$CH_3CH(OTBS)$	B	(65)	70:30	(69)	60:40
$CH_3CH(OTBS)$	C	(58)	94:6	(65)	90:10
$CH_3CH(OTBS)$	D	(63)	96:4	(70)	91:9

		Act = PT	
R			(*E*)/(*Z*)*
c-C_6H_{11}	A	(73)	65:35
c-C_6H_{11}	B	(63)	51:49
c-C_6H_{11}	C	(59)	77:23
c-C_6H_{11}	D	(68)	82:18
$BnOCH_2$	A	(69)	55:45
$BnOCH_2$	B	(59)	66:34
$BnOCH_2$	C	(55)	75:25
$BnOCH_2$	D	(56)	74:26
$TBDPSOCH_2CH(OBn)$	A	(82)	62:38
$TBDPSOCH_2CH(OBn)$	B	(69)	54:46
$TBDPSOCH_2CH(OBn)$	C	(50)	83:17
$TBDPSOCH_2CH(OBn)$	D	(62)	82:18

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 ArCHO	**A**: KHMDS, THF, –78° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde *or* **B**: KHMDS, DMF, –55° *or* **D**: 1. KHMDS, DMF-TDA1, –60°, 2 min 2. Aldehyde		31

		Act = PT		Act = BT	
Ar			$(E)/(Z)^*$		$(E)/(Z)^*$
4-ClC_6H_4	A	(64)	55:45	(56)	49:51
4-ClC_6H_4	B	(55)	51:49	(49)	45:55
4-ClC_6H_4	C	(51)	76:24	(53)	72:28
4-ClC_6H_4	D	(58)	74:26	(55)	78:22
$4\text{-O}_2\text{NC}_6H_4$	A	(70)	56:44		
$4\text{-O}_2\text{NC}_6H_4$	B	(60)	48:52		
$4\text{-O}_2\text{NC}_6H_4$	C	(65)	86:14		
$4\text{-O}_2\text{NC}_6H_4$	D	(63)	89:11		

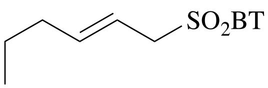
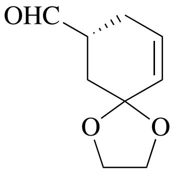
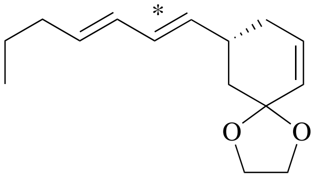
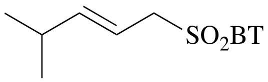
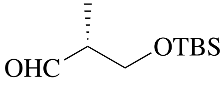
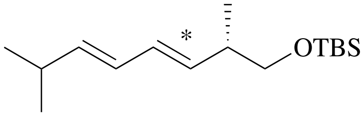
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	1. LiHMDS, –78°, 1 h 2. Aldehyde, 2 h	 (70) $(E)/(Z)^* = —$	517
	 	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt, 1 h	 (75) $(E)/(Z)^* = 80:20$	518

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

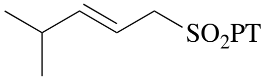
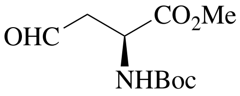
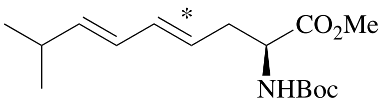
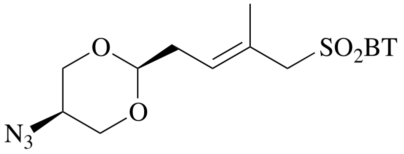
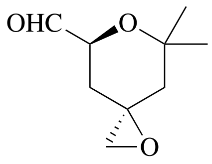
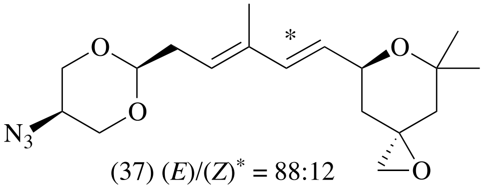
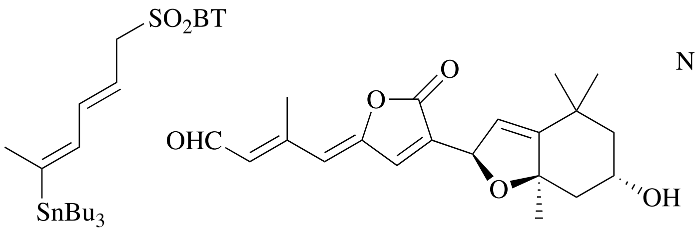
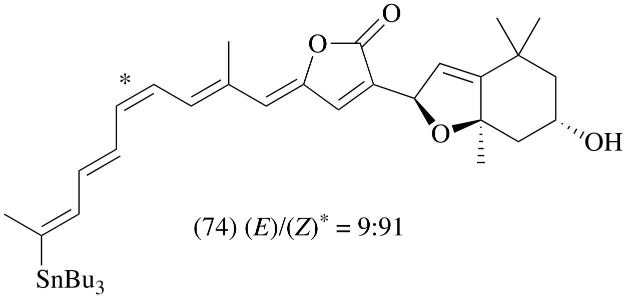
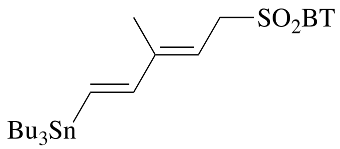
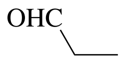
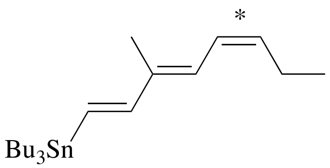
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	 	KHMDS, DMF-HMPA	 (>70) (*E*)/(*Z*)* = 80:20	519
	 	1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 1.5 h; rt, 12 h	 (37) (*E*)/(*Z*)* = 88:12	520
		NaHMDS, THF, –78°, 2 h	 (74) (*E*)/(*Z*)* = 9:91	80
	 	1. KHMDS, THF, –78°, 8 min 2. Aldehyde, –78° to rt, 4 h	 (58) (*E*)/(*Z*)* = 14:86	74

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

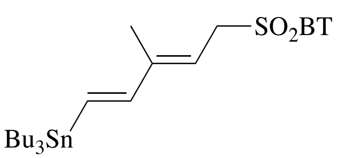
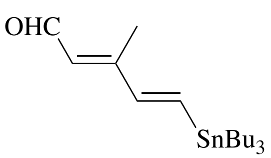
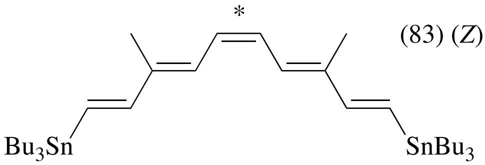
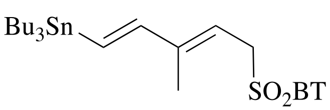
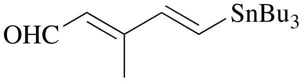
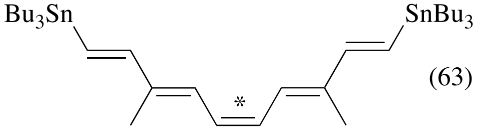
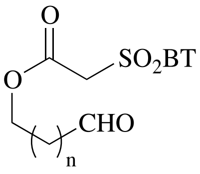
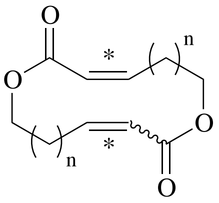
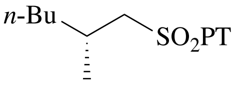
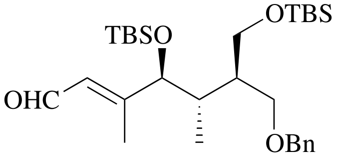
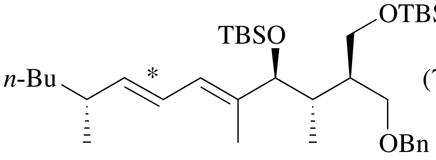
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6	 	1. NaHMDS, THF, –78° 2. Aldehyde, –78° to rt, 12 h	 (83) (*Z*)*-isomer only	521 522 74
	 	KHMDS, THF, –78° to rt	 (63) (*E*)/(*Z*)* = 6:94	75
C_{6-11}		syringe pump addition to DBU, CH_2Cl_2, temp to rt, 14-18 h	 n / Temp / / (*EZ*)/(*ZZ*)* 2 / –78° / (31) / 15:85 2 / rt / (27) / 11:89 3 / rt / (70) / 33:67 4 / rt / (13) / 37:63 5 / –78° / (44) / 35:65	146
C_7	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 17 h	 (73) (*E*)/(*Z*)* > 95:5	523

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

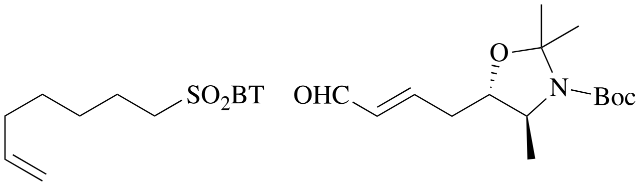
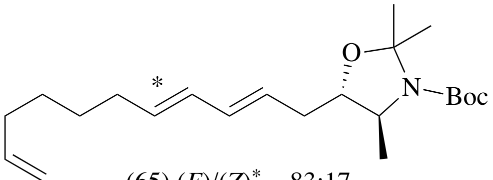
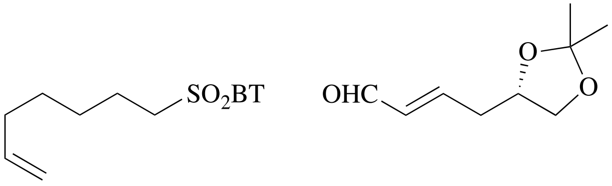
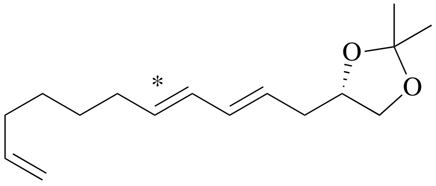
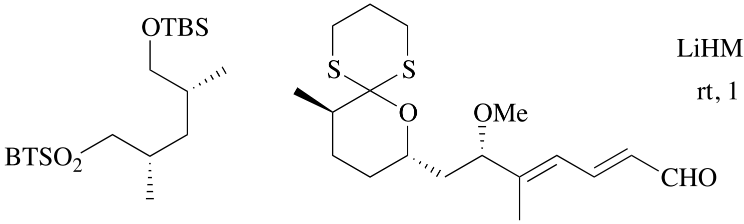
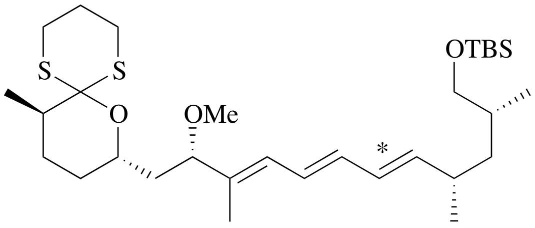
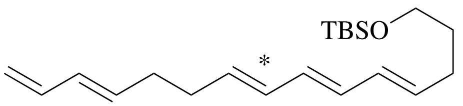
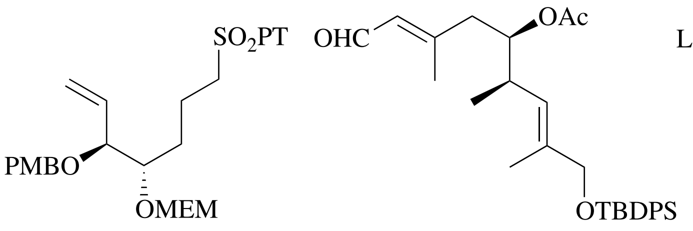
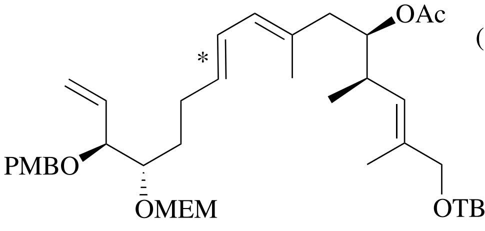
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		KHMDS, THF	 (65) (*E*)/(*Z*)* = 83:17	396
		KHMDS, THF	 (62) (*E*)/(*Z*)* —	524
		LiHMDS, THF, –80°, 3 h; rt, 1 h	 (68) (*E*)/(*Z*)* = 95:5	21
		KHMDS, THF, –78°	 (65) (*E*)/(*Z*)* = 90:10	483
		LiHMDS, THF, –78°, 1 h	 (60) (*E*)/(*Z*)* = 92:8	69

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

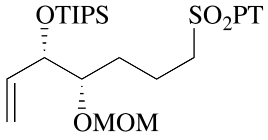
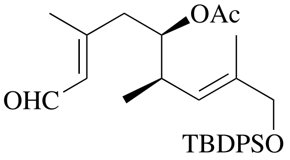
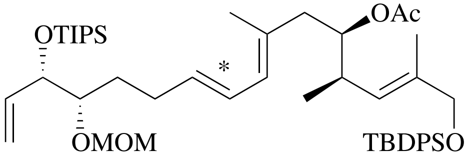
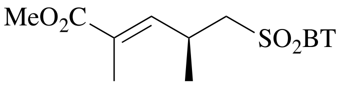
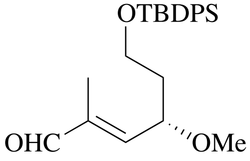
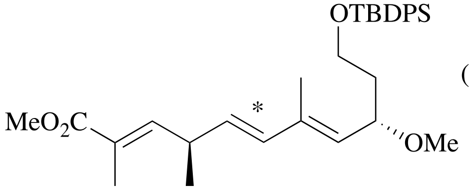
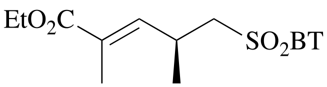
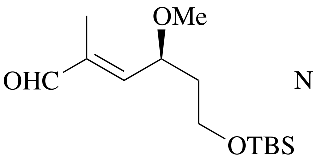
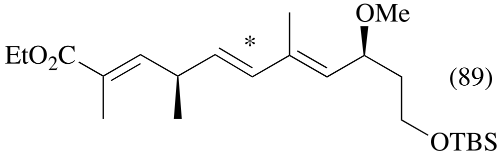
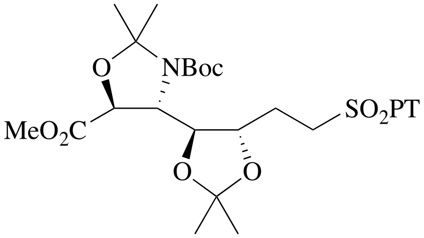
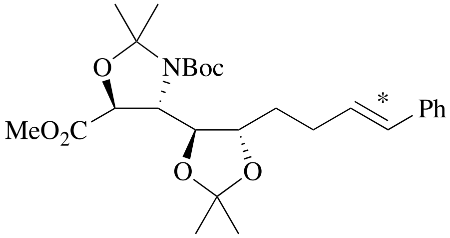
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7						
			LiHMDS, THF, –78°, 45 min		(80) (*E*)/(*Z*)* = 95:5	525 69
			LiHMDS, THF, –78°, 30 min; 23°, 2 h		(97) (*E*)/(*Z*)* = 96:4	526
			NaHMDS, THF, –78° to rt		(89) (*E*)/(*Z*)* = 80:20	527
		PhCHO	KHMDS, THF, –78°, 30 min		(28) (*E*)/(*Z*)* > 99:1	528

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

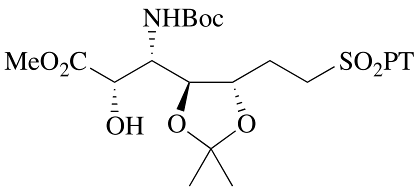
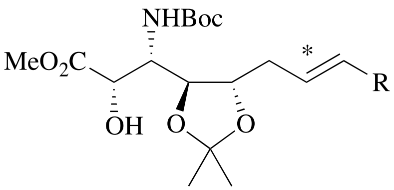
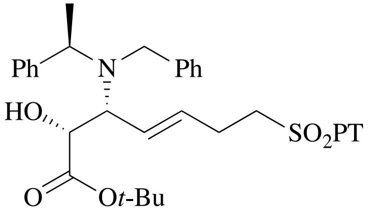
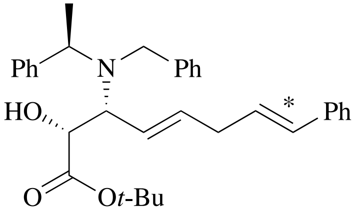
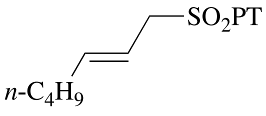
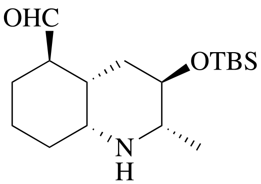
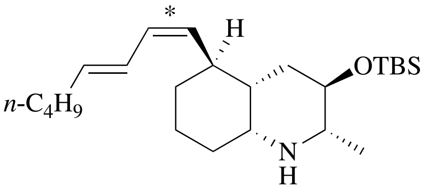
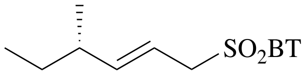
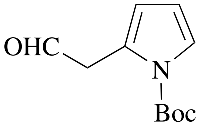
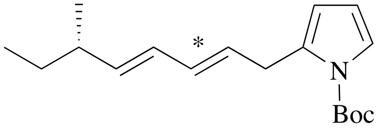
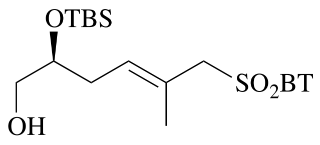
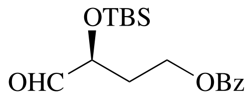
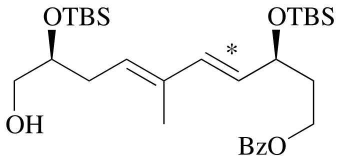
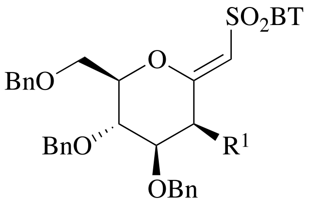
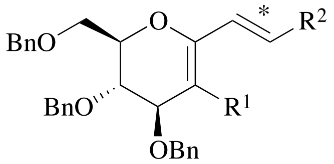
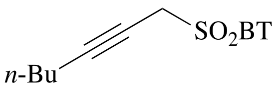
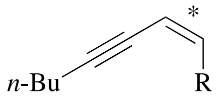
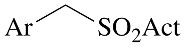
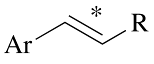
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7		RCHO	KHMDS, THF, –78°, 30 min	 R | | $(E)/(Z)^*$ Ph | (79) | — (E)-4-$EtOC_6H_4CH{=}CH$ | (23) | >99:1		528
		PhCHO	KHMDS, THF, –78°, 30 min		(66) $(E)^*$-isomer	528
			KHMDS		(90) $(Z)^*$-isomer only	299
			1. LDA, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 5 h		(—) $(E)/(Z)^*$ = 40:60	482

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7						
			1. LDA (2 eq), THF, –78°, 5 min 2. Aldehyde, –78° to rt, 3 h		(57) (*E*)*-isomer	529
		R^2CHO	LiHMDS, THF, –78°, 30 min; rt, 1 h		(*E*)*-isomer only throughout	530
	R^1 R^2		R^1 R^2	R^1 R^2		
	H Me (24)		H 2-furanyl (70)	H 2-naphthyl (54)		
	H 4-ClC_6H_4 (72)		H 3,4,5-$(MeO)_3C_6H_2$ (66)	H 2-9*H*-fluorenyl (50)		
	OBn 4-ClC_6H_4 (0)		H 2-pyridinyl (85)	H 2-pyrrolyl (65)		
	H 3-$MeOC_6H_4$ (64)		H 3-$MeOC_6H_4$ (66)			
		RCHO	**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt *or* **B**: LDA, THF, –78°, 3 h; rt, 1 h		R *n*-Bu **A** (27) 3:97 *n*-Bu **B** (37) 5:95 *n*-C_7H_{15} **A** (26) <1:99 *n*-C_7H_{15} **B** (22) <1:99 4-$MeOC_6H_4$ **A** (70) 16:84 4-$MeOC_6H_4$ **B** (59) 12:88 2-furyl **A** (32) <1:99	3

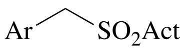
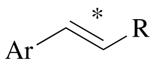
Column header of last sub-table: R — (*E*)/(*Z*)*

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		RCHO	**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt *or* **B**: LDA, THF, –78°, 3 h; rt, 1 h *or* **C**: 1. *n*-BuLi, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt		3

Ar	Act	R (alkyl)			$(E)/(Z)^*$	Ar	Act	R (alkyl)			$(E)/(Z)^*$
Ph	BT	n-C_8H_{17}	**A**	(81)	37:63	Ph	BT	*t*-Bu	**B**	(63)	>99:1
Ph	BT	n-C_8H_{17}	**B**	(80)	23:77	Ph	BT	c-C_6H_{11}	**A**	(78)	50:50
Ph	PYR	n-C_8H_{17}	**C**	(42)	10:90	Ph	BT	c-C_6H_{11}	**B**	(67)	60:40
Ph	PYM	n-C_8H_{17}	**C**	(74)	74:26	4-$MeOC_6H_4$	BT	Et	**A**	(73)	30:70
Ph	BT	*i*-Pr	**A**	(51)	90:10	4-$MeOC_6H_4$	PYR	Et	$\mathbf{A}^{a}$	(12)	12:82
Ph	BT	*i*-Pr	**B**	(69)	45:55	4-$MeOC_6H_4$	PYR	Et	$\mathbf{A}^{a,b}$	(18)	8:92

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7	 RCHO	**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt *or* **B**: LDA, THF, –78°, 3 h; rt, 1 h *or* **C**: 1. *n*-BuLi, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; rt		3

Ar	Act	R (α,β-unsat.)			$(E)/(Z)^*$
Ph	BT	PhC≡C	**A**	(82)	46:56
Ph	BT	Me_2C=CH	**A**	(53)	98:2
Ph	BT	Me_2C=CH	**B**	(70)	98:2
Ph	BT	CH_2=CMe	**A**	(93)	90:10
Ph	BT	CH_2=CMe	**B**	(73)	93:7
Ph	BT	1-cyclohexenyl	**A**	(30)	99:1
Ph	BT	1-cyclohexenyl	**B**	(71)	>99:1
Ph	BT	1-furyl	**A**	(64)	>99:1

Ar	Act	R (α,β-unsat.)			$(E)/(Z)^*$
Ph	BT	4-$MeOC_6H_4$	**A**	(57)	98:2
Ph	BT	4-MeC_6H_4	**A**	(74)	98:2
Ph	BT	4-ClC_6H_4	**A**	(69)	98:2
Ph	PYR	Ph	**C**	(76)	98:2
Ph	PYM	Ph	**A**	(75)	98:2
4-$MeOC_6H_4$	BT	Me_2C=CH	**A**	(61)	88:12
4-$MeOC_6H_4$	BT	Ph	**A**	(84)	97:3

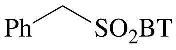
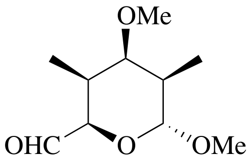
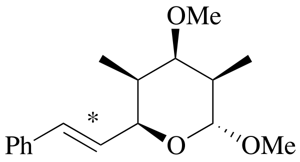
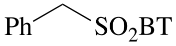
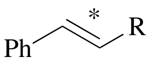
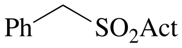
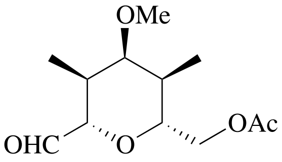
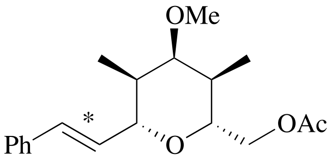
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	1. LiHMDS, THF, –78° 2. Aldehyde	 (>50) $(E)/(Z)^*$ = —	505

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

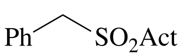
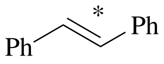
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7	 RCHO	**A**: KHMDS, THF, –78° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde *or* **B**: KHMDS, DMF, –55° *or* **D**: 1. KHMDS, DMF-TDA1, –60°, 2 min 2. Aldehyde		31
	 	MN(SiMe$_3$)$_2$, Solvent, Temp, 30 min; to 0°, 30 min		531

R			$(E)/(Z)^*$
Ph(CH$_2$)$_2$	A	(95)	48:52
Ph(CH$_2$)$_2$	B	(92)	42:58
Ph(CH$_2$)$_2$	C	(74)	15:85
Ph(CH$_2$)$_2$	D	(73)	14:86
BnOCH$_2$	A	(85)	42:58
BnOCH$_2$	B	(70)	32:68
BnOCH$_2$	C	(91)	81:19
BnOCH$_2$	D	(92)	83:17

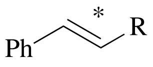
Act	M	Solvent	Temp		$(E)/(Z)^*$
BT	Na	THF	–78°	(85)	85:15
BT	Na	DME	–60°	(75)	81:19
BT	K	THF	–78°	(85)	86:14
BT	K	DME	–60°	(87)	87:13

Act	M	Solvent	Temp		$(E)/(Z)^*$
PT	Na	THF	–78°	(76)	81:19
PT	Na	DME	–60°	(87)	79:21
PT	K	THF	–78°	(72)	63:37
PT	K	DME	–60°	(72)	89:11

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

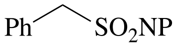
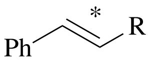
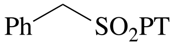
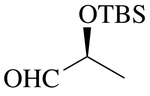
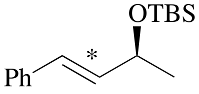
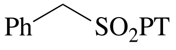
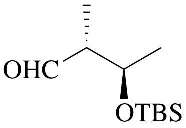
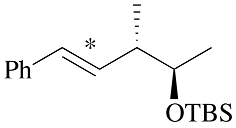
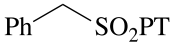
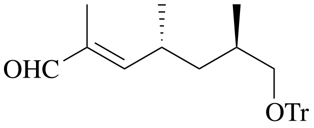
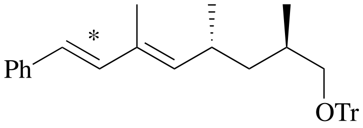
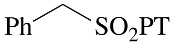
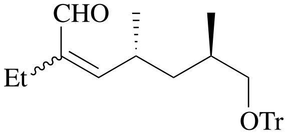
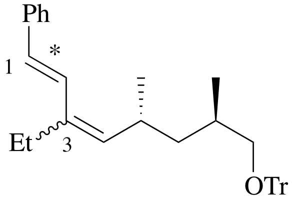
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 PhCHO	1. Base, solvent, temp 2. Aldehyde, 16 h		56

Base	Solvent	Temp	Act = BTFP	$(E)/(Z)^*$	Act = BT	$(E)/(Z)^*$	Act = PT	$(E)/(Z)^*$	Act = TBT	$(E)/(Z)^*$
KOH, n-Bu_4NBr	THF	rt	(78)	84:16	(45)	75:25	(50)	66:34	(53)	60:40
P4-t-Bu	THF	–78°	(65)	98:2	(55)	85:15	(30)	95:5	(35)	95:5
P4-t-Bu	THF-HMPA	–78°	(78)	95:5						
P2-Et	THF	–78°	(67)	97:3						
LDA	THF	–78°	(<5)	—						
KHMDS	DME	–60° to rt	(20)	99:1						
t-BuOK	THF	rt	(<5)	—						
DBU	CH_2Cl_2	rt	(<5)	—						

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 RCHO	1. Base, THF, temp 2. Aldehyde, 16 h		56

R	Base	Temp		$(E)/(Z)^*$
4-$MeOC_6H_4$	KOH, n-Bu_4NBr	rt	(52)	86:14
4-$MeOC_6H_4$	P4-t-Bu	–78°	(81)	94:6
4-$NO_2C_6H_4$	KOH, n-Bu_4NBr	rt	(12)	66:34
4-$NO_2C_6H_4$	P4-t-Bu	0°	(67)	40:60
c-C_6H_{11}	KOH, n-Bu_4NBr	rt	(14)	34:66
c-C_6H_{11}	P4-t-Bu	rt	(86)	50:50
c-C_6H_{11}	P2-Et	rt	(75)	25:75

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7						
		RCHO	NaH, DMF, rt, 1 h			459
			1. KHMDS, DME, –78°, 30 min 2. Aldehyde; rt		(73) $(E)/(Z)^*$ = 91:9	532
			1. KHMDS, THF, –78°, 30 min 2. Aldehyde; rt		(69) $(E)/(Z)^*$ = 54:46	181
			1. LiHMDS, THF, 0°, 20 min 2. Aldehyde, –78° to rt, 12 h		(80) $(E)/(Z)^*$ = 91:9	533 534
		 $(E)/(Z)$ = 17:83	1. LiHMDS, THF, 0°, 20 min 2. Aldehyde, –78° to rt, 12 h		(78) $(1E,3Z)/(1E,3E)/(1Z,3Z)/(1Z,3E)$ = 72:15:10:3	534

R		$(E)/(Z)^*$	R		$(E)/(Z)^*$	R		$(E)/(Z)^*$
Ph	(73)	63:37	$2\text{-}NO_2C_6H_4$	(85)	50:50	$3,4\text{-}(MeO)_2C_6H_3$	(92)	61:39
$4\text{-}ClC_6H_4$	(78)	54:46	2-Me	(97)	55:45	$3,5\text{-}(MeO)_2C_6H_3$	(92)	65:35
$4\text{-}BrC_6H_4$	(47)	56:44	$2\text{-}Cl\text{-}5\text{-}NO_2C_6H_3$	(87)	81:19	$2,4,6\text{-}(MeO)_3C_6H_2$	(97)	>99:1
$4\text{-}NO_2C_6H_4$	(97)	70:30	$4\text{-}(Me_2N)C_6H_4$	(88)	58:42	$3,4,5\text{-}(MeO)_3C_6H_2$	(92)	74:26
$3\text{-}NO_2C_6H_4$	(94)	51:49	$4\text{-}MeOC_6H_4$	(78)	53:47	(*E*)-PhCH=CH	(77)	—

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

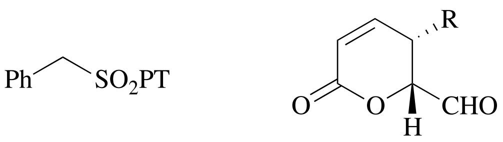
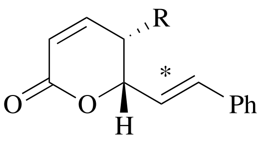
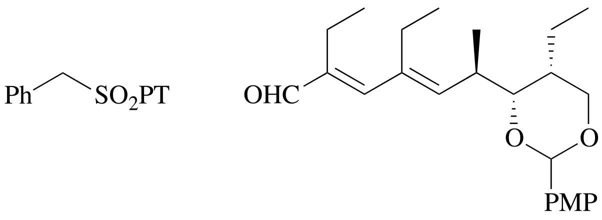
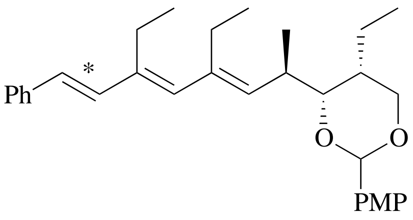
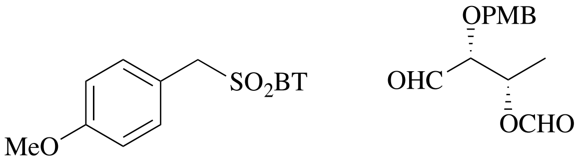
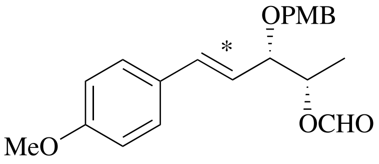
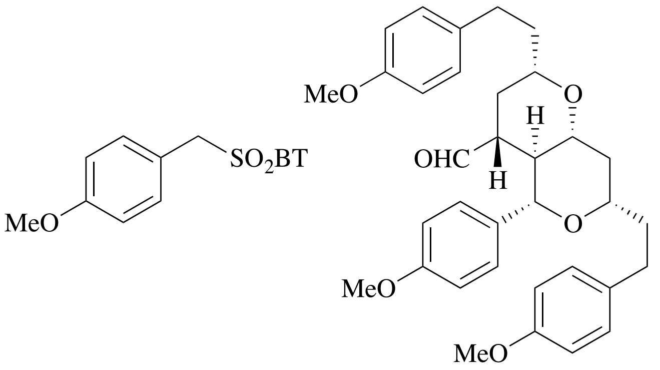
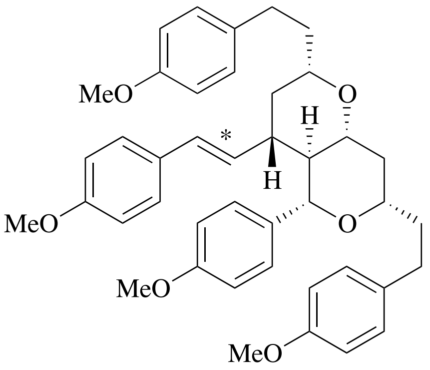
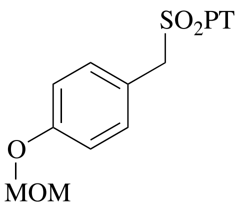
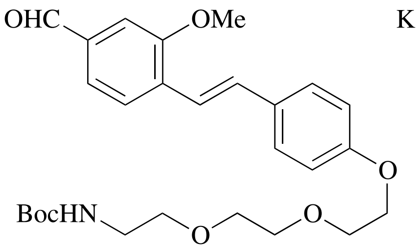
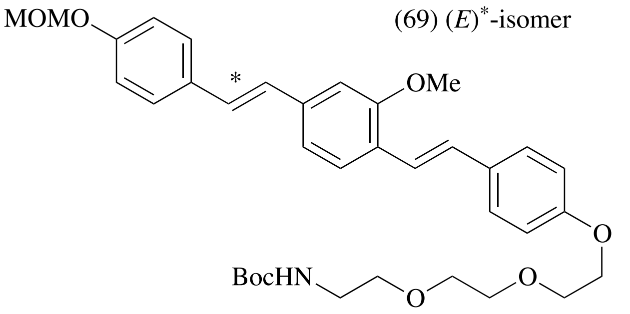
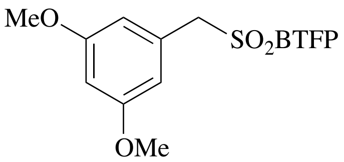
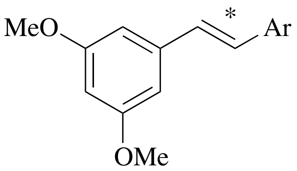
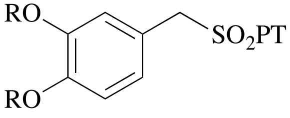
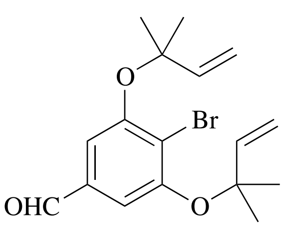
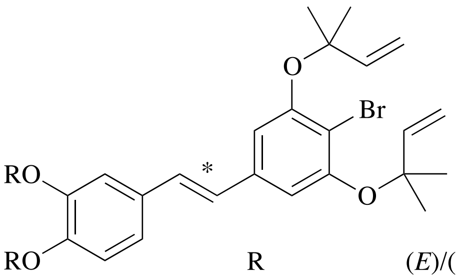
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. KHMDS, THF, 0° to rt, 20 min 2. Aldehyde, –78°, 3 h; rt, 8 h	 R (E)/(Z)* OTBS (40) > 93:7 H (20) —	535 536 537
		LiHMDS, THF	 (82) (E)*-isomer	538
		1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt, 3 h	 (>72) (E)/(Z)* = —	539 540
		1. LiHMDS, THF, –78°, 20 min 2. Aldehyde, 3 h, –78°; rt, 3 h	 (77) (E)/(Z)* = 98:2	541 542

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 	KHMDS, DMF-DMPU, –65° to rt, 12 h	 (69) (*E*)*-isomer	543
	 ArCHO	**A**: KOH, *n*-Bu$_4$NBr, THF, rt, 16 h *or* **B**: P4-*t*-Bu, THF-HMPA, –78°, 16 h		56

Ar			(*E*)/(*Z*)*
4-MeOC$_6$H$_4$	**A**	(81)	75:25
4-MeOC$_6$H$_4$	**B**	(74)	98:2
2,4-(MeO)$_2$C$_6$H$_3$	**A**	(35)	86:14
3,4-(MeO)$_2$C$_6$H$_3$	**A**	(40)	86:14
3,5-(MeO)$_2$C$_6$H$_3$	**A**	(32)	85:15

Ar			(*E*)/(*Z*)*
3,4,5-(MeO)$_3$C$_6$H$_2$	**A**	(26)	96:4
2-thienyl	**A**	(55)	87:13
2-thienyl	**B**	(73)	90:10
3-furyl	**A**	(40)	71:29
4-pyridyl	**A**	(60)	75:25

	 	1. KHMDS, THF, –78°, 30 min 2. Aldehyde, –78 to 23°, 3 h		544

R		(*E*)/(*Z*)*
Boc	(80)	100:0
TBS	(95)	67:33

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

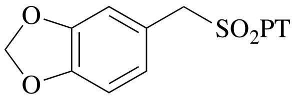
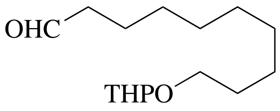
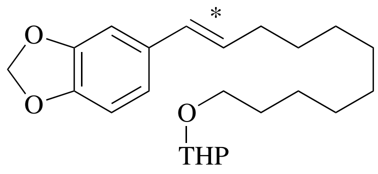
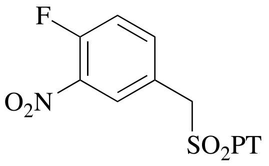
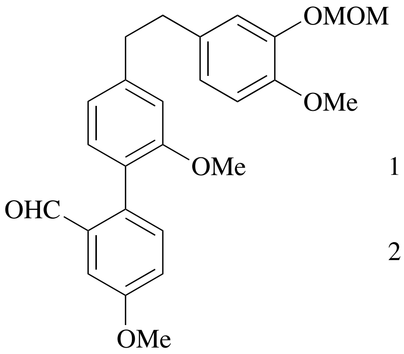
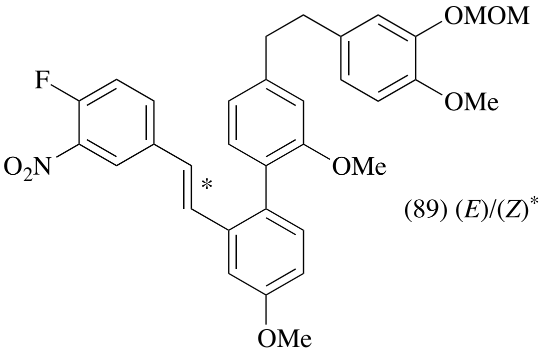
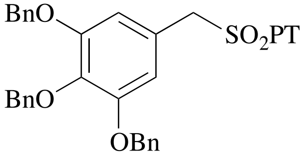
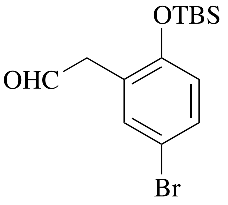
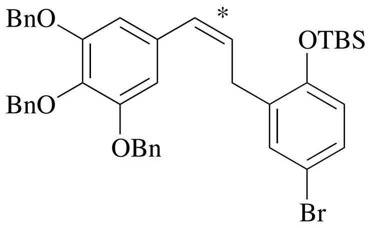
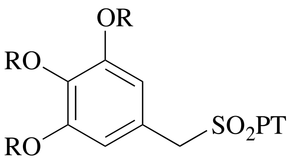
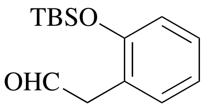
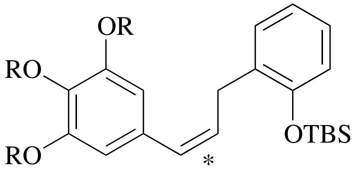
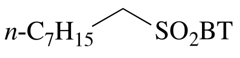
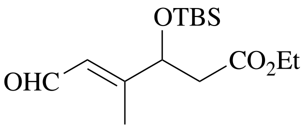
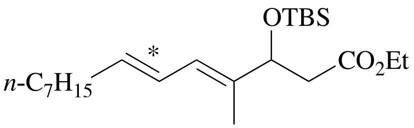
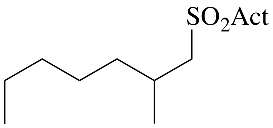
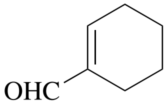
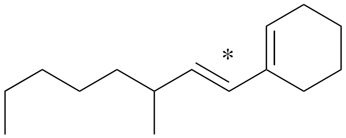
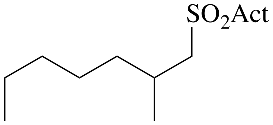
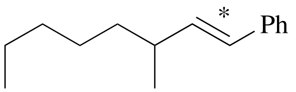
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7						
			LiHMDS, THF, –78° to rt, 12 h		(70) (*E*)/(*Z*)* = —	545
			1. LiHMDS, THF, –78 to 0°, 30 min 2. Aldehyde, THF, –78 to 0°, 3 h		(89) (*E*)/(*Z*)* = 94:6	546
			1. LiHMDS, THF, 0°, 30 min 2. Aldehyde, 2 h		(87) (*Z*)*-isomer only	547
			LiHMDS, THF		R — (*E*)/(*Z*)* Bn (95) 0:100 TBS (75) 9:91 Ms (12) 50:50	548

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

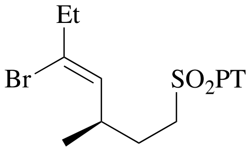
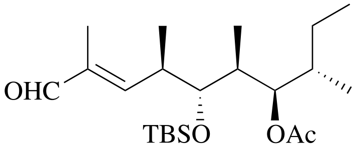
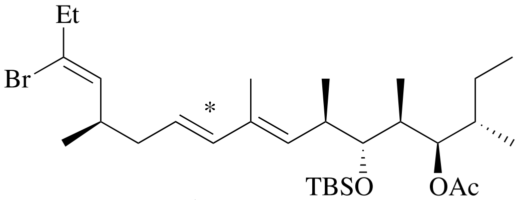
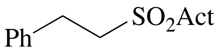
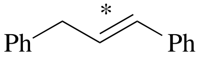
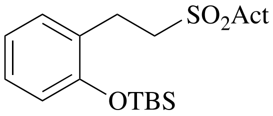
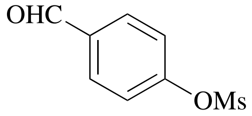
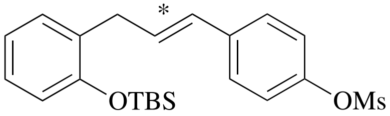
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_8			KHMDS, THF, –78°; rt, 2 h		(72) $(E)/(Z)^*$ = 94:6	35
			1. $MN(SiMe_3)_2$, temp, 30 min 2. Aldehyde, temp, 3 h; rt			20

Solvent	Temp	M	Act = BT		Act = PT	
				$(E)/(Z)^*$		$(E)/(Z)^*$
PhMe	–78°	Li	(69)	98:2	(71)	94:6
PhMe	–78°	Na	(98)	97:3	(90)	82:18
PhMe	–78°	K	(70)	97:3	(27)	55:45
Et_2O	–78°	Li	(16)	97:3	(79)	95:5
Et_2O	–78°	Na	(89)	97:3	(85)	79:21
Et_2O	–78°	K	(88)	96:4	(31)	50:50
THF	–78°	Li	(96)	>99:1	(100)	98:2
THF	–78°	Na	(96)	94:6	(78)	85:15
THF	–78°	K	(76)	86:14	(44)	58:42
DME	–60°	Li	(93)	>99:1	(83)	99:1
DME	–60°	Na	(100)	91:9	(48)	92:8
DME	–60°	K	(94)	72:28	(38)	81:19

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
		PhCHO	LDA, THF, –78°, 1 h; rt, 3 h		20

Act		$(E)/(Z)^*$
BT	(39)	>99:1
TZ	(39)	62:38
IQ	(39)	96:4
PT	(90)	>99:1

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 	KHMDS, DME, –60°	 (54) (*E*)/(*Z*)* = 88:12	549
	 PhCHO	Barbier conditions. See table.		550
	 	**A**: LiHMDS, THF, –78° *or* **B**: DBU, LiCl, MeCN, 0°		550

			Act = p-NPT		Act = m-NPT	
Base	Solvent	Temp		(*E*)/(*Z*)*		(*E*)/(*Z*)*
LiHMDS	THF	–78°	(46)	95:5	(76)	96:4
Cs_2CO_3	MeCN	rt	(37)	91:9	(41)	90:10
DBU	MeCN	0°	(<5)	83:17	(50)	91:9
DBU, LiCl	MeCN	0°	(28)	90:10	(86)	88:12
DBU, NaI	MeCN	0°	(—)	—	(77)	96:4

Act			(*E*)/(*Z*)*
PT	**A**	(46)	–
m-NPT	**B**	(79)	–

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

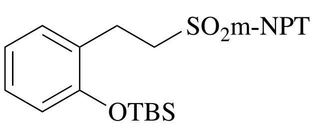
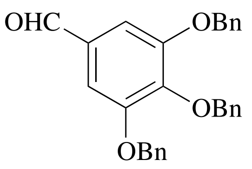
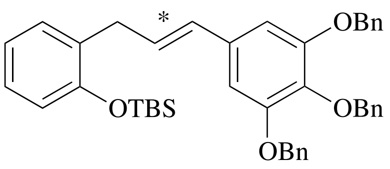
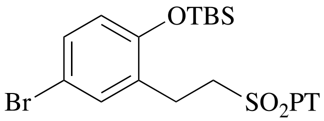
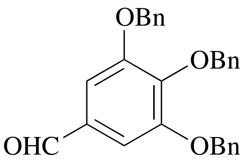
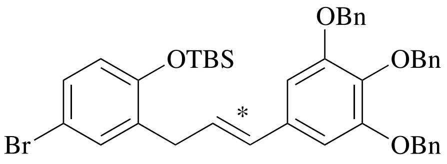
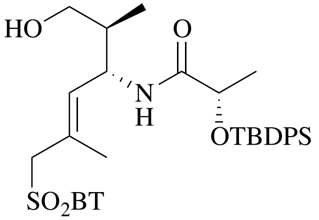
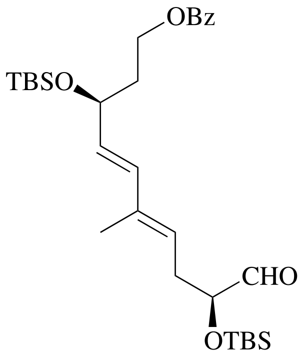
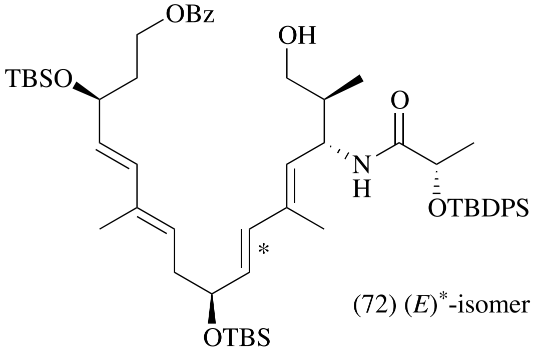
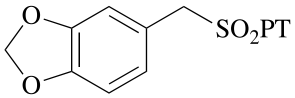
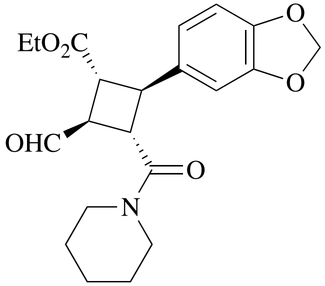
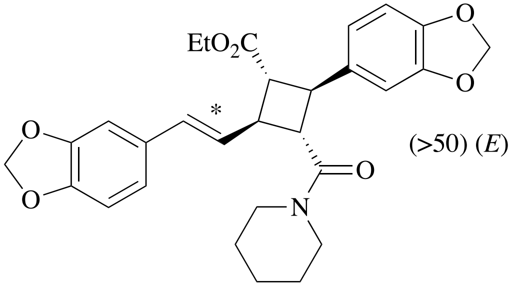
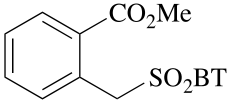
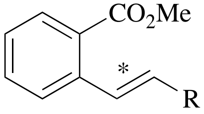
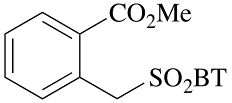
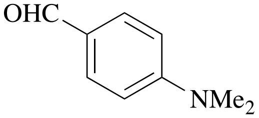
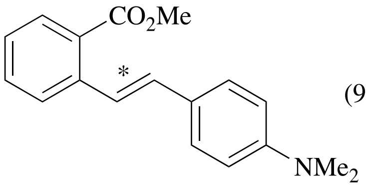
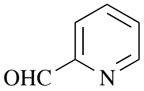
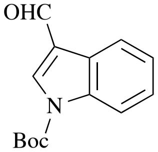
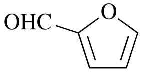
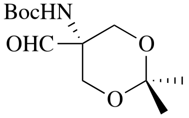
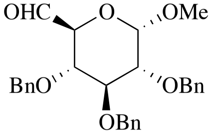
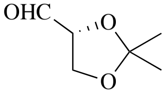
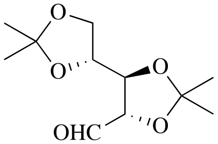
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 	DBU, LiCl, MeCN, 0°	 (81) (*E*)/(*Z*)* = 96:4	550
	 	1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, 2 h	 (96) (*E*)*-isomer only	547
	 	1. LDA (2 eq), THF, –78°, 5 min 2. Aldehyde, –78° to rt	 (72) (*E*)*-isomer	529
	 	KHMDS, DMF-HMPA, –35° to rt, 6 h	 (>50) (*E*)/(*Z*)* = 100:0	551

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_8		RCHO	**A**: K_2CO_3, DMF, 70°, 12 h *or* **B**: 1. NaH, DMF, 0°, 10 min 2. Aldehyde; rt, 1 h			552
			K_2CO_3, DMF, 70°, 12 h		(90) $(E)^*$-isomer only	553

RCHO			$(E)/(Z)^*$
	**A**	(87)	100:0
	**A**	(75)	80:20
	**A**	(79)	80:20
$2\text{-}NO_2C_6H_4CHO$	**A**	(80)	100:0
$2,4,6\text{-}(MeO)_3C_6H_2CHO$	**A**	(75)	80:20
$2\text{-}ClC_6H_4CHO$	**A**	(86)	96:4
EtCHO	**A**	(84)	50:50

RCHO			$(E)/(Z)^*$
	**A**	(80)	100:0
	**B**	(50)	100:0
	**B**	(65)	83:17
	**B**	(64)	94:6

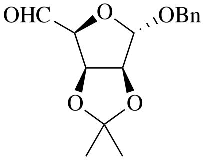
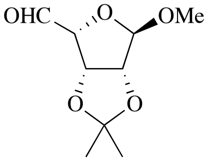
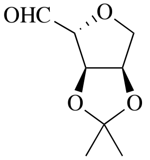
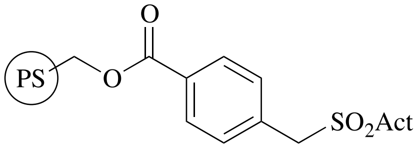
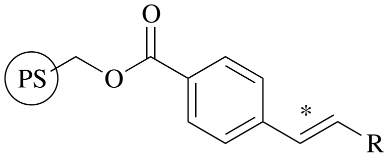
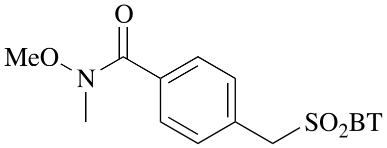
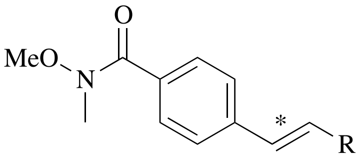
RCHO			$(E)/(Z)^*$
	**B**	(65)	86:14
	**B**	(56)	100:0
	**B**	(75)	100:0

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 RCHO PS = polymer support	1. DBU, CH_2Cl_2, rt, 15 min 2. Aldehyde, rt, 24 h		554

Act	R		$(E)/(Z)^*$
BT	Ph	(64)	100:0
BT	4-BrC_6H_4	(77)	—
BT	4-ClC_6H_4	(66)	—
BT	4-$NO_2C_6H_4$	(50)	67:33
BT	4-$NMe_2C_6H_4$	(40)	—
BT	4-MeC_6H_4	(32)	80:20
BT	4-$MeOC_6H_4$	(10)	—
BT	2-BrC_6H_4	(0)	—

Act	R		$(E)/(Z)^*$
BT	(*E*)-PhCH=CH	(70)	57:43
BT	$(Ph)_2C$=CH	(58)	50:50
BT	*c*-C_6H_{11}	(60)	—
BT	Bn	(40)	50:50
PT	4-BrC_6H_4	(50)	—
PT	4-$MeOC_6H_4$	(15)	—
PT	*c*-C_6H_{11}	(70)	—
PT	Bn	(50)	100:0

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 RCHO	K_2CO_3, 70°, 17 h		555

R	Solvent		$(E)/(Z)^*$
Ph	THF-DMF	(72)	67:33
4-$CHOC_6H_4$	THF-DMF	(57)	90:10
2-$NO_2C_6H_4$	THF-DMF	(70)	90:10
3,4-$(MeO)_2C_6H_3$	THF-DMF	(66)	75:25
2-furanyl	THF-DMF	(75)	55:45
n-C_3H_7	THF-DMF	(78)	67:33
N-Boc-3-indolyl	THF-DMF	(56)	60:40

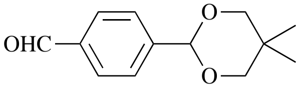
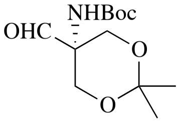
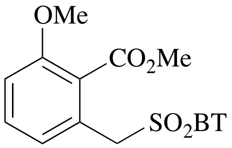
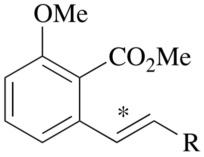
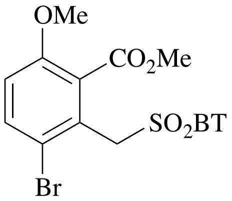
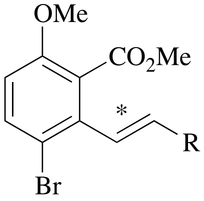
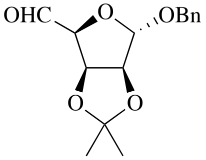
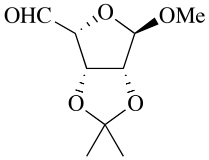
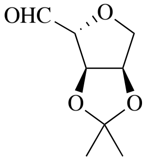
RCHO	Solvent		$(E)/(Z)^*$
	THF-DMF	(64)	75:25
	THF-DMF	(55)	—
	DMF	(70)	100:0

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 RCHO	1. NaH, DMF, 0°, 10 min 2. Aldehyde; rt, 1 h		552
	 RCHO	1. NaH, DMF, 0°, 10 min 2. Aldehyde; rt, 1 h		552

RCHO		$(E)/(Z)^*$
	(70)	80:20
	(77)	90:10
	(67)	100:0

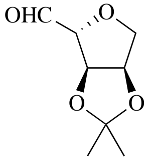
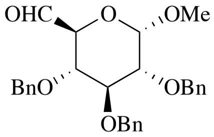
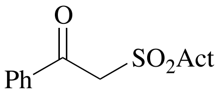
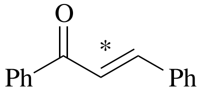
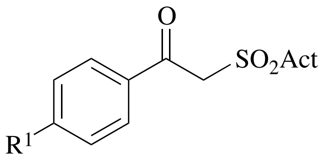
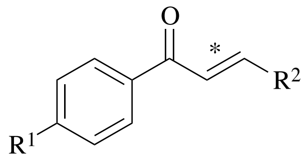
RCHO		$(E)/(Z)^*$
	(54)	100:0
	(77)	100:0

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 PhCHO	1. Base, solvent, temp 2. Aldehyde, time. See table.		82

Act	Base	Solvents	Temp	Time		(*E*)/(*Z*)*
BT	LiHMDS	THF	0°	14 h	(36)	98:2
BT	P_4-*t*-Bu	THF	0°	16 h	(37)	95:5
BT	DBU	THF	0°	16 h	(81)	99:1
BT	DBU	CH_2Cl_2	0°	—	(45)	—
BT	DBU	$CHCl_3$	0°	—	(38)	—
BT	DBU	CH_3CN	0°	—	(33)	—
BT	DBU	MeOH	0°	—	(0)	—
BT	DBU	THF	–78°	—	(46)	—
BT	*t*-BuOK	THF	0°	—	(0)	—
BT	DABCO	THF	0°	—	(0)	—

Act	Base	Solvents	Temp	Time		(*E*)/(*Z*)*
PT	LiHMDS	THF	0°	18 h	(23)	—
PT	P_4-*t*-Bu	THF	0°	19 h	(26)	—
PT	DBU	THF	0°	16 h	(79)	99:1
PYR	LiHMDS	THF	0°	18 h	(<5)	—
PYR	P_4-*t*-Bu	THF	0°	19 h	(12)	—
PYR	DBU	THF	0°	24 h	(37)	—
BTFP	LiHMDS	THF	0°	—	—	—
BTFP	P_4-*t*-Bu	THF	0°	—	—	—
BTFP	DBU	THF	0°	24 h	(<10)	—

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	 R^2CHO	1. DBU, THF 2. Aldehyde, 13-21 h	 (*E*)/(*Z*)* > 99:1	82

R^1	R^2	Act = BT	Act = PT
H	Ph	(81)	(74)
MeO	Ph	(79)	(69)
H	4-$MeOC_6H_4$	(84)	(69)
MeO	4-$MeOC_6H_4$	(76)	(64)
H	4-$[Cl(CH_2)_2O]C_6H_4$	(86)	(75)
H	4-FC_6H_4	(77)	(59)
H	1-naphthyl	(63)	(71)
H	(*E*)-PhCH=CH	(88)	(82)

R^1	R^2	Act = BT	Act = PT
H	4-ClC_6H_4	(74)	(63)
H	3-indolyl	(67)	(24)
MeO	3-indolyl	(69)	(43)
H	4-$(AcNH)C_6H_4$	(66)	(—)
H	4-$(AcO)C_6H_4$	(74)	(—)
H	4-MeC_6H_4	(73)	(46)
H	ferrocenyl	(78)	(64)
MeO	3-$MeOC_6H_4$	(81)	(80)

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

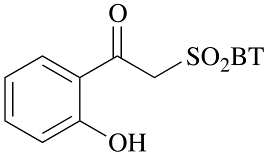
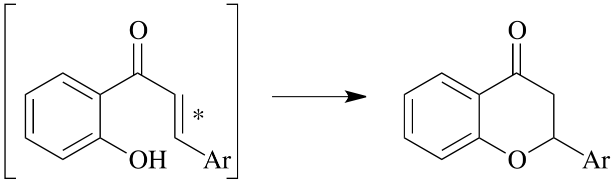
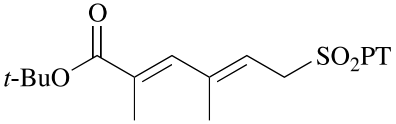
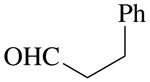
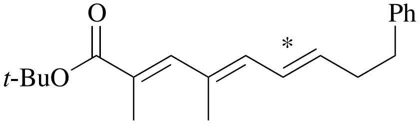
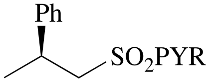
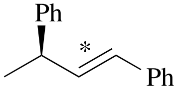
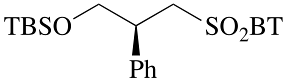
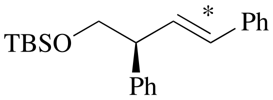
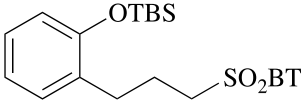
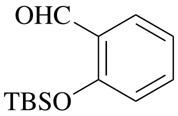
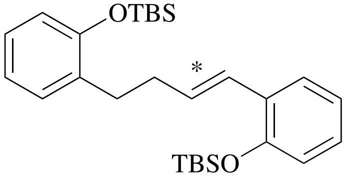
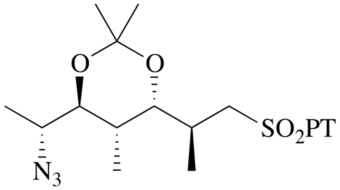
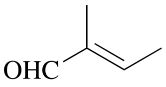
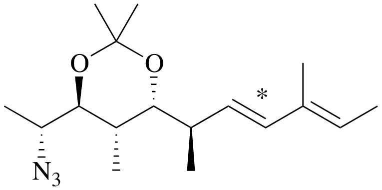
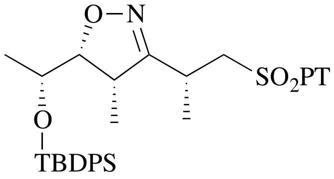
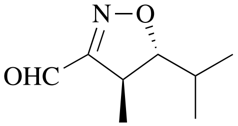
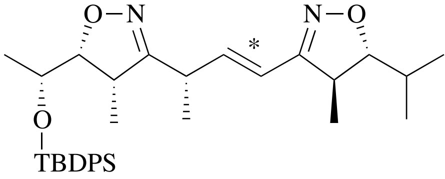
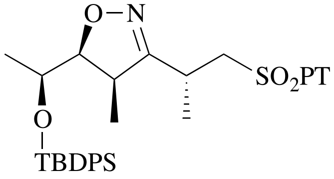
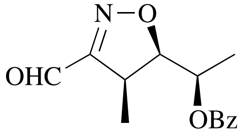
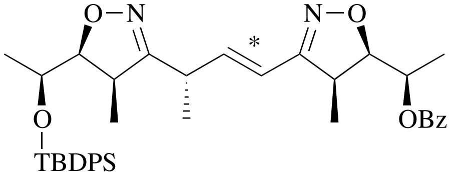
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		ArCHO	DBU, THF, Δ, time. See table.	 Ar — Time Ph — 13 h — (62) 4-$MeOC_6H_4$ — 11 h — (68) 4-HOC_6H_4 — 18 h — (40) 4-BrC_6H_4 — 16 h — (65)	82
			*n*-BuLi, THF, –78°	 (<10) (*E*)/(*Z*)* = —	556
C_9		PhCHO	1. KHMDS, DME, –78°, 3 min 2. Aldehyde, –78°, 2 h	 (87) predominantly (*E*)*	557
		PhCHO	1. KHMDS, THF, –55°, 30 min 2. Aldehyde, –55° to rt	 (82) (*E*)*-isomer only	558
			1. LDA, THF, –80°, 1 h 2. Aldehyde, 90 min, rt	 (79) (*E*)*-isomer	559

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_9			LiHMDS, DME, –65° to rt		(72) (*E*)/(*Z*)* = 94:6	560
			1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1.5 h; rt, 30 min		(75) (*E*)/(*Z*)* = 45:55	561
			1. Base, solvent, –78°, 40 min 2. Aldehyde, –78°, 1 h; rt			561

Base	Solvent		(*E*)/(*Z*)*
LDA	PhMe	(55-95)	28:72
LDA	THF	(55-95)	39:61
LDA	DME	(55-95)	42:58

Base	Solvent		(*E*)/(*Z*)*
KHMDS	PhMe	(55-95)	27:73
KHMDS	THF	(96)	32:68
KHMDS	DME	(55-95)	41:59
KHMDS	DMF	(55-95)	49:51

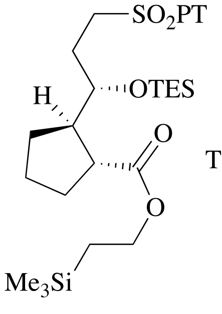
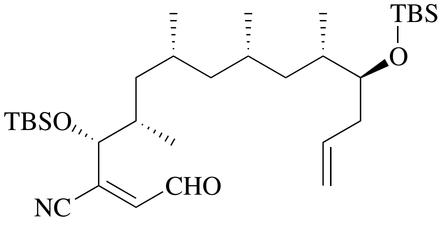
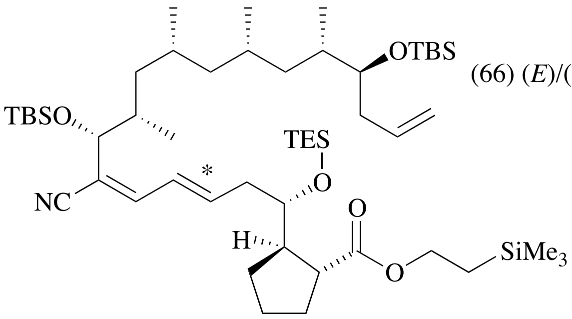
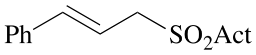
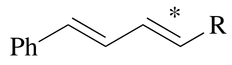
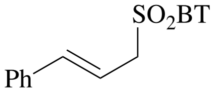
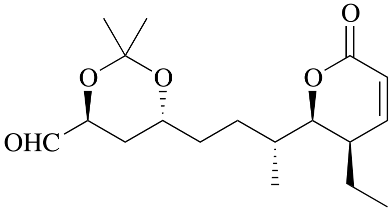
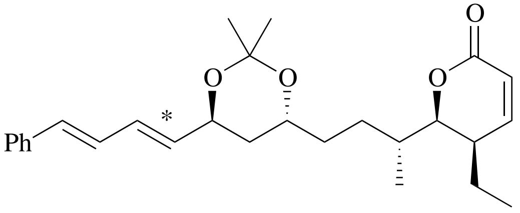
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. NaHMDS, 15-crown-5, THF, –78°, 15 min 2. Aldehyde, –78°, 30 min; rt, 1.5 h		(66) (*E*)/(*Z*)* = 83:17	562

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

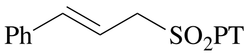
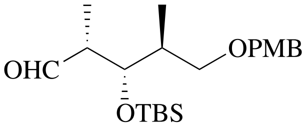
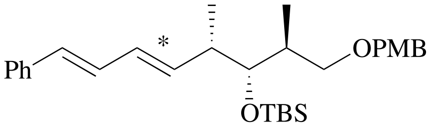
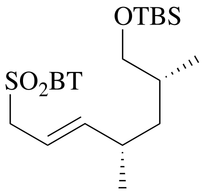
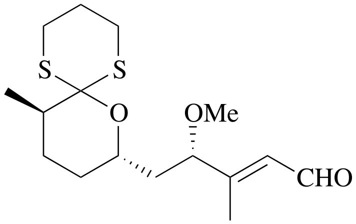
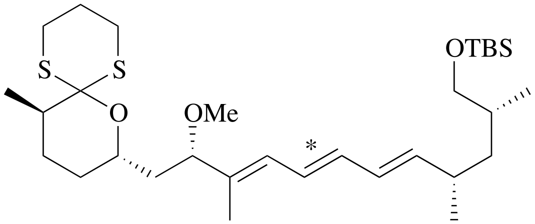
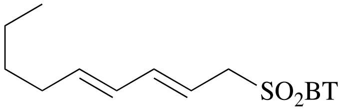
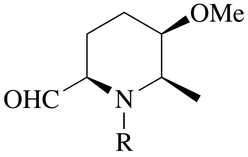
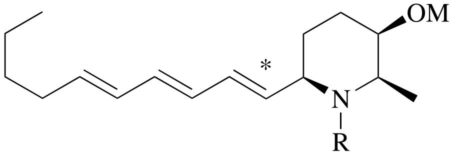
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9	 RCHO	**A**: KHMDS, THF, –78° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde *or* **B**: KHMDS, DMF, –55° *or* **D**: 1. KHMDS, DMF-TDA1, –60°, 2 min 2. Aldehyde		31
	 	1. $MN(SiMe_3)_2$, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt, 1 h		563

R		Act = PT		Act = BT	
			$(E)/(Z)^*$		$(E)/(Z)^*$
$Ph(CH_2)_2$	**A**	(68)	56:44	(86)	57:43
$Ph(CH_2)_2$	**B**	(69)	52:48	(79)	55:45
$Ph(CH_2)_2$	**C**	(59)	16:84	(82)	18:82
$Ph(CH_2)_2$	**D**	(60)	14:86	(85)	15:85
t-Bu	**A**	(66)	58:42		
t-Bu	**B**	(52)	69:21		
t-Bu	**C**	(45)	92:8		
t-Bu	**D**	(49)	95:5		

R		Act = PT	
			$(E)/(Z)^*$
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	**A**	(57)	65:35
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	**B**	(53)	60:40
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	**C**	(36)	15:85
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	**D**	(48)	14:86
$BnOCH_2$	**A**	(81)	42:58
$BnOCH_2$	**B**	(63)	55:45
$BnOCH_2$	**C**	(55)	60:40
$BnOCH_2$	**D**	(69)	56:44
$TBDPSOCH_2CH(OBn)$	**A**	(81)	55:45
$TBDPSOCH_2CH(OBn)$	**B**	(75)	63:47
$TBDPSOCH_2CH(OBn)$	**C**	(72)	88:12
$TBDPSOCH_2CH(OBn)$	**D**	(80)	82:18

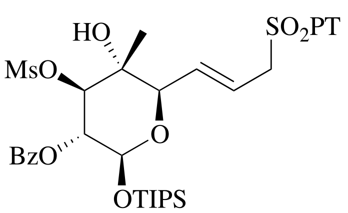
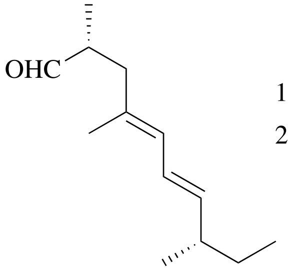
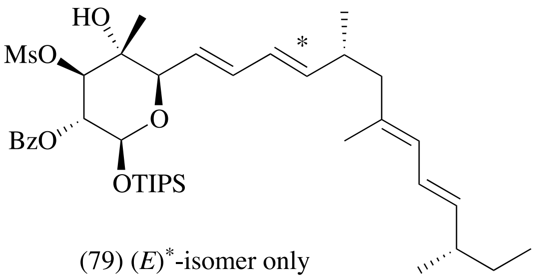
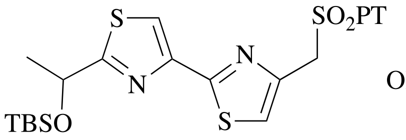
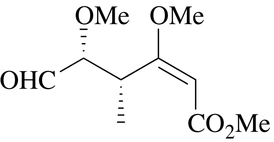
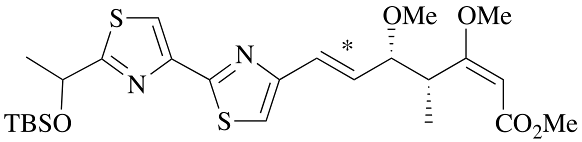
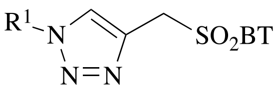
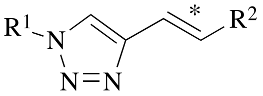
M		$(E)/(Z)^*$
Li	(>56)	66:33
Na	(—)	29:71
K	(—)	17:83

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

<table>
<tr><th></th><th colspan="2">Sulfone and Aldehyde</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_9</td><td></td><td></td><td>1. KHMDS, DME, –60°, 30 min
2. Aldehyde, –60°, 30 min; rt</td><td>
(68) (<i>E</i>)/(<i>Z</i>)* = 50:50</td><td>564</td></tr>
<tr><td></td><td></td><td></td><td>MN(SiMe$_3$)$_2$, THF, –80°
<table>
<tr><th>M</th><th></th><th>(<i>E</i>)/(<i>Z</i>)*</th></tr>
<tr><td>Li</td><td>(—)</td><td>29:71</td></tr>
<tr><td>Na</td><td>(79)</td><td>43:57</td></tr>
<tr><td>K</td><td>(—)</td><td>18:82</td></tr>
</table></td><td></td><td>21</td></tr>
<tr><td></td><td></td><td></td><td>1. MN(SiMe$_3$)$_2$, THF, 30 min
2. Aldehyde, 2 h</td><td></td><td>566</td></tr>
</table>

R	Additive	M	Temp		(*E*)/(*Z*)*
Me	none	Li	–78°	(25)	50:50
Me	none	K	–78°	(32)	50:50
Boc	none	Li	–78°	(83)	50:50
Boc	12-crown-4	Li	–78°	(80)	50:50
Boc	none	K	–78°	(71)	50:50
Boc	HMPA	K	–78°	(83)	67:33
Boc	18-crown-6	K	–78°	(78)	75:25
Boc	18-crown-6	K	–100°	(53)	75:25

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			1. KHMDS (2 eq), THF, –78° 2. Aldehyde, –78°, 3 h; rt	 (79) $(E)^*$-isomer only	565
			1. LiHMDS, THF, 0°, 15 min 2. Aldehyde, 0°	 (73) $(E)/(Z)^* = 91{:}9$	567
C_{9-12}		R^2CHO	LiHMDS, DMF-DMPU, –78°		568

R^1	R^2		$(E)/(Z)^*$
4-$MeOC_6H_4$	2,4,6-$Me_3C_6H_2$	(73)	33:67
$Ph(CH_2)_3$	2,4,6-$Me_3C_6H_2$	(85)	15:85
$Ph(CH_2)_3$	4-$MeOC_6H_4$	(65)	72:28
$Ph(CH_2)_3$	4-$NO_2C_6H_4$	(44)	83:17

R^1	R^2		$(E)/(Z)^*$
4-$MeOC_6H_4$	Et_2CH	(67)	86:14
$Ph(CH_2)_3$	Et_2CH	(41)	77:23
4-$MeOC_6H_4$	n-C_7H_{15}	(71)	72:28
$Ph(CH_2)_3$	n-C_7H_{15}	(31)	7:93

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

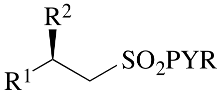
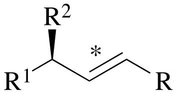
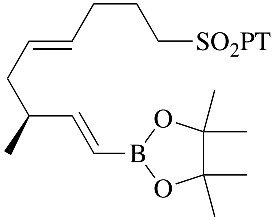
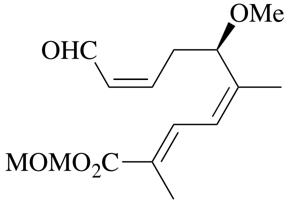
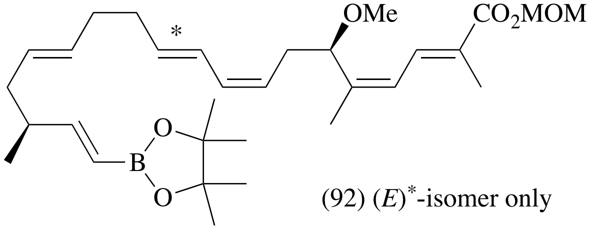
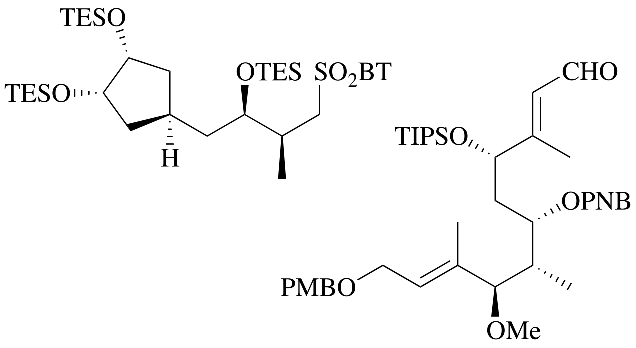
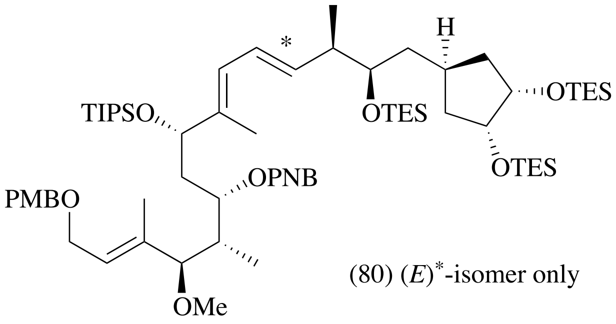
<table>
<tr><th></th><th>Sulfone and Aldehyde</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_{9-13}</td><td> ArCHO</td><td>1. KHMDS, DME, –78°, 3 min
2. Aldehyde, –78°, 2 h</td><td>
<table>
<tr><th>R^1</th><th>R^2</th><th>Ar</th><th></th><th>$(E)/(Z)^*$</th></tr>
<tr><td>Me</td><td>Ph</td><td>Ph</td><td>(94)</td><td>99:1</td></tr>
<tr><td>Me</td><td>Ph</td><td>4-FC_6H_4</td><td>(90)</td><td>90:10</td></tr>
<tr><td>Me</td><td>Ph</td><td>CH=CHPh</td><td>(89)</td><td>87:13</td></tr>
<tr><td>Me</td><td>4-FC_6H_4</td><td>Ph</td><td>(93)</td><td>99:1</td></tr>
<tr><td>n-C_5H_{11}</td><td>Ph</td><td>Ph</td><td>(92)</td><td>99:1</td></tr>
</table></td><td>365</td></tr>
<tr><td>C_{10}</td><td> </td><td>1. KHMDS, THF, –78°
2. Aldehyde, –78°</td><td>
(92) $(E)^*$-isomer only</td><td>569</td></tr>
<tr><td></td><td></td><td>1. LiHMDS, THF, –78°, 40 min
2. Aldehyde, –78°, 1 h; rt, 30 min</td><td>
(80) $(E)^*$-isomer only</td><td>570</td></tr>
</table>

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

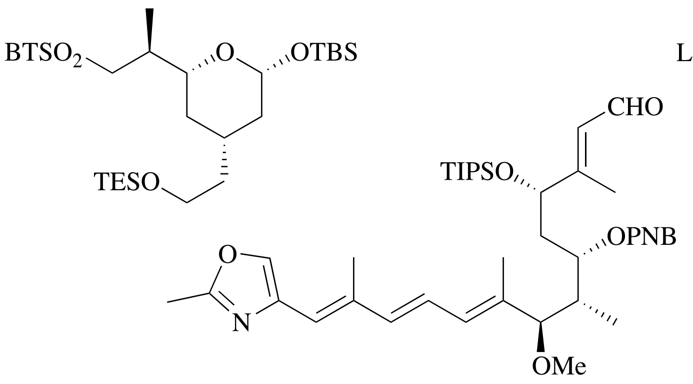
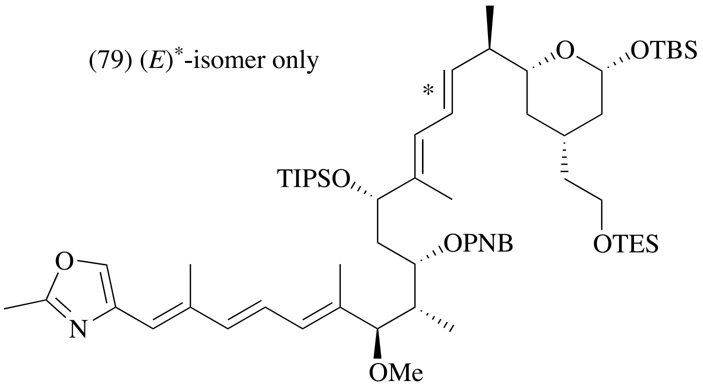
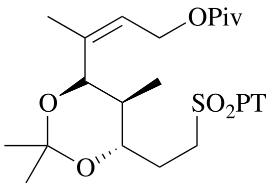
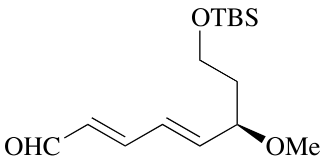
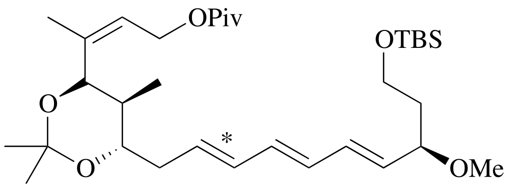
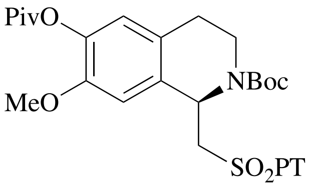
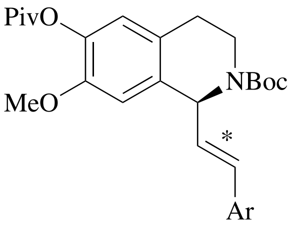
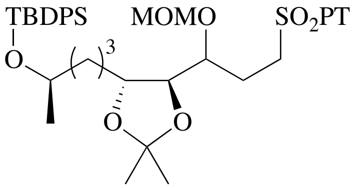
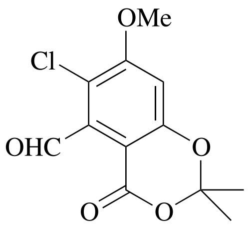
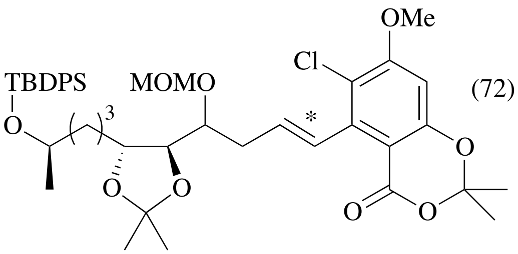
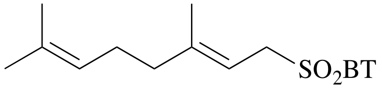
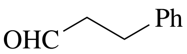
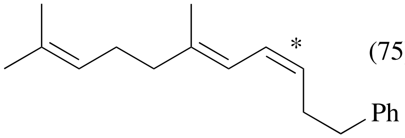
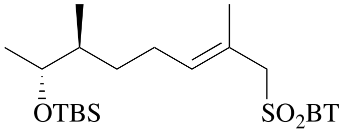
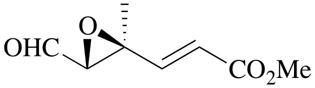
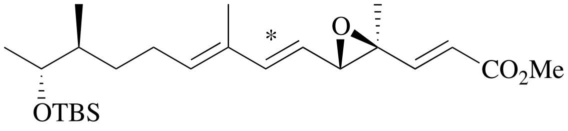
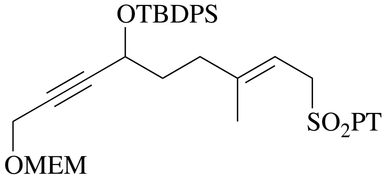
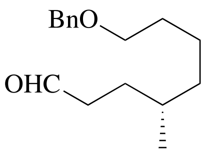
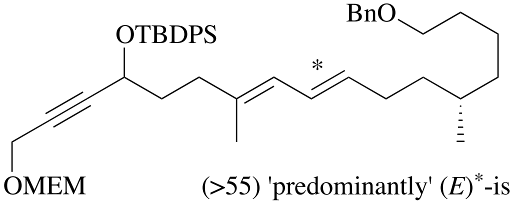
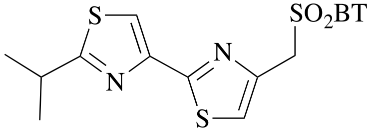
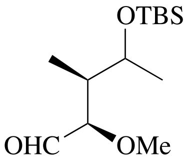
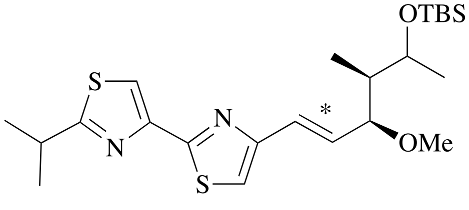
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		LiHMDS, THF, –78°, 2 h; rt	(79) $(E)^*$-isomer only 	571 572
	 	1. KHMDS, THF, –78°, 20 min 2. Aldehyde, –78°, 1 h; rt, 1 h	 (85) $(E)/(Z)^* = 91:9$	573 574
	 ArCHO	LiHMDS, THF, –35°, 1 h	 Ar — $(E)/(Z)^*$ 3,4-$(OCH_2O)C_6H_3$ (85) 100:0 4-$PivOC_6H_4$ (79) 100:0 4-$MeOC_6H_4$ (86) 100:0	575
	 	1. KHMDS, 18-crown-6, THF, –78°, 30 min 2. Aldehyde, –78° to rt, 2 h	 (72) $(E)/(Z)^* = 92:8$	576

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	 	LiHMDS (2 eq), CH_2Cl_2, rt	 (75) $(E)/(Z)^* = 13{:}87$	33 34
	 	LiHMDS, THF, see table		577
	 	KHMDS, THF, –78°	 (>55) 'predominantly' $(E)^*$-isomer	578
	 	1. LiHMDS, THF, 0°, 15 min 2. Aldehyde, 0°, 10 min	 (96) $(E)/(Z)^* = 65{:}35$	579

Additive	Temp		$(E)/(Z)^*$
none	–78°	(≥14)	50:50
none	–98°	(≥62)	38:62
HMPA, 4Å MS	–98°	(≥52)	70:30

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

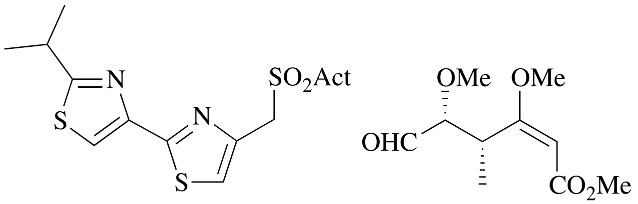
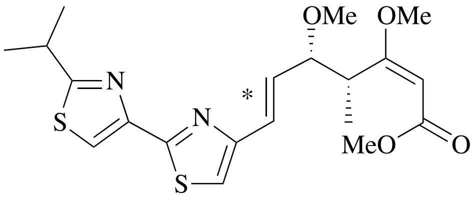
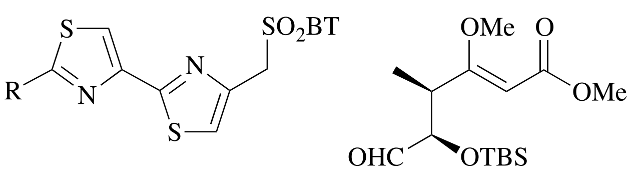
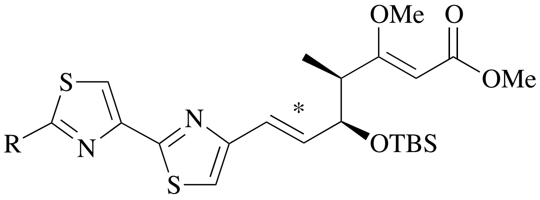
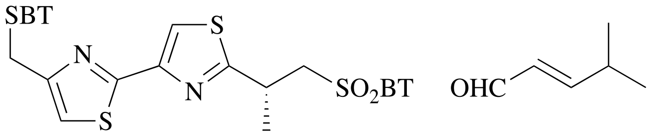
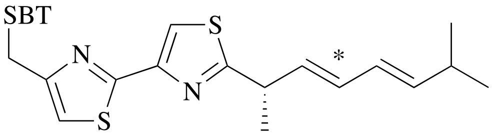
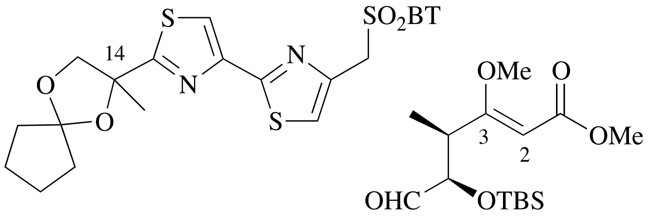
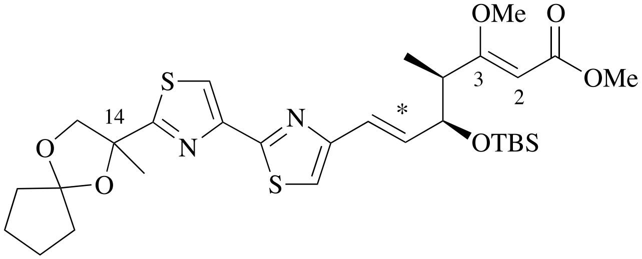
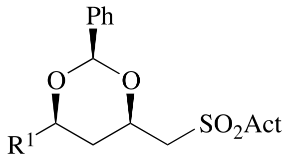
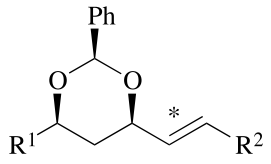
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		1. LiHMDS, THF, 0°, 15 min 2. Aldehyde, 0°, 10 min	 Act (E)/(Z)* BT (64) 94:6 PT (66) 80:20	580
		1. LiHMDS, THF, Temp., 15 min 2. Aldehyde, Temp., 30 min	 R / Temp. / (E)/(Z)* $C(OH)Me_2$ –78° (55) 94:6 $CHMe_2$ –50° (84) 95:5 $C(=CH_2)Me$ –60° (53) 96:4	581 582 582
		LiHMDS, THF, –78°, 15 min	 (77) (E)/(Z)* = 77:23	583
		1. LiHMDS, THF, –78 to –30° 15 min 2. Aldehyde, –78 to 0°, 30min	 C8 C2/C3 (E)/(Z)* (R) (E) (76) 100:0 (R) (Z) (80) 95:5 (S) (Z) (75) 90:10	581

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-12}	 R_2CHO	See table.		49

Act	R^1	R^2	Base	Solvent	Temp		$(E)/(Z)^*$
BT	n-C_6H_{13}	Ph	LiHMDS	THF	–78 to 20°	(41)	83:17
BT	n-C_6H_{13}	Ph	NaHMDS	THF	–78 to 20°	(75)	83:17
BT	n-C_6H_{13}	Ph	KHMDS	THF	–78°	(81)	75:25
BT	n-C_6H_{13}	Ph	KHMDS	DMF	–60°	(78)	88:12
BT	n-C_6H_{13}	Ph	NaH	THF	20°	(71)	97:3
BT	n-C_6H_{13}	PhCH=CH	NaH	THF	20°	(93)	64:36
PYR	$Ph(CH_2)_2$	Ph	NaH	THF	20°	(<5)	—
PYR	$Ph(CH_2)_2$	Ph	NaH	DMF	20°	(50)	89:11
PYR	$Ph(CH_2)_2$	Ph	KHMDS	THF	–78 to 20°	(40)	83:17
PYR	$Ph(CH_2)_2$	Ph	KHMDS	PhMe	–78 to 20°	(44)	90:10
PYR	$Ph(CH_2)_2$	Ph	KHMDS	CH_2Cl_2	–78 to 20°	(47)	94:6

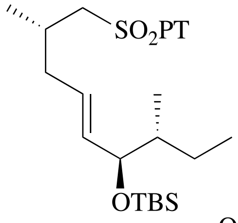
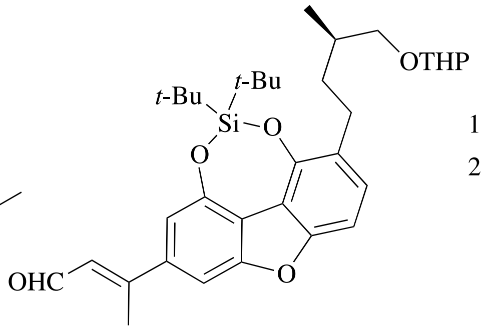
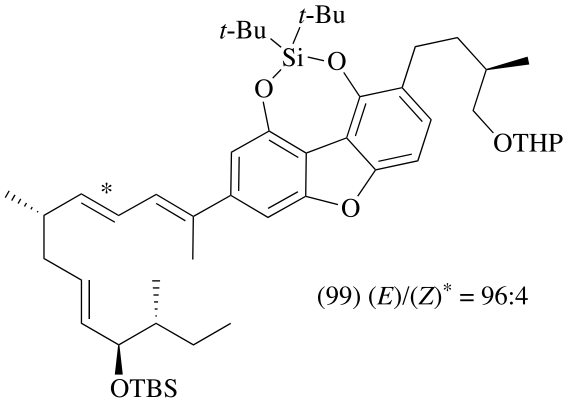
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}	 	1. LiHMDS, THF, –78°, 10 min 2. Aldehyde, –78°, 20 min	 (99) $(E)/(Z)^* = 96:4$	111

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

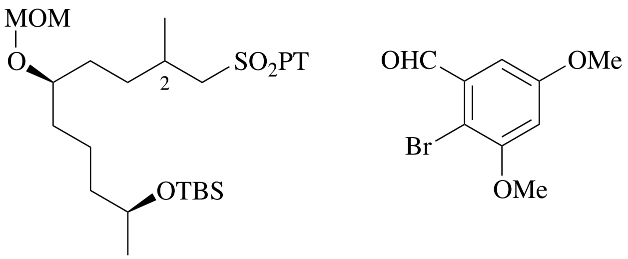
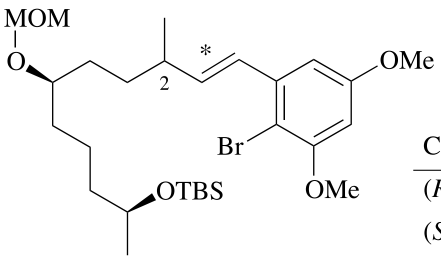
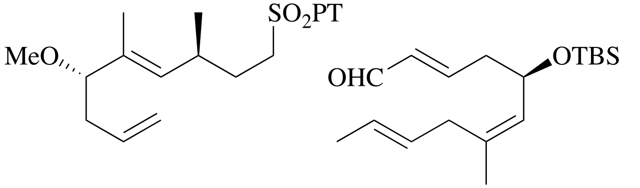
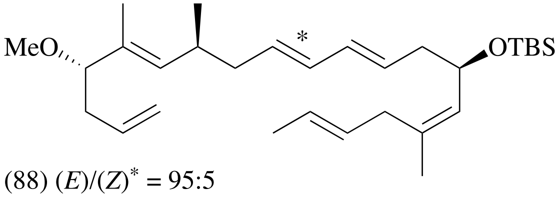
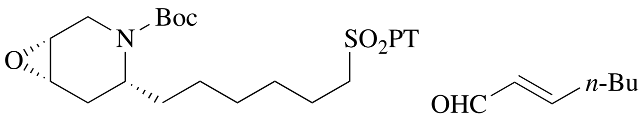
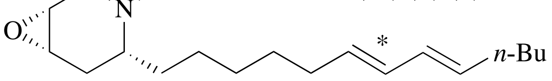
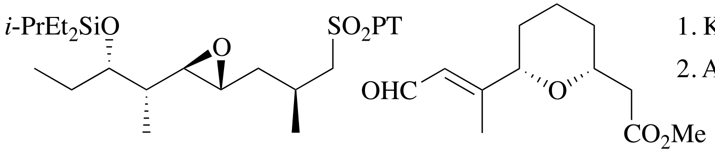
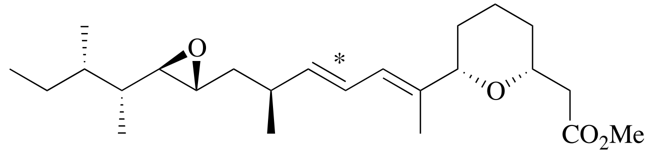
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		1. KHMDS, THF, –80°, 45 min 2. Aldehyde, 30 min; rt, 1 h	 C2 (*R*) (70) (*E*)*-isomer (*S*) (81) (*E*)*-isomer	584
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1 h; rt	 (88) (*E*)/(*Z*)* = 95:5	585
		KHMDS, THF, –78°, 30 min	 (82) (*E*)/(*Z*)* = 90:10	586
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1 h	 (46) (*E*)/(*Z*)* = 93:7	587

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

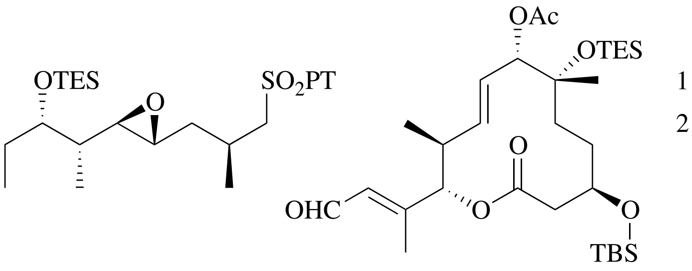
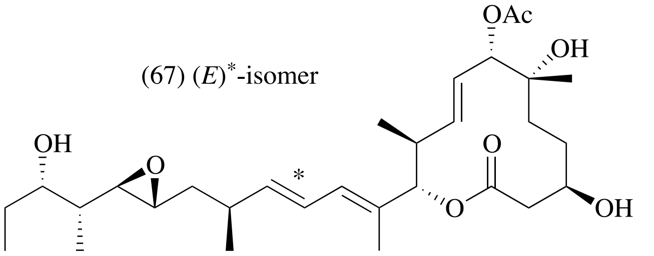
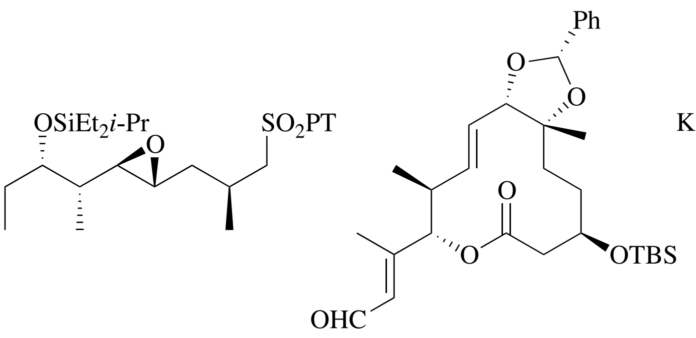
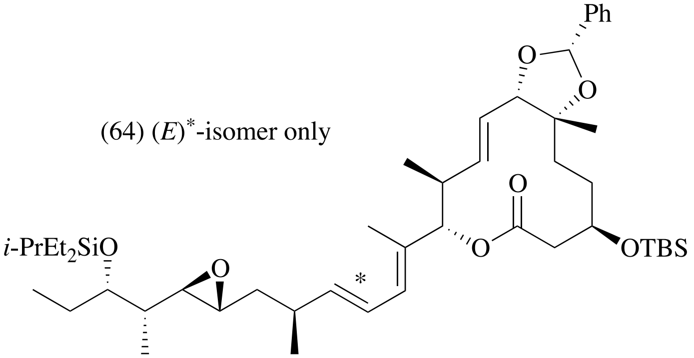
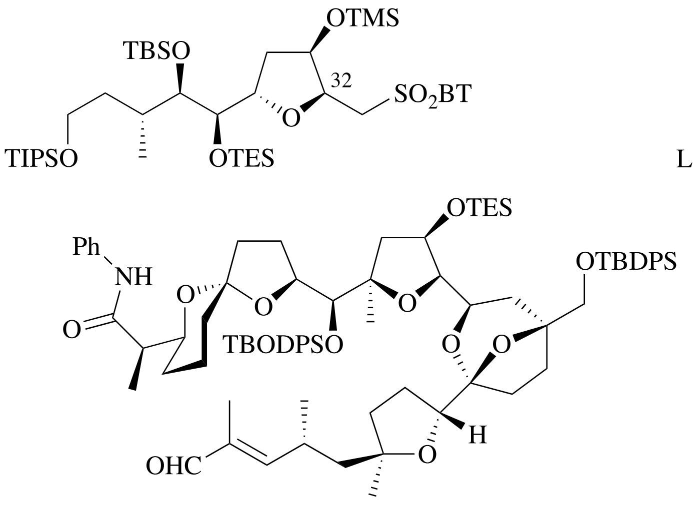
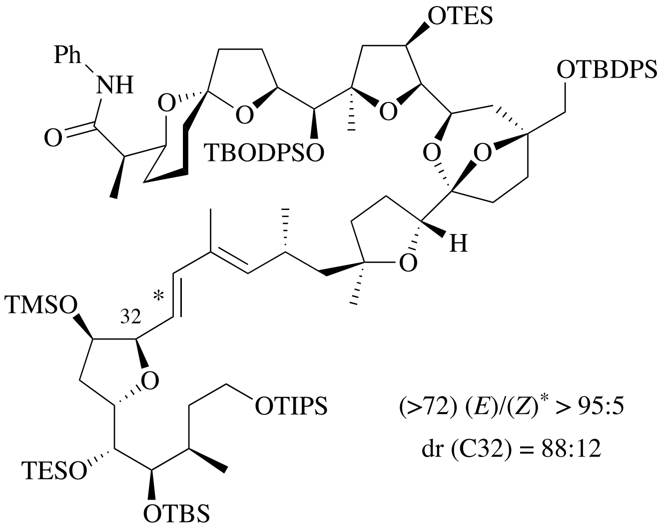
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		1. KHMDS, THF, –78°, 15 min 2. Aldehyde, –78°, 1 h	(67) $(E)^*$-isomer 	588
		KHMDS, THF, –78°	(64) $(E)^*$-isomer only 	265
		LiHMDS, THF, –78° to rt	 (>72) $(E)/(Z)^* > 95:5$ dr (C32) = 88:12	117

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

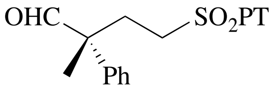
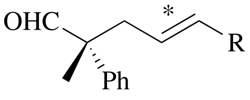
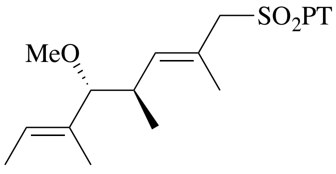
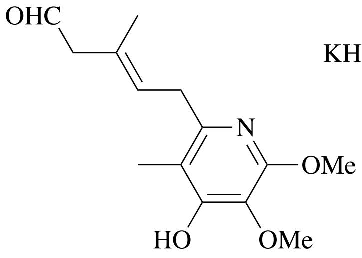
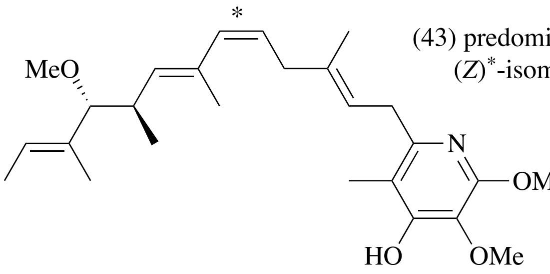
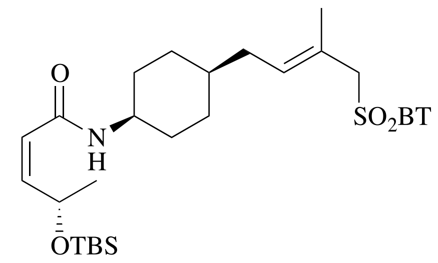
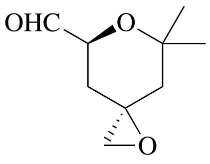
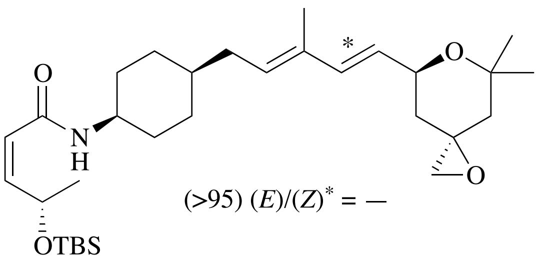
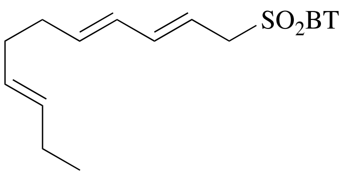
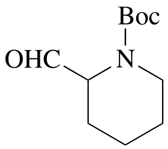
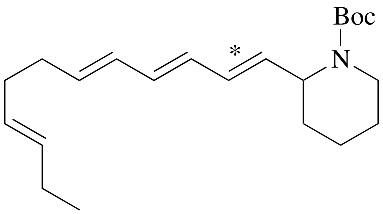
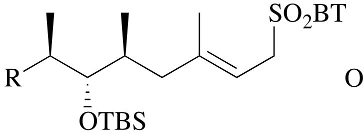
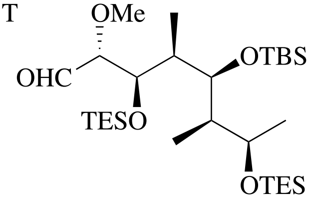
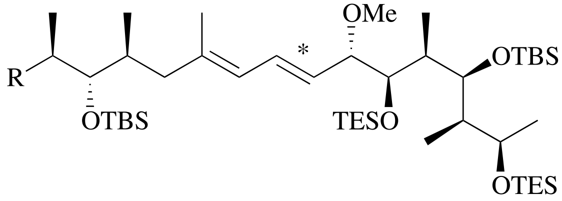
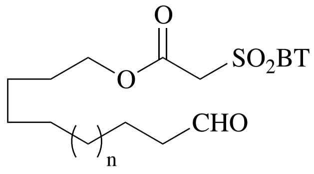
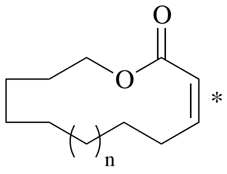
	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{11}		ArCHO	**A**: NaHMDS, DME, –78° *or* **B**: 1. Ethylene glycol, *p*-TsOH, PhH 2. Aldehyde KHMDS, DME, –78° 3. HCl, THF, 50°		R — — $(E)/(Z)^*$ Ph **A** (48) 91:9 Ph **B** (72) 91:9 4-$NO_2C_6H_4$ **B** (77) 90:10 4-$MeOC_6H_4$ **B** (60) 91:9	51
			KHMDS, THF, –78°, 12 h		(43) predominantly $(Z)^*$-isomer	589
			1. LiHMDS, THF, –78°, 10 min 2. Aldehyde, –78°, 1 h; rt, 2 h		(>95) $(E)/(Z)^*$ = —	590
			1. KHMDS, 18-crown-6, THF –80°, 1 h 2. Aldehyde, THF, –80°, 2.5 h; rt		(98) $(E)^*$-isomer only	591

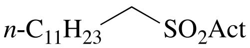
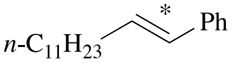
TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-14}	 	See table.		592

R	Eq sulfone	Base	Eq base	Temp		$(E)/(Z)^*$
$TESOCH_2$	1.2	LiHMDS	2.0	–78°, 2 h; rt	(85)	76:24
$TESOCH_2$	1.2	NaHMDS	2.0	–78°, 2 h; rt	(68)	81:19
$TESOCH_2$	1.2	NaHMDS	1.2	–78°, 1 h; 0°	(81)	71:29
$TESOCH_2$	1.2	KHMDS	2.0	–78°, 2 h; rt	(90)	58:42
(*E*)-$EtO_2CC(Me)=CH$	1.1	LiHMDS	2.3	–78°, 20 min; –40, 40 min; 0°	(75)	50:50
(*E*)-$EtO_2CC(Me)=CH$	1.1	NaHMDS	2.2	–78, 2 h; –40, 10 min; 0°	(56)	80:20
(*E*)-$EtO_2CC(Me)=CH$	1.1	NaHMDS	1.1	–78, 30 min; –40, 20 min; 0°	(40)	80:20
(*E*)-$EtO_2CC(Me)=CH$	0.8	NaHMDS	1.2	–78, 30 min; –40, 10 min; 0°	(86)	66:34
(*E*)-$EtO_2CC(Me)=CH$	1.1	KHMDS	2.2	–78, 70 min; –40, 20 min; 0°	(39)	75:25
(*E*)-$HOCH_2C(Me)=CH$	0.8	NaHMDS	1.7	–78, 1 h; –40, 10 min; 0°	(65)	78:22

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
		syringe pump addition to DBU, CH_2Cl_2, rt, 14 h		146

n		$(E)/(Z)^*$
1	(44)	13:87
2	(24)	22:78
4	(25)	20:80

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}	 PhCHO	LDA, THF, –78°, 1 h; rt, 3 h		20

Act		$(E)/(Z)^*$
BT	(30)	79:21
IM	(<1)	54:46
TZ	(44)	38:62
IQ	(40)	74:26

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

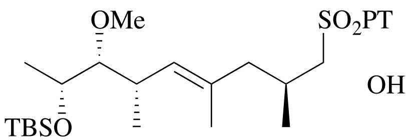
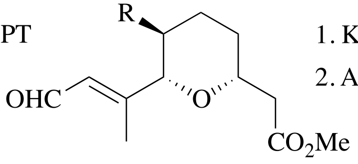
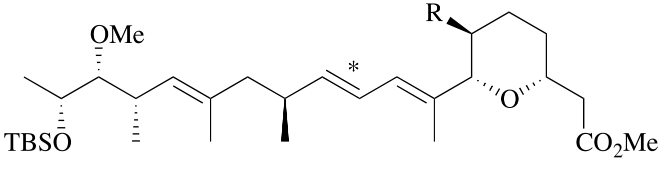
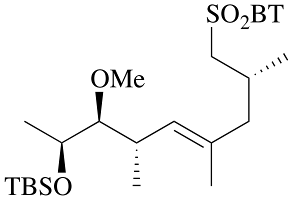
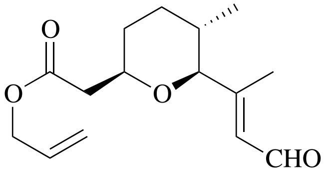
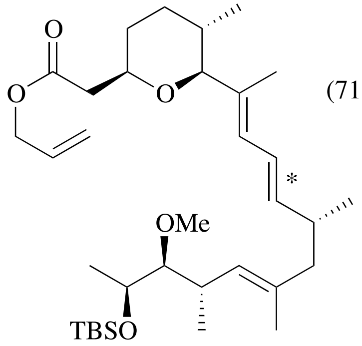
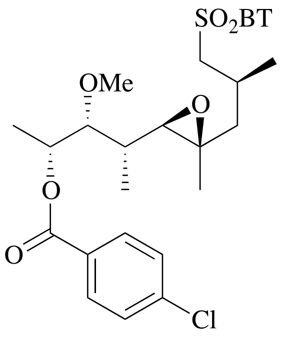
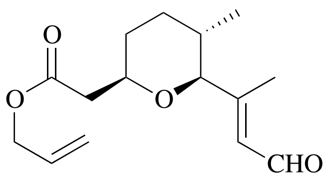
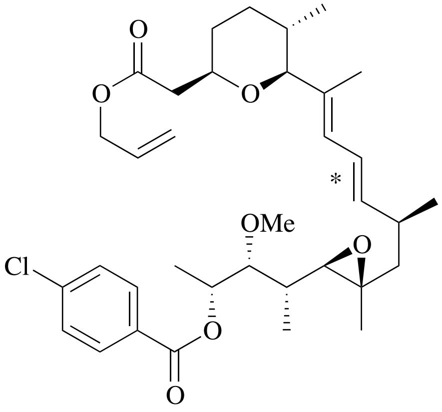
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		1. KHMDS, THF, –78°, 1 h 2. Aldehyde; rt	 R — (E)/(Z)* H (45) 78:22 Me (92) 78:22	587
		1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 1.5 h; rt	 (71) (*E*)/(*Z*)* = 92:8	22
		1. LDA, THF, –78°, 15 min 2. Aldehyde, –78° to –20°, 1.5 h	 (81) (*E*)/(*Z*)* = 91:9	58

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

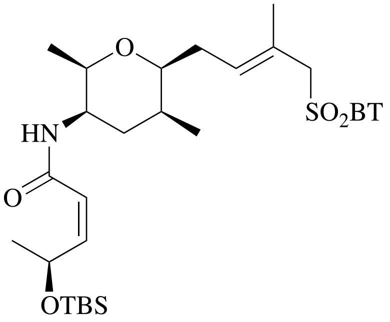
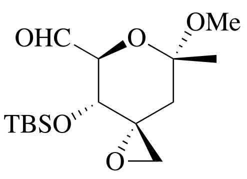
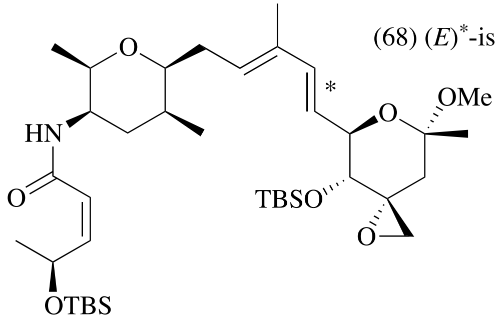
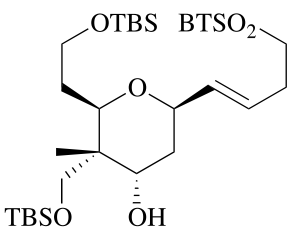
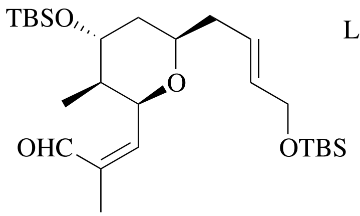
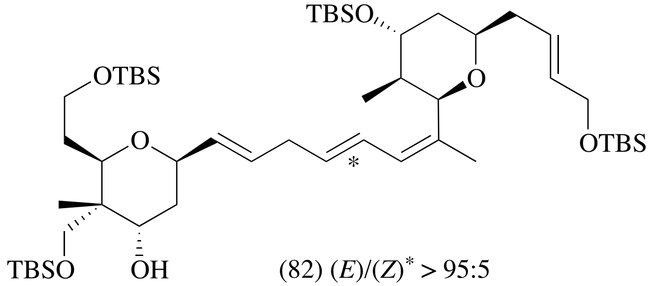
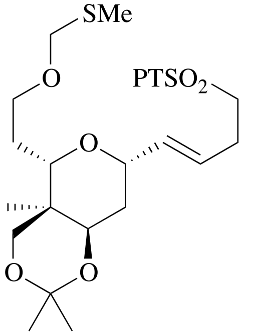
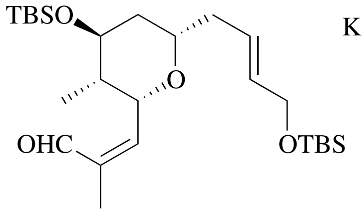
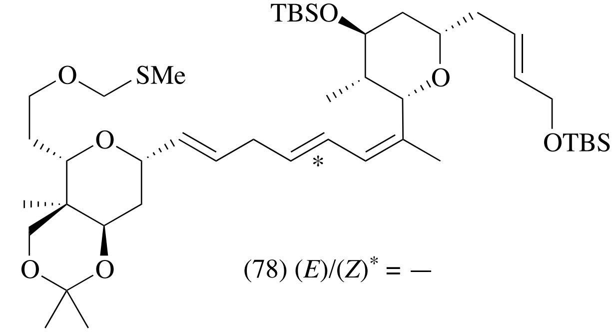
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}	 	1. LiHMDS, THF, –78°, 10 min 2. Aldehyde, –78°, 1 h; rt, 2 h	 (68) (*E*)*-isomer only	593
C_{13}	 	LiHMDS, DME, –70° to rt	 (82) (*E*)/(*Z*)* > 95:5	114 216
	 	KHMDS, THF, –78°, 1 h; rt	 (78) (*E*)/(*Z*)* = —	52 594

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

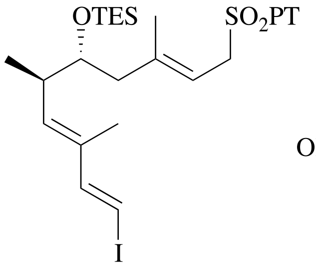
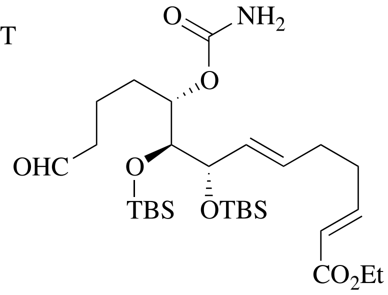
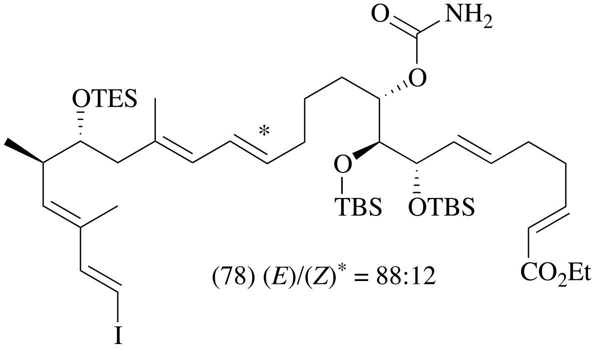
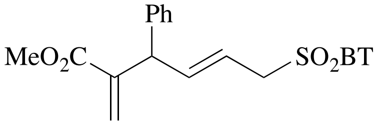
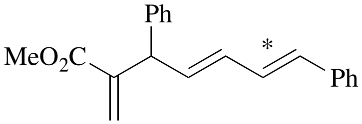
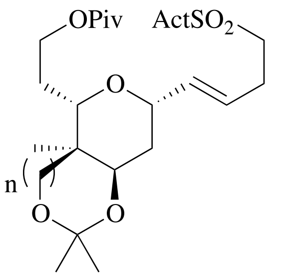
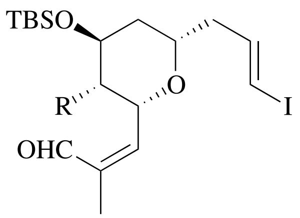
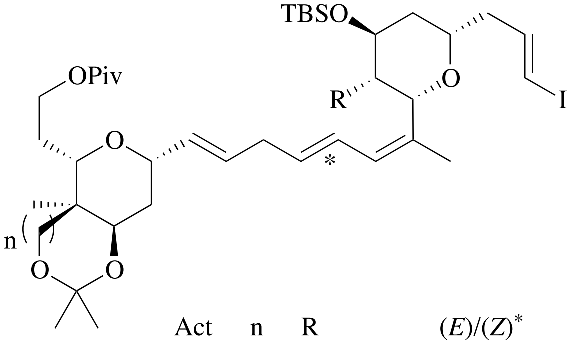
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}	 	1. NaHMDS, THF, –78°, 5 min 2. Aldehyde, –78° to –50°, 1 h	 (78) (*E*)/(*Z*)* = 88:12	595
	 PhCHO	LDA, DME, –50°, 8 h	 (70) (*E*)/(*Z*)* = 11:89	596
$C_{13–14}$	 	1. LiHMDS, THF, –78° 2. Aldehyde, –78° to rt		
			Act n R (*E*)/(*Z*)*	
			BT 1 Me (70) 95:5	597
			PT 1 Me (86) 95:5	206
			PT 1 H (—) (—)	207
			PT 2 Me (—) (—)	207

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

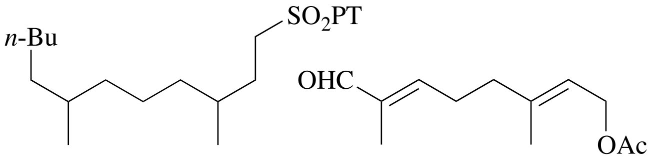
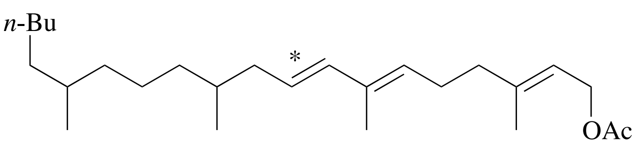
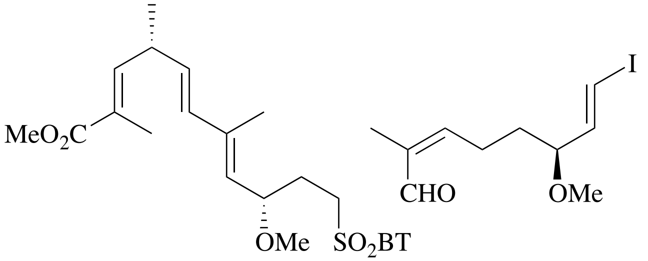
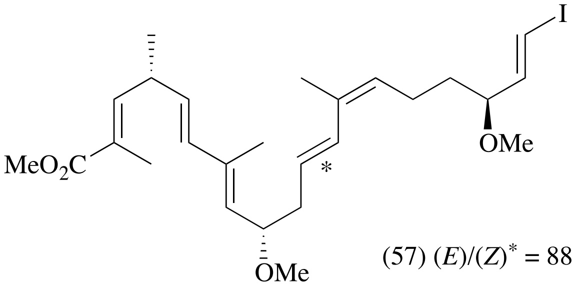
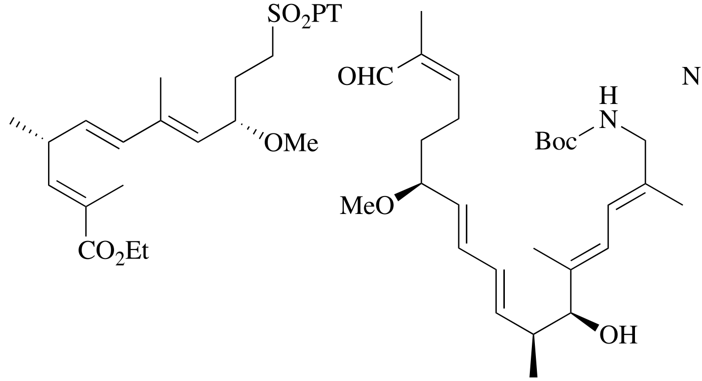
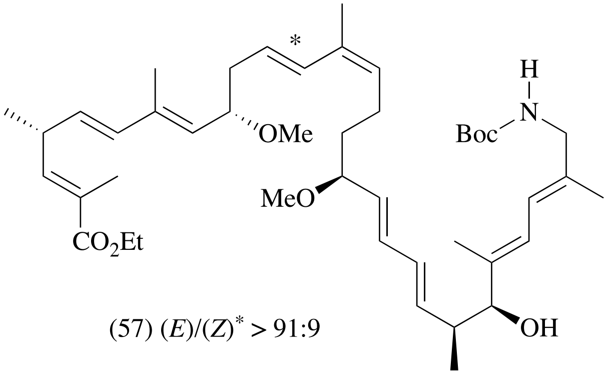
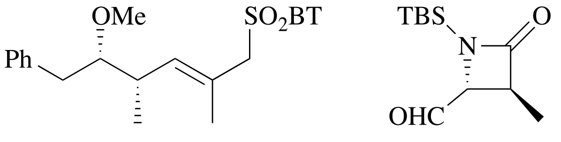
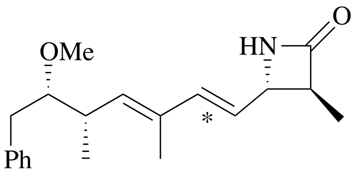
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
		1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt	 (90) $(E)/(Z)^* = —$	452
		LiHMDS, THF, –78°, 2 h; 23°, 30 min	 (57) $(E)/(Z)^* = 88{:}12$	598 526
		NaHMDS, THF, –78° to rt	 (57) $(E)/(Z)^* > 91{:}9$	527
		1. $MN(SiMe_3)_2$, THF 2. KF	 M — $(E)/(Z)^*$ Li (—) ~ 66:34 Na (20-25) ~ 80:20 K (40-45) ~ 75:25	599

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

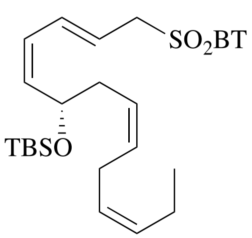
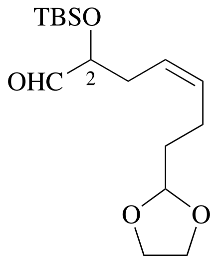
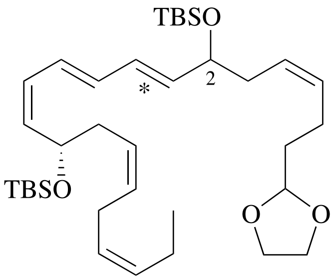
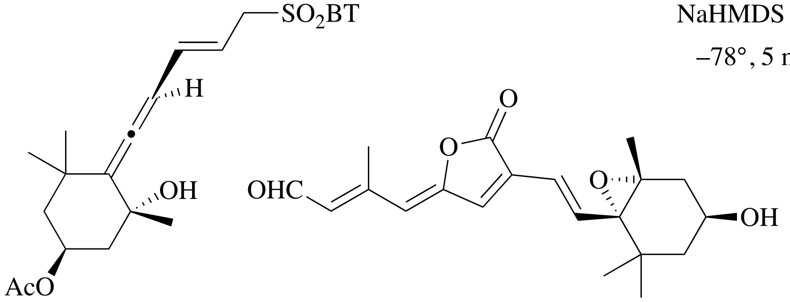
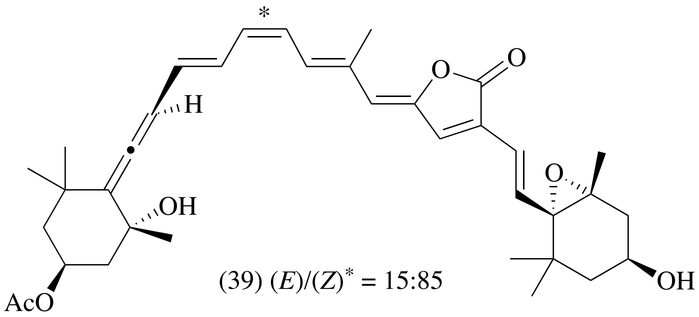
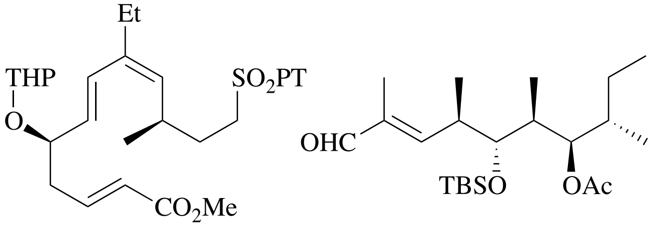
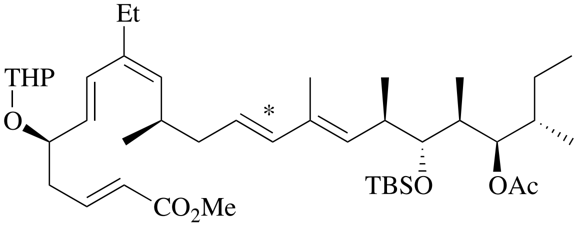
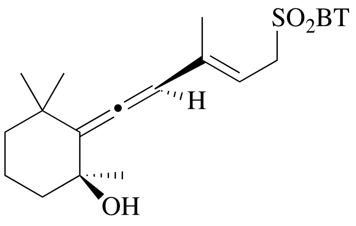
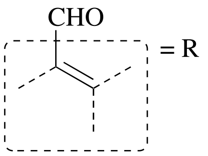
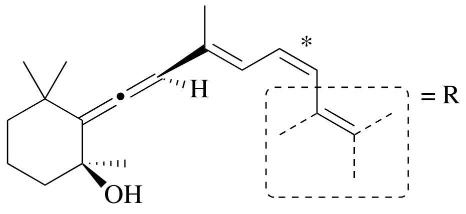
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
	 	P_4-*t*-Bu, MeCN, –40° to rt, 2 h	 C2 (*E*)/(*Z*)* (*R*) (56) 61:39 (*S*) (63) 56:44	600
		NaHMDS (3 eq), THF, –78°, 5 min, dark	 (39) (*E*)/(*Z*)* = 15:85	601
C_{15}				
		KHMDS, DME, –60°	 (38) (*E*)/(*Z*)* > 95:5	549

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			1. NaHMDS, THF, –78° 2. Aldehyde, –78° to rt		522

R (α,β-unsaturated)		$(E)/(Z)^*$
(*E*)-MeCH=CH	(0)	—
(*E*)-PhCH=CH	(83)	22:78
(*E*)-$Bu_3SnCH=CH$	(82)	14:86
$Me_2CH=CH$	(86)	8:92
(*E*)-$TBSOCH_2CH=CMe$	(78)	29:71

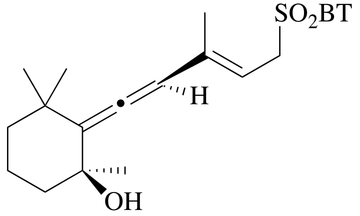
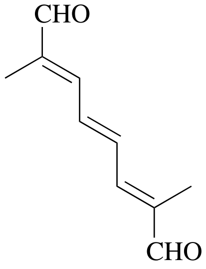
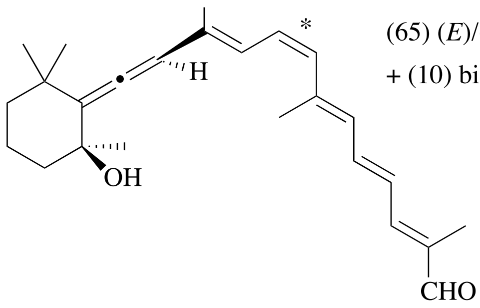
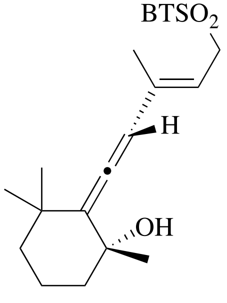
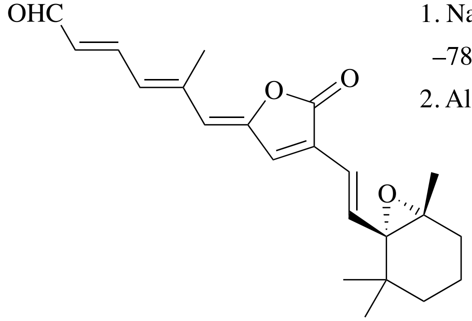
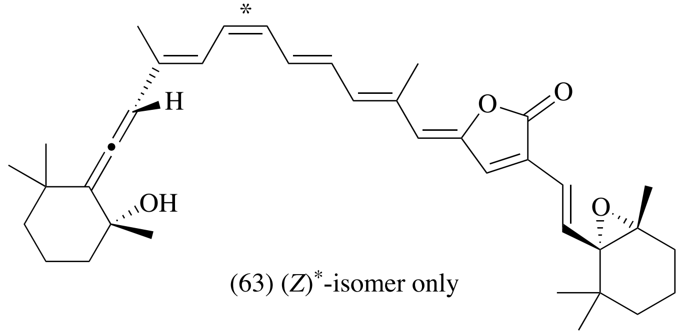
			1. NaHMDS, THF, –78° 2. Dialdehyde, –78° to rt	 (65) $(E)/(Z)^*$ = 0:100 + (10) bis-olefination product	522
			1. NaHMDS (2.5 eq), THF, –78°, 30 min 2. Aldehyde, –78 to 0°, 2 h	 (63) $(Z)^*$-isomer only	522 78

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

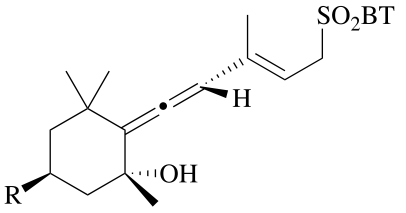
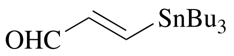
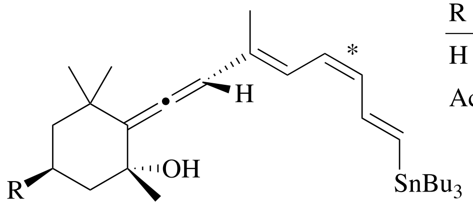
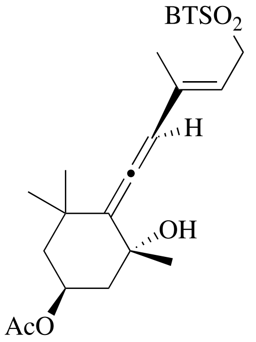
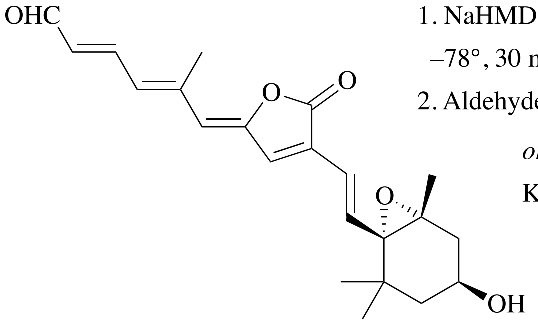
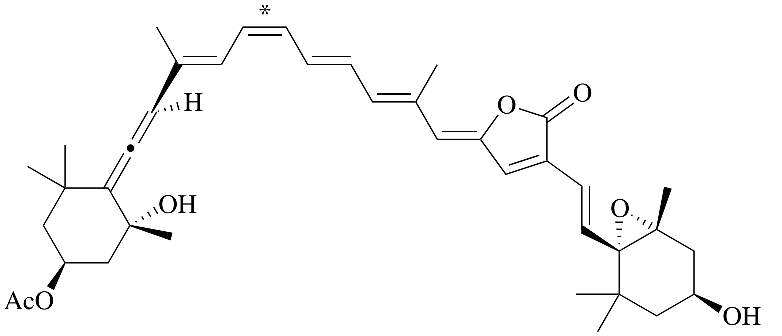
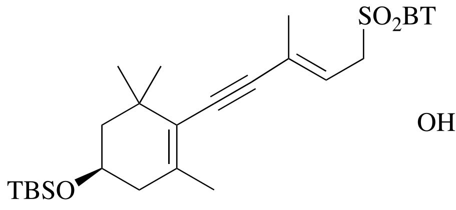
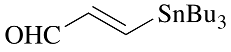
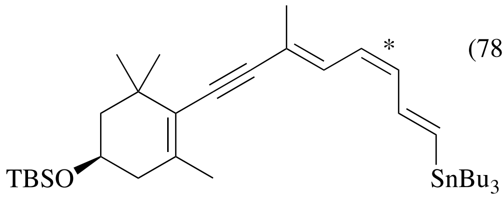
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}				
	 	1. NaHMDS (3 eq), THF, –78°, 30 min 2. Aldehyde, –78°, 2 h	 R — (E)/(Z)* H (79) 17:83 AcO (70) 25:75	602, 78
	 	**A**: 1. NaHMDS (3 eq), BHT, THF, –78°, 30 min 2. Aldehyde, –78 to –30°, 6 h *or* **B**: KHMDS (5 eq), THF, BHT, –78°, 5 min	 **A** (53) (Z)*-isomer isolated **B** (54) (Z)*-isomer isolated	78 43
	 	1. NaHMDS (3 eq), THF, –78°, 30 min 2. Aldehyde, –78°, 2 h	 (78) (Z)*-isomer only	603

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

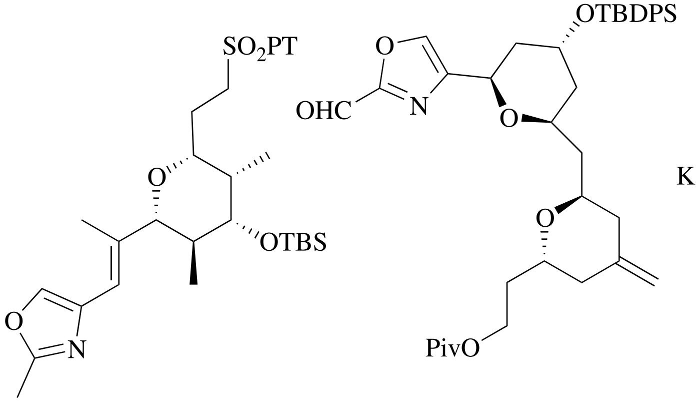
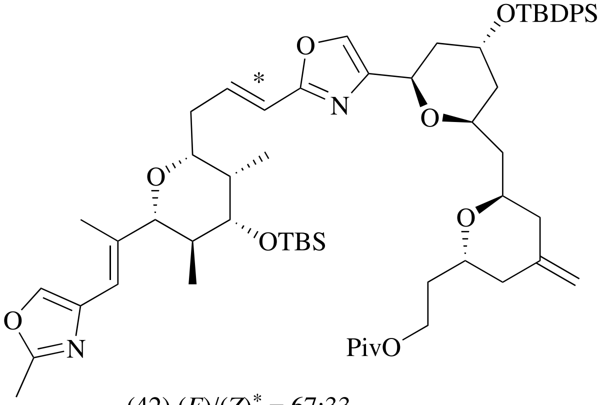
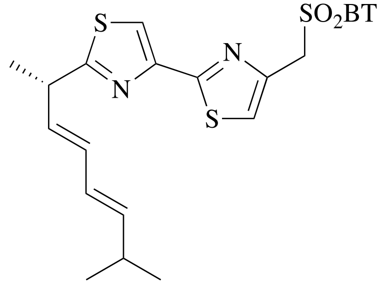
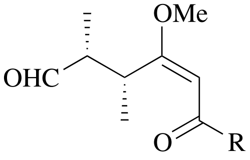
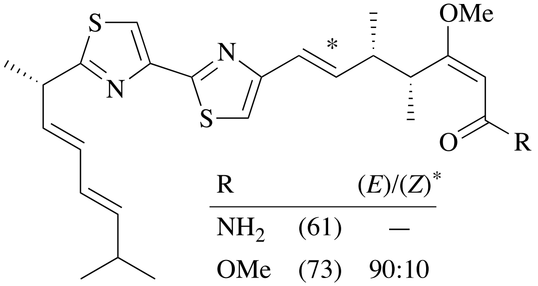
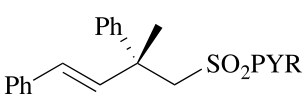
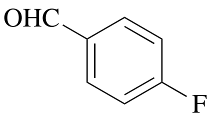
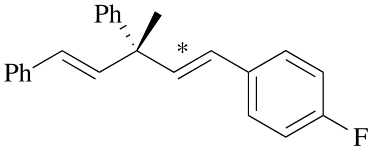
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}		KHMDS, DME, –65 to 0°	 (42) (*E*)/(*Z*)* = 67:33	604
	 	1. LiHMDS, THF, –78 to –30° 30 min 2. Aldehyde, –78 to –60°	 R (*E*)/(*Z*)* NH_2 (61) — OMe (73) 90:10	583
C_{17}	 	1. KHMDS, DME, –78°, 3 min 2. Aldehyde, –78°, 2 h	 (89) (*E*)*-isomer only	605

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

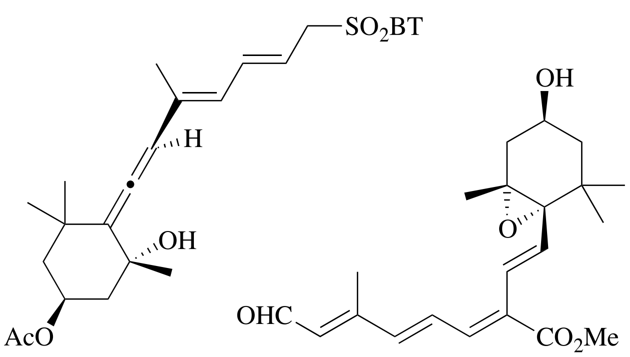
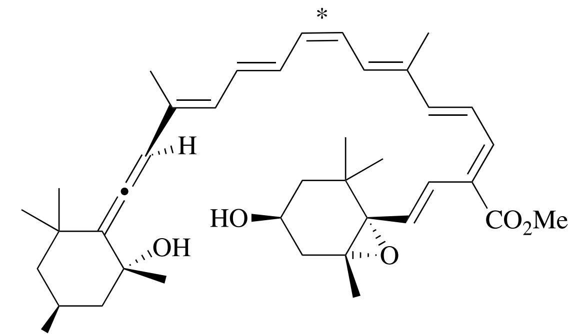
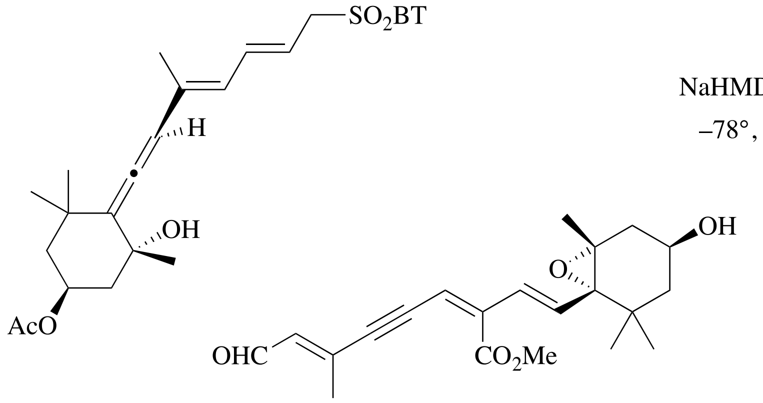
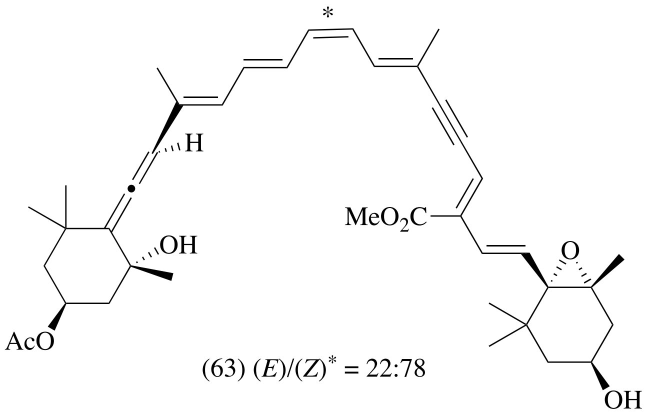
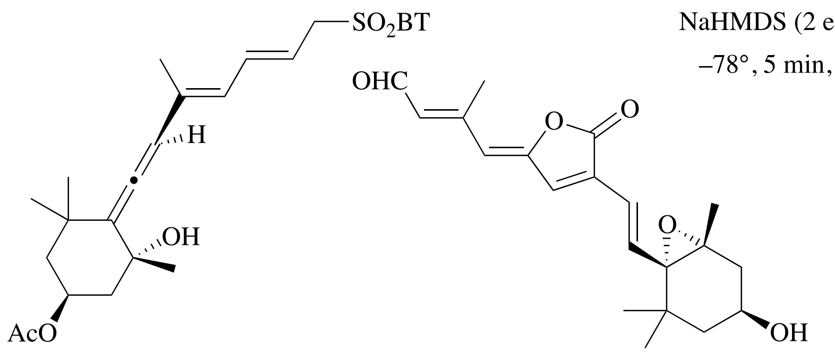
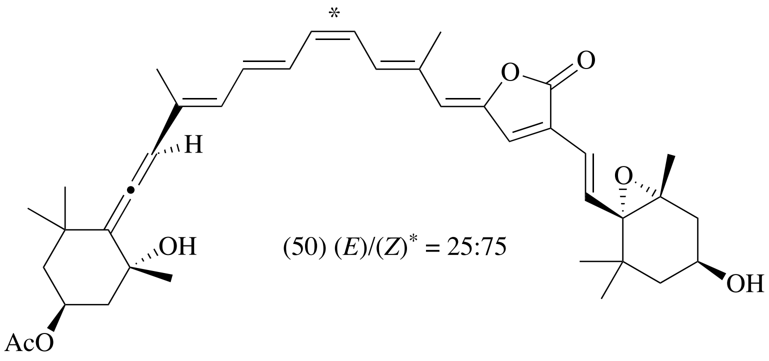
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		NaHMDS (3 eq), THF, –78°, 5 min, dark	 (48) 'mixture of isomers'	606
		NaHMDS (3 eq), THF, –78°, 5 min, dark	 (63) (*E*)/(*Z*)* = 22:78	606
		NaHMDS (2 eq), THF, –78°, 5 min, dark	 (50) (*E*)/(*Z*)* = 25:75	607 77

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

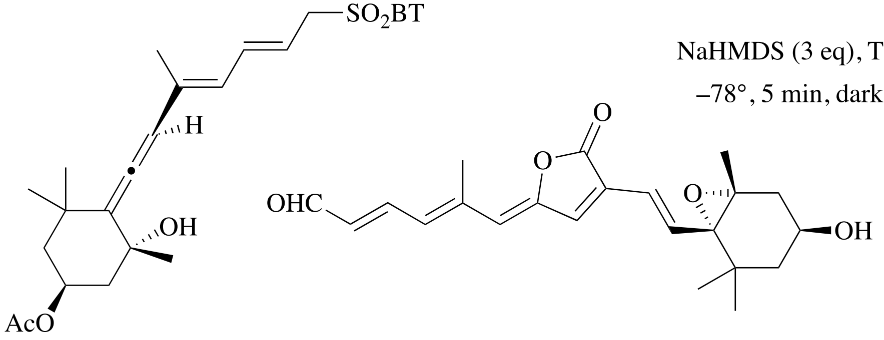
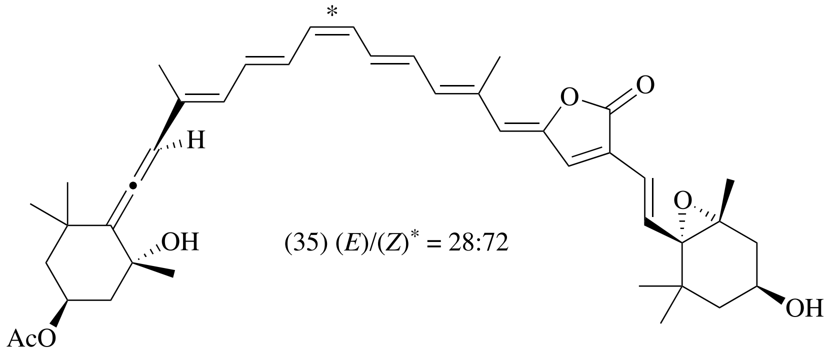
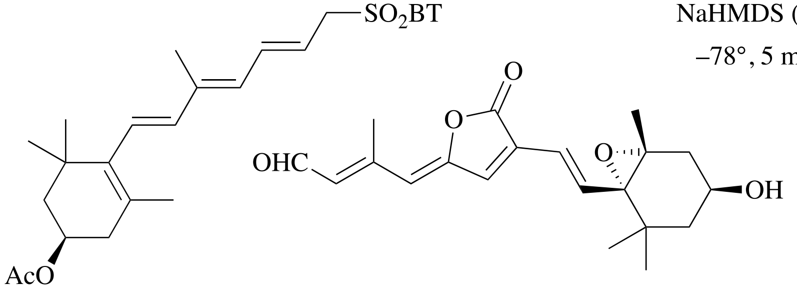
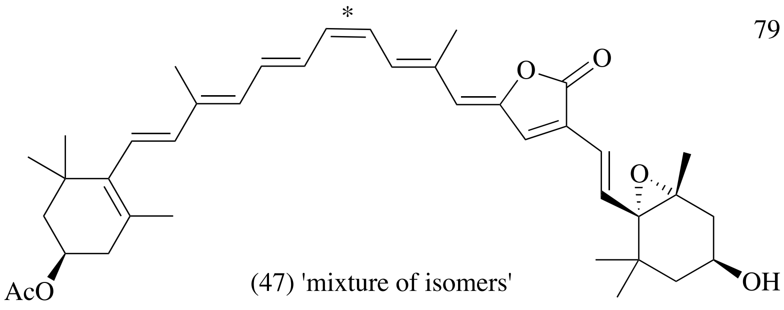
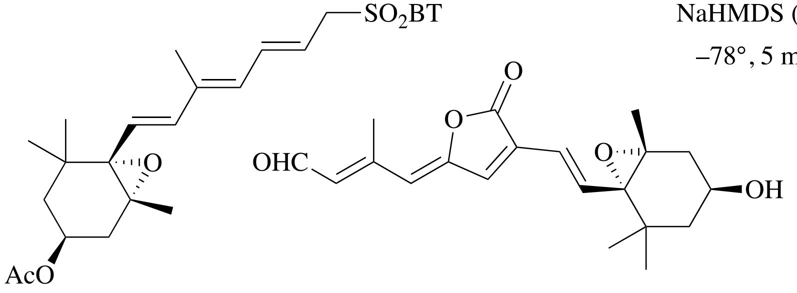
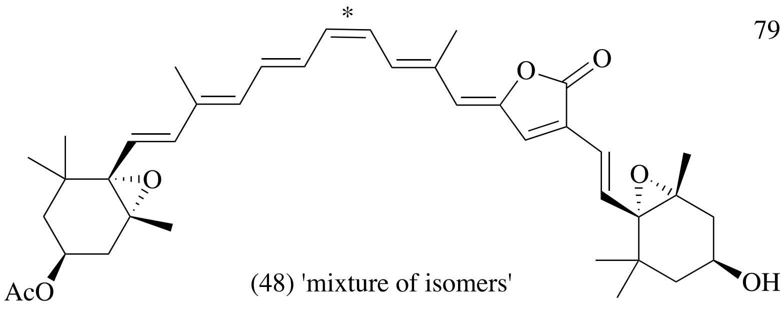
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		NaHMDS (3 eq), THF, –78°, 5 min, dark	 (35) $(E)/(Z)^{*} = 28:72$	601
		NaHMDS (3 eq), THF, –78°, 5 min, dark	 (47) 'mixture of isomers'	79
		NaHMDS (3 eq), THF, –78°, 5 min, dark	 (48) 'mixture of isomers'	79

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

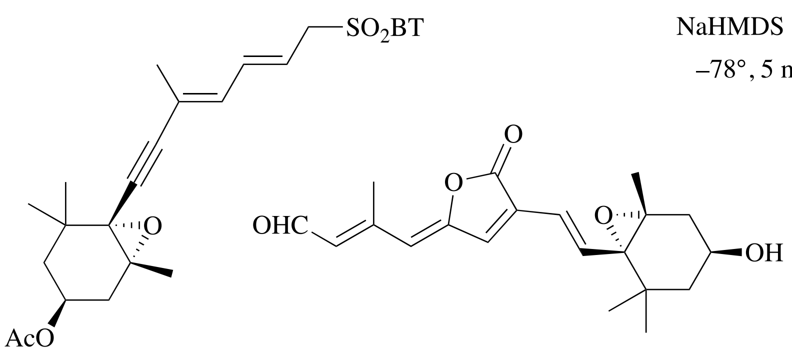
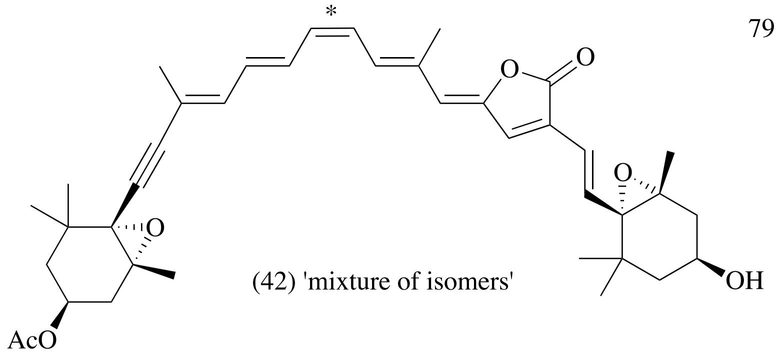
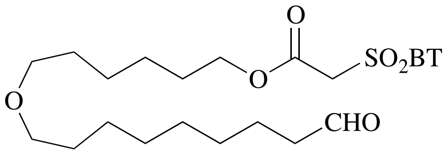
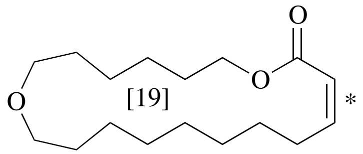
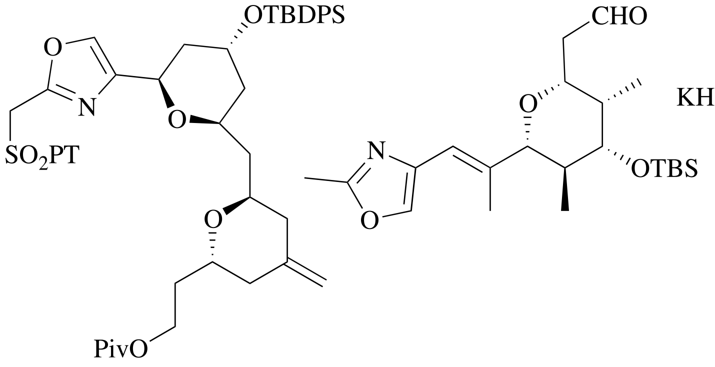
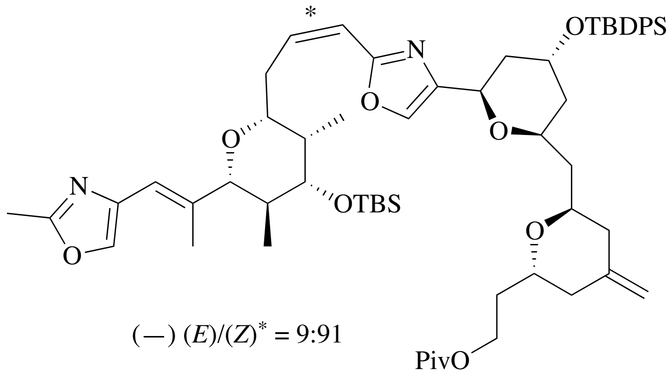
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		NaHMDS (2.7 eq), THF, –78°, 5 min, dark	 (42) 'mixture of isomers'	79
		syringe pump addition to DBU, CH_2Cl_2, –78° to rt, 14 h	 (43) (*E*)/(*Z*)* = 15:85	146
C_{18}		KHMDS, DME, –65 to 0°	 (—) (*E*)/(*Z*)* = 9:91	497

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

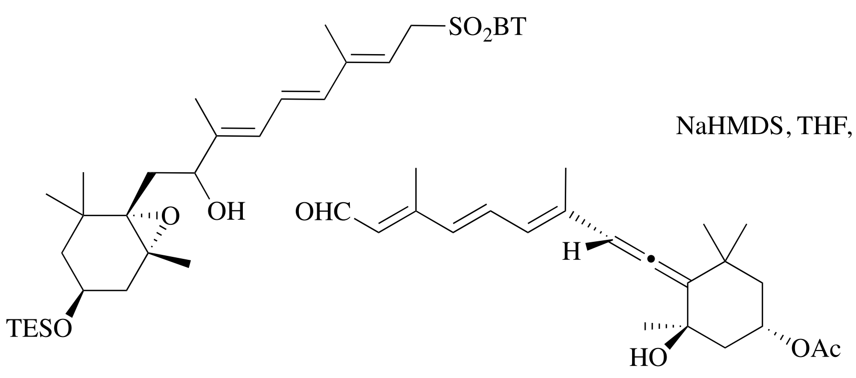
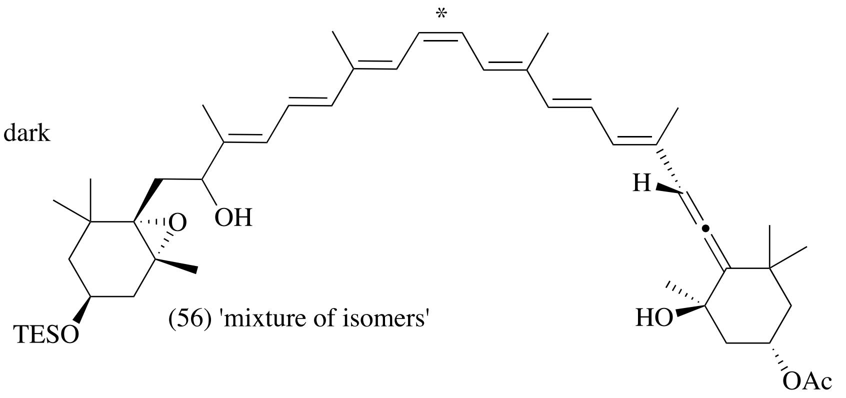
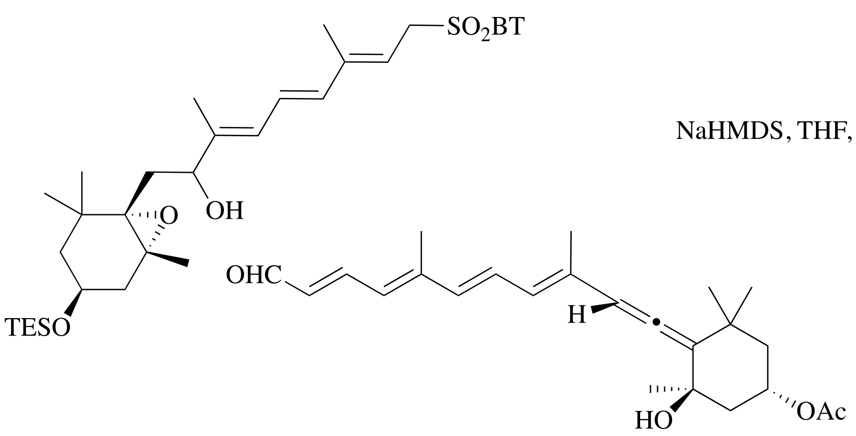
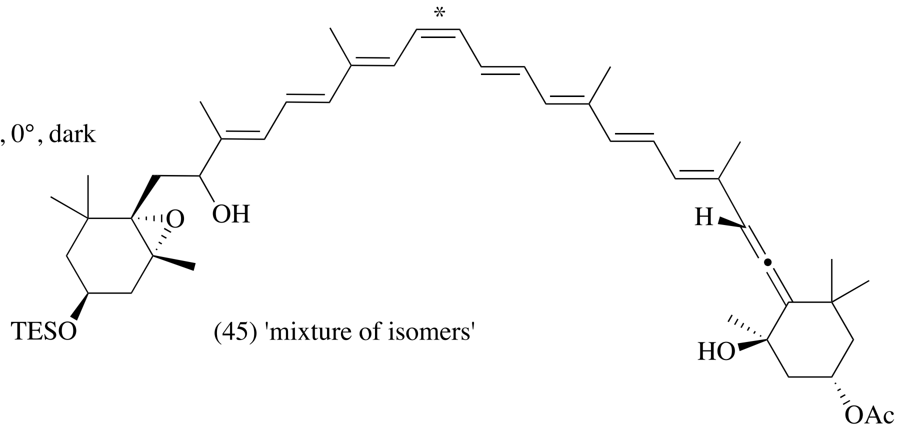
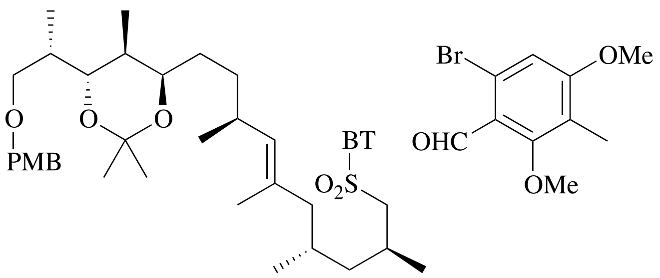
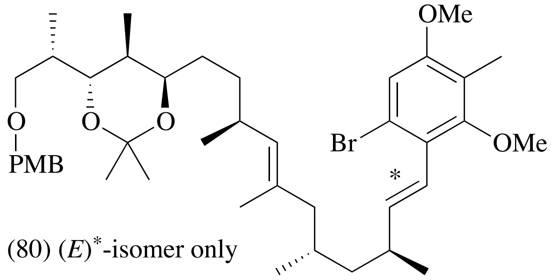
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}		NaHMDS, THF, 0°, dark	 (56) 'mixture of isomers'	608
		NaHMDS, THF, 0°, dark	 (45) 'mixture of isomers'	608
C_{21}		1. LDA, THF, –78°, 25 min 2. Aldehyde, THF; rt, 1 h	 (80) $(E)^*$-isomer only	609

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

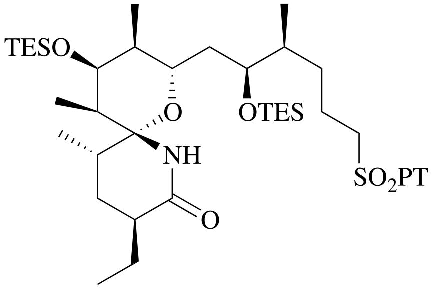
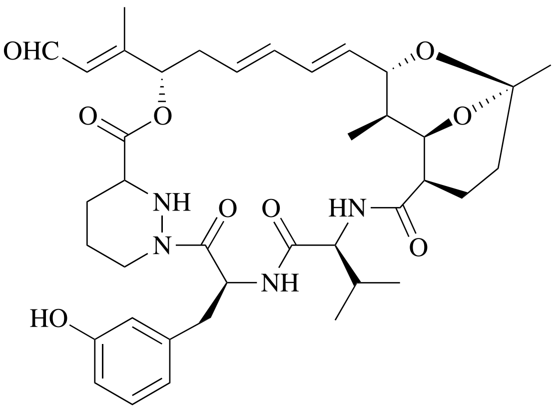
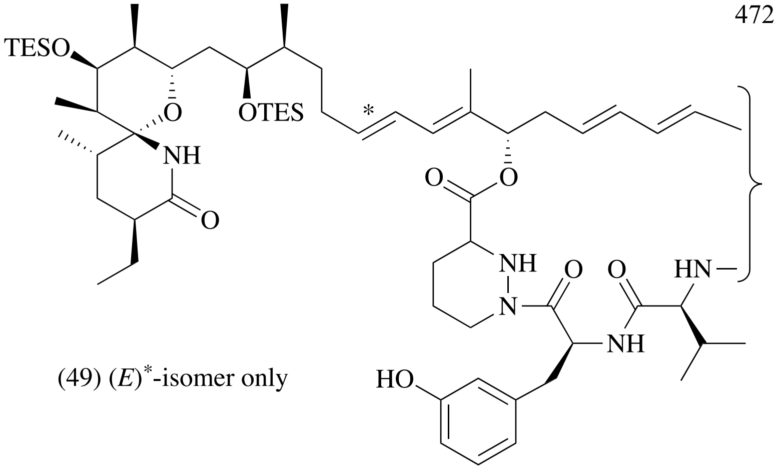
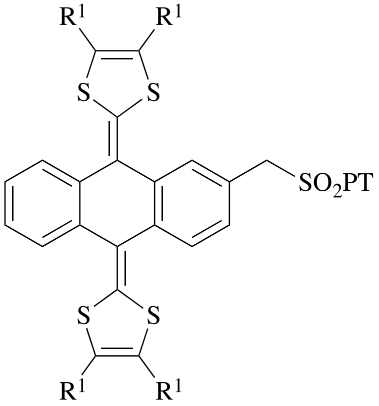
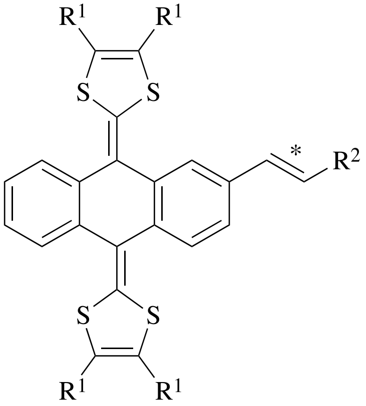
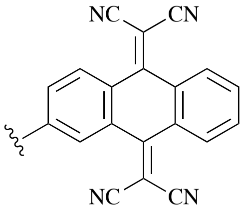
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}				
	 	NaHMDS, DME, –78°, 8 h	 (49) $(E)^*$-isomer only	472
	 R^2CHO	1. NaHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 3 h	 R^1 R^2 Yield of $(E)^*$-isomer H Ph (71) SMe  (94)	610

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

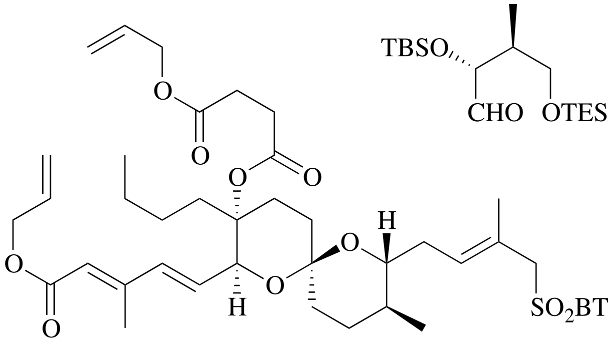
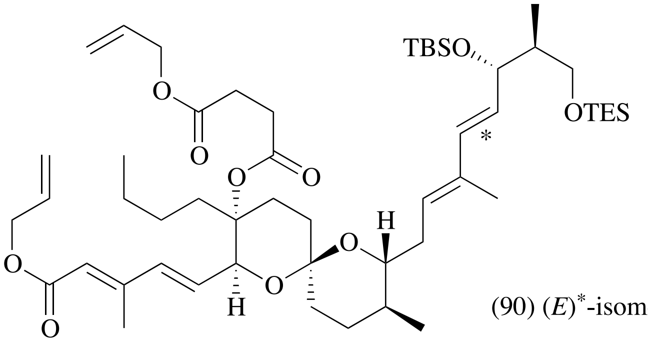
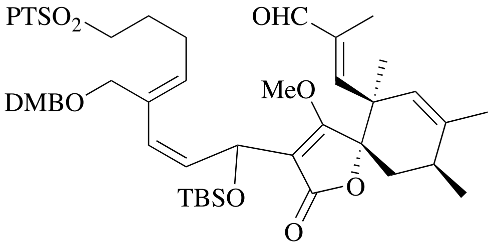
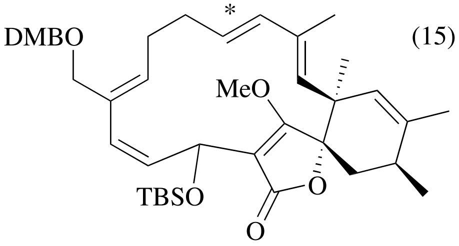
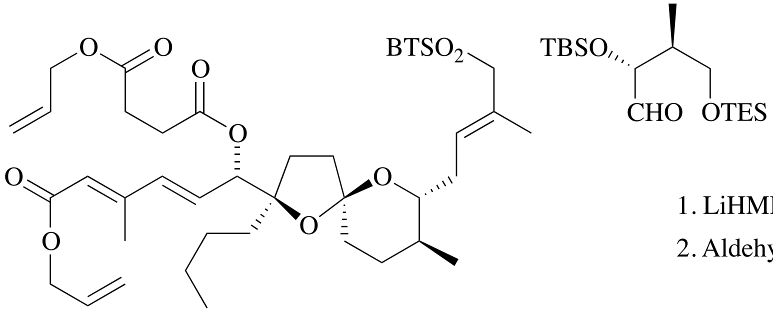
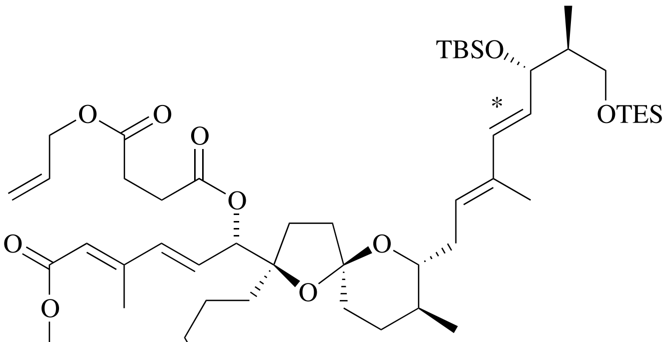
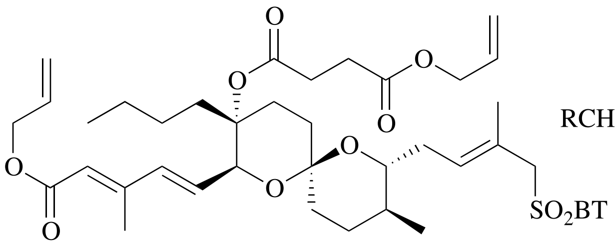
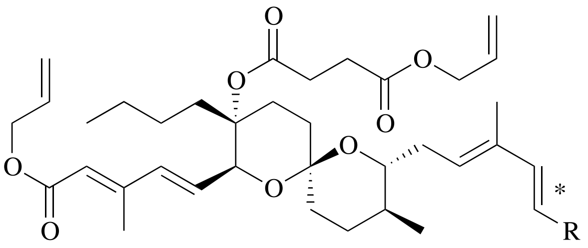
	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24}		LiHMDS, THF, –78° to rt	 (90) (E)*-isomer only	611
C_{25}		KHMDS, THF, –78°, 0.5 h; rt, 1.5 h	 (15) (E)/(Z)* = 100:0	612
		1. LiHMDS, THF, –78° 2. Aldehyde, –78 to 0°	 (56) (E)*-isomer	613

TABLE 3. SYNTHESIS OF CONJUGATED 1,2-DISUBSTITUTED ALKENES

	Sulfone and Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{25}				
	 RCHO	$MN(SiMe_3)_2$, THF, –78°		614 615

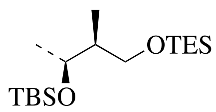
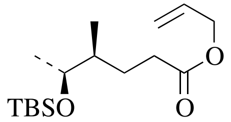
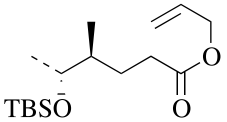
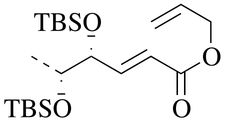
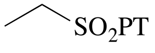
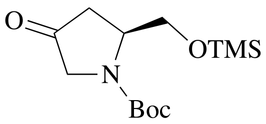
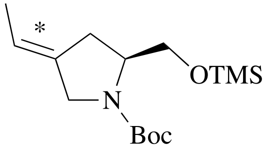
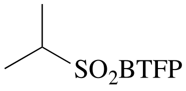
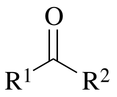
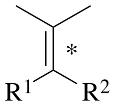
R	M		(*E*)/(*Z*)*
	Li	(90)	—
	K	(55)	—
	Li	(72)	—
	Li	(41)	—

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_2			1. LDA, THF, –78°, 10 min 2. Ketone, –78°, 30 min		(50) (*E*)/(*Z*)* = 67:33	616
C_3			Sulfone (2 eq), carbonyl (1 eq), base (≥2 eq), THF, 12 h			92

R^1	R^2	Base	Temp	
6-MeO-2-naphthyl	H	KOH, Bu_4NBr	rt	(71)
6-MeO-2-naphthyl	H	KHMDS	rt	(<5)
6-MeO-2-naphthyl	H	BEMP	rt	(<5)
6-MeO-2-naphthyl	H	P4-*t*-Bu	rt	(95)
(*E*)-PhCH=CH	H	P4-*t*-Bu	rt	(89)
$Ph(CH_2)_2$	H	P4-*t*-Bu	rt	(52)
n-C_9H_{19}	H	P4-*t*-Bu	rt	(67)

R^1	R^2	Base	Temp	
4-ClC_6H_4	4-ClC_6H_4	KOH	rt	(<5)
4-ClC_6H_4	4-ClC_6H_4	P4-*t*-Bu	0° to rt	(30)
4-ClC_6H_4	4-ClC_6H_4	P4-*t*-Bu	rt to reflux	(71)
4-ClC_6H_4	Ph	P4-*t*-Bu	rt to reflux	(70)
Ph	Ph	P4-*t*-Bu	rt to reflux	(40)
4-$MeOC_6H_4$	4-$MeOC_6H_4$	P4-*t*-Bu	rt to reflux	(10)
$–(CH_2)_2C(OCH_2CH_2O)(CH_2)_2–$		P4-*t*-Bu	rt to reflux	(35)

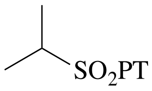
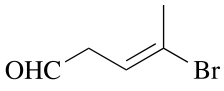
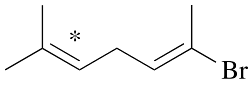
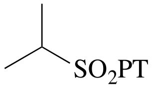
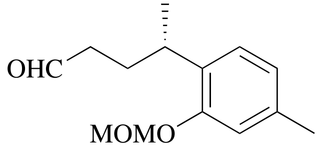
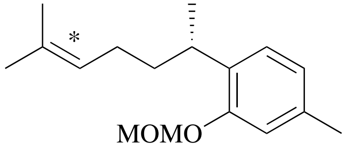
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. LiHMDS, THF, –78°, 35 min 2. Aldehyde, –78° to rt, 16 h		(70)	617
			1. LiHMDS, THF, –78° 2. Aldehyde; rt		(88)	618

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

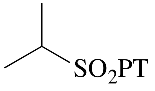
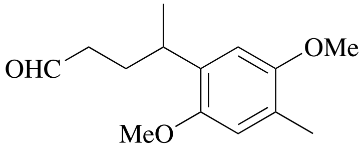
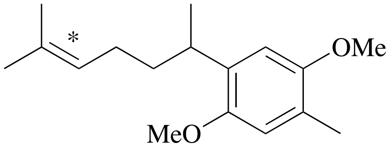
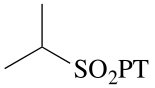
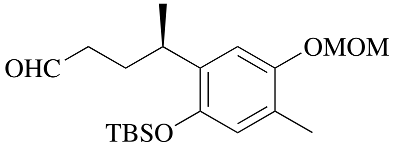
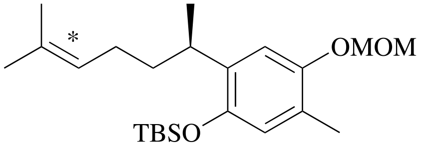
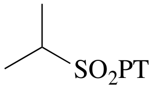
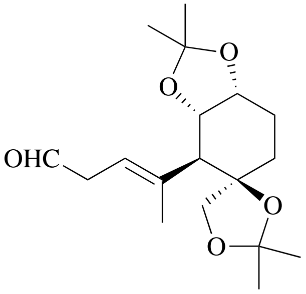
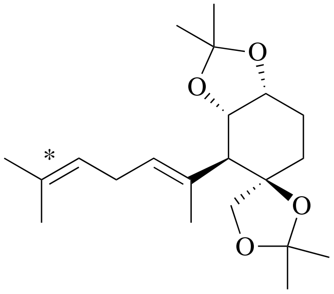
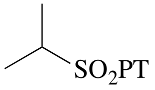
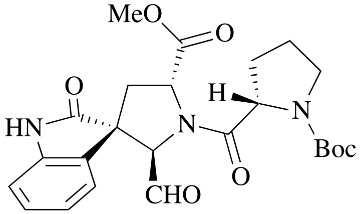
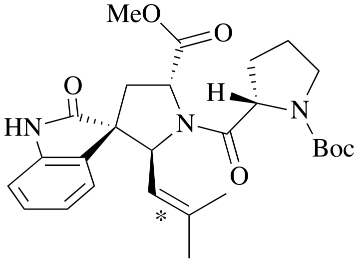
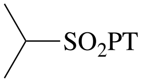
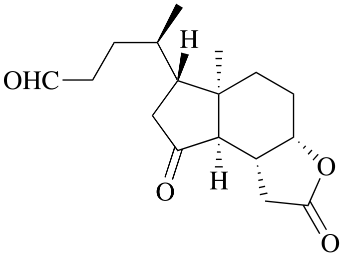
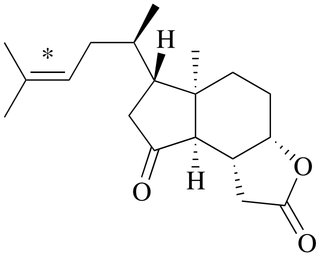
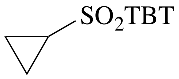
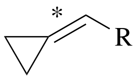
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_3			1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, THF, –78°, 3 h; rt		(88)	163
			LiHMDS, THF, –78° to rt		(98)	619
			1. LiHMDS, THF, –78°, 30 min 2. Aldehyde, –78°, 2 h; rt, 3 h		(>42)	620
			1. LiHMDS (2.3 eq), THF, –78°, 30 min 2. Aldehyde, –78°, 3 h; rt, 8 h		(78)	83

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_3			1. LiHMDS, THF, –78°, 1 h 2. Aldehyde, 50 min		(68)	621
		RCHO	Cs_2CO_3, THF-DMF, 70°, 40 h			84

R		R	
$4\text{-}PhC_6H_4$	(76)	$2\text{-}Br\text{-}4,5\text{-}(MeO)_2C_6H_2$	(59)
$4\text{-}BnOC_6H_4$	(56)	$4\text{-}MeO_2CC_6H_4$	(60)
$3\text{-}BnOC_6H_4$	(66)	$2\text{-}(CH_2CHCH_2)O\text{-}3\text{-}MeOC_6H_3$	(80)
$3,4\text{-}(MeO)_2C_6H_3$	(62)	$TBSO(CH_2)_3$	(43)
$2,5\text{-}(MeO)_2C_6H_3$	(64)		

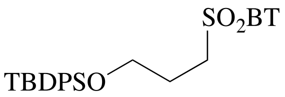
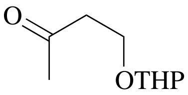
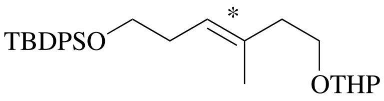
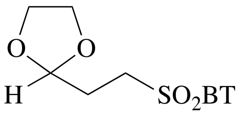
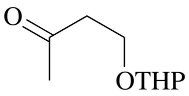
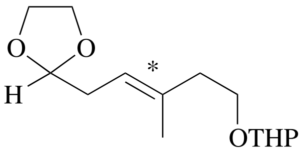
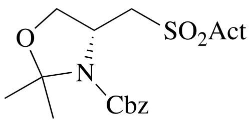
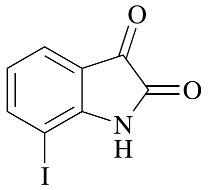
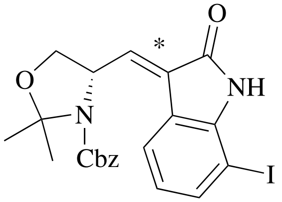
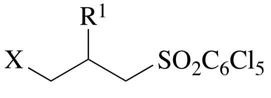
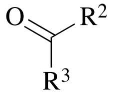
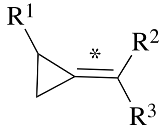
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
			LiHMDS, THF, –78°, 1.5 h		(91) (*E*)/(*Z*)* = 50:50	622
			LiHMDS, THF, –78°, 2 h		(100) (*E*)/(*Z*)* = 67:33	622

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_3			Barbier conditions. See table.		(≥79)	623 624

Act	Base	Solvent	Temp	$(E)/(Z)^*$
PT	NaHMDS	THF	–78°	50:50
PT	LiHMDS	DMF-DMPU	–45°	66:34
BT	NaHMDS	THF	–78°	50:50
BT	LiHMDS	DMF-DMPU	–78°	71:29
BT	LiHMDS	DMF-DMPU	–45°	75:25
BT	LiHMDS	DMF-DMPU	0°	83:17

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{3-4}			1. *t*-BuOK, DMF, –30° 2. Carbonyl, *t*-BuOK, –35 to 60°			85

R^1	R^2	R^3	X		$(E)/(Z)^*$
H	H	4-$Me_2NC_6H_4$	Br	(52)	—
H	H	4-$MeOC_6H_4$	Br	(57)	—
H	H	4-MeC_6H_4	Br	(63)	—
H	H	Ph	Br	(54)	—
H	H	4-ClC_6H_4	Br	(55)	—
H	Ph	Ph	Br	(60)	—
Me	H	4-MeC_6H_4	Cl	(47)	23:77
Me	H	4-$MeOC_6H_4$	Cl	(57)	23:77

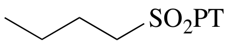
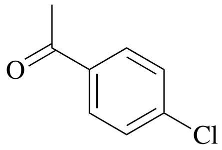
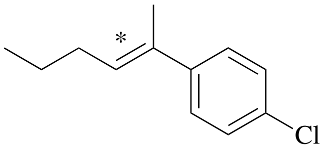
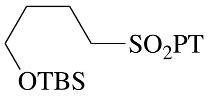
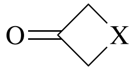
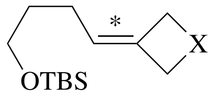
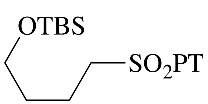
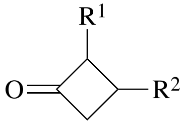
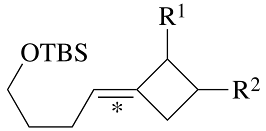
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_4			1. LiHMDS, 12-crown-4 (2 eq) THF, 0.5 min 2. Ketone, –78°, 30 min		(87) $(E)/(Z)^*$ = 72:28	25

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 	NaHMDS, THF, –78°; rt	 X: CPh_2 (51) NC(O)Ph (45) NC(O)O*t*-Bu (74) NTs (>52)	625
	 	**A**: NaHMDS, THF, –78° to rt *or* **B**: LiHMDS, PhMe, –78° to rt		626

R^1	R^2			(*E*)/(*Z*)*
n-C_7H_{15}	H	**A**	(51)	70:30
n-Pr(Ts)N$(CH_2)_3$	H	**A**	(50)	60:40
Ph	H	**B**	(66)	50:50
2-$BnOC_6H_4$	H	**A**	(39)	70:30

R^1	R^2			(*E*)/(*Z*)*
4-$BnOC_6H_4$	H	**A**	(32)	56:44
2,4-$Cl_2C_6H_3$	H	**B**	(75)	50:50
4-$MeO_2CC_6H_4$	H	**B**	(37)	50:50
(*R*)-Ph	(*R*)-Ph	**B**	(49)	45:55

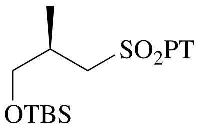
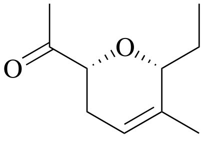
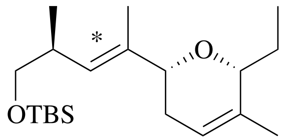
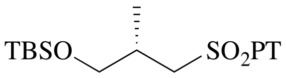
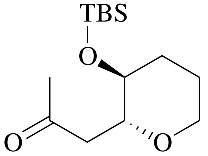
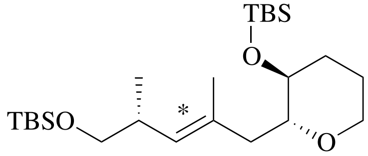
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	LiHMDS, CH_2Cl_2	 (—) (*E*)/(*Z*)* = 75:25	430
	 	1. LDA, THF, –78° 2. Ketone, Additive, THF –78 to 0°, 70 min	 Additive: $CeCl_3$ (80) (*E*)/(*Z*)* 62:38 none (38) 50:50	86

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

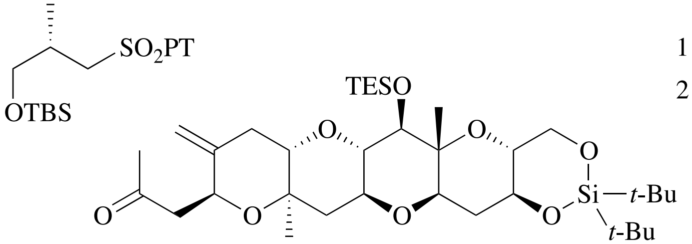
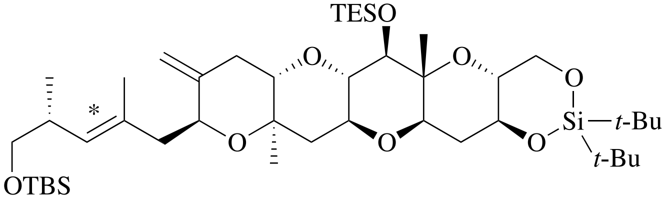
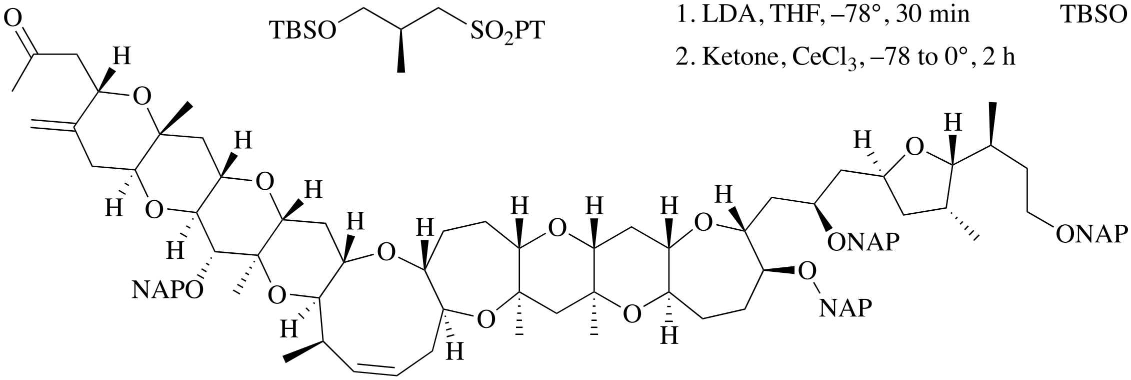
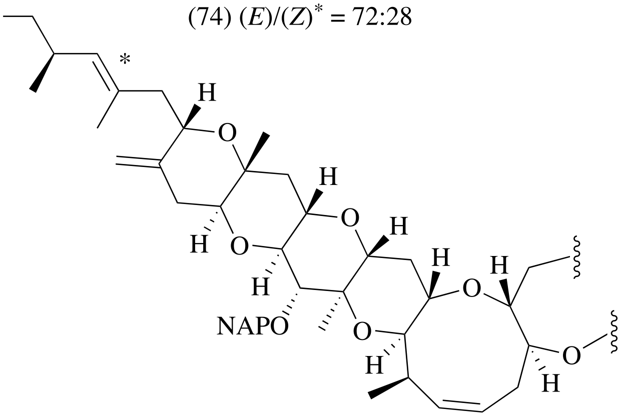
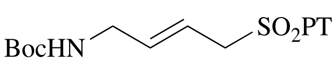
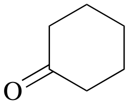
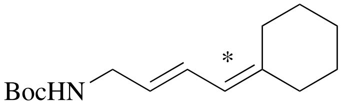
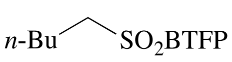
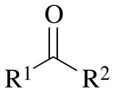
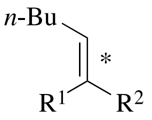
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4		1. LDA, THF, -78° 2. Ketone, $CeCl_3$, THF –78 to 0°, 2 h	 (76) (*E*)/(*Z*)* = 76:24	86
		1. LDA, THF, –78°, 30 min 2. Ketone, $CeCl_3$, –78 to 0°, 2 h	 (74) (*E*)/(*Z*)* = 72:28	88
	 	1. KHMDS (2.1 eq), 18-crown-6, THF, –78°, 30 min 2. Sulfone metallate added to ketone, –78°; rt	 (76)	478

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	P4-*t*-Bu, THF, 12 h		92

R^1	R^2	Eq sulfone	Eq base	Temp		$(E)/(Z)^*$
4-ClC_6H_4	4-ClC_6H_4	1.0	2.4	0° to rt	(97)	—
4-ClC_6H_4	4-ClC_6H_4	2.0	1.2	0° to rt	(40)	—
4-ClC_6H_4	Ph	2.0	2.4	0° to rt	(75)	55:45
4-ClC_6H_4	Ph	2.0	2.4	rt to reflux	(77)	40:60
Ph	Ph	2.0	2.4	0° to rt	(40)	—
Ph	Ph	3.0	3.6	0° to rt	(84)	—
c-C_3H_5	*c*-C_3H_5	2.0	2.4	0° to rt	(35)	—
$–(CH_2)_2CH(t\text{-Bu})(CH_2)_2–$		1.0	1.2	0° to rt	(16)	—
$–(CH_2)_2CH(t\text{-Bu})(CH_2)_2–$		2.0	2.4	0° to rt	(60)	—
$–(CH_2)_2C(OCH_2CH_2O)(CH_2)_2–$		1.0	1.2	0° to rt	(26)	—
$–(CH_2)_2C(OCH_2CH_2O)(CH_2)_2–$		2.0	2.4	0° to rt	(90)	—

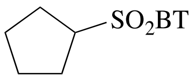
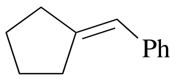
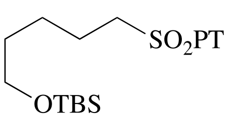
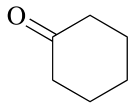
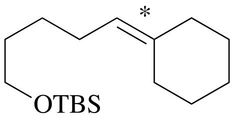
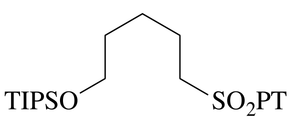
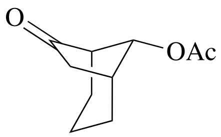
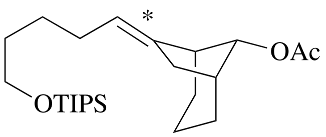
	 PhCHO	LDA, THF, –78°, 3 h; rt, 1h	 (38)	3
	 	NaHMDS, THF, –78°, 30 min	 (74)	627
	 	LiHMDS, THF, –10°	 (87) $(E)/(Z)^*$ = 50:50	628

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

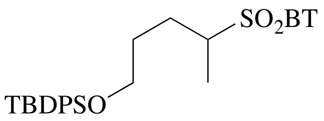
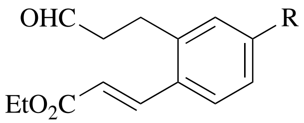
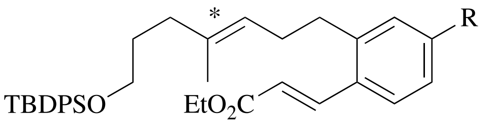
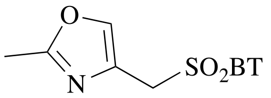
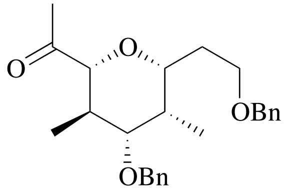
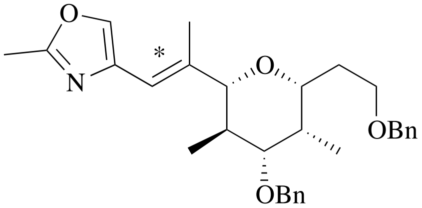
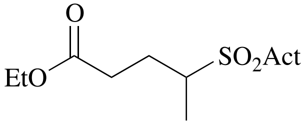
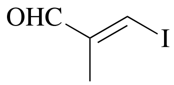
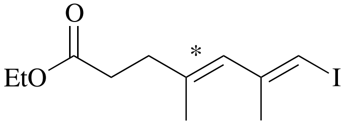
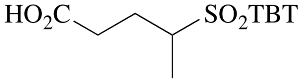
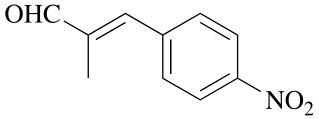
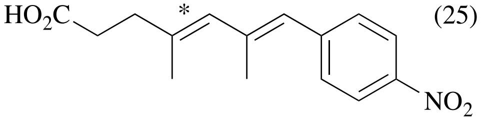
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5	 	NaHMDS, THF, –78° to rt, 12 h	 R = H, OMe (38-55) (*E*)/(*Z*)* = 60:40	629
	 	NaHMDS, THF, –78° to rt, 4 h	 (70) (*E*)/(*Z*)* = 90:10	630
	 	KHMDS, DME, –60°, 3 h	 Act (*E*)/(*Z*)* PT (48) 73:27 TBT (60) 63:37	631
	 	KHMDS, DME, –60°	 (25) (*E*)/(*Z*)* = 62:38	632

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

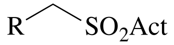
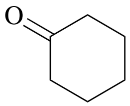
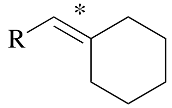
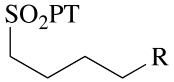
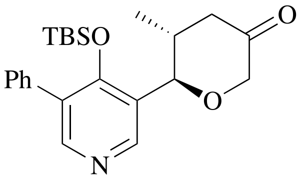
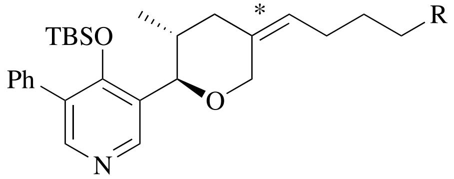
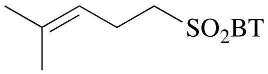
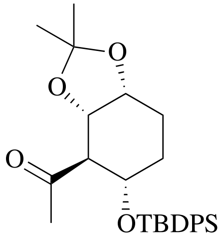
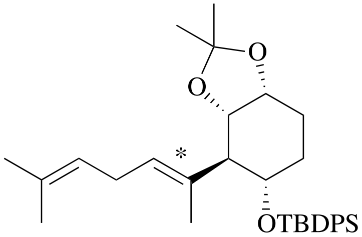
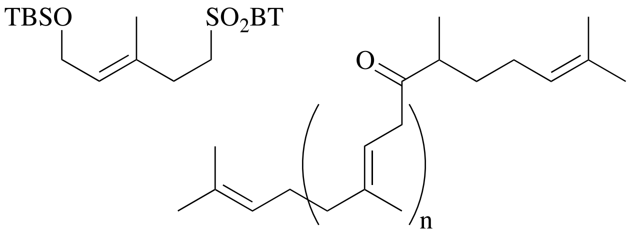
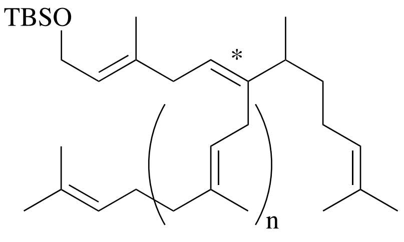
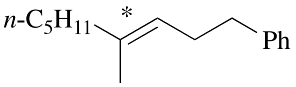
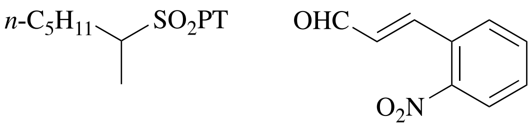
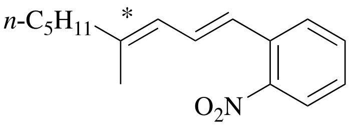
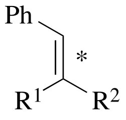
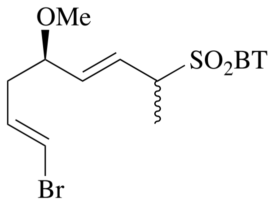
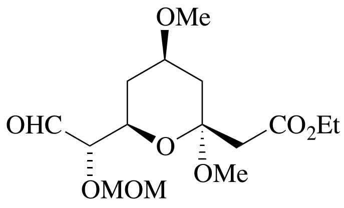
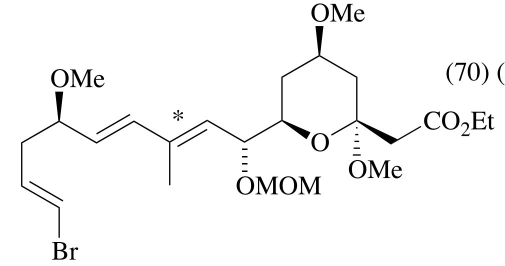
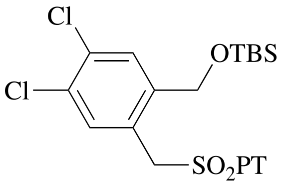
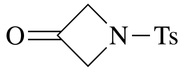
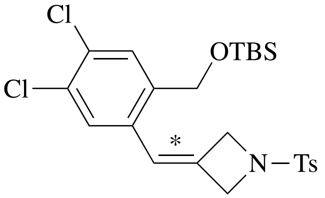
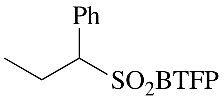
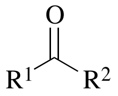
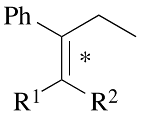
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-9}			**A**: 1. LDA, THF, –78°, 1 h 2. Ketone, –78°, 3 h; rt *or* **B**: LDA, THF, –78°, 3 h; rt, 1 h [a] Lithiation conducted with *n*-BuLi. [b] Acetone used in place of cyclohexanone.	 R Act Me$_2$C=CH BT **A** (56) Me$_2$C=CH BT **B** (68) Me$_2$C=CH PYR **A**[a] (43) Ph BT **A** (61) Ph PYM **A** (81) (*E*)-PhCH=CH BT **A**[b] (51) (*E*)-PhCH=CH BT **A** (40) (*E*)-PhCH=CH PYM **A** (50)	3
C_{5-14}			1. LiHMDS, DME, –78°, 15 min 2. Ketone, –78°, 30 min	 R (*E*)/(*Z*)* Me (—) — (*R*)-EtMeCHCH$_2$ (69) 50:50 (*S*)-EtMeCHCH$_2$ (69) 50:50 *n*-C$_{10}$H$_{21}$ (—) —	633 634
C_6			LiHMDS, THF, –78°, 1.5 h; rt, 10 min	 (87) (*E*)/(*Z*)* = 14:86	635

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		LiHMDS, THF, –65°, 3 h; rt, 16 h	 Yield of (E)*-isomer: n = 0 (32) n = 1 (24) n = 2 (27)	636
C_7		1. LiHMDS, 12-crown-4 (2 eq) THF, 0.5 min 2. Aldehyde, –78°, 30 min	 (97) (E)/(Z)* = 55:45	25
		1. LiHMDS, 12-crown-4 (2 eq) THF, 0.5 min 2. Aldehyde, –78°, 30 min	 (75) (E)/(Z)* = 55:45	25
		Sulfone (2 eq), ketone (1 eq), P4-t-Bu (2.4 eq), THF, 12 h 0° to rt		92

R^1	R^2	
4-ClC_6H_4	4-ClC_6H_4	(<5)
c-C_3H_5	c-C_3H_5	(50)
–$(CH_2)_2CH(t\text{-}Bu)(CH_2)_2$–		(25)
–$(CH_2)_2C(OCH_2CH_2O)(CH_2)_2$–		(90)

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_8			NaHMDS, THF, –78°		(70) $(E)/(Z)^* = 50:50$	89
C_8			NaHMDS, THF, –78° to rt		(62)	625
C_9			Sulfone (2 eq), carbonyl (1 eq), P4-*t*-Bu (2.4 eq), THF, 12 h			92

R^1	R^2	Temp		$(E)/(Z)^*$
Ph	H	–78° to rt	(77)	30:70
Ph	H	–78°	(50)	15:85
6-MeO-2-naphthyl	H	–78° to rt	(50)	35:65
(*E*)-PhCH=CH	H	–78° to rt	(63)	7:93
4-ClC_6H_4	4-ClC_6H_4	rt to reflux	(<5)	—

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

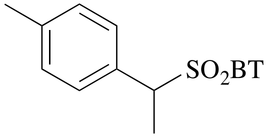
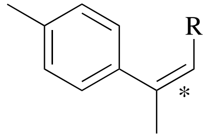
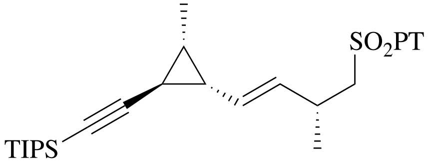
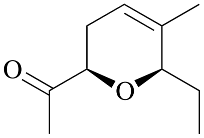
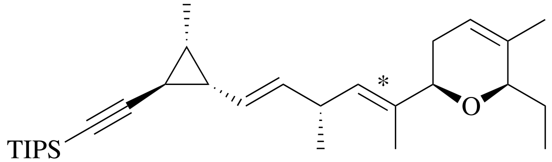
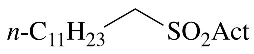
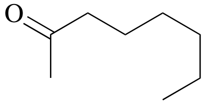
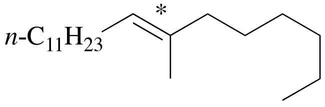
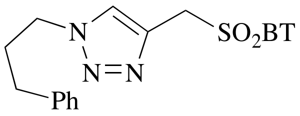
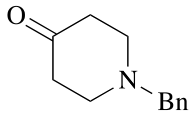
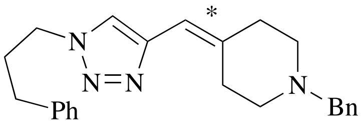
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		RCHO	LDA, THF, –78°; rt, 15 h		90
				R (E)/(Z)* 4-$CO_2MeC_6H_4$ (67) 5:95 4-$CF_3C_6H_4$ (64) 5:95 4-ClC_6H_4 (82) 5:95 4-$NO_2C_6H_4$ (50) 7:93 4-$MeOC_6H_4$ (90) 5:95 4-NCC_6H_4 (38) 8:92	
				R (E)/(Z)* 4-$Me_2NC_6H_4$ (85) 10:90 Ph (75) 5:95 3-Furanyl (97) 5:95 3-Thienyl (68) 5:95 2-Thienyl (81) 5:95	
C_{11}			LiHMDS	 (—) (E)/(Z)* = 75:25	637
C_{12}			LDA, THF, –78°, 1 h; rt, 3 h	 Act (E)/(Z)* BT (60) 34:67 IM (4) 31:69 TZ (15) 22:78 IQ (56) 47:53	20
			LiHMDS, DMF-DMPU, –78°	 (59)	568

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

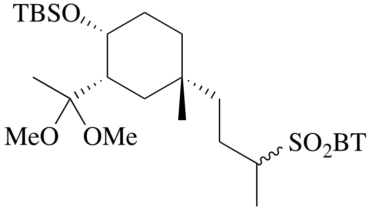
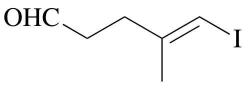
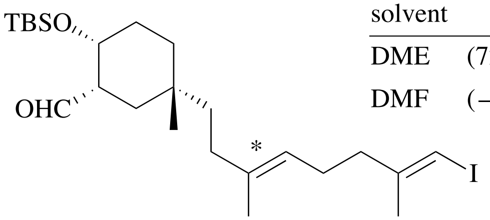
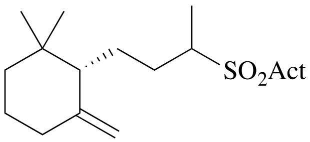
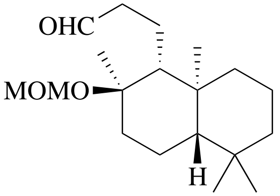
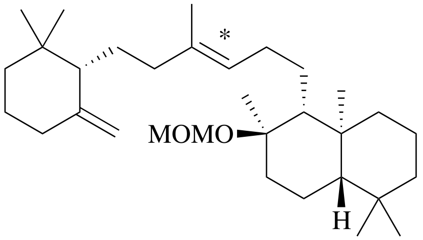
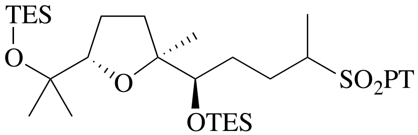
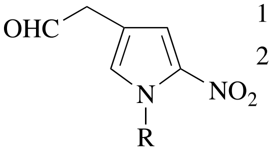
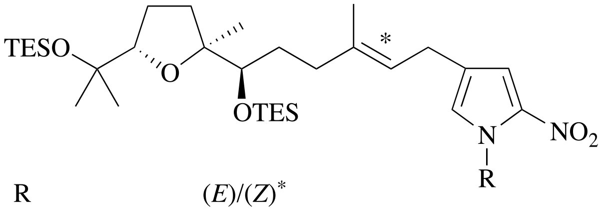
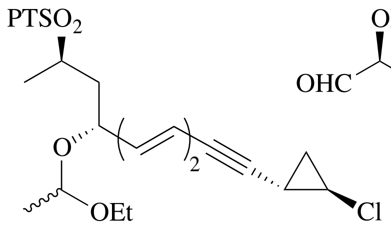
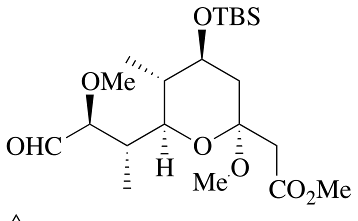
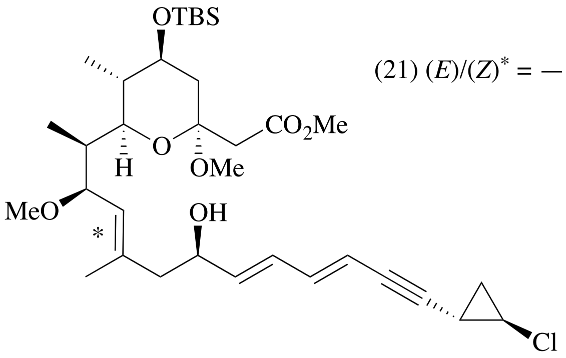
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}	 	1. NaHMDS, solvent, –78° 2. Aldehyde, –78°, 1 h; rt 3. AcOH-THF-H_2O, 45 °C, 8 h	 solvent (*E*)/(Z)* DME (72) 57:43 DMF (—) 33:67	638
C_{13}	 	1. LiHMDS, THF, –78° 20-30 min 2. Aldehyde, 0°, 0.5-1 h	 Act (*E*)/(*Z*)* BT (52) 50:50 PT (89) 50:50	639
	 	1. NaHMDS, THF, –78° 2. Aldehyde, –78° to rt	 R (*E*)/(*Z*)* BOM (42) 53:47 $BzOCH_2$ (30) 53:47	87
	 	1. LiHMDS, THF, –78° 2. Aldehyde, –78° to rt 3. PPTS, MeOH	 (21) (*E*)/(*Z*)* = —	640

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

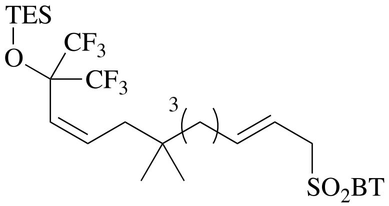
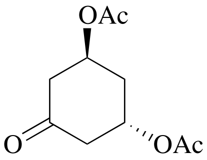
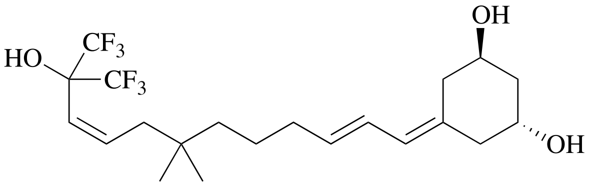
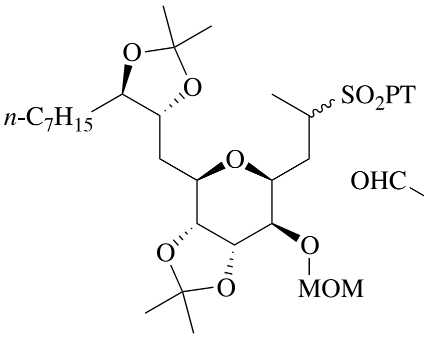
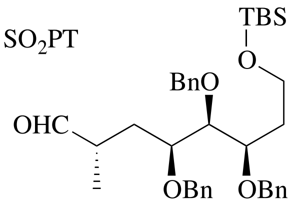
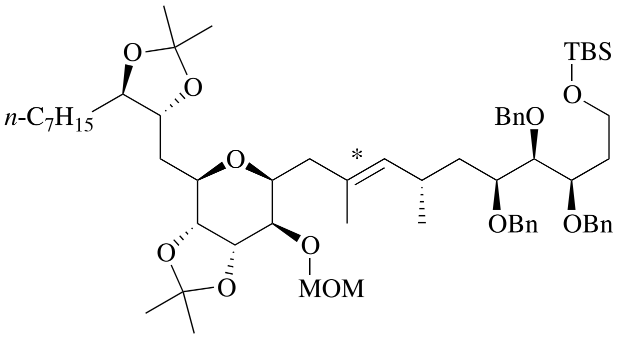
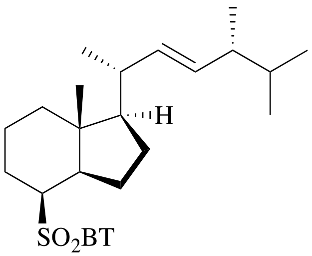
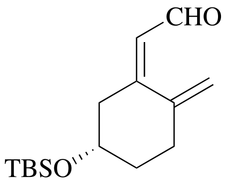
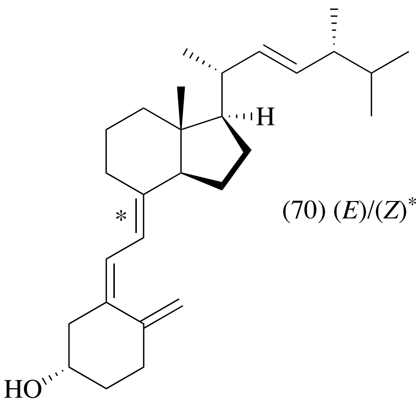
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}	 	1. LiHMDS, THF, –78°, 1.3 h 2. Ketone, –78°, 4 h; rt, 18 h 3. K_2CO_3, MeOH-H_2O, 22 h	 (85)	641
C_{18}	 	1. Base, THF, –78°, 15 min 2. Aldehyde, –78 to –40°, 30 min Base — (*E*)/(*Z*)* LDA (61) 60:40 LiHMDS (43) 50:50 NaHMDS (<5) — KHMDS (<5) —		642
C_{19}	 	1. NaHMDS, Et_2O, –78°, 1 h 2. Aldehyde, –100° to rt, 12 h 3. Bu_4NF, THF, rt, 12 h	 (70) (*E*)/(*Z*)* = 72:28	38

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

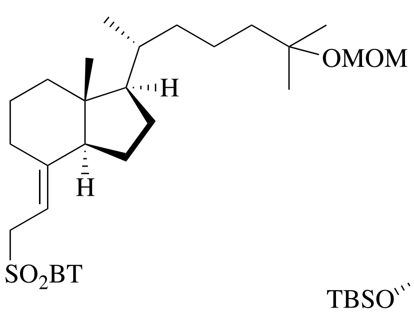
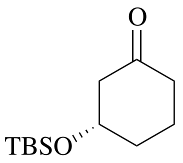
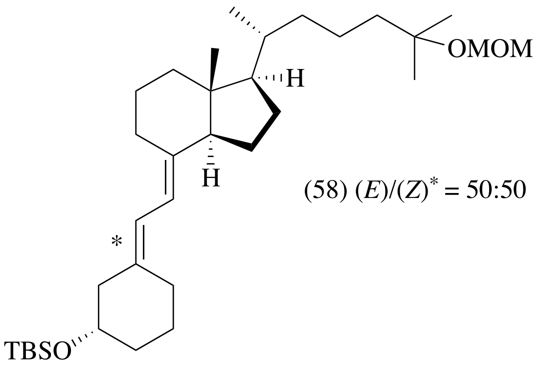
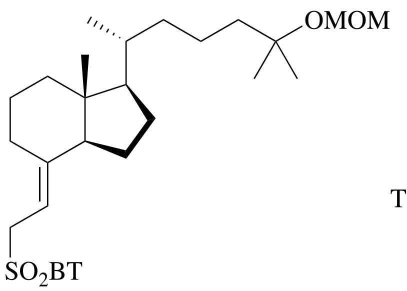
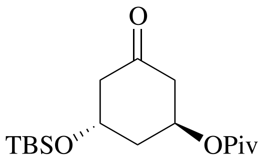
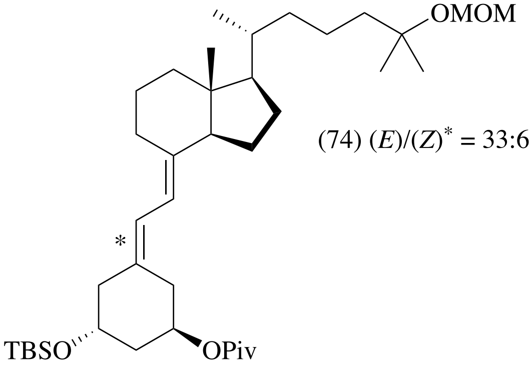
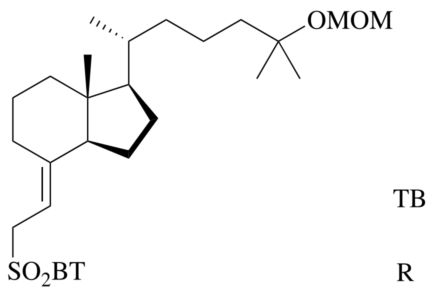
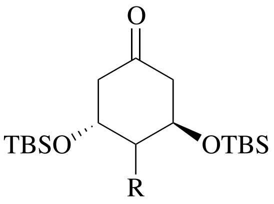
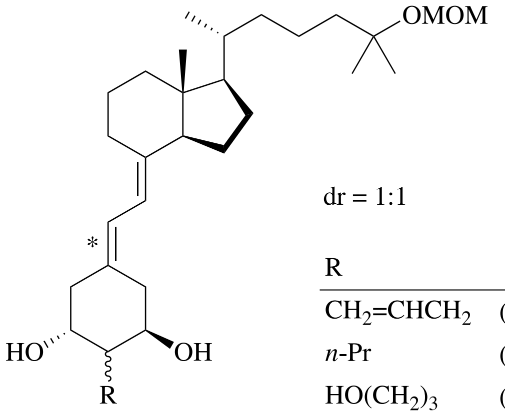
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}				
	 	1. LiHMDS, THF, –78°, 65 min 2. Ketone, –78°, 3 h 3. CSA, MeOH, rt, 20 h	 (58) (*E*)/(*Z*)* = 50:50	643
	 	1. LiHMDS, THF, –78, 30 min 2. Aldehyde, –78 to 0°, 1 h	 (74) (*E*)/(*Z*)* = 33:67	644
	  R CH_2=$CHCH_2$ *n*-Pr TBSO$(CH_2)_3$	1. LiHMDS, THF, –78 to 0° 2. CSA, MeOH	 dr = 1:1 R CH_2=$CHCH_2$ (47) *n*-Pr (51) HO$(CH_2)_3$ (62)	645 646

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

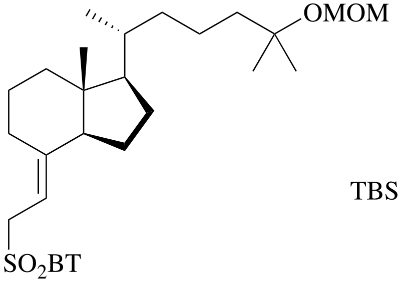
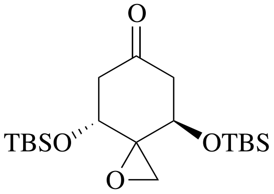
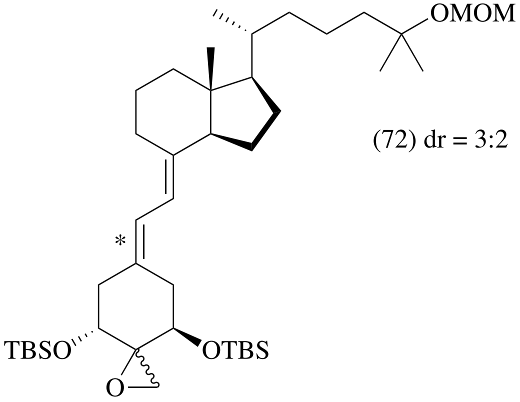
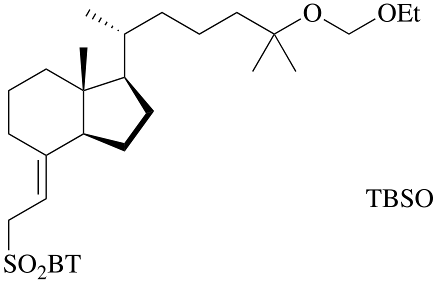
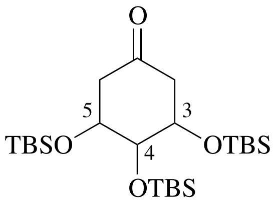
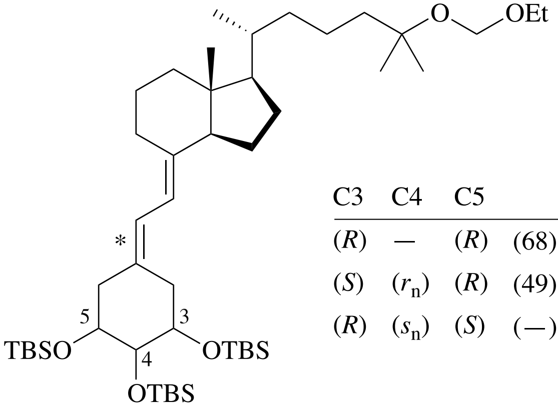
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}	 	1. LiHMDS, THF, –78, 30 min 2. Aldehyde, –78 to 0°, 1 h	 (72) dr = 3:2	644
	 	1. LiHMDS, THF, –50, 2 h 2. Ketone, –50°, 5 h;	 C3 C4 C5 dr (*R*) — (*R*) (68) 76:24 (*S*) (r_n) (*R*) (49) 50:50 (*R*) (s_n) (*S*) (—) 70:30	647

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

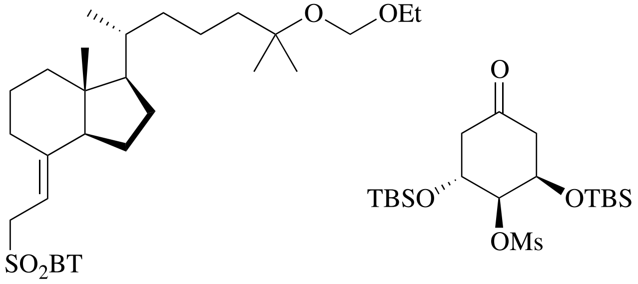
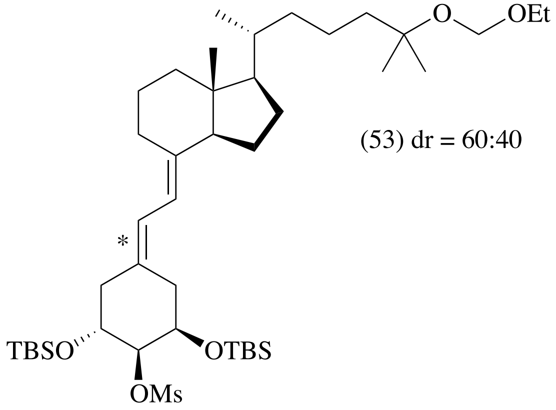
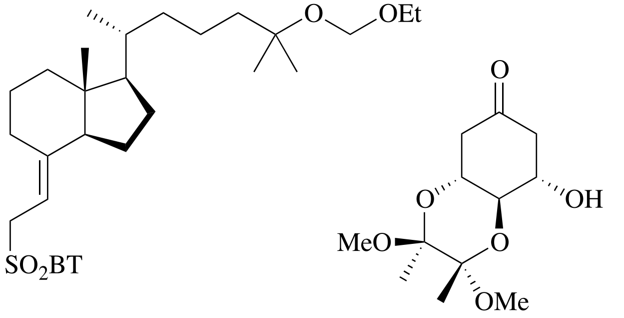
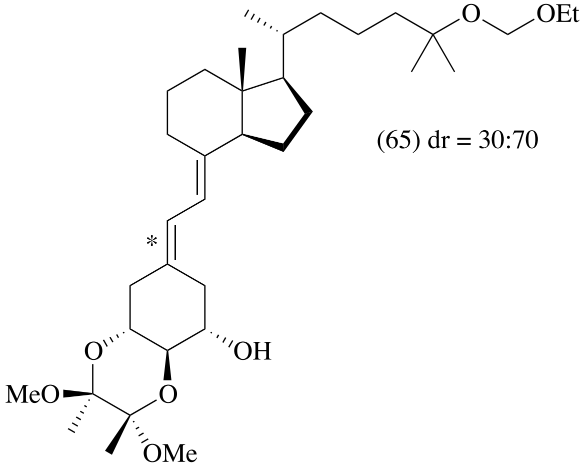
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}				
		1. LiHMDS, THF, –50, 2 h 2. Ketone, –50°, 5 h;	 (53) dr = 60:40	647
		1. LiHMDS, THF, –50, 2 h 2. Ketone, –50°, 5 h	 (65) dr = 30:70	647

TABLE 4. SYNTHESIS OF TRISUBSTITUTED AND TETRASUBSTITUTED ALKENES

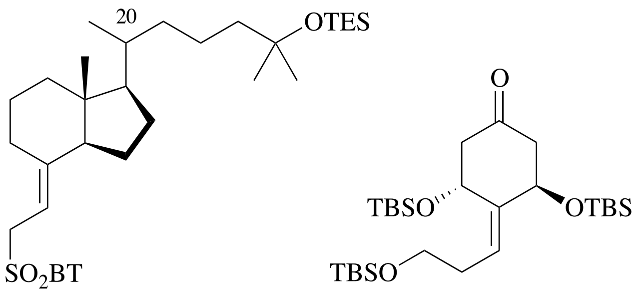
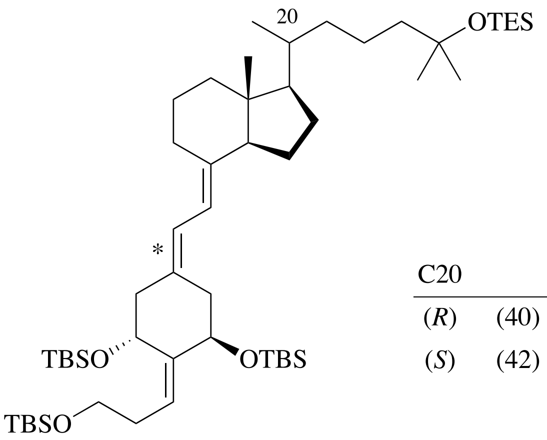
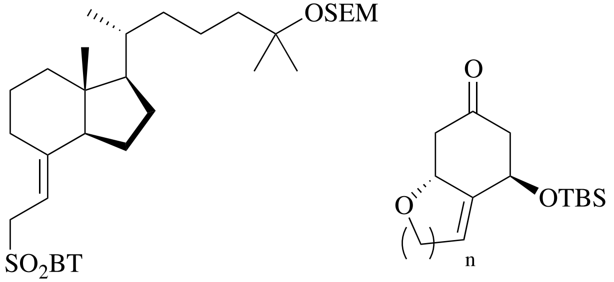
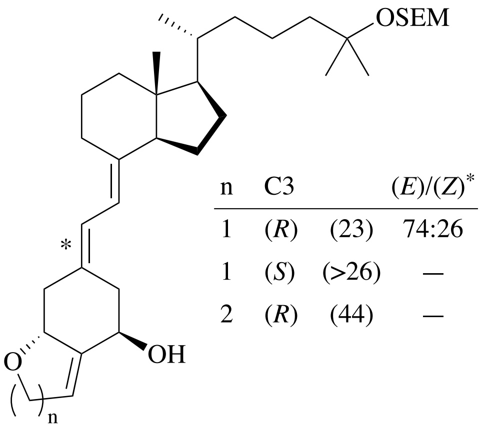
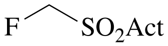
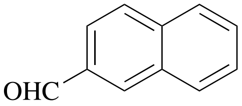
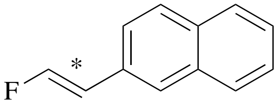
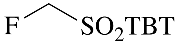
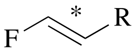
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}				
		1. LiHMDS, THF, –78, 1 h 2. Ketone, –78°, 2 h; –50°, 50 min	 C20 (E)/(Z)* (R) (40) 57:43 (S) (42) 57:43	648
		1. LiHMDS, THF, –78, 20 min 2. Ketone, –78°, 1.5 h; –10°, 1.5 h 3. CSA, MeOH	 n C3 (E)/(Z)* 1 (R) (23) 74:26	649
			1 (S) (>26) —	650
			2 (R) (44) —	651

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1			$MN(SiMe_3)_2$, solvent, temp		93

Act	M	Eq Base	Solvent	Temp		(*E*)/(*Z*)*
BT	Li	2.4	THF	0°	(0)	—
BT	Li	2.4	THF-HMPA	0°	(68)	50:50
PT	Li	2.4	THF	0°	(39)	36:64
PT	Li	2.4	THF-HMPA	0°	(66)	54:46
TBT	Li	2.4	THF	0°	(31)	22:78
TBT	Li	2.4	THF-HMPA	0°	(75)	45:55
TBT	Li	1.5	THF-HMPA	0°	(88)	42:58
TBT	Na	1.5	THF-HMPA	0°	(63)	57:43
TBT	K	1.5	THF-HMPA	0°	(47)	74:26
TBT	Li	1.5	DMF-HMPA	–78°	(>80)	75:25
TBT	Li	1.5	Et_2O-PhMe	0°	(>80)	25:75

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
		RCHO	LiHMDS, THF-HMPA, 0°		93

R		(*E*)/(*Z*)*
4-BnOC_6H_4	(87)	34:66
$2,5\text{-(MeO)}_2C_6H_3$	(90)	47:53
3-BnO-4-MeOC_6H_3	(81)	35:65
$3,4\text{-(OCH}_2\text{O)C}_6H_3$	(78)	34:66
4-PhC_6H_4	(86)	42:58
$2,4\text{-Cl}_2C_6H_3$	(78)	50:50
4-BrC_6H_4	(73)	47:53
$Ph(CH_2)_2$	(51)	48:52

TABLE 5. SYNTHESIS OF VINYL HALIDES

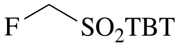
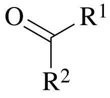
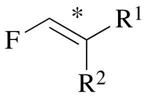
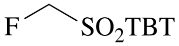
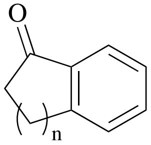
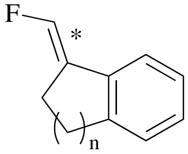
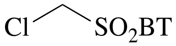
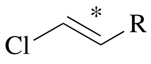
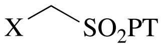
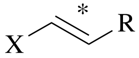
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)					Refs.
C_1			LiHMDS, THF-HMPA, 0°		R^1	R^2		$(E)/(Z)^*$	93
					Ph	Me	(75)	30:70	
					4-$MeOC_6H_4$	Me	(69)	30:70	
					4-MeC_6H_4	Me	(60)	33:67	
					4-ClC_6H_4	Me	(86)	25:75	
					4-BrC_6H_4	Me	(84)	28:72	
					Ph	Ph	(89)	—	
					$Ph(CH_2)_2$	Me	(52)	49:51	
C_1			LiHMDS, THF-HMPA, 0°		n			$(E)/(Z)^*$	93
					1		(67)	76:24	
					2		(66)	59:41	
		RCHO	LDA, THF, –78°, 3 h; rt, 1h		R			$(E)/(Z)^*$	3
					n-C_8H_{17}		(92)	48:52	
					4-$MeOC_6H_4$		(95)	83:17	

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_1						
		RCHO	**A**: LiHMDS, $MgBr_2$•OEt_2, THF, rt, 2 h *or* **B**: LiHMDS, HMPA, THF, rt, 30 min			103

R	X	Method **A**		Method **B**	
			(*E*)/(*Z*)*		(*E*)/(*Z*)*
4-(MeO)C_6H_4	Cl	(69)	94:6	(95)	10:90
4-(MeO)C_6H_4	Br	(—)	—	(70)	5:95
2-MeC_6H_4	Cl	(43)	12:88	(99)	10:90
2-MeC_6H_4	Br	(—)	—	(69)	5:95
4-IC_6H_4	Cl	(38)	27:73	(79)	18:82
4-IC_6H_4	Br	(—)	—	(63)	7:93
2-naphthyl	Cl	(47)	71:29	(86)	9:91
2-naphthyl	Br	(—)	—	(79)	5:95

R	X	Method **B**	
			(*E*)/(*Z*)*
3,4-(OCH_2O)C_6H_3	Cl	(80)	9:91
3,4-(OCH_2O)C_6H_3	Br	(75)	6:94
2-Cl-5-(NO_2)C_6H_3	Cl	(48)	62:38
2-Cl-5-(NO_2)C_6H_3	Br	(73)	55:45
2-Cl-quinol-3-yl	Cl	(62)	52:48
2-Cl-quinol-3-yl	Br	(50)	50:50
(*E*)-PhCH=CH	Cl	(75)	14:86
(*E*)-PhCH=CH	Br	(69)	8:92
Ph(CH_2)$_2$	Cl	(64)	35:65
Ph(CH_2)$_2$	Br	(73)	23:77

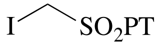
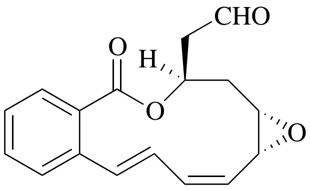
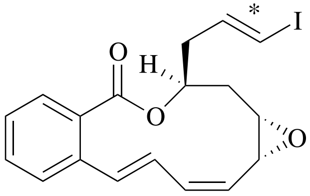
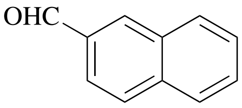
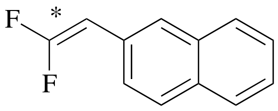
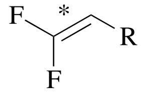
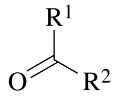
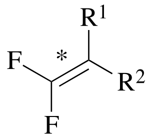
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. NaHMDS, THF, –78°, 5 min 2. Aldehyde, –78° to rt, 12 h		(62) (*E*)/(*Z*)* = 50:50	104
	$ActSO_2CHF_2$		*t*-BuOK, DMF, –50 to –20°, 3 h		Act PYR (92) BT (42) PT (0) TBT (0)	94

TABLE 5. SYNTHESIS OF VINYL HALIDES

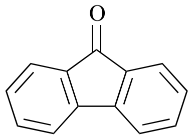
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
	$PYRSO_2CHF_2$ RCHO	Base, DMF, –50 to –20°, 3 h		94

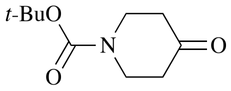
R	Base	
4-$MeOC_6H_4$	*t*-BuOK	(86)
4-*t*-BuC_6H_4	*t*-BuOK	(74)
2,4-$Cl_2C_6H_3$	*t*-BuOK	(72)
3-$NO_2C_6H_4$	*t*-BuOK	(72)
4-$NMe_2C_6H_4$	*t*-BuOK	(91)

R	Base	
4-BrC_6H_4	*t*-BuOK	(72)
3,4-$(OCH_2O)C_6H_3$	*t*-BuOK	(93)
(*E*)-PhCH=CH	*t*-BuOK	(62)
$Ph(CH_2)_2$	LiHMDS	(40)

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PYRSO_2CHF_2$ 	Base, DMF, –50°; –20°, 3 h		94

R^1	R^2	Base	
4-BrC_6H_4	Me	*t*-BuOK	(77)
4-PhC_6H_4	Me	*t*-BuOK	(81)
(*E*)-PhCH=CH	Me	*t*-BuOK	(80)
$Ph(CH_2)_2$	Me	LiHMDS	(72)

Ketone	Base	
	*t*-BuOK	(87)

Ketone	Base	
	*t*-BuOK	(84)

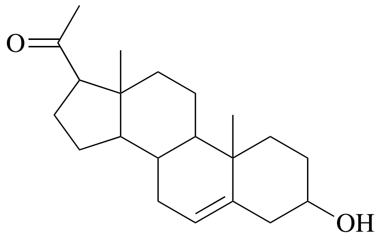
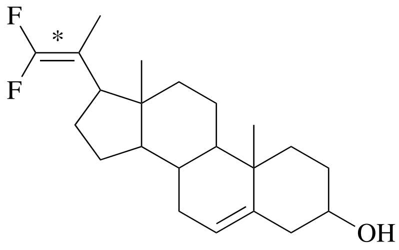
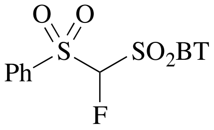
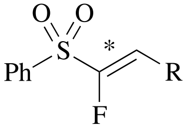
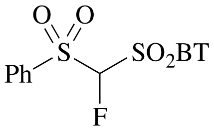
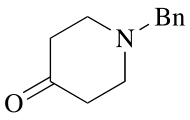
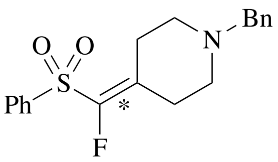
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PYRSO_2CHF_2$ 	LiHMDS, THF, HMPA –78° to rt	 (57)	94

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1	 RCHO	DBU (1.5 eq), solvent, additive, rt		652

R	Solvent	Additive	Time		(*E*)/(*Z*)*
2-naphthyl	CH_2Cl_2	none	120 min	(94)	16:84
Ph	CH_2Cl_2	none	80 min	(90)	16:84
4-$NO_2C_6H_4$	CH_2Cl_2	none	90 min	(85)	22:78
4-$NO_2C_6H_4$	THF	$MgBr_2$	90 min	(84)	29:71
4-ClC_6H_4	CH_2Cl_2	none	70 min	(89)	17:83
4-$MeOC_6H_4$	CH_2Cl_2	none	90 min	(90)	12:88
2-$MeOC_6H_4$	CH_2Cl_2	none	120 min	(75)	48:52
2-$MeOC_6H_4$	THF	$MgBr_2$	120 min	(91)	36:64

R	Solvent	Additive	Time		(*E*)/(*Z*)*
2-thienyl	CH_2Cl_2	none	90 min	(82)	11:89
2-thienyl	THF	$MgBr_2$	90 min	(96)	9:91
ferrocenyl	CH_2Cl_2	none	80 min	(72)	44:56
(*E*)-PhCH=CH	CH_2Cl_2	none	40 min	(87)	13:87
n-C_7H_{15}	CH_2Cl_2	none	90 min	(85)	22:78
n-C_7H_{15}	THF	$MgBr_2$	90 min	(95)	4:96
$Ph(CH_2)_2$	CH_2Cl_2	none	35 min	(66)	23:77
Et_2CH	CH_2Cl_2	none	90 min	(59)	23:77

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	Base, solvent, rt. See table.		652

Base	Solvent	Time	
DBU	CH_2Cl_2	24 h	(47)
DBU	THF	6 h	(65)
LiHMDS	THF	—	(70)

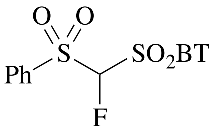
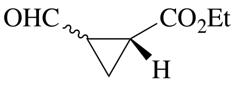
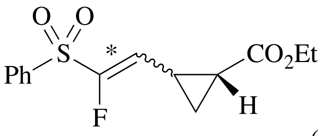
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	  trans:cis = 90:10	DBU, CH_2Cl_2, rt	 (—) (*E*)/(*Z*)* (cis epoxide) = 25:75 (*E*)/(*Z*)* (trans epoxide) = 22:78	652

TABLE 5. SYNTHESIS OF VINYL HALIDES

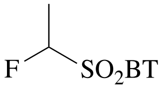
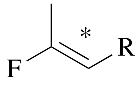
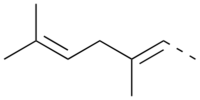
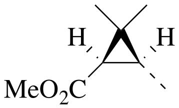
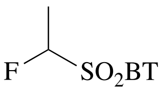
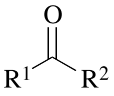
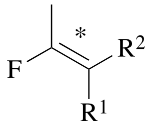
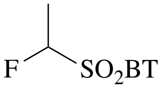
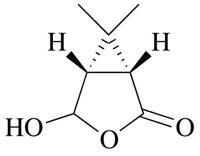
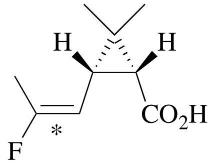
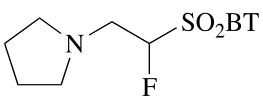
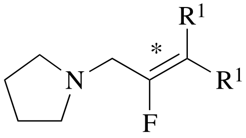
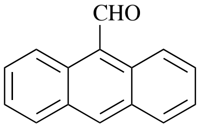
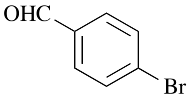
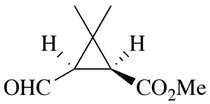
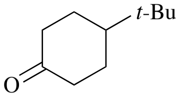
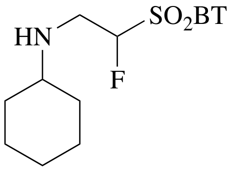
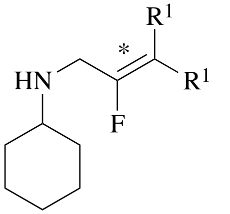
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)					Refs.
C_2		RCHO	**A**: *t*-BuOK, THF, –17°, 30 min *or* **B**: NaHMDS, THF		R			$(E)/(Z)^*$	653
					4-$NO_2C_6H_4$	**A**	(88)	61:39	
					2-$NO_2C_6H_4$	**A**	(86)	63:37	
					4-(HO)-3-(MeO)C_6H_3	**A**	(48)	49:51	
					(*E*)-PhCH=CH	**A**	(55)	62:38	
						**A**	(71)	52:48	
						B	(74)	—	
						**A**	(80)	45:55	
			NaHMDS, THF, –78°, 2 h; rt		R^1	R^2			653
					Ph	Ph	(49)		
					Ph	CF_3	(45)		
					–$(CH_2)_2CH(t\text{-Bu})(CH_2)_2$–		(69)		
			*t*-BuOK, THF, –17°, 30 min		(82) $(E)/(Z)^* = 55:45$				653

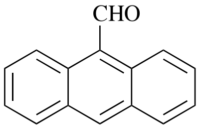
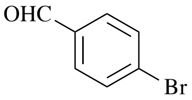
TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2		R^1R^2CO	**A**: *t*-BuOK, –17°, THF, 1 h *or* **B**: NaHMDS, THF, –78 to 0°, 3 h		654

R^1R^2CO			$(E)/(Z)^*$
	**A**	(60)	—
	B	(83)	—
	**A**	(53)	55:45
	B	(70)	60:40

R^1R^2CO			$(E)/(Z)^*$
	**A**	(31)	—
	B	(74)	45:55
	**B**	(73)	40:60
	**A**	(34)	—
	B	(95)	—

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
		R^1R^2CO	**A**: *t*-BuOK, –17°, THF, 1 h *or* **B**: NaHMDS, THF, –78 to 0°, 3 h		654

R^1R^2CO			$(E)/(Z)^*$
	**A**	(68)	15:85
	**A**	(88)	70:30

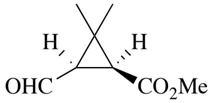
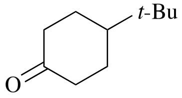
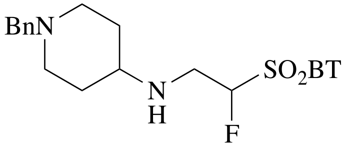
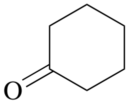
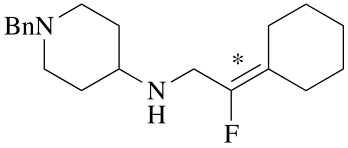
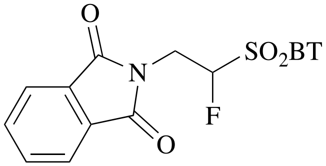
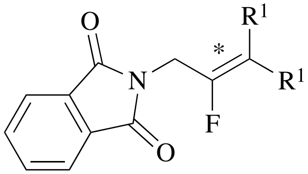
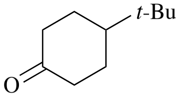
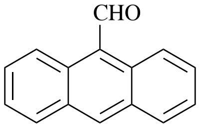
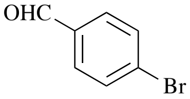
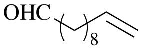
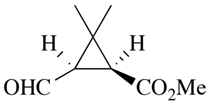
R^1R^2CO			$(E)/(Z)^*$
	**A**	(79)	45:55
	**A**	(62)	40:60
	**A**	(24)	—
	B	(78)	—

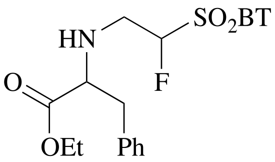
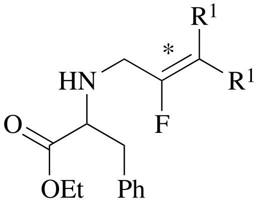
TABLE 5. SYNTHESIS OF VINYL HALIDES

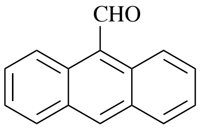
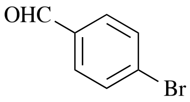
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2	 	NaHMDS, THF, –78°; rt		50
	 R^1R^2CO	**A**: *t*-BuOK, –17°, THF, 1 h *or* **B**: NaHMDS, THF, –78 to 0°, 3 h		654

R^1R^2CO			$(E)/(Z)^*$
TBDPSO$(CH_2)_2$CHO	**A**	(—)	—
BnO$(CH_2)_2$CHO	**A**	(77)	46:54
	**B**	(63)	—

R^1R^2CO			$(E)/(Z)^*$
	**B**	(70)	15:85
	**B**	(56)	10:90

R^1R^2CO			$(E)/(Z)^*$
	**B**	(66)	38:62
	**B**	(50)	52:48

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	 R^1R^2CO	NaHMDS, THF, –78 to 0°, 3 h		654

R^1R^2CO		$(E)/(Z)^*$
	(60)	80:20
	(58)	48:52

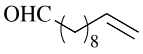
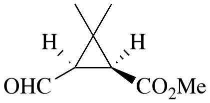
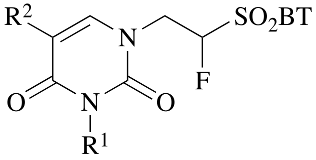
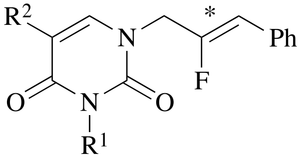
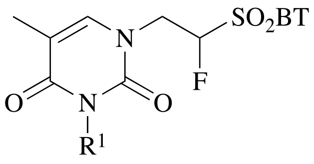
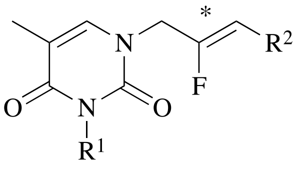
R^1R^2CO		$(E)/(Z)^*$
	(21)	40:60
	(20)	30:70

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2	 PhCHO	NaHMDS, THF, –78 to –20°		50

R^1	R^2		(Z)/(E)*
Bz	Me	(87)	5:95
Bz	H	(69)	6:94
H	F	(69)	47:53
Bz	F	(39)	5:95

	 R^2CHO	NaHMDS, THF, –78° to Temp.		50

R^1	R^2	Temp.		(E)/(Z)*
Bz	4-$MeOC_6H_4$	–20°	(79)	4:96
H	4-$MeOC_6H_4$	20°	(76)	7:93
Bz	4-BrC_6H_4	–20°	(86)	8:92
H	4-BrC_6H_4	20°	(55)	17:83
Bz	4-$NO_2C_6H_4$	–20°	(63)	32:68
Bz	Ph_3C	–20°	(82)	17:83
H	Ph_3C	20°	(65)	15:85
Bz	3-pyridyl	–20°	(61)	16:84
H	3-pyridyl	20°	(66)	12:88
Bz	c-C_6H_{11}	–20°	(83)	28:72
H	c-C_6H_{11}	20°	(57)	21:79
Bz	Me	–20°	(88)	41:59
H	Me	20°	(82)	39:61
Bz	n-C_6H_{13}	–20°	(61)	29:71
H	n-C_6H_{13}	20°	(67)	30:70
Bz	n-C_8H_{17}	–20°	(52)	30:70
H	n-C_8H_{17}	20°	(78)	28:72
Bz	$BnO(CH_2)_3$	–20°	(66)	32:68
H	$BnO(CH_2)_3$	20°	(59)	30:70
Bz	$BnO(CH_2)_4$	–20°	(52)	29:71
H	$BnO(CH_2)_4$	20°	(57)	27:73
Bz	$BnO(CH_2)_5$	–20°	(61)	30:70
H	$BnO(CH_2)_5$	20°	(63)	27:73

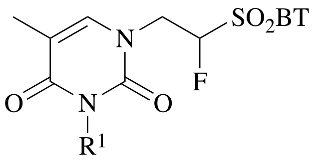
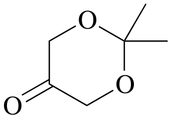
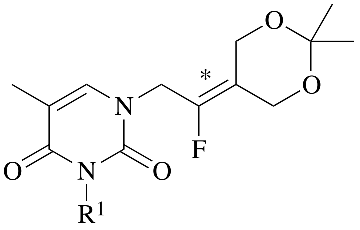
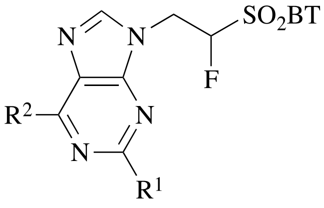
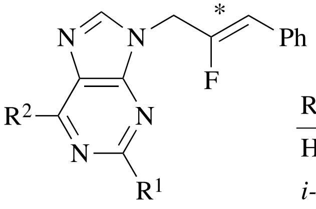
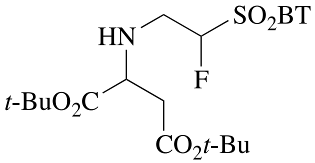
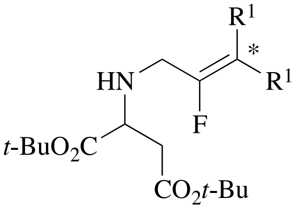
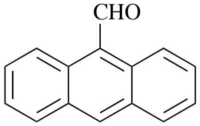
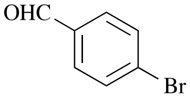
	 	NaHMDS, THF, –78 to –20°	 (60)	50

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
		PhCHO	t-BuOK, THF, –17° to rt		50
		R^1R^2CO	NaHMDS, THF, –78 to 0°, 3 h		654

R^1	R^2		$(Z)/(E)^*$
H	Cl	(61)	55:45
i-PrCONH	OH	(55)	40:60

R^1R^2CO		$(E)/(Z)^*$
	(74)	30:70
	(72)	40:60

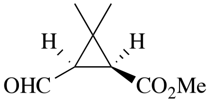
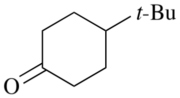
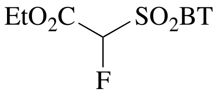
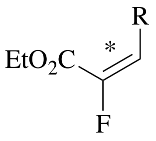
R^1R^2CO		$(E)/(Z)^*$
	(75)	25:75
	(77)	41:59
	(27)	—

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2	 $EtO_2CCH(F)SO_2BT$ RCHO	**A**: NaHMDS, THF, 20°, 2 h *or* **B**: DBU, THF, –78°, 30 min; 1.5 h, 20° *or* **C**: DBU, $MgBr_2$, THF, 20°, 2 h	 $EtO_2CC(F)=CHR$	99

R	Protocol **A**	$(E)/(Z)^*$	Protocol **B**	$(E)/(Z)^*$	Protocol **C**	$(E)/(Z)^*$
n-C_8H_{17}	(76)	48:52	(66)	76:24	(87)	12:88
c-C_6H_{11}	(56)	35:65	(86)	72:28	(77)	10:90
Ph	(69)	15:85	(70)	76:24	(71)	8:92
4-$NO_2C_6H_4$	(85)	16:84	(72)	88:12	(66)	6:94
3-$MeOC_6H_4$	(75)	15:85	(74)	85:15	(49)	13:87
2-furyl	(71)	29:71	(77)	98:2	(37)	49:51
2-thienyl	(75)	23:77	(83)	98:2	(45)	24:76
2-pyridyl	(78)	24:76	(90)	61:39	(27)	22:78

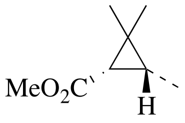
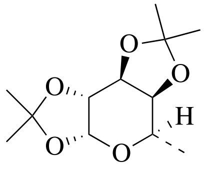
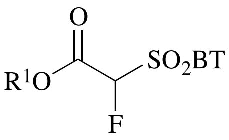
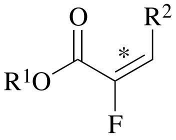
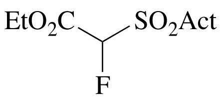
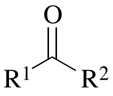
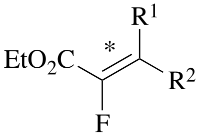
R	Protocol **A**	$(E)/(Z)^*$	Protocol **B**	$(E)/(Z)^*$	Protocol **C**	$(E)/(Z)^*$
	(87)	55:45	(83)	65:35	(90)	20:80
	(81)	25:75	(82)	49:51	(72)	6:94

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	 R^2CHO	DBU, CH_2Cl_2, 0.5-3 h		98

R^1	R^2	Temp		$(E)/(Z)^*$
Et	2-naphthyl	rt	(78)	78:22
t-Bu	2-naphthyl	rt	(93)	77:23
t-Bu	2-naphthyl	–78°	(70)	88:12
8-Ph-menthyl	2-naphthyl	rt	(92)	73:27
Et	2-thienyl	rt	(94)	87:13
t-Bu	2-thienyl	rt	(88)	85:15
8-Ph-menthyl	2-thienyl	rt	(70)	86:14
Et	ferrocenyl	rt	(71)	54:46
t-Bu	ferrocenyl	rt	(83)	57:43
t-Bu	Ph	rt	(78)	75:25
t-Bu	4-$NO_2C_6H_4$	rt	(84)	72:28
t-Bu	4-$MeOC_6H_4$	rt	(87)	83:17

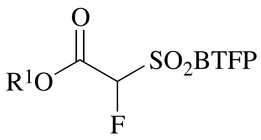
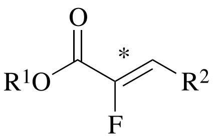
R^1	R^2	Temp		$(E)/(Z)^*$
t-Bu	2-benzofuranyl	rt	(93)	82:18
8-Ph-menthyl	2-benzofuranyl	rt	(79)	85:15
t-Bu	5-benzofuranyl	rt	(99)	80:20
t-Bu	*N*-Ts-4-imidazolyl	rt	(99)	74:26
t-Bu	*N*-Ts-3-indolyl	rt	(90)	83:17
t-Bu	(*E*)-PhCH=CH	rt	(93)	76:24
8-Ph-menthyl	(*E*)-PhCH=CH	rt	(80)	75:25
t-Bu	Et_2CH	rt	(77)	64:36
8-Ph-menthyl	Et_2CH	rt	(65)	61:39
t-Bu	*n*-C_7H_{15}	rt	(82)	71:29
t-Bu	*n*-C_7H_{15}	–78°	(75)	83:17

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	DBU, THF, rt, 6 h	 $(E)/(Z)^* = —$	655

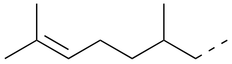
Act	Ketone	
BT	acetone	(10)
BT	cyclopentanone	(40)
BT	3-methylcyclopentanone	(70)
BT	cyclohexanone	(57)
BT	3-methylcyclohexanone	(60)

Act	Ketone	
BT	4-tert-butylcyclohexanone	(82)
PT	4-tert-butylcyclohexanone	(47)
PYM	4-tert-butylcyclohexanone	(46)
BT	3-decalinone	(60)
BT	α-tetralone	(0)

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_2$				
	 R^{2}CHO	1. K$_2$CO$_3$, Bu$_4$NBr, DMF rt, 15 min 2. Aldehyde, rt, 18 h		102

R^1	R^2		$(E)/(Z)^*$
Me	Ph	(>95)	7:93
t-Bu	Ph	(75)	18:82
Me	4-CF$_3$C$_6$H$_4$	(50)	6:94
t-Bu	4-CF$_3$C$_6$H$_4$	(42)	12:88
Me	4-ClC$_6$H$_4$	(60)	8:92
t-Bu	4-ClC$_6$H$_4$	(68)	17:83
t-Bu	4-MeOC$_6$H$_4$	(94)	39:61
Me	2-naphthyl	(47)	9:91
t-Bu	2-naphthyl	(72)	21:79

R^1	R^2		$(E)/(Z)^*$
Me	2-ClC$_6$H$_4$	(68)	10:90
Me	Ph(CH$_2$)$_2$	(66)	52:48
t-Bu	Ph(CH$_2$)$_2$	(92)	77:23
Me	c-C$_6$H$_{11}$	(71)	7:93
t-Bu	c-C$_6$H$_{11}$	(91)	15:85
Me		(61)	57:43
t-Bu		(75)	81:19

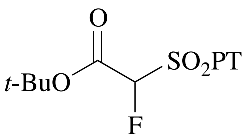
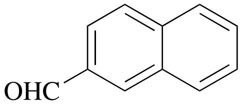
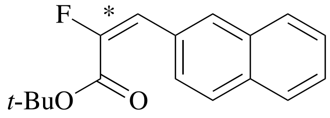
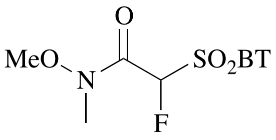
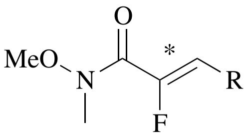
	 	DBU, CH$_2$Cl$_2$, rt	 (95) $(E)/(Z)^*$ = 75:25	98

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2		RCHO	**A**: NaH, THF, rt, 1-1.5 h *or* **B**: DBU, THF, –78°, 2.5-4 h *or* **C**: DBU, DMPU, rt, 16-17 h		100

	protocol A		protocol B		protocol C	
R		$(E)/(Z)^*$		$(E)/(Z)^*$		$(E)/(Z)^*$
n-C_8H_{17}	(83)	<1:99	(74)	54:46	(69)	67:33
4-$NO_2C_6H_4$	(85)	<1:99	(92)	3:97	(83)	67:33
2-naphthyl	(90)	0:100	(86)	6:94	(93)	78:22
2-thienyl	(99)	2:98	(78)	74:26	(81)	86:14
Et_2CH	(71)	0:100				
2-MeC_6H_4	(80)	<1:99				
4-$MeOC_6H_4$	(89)	1:99				
ferrocenyl	(100)	0:100				

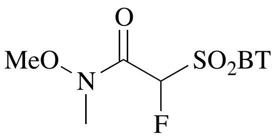
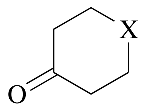
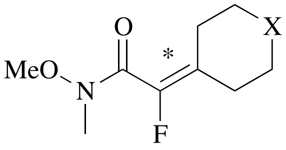
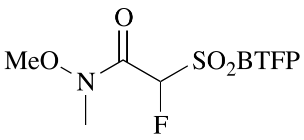
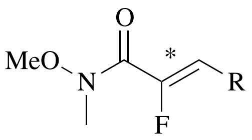
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. Cs_2CO_3, DMF, rt, 30 min 2. Ketone, rt, 30 h		X CH_2 (42) BnN (59)	100

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	 RCHO	1. K_2CO_3, Bu_4NBr, DMF rt, 15 min 2. Aldehyde, rt, 18 h	 (*Z*)*-isomer only	102

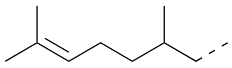
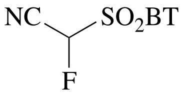
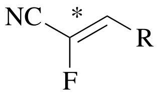
R		R	
Ph	(83)	*n*-C_9H_{19}	(56)
4-$CF_3C_6H_4$	(63)	$Ph(CH_2)_2$	(57)
4-ClC_6H_4	(62)	PhCH(Me)	(46)
4-$MeOC_6H_4$	(45)	*c*-C_5H_9	(51)
2-naphthyl	(81)	*c*-C_6H_{11}	(65)
6-MeO-2-naphthyl	(55)		(63)
2-ClC_6H_4	(99)		

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
		RCHO	1. Aldehyde (1 eq), DBU (4 eq), CH_2Cl_2, temp 2. Sulfone (2 eq), temp, 1 h; rt		101

R	Temp		$(E)/(Z)^*$
n-C_7H_{15}	rt	(97)	23:77
n-C_7H_{15}	–78°	(90)	16:84
$Ph(CH_2)_2$	rt	(80)	23:77
$Ph(CH_2)_2$	–78°	(81)	12:88
Et_2CH	rt	(76)	15:85
Et_2CH	–78°	(77)	8:92
(*E*)-PhCH=CH	rt	(81)	17:83
Ph	rt	(93)	19:81
4-$MeOC_6H_4$	rt	(95)	16:84
2-$MeOC_6H_4$	rt	(91)	37:63
2-$MeOC_6H_4$	–78°	(91)	27:73

R	Temp		$(E)/(Z)^*$
2-MeC_6H_4	rt	(94)	17:83
4-$NO_2C_6H_4$	rt	(72)	17:83
2-$NO_2C_6H_4$	rt	(60)	15:85
2-FC_6H_4	rt	(91)	16:84
2-naphthyl	rt	(98)	15:85
2-naphthyl	–78°	(97)	8:92
2-thienyl	rt	(96)	17:83
3-Boc-5-imidazolyl	rt	(59)	18:82
N-Boc-3-indolyl	rt	(86)	20:80
ferrocenyl	rt	(92)	17:83

TABLE 5. SYNTHESIS OF VINYL HALIDES

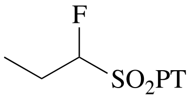
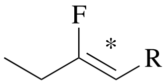
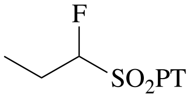
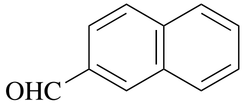
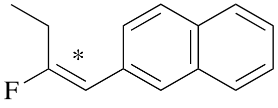
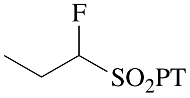
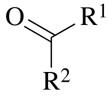
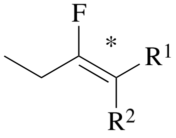
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C_3						
		RCHO	**A**: LiHMDS, $MgBr_2•OEt_2$, THF, rt, 3 h *or* **B**: KHMDS, THF, –78 to –60°, 2 h		R | | | (*E*)/(*Z*)* *n*-C_7H_{15} | A | (71) | 44:56 *n*-C_7H_{15} | B | (74) | 27:73 2-MeC_6H_4 | A | (77) | 18:82 4-$MeOC_6H_4$ | A | (87) | 3:97 4-$NO_2C_6H_4$ | A | (66) | 50:50 4-$NO_2C_6H_4$ | B | (90) | 67:33 2-naphthyl | A | (94) | 14:86 2-naphthyl | B | (64) | 73:27 2-thienyl | A | (75) | 1:99 (*E*)-PhCH=CH | A | (72) | 19:81	95
			LiHMDS, THF, 0°, 2 h		(92) (*E*)/(*Z*)* = 57:43	656
			LiHMDS, THF, 0°, 2 h		Ketone | | (*E*)/(*Z*)* acetophenone | (88) | 26:74 benzophenone | (99) | — *α*-indanone | (77) | 78:22 *N*-benzylpiperidin-4-one | (77) | —	95

TABLE 5. SYNTHESIS OF VINYL HALIDES

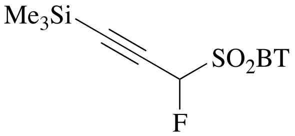
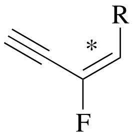
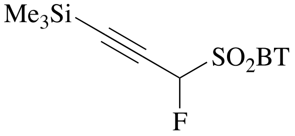
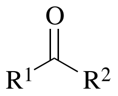
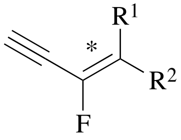
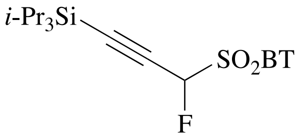
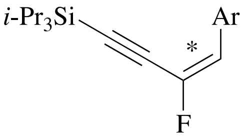
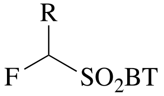
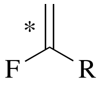
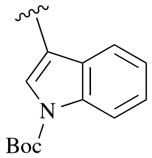
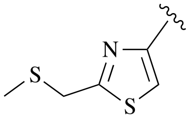
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)						Refs.
C_3		RCHO	**A:** 1. DBU, CH_2Cl_2, –55° 2. n-$Bu_4N^+ F^–$ *or* **B:** 1. LiHMDS, THF, –78° 2. n-$Bu_4N^+ F^–$			protocol A		protocol B		96
					R		$(E)/(Z)^*$		$(E)/(Z)^*$	
					Ph	(90)	76:24	(59)	94:6	
					4-$O_2NC_6H_4$	(59)	51:49	(81)	72:28	
					4-ClC_6H_4	(81)	70:30	(95)	94:6	
					4-$MeOC_6H_4$	(92)	81:19	(97)	95:5	
					2-$MeOC_6H_4$	(92)	78:22	(87)	90:10	
					2-naphthyl	(95)	74:26	(97)	88:12	
					ferrocenyl	(95)	83:17	(98)	90:10	
					3-indolinyl	(95)	75:25	(92)	91:9	
					2-thienyl	(78)	75:25	(78)	91:9	
					(E)-PhCH=CH	(95)	72:28	(96)	80:20	
					$Ph(CH_2)_2$	(54)	80:20	(63)	70:30	
					n-C_7H_{15}	(79)	85:15			
			1. LiHMDS, THF, –78° 2. n-$Bu_4N^+ F^–$		R^1	R^2		$(E)/(Z)^*$		96
					Ph	Me	(88)	100:0		
					$(CH_2)_2NBn(CH_2)_2$		(77)	—		
		ArCHO	**A:** DBU, CH_2Cl_2, –55° *or* **B:** LiHMDS, THF, –78°		Ar			$(E)/(Z)^*$		96
					2-naphthyl	A	(87)	71:29		
					4-$NO_2C_6H_4$	A	(64)	67:33		
					4-$NO_2C_6H_4$	B	(87)	76:24		

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-11}	 $[CH_2O]_n$	Base, solvent, rt, 15 h		97

R	Base	Eq base	Solvent
Ph	DBU	10	CH_2Cl_2 (71)
Ph	Cs_2CO_3	2	CH_2Cl_2 (86)
2-BrC_6H_4	DBU	10	CH_2Cl_2 (57)
2-BrC_6H_4	DBU	3	CH_2Cl_2 (51)
2-BrC_6H_4	Cs_2CO_3	2	CH_2Cl_2 (61)
2-BrC_6H_4	Cs_2CO_3	2	THF (54)
3,4,5-$(MeO)_2C_6H_2$	DBU	10	CH_2Cl_2 (92)
3,4,5-$(MeO)_2C_6H_2$	DBU	3	CH_2Cl_2 (95)
3,4,5-$(MeO)_2C_6H_2$	Cs_2CO_3	2	CH_2Cl_2 (81)
3,4,5-$(MeO)_2C_6H_2$	Cs_2CO_3	2	THF (90)
4-$NO_2C_6H_4$	DBU	3	CH_2Cl_2 (76)
4-$NO_2C_6H_4$	Cs_2CO_3	2	CH_2Cl_2 (78)

R	Base	Eq base	Solvent
4-$NO_2C_6H_4$	Cs_2CO_3	2	THF (71)
2-naphthyl	DBU	10	CH_2Cl_2 (69)
2-naphthyl	DBU	3	CH_2Cl_2 (92)
2-naphthyl	Cs_2CO_3	2	CH_2Cl_2 (74)
2-naphthyl	Cs_2CO_3	2	THF (91)
	Cs_2CO_3	2	CH_2Cl_2 (53)
	Cs_2CO_3	2	THF (63)
	DBU	10	CH_2Cl_2 (99)
	Cs_2CO_3	2	CH_2Cl_2 (92)
	Cs_2CO_3	2	THF (83)

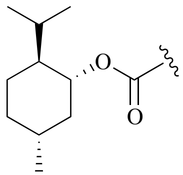
R	Base	Eq base	Solvent
$PhSO_2$	Cs_2CO_3	2	CH_2Cl_2 (75)
$PhSO_2$	Cs_2CO_3	2	THF (39)
EtOC(O)	Cs_2CO_3	2	CH_2Cl_2 (64)
$PhCH_2OC(O)$	DBU	3	CH_2Cl_2 (54)
$PhCH_2OC(O)$	Cs_2CO_3	2	CH_2Cl_2 (66)
(MeO)N(Me)C(O)	Cs_2CO_3	2	CH_2Cl_2 (89)
	Cs_2CO_3	2	CH_2Cl_2 (68)

TABLE 5. SYNTHESIS OF VINYL HALIDES

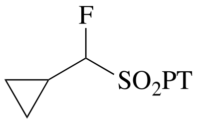
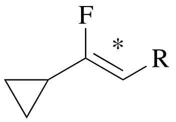
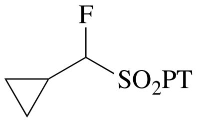
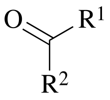
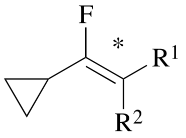
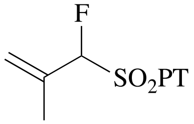
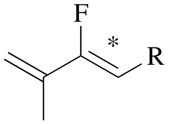
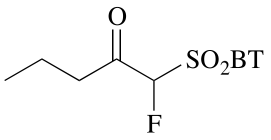
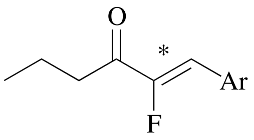
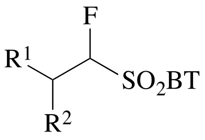
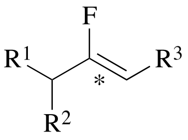
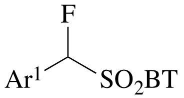
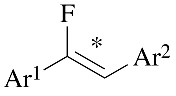
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)					Refs.
C_4		RCHO	**A**: LiHMDS, $MgBr_2$•OEt_2, THF, rt, 3 h *or* **B**: KHMDS, THF, –78 to –60°, 2 h		R			(*E*)/(*Z*)*	95
					n-C_7H_{15}	A	(63)	42:58	
					n-C_7H_{15}	B	(72)	36:64	
					2-MeC_6H_4	A	(72)	50:50	
					4-$MeOC_6H_4$	A	(57)	5:95	
					4-$NO_2C_6H_4$	A	(45)	73:27	
					4-$NO_2C_6H_4$	B	(71)	67:33	
					2-naphthyl	A	(70)	38:62	
					2-naphthyl	B	(83)	50:50	
					2-thienyl	A	(60)	9:91	
					(*E*)-PhCH=CH	A	(53)	49:51	
			LiHMDS, THF, 0°, 2 h		Ketone			(*E*)/(*Z*)*	95
					acetophenone		(96)	25:75	
					benzophenone		(91)	—	
					α-indanone		(88)	78:22	
					N-benzylpiperidin-4-one		(71)	—	
		RCHO	**A**: LiHMDS, $MgBr_2$•OEt_2, THF, rt, 3 h *or* **B**: KHMDS, THF, –78 to –60°, 2 h		R			(*E*)/(*Z*)*	95
					n-C_7H_{15}	A	(63)	80:20	
					n-C_7H_{15}	B	(83)	50:50	
					2-MeC_6H_4	A	(77)	28:72	
					4-$MeOC_6H_4$	A	(60)	<1:99	
					4-$NO_2C_6H_4$	A	(61)	73:27	
					2-naphthyl	A	(78)	16:84	
					2-naphthyl	B	(73)	46:54	
					2-thienyl	A	(78)	0:100	
					(*E*)-PhCH=CH	A	(—)	38:62	

TABLE 5. SYNTHESIS OF VINYL HALIDES

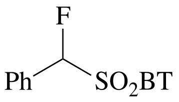
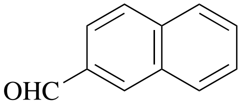
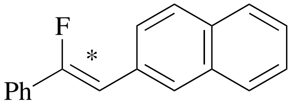
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		ArCHO	DBU, THF, reflux, 0.5 h		100
C_{5-11}		R^3CHO	NaHMDS, THF, –78°; rt, 3 h		45
C_{6-8}		Ar^2CHO	LiHMDS, THF, 0°, 1.5 h		657

Ar		(*E*):(*Z*)*
Ph$(CH_2)_2$	(73)	0:100
4-MeOC_6H_4	(89)	0:100
4-$NO_2C_6H_4$	(86)	0:100
5-benzofuranyl	(90)	0:100

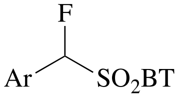
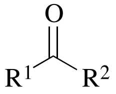
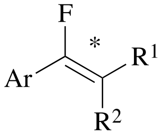
R^1	R^2	R^3		(*E*)/(*Z*)*
Et	Me	4-BrC_6H_4	(63)	71:29
CH_2=CH	Me	4-BrC_6H_4	(68)	75:25
Ph$(CH_2)_2$	Me	4-BrC_6H_4	(66)	69:31
Ph	Me	Ph	(72)	60:40
Ph	Me	4-MeOC_6H_4	(57)	51:49
Ph	Me	*n*-C_8H_{17}	(58)	17:83
2-BrC_6H_4	Me	4-BrC_6H_4	(49)	76:24
–$(CH_2)_4$–		4-BrC_6H_4	(87)	74:26

Ar^1	Ar^2		(*E*)/(*Z*)*
2-BrC_6H_4	2-$CF_3C_6H_4$	(61)	77:23
2-BrC_6H_4	2-Cl-3-pyridyl	(57)	100:0
2-BrC_6H_4	4-pyridyl	(51)	82:18
4-C_6H_4	2-$CF_3C_6H_4$	(65)	29:71
2-$CF_3C_6H_4$	2-BrC_6H_4	(20)	0:100
4-$CF_3C_6H_4$	2-F-3-pyridyl	(85)	86:14
2-Cl-pyrid-3-yl	2-BrC_6H_4	(60)	71:29

TABLE 5. SYNTHESIS OF VINYL HALIDES

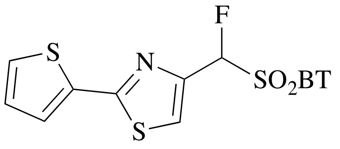
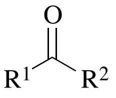
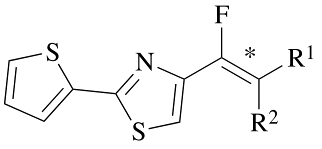
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7	 	$MN(SiMe_3)_2$, solvent, temp		656

M	Solvent	Temp		(*E*)/(*Z*)*
Li	DMF-DMPU	–78°, 40 min; –45°, 35 min; rt, 2 h	(—)	8:92
Li	DMF-DMPU	0°, 1.5 h	(—)	22:78
Li	DMF-DMPU	rt, 2 h	(—)	42:58
Li	THF	–78°, 40 min; –45°, 35 min; rt, 2 h	(—)	69:31
Li	THF	0°, 2 h	(100)	69:31
Na	THF	–78°, 40 min; –45°, 35 min; rt, 2 h	(—)	67:33

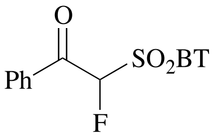
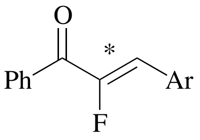
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}	 	LiHMDS, THF, 0°, 1.5-2 h		656

Ar	R^1	R^2		(*E*)/(*Z*)*
Ph	(*E*)-PhCH=CH	H	(90)	50:50
Ph	*n*-C_7H_{15}	H	(100)	66:34
Ph	2-thienyl	H	(98)	68:32
Ph	ferrocenyl	H	(100)	0:100
Ph	–$(CH_2)_2N(Bn)(CH_2)_2$–		(100)	—
Ph	R^1R^2CO = 1-indanone		(91)	94:6
2-naphthyl	2-naphthyl	H	(98)	78:22
2-naphthyl	(*E*)-PhCH=CH	H	(90)	36:64
2-naphthyl	*n*-C_7H_{15}	H	(100)	66:34
2-naphthyl	2-thienyl	H	(100)	72:28
2-naphthyl	ferrocenyl	H	(100)	0:100
2-naphthyl	–$(CH_2)_2N(Bn)(CH_2)_2$–		(100)	—
2-naphthyl	R^1R^2CO = 1-indanone		(87)	95:5
2-thienyl	2-naphthyl	H	(100)	73:27
2-thienyl	(*E*)-PhCH=CH	H	(86)	42:58
2-thienyl	*n*-C_7H_{15}	H	(95)	62:38
2-thienyl	2-thienyl	H	(91)	82:18
2-thienyl	ferrocenyl	H	(100)	6:94
2-thienyl	–$(CH_2)_2N(Bn)(CH_2)_2$–		(100)	—
2-thienyl	R^1R^2CO = 1-indanone		(85)	92:8

TABLE 5. SYNTHESIS OF VINYL HALIDES

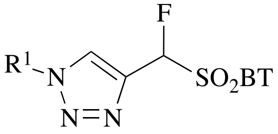
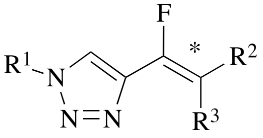
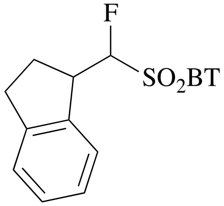
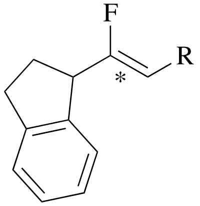
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	 	LiHMDS, THF, 0°, 1.5-2 h		656

R^1	R^2		$(E)/(Z)^*$
2-naphthyl	H	(97)	40:60
(*E*)-PhCH=CH	H	(87)	21:79
n-C_7H_{15}	H	(100)	42:58
2-thienyl	H	(93)	40:60
ferrocenyl	H	(96)	4:96
$-(CH_2)_2N(Bn)(CH_2)_2-$		(100)	—
R^1R^2CO = 1-indanone		(62)	78:22

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
	 ArCHO	DBU, THF, reflux, 0.5 h		100

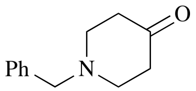
Ar		$(E):(Z)^*$
4-$MeOC_6H_4$	(61)	0:100
2-$MeOC_6H_4$	(64)	0:100
4-$NO_2C_6H_4$	(81)	0:100
2-thienyl	(71)	0:100

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-12}		R^2COR^3	LiHMDS, DMF, DMPU, –78°		568
C_{10}		RCHO	NaHMDS, THF, –78°; rt, 3 h		45

Products for C_{9-12} (ref. 568):

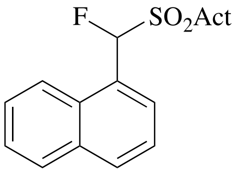
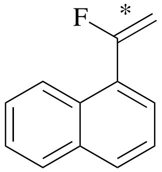
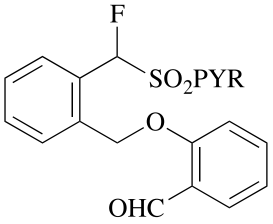
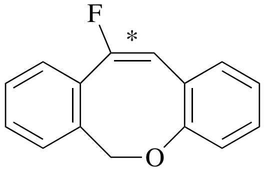
R^1	Carbonyl compound		$(E)/(Z)^*$
$Ph(CH_2)_3$	2,4,6-$Me_3C_6H_2CHO$	(47)	26:74
4-$MeOC_6H_4$	4-$MeOC_6H_4CHO$	(72)	14:86
$Ph(CH_2)_3$	4-$MeOC_6H_4CHO$	(90)	7:93
$Ph(CH_2)_3$	4-$NO_2C_6H_4CHO$	(76)	38:62
4-$MeOC_6H_4$	Et_2CHCHO	(60)	15:85

R^1	Carbonyl compound		$(E)/(Z)^*$
$Ph(CH_2)_3$	Et_2CHCHO	(57)	19:81
4-$MeOC_6H_4$	n-$C_7H_{15}CHO$	(68)	34:66
$Ph(CH_2)_3$	n-$C_7H_{15}CHO$	(63)	36:64
4-$MeOC_6H_4$		(87)	—

Products for C_{10} (ref. 45):

R		$(E)/(Z)^*$
n-C_8H_{17}	(51)	38:62
4-BrC_6H_4	(51)	71:29

TABLE 5. SYNTHESIS OF VINYL HALIDES

	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}	 [CH_2O]$_n$ or aq. CH_2O	**A**: Paraformaldehyde Base, solvent, rt *or* **B**: 37% aq. CH_2O Base, solvent, rt		97
C_{15}		*t*-BuOK, DMF, –50° to rt	 (80) (*E*)* only	658

Act	Base	Eq base	Solvent		
BT	NEt_3	10	CH_2Cl_2	**A**	(0)
BT	K_2CO_3	10	Acetone	**A**	(0)
BT	K_2CO_3	10	THF/H_2O	**A**	(23)
BT	Cs_2CO_3	10	CH_2Cl_2	**A**	(57)
BT	Cs_2CO_3	2	CH_2Cl_2	**A**	(49)
BT	Cs_2CO_3	10	THF	**A**	(67)
BT	Cs_2CO_3	2	THF	**A**	(71)

Act	Base	Eq base	Solvent		
BT	Cs_2CO_3	2	THF	**B**	(0)
BT	TMG	10	CH_2Cl_2	**A**	(25)
BT	DBU	10	CH_2Cl_2	**A**	(67)
BT	DBU	3	CH_2Cl_2	**A**	(62)
BT	DBU	10	THF	**A**	(68)
BT	DBU	10	THF	**B**	(8)
PT	DBU	—	CH_2Cl_2	**A**	(—)

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

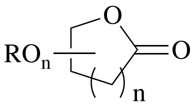
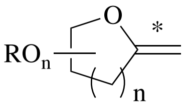
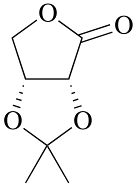
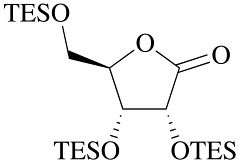
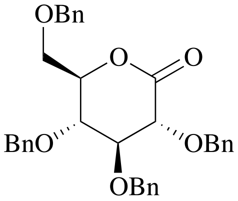
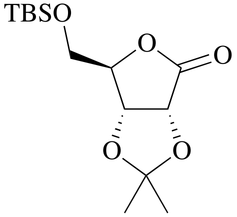
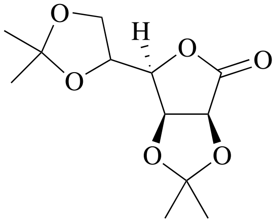
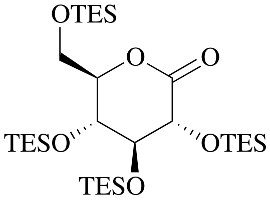
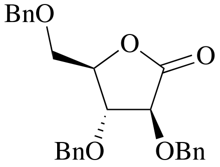
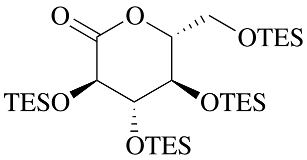
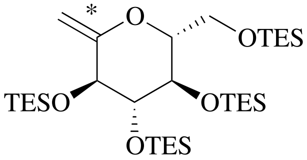
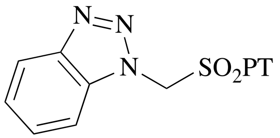
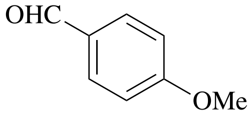
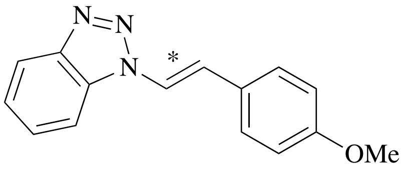
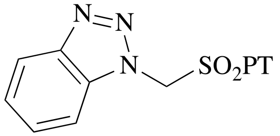
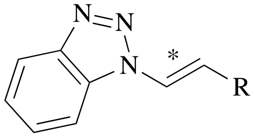
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
	$BTSO_2Me$ 	1. LiHMDS, THF, –78°, 30 min 2. AcOH 3. DBU, THF, rt, 1 h		107
	Lactone	Lactone	Lactone	
	 (51)	 (46)	 (53)	
	 (58)	 (66)	 (74)	
	 (66)			
	$BTSO_2Me$ 	1. LiHMDS, THF, –78°, 30 min 2. DBU, THF, rt, 1 h	 (74)	659

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1			See table.		109

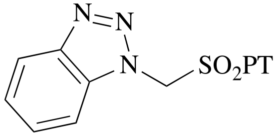
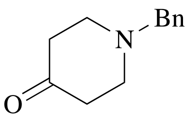
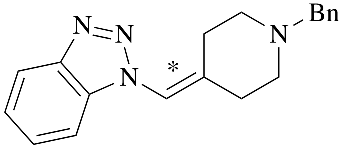
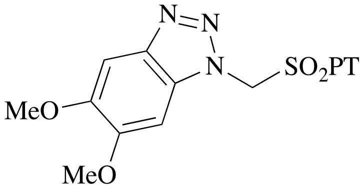
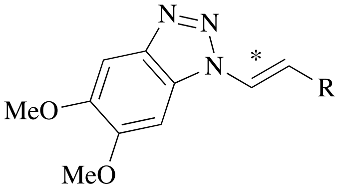
Base	Eq. base	Solvent	Additive	Temp.	Time		$(E)/(Z)^*$
LiHMDS	2.4	THF	none	0°	4 h	(76)	79:21
LiHMDS	4.0	THF	none	–78°	32 h	(—)	28:72
LiHMDS	2.4	THF	none	66°	2 h	(81)	70:30
LiHMDS	3.0	THF	$MgBr_2 \cdot Et_2O$	23°	5 h	(30)	77:23
LiHMDS	2.4	DMF/DMPU	none	–50°	20 h	(—)	57:43
NaHMDS	2.4	THF	none	0°	0.5 h	(45)	60:40
KHMDS	2.4	THF	none	0°	0.5 h	(66)	60:40
DBU	2.0	THF	none	66°	2 h	(47)	26:74

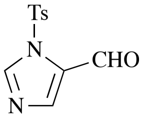
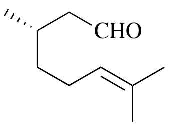
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
		RCHO	**A:** LiHMDS, THF, 0° *or* **B:** DBU, THF, reflux		109

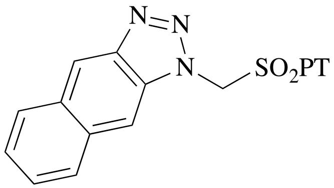
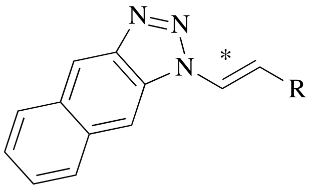
R		Time		$(E)/(Z)^*$
2-MeOC_6H_4	**A**	0.5 h	(86)	93:7
2-MeOC_6H_4	**B**	5 h	(57)	15:85
2-FC_6H_4	**A**	0.5 h	(83)	41:59
2-FC_6H_4	**B**	5 h	(57)	11:89
$4\text{-CF}_3C_6H_4$	**A**	2 h	(62)	29:71
2-Thienyl	**A**	0.5 h	(90)	40:60
2-Thienyl	**B**	5 h	(47)	25:75
5-Benzofuranyl	**A**	1 h	(65)	64:36
5-Benzofuranyl	**B**	14 h	(60)	20:80

R		Time		$(E)/(Z)^*$
3-(1-Tosyl-1*H*-indolyl)	**A**	3 h	(72)	71:29
5-(1-Tosyl-1*H*-imidazolyl)	**A**	2 h	(71)	29:71
$n\text{-}C_7H_{15}$	**A**	0.5 h	(67)	4:96
Et_2CH	**A**	0.5 h	(73)	22:78
Et_2CH	**B**	16 h	(50)	3:97
$c\text{-}C_6H_{11}$	**A**	2 h	(53)	20:80
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	**A**	1 h	(80)	16:84

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1					
			LiHMDS, THF, 0°, 3 h	 (77)	109
		RCHO	LiHMDS, THF, 0°, 25 min		109

RCHO		$(E)/(Z)^*$	RCHO		$(E)/(Z)^*$
	(80)	60:40		(69)	41:59

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
		RCHO	**A:** LiHMDS, Solvent, 0° *or* **B:** DBU, THF, reflux		109

R		Solvent	Time		$(E)/(Z)^*$
3,4,5-$(MeO)_3C_6H_2$	**A**	THF	20 min	(80)	65:35
3,4,5-$(MeO)_3C_6H_2$	**A**	DMF	40 min	(93)	37:63
3,4,5-$(MeO)_3C_6H_2$	**B**	THF	4 h	(52)	25:75
4-$CF_3C_6H_4$	**A**	THF	20 min	(56)	44:56
4-$CF_3C_6H_4$	**A**	DMF	40 min	(62)	41:59
Et_2CH	**A**	THF	25 min	(54)	22:78
Et_2CH	**A**	DMF	40 min	(74)	33:67

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

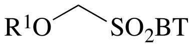
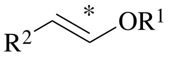
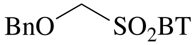
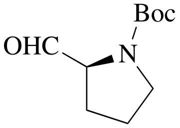
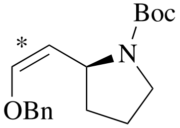
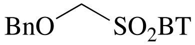
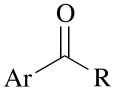
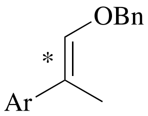
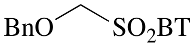
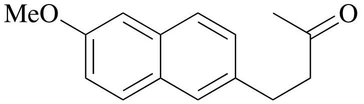
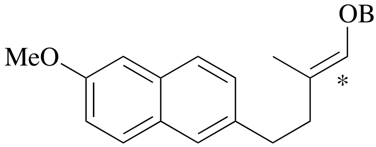
<table>
<tr><th></th><th colspan="2">Sulfone and Carbonyl Compound</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td>C_1</td><td> </td><td>R^2CHO</td><td>LiHMDS, THF, 0°, 1.5 h</td><td>
<table>
<tr><th>R^1</th><th>R^2</th><th></th><th>$(E)/(Z)^*$</th></tr>
<tr><td>Bn</td><td>4-MeC_6H_4</td><td>(73)</td><td>50:50</td></tr>
<tr><td>4-ClC_6H_4</td><td>4-MeC_6H_4</td><td>(83)</td><td>55:45</td></tr>
<tr><td>Bn</td><td>benzothien-2-yl</td><td>(71)</td><td>67:33</td></tr>
<tr><td>Bn</td><td>$Ph(CH_2)_2$</td><td>(46)</td><td>52:48</td></tr>
</table></td><td>105</td></tr>
<tr><td></td><td> </td><td> </td><td>LiHMDS, THF, 0°, 5 min;
rt, 30 min</td><td> (61) $(E)/(Z)^* = 33:67$</td><td>660</td></tr>
<tr><td></td><td> </td><td> </td><td>LiHMDS, THF, 0°, 1.5 h</td><td>
<table>
<tr><th>Ar</th><th>R</th><th></th><th>$(E)/(Z)^*$</th></tr>
<tr><td>4-MeOC_4H_6</td><td>Me</td><td>(87)</td><td>50:50</td></tr>
<tr><td>$3,4\text{-}(OCH_2O)C_6H_3$</td><td>Me</td><td>(86)</td><td>50:50</td></tr>
<tr><td>2-MeC_6H_4</td><td>Me</td><td>(79)</td><td>68:32</td></tr>
<tr><td>4-IC_6H_4</td><td>Me</td><td>(75)</td><td>50:50</td></tr>
<tr><td>4-FC_6H_4</td><td>Me</td><td>(90)</td><td>52:48</td></tr>
<tr><td>Ph</td><td>CF_3</td><td>(82)</td><td>64:36</td></tr>
</table></td><td>105</td></tr>
<tr><td></td><td> </td><td> </td><td>LiHMDS, THF, 0°, 1.5 h</td><td> (86) $(E)/(Z)^* = 60:40$</td><td>105</td></tr>
</table>

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

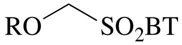
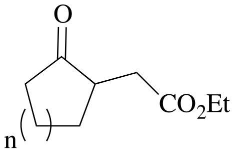
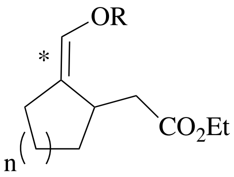
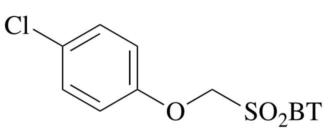
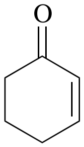
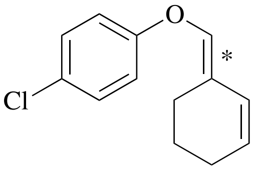
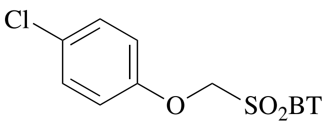
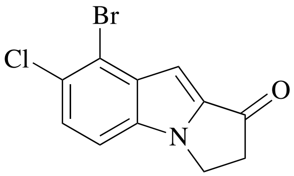
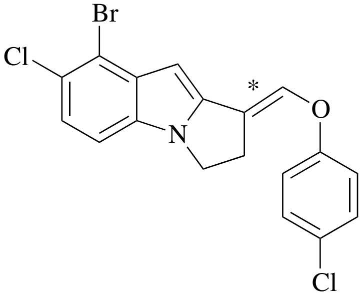
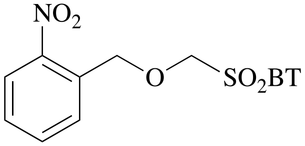
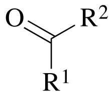
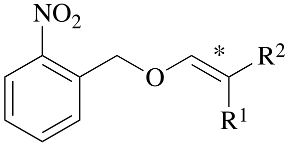
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
	 	LiHMDS, THF, 0°, 1.5 h	 R — n — — $(E)/(Z)^*$ Bn — 1 — (70) — 50:50 Bn — 2 — (71) — 67:33 4-ClC_6H_4 — 1 — (75) — 50:50 4-ClC_6H_4 — 2 — (76) — 67:33	105
	 	LiHMDS, THF, 0°, 1.5 h	 (71) $(E)/(Z)^* = 57{:}43$	105
	 	LiHMDS, THF, 0°, 1.5 h	 (65) $(E)/(Z)^* = 74{:}26$	105
	 	LiHMDS, THF, 0°, 5 h	 R^1 — R^2 — — $(E)/(Z)^*$ Ph — Ph — (62) — — Me — Ph — (97) — 33:67 Me — 2-MeC_6H_4 — (51) — 14:86 Me — 4-$MeOC_6H_4$ — (27) — 50:50 $-(CH_2)_5-$ — (82) — —	661

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

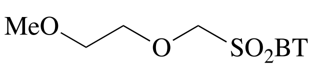
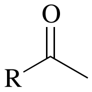
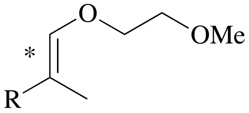
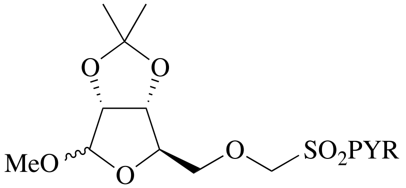
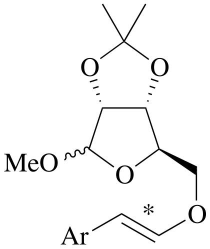
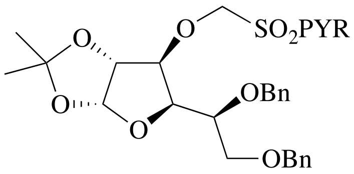
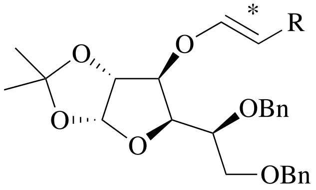
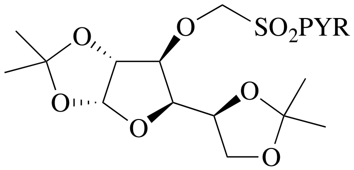
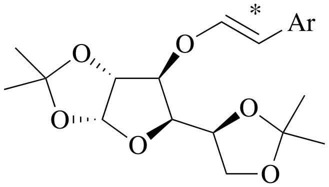
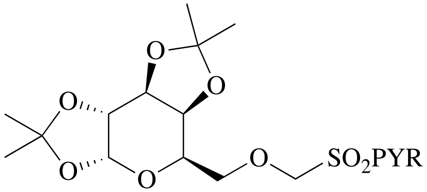
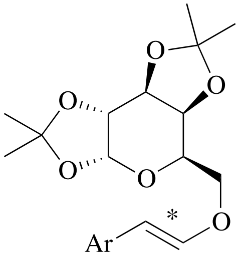
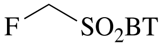
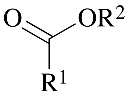
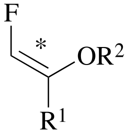
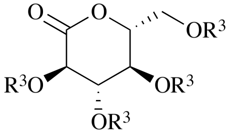
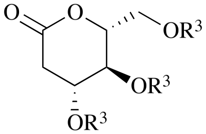
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
	 	LiHMDS, THF, 0°, 1.5 h	 R / / $(E)/(Z)^*$ Ph / (86) / 57:43 4-ClC_6H_4 / (87) / 62:38 3,4-$(OCH_2O)C_6H_3$ / (76) / 57:43 $Ph(CH_2)_2$ / (83) / 57:32	105
	 ArCHO	KOH, Bu_4NBr, THF, rt, 24 h	 Ar / / $(E)/(Z)^*$ Ph / (72) / 94:6 4-$MeOC_6H_4$ / (88) / 78:22 2-$MeOC_6H_4$ / (83) / 71:29 4-ClC_6H_4 / (48) / 92:8 2-ClC_6H_4 / (45) / 78:22 4-$Me_2NC_6H_4$ / (81) / 86:14 4-MeO-2-naphthyl / (70) / 81:19 2-furyl / (92) / 67:33	106
	 RCHO	KOH, Bu_4NBr, THF, rt, 24 h	 Ar / / $(E)/(Z)^*$ *t*-Bu / (31) / <1:99 Ph / (78) / 71:29 4-FC_6H_4 / (58) / 69:31	106
	 ArCHO	KOH, Bu_4NBr, THF, rt, 24 h	 Ar / / $(E)/(Z)^*$ Ph / (63) / 75:25 4-FC_6H_4 / (54) / 75:25	106

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1					
		ArCHO	KOH, Bu_4NBr, THF, rt, 24 h		106
			1. LiHMDS, Additive, THF, –78°, 45 min 2. DBU, THF, rt, 1 h		662

Ar		$(E)/(Z)^*$
Ph	(71)	96:4
4-$MeOC_6H_4$	(91)	89:11
2-$MeOC_6H_4$	(78)	89:11
4-FC_6H_4	(40)	93:7

$R^1CO_2R^2$	R^3	Additive		$(E)/(Z)^*$
	Bn	—	(85)	60:40
	TES	$BF_3·OEt_2$	(94)	80:20
	Bn	—	(82)	30:70

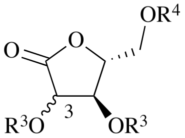
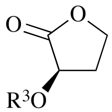
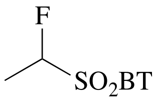
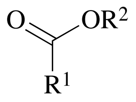
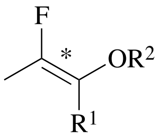
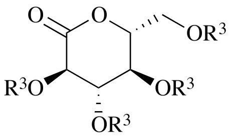
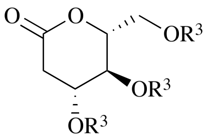
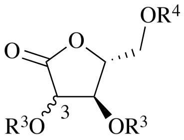
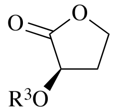
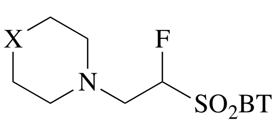
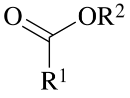
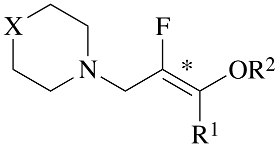
$R^1CO_2R^2$	R^3/R^4	Additive		$(E)/(Z)^*$
	R^3, R^4 = Bn, C3: (*S*)	—	(77)	70:30
	R^3, R^4 = TBS, C3: (*R*)	—	(46)	70:30
	R^3, R^4 = TBS, C3: (*R*)	$BF_3·OEt_2$	(43)	70:30
	R^3 = *i*-Pr, R^4 = TBS, C3: (*R*)	—	(70)	60:40
	Bn	—	(60)	60:40
	TES	—	(20)	40:60
	TES	$BF_3·OEt_2$	(68)	50:50

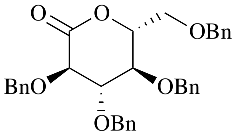
TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

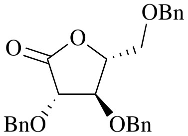
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			1. LiHMDS, Additive, THF, –78°, 45 min 2. DBU, THF, rt, 1 h		662

$R^1CO_2R^2$	R^3	Additive		$(E)/(Z)^*$
	Bn	—	(85)	40:60
	TES	$BF_3·OEt_2$	(93)	40:60
	Bn	—	(58)	70:30

$R^1CO_2R^2$	R^3/R^4	Additive		$(E)/(Z)^*$
	R^3, R^4 = Bn, C3: (*S*)	—	(70)	30:70
	R^3, R^4 = TBS, C3: (*R*)	—	(37)	30:70
	R^3, R^4 = TBS, C3: (*R*)	$BF_3·OEt_2$	(27)	20:80
	R^3 = *i*-Pr, R^4 = TBS, C3: (*R*)	—	(83)	30:70
	R^3 = *i*-Pr, R^4 = TBS, C3: (*R*)	$BF_3·OEt_2$	(40)	30:70
	Bn	—	(60)	30:70
	TES	—	(29)	20:80
	TES	$BF_3·OEt_2$	(68)	30:70

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
			1. LiHMDS, THF, –78°, 45 min 2. DBU, THF, rt, 1 h		662

$R^1CO_2R^2$	X		$(E)/(Z)^*$
	O	(54)	20:80

$R^1CO_2R^2$	X		$(E)/(Z)^*$
	O	(61)	20:80
	CH_2	(41)	0:100

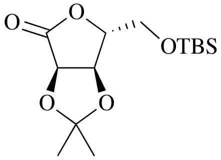
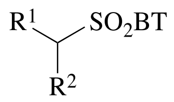
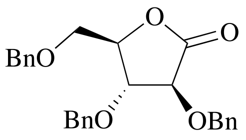
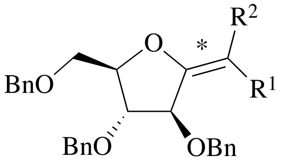
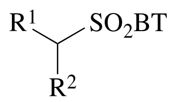
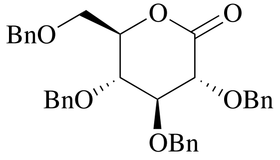
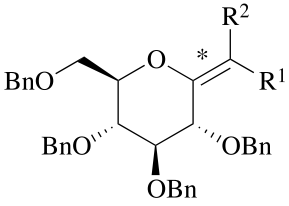
$R^1CO_2R^2$	X		$(E)/(Z)^*$
	O	(91)	20:80
	CH_2	(39)	5:95

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-7}					
			1. LiHMDS, THF, –78°, 30 min 2. AcOH 3. DBU, THF, rt, 1 h		108

R^1	R^2		(*E*)/(*Z*)*
Me	H	(77)	80:20
n-C_6H_{13}	H	(63)	90:10
CH_2=CHCH_2	H	(64)	>90:10
THPO(CH_2)$_3$	H	(63)	90:10
Me	Me	(60)	—
–(CH_2)$_4$–		(61)	—

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
			1. LiHMDS, THF, –78°, 30 min 2. AcOH 3. DBU, THF, rt, 1 h		108

R^1	R^2		(*E*)/(*Z*)*
Me	H	(62)	60:40
n-C_6H_{13}	H	(33)	50:50
CH_2=CHCH_2	H	(33)	80:20
THPO(CH_2)$_3$	H	(49)	50:50
Me	Me	(35)	—
–(CH_2)$_4$–		(28)	—

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

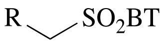
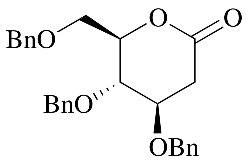
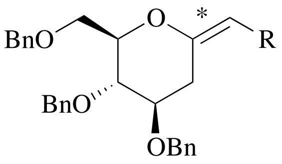
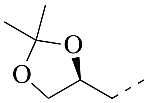
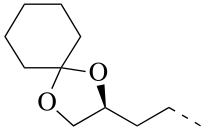
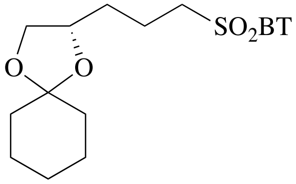
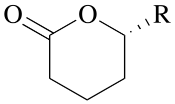
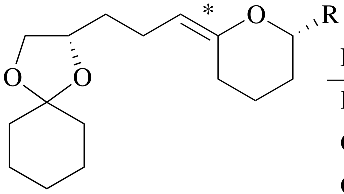
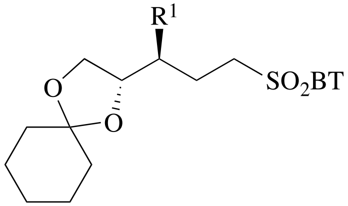
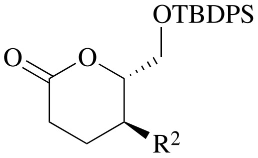
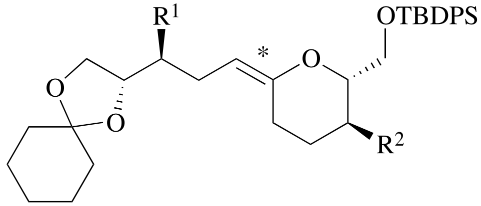
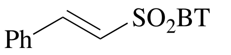
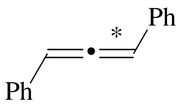
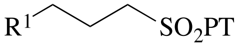
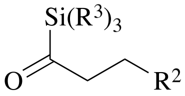
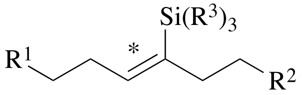
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-5}					
			1. LiHMDS, THF, –78°, 30 min 2. AcOH 3. DBU, THF, rt, 1 h	 R | | $(E)/(Z)^*$ $THPO(CH_2)_3$ | (67) | 60:40  | (54) | 40:60  | (59) | 60:40	663
C_{5-6}					
			**A:** LiHMDS, $BF_3•Et_2O$ THF, –78°; then DBU, THF, rt *or* **B:** LiHMDS, $BF_3•Et_2O$, THF, –78°	 R | | $(E)^*$-isomer H | B | (60) CH_2OBn | A | (55) $CH_2OTBDPS$ | A | (31)	664

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

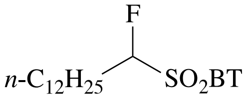
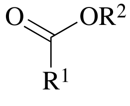
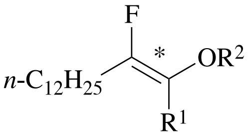
	Sulfone and Carbonyl Compound	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_{5-6}$				
	 	1. LiHMDS, LiCl THF, –78° 2. AcOH 3. DBU, THF, rt, 1 h		232 233

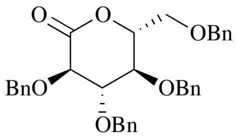
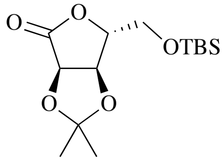
R^1	R^2		$(E)/(Z)^*$
Me	H	(23)	—
H	Me	(23)	—

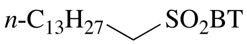
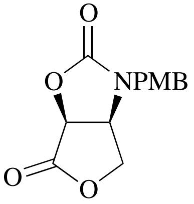
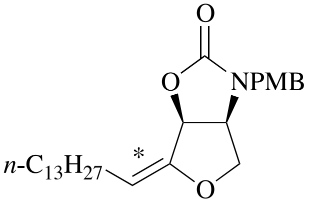
	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)		Refs.
C$_8$						
		PhCHO	1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 2 h; rt		(26)	3
C$_{9-12}$						
			LiHMDS, solvent, –78°, 30 min			110

R^1	R^2	R^3	Solvent		$(E)/(Z)^*$
Ph	Ph	Me	THF	(93)	64:36
Ph	Ph	Et	THF	(24)	50:50
Ph	Ph	Me	PhMe	(74)	33:67
Ph	Bn	Me	THF	(78)	62:38
Ph	Bn	Me	PhMe	(76)	32:68
n-C$_9$H$_{19}$	Ph	Me	THF	(79)	65:35
n-C$_9$H$_{19}$	Ph	Me	PhMe	(69)	39:61
n-C$_9$H$_{19}$	Bn	Me	THF	(84)	68:32
n-C$_9$H$_{19}$	Bn	Me	PhMe	(61)	42:58

TABLE 6. SYNTHESIS OF MISCELLANEOUS ALKENE CLASSES

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			1. LiHMDS, THF, –78°, 45 min 2. DBU, THF, rt, 1 h		662

$R^1CO_2R^2$		$(E)/(Z)^*$	$R^1CO_2R^2$		$(E)/(Z)^*$
	(53)	30:70		(83)	20:80

	Sulfone and Carbonyl Compound		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			LiHMDS, THF, –78°, 30 min	 (55) $(E)/(Z)^* = 67{:}33$	665

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