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Syntheses of Highly Substituted Enantiopure C6 and C7 Enones[1]

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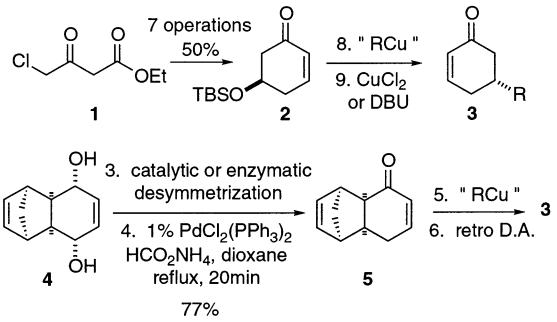
Abstract: Enantiopure epoxyvinyl sulfones ***SS*-9a**, ***SS*-9b**, produced from Jacobsen epoxidation of 2-phenylsulfonyl 1,3-cyclohexa- and cycloheptadiene, are used as a template for the construction of substituted cycloalkenones and as chiral synthetic equivalents of enones **a** and **b**. The addition of carbon nucleophiles to ***SS*-9a**, ***SS*-9b** is high yielding and stereospecific. Enantiopure α,β- and γ-substituted cycloalkenones are easily constructed using a variety of methods.

Introduction

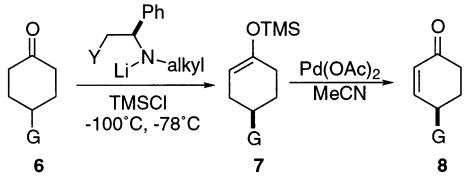
Development of chiral 2,5-cyclohexadienone synthons has received only modest attention in the literature. A differentiated pair of enones that can enantiospecifically add nucleophiles, trap electrophiles, or participate in Diels−Alder reactions are valuable in the synthesis of multifunctionalized cyclohexane molecules, providing access to the substrate is efficient. Two current methods are shown in Scheme 1. The first involves enantiopure 5-silyloxy-cyclohexenone **2** which directs Michael addition through avoidance of 1,3 diaxial interactions, followed by β-elimination of OTBS to generate enone **3**.[2] Synthesis of **2** from commercially available **1** requires seven operations, 50% yield.[3] The second strategy employs tricyclic enone **5**, which masks one of the olefins as a Diels−Alder adduct. Directed Michael addition followed by retro Diels−Alder then reveals the functionalized enone **3**.[4] Substrate **5** is synthesized either through enzymatic or catalytic desymmetrization (Scheme 1).[5,6] Regardless of the brevity of the latter synthesis using catalytic desymmetrization, the catalyst is prohibitively expensive ($60/50 mg, $1.2 M/mol, used at 5%). The lipase-mediated desymmetrization of compound **4** occurs in 79% yield, but requires 16 days reaction time.

In 1993, Koga et al. demonstrated a general method for the construction of 4-alkyl and 4-aryl cyclohexenones **8** using chiral lithium amides.[7] The method is very sound; however, it requires a stoichiometric equivalent of chiral base. Also, if more elaborate substituents are desired, the synthesis of the prochiral 4-substituted cyclohexanone **6** must be performed (Scheme 2). The method is further limited by symmetry to cycloalkanones with an even number of carbons.

Scheme 1



Scheme 2 [a]



[a] G = Me 86% ee, *i*-Pr 95% ee, *t*-Bu 92% ee, Ph 93% ee.

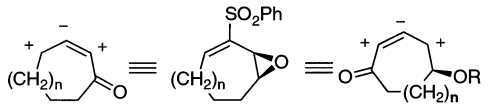
Results and Discussion

We are pleased to report epoxy vinyl sulfone chemistry provides improved methodology for the general synthesis of chiral 4-alkylcycloalkenones and for enantiopure 2,5-cyclohexadienone synthons. By analogy to our previous report in the racemic series,[8] epoxyvinyl sulfone ***SS*-9a** can be considered as a synthon for both unpoled enone **10a** as well as chiral 2,5-cyclohexadienone equivalent **11a** in which one masked enone is charge-inverted, and the latent enone is normally polarized (Scheme 3).

* To whom correspondence should be addressed. E-mail: pfuchs@purdue.edu.

(1) Syntheses via vinyl sulfones 85 and Chiral Carbon Catalog #8. For previous paper, see: Myers, D.; Fuchs, P. L. *J. Org. Chem.* **2002**, *67*, 200.
(2) Hikichi, S.; Hareau, G. P.-J.; Sato, F. *Tetrahedron Lett.* **1997**, *38*, 8299.
(3) Kitamura, M.; Ohkuma, T.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1988**, *29*, 1555.
(4) Hiroya, K.; Zhang, H.; Ogasawara, K. *Synlett* **1999**, 529. Kamikubo, T.; Ogasawara, K. *Chem. Commun.* **1995**, 1951. Shimizu, M.; Kamikubo, T.; Ogasawara, K. *Synlett* **1998**, 655.
(5) Takano, S.; Higashi, Y.; Kamikubo, T.; Moriya, M.; Ogasawara, K. *Synthesis* **1993**, 948.
(6) Ogasawara, K.; Kurihara, Y.; Hiroya, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2287.
(7) Aoki, K.; Nakajima, M.; Tomioka, K.; Koga, K. *Chem. Pharm. Bull.* **1993**, *41*, 994.
(8) Jin, Z.; Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 5995. (The six- and seven-membered 2-phenylsulfonyl-1,3-dienes are commercially available from Aldrich Chemical Co.)

Scheme 3



10a n=0 **9a** n=0 **11a** n=0

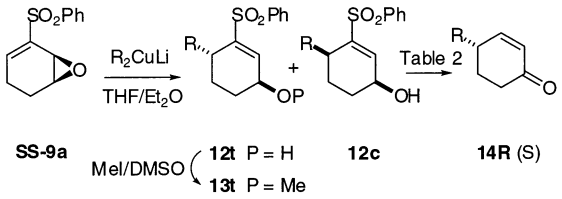
10b n=1 **9b** n=1 **11b** n=1

Table 1. Alkyl Cuprate Additions to ***SS*-9a**

R =	M =	% yield **12t,c**	HPLC ratio **12t/12c**	% yield
Me[a]	Li	98	>50/1	**13t-Me** 99
Et	MgBr	92	>50/1	**13t-Et** 97
i-Pr	MgCl	94	>50/1	**13t-Pr** 99
t-Bu	Li	93	>50/1	**13t-tBu** 98
$PhMe_2Si$	Li	87	>50/1	**13t-PhMe$_2$Si** 93
Ph	MgBr	90	3/1	not run

[a] 20% MeLi/20% CuI, 1.2 equiv of Me_3Al.

Scheme 4

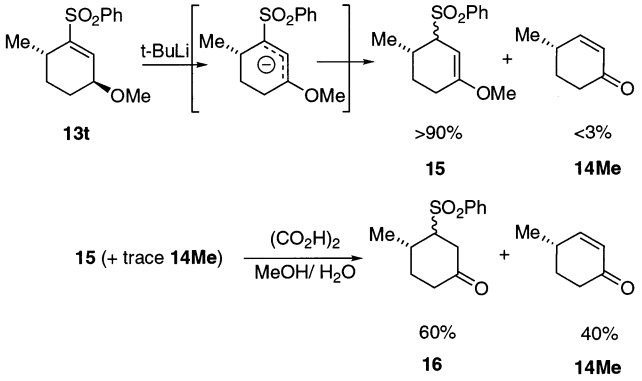


SS-9a MeI/DMSO **12t** P = H **13t** P = Me **12c** **14R** (S)

The enone synthesis begins with an update of our overly conservative NMR estimate that methylation of epoxyvinyl sulfone ***SS*-9**[9] proceeds with ~96/4 trans/cis specificity[10] for trans adduct **14**. Duplication of this reaction with enantiopure ***SS*-9** using chiral HPLC analysis reveals that the reaction is essentially stereospecific (Table 1, entry 1). Repetition of the process for the additional alkyl groups shown in Table 1 can be conveniently conducted with cuprates derived from both lithium and Grignard reagents *without the need for addition of any alkyl aluminum reagent* (Scheme 4). The reactions are all high yielding, and the product can be directly O-methylated as crude material. Methylation using MeI in basic DMSO is high yielding, fast, and does not require chromatography either before or after the process (Table 1). Substantial empirical efforts failed to increase the selectivity of phenyl addition beyond 3:1.

Addition of *t*-BuLi at −78 °C to **13t** generates a bright orange solution which, after 15 min, is quenched with saturated $NaHCO_3$ providing a mixture of sulfone diastereomers **15** in high yield accompanied by less than 3% of the desired enone **14Me** by NMR (Scheme 5). An attempt to hydrolyze diastereomeric vinyl ethers **15** to ketone **14Me** using 5% oxalic acid in 1:1 methanol/water was interrupted after 1 h at 25 °C. TLC analysis incorrectly suggested that the reaction contained only the mixture of starting vinyl ethers **15**. It was later revealed that **15**, **14Me**, and **16** have the same *Rf* value on TLC in the assay system employed. During workup, 10% NaOH was added to the diluted reaction mixture, which was then extracted with CH_2Cl_2. NMR analysis showed that **15** had been completely hydrolyzed to **16** with approximately 40% conversion to enone **14Me**. Et_3N was added to a mixture of γ-ketosulfones **16** and enone **14Me** in CH_2Cl_2. The ratio did not change. Heating the mixture to reflux in CH_2Cl_2, then in dichloroethane, and finally adding DBU, did not positively affect the ratio, and side products began to dominate the crude NMR. Because acidic conditions seemed to facilitate elimination, the process was repeated, and the oxalic acid hydrolysis step was allowed to stir overnight. The ratio, as analyzed by NMR, was worse, 75% **16** and 25% **14Me**.

Scheme 5



13t >90% **15** <3% **14Me**

15 (+ trace **14Me**) 60% **16** 40% **14Me**

Table 2. Cyclohexenones **14** from γ-MeO-Vinyl Sulfones

R	% yield	% ee[a]	% de
Me	**14Me** 93	93[b]	>99
Et	**14Et** 93	93.7	>99
i-Pr	**14Pr** 94	94.8[c]	>99[c]
t-Bu	**14tBu** 89	91.2	98
$PhMe_2Si$	NR		

[a] HPLC analysis. [b] By rotation, HPLC inseparable. [c] Enriched by crystallization.[16]

Adding the crude **16/14Me** mixture to THF/water containing 3% Et_3N and allowing the reaction to stir at 25 °C for 9 h was highly effective. *The ratio of THF to water is critical*. The substrate is dissolved in THF (approximately 0.09 M), water is added until the reaction becomes slightly cloudy, and then the minimum amount of THF is added to establish homogeneity. This process is ineffective without an aqueous wash of the initial reaction, because the lithium salt content does not allow the THF and water to be completely miscible.

Presumably, the basic aqueous conditions are more effective than those in CH_2Cl_2 because of the greater polarity of the media. Furthermore, the literature reveals that elimination of sulfinate from γ-ketosulfones is a reversible process and that the equilibrium lies far toward the side of the β-ketosulfone under acidic conditions.[11]

With a convenient method for conversion of the isomerized allyl sulfone to the desired enone finally in hand, 4-methylcyclohex-2-en-1-one **14Me** was produced in 93% yield. It is significant that the sp^3 cuprate additions to ***SS*-9a** are ~100% anti throughout the series of methyl, ethyl, isopropyl, and *tert*-butyl substituents as assayed by chiral HPLC of the resulting enones (**14**) shown in Table 2.

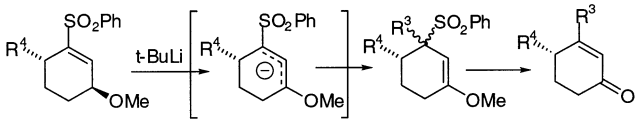
Epoxy vinyl sulfone ***SS*-9a** can be obtained in >99% ee, but in this experiment the ee of epoxide ***SS*-9a** was fixed at 93% by doping with racemic material, providing an unambiguous HPLC control. Except for **14Me** (chiral HPLC inseparable; 93% by rotation), all of the ee values in Table 2 were determined by HPLC analysis. With the possible exception of the *tert*-butyl

(9) Both enantiomers are equally available by catalytic epoxidation of the 2-phenylsulfonyl-1,3-dienes via Jacobsen epoxidation: Hentemann, M. F.; Fuchs, P. L. *Tetrahedron Lett.* **1997**, *38*, 5615.

(10) Saddler, J. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2112.

(11) Girlanda-Junges, C.; Keyling-Bilger, F.; Schmitt, G.; Luu, B. *Tetrahedron* **1998**, *54*, 7735.

Scheme 6



13ta R^4 = Me
13tb R^4 = i-Pr

15a $R^3 = R^4$ = Me **14a**
15b R^3 = allyl; R^4 = Me **14b**
15d R^3 = Me; R^4 = *i*-Pr **14d**
15e R^3 = allyl; R^4 = *i*-Pr **14e**
15f R^3 = *i*-Pr; R^4 = *i*-Pr **14f**
15g R^3 = Bu; R^4 = *i*-Pr **14g**

Table 3. Enantiopure 3,4-Disubstituted Enones

R^4	R^3	% yield	% ee or rotation
Me	Me[a]	**14a** 92	106°
Me	allyl[a]	**14b** 96	−153°
i-Pr	Me[a]	**14d** 90	93
i-Pr	allyl[a]	**14e** trace	
i-Pr	*i*-Pr[a]	**14f** no rxn	
i-Pr	Bu[a]	**14g** no rxn	
i-Pr	allyl[b]	**14e** 92	−69°
i-Pr	*i*-Pr[b]	**14f** trace	
i-Pr	Bu[b]	**14g** 84	−12°

[a] No HMPA added. [b] HMPA added.

Table 4. 3,4-Disubstituted Enones from **17** + Cuprates

R^4	R^3	% yield	% ee or rotation
17a Me	Me	**14a** 92	+106°
17a Me	allyl	**14b** 96	−153°
17a Me	*i*-Pr	**14c** 45	+119°
17b *i*-Pr	Me	**14d** 60	92

experiment, the reactions in Table 2 are held to be 100% enantiospecific within the limits of experimental detection.

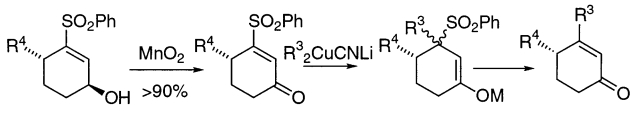
As previously reported, γ-methoxyallyl sulfone anions can be quenched with electrophiles.[8] Extension of this method to the more highly functionalized materials prepared in this study reveals that alkylations of proximally substituted γ-methoxyallyl sulfone anions are strongly influenced by the steric demands of the electrophile (Scheme 6). As can be seen in Table 3, synthesis of 3-substituted-4-alkyl cyclohex-2-en-1-ones bearing a secondary substituent in the 4-position are reluctant to alkylate under "standard" conditions, but can be successfully alkylated *provided that HMPA is added to the γ-methoxyallyl sulfone anion during the alkylation phase.* Still, these conditions cannot overcome the steric demands of the electrophile, with the 3,4-bisisopropyl adduct only being formed in 5−10% yield even using the HMPA protocol.

A complementary method for synthesis of 3-substituted-4-alkyl cyclohex-2-en-1-ones **14** involves reversing the role of nucleophile and electrophile. Oxidation of allylic alcohols **12ta** and **12tb** to β-sulfonyl enones **17a** and **17b**, respectively, using activated MnO_2 is high yielding. Michael addition of hetero-cuprates with subsequent β-elimination of sulfinate gives the desired 3,4-disubstituted enones **14** in fair yield (Table 4, Scheme 7). While cuprate reactions are well known for vinylogous thiolesters,[12] this is apparently the first report with vinylogous acyl sulfones **17** (β-sulfonyl enones).

2-Substituted 4-alkylcyclohexenones are also available by the addition of 2 equiv of alkyl or aryllithium followed by oxidation

(12) Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029. Dieter, R. K.; Silks, L. A., III. *J. Org. Chem.* **1986**, *51*, 4687. Coates, R. M.; Sandefur, L. O. *J. Org. Chem.* **1974**, *39*, 275.

Scheme 7



12ta R^4 = Me
12tb R^4 = i-Pr

17a R^4 = Me
17b R^4 = i-Pr

15a $R^3 = R^4$ = Me **14a**
15b R^3 = allyl, R^4 = Me **14b**
15c R^3 = i-Pr; R^4 = Me **14c**
15d R^3 = Me; R^4 = i-Pr **14d**

Scheme 8

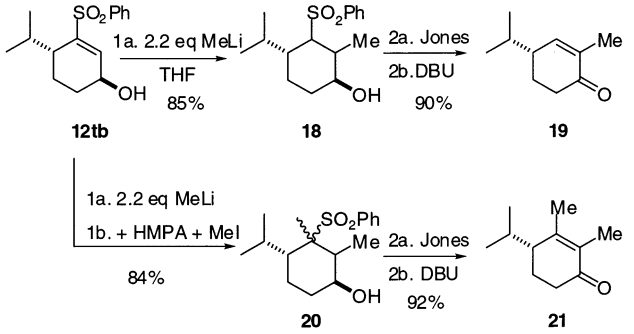


Table 5. Synthesis of Enones **24**

R =	yield **21**	yield **22**	yield **23**	yield **24**
Me	90	96	87	93
i-Pr	94	98	99	92

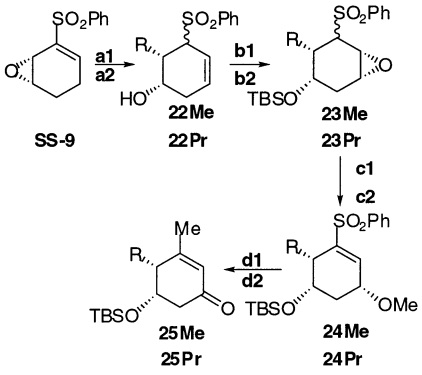
and elimination to the desired enone.[7,13] Application of this technology to **12tb** gives enone **19** in 90% yield (Scheme 8). Extension of the strategy for synthesis of 2,3,4-trisubstituted enones was also examined beginning with alcohol **12tb**. In this instance, addition of the methyllithium and subsequent capture of the anion with the methyl iodide produce **20** as a mixture of isomers. Oxidation of **20** followed by elimination furnishes trisubstituted enone **21** in excellent yield (92%).

Enantiopure epoxyvinyl sulfone ***SS*-9a** also can serve as a synthon for differentiated cyclohexa-2,5-dienones. Treatment of ***SS*-9a** with 1 equiv of LiHMDS followed by addition of methyl- or isopropyl-lithium proceeds via sequential γ-metalation/epoxide fragmentation followed by OM-directed conjugate-addition with quenching α to the sulfone moiety to generate **22** as shown in Table 5 and Scheme 9. $Mo(CO)_3$-catalyzed directed epoxidation with *t*Bu-OOH gives **23**; DBU treatment of **23** for the absolute minimal time (<1 h) cleanly effects β-elimination of the epoxide moiety. Methylation of the resulting γ-sulfonyl allyl alcohol may be done in the same operation to provide **24** in the yields indicated in Table 5. Treatment of **24** with *tert*-butyllithium affords an allylic anion which reacts with methyl iodide (HMPA essential) to give enantiopure enones **25** in >92% yield. Hydrolysis of the highly substituted substrates to their corresponding enones was found to work better under slightly acidic media (SiO_2).

2-Phenylsulfonyl-1,3-cycloheptadiene gives epoxide ***SS*-9b** in high yield and ee with Jacobsen's AE.[9] Nucleophilic methylation of ***SS*-9b** is regio- and stereospecific providing vinyl sulfone **26**. In contrast to the cyclohexyl examples, use of aluminum reagents is required to get clean conversion and high yield. Conversion to 4-methylcyclohept-2-en-1-one **28** is high yielding, but 3 days is required to convert **27** to enone **28**. As

(13) Conrad, P. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 346.

Scheme 9 [a]



Me series, R = Me; Pr series, R = *i*-Pr.

[a] a1. 1.1 equiv of LiHMDS, THF, −78 °C; a2. MeLi or *i*-PrMgCl (4 equiv), −78 °C, 2 h; b1. 2% $Mo(CO)_6$, 1.1 equiv of TBHP, C_6H_6, 80 °C, 2 h; b2. 1.2 equiv of TBSOTf, 1.5 equiv of Et_3N, CH_2Cl_2, 0.5 h, 25 °C; c1. 1.1 equiv of DBU, THF, reflux, 50 min; c2. 10 equiv of MeI, KOH, DMSO, 25 °C, 20 min; d1. 2.0 equiv of *t*-BuLi, −78 °C, 5.0 equiv of HMPA, 0.1 M THF, 20 min, then 5 equiv of MeI; d2. SiO_2, $CHCl_3$, 3 h, 25 °C.

previously demonstrated,[8] metalation/fragmentation/silylation of ***SS*-9b** provides **29**,[14] in near-quantitative yield. This substrate undergoes ready conjugate-addition to provide allyl sulfone **30**. Oxidation of allyl sulfone **30** yielded epoxide **31**, which was treated with DBU to afford vinyl sulfone **32** whose structure was verified by single-crystal X-ray analysis of the methyl derivative **33**.[15] Alcohol methylation followed by metalation/alkylation/elimination of **32** provides enantiopure enone **34**, while nucleophilic methylation/oxidation/elimination generates isomeric enone **36** with equal facility (Scheme 10).

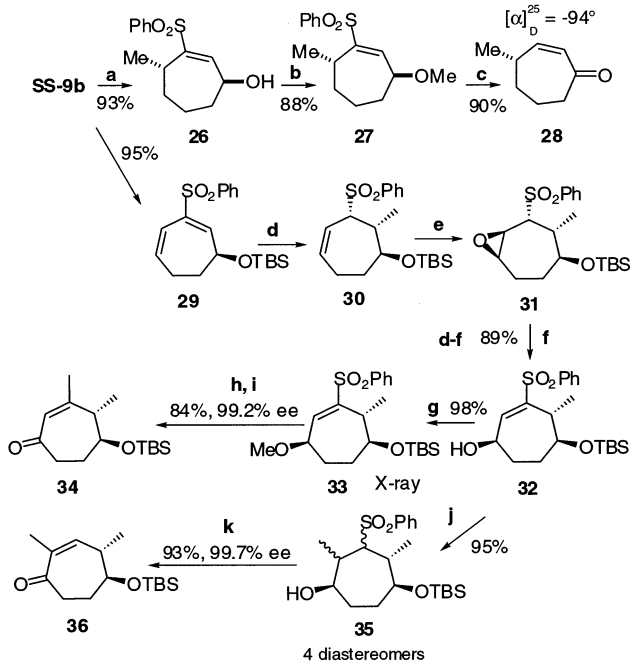
Conclusion

S_N2' addition of alkyl organometallic reagents to cross-conjugated six- and seven-membered epoxyvinyl sulfones results in enantiospecific anti 1,4-addition. These initial vinyl sulfone adducts may be further functionalized to ultimately give high yields of enones which have been alkylated in the α,*β*- and *γ*-positions. The cyclohexyl substrate may be elaborated to an enone bearing both a reactive and a latent enone, thus providing improved access to the enantiopure cyclohexadienone synthon. Similar processing has also been accomplished on the cycloheptyl substrate generating enones alkylated in the α,*β*-, *γ*-, and *δ*-positions, which also bear a protected alcohol moiety in the *δ*-position.

Experimental Procedures

All purchased reagents were used as received. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Benzene, toluene, dichloromethane (CH_2Cl_2), anhydrous methanol dimethyl sulfoxide (DMSO), and dimethyl formamide (DMF) were distilled from calcium hydride. Acetonitrile (CH_3CN), chloroform ($CHCl_3$), and methanol were spectra-grade. *n*-BuLi and *t*-BuLi were titrated prior to use by dropwise addition to a solution of *N*-benzylbenzamide in THF at −78 to 0 °C. Sodium sulfate (Na_2SO_4) and magnesium sulfate ($MgSO_4$) were used as received. Powdered 4

Scheme 10 [a]



[a] a. MeCu (cat), $AlMe_3$, THF, Et_2O, −78 °C, 2 h; b. MeI (10 equiv), KOH, DMSO, 15 min; c1. *t*-BuLi, THF, −78 °C, 10 min; c2. Et_3N, THF, H_2O, 3 d; d. MeLi, THF, −78 °C, 0.5 h; e. 2.5 equiv of *m*-CPBA, CH_2Cl_2, 24 h, 25 °C; f. DBU, THF reflux, 18 h; g. MeI (10 equiv), KOH, DMSO, 5 min; h1. *t*-BuLi, THF, −78 °C, 10 min; h2. MeI, warm to 25 °C, 15 min; i. SiO_2, $CHCl_3$, 6 h, 25 °C; j. 3.0 equiv of MeLi, THF, −50 to 0 °C, 1 h; k. PCC, CH_2Cl_2, 5 h, 25 °C, then 10% NaOH, THF, 8 h, 25 °C.

Å molecular sieves (Aldrich) were oven and/or flame activated under vacuum prior to use. Glassware was oven dried and/or flame dried. All reactions were carried out under a positive pressure of argon in anhydrous solvents (unless otherwise indicated), and the reaction flasks were fitted with rubber septa for the introduction of substrates and reagents via syringe. Unless otherwise noted, all reactions were worked up using standard conditions. Standard workup conditions are the addition of an equal volume of the stated organic solvent followed by two equal volumes of water or aqueous solution. All subsequent washes are perfomed with volumes equal to the organic solution being washed. The progress of reactions was monitored by thin-layer chromatography (TLC) in comparison with the starting material(s). TLC was performed on glass-backed silica gel 60 F 254 plates (EM reagents, 0.25 mm) and eluted with (v/v) ethyl acetate (EA) in hexanes (Hex) or the specified solvent solutions. The TLC plates were visualized with a UV lamp (254 nm) and/or with TLC visualizing solutions activated with heat. The two commonly employed TLC visualizing solutions were (i) *p*-anisaldehyde solution (1350 mL of absolute ethanol, 50 mL of concentrated H_2SO_4, 15 mL of glacial acetic acid, 37 mL of *p*-anisaldehyde), and (ii) permanganate solution (weight percents of 1% $KmnO_4$ and 2% Na_2CO_3 in H_2O). All organic extracts were dried with $MgSO_4$ unless otherwise noted. Analytical samples were obtained from flash silica gel chromatography (SGC), using silica gel of 230−400 mesh, or from recrystallization of the crude products. Silica gel was washed with Et_3N and acetone to render it deactivated. Melting points were obtained on a MEL-TEMP capillary melting point apparatus and uncorrected. Optical rotations were taken on a Rudolph Research Autopol III instrument at 25 °C. ^1H NMR spectra were recorded on Varian INOVA-300 (300 MHz) and Varian VXR (500 MHz) spectrometers. ^{13}C NMR spectra were recorded on Varian INOVA-300 (75 MHz) and Varian VXR (125 MHz) spectrometers. NMR spectra were determined in chloroform-d_1 ($CDCl_3$) solution and are reported in parts per million (ppm) from the residual chloroform (7.26 and 77.00 ppm). Peak multiplicities in ^1H NMR spectra, when reported, are abbreviated as s (singlet), d (doublet), t (triplet), m (multiplet), and b (broad). Mass

(14) Jiang, W.; Lantrip, D. A.; Fuchs, P. L. *Org. Lett.* **2000**, *2*, 2181.
(15) X-ray data for compounds **23Me a**, **23Pr a**, and **33** have been submitted to the Cambridge Crystallographic database. A depiction of the X-ray structure of **33** has been included in the Supporting Information.
(16) The ee of the starting epoxide ***SS*-9a** was 93%, and the ee of **18** was calculated to be 93% by rotation value. ***SS*-9a** can be obtained in >99% ee, but, to aid in HPLC analysis, the normally enantiopure material was doped with racemic epoxide to give 93% ee.

spectra were run by the Purdue University campus wide mass spectrometry facility. The low resolution EI and CI (isobutane) spectra were obtained on a Finnigan 4000 mass spectrometer with a Nova 4 data system with the molecular ion designated as "$M^{+\cdot}$" (all mass-to-charge ratios are reported as *m*/*z*). The high-resolution mass spectra were obtained on a Kratos MS-50 instrument.

General Procedure for the Addition of Mixed Alkyl Cuprates to Epoxyvinyl Sulfone *SS*-9a. To 530 mg (5.9 mmol) of anhydrous CuCN in 25 mL of THF cooled to −78 °C was added 1.15 equiv (4.86 mmol) of the desired alkyllithium or Grignard reagent. The stirred mixture was allowed to warm to −20 °C for 15 min. The reaction temperature was returned to −78 °C, and 1.0 g (4.23 mmol) of ***SS*-9a** in 10 mL of THF was added via cannula. The reaction was then allowed to stir for 4−6 h without further cooling. When complete by TLC, the reaction was quenched with saturated NH_4Cl and extracted with ether. The organic layer was then washed again with 5% HCl. After being dried and the solvent was removed in vacuo, the resulting material can typically be used without purification and was 95% pure by NMR.

General Procedure for the Etherification of γ-Hydroxy Vinyl Sulfones. Crude γ-hydroxy vinyl sulfone (4.0 mmol) was dissolved and rapidly stirred in 30 mL of anhydrous DMSO and cooled in a 25 °C water bath. Next 20−30 equiv of MeI was added. Powdered KOH was added slowly, approximately one pellet every 3 min for a total of five pellets. When complete by TLC, the dark mixture was poured into ice water. The mixture was extracted with ether three times, and the solvent was removed in vacuo. SGC, 6:4 Hex/EA, provided the desired methyl ethers in nearly quantitative yield.

General Procedure for the Conversion of γ-Methoxy Vinyl Sulfones to Enones. First, 1.2 equiv of *t*-BuLi (0.61 mmol) was added to the γ-methoxy vinyl sulfone (0.51 mmol) in 20 mL of THF at −78 °C over 2 min. The resulting bright orange reaction was stirred at this temperature for 25 min. Ten milliliters of a saturated solution of $NaHCO_3$ was added, and the reaction was allowed to warm to room temperature. The mixture was extracted into 40 mL of ether and concentrated. Fifteen milliliters of THF was added followed by water until the two solvents begin to separate. More THF was added just until the solution becomes homogeneous. Next 0.5 mL of Et_3N was added, and the reaction was stirred for 15 h. Monitoring the reaction was best accomplished by NMR. When complete, ether and water were added, the organic layer was separated, and the solvent was removed in vacuo. SGC, 8:2 Hex/EA, provided the desired enones in good yield.

(3*S*,6*S*)-(3-Methoxy-6-methylcyclohex-1-enesulfonyl)-benzene (13t-Me). Quantitative yield. clear oil. ^{1}H NMR ($CDCl_3$): δ 7.85 (d, *J* = 9.5 Hz, 2H), 7.60 (m, 3H), 7.03 (d, *J* = 2.6 Hz, 1H), 3.86 (m, 1H), 3.40 (s, 3H), 2.45 (m, 1H), 1.93−1.60 (m, 3H), 1.38 (m, 1H), 1.17 (d, *J* = 7 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 147.17, 139.71, 136.63, 133.27, 129.13, 128.02, 73.04, 56.74, 28.68, 27.26, 23.90, 19.02. LRMS: (EI) 266 (highest mass), 125 (base peak). (CI) 129 (M + H). HRMS: calculated for $C_{14}H_{18}O_3S$ 267.1055, found 267.1053. $[\alpha]_D$ (*c* 2.28, $CHCl_3$) = −132°.

(*S*)-4-Methylcyclohex-2-enone (14Me). 93% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.80 (ddd, *J* = 10.2, 4.8, 2.2 Hz, 1H), 5.94 (dd, *J* = 10.2, 4.8 Hz, 1H), 2.60−2.30 (m, 3H), 2.10 (m, 1H), 1.67 (m, 1H), 1.16 (d, *J* = 7 Hz, 3H). $[\alpha]_D$ (*c* 0.56, $CHCl_3$) = −116°.

(1*S*,4*S*)-3-Benzenesulfonyl-4-ethylcyclohex-2-enol (12t-Et). 92% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.85 (d, *J* = 9.5 Hz, 2H), 7.60 (m, 3H), 6.98 (d, *J* = 3.4 Hz, 1H), 4.32 (m, 1H), 3.16 (d, *J* = 6 Hz, 1H), 2.29 (m, 1H), 2.00−1.40 (m, 5H), 1.22 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 145.61, 139.89, 139.61, 133.24, 129.06, 127.74, 64.03, 34.80, 26.93, 24.07, 21.55, 11.28. LRMS: (EI) 266 (highest mass), 125 (base peak). (CI) 267 (M + H). HRMS: calculated for $C_{14}H_{18}O_3S$ 266.0977, found 266.0975. $[\alpha]_D$ (*c* 9.07, $CHCl_3$) = −87°.

(3*S*,6*S*)-(6-Ethyl-3-methoxycyclohex-1-enesulfonyl)-benzene (13t-Et). 97% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.85 (d, *J* = 9.5 Hz, 2H), 7.60 (m, 3H), 7.05 (d, *J* = 3.2 Hz, 1H), 3.86 (m, 1H), 3.42 (s, 3H), 2.29 (m, 1H), 2.00−1.40 (m, 5H), 1.32 (m, 1H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 146.52, 139.75, 137.28, 133.20, 129.07, 127.92, 72.91, 56.64, 35.05, 24.21, 23.76, 21.92, 11.39. LRMS: (EI) 280 (highest mass), 139 (base peak). (CI) 281 (M + H). HRMS: calculated for $C_{15}H_{20}O_3S$ 280.1133, found 280.1132. $[\alpha]_D$ (*c* 2.30, $CHCl_3$) = −150°.

(*S*)-4-Ethylcyclohex-2-enone (14Et). 93% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.90 (ddd, *J* = 10.2, 2.6, 1.4 Hz, 1H), 6.01 (ddd, *J* = 10.2, 2.4, 0.8 Hz, 1H), 2.54 (dt, *J* = 16.8, 5.3 Hz, 1H), 2.40 (m, 2H), 2.16 (m, 1H), 1.60 (m, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). 93.7% ee HPLC Chiralcel AD 0.75 mL/min 99.5:0.5 Hex:2-propanol. 15.57 min minor enantiomer, 16.59 min major enantiomer.

(1*S*,4*R*)-3-Benzenesulfonyl-4-isopropylcyclohex-2-enol (12t-Pr). 94% yield. White solid. mp 105 °C. ^{1}H NMR ($CDCl_3$): δ 7.85 (d, *J* = 9.5 Hz, 2H), 7.60 (m, 3H), 7.10 (m, 1H), 4.32 (m, 1H), 2.94 (d, *J* = 5.8 Hz, 1H), 2.50 (m, 2H), 2.1 (m, 1H), 1.80 (m, 1H), 1.4 (m, 2H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.50 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 144.77, 143.97, 140.00, 133.19, 129.04, 127.91, 66.57, 39.73, 30.33, 27.98, 20.19, 19.07, 15.80. LRMS: (EI) 262 (highest mass), 77 (base peak). (CI) 281 (M + H). HRMS: calculated for $C_{15}H_{20}O_3S$ 280.1133, found 280.1129. mp 105 °C. $[\alpha]_D$ (*c* 5.22, $CHCl_3$) = −24°.

(3*S*,6*R*)-(6-Isopropyl-3-methoxycyclohex-1-enesulfonyl)-benzene (13t-Pr). Quantitative yield. White solid. mp 113 °C. ^{1}H NMR ($CDCl_3$): δ 7.95 (m, 2H), 7.60 (m, 3H), 7.13 (m, 1H), 3.87 (m, 1H), 3.44 (s, 3H), 2.50 (m, 2H), 2.1 (m, 1H), 1.80 (m, 1H), 1.4 (m, 2H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 144.58, 141.72, 133.16, 129.03, 128.04, 75.29, 56.35, 39.93, 28.13, 27.10, 20.21, 15.95. LRMS: (EI) 294 (highest mass), 110 (base peak). (CI) 295 (M + H). HRMS: calculated for $C_{16}H_{22}O_3S$ 294.1290, found 294.1282. mp 113 °C. $[\alpha]_D$ (*c* 1.44, $CHCl_3$) = −87°.

(*R*)-4-Isopropylcyclohex-2-enone (14iPr). 94% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.94 (dt, *J* = 10.4, 2.1 Hz, 1H), 6.04 (dd, *J* = 10.4, 2.6 Hz, 1H), 2.56 (dt, *J* = 16.6, 4.3 Hz, 1H), 2.40 (m, 2H), 2.10 (m, 1H), 1.80 (m, 2H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H). 94.7% ee HPLC Chiralcel AD 0.75 mL/min 99.5:0.5 Hex:2-propanol. 21.20 min minor enantiomer, 24.70 min major enantiomer.

(1*S*,4*R*)-3-Benzenesulfonyl-4-*tert*-butylcyclohex-2-enol (12t-tBu). 93% yield. Sticky clear, colorless film. ^{1}H NMR ($CDCl_3$): δ 7.85 (d, *J* = 9.5 Hz, 2H), 7.60 (m, 3H), 6.86 (d, *J* = 2.1 Hz, 1H), 4.32 (m, 1H), 2.56 (m, 2H), 2.17 (m, 1H), 1.84 (m, 1H), 1.53 (m, 1H), 1.37 (m, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 145.92, 144.25, 140.19, 133.16, 129.06, 128.03, 64.20, 42.10, 34.92, 29.88, 29.12, 22.40. LRMS: (EI) 261 (highest mass), 220 (base peak). (CI) 295 (M + H). HRMS: calculated for $C_{16}H_{22}O_3S$ 294.1290, found 294.1277. $[\alpha]_D$ (*c* 7.35, $CHCl_3$) = −107°.

(3*S*,6*R*)-(6-*tert*-Butyl-3-methoxycyclohex-1-enesulfonyl)-benzene (13t-tBu). 98% yield. White oily solid. ^{1}H NMR ($CDCl_3$): δ 7.85 (d, *J* = 9.5 Hz, 2H), 7.60 (m, 3H), 6.91 (d, *J* = 2.6 Hz, 1H), 3.85 (m, 1H), 3.32 (s, 3H), 2.59 (dd, *J* = 6.1, 3.1 Hz, 1H), 2.14 (m, 1H), 1.84 (m, 1H), 1.54 (m, 1H), 1.31 (m, 1H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 146.54, 142.28, 140.53, 133.14, 129.09, 128.11, 73.09, 56.42, 42.56, 35.22, 29.88, 26.12, 22.71, 10.22. LRMS: (EI) 293 (highest mass), 220 (base peak). (CI) 309 (M + H). HRMS: calculated for $C_{17}H_{24}O_3S$ 308.1446, found 308.1436. $[\alpha]_D$ (*c* 4.47, $CHCl_3$) = −142°.

(*S*)-4-*tert*-Butylcyclohex-2-enone (14tBu). 89% yield. ^{1}H NMR ($CDCl_3$): δ 7.05 (dt, *J* = 10.5, 2.0 Hz, 1H), 6.07 (ddd, *J* = 10.5, 2.9, 1.2 Hz, 1H), 2.56 (dt, *J* = 16.5, 3.4 Hz, 1H), 2.40 (m, 1H), 2.23 (m, 1H), 2.18 (m, 1H), 1.8 (m, 1H), 1.01 (s, 9H). 91% ee HPLC Chiralcel AD 1.0 mL/min 99:1 Hex:2-propanol. 10.60 min minor enantiomer, 13.86 min major enantiomer.

(1*S*,4*S*)-3-Benzenesulfonyl-4-(dimethylphenylsilanyl)cyclohex-2-enol (12t-PhMe$_2$Si). 87% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.76−7.33 (m, 10H), 6.80 (d, *J* = 3.7 Hz, 1H), 4.20 (m,

1H), 2.06 (m, 2H), 1.60 (m, 4H), 0.55 (s, 3H), 0.48 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 146.48, 138.72, 137.96, 134.81, 134.08, 133.25, 129.04, 128.11, 127.64, 62.97, 29.41, 24.90, 21.39, 13.65, 10.35, −1.83, −1.94. LRMS: (EI) 372 (highest mass), 135 (base peak). (CI) 372 (M+). HRMS: calculated for $C_{20}H_{24}O_3SSi$ 372.1215, found 372.1197. $[\alpha]_D$ (c 3.49, $CHCl_3$) = −174°.

(1*S*,4*S*)-(2-Benzenesulfonyl-4-methoxycyclohex-2-enyl)-1-dimethylphenylsilane (13t-PhMe$_2$Si). 93% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.76−7.35 (m, 10H), 6.92 (m, 1H), 3.66 (m, 1H), 3.36 (s, 3H), 2.01 (m, 1H), 1.60 (m, 4H), 1.40 (m, 1H), 0.56 (s, 3H), 0.49 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 146.63, 138.94, 138.06, 134.10, 133.24, 133.15, 129.03, 129.00, 128.09, 127.63, 71.83, 56.61, 26.07, 25.00, 21.86, −1.86, −1.95. LRMS: (EI) 386 (highest mass), 135 (base peak). HRMS: calculated for $C_{21}H_{26}O_3SSi$ 386.1372, found 386.1355. $[\alpha]_D$ (c 3.00, $CHCl_3$) = −186°.

(1*S*,4*S*)-3-Benzenesulfonyl-4-methylcyclohept-2-enol (25). 93% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 2H), 7.55 (m, 3H), 7.20 (m, 1H), 4.63 (m, 1H), 3.40 (d, J = 4.9 Hz, 1H), 2.78 (m, 1H), 2.00−1.40 (m, 5H), 1.20 (m, 1H), 0.95 (d, J = 6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 148.27, 143.80, 138.76, 133.17, 129.03, 127.95, 70.71, 35.83, 31.94, 31.71, 20.52, 16.10. LRMS: (EI) 237 (highest mass), 125 (base peak). (CI) 267 (M + H). HRMS: calculated for $C_{14}H_{18}O_3S$ 266.0977, found 266.0964. $[\alpha]_D$ (c 2.26, $CHCl_3$) = −21°.

(3*S*,7*S*)-1-Benzenesulfonyl-3-methoxy-7-methylcycloheptene (26). 88% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 2H), 7.55 (m, 3H), 7.20 (m, 1H), 4.63 (dt, J = 11.4, 2.1 Hz, 1H), 2.80 (m, 1H), 2.00−1.20 (m, 6H), 1.00 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 145.45, 145.08, 138.95, 133.11, 129.00, 128.02, 79.80, 56.60, 32.23, 31.93, 31.79, 20.72, 16.24. LRMS: (EI) 280 (highest mass), 239 (base peak). (CI) 281 (M + H). HRMS: calculated for $C_{15}H_{20}O_3S$ 280.1133, found 280.1126. $[\alpha]_D$ (c 8.06, $CHCl_3$) = −74°.

(*S*)-4-Methylcyclohept-2-enone (27). 90% yield. Conversion to enone required 3 days. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 6.36 (ddd, J = 12.2, 3.6, 0.8 Hz, 1H), 5.96 (dd, J = 12.2, 2.4 Hz, 1H), 2.63 (m, 3H), 1.96 (m, 1H), 1.83 (m, 2H), 1.55 (m, 1H), 1.20 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 204.42, 151.68, 130.61, 43.60, 35.65, 34.27, 21.88, 20.63. $[\alpha]_D$ (c 2.03, $CHCl_3$) = −94°.

General Procedure for Generation of β-Substituted Enones via Electrophile Capture. Following the general procedure for the conversion of γ-methoxy vinyl sulfones to enones, the orange anionic solution was quenched with 1.1 equiv of the desired electrophile. The reaction decolorizes at −78 °C after 15 min. A saturated solution of $NaHCO_3$ was added followed by ether. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was dissolved in $CHCl_3$ 1 mL/mmol, and SiO_2 250 mg/mmol was added. After 2 h, the solution was filtered, and the solvent was removed in vacuo. The enones are typically 90−95% pure. Silica gel chromatography can be used if necessary.

HMPA-Modified Procedure for Generation of β-Substituted Enones via Electrophile Capture. First, 1.2 equiv of t-BuLi (0.61 mmol) was added to the mixture of γ-methoxy vinyl sulfone (0.51 mmol) and HMPA (2.5 mmol) in 20 mL of THF at −78 °C over 2 min. The resulting dark orange reaction was stirred at this temperature for 10 min. The solution was quenched with 3.1 equiv of the desired electrophile. The reaction decolorizes at −78 °C after 15 min. A saturated solution of $NaHCO_3$ was added followed by ether. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was dissolved in $CHCl_3$ 1 mL/mmol, and SiO_2 250 mg/mmol was added. After 3 h, the solution was filtered, and the solvent was removed in vacuo. The enones are typically 90−95% pure. Silica gel chromatography can be used if necessary.

General Procedure for the Oxidation of γ-Hydroxy Vinyl Sulfones. First, 2 mmol of γ-hydroxy vinyl sulfone was dissolved in 100 mL of ether. Activated MnO_2 was added portionwise with rapid stirring until the reaction was complete as determined by TLC. The reaction was filtered through a 1:1 mixture of Celite and SiO_2. The resulting enones did not require purification and were routinely used crude.

General Procedure for Generation of β-Substituted Enones via Addition/Elimination. Alkyl cuprates, prepared as above, were added to β-sulfonyl-enones at −78 °C in THF. The reactions were allowed to warm slowly to room temperature overnight. Ether and water were added to the reactions. The organic layer was dried and concentrated in vacuo. SGC, 8:2, Hex:EA, provided the desired enones in the yields indicated with the remaining mass recovered as unreacted starting material.

(*S*)-3-Benzenesulfonyl-4-methylcyclohex-2-enone (17a). 92% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.95 (m, 2H), 7.69 (m, 3H), 6.57 (s, 1H), 2.93 (m, 1H), 2.63 (ddd, J = 18.7, 13.6, 5.2 Hz, 1H), 2.44 (dt, J = 17.9, 3.8 Hz, 1H), 2.09 (m, 1H), 1.94 (m, 1H), 1.33 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 197.78, 163.83, 137.82, 134.35, 130.00, 129.54, 128.66, 32.86, 30.13, 28.50, 18.19. LRMS: (EI) 250 (highest mass), 81 (base peak). (CI) 251 (M + H). HRMS: calculated for $C_{13}H_{14}O_3S$ 250.0664, found 250.0660. $[\alpha]_D$ (c 5.19, $CHCl_3$) = −11°.

(*R*)-3-Benzenesulfonyl-4-isopropylcyclohex-2-enone (17b). 91% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.95 (m, 2H), 7.68 (m, 3H), 6.61 (m, 1H), 2.82 (m, 1H), 2.65−2.30 (m, 3H), 2.20 (m, 1H), 1.92 (m, 1H), 1.12 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 198.14, 162.75, 138.33, 134.25, 131.89, 129.50, 128.60, 39.38, 34.81, 30.29, 22.92, 21.55, 18.79. LRMS: (EI) 278 (highest mass), 236 (base peak). (CI) 279 (M + H). HRMS: calculated for $C_{15}H_{18}O_3S$ 278.0977, found 278.0968. $[\alpha]_D$ (c 1.71, $CHCl_3$) = −75°.

(*S*)-3,4-Dimethylcyclohex-2-enone (14a). 92% yield. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.80 (t, J = 1.2 Hz, 1H), 2.50−2.20 (m, 3H), 2.10 (m, 1H), 1.75 (m, 1H), 1.18 (d, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 199.60, 166.59, 126.26, 34.48, 34.29, 30.24, 22.66, 17.66. $[\alpha]_D$ (c 0.51, $CHCl_3$) = +106°.

(*S*)-3-Allyl-4-methylcyclohex-2-enone (14b). 96% allyl bromide capture. Clear, light yellow oil. ^{1}H NMR ($CDCl_3$): δ 5.86 (s, 1H), 5.83 (m, 1H), 5.19 (m, 2H), 3.00 (d, J = 7.0 Hz, 2H), 2.53 (m, 2H), 2.36 (m, 1H), 2.16 (m, 1H), 1.83 (m, 1H), 1.24 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 199.41, 167.93, 133.52, 125.68, 118.11, 39.80, 34.12, 32.84, 30.10, 17.53. LRMS: (EI) 150 (highest mass), 79 (base peak). (CI) 151 (M + H). HRMS: calculated for $C_{10}H_{14}O$ 150.1045, found 150.1043. $[\alpha]_D$ (c 1.40, $CHCl_3$) = −153°.

(*S*)-3-Isopropyl-4-methylcyclohex-2-enone (14c). 45% yield, i-PrCu(CN)Li addition. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.87 (m, 1H), 2.53 (m, 2H), 2.34 (dt, J = 17.4, 5.1 Hz, 1H), 2.12 (m, 1H), 1.84 (m, 1H), 1.24 (d, J = 6.9 Hz, 3H), 1.15 (d, J = 6.6 Hz, 3H), 1.13 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 200.09, 176.52, 122.43, 33.64, 32.93, 32.38, 30.26, 22.30, 20.68, 17.89. LRMS: (EI) 152 (highest mass), 109 (base peak). (CI) 153 (M + H). HRMS: calculated for $C_{10}H_{16}O$ 152.1201, found 152.1199. $[\alpha]_D$ (c 0.43, $CHCl_3$) = +119°.

(*R*)-4-Isopropyl-3-methylcyclohex-2-enone (14d). 90% yield MeI capture, 60% yield MeCu(CN)Li addition. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.95 (m, 1H), 2.48 (ddd, J = 17.1, 7.2, 5.1 Hz, 1H), 2.27 (m, 2H), 2.00 (m, 1H), 1.99 (m, 3H), 1.93 (m, 2H), 1.06 (d, J = 6.9 Hz, 3H), 0.86 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 200.32, 165.75, 128.86, 45.94, 36.51, 29.18, 23.82, 22.61, 21.92, 18.38. 93% ee HPLC Chiralcel AD 1.0 mL/min 97.5:2.5 Hex:2-propanol. 7.68 min minor enantiomer, 8.36 min major enantiomer.

(4*S*)-3-Allyl-4-isopropylcyclohex-2-enone (14e). Using HMPA, 92% yield allyl bromide capture. Clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.92 (m, 1H), 5.77 (m, 1H), 2.98 (d, J = 6.9 Hz, 2H), 2.47 (m, 1H), 2.22 (m, 3H), 1.94 (m, 2H), 1.03 (d, J = 6.7 Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 199.75, 166.74, 133.85, 127.47, 43.83, 40.49, 35.46, 28.83, 22.43, 21.47, 18.39. LRMS: (EI) 178 (highest mass), 135 (base peak). HRMS: calculated for $C_{12}H_{18}O$ 178.1358, found 178.1354. $[\alpha]_D$ (c 6.80, $CHCl_3$) = −69°.

(4*R*)-3-Butyl-4-isopropylcyclohex-2-enone (14g). Using HMPA, 84% yield butyl iodide capture. Clear colorless oil. ^{1}H NMR ($CDCl_3$):

δ 5.91 (m, 1H), 2.46 (m, 1H), 2.20 (m, 5H), 1.93 (m, 2H), 1.42 (m, 4H), 1.03 (d, J = 6.7 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 199.93, 169.32, 126.64, 43.90, 36.70, 35.47, 29.85, 28.98, 22.48, 21.51, 18.46, 13.85. LRMS: (EI) 194 (highest mass), 110 (base peak). HRMS: calculated for $C_{13}H_{22}O$ 194.1671, found 1941675. $[\alpha]_D$ (c 5.8, $CHCl_3$) = −12°.

(*R*)-4-Isopropyl-2-methylcyclohex-2-enone (19). Three equivalents of MeLi (1.5 mmol) was added to 140 mg (0.5 mmol) of **12t-iPr** in 20 mL of THF at −78 °C. After 1 h, ether and water were added to the reaction. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was dissolved in 20 mL of acetone and cooled to 0 °C. Jones reagent was added until an orange color persisted. Several drops of 2-propanol were added to bring the reaction back to green. The entire contents of the flask were filtered through a plug of fluorosil, and the solvent was removed in vacuo. The residue was dissolved in 20 mL of $CHCl_3$, 0.76 g (0.5 mmol) of DBU was added, and the reaction was heated to reflux for 2 h. The solvent was removed in vacuo. The crude material was loaded directly onto silica. SGC, 8:2, Hex:EA, provided **19** as a clear colorless liquid. 57 mg, 75% yield. ^{1}H NMR ($CDCl_3$): δ 6.68 (m, 1H), 2.56 (dt, J = 16.6, 4.3 Hz, 1H), 2.33 (m, 2H), 2.00 (m, 1H), 1.81 (dd, J = 2.4, 1.4 Hz, 3H), 1.76 (m, 2H), 0.99 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 200.35, 149.45, 135.45, 42.82, 37.61, 31.70, 25.62, 19.64, 19.40, 16.10. 91.2% ee HPLC Chiralcel AD 1.0 mL/min 99:1 Hex:2-propanol. 5.79 min minor enantiomer, 6.49 min major enantiomer.

(4*R*)-4-Isopropyl-2,3-dimethylcyclohex-2-enone (21). Three equivalents of MeLi (1.65 mmol) was added to a mixture of 157 mg (0.55 mmol) of **12t-iPr** and HMPA (0.48 mL, 2.75 mmol) in 6 mL of THF at −78 °C. After 30 min, methyl iodide (0.17 mL, 2.75 mmol) was added, and the temperature was allowed to rise to −30 °C. Ether (10 mL) and water (5 mL) were added to the reaction, and the mixture was then extracted. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was dissolved in 10 mL of acetone and cooled to 0 °C. Jones reagent was added until an orange color persisted. Several drops of 2-propanol were added to bring the reaction back to green. The entire contents of the flask were filtered through a plug of fluorosil, and the solvent was removed in vacuo. The residue was dissolved in 20 mL of $CHCl_3$, 0.123 mL (0.83 mmol) of DBU was added, and the reaction was heated to reflux for 2 h. The solvent was removed in vacuo. The crude material was loaded directly onto silica. SGC, 8:2, hexane:ethyl acetate, provided **21** as a clear colorless liquid. 83.7 mg, 92% yield. ^{1}H NMR ($CDCl_3$): δ 2.50 (m, 1H), 2.29 (m, 1H), 2.14 (m, 2H), 1.90 (m, 9H), 1.02 (d, J = 6.6 Hz, 3H), 0.85 (d, J + 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 199.01, 158.04, 132.11, 46.86, 35.24, 29.44, 22.15, 21.51, 20.67, 18.68, 11.32. LRMS: (EI) 166 (highest mass), 124 (base peak). HRMS: calculated for $C_{11}H_{18}O$ 166.1358, found 166.1355. $[\alpha]_D$ (c 1.40, $CHCl_3$) = +10°.

Procedure for Nucleophilic Addition to γ-Hydroxy Dienyl Sulfones. (1*S*,5*S*,6*S*)-5-Benzenesulfonyl-6-methylcyclohex-3-enol (22Me). To a solution of epoxy-dienyl sulfone ***SS*-9a** (0.377 g, 1.6 mmol) in THF (10 mL) at −78 °C was slowly added LiHMDS (1.8 mL, 1.8 mmol). The solution was stirred for 30 min, followed by addition of saturated solution of NH_4Cl (5 mL). Et_2O (5 mL) was added to the mixture and separated. The aqueous layer was extracted with Et_2O (2 × 5 mL), and the organic layers are combined, dried over $MgSO_4$, and concentrated. The resulting solid was dissolved in THF (10 mL) at −78 °C, and MeLi (3.4 mL, 4.8 mmol) in Et_2O was added over a period of 15 min; addition must be done slowly to minimize aromatization. The orange solution was stirred for 20 min and then quenched by slowly adding a solution of saturated NH_4Cl (5 mL). The temperature was allowed to rise to 25 °C, and diethyl ether was added (10 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated. The resultant mixture was filtered through a 1 in. silica gel plug eluting with a 3:1 mixture of ethyl acetate/hexanes to give 0.370 g of the desired sulfone as an oil in 92% yield and a 9:1 ratio of diastereomers. ^{1}H NMR ($CDCl_3$): δ 7.88 (m, 2H), 7.61 (m, 3H), 5.97 (m, 1H), 5.54 (m, 1H), 4.17 (m, 1H), 3.62 (m, 1H), 2.47 (m, 1H), 2.28 (m, 1H), 2.05 (m, 1H), 1.77 (m, 1H), 1.07 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 137.9, 133.7, 132.3, 129.1, 128.9, 117.5, 68.6, 66.2, 32.7, 30.3, 15.5. LRMS: (CI) highest mass 253 (M + H), base peak 143. HRMS: (CI) calculated for $C_{13}H_{16}O_3S$ 253.0898, found 253.0905.

(1*S*,5*S*,6*S*)-5-Benzenesulfonyl-6-isopropylcyclohex-3-enol (22Pr). To a solution of epoxy-dienyl sulfone ***SS*-9a** (0.350 g, 1.5 mmol) in THF (10 mL) at −78 °C was slowly added LiHMDS (1.6 mL, 1.6 mmol). The solution was stirred for 30 min, followed by addition of a saturated solution of NH_4Cl (5 mL). Et_2O (5 mL) was added to the mixture and separated. The aqueous layer was extracted with Et_2O (2 × 5 mL), and the organic layers are combined, dried over $MgSO_4$, and concentrated. To the resulting solid in THF (10 mL) at −78 °C was slowly added *i*PrMgCl (3.7 mL, 7.4 mmol) over a period of 15 min; addition must be done slowly to minimize aromatization. The orange solution was stirred for 20 min, and the temperature was allowed to slowly rise to −10 °C over a period of 1 h. The solution was quenched by slowly adding a solution of saturated NH_4Cl (10 mL). The temperature was allowed to rise to 25 °C, and diethyl ether was added (10 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated. The resultant mixture was filtered through a 1 in. silica gel plug eluting with a 3:1 mixture of ethyl acetate:hexanes to give 0.375 g of the desired sulfone as an oil in 89% yield and a 30:1 ratio of diastereomers. ^{1}H NMR ($CDCl_3$): δ 7.88 (m, 2H), 7.59 (m, 3H), 5.99 (m, 1H), 5.66 (m, 1H), 4.31 (m, 1H), 3.77 (m, 1H), 2.17 (m, 4H), 0.81 (d, J = 6.9 Hz, 3H), 0.76 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 137.6, 133.7, 133.2, 129.1, 129.0, 118.5, 65.6, 63.9, 42.6, 31.5, 24.8, 22.1, 19.7. LRMS: (CI) highest mass 281 (M + H), base peak 143. HRMS: (CI) calculated for $C_{15}H_{20}O_3S$ 281.1211, found 281.1199.

(2*R*,3*S*,4*S*)-(3-Benzenesulfonyl-2-methylcyclohept-4-enyloxy)-*tert*-butyldimethylsilane (30). To a solution of dienyl sulfone **29** (0.322 g, 0.89 mmol) in THF (9 mL) at −78 °C was slowly added MeLi (1.8 mL, 1.95 mmol) in Et_2O over a period of 10 min. The orange solution was stirred for 20 min and was then quenched by slowly adding a solution of saturated NH_4Cl (10 mL). The temperature was allowed to rise to 25 °C, and diethyl ether was added (10 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated. The resultant mixture was filtered through a 1 in. silica gel plug eluting with a 3:1 mixture of ethyl acetate:hexanes to give 0.317 g of the desired sulfone as an oil in 94% yield and a 20:1 ratio of diastereomers. ^{1}H NMR ($CDCl_3$): δ 7.87 (m, 2H), 7.58 (m, 3H), 6.03 (m, 1H), 5.87 (m, 1H), 4.60 (m, 1H), 3.83 (m, 1H), 2.42 (m, 4H), 1.77 (m, 1H), 1.63 (m, 1H), 1.41 (m, 1H), 1.09 (d, J = 7.0 Hz, 3H), 0.85 (s, 9H), −0.02 (s, 3H), −0.08 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.0, 134.9, 133.4, 129.1, 128.5, 123.2, 73.6, 62.3, 35.9, 27.1, 25.7, 20.0, 17.9, 12.3, −5.1. LRMS: (CI) highest mass 381 (M + H), base peak 249. HRMS: (CI) calculated for $C_{20}H_{32}O_3SSi$ 381.1920, found 381.1917.

General Procedure for Molybdenum-Catalyzed Epoxidations. To a solution of hydroxy allyl sulfone (0.98 mmol) in benzene (10 mL) was added solid molybdenum hexacarbonyl (0.005 g, 0.021 mmol, 5 mol %). The solution was heated to reflux, and *tert*-butyl hydrogen-peroxide (0.312 mL, 1.56 mmol) in decanes was slowly added over a period of 5 min. The solution was heated at reflux for 1.5 h. The reaction was allowed to cool to 25 °C, and diethyl ether (10 mL) was added to the reaction mixture. The mixture was washed with a saturated solution of sodium bisulfite (5 mL), and the organic layer was concentrated. The resultant mixture was filtered through a 1 in. silica gel plug eluting with a 1:1 mixture of ethyl acetate/hexanes, which upon concentration affords epoxy sulfone as a crystalline solid in a high yields and the same ratio as that of the corresponding starting material. The crystalline

product can be further recrystallized from chloroform and hexanes to separate the diastereomers.

(1*R*,3*S*,4*S*,5*R*,6*R*)-5-Benzenesulfonyl-4-methyl-7-oxabicyclo[4.1.0]-heptan-3-ol (23Me a). 99% yield 6:1 ratio, after recrystallization 83% yield 30:1 ratio. ^{1}H NMR ($CDCl_3$): δ 7.96 (m, 2H), 7.67 (m, 3H), 3.64 (m, 1H), 3.58 (d, J = 3.8 Hz, 1H), 3.51 (d, J = 9.3 Hz, 1H), 3.40 (m, 1H), 2.68 (d, J = 10.8 Hz, 1H, (OH)), 2.40 (ddd, J = 15.7 Hz, 5.6 Hz, 2.7 Hz, 1H), 2.03 (m, 1H), 1.90 (dddd, 15.7 Hz, 5.0 Hz, 3.8 Hz, 1.2 Hz, 1H), 1.25 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 137.9, 134.3, 129.6, 128.7, 69.2, 64.0, 53.4, 51.2, 32.4, 29.8, 18.8. LRMS: (CI) highest mass 269 (M + H), base peak 233. HRMS: (CI) calculated for $C_{13}H_{16}O_4S$ 269.0848, found 269.0852. mp 133.5−134.0 °C. $[\alpha]_D$ (c 2.90, $CHCl_3$) = +27°.

(1*R*,3*S*,4*S*,5*R*,6*R*)-5-Benzenesulfonyl-4-isopropyl-7-oxabicyclo-[4.1.0]heptan-3-ol (23Pr a). 95% >50:1 ratio. ^{1}H NMR ($CDCl_3$): δ 7.94 (m, 2H), 7.67 (m, 3H), 4.05 (m, 1H), 3.89 (d, J = 8.4 Hz, 1H), 3.61 (d, J = 3.7 Hz, 1H), 3.38 (m, 1H), 2.28 (m, 2H), 1.88 (m, 1H), 1.74 (m, 1H), 1.06 (d, J = 7.5 Hz, 3H), 1.03 (d, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 138.0 134.2, 129.5, 128.7, 64.8, 60.7, 53.4, 51.7, 30.2, 29.5, 20.6, 18.3. LRMS: (CI) highest mass 269 (M + H), base peak 233. HRMS: (CI) calculated for $C_{15}H_{20}O_4S$ 297.1161, found 297.1173. mp 147.5−148.0 °C. >99% ee HPLC Chiralcel OD 1.0 mL/min 90:10 Hex:2-propanol. 16.04 min minor enantiomer, 14.60 min major enantiomer. $[\alpha]_D$ (c 3.1, $CHCl_3$) = +63°.

(1*R*,2*R*,3*R*,4*S*,7*R*)-(2-Benzenesulfonyl-3-methyl-8-oxabicyclo[5.1.0]-oct-4-yloxy)-*tert*-butyldimethylsilane (31). To a stirring solution of allyl sulfone **30** (0.884 g, 2.33 mmol) in CH_2Cl_2 (23 mL) at room temperature was added *m*-CPBA (1.56 g, 6.33 mmol). The mixture was stirred for 18 h, at which point diethyl ether (20 mL) was added followed by a saturated solution of sodium bisulfite (20 mL). The organic phase was separated and washed with 10% NaOH (2 × 20 mL), and then dried over $MgSO_4$ and concentrated to give 0.848 g of the desired epoxy sulfone as a single diastereomer in 92% yield. ^{1}H NMR ($CDCl_3$): δ 7.92 (m, 2H), 7.61 (m, 3H), 3.86 (m, 1H), 3.42 (m, 2H), 3.06 (m, 1H), 2.68 (m, 1H), 1.91 (m, 1H), 1.75 (m, 1H), 1.53 (m, 2H), 1.25 (d, J = 7.5 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 3H), −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.4, 133.7, 129.2, 128.5, 72.2, 63.6, 53.2, 51.6, 37.6, 26.3, 25.6, 22.1, 17.8, 13.0, −5.1, −5.2. LRMS: (EI) highest mass 359 (M − C_4H_9), base peak 73. HRMS: (EI) calculated for $C_{20}H_{32}O_4SSi$ 396.1791, found 396.1782.

General Procedure for Silyl Protection of the Epoxy Alcohols. To a stirring solution of the epoxy sulfone (0.42 mmol) and triethylamine (0.63 mmol) in CH_2Cl_2 (4.0 mL) at room temperature was added *tert*-butyldimethylsilyl triflouromethylsulfonate (0.50 mmol). The solution was stirred for 30 min. Diethyl ether (10 mL) was added, and the crude mixture was concentrated. The mixture was then filtered through a 1 in. silica plug eluting with a 1:3 solution of ethyl acetate/hexanes to give, after concentration, the desired protected alcohol in quantitative yield.

(1*R*,3*S*,4*S*,5*R*,6*R*)-(5-Benzenesulfonyl-4-methyl-7-oxa-bicyclo[4.1.0]-hept-3-yloxy)-*tert*-butyldimethylsilane (23Me b). Quantitative yield. ^{1}H NMR ($CDCl_3$): δ 7.91 (m, 2H), 7.62 (m, 3H), 4.15 (ddd, J = 10.4 Hz, 6.3 Hz, 4.4 Hz, 1H), 3.59 (d, J = 2.4 Hz, 1H), 3.35 (d, J = 3.5 Hz, 1H), 3.25 (dd, J = 5.0 Hz, 4.3 Hz, 1H), 2.32 (m, 1H), 1.98 (m, 2H), 1.01 (d, J = 7.2 Hz, 3H), 0.86 (s, 9H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 138.3 134.0, 129.4, 128.4, 65.7, 65.3, 52.1, 49.4, 31.8, 28.5, 14.1, −4.8, −4.9. LRMS: (CI) highest mass 383 (M + H), base peak 383. HRMS: (CI) calculated for $C_{19}H_{30}O_4SSi$ 383.1712, found 383.1700. $[\alpha]_D$ (c 5.0, $CHCl_3$) = +16°.

(1*R*,3*S*,4*S*,5*R*,6*R*)-(5-Benzenesulfonyl-4-isopropyl-7-oxa-bicyclo-[4.1.0]hept-3-yloxy)-*tert*-butyldimethylsilane (23Pr b). Quantitative yield. ^{1}H NMR ($CDCl_3$): δ 7.93 (m, 2H), 7.64 (m, 3H), 4.41 (ddd, J = 11.1 Hz, 6.9 Hz, 4.3 Hz, 1H), 3.84 (m, 1H), 3.42 (m, 1H), 3.31 (m, 1H), 1.98 (m, 4H), 0.91 (d, J = 6.6 Hz, 3H), 0.88 (s, 9H), 0.66 (d, J = 6.4 Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.3, 134.0, 129.4, 128.5, 67.0, 62.6, 52.5, 48.8, 42.6, 29.0, 26.9, 25.8, 23.5, 22.0, 17.9, −4.7, −5.0. LRMS: (CI) highest mass 411 (M + H), base peak 137. HRMS: (CI) calculated for $C_{21}H_{34}O_4SSi$ 411.2025, found 411.2005. $[\alpha]_D$ (c 38.0, $CHCl_3$) = −1°.

General Procedure for Base-Induced Epoxide Opening Followed by Etherification of γ-Hydroxy Vinyl Sulfones. To a solution of the silylated epoxy sulfone (0.25 mmol) in THF (2.5 mL) was added DBU (0.30 mmol). The stirring solution was heated to reflux for 1 h. The temperature was lowered to room temperature, and diethyl ether (5 mL) was added to the mixture followed by water (5 mL). The organic phase was separated and concentrated. The resulting mixture was filtered through a 1 in. silica gel plug eluting with a 1:1 solution of ethyl acetate/hexanes, which upon concentration gives the vinyl sulfone in high yield. Etherification is performed as explained previously.

(1*R*,4*S*,5*S*)-3-Benzenesulfonyl-5-(*tert*-butyldimethylsilanyloxy)-4-methylcyclohex-2-enol (24Me a). 96% yield. ^{1}H NMR ($CDCl_3$): δ 7.88 (m, 2H), 7.58 (m, 3H), 6.92 (d, J = 3.2 Hz, 1H), 4.43 (m, 1H), 3.75 (m, 1H), 2.60 (m, 1H), 1.98 (m, 1H), 1.83 (m, 1H), 1.02 (d, J = 6.9 Hz, 3H), 0.82 (s, 9H), 0.01 (s, 3H), −0.04 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.1, 139.9, 138.7, 133.4, 129.2, 128.0, 69.0, 66.0, 35.3, 35.2, 25.7, 18.0, 13.7, −4.8, −5.0. LRMS: (CI) highest mass 383 (M + H), base peak 365. HRMS: (CI) calculated for $C_{19}H_{30}O_4SSi$ (M + H − H_2O) 365.1607, found 365.1595. $[\alpha]_D$ (c 88.0, $CHCl_3$) = −2°.

(2*S*,3*S*,5*R*)-(3-Benzenesulfonyl-5-methoxy-2-methylcyclohex-3-enyloxy)-*tert*-butyldimethylsilane (24Me b). Reaction time: 10 min; 98% yield. ^{1}H NMR ($CDCl_3$): δ 7.87 (m, 2H), 7.57 (m, 3H), 6.92 (d, J = 2.4 Hz, 1H), 4.03 (m, 1H), 3.65 (m, 1H), 3.40 (s, 3H), 2.59 (m, 1H), 1.97 (m, 1H), 1.70 (m, 1H), 0.95 (d, J = 6.9 Hz, 3H), 0.83 (s, 9H), −0.03 (s, 3H), −0.04 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 146.4, 139.8, 136.0, 133.4, 129.2, 128.1, 68.4, 56.3, 35.0, 31.6, 25.6, 18.0, 13.1, −4.9. LRMS: (CI) highest mass 397 (M + H), base peak 263. HRMS: (CI) calculated for $C_{20}H_{32}O_4SSi$ 396.1791, found 396.1787. $[\alpha]_D$ (c 27.0, $CHCl_3$) = −0.5°.

(1*R*,4*S*,5*S*)-3-Benzenesulfonyl-5-(*tert*-butyldimethylsilanyloxy)-4-isopropylcyclohex-2-enol (24Pr a). 99% yield. ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 2H), 7.58 (m, 3H), 6.88 (d, J = 3.4 Hz, 1H), 4.45 (m, 1H), 3.40 (dt, J = 12.7 Hz, 4.0 Hz, 1H), 2.27 (m, 1H), 2.01 (m, 2H), 1.74 (m, 1H), 1.14 (d, J = 7.0 Hz, 3H), 0.97 (d, J = 7.3 Hz, 3H), 0.80 (s, 9H), −0.13 (s, 3H), −0.16 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 144.1, 139.1, 133.4, 129.2, 128.4, 70.4, 66.2, 46.0, 35.8, 25.7, 25.2, 24.4, 21.8, 18.0, −5.1, −5.2. LRMS: (CI) highest mass 411 (M + H), base peak 137. HRMS: (CI) calculated for $C_{21}H_{34}O_4SSi$ 411.2025, found 411.2012. mp 133.5−134.5 °C. $[\alpha]_D$ (c 5.0, $CHCl_3$) = −60°.

(1*S*,2*S*,5*R*)-(3-Benzenesulfonyl-2-isopropyl-5-methoxycyclohex-3-enyloxy)-*tert*-butyldimethylsilane (24Pr b). Reaction time: 10 min; 98% yield. mp 133.5−134.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 2H), 7.57 (m, 3H), 6.97 (d, J = 3.5 Hz, 1H), 4.01 (m, 1H), 3.41 (s, 3H), 3.38 (m, 1H), 2.24 (m, 2H), 1.97 (m, 1H), 1.74 (m, 1H), 1.13 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H), 0.80 (s, 9H), −0.13 (s, 3H), −0.16 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 144.7, 139.2, 136.6, 133.3, 129.1, 128.4, 74.6, 70.5, 56.6, 49.1, 32.8, 25.7, 25.3, 24.5, 21.6, 18.0, −5.1, −5.2. LRMS: (CI) highest mass 424 (M + H), base peak 133. HRMS: (CI) calculated for $C_{21}H_{34}O_4SSi$ 425.2182, found 425.2176. $[\alpha]_D$ (c 3.0, $CHCl_3$) = −39°.

(1*R*,4*R*,5*S*)-3-Benzenesulfonyl-5-(*tert*-butyldimethylsilanyloxy)-4-methylcyclohept-2-enol (32). Reaction time: 5 h; 97% yield. ^{1}H NMR ($CDCl_3$): δ 7.87 (m, 2H), 7.55 (m, 3H), 7.19 (d, J = 3.5 Hz, 1H), 4.51 (m, 1H), 3.80 (ddd, J = 7.2 Hz, 4.6 Hz, 2.3 Hz, 1H), 2.86 (dq, J = 7.3 Hz, 2.1 Hz, 1H), 2.65 (d, J = 6.6 Hz, 1H, (OH)), 2.14 (m, 1H), 1.92 (m, 1H), 1.80 (m, 1H), 1.69 (m, 1H), 0.97 (d, J = 7.3 Hz, 3H), 0.75 (s, 9H), −0.07 (s, 3H), −0.19 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.5, 142.5, 139.5, 133.1, 129.1, 128.5, 71.0, 70.0, 40.0, 28.6, 28.0, 25.8, 18.0, 16.3, −5.0, −5.5. LRMS: (EI) highest mass 339 (M − C_4H_9), base peak 75. (CI) highest mass 397 (M + H), base peak 379. HRMS: (EI) calculated for $C_{20}H_{32}O_4SSi$ 396.1791, found 396.1772.

(1*S*,2*R*,5*R*)-(3-Benzenesulfonyl-5-methoxy-2-methylcyclohept-3-enyloxy)-*tert*-butyldimethylsilane (33). Reaction time: 10 min; 98%

yield. White solid. mp 116.0−117.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.84 (m, 2H), 7.52 (m, 3H), 7.19 (m, 1H), 3.95 (dt, J = 11.4 Hz, 2.9 Hz, 1H), 3.74 (m, 1H), 3.38 (s, 3H), 2.82 (dq, J = 12.1 Hz, 7.3 Hz, 1H), 1.78 (m, 4H), 0.93 (d, J = 7.5 Hz, 3H), 0.72 (s, 9H), −0.10 (s, 3H), −0.21 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.5, 142.5, 139.5, 133.1, 129.1, 128.5, 71.0, 70.0, 40.0, 28.6, 28.0, 25.8, 18.0, 16.3, −5.0, −5.5. LRMS: (CI) highest mass 411 (M + H), base peak 411. HRMS: (CI) calculated for $C_{21}H_{34}O_4SSi$ 411.2025, found 411.2030.

Enone Formation. (4*R*,5*S*)-5-(*tert*-Butyldimethylsilanyloxy)-3,4-dimethylcyclohex-2-enone (25Me). *t*-BuLi (0.32 mL, 0.38 mmol) was slowly added to a mixture of HMPA (0.17 mL, 0.95 mmol) and γ-methoxy vinyl sulfone **24Me** (0.08 g, 0.19 mmol) in 2 mL of THF at −78 °C. The resulting bright orange mixture was stirred at −78 °C for 5 min. Iodomethane (0.06 mL, 0.95 mmol) was added and was stirred for 15 min. One milliliter of a saturated solution of $NaHCO_3$ was added, and the reaction was allowed to warm to room temperature. The mixture was extracted into diethyl ether (4 mL) and concentrated in vacuo. $CHCl_3$ (1 mL) was added followed by SiO_2 (0.500 g), and the reaction was stirred for 2 h. Monitoring the reaction was best accomplished by ^{1}H NMR. When complete, the silica was filtered, and the solution was concentrated. Silica gel column purification eluting with 1:4 ethyl acetate/hexanes provided the desired enone in 0.044 g, 93% yield. ^{1}H NMR ($CDCl_3$): δ 5.83 (s, 1H), 4.17 (dt, J = 10.7 Hz, 5.2 Hz, 1H), 2.32 (m, 3H), 1.99 (s, 3H), 1.16 (d, J = 7.2 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 198.4, 165.5, 126.1, 69.2, 42.2, 41.8, 25.7, 23.1, 18.0, 11.7, −4.7, −4.9. LRMS: (CI) highest mass 255 (M + H), base peak 255. HRMS: (CI) calculated for $C_{14}H_{26}O_2Si$ 255.1780, found 255.1779. 98.7% ee HPLC Chiralcel OD 1.0 mL/min 90.0:10.0 Hex:2-propanol. 5.25 min minor enantiomer, 4.46 min major enantiomer. $[\alpha]_D$ (c 9.9, $CHCl_3$) = −41°.

(4*R*,5*S*)-5-(*tert*-Butyldimethylsilanyloxy)-4-isopropyl-3-methylcyclohex-2-enone (25Pr). *t*-BuLi (0.15 mL, 0.18 mmol) was slowly added to a mixture of HMPA (0.08 mL, 0.45 mmol) and γ-methoxy vinyl sulfone **24Pr** (0.0382 g, 0.09 mmol) in 2 mL of THF at −78 °C. The resulting bright orange mixture was stirred at −78 °C for 5 min. Iodomethane (0.03 mL, 0.45 mmol) was added and was stirred for 15 min. Saturated $NaHCO_3$ (2 mL) was added, and the reaction was allowed to warm to room temperature. The mixture was extracted into diethyl ether (5 mL) and concentrated in vacuo. $CHCl_3$ (1 mL) was added followed by SiO_2 (0.500 g), and the reaction was stirred for 3 h. Monitoring the reaction was best accomplished by ^{1}H NMR. When complete, the silica was filtered, and the solution was concentrated. Silica gel column purification eluting with 1:4 ethyl acetate/hexanes provided the desired enone in 0.023 g, 91% yield. ^{1}H NMR ($CDCl_3$): δ 5.92 (s, 1H), 4.21 (dt, J = 11.4 Hz, 5.8 Hz, 1H), 2.46 (m, 3H), 2.25 (m, 1H), 2.01 (d, J = 1.4 Hz, 1H), 1.14 (d, J = 7.0 Hz, 3H), 0.90 (s, 9H), 0.88 (d, J = 7.2 Hz, 3H), 0.070 (s, 3H), 0.065 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 199.0, 163.9, 127.8, 69.9, 53.1, 42.9, 26.0, 25.7, 25.4, 24.5, 21.0, −4.7, −4.8. LRMS: (CI) highest mass 283 (M + H), base peak 283. HRMS: (CI) calculated for $C_{16}H_{30}O_2Si$ 283.2093, found 283.2094. 97.7% ee HPLC Chiralcel OD 1.0 mL/min 90.0:10.0 Hex:2-propanol. 4.67 min minor enantiomer, 4.13 min major enantiomer. $[\alpha]_D$ (c 4.0, $CHCl_3$) = −68°.

(4*S*,5*S*)-5-(*tert*-Butyldimethylsilanyloxy)-3,4-dimethylcyclohept-2-enone (34). *t*-BuLi (0.06 mL, 0.07 mmol) was added to the γ-methoxy vinyl sulfone **33** (0.02 g, 0.05 mmol) in 1 mL of THF at −78 °C over 2 min. The resulting bright orange solution was stirred at −78 °C for 5 min. Iodomethane (0.02 mL, 0.25 mmol) was added and was stirred for 15 min. Saturated $NaHCO_3$ (1 mL) was added, and the reaction was allowed to warm to room temperature. The mixture was extracted into diethyl ether (5 mL) and concentrated in vacuo. $CHCl_3$ (1 mL) was added followed by SiO_2 (0.500 g), and the reaction was stirred for 4 h. Monitoring the reaction was best accomplished by NMR. When complete, the silica was filtered, and the solution was concentrated. Silica gel chromatography eluting with 1:4 ethyl acetate/hexanes provided the desired enone in 0.011 g, 84% yield. ^{1}H NMR ($CDCl_3$): δ 5.85 (s, 1H), 3.87 (ddd, J = 8.1 Hz, 5.6 Hz, 2.4 Hz, 1H), 2.84 (dq, J = 16.3 Hz, 10.8 Hz, 1H), 2.49 (m, 2H), 2.04 (m, 1H), 1.92 (d, J = 1.2 Hz, 3H), 1.82 (m, 1H), 1.14 (d, J = 7.3 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 204.2, 155.4, 128.5, 72.7, 47.6, 37.8, 27.5, 26.4, 18.1, 18.0, −4.7, −4.9. LRMS: (EI) highest mass 211 (M + H − C_4H_9), base peak 75. HRMS: (EI) calculated for $C_{15}H_{28}O_2Si$ 268.1859, found 268.1848. 99.2% ee HPLC Chiralcel AD 1.0 mL/min 99.0:1.0 Hex:2-propanol. 11.18 min minor enantiomer, 9.27 min major enantiomer. $[\alpha]_D$ (c 0.4, $CHCl_3$) = +50°.

(4*S*,5*S*)-5-(*tert*-Butyldimethylsilanyloxy)-2,4-dimethylcyclohept-2-enone (36). To a solution of hydroxy dienyl sulfone **32** (0.132 g, 0.33 mmol) in THF (3.3 mL) at −78 °C was slowly added MeLi (0.83 mL, 0.99 mmol) in Et_2O over a period of 10 min. The temperature was allowed to slowly rise to −10 °C and was then quenched by slow addition of a solution of saturated NH_4Cl (5 mL). The temperature was allowed to rise to 25 °C, and diethyl ether was added (10 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated. CH_2Cl_2 (6 mL) was added to the mixture followed by PCC (0.310 g, 1.44 mmol). The mixture was allowed to stir for 2 h. THF (5 mL) was added followed by 10% NaOH (2 mL), and the mixture was allowed to stir for 10 h. At this point, H_2O (5 mL) was added followed by diethyl ether (10 mL), the mixture separated, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic layer was dried over $MgSO_4$ and concentrated. Purification was done by silica gel chromatography eluting with a 1:9 solution of ethyl acetate/hexanes to give 0.84 g of the desired enone as an oil in 88% yield. ^{1}H NMR ($CDCl_3$): δ 6.06 (m, 1H), 3.65 (dt, J = 8.2 Hz, 3.8 Hz, 1H), 2.75 (m, 1H), 2.59 (m, 1H), 2.48 (m, 1H), 1.95 (m, 1H), 1.80 (s, 3H), 1.79 (m, 1H), 1.17 (d, J = 6.9 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 205.4, 144.1, 137.3, 73.8, 40.2, 37.9, 30.8, 25.8, 19.3, 18.0, −4.3, −4.8. LRMS: (EI) highest mass 268 (M + H), base peak 73. (CI) highest mass 269 (M + H), base peak 269. HRMS: (CI) calculated for $C_{15}H_{28}O_2Si$ 269.1937, found 269.1930. 99.7% ee HPLC Chiralcel AD 1.0 mL/min 99.0:1.0 Hex:2-propanol. 3.70 min minor enantiomer, 4.08 min major enantiomer. $[\alpha]_D$ (c 11.0, $CHCl_3$) = +139°.

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Supporting Information Available: Copies of spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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