JOC Article

Highly Stereoselective Synthesis of Functionalized β,β-Di- and Trisubstituted Vinylic Sulfoxides by Cu-Catalyzed Conjugate Addition of Organozinc Reagents

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β,β-Disubstituted chiral vinylic sulfoxides bearing functionalities have been synthesized via Cu-catalyzed conjugate addition of organozinc reagents to chiral 1-alkynyl sulfoxides. Due to the availability of functionalized organozinc reagents and high *syn*-selectivity of the reaction, both geometric β,β-disubstituted vinylic sulfoxides were selectively synthesized. Furthermore, 1-alkynyl sulfoxides were derivatized into trisubstituted vinylic sulfoxides by trapping the resulting α-sulfinyl vinylic carbanion with electrophiles. Highly diastereoselective THF and THP ring formations were accomplished by means of this methodology followed by an intramolecular Michael addition.

Introduction

Vinylic sulfoxides are a well-known chiral building block and have been applied to various asymmetric reactions, in which high diastereoselectivity was often realized. In addition, the sulfinyl group can be converted into various functional groups by reduction, oxidation, thermolysis, Pummerer reaction, α-deprotonation, and so on.[1] Therefore, the synthetic procedures have been extensively studied. Although some useful methods to synthesize (*E*)- and (*Z*)-β-monosubstituted vinylic sulfoxides are available,[2] there are few methods for the synthesis of acyclic β,β-disubstituted vinylic sulfoxides.[3] One widely used methodology is the *syn*-selective conjugate addition of an organocopper reagent to 1-alkynyl sulfoxides.[4] However, application of this method has been limited to introduction of relatively simple alkyl groups. One reason is that organocopper reagents are regularly prepared from reactive organolithium or Grignard reagents. To solve this problem, we have developed a novel synthesis of β,β-disubstituted vinylic sulfoxides by Cu-catalyzed carbozincation of the chiral 1-alkynyl sulfoxides with organozinc reagents, which can be prepared straightforwardly from alkyl halides by a halogen−zinc exchange reaction and many functionalities are compatible due to its mild reactivity, and the results have been reported in a communication.[5] Herein, we report full details of a highly *syn*-selective Cu-catalyzed conjugate addition of an organozinc reagent with 1-alkynyl sulfoxide including a geometrically selective synthesis of functionalized trisubstituted vinylic sulfoxides by trap of the resulting α-sulfinylzinc species with electrophiles. In addition, we accomplished a synthesis of chiral α,α-disubstituted THF and THP compounds with very high diastereoselectivity, and the results are also described.

Result and Discussion

Cu-Catalyzed Carbozincation of 1-Alkynyl Sulfoxides. First, we examined the Cu- or Ni-catalyzed conjugate addition of Et_2Zn to a chiral 1-alkynyl sulfoxide

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(2) For geometric selective synthesis of β-monosubstituted vinylic sulfoxides, see: (a) van Steenis, J. H.; van Es, J. J. G. S.; van der Gen, A. *Eur. J. Org. Chem.* **2000**, *65*, 2787−2793. (b) Segorbe, M. M.; Adrio, J.; Carretero, J. C. *Tetrahedron Lett.* **2000**, *41*, 1983−1986. (c) Mikolajczyk, M.; Perlikowska, W.; Omelañczuk, J.; Cristau, H.-J.; Perraud-Darcy, A. *J. Org. Chem.* **1998**, *63*, 9716−9722. (d) Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, *52*, 1078−1082. (e) Kosugi, H.; Kitaoka, M.; Tagami, K.; Uda, H. *Chem. Lett.* **1985**, 805−808. (f) Posner, G. H.; Tang, P.-W. *J. Org. Chem.* **1978**, *43*, 4131−4136. (g) Abbott, D. J.; Colonna, S.; Stirling, J. M. *J. Chem. Soc. D* **1971**, 471.

(3) For geometric selective synthesis of β,β-disubstituted vinylic sulfoxides, see: (a) Alonso, I.; Carretero, J. C. *J. Org. Chem.* **2001**, *66*, 4453−4456. (b) Ruano, J. L. G.; de Diego, S. A. A.; Blanco, D.; Castro, A. M. M.; Martin, M. R.; Ramos, J. H. R. *Org. Lett.* **2001**, *3*, 3173−3176. (c) Ruano, J. L. G.; Gamboa, A. E.; Castro, A. M. M.; Rodríguez, J. H.; López-Solera, M. I. *J. Org. Chem.* **1998**, *63*, 3324−3332 and ref 2d.

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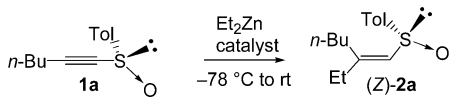
TABLE 1. Synthesis of β,β-Disubstituted Vinylic Sulfoxides with Et_2Zn[a]



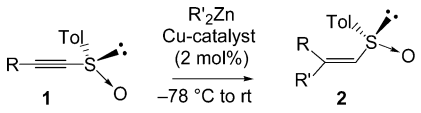
entry	catalyst (mol %)	Et_2Zn[b] (mol per 1 mol of **1a**)	concn (M)	yield (%)
1	CuI (2)	1	0.1	15
2	CuI (2)	2	0.1	72
3	CuI (2)	4	0.1	57
4	CuI (0.5)	2	0.1	35
5	CuI (10)	2	0.1	46
6	CuI (2)	2	1	97
7	CuCN (2)	2	1	86
8	$Cu(OTf)_2$ (2)	2	1	69
9	$Ni(acac)_2$ (20)[c]	2	0.1	46
10	$Ni(acac)_2$ (20)[c]	2	1	34

[a] All reactions were carried out in THF at −78 °C to rt for 2 h. [b] Hexane solution. [c] Reactions were carried out in THF at −20 °C to rt.

1a as shown in Table 1. Upon treatment of **1a** with Et_2Zn (1 mol per 1 mol of **1a**) in the presence of 2 mol % of CuI, the β,β-disubstituted vinylic sulfoxide (*Z*)-**2a** was obtained as the sole geometric isomer,[6] but in only 15% yield (entry 1). However, the yield could be improved to 72% by using Et_2Zn (2 mol per 1 mol of **1a**) (entry 2). Use of Et_2Zn (4 mol per 1 mol of **1a**) rather diminished the yield, giving 57% of (*Z*)-**2a** (entry 3). The amount of CuI is important to obtain high yield, and 2 mol % of CuI afforded the best results. We found that the reaction proceeds almost quantitatively at the higher concentration (entry 6). In all cases, the reaction always shows excellent stereoselectivity, giving *syn*-adducts exclusively. The Cu-salts such as CuCN or $Cu(OTf)_2$ also provided the adduct in moderate to good yields, but the yield was not higher than that using CuI (entries 7 and 8). Although $Ni(acac)_2$ catalyzes the carbometalation of organozinc reagents to alkynes,[7] the catalyst was less effective than Cu salts (entries 9 and 10).

Next, the procedure was applied to a synthesis of β,β-disubstituted vinylic sulfoxides using 1-alkynyl sulfoxides **1a**−**f** (Table 2). Functional groups such as TBSO, AcO, and I are compatible under these reaction conditions (entries 1−3). It should be noted that a nucleophile-sensitive acetoxy group was not affected under the conditions and no Cu-catalyzed iodine−zinc exchange reaction[8] was observed. In the case of the substrate **1d** [R = $(CH_2)_4I$], the yield was improved by sonication (entry 4) and the use of CuCN or $Cu(OTf)_2$ was also effective (entries 5 and 6). The alkynyl sulfoxide bearing a proton or a hindered *t*-Bu group at the β-position showed considerably low yields (entries 7 and 8). *syn*-Selective methylation of **1a** was also accomplished using Me_2Zn in the presence of CuI catalyst to give **2g**[2d] in 81% yield (entry 9).

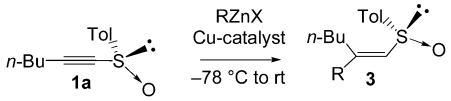
TABLE 2. Synthesis of β,β-Disubstituted Vinylic Sulfoxides with $R_2'Zn$[a]



entry	substrate	R	R′	Cu-catalyst	product (yield, %)
1	**1b**	$TBSO(CH_2)_2$	Et	CuI	**2b** (78)
2	**1c**	$AcO(CH_2)_2$	Et	CuI	**2c** (84)
3	**1d**	$I(CH_2)_4$	Et	CuI	**2d** (71)
4	**1d**	$I(CH_2)_4$	Et	CuI,)))	**2d** (79)
5	**1d**	$I(CH_2)_4$	Et	CuCN	**2d** (86)
6	**1d**	$I(CH_2)_4$	Et	$Cu(OTf)_2$	**2d** (83)
7	**1e**	H	Et	CuI	**2e** (24)[b]
8	**1f**	*t*-Bu	Et	CuI	**2f** (21)[c]
9	**1a**	*n*-Bu	Me	CuI	**2g** (81)[d]

[a] All reactions were carried out in THF using Et_2Zn (hexane solution, 2 mol per 1 mol of **1**) at −78 °C to rt unless otherwise stated. [b] (*Z*)-Isomer was produced in 21% yield. [c] (*E*)-Isomer. [d] Reaction was carried out at −78 to 0 °C.

TABLE 3. Synthesis of β,β-Disubstituted Vinylic Sulfoxides with RZnX[a]



entry	RZnX (equiv)[b]	Cu-catalyst (mol%)	product (yield, %)
1	AllylZnBr (2)	CuI (2)	**3a** (72)
2	AllylZnBr (2)	CuCN (2)	**3a** (73)
3	AllylZnBr (2)	$Cu(OTf)_2$ (2)	**3a** (81)
4	AllylZnBr (1.1)	$Cu(OTf)_2$ (2)	**3a** (67)
5	AllylZnBr (2)	$Cu(OTf)_2$ (5)	**3a** (80)
6	BnZnBr (2)	$Cu(OTf)_2$ (2)	**3b** (81)
7	*t*-$BuCO_2CH_2ZnI$ (3)	$Cu(OTf)_2$ (2)	**3c** (75)
8	$EtO_2C(CH_2)_3ZnI$ (10)	$Cu(OTf)_2$ (2)	**3d** (70)
9	 (2)	$Cu(OTf)_2$ (2)	**3e** (87)
10	$BocNH(CH_2)_3ZnI$ (10)	$Cu(OTf)_2$ (2)	**3f** (84)
11	$TMSCH_2ZnX$[c] (2)	$Cu(OTf)_2$ (2)	**3g** (94)

[a] All reactions were carried out in THF using RZnX in the presence of Cu salt at −78 °C to rt. [b] Organozinc reagents were prepared from RX and Zn (powder) using TMSCl and dibromoethane as initiators unless otherwise cited. [c] Prepared from $TMSCH_2MgCl$ and $ZnBr_2$.

A wide range of multi-functionalized organozinc halides can be prepared by the halogen−zinc exchange reaction.[9] Consequently, reaction of these species with 1-alkynyl sulfoxides affords a versatile method to prepare functionalized β,β-disubstituted vinylic sulfoxides. The results of Cu-catalyzed conjugate addition with RZnX are summarized in Table 3. Allylzinc bromide prepared by reaction of allyl bromide with Zn dust activated with TMSCl and 1,2-dibromoethane underwent carbozincation to **1a** in the presence of 2 mol % of CuI, leading (*E*)-vinylic sulfoxide **3a** in 72% yield as a single product (entry 1).

(6) The assignment of the olefin geometry was conducted by NOE experiment between the olefinic proton and the *cis*-substituent. High optical purity of **4a** was confirmed by chiral HPLC (Daisel Chiralcel OB) in comparison with the racemic sample.

(7) Houpis, I. N.; Lee, J. *Tetrahedron* **2000**, *56*, 817−846.

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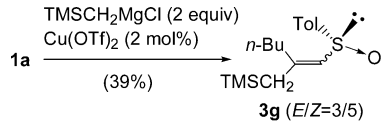
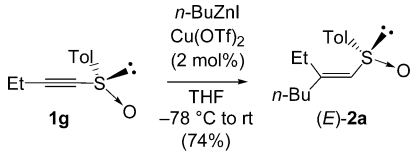
SCHEME 1



SCHEME 2



In this case, $Cu(OTf)_2$ was the most efficient among the Cu salts we tested to give **3a** in 81% yield (entries 1−3). Although a small excess of allylzinc bromide provided **3a** in 67% yield, the yield was lower than that in entry 3 (entry 4). An increase of Cu-catalyst did not improve the yield (entry 5). Using the optimized reaction conditions, various functionalized organozinc halides were reacted with the 1-alkynyl sulfoxide **1a** (entries 6−11). The substituents bearing a variety of nucleophile-sensitive functional groups were introduced stereospecifically in moderate to good yields. In sharp contrast to the result that $TMSCH_2ZnX$ ($TMSCH_2MgCl + ZnBr_2$) afforded *syn*-adduct exclusively in the presence of Cu-catalyst (entry 11), the Cu-catalyzed addition with $TMSCH_2MgCl$ afforded an *E*/*Z*-mixture of **3g** in 39% combined yield with poor selectivity (*E*/*Z* = 3/5) (Scheme 1). The results indicate an advantage of organozinc reagents over the Grignard reagent.[10]

Using the method, the (*E*)-isomer of the vinylic sulfoxide **2a** was synthesized in 74% yield by the reaction of 1-alkynyl sulfoxide **1g** and *n*-butylzinc iodide in the presence of $Cu(OTf)_2$. Because the corresponding (*Z*)-isomer was also synthesized as shown in Table 1, this method affords a powerful tool for stereoselective synthesis of both geometric isomers of the β,β-disubstituted vinylic sulfoxides by changing the combination of 1-alkynyl sulfoxide and the organozinc reagent (Scheme 2).

There are few methods for a geometrically selective synthesis of trisubstituted vinylic sulfoxides.[11] Next, we examined the stereoselective synthesis of trisubstituted vinylic sulfoxides by trapping the vinylzinc intermediate generated by carbozincation with allyl bromide (Table 4).

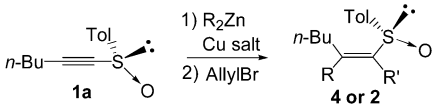
One equivalent of CuCN·2LiCl was added for transmetalation of the α-sulfinyl vinylzinc intermediate generated by CuCN-catalyzed carbozincation.[12] The trisubstituted vinylic sulfoxide **4a** was obtained in 40% yield after quenching the intermediate with 5 equiv of allyl bromide (entry 1). The yield was improved to 88% yield when 1 equiv of CuCN·2LiCl was used for both carbozincation and transmetalation (entry 2). This procedure is more convenient than that of entry 1. CuI and CuCN also afforded **4a** in acceptable yields, while $Cu(OTf)_2$ furnished (*Z*)-**2a** mainly rather than **4a** (entries 3−5).

Reducing the Cu salt is important from the viewpoint of green chemistry. Therefore, we examined the reaction using a catalytic amount of the Cu salt (entries 6−9). The adduct **4a** was obtained in moderate yield by using only 2 mol % of Cu salt. Interestingly, catalytic $Cu(OTf)_2$ showed greater yield than that with stoichiometric $Cu(OTf)_2$ (entries 5 and 9). β-Methylated product **4b** was also synthesized with Me_2Zn in the presence of CuCN·2LiCl or catalytic CuI in 77% and 68% yields, respectively (entries 10 and 11).

Table 5 shows results of a synthesis of trisubstituted vinylic sulfoxides by carbometalation of **1a** with RZnX (X = Br or I) followed by allylation of the resulting α-sulfinyl vinylic carbanion. Functionalized trisubstituted vinylic sulfoxides **5a**−**c** were synthesized in moderate to good yields in the presence of stoichiometric or catalytic Cu-salt. The addition is stereospecific, giving *syn*-adducts as a single isomer.

Application to Diastereoselective Synthesis of Cyclic Ethers. Previously, we have reported a diastereoselective intramolecular conjugate addition of alkoxide to chiral vinylic sulfoxides. The methodology was applied successfully to asymmetric synthesis of dioxaspiro natural products. In the reactions, cyclic vinylic sulfoxides were used as an acceptor and the intramolecular conjugate addition of an alkoxide proceeded with high diastereoselectivity. It is of interest if high diastereoselectivity can be achieved by using acyclic β,β-disubstituted vinylic sulfoxides bearing an alcohol *anti*- or *syn*-sub-

TABLE 4. Synthesis of Trisubstituted Vinylic Sulfoxides with R_2Zn[a]



			yield (%)	
entry	R	Cu salt (equiv)	R′ = allyl	R′ = H
1	Et	CuCN·2LiCl (1)[b]	**4a** (40)	(*Z*)-**2a** (22)
2	Et	CuCN·2LiCl (1)	**4a** (88)	(*Z*)-**2a** (3)
3	Et	CuI (1)	**4a** (74)	(*Z*)-**2a** (13)
4	Et	CuCN (1)	**4a** (68)	(*Z*)-**2a** (15)
5	Et	$Cu(OTf)_2$ (1)	**4a** (6)	(*Z*)-**2a** (53)
6	Et	CuCN·2LiCl (0.02)	**4a** (64)	(*Z*)-**2a** (17)
7	Et	CuI (0.02)	**4a** (66)	(*Z*)-**2a** (10)
8	Et	CuCN (0.02)	**4a** (53)	(*Z*)-**2a** (16)
9	Et	$Cu(OTf)_2$ (0.02)	**4a** (53)	(*Z*)-**2a** (22)
10	Me	CuCN·2LiCl (1)	**4b** (77)	**2g** (9)
11	Me	CuI (0.02)	**4b** (68)	**2g** (7)

[a] All reactions were carried out in THF using R_2Zn (1.5 mol per 1 mol of **1a**) in the presence of Cu salt at −78 °C to rt, and then allyl bromide (5 equiv) was added to the mixture. [b] Carbozincation was conducted using 2 mol % of CuCN, and then CuCN·2LiCl was added before the addition of allyl bromide.

(10) Posner and Okamura independently reported that α-sulfinyl vinyllithium generated by α-deprotonation of (*Z*)-vinylic sulfoxide immediately isomerizes to thermodynamically stable (*E*)-isomer (Posner, G. H.; Tang, P.-W.; Mallamo, J. P. *Tetrahedron Lett.* **1978**, 3995−3998. Okamura, H.; Mitsuhira, Y.; Miura, M.; Takei, H. *Chem. Lett.* **1978**, 517−520). In sharp contrast, no *E*/*Z*-isomerization was observed in α-sulfinyl vinylic carbanion generated by conjugate addition of organocopper reagents to 1-alkynyl sulfoxides (ref 4). The difference presumably arises from the ionic nature of the carbon−lithium bond as compared with the carbon−copper bond. With these facts in mind, we speculate that the organomagnesium intermediate in the reaction of Scheme 1 is geometrically more unstable due to its ionic nature than the corresponding organozinc intermediate in carbozincation, thereby suffering from *E*/*Z*-isomerization.

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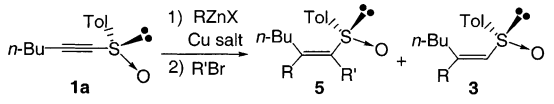
(12) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390−2392.

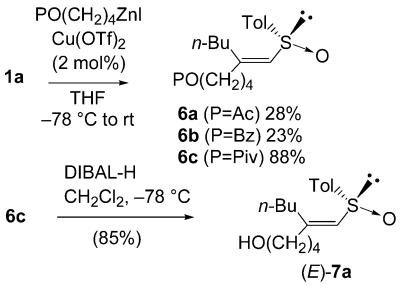
TABLE 5. Synthesis of Trisubstituted Vinylic Sulfoxides with RZnX[a]



entry	RZnX[b]	R'Br	Cu salt (equiv)	yield (%)	
1	AllylZnBr	AllylBr	CuCN•2LiCl (1)	**5a** (82)	**3a** (11)
2	AllylZnBr	AllylBr	CuCN•2LiCl (0.02)	**5a** (74)	**3a** (2)
3	AllylZnBr	AllylBr	$Cu(OTf)_2$ (0.02)	**5a** (66)	**3a** (8)
4		AllylBr	CuCN•2LiCl (1)	**5b** (52)	**3e** (8)
5		AllylBr	CuI (0.02)	**5b** (72)	**3e** (14)
6	AllylZnBr		CuCN•2LiCl (1)	**5c** (86)	**3a** (4)
7	AllylZnBr		CuI (0.02)	**5c** (59)	**3a** (25)

[a] All reactions were carried out in THF using RZnX (2 equiv) in the presence of Cu salt at −78 °C to rt, and then R′X (5 equiv) was added to the mixture. [b] Organozinc reagents were prepared from RX and Zn (powder) using TMSCl and dibromoethane as initiators.

SCHEME 3



stituent on the vinylic sulfoxide. The reaction affords cyclic ethers with a stereogenic center neighboring to the ether oxygen, whose structure is included in natural products such as ionomycin and malyngolide. As an extension of our method, we investigated the synthesis of chiral cyclic ethers.[13]

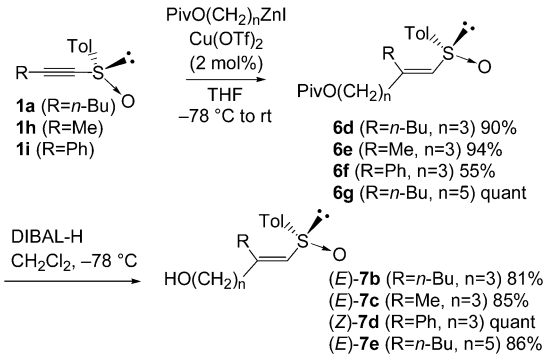
An attempt to introduce 3-acetoxy- and 3-benzoyloxybutylzinc iodide afforded the (*E*)-vinylic sulfoxide **6a** and **6b** in poor yields (Scheme 3). We found that an organozinc reagent bearing a pivaloyl protection furnished the adduct **6c** in 88% yield. The pivaloyl group was deprotected with DIBAL-H at −78 °C without affecting the vinylic sulfoxide to give 85% of (*E*)-**7a** as a single isomer.

Substrates **7b**−**e** (*E*-isomers except for **7d**) with different substituents were also synthesized in good yield by the same procedure (Scheme 4).

On the other hand, the corresponding geometric isomers of **7a**−**d** were prepared by carbozincation of **1j** and **1k** (Scheme 5).

With the substrates in hand, we next examined the intramolecular conjugate addition. Upon treatment of the substrates **7b**−**d** (*E*-isomers except for **7d**) with NaH in THF at 0 °C, the intramolecular conjugate addition took place to give the THF compounds **9b**−**d** in 83−93% yields (Table 6, entries 2−4). The diastereoselectivity was very

SCHEME 4



SCHEME 5

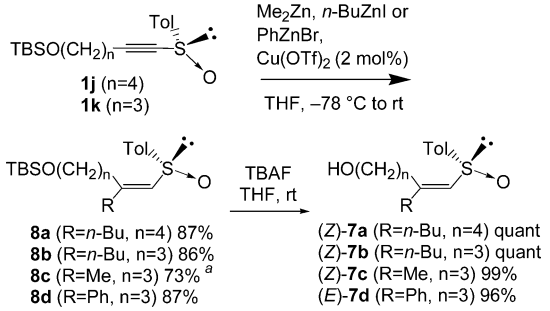
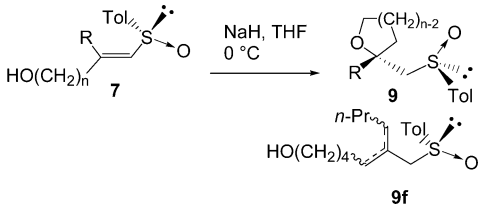


TABLE 6. Diastereoselective Synthesis of Cyclic Ethers 9a−d[a]



entry	substrate	R	n	product	yield (%)	dr[b]
1	(*E*)-**7a**	*n*-Bu	4	**9a**	86	>98:2
2	(*E*)-**7b**	*n*-Bu	3	**9b**	90	>98:2
3	(*E*)-**7c**	Me	3	**9c**	93	96:4
4	(*Z*)-**7d**	Ph	3	**9d**	83	>98:2
5	(*E*)-**7e**	*n*-Bu	5	**9e**	NR	

[a] All reactions were carried out at 0.03 M of the substrate in THF using NaH (5 equiv) at 0 °C. [b] Determined by ^{1}H NMR spectroscopic data.

high (>98:2) except that **9c** (R = Me) afforded slightly reduced diastereoselectivity (dr = 96:4). High diastereoselectivity was observed even in the THP ring formation (entry 1). However, in vinylic sulfoxide (*E*)-**7e** giving a seven-membered ring ether, no cyclized product **9e** was obtained, and, instead, deconjugation of the vinylic sulfoxide proceeded, giving β,γ-unsaturated sulfoxide **9f**[14] in 80% yield (entry 5).

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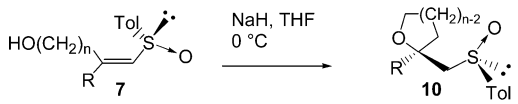
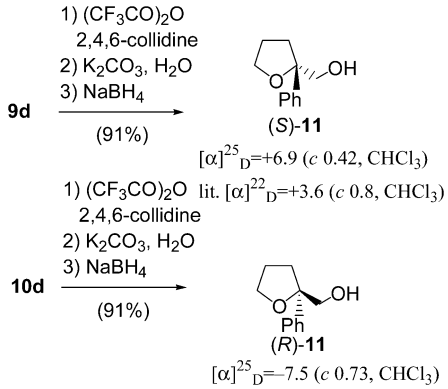
TABLE 7. Diastereoselective Synthesis of Cyclic Ethers 10a−d[a]



entry	substrate	R	n	product	yield (%)	dr[b]
1	(*Z*)-**7a**	*n*-Bu	4	**10a**	87	>98:2
2	(*Z*)-**7b**	*n*-Bu	3	**10b**	79	>98:2
3	(*Z*)-**7c**	Me	3	**10c**	89	>98:2
4	(*E*)-**7d**	Ph	3	**10d**	74	>98:2

[a] All reactions were carried out at 0.03 M of the substrate in THF using NaH (5 equiv) at 0 °C. [b] Determined by ^{1}H NMR spectroscopic data.

SCHEME 6



On the other hand, the vinylic sulfoxides (*Z*)-**7a**−**c** and (*E*)-**7d** were also cyclized on treatment with NaH in THF with very high diastereoselectivities (Table 7). In all cases, the products were epimers of the cyclic ether compounds synthesized from the corresponding geometric isomers.

Stereochemistry of the products was determined by conversion of **9d** and **10d** into the known compound **11** (Scheme 6).[15] Conversion of **9d** into **11** was carried out by a sequential reaction: (1) Pummerer reaction with $(CF_3CO)_2O$; (2) hydrolysis of *O*,*S*-acetal with aqueous K_2CO_3; and (3) reduction of the resulting aldehyde with $NaBH_4$. The THF compound **11** derived from **9d** shows the same sign of specific rotation as that of (*S*)-**11**, while the sign of the specific rotation of compound **11** derived from **10d** exhibited minus value. As a result, we concluded that **9d** and **10d** were (*R*s,2*S*)- and (*R*s,2*R*)-isomers, respectively.

The stereochemical outcome can be explained by the previously proposed reaction mechanism.[13e,f] Conformation of the sulfinyl group was situated to minimize $A^{(1,3)}$-strain. The metal cation of alkoxide would coordinate to the sulfinyl oxygen, thereby directing the approach of the alkoxide. In the vinylic sulfoxide (*E*)-**7c** bearing a small methyl group *syn* to the sulfinyl group, the $A^{(1,3)}$-strain would be slightly decreased, thereby lowering the diastereoselectivity.

Conclusion

We have developed geometrically selective syntheses of β,β-di- and trisubstituted vinylic sulfoxides via the Cu-catalyzed addition of organozinc reagent to 1-alkynyl sulfoxides. A variety of functionalized vinylic sulfoxides can be synthesized due to the mild reactivity of the organozinc reagents. The high *syn*-selectivity of the carbozincation enables the stereoselective synthesis of both geometric isomers. The method was applied to a stereoselective synthesis of two isomers of cyclic ethers.

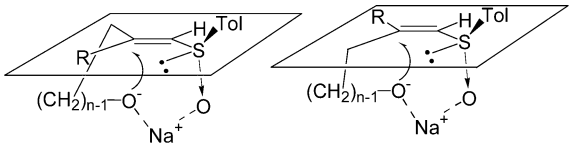


FIGURE 1. Plausible reaction mechanism.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ solution at 500 MHz (^{1}H) and 125, 75, or 67.8 MHz (^{13}C). IR absorption spectra (FT: diffuse reflectance spectroscopy) were recorded with KBr powder, and only noteworthy absorptions (cm^{-1}) are listed. Column chromatography was carried out using Merck silica gel 60 (70−230 mesh). All air- or moisture-sensitive reactions were carried out in flame-dried glassware under an atmosphere of N_2 or Ar. All solvents were dried and distilled according to standard procedures. All organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated with a rotary evaporator under reduced pressure. Allylzinc bromide, *n*-BuZnI, and 3-oxo-1-cyclohexen-1-ylzinc iodide were prepared in situ according to the literature[12] [organozinc halide (reaction temperature, reaction time): allylzinc bromide (0 °C, 4 h), BnZnBr (0 °C, 2 h), 3-oxo-1-cyclohexen-1-ylzinc iodide (25 °C, 2 h)], and the concentration was determined by GC analysis of a hydrolyzed reaction aliquot using *n*-decane as an internal standard.[16] CuCN·2LiCl was prepared according to the literature.[16] 1-Alkynylsulfoxides **1a**,[17] **1b**−**d**,[18] **1e**,[3e,4b] **1f**,[4b] **1g**,[19] **1h**,**i**,[20] and **1j**,**k**[21] were synthesized according to the procedure described in the literature. Characterization data and ^{1}H and ^{13}C NMR spectra of (*Z*)-**2a**, (*E*)-**2a**, and **3a** were reported in the Supporting Information of ref 5.

General Procedure for Cu-Catalyzed Conjugate Addition of R_2Zn to 1-Alkynyl Sulfoxide: (*R*)-[(*Z*)-4-(*tert*-Butyldimethylsilyloxy)-2-ethyl-1-butenyl] *p*-Tolyl Sulfoxide (2b). Et_2Zn (0.99 M in hexane) (1.11 mL, 1.11 mmol) was slowly added to a mixture of **1b** (179 mg, 0.553 mmol) and CuI (2.10 mg, 0.011 mmol) in THF (0.55 mL) with stirring at −78 °C. The stirring was continued for 15 min at −78 °C and at rt for 3.5 h. The reaction was quenched with 28% NH_4OH, and the mixture was extracted with Et_2O. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (2:1) to give **2b** (156 mg, 78%) as a yellow oil. $[\alpha]^{24}_D$ −146 (*c* 1.02, $CHCl_3$). ^{1}H NMR: δ 0.08 (s, 6H), 0.90 (s, 9H), 1.04 (t, J = 7.3 Hz, 3H), 2.24 (ddd, J = 14.7, 7.3, 1.3

(14) The product **9f** was a 1.8:1 mixture of two isomers, but the structures were not determined.

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Hz, 2H), 2.40 (s, 3H), 2.70 (dt, J = 13.2, 6.6 Hz, 1H), 2.95 (dt, J = 13.2, 6.6 Hz, 1H), 3.82 (t, J = 6.6 Hz, 2H), 6.01 (s, 1H), 7.29 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H). ^{13}C NMR: δ −5.4 (2C), 11.4, 18.2, 21.2, 25.8 (3C), 29.9, 35.7, 62.0, 124.2 (2C), 129.7 (2C), 132.2, 140.6, 141.8, 154.8. IR: 2927 (CH), 1493 (C=C), 1043 (S=O). MS (FAB) *m/z* 353 (MH^+). HRMS (FAB) calcd for $C_{19}H_{33}O_2SSi$ (MH^+), 353.1971; found, 353.1974.

General Procedure for Cu-Catalyzed Conjugate Addition of RZnX to 1-Alkynyl Sulfoxide: (*R*)-[(*E*)-2-Benzyl-1-hexenyl] *p*-Tolyl Sulfoxide (3b). Benzylzinc bromide (0.88 M in THF) (0.57 mL, 0.505 mmol) was slowly added to a mixture of **1a** (55.6 mg, 0.252 mmol) and $Cu(OTf)_2$ (1.82 mg, 5.05 μmol) in THF (0.25 mL) with stirring at −78 °C. The stirring was continued for 15 min at −78 °C and at rt for 2 h. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with Et_2O. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (5:1) to give **3b** (63.5 mg, 81%) as a yellow oil. $[\alpha]^{25}_D$ −154 (*c* 0.80, $CHCl_3$). ^{1}H NMR: δ 0.94 (t, J = 7.3 Hz, 3H), 1.39 (qt, J = 7.3, 7.3 Hz, 2H), 1.45−1.52 (m, 1H), 1.55−1.64 (m, 1H), 2.40 (s, 3H), 2.48 (ddd, J = 13.4, 9.8, 6.1 Hz, 1H), 2.55 (ddd, J = 13.4, 9.8, 5.5 Hz, 1H), 3.45 (s, 2H), 6.02 (s, 1H), 7.11 (d, J = 7.3 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 7.26 (t, J = 7.3 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 13.8, 21.3, 22.5, 30.8, 31.4, 42.7, 124.1 (2C), 126.7, 128.5 (2C), 129.0 (2C), 129.8 (2C), 133.5, 136.9, 140.8, 141.6, 154.9. IR: 2954 (CH), 1493 (C=C), 1039 (S=O). MS (FAB) *m/z* 313 (MH^+). HRMS (FAB) calcd for $C_{20}H_{25}OS$ (MH^+), 313.1626; found, 313.1637.

General Procedure for Cu-Catalyzed Conjugate Addition Followed by Alkylation: (*R*)-[(*Z*)-5-Ethyl-1,4-nonadien-4-yl] *p*-Tolyl Sulfoxide (4a, Table 4, Entry 2). Et_2Zn (1.01 M in hexane) (0.35 mL, 0.350 mmol) was slowly added to a mixture of **1a** (51.4 mg, 0.233 mmol) and CuCN·2LiCl (1.00 M in THF) (0.23 mL, 0.233 mmol) with stirring at −78 °C. The stirring was continued for 15 min at −78 °C and at rt for 2 h. Allyl bromide (0.10 mL, 1.17 mmol) was added to the mixture, and the whole was stirred at rt for 3 h. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (5:1) to give **4a** (56.9 mg, 88%) as a yellow oil along with (*Z*)-**2a** (1.6 mg, 3%). $[\alpha]^{24}_D$ −250 (*c* 0.80, $CHCl_3$). ^{1}H NMR: δ 0.97 (t, J = 7.3 Hz, 3H), 1.04 (t, J = 7.3 Hz, 3H), 1.42−1.55 (m, 3H), 1.58−1.66 (m, 1H), 2.20 (q, J = 7.3 Hz, 2H), 2.39 (s, 3H), 2.61 (ddd, J = 13.4, 9.8, 5.5 Hz, 1H), 2.71 (ddd, J = 13.4, 9.8, 6.1 Hz, 1H), 2.80 (dd, J = 16.5, 6.1 Hz, 1H), 3.05 (dd, J = 16.5, 6.1 Hz, 1H), 4.74 (dd, J = 10.4, 1.8 Hz, 1H), 4.78 (dd, J = 17.1, 1.8 Hz, 1H), 5.24 (ddt, J = 17.1, 10.4, 6.1 Hz, 1H), 7.26 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 12.1, 13.9, 21.3, 22.9, 25.5, 27.5, 31.3, 31.7, 115.0, 124.5 (2C), 129.5 (2C), 136.1, 136.3, 139.9, 140.2, 154.2. IR: 2964 (CH), 1493 (C=C), 1043 (S=O). MS (FAB) *m/z* 291 (MH^+). HRMS (FAB) calcd for $C_{18}H_{27}OS$ (MH^+), 291.1783; found, 291.1780.

(*R*)-[(*E*)-5-Butyl-1,4,7-octatrien-4-yl] *p*-Tolyl Sulfoxide (5a, Table 5, Entry 1). Allylzinc bromide (1.00 M in THF) (0.45 mL, 0.454 mmol) was slowly added to a mixture of **1a** (50.0 mg, 0.227 mmol) and CuCN·2LiCl (1.00 M in THF) (0.23 mL, 0.23 mmol) with stirring at −78 °C. The stirring was continued for 15 min at −78 °C and at 0 °C for 2 h. Allyl bromide (0.10 mL, 1.13 mmol) was added to the mixture at −78 °C. The whole was stirred at the temperature for 30 min and at 0 °C for 12 h. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (5:1) to give **5a** (56.6 mg, 82%) as a yellow oil along with **3a** (6.5 mg, 11%). $[\alpha]^{25}_D$ −276 (*c* 1.29, $CHCl_3$). ^{1}H NMR: δ 0.97 (t, J = 7.3 Hz, 3H), 1.40−1.55 (m, 3H), 1.58−1.66 (m, 1H), 2.39 (s, 3H), 2.59 (ddd, J = 13.4, 10.4, 4.9 Hz, 1H), 2.72 (ddd, J = 13.4, 10.4, 6.1 Hz, 1H), 2.83 (dd, J = 16.5, 6.1 Hz, 1H), 2.96 (d, J = 6.1 Hz, 2H), 3.06 (dd, J = 16.5, 6.1 Hz, 1H), 4.76 (dd, J = 10.4, 1.2 Hz, 1H), 4.79 (dd, J = 17.1, 1.2 Hz, 1H), 5.08 (dd, J = 17.1, 1.2 Hz, 1H), 5.08 (dd, J = 10.4, 1.2 Hz, 1H), 5.24 (ddt, J = 17.1, 10.4, 6.1 Hz, 1H), 5.70 (ddt, J = 17.1, 10.4, 6.1 Hz, 1H), 7.27 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 13.9, 21.3, 22.8, 27.6, 31.4, 31.9, 36.9, 115.3, 117.3, 124.4 (2C), 129.6 (2C), 133.8, 135.9, 138.1, 139.8, 140.4, 149.8. IR: 2956 (CH), 1493 (C=C), 1043 (S=O). MS (FAB) *m/z* 303 (MH^+). HRMS (FAB) calcd for $C_{19}H_{27}OS$ (MH^+), 303.1783; found, 303.1795.

3-[(*E*)-4-[(*R*)-(*p*-Tolyl)sulfinyl]-1,4-nonadien-5-yl]-2-cyclohexenone (5b, Table 5, Entry 5). 3-Oxo-1-cyclohexen-1-ylzinc iodide (0.67 M in THF) (0.67 mL, 0.448 mmol) was slowly added to a mixture of **1a** (49.4 mg, 0.224 mmol) and CuI (0.9 mg, 4.48 μmol) with stirring at −78 °C. The stirring was continued for 15 min at −78 °C and at rt for 2 h. Allyl bromide (0.10 mL, 1.12 mmol) was added to the mixture at −78 °C. The whole was stirred at rt for 12 h. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (2:1) to give **5b** (57.8 mg, 72%) as a yellow oil along with **3e** (10.1 mg, 14%). $[\alpha]^{25}_D$ −90.0 (*c* 0.98, $CHCl_3$). ^{1}H NMR: δ 0.95 (t, J = 7.3 Hz, 3H), 1.39−1.53 (m, 4H), 2.02−2.07 (m, 2H), 2.29−2.44 (m, 4H), 2.41 (s, 3H), 2.73−2.85 (m, 3H), 3.01 (dd, J = 15.9, 6.7 Hz, 1H), 4.72 (dd, J = 17.1, 1.2 Hz, 1H), 4.75 (dd, J = 10.4, 1.2 Hz, 1H), 5.20 (ddt, J = 17.1, 10.4, 6.7 Hz, 1H), 5.82 (s, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 13.8, 21.3, 22.6, 22.7, 28.5, 28.5, 30.7, 31.4, 37.2, 116.1, 124.3 (2C), 127.9, 129.9 (2C), 135.9, 139.3 (2C), 140.9, 149.9, 160.5, 198.6. IR: 2956 (CH), 1676 (C=O), 1491 (C=C), 1045 (S=O). MS (FAB) *m/z* 357 (MH^+). HRMS (FAB) calcd for $C_{22}H_{29}O_2S$ (MH^+), 357.1888; found, 357.1884.

Methyl (*E*)-5-Butyl-2-methylene-4-[(*R*)-(*p*-tolyl)sulfinyl]-4,7-octadienoate (5c, Table 5, Entry 6). Allylzinc bromide (1.00 M in THF) (0.38 mL, 0.376 mmol) was slowly added to a mixture of **1a** (41.4 mg, 0.188 mmol) and CuCN·2LiCl (1.00 M in THF) (0.19 mL, 0.188 mmol) with stirring at −78 °C. The stirring was continued for 15 min at −78 °C and at 0 °C for 2 h. Methyl 2-(bromomethyl)acrylate (0.07 mL, 0.564 mmol) was added to the mixture at −78 °C. The whole was stirred at rt for 11 h. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (5:1) to give **5c** (58.1 mg, 86%) as a yellow oil along with **3a** (1.9 mg, 4%). $[\alpha]^{26}_D$ −185 (*c* 1.11, $CHCl_3$). ^{1}H NMR: δ 0.99 (t, J = 7.3 Hz, 3H), 1.42−1.58 (m, 3H), 1.60−1.69 (m, 1H), 2.38 (s, 3H), 2.60 (ddd, J = 13.4, 10.4, 4.9 Hz, 1H), 2.80 (ddd, J = 13.4, 10.4, 6.1 Hz, 1H), 2.82 (d, J = 6.7 Hz, 2H), 3.00 (d, J = 18.3 Hz, 1H), 3.33 (d, J = 18.3 Hz, 1H), 3.70 (s, 3H), 5.05 (dd, J = 16.8, 1.8 Hz, 1H), 5.07 (dd, J = 10.4, 1.8 Hz, 1H), 5.30 (s, 1H), 5.67 (ddt, J = 16.8, 10.4, 6.7 Hz, 1H), 6.01 (s, 1H), 7.24 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 13.9, 21.3, 22.8, 25.0, 31.4, 31.8, 37.6, 51.8, 117.6, 124.3 (2C), 125.2, 129.7 (2C), 133.4, 137.0, 137.6, 139.8, 140.6, 150.6, 167.0. IR: 2954 (CH), 1720 (C=O), 1493 (C=C), 1043 (S=O). MS (FAB) *m/z* 361 (MH^+). HRMS (FAB) calcd for $C_{21}H_{29}O_2S$ (MH^+), 361.1837; found, 361.1829.

(*E*)-5-Butyl-6-[(*R*)-(*p*-tolyl)sulfinyl]-5-hexen-1-ol [(*E*)-7a]. DIBAL-H (1.01 M in toluene, 0.16 mL, 0.16 mmol) was added to a solution of **6c** (29.9 mg, 0.0790 mmol) in CH_2Cl_2 (1 mL) with stirring at −78 °C, and additional DIBAL-H (0.23 mL, 0.23 mmol) was added to the mixture after 1 h. After the stirring was continued for 10 min, saturated Rochelle salt was gradually added to the mixture. The whole was stirred at rt for 30 min. The mixture was extracted with EtOAc, and the extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with EtOAc to give (*E*)-**7a** (19.8 mg, 85%) as a

colorless oil. $[\alpha]^{25}_D$ −149 (*c* 0.94, $CHCl_3$). ^1H NMR: δ 0.96 (t, J = 7.3 Hz, 3H), 1.37−1.62 (m, 8H), 1.82 (br s, 1H), 2.18 (br t, J = 6.7 Hz, 2H), 2.40 (s, 3H), 2.53 (ddd, J = 13.4, 9.8, 6.1 Hz, 1H), 2.62 (ddd, J = 13.4, 9.8, 5.5 Hz, 1H), 3.61 (br t, J = 5.5 Hz, 2H), 6.02 (s, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 14.0, 21.4, 22.8, 23.6, 31.0, 32.2, 32.2, 36.1, 62.4, 124.1 (2C), 129.8 (2C), 131.7, 140.7, 141.7, 156.1. IR: 3024 (OH), 2931 (CH), 1493 (C=C), 1024 (S=O). MS (FAB) *m/z* 295 (MH^+). HRMS (FAB) calcd for $C_{17}H_{27}O_2S$ (MH^+), 295.1732; found, 295.1721.

(*Z*)-4-Butyl-5-[(*R*)-(*p*-tolyl)sulfinyl]-4-penten-1-ol [(*Z*)-7b]. TBAF (1.0 M in THF, 0.18 mL, 0.178 mmol) was added to a stirred solution of **8b** (70.2 mg, 0.178 mmol) in THF (28 mL) at 0 °C. After the mixture was stirred at rt for 1.5 h, saturated NH_4Cl was added, and the mixture was extracted with EtOAc. The organic phase was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with EtOAc to give (*Z*)-**7b** (53.0 mg, quant) as a yellow oil. $[\alpha]^{23}_D$ −81.7 (*c* 0.96, $CHCl_3$). ^1H NMR: δ 0.88 (t, J = 7.3 Hz, 3H), 1.25−1.35 (m, 2H), 1.38−1.47 (m, 2H), 1.77−1.87 (m, 2H), 2.15−2.18 (m, 2H), 2.41 (s, 3H), 2.53 (ddd, J = 13.4, 7.9, 6.1 Hz, 1H), 2.92 (br s, 1H), 2.94 (ddd, J = 13.4, 6.7, 6.7 Hz, 1H), 3.69 (br t, J = 7.9 Hz, 2H), 6.10 (s, 1H), 7.31 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 13.7, 21.3, 22.2, 28.4, 29.2, 31.0, 35.8, 60.9, 124.1 (2C), 129.9 (2C), 131.8, 140.9, 141.1, 157.2. IR: 3388 (OH), 2929 (CH), 1493 (C=C), 1038 (S=O). MS (FAB) *m/z* 281 (MH^+). HRMS (FAB) calcd for $C_{16}H_{25}O_2S$ (MH^+), 281.1575; found, 281.1575.

General Procedure for Intramolecular Michael Addition to Vinylic Sulfoxides: (2*R*)-2-Butyl-2-[(*R*)-(*p*-tolyl)-sulfinylmethyl]tetrahydrofuran (9b). NaH (60% in oil) (66.8 mg, 1.67 mmol) was washed with *n*-hexane under Ar and suspended in THF (6 mL). A solution of (*E*)-**7b** (93.7 mg, 0.334 mmol) in THF (4 mL) was added to the suspension with stirring at 0 °C. The stirring was continued for 30 min. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (2:1) to give **9b** (84.6 mg, 90%) as a colorless oil. $[\alpha]^{25}_D$ +131 (*c* 1.12, $CHCl_3$). ^1H NMR: δ 0.88 (t, J = 6.7 Hz, 3H), 1.28−1.29 (m, 4H), 1.60 (t, J = 6.7 Hz, 2H), 1.88 (dt, J = 12.2, 6.1 Hz, 1H), 1.96−2.04 (m, 1H), 2.08−2.16 (m, 1H), 2.36 (dt, J = 12.2, 6.1 Hz, 1H), 2.41 (s, 3H), 2.89 (d, J = 13.4 Hz, 1H), 3.05 (d, J = 13.4 Hz, 1H), 3.91 (q, J = 7.3 Hz, 1H), 4.04 (q, J = 7.3 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 14.0, 21.3, 23.0, 26.3 (2C), 34.2, 40.7, 68.5, 68.9, 83.2, 123.9 (2C), 129.9 (2C), 141.1, 142.2. IR: 2954 (CH), 1495 (C=C), 1041 (S=O). MS (FAB) *m/z* 281 (MH^+). HRMS (FAB) calcd for $C_{16}H_{25}O_2S$ (MH^+), 281.1575; found, 281.1595.

(*S*)-(2-Phenyltetrahydrofuran-2-yl)methanol [(*S*)-11]. Trifluoroacetic anhydride (0.02 mL, 0.170 mmol) was added to a solution of **9d** (25.6 mg, 0.0852 mmol) and 2,4,6-collidine (0.02 mL, 0.170 mmol) in MeCN (0.61 mL) with stirring at 0 °C. After being stirred at this temperature for 10 min, the reaction was quenched with water (0.03 mL). The mixture was neutralized with K_2CO_3, and the whole was stirred at rt for 2 h. $NaBH_4$ (9.7 mg, 0.256 mmol) was added to the mixture, and the stirring was continued at rt for 15 min. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The organic phase was washed with 5% HCl and saturated $NaHCO_3$ prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexanes−EtOAc (3:1) to give (*S*)-**11** (13.8 mg, 91%) as a colorless oil. $[\alpha]^{25}_D$ +6.9 (*c* 0.42, $CHCl_3$) (lit.[13] $[\alpha]^{22}_D$ +3.6 (*c* 0.8, $CHCl_3$)). ^1H NMR: δ 1.80−1.89 (m, 1H), 1.94−2.02 (m, 1H), 2.07 (br s, 1H), 2.11 (ddd, J = 12.2, 7.9, 4.9 Hz, 1H), 2.35 (dt, J = 12.2, 7.9 Hz, 1H), 3.66 (s, 2H), 3.94 (q, J = 7.3 Hz, 1H), 4.03 (q, J = 7.3 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.34 (dd, J = 7.9, 7.3 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H). ^{13}C NMR: δ 26.1, 34.0, 68.4, 69.0, 87.3, 125.3 (2C), 127.0, 128.3 (2C), 144.2. IR: 3439 (OH), 2872 (CH), 1446 (C=C), 1065 (CH_2OC). MS (FAB) *m/z* 201 (MNa^+). HRMS (FAB) calcd for $C_{11}H_{14}NaO_2$ (MNa^+), 201.0891; found, 201.0890.

Supporting Information Available: Characterization data of **2c**−**f**, **3c**−**g**, **4b**, **6a**−**g**, (*E*)-**7b**−**e**, (*Z*)-**7a**, (*Z*)-**7c**,**d**, **8a**−**d**, **9a**, **9c**, **9d**, **9f**, **10a**−**d**, (*R*)-**11**. ^1H and ^{13}C NMR spectra of **4a**, **5a**, (*E*)-**7a**, (*Z*)-**7a**, **9a**, and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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