Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 9895–9906

TETRAHEDRON

Synthesis of chiral vinylic sulfoxides by Pd-catalyzed asymmetric sulfinylzincation

Naoyoshi Maezaki,[a,*] Suguru Yagi,[a] Shizuka Ohsawa,[a] Hirofumi Ohishi[b] and Tetsuaki Tanaka[a,*]

[a]*Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan*
[b]*Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-1094, Japan*

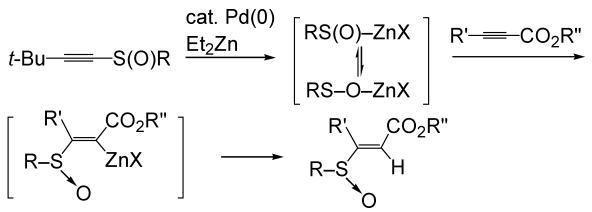
Received 7 July 2003; revised 12 October 2003; accepted 14 October 2003

Abstract—Novel asymmetric sulfinylzincation of alkynoates has been accomplished via a Pd-catalyzed sulfinylzincation using 1-alkynyl sulfoxides bearing chiral auxiliaries as a sulfinylating reagent. The reaction proceeded in a highly *syn*-selective fashion, giving the (*E*)-β-sulfinyl α,β-unsaturated ester exclusively. Among the chiral sulfinylating reagents tested, an isoborneol-type compound (*R*s)-**4** showed the best results in terms of both yield and diastereoselectivity. As a result of optimization of the reaction, the selectivity was improved up to 92:8 dr, and stereochemistry of the newly formed sulfur stereogenic center was revealed as (*S*s)-configuration.

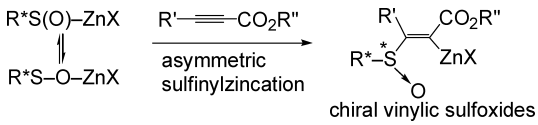
1. Introduction

The synthesis of chiral sulfoxides has been extensively studied due to its high ability of asymmetric induction. Several methods are presently available for the synthesis of optically active sulfoxides. Representative methods are (1) optical resolution of racemic sulfoxides, (2) asymmetic oxidation of sulfides, (3) nucleophilic substitution on chiral sulfur derivatives.[1] Addition of sulfenic acid to an unsaturated bond affords an alternative option. Aversa and co-workers reported an asymmetric addition of a sulfenic acid to unsaturated bonds.[2] However, the stereoselectivity of sulfinylation was not sufficiently high. The asymmetric addition of a chiral sulfenic anion has not hitherto been investigated, to the best of our knowledge.[3] We have recently found that unusual sulfinylation proceeds on treatment of 1-alkynyl sulfoxides with a Pd(0)-catalyst and Et_2Zn, wherein a sulfinylzinc (or zinc sulfenate) species is assumed to be generated via oxidative addition of the 1-alkynyl sulfoxide to the Pd(0)-catalyst followed by transmetalation with Et_2Zn (Scheme 1).[4] This methodology allows easy introduction of a sulfinyl group into activated alkynes in a highly *syn*-selective manner, thereby enabling a compensative procedure against an *anti*-selective conjugate addition of thiolate followed by oxidation to sulfoxide.[5]

In this research, we found that the chirality on the sulfur atom was lost during the reaction presumably as a result of rapid sulfinyl-sulfenate tautomerization. We assumed that the chiral sulfoxides could be synthesized by employing the sulfenate (sulfinyl) anion with a chiral substitutent (R^*) as shown in Scheme 2.



Scheme 1.



Scheme 2.

To confirm our working hypothesis to develop a novel asymmetric reaction, we designed four kinds of chiral 1-alkynyl sulfoxides **1**–**4** bearing various chiral auxiliaries (Fig. 1).

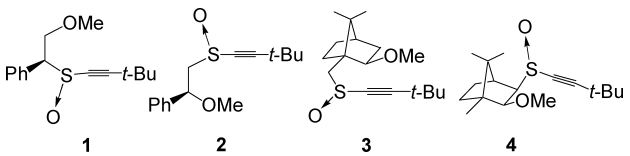


Figure 1. Structure of chiral sulfinylating reagents.

Keywords: sulfoxides; asymmetric reaction; palladium catalyst; sulfinylzincation.
* Corresponding authors. Tel.: +81-6-6879-8213; fax: +81-6-6879-8214; e-mail: maezaki@phs.osaka-u.ac.jp; *Tel.: +81-6-6879-8210; fax: +81-6-6879-8214; e-mail: t-tanaka@phs.osaka-u.ac.jp

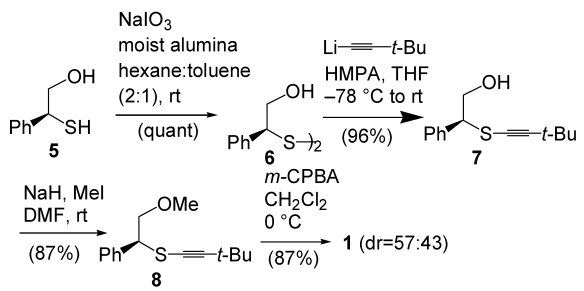
0040–4020/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2003.10.037

In this paper, we report the full details of asymmetric sulfinylzincation using these 1-alkynyl sulfoxides.[6]

2. Results and discussion

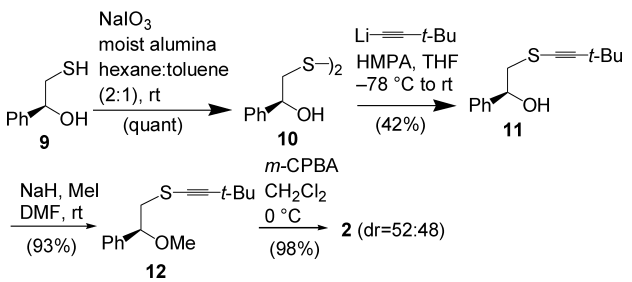
2.1. Preparation of chiral 1-alkynyl sulfoxides

The 1-alkynyl sulfoxide **1** having a stereogenic center adjacent to the sulfoxide was synthesized starting from known hydroxylated thiol **5** prepared from ethyl (*R*)-mandelate according to the procedure described in the literature (Scheme 3).[7] After conversion of **5** into disulfide **6** with $NaIO_3$ and moist aluminum,[8] lithium acetylide generated from 3,3-dimethylbutyne was reacted with **6** in the presence of HMPA, giving sulfide **7** in 96% in two steps. Methylation of the primary alcohol (NaH, MeI) to give **8** followed by *m*-CPBA oxidation of the sulfide furnished the sulfoxide **1** as a 57:43 diastereomeric mixture in 76% yield in two steps.



Scheme 3.

On the other hand, the substrate **2** bearing a stereogenic center at the β-position of the sulfoxide was synthesized as a 52:48 diastereomeric mixture from known hydroxylated thiol **9**[7] following the same procedure for **1** (Scheme 4).

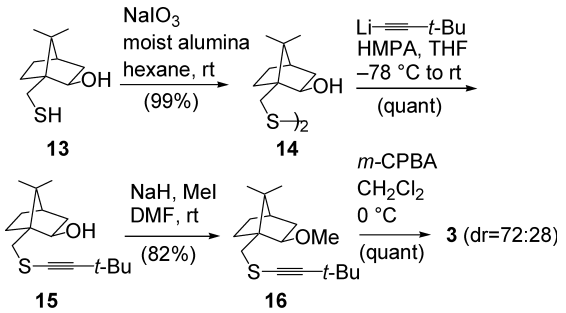


Scheme 4.

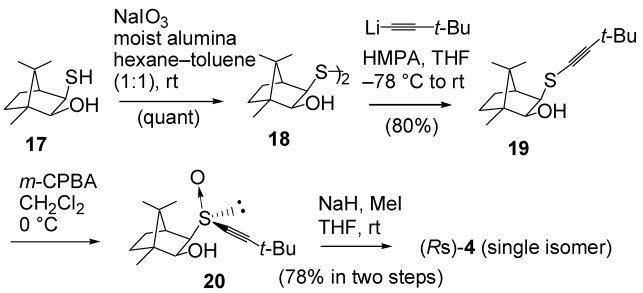
The 1-alkynyl sulfoxides **3** and **4** with the conformationally restricted chiral auxiliaries were also prepared from the known mercaptoisoborneol derivatives **13**[9] and **17**.[10] Thus, the 1-alkynyl sulfoxide **3** was obtained as a 72:28 diastereomeric mixture by the same method described for the 1-alkynyl sulfoxide **1** (Scheme 5).

The 1-alkynyl sulfoxide (*R*s)-**4** was selectively synthesized by *m*-CPBA oxidation of alcohol **19** followed by methylation of the hydroxy group (Scheme 6).[11]

The diastereomeric (*S*s)-**4** was also synthesized mainly by

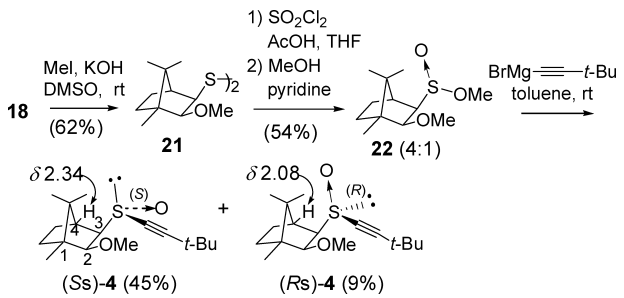


Scheme 5.



Scheme 6.

changing the procedure as depicted in Scheme 7. The hydroxylated disulfide **18** was methylated (MeI, KOH) in 62% yield. The resulting disulfide **21** was transformed into a methyl sulfinate by the reaction with SO_2Cl_2 in AcOH followed by methanolysis in pyridine,[12] giving **22** as a 5:1 diastereomeric mixture in 54% yield in two steps.[13] Finally, the mixture was treated with 3,3-dimethyl-1-butynylmagnesium bromide to give the alkynylsulfoxide (*S*s)-**4** in 45% yield along with 9% of (*R*s)-**4**.



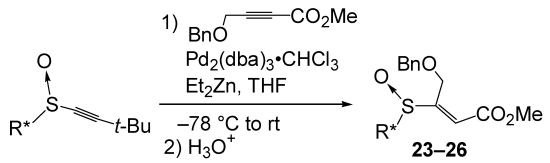
Scheme 7.

These two procedures shown in Schemes 6 and 7 afforded the 1-alkynyl sulfoxides with an opposite configuration. The absolute configuration on the sulfur atom in (*R*s)- and (*S*s)-**4** was assumed by an empirical rule reported by Goodridge and co-workers.[10] They reported that the signal for the H_4-proton in (*R*s)-isomers of 3-*exo*-(alkylsulfinyl)isoborneols appears at lower field than that of the corresponding (*S*s)-isomers due to anisotropic effect of the S=O bond to the H_4-proton in the (*R*s)-isomer.[14] Since the stereochemistry on the sulfoxides in the 3-*exo*-(alkynylsulfinyl)isoborneol derivatives is opposite to that in the 3-*exo*-(alkylsulfinyl)-isoborneols due to the change of priority groups, the isomers having the H_4-proton at 2.34 and 2.08 ppm were assigned as (*S*s)- and (*R*s)-isomers, respectively.

2.2. Asymmetric sulfinylzincation

Asymmetric sulfinylzincation using these 1-alkynyl sulfoxides **1**–**4** was applied to the alkynoate, and the results are summarized in Table 1. A mixture of (*R*)- and (*S*)-sulfoxides was used in the reactions except for entry 4. Upon treatment of the 1-alkynyl sulfoxides with 2 mol% of $Pd_2(dba)_3{\cdot}CHCl_3$ and Et_2Zn in the presence of a γ-functionalized alkynoate, sulfinylzincation proceeded to give the sulfinylated adducts in moderate yields after protonation of the resulting β-sulfinylic vinyl anion. The position of the stereogenic center in the chiral auxiliary considerably affected the diastereoselectivity. Thus, diastereoselectivity was markedly reduced in the substrates **2** and **3** bearing a stereogenic center far from the sulfoxide (entries 2 and 3). On the other hand, 1-alkynyl sulfoxides **1** and **4** with a stereogenic center adjacent to the sulfoxide showed better selectivity. We selected compound (*R*s)-**4** for the further study owing to the higher yield and cheapness of the material.

Table 1. Influence of structure of chiral auxiliaries

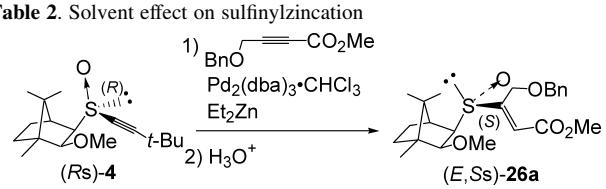


Entry	Substrate	Product	Yiled (%)	dr[a]
1	**1**	**23**	63	83:17[b]
2	**2**	**24**	41	59:41[b]
3	**3**	**25**	68	72:28[b]
4	(*R*s)-**4**	(*E*,*S*s)-**26a**	69	82:18

The reactions were carried out with alkynoate (3 equiv.), Et_2Zn (2 equiv.), and $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol%) in THF overnight under Ar.
[a] Determined by ^1H NMR spectroscopic data.
[b] Stereochemistry was not determined.

To improve the selectivity, solvent effect on the sulfinylzincation was examined. We found that dioxane was the best solvent, giving (*E*,*S*s)-**26a** with 91:9 dr (Table 2). Therefore, dioxane was used in the following experiments.

Table 2. Solvent effect on sulfinylzincation

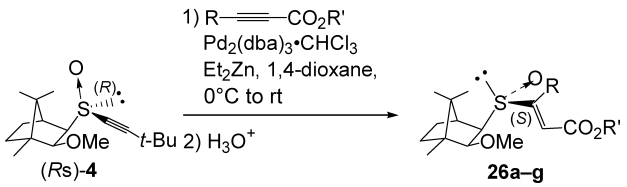


Entry	Solvent	Temperature (°C)	Yiled (%)	dr[a]
1	Toluene	−78°C to rt	86	86:14
2	Et_2O	−78°C to rt	69	88:12
3	THF	−78°C to rt	69	82:18
4	Dioxane	0°C to rt	99	91:9

The reactions were carried out with alkynoate (3 equiv.), Et_2Zn (2 equiv.), and $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol%) in solvent overnight under Ar.
[a] Determined by ^1H NMR spectroscopic data.

Next, we examined the asymmetric sulfinylzincation of various alkynoate derivatives (3 equiv.) with Et_2Zn (2 equiv.) and 2 mol% of catalytic $Pd_2(dba)_3{\cdot}CHCl_3$ in dioxane using the 1-alkynylsulfoxide (*R*s)-**4** as a sulfinyl source. The results are summarized in Table 3.

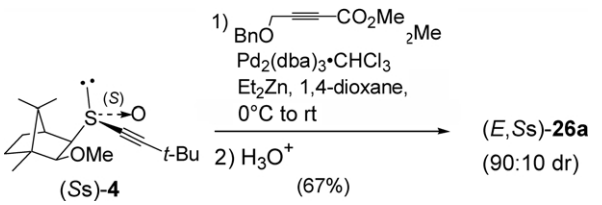
Table 3. Sulfinylzincation of various alkynoates with (*R*s)-**4**



Entry	R	R′	Product	Yiled (%)	dr[a]
1	$BnOCH_2$	Me	(*E*,*S*s)-**26a**	99	91:9
2	$AcOCH_2$	Me	**26b**	51	92:8[b]
3	$TBSOCH_2$	Me	**26c**	98	90:10
4	$BnSCH_2$	Me	**26d**	100	91:9[b]
5	H	Me	**26e**	30	85:15[b,c]
6	Me	Et	**26f**	100	90:10[b,c]
7	Me	Et	**26f**	82	91:9[b,c,d]
8	$BnOCH_2$	4-$O_2NC_6H_4CH_2$	**26g**	72	86:14

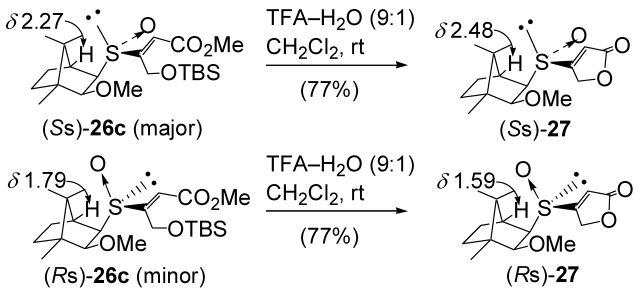
The reactions were carried out with alkynoate (3 equiv.), Et_2Zn (2 equiv.), and $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol%) in 1,4-dioxane overnight under Ar unless otherwise stated.
[a] Determined by ^1H NMR spectroscopic data.
[b] Diastereomeric isomers were inseparable.
[c] 10 equiv. of alkynoates were used.
[d] 1 equiv. of Et_2Zn was used.

Upon treatment of (*R*s)-**4** with 3 equiv. of alkynoate and 2 equiv. of Et_2Zn and 2 mol% of $Pd_2(dba)_3{\cdot}CHCl_3$, the sulfinylzincation proceeded in good yields in the presence of various functional group, except that the β-unsubstituted alkynoate afforded the product in poor yield (entry 5). By use of one equivalent of Et_2Zn, the yield was reduced (entries 6 and 7). Interestingly, the chirality on the sulfur atom was reversed during the reactions. The vinylic sulfoxides with an (*S*)-sulfoxide were obtained preferentially with ca. 9:1 dr, except that **26e** and **26g** exhibited reduced selectivity (ca. 6:1 dr). The selectivity was not affected even if the (*S*s)-isomer of **4** was used, although the yield was slightly reduced (Scheme 8). The results support the speculation that the reaction proceeds via the same zinc sulfenate (or sulfinylzinc) intermediate generated from both epimers of the 1-alkynylsulfoxide (*S*s)- and (*R*s)-**4**.



Scheme 8.

Stereochemistry of the adducts was determined as follows. The geometry of the olefins was deduced as (*E*)-configuration based on our previous results,[4] and was confirmed by lactone formation on treatment of two isomers of **26c** with TFA (Scheme 9). The stereochemistry of the sulfoxide was assumed by the above-mentioned empirical rule. In the ^1H NMR spectra, the major product (*S*s)-**26c** and the corresponding lactone (*S*s)-**27** showed a downfield shift in comparison with the minor adduct (*R*s)-**26c** and the lactone



Scheme 9.

(*R*s)-**27** in signals due to the H_4-protons in the isoborneol skeleton.

This speculation was confirmed by X-ray single crystal analysis of the γ-lactone (*S*s)-**27** (Fig. 2).

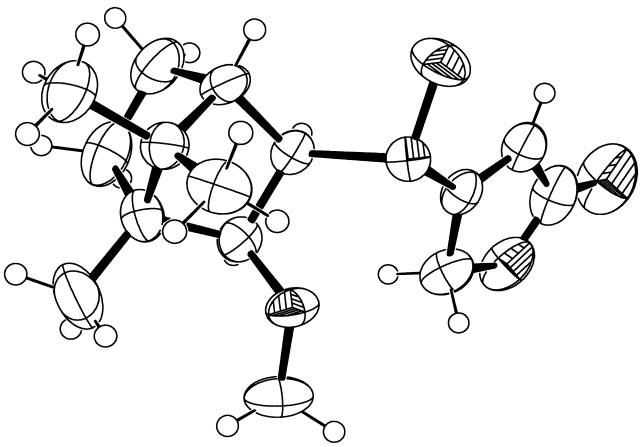


Figure 2. ORTEP drawing of (*S*s)-**27**.

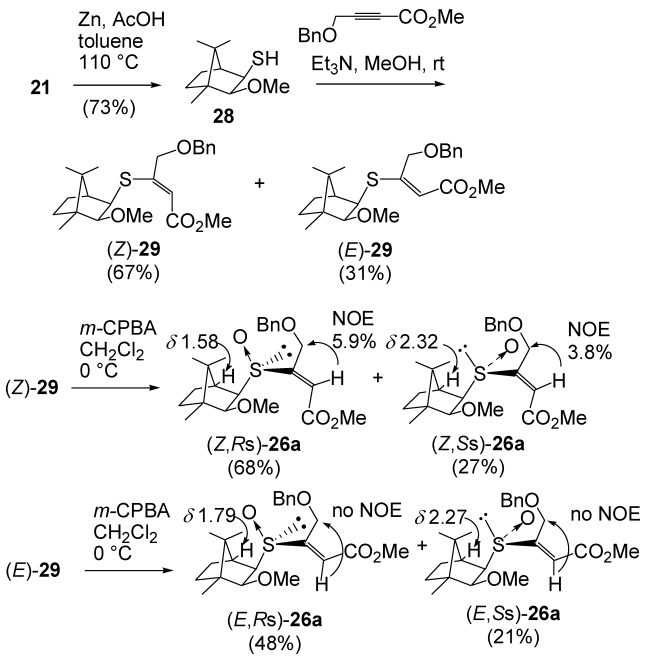
Table 4 shows the chemical shifts of the H_4-proton in the adducts **26a**–**g**. The chemical shifts are varied ranging from 2.27 to 2.42 for major adducts, and ranging from 1.63 to 1.86 for minor adducts. Accordingly, the major and minor sulfoxides are assumed to possess (*S*s)- and (*R*s)-configuration, respectively, by the above-mentioned empirical rule.[10]

Table 4. Comparison of chemical shifts due to H_4-proton for adducts **26a**–**g**

Compound	Substrate	
	Major [(*S*s)-form] (ppm)	Minor [(*R*s)-form] (ppm)
26a	2.27	1.79
26b	2.38	1.68
26c	2.27	1.86
26d	2.37	1.63
26e	2.42	–[a]
26f	2.39	–[a]
26g	2.27	1.82

[a] Not assigned due to overlap with other signals.

Addition of thiolate to alkynoates is known to proceed in an *anti*-selective fashion. To compare the stereochemical outcome with the sulfinylzincation, conjugate addition of thiol **28** was investigated (Scheme 10). The disulfide **21** was reduced with Zn and AcOH to give the thiol **28**, which was reacted with methyl 4-benzyloxy-2-butynoate in the presence of Et_3N in MeOH. Unexpectedly, the reaction proceeded with low selectivity, giving (*Z*)-**29** in 67% yield along with 31% of (*E*)-**29**. In addition, the diastereoselectivity of *m*-CPBA oxidation of (*Z*)- and (*E*)-**29** was also very poor. These results are in sharp contrast to the finding that the sulfinylzincation proceeds with high diastereo- and *syn*-selectivity (Table 3, entry 1). The stereochemistry of the products was confirmed by the empirical rule and NOE experiments.



Scheme 10.

The diastereoselectivity in the sulfinylzincation can be interpreted as follows. In the preferred conformers of the zinc sulfenate and sulfinylzinc species, the smallest lone pair electron would situate at the most crowded space near one of the C_7-Me and C_2-MeO groups (Fig. 3). The X-ray data of (*S*s)-**27** supports this speculation. Although intermediate (b) seems to be more stable than intermediate (a) by

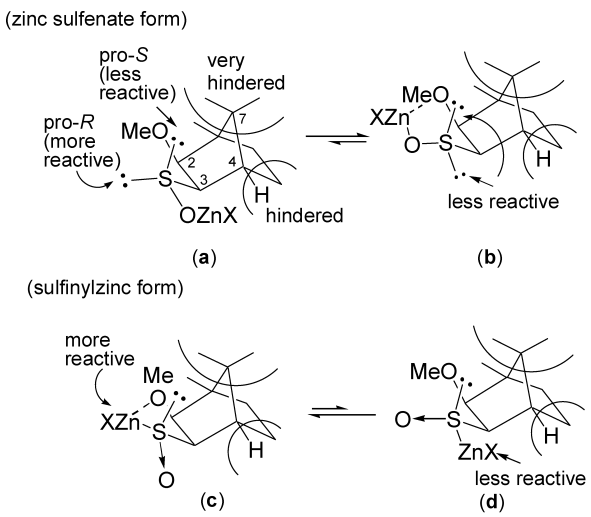


Figure 3. Plausible reaction mechanism for the asymmetric sulfinylzincation reaction (only relevant protons are shown).

the coordination of the methoxy group to the zinc cation, both lone pair electrons on the sulfur atom are shielded by the isoborneol moiety in the intermediate (b). Therefore, the reaction occurred at the pro-*R* lone pair electrons in the intermediate (a) having the least steric demand (Fig. 3(a) and (b)). In comparison with the sulfinylzinc intermediates (c) and (d), the intermediate (c) with an unshielded zinc anion would preferentially react with alkynoates rather than the intermediate (d) (Fig. 3(c) and (d)). Thus, the reactions would proceed via intermediate (a) or (c) to give sulfoxides with (*S*s)-configuration.

3. Conclusion

In conclusion, we have investigated a Pd-catalyzed asymmetric sulfinylzincation using 1-alkynyl sulfoxides bearing chiral auxiliaries. We found that the isoborneol derivative (*R*s)-**4** was the most efficient chiral auxiliary among those we tested. The addition to various alkynoates proceeded in a highly *syn*-selective fashion and the diastereoselectivities exceeded 90:10 dr in many cases. The absolute configuration of the resulting sulfoxide depended on that of the chiral auxiliary rather than that of the original sulfoxide.

4. Experimental

4.1. General

Melting points are uncorrected. Optical rotations were measured using a JASCO DIP-360 digital polarimeter. ^{1}H NMR spectra were recorded in $CDCl_3$ solution at 300 or 500 MHz with a JMN-AL-300 or a JEOL JNM-GX500 spectrometer, respectively. ^{13}C NMR spectra were recorded in $CDCl_3$ at 75 or 125 MHz with a JEOL JMN-AL-300 or a JEOL JNM-GX500 spectrometer, respectively. Chemical shifts of ^{1}H NMR are expressed in ppm downfield from tetramethylsilane as an internal standard (δ=0). Chemical shifts of ^{13}C NMR are expressed as ppm in $CDCl_3$ as an internal standard (δ=77). IR spectra were measured with a Horiba FT-210 IR spectrometer. EI-MS spectra were taken with a JMS-600H mass spectrometer. FAB-MS spectra were measured by a JEOL JMS-700. Kanto Chemical Silica Gel 60 was used as an adsorbent for column chromatography. All air- or moisture-sensitive reactions were carried out in flame-dried glassware under Ar or N_2 atmosphere. All organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated with a rotary evaporator under reduced pressure unless otherwise cited.

4.1.1. Bis[(*S*)-2-hydroxy-1-phenylethyl]disulfide (6). A mixture of **5** (1.73 g, 11.2 mmol), $NaIO_3$ (4.50 g, 22.7 mmol), and 17% wet alumina (11.23 g) in hexane–toluene (1:1) (150 mL) was vigorously stirred at room temperature under Ar. After 1 h, the mixture was filtered and the solid was rinsed with AcOEt. The combined organic layers were washed with 5% $NaHSO_3$ aqueous solution and brine prior to drying and solvent evaporation. The crude was chromatographed on silica gel with *n*-hexane–AcOEt (7:3) to give **6** (1.75 g, quant) as a colorless oil. $[\alpha]_D^{22}$=+134.0 (*c* 2.13, $CHCl_3$). ^{1}H NMR (500 MHz) δ: 2.04 (br s, 2H, OH), 3.74 (t, *J*=7.0 Hz, 2H, 1-H), 3.95 (dd, *J*=11.6, 7.0 Hz, 2H, 2-H), 3.99 (dd, *J*=11.6, 7.0 Hz, 2H, 2-H), 7.23–7.37 (m, 10H, Ar-H). ^{13}C NMR (75 MHz) δ: 57.36 (2C), 64.64 (2C), 128.18 (2C), 128.38 (4C), 128.77 (4C), 138.05 (2C). IR 3321 (OH), 3027 (=CH), 2872 (CH), 1378 (*t*-Bu). MS (FAB) *m/z*: 329 (MNa^+). HRMS (FAB) calcd for $C_{16}H_{18}NaO_2S_2$ (MNa^+): 329.0646. Found: 329.0652.

4.1.2. (*S*)-2-(3,3-Dimethyl-1-butynylthio)-2-phenylethanol (7). *n*-BuLi (1.59 M in hexane) (12.2 mL, 19.43 mmol) was added slowly to a solution of 3,3-dimethyl-1-butyne (2.40 mL, 19.4 mmol) in THF (20 mL) with stirring at −78°C. After 30 min, HMPA (3.40 mL, 19.4 mmol) and the disulfide **6** (1.70 g, 5.55 mmol) was successively added to the mixture. After 15 min, the reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (9:1) to give **7** (1.25 g, 96%) as a colorless powder. Mp 40.0–41.5°C. $[\alpha]_D^{23}$=−15.1 (*c* 1.20, $CHCl_3$). ^{1}H NMR (500 MHz) δ: 1.18 (s, 9H, *t*-Bu), 4.04–4.18 (m, 3H, H-1 and 2), 7.23–7.37 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) δ: 28.57, 30.62 (3C), 54.02, 64.18, 64.72, 104.58, 127.84 (2C), 127.88, 128.39 (2C), 137.56. IR 3379 (OH), 3024 (=CH), 2967 (CH), 1362 (*t*-Bu). MS (FAB) *m/z*: 235 (MH^+). HRMS (FAB) calcd for $C_{14}H_{19}OS$ (MH^+): 235.1157. Found: 235.1175.

4.1.3. (*S*)-1-Methoxy-2-(3,3-dimethyl-1-butynylthio)-2-phenylethane (8). 60% NaH (62 mg, 1.54 mmol) was added to a solution of **7** (300 mg, 1.28 mmol) in DMF (3 mL) with stirring at 0°C. After stirring at room temperature for 1 h, MeI (0.12 mL, 1.92 mmol) was added to the mixture. The whole was stirred at this temperature for 4 h. The reaction was quenched with water and extracted with AcOEt. The extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (95:5) to give **8** (276 mg, 87%) as a colorless oil. $[\alpha]_D^{21}$=+36.1 (*c* 1.24, $CHCl_3$). ^{1}H NMR (500 MHz) δ: 1.17 (s, 9H, *t*-Bu), 3.39 (s, 3H, OCH_3), 3.91 (d, *J*=7.3 Hz, 2H, H-1), 4.20 (t, *J*=7.3 Hz, 1H, H-2), 7.28–7.51 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) δ: 28.68, 30.76 (3C), 51.58, 58.93, 65.40, 74.15, 104.73, 127.83, 127.99 (2C), 128.38 (2C), 138.15. IR 3029 (=CH), 2968 (CH), 1362 (*t*-Bu). MS (FAB) *m/z*: 249 (MH^+). HRMS (FAB) calcd for $C_{15}H_{21}OS$ (MH^+): 249.1313. Found: 249.1318.

4.1.4. (2*S*)-1-Methoxy-2-(3,3-dimethyl-1-butynylsulfinyl)-2-phenylethane (1). *m*-CPBA (containing 30% of water) (158 mg, 0.64 mmol) was added to a solution of the sulfide **8** (150 mg, 0.64 mmol) in CH_2Cl_2 (2 mL) with stirring at 0°C. After 1.5 h, the reaction was quenched with 1N NaOH. The mixture was extracted with AcOEt and the extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (4:1) to give **1** (147 mg, 87%) as a colorless oil (57:43 diasteromeric mixture). ^{1}H NMR (500 MHz) δ: 1.13 (s, 0.43×9H, *t*-Bu), 1.14 (s, 0.57×9H, *t*-Bu), 3.42 (s, 0.57×3H, OCH_3), 3.46 (s, 0.43×3H, OCH_3), 3.96–4.31 (m, 3H, H-1 and 2), 7.35–7.51 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) (major) δ: 28.23, 29.76 (3C), 59.31,

69.59, 69.83, 74.79, 113.06, 128.36 (2C), 128.73, 129.39 (2C), 132.56. (minor) δ: 28.23, 29.73 (3C), 59.19, 69.27, 71.57, 74.39, 113.82, 128.19 (2C), 128.69, 129.57 (2C), 131.69. IR 3032 (=CH), 2971 (CH), 2195 (C≡C), 1363 (*t*-Bu), 1065 (S=O). MS (FAB) *m/z*: 265 (MH^+). HRMS (FAB) calcd for $C_{15}H_{21}O_2S$ (MH^+): 265.1262. Found: 265.1254. Anal. calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62; S, 12.13. Found: C, 67.74; H, 7.67; S, 12.27.

4.1.5. Bis[(*S*)-2-hydroxy-2-phenylethyl]disulfide (10). In a manner similar to that described for **6**, the thiol **5** (1.78 g, 11.5 mmol) was converted into **10** (1.78 g, quant) as a colorless powder. Mp 75.0–76.0°C. $[\alpha]_D^{24}=+169.0$ (*c* 1.20, $CHCl_3$). ^1H NMR (500 MHz) δ: 2.43 (br s, 2H, OH), 2.96 (dd, *J*=14.0, 9.2 Hz, 2H, H-1), 3.08 (dd, *J*=14.0, 3.1 Hz, 2H, H-1), 4.98 (dd, *J*=9.2, 3.1 Hz, 2H, H-2), 7.28–7.38 (m, 10H, Ar-H). ^{13}C NMR (75 MHz) δ: 47.73 (2C), 72.06 (2C), 125.87 (4C), 127.96 (2C), 128.55 (4C), 142.04 (2C). IR 3361 (OH), 3029 (=CH), 2910 (CH). MS (FAB) *m/z*: 329 (MNa^+). HRMS (FAB) calcd for $C_{16}H_{18}NaO_2S_2$ (MNa^+): 329.0646. Found: 329.0665.

4.1.6. (*S*)-2-(3,3-Dimethyl-1-butynylthio)-1-phenylethanol (11). In a manner similar to that described for **7**, the disulfide **10** (1.70 g, 5.55 mmol) was converted into **11** (541 mg, 42%) as a colorless oil. $[\alpha]_D^{22}=-23.4$ (*c* 0.41, $CHCl_3$). ^1H NMR (500 MHz) δ: 1.26 (s, 9H, *t*-Bu), 2.80 (dd, *J*=13.4, 9.2 Hz, 1H, H-2), 3.02 (dd, *J*=13.4, 3.1 Hz, 1H, H-2), 2.82 (br s, 1H, OH), 4.99 (dt, *J*=9.2, 3.1 Hz, 1H, H-1), 7.29–7.41 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) δ: 28.70, 30.86 (3C), 44.54, 65.78, 72.13, 102.96, 125.81 (2C), 127.93, 128.51 (2C), 141.79. IR 3379 (OH), 3029 (=CH), 2968 (CH), 1362 (*t*-Bu). MS (FAB) *m/z*: 257 (MNa^+). HRMS (FAB) calcd for $C_{14}H_{18}NaOS$ (MNa^+): 257.0976. Found: 257.0980.

4.1.7. (*S*)-1-Methoxy-2-(3,3-dimethyl-1-butynylthio)-1-phenylethane (12). In a manner similar to that described for **8**, the alcohol **11** (150 mg, 0.64 mmol) was converted into **12** (147 mg, 93%) as a colorless oil. $[\alpha]_D^{21}=-20.7$ (*c* 1.05, $CHCl_3$). ^1H NMR (500 MHz) δ: 1.24 (s, 9H, *t*-Bu), 2.87 (dd, *J*=13.1, 4.9 Hz, 1H, H-2), 3.00 (dd, *J*=13.1, 8.5 Hz, 1H, H-2), 3.30 (s, 3H, OCH_3), 4.41 (dd, *J*=8.5, 4.9 Hz, 1H, 1-H), 7.30–7.39 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) δ: 28.71, 31.00 (3C), 42.86, 57.16, 66.82, 81.71, 102.55, 126.69 (2C), 128.14, 128.57 (2C), 140.17. IR 3028 (=CH), 2968 (CH), 1362 (*t*-Bu). MS (FAB) *m/z*: 271 (MNa^+). HRMS (FAB) calcd for $C_{15}H_{20}NaOS$ (MNa^+): 271.1133. Found: 271.1131.

4.1.8. (2*S*)-1-Methoxy-2-(3,3-dimethyl-1-butynylsulfinyl)-1-phenylethane (2). In a manner similar to that described for **1**, the sulfide **12** (100 mg, 0.40 mmol) was converted into **2** (104 mg, 98%) as a colorless oil (52:48 diasteromeric mixture). ^1H NMR (500 MHz) δ: 1.25 (s, 0.48×9H, *t*-Bu), 1.33 (s, 0.52×9H, *t*-Bu), 3.19 (dd, *J*=13.7, 11.0 Hz, 0.48H, H-2), 3.21 (dd, *J*=12.8, 4.6 Hz, 0.52H, H-2), 3.24 (s, 0.52×3H, OCH_3), 3.30 (s, 0.48×3H, OCH_3), 3.44 (dd, *J*=13.7, 2.4 Hz, 0.48H, H-2), 3.63 (dd, *J*=12.8, 8.9 Hz, 0.52H, H-2), 4.64 (dd, *J*=8.9, 4.6 Hz, 0.52H, H-1), 4.65 (dd, *J*=11.0, 2.4 Hz, 0.48H, H-1), 7.33–7.42 (m, 5H, Ar-H). ^{13}C NMR (125 MHz) (major) δ: 28.48, 29.91 (3C), 56.80, 65.22, 76.36, 78.82, 113.00, 126.61 (2C), 128.56, 128.84 (2C), 138.75. (minor) δ: 28.34, 30.03 (3C), 56.87, 64.10, 76.42, 78.78, 112.06, 126.55 (2C), 128.43, 128.87 (2C), 138.91. IR 3030 (=CH), 2972 (CH), 2193 (C≡C), 1363 (*t*-Bu), 1063 (S=O). MS (FAB) *m/z*: 265 (MH^+). HRMS (FAB) calcd for $C_{15}H_{21}O_2S$ (MH^+): 265.1262. Found: 265.1267.

4.1.9. (1*S*,2*R*)-Bis(2-hydroxybornane-10-yl)disulfide (14). In a manner similar to that described for **6**, the thiol **13** (1.50 g, 8.05 mmol) was converted into **14** (1.48 g, 99%) as a colorless oil. The spectral data was identified with the reported data.[15]

4.1.10. (1*S*,2*R*)-2-Hydroxy-10-(3,3-dimethyl-1-butynylthio)bornane (15). In a manner similar to that described for **7**, the disulfide **14** (2.61 g, 7.03 mmol) was converted into **15** (1.84 g, quant) as a colorless powder. Mp 34.0–36.0°C. $[\alpha]_D^{22}=+48.1$ (*c* 0.95, $CHCl_3$). ^1H NMR (500 MHz) δ: 0.80 (s, 3H, CH_3), 0.99–1.08 (m, 1H), 1.04 (s, 3H, CH_3), 1.21 (s, 9H, *t*-Bu), 1.32–1.37 (m, 1H), 1.47 (td, *J*=11.6, 4.3 Hz, 1H), 1.64–1.81 (m, 4H), 2.48 (d, *J*=3.7 Hz, 1H), 2.55 (d, *J*=13.4 Hz, 1H, H-10), 3.15 (d, *J*=13.4 Hz, 1H, H-10), 4.29 (dt, *J*=7.9, 4.3 Hz, 1H, H-2). ^{13}C NMR (75 MHz) δ: 19.88, 20.53, 26.92, 28.71, 30.64, 30.80 (3C), 36.01, 38.96, 45.67, 47.76, 53.25, 68.93, 76.39, 101.62. IR 3550 (OH), 2966 (CH), 1362 (*t*-Bu). MS (FAB) *m/z*: 267 (MH^+). HRMS (FAB) calcd for $C_{16}H_{27}OS$ (MH^+): 267.1783. Found: 267.1794.

4.1.11. (1*S*,2*R*)-2-Methoxy-10-(3,3-dimethyl-1-butynylthio)bornane (16). In a manner similar to that described for **8**, the alcohol **15** (300 mg, 1.14 mmol) was converted into **16** (262 mg, 82%) as a colorless oil. $[\alpha]_D^{20}=-135.6$ (*c* 1.10, $CHCl_3$). ^1H NMR (300 MHz) δ: 0.85 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.03–1.08 (m, 1H), 1.22 (s, 9H, *t*-Bu), 1.26–1.43 (m, 1H), 1.57–1.81 (m, 5H), 2.63 (d, *J*=12.3 Hz, 1H, SCH_2), 3.07 (d, *J*=12.3 Hz, 1H, SCH_2), 3.23 (s, 3H, OCH_3), 3.38 (dd, *J*=7.9, 3.3 Hz, 1H, 2-H). ^{13}C NMR (75 MHz) δ: 20.22, 20.41, 27.14, 28.64, 30.95, 30.98 (3C), 36.51, 37.48, 45.54, 47.91, 53.41, 56.31, 69.43, 85.42, 100.33. IR 2931 (CH), 1362 (*t*-Bu). MS (FAB) *m/z*: 303 (MNa^+). HRMS (FAB) calcd for $C_{17}H_{28}NaOS$ (MNa^+): 303.1759. Found: 303.1756.

4.1.12. (1*S*,2*R*)-2-Methoxy-10-(3,3-dimethyl-1-butynylsulfinyl)bornane (3). In a manner similar to that described for **1**, the sulfide **16** (260 mg, 0.93 mmol) was converted into **3** (275 mg, quant) as a colorless oil (72:28 diastereomeric mixture). ^1H NMR (500 MHz) δ: 0.88 (s, 3H, CH_3), 1.04 (s, 0.28×3H, CH_3), 1.05 (s, 0.72×3H, CH_3), 1.00–1.86 (m, 7H), 1.295 (s, 0.72×9H, *t*-Bu), 1.300 (s, 0.28×9H, *t*-Bu), 3.04 (d, *J*=12.8 Hz, 0.72H, H-10), 3.09 (d, *J*=12.8 Hz, 0.28H, H-10), 3.23 (s, 0.28×3H, OCH_3), 3.25 (s, 0.72×3H, OCH_3), 3.28 (d, *J*=12.8 Hz, 0.28H, H-10), 3.35 (dd, *J*=7.3, 3.1 Hz, 0.72H, H-2), 3.54 (dd, *J*=7.3, 3.1 Hz, 0.28H, H-2), 4.12 (d, *J*=12.8 Hz, 0.72H, H-10). ^{13}C NMR (75 MHz) (major) δ: 20.12, 20.21, 27.31, 28.31, 29.87 (3C), 30.72, 37.74, 44.48, 48.76, 50.17, 56.03, 57.93, 77.20, 85.17, 111.61. (minor) δ: 20.07, 20.21, 27.43, 28.28, 29.97 (3C), 31.29, 37.52, 44.41, 48.77, 50.87, 55.85, 58.65, 77.63, 85.23, 111.45. IR 2931 (CH), 2193 (C≡C), 1363 (*t*-Bu), 1063 (S=O). MS (FAB) *m/z*: 297 (MH^+). HRMS (FAB) calcd for $C_{17}H_{29}O_2S$ (MH^+): 297.1888. Found: 297.1885.

Anal. calcd for $C_{17}H_{28}O_2S$: C, 68.87; H, 9.52; S, 10.82. Found: C, 68.60; H, 9.36; S, 10.67.

4.1.13. (1*R*,2*S*,3*R*)-Bis(2-hydroxybornane-3-yl)disulfide (18). In a manner similar to that described for **6**, the thiol **17** (250 mg, 1.34 mmol) was converted into **18** (248 mg, quant) as a colorless powder. The spectral data was identified with the reported data.[16]

4.1.14. (1*R*,2*S*,3*R*)-2-Hydroxy-3-(3,3-dimethyl-1-butynylthio)bornane (19). In a manner similar to that described for **7**, the disulfide **18** (250 mg, 0.67 mmol) was converted into **19** (142 mg, 80%) as a colorless oil. $[\alpha]_D^{28}$=+22.7 (*c* 1.03, $CHCl_3$). ^{1}H NMR (500 MHz) δ: 0.80 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.22 (s, 9H, *t*-Bu), 1.06–1.26 (m, 2H, H-5 and 6), 1.48–1.54 (m, 1H, H-6), 1.78–1.84 (m, 1H, H-5), 1.95 (d, *J*=4.3 Hz, 1H, H-4), 2.32 (d, *J*=3.4 Hz, 1H, OH), 3.38 (d, *J*=7.3 Hz, 1H, H-3), 3.83 (dd, *J*=7.3, 3.4 Hz, 1H, H-2). ^{13}C NMR (125 MHz) δ: 11.53, 21.14, 21.43, 28.67, 28.78, 29.75, 30.93 (3C), 33.25, 45.86, 48.14, 51.57, 61.16, 79.93, 101.27. IR 3542 (OH), 2983 (CH), 2164 (C≡C), 1361 (*t*-Bu). MS (FAB) *m*/*z*: 289 (MNa^+). HRMS (FAB) calcd for $C_{16}H_{26}NaOS$ (MNa^+): 289.1602. Found: 289.1603.

4.1.15. (*R*s,1*R*,2*S*,3*R*)-2-Methoxy-3-(3,3-dimethyl-1-butynylsulfinyl)bornane [(*R*s)-4]. *m*-CPBA (containing 30% of water) (679 mg, 2.75 mmol) was added to a solution of **19** (734 mg, 2.75 mmol) in CH_2Cl_2 (5 mL) with stirring at 0°C. After 1.5 h, the reaction was quenched with 1N NaOH. The mixture was extracted with AcOEt and the extract was washed with brine prior to drying and solvent evaporation. 60% NaH (165 mg, 4.13 mmol) was added to a solution of the crude sulfoxide in DMF (3 mL) with stirring at 0°C. After stirring at room temperature for 1 h, MeI (0.34 mL, 5.50 mmol) was added to the mixture. The whole was stirred at this temperature for 12 h. The reaction was quenched with water and extracted with AcOEt. The extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (4:1) to give (*R*s)-**4** (639 mg, 78% in two steps) as a colorless powder. Mp 92.0–95.0°C. $[\alpha]_D^{25}$=−57.1 (*c* 1.02, $CHCl_3$). ^{1}H NMR (500 MHz) δ: 0.79 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.08–1.12 (m, 1H, H-5 or 6), 1.13–1.22 (m, 1H, H-5 or 6), 1.30 (s, 9H, *t*-Bu), 1.55 (td, *J*=12.2, 3.7 Hz, 1H, H-6), 1.80–1.88 (m, 1H, H-5), 2.08 (d, *J*=4.3 Hz, 1H, H-4), 3.45 (s, 2H, H-2 and 3), 3.49 (s, 3H, OCH_3). ^{13}C NMR (125 MHz) δ: 11.14, 20.48, 21.08, 28.00, 28.32, 30.00 (3C), 32.87, 46.39, 50.78, 51.06, 61.92, 76.87, 79.43, 89.74, 112.17. IR 2964 (CH), 2156 (C≡C), 1371 (*t*-Bu), 1057 (S=O). MS (FAB) *m*/*z*: 297 (MH^+). HRMS (FAB) calcd for $C_{17}H_{29}O_2S$ (MH^+): 297.1888. Found: 297.1904. Anal. calcd for $C_{17}H_{28}O_2S$: C, 68.87; H, 9.52; S, 10.82. Found: C, 68.73; H, 9.40; S, 10.64.

4.1.16. Bis[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]disulfide (21). The disulfide **18** (135 mg, 0.36 mmol) and MeI (0.13 mL, 20.8 mmol) were added to a solution of KOH (264 mg, 4.00 mmol) in DMSO (2 mL) with stirring at room temperature. After 2 h, water was added to the mixture and the mixture was extracted with AcOEt. The organic layer was washed with brine prior to dying and solvent evaporation. The residue was chromatographed on silica gel with hexane–ether (98:2) to give **21** (88 mg, 62%) as a colorless powder. Mp 77.5–80.0°C. $[\alpha]_D^{25}$=−54.1 (*c* 1.03, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.78 (s, 6H, CH_3), 0.88 (s, 6H, CH_3), 1.08 (s, 6H, CH_3), 1.03–1.14 (m, 4H, H-5 and 6), 1.45–1.58 (m, 2H, H-5), 1.72–1.85 (m, 2H, H-6), 2.02 (d, *J*=4.2 Hz, 2H, H-4), 3.247 (s, 4H, H-2 and 3), 3.42 (s, 6H, OCH_3). ^{13}C NMR (125 MHz) δ: 11.64 (2C), 21.04 (2C), 21.66 (2C), 28.59 (2C), 33.74 (2C), 46.96 (2C), 50.36 (2C), 52.75 (2C), 61.16 (2C), 65.59 (2C), 91.38 (2C). IR 2950 (CH), 557 (S-S). MS (FAB) *m*/*z*: 421 (MNa^+). HRMS (FAB) calcd for $C_{22}H_{38}NaO_2S_2$ (MNa^+): 421.2211. Found: 421.2219.

4.1.17. (1*R*,2*S*,3*R*)-2-Methoxy-3-(methoxysulfinyl)-bornane (22). SO_2Cl_2 (200 mg, 1.50 mmol) was added dropwise to a solution of the disulfide **21** (200 mg, 0.50 mmol) and acetic acid (60 mg, 1.00 mmol) in CH_2Cl_2 (2 mL) with stirring at −10°C. The mixture was stirred at room temperature for 2 h and then at 35°C for 1 h. The solvent was evaporated and the residue was dissolved in MeOH (2 mL) and pyridine (158 mg, 2.00 mmol) was added to the mixture. The whole was stirred at room temperature fro 2 h. The reaction was quenched with 1N HCl and the mixture was extracted with AcOEt. The organic layer was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (85:15) to give **22** (134 mg, 54%) as a colorless oil (4:1 diastreomeric mixture). ^{1}H NMR (300 MHz) δ: 0.81 (s, 0.8×3H, CH_3), 0.82 (s, 0.2×3H, CH_3), 0.96 (s, 3H, CH_3), 0.99–1.09 (m, 2H, H-5 and 6), 1.12 (s, 0.8×3H, CH_3), 1.16 (s, 0.2×3H, CH_3), 1.47–1.58 (m, 1H, H-6), 1.72–1.88 (m, 1H, H-5), 2.05 (d, *J*=3.1 Hz, 0.8H, H-4), 2.22 (d, *J*=4.4 Hz, 0.2H, H-4), 3.02 (d, *J*=7.9 Hz, 0.8H, H-3), 3.08 (d, *J*=7.9 Hz, 0.2H, H-3), 3.34 (d, *J*=8.1 Hz, 0.2H, H-2), 3.38 (s, 0.2×3H, OCH_3), 3.41 (d, *J*=8.1 Hz, 0.8H, H-2), 3.44 (s, 0.8×3H, OCH_3), 3.71 (s, 0.8×3H, $S(O)_2CH_3$), 3.83 (s, 0.2×3H, $S(O)_2CH_3$). ^{13}C NMR (125 MHz) (major) δ: 10.92, 20.45, 21.09, 27.81, 32.75, 46.64, 48.52, 50.37, 52.62, 61.46, 78.66, 90.12. (minor) δ: 11.01, 20.70, 27.96, 32.96, 46.63, 46.80, 47.14, 50.39, 50.61, 55.04, 61.00, 90.31. IR 2948 (CH), 1132 (S=O). MS (FAB) *m*/*z*: 247 (MNa^+). HRMS (FAB) calcd for $C_{12}H_{23}O_3S$ (MH^+): 247.1368. Found: 247.1370.

4.1.18. (*S*s,1*R*,2*S*,3*R*)-2-Methoxy-3-(3,3-dimethyl-1-butynylsulfinyl)bornane [(*S*s)-4]. EtMgBr (3 M in ether) (0.33 mL, 1.20 mmol) was added slowly to a solution of 3,3-dimethyl-1-butyne (0.12 mL, 1.00 mmol) in ether (2 mL) with stirring at room temperature under N_2. A solution of **22** (100 mg, 0.41 mmol) in toluene (5 mL) was added to the mixture. The whole was stirred at 60°C for 5 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (85:15) to give (*R*s)-**4** (55 mg, 45%) as a colorless powder along with (*R*s)-**4** (11 mg, 9%). Mp 63.0–65.0°C. $[\alpha]_D^{28}$=+55.2 (*c* 1.15, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.84 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.02–1.16 (m, 1H, H-5 or 6), 1.20–1.45 (m, 1H, H-5 or 6), 1.23 (s, 3H, CH_3), 1.32 (s, 9H, *t*-Bu), 1.50–1.61 (m, 1H, H-6), 1.80–1.93 (m, 1H, H-5), 2.34 (d, *J*=4.4 Hz, 1H, H-4), 3.37

(s, 3H, OCH_3), 3.39 (d, J=7.9 Hz, 1H, H-3), 3.71 (d, J=7.9 Hz, 1H, H-2). ^{13}C NMR (125 MHz) δ: 11.24, 20.32, 21.24, 28.28, 30.10, 30.29 (3C), 32.67, 45.39, 47.37, 51.07, 61.62, 78.25, 79.52, 80.67, 109.81. IR 2964 (CH), 2158 (C≡C), 1371 (*t*-Bu), 1055 (S=O). MS (FAB) *m/z*: 297 (MH^+). HRMS (FAB) calcd for $C_{17}H_{29}O_2S$ (MH^+): 297.1888. Found: 297.1879.

4.2. General procedure of sulfinylzincation with 1–3 (Table 1)

Et_2Zn (0.99 M in hexane) (0.30 mL, 0.30 mmol) was slowly added to a solution of the 1-alkynyl sulfoxide **1** (42 mg, 0.15 mmol), methyl 4-benzyloxy-2-butynoate (92 mg, 0.45 mmol), and $Pd_2(dba)_3{\cdot}CHCl_3$ (3 mg, 0.003 mmol) in THF (0.2 mL) with stirring at −78°C. The stirring was continued at this temperature for 10 min and at room temperature for 2 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (4:1) to give **23** (36 mg, 63%) as a pale yellow oil (83:17 diastereomeric mixture).

4.2.1. Methyl (*E*)-4-benzyloxy-3-[(1*S*)-(2-methoxy-1-phenylethyl)sulfinyl]-2-butenoate (23). Pale yellow oil (83:17 diastereomeric mixture). ^{1}H NMR (500 MHz) δ: 3.20 (s, 0.83×3H, OCH_3), 3.44 (s, 0.17×3H, OCH_3), 3.57 (s, 0.83×3H, CO_2CH_3), 3.77 (s, 0.17×3H, CO_2CH_3), 3.71–3.82 (m, 1.17H, CH_2OMe), 4.05 (dd, J=11.0, 8.0 Hz, 0.83H, CH_2OMe), 4.53–4.70 (m, 1.51H, CHS, CH_2Ph, and 4-H), 4.55 (d, J=11.3 Hz, 0.83H, CH_2Ph), 4.60 (d, J=11.3 Hz, 0.83H, CH_2Ph), 4.82 (dd, J=16.5, 2.1 Hz, 0.17H, 4-H), 4.88 (dd, J=15.6, 2.1 Hz, 0.83H, 4-H), 5.11 (dd, J=15.6, 2.1 Hz, 0.83H, 4-H), 5.76 (t, J=2.1 Hz, 0.17H, 2-H), 6.50 (t, J=2.1 Hz, 0.83H, 2-H), 7.06–7.42 (m, 10H, Ar-H). ^{13}C NMR (75 MHz) (major) δ: 29.22, 51.80, 58.21, 65.83, 67.01, 68.25, 73.81, 118.09, 128.02 (2C), 128.07, 128.48 (2C), 128.72 (2C), 128.82 (2C), 134.93, 136.92, 161.03, 164.81. (minor) δ: 31.67, 51.55, 59.02, 66.17, 67.81, 70.42, 73.92, 119.49, 128.01 (2C), 128.11, 128.51 (2C), 128.56 (2C), 128.70 (2C), 134.93, 136.78, 161.64, 164.26. IR 3030 (=CH), 2929 (CH), 1716 (C=O), 1116 (S=O). MS (FAB) *m/z*: 389 (MH^+). HRMS (FAB) calcd for $C_{21}H_{25}O_5S$ (MH^+): 389.1423. Found: 389.1421.

4.2.2. Methyl (*E*)-4-benzyloxy-3-[(1*S*)-(2-methoxy-2-phenylethyl)sulfinyl]-2-butenoate (24). Pale yellow oil (59:41 diastereomeric mixture). ^{1}H NMR (500 MHz) δ: 3.07 (s, 0.41×3H, OCH_3), 3.25–3.36 (m, 1H, CH_2S), 3.33 (s, 0.59×3H, OCH_3), 3.59 (t, J=11.6 Hz, 0.59H, CH_2S), 3.65–3.80 (m, 0.41H, CH_2S), 3.73 (s, 0.59×3H, CO_2CH_3), 3.77 (s, 0.41×3H, CO_2CH_3), 4.49–5.04 (m, 5H, CH_2Ph, CHOCH$_3$, and H-4), 6.57 (t, J=1.8 Hz, 0.59H, H-2), 6.61 (t, J=1.8 Hz, 0.41H, H-2), 7.25–7.42 (m, 10H, Ar-H). ^{13}C NMR (75 MHz) (major) δ: 29.22, 51.86, 56.03, 62.64, 66.64, 73.60, 76.78, 118.33, 126.66 (2C), 127.83 (2C), 128.34, 128.45 (2C), 136.85, 128.73 (2C), 139.69, 164.37, 164.67. (minor) δ: 31.69, 51.81, 56.93, 59.88, 67.91, 73.65, 75.29, 117.47, 126.61 (2C), 127.98 (2C), 128.21, 128.49 (2C), 128.71 (2C), 136.80, 139.24, 163.97, 164.77. IR 3029 (=CH), 2948 (CH), 1716 (C=O), 1105 (S=O). MS (FAB) *m/z*: 389 (MH^+). HRMS (FAB) calcd for $C_{21}H_{25}O_5S$ (MH^+): 389.1423. Found: 389.1406.

4.2.3. Methyl (*E*)-4-benzyloxy-3-[[(1*S*,2*R*)-2-methoxybornane-10-yl]sulfinyl]-2-butenoate (25). Pale yellow oil (72:28 diastereomeric mixture). ^{1}H NMR (500 MHz) δ: 0.74 (s, 0.28×3H, CH_3), 0.81 (s, 0.72×3H, CH_3), 0.93 (s, 0.28×3H, CH_3), 1.02 (s, 0.72×3H, CH_3), 0.80–1.84 (m, 7H), 2.32 (d, J=12.8 Hz, 0.72H, SCH_2), 3.02–3.10 (m, 0.28×2H, SCH_2), 3.14 (s, 0.72×3H, OCH_3), 3.23 (s, 0.28×3H, OCH_3), 3.40–3.62 (m, 1H, CHO), 3.60 (d, J=12.8 Hz, 0.72H, SCH_2), 3.755 (s, 0.28×3H, CO_2CH_3), 3.760 (s, 0.72×3H, CO_2CH_3), 4.50–5.00 (m, 4H, CH_2-OCH_2Ph), 6.64 (s, 0.28H, H-2), 6.66 (s, 0.72H, H-2), 7.28–7.37 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) (major) δ: 20.10, 20.33, 27.49, 31.58, 37.55, 44.68, 48.83, 51.36, 51.82, 55.60, 55.67, 64.88, 73.49, 85.41, 119.79, 127.91 (2C), 127.98, 128.35 (2C), 128.39, 137.12, 163.64. (minor) δ: 20.08, 20.31, 27.19, 29.20, 30.30, 38.12, 44.92, 51.76, 53.73, 56.16, 67.14, 73.64, 77.20, 85.96, 118.15, 126.85, 127.83 (2C), 128.01 (2C), 128.40 136.78, 164.77. IR 2952 (CH), 1716 (C=O), 1041 (S=O). MS (FAB) *m/z*: 421 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_5S$ (MH^+): 421.2049. Found: 421.2037. Anal. calcd for $C_{23}H_{32}O_5S$: C, 65.68; H, 7.67; S, 7.62. Found: C, 65.66; H, 7.63; S, 7.40.

4.3. General procedure of sulfinylzincation with 4 (Table 3)

Et_2Zn (0.99 M in hexane) (0.20 mL, 0.20 mmol) was slowly added to a solution of the 1-alkynyl sulfoxide (*R*s)-**4** (30 mg, 0.10 mmol), methyl 4-benzyloxy-2-butynoate (61 mg, 0.30 mmol), and $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mg, 0.002 mmol) in 1,4-dioxane (0.5 mL) with stirring at 0°C. The stirring was continued at this temperature for 10 min and at room temperature for 12 h. The reaction was quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (85:15) to give (*E*,*R*s)-**26a** (43 mg, 99%) as a pale yellow oil (91:9 diastereomeric mixture). Analytical sample was purified by column chromatography with hexane–AcOEt (9:1).

4.3.1. Methyl (*E*)-4-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate [(*E*)-26a]. *Compound* (*E*,*S*s)-**26a**. Pale yellow powder. Mp 50.0–51.0°C. $[\alpha]_D^{26}$=−23.5 (*c* 1.06, $CHCl_3$). ^{1}H NMR (500 MHz) δ: 0.81 (s, 3H, CH_3), 0.84–0.98 (m, 2H, H-5′ and 6′), 0.94 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.42–1.51 (m, 1H, H-6′), 1.77–1.85 (m, 1H, H-5′), 2.27 (d, J=4.3 Hz, 1H, H-4′), 3.18 (d, J=7.9 Hz, 1H, H-2′ or 3′), 3.23 (s, 3H, OCH_3), 3.49 (d, J=7.9 Hz, 1H, H-2′ or 3′), 3.77 (s, 3H, CO_2CH_3), 4.57 (d, J=11.3 Hz, 1H, CH_2Ph), 4.66 (d, J=11.3 Hz, 1H, CH_2Ph), 4.71 (d, J=12.8, 1H, H-4), 4.92 (d, J=12.8, 1H, H-4), 6.58 (s, 1H, H-2), 7.27–7.37 (m, 5H, Ar-H). ^{13}C NMR (125 MHz) δ: 11.52, 20.95, 21.08, 29.66, 32.86, 45.08, 47.23, 50.93, 51.90, 61.07, 61.74, 71.21, 73.39, 90.92, 124.07, 127.85 (2C), 127.88, 128.37 (2C), 137.51, 160.23, 164.71. IR 2953 (CH), 1718 (C=O), 1024 (S=O). MS

(FAB) *m/z*: 421 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_5S$ (MH^+): 421.2049. Found: 421.2033. Anal. calcd for $C_{23}H_{32}O_5S$: C, 65.68; H, 7.67; S, 7.62. Found: C, 65.76; H, 7.60; S, 7.34.

Compound (*E*,*R*s)-**26a**. Pale yellow oil. $[\alpha]_D^{27}=+37.0$ (*c* 1.07, $CHCl_3$). ^1H NMR (500 MHz) 0.73 (s, 3H, CH_3), 0.83–1.22 (m, 2H, H-5′ and 6′), 0.96 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.46 (ddd, *J*=12.5, 12.0, 3.5 Hz, 1H, H-6′), 1.57–1.60 (m, 1H, H-5′), 1.79 (d, *J*=3.6 Hz, 1H, H-4′), 3.17 (d, *J*=7.3 Hz, 1H, H-2′ or 3′), 3.43 (d, *J*=7.9 Hz, 1H, H-2′ or 3′), 3.53 (s, 3H, OCH_3), 3.76 (s, 3H, CO_2CH_3), 4.60 (s, 2H, CH_2Ph), 4.64 (d, *J*=12.8 Hz, 1H, H-4), 4.90 (d, *J*=12.8 Hz, 1H, H-4), 6.53 (s, 1H, H-2), 7.28–7.35 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) *δ*: 11.17, 20.50, 21.70, 28.11, 32.50, 46.75, 48.80, 50.64, 51.93, 61.85, 62.05, 73.41, 77.33, 90.53, 124.32, 127.75, 127.96 (2C), 128.24 (2C), 137.30, 161.19, 164.34. IR 2950 (CH), 1724 (C═O), 1024 (S═O). MS (FAB) *m/z*: 421 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_5S$ (MH^+): 421.2049. Found: 421.2043.

4.3.2. Methyl (*E*)-4-acetoxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate (26b). Pale yellow oil. ^1H NMR (500 MHz) *δ*: 0.78 (s, 0.08×3H, CH_3), 0.85 (s, 0.92×3H, CH_3), 0.94–1.16 (m, 2H, H-5′ and 6′), 1.01 (s, 0.92×3H, CH_3), 1.12 (s, 0.08×3H, CH_3), 1.26 (s, 0.08×3H, CH_3), 1.28 (s, 0.92×3H, CH_3), 1.51–1.75 (m, 1H, H-6′), 1.68 (d, *J*=4.3 Hz, 0.08H, H-4′), 1.87–1.92 (m, 1H, H-5′), 2.10 (s, 3H, Ac), 2.38 (d, *J*=4.3 Hz, 0.92H, H-4′), 3.29 (s, 2H, H-2′ and 3′), 3.30 (s, 3H, OCH_3), 3.80 (s, 3H, CO_2CH_3), 5.03 (d, *J*=12.8 Hz, 0.08H, H-4), 5.13 (d, *J*=12.8, 0.92H, H-4), 5.40 (d, *J*=12.8 Hz, 0.92H, H-4), 5.56 (d, *J*=12.8 Hz, 0.08H, H-4), 6.55 (s, 0.08H, H-2), 6.67 (s, 0.92H, H-2). ^{13}C NMR (125 MHz) (major) *δ*: 11.83, 20.66, 20.70, 21.15, 28.64, 33.02, 45.67, 47.27, 51.41, 52.22, 55.80, 61.11, 73.18, 90.83, 125.97, 157.99, 164.33, 169.94. IR 2956 (CH), 1749 (C═O), 1740 (C═O), 1030 (S═O). MS (FAB) *m/z*: 373 (MH^+). HRMS (FAB) calcd for $C_{18}H_{29}O_6S$ (MH^+): 373.1685. Found: 373.1684.

4.3.3. Methyl (*E*)-4-(*tert*-butyldimethylsilyloxy)-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate (26c). *Compound* (*S*s)-**26c**. Pale yellow powder. Mp 63.0–65.5°C. $[\alpha]_D^{28}=-34.4$ (*c* 1.03, $CHCl_3$). ^1H NMR (500 MHz) *δ*: 0.14 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.83 (s, 3H, CH_3), 0.87–1.05 (m, 2H, H-5′and 6′), 0.92 (s, 9H, Si*t*-Bu), 0.93 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.49–1.56 (m, 1H, H-6′), 1.72–1.93 (m, 1H, H-5′), 2.27 (d, *J*=4.2 Hz, 1H, H-4′), 3.31 (d, *J*=8.0 Hz, 1H, H-2′ or 3′), 3.30 (s, 3H, OCH_3), 3.62 (d, *J*=8.0 Hz, 1H, H-2′ or 3′), 3.78 (s, 3H, CO_2CH_3), 4.76 (d, *J*=13.0 Hz, 1H, H-4), 5.11 (d, *J*=13.0 Hz, 1H, H-4), 6.47 (s, 1H, H-2). ^{13}C NMR (125 MHz) *δ*: −5.63, −5.46, 11.40, 18.17, 20.88, 21.14, 25.73 (3C), 28.92, 32.88, 45.11, 47.20, 50.93, 51.74, 54.88, 61.22, 70.31, 91.02, 123.32, 161.53, 164.56. IR 2954 (CH), 1718 (C═O), 1024 (S═O). MS (FAB) *m/z*: 445 (MH^+). HRMS (FAB) calcd for $C_{22}H_{41}O_5SSi$ (MH^+): 445.2444. Found: 445.2475. Anal. calcd for $C_{22}H_{40}O_5SSi$: C, 59.42; H, 9.07; S, 7.21. Found: C, 59.73; H, 8.96; S, 6.87.

Compound (*R*s)-**26c**. Pale yellow oil. $[\alpha]_D^{28}=+6.6$ (*c* 1.05, $CHCl_3$). ^1H NMR (500 MHz) *δ*: 0.12 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.77 (s, 3H, CH_3), 0.90 (s, 9H, Si*t*-Bu), 0.97 (s, 3H, CH_3), 1.00–1.10 (m, 2H, H-5′ and 6′), 1.12 (s, 3H, CH_3), 1.47–1.54 (m, 1H, H-6′), 1.64–1.76 (m, 1H, H-5′), 1.86 (d, *J*=4.4 Hz, 1H, H-4′), 3.12 (d, *J*=7.5 Hz, 1H, H-2′ or 3′), 3.44 (d, *J*=7.5 Hz, 1H, H-2′ or 3′), 3.53 (s, 3H, OCH_3), 3.78 (s, 3H, CO_2CH_3), 4.68 (d, *J*=13.6 Hz, 1H, H-4), 5.12 (d, *J*=13.6 Hz, 1H, H-4), 6.47 (s, 1H, H-2). ^{13}C NMR (125 MHz) *δ*: −5.32, −5.28, 11.28, 18.54, 20.65, 22.00, 25.95 (3C), 28.56, 32.63, 46.86, 48.67, 50.67, 51.94, 56.27, 62.17, 77.77, 90.72, 122.86, 163.65, 164.63. IR 2953 (CH), 1724 (C═O), 1045 (S═O). MS (FAB) *m/z*: 445 (MH^+). HRMS (FAB) calcd for $C_{22}H_{41}O_5SSi$ (MH^+): 445.2444. Found: 445.2449.

4.3.4. Methyl (*E*)-4-benzylthio-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate (26d). Pale yellow oil. ^1H NMR (500 MHz) *δ*: 0.77 (s, 0.09×3H, CH_3), 0.84 (s, 0.91×3H, CH_3), 0.96–1.17 (m, 2H, H-5′ and 6′), 0.98 (s, 0.91×3H, CH_3), 1.08 (s, 0.09×3H, CH_3), 1.25 (s, 0.09×3H, CH_3), 1.29 (s, 0.91×3H, CH_3), 1.48–1.54 (m, 1H, H-6′), 1.63 (d, *J*=4.3 Hz, 0.09H, H-4′), 1.69–1.91 (m, 1H, H-5′), 2.37 (d, *J*=4.3 Hz, 0.91H, H-4′), 3.25 (d, *J*=13.4 Hz, 0.09H, CH_2Ph), 3.25 (s, 3H, OCH_3), 3.26 (d, *J*=7.3 Hz, 0.09H, H-2′ or 3′), 3.43 (d, *J*=7.3 Hz, 0.09H, H-2′ or 3′), 3.29 (d, *J*=8.5 Hz, 0.91H, H-2′ or 3′), 3.32 (d, *J*=13.4 Hz, 0.09H, CH_2Ph), 3.41 (d, *J*=8.0 Hz, 0.91H, H-2′ or 3′), 3.45 (s, 3H, CO_2Me), 3.64 (d, *J*=12.8 Hz, 0.91H, H-4), 3.80 (d, *J*=12.8 Hz, 0.09H, H-4), 3.84 (d, *J*=12.8 Hz, 0.91H, CH_2Ph), 3.88 (d, *J*=12.8 Hz, 0.91H, CH_2Ph), 3.99 (d, *J*=12.8 Hz, 0.09H, H-4), 4.26 (d, *J*=12.8 Hz, 0.91H, H-4), 6.32 (s, 0.09H, H-2), 6.51 (s, 0.91H, H-2), 7.23–7.35 (m, 5H, Ar-H). ^{13}C NMR (125 MHz) (major): *δ*: 11.78, 20.61, 21.09, 24.84, 28.47, 32.90, 37.65, 45.80, 47.42, 51.38, 51.90, 61.01, 73.04, 90.73, 122.27, 127.18, 128.52 (2C), 128.99 (2C), 137.58, 162.42, 164.90. IR 2951 (CH), 1716 (C═O), 1038 (S═O). MS (FAB) *m/z*: 437 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_4S_2$ (MH^+): 437.1820. Found: 437.1827.

4.3.5. Methyl (*E*)-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]propenoate (26e). Pale yellow oil. ^1H NMR (300 MHz) *δ*: 0.81 (s, 0.15×3H, CH_3), 0.87 (s, 0.85×3H, CH_3), 1.01 (s, 0.15×3H, CH_3), 1.03 (s, 0.85×3H, CH_3), 1.04–1.12 (m, 2H, H-5′ and 6′), 1.26 (s, 0.15×3H, CH_3), 1.30 (s, 0.85×3H, CH_3), 1.45–1.57 (m, 1H, H-6′), 1.84–1.92 (m, 1.15H, H-4′ and 5′), 2.42 (d, *J*=4.4 Hz, 0.85H, H-4′), 3.07 (d, *J*=8.1 Hz, 0.15H, H-2′ or 3′), 3.09 (d, *J*=8.1 Hz, 0.85H, H-2′ or 3′), 3.40 (d, *J*=8.1 Hz, 0.85H, H-2′ or 3′), 3.45 (s, 0.85×3H, OCH_3), 3.51 (d, *J*=8.1 Hz, 0.15H, H-2′ or 3′), 3.55 (s, 0.15×3H, OCH_3), 3.81 (s, 3H, CO_2CH_3), 6.66 (d, *J*=5.1 Hz, 0.15H, H-2), 6.71 (d, *J*=5.5 Hz, 0.85H, H-2), 7.78 (d, *J*=4.9, 0.15H, H-3), 7.85 (d, *J*=5.1, 0.85H, H-3). ^{13}C NMR (125 MHz) (major): *δ*: 11.77, 20.28, 21.30, 28.32, 32.78, 45.94, 47.42, 51.39, 52.20, 60.98, 75.85, 90.39, 124.67, 152.16, 164.87. IR 2954 (CH), 1724 (C═O), 1057 (S═O). MS (FAB) *m/z*: 301 (MH^+). HRMS (FAB) calcd for $C_{15}H_{25}O_4S$ (MH^+): 301.1474. Found: 301.1487.

4.3.6. Ethyl (*E*)-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate (26f). Pale yellow oil. ^1H NMR (500 MHz) *δ*: 0.77 (s, 0.1×3H, CH_3), 0.85 (s, 0.9×3H, CH_3), 0.98 (s, 0.1×3H, CH_3), 1.00 (s, 0.9×3H, CH_3), 0.97–1.10 (m, 2H, H-5′ and 6′), 1.26 (s, 0.1×3H, CH_3), 1.30 (s,

0.9×3H, CH_3), 1.30 (t, J=7.0 Hz, 3H, CH_2CH_3), 1.50–1.58 (m, 1H, H-6′), 1.73–1.95 (m, 1.1H, H-4′ and 5′), 2.37 (d, J=1.8 Hz, 0.1×3H, H-4), 2.39 (d, J=4.3 Hz, 0.9H, H-4), 2.39 (d, J=1.2 Hz, 0.9×3H, H-4), 3.00 (d, J=7.3 Hz, 0.1H, H-2′ or 3′), 3.15 (d, J=7.9 Hz, 0.9H, H-2′ or 3′), 3.24 (d, J=7.9 Hz, 0.9H, H-2′ or 3′), 3.27 (s, 0.9×3H, OCH_3), 3.49 (d, J=7.3 Hz, 0.1H, H-2′ or 3′), 3.54 (s, 0.1×3H, OCH_3), 4.23 (q, J=7.0 Hz, 2H, CH_2CH_3), 6.33 (d, J=1.8 Hz, 0.1H, H-2), 6.45 (d, J=1.2 Hz, 0.9H, H-2). ^{13}C NMR (125 MHz) (major): δ: 10.48, 11.77, 14.16, 20.56, 21.09, 28.53, 32.96, 45.61, 47.27, 51.51, 60.62, 61.16, 71.61, 90.70, 121.54, 161.69, 164.97. IR 2956 (CH), 1718 (C═O), 1035 (S═O). MS (FAB) m/z: 329 (MH^+). HRMS (FAB) calcd for $C_{17}H_{29}O_4S$ (MH^+): 329.1787. Found: 329.1793.

4.3.7. 4-Nitrobenzyl (*E*)-4-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate (26g). *Compound* (*S*s)-**26g**. Pale yellow oil. $[\alpha]_D^{25}$=−7.3 (c 0.93, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.81 (s, 3H, CH_3), 0.86–0.99 (m, 2H, H-5′ and 6′), 0.94 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.41–1.51 (m, 1H, H-6′), 1.77–1.86 (m, 1H, H-5′), 2.27 (d, J=4.4 Hz, 1H, H-4′), 3.19 (d, J=8.1 Hz, 1H, H-2′ or 3′), 3.24 (s, 3H, OCH_3), 3.44 (d, J=8.0 Hz, 1H, H-2′ or 3′), 4.54 (d, J=11.6 Hz, 1H, CH_2Ph), 4.62 (d, J=11.6 Hz, 1H, CH_2Ph), 4.72 (dd, J=12.8, 0.9 Hz, 1H, H-4), 4.89 (dd, J=12.8, 0.9 Hz, 1H, H-4), 5.29 (s, 2H, CO_2CH_2Ar), 6.66 (s, 1H, H-2), 7.27–7.38 (m, 5H, Ar-H), 7.51 (d, J=8.8 Hz, 2H, Ar-H), 8.21 (d, J=8.8 Hz, 2H, Ar-H). ^{13}C NMR (125 MHz): δ: 11.53, 21.02, 21.08, 28.69, 32.86, 45.02, 47.24, 50.94, 61.07, 62.24, 65.11, 71.29, 73.47, 90.96, 122.88, 123.77, 127.85 (2C), 128.02 (2C), 128.29 (2C), 128.43 (2C), 137.29, 142.54, 147.74, 162.18, 163.73. IR 2954 (CH), 1724 (C═O), 1522 (N═O), 1346 (N═O), 1022 (S═O). MS (FAB) m/z: 542 (MH^+). HRMS (FAB) calcd for $C_{29}H_{36}NO_7S$ (MH^+): 542.2212. Found: 542.2222.

Compound (*R*s)-**26g**. Pale yellow oil. 1H NMR (300 MHz) δ: 0.74 (s, 3H, CH_3), 0.88–1.01 (m, 2H, H-5′ and 6′), 0.97 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.42–1.65 (m, 2H, H-5′ and 6′), 1.82 (d, J=4.0 Hz, 1H, H-4′), 3.10 (d, J=7.3 Hz, 1H, H-2′ or 3′), 3.43 (d, J=7.7 Hz, 1H, H-2′ or 3′), 3.53 (s, 3H, OCH_3), 4.57 (s, 2H, CH_2Ph), 4.64 (dd, J=13.4, 1.1 Hz, 1H, H-4), 4.87 (dd, J=13.4, 1.1 Hz, 1H, H-4), 5.27 (s, 2H, CO_2CH_2Ar), 6.63 (t, J=1.1 Hz, 1H, H-2), 7.21–7.36 (m, 5H, Ar-H), 7.50 (d, J=8.8 Hz, 2H, Ar-H), 8.20 (d, J=8.8 Hz, 2H, Ar-H). IR 2954 (CH), 1720 (C═O), 1527 (N═O), 1348 (N═O), 1034 (S═O). MS (FAB) m/z: 542 (MH^+). HRMS (FAB) calcd for $C_{29}H_{36}NO_7S$ (MH^+): 542.2212. Found: 542.2197.

4.3.8. 4-[(*S*s)-[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-5*H*-furan-2-one [(*S*s)-27]. A mixture of (*S*s)-**26c** (150 mg, 0.34 mmol) and TFA-water (9:1) (1 mL) in CH_2Cl_2 (2 mL) was stirred at room temperature for 4 days. Water was added to the mixture and the mixture was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (3:2) to give (*S*s)-**27** (78 mg, 77%) as a colorless needles. Mp 196.0–198.0°C (diisopropyl ether). $[\alpha]_D^{28}$=+106 (c 1.00, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.89 (s, 3H, CH_3), 1.03–1.14 (m, 2H, H-5′ and 6′), 1.08 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.50–1.64 (m, 1H, H-6′), 1.86–2.04 (m, 1H, H-5′), 2.48 (d, J=4.6 Hz, 1H, H-4′), 3.38 (s, 3H, OCH_3), 3.44 (d, J=8.2 Hz, 1H, H-2′ or 3′), 3.48 (d, J=8.2 Hz, 1H, H-2′ or 3′), 5.01 (dd, J=17.7, 1.7 Hz, 1H, H-4), 5.09 (dd, J=17.7, 1.7 Hz, 1H, H-4), 6.52 (t, J=1.7 Hz, 1H, H-2). ^{13}C NMR (125 MHz) δ: 12.38, 20.06, 21.25, 28.18, 32.88, 45.56, 47.39, 51.87, 60.90, 69.65, 74.07, 90.51, 120.98, 170.27, 174.41. IR 2951 (CH), 1747 (C═O) 1053 (S═O). MS (FAB) m/z: 299 (MH^+). HRMS (FAB) calcd for $C_{15}H_{23}O_4S$ (MH^+): 299.1317. Found: 299.1317. Anal. calcd for $C_{15}H_{22}O_4S$: C, 60.38; H, 7.43; S, 10.75. Found: C, 60.31; H, 7.27; S, 10.63.

4.3.9. 4-[(*R*s)-[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-5*H*-furan-2-one [(*R*s)-27]. In a manner similar to that described for (*S*s)-**27**, the ester (*R*s)-**26c** (150 mg, 0.34 mmol) was converted into (*R*s)-**27** (78 mg, 77%) as a pale yellow oil. Mp 174.0–176.0°C (diisopropyl ether). $[\alpha]_D^{28}$=−11.7 (c 1.01, $CHCl_3$). ^{1}H NMR (500 MHz) δ: 0.80 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.04–1.16 (m, 2H, H-5′ and 6′), 1.08 (s, 3H, CH_3), 1.56–1.61 (m, 1H, H-6′), 1.59 (d, J=4.3 Hz, 1H, H-4′), 1.80–1.87 (m, 1H, H-5′), 3.29 (d, J=7.3 Hz, 1H, H-2′ or 3′), 3.54 (s, 3H, OCH_3), 3.56 (d, J=7.3 Hz, 1H, H-2′ or 3′), 5.05 (dd, J=18.3, 1.8 Hz, 1H, H-4), 5.29 (dd, J=18.3, 1.8 Hz, 1H, H-4), 6.40 (t, J=1.8 Hz, 1H, H-2). ^{13}C NMR (125 MHz) δ: 10.99, 20.47, 21.63, 28.25, 32.49, 46.99, 49.30, 50.93, 62.22, 69.68, 76.64, 90.10, 122.05, 170.26, 171.50. IR 2956 (CH), 1751 (C═O), 1055 (S═O). Anal. calcd for $C_{15}H_{22}O_4S$: C, 60.38; H, 7.43; S, 10.75. Found: C, 60.28; H, 7.32; S, 10.59.

4.3.10. (1*R*,2*S*,3*R*)-2-methoxybornane-3-thiol (28). Acetic acid (0.60 mL, 9.52 mmol) was added to a mixture of **21** (466 mg, 1.17 mmol) and Zn (900 mg, 13.8 mmol) in toluene (5 mL) with stirring at 110°C for 4 h. After cooling, the mixture was filtrated and the solid was rinsed with AcOEt. The combined filtrates were washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (99:1) to give **28** (343 mg, 73%) as a colorless oil. The ^{1}H NMR data was identified with the reported data.[17] $[\alpha]_D^{26}$=−79.9 (c 1.03, $CHCl_3$).

4.3.11. Methyl (*Z*)-4-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]thio]-2-butenoate [(*Z*)-29] and methyl (*E*)-4-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]thio]-2-butenoate [(*E*)-29]. Et_3N (0.17 mL, 1.20 mmol) was added to a solution of **28** (200 mg, 1.00 mmol) and methyl 4-benzyloxy-2-butynoate (204 mg, 1.00 mg) in MeOH (5 mL) with stirring at room temperature. The stirring was continued at this temperature overnight. The mixture was diluted with AcOEt, and washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (97:3) to give (*Z*)-**29** (270 mg, 67%) and (*E*)-**29** (126 mg, 31%) each as a colorless oil. (*Z*)- 29: $[\alpha]_D^{26}$=+1.7 (c 1.01, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.76 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.94–1.08 (m, 2H, H-5′ and 6′), 1.14 (s, 3H, CH_3), 1.42–1.53 (m, 1H, H-6′), 1.65–1.75 (m, 2H, H-4′ and 5′), 3.17 (d, J=7.5 Hz, 1H, H-2′ or 3′), 3.37 (s, 3H, OCH_3), 3.65 (d, J=7.5 Hz, 1H, H-2′ or 3′), 3.72 (s, 3H, CO_2CH_3), 4.23 (d, J=13.6 Hz, 1H, CH_2Ph), 4.30 (d, J=13.6 Hz, 1H, CH_2Ph), 4.56 (d, J=1.6 Hz, 2H, H-4),

6.05 (t, J=1.6 Hz, 1H, H-2), 7.28–7.39 (m, 5H, Ar-H). ^{13}C NMR (125 MHz) δ: 11.67, 21.12, 21.28, 28.25, 33.41, 47.23, 50.27, 50.72, 50.91, 53.20, 61.16, 71.97, 72.22, 91.53, 112.31, 127.82 (3C), 128.42 (2C), 137.29, 156.92, 166.22. IR 2948 (CH), 1709 (C=O). MS (FAB) *m/z*: 405 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_4S$ (MH^+): 405.2100. Found: 405.2075.

Compound (*E*)-**29**. $[\alpha]_D^{22}=-15.5$ (*c* 1.34, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.80 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 1.10–1.25 (m, 2H, H-5′ and 6′), 1.15 (s, 3H, CH_3), 1.53–1.61 (m, 1H, H-6′), 1.80–1.89 (m, 2H, H-4′ and 5′), 3.28 (d, J=7.7 Hz, 1H, H-2′ or 3′), 3.33 (d, J=7.7 Hz, 1H, H-2′ or 3′), 3.41 (s, 3H, OCH_3), 3.67 (s, 3H, CO_2CH_3), 4.59 (s, 2H, CH_2Ph), 4.85 (d, J=1.3 Hz, 2H, H-4), 5.45 (t, J=1.3 Hz, 1H, H-2), 7.24–7.41 (m, 5H, Ar-H). ^{13}C NMR (125 MHz) δ: 11.51, 20.64, 21.25, 28.40, 33.47, 47.23, 50.26, 50.58, 50.88, 53.23, 61.57, 69.54, 72.95, 91.25, 108.16, 127.57, 127.86 (2C), 128.26 (2C), 137.93, 163.82, 165.19. IR 2949 (CH), 1705 (C=O). MS (FAB) *m/z*: 405 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_4S$ (MH^+): 405.2100. Found: 405.2108.

4.3.12. Methyl (*Z*,*R*s)-4-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate [(*Z*,*R*s)-26a] and methyl (*Z*,*S*s)-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate [(*Z*,*S*s)-26a]. In a manner similar to that described for **1**, the sulfide (*Z*)-**29** (150 mg, 0.37 mmol) was converted into (*Z*,*R*s)-**26a** (106 mg, 68%) and (*Z*,*S*s)-**26a** (41 mg, 27%) each as a colorless oil. (*Z*,*R*s)-**26a**: $[\alpha]_D^{28}=+53.7$ (*c* 1.27, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.73 (s, 3H, CH_3), 0.86–1.20 (m, 2H, H-5′ and 6′), 0.97 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.48 (td, J=12.2, 3.7 Hz, 1H, H-6′), 1.58 (d, J=4.0 Hz, 1H, H-4′), 1.61–1.72 (m, 1H, H-5′), 3.25 (d, J=7.5 Hz, 1H, H-2′ or 3′), 3.43 (d, J=7.5 Hz, 1H, H-2′ or 3′), 3.50 (s, 3H, OCH_3), 3.76 (s, 3H, CO_2CH_3), 4.50 (dd, J=14.9, 1.5 Hz, 1H, H-4), 4.57 (dd, J=14.9, 1.5 Hz, 1H, H-4), 4.56 (d, J=11.9 Hz, 1H, CH_2Ph), 4.63 (d, J=11.9 Hz, 1H, CH_2Ph), 6.60 (t, J=1.5 Hz, 1H, H-2), 7.27–7.39 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) δ: 11.22, 20.64, 21.66, 28.46, 32.50, 46.89, 48.28, 50.62, 51.95, 61.97, 63.78, 72.89, 73.05, 90.50, 124.90, 127.68 (2C), 127.86, 128.39 (2C), 137.16, 156.00, 164.07. IR 2953 (CH), 1728 (C=O), 1028 (S=O). MS (FAB) *m/z*: 421 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_5S$ (MH^+): 421.2049. Found: 421.2049.

Compound (*Z*,*S*s)-**26a**. $[\alpha]_D^{28}=-97.7$ (*c* 0.94, $CHCl_3$). ^{1}H NMR (300 MHz) δ: 0.82 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 0.90–1.05 (m, 2H, H-5′ and 6′), 1.18 (s, 3H, CH_3), 1.45–1.55 (m, 1H, H-6′), 1.77–1.88 (m, 1H, H-5′), 2.32 (d, J=4.4 Hz, 1H, H-4′), 3.25 (s, 2H, H-2′ and 3′), 3.31 (s, 3H, OCH_3), 3.76 (s, 3H, CO_2CH_3), 4.44 (dd, J=14.9, 1.5 Hz, 1H, H-4), 4.58 (d, J=11.7 Hz, 1H, CH_2Ph), 4.66 (d, J=11.7 Hz, 1H, CH_2Ph), 4.67 (dd, J=14.9, 1.5 Hz, 1H, H-4), 6.49 (t, J=1.5 Hz, 1H, H-2), 7.29–7.39 (m, 5H, Ar-H). ^{13}C NMR (75 MHz) δ:11.36, 21.05, 21.21, 28.94, 32.75, 45.73, 47.39, 50.52, 51.90, 61.29, 64.75, 73.12, 73.47, 91.24, 122.45, 127.74 (2C), 127.97, 128.49 (2C), 137.32, 159.70, 164.47. IR 2950 (CH), 1716 (C=O), 1030 (S=O). MS (FAB) *m/z*: 421 (MH^+). HRMS (FAB) calcd for $C_{23}H_{33}O_5S$ (MH^+): 421.2049. Found: 421.2013.

4.3.13. Methyl (*E*,*R*s)-4-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate [(*E*,*R*s)-29] and methyl (*E*,*S*s)-benzyloxy-3-[[(1*R*,2*S*,3*R*)-2-methoxybornane-3-yl]sulfinyl]-2-butenoate [(*E*,*S*s)-29]. In a manner similar to that described for **1**, the sulfide (*E*)-**29** (60 mg, 0.15 mmol) was converted into (*E*,*R*s)-**26a** (30 mg, 48%) and (*E*,*S*s)-**26a** (13 mg, 21%) each as a colorless oil. The data of these compounds were identified with those of the corresponding products synthesized by sylfinylzincation.

4.4. X-Ray analysis

Crystal data for (*R*s)-**27**. $C_{15}H_{22}O_4S$, M=298.39, orthorhombic, space group $P2_12_12_1$, a=12.520(6), b=14.047(6), c=8.703(6) Å, volume=1530.5(14) Å^3, Z=4, D_c=1.295 g cm^{-3}, μ=1.973 mm^{-1}, crystal dimensions 0.5×0.3×0.2 mm^3, F(000)=640, T=293(2) K, θ=4.73–67.33°. 1513 reflections measured, unique reflections 1510 [R_{int}=0.0797], min and max. Absorption correction factor 0.816 and 1.000, $R1$=0.0566, $wR2$=0.1067 for 1331 reflections with $I>2\sigma(I)$ and $R1$=0.0701, $wR2$=0.1737 for all reflections and 186 refined parameters. Final electron density 0.433 and −0.433 e Å^{-3}, S=1.898, absolute Flack structure parameter 0.08(6).

The data set was collected on a Rigaku AFC5R diffractometer with Cu·Kα radiation (λ=1.5418 Å). The structure was solved by direct methods using SHELX-97[18] and refined by full matrix least squares on F^2 by SHELXL-97.[19] Non-hydrogen atoms were refined by anisotropic temperature factor and hydrogens were isotropic. The hydrogens were placed by riding method. The molecular views were realized by ORTEP-III.[20]

Crystal and data collections parameters were deposited with the Cambridge Crystallographic Data Center. The data will be sent on quoting the CCDC-213314 number (e-mail: deposit@ccdc.cam.ac.uk).

References

1. Carreño, M. C. *Chem. Rev.* **1995**, *95*, 1717–1760.
2. Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P.; Policicchio, M. *J. Org. Chem.* **2001**, *66*, 4845–4851. Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P.; Nicolò, F. *J. Org. Chem.* **1999**, *64*, 2114–2118. Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P.; Jones, D. N. *J. Org. Chem.* **1997**, *62*, 4376–4384.
3. Reports regarding sulfenyl anion, see: Furukawa, N.; Konno, Y.; Tsuruoka, M.; Fujihara, H.; Ogawa, S. *Chem. Lett.* **1989**, 1501–1504. Hogg, D. R.; Stewart, J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 43–47.
4. Maezaki, N.; Yagi, S.; Yoshigami, R.; Maeda, J.; Suzuki, T.; Ohsawa, S.; Tsukamoto, K.; Tanaka, T. *J. Org. Chem.* **2003**, *68*, 5550–5558. Maezaki, N.; Yoshigami, R.; Maeda, J.; Tanaka, T. *Org. Lett.* **2001**, *3*, 3627–3629.
5. Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Baldwin, J. E., Magnus, P. D., Eds.; Pergamon: Oxford, 1992; Vol. 9, pp 353–354 and references cited therein.
6. For communication of this report, see: Maezaki, N.; Yagi, S.;

Ohsawa, S.; Ohishi, H.; Tanaka, T. *Tetrahedron: Asymmetry* **2002**, *13*, 1961–1964.
7. Aversa, M. C.; Bonaccorsi, P.; Giannetto, P. *Tetrahedron: Asymmetry* **1994**, *5*, 805–808, and references cited therein.
8. Hirano, M.; Yakabe, S.; Ando, K.; Morimoto, T. *J. Chem. Res. (S)* **1998**, 816–817.
9. Lucchi, O. D.; Lucchini, V.; Marchioro, C.; Valle, G.; Modena, G. *J. Org. Chem.* **1986**, *51*, 1457–1466.
10. Goodridge, R. J.; Hambley, T. W.; Haynes, R. K.; Ridley, D. D. *J. Org. Chem.* **1988**, *53*, 2881–2889.
11. Similar diastereoselectivity was observed in oxidation of 3-*exo*-(alkenylthio)isoborneols, and is explained by a hydrogen bonding of the 2-OH group with *m*-CPBA, see: Yang, T.-K.; Chu, H.-Y.; Lee, D.-S.; Jiang, Y. Z.; Chou, T.-S. *Tetrahedron Lett.* **1996**, *37*, 4537–4540.
12. Youn, J.-H.; Herrmann, R. *Tetrahedron Lett.* **1986**, *27*, 1493–1494.
13. Stereochemistry of the major sulfoxide was assumed as (*S*s)-configuration, since the nucleophilic reaction to sulfenates is known to proceed with inversion of the chirality, see: Walker, A. J. *Tetrahedron: Asymmetry* **1992**, *3*, 961–998, and references cited therein.
14. Green, C. H.; Hellier, D. G. *J. Chem. Soc., Perkin Trans. 2* **1972**, 458–463, and references cited therein.
15. Arai, Y.; Hayashi, K.; Matsui, M.; Koizumi, T.; Shiro, K. *J. Chem. Soc., Perkin Trans. 1* **1991**, *7*, 1709–1716.
16. Yang, T.-K.; Chen, R.-Y.; Lee, D.-S.; Peng, W.-S.; Jiang, Y.-Z.; Mi, A.-Q.; Jong, T.-T. *J. Org. Chem.* **1994**, *59*, 914–921.
17. Li, Y.; Yang, G.; Jiang, Y.; Yang, T. *Synth. Commun.* **1995**, *25*, 1551–1556.
18. Sheldrick, G. M. *SHELX97: Program for the Direct method for Crystal Structures*; University of Goettingen: Germany, 1997.
19. Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Goettingen: Germany, 1997.
20. Burnett, M. N.; Johnson, C. K. *ORTEP-III: Report ORNL-6895*; Oak Ridge National Laboratory: Tennessee, USA, 1996.