Aryl *tert*-butyl sulfoxide-promoted highly enantioselective addition of allyltrichlorosilane to aldehydes†

Peng Wang,[a,b] Junmin Chen,[a,b,c] Linfeng Cun,[a] Jingen Deng,[a,b] Jin Zhu[a,b] and Jian Liao*[a,b]

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A series of enantiomerically pure mono- and bis-aryl *tert*-butyl sulfoxides were synthesised to promote the enantioselective allylation of aldehydes with allyltrichlorosilane. Moderate to good yields and modest to high enantioselectivities were achieved. The absence of nonlinear effect, spacer effect, promoter loading and concentration effect indicate that only one molecule of aryl *tert*-butyl sulfoxide is involved in the stereodetermining step.

Introduction

The asymmetric addition of allylic organometallic reagents to aldehydes represents an important method for enantioselective carbon–carbon bond formation. The homoallylic alcohol products are useful chiral building blocks in organic synthesis and can be readily converted to other functionalised molecules that are of great value to the pharmaceutical and fine-chemicals industries.[1] Different strategies, including the use of chirally modified allylmetal reagents,[2] chiral Lewis acid-catalysed addition of allylmetal reagents to aldehydes,[3–5] and chiral Lewis base-catalysed allylation of aldehydes with allyltrichlorosilane,[6] have been applied to achieve this transformation. Pioneered by Kobayashi[7] and Denmark,[8] the chiral Lewis base strategy features a catalytic format and excellent diastereoselectivity originating from a closed transition state structure and, therefore, has attracted great attention in the last decades. A wide variety of chiral Lewis bases has been demonstrated to be effective in the enantioselective addition of allyltrichlorosilane to aldehydes. Among these are chiral phosphoramides,[9] *N*-oxides,[10] formamides,[11] phosphine oxides,[12] amines[13] and ureas.[14] In 2003, Rowlands and Massa independently reported that chiral sulfoxides were effective in promoting the enantioselective allylation of aldehydes with allyltrichlorosilane.[15] However, two major disadvantages existed. First, the enantioselectivities achieved by these chiral sulfoxides were modest. Second, stoichiometric or more than stoichiometric amounts of the promoters were needed to attain satisfying yields. Very recently, Massa found that with the use of a tetradentate bis-sulfoxide, the reaction can be rendered catalytic and satisfying yields can be obtained. Still, modest enantioselectivities were observed.[16] In this context, we became interested in improving the enantioselectivity of this reaction using chiral sulfoxides as promoters.

It is well documented that the *S*-chiral *tert*-butylsulfinyl moiety is an excellent stereocontrolling element that has been involved in chiral auxiliaries,[17] ligands[18] and the Lewis base catalysts used for the asymmetric reduction of ketimines with trichlorosilane.[19] However, the utilisation of *tert*-butyl sulfoxides as promoters for the allylation of aldehydes with allyltrichlorosilane so far has seen little success. Rowlands found that oxazoline-based *tert*-butyl sulfoxide was ineffective in promoting this reaction.[15a] Khiar also found *tert*-butylsulfinylferrocene and bis(*tert*-butylsulfinyl)ethane less stereoselective than their less hindered sulfoxide counterparts in the allylation of acyl hydrazones with allyltrichlorosilane.[20] Nonetheless, finding out whether *tert*-butyl sulfoxides can be developed into highly stereoselective Lewis base catalysts requires a systematic study that includes fine-tuning the substituents on the sulfinyl sulfur. Herein, we report our preliminary study on the synthesis of mono- and bis-aryl *tert*-butyl sulfoxides and their application in promoting the asymmetric allylation of aldehydes with allyltrichlorosilane. The results are encouraging not only because these sulfoxides represent the most enantioselective Lewis base catalysts for this reaction (up to 90% ee), but also because the mechanistic study indicates that only one sulfoxide is involved in the stereodetermining step, which is unknown for sulfoxide-promoted allylation reactions.

Results and discussion

We first synthesised a series of enantiomerically pure mono-aryl *tert*-butyl sulfoxides with different electronic and steric properties and evaluated these in promoting the allylation of benzaldehyde with allyltrichlorosilane. Sulfoxides **3a–e** were prepared in one step with high yields (72–92%) according to a literature procedure.[21] Starting from **3e**, sulfoxides **5a–d** can also be readily prepared in two steps (Scheme 1).

The model reaction was carried out on a 0.4 mmol scale of benzaldehyde **6a** in CH_2Cl_2. Similar to methyl-*p*-tolyl sulfoxide,[15b] the use of phenyl *tert*-butyl sulfoxide **3a** resulted in moderate yield (48%) and enantioselectivity (59% ee, Table 1, entry 1). Gratifyingly, it was found that the substituents on the phenyl ring played an important role in the enantioselectivity. While the use of **3b** and **3d** bearing *ortho*-methyl and *para*-methoxy substituents

[a]*National Engineering Research Center of Chiral Drugs and Key Laboratory of Asymmetric Synthesis and Chirotechnology of Sichuan Province, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, China. E-mail: jliao10@cioc.ac.cn; Fax: +86 28 8522 3978; Tel: +86 28 8522 9250*
[b]*Graduate School of Chinese Academy of Sciences, Beijing, 100049, China*
[c]*College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, China*

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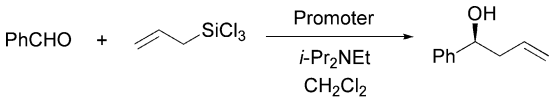
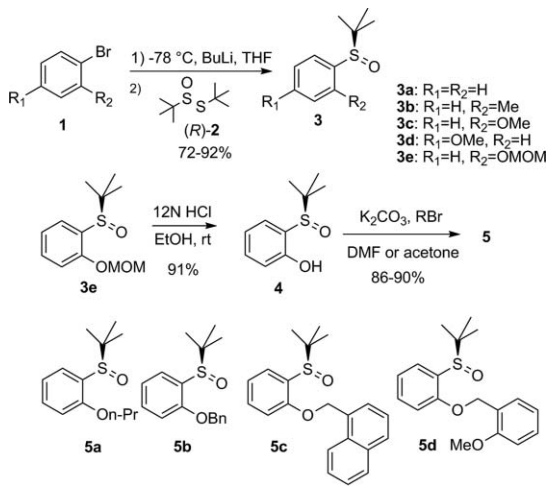
Table 1 Enantioselective allylation of benzaldehyde **6a** with allyltrichlorosilane promoted by mono-aryl *tert*-butyl sulfoxides



6a **7** **8a**

Entry[a]	Promoter	**7**/equiv.	Time/h	Yield[c] (%)	ee[d] (*S*, %)
1	**3a**	1.5	12	48	59
2	**3b**	1.5	12	58	43
3	**3c**	1.5	12	68	72
4	**3d**	1.5	12	56	39
5	**3e**	1.5	12	67	78
6	**5a**	1.5	12	69	79
7	**5b**	1.5	12	67	86
8	**5c**	1.5	12	52	87
9	**5d**	1.5	12	46	89
10[b]	**5d**	1.5	12	55	58
11	**5d**	3.0	6	72	86
12	**5d**	3.0	12	74	85
13	**5d**	3.0	24	75	84

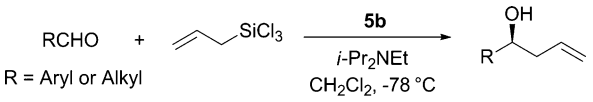
[a] Unless otherwise stated, the allylation was carried out with 0.4 mmol (1 equiv.) of **6a**, 3 equiv. of the promoter and 5 equiv. of *i*-Pr_2NEt in 2 ml CH_2Cl_2 at –78 °C. [b] At –40 °C. [c] Isolated yield. [d] ee was determined by chiral HPLC analysis and the absolute configuration of **8a** was determined by comparison of optical rotation values in the literature.



Scheme 1 Synthesis of mono-aryl *tert*-butyl sulfoxides.

led to an increase in yield (58% and 56%, respectively) and a drop in enantioselectivity (43% ee and 39% ee, respectively, Table 1, entries 2 and 4), improved enantioselectivities (72% ee and 78% ee) and yields (60% and 67%, Table 1, entries 3 and 5) were observed when using **3c** and **3e** with *ortho*-methoxy and *ortho*-methoxymethoxy substituents as the promoters, which might be attributed both to the electron donating character of these alkoxy substituents and to the silicon coordination ability of the *ortho*-alkoxy group. Inspired by these results, a series of *ortho*-alkoxyphenyl *tert*-butyl sulfoxides, **5a–d**, were further evaluated in promoting the model reaction. Moderate to good yields (46–69%) as well as high enantioselectivities (up to 89% ee) were obtained (Table 1, entries 6–9). Since sulfoxide **5b** has a superior reactivity to sulfoxides **5c** and **5d**, it was chosen as the promoter for further investigation. In line with the observation by Massa,[15b] low

Table 2 Enantioselective allylation of aromatic aldehydes promoted by **5b**[a]



6a-l **7** **8a-l**

Entry	**6** (Ar)	Time/h	Yield[b] (%)	ee[c] (*S*, %)
1	**6a** (Ph)	6	72	86
2	**6b** (*o*-$MeOC_6H_4$)	4	89	81
3[d]	**6c** (*p*-$MeOC_6H_4$)	6	65	59
4	**6d** (*p*-BrC_6H_4)	6	47	84
5	**6e** (*o*-BrC_6H_4)	8	62	88
6	**6f** (*p*-ClC_6H_4)	8	45	83
7[e]	**6g** (*o*-ClC_6H_4)	8	53	81
8	**6h** (*p*-MeC_6H_4)	8	57	79
9	**6i** (*m*-$O_2NC_4H_6$)	6	80	82
10	**6j** (1-naphthyl)	5	68	76
11	**6k** ((*E*)-$C_6H_5CH{=}CH$)	3	82	63
12	**6l** ($C_6H_5CH_2CH_2$)	6	35	80 (*R*)

[a] The reaction was carried out with 0.4 mmol of **6** (1 equiv.), 3 equiv. of **5b**, 3 equiv. of **7** and 5 equiv. of *i*-Pr_2NEt in 2.0 ml CH_2Cl_2 at –78 °C. [b] Isolated yield. [c] ee was determined by chiral GC-HPLC analysis and the absolute configuration of **8a–k** was determined by comparison of optical rotation to the literature. [d] The aldehyde was purified by silica gel chromatography before use. [e] The ee was determined after acetylation.

temperature is a prerequisite for high enantioselectivity. Increasing the temperature to –40 °C led to a decreased enantioselectivity (65% ee, Table 1, entry 10). With an increased amount of allyltrichlorosilane (3.0 equiv.), the yield was improved to 72% after only 6 h and the enantioselectivity was not affected (Table 1, entry 11). In addition, the promoter can be recovered in 97% yield and >99% ee (Table 1, entry 11) by eluting with EtOAc. Prolonged reaction time resulted in a slight decrease in the ee values and a slight increase in yields after 12 h and 24 h (Table 1, entries 14 and 15), which means that 6 h is a very reasonable, if not the best, time for the model reaction.

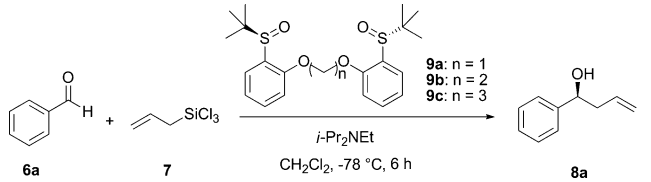
Next, we tested the substrate scope by using **5b** as promoter. The reactions of aldehydes with allyltrichlorosilane were monitored by thin layer chromatography (TLC) and quenched when the aldehydes were not being consumed at an appreciable rate. The results are shown in Table 2.

All the aromatic and α,β-unsaturated aldehydes we used to test the substrate scope were converted to the corresponding homoallylic alcohols in moderate to high yields (45–89%) and good to high enantioselectivities (59–88% ee). Even for aliphatic aldehyde **6l**, the enantioselectivity is good (80% ee), although the yield is moderate (35%, Table 2, entry 12). It is noteworthy that **5b** exhibits quite different reactivities and selectivities towards *ortho*-methoxy benzaldehyde **6b** and *para*-methoxy benzaldehyde **6c** (Table 2, entries 2–3), which again demonstrates the significant yet unknown effect of the "*ortho*-oxygen" on the enantioselectivities.

To make a comparison with the allylation of aldehydes promoted by mono-aryl *tert*-butyl sulfoxides, bis-aryl *tert*-butyl sulfoxides **9a–c** with varying tether lengths from one to three carbons were also synthesised (Scheme 2). The *ortho*-oxygen was incorporated into the structures of **9a–c** to ensure a better comparison with the most stereoselective mono-sulfoxides.

We found that bis-sulfoxide **9b** with a two-carbon tether was the most stereoselective bis-sulfoxide for the allylation of

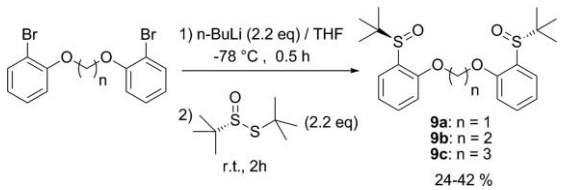
Table 3 Allylation of benzaldeyde promoted by bidentate aryl *tert*-butyl sulfoxides with varying tether lengths[a]



6a 7 8a

Entry	Promoter	Yield[b](%)	ee[c](*S*, %)
1	**9a**	74	86
2	**9b**	77	90
3	**9c**	76	88

[a] The allylation was carried out with 0.4 mmol (1 equiv.) **6a**, 1.5 equiv. of **9**, 1.5 equiv. of **7** and 5 equiv. of *i*-Pr_2NEt in 2 ml CH_2Cl_2 at –78 °C for 6 h. [b] Isolated yield. [c] ee was determined by chiral HPLC analysis and the absolute configuration of **8a** was determined by comparison of optical rotation values in the literature.



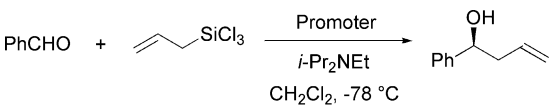
Scheme 2 Synthesis of bis-aryl *tert*-butyl sulfoxides.

benzaldehyde with allyltrichlorosilane (Table 3, entry 2). High enantioselectivity (90%) and high yield (77%) were obtained, which represents the best result of this reaction promoted by chiral sulfoxides. What attracted us more is that bis-sulfoxides **9a–c** demonstrated similar reactivities and enantioselectivities (Table 3, entries 1–3). These results are in sharp contrast to those of the bis-phosphoramide-catalysed allylation of benzaldehyde with allyltrichlorosilane where a great dependence of enantioselectivities on the tether lengths was observed,[9b,e] suggesting that the two sulfoxide moieties might be operating independently rather than cooperatively, *i.e.*, only one sulfoxide moiety is involved in the coordination sphere of the allyltrichlorosilane.

To find further support for the hypothesis that only one sulfoxide moiety is involved in the stereodetermining step in our case, we examined whether there is a nonlinear effect in the model reaction promoted by non-substituted sulfoxide **3a** and sulfoxide **5d** bearing an *ortho*-benzyloxy group. In the allylation of benzaldehyde (0.4 mmol, 1 equiv.) with allyltrichlorosilane (0.6 mmol, 1.5 equiv.) promoted either by **3a** or **5d** (1.2 mmol, 3 equiv.), a linear relationship between the enantiomeric excess of the promoter and the product was observed (Fig. 1), which bolstered our assumption that only one molecule of the aryl *tert*-sulfoxide was involved in the stereodetermining step.

Finally, we investigated the influence of the promoter loading and concentration on the enantioselectivity, which were previously studied by Khiar to probe the operating pathway of the allylation of acyl hydrazones with allyltrichlorosilane promoted by chiral sulfoxides.[20b] We selected three representative promoters, **3a**, **3c** and **5d**, to see if there is any promoter loading and concentration effect. The results are shown in Table 4. For all the chosen promoters, no significant change in enantioselectivity was found when both the promoter loading and concentration decreased (Table 4, entries 1–6). This is in contrast with Khiar's observation that decreasing the promoter loading or concentration leads to a dramatic decline in enantioselectivity.[20b] The independence of enantioselectivity on the promoter loading and concentration in our case indicates that there might be only one coordination pattern of sulfoxide to allylsilane (if not, then high promoter loading and concentration will favor two-sulfoxide coordination pattern, which is supposed to be more enantioselective). Combined with our previous findings that there was no spacer or nonlinear effect, we assume that only one molecule of aryl *tert*-butyl sulfoxide is coordinated to the allylsilane in the stereodetermining

Table 4 Enantioselective allylation of benzaldehyde with the use of sulfoxides **3a**, **3c** and **5b**[a]



6a 7 8a

Entry	Promoter	Equiv.	[P]/M	Yield[b](%)	ee[c] (%)
1	**3a**	3.0	0.6	48	59
2	**3a**	1.0	0.2	36	61
3	**3c**	3.0	0.6	68	72
4	**3c**	1.0	0.2	46	71
5	**5b**	3.0	0.6	67	86
6	**5b**	1.0	0.2	41	86

[a] The reaction was carried out with 1.5 equiv. of allyltrichlorosilane and 5 equiv. of *i*-Pr_2NEt in 2 ml CH_2Cl_2 at –78 °C for 12 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

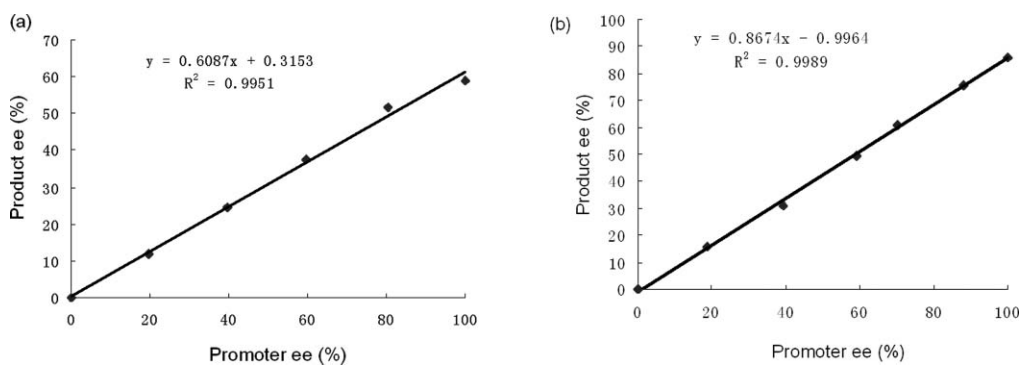


Fig. 1 (a) Linear effect of allylation with promoter **3a**. (b) Linear effect of allylation with promoter **5b**.

step. Although apparently, differently from Khiar's two-sulfoxide coordination mechanism, these observations can also be well understood: due to the steric bulkiness of the *tert*-butyl group, the coordination sphere of the silicon of the allyltrichlorosilane can only accommodate one molecule of aryl *tert*-butyl sulfoxide.

Conclusion

In summary, we have synthesised a series of enantiomerically pure mono- and bis-aryl *tert*-butyl sulfoxides and evaluated their ability to promote the asymmetric allylation of aldehydes with allyltrichlorosilane. We found that the *ortho*-oxygen on the phenyl group of the sulfoxide was a prerequisite for high enantioselectivities and good yields. The highest enantioselectivity (90% ee) was achieved by bis-sulfoxide **9b** with a two-carbon linkage, which is also the highest enantioselectivity ever known for this reaction promoted by a chiral sulfoxide. Besides, the method developed here is quite general for aromatic aldehydes and α,β-unsaturated aldehydes. Even for aliphatic aldehydes, the enantioselectivity is good, although the yield is moderate. Mechanistic studies, including the investigation of spacer effect, nonlinear effect, promoter loading and concentration effect, indicate that the activation of allyltrichlorosilane is through the coordination of one molecule of aryl *tert*-butyl sulfoxide to the allyltrichlorosilane.

Experimental

General methods

Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. (*R*)-*tert*-Butyl *tert*-butanethiosulfinate was prepared according to our method.[21] All reactions were performed under an argon atmosphere in flame-dried glassware. ^{1}H NMR and ^{13}C NMR spectra were acquired at 300 MHz and 75 MHz, respectively. Melting points were measured with BUCHI melting point B-545. Optical rotations were recorded on a PE Polarimeter-341. Enantiomeric excess was determined by chiral HPLC or chiral GLC. Electrospray ionisation high-resolution mass spectra (ESI-HRMS) were recorded on a Bruker P-SIMS-Gly FT-ICR mass spectrometer. THF was dried with sodium/benzophenone. CH_2Cl_2 was dried with CaH_2.

General procedure for the synthesis of sulfoxides 3a–e

At −78 °C, *n*-BuLi (4.4 ml, 2.5 M in hexane, 11.0 mmol, 1.1 equiv.) was added dropwise to the solution of the corresponding bromobenzene (1.05 ml, 10.0 mmol) or its derivatives in anhydrous THF (50 ml) over 3 min. The resulting mixture was stirred for 30 min at −78 °C and a solution of (*R*)-*tert*-butyl *tert*-butanethiosulfinate (2.13 g, 11.0 mmol, 1.1 equiv.) in THF (10 ml) was added. The resulting mixture was stirred for 2 h at −78 °C and then quenched with H_2O (5 ml). The solvent was evaporated under reduced pressure. The aqueous layer was extracted with CH_2Cl_2 (30 ml × 3). The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (7 : 1 petroleum ether : ethyl acetate).

(*R*)-(+)-*tert*-Butylsulfinylbenzene (3a). White solid. Yield 92%. mp = 89–91 °C. $[\alpha]_D^{25}$ = +295.5 (*c* 1.0, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59–7.56 (m, 2H), 7.48–7.46 (m, 3H), 1.15 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.8, 131.1, 128.3, 126.3, 55.8, 22.7. IR (KBr) (cm^{-1}): 2863–3070, 1440, 1362, 1034, 751. HRMS: Calcd. for $C_{10}H_{14}OS$ + Na: 205.1099, found: 205.0653.

1-(*R*)-(+)-*tert*-Butylsulfinyl-2-methylbenzene (3b). Pale yellow oil. Yield 72%. $[\alpha]_D^{25}$ = +112.4 (*c* 1.0, EtOAc). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83–7.79 (m, 1H), 7.39–7.34 (m, 2H), 7.21–7.18 (m, 1H), 2.43 (s, 3H), 1.20 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.1, 137.5, 130.8, 130.5, 126.5, 126.2, 57.5, 23.0, 19.5. IR (KBr) (cm^{-1}): 2875–3084, 1463, 1440, 1360, 1028, 759. HRMS: Calcd. for $C_{11}H_{16}OS$ + Na: 219.0814, found: 219.0811.

1-(*R*)-(+)-*tert*-Butylsulfinyl-2-methoxybenzene (3c). Pale yellow oil. Yield 84%. $[\alpha]_D^{25}$ = +281.9 (*c* 1.0, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.43–7.38 (m, 1H), 7.13–7.08 (m, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 3H), 1.17 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.1, 132.2, 128.6, 127.3, 120.9, 110.6, 57.3, 55.4, 22.8. IR (KBr) (cm^{-1}): 2863–3070, 1478, 1361, 1278, 1031, 756. HRMS: Calcd. for $C_{11}H_{16}O_2S$ + Na: 235.0763, found: 235.0781.

1-(*R*)-(+)-(*tert*-Butylsulfinyl)-4-methoxybenzene (3d). White solid. Yield 81%. mp = 80–82 °C. $[\alpha]_D^{25}$ = +171.5 (*c* 1.0, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51 (dd, *J* = 6.8 Hz, 2.0 Hz, 2H), 6.99 (dd, *J* = 6.9 Hz, 2.0 Hz, 2H), 3.85 (s, 3H), 1.14 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.0, 130.9, 127.9, 113.9, 55.6, 55.4, 22.7. IR (KBr) (cm^{-1}): 2861–3086, 1493, 1404, 1250, 1030, 793. HRMS: Calcd. for $C_{11}H_{16}O_2S$ + Na: 235.0763, found: 235.0767.

1-(*R*)-(+)-*tert*-Butylsulfinyl-2-(methoxymethoxy)benzene (3e). White solid. Yield 91%. mp = 81–82 °C. $[\alpha]_D^{25}$ = +323.8 (*c* 1.0, EtOAc). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.43–7.37 (m, 1H), 7.20–7.13 (m, 2H), 5.19 (AB, *J* = 6.9 Hz, 2H), 3.47 (s, 3H), 1.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.0, 132.3, 129.1, 127.4, 122.1, 114.1, 94.8, 57.5, 56.5, 22.9. IR (KBr) (cm^{-1}): 2865–3026, 1471, 1365, 1268, 1033, 776. HRMS: Calcd. for $C_{12}H_{18}O_3S$ + Na: 265.0874, found: 265.0877.

General procedure for the synthesis of sulfoxides 5a–d

Synthesis of 4. To a solution of **3e** (2.42 g, 10 mmol) was added 12 M HCl (40 ml). The resulting mixture was stirred at room temperature for 12 h and then the solvent was evaporated under reduced pressure. The aqueous layer was extracted with CH_2Cl_2 (50 ml × 3). The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (9 : 1 petroleum ether : ethyl acetate) to yield pure **4** as a white solid (1.80 g, 91% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.9 (br, 1H), 7.36–7.33 (m, 1H), 6.94–6.91 (m, 1H), 6.90–6.87 (m, 2H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.8, 132.9, 127.8, 119.6, 118.7, 116.4, 58.8, 22.9. HRMS: Calcd. for $C_{10}H_{14}O_2S$ + H: 199.0793, found: 199.0792.

Synthesis of 5a–d. To a mixture of **4** (1.98 g, 10 mmol) and anhydrous K_2CO_3 (13.8 g, 100 mmol) in DMF (50 ml) was added the corresponding bromoalkane (12 mmol). The resulting mixture was stirred at 60 °C for 1 h and then filtered. The DMF was removed under reduced pressure and H_2O (10 ml) was added. The mixture was extracted with CH_2Cl_2 (50 ml × 3). The organic layer

was washed with brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (7 : 1 petroleum ether : ethyl acetate).

1-(*R*)-(+)-*tert*-Butylsulfinyl-2-propoxybenzene (5a). Pale yellow oil. Yield 87%. $[\alpha]_D^{25}$ = +255.0 (*c* 1.0, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70 (dd, J = 7.8 Hz, 1.7 Hz, 1H), 7.38–7.32 (m, 1H), 7.08–7.03 (m, 1H), 6.85 (d, J = 8.2 Hz, 1H), 3.99–3.82 (m, 2H), 1.82–1.70 (m, 2H), 1.15 (s, 9H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.6, 132.1, 128.7, 127.3, 120.6, 111.5, 70.0, 57.2, 22.9, 22.3, 10.5. IR (KBr) (cm^{-1}): 2866–3057, 1457, 1360, 1272, 1031, 755. HRMS: Calcd. for $C_{13}H_{20}O_2S$ + Na: 263.1076, found: 263.1075.

1-(*R*)-(+)-(Benzyloxy)-2-(*tert*-butylsulfinyl)benzene (5b). Pale yellow solid. Yield 90%. mp = 75–76 °C. $[\alpha]_D^{25}$ = +187.8 (*c* 1.0, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (dd, J = 7.8 Hz, 1.7 Hz, 1H), 7.39–7.33 (m, 6H), 7.10 (d, J = 0.7 Hz, 1H), 6.93 (dd, J = 8.3 Hz, 0.6 Hz, 1H), 5.06 (s, 2H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.1, 135.9, 132.0, 129.0, 128.4, 127.9, 127.3, 126.9, 121.1, 112.1, 70.4, 57.3, 22.8. IR (KBr) (cm^{-1}): 2860–3058, 1478, 1361, 1277, 1020, 756. HRMS: Calcd. for $C_{17}H_{20}O_2S$ + Na: 311.1076, found: 311.1074.

1-(*R*)-(+)-((2-(*tert*-Butylsulfinyl)phenoxy)methyl)naphthalene (5c). Pale yellow oil. Yield 88%. $[\alpha]_D^{25}$ = +188.2 (*c* 1.0, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.99–7.81 (m, 4H), 7.58–7.44 (m, 5H), 7.17–7.09 (m, 2H), 5.52 (s, 2H), 1.15 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.4, 133.6, 132.2, 131.4, 131.0, 129.4, 129.0, 128.6, 127.6, 126.4, 126.0, 125.9, 125.2, 123.3, 121.4, 112.3, 69.1, 57.3, 22.9. IR (KBr) (cm^{-1}): 2863–3057, 1467, 1362, 1273, 1029, 754. HRMS: Calcd. for $C_{21}H_{22}O_2S$ + Na: 361.1233, found: 361.1236.

1-(*R*)-(+)-(2-Methoxybenzyloxy)-2-(*tert*-butylsulfinyl)benzene (5d). White solid. Yield 86%. mp = 72–74 °C. $[\alpha]_D^{25}$ = +245.3 (*c* 1.0, EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (dd, J = 7.7 Hz, 1.6 Hz, 1H), 7.46–7.37 (m, 2H), 7.31–7.26 (m, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.02–6.88 (m, 3H), 5.14 (dd, J = 14.7 Hz, 12.9 Hz, 2H), 3.85 (s, 3H), 1.20 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.6, 132.2, 129.1, 129.0, 128.2, 127.5, 124.5, 121.0, 120.6, 112.2, 110.1, 65.7, 57.4, 55.2, 23.0. IR (KBr) (cm^{-1}): 2835–3063, 1476, 1361, 1271, 1240, 1032, 762. HRMS: Calcd. for $C_{18}H_{22}O_3S$ + Na: 341.1182, found: 341.1183.

General procedure for the synthesis of bis-sulfoxides 9a–c

At −78 °C, *n*-BuLi (8.8 ml, 2.5 M in hexane, 22.0 mmol, 2.2 equiv.) was added dropwise to the solution of the corresponding dibromo compounds (10.0 mmol) in anhydrous THF (50 ml) over 6 min. The resulting mixture was stirred for 30 min at −78 °C and a solution of (*R*)-*tert*-butyl *tert*-butanethiosulfinate (4.26 g, 22.0 mmol, 2.2 equiv.) in THF (10 ml) was added. The resulting mixture was stirred for 2 h at −78 °C and then quenched with H_2O (10 ml). The solvent was evaporated under reduced pressure and the aqueous layer was extracted with CH_2Cl_2 (50 ml × 3). The organic layer was washed with brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (4 : 1 petroleum ether : ethyl acetate).

Bis(2-((*R*)-*tert*-butylsulfinyl)phenoxy)methane (9a). White solid. Yield 42%. mp = 113–115 °C. $[\alpha]_D^{25}$ = +260.4 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.2 Hz, 2H), 7.29–7.19 (m, 4H), 5.75 (s, 2H), 1.19 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.5, 132.5, 130.0, 127.9, 123.3, 114.4, 92.0, 57.6, 23.0. IR (KBr) (cm^{-1}): 2866–3071, 1475, 1365, 1272, 1031, 769. HRMS: Calcd. for $C_{21}H_{28}O_4S_2$ + H: 409.15, found: 409.1499.

1,2-Bis(2-((*R*)-*tert*-butylsulfinyl)phenoxy)ethane (9b). White solid. Yield 28%. mp = 188–190 °C. $[\alpha]_D^{25}$ = +182.2 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, J = 7.8 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.10 (t, J = 7.5 Hz, 2H), 6.68 (d, J = 8.3 Hz, 2H), 4.42–4.32 (m, 4H), 1.16 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.0, 132.3, 129.5, 127.7, 121.9, 112.4, 67.4, 57.5, 22.9. IR (KBr) (cm^{-1}): 2922–3062, 1479, 1379, 1279, 1028, 762. HRMS: Calcd. for $C_{22}H_{30}O_4S_2$ + H: 423.17, found: 423.1668.

1-((*R*)-*tert*-Butylsulfinyl)-2-(3-(2-((*R*)-*tert*-butylsulfinyl)phenoxy)propoxy)benzene (9c). Colorless oil. Yield 24%. $[\alpha]_D^{25}$ = +155.1 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (dd, J = 7.8 Hz, 1.6 Hz, 2H), 7.39–7.33 (m, 2H), 7.10–7.04 (m, 2H), 6.87 (d, J = 8.1 Hz, 2H), 4.24–4.03 (m, 4H), 2.24–2.16 (m, 2H). 1.13 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.0, 132.3, 128.5, 127.3, 121.0, 111.4, 64.6, 57.2, 28.8, 22.8. IR (KBr) (cm^{-1}): 2922–3062, 1479, 1379, 1279, 1028, 762. HRMS: Calcd. for $C_{23}H_{32}O_4S_2$ + H: 437.18, found: 437.1815.

General procedure for the enantioselective allylation of aldehydes with allyltrichlorosilane promoted by mono-aryl *tert*-butyl sulfoxides

The procedure described here is under optimized reaction conditions. Under an argon atmosphere, allyltrichlorosilane (0.173 ml, 1.2 mmol, 3 equiv.) was added to a solution of aldehyde (0.4 mmol, 1 equiv.), aryl *tert*-butyl sulfoxide (1.2 mmol, 3 equiv.) and diisopropylethylamine (0.348 ml, 2.0 mmol, 5 equiv.) in CH_2Cl_2 (2 ml) at −78 °C. The reaction was monitored by TLC and quenched with saturated aqueous solution of $NaHCO_3$ (1 ml). The mixture was allowed to warm to room temperature and extracted with CH_2Cl_2 (10 ml × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After filtration, the solution was concentrated under reduced pressure. The product was purified by silica gel column chromatography to afford pure compound **8**, followed by ethyl acetate to recover the sulfoxide.

(*S*)-1-Phenyl-3-buten-1-ol (8a)[10e]. Colorless oil. Yield 72%. $[\alpha]_D^{25}$ = −62.3 (*c* 1.0, $CHCl_3$) (lit.[10e] (*R*)-**8a** (87% ee) $[\alpha]_D^{25}$ = +62 (*c* 1.0, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37–7.28 (m, 5H), 5.86–5.74 (m, 1H), 5.19–5.13 (m, 2H), 4.69 (dt, J = 6.5 Hz, 3.1 Hz, 1H), 2.59 (d, J = 3.2 Hz, 1H), 2.49–2.54 (m, 2H). The enantiomeric excess (86% ee, *S*-isomer major) was determined by HPLC (Chiracel OD column, hexane : propan-2-ol = 95 : 5; flow rate 1.0 ml min^{-1}; UV 254 nm; t_{minor} = 7.4 min, t_{major} = 8.2 min).

(*S*)-1-(2-Methoxyphenyl)-3-buten-1-ol (8b)[10c]. Colorless oil. Yield 89%. $[\alpha]_D^{25}$ = −48.8 (*c* 1.0, CH_2Cl_2) (lit.[10c] (*S*)-**8b** (89% ee) $[\alpha]_D$ = −25.6 (*c* 0.47, CH_2Cl_2)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (dd, J = 7.5 Hz, 1.6 Hz, 1H), 7.24 (dd, J = 8.1 Hz, 1.8 Hz, 1H), 6.98 (dd, J = 7.5 Hz, 0.9 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 5.91–5.75 (m, 1H), 5.17–5.09 (m, 2H), 4.98–4.95

(dt, J = 6.5, 3.1 Hz, 1H), 3.85 (s, 3H), 2.63–2.48 (m, 3H). The enantiomeric excess (81% ee, *S*-isomer major) was determined by HPLC (Chiracel OD column, hexane : propan-2-ol = 98 : 2; flow rate 1.0 ml min^{-1}; UV 254 nm; t_{major} = 13.9 min, t_{minor} = 15.4 min).

(*S*)-1-(4-Methoxyphenyl)-3-buten-1-ol (8c)[10e]. Pale yellow oil. Yield 65%. $[\alpha]_D^{25}$ = −35.7 (*c* 1.0, $CHCl_3$) (lit.[10e] (*R*)-**8c** (87% ee) $[\alpha]_D^{25}$ = +57 (*c* 1.0, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30–7.26 (m, 2H), 6.91–6.87 (m, 2H), 5.84–5.75 (m, 1H), 5.19–5.11 (m, 2H), 4.69 (t, J = 6.5 Hz, 1H), 3.80 (s, 3H), 2.50 (t, J = 6.5 Hz, 2H), 2.02 (br, 1H). The enantiomeric excess (59% ee, *S*-isomer major) was determined by HPLC (Chiracel OD column, hexane : propan-2-ol = 98 : 2; flow rate 1.0 ml min^{-1}; UV 254 nm; t_{minor} = 18.1 min, t_{major} = 21.4 min).

(*S*)-1-(4-Bromophenyl)-3-buten-1-ol (8d)[5]. Pale yellow oil. Yield 47%. $[\alpha]_D^{23}$ = −21.3 (*c* 1.0, benzene) (lit.[5] (*S*)-**8d** (96% ee) $[\alpha]_D^{23}$ = −26.1 (*c* 1.1, benzene)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48–7.44 (m, 2H), 7.26–7.20 (m, 2H), 5.78–5.72 (m, 1H), 5.18–5.16 (m, 1H), 5.13–5.12 (m, 1H), 4.69–4.66 (m, 1H), 2.49–2.40 (m, 2H), 2.23 (d, J = 3.1 Hz, 1H). The enantiomeric excess (84% ee, *S*-isomer major) was determined by chiral GLC (Supelco Beta Dex 120, 160 °C, 12 psi, t_{minor} = 36.4 min, t_{major} = 37.1 min).

(*S*)-1-(2-Bromophenyl)-3-buten-1-ol (8e)[10e]. White solid. Yield 62%. mp 45–46 °C. $[\alpha]_D^{25}$ = −82.6 (*c* 1.0, $CHCl_3$) (lit.[10e] (*R*)-**8e** (82% ee) $[\alpha]_D^{25}$ = +77 (*c* 1.0, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57–7.50 (m, 2H), 7.36–7.31 (m, 1H), 7.15–7.10 (m, 1H), 5.89–5.83 (m, 1H), 5.22–5.16 (m, 2H), 5.12–5.07 (m, 1H), 2.67–2.59 (m, 1H), 2.40–2.30 (m, 2H). The enantiomeric excess (88% ee, *S*-isomer major) was determined by chiral GLC (Supelco Beta Dex 120, 150 °C, 12 psi, t_{minor} = 42.3 min, t_{major} = 43.1 min).

(*S*)-1-(4-Chlorophenyl)-3-buten-1-ol (8f)[10e]. Pale yellow oil. Yield 45%. $[\alpha]_D^{25}$ = −63.5 (*c* 1.0, $CHCl_3$) (lit.[10e] (*R*)-**8f** (84% ee) $[\alpha]_D^{25}$ = +62 (*c* 1.0, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33–7.26 (m, 4H), 5.79–5.73 (m, 1H), 5.19–5.13 (m, 2H), 4.73–4.68 (m, 1H), 2.53–2.41 (m, 2H), 2.14 (d, J = 3.2 Hz, 1H). The enantiomeric excess (83% ee, *S*-isomer major) was determined by chiral GLC (Supelco Beta Dex 120, 140 °C, 12 psi, t_{minor} = 52.1 min, t_{major} = 53.4 min).

(*S*)-1-(2-Chlorophenyl)-3-buten-1-ol (8g)[10h]. Pale yellow oil. Yield 53%. $[\alpha]_D^{25}$ = −61.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (dd, J = 7.5, 1.6 Hz, 1H), 7.34–7.27 (m, 2H), 7.21 (dd, J = 8.2, 1.8 Hz, 1H), 5.90–5.73 (m, 1H), 5.21–5.13 (m, 3H), 2.65–2.59 (m, 1H), 2.40–2.35 (m, 1H), 2.25 (s, 1H). The enantiomeric excess (81% ee, *S*-isomer major) was determined by HPLC (Chiracel OD column, hexane : propan-2-ol = 99 : 1; flow rate 0.6 ml min^{-1}; UV 254 nm; t_{minor} = 7.1 min, t_{major} = 9.3 min) after acetylation.

(*S*)-1-(4-Methylphenyl)-3-buten-1-ol (8h)[10a]. Pale yellow oil. Yield 57%. $[\alpha]_D^{25}$ = −31.5 (*c* 1.0, $CHCl_3$) (lit.[10a] (*S*)-**8h** (87% ee) $[\alpha]_D$ = −31.1 (*c* 0.9, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27–7.17 (m, 4H), 5.86–5.77 (m, 1H), 5.20–5.13 (m, 2H), 4.68 (t, J = 6.5 Hz, 1H), 2.53–2.47 (m, 3H), 2.38 (s, 3H). The enantiomeric excess (79% ee, *S*-isomer major) was determined by HPLC (Chiracel AD column, hexane : propan-2-ol = 95 : 5; flow rate 0.5 ml min^{-1}; UV 254 nm; t_{minor} = 15.9 min, t_{major} = 16.8 min).

(*S*)-1-(3-Nitrophenyl)-3-buten-1-ol (8i)[10e]. Yellow oil. Yield 80%. $[\alpha]_D^{25}$ = −54.1 (*c* 1.0, $CHCl_3$) (lit.[10e] (*R*)-**8i** (72% ee) $[\alpha]_D^{25}$ = +47 (*c* 1.0, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.20 (t, J = 1.9 Hz, 1H), 8.11–8.07 (m, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 5.76–5.72 (m, 1H), 5.18–5.12 (m, 2H), 4.82 (dd, J = 4.6 Hz, 2.6 Hz, 1H), 2.58–2.43 (m, 3H). The enantiomeric excess (82% ee, *S*-isomer major) was determined by HPLC (Chiracel AS column, hexane : propan-2-ol = 98 : 2; flow rate 1.0 ml min^{-1}; UV 254 nm; t_{minor} = 45.7 min, t_{major} = 49.4 min).

(*S*)-1-(1-Naphthyl)-3-buten-1-ol (8j)[10e]. Yellow oil. Yield 68%. $[\alpha]_D^{25}$ = −82.2 (*c* 1.0, $CHCl_3$) (lit.[10e] (*R*)-**8j** (79% ee) $[\alpha]_D^{25}$ = +84 (*c* 1.0, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.09 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 6.8 Hz, 1H), 7.55–7.47 (m, 3H), 5.96–5.78 (m, 1H), 5.55 (t, J = 4.2 Hz, 1H), 5.27–5.18 (m, 2H), 2.82–2.74 (m, 1H), 2.66–2.56 (m, 1H), 2.18 (d, J = 3.3 Hz, 1H). The enantiomeric excess (76% ee, *S*-isomer major) was determined by HPLC (Chiracel OD column, hexane : propan-2-ol = 90 : 10; flow rate 1.0 ml min^{-1}; UV 254 nm; t_{minor} = 8.3 min, t_{major} = 14.0 min).

(1*E*,3*S*)-1-Phenyl-1,5-hexadiene-3-ol (8k)[10e]. Yellow oil. Yield 82%. $[\alpha]_D^{25}$ = −19.8 (*c* 1.0, $CHCl_3$) (lit.[10e] (*R*)-**8k** (71% ee) $[\alpha]_D^{25}$ = +23 (*c* 1.0, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41–7.23 (m, 5H), 6.61 (d, J = 16.0 Hz, 1H), 6.25 (dd, J = 16.0 Hz, 6.4 Hz, 1H), 5.92–5.83 (m, 1H), 5.23–5.16 (m, 2H), 4.36 (dd, J = 12.2 Hz, 5.9 Hz, 1H), 2.45–2.39 (m, 2H), 2.11 (br, 1H). The enantiomeric excess (63% ee, *S*-isomer major) was determined by HPLC (Chiracel OD column, hexane : propan-2-ol = 85 : 15; flow rate 1.0 ml min^{-1}; UV 254 nm; t_{minor} = 6.2 min, t_{major} = 8.7 min).

(*R*)-1-Phenylhex-5-en-3-ol (8l)[5]. Colorless oil. Yield 35%. $[\alpha]_D^{23}$ = +23.2 (*c* 1.0, benzene) (lit.[5] (*R*)-**8l** (88% ee) $[\alpha]_D^{23}$ = +25.3 (*c* 1.0, benzene)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33–7.28 (m, 2H), 7.26–7.20 (m, 3H), 5.93–5.74 (m, 1H), 5.18–5.13 (m, 2H), 3.74–3.62 (m, 1H), 2.83–2.70 (m, 2H), 2.43–2.28 (m, 1H), 2.25–2.18 (m, 1H), 1.84–1.77 (m, 2H), 1.71 (s, 1H). The enantiomeric excess (80% ee, *R*-isomer major) was determined by HPLC (Chiracel OD column, hexane : propan-2-ol = 95 : 5; flow rate 1.0 ml min^{-1}; UV 254 nm; t_{minor} = 9.5 min, t_{major} = 14.4 min).

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