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Enantioselective hydrogen atom transfer to α-sulfonyl radicals controlled by selective coordination of a chiral Lewis acid to an enantiotopic sulfonyl oxygen

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Abstract—Enantioselective hydrogen atom transfer to α-sulfonyl radicals generated from the alkyl radical addition to 2-propenyl and 1-phenylethenyl sulfones in the presence of chiral Lewis acids affords products with high enantioselectivity. The stereochemical course is discussed with the transition states involving selective coordination of a chiral Lewis acid to an enantiotopic sulfonyl oxygen.

1. Introduction

Free radical reactions are powerful and versatile tools for carbon–carbon bond formations. High diastereoselectivity has been observed in both substrate- and auxiliary-controlled reactions.[1] Sulfoxides have been widely used as important chiral auxiliaries in asymmetric radical reactions.[2] On the other hand, the sulfonyl group is achiral in itself, but has prochiral oxygens. Studies on asymmetric reactions focusing on prochiral sulfonyl oxygens are extremely attractive, but the application of sulfonyl compounds to enantioselective reactions has been limited.[3] We have reported a highly diastereoselective radical reaction of α-sulfonyl radicals specifically coordinated to prochiral sulfonyl oxygens controlled by intramolecular hydrogen bonding and chelation with Lewis acids.[4] From these results, we envisaged that a stereogenic sulfur newly created by enantioselective coordination to one of the sulfonyl oxygens would control the enantioselective radical reaction (Fig. 1).[5]

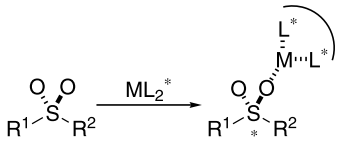

Figure 1. Asymmetric induction through the sulfonyl group.

Indeed, we recently communicated a highly enantioselective radical allylation of the α-sulfonyl radical in the presence of a chiral Lewis acid prepared from $Zn(OTf)_2$ and bis(oxazoline).[6] We now report a highly enantioselective hydrogen atom transfer to α-sulfonyl radicals using the benzimidazolyl sulfonyl group as a stereoinducer.

2. Results

Scheme 1 illustrates the preparation of various vinyl sulfones **6a–g** which were subjected to enantioselective radical addition-hydrogen atom transfer reactions. *N*-Arylmethylation or *N*-methylation of sulfides of **1** and **2** afforded sulfides **3a–g** (method A or B), which were oxidized with *m*-CPBA giving sulfones **4a–g** in high yields. Selenosulfones **5a,d–g** (method C) were prepared on treatment of the corresponding sulfones **4a,d–g** with 2 equiv. of LHMDS and subsequently with phenylselenyl bromide, whereas selenosulfones **5b,c** were obtained on treatment of **4b,c** with 2 equiv. of LDA and diphenyl diselenide (method D).[7] Oxidation of **5a–g** with *m*-CPBA at 0°C followed by warming the mixture gave vinylsulfones **6a–g**.

We first examined the hydrogen atom transfer to the α-sulfonyl radical generated from the addition of a *tert*-butyl radical to 2-propenyl sulfones **6a–d**. The addition-hydrogen atom transfer to **6a–d** was carried out by treatment with *tert*-butyl iodide (2 equiv.), tributyltin hydride (2 equiv.), and triethylborane (2 equiv.)

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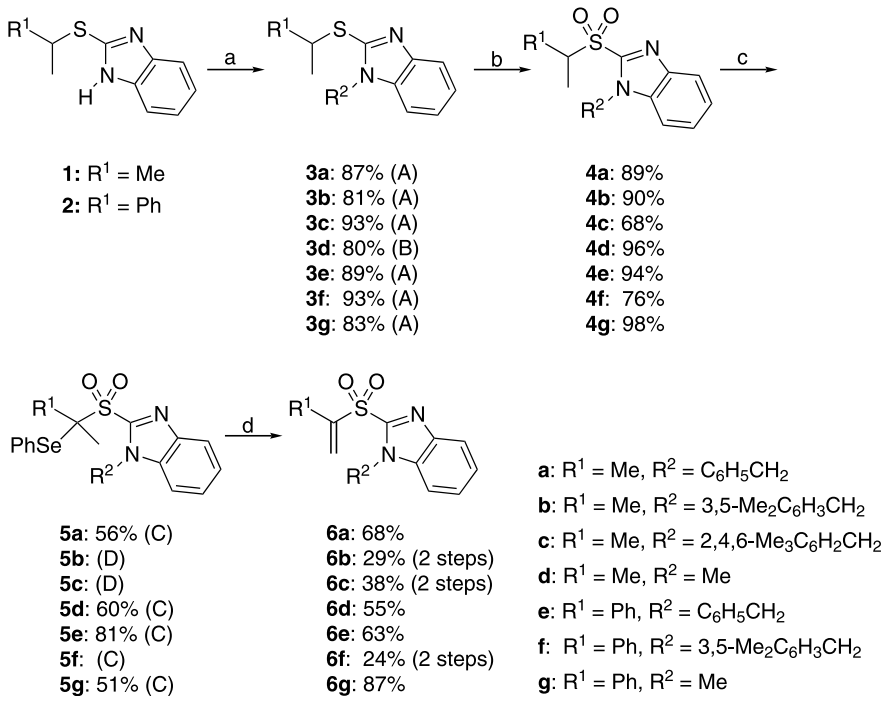


Scheme 1. *Reagents and conditions*: (a) (A): arylmethyl halides, KOH, THF, reflux, or (B): methyl iodide, *n*-BuLi, THF, 0°C→rt; (b) *m*-CPBA, CH_2Cl_2, 0°C→rt; (c) (C): LHMDS, HMPA, PhSeBr, THF, −78°C→rt, or (D): LDA, HMPA, $(PhSe)_2$, THF, −78°C→rt; (d) *m*-CPBA, CH_2Cl_2, 0°C→rt.

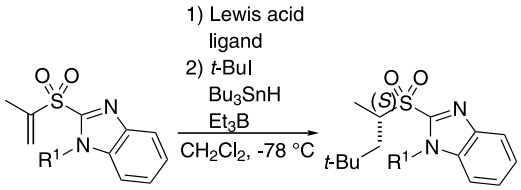
in the presence of a chiral Lewis acid (1 equiv.). The results are shown in Table 1.[8] No addition-hydrogen atom transfer product **7a** was obtained using the chiral Lewis acid derived from $Cu(OTf)_2$ and bis(oxazoline)-Ph **8** (entry 1), whereas the reaction in the presence of $ZnBr_2$-bis(oxazoline)-Ph **8** afforded the product **7a** in high yield but with no enantioselectivity (entry 2). The reaction using $Zn(OTf)_2$ as a Lewis acid gave **7a** with good enantioselectivity (entry 3). The addition-hydrogen atom transfer in the presence of $Mg(ClO_4)_2$-**8** or $Mg(OTf)_2$-**8** did not improve the enantioselectivity (entries 4 and 5). Bis(oxazoline)-Ph **8** gave the best stereoselectivity with $Zn(OTf)_2$ among other bis(oxazoline)s **9**, **10**, **11**, **12**,[9] **13**[10] (entries 6–10). So it was with *N*-(3,5-dimethylphenyl)methyl sulfone **6b**. The reaction of **6d** with $Zn(OTf)_2$-bis(oxazoline)-Ph **8** gave **7d** in 97% yield with 82% ee (entry 11). The reaction of *N*-(2,4,6-trimethylphenyl)methyl sulfone **6c** and *N*-methyl sulfone **6d** afforded the products **7c** and **7d** with lower enantioselectivity in comparison with that from *N*-benzyl sulfone **6a** (entries 12 and 13 versus entry 3).

Table 2 shows the results obtained in the reaction using various hydrogen atom donors and alkyl halides. When an excess amount of tributyltin hydride was used, the hydrogenated product was formed in 19% yield with 39% ee (entry 2), and the enantioselectivity was decreased (entry 1). The reaction using tributyltin deuteride proceeded sluggishly, and formation of the deuterated product was not observed. The reaction using triphenyltin hydride proceeded slowly (entry 3). The reaction using trimethytin hydride as a less hindered hydride afforded the product **7a** in high yield but with low enantioselectivity (entry 4 and entry 5). In the reaction with several alkyl radicals using a $Zn(OTf)_2$-bis(oxazoline)-Ph complex and tributyltin hydride, the addition-hydrogen atom transfer to **6a** with ethyl, isopropyl and *c*-hexyl radicals afforded the products **14**–**16** (entries 7–9) in high yields but with low enantioselectivity. These results suggest that the stereoselectivity obtained depends on the steric bulkiness of the alkyl radicals and the tin reagents.

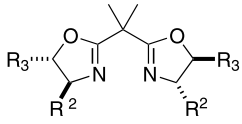
The absolute configuration of **7a** was determined as follows (Scheme 2): Treatment of (*S*)-4,4-dimethyl-2-pentanol[11] **17** with triphenylphosphine and 1-benzylbenzimidole-2-thiol[12] gave (*R*)-sulfide **18** with 95% ee.[13] (*R*)-Sulfide **18** was oxidized with *m*-CPBA to afford sulfone (*R*)-**7a** quantitatively with 95% ee. The stereochemistry of the product **7a** formed in the enantioselective hydrogen atom transfer to the α-sulfonyl radical was determined to be *S* in comparison with the specific rotation. The absolute configuration of **7b** was deduced to be *S*.

Next, we examined the addition-hydrogen atom transfer to 1-phenylethenyl sulfones **6e**–**g**. The results are shown in Table 3.[14] Surprisingly, the reaction of **6e**–**g** with *tert*-butyl iodide, tributyltin hydride, and triethyl borane in the presence of $Zn(OTf)_2$-bis(oxazoline)-Ph **8** did not afford the addition hydrogen atom transfer product **7** at all, whereas the reaction with ethyl iodide proceeded smoothly. Thus, the reaction of *N*-benzylbenzimidazolyl sulfone **6e** with 2 equiv. of ethyl iodide, 2 equiv. of tributyltin hydride, and 4 equiv. of triethyl

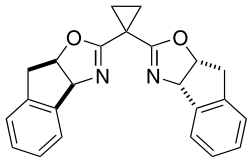
Table 1. Addition-hydrogen atom transfer to 2-propenyl sulfones **6a–d** with various chiral ligands



6a-d **7a-d**



8 : R^2 = Ph, R^3 = H
9 : R^2 = *i*-Pr, R^3 = H
10 : R^2 = *t*-Bu, R^3 = H
11 : R^2 = Bn, R^3 = H
12 : R^2 = Ph, R^3 = Ph



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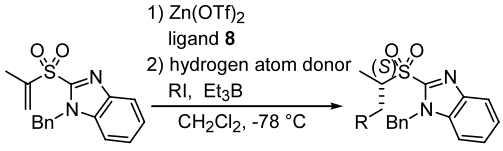
Entry	Vinyl sulfone	R^1	Lewis acid	Ligand	Time (min)	Product	Yield (%)	Ee (%)[a]
1	**6a**	$C_6H_5CH_2$	$Cu(OTf)_2$	**8**	360	**7a**	Trace	–
2	**6a**	$C_6H_5CH_2$	$ZnBr_2$	**8**	30	**7a**	95	0
3	**6a**	$C_6H_5CH_2$	$Zn(OTf)_2$	**8**	60	**7a**	88	56
4	**6a**	$C_6H_5CH_2$	$Mg(ClO_4)_2$	**8**	60	**7a**	97	27
5	**6a**	$C_6H_5CH_2$	$Mg(OTf)_2$	**8**	60	**7a**	94	0
6	**6a**	$C_6H_5CH_2$	$Zn(OTf)_2$	**9**	30	**7a**	99	1
7	**6a**	$C_6H_5CH_2$	$Zn(OTf)_2$	**10**	30	**7a**	98	5
8	**6a**	$C_6H_5CH_2$	$Zn(OTf)_2$	**11**	60	**7a**	98	4
9	**6a**	$C_6H_5CH_2$	$Zn(OTf)_2$	**12**	60	**7a**	98	2
10	**6a**	$C_6H_5CH_2$	$Zn(OTf)_2$	**13**	60	**7a**	99	6
11	**6b**	3,5-$Me_2C_6H_3CH_2$	$Zn(OTf)_2$	**8**	60	**7b**	97	82
12	**6c**	2,4,6-$Me_3C_6H_2CH_2$	$Zn(OTf)_2$	**8**	90	**7c**	95	5
13	**6d**	Me	$Zn(OTf)_2$	**8**	60	**7d**	99	26

[a] Ee was determined by HPLC analysis using CHIRALCEL® OD-H.

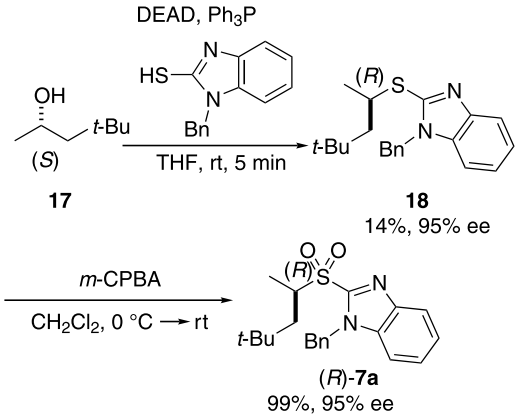
Table 2. Addition-hydrogen atom transfer to 2-propenyl sulfone **6a** with various hydrogen atom donors



6a **7a, 14,15,16**

Entry	R	Hydrogen atom donor (equiv.)	Time (min)	Product	Yield (%)	Ee (%)[a]
1	*t*-Bu	Bu_3SnH (10)	10	**7a**	98	20
2	*t*-Bu	Bu_3SnD (4)	2 days	**7a**	19[b]	39
3	*t*-Bu	Ph_3SnH (2)	360	**7a**	8	38
4	*t*-Bu	Me_3SnH (2)	60	**7a**	99	36
5	*t*-Bu	Me_3SnH (10)	15	**7a**	98	38
6	*t*-Bu	$(TMS)_3SiH$ (2)	1 week	**7a**	35	0
7	Et	Bu_3SnH[c] (2)	210	**14**	79	5
8	*i*-Pr	Bu_3SnH[c] (2)	90	**15**	89	24
9	*c*-Hex	Bu_3SnH[c] (2)	210	**16**	74	8

[a] Ee was determined by HPLC analysis.
[b] The yield of hydrogenated product. The deuterated product was not formed.
[c] RI (4 equiv.), Bu_3SnH (4 equiv.), and Et_3B (4 equiv.) were used.



Scheme 2.

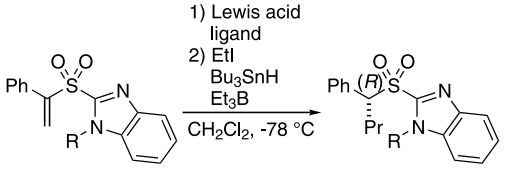
borane gave **7e** in high yield, but, unfortunately, HPLC analysis of **7e** with various chiral columns failed to determine the enantioselectivity. The reaction of *N*-(3,5-dimethyphenyl)methylbenzimidazolyl sulfone **6f** gave the product **7f** with 68% ee (entry 2). On the other hand, *N*-methylbenzimidazolyl sulfone **6g** showed high enantioselectivity. Thus, the addition of an ethyl radical and hydrogen atom transfer from tributyltin hydride in the presence of $Zn(OTf)_2$-bis(oxazoline)-Ph **8** gave **7g** in high yield with 91% ee (entry 3). The reaction using a catalytic amount of $Zn(OTf)_2$-**8** gave **7g** with good enantioselectivity (entry 4). $Mg(ClO_4)_2$-**8** or $Mg(OTf)_2$-**8** showed almost no enantioselectivity (entries 5 and 6). Other bis(oxazoline)s **9**–**12** did not improve the enantioselectivity (entries 7–10). The reaction using 10 equiv. of tributyltin hydride proceeded rapidly to give **6e** with enantioselectivity as high as that obtained in the reaction using 2 equiv. of tributyltin hydride (entry 11). Notably, when triphenyltin hydride and tris(trimethylsilyl)silane were used as hydrogen donors, the reaction proceeded slowly, but the enantioselectivities were substantially the same as that obtained with tributyltin hydride (entries 12 and 13 versus entry 3).

The stereochemistry of **7g** was determined by stereospecific transformation from (*R*)-1-phenyl-1-butanol[15] **19** as shown in Scheme 3. (*R*)-**19** was subjected to the Mitsunobu reaction to give (*S*)-benzimidazolyl sulfide (*S*)-**20** which was transformed to (*S*)-benzimidazolyl sulfone (*S*)-**7g**. By comparison of specific rotations, the absolute configuration of **7g** formed from sulfone **6g** was deduced to be *R*.

3. Discussion

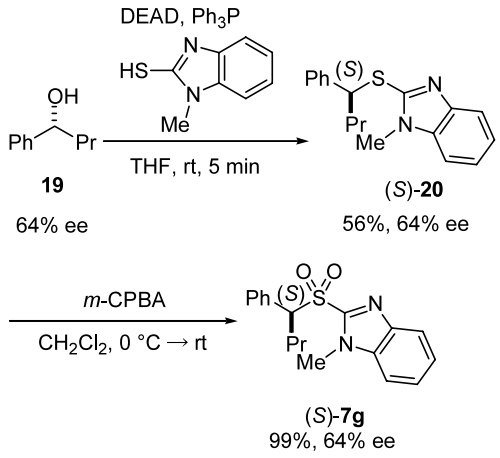
We assumed the reaction mechanism involved the radical hydrogen atom transfer to 2-propenyl sulfone **6a**. Previously, we have reported that the reaction of vinyl sulfone **21** with *tert*-butyl iodide and triethyl borane in the presence of $Zn(OTf)_2$ and bis(oxazoline)-Ph formed the carbon radical which was trapped with diallyl-

Table 3. Addition-hydrogen atom transfer to 1-phenylethenyl sulfones **6e–g**

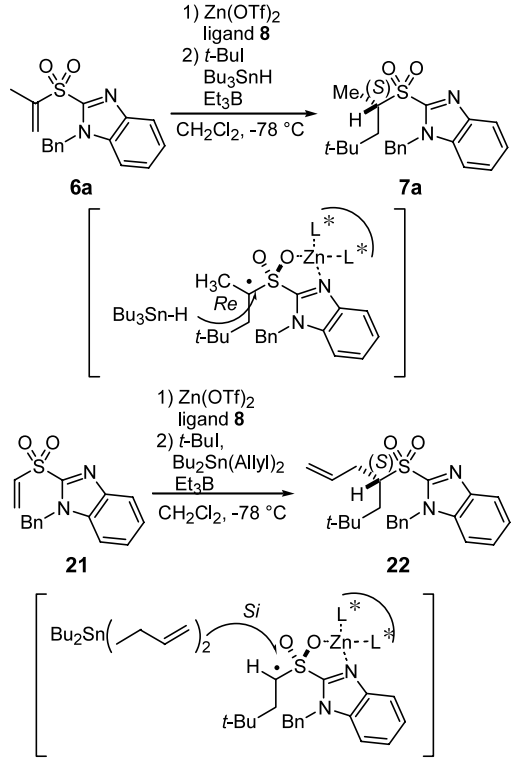


Entry	Vinyl sulfone		Lewis acid	Ligand	Hydrogen atom donor (equiv.)	Time (min)	Product	Yield (%)	Ee (%)[a]
		R							
1	**6e**	$C_6H_5CH_2$	$Zn(OTf)_2$	**8**	Bu_3SnH (2)	120	**7e**	85	–
2	**6f**	3,5-$Me_2C_6H_3CH_2$	$Zn(OTf)_2$	**8**	Bu_3SnH (2)	120	**7f**	75	68
3	**6g**	Me	$Zn(OTf)_2$	**8**	Bu_3SnH (2)	120	**7g**	99	91
4	**6g**	Me	$Zn(OTf)_2$[b]	**8**	Bu_3SnH (2)	120	**7g**	67	55
5	**6g**	Me	$Mg(OTf)_2$	**8**	Bu_3SnH (2)	120	**7g**	68	0
6	**6g**	Me	$Mg(OCl_4)_2$	**8**	Bu_3SnH (2)	120	**7g**	77	4
7	**6g**	Me	$Zn(OTf)_2$	**9**	Bu_3SnH (2)	120	**7g**	99	0
8	**6g**	Me	$Zn(OTf)_2$	**10**	Bu_3SnH (2)	120	**7g**	99	17
9	**6g**	Me	$Zn(OTf)_2$	**11**	Bu_3SnH (2)	120	**7g**	76	16
10	**6g**	Me	$Zn(OTf)_2$	**12**	Bu_3SnH (2)	120	**7g**	65	35
11	**6g**	Me	$Zn(OTf)_2$	**8**	Bu_3SnH (10)	30	**7g**	64	91
12	**6g**	Me	$Zn(OTf)_2$	**8**	Ph_3SnH[c] (2)	360	**7g**	55	93
13	**6g**	Me	$Zn(OTf)_2$	**8**	$(TMS)_3SiH$[d] (4)	1 week	**7g**	25	89

[a] Ee was determined by HPLC analysis using CHIRALCEL® OD-H.
[b] $Zn(OTf)_2$ (0.3 equiv.) and **8** (0.3 equiv.) were used.
[c] EtI (2 equiv.), Ph_3SnH (2 equiv.), and Et_3B (6 equiv.) were used.
[d] EtI (2 equiv.), $(TMS)_3SiH$ (4 equiv.), and Et_3B (4 equiv.) were used.



Scheme 3.



Scheme 4.

dibutyltin to give (*S*)-benzimidazolyl sulfone **22** with high enantioselectivity. Surprisingly, in this reaction, diallyldibutyltin approaches the *Si* face of the carbon radical from the direction opposite to the direction from which the tin hydride approaches the radical center generated in the reaction of **6a** (Scheme 4). The opposite stereochemical course[16] in the allylation and the hydrogen atom transfer to similar α-sulfonyl radicals could not be explained by the difference in stability of the radical intermediates. Therefore, the obtained stereoselectivity should be discussed with the stability of the transition states involving an interaction between the carbon radical and the hydrogen atom donor.

The plausible transition states for both reactions are shown in Figs. 2 and 3. The radical allylation and hydrogen atom transfer using the same chiral Lewis acid would proceed through transition states having tetrahedral zinc, chelating between the sulfonyl oxygen and the nitrogen atom in the benzimidazolyl group.[17] The *pro-R* oxygen of the sulfonyl group preferably coordinates with cationic zinc because of the steric repulsion between the neopentyl and the phenyl groups on the bis(oxazoline) ring. The bulkiest benzimidazolyl group occupies the open space. The second bulkiest group is supposed to be tributyltin hydride which approaches from the direction antiperiplanar to the benzimidazolyl group. A linear C–H–Sn geometry is preferable in the intermolecular hydrogen atom transfer from Bu_3SnH.[18] On the other hand, in the allylation of the α-sulfonyl radical derived from **21**, the neopentyl group is supposed to occupy the position antiperiplanar to the benzimidazolyl group and diallyldibutyltin approaches the *Si* face to form (*S*)-**22** through an S_H2' pathway (Fig. 3).[19]

It is not clear why 1-phenylethenyl sulfone **6g** showed higher enantioselectivity than 2-propenyl sulfone **6b**. It is surprising that a large excess amount of tributyltin hydride and hydrogen atom donors with low reactivity, the latter of which needed prolonged reaction time to complete the reaction, showed substantially the same high enantioselectivity as tributyltin hydride showed (Table 3, entries 11 and 12 versus entry 3). These results indicate that the stable chelating intermediate is formed. A plausible transition state forming (*R*)-**7g** through a considerably stabilized carbon radical adjacent to the phenyl group is depicted in Figure 4.

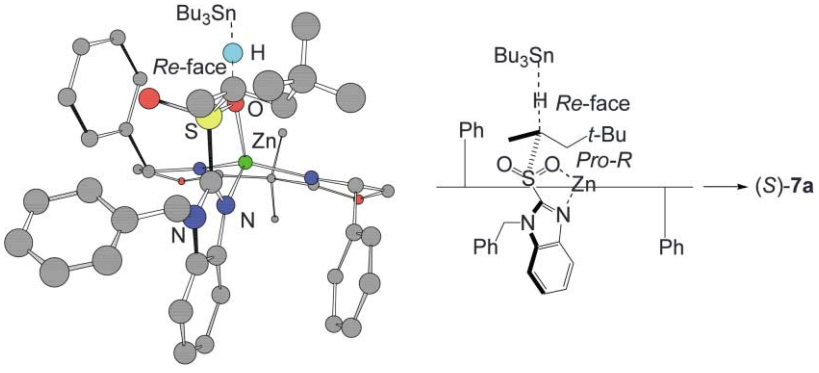


Figure 2. Plausible transition state for the hydrogen atom transfer to α-sulfonyl radical derived from **6a**.

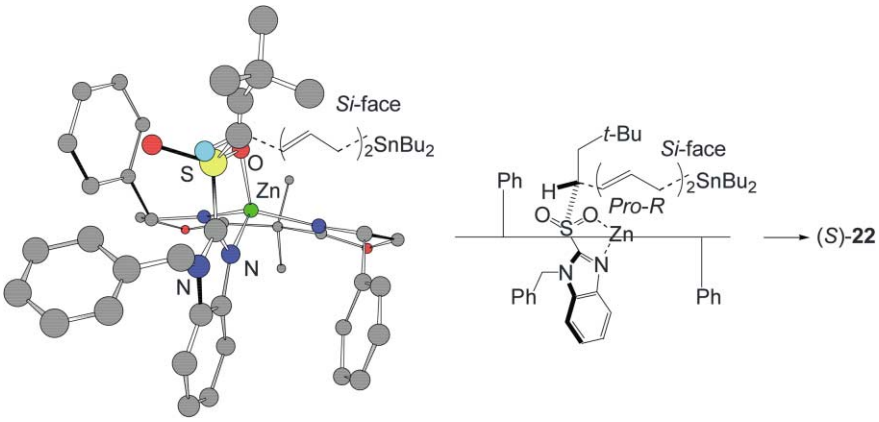


Figure 3. Plausible transition state for the allylation α-sulfonyl radical derived from **21**.

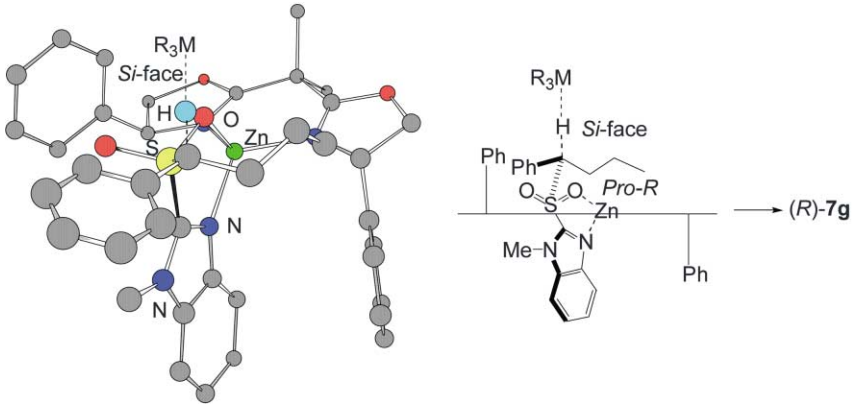


Figure 4. Plausible transition state for the hydrogen atom transfer to α-sulfonyl radical derived from **6g**.

4. Conclusion

Hydrogen atom transfer to α-sulfonyl radicals generated from the alkyl radical addition to 2-propenyl and 1-phenyletheny sulfones in the presence of a chiral Lewis acid afforded the addition-hydrogen atom transfer products with high enantioselectivity. The stereochemical courses of these reactions were elucidated with the assumed transition state involving selective coordination of a chiral Lewis acid to one of the enantiotopic sulfonyl oxygens. The use of achiral sulfonyl groups as stereo-inducers has significant potential for further extension to asymmetric reactions. Currently, studies are in progress in this direction.

5. Experimental

5.1. 2-[(1-Methylethyl)thio]-1-(phenylmethyl)benzimidazole, 3a

A mixture of 2-(1-methylthio)benzimidazole **1** (3.16 g, 16.4 mmol), potassium hydroxide (1.40 g, 21.3 mmol) and benzyl chloride (2.27 mL, 19.7 mol) in THF (30.0 mL) was heated under reflux for 1 h. After cooling, water was added and extracted with CH_2Cl_2, the combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure to leave a solid which was washed with hexane (30 mL) to afford **3a** (4.02 g, 87%): mp 126.4–127.1°C, R_f = 0.38 (hexane/ethyl acetate = 80/20); ^{1}H NMR δ 1.47 (d, J = 6.8 Hz, 6H), 4.15 (sep, J = 6.8 Hz, 1H), 5.33 (s, 2H), 7.17–7.28 (m, 8H), 7.68–7.79 (m, 1H); ^{13}C NMR δ 23.5, 38.9, 47.5, 109.2, 118.4, 121.9, 122.0, 126.8, 126.9, 127.8, 128.8, 135.83, 143.8, 151.8; IR (KBr) 3023, 2969, 1458, 1421, 1376, 1346, 1241, 741, 722 cm^{-1}; EIMS m/z (rel. intensity) 282 (M^+, 18), 240 (30), 207 (25), 91 (100). Anal calcd for $C_{17}H_{18}N_2S$; C, 72.30, H, 6.42, N, 9.92. Found: C, 72.32, H, 6.55, N, 9.77.

5.2. 1-[(3,5-Dimethylphenyl)methyl]-2-[(1-methyethyl)-thio]benzimidazole, 3b

The reaction was carried out as described above except for using **1** (1.51 g, 7.85 mmol), potassium hydroxide (673 mg, 10.2 mmol) and (3,5-dimethylphenyl)methyl bromide (1.72 g, 8.64 mmol) in THF (30.0 mL) was heated under reflux for 12 h. Work-up as above gave a solid which was purified by column chromatography (silica gel 70 g, hexane/ethyl acetate = 95/5) to afford **3b** (1.97 g, 81%): R_f = 0.21 (hexane/ethyl acetate = 95/5); ^{1}H NMR δ 1.48 (d, J = 6.8 Hz, 6H), 2.25 (s, 6H), 4.16

(sep, $J=6.8$ Hz, 1H), 5.25 (s, 2H), 6.77 (s, 2H), 6.89 (s, 1H), 7.10–7.35 (m, 3H), 7.64–7.83 (m, 1H); ^{13}C NMR δ 21.4, 23.6, 39.0, 47.6, 109.2, 118.1, 121.7, 121.8, 124.4, 129.2, 135.4, 138.1, 143.3, 151.5; IR (neat) 2965, 2921, 1429, 1365, 1242, 741 cm^{-1}; EIMS m/z (rel. intensity) 310 (M^+, 32), 268 (36), 235 (24), 119 (55), 86 (29), 84 (45), 49 (60), 28 (100). Anal calcd for $C_{19}H_{22}N_2S$; C, 73.51, H, 7.14, N, 9.02. Found: C, 73.27; H, 7.34, N, 9.03.

5.3. 2-[(1-Methylethyl)thio]-1-[(2,4,6-trimethylphenyl)-methyl]benzimidazole, 3c

The reaction was carried out as described above except for using **1** (1.50 g, 7.78 mmol), potassium hydroxide (558 mg, 11.7 mmol) and (2,4,6-trimethylphenyl)methyl bromide (1.42 g, 8.58 mmol). The obtained crude product was purified by column chromatography (silica gel 30 g, hexane/ethyl acetate = 90/10) to afford **3c** (2.58 g, 93%): mp 104.2–106.0°C; $R_f=0.51$ (hexane/ethyl acetate = 80/20); ^{1}H NMR δ 1.51 (d, $J=5.9$ Hz, 6H), 2.20 (s, 6H), 2.30 (s, 3H), 4.21 (sep, $J=5.9$ Hz, 1H), 5.21 (s, 2H), 6.47–6.60 (m, 1H), 6.81–6.95 (m, 3H), 7.02–7.16 (m, 1H), 7.55–7.70 (m, 1H); ^{13}C NMR δ 20.2, 21.0, 23.5, 38.7, 44.2, 110.0, 118.2, 121.4, 121.6, 127.9, 130.0, 135.6, 137.6, 138.0, 143.9, 152.1; IR (KBr) 2959, 1422, 740 cm^{-1}; EIMS m/z (rel. intensity) 324 (M^+, 51), 249 (37), 191 (23), 133 (100). Anal calcd for $C_{20}H_{24}N_2S$; C, 74.03, H, 7.46, N, 8.63. Found: C, 74.08, H, 7.61, N, 8.43.

5.4. 1-Methyl-2-[(1-methylethyl)thio]benzimidazole, 3d

To a solution of 2-(1-methylthio)benzimidazole **1** (1.20 g, 6.24 mmol) in THF (30.9 mL) was added n-butyllithium (1.72 mol L^{-1}, solution in hexane, 3.99 mL, 6.86 mmol) at −10°C and the mixture was stirred for 15 min, methyl iodide (0.582 mL, 9.36 mmol) was then added. After stirring for 2 h, standard work-up described in the preparation of **3a** gave a solid which was purified by column chromatography (silica gel 30 g, hexane/ethyl acetate = 90/10) to afford **3d** (1.03 g, 80%): mp 30.0–32.0°C; $R_f=0.41$ (hexane/ethyl acetate = 90/10); ^{1}H NMR δ 1.47 (d, $J=6.9$ Hz, 6H), 3.94 (sep, $J=6.9$ Hz, 1H), 4.18 (s, 3H), 7.34–7.51 (m, 3H), 7.81–7.83 (m, 1H); ^{13}C NMR δ 15.0, 23.3, 31.7, 55.1, 110.4, 121.7, 124.0, 125.8, 136.0, 141.0, 146.2; IR (neat) 2982, 1462, 1321, 1149, 1127, 813, 747, 704, 627 cm^{-1}; EIMS m/z (rel. intensity) 238 (M^+, 15), 132 (100), 104 (10). Anal calcd for $C_{11}H_{14}N_2S$; C, 55.44, H, 5.95, N, 11.76. Found: C, 55.56, H, 6.01, N, 11.55.

5.5. 2-[(1-Phenylethyl)thio]-1-(phenylmethyl)-benzimidazole, 3e

The reaction was carried out as described in the preparation of **3a** except for using 2-[(1-phenylethyl)-thio]benzimidazole **2** (2.54 g, 9.99 mmol), potassium hydroxide (990 mg, 15.0 mmol) and benzyl chloride (1.72 mL, 15.0 mol). Standard work-up gave a solid which was purified by column chromatography (silica gel 60 g, hexane/ethyl acetate = 80/20) to afford **3e** (3.08 g, 89%): mp 100.1–101.8°C; $R_f=0.42$ (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 1.80 (d, $J=7.1$ Hz, 3H), 5.19 (q, $J=7.1$ Hz, 1H), 5.13 (d, $J=16.1$ Hz, 1H), 5.23 (d, $J=16.1$ Hz, 1H), 6.95–7.55 (m, 13H), 7.85–8.11 (m, 1H); ^{13}C NMR δ 22.3, 47.5, 109.5, 118.6, 122.0, 122.3, 126.7, 127.1, 127.2, 127.6, 127.1, 127.2, 127.6, 127.7, 128.6, 128.7, 135.7, 142.1, 143.7, 150.9; IR (KBr) 3651, 2345, 1434, 1352, 738 cm^{-1}; EIMS m/z (rel. intensity) 344 (M^+, 50), 240 (100), 239 (25), 207 (32), 105 (75). Anal calcd for $C_{22}H_{20}N_2S$; C, 76.71, H, 5.85, N, 8.19. Found: C, 76.03, H, 5.91, N, 8.15.

5.6. 1-[(3,5-Dimethylphenyl)methyl]-2-[(1-phenylethyl)-thio]benzimidazole, 3f

The reaction of **2** (2.00 g, 7.86 mmol), potassium hydroxide (678 mg, 12.1 mmol) and (3,5-dimethylphenyl)methyl bromide (1.72 g, 8.65 mmol) followed by standard work-up gave the crude product which was purified by column chromatography (silica gel 70 g, hexane/ethyl acetate = 90/10) to afford **3f** (2.76 g, 93%): mp 71.0–72.0°C; $R_f=0.63$ (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 1.84 (d, $J=7.0$ Hz, 3H), 2.21 (s, 6H), 5.13 (s, 2H), 5.20 (q, $J=7.0$ Hz, 1H), 6.89 (s, 2H), 6.90 (s, 1H) 7.25–7.50 (m, 8H), 7.85–7.96 (m, 1H); ^{13}C NMR δ 21.5, 22.6, 47.7, 109.6, 118.2, 122.1, 124.2, 127.1, 127.5, 128.4, 129.3, 135.2, 138.2, 141.7, 150.6; IR (KBr) 2920, 1424, 1368, 1189, 746, 700 cm^{-1}; EIMS m/z (rel. intensity) 372 (M^+, 0.7), 267 (77), 234 (24), 118 (55), 104 (38). Anal calcd for $C_{24}H_{24}N_2S$; C, 77.38, H, 6.49, N, 7.53. Found: C, 77.46, H, 6.55, N, 7.37.

5.7. 1-Methyl-2-[(1-phenylethyl)thio]benzimidazole, 3g

The reaction was carried out as described in the preparation of **3d** except for using **2** (111 mg, 0.437 mmol), n-butyllithium (1.99 mol L^{-1}, solution in hexane, 0.241 mL, 0.480 mmol), methyl iodide (0.030 mL, 0.480 mmol). Standard work-up as above gave a solid which was purified by column chromatography (silica gel 1 g, hexane/ethyl acetate = 90/10) afford **3g** (97.8 mg, 83%): mp 73.1–75.4°C; $R_f=0.46$ (hexane/ethyl acetate = 80/20); ^{1}H NMR δ 1.85 (d, $J=7.0$ Hz, 3H), 3.54 (s, 3H), 5.13 (q, $J=7.0$ Hz, 1H), 7.10–7.50 (m, 8H), 7.65–7.72 (m, 1H); ^{13}C NMR δ 22.2, 30.0, 47.3, 108.8, 118.6, 121.9, 122.1, 127.2, 127.7, 128.6, 136.3, 142.1, 143.5, 150.6; IR (KBr) 3050, 1451, 1415, 1047, 740, 696 cm^{-1}; EIMS m/z (rel. intensity) 268 (M^+, 29), 164 (100), 105 (58). Anal calcd for $C_{16}H_{16}N_2S$; C, 71.60, H, 6.01, N, 10.44. Found: C, 71.58, H, 6.06, N, 10.42.

5.8. 2-[(1-Methylethyl)sulfonyl]-1-(phenylmethyl)-benzimidazole, 4a

To a solution of sulfide **3a** (3.10 g, 11.0 mmol) in CH_2Cl_2 (40.0 mL) was added m-CPBA (5.42 g, 22.0 mmol) at 0°C and the mixture was warmed to room temperature over a period of 12 h. And then saturated aqueous $NaHCO_3$ was added and extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 60 g, hexane/ethyl acetate = 80/20) to afford **4a** (3.08 g, 89%): mp 126.4–127.1°C; $R_f=0.38$ (hexane/ethyl acetate = 80/20);

^{1}H NMR δ 1.41 (d, J=6.9 Hz, 6H), 3.79 (sep, J=6.9 Hz, 1H), 5.84 (s, 2H), 7.10–7.45 (m, 8H), 7.80–7.90 (m, 1H); ^{13}C NMR δ 14.9, 48.7, 55.1, 111.4, 121.8, 124.0, 126.0, 126.9, 127.1, 128.1, 128.8, 135.4, 135.6, 141.2, 146.2; IR (KBr) 3023, 2969, 1458, 1421, 1376, 1346, 1241, 741, 722 cm^{-1}; EIMS m/z (rel. intensity) 314 (M$^+$, 17), 207 (100), 159 (5), 91 (56). Anal calcd for $C_{17}H_{18}N_2O_2S$; C, 64.94, H, 5.77, N, 8.91. Found: C, 65.14, H, 5.82, N, 8.91.

5.9. 1-[(3,5-Dimethylphenyl)methyl]-2-[(1-methylethyl)-sulfonyl]benzimidazole, 4b

The reaction was carried out as described above except for using **3b** (1.65 g, 5.31 mmol) and *m*-CPBA (2.62 g, 10.6 mmol). Standard work-up gave the crude product which was purified by column chromatography (silica gel 70 g, hexane/ethyl acetate=90/10) to afford **4b** (1.63 g, 90%): mp 133.0–134.5°C; R_f=0.25 (hexane/ethyl acetate=90/10); ^{1}H NMR δ 1.42 (d, J=7.1 Hz, 6H), 2.24 (s, 6H), 3.76 (sep, J=7.1 Hz, 1H), 5.76 (s, 2H), 6.83 (s, 2H), 6.91 (s, 1H), 7.30–7.50 (m, 3H), 7.80–7.95 (m, 1H); ^{13}C NMR δ 15.1, 21.5, 48.9, 55.2, 111.4, 121.6, 123.9, 124.5, 125.8, 129.6, 135.1, 135.5, 138.2, 141.0, 145.9; IR (KBr) 2965, 1458, 1321, 1121, 754 cm^{-1}; EIMS m/z (rel. intensity) 342 (M$^+$, 25), 235 (100), 119 (31). Anal calcd for $C_{19}H_{22}N_2O_2S$; C, 66.64, H, 6.48, N, 8.18. Found: C, 66.88, H, 6.49, N, 7.98.

5.10. 2-[(1-Methylethyl)sulfonyl]-1-[(2,4,6-trimethyl-phenyl)methyl]benzimidazole, 4c

The reaction was carried out as described above except for using **3c** (2.28 g, 7.03 mmol) and *m*-CPBA (3.47 g, 14.1 mmol). Standard work-up gave the crude product which was purified by column chromatography (silica gel 100 g, hexane/ethyl acetate=90/10) to afford **4c** (1.69 g, 68%): mp 133.5–136.0°C; R_f=0.59 (hexane/ethyl acetate=70/30); ^{1}H NMR δ 1.55 (d, J=6.9 Hz, 6H), 2.22 (s, 6H), 2.31 (s, 3H), 4.18 (sep, J=6.9 Hz, 1H), 5.90 (s, 2H), 6.45–6.55 (m, 1H), 6.90 (s, 2H), 7.00–7.18 (m, 1H), 7.20–7.32 (m, 1H), 7.70–7.85 (m, 1H); ^{13}C NMR δ 15.2, 20.0, 21.0, 45.6, 54.6, 112.4, 121.4, 123.4, 126.0, 127.3, 130.0, 135.2, 137.9, 138.5, 141.2, 147.0; IR (KBr) 3650, 2978, 1445, 1312, 1132, 1054, 755, 695 cm^{-1}; EIMS m/z (rel. intensity) 356 (M$^+$, 17), 249 (23), 133 (100). Anal calcd for $C_{20}H_{24}N_2O_2S$; C, 67.38, H, 6.79, N, 7.86. Found: C, 67.45, H, 6.89, N, 7.68.

5.11. 1-Methyl-2-[(1-methylethyl)sulfonyl]benzimidazole, 4d

The reaction was carried out as described above except for using **3d** (812 mg, 3.94 mmol) and *m*-CPBA (1.94 g, 7.87 mmol). Standard work-up gave the crude product, which was purified by column chromatography (silica gel 20 g, hexane/ethyl acetate=90/10) to afford **4d** (902 mg, 96%): R_f=0.64 (hexane/ethyl acetate=80/20); ^{1}H NMR δ 1.47 (d, J=6.9 Hz, 6H), 3.94 (sep, J=6.9 Hz, 1H), 4.18 (s, 3H), 7.34–7.51 (m, 3H), 7.81–7.83 (m, 1H); ^{13}C NMR δ 15.0, 23.3, 31.7, 55.1, 110.4, 121.7, 124.0, 125.8, 136.0, 141.0, 146.2; IR (neat) 2982, 1462, 1321, 1149, 1127, 813, 747, 704, 627 cm^{-1}; EIMS m/z (rel. intensity) 238 (M$^+$, 15), 132 (100), 104 (10). Anal calcd for $C_{11}H_{14}N_2S$; C, 55.44, H, 5.95, N, 11.76. Found: C, 55.56, H, 6.01, N, 11.55.

5.12. 2-[(1-Phenylmethyl)sulfonyl]-1-(phenylmethyl)benzimidazole, 4e

The reaction was carried out as described above except for using **3e** (2.86 g, 8.31 mmol) and *m*-CPBA (4.51 g, 18.2 mmol). Standard work-up gave the crude product, which was purified by column chromatography (silica gel 60 g, hexane/ethyl acetate=80/20) to afford **4e** (2.94 g, 94%): mp 117.0–119.0°C; R_f=0.61 (hexane/ethyl acetate=50/50); ^{1}H NMR δ 1.89 (d, J=7.2 Hz, 3H), 4.86 (q, J=7.2 Hz, 1H), 5.13 (d, J=14.9 Hz, 1H), 5.25 (d, J=14.9 Hz, 1H), 6.95–7.50 (m, 13H), 7.85–8.11 (m, 1H); ^{13}C NMR δ 13.5, 48.2, 65.7, 111.5, 121.9, 124.1, 126.1, 126.8, 127.1, 127.9, 128.6, 128.7, 129.3, 129.8, 132.1, 135.3, 141.3, 145.9; IR (KBr) 3651, 2345, 1455, 1317, 1146, 1128, 722, 701 cm^{-1}; EIMS m/z (rel. intensity) 376 (M$^+$, 30), 311 (46), 207 (63), 105 (100). Anal calcd for $C_{22}H_{20}N_2O_2S$; C, 70.19, H, 5.35, N, 7.44. Found: C, 70.14, H, 5.47, N, 7.37.

5.13. 1-[(3,5-Dimethylphenyl)methyl]-2-[(1-phenylethyl)-sulfonyl]benzimidazole, 4f

The reaction was carried out as described above except for using **3f** (2.22 g, 5.96 mmol) and *m*-CPBA (2.93 g, 11.9 mmol). Standard work-up gave the crude product, which was purified by column chromatography (silica gel 60 g, hexane/ethyl acetate=80/20) to afford **4f** (1.83 g, 76%): mp 135.0–136.0°C; R_f=0.63 (hexane/ethyl acetate=70/30); ^{1}H NMR δ 1.87 (d, J=7.2 Hz, 3H), 2.20 (s, 6H), 4.77 (q, J=7.2 Hz, 1H), 4.95 (d, J=16.2 Hz, 1H), 5.14 (d, J=16.2 Hz, 1H), 6.65 (s, 2H), 6.84 (s, 1H), 7.13–7.25 (m, 8H), 7.90–8.10 (m, 1H); ^{13}C NMR δ 13.6, 21.3, 48.1, 65.7, 111.4, 121.5, 123.8, 124.2, 125.8, 128.3, 129.0, 129.4, 131.7, 134.9, 135.1, 138.0, 140.9, 145.4; IR (KBr) 2919, 1322, 1146, 1129, 759 cm^{-1}; EIMS m/z (rel. intensity) 404 (M$^+$, 40), 340 (42), 236 (65), 106 (59), 27 (100). Anal calcd for $C_{24}H_{24}N_2O_2S$; C, 71.26, H, 5.93, N, 6.93. Found: C, 71.42, H, 5.98, N, 6.71.

5.14. 1-Methyl-2-[(1-phenylethyl)sulfonyl]benzimidazole, 4g

The reaction was carried out as described above except for using **3g** (1.32 g, 4.91 mmol) and *m*-CPBA (2.42 g, 9.82 mmol). Standard work-up gave the crude product, which was purified by column chromatography (silica gel 80 g, hexane/ethyl acetate=70/30) to afford **3g** (1.45 g, 98%): mp 139.0–140.5°C; R_f=0.46 (hexane/ethyl acetate=80/20); ^{1}H NMR δ 1.94 (d, J=7.2 Hz, 3H), 3.38 (s, 3H), 4.80 (q, J=7.2 Hz, 1H), 7.10–7.54 (m, 8H), 7.85–8.00 (m, 1H); ^{13}C NMR δ 13.0, 30.7, 66.1, 110.5, 121.9, 124.0, 125.9, 128.5, 129.3, 129.6, 132.2, 135.7, 141.1, 145.5; IR (KBr) 2365, 2345, 1459, 1324, 1156, 1132, 815, 747 cm^{-1}; EIMS m/z (rel. intensity) 300 (M$^+$, 10), 235 (58), 132 (26), 105 (100). Anal calcd for $C_{16}H_{16}N_2O_2S$; C, 63.94, H, 5.37, N, 9.33. Found: C, 63.94, H, 5.42, N, 9.32.

5.15. 2-{[1-Methyl-2-(phenylseleno)ethyl]sulfonyl}-1-(phenylmethyl)benzimidazole, 5a

To a solution of 1,1,1,3,3,3-hexamethyldisilazane (1.47 mL, 6.69 mmol) in THF (4.0 mL) was added *n*-butyllithium (1.99 mol L^{-1} in hexane, 3.50 mL, 6.69 mmol) at 0°C, and the mixture was stirred for 30 min. After cooling the mixture at −78°C, a solution of sulfone **4a** (1.10 g, 3.48 mmol) in THF (10 mL) and a solution of hexamethyphosphoramide (0.219, 6.69 mmol) in THF (3.0 mL) were added. After stirring for 30 min, a solution of phenylselenyl bromide (1.23 g, 5.22 mmol) in THF (0.5 mL) was then added. The reaction mixture was warmed up and water (10 mL) was then added. The combined organic solution was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 80 g, benzene/ethyl acetate = 97/3) to afford **5a** (924 mg, 56%): mp 142.7–144.5°C; R_f = 0.49 (hexane/ethyl acetate = 60/40); ^{1}H NMR δ 1.77 (s, 6H), 5.91 (s, 2H), 7.14–7.50 (m, 11H), 7.55–7.70 (m, 2H), 7.80–7.92 (m, 1H); ^{13}C NMR δ 24.8, 49.4, 69.0, 111.6, 122.0, 124.1, 125.9, 126.1, 127.0, 128.0, 128.8, 129.7, 135.6, 135.7, 138.3, 141.5, 144.7; IR (KBr) 3056, 1605, 1453, 1323, 1145, 1131, 741, 722 cm^{-1}; EIMS *m*/*z* (rel. intensity) 470 (M^+, 0.3), 365 (4), 208 (44), 91 (100). Anal calcd for $C_{23}H_{22}N_2O_2SSe$; C, 58.84, H, 4.72, N, 5.97. Found: C, 58.88, H, 4.83, N, 5.82.

5.16. 1-Methyl-2-{[1-methyl-1-(phenylseleno)ethyl]-sulfonyl}benzimidazole, 5d

The reaction was carried out as described above except for using **4d** (150 mg, 0.269 mmol) to afford **5d** (148 mg, 60%): mp 127–128°C; R_f = 0.27 (hexane/ethyl acetate = 80/20); ^{1}H NMR δ 1.81 (s, 6H), 4.22 (s, 3H), 7.15–7.68 (m, 8H), 7.82–7.91 (m, 1H); ^{13}C NMR δ 24.7, 32.4, 68.5, 110.6, 121.9, 124.0, 125.7, 125.9, 128.8, 129.7, 136.1, 138.2, 141.3, 144.5; IR (KBr) 1456, 1322, 1146, 1131, 1095, 811, 762, 694 cm^{-1}; EIMS *m*/*z* (rel. intensity) 394 (M^+, 6), 199 (100) 197 (71), 157 (31), 132 (57), 131 (36), 119 (38). Anal calcd for $C_{17}H_{18}N_2O_2SSe$; C, 51.91, H, 4.61, N, 7.12. Found: C, 51.88, H, 4.61, N, 7.16.

5.17. 2-{[1-Phenyl-1-(phenylseleno)ethyl]sulfonyl}-1-(phenylmethyl)benzimidazole, 5e

The reaction was carried out as described above except for using sulfone **4e** (1.04 g, 2.77 mmol) to afford **5e** (1.19 g, 81%): mp 138.8–140.4°C; R_f = 0.20 (benzene); ^{1}H NMR δ 2.17 (s, 3H), 4.30 (d, *J* = 15.8 Hz, 1H), 5.00 (d, *J* = 15.8 Hz, 1H), 6.90–7.55 (m, 17H), 7.70–8.11 (m, 2H); ^{13}C NMR δ 22.4, 47.8, 73.6, 111.6, 121.9, 123.9, 126.0, 126.3, 126.8, 127.1, 127.8, 128.4, 128.6, 128.7, 128.9, 129.5, 130.1, 135.2, 135.3, 139.1, 141.4, 144.0; IR (KBr) 3070, 1327, 1146, 744, 723, 693 cm^{-1}; SIMS (rel. intensity) 532 (M^+, 4.6), 272 (74), 240 (5.2), 208 (100). Anal calcd for $C_{28}H_{24}N_2O_2SSe$; C, 63.27, H, 4.55, N, 5.27. Found: C, 63.23, H, 4.64, N, 5.22.

5.18. 1-Methyl-2-{[1-phenyl-1-(phenylseleno)ethyl]-sulfonyl}benzimidazole, 5g

The reaction was carried out as described above except for using sulfone **4g** (1.45 g, 4.83 mmol) to afford **5g** (1.13 g, 51%): mp 162.0–165.0°C; R_f = 0.43 (benzene/ethyl acetate = 95/5); ^{1}H NMR δ 2.10 (s, 3H), 3.13 (s, 3H), 7.15–7.25 (m, 13H), 7.75–7.90 (m, 1H); ^{13}C NMR δ 22.4, 30.7, 73.1, 110.3, 121.6, 123.7, 125.6, 126.0, 128.1, 128.6, 129.1, 129.8, 135.0, 135.5, 138.8, 140.7, 143.3; IR (KBr) 1467, 1326, 1156, 1133, 810, 750, 696 cm^{-1}; SIMS (rel. intensity) 456 (M^+, 66), 307 (100), 300 (27). Anal calcd for $C_{22}H_{20}N_2O_2SSe$; C, 58.02, H, 4.43, N, 6.15. Found: C, 58.00, H, 4.42, N, 6.15.

5.19. 2-[(1-Methylethenyl)sulfonyl]-1-(phenylmethyl)-benzimidazole, 6a

To a solution of sulfide **5a** (808 mg, 1.72 mmol) in CH_2Cl_2 (3.0 mL) was added *m*-CPBA (594 mg, 2.41 mmol) at 0°C and the mixture was warmed to room temperature over a period of 2 h. Then saturated aqueous $NaHCO_3$ was added and extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 60 g, hexane/ethyl acetate = 80/20) to afford **6a** (1.69 g, 68%): mp 126.9–128.2°C; R_f = 0.30 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 2.18 (s, 3H), 5.82 (s, 2H), 5.85 (s, 1H), 6.30 (s, 1H), 7.12–7.49 (m, 8H), 7.84–7.98 (m, 1H); ^{13}C NMR δ 16.8, 48.8, 111.4, 122.0, 124.1, 126.1, 126.8, 127.2, 127.4, 128.1, 128.8, 135.2, 135.9, 141.3, 144.9, 146.7; IR (KBr) 3651, 2349, 1460, 1324, 1121, 817, 730, 698 cm^{-1}; EIMS *m*/*z* (rel. intensity) 312 (M^+, 31), 247 (43), 207, (48), 91 (100). Anal calcd for $C_{17}H_{16}N_2O_2S$; C, 65.36, H, 5.16, N, 8.97. Found: C, 65.36, H, 5.19, N, 8.94.

5.20. 1-[(3,5-Dimethylphenyl)methyl]-2-[(1-methylethenyl)sulfonyl]benzimidazole, 6b

To a solution of diisopropylamine (0.245 mL, 1.77 mmol) in THF (1.2 mL) was added *n*-butyllithium (1.48 mol L^{-1} in hexane, 1.19 mL, 1.77 mmol) at 0°C, and the mixture was stirred for 30 min. After cooling at −78°C, a solution of sulfone **4b** (302 mg, 0.882 mmol) in THF (3.0 mL) and a solution of hexamethyphosphoramide (0.307 mL, 1.77 mmol) in THF (2.0 mL) were added. The mixture was stirred for 30 min, and a solution of diphenyl diselenide (551 mg, 1.77 mmol) in THF (2.0 mL) was then added. The reaction mixture was warmed to room temperature, and water (5.0 mL) was then added. The mixture was extracted with CH_2Cl_2. The combined organic solution was dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue from which excess diphenyl diselenide was removed by column chromatography (silica gel 10 g, hexane/ethyl acetate = 95/5). The obtained solution was concentrated under reduced pressure. The residue was dissolved in CH_2CH_2 (5.0 mL). Then, *m*-CPBA (218 mg, 0.883 mmol) was added at 0°C, the mixture was warmed to room temperature over a period of 2 h. Saturated aqueous $NaHCO_3$ was added and extracted

with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 30 g, hexane/ethyl acetate = 90/10) to afford **6b** (85.9 mg, two steps 29%): mp 138.9–141.7°C; R_f = 0.33 (hexane/ethyl acetate = 80/20); ^{1}H NMR δ 2.18 (s, 3H), 2.24 (s, 6H), 5.72 (s, 2H), 5.86 (s, 1H), 6.31 (s, 1H), 6.76 (s, 2H), 6.89 (s, 1H), 7.10–7.20 (m, 3H), 7.85–8.10 (m, 1H); ^{13}C NMR δ 16.9, 21.4, 48.8, 111.4, 121.6, 123.8, 124.2, 125.8, 127.0, 129.4, 134.8, 135.6, 138.1, 140.9, 144.6, 146.2; EIMS m/z (rel. intensity) 340 (M^+, 11), 275 (69), 236 (55), 118 (100). Anal calcd for $C_{19}H_{20}N_2O_2S$; C, 67.03, H, 5.92, N, 8.23. Found: C, 67.09; H, 5.94, N, 8.14.

5.21. 2-[(1-Methylethenyl)sulfonyl]-1-[(2,4,6-trimethylphenyl)methyl]benzimidazole, 6c

The reaction as described above starting from **4c** (1.20 g, 3.37 mmol) afforded **6c** (654 mg, 2 steps 38%): mp 153.0–157.2°C; R_f = 0.38 (hexane/ethyl acetate = 80/20); ^{1}H NMR δ 2.21 (s, 6H), 2.33 (s, 6H), 5.85 (s, 2H), 6.08 (s, 1H), 6.50–6.67 (m, 1H), 6.50 (s, 1H), 6.91 (s, 2H) 7.00–7.18 (m, 1H), 7.20–7.35 (m, 1H), 7.75–7.90 (m, 1H); ^{13}C NMR δ 17.3, 19.9, 21.0, 45.7, 112.4, 121.7, 123.4, 125.7, 127.1, 127.8, 129.7, 135.5, 137.9, 138.6, 141.3, 145.0, 147.3; IR (KBr) 3650, 1459, 1315, 1121, 741 cm^{-1}; EIMS m/z (rel. intensity) 354 (M^+, 12), 248 (81), 247 (57), 133 (100), 117 (41), 91 (43). Anal calcd for $C_{20}H_{22}N_2O_2S$; C, 67.77, H, 6.26, N, 7.90. Found: C, 67.70, H, 6.37, N, 7.86

5.22. 1-Methyl-2-[(1-methylethenyl)sulfonyl]-benzimidazole, 6d

The reaction as described above staring from **5d** (141 mg, 0.358 mmol) afforded **6d** (46.5 mg, 55%): mp 94.8–95.7°C; R_f = 0.21 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 2.24 (s, 3H), 4.12 (s, 3H), 6.02 (s, 1H), 6.47 (s, 1H), 7.21–7.65 (m, 3H), 7.82–7.98 (m, 1H); ^{13}C NMR δ 16.7, 31.5, 110.4, 121.8, 123.9, 125.8, 127.2, 136.2, 141.0, 145.0, 146.5; IR (KBr) 1451, 1323, 1151, 1126, 1105, 818, 742, 695 cm^{-1}; EIMS m/z (rel. intensity) 236 (M^+, 48), 132 (100), 131 (56). Anal calcd for; $C_{11}H_{12}N_2O_2S$; C, 55.91, H, 5.12, N, 11.86. Found: C, 55.88, H, 5.14, N, 11.87.

5.23. 2-[(1-Phenylethenyl)sulfonyl]-1-(phenylmethyl)-benzimidazole, 6e

The reaction as described above using **5e** (398 mg, 0.713 mmol) afforded **6e** (179 mg, 63%): mp 163.8–165.2°C; R_f = 0.40 (benzene/ethyl acetate = 90/10); ^{1}H NMR δ 5.57 (s, 2H), 6.14 (s, 1H), 6.77 (s, 1H), 6.95–7.10 (m, 2H), 7.20–7.43 (m, 11H), 7.81–8.05 (m, 1H); ^{13}C NMR δ 48.6, 111.5, 122.0, 124.0, 126.1, 126.7, 127.9, 128.4, 128.7, 129.4, 129.6, 131.3, 135.1, 135.7, 141.4, 146.7, 149.1; IR (KBr) 3651, 2349, 1460, 1329, 1146, 826, 745, 733, 695 cm^{-1}; EIMS m/z (rel. intensity) 374 (M^+, 87), 309 (25) 207 (40), 91 (100). Anal calcd for $C_{22}H_{18}N_2O_2S$; C, 70.57, H, 4.85, N, 7.48. Found: C, 70.57, H, 4.93, N, 7.48.

5.24. 1-[(3,5-Dimethylphenyl)methyl]-2-[(1-phenylethenyl)sulfonyl]benzimidazole, 6f

The reaction starting from sulfone **4f** (1.44 g, 3.87 mmol) afforded **6f** (147mg, two steps 24%): mp 117.8–120.3°C; R_f = 0.43 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 2.20 (s, 6H), 5.45 (s, 2H), 6.10 (s, 1H), 6.62 (s, 2H), 6.72 (s, 1H), 6.86 (s, 1H), 7.00–7.85 (m, 8H), 7.90–8.10 (m, 1H); ^{13}C NMR δ 21.4, 48.7, 111.5, 121.8, 123.8, 124.2, 125.9, 128.2, 128.4, 129.0, 129.4, 131.0, 134.7, 135.6, 138.1, 141.0, 146.4, 148.7; IR (KBr) 2919, 1327, 1148, 960, 821, 758 cm^{-1}; EIMS m/z (rel. intensity) 402 (M^+, 5.9), 337 (13), 118 (52), 27 (100). Anal calcd for $C_{24}H_{22}N_2O_2S$; C, 71.61, H, 5.51, N, 6.96. Found: C, 71.88, H, 5.52, N, 6.67.

5.25. 1-Methyl-2-[(1-phenylethenyl)sulfonyl]-benzimidazole, 6g

The reaction starting from sulfone **5g** (803 mg, 1.76 mmol) afforded **6g** (457 mg, 87%): mp 83.5–86.5°C; R_f = 0.37 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 3.75 (s, 3H), 6.20 (s, 1H), 6.85 (s, 1H), 7.10–7.60 (m, 8H), 7.80–7.95 (m, 1H); ^{13}C NMR δ 31.5, 110.3, 121.7, 123.8, 125.7, 128.2, 128.3, 129.2, 129.5, 131.0, 135.8, 140.8, 146.3, 148.9; IR (KBr) 1457, 1330, 1156, 729, 749 cm^{-1}; EIMS m/z (rel. intensity) 298 (M^+, 99), 233 (77), 132 (48), 103 (100). Anal calcd for $C_{16}H_{14}N_2O_2S$; C, 64.41, H, 4.73, N, 9.39. Found: C, 64.50, H, 4.79, N, 9.24.

General procedure for the chiral Lewis acid-mediated intermolecular radical reaction of vinyl sulfones 6a–g

A 0.01 mol/L CH_2Cl_2 solution of 1.1 equiv. of Lewis acid and 1.2 equiv. of bis(oxazoline) was stirred at room temperature for 1 h, and then to this mixture was added vinylsulfones **6a**–**g**. After stirred for 1 h, the mixture was cooled to −78°C and alkyl iodide (2 equiv.), tributyltin hydride (2 equiv.) and triethylborane (2 equiv.) were added. The reaction mixture was stirred at −78°C for 1 h. When the reaction was not completed, another 2 equiv. of tributyltin hydride and triethylborane were added, and the reaction was continued for an additional 1 h. Then 8% KF solution was added, and stirred for 1 h at room temperature. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by flash column chromatography to afford **7a**–**g**.

5.26. (*S*)-1-(Phenylmethyl)-2-[(1,3,3-trimethylbutyl)-sulfonyl]benzimidazole, 7a

$[\alpha]_D^{20}$ −5.32 (c 0.224, $CHCl_3$, 56% ee); mp 125.2–127.0°C; R_f = 0.30 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 0.85 (s, 9H), 1.34 (dd, J = 8.1 Hz, J = 14.5 Hz, 1H), 1.43 (d, J = 6.9 Hz, 3H), 2.12 (dd, J = 1.7 Hz, J = 14.5 Hz, 1H), 3.40–3.60 (m, 1H), 5.80 (d, J = 16.0 Hz, 1H), 5.92 (d, J = 16.0 Hz, 1H), 7.10–7.45 (m, 8H), 7.82–8.05 (m, 1H); ^{13}C NMR δ 16.2, 29.4, 30.9, 41.4, 48.6, 57.3, 111.3, 121.9, 124.1, 126.0, 126.9, 128.1,

128.9, 135.6, 135.8, 141.3, 146.1; IR (KBr) 2948, 1310, 1128, 756, 638 cm^{-1}; EIMS m/z (rel. intensity) 370 (M^+, 6), 313 (40), 207 (100), 91 (98), 57 (59). Anal calcd for $C_{21}H_{26}N_2O_2S$; C, 68.08, H, 7.07, N, 7.56. Found: C, 68.10, H, 7.22, N, 7.40; HPLC (Chiralcel OD-H, hexane/*i*-PrOH 8=97:3, flow rate 0.5 mL min^{-1}) t_R 40.6 (*S*), 47.3 (*R*) min.

5.27. (*S*)-1-[(3,5-Dimethylphenyl)methyl]-2-[(1,3,3-trimethylbutyl)sulfonyl]benzimidazole, 7b

$[\alpha]_D^{20}$ −8.29 (*c* 0.338, $CHCl_3$, 82% ee) mp 91.9–94.2°C; R_f=0.20 (hexane/ethyl acetate=90/10); ^1H NMR δ 0.81 (s, 9H), 1.10–1.25 (m, 4H), 2.00–2.20 (m, 7H), 3.15–3.32 (m, 1H), 5.70 (d, J=16.0 Hz, 1H), 5.83 (d, J=16.0 Hz, 1H), 6.80 (s, 2H), 6.90 (s, 1H), 7.10–7.28 (m, 3H), 7.80–8.15 (m, 1H); ^{13}C NMR δ 16.3, 21.4, 29.4, 30.9, 41.4, 48.6, 57.2, 111.2, 121.6, 123.8, 124.3, 125.8, 129.5, 135.2, 138.2, 140.9, 145.6; IR (KBr) 3651, 2960, 1370, 1146, 722 cm^{-1}; EIMS m/z (rel. intensity) 398 (M^+, 9.4), 236 (100), 118 (35). Anal calcd for $C_{23}H_{30}N_2O_2S$; C, 69.31, H, 7.59, N, 7.03. Found: C, 69.22, H, 7.87, N, 6.90. HPLC (Chiralcel OD-H, hexane/*i*-PrOH=97:3, flow rate 0.5 mL min^{-1}) t_R 30.5 (*S*), 33.3 (*R*) min.

5.28. 2-[(1,3,3-Trimethylbutyl)sulfonyl]-1-[2,4,6-(trimethylphenyl)methyl]benzimidazole, 7c

Mp 105.4–108.1°C; R_f=0.33 (hexane/ethyl acetate=90/10); ^1H NMR δ 0.99 (s, 9H), 1.49 (dd, J=8.0 Hz, J=14.0 Hz, 1H), 1.60 (d, J=8.0 Hz, 3H), 2.10–2.40 (m, 10H), 3.87–4.10 (m, 1H), 5.91 (s, 2H), 6.41–6.55 (m, 1H), 6.90 (s, 2H), 7.00–7.15 (m, 1H), 7.16–7.32 (m, 1H), 7.82–7.90 (m, 1H); ^{13}C NMR δ 16.9, 20.3, 21.3, 29.9, 31.4, 41.7, 45.9, 57.2, 112.7, 121.8, 123.7, 125.8, 127.6, 130.0, 135.5, 138.1, 138.8, 141.5, 147.2; IR (KBr) 2959, 1318, 1141, 744 cm^{-1}; MS (CI) m/e 413 ([M+H]$^+$, 100), 251 (31), 133 (68). Anal calcd for $C_{24}H_{32}N_2O_2S$; C, 69.87, H, 7.82, N, 6.79. Found: C, 69.81, H, 7.97, N, 6.70. HPLC (Chiralcel OD-H, hexane/*i*-PrOH=97:3, flow rate 0.2 mL min^{-1}) t_R 29.2, 31.5 min.

5.29. 1-Methyl-2-[(1,3,3-trimethylbutyl)sulfonyl]-benzimidazole, 7d

Mp 94.9–97.2°C; R_f=0.39 (hexane/ethyl acetate=80/20); ^1H NMR δ 0.93 (s, 9H), 1.41 (dd, J=8.0 Hz, J=14.5 Hz, 1H), 1.43 (d, J=4.4 Hz, 3H), 2.19 (dd, J=2.0 Hz, J=14.5 Hz, 1H), 3.60–3.80 (m, 1H), 4.17 (s, 3H), 7.30–7.55 (m, 3H), 7.82–7.96 (m, 1H); ^{13}C NMR δ 16.3, 29.5, 31.0, 31.7, 41.7, 57.3 110.4, 121.7, 123.9, 125.7, 136.0, 141.1, 146.2; IR (KBr) 2960, 1317, 1152, 745 cm^{-1}; EIMS m/z (rel. intensity) 294 (M^+, 0.8), 132 (100), 57 (38). Anal calcd for; $C_{15}H_{22}N_2O_2S$; C, 61.19, H, 7.53, N, 9.52. Found: C, 61.31, H, 7.69, N, 9.23. HPLC (Chiralcel OD-H, hexane/*i*-PrOH=97:3, flow rate 0.5 mL min^{-1}) t_R 41.1, 46.1 min.

5.30. 2-[(1-Methylbutyl)sulfonyl]-1-(phenylmethyl)-benzimidazole, 14

Mp 83.9–85.7°C; R_f=0.64 (hexane/ethyl acetate=70/30); ^1H NMR δ 0.87 (t, J=7.1 Hz, 3H), 1.10–1.75 (m, 6H), 1.80–2.20 (m, 1H), 3.40–3.70 (m, 1H), 5.84 (s, 2H), 7.17–7.50 (m, 8H), 7.82–8.00 (m, 1H); ^{13}C NMR δ 12.4, 13.6, 19.5, 30.1, 48.6, 59.3, 111.3, 121.8, 124.0, 126.0, 126.9, 128.1, 128.8, 135.5, 135.9, 141.2, 146.3; IR (KBr) 2964, 1332, 1298, 1128, 725 cm^{-1}; EIMS m/z (rel. intensity) 342 (M^+, 0.9), 207 (100), 91 (90). Anal calcd for $C_{19}H_{22}N_2O_2S$; C, 66.64, H, 6.48, N, 8.18. Found: C, 66.50, H, 6.55, N, 8.26. HPLC (Chiralcel OD-H, hexane/*i*-PrOH=97:3, flow rate 0.5 mL min^{-1}) t_R 41.1, 46.1 min.

5.31. 2-[(1,3-Dimethylbutyl)sulfonyl]-1-(phenylmethyl)-benzimidazole, 15

Mp 103.6–105.2°C; R_f=0.38 (hexane/ethyl acetate=80/20); ^1H NMR δ 0.78 (d, J=6.1 Hz, 3H), 0.91 (d, J=6.1 Hz, 3H), 1.33 (d, J=6.8 Hz, 3H), 1.40–1.85 (m, 3H), 3.50–3.72 (m, 1H), 5.84 (s, 2H), 7.14–7.50 (m, 8H), 7.81–8.00 (m, 1H); ^{13}C NMR δ 12.7, 20.7, 23.4, 25.0, 36.5, 48.6, 58.1, 111.3, 121.8, 124.0, 126.0, 126.8, 128.1, 128.8, 135.5, 136.6, 135.7, 141.2, 146.2; IR (KBr) 2956, 1305, 1126, 755, 637 cm^{-1}; MS (CI) m/e 357 ([M+H]$^+$, 100), 250 (8), 209 (16). Anal calcd for $C_{20}H_{24}N_2O_2S$; C, 67.38, H, 6.79, N, 7.86. Found: C, 67.37, H, 6.95, N, 7.71. HPLC (Chiralpac AD-H, hexane/*i*-PrOH=97:3, flow rate 1.0 mL min^{-1}) t_R 33.1, 42.1 min.

5.32. 2-[(2-Cyclohexyl-1-methylethyl)sulfonyl]-1-(phenylmethyl)benzimidazole, 16

Mp 77.0–79.5°C; R_f=0.34 (hexane/ethyl acetate=80/20); ^1H NMR δ.60–2.25 (m, 16H), 3.50–3.70 (m, 1H), 5.84 (d, J=18.1 Hz, 2H), 7.10–7.45 (m, 8H), 7.81–8.00 (m, 1H); ^{13}C NMR δ 12.8, 25.6, 25.9, 26.1, 31.4, 33.8, 34.2, 35.0, 48.5, 57.3, 111.2, 121.7, 123.9, 125.9, 126.7, 127.9, 128.7, 135.5, 135.6, 141.1, 146.1; IR (KBr) 2921, 1459, 1313, 1127, 751, 726 cm^{-1} SIMS (rel. intensity) 396 (M^+, 100), 272 (29), 208 (28), 206 (36). Anal calcd for; $C_{23}H_{28}N_2O_2S$; C, 69.66, H, 7.12, N, 7.06. Found: C, 69.61, H, 7.28, N, 6.94; HPLC (Chiralcel OD-H, hexane/*i*-PrOH=97:3, flow rate 0.5 mL min^{-1}) t_R 38.8, 42.5 min.

5.33. 2-[(1-Phenylbutyl)sulfonyl]-1-(phenylmethyl)-benzimidazole, 7e

Mp 85.1–87.6°C; R_f=0.28 (hexane/ethyl acetate=80/20); ^1H NMR δ 0.88 (t, J=7.3 Hz, 3H), 1.10–1.50 (m, 2H), 2.10–2.70 (m, 2H), 4.68 (dd, J=4.0, 11.4 Hz, 1H), 5.08 (d, J=15.3 Hz, 1H), 5.25 (d, J=15.3 Hz, 1H), 6.80–7.50 (m, 13H), 7.80–8.10 (m, 1H); ^{13}C NMR δ 13.7, 20.0, 28.8, 48.2, 70.8, 111.3, 121.7, 123.9, 125.8, 126.6, 127.7, 128.4, 128.5, 129.0, 130.0, 130.5, 135.0, 135.1, 141.1, 145.8; IR (KBr) 2961, 1320, 1146, 752 cm^{-1} EIMS m/z (rel. intensity) 404 (M^+, 23), 208 (39), 150 (36), 92 (79), 28 (100). Anal calcd for $C_{24}H_{24}N_2O_2S$, C, 71.26, H, 5.98, N, 6.93. Found: C, 71.39, H, 5.98, N, 6.79.

5.34. (*R*)-1-[(3,5-Dimethylphenyl)methyl]-2-[(1-phenylbutyl)sulfonyl]benzimidazole, 7f

$[\alpha]_D^{20}$ +52.7 (*c* 0.228, $CHCl_3$, 68% ee); mp 34.2–36.5°C; R_f = 0.43 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 0.86 (t, *J* = 7.4 Hz, 3H), 1.05–1.59 (m, 2H), 2.0–2.7 (m, 8H), 4.55 (dd, *J* = 4.2 Hz, *J* = 11.2 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H), 5.19 (d, *J* = 16.0 Hz, 1H), 6.65 (s, 2H), 7.19 (s, 1H), 7.00–7.65 (m, 8H), 7.85–8.28 (m, 1H); ^{13}C NMR δ 13.8, 20.0, 21.4, 28.9, 48.2, 70.9, 111.4, 121.0, 124.0, 124.4, 125.9, 128.4, 129.0, 129.4, 130.0, 130.4, 135.0, 135.1, 138.1, 140.8, 145.7; IR (KBr) 2961, 2873, 1329, 1145, 1129, 747, 699 cm^{-1}; EIMS *m*/*z* (rel. intensity) 432 (M^+, 32), 367 (32), 235 (69), 119 (39), 91 (100). Anal calcd for $C_{26}H_{28}N_2O_2S$; C, 72.19, H, 6.52, N, 6.48. Found: C, 72.30, H, 6.65, N, 6.23. HPLC (Chiralpac AD-H, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL min^{-1}) t_R 41.8 (*R*), 57.8 (*S*) min.

5.35. (*R*)-1-Methyl-2-[(1-phenylbutyl)sulfonyl]-benzimidazole, 7g

$[\alpha]_D^{20}$ +82.5 (*c* 0.220, $CHCl_3$, 91% ee); R_f = 0.43 (hexane/ethyl acetate = 70/30); ^{1}H NMR δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.05–2.00 (m, 2H), 2.10–2.35 (m, 2H), 3.34 (s, 3H), 4.64 (dd, *J* = 4.2, 11.4 Hz, 1H), 6.80–7.60 (m, 8H), 7.80–8.00 (m, 1H); ^{13}C NMR δ 13.7, 20.0, 28.2, 30.9, 71.2, 110.1, 121.2, 124.1, 125.9, 127.9, 128.3, 129.7, 133.0, 134.2, 135.0, 140.0, 145.2, 168.9; IR (neat) 3062, 2961, 1336, 1156 747, 633 cm^{-1}; EIMS *m*/*z* (rel. intensity) 328 (M^+, 15), 263 (67), 133 (44), 132 (36), 91 (100). Anal calcd for $C_{18}H_{20}N_2O_2S$; C, 65.83, H, 6.14, N, 8.53. Found: C, 65.73, H, 6.44, N, 8.32; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 90:10, flow rate 0.5 mL min^{-1}) t_R 28.1 (*R*), 35.2 (*S*) min.

Determination of absolute configuration of 7a and 7g

5.36. (*S*)-4,4-Dimethyl-2-pentanol, 17

A solution of (*S*)-propylene oxide (0.301 mL, 4.31 mmol) containing cat. copper iodide (12.3 mg, 0.0647 mmol) in diethyl ether was cooled to −30°C. To this solution *t*-butylmagnesium chloride (1.82 mol L^{-1}, solution in ether, 3.55 mL, 6.46 mmol) was added dropwise over a period of 10 min. After stirring for 2 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 30 g, CH_2Cl_2) to afford **17** (341 mg, 68%) $[\alpha]_D^{25}$ +26.3 (*c* 0.638 EtOH) lit.[11] $[\alpha]_D^{25}$ −39.4 (*c* 2.25 EtOH, 98.4% ee (*R*)).

5.37. (*R*)-1-(Phenylmethyl)-2-[(1,3,3-trimethylbutyl)thio]-benzimidazole, (*R*)-18

To a solution of (*S*)-4,4-dimethylpentanol **17** (124 mg, 1.07 mmol) in THF (3.0 mL) was added slowly diethyl azodicarboxylate (0.397 mL, 2.57 mmol). After stirring for 5 min, a solution of triphenylphosphine in THF (3.0 mL) and successively a solution of 1-benzylbenzimidazole-2-thiol (692 mg, 2.88 mmol) in THF (3.0 mL) were added. After stirring for 5 min saturated aqueous $NaHCO_3$ was added. The mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 15 g, hexane/ethyl acetate = 95/5) to afford **18** (48.8 mg, 14%): $[\alpha]_D^{20}$ −35.3 (*c* 0.928, $CHCl_3$); mp 66.5–68.0°C; R_f = 0.37 (hexane/ethyl acetate = 90/10); ^{1}H NMR δ 0.98 (s, 9H), 1.51 (d, *J* = 6.6 Hz, 3H), 1.54 (dd, *J* = 5.5, 14.6 Hz, 1H), 1.70 (dd, *J* = 6.1, 14.6 Hz, 1H), 3.90–4.10 (m, 1H), 5.34 (s, 2H), 7.06–7.35 (m, 8H), 7.61–7.80 (m, 1H); ^{13}C NMR δ 24.9, 29.9, 31.4, 40.4, 47.5, 50.5, 109.2, 118.5, 121.9, 122.0, 126.8, 127.7, 128.7, 135.8, 135.9, 143.8, 151.8; IR (KBr) 2964, 1421, 1374, 742 cm^{-1}; EIMS *m*/*z* (rel. intensity) 338 (M^+, 9), 240 (77) 207 (23), 91 (100), 57 (31). Anal calcd for $C_{21}H_{26}N_2S$; C, 74.51, H, 7.74, N, 8.28. Found: C, 74.54, H, 7.95, N, 8.05; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 97:3, flow rate 0.3 mL min^{-1}) t_R 25.1 (*S*), 27.0 (*R*) min.

5.38. (*R*)-1-(Phenylmethyl)-2-[(1,3,3-trimethylbutyl)sulfonyl]benzimidazole, (*R*)-7a

To a solution of sulfide **18** (25.3 mg, 0.0747 mmol) in CH_2Cl_2 (4.0 mL) was added *m*-CPBA (36.9 mg, 0.149 mmol) at 0°C and the mixture was gradually warmed to room temperature over a period of 2 h. Saturated aqueous $NaHCO_3$ was added and extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate = 90/10) to afforded (*R*)-**7a** (27.6 mg, 99%): $[\alpha]_D^{20}$ +7.22 (*c* 0.460, $CHCl_3$); HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 97:3, flow rate 0.5 mL min^{-1}) t_R 30.6 (*S*), 37.0 (*R*) min.

5.39. (*S*)-1-Methyl-2-[(1-phenylbutyl)thio]benzimidazole, (*S*)-20

The reaction as described in the preparation of **18** was performed for **19** (75.4 mg, 0.502 mmol) to afforded (*S*)-**20** (83.4 mg, 56%): $[\alpha]_D^{20}$ −197 (*c* 1.04, $CHCl_3$, 64% ee); R_f = 0.29 (benzene); ^{1}H NMR δ 1.91 (t, *J* = 7.2 Hz, 3H), 1.20–1.60 (m, 2H), 1.90–2.40 (m, 2H), 3.49 (s, 3H), 4.80–5.20 (m, 1H), 7.15–7.25 (m, 8H), 7.65–7.90 (m, 1H); ^{13}C NMR δ 13.9, 20.9, 30.0, 38.1, 52.6, 108.6, 118.4, 121.6, 121.9, 127.1, 127.3, 128.0, 128.1, 135.9, 141.1, 142.99, 149.9; IR (neat) 2958, 1358, 1152, 737 cm^{-1}; EIMS *m*/*z* (rel. intensity) 296 (M^+, 18), 164 (89), 91 (49), 49 (30), 28 (100). Anal calcd for $C_{18}H_{20}N_2S$; C, 72.93, H, 6.80, N, 9.45. Found: C, 73.07, H, 6.76, N, 9.34. HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 0.5 mL min^{-1}) t_R 16.4 (*S*), 21.0 (*R*) min.

5.40. (*S*))-1-Methyl-2-[(1-phenylbutyl)sulfonyl]-benzimidazole, (*S*)-7g

A solution of sulfide (*S*)-**20** (43.2 mg, 0.146 mmol) was treated as in the preparation of (*R*)-**7a** to afford (*S*)-**7g** (48.0 mg, 100%): $[\alpha]_D^{20}$ −62.8 (*c* 0.946, $CHCl_3$, 64% ee); HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 1.0 mL min^{-1}) t_R 16.6 (*R*), 21.0 (*S*) min.

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References

1. (a) Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*; VCH: Weinhein, 1995; (b) Porter, N. A.; Giese, B.; Curran, D. P. *Acc. Chem. Res.* **1991**, *24*, 296–304.
2. (a) Delouvrie, B.; Fensterbank, L.; Lacote, E.; Malacria, M. *J. Am. Chem. Soc.* **1999**, *121*, 11395–11401; (b) Lacote, E.; Delouvrie, B.; Fensterbank, L.; Malacria, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2116–2118; (c) Renaud, P.; Bourquard, T.; Carrupt, P.-A.; Gerster, M. *Helv. Chim. Acta* **1998**, *81*, 1048–1063; (d) Mase, N.; Watanabe, Y.; Toru, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2957–2965; (e) Mase, N.; Watanabe, Y.; Ueno, Y.; Toru, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1613–1618; (f) Mase, N.; Watanabe, Y.; Toru, T. *J. Org. Chem.* **1998**, *63*, 3899–3904; (g) Mase, N.; Watanabe, Y.; Ueno, Y.; Toru, T. *J. Org. Chem.* **1997**, *62*, 7794–7800; (h) Angelaud, R.; Landais, Y. *Tetrahedron Lett.* **1997**, *38*, 233–236; (i) Zahouily, M.; Carton, G.; Carrupt, P.-A.; Knouzi, N.; Renaud, P. *Tetrahedron Lett.* **1996**, *37*, 8387–8390.
3. For enantioselective reactions using sulfonyl compounds, see: (a) Sibi, M. P.; Sausker, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 984–991; (b) Yao, S.; Saddy, S.; Hazell, R. G.; Jørgensen, K. A. *Chem. Eur. J.* **2000**, *6*, 2435–2448; (c) Hiroi, K.; Ishi, M. *Tetrahedron Lett.* **2000**, *41*, 7071–7074; (d) Wada, E.; Pei, W.; Kanamasa, S. *Chem. Lett.* **1994**, 2345–2348; (e) Wada, E.; Yasuoka, H.; Kanemasa, S. *Chem. Lett.* **1994**, 1637–1640; (f) Wada, E.; Yasuoka, H.; Kanemasa, S. *Chem. Lett.* **1994**, 145–148; (g) Wan, Z.-K.; Choi, H.-W.; Kang, F.-A.; Nakajima, K.; Demeki, D.; Kishi, Y. *Org. Lett.* **2002**, *4*, 4431–4434. For diastereoselective reactions using sulfonyl compounds, see: (h) Metallinos, C.; Snieckus, V. *Org. Lett.* **2002**, *4*, 1935–1938; (i) Bernabeu, M. C.; Chinchilla, R.; Falvello, L. R.; Nájera, C. *Tetrahedron: Asymmetry* **2001**, *12*, 1811–1815; (j) Enders, D.; Muller, S. F.; Raabe, G.; Runsink, J. *Eur. J. Org. Chem.* **2000**, *8*, 879–892; (k) Sarakinos, G.; Corey, E. J. *Org. Lett.* **1999**, *1*, 1741–1744; (l) Miyabe, H.; Fuji, K.; Naito, T. *Org. Lett.* **1999**, *1*, 569–572; (m) Marcantoni, E.; Cingolani, S.; Bartoli, G.; Bosco, M.; Sambri, L. *J. Org. Chem.* **1998**, *63*, 3624–3630; (n) Marino, J. P.; Anna, L. J.; Fernández, de La Paradilla, R.; Martínez, M. V.; Montero, C.; Viso, A. *J. Org. Chem.* **2000**, *65*, 6462–6473.
4. (a) Mase, N.; Watanabe, Y.; Toru, T. *Tetrahedron Lett.* **1999**, *40*, 2797–2800; (b) Mase, N.; Watanabe, Y.; Toru, T.; Kakumoto, T.; Hagiwara, T. *J. Org. Chem.* **2000**, *65*, 7083–7090.
5. For chiral relay in enantioselective reactions, see: Corminboeuf, O.; Quaranta, L.; Renaud, P.; Liu, M.; Jasperse, C. P.; Sibi, M. P. *Chem. Eur. J.* **2003**, *9*, 28–35.
6. Watanabe, Y.; Mase, N.; Furue, R.; Toru, T. *Tetrahedron Lett.* **2001**, *42*, 2981–2984.
7. LHMDS abstracted the benzyl proton instead of that α to the sulfonyl group.
8. The addition-hydrogenation of 2-propenyl 2-pyridyl sulfone with *tert*-BuI (2 equiv.), Bu_3SnH (2 equiv.), and Et_3B (2 equiv.) in the presence of $Zn(OTf)_2$-bis(oxazoline)-Ph gave the product in 91% yield but with low enantioselectivity.
9. Desimoni, G.; Faita, G.; Mella, M. *Tetrahedron* **1996**, *52*, 13649–13654.
10. Davies, I. W.; Gerena, L.; Castronguay, L.; Senanayake, C. H.; Larsen, R. D.; Verhoeven, T. R.; Reider, P. J. *J. Chem. Soc., Chem. Commun.* **1996**, 1753–1754.
11. Imai, T.; Tamura, T.; Yamamuro, A. *J. Am. Chem. Soc.* **1986**, *108*, 7402–7404.
12. El'tsov, A. V.; Krivozheiko, K. M.; Kolesova, M. B. *J. Org. Chem. USSR (Engl. Transl.)* **1967**, *3*, 1518–1528.
13. Smith, A. B., III; Wan, Z. *J. Org. Chem.* **2000**, *65*, 3738–3753.
14. α-Substituted benzyl heteroaryl sulfones have been reported as selective HIV-2 inhibitors: Balzarini, J.; Stevens, M.; Andrei, G.; Snoeck, R.; Strunk, R.; Pierce, J. B.; Lacadie, J. A.; Clercq, E. D.; Pannecouque, C. *Helv. Chim. Acta* **2002**, *85*, 2961–2974.
15. Ituso, S.; Nakano, M.; Miyazaki, K.; Masuda, H.; Ito, K. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2039–2044.
16. It has been reported that the deuteration of the carbon radical α to the carbonyl with Bu_3SnD slightly reverses diastereoselectivity in the allylation with allyltributyltin: Hart, D. J.; Krishnamurthy, R. *J. Org. Chem.* **1992**, *57*, 4457–4470.
17. Crosignani, S.; Desimoni, G.; Faita, G.; Flippone, S.; Mortoni, A.; Righetti, P.; Zema, M. *Tetrahedron Lett.* **1999**, *40*, 7007–7010.
18. (a) Sordo, T. L.; Dannenberg, J. J. *J. Org. Chem.* **1999**, *64*, 1922–1924; (b) Zipse, H.; He, J.; Houk, H. N.; Giese, B. *J. Am. Chem. Soc.* **1991**, *113*, 4324–4325.
19. (a) Curran, D. P.; van Elburg, P. A. *Tetrahedron Lett.* **1990**, *31*, 2861–2864; (b) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079–4094.