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STEREOSELECTIVE SYNTHESIS OF CHIRAL α,β-UNSATURATED *tert*-BUTYL SULFOXIDES DERIVATIVES BY THE HORNER-WADSWORTH-EMMONS REACTION

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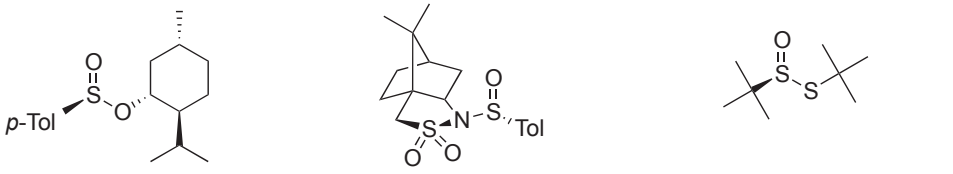
Abstract – A series of chiral α,β-unsaturated *tert*-butyl sulfoxides derivatives was synthesized by the Horner-Wadsworth-Emmons reaction in good (*E*)/(*Z*) ratios. The enantioselectivity up to 89% and the yield up to 90% were achieved. These sulfoxides could be important intermediates in asymmetric synthesis.

Sulfoxides are widely used in organic synthesis.[1-5] They often are valuable intermediates of biologically active compounds (for example, Omeprazole and Lansoprazole) and are good auxiliary or ligands in asymmetric synthesis.[6] In particular, α,β-unsaturated sulfoxides are often employed in carbon-carbon bond-forming reactions as the contained double bond is reactive towards addition[7] and can serve as a dienophile in Diels-Alder reaction.[8] There are two general methods for the preparation of α,β-unsaturated sulfoxides. One may be achieved through the use of vinylic Grignard reagents. As many Grignard reagents can not be prepared easily, this approach is not very practical. The other method is based on Horner-Wittig reaction[9] or Horner-Wadsworth-Emmons Reaction. However, the chirality is often ignored during the preparation, leading to the synthesis of α,β-unsaturated sulfoxide compounds with no or low enantioselectivity. Therefore, the design and synthesis of new chiral α,β-unsaturated sulfoxides attracted



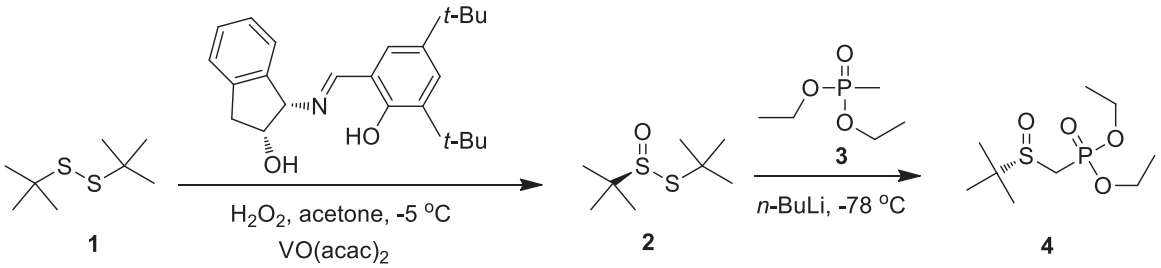
(*S*)-mentyhl *p*-toluenesulfinate *N*-sulfinylsultam *tert*-butyl *tert*-butanethiosulfinate

Figure 1

more attention.[10-13] Optically active sulfoxides were successfully generated from (*S*)-menthyl *p*-toluenesulfinates by Anderson,[14] *N*-sulfinylsultams by Oppolzer[15] and *tert*-butyl *tert*-butanethiosulfinates by Ellman (Figure 1).[16]

Given that *tert*-butylsulfinyl group is a very useful chiral auxiliary in organic synthesis as it has shown high levels of asymmetric induction in a variety of processes, we demonstrate here an approach for the synthesis of chiral α,β-unsaturated sulfoxides containing tertiary butyl group using Horner-Wadsworth-Emmons Reaction (HWE reaction) to achieve good enantioselectivities and (*E*)/(*Z*) ratios. HWE reaction has some advantages over traditional Wittig reaction: 1) the preparation of the starting alkyl phosphonates is easier and cheaper; 2) the phosphonate carbanions are more nucleophilic towards all aldehydes under milder reaction conditions.

α,β-Unsaturated *tert*-butyl sulfoxides were prepared via HWE reaction between diethyl methylphosphonate sulfoxide **4** and aldehydes. The chiral substrate **4** was prepared in good yield and with good enantioselectivity as shown in Scheme 1: the oxidation of disulfide **1** with a chiral ligand in the presence of H_2O_2, followed by nucleophilic substitution reaction with diethyl methylphosphonate **3** using *n*-BuLi in THF at -78 °C. The enantiomeric excess (ee) of **2** was 92% as checked by HPLC analysis, while for **4** was about 89% (if the reaction temperature was -100 °C, ee could be higher by another 1%-3%[17]). For α,β-unsaturated *tert*-butyl sulfoxides, our investigations started with the examination of effects of different bases on the yields and (*E*)/(*Z*) ratios. As shown in Table 1, we found that *n*-BuLi gave the best performance and resulted in 90% yield of *E*-isomer. Other strong and bulky bases such as LiHMDS, LDA or LTMP all gave less yield and (*E*)/(*Z*) ratio. When toluene was used instead of THF as the reaction solvent, both yield and (*E*)/(*Z*) ratio were decreased.



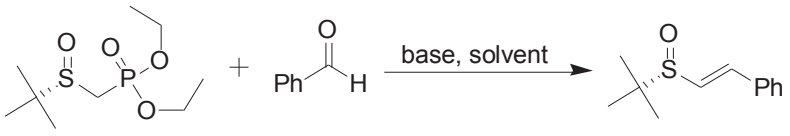
Scheme 1. Synthesis of chiral diethyl methylphosphonate sulfoxide **4**

Using the optimized conditions (entry 1 in Table 1), we shifted to survey the scope of the reaction. A wide range of aryl-, alkyl-, and α,β-unsaturated aldehydes were tested. The results are summarized in Table 2. All substrates could smoothly lead to α,β-unsaturated *tert*-butyl sulfoxides with the *E*-isomers as the major product. It seemed that the 4-substitued aromatic aldehydes with electron-donating group gave

higher (*E*)/(*Z*) ratios and yields than that with electron-withdrawing group. For any 2-substitued aromatic aldehydes, (*E*)/(*Z*) ratios decreased. In addition, the aliphatic aldehydes gave lower yields and (*E*)/(*Z*) ratios.

In order to check if the enantioselectivity was loss or not in the Horner-Wadsworth-Emmons reaction, all *E*-products were subjected HPLC analysis using a chiralpak column. The resulting ee values were also listed in Table 2.

Table 1. Investigations of the effects of different bases and solvents on the Horner-Wadsworth-Emmons reaction[a]

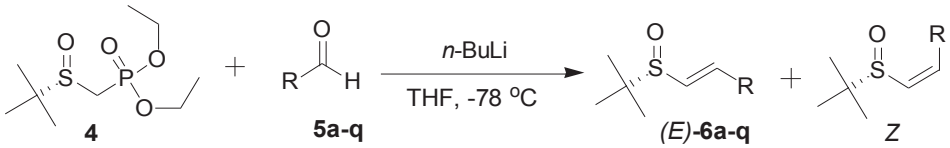


4 **5a** **6a**

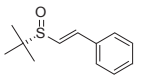
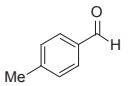
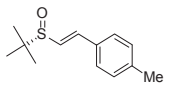
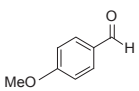
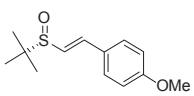
Entry	Base	Solvent	(*E*)/(*Z*) ratio[b]	Yield (%)[c]
1	*n*-BuLi	THF	10/1.0	90
2	LDA	THF	10/2.3	80
3	LTMP	THF	10/2.6	75
4	NaHMDS	THF	10/2.8	78
5	LiHMDS	THF	10/2.3	81
6	*t*-BuOK	THF	10/6.1	15
7	*n*-BuLi	toluene	10/4.3	70

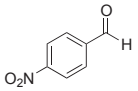
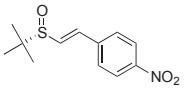
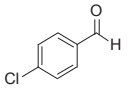
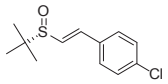
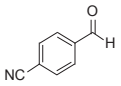
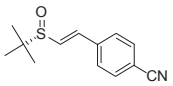
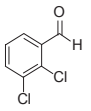
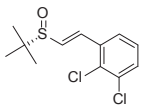
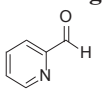
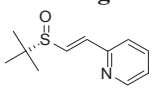
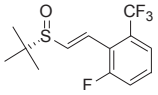
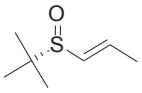
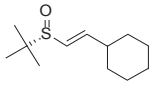
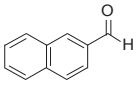
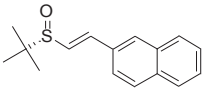
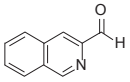
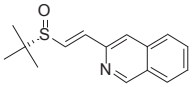
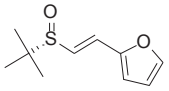
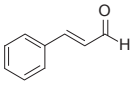
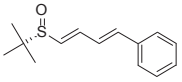
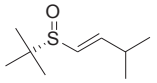
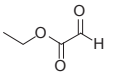
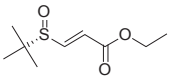
[a]All reactions were carried out using **4** (1.0 mmol), **5a** (2.0 mmol), and base (1.1 mmol) in solvent (5.0 mL) at -78 °C. [b]Determined by ^{1}H NMR analysis of crude product. [c]Isolated yield.

Table 2. The scope of the synthesis of α,β-unsaturated *tert*-butyl sulfoxides using Horner-Wadsworth-Emmons reaction[a]



4 **5a-q** ***(E)*-6a-q** ***Z***

Entry	R	(*E*)/(*Z*) ratio[b]	Major Product (*E*)	Yield (%)[c]	ee (%)[d]
1	 **5a**	10/1.0	 **6a**	90	91
2	 **5b**	10/0.6	 **6b**	87	89
3	 **5c**	10/0.8	 **6c**	88	89

4	 **5d**	10/1.0	 **6d**	65	89
5	 **5e**	10/0.9	 **6e**	70	88
6	 **5f**	10/1.1	 **6f**	64	90
7	 **5g**	10/1.0	 **6g**	67	89
8	 **5h**	10/2.1	 **6h**	61	89
9	 **5i**	10/2.3	 **6i**	67	90
10	 **5j**	10/4.1	 **6j**	72	87
11	 **5k**	10/2.1	 **6k**	80	87
12	 **5l**	10/1.7	 **6l**	77	90
13	 **5m**	10/1.3	 **6m**	62	88
14	 **5n**	10/1.0	 **6n**	65	89
15	 **5o**	10/3.4	 **6o**	73	90
16	 **5p**	10/2.3	 **6p**	68	88
17	 **5q**	10/1.8	 **6q**	70	89

[a]All reactions were carried out using **4** (1.0 mmol), **5** (2.0 mmol), and *n*-BuLi (1.1 mmol) in THF (5.0 mL) at -78 °C. [b]Determined by ^{1}H NMR analysis of crude product. [c]Isolated yield. [d]Determined by HPLC analysis using a chiralpak column.

In summary, we have demonstrated the synthesis of chiral α,β-unsaturated *tert*-butyl sulfoxides using Horner-Wadsworth-Emmons reaction. Up to 90% yield of *E*-isomer was achieved. The enantioselectivity in the starting material **4** could be retained in the HWE reaction, resulting in α,β-unsaturated *tert*-butyl sulfoxides in about 89% ee. As they were important intermediates in the organic synthesis, further applications of these chiral α,β-unsaturated *tert*-butyl sulfoxides such as asymmetric Diels-Alder reaction are in progress.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ operating at 400 MHz and 100 MHz respectively. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (7.28 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.00 ppm). Data are represented as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant in Hertz (Hz), and integration. Products were identified by comparison to spectral data reported in the literature. Mass spectra (both at low resolution and at high resolution) were recorded on a time-of-flight mass spectrometer with an ESI source. High performance liquid chromatography (HPLC) was performed using a chromatograph equipped with a Chiral pak column (250 mm × 4.6 mm) with 10%-1% *i*-PrOH in hexane as the eluent and a flow rate of 1.0-0.7 mL/min. The retention times were 6.4 (R) and 7.9 (S) min for **2** (AS-H column, 1 mL/min, 97:3 hexanes:*i*-PrOH, 254 nm detector wavelength), 11.9 (R) and 12.4 (S) min for **6a** (OJ-H column, 1 mL/min, 97:3 hexanes:*i*-PrOH, 254 nm detector wavelength), 22.5 (R) and 23.4 (S) min for **6b** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 23.5 (R) and 24.8 (S) min for **6c** (OJ-H column, 1 mL/min, 97:3 hexanes:*i*-PrOH, 254 nm detector wavelength), 15.3 (S) and 18.4 (R) min for **6d** (OJ-H column, 1 mL/min, 98:2 hexanes:*i*-PrOH, 254 nm detector wavelength), 36.1 (R) and 40.2 (S) min for **6e** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 13.9 (S) and 14.6 (R) min for **6f** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 45.7 (S) and 49.9 (R) min for **6g** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 31.9 (R) and 35.2 (S) min for **6h** (AS-H column, 0.7 mL/min, 90:10 hexanes:*i*-PrOH, 254 nm detector wavelength). 15.8 (R) and 16.5 (S) min for **6i** (OJ-H column, 0.7 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 11.5 (R) and 14.5 (S) min for **6j** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 8.5 (S) and 9.1 (R) min for **6k** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 37.7 (S) and 41.2 (R) min for **6l** (AS-H column, 1 mL/min, 95:5 hexanes:*i*-PrOH, 254 nm detector wavelength), 27.9 (R) and 30.7 (S) min for **6m** (OJ-H column, 1 mL/min, 98:2 hexanes:*i*-PrOH, 254 nm detector wavelength), 14.2 (R) and 14.8 (S) min for **6n** (OJ-H column, 0.8 mL/min, 98:2 hexanes:*i*-PrOH, 254 nm detector wavelength), 15.0 (S) and 15.9

(R) min for **6o** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 6.4 (R) and 7.3 (S) min for **6p** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), 14.2 (S) and 14.9 (R) min for **6q** (OJ-H column, 1 mL/min, 99:1 hexanes:*i*-PrOH, 254 nm detector wavelength), Optical rotation measurements and HPLC analyses were performed at 30 °C.

Typical procedure for synthesis of 4.

(*S*)-(2-Methylpropane-2-sulfinylmethyl)phosphonic acid diethyl ester (4): A solution of diethyl methylphosphonate **3** (3.0 g, 19.68 mmol) was dissolved in THF (30 mL) under nitrogen. *n*-BuLi (21.65 mmol, 1.6 M in hexanes) was added at -78 °C. After stirring for 10 min at this temperature, a solution of (*R*)-*tert*-butyl *tert*-butanethiosulfinate **2** (1.86 g, 9.84 mmol) in THF (10 mL) was added, and stirring was continued until the reaction reached completion (as checked by TLC). This usually took 1 h. Saturated aqueous ammonium chloride solution (10 mL) was added and the layers were separated. The water layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried with magnesium sulfate. After filtration, the solvents were removed under reduced pressure. The residue was purified using silica gel chromatography with EtOAc as eluent to afford the desired product **4** (1.69 g, 68%); pale green oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23-4.16 (m, 4H), 3.10-2.77 (m, 2H), 1.34 (t, J = 7.2 Hz, 6H), 1.24 (s, 9H).

Typical procedure for synthesis of 6a-q.

(*S*)-(*E*)-[2-(2-Methylpropane-2-sulfinyl)vinyl]benzene (6a): (*S*)-(2-Methylpropane-2-sulfinylmethyl)-phosphonic acid diethyl ester **4** (0.256 g, 1mmol) was dissolved in THF (3 mL) under nitrogen. *n*-BuLi (1.1 mmol, 1.6 M in hexanes) was added at -78 °C. After stirring for 30 min at this temperature, the aldehyde **5a** (0.212 g, 2 mmol) in THF (2 mL) was added, and stirring was continued until the reaction reached completion (as checked by TLC). This usually took 0.5-1 h. Saturated aqueous ammonium chloride solution (10 mL) was added and the layers were separated. The water layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried with magnesium sulfate. After filtration, the solvents were removed under reduced pressure. The crude product was analyzed by ^{1}H NMR. Column chromatography afforded the (*E*)-vinyl sulfoxides and the corresponding (*Z*)-vinyl sulfoxides, as mentioned in Table 2. The residue was loaded on a silica gel using PE / EtOAc (10/1 to 4/1) to afford the desired product **6a** (0.187 g, 90%). The coupling constant of between alkene hydrogen atom is 15.5 Hz, between 12-18 Hz, therefore the absolute configuration of **6a** is (*E*)-vinyl sulfoxides. White solid; mp 80-81 °C; $[\alpha]_D^{20}$ +13.52 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.42 (m, 2H), 7.41-7.37 (m, 3H), 7.25 (d, J = 15.6 Hz, 1H), 6.81(d, J = 15.5 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.1, 129.6, 128.9, 127.6, 126.5, 55.7, 23.1. MS (ESI-TOF) *m/z*: 209.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{16}OS^+$ $[M]^+$ 209.0995, Found: 209.0995.

(*S*)-(*E*)-1-Methyl-4-[2-(2-methylpropane-2-sulfinyl)vinyl]benzene (6b): white solid (0.194 g, 87%); mp 93-94 °C; $[\alpha]_D^{20}$ +8.82 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.25-7.19 (m, 3H), 6.75 (d, *J* = 15.6 Hz, 1H), 2.39 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.1, 131.3, 129.6, 127.6, 124.7, 55.7, 23.1, 21.4. MS (ESI-TOF) *m/z*: 223.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{13}H_{18}OS^+$ $[M]^+$ 223.1151, Found: 223.1149.

(*S*)-(*E*)-1-Methoxy-4-[2-(2-methylpropane-2-sulfinyl)vinyl]benzene (6c): white solid (0.210 g, 88%); mp 114-115 °C; $[\alpha]_D^{20}$ +10.20 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 15.2 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 15.5 Hz, 1H), 3.86 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 138.8, 129.2, 126.8, 123.3, 114.3, 55.5, 55.4, 23.1. MS (ESI-TOF) *m/z*: 239.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{13}H_{18}O_2S^+$ $[M]^+$ 239.1100, Found: 239.1103.

(*S*)-(*E*)-1-[2-(2-Methylpropane-2-sulfinyl)vinyl]-4-nitrobenzene (6d): colorless oil (0.165 g, 65%); $[\alpha]_D^{20}$ +35.80 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 15.2 Hz, 1H), 7.06 (d, *J* = 15.2 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 140.2, 135.3, 132.0, 128.1, 124.3, 56.6, 23.2. MS (ESI-TOF) *m/z*: 254.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{15}NO_3S^+$ $[M]^+$ 254.0845, Found: 254.0841.

(*S*)-(*E*)-1-Chloro-4-[2-(2-methylpropane-2-sulfinyl)vinyl]benzene (6e): white solid (0.169 g, 70%); mp 92-93 °C; $[\alpha]_D^{20}$ +22.16 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 21.6, 8.4 Hz, 4H), 7.20 (d, *J* = 15.2 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 136.8, 135.4, 132.6, 129.2, 128.7, 127.3, 55.9, 23.1. MS (ESI-TOF) *m/z*: 243.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{15}ClOS^+$ $[M]^+$ 243.0605, Found: 243.0600.

(*S*)-(*E*)-4-[2-(2-Methylpropane-2-sulfinyl)vinyl]benzonitrile (6f): white solid (0.149 g, 64%); mp 86-87 °C; $[\alpha]_D^{20}$ +34.71 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* =15.2 Hz 1H), 6.99 (d, *J* = 15.6 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.8, 132.7, 131.0, 128.0, 126.1, 118.4, 112.7, 56.4, 23.2. MS (ESI-TOF) *m/z*: 234.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{13}H_{15}NOS^+$ $[M]^+$ 234.0947, Found: 234.0944.

(*S*)-(*E*)-1,2-Dichloro-3-[2-(2-methylpropane-2-sulfinyl)vinyl]benzene (6g): white solid (0.186 g, 67%); mp 92-93 °C; $[\alpha]_D^{20}$ +8.34 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 15.6 Hz, 1H), 7.49-7.44 (m, 2H), 7.24 (t, *J* = 8 Hz, 1H), 6.86 (d, *J* = 15.6 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.7, 134.0, 132.2, 131.8, 130.8, 127.4, 126.2, 56.0, 23.1. MS (ESI-TOF) *m/z*: 277.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{14}Cl_2OS^+$ $[M]^+$ 277.0215, Found: 277.0210.

(*S*)-(*E*)-2-[2-(2-Methylpropane-2-sulfinyl)vinyl]pyridine (6h): colorless oil (0.127 g, 61%); $[\alpha]_D^{20}$ +21.35 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.0 Hz, 1H), 7.75-7.71 (m,1H), 7.54 (d, *J* = 14.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.28-7.24 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 152.3, 149.8, 137.2, 136.1, 132.1, 124.3, 123.7, 56.2, 23.2. MS (ESI-TOF) *m/z*: 210.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{11}H_{15}NOS^+$ $[M]^+$ 210.0947, Found: 210.0946.

(*S*)-(*E*)-1-Fluoro-2-[2-(2-methylpropane-2-sulfinyl)vinyl]-3-trifluoromethylbenzene (6i): colorless oil (0.197 g, 67%); $[\alpha]_D^{20}$ +128.83 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* =5.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 15.6 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 159.5, 136.3, 136.2, 129.8, 129.7, 126.3, 122.2, 122.1, 122.1, 122.1, 120.0, 119.8, 56.2, 23.0. MS (ESI-TOF) *m/z*: 295.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{13}H_{14}F_4OS^+$ $[M]^+$ 295.0774, Found: 295.0776.

(*S*)-(*E*)-1-(2-Methylpropane-2-sulfinyl)propene (6j): colorless oil (0.105 g, 72%); $[\alpha]_D^{20}$ +27.20 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50-6.38 (m, 1H), 6.13 (dd, *J* = 15.2, 1.6 Hz, 1H), 1.93 (dd, *J* = 6.8, 1.2 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 129.1, 54.23, 22.80, 18.02. MS (ESI-TOF) *m/z*: 147.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_7H_{14}OS^+$ $[M]^+$ 147.0838, Found: 147.0837.

(*S*)-(*E*)-[2-(2-Methylpropane-2-sulfinyl)vinyl]cyclohexane (6k): colorless oil (0.171 g, 80%); $[\alpha]_D^{20}$ +98.22 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (dd, *J* = 15.2, 6.4 Hz, 1H), 6.03 (d, *J* = 15.6 Hz, 1H), 2.20-2.18 (m, 1H), 1.78-1.64 (m, 5H), 1.28 (dd, *J* = 24.4, 11.6 Hz, 3H), 1.19 (s, 9H), 1.14 (d, *J* = 11.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 125.8, 54.3, 40.6, 32.1, 32.0, 25.9, 25.7, 22.8. MS (ESI-TOF) *m/z*: 215.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{12}H_{22}OS^+$ $[M]^+$ 215.1464, Found: 215.1462.

(*S*)-(*E*)-2-[2-(2-Methylpropane-2-sulfinyl)vinyl]naphthalene (6l): white solid (0.199 g, 77%); mp 85-86 °C; $[\alpha]_D^{20}$ +85.43 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 15.2 Hz, 1H), 7.91-7.89 (m, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.60-7.55 (m, 2H), 7.53-7.45 (m, 1H), 6.89 (d, *J* = 15.6 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 133.7, 132.0, 131.1, 129.8, 129.6, 128.6, 126.8, 126.3, 125.4, 124.8, 123.6, 55.8, 23.2. MS (ESI-TOF) *m/z*: 259.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{16}H_{18}OS^+$ $[M]^+$ 259.1151, Found: 259.1144.

(*S*)-(*E*)-3-[2-(2-Methylpropane-2-sulfinyl)vinyl]isoquinoline (6m): white solid (0.161 g, 62%); mp 130-131 °C; $[\alpha]_D^{20}$ +21.97 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.77-7.60 (m, 2H), 7.59-7.52 (m,2H), 7.47 (d, *J* = 15.2 Hz 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 147.6, 138.5, 138.1, 136.4, 130.0, 129.5, 127.6, 127.3, 122.1, 121.3, 57.7, 23.7. MS (ESI-TOF) *m/z*: 260.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{15}H_{17}NOS^+$ $[M]^+$ 260.1104, Found: 260.1097.

(*S*)-(*E*)-2-[2-(2-Methylpropane-2-sulfinyl)vinyl]furan (6n): colorless oil (0.129 g, 65%); $[\alpha]_D^{20}$ +3.72 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.01 (d, *J* = 15.2 Hz, 1H), 6.69 (d, *J* = 15.2 Hz, 1H), 6.51-6.39 (m, 2H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 143.8, 125.1, 124.3, 112.4, 112.0, 55.8, 23.0. MS (ESI-TOF) *m/z*: 199.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{10}H_{14}O_2S^+$ $[M]^+$

199.0787, Found: 199.0783.

(*S*)-(*E*)-[4-(2-Methylpropane-2-sulfinyl)buta-1,3-dienyl]benzene (6o): white solid (0.170 g, 73%); mp 82-83 °C; $[\alpha]_D^{20}$ +52.83 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8 Hz, 2H), 7.42-7.30 (m, 3H), 7.05 (dd, *J* = 14.8, 10.4 Hz, 1H), 6.99-6.88 (m, 1H), 6.83 (d, *J* = 15.6 Hz, 1H), 6.41 (d, *J* = 14.8 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.0, 136.1, 129.2, 128.8, 128.8, 127.0, 125.1, 55.7, 23.0. MS (ESI-TOF) *m/z*: 235.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_{14}H_{18}OS^+$ $[M]^+$ 235.1151, Found: 235.1155.

(*S*)-(*E*)-3-Methyl-1-(2-methylpropane-2-sulfinyl)but-1-ene (6p): colorless oil (0.118 g, 68%); $[\alpha]_D^{20}$ +34.10 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (dd, *J* = 15.6, 6.8 Hz, 1H), 6.05 (dd, *J* = 15.6, 1.2 Hz, 1H), 2.53 (dd, *J* = 13.2, 6.8 Hz, 1H), 1.21 (s, 9H), 1.08 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 125.5, 54.3, 31.3, 22.8, 21.6, 21.5. MS (ESI-TOF) *m/z*: 175.1 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_9H_{18}OS^+$ $[M]^+$ 175.1151, Found: 175.1154.

(*S*)-(*E*)-3-(2-Methylpropane-2-sulfinyl)acrylic acid ethyl ester (6q): colorless oil (0.143 g, 70%); $[\alpha]_D^{20}$ +20.15 (c 1.0, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 14.8 Hz, 1H), 6.66 (d, *J* = 14.8 Hz, 1H), 4.28 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 146.2, 128.2, 61.3, 57.0, 23.3, 14.1. MS (ESI-TOF) *m/z*: 205.0 $[M+H]^+$. HRMS (ESI-TOF) calcd for $C_9H_{16}O_3S^+$ $[M]^+$ 205.0893, Found: 205.0897.

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