Supporting Information for:

***A Highly Stereoselective Vinylogous Pummerer
Reaction Mediated by Me_3SiX***

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Experimental Section

General Method: ^1H -NMR spectra were acquired at either 200 or 300 MHz and ^{13}C -NMR were acquired at 75 MHz (unless otherwise indicated). Chemical shifts (δ) are reported in ppm relative to CDCl_3 (7.26 and 77.0 ppm). Mass spectra (MS) were determined at ionizing voltage of 70 eV. All reactions were carried out in anhydrous solvents and under an Argon atmosphere. THF and Et_2O were distilled from sodium-benzophenone under Argon. $i\text{-Pr}_2\text{NH}$ was distilled from KOH. Flash silica gel column chromatography was performed using silica gel Merk-60 (230-400 mesh). $n\text{-BuLi}$ (2.5 M solution in hexane) was purchased from Aldrich.

(S)-1-Methyl-2-(p-tolylsulfinyl)benzene (8)¹; mp 76-78 °C; $[\alpha]_{\text{D}}^{20}$ -91.0 (c=2.00, acetone); ^1H -NMR (300 MHz) 7.94 (dd, J = 9.3 and 1.6 Hz, 1H), 7.40-7.30 (m, 4H), 7.20 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 7.6 Hz, 1H), 2.32 (s, 3H), and 2.28 (s, 3H).

(S)-1-Ethyl-2-(p-tolylsulfinyl)benzene (9)¹; mp 42-43 °C; $[\alpha]_{\text{D}}^{20}$ -106.4 (c=1.00, CHCl_3); ^1H -NMR (300 MHz) δ 7.94 (m, 1H), 7.52-7.38 (m, 4H), 7.24 (m, 3H), 2.75 (m, 2H), 2.35 (s, 3H), and 1.14 (t, J = 7.5 Hz, 3H).

(S)-Trimethyl-[2-(p-tolylsulfinyl)benzyl]silane (10); A solution of $n\text{-BuLi}$ (0.6 mmol, 2.3 M in hexane) was added to $i\text{Pr}_2\text{NH}$ (0.9 mmol) in THF (3 mL) at 0 °C. After stirring for 20 min, the mixture was cooled to -78 °C. A solution of sulfoxide **8** (0.5 mmol) in THF (2 mL) was added. After stirring for 1 h, Me_3SiBr (2 mmol) was added at -78 °C. When the reaction was completed (less than 1 min), the mixture was hydrolysed (saturated NH_4Cl), extracted (3x10 mL Et_2O), washed (2x10 mL NH_4Cl sat.), dried (MgSO_4) and the solvent was removed under reduced pressure. Compound **10** was purified by flash silica gel column chromatography: 6:1 hexane/ AcOEt ; 63%; colorless oil; $[\alpha]_{\text{D}}^{20}$ +48.3 (c=1.20, CHCl_3); IR (NaCl) 2952, 1590, 1492, 1468, 1248, 1035, and 850 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3) δ 7.83 (dd, J = 7.6 and 1.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.31-7.22 (m, 2H), 7.21 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 8.8 Hz, 1H), 2.33

(s, 3H), 2.29 (d, $J = 14.0$ Hz, 1H), 2.13 (d, $J = 14.0$ Hz, 1H), and 0.03 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 141.7, 141.4, 141.3, 139.0, 130.7, 129.9, 129.5, 125.9, 125.5, 124.9, 23.3, 21.3, and -1.4; MS (FAB) m/z 302 ($M+1$, 15), 287 (27), 211 (55), 197 (100); HRMS [$M+1$] Calcd. for $\text{C}_{17}\text{H}_{22}\text{OS}$: 302.1160. Found: 302.1151; Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{OSSi}$; C, 67.50; H, 7.33; S, 10.60. Found: C, 67.45; H, 7.39; S, 10.90.

(1R)-{1-[2-(*p*-Tolylthio)phenyl]ethoxy}trimethylsilane (11). A solution of *n*-BuLi (0.6 mmol, 2.3 M in hexane) was added to $^i\text{Pr}_2\text{NH}$ (0.89 mmol) in THF (3 mL) at 0 °C. After stirring for 30 min, the mixture was cooled to -78 °C. A solution of sulfoxide **9** (0.5 mmol) in THF (2 mL) was then added. After stirring for 1 h, redistilled Me_3SiCl (1.5 mmol) was added at -78 °C. When the reaction was completed (less than 1 min), the mixture was hydrolysed at -78 °C with H_2O (2 mL), extracted (2x10 mL Et_2O), dried (MgSO_4) and the solvent was removed under reduced pressure. Compound **11** was purified by flash silica gel column chromatography using a 50:1 *n*-hexane/ AcOEt mixture; 70%; colorless oil; $[\alpha]_{\text{D}}^{20}$ -62.7 ($c=1.10$, CHCl_3); IR (NaCl) 2957, 2925, 1492, 1466, 1250 cm^{-1} ; ^1H -NMR (75 MHz, CDCl_3) δ 7.67 (d, $J = 7.9$ Hz, 1H), 7.35-7.13 (m, 7H), 5.42 (q, $J = 6.3$ Hz, 1H), 2.37 (s, 3H), 1.41 (d, $J = 6.3$ Hz, 3H), and 0.08 (s, 9H); ^{13}C -NMR (300 MHz, CDCl_3) δ 147.5, 136.8, 132.4, 132.2, 131.7, 130.8, 129.9, 127.6, 127.4, 126.4, 67.5, 26.2, 21.0, and -0.01.

General Procedure Used for Table 2.

A solution of *n*-BuLi (0.5 mmol, 2.3 M in hexane) was added to $^i\text{Pr}_2\text{NH}$ (0.9 mmol) in THF (3 mL) at 0 °C. After stirring for 30 min, the mixture was cooled to -78 °C. A solution of sulfoxide **8** (0.5 mmol) in THF (2 mL) was added. After stirring for 1 h, the corresponding alkyl iodide or bromide (0.8 mmol) was added at -78 °C. When the reaction was completed (less than 1 min), the mixture was hydrolysed (saturated NH_4Cl), extracted (3x10 mL Et_2O), washed (2x10 mL NH_4Cl sat.), dried (MgSO_4) and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column.

(S)-1-Ethyl-2-(p-tolylsulfinyl)benzene (9); Electrophile used: methyl iodide; 3:1 *n*-hexane/AcOEt mixture; 98 %; mp 42-43 °C; $[\alpha]_D^{20}$ -106.4 (c=1.0, CHCl₃); ¹H-NMR (300 MHz) δ 7.94 (m, 1H), 7.52-7.38 (m, 4H), 7.24 (m, 3H), 2.75 (m, 2H), 2.35 (s, 3H), and 1.14 (t, *J* = 7.5 Hz, 3H).

(S)-1-Propyl-2-(p-tolylsulfinyl)benzene (12); Electrophile used: ethyl iodide; 4:1 *n*-hexane/AcOEt mixture; 92%; colorless oil; $[\alpha]_D^{20}$ -123.4 (c=1.00, CHCl₃); IR (NaCl) 2960, 2931, 2871, 1594, 1493, 1468 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.94–7.85 (m, 1H), 7.49-7.12 (m, 7H), 2.72-2.65 (m, 2H), 2.35 (s, 3H), 1.70-1.60 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 142.7, 142.1, 141.9, 141.5, 130.9, 129.9 (2C), 129.5, 127.1, 125.9 (2C), 124.8, 33.8, 24.0, 21.3, 13.9; HRMS [M+1] Calcd. for C₁₆H₁₈OS: 258.1070. Found: 258.1078.

(S)-1-Benzyl-2-(p-tolylsulfinyl)benzene (13); Electrophile used: benzyl bromide; 3:1 *n*-hexane/AcOEt mixture; 93%; colorless oil; $[\alpha]_D^{20}$ -177.4 (c=1.10, CHCl₃); IR (NaCl) 2923, 1595, 1493, 1453 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.97 (d, *J* = 9.3 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.45-7.20 (m, 8H), 7.17 (d, *J* = 8.3 Hz, 2H), 3.20-3.10 (m, 1H), 3.07-2.88 (m, 2H), 2.85-2.70 (m, 1H), and 2.39 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 142.9, 141.8, 141.6, 140.8, 139.6, 131.0, 130.0, 129.8, 128.4, 128.3, 127.5, 126.2, 125.9, 125.1, 37.0, 33.8, and 21.3; MS (FAB) *m/z* 321 (M+1, 100), 303 (22), 154 (31), 137 (22), 136 (25), 132 (24); HRMS [M+1] Calcd. for C₂₁H₂₁OS: 321.1313. Found: 321.1223.

(S)-1-(2-Phenylethyl)-2-(p-tolylsulfinyl)benzene (14); Electrophile used: 2-phenylethyl iodide; 3:1 *n*-hexane/AcOEt mixture; 81%; colorless oil; $[\alpha]_D^{20}$ -125.5 (c=1.00, CHCl₃); IR (NaCl) 2925, 2860, 1595, 1494, 1470 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 8.00 (d, *J* = 9.2 Hz, 1H), 7.55-7.10 (m, 12H), 2.90-2.72 (m, 1H), 2.70-2.56 (m, 3H), 2.37 (s, 3H), 2.00-1.84 (m, 1H), and 1.80-1.60 (m, 1H); ¹³C-NMR (75 MHz, CDCl₃) δ 142.7, 141.6, 141.5, 140.0, 130.9, 129.9, 129.6, 128.4, 128.3, 127.2, 126.1, 126.0, 125.9, 124.7, 35.6, 32.2, 31.4, and 21.3; MS (FAB) *m/z* 335 (M+1, 100), 271 (27), 155

(27), 154 (94), 137 (62), 136 (67); HRMS [M+1] Calcd. for C₂₂H₂₃OS: 335.1469.

Found: 335.1480.

(S)-1-[2-(3,4-Dimethoxyphenyl)ethyl]-2-(p-tolylsulfinyl)benzene (15); Electrophile used: 2-(3,4-dimethoxyphenyl)ethyl iodide; 1:1 *n*-hexane/AcOEt mixture; 85%; colorless oil; $[\alpha]_D^{20}$ -145.0 (*c*=0.10, CHCl₃); IR (NaCl) 2934, 1591, 1515, 1564 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 9.3 Hz, 1H), 7.40-7.30 (m, 4H), 7.20-7.24 (m, 3H), 6.78 (d, *J* = 8.6 Hz, 1H), 6.68 (m, 2H), 3.84 (s, 6H), 2.81-2.70 (m, 4H), 2.31 (s, 3H), and 2.01-1.67 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 148.7, 147.1, 142.7, 141.8, 141.4, 140.0, 134.0, 130.8, 129.8, 129.5, 127.1, 125.9, 124.6, 120.1, 111.7, 112.2, 55.7, 55.6, 35.0, 32.3, 31.3, and 21.2; MS (FAB) *m/z* 394 (M+1, 35), 377 (96), 213 (90), 151 (100); HRMS [M+1] Calcd. for C₂₄H₂₆O₃S: 394.1602. Found: 394.1614; Anal. Calcd for C₂₄H₂₆O₃S: C, 73.06; H, 6.64; S, 8.13. Found: C, 72.82; H, 6.55; S, 8.06.

(S)-1-Allyl-2-(p-tolylsulfinyl)benzene (16); Electrophile used: allyl bromide; 3:1 *n*-hexane/AcOEt mixture; 82%; colorless oil; $[\alpha]_D^{20}$ -145.5 (*c*=1.00, CHCl₃); IR (NaCl) 2924, 1640, 1595, 1493, 1471 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 9.3 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.42-7.35 (m, 2H), 7.24-7.16 (m, 3H), 5.86-5.70 (m, 1H), 5.02-4.92 (m, 2H), 2.93-2.80 (m, 1H), 2.77-2.64 (m, 1H), 2.34 (s, 3H), 2.32-2.12 (m, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 142.9, 141.8, 141.6, 139.6, 136.9, 130.9, 129.9, 129.6, 127.3, 125.9, 124.8, 115.5, 34.5, 31.1, 21.3; MS (FAB) *m/z* 271 (M+1, 100), 253 (17), 154 (40), 137 (279), 136 (29), 107 (12); HRMS [M+1] Calcd. for C₁₇H₁₉OS: 271.1156. Found: 271.1145; Anal. Calcd for C₁₇H₁₈OS: C, 75.51; H, 6.71; S, 11.86. Found: C, 74.98; H, 6.76; S, 11.69.

(S)-1-(2-Methoxyethyl)-2-(p-tolylsulfinyl)benzene (17); Electrophile used: iodomethyl methyl ether; 1:1 *n*-hexane/AcOEt mixture; 94%; pale yellow oil; $[\alpha]_D^{20}$ -89.8 (*c*=1.18, CHCl₃); IR (NaCl) 2924, 1492, 1471, 1442, 1397, 1382 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.93 (d, *J* = 9.3 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.45-7.30 (m, 2H), 7.30-7.16 (m, 3H), 3.60-3.55 (m, 2H), 3.30 (s, 3H), 3.10-2.90 (m, 2H), and 2.37 (m, 3H); ¹³C-NMR

(75 MHz, CDCl₃) δ 143.5, 141.7, 141.5, 136.9, 130.9, 130.1, 129.9, 127.7, 125.9, 125.1, 72.2, 58.5, 31.9, 21.3; Anal. Calcd for C₁₆H₁₈O₂S: C, 70.04; H, 6.61; S, 11.69. Found: C, 69.90; H, 6.46; S, 11.28.

[3-(2-*p*-Tolylsulfinylbenzene)propoxy]triisopropylsilane (18); Electrophile used: (3-iodopropoxy)triisopropylsilane; 2:1 *n*-hexane/AcOEt mixture; 53%; pale yellow oil; $[\alpha]_D^{20}$ -54.0 (*c*=0.5, CHCl₃); IR (NaCl) 2865, 1595, 1493, 1465 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.93 (d, *J* = 9.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.42-7.39 (m, 2H), 7.23-7.18 (m, 3H), 3.69 (t, *J* = 6.1 Hz, 2H), 3.00-2.70 (m, 2H), 2.32 (s, 3H), 1.86-1.60 (m, 2H), and 1.10-1.01 (m, 21H); ¹³C-NMR (75 MHz, CDCl₃) δ 142.9, 142.0, 141.4, 140.1, 130.8, 129.8, 129.5, 127.0, 125.9, 124.6, 62.4, 33.7, 28.2, 21.2, 17.9, and 11.9; Anal. Calcd for C₂₅H₃₈O₂SSi: C, 69.71; H, 8.89; S, 7.44. Found: C, 69.95; H, 8.41; S, 7.55.

***N*-(3-(2-*p*-Tolylsulfinylbenzene)propyl)phthalimide (19);** Electrophile used: *N*-(2-iodoethyl)phthalimide; 1:2 *n*-hexane/AcOEt mixture; 51%; pale yellow oil; $[\alpha]_D^{20}$ -72.3 (*c*=1.1, CHCl₃); IR (NaCl) 1717, 1492, 1362, 1015 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 7.78 (d, *J* = 7.3 Hz, 1H), 7.75-7.52 (m, 4H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.39-7.24 (m, 5H), 4.10-3.60 (m, 4H), 3.20-3.05 (m, 1H), 2.75-2.60 (m, 1H), and 2.37 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃) δ 169.6, 133.8, 133.3, 131.9, 131.4, 127.2, 126.4, 125.9, 125.6, 121.9, 121.7, 121.1, 121.0, 119.9, 118.4, 39.3, 34.9, 33.9, and 16.9.

General Procedure Used for Table 3. A solution of *n*-BuLi (0.6 mmol, 2.3 M in hexane) was added to ^{*i*}Pr₂NH (0.89 mmol) in THF (3 mL) at 0 °C. After stirring for 30 min, the mixture was cooled to -78 °C. A solution of the appropriate sulfoxide (*i.e.* **12-19**) (0.5 mmol) in THF (2 mL) was then added. After stirring for 1 h, freshly distilled TMSCl (1.5 mmol) was added at -78 °C. When the reaction was completed (less than 1 min), the mixture was hydrolysed (a mixture of 1 mL NH₄Cl sat mixture and 1 mL of CH₃CN² or 1 mL HF*py at -78 °C), increasing the temperature to rt overnight. The mixture was extracted (3x10 mL Et₂O), washed (2x10 mL NH₄Cl sat.), dried (MgSO₄) and the solvent

was removed under reduced pressure. The residue was purified by flash silica gel column chromatography.

(1R)-1-[2-(*p*-Tolylsulfanyl)phenyl]ethan-1-ol (20); 2:1 *n*-hexane/AcOEt mixture; 69%; colorless oil; $[\alpha]_D^{20}$ -60.0 ($c=0.76$, CHCl_3); IR (NaCl) 3385 (bs), 2970, 2924, 2855, 1590, 1491, 1090, and 1016 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.58 (dd, $J = 7.3$ Hz and 0.8 Hz, 1H), 7.29 (dt, $J = 6.5$ and 2.4 Hz, 1H), 7.21-7.07 (m, 6H), 5.39 (dq, $J = 6.5$ and 3.6 Hz, 1H), 2.30 (s, 3H), 2.03 (d, $J = 3.6$ Hz, 1H), and 1.45 (d, $J = 6.5$ Hz, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 146.1, 137.1, 132.8, 132.5, 132.0, 130.8, 130.1, 128.0, 127.8, 125.8, 67.3, 24.0, 21.0; MS (FAB) m/z 245 ($M+1$, 21), 154 (100), 136 (71), 107 (28); HRMS $[M+1]$ Calcd. for $\text{C}_{15}\text{H}_{16}\text{OS}$: 244.0921. Found: 244.0917.

(1R)-1-[2-(*p*-Tolylsulfanyl)phenyl]propan-1-ol (21); 2:1 *n*-hexane/AcOEt mixture; 67%; colorless oil; $[\alpha]_D^{20}$ -23.4 ($c=1.8$, CHCl_3); IR (NaCl) 3405 (bs), 1641, 1491, 1462, 1437 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.59 (dd, $J = 7.3$ and 0.8 Hz, 1H), 7.38-7.18 (m, 5H), 7.14 (d, $J = 8.1$ Hz, 2H), 5.20 (t, $J = 6.6$ Hz, 1H), 2.37 (s, 3H), 2.09 (bs, 1H), 1.86-1.79 (m, 2H), and 1.01 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C-NMR}$ (75 MHz) δ 145.1, 137.1, 132.4, 130.9(2C), 130.1, 127.9(2C), 127.6, 127.4, 72.6, 31.0, 21.0, and 10.3; Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{OS}$: C, 74.38; H, 7.02; S, 12.41. Found: C, 74.20; H, 6.66; S, 12.29.

(1R)-2-Phenyl-1-[2-(*p*-tolylsulfanyl)phenyl]ethan-1-ol (22); 2:1 *n*-hexane/AcOEt mixture; 51%; colorless oil; $[\alpha]_D^{20}$ -41.5 ($c=1.4$, CHCl_3); IR (NaCl) 3375 (bs), 2919, 1602, 1491, 1453 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz) δ 7.65 (d, $J = 7.9$ Hz, 1H), 7.38-7.17 (m, 10H), 7.12 (d, $J = 8.6$ Hz, 2H), 5.44 (dt, $J = 9.5$ and 3.2 Hz, 1H), 3.12 (dd, $J = 13.4$ and 3.2 Hz, 1H), 2.80 (dd, $J = 13.4$ and 9.5 Hz, 1H), 2.33 (s, 3H), 2.04 (d, $J = 3.3$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 144.5, 138.5, 137.0, 132.8, 132.5, 132.0, 130.8, 130.1, 129.5, 128.5, 128.0, 127.8, 126.6, 126.3, 72.2, 45.0, and 21.0; Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{OS}$: C, 78.71; H, 6.29; S, 10.01. Found: C, 78.58; H, 6.20; S, 10.01.

(1R)-3-Phenyl-1-[2-(*p*-tolylsulfanyl)phenyl]propan-1-ol (23); 2:1 *n*-hexane/AcOEt mixture; 54%; colorless oil; $[\alpha]_D^{20}$ -17.1 ($c=0.8$, CHCl_3); IR (NaCl) 3405, 2921, 2859,

1602, 1589, 1492, 1454 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3) δ 7.68 (d, $J = 7.7$ Hz, 1H), 7.40-7.05 (m, 12H), 5.26 (m, 1H), 2.90-2.60 (m, 2H), 2.32 (s, 3H), 2.10-1.90 (m, 3H); ^{13}C -NMR (75 MHz, CDCl_3) δ 145.4, 141.8, 137.0, 132.9, 130.7 (2C), 130.0 (2C), 128.4, 128.3, 128.0, 127.9, 126.5, 125.7, 70.9, 39.6, 32.4, and 20.1; MS (FAB) m/z 334 ($M+1$, 75), 225 (84), 137 (100), 91 (65); HRMS [$M+1$] Calcd. for $\text{C}_{22}\text{H}_{22}\text{OS}$: 334.1391. Found: 334.1392.

(1R)-3-(3,4-Dimethoxyphenyl)-1-[2-(*p*-tolylsulfanyl)phenyl]-propan-1-ol (24); 2:1 *n*-hexane/AcOEt mixture; 58%; colorless oil; $[\alpha]_{\text{D}}^{20}$ -80.8 ($c=1.2$, CHCl_3); IR (NaCl) 3357 (bs), 2923, 1682, 1639, 1545, 1492 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3) δ 7.58 (dd, $J = 7.7$ and 1.1 Hz, 1H), 7.38-7.14 (m, 7H), 6.80-6.68 (m, 3H), 5.24 (t, $J = 6.4$ Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.90-2.60 (m, 2H), 2.32 (s, 3H), 2.1 (bs, 1H), and 2.01 (m, 2H); ^{13}C -NMR (75 MHz, CDCl_3) δ 148.8, 147.1, 145.3, 137.0, 134.4, 132.7, 130.7 (2C), 130.0, 127.9, 127.8, 126.4 (2C), 120.2, 111.7, 111.2, 70.7, 55.8, 55.7, 39.7, 21.9, and 21.0; Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{O}_3\text{S}$: C, 73.06; H, 6.64; S, 8.13. Found: C, 72.93; H, 6.77; S, 7.94.

(1R)-1-[2-(*p*-Tolylsulfanyl)phenyl]-3-buten-1-ol (25); 2:1 *n*-hexane/AcOEt mixture; 65%; pale yellow oil; $[\alpha]_{\text{D}}^{20}$ -99.5 ($c=0.9$, CHCl_3); IR (NaCl) 3405 (bs), 2932, 1591, 1515, 1463, cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3) δ 7.57 (dd, $J = 8.1$ and 0.8 Hz, 1H), 7.38-7.14 (m, 5H), 7.11 (d, $J = 8.5$ Hz, 2H), 5.92-5.78 (m, 1H), 5.32-5.25 (m, 1H), 5.24-5.00 (m, 2H), 2.60-2.30 (m, 2H), 2.32 (s, 3H), 2.16 (d, $J = 3.4$ Hz, 1H); ^{13}C -NMR (75 MHz, CDCl_3) δ 144.4, 137.1, 134.7, 132.9, 132.5, 132.0, 130.8, 130.1, 128.1, 127.7, 126.4, 118.4, 70.1, 42.7, and 21.1; Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{OS}$: C, 75.51; H, 6.71; S, 11.86. Found: C, 75.64; H, 6.71; S, 11.19.

(1R)-1-[2-(*p*-Tolylsulfanyl)phenyl]-propan-1-3-diol (26); 1:1 *n*-hexane/AcOEt mixture; 56%; colorless oil; $[\alpha]_{\text{D}}^{20}$ -58.4 ($c=0.9$, CHCl_3); IR (NaCl) 3356 (bs), 2922, 1698, 1491, 1049 cm^{-1} ; ^1H -NMR (300 MHz) δ 7.62 (d, $J = 9.3$ Hz, 1H), 7.33-7.12 (m, 5H), 7.10 (d, $J = 8.1$ Hz, 2H), 5.46 (dd, $J = 7.6$ and 4.2 Hz, 1H), 3.88-3.75 (m, 2H), 3.15 (bs, 1H), 2.56

(bs, 1H), 2.32 (s, 3H), 1.90-1.80 (m, 2H); ^{13}C -NMR (75 MHz) δ 144.7, 137.2, 132.7, 132.3, 130.9, 130.1 (2C), 128.0, 127.8, 126.4, 71.4, 61.8, 39.4, and 21.0.

(1R)-1-[2-(*p*-Tolylsulfanyl)]phenyl]ethene (27); 1:1 *n*-hexane/AcOEt mixture; 31%; colorless oil; $[\alpha]_{\text{D}}^{20}$ -135.8 ($c=0.6$, CHCl_3); ^1H -NMR (300 MHz, CDCl_3) δ 7.97 (dd, $J=7.2$ and 2.1 Hz, 1H), 7.60-7.10 (m, 8H), 5.70 (dd, $J=17.3$ and 0.9 Hz, 1H), 5.37 (dd, $J=10.9$ and 0.9 Hz, 1H), 2.33 (s, 3H); ^{13}C -NMR (75 MHz, CDCl_3) δ 141.4, 131.8, 130.9, 130.0, 129.9, 128.9, 128.5, 128.4, 126.1, 125.3, 124.3, 118.1, and 21.4; MS (FAB) m/z 242 ($M+1$, 11), 211 (43), 174 (21), 137 (100); HRMS [$M+1$] Calcd. for $\text{C}_{15}\text{H}_{14}\text{OS}$: 242.0765. Found: 244.0758.

General Procedure Used for Mosher's Ester Preparation.³

To a solution of the appropriate alcohol **20-25** (0.05 mmol) in CH_2Cl_2 (1 mL) was added Et_3N (14 μL , 0.1 mmol), DMAP (0.01 mmol) and (*S*)-MTPA-Cl or (*R*)-MTPA-Cl (0.1 mmol) under an Argon atmosphere. When the reaction was completed, the mixture was hydrolysed (HCl 5%, 1 mL), extracted (3x1 mL, CH_2Cl_2), washed (2x2 mL NaHCO_3 sat), dried (Na_2SO_4) and the solvent was removed under reduced pressure.

(1R)-1-[2-(*p*-Tolylsulfanyl)]phenyl]ethan-1-ol O-(*R*)-MTPA Ester (29a); ^1H -NMR (400 MHz, CDCl_3) δ 7.47 (d, $J=7.2$ Hz, 1H), 7.41-7.12 (m, 7H), 7.10 (d, $J=8.0$ Hz, 2H), 6.63 (q, $J=6.8$ Hz, 1H), 3.55 (s, 3H), 2.31 (s, 3H), 1.53 (d, $J=6.8$ Hz, 3H).

(1R)-1-[2-(*p*-Tolylsulfanyl)]phenyl]ethan-1-ol O-(*S*)-MTPA Ester (29b); ^1H -NMR (400 MHz, CDCl_3) δ 7.48 (d, $J=8.0$ Hz, 1H), 7.42-7.16 (m, 7H), 7.10 (d, $J=8.0$ Hz, 2H), 6.68 (q, $J=6.8$ Hz, 1H), 3.50 (s, 3H), 2.32 (s, 3H), 1.47 (d, $J=6.8$ Hz, 3H).

(1R)-1-[2-(*p*-Tolylsulfanyl)]phenyl]propan-1-ol O-(*R*)-MTPA Ester (30a); ^1H -NMR (300 MHz, CDCl_3) δ 7.50-7.15 (m, 6H), 7.11 (d, $J=7.9$ Hz, 2H), 6.55 (dd, $J=8.1$ and 5.4 Hz, 1H), 3.50 (s, 3H), 2.32 (s, 3H), 1.95-1.75 (m, 2H), 0.85 (t, $J=7.3$ Hz, 3H).

(1R)-1-[2-(*p*-Tolylsulfanyl)]phenyl]propan-1-ol O-(*S*)-MTPA Ester (30b); ^1H -NMR (300 MHz, CDCl_3) δ 7.50-7.07 (m, 8H), 6.44 (dd, $J=8.4$, 4.7 Hz, 1H), 3.56 (s, 3H), 2.32 (s, 3H), 1.90-1.79 (m, 2H), 0.95 (t, $J=7.3$ Hz, 3H).

(1R)-2-Phenyl-1-[2-(*p*-tolylsulfanyl)phenyl]ethan-1-ol O-(*R*)-MTPA Ester (31a); ¹H-NMR (300 MHz, CDCl₃) δ 7.60-7.50 (m, 1H), 7.50-7.11 (m, 17H), 6.71 (dd, *J* = 10.2 and 3.5 Hz, 1H), 3.23 (s, 3H), 3.12-2.95 (m, 2H), 2.32 (s, 3H).

(1R)-2-Phenyl-1-[2-(*p*-tolylsulfanyl)phenyl]ethan-1-ol O-(*S*)-MTPA Ester (31b); ¹H-NMR (300 MHz, CDCl₃) δ 7.54 (m, 1H), 7.42-7.04 (m, 17H), 6.87 (dd, *J* = 8.3 and 5.4 Hz, 1H), 3.30 (s, 3H), 3.10-3.03 (m, 2H), 2.31 (s, 3H).

(1R)-3-Phenyl-1-[2-(*p*-tolylsulfanyl)phenyl]propan-1-ol O-(*R*)-MTPA Ester (32a); ¹H-NMR (300 MHz, CDCl₃) δ 7.50-7.08 (m, 15H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.65 (dd, *J* = 8.8 and 3.8 Hz, 1H), 3.51 (s, 3H), 2.80-2.40 (m, 2H), 2.32 (s, 3H), and 2.10-1.98 (m, 2H).

(1R)-3-Phenyl-1-[2-(*p*-tolylsulfanyl)phenyl]propan-1-ol O-(*R*)-MTPA Ester (32b); ¹H-NMR (300 MHz, CDCl₃) δ 7.52-7.10 (m, 15H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.58 (dd, *J* = 8.7, 4.1 Hz, 1H), 3.57 (s, 3H), 2.55-2.40 (m, 2H), 2.32 (s, 3H), 2.00-1.80 (m, 2H).

(1R)-3-(3,4-Dimethoxyphenyl)-1-[2-(*p*-tolylsulfanyl)phenyl]propan-1-ol O-(*R*)-MTPA Ester (33a); ¹H-NMR (300 MHz, CDCl₃) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.41-7.18 (m, 10H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.77-6.55 (m, 1H), 6.64 (dd, *J* = 8.9 and 4.1 Hz, 1H), 6.58-6.48 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.51 (s, 3H), 2.60-2.40 (m, 2H), 2.31 (s, 3H), 2.20-1.90 (m, 2H).

(1R)-3-(3,4-Dimethoxyphenyl)-1-[2-(*p*-tolylsulfanyl)phenyl]propan-1-ol O-(*S*)-MTPA Ester (33b); ¹H-NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.41-7.10 (m, 12H), 6.75 (m, 3H), 6.60 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.51 (s, 3H), 2.52-2.44 (m, 2H), 2.31 (s, 3H), 2.20-1.91 (m, 2H).

(1R)-1-[2-(*p*-Tolylsulfanyl)phenyl]-3-buten-1-ol O-(*R*)-MTPA Ester (34a); ¹H-NMR (300 MHz, CDCl₃) δ 7.50-7.45 (m, 1H), 7.40-7.07 (m, 12H), 6.58 (dd, *J* = 8.1 and 4.9 Hz, 1H), 5.68-6.64 (m, 1H), 4.95-4.86 (m, 2H), 3.49 (s, 3H), 2.60-2.50- (m, 2H), and 2.32 (s, 3H).

(1R)-1-[2-(*p*-Tolylsulfanyl)phenyl]-3-buten-1-ol O-(*S*)-MTPA Ester (34b); ¹H-NMR (300 MHz, CDCl₃) δ 7.50-7.45 (m, 1H), 7.40-7.18 (m, 10H), 7.10 (d, *J* = 8.0 Hz, 2H),

6.68 (dd, $J = 8.6, 4.4$ Hz, 1H), 5.73-5.68 (m, 1H), 5.08-4.98 (m, 2H), 3.55 (s, 3H), 2.65-2.53 (m, 2H), and 2.32 (s, 3H).

Procedure for the Preparation of the Mosher Ester³ of Diol 26. To a solution of diol **26** (0.1 mmol) in CH_2Cl_2 (2 mL) was added Et_3N (28 μL , 0.1 mmol), DMAP (0.02mmol) and TBSCl (0.1 mmol). After stirring for 12 h, the mixture was hydrolysed (NH_4Cl sat.), washed (2x5 ml NH_4Cl sat), and the solvent was removed under reduced pressure. To the crude reaction residue in CH_2Cl_2 (1 mL) was added Et_3N (28 μL , 0.1 mmol), DMAP (0.02mmol) and (*S*)-MTPA-Cl or (*R*)-MTPA-Cl (0.1 mmol) under an Argon atmosphere. When the reaction was completed, the mixture was hydrolysed (HCl 5%, 1 mL), extracted (3x1 mL, CH_2Cl_2), washed (2x2 mL NaHCO_3 sat), dried (Na_2SO_4) and the solvent was removed under reduced pressure.

(1*R*)-3-*tert*-Butyldimethylsilyloxy-1-[2-(*p*-tolylsulfanyl)phenyl]propan-1-ol O-(*R*)-MTPA Ester (35a); $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.45 (d, $J = 6.4$ Hz, 1H), 7.40-7.15 (m, 5H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.73 (dd, $J = 9.2$ and 4.1 Hz, 1H), 3.60-3.45 (m, 2H), 3.49 (s, 3H), 2.35 (s, 3H), 2.05-1.95 (m, 2H), 0.86 (s, 9H), and -0.01 (s, 6H).

(1*R*)-3-*tert*-Butyldimethylsilyloxy-1-[2-(*p*-tolylsulfanyl)phenyl]propan-1-ol O-(*S*)-MTPA Ester (35b); $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.45-7.08 (m, 8H), 6.67 (dd, $J = 9.2, 4.2$ Hz, 1H), 3.75-3.65 (m, 2H), 3.54 (s, 3H), 2.35 (s, 3H), 2.05-2.00 (m, 2H), 0.87 (s, 9H), and 0.02 (s, 6H).

References:

- (1) Sulfoxides **8** and **9** were prepared following described procedures, see: (a) García Ruano, J. L.; Aranda, M.; Carreño, M. C.; Toledo, M. A. *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 2376. (b) García Ruano, J. L.; Alemán J.; Soriano, J. F. *Org. Lett.*, **2003**, 5, 677.
- (2) Shaabani, A.; Karimi, A. R.; Alamshahi, A. R. *Indian J. Chem.* **2002**, 41, 1972.

- (3) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092.