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Supporting Information

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Highly Enantioselective Reactions of α-Sulfonyl Carbanion of Trifluoromethyl Sulfones

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General. All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silicagel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or p-anisaldehyde in ethanol/ heat. Column chromatography was carried out on a column packed with silicagel 60N spherical neutral size 63-210 μm. The ^{1}H-NMR (200 MHz), ^{19}F-NMR (188 MHz), and ^{13}C-NMR (50.3 MHz) spectra for solution in $CDCl_3$, were recorded on a Varian Gemini-200. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or $CHCl_3$. HPLC analyses were performed on a JASCO PU-2080 Plus or SHIMADZU LC-2010A HT using 4.6 x 250 mm CHIRALPAK AD-H or CHIRALCEL OJ-H or CHIRALCEL OD-H or CHIRALPAK AS-H column. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer.

General procedure for the enantioselective reaction of α-sulfonyl carbanions using bis(oxazoline)s: 1,2-Diphenyl-2-trifluoromethanesulfonylethanol (2f): *n*BuLi (0.11 mL, 0.142 mmol) was added at –30 ^{o}C to a solution of bis(oxazoline) **3g** (17.3 mg, 0.035 mmol) and sulfone **1f** (26.5 mg, 0.118 mmol) in toluene (1.5 mL) and the solution was stirred for 15 min. Benzaldehyde (0.018 ml, 0.177 mmol) was then added. After stirring for 1 h, TMSCl (0.017 ml, 0.13 mmol) was added and the mixture was stirred for an additional 12 h. Aqueous NH_4Cl was added to the reaction mixture and the aqueous layer was extracted with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product which was purified by column chromatography (silica gel 15 g, hexane/ethyl acetate = 90:10) to give *syn*-**2f** (28.4 mg, 74%, 94% ee). The enantiomer ratio was determined

by HPLC analysis using chiralpak AD-H. *syn*-**2f**; $[\alpha]_D^{26}$ +1.03 (*c* 0.59, $CHCl_3$, 90% ee); ^{1}H NMR δ 3.01 (br, 1H), 4.76 (d, *J* = 9.9 Hz, 1H), 5.59 (d, *J* = 9.9 Hz, 1H), 7.11-7.26 (m, 10H); ^{13}C NMR δ 74.0, 75.1, 116.4, 122.9, 126.7, 126.9, 128.0, 128.2, 128.5, 129.5, 130.0, 138.5; ^{19}F NMR δ –73.2; IR (KBr) 3538, 3067, 3035, 2924, 2853, 2359, 1716, 1493, 1455, 1346, 1296, 1203, 1105, 1053, 1034, 917, 857, 802, 763, 698, 651, 632, 620 cm^{-1}; EIMS *m/z* 330 (M^+,12), 197 (14), 165 (22), 107, (100), 91 (77), 79 (83). HPLC (CHIRALPAK AD-H hexane/*i*PrOH = 95/5, flow rate 1.0 ml/min) t_R 15.7 (minor) and 17.8 (major) min. *anti*-**2f**; ^{1}H NMR δ 2.80 (br, 1H), 4.46 (d, *J* = 7.2 Hz, 1H), 5.99 (s, 1H), 6.99-7.43 (m, 10H); ^{19}F NMR δ -74.4 (s).

1,2-Diphenyl-2-methanesulfonylethanol (2a): (starting **1a**: 21 mg, 0.123mmol; product **2a**: 6.5 mg (19%), *syn*-**2a:** 10% ee, *anti*-**2a**: 1% ee); *syn*-**2a**; ^{1}H NMR δ 2.96 (s, 3H), 3.55 (d, *J* = 2.2 Hz, 1H), 4.40 (d, *J* = 9.8 Hz, 1H), 5.61 (dd, *J* = 2.2, 9.8 Hz, 1H), 7.15-7.27 (m, 10H); IR (KBr): 3473, 3051, 3010, 2934, 2360, 1494, 1454, 1411, 1287, 1200, 1135, 1051, 966, 916, 861, 841, 788, 751, 695 cm^{-1}; EIMS *m/z* 276 (M^+, 17), 170 (100), 105 (55), 91, (93), 77 (63). HPLC (CHIRALCEL OD-H hexane:*i*PrOH = 70:30, flow rate 0.5 ml/min), t_R 14.8 (major) and 18.6 (minor) min. *anti*-**2a**; ^{1}H NMR δ 2.71 (s, 3H), 3.91 (d, *J* = 2.7 Hz, 1H), 4.16 (d, *J* = 2.7 Hz, 1H), 6.01 (br, 1H), 7.21-7.41 (m, 10H); IR (KBr) 3452, 2921, 2853, 2356, 1496, 1454, 1297, 1218, 1193, 1136, 1060, 973, 818, 760, 700 cm^{-1}; EIMS *m/z* 276 (M^+, 14), 170 (83), 105 (30), 91 (100), 77, (71), 64 (35). HPLC (CHIRALCEL OD-H hexane: ^{i}PrOH = 80:20, flow rate 0.5 ml/min), t_R 21.7 (major) and 29.6 (minor) min

1,2-Diphenyl-2-(2,2-dimethylethane)sulfonylethanol (2b): (starting **1b**: 24.2 mg, 0.114 mmol; product **2b**: 25.8 mg (71%), *syn*-**2b:** 29% ee, *anti*-**2b**: 21% ee); *syn*-**2b**; ^{1}H NMR δ 1.25 (s, 9H), 4.56 (d, *J* = 9.2 Hz, 1H) 5.06 (d, *J* = 1.3 Hz, 1H), 5.62 (dd, *J* = 1.3, 9.2 Hz, 1H), 7.06-7.27 (m, 10H); ^{13}C NMR δ 24.1, 63.5, 70.7, 74.6, 127.2, 127.7, 128.2, 128.3, 130.0, 131.7, 138.9; IR (KBr) 3478, 2979, 2916, 2360, 1558, 1495, 1455, 1399, 1274, 1241, 1199, 1099, 1037, 916, 782, 764, 701, 669, 625 cm^{-1}; EIMS *m/z* 318 (M^+, 1), 212 (27), 156 (61), 139 (29), 91 (24), 57 (100). HPLC (CHIRALPAK AD-H hexane:*i*PrOH = 80:20, flow rate 1.0 ml/min), t_R 16.7 (minor) and 22.5 (major) min. *anti*-**2b**; ^{1}H NMR 1.25 (s, 9H), 3.55 (d, *J* = 3.6 Hz, 1H), 4.25 (d, *J* = 3.6 Hz, 1H), 6.13 (br, 1H), 7.15-7.32 (m, 10H); IR (KBr) 3434, 2933, 2362, 1558, 1493, 1455, 1365, 1280, 1214, 1107, 1059, 791, 761, 715, 700, 659 cm^{-1}; EIMS *m/z* 318 (M^+, 6), 212 (33), 156 (100), 107 (48), 105 (42), 91 (39), 57 (93). Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.90; H, 6.96. Found: C, 67.57; H, 7.29. HPLC (CHIRALPAK AD-H hexane:*i*PrOH = 90:10, flow rate 1.0 ml/min), t_R 17.1 (major) and 24.5 (minor) min.

1, 2-Diphenyl-2-benzenesulfonylethanol (2c): (starting **1c**: 26.5 mg, 0.114 mmol; product **2c**: 32.2 mg (83%), *syn*-**2c:** 32% ee, *anti*-**2c**: 41% ee); *syn*-**2c**; ^{1}H NMR δ 4.45 (d, *J* = 9.6 Hz, 1H), 4.53 (br, 1H) 5.76 (d, *J* = 9.6Hz, 1H), 6.89-7.56 (m, 15H); ^{13}C NMR δ 73.9, 74.6, 127.2, 127.9, 128.3, 128.5, 128.7, 130.1, 130.5, 133.6, 137.3, 139.2; IR (KBr) 3480, 2927, 1507, 1455, 1290, 1139, 1085, 802, 756, 697 cm^{-1}; EIMS *m/z* 338 (M^+, 7), 232 (99), 197 (15), 105 (58), 91 (88), 77 (100). Anal. Calcd for $C_{20}H_{18}O_3S$: C, 70.98; H, 5.36. Found: C, 70.87; H, 5.37. HPLC (CHIRALCEL OD-H hexane:*i*PrOH = 70:30, flow rate 1.2 ml/min), t_R 10.0 (major) and 24.7 (minor) min. *anti*-**2c**; ^{1}H NMR δ 3.48 (d, *J* = 2.7 Hz, 1H), 4.17 (d, *J* = 2.7 Hz, 1H), 6.02 (br, 1H), 7.04-7.66 (m, 15H); IR (KBr) 3477, 2976, 1495, 1455, 1274, 1198, 1100, 1037, 783, 764, 701 cm^{-1}; EIMS *m/z* 338 (M^+, 6), 232 (100), 197 (12), 91 (91), 77 (64). HPLC (CHIRALCEL OD-H hexane:*i*PrOH = 90:10, flow rate 0.6 ml/min), t_R 19.7 (major) and 24.0 (minor) min.

1,2-Diphenyl-2-pentafluorobenzenesulfonylethanol (2d): (starting **1d**: 36.3 mg, 0.113 mmol; product **2d**: 34.4 mg (71%), *syn*-**2d:** 23% ee, *anti*-**2d**: 14% ee); *syn*-**2d**; ^{1}H NMR δ 2.88 (br, 1H), 4.72 (d, *J* = 9.9 Hz, 1H), 5.70 (d, *J* = 9.9 Hz, 1H), 7.13-7.34 (m, 10H); ^{13}C NMR δ 73.9, 74.6, 127.2, 127.9, 128.3, 128.5, 128.7, 130.1, 130.5, 133.6, 137.3, 139.2; ^{19}F NMR δ –158.2- –134.8 (m, **F**-); IR (KBr) 3507, 2954, 1644, 1522, 1495, 1455, 1401, 1323, 1299, 1150, 1103, 1060, 987, 755, 715, 696, 659, 616 cm^{-1}; EIMS *m/z* 428(M^+, 3), 107 (100), 91 (48), 77 (37). Anal. Calcd for $C_{20}H_{13}F_5O_3S$: C, 56.08; H, 3.06. Found: C, 55.70; H, 3.44. HPLC (CHIRALCEL OD-H hexane:*i*PrOH = 95:5, flow rate 1.2 ml/min), t_R 17.3 (minor) and 28.5 (major) min. *anti*-**2d**; ^{1}H NMR δ 3.48 (d, *J* = 2.7 Hz, 1H), 4.17 (d, *J* = 2.7 Hz, 1H), 6.02 (br, 1H), 7.04-7.66 (m, 15H); ^{19}F NMR δ –157.7- –133.9 (m); IR (KBr) 3540, 2922, 1646, 1522, 1494, 1456, 1397, 1337, 1294, 1148, 1100, 1026, 988, 765, 719, 703, 658, 611 cm^{-1}; EIMS *m/z* 428 (M^+, 3), 322 (6), 107 (100), 91 (52), 77 (34), 51 (10). HPLC (CHIRALCEL OD-H hexane: *i*PrOH = 95:5, flow rate 1.2 ml/min), t_R 26.0 (minor) and 34.1 (major) min

1,2-Diphenyl-2-(2-pyridylsulfonyl)ethanol (2e): (starting **1e**: 22.5 mg, 0.096 mmol; product **2e**: 21.5 mg (66%), *syn*-**2e:** 4% ee, *anti*-**2e**: 8% ee): *syn*-**2e**; ^{1}H NMR δ 4.04 (*d*, 1H, *J* = 2.4 Hz), 5.11 (*d*, 1H, *J* = 9.8 Hz), 5.73 (*dd*, 1H, *J* = 2.0, 10.0 Hz,), 7.04-7.18 (*m*, 10H), 7.42-7.47 (m, 1H), 7.72-7.76 (*m*, 2H), 8.71-8.75 (*m*, 1H); IR (KBr) 3276, 3031, 2979, 1654, 1455, 1308, 1147, 1113, 982, 916, 761, 699, 648 cm^{-1}; EIMS *m/z* 339 (M^+, 3), 274 (10), 169 (27), 149 (58), 84 (37), 57 (100). HPLC(CHIRALCEL AD-H hexane: *i*PrOH = 85:15, flow rate 1.0 ml/min), t_R 37.3 (major) and 41.8 (minor) min. *anti*-**2e**; ^{1}H NMR δ 3.89 (*d*, *J* = 2.6 Hz, 1H), 4.88 (*d*, *J* = 3.0 Hz, 1H), 5.97 (*t*, *J* = 2.7 Hz, 1H), 7.06-7.35 (*m*, 10H), 7.41-7.48 (m, 1H), 7.74-7.70 (*m*,

2H), 8.70-8.73 (*m*, 1H); IR (KBr) 3467, 27924, 1578, 1453, 1312, 1160, 1109, 799, 701 cm^{-1}; EIMS *m/z* 339 (M^+, 15), 167 (18), 149 (36), 71 (39), 57 (100). HPLC(CHIRALPAK AD-H hexane: *i*PrOH = 85:15, flow rate 1.0 ml/min), t_R 25.2 (major) and 35.0 (minor) min.

1-(4-Methylphenyl)-2-phenyl-2-(trifluoromethanesulfonyl)ethanol (5): (starting **1f**: 24.0 mg, 0.107 mmol; product **5**: 25.9 mg (70%), *syn*-**5:** 94% ee): *syn*-**5**; $[\alpha]_D^{26}$ +10.4 (*c* 0.79, $CHCl_3$, 94% ee);^{1}H NMR δ 2.22 (s, 3H), 2.95 (br, 1H), 4.75 (d, *J* = 9.9 Hz, 1H), 5.56 (d, *J* = 9.9 Hz, 1H), 6.98-7.28 (m, 9H); ^{19}F NMR δ −73.3 (s); IR (KBr) 3572, 2925, 1613, 1517, 1493, 1455, 1352, 1261, 1195, 1106, 819, 794, 727, 697, 646, 618 cm^{-1}; EIMS *m/z* 344 (M^+, 1), 121 (100), 105 (14), 91 (12), 77 (25). Anal. Calcd for $C_{16}H_{15}F_3O_3S$: C, 55.81; H, 4.39. Found: C, 55.62; H, 4.59. HPLC (CHIRALPAK AD-H×2 hexane/*i*PrOH = 95/5, flow rate 1.0 ml/min) t_R 37.8 (minor) and 44.5 (major) min.

1-(4-Methoxyphenyl)-2-phenyl-2-(trifluoromethanesulfonyl)ethanol (6): (starting **1f**: 23.3 mg, 0.104 mmol; product **6**: 21.3 mg (57%), *syn*-**6:** 98% ee): *syn*-**6**; $[\alpha]_D^{26}$ +15.4 (*c* 0.33, $CHCl_3$, 98% ee); ^{1}H NMR δ 2.95 (br, 1H), 3.70 (s, 3H), 4.73 (d, *J* = 10.0 Hz, 1H), 5.54 (d, *J* = 10.0 Hz, 1H), 6.65-7.35 (m, 9H); ^{19}F NMR δ −73.2; IR (KBr) cm^{-1}; EIMS *m/z*360 (M^+, 6), 210 (21), 137 (100), 109 (33), 91 (33), 77 (31). HPLC (CHIRALPAK AD-H hexane/^{i}PrOH = 95/5, flow rate 1.0 ml/min) t_R 22.9 (minor) and 31.4 (major) min.

1-(4-Chlorophenyl)-2-phenyl-(2-trifluoromethanesulfonyl)ethanol (7): (starting **1f**: 23.3 mg, 0.104 mmol; product **7**: 25.1 mg (66%), *syn*-**7:** 84% ee): *syn*-**7**; $[\alpha]_D^{20}$ +10.8 (*c* 0.78, $CHCl_3$, 84% ee); ^{1}H NMR δ 3.19 (br, 1H), 4.69 (d, *J* = 9.8 Hz, 1H), 5.59 (d, *J* = 9.8 Hz, 1H), 7.02-7.31 (m, 9H); ^{13}C NMR δ 73.6, 75.0, 126.9, 128.0, 128.5, 128.9, 129.9, 130.1, 134.4, 136.9; ^{19}F NMR δ −73.23 (s, C**F**$_3$-); IR (KBr) 3526, 3066, 2945, 2358, 1596, 1492, 1455, 1334, 1296, 1194, 1102, 1079, 1014, 826, 735, 699, 685, 644, 619, 602 cm^{-1}; EIMS *m/z* 364 (M^+, 9), 165 (18), 141 (100), 113 (60), 91 (85), 77 (85). HPLC (CHIRALPAK AD-H hexane/*i*PrOH = 95/5, flow rate 1.0 ml/min) t_R 17.8 (minor) and 22.4 (major) min.

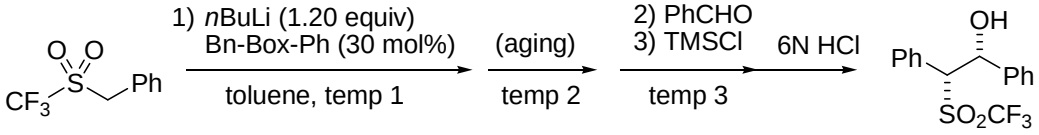
1-(2-Naphthyl)-2-phenyl-2-(trifluoromethanesulfonyl)ethanol (8): (starting **1f**: 22.8 mg, 0.102 mmol; product **8**: 20.9 mg (54%), *syn*-**8:** 96% ee): *syn*-**8**; $[\alpha]_D^{20}$ +4.3 (*c* 0.72, $CHCl_3$, 90% ee); ^{1}H NMR δ 2.22 (s, 3H), 2.95 (br, 1H), 4.75 (d, *J* = 9.9 Hz, 1H), 5.56 (d, *J* = 9.9 Hz, 1H), 6.98-7.28 (m, 9H); ^{19}F NMR δ −73.3; IR (KBr) 3527, 2941, 1683, 1507, 1456, 1356, 1218, 1203, 1104, 1046, 868, 837, 761, 695, 664, 630 cm^{-1};

EIMS *m/z* 380 (M^+, 10), 185 (34), 127 (36), 91 (100). HPLC (CHIRALPAK AD-H×2 hexane/*i*PrOH = 97/3, flow rate 2.0 ml/min) t_R 48.8 (minor) and 54.8 (major) min.

1-(2-(Furanyl)-2-phenyl-2-(trifluoromethanesulfonyl)ethanol (9): (starting **1f**: 23.3 mg, 0.104 mmol; product **9**: 11.7 mg (35%), *syn*-**9:** 90% ee): *syn*-**9**; $[\alpha]_D^{20}$ –1.1 (*c* 0.13, $CHCl_3$, 90% ee); ^{1}H NMR δ 3.05 (*br*, 1H), 5.04 (*d*, *J* = 9.8 Hz, 1H), 5.65 (*d*, *J* = 9.8 Hz, 1H), 6.09-6.14 (*m*, 3H), 7.21-7.37 (m, 10H); ^{19}F NMR δ –73.3; IR (KBr) 3435, 2953, 1497, 1456, 1346, 1199, 1109, 1015, 926, 809, 739, 697, 648 cm^{-1}; EIMS *m/z* 320 (M^+, 1), 105 (19), 91 (100), 77 (18). HPLC (Daicel CHIRALPAK AD-H, hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) t_R 20.5 (minor) and 30.7 (major) min.

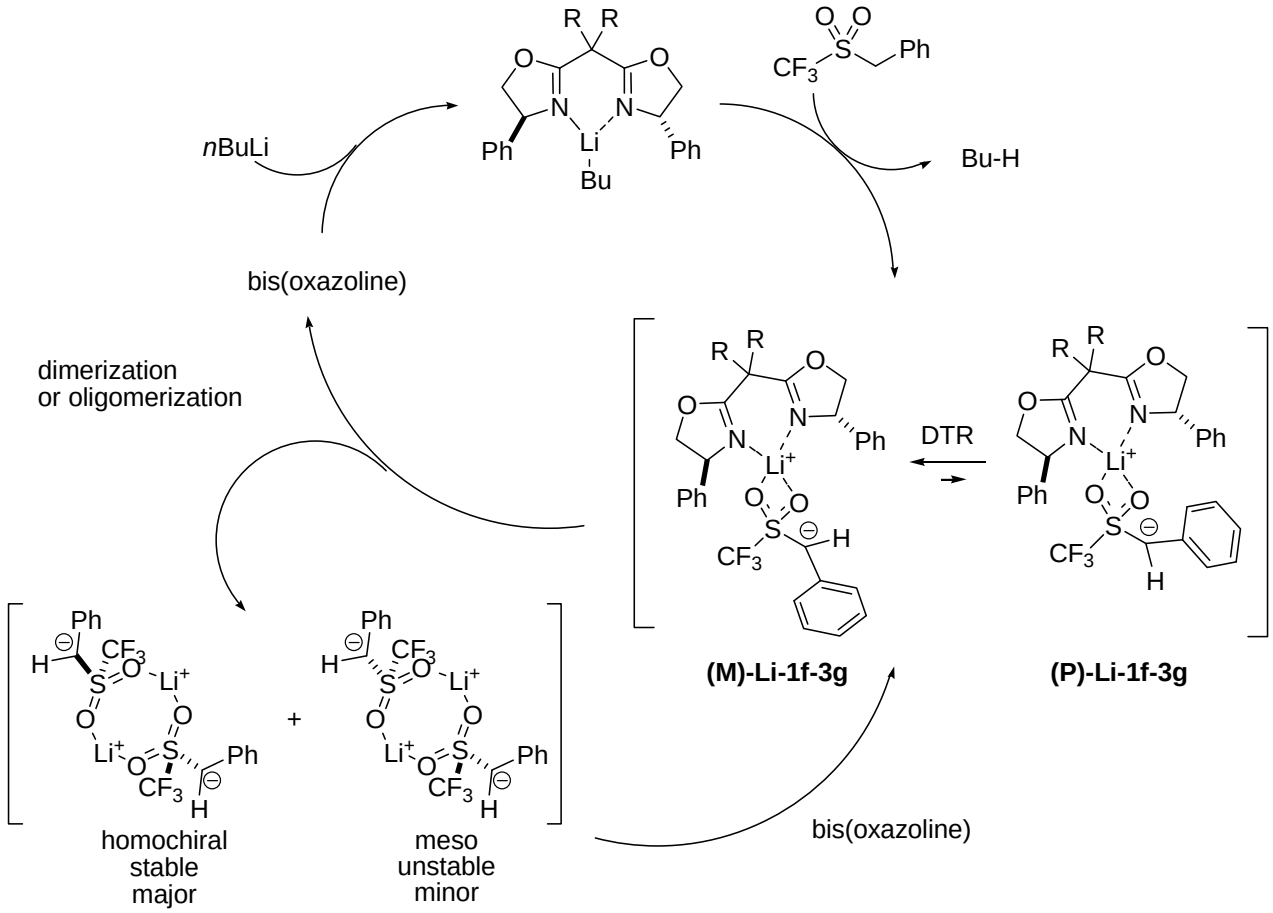
(*R*)-1-Fluoro-1-phenylmethyl trifluoromethyl sulfone (10): (starting **1f**: 26.3 mg, 0.117 mmol; product **10**: 14.0 mg (50%), **10:** 99% ee): $[\alpha]_D^{20}$ +28.2 (*c* 0.18, $CHCl_3$, 83% ee); ^{1}H NMR δ 6.42 (d, *J* = 47.6 Hz, 1H), 7.52-7.61 (m, 5H); ^{13}C NMR δ 98.0, 102.5, 123.6, 128.3, 128.4, 129.0, 132.2; ^{19}F NMR δ –73.5 (d, *J* = 8.4 Hz), –172.4 (dd, *J* = 8.4 Hz, 47.6 Hz); IR (KBr) 2970, 2923, 2852, 2358, 1496, 1457, 1373, 1313, 1293, 1207, 1123, 1051, 1027, 786, 724, 694 cm^{-1}; EIMS *m/z* 242 (M^+, 3), 168 (10), 149 (15), 109 (100), 91 (48), 57 (80); HPLC (CHIRALCEL OB-H hexane/*i*PrOH = 98/2, flow rate 0.5 ml/min), t_R 13.0 (major) and 22.9 (minor) min.

Warm-cool procedure



temp 1 (°C)	temp 2 (°C)	temp 3 (°C)	yield (%)	*syn* : *anti*	er *(syn)*
–95	–95	–95	65	95 : 5	86 : 14
–95	–78	–95	60	95 : 5	92 : 8
–78	–78	–78	67	97 : 3	93 : 7

Plausible Catalytic Cycle



Complete ref. 3b: J. P. Scott, S. F. Oliver, K. M. J. Brands, S. E. Brewer, A. J. Davies, A. D. Gibb, D. Hands, S. P. Keen, F. J. Sheen, R. A. Reamer, R. D. Wilson, U. Dolling, *J. Org. Chem.* **2006**, *71*, 3086-3092.