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Supporting Information

Ethyl (S)-3-(2'-Hydroxyethoxy)-2,2-dimethyl-3-phenylpropanoate (4a): ^1H NMR (300 MHz, CDCl_3) δ 1.01 (3H, s), 1.10 (3H, s), 1.28 (3H, t, J = 7.2 Hz), 2.44 (1H, br t, J = 6.3 Hz), 3.30 (1H, ddd, J = 4.1, 5.7, and 10.5 Hz), 3.50 (1H, ddd, J = 3.2, 5.1, and 10.5 Hz), 3.62-3.68 (2H, m), 4.19 (2H, q, J = 7.2 Hz), 4.71 (1H, s), 7.26-7.37 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 14.2, 18.0, 23.2, 47.8, 60.8, 61.7, 70.5, 85.8, 127.8, 127.9, 128.4, 137.2, 177.3; IR (liquid film) 3450 (br), 2980, 1720, 770, 750, 705 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4$: C, 67.65; H, 8.33. Found: C, 67.42; H, 8.56.

Ethyl (S)-3-(2-Hydroxyethoxy)-2,2-dimethyl-3-(4-methoxyphenyl)propanoate (4b): ^1H NMR (300 MHz, CDCl_3) δ 0.98 (3H, s), 1.09 (3H, s), 1.28 (3H, t, J = 7.2 Hz), 2.43 (1H, br t, J = 6.3 Hz), 3.28 (1H, ddd, J = 3.9, 6.2, and 10.3 Hz), 3.48 (1H, ddd, J = 3.2, 5.0, and 10.3 Hz), 3.61-3.67 (2H, m), 3.80 (3H, s), 4.18 (2H, q, J = 7.2 Hz), 4.66 (1H, s), 6.85-6.88 (2H, m), 7.18-7.21 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 14.2, 18.0, 23.2, 47.9, 55.2, 60.8, 61.7, 70.3, 85.4, 113.3, 129.1, 129.5, 159.3, 177.4; IR (liquid film) 3480 (br), 2970, 1715, 805 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_5$: C, 64.84; H, 8.16. Found: C, 64.59; H, 8.31.

Ethyl (R)-3-(2-Hydroxyethoxy)-2,2-dimethyl-3-(2-furyl)propanoate (4e): ^1H NMR (300 MHz, CDCl_3) δ 1.04 (3H, s), 1.26 (3H, s), 1.27 (3H, t, J = 7.0 Hz), 2.40 (1H, br t, J = 6.4 Hz), 3.39 (1H, ddd, J = 3.3, 6.4, and 10.0 Hz), 3.52 (1H, ddd, J = 2.9, 5.8, and 10.0 Hz), 3.57-3.73 (2H, m), 4.17 (2H, q, J = 7.0 Hz), 4.75 (1H, s), 6.30 (1H, d, J = 3.2 Hz), 6.34-6.36 (1H, m), 7.39-7.40 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 18.6, 22.7, 47.5, 60.9, 61.6, 70.7, 79.9, 109.6, 110.1, 142.5, 151.7, 176.7; IR (liquid film) 3450 (br), 2940, 1730, 740 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_5$: C, 60.92; H, 7.87. Found: C, 60.74; H, 8.07.

Ethyl (E)-(R)-3-(2-Hydroxyethoxy)-2,2-dimethyl-5-phenyl-4-pentenoate (4f): ^1H NMR (300 MHz, CDCl_3) δ 1.13 (3H, s), 1.24 (3H, s), 1.27 (3H, t, J = 7.1 Hz), 2.37-3.46 (1H, m), 3.37-3.46 (1H, m), 3.62-3.72 (3H, m), 4.17 (2H, q, J = 7.1 Hz), 4.18 (1H, dd, J = 0.6 and 8.3 Hz), 6.08 (1H, dd, J = 8.3 and 16.0 Hz), 6.60 (1H, d, J = 16.0 Hz), 7.23-7.42 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 14.2, 18.8, 22.8, 47.3, 60.7, 61.7, 70.0, 85.3, 125.3, 126.6, 128.0, 128.6, 135.1, 136.2, 176.9; IR (liquid film) 3490 (br), 2980, 1720, 750, 730, 695 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: C, 69.84; H, 8.27. Found: C, 69.65; H, 8.18.

S-tert-Butyl (R)-3-(2-Hydroxyethoxy)-3-(4-methoxyphenyl)propanthioate (4c): ^1H NMR (300 MHz, CDCl_3) δ 1.46 (9H, s), 2.53 (1H, dd, J = 6.0 and 7.0 Hz), 2.66 (1H, dd, J = 3.6 and 15.3 Hz), 2.97 (1H, dd, J = 9.9 and 15.3 Hz), 3.34 (1H, ddd, J = 4.1, 6.0, and 10.3 Hz), 3.49 (1H, ddd, J = 3.3, 4.9, and 10.3 Hz), 3.64-3.70 (2H, m), 3.80 (3H, s), 4.78 (1H, dd, J = 3.6 and 9.9 Hz), 6.85-6.90 (2H, m), 7.20-7.26 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 29.7, 48.4, 52.6, 55.3, 61.7, 69.9, 78.0, 114.0, 127.6, 132.5, 159.5, 198.4; IR (liquid

film) 3480 (br), 2950, 1680, 795 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_4\text{S}$: C, 61.51; H, 7.74; S, 10.26. Found: C, 61.23; H, 7.67; S, 10.35.

(3R)-3-(2-Hydroxyethoxy)-3-(4-methoxyphenyl)-1-phenyl-1-propanone (4d): ^1H NMR (300 MHz, CDCl_3) δ 3.00 (1H, dd, $J = 5.6$ and 7.2 Hz), 3.09 (1H, dd, $J = 3.2$ and 17.3 Hz), 3.40 (1H, ddd, $J = 3.1$, 6.8 , and 10.9 Hz), 3.54 (1H, ddd, $J = 2.9$, 5.6 , and 10.9 Hz), 3.60-3.78 (2H, m), 3.60 (1H, dd, $J = 9.5$ and 17.3 Hz), 3.81 (3H, s), 5.04 (1H, dd, $J = 3.1$ and 9.5 Hz), 6.89-6.94 (2H, m), 7.29-7.34 (2H, m), 7.42-7.48 (2H, m), 7.53-7.59 (1H, m), 7.94-7.98 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 47.1, 55.3, 60.8, 61.7, 69.8, 76.9, 114.4, 127.7, 128.2, 128.6, 133.3, 137.0, 159.4, 198.2; IR (liquid film) 3425 (br), 2925, 1680, 795, 755, 690 cm^{-1} ; HRMS (EI). calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4$: 300.1361. Found: 300.1360.

(S)-MTPA ester of 4a: ^1H NMR (300 MHz, CDCl_3) δ 0.98 (3H, s), 1.09 (3H, s), 1.24 (3H, t, $J = 7.1$ Hz), 3.49 (1H, ddd, $J = 3.2$, 5.0 , and 11.2 Hz), 3.55-3.64 (4H, m), 4.04-4.20 (2H, m), 4.29 (1H, ddd, $J = 3.1$, 5.0 , and 11.7 Hz), 4.47 (1H, ddd, $J = 3.2$, 7.5 , and 11.7 Hz), 4.65 (1H, s), 7.20-7.29 (5H, m), 7.40-7.44 (3H, m), 7.53-7.58 (2H, m) [a minor diastereomer resonated at 0.97 (3H, s), 1.08 (3H, s), 1.20 (3H, t, $J = 7.1$ Hz), 4.36-4.39 (2H, m), and 4.63 (1H, s)].

(S)-MTPA ester of 4b: ^1H NMR (300 MHz, CDCl_3) δ 0.96 (3H, s), 1.08 (3H, s), 1.24 (3H, t, $J = 7.1$ Hz), 3.47 (1H, ddd, $J = 3.3$, 5.0 , and 11.2 Hz), 3.55-3.63 (4H, m), 3.79 (3H, s), 4.03-4.20 (2H, m), 4.28 (1H, ddd, $J = 3.2$, 5.0 , and 11.7 Hz), 4.46 (1H, ddd, $J = 3.3$, 7.6 , and 11.7 Hz), 4.60 (1H, s), 6.78-6.82 (2H, m), 7.11-7.16 (2H, m), 7.39-7.44 (3H, m), 7.53-7.57 (2H, m) [a minor diastereomer resonated at 0.95 (3H, s), 1.07 (3H, s), 1.20 (3H, t, $J = 7.1$ Hz), 4.35-4.38 (2H, m), and 4.58 (1H, s)].

(S)-MTPA ester of 4c: ^1H NMR (300 MHz, CDCl_3) δ 1.41 (9H, s), 2.63 (1H, dd, $J = 5.0$ and 15.0 Hz), 2.92 (1H, dd, $J = 8.5$ and 15.0 Hz), 3.48-3.60 (5H, m), 3.78 (3H, s), 4.29 (1H, ddd, $J = 3.6$, 5.1 , and 11.7 Hz), 4.50 (1H, ddd, $J = 3.9$, 6.6 , and 11.7 Hz), 4.72 (1H, dd, $J = 5.0$ and 8.5 Hz), 6.79-6.84 (2H, m), 7.10-7.18 (2H, m), 7.38-7.43 (3H, m), 7.54-7.57 (2H, m) [a minor diastereomer resonated at 2.90 (1H, dd, $J = 8.5$ and 14.6 Hz) and 4.38-4.41 (2H, m)].

(S)-MTPA ester of 4d: ^1H NMR (300 MHz, CDCl_3) δ 3.04 (1H, dd, $J = 4.6$ and 16.6 Hz), 3.46-3.59 (6H, m), 3.79 (3H, s), 4.28-4.35 (1H, m), 4.41-4.49 (1H, m), 4.96 (1H, dd, $J = 4.6$ and 8.2 Hz), 6.83-6.86 (2H, m), 7.27-7.57 (10H, m), 7.88-7.91 (2H, m) [a minor diastereomer resonated at 3.86 (3H, s)].

(S)-MTPA ester of 4e: ^1H NMR (300 MHz, CDCl_3) δ 1.02 (3H, s), 1.22 (3H, s), 1.22 (3H, t, $J = 7.1$ Hz), 3.50-3.58 (4H, m), 3.65 (1H, ddd, $J = 3.1$, 7.2 , and 11.1 Hz), 4.06-4.18 (2H, m), 4.26 (1H, ddd, $J = 3.1$, 5.3 , and 11.8 Hz), 4.50 (1H, ddd, $J = 3.3$, 7.2 , and 11.8 Hz), 4.70 (1H, s), 6.23 (1H, d, $J = 3.2$ Hz), 6.30 (1H, dd, $J = 1.8$ and 3.3 Hz), 7.34-7.35 (1H, m), 7.38-7.43 (3H, m), 7.53-7.56 (2H, m) [a minor diastereomer resonated at 1.18 (3H, t, $J = 7.2$ Hz), 4.34-4.40 (2H, m), 4.69 (1H, s), and 6.21 (1H, d, $J = 3.5$ Hz)].

(S)-MTPA ester of 4f: ^1H NMR (300 MHz, CDCl_3) δ 1.10 (3H, s), 1.19 (3H, s), 1.23 (3H, t, $J = 7.1$ Hz), 3.54-3.60 (4H, m), 3.79 (1H, ddd, $J = 3.1, 7.3$, and 11.3 Hz), 4.08-4.15 (3H, m), 4.31 (1H, ddd, $J = 3.1, 5.3$ and 11.7 Hz), 4.51 (1H, ddd, $J = 3.1, 7.3$ and 11.7 Hz), 6.03 (1H, dd, $J = 8.1$ and 16.0 Hz), 6.55 (1H, d, $J = 16.0$ Hz), 7.23-7.41 (8H, m), 7.52-7.56 (2H, m) [a minor diastereomer resonated at 4.39-4.43 (2H, m), 6.01 (1H, dd, $J = 8.3$ and 15.9 Hz), and 6.54 (1H, d, $J = 15.9$ Hz)].

Ethyl (S)-3-(2'-Iodoethoxy)-2,2-dimethyl-3-phenylpropanoate. To a solution of **4a** (33.5 mg, 0.13 mmol), imidazole (20 mg, 0.31 mmol), and triphenylphosphine (80 mg, 0.31 mmol) in benzene (1.2 mL) at rt was added iodine (62 mg, 0.25 mmol). After being stirred for 0.5 h, the mixture was poured into aq Na_2SO_3 , extracted twice with hexane. The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica gel flash column chromatography gave 45.1 mg (95% yield) of the iodide: ^1H NMR (300 MHz, CDCl_3) δ 1.00 (3H, s), 1.14 (3H, s), 1.27 (3H, t, $J = 7.2$ Hz), 3.10-3.23 (2H, m), 3.48 (1H, ddd, $J = 6.1, 7.3$, and 10.6 Hz), 3.60 (1H, ddd, $J = 6.7, 6.9$, and 10.6 Hz), 4.17 (2H, q, $J = 7.2$ Hz), 4.67 (1H, s), 7.25-7.36 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 2.9, 14.2, 18.7, 22.5, 47.9, 60.6, 70.0, 86.0, 127.8, 128.0, 128.4, 137.4, 176.5; IR (liquid film) 2980, 1730, 770, 750, 705 cm^{-1} .

S-tert-Butyl (R)-3-(2-Iodoethoxy)-3-(4-methoxyphenyl)propanethioate. The iodide was prepared in 83% yield by a procedure similar to that described above. ^1H NMR (300 MHz, CDCl_3) δ 1.44 (9H, s), 2.63 (1H, dd, $J = 4.6$ and 14.9 Hz), 2.96 (1H, dd, $J = 9.1$ and 14.9 Hz), 3.13 (1H, ddd, $J = 6.6, 7.6$, and 9.8 Hz), 3.20 (1H, ddd, $J = 6.1, 7.5$, and 9.8 Hz), 3.50 (1H, ddd, $J = 6.1, 7.6$, and 10.7 Hz), 3.58 (1H, ddd, $J = 6.6, 7.5$, and 10.7 Hz), 3.79 (3H, s), 4.76 (1H, dd, $J = 4.6$ and 9.1 Hz), 6.84-6.89 (2H, m), 7.20-7.25 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 2.7, 29.8, 48.2, 52.7, 55.3, 69.6, 78.1, 114.0, 127.8, 132.4, 159.5, 197.3; IR (liquid film) 2960, 1680, 795 cm^{-1} .

Ethyl (S)-2,2-Dimethyl-3-hydroxy-3-phenylpropanoate (5a). A mixture of ethyl (S)-3-(2'-iodoethoxy)-2,2-dimethyl-3-phenylpropanoate (45.1 mg, 0.12 mmol) and zinc powder (41 mg, 0.48 mmol) in ethanol (0.4 mL) was stirred at 60 $^\circ\text{C}$ for 1 h. Extractive work-up followed by purification of the crude product with silica gel flash column chromatography gave 21.3 mg (80% yield) of **5a**: ^1H NMR (300 MHz, CDCl_3) δ 1.10 (3H, s), 1.13 (3H, s), 1.26 (3H, t, $J = 7.2$ Hz), 3.19 (1H, br s), 4.17 (2H, q, $J = 7.2$ Hz), 4.88 (1H, s), 7.29-7.32 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 19.1, 23.0, 47.5, 60.9, 78.7, 127.7 (3C), 140.0, 177.7; IR (liquid film) 3500, 2980, 1720, 710 cm^{-1} .

(S)-MTPA ester of **5a**: ^1H NMR (300 MHz, CDCl_3) δ 1.07 (3H, s), 1.20 (3H, s), 1.23 (3H, t, $J = 7.2$ Hz), 3.47 (3H, m), 4.03-4.19 (2H, m), 6.26 (1H, s), 7.12-7.43 (10H, m) [a minor diastereomer resonated at 1.19 (3H, s), 1.33 (3H, t, $J = 7.2$ Hz), 3.56 (3H, m), and 6.32 (1H, s)].

S-tert-Butyl (R)-3-Hydroxy-3-(4-methoxyphenyl)propanthioate (5b): The compound was prepared in 96% yield by a procedure similar to that described above except that THF was used as a solvent. ^1H NMR (300 MHz, CDCl_3) δ 1.46 (9H, s), 2.78 (1H, dd, $J = 3.6$ and 15.7 Hz), 2.88 (1H, dd, $J = 8.9$ and 15.7 Hz), 3.08 (1H, d, $J = 3.1$ Hz), 3.79 (3H, s), 5.09 (1H, ddd, $J = 3.1, 3.6$, and 8.9 Hz), 6.84-6.89 (2H, m), 7.20-7.29 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 29.7, 48.6, 52.8, 55.3, 70.5, 113.9, 126.9, 134.6, 159.2, 199.9; IR (liquid film) 3450 (br), 2960, 1680, 795 cm^{-1} ; HRMS (EI). calcd for $\text{C}_{14}\text{H}_{23}\text{O}_3\text{S}$: 268.1133. Found: 268.1141.

(S)-MTPA ester of **5b**: ^1H NMR (300 MHz, CDCl_3) δ 1.44 (9H, s), 2.82 (1H, dd, $J = 3.7$ and 16.3 Hz), 3.21 (1H, dd, $J = 10.1$ and 16.3 Hz), 3.51 (3H, m), 3.79 (3H, s), 6.34 (1H, dd, $J = 3.7$ and 10.1 Hz), 6.78-6.83 (2H, m), 7.12-7.17 (2H, m), 7.24-7.38 (5H, m) [a minor diastereomer resonated at 1.39 (9H, s), 2.84 (1H, dd, $J = 4.6$ and 16.0 Hz), 3.41 (3H, m), 3.81 (3H, s), 6.41 (1H, dd, $J = 4.6$ and 9.5 Hz), and 6.86-6.89 (2H, m)].