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Supporting Information

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Aqueous Asymmetric Mukaiyama Aldol Reaction Catalyzed by Chiral Gallium Lewis Acid with Trost-Type Semi-Crown Ligands

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Supporting Information

Chiral ligand **1a**^[1] is a known compound. Characterization data of other chiral ligands (**1c-h**) are as follows:

Ligand (S,S)-1c^[2]: A light yellow solid, mp: 90-92°C. $[\alpha]_D = +48.0$ (c 1.0, CH₂Cl₂). IR $\nu = 3416, 3058, 2964, 1471, 1449, 1377, 1268, 1217, 1004, 870, 767, 748, 703$ cm⁻¹. ¹H NMR: $\delta = 1.67-1.65$ (4H, m), 1.89-1.85 (2H, m), 2.05-2.02 (2H, m), 2.42-2.38 (2H, m), 2.89-2.77 (2H, m), 3.28 (4H, dd, $J = 27.3, 13.2$ Hz), 3.98 (2H, dd, $J = 9.1, 4.8$ Hz), 6.55 (2H, d, $J = 8.7$ Hz), 7.58 (4H, d, $J = 7.5$ Hz), 7.69 (d, $J = 7.8$ Hz, 4H). ¹³C NMR: $\delta = 24.1, 29.6, 55.2, 57.4, 71.4, 79.0, 114.3$ (d, ² $J_{C-F} = 22.6$ Hz), 125.3 (d, ⁴ $J_{C-F} = 6.8$ Hz), 125.9, 126.0, 126.1, 126.7 (d, ³ $J_{C-F} = 12.8$ Hz), 128.1, 128.3, 146.9, 151.0, 155.3 (d, ¹ $J_{C-F} = 270.0$ Hz). HRMS (FAB): calcd. for C₄₂H₄₄FN₂O₃ (M+H): 643.3330, found: 643.3332.

Ligand (S,S)-1d: A white solid, mp: 144-6°C. $[\alpha]_D = +145$ (c 1.0, CH₂Cl₂). IR: $\nu = 3386, 3056, 2959, 1641, 1602, 1484, 1401, 1298, 1213, 1006, 838, 765, 742, 696$ cm⁻¹. ¹H NMR: $\delta = 1.18$ (9H, s), 1.52-2.11 (8H, m), 2.41-2.48 (2H, m), 2.77-2.79 (2H, m), 3.21 (1H, d, $J = 12.6$ Hz), 3.47 (1H, d, $J = 12.7$ Hz), 4.21 (2H, dd, $J = 9.2, 5.0$ Hz), 6.72 (2H, s), 7.70-7.98 (24H, m), 8.18 (1H, s), 8.47 (1H, s); ¹³C NMR: $\delta = 19.5, 23.7, 24.1, 29.9, 31.7, 33.7, 55.1, 58.0, 70.1, 79.2, 123.4, 124.5, 124.7, 124.8, 125.4, 125.7, 126.0, 127.0, 127.5, 127.8, 127.9, 128.3, 128.8, 132.2, 133.2, 133.3, 140.7, 143.9, 144.5, 152.8$. HRMS (FAB): calcd. for C₇₀H₆₇N₂O₃ (M-H): 983.5130, found: 983.5137.

Ligand (S,S)-1e: A light yellow solid, mp: 146-7°C. $[\alpha]_D = +92.0$ (c 1.0, CH₂Cl₂). IR: $\nu = 3425, 3055, 2959, 1629, 1600, 1482, 1362, 1300, 1271, 1210, 857, 814, 790, 747$ cm⁻¹. ¹H NMR: $\delta = 1.24$ (9H, s), 1.53-2.08 (8H, m), 2.44-2.47 (2H, m), 2.83-2.86 (2H, m), 3.30 (2H, d, $J = 12.6$ Hz), 3.64 (2H, d, $J = 12.3$ Hz), 4.06 (2H, dd, $J = 9.0, 5.1$ Hz), 6.84 (2H, s), 6.46-7.29 (14H, m), 7.56-7.63 (14H, m), 7.70 (2H, d, $J = 8.4$ Hz), 8.87 (2H, d, $J = 8.4$ Hz); ¹³C NMR: $\delta = 20.1, 23.8, 24.3, 29.1, 32.7, 33.7, 54.1, 58.0, 71.1, 78.2, 124.7, 126.0, 126.3, 126.5, 26.8, 127.9, 128.3, 128.8, 129.2, 139.2, 139.3, 140.6, 140.7, 145.6, 146.5, 152.3$. HRMS (FBA): calcd. for C₆₂H₅₉N₂O₃ (M-H): 879.4531, found: 879.4547.

Ligand (S,S)-1f: A white solid, mp: 194-6°C. $[\alpha]_D = +46.0$ (c 1.0, CH₂Cl₂). IR: $\nu = 3403, 3059, 3027, 2963, 2871, 2809, 1601, 1490, 1448, 1103$ cm⁻¹. ¹H NMR: $\delta = 1.24$ (9H, s), 1.50-1.64 (4H, m), 1.87-1.99 (4H, m), 2.35-2.38 (2H, m), 2.85-2.94 (2H, m), 3.12 (4H, dd, $J = 13.9, 12.3$ Hz), 3.99 (2H, dd, $J = 9.0, 4.2$ Hz), 5.00 (2H, bs), 6.57 (1H, s), 6.82 (2H, s), 7.09-7.19 (4H, m), 7.26-7.33 (8H, m), 7.60 (4H, d, $J = 7.5$ Hz), 7.77 (4H, d, $J = 7.8$ Hz); ¹³C NMR: $\delta = 26.7, 23.5, 31.7, 34.0, 55.0, 57.7, 71.4,$

78.9, 124.0, 125.9, 126.0, 126.4, 127.1, 128.0, 128.2, 128.8, 146.4, 147.0, 152.6. HRMS (FAB): calcd for C₄₆H₅₂N₂O₂: 665.4083, found: 665.4084.

Ligand (S,S)-1g: A white solid, mp: 211-2^oC. [α]_D = +48.6 (*c* 2.0, CH₂Cl₂). IR: ν = 3353, 3060, 3025, 2943, 2871, 1590, 1491, 1449, 1375, 1112, 1033, 747, 705 cm⁻¹. ¹H NMR: δ = 7.70 (4H, d, *J* = 7.61 Hz), 7.62 (4H, d, *J* = 7.62 Hz), 7.47 (1H, t, *J* = 7.69 Hz), 7.39-7.28 (6H, m), 7.25-7.16 (6H, m), 7.09 (2H, q, *J* = 6.73 Hz), 6.88 (2H, d, *J* = 7.57 Hz), 5.24 (2H, s), 4.13 (4H, t, *J* = 6.91 Hz), 3.36 (2H, d, *J* = 5.76 Hz), 2.95 (2H, s), 2.52 (2H, q, *J* = 8.01 Hz), 2.04-1.91 (2H, m), 1.80-1.76 (2H, m), 1.36-1.17 (2H, m), 0.90 (2H, br); ¹³C NMR: δ = 158.81, 147.92, 146.63, 136.55, 128.18, 128.09, 128.02, 127.87, 126.33, 126.27, 125.89, 125.80, 125.63, 120.40, 78.13, 70.74, 61.65, 55.61, 29.78, 24.44.; HRMS (FAB): calcd. for C₄₁H₄₄N₃O₂ (M+H): 610.3429, found: 610.3412.

Ligand (S)-1h: A white solid, mp: 132-4^oC. [α]_D = +36.0 (*c* 1.0, CH₂Cl₂). IR: ν = 3423, 3060, 2960, 1631, 1502, 1449, 1362, 1249, 1167, 1125, 1031 cm⁻¹. ¹H NMR: δ = 1.22, (9H, s), 1.68-1.72 (1H, m), 1.85-1.90 (1H, m), 2.04-2.08 (1H, m), 2.40-2.44 (1H, m), 2.89-2.92 (1H, m), 3.27, 3.61 (2H, ABq, *J* = 13.2 Hz), 3.97, 4.02 (1H, dd, *J* = 4.8, 9.3 Hz), 6.66 (1H, d, *J* = 8.4 Hz), 6.83 (1H, d, *J* = 1.8 Hz), 7.25-7.33 (4H, m), 7.54 (1H, d, *J* = 7.8 Hz), 7.62 (1H, d, *J* = 7.8 Hz); ¹³C NMR: δ = 24.2, 29.3, 31.6, 33.9, 55.3, 61.1, 72.4, 79.8, 115.0, 122.3, 125.3, 125.7, 125.8, 126.8, 127.0, 128.2, 128.5, 141.7, 145.8, 146.1, 154.1. HRMS (FAB): calcd. for C₂₆H₃₀NO₂: 388.2271, found: 388.2278.

Most of silyl enol ethers used are known compounds except **2e-h**.

(Z)-1-(b-naphthyl)-1-trimethylsiloxyprop-1-ene (2e): A colorless oil; Yield: 95%. IR (film): ν = 3055, 2961, 2909, 2859, 1644, 1320, 1252, 1070 cm⁻¹. ¹H NMR: δ = 0.18 (9H, s), 1.83 (3H, d, *J* = 7.3 Hz), 5.54 (1H, q, *J* = 7.3 Hz), 7.46-7.50 (2H, m), 7.65 (1H, dd, *J* = 8.6, 1.6 Hz), 7.77-7.94 (4H, m); ¹³C NMR: δ = -0.46, -0.39, -0.30, 11.2, 105.5, 123.8, 124.8, 125.1, 125.5, 126.9, 127.2, 127.6, 132.2, 132.7, 135.8, 149.2. HRMS (FAB): calcd: for C₁₆H₂₀OSi: 256.1283, found: 256.1281.

(Z)-1-(a-naphthyl)-1-trimethylsiloxyprop-1-ene (2f): A colorless oil, Yield: 94%. IR (film): ν = 3048, 2959, 2915, 2859, 1661, 1309, 1251, 1062, 1036 cm⁻¹. ¹H NMR: δ = 0.15 (9H, s), 1.97 (3H, d, *J* = 6.7Hz), 5.23 (1H, q, *J* = 6.7 Hz), 7.56-7.65 (4H, m), 7.92-d below.7.99 (2H, m), 8.40 (1H, d, *J* = 7.9 Hz); ¹³C NMR: δ = -0.75, -0.39, 0.39, 11.0, 108.5, 124.8, 125.4, 125.5, 125.9, 126.4, 127.8, 127.9, 131.2, 133.4, 137.8, 149.6. HRMS (FAB): calcd for C₁₆H₂₀OSi: 256.1283, found: 256.1281.

(Z)-1-(4'-*t*-butylphenyl)-1-trimethylsiloxy-prop-1-ene (2g): A colorless oil, Yield: 47%. IR (film): ν = 3032, 2963, 2905, 1685, 1644, 1602 cm⁻¹. ¹H NMR: δ = -0.11 (9H, s), 1.24 (3H, s), 1.66 (3H, d, *J* = 6.8 Hz), 4.45 (1H, q, *J* = 6.8 Hz), 7.15 (2H, d, *J* = 7.8 Hz), 7.25 (2H, d, *J* = 7.8 Hz); ¹³C NMR: δ = -0.46, -0.39, 0.39, 0.45, 11.5, 31.3, 34.3, 104.3, 124.7, 125.1, 125.4, 136.1, 142.1, 149.4, 149.7, 150.0. HRMS (FAB): calcd. for C₁₆H₂₆OSi: 262.1813, found: 262.1814.

(Z)-1-(*p*-biphenyl)-1-trimethylsiloxyprop-1-ene (2h): A white solid, Yield: 96%. IR (film): ν = 3032, 2963, 2905, 1685, 1644, 1602, 1323, 1251, 1116, 1069 cm⁻¹. ¹H NMR: δ = 0.17 (9H, s), 1.75 (3H, d, *J* = 6.9Hz), 5.34 (1H, q, *J* = 6.9 Hz), 7.34 (1H, t, *J* = 7.3 Hz), 7.42, (4H, d, *J* = 8.6 Hz), 7.54 (4H, m), 7.61 (2H, d, *J* = 8.6Hz); ¹³C NMR: δ = -0.46, -0.39, -0.30, 11.2, 104.9, 124.9, 126.1, 126.3, 126.6, 28.1, 137.5, 139.3, 140.1, 148.9. HRMS (FAB): calcd for C₁₈H₂₂OSi: 282.1440, found: 282.1434.

Aldol products, **4a**,^[3] **4b**,^[8] **4c**,^[5] **4d**,^[4] **4e**,^[3] **4f**,^[5] **4g**,^[8] **4h**,^[4] **7a**,^[7] **7b**,^[9] **7c**,^[10] **7d**,^[11] **7e**,^[12] **10a**,^[6] **10b**,^[5] **13a**,^[4] **13c**,^[5] **13e**^[5] are known compounds.

1-(4'-Methylphenyl)-3-phenyl-3-hydroxy-2-methyl-propan-1-one (syn-4i): A colorless oil. [α] = -11.4 (*c* 0.2, CH₂Cl₂). IR (film): ν = 3465, 3030, 2927, 1669, 1605, 1453, 1409, 1339, 1225, 1204,

1183 cm^{-1} . ^1H NMR: δ = 1.21 (3H, d, J = 7.2 Hz), 2.44 (3H, s), 3.66-3.73 (1H, m), 3.80 (1H, bs), 5.26 (1H, d, J = 2.7 Hz), 7.17-7.85 (7H, m), 7.88 (2H, d, J = 8.1 Hz); ^{13}C NMR: δ = 11.2, 21.7, 46.8, 73.0, 126.1, 127.3, 128.3, 128.7, 129.5, 133.1, 141.9, 144.7, 205.6. HRMS (FAB): calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$: 255.1379, found: 255.1379. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 9/1, flow rate = 0.8 mL/min): t_{R} = 42.39 (major) and 59.60 min (minor).

1-(4'-Methoxyphenyl)-3-phenyl-3-hydroxyl-2-methyl-propan-1-one (syn-4j): A colorless oil. $[\alpha]_{\text{D}}$ = -17.3 (c 0.4, CH_2Cl_2). IR (film): ν = 3484, 2929, 2851, 1666, 1600, 1510, 1456, 1419, 1312, 1261, 1221, 1173, cm^{-1} . ^1H NMR: δ = 1.21(3H, d, J = 7.2 Hz), 3.63-3.65 (1H, m), 3.88 (3H, s), 5.23(1H, d, J = 1.8 Hz), 6.90-7.42 (7H, m), 7.93 (2H, d, J = 8.4 Hz); ^{13}C NMR: δ = 19.2, 31.0, 55.6, 73.0, 127.1, 128.4, 129.3, 129.7, 130.3, 134.1, 143.5, 146.7, 207.9. HRMS (FAB): calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Na}$ (M+Na): 293.1148, found: 293.1148. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 200/1, flow rate = 0.8 mL/min): t_{R} = 21.69 (major) and 24.52 min (minor).

1-(4'-Chlorophenyl)-3-phenyl-3-hydroxyl-2-methyl-propan-1-one (syn-4k): A colorless oil. $[\alpha]_{\text{D}}$ = -12.0 (c 0.5, CH_2Cl_2). IR (film): ν = 3461, 2970, 2877, 1675, 1589, 1489, 1454, 1401, 1339, 1212, 1091 cm^{-1} . ^1H NMR: δ = 1.20 (3H, d, J = 7.2 Hz), 3.46 (1H, bs), 3.62-3.69 (1H, m), 5.21 (1H, d, J = 1.8 Hz), 7.24-7.45 (7H, m), 7.86 (2H, d, J = 8.4 Hz); ^{13}C NMR: δ = 11.5, 29.7, 47.3, 73.3, 127.5, 128.4, 129.1, 134.0, 135.2, 140.0, 142.1, 143.1, 204.2. HRMS (FAB): calcd. for $\text{C}_{17}\text{H}_{17}\text{O}_2\text{Cl}$: 275.0833, found: 275.0837. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 300/1, flow rate = 0.8 mL/min): t_{R} = 51.85 (major) and 58.78 min (minor).

1-(b-Naphthyl)-3-phenyl-3-hydroxyl-2-methyl-propan-1-one (syn-4l): A colorless oil. $[\alpha]_{\text{D}}$ = +73.9 (c 0.2, CHCl_3). IR (film): ν = 3482, 3059, 2928, 1669, 1662, 1596, 1493, 1454, 1358, 1276, 1182 cm^{-1} . ^1H NMR: δ = 1.26 (3H, d, J = 7.2 Hz), 3.77 (1H, bs), 3.78-3.91 (1H, m), 5.31 (1H, d, J = 2.7 Hz), 7.21-8.00 (11H, m), 8.45 (1H, d, J = 1.8 Hz); ^{13}C NMR: δ = 11.0, 51.3, 73.4, 124.4, 125.6, 126.1, 126.6, 126.8, 127.0, 127.4, 128.0, 128.4, 128.5, 128.6, 130.4, 132.8, 134.0, 135.8, 141.9, 209.2. HRMS (FAB): calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Na}$ (M+Na): 313.1199, found: 313.1198. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 90/1, flow rate = 0.8 mL/min): t_{R} = 24.09 (major) and 29.49 min (minor).

1-(a-Naphthyl)-3-phenyl-3-hydroxyl-2-methyl-propan-1-one (syn-4m): A colorless oil. $[\alpha]_{\text{D}}$ = +101.5 (c 1.0, CHCl_3). IR (film): ν = 3461, 2970, 2931, 2877, 1675, 1589, 1489, 1454, 1401, 1339, 1212, 1091 cm^{-1} . ^1H NMR: δ = 1.24 (1H, d, J = 7.2 Hz), 3.37 (1H, bs), 3.67-3.78 (1H, m), 5.32 (1H, d, J = 1.8 Hz), 7.22-8.45 (12H, m); ^{13}C NMR: δ = 10.9, 51.3, 73.4, 124.3, 125.6, 126.1, 126.6, 126.8, 127.0, 127.4, 128.0, 128.3, 128.5, 130.4, 132.7, 134.0, 135.7, 142.0, 209.2. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2$: 291.1379, found: 291.1382. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 90/1, flow rate = 0.8 mL/min): t_{R} = 15.63 (major) and 21.34 min (minor).

1-(4'-*t*-Butylphenyl)-3-phenyl-3-hydroxyl-2-methyl-propan-1-one (syn-4n): A colorless oil. $[\alpha]_{\text{D}}$ = -14.1 (c 0.2, CH_2Cl_2). IR (film): ν = 3409, 3030, 2963, 2872, 1668, 1605, 1459, 1408, 1364, 1268, 1221, 1194 cm^{-1} . ^1H NMR: δ = 1.14 (3H, d, J = 7.2 Hz), 1.29 (9H, s), 3.59-3.60 (1H, m), 3.81 (1H, bs), 5.25 (1H, d, J = 2.7 Hz), 7.19-7.41 (5H, m), 7.47 (2H, d, J = 7.2 Hz), 7.89 (2H, d, J = 7.2 Hz); ^{13}C NMR: δ = 10.3, 31.4, 34.8, 46.8, 73.0, 125.5, 125.9, 127.3, 128.3, 128.6, 141.7, 150.4, 157.6, 205.6. HRMS (FAB): calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Na}$ (M+Na): 319.1668, found: 319.1669. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 90/1, flow rate = 0.8 mL/min): t_{R} = 17.09 (major) and 21.22 min (minor).

1-(*p*-Biphenyl)-3-phenyl-3-hydroxyl-2-methyl-propan-1-one (syn-4o): A white solid, mp: 95-6°C. $[\alpha]_{\text{D}}$ = -13.9 (c 2.0, CH_2Cl_2). IR (film): ν = 3499, 3057, 3029, 2979, 2938, 2873, 1669, 1603, 1556, 1490, 1447, 1404, 1329, 1230, 1189 cm^{-1} . ^1H NMR: δ = 1.26 (3H, d, J = 6.9 Hz), 3.61 (1H, bs),

3.62-3.77 (1H, m), 5.28 (1H, d, $J = 2.7$ Hz), 7.21-7.75 (12H, m), 8.05 (2H, d, $J = 7.2$ Hz). ^{13}C NMR: $\delta = 10.3, 47.1, 73.2, 126.1, 127.1, 127.4, 127.5, 128.3, 128.4, 128.8, 129.1, 134.3, 139.7, 141.2, 146.3, 205.4$. HRMS (FAB) calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_2\text{Na}$ (M+Na): 339.1355, found: 339.1360. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 9/1, flow rate = 0.8 mL/min): $t_{\text{R}} = 21.91$ (major) and 28.50 min (minor).

1-(*p*-Biphenyl)-3-(4'-methylphenyl)-3-hydroxyl-2-methyl-propan-1-one (*syn-4p*): A white solid, mp: 111-2°C. $[\alpha]_{\text{D}} = -105.4$ (c 0.3, CH_2Cl_2). IR (film): $\nu = 3495, 2987, 2934, 2933, 2876, 1661, 1602, 1515, 1453, 1405, 1333, 1224, 1198, 1123, 1069$ cm^{-1} . ^1H NMR: $\delta = 1.23$ (3H, d, $J = 7.2$ Hz), 2.35 (3H, s), 3.61 (1H, s), 3.72 (1H, q, $J = 3.4$ Hz), 5.24 (1H, d, $J = 1.8$ Hz), 7.17 (2H, d, $J = 7.9$ Hz), 7.31 (2H, d, $J = 7.9$ Hz), 7.41-7.51 (3H, m), 7.63 (2H, d, $J = 7.0$ Hz), 7.70 (2H, d, $J = 8.4$ Hz), 8.01 (2H, d, $J = 8.4$ Hz); ^{13}C NMR: $\delta = 11.3, 21.1, 47.2, 73.1, 126.0, 126.7, 127.3, 128.4, 128.9, 129.0, 129.1, 134.4, 136.9, 138.9, 139.7, 146.3, 205.3$. HRMS (FAB): calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_2\text{Na}$ (M+Na): 353.1512, found: 353.1509. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 9/1, flow rate = 0.8 mL/min): $t_{\text{R}} = 22.23$ (major) and 30.34 min (minor).

1-(*p*-Biphenyl)-3-(4'-chlorophenyl)-3-hydroxyl-2-methyl-propan-1-one (*syn-4q*): A white solid, mp: 96-8°C. $[\alpha]_{\text{D}} = -31.2$ (c 1.7, CH_2Cl_2). IR (film): $\nu = 3461, 2970, 2931, 2877, 1675, 1589, 1489, 1454, 1401, 1339, 1212, 1091$ cm^{-1} . ^1H NMR (300 MHz, CDCl_3) $\delta = 1.19$ (d, $J = 7.2$ Hz, 3H), 3.53 (bs, 1H), 3.60-3.69 (m, 1H), (4.91), 5.32 (d, $J = 2.7$ Hz, 1H), 7.23-7.44 (m, 9H), 7.83-7.93 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) $\delta = 11.5, 32.0, 47.3, 73.3, 126.1, 126.7, 127.3, 127.4, 127.5, 128.1, 128.3, 128.5, 128.6, 129.0, 129.1, 129.9, 134.9, 140.0, 141.9, 204.2$. HRMS calcd. for $\text{C}_{22}\text{H}_{19}\text{O}_2\text{ClNa}$ (M+Na): 373.0966, Found: 373.0966. HPLC (Daicel Chiralpak OD, hexane/isopropanol = 30/1, flow rate = 0.8 mL/min): $t_{\text{R}} = 23.25$ (major) and 26.46 min (minor).

1-(*p*-Biphenyl)-3-(4'-bromophenyl)-3-hydroxyl-2-methyl-propan-1-one (*syn-4r*): A white solid, mp: 90-2°C. $[\alpha]_{\text{D}} = -28.9$ (c 1.7, CH_2Cl_2). IR (film): $\nu = 3474, 2981, 2939, 2887, 1695, 1594, 1232, 1110$ cm^{-1} . ^1H NMR: $\delta = 1.21$ (3H, d, $J = 7.2$ Hz), 3.59-3.77 (1H, m), 3.86 (1H, bs), 5.22 (1H, d, $J = 1.8$ Hz), 7.21-7.78 (7H, m), 8.05 (2H, d, $J = 7.2$ Hz); ^{13}C NMR: $\delta = 11.2, 46.8, 72.5, 121.2, 127.3, 127.6, 127.9, 128.5, 129.0, 129.2, 131.4, 134.0, 139.6, 140.9, 146.5, 205.3$. HRMS calcd. for $\text{C}_{22}\text{H}_{19}\text{O}_2\text{Br}$: 394.0574 and 396.0553, found: 394.0569 and 396.0551. HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 9/1, flow rate = 0.8 mL/min): $t_{\text{R}} = 20.65$ (major) and 26.75 min (minor).

***S-t*-Butyl-3-hydroxy-2-methyl-3-(4'-methylphenyl)-1-propanthioate (*syn-13b*):** Colorless liquid. $[\alpha]_{\text{D}} = -20.8$ (c 0.2, CHCl_3). IR: $\nu = 3382, 2963, 2925, 1704, 1607, 1455, 1366, 1260, 1172, 1036, 959, 810$ cm^{-1} . ^1H NMR: $\delta = 1.15$ (3H, d, $J = 7.1$ Hz), 1.41 (9H, s), 2.41 (3H, s), 2.79-2.84 (1H, m), 2.98 (1H, bs), 5.04 (1H, d, $J = 4.4$ Hz), 7.09-7.18 (2H, m), 7.21-7.29 (2H, m); ^{13}C NMR: $\delta = 11.4, 21.1, 29.7, 48.2, 55.1, 73.7, 126.0, 128.9, 137.1, 138.3, 205.2$. HRMS (FAB): calcd. for $\text{C}_{15}\text{H}_{23}\text{O}_2\text{S}$ (M+H): 267.1413, found: 267.1411. HPLC (Daicel Chiralpak OD, hexane/isopropanol = 30/1, flow rate = 0.8 mL/min): $t_{\text{R}} = 13.40$ (major) and 15.37 min (minor).

***S-t*-Butyl-3-hydroxy-2-methyl-3-(4'-chlorophenyl)-1-propanthioate (*syn-13d*):** A colorless liquid. $[\alpha]_{\text{D}} = 101.3$ (c 0.5, CHCl_3). IR: $\nu = 3383, 2967, 2925, 1703, 1679, 1591, 1455, 1366, 1259, 1173, 1090, 1038, 961, 821$ cm^{-1} . ^1H NMR: $\delta = 1.11$ (3H, d, $J = 7.1$ Hz), 1.45 (9H, s), 2.75-2.82 (1H, m), 3.10 (1H, bs), 5.09 (1H, d, $J = 4.4$ Hz), 7.21-7.39 (4H, m). ^{13}C NMR: $\delta = 11.4, 29.7, 48.5, 54.8, 73.2, 127.5, 128.4, 133.1, 139.7, 205.2$. HRMS (FAB): calcd. for $\text{C}_{14}\text{H}_{18}\text{ClOS}$ (M-OH): 269.0761, found: 269.0756. HPLC (Daicel Chiralpak OD, hexane/isopropanol = 30/1, flow rate = 0.8 mL/min): $t_{\text{R}} = 17.09$ (major) and 19.34 min (minor).

S-*t*-Butyl-3-hydroxy-2-methyl-3-(α -naphthyl)-1-propanthioate (syn-13f): A colorless liquid. $[\alpha]_D = 121.1$ (*c* 0.2, CHCl₃). IR: $\nu = 3469, 2966, 2925, 1685, 1589, 1512, 1456, 1366, 1266, 1177, 1055, 1034, 959, 884, 804, 773$ cm⁻¹. ¹H NMR: $\delta = 1.21$ (3H, d, *J* = 7.1 Hz), 1.47 (9H, s), 2.77-2.98 (1H, m), 3.05 (1H, bs), 5.14 (1H, d, *J* = 3.6 Hz), 7.42-7.49 (7H, m). ¹³C NMR: $\delta = 10.7, 29.8, 48.5, 53.0, 70.1, 122.5, 124.2, 125.3, 125.4, 126.2, 128.0, 129.1, 129.7, 133.7, 136.2, 205.6$. HRMS (FAB): calcd. for C₁₈H₂₂O₂SNa (M+Na): 325.1233, found: 325.1231. HPLC (Daicel Chiralpak OD, hexane/isopropanol = 30/1, flow rate = 0.8 mL/min): *t*_R = 6.13 (major) and 8.68 min (minor).

References

- 1 B. M. Trost, H. Ito, *J. Am. Chem. Soc.*, **2000**, *122*, 12003-12004
- 2 B. M. Trost, E. R. Silcoff, H. Ito, *Org. Lett.*, **2001**, *3*, 2497-2500
- 3 S. E. Denmark, K. T. Wang, R. A. Stavenger, *J. Am. Chem. Soc.*, **1997**, *119*, 2333-2334
- 4 S. Nagayama, S. Kobayashi, *J. Am. Chem. Soc.*, **2000**, *122*, 11531-11532
- 5 T. Hamada, K. Manabe, S. Ishikawa, S. Nagayama, M. Shiro, S. Kobayashi, *J. Am. Chem. Soc.*, **2003**, *125*, 2989-2996.
- 6 A. Yanagisawa, Y. Nakatsuka, K. Asakawa, M. Wadamoto, H. Kageyama, H. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1477
- 7 E. J. Corry, C. L. Cywn, T. D. Roper, *Tetrahedron Lett.* **1992**, *33*, 6907
- 8 S. Ikuya, S. Toshihiro, S. Hideaki, B. Akio, *Org. Lett.* **2002**, *4*, 301-304
- 9 I. Katsuyuki, I. Tatsuya, S. Ikuya, B. Akio, *Adv. Synth. Catal.* **2002**, *344*, 283-287
- 10 O. Yuhki, K. Kiichirou, I. Taketo, Y. Tohru, *Org. Lett.* **2001**, *3*, 2543-2546
- 11 S. Ikuya, K. Hirofumi, I. Tatsuya, Y. Makoto, B. Akio, *Angew. Chem. Int. Ed.* **2004**, *43*, 711-714
- 12 H. Makoto, H. Hajime, I. Hajime, H. Akira, *J. Am. Chem. Soc.* **1997**, *119*, 5459-5460