Supporting Information

for

CATALYTIC ASYMMETRIC RING-OPENING OF σ-SYMMETRIC CYCLIC CARBONATES WITH CHIRAL AMINO SULFONAMIDE CATALYSTS

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Enzymatic acetylation of σ-symmetric 1,3-diols 15a-c

To a solution of 1,3-diol **15a** (100 mg, 0.319 mmol) in vinyl acetate (6.38 mL) was added PPL (95.7 mg, 16200 units/mmol) at room temperature. After stirring for 4 h, the reaction mixture was filtered and concentrated in *vacuo*. The residue was purified by column chromatography [Silica Gel 60N: *n*-hexane–AcOEt (1:2)] to afford (*R*)-**16a** (45.4 mg, 40%, 98% ee). The enantiomeric excess of (*R*)-**16a** was determined by HPLC analysis [CHIRALPAK IB, *n*-hexane–2-propanol (4:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 12.62 min, t_R (minor) = 15.96 min].

(*R*)-2-{{[(9*H*-Fluoren-9-yl)methoxy]carbonyl}amino}-3-hydroxypropyl Acetate [(*R*)-**16a**]

White solid; mp 129–131 °C; $[\alpha]_D^{18}$ +2.0 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.27 (brt, 1H), 3.61–3.74 (m, 2H), 3.90–4.00 (m, 1H), 4.22 (brs, 3H), 4.43 (d, *J* = 6.5 Hz, 2H), 5.18 (brd, 1H), 7.32 (td, *J* = 1.1, 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H); IR (KBr) 3337, 2958, 1716, 1697, 1542, 1273 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{21}NO_5Na$: 378.1317; found: 378.1325.

(*R*)-2-{[(Benzyloxy)carbonyl]amino}-3-hydroxypropyl Acetate [(*R*)-**16b**]

99% ee, HPLC analysis [CHIRALCEL OJ-H, *n*-hexane–2-propanol (2:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 12.84 min, t_R (minor) = 10.59 min].

White solid; mp 48–50 °C; $[\alpha]_D^{17}$ +1.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.28 (brs, 1H), 3.62–3.73 (m, 2H), 4.00 (brs, 1H), 4.22 (d, *J* = 5.7 Hz, 2H), 5.11 (s, 2H), 5.18 (brs, 1H), 7.31–7.39 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 51.6, 61.7, 62.9, 67.1, 128.1, 128.2, 128.6, 136.2, 156.3, 171.4; IR (KBr) 3341, 1715, 1693, 1543, 1269, 1036 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{17}NO_5Na$: 290.1004; found: 290.1003.

(*R*)-2-[(*tert*-Butoxycarbonyl)amino]-3-hydroxypropyl Acetate [(*R*)-**16c**]

100% ee, HPLC analysis [CHIRALPAK AD-H, *n*-hexane–EtOH (5:1), flow rate: 1.0 mL/min; detection: 220 nm; t_R (major) = 6.52 min].

Pale yellow oil; $[\alpha]_D^{17}$ +5.1 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.45 (s, 9H), 2.09 (s, 3H), 2.39 (brs, 1H), 3.60–3.71 (m, 2H), 3.88 (brs, 1H), 4.21 (d, *J* = 5.7 Hz, 2H), 4.94 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 28.4, 51.1, 62.0, 63.1, 80.0, 155.8, 171.4; IR (neat) 3366, 2979, 1694, 1525, 1392, 1367, 1245 cm^{-1}; HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{10}H_{19}NO_5Na$: 256.1161; found: 256.1154.

Synthesis of (*S*)-17a-c by Cbz protection of (*R*)-16a-c

To a solution of (*R*)-**16a** (34.0 mg, 0.0957 mmol, 98% ee) and pyridine (46.0 μL, 0.574 mmol) in anhydrous THF (1 mL) was added CbzCl (41.0 μL, 0.287 mmol) at room temperature. After stirring at 50 °C for 20.5 h, 1N HCl (5 mL) was added and then extracted with $CHCl_3$ (3 x 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was purified by column chromatography [Silica Gel 60N: *n*-hexane–AcOEt (3:2)] to afford (*S*)-**17a** (16.7 mg, 36%, 97% ee). The enantiomeric excess of (*S*)-**17a** was determined by HPLC analysis [CHIRALPAK IA, *n*-hexane–2-propanol (4:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 14.12 min, t_R (minor) = 19.94 min].

(*S*)-2-{{[(9*H*-Fluoren-9-yl)methoxy]carbonyl}amino}-3-{[(benzyloxy)carbonyl]oxy}propyl Acetate [(*S*)-**17a**]

White solid; mp 57–59 °C; $[\alpha]_D^{19}$ –4.9 (*c* 0.50, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.06 (s, 3H), 4.08–4.15 (m, 1H), 4.16–4.26 (m, 4H), 4.27–4.34 (m, 1H), 4.42 (d, *J* = 6.5 Hz, 2H), 5.08 (brd, 1H), 5.17 (s, 2H), 7.31 (td, *J* = 0.9, 7.4 Hz, 2H), 7.31–7.41 (m, 7H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 47.2, 49.1, 62.8, 66.4, 67.0, 70.1, 120.0, 125.0, 127.1, 127.8, 128.5, 128.68, 128.74, 134.8, 141.3, 143.7, 143.8, 154.8, 155.7, 170.6; IR (KBr) 3329,

3069, 2960, 1739, 1688, 1547, 1287 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{27}NO_7Na$: 512.1685; found: 512.1685.

(*S*)-2-{[(Benzyloxy)carbonyl]amino}-3-{[(benzyloxy)carbonyl]oxy}propyl Acetate [(*S*)-**17b**]

96% ee, HPLC analysis [CHIRALPAK IB, *n*-hexane–2-propanol (4:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 13.00 min, t_R (minor) = 11.57 min].

White solid; mp 69–71 °C; $[\alpha]_D^{19}$ –5.1 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.03 (s, 3H), 4.07–4.17 (m, 1H), 4.17–4.26 (m, 3H), 4.26–4.33 (m, 1H), 5.06–5.14 (m, 1H), 5.10 (s, 2H), 5.16 (s, 2H), 7.30–7.42 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 49.0, 62.8, 66.4, 67.1, 70.1, 128.2, 128.3, 128.4, 128.56, 128.66, 128.70, 134.9, 136.1, 154.8, 155.7, 170.1; IR (KBr) 3278, 2900, 1750, 1689, 1376, 1278, 1232 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{23}NO_7Na$: 424.1372; found: 424.1359.

(*S*)-3-{[(Benzyloxy)carbonyl]oxy}2-[(*tert*-butoxycarbonyl)amino]propyl Acetate [(*S*)-**17c**]

100% ee, HPLC analysis [CHIRALPAK IA, *n*-hexane–2-propanol (6:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 10.80 min].

Colorless oil; $[\alpha]_D^{19}$ –4.5 (*c* 1.66, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.06 (s, 3H), 4.08–4.23 (m, 4H), 4.23–4.32 (m, 1H), 4.85 (brd, 1H), 5.16 (s, 2H), 7.32–7.43 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 28.3, 48.3, 63.0, 66.6, 70.0, 80.1, 128.4, 128.66, 128.70, 134.9, 154.8, 155.1, 170.6; IR (neat) 3365, 2978, 1748, 1715, 1522, 1392, 1367, 1240 cm^{-1}; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{25}NO_7Na$: 390.1529; found: 390.1543.

Synthesis of (*S*)-17a-c by acetylation of (*S*)-3a-c

To a solution of (*S*)-**3a** (40.0 mg, 0.0894 mmol, 81% ee) and pyridine (17.2 μL, 0.215 mmol) in anhydrous CH_2Cl_2 (0.42 mL) was added Ac_2O (10.1 μL, 0.107 mmol) at room temperature. After

stirring for 22 h, 1N HCl (3 mL) was added and then extracted with $CHCl_3$ (3 x 5 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was purified by column chromatography [Silica Gel 60N: *n*-hexane–AcOEt (3:2)] to afford (*S*)-**17a** (17.6 mg, 40%, 83% ee). The enantiomeric excess of (*S*)-**17a** was determined by HPLC analysis [CHIRALPAK IA, *n*-hexane–2-propanol (4:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 14.07 min, t_R (minor) = 19.76 min].

(*S*)-2-{{[(9*H*-Fluoren-9-yl)methoxy]carbonyl}amino}-3-{[(benzyloxy)carbonyl]oxy}propyl Acetate [(*S*)-**17a**]

White solid; mp 101–103 °C; $[\alpha]_D^{20}$ –3.7 (*c* 0.50, $CHCl_3$); HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{27}NO_7Na$: 512.1685; found: 512.1668.

(*S*)-2-{[(Benzyloxy)carbonyl]amino}-3-{[(benzyloxy)carbonyl]oxy}propyl Acetate [(*S*)-**17b**]

78% ee, HPLC analysis [CHIRALPAK IB, *n*-hexane–2-propanol (4:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 13.00 min, t_R (minor) = 11.50 min].

White solid; mp 66–68 °C; $[\alpha]_D^{17}$ –3.9 (*c* 1.00, $CHCl_3$); HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{23}NO_7Na$: 424.1372; found: 424.1357.

(*S*)-3-{[(Benzyloxy)carbonyl]oxy}2-[(*tert*-butoxycarbonyl)amino]propyl Acetate [(*S*)-**17c**]

70% ee, HPLC analysis [CHIRALPAK IA, *n*-hexane–2-propanol (6:1), flow rate: 1.0 mL/min; detection: 254 nm; t_R (major) = 10.71 min, t_R (minor) = 9.65 min].

Colorless oil; $[\alpha]_D^{18}$ –2.2 (*c* 1.66, $CHCl_3$); HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{25}NO_7Na$: 390.1529; found: 390.1498.