Supporting Information

Chiral Ligand-Controlled Asymmetric Conjugate Addition of Lithium Amide to Enoates

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General

¹H-NMR (500 MHz) and ¹³C-NMR (125 MHz) were measured in CDCl₃. Chemical shift values were expressed in ppm downfield from internal tetramethylsilane.

***tert*-Butyl 3-(2-naphthyl)-2-propenoate (3f).** To a suspension of *tert*-butyl triphenylphosphorane diylacetate (8.82 g, 23.4 mmol) in toluene (15 mL) was added 2-naphthaldehyde (2.82 g, 18.0 mmol) in toluene (15 mL). The mixture was stirred for 18 h at rt and was filtrated. Concentration, silica gel column chromatography (AcOEt/hexane = 1/30) and recrystallization (MeCN/H₂O=1/2) gave **3f** (4.1 g, 91%) as colorless plates of mp 74–75 °C. ¹H NMR: 1.57 (9H, s), 6.49 (1H, d, *J* = 15.9 Hz), 7.49–7.51 (2H, m), 7.66 (1H, d, *J* = 8.3 Hz), 7.75 (1H, d, *J* = 15.9 Hz), 7.81–7.86 (3H, m), 7.91 (1H, s). ¹³C NMR: 28.2, 80.5, 120.4, 123.6, 126.6, 127.1, 127.8, 128.5, 128.6, 129.6, 132.2, 133.3, 134.1, 143.6, 166.4. IR (nujol): 1713, 1150 cm⁻¹. EIMS *m/z*: 254 (M⁺). Anal. Calcd. for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.5; H, 7.13.

General Procedure for the External Chiral Ligand 1-Controlled Asymmetric Conjugate Addition of Lithium *N*-benzyltrimethylsilylamide (2c) to Enoates (method A). Under Ar atmosphere, *n*-BuLi (0.9 mL, 1.6 M in hexane solution, 1.5 mmol) was added to a solution of *N*-benzyltrimethylsilylamine (0.3 mL, 1.5 mmol) in toluene (4 mL) at –78 °C over 5 min. After stirring for 0.5 h, **1** (436 mg, 1.8 mmol) in toluene (2 mL) was added and the mixture was stirred for 0.5 h at –78 °C. A toluene solution of **3** (1.0 mmol) and TMSCl (0.63 mL, 5.0 mmol) was added over 5 min. The mixture was stirred at –78 °C for the indicated time and was quenched with satd. NH₄Cl (1.5 mL). After addition of satd. NaHCO₃ (20 mL), the mixture was extracted with AcOEt. The organic layer was washed with brine and dried over Na₂SO₄. Concentration and silica gel column chromatography gave **4** (or **5**).

Method B. The similar procedure as the method A excluding no addition of TMSCl.

General Procedure for Debenzylation. A mixture of **4c** (115 mg, 0.37 mmol) and Pearlman's catalyst (30.8 mg, 0.074 mmol) in MeOH (1.5 mL) was stirred under hydrogen atmosphere (7 atm) at rt. The reaction mixture was filtered and concentrated. Silica gel

column chromatography (AcOEt/hexane = 1/2) gave **4** ($R^1=R^2=H$) (77 mg, 94%).

tert-Butyl 3-(diisopropylamino)-3-phenylpropanoate (4a): Chromatography (AcOEt/hexane = 1/90) gave a colorless oil of $[\alpha]^{25}_D +32.5$ (c 0.72, $CHCl_3$). 68% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=500/1, 0.5 mL/min, 254 nm, major 13.1 min and minor 18.9 min). 1H NMR: 0.93 and 1.10 (each 6H, d, $J = 6.8$ Hz), 1.32 (9H, s), 2.72 (1H, dd, $J = 4.9, 15.0$ Hz), 2.84 (1H, dd, $J = 10.4, 15.0$ Hz), 3.15 (2H, sept, $J = 6.8$ Hz), 4.47 (1H, dd, $J = 4.9, 10.4$ Hz), 7.17 (1H, t, $J = 7.3$ Hz), 7.25 (2H, dd, $J = 7.3, 7.6$ Hz), 7.38 (2H, d, $J = 7.6$ Hz). ^{13}C NMR: 23.0, 23.2, 28.2, 41.2, 45.5, 55.2, 80.4, 126.5, 127.9, 128.3, 144.1, 171.8. IR (neat): 3400, 1728, 1130 cm^{-1} . EIMS m/z : 305 (M^+), 262 ($M - i\text{-Pr}$), 206 ($262 - t\text{-Bu}$), 190 ($M - CO_2t\text{-Bu}$). HRMS (m/z): M^+ Calcd for $C_{19}H_{31}NO_2$, 305.2357; Found, 305.2355.

tert-Butyl 3-(dibenzylamino)-3-phenylpropanoate (4b): Chromatography (AcOEt/hexane = 1/70) gave a colorless oil. 4% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=250/1, 1.0 mL/min, 254 nm, major 10.6 min and minor 7.7 min). 1H NMR: 1.33 (9H, s), 2.71 (1H, dd, $J = 8.7, 14.5$ Hz), 2.99 (1H, dd, $J = 6.9, 14.5$ Hz), 3.28 (1H, d, $J = 13.8$ Hz), 3.71 (1H, d, $J = 13.8$ Hz), 4.27 (1H, dd, $J = 6.9, 8.7$ Hz), 7.20–7.36 (15H, m). ^{13}C NMR: 27.9, 37.3, 53.9, 59.2, 80.4, 126.9, 127.2, 127.9, 128.1, 128.7, 128.8, 138.3, 139.8, 171.0. IR (neat): 3425, 1728, 1153 cm^{-1} . EIMS m/z : 401 (M^+), 344 ($M - t\text{-Bu}$), 310 ($M - Bn$), 286 ($M - CO_2t\text{-Bu}$). These are identical to those reported in Bull, S. D.; Davies, S. G.; Fenton, G.; Mulvaney, A. W.; Prasad, R. S.; Smith, A. D. *J. Chem. Soc. Perkin Trans.1*, **2000**, 3765–3774.

tert-Butyl (R)-3-(benzylamino)-3-phenylpropanoate (4c): Chromatography (AcOEt/hexane = 1/25) gave a colorless oil of $[\alpha]^{25}_D +32.5$ (c 1.35, $CHCl_3$). 97% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=100/1, 1.0 mL/min, 254 nm, major 5.7 min and minor 6.7 min). 1H NMR: 1.37 (9H, s), 2.11 (1H, brs), 2.53 (1H, dd, $J = 5.2, 15.3$ Hz), 2.64 (1H, dd, $J = 8.9, 15.3$ Hz), 3.54 and 3.64 (each 1H, d, $J = 13.1$ Hz), 4.07 (1H, dd, $J = 5.2, 8.9$ Hz), 7.21–7.37 (10H, m). ^{13}C NMR: 28.0, 44.3, 51.4, 59.2, 80.6, 126.8, 127.25, 127.34, 128.1, 128.3, 128.5, 140.4, 142.7, 171.1. IR (neat): 3333, 1724, 1150 cm^{-1} . EIMS m/z : 311 (M^+), 254 ($M - t\text{-Bu}$), 220 ($M - Bn$), 196 ($M - CO_2t\text{-Bu}$), 164 ($256 - Bn$). These are identical to those reported in Bull, S. D.; Davies, S. G.; Fenton, G.; Mulvaney, A. W.; Prasad, R. S.; Smith, A. D. *J. Chem. Soc. Perkin Trans.1*, **2000**, 3765–3774.

tert-Butyl 3-(benzylamino)butanoate (5b): Chromatography (AcOEt/hexane = 1/10) gave a colorless oil of $[\alpha]^{25}_D +13.8$ (c 1.03, $CHCl_3$). 97% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=400/1, 1.0 mL/min, 254 nm, major 21.8 min and minor 19.0 min). 1H NMR: 1.14 (3H, d, $J = 6.1$ Hz), 1.44 (9H, s), 1.72 (1H, brs), 2.29 (1H, dd, $J = 5.8, 15.0$ Hz), 2.41 (1H, dd, $J = 7.0, 15.0$ Hz), 3.12 (1H, ddq, $J = 5.8, 6.1, 7.0$ Hz), 3.75 and 3.82 (each 1H, d, $J = 12.8$ Hz), 7.22–7.33 (5H, m). ^{13}C NMR: 20.4, 28.1, 42.8, 49.9, 51.2, 80.3, 126.8, 128.1, 128.3, 140.5, 171.7. IR (neat): 3329, 1724, 1157 cm^{-1} . EIMS m/z : 249 (M^+), 192 ($M - t\text{-Bu}$),

134 (M – CO₂*t*-Bu). Anal. Calcd. for C₁₅H₂₃NO₂: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.47; H, 9.12; N, 5.39.

***tert*-Butyl 3-(benzylamino)-4-methylpentanoate (5c):** Chromatography (AcOEt/hexane = 1/30) gave a colorless oil of [α]_D²⁵ +6.33 (c 1.09, CHCl₃). 99% ee (HPLC, Daicel Chiralpak OJ, Hexane/*i*-PrOH=1000/1, 0.5 mL/min, 254 nm, major 13.4 min and minor 16.3 min). ¹H NMR: 0.90 and 0.92 (each 3H, d, *J* = 7.1 Hz), 1.44 (9H, s), 1.51 (1H, brs), 1.88 (1H, dq, *J* = 7.1, 8.7 Hz), 2.26 (1H, dd, *J* = 8.2, 15.0 Hz), 2.36 (1H, dd, *J* = 4.6, 15.0 Hz), 2.86 (1H, ddd, *J* = 4.6, 8.2, 8.7 Hz), 3.76 and 3.79 (each 1H, d, *J* = 12.8 Hz), 7.21–7.35 (5H, m). ¹³C NMR: 17.6, 18.8, 28.1, 30.4, 37.4, 51.6, 59.9, 80.3, 126.8, 128.1, 128.2, 140.9, 172.5. IR (neat): 3352, 1728, 1153 cm⁻¹. EIMS *m/z*: 278 (M⁺), 234 (M – *i*-PrH), 221 (M – *t*-Bu), 162 (M – CO₂*t*-Bu). Anal. Calcd. for C₁₇H₂₇NO₂: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.42; H, 9.51; N, 5.04.

***tert*-Butyl 3-(benzylamino)-4-hexenoate (5d):** Chromatography (AcOEt/hexane = 1/20) gave a colorless oil of [α]_D²⁵ +13.0 (c 1.01, CHCl₃). 98% ee (HPLC, Daicel Chiralpak OB-H, Hexane/*i*-PrOH=1000/1, 1.0 mL/min, 254 nm, major 7.6 min and minor 9.0 min). ¹H NMR: 1.42 (9H, s), 1.70 (3H, d, *J* = 6.4 Hz), 2.35 (1H, dd, *J* = 6.4, 14.8 Hz), 2.44 (1H, dd, *J* = 7.7, 14.8 Hz), 3.43 (1H, ddd, *J* = 6.4, 7.6, 7.7 Hz), 3.80 and 3.64 (each 1H, d, *J* = 13.2 Hz), 5.32 (1H, dd, *J* = 7.6, 15.3 Hz), 5.61 (1H, dq, *J* = 6.4, 15.3 Hz), 7.21–7.31 (5H, m). ¹³C NMR: 17.7, 28.1, 42.3, 51.2, 57.2, 80.5, 126.8, 127.7, 128.2, 128.3, 132.5, 140.5, 171.3. IR (neat): 3329, 1728, 1157 cm⁻¹. EIMS *m/z*: 275 (M⁺), 218 (M – *t*-Bu), 184 (M – Bn), 160 (M – CO₂*t*-Bu). Anal. Calcd. for C₁₇H₂₅NO₂: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.36; H, 9.33; N, 5.22.

***tert*-Butyl 3-(benzylamino)-3-(1-naphthyl)propanoate (5e):** Chromatography (ether/hexane = 1/15) gave a colorless oil of [α]_D²⁵ +4.9 (c 0.94, CHCl₃). 91% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=100/1, 1.0 mL/min, 254 nm, major 9.5 min and minor 14.3 min). ¹H NMR: 1.37 (9H, s), 2.04 (1H, brs), 2.67–2.75 (2H, m), 3.62 and 3.72 (each 1H, d, *J* = 13.1 Hz), 4.97 (1H, dd, *J* = 4.9, 8.3 Hz), 7.22–7.29 (5H, m), 7.41–7.52 (3H, m), 7.74–7.79 (2H, m), 7.81–7.89 (1H, m), 8.23 (1H, d, *J* = 7.4 Hz). ¹³C NMR: 28.0, 43.7, 51.6, 80.8, 123.0, 123.9, 125.4, 125.6, 126.0, 126.9, 127.7, 128.2, 128.3, 128.9, 131.4, 134.0, 138.1, 140.4, 171.4. IR (neat): 3333, 1724, 1150 cm⁻¹. EIMS *m/z*: 361 (M⁺), 304 (M – *t*-Bu), 270 (M – Bn), 246 (M – CO₂*t*-Bu). Anal. Calcd. for C₂₄H₂₇NO₂: C, 79.74; H, 7.53; N, 3.87. Found: C, 79.76; H, 7.59; N, 3.69.

***tert*-Butyl 3-(benzylamino)-3-(2-naphthyl)propanoate (5f):** Chromatography (ether/hexane = 1/10) gave a colorless oil of [α]_D²⁵ +35.5 (c 1.10, CHCl₃). 94% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=100/1, 1.0 mL/min, 254 nm, major 8.1 min and minor 9.6 min). ¹H NMR: 1.36 (9H, s), 2.01 (1H, brs), 2.61 (1H, dd, *J* = 5.2, 15.3 Hz), 2.72 (1H, dd, *J*

= 8.9, 15.3 Hz), 3.58 and 3.66 (each 1H, d, J = 13.1 Hz), 4.25 (1H, dd, J = 5.2, 8.9 Hz), 7.22–7.32 (5H, m), 7.45–7.54 (3H, m), 7.79–7.86 (4H, m). ^{13}C NMR: 28.0, 44.2, 51.4, 59.3, 80.7, 125.0, 125.7, 126.0, 126.3, 126.9, 127.7, 127.8, 128.2, 128.3, 128.4, 133.0, 133.4, 140.1, 140.3, 171.1. IR (neat): 3333, 1724, 1150 cm^{-1} . EIMS m/z : 361 (M^+), 304 ($\text{M} - t\text{-Bu}$), 270 ($\text{M} - \text{Bn}$) 246 ($\text{M} - \text{CO}_2t\text{-Bu}$). Anal. Calcd. for $\text{C}_{24}\text{H}_{27}\text{NO}_2$: C, 79.74; H, 7.53; N, 3.87. Found: C, 79.49; H, 7.52; N, 3.88.

***tert*-Butyl (1*R*,2*S*)-2-(benzylamino)cyclopentanecarboxylate (*cis*-5*g*):** Chromatography (AcOEt/hexane = 1/20) gave a colorless oil of $[\alpha]_{\text{D}}^{25} -29.4$ (c 1.18, CHCl_3). 92% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=400/1, 1.0 mL/min, 254 nm, major 11.3 min and minor 9.7 min). ^1H NMR: 1.45 (9H, s), 1.51–2.01 (6H, m), 1.74 (1H, brs), 2.84 (1H, m), 3.27 (1H, m), 3.80 (2H, s), 7.21–7.33 (5H, m). ^{13}C NMR: 22.1, 27.5, 28.2, 31.6, 48.3, 52.3, 61.4, 80.1, 126.7, 128.0, 128.3, 140.7, 174.0. IR (neat): 3337, 1720, 1150 cm^{-1} . EIMS m/z : 275 (M^+), 218 ($\text{M} - t\text{-Bu}$), 184 ($\text{M} - \text{Bn}$). Anal. Calcd. for $\text{C}_{17}\text{H}_{25}\text{NO}_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.86; H, 9.33; N, 4.98.

***tert*-Butyl (1*S*, 2*S*)-2-(benzylamino)cyclopentanecarboxylate (*trans*-5*g*):** Chromatography (AcOEt/hexane = 1/2) gave a colorless oil of $[\alpha]_{\text{D}}^{25} + 49.8$ (c 0.51, CHCl_3). 97% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=100/1, 1.0 mL/min, 254 nm, major 7.3 min and minor 6.2 min). ^1H NMR: 1.43 (9H, s), 1.61–2.05 (6H, m), 2.05 (1H, brs), 2.52 (1H, m), 3.26 (1H, m), 3.75 and 3.82 (each 1H, d, J = 13.1 Hz), 7.24–7.32 (5H, m). ^{13}C NMR: 23.5, 28.1, 28.5, 33.1, 51.8, 52.5, 62.7, 80.2, 126.9, 128.1, 128.4, 140.2, 175.0. IR (neat): 3325, 1724, 1150 cm^{-1} . EIMS m/z : 275 (M^+), 218 ($\text{M} - t\text{-Bu}$), 184 ($\text{M} - \text{Bn}$). HRMS (m/z): M^+ Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2$, 275.1885; Found, 275.1893.

Methyl 3-(benzylamino)butanoate: Chromatography (AcOEt/hexane = 1/5) gave a colorless oil of $[\alpha]_{\text{D}}^{25} + 15.3$ (c 0.70, CHCl_3). 82% ee (HPLC, Daicel Chiralpak OD-H, Hexane/*i*-PrOH=100/1, 1.0 mL/min, 254 nm, major 16.0 min and minor 12.6 min). ^1H NMR: 1.16 (3H, d, J = 6.1 Hz), 1.67 (1H, brs), 2.39 (1H, dd, J = 6.1, 15.3 Hz), 2.50 (1H, dd, J = 7.0, 15.3 Hz), 3.16 (1H, ddq, J = 6.1, 6.1, 7.0 Hz), 3.67 (3H, s), 3.76 and 3.83 (each 1H, d, J = 13.2 Hz), 7.22–7.32 (5H, m). ^{13}C NMR: 20.4, 41.4, 49.6, 51.2, 51.5, 126.9, 128.1, 128.4, 140.4, 172.7. IR (neat): 3329, 1736, 1176 cm^{-1} . EIMS m/z : 208 (M^+), 193 ($\text{M} - t\text{-Bu}$), 134 ($\text{M} - \text{CO}_2\text{Me}$).

Asao, N.; Uyehara, T.; Yamamoto, Y. *Tetrahedron* **1988**, *44*, 4173–4180.

***tert*-Butyl (R)-3-amino-3-phenylpropionate:** Chromatography (AcOEt/hexane = 1/2) gave a colorless oil of $[\alpha]_{\text{D}}^{25} + 18.8$ (c 0.75, CHCl_3). ^1H NMR: 1.42 (9H, s), 1.89 (2H, brs), 2.59 (2H, d, J = 6.8 Hz), 4.38 (1H, t, J = 6.8 Hz), 7.23–7.37 (5H, m). ^{13}C NMR: 28.0, 45.3, 52.7, 80.7, 126.3, 127.3, 128.5, 144.7, 171.3. IR (neat): 3383, 2978, 1724, 1150 cm^{-1} . EIMS m/z :

221 (M⁺), 164 (M – *t*-Bu), 106 (M – CO₂*t*-Bu).

Davies, S. G.; Garrido, N. M.; Ichihara, O.; Walters, I. A. S. *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1153–1155.

***tert*-Butyl (1*R*,2*S*)-2-aminocyclopentanecarboxylate** : Chromatography (MeOH/ether = 1/2) gave a colorless oil of [α]_D²⁵ –4.0 (c 1.0, CHCl₃). ¹H NMR: 1.47 (9H, s), 1.49–1.60 (4H, m), 1.79–2.02 (4H, m), 2.67–2.72 (1H, m), 3.54–3.58 (1H, m). ¹³C NMR: 22.3, 26.2, 28.2, 34.8, 51.1, 54.9, 80.3, 173.6. IR (neat): 3383, 1724, 1366, 1153 cm^{–1}. EIMS *m/z*: 185 (M⁺), 128 (M – *t*-Bu), 84 (M – CO₂*t*-Bu).

Davies, S. G.; Ichihara, O.; Lenoir, I.; Walters, I. A. S. *J. Chem. Soc., Perkin Trans. 1*, **1994**, 1141–1145.

***tert*-Butyl (Z)-2-trimethylsilylcinnamate** : Chromatography (ether/hexane = 1/50) gave a colorless oil. ¹H NMR: 0.24 (9H, s), 1.45 (9H, s), 6.75 (1H, s), 7.24–7.31 (3H, m), 7.37–7.39 (2H, m). ¹³C NMR: –1.62, 28.0, 81.0, 128.1, 128.2, 128.3, 136.8, 140.0, 140.4, 171.1. IR (neat): 1701, 1149 cm^{–1}. EIMS *m/z*: 276 (M⁺), 220 (M+1 – *t*-Bu), 205 (M – TMS).

Saito, Y.; Takeuchi, S. *Synthesis* **1983**, 734–735.

68% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 500/1, 0.5 ml/min, 254 nm, major 13.1 min and minor 18.9 min)

$^1\text{H-NMR}$ of **4b** in CDCl_3
(Table 1, Entry 2)

$^{13}\text{C-NMR}$ of **4b** in CDCl_3
(Table 1, Entry 2)

4% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 250/1, 1.0 ml/min, 254 nm, major 10.6 min and minor 7.7 min)

97% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 100/1, 1.0 ml/min, 254 nm, major 5.7 min and minor 6.7 min)

82% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 100/1, 1.0 ml/min, 254 nm, major 16.0 min and minor 12.6 min)

97% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 400/1, 1.0 ml/min, 254 nm, major 21.8 min and minor 19.0 min)

¹H-NMR of **4a** in CDCl₃
(Table 2, Entry 3 and 4)

¹³C-NMR of **5d** in CDCl₃
(Table 2, Entry 3 and 4)

98% ee (HPLC, Daicel Chiralpak OJ, hexane/*i*-PrOH = 1000/1, 0.5 ml/min, 254 nm, major 12.9 min and minor 15.7 min)

98% ee (HPLC, Daicel Chiralpak OB-H, hexane/*i*-PrOH = 1000/1, 1.0 ml/min, 254 nm, major 9.0 min and minor 7.6 min)

¹H-NMR of **5e** in CHCl₃
(Table 2, Entry 7 and 8)

¹³C-NMR of **5e** in CHCl₃
(Table 2, Entry 7 and 8)

92% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 100/1, 1.0 ml/min, 254 nm, major 9.4 min and minor 14.2 min)

94% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 100/1, 1.0 ml/min, 254 nm, major 8.1 min and minor 9.6 min)

^1H -NMR of *cis*-**5g** in CDCl_3
(Table 2, Entry 11 and 12)

^{13}C -NMR of *cis*-**5g** in CDCl_3
(Table 2, Entry 11 and 12)

cis **5g** (Table 2, entry 11)

92% ee (HPLC, Daicel Chiralpak OD-H, hexane/*i*-PrOH = 400/1, 1.0 ml/min, 254 nm, major 11.3 min and minor 9.7 min)

¹H-NMR of *trans*-**5g** in CDCl₃
(Table 2, Entry 11 and 12)