Supporting Information

Asymmetric Synthesis of β -Amino Esters by Aza-Michael reaction of α,β -Unsaturated Amides Using (*S,S*)-(+)-Pseudoephedrine as Chiral Auxiliary

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1.- Diastereoselective conjugate addition of lithium benzylamides to α,β -unsaturated amides **1a-e**.

General procedures:

PROCEDURE A: A solution of *n*-BuLi (4 mmol) was added to a solution of dibenzylamine or *N*-Methylbenzylamine (4 mmol) in dry toluene (40 mL) at -78°C and the reaction was stirred at this temperature for 30 min. This mixture was slowly added within 2 h over a cooled (-90°C) solution of the corresponding amide **1a-e** (1 mmol) in dry toluene (20 mL). The reaction was stirred for further 20h. at this temperature, after which it was quenched with a saturated NH_4Cl solution (30 mL). The mixture was extracted with CH_2Cl_2 (3 x 15ml) and the combined organic fractions were collected, dried over Na_2SO_4 , filtered and the solvent removed *in vacuo* affording the wanted amides after flash column chromatography purification (hexanes:AcOEt 1:1)

PROCEDURE B: A solution of *n*-BuLi (2 mmol) was added to a solution of the benzylamine (2 mmol) and TMEDA (2 mmol) in dry toluene (40 mL) at -78°C and the reaction was stirred at this temperature for 30 min. The mixture was cooled to -90°C and a solution of the corresponding amide **1a-e** (1 mmol) in dry toluene (20 mL) was added within 30 min. The reaction was stirred for further 7h. at this temperature, after which it was quenched with a saturated NH_4Cl solution (30 mL). The mixture was extracted with CH_2Cl_2 (3 x 15ml) and the combined organic fractions were collected, dried over Na_2SO_4 , filtered and the solvent removed *in vacuo* affording the wanted amides after flash column chromatography purification (hexanes:AcOEt 1:1)

(+)-(1'S,2'S,3R)-3-dibenzylamino-*N*-methyl-*N*-(2'-phenyl-2'-hydroxy-1'-methylethyl)butanamide (2a).

Amide **2a** was prepared in >99% de (Chiralcel OD column, UV detector, *iso*-propanol/hexanes 2/98, flow rate: 1.00mL/min.), according to procedure A. Yield: 85%. Mp. $117-119^{\circ}\text{C}$ (hexanes/*i*PrOH). $[\alpha]_{\text{D}}^{20}$: +67.1 (0.31, CH_2Cl_2). $^1\text{H-NMR}$ (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.65* (d, 3H, $J=6.7$ Hz); 0.75 (d, 3H, $J=6.7$ Hz); 1.11 (t, 3H, $J=6.1$ Hz); 2.31 (dd, $J=14.2$, 8.3Hz, 2H); 2.57 (s, 3H); 2.65 (dd, $J=13.4$, 8.3Hz, 2H); 2.86* (s, 3H); 3.18 (m, 1H); 3.53 (d, 2H, $J=13.8$ Hz); 3.64 (d, 2H, $J=13.8$ Hz); 4.46 (m, 1H); 4.55 (d, 1H); 7.29 (m, 15H). $^{13}\text{C-NMR}$ (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 14.2; 14.3*; 26.8; 33.1; 37.8*; 39.2; 50.54; 51.3*; 53.5. 58.4; 75.4*; 76.4; 126.1; 126.8; 127.4; 128.0; 128.2; 139.4;

140.4*; 141.2*; 142.3; 172.8*; 174.0. IR (KBr): 3358 (OH); 1610 (C=O). MS (EI) m/z (Rel. Int.): 339 (40), 321.4 (10), 224 (30), 196 (20), 148 (20); 132 (20), 107 (10), 91 (100), 79 (10), 65 (10). Anal. Calcd for C₂₈H₃₄N₂O₂: C, 78.10; H, 7.96; N, 6.51. Found. C, 78.16; H, 8.08; N, 6.42.

(+)-(1'S,2'S,3R)-3-dibenzylamino-N-methyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)pentanamide (2b)

Amide **2b** was prepared in 88% de (Chiralcel OD column, UV detector, *iso*-propanol/hexanes 2/98, flow rate: 1.00mL/min.), according to procedure B. Yield: 85%. ¹H-NMR (δ, ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.65* (d, 3H, J = 6.73 Hz); 0.96 (t, 3H, J = 7.3Hz); 1.07 (d, 3H, J = 6.3 Hz); 1.36 (m, 1H); 1.60 (m, 1H); 2.27 (dd, 1H, J = 14.5, J = 8.9Hz); 2.62 (dd, 1H, J = 14.5, J = 8.9Hz); 2.72 (s, 3H); 2.84* (s, 3H); 3.0 (m, 1H); 3.46 (d, 2H, J = 13.4Hz); 4.49 (m, 1H); 4.57 (d, 1H, J = 7.3Hz); 7.29 (m, 15H). ¹³C-NMR (δ, ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 11.6; 14.4; 14.8*; 24.2; 32.9*; 34.3; 53.1; 56.8; 57.5*; 58.4; 75.4*; 76.4; 126.2; 126.6; 126.8; 126.9; 127.2; 127.2; 127.9; 128.2; 128.3; 128.57; 128.7; 128.9; 139.8; 140.3*; 141.3*; 142.3; 173.5*; 174.5. IR (CHCl₃): 3358 (OH); 1610 (C=O). MS (EI) m/z (Rel. Int.): 415 (M⁺-18, 1), 353 (24), 335 (3), 250 (2), 238 (19), 196 (16), 188 (3), 146 (17), 132 (4), 91 (100), 79 (13), 58 (15). Anal. Calcd for C₂₉H₃₆N₂O₂: C, 78.34; H, 8.16; N, 6.30. Found. C, 77.41; H, 8.16; N, 6.24.

(+)-(1'S,2'S,3R)-3-dibenzylamino-N,4-dimethyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)pentanamide (2c)

Amide **2c** was prepared in 64% de (Chiralcel OD column, UV detector, *iso*-propanol/hexanes 4/96, flow rate: 0.80mL/min.), according to procedure B. Yield: 62%. ¹H-NMR (δ, ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.84 (d, 3H, J = 7.14Hz); 1.04 (d, 3H, J = 6.3Hz); 1.15 (d, 3H, J = 7.1Hz); 1.81 (m, 1H); 2.33 (m, 1H); 2.53 (m, 1H); 2.8 (s, 3H); 2.86* (s, 3H); 3.14 (m, 1H); 3.41 (d, 2H, J = 13.8Hz); 3.78 (d, 2H, J = 13.8Hz); 4.53 (m, 1H); 4.63 (d, 1H, J = 7.9Hz); 7.33 (m, 15H). ¹³C-NMR (δ, ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 14.4; 15.0*; 19.8*; 21.2; 31.2*; 31.4; 31.8; 33.1; 54.0*; 54.5; 60.9; 76.5*; 76.5; 126.6; 126.4; 126.6; 126.7; 127.5; 127.6; 127.9; 128.3; 128.6; 129.0; 129.0; 140.0; 140.3*; 141.3; 142.3; 174.0; 174.7. IR (CHCl₃): 3347 (OH); 1605 (C=O). MS (EI) m/z (Rel. Int.): 455 (1),

415 (4), 367 (12), 308 (1), 290 (3), 252 (11), 220 (3), 196 (12), 160 (8), 148 (13), 107 (16), 91 (100), 58 (24). Anal. Calcd for C₃₀H₃₈N₂O₂: C, 78.56; H, 8.35; N, 6.11. Found. C, 78.44; H, 8.43; N, 6.23.

(+)-(1'S,2'S,3R)-3-dibenzylamino-N,4,4-trimethyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)pentanamide (2d)

Amide **2d** was prepared in >99% de (Chiralcel OD column, UV detector, *iso*-propanol/hexanes 4/96, flow rate: 0.80mL/min.), according to procedure A. Yield: 33%. $[\alpha]_D^{20} = +52.9$ (c = 0.58, CH₂Cl₂). ¹H-NMR (δ, ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.87 (m, 9H); 1.14 (d, 3H, *J* = 7.1Hz); 2.31 (m, 1H); 2.52 (m, 1H); 2.80 (s, 3H); 2.87* (s, 3H); 3.12 (m, 1H); 3.38 (d, 2H, *J* = 13.8Hz); 3.75 (d, 2H, *J* = 13.8Hz); 4.48 (m, 1H); 4.61 (m, 1H); 7.29 (m, 15H). ¹³C-NMR (δ, ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 14.4; 19.8*; 20.8; 31.4; 31.8; 33.1; 54.0*; 54.5; 60.7; 60.9*; 75.8*; 76.3; 126.2; 126.5; 127.4; 127.7; 128.3; 140.0; 140.3*; 141.8*; 142.4; 174.0*; 174.6. IR (CHCl₃): 3358 (OH); 1610 (C=O). MS (EI) *m/z* (Rel. Int.): 415 (4), 367 (4); 347 (2); 290 (83); 252 (11); 220 (3); 196 (15); 160 (10); 148 (15); 107 (12); 91 (100); 58 (17). Anal. Calcd for C₃₁H₄₀N₂O₂: C, 78.77; H, 8.53; N, 5.93. Found. C, 78.83; H, 8.74; N, 6.71.

(+)-(1'S,2'S,3S)-3-dibenzylamino-N-methyl-3-phenyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)propanamide (2e)

Amide **2e** was prepared in 96% de (Chiralcel OD column, UV detector, *iso*-propanol/hexanes 4/96, flow rate: 0.80mL/min.), according to procedure A. Yield: 15%. $[\alpha]_D^{20} = +46.9$ (c = 0.24, CH₂Cl₂). ¹H-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 0.95 (d, 3H, *J* = 6.7Hz); 1.01 (d, 3H, *J* = 6.7Hz); 2.65 (s, 3H); 2.67* (s, 3H); 2.90 (m, 3H); 3.33 (m, 2H); 3.67 (m, 2H); 4.52 (m, 2H); 7.32 (m, 20H). ¹³C-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 14;3; 14;7; 32;6; 36;4; 36;8*; 54;1*; 54;3; 60;2; 60;9*; 75;2*; 75;4; 126;4; 126;8; 127;2; 127;3; 127;5; 127;9; 128;1; 128;2; 128;3; 128;4; 128;6; 128;7; 138;5*; 138;9; 141;1*; 142;2; 173;2; 173;3*. IR (CHCl₃): 3358 (OH), 1610 (C=O). MS (EI) *m/z* (Rel. Int.): 493 (M⁺, 1), 401 (24), 286 (19), 236 (6), 196 (49), 148 (13), 107 (8), 91 (100), 58 (11). Anal. Calcd for C₂₇H₃₂N₂O₂: C, 77.85; H, 7.74; N, 6.73. Found. C, 77.77; H, 7.76; N, 6.93.

(+)-(1'S,2'S,3R)-3-(benzylmethylamino)-N-methyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)butanamide (3a)

Amide **3a** was prepared in >99% de (Chiralcel OD column, UV detector, isopropanol/hexanes 2/98, flow rate: 1.00mL/min.), according to procedure A. Yield: 88%. $[\alpha]_D^{20} = +57.1$ (c = 0.16, CH₂Cl₂). ¹H-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 0.9* (d, 3H, J= 6.3Hz); 1.01 (d, 3H, J= 6.3Hz); 1.07 (d, 3H, J= 6.3Hz); 2.14 (s, 3H); 2.21* (s, 3H); 2.3 (dd, J=14.0, 9.1Hz, 2H); 2.57 (dd, J=14.2, 8.3Hz, 2H); 2.73 (s, 3H); 2.87* (s, 3H); 3.26 (m, 1H); 3.51 (m, 2H); 4.5 (d, 1H, J= 6.74Hz); 4.7 (m, 1H); 7.32 (m, 10H). ¹³C-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 13.6*; 14.0; 14.5; 15.3; 26.8; 31.7; 36.4; 38.5*; 54.4; 55.2*; 57.3; 58.0*; 58.4; 74.8*; 75.6; 126.4; 126.7; 127.3; 127.7; 128.0; 128.2; 128.6; 128.7; 139.0; 139.1*; 141.8*; 142.0; 172.6*; 173.4. IR (CHCl₃): 3358 (OH), 1610 (C=O). MS (EI) m/z (Rel. Int.): 263 (85), 247 (1), 234 (3), 219 (5), 205 (5), 190 (5), 165 (2), 148 (27), 126 (15), 120 (64), 91 (100), 58 (62), 56 (20). Anal. Calcd for C₂₂H₃₀N₂O₂: C, 74.54; H, 8.53; N, 7.90. Found. C, 74.64; H, 8.39; N, 7.85.

(+)-(1'S,2'S,3R)-3-(benzylmethylamino)-N-methyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)pentanamide (3b)

Amide **3b** was prepared in 48% de (Chiralcel OD column, UV detector, isopropanol/hexanes 2/98, flow rate: 1.00mL/min.), according to procedure A. Yield: 62%. ¹H-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 0.93 (t, 3H, J= 7.1Hz); 1.05 (d, 3H, J= 6.3Hz); 1.35 (m, 1H); 1.63 (m, 1H); 2.17 (s, 3H); 2.27* (s, 3H); 2.38 (m, 1H); 2.59 (m, 1H); 2.79 (s, 3H); 2.84* (s, 3H); 3.08 (m, 1H); 3.62 (m, 2H); 4.56 (m, 1H); 4.6 (d, 1H, J=6.7Hz); 7.29 (m, 10H). ¹³C-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 11.5; 14.1; 23.3; 23.8*; 27.0; 35.0; 36.5*; 36.9; 57.5; 57.9*; 58.6; 58.8*; 61.4; 61.9*; 75.3*; 76.3; 126.4; 126.6; 126.9; 127.6; 127.7; 127.9; 128.1; 128.3; 128.4; 128.5; 128.7; 128.9; 129.1; 139.5; 142.1; 142.3*; 174.6; 174.7*. IR (CHCl₃): 3350 (OH), 1605 (C=O). MS (EI) m/z (Rel. Int.): 339 (1), 311 (1), 277 (8), 229 (3), 204 (3); 174 (3); 162 (26), 148 (16), 120 (54), 91 (100), 79 (23), 58 (69). Anal. Calcd for C₂₃H₃₂N₂O₂: C, 74.96; H, 8.75; N, 7.60. Found. C, 75.09; H, 8.89; N, 7.73.

(+)-(1'S,2'S,3R)-3-(benzylmethylamino)-N,4-dimethyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)pentanamide (3c)

Amide **3c** was prepared in 60% de (Chiralcel OD column, UV detector, isopropanol/hexanes 4/96, flow rate: 0.80mL/min.), according to procedure A. Yield: 53%.

¹H-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 0.92 (m, 6H); 1.07 (d, 3H, *J*= 6.7Hz); 1.80 (m, 1H); 2.12 (s, 3H); 2.18* (s, 3H); 2.40 (m, 2H); 2.88 (s, 3H); 2.91* (s, 3H); 3.11 (m, 1H); 3.60 (m, 2H); 4.35 (s, 1H); 4.57 (m, 2H); 7.27 (m, 10H). ¹³C-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 14.4; 15.5*; 20.1; 31.4; 31.5; 31.8*; 36.5*; 37.0; 58.8; 59.2*; 66.4; 75.5*; 76.6; 126.4; 126.5; 126.6; 127.7; 128.1; 128.3; 128.5; 128.6; 128.7; 140.2; 140.3*; 141.3*; 142.4; 173.9*; 175.1. IR (CHCl₃): 3400 (OH), 1625 (C=O). MS (EI) *m/z* (Rel. Int.): 383 (3), 339 (33), 295 (3), 291 (19), 263 (2), 218 (7), 207 (2), 176 (40), 148 (45), 120 (51), 91 (100), 79 (17), 58 (15). Anal. Calcd for C₂₄H₃₄N₂O₂: C, 75.35; H, 8.96; N, 7.32. Found. C, 75.53; H, 8.78; N, 7.27.

(+)-(1'S,2'S,3S)-3-(benzylmethylamino)-N,4,4-trimethyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)pentanamide (3d)

Amide **3d** was prepared in 76% de (Chiralcel OD column, UV detector, isopropanol/hexanes 2/98, flow rate: 0.80mL/min.), according to procedure A. Yield: 52%.

¹H-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 0.86 (d, 3H, *J*= 6.7Hz); 1.06 (d, 9H, *J*= 5.9Hz); 2.13 (s, 3H); 2.25 (m, 1H); 2.61 (m, 1H); 2.88* (s, 3H); 2.92 (s, 3H); 3.09 (m, 1H); 3.60 (m, 2H); 4.59 (m, 2H); 7.31 (m, 10H). ¹³C-NMR (CDCl₃); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ, ppm): 14.5; 20.2*; 21.0; 29.7; 31.5; 31.8; 36.9; 58.6; 58.8; 66.2; 75.5; 126.5; 126.7; 126.9; 127.7; 128.1; 128.4; 128.5; 140.0; 142.4; 175.4. IR (CHCl₃): 3400 (OH), 1625 (C=O). MS (EI) *m/z* (Rel. Int.): 383 (1), 339 (19), 291 (13), 243 (6), 218 (5), 207 (2), 176 (36), 148 (42), 120 (49), 91 (100), 83 (20), 58 (24). Anal. Calcd for C₂₅H₃₆N₂O₂: C, 75.72; H, 9.15; N, 7.06. Found. C, 75.60; H, 9.26; N, 7.00.

(+)-(1'S,2'S,3S)-3-(benzylmethylamino)-N-methyl-3-phenyl-N-(2'-phenyl-2'-hydroxy-1'-methylethyl)propanamide (3e)

Amide **3e** was prepared in 44% de (Chiralcel OD column, UV detector, isopropanol/hexanes 4/96, flow rate: 0.80mL/min.), according to procedure A. Yield: 94%.

$[\alpha]_D^{20} = +119.8$ ($c = 0.36$, CH_2Cl_2). $^1\text{H-NMR}$ (CDCl_3); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ , ppm): 0.66* (d, 3H, $J = 6.7\text{Hz}$); 0.93 (d, 3H, $J = 6.7\text{Hz}$); 2.13 (s, 3H); 2.23* (s, 3H); 2.75 (s, 3H); 2.78* (s, 3H); 2.80 (m, 1H); 3.0 (m, 2H); 3.44 (m, 2H); 4.17 (m, 1H); 4.47 (d, 1H, $J = 3.9\text{Hz}$); 7.31 (m, 15H). $^{13}\text{C-NMR}$ (CDCl_3); (3:1 rotamer ratio: * indicates minor rotamer resonances); (δ , ppm): 14.1; 15.2*; 27.0; 32.5; 37.2*; 37.7; 38.4; 59.2; 59.3*; 65.1; 65.4*; 75.2*; 75.9; 126.5; 126.8; 127.1; 127.3; 127.5; 127.8; 128.1; 128.2; 128.3; 128.5; 128.7; 129.2; 129.7; 139.5; 140.4*; 142.1; 143.2; 172.2*; 173.2. IR (CHCl_3): 3360 (OH), 1615 (C=O). MS (EI) m/z (Rel. Int.): 417 (15), 325 (43), 309 (5), 278 (3), 252 (3), 210 (52), 188 (13), 160 (12), 131 (30), 120 (60), 91 (100), 58 (32). Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_2$: C, 77.85; H, 7.74; N, 6.73. Found. C, 77.77; H, 7.76; N, 6.93.

2.- Conversion of amides **2a-e** into β -amino esters **4a-e**.

Dimethylcarbonate (7.5 mmol) and MeONa (10 mmol) were added to a solution of the corresponding β -amino amide **2a-e** (1 mmol) in CH_2Cl_2 (20 mL) at rt. The mixture was stirred at this temperature for 24h., after which it was quenched with sat. NH_4Cl . The mixture was extracted with CH_2Cl_2 (3 x 15ml) and the combined organic fractions were collected, dried over Na_2SO_4 , filtered and the solvent removed *in vacuo* affording the wanted β -amino esters after column chromatography purification (hexanes:AcOEt 8:2)

(-)-(3R)-Methyl 3-dibenzylaminobutanoate (**4a**)

Yield: 73%, >99%ee (determined by chiral HPLC: Chiralcel OJ column, UV detector, *iso*-propanol/hexanes 5/95, flow rate: 0.85mL/min). $[\alpha]_D^{20} = -9.7$ ($c = 0.21$, CH_2Cl_2). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 1.10 (d, 3H, $J = 6.7\text{Hz}$); 2.29 (dd, 1H, $J = 13.8, 6.7\text{Hz}$); 2.65 (dd, 1H, $J = 13.8, 6.7\text{Hz}$); 3.31 (m, 1H); 3.45 (d, 2H, $J = 13.8\text{Hz}$); 3.65 (d, 2H, $J = 13.8\text{Hz}$); 3.60 (s, 3H); 7.27 (m, 10H). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 14.1; 39.3; 50.2; 51.1; 53.5; 127.1; 128.3; 128.5; 140.2; 173.6. IR (CHCl_3): 1605 (C=O). MS (EI) m/z (Rel. Int.): 297 (2), 282 (7), 224 (100), 206 (7), 181 (11), 132 (5), 91 (97), 65 (3), 56 (12). Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_2$: C, 76.73; H, 7.80; N, 4.71. Found. C, 76.60; H, 8.06; N, 4.72.

(-)-(3R)-Methyl 3-dibenzylaminopentanoate (4b)

Yield: 75%, 88%ee (determined by chiral HPLC: Chiralcel OJ column, UV detector, *iso*-propanol/hexanes 5/95, flow rate: 0.85mL/min). ¹H-NMR (CDCl₃, δ, ppm): 0.91 (t, 3H, *J*= 7.5Hz); 1.31 (m, 1H); 1.71 (m, 1H); 2.31 (dd, 1H, *J*= 13.8, 7.1Hz); 2.63 (dd, 1H, *J*= 13.8, 7.1Hz); 2.99 (m, 1H); 3.58 (m, 4H); 3.63 (s, 3H); 7.25 (m, 10H). ¹³C-NMR (CDCl₃, δ, ppm): 11.6; 23.1; 35.3; 51.5; 53.3; 57.2; 126.8; 128.1; 128.9; 139.9; 173.4. IR (CHCl₃): 1605 (C=O). MS (EI) *m/z* (Rel. Int.): 311 (1), 282 (15), 238 (12); 220 (2), 181 (6), 169 (2), 149 (4), 122 (7), 105 (65), 91 (100), 77 (52), 57 (61). Anal. Calcd for C₂₀H₂₅NO₂: C, 77.14; H, 8.09; N, 4.50. Found. C, 76.97; H, 8.17; N, 4.47.

(-)-(3R)-Methyl 3-dibenzylamino-4-methylpentanoate (4c)

Yield: 52%, 60%ee (determined by chiral HPLC: Chiralcel OJ column, UV detector, *iso*-propanol/hexanes 5/95, flow rate: 0.85mL/min). ¹H-NMR (CDCl₃, δ, ppm): 0.83 (d, 3H, *J*= 6.7Hz); 1.0 (d, 3H, *J*= 6.7Hz); 1.89 (m, 1H); 2.31 (m, 1H); 2.70 (m, 1H); 2.86 (m, 1H); 3.41 (d, 2H, *J*= 13.4Hz); 3.73 (d, 2H, *J*= 13.4Hz); 7.30 (m, 10H). ¹³C-NMR (CDCl₃, δ, ppm): 19.8; 21.2; 30.8; 32.6; 51.6; 54.1; 61.3; 126.8; 128.1; 129.0; 139.8; 174.2. IR (CHCl₃): 1605 (C=O). MS (EI) *m/z* (Rel. Int.): 282 (44), 252 (4), 181 (10), 160 (2), 158 (2), 132 (3), 114 (3), 92 (8), 91 (100), 65 (9), 55 (2). Anal. Calcd for C₂₁H₂₇NO₂: C, 77.50; H, 8.36; N, 4.30. Found. C, 77.45; H, 8.54; N, 4.19.

(-)-(3S)-Methyl 3-dibenzylamino-4,4-dimethylpentanoate (4d)

Yield: 70%, >99%ee (determined by chiral HPLC: Chiralcel OJ column, UV detector, *iso*-propanol/hexanes 5/95, flow rate: 0.85mL/min). $[\alpha]_D^{20} = -5.0$ (c = 0.12, CH₂Cl₂). ¹H-NMR (CDCl₃, δ, ppm): 0.81 (s, 3H); 0.98 (s, 3H); 1.28 (s, 3H); 2.30 (dd, 1H, *J*= 14.9, 6.7Hz); 2.69 (dd, 1H, *J*= 14.9, 6.7Hz); 2.85 (m, 1H); 3.40 (d, 2H, *J*= 13.4Hz); 3.65 (s, 3H); 3.73 (d, 2H, *J*= 13.4Hz); 7.29 (m, 10H). ¹³C-NMR (CDCl₃, δ, ppm): 19.8; 21.2; 22.5; 29.7; 35.6; 51.6; 54.1; 61.3; 126.8; 128.1; 129.0; 140.1; 174.1. IR (CHCl₃): 1605 (C=O). MS (EI) *m/z* (Rel. Int.): 282 (23), 252 (2), 181 (6), 132 (2), 114 (2), 92 (8), 91 (100), 65 (11), 55 (2). Anal. Calcd for C₂₂H₂₉NO₂: C, 77.84; H, 8.61; N, 4.13. Found. C, 78.02; H, 8.55; N, 4.02.

(-)-(3*S*)-Methyl 3-dibenzylamino-3-phenylpropanoate (4e)

Yield: 63%, 96%ee (determined by chiral HPLC: Chiralcel OJ column, UV detector, *iso*-propanol/hexanes 5/95, flow rate: 0.85mL/min). $[\alpha]_D^{20} = -5.1$ ($c = 0.12$, CH_2Cl_2). ^1H -NMR (CDCl_3 , δ , ppm): 2.73 (dd, 1H, $J = 14.1, 6.7\text{Hz}$); 3.15 (m, 3H); 3.65 (s, 3H); 3.83 (d, 2H, $J = 13.4\text{Hz}$); 4.3 (m, 1H). ^{13}C -NMR (CDCl_3 , δ , ppm): 36.6; 51.6; 53.6; 58.8; 126.9; 128.1; 128.1; 128.2; 128.6; 128.8; 139.8; 144.9; 172.1. IR (CHCl_3): 1605 (C=O). MS (EI) m/z (Rel. Int.): 286 (12), 268 (1), 252 (1), 238 (1), 210 (2), 196 (23), 181 (2), 162 (6), 147 (2), 121 (13), 103 (14), 77 (22), 51 (62). Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2$: C, 80.19; H, 7.01; N, 3.90. Found. C, 80.16; H, 7.11; N, 3.77.