Supporting Information 1
for Highly Enantioselective Phase-Transfer-Catalyzed Alkylation of Protected
 α -Amino Acid Amides toward Practical Asymmetric Synthesis of Vicinal Diamines,
 α -Amino Ketones and α -Amino Alcohols

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General Procedure for the Preparation of Glycine Amide-Benzophenone Schiff Base 1:

To a solution of Z-Gly (2.1 g, 10 mmol) and *N*-methylmorpholine (0.98 mL, 11 mmol) in CH₂Cl₂ (30 mL) was added ethyl chloroformate (1.1 mL, 11 mmol) at 0 °C under argon atmosphere and the mixture was stirred for 30 min. Then, a solution of amine (11 mmol) in CH₂Cl₂ (5 mL) was added dropwise at 0 °C and the whole mixture was allowed to warm to room temperature. After stirring for 5 h, the resulting mixture was poured into water, extracted with CH₂Cl₂ and the combined organic layer was dried over Na₂SO₄. The residue obtained by filtration and subsequent evaporation was diluted with ether, and resulting precipitate was collected by filtration. The resulting solid material was suspended in MeOH (10 mL) and ethyl acetate (10 mL) in the presence of 10% Pd/C (0.25 g) and an equivalent amount of acetic acid (0.57 mL, 10 mmol), and stirred for 10 h at room temperature under hydrogen gas atmosphere. Subsequent filtration and concentration gave the corresponding amino acid amide acetate. To the slurry of the solid material in CH₂Cl₂ (20 mL) under argon atmosphere was added benzophenone imine (1.7 mL, 10 mmol) dropwise at room temperature and the mixture was vigorously stirred for 10 h. The resulting mixture was poured into water, extracted with ethyl acetate, dried over Na₂SO₄ and concentrated. Recrystallization of the residue from hexane/ethyl acetate afforded the desired glycine amide-benzophenone Schiff base as a white solid (82–90%).

Characterization of Schiff Base Protected Glycine Amides

Glycine Benzylamide-Benzophenone Schiff Base (1a): ¹H NMR (400 MHz, CDCl₃) δ 7.81 (1H, br, NH), 7.60-7.58 (2H, m, ArH), 7.50-7.40 (4H, m, ArH), 7.37-7.25 (7H, m, ArH), 7.13 (2H, dd, *J* = 1.8, 7.8 Hz, ArH), 4.60 (2H, d, *J* = 6.4 Hz, NCH₂CO), 4.03 (2H, s, PhCH₂); ¹³C NMR (100 MHz,

CDCl₃) δ 170.5, 170.1, 138.5, 138.3, 135.9, 130.6, 128.9, 128.8, 128.6, 128.3, 128.1, 127.4, 127.3, 127.1, 56.7, 43.1; IR (KBr) 3362, 3055, 3028, 2941, 2889, 1647, 1526, 1495, 1448, 1435, 1394, 1360, 1317, 1285, 1258, 1186, 1155, 1078, 1049, 1032, 1001, 941, 910, 787, 752, 731, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₂H₂₁N₂O ([M+H]⁺): 329.1648, Found: 329.1646.

Glycine Diphenylmethanamide–Benzophenone Schiff Base (1b): ¹H NMR (400 MHz, CDCl₃) δ 8.30 (1H, d, J = 8.8 Hz, NH), 7.59-7.57 (2H, m, ArH), 7.48-7.41 (4H, m, ArH), 7.38-7.26 (12H, m, ArH), 7.15-7.12 (2H, m, ArH), 6.37 (1H, d, J = 8.8 Hz, Ph₂CH), 4.04 (2H, s, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 169.6, 141.7, 138.6, 135.9, 130.6, 129.0, 128.8, 128.6, 128.3, 128.2, 127.3, 127.2, 127.1, 56.6, 56.4; IR (KBr) 3354, 3057, 3028, 1682, 1647, 1599, 1576, 1495, 1447, 1394, 1292, 1213, 1180, 1153, 1074, 1030, 1001, 988, 783, 760, 735, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₈H₂₅N₂O ([M+H]⁺): 405.1961, Found: 405.1972.

Characterization of the Alkylation Products 2b (Table 1)

Ph₂C=NCHBnCONHCHPh₂ (2ba, entry 1): 92% ee (*R*), $[\alpha]_D^{25} = +100.5^\circ$ (*c* 0.64, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.52 (3H, m, ArH), 7.42-7.14 (18H, m, ArH), 7.04-7.02 (2H, m, ArH), 6.45 (2H, d, J = 7.2 Hz, ArH), 6.29 (1H, d, J = 8.4 Hz, Ph₂CH), 4.23 (1H, dd, J = 3.6, 9.2 Hz, NCHCO), 3.19 (1H, dd, J = 3.6, 13.6 Hz, CH₂), 3.08 (1H, dd, J = 9.2, 13.6 Hz, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 169.9, 141.6, 141.5, 138.9, 137.5, 135.3, 130.4, 130.1, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.2, 127.1, 126.2, 67.7, 56.3, 41.5; IR (liquid film) 3385, 3028, 1738, 1680, 1495, 1242, 1047, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₅H₃₁N₂O ([M+H]⁺): 495.2431, Found: 495.2425. HPLC condition: DAICEL Chiralcel OD, hexane/*i*-PrOH = 30:1, flow rate = 0.5 mL/min, t_R = 17.4 (*S*) and 31.4 (*R*) min.

Ph₂C=NCH(allyl)CONHCHPh₂ (2bb, entry 2): 98% ee (*R*), $[\alpha]_D^{26} = +0.62^\circ$ (*c* 1.02, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (1H, d, J = 8.8 Hz, NH), 7.60-7.58 (2H, m, ArH), 7.43-7.20 (16H, m, ArH), 7.08-7.05 (2H, m, ArH), 6.31 (1H, d, J = 8.8 Hz, Ph₂CH), 5.73-5.63 (1H, m, CH₂=CH), 5.04-4.97 (2H, m, CH=CH₂), 4.14-4.10 (1H, m, NCHCO), 2.62-2.50 (2H, m, CH₂=CHCH₂); ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 169.6, 141.7, 141.6, 139.1, 135.6, 133.8, 130.5, 128.7, 128.5, 128.5, 128.5, 128.4, 128.1, 127.6, 127.3, 127.2, 127.1, 117.7, 65.8, 56.3, 39.9; IR (liquid film) 3383, 3061, 2359, 1736, 1680, 1495, 1242, 1047, 916, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₁H₂₉N₂O

([M+H]⁺): 445.2274, Found: 445.2270. HPLC condition: DAICEL Chiralcel OD-H, hexane/*i*-PrOH = 400:1, flow rate = 1.0 mL/min, *t*_R = 58.2 (*R*) and 67.9 (*S*) min.

Ph₂C=NCHBuCONHCHPh₂ (2bc, entry 3): 97% ee (*R*), [α]_D²⁴ = +16.3° (*c* 0.78, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.59 (3H, m, ArH and NH), 7.44-7.39 (4H, m, ArH), 7.38-7.20 (12H, m, ArH), 7.09-7.04 (2H, m, ArH), 6.31 (1H, d, *J* = 8.8 Hz, Ph₂CH), 4.03 (1H, dd, *J* = 5.0, 7.0 Hz, NCHCO), 1.85-1.73 (2H, m, CH₃(CH₂)₂CH₂), 1.28-1.13 (4H, m, CH₃(CH₂)₂), 0.80 (3H, t, *J* = 7.2 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 169.1, 141.8, 141.7, 139.1, 135.7, 130.4, 128.7, 128.6, 128.5, 128.5, 128.4, 128.1, 127.6, 127.2, 127.2, 127.1, 66.2, 56.2, 35.4, 27.8, 22.7, 14.0; IR (liquid film) 3383, 3061, 3028, 2955, 2870, 1682, 1624, 1495, 1315, 1447, 1285, 1117, 1030, 760, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₂H₃₃N₂O ([M+H]⁺): 461.2587, Found: 461.2591. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 20:1, flow rate = 0.5 mL/min, *t*_R = 62.7 (*S*) and 80.3 (*R*) min.

Ph₂C=NCH(CH₂*c*-Hex)CONHCHPh₂ (2bd, entry 4): 98% ee (*R*), [α]_D²⁶ = +35.9° (*c* 1.23, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.58 (3H, m, ArH and NH), 7.44-7.40 (4H, m, ArH), 7.37-7.32 (4H, m, ArH), 7.30-7.20 (8H, m, ArH), 7.08-7.04 (2H, m, ArH), 6.30 (1H, d, *J* = 8.8 Hz, Ph₂CH), 4.13 (1H, t, *J* = 6.6 Hz, NCHCO), 1.70 (2H, dd, *J* = 6.6, 6.6 Hz, *c*-HexCH₂), 1.61-1.50 (4H, m, C₆H₁₁), 1.29-1.01 (5H, m, C₆H₁₁), 0.84-0.62 (2H, m, C₆H₁₁); ¹³C NMR (100 MHz, CDCl₃) δ 172.8, 168.8, 141.8, 139.2, 135.6, 130.4, 128.7, 128.5, 128.5, 128.5, 128.5, 128.1, 127.6, 127.2, 127.2, 127.1, 64.3, 56.2, 43.4, 34.1, 33.9, 32.9, 26.5, 26.4, 26.1; IR (liquid film) 3389, 3061, 3028, 2922, 2851, 1676, 1495, 1447, 1286, 1030, 754, 696 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₅H₃₇N₂O ([M+H]⁺): 501.2900, Found: 501.2898. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 20:1, flow rate = 1.0 mL/min, *t*_R = 48.4 (*S*) and 50.6 (*R*) min.

Ph₂C=NCH(*c*-Pent)CONHCHPh₂ (2bf, entry 8): 96% ee, [α]_D²⁵ = +53.3° (*c* 0.58, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.60 (2H, m, ArH), 7.44-7.17 (16H, m, ArH), 7.03-7.00 (2H, br, ArH), 6.32 (1H, d, *J* = 8.8 Hz, Ph₂CH), 4.00 (1H, d, *J* = 5.6 Hz, NCHCO), 2.40 (1H, br, (CH₂)₄CH), 1.63-1.47 (6H, m, CH(CH₂)₄), 1.26 (2H, br, CH(CH₂)₄); ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 169.4, 141.7, 141.7, 139.3, 135.7, 130.4, 128.6, 128.5, 128.5, 128.5, 128.5, 128.1, 127.7, 127.3, 127.2, 127.1, 127.0, 69.3, 56.1, 45.2, 29.0, 28.0, 25.2, 25.0; IR (liquid film) 3391, 3061, 3028, 2955, 2868, 1676,

1622, 1495, 1447, 1313, 1285, 1030, 910, 733, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 473.2587, Found: 473.2580. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 20:1, flow rate = 1.0 mL/min, t_{R} = 31.3 (major) and 52.9 (minor) min.

$\text{Ph}_2\text{C}=\text{NCH}(\text{c-Hex})\text{CONHCHPh}_2$ (2bg, entry 9): 95% ee, $[\alpha]_{\text{D}}^{25} = +41.2^\circ$ (*c* 0.75, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.61 (2H, m, ArH), 7.42-7.16 (16H, m, ArH), 7.02-6.99 (2H, m, ArH), 6.33 (1H, d, $J = 8.8$ Hz, Ph_2CH), 3.88 (1H, d, $J = 4.4$ Hz, NCHCO), 1.92-1.88 (1H, m, $(\text{CH}_2)_5\text{CH}$), 1.66-1.58 (3H, m, $\text{CH}(\text{CH}_2)_5$), 1.47-1.44 (1H, m, $\text{CH}(\text{CH}_2)_5$), 1.37-0.93 (6H, m, $\text{CH}(\text{CH}_2)_5$); ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 169.5, 141.7, 139.2, 135.7, 130.4, 128.5, 128.5, 128.4, 128.1, 127.7, 127.4, 127.3, 127.1, 127.0, 71.5, 56.2, 43.8, 30.2, 28.0, 26.4, 26.4, 26.3; IR (liquid film) 3389, 3061, 3028, 2928, 2853, 1676, 1622, 1495, 1448, 1315, 1281, 1030, 908, 731, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{34}\text{H}_{35}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 487.2744, Found: 487.2758. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 20:1, flow rate = 1.0 mL/min, t_{R} = 33.6 (major) and 73.8 (minor) min.

$\text{Ph}_2\text{C}=\text{NCH}(\text{c-Hept})\text{CONHCHPh}_2$ (2bh, entry 10): 89% ee, $[\alpha]_{\text{D}}^{24} = +39.2^\circ$ (*c* 0.61, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.60 (2H, m, ArH), 7.42-7.32 (8H, m, ArH), 7.29-7.21 (6H, m, ArH), 7.19-7.17 (2H, m, ArH), 7.00-6.98 (2H, m, ArH), 6.34 (1H, d, $J = 8.8$ Hz, Ph_2CH), 3.94 (1H, d, $J = 4.0$ Hz, NCHCO), 2.12-2.04 (1H, br, $(\text{CH}_2)_6\text{CH}$), 1.77-1.69 (1H, br, $\text{CH}(\text{CH}_2)_6$), 1.60-1.17 (11H, m, $\text{CH}(\text{CH}_2)_6$); ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 169.7, 141.7, 141.7, 139.3, 135.7, 130.3, 128.6, 128.5, 128.5, 128.4, 128.1, 127.7, 127.4, 127.2, 127.1, 127.0, 72.2, 56.2, 45.3, 31.9, 29.9, 28.2, 26.8, 26.6; IR (liquid film) 3393, 3061, 3028, 2926, 2855, 1738, 1680, 1620, 1493, 1447, 1285, 1242, 1117, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{35}\text{H}_{37}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 501.2900, Found: 501.2908. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 20:1, flow rate = 1.0 mL/min, t_{R} = 37.2 (major) and 65.5 (minor) min.

Characterization of β -Chiral Primary Alkyl Halide 5¹

(*S*)-PhCH(Me)CH₂I [(*S*)-5a]: 97% ee, $[\alpha]_{\text{D}}^{31} = -31.17^\circ$ (*c* 1.16, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.30 (2H, m, ArH), 7.27-7.18 (3H, m, ArH), 3.40 (1H, dd, $J = 6.5, 9.7$ Hz, CH_2I), 3.32 (1H, dd, $J = 7.9, 9.7$ Hz, CH_2I), 3.08-3.00 (1H, m, PhCH), 1.42 (3H, d, $J = 7.1$ Hz, PhCHCH_3).

(*p*-Tolyl)CH(Me)CH₂I (5b): ^1H NMR (400 MHz, CDCl_3) δ 7.13 (2H, d, $J = 8.3$ Hz, $\text{CH}_3\text{C}_6\text{H}_4$),

7.09 (2H, d, $J = 8.3$ Hz, $\text{CH}_3\text{C}_6\text{H}_4$), 3.38 (1H, dd, $J = 5.9, 9.7$ Hz, CH_2I), 3.30 (1H, dd, $J = 7.9, 9.7$ Hz, CH_2I), 3.05-2.96 (1H, m, (*p*-tolyl)CH), 2.33 (3H, s, $\text{C}_6\text{H}_4\text{CH}_3$), 1.40 (3H, d, $J = 7.1$ Hz, (*p*-tolyl)CHCH₃).

(*c*-Hex)CH(Me)CH₂I (5c): ^1H NMR (400 MHz, CDCl_3) δ 3.29 (1H, dd, $J = 4.4, 9.5$ Hz, CH_2I), 3.18 (1H, dd, $J = 6.3, 9.5$ Hz, CH_2I), 1.76-1.63 (5H, m, (*c*-Hex)CH and C_6H_{11}), 1.36-1.05 (5H, m, C_6H_{11}), 1.02-0.91 (2H, m, C_6H_{11}), 0.97 (3H, d, $J = 6.3$ Hz, CH_3).

PhCH(Bu)CH₂I (5d): ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.29 (2H, m, ArH), 7.26-7.22 (1H, m, ArH), 7.15-7.13 (2H, m, ArH), 3.42-3.32 (2H, m, CH_2I), 2.86-2.79 (1H, m, PhCH), 1.93-1.84 (1H, m, $\text{CH}_3(\text{CH}_2)_3$), 1.67-1.57 (1H, m, $\text{CH}_3(\text{CH}_2)_3$), 1.34-1.08 (4H, m, $\text{CH}_3(\text{CH}_2)_3$), 0.84 (3H, t, $J = 7.1$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 128.4, 127.3, 126.8, 48.3, 35.6, 29.8, 22.6, 14.2, 14.0; IR (neat) 3026, 2955, 2926, 2857, 1495, 1452, 1175, 756, 698 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{I}$: C, 50.02; H, 5.95; I, 44.04. Found: C, 50.30; H, 5.88; I, 43.85.

Characterization of Product 2b of the Stereoselective Alkylation of 1b with β -Chiral Primary Alkyl Halide 5 (Table 2)

(2*R,4*R**)-Ph₂C=NCH(CH₂CH(Me)*p*-tolyl)CONHCHPh₂ (2bk, entry 2):** 97% ee, $[\alpha]_{\text{D}}^{29} = +4.58^\circ$ (*c* 0.80, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.55 (2H, m, ArH), 7.48-7.17 (17H, m, ArH and NH), 6.99-6.95 (6H, m, ArH), 6.27 (1H, d, $J = 8.3$ Hz, Ph_2CH), 4.06 (1H, dd, $J = 5.7, 7.7$ Hz, NCHCO), 2.78-2.69 (1H, m, $\text{CH}_3\text{CH}(\textit{p}\text{-tolyl})$), 2.28 (3H, s, $\text{C}_6\text{H}_4\text{CH}_3$), 2.16-2.00 (2H, m, NCHCH₂), 0.97 (3H, d, $J = 7.1$ Hz, (*p*-tolyl)CHCH₃); ^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 169.2, 143.8, 141.6, 141.5, 139.1, 135.2, 134.9, 130.3, 128.7, 128.5, 128.4, 128.4, 128.4, 127.9, 127.5, 127.1, 127.1, 127.0, 126.6, 64.7, 56.1, 44.3, 35.6, 21.6, 20.9; IR (neat) 3389, 3059, 3026, 2957, 2922, 2868, 1678, 1622, 1493, 1447, 1287, 1030, 912, 816, 733, 696 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 537.2900, Found: 537.2896. HPLC condition: DAICEL Chiralpak AD-H, hexane/EtOH = 20:1, flow rate = 0.5 mL/min, t_{R} = 16.6 (major) and 20.2 (minor) min.

(2*R,4*S**)-Ph₂C=NCH(CH₂CH(Me)*p*-tolyl)CONHCHPh₂ (2bk, entry 2):** ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.47 (2H, m, ArH), 7.42-7.17 (17H, m, ArH and NH), 6.95 (2H, d, $J = 8.1$ Hz, $\text{CH}_3\text{C}_6\text{H}_4$), 6.87 (2H, d, $J = 8.1$ Hz, $\text{CH}_3\text{C}_6\text{H}_4$), 6.81-6.79 (2H, m, ArH), 6.32 (1H, d, $J = 8.3$ Hz, Ph_2CH), 3.99 (1H, dd, $J = 5.7, 7.5$ Hz, NCHCO), 2.86-2.77 (1H, m, $\text{CH}_3\text{CH}(\textit{p}\text{-tolyl})$), 2.26 (3H, s,

C₆H₄CH₃), 2.24-2.17 (1H, ddd, $J = 5.7, 8.3, 13.9$ Hz, NCHCH₂), 2.08-2.01 (1H, m, NCHCH₂), 1.09 (3H, d, $J = 7.1$ Hz, (*p*-tolyl)CHCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.3, 169.5, 143.3, 141.6, 139.1, 135.2, 134.9, 130.2, 128.8, 128.4, 128.4, 128.3, 128.3, 128.1, 127.8, 127.3, 127.2, 127.1, 127.0, 126.6, 64.7, 56.1, 43.1, 35.8, 23.3, 20.9; IR (neat) 3393, 3059, 3026, 2957, 2920, 2868, 1678, 1493, 1447, 1287, 1030, 912, 816, 731, 696 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₈H₃₆N₂O ([M+H]⁺): 537.2900, Found: 537.2899. HPLC condition: DAICEL Chiralpak AD-H, hexane/EtOH = 20:1, flow rate = 0.5 mL/min, t_R = 18.0 (major) and 23.5 (minor) min.

(2R*,4R*)-Ph₂C=NCH(CH₂CH(Me)*c*-Hex)CONHCHPh₂ (2bl, entry 3): 97% ee, $[\alpha]_D^{30} = +40.26^\circ$ (*c* 2.04, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.59 (2H, m, ArH), 7.48 (1H, d, $J = 8.9$ Hz, NH), 7.43-7.19 (16H, m, ArH), 7.05-7.03 (2H, m, ArH), 6.31 (1H, d, $J = 8.9$ Hz, Ph₂CH), 4.08 (1H, dd, $J = 4.0, 9.1$ Hz, NCHCO), 1.90 (1H, ddd, $J = 4.0, 9.1, 13.5$ Hz, NCHCH₂), 1.68-0.88 (13H, m, NCHCH₂, CH₃CH(*c*-Hex) and C₆H₁₁), 0.52 (3H, d, $J = 6.7$ Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 169.2, 141.8, 141.8, 139.3, 135.6, 130.4, 128.7, 128.5, 128.5, 128.5, 128.1, 127.8, 127.3, 127.2, 127.2, 127.1, 65.0, 56.2, 43.1, 40.4, 34.3, 30.5, 28.6, 26.9, 26.8, 15.9; IR (neat) 3391, 3059, 3028, 2922, 2851, 1678, 1620, 1493, 1447, 1315, 1285, 1030, 912, 731, 696 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₇H₄₀N₂O ([M+H]⁺): 529.3213, Found: 529.3207. HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 10:1, flow rate = 0.5 mL/min, t_R = 29.4 (major) and 40.4 (minor) min.

(2R*,4S*)-Ph₂C=NCH(CH₂CH(Me)*c*-Hex)CONHCHPh₂ (2bl, entry 3): ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.58 (3H, m, ArH and NH), 7.43-7.21 (16H, m, ArH), 7.08-7.06 (2H, m, ArH), 6.29 (1H, d, $J = 8.7$ Hz, Ph₂CH), 4.08 (1H, t, $J = 6.5$ Hz, NCHCO), 1.99-1.93 (1H, m, NCHCH₂), 1.62-1.38 (7H, m, NCHCH₂, CH₃CH(*c*-Hex) and C₆H₁₁), 1.06-0.82 (6H, m, C₆H₁₁), 0.66 (3H, d, $J = 6.7$ Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 168.5, 141.7, 139.1, 135.4, 130.2, 128.6, 128.4, 128.4, 128.3, 127.9, 127.5, 127.2, 127.1, 127.1, 127.0, 64.9, 56.1, 41.6, 40.4, 34.2, 30.6, 27.6, 26.8, 26.6, 16.2; IR (neat) 3391, 3059, 3028, 2922, 2851, 1680, 1622, 1493, 1447, 1287, 1030, 912, 745, 696 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₇H₄₀N₂O ([M+H]⁺): 529.3213, Found: 529.3218. HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 10:1, flow rate = 0.5 mL/min, t_R = 27.5 (minor) and 35.3 (major) min.

(2*R,4*R**)-Ph₂C=NCH(CH₂CH(Bu)Ph)CONHCHPh₂ (2bm, entry 4):** 98% ee, $[\alpha]_D^{33} = +18.31^\circ$ (*c* 1.35, CHCl₃); ¹H NMR (400 MHz, CDCl₃) 7.54-7.49 (3H, m, ArH and NH), 7.42-7.07 (19H, m, ArH), 7.04-7.02 (2H, m, ArH), 6.93-6.91 (2H, m, ArH), 6.26 (1H, d, *J* = 7.1 Hz, Ph₂CH), 4.03 (1H, t, *J* = 6.7 Hz, NCHCO), 2.64-2.57 (1H, m, BuCHPh), 2.26-2.20 (1H, m, NCHCH₂), 2.00-1.93 (1H, m, NCHCH₂), 1.38-1.32 (2H, m, CH₃(CH₂)₃), 1.13-1.06 (2H, m, CH₃(CH₂)₃), 1.00-0.93 (2H, m, CH₃(CH₂)₃), 0.74 (3H, t, *J* = 7.3 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 169.0, 145.3, 141.8, 141.7, 139.3, 135.2, 130.3, 128.6, 128.5, 128.5, 128.4, 128.0, 127.6, 127.5, 127.2, 127.2, 127.1, 125.7, 64.6, 56.2, 43.2, 42.1, 35.9, 29.7, 22.8, 14.1; IR (neat) 3385, 3059, 3026, 2953, 2926, 2855, 1738, 1680, 1493, 1447, 1366, 1287, 1217, 931, 905, 762, 729, 696 cm⁻¹. HRMS (ESI-TOF) Calcd for C₄₀H₄₀N₂O ([M+H]⁺): 565.3213, Found: 565.3218. HPLC condition: DAICEL Chiralpak AD-H, hexane/EtOH = 50:1, flow rate = 0.5 mL/min, *t*_R = 24.0 (major) and 34.4 (minor) min.

(2*R,4*S**)-Ph₂C=NCH(CH₂CH(Bu)Ph)CONHCHPh₂ (2bm, entry 4):** ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.44 (2H, m, ArH), 7.42-7.05 (20H, m, ArH and NH), 6.92-6.90 (2H, m, ArH), 6.75-6.73 (2H, m, ArH), 6.32 (1H, d, *J* = 8.7 Hz, Ph₂CH), 3.94 (1H, dd, *J* = 5.9, 7.1 Hz, NCHCO), 2.68-2.61 (1H, m, BuCHPh), 2.21-2.18 (2H, m, NCHCH₂), 1.53-1.47 (1H, m, CH₃(CH₂)₃), 1.42-1.32 (1H, m, CH₃(CH₂)₃), 1.21-0.97 (4H, m, CH₃(CH₂)₃), 0.77 (3H, t, *J* = 7.3 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 169.9, 144.8, 141.7, 139.2, 135.3, 130.3, 128.6, 128.5, 128.5, 128.5, 128.3, 128.1, 128.0, 127.7, 127.4, 127.3, 127.3, 127.2, 127.1, 125.6, 64.7, 56.2, 42.0, 41.8, 37.5, 29.5, 22.8, 14.1; IR (neat) 3393, 3059, 3026, 2953, 2926, 2855, 1790, 1680, 1493, 1447, 1395, 1287, 1180, 758, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₄₀H₄₀N₂O ([M+H]⁺): 565.3213, Found: 565.3219. HPLC condition: DAICEL Chiralpak AD-H, hexane/EtOH = 50:1, flow rate = 0.5 mL/min, *t*_R = 25.6 (major) and 38.7 (minor) min.

Characterization of Dpm-Protected Vicinal Diamines 3 (Table 3)

H₂NCHBnCH₂NHCHPh₂ (3a, entry 1): 92% ee, $[\alpha]_D^{30} = -16.5^\circ$ (*c* 0.46, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.36 (4H, m, ArH), 7.29-7.24 (6H, m, ArH), 7.22-7.13 (5H, m, ArH), 4.79 (1H, s, Ph₂CH), 3.13-3.06 (1H, m, NH₂CH), 2.77 (1H, dd, *J* = 4.8, 13.6 Hz, PhCH₂), 2.68 (1H, dd, *J* = 4.4, 12.0 Hz, NCH₂), 2.51-2.44 (2H, m, PhCH₂ and NCH₂), 1.69 (2H, br, NH₂); ¹³C NMR (100 MHz, CDCl₃) δ 144.1, 143.8, 139.1, 129.1, 128.3, 127.2, 127.1, 126.8, 126.1, 67.5, 54.4, 52.9, 42.6; IR

(KBr) 3250, 3020, 2800, 1595, 1452, 1215, 1099, 900, 885, 741, 706 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2$ ($[\text{M}+\text{H}]^+$): 317.2012, Found: 317.2017.

$\text{H}_2\text{NCH(allyl)CH}_2\text{NHCHPh}_2$ (3b, entry 2): 98% ee, $[\alpha]_{\text{D}}^{30} = -7.31^\circ$ (*c* 0.30, MeOH); ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.37 (4H, m, ArH), 7.30-7.24 (4H, m, ArH), 7.21-7.17 (2H, m, ArH), 5.79-5.68 (1H, m, $\text{CH}_2=\text{CH}$), 5.09-5.04 (2H, m, $\text{CH}=\text{CH}_2$), 4.79 (1H, s, Ph_2CH), 2.95-2.88 (1H, m, NH_2CH), 2.64 (1H, dd, $J = 4.4, 12.0$ Hz, NCH_2), 2.44 (1H, dd, $J = 4.4, 12.0$ Hz, NCH_2), 2.25-2.20 (3H, m, NH_2 and $\text{CH}_2=\text{CHCH}_2$), 2.08-2.01 (1H, m, $\text{CH}_2=\text{CHCH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0, 143.8, 135.0, 128.3, 127.2, 127.1, 126.9, 117.4, 67.5, 54.0, 50.9, 40.2; IR (KBr) 2931, 1636, 1541, 1404, 746, 706 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_2$ ($[\text{M}+\text{H}]^+$): 267.1856, Found: 267.1849.

$\text{H}_2\text{NCHBuCH}_2\text{NHCHPh}_2$ (3c, entry 3): 97% ee, $[\alpha]_{\text{D}}^{30} = -7.95^\circ$ (*c* 0.40, MeOH); ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.37 (4H, m, ArH), 7.29-7.25 (4H, m, ArH), 7.20-7.16 (2H, m, ArH), 4.79 (1H, s, Ph_2CH), 2.80 (1H, m, NH_2CH), 2.62 (1H, dd, $J = 4.0, 12.0$ Hz, NCH_2), 2.36 (1H, dd, $J = 8.8, 12.0$ Hz, NCH_2), 2.09 (2H, br, NH_2), 1.39-1.25 (6H, m, $\text{CH}_3(\text{CH}_2)_3$), 0.87 (3H, t, $J = 6.8$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 143.9, 128.3, 127.2, 127.1, 126.8, 67.5, 54.5, 51.4, 35.5, 28.3, 22.8, 14.1; IR (KBr) 3300, 2931, 1638, 1541, 1396, 1339, 745, 704 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_2$ ($[\text{M}+\text{H}]^+$): 283.2169, Found: 283.2166.

$\text{H}_2\text{NCH}(\text{CH}_2\text{c-Hex})\text{CH}_2\text{NHCHPh}_2$ (3d, entry 4): 98% ee, $[\alpha]_{\text{D}}^{30} = -6.60^\circ$ (*c* 0.30, MeOH); ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.37 (4H, m, ArH), 7.29-7.25 (4H, m, ArH), 7.20-7.16 (2H, m, ArH), 4.79 (1H, s, Ph_2CH), 2.95-2.88 (1H, m, NH_2CH), 2.60 (1H, dd, $J = 3.6, 12.0$ Hz, NCH_2), 2.33 (1H, dd, $J = 8.8, 12.0$ Hz, NCH_2), 1.98 (2H, br, NH_2), 1.71-1.60 (5H, m, $\text{CH}_2\text{C}_6\text{H}_{11}$), 1.36-1.07 (6H, m, $\text{CH}_2\text{C}_6\text{H}_{11}$), 0.92-0.76 (2H, m, $\text{CH}_2\text{C}_6\text{H}_{11}$); ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 143.9, 128.3, 127.2, 127.1, 126.8, 67.5, 55.0, 48.5, 43.7, 34.2, 34.1, 33.0, 26.6, 26.4, 26.3; IR (KBr) 2920, 2370, 1558, 1450, 1230, 745, 702 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{22}\text{H}_{31}\text{N}_2$ ($[\text{M}+\text{H}]^+$): 323.2482, Found: 323.2494.

$\text{H}_2\text{NCH}(\text{c-Pent})\text{CH}_2\text{NHCHPh}_2$ (3f, entry 6): 96% ee, $[\alpha]_{\text{D}}^{30} = -19.59^\circ$ (*c* 0.33, MeOH); ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.37 (4H, m, ArH), 7.29-7.24 (4H, m, ArH), 7.20-7.15 (2H, m, ArH), 4.79 (1H, s, Ph_2CH), 2.70 (1H, dd, $J = 3.2, 11.6$ Hz, NCH_2), 2.62 (1H, dt, $J = 3.2, 8.8$ Hz, NH_2CH),

2.36 (1H, dd, $J = 8.8, 11.6$ Hz, NCH₂), 1.89 (2H, br, NH₂), 1.79-1.46 (7H, m, C₅H₉), 1.26-1.05 (2H, m, C₅H₉); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 143.9, 128.3, 128.2, 127.2, 127.1, 126.8, 67.6, 56.4, 53.6, 45.3, 29.6, 29.6, 25.5, 25.3; IR (KBr) 2949, 2360, 1558, 1452, 1396, 746, 704 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₀H₂₇N₂ ([M+H]⁺): 295.2169, Found: 295.2156.

H₂NCH(c-Hex)CH₂NHCHPh₂ (3g, entry 7): 95% ee, $[\alpha]_D^{30} = -15.53^\circ$ (c 0.39, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (4H, m, ArH), 7.29-7.25 (4H, m, ArH), 7.20-7.16 (2H, m, ArH), 4.78 (1H, s, Ph₂CH), 2.67 (1H, dd, $J = 3.2, 11.6$ Hz, NCH₂), 2.60 (1H, ddd, $J = 3.2, 5.6, 8.8$ Hz, NH₂CH), 2.38 (1H, dd, $J = 8.8, 11.6$ Hz, NCH₂), 1.85 (2H, br, NH₂), 1.73-1.57 (5H, m, C₆H₁₁), 1.28-0.90 (6H, m, C₆H₁₁); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 144.0, 128.3, 127.2, 127.1, 126.8, 67.6, 56.3, 52.1, 42.3, 29.8, 28.5, 26.6, 26.4, 26.3; IR (KBr) 2924, 2851, 2370, 1558, 1452, 745, 704 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₁H₂₉N₂ ([M+H]⁺): 309.2325, Found: 309.2318.

H₂NCH(c-Hept)CH₂NHCHPh₂ (3h, entry 8): 89% ee, $[\alpha]_D^{30} = -20.0^\circ$ (c 0.41, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (4H, m, ArH), 7.29-7.25 (4H, m, ArH), 7.20-7.16 (2H, m, ArH), 4.78 (1H, s, Ph₂CH), 2.72 (1H, ddd, $J = 4.0, 4.0, 9.2$ Hz, NH₂CH), 2.63 (1H, dd, $J = 4.0, 11.6$ Hz, NCH₂), 2.37 (1H, dd, $J = 9.2, 11.6$ Hz, NCH₂), 1.71 (2H, br, NH₂), 1.68-1.34 (11H, m, C₇H₁₃), 1.27-1.19 (2H, m, C₇H₁₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 144.0, 128.3, 127.2, 127.1, 126.8, 67.6, 57.1, 52.3, 43.8, 31.2, 29.3, 28.3, 28.2, 27.3, 27.0; IR (KBr) 3281, 2370, 1558, 1450, 853, 743, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₂H₃₁N₂ ([M+H]⁺): 323.2482, Found: 323.2481.

(2R,4R)-H₂NCH(CH₂CH(Me)Ph)CH₂NHCHPh₂ (3i, entry 9): 99% ee, $[\alpha]_D^{29} = -41.69^\circ$ (c 1.97, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.34 (4H, m, ArH), 7.30-7.21 (6H, m, ArH), 7.21-7.14 (3H, m, ArH), 7.12-7.10 (2H, m, ArH), 4.73 (1H, s, Ph₂CH), 2.80-2.71 (2H, m, NH₂CH and CH₃CHPh), 2.67 (1H, dd, $J = 3.6, 11.9$ Hz, NCH₂), 2.46 (2H, br, NH₂), 2.39 (1H, dd, $J = 8.3, 11.9$ Hz, NCH₂), 1.66 (2H, t, $J = 7.3$ Hz, PhCHCH₂), 1.19 (3H, d, $J = 7.1$ Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 143.9, 143.6, 128.2, 128.2, 127.1, 127.0, 126.7, 126.7, 126.6, 125.8, 67.3, 53.7, 49.4, 43.8, 36.7, 22.4; IR (neat) 3296, 3024, 2957, 2922, 2847, 1601, 1493, 1452, 1182, 1115, 1028, 912, 762, 744, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₄H₂₈N₂ ([M+H]⁺): 345.2325 Found: 345.2328.

(2R*,4R*)-H₂NCH(CH₂CH(Me)c-Hex)CH₂NHCHPh₂ (3j, entry 10): 97% ee, $[\alpha]_D^{27} = -5.49^\circ$ (c 0.78, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.38 (4H, m, ArH), 7.30-7.26 (4H, m,

ArH), 7.21-7.17 (2H, m, ArH), 4.78 (1H, s, Ph₂CH), 2.94-2.87 (1H, m, NH₂CH), 2.71 (2H, br, NH₂), 2.62 (1H, dd, *J* = 3.8, 11.9 Hz, NCH₂), 2.44 (1H, dd, *J* = 8.7, 11.9 Hz, NCH₂), 1.71-0.88 (14H, m, (*c*-Hex)CHCH₂, CH₃CH(*c*-Hex) and C₆H₁₁), 0.78 (3H, d, *J* = 6.7 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.0, 143.8, 128.4, 127.2, 126.9, 126.9, 67.5, 49.5, 43.1, 34.3, 30.5, 28.6, 27.0, 26.9, 26.8, 15.9; IR (neat) 3294, 3024, 2920, 2849, 1491, 1449, 1379, 1186, 1119, 1028, 839, 745, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₄H₃₄N₂ ([M+H]⁺): 351.2795, Found: 351.2796.

Boc-Protection of 3 and Subsequent Removal of Dpm Group by Hydrogenolysis: As exemplified below, re-protection of the free amine moiety of **3e** (R¹ = *i*-Pr) and subsequent deprotection of Dpm group by simple hydrogenolysis gave the other partially protected diamine. Thus, to a solution of **3e** (R¹ = *i*-Pr) (54 mg, 0.20 mmol) in CH₂Cl₂ (3 mL) was added triethylamine (0.31 mL, 0.22 mmol) and di-*tert*-butyl dicarbonate ((Boc)₂O, 0.51 mL, 0.22 mmol) at room temperature. After stirring for 2 h, the reaction solution was poured into water and extracted with ethyl acetate. The organic extracts were dried over Na₂SO₄ and concentrated. Purification of the residue by column chromatography on silica gel (hexane/ethyl acetate = 10:1 as eluent) gave the fully protected diamine in quantitative yield (74 mg, 0.20 mmol). This white solid material and 10% Pd/C (5.0 mg) were suspended in MeOH (3 mL) under hydrogen gas atmosphere at room temperature and the mixture was stirred for 10 h. After filtration, a 2 M ethereal solution of HCl (0.12 mL, 0.24 mmol) was added and the solution was stirred for 1 h at room temperature. Evaporation of solvents afforded the corresponding partially protected diamine hydrochloride as a white solid, which was washed with hexane/ether (1:1) and dried *in vacuo* (44 mg, 0.18 mmol, 91 %): [α]_D³⁰ = -11.4° (*c* 1.00, MeOH); ¹H NMR (400 MHz, D₂O) δ 3.51-3.46 (1H, m, NCH), 3.15-3.10 (1H, m, CH₂), 2.85-2.79 (1H, m, CH₂), 1.73-1.67 (1H, m, CH₃CH), 1.34 (9H, s, C(CH₃)₃), 0.82 (3H, d, *J* = 6.8 Hz, CHCH₃), 0.79 (3H, d, *J* = 6.8 Hz, CHCH₃); ¹³C NMR (100 MHz, D₂O) δ 158.5, 81.8, 54.7, 42.2, 31.1, 28.3, 19.1, 17.6; IR (KBr) 3377, 2870, 1682, 1518, 1458, 1371, 1250, 1165 cm⁻¹. HRMS (ESI-TOF) Calcd for C₁₀H₂₂N₂O₂Na ([M+Na]⁺): 225.1574, Found: 225.1572.

Hydrolysis of the Imine Moiety of 7ac: To a solution of **7ac** (72 mg, 0.16 mmol) in THF (2 mL) was added 1 N HCl (2 mL) at 0 °C and the mixture was allowed to warm to room temperature. After stirring for 1 h, the mixture was basified by 1 M NaOH and extracted with ethyl acetate. Purification by column chromatography on silica gel (ethyl acetate as eluent) gave the desired α -amino acid amide **8** quantitatively (90% ee, *R*): $[\alpha]_D^{28} = +28.1^\circ$ (*c* 0.99, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.48 (1H, d, *J* = 8.0 Hz, NH), 7.34-7.29 (4H, m, ArH), 7.27-7.21 (6H, m, ArH), 6.18 (1H, d, *J* = 8.4 Hz, Ph₂CH), 2.53-2.44 (1H, m, (CH₂)₄CH), 1.76-1.69 (1H, m, CH(CH₂)₄), 1.62-1.49 (3H, m, CH(CH₂)₄), 1.30 (3H, s, CH₃), 1.28-1.13 (4H, m, CH(CH₂)₄); ¹³C NMR (100 MHz, CDCl₃) δ 176.1, 142.0, 141.9, 128.5, 128.4, 127.3, 127.2, 127.1, 127.1, 59.1, 56.5, 47.4, 27.1, 26.9, 26.4, 25.9, 25.7; IR (KBr) 3350, 3302, 3030, 2953, 2862, 1653, 1601, 1495, 1447, 1367, 1302, 1202, 1157, 1030, 866, 822, 764, 741, 702 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₁H₂₇N₂O ([M+H]⁺): 323.2118, Found: 323.2127. HPLC condition: DAICEL Chiralpak AD-H, hexane/EtOH = 10:1, flow rate = 0.5 mL/min, *t*_R = 30.5 (*R*) and 45.1 (*S*) min.

General Procedure for the Preparation of α -Amino Acid Diphenylmethanamide–Aldimine Schiff Base 6: To a solution of Z-Ala (2.2 g, 10 mmol) and *N*-methylmorpholine (0.98 mL, 11 mmol) in CH₂Cl₂ (30 mL) was added ethyl chloroformate (1.1 mL, 11 mmol) at 0 °C under argon atmosphere and the mixture was stirred for 30 min. Then, a solution of diphenylmethanamine (1.9 mL, 11 mmol) in CH₂Cl₂ (5 mL) was added dropwise at 0 °C and the whole mixture was allowed to warm to room temperature. After stirring for 3 h, the resulting mixture was poured into water. Extractive workup was performed with CH₂Cl₂ and the combined organic layer was dried over Na₂SO₄. The residue obtained by filtration and subsequent evaporation was diluted with hexane, and resulting precipitate was collected by filtration. The solid material and 10% Pd/C (0.21 g) were suspended in MeOH (20 mL) under hydrogen gas atmosphere at room temperature and the mixture was stirred for 1 d. After filtration, the solution was concentrated under reduced pressure and the residue was dissolved in benzene (12 mL). To the solution was added trimethyl orthoformate (1.4 mL, 13 mmol) and *p*-chlorobenzaldehyde (0.59 g, 4.2 mmol) at room temperature under argon atmosphere and the mixture was stirred for 10 h. The reaction solution was poured into water and extracted with ethyl acetate. The combined extracts were dried over Na₂SO₄, concentrated and the

resulting white solid was simply washed with hexane/ether (4:1). **6a** ($R^1 = \text{Me}$) (3.2 g, 8.6 mmol, 86%): ^1H NMR (400 MHz, CDCl_3) δ 8.25 (1H, s, ArCH=N), 7.67 (2H, d, $J = 8.6$ Hz, $p\text{-Cl-C}_6\text{H}_4$), 7.62 (1H, d, $J = 8.4$ Hz, NH), 7.41 (2H, d, $J = 8.6$ Hz, $p\text{-Cl-C}_6\text{H}_4$), 7.35 (2H, d, $J = 6.8$ Hz, ArH), 7.30-7.19 (8H, m, ArH), 6.30 (1H, d, $J = 8.8$ Hz, Ph_2CH), 4.05 (1H, q, $J = 7.2$ Hz, NCHCO), 1.50 (3H, d, $J = 7.2$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 160.6, 141.8, 141.6, 137.4, 133.9, 129.4, 129.1, 128.7, 128.6, 127.4, 127.4, 127.2, 127.2, 68.2, 56.2, 21.4; IR (KBr) 3271, 3053, 2977, 2928, 1649, 1595, 1541, 1495, 1447, 1306, 1294, 1232, 1084, 1013, 829, 760, 741, 700 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{23}\text{H}_{21}\text{ClN}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 399.1235, Found: 399.1249.

***p*-Cl-C₆H₄CH=NCH(Bn)CONHCHPh₂ (6b, $R^1 = \text{CH}_2\text{Ph}$):** ^1H NMR (400 MHz, CDCl_3) δ 7.61 (1H, d, $J = 9.0$ Hz, NH), 7.54 (1H, s, ArCH=N), 7.50 (2H, d, $J = 8.4$ Hz, $p\text{-Cl-C}_6\text{H}_4$), 7.36 (2H, d, $J = 8.4$ Hz, $p\text{-Cl-C}_6\text{H}_4$), 7.33-7.18 (13H, m, ArH), 7.09-7.06 (2H, m, ArH), 6.31 (1H, d, $J = 9.0$ Hz, Ph_2CH), 4.04 (1H, dd, $J = 3.2, 9.6$ Hz, NCHCO), 3.42 (1H, dd, $J = 3.2, 13.2$ Hz, PhCH_2), 2.98 (1H, dd, $J = 9.6, 13.2$ Hz, PhCH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 161.3, 141.5, 141.4, 137.2, 137.1, 133.7, 130.0, 129.2, 128.9, 128.6, 128.5, 128.1, 127.3, 127.2, 127.1, 126.5, 74.8, 56.4, 41.3; IR (KBr) 3288, 3030, 2920, 2851, 1651, 1593, 1539, 1489, 1234, 1085, 824, 743, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{29}\text{H}_{26}\text{ClN}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 453.1728, Found: 453.1722.

Characterization of the Quaternization Products 7 (Table 4)

***p*-Cl-C₆H₄CH=NCMe(allyl)CONHCHPh₂ (7aa, entry 1):** 93% ee, $[\alpha]_{\text{D}}^{26} = -22.2^\circ$ (c 1.85, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.33 (1H, d, $J = 8.4$ Hz, NH), 8.23 (1H, s, ArCH=N), 7.65 (2H, d, $J = 8.6$ Hz, $p\text{-Cl-C}_6\text{H}_4$), 7.40 (2H, d, $J = 8.6$ Hz, $p\text{-Cl-C}_6\text{H}_4$), 7.35-7.22 (10H, m, ArH), 6.26 (1H, d, $J = 8.4$ Hz, Ph_2CH), 5.64-5.53 (1H, m, $\text{CH}_2=\text{CH}$), 4.98-4.96 (2H, m, $\text{CH}=\text{CH}_2$), 2.75 (1H, dd, $J = 7.6, 14.0$ Hz, $\text{CH}_2=\text{CHCH}_2$), 2.51 (1H, dd, $J = 7.6, 14.0$ Hz, $\text{CH}_2=\text{CHCH}_2$), 1.48 (3H, s, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 157.4, 141.9, 141.8, 137.1, 134.2, 132.3, 129.1, 129.0, 128.5, 128.5, 127.2, 127.2, 127.0, 119.0, 67.6, 56.7, 44.1, 22.1; IR (neat) 3367, 3063, 2976, 2926, 1672, 1595, 1490, 1452, 1375, 1265, 1167, 1088, 918, 824, 758, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{26}\text{H}_{26}\text{ClN}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 417.1728, Found: 417.1731. HPLC condition: DAICEL Chiralpak AD-H, hexane/EtOH = 20:1, flow rate = 0.5 mL/min, t_{R} = 23.9 (minor) and 25.7 (major) min.

***p*-Cl-C₆H₄CH=NCMe(Bu)CONHCHPh₂ (7ab, entry 2):** 93% ee, $[\alpha]_{\text{D}}^{26} = -23.3^\circ$ (c 1.45,

CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.44 (1H, d, *J* = 8.8 Hz, NH), 8.25 (1H, s, ArCH=N), 7.66 (2H, d, *J* = 8.6 Hz, *p*-Cl-C₆H₄), 7.41 (2H, d, *J* = 8.6 Hz, *p*-Cl-C₆H₄), 7.36-7.22 (10H, m, ArH), 6.28 (1H, d, *J* = 8.8 Hz, Ph₂CH), 2.09-2.02 (1H, m, CH₃(CH₂)₂CH₂), 1.69-1.62 (1H, m, CH₃(CH₂)₂CH₂), 1.45 (3H, s, NCCH₃), 1.24-1.04 (4H, m, CH₃(CH₂)₂), 0.78 (3H, t, *J* = 7.0 Hz, (CH₂)₃CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 156.8, 142.1, 141.9, 137.1, 134.4, 129.1, 129.0, 128.5, 128.5, 127.2, 127.2, 127.2, 127.0, 67.8, 56.7, 40.5, 26.2, 23.4, 23.0, 14.0; IR (neat) 3367, 3061, 3028, 2955, 2928, 2870, 1670, 1593, 1489, 1454, 1167, 1090, 824, 756, 741, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₇H₃₀ClN₂O ([M+H]⁺): 433.2041, Found: 433.2043. HPLC condition: DAICEL Chiralpak AD-H, hexane/*i*-PrOH = 10:1, flow rate = 0.5 mL/min, *t*_R = 31.9 (minor) and 39.4 (major) min.

***p*-Cl-C₆H₄CH=NCBn(allyl)CONHCHPh₂ (7ba, entry 4):** 82% ee, [α]_D²⁶ = -8.90° (*c* 2.16, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.43 (1H, d, *J* = 8.4 Hz, NH), 7.99 (1H, s, ArCH=N), 7.53 (2H, d, *J* = 8.4 Hz, *p*-Cl-C₆H₄), 7.38 (2H, d, *J* = 8.4 Hz, *p*-Cl-C₆H₄), 7.30-7.19 (8H, m, ArH), 7.17-7.07 (3H, m, ArH), 7.03-7.01 (2H, m, ArH), 6.96-6.94 (2H, m, ArH), 6.26 (1H, d, *J* = 8.4 Hz, Ph₂CH), 5.52-5.45 (1H, m, CH₂=CH), 5.00-4.92 (2H, m, CH=CH₂), 3.32 (1H, d, *J* = 13.6 Hz, PhCH₂), 3.09 (1H, dd, *J* = 6.6, 14.6 Hz, CH₂=CHCH₂), 3.04 (1H, d, *J* = 13.6 Hz, PhCH₂), 2.59 (1H, dd, *J* = 7.8, 14.6 Hz, CH₂=CHCH₂); ¹³C NMR (100 MHz, CDCl₃) δ 172.3, 159.3, 141.8, 141.6, 137.2, 135.5, 134.0, 132.1, 129.0, 129.0, 128.4, 127.7, 127.2, 127.2, 127.1, 127.0, 126.4, 118.8, 71.1, 56.7, 45.0, 40.4; IR (neat) 3366, 3061, 3028, 2918, 1670, 1593, 1491, 1454, 1088, 918, 824, 745, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₂H₃₀ClN₂O ([M+H]⁺): 493.2041, Found: 493.2042. HPLC condition: DAICEL Chiralpak AD-H, hexane/EtOH = 4:1, flow rate = 0.5 mL/min, *t*_R = 25.2 (major) and 35.2 (minor) min.

Characterization of the Chiral Vicinal Diamine 9 (Scheme 6)

H₂NCMe(*c*-Pent)CH₂NHCHPh₂ (9): 90% ee, [α]_D²⁶ = +0.48° (*c* 0.30, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.37 (4H, m, ArH), 7.32-7.25 (4H, m, ArH), 7.20-7.16 (2H, m, ArH), 4.75 (1H, s, Ph₂CH), 2.44 (2H, s, NCH₂), 1.98-1.92 (1H, m, (CH₂)₄CH), 1.60-1.47 (6H, m, CH(CH₂)₄), 1.31-1.18 (2H, m, CH(CH₂)₄), 1.03 (3H, s, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 128.3, 127.2, 127.1, 126.8, 68.0, 58.3, 54.0, 48.2, 27.2, 26.5, 25.8, 23.5; IR (KBr) 2957, 1558, 1454, 1398, 745, 702 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₁H₂₉N₂ ([M+H]⁺): 309.2325, Found: 309.2316.

Determination of the Absolute Stereochemistry at α -Carbon of α,α -Dialkyl- α -Amino Amide

7ac

Scheme 1. Preparation of Dipeptide **19** from **7ac**.

Preparation and Crystallization of Dipeptide 19: To a solution of Z-L-Ala (0.12 g, 0.55 mmol) and *N*-methylmorpholine (60 μ L, 0.55 mmol) in CH₂Cl₂ (2 mL) was added ethyl chloroformate (52 μ L, 0.55 mmol) at 0 °C and the mixture was stirred for 30 min. α -Amino acid amide **8** (0.16 g, 0.5 mmol) was added in one portion to the mixture at the same temperature. Then, the resulting mixture was allowed to warm to room temperature and stirred for 5 h. The reaction mixture was poured into water and extracted with ethyl acetate. The combined extracts were dried over Na₂SO₄ and concentrated. Purification of the residue by column chromatography on silica gel (hexane/ethyl acetate = 5:1 as eluent) gave dipeptide **19** (0.20 g, 0.38 mmol, 76%) as a white solid. Recrystallization of **19** was performed from MeOH: $[\alpha]_D^{27} = -51.0^\circ$ (*c* 0.57, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.58 (1H, br, NH), 7.33–7.21 (15H, m, ArH), 6.25 (1H, d, *J* = 8.4 Hz, Ph₂CH), 6.20 (1H, s, NH), 5.06 (1H, br, NH), 4.80 (1H, d, *J* = 12.2, PhCH₂), 4.55 (1H, d, *J* = 12.2 Hz, PhCH₂), 4.03–3.98 (1H, m, NCHCO), 2.50–2.40 (1H, br, (CH₂)₄CH), 1.56 (3H, s, NC(*c*-Pent)CH₃), 1.49 (6H, br, CH(CH₂)₄), 1.34 (3H, d, *J* = 7.2 Hz, CHCH₃), 1.27–1.20 (2H, br, CH(CH₂)₄); ¹³C NMR (100 MHz, CDCl₃) δ 172.1, 172.0, 141.7, 135.8, 128.4, 128.2, 128.2, 128.0, 127.8, 127.3, 127.1, 126.9, 67.1, 62.7, 57.0, 51.7, 47.4, 27.0, 26.9, 25.7, 25.6, 20.0, 17.3; IR (liquid film) 3408, 3314, 3061, 3032, 2957, 2870, 1709, 1695, 1639, 1522, 1454, 1367, 1319, 1242, 1074, 1026, 741, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₂H₃₇N₃O₄Na ([M+Na]⁺): 550.2676, Found: 550.2671.

Experimental Details of X-ray Analysis

Empirical Formula	$C_{34}H_{45}O_6N_3$	μ (MoK α), cm^{-1}	0.84
Formula Weight	591.75	No. of Reflns Meased	14368
Crystal Color, Habit	colorless, prism	No. of Reflns Obsd	3827
Crystal Dimensions	0.4 _ 0.2 _ 0.1 mm	No. of Variable	389
Crystal System	monoclinic	R_I	0.053
Space Group	$P2_1$ (No. 4)	R_w	0.122
a , Å	10.731(8)	Goodness of Fit	1.52
b , Å	10.679(6)	Max Shift/Error in Final Cycle	0.004
c , Å	14.299(9)		
V , Å ³	1597(1)		
Z	2		
D_{calc} , g/cm ³	1.230		
T , °C	-150

Figure 1. ORTEP Diagram of Dipeptide **19**.

Preparation of Z-Protected Glycine Weinreb Amides

Z-Gly-N(OMe)Me: To a stirred solution of Z-Gly (2.1 g, 10 mmol) and *N*-methylmorpholine (2.2 mL, 20 mmol) in CH₂Cl₂ (50 mL) was added ethyl chloroformate (0.96 mL, 10 mmol) at 0 °C and the mixture was stirred for 15 min at the same temperature. Powdered *N,O*-dimethylhydroxylamine hydrochloride (0.98 g, 10 mmol) was added in one portion and the mixture was stirred for 30 min at 0 °C and for 3 h at room temperature. The resulting mixture was treated with water and then extracted with ether. The combined extracts were washed with brine, dried over Na₂SO₄ and concentrated. Purification of the crude products by column chromatography on silica gel (hexane/ethyl acetate = 1:1 to 1:2 as eluent) gave Z-Gly-N(OMe)Me as colorless viscous oil (2.2 g, 8.6 mmol, 86%): ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.29 (5H, m, ArH), 5.55 (1H, br, NH), 5.13 (2H, s, PhCH₂), 4.15 (2H, d, *J* = 4.4 Hz, NCH₂CO), 3.72 (3H, s, OCH₃), 3.21 (3H, s, NCH₃); IR (KBr) 3414, 3333, 3070, 3036, 2966, 2941, 1724, 1672, 1526, 1456, 1393, 1275, 1250, 1167, 1049, 988, 925, 775, 743, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₁₂H₁₆N₂O₄Na ([M+Na]⁺): 275.1002, Found: 275.1002.

Z-Gly-N(OMe)CH₂Ph: This compound was synthesized by the same procedure described above using *N*-benzyl-*O*-methylhydroxylamine² instead of *N,O*-dimethylhydroxylamine hydrochloride and a half amount of *N*-methylmorpholine. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate = 1.5:1 to 1:1 as eluent) gave Z-Gly-N(OMe)CH₂Ph as colorless viscous oil (79%): ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.29 (10H, m, ArH), 5.57 (1H, s, NH), 5.13 (2H, s, PhCH₂O), 4.79 (2H, s, PhCH₂N), 4.19 (2H, d, *J* = 4.4 Hz, NCH₂CO), 3.65 (3H, s, OCH₃); IR (KBr) 3261, 3065, 3009, 2949, 1703, 1641, 1547, 1497, 1452, 1421, 1340, 1279, 1270, 1242, 1165, 1132, 1053, 1003, 970, 739, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₁₈H₂₀N₂O₄Na ([M+Na]⁺): 351.1315, Found: 351.1325.

Preparation of Schiff Base Protected Glycine Weinreb Amides

Ph₂C=NHCH₂CON(OMe)Me (10a): Z-Gly-N(OMe)Me (2.16 g, 8.56 mmol) was dissolved in MeOH (40 mL) and the Z group was deprotected by hydrogenation with 10% Pd/C (90 mg) under hydrogen gas atmosphere. After stirring for 12 h at room temperature, the resulting mixture was filtered through a pad of celite. Then, a 1 M MeOH solution of HCl (9.5 mL, 9.5 mmol) was added

to the filtrate at 0 °C, and the solution was allowed to warm to room temperature and stirred there for 20 min. The volatiles were removed by evaporation and the residue was suspended in CH₂Cl₂ (43 mL). Benzophenone imine (1.4 mL, 8.6 mmol) was added and the whole mixture was stirred for 6 h at room temperature. The resulting white suspension was filtered through celite and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 1:1 to 1:3 as eluent) to give glycine Weinreb amide–benzophenone Schiff base **10a** as colorless viscous oil (1.9 g, 6.8 mmol, 68%): ¹H NMR (400 MHz, CDCl₃) δ 7.67-7.65 (2H, m, ArH), 7.49-7.37 (4H, m, ArH), 7.33 (2H, t, *J* = 7.2 Hz, ArH), 7.24-7.22 (2H, m, ArH), 4.35 (2H, s, NCH₂CO), 3.64 (3H, s, OCH₃), 3.21 (3H, s, NCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 171.1, 139.3, 136.0, 130.1, 128.6, 128.6, 128.5, 128.4, 128.4, 127.8, 127.8, 127.7, 127.7, 61.4, 54.8, 32.4; IR (KBr) 3070, 3030, 2975, 2939, 1672, 1628, 1599, 1576, 1491, 1462, 1447, 1421, 1385, 1315, 1290, 1180, 1119, 1074, 1028, 1007, 982, 939, 783, 775, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₁₇H₁₉N₂O₂ ([M+H]⁺): 283.1441, Found: 283.1446.

Ph₂C=NHCH₂CON(OMe)CH₂Ph (10b): This compound was prepared by similar procedure described above. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate = 1.5:1 to 1:1 as eluent) gave **10b** as colorless viscous oil (79%). ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.65 (2H, m, ArH), 7.44-7.27 (11H, m, ArH), 7.22-7.20 (2H, m, ArH), 4.81 (2H, s, PhCH₂N), 4.40 (2H, s, NCH₂CO), 3.56 (3H, s, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 170.7, 138.8, 135.8, 135.5, 129.7, 128.2, 128.1, 128.0, 127.9, 127.7, 127.4, 127.2, 127.0, 61.7, 54.7, 48.7; IR (KBr) 3439, 3061, 3028, 2937, 1672, 1626, 1578, 1495, 1447, 1406, 1315, 1292, 1240, 1028, 1001, 783, 700 cm⁻¹. HRMS (ESI-TOF) Calcd for C₂₃H₂₃N₂O₂ ([M+H]⁺): 359.1754, Found: 359.1738.

Characterization of Product 11b of the Asymmetric Alkylation of Glycine Weinreb Amide–Benzophenone Schiff Base 10 under Phase-Transfer Conditions (Table 5)

Ph₂C=NCH(allyl)CON(OMe)CH₂Ph (11b, R¹ = CH₂CH=CH₂; entry 3): 97% ee (*R*), [α]_D²³ = +23.4° (*c* 1.00, EtOH); ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.62 (2H, m, ArH), 7.46-7.25 (11H, m, ArH), 7.19-7.16 (2H, m, ArH), 5.74 (1H, ddt, *J* = 6.8, 10.0, 17.2 Hz, CH₂=CH), 5.05-4.97 (2H, m, CH=CH₂), 4.76 (2H, s, PhCH₂), 4.40 (1H, t, *J* = 6.8 Hz, NCHCO), 3.17 (3H, s, OCH₃), 2.82 (1H, ddd,

$J = 6.8, 6.8, 13.6$ Hz, $\text{CH}_2=\text{CHCH}_2$), 2.48 (1H, ddd, $J = 6.8, 6.8, 13.6$ Hz, $\text{CH}_2=\text{CHCH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 172.3, 169.6, 139.3, 136.6, 136.1, 134.5, 130.0, 128.6, 128.2, 128.2, 128.1, 128.0, 128.0, 127.7, 127.7, 127.3, 117.1, 63.0, 61.6, 48.9, 37.7; IR (KBr) 3063, 3030, 2976, 2936, 1672, 1622, 1576, 1497, 1447, 1402, 1354, 1315, 1288, 1231, 1180, 1076, 1030, 991, 914, 781, 770, 731, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 399.2067, Found: 399.2085. HPLC condition: DAICEL Chiralcel OD-H, hexane/EtOH = 50:1, flow rate = 0.5 mL/min, $t_R = 21.6$ (R) and 24.8 (S) min.

$\text{Ph}_2\text{C}=\text{NCH}(\text{methallyl})\text{CON}(\text{OMe})\text{CH}_2\text{Ph}$ (11b, $\text{R}^1 = \text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$; entry 4): 97 % ee (R), $[\alpha]_D^{23} = +50.3^\circ$ (c 1.00, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 7.65 (2H, m, ArH), 7.44-7.25 (11H, m, ArH), 7.18-7.16 (2H, m, ArH), 4.78-4.69 (4H, m, $\text{CH}_3\text{C}=\text{CH}_2$ and PhCH_2), 4.52 (1H, t, $J = 6.0$ Hz, NCHCO), 3.20 (3H, s, OCH_3), 2.78 (1H, dd, $J = 6.0, 13.6$ Hz, $\text{CH}_2=\text{CCH}_2$), 2.44 (1H, dd, $J = 6.0, 13.6$ Hz, $\text{CH}_2=\text{CCH}_2$), 1.53 (3H, s, $\text{CH}_2=\text{CCH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 169.5, 141.7, 139.4, 136.6, 136.2, 130.0, 128.7, 128.3, 128.3, 128.2, 127.9, 127.7, 127.3, 113.1, 61.9, 61.6, 49.0, 41.3, 22.8; IR (KBr) 3059, 2966, 2934, 1674, 1622, 1576, 1497, 1447, 1402, 1315, 1290, 1231, 1180, 1076, 1030, 989, 893, 781, 770, 729, 696 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 413.2224, Found: 413.2205. HPLC condition: DAICEL Chiralcel OD, hexane/*i*-PrOH = 10:1, flow rate = 0.5 mL/min, $t_R = 16.0$ (S) and 17.8 (R) min.

$\text{Ph}_2\text{C}=\text{NCH}(\text{propargyl})\text{CON}(\text{OMe})\text{CH}_2\text{Ph}$ (11b, $\text{R}^1 = \text{CH}_2\text{C}\equiv\text{CH}$; entry 5): 96% ee (R), $[\alpha]_D^{23} = +18.0^\circ$ (c 1.00, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.61 (2H, m, ArH), 7.44-7.37 (4H, m, ArH), 7.33-7.22 (9H, m, ArH), 4.84 (1H, d, $J = 15.6$ Hz, PhCH_2), 4.72 (1H, d, $J = 15.6$ Hz, PhCH_2), 4.60 (1H, t, $J = 6.6$ Hz, NCHCO), 3.18 (3H, s, OCH_3), 3.02 (1H, ddd, $J = 2.8, 6.6, 16.4$ Hz, $\text{C}\equiv\text{CCH}_2$), 2.62 (1H, ddd, $J = 2.8, 6.6, 16.4$ Hz, $\text{C}\equiv\text{CCH}_2$), 1.95 (1H, t, $J = 2.8$ Hz, $\text{C}\equiv\text{CH}$); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 170.9, 139.3, 136.1, 136.0, 130.3, 128.9, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 81.2, 70.2, 62.1, 61.8, 49.0, 23.3; IR (KBr) 3061, 3030, 2934, 1672, 1620, 1576, 1497, 1447, 1315, 1290, 1234, 1180, 1080, 1030, 989, 783, 731, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 397.1911, Found: 397.1914. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 4:1, flow rate = 0.5 mL/min, $t_R = 14.6$ (R) and 23.3 (S) min.

Ph₂C=NCH(CH₂α-Np)CON(OMe)CH₂Ph (11b, R¹ = CH₂α-Np; entry 6): 97% ee (*R*), $[\alpha]_{\text{D}}^{23} = +183.1^{\circ}$ (*c* 1.00, EtOH); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (1H, d, *J* = 8.4 Hz, ArH), 7.69 (1H, d, *J* = 8.4 Hz, ArH), 7.62-7.59 (3H, m, ArH), 7.40-7.19 (13H, m, ArH), 7.09 (2H, t, *J* = 7.4 Hz, ArH), 6.50 (2H, br, ArH), 4.86 (1H, d, *J* = 15.6 Hz, PhCH₂), 4.86 (1H, dd, *J* = 5.6, 8.2 Hz, NCHCO), 4.65 (1H, d, *J* = 15.6 Hz, PhCH₂), 3.77 (1H, dd, *J* = 5.6, 13.3 Hz, NpCH₂), 3.44 (1H, dd, *J* = 8.2, 13.3 Hz, NpCH₂), 2.98 (3H, s, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 169.7, 139.1, 136.3, 136.2, 133.7, 133.5, 132.1, 130.0, 128.6, 128.3, 128.3, 128.0, 127.8, 127.8, 127.7, 127.4, 127.3, 127.0, 125.4, 125.3, 125.0, 123.5, 63.2, 61.8, 49.3, 36.7; IR (KBr) 3055, 2961, 2932, 1670, 1620, 1595, 1576, 1510, 1497, 1447, 1396, 1356, 1313, 1288, 1232, 1184, 1076, 1028, 988, 797, 777, 697 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₄H₃₁N₂O₂ ([M+H]⁺): 499.2380, Found: 499.2371. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 4:1, flow rate = 0.5 mL/min, *t*_R = 16.8 (*R*) and 23.5 (*S*) min.

Ph₂C=NCH(CH₂β-Np)CON(OMe)CH₂Ph (11b, R¹ = CH₂β-Np; entry 7): 91% ee (*R*), $[\alpha]_{\text{D}}^{23} = +73.5^{\circ}$ (*c* 1.00, EtOH); ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.62 (5H, m, ArH), 7.52 (1H, s, ArH), 7.44-7.27 (8H, m, ArH), 7.20-7.10 (6H, m, ArH), 6.84 (2H, d, *J* = 7.2 Hz, ArH), 4.81 (1H, d, *J* = 15.6 Hz, PhCH₂), 4.72 (1H, t, *J* = 6.8 Hz, NCHCO), 4.66 (1H, d, *J* = 15.6 Hz, PhCH₂), 3.56 (1H, dd, *J* = 6.8, 12.8 Hz, NpCH₂), 3.14 (1H, dd, *J* = 6.8, 12.8 Hz, NpCH₂), 3.09 (3H, s, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 172.2, 170.1, 139.2, 136.5, 136.1, 135.7, 133.3, 132.0, 130.1, 128.7, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.6, 127.5, 127.5, 127.4, 127.3, 125.6, 125.2, 65.1, 61.8, 49.0, 39.8; IR (KBr) 3055, 3028, 2963, 2934, 1670, 1616, 1597, 1576, 1510, 1497, 1445, 1402, 1356, 1313, 1290, 1232, 1180, 1153, 1124, 1076, 1030, 991, 856, 820, 781, 748, 698 cm⁻¹. HRMS (ESI-TOF) Calcd for C₃₄H₃₁N₂O₂ ([M+H]⁺): 499.2380, Found: 499.2347. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 4:1, flow rate = 1.0 mL/min, *t*_R = 12.3 (*R*) and 14.2 (*S*) min.

Ph₂C=NCHEtCON(OMe)CH₂Ph (11b, R¹ = Et; entry 8): 94% ee (*R*), $[\alpha]_{\text{D}}^{23} = +23.4^{\circ}$ (*c* 1.00, EtOH); ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.64 (2H, m, ArH), 7.45-7.25 (11H, m, ArH), 7.18-7.15 (2H, m, ArH), 4.80 (1H, d, *J* = 15.4 Hz, PhCH₂), 4.73 (1H, d, *J* = 15.4 Hz, PhCH₂), 4.24 (1H, t, *J* = 6.6 Hz, NCHCO), 3.16 (3H, s, OCH₃), 2.13-2.03 (1H, m, CH₃CH₂), 1.82-1.71 (1H, m, CH₃CH₂), 0.87 (3H, t, *J* = 7.4 Hz, CH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 173.0, 169.4, 139.5, 136.9, 136.4, 130.0, 128.7, 128.3, 128.3, 128.2, 128.2, 128.2, 127.8, 127.4, 64.6, 61.6, 49.0, 26.9,

11.0; IR (KBr) 3061, 3032, 2968, 2932, 1672, 1620, 1578, 1497, 1447, 1398, 1315, 1294, 1225, 1180, 1075, 1030, 1001, 984, 783, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 387.2067, Found: 387.2065. HPLC condition: DAICEL Chiralcel OD, hexane/*i*-PrOH = 50:1, flow rate = 0.5 mL/min, t_R = 41.6 (*S*) and 46.3 (*R*) min.

$\text{Ph}_2\text{C}=\text{NCHBuCON}(\text{OMe})\text{CH}_2\text{Ph}$ (11b, $\text{R}^1 = \text{Bu}$; entry 9): 92% ee (*R*), $[\alpha]_{\text{D}}^{23} = +19.3^\circ$ (*c* 1.00, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 7.65 (2H, d, $J = 7.2$ Hz, ArH), 7.44-7.25 (11H, m, ArH), 7.17-7.15 (2H, m, ArH), 4.79 (1H, d, $J = 15.4$ Hz, PhCH_2), 4.73 (1H, d, $J = 15.4$ Hz, PhCH_2), 4.31 (1H, t, $J = 6.6$ Hz, NCHCO), 3.16 (3H, s, OCH_3), 2.08-1.99 (1H, m, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$), 1.79-1.70 (1H, m, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$), 1.32-1.18 (4H, m, $\text{CH}_3(\text{CH}_2)_2$), 0.83 (3H, t, $J = 7.2$ Hz, $(\text{CH}_2)_3\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 169.2, 139.3, 136.8, 136.2, 129.9, 128.5, 128.2, 128.1, 128.1, 128.1, 127.7, 127.7, 127.3, 63.0, 61.5, 48.9, 33.1, 28.4, 22.4, 13.9; IR (KBr) 3061, 3032, 2957, 2930, 2858, 1670, 1622, 1576, 1497, 1447, 1398, 1315, 1286, 1231, 1182, 1076, 1030, 988, 781, 729, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 415.2380, Found: 415.2390. HPLC condition: DAICEL Chiralpak AD, hexane/EtOH = 50:1, flow rate = 0.5 mL/min, t_R = 37.5 (*S*) and 43.4 (*R*) min.

Characterization of α -Amino Ketone 12 (Table 6)

(4*R*)-*N*-Benzoyl-4-aminoct-1,7-dien-5-one (entry 2): For the preparation of this compound, 1 N HCl treatment was performed within 5 min and the crude amino ketone hydrochloride was protected without concentration step: 97% ee, $[\alpha]_{\text{D}}^{21} = +43.5^\circ$ (*c* 1.00, EtOH); ^1H NMR (400 MHz, CDCl_3)

Figure 2.

δ 7.79 (2H, d, $J = 7.2$ Hz, ArH), 7.52 (1H, t, $J = 7.2$ Hz, ArH), 7.44 (2H, t, $J = 7.2$ Hz, ArH), 6.90 (1H, br d, $J = 5.6$ Hz, NH), 5.94 (1H, ddt, $J = 7.0, 10.4, 17.2$ Hz, $\text{COCH}_2\text{CH}=\text{CH}_2$), 5.71 (1H, ddt, $J = 7.2, 9.8, 17.4$ Hz, $\text{CHCH}_2\text{CH}=\text{CH}_2$), 5.26-5.12 (4H, m, $2\text{CH}=\text{CH}_2$), 4.95 (1H, dt, $J = 5.6, 6.8$ Hz, NCHCO), 3.42-3.31 (2H, m, $\text{CH}_2=\text{CHCH}_2\text{CO}$), 2.80 (1H, ddd, $J = 6.8, 7.2, 14.4$ Hz, $\text{CH}_2=\text{CHCH}_2\text{CH}$), 2.59 (1H, ddd, $J = 6.8, 7.2, 14.4$ Hz, $\text{CH}_2=\text{CHCH}_2\text{CH}$); ^{13}C NMR (100 MHz, CDCl_3) δ 205.8, 166.7, 133.8, 131.9, 131.7, 129.3, 128.5, 126.9, 119.6, 119.4, 57.5, 45.0, 35.7; IR (KBr) 3283, 3078, 3069, 2978, 1722, 1638, 1605, 1582, 1531, 1491, 1435, 1391, 1329, 1296, 1155, 989, 914, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 266.1152, Found: 266.1160. HPLC condition: DAICEL Chiralcel OJ, hexane/EtOH = 30:1, flow rate = 0.5 mL/min, t_R = 38.6 (*S*) and 45.8 (*R*) min.

(4R)-N-Benzoyl-4-aminohept-1-en-5-one (entry 3): This compound was also synthesized with precaution noted above: 97% ee, $[\alpha]_{\text{D}}^{20} = +34.5^{\circ}$ (*c* 1.00, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 7.80 (2H, dt, $J = 1.4, 7.4$ Hz, ArH), 7.54-

Figure 3.

7.42 (3H, m, ArH), 6.97 (1H, br, NH), 5.75-5.65 (1H, m, $\text{CH}_2=\text{CH}$), 5.17-5.12 (2H, m, $\text{CH}=\text{CH}_2$), 4.90 (1H, dd, $J = 5.4, 12.8$ Hz, NCHCO), 2.83-2.52 (4H, m, $\text{CH}_2=\text{CHCH}_2$ and $\text{CH}_3\text{CH}_2\text{CO}$), 1.12 (3H, d, $J = 7.2$ Hz, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 208.5, 166.7, 133.9, 132.0, 131.6, 128.5, 126.9, 119.1, 57.6, 36.0, 33.4, 7.6; IR (KBr) 3287, 3063, 2976, 2937, 1722, 1638, 1580, 1533, 1487, 1433, 1408, 1331, 1296, 1269, 1246, 1153, 1111, 1096, 993, 934, 916, 874, 802, 702 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 254.1152, Found: 254.1158. HPLC condition: DAICEL Chiralpak AD, hexane/*i*-PrOH = 30:1, flow rate = 0.5 mL/min, $t_{\text{R}} = 36.0$ (*R*) and 48.5 (*S*) min.

(2R)-N-Boc-2-amino-3-(1-naphthyl)-1-phenylpropan-1-one (12, $\text{R}^1 = \text{CH}_2\alpha\text{-Np}$, $\text{R}^2 = \text{Ph}$; entry 4): 97% ee, $[\alpha]_{\text{D}}^{23} = -12.8^{\circ}$ (*c* 1.00, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 8.10 (1H, d, $J = 8.4$ Hz, ArH), 7.78-7.75 (3H, m, ArH), 7.63 (1H, d, $J =$

Figure 4.

6.8 Hz, ArH), 7.53-7.44 (3H, m, ArH), 7.31-7.20 (3H, m, ArH), 7.11 (1H, d, $J = 6.8$ Hz, ArH), 5.72 (1H, dt, $J = 8.0, 6.8$ Hz, NCHCO), 5.48 (1H, d, $J = 8.0$ Hz, NH), 3.54 (2H, d, $J = 6.8$ Hz, NpCH_2), 1.40 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 154.9, 134.9, 133.5, 133.2, 132.1, 132.0, 128.4, 128.2, 127.5, 127.3, 125.9, 125.3, 124.8, 123.4, 79.5, 55.0, 36.4, 28.2; IR (KBr) 3364, 3067, 3003, 2978, 2961 2928, 1684, 1599, 1582, 1514, 1448, 1393, 1366, 1317, 1292, 1269, 1248, 1223, 1165, 1053, 1022, 988, 795, 773, 758, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 398.1727, Found: 398.1706. HPLC condition: DAICEL Chiralpak AD, hexane/EtOH = 50:1, flow rate = 0.5 mL/min, $t_{\text{R}} = 29.4$ (*R*) and 43.7 (*S*) min.

(2R)-N-Boc-2-amino-1-phenylbutan-1-one (12, $\text{R}^1 = \text{Et}$, $\text{R}^2 = \text{Ph}$; entry 5):

94% ee, $[\alpha]_{\text{D}}^{22} = +3.0^{\circ}$ (*c* 1.00, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (2H, d, $J = 7.6$ Hz, ArH), 7.60 (1H, t, $J = 7.6$ Hz, ArH), 7.49 (2H, t, $J = 8.0$ Hz, ArH), 5.51 (1H, br d, $J = 7.6$ Hz, NH), 5.27 (1H, dt, $J = 7.6, 12.2$ Hz, NCHCO), 2.03-

Figure 5.

1.92 (1H, m, CH_3CH_2), 1.67-1.56 (1H, m, CH_3CH_2), 1.46 (9H, s, $\text{C}(\text{CH}_3)_3$), 0.89 (3H, t, $J = 7.4$ Hz, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 155.4, 134.7, 133.5, 128.7, 128.5, 128.2, 79.6, 56.1,

28.5, 26.7, 9.3; IR (KBr) 3358, 2976, 2936, 1715, 1684, 1599, 1580, 1501, 1448, 1393, 1366, 1285, 1244, 1219, 1167, 1078, 1053, 1003, 874, 862, 777, 700 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 286.1414, Found: 286.1429. HPLC condition: DAICEL Chiralcel OD, hexane/*i*-PrOH = 50:1, flow rate = 0.5 mL/min, t_{R} = 11.5 (*R*) and 15.8 (*S*) min.

Determination of Absolute Configuration of α -Amino Alcohols 14, 16 and 17: General Procedure for the Preparation of Oxazolidin-2-one Derivatives: Absolute configuration of α -amino alcohols was determined by ^1H NMR (comparison of the vicinal coupling constants, J_{vic} , between the methine protons)³ and NOE analyses after conversion to oxazolidin-2-one derivatives from *Z*-protected α -amino alcohols. Thus, to a solution of *Z*-protected α -amino alcohol in THF (0.1–0.2 M) was added a 1.0 M THF solution of lithium bis(trimethylsilyl)amide (2.0 equiv) at 0 °C and the solution was stirred at 0 °C or room temperature. After the reaction was completed, the resulting mixture was treated with saturated NH_4Cl and extractive workup was performed with ethyl acetate. The combined extracts were washed with brine and dried over Na_2SO_4 . Removal of solvents and purification of the residue by column chromatography on silica gel (hexane/ethyl acetate as eluent) gave the corresponding oxazolidin-2-one derivative as white solid.

(4*R*,5*R*)-4-Allyl-5-phenyloxazolidin-2-one (from 14, $\text{R}^1 = \text{CH}_2\text{CH}=\text{CH}_2$):

$[\alpha]_{\text{D}}^{25} = +55.1^\circ$ (*c* 0.50, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.34 (5H, m, ArH), 5.99 (1H, br, NH), 5.75 (1H, ddt, $J = 7.2, 10.4, 16.8$ Hz, $\text{CH}_2=\text{CH}$), 5.25–5.21 (2H, m, $\text{CH}=\text{CH}_2$), 5.17 (1H, d, $J_{\text{vic}} = 6.0$ Hz, OCHPh), 3.79 (1H, ddd, $J = 6.0, 6.0,$

Figure 6.

7.2 Hz, NCH), 2.51 (1H, ddd, $J = 6.0, 7.2, 13.0$ Hz, $\text{CH}_2=\text{CHCH}_2$), 2.40 (1H, ddd, $J = 7.2, 7.2, 13.0$ Hz, $\text{CH}_2=\text{CHCH}_2$); IR (KBr) 3267, 3150, 3080, 2932, 2899, 1757, 1641, 1499, 1458, 1431, 1385, 1342, 1273, 1221, 1134, 1016, 930, 891, 766, 702 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 204.1019, Found: 204.1029.

(4*R*,5*S*)-4-Allyl-5-phenyloxazolidin-2-one (from 16, $\text{R}^1 = \text{CH}_2\text{CH}=\text{CH}_2$):

$[\alpha]_{\text{D}}^{25} = +138.4^\circ$ (*c* 0.50, EtOH); ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.29 (5H, m, ArH), 5.76 (1H, d, $J_{\text{vic}} = 8.0$ Hz, OCHPh), 5.56 (1H, ddt, $J = 7.2, 10.4, 16.8$ Hz, $\text{CH}_2=\text{CH}$), 5.45 (1H, s, NH), 5.10 (1H, d, $J = 10.4$ Hz, $\text{CH}=\text{CH}_2$), 5.02 (1H, dt, $J =$

Figure 7.

1.2, 16.8 Hz, $\text{CH}=\text{CH}_2$), 4.05 (1H, ddd, $J = 5.6, 8.0, 8.4$ Hz, NCH), 1.79–1.73 (2H, m, $\text{CH}_2=\text{CHCH}_2$);

IR (KBr) 3251, 3167, 3074, 2932, 1751, 1724, 1641, 1499, 1454, 1431, 1391, 1350, 1310, 1265, 1244, 1215, 1134, 1101, 1082, 1057, 1018, 970, 951, 935, 910, 887, 783, 735, 700 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 204.1019, Found: 204.1037.

(4*R*,5*R*)-4-(1-Naphthylmethyl)-5-phenyloxazolidin-2-one (from 14, $\text{R}^1 = \text{CH}_2\alpha\text{-Np}$): $[\alpha]_{\text{D}}^{23} = +3.5^\circ$ (c 0.50, THF); ^1H NMR (400 MHz, CDCl_3) δ 7.89-7.86 (1H, m, ArH), 7.81-7.78 (2H, m, ArH), 7.52-7.46 (2H, m, ArH), 7.44 (1H, t, $J = 7.4$ Hz, ArH), 7.38-7.36 (4H, m, ArH), 7.26-7.24 (2H, m, ArH), 5.35 (1H, d, $J_{\text{vic}} = 6.0$ Hz, OCHPh), 5.22 (1H, s, NH), 4.10 (1H, ddd, $J = 4.8, 6.0, 9.2$ Hz, NCH), 3.55 (1H, dd, $J = 4.8, 14.0$ Hz, NpCH_2), 3.34 (1H, dd, $J = 9.2, 14.0$ Hz, NpCH_2); IR (KBr) 3298, 3063, 3040, 2932, 1771, 1597, 1510, 1456, 1396, 1339, 1306, 1259, 1215, 1099, 1082, 1015, 943, 779, 731, 698 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 304.1332, Found: 304.1339.

Figure 8.

(4*R*,5*S*)-4-(1-Naphthylmethyl)-5-phenyloxazolidin-2-one (from 16, $\text{R}^1 = \text{CH}_2\alpha\text{-Np}$): $[\alpha]_{\text{D}}^{26} = +64.8^\circ$ (c 0.50, THF); ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.85 (1H, m, ArH), 7.76 (1H, d, $J = 8.0$ Hz, ArH), 7.70 (1H, d, $J = 8.0$ Hz, ArH), 7.54-7.36 (8H, m, ArH), 7.21 (1H, d, $J = 6.8$ Hz, ArH), 5.88 (1H, d, $J_{\text{vic}} = 8.0$ Hz, OCHPh), 4.82 (1H, s, NH), 4.36 (1H, ddd, $J = 2.8, 8.0, 11.6$ Hz, NCH), 2.84 (1H, dd, $J = 2.8, 14.0$ Hz, NpCH_2), 2.56 (1H, dd, $J = 11.6, 14.0$ Hz, NpCH_2); IR (KBr) 3418, 3275, 3065, 2926, 1759, 1597, 1510, 1500, 1456, 1394, 1350, 1232, 1084, 1040, 1011, 966, 793, 775, 741, 700 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 304.1332, Found: 304.1339.

Figure 9.

(4*R*,5*S*)-4-(1-Naphthylmethyl)-5-ethyl-5-phenyloxazolidin-2-one (from (2*R*,3*S*)-17): ^1H NMR (400 MHz, CDCl_3) δ 7.86 (1H, dd, $J = 1.2, 8.4$ Hz, ArH), 7.75 (2H, d, $J = 8.4$ Hz, ArH), 7.57-7.48 (6H, m, ArH), 7.41-7.35 (2H, m, ArH), 7.19 (1H, d, $J = 6.8$ Hz, ArH), 4.76 (1H, s, NH), 4.00 (1H, dd, $J = 2.6, 11.8$ Hz, NCH), 2.96 (1H, dd, $J = 2.6, 13.8$ Hz, NpCH_2), 2.36-2.16 (3H, m, NpCH_2 and CH_3CH_2), 0.89 (3H, t, $J = 7.2$ Hz, CH_2CH_3), NOE analysis of this compound was performed using C_6D_6 as solvent. ^1H NMR (400 MHz, C_6D_6) δ 7.66 (1H, d, $J = 8.4$ Hz, ArH), 7.63 (1H, d, $J = 8.4$ Hz, ArH), 7.51 (1H, d, $J = 8.4$ Hz, ArH), 7.33-7.23 (4H, m, ArH), 7.15-7.09 (3H, m, ArH), 7.04 (1H, t, $J = 7.4$ Hz, ArH), 6.76 (1H, d, $J = 6.8$ Hz, ArH), 4.69 (1H, s, NH), 3.49 (1H, dd, $J = 2.6, 11.5$ Hz, NCH), 2.71 (1H, dd, $J = 2.4, 14.0$ Hz, NpCH_2), 2.15 (1H, dd, $J = 11.5, 14.0$ Hz, NpCH_2), 1.87 (1H, dq, $J =$

7.2, 7.2 Hz, CH_3CH_2), 1.69 (1H, dq, $J = 7.2, 7.2$ Hz, CH_3CH_2), 0.76 (3H, t, $J = 7.2$ Hz, CH_2CH_3); IR (KBr) 3271, 3063, 2972, 2934, 2878, 1753, 1597, 1510, 1500, 1448, 1396, 1379, 1300, 1283, 1246, 1231, 1184, 1121, 1078, 1032, 984, 951, 785, 766, 702 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 332.1645, Found: 332.1642.

Figure 10. NOE Experiment in C_6D_6 .

(4R,5R)-4-(1-Naphthylmethyl)-5-ethyl-5-phenyloxazolidin-2-one (from (2R,3R)-17): ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.83 (2H, m, ArH), 7.79 (1H, d, $J = 8.4$ Hz, ArH), 7.53-7.33 (9H, m, ArH), 4.59 (1H, s, NH), 4.12 (1H, dd, $J = 2.4, 11.7$ Hz, NCH), 3.71 (1H, dd, $J = 2.4, 13.6$ Hz, NpCH_2), 3.24 (1H, dd, $J = 11.7, 13.6$ Hz, NpCH_2), 2.42 (1H, dq, $J = 7.2, 7.2$ Hz, CH_3CH_2), 2.22 (1H, dq, $J = 7.2, 7.2$ Hz, CH_3CH_2), 0.91 (3H, t, $J = 7.2$ Hz, CH_2CH_3); IR (KBr) 3449, 3437, 3132, 3069, 2974, 2926, 2895, 2853, 1751, 1597, 1508, 1500, 1448, 1383, 1358, 1312, 1295, 1280, 1269, 1221, 1157, 1142, 1105, 1094, 1074, 1053, 1036, 1015, 991, 959, 910, 895, 789, 766, 739, 704 cm^{-1} . HRMS (ESI-TOF) Calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_2$ ($[\text{M}+\text{H}]^+$): 332.1645, Found: 332.1645.

Figure 11. NOE Experiment in CDCl_3 .

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