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New Auxiliaries for Copper-Catalyzed Asymmetric Michael Reactions: Generation of Quaternary Stereocenters at Room Temperature

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General procedure 1 (GP1), synthesis of auxiliaries 2a-p: To a solution of the respective *N*-Boc-protected compound **9a–l** and **11m–p** in CH_2Cl_2 trifluoroacetic acid (ca. 2.3 eq) was added and the reaction mixture was stirred for 14–24 h at 23°C. All volatile materials were removed *in vacuo*. The residue was dissolved in water and treated with KOH (10% aqueous solution) at 0°C. The resulting mixture was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. After filtration and evaporation of the solvent the crude product was purified by Kugelrohr distillation (1 mbar). The amines **2a–p** are very hygroscopic and sensitive to CO_2 and were therefore stored under nitrogen.

L-Valine Dimethylamide (2a): Deprotection of **9a** (8.200 g, 33.56 mmol) yielded **2a** after Kugelrohr distillation (100°C, oven temp.) as a colorless oil (3.122 g, 21.65 mmol, 65%). $[\alpha]_{23}^{D}$ = +65.8 (*c* = 12.3 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.8 Hz, 3 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 1.65 (s, 2 H), 1.76–1.94 (m, 1 H), 2.96 (s, 3 H), 3.03 (s, 3 H), 3.49 (d, *J* = 5.4 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.81 (CH_3), 19.96 (CH_3), 32.00 (CH), 35.69 (CH_3), 37.03 (CH_3), 56.23 (CH), 175.15 (C=O); $C_7H_{16}N_2O$ (144.12).

L-Valine Diethylamide (2b): Deprotection of **9b** (10.02 g, 36.79 mmol) yielded **2b** after Kugelrohr distillation (115°C, oven temp.) as a colorless oil (5.265 g, 30.56 mmol, 83%). $[\alpha]_{23}^{D}$ = +57.1 (*c* = 10.3 in MeOH), ref.[35] $[\alpha]_{23}^{D}$ = +53.5 (*c* = 10 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (d, *J* = 6.7 Hz, 3 H), 0.94 (d, *J* = 6.8 Hz, 3 H), 1.11 (t, *J* = 7.1 Hz, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H), 1.62 (s, 2 H), 1.79–1.88 (m, 1 H), 3.12–3.28 (m, 2 H), 3.34 (d, *J*

= 6.1 Hz, 1 H), 3.37–3.46 (m, 1 H), 3.55–3.64 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.02 (CH_3), 14.74 (CH_3), 17.20 (CH_3), 20.06 (CH_3), 32.50 (CH), 40.34 (CH_2), 41.63 (CH_2), 56.55 (CH), 180.01 (C=O); $C_9H_{20}N_2O$ (172.27).

L-Leucine Dimethylamide (2d): Deprotection of **9d** (3.250 g, 12.63 mmol) yielded **2d** after Kugelrohr distillation (110°C, oven temp.) as a colorless oil (1.759 g, 11.12 mmol, 88%). $[\alpha]_{23}^{D}$ = +5.37 (*c* = 17.0 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.93 (d, *J* = 6.7 Hz, 3 H), 0.94 (d, *J* = 6.6 Hz, 3 H), 1.29–1.39 (m, 2 H), 1.62 (s, 2 H), 1.75–1.93 (m, 1 H), 2.96 (s, 3 H), 3.02 (s, 3 H), 3.68–3.76 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.44 (CH_3), 23.57 (CH_3), 24.64 (CH), 35.82 (CH_3), 36.63 (CH_3), 44.43 (CH_2), 49.39 (CH), 176.03 (C=O); $C_8H_{18}N_2O$ (158.24).

L-Isoleucine Dimethylamide (2e): Deprotection of **9e** (3.300 g, 12.77 mmol) yielded **2e** after Kugelrohr distillation (120°C, oven temp.) as a colorless oil (1.509 g, 9.536 mmol, 75%). $[\alpha]_{23}^{D}$ = +63 (*c* = 5.6 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 1.03–1.22 (m, 1 H), 1.48–1.69 (m, 2 H), 1.60 (s, br, 2 H), 2.97 (s, 3 H), 3.03 (s, 3 H), 3.52 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.43 (CH_3), 16.15 (CH_3), 23.56 (CH_2), 35.73 (CH_3), 37.13 (CH_3), 38.92 (CH), 55.66 (CH), 175.30 (C=O); $C_8H_{18}N_2O$ (158.24).

L-Phenylalanine Dimethylamide (2h): Deprotection of **9h** (2.100 g, 7.182 mmol) yielded **2h** after Kugelrohr distillation (180°C, oven temp.) as a colorless oil (834 mg, 4.34 mmol, 60%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.80 (s, 2 H), 2.73 (s, 3 H), 2.77 (dd, *J* = 13.2, 7.4 Hz, 1 H), 2.91 (s, 3 H), 2.94 (dd, *J* = 13.2, 6.8 Hz, 1 H), 3.94 (t, *J* = 7.2 Hz, 1 H), 7.15–7.34 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 35.68 (CH_3), 36.60 (CH_3), 42.77 (CH_2), 52.80 (CH), 126.73 (CH), 128.47 (2 CH), 129.26 (2 CH), 137.74 (C), 174.50 (C=O); $C_{11}H_{16}N_2O$ (192.26).

L-Valine Piperidide (2i): Deprotection of **9i** (3.400 g, 11.95 mmol) yielded **2i** after Kugelrohr distillation (140°C, oven temp.) as a colorless oil (1.988 g, 10.79 mmol, 90%). $[\alpha]_{23}^{D}$ = +61.4 (*c* = 9.35 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.8 Hz, 3 H), 0.97 (d, *J* = 6.8 Hz, 3 H), 1.48–1.72 (m, 6 H), 1.68 (s, 2 H), 1.73–1.91 (m, 1 H), 3.36–3.45 (m, 2 H), 3.51 (d, *J* = 4.9 Hz, 1 H), 3.52–3.62 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.49 (CH_3), 20.15 (CH_3), 24.59 (CH_2), 25.66 (CH_2), 26.55 (CH_2), 31.90 (CH), 43.11 (CH_2),

46.42 (CH_2), 55.96 (CH), 173.30 (C=O); IR (ATR): ν = 1636, 1443; MS (EI, 70 eV): *m/z* (%) = 184 (1) $[M]^+$, 141 (11), 84 (14), 72 (100); HR-MS: $C_{10}H_{20}N_2O$ (184.28): calcd 184.1576; found 184.1574.

L-Leucine Pyrrolidide (2j): Deprotection of **9j** (3.700 g, 13.01 mmol) yielded **2j** after Kugelrohr distillation (145°C, oven temp.) as a colorless oil (2.371 g, 12.87 mmol, 99%). $[\alpha]_{23}^{D}$ = –12 (*c* = 4.4 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.8 Hz, 6 H), 1.29–1.43 (m, 2 H), 1.74 (s, br, 2 H), 1.78–1.88 (m, 3 H), 1.91–1.99 (m, 2 H), 3.33–3.45 (m, 2 H), 3.46–3.55 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.43 (CH_3), 23.45 (CH_3), 23.94 (CH_2), 24.51 (CH), 25.99 (CH_2), 44.30 (CH_2), 45.81 (2 CH_2), 51.21 (CH), 174.35 (C=O); IR (ATR): ν = 1639; MS (EI, 70 eV): *m/z* (%) = 184 (2) $[M]^+$, 127 (10), 98 (6), 86 (100), 70 (33); HR-MS: $C_{10}H_{20}N_2O$ (184.28): calcd 184.1576; found 184.1577.

L-Isoleucine Pyrrolidide (2k): Deprotection of **9k** (4.340 g, 15.26 mmol) yielded **2k** after Kugelrohr distillation (135°C, oven temp.) as a colorless oil (2.213 g, 12.01 mmol, 79%). $[\alpha]_{23}^{D}$ = +22.4 (*c* = 5.45 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.5 Hz, 3 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 1.08–1.20 (m, 1 H), 1.57–1.70 (m, 2 H), 1.79 (s, br, 2 H), 1.81–1.90 (m, 2 H), 1.90–1.98 (m, 2 H), 3.32 (d, *J* = 6.4 Hz, 1 H), 3.39–3.56 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.32 (CH_3), 16.05 (CH_3), 23.86 (CH_2), 24.13 (CH_2), 26.12 (CH_2), 38.88 (CH), 45.80 (CH_2), 46.44 (CH_2), 57.87 (CH), 173.73 (C=O); IR (ATR): ν = 1635, 1437; MS (EI, 70 eV): *m/z* (%) = 184 (3) $[M]^+$, 127 (18), 86 (100), 70 (6); HR-MS: $C_{10}H_{20}N_2O$ (184.28): calcd 184.1576; found 184.1574.

L-Isoleucine Piperidide (2l): Deprotection of **9l** (7.150 g, 23.96 mmol) yielded **2l** after Kugelrohr distillation (175°C, oven temp.) as a colorless oil (2.861 g, 14.43 mmol, 60%). $[\alpha]_{23}^{D}$ = +49.1 (*c* = 8.35 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 3 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 1.06–1.19 (m, 1 H), 1.48–1.69 (m, 8 H), 2.09 (s, br, 2 H), 3.38–3.44 (m, 2 H), 3.52–3.65 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.66 (CH_3), 16.42 (CH_3), 23.32 (CH_2), 24.57 (CH_2), 25.64 (CH_2), 26.56 (CH_2), 38.74 (CH), 43.17 (CH_2), 46.52 (CH_2), 55.50 (CH), 173.13 (C=O); IR (ATR): ν = 1636, 1443; MS (EI, 70 eV): *m/z* (%) = 199 (18) $[M + H]^+$, 86 (100), 84 (5), 69 (11); HR-MS: $C_{11}H_{22}N_2O$ (198.31): calcd 199.1810; found 199.1811 $(M + H)^+$.

(*S*)-2-Amino-1-(dimethylamino)-3-phenylpropane (2p): Deprotection of **11p** (436 mg, 1.57 mmol) yielded **2p** as a colorless oil (394 mg, 2.73 mmol, 83%), which could be used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (s, br, 2 H), 2.11–2.35 (m, 2 H), 2.24 (s, 6 H), 2.48 (dd, *J* = 13.3, 8.6 Hz, 1 H), 2.74 (dd, *J* = 13.3, 4.5 Hz, 1 H), 3.07–3.22 (m, 1 H), 7.16–7.35 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.20 (CH_2), 45.77 (2 CH_3), 49.97 (CH), 66.26 (CH_2), 126.11 (CH), 128.32 (2 CH), 129.18 (2 CH), 139.19 (C=O); $C_{11}H_{18}N_2$ (178.28).

General procedure 5 (GP5), synthesis of *N*-Boc-protected amino acid amides 9a–l: To a solution of *N*-Boc-protected amino acid **8a**–**f** in CH_2Cl_2 dicyclohexylcarbodiimide (DCC) was added in small portions at 0°C, followed by addition of the respective amine dissolved in CH_2Cl_2. The mixture was stirred overnight at 23°C, filtered through SiO_2 (eluent: MTB), and all volatile materials were removed in vacuo. The residue was chromatographed on SiO_2 (eluent: MTB/PE) to give the title compounds **9a**–**l**.

***N*-(*tert*-Butyloxycarbonyl)-L-valine Dimethylamide (9a)**: *N*-Boc-L-valine (**8a**) (8.960 g, 41.24 mmol) and DCC (9.785 g, 47.43 mmol) in CH_2Cl_2 (45 ml) were converted according to GP5 with $HNMe_2$ (5.6 ml, 82 mmol) in CH_2Cl_2 (15 ml) to yield **9a** after chromatography (MTB/PE = 1 : 1, R_f = 0.21) as a colorless, viscous oil (8.338 g, 34.13 mmol, 83%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.8 Hz, 3 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 1.43 (s, 9 H), 1.84–2.02 (m, 1 H), 2.96 (s, 3 H), 3.09 (s, 3 H), 4.47 (dd, *J* = 9.2, 5.8 Hz, 1 H), 5.30 (d, br, *J* = 9.2 Hz, 1 H); $C_{12}H_{24}N_2O_3$ (244.33).

***N*-(*tert*-Butyloxycarbonyl)-L-leucine Dimethylamide (9d)**: *N*-Boc-L-leucine (**8b**) (4.470 g, 20.25 mmol) and DCC (4.894 g, 23.72 mmol) in CH_2Cl_2 (20 ml) were converted according to GP5 with $HNMe_2$ (3.6 ml, 55 mmol) in CH_2Cl_2 (8 ml) to yield **9d** after chromatography (MTB/PE = 1 : 1, R_f = 0.20) as a colorless solid (3.434 g, 13.34 mmol, 65%). M.p. 50–51°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.5 Hz, 3 H), 0.99 (d, *J* = 6.5 Hz, 3 H), 1.42 (s, 9 H), 1.32–1.51 (m, 2 H), 1.61–1.80 (m, 1 H), 2.95 (s, 3 H), 3.07 (s, 3 H), 4.58–4.72 (m, 1 H), 5.26 (d, br, *J* = 9.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.52 (CH_3), 23.18 (CH_3), 24.34 (CH), 28.09 (3 CH_3), 35.42 (CH_3), 36.66 (CH_3), 42.39 (CH_2), 48.34 (CH), 79.00 (C), 155.42 (C=O), 172.66 (C=O); IR (ATR): ν = 1707, 1646, 1172; MS (EI, 70 eV): *m/z* (%) = 258 (3) $[M]^+$, 186 (34), 185 (29), 130 (28), 128 (6), 86 (36), 72 (89), 59 (31), 57 (100); HR-

MS: $C_{13}H_{26}N_2O_3$ (258.36): calcd 258.1943; found 258.1945.

***N*-(*tert*-Butyloxycarbonyl)-L-isoleucine Dimethylamide (9e)**: *N*-Boc-L-isoleucine (**8c**) (5.200 g, 22.48 mmol) and DCC (5.335 g, 25.85 mmol) in CH_2Cl_2 (25 ml) were converted according to GP5 with $HNMe_2$ (3.4 ml, 49 mmol) in CH_2Cl_2 (10 ml) to yield **9e** after chromatography (MTB/PE = 1 : 1, R_f = 0.20) as a colorless, viscous oil (5.149 g, 19.30 mmol, 87%). $[\alpha]_{23}^{D}$ = +17.4 (*c* = 5.05 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 3 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 0.99–1.18 (m, 1 H), 1.41 (s, 9 H), 1.46–1.76 (m, 2 H), 2.96 (s, 3 H), 3.09 (s, 3 H), 4.47 (dd, *J* = 9.3, 6.5 Hz, 1 H), 5.25 (d, br, *J* = 9.5 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.10 (CH_3), 15.39 (CH_3), 23.74 (CH_2), 28.09 (3 CH_3), 35.32 (CH_3), 37.14 (CH_3), 37.90 (CH), 54.04 (CH), 79.00 (C), 155.57 (C=O), 172.14 (C=O); IR (ATR): ν = 1706, 1643, 1173; MS (EI, 70 eV): *m/z* (%) = 259 (3) $[M + H]^+$, 203 (100), 159 (95), 130 (13), 86 (13), 72 (7), 57 (21); HR-MS: $C_{13}H_{26}N_2O_3$ (258.36): calcd 259.2022; found 259.2022 $(M + H)^+$.

***N*-(*tert*-Butyloxycarbonyl)-L-phenylalanine Dimethylamide (9h)**: *N*-Boc-L-phenylalanine (**8f**) (5.300 g, 19.98 mmol) and DCC (4.907 g, 23.78 mmol) in CH_2Cl_2 (30 ml) were converted according to GP5 with $HNMe_2$ (4.1 ml, 60 mmol) in CH_2Cl_2 (10 ml) to yield **9h** after chromatography (MTB/PE = 1 : 1, R_f = 0.19) as a colorless resin (3.219 g, 11.01 mmol, 55%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.41 (s, 9 H), 2.60 (s, 3 H), 2.85 (s, 3 H), 2.91–3.00 (m, 2 H), 4.73–4.88 (m, 1 H), 5.41 (d, br, *J* = 8.5 Hz, 1 H), 7.13–7.32 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.31 (3 CH_3), 35.45 (CH_3), 36.73 (CH_3), 40.31 (CH_2), 51.34 (CH), 79.55 (C), 126.83 (CH), 128.33 (2 CH), 129.38 (2 CH), 136.49 (C), 155.04 (C=O), 171.53 (C=O); $C_{16}H_{24}N_2O_3$ (292.38).

***N*-(*tert*-Butyloxycarbonyl)-L-valine Piperidide (9i)**: *N*-Boc-L-valine (**8a**) (4.250 g, 19.56 mmol) and DCC (4.238 g, 20.54 mmol) in CH_2Cl_2 (30 ml) were converted according to GP5 with piperidine (1.832 g, 21.52 mmol) in CH_2Cl_2 (10 ml) to yield **9i** after chromatography (MTB/PE = 1 : 4, R_f = 0.26) as a colorless solid (3.446 g, 12.12 mmol, 62%). M.p. 49°C; $[\alpha]_{23}^{D}$ = +32 (*c* = 3.3 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H), 1.42 (s, 9 H), 1.49–1.73 (m, 6 H), 1.80–1.99 (m, 1 H), 3.40–3.50 (m, 2 H), 3.50–3.61 (m, 2 H), 4.47 (dd, *J* = 9.1, 5.3 Hz, 1 H), 5.39 (d, br, *J* = 9.2 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.97 (CH_3), 19.68 (CH_3), 24.47 (CH_2), 25.59 (CH_2), 26.48

(CH_2), 28.32 (3 CH_3), 31.57 (CH), 43.09 (CH_2), 46.78 (CH_2), 54.61 (CH), 79.21 (C), 155.88 (C=O), 170.23 (C=O); IR (ATR): ν = 1707, 1638, 1443, 1172; MS (EI, 70 eV): *m/z* (%) = 284 (4) $[M]^+$, 228 (12), 211 (23), 186 (14), 172 (17), 167 (6), 141 (5), 130 (56), 127 (8), 116 (38), 112 (20), 98 (31), 86 (64), 72 (53), 69 (36), 57 (100); HR-MS: $C_{15}H_{28}N_2O_3$: calcd 284.2100; found 286.2098; elemental analysis calcd (%) for $C_{15}H_{28}N_2O_3$ (284.40): C 63.35, H 9.92, N 9.85; found C 63.23, H 9.74, N 9.85.

***N*-(*tert*-Butyloxycarbonyl)-L-leucine Pyrrolidide (9j)**: *N*-Boc-L-leucine (**8b**) (5.250 g, 22.70 mmol) and DCC (5.152 g, 24.97 mmol) in CH_2Cl_2 (30 ml) were converted according to GP5 with pyrrolidine (1.937 g, 27.24 mmol) in CH_2Cl_2 (10 ml) to yield **9j** after chromatography (MTB/PE = 1 : 2, R_f = 0.10) as a colorless solid (3.914 g, 13.76 mmol, 61%). M.p. 59°C; $[\alpha]_{23}^{D}$ = –6.9 (*c* = 10.1 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.5, 3 H), 0.98 (d, *J* = 6.5 Hz, 3 H), 1.29–1.54 (m, 2 H); 1.42 (s, 9 H), 1.62–2.02 (m, 5 H), 3.32–3.56 (m, 3 H), 3.56–3.74 (m, 1 H), 4.38–4.52 (m, 1 H), 5.23 (d, br, *J* = 8.9 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.83 (CH_3), 23.44 (CH_3), 24.15 (CH_2), 24.60 (CH), 26.04 (CH_2), 28.35 (3 CH_3), 42.59 (CH_2), 45.89 (CH_2), 46.24 (CH_2), 50.40 (CH), 79.35 (C), 155.63 (C=O), 171.41 (C=O); IR (ATR): ν = 1708, 1641, 1433, 1168; MS (EI, 70 eV): *m/z* (%) = 284 (2) $[M]^+$, 228 (5), 211 (16), 186 (15), 172 (5), 130 (70), 98 (55), 86 (95), 70 (25), 57 (100); HR-MS: $C_{15}H_{28}N_2O_3$: calcd 284.2100; found 286.2102; elemental analysis calcd (%) for $C_{15}H_{28}N_2O_3$ (284.40): C 63.35, H 9.92, N 9.85; found C 63.14, H 9.62, N 9.80.

***N*-(*tert*-Butyloxycarbonyl)-L-isoleucine Piperidide (9l)**: *N*-Boc-L-isoleucine (**8c**) (8.150 g, 35.24 mmol) and DCC (8.361 g, 40.52 mmol) in CH_2Cl_2 (40 ml) were converted according to GP5 with piperidine (4.501 g, 52.86 mmol) in CH_2Cl_2 (10 ml) to yield **9l** after chromatography (MTB/PE = 1 : 2, R_f = 0.29) as a colorless solid (7.486 g, 25.08 mmol, 71%). M.p. 49°C; $[\alpha]_{23}^{D}$ = +23 (*c* = 4.1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.4 Hz, 3 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 1.02–1.15 (m, 1 H), 1.41 (s, 9 H), 1.43–1.69 (m, 8 H), 3.44–3.51 (m, 2 H), 3.51–3.62 (m, 2 H), 4.49 (dd, *J* = 9.2, 6.0 Hz, 1 H), 5.32 (d, br, *J* = 8.6 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.52 (CH_3), 15.93 (CH_3), 23.76 (CH_2), 24.50 (CH_2), 25.61 (CH_2), 26.53 (CH_2), 28.32 (3 CH_3), 38.28 (CH), 43.11 (CH_2), 46.86 (CH_2), 54.20 (CH), 79.24 (C), 155.83 (C=O), 170.43 (C=O); IR (ATR): ν = 1705, 1634, 1443, 1172; MS (EI, 70 eV): *m/z* (%) = 298 (3) $[M]^+$, 225 (15), 186 (29), 168 (11), 130 (90), 112 (61), 86 (100), 84 (19), 69 (28), 57 (78); HR-MS: $C_{16}H_{30}N_2O_3$: calcd 298.2256; found 298.2251;

elemental analysis calcd (%) for $C_{16}H_{30}N_2O_3$ (298.43): C 64.40, H 10.13, N 9.39; found C 64.59, H 10.30, N 9.54.

***tert*-Butyl (*S*)-*N*-[1-(Ethylsulfanylmethyl)-2-phenylethyl]carbamate (11o)**: According to the procedure given above for compound **11m** tosylate **10b** (1.700 g, 4.192 mmol) was converted with NaSEt (80%, 1.102 g, 10.48 mmol) to afford **11o** after chromatography on SiO_2 (MTB/PE = 1 : 6, R_f = 0.31) as a colorless solid (1.130 g, 3.825 mmol, 91%). M.p. 58°C; $[\alpha]_{23}^{D}$ = +4.9 (*c* = 4.3 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.3 Hz, 3 H), 1.41 (s, 9 H), 2.56 (q, *J* = 7.5 Hz, 2 H), 2.59–2.63 (m, 2 H), 2.84–2.91 (m, 2 H), 3.73–4.21 (m, br, 1 H), 4.69 (s, br, 1 H), 7.18–7.25 (m, 3 H), 7.27–7.33 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.86 (CH_3), 26.74 (CH_2), 28.35 (3 CH_3), 35.56 (CH_2), 39.51 (CH_2), 51.09 (CH), 79.40 (C), 126.48 (CH), 128.45 (2 CH), 129.41 (2 CH), 137.69 (C), 155.23 (C=O); IR (ATR): ν = 1713, 1701, 1496, 1366, 1249, 1169, 700; MS (EI, 70 eV): *m/z* (%) = 295 (2) $[M]^+$, 220 (16), 204 (22), 178 (16), 148 (13), 120 (70), 117 (18), 104 (30), 91 (29), 75 (15), 57 (100); HR-MS: $C_{16}H_{25}NO_2S$: calcd 295.1506; found 295.1606; elemental analysis calcd (%) for $C_{16}H_{25}NO_2S$ (295.45): C 65.05, H 8.53, N 4.74; found C 65.07, H 8.47, N 4.86.