Supporting Information

Tandem Asymmetric Conjugate Addition/ α -Alkylation using (*S,S*)-(+)-Pseudoephedrine as Chiral Auxiliary.

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1. General methods:

Melting points were determined in unsealed capillary tubes and are uncorrected. IR spectra were obtained on KBr pellets (solids) or CHCl_3 solution (oils). NMR spectra were recorded at 20-25°C, running at 250 MHz for ^1H and 62.8 MHz for ^{13}C in CDCl_3 solution and resonances are reported in ppm relative to tetramethylsilane unless otherwise stated. Mass spectra were recorded under electron impact at 70 eV. TLC was carried out with 0.2 mm. thick silica gel plates (Merck Kiesegel GF₂₅₄) and visualization was accomplished by UV light or by spraying with phosphomolybdic acid. Flash column chromatography on silica gel was performed with Merck Kiesegel 60 (230-400 mesh). All solvents used in reactions were dried and purified according to standard procedures. All air- or moisture-sensitive reactions were performed under argon. The glassware was oven dried (140°C) overnight and purged with argon prior to use. Organolithium reagents were titrated periodically with diphenylacetic acid. All other reagents were used as purchased. Diastereomeric ratios (d.r.) were determined by HPLC under conditions specified in each case.

2.- Diastereoselective tandem conjugate addition/alkylation.

General procedure:

A solution of organolithium reagent (2.05 mmol) was carefully added to a suspension of the enamide (1.00 mmol) and LiCl (5.00 mmol) in dry THF (30 mL) at -105°C and the reaction was stirred at this temperature until TLC analysis of aliquots indicated complete consumption of the starting material (typically 30 min.). The corresponding alkyl halide (4.00 mmol) was added at once and the mixture was allowed to warm to 0°C at which temperature it was stirred for further 5h. The reaction was quenched with a saturated NH_4Cl solution (20 mL), extracted with CH_2Cl_2 (3 x 10mL) and the combined organic fractions were collected, dried over Na_2SO_4 , filtered and the solvent removed *in vacuo* affording the tandem pure products after flash column chromatography.

(+)-(1'S,2'S,2S,3R)-N-(2'-Hydroxy-1'-methyl-2'-phenylethyl)-2,N-dimethyl-3-phenylbutanamide (3a)

Amide **3a** (0.50g, 1.54mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and MeI (0.50mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 93:4:3:<1 diastereomeric ratio: t_R for the major isomer: 37.75min. (93%). The other isomers eluted at 17.55min. (<1%), 24.71min. (4%) and 28.07min. (3%). Amide **3a** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 77%. $[\alpha]_D^{20} = +116.1$ ($c=1.0$, CH_2Cl_2). ^1H -NMR (δ , ppm) (4:1 rotamer ratio; *indicates minor rotamer resonances): 0.75 (d, 3H, $J=6.7$ Hz); 0.89* (d, 3H, $J=5.0$ Hz); 1.00* (d, 3H, $J=6.7$ Hz); 1.15 (d, 3H, $J=6.7$ Hz); 1.22 (d, 3H, $J=7.0$ Hz); 2.73 (m, 1H); 2.82 (s, 3H); 2.94* (s, 3H); 2.98 (m, 1H); 4.19* (m, 1H); 4.34 (m, 1H); 4.57* (m, 1H); 4.65 (m, 1H); 5.07 (bs, 1H); 7.15-7.33 (m, 10H). ^{13}C -NMR (δ , ppm) (4:1 rotamer ratio; *indicates minor rotamer resonances): 14.3; 15.4*; 16.6; 16.9*; 20.3*; 20.5; 27.1*; 34.3; 42.4*; 43.6; 43.9; 44.2*; 58.4; 60.0*;

75.1*; 76.1; 126.0; 126.1*; 126.2; 126.7*; 127.5; 127.6; 128.0*; 128.1; 128.2*; 128.3; 128.5*; 141.6*; 142.4; 144.8; 145.1*; 177.1*; 178.2. IR (CHCl₃): 3380 (OH); 1716 (C=O). MS (EI) *m/z* (Rel. Int.): 307 (M⁺-18, 1), 218 (10), 204 (10), 202 (15), 147 (16), 145 (15), 117 (11), 115 (10); 105 (27), 91 (37), 58 (100). Anal. Calcd. for C₂₁H₂₇NO₂: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.76; H, 8.51; N, 4.50.

(+)-(1'S,2'S,2S,3R)-2-Ethyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylbutanamide (3b)

Amide **3b** (0.65g, 1.92mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and EtI (0.63mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 98:2, flow rate 0.85 mL/min) indicated a 95:5:<1:<1 diastereomeric ratio: *t_R* for the major isomer: 33.64min. (95%). The other isomers eluted at 23.11min. (5%), 29.95min. (<1%) and 47.16min. (<1%). Amide **3b** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 96%. [α]_D²⁰ = +76.2 (*c*=1.0, CH₂Cl₂). ¹H-NMR (δ , ppm) (5:1 rotamer ratio; *indicates minor rotamer resonances): 0.61 (t, 3H, *J*= 7.1 Hz); 0.88* (t, 3H, *J*= 5.6 Hz); 1.13 (d, 3H, *J*= 6.0 Hz); 1.17 (d, 3H, *J*= 6.7 Hz); 1.28* (d, 3H, *J*= 7.1 Hz); 1.47 (m, 2H); 1.57* (m, 2H); 2.76 (m, 1H); 2.94 (s, 3H); 3.00* (s, 3H); 3.15 (m, 1H), 4.17* (m, 1H); 4.63 (m, 3H); 7.17-7.41 (m, 10H). ¹³C-NMR (δ , ppm) (5:1 rotamer ratio; *indicates minor rotamer resonances): 11.4; 12.0*; 14.6; 15.0*; 18.7*; 20.1; 23.9*; 25.1; 27.0*; 33.1; 42.3*; 43.3; 49.0*; 50.1; 58.2; 58.4*; 75.1*; 76.0; 126.2*; 126.3; 126.4*; 126.9; 127.2*; 127.4; 127.6*; 128.0; 128.1*; 128.2; 128.3; 128.5*; 141.5*; 142.3; 145.2; 145.4*; 176.2*; 177.7. IR (CHCl₃): 3375 (OH); 1630 (C=O). MS (EI) *m/z* (Rel. Int.): 261 (M⁺-78, 1), 232 (4), 147 (6), 105 (26), 91 (15), 58 (100). Anal. Calcd. for C₂₂H₂₉NO₂: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.71; H, 8.85; N, 4.28.

(+)-(1'S,2'S,2S,3R)-2-Allyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylbutanamide (3c)

Amide **3c** (0.49g, 1.42mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and allyl iodide (0.73mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 98:2, flow rate 0.85 mL/min) indicated a 93:4:2:1 diastereomeric ratio: t_R for the major isomer: 30.39min. (93%). The other isomers eluted at 21.06min. (4%), 22.69min. (2%) and 41.43min. (1%). Amide **3c** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). and it was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 70%. $[\alpha]_D^{20} = +75.9$ ($c=1.0$, CH_2Cl_2). $^1\text{H-NMR}$ (δ , ppm) (4:1 rotamer ratio; *indicates minor rotamer resonances): 0.72* (d, 3H, $J=6.7$ Hz); 0.85* (d, 3H, $J=6.6$ Hz); 1.08 (d, 3H, $J=6.3$ Hz); 1.18 (d, 3H, $J=6.7$ Hz); 1.85 (m, 1H); 2.24 (m, 1H); 2.48 (m, 1H); 2.88* (s, 3H); 2.91 (s, 3H); 3.07 (m, 1H), 4.11* (m, 1H); 4.41 (m, 1H); 4.63 (m, 2H); 4.83 (m, 2H); 5.48 (m, 1H); 5.82* (m, 1H); 7.18-7.41 (m, 10H). $^{13}\text{C-NMR}$ (δ , ppm) (4:1 rotamer ratio; *indicates minor rotamer resonances): 14.5; 15.0*; 19.6*; 20.0; 27.0*; 32.9; 35.1*; 36.4; 42.9*; 43.1; 47.7*; 48.7; 58.1*; 58.5; 75.1*; 75.9; 116.4; 116.7*; 126.3; 126.7*; 126.9; 127.2*; 127.3*; 127.5; 128.0*; 128.2; 128.3*; 128.4; 128.6; 135.3; 136.6*; 141.1*; 142.2; 144.7; 145.1*; 175.4*; 176.7. IR (CHCl_3): 3382 (OH); 1615 (C=O). MS (EI) m/z (Rel. Int.): 244 (M^+-107 , 8), 117 (7), 105 (26), 91 (8), 58 (100). Anal. Calcd. for $\text{C}_{23}\text{H}_{29}\text{NO}_2$: C, 78.59; H, 8.32; N, 3.99. Found: C, 78.64; H, 8.45; N, 3.78.

(+)-(1'S,2'S,2S,3R)-2-Benzyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylbutanamide (3d)

Amide **3d** (0.63g, 1.56mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and benzyl bromide (0.94mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00

mL/min) indicated a 96:4:<1:<1 diastereomeric ratio: t_R for the major isomer: 18.64min. (93%). The other isomers eluted at 12.44min. (<1%), 13.58min. (4%) and 20.77min. (<1%). Amide **3d** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 78%. $[\alpha]_D^{20} = +10.9$ ($c=1.0$, CH_2Cl_2). ^1H -NMR (δ , ppm) (6:1 rotamer ratio; *indicates minor rotamer resonances): 0.41* (d, 3H, $J=6.5$ Hz); 0.68 (d, 3H, $J=6.7$ Hz); 0.72* (d, 3H, $J=6.1$ Hz); 1.24 (d, 3H, $J=6.5$ Hz); 2.44* (s, 3H); 2.52 (s, 3H); 2.73 (m, 1H); 3.15 (m, 2H); 3.61 (m, 1H); 4.12* (m, 1H); 4.48 (m, 1H); 4.70 (m, 1H); 6.93-7.44 (m, 15H). ^{13}C -NMR (δ , ppm) (6:1 rotamer ratio; *indicates minor rotamer resonances): 14.1; 14.9*; 19.8*; 20.4; 27.1*; 30.8; 37.4*; 38.5; 42.4*; 43.5; 50.8*; 51.8; 56.2; 58.2*; 74.9*; 76.2; 126.1; 126.2*; 126.5; 126.7; 126.9*; 127.0*; 127.1; 127.2*; 127.3*; 127.5; 127.7*; 128.1; 128.3; 128.4*; 128.5*; 128.6; 128.7; 129.1*; 139.8; 140.4*; 141.1*; 142.0; 145.0; 145.1*; 175.8*; 176.9. IR (CHCl_3): 3382 (OH); 1614 (C=O). MS (EI) m/z (Rel. Int.): 294 (M^+-107 , 7), 131 (7), 105 (34), 91 (17), 58 (100). Anal. Calcd. for $\text{C}_{27}\text{H}_{31}\text{NO}_2$: C, 80.76; H, 7.78; N, 3.49. Found: C, 80.59; H, 7.91; N, 3.62.

(+)-(1'S,2'S,2S,3S)-N-(2'-Hydroxy-1'-methyl-2'-phenylethyl)-2,3,N-trimethylheptanamide (3e)

Amide **3e** (0.41g, 1.34mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), $n\text{BuLi}$ (4.43mL of a 1.0M solution in hexanes) and MeI (0.50mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 91:5:3:<1 diastereomeric ratio: t_R for the major isomer: 28.63min. (91%). The other isomers eluted at 15.46min. (5%), 21.12. (3%) and 34.53min. (<1%). Amide **3e** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 67%. $[\alpha]_D^{20} = +111.1$ ($c=0.8$, CH_2Cl_2). ^1H -NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.73-1.32 (m, 16H); 1.41 (m, 1H); 1.62 (m, 1H); 2.33 (m, 1H); 2.71 (s, 3H); 2.80* (s, 3H); 2.94 (m, 1H); 4.02* (m, 1H); 4.21 (m, 1H); 4.52 (m, 2H); 7.32 (m, 5H). ^{13}C -NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 14.1; 14.3*; 14.6; 14.8*; 15.2*; 15.7; 18.3; 18.6*; 22.4; 22.6*; 30.5; 32.3*; 33.1; 35.4*; 36.3*; 36.5; 38.4; 39.2*; 41.5*; 42.3; 51.2;

51.7*; 74.5*; 76.0; 126.2; 126.7*; 127.1*; 127.3; 127.5*; 128.5; 141.7*; 144.2; 176.4*; 178.5. IR (CHCl₃): 3371 (OH); 1616 (C=O). MS (EI) *m/z* (Rel. Int.): 216 (M⁺-89, 1), 198 (7), 147 (6), 113 (5), 71 (16), 58 (100). Anal. Calcd. for C₁₉H₃₁NO₂: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.56; H, 9.97; N, 4.48.

(+)-(1'S,2'S,2S,3S)-2-Ethyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-3,N,-dimethylheptanamide (3f)

Amide **3f** (0.47g, 1.46mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), ⁿBuLi (4.43mL of a 1.0M solution in hexanes) and EtI (0.63mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 93:7, flow rate 0.85 mL/min) indicated a 91:6:2:<1 diastereomeric ratio: *t_R* for the major isomer: 10.07min. (91%). The other isomers eluted at 7.41min. (<1%), 8.56min. (6%) and 11.84min. (2%). Amide **3f** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 73%. [α]_D²⁰ = +64.7 (*c*=1.0, CH₂Cl₂). ¹H-NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.73-1.32 (m, 16H); 1.41 (m, 1H); 1.62 (m, 1H); 2.33 (m, 1H); 2.71 (s, 3H); 2.80* (s, 3H); 2.94 (m, 1H), 4.02* (m, 1H); 4.21 (m, 1H); 4.52 (m, 2H); 7.32 (m, 5H). ¹³C-NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 11.7; 12.2*; 13.9*; 14.1; 14.3; 14.5*; 15.1*; 15.4; 18.3; 18.6*; 22.3; 22.4*; 27.3*: 27.5; 30.2; 32.4*; 36.0*; 36.3; 39.0; 39.3*; 41.5*; 42.4; 51.3; 51.7*; 74.5*; 76.0; 126.0; 126.5*; 127.3*; 127.7; 127.1*; 128.3; 142.0*; 144.2; 176.4*; 178.5. IR (CHCl₃): 3392 (OH); 1615 (C=O). MS (EI) *m/z* (Rel. Int.): 212 (M⁺-107, 7), 148 (5), 107 (5), 85 (16), 79 (7), 71 (25), 58 (100), 55 (8). Anal. Calcd. for C₂₀H₃₃NO₂: C, 75.19; H, 10.41; N, 4.38. Found: C, 75.54; H, 10.65; N, 4.30.

(+)-(1'S,2'S,2S,3S)-2-Allyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-3,N,-dimethylheptanamide (2g)

Amide **3g** (0.47g, 1.43mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), ⁿBuLi (4.43mL of a 1.0M solution in hexanes) and allyl iodide (0.73mL, 8.00mmol). HPLC analysis of the crude reaction

mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 86:10:4:<1 diastereomeric ratio: t_R for the major isomer: 10.46min. (86%). The other isomers eluted at 5.43min. (<1%), 9.10min. (4%) and 14.07min. (10%). Amide **3g** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 71%. $[\alpha]_D^{20} = +67.8$ ($c=1.0$, CH₂Cl₂). ¹H-NMR (δ , ppm) (4:1 rotamer ratio; *indicates minor rotamer resonances): 0.58* (d, 3H, $J=6.8$ Hz); 0.73-1.38 (m, 13H); 1.46 (m, 1H); 1.68 (m, 1H); 2.27 (m, 1H); 2.47 (m, 1H); 2.74 (s, 3H); 2.78* (s, 3H); 4.06* (m, 1H); 4.38-4.62 (m, 3H); 4.87 (m, 2H); 5.02* (m, 2H); 5.57 (m, 1H); 5.83* (m, 1H); 7.44 (m, 5H). ¹³C-NMR (δ , ppm) (4:1 rotamer ratio; indicates minor rotamer resonances): 13.9; 14.4; 15.2*; 15.8*; 17.3; 17.5*; 22.7; 26.8*; 28.7; 29.1*; 29.3; 31.2*; 32.7; 32.8*; 34.3; 34.6*; 35.2; 35.5*; 47.3*; 47.5; 58.2; 58.7*; 75.9; 76.5*; 115.9*; 116.1; 126.2; 126.5*; 126.8*; 127.2; 127.3*; 128.0; 136.0; 136.3*; 142.1*; 142.3; 177.1*; 177.3. IR (CHCl₃): 3386 (OH); 1617 (C=O). MS (EI) m/z (Rel. Int.): 224 (M⁺-107, 5), 97 (7), 83 (15), 58 (100), 55 (6). Anal. Calcd. for C₂₁H₃₃NO₂: C, 76.09; H, 10.03; N, 4.23. Found: C, 76.22; H, 9.87; N, 4.37.

(+)-(1'S,2'S,2S,3S)-2-Benzyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-3,N,-dimethylheptanamide (3h)

Amide **3h** (0.48g, 1.26mmol) was prepared according to the general procedure starting from enamide **1a** (0.46g, 2.00mmol), LiCl (0.42g, 10.00mmol), ⁿBuLi (4.43mL of a 1.0M solution in hexanes) and benzyl bromide (0.73mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 90:10, flow rate 1.00 mL/min) indicated a 89:8:3:<1 diastereomeric ratio: t_R for the major isomer: 14.49min. (89%). The other isomers eluted at 7.38min. (<1%), 9.59min. (3%) and 11.20min. (8%). Amide **3h** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 63%. M.p.: 69-72°C (hexanes/AcOEt 1:1). $[\alpha]_D^{20} = -6.5$ ($c=1.0$, CH₂Cl₂). ¹H-NMR (δ , ppm) (5:1 rotamer ratio; *indicates minor rotamer resonances): 0.61 (d, 3H, $J=6.7$ Hz); 0.68* (d, 3H, $J=6.8$ Hz); 0.82 (m, 6H); 1.36 (m, 4H); 1.62 (m, 1H); 1.84 (m, 1H); 2.22* (s, 3H); 2.43 (s, 3H); 2.83 (m, 3H); 3.84 (m, 1H); 4.47 (m, 2H); 7.08-7.43 (m, 10H). ¹³C-NMR (δ , ppm) (5:1 rotamer ratio; indicates minor rotamer resonances): 14.0; 15.0*; 16.3*; 17.6; 22.7*; 22.9; 26.9*; 28.7; 29.4*;

31.4; 33.1; 33.4*; 35.5*; 35.6; 36.5*; 36.7; 49.5*; 50.5; 56.8*; 58.1; 64.7; 76.2*; 76.5; 126.0; 126.3*; 126.5*; 126.6; 127.2*; 127.5; 127.6*; 128.1; 128.2; 128.4*; 128.5*; 128.9; 140.2; 140.4*; 141.8*; 142.1; 175.7*; 177.5. IR (KBr): 3385 (OH); 1615 (C=O). MS (EI) m/z (Rel. Int.): 274 (M^+ -107, 5), 178 (6), 119 (6), 105 (9), 91 (23), 58 (100). Anal. Calcd. for $C_{25}H_{35}NO_2$: C, 78.70; H, 9.25; N, 3.67. Found: C, 78.59; H, 9.13; N, 3.77.

(+)-(1'S,2'S,2S,3R)-N-(2'-Hydroxy-1'-methyl-2'-phenylethyl)-2,N-dimethyl-3-phenylpentanamide (3i)

Amide **3i** (0.51g, 1.51mmol) was prepared according to the general procedure starting from enamide **1b** (0.49g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and MeI (0.50mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 95:4:<1:<1 diastereomeric ratio: t_R for the major isomer: 30.16min. (95%). The other isomers eluted at 13.76min. (<1%), 16.62min. (<1%) and 21.60min. (4%). Amide **3i** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 75%. $[\alpha]_D^{20} = +130.4$ ($c=1.0$, CH_2Cl_2). 1H -NMR (δ , ppm) (3:2 rotamer ratio; *indicates minor rotamer resonances): 0.58 (t, 3H, $J=7.5$ Hz); 0.64 (d, 3H, $J=6.1$ Hz); 0.83* (d, 3H, $J=6.2$ Hz); 1.02* (d, 3H, $J=6.7$ Hz); 1.21 (d, 3H, $J=6.7$ Hz); 1.33 (m, 1H); 1.58 (m, 1H); 2.71 (m, 2H); 2.86 (s, 3H); 2.91* (s, 3H); 4.17* (m, 1H); 4.39 (m, 1H); 4.53* (m, 1H); 4.64 (m, 1H); 5.02 (bs, 1H); 7.08-7.35 (m, 10H). ^{13}C -NMR (δ , ppm) (3:2 rotamer ratio; indicates minor rotamer resonances): 12.3*; 12.6; 14.4; 14.7*; 17.5; 17.8*; 26.3; 26.4*; 32.1; 41.2*; 41.6; 50.4; 51.6*; 58.2; 59.0*; 75.4*; 76.1; 126.0; 126.2*; 126.4; 126.8; 127.2*; 127.3; 127.5; 127.6*; 128.0*; 128.2; 141.4*; 142.0; 143.6; 144.1*; 177.3*; 178.5. IR ($CHCl_3$): 3372 (OH); 1615 (C=O). MS (EI) m/z (Rel. Int.): 321 (M^+ -18, 2), 232 (16), 216 (14), 147 (29), 145 (18), 119 (34), 117 (40), 115 (29); 105 (81), 91 (100), 77 (45), 58 (16). Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.79; H, 8.28; N, 4.28.

(+)-(1'S,2'S,2S,3R)-2-Ethyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylpentanamide (3j)

Amide **3j** (0.56g, 1.62mmol) was prepared according to the general procedure starting from enamide **1b** (0.49g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and EtI (0.63mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 97:2:<1:<1 diastereomeric ratio: t_R for the major isomer: 15.37min. (97%). The other isomers eluted at 11.85min. (2%), 12.69min. (<1%) and 19.50min. (<1%). Amide **3j** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 80%. $[\alpha]_D^{20} = +94.7$ ($c=1.0$, CH_2Cl_2). $^1\text{H-NMR}$ (δ , ppm) (3:2 rotamer ratio; *indicates minor rotamer resonances): 0.52 (t, 6H, $J=7.1$ Hz); 0.61* (t, 6H, $J=7.1$ Hz); 0.68* (t, 3H, $J=6.9$ Hz); 0.97* (d, 3H, $J=6.7$ Hz); 1.05 (m, 1H); 1.13 (d, 3H, $J=6.7$ Hz); 1.45 (m, 2H); 1.53 (m, 1H); 2.69 (m, 1H); 2.75 (m, 1H); 2.88* (s, 3H); 2.94 (s, 3H); 4.21* (m, 1H); 4.57 (m, 2H); 4.69; 5.02 (bs, 1H); 7.10-7.41 (m, 10H). $^{13}\text{C-NMR}$ (δ , ppm) (3:2 rotamer ratio; indicates minor rotamer resonances): 12.1; 12.3*; 14.5*; 14.7; 16.4; 16.6*; 23.2*; 24.6; 27.5; 27.7*; 32.5; 49.8; 50.2*; 52.4; 52.5*; 58.6; 58.9*; 76.5*; 76.7; 126.1; 126.7; 126.9*; 127.1; 127.3*; 127.6; 127.8; 128.1; 128.5*; 143.2*; 145.4; 145.7; 146.1*; 177.1*; 178.0. IR (CHCl_3): 3365 (OH); 1612 (C=O). MS (EI) m/z (Rel. Int.): 335 (M^+-18 , 2), 246 (15), 161 (24), 159 (21), 147 (18), 131 (13), 119 (55), 117 (22), 115 (20); 105 (61), 91 (100), 77 (39), 58 (14). Anal. Calcd. for $\text{C}_{23}\text{H}_{31}\text{NO}_2$: C, 78.15; H, 8.84; N, 3.96. Found: C, 78.01; H, 8.66; N, 3.79.

(+)-(1'S,2'S,2S,3R)-2-Allyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylpentanamide (3k)

Amide **3k** (0.56g, 1.54mmol) was prepared according to the general procedure starting from enamide **1b** (0.49g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and allyl bromide (0.73mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 95:4:1:<1 diastereomeric ratio: t_R for the major isomer: 15.60min. (95%). The other isomers eluted at 10.39min. (<1%), 12.51min. (4%) and 18.65min.

(1%). Amide **3k** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 77%. $[\alpha]_D^{20} = +74.6$ ($c=1.0$, CH_2Cl_2). ^1H -NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.50 (t, 3H, $J=7.2$ Hz); 0.58* (t, 3H, $J=7.2$ Hz); 0.82* (d, 3H, $J=6.7$ Hz); 1.02 (d, 3H, $J=6.5$ Hz); 1.31 (m, 1H); 1.52 (m, 1H); 1.71 (m, 1H); 2.06 (m, 1H); 2.67 (m, 1H); 2.79 (m, 1H); 2.84* (s, 3H); 2.87 (s, 3H); 4.20* (m, 1H); 4.51 (m, 2H); 4.73 (m, 2H); 4.67* (m, 2H); 5.37 (m, 1H); 5.71* (m, 1H); 7.07-7.38 (m, 10H). ^{13}C -NMR (δ , ppm) (3:1 rotamer ratio; indicates minor rotamer resonances): 13.0; 13.2*; 15.4; 15.5*; 27.6; 28.1*; 32.4; 36.5*; 38.3; 48.7*; 49.2; 51.6; 51.9*; 58.4; 59.7; 75.4*; 76.7; 114.2; 114.5*; 125.8; 125.9*; 126.4; 126.6; 127.1*; 127.2; 127.6; 128.1; 128.3*; 136.2; 137.0*; 141.1*; 141.9; 142.2; 142.3*; 175.4*; 177.0. IR (CHCl_3): 3389 (OH); 1613 (C=O). MS (EI) m/z (Rel. Int.): 318 (M^+-47 , 6), 258 (18), 229 (8), 147 (20), 131 (22), 129 (15), 117 (31), 115 (23); 105 (46), 91 (100), 77 (40), 58 (14). Anal. Calcd. for $\text{C}_{24}\text{H}_{31}\text{NO}_2$: C, 78.86; H, 8.55; N, 3.83. Found: C, 78.76; H, 8.58; N, 3.82.

(+)-(1'S,2'S,2S,3R)-2-Benzyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylpentanamide (3l)

Amide **3l** (0.56g, 1.34mmol) was prepared according to the general procedure starting from enamide **1b** (0.49g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and benzyl bromide (0.94mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 99:<1:<1:<1 diastereomeric ratio: t_R for the major isomer: 17.41min. (99%). The other isomers eluted at 12.16min. (<1%), 13.76min. (<1%) and 24.95min. (<1%). Amide **3l** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 67%. M.p.: 176-178°C (hexanes/AcOEt 1:1). $[\alpha]_D^{20} = +14.6$ ($c=1.0$, CH_2Cl_2). ^1H -NMR (δ , ppm) (6:1 rotamer ratio; *indicates minor rotamer resonances): 0.58 (m, 6H); 0.83* (d, 3H, $J=6.7$ Hz); 1.46 (m, 1H); 1.61 (m, 1H); 2.34 (dd, 1H, $J=12.8, 3.4$ Hz); 2.48 (s, 3H); 2.66 (dd, 1H, $J=1.8, 11.5$ Hz); 2.75* (s, 3H); 2.83 (dt, 1H, $J=3.1, 11.2$ Hz); 3.11 (dt, 1H, $J=3.5, 11.1$ Hz); 3.50 (bs, 1H); 4.48 (m, 1H); 4.64 (m, 1H); 6.94 (d, 2H, $J=6.9$ Hz); 7.12-7.35 (m, 15H). ^{13}C -NMR (δ , ppm) (6:1 rotamer ratio; indicates minor rotamer resonances):

12.5; 12.6*; 13.8; 14.5*; 26.3; 26.4*; 31.2; 39.8; 51.7*; 51.9; 52.4; 53.1*; 56.7; 59.2*; 74.6*; 75.9; 125.9; 126.5*; 126.6; 127.0; 127.2*; 127.8; 128.0*; 128.3; 128.6; 128.7*; 128.9*; 129.1; 129.3; 129.4*; 129.6; 129.8*; 140.1; 140.8*; 141.2; 143.6; 175.4*; 177.0. IR (KBr): 3385 (OH); 1614 (C=O). MS (EI) m/z (Rel. Int.): 308 ($M^+ - 107$, 1), 221 (14), 189 (17), 145 (20), 119 (39), 115 (15); 105 (30), 91 (100), 77 (37). Anal. Calcd. for $C_{28}H_{33}NO_2$: C, 80.93; H, 8.00; N, 3.37. Found: C, 80.78; H, 7.92; N, 3.22.

(+)-(1'S,2'S,2S,3R)-N-(2'-Hydroxy-1'-methyl-2'-phenylethyl)-2,N-dimethyl-3-phenylhexanamide (3m)

Amide **3m** (0.61g, 1.67mmol) was prepared according to the general procedure starting from enamide **1c** (0.52g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and MeI (0.50mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 93:7, flow rate 0.85 mL/min) indicated a 99:<1:<1:<1 diastereomeric ratio: t_R for the major isomer: 18.50min. (99%). The other isomers eluted at 11.85min. (<1%), 13.00min. (<1%) and 29.42min. (<1%). Amide **3m** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 86%. $[\alpha]_D^{20} = +136.0$ ($c=1.0$, CH_2Cl_2). M.p.: 161-164°C (hexanes/AcOEt 1:1). 1H -NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.71 (d, 3H, $J=6.3$ Hz); 0.77 (t, 3H, $J=7.1$ Hz); 0.84* (t, 3H, $J=5.6$ Hz); 0.93* (d, 3H, $J=6.1$ Hz); 1.12* (d, 3H, $J=5.9$ Hz); 1.23 (d, 3H, $J=6.5$ Hz); 1.54 (m, 4H); 2.54 (m, 1H); 2.63 (m, 1H); 2.83 (s, 3H); 2.96* (s, 3H); 3.12* (m, 1H); 4.31 (m, 1H); 4.62 (m, 1H); 5.03 (bs, 1H); 7.12-7.34 (m, 10H). ^{13}C -NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 11.9*; 13.8; 14.3; 15.5*; 16.5; 16.8*; 20.5; 20.6*; 27.1*; 34.4; 36.3; 36.5*; 41.9*; 42.5; 49.2; 49.7*; 58.3*; 60.2; 75.1*; 76.2; 126.0; 126.2; 126.3*; 126.7*; 127.3; 127.4*; 127.9*; 128.1; 128.1; 128.3; 128.5*; 141.6*; 142.4; 142.8; 143.2*; 177.3*; 178.5. IR (KBr): 3378 (OH); 1616 (C=O). MS (EI) m/z (Rel. Int.): 354 (M^+ , 4), 246 (23), 161 (8), 133 (13), 105 (19), 91 (38), 79 (5), 77 (6), 58 (100). Anal. Calcd. for $C_{23}H_{31}NO_2$: C, 78.15; H, 8.84; N, 3.96. Found: C, 78.28; H, 8.54; N, 4.03.

(+)-(1'S,2'S,2S,3R)-2-Ethyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylhexanamide (3n)

Amide **3n** (0.60g, 1.64mmol) was prepared according to the general procedure starting from enamide **1c** (0.52g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and EtI (0.63mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 95:4:1:<1 diastereomeric ratio: t_R for the major isomer: 13.11min. (93%). The other isomers eluted at 11.78min. (1%), 15.58min. (4%) and 28.36min. (<1%). Amide **3n** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 82%. $[\alpha]_D^{20} = +70.7$ ($c=1.0$, CH₂Cl₂). ¹H-NMR (δ , ppm) (10:1 rotamer ratio; *indicates minor rotamer resonances): 0.57 (t, 3H, $J=7.0$ Hz); 0.73 (d, 3H, $J=6.7$ Hz); 0.88 (t, 3H, $J=6.1$ Hz); 1.10 (m, 2H); 1.48 (m, 4H); 2.73 (m, 2H); 2.78* (s, 3H); 2.93 (s, 3H); 4.21* (m, 1H), 4.73 (m, 3H); 7.07-7.43 (m, 10H). ¹³C-NMR (δ , ppm) (10:1 rotamer ratio; *indicates minor rotamer resonances): 11.3; 12.5*; 14.7; 15.3; 16.2*; 19.3*; 20.4; 20.6*; 24.3*; 26.8*; 30.1*; 33.6; 37.5; 37.8*; 49.6; 49.9*; 50.2; 58.1*; 59.3; 75.7*; 76.6; 126.0; 126.4; 126.7*; 127.2; 127.9; 128.1; 128.3; 128.7*; 141.0*; 142.3; 142.7; 177.2*; 178.9. IR (CHCl₃): 3392 (OH); 1616 (C=O). MS (EI) m/z (Rel. Int.): 302 ($M^+ - 65$, 2), 256 (3), 148 (6), 115 (7), 97 (6), 91 (4), 79 (5), 77 (6), 69 (10), 58 (100), 55 (13). Anal. Calcd. for C₂₄H₃₃NO₂: C, 78.43; H, 9.05; N, 3.81. Found: C, 78.59; H, 9.19; N, 3.82.

(+)-(1'S,2'S,2S,3R)-2-Allyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylhexanamide (3o)

Amide **3o** (0.53g, 1.40mmol) was prepared according to the general procedure starting from enamide **1c** (0.52g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and allyl iodide (0.73mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 98:2, flow rate 0.85 mL/min) indicated a 96:4:<1:<1 diastereomeric ratio: t_R for the major isomer: 19.41min. (96%). The other isomers eluted at 15.69min. (<1%), 17.44min. (4%) and 22.80min.

(<1%). Amide **3o** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 70%. $[\alpha]_D^{20} = +72.8$ ($c=1.0$, CH_2Cl_2). ^1H -NMR (δ , ppm) (9:1 rotamer ratio; *indicates minor rotamer resonances): 0.63 (t, 3H, $J=7.2$ Hz); 0.91* (t, 3H, $J=6.8$ Hz); 1.03* (d, 3H, $J=5.9$ Hz); 1.12 (d, 3H, $J=6.7$ Hz); 1.43 (m, 4H); 1.81 (m, 1H); 2.16 (m, 1H); 2.81 (m, 2H), 2.93 (s, 3H); 4.28 (m, 1H), 4.53 (m, 2H); 4.82 (m, 2H); 5.01* (m, 2H); 5.47 (m, 1H); 5.80* (m, 1H); 7.13-7.48 (m, 10H). ^{13}C -NMR (δ , ppm) (10:1 rotamer ratio; *indicates minor rotamer resonances): 13.8; 14.7; 15.2*; 20.6; 20.7*; 27.0*; 33.3; 35.5*; 35.9; 36.1*; 36.5; 47.8*; 48.5; 48.8; 49.2*; 58.8; 59.7*; 75.2*; 76.3; 116.5; 117.1*; 126.4*; 126.5; 127.0; 127.4*; 127.6; 128.1*; 128.3; 128.4; 128.5; 128.7*; 135.5; 136.7*; 140.8*; 142.3; 142.8; 143.2*; 175.9*; 177.4. IR (CHCl_3): 3384 (OH); 1616 (C=O). MS (EI) m/z (Rel. Int.): 379 (M^+ , 7), 272 (20), 215 (5), 148 (6), 145 (7), 133 (23), 117 (8), 105 (9), 91 (50), 79 (7), 58 (100). Anal. Calcd. for $\text{C}_{25}\text{H}_{33}\text{NO}_2$: C, 79.11; H, 8.76; N, 3.69. Found: C, 79.34; H, 8.91; N, 3.65.

(-)-(1'S,2'S,2S,3R)-2-Benzyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-phenylhexanamide (3p)

Amide **3p** (0.63g, 1.46mmol) was prepared according to the general procedure starting from enamide **1c** (0.52g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and benzyl bromide (0.94mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 0.65 mL/min) indicated a >99:<1:<1:<1 diastereomeric ratio: t_R for the major isomer: 19.54min. (>99%). The other isomers eluted at 15.30min. (<1%), 18.58min. (<1%) and 24.91min. (<1%). Amide **3p** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 73%. $[\alpha]_D^{20} = -14.4$ ($c=1.0$, CH_2Cl_2). M.p.: 143-145°C (hexanes/AcOEt 1:1). ^1H -NMR (δ , ppm) (10:1 rotamer ratio; *indicates minor rotamer resonances): 0.61 (d, 3H, $J=6.8$ Hz); 0.79 (t, 3H, $J=7.2$ Hz); 1.08 (m, 2H); 1.56 (m, 2H); 2.23 (m, 1H); 2.50 (s, 3H); 2.61* (s, 3H); 2.73 (m, 1H), 3.02 (m, 1H); 3.12 (m, 1H); 3.61 (bs, 1H); 4.12* (m, 1H); 4.48 (m, 1H); 4.62 (m, 1H); 6.83-7.51 (m, 15H). ^{13}C -NMR (δ , ppm) (10:1 rotamer ratio; *indicates minor rotamer resonances): 13.7; 14.0; 14.9*; 20.5; 20.7*; 27.1*; 30.8; 36.3; 38.5; 49.0; 49.7*; 50.9*;

51.4; 56.2; 58.2*; 74.8*; 76.3; 126.0; 126.2*; 126.4; 126.5*; 126.6; 126.9*; 127.0*; 127.7; 128.0; 128.2; 128.3*; 128.4; 128.5; 128.7; 129.0*; 139.7; 140.3*; 140.7*; 141.9; 143.0; 175.6*; 177.3. IR (KBr): 3370 (OH); 1613 (C=O). MS (EI) m/z (Rel. Int.): 322 (M^+ -107, 4), 159 (4), 133 (11), 117 (6), 91 (23), 71 (5), 58 (100). Anal. Calcd. for $C_{29}H_{35}NO_2$: C, 81.08; H, 8.21; N, 3.26. Found: C, 81.25; H, 8.37; N, 3.31.

(+)-(1'S,2'S,2S,3S)-2-Allyl-N-(2'-Hydroxy-1'-methyl-2'-phenylethyl)-N-methyl-3-propylheptanamide (3q)

Amide **3q** (0.55g, 1.54mmol) was prepared according to the general procedure starting from enamide **1c** (0.52g, 2.00mmol), LiCl (0.42g, 10.00mmol), n BuLi (4.43mL of a 1.0M solution in hexanes) and allyl bromide (0.73mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 0.65 mL/min) indicated a 96:3:1:<1 diastereomeric ratio: t_R for the major isomer: 10.08min. (96%). The other isomers eluted at 6.61min. (3%), 8.22min. (<1%) and 11.33min. (1%). Amide **3q** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 77%. $[\alpha]_D^{20} = +71.8$ ($c=1.0$, CH_2Cl_2). 1H -NMR (δ , ppm) (4:1 rotamer ratio; *indicates minor rotamer resonances): 0.75 (m, 6H); 0.82* (d, 3H, $J = 6.5$ Hz); 1.07 (d, 3H, $J = 6.3$ Hz); 1.21-1.49 (m, 10H); 1.51 (m, 1H); 2.51 (m, 1H); 2.36 (m, 1H); 2.58 (m, 1H); 2.74 (s, 3H); 2.86* (s, 3H); 4.02* (m, 1H); 4.17 (m, 1H); 4.56 (m, 1H); 4.63 (bs, 1H); 5.02 (m, 1H); 5.11* (m, 1H); 5.54 (m, 1H); 5.73* (m, 1H), 7.37 (m, 5H). ^{13}C -NMR (δ , ppm) (4:1 rotamer ratio; *indicates minor rotamer resonances): 13.9*; 14.2; 14.4; 15.3*; 20.0; 20.4*; 22.7*; 22.9; 26.9*; 28.3; 28.8; 29.1*; 30.7; 31.5*; 31.9; 33.1*; 33.3; 33.8; 39.3; 39.4*; 44.5*; 44.8; 57.7; 59.2*; 75.0*; 75.9; 115.5*; 115.8; 126.1*; 126.7; 127.1*; 127.6; 128.0; 128.3*; 136.3; 137.6*; 142.3; 175.6*; 177.1. IR ($CHCl_3$): 3381 (OH); 1619 (C=O). MS (EI) m/z (Rel. Int.): 252 (M^+ -107, 6), 196 (5), 140 (3), 111 (9), 97 (11), 83 (10), 69 (12), 58 (100). Anal. Calcd. for $C_{23}H_{37}NO_2$: C, 76.83; H, 10.37; N, 3.90. Found: C, 76.92; H, 10.41; N, 4.02.

(+)-(1'S,2'S,2S,3S)-N-(2'-Hydroxy-1'-methyl-2'-phenylethyl)-2,4,4,N-tetramethyl-3-phenylpentanamide (3r)

Amide **3r** (0.51g, 1.40mmol) was prepared according to the general procedure starting from enamide **1d** (0.55g, 2.00mmol), LiCl (0.42g, 10.00mmol), PhLi (4.43mL of a 1.0M solution in dibutylether) and MeI (0.50mL, 8.00mol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 98:2, flow rate 0.85 mL/min) indicated a 96:3:2:<1 diastereomeric ratio: t_R for the major isomer: 30.81min. (93%). The other isomers eluted at 28.97min. (3%), 34.86min. (2%) and 41.51min. (<1%). Amide **3r** was isolated in pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 70%. M.p.: 103-105°C (hexanes/AcOEt 1:1). $[\alpha]_D^{20} = +124.8$ ($c=0.5$, CH₂Cl₂). ¹H-NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 0.56 (d, 3H, $J=6.7$ Hz); 0.82 (s, 9H); 1.10* (d, 3H, $J=6.8$ Hz); 1.28 (d, 3H, $J=7.1$ Hz); 2.88 (s, 3H); 2.91* (s, 3H); 2.98 (m, 1H); 3.18 (m, 1H), 4.07 (m, 1H); 4.69* (m, 1H); 4.60* (m, 1H); 4.73 (m, 1H); 5.44 (bs, 1H); 7.11-1.37 (m, 10H). ¹³C-NMR (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 14.0; 15.0*; 19.0; 19.3*; 27.3*; 29.0; 34.3*; 34.4; 34.9; 35.9*; 56.8; 58.0*; 58.5; 62.6; 75.3*; 76.5; 125.8; 126.9*; 127.1; 127.2; 127.3; 128.0; 128.2*; 128.6; 141.3; 141.6*; 142.1*; 142.5; 178.3*; 179.6. IR (KBr): 3378 (OH); 1620 (C=O). MS (EI) m/z (Rel. Int.): 260 (M⁺, 107, 7), 204 (5), 147 (7), 105 (25), 91 (7), 58 (100). Anal. Calcd. for C₂₄H₃₃NO₂: C, 78.43; H, 9.05; N, 3.81. Found: C, 78.27; H, 9.13; N, 3.76.

(+)-(1'S,2'S,2S,3S)-3-tert-Butyl-N-(2'-hydroxy-1'-methyl-2'-phenylethyl)-2,N-dimethylheptanamide (3s)

Amide **3s** (0.24g, 0.71mmol) was prepared according to the general procedure starting from enamide **1d** (0.55g, 2.00mmol), LiCl (0.42g, 10.00mmol), ⁿBuLi (4.43mL of a 1.0M solution in hexanes) and MeI (0.50mL, 8.00mmol). HPLC analysis of the crude reaction mixture (Chiracel OD column, hexanes/*iso*-propanol 95:5, flow rate 1.00 mL/min) indicated a 97:2:<1:<1 diastereomeric ratio: t_R for the major isomer: 10.11min. (93%). The other isomers eluted at 12.01min. (<1%), 13.81min. (<1%) and 15.42min. (2%). Amide **3s** was isolated in

pure form as a yellowish oil after flash column chromatography (hexanes/AcOEt 1:1). Yield: 35%. $[\alpha]_D^{20} = +91.7$ ($c=1.0$, CH_2Cl_2). $^1\text{H-NMR}$ (δ , ppm) (5:1 rotamer ratio; *indicates minor rotamer resonances): 0.84 (m, 15H); 0.97* (d, 3H, $J=6.6$ Hz); 1.08 (d, 3H, $J=6.7$ Hz); 1.25 (m, 4H), 1.72 (m, 1H); 2.07 (m, 1H); 2.22 (m, 1H); 2.70 (s, 3H); 2.82* (s, 3H); 2.86 (m, 1H); 4.02* (m, 1H); 4.43 (m, 1H); 4.57 (m, 1H); 7.31 (m, 5H). $^{13}\text{C-NMR}$ (δ , ppm) (3:1 rotamer ratio; *indicates minor rotamer resonances): 13.8*; 14.0; 14.3; 15.3*; 23.1; 27.1*; 27.4; 29.6; 30.4*; 30.9; 31.0; 31.6*; 32.9*; 33.4; 33.6*; 33.9*; 34.2; 35.5; 43.7; 44.4*; 58.2; 58.8*; 75.4*; 76.5; 126.3; 126.4*; 126.8*; 127.4; 128.1*; 128.2; 141.4*; 142.5; 175.9; 176.0*. IR (CHCl_3): 3378 (OH); 1619 (C=O). MS (EI) m/z (Rel. Int.): 332 (M^+-15 , 1), 226 (9), 170 (7), 100 (5), 85 (10), 71 (7), 58 (100). Anal. Calcd. for $\text{C}_{22}\text{H}_{37}\text{NO}_2$: C, 76.03; H, 10.73; N, 4.03. Found: C, 76.15; H, 10.96; N, 4.14.

3.- Removal of the chiral auxiliary. Synthesis of alcohols 6a-s

General procedure:

A solution of the starting amide **3a-s** (1.0 mmol) in AcOH (10.0 mL) was refluxed for 12h after which the solvent was removed under reduced pressure yielding the crude esters **7a-s** which were used in the next step without further purification. Next, LAH (3.0 mmol) was added at once over a cooled (0°C) solution of the ester **7a-s** (1.0 mmol) in dry THF (15 mL). The mixture was refluxed for 3h, quenched with 1M HCl (15mL) and extracted with CH₂Cl₂ (3 x 15mL). The organic fractions were collected, dried over Na₂SO₄, filtered and the solvent removed *in vacuo* affording the wanted alcohols **6a-s** after flash column chromatography purification. The chiral auxiliary could be recovered from the aqueous layer after basifying (pH=10) with a 4M NaOH solution and extracting with CH₂Cl₂ (3 x 15mL), filtering and removing the solvent. (*S,S*)-(+)-pseudoephedrine was isolated in c.a. 75% yield after crystallization (hexanes/AcOEt) and with no loss of optical purity as the measurement of its $[\alpha]_D^{20}$ value indicated.

(-)-(2*S*,3*R*)-2-Methyl-3-phenylbutan-1-ol (**6a**).

Alcohol **6a** (203mg, 1.21mmol) was prepared according to the general procedure starting from amide **3a** (487mg, 1.48mmol), AcOH (30 mL) and LAH (168mg 4.44mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 82%. $[\alpha]_D^{20} = -19.5$ ($c=0.4$, CHCl₃). ¹H-NMR (δ , ppm): 0.64 (d, 3H, $J=6.8$ Hz); 1.23 (d, 3H, $J=6.7$ Hz); 1.74 (m, 1H); 2.68 (m, 1H); 3.46 (m, 1H); 3.53 (m, 1H); 7.24 (m, 5H). ¹³C-NMR (δ , ppm): 14.4; 19.1; 37.6; 41.6; 65.9; 125.9; 126.0; 128.3; 146.4. IR (CHCl₃): 3369 (OH). MS (EI) m/z (Rel. Int.): 164 (M^+ , 1), 146 (8), 105 (15), 91 (19), 77 (4), 58 (100). Anal. Calcd. for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.32; H, 9.73.

(-)-(2*S*,3*R*)-2-Ethyl-3-phenylbutan-1-ol (**6b**).

Alcohol **6b** (63mg, 0.35mmol) was prepared according to the general procedure starting from amide **3b** (166mg, 0.47mmol), AcOH (10 mL) and LAH (40mg 1.04mmol) and isolated as a colourless oil after flash column chromatography purification

(hexanes/AcOEt 9:1). Yield: 75%. $[\alpha]_D^{20} = -9.9$ ($c=0.3$, CHCl_3). $^1\text{H-NMR}$ (δ , ppm): 0.76 (t, 3H, $J=7.3$ Hz); 1.09 (d, 3H, $J=6.9$ Hz); 1.53 (m, 2H); 2.81 (m, 2H); 3.37 (dd, 1H, $J=10.2, 2.2$ Hz); 3.49 (dd, 1H, $J=10.2, 2.7$ Hz); 3.71 (bs, 1H); 7.13 (m, 2H); 7.28 (m, 3H). $^{13}\text{C-NMR}$ (δ , ppm): 11.7; 18.5; 20.4; 40.0; 48.3; 62.8; 126.0; 127.4; 128.4; 146.4. IR (CHCl_3): 3354 (OH). MS (EI) m/z (Rel. Int.): 178 (M^+ , 3), 160 (6), 131 (9), 105 (100), 91 (24), 79 (7), 77 (8). Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.85; H, 10.18. Found: C, 80.65; H, 9.97.

(-)-(2*S*,3*R*)-2-Allyl-3-phenylbutan-1-ol (6c).

Alcohol **6c** (75mg, 0.39mmol) was prepared according to the general procedure starting from amide **3c** (189mg, 0.54mmol), AcOH (10mL) and LAH (62mg 1.62mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 73%. $[\alpha]_D^{20} = -21.8$ ($c=0.1$, CHCl_3). $^1\text{H-NMR}$ (δ , ppm): 1.12 (d, 3H, $J=6.9$ Hz); 0.84 (d, 3H, $J=6.9$ Hz); 2.03 (m, 2H); 2.69 (m, 1H); 2.83 (m, 1H); 3.58 (dd, 1H, $J=9.8, 2.5$ Hz); 3.81 (dd, 1H, $J=9.8, 1.3$ Hz); 4.91 (m, 2H); 5.83 (m, 1H); 7.16 (m, 2H); 7.33 (m, 3H). $^{13}\text{C-NMR}$ (δ , ppm): 12.5; 29.7; 35.1; 44.3; 66.6; 113.2; 125.5; 125.8; 128.1; 136.3; 141.8. IR (CHCl_3): 3338 (OH). MS (EI) m/z (Rel. Int.): 190 (M^+ , 1), 157 (6), 146 (7), 133 (31), 117 (7), 91 (100), 77 (4), 65 (4). Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 81.89; H, 9.67.

(-)-(2*S*,3*R*)-2-Benzyl-3-phenylbutan-1-ol (6d).

Alcohol **6d** (44mg, 0.18mmol) was prepared according to the general procedure starting from amide **3d** (93mg, 0.23mmol), AcOH (5mL) and LAH (26mg 0.69mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 80%. $[\alpha]_D^{20} = -17.2$ ($c=0.2$, CHCl_3). $^1\text{H-NMR}$ (δ , ppm): 1.07 (d, 3H, $J=6.8$ Hz); 1.71 (m, 2H); 2.58 (m, 1H); 2.81 (m, 1H); 3.53 (dd, 1H, $J=9.9, 2.1$ Hz); 3.67 (dd, 1H, $J=9.9, 1.2$ Hz); 7.12-7.43 (m, 10H). $^{13}\text{C-NMR}$ (δ , ppm): 14.1; 22.6; 31.6; 49.2; 62.3; 125.9; 126.2; 127.7; 127.8; 128.4; 129.1; 141.1; 142.9. IR (CHCl_3): 3387 (OH). MS (EI) m/z (Rel. Int.): 240 (M^+ , 2), 146 (6), 91 (100), 89 (12), 87 (10), 65 (22). Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{O}$: C, 84.96; H, 8.39. Found: C, 85.08; H, 8.41.

(-)-(2*S*,3*S*)-2,3-dimethylheptan-1-ol (6e).

Alcohol **6e** (46mg, 0.32mmol) was prepared according to the general procedure starting from amide **3e** (123mg, 0.40mmol), AcOH (10mL) and LAH (46mg 1.21mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 86%. $[\alpha]_D^{20} = -19.7$ ($c=0.1$, CHCl₃). ¹H-NMR (δ , ppm): 0.75 (t, 3H, $J=7.5$ Hz); 1.98 (m, 6H); 4.12-1.49 (m, 6H); 1.67 (m, 2H); 3.54 (m, 2H). ¹³C-NMR (δ , ppm): 13.2; 14.5; 14.8; 22.5; 29.8; 33.6; 39.5; 41.2; 68.1. IR (CHCl₃): 3410 (OH). MS (EI) m/z (Rel. Int.): 144 (M^+ , 1), 126 (5), 85 (7), 83 (100), 69 (43), 57 (22). Anal. Calcd. for C₉H₂₀O: C, 74.93; H, 13.97. Found: C, 75.10; H, 14.08.

(-)-(2*S*,3*S*)-2-Ethyl-3-methylheptan-1-ol (6f).

Alcohol **6f** (68mg, 0.43mmol) was prepared according to the general procedure starting from amide **3f** (141mg, 0.44mmol), AcOH (10mL) and LAH (50mg 1.33mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 98%. $[\alpha]_D^{20} = -6.5$ ($c=0.1$, CHCl₃). ¹H-NMR (δ , ppm): 0.78 (m, 9H); 1.35 (m, 6H); 1.47 (m, 2H); 1.60 (m, 2H); 3.61 (m, 2H). ¹³C-NMR (δ , ppm): 14.5; 15.2; 19.6; 21.2; 22.7; 23.0; 29.4; 32.0; 47.1; 63.7. IR (CHCl₃): 3343 (OH). MS (EI) m/z (Rel. Int.): 140 (M^+-18 , 52), 111 (12), 97 (31), 84 (90), 83 (100), 69 (93), 67 (33). Anal. Calcd. for C₁₀H₂₂O: C, 75.88; H, 14.01. Found: C, 76.11; H, 13.89.

(-)-(2*S*,3*S*)-2-Allyl-3-methylheptan-1-ol (6g).

Alcohol **6g** (63mg, 0.37mmol) was prepared according to the general procedure starting from amide **3g** (153mg, 0.46mmol), AcOH (10mL) and LAH (53mg 1.38mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 80%. $[\alpha]_D^{20} = -8.1$ ($c=0.1$, CHCl₃). ¹H-NMR (δ , ppm): 0.81 (m, 6H); 1.11-1.42 (m, 6H); 1.95 (m, 1H); 2.15 (m, 1H); 3.62 (m, 2H); 5.01 (m, 2H); 5.88 (m, 1H). ¹³C-NMR (δ , ppm): 14.1; 16.1; 22.9; 29.7; 32.2; 32.8; 33.2; 45.2; 64.3; 115.7; 138.2. IR (CHCl₃): 3374 (OH). MS (EI) m/z (Rel. Int.): 155 (M^+-15 , 5), 152 (M^+-18 , 30), 109 (56), 95 (100), 81 (89), 79 (24), 69 (90), 67 (88). Anal. Calcd. for C₁₁H₂₂O: C, 77.58; H, 13.02. Found: C, 77.67; H, 12.88.

(-)-(2*S*,3*S*)-2-Benzyl-3-methylheptan-1-ol (6h).

Alcohol **6h** (88mg, 0.40mmol) was prepared according to the general procedure starting from amide **3h** (156mg, 0.41mmol), AcOH (10mL) and LAH (50mg 1.23mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 98%. $[\alpha]_D^{20} = -9.7$ ($c=0.1$, CHCl₃). ¹H-NMR (δ, ppm): 0.83 (m, 6H); 1.08-1.47 (m, 4H); 1.54 (m, 1H); 1.82 (m, 2H); 2.49 (m, 1H); 2.67 (m, 2H); 3.55 (m, 2H); 7.12-7.33 (m, 5H). ¹³C-NMR (δ, ppm): 14.1; 16.1; 22.9; 29.8; 32.8; 33.5; 35.2; 47.5; 62.8; 125.8; 128.3; 128.4; 141.5. IR (CHCl₃): 3335 (OH). MS (EI) m/z (Rel. Int.): 202 ($M^+ - 18$, 34), 145 (100), 131 (62), 117 (74), 104 (65), 91 (90), 69 (98). Anal. Calcd. for C₁₅H₂₄O: C, 81.76; H, 10.98. Found: C, 81.97; H, 11.15.

(-)-(2*S*,3*R*)-2-Methyl-3-phenylpentan-1-ol (6i).

Alcohol **6i** (90mg, 0.50mmol) was prepared according to the general procedure starting from amide **3i** (203mg, 0.59mmol), AcOH (12mL) and LAH (70mg 1.80mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 87%. $[\alpha]_D^{20} = -7.5$ ($c=0.1$, CHCl₃). ¹H-NMR (δ, ppm): 0.81 (m, 6H); 1.63 (m, 1H); 1.84 (m, 1H); 2.27 (m, 1H); 2.53 (m, 1H); 3.48 (m, 2H); 7.10-7.41 (m, 5H). ¹³C-NMR (δ, ppm): 12.4; 13.7; 25.7; 40.2; 48.9; 66.3; 125.9; 127.9; 128.8; 142.7. IR (CHCl₃): 3378 (OH). MS (EI) m/z (Rel. Int.): 160 ($M^+ - 18$, 56), 145 (49), 131 (100), 128 (25), 119 (25), 117 (48), 115 (50), 91 (86), 77 (28), 65 (20). Anal. Calcd. for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.78; H, 10.25.

(-)-(2*S*,3*R*)-2-Ethyl-3-phenylpentan-1-ol (6j).

Alcohol **6j** (86mg, 0.45mmol) was prepared according to the general procedure starting from amide **3j** (236mg, 0.67mmol), AcOH (15mL) and LAH (76mg 2.01mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 67%. $[\alpha]_D^{20} = -21.2$ ($c=0.1$, CHCl₃). ¹H-NMR (δ, ppm): 0.68 (t, 3H, $J=7.1$ Hz); 0.82 (t, 3H, $J=6.9$ Hz); 1.26 (m, 2H); 1.53 (m, 2H); 1.81 (m, 1H); 2.60 (m, 1H); 3.67 (dd, 1H, $J=14.4, 3.1$ Hz); 3.75 (dd, 1H, $J=14.4, 2.6$ Hz); 7.12-7.40 (m, 5H). ¹³C-NMR (δ, ppm): 11.8; 12.4; 21.2; 25.6; 29.5; 47.2; 62.3; 125.9; 128.1;

128.3; 144.8. IR (CHCl₃): 3378 (OH). MS (EI) *m/z* (Rel. Int.): 174 (M⁺-18, 50), 145 (100), 131 (42), 128 (39), 119 (34), 117 (71), 115 (48), 91 (82), 77 (31), 65 (19). Anal. Calcd. for C₁₃H₂₀O: C, 81.20; H, 10.48. Found: C, 81.36; H, 10.45.

(-)-(2*S*,3*R*)-2-Allyl-3-phenylpentan-1-ol (6k).

Alcohol **6k** (129mg, 0.64mmol) was prepared according to the general procedure starting from amide **3k** (268mg, 0.73mmol), AcOH (15mL) and LAH (84mg 2.21mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 87%. $[\alpha]_D^{20} = -19.7$ (*c*=0.1, CHCl₃). ¹H-NMR (δ, ppm): 0.65 (t, 3H, *J*=7.2 Hz); 1.61 (m, 1H); 1.89 (m, 2H); 2.01 (m, 1H); 2.33 (m, 1H); 2.64 (m, 1H); 3.62 (dd, 1H, *J*=9.6, 2.9 Hz); 3.71 (dd, 1H, *J*=9.6, 2.8 Hz); 4.97 (m, 2H); 5.73 (m, 1H); 7.15-7.38 (m, 5H). ¹³C-NMR (δ, ppm): 12.3; 25.4; 33.4; 45.3; 47.7; 62.9; 116.2; 126.0; 128.1; 128.6; 137.4; 143.2. IR (CHCl₃): 3364 (OH). MS (EI) *m/z* (Rel. Int.): 186 (M⁺-18, 36), 169 (64), 157 (88), 145 (36), 143 (36), 129 (97), 115 (80), 91 (100), 77 (33), 65 (17). Anal. Calcd. for C₁₄H₂₀O: C, 82.30; H, 9.87. Found: C, 82.24; H, 10.11.

(-)-(2*S*,3*R*)-2-Benzyl-3-phenylpentan-1-ol (6l).

Alcohol **6l** (75mg, 0.30mmol) was prepared according to the general procedure starting from amide **3l** (155mg, 0.37mmol), AcOH (8mL) and LAH (84mg 1.12mmol) and isolated as a colourless oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 80%. $[\alpha]_D^{20} = -19.7$ (*c*=0.1, CHCl₃). ¹H-NMR (δ, ppm): 0.82 (t, 3H, *J*=7.1 Hz); 1.68 (m, 1H); 1.86 (m, 1H); 2.21 (m, 1H); 2.60 (m, 2H); 2.77 (m, 1H); 3.47 (dd, 1H, *J*=9.8, 3.2 Hz); 3.71 (dd, 1H, *J*=9.9, 3.2 Hz); 7.06-7.41 (m, 10H). ¹³C-NMR (δ, ppm): 13.4; 25.3; 29.7; 34.7; 47.8; 61.7; 125.8; 126.1; 128.2; 128.3; 128.7; 129.0; 141.2; 143.2. IR (CHCl₃): 3370 (OH). MS (EI) *m/z* (Rel. Int.): 254 (M⁺-18, 39), 207 (57), 145 (48), 129 (68), 117 (49), 115 (44), 91 (100), 77 (20), 65 (19). Anal. Calcd. for C₁₈H₂₂O: C, 84.99; H, 8.72. Found: C, 84.86; H, 8.95.

(-)-(2*S*,3*R*)-2-Methyl-3-phenylhexan-1-ol (6m).

Alcohol **6m** (109mg, 0.57mmol) was prepared according to the general procedure starting from amide **3m** (205mg, 0.58mmol), AcOH (15mL) and LAH (73mg 1.75mmol) and isolated as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 98%. $[\alpha]_D^{20} = -17.1$ ($c=0.9$, CHCl₃). ¹H-NMR (δ , ppm): 0.75 (t, 3H, $J=7.1$ Hz); 0.91 (d, 3H, $J=6.7$ Hz); 1.12 (m, 2H); 1.63 (m, 2H); 1.81 (m, 1H); 2.73 (m, 1H); 3.51 (m, 2H); 7.16 (m, 3H); 7.27 (m, 2H). ¹³C-NMR (δ , ppm): 13.8; 14.1; 20.9; 35.2; 40.5; 46.8; 66.2; 125.9; 127.9; 128.7; 142.9. IR (CHCl₃): 3350 (OH). MS (EI) m/z (Rel. Int.): 192 (M^+ , 4), 133 (29), 117 (8), 91 (100), 77 (5). Anal. Calcd. for C₁₃H₂₀O: C, 81.20; H, 10.48. Found: C, 81.29; H, 10.23.

(-)-(2*S*,3*R*)-2-Ethyl-3-phenylhexan-1-ol (6n).

Alcohol **6n** (120mg, 0.58mmol) was prepared according to the general procedure starting from amide **3n** (307mg, 0.84mmol), AcOH (17mL) and LAH (95mg 2.49mmol) and isolated as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 70%. $[\alpha]_D^{20} = -4.3$ ($c=0.9$, CHCl₃). ¹H-NMR (δ , ppm): 0.83 (t, 6H, $J=7.3$ Hz); 1.09 (m, 4H); 1.57 (m, 2H); 2.16 (m, 1H); 2.77 (m, 1H); 3.64 (dd, 1H, $J=12.2, 3.1$ Hz); 3.76 (dd, 1H, $J=12.2, 3.0$ Hz); 7.12-7.43 (m, 5H). ¹³C-NMR (δ , ppm): 11.8; 14.1; 20.6; 20.9; 34.7; 45.8; 47.4; 62.1; 128.0; 128.4; 128.5; 143.8. IR (CHCl₃): 3367 (OH). MS (EI) m/z (Rel. Int.): 188 (M^+ -18, 52), 158 (24), 145 (100), 131 (52), 127 (38), 116 (82), 114 (52), 91 (90), 77 (33), 65 (26). Anal. Calcd. for C₁₄H₂₂O: C, 81.50; H, 10.75. Found: C, 81.68; H, 10.61.

(-)-(2*S*,3*R*)-2-Allyl-3-phenylhexan-1-ol (6o).

Alcohol **6o** (127mg, 0.58mmol) was prepared according to the general procedure starting from amide **3o** (243mg, 0.64mmol), AcOH (15mL) and LAH (82mg 1.92mmol) and isolated as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 91%. $[\alpha]_D^{20} = -17.8$ ($c=0.2$, CHCl₃). ¹H-NMR (δ , ppm): 0.83 (t, 3H, $J=7.1$ Hz); 1.18 (m, 2H); 1.54 (m, 2H); 2.08 (m, 2H); 2.69 (m, 1H); 2.86 (m, 1H); 3.51 (m, 1H); 3.51 (dd, 1H, $J=10.0, 1.1$ Hz); 3.62

(dd, 1H, J = 10.0, 1.5 Hz); 4.96 (m, 2H); 5.72 (m, 1H); 7.12 (m, 3H); 7.25 (m, 2H). ^{13}C -NMR (δ , ppm): 14.1; 20.8; 33.5; 34.9; 37.9; 45.6; 62.9; 116.5; 126.0; 127.9; 128.5; 137.7; 143.5. IR (CHCl_3): 3405 (OH). MS (EI) m/z (Rel. Int.): 200 (M^+ -18, 34), 169 (83), 157 (84), 143 (52), 129 (96), 115 (77), 91 (100), 77 (27). Anal. Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}$: C, 82.52; H, 10.16. Found: C, 82.47; H, 10.33.

(-)-(2*S*,3*R*)-2-Benzyl-3-phenylhexan-1-ol (6p).

Alcohol **6p** (64mg, 0.24mmol) was prepared according to the general procedure starting from amide **3p** (150mg, 0.35mmol), AcOH (10mL) and LAH (40mg 1.05mmol) and isolated as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 68%. $[\alpha]_{\text{D}}^{20}$ = -5.9 (c =0.1, CHCl_3). ^1H -NMR (δ , ppm): 0.73 (t, 3H, J = 7.0 Hz); 1.15 (m, 2H); 1.46 (m, 1H); 1.57 (m, 1H); 2.01 (m, 1H); 2.43 (m, 1H); 2.67 (m, 1H); 3.02 (m, 1H); 3.47 (dd, 1H, J = 9.7, 2.3 Hz); 3.55 (dd, 1H, J = 9.7, 2.3 Hz); 7.11-7.54 (m, 10H). ^{13}C -NMR (δ , ppm): 13.8; 20.6; 29.8; 35.0; 37.3; 44.2; 63.5; 129.8; 126.2; 126.4; 127.3; 128.0; 128.5; 143.2; 144.1. IR (CHCl_3): 3695 (OH). MS (EI) m/z (Rel. Int.): 268 (M^+ , 1), 250 (10), 133 (17), 117 (10), 91 (100), 77 (10). Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{O}$: C, 85.03; H, 9.01. Found: C, 84.90; H, 8.88.

(-)-(2*S*,3*S*)-2-Allyl-3-propylheptan-1-ol (6q).

Alcohol **6q** (51mg, 0.26mmol) was prepared according to the general procedure starting from amide **3q** (136mg, 0.38mmol), AcOH (8mL) and LAH (43mg 1.14mmol) and isolated as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 68%. $[\alpha]_{\text{D}}^{20}$ = -3.7 (c =0.1, CHCl_3). ^1H -NMR (δ , ppm): 0.78 (t, 6H, J = 7.1 Hz); 1.03-1.31 (m, 10H); 1.47 (m, 1H); 1.61 (m, 1H); 2.07 (m, 2H); 3.55 (m, 2H); 4.98 (m, 2H); 5.77 (m, 1H). ^{13}C -NMR (δ , ppm): 14.1; 14.4; 20.8; 23.0; 23.1; 30.0; 30.3; 33.2; 37.9; 42.6; 64.1; 115.7; 138.4. IR (CHCl_3): 3399 (OH). MS (EI) m/z (Rel. Int.): 180 (M^+ -18, 1), 156 (5), 137 (13), 123 (16), 113 (18), 99 (22), 95 (32), 83 (67), 55 (100). Anal. Calcd. for $\text{C}_{13}\text{H}_{26}\text{O}$: C, 78.72; H, 13.21. Found: C, 78.60; H, 13.33.

(+)-(2*S*,3*S*)-2,4,4-trimethyl-3-phenylpentan-1-ol (6r).

Alcohol **6r** (80mg, 0.39mmol) was prepared according to the general procedure starting from amide **3r** (189mg, 0.51mmol), AcOH (10mL) and LAH (59mg, 1.54mmol) and isolated as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 76%. $[\alpha]_D^{20} = +13.1$ ($c=1.0$, CHCl₃). ¹H-NMR (δ , ppm): 0.78 (d, 3H, $J=6.8$ Hz); 1.06 (s, 9H); 2.21 (m, 1H); 2.61 (d, 1H, $J=0.8$ Hz); 3.33 (d, 2H, $J=6.7$ Hz); 7.23 (m, 5H). ¹³C-NMR (δ , ppm): 15.0; 29.7; 34.5; 36.1; 56.4; 67.9; 125.9; 127.5; 128.3; 141.2. IR (CHCl₃): 3343 (OH). MS (EI) m/z (Rel. Int.): 173 (M^+ -33, 1), 150 (16), 132 (57), 117 (42), 105 (21), 91 (100), 57 (49). Anal. Calcd. for C₁₄H₂₂O: C, 81.50; H, 10.75. Found: C, 81.68; H, 10.68.

(+)-(2*S*,3*S*)-3-*tert*-Butyl-2-methylheptan-1-ol (6s).

Alcohol **6s** (96mg, 0.52mmol) was prepared according to the general procedure starting from amide **3s** (220mg, 0.63mmol), AcOH (15mL) and LAH (72mg, 1.90mmol) and isolated as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 9:1). Yield: 82%. $[\alpha]_D^{20} = +51.3$ ($c=1.0$, CHCl₃). ¹H-NMR (δ , ppm): 0.81 (bs, 12H); 1.07 (d, 2H, $J=6.7$ Hz); 1.13-1.43 (m, 6H); 1.98 (m, 1H); 2.47 (m, 1H); 3.57 (m, 2H). ¹³C-NMR (δ , ppm): 14.1; 23.2; 27.5; 29.7; 31.2; 33.5; 34.8; 35.6; 43.8; 63.3. IR (CHCl₃): 3370 (OH). MS (EI) m/z (Rel. Int.): 168 (M^+ -18, 1), 117 (25), 88 (15), 77 (36), 55 (100), 53 (27). Anal. Calcd. for C₁₂H₂₆O: C, 77.35; H, 14.06. Found: C, 77.43; H, 14.11.

4.- Stereochemical assignment

4.1.- Acid hydrolysis of amide **2a**. Synthesis of (-)-(*R*)-3-Phenylbutanoic acid.

4M H₂SO₄ (10 mL) was slowly added over a cooled (0°C) solution of amide **2a** (0.17g, 0.96mmol) in 1,4-dioxane (10 mL). The reaction was refluxed for 6h after which it was cooled down to r.t. Water (20 mL) was added and the mixture was carefully basified to pH=12 and washed with EtOAc (3x20mL). The aqueous layer was carefully driven to pH=3 and extracted with CH₂Cl₂ (3x20mL). The collected organic acidic fractions were dried over Na₂SO₄, filtered and the solvent was removed *in vacuo* yielding pure acid (0.35g, 1.12mmol) as a yellowish oil. Yield: 91%. $[\alpha]_D^{20} = -42.3$ ($c=0.70$, C₆H₆) (Lit.¹ $[\alpha]_D^{20} = -45.8$, $c=0.77$, C₆H₆). ¹H-NMR (δ , ppm): 1.36 (d, 3H, $J=7.2$ Hz); 2.68 (m, 2H); 3.35 (m, 1H); 7.33 (m, 5H); 11.2-11.9 (bs, 1H). ¹³C-NMR (δ , ppm): 21.8; 36.0; 42.5; 126.4; 126.6; 128.5; 145.3; 179.1. IR (CHCl₃): 3028 (OH); 1707 (C=O). MS (EI) m/z (Rel. Int.): 164 (M⁺, 17), 118 (16), 105 (100), 85 (23), 79 (16), 77 (17), 57 (15).

4.2.- Acid hydrolysis of amide **3a**. Synthesis of (+)-(*2S,3R*)-2-methyl-3-phenylbutanoic acid (**4a**).

4M H₂SO₄ (10 mL) was slowly added over a cooled (0°C) solution of amide **3a** (0.31g, 0.95mmol) in 1,4-dioxane (10 mL). The reaction was refluxed for 12h after which it was cooled down to r.t. Water (20 mL) was added and the mixture was carefully basified to pH=12 and washed with EtOAc (3x20mL). The aqueous layer was carefully driven to pH=3 and extracted with CH₂Cl₂ (3x20mL). The collected organic acidic fractions were dried over Na₂SO₄, filtered and the solvent was removed *in vacuo* yielding pure acid **4a** (166mg, 0.93mmol) as a yellowish oil. Yield: 98%. $[\alpha]_D^{20} = +11.3$ ($c=0.30$, CHCl₃). ¹H-NMR (δ , ppm): 1.02 (d, 3H, $J=7.2$ Hz); 1.38 (d, 3H, $J=7.2$ Hz); 2.61 (m, 1H); 2.98 (m, 1H); 7.33 (m, 5H); 9.2-10.4 (bs, 1H). ¹³C-NMR (δ , ppm): 16.2; 20.8; 43.1; 46.8; 126.6; 127.6; 128.5; 143.9; 183.1. IR (CHCl₃): 1964 (OH); 1889 (C=O). MS (EI) m/z (Rel. Int.): 178 (M⁺, 5), 117 (4), 105 (73), 85 (69), 83 (100), 87 (15).

¹ Suzuki, I.; Kin, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1993**, *115*, 10139.

4.3.- Intramolecular Friedel-Crafts acylation. Synthesis of (+)-(2*S*,3*R*)-2,3-dimethylindan-1-one (**5a**).

Oxalyl chloride (0.14 mL, 1.10 mmol) was slowly added over a cooled (0°C) solution of the acid **4a** (0.18 g, 1.00 mmol) in dry CH₂Cl₂ (20 mL). The mixture was stirred for 1h. at this temperatures and the volatiles were removed under reduced pressure. The resulting yellowish oil was dissolved in dry CH₂Cl₂ (20 mL), the mixture was cooled to 0°C and AlCl₃ (0.26 g, 2.00 mmol) was added at once. After stirring for 1h. at 0°C, the reaction was quenched with sat. NH₄Cl and extracted with CH₂Cl₂ (3 x 15mL). The organic fractions were collected, dried over Na₂SO₄, filtered and the solvent removed under reduced pressure affording pure indanone **5a** (166mg, 0.93mmol) as a yellowish oil after flash column chromatography purification (hexanes/AcOEt 8:2). Yield: 60%. [α]_D²⁰ = +58.6 (*c*=0.30, CHCl₃). ¹H-NMR (δ , ppm): 1.18 (d, 3H, *J*=5.3Hz); 1.27 (d, 3H, *J*=5.2Hz); 2.82 (m, 1H); 3.51 (m, 1H); 7.34 (t, 1H, *J*=7.6Hz); 7.46 (d, 1H, *J*=7.4Hz); 7.53 (t, 1H, *J*=7.1Hz); 7.71 (d, 1H, *J*=7.6Hz). ¹³C-NMR (δ , ppm): 14.3; 21.2; 43.1; 45.4; 126.2; 127.5; 128.1; 153.0; 202.4. IR (CHCl₃): 1711 (C=O).

5.- ^1H - and ^{13}C -NMR spectra of amides **3a-s**.

5.1.- ^1H - and ^{13}C -NMR spectra of amide **3a**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3b**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3c**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3d**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3e**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3f**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3g**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3h**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3i**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3j**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3k**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **31**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3m**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3n**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3o**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3p**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3q**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3r**.

5.1.- ^1H - and ^{13}C -NRM spectra of amide **3s**.