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Supporting Information

Asymmetric Rhodium-Catalysed Hydrogenation Meets Gold-Catalysed Cyclisation: Enantioselective Synthesis of 8-Hydroxytetrahydroisquinolines

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Experimental Section

General methods: Chemicals (Aldrich, Fluka, Lancaster, and Merck) were used without further purification. All solvents were distilled before use. $[\mu\text{-Cl}(AuPPh_3)_2]BF_4$[1] and $[\mu\text{-Cl}(AuPMes_3)_2]BF_4$[2] were prepared according to published procedures. Enantiomeric excess was determined by HPLC on a chiral stationary phase (Chiracel OD, 4.6 mm I.D. x 250mm or Chiralcel OD-H 5µ, 4.6 mm I.D. x 150 mm). Optical rotation was recorded on a Perkin Elmer 241 polarimeter (Na, 589 nm). NMR spectra were recorded on Bruker ARX500 and AMX300 spectrometers. Chemical shifts were referenced to residual solvent protons. Signal multiplicity as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet). ^{13}C assignment was achieved via DEPT90 and DEPT135 spectra. MS spectra were recorded on a Finnigan MAT 90 or Varian 711. IR spectra were recorded on a Bruker Vector 22.

General procedure 1 (GP 1) - Horner-Wadsworth-Emmons reaction of furfurals:[3] At -78 °C 1 equivalent KO*t*Bu was suspended in dichloromethane (6 mmol/mL). Then a solution of 1 equivalent of methyl 2-benzyloxycarbonylamino-2-(dimethoxyphosphinyl)-acetate **14** in dichloromethane (667 µmol/mL) and a solution of 1 equivalent of furfural **13** in dichloromethane (6 mmol/mL) were added. After the reaction mixture was stirred for additional 2 h at room temperature, the solvent was removed under reduced pressure, the residue dissolved in EtOAc, washed with water and saturated aqueous NH_4Cl, dried over anhydrous sodium sulfate. After removing of the solvent under reduced pressure, the crude product **15** was obtained and purified either by recrystallisation or by column chromatography on silica gel (hexanes/EtOAc).

General procedure 2 (GP 2) - Asymmetric hydrogenation: Under an atmosphere of nitrogen, 1 equivalent of the (*Z*)-dehydroamino acid **15**, 1 mol% $[Rh(nbd)_2]BF_4$ and 1 mol% Mandyphos(OMe) **22** were weighed into a glass pressure bottle and dissolved in MeOH/toluene (1/1,

v/v), the nitrogen atmosphere was exchanged for hydrogen (5 bars), then the reaction mixture was left at room temperature (5.5 to 120 h). After removing of the solvent under reduced pressure the product **16** was isolated by column chromatography on silica gel (hexanes/EtOAc).

General procedure 3 (GP 3) – Cleavage of Cbz protecting group and subsequent protection as brosylate:[4] Under an atmosphere of nitrogen, 1 equivalent of the Cbz protected compound was dissolved in dry MeOH. Pd/C (Fluka 75990, Assay 10% Pd) (50 mg/mmol) and freshly distilled cyclohexene (2.1 mL/mmol) were added and refluxed for 1 h. The reaction mixture was allowed to cool, filtered over celite and then the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, triethylamine (1.5 equivalents) was added and cooled to 0 °C, followed by addition of 4-bromobenzenesulfonyl chloride (1.1 equivalents) in portions and the reaction mixture was stirred at room temperature. After completion (monitored by TLC) water was added, the layers were separated and the aqueous layer was extracted with dichloromethane twice, dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 4 (GP 4) – Propargylation of sulfonamides: 1 equivalent of sulfonamide was dissolved in acetone at room temperature and 3 equivalents of caesium carbonate and 3 equivalents of propargyl bromide (80 wt% solution in toluene) were added and stirred over night. The solvent was removed under reduced pressure, the residue was dissolved in water, extracted with dichloromethane, dried over anhydrous sodium sulfate and the solvent was removed in vacuo. Column chromatography on silica gel (hexanes/EtOAc/DCM) furnished the propargylated sulfonamides.

General procedure 5 (GP 5) – Reduction of methyl esters with DIBALH:[5] Under an atmosphere of nitrogen, 1 equivalent of the

methyl ester was dissolved in dry tetrahydrofuran and cooled to -78 °C. 2.6 equivalents of DIBALH (1.0 M in hexane) were added dropwise and the mixture was allowed to reach room temperature. The reaction progress was checked by TLC. After completion MeOH, 0.5 M hydrochloric acid and saturated aqueous potassium sodium tartrate were added and stirred over night to get a powdery precipitate, which was filtered off. The aqueous layer was extracted three times with diethyl ether, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc) or was used in the following reaction without purification.

General procedure 6 (GP 6) – Protection of alcohols with TBDMSCl:[6] Under an atmosphere of nitrogen, 1 equivalent of alcohol was dissolved in dry dimethyl formamide at room temperature. Then 2.5 equivalents imidazole and 2 equivalents TBDMSCl were added subsequently and monitored by TLC. After completion, the mixture was diluted with water and the aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with 0.5 M hydrochloric acid and brine, and then dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure the crude product was purified by column chromatography on silca gel (hexanes/EtOAc).

General procedure 7 (GP 7) – Propargylation of carbamates: Under an atmosphere of nitrogen, 1 equivalent of carbamate was dissolved in dry dimethyl formamide and 1.2 equivalents sodium hydride were added. After 15 min of stirring, 1.2 equivalents propargyl bromide (80 wt% solution in toluene) were added dropwise. The reaction was monitored by TLC. After completion the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted three times with diethyl ether, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 8 (GP 8) – Propargylation of carbamates with free hydroxy group: Under an atmosphere of nitrogen, 1 equivalent of carbamate was dissolved in dry dimethyl formamide and 3 equivalents sodium hydride were added. After 15 min of stirring, 1.2 equivalents propargyl bromide (80 wt% solution in toluene) were added dropwise. The reaction was monitored by TLC. After completion the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted three times with diethyl ether, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 9 (GP 9) – Gold catalysis: In a NMR tube 1 equivalent of starting material was dissolved in 600 µL of the corresponding deuterated solvent. Then 1 or 5 mol% of the catalyst precursor was added and the reaction was monitored by ^1H NMR. After completion the solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel (hexanes/EtOAc).

General procedure 10 (GP 10) – Gold catalysis under nitrogen: Under an atmosphere of nitrogen, 1 equivalent of starting material was dissolved in dry dichloroethane. Then 1 mol% of the catalyst precursor was added and the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel (hexanes/EtOAc).

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-(furan-2-yl)acrylate (15a):[7] As described in GP 1, KO*t*Bu (1.36 g, 12.1 mmol) in dichloromethane (2 mL), **14** (4.00 g, 12.1 mmol) in dichloromethane (18 mL) and freshly distilled furfural **13a** (1.00 mL, 1.16 g, 12.1 mmol) in dichloromethane (2 mL) furnished pure **15a** (2.95 g, 9.79 mmol, 81%) as colourless solid after recrystallisation from

EtOAc. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.79 (s, 3H), 5.17 (s, 2H), 6.46 (dd, *J* = 1.8 Hz, 3.5 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 6.80 (br s, 1H), 7.00 (s, 1H), 7.32-7.38 (m, 5H), 7.48 (d, *J* = 1.8 Hz, 1H).

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-(5-methyl-2-furyl)acrylate (15b): As described in GP 1, KO*t*Bu (224 mg, 2.00 mmol) in dichloromethane (2 mL), **14** (663 mg, 2.00 mmol) in dichloromethane (5 mL) and 5-methylfurfural **13b** (200 µL, 220 mg, 2.00 mmol) in dichloromethane (1 mL) furnished pure **15b** (448 mg, 1.42 mmol, 71%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 5/1). Mp. 66-68 °C. R_f (hexanes/EtOAc, 5/1) = 0.10. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.30 (s, 3H), 3.78 (s, 3H), 5.18 (s, 2H), 6.08 (dd, *J* = 0.6 Hz, 3.3 Hz, 1H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.61 (br s, 1H), 7.01 (s, 1H), 7.31-7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.6 (q), 52.1 (q), 67.0 (t), 108.6 (d), 117.0 (d), 118.2 (d), 120.4 (s), 127.8 (d, 2C), 127.9 (d), 128.2 (d, 2C), 136.0 (s), 148.0 (s), 153.8 (s), 155.0 (s), 165.3 (s). IR (neat): $\tilde{n}$ = 3291, 3088, 1727, 1686, 1618, 1504, 1438, 1372, 1300, 1214, 1133, 1053, 875, 787, 765, 749, 697 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 315 (31)[M^+], 207 (19), 180 (30), 120 (48), 91 (100). $C_{17}H_{17}NO_5$ (315.32): calcd. C 64.75, H 5.43, N 4.44; found C 64.45, H 5.43, N 4.32.

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-(5-ethyl-2-furyl)acrylate (15c): As described in GP 1, KO*t*Bu (1.68 g, 15.0 mmol) in dichloromethane (5 mL), **14** (4.97 g, 15.0 mmol) in dichloromethane (25 mL) and 5-ethyl furfural **13c** (1.77 mL, 1.86 g, 15.0 mmol) in dichloromethane (10 mL) furnished pure **15c** (2.40 g, 7.29 mmol, 49%) as yellowish solid after recrystallisation from EtOAc. Mp. 80-81 °C. R_f (hexanes/EtOAc, 1/1) = 0.50. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.22 (t, *J* = 7.6 Hz, 3H), 2.64 (q, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 5.17 (s, 2H), 6.08 (d, *J* = 3.3 Hz, 1H), 6.53 (d, *J* = 3.3 Hz, 1H), 6.65 (br s, 1H), 7.03 (s, 1H), 7.30-7.39 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.7 (q), 21.6 (t), 52.4 (q), 67.4 (t),

107.2 (d), 117.1 (d), 118.0 (d), 120.6 (s), 128.1 (d, 2C), 128.2 (d), 128.5 (d, 2C), 136.1 (s), 148.0 (s), 154.0 (s), 160.8 (s), 165.5 (s). IR (neat): $\tilde{n}$ = 3281, 2964, 1728, 1684, 1662, 1520, 1506, 1437, 1366, 1292, 1213, 1133, 1051, 1031 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 329 (70)[M^+], 221 (30), 194 (41), 134 (33), 91.1 (100), 43 (23), 28.1 (68). $C_{18}H_{19}NO_5$ (329.35): calcd. C 65.64, H 5.81, N 4.25; found C 65.68, H 5.84, N 4.20.

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-(4,5-dimethyl-2-furyl)acrylate (15d): As described in GP 1, KO*t*Bu (907 mg, 8.08 mmol) in dichloromethane (3 mL), **14** (2.68 g, 8.08 mmol) in dichloromethane (12 mL) and 4,5-dimethyl furfural **13d** (984 µL, 1.00 mg, 8.08 mmol) in dichloromethane (3 mL) furnished pure **15d** (1.87 g, 5.67 mmol, 70%) as bright yellow solid after column chromatography on silica gel (hexanes/EtOAc, 10/1). Mp. 76-77 °C. R_f (hexanes/EtOAc, 1/1) = 0.49. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.92 (s, 3H), 2.20 (s, 3H), 3.76 (s, 3H), 5.17 (s, 2H), 6.41 (s, 1H), 6.60 (br s, 1H), 6.99 (s, 1H), 7.27-7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 9.6 (q), 11.7 (q), 52.3 (q), 67.3 (t), 117.5 (s), 118.2 (d), 119.5 (d), 120.1 (s), 128.0 (d, 2C), 128.1 (d), 128.4 (d, 2C), 136.2 (s), 146.8 (s), 151.1 (s), 154.4 (s), 165.6 (s). IR (neat): $\tilde{n}$ = 3290, 2951, 1700, 1644, 1610, 1537, 1494, 1438, 1358, 1262, 1229, 1157, 1130, 1067, 1004 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 329 (46)[M^+], 221 (11), 194 (40), 162 (22), 135 (15), 134 (32), 91 (100), 43 (15). $C_{18}H_{19}NO_5$ (329.35): calcd. C 65.64, H 5.81, N 4.25; found C 65.55, H 5.83, N 4.20.

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-[(5-*tert*-butyl(dimethyl)silyl)-2-furyl]acrylate (15e): As described in GP 1, KO*t*Bu (1.68 g, 15.0 mmol) in dichloromethane (5 mL), **14** (4.97 g, 15.0 mmol) in dichloromethane (25 mL) and 5-*tert*-butyldimethylsilyl furfural **13e** (3.16 g, 15.0 mmol) in dichloromethane (5 mL) furnished pure **15e** (4.97 g, 12.0 mmol, 80%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 10/1). Mp. 92-93 °C. R_f (hexanes/EtOAc, 10/1) =

0.09. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.22 (s, 6H), 0.89 (s, 9H), 3.81 (s, 3H), 5.17 (s, 2H), 6.57 (d, *J* = 3.4 Hz, 1H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.95 (s, 1H), 7.05 (br s, 1H), 7.30 - 7.36 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -6.55 (q, 2C), 16.86 (s), 26.23 (q, 3C), 52.46 (q), 67.49 (t), 115.04 (d), 115.54 (d), 122.75 (s), 123.00 (d), 128.19 (d), 128.22 (d, 2C), 128.45 (d, 2C), 135.92 (s), 153.66 (s), 153.74 (s), 162.22 (s), 165.29 (s). IR (neat): $\tilde{n}$ = 3175, 3100, 2936, 2856, 1704, 1635, 1554, 1442, 1406, 1333, 1277, 1201, 1120, 1040, 999, 926, 808, 768, 705 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 415 (21)[M^+], 307 (15), 250 (46), 222 (15), 108 (19), 91 (100), 56 (15). $C_{22}H_{29}NO_5Si$ (415.55): calcd. C 63.59, H 7.03, N 3.37; found C 63.72, H 7.10, N 3.29.

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-[5-(3-trifluoromethyl-phenyl)-2-furyl)acrylate (15f): As described in GP 1, KO*t*Bu (930 mg, 8.33 mmol) in dichloromethane (5 mL), **14** (2.76 g, 8.33 mmol) in dichloromethane (15 mL) and 5-[3-(trifluoromethyl)phenyl] furfural **13f** (1.77 mL, 2.00 g, 8.33 mmol) in dichloromethane (10 mL) furnished pure **15f** (1.25 g, 2.80 mmol, 34%) as colourless solid after recrystallisation from EtOAc. Mp. 116-118 °C. R_f (hexanes/EtOAc, 1/1) = 0.20. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.83 (s, 3H), 5.18 (s, 2H), 6.71 (d, *J* = 3.6 Hz, 1H), 6.75 (br s, 1H), 6.81 (d, *J* = 3.6 Hz, 1H), 7.16 (s, 1H), 7.28-7.38 (m, 5H), 7.38-7.47 (m, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.88 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.7 (q), 67.7 (t), 108.8 (d), 117.4 (d), 118.0 (d), 120.8 (dq, $^{3}J_{CF}$ = 3.8 Hz), 121.9 (s), 123.8 (sq, $^{1}J_{CF}$ = 272.5 Hz), 124.6 (dq, $^{3}J_{CF}$ = 3.8 Hz), 127.0 (d), 128.2 (d, 3C, not resolved), 128.4 (d, 2C), 129.4 (d), 130.3 (s), 131.3 (sq, $^{2}J_{CF}$ = 32.5 Hz), 135.8 (s), 149.7 (s), 153.7 (s), 154.1 (s), 165.1 (s). IR (neat): $\tilde{n}$ = 3317, 2954, 1722, 1694, 1641, 1524, 1489, 1452, 1438, 1366, 1334, 1273, 1227, 1206, 1165, 1100, 1060, 940 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 445 (28)[M^+], 337 (86), 310 (21), 251 (20), 250 (100), 108 (38), 91 (95), 28 (36). $C_{23}H_{18}F_3NO_5$ (445.39): calcd. C 62.02, H 4.07, N 3.14; found C 62.13, H 4.06, N 3.10.

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-[(4-bromophenyl)-2-furyl]acrylate (15g): As described in GP 1, KO*t*Bu (715 mg, 6.37 mmol) in dichloromethane (2 mL), **14** (2.11 g, 6.37 mmol) in dichloromethane (9 mL) and 5-(4-bromophenyl) furfural **13g** (1.60 g, 6.37 mmol) in dichloromethane (20 mL) furnished pure **15g** (2.37 g, 5.19 mmol, 82%) as bright yellow solid after recrystallisation from EtOAc. Mp. 95-97 °C. R_f (hexanes/EtOAc, 1/1) = 0.57. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.83 (s, 3H), 5.17 (s, 2H), 6.69 (d, *J* = 3.6 Hz, 1H), 6.71 (br s, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 7.14 (s, 1H), 7.34 (s, 5H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.6 (q), 67.6 (t), 108.1 (d), 117.6 (d), 118.3 (d), 121.6 (s), 122.3 (s), 125.6 (d, 2C), 128.3 (d, 2C), 128.4 (d), 128.5 (s), 128.6 (d, 2C), 132.0 (d, 2C), 135.8 (s), 149.4 (s), 153.8 (s), 154.8 (s), 165.3 (s). IR (neat): $\tilde{n}$ = 3342, 3065, 2953, 1895, 1693, 1643, 1566, 1524, 1471, 1366, 1282, 1233, 1132, 1067, 995, 962, 910, 858, 819, 779, 759, 696 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 457 (20)[^{81}Br-M$^+$], 455 (20)[^{79}Br-M$^+$], 349 (35), 347 (35), 322 (24), 320 (24), 262 (48), 260 (48), 91 (100). $C_{22}H_{18}BrNO_5$ (456.29): calcd. C 57.91, H 3.98, N 3.07; found 57.69, H 4.01, N 3.00.

Methyl (2*Z*)-2-{[(Benzyloxy)carbonyl]amino}-3-furan-3-yl acrylate (15h):[7] As described in GP 1, KO*t*Bu (1.68 g, 15.0 mmol) in dichloromethane (5 mL), **14** (4.97 g, 15.0 mmol) in dichloromethane (25 mL) and furan-3-carbaldehyde **13h** (1.77 mL, 1.86 g, 15.0 mmol) in dichloromethane (10 mL) furnished pure **15h** (2.89 g, 9.60 mmol, 63%) as colourless solid after recrystallisation from EtOAc. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 3.69 (s, 3H), 5.09 (s, 2H), 6.74 (s, 1H), 7.25-7.45 (m, 6 H), 7.74 (s, 1H), 8.09 (s, 1H), 9.00 (s, 1H).

Methyl (2*R*)-(-)-2-[(Benzyloxy)carbonylamino]-3-furan-3-ylpropanoate (16a):[7] As described in GP 2, **15a** (1.00 g, 3.32 mmol), [Rh(nbd)$_2$]BF_4 (12.4 mg, 33.2 µmol) and MandyPhos(OMe) **22** (35.0 mg, 33.2 µmol) in 30 mL MeOH/toluene are converted for

5.5 h with 5 bars hydrogen pressure. Column chromatography on silica gel (hexanes/EtOAc, 2/1) furnished pure **16a** (977 mg, 3.22 mmol, 97%) as light yellow oil. R_f (hexanes/EtOAc, 3/1) = 0.56. HPLC: 98% *ee*, Chiralcel OD (eluent: hexane/^{i}PrOH: 9/1; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 7.43 min, (-)-enantiomer: 9.97 min. $[\alpha]_D^{20}$=-47.5 (98% *ee*, c=1.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.11-3.19 (m, 2H), 3.75 (s, 3H), 4.61-4.68 (m, 1H), 5.11 (s, 2H), 5.40 (br d, *J* = 7.6 Hz, 1H), 6.06 (dd, *J* = 0.6 Hz, *J* = 3.1 Hz, 1H), 6.27 (dd, *J* = 1.8 Hz, *J* = 3.1 Hz, 1H), 7.30 (dd, *J* = 1.8 Hz, 0.6 Hz, 1H), 7.34-7.36 (m, 5H).

Methyl (2*R*)-(-)-2-Benzyloxycarbonylamino-3-(5-methylfuran-2-yl)propanoate (16b): As described in GP 2, **15b** (3.02 g, 9.57 mmol), $[Rh(nbd)_2]BF_4$ (35.8 mg, 95.7 µmol) and MandyPhos(OMe) **22** (101 mg, 95.7 µmol) in 90 mL MeOH/toluene are converted for 16.5 h with 5 bars hydrogen pressure. Column chromatography on silica gel (hexanes/EtOAc, 6/1) furnished pure **16b** (2.98 g, 9.38 mmol, 98%) as light yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.67. HPLC: 96% *ee*, Chiralcel OD (eluent: hexane/^{i}PrOH: 9/1; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 6.63 min, (-)-enantiomer: 8.47 min. $[\alpha]_D^{20}$=-48.3 (96% *ee*, c=1.17, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.21 (s, 3H), 3.05-3.16 (m, 2H), 3.75 (s, 3H), 4.60-4.63 (m, 1H), 5.01-5.14 (m, 2H), 5.41 (br d, *J* = 8.0 Hz, 1H), 5.83 (dd, *J* = 0.9 Hz, 3.1 Hz, 1H), 5.94 (d, *J* = 3.1 Hz, 1H), 7.30-7.38 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 13.44 (q), 30.89 (t), 52.36 (q), 53.13 (d), 66.93 (t), 106.12 (d), 108.70 (d), 128.03 (d, 2C), 128.10 (d), 128.46 (d, 2C), 148.03 (s), 151.73 (s), 155.64 (s), 162.38 (s), 171.65 (s). IR (neat): $\tilde{n}$ = 3368, 2953, 2352, 1960, 1726, 1516, 1437, 1344, 1214, 1063, 889, 631 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 317 (1.6)[M^+], 166 (61), 95 (100). $C_{17}H_{19}NO_5$ (317.34): calcd. C 64.34, H 6.03, N 4.41; found C 64.50, H 6.11, N 4.39. **Racemic:** As described in GP 2, **15b** (937 g, 2.97 mmol) and $RhCl(PPh_3)_3$ (275 mg, 297 µmol) in 40 mL MeOH/toluene are converted for 24 h with 5 bars hydrogen pressure. Column

chromatography on silica gel (hexanes/EtOAc, 5/1) furnished pure (±)-**16b** (867 mg, 2.73 mmol, 92%) as light yellow oil.

Methyl (2*R*)-(-)-2-Benzyloxycarbonylamino-3-(5-ethylfuran-2-yl)propanoate (16c): As described in GP 2, **15c** (849 mg, 2.58 mmol), $[Rh(nbd)_2]BF_4$ (9.60 mg, 25.8 µmol) and MandyPhos(OMe) **22** (27.1 mg, 25.8 µmol) in 25 mL MeOH/toluene are converted for 17.5 h with 5 bars hydrogen pressure. Column chromatography on silica gel (hexanes/EtOAc, 6/1) furnished pure **16c** (756 mg, 2.28 mmol, 88%) as light yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.64. HPLC: 95% *ee*, Chiralcel OD (eluent: hexane/^{i}PrOH: 95/5; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 8.15 min, (-)-enantiomer: 11.75 min. $[\alpha]_D^{20}$=-57.6 (95% *ee*, c=1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.18 (t, *J* = 7.5 Hz, 3H), 2.57 (q, *J* = 7.5 Hz, 2H), 3.11 (dd, *J* = 15.2 Hz, 5.2 Hz, 1H), 3.15 (dd, *J* = 15.2 Hz, 5.3 Hz, 1H), 3.75 (s, 3H), 4.62 (*app.* dt, *J* = 8.3 Hz, 5.3 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 5.42 (d, *J* = 8.0 Hz, 1H), 5.84 (d, *J* = 2.9 Hz, 1H), 5.95 (d, *J* = 2.9 Hz, 1H), 7.29-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 12.0 (q), 21.3 (t), 30.9 (t), 52.4 (d), 53.2 (q), 67.0 (t), 104.6 (d), 108.5 (d), 128.0 (d, 2C), 128.1 (d), 128.5 (d, 2C), 136.3 (s), 148.0 (s), 155.7 (s), 157.5 (s), 171.7 (s). IR (neat): $\tilde{n}$ = 3340, 2970, 1720, 1509, 1454, 1437, 1343, 1207, 1178, 1057, 1025 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 331 (3)[M^+], 180 (56), 109 (100), 91 (46), 28 (17), 18 (28). $C_{18}H_{21}NO_5$ (331.36): calcd. C 65.24, H 6.39, N 4.23; found C 65.26, H 6.40, N 4.11.

Methyl (2*R*)-(-)-2-Benzyloxycarbonylamino-3-(4,5-dimethylfuran-2-yl)propanoate (16d): As described in GP 2, **15d** (1.00 g, 3.04 mmol), $[Rh(nbd)_2]BF_4$ (10.0 mg, 30.4 µmol) and MandyPhos(OMe) **22** (32.0 mg, 30.4 µmol) in 30 mL MeOH/toluene are converted for 64 h with 5 bars hydrogen pressure. Column chromatography on silica gel (hexanes/EtOAc, 6/1) furnished pure **16d** (830 mg, 2.50 mmol, 82%) as yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.64. HPLC: 87% *ee*, Chiralcel OD (eluent: hexane/^{i}PrOH: 9/1; flow

1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 6.28 min, (-)-enantiomer: 7.88 min. $[\alpha]_D^{20}$=-40.6 (87% *ee*, c=1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.86 (s, 3H), 2.11 (s, 3H), 3.04 (dd, *J* = 15.2 Hz, 5.2 Hz, 1H), 3.10 (dd, *J* = 15.2 Hz, 5.4 Hz, 1H), 3.75 (s, 3H), 4.59 (*app.* dt, actual ddd, *J* = 8.1 Hz, 5.4 Hz, 5.2 Hz 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 5.39 (d, *J* = 8.1 Hz, 1H), 5.82 (s, 1H), 7.28-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 9.8 (q), 11.2 (q), 30.8 (t), 52.4 (q), 53.1 (d), 66.9 (t), 111.2 (d), 114.5 (s), 128.0 (d, 2C), 128.1 (d), 128.5 (d, 2C), 136.3 (s), 146.7 (s), 146.9 (s), 155.7 (s), 171.7 (s). IR (neat): $\tilde{n}$ = 3342, 2950, 1723, 1511, 1437, 1345, 1212, 1058, 1027, 902, 698, 631 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 331 (4)[M^+], 180 (4), 110 (9), 109 (100), 91 (34), 43 (12). $C_{18}H_{21}NO_5$ (331.36): calcd. C 65.24, H 6.39, N 4.23; found C 65.09, H 6.44, N 4.15.

Methyl (2*R*)-(-)-2-Benzyloxycarbonylamino-3-[(5-*tert*-butyldimethylsilyl)furan-2-yl]propanoate (16e): As described in GP 2, **15e** (2.01 g, 4.83 mmol), $[Rh(nbd)_2]BF_4$ (9.0 mg, 24.2 µmol) and MandyPhos(OMe) **22** (25.4 mg, 24.2 µmol) in 50 mL MeOH/toluene are converted for 120 h with 5 bars hydrogen pressure. Column chromatography on silica gel (hexanes/EtOAc, 6/1) furnished pure **16e** (2.01 g, 4.82 mmol, 99%) as colourless viscous oil. R_f (hexanes/EtOAc, 1/1) = 0.63. HPLC: 80% *ee*, Chiralcel OD (eluent: hexane/^{i}PrOH: 96/4; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 6.35 min, (-)-enantiomer: 8.45 min. $[\alpha]_D^{20}$=-27.9 (80% *ee*, c=1.07, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.20 (s, 6H), 0.90 (s, 9H), 3.11-3.31 (br m, 2H), 3.73 (s, 3H), 4.61-4.68 (m, 1H), 5.11 (s, 2H), 5.42 (br d, *J* = 8.1 Hz, 1H), 6.06 (d, *J* = 3.1 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 7.30-7.36 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = -6.46 (q), -6.39 (q), 16.70 (s), 26.25 (q, 3C), 30.79 (t), 52.38 (q), 53.04 (d), 66.88 (t), 107.99 (d), 121.59 (d), 127.94 (d, 2C), 128.06 (d), 128.43 (d, 2C), 136.23 (s) 154.21 (s), 155.60 (s), 158.66 (s), 171.48 (s). IR (neat): $\tilde{n}$ = 3302, 2941, 2892, 2856, 1726, 1698, 1540, 1503, 1443, 1328, 1256,

1216, 1051, 1007, 928, 825, 771, 685, 630 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 417 (4)[M^+], 360 (10), 316 (28), 266 (74), 209 (30), 195 (40), 91 (100). $C_{22}H_{31}NO_5Si$ (417.57): calcd. C 63.28, H 7.48, N 3.35; found C 63.27, H 7.52, N 3.30.

Methyl (2*R*)-(-)-2-Benzyloxycarbonylamino-3-[5-(3-trifluoromethylphenyl)furan-2-yl]propanoate (16f): As described in GP 2, **15f** (1.00 g, 2.25 mmol), $[Rh(nbd)_2]BF_4$ (8.4 mg, 22.5 µmol) and MandyPhos(OMe) **22** (23.6 mg, 22.5 µmol) in 25 mL MeOH/toluene are converted for 18 h with 5 bars hydrogen pressure. Column chromatography on silica gel (hexanes/EtOAc, 6/1) furnished pure **16f** (369 mg, 820 µmol, 37%) as colourless viscous oil. Mp. 83-84 °C. R_f (hexanes/EtOAc, 1/1) = 0.66. HPLC: 87% *ee*, Chiralcel OD (eluent: hexane/^{i}PrOH: 96/4; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 5.45 min, (-)-enantiomer: 6.47 min. $[\alpha]_D^{20}$=-73.6 (87% *ee*, c=1.02, $CHCl_3$). One recrystallisation afforded 92% *ee*: $[\alpha]_D^{20}$=-85.5 (92% *ee*, c=1.027, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.28 (d, *J* = 5.2 Hz, 2H), 3.80 (s, 3H), 4.70 (dt, *J* = 5.2 Hz, 7.9 Hz, 1H), 5.11 (s, 2H), 5.44 (d, *J* = 7.9 Hz, 1H), 6.19 (d, *J* = 3.3 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 7.27-7.38 (m, 5H), 7.44-7.51 (m, 2H), 7.70-7.75 (m, 1H), 7.81 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 31.1 (t), 52.6 (q), 53.0 (d), 67.1 (t), 107.1 (d), 110.5 (d), 120.2 (dq, $^3J_{CF}$ = 3.8 Hz), 124.1 (sq, $^1J_{CF}$ = 272.5 Hz), 123.7 (dq, $^3J_{CF}$ = 3.8 Hz), 126.5 (d), 128.1 (d, 2C), 128.2 (d), 128.5 (d, 2C), 129.2 (d), 131.2 (sq, $^2J_{CF}$ = 32.3 Hz), 131.4 (s), 136.2 (s), 150.1 (s), 152.1 (s), 155.6 (s), 171.5 (s). IR (neat): $\tilde{n}$ = 3325, 1745, 1682, 1339, 1302, 1267, 1202, 1155, 1111, 1075, 1023, 960, 934, 895, 853, 784, 753, 693 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 447 (5)[M^+], 324 (7), 296 (61), 242 (10), 225 (100), 173 (7), 91 (32). HRMS (EI, 70eV): $C_{23}H_{20}F_3NO_5$ calcd. 447.1294; found 447.1294.

Methyl (2*R*)-(-)-2-Benzyloxycarbonylamino-3-[(5-(3-trifluoromethylphenyl)furan-2-yl]propanoate (16h):[7] As described in GP 2, **15h** (1.00 g, 3.32 mmol), $[Rh(nbd)_2]BF_4$ (12.4 mg,

33.2 µmol) and MandyPhos(OMe) **22** (35.0 mg, 33.2 µmol) in 30 mL MeOH/toluene are converted for 14.5 h with 5 bars hydrogen pressure. Column chromatography on silica gel (hexanes/EtOAc, 6/1) furnished pure **16h** (853 mg, 2.81 mmol, 85%) as yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.56. HPLC: 93% *ee*, Chiralcel OD (eluent: hexane/^{i}PrOH: 9/1; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 7.80 min, (-)-enantiomer: 9.68 min. $[\alpha]_D^{20}$=-38.6 (93% *ee*, c=1.04, $CHCl_3$). ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 2.71 (dd, *J* = 14.5 Hz, 9.7 Hz, 1H), 2.85 (dd, *J* = 14.5 Hz, 5.1 Hz, 1H), 3.63 (s, 3H), 4.20 (*app.* dt, actual ddd, *J* = 9.7 Hz, 7.9 Hz, 5.1 Hz, 1H), 5.01 (s, 2H), 6.40 (s, 1H), 7.27-7.40 (m, 5H), 7.46 (s, 1H), 7.55 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H).

Methyl (2*R*)-(-)-2-{[(4-Bromophenyl)sulfonyl]amino}-3-(2-furyl)propanoate (23a): As described in GP 3, furyl alanine **16a** (934 mg, 3.08 mmol), Pd/C (50 mg) and cyclohexene (6.50 mL) in MeOH (20 mL) furnished the crude amine. Triethylamine (229 µL, 166 mg, 1.64 mmol), 4-bromobenzenesulfonyl chloride (307 mg, 1.20 mmol) in dichloromethane (5 mL) furnished the pure sulfonamide **23a** (262 mg, 674 µmol, 24%) after chromatography on silica gel (hexanes/DCM, 1/1) as colourless solid. Mp. 95-97 °C. R_f (hexanes/DCM, 1/1) = 0.09. $[\alpha]_D^{20}$=-13.04 (c=1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.07 (dd, *J* = 15.1 Hz, 5.4 Hz, 1H), 3.11 (dd, *J* = 15.1 Hz, 5.9 Hz, 1H), 3.58 (s, 3H), 4.23 (ddd, *J* = 9.1 Hz, 5.9 Hz, 5.4 Hz, 1H), 5.36 (d, *J* = 9.1 Hz, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 6.24 (dd, *J* = 3.2 Hz, 1.9 Hz, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 32.0 (t), 52.7 (q), 54.7 (d), 108.5 (d), 110.4 (d), 127.7 (s), 128.7 (d, 2C), 132.2 (d, 2C), 138.9 (s), 142.3 (d), 149.0 (s), 170.7 (s). IR (neat): $\tilde{n}$ = 3277, 1747, 1610, 1323, 1151, 1107, 1086, 1069, 1008, 938, 839, 737 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 386 (1)[M^+], 220 (29), 152 (100), 81 (59). $C_{14}H_{14}BrNO_5S$ (388.23): calcd. C 43.31, H 3.63, N 3.61; found C 43.38, H 3.63, N 3.61.

Methyl (+)-(2*R*)-[(4-Bromobenzenesulfonyl)-prop-2-ynyl-amino]-3-furan-2-yl-propanoate (24a): As described in GP 4, sulfonamide **23a** (109 mg, 282 µmol), caesium carbonate (275 mg, 845 µmol) and propargylbromide (80 wt% solution in toluene) (73 µL, 101 mg, 845 µmol) in acetone (5 mL) furnished propargylated sulfonamide **24a** (102 mg, 239 µmol, 85%) after column chromatography on silica gel (hexanes/EtOAc, 5/1) as light yellow solid. Mp. 53-55°C. R_f (hexanes/EtOAc, 5/1) = 0.23. $[\alpha]_D^{20}$=+52.73 (c=1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.18 (t, *J* = 2.5 Hz, 1H), 3.14 (dd, *J* = 15.5 Hz, 8.8 Hz, 1H), 3.35 (dd, *J* = 15.5 Hz, 6.4 Hz, 1H), 3.61 (s, 3H), 4.13 (dd, *J* = 18.7 Hz, 2.5 Hz, 1H), 4.25 (dd, *J* = 18.7 Hz, 2.5 Hz, 1H), 4.91 (dd, *J* = 8.8 Hz, 6.4 Hz, 1H), 6.09 (dd, *J* = 3.2 Hz, 0.8 Hz, 1H), 6.24 (dd, *J* = 3.2 Hz, 0.8 Hz, 1H), 7.27 (dd, *J* = 1.8 Hz, 0.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 29.0 (t), 34.4 (t), 52.5 (q), 58.6 (d), 73.5 (d), 78.3 (s), 108.3 (d), 110.6 (d), 127.8 (s), 129.5 (d, 2C), 132.1 (d, 2C), 139.1 (s), 142.0 (d), 150.0 (s), 170.2 (s). IR (film): $\tilde{n}$ = 3280, 3088, 2951, 1776, 1574, 1435, 1351, 1277, 1223, 1160, 1092, 1068, 1009, 904, 883, 822 cm^{-1}. MS (CI (+), 70eV): *m/z* (%): 445 (100)[^{81}Br-M + NH_4^+], 443 (98)[^{79}Br-M + NH_4^+], 428 (6)[^{81}Br-M^+], 426 (6)[^{79}Br-M^+], 346 (18), 344 (17), 152 (44). $C_{17}H_{16}BrNO_5S$ (426.28): calcd. C 47.90, H 3.78, N 3.29; found C 47.83, H 3.84, 3.25.

(+)-Methyl (3*R*)-2-[(4-Bromophenyl)sulfonyl]-8-hydroxy-1,2,3,4-tetrahydroisoquinoline-3-carboxylate (25aa) and **(+)-Methyl (3*R*)-2-[(4-Bromophenyl)sulfonyl]-7-hydroxy-1,2,3,4-tetrahydroisoquinoline-3-carboxylate (25ab):** As described in GP 9, alkyne **24a** (81.4 mg, 191 µmol) and $[\mu\text{–}Cl(AuPMes_3)_2]BF_4$ (2.50 mg, 1.91 µmol) in $CDCl_3$ (600 µL) furnished phenol **25aa** (23.1 mg, 54.2 µmol, 28%) as light yellow solid and phenol **25ab** 15.9 mg, 37.0 µmol, 20%) as yellow oil after column chromatography on silica gel (hexanes/EtOAc, 5/1). **25aa**: Mp. 63-65°C. R_f (hexanes/EtOAc, 3/1) = 0.26. $[\alpha]_D^{20}$=+28.86 (c=0.14, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.20 (br s, 1H), 3.22 (br s, 1H), 3.46 (s,

3H), 4.30 (d, *J* = 16.1 Hz, 1H), 4.74 (d, *J* = 16.1 Hz, 1H), 5.04 (dd, *J* = 4.7 Hz, 3.9 Hz, 1H), 5.21 (br s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 7.01 (*app.* t, *J* = 7.8 Hz (actual dd, only mean coupling constant), 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 31.76 (t), 40.41 (t), 52.34 (d), 53.71 (q), 112.92 (d), 118.42 (s), 121.01 (d), 127.45 (d), 127.66 (s), 128.93 (d, 2C), 132.14 (d, 2C), 137.99 (s), 151.77 (s), 170.45 (s) [1C (s) not detected!]. IR (neat): $\tilde{n}$ = 3414, 3091, 2954, 1735, 1585, 1466, 1440, 1385, 1327, 1277, 1208, 1155, 1095, 1063, 1005, 964, 874, 826, 779, 748, 704, 650, 596 cm^{-1}. MS (CI (+)): *m/z* (%): 428 (45)[^{81}Br-M +H$^+$], 426 (48)[^{79}Br-M + H$^+$ + ^{81}Br-M$^+$], 424 (7)[^{79}Br-M$^+$], 368 (69), 366 (66), 206 (100). HRMS (CI (+)): $C_{17}H_{16}BrNO_5S$: [^{79}Br-M - H]$^+$ calcd. 423.9855; found 423.9844. **25ab:** R_f (hexanes/EtOAc, 3/1) = 0.21. $[a]_D^{20}$=+13.08 (c=0.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.10-3.15 (m, 2H), 3.48 (s, 3H), 4.40 (d, *J* = 15.4 Hz, 1H), 4.64 (d, *J* = 15.4 Hz, 1H), 4.85 (br s, 1H), 4.98 (dd, *J* = 5.3 Hz, 3.6 Hz, 1H), 6.50 (d, *J* = 2.7 Hz, 1H), 6.64 (dd, *J* = 8.3 Hz, 2.7 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 31.18 (t), 44.46 (t), 52.37 (q), 54.19 (d), 112.47 (d), 114.60 (d), 121.10 (s), 122.58 (s), 127.77 (s), 128.85 (d, 2C), 130.01 (d), 132.20 (d, 2C), 137.99 (s), 154.45 (s), 170.62 (s). IR (film): $\tilde{n}$ = 3434, 2952, 1739, 1623, 1574, 1508, 1444, 1384, 1345, 1284, 1208, 1161, 1093, 1059, 1010, 946, 910, 822, 751, 648, 603 cm^{-1}. MS (CI (+)): *m/z* (%): 428 (22)[^{81}Br-M + H$^+$], 426 (27)[^{79}Br-M + H$^+$ + ^{81}Br-M$^+$], 424 (7)[^{79}Br-M$^+$], 368 (32), 366 (30), 206 (100), 204 (43). HRMS (CI (+)): $C_{17}H_{16}BrNO_5S$: [^{79}Br-M - H]$^+$ calcd. 423.9855; found 423.9837.

Methyl (2*R*)-(-)-2-{[(4-Bromophenyl)sulfonyl]amino}-3-(5-methyl-2-furyl)propanoate (23b): As described in GP 3, furyl alanine **16b** (1.25 g, 3.95 mmol), Pd/C (50 mg) and cyclohexene (8.30 mL) in MeOH (25 mL) furnished the crude amine. Triethylamine (830 µL, 599 mg, 5.92 mmol), 4-bromobenzenesulfonyl chloride (1.11 g, 4.34 mmol) in dichloromethane (25 mL) furnished the pure

sulfonamide **23b** (1.22 g, 3.04 mmol, 77%) after chromatography on silica gel (hexanes/EtOAc/DCM, 5/1/1) as colourless solid. Mp. 92-93 °C. R_f (hexanes/EtOAc/DCM, 5/1/1) = 0.24. $[\alpha]_D^{20}$=-8.61 (c=1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.17 (d, *J* = 1.0 Hz, 3H), 2.99 (dd, *J* = 15.1 Hz, 5.6 Hz, 1H), 3.04 (dd, *J* = 15.1 Hz, 6.1 Hz, 1H), 3.59 (s, 3H), 4.20 (ddd, *J* = 9.1 Hz, 6.1 Hz, 5.6 Hz, 1H), 5.37 (d, *J* = 9.1 Hz, 1H), 5.80 (dd, *J* = 3.1 Hz, 1.0 Hz, 1H), 5.92 (d, *J* = 3.1 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 13.4 (q), 32.0 (t), 52.6 (q), 54.9 (d), 106.2 (d), 109.3 (d), 127.7 (s), 128.7 (d, 2C), 132.2 (d, 2C), 139.0 (s), 147.0 (s), 151.9 (s), 170.9 (s). IR (neat): $\tilde{n}$ = 3281, 3089, 2960, 1724, 1574, 1473, 1427, 1343, 1316, 1271, 1241, 1162, 1090, 1069, 1029, 969, 910, 829 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 401 (2)[M - H^+], 166 (12), 96 (9), 95 (100), 43 (5). $C_{15}H_{16}BrNO_5S$ (402.26): calcd. C 44.79, H 4.01, N 3.48; found C 44.83, H 4.04, N 3.42.

Racemic: As described in GP 3, furyl alanine (±)-**16b** (1.20 g, 3.78 mmol), Pd/C (190 mg) and cyclohexene (8.00 mL) in MeOH (50 mL) furnished the crude amine. Triethylamine (800 µL, 577 mg, 5.70 mmol), 4-bromobenzenesulfonyl chloride (1.07 g, 4.18 mmol) in dichloromethane (25 mL) furnished the pure sulfonamide (±)-**23b** (1.18 g, 2.93 mmol, 78%) after chromatography on silica gel (hexanes/EtOAc, 4/1) as colourless solid.

Methyl (*R*)-(+)-2-[(4-Bromobenzenesulfonyl)prop-2-ynylamino]-3-(5-methylfuran-2-yl)propanoate (24b): As described in GP 4, sulfonamide **23b** (208 mg, 518 µmol), caesium carbonate (463 mg, 1.42 mmol) and propargylbromide (80 wt% solution in toluene) (158 µL, 169 mg, 1.42 mmol) in acetone (25 mL) furnished propargylated sulfonamide **24b** (153 mg, 347 µmol, 67%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as light yellow oil. R_f (hexanes/EtOAc, 5/1) = 0.21. $[\alpha]_D^{20}$=+31.41 (c=1.07, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.18 (m, 4H), 3.06 (dd, *J* = 15.4 Hz, 8.9 Hz, 1H), 3.28 (dd, *J* = 15.4 Hz, 6.2 Hz, 1H), 3.62 (s, 3H), 4.13 (dd, *J* = 18.8 Hz, 2.5 Hz, 1H), 4.25 (dd, *J* = 18.8 Hz, 2.5 Hz,

1H), 4.86 (dd, *J* = 8.9 Hz, 6.2 Hz, 1H), 5.79 (d, *J* = 3.1 Hz, 1H), 5.94 (d, *J* = 3.1 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H). ^{1}H NMR (CD_3CN, 300 MHz): δ = 2.17 (s, 3H), 2.61 (*app.* t, *J* = 2.5 Hz, 1H), 3.07 (dd, *J* = 15.6 Hz, 9.6 Hz, 1H), 3.23 (dd, *J* = 15.6 Hz, 5.5 Hz, 1H), 3.55 (s, 3H), 4.11 (dd, *J* = 18.8 Hz, 2.5 Hz, 1H), 4.21 (dd, *J* = 18.8 Hz, 2.5 Hz, 1H), 4.81 (dd, *J* = 9.6 Hz, 5.5 Hz, 1H), 5.84 (d, *J* = 3.0 Hz, 1H), 5.99 (d, *J* = 3.0 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 13.4(q), 28.8 (t), 34.2 (t), 52.2 (q), 58.6 (d), 73.2 (d), 78.3 (s), 106.2 (d), 108.8 (d), 127.5 (s), 129.0 (d, 2C), 131.8 (d, 2C), 139.0 (s), 147.8 (s), 151.3 (s), 170.2 (s). IR (film): $\tilde{n}$ = 3281, 2951, 1739, 1573, 1472, 1435, 1389, 1343, 1276, 1252, 1214, 1158, 1091, 1068, 1008, 903, 878, 822, 786, 740 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 441 (2)[^{81}Br-M^{+}], 439 (2)[^{79}Br-M^{+}], 346 (8), 344 (7), 221 (7), 219 (6), 166 (38), 124 (8), 96 (11), 95 (100), 66 (7), 43 (8), 28 (15). HRMS (EI (+), 70 eV): $C_{18}H_{18}{}^{79}BrNO_5S$: calcd. 439.0089; found 439.0089.

Racemic: As described in GP 4, sulfonamide (±)-**23b** (400 mg, 994 µmol), caesium carbonate (972 mg, 2.98 mmol) and propargylbromide (80 wt% solution in toluene) (331 µL, 355 mg, 2.98 mmol) in acetone (20 mL) furnished propargylated sulfonamide (±)-**24b** (319 mg, 725 µmol, 73%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as light yellow oil.

(+)-Methyl (3*R*)-2-[(4-Bromophenyl)sulfonyl]-8-hydroxy-7-methyl-1,2,3,4-tetrahydroisoquinoline-3-carboxylate (25b): As described in GP 9, alkyne **24b** (82.6 mg, 188 µmol) and [µ–Cl(AuPPh$_3$)$_2$]BF$_4$ (9.80 mg, 9.38 µmol) in $CDCl_3$ (600 µL) furnished phenol **25b** (53.1 mg, 117 µmol, 62%) as yellow solid after column chromatography on silica gel (hexanes/EtOAc/DCM, 5/1/1). Mp. 54-55 °C. R_f (hexanes/EtOAc/DCM, 5/1/1) = 0.23. HPLC: 94% *ee*, Chiralcel OD-H 5µ (eluent: hexane/EtOH: gradient 15-50% EtOH; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 5.19 min, (-)-enantiomer: 8.11 min. $[\alpha]_D^{20}$=+11.72 (94% *ee*, c=0.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.18 (s, 3H), 3.18 (*app.* d, *J* =

3.4 Hz, 2H), 3.46 (s, 3H), 4.33 (d, *J* = 16.0 Hz, 1H), 4.74 (d, *J* = 16.0 Hz, 1H), 4.76 (br s 1H), 5.02 (dd, *J* = 5.0 Hz, 3.7 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H). ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.56 (s, 3H), 2.83 (s, 3H), 2.88 (dd, *J* = 16.0 Hz, 6.2 Hz, 1H), 3.01 (dd, *J* = 16.0 Hz, 2.3 Hz, 1H), 4.33 (bs, 1H), 4.65 (dd, *J* = 16.0 Hz, 1.0 Hz, 1H), 5.07 (dd, *J* = 6.2 Hz, 2.3 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 6.38 (d, *J* = 7.7 Hz, 1H), 6.62 (dd, *J* = 7.7 Hz, 0.6 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 15.19 (q), 31.62 (t), 40.65 (t), 52.28 (q), 53.74 (d), 106.58 (s), 118.16 (s), 120.18 (s), 120.68 (d), 127.56 (d), 128.92 (d, 2C), 129.79 (d), 132.11 (d, 2C), 138.18 (s), 149.98 (s), 170.46 (s). IR (neat): $\tilde{\nu}$ = 3489, 2953, 1740, 1578, 1466, 1438, 1384, 1334, 1160, 1100, 1074, 1043, 1011, 966, 910, 867, 756 cm^{-1}. MS (CI (-)): *m/z* (%): 441 (100)[^{81}Br-M^{+}], 441 (97)[^{79}Br-M^{+}], 221 (71), 219 (70). HRMS (CI (-)): $C_{18}H_{18}{}^{81}BrNO_5S$: calcd. 441.0069; found 441.0064; $C_{18}H_{18}{}^{79}BrNO_5S$: calcd. 439.0089; found 439.0079.

Racemic: As described in GP 9, alkyne (±)-**24b** (30.0 mg, 68.1 µmol) and [µ–Cl(AuPPh$_3$)$_2$]BF$_4$ (3.55 mg, 3.41 µmol) in $CDCl_3$ (600 µL) furnished phenol (±)-**25b** (18.6 mg, 42.2 µmol, 62%) as yellow solid after column chromatography on silica gel (hexanes/EtOAc, 4/1).

(+)-4-Bromo-*N*-{(1*R*)-[1-hydroxymethyl-2-(5-methyl-2-furyl)ethyl]benzenesulfonamide (**26b**)**:** As described in GP 5, methyl ester **23b** (905 mg, 2.25 mmol), DIBALH (1.0 M in hexane) (5.85 mL) in THF (20 mL) are converted. Addition of MeOH (5 mL), 0.5 M hydrochloric acid (5 mL) and saturated aqueous potassium sodium tartrate (5 mL) furnished alcohol **26b** (738 mg, 1.97 mmol, 88%) after column chromatography on silica gel (hexanes/EtOAc/DCM, 10/1/1) as colourless solid. Mp. 87-88 °C. R_f (hexanes/EtOAc, 1/1) = 0.40. $[\alpha]_D^{20}$=+18.20 (c=1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.14 (s, 3H), 2.31 (br s, 1H), 2.71 (d, *J* = 6.8 Hz, 2H), 3.46 – 3.53 (m, 1H), 3.58 (dd, *J* = 11.3 Hz, 4.6 Hz, 1H), 3.67 (dd, *J* = 11.3 Hz, 4.2 Hz, 1H), 5.20 (d, *J* = 7.4 Hz, 1H), 5.76 (dd, *J* = 3.0

Hz, 1.1 Hz, 1H), 5.85 (d, *J* = 3.0 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 13.5 (q), 30.2 (t), 54.6 (d), 64.5 (t), 106.2 (d), 108.8 (d), 127.5 (s), 128.5 (d, 2C), 132.2 (d, 2C), 139.1 (s), 148.5 (s), 151.6 (s). IR (film): $\tilde{n}$ = 3542, 3304, 3154, 2917, 1572, 1470, 1448, 1415, 1324, 1279, 1242, 1155, 1090, 1067, 1040, 1015, 996, 942, 822, 794, 776, 738 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 375 (5)[^{81}Br-M$^+$], 373 (5)[^{79}Br-M$^+$], 280 (46), 278 (46), 221 (34), 219 (34), 157 (22), 155 (22), 95 (100). HRMS (EI (+), 70 eV): $C_{14}H_{16}{}^{79}BrNO_4S$: calcd. 372.9983; found 372.9984.

Racemic: As described in GP 5, methyl ester (±)-**23b** (752 mg, 1.87 mmol), DIBALH (1.0 M in hexane) (4.90 mL) in THF (20 mL) are converted. Addition of MeOH (5 mL), 0.5 M hydrochloric acid (5 mL) and saturated aqueous potassium sodium tartrate (5 mL) furnished alcohol (±)-**26b** (611 mg, 1.63 mmol, 87%) after column chromatography on silica gel (hexanes/EtOAc, 3/1) as colourless solid.

(+)-4-Bromo-*N*-{(1*R*)-2-hydroxy-1-[(5-methyl-2-furyl)methyl]ethyl}-*N*-prop-2-ynylbenzenesulfonamide (27b): As described in GP 4, sulfonamide **26b** (700 mg, 1.87 mmol), caesium carbonate (1.83 g, 5.61 mmol) and propargylbromide (80 wt% solution in toluene) (600 µL, 667 mg, 5.61 mmol) in acetone (25 mL) furnished propargylated sulfonamide **27b** (625 mg, 1.51 mmol, 81%) after column chromatography on silica gel (hexanes/EtOAc, 2/1) as viscous yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.20. $[\alpha]_D^{20}$=+24.20 (c=3.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.99 (br s, 1H), 2.19 (s, 3H), 2.26 (*app.* t, *J* = 2.5 Hz, 1H), 2.77 (dd, *J* = 15.2 Hz, 6.9 Hz, 1H), 2.84 (dd, *J* = 15.2 Hz, 7.7 Hz, 1H), 3.72 (dd, *J* = 12.3 Hz, 4.5 Hz, 1H), 3.77 (dd, *J* = 12.3 Hz, 7.9 Hz, 1H), 4.08 (dd, *J* = 18.8 Hz, 2.5 Hz, 1H), 4.21-4.26 (m, 1H), 4.25 (dd, *J* = 18.8 Hz, 2.5 Hz, 1H), 5.79 (dd, *J* = 3.0 Hz, 0.9 Hz, 1H), 5.87 (d, *J* = 3.0 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 13.5 (q), 28.3 (t), 32.7 (t), 59.6 (d), 62.9 (t), 73.0 (d), 79.6 (s), 106.2 (d), 108.3 (d), 127.6 (s),

129.0 (d, 2C), 132.0 (d, 2C), 139.3 (s), 148.8 (s), 151.3 (s). IR (film): $\tilde{n}$ = 3284, 2923, 1572, 1471, 1435, 1388, 1336, 1217, 1095, 1067, 1012, 882, 747 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 413 (7)[^{81}Br-M^+], 411 (6)[^{79}Br-M^+], 318 (100), 316 (98), 221 (31), 220 (30), 156 (40), 155 (41), 95 (73). HRMS (EI (+), 70 eV): $C_{17}H_{18}{}^{79}BrNO_4S$: calcd. 411.0140; found 411.0128.

Racemic: As described in GP 4, sulfonamide (±)-**26b** (609 mg, 1.63 mmol), caesium carbonate (1.59 g, 4.88 mmol) and propargylbromide (80 wt% solution in toluene) (500 µL, 580 mg, 4.88 mmol) in acetone (25 mL) furnished propargylated sulfonamide (±)-**27b** (539 mg, 1.31 mmol, 80%) after column chromatography on silica gel (hexanes/EtOAc, 5/1) as viscous yellow oil.

(-)-(3*R*)-4-[(4-Bromophenyl)sulfonyl]-6-methyl-3-[(5-methyl-2-furyl)methyl]-3,4-dihydro-2*H*-1,4-oxazine (28b): As described in GP 9, alkyne **27b** (11.1 mg, 269 µmol) and gold(III) chloride (5 wt% in CD_3CN) (8.20 mg, 1.35 µmol) in CD_3CN (600 µL) furnished compound **28b** (11.0 mg, 267 µmol, 99%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 10/1). Mp. 99-101°C. R_f (hexanes/EtOAc, 1/1) = 0.77. $[a]_D^{20}$=-180.00 (c=0.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.79 (d, *J* = 0.8 Hz, 3H), 2.25 (s, 3H), 2.75-2.84 (m, 3H), 3.82 (dd, *J* = 11.0 Hz, 1.1 Hz, 1H), 3.99-4.04 (m, 1H), 5.79 (s, 1H), 5.85 (dd, *J* = 2.9 Hz, 0.8 Hz, 1H), 5.99 (d, *J* = 2.9 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 13.58 (q), 17.72 (q), 29.15 (t), 51.03 (d), 63.67 (t), 97.71 (d), 106.15 (d), 108.60 (d), 127.92 (s), 128.88 (d, 2C), 132.43 (d, 2C), 136.15 (s), 140.56 (s), 149.06 (s), 151.45 (s). IR (neat): $\tilde{n}$ = 3097, 2921, 1678, 1570, 1461, 1353, 1301, 1199, 1163, 1072, 1032, 1010, 958, 916, 884, 779, 740, 702, 648 cm^{-1}. MS (FAB (+)): *m/z* (%): 413 (100)[^{81}Br-M^+], 411 (95)[^{79}Br-M^+], 318 (58), 316 (56), 193 (58), 95 (64). HRMS (FAB (+)): $C_{17}H_{18}{}^{81}BrNO_4S$: calcd. 413.0119; found 413.0127. $C_{17}H_{18}{}^{79}BrNO_4S$: calcd. 411.0139; found 411.0138.

(+)-4-Bromo-*N*-{(1*R*)-2-{[*tert*-butyl(dimethyl)silyl]oxy}-1-[(5-methyl-2-furyl)methyl]ethyl}-*N*-prop-2-ynylbenzenesulfonamide (29b): As described in GP 6, alcohol **27b** (288 mg, 700 µmol), imidazole (119 mg, 1.75 mmol) and TBDMSCl (127 mg, 839 µmol) in dimethyl formamide (6 mL) furnished protected alcohol **29b** (245 mg, 465 µmol, 66%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as colourless solid. Mp. 54-55°C. R_f (hexanes/EtOAc, 5/1) = 0.46. $[\alpha]_D^{20}$=+47.30 (c=1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.016 (s, 3H), 0.024 (s, 3H), 0.88 (s, 9H), 2.17 (t, *J* = 2.5 Hz, 1H), 2.19 (s, 3H), 2.80 (dd, *J* = 15.1 Hz, 6.8 Hz, 1H), 3.06 (dd, *J* = 15.1 Hz, 8.0 Hz, 1H), 3.74 (dd, *J* = 10.7 Hz, 4.9 Hz, 1H), 3.79 (dd, *J* = 10.7 Hz, 4.5 Hz, 1H), 4.11-4.15 (m, 1H), 4.27 (dd, *J* = 18.6 Hz, 2.5 Hz, 1H), 4.31 (dd, *J* = 18.6 Hz, 2.5 Hz, 1H), 5.79 (dd, *J* = 3.0 Hz, 1.0 Hz, 1H), 5.85 (d, *J* = 3.0 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -5.7 (q), -5.6 (q), 13.5 (q), 18.2 (s), 25.8 (q, 3C), 28.1 (t), 33.8 (t), 58.9 (d), 64.5 (t), 72.7 (d), 79.9 (s), 106.1 (d), 108.0 (d), 127.3 (s), 129.0 (d, 2C), 131.9 (d, 2C), 139.8 (s), 149.7 (s), 150.9 (s). IR (film): $\tilde{n}$ = 3268, 2931, 2859, 1571, 1466, 1433, 1388, 1258, 1214, 1118, 1091, 1049, 929, 902, 709, 677, 627 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 527 (1)[^{81}Br-M^+], 525 (1)[^{79}Br-M^+], 512 (1), 510 (1), 470 (32), 468 (28), 432 (11), 430 (10), 211 (100). HRMS (EI (+), 70 eV): $C_{23}H_{32}{}^{81}BrNO_4SSi$: calcd. 527.0984; found 527.0975; $C_{23}H_{32}{}^{79}BrNO_4SSi$: calcd. 525.1005; found 525.0989.

Racemic: As described in GP 6, alcohol (±)-**27b** (536 mg, 1.30 mmol), imidazole (230 mg, 3.38 mmol) and TBDMSCl (392 mg, 2.60 mmol) in dimethyl formamide (3 mL) furnished protected alcohol (±)-**29b** (620 mg, 1.18 mmol, 91%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as colourless solid.

(-)-(3*R*)-2-[(4-Bromophenyl)sulfonyl]-3-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-7-methyl-1,2,3,4-tetrahydroisoquinolin-8-ol (30b): As described in GP 9, alkyne **29b**

(87.0 mg, 165 µmol) and [µ–Cl(AuPPh$_3$)$_2$]BF$_4$ (1.72 mg, 1.65 µmol) in CDCl$_3$ (600 µL) furnished phenol **30b** (60.5 mg, 115 µmol, 70%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 5/1). Mp. 138-140 °C. R_f (hexanes/EtOAc, 5/1) = 0.06. HPLC: 96% *ee*, Chiralcel OD-H 5µ (eluent: isocratic 5% EtOH in hexane; flow 1 mL/min; temperature: 25 °C). Retention time: (+)-enantiomer: 4.38 min, (-)-enantiomer: 5.33 min. $[a]_D^{20}$=-5.30 (96% *ee*, c=0.16, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 500 MHz): δ = -0.03 (s, 3H), -0.02 (s, 3H), 0.84 (s, 9H), 2.17 (s, 3H), 2.74 (dd, *J* = 15.9 Hz, 6.0 Hz, 1H), 2.81 (dd, *J* = 15.9 Hz, 3.8 Hz, 1H), 3.50 (dd, *J* = 9.9 Hz, 8.1 Hz, 1H), 3.65 (dd, *J* = 9.9 Hz, 5.2 Hz, 1H), 4.14-4.18 (m, 1H), 4.20 (d, *J* = 16.6 Hz, 1H), 4.68 (d, *J* = 16.6 Hz, 1H), 4.88 (s, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (CDCl$_3$, 125.8 MHz): δ = -5.52 (q), -5.48 (q), 15.27 (q), 18.17 (s), 25.79 (q, 3C), 29.05 (t), 40.00 (t), 53.50 (d), 63.42 (t), 118.84 (s), 119.93 (s), 120.85 (d), 127.18 (s), 128.60 (s), 128.93 (d, 2C), 131.79 (d), 132.00 (d, 2C), 139.01 (s), 149.67 (s). IR (neat): $\tilde{n}$ = 3475, 2929, 2856, 2360, 1579, 1467, 1387, 1333, 1255, 1159, 1109, 1005, 906, 839, 780, 741, 631 cm^{-1}. MS (FAB(+)): *m/z* (%): 550 (100)[^{81}Br-M + Na$^+$], 548 (91)[^{79}Br-M + Na$^+$], 527 (13)[^{81}Br-M$^+$], 525 (13)[^{79}Br-M$^+$], 470 (24), 468 (20), 396 (13), 394 (12), 382 (12), 380 (13). $C_{23}H_{32}BrNO_4SSi$ (526.56): calcd. C 52.46, H 6.13, N 2.66; found C 52.48, H 6.10, N 2.61.

Racemic: As described in GP 9, alkyne (±)-**29b** (65.0 mg, 123 µmol) and [µ–Cl(AuPPh$_3$)$_2$]BF$_4$ (6.40 mg, 6.20 µmol) in CDCl$_3$ (600 µL) furnished phenol (±)-**30b** (40.4 mg, 76.7 µmol, 62%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 5/1).

(-)-Benzyl (1*R*)-[2-(5-methyl-2-furyl)-1-(hydroxymethyl)ethyl]carbamate (31b): As described in GP 5, methyl ester **16b** (750 mg, 2.36 mmol), DIBALH (1.0 M in hexane) (6.10 mL) in THF (30 mL) are converted. Addition of MeOH (10 mL), 0.5 M hydrochloric acid (10 mL) and saturated aqueous potassium sodium

tartrate (10 mL) furnished alcohol **31b** (552 mg, 1.91 mmol, 81%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as colourless solid. Mp. 42-43°C. R_f (hexanes/EtOAc, 3/1) = 0.46. $[\alpha]_D^{20}$=-8.32 (c=0.12, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.16 (br s, 1H), 2.23 (s, 3H), 2.85 (d, *J* = 6.5 Hz, 2H), 3.62 (dd, *J* = 11.2 Hz, 5.2 Hz, 1H), 3.67 (dd, *J* = 11.2 Hz, 4.2 Hz, 1H), 3.94-4.00 (m, 1H), 5.10 (s, 2H), 5.14 (br s, 1H), 5.85 (dd, *J* = 3.0 Hz, 0.9 Hz, 1H), 5.96 (d, *J* = 3.0 Hz, 1H), 7.30-7.38 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 13.5 (q), 29.8 (t), 52.2 (d), 64.5 (t), 66.8 (t), 106.6 (d), 108.7 (d), 128.0 (d, 2C), 128.1 (d), 128.5 (d, 2C), 136.4 (s), 149.7 (s), 151.4 (s), 162.4 (s). IR (neat): $\tilde{n}$ = 3314, 2926, 2361, 1688, 1538, 1456, 1426, 1377, 1317, 1270, 1233, 1137, 1085, 1017, 964, 892, 841, 777, 734, 688 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 289 (12)[M^+], 194 (13), 138 (13), 95 (39), 91 (100). HRMS (EI (+), 70 eV): $C_{16}H_{19}NO_4$: calcd. 289.1314; found 289.1315.

(+)-Benzyl (1*R*)-2-(5-methyl-2-furyl)-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethylcarbamate (32b): As described in GP 6, alcohol **31b** (222 mg, 768 µmol), imidazole (131 mg, 1.92 mmol) and TBDMSCl (139 mg, 922 µmol) in dimethyl formamide (5 mL) furnished protected alcohol **32b** (227 mg, 561 µmol, 73%) after column chromatography on silica gel (hexanes/EtOAc, 5/1) as light yellow oil. R_f (hexanes/EtOAc, 3/1) = 0.63. $[\alpha]_D^{20}$=+32.40 (c=1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.04 (s, 3H), 0.05 (s, 3H), 0.90 (s, 9H), 2.23 (d, *J* = 1.1 Hz, 3H), 2.84 (d, *J* = 6.7 Hz, 2H), 3.57 (dd, *J* = 10.0 Hz, 4.6 Hz, 1H), 3.62 (dd, *J* = 10.0 Hz, 3.5 Hz, 1H), 3.97 (br s, 1H), 5.06 (br s, 1H), 5.10 (s, 2H), 5.85 (dd, *J* = 3.0 Hz, 1.1 Hz, 1H), 5.94 (d, *J* = 3.0 Hz, 1H), 7.35-7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = -5.5 (q, 2C), 13.5 (q), 18.3 (s), 25.9 (q, 3C), 29.8 (t), 51.6 (d), 63.4 (t), 66.6 (t), 106.0 (d), 107.7 (d), 128.1 (br d, 3C), 128.5 (d, 2C), 136.6 (s), 150.4 (s), 151.0 (s), 155.8 (s). IR (neat): $\tilde{n}$ = 3326, 2929, 2856, 1707, 1505, 1464, 1387, 1252, 1220, 1113, 1055, 837, 778, 739, 697, 669, 631 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 403 (1)[M^+], 346 (7), 264

(14), 252 (28), 195 (14), 91 (100). $C_{22}H_{33}NO_4Si$ (403.59): calcd. C 65.47, H 8.24, N 3.47; found C 65.23, H 8.26, N 3.42.

(+)-Benzyl (1*R*)-2-(5-Methyl-2-furyl)-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethyl(prop-2-ynyl)carbamate (33b): As described in GP 7, carbamate **32b** (49.4 mg, 122 µmol), sodium hydride (3.50 mg, 147 µmol) and propargyl bromide (80 wt% solution in toluene) (16.0 µL, 17.5 mg, 147 µmol) in dimethyl formamide (5 mL) furnished propargylated carbamate **33b** (63.1 mg, 143 µmol, 87%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as light yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.74. $[\alpha]_D^{20}$=+18.30 (c=0.38, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) [due to superimposition of rotamers no determination of coupling constants possible]: δ = 0.01 (s, 3H), 0.02 (s, 3H), 0.88 (s, 9H), 2.14 (br m, 0.5H), 2.17 (br m, 0.5H), 2.19 (br s, 1.5H), 2.22 (br s, 1.5H), 2.94 (*app.* br d, *J* = 7.4 Hz, 1H), 3.03 (*app.* br d, *J* = 7.5 Hz, 1H), 3.71-3.87 (br m, 2H), 4.04-4.17 (br m, 2H), 4.19-4.32 (br m, 1H), 5.08-5.17 (br m, 2H), 5.81 (br s, 1H), 5.85-5.89 (br m, 1H), 7.28-7.42 (m, 5H). ^{13}C NMR ($CDCl_3$ (250.2K), 125.8 MHz) [superimposition of rotamers]: δ = -5.63 (q), -5.60 (q), -5.52 (q, 2C), 13.57 (q), 13.63 (q), 18.06 (s of both rotamers, hence 2C), 25.67 (q, 3C), 25.71 (q, 3C), 27.28 (t of both rotamers, hence 2C), 27.89 (t 2C), 57.54 (d of both rotamers, hence 2C), 63.21 (t), 63.43 (t), 66.98 (t), 67.35 (t), 70.65 (d), 70.72 (d), 80.60 (s), 80.67 (s), 105.85 (d), 105.92 (d), 107.27 (d), 107.51 (d), 127.43 (d of both rotamers, hence 2C), 127.77 (d of both rotamers, hence 3C), 127.93 (d), 128.32 (d of both rotamers, hence 2C), 128.38 (d of both rotamers, hence 2C), 136.09 (s), 136.40 (s), 150.06 (s), 150.29 (s), 150.64 (s), 150.70 (s), 155.13 (s), 155.85 (s). IR (neat): $\tilde{n}$ = 3297, 2935, 2858, 1703, 1458, 1419, 1247, 1113, 1016, 840, 778, 663 cm^{-1}. MS (DCI(+)): *m/z* (%): 442 (73)[M$^+$], 302 (30), 252 (91), 91 (100). HRMS (DCI(+)): $C_{25}H_{35}NO_4Si$: calcd. 441.2335; found 442.2404.

(-)-Benzyl (3*R*)–3-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-8-hydroxy-7-methyl-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (34b): As described in GP 9, alkyne **33b** (42.5 mg, 96.2 µmol) and [µ–Cl(AuPPh$_3$)$_2$]BF$_4$ (4.80 mg, 4.61 µmol) in CDCl$_3$ (600 µL) furnished phenol **34b** (35.9 mg, 81.3 µmol, 84%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 20/1). Mp. 103-105 °C. R_f (hexanes/EtOAc, 1/1) = 0.69. $[\alpha]_D^{20}$=-4.00 (c=0.11, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 500 MHz, 250 K) [superimposition of rotamers; * = main rotamer; ratio of rotamers = 2:1]: δ = -0.096 (s*, 3H), -0.091 (s*, 3H), -0.062 (s, 3H), -0.058 (s, 3H), 0.806 (s*, 9H), 0.812 (s, 9H), 2.22 (s, 3H), 2.25 (s*, 3H), 2.79 (dd*, *J* = 16.1 Hz, 2.3 Hz, 1H), 2.83 (dd, *J* = 16.2 Hz, 2.2 Hz, 1H), 2.93 (dd*, *J* = 16.1 Hz, 6.0 Hz, 1H), 2.97 (dd, *J* = 16.2 Hz, 6.0 Hz, 1H), 3.35 (dd*, *J* = 10.0 Hz, 7.7 Hz, 1H), 3.39 (dd, *J* = 10.0 Hz, 7.9 Hz, 1H), 3.51 (dd*, J = 10.0 Hz, 7.1 Hz, 1H), 3.53 (dd, *J* = 10.0 Hz, 7.1 Hz, 1H), 4.24 (d, *J* = 17.4 Hz, 1H), 4.33 (d*, *J* = 17.6 Hz, 1H), 4.52 (dddd*, *J* = 7.7 Hz, 7.1 Hz, 6.0 Hz, 2.3 Hz, 1H), 4.64 (dddd, *J* = 7.9 Hz, 7.1 Hz, 6.0 Hz, 2.2 Hz, 1H), 4.80 (d, *J* = 17.4 Hz, 1H), 4.90 (d*, *J* = 17.6 Hz, 1H), 4.99 (s, 1H), 5.15 (d*, *J* = 12.5 Hz, 1H), 5.18 (d*, *J* = 12.5 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.22 (d, *J* = 12.4 Hz, 1H), 6.53 (br s, 1H), 6.62 (d*, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.95 (d*, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 7.31-7.42 (m of both rotamers, 10H). ^{13}C NMR (CDCl$_3$, 125.8 MHz, 250K) [superimposition of rotamers; * = main rotamer; ratio of rotamers = 2:1]: δ = -5.15 (q, 2C), -5.11 (q*, 2C), 16.00 (q), 16.30 (q*), 18.49 (s), 18.54 (s*), 26.12 (q, 3C), 26.15 (q*, 3C), 29.13 (t), 29.47 (t*), 39.33 (t), 39.69 (t*), 50.79 (d), 51.49 (d*), 61.77 (t), 62.18 (t*), 67.49 (t), 67.69 (t*), 119.21 (s), 119.66 (s*), 119.89 (s), 120.76 (s*), 121.26 (d), 121.45 (d*), 128.38 (d of both rotamers, hence 4C), 128.46 (d of both rotamers, hence 2C), 128.90 (d of both rotamers, hence 6C), 131.29 (s*), 132.13 (s), 136.85 (s*), 137.05 (s), 150.20 (s), 150.94 (s*), 156.48 (s), 156.75 (s*). ^{13}C NMR (CD$_2$Cl$_2$, 125.8 MHz) [superimposition of rotamers; * = main rotamers; ratio of rotamers = 2:1]: δ = -5.46 (q of both rotamers, hence 4C), 15.52

(q), 15.62 (q*), 18.38 (s of both rotamers, hence 2C), 25.92 (q of both rotamers, hence 6C), 29.33 (t), 29.63 (t*), 39.44 (t), 39.57 (t*), 51.22 (t), 51.72 (t*), 62.23 (t), 62.56 (t*), 67.33 (t), 67.41 (t*), 119.62 (s), 119.78 (s*), 120.28 (s), 120.82 (s*), 121.13 (d), 121.45 (d*), 128.23 (d of both rotamers, hence 4C), 128.27 (d of both rotamers, hence 2C), 128.82 (d of both rotamers, hence 4C), 128.93 (d of both rotamers, hence 2C), 131.96 (s*), 132.35 (s), 137.41 (s), 137.62 (s*), 150.32 (s), 150.58 (s*), 156.23 (s), 156.40 (s*). IR (neat): $\tilde{n}$ = 3388, 2936, 2859, 2356, 1673, 1430, 1360, 1302, 1245, 1217, 1103, 1044, 999, 943, 901, 843, 774, 696 cm^{-1}. MS (EI(+), 70 eV): *m/z* (%): 441 (<1)[M^+], 426 (1), 384 (25), 340 (5), 306 (46), 252 (52), 91 (100). $C_{25}H_{35}NO_4Si$ (441.64): calcd. C 67.99, H 7.99, N 3.17; found C 68.01, H 8.05, N 3.08.

(-)-(4*R*)-4-[(5-Methyl-2-furyl)methyl]-3-prop-2-ynyl-1,3-oxazolidin-2-one (37b): As described in GP 8, alcohol **31b** (552 mg, 1.91 mmol), sodium hydride (138 mg, 5.73 mmol) and propargyl bromide (80 wt% solution in toluene) (320 µL, 341 mg, 2.87 mmol) in dimethyl formamide (5 mL) furnished propargylated carbamate **37b** (322 mg, 1.47 mmol, 77%) after column chromatography on silica gel (hexanes/EtOAc, 5/1) as light yellow oil. R_f (hexanes/EtOAc, 5/1) = 0.09. $[\alpha]_D^{20}$=-92.91 (c=0.86, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.24 (s, 3H), 2.30 (t, *J* = 2.5 Hz, 1H), 2.83 (dd, *J* = 15.0 Hz, 7.6 Hz, 1H), 3.05 (dd, *J* = 15.0 Hz, 3.9 Hz, 1H), 3.83 (dd, *J* = 17.9 Hz, 2.5 Hz, 1H), 4.13 (dd, *J* = 8.2 Hz, 6.3 Hz, 1H), 4.17-4.26 (m, 1H), 4.36-4.43 (m, 2H), 5.87 (dd, *J* = 3.0 Hz, 1.0 Hz, 1H), 5.99 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.47 (q), 30.54 (t), 32.22 (t), 53.52 (d), 67.07 (t), 73.23 (d), 76.83 (s), 106.23 (d), 108.73 (d), 147.36 (s), 151.99 (s), 157.54 (s). IR (neat): $\tilde{n}$ = 3287, 2358, 1755, 1569, 1432, 1353, 1252, 1092, 1022, 940, 896, 790, 644 cm^{-1}. MS (EI, 70 eV): *m/z* (%): 219 (15)[M^+], 177 (7), 124 (100). $C_{12}H_{13}NO_3$ (219.24.): calcd. C 65.74, H 5.98, N 6.39; found C 65.90, H 6.10, N 6.13.

(+)-(10a*R*)-6-Hydroxy-7-methyl-1,5,10,10a-tetrahydro[1,3]oxazolo[3,4-*b*]isochinolin-3-one (38b): As described in GP 9, alkyne **37b** (40.0 mg, 182 µmol) and [µ–Cl(AuPPh$_3$)$_2$]BF$_4$ (1.89 mg, 1.82 µmol) in $CDCl_3$ (600 µL) furnished phenol **38b** (19.9 mg, 90.8 µmol, 50%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 2/1). Mp. 110-112°C. R_f (hexanes/EtOAc, 1/1) = 0.17. $[\alpha]_D^{20}$=+121.36 (c=0.22, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.25 (s, 3H), 2.80-2.85 (*app.* m, actual dd, *J* = 15.1 Hz, 10.9 Hz, 1H), 2.91 (dd, *J* = 15.1 Hz, 4.1 Hz, 1H), 3.93-3.98 (dddd, *J* = 10.9 Hz, 7.9 Hz, 5.4 Hz, 4.1 Hz, 1H), 4.13 (dd, *J* = 8.6 Hz, 5.4 Hz, 1H), 4.33 (d, *J* = 17.5 Hz, 1H), 4.60 (*app.* t, actual dd, *J* = 8.6 Hz, 7.9 Hz, 1H), 4.91 (d, *J* = 17.5 Hz, 1H), 5.57 (br s, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 15.34 (q), 33.98 (t), 39.79 (t), 51.24 (d), 68.57 (t), 118.86 (s), 120.86 (d), 120.95 (s), 128.90 (d), 130.70 (s), 150.86 (s), 157.73 (s). IR (neat): $\tilde{n}$ = 3326, 2907, 1712, 1584, 1446, 1318, 1281, 1216, 1077, 1018, 809, 758, 720, 652, 611 cm^{-1}. MS (EI(+), 70 eV): *m/z* (%): 219 (100)[M$^+$], 204 (7), 175 (13), 158 (25), 142 (59), 134(93), 95 (32). $C_{12}H_{13}NO_3$ (219.24): calcd. C 65.74, H 5.98, N 6.39; found C 65.53, H 6.14, N 6.21.

(+)-Benzyl (1*R*)-2-(5-ethyl-2-furyl)-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethylcarbamate (32c): As described in GP 5, methyl ester **16c** (754 g, 2.28 mmol), DIBALH (1.0 M in hexane) (5.90 mL) in THF (10 mL) are converted. Addition of MeOH (5 mL), 0.5 M hydrochloric acid (5 mL) and saturated aqueous potassium sodium tartrate (5 mL) furnished the crude alcohol (654 mg) which was used in the next step without purification. As described in GP 6, the crude alcohol, imidazole (387 mg, 5.69 mmol) and TBDMSCl (686 mg, 4.55 mmol) in dimethyl formamide (15 mL) furnished protected alcohol (*R*)-**32c** (565 mg, 1.35 mmol, 59% overall) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as colourless oil. R_f (hexanes/EtOAc, 1/1) = 0.77. $[\alpha]_D^{20}$=+39.30 (c=1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.04

(s, 3H), 0.05 (s, 3H), 0.90 (s, 9H), 1.20 (t, *J* = 7.5 Hz, 3H), 2.58 (q, *J* = 7.5 Hz, 2H), 2.85 (d, *J* = 6.7 Hz, 2H), 3.55-3.65 (m, 2H), 3.90-4.05 (b m, 1H), 5.05 (bs, 1H), 5.10 (s, 2H), 5.85 (d, *J* = 3.0 Hz, 1H), 5.95 (d, *J* = 3.0 Hz, 1H), 7.31-7.27 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = -5.5 (q, 2C), 12.2 (q), 18.3 (s), 21.3 (t), 25.9 (q, 3C), 29.8 (t), 51.7 (d), 63.4 (t), 66.6 (t), 104.4 (d), 107.5 (d), 128.0 (br d, 3C), 128.5 (d, 2C), 136.6 (s), 150.3 (s), 155.8 (s), 156.8 (s). IR (neat): $\tilde{n}$ = 3445, 2932, 1718, 1507, 1464, 1253, 1114, 1062, 894, 838, 779 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 417 (<1)[M^+], 402 (1), 360 (11), 266 (53), 209 (28), 109 (29), 91 (100). $C_{23}H_{35}NO_4Si$ (417.61): calcd. C 66.15, H 8.45, N 3.35; found C 66.23, H 8.44, N 3.34.

(+)-Benzyl (1*R*)-2-(5-Ethyl-2-furyl)-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethyl(prop-2-ynyl)carbamate (33c): As described in GP 7, carbamate **32c** (211 mg, 505 µmol), sodium hydride (17.2 mg, 718 µmol) and propargyl bromide (80 wt% solution in toluene) (80.0 µL, 85.4 mg, 718 µmol) in dimethyl formamide (5 mL) furnished propargylated carbamate **33c** (229 mg, 503 µmol, >99%) after column chromatography on silica gel (hexanes/EtOAc, 50/1) as light yellow oil. R_f (hexanes/EtOAc, 3/1) = 0.53. $[\alpha]_D^{20}$=+28.00 (c=1.36, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.01 (s, 3H), 0.03 (s, 3H), 0.88 (s, 9H), 1.18 (*app.* td, *J* = 7.5 Hz, 1.5 Hz, 3H), 2.10-2.20 (m, 1H), 2.56 (*app.* quint, *J* = 7.3 Hz, 2H), 2.95 (*app.* d, *J* = 7.4 Hz, 1H), 3.03 (*app.* d, *J* = 7.5 Hz, 1H), 3.76-3.88 (m, 2H), 4.00-4.15 (m, 2H), 4.21-4.32 (m, 1H), 5.08-5.20 (m, 2H), 5.80-5.85 (m, 1H), 5.85-5.94 (m, 1H), 7.28-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) [superimposition of rotamers]: δ = -5.60 (q of both rotamers, hence 2C), -5.55 (q of both rotamers, hence 2C), 12.22 (q of both rotamers, hence 2C), 18.16 (s of both rotamers, hence 2C), 21.32 (t of both rotamers, hence 2C), 25.82 (q of both rotamers, hence 6C), 27.62 (t), 28.29 (t), 34.65 (t), 35.27 (t), 57.88 (d), 58.27 (d), 63.48 (t), 63.73 (t), 67.05 (t), 67.46 (t), 70.74 (d), 70.86 (d), 80.72 (s), 80.76 (s), 104.40 (d of both rotamers, hence 2C), 107.12 (d), 107.21 (d), 127.57 (d of

both rotamers, hence 2C), 127.80 (d of both rotamers, hence 2C), 127.91 (d of both rotamers, hence 2C), 128.37 (d of both rotamers, hence 4C), 136.44 (s), 136.73 (s), 150.29 (s), 150.48 (s), 155.18 (s), 155.93 (s), 156.47 (s), 156.52 (s). IR (neat): $\tilde{n}$ = 3434, 2957, 1704, 1459, 1246, 1115, 1010, 893, 838, 773, 697, 631 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 455 (1)[M^+], 302 (27), 266 (58), 209 (14), 91 (100). $C_{26}H_{37}NO_4Si$ (455.66): calcd. C 68.53, H 8.18, N 3.07; found C 68.55, H 8.22, N 2.99.

(-)-Benzyl (3*R*)–3-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-8-hydroxy-7-ethyl-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (34c): As described in GP 9, alkyne **33c** (37.4 mg, 82.1 µmol) and [µ–$Cl(AuPPh_3)_2]BF_4$ (4.30 mg, 4.13 µmol) in $CDCl_3$ (600 µL) furnished phenol **34c** (29.9 mg, 65.7 µmol, 80%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 20/1). Mp. 79-81 °C. R_f (hexanes/EtOAc, 3/1) = 0.49. $[\alpha]_D^{20}$=-26.63 (c=0.89, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) [superimposition of rotamers; * = main rotamers; ratio of rotamers = 3:2]: δ = -0.07 (br s*, 3.6H), -0.04 (br s, 2.4H), 0.83 (s, 9H), 1.24 (t, 3H), 2.54-2.66 (br m, 2H), 2.80-2.99 (br m, 2H), 3.36-3.48 (br m, 1H), 3.53-3.61 (br m, 1H), 4.25-4.37 (br m, 1H), 4.45-4.55 (br m*, 0.6H), 4.57-4.67 (br m, 0.4H), 4.75-4.90 (br m, 1H), 4.93 (br s, 0.4H), 5.21 (s, 2H), 5.64 (br s*, 0.6H), 6.66-6.71 (br m, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 7.29-7.43 (m, 5H). ^{13}C NMR (CD_2Cl_2, 125.8 MHz) [superimposition of rotamers; * = main rotamers; ratio of rotamers = 3:2]: δ = -5.45 (q of both rotamers, hence 4C), 14.29 (q of both rotamers, hence 2C), 18.39 (s of both rotamers, hence 2C), 22.87 (t*), 22.98 (t), 25.93 (q of both rotamers, hence 6C), 29.36 (t), 29.66 (t*), 39.50 (t), 39.67 (t*), 51.22 (d), 51.76 (d*), 62.34 (t), 62.63 (t*), 67.34 (t), 67.47 (t*), 119.80 (s), 119.96 (s*), 121.22 (d*), 121.62 (d), 126.53 (s), 127.21 (s*), 127.22 (d of both rotamers, hence 2C), 128.22 (d of both rotamers, hence 4C), 128.27 (d of both rotamers, hence 2C), 128.81 (d of both rotamers, hence 4C), 131.81 (s), 132.25 (s*), 137.43 (s*), 137.61 (s), 149.80 (s), 150.17 (s*), 156.24 (s), 156.48 (s*). IR (neat): $\tilde{n}$ = 3380, 3031, 2857, 1672,

1431, 1358, 1303, 1254, 1208, 1177, 1107, 1022, 998, 941, 889, 841, 772, 744, 696, 671, 628 cm^{-1}. MS (EI(+), 70 eV): *m/z* (%): 455 (3)[M^+], 440 (3), 398 (52), 320 (100), 266 (66), 91 (69). HRMS (EI, 70 eV): $C_{26}H_{37}NO_4Si$: calcd. 455.2492; found 455.2491.

(-)-Benzyl (1*R*)-[2-(4,5-dimethyl-2-furyl)-1-(hydroxymethyl)ethyl]carbamate (31d): As described in GP 5, methyl ester **16d** (1.42 g, 4.26 mmol), DIBALH (1.0 M in hexane) (11.1 mL) in THF (30 mL) are converted. Addition of MeOH (10 mL), 0.5 M hydrochloric acid (10 mL) and saturated aqueous potassium sodium tartrate (10 mL) furnished alcohol **31d** (768 mg, 2.53 mmol, 60%) after column chromatography on silica gel (hexanes/EtOAc, 2/1) as colourless solid. Mp. 76-78 °C. R_f (hexanes/EtOAc, 2/1) = 0.14. $[a]_D^{20}$=-3.55 (c=0.31, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.87 (s, 3H), 2.14 (s, 3H), 2.18 (br s, 1H), 2.80 (s, 1H), 2.82 (s, 1H), 3.59–3.70 (br m, 2H), 3.90–3.99 (br m, 1H), 5.10 (br s, 2H + 1H), 5.85 (s, 1H), 7.30–7.36 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 9.78 (q), 11.27 (q), 29.73 (t), 52.19 (d), 64.54 (t), 66.83 (t), 110.85 (d), 114.52 (s), 128.07 (d, 2C), 128.13 (d), 128.51 (d, 2C), 136.36 (s), 146.54 (s), 148.25 (s), 156.46 (s). IR (neat): $\tilde{n}$ = 3313, 2927, 2882, 1684, 1537, 1456, 1434, 1317, 1252, 1149, 1076, 1019, 739, 687, 612, 582 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 303 (11)[M^+], 194 (8), 152 (37), 109 (67), 91 (100). $C_{17}H_{21}NO_4$ (303.35): calcd. C 67.31, H 6.98, N 4.62; found C 67.26, H 7.00, N 4.50.

(+)-Benzyl (1*R*)-2-(4,5-dimethyl-2-furyl)-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethylcarbamate (32d): As described in GP 6, alcohol **31d** (545 mg, 1.80 mmol), imidazole (307 mg, 4.50 mmol) and TBDMSCl (543 mg, 3.60 mmol) in dimethyl formamide (4 mL) furnished protected alcohol **32d** (698 mg, 1.67 mmol, 93%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as colourless oil. R_f (hexanes/EtOAc, 2/1) = 0.66. $[a]_D^{20}$=+12.80 (c=1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.04 (s, 3H), 0.05 (s, 3H), 0.90 (s, 9H), 1.88 (s, 3H), 2.14 (s, 3H), 2.80 (br d, *J* = 6.5 Hz, 2H), 3.56 (dd, *J* = 9.9 Hz, 4.8 Hz, 1H), 3.62 (dd, *J* = 9.9 Hz,

2.8 Hz, 1H), 3.82-4.00 (br m, 1H), 4.84-5.13 (m, 3H, superimposition of rotamers, benzyl. CH_2 + NH), 5.83 (s, 1H), 7.30-7.38 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -5.50 (q, 2C), 9.82 (q), 11.25 (q), 18.27 (s), 25.87 (q, 3C), 29.69 (t), 51.69 (d), 63.48 (t), 66.56 (t), 110.32 (d), 114.32 (s), 128.03 (d, 2C), 128.06 (d), 128.48 (d, 2C), 136.67 (s), 146.10 (s), 149.08 (s), 155.82 (s). IR (neat): $\tilde{n}$ = 2939, 2855, 1718, 1506, 1458, 1251, 1114, 1060, 997, 893, 836, 773, 704 cm^{-1}. MS (EI, 70 eV): *m/z* (%): 417 (2)[M^+], 360 (6), 266 (60), 209 (26), 135 (16), 109 (43), 91 (100). $C_{23}H_{35}NO_4Si$ (417.61): calcd. C 66.15, H 8.45, N 3.35; found C 66.12, H 8.51, N 3.30.

(+)-Benzyl (1*R*)-2-(4,5-Dimethyl-2-furyl)-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethyl(prop-2-ynyl)carbamate (33d): As described in GP 7, carbamate **32d** (252 mg, 604 µmol), sodium hydride (17.4 mg, 724 µmol) and propargyl bromide (80 wt% solution in toluene) (76.0 µL, 80.4 mg, 724 µmol) in dimethyl formamide (5 mL) furnished propargylated carbamate **33d** (243 mg, 533 µmol, 88%) after column chromatography on silica gel (hexanes/EtOAc, 50/1) as light yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.80. $[\alpha]_D^{20}$=+66.80 (c=0.50, $CHCl_3$). ^1H NMR ($CDCl_3$, 250 MHz) [due to superimposition of rotamers no determination of coupling constants possible]: δ = 0.01 (s, 3H), 0.02 (s, 3H), 0.88 (s, 9H), 1.86 (s, 3H), 2.10-2.17 (br m, 4H), 2.89 (*app.* br d, *J* = 7.4 Hz, 1H), 2.98 (*app.* br d, *J* = 7.5 Hz, 1H), 3.71-3.87 (br m, 2H), 4.03-4.15 (br m, 2H), 4.16-4.32 (br m, 1H), 5.08-5.17 (br m, 2H), 5.77 (*app.* br d, *J* = 13.0 Hz, 1H), 7.28-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) [superimposition of rotamers]: δ = -5.59 (q of both rotamers, hence 2C), -5.54 (q of both rotamers, hence 2C), 9.84 (q of both rotamers, hence 2C), 11.22 (q of both rotamers, hence 2C), 18.16 (s of both rotamers, hence 2C), 25.83 (q of both rotamers, hence 6C), 27.56 (t), 28.21 (t), 34.54 (t), 35.30 (t), 57.83 (d), 58.31 (d), 63.47 (t), 63.76 (t), 67.04 (t), 67.44 (t), 70.72 (d), 70.84 (d), 80.76 (s), 80.80 (s), 109.90 (d), 110.01 (d), 114.31 (s of both rotamers, hence 2C), 127.57 (d of both rotamers, hence 2C),

127.79 (d), 127.90 (d of both rotamers, hence 3C), 128.40 (d of both rotamers, hence 4C), 136.47 (s), 136.76 (s), 145.82 (s of both rotamers, hence 2C), 149.09 (s), 149.31 (s), 155.21 (s), 155.98 (s). IR (neat): $\tilde{n}$ = 3300, 2936, 2860, 1701, 1578, 1456, 1418, 1328, 1245, 1111, 1003, 839, 774, 631 cm^{-1}. MS (CI (+)): *m/z* (%): 489 (29) [M + 2 NH_3^+], 488 (54), 472 (83)[M + NH_3^+], 470 (76), 454 (24)[M - H^+], 430 (48), 414 (100). $C_{26}H_{37}NO_4Si$ (455.66): calcd. C 68.53, H 8.18, N 3.07; found C 68.60, H 8.18, N 2.88.

(+)-4-Bromo-*N*-{(1*R*)-2-{[*tert*-butyl(dimethyl)silyl]oxy}-1-[(4,5-dimethyl-2-furyl)methyl]ethyl}benzenesulfonamide (35d): As described in GP 3, furyl alanine **32d** (695 mg, 1.66 mmol), Pd/C (83 mg) and cyclohexene (3.50 mL) in MeOH (30 mL) furnished the crude amine. Triethylamine (347 µL, 252 mg, 2.49 mmol), 4-bromobenzenesulfonyl chloride (468 mg, 1.83 mmol) and additional DMAP (20.3 mg, 166 µmol) in dichloromethane (30 mL) furnished the pure sulfonamide **35d** (837 mg, 1.66 mmol, >99%) after chromatography on silica gel (hexanes/EtOAc, 3/1) as colourless solid. Mp. 78-79 °C. R_f (hexanes/EtOAc, 3/1) = 0.43. $[a]_D^{20}$=+12.55 (c=0.51, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.02 (s, 3H), 0.03 (s, 3H), 0.88 (s, 9H), 1.83 (d, *J* = 0.5 Hz, 3H), 2.06 (s, 3H), 2.65 (dd, *J* = 15.0 Hz, 6.9 Hz, 1H), 2.71 (dd, *J* = 15.0 Hz, 6.2 Hz, 1H), 3.43-3.49 (m, 1H), 3.49 (dd, *J* = 9.7 Hz, 5.2 Hz, 1H), 3.59 (dd, *J* = 9.7 Hz, 3.1 Hz, 1H), 4.84 (br d, *J* = 7.7 Hz, 1H), 5.70 (s, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -5.53 (q, 2C), 9.75 (q), 11.23 (q), 18.23 (s), 25.82 (q, 3C), 30.26 (t), 54.44 (d), 64.25 (t), 110.88 (d), 114.46 (s), 127.20 (s), 128.49 (d, 2C), 132.01 (d, 2C), 139.71 (s), 146.35 (s), 147.97 (s). IR (neat): $\tilde{n}$ = 3300, 2926, 2856, 1641, 1576, 1466, 1389, 1328, 1251, 1158, 1121, 1087, 1062, 1000, 936, 832, 774, 736, 698, 605 cm^{-1}. MS (CI (+), 100 eV): *m/z* (%): 532 (4)[^{81}Br-M + $C_2H_5^+$], 530 (4)[^{79}Br-M + $C_2H_5^+$], 504 (54)[^{81}Br-MH^+], 502 (51)[^{79}Br-MH^+], 446 (100), 444 (92), 394 (23), 392 (22), 336 (30), 334 (27), 267 (70), 173 (60) 109 (38). HRMS (EI (+), 70 eV):

$C_{21}H_{32}{}^{81}BrNO_4SSi$: calcd. 503.0984; found 503.0990; $C_{21}H_{32}{}^{79}BrNO_4SSi$: calcd. 501.1005; found 501.1005.

(+)-4-Bromo-*N*-{(1*R*)-2-{[*tert*-butyl(dimethyl)silyl]oxy}-1-[(4,5-dimethyl-2-furyl)methyl]ethyl}-*N*-prop-2-ynylbenzenesulfonamide (29d): As described in GP 4, sulfonamide **35d** (754 mg, 1.50 mmol), caesium carbonate (1.47 g, 4.50 mmol) and propargylbromide (80 wt% solution in toluene) (250 µL, 268 mg, 2.25 mmol) in acetone (20 mL) furnished propargylated sulfonamide **29d** (747 mg, 1.38 mmol, 92%) after column chromatography on silica gel (hexanes/EtOAc, 20/1) as colourless solid. Mp. 46-48 °C. R_f (hexanes/EtOAc, 20/1) = 0.19. $[\alpha]_D^{20}$=+33.8 (c=0.55, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.028 (s, 3H), 0.033 (s, 3H), 0.88 (s, 9H), 1.84 (s, 3H), 2.09 (s, 3H), 2.18 (t, *J* = 2.5 Hz, 1H), 2.76 (dd, *J* = 15.1 Hz, 7.1 Hz, 1H), 3.00 (dd, *J* = 15.1 Hz, 7.5 Hz, 1H), 3.75 (dd, *J* = 10.6 Hz, 4.9 Hz, 1H), 3.81 (dd, *J* = 10.6 Hz, 4.7 Hz, 1H), 4.06-4.14 (m, 1H), 4.26 (dd, *J* = 18.6 Hz, 2.5 Hz, 1H), 4.32 (dd, *J* = 18.6 Hz, 2.5 Hz, 1H), 5.71 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = -5.68 (q), -5.59 (q), 9.80 (q), 11.21 (q), 18.16 (s), 25.80 (q, 3C), 27.89 (t), 33.75 (t), 58.99 (d), 64.70 (t), 72.64 (d), 79.98 (s), 110.51 (d), 114.44 (s), 127.12 (s), 128.91 (d, 2C), 131.78 (d, 2C), 139.72 (s), 145.98 (s), 148.37 (s). IR (neat): $\tilde{n}$ = 2927, 2856, 1575, 1464, 1388, 1345, 1255, 1159, 1094, 1003, 832, 777, 754, 608 cm^{-1}. MS (CI (+), 100 eV): *m/z* (%): 570 (3)[^{81}Br-M + $C_2H_5^+$], 568 (3)[^{79}Br-M + $C_2H_5^+$], 541 (26)[^{81}Br-M^+], 539 (24)[^{79}Br-M^+], 526 (18), 524 (16), 484 (73), 482 (68), 432 (34), 430 (30), 267 (89), 211 (100), 109 (38). MS (CI (-), 100 eV): *m/z* (%): 541 (1)[^{81}Br-M^+], 539 (1)[^{79}Br-M^+], 502 (4), 500 (4), 220 (100), 218 (98). $C_{24}H_{34}BrNO_4SSi$ (540.59): calcd. C 53.32, H 6.34, N 2.59; found C 53.47, H 6.33, N 2.59.

(-)-(3*R*)-2-[(4-Bromophenyl)sulfonyl]-3-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-6,7-dimethyl-1,2,3,4-tetrahydroisoquinolin-8-ol (30d): As described in GP 10, alkyne

29d (100 mg, 185 µmol) and [µ–Cl(AuPMes$_3$)$_2$]BF$_4$ (2.40 mg, 1.85 µmol) in dichloroethane (6 mL) furnished phenol **30d** (37.2 mg, 68.8 µmol, 37%) as light yellow solid after column chromatography on silica gel (hexanes/EtOAc, 20/1). Mp. 35-37 °C. R_f (hexanes/EtOAc, 5/1) = 0.26. $[\alpha]_D^{20}$=-21.43 (c=0.14, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 500 MHz): δ = -0.03 (s, 3H), -0.01 (s, 3H), 0.84 (s, 9H), 2.07 (s, 3H), 2.19 (s, 3H), 2.70 (dd, *J* = 15.9 Hz, 5.9 Hz, 1H), 2.75 (dd, *J* = 15.9 Hz, 3.7 Hz, 1H), 3.49 (dd, *J* = 9.9 Hz, 8.2 Hz, 1H), 3.65 (dd, *J* = 9.9 Hz, 5.3 Hz, 1H), 4.16 (d, *J* = 16.4 Hz, 1H), 4.14-4.18 (m, 1H), 4.64 (d, *J* = 16.4 Hz, 1H), 4.80 (s, 1H), 6.47 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (CDCl$_3$, 125.8 MHz): δ = -5.52 (q), -5.48 (q), 11.20 (q), 18.17 (s), 20.02 (q), 25.78 (q, 3C), 28.82 (t), 39.99 (t), 53.48 (d), 63.30 (t), 116.39 (s), 118.66 (s), 122.53 (d), 127.11 (s), 128.59 (d, 2C), 130.53 (s), 131.97 (d, 2C), 136.05 (s), 139.07 (s), 149.44 (s). IR (neat): $\tilde{n}$ = 3481, 2929, 2857, 1577, 1463, 1386, 1333, 1248, 1204, 1156, 1080, 1011, 832, 780, 743, 708, 661, 599 cm^{-1}. MS (CI(+)): *m/z* (%): 542 (100)[^{81}Br-M + H$^+$], 540 (93)[^{79}Br-M + H$^+$], 484 (28), 482 (25), 320 (90). HRMS (CI(+)): $C_{24}H_{34}BrNO_4SSi$: ^{81}Br-M + H$^+$: calcd. 542.1219; found 542.1220; ^{79}Br-M + H$^+$: calcd. 540.1239; found 540.1215.

(-)-(4*R*)-4-[(4,5-Dimethyl-2-furyl)methyl]-3-prop-2-ynyl-1,3-oxazolidin-2-one (37d): As described in GP 8, alcohol **31d** (200 mg, 659 µmol), sodium hydride (47.5 mg, 1.98 mmol) and propargyl bromide (80 wt% solution in toluene) (110 µL, 118 mg, 989 µmol) in dimethyl formamide (5 mL) furnished propargylated carbamate **37d** (126 mg, 541 µmol, 82%) after column chromatography on silica gel (hexanes/EtOAc, 5/1) as yellow oil. R_f (hexanes/EtOAc, 2/1) = 0.28. $[\alpha]_D^{20}$=-133.10 (c=0.42, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 1.88 (s, 3H), 2.14 (s, 3H), 2.30 (t, *J* = 2.5 Hz, 1H), 2.78 (dd, *J* = 15.1 Hz, 7.8 Hz, 1H), 3.00 (dd, *J* = 15.1 Hz, 3.9 Hz, 1H), 3.83 (dd, *J* = 17.9 Hz, 2.5 Hz, 1H), 4.12 (dd, *J* = 8.5 Hz, 6.5 Hz, 1H), 4.17-4.22 (m, 1H), 4.36-4.41 (m, 2H), 5.88 (s, 1H). ^{13}C NMR (CDCl$_3$, 125.8 MHz): δ = 9.75 (q), 11.25 (q), 30.44 (t), 32.22 (t), 53.55 (d),

67.10 (t), 73.21 (d), 76.88 (s), 111.25 (d), 114.63 (s), 146.06 (s), 147.14 (s), 157.59 (s). IR (neat): $\tilde{n}$ = 3286, 2922, 1758, 1641, 1574, 1432, 1353, 1250, 1189, 1092, 1022, 645 cm^{-1}. MS (CI (+), 100 eV): *m/z* (%): 234 (41)[MH^+], 233 (9)[M^+], 135 (15), 124 (32), 109 (100). HRMS (CI (+)): $C_{13}H_{15}NO_3$: calcd. 233.1052; found 233.1056.

(+)-(9a*R*)-2,3-Dimethyl-4-methylene-4,9,9a,10-tetrahydro-5*H*-furo[2,3-*d*][1,3]oxazolo[3,4-*a*]azepin-7-one (39d): As described in GP 9, alkyne **37d** (20.1 mg, 81.2 µmol) and [µ–Cl($AuPPh_3$)$_2$]BF_4 (8.97 mg, 8.12 µmol) in $CDCl_3$ (600 µL) furnished product **39d** (6.30 mg, 27.0 µmol, 33%) as colourless solid after column chromatography on silica gel (hexanes/EtOAc, 2/1). Mp. 111-113°C. R_f (hexanes/EtOAc, 2/1) = 0.23. $[a]_D^{20}$=+52.22 (c=0.45, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.94 (s, 3H), 2.18 (s, 3H), 2.97 (br s, 1H), 2.98 (*app.* d, *J* = 2.4 Hz, 1H), 3.81 (dd, *J* = 13.9 Hz, 1.1 Hz, 1H), 3.95 (dd, *J* = 8.6 Hz, 5.8 Hz, 1H), 4.02-4.08 (m, 1H), 4.40 (d, *J* = 13.9 Hz, 1H), 4.47 (*app.* t, *J* = 8.4 Hz, 1H), 5.17 (d, *J* = 1.1 Hz, 1H), 5.38 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 9.55 (q), 11.33 (q), 34.19 (t), 51.71 (t), 54.32 (d), 67.46 (t), 113.97 (s), 116.91 (t), 122.88 (s), 135.03 (s), 144.96 (s), 146.47 (s), 157.48 (s). IR (neat): $\tilde{n}$ = 2916, 1736, 1622, 1419, 1293, 1249, 1079, 1031, 995, 913, 838, 794, 757, 701, 651, 610 cm^{-1}. MS (CI (+)): *m/z* (%): 234 (100) [M + H^+], 233 (75)[M^+]. HRMS (CI (+)): $C_{13}H_{15}NO_3$: [$MH]^+$: calcd. 234.1130; found 234.1131; M^+: calcd. 233.1052; found 233.1054.

(-)-Benzyl (1*R*)-2-{5-[*tert*-butyl(dimethyl)silyl]-2-furyl}-1-(hydroxymethyl)ethyl]carbamate (31e): As described in GP 5, methyl ester **16e** (1.09 g, 2.61 mmol), DIBALH (1.0 M in hexane) (6.80 mL) in THF (30 mL) are converted. Addition of MeOH (10 mL), 0.5 M hydrochloric acid (10 mL) and saturated aqueous potassium sodium tartrate (10 mL) furnished alcohol **31e** (593 mg, 1.52 mmol, 58%) after column chromatography on silica gel (hexanes/EtOAc, 4/1) as colourless solid. R_f (hexanes/EtOAc, 4/1) = 0.09. $[a]_D^{20}$=-7.63

(c=3.00, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.20 (s, 6H), 0.90 (s, 9H), 2.17 (br s, 1H), 2.95 (d, *J* = 6.3 Hz, 2H), 3.59 (dd, *J* = 11.1 Hz, 5.1 Hz, 1H), 3.65 (dd, *J* = 11.1 Hz, 4.0 Hz, 1H), 3.97-4.03 (m, 1H), 5.09 (s, 2H), 5.18 (br d, *J* = 6.7 Hz, 1H), 6.09 (d, *J* = 3.1 Hz, 1H), 6.54 (d, *J* = 3.1 Hz, 1H), 7.29-7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -6.37 (q), -6.35 (q), 16.69 (s), 26.29 (q, 3C), 29.83 (t), 52.28 (d), 64.54 (t), 66.83 (t), 107.58 (d), 121.77 (d), 128.03 (d), 128.10 (d, 2C), 128.48 (d, 2C), 136.33 (s), 155.79 (s), 156.44 (s), 158.26 (s). IR (film): $\tilde{n}$ = 3315, 2930, 2856, 2360, 1699, 1524, 1461, 1418, 1346, 1253, 1057, 935, 803, 779, 631 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 389 (1)[M^+], 332 (6), 224 (100). $C_{21}H_{31}NO_4Si$ (389.56): calcd. C 64.75, H 8.02, N 3.60; found C 64.88, H 8.07, N 3.56.

(+)-Benzyl (1*R*)-2-{5-[*tert*-Butyl(dimethyl)silyl]-2-furyl}-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethylcarbamate (32e): As described in GP 6, alcohol **31e** (205 mg, 526 µmol), imidazole (89.5 mg, 1.32 mmol) and TBDMSCl (159 mg, 1.05 mmol) in dimethyl formamide (2 mL) furnished protected alcohol **32e** (252 mg, 500 µmol, 95%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as colourless solid. Mp. 43-45°C. R_f (hexanes/EtOAc, 1/1) = 0.80. $[\alpha]_D^{20}$=+6.93 (c=1.40, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.02 (s, 3H), 0.03 (s, 3H), 0.19 (s, 6H), 0.89 (s, 9H), 0.90 (s, 9H), 2.94 (br d, *J* = 6.6 Hz, 2H), 3.55 (dd, *J* = 9.9 Hz, 4.9 Hz, 1H), 3.59 (dd, *J* = 9.9 Hz, 3.4 Hz, 1H), 3.95-4.05 (br m, 1H), 4.75-5.15 (m, 3H, superimposition of rotamers, benzyl. CH_2 + NH), 6.01-6.10 (br m, superimposition of rotamers, 1H), 6.53 (d, *J* = 3.1 Hz, 1H), 7.29-7.39 (m, 5H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -6.31 (q), -6.29 (q), -5.50 (q), -5.49 (q), 16.74 (s), 18.24 (s), 25.86 (q, 3C), 26.35 (q, 3C), 29.80 (t), 51.72 (d), 63.48 (t), 66.56 (t), 107.16 (d), 121.69 (d), 128.02 (d, 2C + d, 1C), 128.47 (d, 2C), 136.61 (s), 155.77 (s), 155.60 (s), 157.72 (s). IR (neat): $\tilde{n}$ = 3287, 2932, 2889, 2855, 1695, 1548, 1496, 1462, 1290, 1249, 1105, 1066, 1036, 1008, 935, 830, 773, 674 cm^{-1}. MS (FAB (+)): *m/z* (%): 526 (37)[M + Na^+], 504 (5)[MH^+], 446 (15),

91 (100). $C_{27}H_{45}NO_4Si_2$ (503.82): calcd. C 64.37, H 9.00, N 2.78; found C 64.16, H 8.94, N 2.79.

(+)-Benzyl (1*R*)-2-{5-[*tert*-Butyl(dimethyl)silyl]-2-furyl}-1-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)ethyl(prop-2-ynyl)carbamate (33e): As described in GP 7, carbamate **32e** (106 mg, 210 µmol), sodium hydride (6.05 mg, 252 µmol) and propargyl bromide (80 wt% solution in toluene) (35.0 µL, 37.4 mg, 314 µmol) in dimethyl formamide (2 mL) furnished propargylated carbamate **33e** (94.5 mg, 174 µmol, 83%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as light yellow oil. R_f (hexanes/EtOAc, 1/1) = 0.74. $[a]_D^{20}$=+16.98 (c=0.43, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz) [superimposition of rotamers]: δ = -0.01-0.02 (m, 6H), 0.18 (s, 3H), 0.19 (s, 3H), 0.86-0.89 (m, 18H), 2.10-2.19 (m, 1H), 2.92-3.13 (m, 2H), 3.51-4.33 (m, 4.5H), 5.05-5.27 (m, 2.5H), 5.97-6.06 (m, 1H), 6.50-6.54 (m, 1H), 7.30-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) [superimposition of rotamers]: δ = -6.31 (q), -6.30 (q), -6.25 (q of both rotamers, hence 2C), -5.56 (q), -5.53 (q of both rotamers, hence 2C), -5.50 (q), 16.72 (s of both rotamers, hence 2C), 18.15 (s), 18.25 (s), 25.83 (q, 3C), 25.85 (q, 3C), 26.35 (q of both rotamers, hence 6C), 27.85 (t), 28.52 (t), 34.77 (t), 35.23 (t), 57.97 (d), 58.40 (d), 63.48 (t), 63.63 (t), 67.10 (t), 67.51 (t), 79.87 (d), 71.00 (d), 80.64 (s), 80.69 (s), 106.75 (d), 107.17 (d), 121.69 (d), 121.75 (d), 127.59 (d of both rotamers, hence 2C), 127.81 (d of both rotamers, hence 2C), 128.02 (d of both rotamers, hence 2C), 128.38 (d of both rotamers, hence 2C), 128.47 (d of both rotamers, hence 2C), 136.60 (s), 136.68 (s), 155.78 (s of both rotamers, hence 2C), 156.60 (s), 156.66 (s), 156.93 (s), 157.35 (s). IR (neat): $\tilde{n}$ = 3525, 3361, 2933, 2889, 1698, 1517, 1461, 1369, 1327, 1237, 1151, 1010, 929, 841, 779, 689 cm^{-1}. MS (FAB (+)): *m/z* (%): 564 (9)[M + Na^+], 542 (5)[MH^+], 484 (9), 434 (5), 352 (16), 91 (100). $C_{30}H_{47}NO_4Si_2$ (541.87): calcd. C 66.50, H 8.74, N 2.58; found C 66.24, H 8.90, N 2.66.

(+)-4-Bromo-*N*-{(1*R*)-2-{[*tert*-butyl(dimethyl)silyl]oxy}-1-{[5-*tert*-butyl(dimethyl)silyl-2-furyl]methyl}ethyl}benzenesulfonamide (35e): As described in GP 3, furyl alanine **32e** (261 mg, 518 µmol), Pd/C (26 mg) and cyclohexene (1.10 mL) in MeOH (10 mL) furnished the crude amine. Triethylamine (108 µL, 78.6 mg, 777 µmol), 4-bromobenzenesulfonyl chloride (146 mg, 570 µmol) and additional DMAP (6.30 mg, 51.8 µmol) in dichloromethane (30 mL) furnished the pure sulfonamide **35e** (148 mg, 251 µmol, 49%) after chromatography on silica gel (hexanes/EtOAc, 20/1) as colourless solid. Mp. 62-64 °C. R_f (hexanes/EtOAc, 20:1) = 0.11. $[\alpha]_D^{20}$=+6.36 (c=0.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = -0.03 (s, 3H), -0.01 (s, 3H), 0.19 (s, 3H), 0.20 (s, 3H), 0.85 (s, 9H), 0.90 (s, 9H), 2.82 (dd, *J* = 14.9 Hz, 7.4 Hz, 1H), 2.89 (dd, *J* = 14.9 Hz, 5.1 Hz, 1H), 3.43 (dd, *J* = 9.9 Hz, 5.0 Hz, 1H), 3.49 (dd, *J* = 9.9 Hz, 4.1 Hz, 1H), 3.50-3.56 (m, 1H), 4.93 (d, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 3.1 Hz, 1H), 6.50 (d, *J* = 3.1 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -6.30 (q), -6.27 (q), -5.55 (q), -5.52 (q), 16.76 (s), 18.21 (s), 25.81 (q, 3C), 26.35 (q, 3C), 30.38 (t), 54.49 (d), 63.62 (t), 107.73 (d), 121.77 (d), 127.47 (s), 128.58 (d, 2C), 132.33 (d, 2C), 139.86 (s), 155.51 (s), 158.17 (s). IR (neat): $\tilde{n}$ = 3287, 3097, 2932, 2856, 1576, 1467, 1398, 1333, 1253, 1163, 1100, 1058, 1009, 979, 930, 830, 777, 739, 674, 648 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 574 (3), 572 (3), 532 (90), 530 (79), 394 (10), 392 (9), 336 (9), 334 (8), 294 (10), 292 (9), 173 (72), 116 (29), 75 (37), 73 (100). $C_{25}H_{42}BrNO_4SSi_2$ (588.75): calcd. C 51.00, H 7.19, N 2.38; found C 51.26, H 7.21, N 2.28.

(+)-4-Bromo-*N*-{(1*R*)-2-{[*tert*-butyl(dimethyl)silyl]oxy}-1-{[5-*tert*-butyl(dimethyl)silyl-2-furyl]methyl}ethyl}-*N*-prop-2-ynylbenzenesulfonamide (29e): As described in GP 4, sulfonamide **35e** (124 mg, 210 µmol), caesium carbonate (206 mg, 631 µmol) and propargylbromide (80 wt% solution in toluene) (70 µL, 74.9 mg, 630 µmol) in acetone (3 mL) furnished propargylated sulfonamide **29e** (108 mg, 174 µmol, 83%) after column chromatography on silica

gel (hexanes/EtOAc, 50/1) as colourless solid. Mp. 50-52 °C. R_f (hexanes/EtOAc, 20/1) = 0.20. $[\alpha]_D^{20}$=+164.86 (c=0.35, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = -0.01 (s, 3H), 0.00 (s, 3H), 0.20 (s, 3H), 0.21 (s, 3H), 0.86 (s, 9H), 0.91 (s, 9H), 2.16 (t, *J* = 2.5 Hz, 1H), 2.86 (dd, *J* = 14.9 Hz, 5.6 Hz, 1H), 3.18 (dd, *J* = 14.9 Hz, 9.0 Hz, 1H), 3.69 (dd, *J* = 10.8 Hz, 5.2 Hz, 1H), 3.76 (dd, *J* = 10.8 Hz, 4.3 Hz, 1H), 4.14-4.19 (m, 1H), 4.28 (d, *J* = 2.5 Hz, 2H), 5.98 (d, *J* = 3.1 Hz, 1H), 6.50 (d, *J* = 3.1 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -6.28 (q), -6.24 (q), -5.69 (q), -5.61 (q), 16.73 (s), 18.14 (s), 25.79 (q, 3C), 26.34 (q, 3C), 28.42 (t), 33.90 (t), 58.78 (d), 64.12 (t), 72.81 (d), 79.79 (s), 107.29 (d), 121.78 (d), 127.36 (s), 129.07 (d, 2C), 131.98 (d, 2C), 139.74 (s), 155.89 (s), 157.81 (s). IR (neat): $\tilde{n}$ = 3303, 2932, 2856, 1578, 1468, 1390, 1350, 1254, 1163, 1098, 1007, 833, 780, 746, 672, 643, 611, 575 cm^{-1}. MS (EI (+), 70 eV): *m/z* (%): 627 (<1)[^{81}Br-M^+], 625 (<1)[^{79}Br-M^+], 612 (2), 610 (2), 570 (42), 568 (35), 432 (9), 430 (8), 352 (16), 211 (100). $C_{28}H_{44}BrNO_4SSi_2$ (626.79): calcd. C 53.65, H 7.08, N 2.23; found C 54.01, H 7.14, N 2.23.

(+)-(7*R*)-6-[(4-bromophenyl)sulfonyl]-2-[*tert*-butyl(dimethyl)silyl]-7-({[*tert*-butyl(dimethyl)silyl]oxy}methyl-4-methylene-5,6,7,8-tetrahydro-4*H*-furo[2,3-*d*]azepine (36e): As described in GP 9, alkyne **29e** (36.1 mg, 50.4 µmol) and [µ–$Cl(AuPPh_3)_2]BF_4$ (5.35 mg, 5.04 µmol) in $CDCl_3$ (600 µL) furnished furo[2,3-*d*]azepine **36e** (26.4 mg, 42.1 µmol, 84%) as colourless viscous oil after column chromatography on silica gel (hexanes/EtOAc, 50/1). R_f (hexanes/EtOAc, 50/1) = 0.20. $[\alpha]_D^{20}$=+46.67 (c=0.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.11 (s, 3H), 0.12 (s, 3H), 0.17 (s, 3H), 0.18 (s, 3H), 0.88 (s, 9H), 0.93 (s, 9H), 2.99 (dd, *J* = 16.1 Hz, 10.0 Hz, 1H), 3.28 (dd, *J* = 16.1 Hz, 11.6 Hz, 1H), 3.82 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 3.89 (dd, *J* = 10.0 Hz, 5.4 Hz, 1H), 4.04-4.13 (m, 1H), 4.32 (d, *J* = 16.7 Hz, 1H), 4.48 (d, *J* = 16.7 Hz, 1H), 4.99 (s, 2H), 6.22 (s, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -

6.30 (q), -6.15 (q), 5.51 (q), -5.41 (q), 16.60 (s), 18.25 (s), 25.91 (q, 3C), 26.32 (q, 3C), 28.37 (t), 49.55 (t), 58.57 (d), 67.08 (t), 110.08 (t), 118.88 (d), 119.51 (s), 126.64 (s), 128.89 (d, 2C), 131.21 (d, 2C), 136.07 (s), 139.18 (s), 153.30 (s), 157.72 (s). IR (neat): $\tilde{n}$ = 2933, 2857, 1641, 1466, 1347, 1250, 1156, 1078, 912, 830, 775, 733, 651, 612 cm^{-1}. MS (CI (+)): *m/z* (%): 627 (40)[^{81}Br-M$^+$], 625 (32)[^{79}Br-M$^+$], 612 (27), 610 (18), 570 (100), 568 (85), 407 (95). HRMS (CI (+)): $C_{28}H_{44}{}^{79}BrNO_4SSi_2$: calcd. 625.1713; found 625.1727.

(-)-(4*R*)-4-{5-[*tert*-Butyl(dimethyl)silyl]-2-furyl}methyl]-3-prop-2-ynyl-1,3-oxazolidin-2-one (37e): As described in GP 8, alcohol **31e** (101 mg, 260 µmol), sodium hydride (9.40 mg, 779 µmol) and propargyl bromide (80 wt% solution in toluene) (45.0 µL, 46.5 mg, 390 µmol) in dimethyl formamide (5 mL) furnished propargylated carbamate **37e** (69.0 mg, 216 µmol, 83%) after column chromatography on silica gel (hexanes/EtOAc, 10/1) as light yellow oil. R_f (hexanes/EtOAc, 1:1) = 0.63. $[\alpha]_D^{20}$=-24.35 (c=0.46, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.20 (s, 6H), 0.90 (s, 9H), 2.30 (t, *J* = 2.5 Hz, 1H), 2.93 (dd, *J* = 15.0 Hz, 7.3 Hz, 1H), 3.15 (dd, *J* = 15.0 Hz, 3.8 Hz, 1H), 3.84 (dd, *J* = 17.8 Hz, 2.5 Hz, 1H), 4.15 (dd, *J* = 7.8 Hz, 6.4 Hz, 1H), 4.18-4.28 (m, 1H), 4.36-4.45 (m, 2H), 6.12 (d, *J* = 3.1 Hz, 1H), 6.55 (d, *J* = 3.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = -6.38 (q), -6.33 (q), 16.72 (s), 26.28 (q, 3C), 30.66 (t), 32.22 (t), 53.60 (d), 67.10 (t), 73.30 (d), 76.82 (s), 108.02 (d), 121.68 (d), 153.49 (s), 157.45 (s), 159.04 (s). IR (neat): $\tilde{n}$ = 3295, 2933, 2858, 2352, 1757, 1430, 1251, 1191, 1094, 1013, 892, 772, 678, 631 cm^{-1}. MS (FAB (+)): *m/z* (%): 342 (100)[M + Na$^+$], 320 (9), 73 (10). HRMS (FAB (+), 70 eV): $C_{17}H_{25}NNaO_3Si$: calcd. 342.1501; found 342.1504.

(+)-(9a*R*)-2-[*tert*-Butyl(dimethyl)silyl]-4-methylene-4,9,9a,10-tetrahydro-5*H*-furo[2,3-*d*][1,3]oxazolo[3,4-*a*]azepin-7-one (39e): As described in GP 9, alkyne **37e** (41.0 mg, 128 µmol) and [µ–$Cl(AuPPh_3)_2$]BF_4 (6.68 mg, 6.42 µmol) in $CDCl_3$ (600 µL) furnished

product **39e** (15.3 mg, 47.9 µmol, 37%) as colourless viscous oil after column chromatography on silica gel (hexanes/EtOAc, 10/1). R_f (hexanes/EtOAc, 3/1) = 0.14. $[\alpha]_D^{20}$=+36.67 (c=0.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.21 (s, 6H), 0.92 (s, 9H), 3.05 (dd, *J* = 16.3 Hz, 9.3 Hz, 1H), 3.17 (dd, *J* = 16.3 Hz, 3.8 Hz, 1H), 3.92 (dt, *J* = 14.6 Hz, 1.3 Hz, 1H), 3.94 (dd, *J* = 8.7 Hz, 6.1 Hz, 1H), 4.11-4.16 (m, 1H), 4.47 (dd, *J* = 14.6 Hz, 0.8 Hz, 1H), 4.48 (*app.* t, *J* = 8.5 Hz (mean coupling constant), 1H), 5.19 (*app.* q, *J* = 1.1 Hz, 1H), 5.26 (*app.* t, *J* = 1.1 Hz, 1H), 6.64 (s, 1H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = -6.30 (q, 2C), 16.73 (s), 26.30 (q, 3C), 34.08 (t), 50.20 (t), 54.61 (d), 67.55 (t), 113.97 (t), 121.37 (d), 122.09 (s), 135.22 (s), 151.29 (s), 157.55 (s), 157.84 (s). IR (neat): $\tilde{n}$ = 2931, 2856, 1747, 1639, 1413, 1250, 1190, 1110, 1010, 937, 898, 815, 770, 679, 649 cm^{-1}. MS (CI (+)): *m/z* (%): 320 (100)[M + H^+], 319 (40)[M^+], 262 (59), 177 (14). HRMS (CI (+)): $C_{17}H_{25}NO_3Si$: [MH]$^+$: calcd. 320.1676; found 320.1666; M^+: calcd. 319.1604; found 319.1603.

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