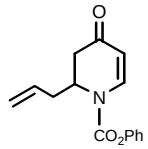
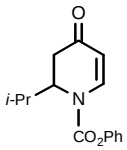
Supplemental Material

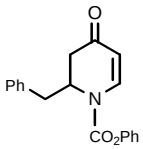
Compounds **6a-c** were prepared according to the general procedure described by Comins, D. L. and Brown, J. D. in *Tetrahedron Lett.* **1986**, *27*, 4549-4552.



6a: IR (KBr) 1738, 1672, 1605, 1332, 1303, 1287, 1259 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90(d, 1H, *J* = 4.9 Hz); 7.13-7.45(m, 5H); 5.80(m, 1H); 5.45(bd, 1H, *J* = 7.6 Hz); 5.14(m, 2H); 4.80(m, 1H); 2.90(m, 1H); 2.60(m, 2H); 2.40(m, 1H); ^{13}C NMR ($CDCl_3$) δ 35.4, 39.5, 53.1, 108.2, 119.4, 121.2, 126.4, 129.6, 132.8, 141.0, 150.4, 192.5 ppm; Exact mass calculated for $C_{15}H_{16}NO_3$, 258.1130, found: 258.1103.

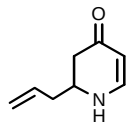


6b: IR (KBr) 1737, 1675, 1606, 1332, 1273, 1262, 1191 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.99(bd, 1H, *J* = 7.6 Hz); 7.20-7.50(m, 5H); 5.35(d, 1H, *J* = 8.4 Hz); 4.37(m, 1H); 2.98(dd, 1H, *J* = 6.5 and 16.5 Hz); 2.50(solvent obscured multiplet, 1H); 2.10(m, 1H); 0.93(d, 6H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 18.9, 19.6, 29.1, 38.4, 59.3, 108.8, 121.2, 126.3, 129.6, 141.5, 150.5, 193.2 ppm; Exact mass calculated for $C_{15}H_{18}NO_3$, 260.1286, found: 260.1288.

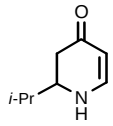


6c: IR (KBr) 1737, 1674, 1606, 1335, 1301, 1261, 1193 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 90°C) δ 7.94(dd, 1H, *J* = 1.7 and 8.5 Hz); 6.9-7.4(m, 10H); 5.42(dd, 1H, *J* = 1.2 and 8.3 Hz); 4.89(bdd, 1H, *J* = 5.0 and 6.0 Hz); 2.88-3.05(m, 3H); 2.32(dt, 1H, *J* = 1.5 and 16.6 Hz); ^{13}C NMR ($CDCl_3$) δ 36.6, 39.0, 55.3, 108.2, 121.3, 126.4, 127.1, 128.8, 129.6, 129.7, 136.4, 141.0, 150.4, 192.7 ppm. Exact mass calculated for $C_{19}H_{18}NO_3$, 308.1286, found: 308.1287.

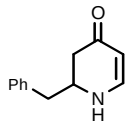
General procedure for the synthesis of 7a-c. To a solution of **6c** (8.5 g, 27.7 mmol) in 50 mL of methanol was added 5 mL of a 25% solution of sodium methoxide in methanol. After stirring for 2 h the reaction was neutralized by the slow addition of 12M HCl. The remaining slurry was concentrated and purified by flash chromatography (SiO_2, EtOAc) to provide 4.61 g (89%) of vinylogous amide **7c**.



7a: IR (KBr) 3245, 1623, 1574, 1407, 1342, 1239, 1214, 1172 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 7.17(t, 1H, *J* = 6.9 Hz); 7.78(m, 1H); 5.23(m, 2H); 5.01(d, 1H, *J* = 7.3 Hz); 3.69(m, 1H); 2.20-2.55(m, 4H); ^{13}C NMR ($CDCl_3$) δ 38.5, 42.0, 52.2, 99.1, 119.3, 133.2, 151.1, 192.8 ppm. Exact mass calculated for $C_8H_{12}NO$, 137.0840, found: 137.0838.

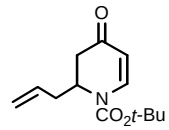


7b: IR (KBr) 3251, 2961, 1621, 1571, 1232, 1173 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 7.37(bs, 1H); 7.22(t, 1H, *J* = 6.9 Hz); 4.61(d, 1H, *J* = 7.3 Hz); 3.29(m, 1H); 2.14(dd, 1H, *J* = 12.8 and 15.8 Hz); 2.05(dd, 1H, *J* = 5.8 and 16.1 Hz); 1.79(m, 1H); 0.86(d, 6H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 18.0, 18.4, 31.0, 38.5, 58.7, 97.9, 152.3, 193.4 ppm; Exact mass calculated for $C_8H_{14}NO$, 140.1075, found: 140.1084.

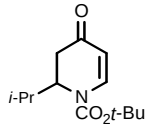


7c: IR (KBr) 3229, 3028, 1622, 1571, 1241, 1196 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 7.38(bd, 1 H); 7.17-7.31(m, 5H); 4.64(d, 1H, *J* = 7.4 Hz); 3.74(m, 1H); 2.86(dd, 1H, *J* = 6.6 and 13.6 Hz); 2.75(dd, 1H, *J* = 7.6 and 13.5 Hz); 2.04-2.08(m, 2H); ^{13}C NMR ($CDCl_3$) δ 40.3, 42.1, 54.4, 99.3, 127.1, 128.9, 129.2, 136.7, 151.0, 192.6 ppm; Exact mass calculated for $C_{12}H_{14}NO$, 188.1075, found: 188.1077.

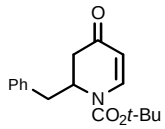
General procedure for the synthesis of 8a-c. To a solution of **7c** (4.4 g, 23.5 mmol) in 50 mL of acetonitrile was added 5.6 g (25.9 mmol) of Boc_2O and 3.2 g (25.9 mmol) of DMAP. After stirring for 12 h the reaction was concentrated, diluted with ether and washed consecutively with 1 N HCl, saturated $NaHCO_3$ and brine. The organic layer was dried over magnesium sulfate, filtered and concentrated. Purification using flash chromatography (SiO_2, 20% EtOAc/hexanes) provided 5.8 g (86%) of **8c**.



8a: IR (KBr) 1721, 1672, 1600, 1332, 1289, 1159 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 7.73(dd, 1H, *J* = 1.5 and 8.5 Hz); 5.70(m, 1H); 5.15(d, 1H, J = 8.5 Hz); 4.98(m, 2H); 4.50(m, 1H); 2.80(dd, 1H, *J* = 6.6 and 16.5 Hz); 2.10-2.35(m, 3H); 1.44(s, 9H); ^{13}C NMR ($CDCl_3$) δ 28.0, 35.1, 39.2, 52.3, 83.3, 106.1, 118.9, 133.1, 142.0, 151.1, 192.9 ppm.

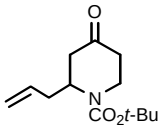


8b: IR (KBr) 1721, 1677, 1600, 1336, 1276, 1156 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 7.78(d, 1H, *J* = 6.6 Hz); 5.14(d, 1H, *J* = 7.3 Hz); 4.16(m, 1H); 2.79(dd, 1H, *J* = 6.6 and 16.9 Hz); 2.36(dt, 1H, *J* = 1.5, 2.9 and 18.3 Hz); 1.89(m, 1H); 1.45(s, 9H); 0.81(t, 6H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 18.9, 19.5, 28.0, 38.2, 58.2, 83.1, 106.7, 142.5, 151.6, 193.5 ppm; Exact mass calculated for $C_{13}H_{22}NO_3$, 240.1599, found: 240.1605.

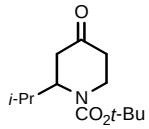


8c: IR (KBr) 1721, 1671, 1600, 1334, 1301, 1155 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.79(bd, 1H, *J* = 8 Hz); 7.06-7.30(m, 5H); 5.25(bd, 1H, *J* = 8.1 Hz); 4.61(m, 1H); 2.66-2.87(m, 3H); 2.14(bd, 1H, *J* = 16.9 Hz); 1.29(s, 9H); ^{13}C NMR ($CDCl_3$) δ 27.9, 36.2, 38.8, 54.4, 83.4, 106.4, 126.8, 128.7, 129.6, 136.8, 142.0, 193.0 ppm; Exact mass calculated for $C_{17}H_{22}NO_3$, 288.1599, found: 288.1585.

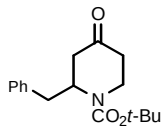
General procedure for the synthesis of 9a-c. A solution of **8c** (5.4 g, 18.8 mmol) and zinc (3.6 g, 56.4 mmol) in 40 mL of glacial acetic was heated at 50° C for 12 h. The reaction mixture was then concentrated, dissolved in EtOAc and the zinc salts removed by filtration. The resulting organic layer was concentrated and purified using flash chromatography (SiO_2, 20% EtOAc/hexanes) providing 4.9 g (91%) of **9c**.



9a: IR (KBr) 1685, 1509, 1414, 1163 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.64(m, 1H); 5.00(m, 2H); 4.42(m, 1H); 4.03(m, 1H); 3.18(m, 1H); 2.61(dd, 1H, *J* = 7.3 and 13.7 Hz); 2.40(m, 1H); 2.18(m, 3H); 1.38(s, 9H); ^{13}C NMR ($CDCl_3$) δ 28.3, 37.1, 38.4, 40.5, 44.4, 51.6,m 80.3, 118.1, 133.5, 154.5 ppm.



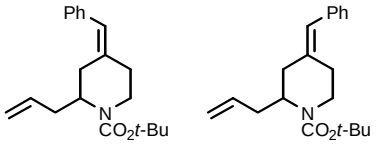
9b: IR (KBr) 1720, 1693, 1413, 1365, 1163 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.13(m, 1H); 3.98(m, 1H); 3.04(bt, 1H, *J* = 12.5 Hz); 2.33-2.55(m, 3H); 2.11(m, 1H); 1.60(m, 1H); 1.39(s, 9H); 0.84(d, 3H, *J* = 6.6 Hz); 0.74(d, 3H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 18.8, 19.6, 28.3, 29.4, 38.7, 40.6, 43.2, 58.3, 80.2, 154.8, 208.5 ppm; Exact mass calculated for $C_{13}H_{24}NO_3$, 242.1756, found: 242.1772.



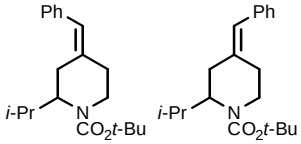
9c: IR (KBr) 1721, 1692, 1411, 1365, 1166 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 90°C) δ 7.1-7.3(m, 5H); 4.64(m, 1H); 4.1(m, 1H); 3.34(ddd, 1H, *J* = 4.2, 11.0 and 13.9 Hz); 2.79(dd, 1H, *J* = 7.9 and 13.6 Hz); 2.71(dd, 1H, *J* = 7.3 and 13.7 Hz); 2.62(ddd, 1H, *J* = 1.0, 6.7 and 15.0 Hz); 2.4-2.52(m, 1H); 2.2-2.3(m, 2H); 1.35(s, 9H); ^{13}C NMR ($CDCl_3$) δ 28.2, 38.7, 39.1, 40.6, 44.0, 53.8, 80.4, 126.6, 128.5, 129.3, 137.4, 154.4, 208.5 ppm; Exact mass calculated for $C_{17}H_{24}NO_3$, 290.1756, found: 290.1754.

General procedure for the synthesis of 10a-c. To a slurry of $(Ph)_3PCH_2PhCl$ (16.2 g, 41.4 mmol) in 50 mL of THF was added 41.6 mL (41.6 mmol) of a 1M THF solution of

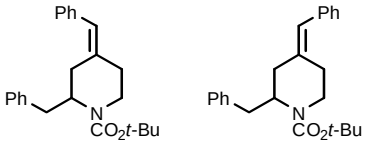
potassium t-butoxide. After stirring for 30 min, a THF solution of **9a** (23.0 mmol) was added and the reaction stirred for 24 h. The reaction mixture was quenched by the addition of 1M HCl, concentrated and the residue extracted with ether. The resulting ether layer was dried over magnesium sulfate, filtered and concentrated. Purification using flash chromatography (SiO_2, 10% EtOAc/hexanes) provided 6.4 g (89%) of a 1:1 mixture of *E* and *Z*-diastereomers **10a**.



10a (as a 1:1 mixture of olefin diastereomers): ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.14-7.32(m, 10H); 6.46(s, 1H); 6.29(s, 1H); 5.67(m, 1H); 5.52(m, 1H); 4.99(m, 2H); 4.79(m, 2H); 4.23(bs, 2H); 3.89(m, 2H); 2.79(m, 2H); 2.66(m, 2H); 2.46(m, 1H); 1.90-2.30(m, 9H); 1.35(s, 18H); Exact mass calculated for $C_{20}H_{28}NO_2$, 314.2120, found: 314.2146.

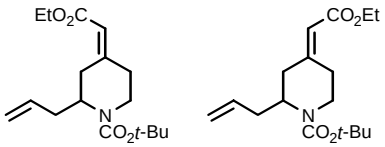


10b (as a 1:1 mixture of olefin diastereomers): ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.14-7.31(m, 10H); 6.43(s, 1H); 6.30(s, 1H); 4.02(m, 2H); 3.75(m, 2H); 2.83(d, 1H, *J* = 13.9 Hz); 2.75(m, 3H); 2.20-2.45(m, 4H); 1.88-2.02(m, 2H); 1.88)m, 1H); 1.70(m, 1H); 1.36(s, 18H); 0.91(d, 3H, *J* = 6.6 Hz); 0.74(d, 3H, *J* = 6.6 Hz); 0.65(d, 3H, *J* = 6.6 Hz); 0.43(d, 3H, *J* = 6.6 Hz); Exact mass calculated for $C_{20}H_{30}NO_2$, 316.2276, found: 316.2295.

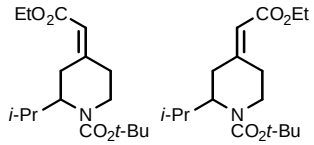


10c (as a 1:1 mixture of olefin diastereomers): ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.79-7.35(m, 20H); 6.55(s, 1H); 6.34(s, 1H); 4.33(m, 2H); 3.29(m, 2H); 3.01(m, 2H); 2.00-2.85(m, 14H); 1.21(s, 18H); Exact mass calculated for $C_{24}H_{30}NO_2$, 364.2276, found: 364.2287.

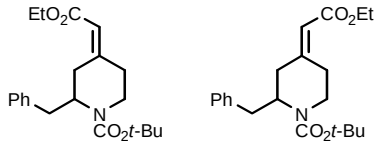
<u>General procedure for the synthesis of 11a-c.</u> To a slurry of $(Ph)_3PCHCO_2Et$ (15.0 g, 42.9 mmol) in 20 mL of toluene was added 3.74 g of ketone **9a** (15.6 mmol). The reaction mixture was heated at reflux for 12 h. The resulting reaction mixture was concentrated *in vacuo*. Purification using flash chromatography (SiO_2, 20% EtOAc/hexanes) provided 4.84 g (100%) of a 1:1 mixture of *E* and *Z*-diastereomers **11a**.



11a (as a 1:1 mixture of olefin diastereomers): ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.82(s, 1H); 5.70(s, 1H); 5.50-5.70(m, 2H); 4.90-5.10(m, 4H); 4.29(m, 2H); 4.04(q, 8H, *J* = 7.3Hz); 3.98(m, 2H); 3.59(bd, 1H, *J* = 13.6 Hz); 3.48(m, 1H); 2.81(m, 2H); 2.40(m, 1H); 2.00-2.25(m, 9H); 1.36(s, 18H); 1.16(t, 3H, *J* = 7.0 Hz); 1.15(t, 3H, *J* = 6.9 Hz); Exact mass calculated for $C_{17}H_{28}NO_4$, 310.2019, found: 310.1998.

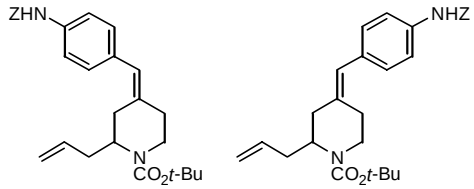


11b (as a 1:1 mixture of olefin diastereomers): ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.80(s, 1H); 5.77(s, 1H); 3.95-4.15(m, 6H); 3.70-3.95(m, 3H); 3.53(bd, 1H, *J* = 14.2 Hz); 2.71(m, 2H); 2.45(m, 1H); 1.95-2.35(m, 7H); 1.65(m, 2H); 1.39(s, 18H); 1.18(t, 3H, *J* = 7.0 Hz); 1.17(t, 3h, *J* = 6.9 Hz); 0.89(t, 6H, *J* = 7.0 Hz); 0.72(t, 6H, *J* = 6.2 Hz); Exact mass calculated for $C_{17}H_{30}NO_4$, 312.2175, found: 312.2174.



11c (as a 1:1 mixture of olefin diastereomers): ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.09-7.27(m, 10H); 5.89(s, 1H); 5.73(s, 1H); 4.49(m, 2H); 4.11(m, 6H); 3.57(m, 2H); 3.04(m, 2H); 2.20-2.79(m, 14H); 1.00-1.25(m, 24H); Exact mass calculated for $C_{21}H_{30}NO_4$, 360.2174, found: 360.2181.

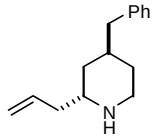
Procedure for the synthesis of 12a. To a –78 °C slurry of $(Ph)_3PCH_2Ph$-4-NHZCl (5.1 g, 9.3 mmol) in 50 mL of THF was added dropwise 20.5 mL (20.5 mmol) of a 1M THF solution of potassium t-butoxide. The resulting purple solution was warmed to room temperature. After stirring for 30 min a THF solution of **9a** (1.4 g, 5.84 mmol) was added and the reaction stirred for 24 h. The reaction mixture was quenched by the addition of 1M HCl, concentrated and the residue extracted with ether. The resulting ether layer was dried over magnesium sulfate, filtered and concentrated. Purification using flash chromatography (SiO_2, 20% EtOAc/hexanes) provided 2.43 g (90%) of a 1:1 mixture of *E* and *Z*-diastereomers **12a**.



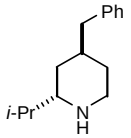
12a: ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.11-7.40(m, 18H); 6.26(s, 2H); 6.42(s, 1H); 6.26(s, 1H); 5.53-5.82(m, 2H); 4.70-5.09(m, 4H); 4.37(bs, 2H); 4.02(bs, 2H); 2.00=2.96(m, 18H); 1.46(s, 18H); Exact mass calculated for $C_{28}H_{35}N_2O_4$, 463.2596, found: 463.2597.

General procedure for the synthesis of 13a-g. To a –78 °C solution of THF (20 mL) and NH_3 (20 mL) was added 0.22 g (> 50 eq) of lithium metal. The resulting blue solution was stirred for 30 min. A THF solution (10 mL) of olefin **12a** (0.287 g) was added dropwise and the resulting mixture was allowed to warm to - 18 °C over 1 h. The

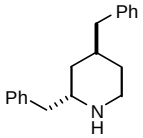
reaction mixture was quenched by the addition of solid NH_4Cl and 0.5 mL of water, warmed to room temperature and stirred until the complete evaporation of ammonia was observed. The mixture was then concentrated and the remaining solids washed with ethyl acetate. The resulting slurry was filtered, dried over magnesium sulfate and concentrated. The resulting residue could be purified by flash chromatography. Typically the crude material was dissolved in 10 mL of 75% TFA/CH_2Cl_2 and stirred for 2 h. Concentration and purification using flash chromatography (SiO_2, 1-10 % MeOH/CH_2Cl_2/2 % conc. NH_4OH:lower phase) provided 0.108 g (76 %) of **13g**.



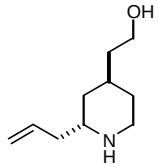
13a: IR (CH_2Cl_2 film) 3026, 2929, 2854, 1674, 1643, 1202, 1175, 1131, 720, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.30(m, 5H); 5.72(m, 1H); 5.09(m, 2H); 3.32(m, 1H); 3.03(m, 2H); 2.62(d, 2H, J = 7.6 Hz); 2.34(m, 2H); 2.07(m, 1H); 1.67-1.77(m, 1H); 1.53(m, 2H); 1.37-1.44(m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.1, 31.5, 31.8, 36.2, 39.3, 39.7, 51.3, 119.4, 126.3, 128.5, 128.9, 132.2, 139.5 ppm; Exact mass calculated for $C_{15}H_{22}N$, 216.1752, found: 216.1763.



13b: IR (CH_2Cl_2 film) 3025, 2933, 2873, 1677, 1202, 1176, 1131, 720, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.12-7.33(m, 5H); 3.06-3.10(m, 2H); 2.83-2.90(m, 1H); 2.70(d, 1H, *J* = 8.1 Hz); 2.17(m, 1H); 1.86(m, 1H); 1.52-1.66(m, 3H); 0.98(d, 3H, *J* = 7.0 Hz); 0.89(d, 3H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 18.3, 19.0, 27.6, 29.9, 30.3, 32.3, 38.4, 40.6, 57.3, 126.2, 128.5, 128.9, 140.1 ppm; Exact mass calculated for $C_{15}H_{24}N$, 218.1909, found: 218.1921.

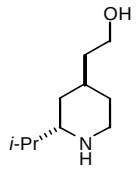


13c: IR (CH_2Cl_2 film) 3025, 2916, 1676, 1495, 1453, 1200, 736, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.08-7.33(m, 10H); 3.21(m, 1H); 2.92(t, 2H, *J* = 5.2 Hz); 2.62-2.84(m, 4H); 2.10(m, 1H); 1.72(m, 1H); 1.54(t, 2H, *J* = 5.5 Hz); 1.40-1.47(m, 1H); ^{13}C NMR ($CDCl_3$) δ 30.0, 33.2, 34.8, 39.9, 40.7, 40.8, 53.2, 126.0, 126.5, 128.3, 128.6, 129.1, 129.2, 138.7, 140.6 ppm; Exact mass calculated for $C_{19}H_{24}N$, 266.1909, found: 266.1894.

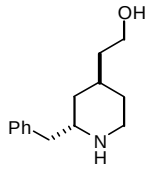


13d: IR (CH_2Cl_2 film) 3266, 3074, 2923, 1058, 912 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.69-5.83(m, 1H); 5.08-5.13(m, 2H); 3.69(t, 2H, *J* = 7.0 Hz); 2.81-2.97(m, 3H); 2.15-2.33(m, 4H); 1.94(m, 1H); 1.75(m,

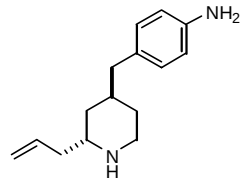
1H); 1.64(q, 2H, *J* = 6.6 Hz); 1.53(t, 2H, *J* = 5.7 Hz); 1.41(m, 1H); ^{13}C NMR ($CDCl_3$) δ 27.5, 30.6, 35.8, 36.3, 39.0, 40.8, 50.8, 60.8, 117.6, 135.2 ppm; Exact mass calculated for $C_{10}H_{20}NO$, 170.1544, found: 170.1540.



13e: IR (CH_2Cl_2 film) 2967, 2935, 2877, 1676, 1202, 1178, 1132, 721 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70(t, 2H, J = 6.5 Hz); 3.03-3.13(m, 2H); 2.85(m, 1H); 2.09(m, 1H); 1.87-1.97(m, 2H); 1.56-1.76(m, 5H); 1.00(d, 3H, J = 6.6 Hz); 0.96(d, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 18.2, 18.8, 26.8, 27.5, 30.0, 30.4, 34.6, 40.5, 57.4, 60l4, 118.6, 161.9, 162.3 ppm; Exact mass calculated for $C_{10}H_{22}NO$, 172.1701 , found: 172.1698.



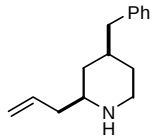
13f: IR (CH_2Cl_2 film) 3289, 3026, 2924, 2851, 1675, 1201, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17(m, 5H); 3.64(t, 1H, *J* = 7.0 Hz); 3.16(m, 3H); 2.70-2.96(m, 4H); 1.95(m, 1H); 1.79(m, 1H); 1.59(m, 4H); 1.43(m, 1H); ^{13}C NMR ($CDCl_3$) δ 27.4, 30.0, 35.2, 36.2, 40.4, 40.6, 53.0, 60.2, 126.5, 128.6, 129.1, 138.3 ppm; Exact mass calculated for $C_{14}H_{22}NO$, 220.1702, found: 220.1686.



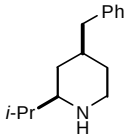
13g: IR (CH_2Cl_2 film) 2914, 2842, 1637, 1621, 1516, 1445, 827 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93(d, 2H, *J* = 8.5 Hz); 6.62(d, 2H, *J* = 8.5 Hz); 5.68-5.82(m, 1H); 5.04-5.11(m, 2H); 3.55(bs, 2H); 2.77-2.95(m, 3H); 2.55(d, 2H, *J* = 7.7 Hz); 2.04-2.22(m, 2H); 1.88-2.00(m, 2H); 1.57-1.70(m, 1H); 1.29-1.52(m, 3H); ^{13}C NMR ($CDCl_3$) δ 30.6, 33.6, 36.2, 39.1, 39.7, 41.0, 50.8, 115.2, 117.1, 129.8, 131.1, 135.9, 144.2 ppm; Exact mass calculated for $C_{15}H_{23}N_2$, 231.1862, found: 231.1847.

General procedure for the synthesis of 14a-g. A solution of **12a** (0.26 g, 0.57 mmol) in 12 ml of 75% TFA/CH_2Cl_2 was stirred for 2 h. The reaction mixture was then concentrated and added dropwise (in 10 mL of THF) to a –78 °C solution of THF (20 mL) and NH_3 (20 mL) containing 0.44 g (> 50 eq) of lithium metal. The resulting mixture was allowed to warm to - 18 °C over 1 h. The reaction mixture was quenched by the addition of solid NH_4Cl and 0.5 mL of water, warmed to room temperature and stirred until the complete evaporation of ammonia was observed. The mixture was then concentrated and the remaining solids washed with ethyl acetate. The resulting slurry was filtered, dried over magnesium sulfate and concentrated. Purification using flash

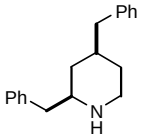
chromatography (SiO_2, 1-10 % MeOH/CH_2Cl_2/2 % conc. NH_4OH:lower phase) provided 0.115 g (88 %) of **14g**.



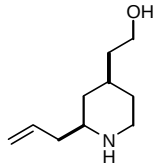
14a: IR (CH_2Cl_2 film) 3025, 2914, 2845, 2802, 1452, 1446, 1321, 913, 747, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.17(m, 5H); 5.68-5.82(m, 1H); 5.07-5.11(m, 2H); 3.04-3.10(m, 1H); 2.43-2.61(m, 3H); 1.99-2.20(m, 3H); 1.57-1.69(m, 3H); 1.13(ddd, 1H, *J* = 4.4, 12.5 and 16.5 Hz); 0.86(q, 1H, *J* = 12.5 Hz); ^{13}C NMR ($CDCl_3$) δ 32.8, 38.6, 39.3, 41.7, 43.8, 46.6, 55.8, 117.3, 125.8, 128.1, 129.1, 135.5, 140.6 ppm; Exact mass calculated for $C_{15}H_{22}N$, 216.1752, found: 216.1765.



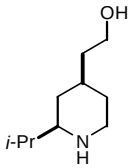
14b: IR (CH_2Cl_2 film) 2955, 2929, 2870, 1453, 1444, 747, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.13-7.30(m, 5H); 3.07-3.13(m, 1H); 2.45-2.60(m, 3H); 2.16-2.23(m, 1H); 1.47-1.71(m, 4H); 1.08(ddd, 1H, *J* = 4.0, 12.4 and 16.5 Hz); 0.91-0.78(m, 7H); ^{13}C NMR ($CDCl_3$) δ 18.8, 19.0, 33.0, 33.3, 36.3, 38.7, 44.1, 47.1, 62.5, 125.7, 128.1, 129.1, 140.7 ppm; Exact mass calculated for $C_{15}H_{24}N$, 218.1909, found: 218.1937.



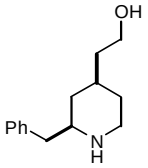
14c: IR (CH_2Cl_2 film) 3025, 2913, 2845, 2800, 1493, 1452, 1320, 746, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.11-7.32(m, 10H); 2.98-3.04(m, 1H); 2.40-2.75(m, 6H); 1.56-1.76(m, 3H); 1.18(m, 1H); 0.99(q, 1H, *J* = 11 Hz); ^{13}C NMR ($CDCl_3$) δ 32.4, 38.6, 39.4, 43,7, 43.8, 46.6, 58.0, 125.9, 126.4, 128.2, 128.6, 129.2, 129.3, 139.0, 140.5 ppm; Exact mass calculated for $C_{19}H_{24}N$, 266.1909, found: 266.1917.



14d: IR (CH_2Cl_2 film) 3267, 3074, 2920, 2850, 2737, 1442, 1058, 996, 912 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.70-5.84(m, 1H); 5.55-5.30(m, 2H); 3.69(t, 2H, *J* = 6.6 Hz); 3.06-3.12(m, 1H); 2.63(dt, 1H, *J* = 2.6 and 12.0 Hz); 4.48-2.56(m, 1H); 2.01-2.22(m, 2H); 1.48-1.73(m, 5H); 1.13(ddd, 1H, *J* = 4.0, 12.4 and 16.8 Hz); 0.83(q, 1H, *J* = 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 32.9, 33.0, 39.4, 40.0, 41.8, 46.6, 55.7, 60.2, 117.3, 135.5 ppm; Exact mass calculated for $C_{10}H_{20}NO$, 170.1544, found: 170.1549.

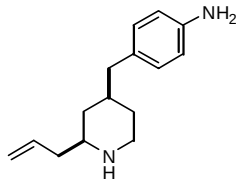


14e: IR (CH_2Cl_2 film) 3286, 2923, 2872, 1057 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.67(t, 2H, *J* = 6.2 Hz); 3.12(m, 1H); 2.62(dt, 1H, *J* = 2.0 and 9.5 Hz); 2.23(m, 1H); 3.13(bs, 1H); 1.47-1.73(m, 6H); 1.07(m, 1H); 0.93(d, 3H, *J* = 6.6 Hz); 0.90(d, 3H, *J* = 6.6 Hz); 0.79(q, 1H, *J* = 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 18.8, 18.9, 33.1, 33.2, 36.1, 40.3, 47.0, 60.0, 62.5 ppm;
Exact mass calculated for $C_{10}H_{22}N0$, 172.1701, found: 172.1684.



14f: IR (CH_2Cl_2 film) 3273, 3060, 3025, 2919, 2849, 2738, 1493, 1453, 1443, 132, 1150, 1114, 1084, 1058, 1029, 748, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.33(m, 5H); 3.68(t, 2H, *J* = 6.6 Hz); 3.03(m, 1H); 2.6802.77(m, 2H); 2.50-2.62(m, 2H); 1.94(bs, 1H); 1.64-1.78(m, 2H); 1.48-1.59(m, 3H); 1.08-1.26(m, 1H); 0.94(q, 1H, *J* = 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 30.2, 32.6, 33.0, 39.4, 40.0, 43.6, 46.6, 58.0, 59.7, 126.3, 128.5, 129.2, 138.9 ppm; Exact mass calculated for $C_{14}H_{22}NO$, 220.1701, found: 220.1721.

14g: IR (CH_2Cl_2 film) 2909, 2841, 1620, 1515, 1444, 1319, 1274, 827 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.93(d, 2H, *J* = 8.4 Hz); 6.62(d, 2H, *J* = 8.4 Hz); 5.6805.82(m, 1H); 5.02-5.12(m, 2H); 3.55(bs, 2H); 3.06(m, 1H); 2.40-2.60(m, 4H); 1.98-2.19(m, 2H); 1.50-1.71(m, 4H); 1.09(dd, 1H, *J* = 4.0 and 12.5 Hz); 0.81(q, 1H, *J* = 11.4 Hz); ^{13}C NMR ($CDCl_3$) δ 32.9, 38.9, 39.4, 41.8, 43.0, 46.7, 55.8, 115.1, 117.2, 129.9, 130.6, 135.6, 144.2 ppm; Exact mass calculated for $C_{15}H_{23}N_2$, 231.1861, found: 231.1876.



Determination of Diastereoselectivities

For all reaction products with a chromophore suitable for UV detection (**13a-c, 13f, 14a-c , 14f**) the following HPLC conditions were used for measuring diastereomeric ratios obtained in this reaction sequence. All traces were verified by a coinjection of the opposite diastereomer in question. All *cis*-derivatives were injected as a solution of the free amine. The crude *trans*-TFA salts were neutralized with a small amount of conc. NH_4OH prior to injection. All other ratios (**13d-g** and **14d –g**) were measured by comparison of the ^1H NMR spectra.

Column: YMC packed PVA-SIL NP silica column (4.4 mm X 250 mm)
Wavelength: 260 nm

For **13a**:
Injection Volume: 5 μL of a 5.6 mg/mL solution in CH_2Cl_2
flowrate: 6 ml/min
solvent system: 1% MeOH/1% conc. NH_4OH/98% CH_2Cl_2/lower phase
retention time: 5.8 min

For **13b**:
Injection Volume: 20 μL of a 1.2 mg/mL solution in CH_2Cl_2
flowrate: 6 ml/min
solvent system: 1% MeOH/1% conc. NH_4OH/98% CH_2Cl_2/lower phase
retention time: 7.1 min

For **13c**:
Injection Volume: 10 μL of a 12.7 mg/mL solution in CH_2Cl_2
flowrate: 6 ml/min
solvent system: 1% MeOH/1% conc. NH_4OH/98% CH_2Cl_2/lower phase
retention time: 3.2 min

For **13f**:
Injection Volume: 10 μL of a 7.7 mg/mL solution in CH_2Cl_2
flowrate: 2 ml/min
solvent system: 2% MeOH/1% conc. NH_4OH/98% CH_2Cl_2/lower phase
retention time: 5.0 min

For **14a**:
Injection Volume: 20 μL of a 1.0 mg/mL solution in CH_2Cl_2
flowrate: 6 ml/min
solvent system: 1% MeOH/1% conc. NH_4OH/98% CH_2Cl_2/lower phase
retention time: 3.2 min

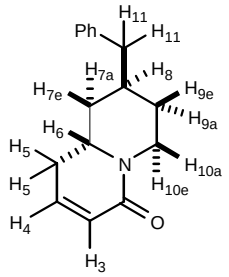
For **14b**:
Injection Volume: 20 μL of a 1.2 mg/mL solution in CH_2Cl_2
flowrate: 6 ml/min
solvent system: 1% MeOH/1% conc. NH_4OH/98% CH_2Cl_2/lower phase
retention time: 4.7 min

For **14c**:
Injection Volume: 10 μL of a 2.0 mg/mL solution in CH_2Cl_2
flowrate: 6 ml/min
solvent system: 1% MeOH/1% conc. NH_4OH/98% CH_2Cl_2/lower phase
retention time: 1.6 min

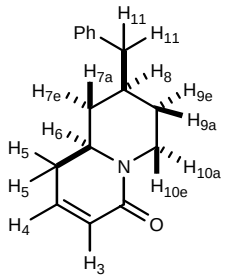
For **14f**:
Injection Volume: 10 μL of a 2.0 mg/mL solution in CH_2Cl_2

flowrate: 2 ml/min
solvent system: 2% MeOH/2% conc. NH_4OH/96% CH_2Cl_2/lower phase
retention time: 4.2 min

Synthesis of 15 and 16. A biphasic solution of **13a** (0.171 g, 0.795 mmol) and acroyl chloride (0.35 mL, 7.95 mmol) in 10 ml of CH_2Cl_2 and 1 mL of saturated $NaHCO_3$ was stirred for 1 h. The organic layer was separated, dried over magnesium sulfate and concentrated. Purification using flash chromatography (SiO_2, 50 % EtOAc/hexanes) provided 0.138 g (65%) of the amide. To a solution of the above amide (0.149 g, 0.55 mmol) in 10 mL of degassed CH_2Cl_2 was added 0.023 g (5 mol %) of $(Cy_3P)_2Ru(IV)=CHPhCl_2$. The reaction mixture was stirred at room temperature for 12h. The resulting reaction mixture was concentrated *in vacuo*. Purification using flash chromatography (SiO_2, 50% EtOAc/hexanes) provided 0.083 g (62%) of **15**.



15: IR (CH_2Cl_2 film) 2931, 2853, 1667, 1614, 1446, 1420, 1337, 1317, 1278, 1266, 814, 739, 701 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.15-7.29(m, 5H, **Ar-H**); 6.55(m, 1H, $\mathbf{H_4}$); 5.72(m, 1H, $\mathbf{H_3}$); 3.86(m, 1H, $\mathbf{H_{10a}}$); 3.74(m, 1H, $\mathbf{H_6}$); 2.72(m, 2H, $\mathbf{2\text{-}H_{11}}$); 2.44(m, 1H, $\mathbf{H5_a}$); 2.00-2.11(m, 2H, H_8 and $\mathbf{H5_e}$); 1.42-1.60(m, 4H, $\mathbf{2\text{-}H_9}$ and $\mathbf{2\text{-}H_7}$); A strong nOe difference between H_{11}, H_{10a} and H_6 is indicative of a *trans* relationship between the 2 and 4 positions. ^{13}C NMR ($CDCl_3$) δ 27.6, 31.3, 32.6, 36.1, 37.3, 49.2, 124.9, 126.1, 128.5, 128.9, 138.1, 140.5, 165.7 ppm; Exact mass calculated for $C_{16}H_{19}NO$, 242.1545, found: 242.1538.



16: IR (CH_2Cl_2 film) 2918, 1667, 1615, 1446, 1422, 1267, 701 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.15-7.29(m, 5H, **Ar-H**); 6.53(m, 1H, $\mathbf{H_4}$); 5.68(m, 1H, $\mathbf{H_3}$); 4.24(m, 1H, $\mathbf{H_{10a}}$); 3.36(m, 1H, $\mathbf{H_6}$); 2.41-2.56(m, 4H, $\mathbf{2\text{-}H_{11}}$, $\mathbf{H_{5a}}$ **and** $\mathbf{H_{10}}$); 2.10(m, 1H, $\mathbf{H_5}$); 1.72(m, 1H, $\mathbf{H_8}$); 1.61(m, 2H, $\mathbf{H_{9a}}$ and $\mathbf{H_{7a}}$); 1.02-1.15(m, 2H, $\mathbf{H_{9e}}$ and $\mathbf{H_{7e}}$); A strong nOe difference between H_8 and H_6 is indicative of a *cis* relationship between the 2 and 4 positions. ^{13}C NMR ($CDCl_3$) δ 31.0, 31.2, 37.7, 39.6, 42.6, 43.1, 54.3, 124.5, 126.1, 128.3, 129.1, 138.1, 139.8, 165.5 ppm; Exact mass calculated for $C_{16}H_{19}NO$, 242.1545, found: 242.1546.