A Highly Selective Organocatalytic Route to Chiral Dihydro-1,2-oxazines

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Supporting Information

General Information

Solvents: Diethyl ether and tetrahydrofuran were distilled from calcium hydride and lithium aluminium hydride prior to use; chloroform, dichloromethane and toluene from calcium hydride. Anhydrous dimethylsulfoxide was used as supplied. Petrol refers to petroleum ether b.p. 40-60°C and ether to diethyl ether, which were distilled before use.

Reagents: All reactions were performed under an argon atmosphere unless otherwise stated. Reagents were used as supplied or purified using standard procedures as necessary.

Chromatography: Flash column chromatography was carried out using Silica Gel 60 (0.040-0.063 mm) 230-400 mesh under pressure unless otherwise indicated. Analytical thin layer chromatography was performed using pre-coated glass-backed plates (Merck Kieselgel 60 F254) and visualised by ultraviolet radiation (254 nm), acidic Cerium Ammonium Molybdate, or basic potassium permanganate solutions as appropriate.

Data Collection: Melting points were performed on a Reichert hot-stage apparatus, and are uncorrected. Optical rotations were measured on a Perkin Elmer 343 digital polarimeter using a sodium lamp (589 nm) as the light source; $[\alpha]_D$ values are reported in $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$. Infrared spectra were recorded as thin films on a Perkin Elmer Spectrum One FT-IR 1600 spectrometer fitted with an ATR sampling accessory. ^1H NMR spectra were recorded at 400 and 600 MHz on Bruker DPX-400 and Bruker DRX-600 spectrometers, respectively with residual protic solvent CDCl_3

as the internal reference ($\delta_{\text{H}} = 7.26$ ppm) and are reported as follows: chemical shift δ /ppm (multiplicity, coupling constant J /Hz, number of protons, assignment). Non-integral proton numbers indicate isomeric species, either rotamers or diastereomers. ^{13}C NMR spectra were recorded at 100 MHz and 150 MHz on Bruker DPX-400 and Bruker DRX-600 spectrometers, respectively. The resonance of CDCl_3 ($\delta_{\text{C}} = 77.0$ ppm, t) was used as an internal reference. ^{13}C DEPT-135 and two-dimensional (COSY, HMQC and HMBC) NMR experiments were used where appropriate, to aid the assignment of signals in the ^1H and ^{13}C spectra. NMR resolution enhancement was also used to assist coupling assignment in most ^1H NMR spectra. Mass spectra and accurate mass data were obtained on an LCT Premier spectrometer by Waters using a Micromass MS software at the Department of Chemistry, University of Cambridge. The enantiomeric excesses (*ee*) were determined by high performance liquid chromatography (HPLC), performing on Hewlett-Packard Agilent 1100 chromatographs using a Chiralpak AD-H (0.46×25 cm) or Chiralcel OD-H (0.46×25 cm) column as noted or gas chromatography (GC), performing on an Agilent 6890N chromatograph using an Astec Chiraldex column. The diastereomeric excesses (*de*) were determined by ^1H NMR spectroscopy of crude products. The racemic materials were prepared using DL-proline catalyst in the same procedure as their corresponding chiral compounds.

General procedure for the synthesis of a 1,2-oxazine catalysed by (2*S*)-5-pyrrolidin-2-yl-1*H*-tetrazole (Table 1, Entries 1-8 and Table 2, Entries 1-2)

To a solution of appropriate aldehyde (2.40 mmol) in DMSO (10 ml) was added (2*S*)-5-pyrrolidin-2-yl-1*H*-tetrazole (56 mg, 0.40 mmol). The resulting suspension was stirred vigorously for 1 min before addition of nitrosobenzene (0.22 g, 2.00 mmol). The bright green reaction mixture was stirred at room temperature until the reaction was determined to be complete by TLC and the disappearance of green colour, resulting in a yellow solution. The reaction mixture was then cooled to 0°C and THF (10 ml) was added. Vinyltriphenylphosphonium bromide (1.14 g, 3.00 mmol) was added, followed by sodium hydride (0.16 g, 4.00 mmol). After 20 min of stirring at 0°C , the reaction mixture was quenched using saturated aqueous NH_4Cl and extracted with ether (3×30 ml). The combined organic layers were dried over MgSO_4 , filtered

and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (solvents noted) to provide the title compounds.

(6*R*)-6-Isopropyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4a)

Prepared according to the general procedure from isovaleraldehyde (0.27 ml, 2.40 mmol) to provide the title compound as a yellow oil (0.29 g, 71%, 99% *ee*) after flash column chromatography (4:1, petrol/toluene). $[\alpha]_D^{25} +34.0$ (*c* 1.72 in CHCl_3); $\nu_{(\text{max})}$ (film) 2961, 2871, 1694, 1599, 1489, 1468, 1454, 1433, 1385, 1367, 1212, 1067, 990.8, 752.3, 724.4, 689.5, 667.8 cm^{-1} ; δ_{H} (600 MHz, CDCl_3) 1.03 (d, *J* 6.8, 3H, $(\text{CH}_3)(\text{CH}'_3)\text{CH}$), 1.06 (d, *J* 6.7, 3H, $(\text{CH}_3)(\text{CH}'_3)\text{CH}$), 1.95 (dq, *J* 6.8, 6.8, 6.7, 1H, $(\text{CH}_3)(\text{CH}'_3)\text{CH}$), 3.73 (app ddt, *J* 15.7, 2.9, 2.0, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 3.89 (m, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 4.33 (m, 1H, $(\text{CH}_3)_2\text{CHCH}(\text{CH}=\text{CH})\text{ONPh}$), 5.94-5.99 (m, 2H, $(\text{CH}_3)_2\text{CHCH}(\text{CH}=\text{CH})\text{ONPh}$), 6.97 (t, *J* 7.4, 1H, *PhH*), 7.12 (d, *J* 7.9, 2H, *PhH*), 7.30 (dd, *J* 7.9, 7.4, 2H, *PhH*); δ_{C} (150 MHz, CDCl_3) 18.3 ($(\text{CH}_3)(\text{C}'\text{H}_3)\text{CH}$), 18.4 ($(\text{CH}_3)(\text{C}'\text{H}_3)\text{CH}$), 31.6 ($\text{CH}_3(\text{C}'\text{H}_3)\text{CH}$), 51.8 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 82.4 ($(\text{CH}_3)_2\text{CHCH}(\text{CH}=\text{CH})\text{ONPh}$), 115.3 ($2\times\text{PhCH}$), 121.8 (*PhCH*), 123.6 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 128.6 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 128.7 ($2\times\text{PhCH}$), 150.8 (*PhC-N*); *m/z* (ES) found 204.1398 ($[\text{MH}^+]$ $\text{C}_{13}\text{H}_{18}\text{NO}$), requires 204.1388; HPLC (Chiralcel OD-H, 99:1, hexanes/*i*PrOH, 0.5 ml min⁻¹, 254 nm, *t*_R(minor) 13.4 min, *t*_R(major) 15.1 min.

(6*R*,2'*Z*)-6-Pent-2'-enyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4b)

Prepared according to the general procedure from *cis*-4-heptenal (0.33 ml, 2.40 mmol) to provide the title compound as a yellow oil (0.23 g, 50%, 99% *ee*) after flash column chromatography (4:1, petrol/toluene). $[\alpha]_D^{25} -55.5$ (*c* 2.83 in CHCl_3); $\nu_{(\text{max})}$ (film) 2962, 1598, 1490, 1454, 1431, 1284, 1211, 1096, 1071, 1046, 994.9, 881.0, 753.5,

718.7, 690.0 cm^{-1} ; δ_{H} (600 MHz, CDCl_3) 1.02 (t, J 7.4, 3H, CH_3CH_2), 2.13 (app qu, J 7.4, 2H, CH_3CH_2), 2.44 (app qu, J 7.4, 1H, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}(\text{H}')$), 2.58 (app qu, J 7.4, 1H, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}(\text{H}')$), 3.80 (app dq, J 15.7, 1.9, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 3.90 (m, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 4.62-4.65 (m, 1H, $\text{CH}=\text{CHCH}_2\text{CH}(\text{CH}=\text{CH})\text{O}$), 5.53-5.63 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2$), 5.96 (app dq, J 10.0, 1.9, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 5.99 (m, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 7.02 (t, J 7.3, 1H, PhH), 7.17 (d, J 8.7, 2H, $2\times\text{PhH}$), 7.34 (dd, J 8.7, 7.3, 2H, $2\times\text{PhH}$); δ_{C} (150 MHz, CDCl_3) 14.2 (CH_3CH_2), 20.8 (CH_3CH_2), 31.4 ($\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2$), 51.6 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 77.7 ($\text{CH}_2\text{CH}(\text{CH}=\text{CH})\text{ONPh}$), 115.5 ($2\times\text{PhCH}$), 121.9 (PhCH), 123.3 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 124.1 ($\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$), 128.8 ($2\times\text{PhCH}$), 129.6 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 134.2 ($\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$), 150.7 (PhC-N); m/z (ES) found 230.1553 ($[\text{MH}^+]$ $\text{C}_{15}\text{H}_{20}\text{NO}$), requires 230.1545; HPLC (Chiralcel OD-H, 99:1, hexanes/ i PrOH, 0.5 ml min^{-1} , 254 nm, $t_{\text{R}}(\text{major})$ 14.1 min, $t_{\text{R}}(\text{minor})$ 14.6 min.

(6*R*,2'*E*)-6-Oct-2'-enyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4c)

Prepared according to the general procedure from *trans*-4-decenal (0.44 ml, 2.40 mmol) to provide the title compound as a yellow oil (0.24 g, 45%) after flash column chromatography (20:1, petrol/EtOAc). $[\alpha]_{\text{D}}^{25}$ -10.1 (c 0.78 in CHCl_3); $\nu_{(\text{max})}$ (film) 3040, 2956, 2924, 2856, 1687, 1599, 1490, 1454, 1431, 1351, 1286, 1211, 1111, 1096, 1072, 1048, 1003, 967.6, 887.9, 752.8, 720.3, 689.0 cm^{-1} ; δ_{H} (600 MHz, CDCl_3) 0.93 (t, J 7.1, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.30-1.39 (m, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.43 (app qu, J 7.1, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 2.08 (app q, J 7.1, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2$), 2.33 (app dt, J 13.8, 6.9, 1H, $\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}(\text{H}')$), 2.51 (app dt, J 13.8, 6.9, 1H, $\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}(\text{H}')$), 3.78 (app dq, J 15.7, 2.3, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 3.88 (app ddt, J 15.7, 3.7, 1.3, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 4.59-4.62 (m, 1H, $\text{CH}=\text{CHCH}_2\text{CH}(\text{CH}=\text{CH})\text{O}$), 5.57 (app dtt, J 10.4, 7.1, 6.9, 2H, $\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2$), 5.94-5.96 (m, 2H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 7.00 (t, J 7.3, 1H, PhH), 7.15 (d, J 8.7, 2H, $2\times\text{PhH}$), 7.32 (dd, J 8.7, 7.3, 2H, $2\times\text{PhH}$); δ_{C} (150 MHz, CDCl_3) 14.1 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 22.6 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 29.2 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$), 31.4 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 32.7 ($\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2$), 36.7 ($\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2$), 51.5

(PhNCH(H')CH=CH), 77.8 (CH₂CH(CH=CH)ONPh), 115.5 (2×PhCH), 121.8 (PhCH), 123.1 (PhNCH(H')CH=CH), 125.3 (CH₂CH₂CH=CHCH₂), 128.7 (2×PhCH), 129.6 (PhNCH(H')CH=CH), 133.8 (CH₂CH₂CH=CHCH₂), 150.6 (PhC-N); *m/z* (ES) found 272.2006 ([MH⁺] C₁₈H₂₆NO), requires 272.2014.

(6*R*)-6-Butyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4d)

Prepared according to the general procedure from hexanal (0.29 ml, 2.40 mmol) to provide the title compound as a pale yellow oil (0.17 g, 39%, 99% *ee*) after flash column chromatography (4:1, petrol/toluene). $[\alpha]_D^{25} +15.7$ (*c* 1.02 in CHCl₃); $\nu_{(\text{max})}$ (film) 3041, 2955, 2931, 2860, 1598, 1490, 1454, 1431, 1349, 1211, 1031, 1003, 752.6, 717.5, 688.8 cm⁻¹; δ_H (600 MHz, CDCl₃) 0.94 (t, *J* 7.3, 3H, CH₃CH₂CH₂), 1.34-1.63 (m, 5H, CH₃CH₂CH₂CH(H')C(H)), 1.69-1.76 (m, 1H, CH₃CH₂CH₂CH(H')C(H)), 3.74 (app dq, *J* 15.8, 2.0, 1H, PhNCH(H')CH=CH), 3.88 (app dtt, *J* 15.8, 2.4, 2.0, 1H, PhNCH(H')CH=CH), 4.56-4.59 (m, 1H, CH₂CH(H')C(H)(CH=CH)O), 5.89 (app dq, *J* 10.1, 2.0, 1H, PhNCH(H')CH=CH), 5.93 (app dqu, *J* 10.1, 2.0, 1H, PhNCH(H')CH=CH), 6.97 (t, *J* 7.3, 1H, PhH), 7.12 (d, *J* 8.7, 2H, 2×PhH), 7.31 (dd, *J* 8.7, 7.3, 2H, 2×PhH); δ_C (150 MHz, CDCl₃) 14.0 (CH₃CH₂CH₂), 22.7 (CH₃CH₂CH₂), 27.8 (CH₃CH₂CH₂), 33.2 (CH₃CH₂CH₂CH₂), 51.6 (PhNCH(H')CH=CH), 77.9 (CH₃(CH₂)₃CH(CH=CH)ONPh), 115.4 (2×PhCH), 121.8 (PhCH), 122.8 (PhNCH(H')CH=CH), 128.8 (2×PhCH), 130.2 (PhNCH(H')CH=CH), 150.7 (PhC-N); *m/z* (ES) found 218.1543 ([MH⁺] C₁₄H₂₀NO), requires 218.1545; HPLC (Chiralcel OD-H, 99:1, hexanes/^{*i*}PrOH, 0.5 ml min⁻¹, 254 nm, *t*_R(major) 13.2 min, *t*_R(minor) 13.8 min.

(6*R*)-6-Allyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4e)

Prepared according to the general procedure from 4-pentenal (0.24 ml, 2.40 mmol) to provide the title compound as a yellow oil (0.18 g, 44%, 99% *ee*) after flash column chromatography (4:1, petrol/toluene). $[\alpha]_D^{25}$ -19.2 (*c* 1.31 in CHCl_3); $\nu_{\text{(max)}}$ (film) 3042, 2859, 2817, 1642, 1598, 1490, 1454, 1430, 1288, 1211, 994.5, 916.1 753.3, 719.2, 689.2 cm^{-1} ; δ_{H} (600 MHz, CDCl_3) 2.39 (app qu, *J* 7.0, 1H, $\text{CH}_2=\text{CHCHH}'$), 2.55 (app qu, *J* 7.0, 1H, $\text{CH}_2=\text{CHCHH}'$), 3.77 (app dq, *J* 15.8, 2.5, 1H, PhNCH(H')CH=CH), 3.87 (app dtt, *J* 15.8, 2.5, 1.9, 1H, PhNCH(H')CH=CH), 4.64 (m, 1H, $\text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH=CH})\text{O}$), 5.14 (dd, *J* 10.3, 1.7, 1H, H'CH=CHCH_2), 5.18 (dd, *J* 17.1, 1.7, 1H, H'CH=CHCH_2), 5.90-5.98 (m, 3H, $\text{H'CH=CHCH}_2\text{CH}(\text{CH=CH})\text{O}$), 6.98 (t, *J* 7.3, 1H, PhH), 7.12 (d, *J* 8.7, 2H, $2\times\text{PhH}$), 7.30 (dd, *J* 8.7, 7.3, 2H, $2\times\text{PhH}$); δ_{C} (150 MHz, CDCl_3) 37.8 ($\text{CH}_2=\text{CHCH}_2$), 51.5 (PhNCH(H')CH=CH), 77.3 ($\text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH=CH})\text{ONPh}$), 115.5 ($2\times\text{PhCH}$), 117.4 ($\text{CH}_2=\text{CHCH}_2$), 121.9 (PhCH), 123.3 (PhNCH(H')CH=CH), 128.7 ($2\times\text{PhCH}$), 129.4 (PhNCH(H')CH=CH), 134.2 ($\text{CH}_2=\text{CHCH}_2$), 150.5 (PhC-N); *m/z* (ES) found 202.1237 ($[\text{MH}^+]$ $\text{C}_{13}\text{H}_{16}\text{NO}$), requires 202.1232; HPLC (Chiralcel OD-H, 99:1, hexanes/*i*PrOH, 0.5 ml min^{-1} , 254 nm, t_{R} (major) 15.7 min, t_{R} (minor) 17.0 min.

(6'*R*)-4-(2'-Phenyl-3',6'-dihydro-2'*H*-[1,2]oxazin-6'-yl)-butyric acid methyl ester (4f)

Prepared according to the general procedure from adipicsemialdehyde methyl ester (0.36 ml, 2.40 mmol) to provide the title compound as a yellow oil (0.26 g, 50%, 99% *ee*) after flash column chromatography (15:1, petrol/EtOAc). $[\alpha]_D^{25}$ -1.0 (*c* 0.84 in CHCl_3); $\nu_{\text{(max)}}$ (film) 2951, 1733, 1598, 1490, 1454, 1435, 1351, 1240, 1211, 1163, 1097, 1054, 1003, 887.2, 754.4, 718.4, 690.8 cm^{-1} ; δ_{H} (600 MHz, CDCl_3) 1.63-1.96 (m, 4H, $\text{CH}_3\text{OCOCH}_2\text{CH}_2\text{CH}_2$), 2.39 (t, *J* 7.4, 2H, $\text{CH}_3\text{OCOCH}_2\text{CH}_2$), 3.67 (s, 3H, $\text{CH}_3\text{OCOCH}_2$), 3.74 (app dq, *J* 15.8, 2.3, 1H, PhNCH(H')CH=CH), 3.87 (app dtt, *J* 15.8, 2.5, 2.3, 1H, PhNCH(H')CH=CH), 4.59 (app tq, *J* 6.9, 2.3, 1H, $\text{CH}_2\text{CH}_2\text{CH}(\text{CH=CH})\text{O}$), 5.87 (app dq, *J* 10.0, 2.3, 1H, PhNCH(H')CH=CH), 5.94 (app dqu, *J* 10.0, 2.3, 1H, PhNCH(H')CH=CH), 6.98 (t, *J* 7.4, 1H, PhH), 7.10 (d, *J* 8.7, 2H, $2\times\text{PhH}$), 7.30 (dd, *J* 8.7, 7.4, 2H, $2\times\text{PhH}$); δ_{C} (150 MHz, CDCl_3) 21.1

(CH₃OCOCH₂CH₂), 32.8 (CH₃OCOCH₂CH₂CH₂), 33.9 (CH₃OCOCH₂CH₂), 51.5 (CH₃OCOCH₂), 51.8 (PhNCH(H')CH=CH), 77.4 (CH₂CH₂CH(CH=CH)ONPh), 115.5 (2×PhCH), 122.0 (PhCH), 123.3 (PhNCH(H')CH=CH), 128.8 (2×PhCH), 129.7 (PhNCH(H')CH=CH), 150.6 (PhC-N), 173.9 (CH₃OCOCH₂); *m/z* (ES) found 262.1443 ([MH⁺] C₁₅H₂₀NO₃), requires 262.1443; HPLC (Chiralcel OD-H, 98:2, hexanes/ⁱPrOH, 1.0 ml min⁻¹, 254 nm, *t*_R(major) 15.2 min, *t*_R(minor) 17.7 min.

(6*R*)-6-Benzyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4g)

Prepared according to the general procedure from 3-phenyl propionaldehyde (0.33 ml, 2.40 mmol) to provide the title compound as a yellow oil (0.20 g, 40%, 99% *ee*) after gradient flash column chromatography (9:1 → 6:1 → 4:1, petrol/DCM). [α]_D²⁵ +36.1 (*c* 3.34 in CHCl₃); $\nu_{\text{(max)}}$ (film) 3028, 2860, 2815, 1598, 1490, 1454, 1430, 1282, 1212, 1076, 1003, 889.3, 873.1, 751.9, 718.9, 689.3 cm⁻¹; δ_{H} (600 MHz, CDCl₃) 2.92 (dd, *J* 13.9, 6.0, 1H, PhCHH'CH(CH=CH)O), 3.13 (dd, *J* 13.9, 8.1, 1H, PhCHH'CH(CH=CH)O), 3.81 (app dq, *J* 15.8, 2.5, 1H, PhNCH(H')CH=CH), 3.87 (app ddt, *J* 15.8, 3.7, 2.5, 1H, PhNCH(H')CH=CH), 4.81 (ddddd, *J* 8.1, 6.0, 3.7, 2.5, 1.9, 1H, PhCH₂CH(CH=CH)O), 5.91 (app dq, *J* 10.1, 2.5, 1H, PhNCH(H')CH=CH), 5.97 (app dtd, *J* 10.1, 2.5, 1.91H, PhNCH(H')CH=CH), 6.97 (d, *J* 7.3, 1H, N-PhH), 7.05 (d, *J* 8.8, 2H, 2×(N-PhH)), 7.24-7.34 (m, 7H, 2×(N-PhH), 5×(CH₂-PhH)); δ_{C} (150 MHz, CDCl₃) 39.9 (PhCH₂CH(CH=CH)O), 51.8 (PhNCH(H')CH=CH), 78.6 (PhCH₂CH(CH=CH)O), 115.5 (2×(N-PhCH)), 121.9 (N-PhCH), 123.4 (PhNCH(H')CH=CH), 126.4 (CH₂-PhC), 128.3 (2×(N-PhCH)), 128.7 (2×(CH₂-PhCH)), 129.2 (PhNCH(H')CH=CH), 129.5 (2×(CH₂-PhCH)), 137.9 (PhC-CH₂), 150.6 (PhC-N); *m/z* (ES) found 252.1386 ([MH⁺] C₁₇H₁₈NO), requires 252.1388; HPLC (Chiralcel OD-H, 98:2, hexanes/ⁱPrOH, 1.0 ml min⁻¹, 254 nm, *t*_R(major) 8.0 min, *t*_R(minor) 8.8 min.

(6*S*)-6-*tert*-Butyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4h)

Prepared according to the general procedure from 3,3-dimethylbutyraldehyde (0.32 ml, 2.40 mmol) to provide the title compound as a pale yellow solid (0.35 g, 82%, 99% *ee*) after flash column chromatography (20:1, petrol/EtOAc). m.p. 86-87°C; $[\alpha]_D^{25} +75.4$ (*c* 0.34 in CHCl_3); $\nu_{\text{(max)}}$ (film) 3071, 2965, 2867, 2840, 2815, 1739, 1599, 1490, 1475, 1462, 1440, 1389, 1363, 1216, 1114, 1005, 984.7, 887.4, 785.3, 754.5, 743.1, 690.3, 662.0 cm^{-1} ; δ_{H} (600 MHz, CDCl_3) 1.03 (s, 9H, $(\text{CH}_3)_3\text{CCH}$), 3.67 (app ddt, *J* 15.4, 3.5, 1.3, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 3.93 (dddd, *J* 15.4, 4.0, 2.9, 1.1, 1H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 4.30 (m, 1H, $(\text{CH}_3)_3\text{CC}(\text{H})(\text{CH}=\text{CH})\text{O}$), 5.97-6.02 (m, 2H, $\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 6.96 (t, *J* 7.3, 1H, PhH), 7.11 (d, *J* 8.7, 2H, $\times\text{PhH}$), 7.30 (dd, *J* 7.3, 8.7, 2H, $2\times\text{PhH}$); δ_{C} (150 MHz, CDCl_3) 25.9 ($(\text{CH}_3)_3\text{CCH}$), 34.2 ($(\text{CH}_3)_3\text{CCH}$), 51.5 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 84.8 ($(\text{CH}_3)_3\text{CCH}(\text{CH}=\text{CH})\text{ONPh}$), 115.3 ($2\times\text{PhCH}$), 121.7 (PhCH), 124.3 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 127.4 ($\text{PhNCH}(\text{H}')\text{CH}=\text{CH}$), 128.7 ($2\times\text{PhCH}$), 150.8 (PhC-N); *m/z* (ES) found 218.1546 ($[\text{MH}^+]$ $\text{C}_{14}\text{H}_{20}\text{NO}$), requires 218.1545; HPLC (Chiralcel OD-H, 99:1, hexanes/*i*PrOH, 0.5 ml min^{-1} , 254 nm, t_{R} (minor) 10.1 min, t_{R} (major) 14.6 min.

(6*R*)-6-Isopropyl-4-methyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4i)

To a solution of isovaleraldehyde (53 μl , 0.48 mmol) in DMSO (2 ml) was added (2*S*)-5-pyrrolidin-2-yl-1*H*-tetrazole (11 mg, 0.08 mmol). The resulting suspension was stirred vigorously for 1 min before addition of nitrosobenzene (44 mg, 0.40 mmol). The bright green reaction mixture was stirred at room temperature until the reaction was determined to be complete by TLC and the disappearance of green colour, resulting in a yellow solution. The reaction mixture was then cooled to 0°C and THF (2 ml) was added. Isopropenyltriphenylphosphonium bromide (230 mg, 0.60 mmol) was added, followed by sodium hydride (32 mg, 0.80 mmol). After 20 min of stirring at 0°C, the reaction mixture was quenched using saturated aqueous NH_4Cl and extracted with ether (3 $\times$ 6 ml). The combined organic layers were dried

over MgSO₄, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (20:1, petrol/EtOAc) to provide the title compound as a yellow oil (46 mg, 53%, 99% *ee*). $[\alpha]_D^{25} +58.2$ (*c* 0.68 in CHCl₃); $\nu_{\text{(max)}}$ (film) 2960, 2863, 2836, 1598, 1491, 1476, 1463, 1216, 1030, 984.5, 887.1, 785.3, 753.2, 689.7 cm⁻¹; δ_{H} (600 MHz, CDCl₃) 1.03 (d, *J* 6.8, 3H, (CH₃)(CH'₃)CH), 1.05 (d, *J* 6.8, 3H, (CH₃)(CH'₃)CH), 1.83 (s, 3H, PhNCH₂C(CH₃)=CH), 1.91 (app sext, *J* 6.8, 1H, (CH₃)(CH'₃)CH), 3.61 (m, 1H, PhNCH(H')C(CH₃)=CH), 3.72 (m, 1H, PhNCH(H')C(CH₃)=CH), 4.24 (app ddt, *J* 6.8, 4.3, 2.1, 1H, (CH₃)₂CHCH(CH=C(CH₃))ONPh), 5.64 (m, 1H, (CH₃)₂CHCH(CH=C(CH₃))ONPh), 6.97 (t, *J* 7.3, 1H, PhH), 7.14 (d, *J* 8.7, 2H, 2×PhH), 7.31 (dd, *J* 7.3, 8.7, 2H, 2×PhH); δ_{C} (150 MHz, CDCl₃) 18.4 ((CH₃)(C'H₃)CH), 18.5 ((CH₃)(C'H₃)CH), 20.3 (PhNCH₂C(CH₃)=CH), 31.7 ((CH₃)₂CH), 55.5 (PhNCH(H')C(CH₃)=CH), 81.9 ((CH₃)₂CHCH(CH=C(CH₃))ONPh), 115.4 (2×PhCH), 121.7 (PhCH), 122.4 (PhNCH₂C(CH₃)=CH), 128.8 (2×PhCH), 131.2 (PhNCH₂C(CH₃)=CH), 150.7 (PhC-N); *m/z* (ES) found 218.1540 ([MH⁺] C₁₄H₂₀NO), requires 218.1545; GC (Chiraldex, 90°C, 25 psi, split 50:1, *t*_R(major) 125.6 min, *t*_R(minor) 125.8 min.

(6*R*,1'*R*)-6-(1',5'-Dimethyl-hex-4'-enyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (4j)

Prepared according to the general procedure from (*R*)-(+)-citronellal (0.48 ml, 2.40 mmol) to provide the title compound as a pale yellow oil (0.37 g, 67%, 83% *de*) after flash column chromatography (4:1, petrol/toluene). $[\alpha]_D^{25} +18.7$ (*c* 1.29 in CHCl₃); $\nu_{\text{(max)}}$ (film) 2965, 2926, 2856, 1725, 1600, 1490, 1453, 1377, 1211, 1066, 1031, 988.2, 884.5, 752.7, 689.8 cm⁻¹; δ_{H} (600 MHz, CDCl₃) 1.02 (d, *J* 6.8, 3H, CH₂CH₂CH(CH₃)), 1.30 (app tdd, *J* 9.4, 5.5, 3.9, 2H, CH₂CH₂CH(CH₃)), 1.62 (s, 3H, (CH₃)CCH'₃=CHCH₂), 1.69 (s, 3H, (CH₃)CCH'₃=CHCH₂), 1.81-1.89 (m, 1H, CH₂CH₂CH(CH₃)), 1.99 (ddt, *J* 15.0, 7.5, 7.5, 1H, (CH₃)CCH'₃=CHCHH'), 2.06-2.14 (m, 1H, (CH₃)CCH'₃=CHCHH'), 3.73 (app dq, *J* 15.7, 2.2, 1H, PhNCH(H')CH=CH), 3.89 (app dtt, *J* 15.7, 2.5, 2.2, 1H, PhNCH(H')CH=CH), 4.45-4.48 (m, 1H, CH₂CH(CH₃)CH(CH=CH)O), 5.10-5.15 (m, 1H, (CH₃)CCH'₃=CHCH₂), 5.93 (app

dq, J 10.1, 2.2, 1H, PhNCH(H')CH=CH), 5.98 (app dqu, J 10.1, 2.2, 1H, PhNCH(H')CH=CH), 6.97 (t, J 7.3, 1H, PhH), 7.12 (d, J 8.7, 2H, 2×PhH), 7.30 (dd, J 8.7, 7.3, 2H, 2×PhH); δ_c (150 MHz, CDCl₃) 15.4 (CH₂CH₂CH(CH₃)), 17.7 (CH₃)CCH'₃=CHCH₂), 25.5 ((CH₃)CCH'₃=CHCHH'), 25.7 ((CH₃)CCH'₃=CHCH₂), 32.3 (CH₂CH₂CH(CH₃)), 35.9 (CH₂CH₂CH(CH₃)), 51.9 (PhNCH(H')CH=CH), 81.6 (CH₂CH(CH₃)CH(CH=CH)O), 115.5 (2×PhCH), 121.8 (PhCH), 123.8 (PhNCH(H')CH=CH), 124.5 (CH₃)CCH'₃=CHCHH'), 128.5 (PhNCH(H')CH=CH), 128.7 (2×PhCH), 131.5 (CH₃)CCH'₃=CHCHH'), 150.8 (PhC-N); m/z (ES) found 272.2003 ([MH⁺] C₁₈H₂₆NO), requires 272.2014.

**(6R,1'S)-6-(1',5'-Dimethyl-hex-4'-enyl)-2-phenyl-3,6-dihydro-2H-[1,2]oxazine
(4k)**

Prepared according to the general procedure from (*S*)-(-)-citronellal (0.45 ml, 2.40 mmol) to provide the title compound as a pale yellow oil (0.33 g, 61%, 99% *de*) after flash column chromatography (4:1, petrol/DCM). $[\alpha]_D^{25} +34.3$ (c 0.88 in CHCl₃); $\nu_{\text{(max)}}$ (film) 2926, 1600, 1490, 1211, 981.0, 753.1, 690.4 cm⁻¹; δ_H (600 MHz, CDCl₃) 1.01 (d, J 6.9, 3H, CH₂CH₂CH(CH₃)), 1.36 (app tdd, J 9.1, 5.7, 2.4, 2H, CH₂CH₂CH(CH₃)), 1.64 (s, 3H, (CH₃)CCH'₃=CHCH₂), 1.72 (s, 3H, (CH₃)CCH'₃=CHCH₂), 1.78-1.84 (m, 1H, CH₂CH₂CH(CH₃)), 2.02-2.16 (m, 2H, (CH₃)CCH'₃=CHCH₂), 3.73 (app dq, J 15.7, 2.8, 1H, PhNCH(H')CH=CH), 3.91 (app dtt, J 15.7, 2.8, 1.8, 1H, PhNCH(H')CH=CH), 4.51-4.54 (m, 1H, CH₂CH(CH₃)CH(CH=CH)O), 5.16 (app tt, J 7.1, 2.4, 1H, (CH₃)CCH'₃=CHCH₂), 5.92 (app dq, J 10.1, 2.4, 1H, PhNCH(H')CH=CH), 5.99 (app ddt, J 10.1, 4.5, 2.4, 1H, PhNCH(H')CH=CH), 6.98 (t, J 7.3, 1H, PhH), 7.13 (d, J 8.7, 2H, 2×PhH), 7.32 (dd, J 8.7, 7.3, 2H, 2×PhH); δ_c (150 MHz, CDCl₃) 14.8 (CH₂CH₂CH(CH₃)), 17.7 (CH₃)CCH'₃=CHCH₂), 25.7 ((CH₃)CCH'₃=CHCH₂), 25.8 (CH₃)CCH'₃=CHCH₂), 33.0 (CH₂CH₂CH(CH₃)), 36.3 (CH₂CH₂CH(CH₃)), 51.7 (PhNCH(H')CH=CH), 80.9 (CH₂CH(CH₃)CH(CH=CH)O), 115.4 (2×PhCH), 121.8 (PhCH), 123.6 (PhNCH(H')CH=CH), 124.6 (CH₃)CCH'₃=CHCH₂), 128.8 (2×PhCH), 129.1

(PhNCH(H')CH=CH), 131.5 (CH₃)CCH'₃=CHCH₂), 150.8 (PhC-N); *m/z* (ES) found 272.2004 ([MH⁺] C₁₈H₂₆NO), requires 272.2014.

(3*R*,4*Z*)-2-Methyl-6-phenylamino-hex-4-en-3-ol (5a)

To a solution of (6*R*)-6-isopropyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine **4a** (0.21 g, 1.02 mmol) in MeOH (10 ml) were added zinc powder (0.34 g, 5.10 mmol) and 3*N* aqueous HCl (3.4 ml, 10.2 mmol). The resulting suspension was stirred vigorously at room temperature for 18 h. The reaction mixture was quenched using saturated aqueous NaHCO₃ (40 ml), diluted with H₂O and extracted with EtOAc (3×40 ml). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (3:1, petrol/EtOAc) to provide the title compound as a pale yellow oil (0.17 g, 83%, 99% *ee*). [α]_D²⁵ +8.2 (*c* 1.47 in CHCl₃); ν_(max) (film) 3376, 2960, 1603, 1505, 1468, 1314, 1255, 1179, 1016, 749.5, 692.6 cm⁻¹; δ_H (600 MHz, CDCl₃) 0.92 (d, *J* 6.7, 3H, (CH₃)(CH'₃)CH), 0.99 (d, *J* 6.7, 3H, (CH₃)(CH'₃)CH), 1.74 (app oct, *J* 6.7, 1H, (CH₃)(CH'₃)CH), 2.81 (br s, 2H, (CH₃)₂CHCH(OH), PhNHCHH'), 3.76 (ddd, *J* 14.0, 6.1, 1.6, 1H, PhNHCHH'), 3.88 (ddd, *J* 14.0, 7.2, 1.6, 1H, PhNHCHH'), 4.21 (dd, *J* 8.8, 6.7, 1H, (CH₃)₂CHCH(OH)), 5.61 (dd, *J* 11.1, 8.8, 1H, PhNHCH₂CH=CH), 5.73 (ddd, *J* 11.1, 7.2, 6.1, 1H, PhNHCH₂CH=CH), 6.65 (d, *J* 8.6, 2H, PhH), 6.76 (t, *J* 7.3, 1H, PhH), 7.20 (dd, *J* 8.6, 7.3, 2H, PhH); δ_C (150 MHz, CDCl₃) 18.1 ((CH₃)₂CH), 34.2 ((CH₃)₂CH), 41.6 (PhNHCH₂), 72.8 (CH₃)₂CHCH(OH), 113.3 (2×PhCH), 118.1 (PhCH), 129.3 (2×PhCH), 129.4 (PhNCH₂CH=CH), 133.9 (PhNCH₂CH=CH), 147.7 (PhC-N); *m/z* (ES) found 206.1550 ([MH⁺] C₁₃H₂₀NO), requires 206.1545; HPLC (Chiralcel OD-H, 95:5, hexanes/^{*i*}PrOH, 1.0 ml min⁻¹, 254 nm, *t*_R(major) 29.1 min, *t*_R(minor) 33.7 min.

(2*Z*,4*R*,6*Z*)-1-Phenylamino-nona-2,6-dien-4-ol (5b)

To a solution of (6*R*,2'*Z*)-6-Pent-2'-enyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine **4b** (0.16 g, 0.685 mmol) in MeOH (7 ml) were added zinc powder (0.23 g, 3.52 mmol) and 3*N* aqueous HCl (2.3 ml, 6.85 mmol). The resulting suspension was stirred vigorously at room temperature for 18 h. The reaction mixture was quenched using saturated aqueous NaHCO₃ (20 ml), diluted with H₂O and extracted with EtOAc (3×20 ml). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (3:1, petrol/EtOAc) to provide the title compound as a yellow oil (0.13 g, 92%, 99% *ee*). $[\alpha]_D^{25} +43.1$ (*c* 1.00 in CHCl₃); $\nu_{(\max)}$ (film) 3351, 3052, 2961, 2933, 2834, 1602, 1503, 1462, 1431, 1313, 1254, 1179, 1024, 991.8, 867.0, 747.0, 691.0 cm⁻¹; δ_H (600 MHz, CDCl₃) 0.98 (t, *J* 7.5, 3H, CH₃CH₂), 2.09 (app qu, *J* 7.5, 2H, CH₃CH₂), 2.26 (app qu, *J* 6.9, 1H, CH₃CH₂CH=CHCH(*H'*)), 2.41 (app qu, *J* 6.9, 1H, CH₃CH₂CH=CHCH(*H''*)), 3.77 (ddd, *J* 14.1, 6.4, 1.5, 1H, PhNHCH(*H'*)CH=CH), 3.86 (ddd, *J* 14.1, 6.4, 1.5, 1H, PhNHCH(*H''*)CH=CH), 4.52 (app dtd, *J* 8.1, 6.9, 1.0, 1H, CH=CHCH₂CH(OH)CH=CH), 5.36 (app dt, *J* 10.1, 6.9, 1H, CH₃CH₂CH=CHCH₂), 5.58-5.65 (m, 2H, CH=CHCH₂CH(OH)CH=CH), 5.69 (app dtd, *J* 11.1, 6.4, 1.0, 1H, PhNHCH₂CH=CH), 6.63 (d, *J* 8.6, 2H, 2×Ph*H*), 6.74 (t, *J* 7.3, 1H, Ph*H*), 7.19 (dd, *J* 8.6, 7.3, 2H, 2×Ph*H*); δ_C (150 MHz, CDCl₃) 14.2 (CH₃CH₂), 20.8 (CH₃CH₂), 35.4 (CH₃CH₂CH=CHCH₂), 41.5 (PhNHCH₂CH=CH), 67.5 (CH₂CH(OH)CH=CH), 113.2 (2×PhCH), 117.9 (PhCH), 123.4 (CH₃CH₂CH=CH), 129.0 (PhNHCH₂CH=CH), 129.2 (2×PhCH), 134.8 (PhNHCH₂CH=CH), 135.6 (CH₃CH₂CH=CH), 147.9 (PhC-N); *m/z* (ES) found 232.1700 ([MH⁺] C₁₅H₂₂NO), requires 232.1701; HPLC (Chiralpak AD-H, 99:1, hexanes/*i*PrOH, 0.5 ml min⁻¹, 254 nm, *t*_R(minor) 154.6 min, *t*_R(major) 162.0 min.

(4*R*)-1-Phenylamino-dodeca-2,6-dien-4-ol (5c)

To a solution of (6*R*,2'*E*)-6-Oct-2'-enyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine **4c** (0.12 g, 0.450 mmol) in MeOH (5 ml) were added zinc powder (0.15 g, 2.27 mmol)

and 3N aqueous HCl (1.5 ml, 4.50 mmol). The resulting suspension was stirred vigorously at room temperature for 18 h. The reaction mixture was quenched using saturated aqueous NaHCO₃ (15 ml), diluted with H₂O and extracted with EtOAc (3×20 ml). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (3:1, petrol/EtOAc) to provide the title compound as a yellow oil (0.10 g, 83%, 99% *ee*). $[\alpha]_D^{25} +33.2$ (*c* 0.98 in CHCl₃); $\nu_{(\max)}$ (film) 3351, 3052, 2924, 2854, 1602, 1504, 1466, 1432, 1313, 1255, 1179, 1010, 970.1, 868.2, 746.9, 690.8 cm⁻¹; δ_H (600 MHz, CDCl₃) 0.89 (t, *J* 7.1, 3H, CH₃CH₂CH₂), 1.24-1.34 (m, 4H, CH₃CH₂CH₂CH₂), 1.37 (app qu, *J* 7.2, 2H, CH₃CH₂CH₂CH₂), 2.03 (app q, *J* 7.2, 2H, CH₂CH₂CH=CHCH₂), 2.26 (app t, *J* 6.6, 2H, CH₂CH₂CH=CHCH₂), 3.77 (ddd, *J* 14.1, 6.2, 1.5, 1H, PhNHCH(H')CH=CH), 3.86 (ddd, *J* 14.1, 7.0, 1.5, 1H, PhNHCH(H')CH=CH), 4.49 (app dtd, *J* 8.1, 6.6, 1.0, 1H, CH=CHCH₂CH(OH)CH=CH), 5.40 (app dt, *J* 15.3, 7.2, 1H, CH₂CH₂CH=CHCH₂), 5.60-5.65 (m, 2H, CH=CHCH₂CH(OH)CH=CH), 5.69 (dddd, *J* 11.1, 6.2, 7.0, 1.0, 1H, PhNHCH₂CH=CH), 6.63 (d, *J* 8.6, 2H, 2×PhH), 6.74 (t, *J* 7.3, 1H, PhH), 7.19 (dd, *J* 8.6, 7.3, 2H, 2×PhH); δ_C (150 MHz, CDCl₃) 14.0 (CH₃CH₂CH₂), 22.5 (CH₃CH₂CH₂), 29.1 (CH₃CH₂CH₂CH₂), 31.4 (CH₃CH₂CH₂), 32.6 (CH₂CH₂CH=CHCH₂), 41.0 (CH₂CH₂CH=CHCH₂), 41.5 (PhNHCH₂CH=CH), 67.2 (CH₂CH(OH)CH=CH), 113.1 (2×PhCH), 117.9 (PhCH), 124.6 (CH₂CH₂CH=CHCH₂), 128.9 (PhNHCH₂CH=CH), 129.2 (2×PhCH), 134.7 (PhNHCH₂CH=CH), 135.4 (CH₂CH₂CH=CHCH₂), 147.9 (PhC-N); *m/z* (ES) found 274.2166 ([MH⁺] C₁₈H₂₈NO), requires 274.2171; HPLC (Chiralpak AD-H, 99:1, hexanes/*i*PrOH, 0.5 ml min⁻¹, 254 nm, *t*_R(minor) 112.9 min, *t*_R(major) 118.1 min.

(2*Z*,4*R*)-1-Phenylamino-oct-2-en-4-ol (5d)

To a solution of (6*R*)-6-butyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine **4d** (21 mg, 0.097 mmol) in MeOH (1.0 ml) were added zinc powder (32 mg, 0.487 mmol) and 3N aqueous HCl (0.3 ml, 0.974 mmol). The resulting suspension was stirred vigorously at room temperature for 18 h. The reaction mixture was quenched using saturated

aqueous NaHCO₃ (5 ml), diluted with H₂O and extracted with EtOAc (3×10 ml). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (3:1, petrol/EtOAc) to provide the title compound as a yellow oil (20 mg, 96%, 99% *ee*) after flash column chromatography (3:1, petrol/EtOAc). $[\alpha]_D^{25} +28.2$ (*c* 0.71 in CHCl₃); $\nu_{\text{(max)}}$ (film) 3347, 3054, 2930, 2855, 1602, 1504, 1466, 1431, 1313, 1256, 1179, 1154, 1001, 871.9, 747.1, 691.1 cm⁻¹; δ_H (600 MHz, CDCl₃) 0.92 (t, *J* 7.0, 3H, CH₃CH₂CH₂), 1.27-1.39 (m, 4H, CH₃CH₂CH₂CH(H')), 1.46-1.52 (m, 1H, CH₃CH₂CH₂CH(H')), 1.61-1.66 (m, 1H, CH₃CH₂CH₂CH(H')), 3.77 (ddd, *J* 14.1, 6.1, 1.5, 1H, PhNHCHH'), 3.87 (ddd, *J* 14.1, 7.1, 1.5, 1H, PhNHCHH'), 4.49 (ddd, *J* 14.7, 7.7, 1.0, 1H, CH₃(CH₂)₃CH(OH)), 5.59 (ddt, *J* 11.0, 7.7, 1.5, 1H, PhNHCH₂CH=CH), 5.67 (dddd, *J* 11.0, 6.1, 7.1, 1.0, 1H, PhNHCH₂CH=CH), 6.64 (d, *J* 8.1, 2H, 2×PhH), 6.74 (t, *J* 7.4, 1H, PhH), 7.19 (dd, *J* 8.1, 7.4, 2H, 2×PhH); δ_C (150 MHz, CDCl₃) 14.0 (CH₃CH₂CH₂), 22.6 (CH₃CH₂CH₂), 27.5 (CH₃CH₂CH₂), 37.2 (CH₃CH₂CH₂CH₂), 41.5 (PhNHCH₂CH=CH), 67.9 (CH₃(CH₂)₃CH(OH)), 113.2 (2×PhCH), 118.0 (PhCH), 128.7 (PhNHCH₂CH=CH), 129.3 (2×PhCH), 135.6 (PhNHCH₂CH=CH), 147.8 (PhC-N); *m/z* (ES) found 220.1700 ([MH⁺] C₁₄H₂₂NO), requires 220.1701; HPLC (Chiralpak AD-H, 99:1, hexanes/ⁱPrOH, 0.5 ml min⁻¹, 254 nm, *t*_R(minor) 157.9 min, *t*_R(major) 164.0 min.