Supplementary Material (ESI) for Chemical Communications

Controlling diastereoselectivity in the reactions of enantiomerically pure α-bromoacyl-imidazolidinones with nitrogen nucleophiles: substitution reactions with retention or inversion of configuration.

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Supplementary Information

General Procedures: All reactions were performed using oven-dried apparatus under a dry atmosphere at room temperature (unless otherwise stated). Reaction solvents were pre-dried and distilled prior to use. Tetrahydrofuran and diethyl ether were pre-dried over sodium wire and distilled from sodium benzophenone under a nitrogen atmosphere. Dichloromethane, dimethyl formamide and acetonitrile were distilled from calcium hydride powder under a nitrogen atmosphere. Methanol was distilled from iodine/magnesium turning under an atmosphere of nitrogen. The term petrol refers to distilled petroleum ether (40-60°C). Flash column chromatography was carried out using Merck 60 silica gel. Analytical thin-layer chromatography (TLC) was performed on E. Merck silica gel 60F-254 pre-coated plates and the spots visualised with a UV lamp and ninhydrin or permanganate dips. Melting points were carried out on a Gallenkamp melting point apparatus and are uncorrected. IR specta were recorded using a Perkin-Elmer FT-IR 298 or 2000 FT spectrometer, NMR spectra were measured using Brüker 300MHz and 500MHz machines whilst coupling constants (*J*) are given in Hertz. Mass spectra were recorded on a Fisons autospec or Micromass Platform instruments. High-resolution spectra were performed at the National Service Centre, University College, Swansea on a Thermoquest Finnigan MAT900XT Spectrometer. Optical rotation measurements were carried out using a Perkin-Elmer 241 polarimeter (cont. Na 589) with a cell length path of 10 cm. The mean value for ten α reading were taken.

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Representative General Procedures

Preparation of (2'*R*) – bromides *via* lithiation bromination.

Preparation of 4a

To an N_2 purged stirring flask containing (4*S*,5R)-1-(3'-phenylpropionyl)-3, 4-dimethyl-5-phenylimidazolidin-2-one (1.0 g, 3.10 mmol), in THF (10 ml) was cooled to -78°C and LHMDS (1.0 M in hexanes, 3.4 ml, 3.4 mmol) was added dropwise. The reaction was allowed to stir for 45 minutes before the addition of bromine (183 μl, 3.57 mmol) dropwise and the reaction allowed to stir for a further 50 minutes. The reaction was quenched by the addition of $NH_4Cl_{(aq)}$ (20 ml) and EtOAc (20 ml). The organic layer was further washed with $NH_4Cl_{(aq)}$ (2 × 20 ml); the aqueous layer back-extracted with EtOAc (5 ml). The organic layers were collected, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude was purified using flash column chromatography [silica] P/EtOAc (4:1) to give **4a** (890 mg, 72%)

Substitution of (2'*R*) – bromides with benzylamine under DKR (epimerising) conditions.

Preparation of 5a

To an N_2 purged stirring flask containing (2*'RS*,4*S*,5*R*)-1-(2'-bromo-3-phenyl-propionyl)-3,4-dimethyl-5-phenylimidazolidin-2-one, (65 mg, 0.16 mmol), and *n*Bu_4NI (12.9 mg. 0.03 mmol) in THF (2 ml) was added benzylamine (106 μl, 0.97 mmol) and allowed to stir at room temperature for 6 days. The reaction was concentrated *in vacuo*, re-dissolved in EtOAc (10 ml) and deionised water (10 ml) added. The organic layer was further washed with deionised water (2 × 10 ml); the aqueous layer back-extracted with EtOAc (5 ml). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude was purified by flash column chromatography [silica] with eluent P/EtOAc (4:1). This afforded **5a** as a white solid (51 mg, 74%).

Direct substitution of (2'*R*) – bromides with TMGA.[6]

Preparation of 6a

To a N_2 purged flask containing (2'*R*,4*S*,5*R*)-1-(2'-bromo-3'-phenylpropionyl)-3,4-dimethyl-5-phenylimidazolidin-2-one (65 mg, 0.16 mmol) in DCM (2 ml) was cooled to 0 °C and TMGA

(90 mg, 0.57 mmol) added. The reaction was stirred at 0 °C *ca* 15 minutes and then allowed to warm to room temperature. The reaction was allowed to stir for 2 hours before quenching by the addition of deionised water (10 ml) and EtOAc (10 ml). The organic layer was washed with $NH_4Cl_{(aq)}$ (2 × 10 ml). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified using flash column chromatography [silica] with eluent P/EtOAc (4:1) to give the product **6a** as a white solid (55.3 mg, 94%), d.e. >95%.

Auxiliary cleavage protocol with NaOMe

Preparation of 7a

To a N_2 purged flask containing (2'*R*,4*S*,5*R*)-1-(2'-benzylamino-3'-phenylpropionoyl)-3,4-dimethyl-5-phenylimidazolidin-2-one (67.4 mg, 0.16 mmol) and NaOMe (8.7mg, 0.16 mmol) was added MeOH (2 ml) initially at 0 °C and then the reaction was allowed to warm to room temperature. The reaction was allowed to stir for 18 hours. The reaction was quenched by the addition of brine (6 ml) and EtOAc (6 ml). The organic layer was washed with brine (2 × 6 ml) and the aqueous layer back extracted with EtOAc (2 ml). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude was purified using flash column chromatography [silica] with eluent P/EtOAc (4:1-1:7) to give the product as a colourless oil (39.6 mg, 92%) and recovered auxiliary (27.9 mg, 92%).

Auxiliary cleavage protocol with LiOOH

Preparation of 8a

To a stirring flask containing (2'*S*,4*S*,5*R*)-1-(2'-azido-3'-phenylpropionyl)-3,4-dimethyl-5-phenylimidazolidin-2-one (52.6 mg, 0.15 mmol) in THF/de-ionized water (3/1, 1.36:045 ml) cooled to 0 °C was added a solution of LiOOH [LiOH (6.6 mg, 0.16 mmol), deionised water (0.16 ml), HOOH (27.5% in water, 64 μl, 0.58 mmol)] dropwise. The reaction mixture was maintained at 0 °C for *ca* 15 min and then allowed to warm to room temperature. The reaction was complete after 1.5 hours and cooled to 0 °C whereupon Na_2SO_3 (91.2 mg, 0.72 mmol) in deionised water (1.6 ml) was added. The reaction was allowed to stir *ca* 15 min and allowed to warm to room temperature. After 1 hour the reaction mixture was tested for peroxides (starch/iodine paper) and checked that the pH of the solution was *ca* 9-10. The aqueous layer was washed with DCM (3 × 10 ml) and the aqueous layer again cooled to 0 °C. HCl (1M) was added dropwise to the cooled aqueous solution until the pH became *ca* 2-1.5. The aqueous layer was washed with EtOAc (3x10 ml). The organic layers were

dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford the product as a colourless oil (27.3 mg, 98%) and recovered auxiliary (25.7 mg, 93%).

Spectroscopic and analytical data

4a

R*f* 0.27 (P/EtOAc, 4:1); υ_{max} (thin film)/cm^{-1} 3086, 3060, 3027, 2981, 2991, 2935, 1710, 1692, 1603, 1585, 1498, 1455, 769, 756, 745, 699; δ_H($CDCl_3$, 300MHz) 7.01-7.19 (m, 8H, Ar**C**H), 6.75 (d, *J* = 6.7 Hz, 2H, Ar**C**H), 6.6. (dd, *J* = 6.3, 9.1 Hz, 1H, **C**HBr), 5.22 (d, *J* = 8.6 Hz, 1H **C**HPh), 3.86 (dq, 1H, *J* = 8.6, 6.6Hz, **C**HCH_3), 3.42 (dd, *J* = 6.3, 13.7 Hz, 1H, **C**H_A**H$_B$**Ph), 3.10 (dd, *J* = 9.1, 13.7 Hz, 1H, **C**$H_A$$H_B$Ph), 2.75 (s, 3H, **CH$_3$**N), 0.68 (d, *J* = 6.6 Hz, 3H, **CH$_3$**CH); δ_C($CDCl_3$, 75MHz) 168.2 (N**C**ON), 154.7 (N**C**O), 137.0 (Ar**C**), 135.7 (Ar**C**), 129.4 (Ar**C**H), 128.5 (Ar**C**H), 127.8 (Ar**C**H), 126.8 (Ar**C**H), 126.6 (Ar**C**H), 59.7 (**C**HPh), 53.6 (**C**HCH_3), 43.6 (**C**HBr), 40.5 (**CH$_2$**Ph), 28.2 (**CH$_3$**N), 14.8 (**CH$_3$**CH); *m/z* (FAB) 402 (MH^+), 321 (M^+-Br), 279, 217(M^+-CHBrCH_2Ph), 189, 77; Accurate mass (ES) $C_{20}H_{21}N_2O_2Br$ Calculated 400.0786 (M^+) Measured 400.0785. $[\alpha]_D^{30}$ -90.7 (*c* = 1.00 DCM); Mpt 150-151 °C.

4b

R*f* 0.48 (P/EtOAc 2:1); υ_{max} (thin film)/cm^{-1} 3062, 3029, 2978, 2937, 1730, 1686, 1604, 1496, 1476, 1454, 754, 737, 701; δ_H($CDCl_3$, 300MHz) 7.22-7.36 (m, 10H, Ar**C**H), 5.91 (t, *J* = 7.4 Hz, 1H, **C**HBr), 5.28 (d, *J* = 8.7 Hz, 1H, **C**HPh), 3.85 (dq, *J* = 8.7, 6.6 Hz, 1H, **C**HCH_3), 2.82 (s, 3H, **CH$_3$**N), 2.63-2.79 (m, 2H, **CH$_2$**Ph), 2.28-2.38 (m, 2H, **CH$_2$**CH_2Ph), 0.77 (d, 3H, *J* = 6.6 Hz, **CH$_3$**CH); δ_C($CDCl_3$, 75MHz) 167.9 (N**C**ON), 154.5 (N**C**O), 140.5 (Ar**C**), 135.4 (Ar**C**), 128.5 (Ar**C**H), 128.4 (Ar**C**H), 128.2 (Ar**C**H), 126.9 (Ar**C**H), 126.1 (Ar**C**H), 59.1 (**C**HPh), 53.6 (**C**HCH_3), 45.5 (**C**HBr), 35.5 (**CH$_2$**CH_2Ph), 34.5 (**CH$_2$**Ph), 28.2 (**CH$_3$**N), 15.1 (**CH$_3$**CH); *m/z* (EI) 416 (MH^+), 335 (MH^+-Br), 325, 310, 231 (M-(Br)CH_2CH_2Ph), 191 (M-CHBrCH_2CH_2Ph), 132, 91, 77; Accurate mass (ES) $C_{21}H_{23}N_2O_2Br$ Calculated 414.0943 (M^+) Measured 414.0939; $[\alpha]_D^{27}$ -60.4 (*c* = 1.00 $CHCl_3$).

4c

R*f* 0.57 (P/EtOAc 2:1; υ_{max} (thin film)/cm^{-1} 3028, 2935, 1730, 1686, 1495, 1454, 1423, 751, 700; δ_H($CDCl_3$, 300MHz) 7.09-7.36 (m, 10H, Ar**C**H), 5.96 (t, *J* = 6.7 Hz, 1H, **C**HBr), 5.29 (d, *J* = 8.7 Hz, 1H, **C**HPh), 3.84 (dq, *J* = 8.7, 6.5Hz, 1H, **C**HCH_3), 2.81 (s, 3H, **C**$\mathbf{H_3}$N), 2.64 (t, *J* = 7.5 Hz, 2H, **C**$\mathbf{H_2}$Ph), 1.97-2.16 (m, 2H, **C**$\mathbf{H_2}CH_2CH_2Ph$), 1.84-1.67 (m, 2H, CH_2**C**$\mathbf{H_2}CH_2Ph$), 0.76 (d, *J* = 6.5 Hz, 3H,**C**$\mathbf{H_3}$CH); δ_C($CDCl_3$, 75MHz) 168.0 (N**C**ON), 154.6 (N**C**O), 141.6 (Ar**C**), 135.5 (Ar**C**), 128.5 (Ar**C**H), 128.4 (Ar**C**H), 128.3 (Ar**C**H), 128.2 (Ar**C**H), 126.9 (Ar**C**H), 125. (Ar**C**H), 125.77 (**ArC**H), 59.1 (**C**HPh), 53.6 (**C**HCH_3), 44.8 (**C**HBr), 35.2 (**C**$\mathbf{H_2}$Ph), 33.3 (**C**$\mathbf{H_2}CH_2CH_2Ph$), 29.1 (CH_2**C**$\mathbf{H_2}CH_2Ph$), 28.3 (**C**$\mathbf{H_3}$N), 15.1 (**C**$\mathbf{H_3}$CH); *m/z* (FAB) 429 (M^+), 349 (M^+-Br), 253, 191, 84, 51; Accurate mass (ES) $C_{22}H_{25}N_2O_2Br$ Calculated 428.1099 (M) Measured 428.1093; $[\alpha]_D^{29}$ –67.7 (*c* = 1.00 $CHCl_3$).

4d

R*f* 0.23 (P/EtOAc 4:1); υ_{max} (thin film)/cm^{-1} 3028, 2932, 2859, 1730, 1688, 1602, 1493, 1454, 1423, 748, 700; δ_H($CDCl_3$, 300MHz) 7.14-7.34 (m, 10H, Ar**C**H), 5.87 (t, *J* = 7.4 Hz, 1H, **C**HBr), 5.32 (d, *J* = 8.8 Hz, 1H, **C**HPh), 3.91 (dq, *J* = 8.8, 6.6, Hz, 1H, **C**HCH_3), 2.85 (s, 3H, **C**$\mathbf{H_3}$N), 2.60 (t, *J* = 7.6 Hz, 2H, **C**$\mathbf{H_2}$Ph), 1.98-2.11 (m, 2H, **C**$\mathbf{H_2}CH_2CH_2CH_2Ph$), 1.45-1.69 (m, 4H, CH_2**C**$\mathbf{H_2}$**C**$\mathbf{H_2}CH_2Ph$), 0.80 (d, *J* = 6.6 Hz, 3H, **C**$\mathbf{H_3}$CH); δ_C($CDCl_3$, 75MHz) 168.7 (N**C**ON), 155.2 (N**C**O), 142.7 (Ar**C**), 135.9 (Ar**C**), 129.0 (Ar**C**H), 128.9 (Ar**C**H), 128.7 (Ar**C**H), 127.5 (Ar**C**H), 126.2 (Ar**C**H), 59.8 (**C**HPh), 54.3 (**C**HCH_3), 45.4 (CH**Br**), 36.1 (**C**$\mathbf{H_2}$Ph), 34.1 (**C**$\mathbf{H_2}CH_2CH_2CH_2Ph$), 31.3 ($CH_2CH_2$**C**$\mathbf{H_2}CH_2Ph$), 28.8 (**C**$\mathbf{H_3}$N), 27.51 ($CH_2$**C**$\mathbf{H_2}CH_2CH_2Ph$), 15.7 (**C**$\mathbf{H_3}$CH); *m/z* (ES) 445 ($Br^{81}$ M^+), 365 (MH^{2+}-Br), 232 (MH^{2+}-(Br)$CH_2CH_2CH_2CH_2Ph$), 191; Accurate mass (ES) $C_{23}H_{27}N_2O_2Br$, Calculated 442.1256 (M) Measured 442.1255; $[\alpha]_D^{27}$ -60.8 (*c* = 1.00 $CHCl_3$).

EPIMER of **4d** also isolated (7%)

R*f* 0.25 (P/EtOAc 4:1)

υ_{max} (thin film)/cm^{-1} 3061, 3030, 2934, 2859 (Aliphatic CH), 1724 (CO), 1691 (CO), 1602, 1492, 1453, 1424 (Ar-C=C), 750, 701 (Ar- monosubstituted), 670 (CBr).

δ_H($CDCl_3$, 300MHz) 7.22-7.31 (m, 5H, Ar**C**H), 7.09-7.15 (m, 5H, Ar**C**H), 5.95 (t, *J* = 7.3 Hz, 1H, **C**HBr), 5.30 (d, *J* = 8.4 Hz, 1H, **C**HPh), 3.95 (dq, *J* = 6.6 8.4 Hz, 1H, **C**HCH_3), 2.84 (s, 3H, **C**$\mathbf{H_3}$N), 2.53 (t, *J* = 7.7 Hz, 2H, **C**$\mathbf{H_2}$Ph), 1.94-2.12 (m, 2H, **C**$\mathbf{H_2}CH_2CH_2CH_2$Ph), 1.55-1.62 (m, 2H, $CH_2CH_2\mathbf{CH_2}CH_2$Ph), 1.26-1.36 (m, 2H, $CH_2\mathbf{CH_2}CH_2CH_2$Ph), 0.80 (d, *J* = 6.6 Hz, 3H,**C**$\mathbf{H_3}$CH).

δ_C($CDCl_3$, 75MHz) 169.1 (N**C**ON), 155.3 (N**C**O), 142.7 (Ar**C**), 136.7 (Ar**C**), 129.0 (Ar**C**H), 128.8 (Ar**C**H), 128.7 (Ar**C**H), 127.3 (Ar**C**H), 126.1 (Ar**C**H), 60.3 (**C**HPh), 54.2 (**C**HCH_3), 45.5 (CH**Br**) 36.1 (**C**$\mathbf{H_2}$Ph), 34.8 (**C**$\mathbf{H_2}CH_2CH_2CH_2$Ph), 31.2 ($CH_2CH_2\mathbf{CH_2}CH_2$Ph), 28.6 (**C**$\mathbf{H_3}$N), 27.3 ($CH_2\mathbf{CH_2}CH_2CH_2$Ph), 15.2 (**C**$\mathbf{H_3}$CH).

m/z (ES) 445 ($Br^{81}M^+$), 365 (M^+-Br), 270, 232(M^+-(Br)$CH_2CH_2CH_2CH_2$Ph), 191.

Accurate mass (ES) $C_{23}H_{27}N_2O_2Br$ Calculated 442.1256 (M) Measured 442.1261.

$[\alpha]_D^{26}$ -72.1 (*c* = 1.00 $CHCl_3$).

Mpt 98.4-99.4 °C.

4e

R*f* 0.24 (P/EtOAc 4:1; υ_{max} (thin film)/cm^{-1} 3061, 3028, 2931, 2858, 1731, 1688, 1603, 1493, 1454, 1423, 750, 700; δ_H($CDCl_3$, 300MHz) 7.13-7.37 (m, 10H, Ar**C**H), 5.88 (t, *J* = 7.3 Hz, 1H, **C**HBr), 5.32 (d, *J* = 8.8 Hz, 1H, **C**HPh), 3.91 (dq, *J* = 8.8, 6.6 Hz 1H, **C**HCH_3), 2.85 (s, 3H, **C**$\mathbf{H_3}$N), 2.58 (t, *J* = 7.7 Hz, 2H, **C**$\mathbf{H_2}$Ph), 1.95-2.13 (m, 2H, **C**$\mathbf{H_2}CH_2CH_2CH_2CH_2$Ph), 1.50-1.64 (m, 2H, $CH_2CH_2CH_2\mathbf{CH_2}CH_2$Ph) 1.32-1.48 (m, 4H, $CH_2\mathbf{CH_2CH_2}CH_2CH_2$Ph) 0.80 (d, *J* = 6.6 Hz, 3H, **C**$\mathbf{H_3}$CH); δ_C($CDCl_3$, 75MHz) 167.0 (N**C**ON), 153.5 (N**C**O), 141.3 (Ar**C**), 134.1 (Ar**C**), 127.2 (Ar**C**H), 127.1 (Ar**C**H), 127.0 (Ar**C**H), 126.9 (Ar**C**H), 125.7 (Ar**C**H), 124.3 (Ar**C**H), 58.0 (**C**HPh), 52.5 (**C**HCH_3), 43.8 (**C**HBr), 34.4 (**C**$\mathbf{H_2}$Ph), 32.4 (**C**$\mathbf{H_2}CH_2CH_2CH_2CH_2$Ph) 29.9 ($CH_2CH_2CH_2\mathbf{CH_2}CH_2$Ph), 27.4 ($CH_2\mathbf{CH_2}CH_2CH_2CH_2$Ph), 27.1 (**C**$\mathbf{H_3}$N), 25.9 ($CH_2CH_2\mathbf{CH_2}CH_2CH_2$Ph,) 13.90 (**C**$\mathbf{H_3}$CH); *m/z* (ES) 457 ($Br^{79}M^+$), 377 (M-Br), 319, 232, 191; Accurate mass (ES) $C_{24}H_{30}N_2O_2Br$ Calculated 456.1412 (M) Measured 456.1417. $[\alpha]_D^{29}$ -56.2 (*c* = 1.00 $CHCl_3$).

EPIMER of **4e** also isolated (10%)

Data for (2'*S*,4*S*,5*R*)1-(2'-Bromo-7'-phenylheptanoyl)-3,4-dimethyl-5-phenylimidazolidin-2-one

R*f* 0.26 (P/EtOAc 4:1)

υ_{max} (thin film)/cm^{-1} 3028, 2931, 2858, (Aliphatic CH), 1731 (CO), 1690 (CO), 1603, 1492, 1454, 1423, (Ar-C=C), 749, 701 (Ar- monosubstituted). δ_H($CDCl_3$, 300MHz) 7.23-7.30 (m, 5H, Ar**CH**), 7.09-7.15 (m, 5H, Ar**CH**), 5.95 (t, *J* = 7.3 Hz, 1H, **CH**Br), 5.30 (d, *J* = 8.5 Hz, 1H, **CH**Ph), 3.96 (dq, *J* = 6.6, 8.5 Hz, 1H, **CH**CH_3), 2.85 (s, 3H, **CH$_3$**N), 2.53 (t, *J* = 7.7 Hz, 2H, **CH$_2$**Ph), 1.92-2.09 (m, 2H, **CH$_2$**$CH_2CH_2CH_2CH_2$Ph), 1.48-1.59 (m, 2H, $CH_2CH_2CH_2$**CH$_2$**CH_2Ph) 1.23-1.38 (m, 4H, CH_2**CH$_2$CH$_2$**CH_2CH_2Ph) 0.81 (d, *J* = 6.6 Hz, 3H,**CH$_3$**CH). δ_C($CDCl_3$, 75MHz) 169.1 (N**CO**N), 155.3 (N**CO**), 143.0 (Ar**C**), 136.7 (Ar**C**), 129.0 (Ar**CH**), 128.8 (Ar**CH**), 128.7 (Ar**CH**), 128.6 (Ar**CH**), 127.3 (Ar**CH**), 126.0 (Ar**CH**), 60.3 (**CH**Ph), 54.2 (**CH**CH_3), 45.5 (**CH**Br), 36.1 (**CH$_2$**Ph), 34.9 (**CH$_2$**$CH_2CH_2CH_2CH_2$Ph), 31.6 ($CH_2CH_2CH_2$**CH$_2$**CH_2Ph), 29.0 (CH_2**CH$_2$**$CH_2CH_2CH_2$Ph), 28.6 (**CH$_3$**N), 27.4 (CH_2CH_2**CH$_2$**CH_2CH_2Ph), 15.2 (**CH$_3$**CH). *m/z* (ES) 457 ($Br^{79}M^+$), 377 (M-Br), 232, 205, 191. Accurate mass (ES) $C_{24}H_{30}N_2O_2Br$ Calculated 456.1412 (M^+) Measured 456.1415. $[\alpha]_D^{26}$ -62.2 (*c* = 1.00 $CHCl_3$).

5a

R*f* 0.54 (P/EtOAc, 4:1); υ_{max} (thin film)/cm^{-1} 3340 (NH), 3062, 3029, 1729, 1679, 1604, 1495, 1454, 1422, 744, 699; δ_H($CDCl_3$, 300MHz) 7.12-7.33 (m, 15H, Ar**CH**), 5.18 (t, *J* = 7.4 Hz, 1H, (CO**CH**), 5.08 (d, *J* = 8.4 Hz, 1H, **CH**Ph), 3.57 (d, J_{gem} = 12.8 Hz, 1H, NH**C**H_A**H$_B$**Ph), 3.47 (d, J_{gem} = 12.8 Hz, H, NH**CH$_A$**H_BPh), 3.45-3.54 (m, 1H, **CH**CH_3), 2.98 (dd, *J* = 7.4, 12.7 Hz, 1H, CH**C**H_A**H$_B$**Ph), 2.92 (dd, *J* = 7.4, 12.7 Hz, 1H, CH**CH$_A$**H_BPh), 2.66 (s, 3H, **CH$_3$**N), 2.43 (br s, 1H, **NH**), 0.71 (d, *J* = 6.6 Hz, 3H, **CH$_3$**CH); δ_C($CDCl_3$, 75MHz) 175.2 (N**CO**N), 155.2 (N**CO**), 139.8 (Ar**C**), 137.9 (Ar**C**), 136.6 (Ar**C**), 129.7 (Ar**CH**), 128.5 (Ar**CH**), 128.2 (Ar**CH**), 128.1 (Ar**CH**), 128.0 (Ar**CH**), 127.9 (Ar**CH**), 126.8 (Ar**CH**), 126.7 (Ar**CH**), 126.2 (Ar**CH**), 60.4 (CO**CH**), 59.5 (**CH**Ph), 53.8 (**CH**CH_3), 51.5 (NH**CH$_2$**Ph), 40.5 (**CH$_2$**Ph), 28.0 (**CH$_3$**N), 14.7 (**CH$_3$**CH). *m/z* (EI) 427 (M^+), 336 (M^+-CH_2Ph), 320 (M^+-HNCH_2PH), 210, 191, 91; Accurate

mass (ES) $C_{27}H_{29}N_3O_2$ Calculated 427.2260 (M^+) Measured 427.2262. $[\alpha]_D^{28}$ -92.0 (*c* = 0.46 MeOH); Mpt 116.8-117.9°C.

5b

R*f* 0.57 (P/EtOAc 2:1); υ_{max} (thin film)/cm^{-1} 3338, 3062, 3029, 2932,2860, 1730, 1679, 1603, 1495, 1454, 1423, 737, 701; δ_H($CDCl_3$, 300MHz) 7.06-7.31 (m, 15H, Ar**C**H), 5.16 (d, *J* = 8.5 Hz, 1H, **C**HPh), 4.68 (dd, *J* = 4.8, 7.9 Hz, 1H, CO**C**H), 3.77 (dq, *J* = 8.5, 6.6 Hz, 1H, **C**HCH_3), 3.47 (d, J_{gem} = 12.8 Hz, 1H, HN**C**$\mathbf{H_A}H_B$Ph) 3.34 (d, J_{gem} = 12.8 Hz, 1H, HN**C**$H_A\mathbf{H_B}$Ph) 2.87 (ddd, *J* = 4.9, 11.1, 16.5 Hz, 1H, CH_2**C**$\mathbf{H_A}H_B$Ph), 2.73 (s, 3H, **C**$\mathbf{H_3}$N), 2.64 (ddd, *J* = 5.7, 11.1, 16.5 Hz, 1H, CH_2**C**$H_A\mathbf{H_B}$Ph), 1.93-2.05 (m, 2H, **C**$\mathbf{H_A}H_B$$CH_2$Ph, **NH**), 1.71-1.78 (m, 1H, **C**$H_A\mathbf{H_B}$$CH_2$Ph), 0.72 (d, *J* = 6.6 Hz, 3H, **C**$\mathbf{H_3}$CH); δ_C($CDCl_3$, 75MHz) 175.6 (N**C**ON), 155.4 (N**C**O), 142.2 (Ar**C**), 140.3 (Ar**C**), 136.7 (Ar**C**), 128.5 (Ar**C**H), 128.3 (Ar**C**H), 128.1 (Ar**C**H), 128.1 (Ar**C**H), 126.9 (Ar**C**H), 126.7 (Ar**C**H), 125.6 (Ar**C**H), 59.8 (CO**C**H), 59.5 (**C**HPh), 53.9 (**C**HCH_3), 51.5 (HN**C**$\mathbf{H_2}$Ph), 35.2 (**C**$\mathbf{H_2}$$CH_2$Ph), 32.4 (**C**$\mathbf{H_2}$Ph), 28.2 (**C**$\mathbf{H_3}$N), 14.8 (**C**$\mathbf{H_3}$CH); *m/z* (EI) 441 ($M^+$), 350 ($M^+$-$CH_2$Ph), 336 ($M^+$-N$CH_2$Ph), 245 ($M^+$-(N$CH_2$Ph)$CH_2$Ph), 224, 191 ($M^+$-COCH(HN$CH_2$Ph)$CH_2CH_2$Ph), 132, 91, 77; Accurate mass (ES) $C_{28}H_{31}N_3O_2$ Calculated 441.2416 (M^+) Measured 441.2419.; $[\alpha]_D^{25}$ -37.1 (*c* = 1.00 $CHCl_3$); Mpt 89.1-90.2 °C.

5c

R*f* 0.45 (P/EtOAc 4:1); υ_{max} (thin film)/cm^{-1} 3340, 3027, 2937, 1720, 1679, 1495, 1454, 1421, 747, 699; δ_H($CDCl_3$, 300MHz) 7.05-7.43 (m, 15H, Ar**C**H), 5.20 (d, *J* = 8.5 Hz, 1H, **C**HPh), 4.67 (dd, *J* = 3.6, 7.7 Hz, 1H, CO**C**H), 3.79 (dq, *J* = 8.5, 6.6 Hz, 1H, **C**HCH_3), 3.42 (d, J_{gem} = 12.8 Hz, 1H, HN**C**$\mathbf{H_A}H_B$Ph), 3.30 (d, J_{gem} = 12.8 Hz, 1H, HN**C**$H_A\mathbf{H_B}$Ph), 2.73 (s, 3H, **C**$\mathbf{H_3}$N), 2.45-4.62 (m, 2H, CH_2CH_2**C**$\mathbf{H_2}$Ph), 1.96 (s, 1H, **NH**) 1.66-1.81 (m, 3H, **C**$\mathbf{H_A}H_B$**C**$\mathbf{H_2}$$CH_2$Ph), 1.43-1.55 (m, 1H, **C**$H_A\mathbf{H_B}$$CH_2CH_2$Ph) 0.72 (d, *J* = 6.6 Hz, 3H, **C**$\mathbf{H_3}$CH); δ_C($CDCl_3$, 75MHz) 177.1 (N**C**ON), 156.5 (N**C**O), 143.6 (Ar**C**), 141.4 (Ar**C**), 137.8 (Ar**C**), 129.5 (Ar**C**H), 129.5 (Ar**C**H), 129.2 (Ar**C**H), 129.0 (Ar**C**H), 128.0 (Ar**C**H), 127.8 (Ar**C**H), 126.6 (Ar**C**H), 60.6 (**C**HPh, CO**C**H), 55.0 (**C**HCH_3), 52.7 (HN**C**$\mathbf{H_2}$Ph) 36.8 (**C**$\mathbf{H_2}$Ph), 34.4 (**C**$\mathbf{H_2}$$CH_2CH_2$Ph), 29.2 (**C**$\mathbf{H_3}$N) 28.7 ($CH_2$**C**$\mathbf{H_2}$$CH_2$Ph), 15.9 (**C**$\mathbf{H_3}$CH); *m/z* (FAB) 456 ($MH^+$), 364 ($M^+$-$CH_2$Ph), 238, 191, 91; Accurate mass (EI) $C_{29}H_{33}N_3O_2$ Calculated 455.2573 (M) Measured 455.2569; $[\alpha]_D^{31}$ -30.2 (*c* = 1.00 $CHCl_3$); Mpt 106.0-108.2 °C.

5d

R*f* 0.17 (P/EtOAc 4.1); υ_{max} (thin film)/cm^{-1} 3331 (NH), 3028, 2931, 2857, 1729, 1678, 1603, 1454, 1422, 745, 698; δ_H($CDCl_3$, 300MHz) 7.13-7.39 (m, 15H, Ar**C**H), 5.29 (d, *J* = 8.5 Hz, 1H, **C**HPh), 4.70 (dd, *J* = 4.8, 6.8Hz, 1H, CO**C**H), 3.89 (dq, *J* = 8.5, 6.6 Hz, 1H, **C**HCH_3), 3.50 (d, J_{gem} = 12.8 Hz, 1H, HN**C**$\mathbf{H_A}H_B$Ph) 3.48 (d, J_{gem} = 12.8 Hz, 1H, HN**C**$\mathbf{H_A}H_B$Ph), 2.82 (s, 3H, **C**$\mathbf{H_3}$N), 2.58 (t, *J* = 7.3 Hz, 2H, **C**$\mathbf{H_2}$Ph), 2.09 (s, 1H, **N**H), 1.72-1.77 (m, 1H, $CH_A\mathbf{H_B}CH_2CH_2CH_2$Ph), 1.61-1.66 (m, 2H, **C**$\mathbf{H_2}CH_2CH_2$Ph) 1.42-1.55 (m, 3H, **C**$\mathbf{H_A}H_BCH_2CH_2CH_2$Ph), 0.78 (d, *J* = 6.6 Hz, 3H, **C**$\mathbf{H_3}$CH); δ_C($CDCl_3$, 75MHz) 176.7 (N**C**ON), 156.0 (N**C**O), 143.3 (Ar**C**), 140.9 (Ar**C**), 137.3 (Ar**C**), 129.0 (Ar**C**H), 128.9 (Ar**C**H), 128.6 (Ar**C**H), 128.6 (Ar**C**H), 128.5 (Ar**C**H), 127.4 (Ar**C**H), 127.2 (Ar**C**H), 126.0 (Ar**C**H), 60.2 (CO**C**H) 60.1 (**C**HPh), 54.4 (**C**HCH_3), 52.1 (NH**C**$\mathbf{H_2}$Ph), 36.4 (**C**$\mathbf{H_2}$Ph), 34.0 (**C**$\mathbf{H_2}CH_2CH_2CH_2$Ph), 31.9 (**C**$\mathbf{H_2}CH_2$Ph), 28.6 (**C**$\mathbf{H_3}$N), 26.2 (CH_2**C**$\mathbf{H_2}CH_2CH_2$Ph), 15.3 (**C**$\mathbf{H_3}$-CH); *m/z* (ES) 470 (MH^+), 312, 302, 272, 191; Accurate mass (ES) $C_{30}H_{35}N_3O_2$ Calculated 469.2729 (M^+) Measured 469.2734; $[\alpha]_D^{28}$ -30.0 (*c* = 1.00 $CHCl_3$); Mpt 109.3-110 °C.

5e

R*f* 0.21 (P/EtOAc 4:1); υ_{max} (thin film)/cm^{-1} 3335, 3058, 3061, 3028, 2931, 2856, 1730, 1679, 1603, 1492, 1454, 1423, 746, 700; δ_H($CDCl_3$, 300MHz) 7.14-7.33 (m, 15H, Ar**C**H), 5.27 (d, *J* = 8.5 Hz, 1H, **C**HPh), 4.67 (dd, *J* = 4.5, 6.8 Hz, 1H, CO**C**H), 3.86 (dq, *J* = 8.5, 6.6 Hz, 1H, **C**HCH_3), 3.50 (d, J_{gem} = 12.8$_{gem}$ Hz, 1H, HN**C**$\mathbf{H_A}H_B$Ph), 3.38 (d, J_{gem} = 12.8 Hz, 1H, HN$CH_A\mathbf{H_B}$Ph), 2.79 (s, 3H, **C**$\mathbf{H_3}$N), 2.58 (t, *J* = 7.7 Hz, 2H, **C**$\mathbf{H_2}$Ph), 2.09 (s, 1H, **N**H) 1.67-1.74 (m, 1H, CH**C**$\mathbf{H_A}H_BCH_2CH_2CH_2CH_2$Ph), 1.55-1.64 (m, 2H, $CHCH_2CH_2CH_2$**C**$\mathbf{H_2}CH_2$Ph), 1.42-1.51 (m, 3H, CH**C**$H_A\mathbf{H_B}$**C**$\mathbf{H_2}CH_2$**C**$\mathbf{H_2}CH_2$Ph), 1.26-1.39 (m, 2H, $CHCH_2CH_2$**C**$\mathbf{H_2}CH_2CH_2$Ph), 0.78 (d, *J* = 6.6 Hz, 3H, **C**$\mathbf{H_3}$CH); δ_C($CDCl_3$, 75MHz) 174.4 (N**C**ON), 154.7 (N**C**O), 142.1 (Ar**C**), 139.7 (Ar**C**), 136.1 (Ar**C**), 127.7 (Ar**C**H), 127.6 (Ar**C**H), 127.5 (Ar**C**H), 127.4 (Ar**C**H), 127.4 (Ar**C**H), 127.3 (Ar**C**H), 126.2 (Ar**C**H), 125.9 (Ar**C**H), 124.7 (Ar**C**H), 59.0 (CO**C**H), 58.8 (**C**HPh), 53.2 (**C**HCH_3), 50.9 (NH**C**$\mathbf{H_2}$Ph), 36.8 (**C**$\mathbf{H_2}$Ph), 36.8 (**C**$\mathbf{H_2}CH_2CH_2$ CH_2CH_2Ph), 30.6 (**C**$\mathbf{H_2}CH_2$Ph), 28.5 (**C**$\mathbf{H_2}CH_2CH_2$Ph), 27.4 (**C**$\mathbf{H_3}$N), 25.0 (CH_2**C**$\mathbf{H_2}CH_2CH_2CH_2$Ph), 14.1 (**C**$\mathbf{H_3}$-CH); *m/z* (ES) 484 (MH^+), 349, 309, 302, 191; Accurate mass (ES) $C_{31}H_{37}N_3O_2$ Calculated 483.2886 (M^+) Measured 483.2884; $[\alpha]_D^{26}$ -29.8 (*c* = 1.00 $CHCl_3$); Mpt 57.1-58.9 °C.

6a

R*f* 0.31 (P/EtOAc 4:1); υ_{max} (thin film)/cm^{-1} 3068, 3032, 2972, 2928, 2121, 1730, 1685, 1603, 1497, 1456, 1425, 745, 702; δ_H($CDCl_3$, 300MHz) 7.22-7.31 (m, 8H, Ar**CH**), 7.04-7.08 (m, 2H, Ar**CH**), 5.41 (dd, *J* = 4.5, 9.7 Hz, 1H, **CH**N_3), 5.35 (d, *J* = 8.6 Hz, 1H, **CH**Ph), 3.96 (dq, *J*= 8.6, 6.6 Hz, 1H, **CH**CH_3), 3.31 (dd, *J* = 4.5, 13.7 Hz, 1H, **CH$_A$**H$_B$Ph), 2.85 (s, 3H, **CH$_3$**N), 2.84 (dd, *J* = 9.7, 13.7 Hz, 1H, **C**H$_A$**H$_B$**Ph), 0.80 (d, *J* = 6.6 Hz, 3H, **CH$_3$**CH); δ_C($CDCl_3$, 75MHz) 169.7 (N**CO**N), 154.9 (N**CO**), 13.4 (Ar**C**), 135.8 (Ar**C**), 129.2 (Ar**CH**), 128.8 (Ar**CH**), 128.5 (Ar**CH**), 128.2 (Ar**CH**), 126.9 (Ar**CH**), 126.8 (Ar**CH**), 61.4 (**CH**N_3), 59.2 (**CH**Ph), 54.0 (**CH**CH_3), 37.3 (**CH$_2$**Ph), 28.1 (**CH$_3$**N), 14.8 (**CH$_3$**CH); *m/z* (FAB) 364 (MH^+), 364**,** 307, 154, 136, 77; Accurate Mass (ES) $C_{20}H_{21}N_5O_2$; Calculated 364.1773 (MH^+) Measured 364.1778; $[\alpha]_D^{25}$ -70.9 (*c* = 1.00 $CHCl_3$); Mpt. 148.0-148.5 °C

6b

R*f* 0.57 (P/EtOAc 2:1); υ_{max} (thin film)/cm^{-1} 3030, 2935, 2864, 2103, 1732, 1686, 1496, 1455, 1424, 756, 701; δ_H($CDCl_3$, 300MHz) 7.25-7.33 (m, 5H, Ar**CH**), 7.11-7.21 (m, 5H, Ar**CH**), 5.35 (d, *J* = 8.6 Hz, 1H, **CH**Ph), 5.17 (dd, *J* = 4.0, 8.8 Hz, 1H, CO**CH**), 3.95 (dq, *J* = 8.6, 6.6 Hz, 1H, **CH**CH_3), 2.83 (s, 3H, **CH$_3$**N), 2.65-2.77 (m, 2H, **CH$_2$**Ph), 2.16-2.25 (m, 1H, **CH$_A$**H$_B$$CH_2$Ph), 1.91-2.04 (m, 1H, **C**H$_A$**H$_B$**CH_2Ph), 0.81 (d, *J* = 6.6 Hz, 3H,**CH$_3$**CH); δ_C($CDCl_3$, 75MHz) 169.9 (N**CO**N), 154.9 (N**CO**), 140.7 (Ar**C**), 135.9 (Ar**C**), 128.6 (Ar**CH**), 128.3 (**ArCH**), 126.8 (**ArCH**), 126.0 (**ArCH**), 125.8 (**ArCH**), 60.3 (**CH**N_3), 59.2 (**CH**Ph), 54.1 (**CH**CH_3), 33.2 (**CH$_2$**Ph), 32.3 (**CH$_2$**CH_2Ph), 28.1 (**CH$_3$**N), 14.8 (**CH$_3$**CH); *m/z* (FAB) 378 (MH^+), 335 (MH^+- N_3), 245, 191, 132, 91; Accurate mass (ES) $C_{21}H_{23}N_5O_2$ Calculated 377.1852 (M^+) Measured 377.1852; $[\alpha]_D^{29}$ -27.7 (*c* = 1.00 $CHCl_3$); Mpt. 120.9-122.0 °C.

6c

R*f* 0.57 (P/EtOAc 2:1); υ_{max} (thin film)/cm^{-1} 3029, 2976, 2863, 2104, 1732, 1687, 1495, 1455, 1423, 750, 701; δ_H($CDCl_3$, 300MHz) 7.17-7.24 (m, 5H, Ar**CH**), 7.01-7.12 (m, 5H, Ar**CH**), 5.26 (d, *J* = 8.6 Hz, 1H, **CH**Ph), 5.10 (dd, *J* = 4.4, 7.8 Hz, 1H, **CH**N_3), 3.83 (dq, *J* = 8.6, 6.6 Hz, 1H, **CH**CH_3), 2.75 (s, 3H, **CH$_3$**N), 2.53-2.60 (m, 2H, **CH$_2$**Ph), 1.83-1.88 (m, 1H, **C**H$_A$**H$_B$**CH_2CH_2Ph)

1.63-1.73 (m, 3H, $\mathbf{CH_A}H_BCH_2CH_2Ph$), 0.73 (d, *J* = 6.6 Hz, 3H, $\mathbf{CH_3}CH$); δ_C($CDCl_3$, 75MHz) 169.4 (N**C**ON), 154.0 (N**C**O), 140.7 (Ar**C**), 135.0 7 (Ar**C**), 127.6 (Ar**C**H), 127.4 (Ar**C**H), 127.3 (Ar**C**H), 125.9 (Ar**C**H), 124.8 (Ar**C**H), 58.9 (**C**HN_3), 58.2 (**C**HPh) 53.0 (**C**HCH_3), 34.3 ($\mathbf{CH_2}$Ph), 30.1 ($\mathbf{CH_2}CH_2CH_2Ph$), 27.1 ($\mathbf{CH_3}N$), 26.7 ($CH_2\mathbf{CH_2}CH_2Ph$), 15.9 ($\mathbf{CH_3}CH$); *m/z* (FAB) 392 (MH^+), 349 (MH^+-N_3), 307, 231(MH^+-$CH_2CH_2CH_2Ph$, N_3); Accurate mass (EI) $C_{22}H_{25}N_5O_2$ Calculated 391.2008 (M^+) Measured 391.2001; $[\alpha]_D^{28}$ -36.5 (*c* = 1.00 $CHCl_3$); Mpt 65.2-66.0 °C.

6d

R*f* 0.23 (P/EtOAc) 4:1; υ_{max} (thin film)/cm^{-1} 3029, 2934, 2102, 1732, 1687, 1423, 747, 700; δ_H($CDCl_3$, 300MHz) 7.23-7.33 (m, 5H, Ar**C**H), 7.09-7.16 (m, 5H, Ar**C**H), 5.32 (d, *J* = 8.6 Hz, 1H, **C**HPh), 5.12 (dd, *J* = 4.3, 9.1 Hz, 1H, **C**HN_3), 3.91 (dq, *J* = 8.6, 6.6Hz, 1H, **C**HCH_3), 2.79 (s, 3H, $\mathbf{CH_3}N$), 2.57 (t, *J* = 7.6 Hz, 2H, $\mathbf{CH_2}$Ph), 1.88-1.94 (m, 1H, $\mathbf{CH_A}H_BCH_2CH_2CH_2Ph$), 1.59-1.75 (m, 3H, $CH_A\mathbf{H_B}CH_2CH_2CH_2Ph$), 1.45-1.54 (m, 2H, $CH_2\mathbf{CH_2}CH_2CH_2Ph$), 0.77 (d, *J* = 6.6 Hz, 3H, $\mathbf{CH_3}CH$); δ_C($CDCl_3$, 75MHz) 170.9 (N**C**ON), 155.4 (N**C**O), 142.8 (Ar**C**), 136.6 (Ar**C**), 129.1 (Ar**C**H), 128.9 (Ar**C**H), 128.8 (Ar**C**H), 128.7 (Ar**C**H), 127.3 (Ar**C**H), 126.1 (Ar**C**H), 60.6 (**C**HN_3) 59.7 (**C**HPh), 54.5 (**C**HCH_3), 36.2 ($\mathbf{CH_2}$Ph), 31.7 ($\mathbf{CH_2}CH_2CH_2CH_2Ph$), 31.4 ($\mathbf{CH_2}CH_2Ph$), 28.6 ($\mathbf{CH_3}N$), 26.2 ($CH_2\mathbf{CH_2}CH_2CH_2Ph$), 15.3 ($\mathbf{CH_3}CH$); *m/z* (ES) 406 ($MH^+$), 378 ($MH^+$-$N_2$), 191; Accurate mass (ES) $C_{23}H_{27}N_5O_2$ Calculated 405.2165 (M^+) Measured 405.2167; $[\alpha]_D^{25}$ -27.2 (*c* = 1.00 $CHCl_3$); Mpt 64.9-66.3 °C.

6e

R*f* 0.23 (P/EtOAc) 4:1; υ_{max} (thin film)/cm^{-1} 3029, 2934, 2102, 1732, 1687, 1423, 747, 700; δ_H($CDCl_3$, 300MHz) 7.23-7.33 (m, 5H, Ar**C**H), 7.09-7.16 (m, 5H, Ar**C**H), 5.32 (d, *J* = 8.6 Hz, 1H, **C**HPh), 5.12 (dd, *J* = 4.3, 9.1 Hz, 1H, **C**HN_3), 3.91 (dq, *J* = 8.6, 6.6Hz, 1H, **C**HCH_3), 2.79 (s, 3H, $\mathbf{CH_3}N$), 2.57 (t, *J* = 7.6 Hz, 2H, $\mathbf{CH_2}$Ph), 1.88-1.94 (m, 1H, $\mathbf{CH_A}H_BCH_2CH_2CH_2Ph$), 1.59-1.75 (m, 3H, $CH_A\mathbf{H_B}CH_2CH_2CH_2Ph$), 1.45-1.54 (m, 2H, $CH_2\mathbf{CH_2}CH_2CH_2Ph$), 0.77 (d, *J* = 6.6 Hz, 3H, $\mathbf{CH_3}CH$); δ_C($CDCl_3$, 75MHz) 170.9 (N**C**ON), 155.4 (N**C**O), 142.8 (Ar**C**), 136.6 (Ar**C**), 129.1 (Ar**C**H), 128.9 (Ar**C**H), 128.8 (Ar**C**H), 128.7 (Ar**C**H), 127.3 (Ar**C**H), 126.1 (Ar**C**H), 60.6 (**C**HN_3) 59.7 (**C**HPh), 54.5 (**C**HCH_3), 36.2 ($\mathbf{CH_2}$Ph), 31.7 ($\mathbf{CH_2}CH_2CH_2CH_2Ph$), 31.4 ($\mathbf{CH_2}CH_2Ph$), 28.6 ($\mathbf{CH_3}N$), 26.2 ($CH_2\mathbf{CH_2}CH_2CH_2Ph$), 15.3 ($\mathbf{CH_3}CH$); *m/z* (ES) 406 ($MH^+$), 378

(MH^+-N_2), 191; Accurate mass (ES) $C_{23}H_{27}N_5O_2$ Calculated 405.2165 (M^+) Measured 405.2167; $[\alpha]_D^{25}$ -27.2 (*c* = 1.00 $CHCl_3$); Mpt 64.9-66.3 °C.

7a

R*f* 0.46 (P/EtOAc 4:1); υ_{max} (thin film)/cm^{-1} 3333 (NH), 3086, 3062, 3028, 2950, 2854, 1736, 1455, 1435, 742, 699; δ_H($CDCl_3$, 300MHz) 7.15-7.31 (m, 10H, Ar**C**H), 3.82 (d, J_{gem} = 13 Hz, 1H, HN**C**$H_A$$H_B$Ph), 3.65 (s, 3H, **C**$H_3$O), 3.64 (d, J_{gem} = 13.0 Hz, 1H, HN**C**H_A**H**$_B$Ph), 3.55 (t, *J* = 7.0 Hz, 1H, **C**HNHCH$_2$Ph) 2.97 (t, *J* = 7.0 Hz, 2H, **C**H_2Ph), 1.84 (s, 1H, N**H**); δ_C($CDCl_3$, 75MHz) 175.0 (**CO**), 139.5 (Ar**C**), 137.2 (Ar**C**), 129.1 (Ar**C**H), 128.3 (Ar**C**H), 128.3 (Ar**C**H), 128.0 (Ar**C**H), 126.9 (Ar**C**H), 126.6 (Ar**C**H), 62.0 (CO**C**H), 51.9 (**C**H_3O), 51.6 (NH**C**H_2Ph) 39.6 (**C**H_2Ph); *m/z* (FAB) 270 (MH^+), 210**,** 178,136, 91; Accurate mass, (ES) $C_{17}H_{19}NO_2$ Calculated 270.1494 (M+H) Measured 270.1492. $[\alpha]_D^{30}$ +8.0 (*c* = 1.00 $CHCl_3$).

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7b

R*f* 0.67 (P/EtOAc 3:1); υ_{max} (thin film)/cm^{-1} 3062, 3027, 2950, 2855, 1734, 1454, 1434, 699; δ_H($CDCl_3$, 300MHz) 7.25-7.28 (m, 4H, Ar**C**H), 7.16-7.23 (m, 3H, Ar**C**H), 7.06-7.12 (m, 3H, Ar**C**H), 3.74 (d, J_{gem} = 12.9 Hz, 1H, HN**C**$H_A$$H_B$Ph), 3.63 (s, 3H, **C**$H_3$CO), 3.54 (d, J_{gem} = 12.9 Hz, 1H, HN**C**H_A**H**$_B$Ph), 3.21 (dd, *J* = 5.8, 7.6 Hz, 1H, CO**C**H), 2.61-2.69 (m, 2H, CH_2**C**H_2Ph), 1.80-1.93 (m, 3H, **NH** + **C**$H_2$$CH_2$Ph);[52] δ_C($CDCl_3$, 75MHz) 176.3 (**CO**), 141.8 (Ar**C**), 140.3 (Ar**C**), 128.9 (Ar**C**H), 128.8 (Ar**C**H), 128.8 (Ar**C**H), 128.7 (Ar**C**H), 127.5 (Ar**C**H), 126.4 (Ar**C**H), 60.5 (CO**C**H), 52.6 (HN**C**H_2Ph) 52.2 (**C**H_3O), 35.5 (CH_2**C**H_2Ph), 30.1 (**C**$H_2$$CH_2$Ph).[52] *m/z* (FAB) 284 (MH^+), 224 (MH^+-MeOCO), 167, 149, 91; Accurate mass (ES) $C_{18}H_{21}NO_2$ Calculated 284.1650 (MH^+) Measured 284.1648. $[\alpha]_D^{28}$ +25.0 (*c* = 1.00 $CHCl_3$).

7c

R*f* 0.65 (P/EtOAc 3:1); υ_{max} (thin film)/cm^{-1} 3348 (NH), 3026, 2948, 2924, 2857, 1735, 1453, 1432, 699; δ_H($CDCl_3$, 300MHz) 7.30-7.38 (m, 4H, Ar**C**H), 7.24-7.25 (m, 3H, Ar**C**H), 7.13-7.19 (m, 3H, Ar**C**H), 3.79 (d, J_{gem} = 13.0 Hz, 1H, HN**C**$H_A$$H_B$Ph), 3.70 (s, 3H, **C**$H_3$O), 3.60 (d, J_{gem} =

13.0 Hz, 1H, HN**C**H_A**H_B**Ph), 3.28 (t, *J* = 6.0 Hz, 1H, COCH), 2.59 (t, *J* = 7.0 Hz, 2H, CH_2Ph), 1.63-1.74 (m, 5H, $CHCH_2CH_2CH_2$Ph, + NH);

δ_C($CDCl_3$, 75MHz) 175.9 (CO), 141.9 (ArC), 139.7 (ArC), 128.3 (ArCH), 128.3 (ArCH), 128.2 (ArCH), 128.2 (ArCH), 126.9 (ArCH), 125.7 (ArCH), 60.4 (COCH), 52.1 ($NHCH_2$Ph), 51. (CH_3O), 35.5 (CH_2Ph), 33.0 ($CH_2CH_2CH_2$Ph), 27.5 ($CH_2CH_2CH_2$Ph); *m/z* (FAB) 298 (MH^+), 238, 197, 136, 91; Accurate mass (ES) $C_{19}H_{23}NO_2$ Calculated 298.1807 (MH^+) Measured 298.1803. $[\alpha]_D^{35}$ +13.0 (*c* = 1.1 MeOH).

7d

R*f* 0.49 (P/EtOAc 4:1); υ_{max} (thin film)/cm^{-1} 3336 (NH), 3085, 3062, 3026, 2931, 2857 (Aliphatic CH), 1735(CO), 1454, 1434, (Ar-C=C), 743, 699; δ_H($CDCl_3$, 300MHz) 7.23-7.38 (m, 4H, Ar**CH**), 7.25-7.27 (m, 3H, Ar**CH**), 7.15-7.20 (m, 3H, Ar**CH**), 3.81 (d, J_{gem} = 13.0 Hz, 1H, HN**C**$\mathbf{H_A}$$H_B$Ph), 3.71 (s, 3H, **C**$\mathbf{H_3}$O), 3.62 (d, J_{gem} = 13.0 Hz, 1H, HN**C**H_A**H_B**Ph), 3.27 (t, *J* = 6.6 Hz, 1H, CO**CH**) 2.60 (t, *J* = 7.6 Hz, 2H, **C**$\mathbf{H_2}$Ph) 1.79 (s, 1H, (**NH**) 1.56-1.69 (m, 4H, **C**$\mathbf{H_2}$$CH_2$**C**$\mathbf{H_2}$$CH_2$Ph,), 1.38-1.46 (m, 2H, CH_2**C**$\mathbf{H_2}$$CH_2CH_2$Ph); δ_C($CDCl_3$, 75MHz) 176.1 (**CO**), 142.4 (Ar**C**), 139.8 (Ar**C**), 129.3 (Ar**CH**), 128.2 (Ar**CH**), 127.0 (Ar**CH**), 125.6 (Ar**CH**), 60.5 (CO**CH**) 52.1 (NH**C**$\mathbf{H_2}$Ph) 51.6 (**C**$\mathbf{H_3}$O), 35.6 (**C**$\mathbf{H_2}$Ph), 33.3 (**C**$\mathbf{H_2}$$CH_2CH_2CH_2$Ph), 31.1 ($CH_2CH_2$**C**$\mathbf{H_2}$$CH_2$Ph), 25.2 ($CH_2$**C**$\mathbf{H_2}$$CH_2CH_2$Ph); *m/z* (FAB) 312 ($MH^+$), 252**,** 207,147, 91; Accurate mass (ES) $C_{20}H_{25}NO_2$ Calculated 312.1963 (MH^+) Measured 312.1966; $[\alpha]_D^{31}$ +19.0 (*c* = 1.00 $CHCl_3$).

7e

R*f* 0.49 (P/EtOAc 4:1); υ_{max} (thin film)/cm^{-1} 3335, 3085, 3062, 3026, 2931, 2856, 1735, 1454, 1435, 741, 698; δ_H($CDCl_3$, 300MHz) 7.29-7.33 (m, 4H, Ar**CH**), 7.25-7.27 (m, 3H, Ar**CH**), 7.15-7.19 (m, 3H, Ar**CH**), 5.81 (d, J_{gem} = 13.0 Hz, 1H, HN**C**$\mathbf{H_A}$$H_B$Ph), 3.71 (s, 3H, **C**$\mathbf{H_3}$O), 3.66 (d, J_{gem} = 13.0 Hz, 1H, HN**C**H_A**H_B**Ph), 3.26 (t, *J* = 6.6 Hz, 1H, CO**CH**), 2.58 (t, *J* = 7.7 Hz, 2H, **C**$\mathbf{H_2}$Ph), 1.76 (s, 1H, (**NH**), 1.58-1.63 (m, 4H, **C**$\mathbf{H_2}$$CH_2CH_2$**C**$\mathbf{H_2}$$CH_2$Ph), 1.31-1.40 (m, 4H, CH_2**C**$\mathbf{H_2}$**C**$\mathbf{H_2}$$CH_2CH_2$Ph); δ_C($CDCl_3$, 75MHz) 176.0 (**CO**), 142.6 (Ar**C**), 139.8 (Ar**C**), 128.3 (Ar**CH**), 128.2 (Ar**CH**), 127.0 (Ar**CH**), 125.8 (Ar**CH**), 125.5 (Ar**CH**), 60.6 (CO**CH**) 52.1 (NH**C**$\mathbf{H_2}$Ph), 51.6 (**C**$\mathbf{H_3}$O), 35.7 (**C**$\mathbf{H_2}$Ph), 33.4 (**C**$\mathbf{H_2}$$CH_2CH_2CH_2CH_2$Ph), 31.2 ($CH_2CH_2CH_2$**C**$\mathbf{H_2}$$CH_2$Ph), 28.9 ($CH_2CH_2$**C**$\mathbf{H_2}$$CH_2CH_2$Ph), 25.5 ($CH_2$**C**$\mathbf{H_2}$$CH_2CH_2CH_2$Ph); *m/z*

(FAB) 351 (MH^+), 326**,** 266, 91; Accurate mass (ES) $C_{21}H_{27}NO_2$ Calculated 326.2120 (MH^+) Measured 326.2127; $[\alpha]_D^{31}$ +18.5 (*c* = 1.00 $CHCl_3$).

8a

R*f* 0.63 ($CHCl_3$/CH_3OH/H_2O/CH_3CO_2H 7.5:3:0.6:0.3); υ_{max} (thin film)/cm^{-1} 3065, 3031, 2928, 2117, 1720, 1497, 1455, 750, 699; δ_H($CDCl_3$, 300MHz) 10.71 (br s, 1H, **OH**), 7.23-7.37 (m, 5H, Ar**CH**), 4.15 (dd, *J* = 4.9, 8.9 Hz, 1H, **CH**N_3), 3.24 (dd, *J* = 4.9, 14.0 Hz, 1H, **CH$_A$**H$_B$Ph), 3.04 (dd, *J* = 8.9, 14.0 Hz, 1H, **C**H$_A$**H$_B$**Ph); δ_C($CDCl_3$, 75MHz) 176.1 (**CO**), 135.5 (Ar**C**), 129.2 (Ar**CH**), 128.7 (Ar**CH**), 127.4 (Ar**CH**), 63.0 (**CH**N_3), 37.4 (**CH$_2$**Ph); *m/z* (EI) 191 (M^+), 177, 163, 149, 131; Accurate mass (ES) $C_9H_9N_3O_2$ Calculated 190.0617 (M-H) Measured 190.0614. $[\alpha]_D^{30}$ -70.9 (*c* = 1.0 $CHCl_3$) Lit $[\alpha]_D$ –68.7 (*c* = 1.07 $CHCl_3$).

See: Roper J. M. and Bauer D. P., *Synthesis*, 1983, **12**, 1041.

8b

R*f* 0.60 ($CHCl_3$/CH_3OH/H_2O/CH_3CO_2H 7.5:3:0.6:0.3); υ_{max} (thin film)/cm^{-1} 3028, 2109, 1717, 1497, 1454, 750, 699; δ_H($CDCl_3$, 300MHz**)** 9.71 (br s, 1H, **OH**), 7.13-7.24 (m, 5H, Ar**CH**), 3.87 (dd, *J* = 4.8, 8.8 Hz, 1H, **CH**N_3), 2.71-2.81 (m, 2H, **CH$_2$**Ph), 2.04-2.20 (m, 2H, **CH$_2$**CH_2Ph,); δ_C($CDCl_3$, 75MHz) 176.6 (**CO**), 139.6 (Ar**C**), 128.5 (Ar**CH**), 128.4 (Ar**CH**), 126.4 (Ar**CH**), 60.7 (**CH**N_3), 32.7 (**CH$_2$**Ph), 31.6 (**CH$_2$**CH_2Ph); *m/z* (ES) 2O4 (M-H^+), 161**,** 130; Accurate mass (ES) $C_{10}H_{11}N_3O_2$ Calculated 204.0773 (M-H) Measured 204.0774; $[\alpha]_D^{34}$ -61.1 (c = 1.0 $CHCl_3$).

8c

R*f* 0.67 (EtOAc/MeOH 23:2); υ_{max} (thin film)/cm^{-1} 3027, 2929, 2862, 2110, 1717, 1496, 1453, 749, 699; δ_H($CDCl_3$, 300MHz) 10.34 (br s, 1H, **OH**), 7.09-7.35 (m, 5H, Ar**CH**), 3.89 (dd, *J* = 4.7, 7.5 Hz, 1H, **CH**N_3), 2.66 (t, 2H, *J* = 7.0 Hz, **CH$_2$**Ph) 1.77-1.95 (m, 4H, **CH$_2$CH$_2$**CH_2Ph); δ_C($CDCl_3$, 75MHz) 176.7 (**CO**), 141.1 (Ar**C**), 128.4 (Ar**CH**), 128.3 (Ar**CH**), 126.1 (Ar**CH**), 61.6 (**CH**N_3), 35.1 (**CH$_2$**Ph), 30.7 (**CH$_2$**CH_2CH_2Ph), 27.3 (CH_2**CH$_2$**CH_2Ph); *m/z* (FAB) 220 (MH^+), 166, 152, 135, 121, 108; Accurate mass (ES) $C_{11}H_{13}N_3O_2$ Calculated 237.1352 ($M+NH_4$) Measured 237.1353; $[\alpha]_D^{28}$ -30.7 (*c* = 1.0 $CHCl_3$); Mpt. 41.5-42.4 °C.

8d

R*f* 0.61 (EtOAc/MeOH 23:2); υ_{max} (thin film)/cm^{-1} 3027, 2932, 2860, 2107, 1717, 1496, 1453, 747, 699; δ_H($CDCl_3$, 300MHz) 11.3 (br s, 1H, **OH**), 7.23-7.30 (m, 2H, Ar**CH**), 7.12-7.20 (m, 3H, Ar**CH**), 3.87 (dd, *J* = 5.2, 8.3 Hz, 1H, **CH**N_3), 2.63 (t, 2H, *J* = 7.6 Hz, **CH$_2$**Ph), 1.78-1.92 (m, 2H, **CH$_2$**$CH_2CH_2CH_2$Ph), 1.62-171 (m, 2H, CH_2CH_2**CH$_2$**CH_2Ph), 1.46-1.55 (m, 2H, CH_2**CH$_2$**CH_2CH_2Ph); δ_C($CDCl_3$, 75MHz) 176.9 (**CO**), 141.9 (Ar**C**), 128.4 (Ar**CH**), 128.3 (Ar**CH**), 125.8 (Ar**CH**), 61.6 (**CH**N_3), 35.5 (**CH$_2$**Ph), 31.1 (**CH$_2$**$CH_2CH_2CH_2$Ph), 30.8 (CH_2CH_2**CH$_2$**CH_2Ph), 25.3 (CH_2**CH$_2$**CH_2CH_2Ph); *m/z* (CI+) 251 (M+NH_4), 215, 208, 177, 162; Accurate mass (ES) $C_{12}H_{15}N_3O_2$ Calculated 251.1508 (M+NH_4) Measured 251.1511; $[\alpha]_D^{24}$ -24.4 (*c* = 1.0 $CHCl_3$).

8e

R*f* 0.64 (EtOAc/MeOH 23:2); υ_{max} (thin film)/cm^{-1} 3062, 3026, 2931, 2858, 2108, 1717, 1495, 1453, 747, 699; δ_H($CDCl_3$, 300MHz) 10.4 (br s, 1H, **OH**), 7.23-7.29 (m, 2H, Ar**CH**), 7.14-7.19 (m, 3H, Ar**CH**), 3.87 (dd, *J* = 5.3, 8.0 Hz, 1H, **CH**N_3), 2.60 (t, 2H, *J* = 7.6 Hz, **CH$_2$**Ph), 1.76-1.88 (m, 2H, **CH$_2$**$CH_2CH_2CH_2CH_2$Ph), 1.58-1.68 (m, 2H, $CH_2CH_2CH_2$**CH$_2$**CH_2Ph), 1.36-1.48 (m, 4H, CH_2**CH$_2$CH$_2$**CH_2CH_2Ph); δ_C($CDCl_3$, 75MHz) 176.8 (**CO**), 142.3 (Ar**C**), 128.4 (Ar**CH**), 128.3 (Ar**CH**), 125.7 (Ar**CH**), 61.6 (**CH**N_3), 35.7 (**CH$_2$**Ph), 31.2 (**CH$_2$**$CH_2CH_2CH_2CH_2$Ph), 31.1 ($CH_2CH_2CH_2$**CH$_2$**CH_2Ph), 28.5 (**CH$_2$**CH_2CH_2Ph), 25.5 (CH_2**CH$_2$**$CH_2CH_2CH_2$Ph); *m/z* (CI+) 265 (M+NH_4), 222, 215, 191, 176; Accurate mass (ES) $C_{13}H_{17}N_3O_2$ Calculated 265.1665 (M+NH_4) Measured 265.1661; $[\alpha]_D^{31}$ -21.0 (*c* = 1.0 $CHCl_3$).

Hydrogenolysis of benzylamino group of 7a

Hydrogenolysis of 7a

To a N_2 flask containing 2*R*-benzylamino-3-phenylpropionic acid methyl ester **7a** (31.9 mg, 0.12 mmol), and pearlmans catalyst[5] (3.2 mg, 10% w/w) was added MeOH (2 ml). The reaction vessel was evacuated and purged with H_2 continuously over a five minute period and allowed to stir for 7 hours. The reaction mixture was filtered through celite™ and purified using flash column chromatography [silica] with eluent EtOAc forming the aminoester as a colourless oil (21.1 mg, 100%). Full characterisation was performed before converting into the hydrochloride salt. The amino ester was dissolved in ice-cold ether before the addition of HCl (2M in ether, *ca.* 4 drops). The solvent was removed *in vacuo* to give the product as a white solid (25.2 mg, 99%).

R*f* 0.36 (DCM/MeOH 10:1); υ_{max} (thin film)/cm^{-1} 3376 (NH), 3063, 3028, 2951, 2854, 1737, 1603, 1496, 1454, 1438, 746, 701; δ_H($CDCl_3$, 300MHz) 7.14-7.30 (m, 5H, Ar**CH**), 3.71 (dd, *J* = 5.2, 7.8 Hz, 1H, CO**CH**), 3.68 (s, 3H, $\mathbf{CH_3}$O), 3.06 (dd, *J* = 5.2, 13.5 Hz, 1H, $\mathbf{CH_A}H_BPh$), 2.83 (dd, *J* = 7.8, 13.5 Hz, 1H, $CH_A\mathbf{H_B}Ph$, 1.79 (br s, 2H, $\mathbf{NH_2}$); δ_C($CDCl_3$, 75MHz) 175.8 (**CO**), 137.6 (Ar**C**), 129.7 (Ar**CH**), 129.0 (Ar**CH**), 127.2 (Ar**CH**), 56.2 (CO**CH**), 52.4 ($\mathbf{CH_3}$O), 41.5 ($\mathbf{CH_2}$Ph). *m/z* (CI**)** (MH^+) 180, 150, 134, 120, 108; Accurate Mass (ES): $C_{10}H_{13}NO_2$ calculated. 180.1024 (M+H); Measured 180.1022 $[\alpha]_D^{30}$ -44.5° (*c* = 2.00 EtOH); $[\alpha]_D^{27}$ -34 (*c* = 1.00 EtOH) Lit –36 *c* = 1, EtOH; Mpt 156-158 °C, Lit 160-161 °C, 153-154 °C

[a]Chen B-C., Skoumbourdis A. P., Guo P., Bednarz M. S., Kocy O. R., Sundeen J. E. and Vite G. D., *J. Org. Chem*., 1999, **64**, 9294, [b]Glaser R. and Geresh S., *Tetrahedron*, 1979, **35**, 2381.

Esterification and hydrogenolysis of 8a

To a stirring solution of 2*S*-azido-3-phenylpropionic acid **8a** (63.9 mg, 0.33 mmol) in MeOH (2 ml), was added Pd(C) 10% (6.4 mg 10% w/w). The reaction vessel was evacuated and filled with H_2 continuously over a five-minute period. The reaction was allowed to stir for 30 minutes. The reaction mixture was filtered through celite™ and concentrated *in vacuo* leaving an off-white solid. The crude was dissolved in the minimum amount of MeOH before the addition of cold ether, whereupon a white precipitate formed. The excess solvent was carefully decanted off and the white solid dried under vacuum forming the product amino acid (47.3 mg, 86%).

R*f* 0.32 ($CHCl_3/CH_3OH/H_2O/CH_3CO_2H$ 7.5:3:0.6:0.3); υ_{max} (KBr)/cm^{-1} 3418, 3031, 2738, 2421, 2123, 1625, 1562; δ_H(D_2O 300MHz) 7.26-7.31 (m, 3H, ArCH), 7.18-7.24 (m, 2H, ArCH), 3.86 (dd, *J* = 5.5, 7.6 Hz, 1H, COCH), 3.16 (dd, *J* = 5.5, 14.5 Hz 1H, CH_AH_BPh), 2.99 (dd, *J* = 7.6, 14.5 Hz 1H, CH_AH_BPh); δ_C(D_2O 75MHz) 173.7 (CO), 134.8 (ArC), 129.1 (ArCH), 128.9 (ArCH), 127.5 (ArCH), 55.8 (COCH), 36.1 (CH_2Ph). *m/z* (EI^+) 165 (M^+), 148, 130; Accurate mass (ES) Calculated 166.0868 (MH^+) Measured 166.0868; $[\alpha]_D^{30}$ -37.1 (*c* = 1.00 H_2O) Lit $[\alpha]_D^{30}$ -34 (*c* = 1.00 H_2O) . Mpt 281-283°C, Lit 283-284 °C.
See Roper J. M. and Bauer D. P., *Synthesis*, 1983, **12**, 1041.

A similar protocol was used for the esterification and hydrogenolysis of 8b and 8c

Data for 8b. R*f* 0.45 ($CHCl_3/CH_3OH/H_2O/CH_3CO_2H$ 7.5:3:0.6:0.3); υ_{max} (KBr)/cm^{-1} 3419 (NH_2), 3006, 2921, (Aliphatic CH), 1738 (CO), 1603, 1495, 1488, (Ar-C=C), 773, (Ar monosubstituted). ; δ_H(D_2O, d-TFA, 300MHz) 7.25-7.30 (m, 2H, ArCH), 7.19-7.21 (m, 3H, ArCH), 3.94 (t, *J* = 6.2 Hz, 1H, COCH), 2.64-2.72 (m, 2H, CH_2Ph), 2.07-2.19 (m, 2H, $CHCH_2CH_2Ph$); δ_C(D_2O, d-TFA, 75MHz) 171.4 (CO), 139.7 (ArC), 128.5 (ArCH), 128.3 (ArCH), 128.2 (ArCH), 51.9 (COCH), 31.2 (CH_2Ph), 30.0 (CH_2CH_2Ph); *m/z* (ES) 180 (MH^+), 148, 132, 116; Accurate mass (ES) Calculated 180.1024 (M+H) Measured 180.1025. $[\alpha]_D^{16}$ +40.2 (*c* = 1.00 3N HCl). Lit $[\alpha]_D^{16}$ +45 (*c* = 1.00 3N HCl). M.p 302-305 °C.

Data for 8c. R*f* 0.28 ($CHCl_3/CH_3OH/H_2O/CH_3CO_2H$ 7.5:3:0.6:0.3). υ_{max} (KBr)/cm^{-1} 3420 (NH), 3060, 3028, 2941, (Aliphatic CH), 1604, 1584. δ_H(D_2O, d-TFA, 300MHz) 6.71-6.76 (m, 2H, ArCH), 6.63-6.68 (m, 3H, ArCH), 3.43 (dd, *J* = 6.0, 9.2 Hz, 1H, COCH), 2.07 (m, 2H, CH_2Ph), 1.30-1.36 (m, 2H, $CH_2CH_2CH_2Ph$), 1.12-1.27 (m, 2H, CH_2CH_2Ph). δ_C(D_2O, d-TFA, 75MHz) 171.3 (CO), 141.1 (ArC), 128.0 (ArCH), 127.9 (ArCH), 125.6 (ArCH) 52.1 (COCH), 33.6 (CH_2Ph), 28.6 ($CHCH_2CH_2$), 25.3 (CH_2CH_2Ph). *m/z* (ES) 193 (M^+), 190, 176, 162. Accurate mass (ES) Calculated 194.1181 (MH^+) Measured 194.1179. $[\alpha]_D^{28}$ +36.4 (*c* 1.16, 5N, HCl/DMF 1:1), Lit $[\alpha]_D$ +39 (*c* 1.16, 5N, HCl/DMF 1:1). Mpt 228-230 °C.

For **8b** and **8c** see: Asano Y., Yamada A., Kato Y., Yamarguchi K., Hibino Y., Hirai K. and Kondo K., *J. Org. Chem*., 1990, **55**, 5567.

Independent Synthesis of 7b from (*R*)-Homophenylalanine

Preparation of 2-(*R*)-amino-4-phenylbutyric acid methyl ester

(*R*)-Homophenylalanine (20.5 mg, 0.11 mmol), was dissolved 2,2-dimethoxypropane (3.0 ml) and HCl (*ca* 2 drops). The reaction was left stirring for 48 hours where the reaction mixture had turned deep red and was complete by tlc. The reaction was quenched by concentrating *in vacuo* dissolution in the minimum amount of MeOH and addition of cold diethyl ether until a precipitate was observed. The 2-(R)-amino-4-phenylbutyric acid methyl ester was formed as white crystals (20.9 mg, 80%). R*f* 0.40 (DCM/MeOH 10:1). δ_H(CD_3OD, 300MHz) 7.13-7.28 (m, 5H, Ar**CH**), 3.70 (s, 3H, $\mathbf{CH_3}O$), 3.45 (t, *J* = 6.4 Hz, 1H, **CH**NH_2), 2.60 (t, *J* = 8.0 Hz, 2H, $\mathbf{CH_2}Ph$) 1.95-2.07 (m, 1H, $CH\mathbf{CH_A}H_BCH_2Ph$,), 1.81-1.93 (m, 1H, $CHCH_A\mathbf{H_B}CH_2Ph$). $[\alpha]_D^{31}$ -45 (*c* = 1.00 MeOH). Mpt 187-190 °C, Lit 194

Rachele J. R., *J. Org. Chem*., 1963, **28**, 2898.

Bourguignon J., Combret Y., Duflos J., Dupas G. and Quéguiner G., *Tetrahedron Asymmetry*, 1993, **4**, 1635.

Preparation of 7b

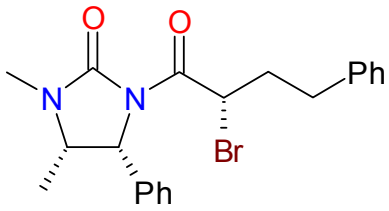
2-(*R*)-amino-4-phenylbutyric acid methyl ester (18.3 mg, 0.08 mmol) was dissolved in DCM (2 ml) and THF (2 ml) to which was added Na_2CO_3 (33.5 mg, 0.3 mmol) in deionised water (90 μl), followed by benzyl bromide (19 μl, 0.16 mmol).[54] The reaction was refluxed at 45 °C for 3 days. The reaction was quenched by dissolving in EtOAc (10 ml) and brine (10 ml). The organic layer was washed with deionised water (2x10 ml); the aqueous layer back extracted with EtOAc (5 ml). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo* to give compound (**7b**) as a colourless oil (15 mg, 66%). R*f* 0.67 (P/EtOAc 3:1). δ_H($CDCl_3$, 300MHz) 7.25-7.28 (m, 4H, Ar**CH**), 7.16-7.23 (m, 3H, Ar**CH**), 7.06-7.12 (m, 3H, Ar**CH**), 3.74 (d, J_{gem} = 12.9 Hz, , 1H, $HN\mathbf{CH_A}H_BPh$), 3.63 (s, 3H, $\mathbf{CH_3}CO$), 3.54 (d, J_{gem} = 12.9 Hz, , 1H, $HNCH_A\mathbf{H_B}Ph$), 3.21 (dd, *J* =

5.8, 7.6 Hz, 1H, CO**CH**), 2.61-2.69 (m, 2H, CH_2**CH_2**Ph), 1.80-1.93 (m, 3H, **NH** + **CH_2**CH_2Ph). $[\alpha]_D^{28}$ +24.0 (*c* = 1.00 $CHCl_3$).

Note the sign of the optical rotation does change from minus to plus in the conversion of 7a to 7b.

Evans P. A., Robinson J. E. and Nelson J. N., *J. Am Chem Soc*., 1999, **121**, 6761

(2'*S*,4*S*,5*R*)-1-(2'-Bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one



The epimer of **4b** (i.e. (2'*S*,4*S*,5*R*)-1-(2'-Bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one) could be prepared by epimerisation of **4b** (Bu_4NBr).

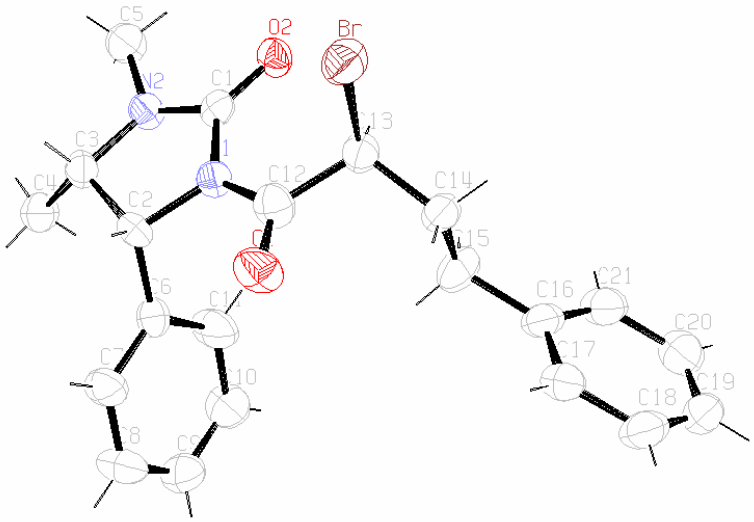
(2'*S*,4*S*,5*R*)-1-(2'-Bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one

To a N_2 purged stirring flask containing (2'*R*,4*S*,5*R*)-1-(2'-bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one **4b** (2.8 g, 6.76 mmol) in THF (86 ml) was added *n*Bu_4NBr (436 mg, 1.35 mmol) and left stirring for 22 hours. The reaction was quenched by the addition of deionised water (50 ml) and EtOAc (50 ml). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude was purified by flash column chromatography [silica] with eluent P/EtOAc (4:1) forming (2'*S*,4*S*,5*R*)-1-(2'-bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one (1.26 g, 45%) as a white solid and **4b** (1.45 g, 52%).

(2'*S*,4*S*,5*R*)-1-(2'-Bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one

R*f* 0.58 (P/EtOAc 2:1). υ_{max} (thin film)/cm^{-1} 3086, 3065, 3029, 2988, 2979, 2968, 2936, 2909, 2856(Aliphatic CH), 1705 (CO), 1687 (CO), 1603, 1496, 1455, (Ar-C=C), 743, 700 (Ar monosubstituted). δ_H($CDCl_3$, 300MHz) 7.24-7.34 (m, 5H, ArCH), 7.11-7.20 (m, 5H, ArCH) 6.02 (t, *J* = 7.0 Hz, 1H, CHBr), 5.32 (d, *J* = 8.5 Hz, 1H, CHPh), 3.88-3.95 (m, 1H, $CHCH_3$), 2.83 (s, 3H, CH_3N), 2.67-2.74 (m, 1H, $CH_2CH_AH_BPh$), 2.54-2.64 (m, 1H, $CH_2CH_AH_BPh$), 2.26-2.38 (m, 2H, CH_2CH_2Ph), 0.78 (d, 3H, *J* = 6.5 Hz, CH_3CH). δ_C($CDCl_3$, 75MHz) 168.2 (NCON), 154.7 (NCO), 140.5 (ArC), 135.3 (ArC), 128.6 (ArCH), 128.5 (ArCH), 128.4 (ArCH), 128.2 (ArCH), 126.8 (ArCH), 126.1 (ArCH), 59.8 (CHPh), 53.6 ($CHCH_3$), 45.0 (CHBr), 36.2 CH_2CH_2Ph), 33.3 (CH_2Ph), 28.2 (CH_3N), 14.8 (CH_3CH). *m/z* (EI) 416 (MH^+), 335 (MH^+-Br), 325, 312, 245 231 (MH^+-(Br)CH_2CH_2Ph), 191 (MH^+-$COCHBrCH_2CH_2Ph$), 132, 91, 77.

Accurate mass (ES) $C_{21}H_{23}N_2O_2Br$ Calculated 414.0943 (M^+) Measured 414.0934. $[\alpha]_D^{30}$ -72.7 (*c* = 1.00 $CHCl_3$). Mpt 119.4-119.9 °C.

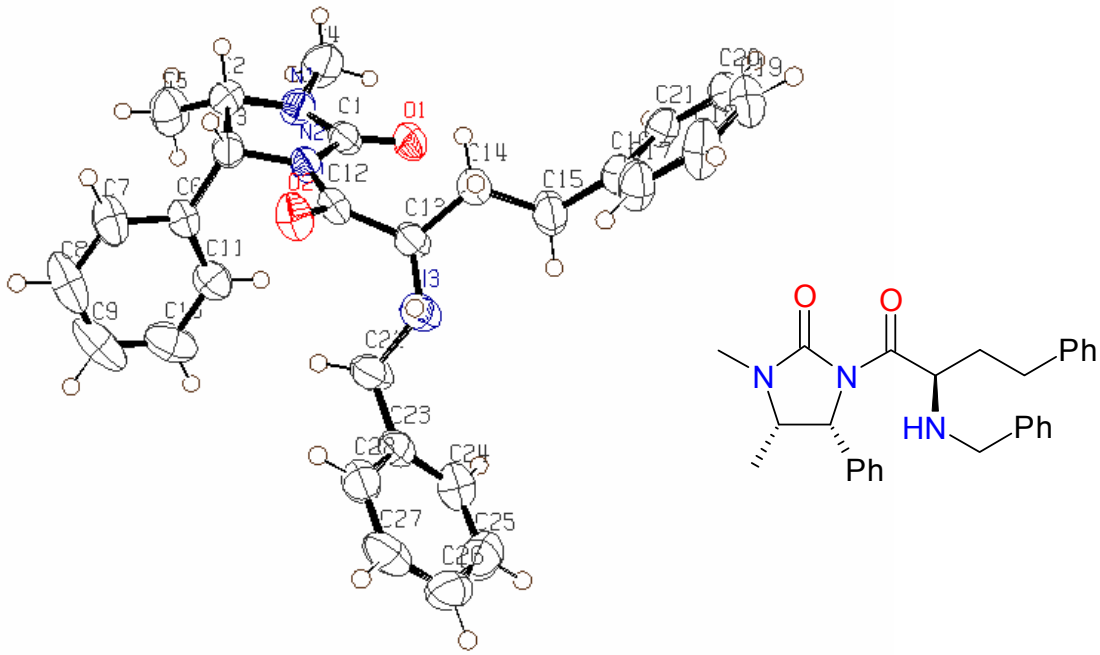


Ortep representation of (2'*S*,4*S*,5*R*)-1-(2'-bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one

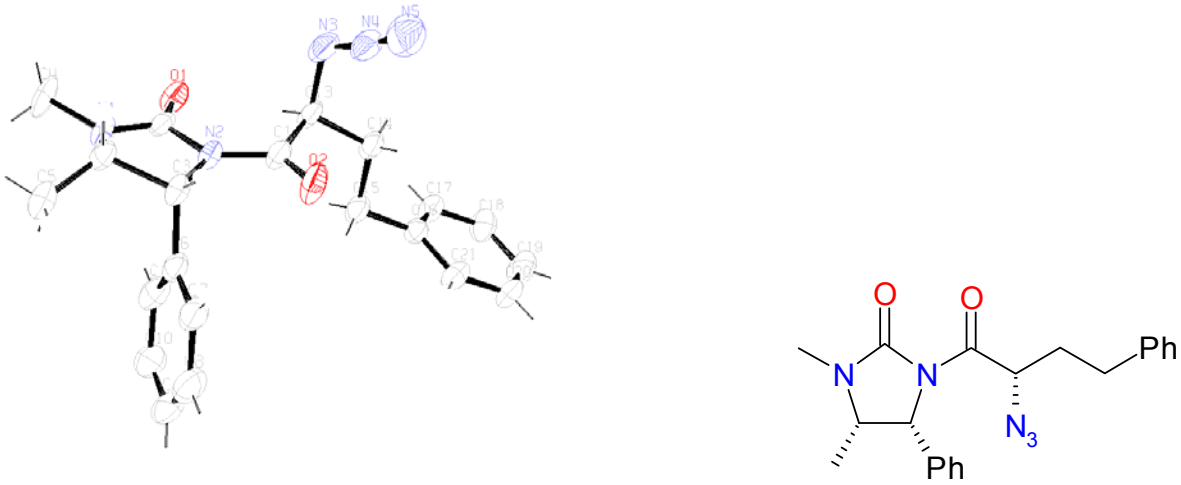
Detailed data sets at the end of the document.

Supplementary Material (ESI) for Chemical Communications

Ortep representation of 5b



Ortep representation of 6b



Detailed data sets at the end of the document.

Crystal data and structure refinement of (2'*S*,4*S*,5*R*)-1-(2'-bromo-4'-phenylbutyryl)-3,4-dimethyl-5-phenylimidazolidin-2-one

Table 1

Empirical formula	C21 H23 Br N2 O2	
Formula weight	415.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$ (No.4)	
Unit cell dimensions	a = 10.3839(12) Å	α= 90°.
	b = 6.2094(4) Å	β= 108.513(4)°.
	c = 15.9554(18) Å	γ = 90°.
Volume	975.53(17) $Å^3$	
Z	2	
Density (calculated)	1.41 Mg/m^3	
Absorption coefficient	2.12 mm^{-1}	
F(000)	428	
Crystal size	0.30 x 0.20 x 0.1 mm^3	
Theta range for data collection	3.88 to 24.99°.	
Index ranges	-12<=h<=12, -7<=k<=6, -15<=l<=18	
Reflections collected	6524	
Independent reflections	3198 [R(int) = 0.077]	
Reflections with I>2sigma(I)	2534	
Completeness to theta = 24.99°	99.3 %	
Tmax. and Tmin.	0.741 and 0.665	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3198 / 1 / 237	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.050, wR2 = 0.095	
R indices (all data)	R1 = 0.073, wR2 = 0.104	
Absolute structure parameter	-0.013(14)	
Largest diff. peak and hole	0.26 and -0.39 $e.Å^{-3}$	

Data collection KappaCCD , Program package WinGX , Abs correction MULTISCAN

Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for dec400. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br	1224(1)	3167(1)	5070(1)	48(1)
O(1)	897(4)	6255(6)	3267(3)	51(1)
O(2)	3873(4)	1423(5)	4166(3)	36(1)
N(1)	2962(4)	4752(6)	3555(3)	31(1)
N(2)	5139(5)	4021(6)	3780(3)	35(1)
C(1)	3997(4)	3195(11)	3876(3)	31(1)
C(2)	3466(5)	6689(8)	3226(4)	31(1)
C(3)	5048(5)	6323(8)	3567(4)	35(1)
C(4)	5780(5)	6884(10)	2912(4)	47(2)
C(5)	6434(5)	2961(12)	4179(4)	47(1)
C(6)	2845(6)	6968(9)	2233(4)	34(2)
C(7)	2509(7)	8994(9)	1897(5)	46(2)
C(8)	1934(7)	9306(11)	991(5)	57(2)
C(9)	1689(6)	7628(10)	423(5)	53(2)
C(10)	2021(8)	5608(11)	740(4)	65(2)
C(11)	2591(8)	5259(9)	1649(5)	62(2)
C(12)	1617(6)	4702(9)	3525(4)	43(2)
C(13)	1087(5)	2673(8)	3841(4)	37(2)
C(14)	-373(5)	2183(9)	3292(4)	39(1)
C(15)	-459(5)	1510(10)	2362(4)	47(2)
C(16)	-1847(6)	699(9)	1820(4)	41(2)
C(17)	-2997(6)	1971(10)	1680(4)	44(2)
C(18)	-4274(6)	1214(11)	1192(4)	55(2)
C(19)	-4424(7)	-819(11)	847(4)	55(2)
C(20)	-3296(7)	-2114(13)	981(4)	54(2)
C(21)	-2013(6)	-1371(9)	1482(4)	50(2)

Table 3. Bond lengths [Å] and angles [°] for dec400.

Br-C(13)	1.945(6)
O(1)-C(12)	1.209(6)
O(2)-C(1)	1.217(7)
N(1)-C(12)	1.383(7)
N(1)-C(1)	1.416(7)
N(1)-C(2)	1.473(6)
N(2)-C(1)	1.344(6)
N(2)-C(5)	1.451(7)
N(2)-C(3)	1.465(6)
C(2)-C(6)	1.518(8)
C(2)-C(3)	1.575(7)
C(3)-C(4)	1.515(8)
C(6)-C(7)	1.369(7)
C(6)-C(11)	1.381(8)
C(7)-C(8)	1.391(9)
C(8)-C(9)	1.351(8)
C(9)-C(10)	1.355(9)
C(10)-C(11)	1.399(9)
C(12)-C(13)	1.524(7)
C(13)-C(14)	1.521(7)
C(14)-C(15)	1.517(8)
C(15)-C(16)	1.512(8)
C(16)-C(21)	1.383(8)
C(16)-C(17)	1.390(8)
C(17)-C(18)	1.390(8)
C(18)-C(19)	1.366(9)
C(19)-C(20)	1.381(9)
C(20)-C(21)	1.396(8)

C(12)-N(1)-C(1)	129.8(5)
C(12)-N(1)-C(2)	118.4(4)
C(1)-N(1)-C(2)	111.8(4)
C(1)-N(2)-C(5)	120.3(5)

C(1)-N(2)-C(3)	113.9(5)
C(5)-N(2)-C(3)	121.8(5)
O(2)-C(1)-N(2)	126.4(5)
O(2)-C(1)-N(1)	126.5(4)
N(2)-C(1)-N(1)	107.1(5)
N(1)-C(2)-C(6)	112.5(4)
N(1)-C(2)-C(3)	102.0(4)
C(6)-C(2)-C(3)	115.4(5)
N(2)-C(3)-C(4)	112.0(5)
N(2)-C(3)-C(2)	101.8(4)
C(4)-C(3)-C(2)	115.1(5)
C(7)-C(6)-C(11)	118.1(6)
C(7)-C(6)-C(2)	119.0(5)
C(11)-C(6)-C(2)	122.9(5)
C(6)-C(7)-C(8)	120.5(6)
C(9)-C(8)-C(7)	121.1(6)
C(8)-C(9)-C(10)	119.5(7)
C(9)-C(10)-C(11)	120.2(7)
C(6)-C(11)-C(10)	120.5(6)
O(1)-C(12)-N(1)	120.1(5)
O(1)-C(12)-C(13)	121.5(5)
N(1)-C(12)-C(13)	118.3(5)
C(14)-C(13)-C(12)	111.9(5)
C(14)-C(13)-Br	110.7(4)
C(12)-C(13)-Br	106.5(4)
C(15)-C(14)-C(13)	110.9(5)
C(16)-C(15)-C(14)	113.6(5)
C(21)-C(16)-C(17)	118.1(5)
C(21)-C(16)-C(15)	120.7(5)
C(17)-C(16)-C(15)	121.1(5)
C(16)-C(17)-C(18)	121.1(6)
C(19)-C(18)-C(17)	120.3(6)
C(18)-C(19)-C(20)	119.6(6)
C(19)-C(20)-C(21)	120.3(7)
C(16)-C(21)-C(20)	120.6(6)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for dec400. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br	44(1)	55(1)	42(1)	-3(1)	11(1)	-4(1)
O(1)	41(2)	45(2)	70(3)	15(2)	24(2)	15(2)
O(2)	35(2)	26(2)	47(3)	-1(2)	12(2)	1(2)
N(1)	27(3)	29(2)	39(3)	0(2)	12(2)	3(2)
N(2)	28(3)	34(2)	44(3)	4(2)	14(2)	2(2)
C(1)	33(3)	26(3)	31(3)	-10(4)	7(2)	2(3)
C(2)	37(3)	24(3)	33(3)	3(2)	15(3)	2(2)
C(3)	39(3)	33(3)	34(3)	-3(2)	11(3)	-7(2)
C(4)	35(3)	55(3)	49(4)	9(3)	12(3)	-8(3)
C(5)	35(3)	49(3)	56(4)	9(4)	15(3)	3(3)
C(6)	37(3)	30(3)	38(4)	-5(3)	15(3)	-3(2)
C(7)	55(4)	33(3)	46(5)	1(3)	9(3)	7(3)
C(8)	67(5)	50(4)	48(5)	17(4)	12(4)	16(3)
C(9)	53(4)	63(6)	39(4)	5(3)	6(3)	-5(3)
C(10)	102(6)	52(4)	29(4)	-11(3)	2(4)	-17(4)
C(11)	98(6)	31(3)	44(5)	-2(3)	3(4)	1(3)
C(12)	45(4)	35(3)	50(4)	-2(3)	18(3)	2(3)
C(13)	33(3)	36(4)	40(3)	-1(2)	9(3)	-2(2)
C(14)	32(3)	49(3)	34(4)	1(3)	7(3)	-5(2)
C(15)	29(3)	66(4)	47(4)	-5(3)	12(3)	-1(3)
C(16)	35(3)	50(4)	33(4)	7(3)	4(3)	4(3)
C(17)	45(4)	44(3)	41(4)	9(3)	11(3)	4(3)
C(18)	40(4)	75(5)	42(4)	16(4)	4(3)	4(3)
C(19)	41(4)	71(4)	44(4)	13(3)	4(3)	-12(3)
C(20)	73(4)	46(4)	39(3)	-5(3)	11(3)	-13(4)
C(21)	55(4)	50(5)	40(4)	5(3)	8(3)	5(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for dec400.

	x	y	z	U(eq)
H(2)	3245	7984	3527	37
H(3)	5453	7168	4123	42
H(4A)	6753	6600	3179	70
H(4B)	5640	8411	2755	70
H(4C)	5420	6002	2379	70
H(5A)	6976	3795	4692	70
H(5B)	6922	2861	3746	70
H(5C)	6280	1511	4370	70
H(7)	2670	10196	2285	56
H(8)	1710	10723	768	68
H(9)	1287	7862	-194	64
H(10)	1866	4424	343	78
H(11)	2806	3836	1867	75
H(13)	1677	1426	3806	44
H(14A)	-731	1012	3577	47
H(14B)	-941	3477	3266	47
H(15A)	-217	2757	2055	57
H(15B)	218	362	2397	57
H(17)	-2909	3381	1923	53
H(18)	-5047	2115	1097	65
H(19)	-5299	-1339	518	65
H(20)	-3392	-3517	731	65
H(21)	-1248	-2295	1592	60

Supplementary Material (ESI) for Chemical Communications

Crystal data and structure refinement for 5b

Table 1

Empirical formula	C28 H31 N3 O2	
Formula weight	441.56	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$ (No.19)	
Unit cell dimensions	a = 9.5902(3) Å	α= 90°.
	b = 10.3216(4) Å	β= 90°.
	c = 24.9928(10) Å	γ = 90°.
Volume	2473.9(2) $Å^3$	
Z	4	
Density (calculated)	1.19 Mg/m^3	
Absorption coefficient	0.07 mm^{-1}	
F(000)	944	
Crystal size	0.4 x 0.3 x 0.1 mm^3	
Theta range for data collection	3.79 to 25.01°.	
Index ranges	-11<=h<=11, -12<=k<=9, -27<=l<=29	
Reflections collected	12753	
Independent reflections	4334 [R(int) = 0.059]	
Reflections with I>2sigma(I)	3264	
Completeness to theta = 25.01°	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4334 / 0 / 305	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.046, wR2 = 0.101	
R indices (all data)	R1 = 0.072, wR2 = 0.112	
Absolute structure parameter	0.3(15)	
Extinction coefficient	0.031(3)	
Largest diff. peak and hole	0.11 and -0.13 $e.Å^{-3}$	

Data collection KappaCCD , Program package WinGX , Abs correction not applied ,

Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for dec1400. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1985(2)	81(2)	1835(1)	52(1)
O(2)	-580(2)	3208(2)	1468(1)	55(1)
N(1)	2649(2)	1449(2)	2514(1)	49(1)
N(2)	1104(2)	2187(2)	1928(1)	42(1)
N(3)	63(2)	1920(2)	507(1)	51(1)
C(1)	1938(2)	1119(2)	2069(1)	43(1)
C(2)	2155(2)	2645(2)	2759(1)	49(1)
C(3)	1277(2)	3270(2)	2300(1)	43(1)
C(4)	3396(3)	461(3)	2813(1)	71(1)
C(5)	3333(3)	3460(3)	2977(1)	71(1)
C(6)	1907(2)	4446(2)	2033(1)	42(1)
C(7)	1603(3)	5671(3)	2222(1)	63(1)
C(8)	2143(3)	6761(3)	1989(2)	83(1)
C(9)	3007(3)	6649(3)	1552(2)	87(1)
C(10)	3322(3)	5448(3)	1356(1)	75(1)
C(11)	2787(2)	4338(3)	1598(1)	54(1)
C(12)	244(2)	2307(2)	1485(1)	43(1)
C(13)	401(2)	1347(2)	1025(1)	45(1)
C(14)	-525(2)	156(2)	1108(1)	46(1)
C(15)	-102(3)	-931(2)	731(1)	60(1)
C(16)	-1167(2)	-2004(2)	688(1)	46(1)
C(17)	-2468(3)	-1750(3)	462(1)	61(1)
C(18)	-3468(3)	-2702(3)	422(1)	69(1)
C(19)	-3171(3)	-3930(3)	600(1)	61(1)
C(20)	-1897(3)	-4204(2)	827(1)	50(1)
C(21)	-910(2)	-3237(2)	870(1)	46(1)
C(22)	994(3)	2969(3)	334(1)	58(1)

C(23)	695(2)	3277(2)	-245(1)	45(1)
C(24)	1268(3)	2553(3)	-653(1)	58(1)
C(25)	974(3)	2799(3)	-1179(1)	70(1)
C(26)	78(3)	3781(3)	-1310(1)	66(1)
C(27)	-508(3)	4527(3)	-917(1)	63(1)
C(28)	-202(2)	4278(3)	-383(1)	54(1)

Table 3. Bond lengths [Å] and angles [°] for dec1400.

O(1)-C(1)	1.221(3)
O(2)-C(12)	1.221(3)
N(1)-C(1)	1.348(3)
N(1)-C(4)	1.453(3)
N(1)-C(2)	1.457(3)
N(2)-C(12)	1.387(3)
N(2)-C(1)	1.406(3)
N(2)-C(3)	1.463(3)
N(3)-C(13)	1.459(3)
N(3)-C(22)	1.469(3)
C(2)-C(5)	1.510(3)
C(2)-C(3)	1.562(3)
C(3)-C(6)	1.511(3)
C(6)-C(11)	1.381(3)
C(6)-C(7)	1.381(3)
C(7)-C(8)	1.368(4)
C(8)-C(9)	1.376(5)
C(9)-C(10)	1.366(5)
C(10)-C(11)	1.393(4)
C(12)-C(13)	1.525(3)
C(13)-C(14)	1.531(3)
C(14)-C(15)	1.520(3)
C(15)-C(16)	1.510(3)
C(16)-C(21)	1.373(3)
C(16)-C(17)	1.395(4)
C(17)-C(18)	1.377(4)
C(18)-C(19)	1.373(4)
C(19)-C(20)	1.376(4)
C(20)-C(21)	1.380(3)
C(22)-C(23)	1.509(3)
C(23)-C(24)	1.378(4)
C(23)-C(28)	1.387(3)
C(24)-C(25)	1.368(4)

C(25)-C(26)	1.369(4)
C(26)-C(27)	1.368(4)
C(27)-C(28)	1.392(4)

C(1)-N(1)-C(4)	119.8(2)
C(1)-N(1)-C(2)	113.29(18)
C(4)-N(1)-C(2)	122.6(2)
C(12)-N(2)-C(1)	127.43(19)
C(12)-N(2)-C(3)	120.43(18)
C(1)-N(2)-C(3)	112.07(17)
C(13)-N(3)-C(22)	115.18(18)
O(1)-C(1)-N(1)	126.7(2)
O(1)-C(1)-N(2)	126.1(2)
N(1)-C(1)-N(2)	107.2(2)
N(1)-C(2)-C(5)	112.4(2)
N(1)-C(2)-C(3)	102.53(18)
C(5)-C(2)-C(3)	115.9(2)
N(2)-C(3)-C(6)	112.31(18)
N(2)-C(3)-C(2)	102.20(17)
C(6)-C(3)-C(2)	116.12(18)
C(11)-C(6)-C(7)	118.1(2)
C(11)-C(6)-C(3)	121.8(2)
C(7)-C(6)-C(3)	120.0(2)
C(8)-C(7)-C(6)	121.9(3)
C(7)-C(8)-C(9)	119.7(3)
C(10)-C(9)-C(8)	119.7(3)
C(9)-C(10)-C(11)	120.5(3)
C(6)-C(11)-C(10)	120.1(3)
O(2)-C(12)-N(2)	118.7(2)
O(2)-C(12)-C(13)	122.2(2)
N(2)-C(12)-C(13)	119.06(19)
N(3)-C(13)-C(12)	112.52(19)
N(3)-C(13)-C(14)	108.49(18)
C(12)-C(13)-C(14)	111.18(18)
C(15)-C(14)-C(13)	110.67(19)

C(16)-C(15)-C(14)	113.89(19)
C(21)-C(16)-C(17)	118.0(2)
C(21)-C(16)-C(15)	122.3(2)
C(17)-C(16)-C(15)	119.7(2)
C(18)-C(17)-C(16)	121.2(2)
C(19)-C(18)-C(17)	119.4(2)
C(18)-C(19)-C(20)	120.4(3)
C(19)-C(20)-C(21)	119.6(2)
C(16)-C(21)-C(20)	121.4(2)
N(3)-C(22)-C(23)	108.83(19)
C(24)-C(23)-C(28)	118.0(2)
C(24)-C(23)-C(22)	121.2(2)
C(28)-C(23)-C(22)	120.8(2)
C(25)-C(24)-C(23)	121.8(3)
C(24)-C(25)-C(26)	119.8(3)
C(27)-C(26)-C(25)	120.2(2)
C(26)-C(27)-C(28)	119.9(3)
C(23)-C(28)-C(27)	120.4(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for dec1400. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	69(1)	33(1)	54(1)	3(1)	-3(1)	3(1)
O(2)	51(1)	44(1)	69(1)	-4(1)	-13(1)	1(1)
N(1)	58(1)	46(1)	42(1)	2(1)	-5(1)	7(1)
N(2)	48(1)	31(1)	46(1)	2(1)	-5(1)	-1(1)
N(3)	51(1)	51(1)	51(1)	10(1)	-8(1)	-11(1)
C(1)	48(1)	34(1)	47(1)	5(1)	5(1)	-3(1)
C(2)	57(1)	47(1)	43(1)	-1(1)	2(1)	1(1)
C(3)	43(1)	37(1)	48(1)	-7(1)	3(1)	-2(1)
C(4)	92(2)	68(2)	53(2)	3(1)	-18(1)	22(2)
C(5)	74(2)	65(2)	73(2)	-8(2)	-27(2)	-4(2)
C(6)	39(1)	33(1)	54(1)	-1(1)	-4(1)	0(1)
C(7)	57(2)	40(2)	92(2)	-7(2)	-2(1)	4(1)
C(8)	69(2)	36(2)	145(3)	0(2)	-21(2)	-3(2)
C(9)	63(2)	53(2)	144(3)	41(2)	-28(2)	-20(2)
C(10)	60(2)	80(2)	84(2)	26(2)	-1(2)	-20(2)
C(11)	49(1)	49(2)	63(2)	4(1)	0(1)	-4(1)
C(12)	45(1)	29(1)	54(1)	3(1)	-1(1)	-5(1)
C(13)	48(1)	40(1)	48(1)	5(1)	-4(1)	-7(1)
C(14)	54(1)	39(1)	46(1)	-1(1)	1(1)	-7(1)
C(15)	64(2)	44(2)	72(2)	-12(1)	11(1)	-7(1)
C(16)	54(1)	39(1)	44(1)	-9(1)	3(1)	1(1)
C(17)	78(2)	41(2)	63(2)	-8(1)	-22(1)	8(1)
C(18)	68(2)	53(2)	86(2)	-22(2)	-29(2)	12(2)
C(19)	57(2)	45(2)	80(2)	-16(1)	-2(1)	-5(1)
C(20)	65(2)	36(1)	50(1)	-1(1)	3(1)	1(1)
C(21)	51(1)	43(2)	44(1)	-8(1)	-3(1)	7(1)
C(22)	63(2)	56(2)	55(1)	16(1)	-8(1)	-19(1)
C(23)	46(1)	39(1)	51(1)	5(1)	-2(1)	-7(1)
C(24)	53(1)	47(2)	73(2)	-6(1)	-6(1)	0(1)
C(25)	66(2)	80(2)	63(2)	-19(2)	6(2)	-16(2)

C(26)	71(2)	80(2)	47(2)	6(2)	-6(1)	-26(2)
C(27)	62(2)	49(2)	79(2)	23(2)	-16(2)	-6(1)
C(28)	55(1)	45(2)	60(2)	-2(1)	4(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for dec1400.

	x	y	z	U(eq)
H(3A)	-840(30)	2190(20)	492(9)	45(6)
H(2)	1514	2418	3060	59
H(3)	341	3511	2445	51
H(4C)	3589	-279	2579	107
H(4B)	2826	176	3116	107
H(4A)	4277	820	2945	107
H(5C)	4034	3593	2697	106
H(5B)	3761	3016	3282	106
H(5A)	2967	4301	3093	106
H(7)	1002	5760	2522	76
H(8)	1921	7592	2128	100
H(9)	3383	7401	1388	104
H(10)	3910	5370	1052	89
H(11)	3027	3507	1463	64
H(13)	1394	1052	1014	54
H(14B)	-443	-144	1483	55
H(14A)	-1511	393	1043	55
H(15B)	57	-562	371	72
H(15A)	791	-1303	856	72
H(17)	-2668	-904	334	73
H(18)	-4355	-2511	273	83
H(19)	-3849	-4596	566	73
H(20)	-1699	-5052	953	60
H(21)	-34	-3428	1029	55
H(22B)	1979	2698	375	70
H(22A)	839	3748	557	70
H(24)	1885	1864	-566	69

H(25)	1390	2289	-1452	84
H(26)	-138	3946	-1675	79
H(27)	-1123	5214	-1009	76
H(28)	-610	4796	-110	64

Crystal data and structure refinement for 6b

Identification code	may2601	
Empirical formula	C21 H23 N5 O2	
Formula weight	377.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2 (No.5)	
Unit cell dimensions	a = 19.2790(16) Å	α= 90°.
	b = 6.0518(8) Å	β= 99.200(8)°.
	c = 17.189(2) Å	γ = 90°.
Volume	1979.7(4) $Å^3$	
Z	4	
Density (calculated)	1.27 Mg/m^3	
Absorption coefficient	0.09 mm^{-1}	
F(000)	800	
Crystal size	0.40 x 0.05 x 0.05 mm^3	
Theta range for data collection	3.79 to 23.01°.	
Index ranges	-19<=h<=20, -6<=k<=6, -18<=l<=17	
Reflections collected	4206	
Independent reflections	2477 [R(int) = 0.087]	
Reflections with I>2sigma(I)	2118	
Completeness to theta = 23.01°	97.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2477 / 1 / 256	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.086, wR2 = 0.229	
R indices (all data)	R1 = 0.098, wR2 = 0.245	
Absolute structure parameter	-8(4)	
Extinction coefficient	0.017(6)	
Largest diff. peak and hole	0.29 and -0.40 e.$Å^{-3}$	

The compound crystallizes as long , very thin, needles, and the diffraction is weak.
Data collection KappaCCD , Program package WinGX , Abs correction not applied ,
Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for may2601. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2754(2)	-34(8)	816(2)	38(1)
O(2)	2256(3)	-4769(8)	2442(3)	51(1)
N(1)	3486(3)	-2879(9)	593(3)	35(1)
N(2)	2842(2)	-3366(8)	1535(2)	30(1)
N(3)	1201(3)	-2053(11)	1299(3)	45(2)
N(4)	872(3)	-3627(12)	1514(3)	48(2)
N(5)	532(4)	-5095(15)	1628(4)	71(2)
C(1)	3009(3)	-1877(11)	951(3)	31(2)
C(2)	3580(3)	-5227(11)	773(3)	35(1)
C(3)	3290(3)	-5340(10)	1580(3)	32(1)
C(4)	3703(4)	-1920(13)	-120(4)	54(2)
C(5)	4301(4)	-6093(15)	780(4)	54(2)
C(6)	3859(3)	-5360(11)	2295(3)	34(1)
C(7)	3983(3)	-7243(12)	2756(3)	44(2)
C(8)	4519(4)	-7298(15)	3393(4)	55(2)
C(9)	4941(4)	-5455(15)	3592(4)	55(2)
C(10)	4826(3)	-3610(13)	3138(4)	48(2)
C(11)	4287(4)	-3535(13)	2502(3)	45(2)
C(12)	2327(3)	-3244(11)	2000(3)	35(1)
C(13)	1806(3)	-1319(11)	1899(3)	36(2)
C(14)	1563(3)	-669(11)	2677(3)	37(2)
C(15)	2169(3)	235(12)	3289(3)	39(2)
C(16)	1873(3)	1074(11)	4006(3)	32(1)
C(17)	1575(3)	3107(12)	4017(3)	42(2)
C(18)	1269(4)	3807(13)	4659(4)	48(2)
C(19)	1294(4)	2414(14)	5309(4)	55(2)
C(20)	1598(4)	410(14)	5311(4)	51(2)
C(21)	1896(3)	-334(12)	4663(3)	41(2)

Table 3. Bond lengths [Å] and angles [°] for may2601.

O(1)-C(1)	1.225(8)
O(2)-C(12)	1.218(8)
N(1)-C(1)	1.332(8)
N(1)-C(2)	1.459(9)
N(1)-C(4)	1.476(7)
N(2)-C(12)	1.372(7)
N(2)-C(1)	1.424(7)
N(2)-C(3)	1.469(8)
N(3)-N(4)	1.234(9)
N(3)-C(13)	1.495(8)
N(4)-N(5)	1.139(10)
C(2)-C(5)	1.484(9)
C(2)-C(3)	1.577(7)
C(3)-C(6)	1.513(8)
C(6)-C(7)	1.386(9)
C(6)-C(11)	1.389(9)
C(7)-C(8)	1.380(9)
C(8)-C(9)	1.391(12)
C(9)-C(10)	1.359(11)
C(10)-C(11)	1.384(9)
C(12)-C(13)	1.530(9)
C(13)-C(14)	1.537(7)
C(14)-C(15)	1.541(9)
C(15)-C(16)	1.526(8)
C(16)-C(17)	1.359(9)
C(16)-C(21)	1.409(9)
C(17)-C(18)	1.398(9)
C(18)-C(19)	1.395(10)
C(19)-C(20)	1.346(11)
C(20)-C(21)	1.407(9)
C(1)-N(1)-C(2)	114.6(5)
C(1)-N(1)-C(4)	120.9(6)

C(2)-N(1)-C(4)	121.2(5)
C(12)-N(2)-C(1)	130.0(5)
C(12)-N(2)-C(3)	119.2(4)
C(1)-N(2)-C(3)	110.7(4)
N(4)-N(3)-C(13)	113.9(5)
N(5)-N(4)-N(3)	172.5(6)
O(1)-C(1)-N(1)	127.8(5)
O(1)-C(1)-N(2)	125.4(5)
N(1)-C(1)-N(2)	106.8(5)
N(1)-C(2)-C(5)	115.5(6)
N(1)-C(2)-C(3)	100.3(5)
C(5)-C(2)-C(3)	116.2(5)
N(2)-C(3)-C(6)	113.2(5)
N(2)-C(3)-C(2)	102.0(4)
C(6)-C(3)-C(2)	113.7(4)
C(7)-C(6)-C(11)	117.8(6)
C(7)-C(6)-C(3)	120.5(6)
C(11)-C(6)-C(3)	121.7(6)
C(8)-C(7)-C(6)	120.8(7)
C(7)-C(8)-C(9)	120.6(7)
C(10)-C(9)-C(8)	118.9(7)
C(9)-C(10)-C(11)	120.8(7)
C(10)-C(11)-C(6)	121.1(7)
O(2)-C(12)-N(2)	119.2(5)
O(2)-C(12)-C(13)	120.6(5)
N(2)-C(12)-C(13)	119.9(5)
N(3)-C(13)-C(12)	106.1(5)
N(3)-C(13)-C(14)	111.4(5)
C(12)-C(13)-C(14)	112.5(5)
C(13)-C(14)-C(15)	112.5(5)
C(16)-C(15)-C(14)	109.2(5)
C(17)-C(16)-C(21)	119.7(6)
C(17)-C(16)-C(15)	121.7(5)
C(21)-C(16)-C(15)	118.5(6)
C(16)-C(17)-C(18)	121.2(6)

C(19)-C(18)-C(17)	119.0(7)
C(20)-C(19)-C(18)	120.4(6)
C(19)-C(20)-C(21)	121.2(6)
C(20)-C(21)-C(16)	118.4(7)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for may2601. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	55(3)	33(3)	29(2)	4(2)	15(2)	2(2)
O(2)	68(3)	49(3)	46(3)	17(2)	35(2)	15(2)
N(1)	45(3)	41(3)	22(2)	1(2)	15(2)	-2(2)
N(2)	38(3)	32(3)	22(2)	0(2)	11(2)	0(2)
N(3)	55(3)	57(4)	24(2)	0(3)	9(2)	11(3)
N(4)	52(3)	63(5)	28(3)	-4(3)	8(2)	6(4)
N(5)	73(5)	84(6)	58(4)	-16(4)	17(3)	-11(5)
C(1)	37(3)	40(4)	17(3)	0(3)	4(2)	-7(3)
C(2)	42(3)	42(4)	23(3)	-7(3)	9(2)	0(3)
C(3)	43(3)	31(4)	25(3)	-4(3)	14(2)	-2(3)
C(4)	81(5)	56(5)	33(3)	4(3)	36(3)	-14(4)
C(5)	58(4)	77(5)	33(3)	-2(3)	20(3)	7(4)
C(6)	40(3)	39(4)	24(3)	-2(3)	12(2)	5(3)
C(7)	49(4)	51(4)	33(3)	6(3)	15(3)	11(3)
C(8)	67(4)	63(5)	39(4)	18(4)	18(3)	21(4)
C(9)	61(4)	80(6)	25(3)	-6(4)	9(3)	17(4)
C(10)	52(4)	57(5)	35(3)	-12(4)	7(3)	4(4)
C(11)	60(4)	48(4)	29(3)	-5(3)	12(3)	2(3)
C(12)	44(3)	39(4)	25(3)	5(3)	12(2)	5(3)
C(13)	49(4)	43(4)	18(3)	2(3)	13(2)	11(3)
C(14)	44(3)	44(4)	25(3)	0(3)	13(2)	5(3)
C(15)	45(4)	49(4)	26(3)	0(3)	13(3)	8(3)
C(16)	33(3)	36(4)	26(3)	-3(3)	6(2)	-3(3)
C(17)	45(3)	54(5)	28(3)	0(3)	11(3)	0(3)
C(18)	56(4)	51(4)	42(4)	-9(3)	21(3)	1(3)
C(19)	70(5)	67(5)	32(4)	-13(3)	19(3)	-6(4)
C(20)	55(4)	74(6)	26(3)	14(3)	11(3)	-5(4)
C(21)	55(4)	43(4)	27(3)	3(3)	9(3)	-8(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for may2601.

	x	y	z	U(eq)
H(2)	3253	-6076	372	42
H(3)	2991	-6689	1585	39
H(4A)	3441	-2630	-589	80
H(4B)	4208	-2162	-106	80
H(4C)	3605	-330	-138	80
H(5A)	4409	-6095	242	82
H(5B)	4331	-7604	988	82
H(5C)	4639	-5152	1115	82
H(7)	3696	-8510	2632	52
H(8)	4600	-8609	3698	66
H(9)	5302	-5484	4037	66
H(10)	5121	-2356	3259	57
H(11)	4207	-2215	2202	54
H(13)	2034	-13	1689	43
H(14A)	1357	-1978	2899	44
H(14B)	1192	470	2569	44
H(15A)	2517	-949	3450	47
H(15B)	2409	1455	3055	47
H(17)	1575	4069	3580	50
H(18)	1047	5210	4652	58
H(19)	1096	2882	5753	66
H(20)	1611	-519	5759	61
H(21)	2107	-1752	4668	50