Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A novel synthesis of pyrrolo-(di)-benzazocinones *via* an endocyclic iminium ion cyclisation

Frank D. King*, Abil E. Aliev, Stephen Caddick and D. A. Tocher

General procedure for the preparation of the N-substituted imides:

A stirred solution of the appropriate alcohol (10 mmol), triphenyl phosphine (11 mmol) and the dried NH-imide (11 mol) was dissolved in DCM (50 ml), cooled to 0^{o}C and treated with DEAD (11 mmol) until the yellow colour remained. The reaction mixture was left overnight at ambient temperatures, the solvent removed and the residue purified by column chromatography on SiO_2, eluting with petrol/DCM.

General procedure for the reduction of the N-substituted succinimides and glutarimides to the hydroxy-amides using $NaBH_4$

A stirred solution of the appropriate N-substituted succinimide (5 mmol) was dissolved in EtOH (30 ml) and saturated aqueous $KHCO_3$ solution (3 ml) added together with H_2O (2 ml). On cooling to 0-5^{o}C, $NaBH_4$ (25 mmol) was added and the reaction stirred at that temperature for 2-4h, until most of the succinimide had been reduced by TLC. Water (150 ml) was then added and the product extracted into DCM (3 x 50 ml), dried (K_2CO_3), concentrated and the residue purified by column chromatography on SiO_2.

General procedure for the reduction of the N-substituted phthalimides to the hydroxy-amides using $NaBH_4$

To a stirred, ethanolic (40 ml) suspension of the phthalimide (5 mmol) and water (4 ml) was added $NaBH_4$ (25 mmol) at ambient temperatures and the reaction stirred at ambient temperatures for 1h until no starting material was observed by TLC. Water (150 ml) was then added and the solid product collected and dried.

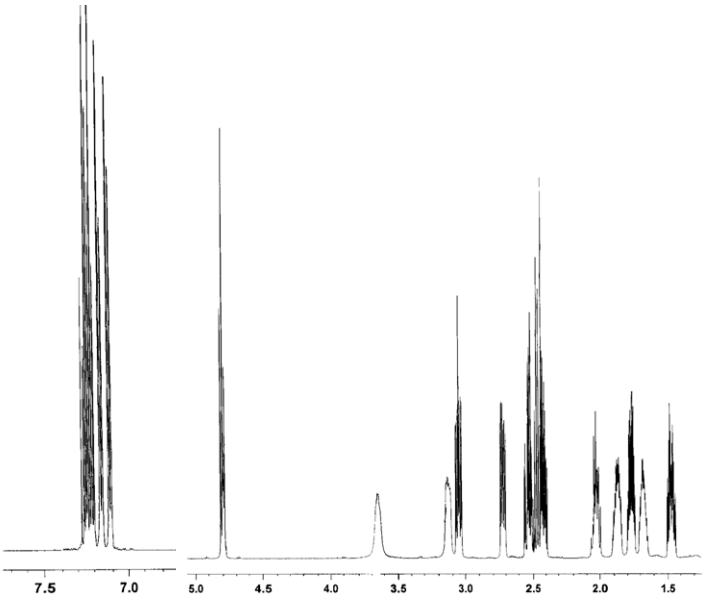
General procedure for the triflic acid-mediated cyclisation:

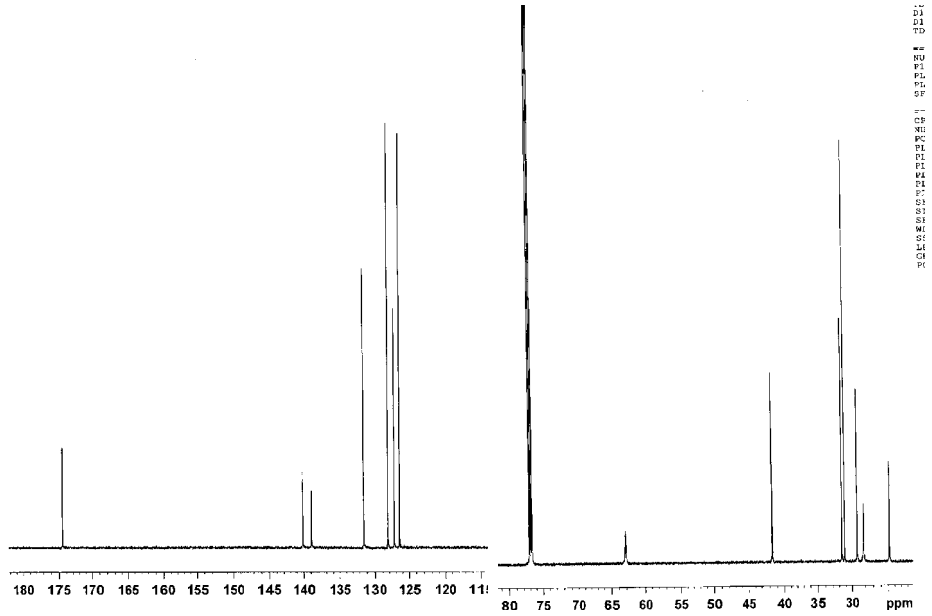
A solution of the hydroxy-amide (5 mmol) in chloroform (10 mL) was added over 10 min to a heated (65^{o}C), stirred mixture of triflic acid (50 mmol) in chloroform (40 mL). The reaction was heated under gentle reflux for a given period. On cooling to ambient temperatures, water (20 ml) was added and the aqueoud layer carefully basified with solid K_2CO_3 (vigorous effervescence). The reaction mixture was transferred to a separating funnel and the lower layer separated. The aqueous layer was extracted with DCM (50 ml) and the combined organic extracts dried (K_2CO_3). Filtration and evaporation *in vacuo* gave the crude products which were separated by column chromatography on silica.

6-Aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2a)

Preparative details in the paper.

^{1}H NMR and ^{13}C NMR of **2a**

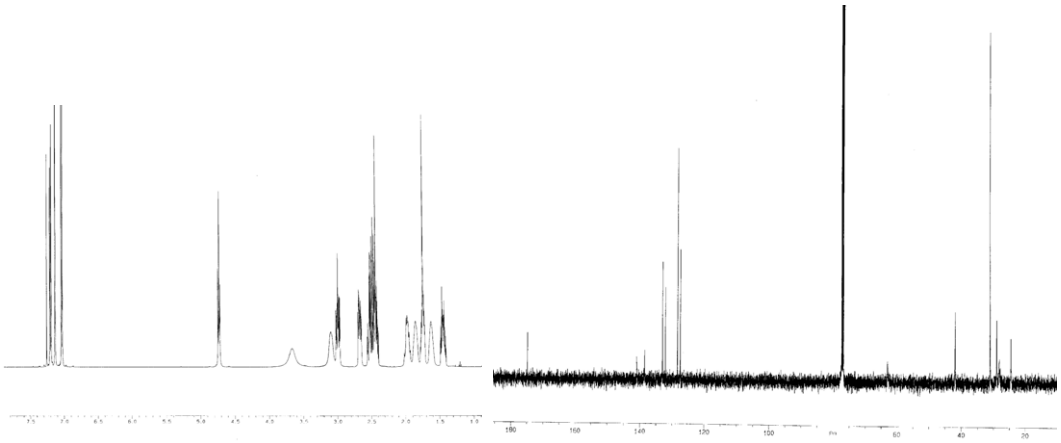




14-Chloro-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2b)

Following the general procedure, 4-(4-chlorophenyl)butan-1-ol (C.K. Lau, S. Tardif, C. Dufresne, and J. Scheigetz, *J. Org. Chem.* 1989; **54**; 491) was converted to the N-substituted succinimide **1b**, eluting with 3:1 DCM:petrol, isolated as a white solid (87% yield) mpt 61-3^{o}C (ether/petrol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.53-1.60 (4H, m), 2.58 (2H, t, *J* = 7.1 Hz), 2.67 (4H, s), 3.51 (2H, t, *J* = 6.8 Hz), 7.07 (2H, d, *J* = 8.3 Hz), 7.22 (2H, d, *J* = 8.3Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.23 (CH_2), 28.22 (CH_2), 28.56 (CH*2*), 34.68 (CH_2), 38.54 (CH_2), 128.49 (CH), 129.83 (CH), 131.61 (C), 140.39 (C), 177.33 (C).. **1b** was reduced with $NaBH_4$ following the general procedure to give the hydroxyamide, purified by column chromatography on SiO_2, eluting with 1:1 DCM/EtOAc (66% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.4-1.60 (4H, m), 1.80 – 1.93 (1H, m), 2.16- 2.32 (2H, m), 2.41-2.62 (3H, m), 3.06-3.15 (1H, m), 3.38-3.47 (1H, m), 5.13 (1H, d, *J* = 5.5 Hz), 7.05 (2H, d, *J* = 8.2 Hz), 7.19 (2H, d, *J* = 8.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.7 (CH_2), 27.7 (CH_2), 28.3 (CH_2), 28.7 (CH_2), 34.4 (CH_2), 39.3 (CH_2), 82.7 (CH), 127.8 (CH), 129.5 (CH), 131.3 (C), 140.2 (C), 174.7 (C). Cyclisation of the hydroxyamide by the general procedure, heating under reflux for 3h gave the title compound 1b (65% yield), mpt = 84-5^{o}C (ether/petrol). HRMS Theoretical Mass: 250.09987; Measured Mass: 250.10050. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 – 1.50 (1H, m), 1.55 – 1.68 (1H, brm), 1.70 – 1.80 (1H, m), 1.80 – 1.90 (1H, brm), 1.91 – 2.01 (1H, m), 2.49 – 2.56 (2H, m), 2.67 (1H, ddd, *J* = 5.0, 5.8, 13.5 Hz), 2.96 – 3.03 (1H, m), 2.99 (1H, ddd, *J* = 4.3, 10.1, 14.0Hz), 3.04 – 3.15 (1H, brm), 3.56 – 3.76 (1H, brm), 4.73 (1H, t, *J* = 7.5 Hz), 7.03 (1H, d, *J* = 8.1 Hz), 7.13 (1H, d, *J* = 2.1 Hz), 7.20 (1H, dd, *J* – 8.1, 2.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.53 (CH_2), 28.21 (CH_2), 29.02 (CH_2), 31.08 (CH_2), 31.14 (CH_2), 41.81 (CH_2), 62.96 (CH), 127.48 (CH), 128.35 (CH), 132.11 (C), 133.01 (C), 138.58 (C), 140.91 (C), 174.87 (C).

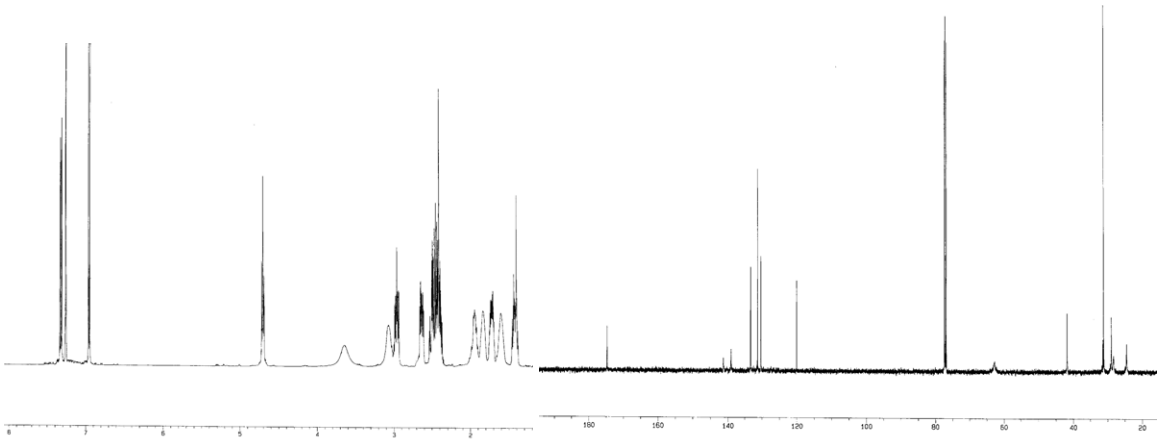
^{1}H NMR and ^{13}C NMR of **2b**



14-Bromo-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2c)

Following the general procedure, 4-(4-bromophenyl)butan-1-ol (M. Zaidlewicz and A. Wolan, *J. Organomet, Chem.* 2002; **657**; 129) was converted to the N-substituted succinimide **1c**, eluting with 3:1 DCM:petrol, isolated as a white solid (85% yield) mpt 86-8^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 – 1.65 (4H, m), 2.60 (2H, t, *J* = 7 Hz), 2.68 (4H, s), 3.51 (2H, t, *J* = 7 Hz), 7.02 (2H, d, *J* = 8 Hz), 7.37 (2H, d, *J* = 8 Hz) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.2 (CH_2), 28.2 (CH_2), 28.4 (CH_2), 34.7 (CH_2), 38.5 (CH_2), 119.6 (C), 130.2 (CH), 131.4 (CH), 140.8 (C), 177.2 (C). . **1c** was reduced with $NaBH_4$ following the general procedure to give the hydroxyamide, purified by column chromatography on SiO_2, eluting with 1:1 DCM/EtOAc (yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 – 1.48 (1H, m), 1.54 – 1.67 (1H, brm), 1.69 – 1.77 (1H, m), 1.79 – 1.89 (brm, 1H), 1.89 – 2.00 (1H, brm), 2.36-2.56 (3H, m), 2.63 (1H, dt, *J* = 5.7, 13.7 Hz), 2.96 (1H, tt, *J* = 4.3, 10.2 Hz), 3.00 – 3.12 (1H, brm), 3.50 – 3.75 (1H, brm), 4.71 (1H, t, *J* = 7.5 Hz), 6.95 (1H, d, *J* = 8.1 Hz), 7.27 (1H, d, *J* = 2.0 Hz), 7.33 (1H, dd, *J* = 2.0, 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.15 (CH_2), 28.34 (CH_2), 28.60 (CH_2), 29.02 (CH_2), 34.88 (CH_2), 39.67 (CH_2), 83.21 (CH), 119.60 (C), 130.24 (CH), 131.44 (CH), 141.07 (C), 175.04 (C).. Cyclisation of the hydroxyamide by the general procedure, heating under reflux for 3h gave the title compound **2c** (73% yield), mpt = 93-4^{o}C (ether/petrol). HRMS Theoretical Mass: 293.04098; Measured Mass: 293.04162. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 – 1.50 (1H, m), 1.55 – 1.68 (1H, brm), 1.70 – 1.80 (1H, m), 1.80 – 1.90 (1H, brm), 1.91 – 2.01 (1H, m), 2.34 – 2.56 (3H, m), 2.64 (1H, ddd, *J* = 5.0, 5.8, 13.5 Hz), 2.92 – 3.00 (1H, m), 3.00 – 3.27 (1H, brm), 3.56 – 3.76 (1H, brm), 4.71 (1H, t, *J* = 7.5 Hz), 6.95 (1H, d, *J* = 8.1 Hz), 7.26 (1H, d, *J* = 3.2 Hz), 7.20 (1H, dd, *J* – 8.1, 3.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.49 (CH_2), 28.34 (CH_2), 28.94 (CH_2), 31.13 (CH_2), 31.35 (CH_2), 41.81 (CH_2), 62.83 (CH), 120.06 (C), 130.37 (CH), 131.31 (CH), 133.32 (C), 138.58 (C), 139.07 (C), 174.84 (C).

^{1}H NMR and ^{13}C NMR of **2c**



13-Bromo-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2d) 9/14 and 15-Bromo-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2e)

A solution of 4 (4-nitrophenyl)butylsuccinimide (see **2k**) (2.0g, 7.2 mmol) and ammonium formate (2.3g, 36mmol) in ethanol (50 ml) was heated to gentle reflux under argon with 10% Pd/C (0.2g) for 2h. The cooled reaction mixture was filtered through celite and concentrated in vacuo to give a pale orange solid of the 4-amino compound (1.8g, 100% yield) used without further purification. Mpt 148-151^{o}C (ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ = δ = 1.50 – 1.61 (4H, m), 2.50 (2H, t, *J* = 6.9 Hz), 2.67 (4H, s), 3.51 (2H, t, *J* = 6.7 Hz), 3.50 – 3.60 (brs, 2H), 6.61 (2H, d, *J* = 8.3 Hz), 6.94 (2H, d, *J* = 8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.30 (CH_2), 28.22 (CH_2), 28.98 (CH_2), 34.52 (CH_2), 38.76 (CH_2), 115.31 (CH), 129.25 (CH), 132.09 (C), 144.33 (C), 177.36 (C).

To a stirred solution of the 4-amino compound (0.6g, 2.4 mmol) in $CHCl_3$ (50 ml) at 0^{o}C was added NBS (0.43g, 2.4mmol) and the reaction warmed to ambient temperatures and stirred for 30 min. The reaction mixture was washed with 1M $NaHSO_3$ solution (20 ml), 1M NaOH solution (30 ml) and dried (K_2CO_3). The organic solution was concentrated in vacuo and the residue purified by column chromatography on silica, eluting with DCM – DCM + 2% MeOH to give the 4-(3-bromo-4-aminophenyl)butylsuccinimide (0.63g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 – 1.60 (4H, m), 2.44 (2H, t, *J* = 6.9 Hz), 2.63 (4H, s), 3.43 (2H, t, *J* = 6.7 Hz), 4.00 (2H, brs), 6.64 (1H, d, *J* = 8.1 Hz), 6.89 (1H, dd, *J* = 1.8, 8.1 Hz), 7.16 (1H, d, *J* = 1.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.19 (CH_2), 28.23 (CH_2), 28.71 (CH_2), 33.82 (CH_2), 38.61 (CH_2), 109.29 (C), 115.86 (CH), 128.47 (CH), 132.17 (CH), 133.25 (C), 131.52 (CH), 142.09 (C), 177.37 (C).

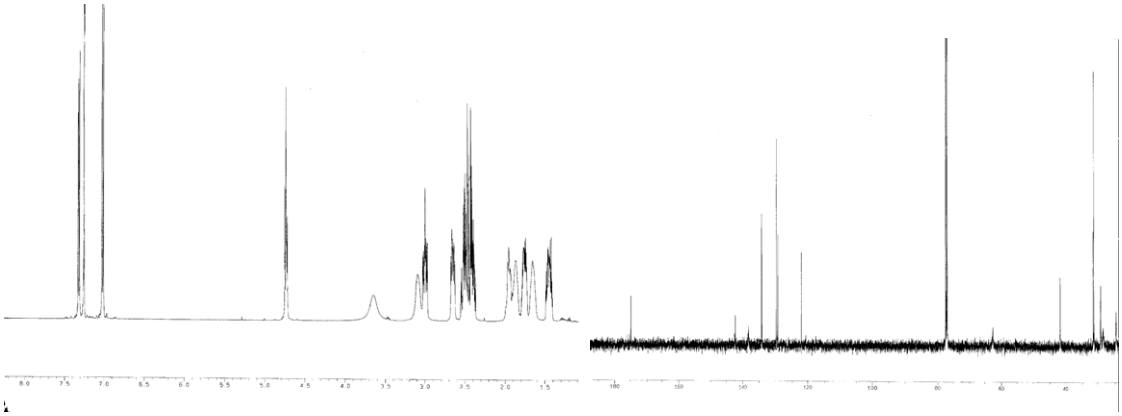
A stirred solution of the 4-(3-bromo-4-aminophenyl)butylsuccinimide (1.0g, 3.1 mmol) in acetic acid (5ml), water (3 ml) and cHCl (1 ml) was cooled to 0^{o}C and treated with a solution of $NaNO_2$ (0.23g) in water (3 ml), and the reaction mixture stirred for 15 min. A solution of 50% H_3PO_2 (5 ml) was added and the reaction mixture maintained at 0-5^{o}C overnight. On dilution with water (50 ml), the solid product was collected, dried and purified by column chromatography on silica, eluting with DCM + 1% Et_2O to give the 4(3-bromophenyl)butylsuccinimide **1d/e** (0.9g, 95% yield), mpt 99-101^{o}C (EtOAc/petrol). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55 – 1.62 (4H, m), 2.60 (2H, t, *J* = 6.9 Hz), 2.70 (4H, s), 3.52 (2H, t, *J* = 6.7 Hz), 7.08 (1H, d, *J* = 7.6 Hz), 7.13 (1H, t, *J* = 7.6 Hz), 7.28 – 7.33 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.25 (CH_2), 28.23 (CH_2), 28.46 (CH_2), 35.03 (CH_2), 38.55 (CH_2), 122.48 (C), 127.17 (CH), 129.07 (CH), 130.00 (CH), 131.52 (CH), 144.31 (C), 177.31 (C).

A stirred solution of **1d/e** (0.62g, 2mmol) in dry THF (10 ml) was cooled to -78^{o}C under Argon and treated with DIBAL (2.2ml of a 1M solution in hexanes) and allow to warm to 0^{o}C over 30 min.. A 2M NaOH solution (1 ml) was carefully added followed by ether (50 ml) and the reaction mixture stirred o/n. K_2CO_3 (2g) was added and the reaction mixture filter through celite, and the solids thoroughly washed with DCM (2 x 50 ml). The combined organics were concentrated in vacuo and the residue purified by column chromatography on silica, eluting with DCM to give recovered starting material (0.3g, 48%), then with 3% MeOH/DCM to give the hydroxyamide 0.23g (37% yield) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 – 1.61 (4H, m), 1.80 – 1.95 (1H, m), 2.20 – 2.33 (2H, m), 2.45 – 2.62 (3H, m), 2.98 – 3.19 (1H, m), 3.39 – 3.50 (1H, m),3.81 (1H, d, *J* = 8.2 Hz), 5.15 (1H, t, *J* = 5.8Hz), 7.07 (1H, d, *J* = 7.6 Hz), 7.12 (1H, t, *J* = 7.6 Hz), 7.27 – 7.32 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.20 (CH_2), 28.40 (CH_2), 28.54 (CH_2), 29.00 (CH_2), 35.16 (CH_2), 39.70 (CH_2), 83.27 (CH), 122.46 (C), 127.17 (CH), 129.03 (CH), 130.00 (CH), 131.48 (CH), 144.51 (C), 174.98 (C).

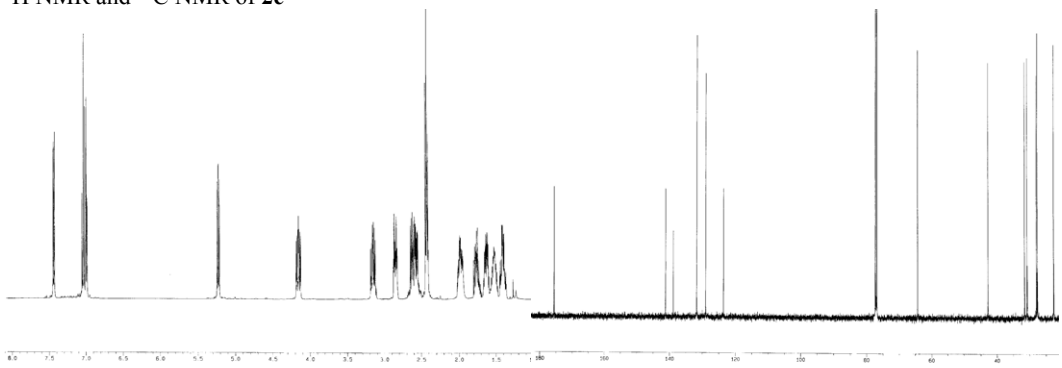
Cyclisation of the hydroxyamide (0.23g, 0.75mmol) by the general procedure, heating under reflux for 3h gave a mixture of 1e and 1f, separated by column chromatography on silica, eluting with Et_2O to give **2e** (40 mgs, 18% yield) mpt = 96-7^{o}C (ether). HRMS Theoretical Mass: 294.04935; Measured Mass: 294.04938. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 – 1.46 (1H, m), 1.47 – 1.68 (2H, m), 1.69 – 1.80 (1H, m), 1.90 – 2.03 (1H, m), 2.43 (2H, t, *J* = 8.6 Hz), 2.50 – 2.69 (2H, m), 2.85 (1H, dt, *J* = 4.4, 13.8 Hz), 3.10 – 3.20 (1H, m), 4.11 – 4.20 (1H, m), 5.23 (1H, dd, *J* = 6.4, 8.2 Hz), 6.99 (1H, dd, *J* = 1.2, 7.5 Hz), 7.04 (1H, t, *J* = 7.6 Hz), 7.44 (1H, dd, *J* = 1.3,7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.77 (CH_2), 27.70 (CH_2), 27.97 (CH_2), 30.81 (CH_2), 31.58 (CH_2), 42.82 (CH_2), 64.29 (CH), 123.64 (C), 129.00 (CH), 131.67 (CH), 131.71 (CH), 138.88 (C), 141.24 (C), 175.66 (C).

Elution with Et2O + 3% MeOH to gave **2d** (220 mgs, 73% yield), mpt 82-4^{o}C (ether/petrol). HRMS Theoretical Mass: 294.04935; Measured Mass: 294.04857. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 – 1.50 (1H, m), 1.59 – 1.69 (1H, brm), 1.70 – 1.80 (1H, m), 1.81 – 2.00 (2H, m), 2.36 – 2.56 (3H, m), 2.60 – 2.70 (1H, m), 2.95 – 3,18 (2H, brm), 3.51 – 3.68 (1H, brm), 4.74 (1H, t, *J* = 7.5 Hz), 7.02 (1H, d, *J* = 8.2 Hz), 7.26 (1H, d, *J* = 2.3 Hz), 7.32 (1H, dd, *J* = 2.3, 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.6 (CH_2), 28.3 (CH_2), 29.0 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 41.7 (CH_2), 62.5 (CH), 122.0 (C), 129.2 (CH), 129.6 (CH), 134.3 (CH), 138.1 (C), 142.5 (C), 174.8 (C)..

^{1}H NMR of **2d**



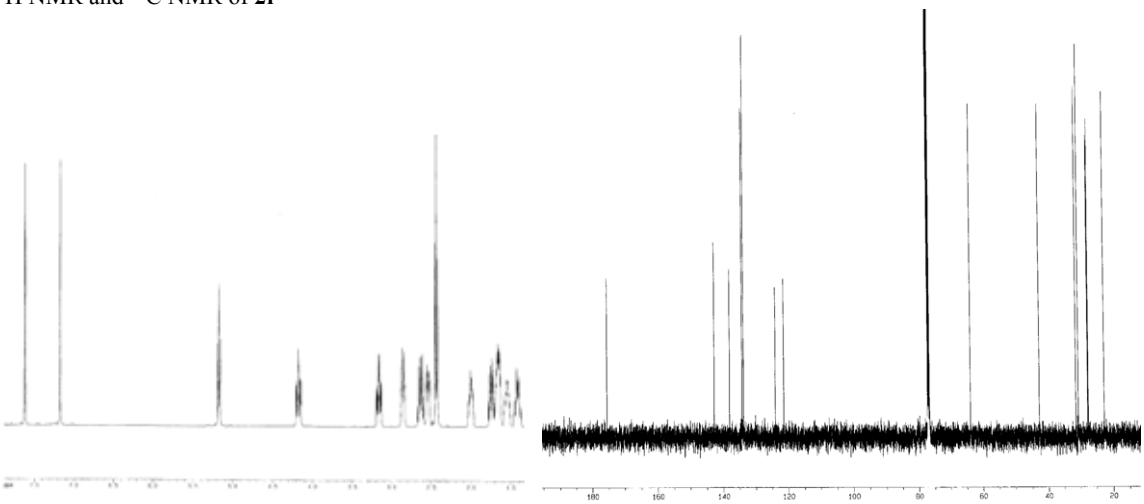
^{1}H NMR and ^{13}C NMR of **2e**



13,15-Dibromo-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2f)

To a stirred solution of the 4-amino compound (0.6g, 2.4 mmol) in $CHCl_3$ (50 ml) at 0^oC was added NBS (0.86g, 4.8 mmol) and the reaction warmed to ambient temperatures and stirred for 2h. The reaction mixture was washed with 1M $NaHSO_3$ solution (20 ml), 1M NaOH solution (30 ml) and dried (K_2CO_3). The organic solution was concentrated in vacuo and the residue purified by column chromatography on silica, eluting with DCM to give the 4-(3,5-dibromo-4-amino-phenyl)butylsuccinimide (0.87g, 90% yield) as an orange solid, mpt 84-6^oC (ether). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.50 – 1.60 (4H, m), 2.47 (2H, t, *J* = 7.2 Hz), 2.71 (4H, s), 3.50 (2H, t, *J* = 7.0 Hz), 4.40 (2H, brs), 7.17 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.14 (CH_2), 28.23 (CH_2), 28.65 (CH_2), 33.85 (CH_2), 38.54 (CH_2), 108.43 (C), 131.65 (CH), 133.56 (C), 140.01 (C), 177.31 (C).
A stirred solution of the 4-(3,5-dibromo-4-aminophenyl)butylsuccinimide (2.9g, 7.2 mmol) in acetic acid (10ml), water (6 ml) and cHCl (2 ml) was cooled to 0^oC and treated with a solution of $NaNO_2$ (0.5g) in water (3 ml), and the reaction mixture stirred for 15 min. A solution of 50% H_3PO_2 (10 ml) was added and the reaction mixture maintained at 0-5^oC overnight. On dilution with water (50 ml), the solid product was collected, dried and purified by column chromatography on silica, eluting with DCM + 1% MeOH to give the 4(3,5-dibromophenyl)butylsuccinimide **1f** (2.5g, 89% yield), mpt 46-8^oC (EtOAc/ petrol). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.53 – 1.60 (4H, m), 2.56 (2H, t, *J* = 6.7 Hz), 2.69 (4H, s), 3.51 (2H, t, *J* = 6.8 Hz), 7.23 (2H, d, *J* = 1.6 Hz), 7.47 (1H, t, *J* = 1.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.20 (CH_2), 28.23 (CH_2), 28.25 (CH_2), 34.77 (CH_2), 38.40 (CH_2), 122.87 (C), 130.37 (CH), 131.67 (CH), 145.91 (C), 177.29 (C).
A stirred solution of **1f** (1.6g, 4.1mmol) in dry THF (20 ml) was cooled to -78^oC under Argon and treated with DIBAL (4.1 ml of a 1M solution in hexanes) and allow to warm to 0^oC over 30 min.. A 2M NaOH solution (1 ml) was carefully added followed by ether (50 ml) and the reaction mixture stirred overnight. K_2CO_3 (2g) was added and the reaction mixture filter through celite, and the solids thoroughly washed with DCM (2 x 50 ml). The combined organics were concentrated *in vacuo* and the residue purified by column chromatography on silica, eluting with DCM to give recovered starting material (0.4g, 25%), then with 2% MeOH/DCM to give the hydroxyamide 0.74g (46% yield) ^1H NMR (500 MHz, $CDCl_3$): δ = 1.48 – 1.61 (4H, m), 1.82 – 1.92 (1H, m), 2.20 – 2.32 (2H, m), 2.45 – 2.60 (3H, m), 3.10 – 3.19 (1H, m), 3.39 – 3.48 (1H, m), 4.52 (1H, d, *J* = 8.3 Hz), 5.14 (1H, t, *J* = 5.9 Hz), 7.21 (2H, d, *J* = 1.7 Hz), 7.45 (1H, t, *J* = 1.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.14 (CH_2), 28.32 (CH_2), 29.06 (CH_2), 34.88 (CH_2), 39.57 (CH_2), 83.22 (CH), 122.86 (C), 130.32 (CH), 131.61 (CH), 146.13 (C), 175.18 (C).
Cyclisation of the hydroxyamide (0.7g, 1.8mmol) by the general procedure, heating under reflux for 3h and purification by column chromatography on silica, eluting with Et_2O + 1% MeOH gave **2f** (0.54g, 80% yield) mpt = 88-90^oC (EtOAc/petrol). HRMS Theoretical Mass: 371.95986; Measured Mass: 371.95844. FT-IR (Neat) 1689, 1572, 1547, 1435, 1387, 1336, 1252, 1229, 1157, 902, 853, 742 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.35 – 1.46 (1H, m), 1.49 – 1.59 (1H, m), 1.60 – 1.79 (3H, m), 1.95 – 2.05 (1H, m), 2.43 (2H, t, *J* = 8.3 Hz), 2.54 (1H, ddd, *J* = 2.2, 4.7, 13.5 Hz), 2.59 – 2.68 (1H, dtt, J = 1.1, 8.0, 13.4 Hz), 2.86 (1H, dt, *J* = 4.3, 8.6 Hz), 3.16 (4.7, 5.5, 12.4Hz), 4.17 (1H, m), 5.17 (dt, J = 1.1, 7.7 Hz), 7.18 (1H, s), 7.63 (1H, t, J = 1.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.66 (CH_2), 27.56 (CH_2), 27.78 (CH_2), 30.69 (CH_2), 31.48 (CH_2), 42.82 (CH_2), 63.96 (CH), 121.47 (C), 124.04 (C), 133.86 (CH), 134.32 (CH), 138.18 (C), 142.85 (C), 175.59 (C).

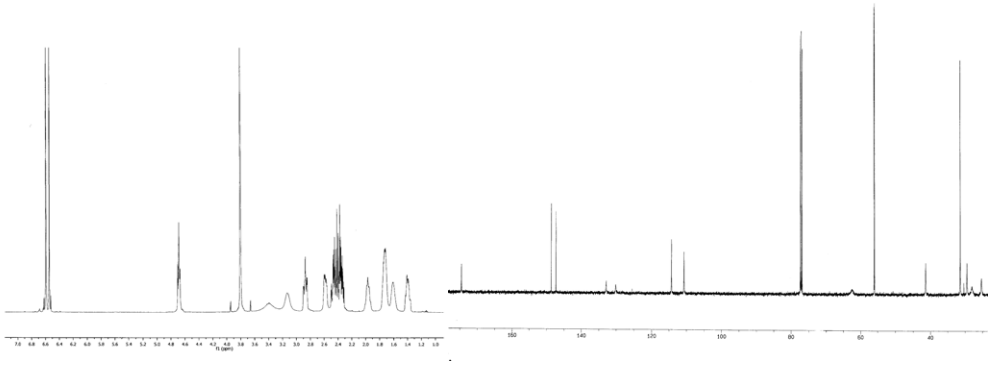
^1H NMR and ^{13}C NMR of **2f**



13,14-Dimethoxy-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2g)

Following the general procedure, 4-(3,4-dimethoxyphenyl)butan-1-ol (R. Heck and S. Winstein; *J. Amer. Chem. Soc.* 1957; **79**; 3114) was converted to the N-substituted succinimide **1g**, eluting with 3:1 DCM:petrol, isolated as a white solid (85% yield), mpt 86-8°C (EtOAC/petrol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 – 1.65 (4h, m), 2.59 (2h, t, *J* = 7Hz), 2.68 (4H, s), 3.51 (2H, t, *J* = 7 Hz) 3.84 (3H, s), 3.87 (3H, s), 6.65 – 6.72 (2H, m), 6.77 (1H, d, J = 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.2 (CH_2), 28.2 (CH_2), 28.8 (CH_2), 34.9 (CH_2), 38.6 (CH_2), 55.8 (CH_3), 55.9 (CH_3), 111.2 (CH), 111.8 (CH), 119.2 (C), 120.2 (CH), 134.6 (C), 147.2 (C), 177.3 (C); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.23 (CH_2), 28.41 (CH_2), 28.97 (CH_2), 35.09 (CH_2), 39.78 (CH_2), 55.92 (CH_3), 56.01 (CH_3), 83.24 (CH), 111.33 (CH), 111.89 (CH), 120.26 (CH), 134.86 (C), 147.22 (C), 148.86 (C), 174.83 (C). **1g** (0.7g, 2.3mmol) was reduced with $NaBH_4$ following the general procedure to give the crude hydroxyamide, used without further purification (~90% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 – 1.62 (4H, m), 1.82 – 1.90 (1H, m), 2.20 – 2.30 (2H, m), 2.45 – 2.60 (3H, m), 3.09 – 3.17 (1H, m), 3.43 – 3.52 (1H, m), 3.83 (3H, s), 3.85 (3H, s), 5.15 (1H, d, *J* = 4.8 Hz), 6.65 – 6.70 (2H, m), 6.76 (1H, d, *J* = 8.6 Hz). Cyclisation of the crude hydroxyamide by the general procedure, heating under reflux for 15 min., and purification by column chromatography on silica, eluting with Et_2O + 1% MeOH gave the title compound **2g** 0.49g (74% overall yield) as an oil. HRMS Theoretical Mass: 275.15160; Measured Mass: 275.15175. FT-IR (Neat) 2932, 1667, 1516, 1450, 1415, 1348, 1252, 1208, 1105, 769 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 – 1.46 (1H, brm), 1.55 – 1.67 (2H, brm), 1.90 – 2.00 (1H, brm), 2.30 – 2.51 (3H, m), 2.55 – 2.62 (1H, m), 2.83 – 2.91 (1H, m), 3.80 (6H, s), 4.68 (1H, t, *J* = 7.4 Hz), 6.54 (1H, s), 6.59 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.91 (CH_2), 27.65 (CH_2), 29.06 (CH_2), 30.95 (CH_2), 40.99 (CH_2), 55.54 (CH_3), 55.67 (CH_3), 62.14 (CH), 110.33 (CH), 113.87 (CH), 129.70 (C), 132.51 (C), 146.92 (C), 148.27 (C), 174.27 (C).

^{1}H NMR and ^{13}C NMR of **2g**



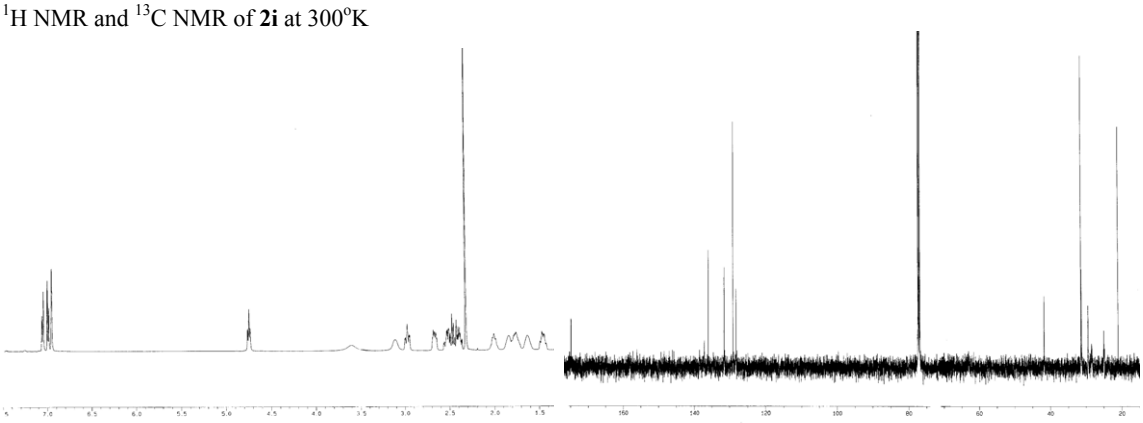
Attempted preparation of 14-Methoxy-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2h)

Following the general procedure, 4-(4-methoxyphenyl)butan-1-ol (A. Pelter, R.S. Ward and R.R. Rao, *Tetrahedron*; 1985; **41**; 2933) was converted to the N-substituted succinimide **1h**, eluting with 3:1 DCM:petrol, isolated as a white solid (85% yield), mpt 62-3°C (Et_2O/petrol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55 – 1.65 (4H, m), 2.54 (2H, t, *J* = 6.8Hz), 2.67 (4H, s), 3.51 (2H, t, *J* = 6.7 Hz), 3.77 (3H, s), 6.80 (2H, d, *J* = 8.6 Hz), 7.06 (2H, d, *J* = 8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.3 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 34.5 (CH_2), 38.7 (CH_2), 55.3 (CH_3), 113.8 (CH), 129.4 (CH), 134.1 (C), 157.9 (C), 177.3 (C).. **1h** was reduced with $NaBH_4$ following the general procedure to give the hydroxyamide, purified by column chromatography on SiO_2, eluting with 1:1 DCM/EtOAc (95% yield) mpt 56-8°C (Et_2O/petrol); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 – 1.61 (4H, m), 1.82 – 1.88 (1H, m), 2.17 – 2.36 (2H, m), 2.40 – 2.55 (3H, m), 3.07 – 3.15 (1H, m), 3.42 – 3.50 (1H, m), 3.74 (3H, s), 4.88 (1H, d, *J* = 8.2 Hz), 5.13 (1H, dt, *J* = 2.1, 8.0 Hz), 6.78 (2H, d, *J* = 8.6 Hz), 7.04 (2H, d, *J* = 8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.1 (CH_2), 28.2 (CH_2), 29.1 (CH_2), 39.7 (CH_2), 55.3 (CH_3), 83.1 (CH), 113.8 (CH), 129.3 (CH), 134.3 (C), 157.8 (C), 175.1 (C). Cyclisation as described under the general procedure gave insoluble, presumed polymeric material only.

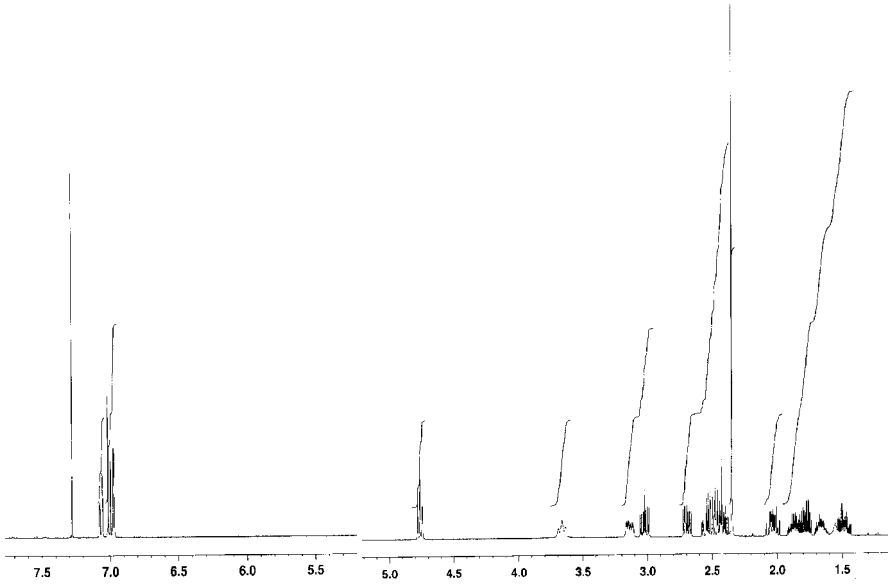
14-Methyl-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2i)

Following the general procedure, 4-(4-methylphenyl)butan-1-ol (V. Huisgen; *Monatsh. Chem.*; 1957; **88**; 517) was converted to the N-substituted succinimide **1i**, eluting with 3:1 DCM:petrol, isolated as a white solid (85% yield), mpt 76-8^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55 – 1.63 (4H, m), 2.31 (3H, s), 2.59 (2H, t, *J* = 6.9 Hz), 2.68 (4H, s), 3.52 (2H, t, *J* = 7.0 Hz), 7.05 (2H, d, *J* = 8.1 Hz), 7.08 (2H, d, *J* = 8.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.06 (CH_3), 27.34 (CH_2), 28.22 (CH_2), 28.80 (CH_2), 34.95 (CH_2), 38.72 (CH_2), 128.36 (CH), 129.09 (CH), 135.33 (C), 138.90 (C), 177.32 (C).. 1**i** (0.6g, 3.3 mmol) was reduced with $NaBH_4$ following the general procedure to give the hydroxyamide, purified by column chromatography on SiO_2, eluting with Et_2O + 4% MeOH, 0.34g (57% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.50 – 1.65 (4H, m), 1.83 – 1.92 (1H, m), 2.23-2.35 (5H, m including 2.31, 3H, s), 2.48 – 2.62 (3H, m), 3.10 – 3.18 (1H, m), 3.41 – 3.53 (2H, m), 5.13 – 5.18 (1H,dd, *J* = 4.6, 6.4 Hz), 7.04 (2H, d, *J* = 8.1 Hz), 7.07 (2H, d, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.06 (CH_3), 27.27 (CH_2), 27.27 (CH_2), 28.41 (CH_2), 28.88 (CH_2), 28.96 (CH_2), 35.08 (CH_2), 39.80 (CH_2), 83.25 (CH), 128.36 (CH), 129.09 (CH), 135.32 (C), 139.06 (C), 174.82 (C).
Cyclisation of the hydroxyamide (0.34g, 1.4mmol) by the general procedure, heating under reflux for 1h, and purification by column chromatography on silica, eluting with Et_2O + 2% MeOH gave the title compound 2**i** 0.25g, (80% yield), mpt = 52-4^{o}C (ether). HRMS theoretical mass 229.14612, measured mass 229.14545. ^{1}H NMR (500 MHz, $CDCl_3$): δ = ; ^{13}C NMR (125 MHz, $CDCl_3$): δ =

^{1}H NMR and ^{13}C NMR of **2i** at 300^{o}K



^{1}H NMR of **2i** at 333^{o}K



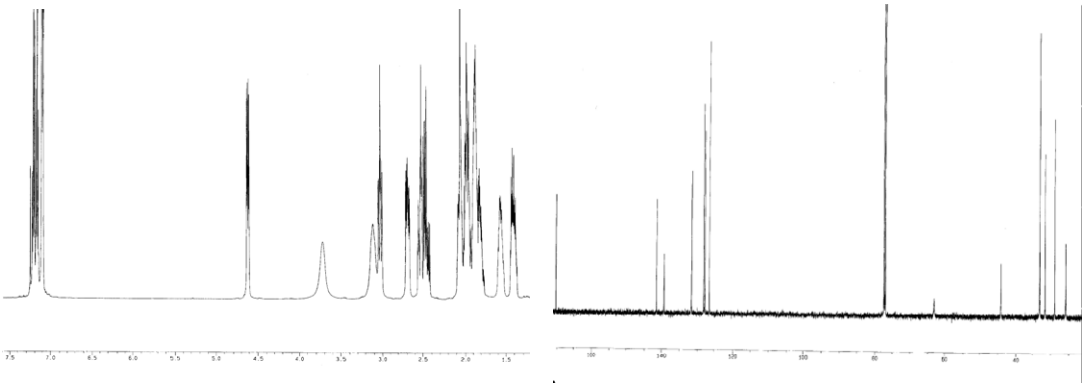
Attempted preparation of 14-Nitro-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (2j)

Following the general procedure, 4-(4-nitrophenyl)butan-1-ol was converted to the N-substituted succinimide **1j**, eluting with 3:1 DCM:petrol, isolated as a white solid (85% yield), mpt 73-5°C (ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.50 – 1.62 (4H, m), 2.51 (2H, t, *J* = 6.8 Hz), 2.67 (4H, s), 3.51 (2H, t, J = 6.8 Hz), 6.62 (2H, d, *J* = 8.5 Hz), 6.94 (2H, d, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.89 (CH_2), 27.82 (CH_2), 28.56 (CH_2), 34.12 (CH_2), 38.35 (CH_2), 115.02 (CH), 128.86 (CH), 131.83 (C), 143.71 (C), 176.96 (C). **1j** (0.37g, 1.3mmol) was reduced with $NaBH_4$ following the general procedure to give the hydroxyamide, purified by column chromatography on SiO_2, eluting with 1:1 DCM/EtOAc, 0.15g (40% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.50 – 1.69 (4H, m), 1.83 – 1.91 (1H, m), 2.20 – 2.30 (2H, m), 2.46 – 2.53 (1H, m), 2.64 – 2.76 (2H, m), 3.11 – 3.20 (1H, m), 3.40 – 3.50 (1H, m), 4.25 (1H, d, *J* = 8.2 Hz), 5.12 – 5.20 (1H, m), 7.29 (2H, d, *J* = 8.7 Hz), 8.08 (2H, d, *J* = 8.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.2 (CH_2), 28.3 (CH_2), 28.4 (CH_2), 29.0 (CH_2), 35.3 (CH_2), 39.6 (CH_2), 83.3 (CH), 123.7 (CH), 129.3 (CH), 146.4 (C), 150.2 (C), 175.2 (C).
Cyclisation of the hydroxyamide (0.15g, 0.5mmol) by the general procedure, heating under reflux for 3h showed only starting material. Prolonged heating for 18h showed no starting material but gave none of the desired product **2j.**

1,2,3,5,6,7,8,12b-Octahydro-4a-aza-dibenzo[a,c]cylcoocten-4-one (4)

Following the general procedure, 4-phenylbutan-1-ol (1.5g, 10mmol) was converted to 4-phenylbutyl-1-glutarimide **3**, purification on silica, eluting with 3:1 DCM:petrol, and isolated as a white solid, 2.1g (85% yield), mpt = 62-4°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 – 1.67 (4H, m), 1.90 (2H, quintet, *J* = 7 Hz), 2.62 (4H, t, *J* = 6.5 Hz), 3.77 (2H, t, *J* = 7.5 Hz), 7.12 – 7.20 (3H, m), 7.27 (2H, dd, *J* = 1.5, 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.3 (CH_2), 27.7 (CH_2), 28.9 (CH_2), 33.0 (CH_2), 35.6 (CH_2), 39.5 (CH_2), 125.8 (CH), 128.4 (CH), 128.5 (CH), 142.3 (C), 172.6 (C). 4-Phenylbutyl-1-glutarimide **3** (0.5g, 2 mmol) was reduced with $NaBH_4$ following the general procedure to give the hydroxyamide (0.5g, ~100% yield), used without further purification. NMR indicates ~1:1 axial: equatorial OH: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.50 – 2.16 (H, m), 2.25 – 2.35 (1.5H, m), 2.38 – 2.52 (1.5H, m), 2.63 (2H, t, *J* = 7.0 Hz), 3.13 – 3.21 (0.5 H, m), 3.46 (1H, t, *J* = 7.0 Hz), 3.65 – 3.72 (0.5H, m), 4.93 (0.5H, t, *J* = 3.5 Hz), 5.11 (0.5H, dt, *J* = 4.4, 7.7 Hz), 5.97 (0.5H, dt, *J* = 1.6, 6.1 Hz), ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.99 (CH_2), 27.84 (CH_2), 28.12 (CH_2), 31.08 (CH_2), 35.21 (CH_2), 45.53 (CH_2), 105.72 (CH), 125.85 (CH), 128.39 (CH), 129.52 (CH), 141.81 (C), 168.96 (C).
The hydroxyamide (0.5g) was cyclised by the general procedure, purification by chromatography on silica, eluting with Et_2O + 1% MeOH gave the title compound **4**, 0.3 g, (65% yield), mpt 77-9°C (Et_2O/petrol). FT-IR (neat) 1720, 1661, 1361, 1277, 1240, 1123, 1044, 753, 698 cm^{-1}. HRMS Theoretical Mass: 229.14612; Measured Mass: 229.14534; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 – 1.46 (1H, m), 1.50 – 1.63 (1H, m), 1.75 – 2.10 (6H, m), 2.40 – 2.57 (2H, m), 2.65 – 2.74 (1H, m), 2.99 – 3.20 (2H, brm including 3.03, 1H, ddd, *J* = 3.1, 10.2, 13.3 Hz), 3.63 - 3.80 (1H, brm), 4.62 (1H, dd, J = 4.4, 9.9 Hz), 7.05 – 7.26 (4H, m); ^{13}C NMR + DEPT (125 MHz, $CDCl_3$): δ = 20.56 (CH_2), 25.73 (CH_2), 28.90 (CH_2), 31.81 (CH_2), 33.13 (CH_2), 33.20 (CH_2), 44.10 (CH_2), 63.23 (CH_2), 126.54 (CH), 127.90 (CH), 128.25 (CH), 131.64 (CH), 139.46 (C), 141.43 (C), 170.39 (C).

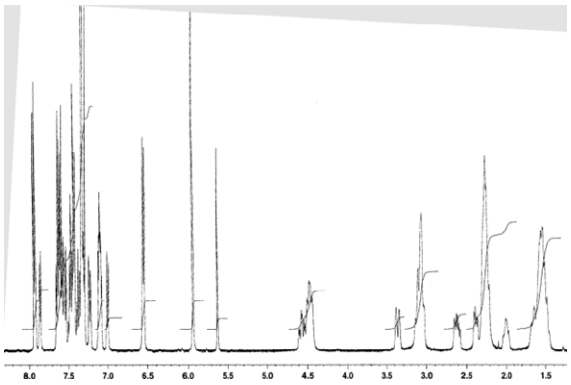
^{1}H-NMR and ^{13}C-NMR of **4**



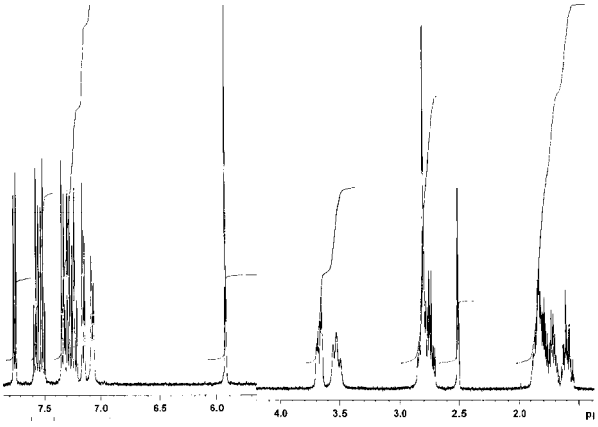
6-Aza-benzo[c]tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (6)

Preparative details in the paper.

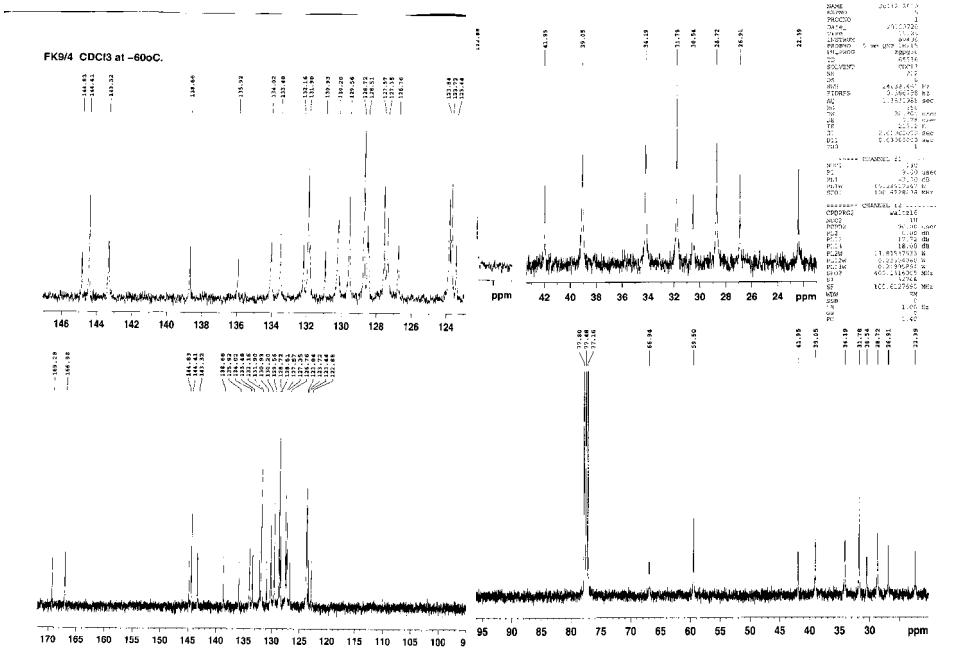
^{1}H-NMR of **6** at -60^{o}C in $CDCl_3$



^{1}H-NMR of **6** at 125^{o}C in d^{6}-DMSO



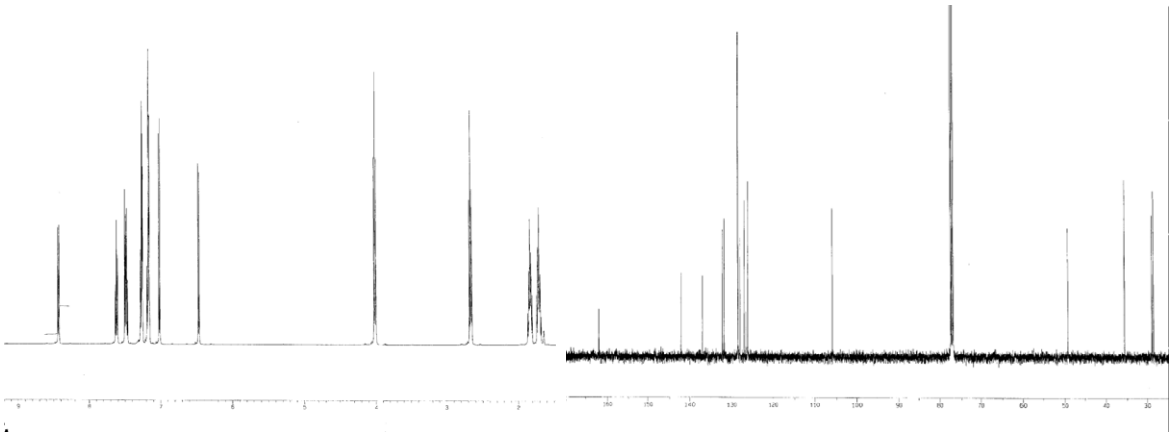
^{13}C-NMR of **6** at -60^{o}C in $CDCl_3$



2-(4-Phenyl-butyl)-2H-isoquinolin-1-one (8b)

Preparative details in the paper

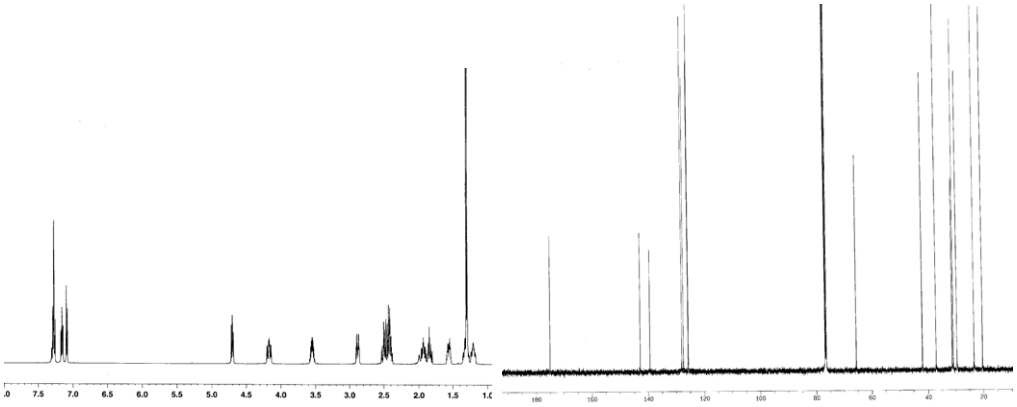
^{1}H NMR and ^{13}C NMR of **8b**



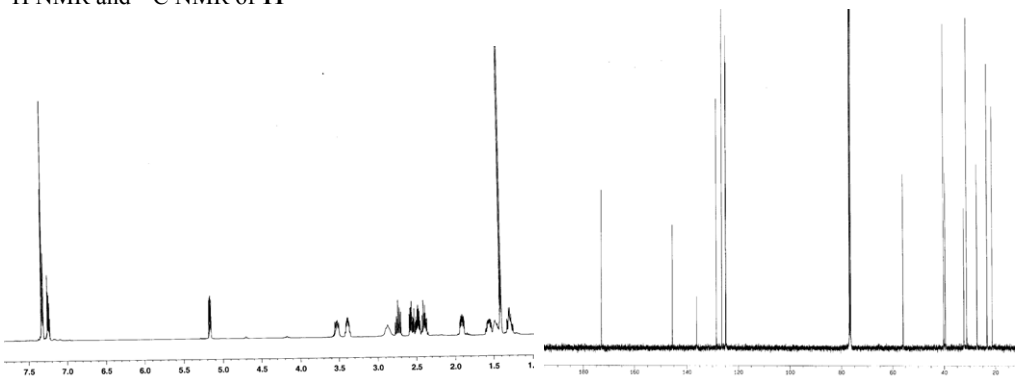
(2R,10S; 2S,10R)-10-Methyl-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (10) and (2R,10R; 2S,10S)-10-Methyl-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (11)

Following the general procedure, 4-phenylpentanol (W.E. Truce, D.N. Burdge and R.J. Steltenkamp, J. Org. Chem., 1962, 27, 3913) was converted to the succinimide **9**, isolated as an oil (87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (3H, d, *J* = 7.0 Hz), 1.35 – 1.45 (1H, m), 1.46 – 1.60 (3H, m), 2.62 (4H, s), 2.68 (1H, hextet, *J* = 7.0 Hz), 3.44 (2H, t, *J* = 7.2 Hz), 7.11 – 7.20 (3H, m), 7.23 – 7.30 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.30 (CH_3), 25.98 (CH_2), 28.31 (CH_2), 35.41 (CH_2), 38.85 (CH_2), 39.63 (CH), 126.10 (CH), 127.13 (CH), 128.68 (CH), 147.01 (C), 177.32 (C). . The succinimide **9** was reduced with NaBH4 and cyclised with triflic acid by the general procedures to give a mixture of **10** and **11**, separated by chromatography on silica, eluting with Et_2O to give initially **10** (76% yield) mpt = 74-6^{o}C (EtOAc/petrol). FT-IR (neat) 1681, 1486, 1445, 1411, 1374, 1271, 1252, 1153, 1139, 926, 878, 830, 761, 706 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17-1.22 (1H, m), 1.23-1.27 (4H, m, including 1.30, 3h, d, *J* = 6.6 Hz), 1.79 – 1.88 (1H, m), 1.89 – 1.98 (1H, m), 2.37 – 2.54 (2H , m), 2.88 (1H, dt, *J* = 4.2, 13.9 Hz), 3.55 (1H, tt, *J* = 6.8, 12.5 Hz), 4.17 (1H, ddd, *J* = 5.0, 12.0, 13.9 Hz), 4.70 (1H, t, *J* = 7.0 Hz), 7.09 (1H, d, *J* = 7.3 Hz), 7.16 (1H, dt, *J* = 2.1, 7.6 Hz), 7.25-7.32 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.68 (CH_3), 23.75 (CH_2), 29.89 (CH_2), 31.24 (CH_2), 31.67 (CH), 37.59 (CH_2), 42.31 (CH_2), 66.01 (CH), 126.05 (CH), 126.14 (CH), 127.83 (CH), 128.41 (CH), 139.39 (C), 142.86 (C), 175.01 (C). Further elution with Et2O gave the **11** (14% yield) as an oil, which crystallised from Et_2O/petrol, m.pt. 102-4^{o}C; FT-IR (neat) 1669, 1451, 1435, 1423, 1247, 755, 744, 662 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 – 1.34 (1H, m), 1.40 (3H, d, *J* = 6.8 Hz), 1.45 – 1.60 (2H, m), 1.87 – 1.95 (1H, m), 2.35 – 2.60 (3H, m), 2.74 (1H, quintet, *J* = 8.7 Hz), 2.81-2.90 (m, 1H), 3.34 – 3.43 (1H, m), 3.53 (1H, dd, *J* = 8.6, 14.0 Hz), 5.17 (1H, dd, *J* = 4.7, 8.0 Hz), 7.21 – 7.26 (1H, m), 7.30 – 7.34 (3H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.65 (CH_3), 23.66 (CH_2), 27.60 (CH_2), 31.64 (CH_2), 32.78 (CH), 40.00 (CH_2), 40.60 (CH_2), 56.331 (CH), 125.08 (CH), 125.28 (CH), 126.71 (CH), 128.92 (CH), 136.16 (C), 145.53 (C), 172.96 (C).

^{1}H NMR and ^{13}C NMR of **10**



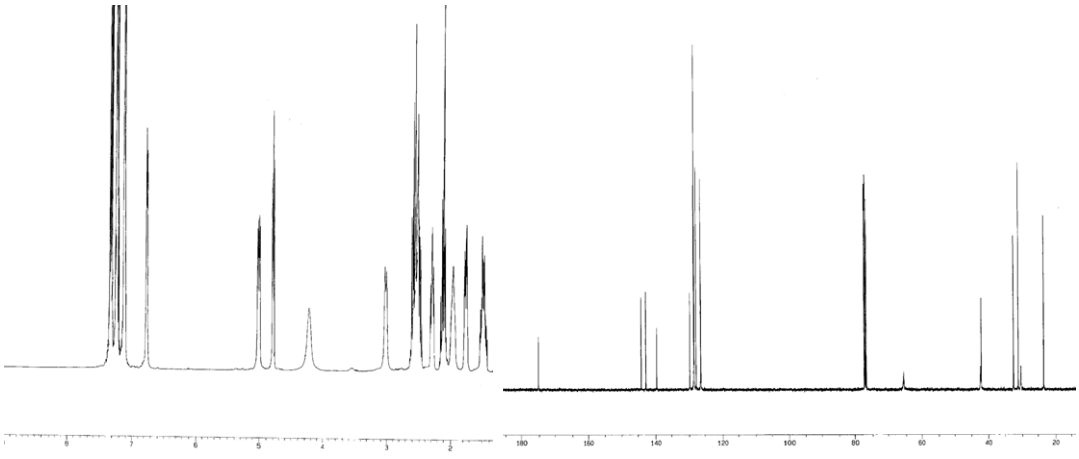
^{1}H NMR and ^{13}C NMR of **11**



(2R,10R; 2S,10S)-10-Phenyl-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (13)

Preparative details in the paper

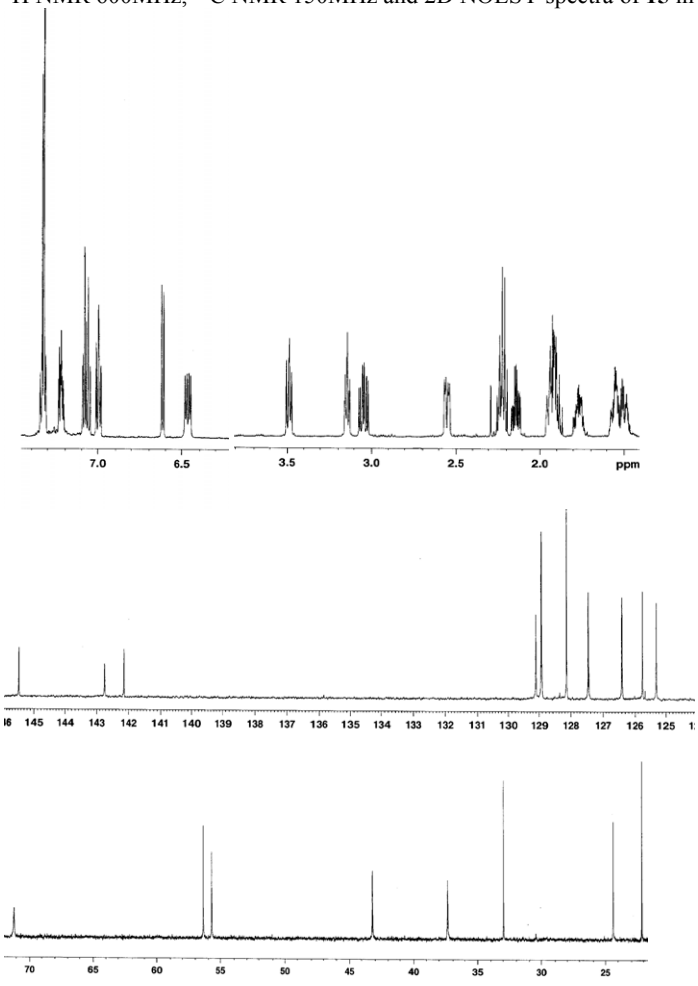
^{1}H NMR 500MHz and 13C NMR 125MHz of **13** in $CDCl_3$ at 300K

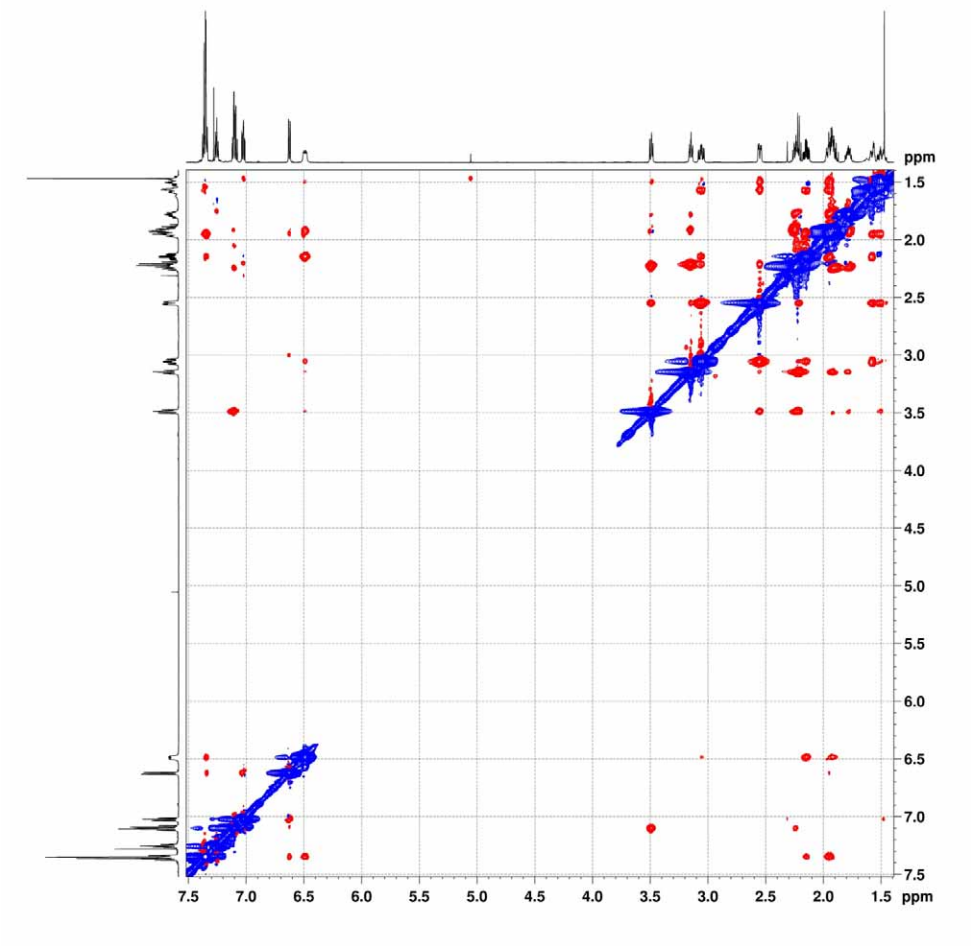


(2R,10R; 2S,10S)-10-Phenyl-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trienene (15)

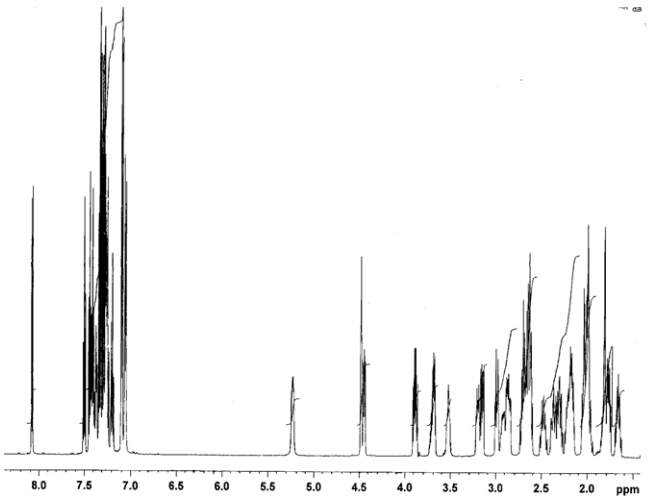
Preparative details in the paper

^{1}H NMR 600MHz, ^{13}C NMR 150MHz and 2D NOESY spectra of **15** in $CDCl_3$ at 327K





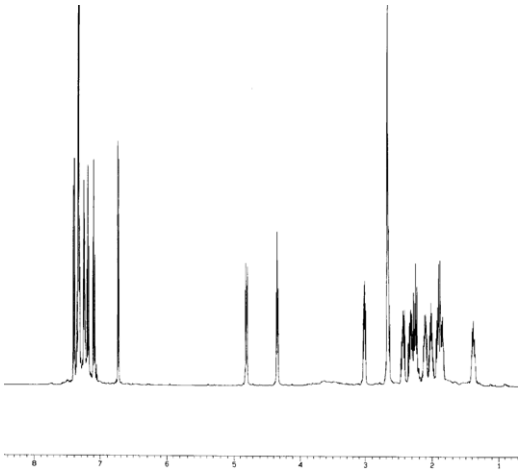
^{1}H NMR 600MHz of **15.HCl** in $CDCl_3$ at 333K

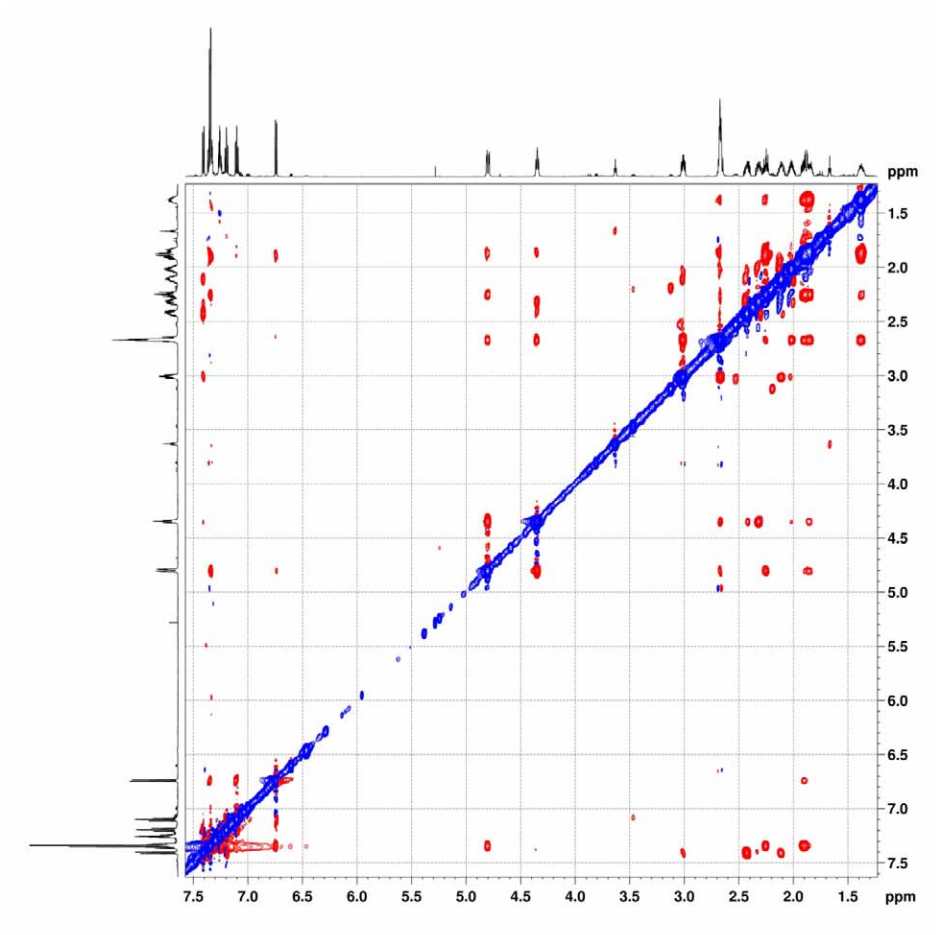


(2R,10S; 2S,10R)-10-Phenyl-6-aza-tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trienene (16)

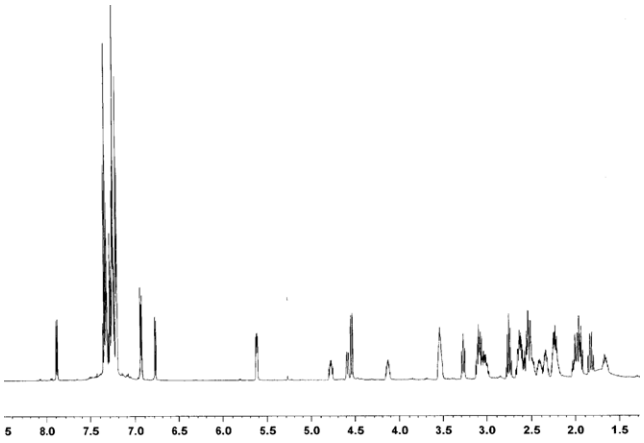
Preparative details in the paper

^{1}H NMR 500MHz and 2D NOESY of **16** in $CDCl_3$ at 300K:





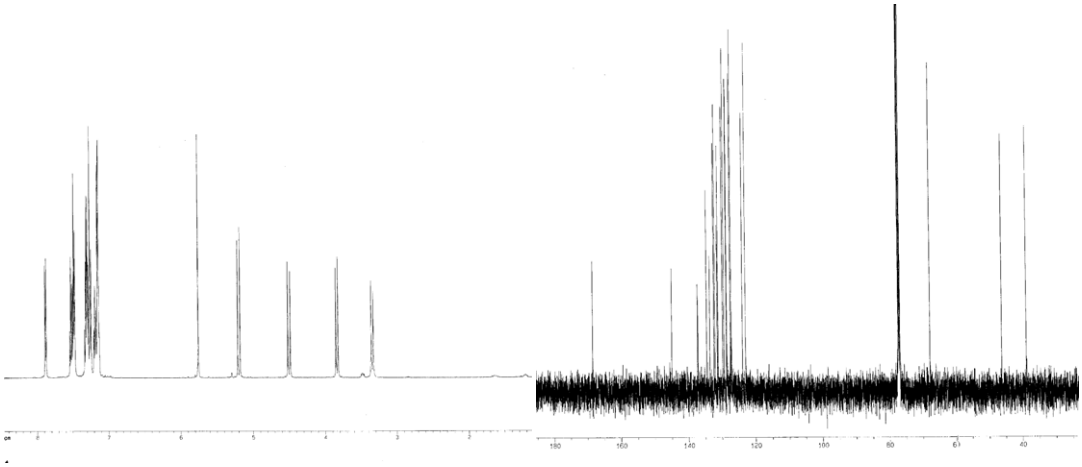
^{1}H NMR 500MHz of **16.HCl** in $CDCl_3$ at 333K



6-Aza-dibenzo[c,f]tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (20)

Preparative details in the paper

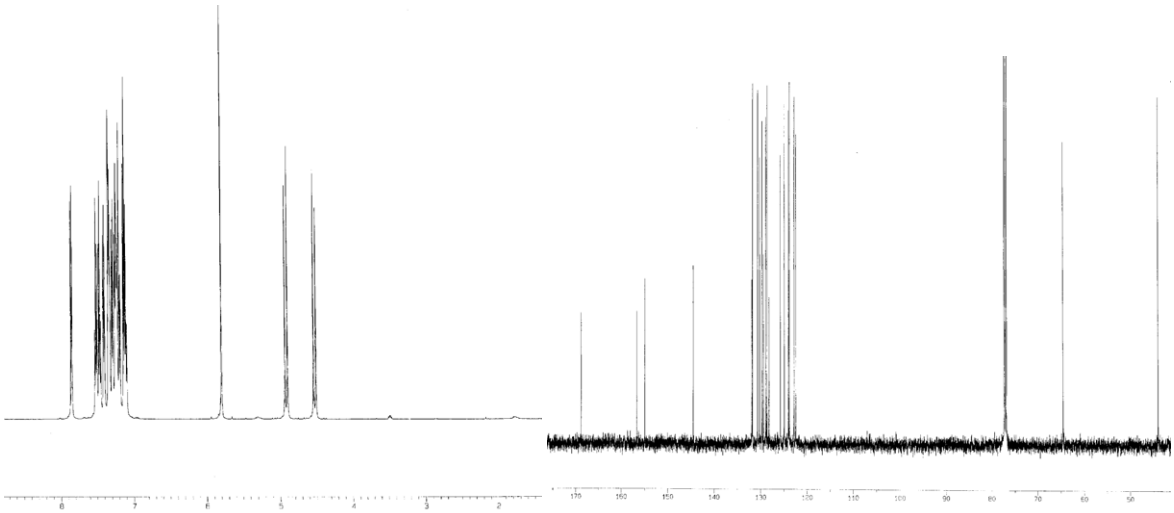
^{1}H NMR and ^{13}C NMR of **20**



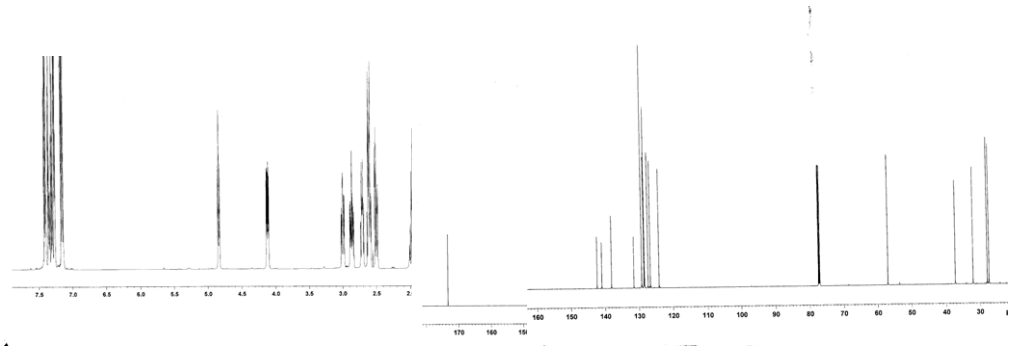
6-Aza-10-oxa-dibenzo[c,f]tricyclo[9.4.0.0*2,6*]pentadeca-1(11),12,14-trien-5-one (21)

Preparative details in the paper.

^{1}H NMR and ^{13}C NMR of **21**



4-Phenyl-5,12b-dihydro-6H-isoindolo[1,2-a]isoquinolin-8-one (25)



Crystal data and structure refinement for 2f: CCDC 787503

Chemical formula $C_{14}H_{15}Br_2NO$; Formula weight 373.09, Temperature 150(2) K, Radiation, wavelength MoKα, 0.71073 Å Crystal system, space group triclinic, P $\bar{1}$, Unit cell parameters a = 5.6309(10) Åα = 88.759(3)°, b = 8.4895(16) Å β = 84.820(3)° c = 14.660(3) Å, γ = 73.866(3)°, Cell volume 670.4(2) $Å^3$, Z 2, Calculated density 1.848 g/cm^3, Absorption coefficient μ 6.033 mm^{-1}, F(000) 368, Crystal colour and size colourless, 0.48 × 0.22 × 0.05 mm^3, Data collection method Bruker SMART APEX diffractometer, ω rotation with narrow frames, θ range for data collection 2.50 to 28.35°, Index rangesh −7 to 7, k −11 to 11, l −19 to 19, Completeness to θ = 26.00° 95.7 %, Reflections collected 5409, Independent reflections 2933 (R_{int} = 0.0369), Reflections with $F^2>2\sigma$ 2476, Absorption correction semi-empirical from equivalents, Min. and max. transmission 0.1598 and 0.7524, Structure solution direct methods, Refinement method Full-matrix least-squares on F^2, Weighting parameters a, b 0.1028, 0.0000, Data/restraints/ parameters 2933 / 0 / 164, Final R indices [$F^2>2\sigma$] R1 = 0.0384, wR2 = 0.1051, R indices (all data) R1 = 0.0436, wR2 = 0.1097, Goodness-of-fit on F^2 0.755, Extinction coefficient 0.036(3), Largest and mean shift/su 0.001 and 0.000, Largest diff. peak and hole 0.978 and −0.896 e $Å^{-3}$.

Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **2f**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Br(1)	1.47882(5)	0.47715(3)	0.676867(19)	0.02340(15)
Br(2)	0.90536(6)	0.82017(4)	0.40581(2)	0.03526(16)
C(1)	0.7205(5)	0.6713(4)	0.9374(2)	0.0234(6)
C(2)	0.7711(6)	0.4978(3)	0.9031(2)	0.0255(6)
C(3)	1.0109(6)	0.4685(3)	0.8395(2)	0.0237(6)
C(4)	1.0376(5)	0.6425(3)	0.81609(19)	0.0178(5)
C(5)	0.9875(5)	0.6940(3)	0.71784(18)	0.0158(5)
C(6)	1.1737(5)	0.6278(3)	0.6480(2)	0.0186(6)
C(7)	1.1561(5)	0.6617(3)	0.5566(2)	0.0241(6)
C(8)	0.9370(6)	0.7676(4)	0.5320(2)	0.0241(6)
C(9)	0.7445(5)	0.8344(4)	0.5963(2)	0.0231(6)
C(10)	0.7643(5)	0.7989(3)	0.6895(2)	0.0184(6)
C(11)	0.5422(5)	0.8828(4)	0.7543(2)	0.0238(6)
C(12)	0.5649(6)	1.0428(4)	0.7955(2)	0.0332(8)
C(13)	0.8134(7)	1.0316(4)	0.8305(2)	0.0322(7)
C(14)	0.8826(6)	0.9104(3)	0.9086(2)	0.0270(7)
O(1)	0.5629(4)	0.7378(3)	0.99854(16)	0.0342(5)
N(1)	0.8748(4)	0.7442(3)	0.88855(16)	0.0196(5)

Table 3. Bond lengths [Å] and angles [°] for **2f**.

Bond lengths			
Br(1)–C(6)	1.911(3)	Br(2)–C(8)	1.906(3)
C(1)–O(1)	1.229(4)	C(1)–N(1)	1.348(4)
C(1)–C(2)	1.509(4)	C(2)–C(3)	1.533(4)
C(3)–C(4)	1.555(4)	C(4)–N(1)	1.462(3)
C(4)–C(5)	1.524(4)	C(5)–C(6)	1.402(4)
C(5)–C(10)	1.415(4)	C(6)–C(7)	1.372(4)
C(7)–C(8)	1.382(4)	C(8)–C(9)	1.372(4)
C(9)–C(10)	1.400(4)	C(10)–C(11)	1.514(4)
C(11)–C(12)	1.540(4)	C(12)–C(13)	1.511(5)
C(13)–C(14)	1.526(5)	C(14)–N(1)	1.461(4)
Angles			
O(1)–C(1)–N(1)	124.9(3)	O(1)–C(1)–C(2)	126.3(3)
N(1)–C(1)–C(2)	108.7(2)	C(1)–C(2)–C(3)	104.9(2)
C(2)–C(3)–C(4)	105.0(2)	N(1)–C(4)–C(5)	116.6(2)
N(1)–C(4)–C(3)	102.8(2)	C(5)–C(4)–C(3)	113.3(2)
C(6)–C(5)–C(10)	116.2(3)	C(6)–C(5)–C(4)	118.0(2)
C(10)–C(5)–C(4)	125.8(2)	C(7)–C(6)–C(5)	124.8(2)
C(7)–C(6)–Br(1)	114.9(2)	C(5)–C(6)–Br(1)	120.3(2)
C(6)–C(7)–C(8)	117.1(3)	C(7)–C(8)–C(9)	121.3(3)
C(7)–C(8)–Br(2)	118.6(2)	C(9)–C(8)–Br(2)	120.0(2)
C(8)–C(9)–C(10)	121.1(3)	C(9)–C(10)–C(5)	119.4(3)
C(9)–C(10)–C(11)	116.3(2)	C(5)–C(10)–C(11)	124.2(3)
C(10)–C(11)–C(12)	113.1(3)	C(13)–C(12)–C(11)	114.9(2)
C(12)–C(13)–C(14)	114.8(3)	N(1)–C(14)–C(13)	114.2(2)
C(1)–N(1)–C(4)	114.9(2)	C(1)–N(1)–C(14)	122.3(2)
C(4)–N(1)–C(14)	122.8(2)		

Anisotropic displacement parameters ($Å^2$) for **2f**.
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	0.01817(19)	0.0290(2)	0.0171(2)	–0.00120(12)	–0.00017(12)	0.00304(12)
Br(2)	0.0373(2)	0.0434(2)	0.0139(2)	0.00384(14)	–0.00248(15)	0.00705(15)
C(1)	0.0244(14)	0.0314(15)	0.0139(15)	0.0022(11)	0.0002(11)	–0.0077(11)
C(2)	0.0336(15)	0.0255(14)	0.0189(16)	0.0047(12)	0.0001(13)	–0.0118(12)
C(3)	0.0293(15)	0.0215(13)	0.0172(15)	0.0003(11)	0.0000(12)	–0.0026(11)
C(4)	0.0173(12)	0.0222(13)	0.0114(13)	–0.0027(10)	0.0021(10)	–0.0023(10)
C(5)	0.0144(11)	0.0202(12)	0.0123(14)	–0.0013(10)	0.0004(10)	–0.0043(9)
C(6)	0.0138(11)	0.0205(13)	0.0175(15)	–0.0017(10)	0.0005(10)	0.0012(9)
C(7)	0.0227(14)	0.0290(15)	0.0152(15)	–0.0018(11)	0.0035(11)	0.0001(11)
C(8)	0.0285(15)	0.0259(14)	0.0143(15)	–0.0002(11)	–0.0008(12)	–0.0016(11)
C(9)	0.0211(13)	0.0247(14)	0.0211(16)	0.0027(11)	–0.0022(12)	–0.0024(10)
C(10)	0.0176(12)	0.0196(12)	0.0158(15)	–0.0004(10)	0.0039(11)	–0.0034(10)
C(11)	0.0154(12)	0.0298(15)	0.0197(16)	0.0034(12)	0.0037(11)	0.0023(10)
C(12)	0.0380(17)	0.0250(15)	0.0268(18)	–0.0022(13)	0.0080(14)	0.0041(13)
C(13)	0.0448(18)	0.0232(14)	0.0277(18)	–0.0092(12)	0.0160(15)	–0.0132(13)
C(14)	0.0319(15)	0.0283(15)	0.0218(17)	–0.0101(12)	0.0046(13)	–0.0114(12)
O(1)	0.0349(12)	0.0412(13)	0.0235(13)	–0.0045(10)	0.0149(10)	–0.0106(10)
N(1)	0.0231(11)	0.0236(11)	0.0117(12)	–0.0042(9)	0.0030(9)	–0.0070(9)

Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **2f**.

	x	y	z	U
H(2A)	0.6328	0.4856	0.8692	0.031
H(2B)	0.7933	0.4193	0.9547	0.031
H(3A)	0.9986	0.4097	0.7832	0.028
H(3B)	1.1548	0.4031	0.8707	0.028
H(4A)	1.2121	0.6420	0.8246	0.021
H(7A)	1.2887	0.6143	0.5120	0.029
H(9A)	0.5954	0.9058	0.5773	0.028
H(11A)	0.5225	0.8066	0.8047	0.029
H(11B)	0.3910	0.9077	0.7209	0.029
H(12A)	0.5327	1.1293	0.7482	0.040
H(12B)	0.4344	1.0774	0.8467	0.040
H(13A)	0.8127	1.1418	0.8516	0.039
H(13B)	0.9436	0.9998	0.7789	0.039
H(14A)	1.0522	0.9062	0.9236	0.032
H(14B)	0.7677	0.9515	0.9634	0.032

Torsion angles [°] for **2f**.

O(1)–C(1)–C(2)–C(3)	−170.6(3)	N(1)–C(1)–C(2)–C(3)	10.5(3)
C(1)–C(2)–C(3)–C(4)	−17.9(3)	C(2)–C(3)–C(4)–N(1)	18.6(3)
C(2)–C(3)–C(4)–C(5)	−108.1(3)	N(1)–C(4)–C(5)–C(6)	163.8(2)
C(3)–C(4)–C(5)–C(6)	−77.1(3)	N(1)–C(4)–C(5)–C(10)	−18.7(4)
C(3)–C(4)–C(5)–C(10)	100.3(3)	C(10)–C(5)–C(6)–C(7)	2.1(4)
C(4)–C(5)–C(6)–C(7)	179.8(3)	C(10)–C(5)–C(6)–Br(1)	−177.41(19)
C(4)–C(5)–C(6)–Br(1)	0.3(3)	C(5)–C(6)–C(7)–C(8)	−0.7(4)
Br(1)–C(6)–C(7)–C(8)	178.8(2)	C(6)–C(7)–C(8)–C(9)	−0.8(5)
C(6)–C(7)–C(8)–Br(2)	179.3(2)	C(7)–C(8)–C(9)–C(10)	0.8(5)
Br(2)–C(8)–C(9)–C(10)	−179.3(2)	C(8)–C(9)–C(10)–C(5)	0.7(5)
C(8)–C(9)–C(10)–C(11)	178.6(3)	C(6)–C(5)–C(10)–C(9)	−2.0(4)
C(4)–C(5)–C(10)–C(9)	−179.5(3)	C(6)–C(5)–C(10)–C(11)	−179.8(3)
C(4)–C(5)–C(10)–C(11)	2.8(4)	C(9)–C(10)–C(11)–C(12)	−94.7(3)
C(5)–C(10)–C(11)–C(12)	83.1(3)	C(10)–C(11)–C(12)–C(13)	−45.8(4)
C(11)–C(12)–C(13)–C(14)	−62.0(4)	C(12)–C(13)–C(14)–N(1)	54.5(4)
O(1)–C(1)–N(1)–C(4)	−176.9(3)	C(2)–C(1)–N(1)–C(4)	2.0(3)
O(1)–C(1)–N(1)–C(14)	4.8(4)	C(2)–C(1)–N(1)–C(14)	−176.3(2)
C(5)–C(4)–N(1)–C(1)	111.3(3)	C(3)–C(4)–N(1)–C(1)	−13.3(3)
C(5)–C(4)–N(1)–C(14)	−70.4(3)	C(3)–C(4)–N(1)–C(14)	165.0(2)
C(13)–C(14)–N(1)–C(1)	−118.3(3)	C(13)–C(14)–N(1)–C(4)	63.5(4)