

Sequential One-Pot Bimetallic Ir(III) / Pd(0) Catalysed Mono- / Bis-Alkylation and Spirocyclisation Processes of 1,3-Dimethylbarbituric Acid and Allenes

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Electronic Supplementary Information

General experimental procedures

Nuclear magnetic resonance spectra were recorded on Bruker Avance instruments operating at 300 and 500 MHz, ¹³C NMR spectra were recorded at 75.5 and 125 MHz respectively. Chemical shifts (δ) are given in parts per million (ppm) downfield relative to tetramethylsilane (TMS). Coupling constants are given in hertz (Hz). Unless otherwise stated deuteriochloroform (CDCl₃) was used as solvent. In assignment of the ¹H NMR spectra, multiplicities and abbreviations used are as follows; Ar = aromatic, Ph = phenyl, Py = pyridyl, Pyr = pyrazinyl, d = doublet, dd = doublet of doublets, dq = doublet of quartets, dt = doublet of triplets, m = multiplet, q = quartet, s = singlet, t = triplet, td = triplet of doublets and tt = triplet of triplets.

Mass spectra were recorded using a Micromass ZMD 2000 electrospray (ES) spectrometer and on a GCT Premier mass spectrometer employing electron impact ionisation (EI) or field ionization (FI).

Melting points were determined on a Griffin hot-stage apparatus and are uncorrected. Infrared spectroscopy was recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer either as a thin film on sodium chloride plates or as a solid using the golden gate solid phase attachment. Thin films were prepared by the evaporation of a solution of the compound in chloroform. Flash column chromatography was performed using FluoroChem 60 (40-60 μm mesh) silica gel and t.l.c on Merck 60 Å F₂₅₄ pre-coated glass-backed plates and visualized by UV (254 nm). Microanalyses were obtained using a Carlo Erba 1108 Elemental Analyser. Unless otherwise noted all reagents were obtained from commercial suppliers and used without further purification. Petrol refers to the fraction of petroleum ether with b.p. 40-60 °C.

General procedure for the [IrCp*Cl₂]₂ catalysed alkylation cascade of 1,3-*N,N'*-dimethylbarbituric acid by alcohols under microwave irradiation (A)

A mixture of 1,3-dimethylbarbituric acid (1.00 mmol), [IrCp*Cl₂]₂ (2.5 mol% based on 1,3-dimethylbarbituric acid), potassium hydroxide (15 mol%) and alcohol (1.50 mmol) in a microwave tube was flushed with nitrogen and sealed. The mixture was melted and thereafter magnetically stirred under microwave irradiation (300 W, sealed reaction vessel) for 10 min (hold time) at 110 °C. The crude product was analysed by ¹HNMR and thereafter purified by column chromatography.

General procedure for the sequential one-pot Ir(III)/Pd(0) catalysed *inter-intra*-molecular cascade (B)

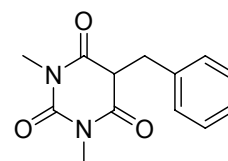
A mixture of 1,3-dimethylbarbituric acid (1.00 or 0.50 mmol), [IrCp*Cl₂]₂ (2.5 mol% based on 1,3-dimethylbarbituric acid), potassium hydroxide (15 mol%) and 2-iodobenzyl alcohol (1.20 or 0.60 mmol) in a microwave tube was flushed with nitrogen and sealed. The mixture was magnetically stirred under microwave irradiation (300 W, sealed reaction vessel) for 10 min (hold time) at 110 °C. Thereafter, sequential addition of Pd₂dba₃ (5 mol%), TFP (20 mol%), K₂CO₃ (2.00 mol equiv.), allene substrate (1.20 mol equiv.) and CH₃CN (2.0 or 1.0 mL) followed by stirring under microwave irradiation (300 W, sealed reaction vessel) for a further 20 min (hold time) at 110 °C. The mixture was diluted (CH₃CN), filtered and the filtrate evaporated to dryness. The residue was analysed by ¹HNMR and thereafter purified by column chromatography.

General procedure for the sequential one-pot Ir(III)/Pd(0) catalysed *inter-inter*-molecular cascade (C)

A mixture of 1,3-dimethylbarbituric acid (1.00 mmol), [IrCp*Cl₂]₂ (2.5 mol% based on 1,3-dimethylbarbituric acid), potassium hydroxide (15 mol%) and alcohol (1.50 mmol) in a microwave tube was flushed with nitrogen and sealed. The mixture was magnetically stirred under microwave irradiation (300 W, sealed reaction vessel) for 10 min (hold time) at 110 °C. Thereafter, sequential addition of Pd₂dba₃ (5 mol%), TFP (20 mol%), K₂CO₃ (2.00 mmol), aryl iodide (1.50 mmol) and CH₃CN (2.0 mL). The microwave tube was resealed, subjected to three freeze/pump/thaw cycles followed by an addition of allene gas (~0.5 bar). The mixture was magnetically stirred under microwave irradiation (300 W, sealed reaction vessel) for a further 20 min (hold time) at 110 °C and thereafter cooled, vented, diluted with CH₃CN, filtered and the filtrate evaporated to dryness. The residue was analysed by ¹HNMR and thereafter purified by column chromatography.

5-Benzyl-1,3-dimethylbarbituric acid (**3a**)

Prepared by the general procedure **A** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and benzyl alcohol (0.162 g, 1.50 mmol). Work up followed by column chromatography

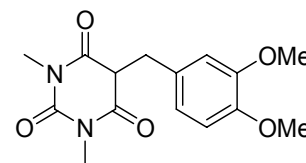


eluting with 1:1 v/v ether-petroleum ether gave **3a** (0.206 g, 84%) as colourless

needles; mp 116-117 °C (lit.¹ 116.5-117.5 °C); δ_H (300 MHz, CDCl₃); 7.27-7.20 (m, 3H, Ph-H), 7.06-6.99 (m, 2H, Ph-H), 3.78 (t, 1H, J 4.9 Hz, CHCH₂), 3.46 (d, 2H, CHCH₂), 3.12 (s, 6H, 2 × NCH₃); δ_C (75.5 MHz, CDCl₃); 168.7 (2 × C=O), 151.4 (C=O), 135.5 (C), 129.3 (2 × CH), 129.0 (2 × CH), 128.2 (CH), 51.1 (CH), 38.3 (CH₂), 28.6 (2 × CH₃); *m/z* (ES) 245 (M-H, 100), H.R.M.S [M-H] C₁₃H₁₃N₂O₃ Calculated 245.0932, found 245.0920.

5-(3,4-Dimethoxybenzyl)-1,3-dimethylbarbituric acid (**3b**)

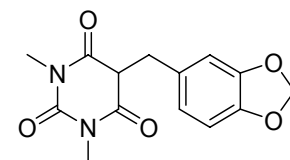
Prepared by the general procedure **A** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,4-dimethoxybenzyl alcohol (0.252 g, 1.50 mmol). Work up followed by column chromatography eluting with 4:1 v/v ether-hexane gave **3b** (0.241 g,



79%) as colourless plates; mp 110-112 °C (lit.¹ 111-112 °C); δ_H (300 MHz, CDCl₃); 6.72 (d, 1H, J 8.3 Hz, 3,4-diMeO-Ph-H₅), 6.58 (d, 1H, J 8.3 Hz, 3,4-diMeO-Ph-H₆), 6.55 (s, 1H, 3,4-diMeO-Ph-H₂), 3.84 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃), 3.75 (t, 1H, J 4.6 Hz, CHCH₂), 3.43 (d, 2H, J 4.6 Hz, CHCH₂), 3.15 (s, 6H, 2 × NCH₃); δ_C (75.5 MHz, CDCl₃); 168.8 (2 × C=O), 151.4 (C=O), 149.2 (C), 148.9 (C), 127.9 (C), 121.5 (CH), 112.2 (CH), 111.4 (CH), 56.2 (2 × CH₃), 51.2 (CH), 37.8 (CH₂), 28.7 (2 × CH₃); *m/z* (FI) 306 (M⁺, 100), H.R.M.S [M⁺] C₁₅H₁₈N₂O₅ Calculated 306.1216, found 306.1204.

5-(Methylene-3,4-di-oxy-phenyl)-1,3-dimethylbarbituric acid (**3c**)

Prepared by the general procedure **A** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,4-dioxymethylenebenzyl alcohol (0.228 g, 1.50 mmol). Work up followed by column chromatography eluting with 1:1 v/v ether-petroleum ether gave **3c**

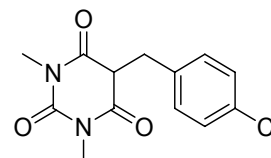


(0.240 g, 83%) as colourless prisms; mp 99-100 °C (lit.¹ 97-98 °C); δ_H (300 MHz, CDCl₃); 6.67 (d, 1H, J 7.9 Hz, Ph-H₅), 6.53 (d, 1H, J 1.1 Hz, Ph-H₂), 6.51 (dd, 1H, J 7.9 and 1.1 Hz, Ph-H₆), 5.92 (s, 2H, OCH₂O), 3.72 (t, 1H, J 4.6 Hz, CHCH₂), 3.39 (d, 2H, J 4.6 Hz, CHCH₂), 3.17 (s, 6H, 2 × NCH₃); δ_C (75.5

MHz, CDCl₃); 168.6 (2 × C=O), 151.5 (C=O), 148.2 (C), 147.5 (C), 129.2 (C), 122.6 (CH), 109.6 (CH), 108.7 (CH), 101.5 (CH₂), 51.2 (CH), 37.7 (CH₂), 28.6 (2 × CH₃); *m/z* (ES) 289 (M-H, 100), H.R.M.S [M-H] C₁₄H₁₃N₂O₅ Calculated 289.0830, found 289.0824.

5-(4-Chlorobenzyl)-1,3-dimethylbarbituric acid (3d)

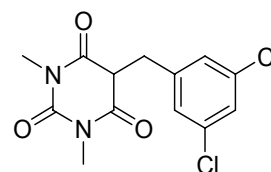
Prepared by the general procedure A from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 4-chlorobenzyl alcohol (0.214 g, 1.50 mmol). Work up followed by column chromatography eluting with 2:1 v/v ether-petroleum ether gave **3d** (0.230 g,



82%) as colourless solid; mp 75-77 °C; δ_H (300 MHz, CDCl₃); 7.21 (dt, 2H, J 8.3 and 2.0 Hz, 4-Cl-Ph-H_{3,5}), 7.02 (dt, 2H, J 8.3 and 2.0 Hz, 4-Cl-Ph-H_{2,6}), 3.76 (t, 1H, J 4.8 Hz, CHCH₂), 3.45 (d, 2H, J 4.8 Hz, CHCH₂Ph), 3.17 (s, 6H, 2 × NCH₃); δ_C (75.5 MHz, CDCl₃); 168.3 (2 × C=O), 151.3 (C=O), 134.4 (C), 134.0 (C), 130.9 (2 × CH), 129.2 (2 × CH), 50.8 (CH), 36.5 (CH₂), 28.8 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2945, 1747, 1671, 1489, 1443, 1379, 1292, 1278, 1111, 1092, 1015; *m/z* (ES) 279 (M-H (³⁵Cl), 100), 281 (M-H (³⁷Cl), 28); H.R.M.S [M-H] (³⁵Cl) C₁₃H₁₂ClN₂O₃ Calculated 279.0542, found 279.0529.

5-(3,5-Dichlorobenzyl)-1,3-dimethylbarbituric acid (3e)

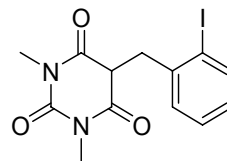
Prepared by the general procedure A from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,5-dichlorobenzyl alcohol (0.266 g, 1.50 mmol) in toluene (0.5 mL). Work up followed by column chromatography eluting with 1:1 v/v ether-petroleum ether



gave **3e** (0.239 g, 76%) as colourless solid; mp 101-102 °C; δ_H (300 MHz, CDCl₃); 7.24 (t, 2H, J 1.8 Hz, 3,5-diCl-Ph-H_{2,6}), 7.02 (d, 1H, J 1.8 Hz, 3,5-diCl-Ph-H₄), 3.77 (t, 1H, J 4.8 Hz, CHCH₂), 3.42 (d, 2H, J 4.8 Hz, CHCH₂), 3.21 (s, 6H, 2 × NCH₃); δ_C (75.5 MHz, CDCl₃); 167.9 (2 × C=O), 151.3 (C=O), 139.6 (C), 135.7 (C), 135.5 (C), 128.3 (CH), 128.1 (2 × CH), 50.6 (CH), 35.7 (CH₂), 28.9 (2 × CH₃); ν_{max} (film)/cm⁻¹ 1674, 1585, 1564, 1436, 1380, 1304, 1280, 1095, 1020; *m/z* (ES) 313 (M-H (³⁵Cl), 100), 315 (M-H (³⁵Cl+³⁷Cl), 54), 317 (M-H (³⁷Cl), 8); H.R.M.S [M-H] (³⁵Cl) C₁₃H₁₁Cl₂N₂O₃ Calculated 313.0152, found 313.0151.

5-(2-Iodobenzyl)-1,3-dimethylbarbituric acid (**3f**)

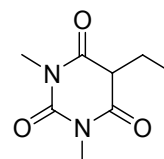
Prepared by the general procedure **A** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 2-iodobenzyl alcohol (0.351 g, 1.50 mmol). Work up followed by column chromatography eluting with 2:1 v/v ether-petroleum ether gave **3f** (0.275 g, 74%) as



colourless solid; mp 114-116 °C; δ_{H} (300 MHz, CDCl₃); 7.83 (d, 1H, J 7.9 Hz, 2-I-Ph-H₃), 7.30 (t, 1H, J 7.7 Hz, 2-I-Ph-H₅), 7.20 (dd, 1H, J 7.7 and 1.5 Hz, 2-I-Ph-H₆), 6.95 (ddd, 1H, J 7.9, 7.7 and 1.5 Hz, 2-I-Ph-H₄), 3.86 (t, 1H, J 6.4 Hz, CHCH₂), 3.52 (d, 2H, J 6.4 Hz, CHCH₂), 3.26 (s, 6H, 2 × NCH₃); δ_{C} (75.5 MHz, CDCl₃); 168.0 (2 × C=O), 151.9 (C=O), 140.3 (CH), 139.5 (C), 131.0 (CH), 129.6 (CH), 128.7 (CH), 100.9 (C), 50.5 (CH), 41.5 (CH₂), 29.2 (2 × CH₃); m/z (FI) 372 (M⁺, 5), H.R.M.S [M⁺] C₁₃H₁₃IN₂O₃ Calculated 371.9971, found 371.9972.

5-Ethyl-1,3-dimethylbarbituric acid (**3g**)²

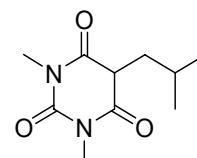
Prepared by the general procedure **A** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and ethanol (1.0 mL). Work up followed by column chromatography eluting with 2:1 v/v ether-petroleum



ether gave **3g** (0.154 g, 84%) as an colourless oil; δ_{H} (300 MHz, CDCl₃); 3.48 (t, 1H, J 5.3 Hz, CHCH₂), 3.31 (s, 6H, 2 × NCH₃), 2.19 (qd, 2H, J 7.5 and 5.3 Hz, CH₂CH₃), 0.94 (t, 3H, J 7.5 Hz, CH₂CH₃); δ_{C} (75.5 MHz, CDCl₃); 169.0 (2 × C=O), 152.0 (C=O), 50.4 (CH), 28.8 (2 × CH₃), 25.2 (CH₂), 10.7 (CH₃); m/z (FI) 184 (M⁺, 50); H.R.M.S [M⁺] C₈H₁₂N₂O₃ Calculated 184.0848, found 184.0851.

5-Isobutyl-1,3-dimethylbarbituric acid (**3h**)

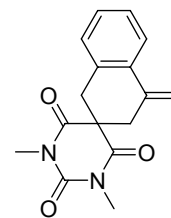
Prepared by the general procedure **A** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 2-methylpropanol (1.0 mL). Work up followed by column chromatography eluting with 3:1 v/v ether-petroleum ether gave **3h** (0.180 g, 85%) as colourless prisms; mp 58-59



°C; δ_{H} (500 MHz, CDCl₃); 3.48 (t, 1H, J 6.6 Hz, CHCH₂), 3.29 (s, 6H, 2 × NCH₃), 1.94 (t, 2H, J 6.6 Hz, CH₂CH(CH₃)₂), 1.88-1.76 (m, 1H, CH(CH₃)₂), 0.94 (d, 6H, J 6.8 Hz, CH(CH₃)₂); δ_{C} (75.5 MHz, CDCl₃); 169.3 (2 × C=O), 152.1 (C=O), 48.2 (CH), 40.9 (CH), 28.9 (2 × CH₃), 26.1 (CH₂), 22.5 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2959, 2873, 1739, 1694, 1665, 1519, 1462, 1421, 1373, 1283, 1246, 1201, 1155, 1089; m/z (ES) 211 (M-H, 100); H.R.M.S [M-H] C₁₀H₁₅N₂O₃ Calculated 211.1088, found 211.1078.

1',3'-Dimethyl-4-methylene-3,4-dihydro-1*H*,2'*H*-spiro[naphthalene-2,5'-pyrimidine]-2',4',6'(1'*H*,3'*H*)-trione (6a)

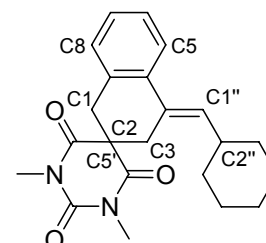
Prepared by the general procedure **B** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 2-iodobenzyl alcohol (0.281 g, 1.20 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), allene gas (0.5 bar) and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with diethyl



ether gave **6a** (0.119 g, 42%) as colourless plates; mp 129-131 °C; δ_H (300 MHz, CDCl₃); 7.61 (d, 1H, J 7.7 Hz, Ar-H₅), 7.24 (t, 1H, J 7.7 Hz, Ar-H₆), 7.19 (t, 1H, J 7.7 Hz, Ar-H₇), 7.14 (d, 1H, J 7.7 Hz, Ar-H₈), 5.61 (s, 1H, C=CH₂), 4.99 (s, 1H, C=CH₂), 3.43 (s, 2H, C(1)H₂), 3.30 (s, 6H, 2 × NCH₃), 2.93 (s, 2H, C(3)H₂); δ_C (75.5 MHz, CDCl₃); 171.1 (2 × C=O), 151.7 (C=O), 138.7 (C), 133.6 (C), 133.2 (C), 128.9 (CH), 128.8 (CH), 126.7 (CH), 124.3 (CH), 111.9 (CH₂), 52.7 (C), 42.5 (CH₂), 34.3 (CH₂), 29.5 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2939, 1750, 1676, 1454, 1415, 1375, 1113, 1067; m/z (FI) 284 (M⁺, 100); H.R.M.S [M⁺] C₁₆H₁₆N₂O₃ Calculated 284.1161, found 284.1173.

(4E)-4-(Cyclohexylmethylene)-1',3'-dimethyl-3,4-dihydro-1H,2H'-spiro[naphthalene-2,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (6b)

Prepared by the general procedure **B** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 2-iodobenzyl alcohol (0.281 g, 1.20 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), 1-cyclohexyl allene (0.146 g, 1.20 mmol) and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **6b** (0.190 g, 52%) as colourless plates; mp 120-122 °C; (Found: C, 72.05; H, 7.15; N, 7.45; C₂₂H₂₆N₂O₃ requires: C, 72.11; H, 7.15; N, 7.64 %); δ_{H} (300 MHz, CDCl₃); 7.56-7.47 (m, 1H, Ar-H₅), 7.21-7.13 (m, 2H, Ar-H_{6,7}), 7.12-7.05 (m, 1H, Ar-H₈), 6.0 (d, 1H, J 9.5 Hz, C(4)=C(1'')H), 3.37 (s, 2H, C(1)H₂), 3.30 (s, 6H, 2 × NCH₃), 2.94 (bd, 2H, J 1.0 Hz, C(3)H₂), 2.29-2.1 (m, 1H, Cy-C(2'')H), 1.81-1.52 (m, 4H, Cy-CH₂), 1.39-1.07 (m, 6H, Cy-CH₂); δ_{C} (75.5 MHz, CDCl₃); 171.3 (2 × C=O), 151.8 (C=O), 135.4 (C), 134.4 (CH), 132.7 (C), 128.6 (CH), 127.9 (C), 127.7 (CH), 126.8 (CH), 123.8 (CH), 52.8 (C), 37.7 (CH), 35.5 (CH₂), 35.0 (CH₂), 33.5 (2 × CH₂), 29.5 (2 × CH₃), 26.3 (CH₂), 26.2 (2 × CH₂); ν_{max} (film)/cm⁻¹ 2923, 2846, 1747, 1678, 1449, 1415, 1371, 1305, 1262, 1111, 1067; *m/z* (ES) 367 (M+H, 21), 389 (M+Na, 100).

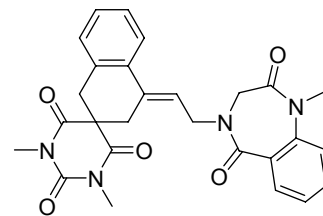
n.O.e for **6b**

Irradiated proton	Enhancement (%)			
	C(2'')H	C(3)H ₂	Ar-H ₅	Ar-H ₈
C(1'')H			19	
C(1)H ₂		1.7		7.3
C(3)H ₂	7.9			

(4E)-1',3'-Dimethyl-4-[2-(1-methyl-2,5-dioxo-1,2,3,5-tetrahydro-4H-1,4-benzodiazepin-4-yl)-ethyldiene]-3,4-dihydro-1H,2'H-spiro[naphthalene-2,5'-pyrimidine]-2',4',6'(1'H,3'H)-trione (6c)

Prepared by the general procedure **B** from 1,3-dimethylbarbituric acid

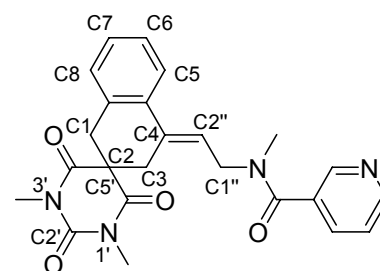
(0.078 g, 0.50 mmol), KOH (4.5 mg, 0.075 mmol), [IrCp*Cl₂]₂ (10 mg, 0.013 mmol) and 2-iodobenzyl alcohol (0.140 g, 0.60 mmol) followed by sequential addition of Pd₂dba₃ (0.023 g, 0.025 mmol), TFP (0.023 g, 0.10 mmol), K₂CO₃ (0.138 g, 1.00 mmol), allene substrate (0.146 g, 0.60 mmol)



and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with 2:1 v/v ethyl acetate/petroleum ether gave **6c** (0.128 g, 53%) as colourless solid; mp 90-92 °C; δ_H (500 MHz, CDCl₃); 7.87 (dd, 1H, J 7.7 and 1.3 Hz, Ar-H), 7.62-7.58 (m, 1H, Ar-H), 7.53 (td, 1H, J 7.7 and 1.3 Hz, Ar-H), 7.30 (t, 1H, J 7.7 Hz, Ar-H), 7.25-7.18 (m, 3H, Ar-H), 7.10-7.06 (m, 1H, Ar-H), 6.23 (app. t, 1H, J 7.3 Hz, CHCH₂), 4.65 (dd, 1H, J 15.4 and 6.0 Hz, CHCH₂), 4.23 (dd, 1H, J 15.4 and 8.8 Hz, CHCH₂), 3.95 (d, 1H, J 15.0 Hz, CH₂), 3.78 (d, 1H, J 15.0 Hz, CH₂), 3.44-3.35 (m, 4H, CH₂ and NCH₃), 3.32 (s, 3H, NCH₃), 3.29 (d, 1H, J 16.7 Hz, CH₂), 3.26 (s, 3H, NCH₃), 3.19 (d, 1H, J 15.0 Hz, CH₂), 3.13 (d, 1H, J 15.0 Hz, CH₂); δ_C (75.5 MHz, CDCl₃); 171.4 (C=O), 171.0 (C=O), 169.2 (C=O), 167.4 (C=O), 151.6 (C=O), 141.5 (C), 135.6 (C), 134.3 (C), 132.7 (C), 132.6 (CH), 131.3 (CH), 129.0 (C), 128.7 (2 × CH), 127.2 (CH), 126.1 (CH), 124.2 (CH), 121.4 (CH), 120.1 (CH), 51.9 (C), 50.7 (CH₂), 45.4 (CH₂), 36.9 (CH₂), 35.4 (CH₃), 33.7 (CH₂), 29.6 (CH₃), 29.4 (CH₃); ν_{max} (film)/cm⁻¹ 2934, 1755, 1677, 1637, 1474, 1454, 1418, 1377, 1314, 1273, 1234, 1131; *m/z* (ES) 487 (M+H), 27, 509 (M+Na, 100); H.R.M.S [M+H] C₂₇H₂₇N₄O₅ Calculated 487.1976, found 487.1977.

***N*-[(2*E*)-2-(1',3'-Dimethyl-2',4',6'-trioxo-1',3',4',6'-tetrahydro-1*H*,2'*H*-spiro[naphthalene-2,5'-pyrimidin]-4(3*H*)-ylidene)ethyl]-*N*-methylnicotinamide (6d)**

Prepared by the general procedure **B** from 1,3-dimethylbarbituric acid (0.078 g, 0.50 mmol), KOH (4.5 mg, 0.075 mmol), [IrCp*Cl₂]₂ (10 mg, 0.013 mmol) and 2-iodobenzyl alcohol (0.140 g, 0.60 mmol) followed by sequential addition of Pd₂dba₃ (0.023 g, 0.025 mmol), TFP (0.023 g, 0.10 mmol), K₂CO₃ (0.138 g, 1.00 mmol), allene substrate (0.113 g, 0.60 mmol) and CH₃CN (2.0 mL). Work up followed by column



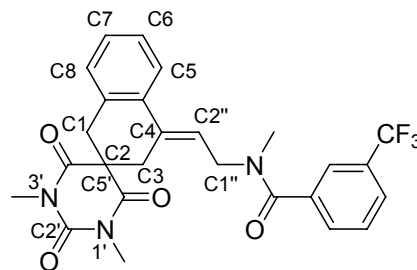
chromatography eluting with diethyl ether gave **6d** (0.127 g, 59%, *E* : *Z*, 87 : 13) as colourless plates; δ_{H} (*E*-isomer, 500 MHz, 60 °C, CDCl₃); 8.68 (s, 1H, Py-H₂), 8.62 (dd, 1H, *J* 4.8 and 1.0 Hz, Py-H₆), 7.74 (dt, 1H, *J* 7.8 and 1.9 Hz, Py-H₄), 7.57 (dd, 1H, *J* 6.5 and 2.6 Hz, Ar-H₃), 7.30 (dd, 1H, *J* 7.8 and 4.8 Hz, Py-H₅), 7.27-7.15 (m, 2H, Ar-H_{4,5}), 7.04 (dd, 1H, *J* 6.0 and 2.5 Hz, Ph-H₆), 6.16 (bs, 1H, CHCH₂), 4.21 (bs, 2H, CH₂NCH₃), 3.26 (bs, 2H, C(1)H₂), 3.24 (s, 6H, 2 × NCH₃), 3.03 (bs, 5H, CH₂NCH₃ + C(3)H₂); δ_{C} (125 MHz, 60 °C, CDCl₃); 170.8 (2 × C=O), 168.8 (C=O), 151.1 (C=O), 150.6 (CH), 148.0 (CH), 135.0 (C), 134.7 (CH), 134.4 (C), 132.15 (C), 132.06 (C), 128.19 (2 × CH), 126.98 (CH), 123.7 (CH), 123.2 (CH), 120.6 (CH), 51.7 (C), 37.3 (2 × CH₂), 32.9 (CH₂), 28.9 (3 × CH₃); ν_{max} (film)/cm⁻¹ 2950, 2917, 1747, 1677, 1454, 1415, 1376, 1303, 1267, 1111, 1075, 1023; *m/z* (ES) 455 (M+Na, 100), 433 (M+H, 18); H.R.M.S [M+H] C₂₄H₂₅N₄O₄ Calculated 433.1870, found 433.1869.

n.O.e for **6d**

Irradiated proton	Enhancement (%)						
	PyH ₄	PyH ₆	C(5)H	C(7)H	C(2'')H	C(1'')H ₂	C(1)H
PyH ₅	9.7	3.3					
C(8)H				4.1			
C(2'')H			14.9				
C(1'')H ₂					5.9		
C(1'')NCH ₃					0.97	1.8	
C(3)H ₂							4.2

***N*-[*(2E)*-2-(1',3'-Dimethyl-2',4',6'-trioxo-1',3',4',6'-tetrahydro-1*H*,2'*H*-spiro[naphthalene-2,5'-pyrimidin]-4(3*H*)-ylidene)ethyl]-*N*-methyl-3-(trifluoromethyl)benzamide (**6e**)**

Prepared by the general procedure **B** from 1,3-dimethylbarbituric acid (0.078 g, 0.50 mmol), KOH (4.5 mg, 0.075 mmol), [IrCp*Cl₂]₂ (10 mg, 0.013 mmol) and 2-iodobenzyl alcohol (0.140 g, 0.60 mmol) followed by sequential addition of Pd₂dba₃ (0.023 g, 0.025 mmol), TFP (0.023 g, 0.10 mmol), K₂CO₃ (0.138 g, 1.00 mmol), allene substrate (0.153 g, 0.60 mmol) and CH₃CN (2.0 mL). Work up



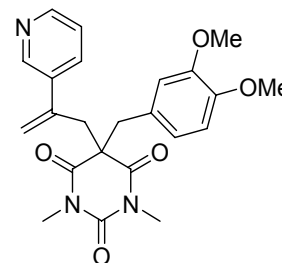
followed by column chromatography eluting with 6:1 v/v diethyl ether/hexane gave **6e** (0.125 g, 50%, *E* : *Z*, 95 : 5) as colourless solid; δ_{H} (*E*-isomer, 500 MHz, 60 °C, CDCl₃); 7.72 (s, 1H, 3-CF₃Ph-H₂), 7.68 (d, 1H, J 7.8 Hz, 3-CF₃Ph-H₄), 7.62 (d, 1H, J 7.8 Hz, 3-CF₃Ph-H₆), 7.59 (d, 1H, J 6.5 Hz, Ar-H₅), 7.53 (t, 1H, J 7.8 Hz, 3-CF₃Ph-H₅), 7.26-7.19 (m, 2H, Ar-H_{6,7}), 7.06 (d, 1H, J 6.5 Hz, Ar-H₈), 6.19 (bs, 1H, CHCH₂), 4.23 (bs, 2H, CHCH₂N), 3.29 (bs, 2H, C(1)H₂), 3.26 (s, 6H, 2 × NCH₃), 3.03 (bs, 5H, NCH₃ + C(3)H₂); δ_{C} (125 MHz, 60 °C, CDCl₃); 170.7 (2 × C=O), 169.7 (C=O), 151.1 (C=O), 137.2 (C), 134.7 (C), 134.4 (C), 132.0 (C), 131.2 (q, 1C, ²J_{CF} 33 Hz), 130.2 (CH), 128.9 (CH), 128.1 (2 × CH), 127.0 (CH), 126.3 (CH), 124.1 (CH), 123.7 (q, 1C, ¹J_{CF} 270 Hz), 123.65 (CH), 120.6 (CH), 51.7 (C), 37.3 (2 × CH₂), 32.8 (CH₂), 28.9 (3 × CH₃); ν_{max} (film)/cm⁻¹ 2956, 2923, 1747, 1678, 1631, 1455, 1421, 1376, 1330, 1259, 1166, 1122, 1068; *m/z* (ES) 522 (M+Na, 100), 500 (M+H, 33); H.R.M.S [M+H] C₂₆H₂₅F₃N₃O₄ Calculated 500.1792, found 500.1782.

n.O.e for **6e**

Irradiated proton	Enhancement (%)						
	C(1)H ₂	C(7)H	C(5)H	C(2'')H	C(1'')H ₂	3-CF ₃ Ph-H ₆	3-CF ₃ Ph-H ₂
C(8)H	7.8	6					
C(2'')H			17.5		3.1		
C(1'')H ₂				3.4			
C(1'')NCH ₃				1	1.4	1.1	1.1

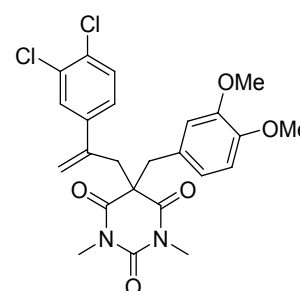
5-(3,4-Dimethoxybenzyl)-1,3-dimethyl-5-(2-(pyridin-3-yl)allyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (8a)

Prepared by the general procedure **C** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,4-dimethoxybenzyl alcohol (0.252 g, 1.50 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), 3-iodopyridine (0.308 g, 1.50 mmol), allene gas (0.5 bar) and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **8a** (0.190 g, 45%) as colourless plates; mp 110-112 °C; (Found: C, 65.00; H, 6.10; N, 9.65; C₂₃H₂₅N₃O₅ requires: C, 65.24; H, 5.95; N, 9.92 %); δ_H (300 MHz, CDCl₃); 8.50 (dd, 1H, J 4.9 and 1.5 Hz, Py-H₆), 8.43 (d, 1H, J 2.1 Hz, Py-H₂), 7.54 (dt, 1H, J 7.8 and 2.1 Hz, Py-H₄), 7.23 (dd, 1H, J 7.8 and 4.9 Hz, Py-H₅), 6.65 (d, 1H, J 8.1 Hz, Ph-H₅), 6.53 (dd, 1H, J 8.1 and 2.0 Hz, Ph-H₆), 6.50 (d, 1H, J 2.0 Hz, Ph-H₁), 5.23 (d, 1H, J 0.5 Hz, C=CH₂), 5.18 (s, 1H, C=CH₂), 3.80 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 3.35 (s, 2H, CH₂), 3.31 (s, 2H, CH₂), 2.85 (s, 6H, 2 × NCH₃); δ_C (75.5 MHz, CDCl₃); 171.0 (2 × C=O), 150.3 (C=O), 149.7 (CH), 149.0 (C), 148.8 (C), 148.2 (CH), 141.4 (C), 135.8 (C), 134.4 (CH), 127.3 (C), 123.3 (CH), 121.9 (CH), 120.3 (CH₂), 112.6 (CH), 111.3 (CH), 59.4 (C), 56.11 (2 × CH₃), 45.4 (CH₂), 45.0 (CH₂), 28.4 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2956, 1679, 1518, 1445, 1418, 1382, 1261, 1141, 1026; *m/z* (ES) 424 (M+H), 100).



5-(3,4-Dimethoxybenzyl)-5-(2-(3,4-dichlorophenyl)allyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (8b)

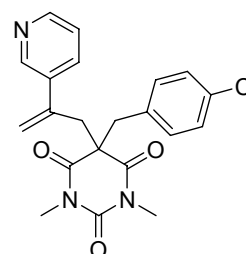
Prepared by the general procedure **C** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,4-dimethoxybenzyl alcohol (0.252 g, 1.50 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), 1,2-dichloro-4-iodobenzene (0.409 g, 1.50 mmol), allene gas (0.5 bar) and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with diethyl ether gave **8b** (0.251 g, 51%) as colourless prisms; mp 121-122 °C; (Found: C, 58.60; H, 4.70; Cl, 14.25; N, 5.80; C₂₄H₂₄Cl₂N₂O₅ requires: C, 58.67; H, 4.92; Cl, 14.43; N, 5.70 %); δ_H (300 MHz, CDCl₃); 7.35 (d, 1H, J 8.3 Hz, 3,4-diClPh-H₅), 7.28 (d, 1H, J 2.0 Hz, 3,4-diCl-Ph-H₂), 7.02 (dd, 1H, J 8.3 and 2.0 Hz, 3,4-diCl-Ph-H₆), 6.65 (d, 1H, J 8.1 Hz, 3,4-diCH₃O-Ph-H₅), 6.53 (dd, 1H, J 8.1 and 2.0 Hz, 3,4-diCH₃O-Ph-H₆), 6.51 (s, 1H, 3,4-diCH₃O-Ph-H₂), 5.19 (d, 1H, J



0.7 Hz, C=CH₂), 5.12 (s, 1H, C=CH₂), 3.80 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 3.30-3.25 (2 × s, 4H, 2 × CH₂), 2.87 (s, 6H, 2 × NCH₃); δ_C (75.5 MHz, CDCl₃); 171.0 (2 × C=O), 150.4 (C=O), 149.1 (C), 148.8 (C), 142.5 (C), 140.3 (C), 132.9 (C), 132.5 (C), 130.6 (CH), 129.1 (CH), 127.4 (C), 126.4 (CH), 122.0 (CH), 119.8 (CH₂), 112.8 (CH), 111.4 (CH), 59.4 (C), 56.1 (2 × CH₃), 45.3 (2 × CH₂), 28.3 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2945, 1725, 1679, 1518, 1444, 1377, 1263, 1144, 1026; *m/z* (ES) 513 (M+Na (³⁵Cl), 12.5), 515 (³⁵Cl + ³⁷Cl) 7), 517 (³⁷Cl) 1).

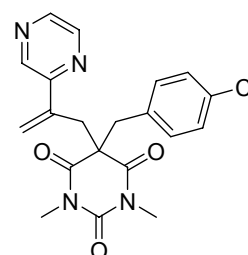
5-(4-Chlorobenzyl)-1,3-dimethyl-5-(2-(pyridin-3-yl)allyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (8c)

Prepared by the general procedure C from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 4-chlorobenzyl alcohol (0.214 g, 1.50 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), 3-iodopyridine (0.308 g, 1.50 mmol), allene gas (0.5 bar) and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with 4:1 v/v ether-petroleum ether gave **8c** (0.258 g, 65%) as a colourless solid; mp 120-122 °C; (Found: C, 63.10; H, 5.00; Cl, 8.90; N, 10.60; C₂₁H₂₀ClN₃O₃ requires: C, 63.40; H, 5.07; Cl, 8.91; N, 10.56 %); δ_H (300 MHz, CDCl₃); 8.50 (dd, 1H, *J* 4.7 and 1.7 Hz, Py-H₆), 8.43 (d, 1H, *J* 2.1 Hz, Py-H₂), 7.52 (dt, 1H, *J* 7.7 and 2.1 Hz, Py-H₄), 7.23 (dd, 1H, *J* 7.7 and 4.7 Hz, Py-H₅), 7.14 (d, 2H, *J* 8.1 Hz, Ph-H_{3,5}), 6.93 (d, 2H, *J* 8.1 Hz, Ph-H_{2,6}), 5.25 (s, 1H, C=CH₂), 5.19 (s, 1H, C=CH₂), 3.34 (s, 2H, CH₂), 3.33 (s, 2H, CH₂), 2.83 (s, 6H, 2 × NCH₃); δ_C (75.5 MHz, CDCl₃); 170.6 (2 × C=O), 150.2 (C=O), 149.8 (CH), 148.1 (CH), 141.1 (C), 135.6 (C), 134.3 (CH), 134.1 (C), 133.6 (C), 131.1 (2 × CH), 129.1 (2 × CH), 123.3 (CH), 120.5 (CH₂), 59.1 (C), 45.4 (CH₂), 44.4 (CH₂), 28.3 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2939, 1744, 1679, 1489, 1443, 1418, 1381, 1130, 1094; *m/z* (ES) 398 (M+H (³⁵Cl), 100), 400 (³⁷Cl), 33).



5-(4-Chlorobenzyl)-1,3-dimethyl-5-(2-(pyrazin-2-yl)allyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (8d)

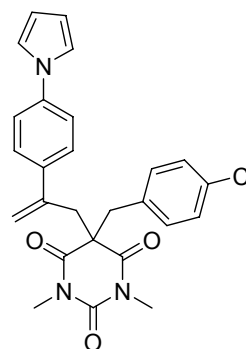
Prepared by the general procedure C from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 4-chlorobenzyl alcohol (0.214 g, 1.50 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), 2-iodopyrazine (0.309 g, 1.50 mmol), allene gas (0.5 bar) and CH₃CN (2.0



mL). Work up followed by column chromatography eluting with 1:1 v/v ether-petroleum ether gave **8d** (0.191 g, 48%) as colourless needles; δ_{H} (300 MHz, CDCl_3); 8.66 (d, 1H, J 0.7 Hz, Pyr-H₃), 8.45 (s, 2H, Pyr-H_{5,6}), 7.17 (d, 2H, J 8.5 Hz, 4-ClPh-H_{3,5}), 6.97 (d, 2H, J 8.5 Hz, 4-ClPh-H_{2,6}), 5.74 (s, 1H, C=CH₂), 5.43 (s, 1H, C=CH₂), 3.49 (s, 2H, CH₂), 3.37 (s, 2H, CH₂), 2.94 (s, 6H, 2 × NCH₃); δ_{C} (75.5 MHz, CDCl_3); 170.7 (2 × C=O), 153.4 (C), 150.6 (C=O), 143.7 (CH), 143.4 (CH), 142.6 (CH), 141.1 (C), 134.0 (C), 133.8 (C), 131.3 (2 × CH), 129.1 (2 × CH), 122.2 (CH₂), 59.0 (C), 44.6 (CH₂), 42.8 (CH₂), 28.5 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2939, 1747, 1678, 1442, 1418, 1381, 1327, 1300, 1278, 1130, 1094, 1016; m/z (ES) 399 (M+H (³⁵Cl), 100), 401 (³⁷Cl), 25), 421 (M+Na (³⁵Cl), 93), 423 (³⁷Cl), 25); H.R.M.S [M+H] (³⁵Cl) C₂₀H₂₀ClN₄O₃ Calculated 399.1218, found 399.1205.

5-(2-(4-(1*H*-Pyrrol-1-yl)phenyl)allyl)-5-(4-chlorobenzyl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (8e)

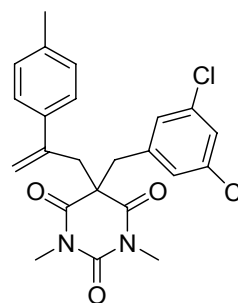
Prepared by the general procedure C from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 4-chlorobenzyl alcohol (0.214 g, 1.50 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), 1-(4-iodophenyl)-1*H*-pyrrole (0.404 g, 1.50 mmol), allene gas (0.5 bar) and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with 1:6 v/v ether-petroleum ether gave **8e** (0.244 g, 53%) as pale yellow solid, mp 55-



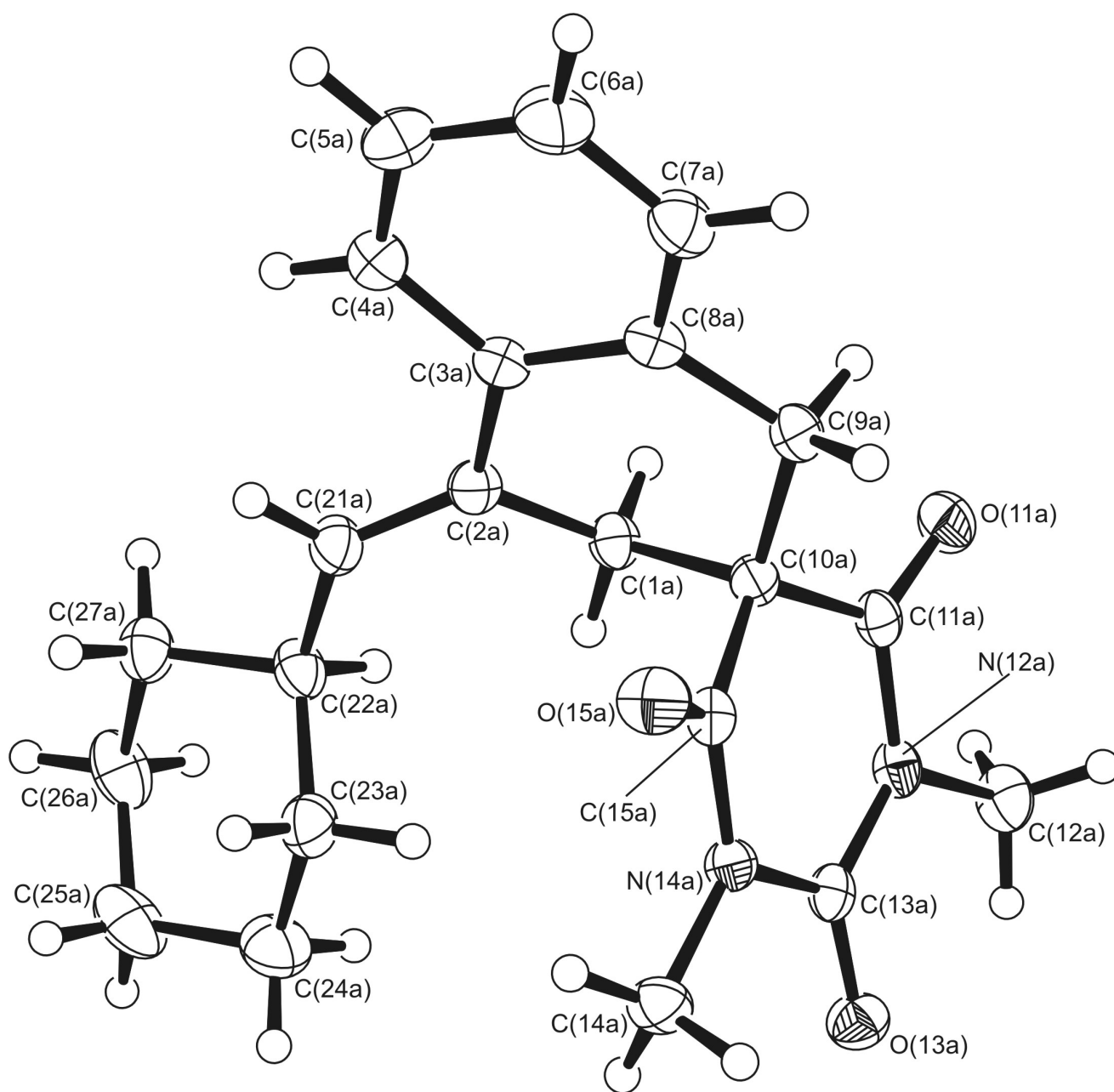
58 °C; (Found: C, 67.85; H, 5.10; Cl, 7.90; N, 8.90; C₂₆H₂₄ClN₃O₃ requires: C, 67.60; H, 5.24; Cl, 7.67; N, 9.10 %); δ_{H} (300 MHz, CDCl_3); 7.31 (dt, 2H, J 6.6 and 2.0 Hz, Ar-H), 7.22 (dt, 2H, J 6.6 and 2.0 Hz, Ar-H), 7.13 (dt, 2H, J 8.5 and 2.0 Hz, 4-ClPh-H_{3,5}), 7.06 (app. t, 2H, J 2.2 Hz, Py-H), 6.95 (dt, 2H, J 8.5 and 2.0 Hz, 4-ClPh-H_{2,6}), 6.35 (app. t, 2H, J 2.2 Hz, Py-H), 5.20 (d, 1H, J 1.1 Hz, C=CH₂), 5.11 (s, 1H, C=CH₂), 3.36 (s, 2H, CH₂), 3.33 (s, 2H, CH₂), 2.80 (s, 6H, 2 × NCH₃); δ_{C} (75.5 MHz, CDCl_3); 170.7 (2 × C=O), 150.5 (C=O), 143.1 (C), 140.8 (C), 136.9 (C), 134.0 (2 × C), 131.3 (2 × CH), 129.1 (2 × CH), 128.3 (2 × CH), 120.3 (2 × CH), 119.4 (2 × CH), 119.0 (CH₂), 111.3 (2 × CH), 59.3 (C), 46.5 (CH₂), 43.8 (CH₂), 28.3 (2 × CH₃); ν_{max} (film)/cm⁻¹ 2939, 1747, 1678, 1607, 1521, 1442, 1381, 1330; m/z (ES) 462 (M+H (³⁵Cl), 21), 464 (³⁷Cl), 11), 484 (M+Na (³⁵Cl), 24), 486 (³⁷Cl), 9).

5-(3,5-Dichlorobenzyl)-1,3-dimethyl-5-(2-*p*-tolylallyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (8f)

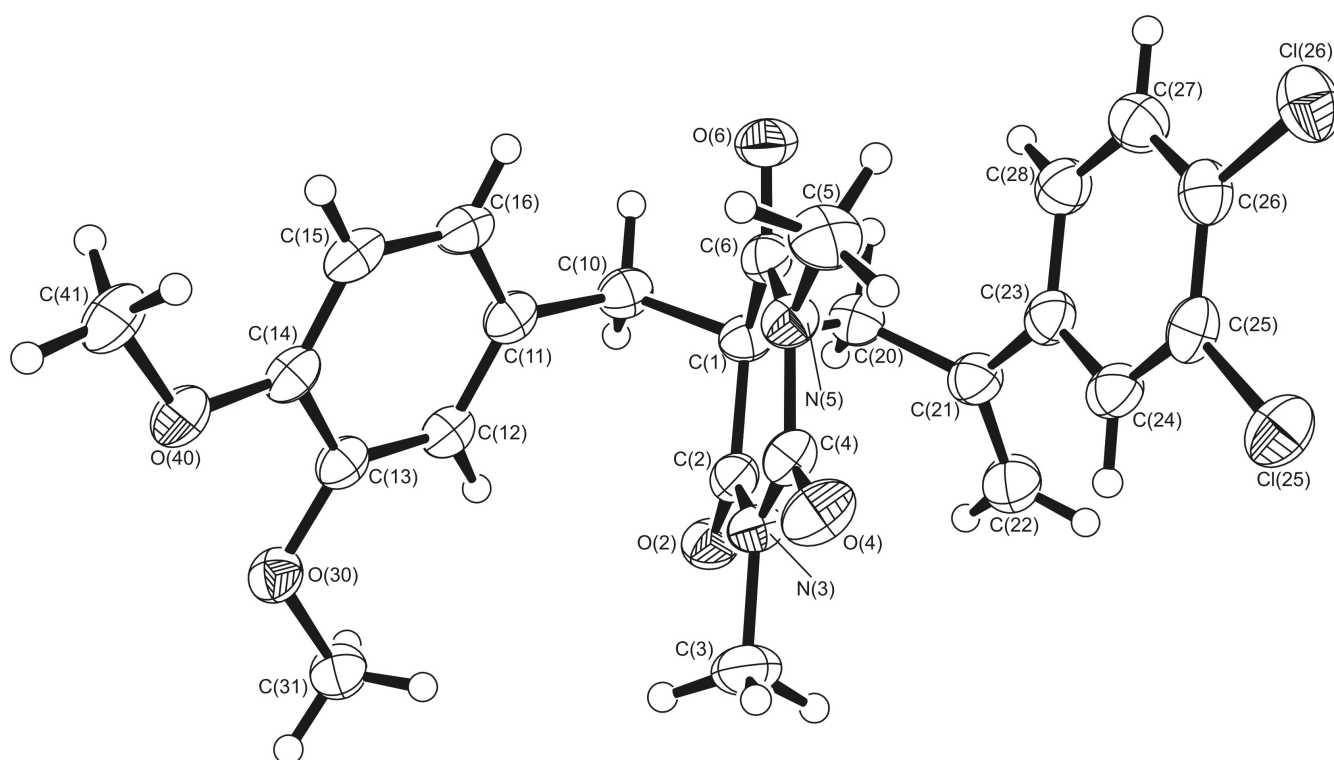
Prepared by the general procedure **C** from 1,3-dimethylbarbituric acid (0.156 g, 1.00 mmol), KOH (9 mg, 0.152 mmol), [IrCp*Cl₂]₂ (0.020 g, 0.025 mmol) and 3,5-dichlorobenzyl alcohol (0.266 g, 1.50 mmol) followed by sequential addition of Pd₂dba₃ (0.046 g, 0.05 mmol), TFP (0.046 g, 0.20 mmol), K₂CO₃ (0.276 g, 2.00 mmol), 4-iodotoluene (0.327 g, 1.50 mmol), allene gas (0.5 bar) and CH₃CN (2.0 mL). Work up followed by column chromatography eluting with 1:9 v/v ether-



petroleum ether gave **8f** (0.249 g, 56%) as colourless plates; mp 75-77 °C; δ_{H} (300 MHz, CDCl₃); 7.17 (t, 1H, J 2.0 Hz, 3,5-diClPh-H₄), 7.10 (d, 2H, J 8.3 Hz, Ph-H_{2,6}), 7.05 (d, 2H, J 8.3 Hz, Ph-H_{3,5}), 6.93 (d, 2H, J 2.0 Hz, 3,5-diClPh-H_{2,6}), 5.16 (d, 1H, J 1.3 Hz, C=CH₂), 5.05 (s, 1H, C=CH₂), 3.32 (s, 2H, CH₂), 3.28 (s, 2H, CH₂), 2.80 (s, 6H, 2 × NCH₃), 2.30 (s, 3H, CH₃) ; δ_{C} (75.5 MHz, CDCl₃); 170.4 (2 × C=O), 150.4 (C=O), 143.7 (C), 139.0 (C), 138.6 (C), 136.7 (C), 135.3 (2 × C), 129.4 (2 × CH), 128.5 (2 × CH), 128.2 (CH), 126.9 (2 × CH), 118.4 (CH₂), 59.1 (C), 46.9 (CH₂), 43.3 (CH₂), 28.3 (2 × CH₃), 21.4 (CH₃); ν_{max} (film)/cm⁻¹ 3076, 2943, 1748, 1682, 1587, 1566, 1512, 1445, 1432, 1382, 1316, 1289, 1122, 1091, 1040; m/z (ES) 467 (M+Na (³⁵Cl), 38), 469 (³⁵Cl + ³⁷Cl), 22), 471 (³⁷Cl), 4.4); H.R.M.S [M+Na] (³⁵Cl) C₂₃H₂₂Cl₂N₂NaO₃ Calculated 467.0900, found 467.0900.



View of **6b**. Ellipsoid probability: 50 %.



View of **8b**. Ellipsoid probability: 50%.

¹ K. A. Krasnov, V.G. Kartsev, A. S. Gorovoi, Chem. Nat. Compd. (Engl. Transl.), 2000, **36**, 192.

² B. S. Jursic, E. D. Stevens, *Tetrahedron Lett.* 2003, **44**, 2203.