

## Experimental

### General

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker DPX 300 spectrometer. [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub><sup>1</sup>, **L1**<sup>2</sup> and **L2**<sup>2</sup> were prepared according to the literature method. All other reagents are commercially available and were used as received. Microanalyses were performed by Mr Ian Blakeley in the University of Leeds, School of Chemistry. Mass spectra were collected by Ms Tanya Marinko-Covell either on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. X-ray data was collected by the author. A suitable single crystal was selected and immersed in an inert oil. The crystal was then mounted onto a glass capillary and attached to a goniometer head on a Bruker X8 Apex diffractor using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and 1.0°  $\phi$ -rotation frames. The crystal was then cooled to 150K by an Oxford cryostream low temperature device.<sup>3</sup> The full data set was recorded and the images processed using DENZO and SCALEPACK programs.<sup>4</sup> The structures were solved by the author. Structure solution by direct methods was achieved through the use of SHELXS86<sup>5</sup>, SIR92<sup>6</sup> or SIR97<sup>7</sup> programs, and the structural model defined by full matrix least squares on F<sup>2</sup> using SHELX97.<sup>5</sup> Molecular graphics were plotted using POV-Ray<sup>8</sup> via the XSeed program. Editing of Crystallographic Information files and construction of tables of bond lengths and angles was achieved using WC<sup>9</sup> and PLATON.<sup>10</sup> Hydrogen atoms were placed using idealised geometric positions (with free rotation for methyl groups), allowed to move in a “riding model” along with the atoms to which they were attached, and refined isotropically.

### Cell Line Testing

The *in vitro* tests were performed at the Institute of Cancer Therapeutics, Bradford, on MCF7 (human breast adenocarcinoma) and HT-29 (human colon adenocarcinoma) cell lines. Cells were incubated in 96-well plates at a concentration of  $2 \times 10^4$  cells/ml. 200  $\mu$ L of growth media (RPMI 1640 supplemented with 10% foetal calf serum, sodium pyruvate (1 mM) and L-glutamine (2 mM)) was added to each well and the plates were incubated for 24 hours at 37 °C in an atmosphere of 5% CO<sub>2</sub> prior to drug exposure. Compounds **1-6**, [IrCp\*Cl<sub>2</sub>]<sub>2</sub>, [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub>, 2-hydroxy-1,4-naphthoquinone and cisplatin were all dissolved in

dimethylsulphoxide at a concentration of 25 mM and diluted further with medium to obtain drug solutions ranging from 250 to 0.49  $\mu\text{M}$ . The final dimethylsulphoxide concentration was 0.1% (v/v) which is non-toxic to cells. Drug solutions were applied to cells and incubated for 5 days at 37 °C in an atmosphere of 5%  $\text{CO}_2$ . 20  $\mu\text{L}$  of MTT (5  $\text{mgml}^{-1}$ ) was added to each well and incubated for 3 hours at 37 °C in an atmosphere of 5%  $\text{CO}_2$ . The solutions were then removed and 150  $\mu\text{L}$  of dimethylsulphoxide was added to each well to dissolve the purple formazan crystals. A Thermo Scientific Multiskan EX microplate photometer was used to measure the absorbance at 540 nm. Lanes containing medium only and cells in medium (no drug) were used as blanks for the spectrophotometer and 100% cell survival respectively. Cell survival was determined as the absorbance of treated cells divided by the absorbance of controls and expressed as a percentage. The  $\text{IC}_{50}$  values were determined from plots of % survival against drug concentration. Each experiment was repeated 3 times and a mean value obtained.

### Synthesis of $\text{C}_{16}\text{H}_{14}\text{NOF}$ (L3)

Sodium ethoxide (2.46 g, 36.2 mmol) was dissolved in ethyl acetate (20 ml), and a mixture of 3'-fluoroacetophenone (5.00 g, 36.2 mmol) and ethyl acetate (20 ml) was added dropwise with stirring over 10 minutes. The reaction mixture was heated under reflux for 1 hour and allowed to stand at room temperature until a precipitate was observed. The solution was transferred to a separating funnel with ice water (100 ml) and the aqueous layer was washed with diethyl ether (3  $\times$  30 ml). The solution was acidified with sulfuric acid (1:1 ice water) until slightly acidic to litmus. The product was extracted with diethyl ether (4  $\times$  30 ml) and dried (anhydrous sodium sulfate) in the freezer overnight. The drying agent was removed by filtration and the solvent was then removed under reduced pressure to give a light brown oil which readily solidified in air. The crude product was recrystallised from methanol to give light brown crystals of 3-fluoro-1-phenylbutan-1,3-dione (1.99 g, 11.1 mmol, 31%).

HCl (0.5ml) was added dropwise to a solution of 3-fluoro-1-phenylbutan-1,3-dione (0.52g, 2.89 mmol) and aniline (1 ml) in toluene (10 ml) until a precipitate formed and the mixture was stirred for 16 hours. The precipitate was filtered and the solvent removed from the filtrate yielding a brown precipitate. The crude product was recrystallised from slow evaporation in ethanol (20 ml) to obtain yellow crystals (0.61 g, 2.9 mmol, 83%).

**Analysis Calculated:** C 75.3, H 5.5, N 5.5%. **Analysis Found:** 75.3, H 5.3, N 5.5%.

**ES-MS (+):**  $m/z$  255.4 [ $M^+$ ]

**$^1H$  NMR** ( $CDCl_3$ , 300 MHz, 300 K)  $\delta$  13.18 (br. s, 1H, NH), 7.74 (d,  $^3J(^1H-^1H) = 7.7$  Hz, 1H, aromatic CH *ortho* to CO and *para* to CF), 7.66 (dt,  $^3J(^1H-^{19}F) = 9.9$  Hz,  $^4J(^1H-^1H) = 1.9$  Hz, 1H, aromatic CH *ortho* to CO and *ortho* to CF), 7.48-7.45 (m, 1H, aromatic CH *meta* to acnac CO and *meta* to CF), 7.43 (br. d, 2H, aniline CH *meta* to acnac NH,  $^3J(^1H-^1H) = 8.0$  Hz), 7.33-7.29 (m, 1H, aniline CH *para* to acnac NH), 7.26-7.22 (m, 2H, aniline CH *ortho* to acnac NH), 7.22-7.16 (m, 1H, aromatic CH *para* to CO and *ortho* to CF), 5.90 (s, 1H, CNHCHCO), 2.20 (s, 3H, CH<sub>3</sub>CNH)

**$^{13}C\{^1H\}$  NMR** ( $CDCl_3$ , 75 MHz, 300 K)  $\delta$  177.2 (quaternary C, C-O), 162.9 (d, C-F *meta* to CO,  $^1J(^{13}C-^{19}F) = 245.5$ ), 142.4 (aniline CNH or acnac CH<sub>3</sub>CNH), 138.5 (aromatic C *ipso* to acnac CO), 129.8 (d,  $^3J(^{13}C-^{19}F) = 29.7$  Hz), CH *meta* to acnac CO and *meta* to CF, 129.2 ( $2 \times$  C, aniline CH *meta* to acnac NH), 126.04 (aniline CH *para* to acnac NH), 124.9 ( $2 \times$  C, aniline CH *ortho* to acnac NH), 122.6 (d,  $^4J(^{13}C-^{19}F) = 9.9$  Hz, aromatic CH *ortho* to acnac CO and *para* to CF), 117.8 (d,  $^2J(^{13}C-^{19}F) = 84.1$  Hz, aromatic CH *para* to acnac CO and *ortho* to CF), 114.0 (d,  $^2J(^{13}C-^{19}F) = 89.0$  Hz, aromatic CH *ortho* to acnac CO and *ortho* to CF), 94.0 (CNHCHCO), 20.4 (CH<sub>3</sub>CNH)

### Synthesis of $IrC_{22}H_{22}N_2OCIF_2$ (1)

2',4'-difluorophenylpicolinamide (0.07 g, 0.30 mmol) and  $[IrCp^*Cl_2]_2$  (0.10 g, 0.13 mmol) were dissolved in ethanol (30 ml) and the solution was refluxed for 30 mins.  $NH_4PF_6$  was added and the mixture was refluxed overnight. The resulting yellow solution was evaporated to dryness, redissolved in dichloromethane (50 ml) and washed with water ( $2 \times 10$  ml) & brine (10 ml), dried using sodium sulfate and filtered. The product was recrystallised by DCM/hexane layer diffusion (0.06 g, mmol, 77%).

**Analysis Calculated:** C 44.3, H 3.7, N 4.7%. **Analysis Found:** C 43.8, H 3.8, N 4.4%

**ES MS (+):** 561.1 [ $M^+$ ]-Cl

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K) 8.58 (br. d, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 5.6 Hz, 1H, pyridyl CH ortho to N), 8.18 (br. d, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 7.5 Hz, pyridyl CH meta to N, ortho to amide), 7.94 (vtd, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 7.8 Hz, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 7.5 Hz, <sup>4</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 1.4 Hz, 1H, pyridyl CH para to N), 7.75 (vbr. q (ddd), <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 8.6 Hz, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 8.6 Hz, <sup>4</sup>J ( <sup>1</sup>H-<sup>19</sup>F) = 8.6 Hz, CH meta to both F), 7.51 (ddd, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 7.3 Hz, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 5.8 Hz, <sup>4</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 1.7 Hz, pyridyl CH para to CO), 6.86 (m, CH ortho to both F and CH ortho and para to F), 1.45 (s, 15H, 5 × CH<sub>3</sub>)

**<sup>13</sup>C {<sup>1</sup>H} NMR** (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 168.4 (NCO), 154.4 (CCON), 159.9 (dd, <sup>1</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 245.1 Hz, <sup>4</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 11.1 Hz, quarternary CF), 157.6 (dd, <sup>1</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 294.4 Hz, <sup>4</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 11.8 Hz, quarternary CF), 149.6 (CH ortho to N on pyridyl ring), 138.6 (C para to N on pyridyl ring), 132.2 (dd, <sup>2</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 13.2 Hz, <sup>4</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 3.9 Hz, quarternary CN), 128.8 (dd, <sup>3</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 9.3 Hz, <sup>3</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 4.1 Hz, C meta to both F), 127.5 (CH meta to N on pyridyl ring), 126.7 (CH on pyridyl ring ortho to CO), 111.0 (dd, <sup>2</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 21.5 Hz, <sup>4</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 3.5 Hz, CH ortho to F and para to F), 103.4 (vt (dd), <sup>2</sup>J ( <sup>13</sup>C-<sup>19</sup>F) = 25.5 Hz, <sup>13</sup>C-<sup>19</sup>F) = 25.5 Hz, CH ortho to both F), 86.6 (5 × quarternary C on Cp\*), 8.4 (5 × CH<sub>3</sub> on Cp\*)

### Synthesis of IrC<sub>22</sub>H<sub>22</sub>N<sub>2</sub>OCIF<sub>2</sub> (2)

2',5'-difluorophenylpicolinamide (0.07 g, 0.30 mmol) and [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (0.10 g, 0.13 mmol) were dissolved in ethanol (30 ml) and the solution was refluxed for 30 mins. NH<sub>4</sub>PF<sub>6</sub> (0.10g, 0.61 mmol) was added and the mixture was refluxed overnight. The resulting yellow solution was evaporated to dryness, redissolved in dichloromethane (50 ml) and washed with water (2 × 10 ml) & brine (10 ml), dried using sodium sulfate and filtered. The product was recrystallised by DCM/hexane layer diffusion (0.07 g, 0.12 mmol, 90%)

**Analysis Calculated:** C 44.3, H 3.7, N 4.7%. **Analysis Found:** C 44.5, H 3.7, N 4.6%

**ES MS (+):** 561.1 [M<sup>+</sup>]-Cl

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 300 K) 8.59 (ddd), <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 5.5 Hz, <sup>4</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 1.4 Hz, <sup>5</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 0.7 Hz, pyridyl CH ortho to N), 8.19 (ddd, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 7.8 Hz, <sup>4</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 1.6 Hz, <sup>5</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 0.7 Hz, pyridyl CH meta to N, ortho to amide), 7.95 (vtd (ddd), <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 7.7 Hz, <sup>3</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 7.7 Hz, <sup>4</sup>J ( <sup>1</sup>H-<sup>1</sup>H) = 1.4 Hz, pyridyl CH para to N), 7.48-7.58 (m, CH

para to CO on pyridyl ring and CH ortho to NCO), 7.07 (vtd (ddd),  $^3J(^1\text{H}-^1\text{H}) = 5.1$  Hz,  $^3J(^1\text{H}-^1\text{H}) = 9.2$  Hz,  $^4J(^1\text{H}-^1\text{H}) = 9.2$  Hz, CH meta to NCO and F), 6.77 – 6.85 (m, CH para to NCO), 1.46 (15H,  $5 \times \text{CH}_3$ )

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ) 168.2 (NCO), 159.8 (dd,  $^1J(^{13}\text{C}-^{19}\text{F}) = 242.5$  Hz,  $^4J(^{13}\text{C}-^{19}\text{F}) = 2.3$  Hz, CF meta to NCO), 154.4 (CCON), 153.4 (dd,  $^1J(^{13}\text{C}-^{19}\text{F}) = 242.4$  Hz,  $^4J(^{13}\text{C}-^{19}\text{F}) = 2.9$  Hz, CF ortho to NCO), 149.6 (CH ortho to N on pyridyl ring), 138.7 (C para to N on pyridyl ring), 137.1 ((dd,  $^2J(^{13}\text{C}-^{19}\text{F}) = 15.7$  Hz,  $^3J(^{13}\text{C}-^{19}\text{F}) = 11.3$  Hz, CN ortho to F), 127.6 (C para to CO on pyridyl ring), 126.8 (C ortho to CO on pyridyl ring), 115.7 (dd,  $^2J(^{19}\text{F}-^{13}\text{C}) = 23.9$  Hz,  $^3J(^{19}\text{F}-^{13}\text{C}) = 9.7$  Hz, CH meta to NCO and F), 114.9 (dd,  $^2J(^{19}\text{F}-^{13}\text{C}) = 24.7$  Hz,  $^3J(^{19}\text{F}-^{13}\text{C}) = 2.9$  Hz, CH ortho to NCO), 112.1 (dd,  $^2J(^{19}\text{F}-^{13}\text{C}) = 24.3$  Hz,  $^3J(^{19}\text{F}-^{13}\text{C}) = 7.9$  Hz, CH para to NCO), 86.7 ( $5 \times \text{CCH}_3$ ), 8.4 ( $5 \times \text{CCH}_3$ ).

### Synthesis of $\text{IrC}_{26}\text{H}_{28}\text{NOCIF}$ (3)

Triethylamine (0.04 ml, 0.29 mmol) was added to a solution of  $[\text{IrCp}^*\text{Cl}_2]_2$  (0.10 g, 0.13 mmol) and **7** (0.07 g, 0.27 mmol) in dichloromethane (25 ml). After 72 hours the solvent was removed and the crude product recrystallised by dichloromethane/hexane layer diffusion to yield large red crystals suitable for X-ray crystallography (0.06 g, 0.10 mmol, 75%).

**Analysis Calculated (with 0.75 equivalents of dichloromethane):** C: 47.2, H: 4.4, N: 2.1%

**Analysis Found:** C: 47.3 H: 4.4 N: 2.1%

**ES MS (+):** 582.2  $[\text{M}^+]\text{-Cl}$

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K) 7.67 (ddd,  $^3J(^1\text{H}-^1\text{H}) = 7.8$  Hz,  $^4J(^1\text{H}-^1\text{H}) = 1.5$  Hz,  $^4J(^1\text{H}-^1\text{H}) = 1.1$  Hz, 1H, CH para to F), 7.59 (ddd,  $^3J(^1\text{H}-^{19}\text{F}) = 10.5$  Hz,  $^4J(^1\text{H}-^1\text{H}) = 2.7$  Hz,  $^4J(^1\text{H}-^1\text{H}) = 1.6$  Hz, 1H, CH ortho to F and CO), 7.50 (td (ddd),  $^3J(^1\text{H}-^1\text{H}) = 7.4$  Hz,  $^4J(^1\text{H}-^1\text{H}) = 1.2$  Hz, 2H,  $2 \times \text{CH}$  meta to N), 7.32-7.42 (m, 3H, CH meta to CO and  $2 \times \text{CH}$  ortho to N), 7.09-7.16 (m, 2H, CH ortho to CO and CH para to N), 5.51 (br. s, 1H, COCHCN), 1.70 (br. s, 3H,  $\text{CH}_3\text{CN}$ ), 1.26 (br. s, 15H,  $5 \times \text{CH}_3$  on Cp\*)

$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 300 K) 174.3 (CO), 163.6 (CN on phenyl ring), 163.5 (d,  $^1J(^{13}\text{C}-^{19}\text{F}) = 244.6$  Hz, CF), 154.5 ( $\text{CH}_3\text{CN}$ ), 142.8 (d,  $^3J(^{13}\text{C}-^{19}\text{F}) = 7.3$  Hz, CCO on phenyl

ring), 130.2 (d,  $^3J(^{13}\text{C}-^{19}\text{F}) = 8.1$  Hz,  $\underline{\text{C}}\text{H}$  meta to F), 129.8 ( $2 \times \underline{\text{C}}\text{H}$  on phenyl ring meta to N), 128.7 ( $2 \times \underline{\text{C}}\text{H}$  on phenyl ring ortho to N), 126.1 ( $\underline{\text{C}}\text{H}$  on phenyl ring para to N), 122.6 (d,  $^4J(^{13}\text{C}-^{19}\text{F}) = 2.8$  Hz,  $\underline{\text{C}}\text{H}$  para to F), 116.5 (d,  $^2J(^{13}\text{C}-^{19}\text{F}) = 21.7$  Hz,  $\underline{\text{C}}\text{H}$  para to CO), 113.9 (d,  $^2J(^{13}\text{C}-^{19}\text{F}) = 22.7$  Hz,  $\underline{\text{C}}\text{H}$  ortho to F and CO), 97.2 (CO $\underline{\text{C}}\text{H}\text{CN}$ ), 86.3 ( $\underline{\text{C}}\text{CH}_3$  on Cp\*), 25.5 ( $\underline{\text{C}}\text{H}_3\text{CN}$ ), 8.7 ( $\underline{\text{C}}\text{H}_3$  on Cp\*)

#### Synthesis of RuC<sub>26</sub>H<sub>27</sub>NOClF (4)

Triethylamine (0.05 ml, 0.39 mmol) and [*p*-cymRuCl<sub>2</sub>]<sub>2</sub> (0.12 g, 0.20 mmol) were added to **7** (0.10 g, 0.39 mmol) in dichloromethane (30 ml). The solution was stirred for 16 hours, and the solvent removed under reduced pressure. The crude product was recrystallised from methanol at 4 °C to yield red crystals (0.12 g, 0.23 mmol, 58%).

**Analysis Calculated:** C 59.5, H 5.2, N 2.7%. **Analysis Found:** C 59.4, H 5.2, N 2.6%

**ES MS (+):** 490.11 [M<sup>+</sup>]-Cl

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz, 300 K)  $\delta$  7.75 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 8.5$  Hz, 1H, aromatic  $\underline{\text{C}}\text{H}$  *ortho* to CO), 7.61-7.56 (m, 2H, aromatic  $\underline{\text{C}}\text{H}$  both *ortho* and *meta* to CO), 7.43 (br. tt,  $^3J(^1\text{H}-^1\text{H}) = 6.9$  Hz and  $^3J(^1\text{H}-^1\text{H}) = 1.6$  Hz, 2H, aniline  $\underline{\text{C}}\text{H}$  *meta* to N), 7.31-7.28 (m, 1H, aniline  $\underline{\text{C}}\text{H}$  *para* to N), 7.26-7.22 (m, 1H, aniline  $\underline{\text{C}}\text{H}$  *ortho* to N), 7.10-7.07 (m, 1H, aniline  $\underline{\text{C}}\text{H}$  *ortho* to N), 7.07-7.03 (m, 1H, aromatic CH *para* to CO and *meta* to CF), 5.41 (s, 1H, C(NH) $\underline{\text{C}}\text{H}\text{CO}$ ), 5.35 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 6.0$  Hz, 1H, *p*-cymene  $\underline{\text{C}}\text{H}$ ), 5.17 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 6.4$  Hz, 1H, *p*-cymene  $\underline{\text{C}}\text{H}$ ), 5.07 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 5.6$  Hz, 1H, *p*-cymene  $\underline{\text{C}}\text{H}$ ), 3.69 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 6.0$  Hz, 1H, *p*-cymene  $\underline{\text{C}}\text{H}$ ), 2.72-2.66 (br. sept,  $^3J(^1\text{H}-^1\text{H}) = 7.0$  Hz, 1H,  $\underline{\text{C}}\text{H}(\text{CH}_3)_2$ ), 2.03 (s, 3H, *p*-cymene  $\underline{\text{C}}\text{H}_3$ ), 1.79 (s, 3H, acnac  $\underline{\text{C}}\text{H}_3$ ,  $\underline{\text{C}}\text{H}_3\text{CNH}$ ), 1.21 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 6.8$  Hz, 3H, *p*-cymene  $\text{CH}(\text{CH}_3)_2$ ), 1.22 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 7.3$  Hz, 3H, *p*-cymene  $\text{CH}(\text{CH}_3)_2$ ), 1.20 (br. d,  $^3J(^1\text{H}-^1\text{H}) = 7.3$  Hz, 3H, *p*-cymene  $\text{CH}(\text{CH}_3)_2$ )

**<sup>13</sup>C {<sup>1</sup>H} NMR** (CDCl<sub>3</sub>, 75 MHz, 300.0 K)  $\delta$  170.0 (d,  $^4J(^{13}\text{C}-^{19}\text{F}) = 2.1$  Hz,  $\underline{\text{C}}\text{O}$ ), 165.1 (aniline  $\underline{\text{C}}$  *ipso* to N or acnac  $\text{CH}_3\underline{\text{C}}\text{NH}$ ), 162.7 (d,  $^1J(^{13}\text{C}-^{19}\text{F}) = 243.3$  Hz,  $\underline{\text{C}}\text{-F}$  *meta* to CO), 157.2 (aniline  $\underline{\text{C}}$  *ipso* to N or acnac  $\text{CH}_3\underline{\text{C}}\text{NH}$ ), 142.0 (d,  $^3J(^{13}\text{C}-^{19}\text{F}) = 6.2$  Hz,  $\underline{\text{C}}$  *ipso* to CO and *meta* to C-F), 129.7 (aniline  $\underline{\text{C}}\text{H}$  *meta* to N), 129.2 (d,  $^3J(^{13}\text{C}-^{19}\text{F}) = 7.2$  Hz, aromatic  $\underline{\text{C}}\text{H}$  *meta* to CO and *meta* to C-F), 127.8 (aniline  $\underline{\text{C}}\text{H}$  *meta* to N), 126.0 (aniline  $\underline{\text{C}}\text{H}$  *para* to N),

125.5 (aniline  $\underline{\text{C}}\text{H}$  *ortho* to N), 123.3 (aniline  $\underline{\text{C}}\text{H}$  *ortho* to N), 122.4 (d,  ${}^4J$  ( ${}^{13}\text{C}$ - ${}^{19}\text{F}$ ) = 2.1 Hz,  $\underline{\text{C}}\text{H}$  *ortho* to CO and *para* to C-F), 116.1 (d,  ${}^2J$  ( ${}^{13}\text{C}$ - ${}^{19}\text{F}$ ) = 20.6 Hz,  $\underline{\text{C}}\text{H}$  *para* to CO and *ortho* to C-F), 114.0 (d,  ${}^2J$  ( ${}^{13}\text{C}$ - ${}^{19}\text{F}$ ) = 22.7 Hz,  $\underline{\text{C}}\text{H}$  *ortho* to CO and *ortho* to C-F), 101.0 (quaternary *p*-cymene  $\underline{\text{C}}$ ), 96.3 (quaternary *p*-cymene  $\underline{\text{C}}$ ), 94.8 (C(N) $\underline{\text{C}}\text{HCO}$ ), 87.1 (*p*-cymene  $\underline{\text{C}}\text{H}$ ), 84.6 (*p*-cymene  $\underline{\text{C}}\text{H}$ ), 84.5 (*p*-cymene  $\underline{\text{C}}\text{H}$ ), 79.6 (*p*-cymene  $\underline{\text{C}}\text{H}$ ), 30.5 (*p*-cymene  $\underline{\text{C}}\text{H}(\text{CH}_3)_2$ ), 24.7 ( $\underline{\text{C}}\text{H}_3\text{C}(\text{N})$ ), 23.4 (*p*-cymene  $\text{CH}(\underline{\text{C}}\text{H}_3)_2$ ), 20.9 (*p*-cymene  $\text{CH}(\underline{\text{C}}\text{H}_3)_2$ ), 18.4 (*p*-cymene  $\underline{\text{C}}\text{H}_3$ )

### Synthesis of $\text{IrC}_{20}\text{H}_{20}\text{O}_3\text{Cl}$ (5)

Triethylamine (0.10 g, 1.00 mmol) to a solution of 2-hydroxy-1,4-naphthoquinone (0.18 g, 1.00 mmol) in dichloromethane (25 ml). After 5 minutes,  $[\text{IrCp}^*\text{Cl}_2]_2$  (0.20 g, 0.33 mmol) was added and the resulting dark purple solution was stirred overnight. After removal of the solvent the crude product was recrystallised with layer diffusion using a dichloromethane/diethyl ether solvent system and washed with diethyl ether to yield dark purple crystals (0.17 g, 0.32 mmol, 64%). Single crystals suitable for X-ray crystallography were obtained from a dichloromethane/pentane vapour diffusion system.

**Analysis Calculated:** C 44.8; H 3.8; Cl 6.6%. **Analysis found:** C 44.6; H 3.9; Cl 6.9%

**ES+MS ( $\text{CH}_3\text{CN}$ ,  $m/z$ ):** 501.1  $[\text{M}-\text{Cl}]^+$

**${}^1\text{H}$  NMR:** ( $\text{CDCl}_3$ , 500 MHz, 300 K)  $\delta$  8.04 (d,  ${}^3J$ ( ${}^1\text{H}$ - ${}^1\text{H}$ ) = 7.5 Hz, 1H, aromatic  $\underline{\text{C}}\text{H}$  *peri* to C=O), 7.99 (d,  ${}^3J$ ( ${}^1\text{H}$ - ${}^1\text{H}$ ) = 7.5 Hz, 1H, aromatic  $\underline{\text{C}}\text{H}$  *peri* to C=O), 7.73 (t,  ${}^3J$ ( ${}^1\text{H}$ - ${}^1\text{H}$ ) = 7.0 Hz, 1H, aromatic  $\underline{\text{C}}\text{H}$  *ortho* to aromatic  $\text{CH}$  *peri* to C=O), 7.52 (t, 1H,  ${}^3J$ ( ${}^1\text{H}$ - ${}^1\text{H}$ ) = 7.0 Hz, aromatic  $\underline{\text{C}}\text{H}$  *ortho* to aromatic  $\text{CH}$  *peri* to C=O), 6.06 (s, 1H, aromatic  $\underline{\text{C}}\text{H}$  *ortho* to C=O), 1.72 (s, 15H,  $\underline{\text{C}}\text{H}_3$ ),

**${}^{13}\text{C}\{{}^1\text{H}\}$  NMR:** ( $\text{CDCl}_3$ , 125 MHz, 300 K)  $\delta$  197.9 (aromatic  $\underline{\text{C}}\text{O}$ ), 184.1 (aromatic  $\underline{\text{C}}\text{O}$ ), 172.6 (aromatic  $\underline{\text{C}}\text{O}$ ), 136.6 (aromatic  $\underline{\text{C}}\text{H}$  *ortho* to aromatic  $\text{CH}$  *peri* to C=O), 133.4 (aromatic  $\underline{\text{C}}$ ), 131.5 (aromatic  $\underline{\text{C}}\text{H}$  *ortho* to aromatic  $\text{CH}$  *peri* to C=O), 129.0 (aromatic  $\underline{\text{C}}$ ), 127.0 (aromatic  $\underline{\text{C}}\text{H}$  *peri* to C=O), 126.7 (aromatic  $\underline{\text{C}}\text{H}$  *peri* to C=O), 113.3 (aromatic  $\underline{\text{C}}\text{H}$  *ortho* and *meta* to C=O), 84.6 ( $\underline{\text{C}}\text{CH}_3$  on Cp\*), 9.4 ( $\underline{\text{C}}\text{CH}_3$  on Cp\*).

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