

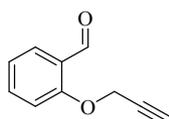
## Supporting information

### Pump-probe XAS investigation of the triplet state of Ir photosensitizer with chromenopyridinone ligands

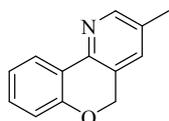
Grigory Smolentsev, Kaj M. van Vliet, Nicolo Azzaroli, Jeroen A. van Bokhoven, Albert M. Brouwer, Bas de Bruin, Maarten Nachtegaal and Moniek Tromp

#### Experimental procedures

**General Procedures.** All chemicals were purchased from commercial suppliers and were used without further purification. The ligand was synthesized according to work by Balci.<sup>1</sup> NMR spectra (<sup>1</sup>H, and <sup>13</sup>C{<sup>1</sup>H}) were measured on a Bruker AV400, AV300 or DRX 500 spectrometer, referenced internally to residual solvent resonance of CHCl<sub>3</sub> ( $\delta = 7.26$  ppm for <sup>1</sup>H,  $\delta = 77.2$  ppm for <sup>13</sup>C). Mass spectra were collected on an AccuTOF LC, JMS-T100LP Mass spectrometer (JEOL, Japan) with a coldspray ionization (CSI) source (JEOL). The CSI apparatus features a liquid nitrogen cooling device to maintain the temperature of the capillary and spray itself between 0 °C and – 50 °C. Typical measurement conditions are as follows: Positive-ion mode; Needle voltage 2000V, Orifice 1 voltage 90V, Orifice 2 voltage 9V, Ring Lens voltage 22V. Ion source temperature 30 0C, spray temperature - 20 0C. Flow injection with a flow rate of 0.01 ml/min. All mass spectra were recorded with an average duration of 0.5 min. The UV-vis absorption spectrum was measured in a quartz cuvette (1 cm, Hellma) on a Shimadzu UV2700 spectrophotometer. The fluorescence emission spectrum was recorded on a SPEX Fluorolog 3 fluorometer and are corrected for fluctuations of the excitation source flux and wavelength dependence of the detection system. All steady-state measurements were done at 21°C.

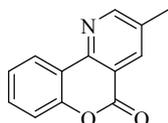


**Synthesis of 2-(2-propyn-1-yloxy)-benzaldehyde.**<sup>1</sup> To a 100 mL round-bottom flask was added salicylaldehyde (4.35 mL, 41 mmol, 1 eq.) and DMF (24 mL). This solution changed to a yellow suspension when K<sub>2</sub>CO<sub>3</sub> (8.6 g, 62 mmol, 1.5 eq.) was added. After addition of propargyl bromide (5.4 mL, 49 mmol, 1.2 eq.) the suspension turned brown. After stirring for 24 h H<sub>2</sub>O (250 mL) was added and the product was extracted with EtOAc (150 mL). The organic layer was washed with H<sub>2</sub>O (2x 250 mL) and dried over MgSO<sub>4</sub>. Evaporation of the solvent gave the product as a yellow solid (6.37 g, 39.8 mmol, 97% yield). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ = 10.49 (s, 1H), 7.87 (dd,  $J = 7.7$  Hz, 1.8 Hz, 1H), 7.57 (ddd,  $J = 8.6$  Hz, 7.2 Hz, 1.8 Hz, 1H), 7.12 (d,  $J = 8.4$  Hz, 1H), 7.09 (t,  $J = 7.6$  Hz, 1H), 4.84 (d,  $J = 2.4$  Hz, 2H), 2.57 (t,  $J = 2.4$  Hz, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ = 189.7, 159.9, 135.9, 128.8, 125.7, 121.9, 113.3, 100.1, 77.8, 76.62, 56.5.

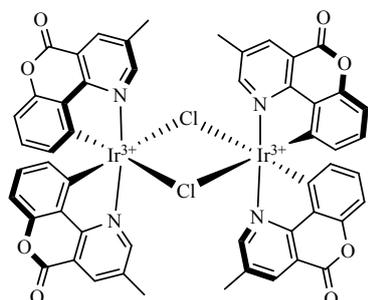


**Synthesis of 3-Methyl-5H-chromeno[4,3-b]pyridine.**<sup>1</sup> To a yellow solution of 2-(2-propyn-1-yloxy)-benzaldehyde (2 g, 12.5 mmol, 1 eq.) in EtOH (60 mL) was added DBU (1.9 mL, 12.7 mmol, 1.02 eq.) at r.t.. To the resulting orange solution was added propargyl amine (1.6 mL, 25 mmol, 2 eq.) and the

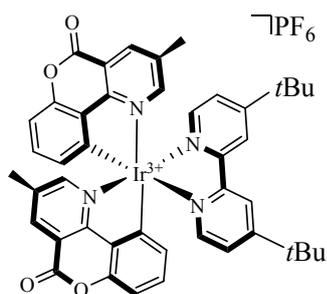
reaction mixture was refluxed at 80 °C for 90 h. Then the reaction mixture was allowed to cool to r.t. and the solvent was evaporated. To the concentrate was added EtOAc (160 mL) and this was washed with water (3x 160 mL) and brine (160 mL), dried over MgSO<sub>4</sub> and concentrated in vacuo to give a black oil. This oil is purified by flash chromatography (20% EtOAc in hexane) to give the product as a pale orange solid (1.85 g, 9.4 mmol, 75% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ= 8.41 (s, 1H), 8.18 (dd, *J*= 7.7 Hz, 1.6 Hz, 1H), 7.29 (dt, *J*= 1.7 Hz, 7.8 Hz, 1H), 7.09 (t, *J*=7.1 Hz, 1H), 6.96 (d, *J*= 8.1 Hz, 1H), 5.18 (s, 2H), 2.36 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ= 156.2, 149.9, 146.2, 132.7, 132.3, 130.9, 125.8, 124.4, 123.4, 122.5, 117.0, 68.0, 18.5.



**Synthesis of 3-Methyl-5H-chromeno[4,3-b]pyridin-5-one (ChpH).**<sup>1</sup> To a mixture of CrO<sub>3</sub> (9.5 g, 95 mmol, 18.6 eq.) and DCM (100 mL) was added pyridine (12.5 mL, 155 mmol, 30 eq.). After 20 minutes of stirring at r.t., the mixture was cooled to 0 °C and a 40 mL DCM solution of 3-Methyl-5H-chromeno[4,3-b]pyridine (1 g, 5.1 mmol) was added dropwise. The reaction mixture was stirred for 21 h at r.t.. The reaction mixture was filtered over a silica plug with DCM and the filtrate was concentrated in vacuo to give the product as a white solid (1.0 g, 4.7 mmol, 93% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ= 8.86 (d, *J*= 2.0 Hz, 1H), 8.56 (d, *J*= 7.7 Hz, 1H), 8.42 (dd, *J*= 2.2 Hz, 0.8 Hz, 1H), 7.56 (dt, *J*= 1.7 Hz, 7.8 Hz, 1H), 7.41 (t, *J*=7.8 Hz, 2H), 7.39 (d, *J*= 7.7 Hz, 1H), 2.52 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ= 161.6, 156.9, 152.4, 149.6, 137.9, 134.2, 131.9, 125.0, 124.6, 119.6, 117.3, 117.0, 18.6.



**Synthesis of [Ir(Chp)<sub>2</sub>Cl]<sub>2</sub>.** To a flame-dried 50 mL Schlenk was added IrCl<sub>3</sub>·*n*H<sub>2</sub>O (200 mg, 0.56 mmol, 1 eq.) and chromenopyridine **1a** (473 mg, 2.24 mmol, 4 eq.). Then H<sub>2</sub>O (degassed, 5 mL) and 2-methoxyethanol (degassed, 15 mL) were added at r.t. and the reaction mixture was refluxed at 120 °C under N<sub>2</sub> for 30h. The reaction was allowed to cool down to r.t. and H<sub>2</sub>O (20 mL) was added to precipitate the product, which was collected by suction filtration. The orange-yellow residue was purified by soxhlet extraction, where excess ligand was extracted with hexane and the complex was extracted with DCM. Evaporation of the solvent gives the complex as a yellow solid (305 mg, 0.23 mmol, 85% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 9.09 (s, 4H), 8.51 (s, 4H), 6.84 (t, *J* = 7.8 Hz, 4H), 6.76 (d, *J* = 8.1 Hz, 4H), 5.70 (d, *J* = 7.6 Hz, 4H), 2.25 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 164.23, 160.68, 156.36, 151.20, 139.91, 138.73, 133.14, 132.51, 127.56, 125.87, 109.48, 19.36.

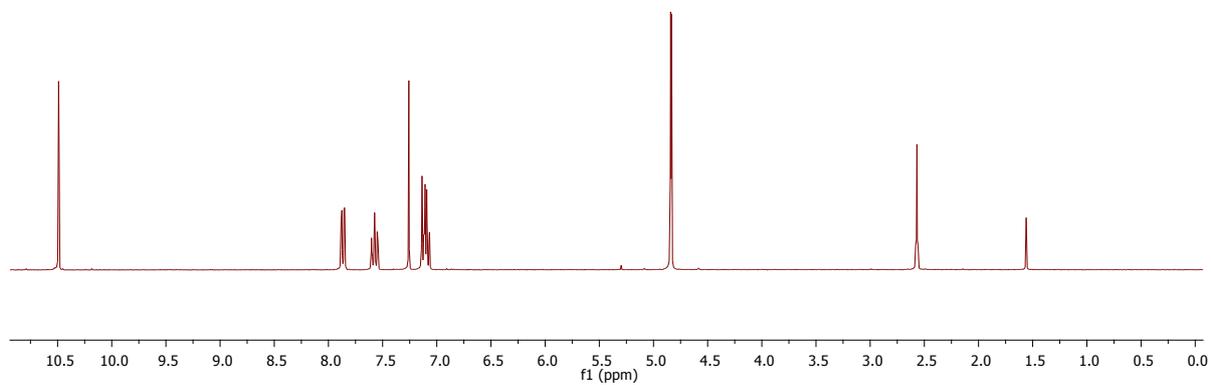
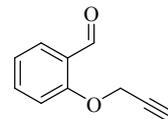


**Synthesis of [Ir(Chp)<sub>2</sub>(dtbbpy)]PF<sub>6</sub>.** To a flame-dried 25 mL schlenk was added [Ir(Chp)<sub>2</sub>Cl]<sub>2</sub> (110 mg, 0.08 mmol), 4,4'-Di-tert-butyl-2,2'-dipyridyl (dtbbpy, 50 mg, 0.18 mmol, 2.25 eq.) and ethylene glycol (4.2 mL). This orange suspension was heated overnight at 150 °C under a nitrogen atmosphere. The resulting orange solution was cooled to room temperature, H<sub>2</sub>O (40 mL) was added the aqueous mixture was washed with diethyl ether (3x20 mL). The aqueous layer was heated to 70 °C and a solution of NH<sub>4</sub>PF<sub>6</sub> (2.6 M, 4.2 mL) was added to give a yellow suspension that was cooled to 0 °C and filtered to give the product as a yellow solid. The crude product was further recrystallized by slow vapor diffusion from chloroform and pentane. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.36 (s, 1H), 7.92 (d, *J* = 5.9 Hz, 1H), 7.65 (s, 1H), 7.46 (d, *J* = 5.9 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 1.45 (s, 11H), 6.10 (d, *J* = 7.3 Hz, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 164.86, 162.86, 160.27, 156.26, 154.43, 151.57, 149.82, 146.72, 139.81, 133.26, 127.73, 126.84, 125.77, 123.07, 109.98, 35.89, 30.18, 18.95. *m/z* (ESI<sup>+</sup>) [C<sub>44</sub>H<sub>40</sub>Ir<sub>1</sub>N<sub>4</sub>O<sub>4</sub>]<sup>+</sup> calc. 881.31 / found 881.27 ; [C<sub>44</sub>H<sub>40</sub>Ir<sub>1</sub>N<sub>4</sub>O<sub>4</sub>+CH<sub>4</sub>O]<sup>+</sup> calc. 913.29 / found 913.26. The isotope pattern for the complex matches with the measurement.

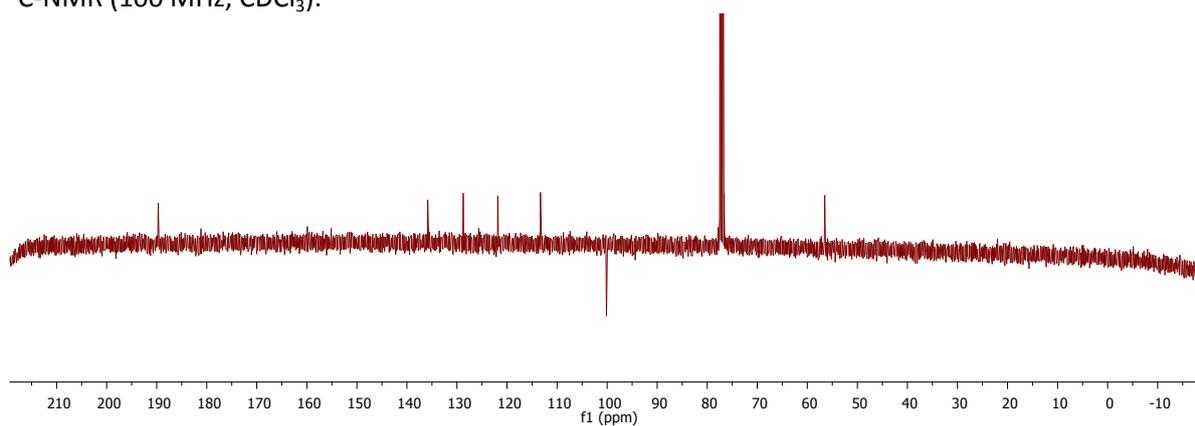
# Spectra

## 2-(2-propyn-1-yloxy)-benzaldehyde

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):

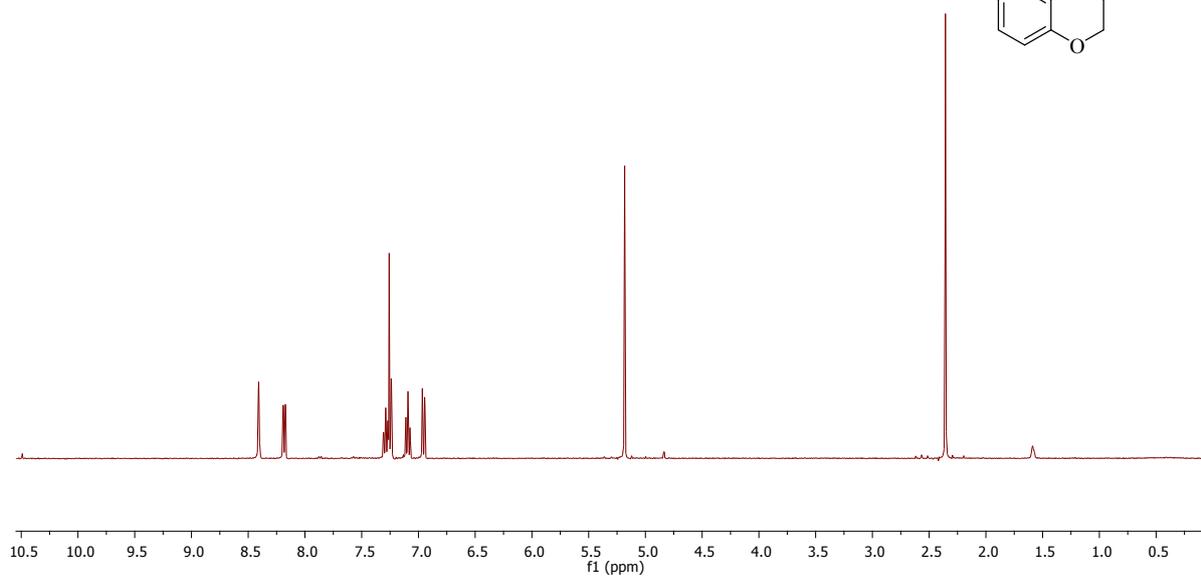
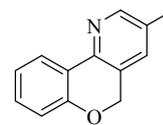


$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):

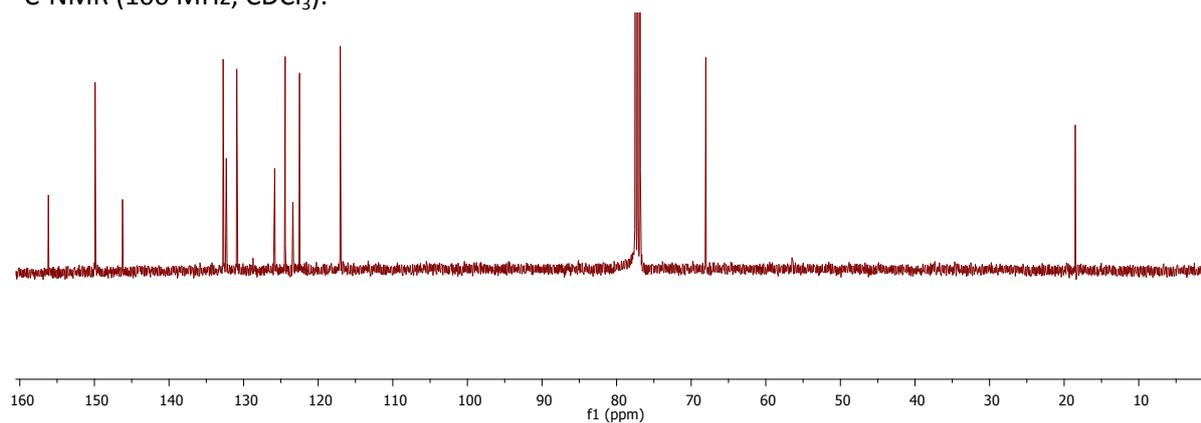


### 3-Methyl-5H-chromeno[4,3-b]pyridine

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )

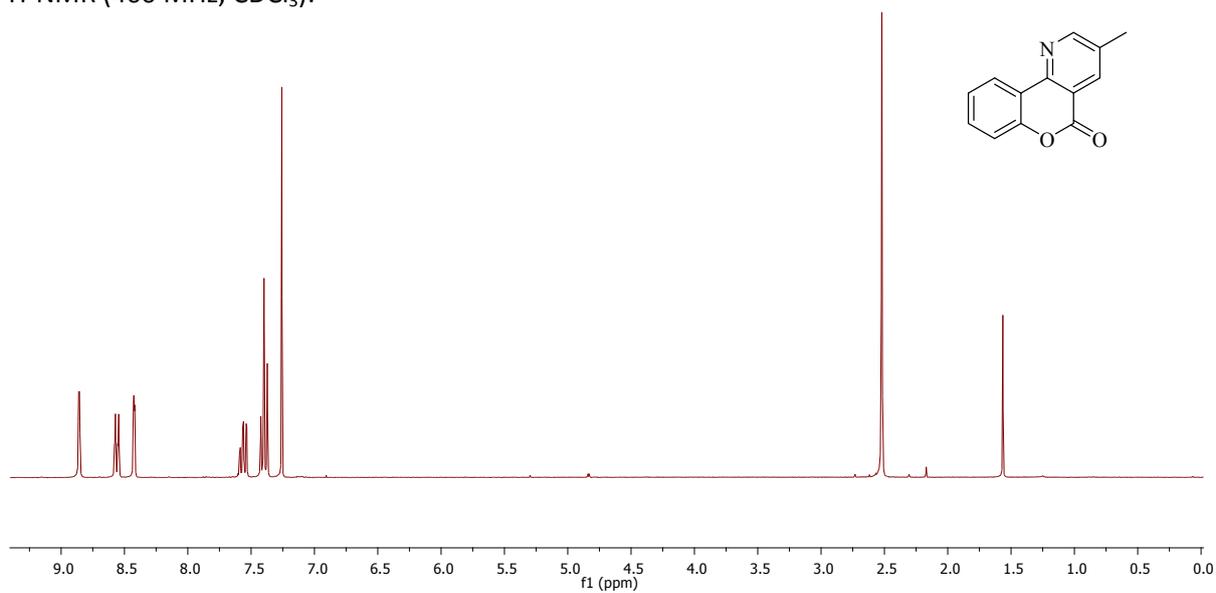


$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):

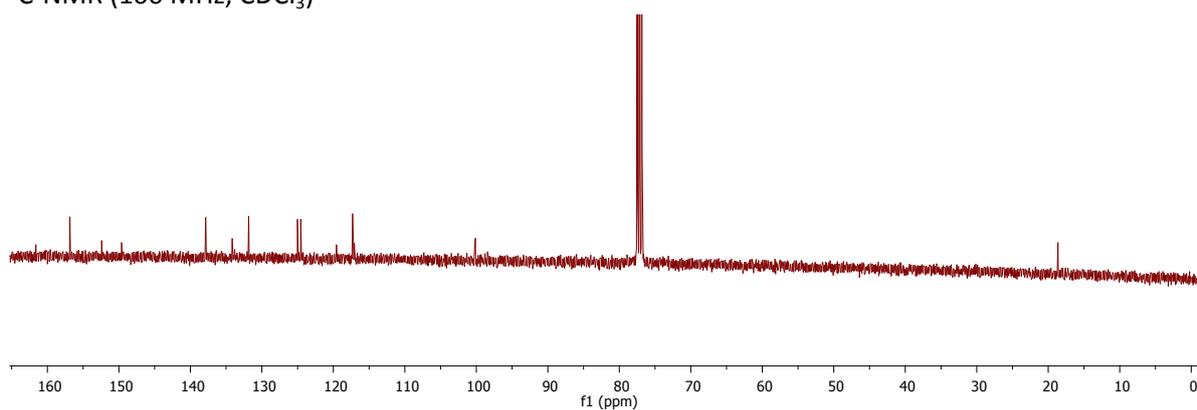


### 3-Methyl-5H-chromeno[4,3-b]pyridin-5-one (ChpH)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):

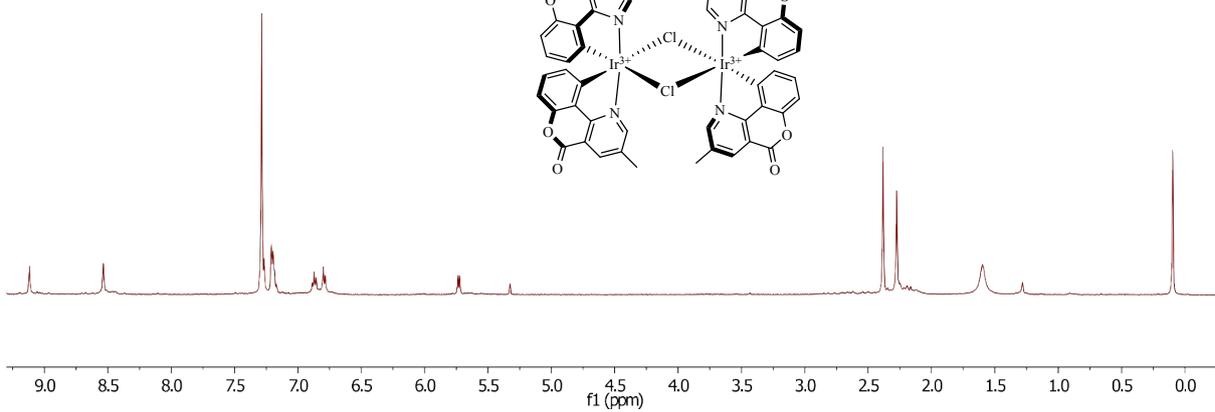
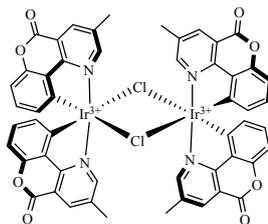


$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )

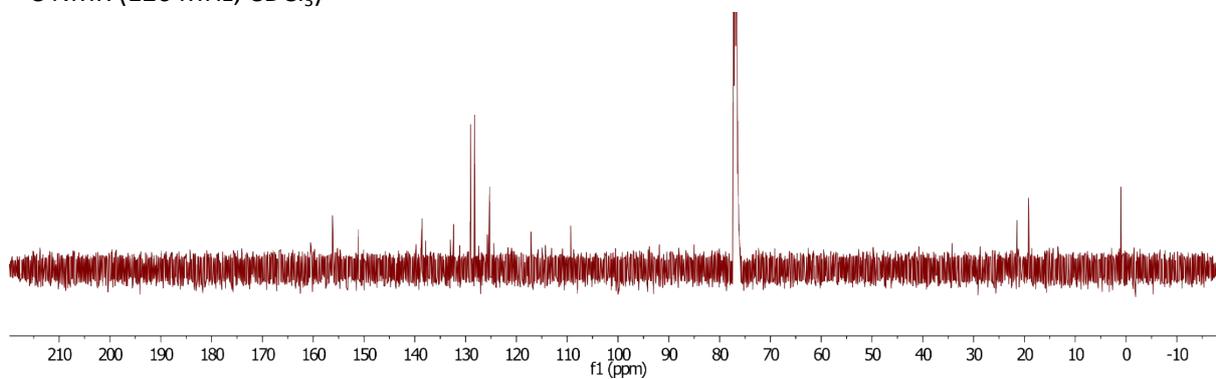


**[Ir(Chp)<sub>2</sub>Cl]<sub>2</sub>**

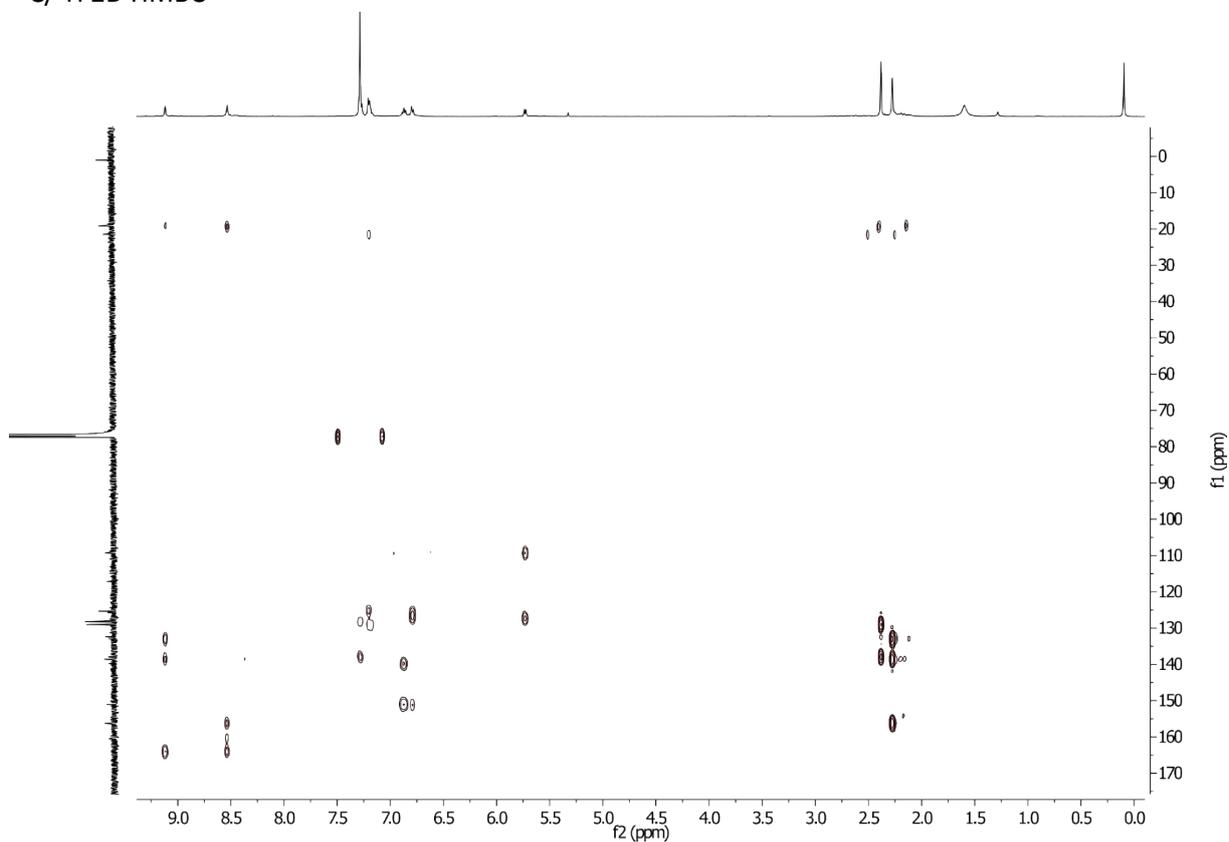
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



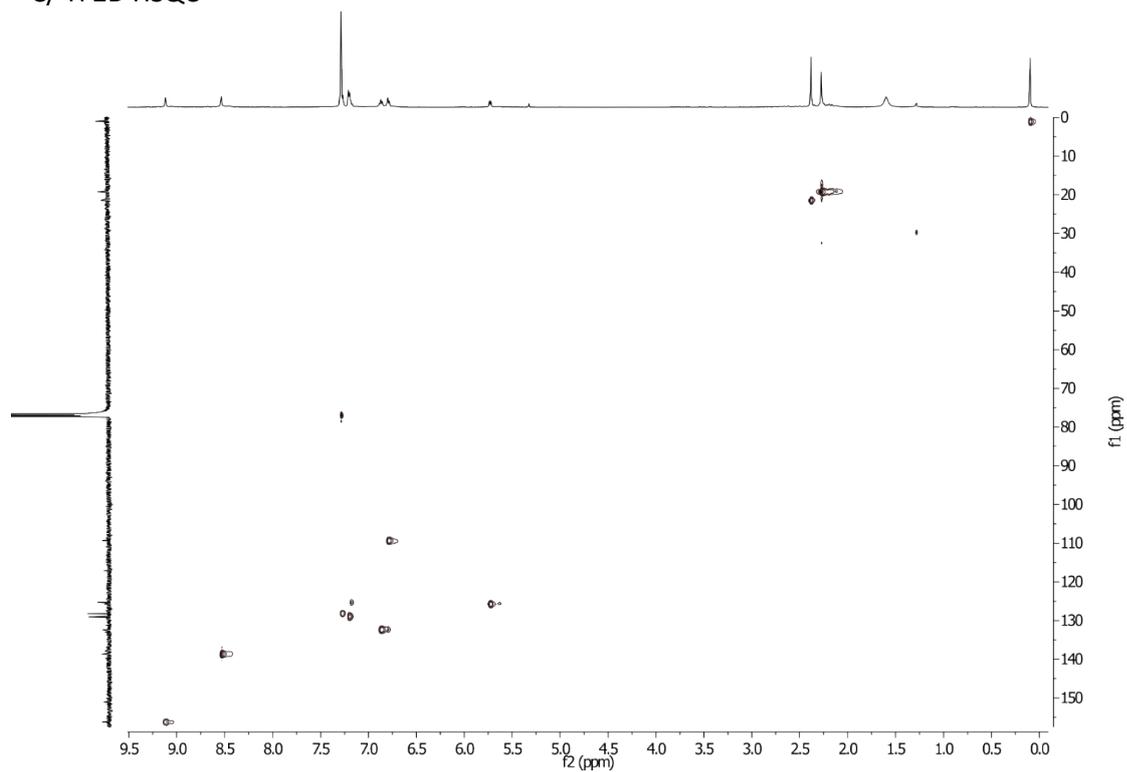
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C/<sup>1</sup>H 2D HMBC

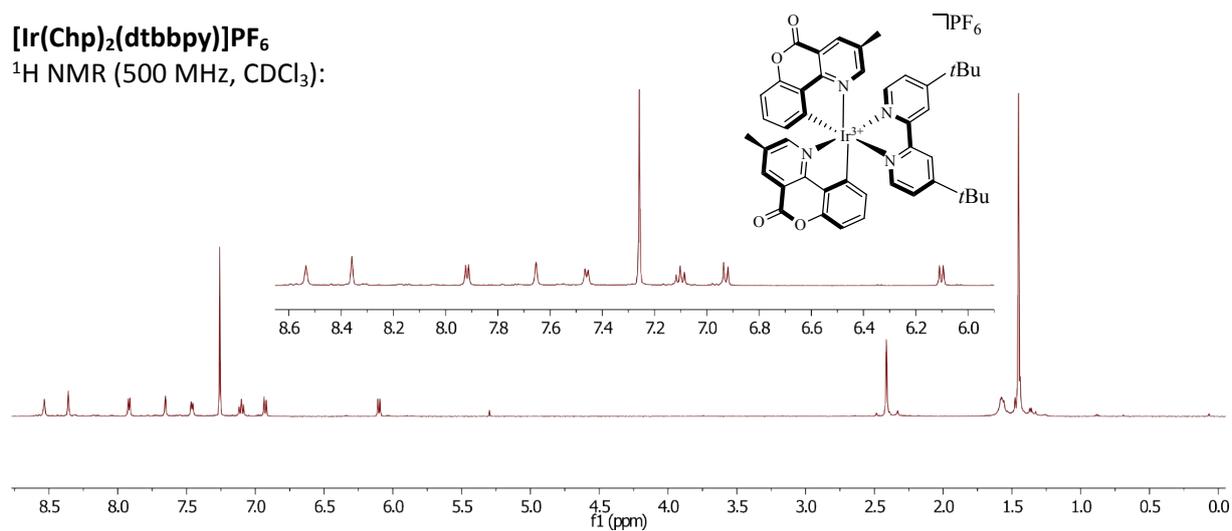


$^{13}\text{C}/^1\text{H}$  2D HSQC

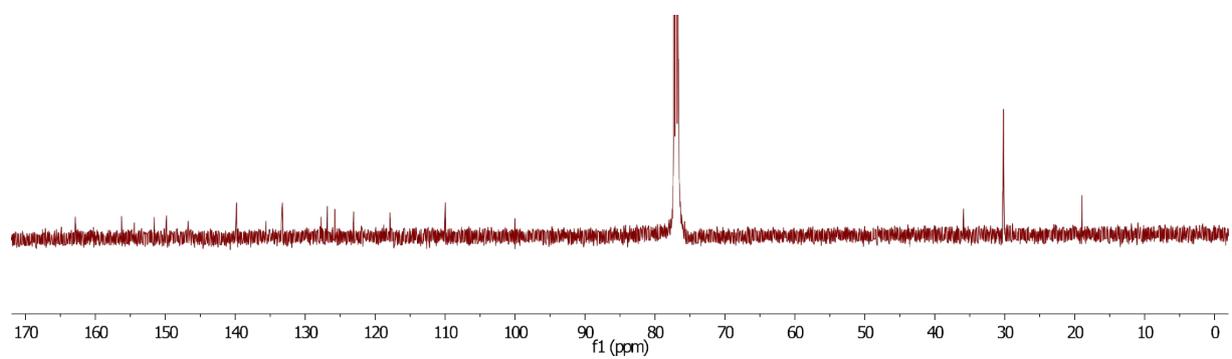


**[Ir(Chp)<sub>2</sub>(dtbbpy)]PF<sub>6</sub>**

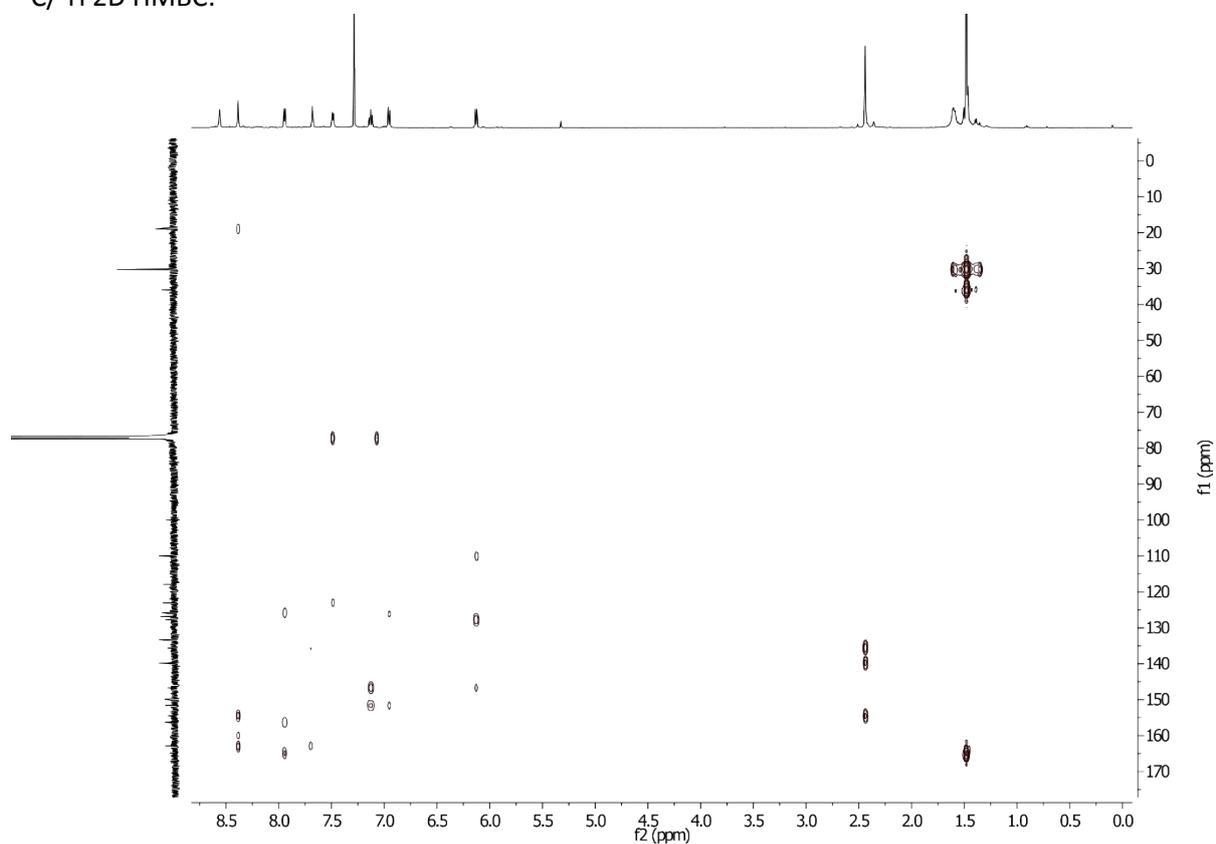
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):



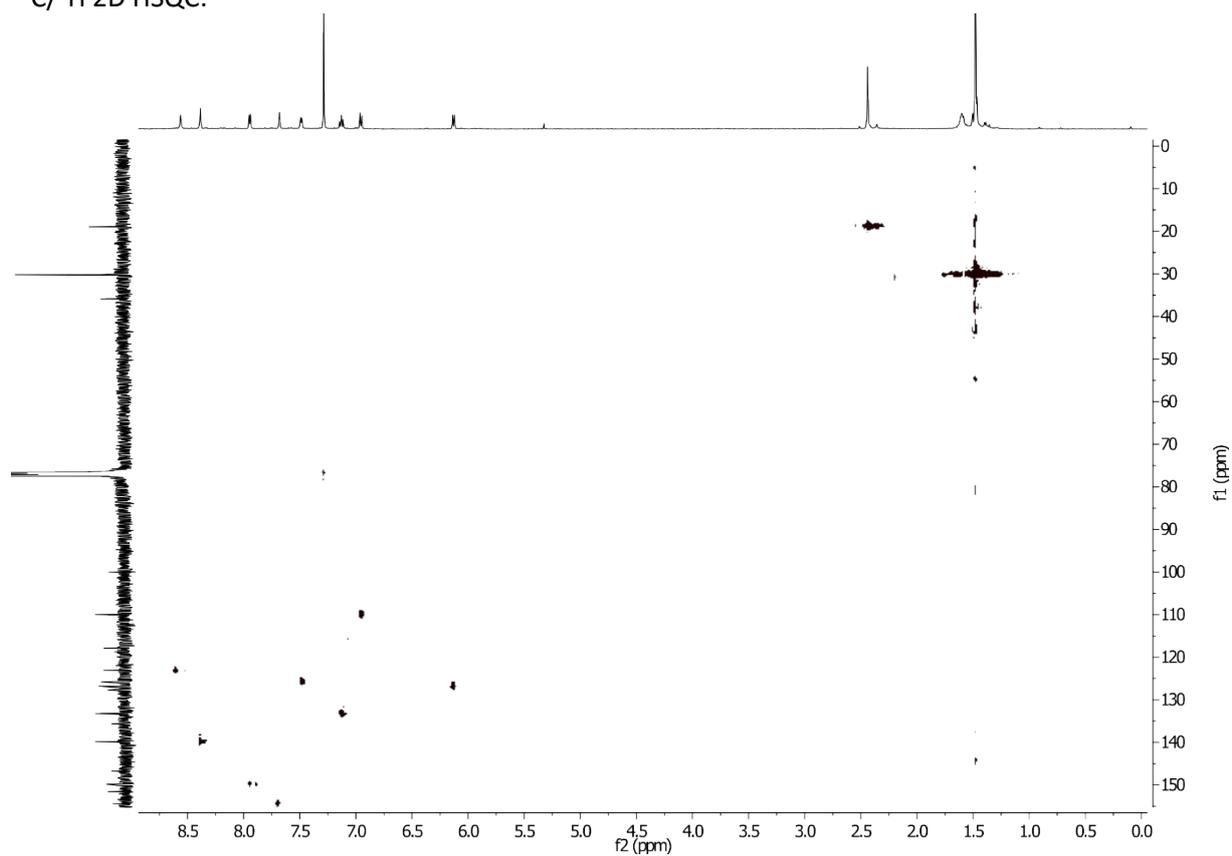
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)



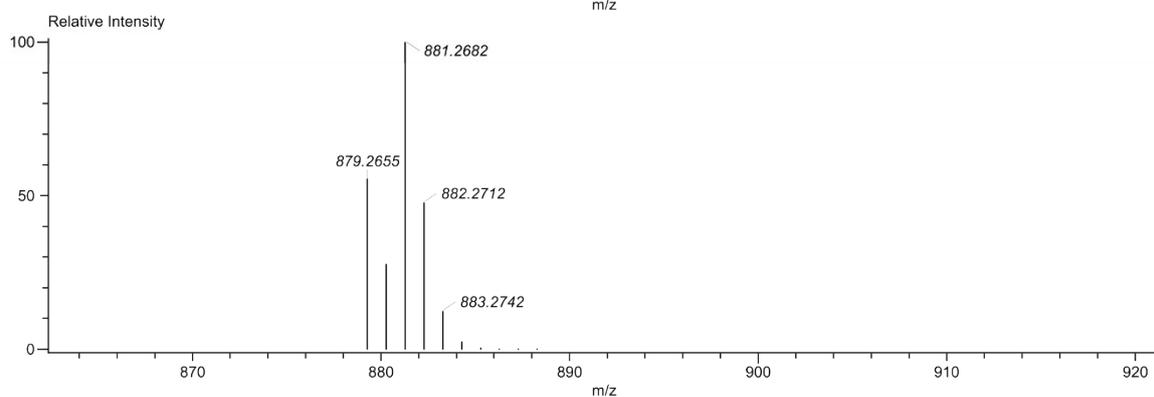
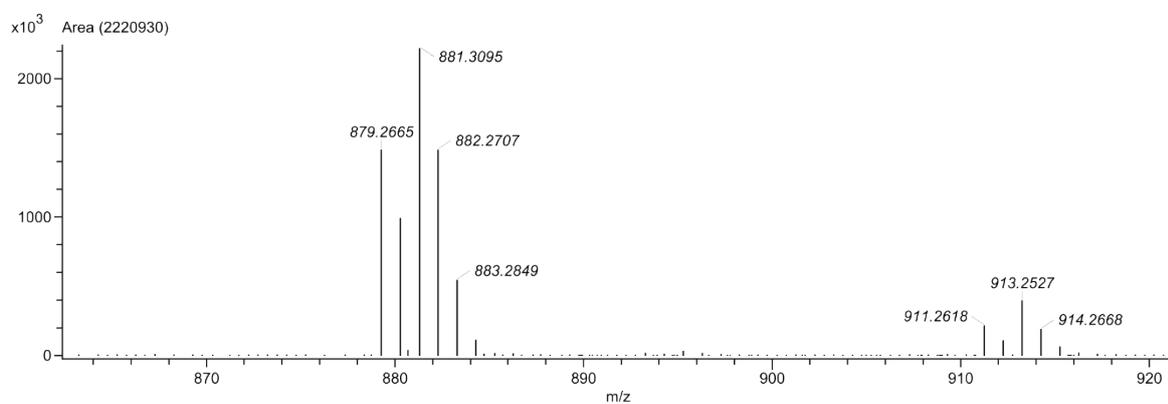
<sup>13</sup>C/<sup>1</sup>H 2D HMBC:



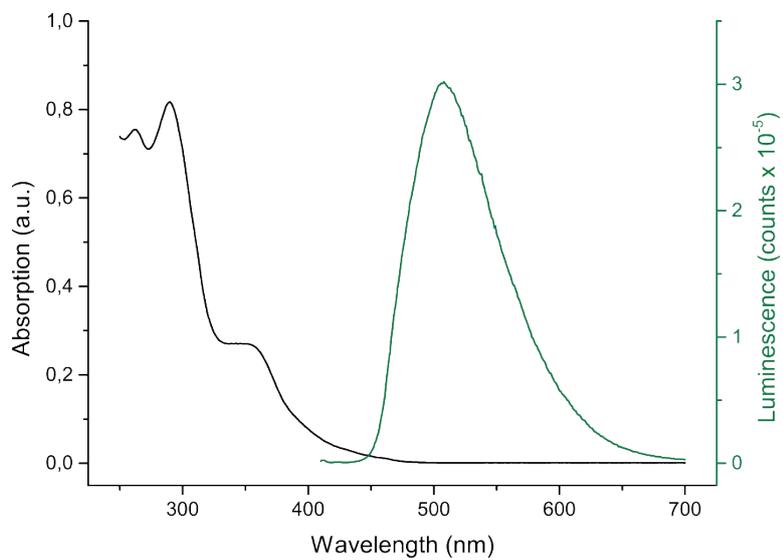
$^{13}\text{C}/^1\text{H}$  2D HSQC:



The measured coldspray<sup>+</sup> ionization mass spectrum (top) and the calculated isotope pattern for  $[\text{Ir}(\text{Chp})_2(\text{dtbbpy})]^+$ .



The measured UV-Vis spectrum of  $[\text{Ir}(\text{Chp})_2(\text{dtbbpy})]\text{PF}_6$  in degassed DCM (black line) and the luminescence spectrum recorded with 400 nm excitation (green line).



## Structures

Optimized structure of Ir complex with two 5-oxo-5*H*-chromeno[4,3-*b*]pyridin-10-ide and one 2,2'-bipyridine ligands

Singlet (ground) state with lowest energy

Atom	X	Y	Z (Angstrom)
Ir	0.000000	0.000000	-0.011508
H	2.915113	3.192577	-4.167602
C	0.618802	0.408927	2.968875
C	1.254419	0.845917	4.142806
H	2.639843	-0.576482	-2.060519
C	-2.927553	-1.935175	2.802238
C	-2.257290	-1.476880	1.669206
N	-1.130358	-0.727719	1.737673
C	-0.618802	-0.408927	2.968875
C	-1.254419	-0.845917	4.142806
C	-2.416202	-1.613003	4.062724
C	2.416202	1.613003	4.062724
H	-3.828835	-2.532564	2.689970
H	-2.615467	-1.699219	0.667734
H	3.828835	2.532564	2.689970
N	1.130358	0.727719	1.737673
H	-2.911209	-1.953550	4.969198
C	2.257290	1.476880	1.669206
C	2.927553	1.935175	2.802238
H	2.911209	1.953550	4.969198
H	2.615467	1.699219	0.667734
O	-0.861900	-4.319072	-2.959089
C	-0.701947	-2.206763	-1.762382
C	-1.326790	-3.032286	-2.714050
C	0.253562	-4.871542	-2.294580
C	2.635772	-3.555542	0.344297
C	2.082852	-2.285738	0.541259
N	0.994873	-1.852130	-0.136976
C	0.426480	-2.706404	-1.055662
C	0.930884	-3.998475	-1.292759
C	2.056206	-4.429943	-0.580240
C	-2.429729	-2.561930	-3.427460
H	3.513149	-3.845047	0.916530
H	2.517617	-1.589792	1.252454
H	-3.727650	-0.876276	-3.713113
C	-1.138804	-0.882584	-1.478020
H	2.456740	-5.425392	-0.757831
C	-2.246295	-0.427185	-2.206259
C	-2.872140	-1.259855	-3.159114
O	0.585908	-6.000454	-2.568004
H	-2.915113	-3.192577	-4.167602
H	-2.639843	0.576482	-2.060519
O	0.861900	4.319072	-2.959089
C	0.701947	2.206763	-1.762382

C	1.326790	3.032286	-2.714050
C	-0.253562	4.871542	-2.294580
C	-2.635772	3.555542	0.344297
C	-2.082852	2.285738	0.541259
N	-0.994873	1.852130	-0.136976
C	-0.426480	2.706404	-1.055662
C	-0.930884	3.998475	-1.292759
C	-2.056206	4.429943	-0.580240
C	2.429729	2.561930	-3.427460
H	-3.513149	3.845047	0.916530
H	-2.517617	1.589792	1.252454
H	3.727650	0.876276	-3.713113
C	1.138804	0.882584	-1.478020
H	-2.456740	5.425392	-0.757831
C	2.246295	0.427185	-2.206259
C	2.872140	1.259855	-3.159114
O	-0.585908	6.000454	-2.568004
H	0.845450	0.592387	5.115736
H	-0.845450	-0.592387	5.115736

Optimized structure of Ir complex with two 5-oxo-5*H*-chromeno[4,3-*b*]pyridin-10-ide and one 2,2'-bipyridine ligands

Triplet (photoexcited) state with lowest energy

Atom	X	Y	Z (Angstrom)
Ir	0.000000	0.000000	-0.063108
H	3.009538	3.297950	-4.011564
C	0.623950	0.364996	2.937463
C	1.335815	0.721833	4.109029
H	2.747653	-0.490944	-1.943114
C	-3.008569	-1.806467	2.755174
C	-2.293836	-1.424476	1.631396
N	-1.130976	-0.717750	1.690686
C	-0.623950	-0.364996	2.937463
C	-1.335815	-0.721833	4.109029
C	-2.517538	-1.437817	4.028277
C	2.517538	1.437817	4.028277
H	-3.925973	-2.377385	2.641188
H	-2.645206	-1.677106	0.635688
H	3.925973	2.377385	2.641188
N	1.130976	0.717750	1.690686
H	-3.058977	-1.707839	4.931885
C	2.293836	1.424476	1.631396
C	3.008569	1.806467	2.755174
H	3.058977	1.707839	4.931885
H	2.645206	1.677106	0.635688
O	-0.884675	-4.363131	-2.892262
C	-0.721250	-2.257848	-1.708618
C	-1.359825	-3.097359	-2.628765
C	0.276173	-4.898337	-2.249540
C	2.699350	-3.511079	0.314893

C	2.142106	-2.244845	0.505017
N	1.027941	-1.837554	-0.161123
C	0.447105	-2.723740	-1.040565
C	0.962852	-4.007154	-1.277266
C	2.116274	-4.414548	-0.584662
C	-2.507538	-2.645811	-3.300875
H	3.590223	-3.780939	0.876100
H	2.581113	-1.530446	1.194332
H	-3.865227	-0.996522	-3.556151
C	-1.178281	-0.931161	-1.429244
H	2.530234	-5.404925	-0.754665
C	-2.338086	-0.501745	-2.113505
C	-2.978655	-1.349016	-3.032438
O	0.610561	-6.019160	-2.539006
H	-3.009538	-3.297950	-4.011564
H	-2.747653	0.490944	-1.943114
O	0.884675	4.363131	-2.892262
C	0.721250	2.257848	-1.708618
C	1.359825	3.097359	-2.628765
C	-0.276173	4.898337	-2.249540
C	-2.699350	3.511079	0.314893
C	-2.142106	2.244845	0.505017
N	-1.027941	1.837554	-0.161123
C	-0.447105	2.723740	-1.040565
C	-0.962852	4.007154	-1.277266
C	-2.116274	4.414548	-0.584662
C	2.507538	2.645811	-3.300875
H	-3.590223	3.780939	0.876100
H	-2.581113	1.530446	1.194332
H	3.865227	0.996522	-3.556151
C	1.178281	0.931161	-1.429244
H	-2.530234	5.404925	-0.754665
C	2.338086	0.501745	-2.113505
C	2.978655	1.349016	-3.032438
O	-0.610561	6.019160	-2.539006
H	0.953342	0.424076	5.080526
H	-0.953342	-0.424076	5.080526

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<sup>1</sup> S. Keskin, M. Balci, *Org. Lett.* **2015**, *17*, 964