

Supporting Information for

Highly Luminescent Cyclometalated Iridium Complexes Generated by Nucleophilic Addition to Coordinated Isocyanides

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Contents

<i>Index</i>	<i>Page</i>
Experimental Section	S2–S7
X-ray crystallographic summary tables	S8–S9
Cyclic voltammograms for new complexes	S10–S13
UV-vis absorption of new complexes	S14–S15
Emission spectra of 3b and 4b	S16
Excitation spectra of 3a , 3b , 4a , and 4b	S17–S18
Photostability data	S19–S20
NMR spectra for all new complexes	S21–S31
References	S32

Experimental Section

Materials. Reactions were performed in ambient conditions unless otherwise stated. Dry solvents were obtained from a Grubbs Solvent Purification System and degassed with argon. Starting materials and reagents, unless otherwise specified, were obtained from commercial sources and used without further purification. Previously reported $\text{Ir}(\text{F}_2\text{ppy})_2(\text{CNAr}^{\text{NO}_2})(\text{Cl})$ (**1b**) was synthesized by the reaction of the chloro bridged Ir dimer $[\text{Ir}(\text{F}_2\text{ppy})_2(\mu\text{-Cl})]_2$ in dichloromethane with 2 equiv of 4-nitrophenyl isocyanide.¹

Physical Methods. ^1H , ^{13}C and ^{19}F NMR spectra were recorded at room temperature using a JEOL ECA-500 or ECA-600 NMR spectrometer. UV-vis absorption spectra were recorded in dichloromethane in screw-capped 1 cm quartz cuvettes using an Agilent Carey 8454 UV-vis spectrophotometer. Steady-state emission and excitation spectra were recorded using a Horiba FluoroMax-4 spectrofluorometer. To exclude air, samples for emission spectra were prepared in a nitrogen-filled glove-box using dry, deoxygenated solvents. Samples for room-temperature emission were housed in 1 cm quartz cuvettes with septum-sealed screw caps, and samples for low-temperature emission were contained in a custom quartz EPR tube with high-vacuum valve and immersed in liquid nitrogen using a finger Dewar. Emission quantum yields were determined relative to a standard of quinine sulfate in 0.05 M sulfuric acid, which has a reported fluorescence quantum yield (Φ_{F}) of 0.52.² The quantum yields of complexes doped into poly(methyl methacrylate) (PMMA) thin films were recorded using a Spectralon-coated integrating sphere (150 mm diameter, Labsphere) exciting at 365 nm. Phosphorescence lifetimes were measured on a Horiba DeltaFlex Lifetime System, using 330 nm excitation. Cyclic voltammetry (CV) experiments were performed with a CH Instruments 602E potentiostat using a three-electrode system in a nitrogen-filled glove-box. A 3 mm diameter glassy-carbon electrode, Pt wire, and silver wire were used as working electrode, counter electrode, and pseudoreference electrode, respectively. Measurements were carried out in acetonitrile solution with 0.1 M TBAPF₆ as a supporting electrolyte at scan rate of 0.1 V/s. Ferrocene was used as an internal standard, and potentials were referenced to the ferrocene/ferrocenium couple. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

PMMA film fabrication. A solution of PMMA (98 mg, 35 kDa) in dichloromethane (1.0 mL) was stirred at room temperature in a nitrogen-filled glove-box. Then, the respective iridium complex (2 mg, 2 wt. %) was added to the solution and stirred, yielding a bright yellow (**3a**, **3b**) or orange (**4a**, **4b**) solution. The resulting solution was drop coated on a quartz substrate and dried at room temperature overnight.

Synthesis

Synthesis of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{CNAr}^{\text{CF}_3})(\text{Cl})$ (1a**).** $[\text{Ir}(\text{F}_2\text{ppy})_2(\mu\text{-Cl})]_2$ (290 mg, 0.238 mmol) was suspended in 30 mL of CH_2Cl_2 inside the glove box. 4-trifluoromethylphenyl isocyanide (84 mg, 0.49 mmol) was added to the mixture. After 12 h of stirring at room temperature the solvent was removed under vacuum. The yellow solid was washed with excess of hexane and dried

under vacuum. Yield: 88 % (327 mg, 0.420 mmol). ^1H and ^{19}F NMR spectra suggest the formation of two isomeric products in a 1:3.8 ratio. Some of the peaks were overlapped and could not be definitively assigned. ^1H NMR (600 MHz, Acetone- d_6): **Major isomer** : δ = 9.93 (d, J = 5.5 Hz, 1H), 9.48 (d, J = 6.2 Hz, 1H), 8.35 (d, J = 8.3 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H), 8.17 (t, J = 7.6 Hz, 1H), 8.12 (t, J = 7.6 Hz, 1H), 7.82 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 5.5 Hz, 1H), 7.44 (t, J = 6.9 Hz, 1H), 6.60–6.56 (m, 1H), 6.53–6.49 (m, 1H), 5.90 (dd, J = 2.75, 8.59 Hz, 1H), 5.46 (dd, J = 2.1, 8.3 Hz, 1H). **Minor isomer** : δ = 9.55 (d, J = 4.8 Hz, 1H), 8.38 (d, J = 8.3 Hz, 1H), 8.21 (d, J = 8.3 Hz, 1H), 7.98 (dd, J = 2.8, 9.3 Hz, 1H), 7.95 (d, J = 5.5 Hz, 1H), 7.65 (d, J = 8.9 Hz, 2H), 7.53 (t, J = 6.2 Hz, 1H), 7.01 (t, J = 6.19 Hz, 1H), 6.89–6.85 (m, 1H), 6.48–6.46 (m, 1H), 5.96 (dd, J = 2.8, 8.3 Hz, 1H). ^{19}F NMR (565 MHz, Acetone- d_6): **Major isomer** : δ = –63.37 (s, CF_3 , 3F), –109.12 (q, J = 8.9 Hz, 1F), –109.59 (q, J = 8.9 Hz, 1F), –109.59 (t, J = 10.5 Hz, 1F), –111.32 (t, J = 9.7 Hz, 1F). **Minor isomer** : –63.34 (s, CF_3 , 3F), –108.50 (q, J = 9.7 Hz, 1F), –110.33 (q, J = 8.9 Hz, 1F), –110.95 (t, J = 9.7 Hz, 1F), –112.08 (t, J = 9.7 Hz, 1F).

Synthesis of $\text{Ir}(\text{bt})_2(\text{CNAr}^{\text{CF}_3})(\text{Cl})$ (2a). $[\text{Ir}(\text{bt})_2(\mu\text{-Cl})]_2$ (160 mg, 0.124 mmol) was suspended in 30 mL of CH_2Cl_2 inside the glove box. 4-trifluoromethylphenyl isocyanide was added (50 mg, 0.29 mmol) to the mixture. After 12 h of stirring at room temperature the solvent was removed under vacuum. The yellow solid was washed with excess of hexane and dried under vacuum. Yield: 76% (153 mg, 0.187 mmol). ^1H NMR (500 MHz, Acetone- d_6): δ = 10.07–10.05 (m, 1H), 8.54 (d, J = 8.6 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.23–8.21 (m, 1H), 7.81 (d, J = 8.6 Hz, 2H), 7.78–7.71 (m, 3H), 7.63–7.58 (m, 5H), 6.92 (q, J = 7.5 Hz, 2H), 6.78 (td, J = 1.2, 7.5 Hz, 1H), 6.74 (td, J = 1.2, 7.5 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 6.28 (d, J = 7.5 Hz, 1H). ^{19}F NMR (470 MHz, Acetone- d_6): δ = –63.33 (s, CF_3 , 3F).

Synthesis of $\text{Ir}(\text{bt})_2(\text{CNAr}^{\text{NO}_2})(\text{Cl})$ (2b). $[\text{Ir}(\text{bt})_2(\mu\text{-Cl})]_2$ (100 mg, 0.0773 mmol) was suspended in 30 mL of CH_2Cl_2 inside the glove box. 4-nitrophenyl isocyanide was added (23 mg, 0.16 mmol) to the mixture. After 12 h of stirring at room temperature the solvent was removed under vacuum. The yellow solid was washed with excess of hexane and dried under vacuum. Yield: 80 % (98 mg, 0.12 mmol). ^1H NMR (500 MHz, Acetone- d_6): δ = 10.06–10.04 (m, 1H), 8.53 (d, J = 8.0 Hz, 1H), 8.31–8.29 (m, 2H), 8.27 (d, J = 8.0 Hz, 1H), 8.23–8.21 (m, 1H), 7.78 (td, J = 1.2, 7.5 Hz, 1H), 7.76–7.72 (m, 2H), 7.65–7.58 (m, 5H), 6.93 (q, J = 7.5 Hz, 2H), 6.79 (td, J = 1.2, 7.5 Hz, 1H), 6.75 (td, J = 1.2, 7.5 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 6.27 (d, J = 7.5 Hz, 1H).

General procedure for preparation of Ir carbene complexes 3a–4d. The complex $\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{CNAr})(\text{Cl})$ (**1a–2b**) was dissolved in a minimum amount of CH_2Cl_2 and combined with excess amine. The resulting reaction mixture was stirred at room temperature for 4–5 d. The crude product was purified by silica column chromatography from CH_2Cl_2 /hexane to give pure product.

$\text{Ir}(\text{F}_2\text{ppy})_2(\text{CNH}(\text{Ar}^{\text{CF}_3})\text{NHPr})$ (3a). Prepared by the general procedure using 230 mg of $\text{Ir}(\text{F}_2\text{ppy})_2(\text{CNAr}^{\text{CF}_3})(\text{Cl})$ (**1a**) and propylamine (5.0 mL) with a reaction time of 5 d. The resulting crude product was purified by silica column chromatography and recrystallization

from CH₂Cl₂/hexane to give a bright yellow solid. Yield: 69 mg, 29 %.

¹H NMR (600 MHz, Acetone-d₆): δ = 10.02 (s, 1H), 8.53 (d, *J* = 5.5 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.18 (m, 2H), 7.86 (t, *J* = 8.3 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.07–7.02 (m, 4H), 6.87 (s, 1H), 6.44 (m, 2H), 6.32 (s, 1H), 6.05 (dd, *J* = 2.1, 7.6 Hz, 1H), 5.87 (dd, *J* = 2.1, 8.3 Hz, 1H), 3.36–3.27 (m, 2H), 1.47–1.39 (m, 2H), 0.68 (t, *J* = 7.6 Hz, 3H). ¹³C{¹H} NMR (151 MHz, Acetone-d₆): δ = 200.4, 179.6, 179.1, 166.2 (d, *J* = 7.4 Hz), 165.2 (d, *J* = 7.4 Hz), 164.1 (dd, *J* = 10.4, 242.5 Hz), 162.2 (dd, *J* = 11.8, 247.3 Hz), 158.2, 152.9, 152.5, 151.3, 136.7, 136.0, 132.81, 132.79, 127.5 (q, *J* = 270.6), 128.1, 127.0, 122.9, 122.8, 122.73, 122.69, 122.6, 120.02, 119.99, 113.1 (d, *J* = 16.3 Hz), 112.0 (d, *J* = 14.8 Hz), 109.7, 96.4 (t, *J* = 26.6 Hz), 95.4 (t, *J* = 26.6 Hz), 44.0, 22.2, 10.2. ¹⁹F NMR (565 MHz, Acetone-d₆): δ = –60.94 (s, 3F, CF₃), –110.92 (q, *J* = 8.1 Hz, 1F, F₂ppy), –111.50 (q, *J* = 8.9 Hz, 1F, F₂ppy), –111.75 (t, *J* = 9.7 Hz, 1F, F₂ppy), –111.48 (t, *J* = 10.5 Hz, 1F, F₂ppy). Anal. Calcd for C₃₃H₂₄F₇IrN₄·0.2C₆H₁₄: C, 50.15; H, 3.18; N, 6.83. Found: C, 50.02; H, 3.18; N, 6.83.

Ir(F₂ppy)₂(CNH(Ar^{CF3})NHCH₂(4-OMe-C₆H₄)) (3b). Prepared by the general procedure using 180 mg of Ir(F₂ppy)₂(CNAr^{CF3})(Cl) (**1a**) and 4-methoxybenzylamine (4.0 mL) with a reaction time of 5 d. The resulting crude product was purified by silica column chromatography and recrystallization from CH₂Cl₂/hexane to give a bright yellow solid. Yield: 36 mg, 18 %.

¹H NMR (600 MHz, Acetone-d₆): δ = 10.03 (s, 1H), 8.47 (d, *J* = 5.5 Hz, 1H), 8.31 (d, *J* = 8.9 Hz, 1H), 8.19 (d, 8.3 Hz, 1H), 8.16 (d, 6.2, 1H), 7.93 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 6.2 Hz, 1H), 7.01–6.97 (m, 3H), 6.90 (s, 1H), 6.86–6.83 (m, 3H), 6.73 (d, *J* = 8.3 Hz, 2H), 6.46–6.38 (m, 2H), 6.02 (dd, *J* = 2.1, 9.3 Hz, 1H), 5.92 (dd, *J* = 2.1, 8.3 Hz, 1H), 4.59 (dd, *J* = 6.9, 15.8 Hz, 1H), 4.46 (dd, *J* = 6.2, 15.5 Hz, 1H), 3.72 (s, 3H). ¹³C{¹H} NMR (151 MHz, Acetone-d₆): δ = 200.6, 179.4, 178.9, 166.3 (d, *J* = 7.39 Hz), 165.1 (d, *J* = 7.39 Hz), 164.1 (dd, *J* = 11.8, 235.5 Hz), 162.1 (dd, *J* = 11.8, 258.0 Hz), 159.1, 158.04, 152.9, 152.8, 151.5, 136.8, 136.0, 132.81, 132.78, 129.2, 128.0, 127.8, 127.0, 125.7 (q, *J* = 270.6 Hz), 123.0, 122.93, 122.86, 122.8, 122.7, 122.6, 119.99, 119.98, 113.9, 113.2 (d, *J* = 14.79 Hz), 112.1 (d, *J* = 11.8 Hz), 109.8, 96.4 (t, *J* = 26.6 Hz), 95.5 (t, *J* = 26.6 Hz), 54.7, 45.3. ¹⁹F NMR (565 MHz, Acetone-d₆): δ = –61.01 (s, 3F, CF₃), –110.96 (q, *J* = 8.9 Hz, 1F, F₂ppy), –111.51 (q, *J* = 8.9 Hz, 1F, F₂ppy), –111.70 (t, *J* = 10.5 Hz, 1F, F₂ppy), –112.47 (t, *J* = 10.1 Hz, 1F, F₂ppy). Anal. Calcd for C₃₈H₂₆F₇IrN₄O: C, 51.87; H, 2.98; N, 6.37. Found: C, 52.45; H, 3.10; N, 6.25.

Ir(F₂ppy)₂(CNH(Ar^{4-NO2})NEt₂) (3c). Prepared by the general procedure using 95 mg of Ir(F₂ppy)₂(CNAr^{NO2})(Cl) (**1b**) and diethylamine (0.7 mL) with a reaction time of 4 d. The resulting crude product was purified by silica column chromatography with CH₂Cl₂ and a bright yellow solid was isolated after washing with hexane. Yield: 75 mg, 75 %.

¹H NMR (600 MHz, Acetone-d₆): δ = 9.85 (s, 1H), 8.48 (d, *J* = 4.8 Hz, 1H), 8.32 (d, *J* = 8.9 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 6.2 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.80 (t, *J* = 8.3 Hz, 1H), 7.65 (dd, *J* = 2.8, 8.3 Hz, 1H), 7.27 (d, *J* = 2.8 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.08 (td, *J* = 1.4, 6.9 Hz, 1H), 7.02 (td, *J* = 1.4, 6.9 Hz, 1H), 6.48 (td, *J* = 2.8, 11.0 Hz, 1H), 6.38 (td, *J* = 2.1, 11.3 Hz, 1H), 5.91 (dd, *J* = 2.1, 7.9 Hz, 1H), 5.60 (dd, *J* = 2.8, 8.3 Hz, 1H),

3.95–3.90 (m, 1H), 3.75–3.69 (m, 1H), 3.62–3.56 (m, 1H), 3.37–3.31 (m, 1H), 1.23 (t, $J = 7.6$ Hz, 1H), 0.47 (t, $J = 6.9$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone- d_6): $\delta = 201.0, 181.8, 175.5, 166.0$ (d, $J = 7.4$ Hz), 164.8 (t, $J = 5.9$ Hz), 164.6 (d, $J = 10.4$ Hz), 163.0 (q, $J = 10.4$ Hz), 162.4 (dd, $J = 10.4, 282.4$ Hz), 161.7 (dd, $J = 11.8, 260.2$ Hz), 161.2, 153.1, 152.6 (dd, $J = 16.3, 36.2$ Hz), 152.1, 142.4, 136.9, 136.6 (d, $J = 11.8$ Hz), 136.2, 131.3, 127.4, 126.8, 123.3 (d, $J = 10.4$ Hz), 123.0 (td, $J = 10.4, 38.4$ Hz), 122.4 (d, $J = 14.8$ Hz), 120.2, 112.7 (d, $J = 16.3$ Hz), 111.1 (d, $J = 16.3$ Hz), 109.5, 96.1 (t, $J = 26.6$ Hz), 95.6 (t, $J = 26.6$ Hz), 52.2, 41.8, 14.2, 12.6. ^{19}F NMR (565 MHz, Acetone- d_6): $\delta = -110.14$ (q, $J = 8.9$ Hz, 1F, F₂ppy), -110.94 (q, $J = 8.1$ Hz, 1F, F₂ppy), -111.50 (t, $J = 10.9$ Hz, 1F, F₂ppy), -111.97 (t, $J = 10.9$ Hz, 1F, F₂ppy). Anal. Calcd for C₃₃H₂₆F₄IrN₅O₂: C, 49.99; H, 3.31; N, 8.83. Found: C, 49.47; H, 3.48; N, 8.96.

Ir(F₂ppy)₂(CNH(Ar^{4-NO₂)NPr₂) (3d).} Prepared by the general procedure using 66 mg of Ir(F₂ppy)₂(CNAr^{NO₂})(Cl) (**1b**) and dipropylamine (1.0 mL) with a reaction time of 4 d. The resulting crude product was purified by silica column chromatography with CH₂Cl₂ and a bright yellow solid was isolated after washing with hexane. Yield: 38 mg, 53 %.

^1H NMR (600 MHz, Acetone- d_6): $\delta = 9.81$ (s, 1H), 8.50 (d, $J = 5.5$ Hz, 1H), 8.32 (d, $J = 8.3$ Hz, 1H), 8.20 (d, $J = 8.9$ Hz, 1H), 7.99 (d, $J = 5.5$ Hz, 1H), 7.88 (t, $J = 7.6$ Hz, 1H), 7.80 (t, $J = 7.6$ Hz, 1H), 7.63 (td, $J = 2.8, 8.3$ Hz, 1H), 7.25 (d, $J = 2.8$ Hz, 1H), 7.10–7.07 (m, 2H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.48 (td, $J = 2.1, 11.0$ Hz, 1H), 6.39 (td, $J = 2.8, 11.0$ Hz, 1H), 5.91 (dd, $J = 2.1, 8.3$ Hz, 1H), 5.59 (dd, $J = 2.8, 8.3$ Hz, 1H), 3.72–3.63 (m, 2H), 3.59–3.54 (m, 1H), 3.20 (td, $J = 4.8, 12.4$ Hz, 1H), 1.77–1.68 (m, 2H), 1.36–1.30 (m, 1H), 0.86 (d, $J = 7.6$ Hz, 3H), 0.72–0.66 (m, 1H), 0.18 (d, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone- d_6): $\delta = 201.2, 182.0, 175.4, 166.0$ (d, $J = 7.4$ Hz), 164.8 (d, $J = 8.9$ Hz), 164.7 (t, $J = 4.4$ Hz), 163.0 (q, $J = 5.9$ Hz), 161.7 (dd, $J = 11.8, 258.8$ Hz), 162.4 (dd, $J = 11.8, 261.7$ Hz), 161.0, 153.2, 153.1, 152.7, 152.0, 142.4, 136.7, 136.4, 131.3, 127.3, 126.8, 123.2, 122.9 (t, $J = 22.2$ Hz), 122.4, 120.0, 112.8 (d, $J = 13.3$ Hz), 111.1 (d, $J = 14.8$ Hz), 109.4, 96.2 (t, $J = 26.6$ Hz), 95.6 (t, $J = 28.1$ Hz), 59.8, 49.0, 22.9, 20.7, 10.5, 9.4. ^{19}F NMR (565 MHz, Acetone- d_6): $\delta = -110.04$ (q, $J = 8.9$ Hz, 1F, F₂ppy), -111.09 (q, $J = 8.1$ Hz, 1F, F₂ppy), -111.42 (t, $J = 9.7$ Hz, 1F, F₂ppy), -111.93 (t, $J = 10.5$ Hz, 1F, F₂ppy). Anal. Calcd for C₃₅H₃₀F₄IrN₅O₂: C, 51.21; H, 3.68; N, 8.53. Found: C, 50.96; H, 3.79; N, 8.56.

Ir(bt)₂(CNH(Ar^{4-CF₃)NHPr) (4a).} Prepared by the general procedure using 97 mg of Ir(bt)₂(CNAr^{CF₃})(Cl) (**2a**) and propylamine (2.0 mL) with a reaction time of 5 d. The resulting crude product was purified by silica column chromatography with CH₂Cl₂ and a bright orange solid was isolated after washing with hexane. The product was partially solvated with hexane after drying in vacuo. Yield: 35 mg, 35 %.

^1H NMR (600 MHz, Acetone- d_6): $\delta = 10.02$ (s, 1H), 8.02 (d, $J = 8.3$ Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 1H), 7.80 (q, $J = 8.3$ Hz, 3H), 7.42–7.32 (m, 3H), 7.23 (d, $J = 8.3$ Hz, 1H), 6.99 (t, $J = 8.3$ Hz, 1H), 6.93–6.85 (m, 5H), 6.72–6.67 (m, 3H), 6.58 (d, $J = 7.6$ Hz, 1H), 6.05 (s, 1H), 3.40–3.34 (m, 1H), 3.31–3.25 (m, 1H), 1.43–1.32 (m, 2H), 0.64 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone- d_6): $\delta = 200.5, 180.8, 179.0, 174.3, 173.9, 159.1, 151.9, 151.1, 148.5, 141.4, 140.2, 134.8, 133.8, 133.71, 133.68, 131.45, 131.39, 130.3, 130.0, 126.8, 126.5, 125.7,$

125.4, 125.3, 125.2, 122.6, 122.44, 122.39 (q, $J = 275.0$ Hz), 122.2, 121.0, 120.2, 119.39, 119.37, 108.9, 44.0, 22.0, 10.2. ^{19}F NMR (565 MHz, Acetone- d_6): $\delta = -60.91$ (s, 3F, CF_3). Anal. Calcd for $\text{C}_{37}\text{H}_{28}\text{F}_3\text{IrN}_4\text{S}_2 \cdot 0.2\text{C}_6\text{H}_{14}$: C, 53.40; H, 3.61; N, 6.52. Found: C, 53.70; H, 3.94; N, 6.34.

$\text{Ir}(\text{bt})_2(\text{CNH}(\text{Ar}^{\text{CF}_3})\text{NHCH}_2(4\text{-OMe-C}_6\text{H}_4))$ (4b). Prepared by the general procedure using 200 mg of $\text{Ir}(\text{bt})_2(\text{CNAr}^{\text{CF}_3})(\text{Cl})$ (**2a**) and 4-methoxybenzylamine (6.0 mL) with a reaction time of 5 d. The resulting crude product was purified by silica column chromatography with CH_2Cl_2 and a bright orange solid was isolated after washing with hexane. Yield: 47 mg, 21 %.

^1H NMR (600 MHz, Acetone- d_6): $\delta = 10.04$ (s, 1H), 8.11 (d, $J = 8.3$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 1H), 7.83 (d, $J = 8.9$ Hz, 1H), 7.77 (dd, $J = 7.6, 15.8$ Hz, 2H), 7.39–7.36 (m, 3H), 7.16 (d, $J = 8.9$ Hz, 1H), 6.98 (t, $J = 8.3$ Hz, 1H), 6.91 (d, $J = 8.3$ Hz, 1H), 6.89–6.85 (m, 3H), 6.82 (td, $J = 2.1, 6.5$ Hz, 1H), 6.71–6.67 (m, 3H), 6.66–6.65 (m, 2H), 6.62 (s, 1H), 6.60 (d, $J = 7.6$ Hz, 1H), 6.52 (d, $J = 8.3$ Hz, 2H), 4.69 (dd, $J = 6.9, 15.8$ Hz, 1H), 4.43 (dd, $J = 5.5, 15.8$ Hz, 1H), 3.66 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone- d_6): $\delta = 200.8, 181.0, 178.9, 174.1, 173.7, 159.0, 158.9, 152.0, 151.0, 148.7, 141.3, 140.2, 134.8, 138.7, 133.60, 133.58, 131.5, 131.4, 130.2, 130.0, 129.0, 127.7, 127.0, 126.6, 125.8, 125.4, 125.3, 122.7, 122.5, 122.4$ (q, $J = 277.9$ Hz), 122.3, 120.9, 120.7, 120.2, 119.4, 119.3, 113.7, 109.0, 54.6, 45.3. ^{19}F NMR (565 MHz, Acetone- d_6): $\delta = -60.93$ (s, 3F, CF_3). Anal. Calcd for $\text{C}_{42}\text{H}_{30}\text{F}_3\text{IrN}_4\text{OS}_2$: C, 54.83; H, 3.29; N, 6.09. Found: C, 55.01; H, 3.23; N, 6.03.

$\text{Ir}(\text{bt})_2(\text{CNH}(\text{Ar}^{4\text{-NO}_2})\text{NHEt})$ (4c). Prepared by the general procedure using 100 mg of $\text{Ir}(\text{bt})_2(\text{CNAr}^{\text{NO}_2})(\text{Cl})$ (**2b**) and diethylamine (1.0 mL) with a reaction time of 4 d. The major product was formed via reaction with a minor impurity of ethylamine. The resulting crude product was purified by silica column chromatography with CH_2Cl_2 and a bright orange solid was isolated after washing with hexane. Yield: 40 mg, 40 %.

^1H NMR (600 MHz, Acetone- d_6): $\delta = 10.25$ (s, 1H), 8.03 (d, $J = 7.6$ Hz, 1H), 8.00 (d, $J = 7.6$ Hz, 1H), 7.81 (d, $J = 7.6$ Hz, 2H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.59 (dd, $J = 2.1, 8.6$ Hz, 1H), 7.47 (d, $J = 2.8$ Hz, 1H), 7.43–7.37 (m, 2H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 8.3$ Hz, 1H), 7.05 (t, $J = 8.3$ Hz, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 6.89 (t, $J = 7.6$ Hz, 1H), 6.72–6.69 (m, 2H), 6.64 (d, $J = 7.6$ Hz, 1H), 6.56 (d, $J = 7.6$ Hz, 1H), 6.38 (s, 1H), 3.52–3.47 (m, 1H), 3.38–3.33 (m, 1H), 0.99 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Acetone- d_6): $\delta = 201.0, 180.9, 179.2, 173.3, 173.2, 162.2, 151.7, 150.9, 149.8, 142.5, 141.3, 140.2, 134.6, 133.7, 131.7, 131.42, 131.40, 130.4, 130.2, 126.9, 126.8, 125.8, 125.6, 125.4, 125.3, 123.2, 122.8, 121.3, 121.1, 120.5, 120.4, 119.5, 109.1, 37.6, 13.7$. Anal. Calcd for $\text{C}_{35}\text{H}_{26}\text{IrN}_5\text{O}_2\text{S}_2$: C, 52.22; H, 3.26; N, 8.70. Found: C, 51.96; H, 3.31; N, 8.55.

$\text{Ir}(\text{bt})_2(\text{CNH}(\text{Ar}^{4\text{-NO}_2})\text{NHPr})$ (4d). Prepared by the general procedure using 64 mg of $\text{Ir}(\text{bt})_2(\text{CNAr}^{\text{NO}_2})(\text{Cl})$ (**2b**) and dipropylamine (1.5 mL) with a reaction time of 4 d. The major product was formed via reaction with a minor impurity of propylamine. The resulting crude product was purified by silica column chromatography with CH_2Cl_2 and a bright orange solid was isolated after washing with hexane. Yield: 51 mg, 77 %.

¹H NMR (600 MHz, Acetone-d₆): δ = 10.26 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.83–7.81 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 2.8, 8.3, 1H), 7.49 (d, *J* = 2.8 Hz, 1H), 7.43–7.37 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.05 (t, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.90 (q, *J* = 7.6 Hz, 2H), 6.74–6.70 (m, 2H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.26 (s, 1H), 3.43–3.38 (m, 1H), 3.36–3.30 (m, 1H), 1.44–1.33 (m, 2H), 0.64 (t, *J* = 7.6 Hz, 3H). ¹³C{¹H} NMR (151 MHz, Acetone-d₆): δ = 200.3, 180.9, 179.2, 173.4, 173.2, 162.1, 151.8, 150.9, 149.6, 142.5, 141.3, 140.2, 134.7, 133.7, 131.7, 131.4, 130.4, 130.2, 126.9, 126.8, 125.8, 125.6, 125.4, 125.3, 123.2, 122.8, 121.3, 121.1, 120.5, 120.4, 119.4, 109.1, 44.3, 22.0, 10.2. Anal. Calcd for C₃₆H₂₈IrN₅O₂S₂: C, 52.80; H, 3.45; N, 8.55. Found: C, 53.06; H, 3.66; N, 8.37.

X-ray Crystallography Details. Single crystals were grown by vapor diffusion of hexane into concentrated CH₂Cl₂ solutions. Crystals were mounted on a Bruker Apex II three-circle diffractometer using MoK α radiation (λ = 0.71073 Å). The data was collected at 123(2) K and was processed and refined within the APEXII software. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the program SHELXL.³ Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all non-hydrogen atoms were refined anisotropically. The crystal structure of **3c** contained electron density corresponding to disordered solvent that could not be satisfactorily refined. The SQUEEZE function in PLATON⁴ was used to remove this residual electron density. The crystal structure of **4c** included a solvent molecule which was modeled as a two-part disorder between a CHCl₃ and a CH₂Cl₂. The 1,2 and 1,3 bond distances of all disordered parts were restrained to be the same, and rigid bond restraints were used on the anisotropic displacement parameters of the disordered atoms. Crystallographic details are summarized in Tables S1 and S2.

Table S1. Crystallographic summary for **3a** and **3c**

	3a	3c
Crystal data		
Chemical formula	C ₃₃ H ₂₄ F ₇ IrN ₄	C ₃₃ H ₂₆ F ₄ IrN ₅ O ₂
M_r	801.76	792.79
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a, b, c (Å)	10.6293 (6), 19.9421 (11), 13.7025 (8)	11.392 (7), 21.133 (14), 13.834 (9)
β (°)	99.2721 (7)	94.876 (8)
V (Å ³)	2866.6 (3)	3318 (4)
μ (mm ⁻¹)	4.74	4.08
Crystal size (mm)	0.64 × 0.30 × 0.15	0.30 × 0.30 × 0.10
Data collection		
T_{\min}, T_{\max}	0.448, 0.746	0.627, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17581, 6539, 6315	20239, 7568, 6935
R_{int}	0.017	0.029
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.650	0.652
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.047, 1.09	0.027, 0.061, 1.12
No. of reflections	6539	7568
No. of parameters	414	413
No. of restraints	2	1
	$w = 1/[\sigma^2(F_o^2) + (0.0899P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0028P)^2 + 10.0836P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	3.72, -3.57	1.40, -1.44

Table S2. Crystallographic summary for **3d** and **4c**

	3d	4c ·1.25CH ₂ Cl ₂
Crystal data		
Chemical formula	C ₃₅ H ₃₀ F ₄ IrN ₅ O ₂	C ₃₆ H _{27.50} Cl _{2.50} IrN ₅ O ₂ S ₂
<i>M_r</i>	820.84	907.07
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>Cc</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.7013 (9), 11.2843 (6), 18.1118 (10)	23.9379 (10), 11.9202 (5), 15.6551 (12)
β (°)	113.5434 (7)	130.05
<i>V</i> (Å ³)	3129.3 (3)	3419.4 (3)
μ (mm ⁻¹)	4.33	4.26
Crystal size (mm)	0.23 × 0.19 × 0.01	0.30 × 0.07 × 0.06
Data collection		
<i>T</i> _{min} , <i>T</i> _{max}	0.597, 0.746	0.585, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	18937, 7153, 6313	10379, 5415, 5122
<i>R</i> _{int}	0.026	0.023
(sin θ/λ) _{max} (Å ⁻¹)	0.649	0.651
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.023, 0.068, 1.16	0.019, 0.041, 0.92
No. of reflections	7153	5415
No. of parameters	429	477
No. of restraints	1	101
Δρ _{max} , Δρ _{min} (e Å ⁻³)	2.00, -1.31	0.91, -0.80
Absolute structure	—	Classical Flack method preferred over Parsons because s.u. lower.
Absolute structure parameter	—	0.005 (5)

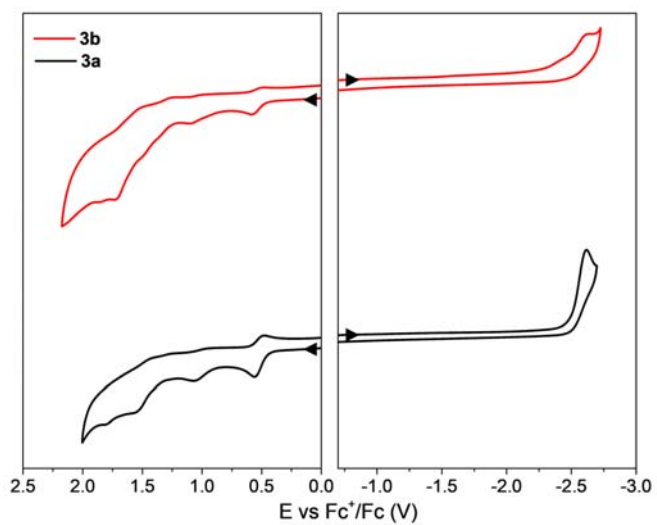


Figure S1. Overlaid cyclic voltammograms of **3a** and **3b**. Currents are normalized to bring the plots onto the same scale.

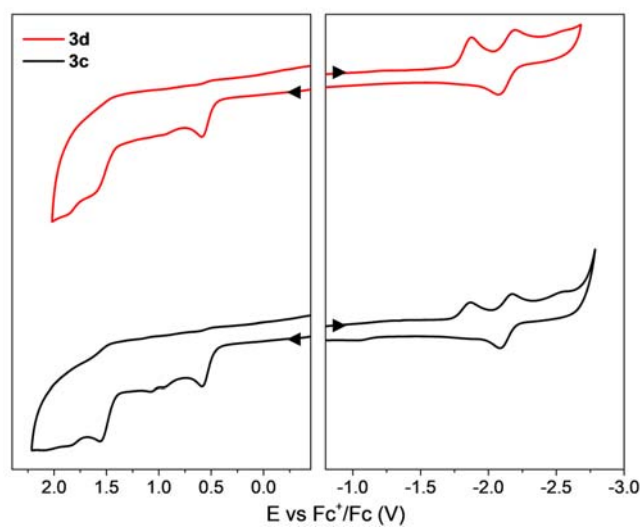


Figure S2. Overlaid cyclic voltammograms of **3c** and **3d**. Currents are normalized to bring the plots onto the same scale.

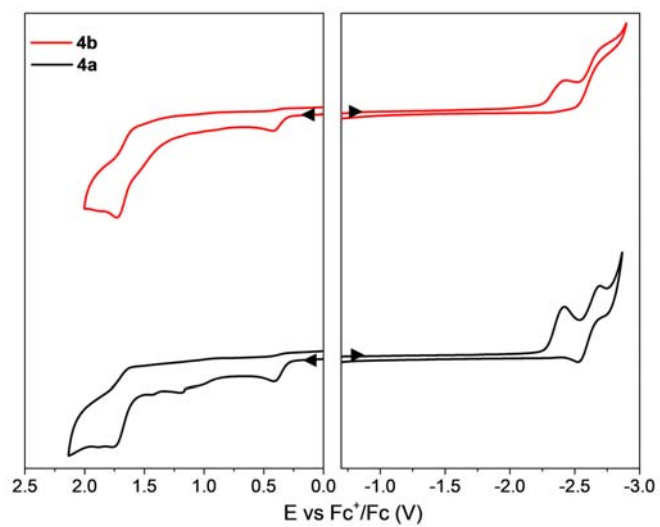


Figure S3. Overlaid cyclic voltammograms of **4a** and **4b**. Currents are normalized to bring the plots onto the same scale.

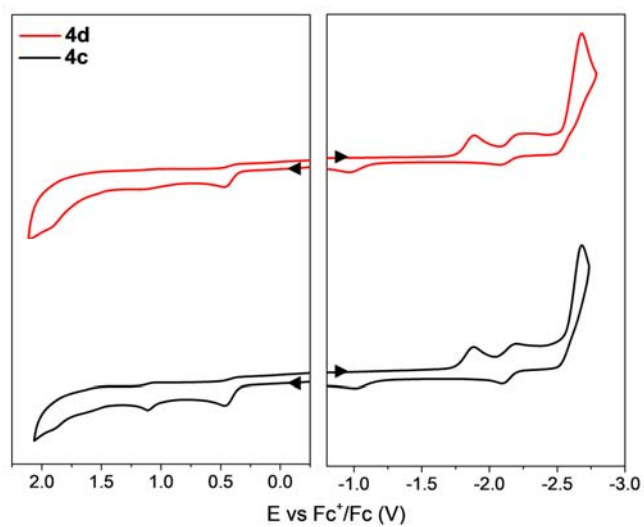


Figure S4. Overlaid cyclic voltammograms of **4c** and **4d**. Currents are normalized to bring the plots onto the same scale.

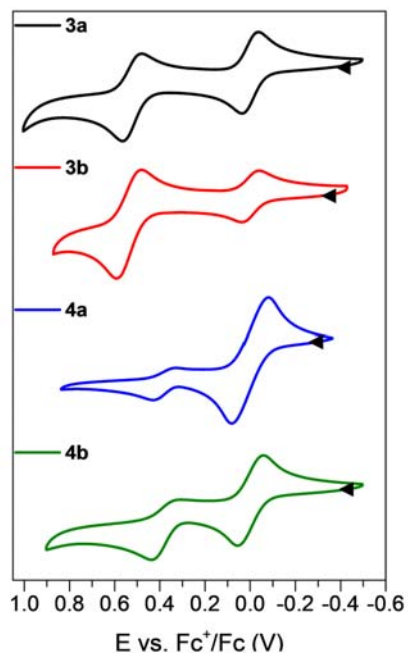


Figure S5. Overlaid cyclic voltammograms of **3a**, **3b**, **4a**, and **4b** (first oxidation wave only). The wave at 0 V corresponds to the internal ferrocene standard. Currents are normalized to bring the plots onto the same scale.

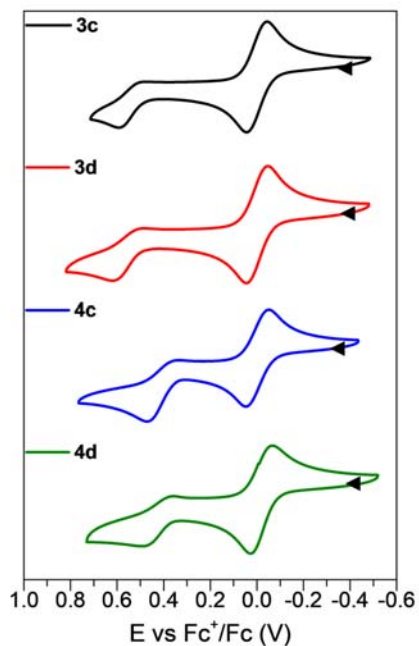


Figure S6. Overlaid cyclic voltammograms of **3c**, **3d**, **4c**, and **4d** (first oxidation wave only). The wave at 0 V corresponds to the internal ferrocene standard. Currents are normalized to bring the plots onto the same scale.

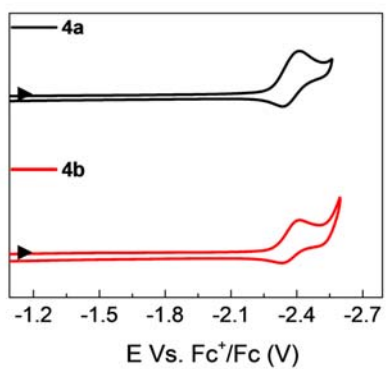


Figure S7. Overlaid cyclic voltammograms of **4a** and **4b** (first reduction wave only). Currents are normalized to bring the plots onto the same scale.

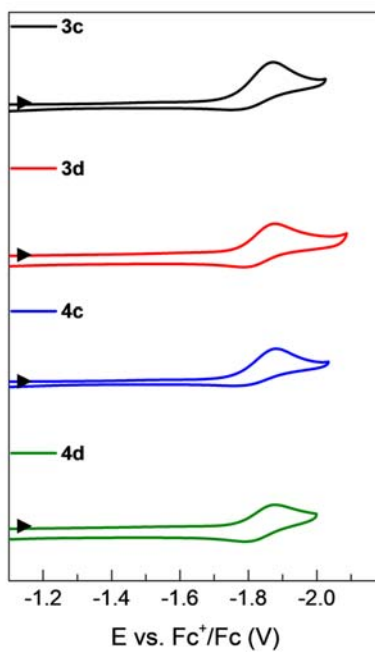


Figure S8. Overlaid cyclic voltammograms of **3c**, **3d**, **4c**, and **4d** (first reduction wave only). Currents are normalized to bring the plots onto the same scale.

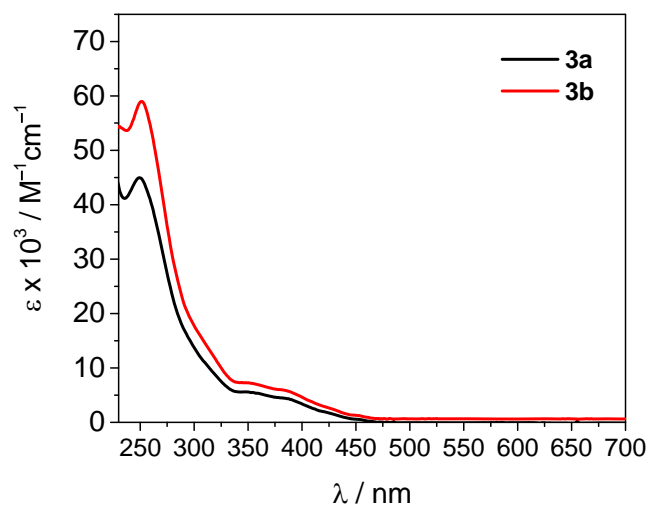


Figure S9. Overlaid UV-vis absorption spectra of **3a** and **3b** in CH_2Cl_2 .

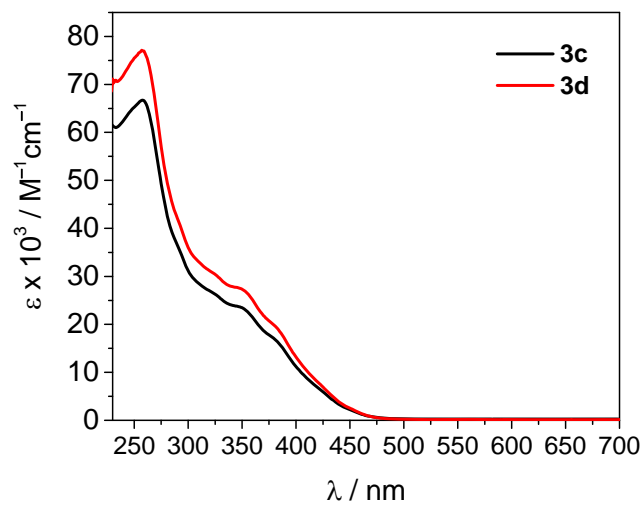


Figure S10. Overlaid UV-vis absorption spectra of **3c** and **3d** in CH_2Cl_2 .

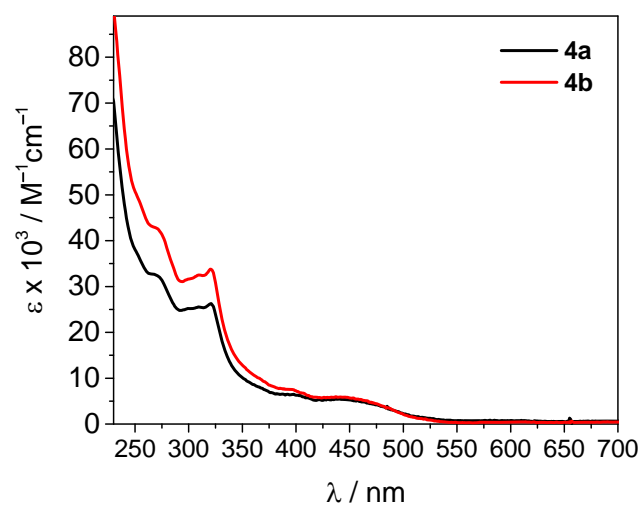


Figure S11. Overlaid UV-vis absorption spectra of **4a** and **4b** in CH₂Cl₂.

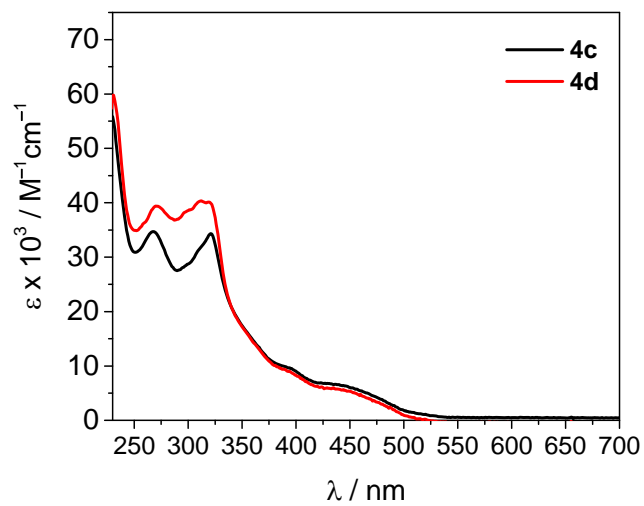


Figure S12. Overlaid UV-vis absorption spectra of **4c** and **4d** in CH₂Cl₂.

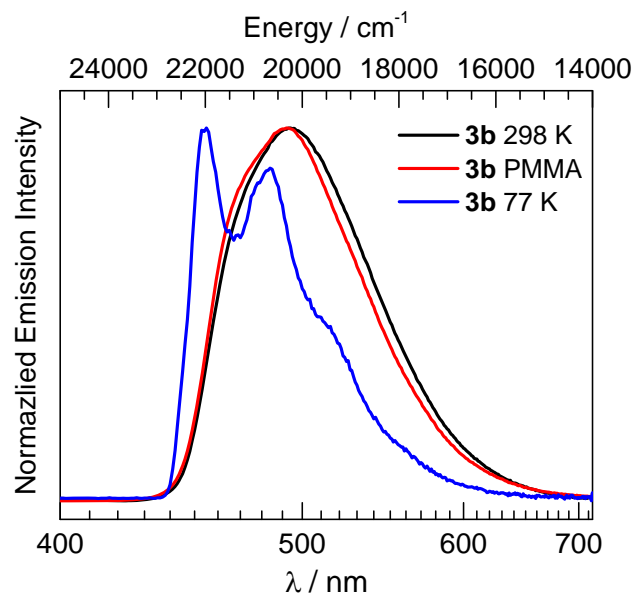


Figure S13. Emission spectra of **3b**, recorded at room temperature (298 K) in CH_2Cl_2 ($\lambda_{\text{exc}} = 310$ nm), PMMA film ($\lambda_{\text{exc}} = 365$ nm) and at low temperature (77 K) in CH_2Cl_2 /toluene (1:3 = v/v) ($\lambda_{\text{exc}} = 310$ nm).

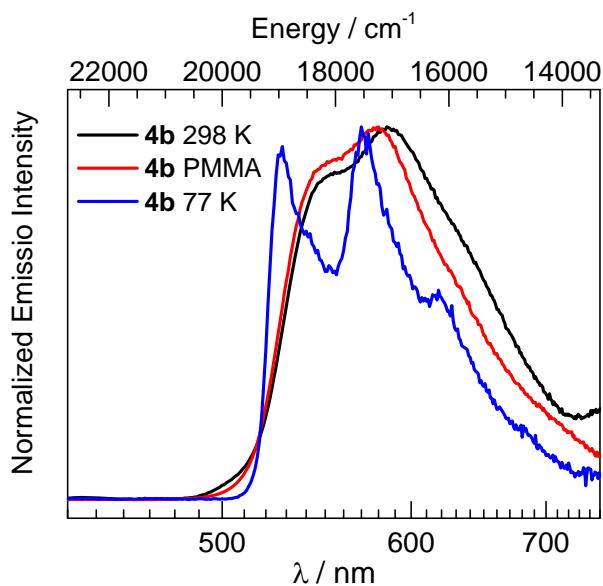


Figure S14. Emission spectra of **4b**, recorded at room temperature (298 K) in CH_2Cl_2 ($\lambda_{\text{exc}} = 310$ nm), PMMA film ($\lambda_{\text{exc}} = 365$ nm) and at low temperature (77 K) in CH_2Cl_2 /toluene (1:3 = v/v) ($\lambda_{\text{exc}} = 310$ nm).

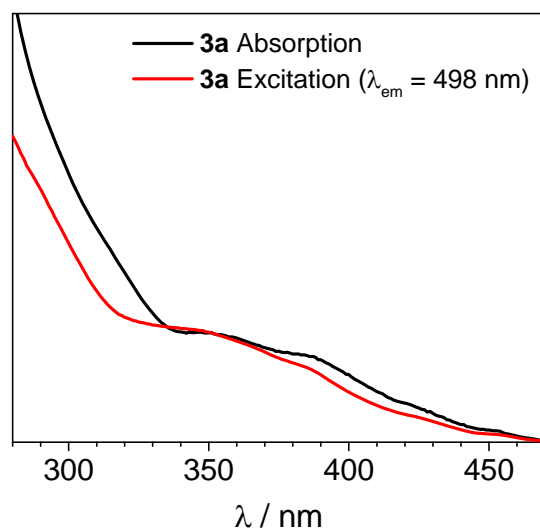


Figure S15. Overlaid UV-vis absorption and excitation spectra of **3a**, recorded in CH_2Cl_2 at room temperature.

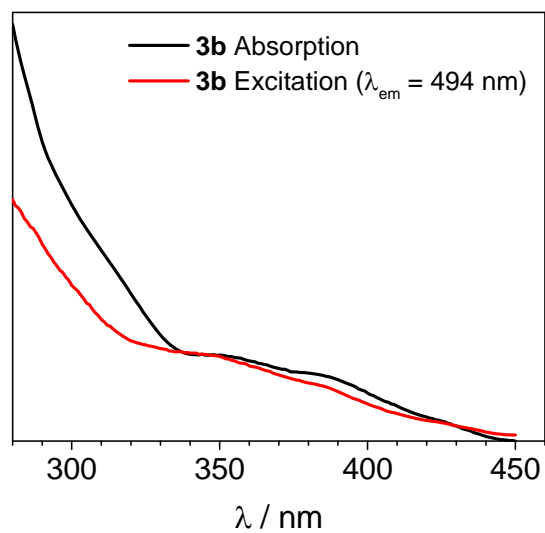


Figure S16. Overlaid UV-vis absorption and excitation spectra of **3b**, recorded in CH_2Cl_2 at room temperature.

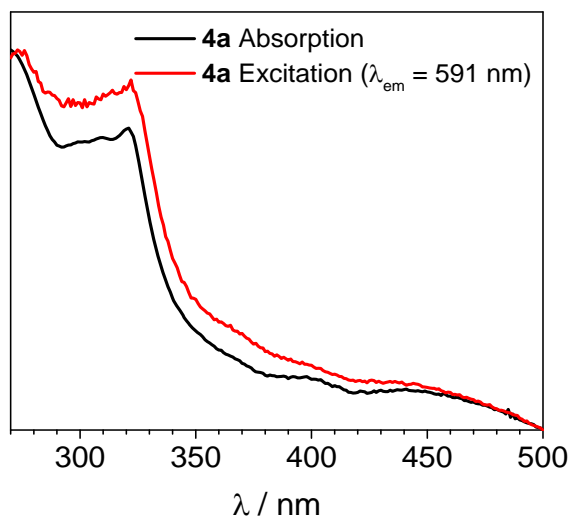


Figure S17. Overlaid UV-vis absorption and excitation spectra of **4a**, recorded in CH_2Cl_2 at room temperature.

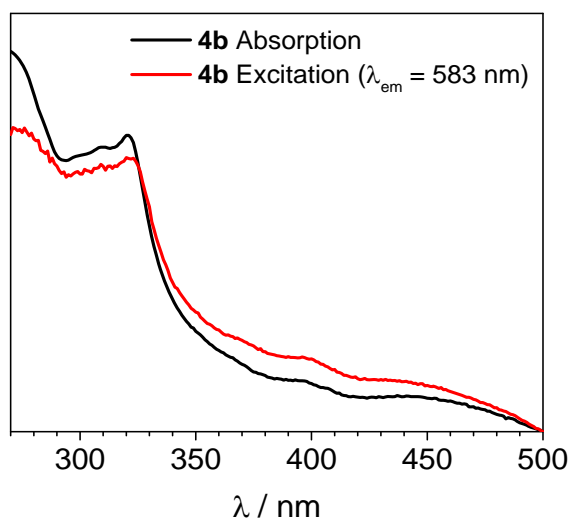


Figure S18. Overlaid UV-vis absorption and excitation spectra of **4b**, recorded in CH_2Cl_2 at room temperature.

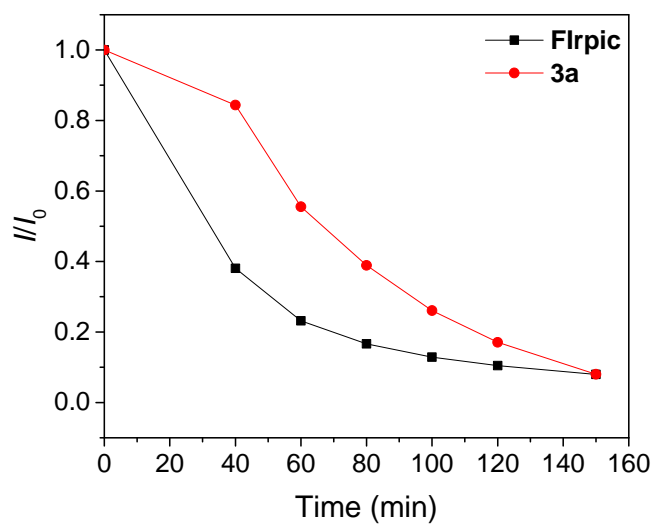


Figure S19. Plot showing the change in normalized emission intensity when samples of Flrpic and **3a** in CH_2Cl_2 are irradiated with blue light at room temperature.

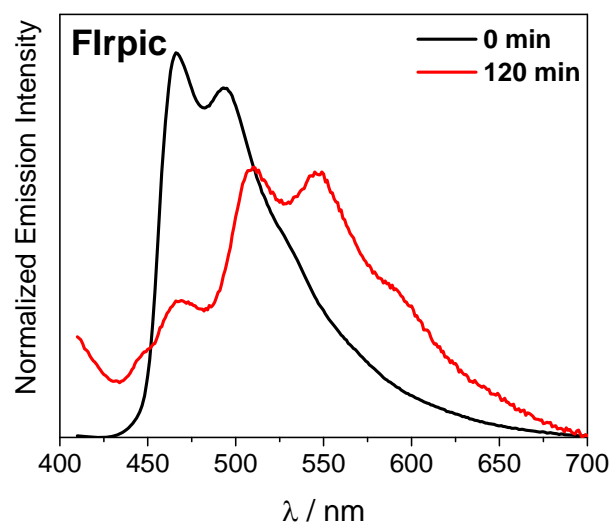


Figure S20. Normalized emission spectra of Flrpic, recorded before and after 120-min of irradiation with blue light. Emission spectra were recorded at room temperature in CH_2Cl_2 .

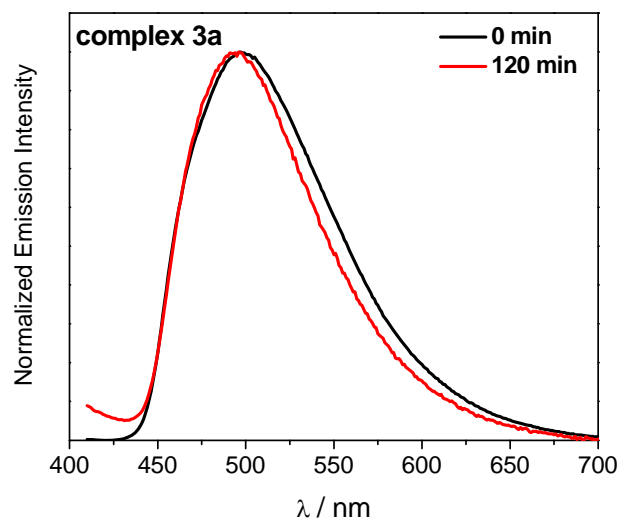


Figure S21. Normalized emission spectra of **3a**, recorded before and after 120-min of irradiation with blue light. Emission spectra were recorded at room temperature in CH_2Cl_2 .

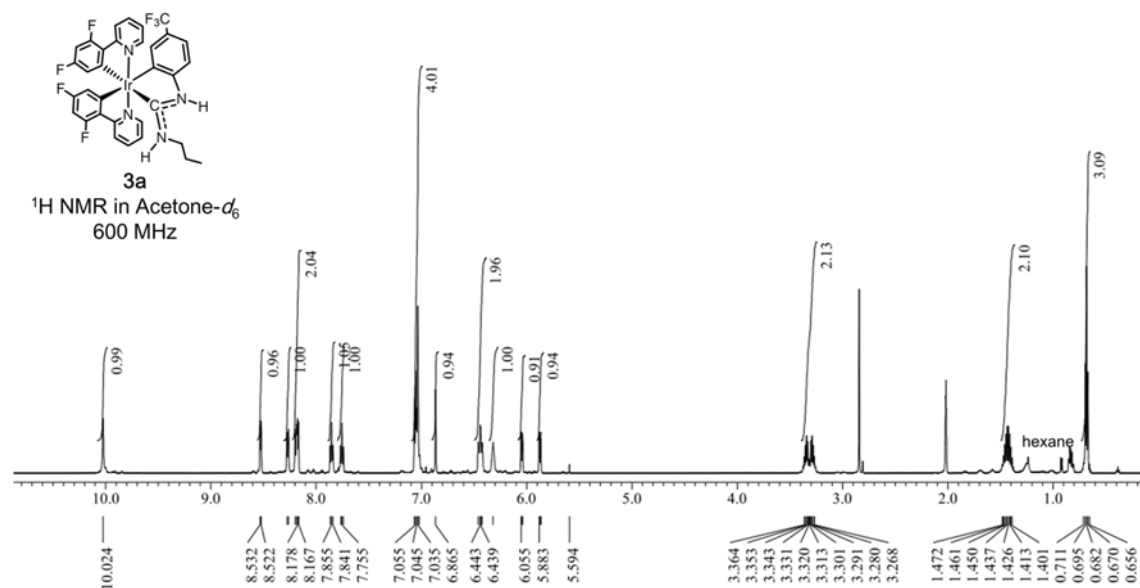


Figure S22. ¹H NMR spectrum of **3a**, recorded in acetone-*d*₆ at 600 MHz.

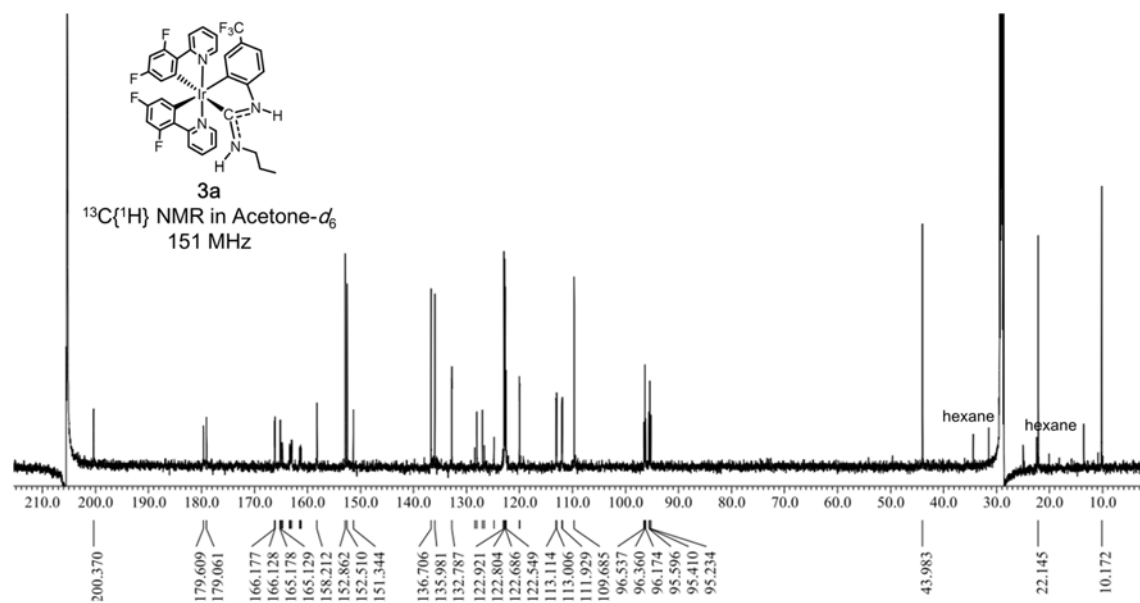


Figure S23. ¹³C NMR spectrum of **3a**, recorded in acetone-*d*₆ at 151 MHz.

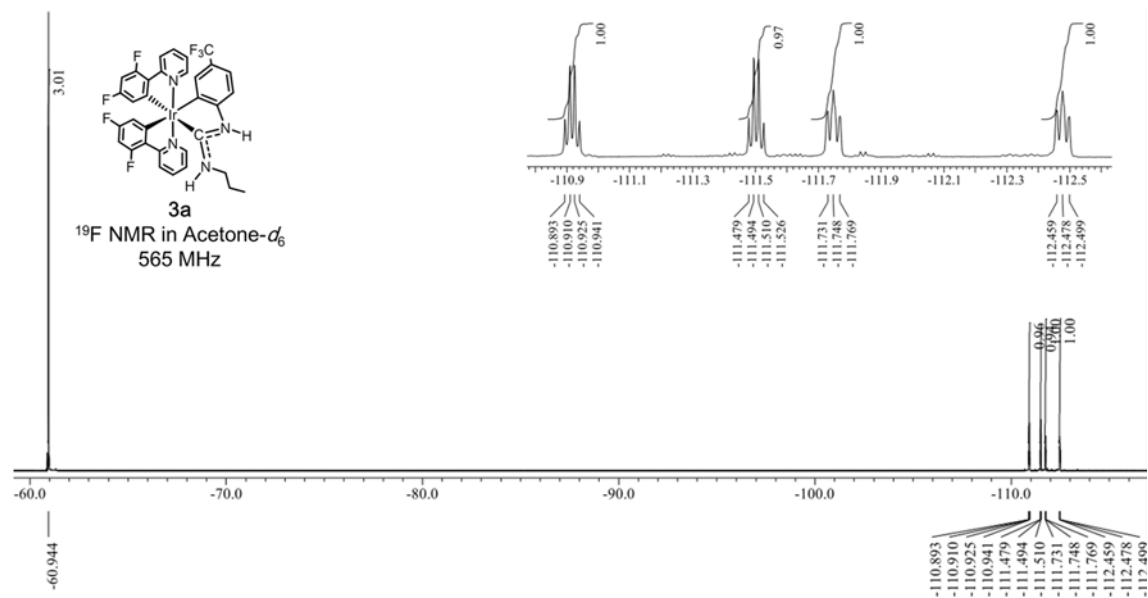


Figure S24. ^{19}F NMR spectrum of **3a**, recorded in acetone- d_6 at 565 MHz.

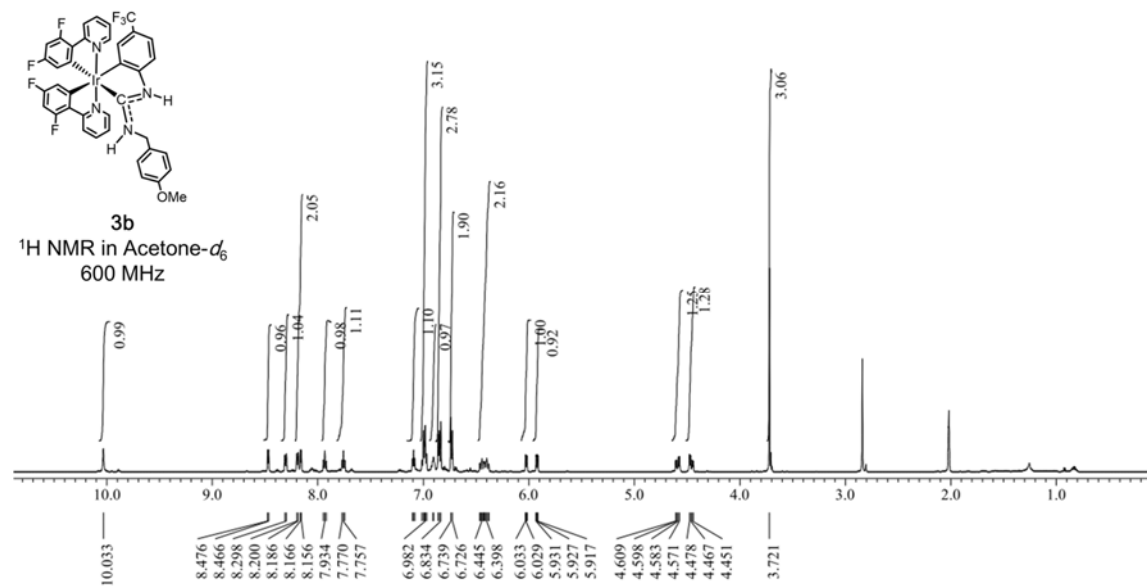


Figure S25. ^1H NMR spectrum of **3b**, recorded in acetone- d_6 at 600 MHz.

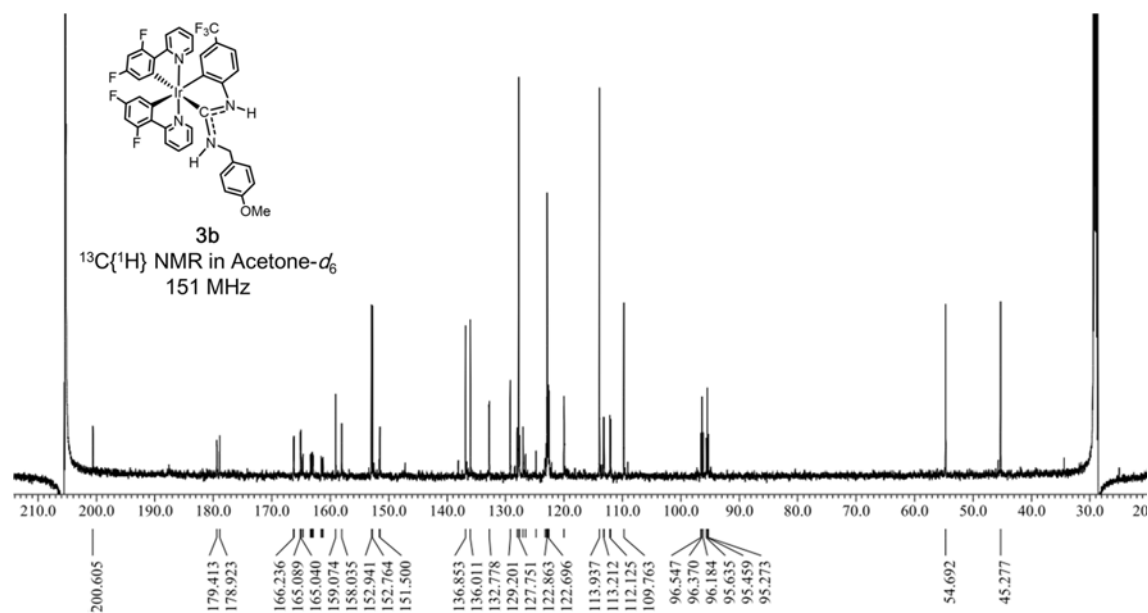


Figure 26. ^{13}C NMR spectrum of **3b**, recorded in acetone- d_6 at 151 MHz.

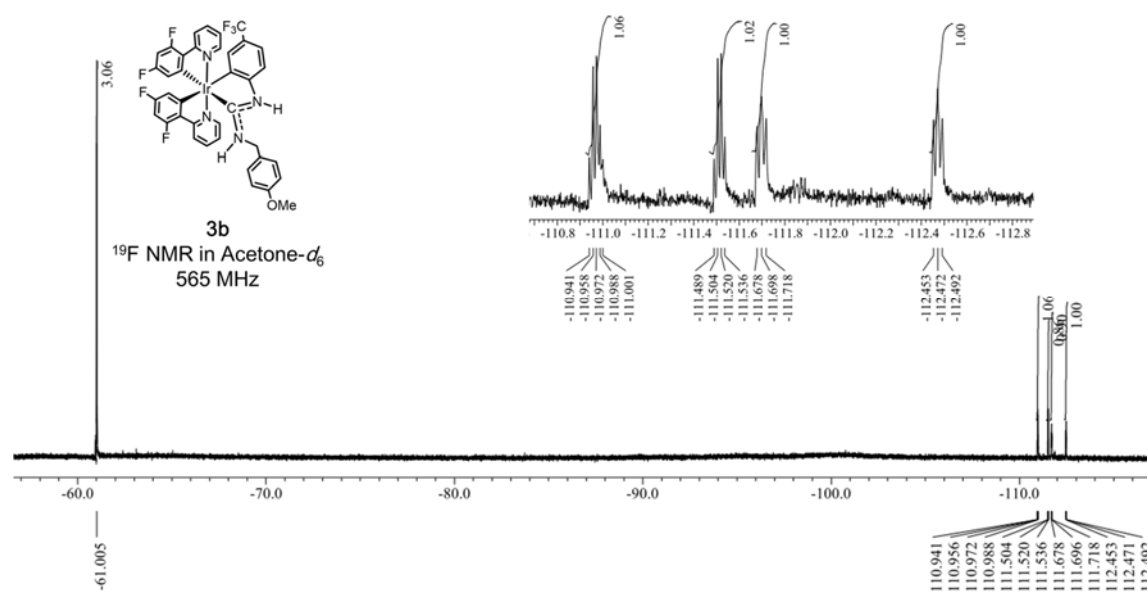


Figure 27. ^{19}F NMR spectrum of **3b**, recorded in acetone- d_6 at 565 MHz.

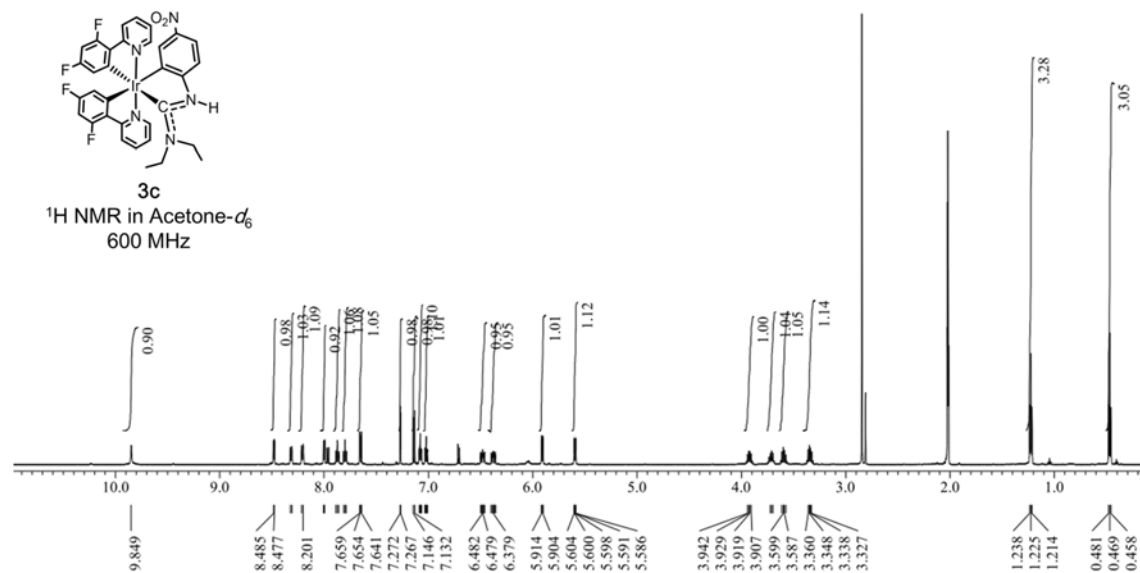


Figure S28. ¹H NMR spectrum of **3c**, recorded in acetone-*d*₆ at 600 MHz.

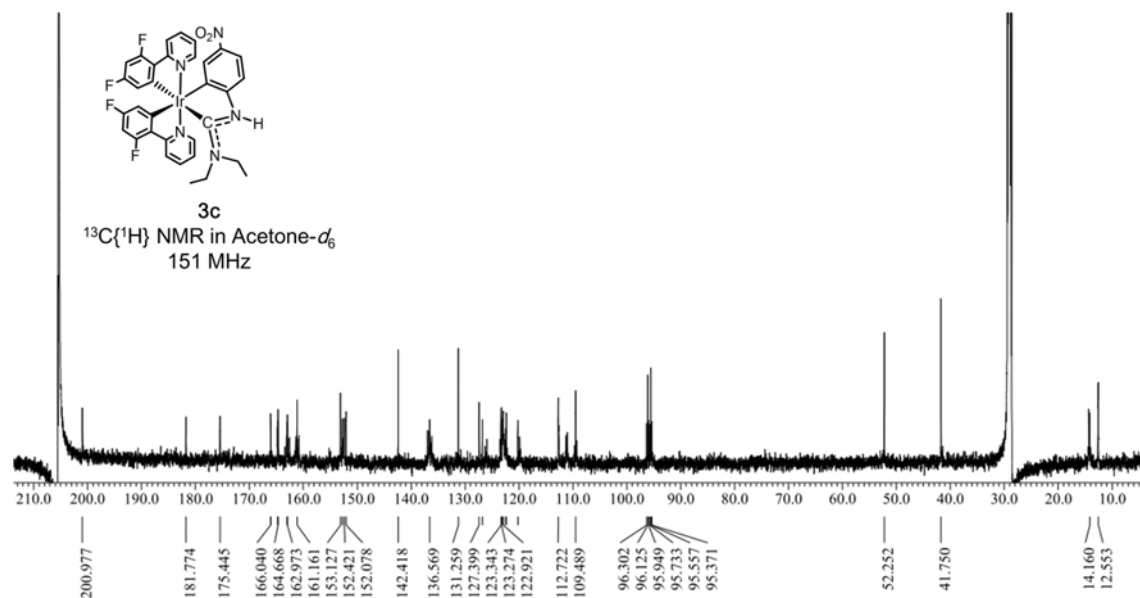


Figure S29. ¹³C NMR spectrum of **3c**, recorded in acetone-*d*₆ at 151 MHz.

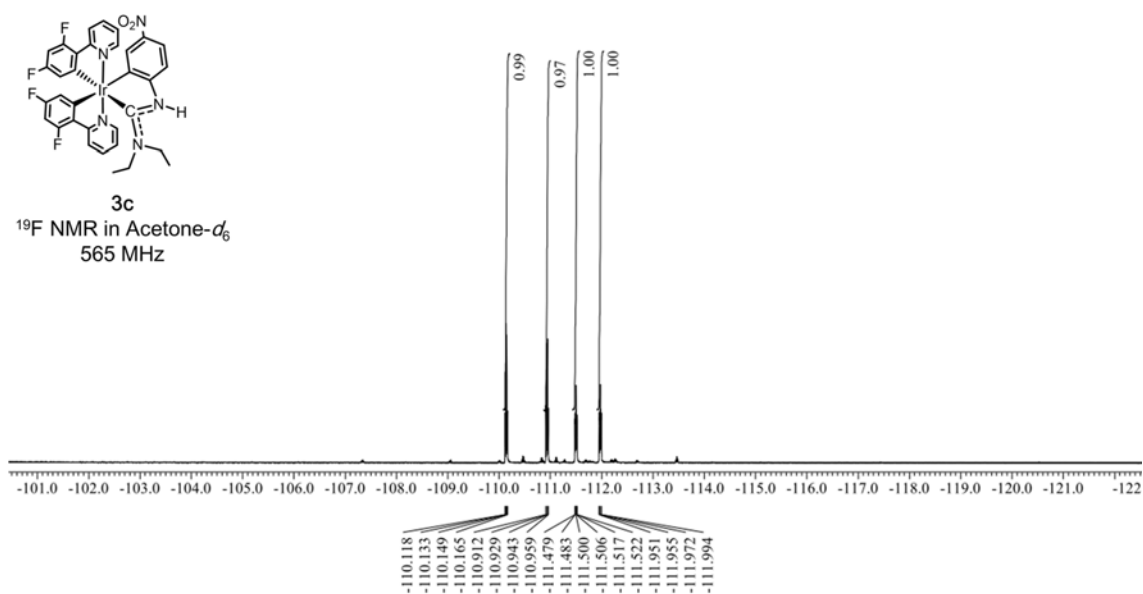


Figure S30. ¹⁹F NMR spectrum of **3c**, recorded in acetone-*d*₆ at 565 MHz.

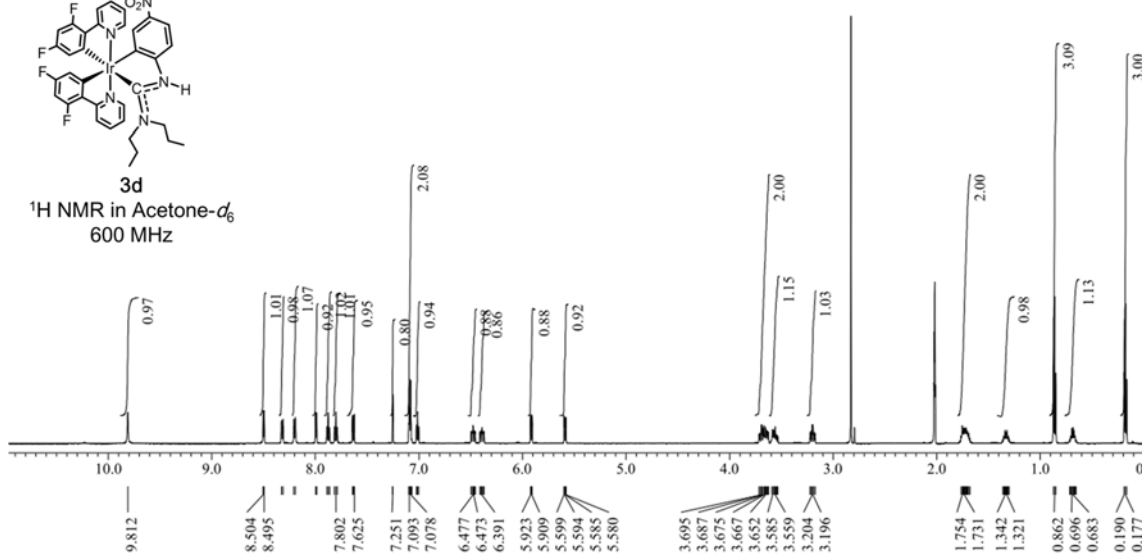


Figure S31. ¹H NMR spectrum of **3d**, recorded in acetone-*d*₆ at 600 MHz.

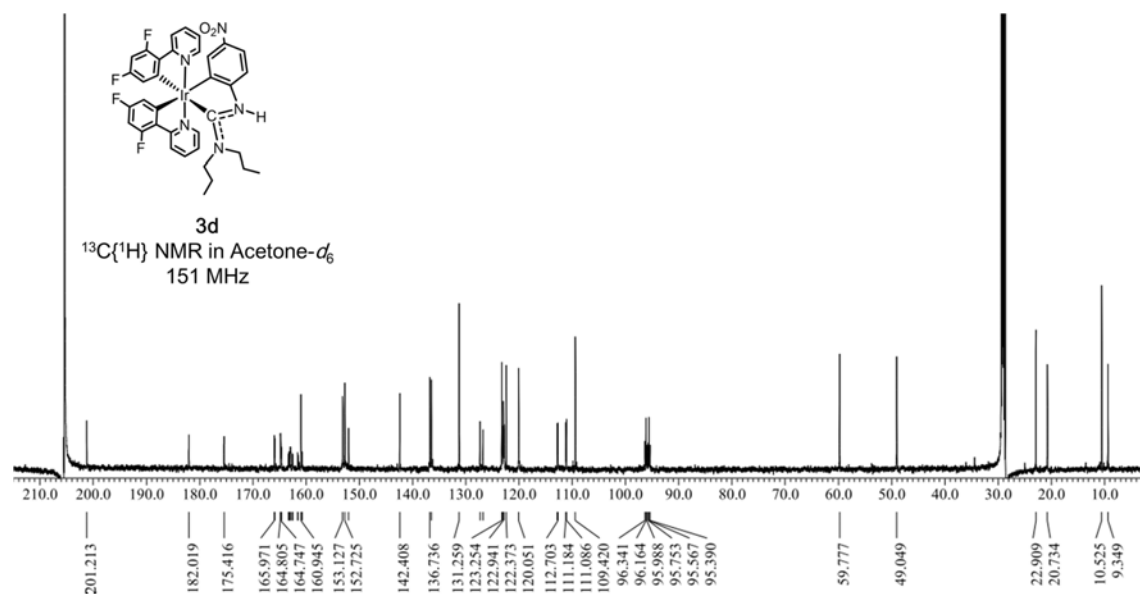


Figure S32. ^{13}C NMR spectrum of **3d**, recorded in acetone- d_6 at 151 MHz.

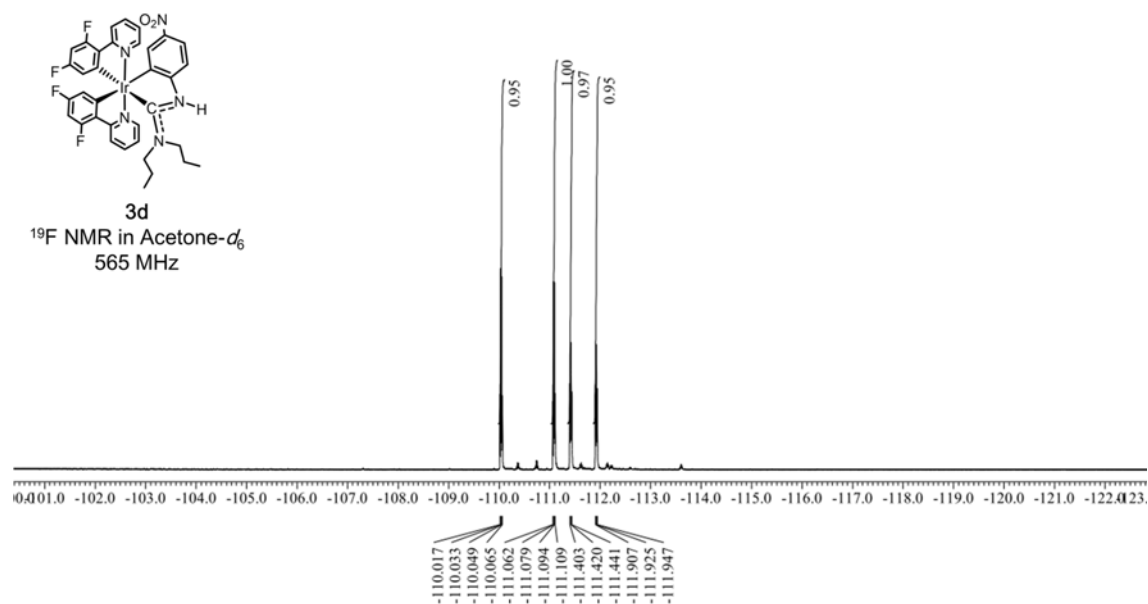


Figure S33. ^{19}F NMR spectrum of **3d**, recorded in acetone- d_6 at 565 MHz.

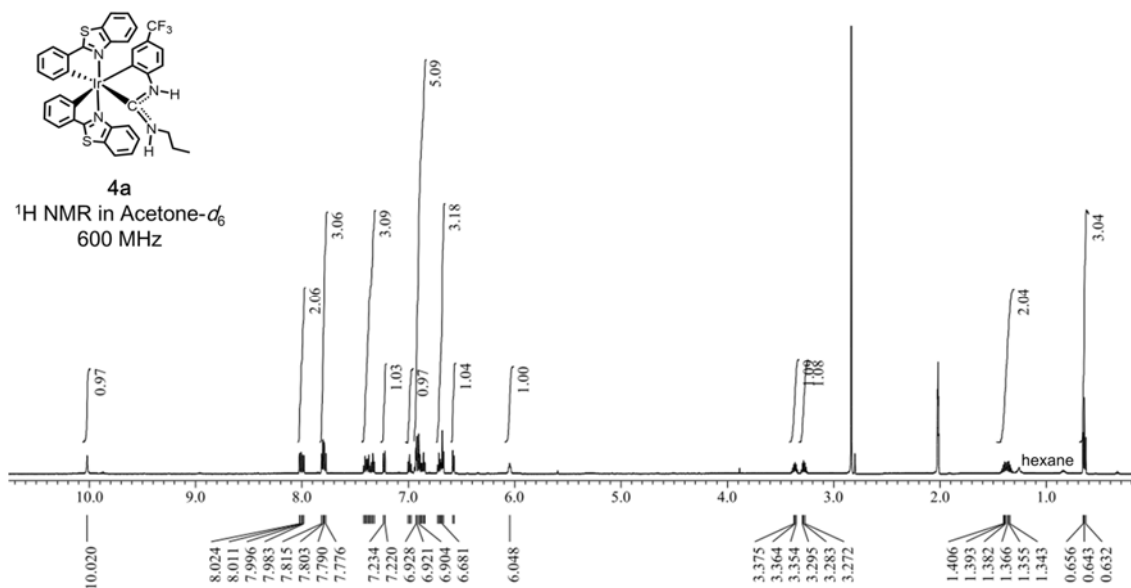


Figure S34. ¹H NMR spectrum of **4a**, recorded in acetone-*d*₆ at 600 MHz.

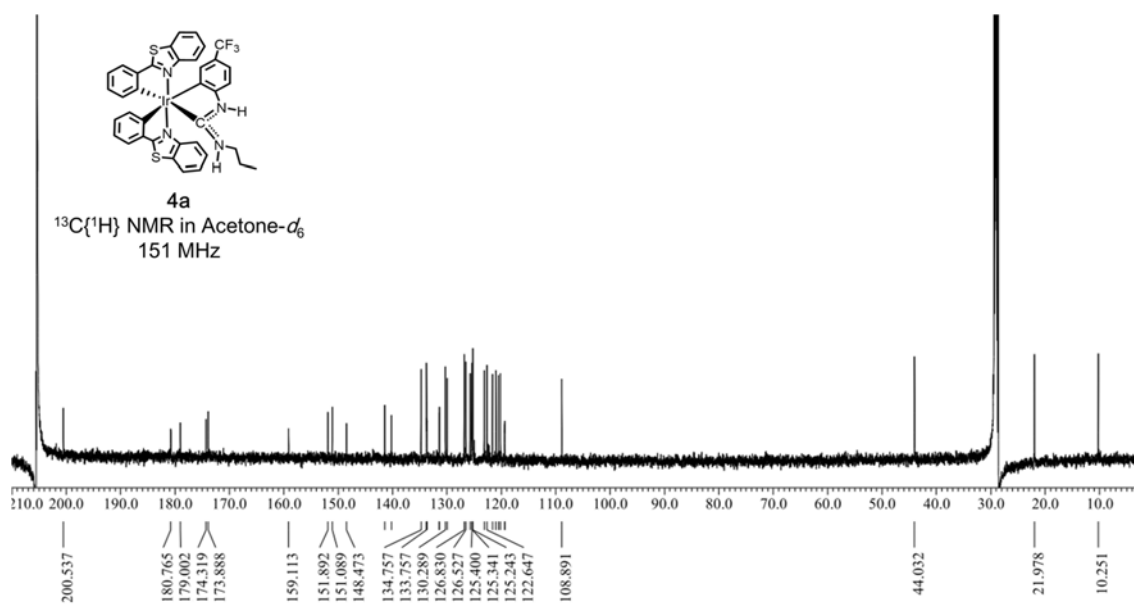


Figure S35. ¹³C NMR spectrum of **4a**, recorded in acetone-*d*₆ at 151 MHz.

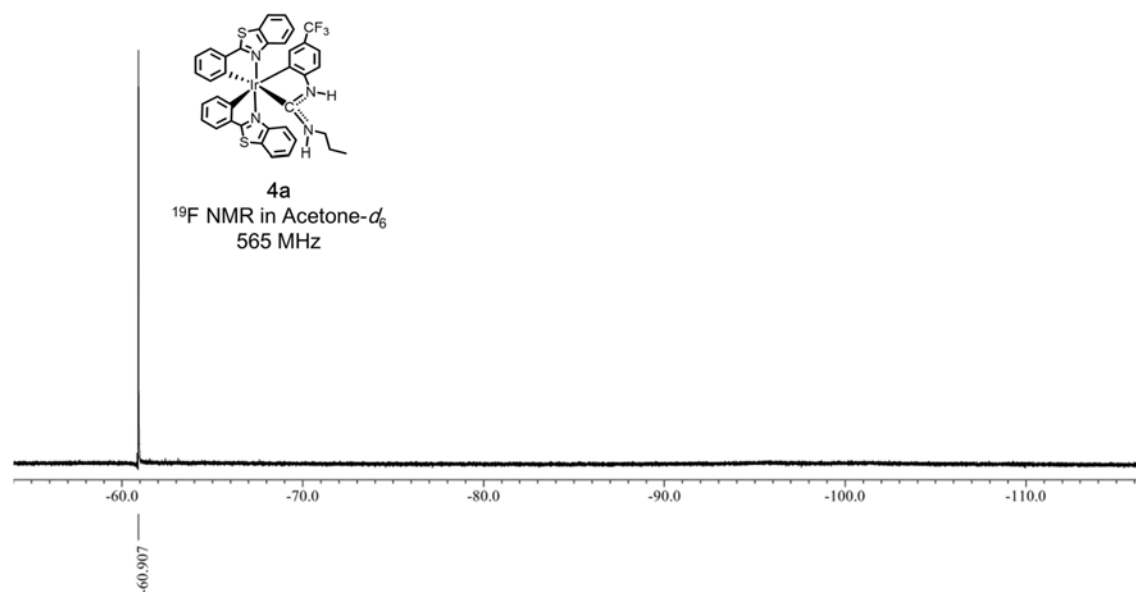


Figure S36. ^{19}F NMR spectrum of **4a**, recorded in acetone- d_6 at 565 MHz.

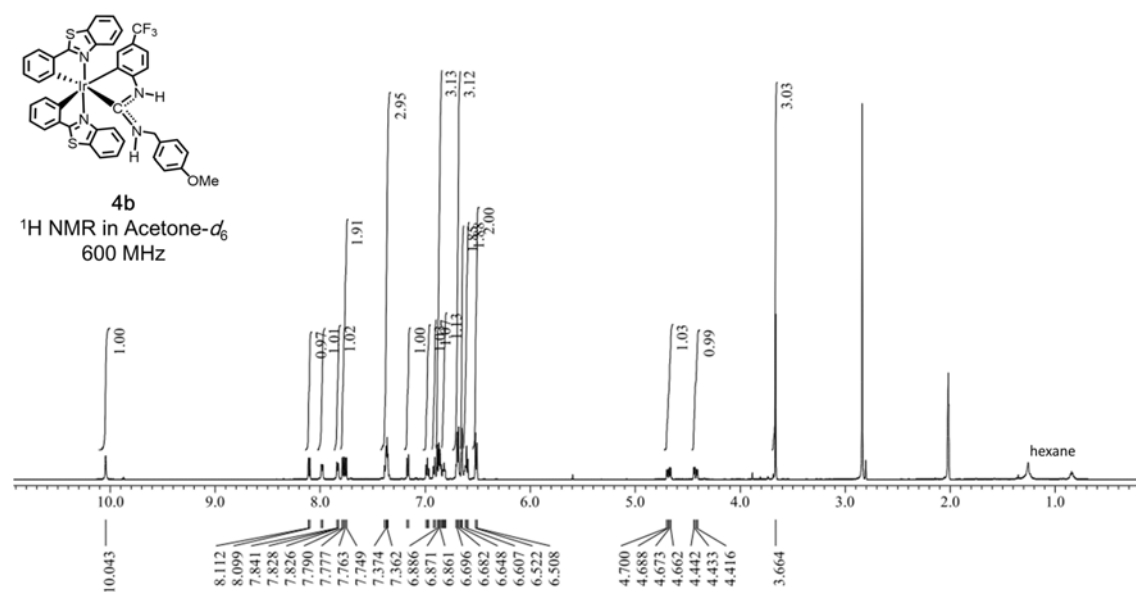


Figure S37. ^1H NMR spectrum of **4b**, recorded in acetone- d_6 at 600 MHz.

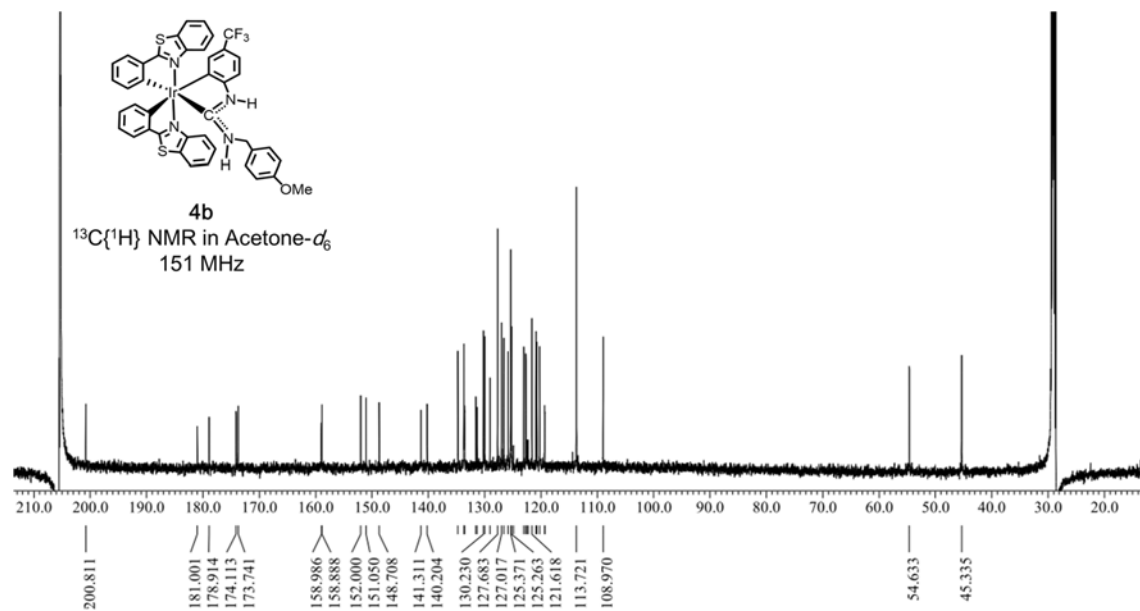


Figure S38. ^{13}C NMR spectrum of **4b**, recorded in acetone- d_6 at 151 MHz.

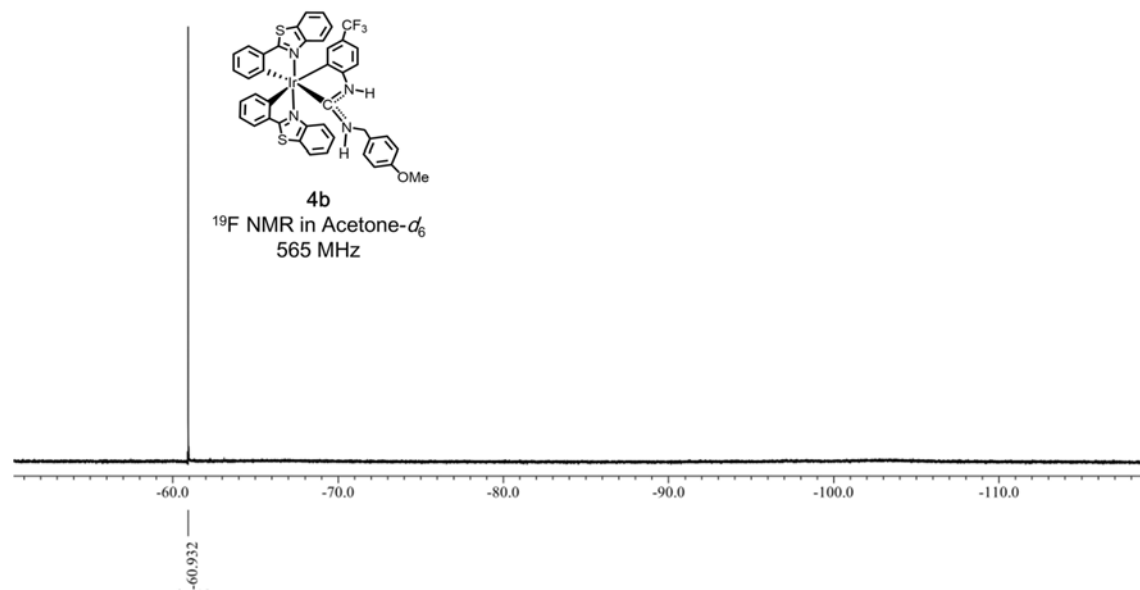


Figure S39. ^{19}F NMR spectrum of **4b**, recorded in acetone- d_6 at 565 MHz.

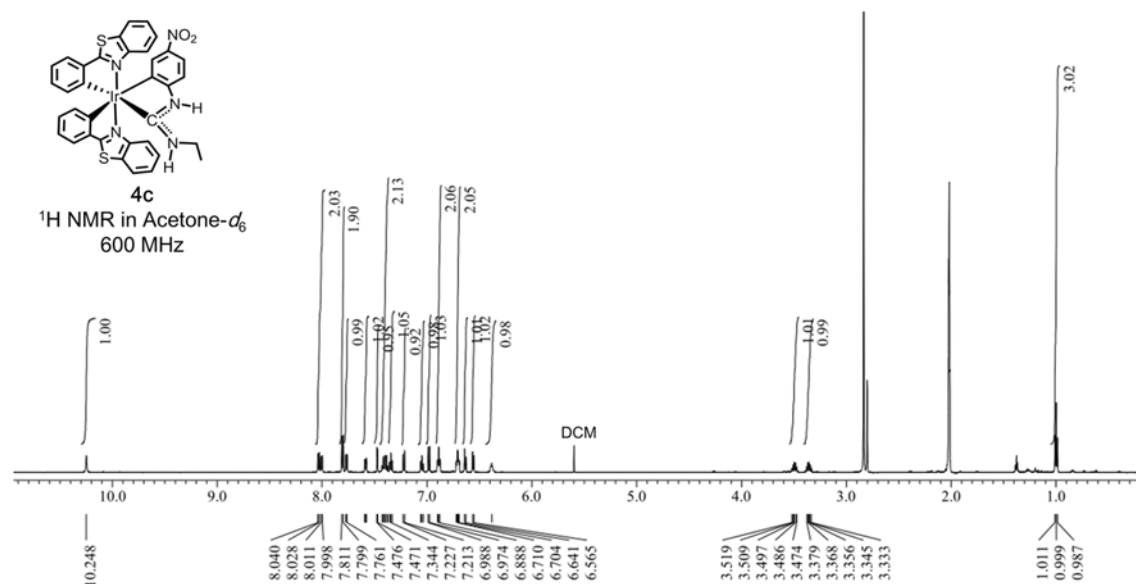


Figure S40. ¹H NMR spectrum of **4c**, recorded in acetone-*d*₆ at 600 MHz.

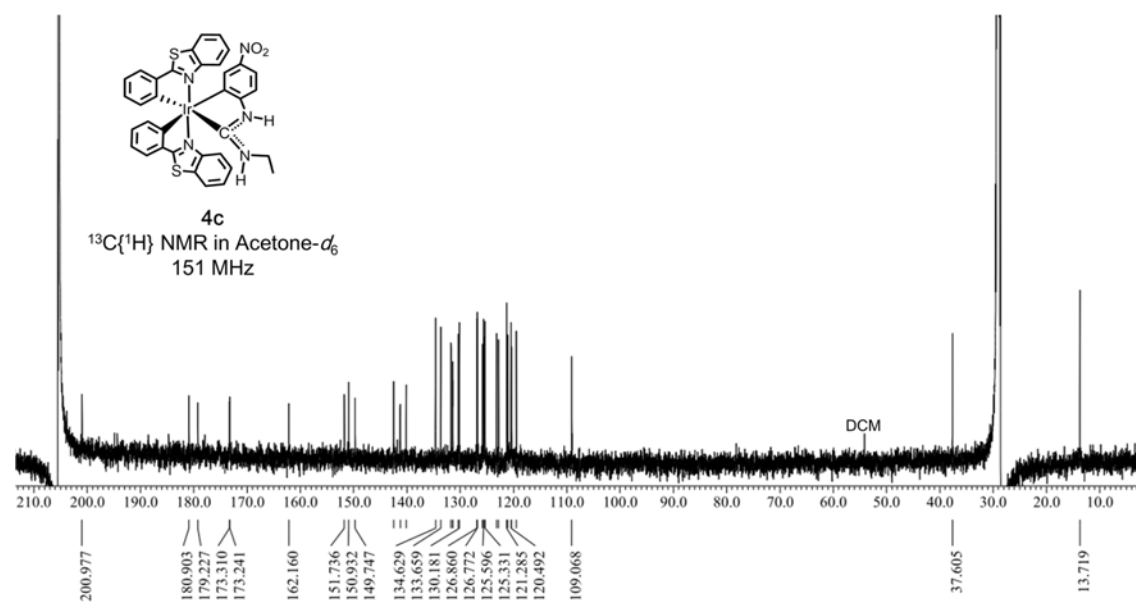


Figure S41. ¹³C NMR spectrum of **4c**, recorded in acetone-*d*₆ at 151 MHz.

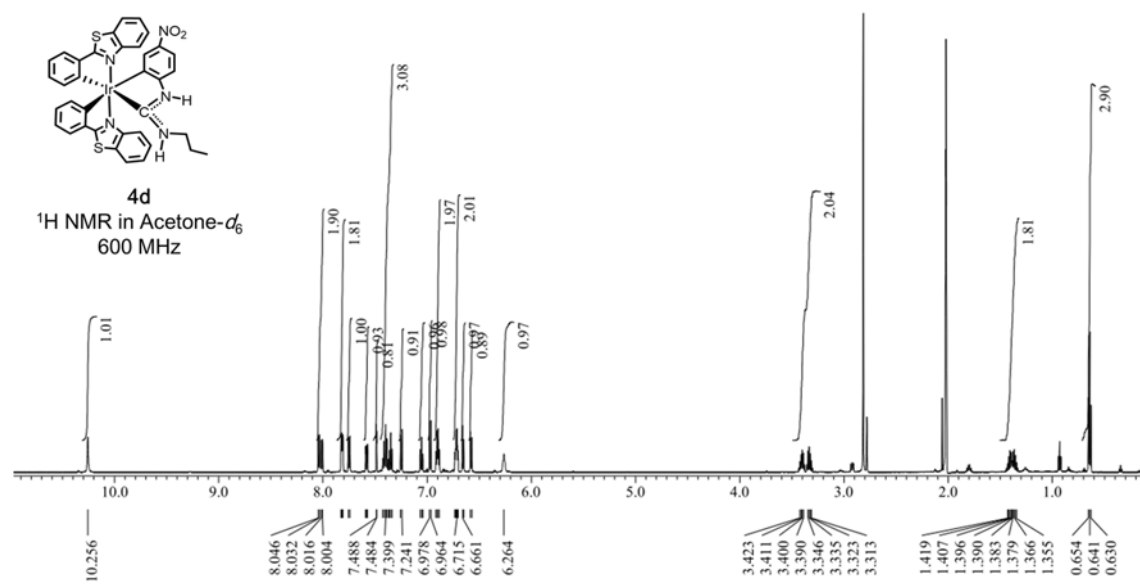


Figure S42. ¹H NMR spectrum of **4d**, recorded in acetone-*d*₆ at 600 MHz.

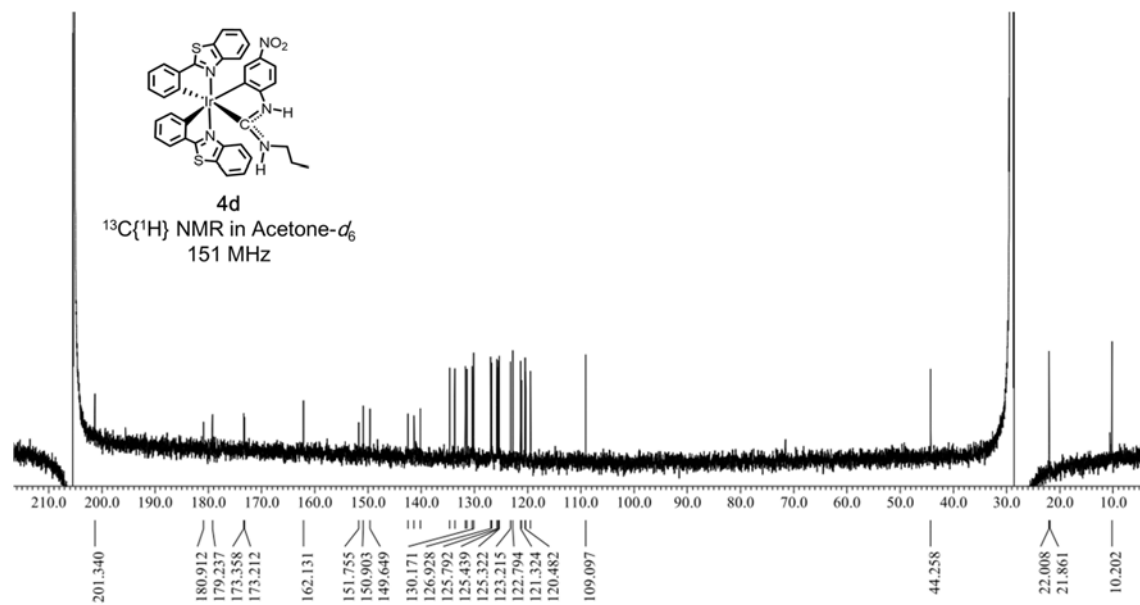


Figure S43. ¹³C NMR spectrum of **4d**, recorded in acetone-*d*₆ at 151 MHz.

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