Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis and Characterization of N-2-Aryl-1,2,3-Triazole Based Iridium Complexes as Photocatalysts with Tuneable Photoredox Potential

Rong Cai,[a] Wuming Yan,[a] Matthew G. Bologna,[a] Kaushalya de Silva,[a] Zhao Ma,[b] Harry O. Finklea,[a] Jeffrey L. Petersen,[a] Minyong Li*[b] and Xiaodong Shi*[a]

[a] *C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, USA*
[b] *Department of Medicinal Chemistry, School of Pharmacy, Shandong University, Jinan, Shandong, 250012, China*
Email: mli@sdu.edu.cn (ML) and Xiaodong.Shi@mail.wvu.edu (XS)

I. General Methods and materials:

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 600 MHz or Agilent 400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CD_3CN (δ 1.94 ppm) for ^{1}H NMR and CD_3CN (δ 1.39 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by UV lamp. ESI-MS were recorded on Thermo Scientific Q-exactive spectrometer.

The UV-Vis spectra were obtained with a Shimadzu UV-1800 UV spectrophotometer in 10 mm path length quartz cuvettes with 1×10^{-5}M Iridium complex solutions in freshly distilled acetonitrile (ACN). The fluorescence spectra were obtained in 10 mm path length quartz cuvettes using Shimadzu RF-5301 PC spectrofluorophotometer with 1×10^{-5}M Iridium complex solutions in ACN.

The fluorescence quantum yields of iridium complexes (Φ_x) were calculated based on equation (1) using $Ru(bpy)_3(PF_6)_2$ in ACN ($\Phi = 0.094$)[1] as a standard. All the samples were tested with 1×10^{-5}M ACN solutions under argon protection.

$$\Phi_x = \frac{n_x^2}{n_{std}^2}\cdot\frac{1-10^{-Abs_{std}}}{1-10^{-Abs_x}}\cdot\frac{I_x}{I_{std}}\cdot\Phi_{std} \qquad (1)$$

Φ is the quantum yield, **I** is integrated emission intensity, **Abs** is the absorption at the excitation wavelength (370nm), and **n** is the refractive index of pure solvents ($n_x = n_{std}$ in this case); 'std' stands for reference standard samples, 'x' stands for samples.

The excited-state lifetime were measured on a Horiba Fluorolog-3 spectrofluorometer with a NanoLED-370nm as the light source. The samples were prepared in ACN (1×10^{-5}M solutions) and tested in 10 mm path length quartz cuvettes. A highly diluted colloidal silica solution (0.01% dilution of LUDOX AS-40 colloidal silica using deionized water) was used to get the prompt spectra. All samples were tested under same conditions.

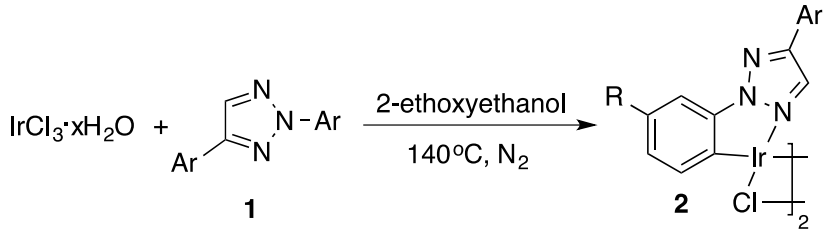
The cyclic voltammetry measurements were conducted on a WaveNow USB potentiostat in a three-compartment cell at 0.1 V/s scan rate using 1 mM Iridium complex solutions in freshly distilled acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. [2] A platinum wire was used as the working electrode and a folded

[1] J. M. Calvert, J. V. Caspar, R. A. Binstead, T. D. Westmoreland and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 6620-6627.
[2] K. N. Swanick, S. Ladouceur, E. Zysman-Colman and Z. Ding, *Chem. Commun.*, 2012, **48**, 3179.

platinum plate was used as the counter electrode. A silver wire was used as the quasi-reference electrode. Potentials were calibrated using Fc^+/Fc redox couple (0.40V in ACN) after each experiment and reported vs. SCE.

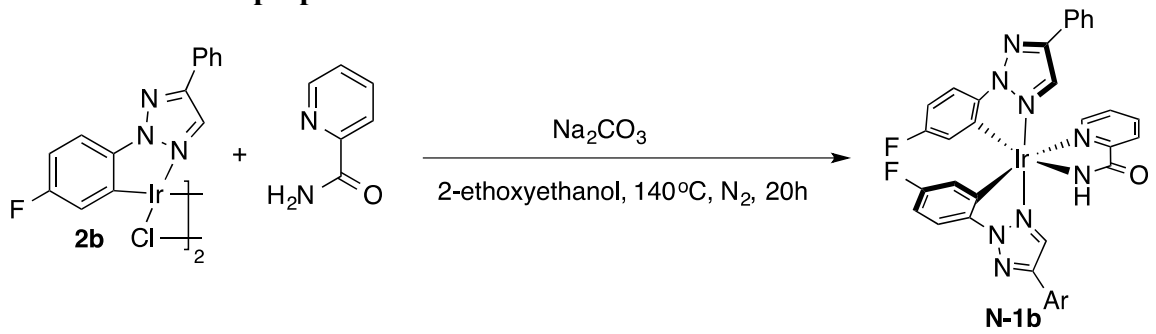
The N-2-aryl triazoles were synthesized according to the literature reported previously[3]. The photocatalytic reactions were performed under same conditions as previous literature reports.[4]

General procedure for the preparation of $[(pta)_2Ir(\mu\text{-}Cl)]_2$:



The preparation $[(pta)_2Ir(\mu\text{-}Cl)]_2$ is adapted from literature report.[5] The pta ligand **1** (2.5 mmol), $IrCl_3 \cdot xH_2O$ (353 mg, 1 mmol) in 32 mL 2-ethoxyethanol/water (3:1) was refluxed at 140 °C under nitrogen or argon atmosphere for 24 h. After cooled to room temperature, the yellow precipitate was isolated by filtration and washed with water and ethanol and allowed to air dry. The yellow solid was used for the next step without further purification. Yields of the μ-dichloro-bridged iridium(III) dimer **2** are ranged from 53% to 95% (**2a**: 63%, **2b**: 92%, **2c**: 53%, **2d**: 78%, **2e**: 87%, **2f**: 89%, **2g**: 95%).

Procedure for the preparation of N-1b:



The procedure is adapted from literature report[6]. The μ-dichloro-bridged iridium(III) dimer **2b** (424 mg, 0.3 mmol), sodium carbonate (350 mg, 3.3 mmol) and the N^N ligand 2-picolinamide (96 mg, 0.78 mmol) was suspended in 22 mL 2-ethoxyethanol. The reaction mixture was stirred at 140 °C for 20 h under nitrogen atmosphere. After the reaction was cooled to room temperature, 150 mL ethyl acetate was added. The solution

---

[3] a) Liu, Y.; Yan, W.; Chen, Y.; Petersen, J. L. ; Shi, X. *Org. Lett.* **2008**, *10*, 5389-5392. b) Yan, W.; Wang, Q.; Lin, Q.; Li, M.; Petersen, J. L. ; Shi, X. *Chem. Eur. J.* **2011**, *17*, 5011-5018.

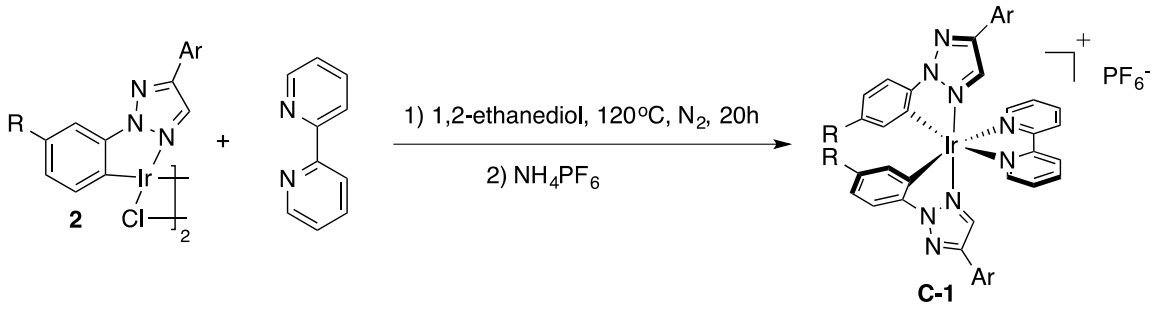
[4] a) A. G. Condie, J. C. González-Gómez and C. R. J. Stephenson, *J. Am. Chem. Soc.*, **2010**, *132*, 1464-1465; b) J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam and C. R. J. Stephenson, *Nat. Chem.*, **2012**, *4*, 854-859.

[5] Fernández-Hernández, J. M.; Yang, C. H.; Beltrán, J. I.; Lemaur, V.; Polo, F.; Fröhlich, R.;et al and De Cola, L. *J. Am. Chem. Soc.* **2011**, *133*, 10543-10558.

[6] You, Y. ; Park, S. Y. *J. Am. Chem. Soc.* **2005**, *127*, 12438-12439.

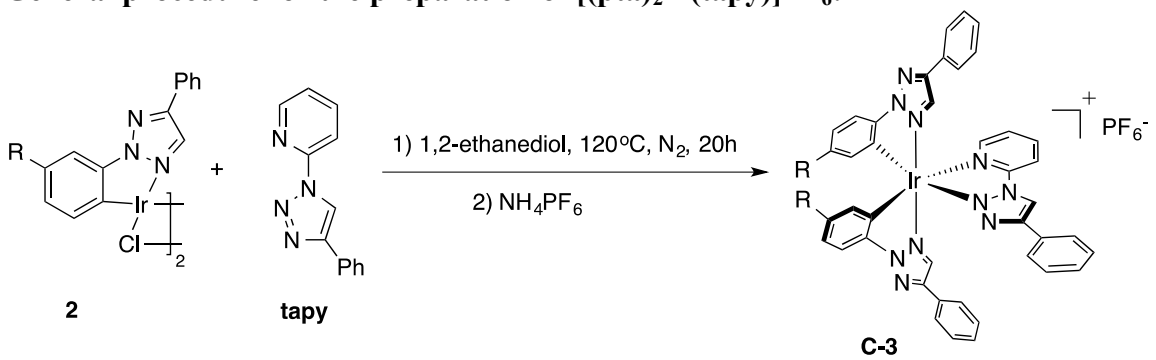
was extracted with water three times. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The solid was then purified by flash chromatography on silica gel using ethyl acetate and recrystallized from ether / hexane to yield **N-1b** in 75% yield.

General procedure for the preparation of $[(pta)_2Ir(ppy)]PF_6$[7]:



The μ-dichloro-bridged iridium(III) dimer **2** (0.15 mmol) and the N^N ligand 2,2'-bispyridine (58 mg, 0.375 mmol) was suspended in 10 mL 1,2-ethanediol. The reaction mixture was stirred at 120 °C for 20 h under nitrogen or argon atmosphere. After the reaction was cooled to room temperature, 150 mL distilled water was added. The solution was extracted with ethyl ether three times to remove the excess bpy. Ammonium hexafluorophosphate solution (1 g in 10 mL water) was added to the aqueous layer to yield a yellow precipitate. The solution was then heated at 70 °C for 10 min. After cooled to room temperature, the yellow precipitate was filtrated and further purified by flash chromatography on silica gel using 10% DCM / acetone eluent. After the column, the solid was re-dissolved in minimum amount of methanol and precipitated again using NH_4PF_6 (1 g in 10 mL water). The yellow precipitate was filtered and washed with water and then recrystallized from minimum amount of hot acetonitrile for further experiments.

General procedure for the preparation of $[(pta)_2Ir(tapy)]PF_6$:

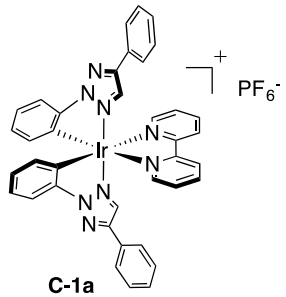


The μ-dichloro-bridged iridium(III) dimer **2** (0.15 mmol) and the N^N ligand tapy (83 mg, 0.375 mmol) was suspended in 10 mL 1,2-ethanediol. The reaction mixture was stirred at 120 °C for 20 h under nitrogen or argon atmosphere. After the reaction was cooled to room temperature, 150 mL distilled water was added, followed by ammonium

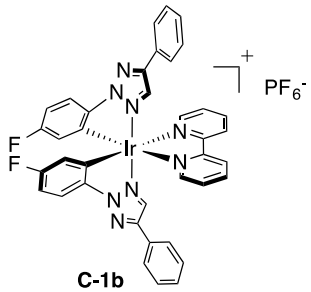
[7] Ladouceur, S.; Fortin, D. ; Zysman-Colman, E. *Inorg. Chem.* **2011**, *50*, 11514-11526.

hexafluorophosphate solution (1 g in 10 mL water) to yield a yellow precipitate. The precipitate was filtered and further purified by flash chromatography on silica gel using 10% acetone/DCM eluent. After the column, the solid was re-dissolved in minimum amount of methanol and precipitated again using NH_4PF_6 (1 g in 10 mL water). The precipitate was filtered and washed with water and then recrystallized from minimum amount of hot acetonitrile for further experiments.

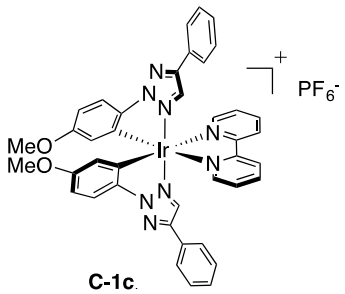
II. Compounds Characterization



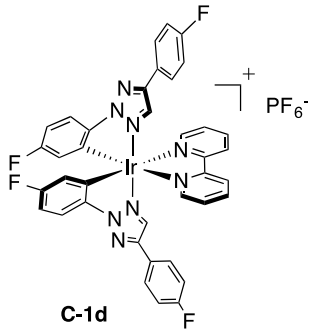
C-1a: Yellow Solid (79% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.58 (d, *J* = 8.2 Hz, 2H), 8.22-8.16 (m, 4H), 7.88 (dd, *J* = 8.1, 1.5 Hz, 4H), 7.84 (s, 2H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.57 (ddd, *J* = 7.6, 5.5, 1.1 Hz, 2H), 7.51-7.45 (m, 6H), 7.19 (td, *J* = 7.7, 1.1 Hz, 2H), 7.00 (td, *J* = 7.5, 1.3 Hz, 2H), 6.52 (dd, *J* = 7.5, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 157.57, 152.88, 150.26, 142.34, 141.07, 133.72, 132.51, 130.81, 130.64, 130.26, 129.65, 129.57, 129.44, 127.01, 125.64, 125.24, 115.46. ESI-MS calculated for $[C_{38}H_{28}IrN_8]^+$: 789.2066, found: 789.2047.



C-1b: Yellow Solid (85% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.57 (d, *J* = 8.2 Hz, 2H), 8.24-8.18 (m, 4H), 7.88-7.83 (m, 6H), 7.80 (s, 2H), 7.59 (ddd, *J* = 7.6, 5.5, 1.3 Hz, 2H), 7.51-7.43 (m, 6H), 6.98 (td, *J* = 8.8, 2.6 Hz, 2H), 6.22 (dd, *J* = 8.8, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.01 (d, *J* = 248.1 Hz), 157.48, 153.12, 150.33, 141.32, 138.90, 133.39 (d, *J* = 6.0 Hz), 132.66, 130.86, 130.25, 129.55, 129.48, 127.05, 125.71, 120.13 (d, *J* = 20.4 Hz), 117.23 (d, *J* = 9.2 Hz), 112.05 (d, *J* = 14.6 Hz); ^{19}F NMR (376 MHz, CD_3CN): δ -73.84 (d, *J* = 706.8 Hz, 6F), -114.80 (m, 2F). ESI-MS calculated for $[C_{38}H_{26}F_2IrN_8]^+$: 825.1878, found: 825.1861.

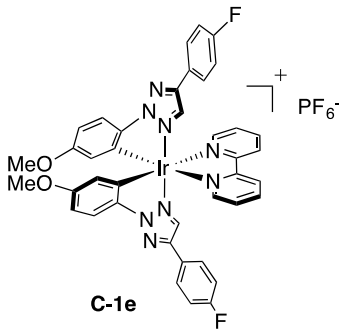


C-1c: Yellow Solid (68% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.55 (d, *J* = 8.2 Hz, 2H), 8.23-8.18 (m, 4H), 7.85 (dd, *J* = 8.1, 1.6 Hz, 4H), 7.75 (d, *J* = 9.1 Hz, 2H), 7.74 (s, 2H), 7.58 (ddd, *J* = 7.7, 5.5, 1.2 Hz, 2H), 7.50-7.41 (m, 6H), 6.77 (dd, *J* = 8.8, 2.6 Hz, 2H), 5.91 (d, *J* = 2.6 Hz, 2H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 160.70, 157.54, 153.00, 149.67, 141.05, 136.24, 132.81, 131.68, 130.66, 130.24, 129.67, 129.42, 126.91, 125.56, 118.95, 116.72, 109.51, 55.96. ESI-MS calculated for $[C_{40}H_{32}IrN_8O_2]^+$: 849.2277, found: 849.2262.



C-1d

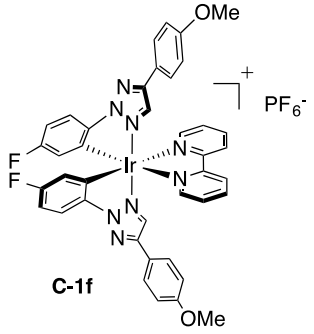
C-1d: Synthesized from one-Pot sequential reactions without isolating the μ-dichloro-bridged iridium(III) dimer. Yellow Solid (62% yield over two steps). ^{1}H NMR (400 MHz, CD_3CN): δ 8.56 (d, *J* = 8.1 Hz, 2H), 8.24-8.17 (m, 4H), 7.91-7.86 (m, 4H), 7.84 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.76 (s, 2H), 7.59 (ddd, *J* = 7.7, 5.5, 1.2 Hz, 2H), 7.26-7.20 (m, 4H), 6.98 (td, *J* = 8.8, 2.7 Hz, 2H), 6.21 (dd, *J* = 8.8, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 164.49 (d, *J* = 246.0 Hz), 163.03 (d, *J* = 248.1 Hz), 157.47, 153.13, 149.44, 141.34, 138.83, 133.35 (d, *J* = 6.0 Hz), 132.53, 129.55, 129.29 (d, *J* = 8.5 Hz), 126.00 (d, *J* = 2.9 Hz), 125.70, 120.13 (d, *J* = 20.5 Hz), 117.20 (d, *J* = 22.1 Hz), 117.24 (d, *J* = 9.2 Hz), 112.02 (d, *J* = 24.7 Hz); ^{19}F NMR (376 MHz, CD_3CN): -73.92 (d, *J* = 706.0 Hz, 6F), -113.59 (m, 2F), -114.77 (m, 2F). ESI-MS calculated for $[C_{38}H_{24}F_4IrN_8]^+$: 861.1689, found: 861.1670.



C-1e

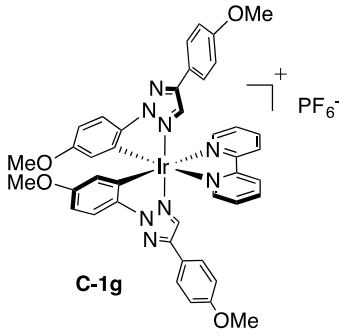
C-1e: Yellow Solid (55% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.56 (d, *J* = 8.1 Hz, 2H), 8.23-8.18 (m, 4H), 7.89-7.84 (m, 4H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.71 (s, 2H), 7.58 (ddd, *J* = 7.7, 5.5, 1.2 Hz, 2H), 7.25-7.19 (m, 4H), 6.76 (dd, *J* = 8.8, 2.6 Hz, 2H), 5.90 (d, *J* = 2.6 Hz, 2H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 164.36 (d, *J* = 246.0 Hz), 160.72, 157.53, 152.98, 148.78, 141.08, 136.19, 132.77, 131.55, 129.42, 129.12 (d, *J* =

8.4 Hz), 126.19 (d, *J* = 3.0 Hz), 125.57, 118.99, 117.16 (d, *J* = 22.0 Hz), 116.72, 109.47, 55.96; ^{19}F NMR (376 MHz, CD_3CN): -73.84 (d, *J* = 706.2 Hz, 6F), -113.93 (m, 2F). ESI-MS calculated for $[C_{40}H_{30}F_2IrN_8O_2]^+$: 885.2089, found: 885.2078.



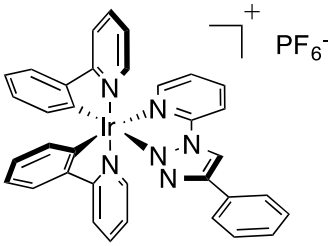
C-1f

C-1f: Yellow Solid (56% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.56 (d, *J* = 8.1 Hz, 2H), 8.23-8.17 (m, 4H), 7.83-7.77 (m, 6H), 7.69 (s, 2H), 7.58 (ddd, *J* = 7.7, 5.5, 1.2 Hz, 2H), 7.04-7.00 (m, 4H), 6.97 (td, *J* = 8.8, 2.7 Hz, 2H), 6.19 (dd, *J* = 8.8, 2.6 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 162.89 (d, *J* = 247.6 Hz), 162.00, 157.47, 153.09, 150.30, 141.28, 138.98, 133.29 (d, *J* = 6.0 Hz), 131.96, 129.53, 128.57, 125.68, 121.90, 120.06 (d, *J* = 20.4 Hz), 117.02 (d, *J* = 9.1 Hz), 115.62, 111.91 (d, *J* = 24.5 Hz), 56.21; ^{19}F NMR (376 MHz, CD_3CN): -73.87 (d, *J* = 705.7 Hz, 6F), -115.13 (m, 2F). ESI-MS calculated for $[C_{40}H_{30}F_2IrN_8O_2]^+$: 885.2089, found: 885.2076.



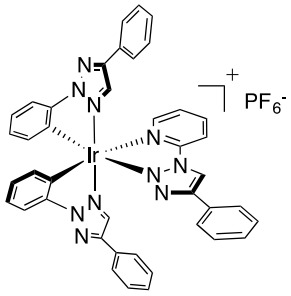
C-1g

C-1g: Yellow Solid (38% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.55 (d, *J* = 8.1 Hz, 2H), 8.22-8.17 (m, 4H), 7.79-7.75 (m, 4H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.64 (s, 2H), 7.59-7.56 (m, 2H), 7.03-6.99 (m, 4H), 6.76 (dd, *J* = 8.8, 2.6 Hz, 2H), 5.89 (d, *J* = 2.6 Hz, 2H), 3.82 (s, 6H), 3.62 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 161.84, 160.55, 157.53, 152.96, 149.65, 141.00, 136.34, 132.70, 130.96, 129.39, 128.41, 125.54, 122.11, 118.96, 116.51, 115.59, 109.37, 56.19, 55.94. ESI-MS calculated for $[C_{42}H_{36}IrN_8O_2]^+$: 909.2489, found: 909.2478.



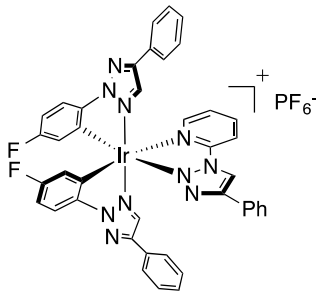
C-2

C-2: Yellow Solid (40% yield). ^{1}H NMR (600 MHz, CD_3CN): δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.26 (td, *J* = 8.0, 1.6 Hz, 1H), 8.09-8.07 (m, 2H), 8.05 (s, 1H), 7.95 (ddd, *J* = 4.6, 3.2, 1.6 Hz, 2H), 7.90-7.88 (m, 3H), 7.82-7.80 (m, 3H), 7.73 (dd, *J* = 5.8, 0.7 Hz, 1H), 7.54-7.49 (m, 4H), 7.10-7.04 (m, 4H), 6.93 (dtd, *J* = 14.5, 7.3, 1.3 Hz, 2H), 6.28 (dd, *J* = 21.6, 7.7 Hz, 2H); ^{13}C NMR (150 MHz, CD_3CN): δ 168.48, 167.95, 153.69, 150.90, 150.83, 150.18, 149.39, 148.19, 145.52, 145.21, 145.19, 143.13, 140.05, 139.98, 136.93, 132.94, 132.38, 131.81, 131.47, 131.03, 130.42, 128.56, 127.76, 127.61, 126.00, 125.74, 124.78, 124.67, 124.12, 123.92, 121.01, 120.97, 115.87. ESI-MS calculated for $[C_{35}H_{26}IrN_6]^+$: 723.1843, found: 723.1858.



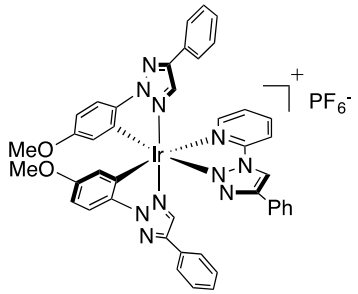
C-3a

C-3a: Light yellow Solid (85% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.46 (d, *J* = 8.4 Hz, 1H), 8.33 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 8.25 (s, 1H), 8.13 (s, 1H), 8.01-7.97 (m, 4H), 7.92-7.90 (m, 4H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.58-7.44 (m, 10H), 7.26-7.19 (m, 2H), 7.02 (dtd, *J* = 10.6, 7.5, 1.3 Hz, 2H), 6.52 (dd, *J* = 7.6, 5.1 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 153.49, 151.48, 150.37, 150.20, 149.76, 143.74, 142.50, 142.24, 138.52, 134.05, 133.56, 133.35, 133.33, 131.88, 130.91, 130.88, 130.51, 130.35, 130.33, 129.64, 129.59, 129.56, 129.26, 128.57, 127.72, 127.69, 127.47, 127.02, 126.98, 125.79, 125.56, 124.70, 115.77, 115.59, 115.37. ESI-MS calculated for $[C_{41}H_{30}IrN_{10}]^+$: 855.2284, found: 855.2269.



C-3b

C-3b: Light yellow Solid (71% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.46 (ddd, *J* = 8.4, 1.2, 0.8 Hz, 1H), 8.34 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 8.32 (s, 1H), 8.10 (s, 1H), 8.03-7.99 (m, 3H), 7.95 (s, 1H), 7.91-7.88 (m, 4H), 7.86 (dd, *J* = 8.8, 4.9 Hz, 2H), 7.59-7.44 (m, 10H), 7.02 (tdd, *J* = 8.8, 6.0, 2.7 Hz, 2H), 6.23 (ddd, *J* = 8.8, 4.3, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 162.80 (d, *J* = 248.1 Hz), 162.64 (d, *J* = 247.9 Hz), 153.59, 151.71, 150.44, 150.27, 149.61, 144.02, 139.10, 139.08, 138.80, 133.45 (d, *J* = 3.6 Hz), 131.95, 130.94 (d, *J* = 2.1 Hz), 130.55, 130.33, 130.31, 130.26, 130.19, 129.48, 129.45, 128.49, 127.71, 127.54, 127.34, 127.28, 127.06, 127.02, 120.56 (d, *J* = 21.0 Hz), 120.12 (d, *J* = 21.1 Hz), 117.36 (d, *J* = 9.3 Hz), 117.05 (d, *J* = 9.3 Hz), 115.84, 112.57 (d, *J* = 19.4 Hz), 112.32 (d, *J* = 19.4 Hz) ; ^{19}F NMR (376 MHz, CD_3CN): -73.92 (d, *J* = 705.9 Hz, 6F), -114.50 (m, 1F), -115.05 (m, 1F). ESI-MS calculated for $[C_{41}H_{28}F_2IrN_{10}]^+$: 891.2096, found: 891.2083.



C-3c

C-3c: Light yellow Solid (44% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 8.45 (dd, *J* = 8.3, 0.6 Hz, 1H), 8.33 (td, *J* = 8.0, 1.5 Hz, 1H), 8.29 (s, 1H), 8.06-8.00 (m, 3H), 8.05 (s, 1H), 7.90 (s, 1H), 7.90-7.87 (m, 4H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.59-7.42 (m, 10H), 6.80 (ddd, *J* = 8.7, 6.2, 2.6 Hz, 2H), 5.91 (dd, *J* = 2.2 Hz, 2H), 3.64 (2s, 6H).; ^{13}C NMR (100 MHz, CD_3CN): δ 160.58, 160.30, 153.47, 151.58, 149.76, 149.71, 149.60, 143.76, 138.54, 136.40, 136.08, 132.50, 132.46, 131.90, 130.74, 130.72, 130.52, 130.31, 130.29, 129.78, 129.66, 129.63, 128.57, 127.72, 127.43, 126.92, 126.88, 126.83, 119.37, 118.81, 116.86, 116.56, 115.74, 110.01, 109.82, 56.02, 55.97. ESI-MS calculated for $[C_{43}H_{34}IrN_{10}O_2]^+$: 915.2495, found: 915.2481.

III. ORTEP Drawing of the Crystal Structures

ORTEP Drawing of the Crystal Structures for complex N-1

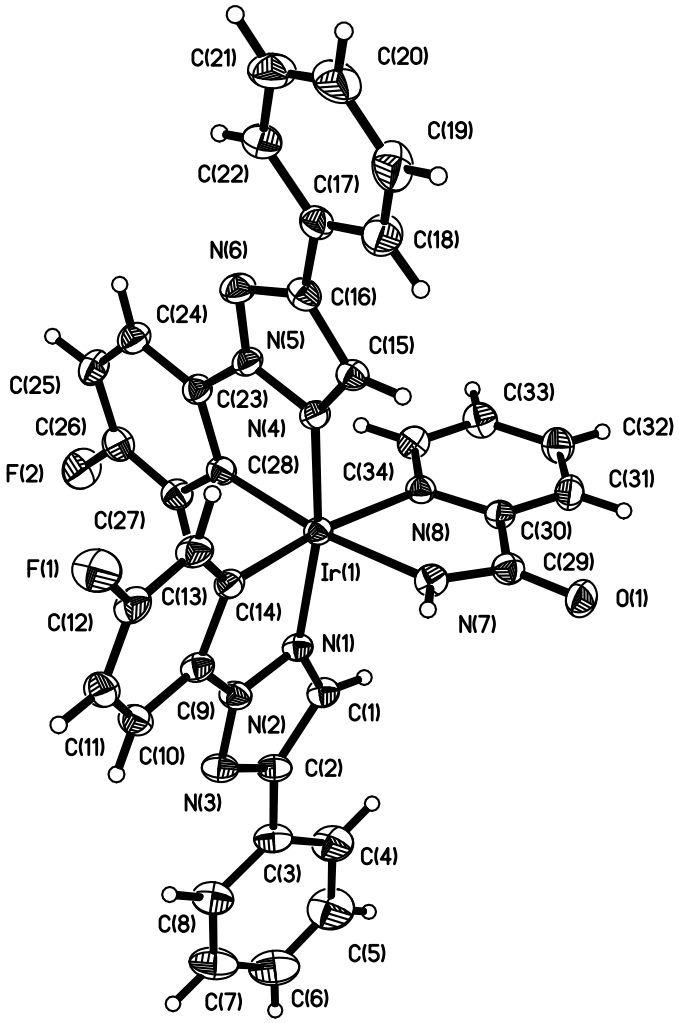


Figure 1. Perspective view of the molecular structure of $Ir(N_3C_{14}H_9F)_2(C_6H_5N_2O)$ with the atom labeling scheme. The thermal ellipsoids are scaled to 30% probability. CCDC number: 1012360

ORTEP Drawing of the Crystal Structures for complex C-1

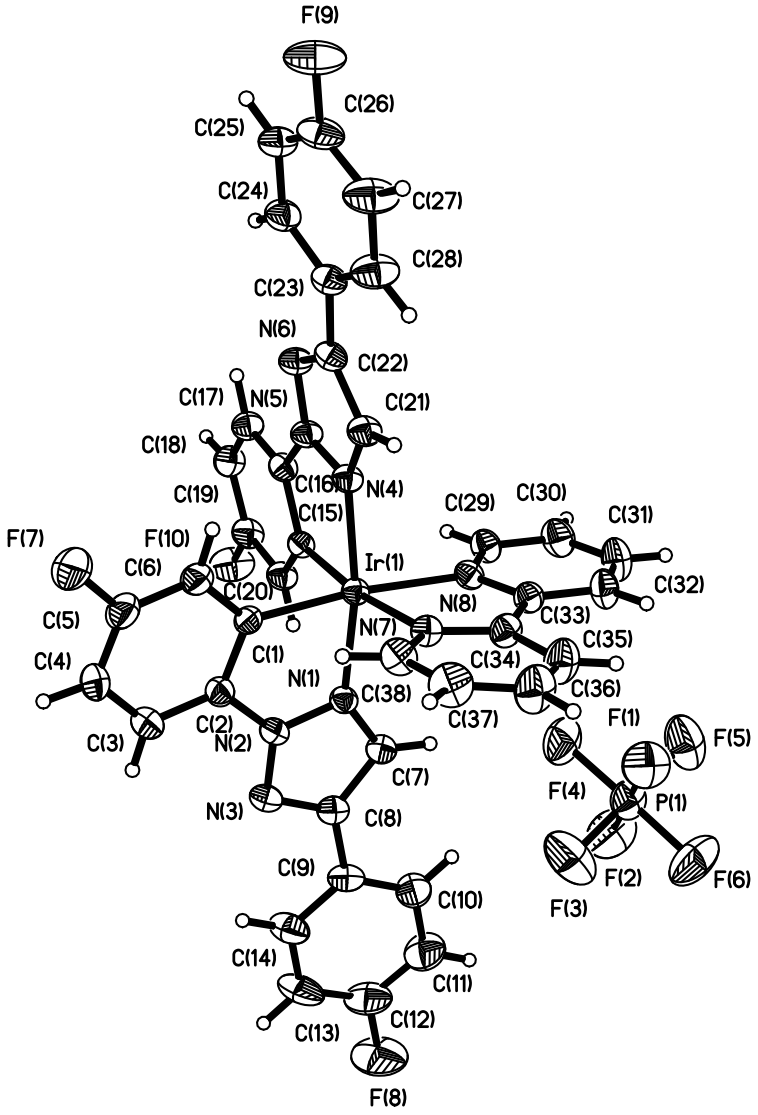
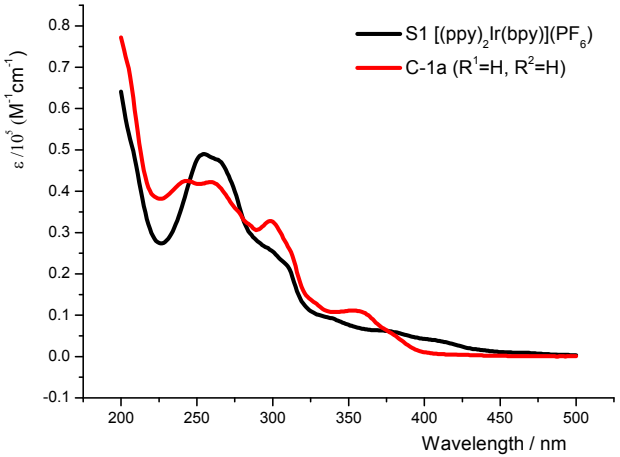
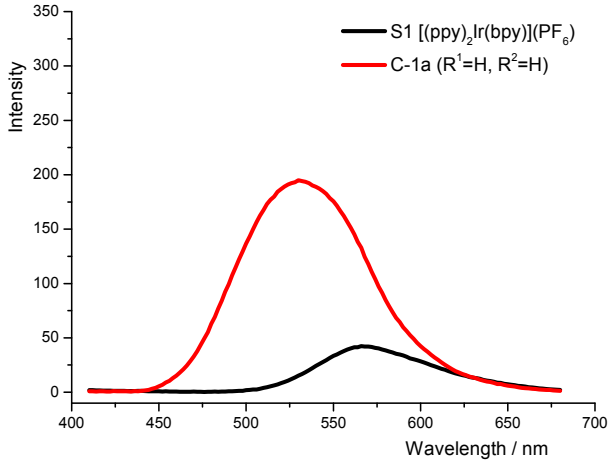
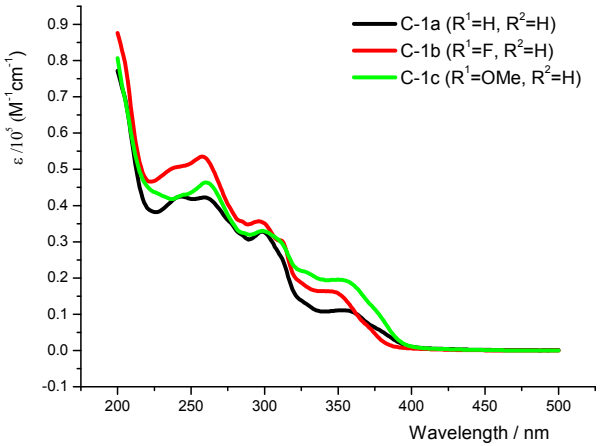


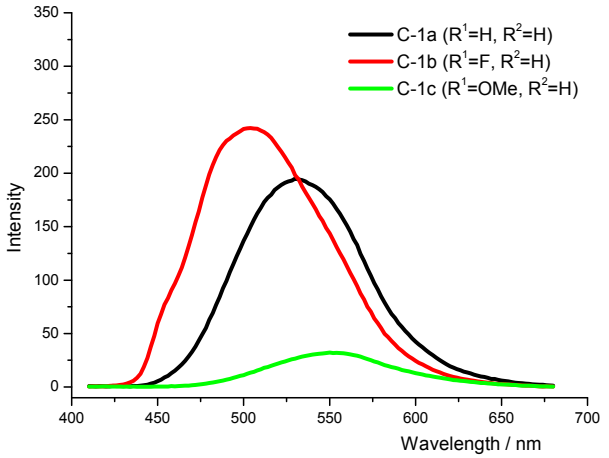
Figure 1. Perspective view of the molecular structure of $[Ir(bpy)(C_{14}H_8N_3F_2)_2]PF_6$ with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 1010939

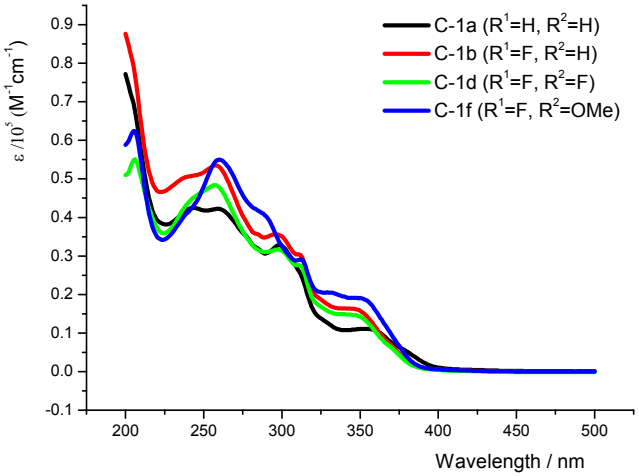
IV. UV-Vis Spectra and Fluorescence Spectra

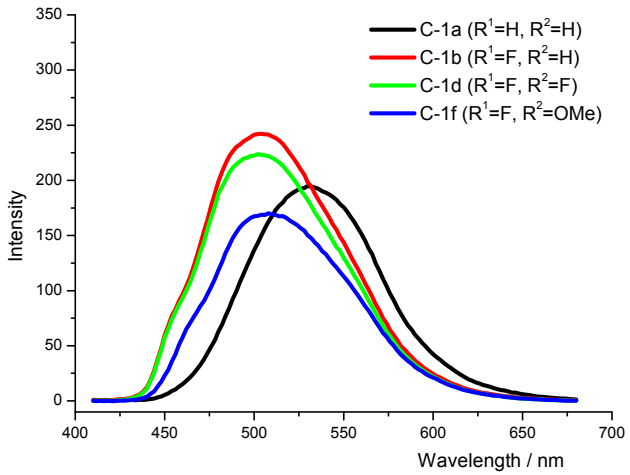


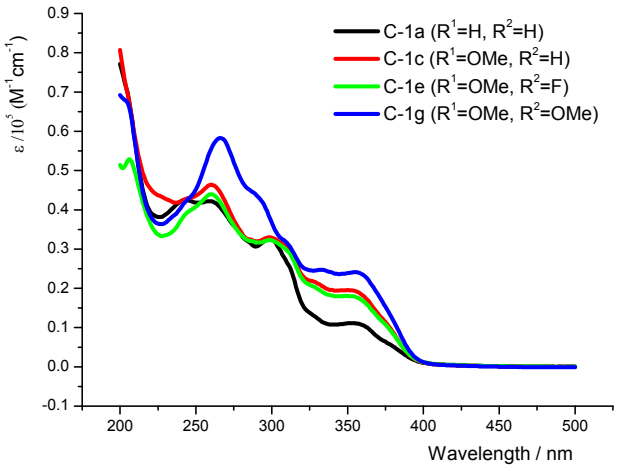


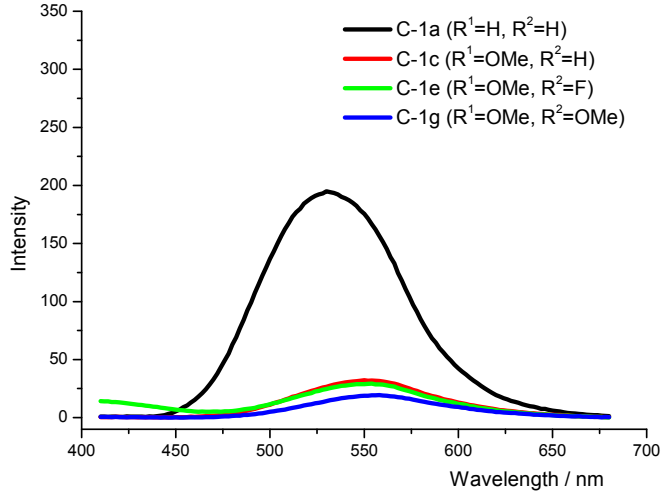


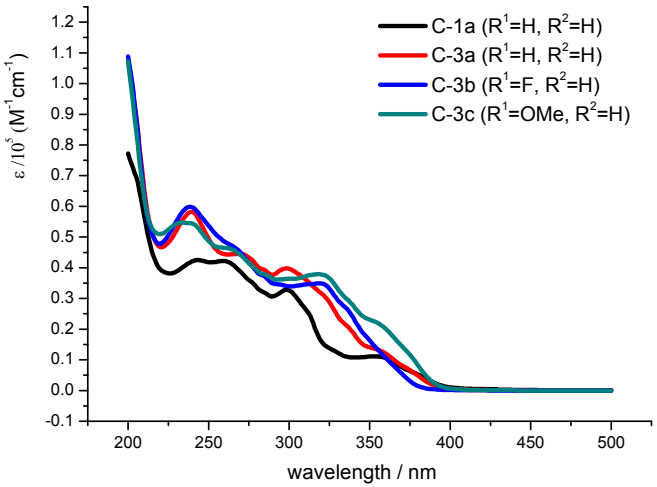


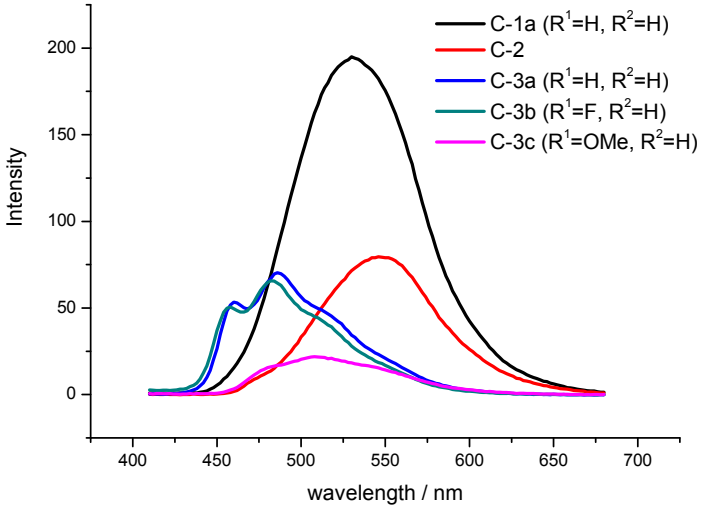

C-1a (R1=H, R2=H)
C-1b (R1=F, R2=H)
C-1d (R1=F, R2=F)
C-1f (R1=F, R2=OMe)
ε /10^5 (M^-1cm^-1)
Wavelength / nm

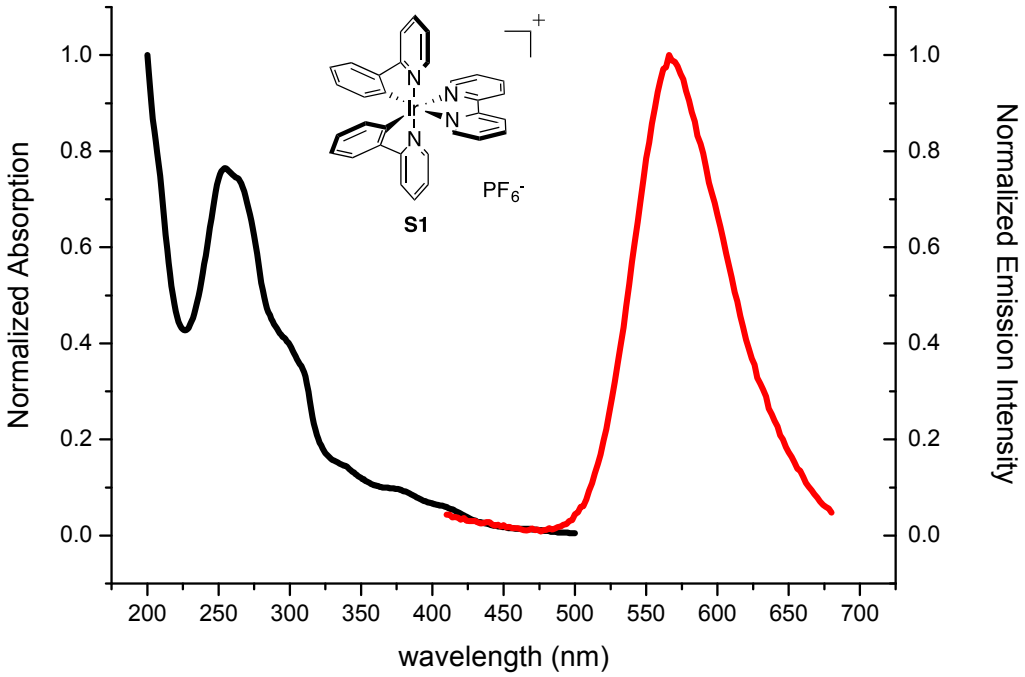

C-1a (R1=H, R2=H)
C-1b (R1=F, R2=H)
C-1d (R1=F, R2=F)
C-1f (R1=F, R2=OMe)
Intensity
Wavelength / nm

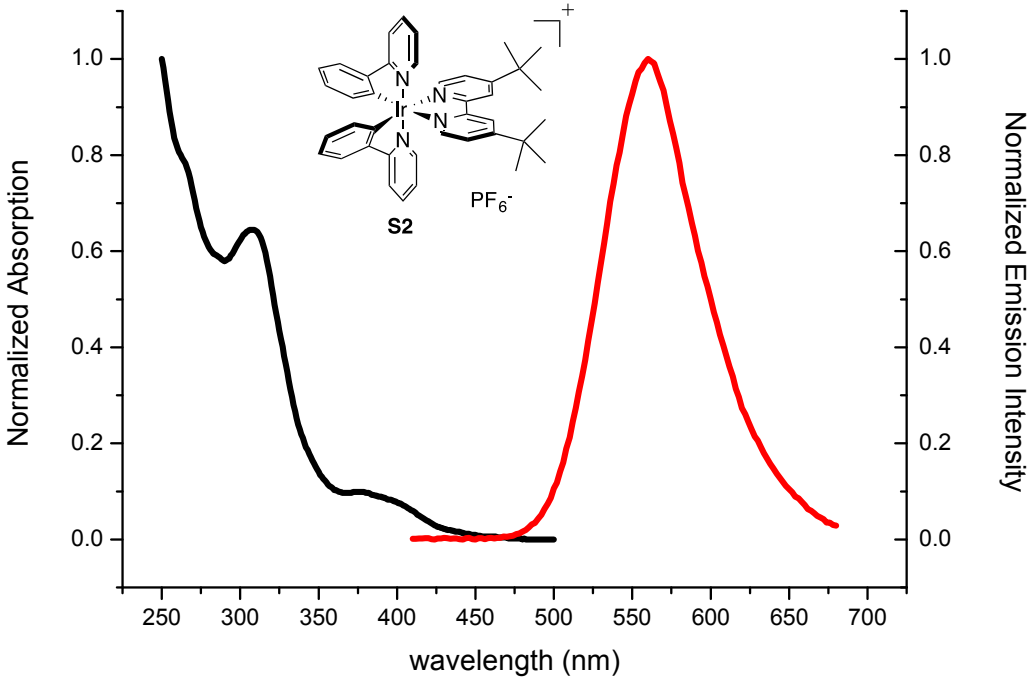

C-1a (R1=H, R2=H)
C-1c (R1=OMe, R2=H)
C-1e (R1=OMe, R2=F)
C-1g (R1=OMe, R2=OMe)
ε /10^5 (M^-1cm^-1)
Wavelength / nm

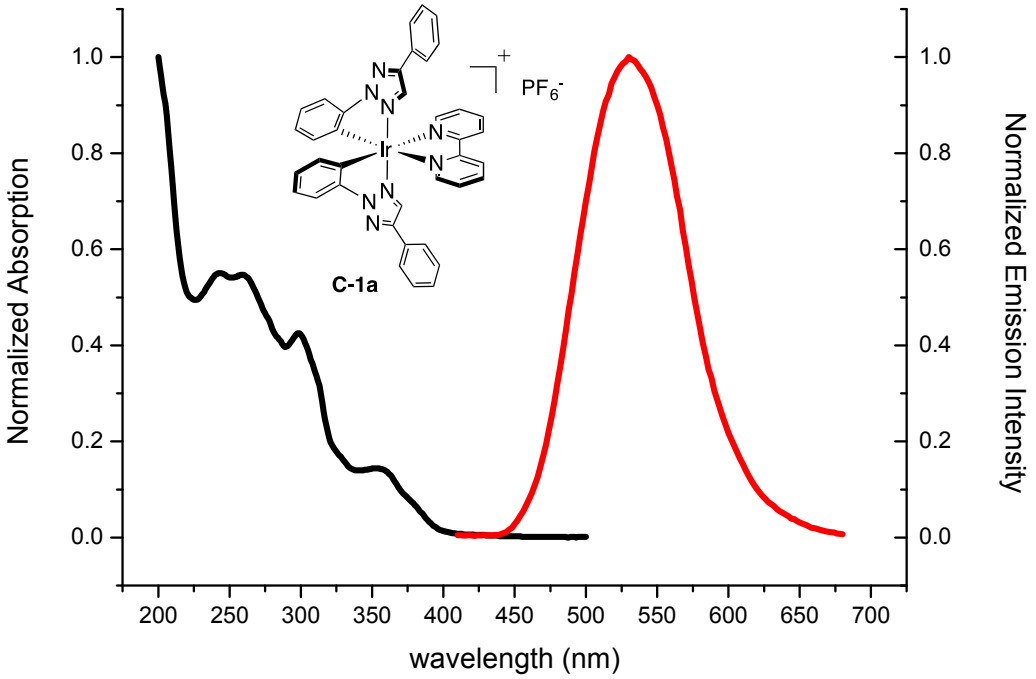

C-1a (R1=H, R2=H)
C-1c (R1=OMe, R2=H)
C-1e (R1=OMe, R2=F)
C-1g (R1=OMe, R2=OMe)
Intensity
Wavelength / nm

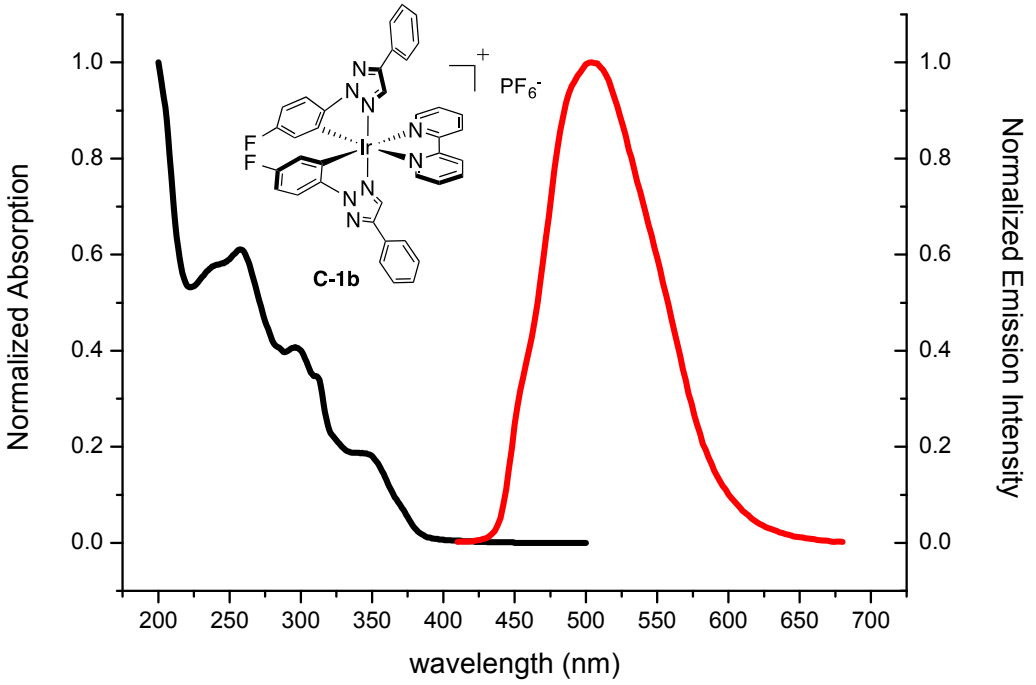

C-1a (R1=H, R2=H)
C-3a (R1=H, R2=H)
C-3b (R1=F, R2=H)
C-3c (R1=OMe, R2=H)
ε /10^5 (M^-1cm^-1)
wavelength / nm

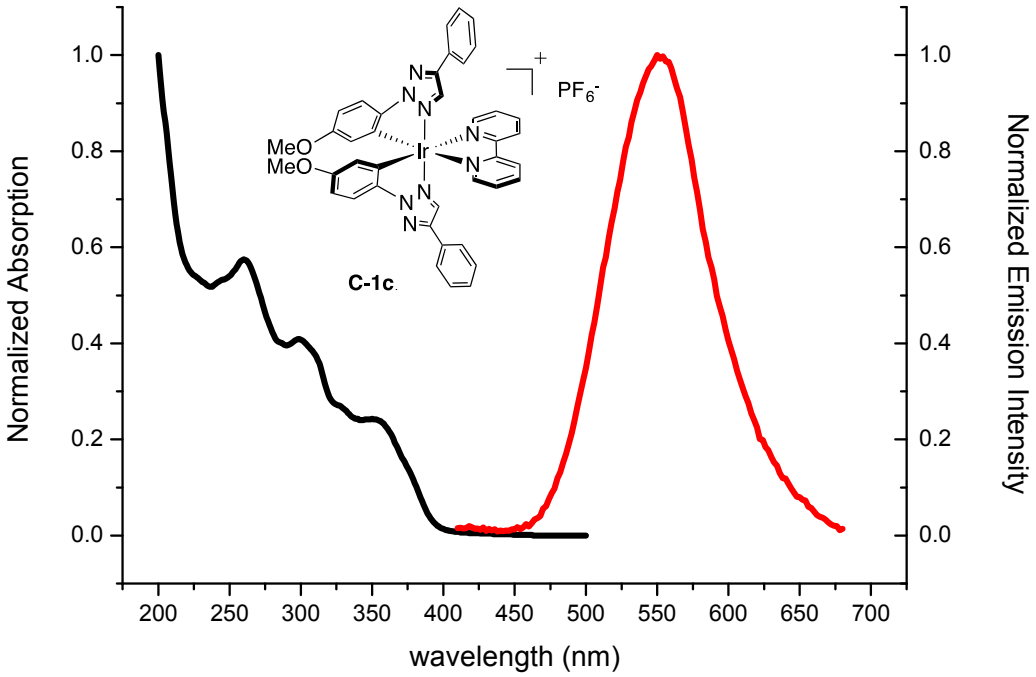

C-1a (R1=H, R2=H)
C-2
C-3a (R1=H, R2=H)
C-3b (R1=F, R2=H)
C-3c (R1=OMe, R2=H)
Intensity
wavelength / nm

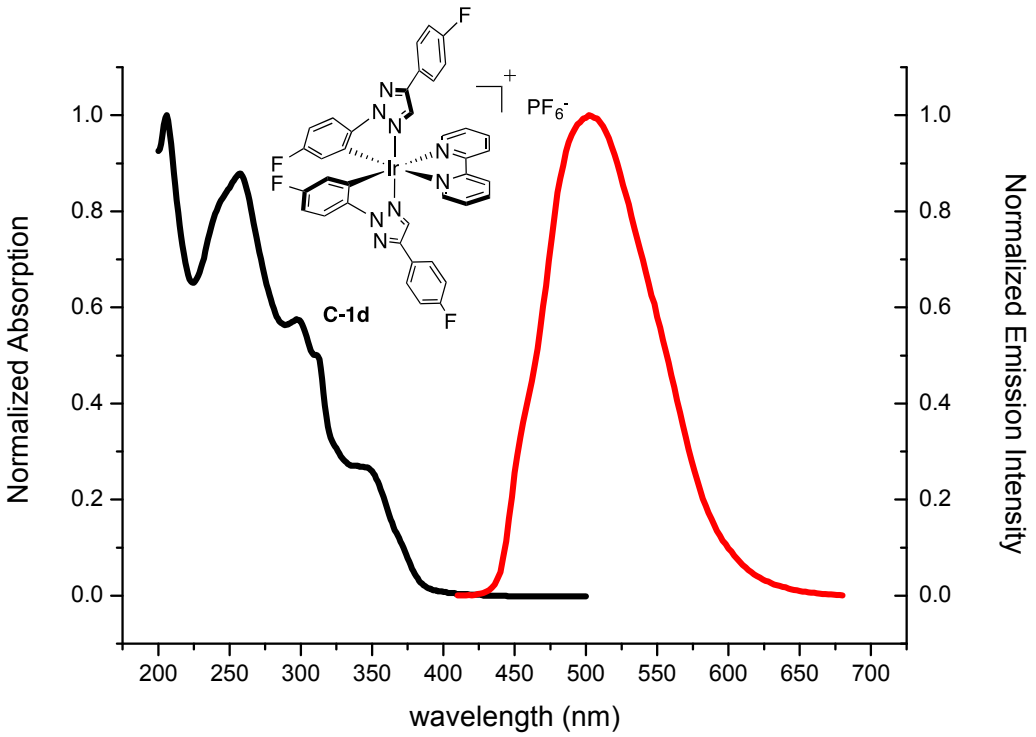

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
PF6-
S1

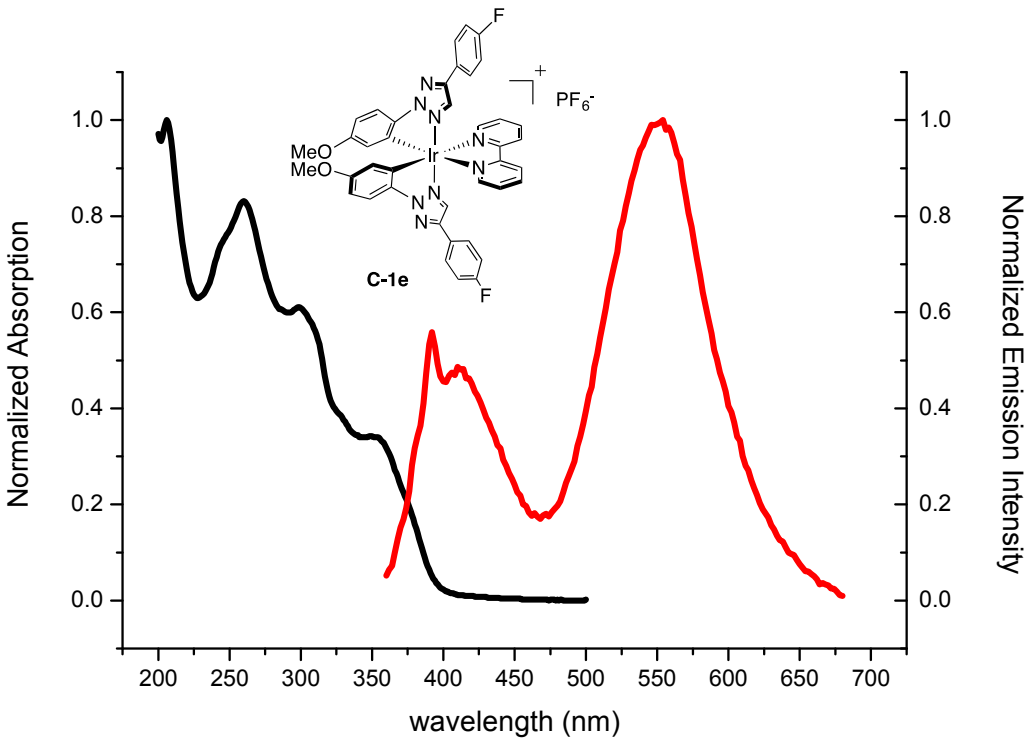

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
PF6-
S2

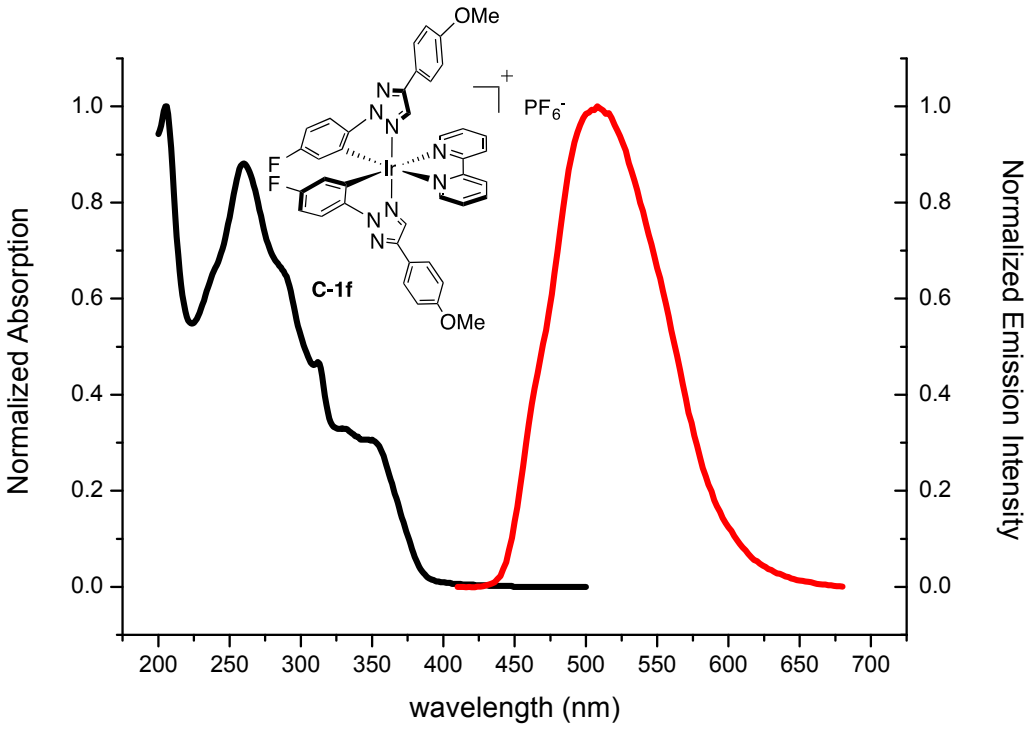

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
C-1a
PF6-

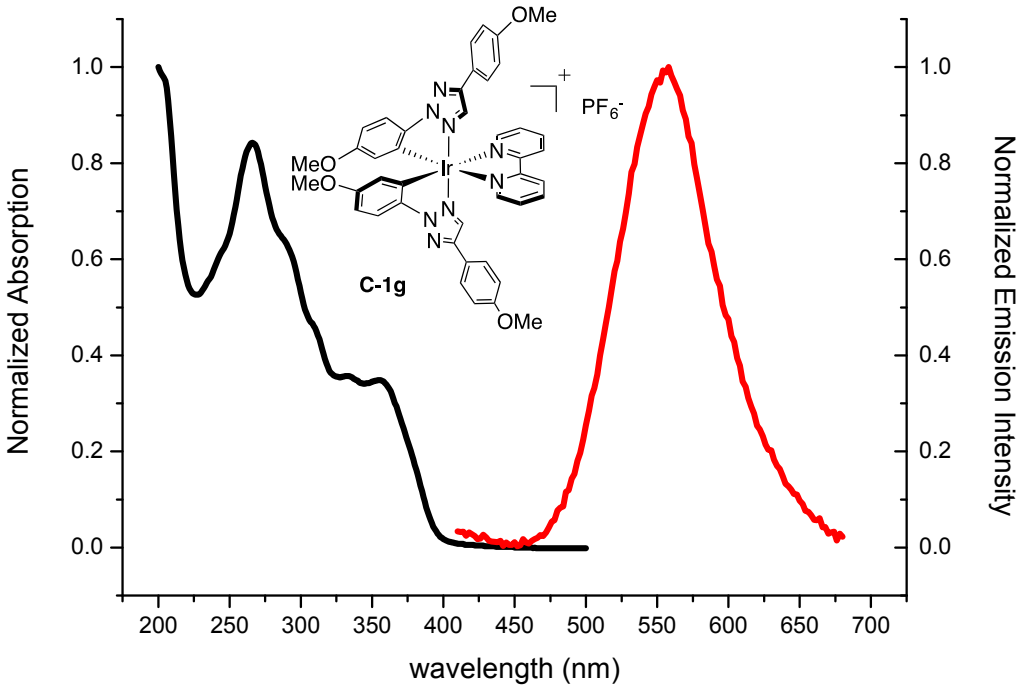

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
C-1b
PF6-

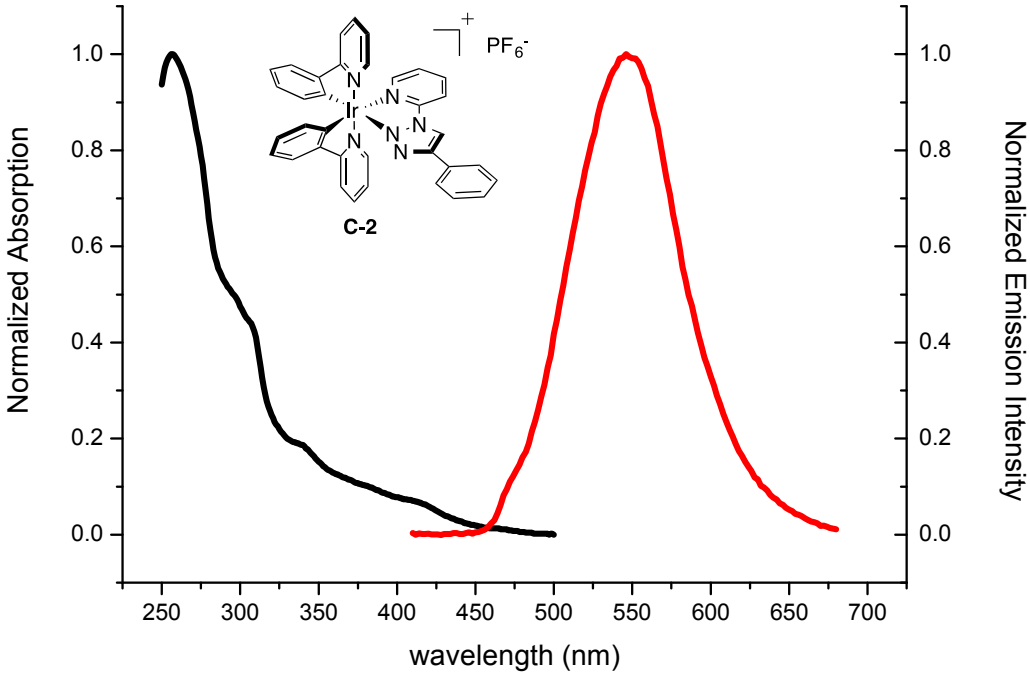

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
C-1c
MeO
MeO
Ir
N
PF6-

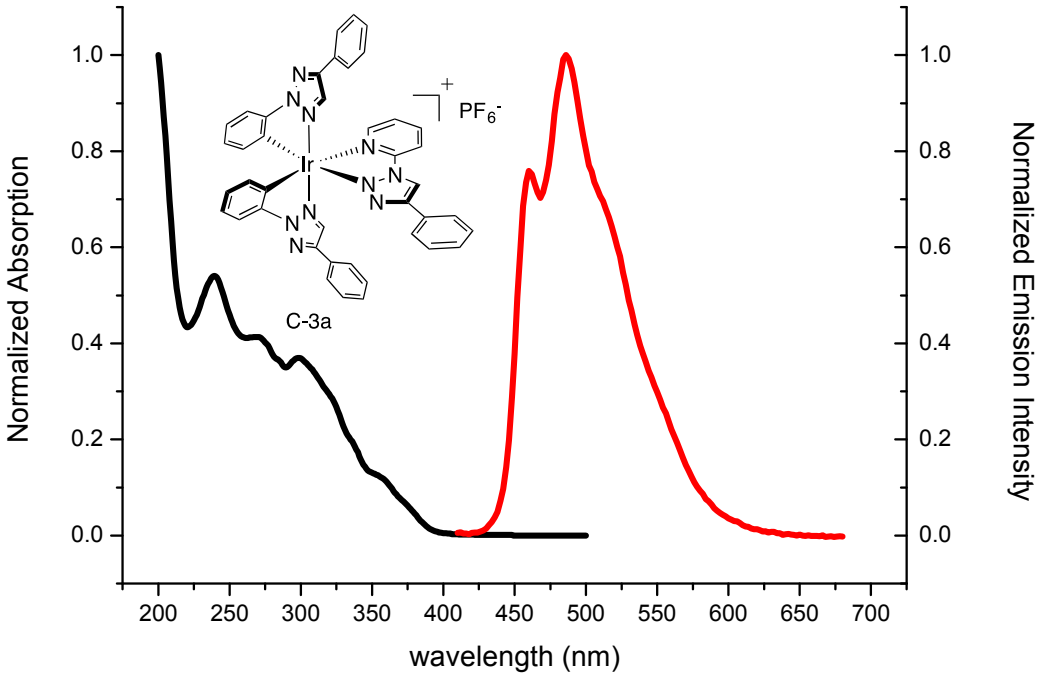

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
C-1d
F
Ir
N
PF6-

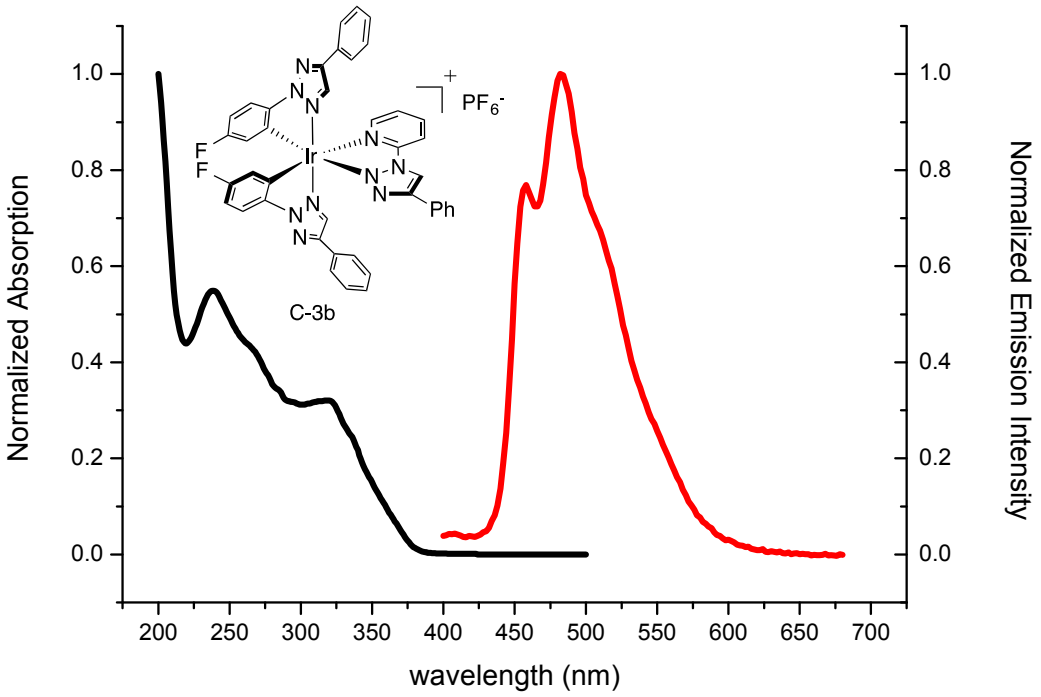

C-1e
PF6-
MeO
MeO
Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
200
250
300
350
400
450
500
550
600
650
700

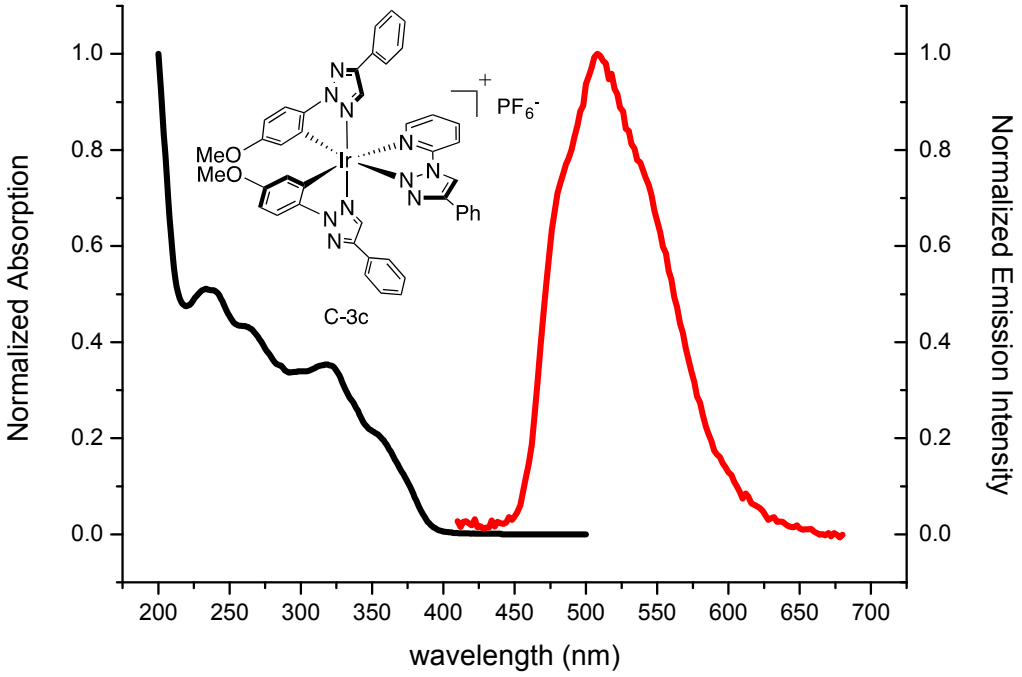

C-1f
PF6-
OMe
OMe
F
F
Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
200
250
300
350
400
450
500
550
600
650
700


OMe
MeO
MeO
Ir
N
PF6-
C-1g
OMe
Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
200
250
300
350
400
450
500
550
600
650
700

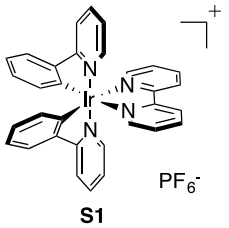

Ir
N
PF6-
C-2
Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
250
300
350
400
450
500
550
600
650
700


Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
C-3a
PF6-

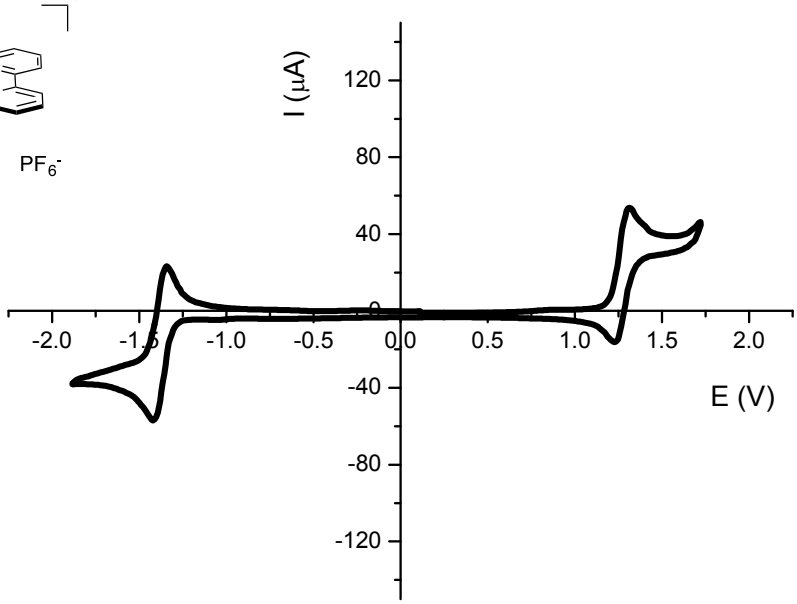

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
C-3b
PF6-
Ph

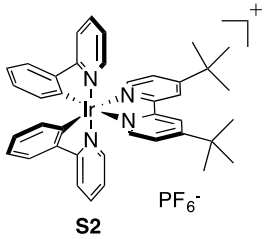

Normalized Absorption
Normalized Emission Intensity
wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
250
300
350
400
450
500
550
600
650
700
MeO
MeO
Ir
N
Ph
PF6-
C-3c

V. Cyclic Voltammetry

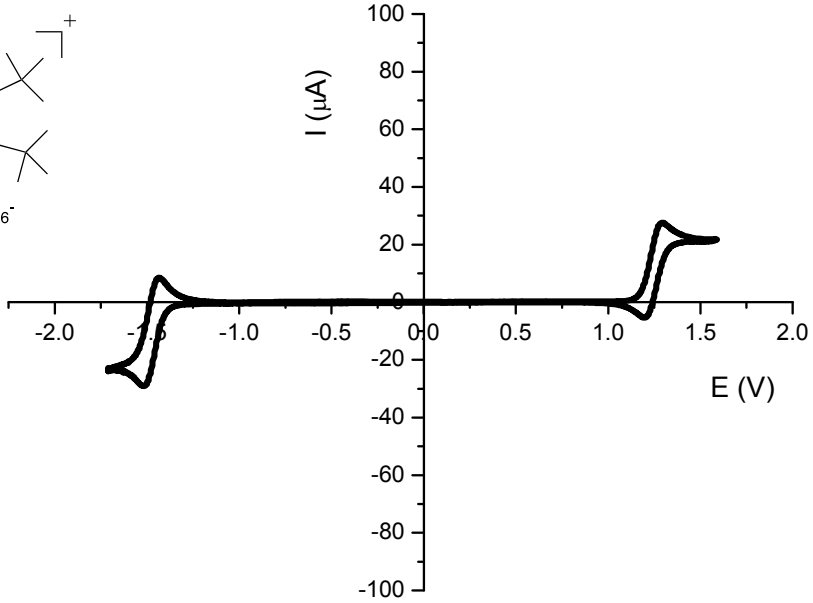


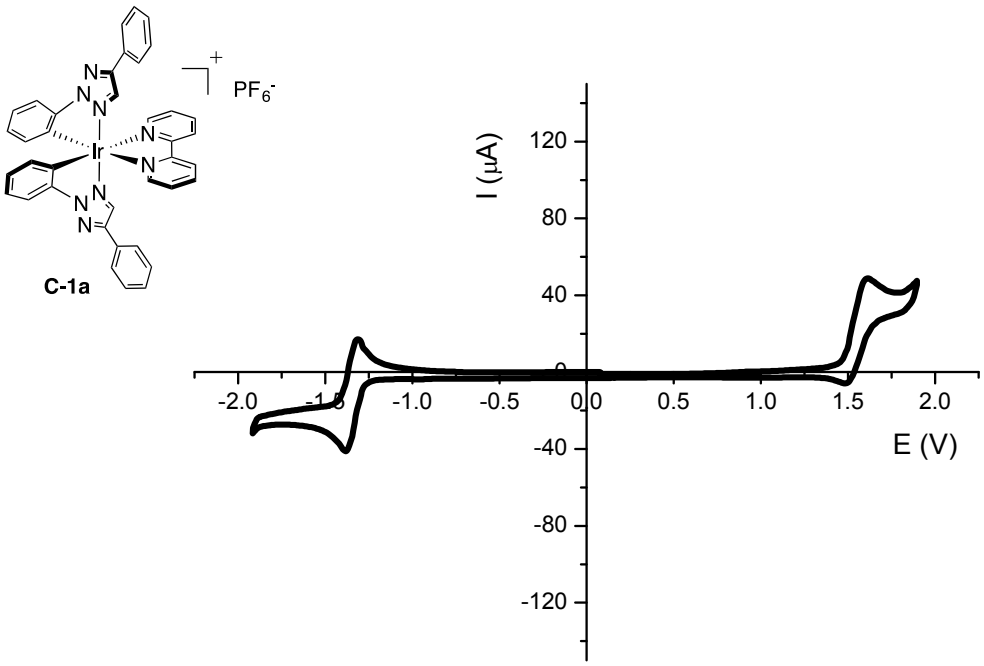
S1

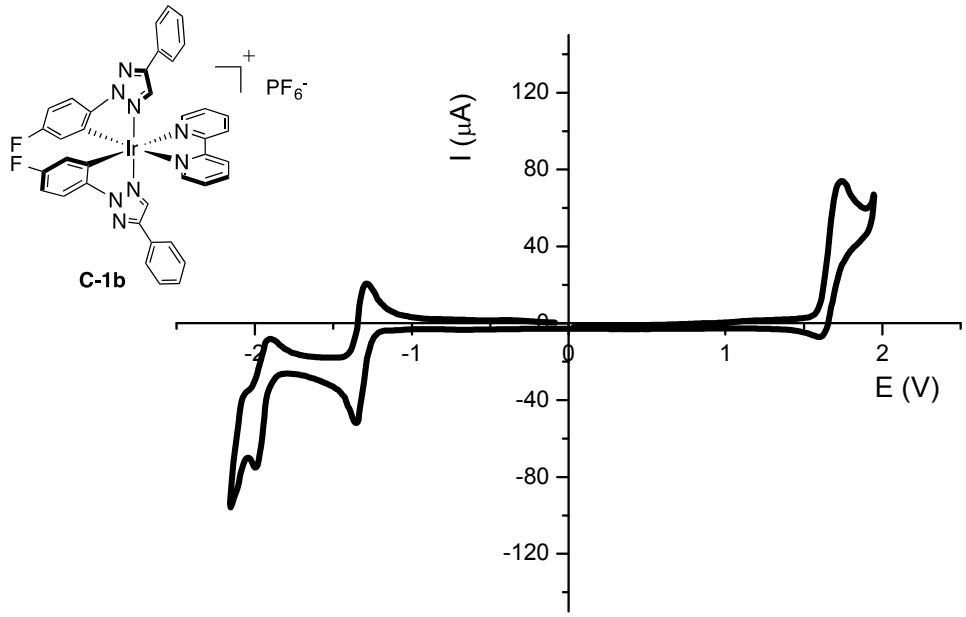


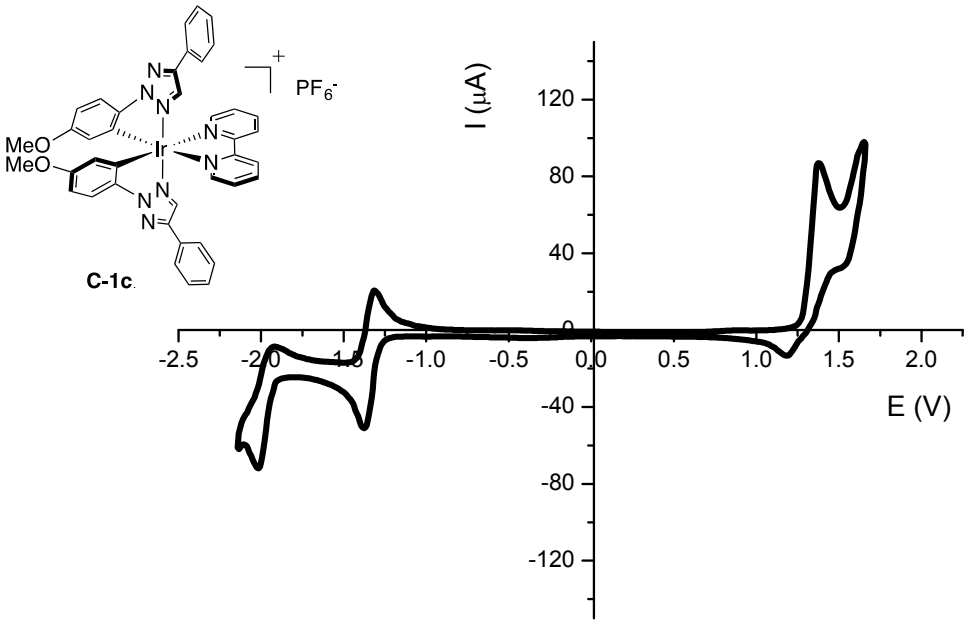


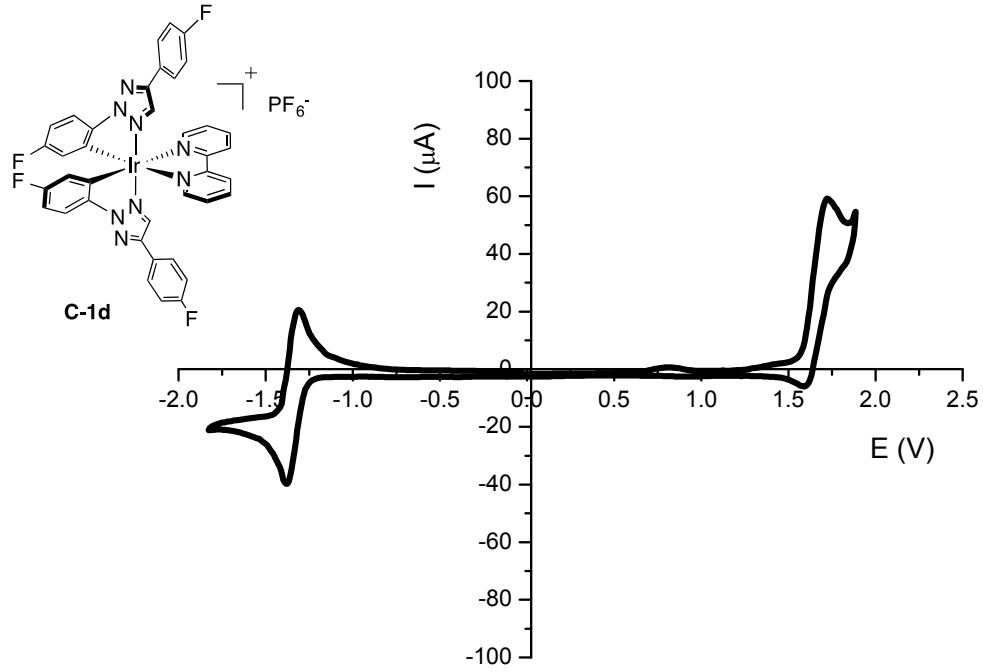
S2

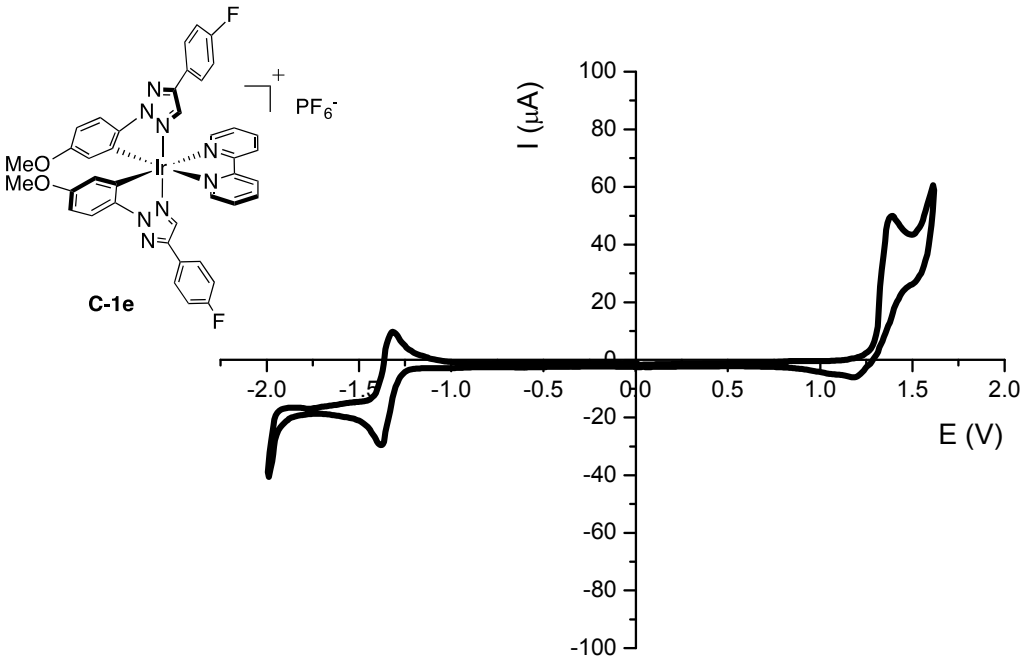


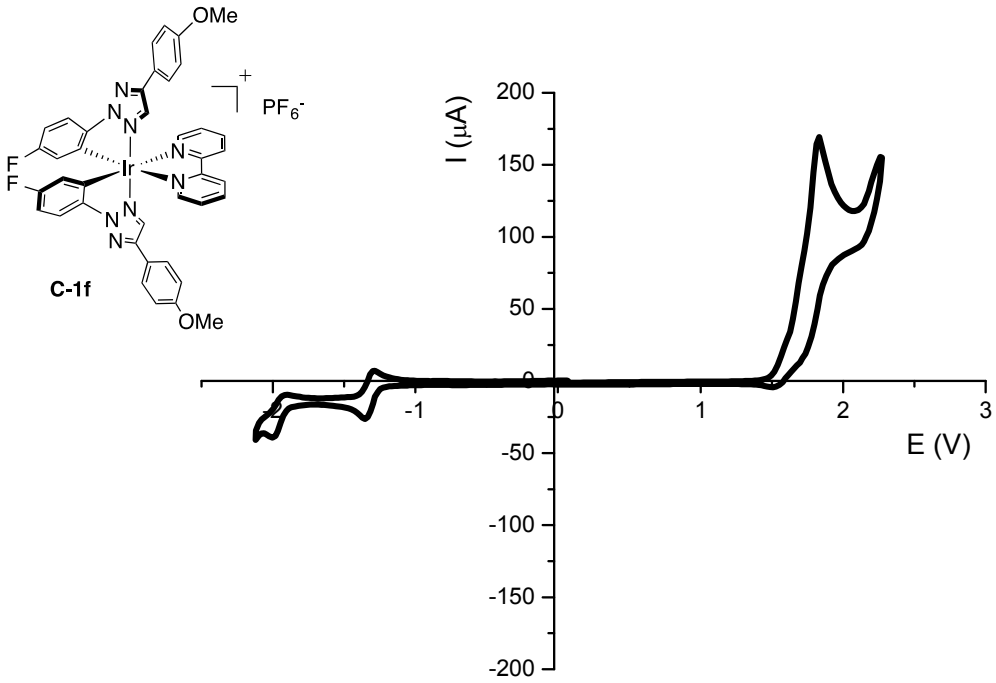

PF6-
C-1a
I (μA)
E (V)
120
80
40
0
-40
-80
-120
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

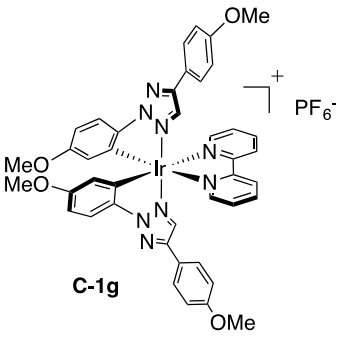

PF6-
C-1b
I (μA)
E (V)
120
80
40
0
-40
-80
-120
-2
-1
0
1
2


MeO
MeO
Ir
N
PF6-
C-1c
I (μA)
E (V)
120
80
40
0
-40
-80
-120
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

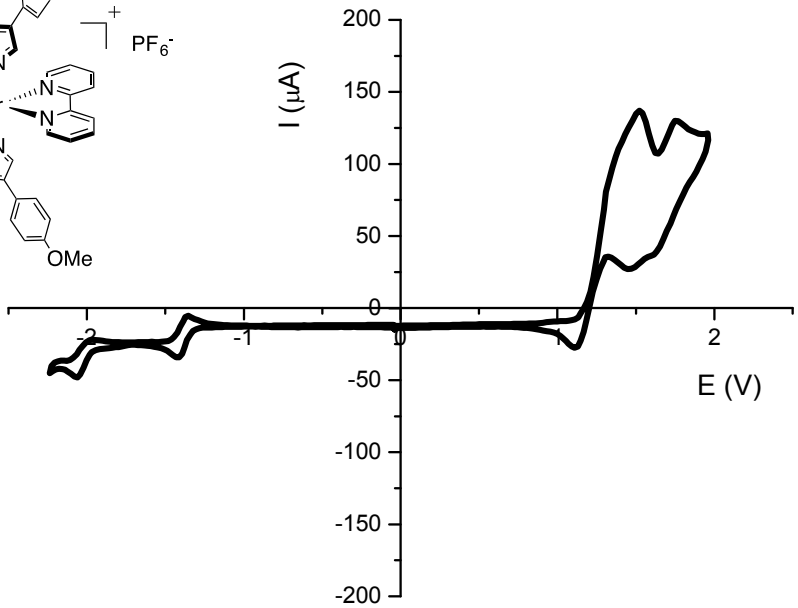

F
F
Ir
N
PF6-
C-1d
I (μA)
E (V)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

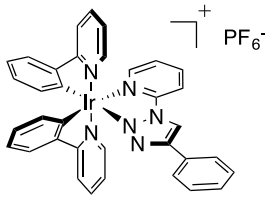

F
MeO
MeO
Ir
N
PF6-
C-1e
I (μA)
E (V)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0


OMe
F
F
Ir
N
PF6-
C-1f
I (μA)
E (V)
200
150
100
50
0
-50
-100
-150
-200
-1
0
1
2
3

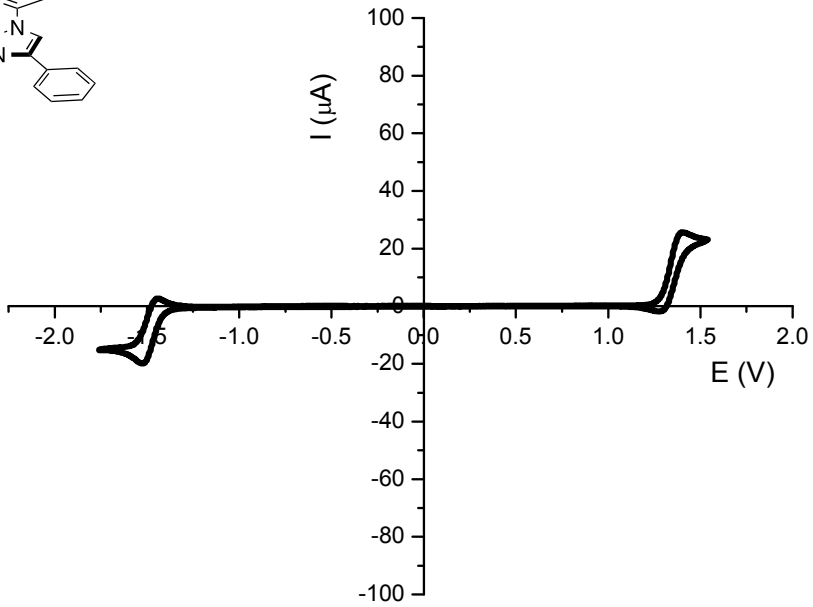

OMe
MeO
MeO
Ir
N
PF6-
OMe

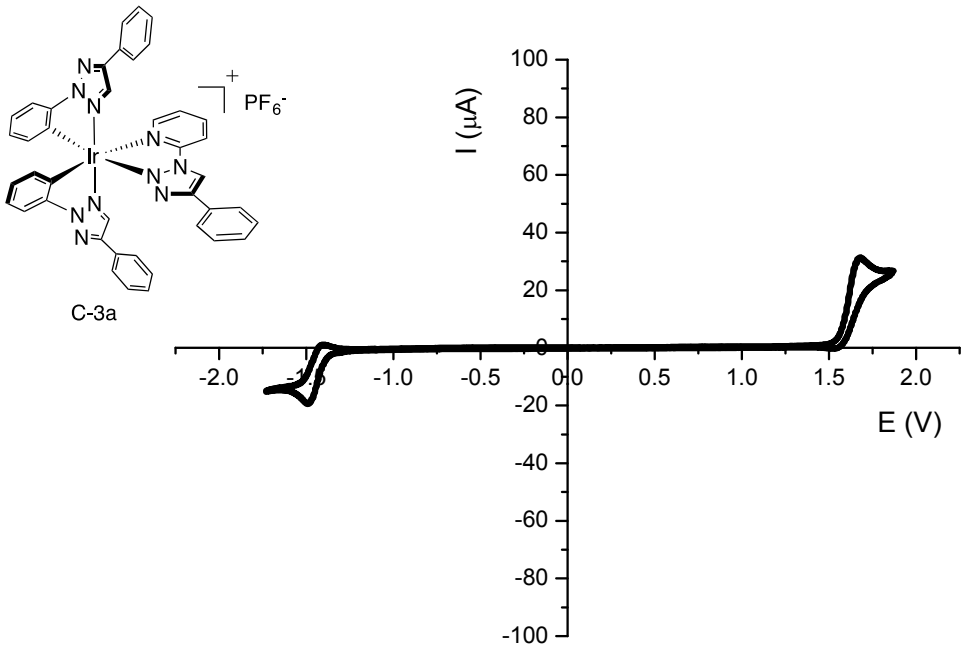
C-1g

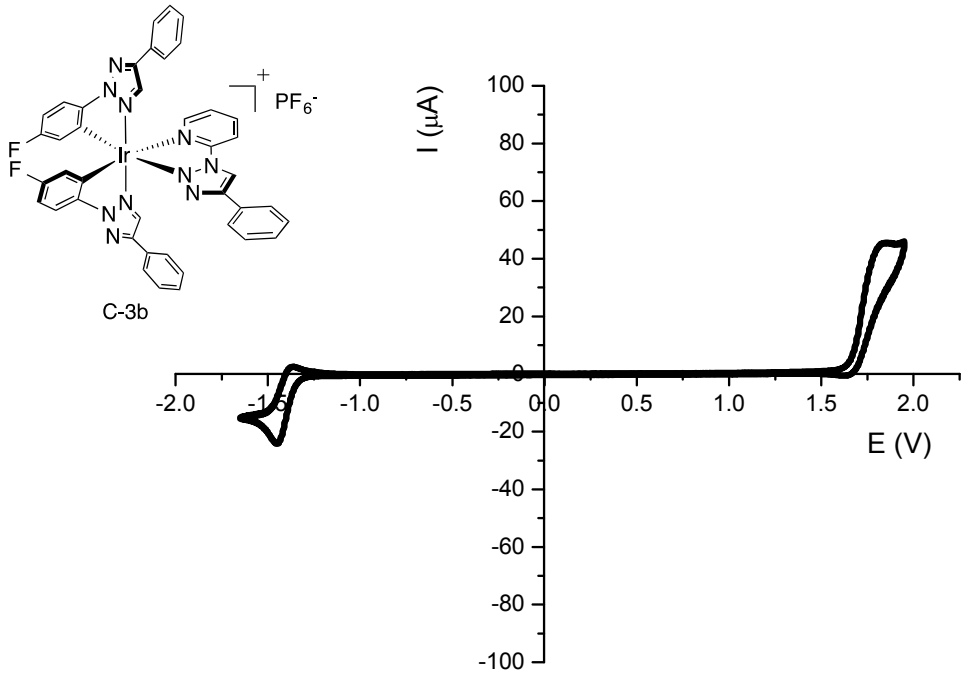

I (μA)
E (V)
200
150
100
50
0
-50
-100
-150
-200
-2
-1
0
2

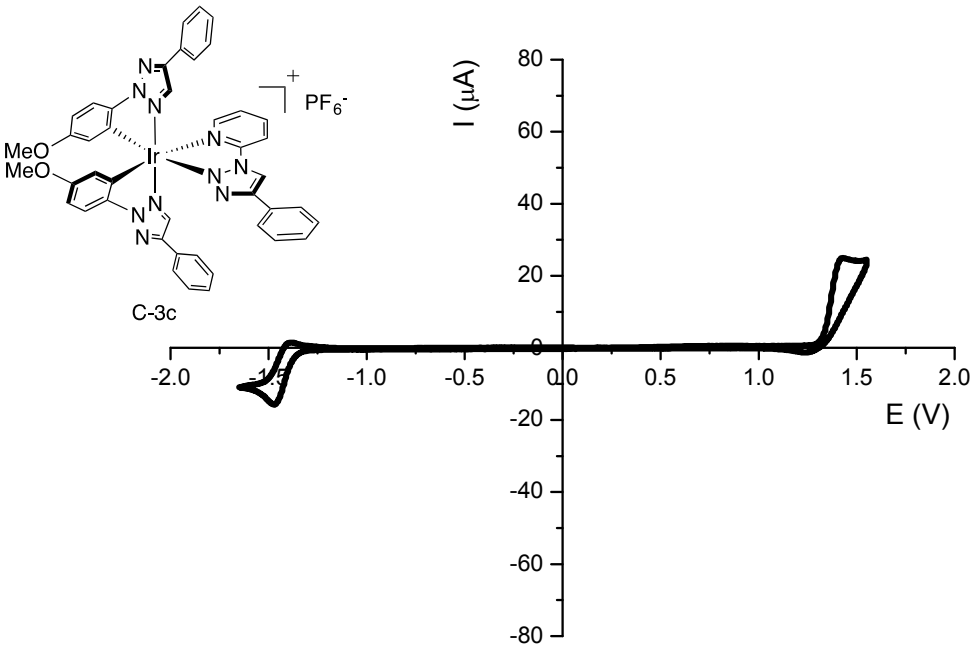

Ir
N
PF6-

C-2


I (μA)
E (V)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0


PF6-
C-3a
I (μA)
E (V)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-2.0
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

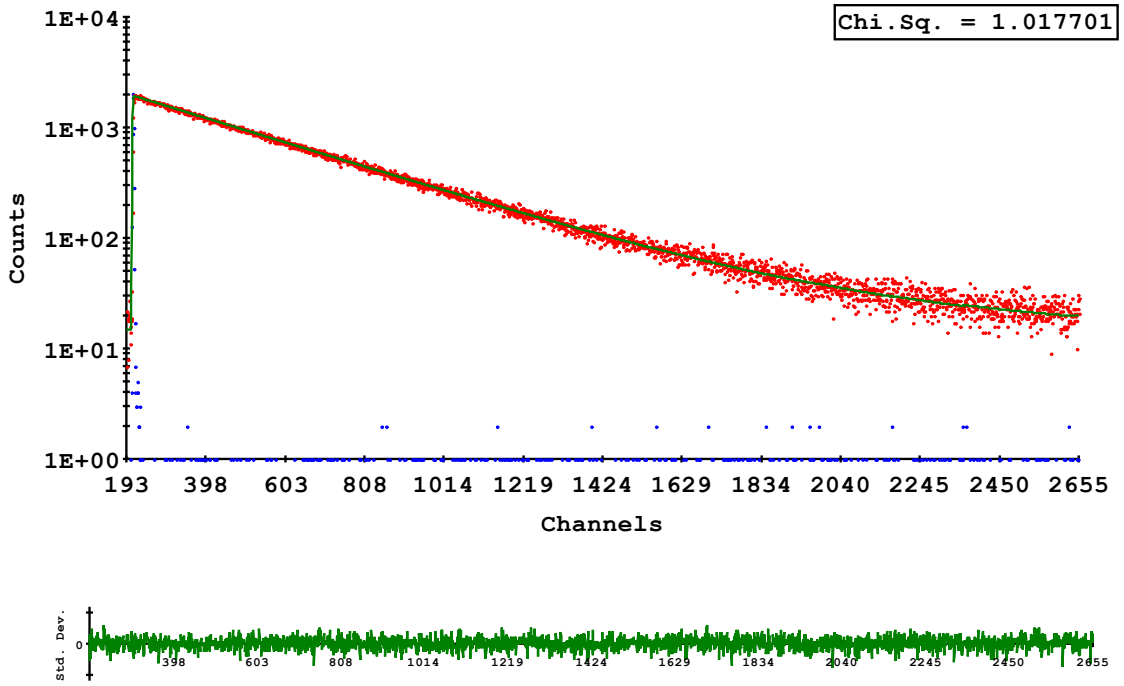

F
F
PF6-
C-3b
I (μA)
E (V)
100
80
60
40
20
0
-20
-40
-60
-80
-100
-2.0
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0


MeO
MeO
Ir
N
PF6-
C-3c
I (μA)
E (V)
80
60
40
20
0
-20
-40
-60
-80
-2.0
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

VI. Excited-state lifetime

All the samples are tested under same conditions as described above (Section I). The sample solutions were degassed with nitrogen bubbles for 20 mins, capped with rubber septum and sealed with Parafilm, followed by protection with nitrogen using freeze/thaw techniques prior to the measurement. For parallel comparison, we tested two literature reported samples under our conditions: $[(ppy)_2Ir(dtbbpy)]PF_6$ (experimental: 175 ns, literature: 557 ns) and $Ru(bpy)_3(PF_6)_2$ (experimental: 382 ns, literature: 1100 ns). Complexes **C-3a**, **C-3b** and **C-3c** were fitted with two exponentials while all the other complexes were fitted with one exponential using DAS6.

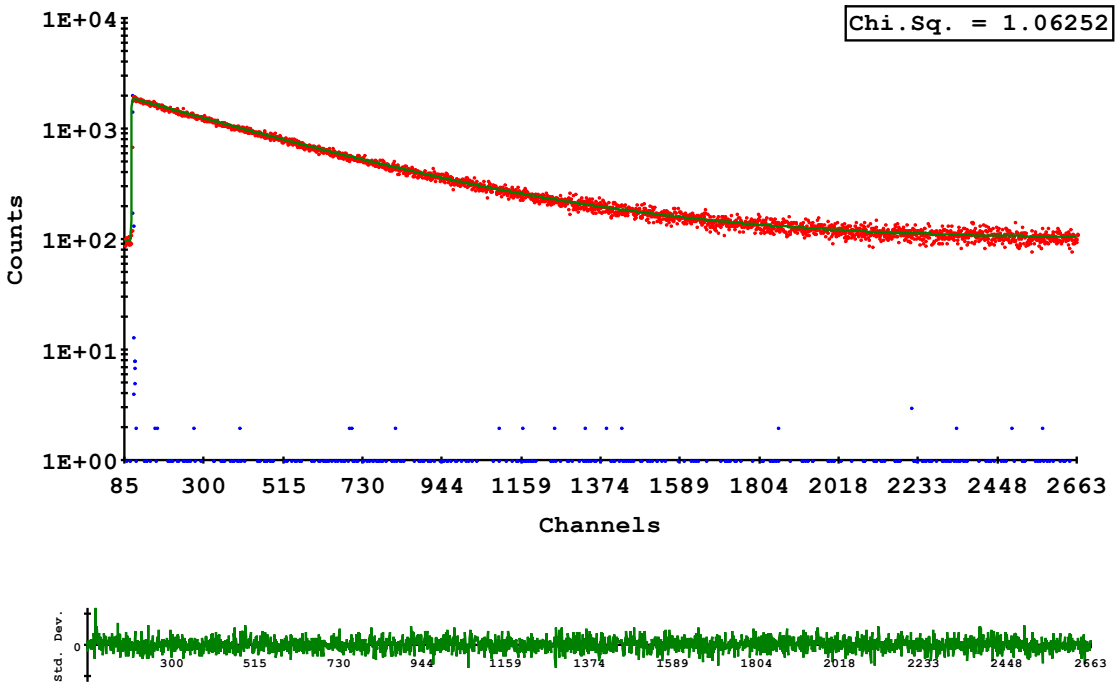
$[(ppy)_2Ir(dtbbpy)]PF_6$




```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         1.75583E-08    sec

 T1 Estimate = 299.4264 ch;         1.314355E-07   sec

 A Free
 B1 Free

 Prompt and decay LO = 193    ch;   8.471879E-08   sec
 Prompt and decay HI = 2695   ch;   1.18299E-06    sec

 Background on prompt = 1 (manual)
 Time calibration = 4.389575E-10 sec/ch

The fitted parameters are:
```

```
 Hi reduced to: 2655 ch

 SHIFT = 0.503097      ch;  2.208382E-10  sec    S.Dev = 1.189053E-11  sec
 T1    = 397.7953      ch;  1.746152E-07  sec    S.Dev = 2.967923E-10  sec
 A     = 14.67546                               S.Dev = 0.1670179
 B1    = 0.3065412     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 3.783242E-04
 Average Life Time = 1.746152E-07  sec
 CHISQ = 1.017701           [ 2459 degrees of freedom ]
```

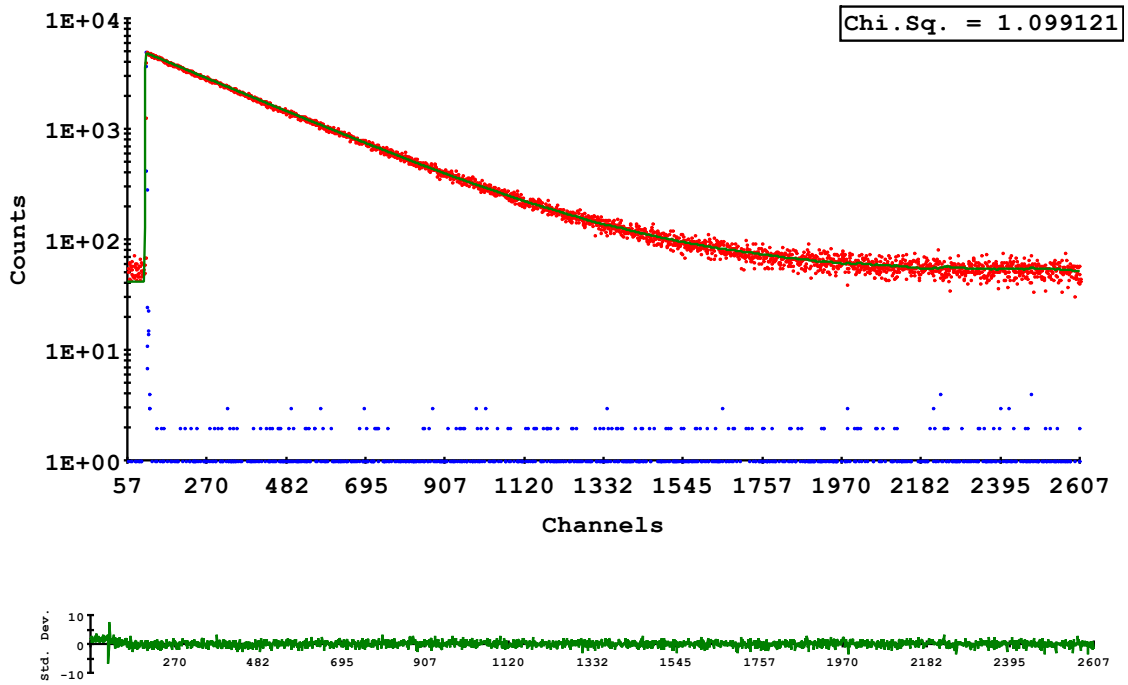
$Ru(bpy)_3(PF_6)_2$




```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;        0              sec
 Shift Limit = 40       ch;        3.51166E-08    sec

 T1 Estimate = 307.987  ch;        2.703864E-07   sec

 A Free
 B1 Free

 Prompt and decay LO = 85     ch;  7.462277E-08   sec
 Prompt and decay HI = 2703   ch;  2.373004E-06   sec

 Background on prompt = 1 (manual)
 Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 2663 ch

 SHIFT = 0.3908297     ch;  3.431153E-10  sec    S.Dev = 2.258932E-11  sec
 T1    = 434.98        ch;  3.818755E-07  sec    S.Dev = 8.897758E-10  sec
 A     = 97.82068                               S.Dev = 0.3045523
 B1    = 0.470622      [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 6.445636E-04
```

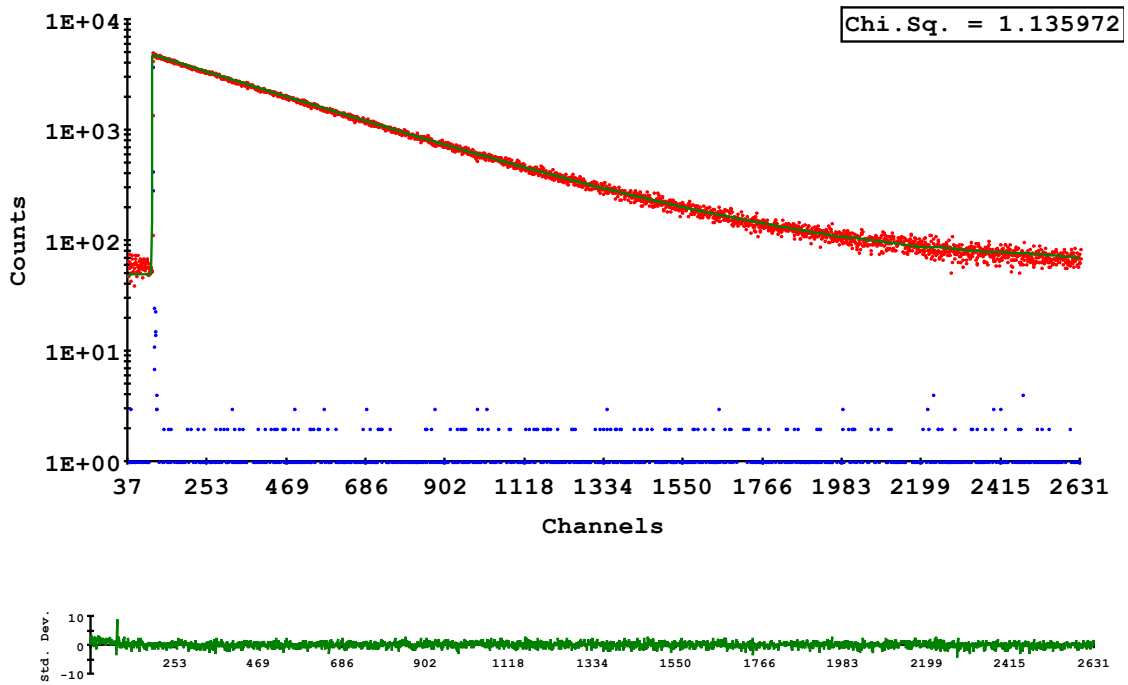
```
Average Life Time = 3.818755E-07  sec
CHISQ = 1.06252            [ 2575 degrees of freedom ]
```

C-1a



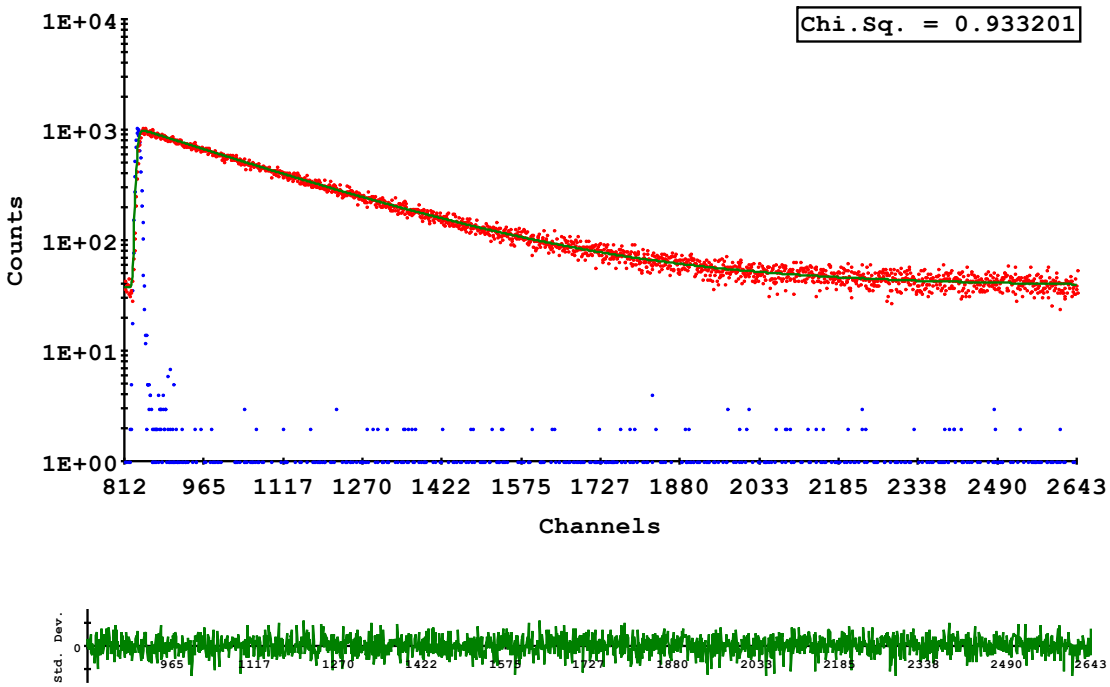

```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;        0              sec
 Shift Limit = 40       ch;        3.51166E-08    sec

 T1 Estimate = 292.838  ch;        2.570869E-07   sec

 A Free
 B1 Free

 Prompt and decay LO = 57     ch;  5.004115E-08   sec
 Prompt and decay HI = 2647   ch;  2.323841E-06   sec

 Background on prompt = 1 (manual)
 Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 2607 ch

 SHIFT = 0.5974014     ch;  5.244676E-10  sec    S.Dev = 1.119862E-11  sec
 T1    = 302.9154      ch;  2.65934E-07   sec    S.Dev = 3.112539E-10  sec
 A     = 41.43258                               S.Dev = 0.2173026
 B1    = 0.5112242     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 4.446301E-04
 Average Life Time = 2.65934E-07   sec
 CHISQ = 1.099121           [ 2547 degrees of freedom ]
```

C-1b




```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         3.51166E-08    sec

 T1 Estimate = 372.2305 ch;         3.267867E-07   sec

 A Free
 B1 Free

 Prompt and decay LO = 37     ch;   3.248285E-08   sec
 Prompt and decay HI = 2671   ch;   2.344911E-06   sec

 Background on prompt = 1 (manual)
 Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 2631 ch

 SHIFT = 0.5086936     ch;  4.465898E-10  sec    S.Dev = 1.235969E-11  sec
 T1    = 407.7457      ch;  3.57966E-07   sec    S.Dev = 4.258433E-10  sec
 A     = 47.75816                               S.Dev = 0.2819181
 B1    = 0.4984699     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 3.910421E-04
 Average Life Time = 3.57966E-07   sec
 CHISQ = 1.135972           [ 2591 degrees of freedom ]
```

C-1c



Calculated using 1 exponential

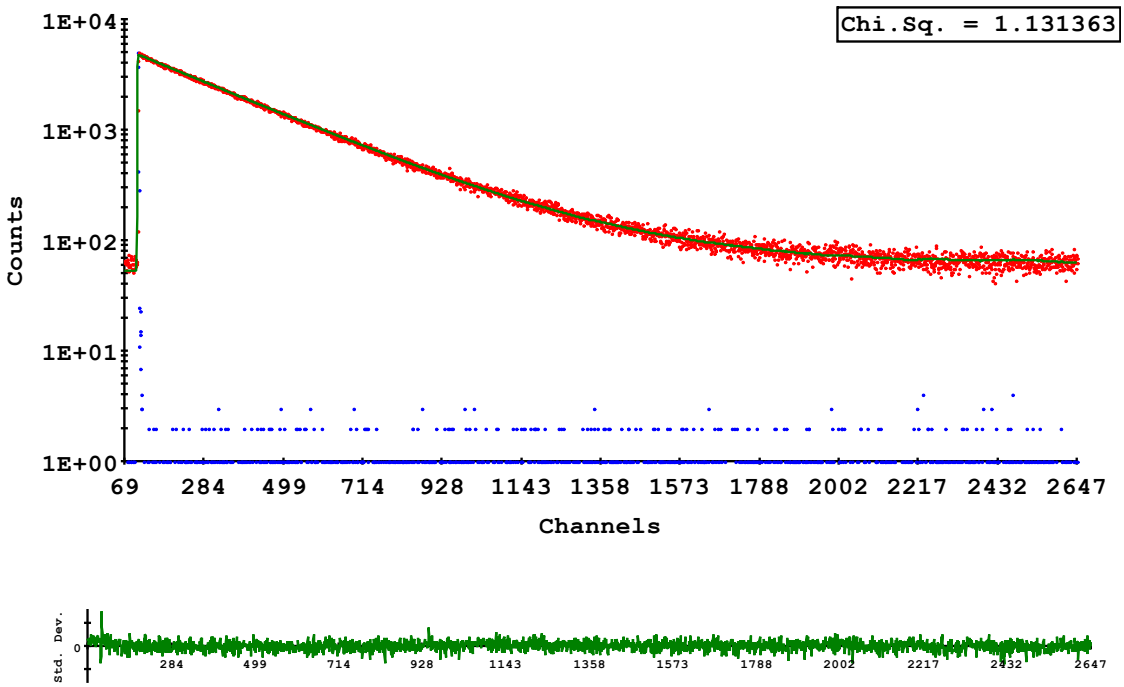
The initial paramters are:

```
 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         4.389575E-09   sec

 T1 Estimate = 169.1614 ch;         1.856367E-08   sec

 A Free
 B1 Free

 Prompt and decay LO = 812    ch;   8.910837E-08   sec
 Prompt and decay HI = 2683   ch;   2.944307E-07   sec

 Background on prompt = 1 (manual)
 Time calibration = 1.097394E-10 sec/ch
```

The fitted parameters are:

```
 Hi reduced to: 2643 ch

 SHIFT = 0.453698      ch;  4.978853E-11  sec    S.Dev = 8.439614E-12  sec
 T1    = 275.3003      ch;  3.021128E-08  sec    S.Dev = 9.846059E-11  sec
 A     = 37.60783                               S.Dev = 0.2243803
 B1    = 8.788235E-02  [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 2.024839E-04
 Average Life Time = 3.021128E-08  sec
 CHISQ = 0.933201           [ 1828 degrees of freedom ]
```

C-1d



Calculated using 1 exponential

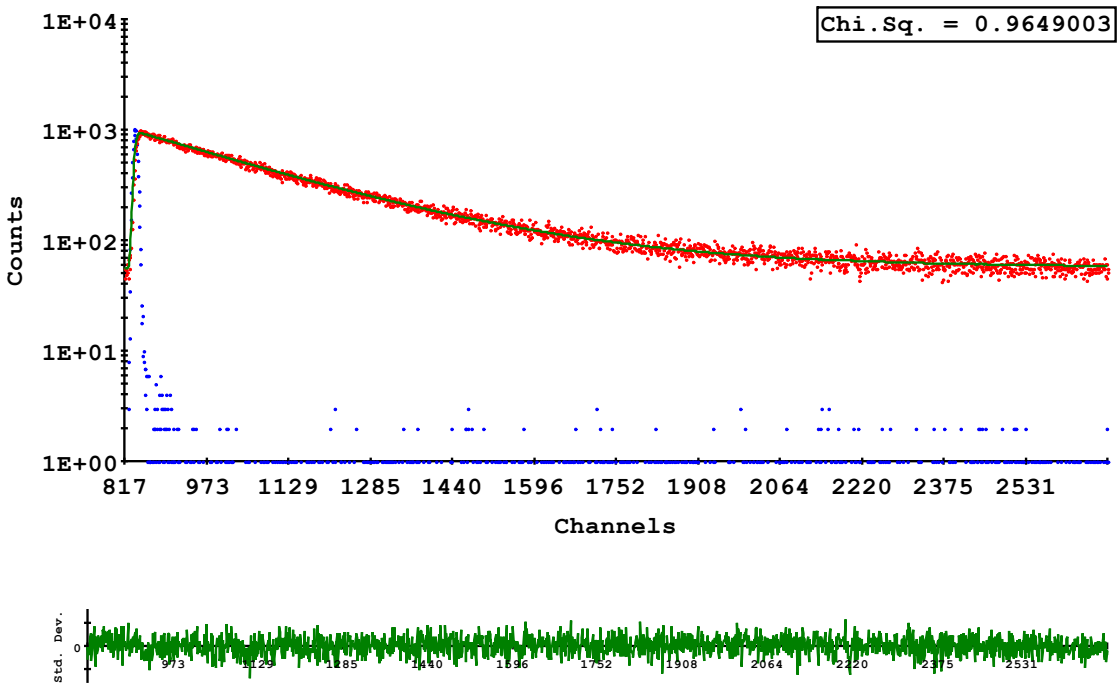
The initial paramters are:

```
 Shift Value = 0        ch;        0              sec
 Shift Limit = 40       ch;        3.51166E-08    sec

 T1 Estimate = 287.6757 ch;        2.525548E-07   sec

 A Free
 B1 Free

 Prompt and decay LO = 69     ch;   6.057613E-08   sec
 Prompt and decay HI = 2687   ch;   2.358958E-06   sec

 Background on prompt = 1 (manual)
 Time calibration = 8.77915E-10 sec/ch
```

The fitted parameters are:

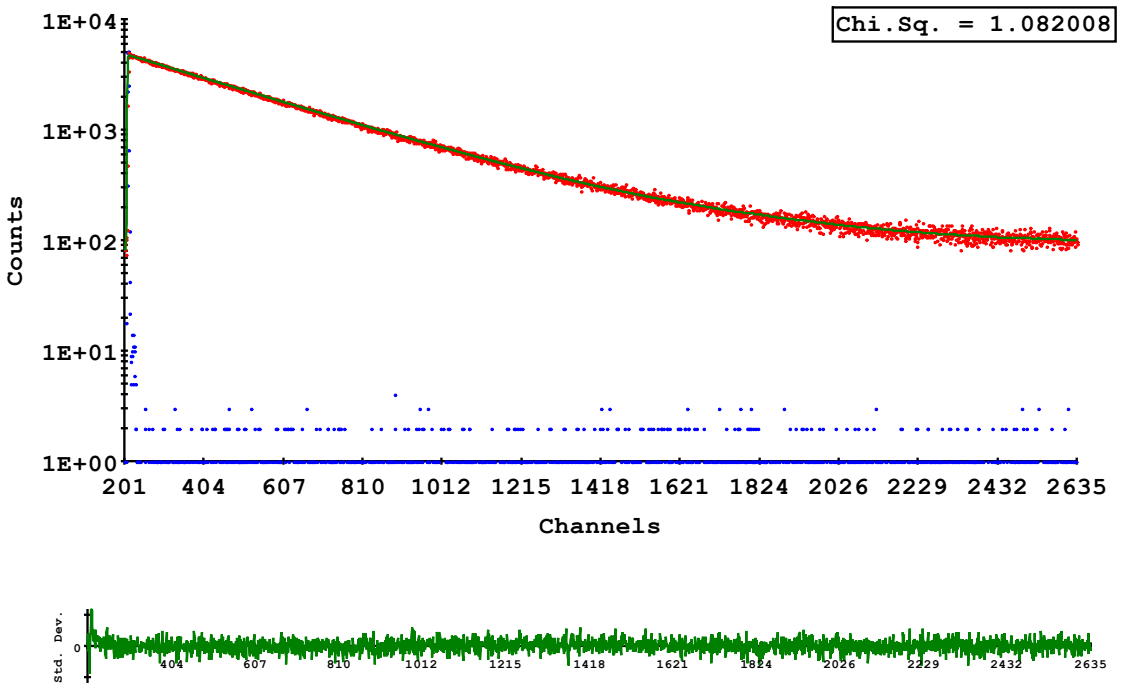
```
 Hi reduced to: 2647 ch

 SHIFT = 0.4703841     ch;  4.129572E-10  sec    S.Dev = 1.27369E-11   sec
 T1    = 308.0277      ch;  2.704222E-07  sec    S.Dev = 3.395406E-10  sec
 A     = 52.95856                               S.Dev = 0.2339391
 B1    = 0.5000985     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 4.39496E-04
 Average Life Time = 2.704222E-07  sec
 CHISQ = 1.131363           [ 2575 degrees of freedom ]
```

C-1e



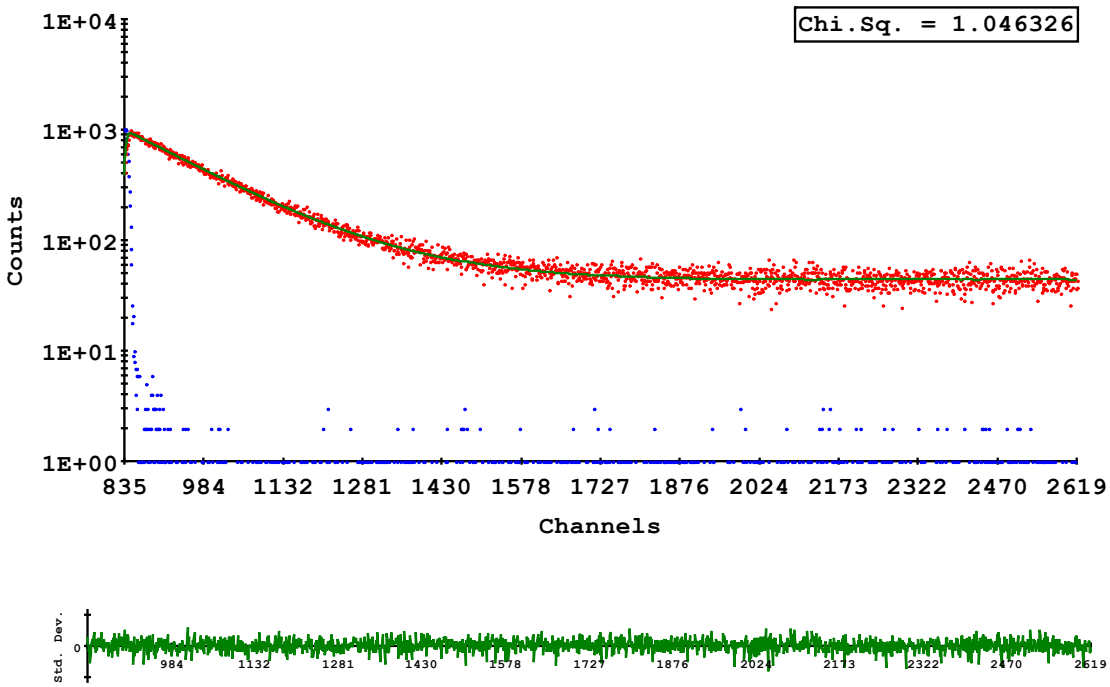

```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         4.389575E-09   sec

 T1 Estimate = 269.9332 ch;         2.96223E-08    sec

 A Free
 B1 Free

 Prompt and decay LO = 817    ch;   8.965706E-08   sec
 Prompt and decay HI = 2727   ch;   2.992593E-07   sec

 Background on prompt = 1 (manual)
 Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 2687 ch

 SHIFT = 9.247364E-03  ch;  1.0148E-12    sec    S.Dev = 9.412315E-12  sec
 T1    = 288.3633      ch;  3.164481E-08  sec    S.Dev = 1.262334E-10  sec
 A     = 56.06471                               S.Dev = 0.260014
 B1    = 8.461874E-02  [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 2.07085E-04
 Average Life Time = 3.164481E-08  sec
 CHISQ = 0.9649003          [ 1867 degrees of freedom ]
```

C-1f



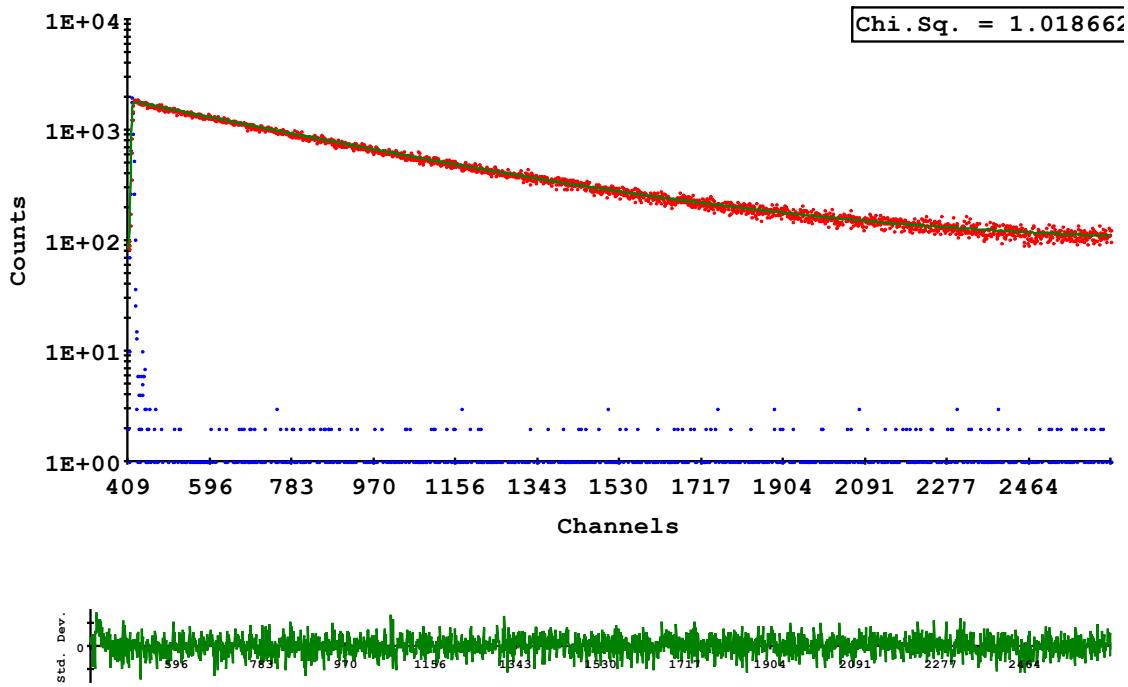

```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;         0               sec
 Shift Limit = 40       ch;         1.75583E-08     sec

 T1 Estimate = 297.8851 ch;         1.307589E-07    sec

 A Free
 B1 Free

 Prompt and decay LO = 201    ch;   8.823045E-08    sec
 Prompt and decay HI = 2675   ch;   1.174211E-06    sec

 Background on prompt = 1 (manual)
 Time calibration = 4.389575E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 2635 ch

 SHIFT = 0.3860314     ch;  1.694514E-10  sec     S.Dev = 8.379197E-12  sec
 T1    = 390.7628      ch;  1.715283E-07  sec     S.Dev = 2.22235E-10   sec
 A     = 82.85342                                S.Dev = 0.3409277
 B1    = 0.2904978     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 2.399315E-04
 Average Life Time = 1.715283E-07  sec
 CHISQ = 1.082008           [ 2431 degrees of freedom ]
```

C-1g



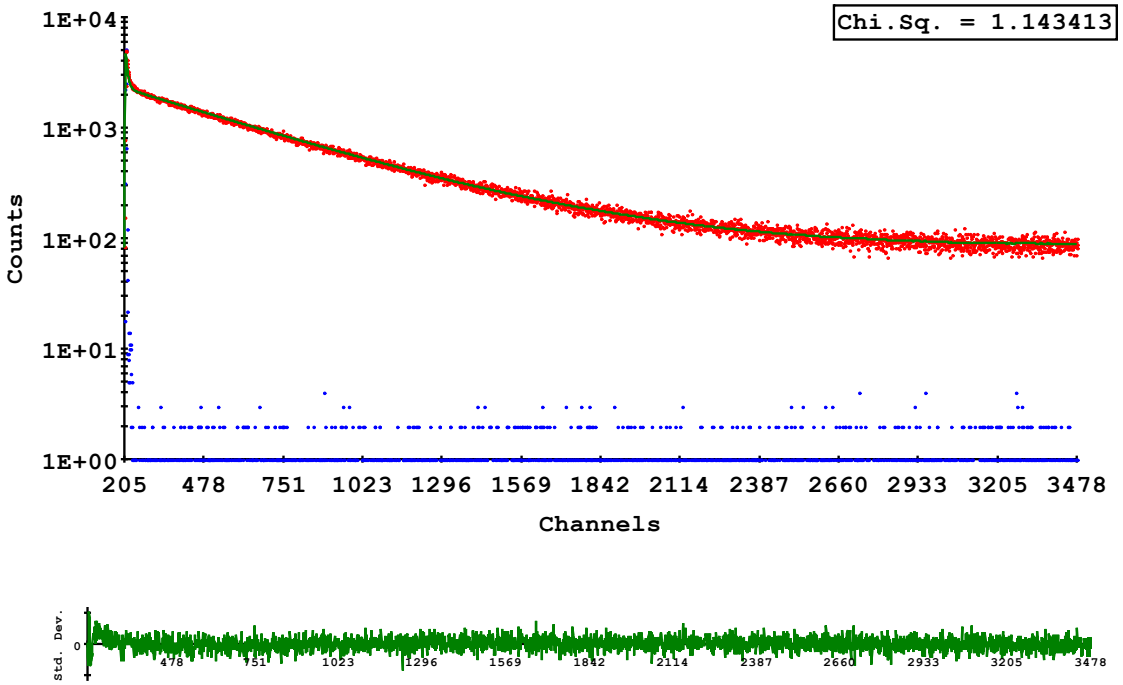

```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         4.389575E-09   sec

 T1 Estimate = 117.7722 ch;         1.292425E-08   sec

 A Free
 B1 Free

 Prompt and decay LO = 835    ch;   9.163237E-08   sec
 Prompt and decay HI = 2659   ch;   2.91797E-07    sec

 Background on prompt = 1 (manual)
 Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 2619 ch

 SHIFT = -1.511307     ch;  -1.658498E-10 sec    S.Dev = 1.129568E-11  sec
 T1    = 164.2944      ch;  1.802956E-08  sec    S.Dev = 8.000964E-11  sec
 A     = 43.13564                               S.Dev = 0.1962022
 B1    = 0.1359902     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 4.017249E-04
 Average Life Time = 1.802956E-08  sec
 CHISQ = 1.046326           [ 1781 degrees of freedom ]
```

C-2



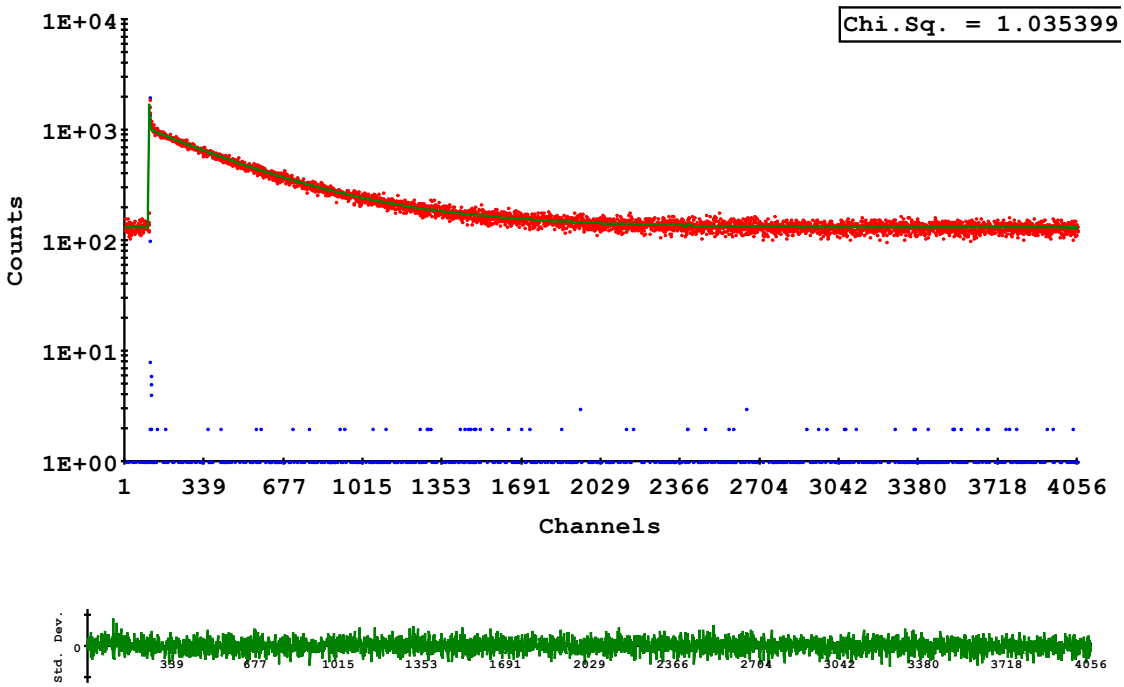

```
Calculated using 1 exponential

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         8.77915E-09    sec

 T1 Estimate = 387.4972 ch;         8.504739E-08   sec

 A Free
 B1 Free

 Prompt and decay LO = 409    ch;   8.976681E-08   sec
 Prompt and decay HI = 2691   ch;   5.906173E-07   sec

 Background on prompt = 1 (manual)
 Time calibration = 2.194787E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 2651 ch

 SHIFT = 0.3212092     ch;  7.049859E-11  sec    S.Dev = 9.764486E-12  sec
 T1    = 501.614       ch;  1.100936E-07  sec    S.Dev = 3.117276E-10  sec
 A     = 84.2297                                S.Dev = 0.392129
 B1    = 0.1542881     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 2.143631E-04
 Average Life Time = 1.100936E-07  sec
 CHISQ = 1.018662           [ 2239 degrees of freedom ]
```

C-3a



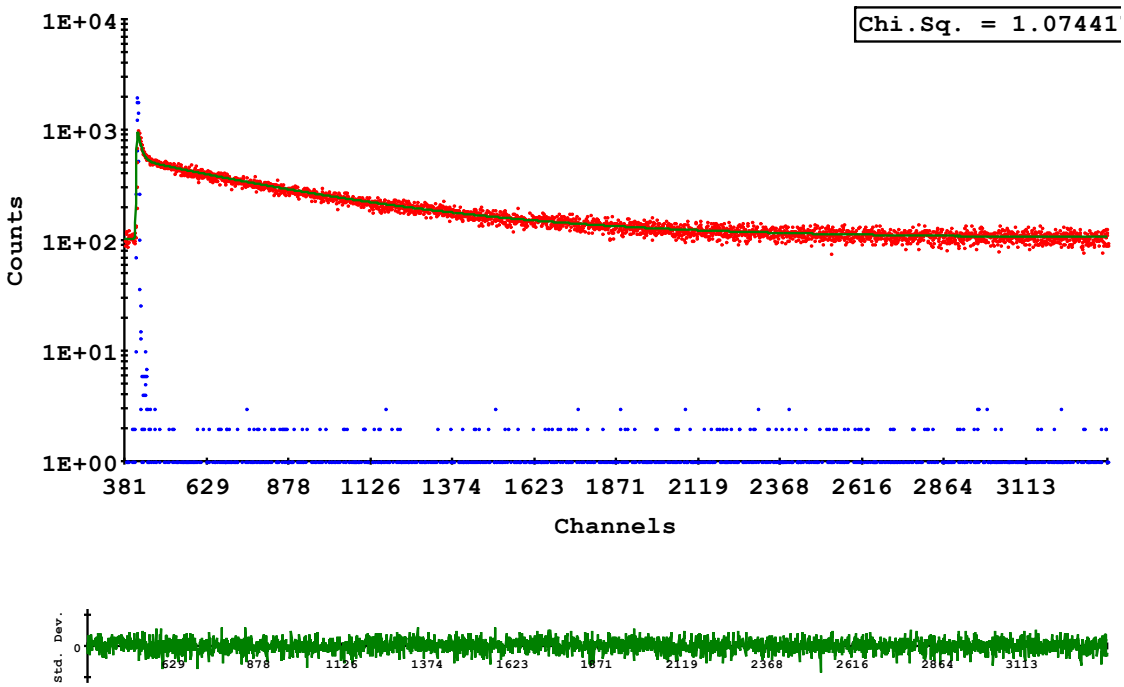

```
Calculated using 2 exponentials

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         1.75583E-08    sec

 T1 Estimate = 150.4275 ch;         6.603126E-08   sec
 T2 Estimate = 601.7099 ch;         2.64125E-07    sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 205    ch;   8.998629E-08   sec
 Prompt and decay HI = 3518   ch;   1.544252E-06   sec

 Background on prompt = 1 (manual)
 Time calibration = 4.389575E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 3478 ch

 SHIFT = 9.356263E-02  ch;  4.107002E-11  sec    S.Dev = 7.121309E-12  sec
 T1    = 6.639951      ch;  2.914656E-09  sec    S.Dev = 9.402936E-11  sec
 T2    = 516.1541      ch;  2.265697E-07  sec    S.Dev = 4.253594E-10  sec
 A     = 77.17587                                S.Dev = 0.2509782
 B1    = 0.2414948     [ 2.24 Rel.Ampl][ 0.64 Alpha] S.Dev = 2.503661E-03
 B2    = 0.135377      [ 97.76 Rel.Ampl][ 0.36 Alpha] S.Dev = 1.506701E-04
 Average Life Time = 8.325431E-08  sec
 CHISQ = 1.143413           [ 3268 degrees of freedom ]
```

C-3b



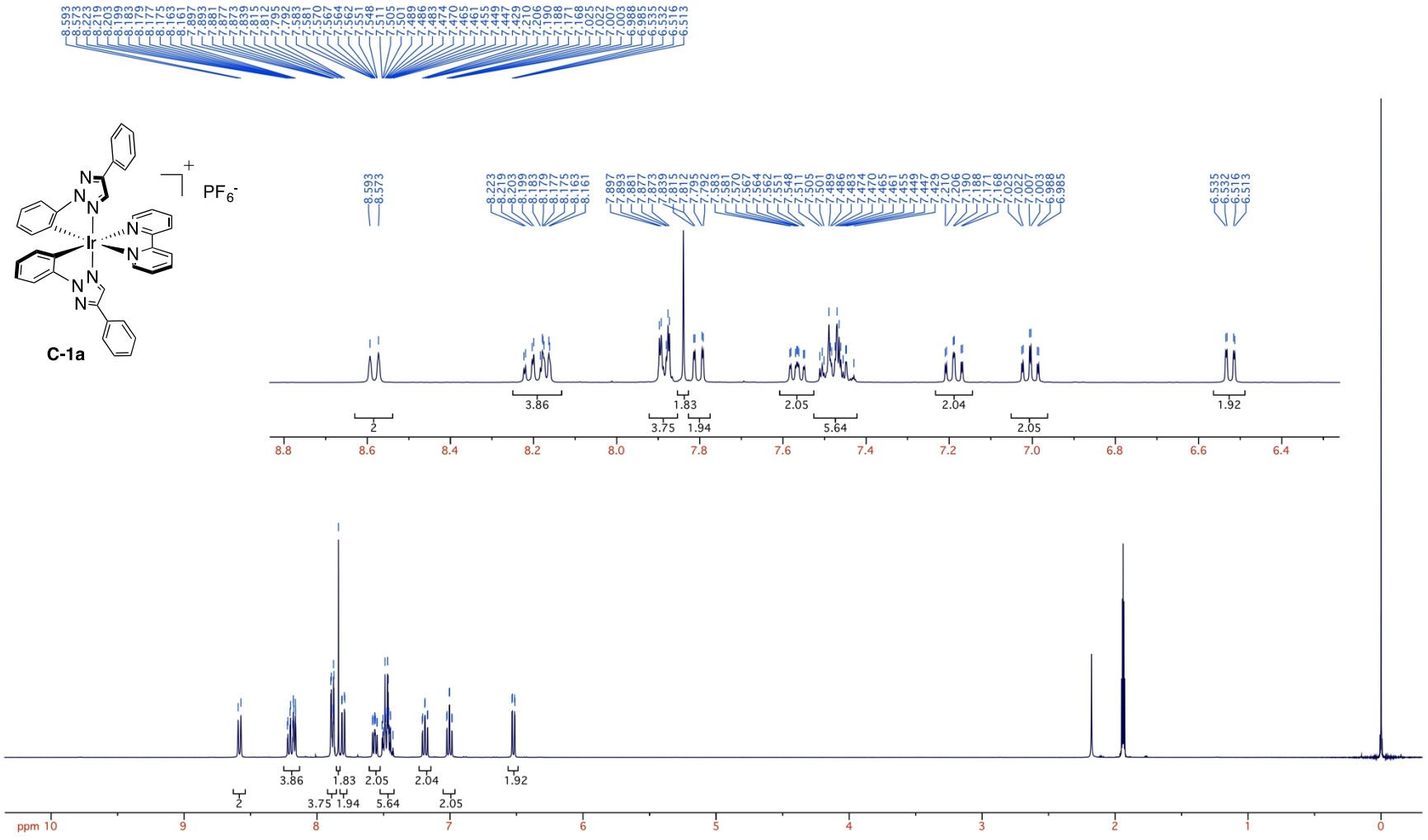

```
Calculated using 2 exponentials

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         3.51166E-08    sec

 T1 Estimate = 106.7029 ch;         9.367609E-08   sec
 T2 Estimate = 426.8117 ch;         3.747044E-07   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 2      ch;   1.75583E-09    sec
 Prompt and decay HI = 4096   ch;   3.59594E-06    sec

 Background on prompt = 1 (manual)
 Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 4056 ch

 SHIFT = 0.1195633     ch;  1.049664E-10  sec    S.Dev = 2.888147E-11  sec
 T1    = 3.303561      ch;  2.900246E-09  sec    S.Dev = 2.73716E-10   sec
 T2    = 438.8091      ch;  3.852371E-07  sec    S.Dev = 1.334552E-09  sec
 A     = 129.7937                                S.Dev = 0.2192968
 B1    = 0.3673247     [ 1.13 Rel.Ampl][ 0.60 Alpha] S.Dev = 1.066362E-02
 B2    = 0.2421349     [ 98.87 Rel.Ampl][ 0.40 Alpha] S.Dev = 5.042904E-04
 Average Life Time = 1.548005E-07  sec
 CHISQ = 1.035399           [ 4050 degrees of freedom ]
```

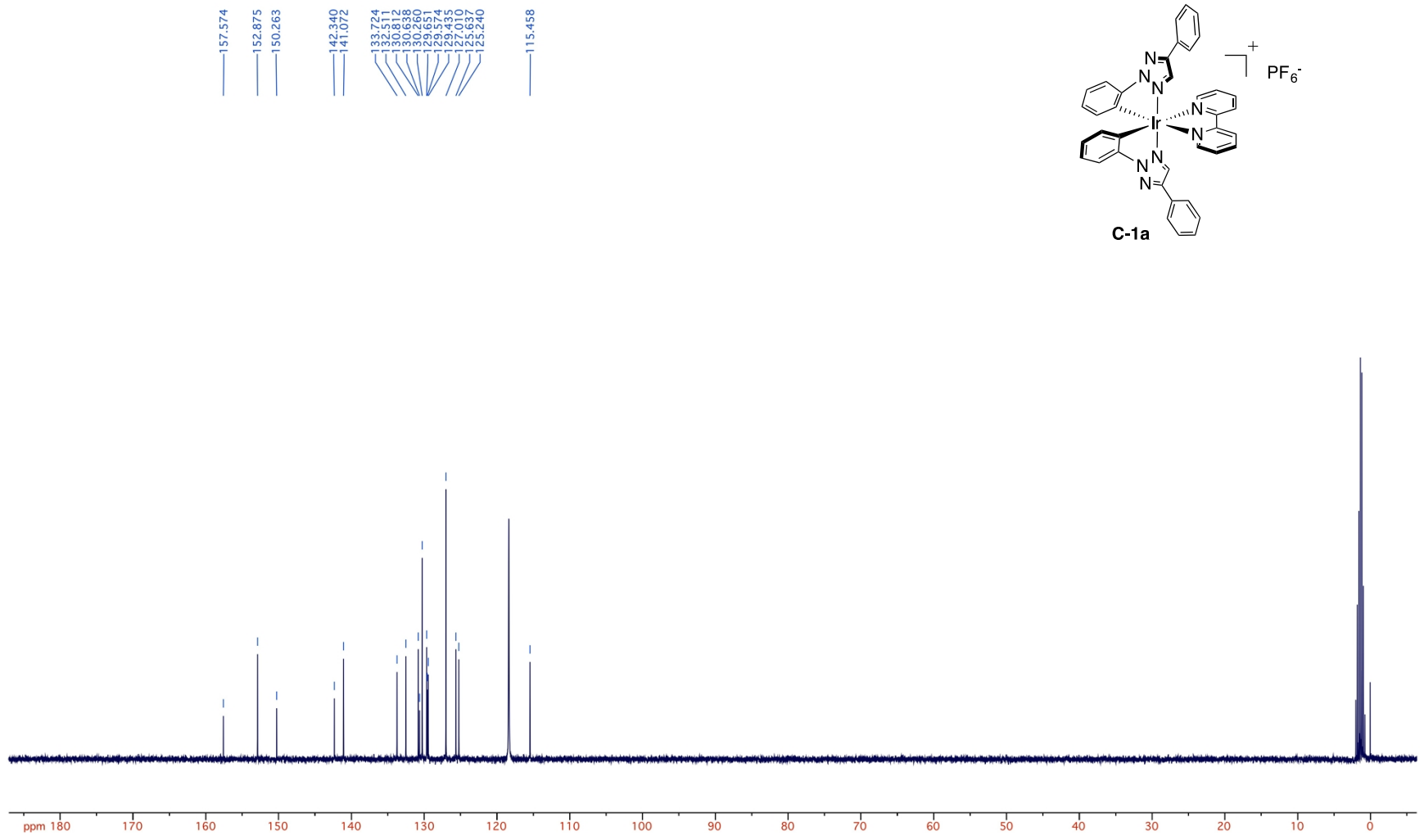
C-3c

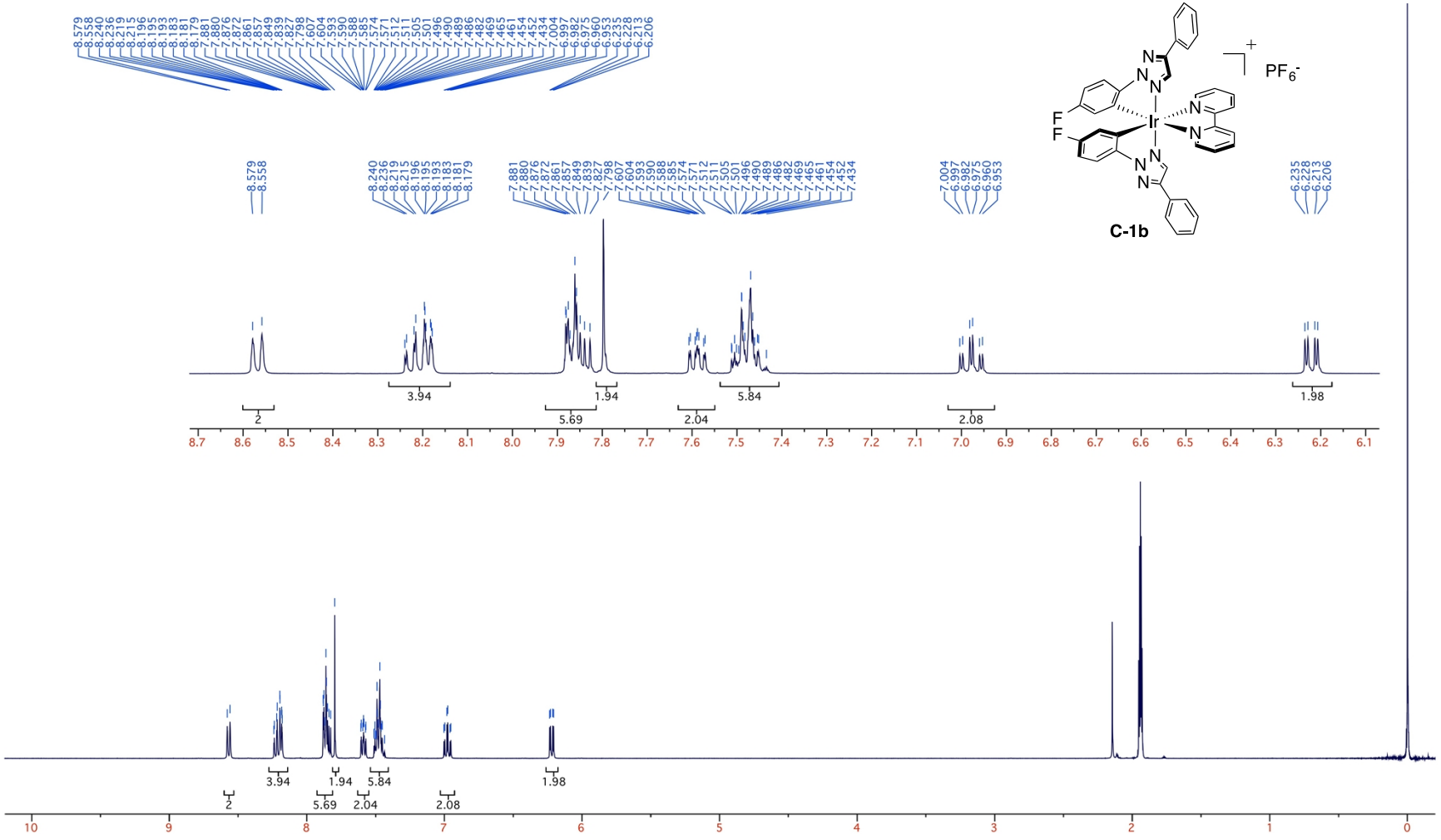


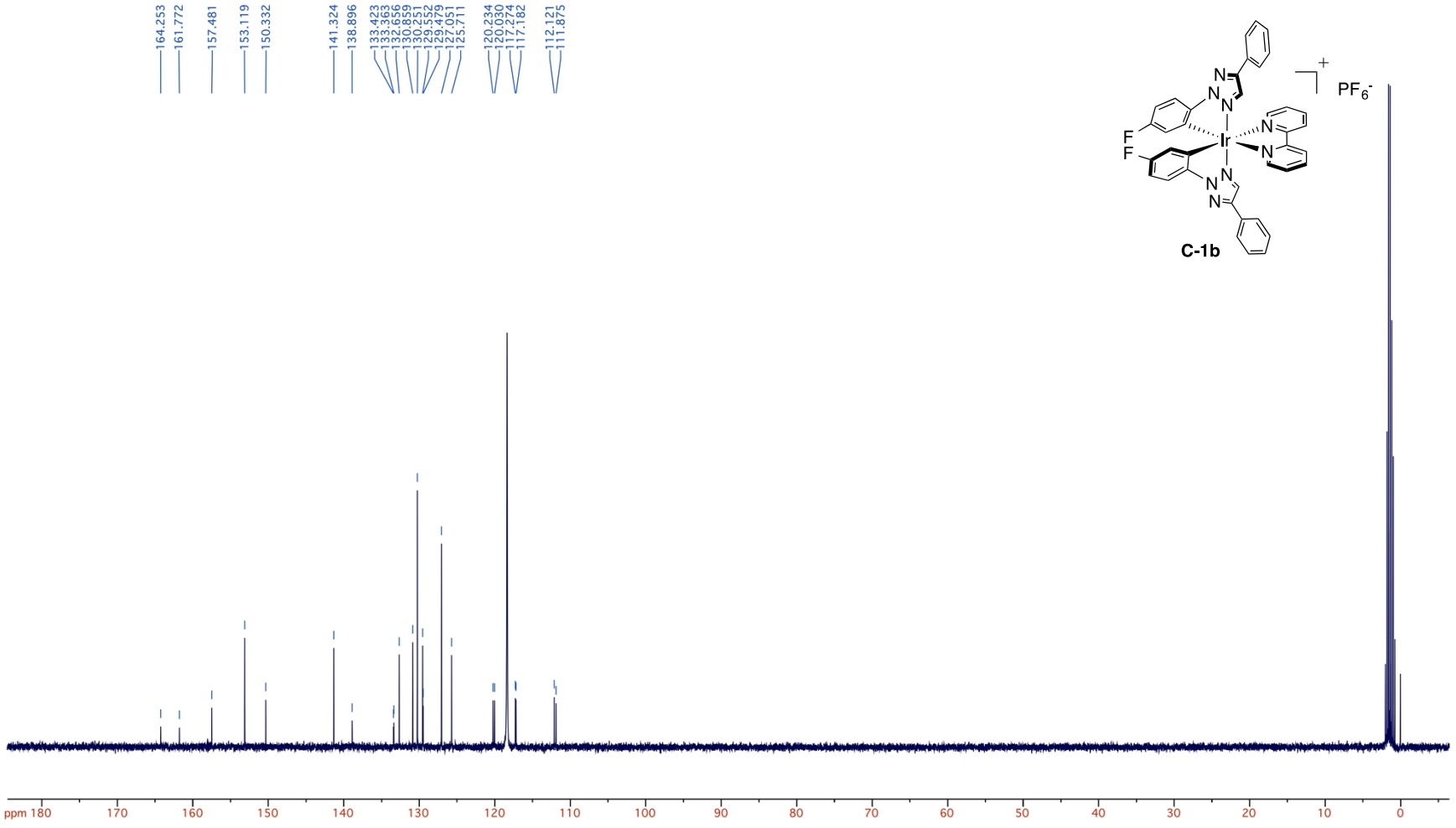

```
Calculated using 2 exponentials

The initial paramters are:

 Shift Value = 0        ch;         0              sec
 Shift Limit = 40       ch;         8.77915E-09    sec

 T1 Estimate = 321.9654 ch;         7.066456E-08   sec
 T2 Estimate = 1287.861 ch;         2.826582E-07   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 381    ch;   8.36214E-08    sec
 Prompt and decay HI = 3401   ch;   7.464472E-07   sec

 Background on prompt = 1 (manual)
 Time calibration = 2.194787E-10 sec/ch

The fitted parameters are:

 Hi reduced to: 3361 ch

 SHIFT = -0.1458581    ch;   -3.201274E-11 sec    S.Dev = 1.377985E-11  sec
 T1    = 10.5551       ch;   2.31662E-09   sec    S.Dev = 1.14752E-10   sec
 T2    = 540.5867      ch;   1.186473E-07  sec    S.Dev = 7.761685E-10  sec
 A     = 103.4928                                 S.Dev = 0.2637861
 B1    = 6.355906E-02  [ 3.13 Rel.Ampl][ 0.62 Alpha] S.Dev = 1.31891E-03
 B2    = 3.844109E-02  [ 96.87 Rel.Ampl][ 0.38 Alpha] S.Dev = 1.240731E-04
 Average Life Time = 4.615849E-08  sec
 CHISQ = 1.074417           [ 2975 degrees of freedom ]
```

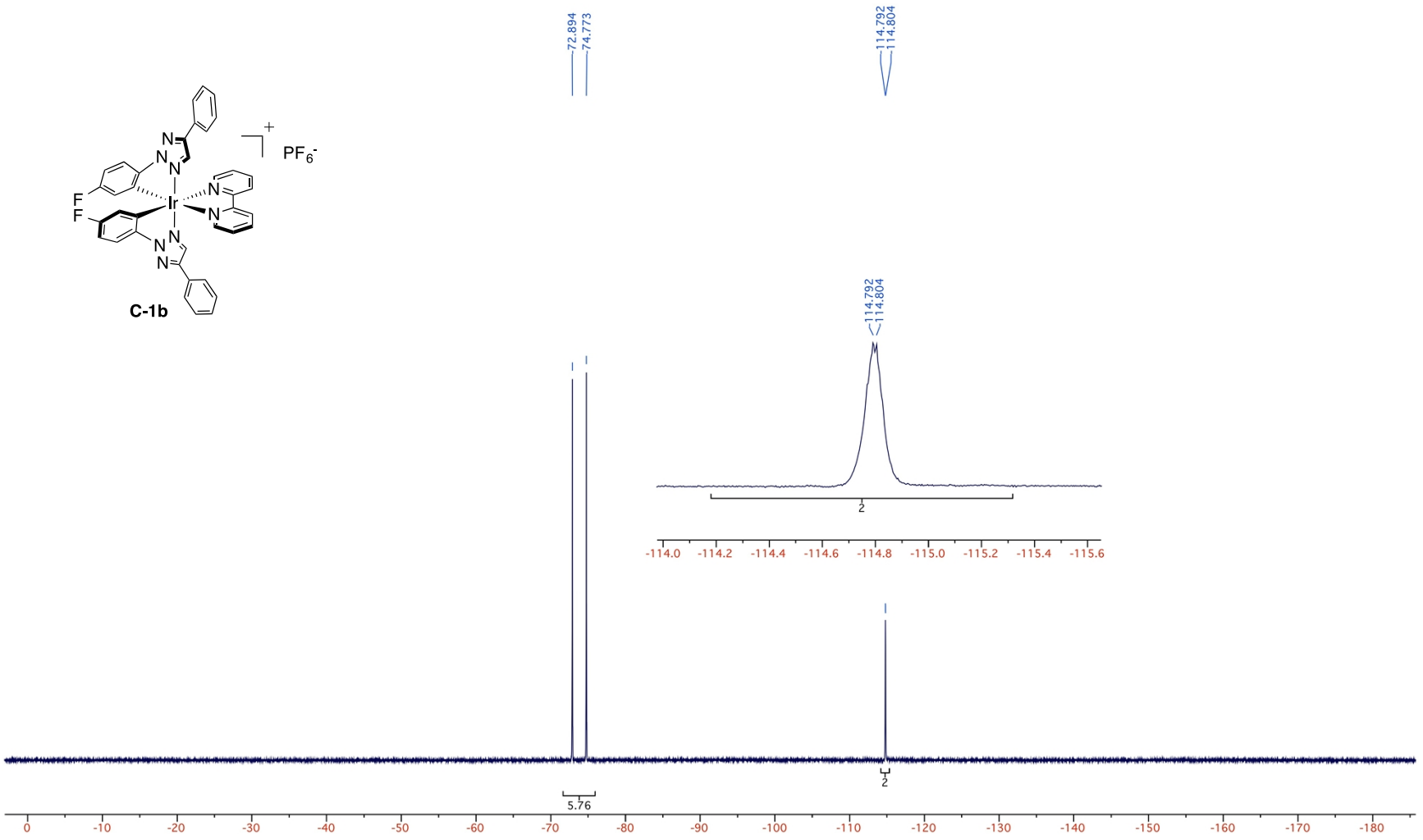
VII. NMR spectra

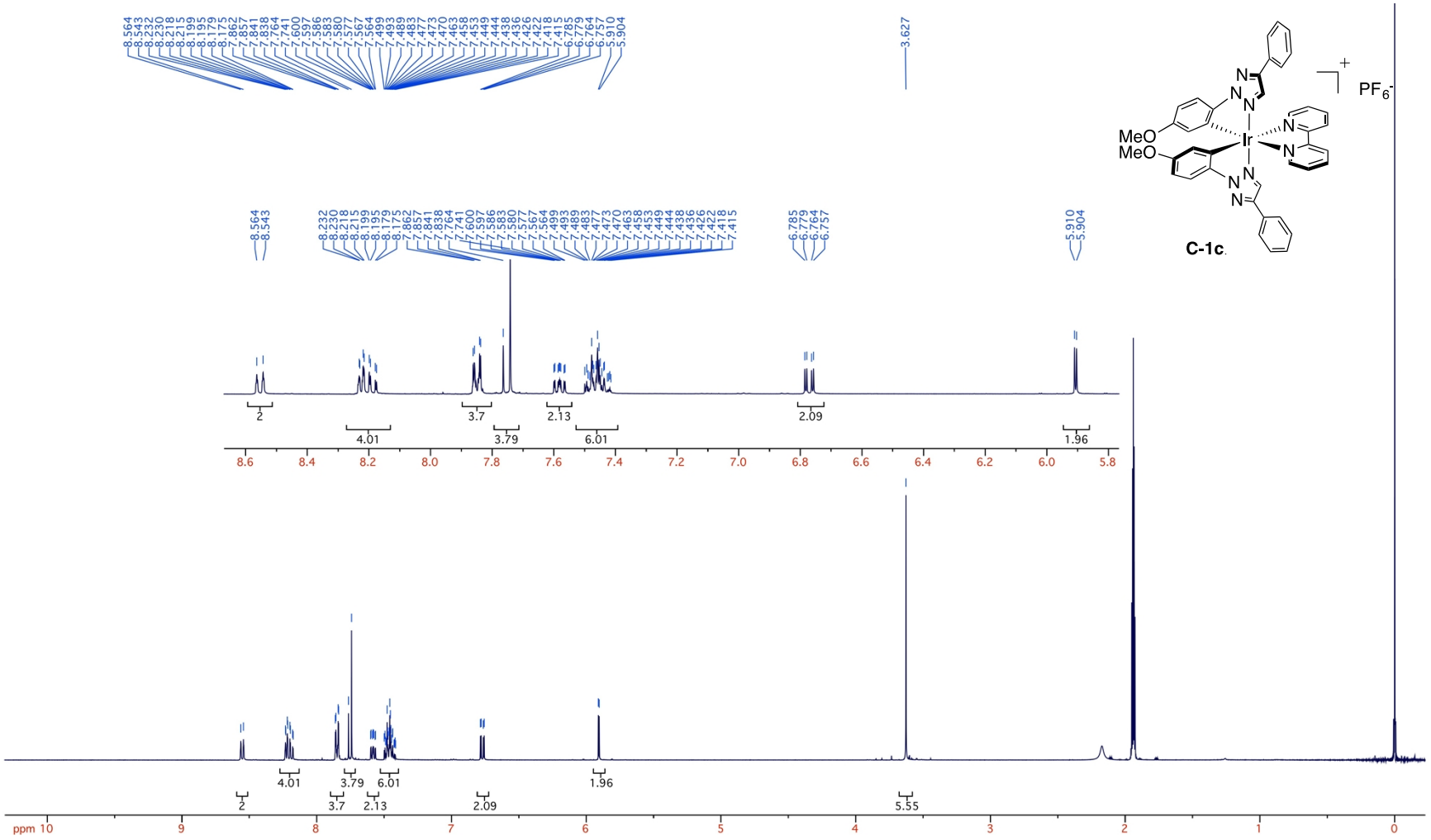


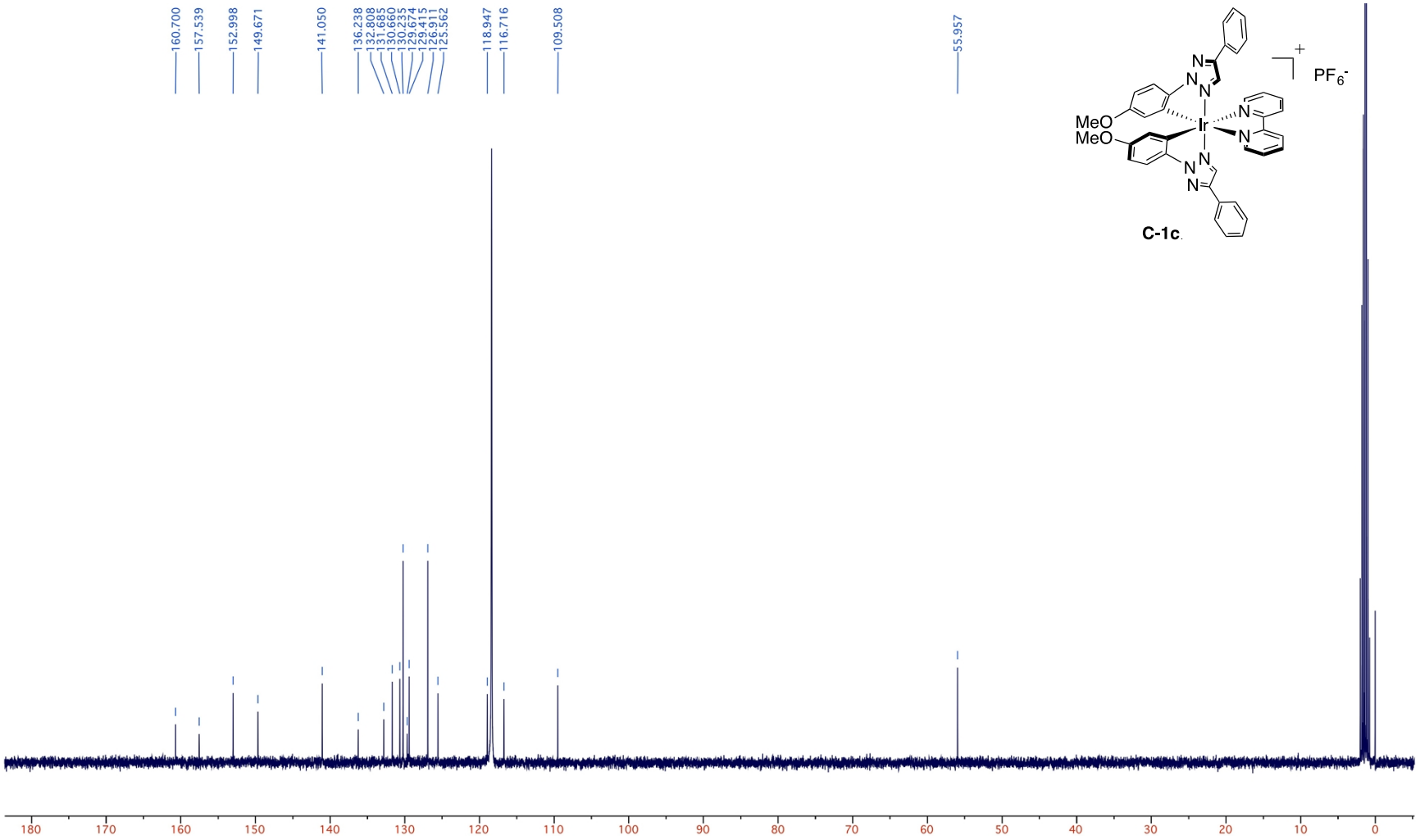

157.574
152.875
150.263
142.340
141.072
133.724
132.511
130.812
130.638
130.260
129.651
129.574
129.435
127.010
125.637
125.240
115.458
PF6-
C-1a
ppm 180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

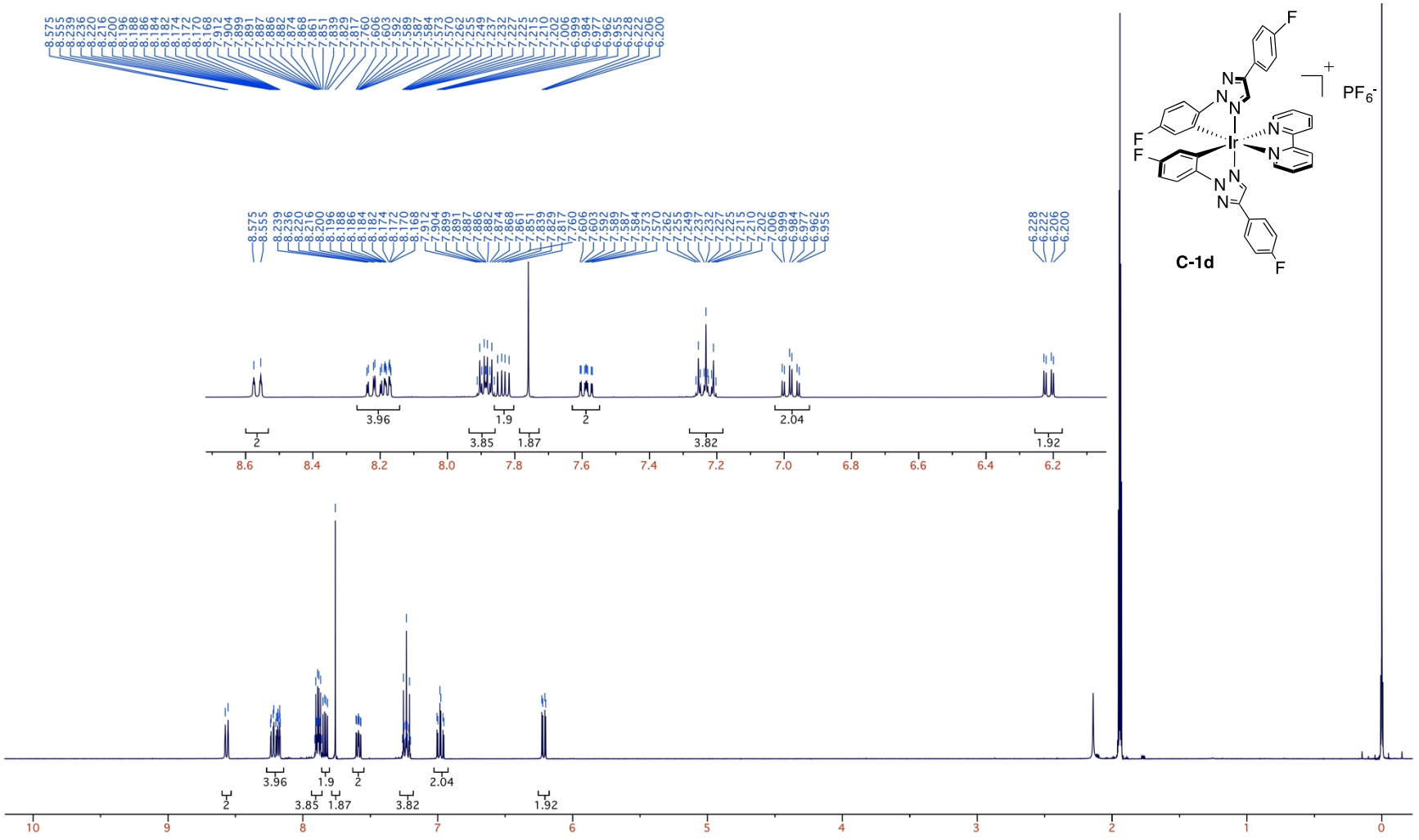

C-1b
PF6-
8.579
8.558
8.240
8.236
8.219
8.215
8.196
8.195
8.193
8.183
8.181
8.179
7.881
7.880
7.876
7.872
7.861
7.857
7.849
7.839
7.827
7.798
7.607
7.604
7.593
7.590
7.588
7.585
7.574
7.571
7.512
7.511
7.505
7.501
7.496
7.490
7.489
7.486
7.482
7.469
7.465
7.461
7.454
7.452
7.434
7.004
6.997
6.982
6.975
6.960
6.953
6.235
6.228
6.213
6.206
3.94
1.94
5.84
1.98
2
5.69
2.04
2.08

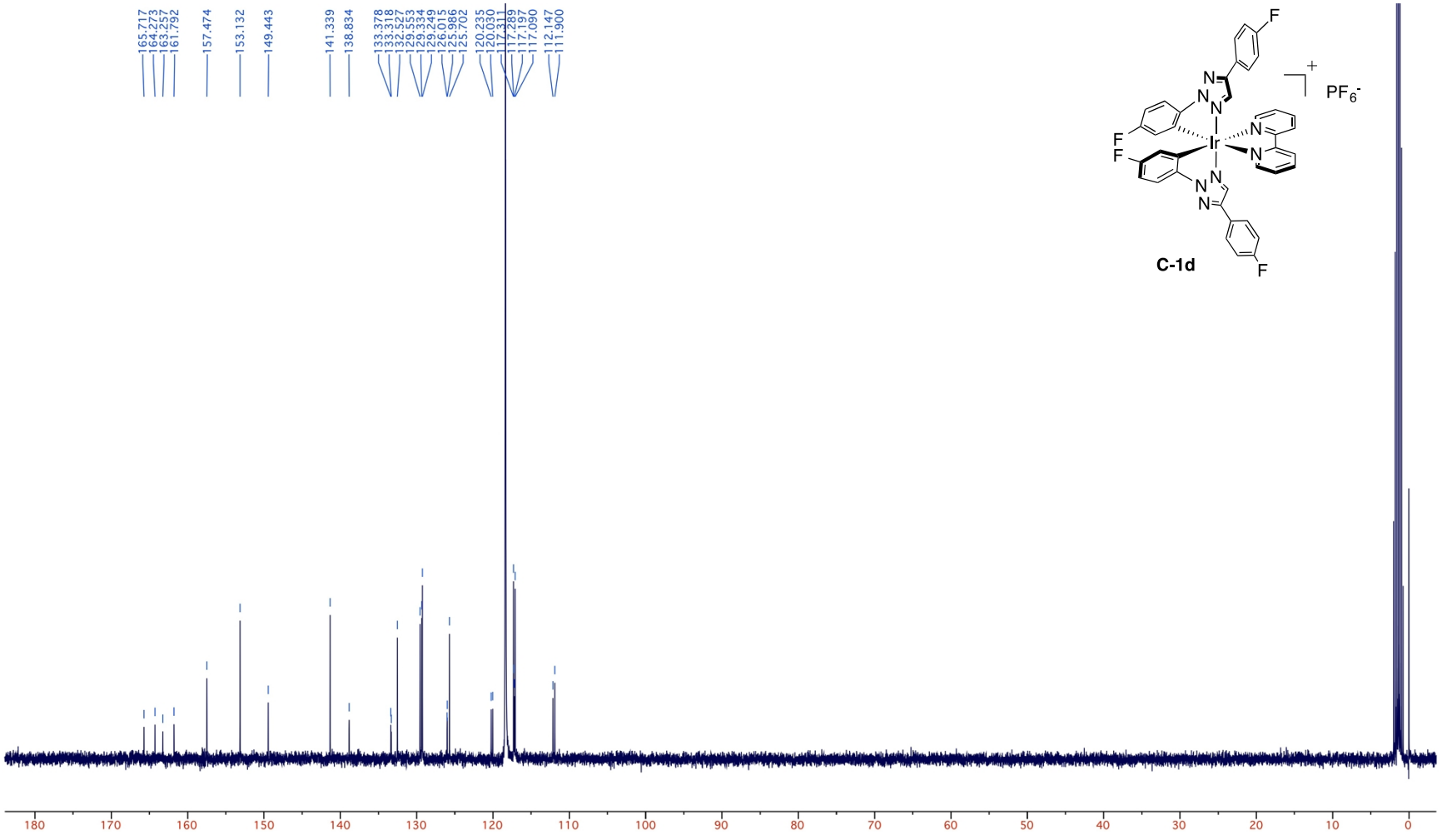

164.253
161.772
157.481
153.119
150.332
141.324
138.896
133.423
133.363
132.656
130.859
130.251
129.552
129.479
127.051
125.711
120.234
120.030
117.274
117.182
112.121
111.875
ppm 180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
F
F
Ir
N
PF6-
C-1b

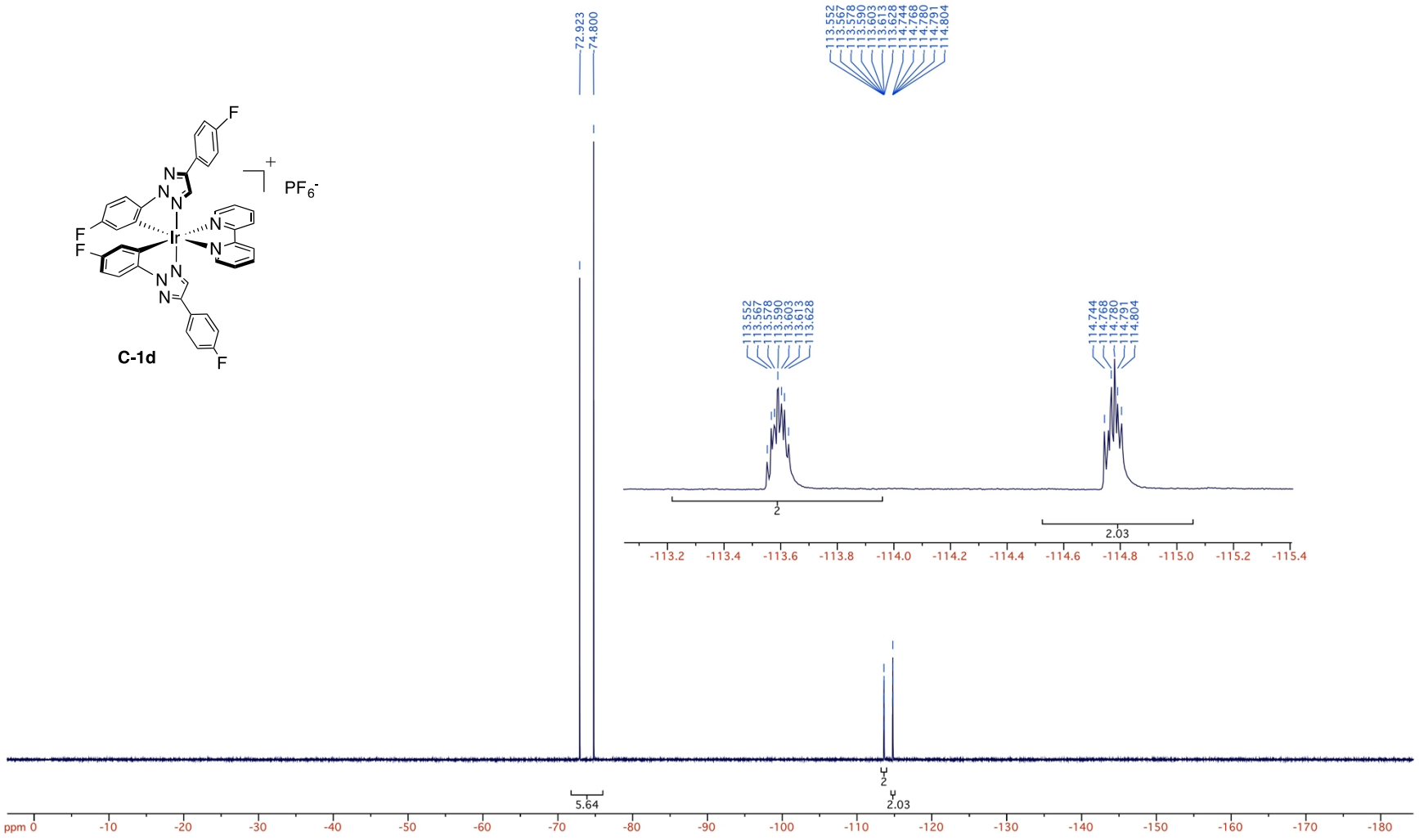

72.894
74.773
114.792
114.804
C-1b
PF6-
F
F
Ir
N
114.792
114.804
2
-114.0
-114.2
-114.4
-114.6
-114.8
-115.0
-115.2
-115.4
-115.6
5.76
2
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180

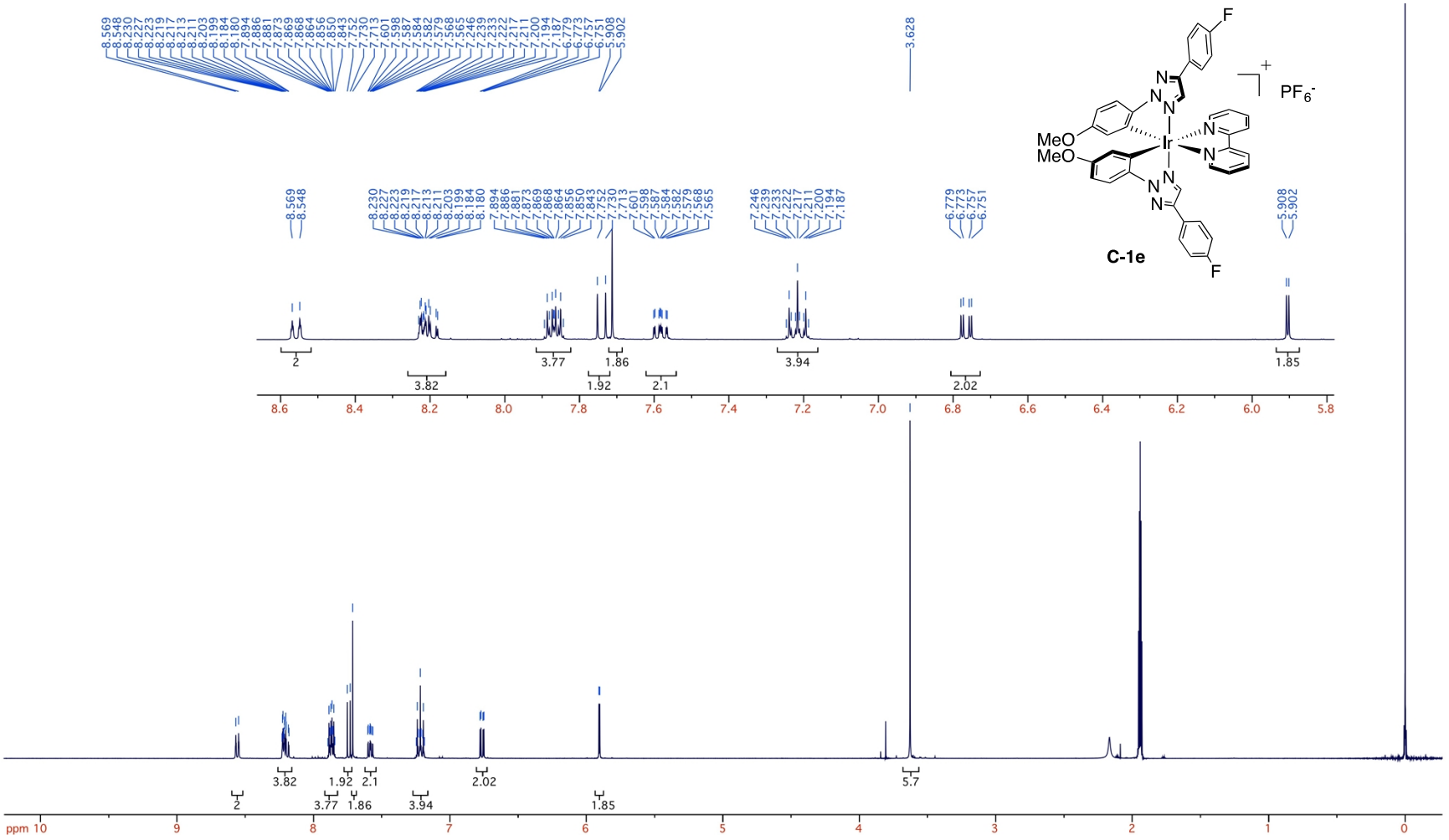

8.564
8.543
8.232
8.230
8.218
8.215
8.199
8.195
8.179
8.175
7.862
7.857
7.841
7.838
7.764
7.741
7.600
7.597
7.586
7.583
7.580
7.577
7.567
7.564
7.499
7.493
7.489
7.483
7.477
7.473
7.470
7.463
7.458
7.453
7.449
7.444
7.438
7.436
7.426
7.422
7.418
7.415
6.785
6.779
6.764
6.757
5.910
5.904
3.627
MeO
MeO
Ir
N
PF6-
C-1c.
2
4.01
3.7
3.79
2.13
6.01
2.09
1.96
5.55
ppm

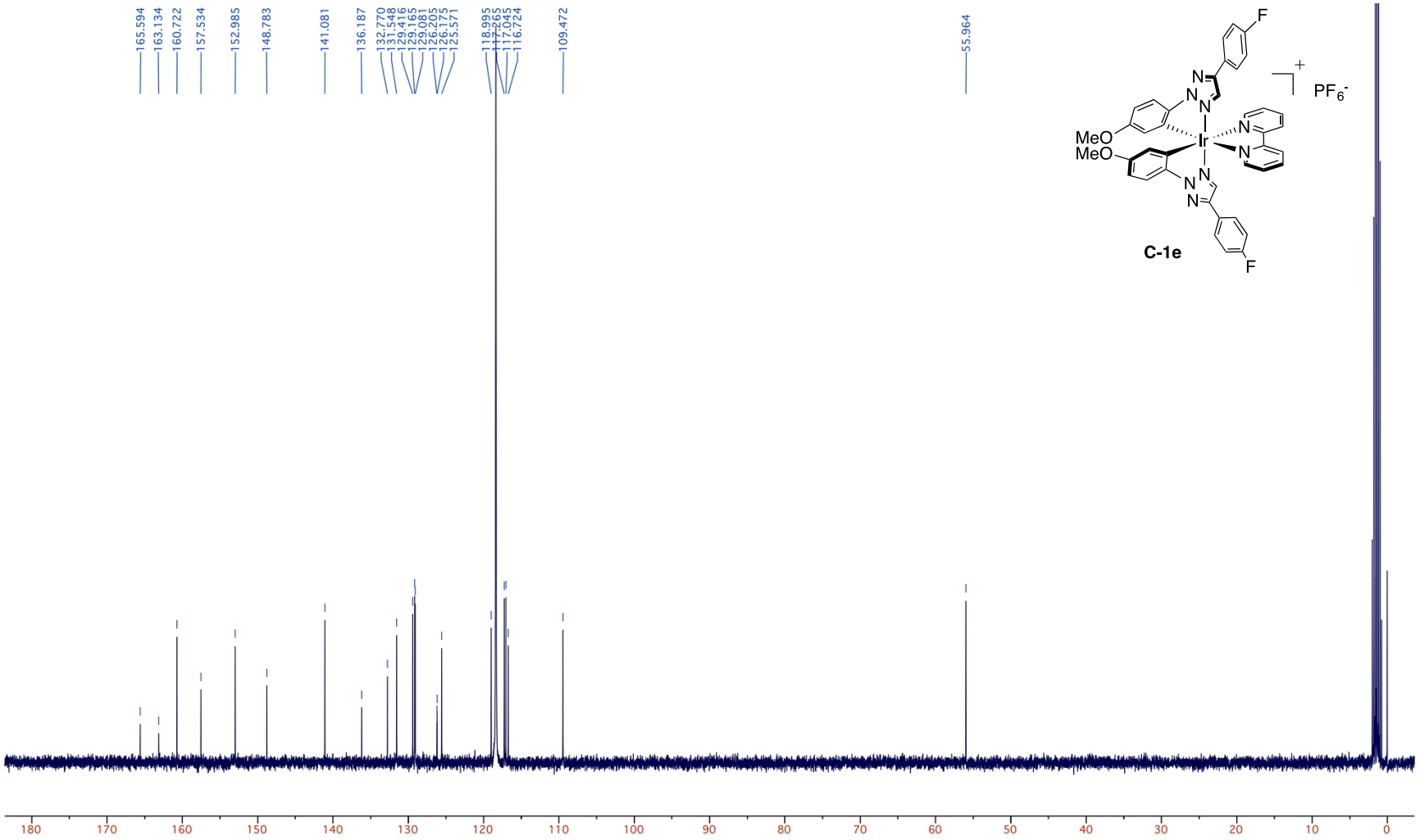

160.700
157.539
152.998
149.671
141.050
136.238
132.808
131.685
130.660
130.235
129.674
129.415
126.911
125.562
118.947
116.716
109.508
55.957
MeO
MeO
Ir
N
PF6-
C-1c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


C-1d
PF6-


165.717
164.273
163.257
161.792
157.474
153.132
149.443
141.339
138.834
133.378
133.318
132.527
129.553
129.334
129.249
126.015
125.986
125.702
120.235
120.030
117.311
117.289
117.197
117.090
112.147
111.900
C-1d
PF6-
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


C-1d
PF6-
72.923
74.800
113.552
113.567
113.578
113.590
113.603
113.613
113.628
114.744
114.768
114.780
114.791
114.804
2
2.03
5.64
ppm 0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-113.2
-113.4
-113.6
-113.8
-114.0
-114.2
-114.4
-114.6
-114.8
-115.0
-115.2
-115.4

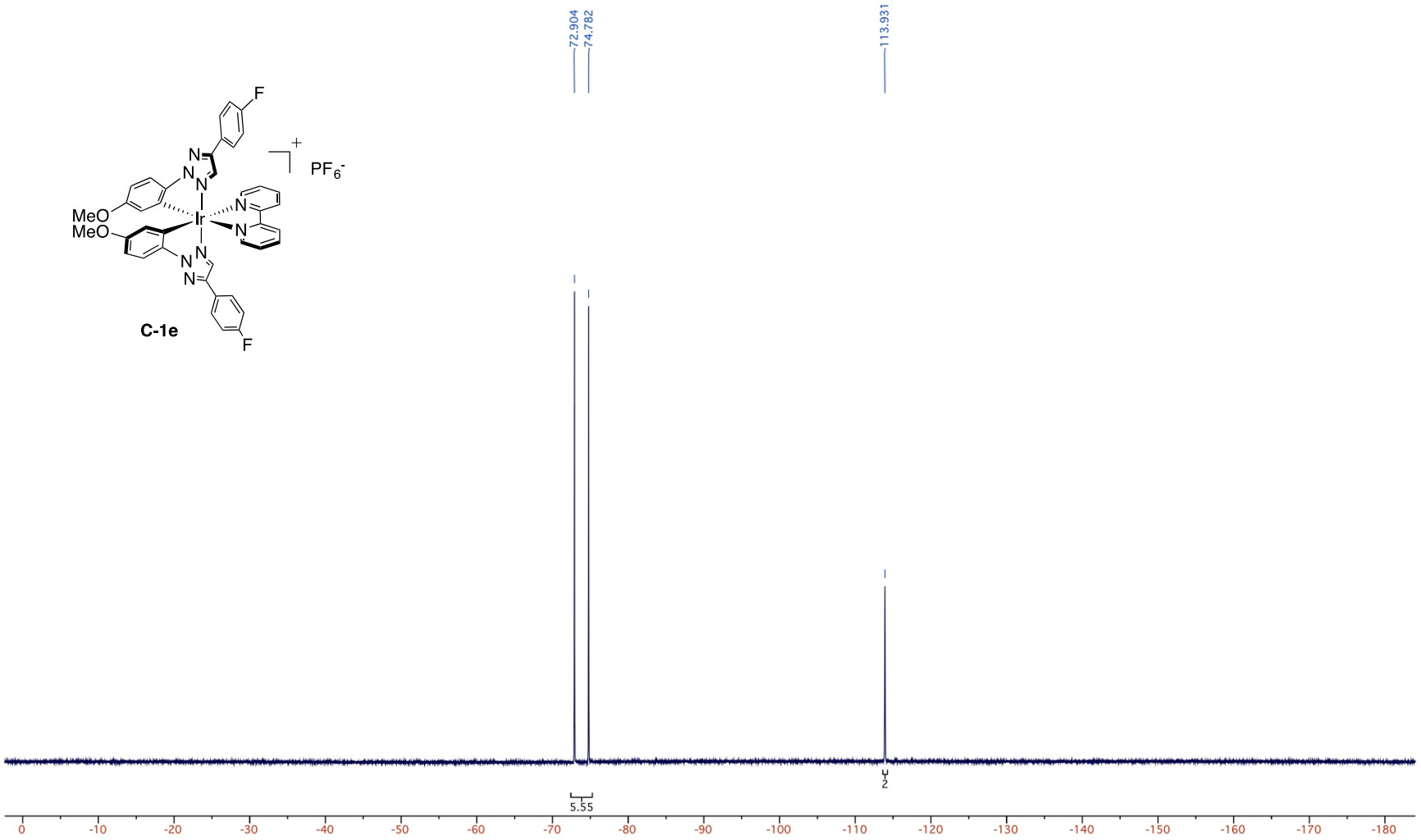

8.569
8.548
8.230
8.227
8.223
8.219
8.217
8.213
8.211
8.203
8.199
8.184
8.180
7.894
7.886
7.881
7.873
7.869
7.868
7.864
7.856
7.850
7.843
7.752
7.730
7.713
7.601
7.598
7.587
7.584
7.582
7.579
7.568
7.565
7.246
7.239
7.233
7.222
7.217
7.211
7.200
7.194
7.187
6.779
6.773
6.757
6.751
5.908
5.902
3.628
F
N
N
N
N
Ir
N
N
MeO
MeO
N
N
F
PF6-
C-1e
2
3.82
3.77
1.86
1.92
2.1
3.94
2.02
1.85
5.7
ppm 10
9
8
7
6
5
4
3
2
1
0

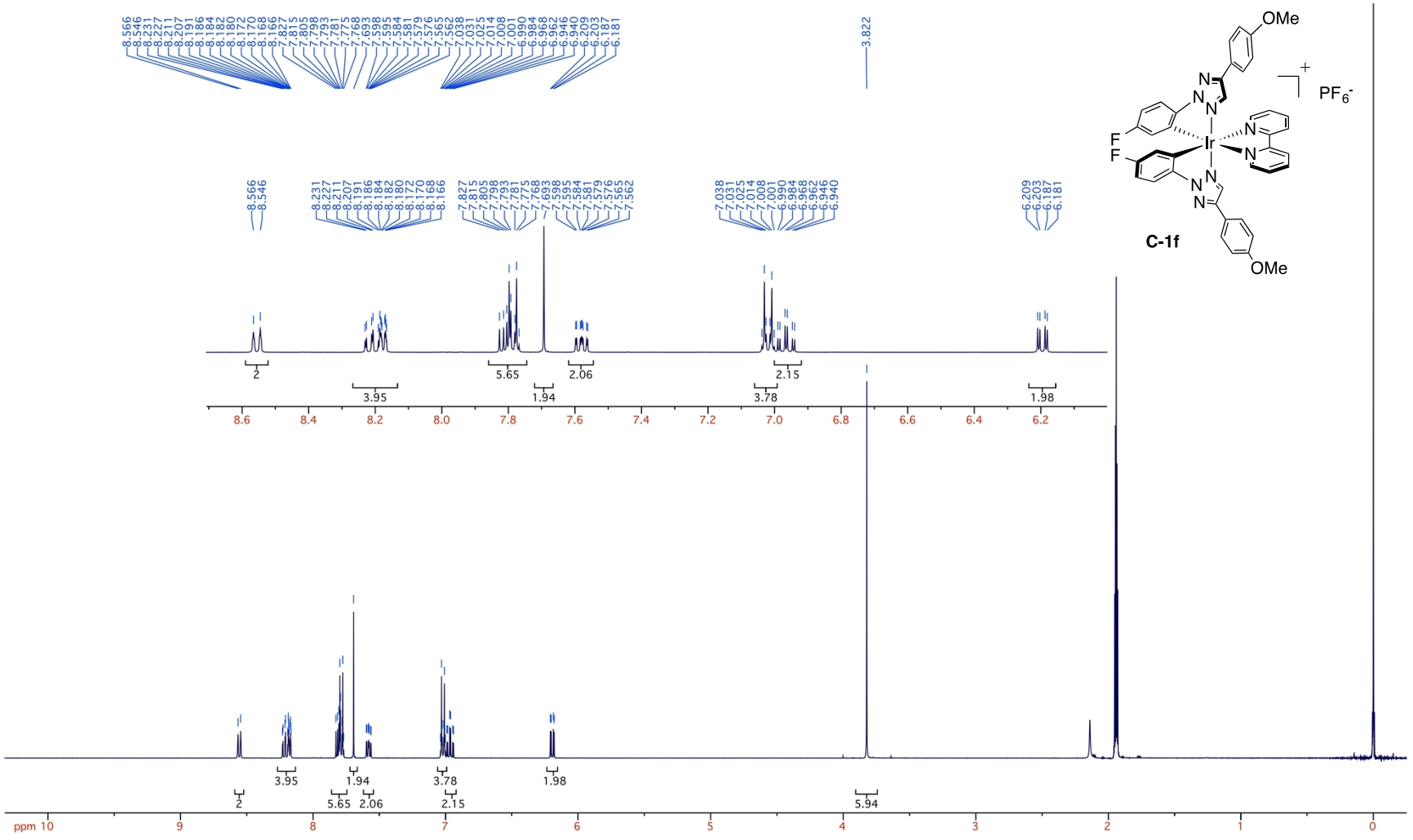

165.594
163.134
160.722
157.534
152.985
148.783
141.081
136.187
132.770
131.548
129.416
129.165
129.081
126.205
126.175
125.571
118.995
117.265
117.045
116.724
109.472
55.964
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

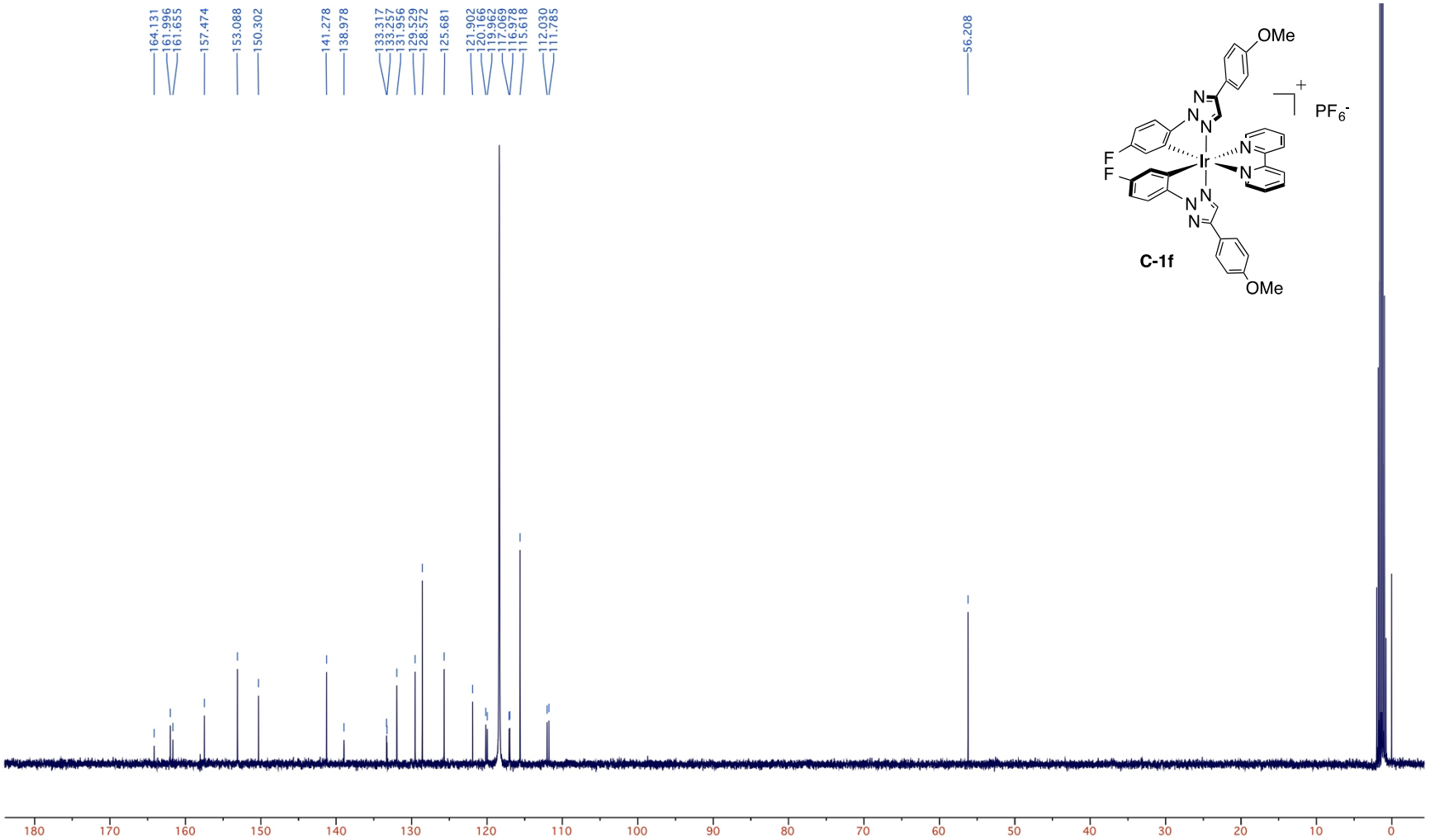
F
N
N
N
MeO
MeO
Ir
N
N
N
N
F
PF6-

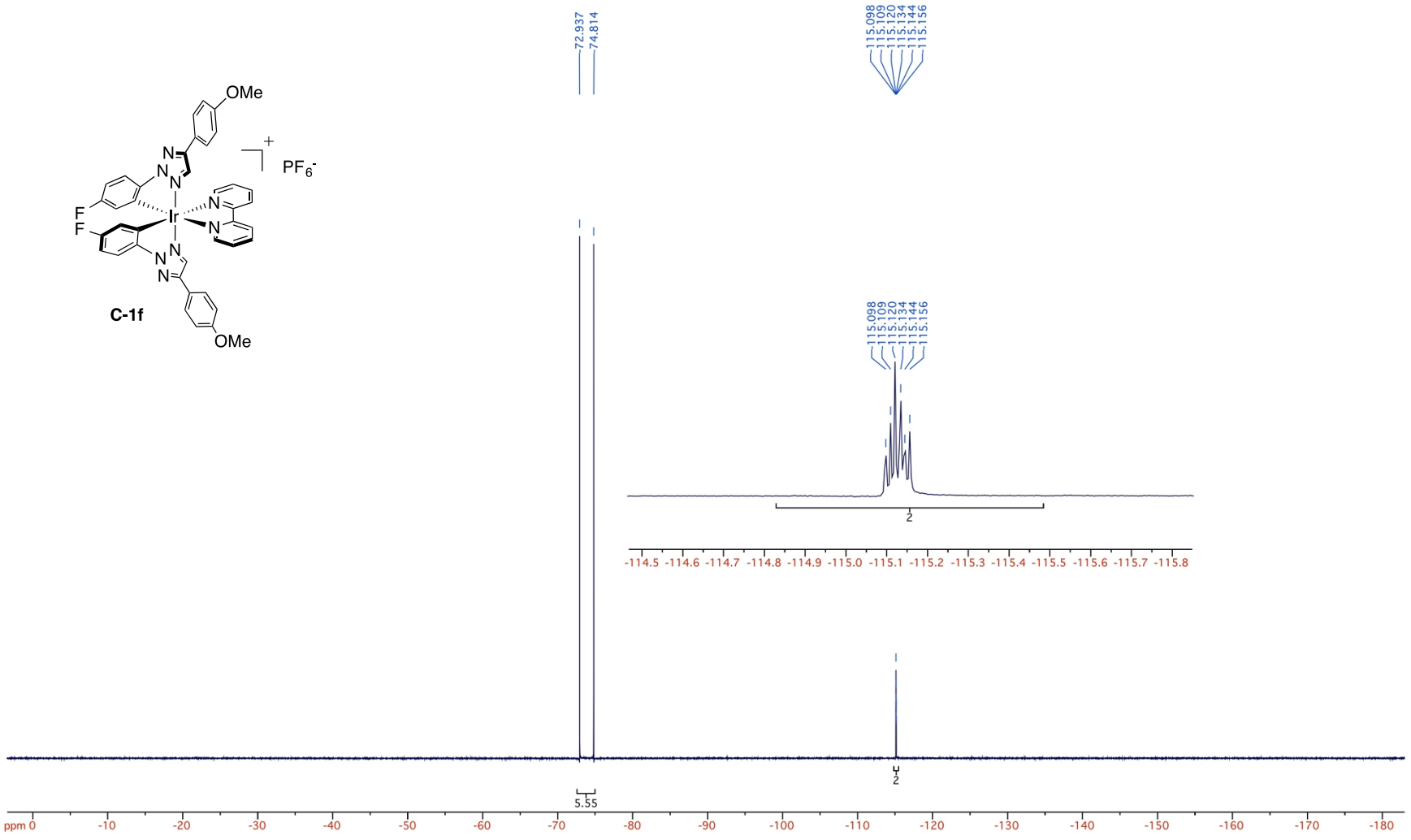
C-1e

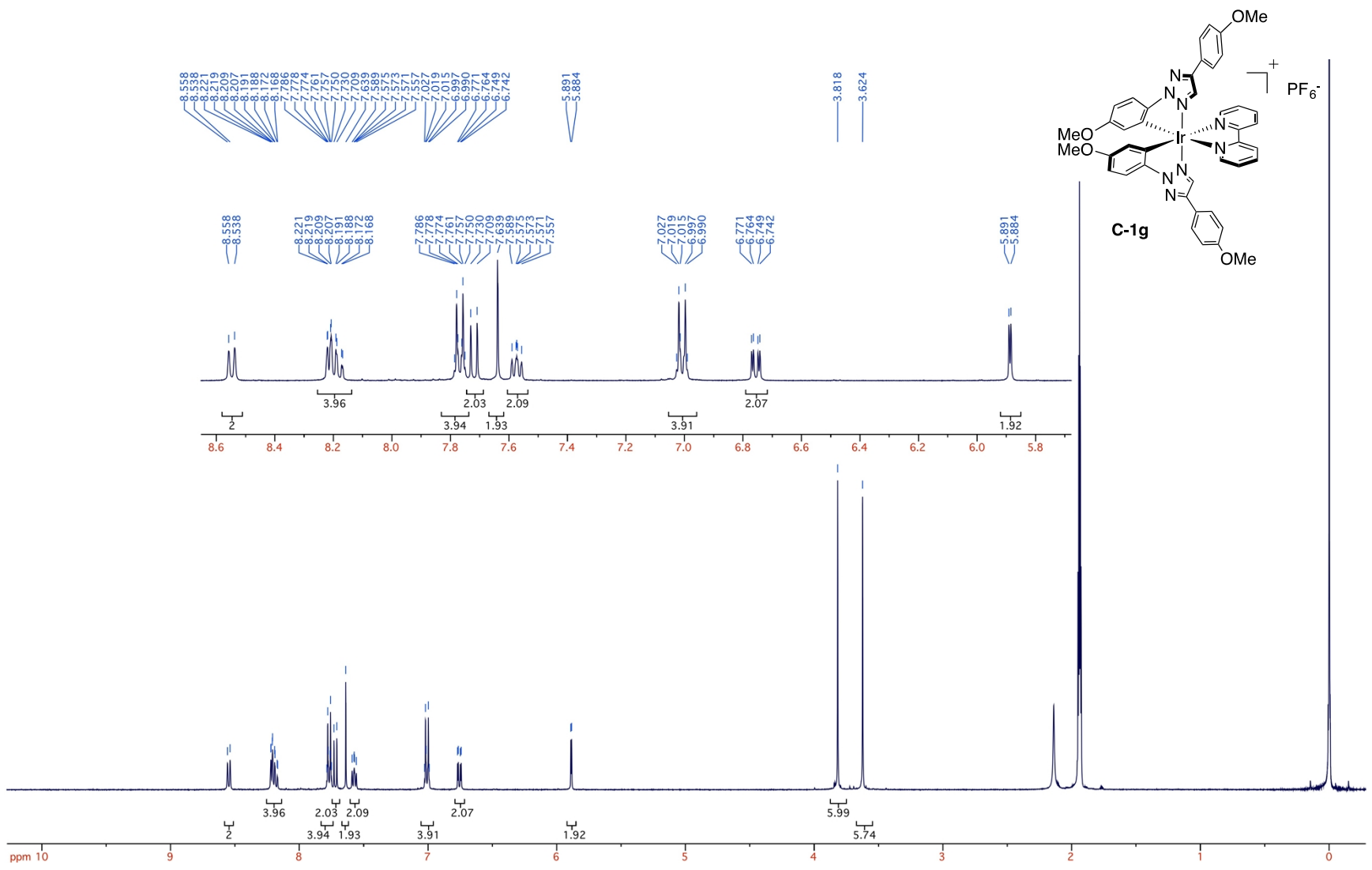
F
N
N
N
MeO
MeO
Ir
N
N
N
N
F
PF6-
C-1e

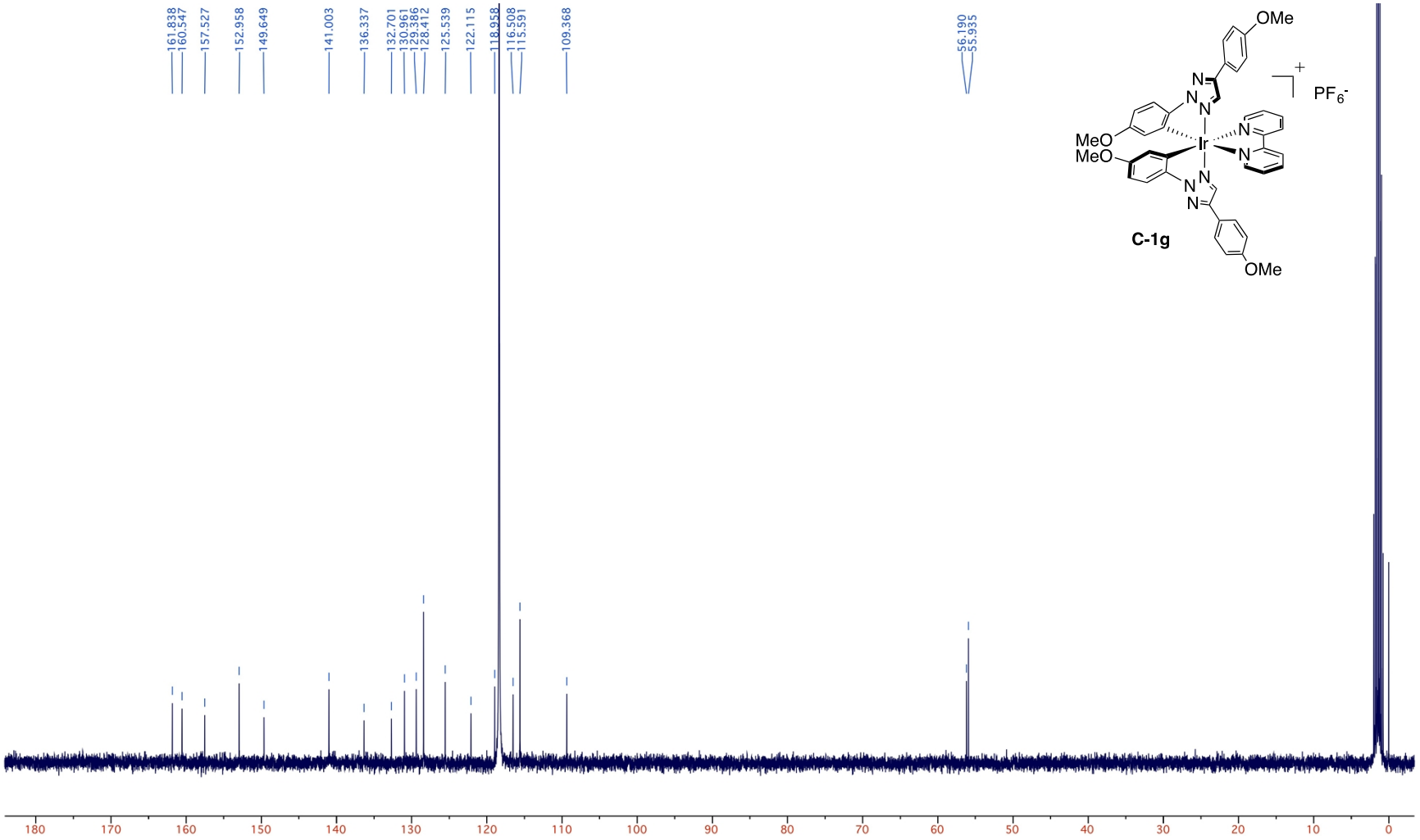

72.904
74.782
113.931
5.55
2
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180

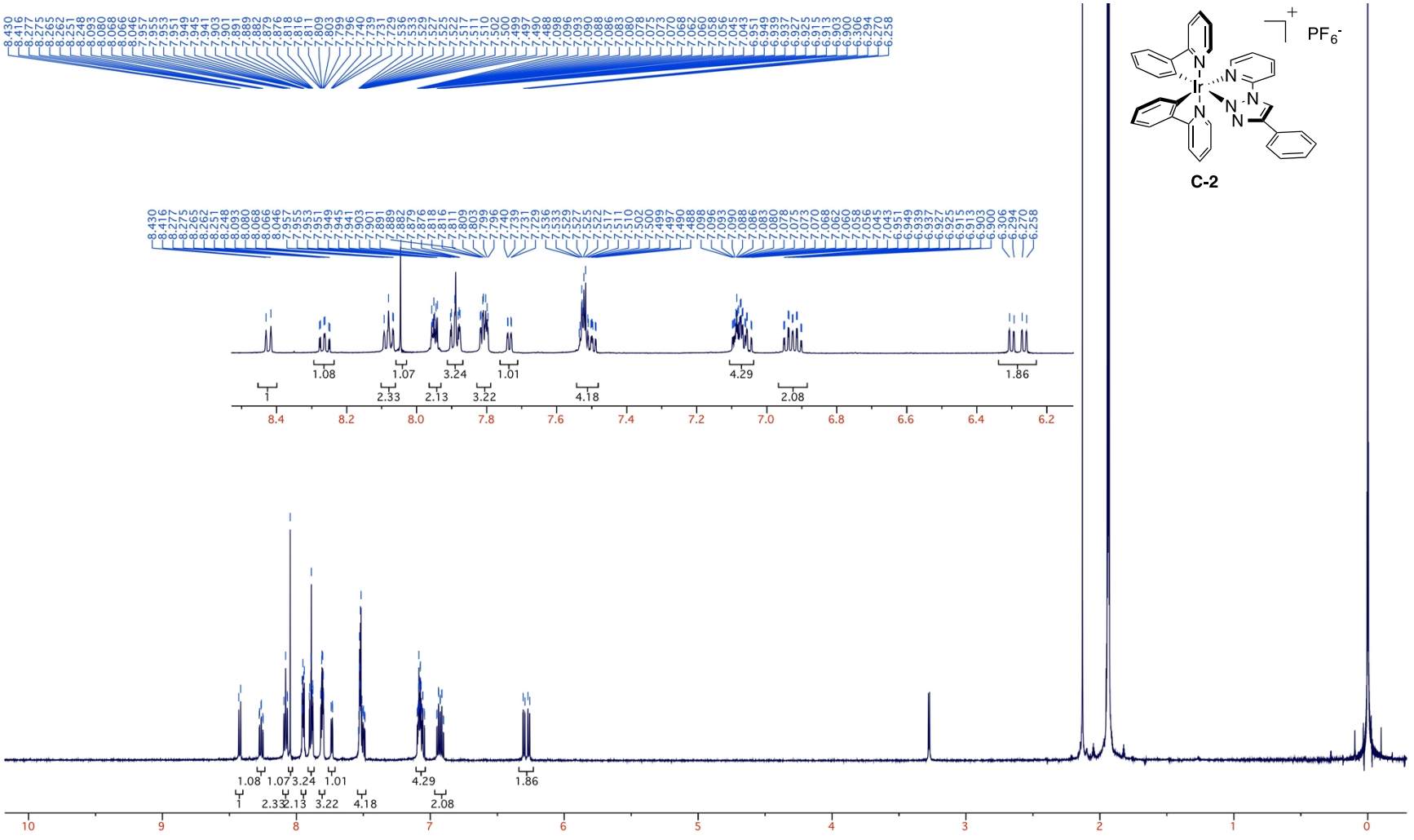

8.566
8.546
8.231
8.227
8.211
8.207
8.191
8.186
8.184
8.182
8.180
8.172
8.170
8.168
8.166
7.827
7.815
7.805
7.798
7.793
7.781
7.775
7.768
7.693
7.598
7.595
7.584
7.581
7.579
7.576
7.565
7.562
7.038
7.031
7.025
7.014
7.008
7.001
6.990
6.984
6.968
6.962
6.946
6.940
6.209
6.203
6.187
6.181
3.822
OMe
PF6-
C-1f
2
3.95
1.94
5.65
2.06
3.78
2.15
1.98
5.94
ppm 10
9
8
7
6
5
4
3
2
1
0

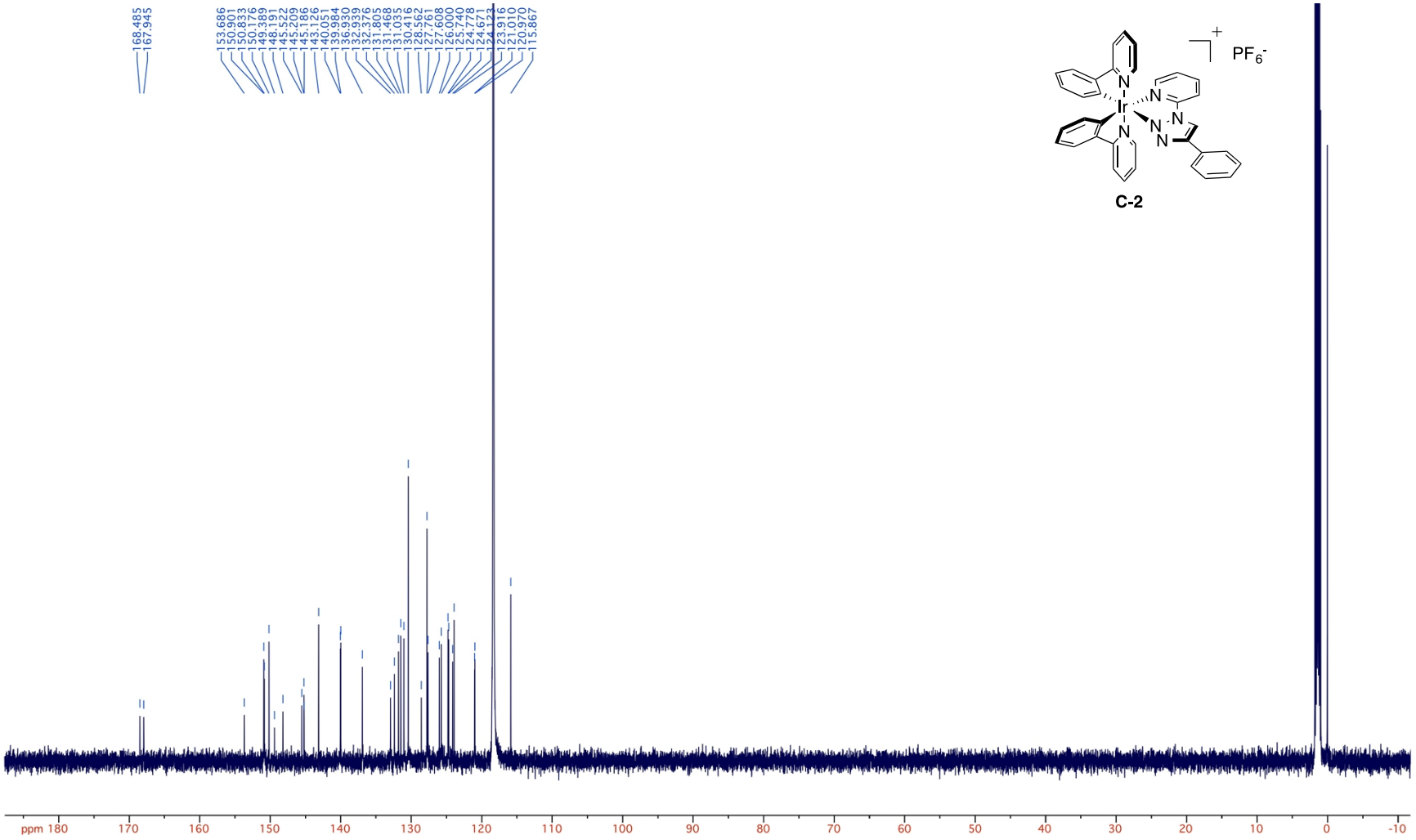

164.131
161.996
161.655
157.474
153.088
150.302
141.278
138.978
133.317
133.257
131.956
129.529
128.572
125.681
121.902
120.166
119.962
117.079
116.978
115.618
112.030
111.785
56.208
OMe
N
N
N
F
F
Ir
N
N
N
N
N
OMe
PF6-
C-1f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

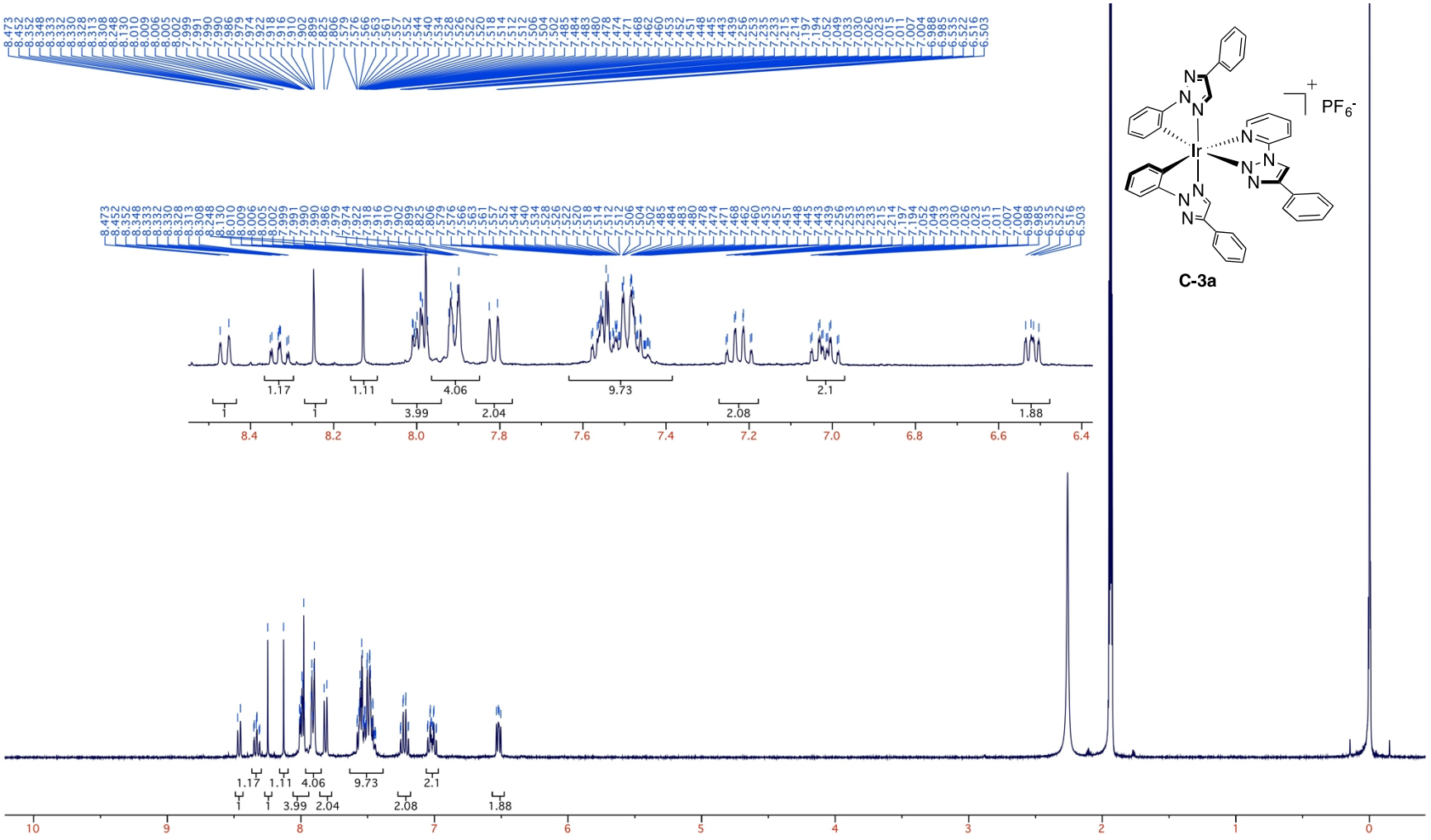

OMe
PF6-
F
F
Ir
N
C-1f
OMe
72.937
74.814
115.098
115.109
115.120
115.134
115.144
115.156
2
-114.5 -114.6 -114.7 -114.8 -114.9 -115.0 -115.1 -115.2 -115.3 -115.4 -115.5 -115.6 -115.7 -115.8
5.55
2
ppm 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180

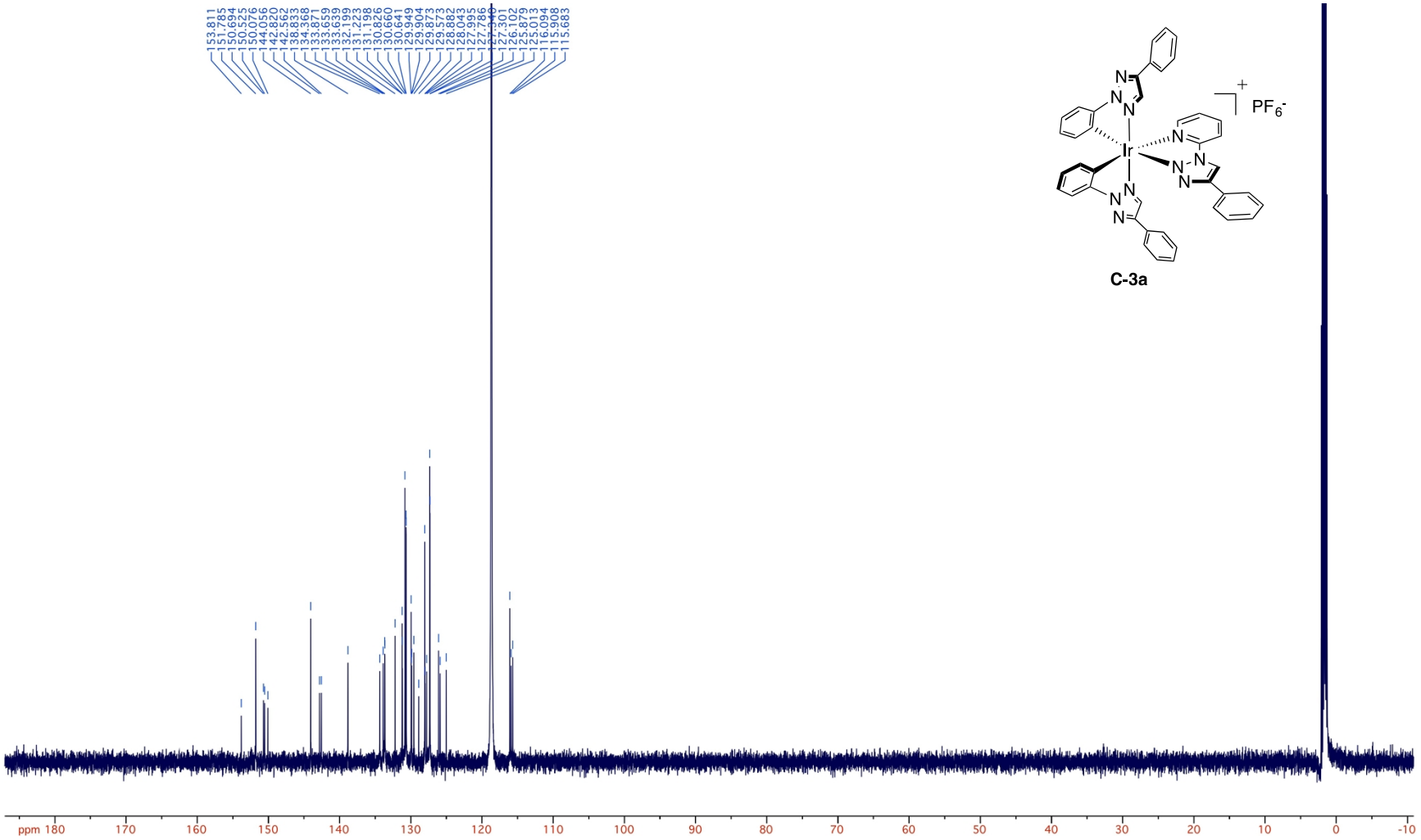

8.558
8.538
8.221
8.219
8.209
8.207
8.191
8.188
8.172
8.168
7.786
7.778
7.774
7.761
7.757
7.750
7.730
7.709
7.639
7.589
7.575
7.573
7.557
7.027
7.019
7.015
6.997
6.990
6.771
6.764
6.749
6.742
5.891
5.884
3.818
3.624
OMe
MeO
MeO
Ir
N
PF6-
C-1g
OMe
3.96
2.03
2.09
2.07
2
3.94
1.93
3.91
1.92
5.99
5.74
ppm 10
9
8
7
6
5
4
3
2
1
0


161.838
160.547
157.527
152.958
149.649
141.003
136.337
132.701
130.961
129.386
128.412
125.539
122.115
118.958
116.508
115.591
109.368
56.190
55.935
OMe
MeO
MeO
Ir
N
PF6-
C-1g
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


C-2
PF6-
1.08
1.07
3.24
1.01
4.29
1.86
1
2.33
2.13
3.22
4.18
2.08

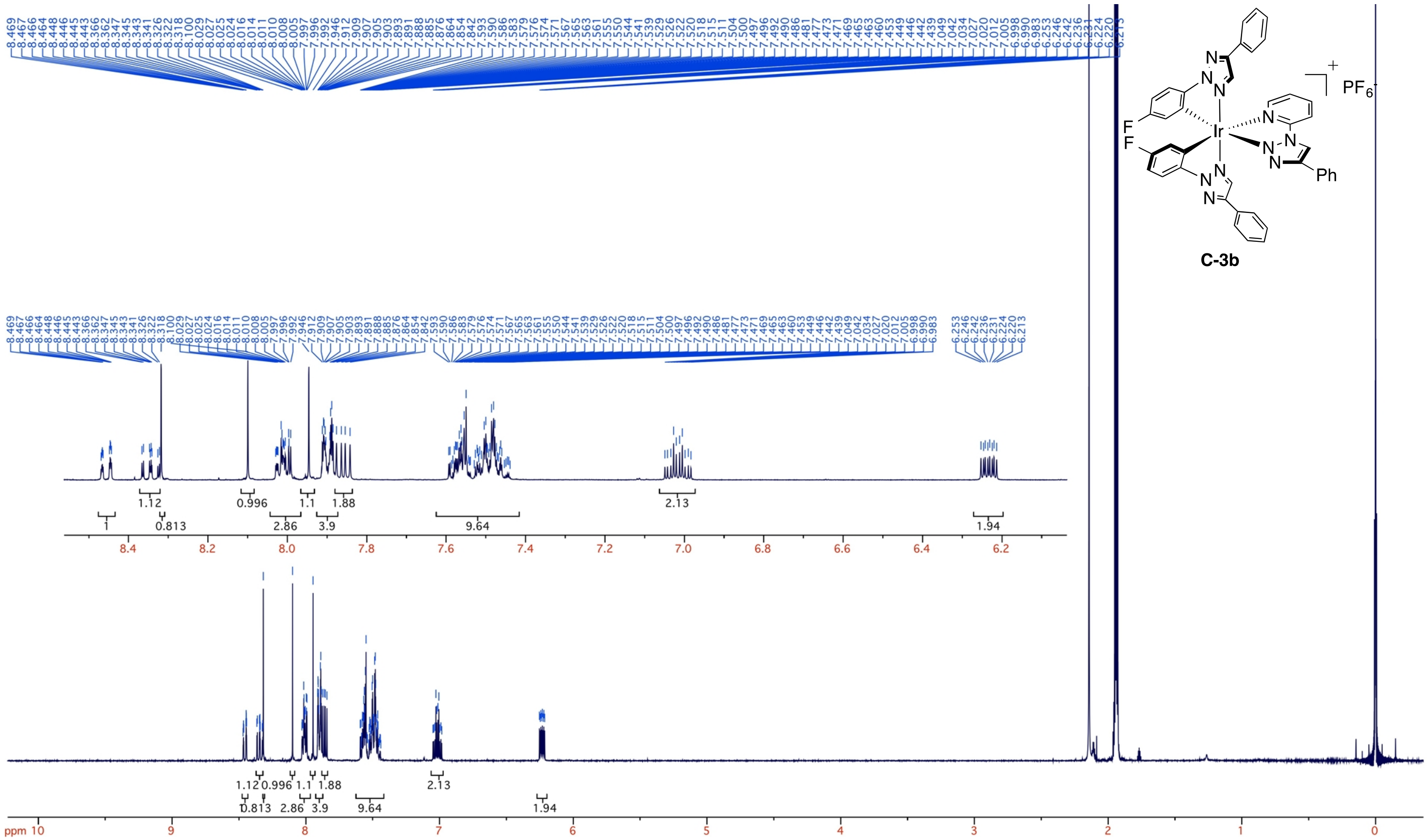

168.485
167.945
153.686
150.901
150.833
150.176
149.389
148.191
145.522
145.209
145.186
143.126
141.051
139.984
136.930
132.939
132.376
131.805
131.468
131.035
130.416
128.562
127.661
127.608
126.000
125.740
124.778
124.671
124.123
123.916
121.010
120.970
115.867
PF6-
C-2
ppm 180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


C-3a
PF6-
1.17
1.11
4.06
9.73
2.1
1
1
3.99
2.04
2.08
1.88

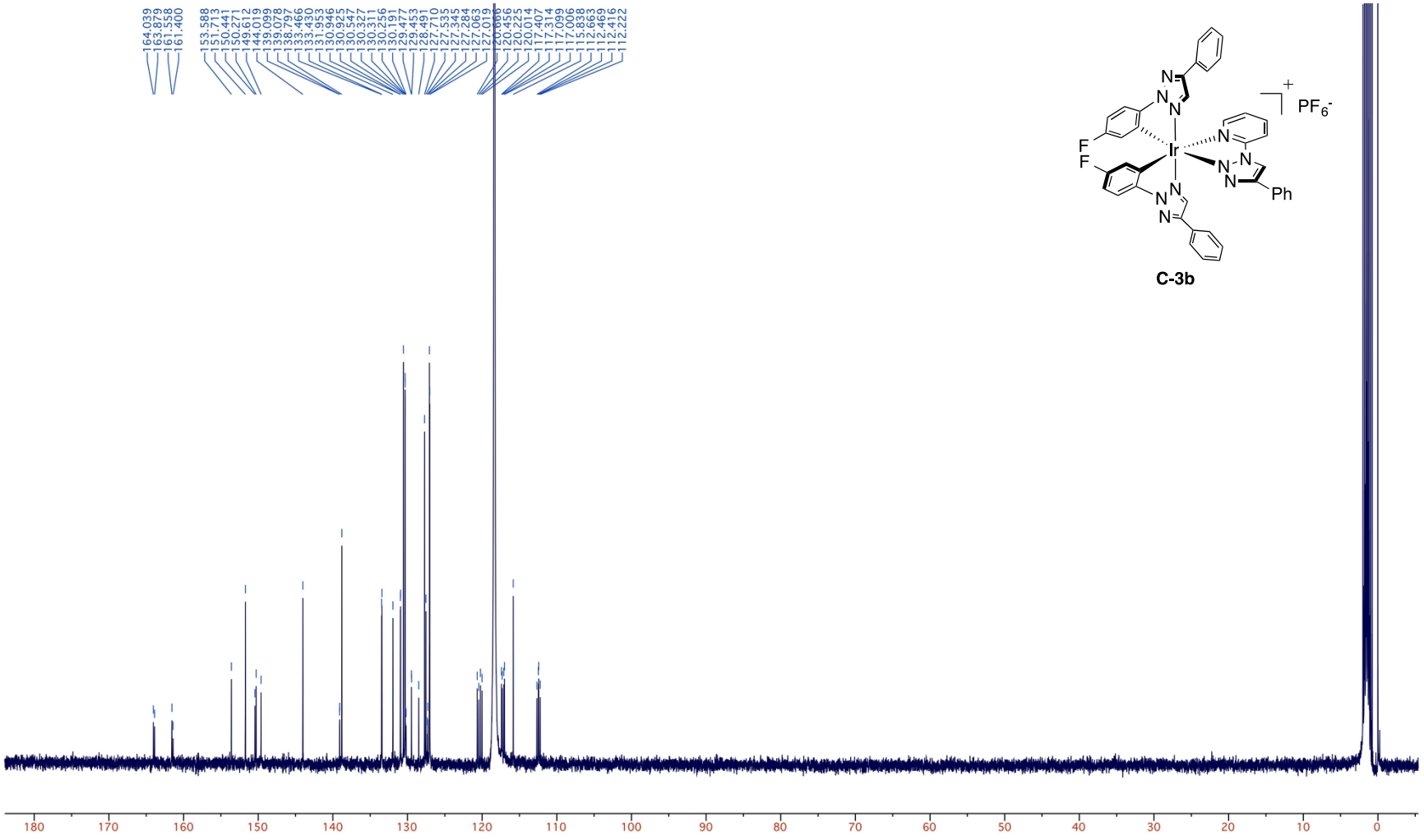

153.811
151.785
150.694
150.525
150.076
144.056
142.820
142.562
138.833
134.368
133.871
133.659
133.639
132.199
131.223
131.198
130.826
130.660
130.641
129.949
129.904
129.873
128.882
128.043
127.995
127.786
127.340
127.301
126.102
125.879
125.013
116.904
116.608
115.683
ppm 180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Ir
N
PF6-

C-3a

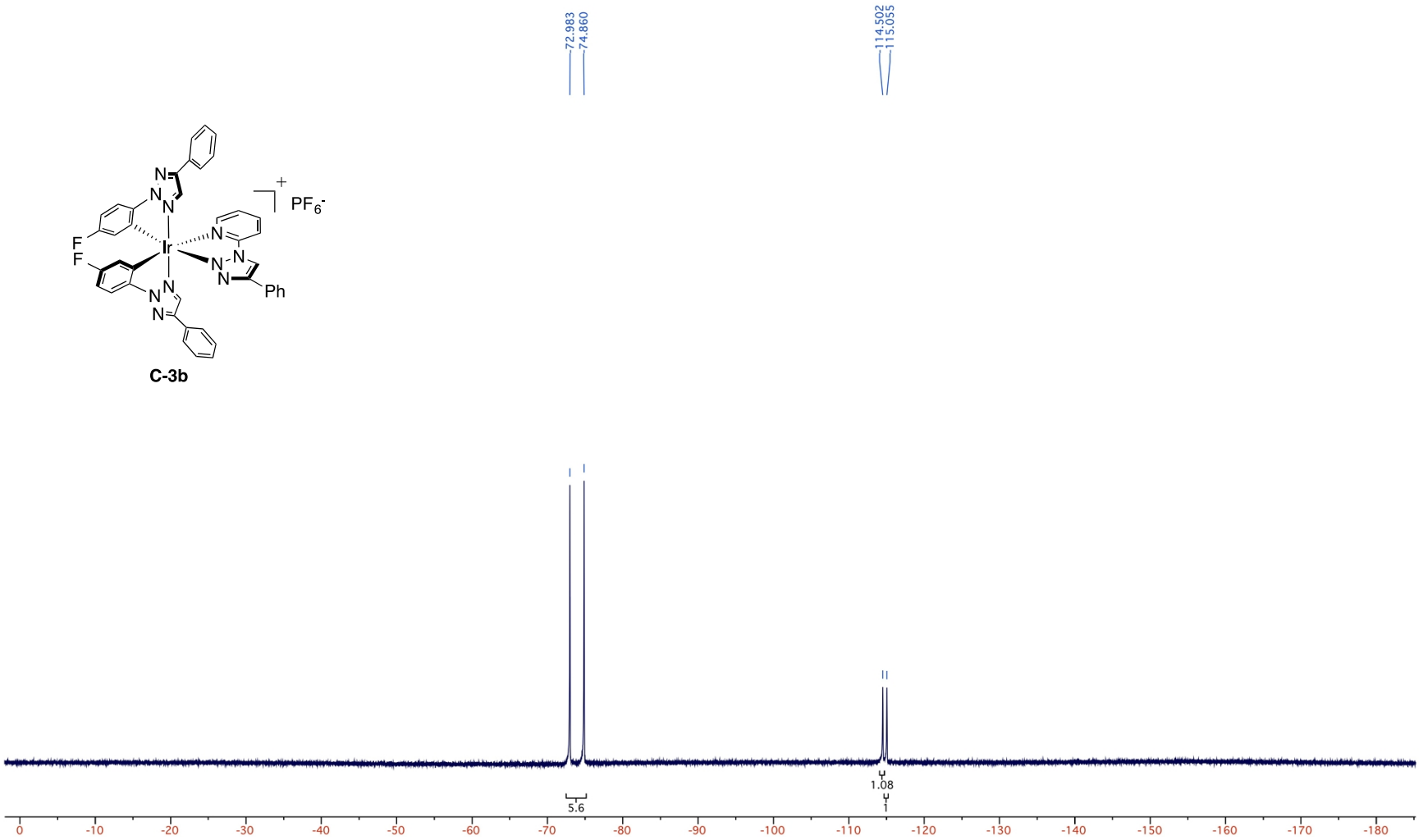


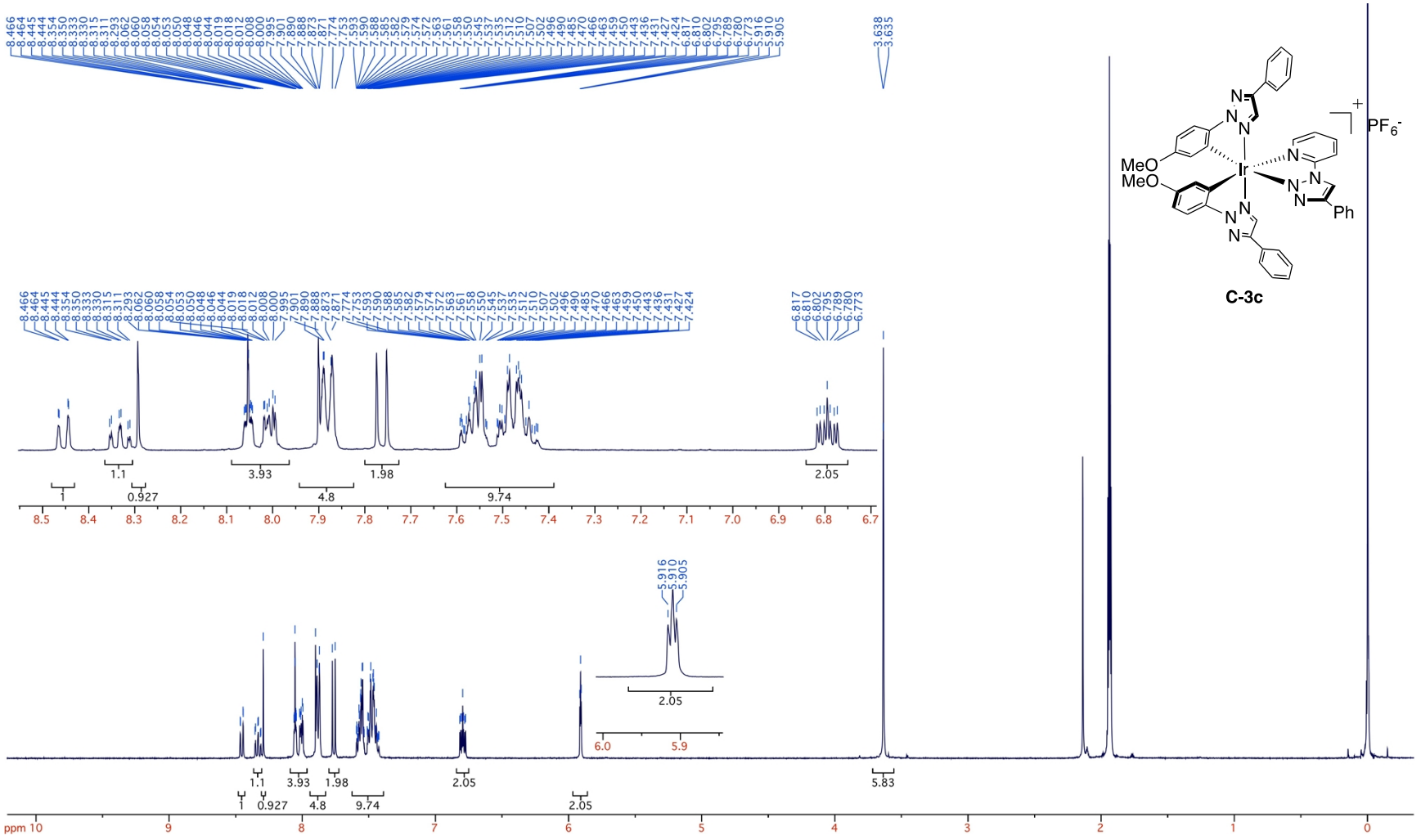
C-3b

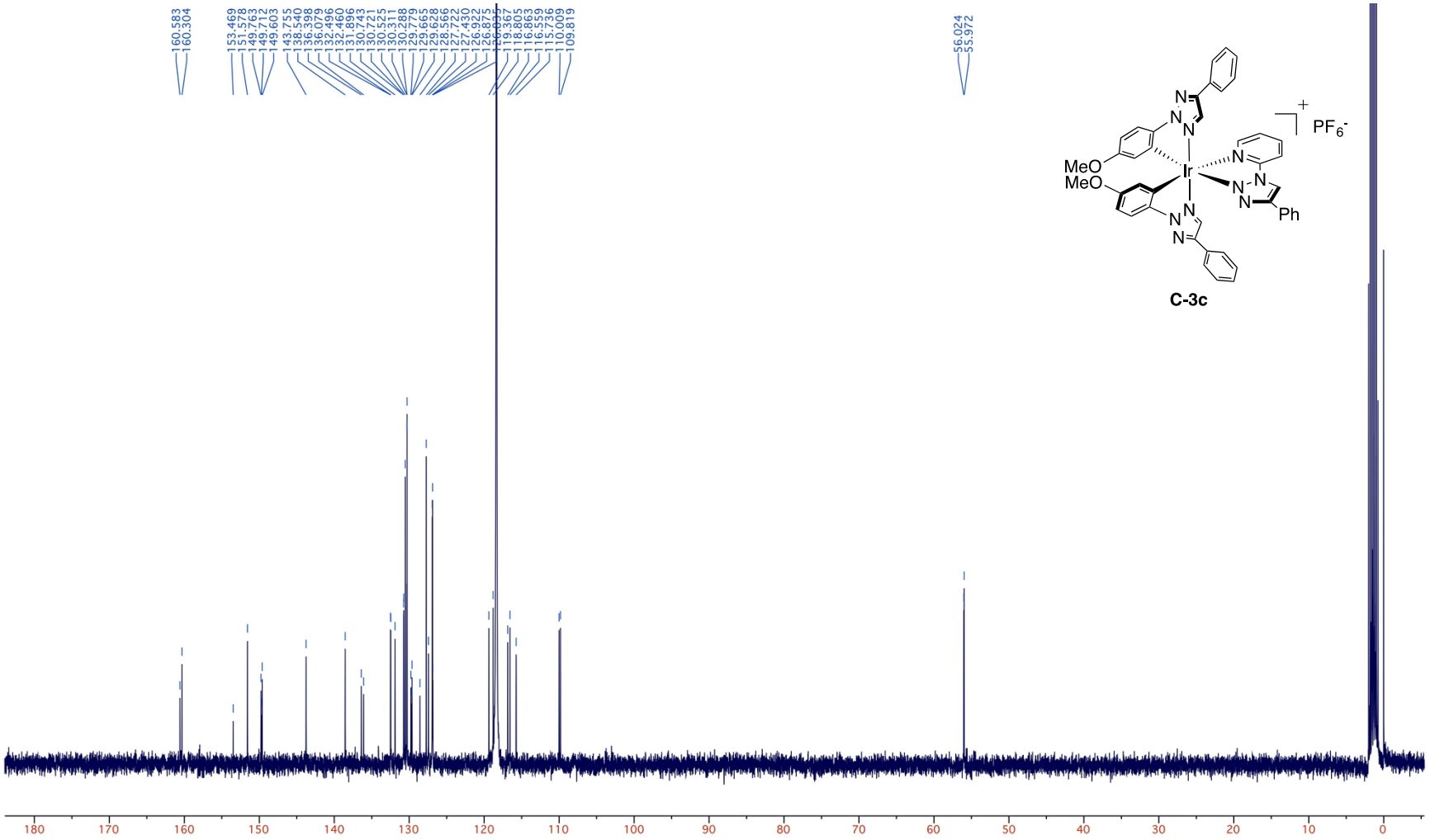

164.039
163.879
161.558
161.400
153.588
151.713
150.441
150.271
149.612
144.019
139.099
139.078
138.797
133.466
133.430
131.953
130.946
130.925
130.547
130.327
130.311
130.256
130.191
129.477
129.453
128.491
127.710
127.535
127.345
127.284
127.263
127.019
120.666
120.456
120.225
120.014
117.407
117.314
117.099
117.006
115.683
112.469
112.416
112.222
F
F
Ir
N
Ph
PF6-
C-3b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

N
N
N
F
F
Ir
N
N
N
N
N
Ph
+
PF6-

C-3b


72.983
74.860
114.502
115.055
5.6
1.08
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180


MeO
MeO
Ir
Ph
PF6-
C-3c


160.583
160.304
153.469
151.578
149.763
149.712
149.603
143.755
138.540
136.398
136.079
132.496
132.460
131.896
130.743
130.721
130.525
130.311
130.288
129.779
129.665
129.628
129.566
127.732
127.432
126.922
126.875
126.032
119.367
118.805
116.863
116.559
115.736
110.009
109.819
56.024
55.972
MeO
MeO
Ir
N
N
N
N
N
N
N
N
Ph
PF6-
C-3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0