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Supporting Information

Palladium-Catalyzed C—H Bond Arylation of Cyclometalated Difluorinated 2-Arylisoquinolinyl Iridium(III) Complexes

Marie Peng, Jinqiang Lin, Wei Lu,* Thierry Roisnel, Véronique Guerchais,* Henri Doucet,* and Jean-François Soulé*

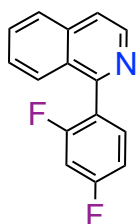
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1) General Information

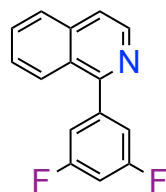
All reactions were carried out under argon atmosphere with standard Schlenk technique. DMA and 2-ethoxyethanol were purchased from Acros Organics and were not purified before use. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV III 400 MHz NMR spectrometer equipped with BBFO probehead. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ^1H ; 77.23 ppm for ^{13}C), constants were reported in Hertz. ^1H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All reagents were weighed and handled in air. HRMS were recorded on a Bruker Ultraflex III mass spectrometer at the corresponding facilities of the Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes 1 (CRMPO). Elemental Analysis were recorded on a Thermo Fisher FLASH 1112 at the corresponding facilities of the CRMPO. UV-Vis spectra were recorded on a HITACHI U-3900 spectrophotometer. The steady-state emission spectra and lifetime studies were measured with Edinburgh FL 900 photon-counting system. Both wavelength-dependent excitation and emission responses of the fluorimeter were calibrated. Spectral grade solvents (Merck) were used as received. To determine the photoluminescence quantum yield in solution, samples were degassed using at least three freeze-pump-thaw cycles. The solution quantum yields are calculated using the standard sample which has a known quantum yield. Cyclic voltammetry was conducted on a CHI621A Electrochemical Analyzer. Ag/Ag^+ (0.01 M AgNO_3) electrode was employed as reference electrode. The oxidation and reduction potentials were measured using a platinum working electrode with 0.1 M of NBu_4PF_6 in CH_2Cl_2 and a gold wire with 0.1 M of NBu_4PF_6 in THF, respectively. The potentials were referenced externally to the ferrocenium/ferrocene (Fc^+/Fc) couple.

2) Procedures and characterization data of iridium complexes

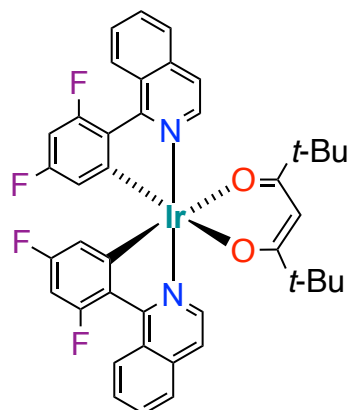


1-(2,4-Difluorophenyl)isoquinoline (1): To a 150 mL oven dried Schlenk tube, 2-chloroisoquinoline (1 g, 6.11 mmol, 1 equiv.) and (2,4-difluorophenyl)boronic acid (1.204 g, 7.64 mmol, 1.25 equiv.), K_2CO_3 (1.69 g, 12.22 mmol, 2 equiv.), toluene (16 mL), MeOH (2 mL) water (2 mL) and $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$ (0.073 g, 0.12 mmol, 2 mol%) were successively added. The atmosphere was replaced with argon via vacuum-argon cycles (5 times) and stirred at 110 °C (oil bath temperature) for 16 hours. After cooling the reaction at room temperature and concentration, the crude mixture was purified by flash chromatography on silica gel (heptane-EtOAc | 80:20) to afford the desired compound **1** as a yellow solid (1.240 g, 84%). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.66 (d, 1H, $J = 5.8$ Hz), 7.94 (d, 1H, $J = 8.2$ Hz), 7.81 (dd, 1H, $J = 2.6$, 5.8 Hz), 7.77-7.73 (m, 2H), 7.62-7.57 (m, 2H), 7.10 (td, 1H, $J = 2.4$, 6.3 Hz), 7.02 (td, 1H, $J = 2.4$, 6.9 Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) δ (ppm): -109.5 (d, $J = 8.2$ Hz), -108.8 (d, $J = 8.2$ Hz). ^{13}C NMR (400 MHz, CDCl_3) δ (ppm): 163.4 (dd, $J = 11.6$, 250.3 Hz), 160.2 (dd, $J = 12.1$, 250.8

Hz), 155.09, 142.3, 136.4, 132.9 (dd, $J = 9.7, 5.1$ Hz), 130.3, 127.5, 127.4, 127.0, 126.9, 123.6 (dd, $J = 16.1, 3.9$ Hz), 120.8, 111.8 (dd, $J = 21.3, 3.7$ Hz), 104.2 (t, $J = 25.7$ Hz). The NMR data were consistent with those reported in the literature.^[S1]

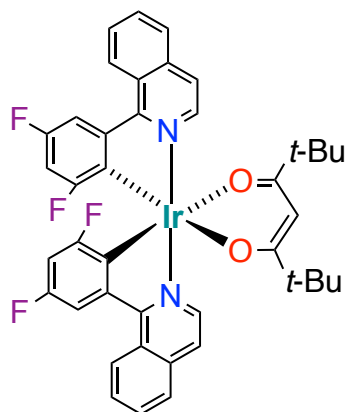


1-(3,5-Difluorophenyl)isoquinoline (2): To a 150 mL oven dried Schlenk tube, 2-chloroisoquinoline (1 g, 6.11 mmol, 1 equiv.) and (3,5-difluorophenyl)boronic acid (1.204 g, 7.64 mmol, 1.25 equiv.), K_2CO_3 (1.69 g, 12.22 mmol, 2 equiv.), toluene (16 mL), MeOH (2 mL) water (2 mL) and $PdCl(C_3H_5)(dppb)$ (0.073 g, 0.12 mmol, 2 mol%) were successively added. The atmosphere was replaced with argon via vacuum-argon cycles (5 times) and stirred at 110 °C (oil bath temperature) for 16 hours. After cooling the reaction at room temperature and concentration, the crude mixture was purified by flash chromatography on silica gel (heptane-EtOAc | 80:20) to afford the desired compound **2** as a yellow solid (0.737 g, 50%). 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (d, 1H, $J = 5.7$ Hz), 8.09 (d, 1H, $J = 8.5$ Hz), 7.94 (d, 1H, $J = 8.3$ Hz), 7.78-7.72 (m, 2H), 7.62 (td, 1H, $J = 7.2$ Hz), 7.29-7.26 (m, 2H), 6.98 (td, 1H, $J = 2.3, 8.9$ Hz). $^{19}F\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ (ppm): -109.5 (s). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 162.9 (dd, $J = 12.7, 249.3$ Hz), 158.0 (t, $J = 2.6$ Hz), 142.7 (t, $J = 9.3$ Hz), 142.1, 136.9, 130.3, 127.8, 127.2, 126.7, 126.3, 120.8, 113.0, 104.3 (t, $J = 25.2$ Hz). The NMR data were consistent with those reported in the literature.^[S2]



Bis[3,5-difluoro-2-(1-isoquinolinyl- κN)phenyl- κC](2,2,6,6-tetramethyl-3,5-heptanedionato- $\kappa O^3, \kappa O^5$)-iridium (III) (3): $IrCl_3 \cdot 6H_2O$ (0.150 g, 0.5 mmol, 1.0 equiv.) and 1-(2,4-difluorophenyl)isoquinoline (**1**) (0.422 g, 1.75 mmol, 3.5 equiv.) were suspended in a mixture of 2-ethoxyethanol/water (20 mL, 3/1). The mixture was heated and kept at 125 °C under stirring. After 24 hours, it was allowed to cool to room temperature. Then water was added (15 mL) and the product was filtered and washed with pentane to give the intermediate $[Ir(C^{\wedge}N)_2Cl]_2$ dimer complex, which was directly engaged in the next step without further purification. In a 150 mL oven-dried Schlenk, the crude mixture of $[Ir(C^{\wedge}N)_2Cl]_2$ (1.0 equiv.), 2,2,6,6-tetramethylheptane-3,5-dione (0.276 g, 1.5 mmol, 3 equiv.) and K_2CO_3 (0.483 g, 3.5 mmol, 7 equiv.) were mixed with 2-ethoxyethanol. The resulting solution was stirred at 125 °C for 3 hours. After cooling to room temperature, the crude product was filtered through celite® and the organic solution was concentrated under reduced pressure. The crude mixture was purified by silica column chromatography to afford the desired cyclometalated complex **3** (320 mg, 75%) as a red powder. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.44 (t, 2H, $J = 8.9$ Hz), 8.21 (d, 2H, $J = 6.3$ Hz), 7.87 (d, 2H, $J = 8.0$ Hz), 7.68-7.57 (m, 4H), 7.51 (d, 2H, $J = 6.3$ Hz), 6.49-6.38 (m, 2H), 5.96-5.88 (m, 2H), 5.43 (s, 1H), 0.79 (s, 18H). $^{19}F\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ (ppm): -96.56 (d, $J = 10.6$ Hz), -108.83 (d, $J = 10.6$ Hz).

^{13}C NMR (500 MHz, CD_2Cl_2) δ (ppm): 194.4, 167.2 (d, $J = 5.2$ Hz), 163.3 (dd, $J = 12.4$, 256.2 Hz), 159.8 (dd, $J = 13.0$, 259.8 Hz), 155.6 (d, $J = 7.0$ Hz), 140, 137.0, 131.1, 129.0, 128.8, 126.7 (d, $J = 2.6$ Hz), 126.2, 126.0, 120.5, 116.0 (dd, $J = 2.5$, 16.4 Hz), 96.8 (t, $J = 25.7$ Hz), 90.1, 41.0, 29.7, 27.7, 27.1, 14.9. The NMR data were consistent with those reported in the literature.^[53]

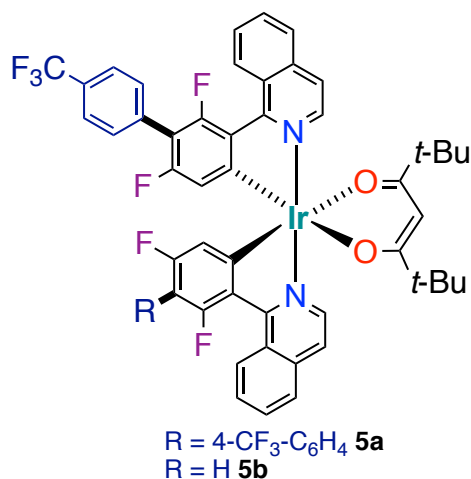


Bis[4,6-difluoro-2-(1-isoquinolinyl- κN)phenyl- κC](2,2,6,6-tetramethyl-3,5-heptanedionato- $\kappa\text{O}^3,\kappa\text{O}^5$)-iridium (III) (4):

$\text{IrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.150 g, 0.5 mmol, 1.0 equiv.) and 1-(3,5-difluorophenyl)isoquinoline (2) (0.422 g, 1.75 mmol, 3.5 equiv.) were suspended in a mixture of 2-ethoxyethanol/water (20 mL, 3/1). The mixture was heated and kept at 125 °C under stirring. After 24 hours, it was allowed to cool to room temperature. Then water was added (15 mL) and the product was filtered and washed with pentane to give the intermediate $[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{Cl}]_2$ dimer complex, which was directly engaged in the

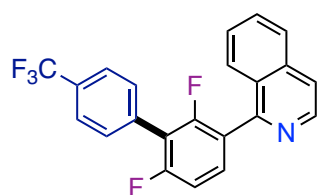
next sept without further purification. In a 150 mL oven-dried Schlenk, the crude mixture of $[\text{Ir}(\text{C}^{\wedge}\text{N})_2\text{Cl}]_2$ (1.0 equiv.), 2,2,6,6-tetramethylheptane-3,5-dione (0.276 g, 1.5 mmol, 3 equiv.) and K_2CO_3 (0.483 g, 3.5 mmol, 7 equiv.) were mixed with 2-ethoxyethanol. The resulting solution was stirred at 125 °C for 3 hours. After cooling to room temperature, the crude product was filtered through celite® and the organic solution was concentrated under reduced pressure. The crude mixture was purified by silica column chromatography to afford the desired cyclometalated complex **4** (171 mg, 40%) as a red powder. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.92-8.89 (m, 2H), 8.27 (d, 2H, $J = 6.4$ Hz), 7.94-7.86 (m, 4H), 7.74-7.69 (m, 4H), 7.41-7.36 (m, 2H), 6.30-6.24 (m, 2H), 5.41 (s, 1H), 0.76 (s, 18H). $^{19}\text{F}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) δ (ppm): -101.25 (d, $J = 5.2$ Hz), -121.77 (d, $J = 5.3$ Hz). ^{13}C NMR (500 MHz, CD_2Cl_2) δ (ppm): 195.4, 169.7 (dd, $J = 11.8$, 236.3 Hz), 168.0 (d, $J = 3.1$ Hz), 159.3 (dd, $J = 12.0$, 235.3 Hz), 151.0 (dd, $J = 8.9$, 17.6 Hz), 141.5, 137.6, 133.2, 132.1 (d, $J = 6.7$ Hz), 131.3, 125.9 (dd, $J = 2.5$, 39.1 Hz), 120.2, 112.6 (dd, $J = 3.6$, 22.7 Hz), 103.8 (dd, $J = 24.4$, 31.9 Hz), 90.8, 41.6, 30.3, 28.2. ESI-HRMS for $\text{C}_{41}\text{H}_{35}\text{N}_2\text{O}_2\text{F}_4^{193}\text{Ir} [\text{M}]^+$: found 856.2255, calcd 856.2258.

Procedure for C–H bond arylation on the iridium complex: To a 15 mL oven dried Schlenk tube, the Ir(III) complex (43 mg, 0.05 mmol, 1 equiv.), aryl bromide (0.2 mmol, 4 equiv.), $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.65 mg, 0.0025 mmol, 5 mol%), dppb (1.07 mg, 0.0025 mmol, 5 mol%) and KOiPr (28 mg, 0.20 mmol, 4 equiv.) and DMA (4 mL) were successively added. The atmosphere was replaced with argon via vacuum-argon cycles (5 times) and stirred at 125 °C for 16 hours. After cooling the reaction to room temperature, the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography to afford the desired arylated cyclometalated complexes.

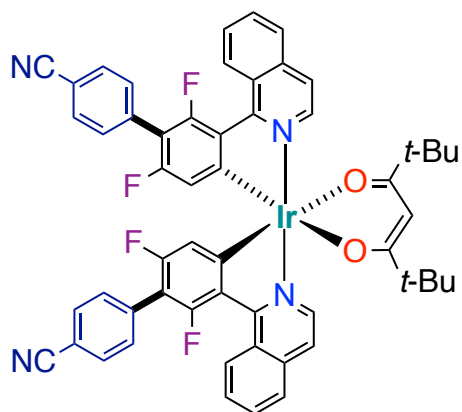


Bis[4-(4-benzotrifluoride)-3,5-difluoro-2-(1-isoquinolinyl- κ N)phenyl- κ C](2,2,6,6-tetramethyl-3,5-heptanedionato- κ O³, κ O⁵)-iridium (III) (5a**):** Following the general procedure using **1** (43 mg, 0.05 mmol, 1 equiv.), 4-bromobenzotrifluoride (45 mg, 0.2 mmol, 4 equiv.) the residue was purified by silica column chromatography (heptane/CH₂Cl₂ | 75-25) to afford the desired compound **5a** as a red powder (51 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.38 (t, 2H, J = 9.6 Hz), 8.25 (d, 2H, J = 6.3 Hz), 7.89 (d, 2H, J = 8.2 Hz), 7.72 (t, 2H, J = 7.3 Hz), 7.67-7.55 (m, 12H), 6.11 (d, 2H, J = 9.5 Hz), 5.47 (s, 1H), 1.61 (s, 18H). ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ (ppm): -62.57, -102.14 (d, J = 10.1 Hz), -112.72 (d, J = 10.4 Hz). ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 201.5, 195.0, 167.4 (d, J = 5.1 Hz), 159.9 (dd, J = 6.7, 258.2 Hz), 156.3 (dd, J = 7.5, 251.3 Hz), 148.5, 140.2, 139.9, 137.2, 137.0, 137.7, 134.0, 132.0, 131.0, 130.9, 130.7, 130.3 (dd, J = 2.3, 6.9 Hz), 129.8, 129.5, 129.1, 129.0, 128.9, 128.3, 127.5, 126.8, 126.7, 126.2, 126.1, 125.6, 125.1 (d, J = 3.7 Hz), 125.0, 124.9, 124.8, 122.9, 122.0, 120.7, 116.6 (dd, J = 2.0, 18.1 Hz), 109.7 (t, J = 20.4 Hz), 90.8, 89.9, 41.2, 39.4, 31.9, 30.9, 29.0, 28.3, 28.0, 27.5, 27.1, 26.2, 25.6, 22.7, 14.1. ESI-HRMS for C₅₅H₄₁N₂O₂F₁₀¹⁹³Ir [M]⁺: found 1144.2627, calcd 1144.2632.

[3,5-difluoro-2-(1-isoquinolinyl- κ N)phenyl- κ C][4-(4-benzotrifluoride)-3,5-difluoro-2-(1-isoquinolinyl- κ N)phenyl- κ C](2,2,6,6-tetramethyl-3,5-heptanedionato- κ O³, κ O⁵)-iridium (III) (5b**)** was isolated as a side product. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.43 (dt, 2H, J = 32.7, 9.2 Hz), 8.30-8.19 (m, 2H), 7.95-7.87 (m, 2H), 7.80-7.51 (m, 10H), 6.48 (m, 1H), 6.09-5.97 (m, 2H), 5.45 (s, 1H), 0.82 (s, 18H). ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ (ppm): -62.57, -96.41 (d, J = 11.3 Hz), -102.33 (d, J = 10.2 Hz), -108.72 (d, J = 10.3 Hz), -112.88 (d, J = 9.9 Hz).

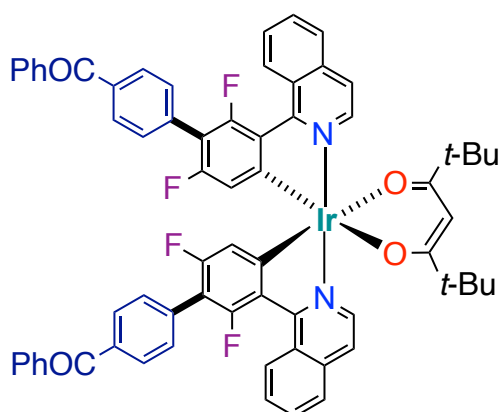


1-(2,6-Difluoro-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)isoquinoline (5c**):** Following the procedure using 1-(2,4-difluorophenyl)isoquinoline **1** (150 mg, 0.625 mmol, 1 equiv.) and 4-(trifluoromethyl)bromobenzene (129 μ L, 0.93 mmol, 1.5 equiv.), the residue was purified by silica column chromatography (Heptane/EtOAc 70:30) to afford the desired compound (157.7 mg, 66 %) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.64 (d, 1H, J = 5.7 Hz), 7.92 (d, 1H, J = 8.2 Hz), 7.86 (dd, 1H, J = 2.2, 8.4 Hz), 7.77-7.69 (m, 6H), 7.62-7.57 (m, 2H), 7.23 (td, 1H, J = 1.3, 8.7 Hz). ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ (ppm): -62.7, -113.1 (d, J = 7.7 Hz), -114.1 (d, J = 7.3 Hz). ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 160.2 (dd, J = 6.3, 251.4 Hz), 157.1 (dd, J = 6.8, 251.6 Hz), 155.0, 142.3, 136.4, 132.8, 132.0 (dd, J = 5.3, 10.2 Hz), 130.9, 130.4, 127.7, 127.6, 127.4, 127.1, 126.8 (d, J = 2.1 Hz), 125.3 (d, J = 3.8 Hz), 124.1 (dd, J = 3.9, 17.5 Hz), 122.7, 121.0, 117.4 (t, J = 18.9 Hz), 112.2 (dd, J = 3.8, 23.0 Hz).



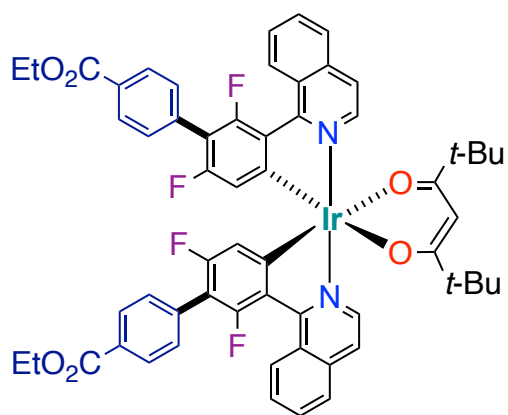
Bis[4-(4-benzonitrile)-3,5-difluoro-2-(1-isoquinolinyl- κ N)phenyl- κ C](2,2,6,6-tetramethyl-3,5-

heptanedionato- κ O³, κ O⁵)-iridium (III) (6): Following the general procedure using **1** (43 mg, 0.05 mmol, 1 equiv.), 4-bromobenzonitrile (36 mg, 0.2 mmol, 4 equiv.) the residue was purified by silica column chromatography (CH₂Cl₂ | 100) to afford the desired compound **6** as a red powder (47 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.39 (t, 2H, J = 9.5 Hz), 8.27 (d, 2H, J = 6.3 Hz), 7.93 (d, 2H, J = 8.1 Hz), 7.78-7.59 (m, 14H), 6.12 (dd, 2H, J = 9.5 Hz), 5.47 (s, 1H), 0.82 (s, 18H). ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ (ppm): -102.3 (d, J = 9.8 Hz), -112.7 (d, J = 9.8 Hz). ¹³C NMR (500 MHz, CD₂Cl₂) δ (ppm): 196.1, 167.6 (d, J = 5.0 Hz), 160.3 (dd, J = 6.4, 258.1 Hz), 156.6 (dd, J = 7.2, 261.7 Hz), 156.2 (d, J = 7.5 Hz), 144.1, 140.6, 137.8, 136.4, 134.1, 133.4, 133.2, 132.4, 131.9, 131.8, 131.1 (dd, J = 2.1, 6.7 Hz), 129.4, 129.2, 128.5, 127.5, 126.9, 126.7, 121.6, 119.4, 119.1, 117.2 (dd, J = 1.07, 17.9 Hz), 112.9, 111.9, 111.6, 109.9 (t, J = 19.7 Hz), 90.8, 41.7, 28.3, 27.7. ESI-HRMS for C₅₅H₄₁N₄O₂F₄¹⁹³Ir [M]⁺: found 1058.2791, calcd 1058.2789.



Bis[4-(4-benzophenone)-3,5-difluoro-2-(1-isoquinolinyl- κ N)phenyl- κ C](2,2,6,6-tetramethyl-3,5-heptanedionato- κ O³, κ O⁵)-iridium (III) (7):

Following the general procedure using **1** (43 mg, 0.05 mmol, 1 equiv.), 4-bromobenzophenone (52 mg, 0.2 mmol, 4 equiv.) the residue was purified by silica column chromatography (CH₂Cl₂ | 100) to afford the desired compound **7** as a red powder (33 mg, 55%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.42 (t, 2H, J = 9.4 Hz), 8.27 (d, 2H, J = 6.3 Hz), 7.99-7.79 (m, 10H), 7.73 (t, 2H, J = 7.4 Hz), 7.67-7.55 (m, 10H), 7.49 (m, 4H), 6.15 (d, 2H, J = 9.4 Hz), 5.46 (s, 1H), 0.96 (s, 18H). ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ (ppm): -101.82 (d, J = 10.2 Hz), -112.32 (d, J = 10.0 Hz). ¹³C NMR (500 MHz, CD₂Cl₂) δ (ppm): 195.9, 195.8, 195.11, 159.9 (dd, J = 6.5, 257.8 Hz), 156.3 (dd, J = 7.4, 260.9), 154.8 (d, J = 7.6 Hz), 143.7, 140.1, 137.7, 137.2, 136.4, 135.3, 132.4, 132.3, 131.3, 130.7, 130.4, 129.9, 129.7, 128.9 (d, J = 20.7 Hz), 128.3, 128.2, 127.1, 126.8, 126.3, 126.1, 120.9, 116.5 (dd, J = 4.8, 21.3 Hz), 110.1 (t, J = 20.4 Hz), 90.8, 90.2, 41.1, 29.7, 27.7, 27.1, 22.7, 13.9, 0.77. ESI-HRMS for C₆₇H₅₁N₂O₄F₄¹⁹³Ir [M]⁺: found 1216.3491, calcd 1216.3487.



Bis[4-(ethyl 4-benzoate)-3,5-difluoro-2-(1-isoquinolinyl- κ N)phenyl- κ C](2,2,6,6-tetramethyl-3,5-heptanedionato- κ O³, κ O⁵)-iridium (III) (8):

Following the general procedure using **1** (43 mg, 0.05 mmol, 1 equiv.), ethyl 4-bromobenzoate (45 mg, 0.2 mmol, 4 equiv.) the residue was purified by silica column chromatography (CH_2Cl_2 | 100) to afford the desired compound **8** as a red powder (25 mg, 44%). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.39 (t, 2H, $J = 9.5$ Hz), 8.25 (d, 2H $J = 6.3$ Hz), 8.16-8.08

(m, 4H), 7.88 (d, 2H, $J = 8.1$ Hz), 7.71 (t, 2H, $J = 7.5$ Hz), 7.67-7.53 (m, 8H), 6.11 (d, 2H, $J = 9.4$), 5.45 (s, 1H), 3.59 (q, $J = 7.0$ Hz, 4H), 1.25 – 1.21 (m, 6H), 0.81 (s, 18H). $^{19}\text{F}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) δ (ppm): -101.84 (d, $J = 9.7$ Hz), -112.34 (d, $J = 10.0$ Hz). ^{13}C NMR (500 MHz, CD_2Cl_2) δ (ppm): 195.7, 167.7 (d, $J = 5.0$ Hz), 166.8, 166.7, 160.5 (dd, $J = 6.6$, 257.6 Hz), 156.9 (dd, $J = 7.4$, 261.1 Hz), 155.4 (d, $J = 7.4$ Hz), 144.8, 140.7, 137.8, 136.2, 131.9, 131.1, 130.8, 130.6, 130.1, 129.7, 129.6, 129.4, 127.8, 127.4 (d, $J = 2.0$ Hz), 126.7, 121.4, 117.1 (dd, $J = 1.5$, 18.0 Hz), 110.74 (t, $J = 20.4$ Hz), 90.8, 61.6, 61.5, 41.7, 28.3, 27.7, 14.7. ESI-HRMS for $\text{C}_{59}\text{H}_{51}\text{N}_2\text{O}_6\text{F}_4^{193}\text{Ir} [\text{M}]^+$: found 1152.3303, calcd 1152.3307.

3) Photophysical data of the iridium complexes

a. Electrochemical properties

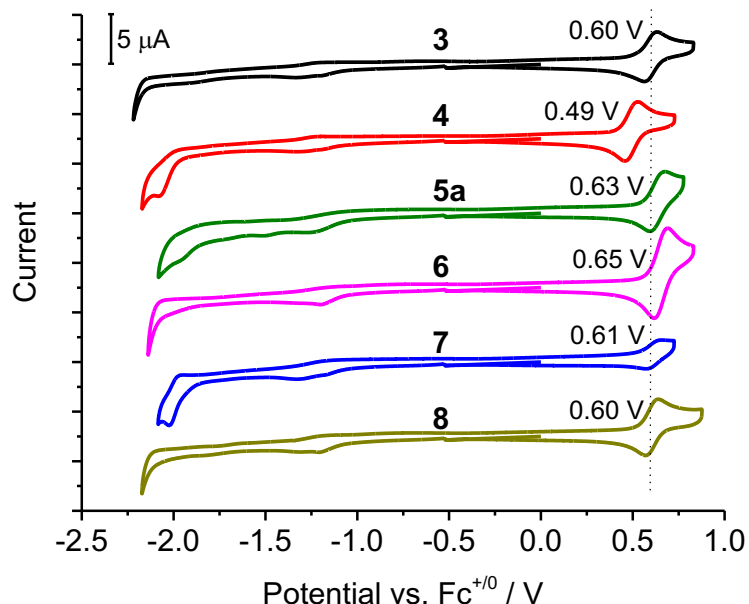


Figure S1. Cyclic voltammograms in deoxygenated CH_2Cl_2 solutions at 298 K.

b. Absorption and emission measurements.

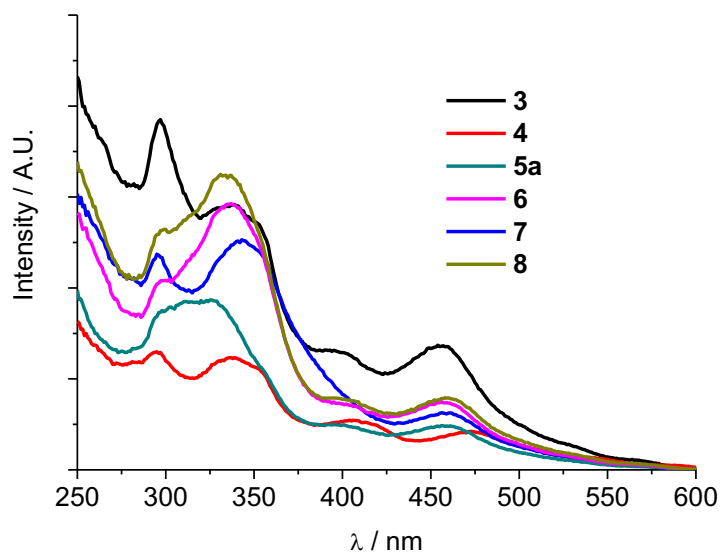


Figure S2. Excitation spectra in deoxygenated CH_2Cl_2 (concentration $\sim 1 \times 10^{-5}$ M) at 298 K.

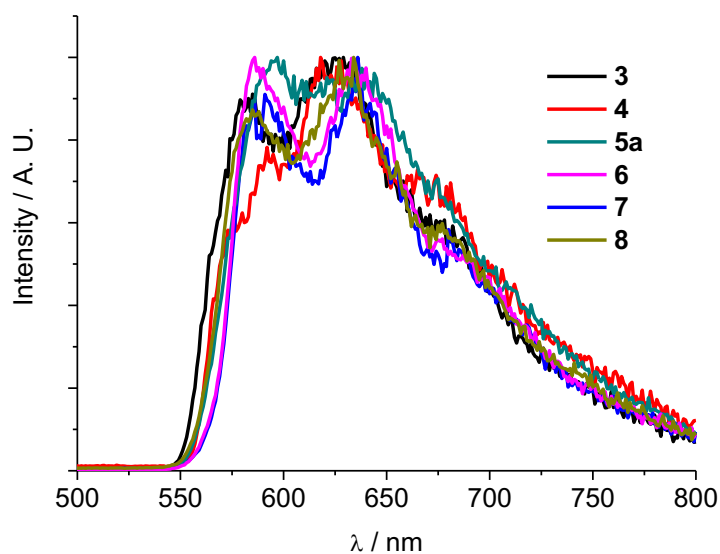


Figure S3. Normalized emission spectra in glassy 2-methyltetrahydrofuran solutions at 77 K (excited at 365 nm, concentration 1×10^{-5} M).

4) Crystallographic data collection and structure refinement

Single crystal X-ray structural analyses for **3**, **4**, **5a**, **7** and **8** were performed on a APEXII, Bruker-AXS diffractometer equipped with a CCD plate detector, Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator), T = 150 K; triclinic P -1 (I.T.#2), a = 9.9255(7), b = 12.1159(8), c

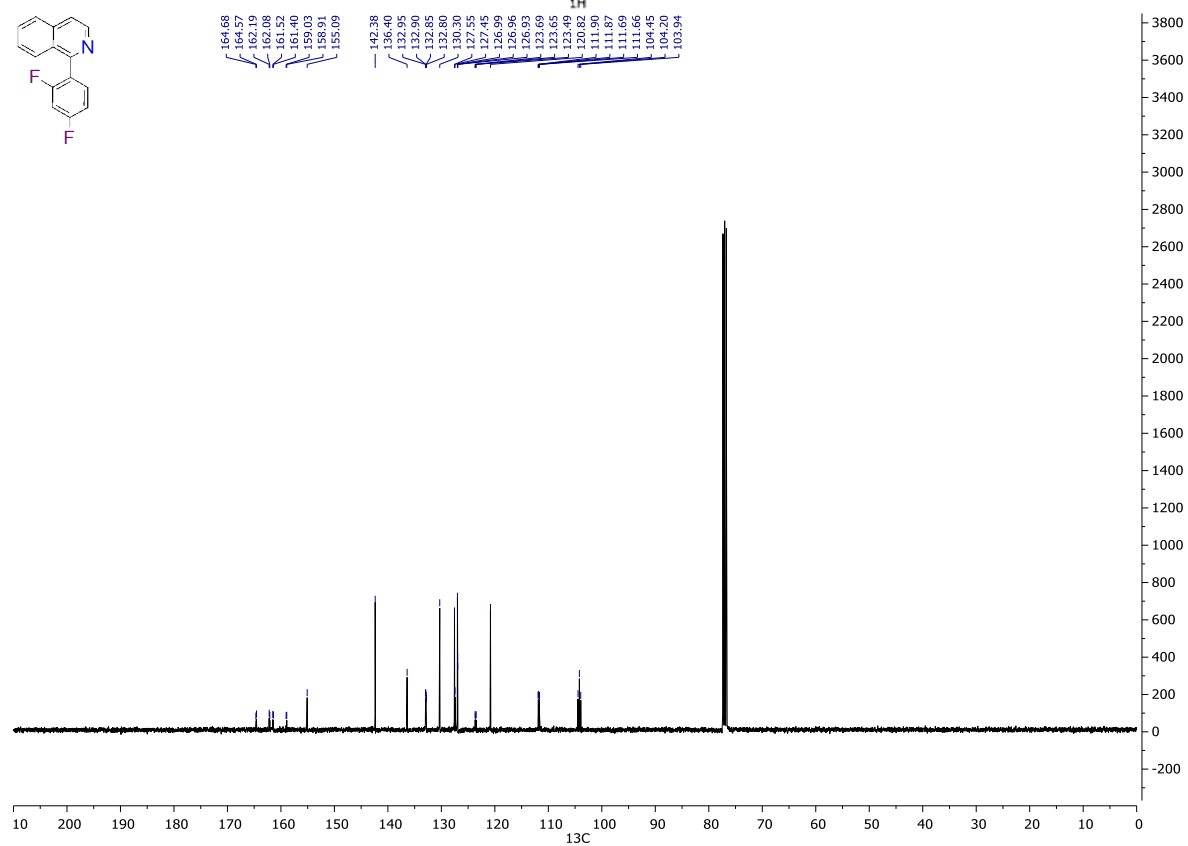
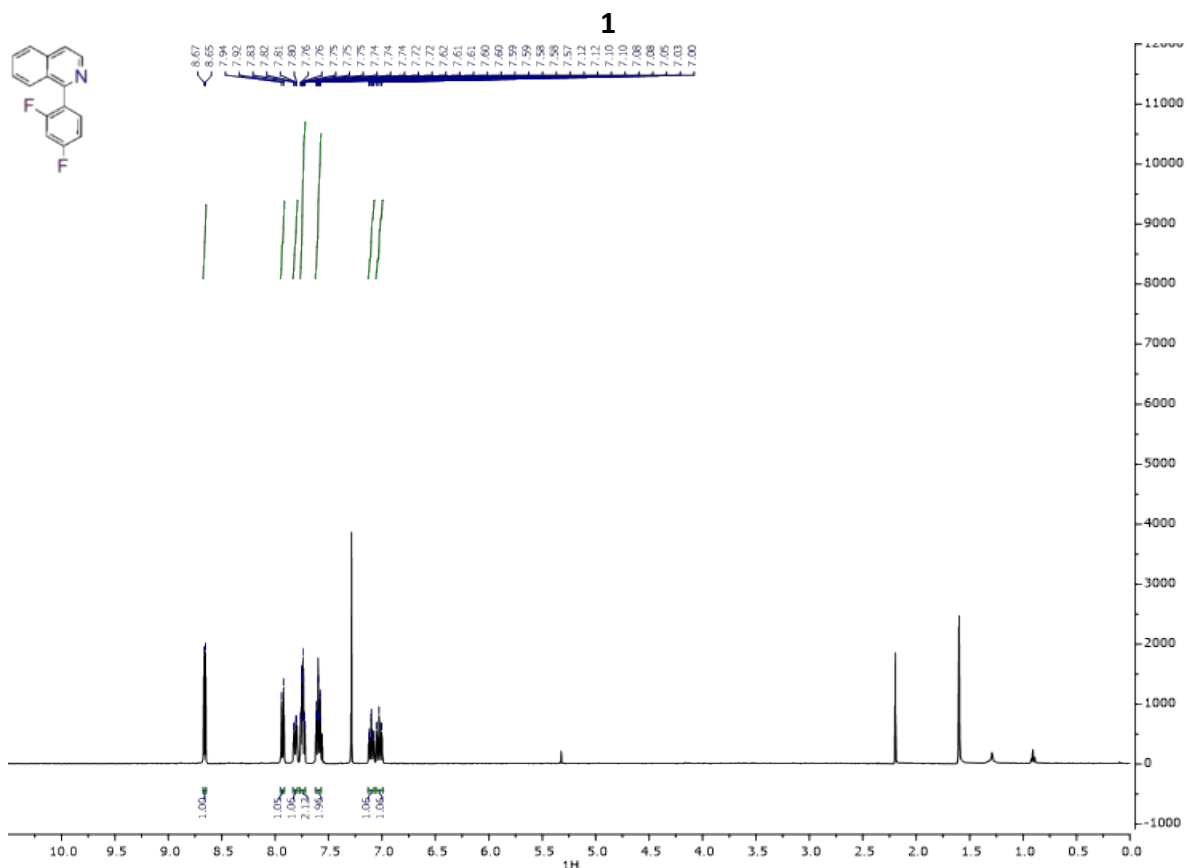
= 20.7316(11) Å, α = 100.693(2), β = 90.621(2), γ = 96.904(2) °, V = 2430.6(3) Å³. Z = 2, d = 1.563 g.cm⁻³, μ = 2.829 mm⁻¹. The structure was solved by dual-space algorithm using the SHELXT program,^[S4] and then refined with full-matrix least-squares methods based on F² (SHELXL).^[S5] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F² with 11082 unique intensities and 628 parameters converged at ω RF2 = 0.0740 (RF = 0.0273) for 10193 observed reflections with $I > 2\sigma(I)$. Details of the structures and their refinement may be obtained from the Cambridge Crystallographic Data Centre by referencing CCDC-2044887 for **3**, CCDC-2044890 for **4**, CCDC-2044888 for **5a**, CCDC-2044889 for **7**, CCDC-2044944 for **8**.

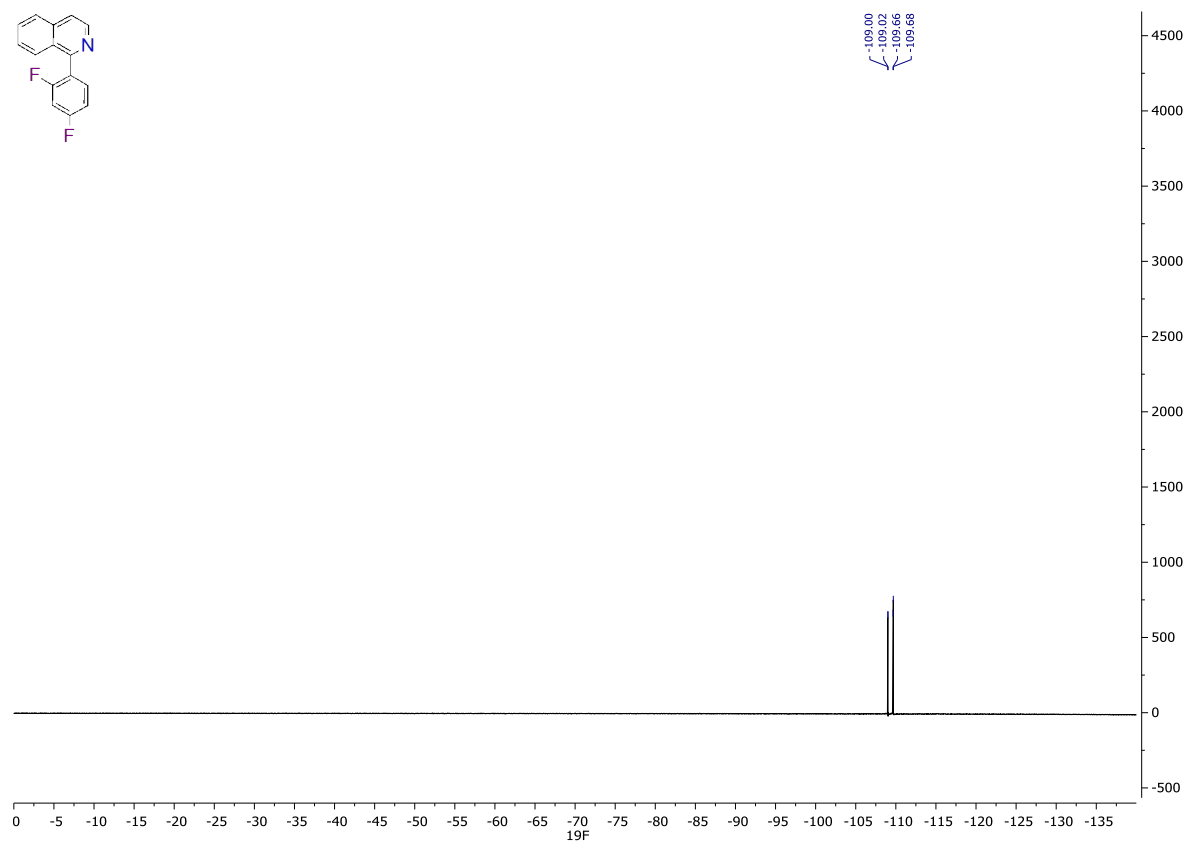
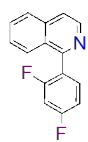
Table S1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **3**, **4**, **5a**, **7**, and **8** with Estimated Standard Deviations (es's) Given in Parentheses.

	Bond length (Å)			Bite angle (°)		Θ ^[a]	Shorter Ir – Ir distance in packing (Å)
	Ir–C	Ir–N	Ir–O	$C_{C^N}-Ir-N_{C^N}$	O–Ir–O		
3	1.987(7)	2.036(6)	2.121(5)	80.5(3)	87.89(17)	–	9.726
	1.987(7)	2.038(5)	2.125(4)	80.0(2)			
4	1.988(10)	2.029(8)	2.095(6)	79.5(3)	89.7(3)	–	9.587
	2.007(9)	2.041(8)	2.117(7)	79.8(4)			
5a	1.982(3)	2.035(3)	2.112(2)	80.33(12)	87.80(9)	52.10(5)	10.088
	1.990(3)	2.039(3)	2.131(2)	80.31(12)		43.00(6)	
7	1.982(6)	2.038(6)	2.127(4)	80.1(2)	86.63(17)	41.6(11)	13.524
	2.000(6)	2.036(6)	2.145(5)	80.7(3)		48.1(10)	
8	1.984(8)	2.036(6)	2.128(6)	80.1(3)	86.9(3)	43.4(13)	13.237
	1.984(8)	2.036(6)	2.128(6)	80.1(3)		43.4(13)	

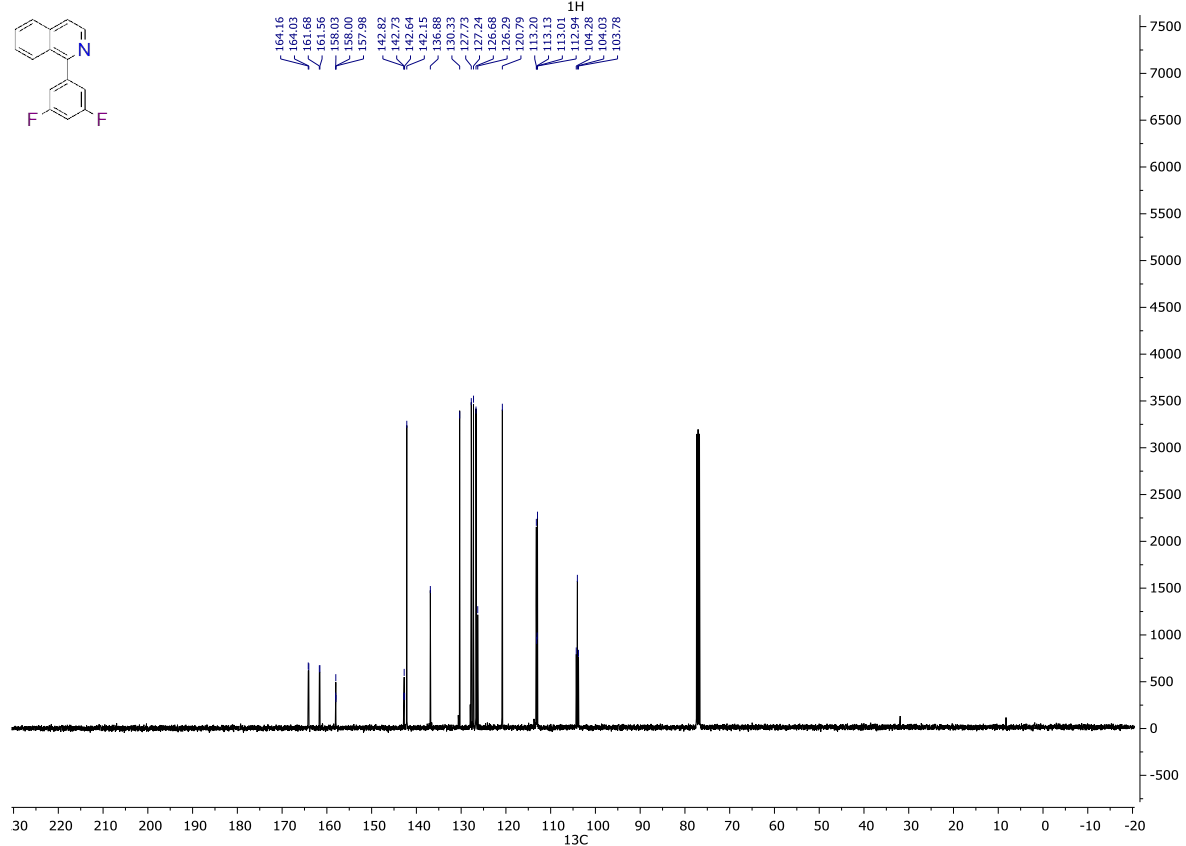
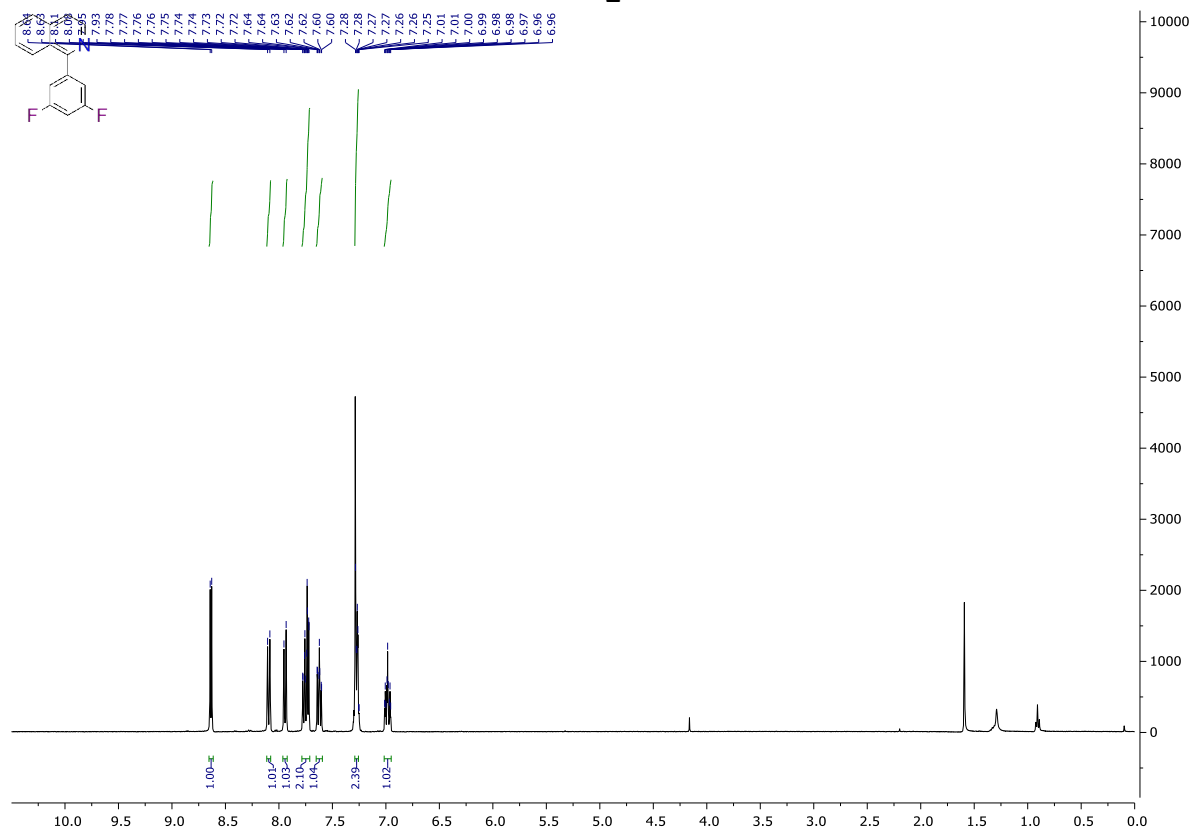
^[a] The dihedral angle between the pendant aryl ring and fluorinated ring in C^N ligands.

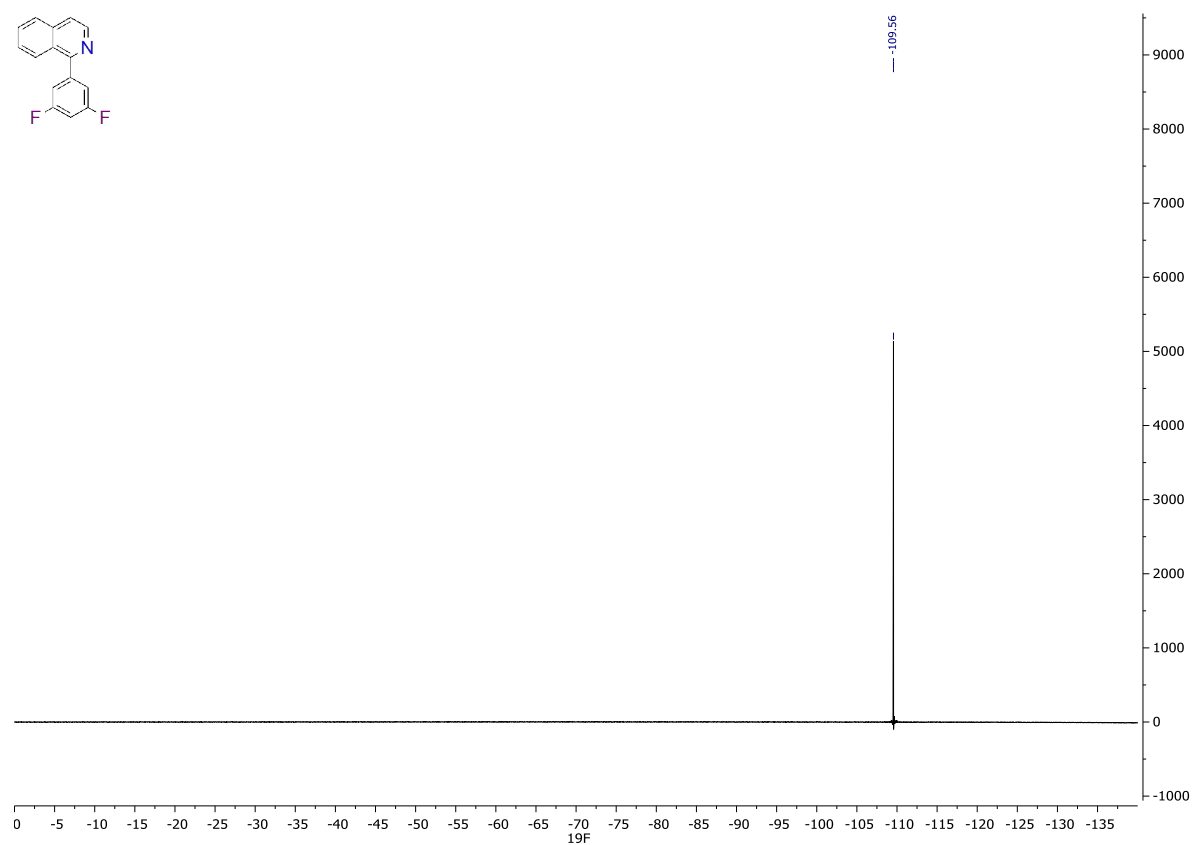
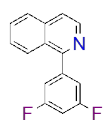
5) [NMR charts](#)



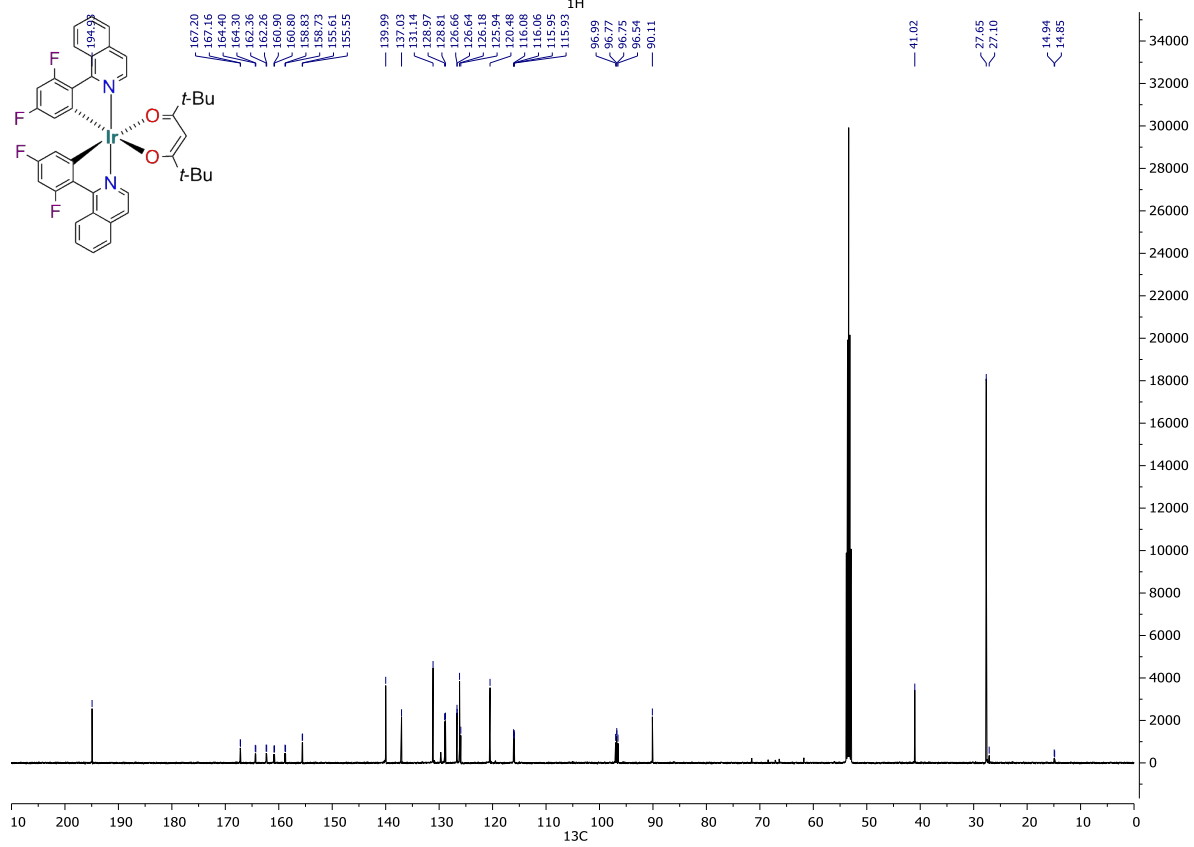
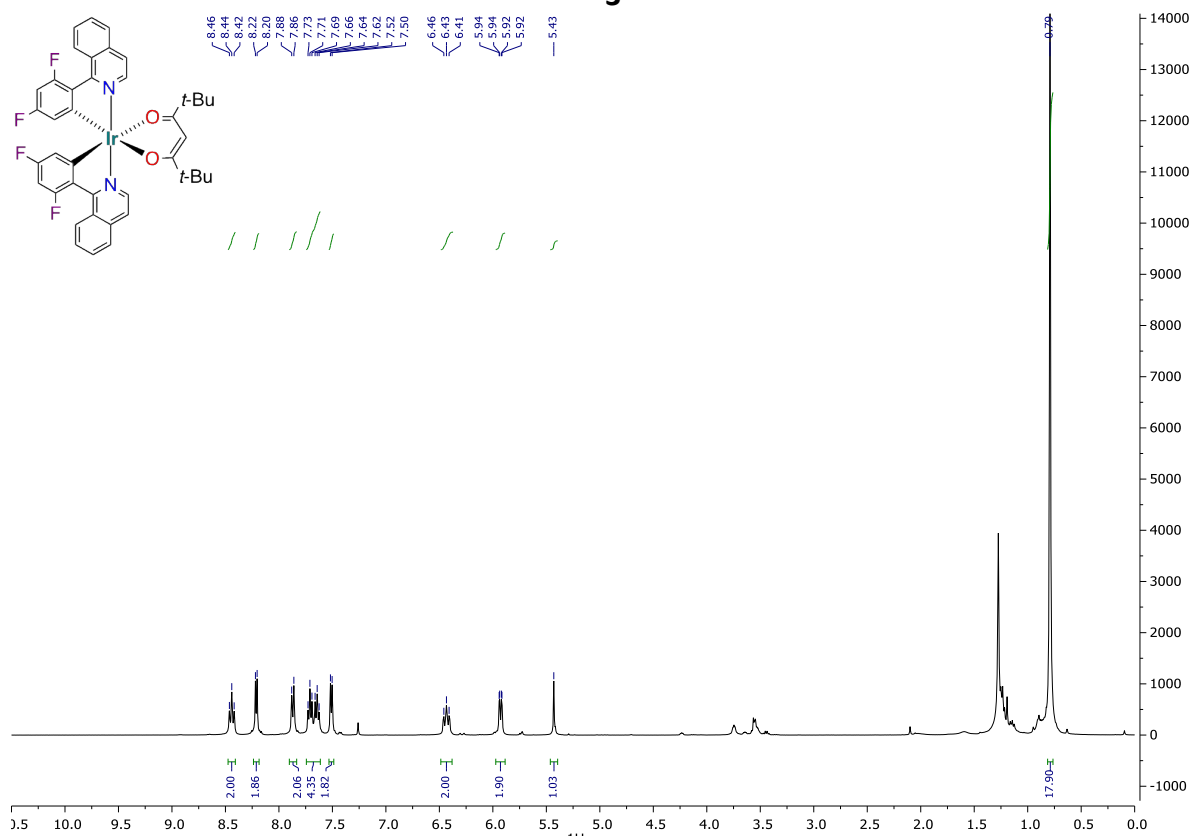


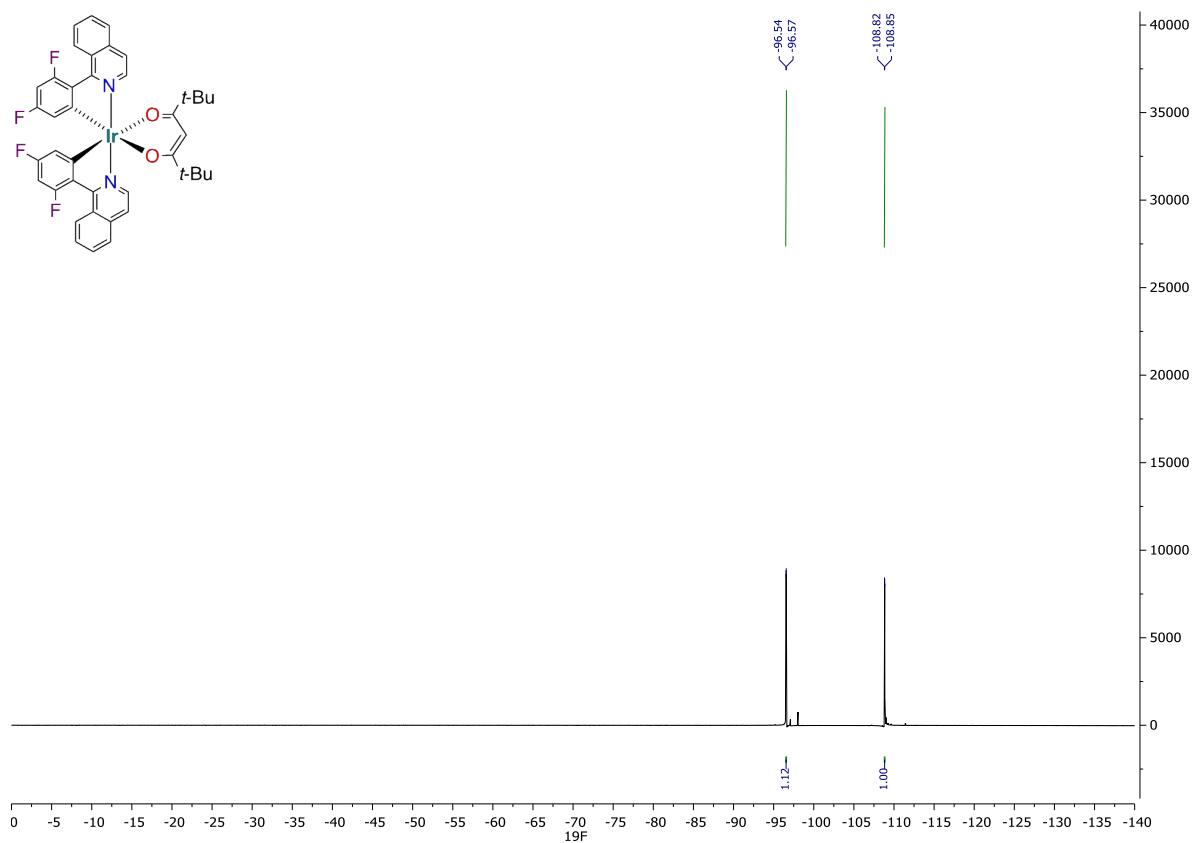
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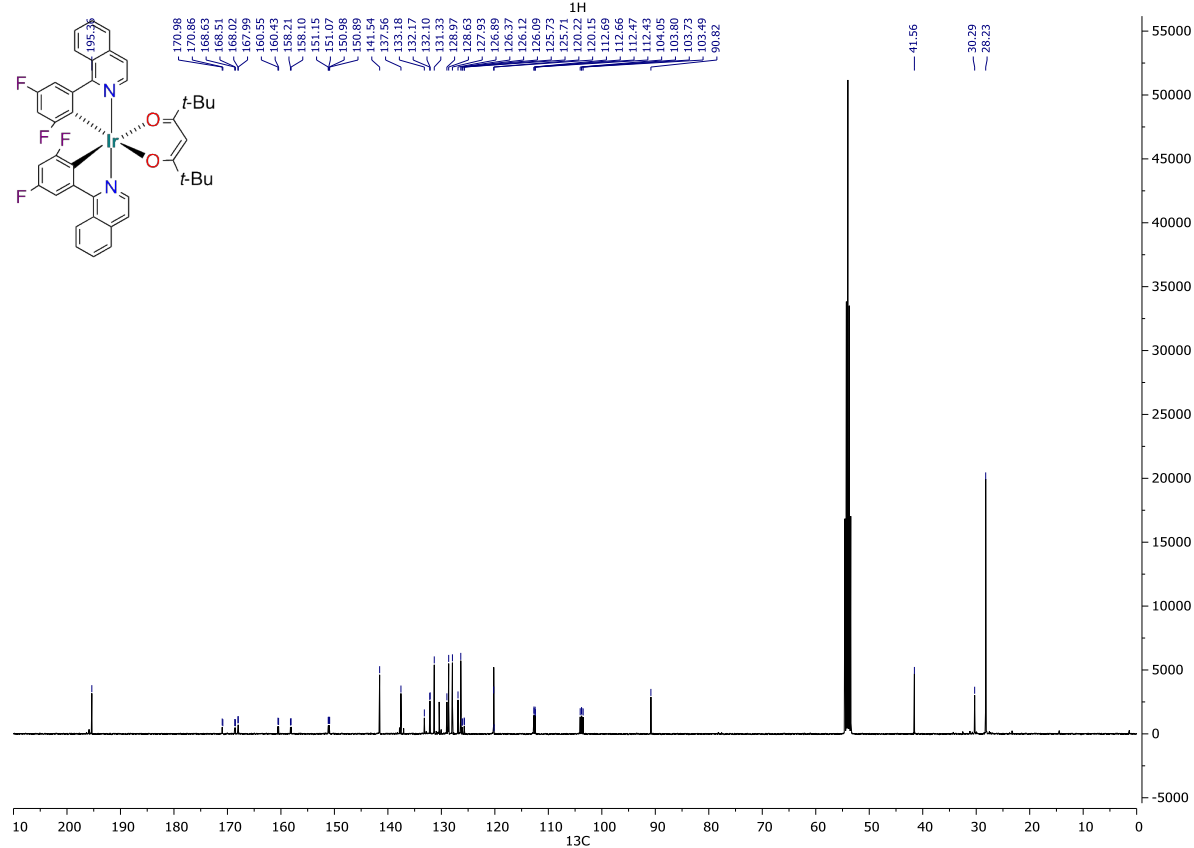
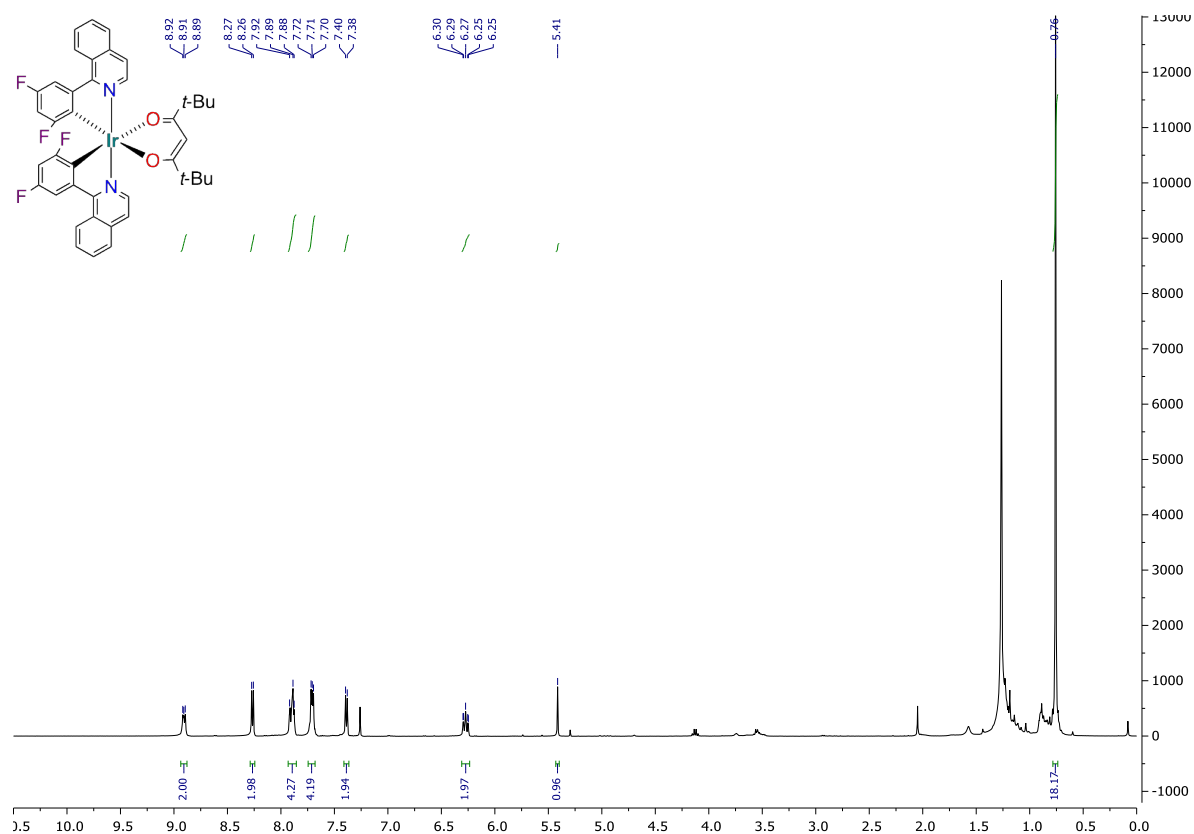


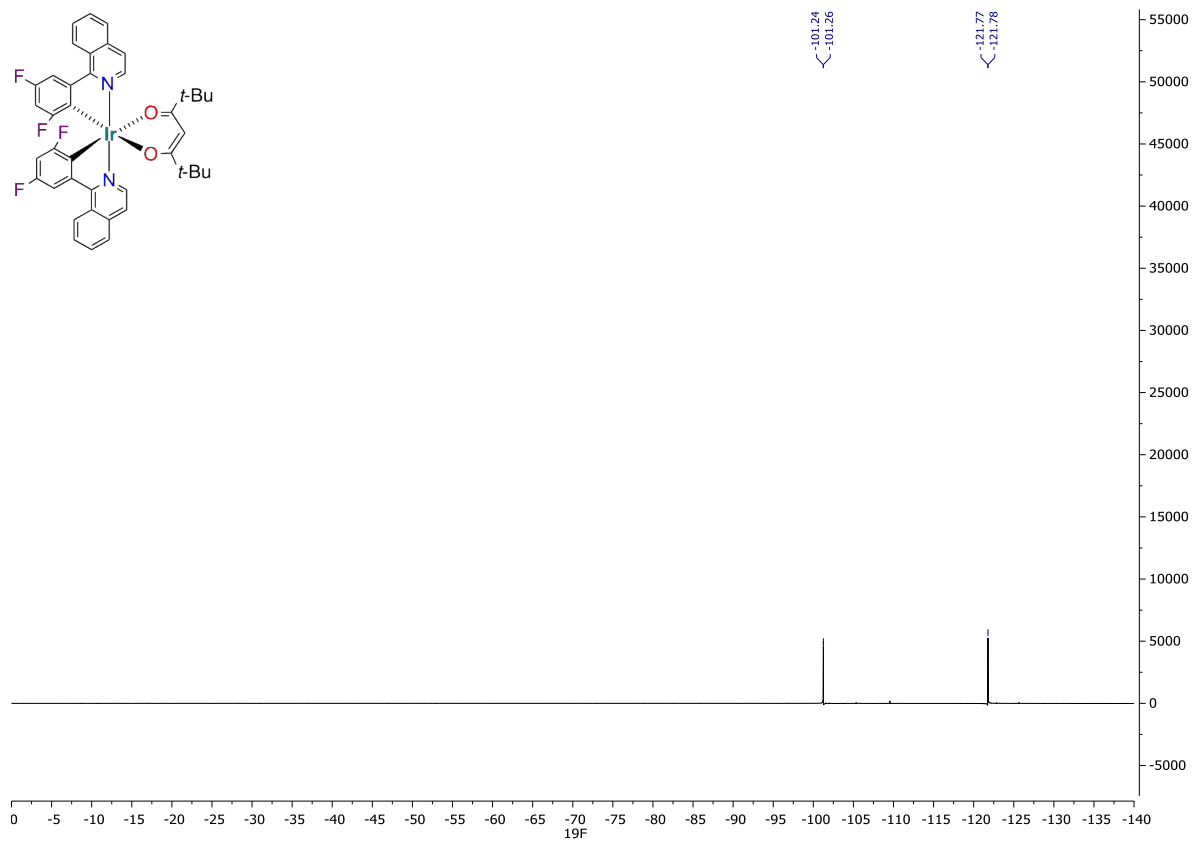


3

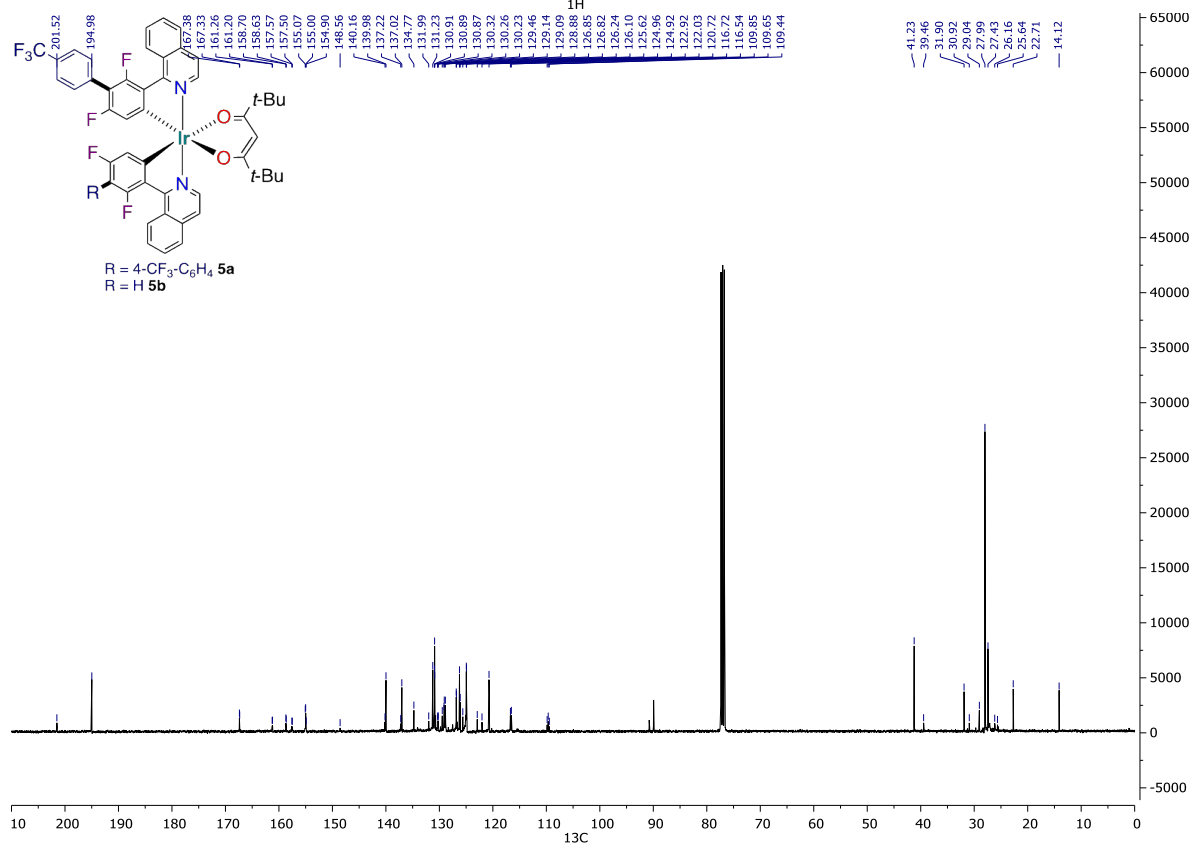
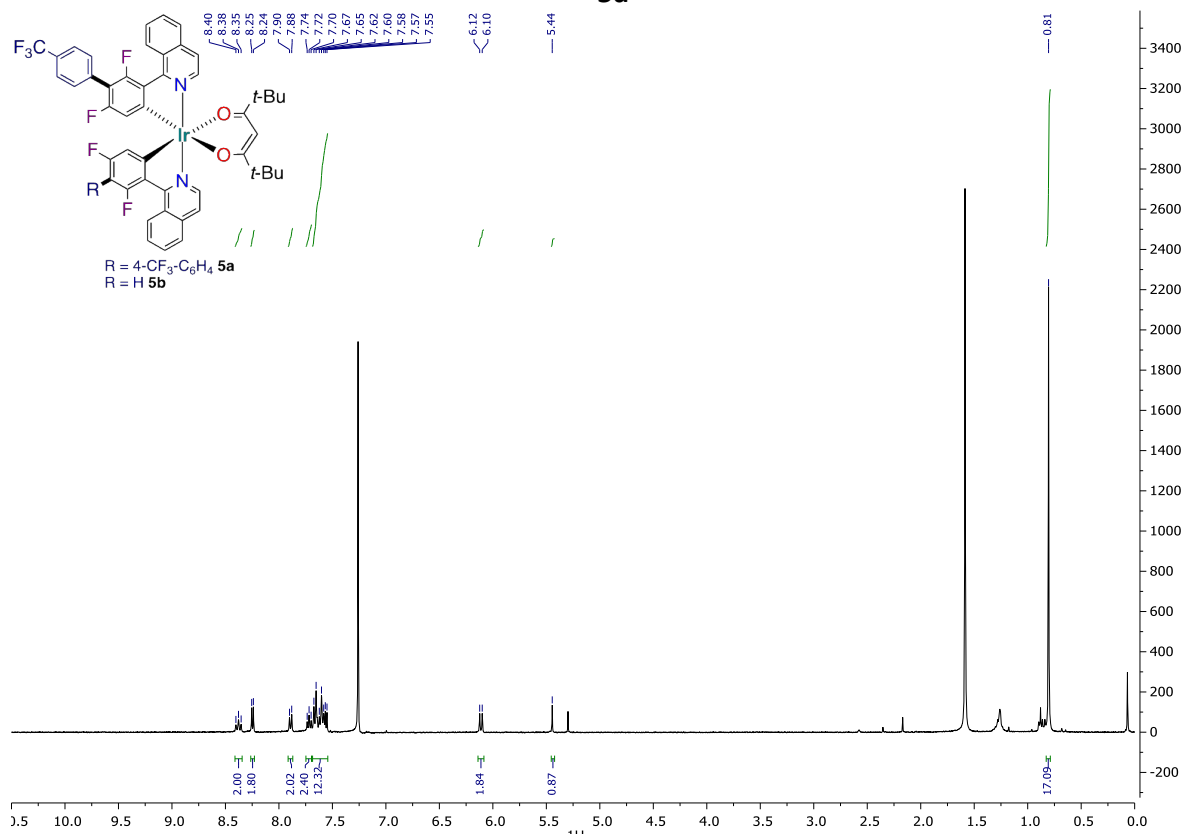


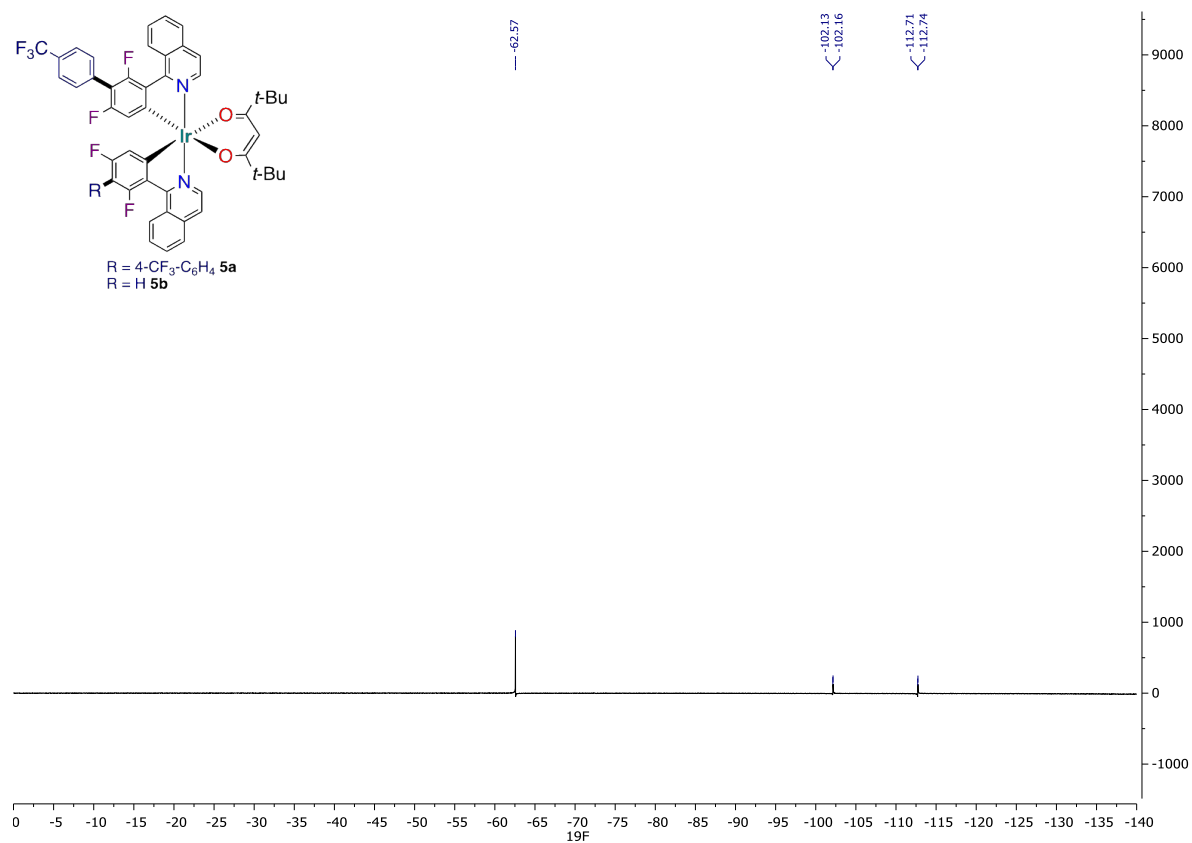


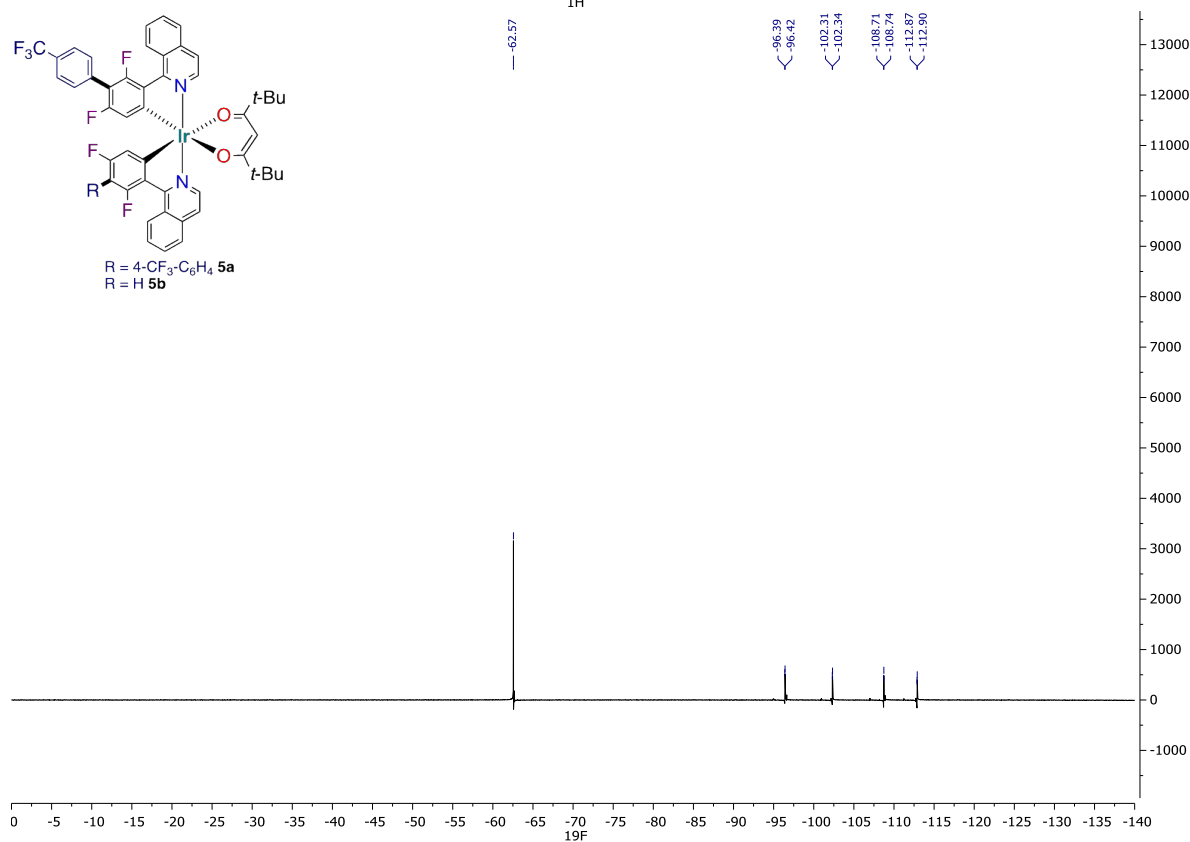
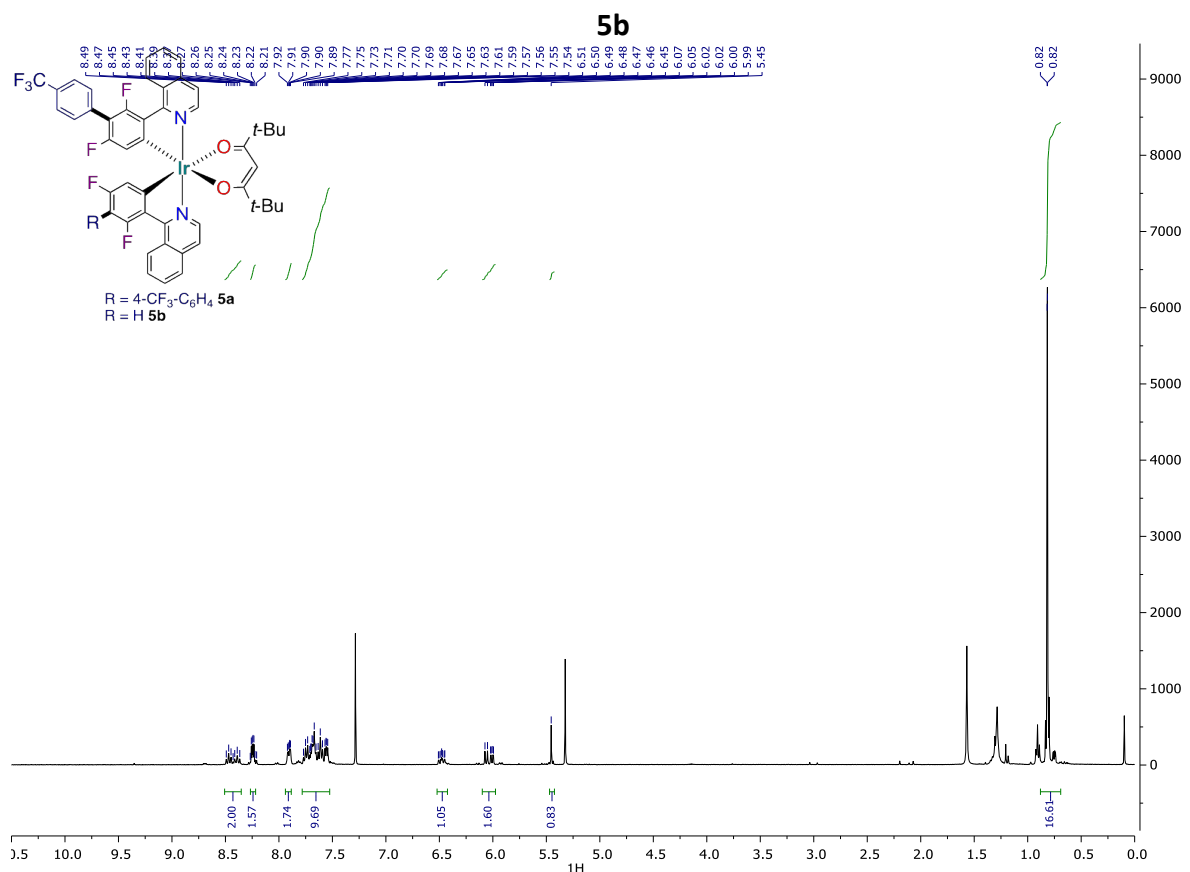


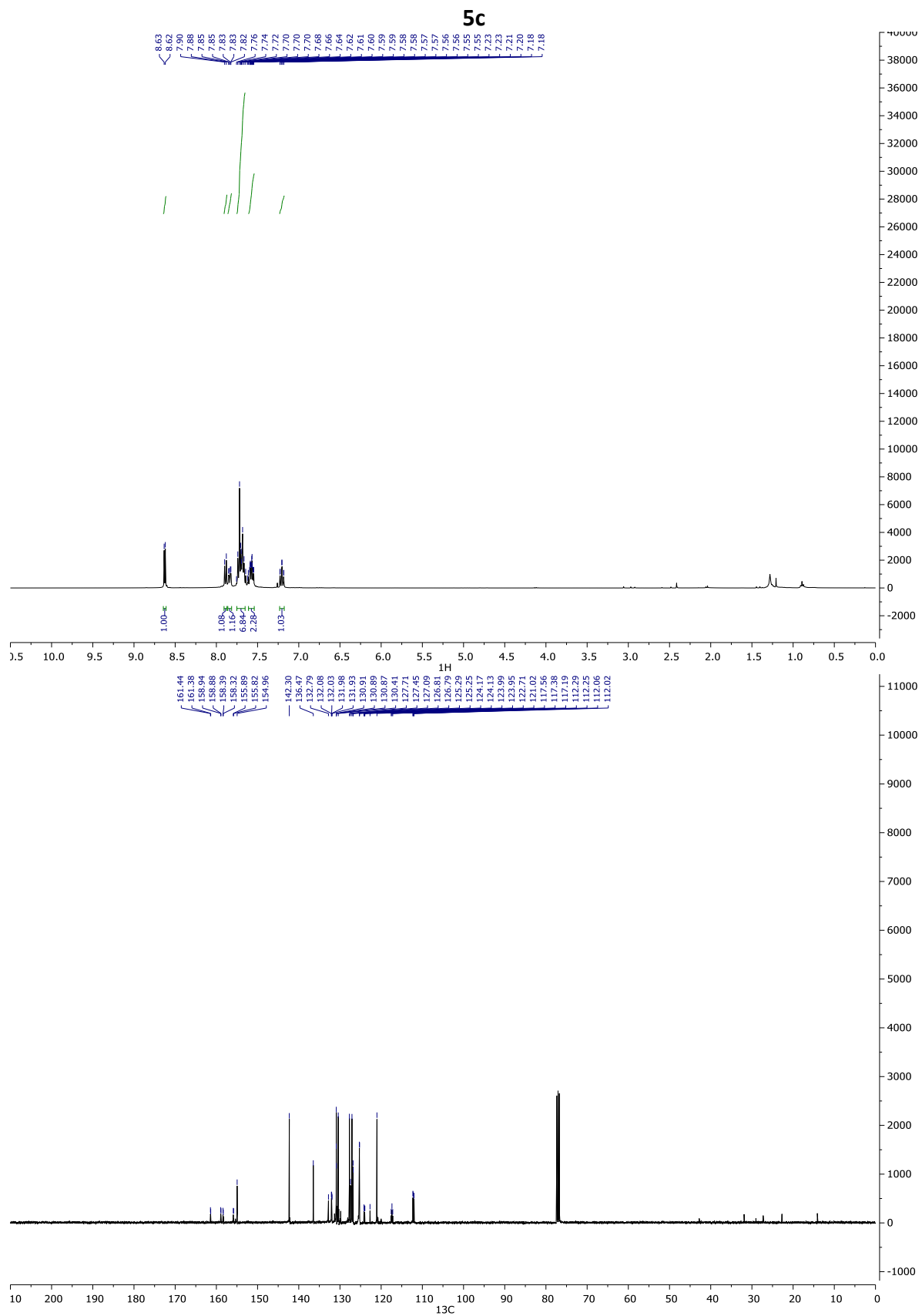


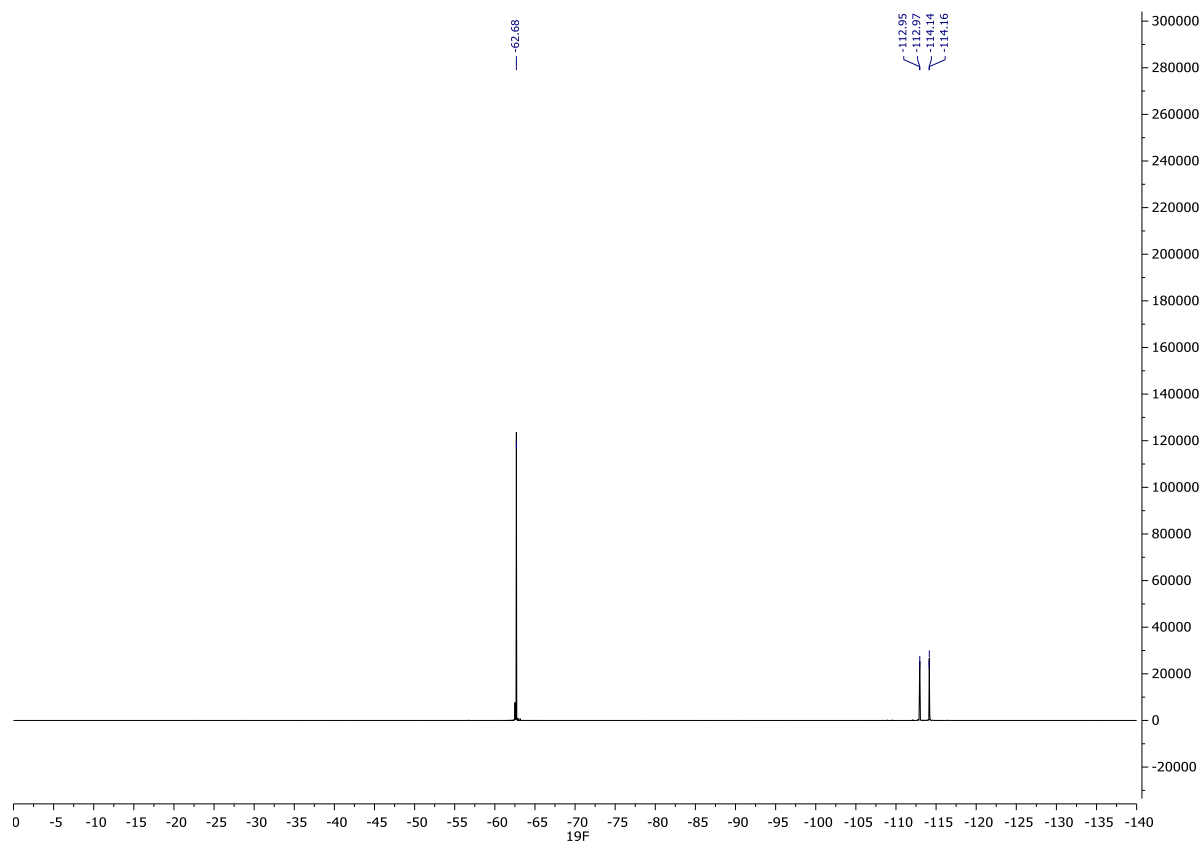
5a



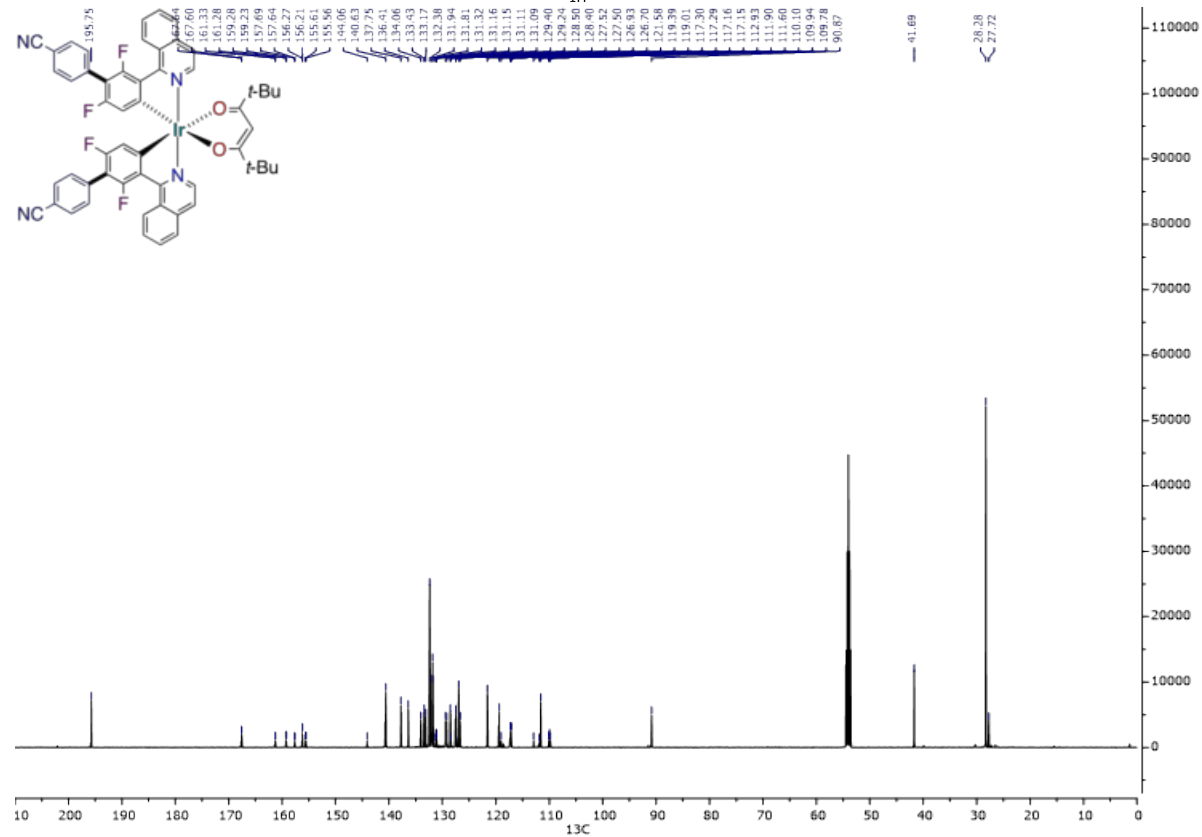
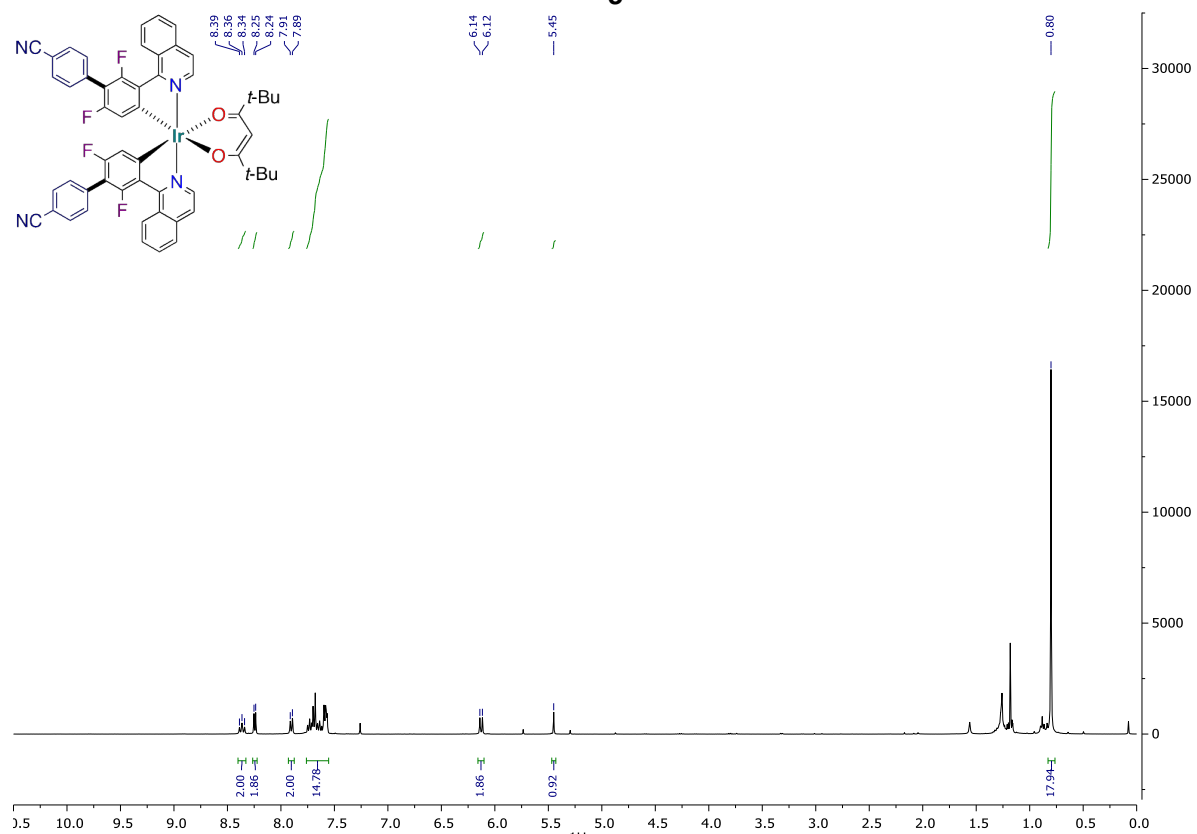


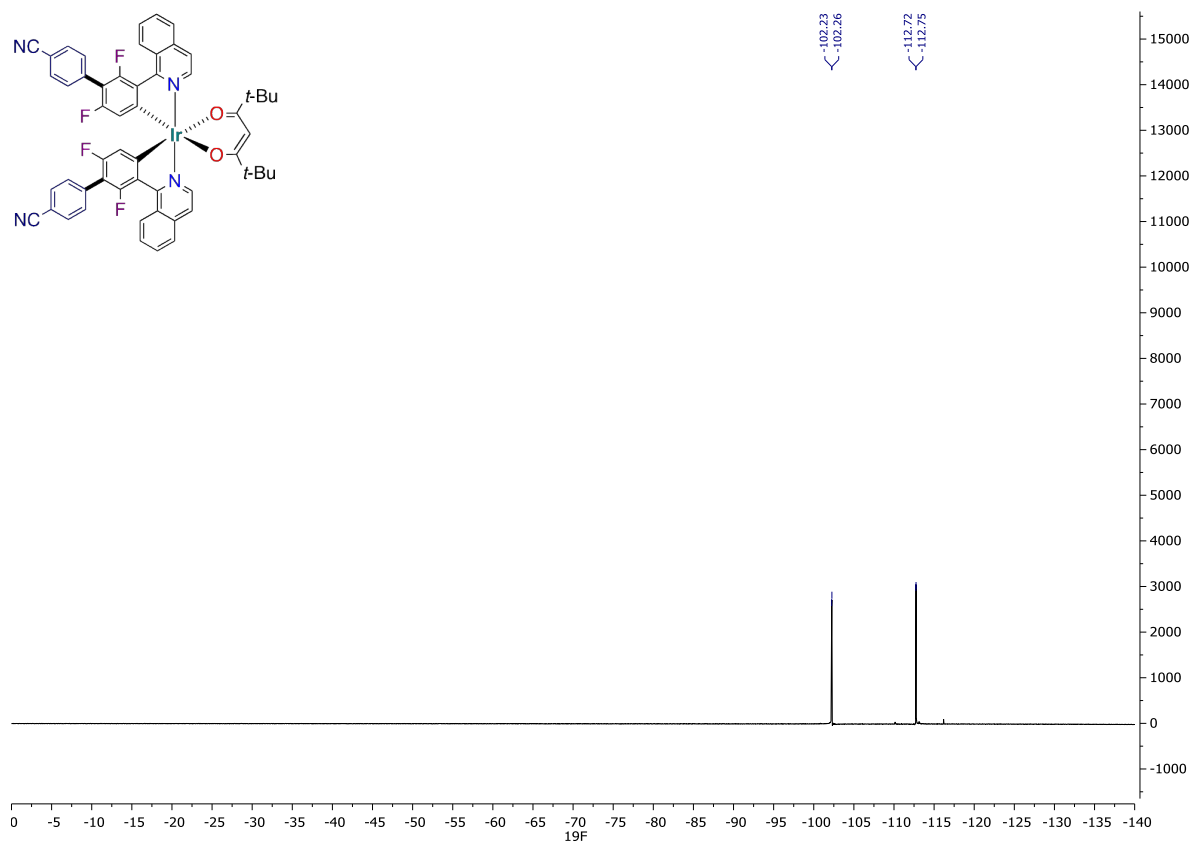


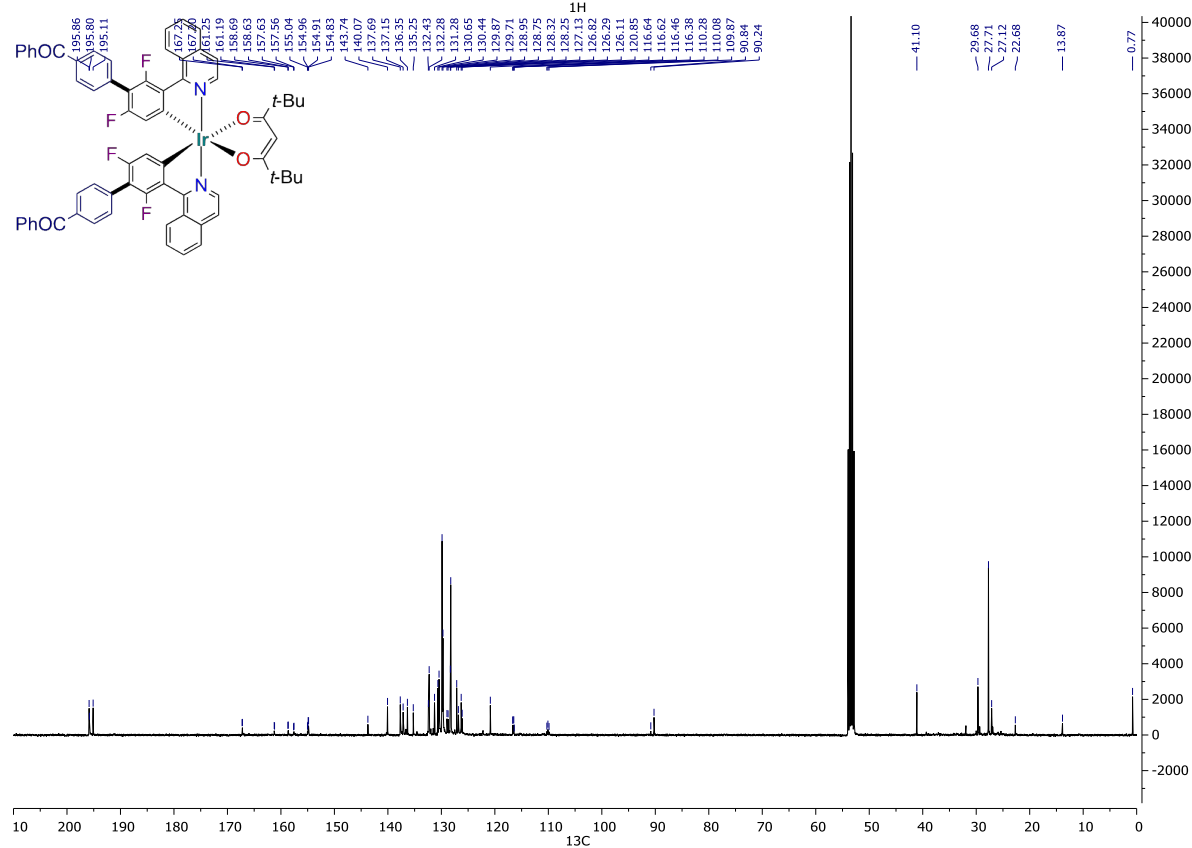
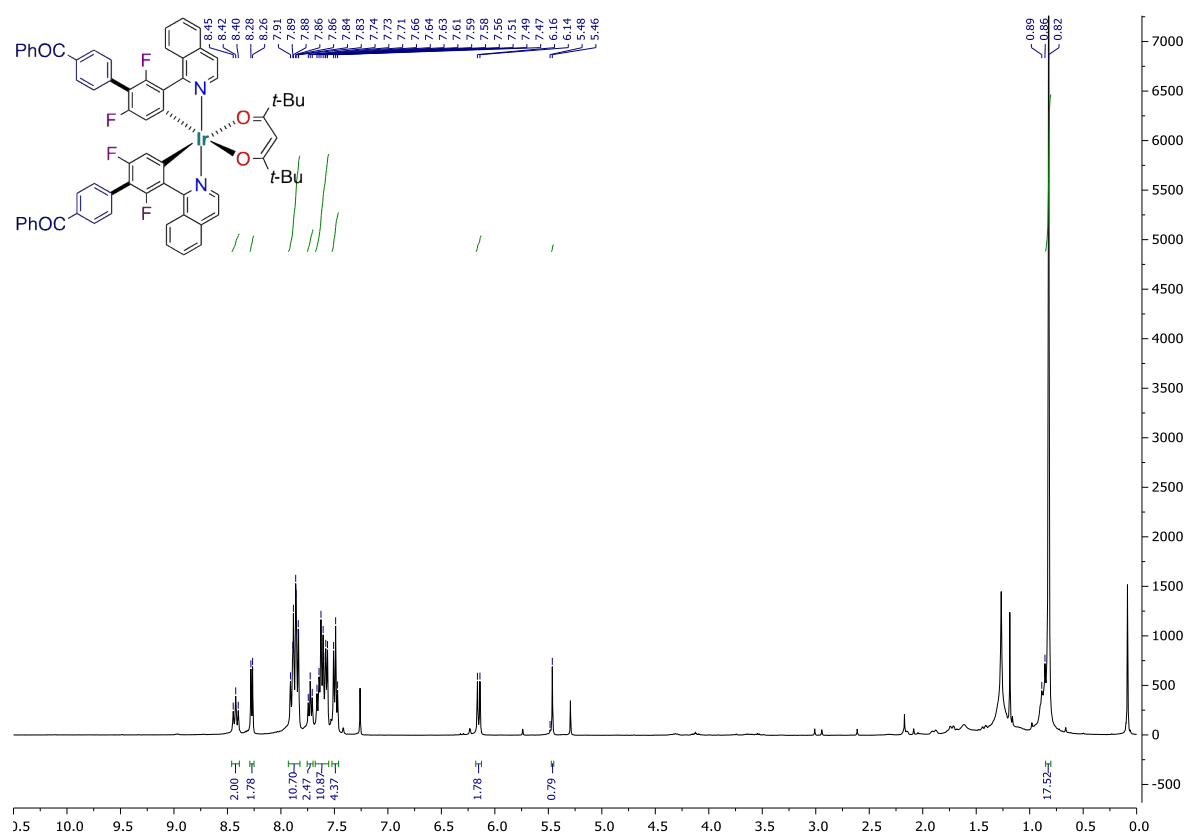


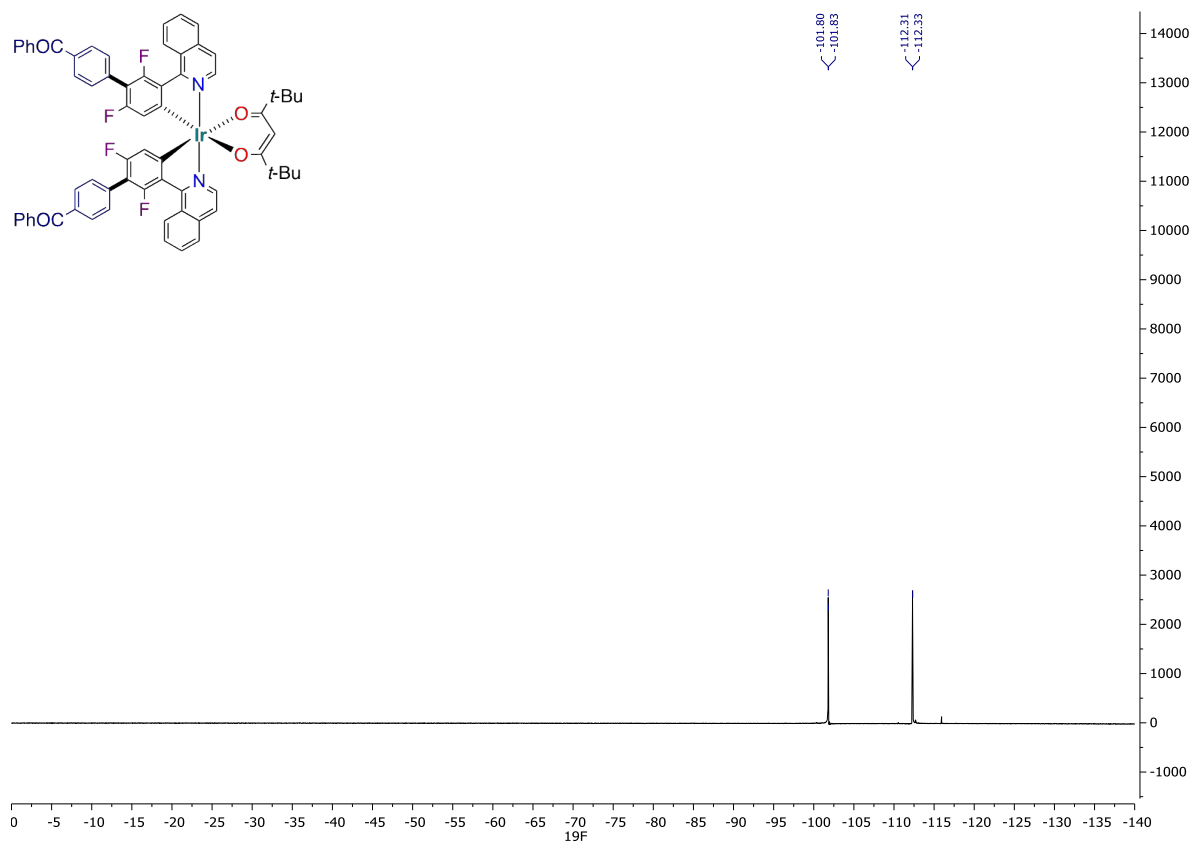


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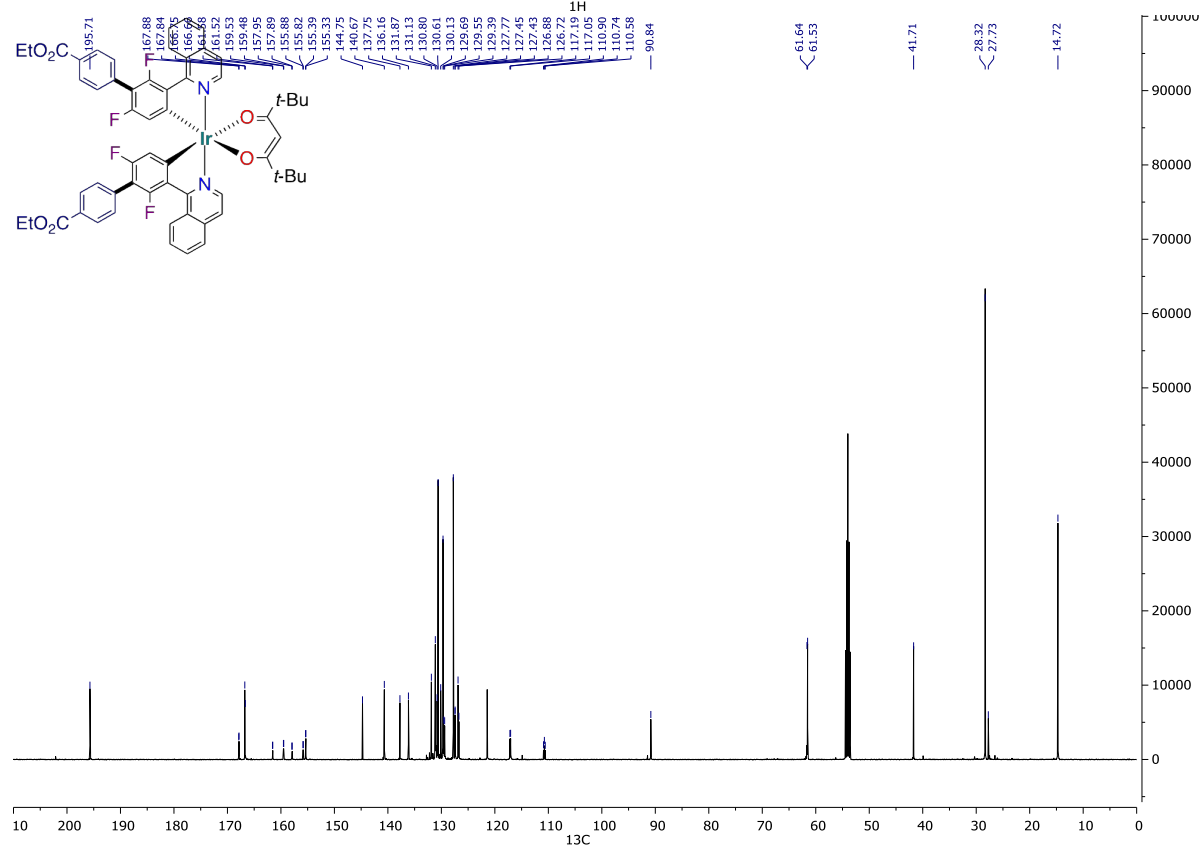
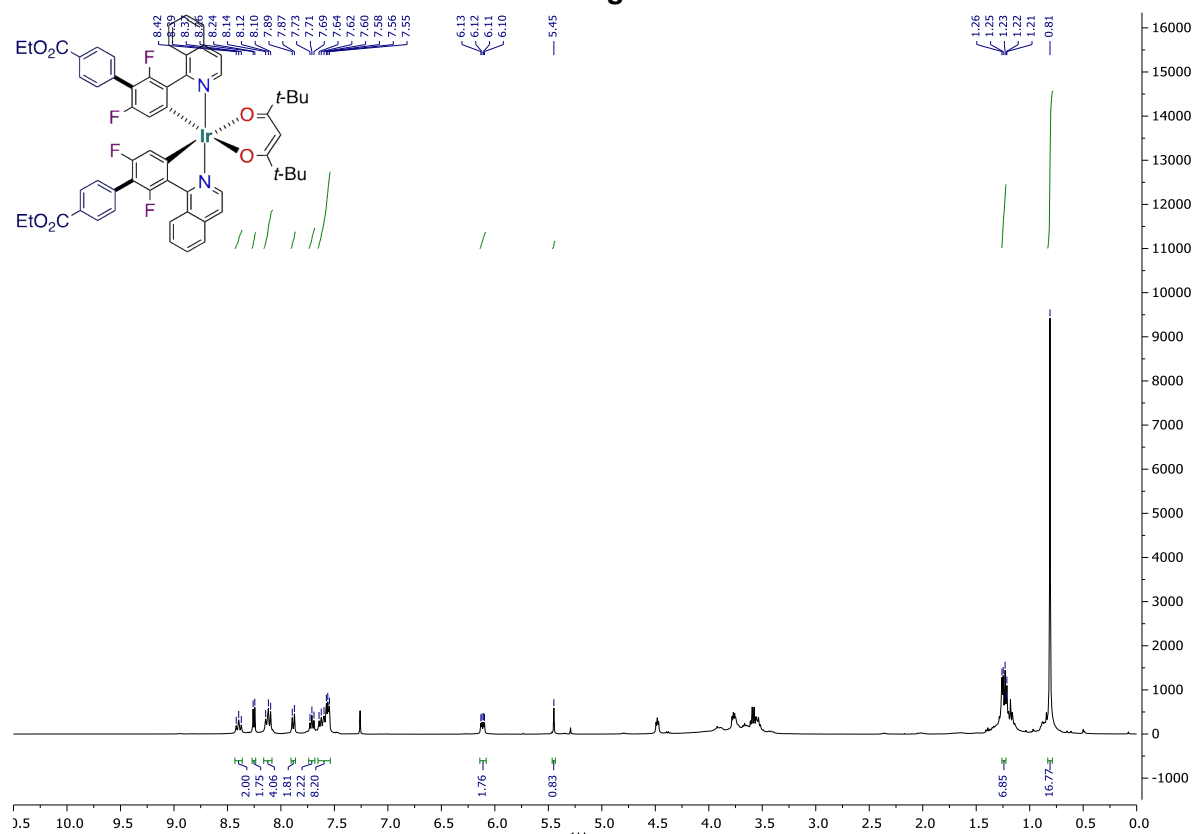


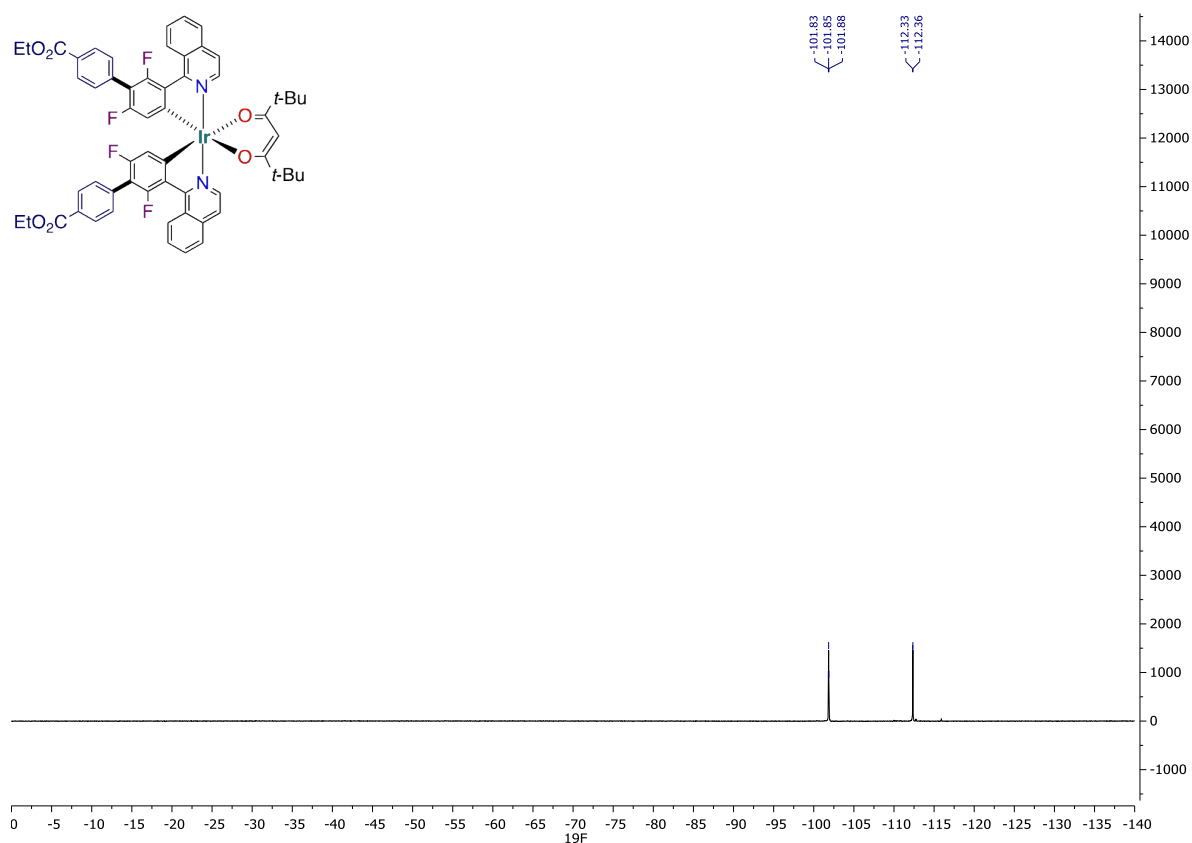






8





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- [S4] G. M. Sheldrick, *Acta Cryst. A* 71 2015 3-8
- [S5] Sheldrick G.M., *Acta Cryst. C* 71 2015 3-8