



Supporting Information

Photoinduced Group Transposition via Iridium-Nitrenoid Leading to Amidative Inner-Sphere Aryl Migration

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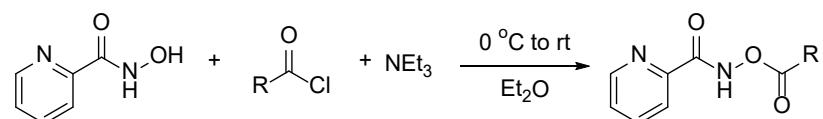
1. General considerations

Reagent preparation. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by UV light (254 nm). Silica-gel chromatography was performed using a CombiFlash® Rf + system with RediSep® Rf Silica columns using a proper eluent. Air-sensitive liquid and solutions were transferred via syringe by using degassed solvents. Concentration of solution was carried out by using a rotary evaporator and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr.

Product characterization: ^1H NMR was recorded on Bruker AVANCE III HD (400 MHz), AVANCE NEO Nanobay (400 MHz), AVANCE NEO (500 MHz), or Agilent Technologies DD2 (600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the residual solvent peak (CHCl_3 in CDCl_3 : 7.26 ppm; CH_2Cl_2 in CD_2Cl_2 : 5.32 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, m = multiplet, br = broad. Coupling constants, J , were reported in hertz (Hz). ^{13}C NMR was obtained on Bruker AVANCE III HD (100 MHz), AVANCE NEO (125 MHz), or Agilent Technologies DD2 (150 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the residual solvent peak. ^{19}F NMR was recorded on Bruker AVANCE III HD (376 MHz) or AVANCE NEO (471 MHz). ^{31}P NMR was recorded on AVANCE NEO (202 MHz). X-band CW electron paramagnetic resonance (EPR) spectroscopy was performed using Bruker EMXplus spectrometer equipped with a standard resonator. Infrared (IR) spectra were acquired on Bruker Alpha ATR FT-IR Spectrometer. Frequencies are given in wave numbers (cm^{-1}), and only selected peaks were reported. The melting point was measured with Buchi Melting Point M-565. High-resolution mass spectra (HRMS) were obtained from KAIST Analysis Center for Research Advancement (KARA) via the electrospray ionization (ESI) method.

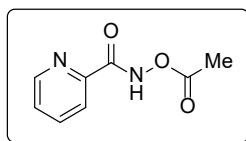
2. Procedures for the preparation of starting materials

2-1. Preparation of ligands



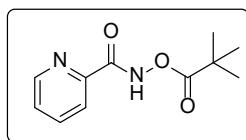
N-Hydroxypicolinamide was prepared by following the previously reported procedure.^[1] A solution of *N*-hydroxypicolinamide in Et₂O (0.1 M) was cooled down to 0 °C. To the reaction mixture were added acyl chloride (1 equiv) followed by NEt₃ (1 equiv). The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched by adding water and extracted with Et₂O for three times. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The desired amide product was obtained via recrystallization in CH₂Cl₂/*n*-pentane or via silica column chromatography (*n*-Hexanes to *n*-Hexanes/EtOAc = 1:1).

N-Acetoxy picolinamide (L1)

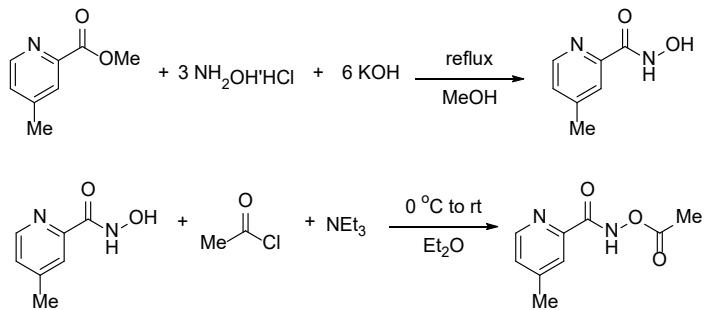


Colorless solid (5.0 mmol scale, 500 mg, 55%); **m.p.** 95–97 °C; **¹H NMR** (600 MHz, CDCl₃) δ 10.92 (br, 1H), 8.56 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.15 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.51 – 7.43 (m, 1H), 2.30 (s, 3H); **¹³C NMR** (151 MHz, CDCl₃) δ 168.5, 161.7, 148.6, 148.4, 137.6, 127.3, 122.9, 18.5; **IR** (cm⁻¹) 3098, 2902, 1783, 1690, 1493, 1435, 1305, 1244, 1091, 1019, 1003, 854, 749; **HRMS** (ESI) *m/z* calcd. for C₈H₉N₂O₃⁺ [M+H]⁺: 181.0608, found: 181.0610.

N-(Pivaloyloxy)picolinamide (L2)



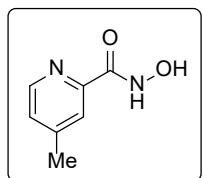
Colorless solid (2.0 mmol scale, 144 mg, 65%); **m.p.** 99–101 °C; **¹H NMR** (400 MHz, CDCl₃) δ 10.85 (br, 1H), 8.62 – 8.50 (m, 1H), 8.13 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.92 – 7.78 (m, 1H), 7.46 (ddd, *J* = 7.8, 4.8, 1.5 Hz, 1H), 1.36 (d, *J* = 2.1 Hz, 9H); **¹³C NMR** (151 MHz, CDCl₃) δ 176.3, 162.0, 148.6, 148.6, 137.6, 127.2, 122.8, 38.6, 27.2; **IR** (cm⁻¹) 3083, 2973, 1722, 1687, 1590, 1565, 1502, 1468, 1363, 1286, 1078, 876, 753, 700, 625; **HRMS** (ESI) *m/z* calcd. for C₁₁H₁₅N₂O₃⁺ [M+H]⁺: 223.1077, found: 223.1081.



Procedure for the preparation of *N*-acetoxy-4-methylpicolinamide. To a solution of methyl 4-methylpicolinate (10 mmol, 1.5 g) in MeOH (0.4 M) were added NH₂OH·HCl (30 mmol, 2.08 g) and KOH (60 mmol, 3.4 g). The reaction mixture was stirred at 90 °C for 12 h, and the crude mixture was cooled down to room temperature. Then, 1N HCl (aq) was added to adjust the pH of the reaction mixture to pH 5~6. The solvent was removed, and the residue was extracted three times with EtOAc. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by recrystallization in CH₂Cl₂/n-pentane to obtain *N*-hydroxy-4-methylpicolinamide.

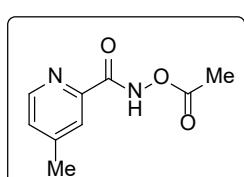
A solution of *N*-hydroxy-4-methylpicolinamide (2.0 mmol, 304 mg) in Et₂O (0.1 M) was cooled down to 0 °C. To the reaction mixture were added acetyl chloride (2.0 mmol, 0.14 mL) followed by NEt₃ (2.0 mmol, 0.28 mL). The reaction mixture was warmed to the room temperature and stirred for 12 h. The reaction mixture was quenched by adding water and extracted with Et₂O for three times. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. ***N*-Acetoxy-4-methylpicolinamide** was obtained via silica column chromatography (*n*-Hexanes to *n*-Hexanes:EtOAc = 1:1).

***N*-Hydroxy-4-methylpicolinamide**

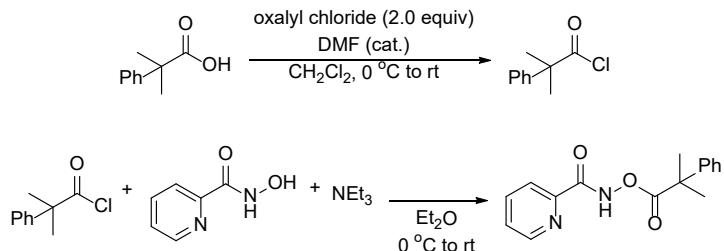


Colorless solid (861 mg, 57%); **m.p.** 84–86 °C; **¹H NMR** (500 MHz, CD₂Cl₂) δ 10.39 (br, 1H), 8.59 (br, 1H), 8.38 (d, *J* = 4.9 Hz, 1H), 7.92 (s, 1H), 7.28 (d, *J* = 6.1 Hz, 1H), 2.42 (s, 3H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 162.7, 149.8, 148.7, 148.3, 127.9, 123.4, 21.3; **IR** (cm⁻¹) 3080, 1667, 1603, 1512, 1448, 1372, 1287, 1222, 1139, 1037, 838, 823, 765, 681; **HRMS** (ESI) *m/z* calcd. for C₇H₉N₂O₂⁺ [M+H]⁺: 153.0659, found: 153.0659.

***N*-Acetoxy-4-methylpicolinamide (L3)**

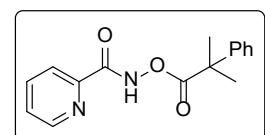


Colorless solid (2 mmol scale, 310 mg, 80%); **m.p.** 99–101 °C; **¹H NMR** (400 MHz, CDCl₃) δ 10.91 (br, 1H), 8.41 (d, *J* = 5.7 Hz, 1H), 7.98 (s, 1H), 7.29 (d, *J* = 5.7 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 168.5, 162.0, 149.3, 148.4, 148.2, 128.1, 123.7, 21.3, 18.6; **IR** (cm⁻¹) 3056, 1790, 1681, 1602, 1467, 1368, 1287, 1248, 1171, 1037, 996, 827, 766; **HRMS** (ESI) *m/z* calcd. for C₉H₁₁N₂O₃⁺ [M+H]⁺: 195.0764, found: 195.0766.

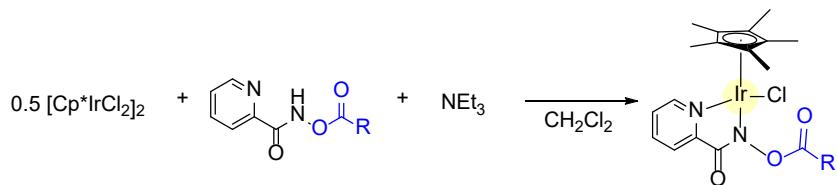


Procedure for the preparation of *N*-{(2-methyl-2-phenylpropanoyl)oxy}picolinamide. To a solution of 2-methyl-2-phenylpropanoic acid (2 mmol, 328 mg) in CH_2Cl_2 (0.1 M) were added oxalyl chloride (2.0 equiv) and DMF (2 drops) at 0 °C. The reaction was allowed to stir at room temperature for 2 h. After completion, the solvent was removed under reduced pressure to afford the crude acid chloride. Then, to the crude acid chloride, Et_2O (0.1 M) and *N*-hydroxypicolinamide (1.0 equiv) were added at 0 °C. To the reaction mixture, NEt_3 (1.0 equiv) was added, and the mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched by adding water and extracted with Et_2O for three times. The organic layer was dried over MgSO_4 and concentrated under reduced pressure. ***N*-{(2-Methyl-2-phenylpropanoyl)oxy}picolinamide** was obtained via silica column chromatography (*n*-Hexanes to *n*-Hexanes: EtOAc = 1:1).

***N*-{(2-Methyl-2-phenylpropanoyl)oxy}picolinamide (L4)**

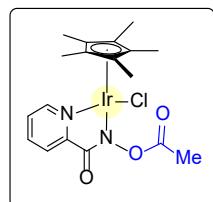
 Colorless resin (407 mg, 72%); **$^1\text{H NMR}$** (600 MHz, CD_2Cl_2) δ 10.70 (s, 1H), 8.56 (d, J = 4.8 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.89 (td, J = 7.8, 1.6 Hz, 1H), 7.50 (dd, J = 7.6, 4.7 Hz, 1H), 7.47 (d, J = 7.3 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.30 (t, J = 7.3 Hz, 1H), 1.73 (s, 6H); **$^{13}\text{C NMR}$** (151 MHz, CD_2Cl_2) δ 175.1, 162.4, 148.9, 148.8, 143.7, 138.0, 128.9, 127.6, 127.6, 126.3, 122.9, 46.5, 26.8; **IR** (cm^{-1}) 3023, 2977, 1777, 1695, 1590, 1460, 1425, 1065, 699; **HRMS (ESI)** m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3^+$ [$\text{M}+\text{H}]^+$: 285.1234, found: 285.1241.

2-2. Preparation of $\text{Cp}^*\text{Ir}(\text{hydroxamate})\text{Cl}$ complexes



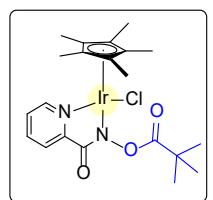
Procedure for the preparation of $\text{Cp}^*\text{Ir}(\text{hydroxamate})\text{Cl}$ complexes. Prepared by following a modified procedure from the literature.^[2] To a solution of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.5 equiv) in CH_2Cl_2 (0.05 M) were added *N*-acyloxy picolinamide (1.0 equiv) and NEt_3 (1.0 equiv). The reaction mixture was stirred at 25 °C for 1 h and washed with water for three times. The organic layer was collected and dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by recrystallization in $\text{CH}_2\text{Cl}_2/n$ -pentane or silica column chromatography (CH_2Cl_2 to $\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 10:1).

Ir1a



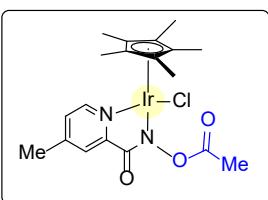
The reaction was conducted with 0.5 mmol of $[\text{Cp}^*\text{IrCl}_2]_2$ and **L1**. Yellow solid (540 mg, 99%); **m.p.** 172–174 °C (decomp.); **$^1\text{H NMR}$** (600 MHz, CD_2Cl_2) δ 8.48 (d, J = 5.6 Hz, 1H), 8.04 (d, J = 9.5 Hz, 1H), 8.00 – 7.92 (m, 1H), 7.55 – 7.47 (m, 1H), 2.26 (s, 3H), 1.69 (s, 15H); **$^{13}\text{C NMR}$** (101 MHz, CD_2Cl_2) δ 169.6, 166.7, 152.5, 150.4, 139.3, 128.0, 125.8, 87.7, 19.0, 9.1; **IR** (cm^{-1}) 2914, 1763, 1644, 1602, 1464, 1362, 1282, 1183, 1094, 1001, 865, 682; **HRMS** (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{22}\text{IrN}_2\text{O}_3^+ [\text{M}-\text{Cl}]^+$: 507.1254, found: 507.1253.

Ir1b



The reaction was conducted with 0.25 mmol of $[\text{Cp}^*\text{IrCl}_2]_2$ and **L2**. Yellow solid (148 mg, 74%); **m.p.** 159–161 °C (decomp.); **$^1\text{H NMR}$** (500 MHz, CD_2Cl_2) δ 8.48 (d, J = 5.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.50 (ddd, J = 7.3, 5.5, 1.6 Hz, 1H), 1.69 (s, 15H), 1.38 (s, 9H); **$^{13}\text{C NMR}$** (101 MHz, CD_2Cl_2) δ 176.6, 166.3, 152.7, 150.2, 139.2, 127.7, 125.7, 87.7, 39.0, 27.9, 9.2; **IR** (cm^{-1}) 2969, 1746, 1647, 1605, 1465, 1363, 1088, 1025, 677; **HRMS** (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{28}\text{IrN}_2\text{O}_3^+ [\text{M}-\text{Cl}]^+$: 549.1724, found: 549.1729.

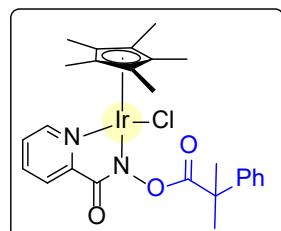
Ir1c



The reaction was conducted with 0.25 mmol of $[\text{Cp}^*\text{IrCl}_2]_2$ and **L3**. Yellow solid (251 mg, 90%); **m.p.** 178–180 °C (decomp.); **$^1\text{H NMR}$** (500 MHz, CD_2Cl_2) δ 8.30 (d, J = 5.6 Hz, 1H), 7.87 (d, J = 2.4 Hz, 1H), 7.31 (dd, J = 5.8, 2.7 Hz, 1H), 2.51 (s, 3H), 2.25 (s, 3H), 1.68 (s, 15H); **$^{13}\text{C NMR}$** (101 MHz, CD_2Cl_2) δ 169.7, 166.8, 152.0, 151.8, 149.7, 128.8, 126.5, 87.5, 21.4, 19.0, 9.1; **IR** (cm^{-1}) 2621, 1767,

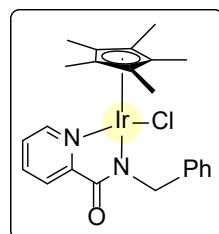
1647, 1616, 1452, 1325, 1187, 1078, 838; **HRMS** (ESI) m/z calcd. for $C_{19}H_{24}IrN_2O_3^+ [M-Cl]^+$: 521.1411, found: 521.1416.

Ir1d



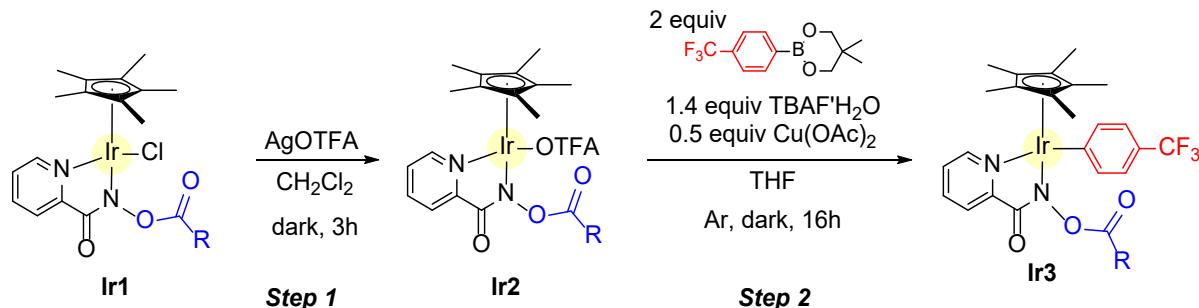
The reaction was conducted with 0.25 mmol of $[Cp^*IrCl_2]_2$ and **L4**. Yellow solid (227 mg, 70%); **m.p.** 135–137 °C (decomp.); **1H NMR** (500 MHz, CD_2Cl_2) δ 8.46 (d, $J = 5.5$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.94 (td, $J = 7.7, 1.5$ Hz, 1H), 7.61 (d, $J = 7.4$ Hz, 2H), 7.48 (ddd, $J = 7.4, 5.5, 1.7$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 2H), 7.26 (t, $J = 7.3$ Hz, 1H), 1.76 (s, 3H), 1.75 (s, 3H), 1.52 (s, 15H); **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 174.3, 166.3, 152.6, 150.1, 144.8, 139.2, 128.6, 127.7, 127.1, 126.9, 125.7, 87.6, 46.5, 27.4, 27.1, 9.0; **IR** (cm^{-1}) 2970, 2904, 1751, 1649, 1604, 1465, 1070, 761, 698; **HRMS** (ESI) m/z calcd. for $C_{26}H_{30}IrN_2O_3^+ [M-Cl]^+$: 611.1880, found: 611.1889.

Ir1e



The reaction was conducted with 0.25 mmol of $[Cp^*IrCl_2]_2$ and *N*-benzylpicolinamide.^[3] Yellow solid (199 mg, 69%); **m.p.** 138–140 °C (decomp.); **1H NMR** (600 MHz, CD_2Cl_2) δ 8.56 (d, $J = 5.1$ Hz, 1H), 8.02 (d, $J = 7.8$ Hz, 1H), 7.92 (t, $J = 7.7$ Hz, 1H), 7.51 – 7.46 (m, 1H), 7.37 (d, $J = 7.6$ Hz, 2H), 7.26 (t, $J = 7.5$ Hz, 2H), 7.17 (t, $J = 7.4$ Hz, 1H), 5.05 (d, $J = 15.1$ Hz, 1H), 4.80 (d, $J = 15.6$ Hz, 1H), 1.56 (s, 15H); **^{13}C NMR** (151 MHz, CD_2Cl_2) δ 171.6, 155.6, 149.9, 141.5, 138.8, 128.1, 127.9, 127.4, 126.2, 125.9, 87.0, 55.1, 9.2; **IR** (cm^{-1}) 2916, 2889, 1619, 1592, 1563, 1449, 1376, 1027, 707; **HRMS** (ESI) m/z calcd. for $C_{23}H_{26}IrN_2O^+ [M-Cl]^+$: 539.1669, found: 539.1673.

2-3. Preparation of $Cp^*Ir(\text{hydroxamate})(\text{Ar})$ complexes



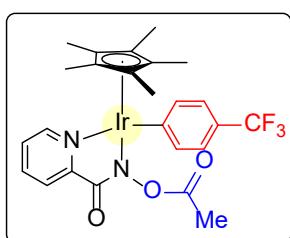
Procedure for the preparation of $Cp^*Ir(\text{hydroxamate})(\text{Ar})$ complexes. Prepared by following a modified procedure from the literature.^[4] 5,5-Dimethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborinane, 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane, 5,5-dimethyl-2-phenyl-1,3,2-

dioxaborinane, 5,5-dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane, and 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane were prepared according the reported procedure.^[4]

Step 1. To a solution of **Ir1** in CH₂Cl₂ (0.05 M) was added silver trifluoroacetate (AgOTFA, 1.0 equiv). The reaction mixture was stirred at 25 °C for 3 h in the dark, and after the reaction, the reaction mixture was filtered through a pad of celite with CH₂Cl₂. The filtered solution was concentrated under reduced pressure. Obtained **Ir2** was directly used for the following step.

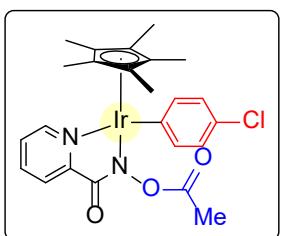
Step2. 5,5-Dimethyl-2-(aryl)-1,3,2-dioxaborinane (2.0 equiv) and *n*-tetrabutylammonium fluoride hydrate (TBAF·H₂O, 1.4 equiv) was dissolved in THF (0.1 M) and premixed for 1 h under Ar atmosphere. Then, **Ir2** (1.0 equiv) and Cu(OAc)₂ (0.5 equiv) were added to the reaction mixture. The reaction mixture was stirred in the dark at 25 °C for 16 h. The reaction mixture was filtered through a pad of silica with acetone. The collected solution was concentrated under reduced pressure, and the residue was purified by silica column chromatography to obtain **Ir3** using *n*-hexanes/acetone = 1:1 mixture as the eluent.

Ir3a



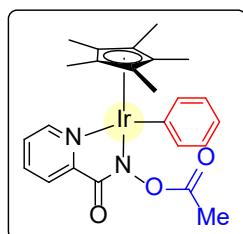
The reaction was conducted with 0.64 mmol of **Ir1a** and 5,5-dimethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborinane. Yellow solid (388 mg, 59%); **m.p.** 195–197 °C (decomp.); **¹H NMR** (600 MHz, CD₂Cl₂) δ 8.51 (d, *J* = 5.9 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 5.6 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 2.33 (s, 3H), 1.59 (s, 15H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 169.1, 165.8, 153.4, 153.0, 150.0, 137.6, 137.5, 127.7, 125.8, 125.7 (q, *J* = 270.5 Hz), 124.8 (d, *J* = 30.3 Hz), 123.7 (q, *J* = 3.8 Hz), 90.0, 19.0, 8.9; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -62.0; **IR** (cm⁻¹) 2912, 1767, 1644, 1588, 1320, 1096, 1073, 867, 758; **HRMS** (ESI) *m/z* calcd. for C₂₅H₂₆F₃IrN₂O₃Na⁺ [M+Na]⁺: 675.1417, found: 675.1418.

Ir3b



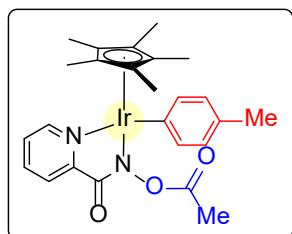
The reaction was conducted with 0.2 mmol of **Ir1a** and 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane. Yellow solid (69.7 mg, 56%); **m.p.** 175–177 °C (decomp.); **¹H NMR** (600 MHz, CD₂Cl₂) δ 8.48 (d, *J* = 5.6 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 6.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H), 1.58 (s, 15H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 169.0, 165.9, 152.9, 150.0, 144.3, 138.4, 137.3, 128.9, 127.6, 127.5, 125.7, 89.8, 18.9, 8.8; **IR** (cm⁻¹) 2911, 1766, 1643, 1601, 1361, 1183, 1004, 867, 757, 680; **HRMS** (ESI) *m/z* calcd. for C₂₄H₂₆ClIrN₂O₃Na⁺ [M+Na]⁺: 641.1153, found: 641.1146.

Ir3c



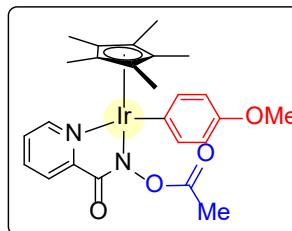
The reaction was conducted with 0.43 mmol of **Ir1a** and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane. Yellow solid (78.4 mg, 31%); **m.p.** 168–170 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.50 (d, *J* = 6.9 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 8.4 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 2.33 (s, 3H), 1.58 (s, 15H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 169.2, 165.8, 153.1, 150.0, 146.1, 137.1, 137.1, 127.8, 127.4, 125.8, 122.8, 89.8, 19.0, 8.9; **IR** (cm⁻¹) 2903, 1765, 1642, 1601, 1460, 1360, 1184, 1065, 798, 680, 650; **HRMS** (ESI) *m/z* calcd. for C₂₄H₂₇IrN₂O₃Na⁺ [M+Na]⁺: 607.1543, found: 607.1547.

Ir3d



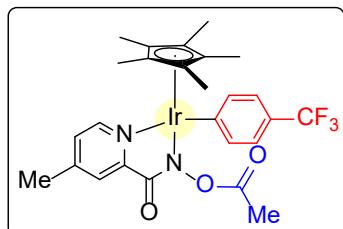
The reaction was conducted with 0.43 mmol of **Ir1a** and 5,5-dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane. Yellow solid (40.6 mg, 16%); **m.p.** 186–188 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.49 (d, *J* = 5.5 Hz, 1H), 7.84 (d, *J* = 6.1 Hz, 1H), 7.76 (t, *J* = 8.4 Hz, 1H), 7.42 (ddd, *J* = 7.4, 5.6, 1.7 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H) δ 2.33 (s, 1H), 2.16 (s, 1H), 1.59 (s, 5H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 169.2, 165.9, 153.0, 150.0, 141.5, 137.0, 136.8, 131.9, 128.7, 127.3, 125.8, 89.7, 20.7, 19.0, 8.9; **IR** (cm⁻¹) 2914, 1767, 1642, 1601, 1361, 1183, 996, 758, 729, 616; **HRMS** (ESI) *m/z* calcd. for C₂₅H₂₉IrN₂O₃Na⁺ [M+Na]⁺: 621.1700, found: 621.1700.

Ir3e



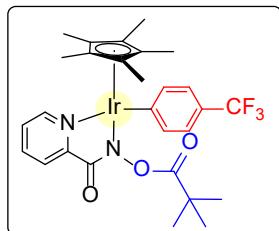
The reaction was conducted with 0.43 mmol of **Ir1a** and 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane. Yellow solid (72.6 mg, 28%); **m.p.** 148–150 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.49 (d, *J* = 5.5 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 8.4 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 8.7 Hz, 2H), 3.63 (s, 3H), 2.33 (s, 3H), 1.59 (s, 15H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 169.2, 165.9, 156.7, 153.0, 150.0, 137.0, 137.0, 134.7, 127.3, 125.8, 113.9, 89.7, 55.1, 19.0, 8.9; **IR** (cm⁻¹) 2911, 1765, 1642, 1601, 1482, 1461, 1361, 1176, 1025, 996, 812; **HRMS** (ESI) *m/z* calcd. for C₂₅H₂₉IrN₂O₄Na⁺ [M+Na]⁺: 637.1649, found: 637.1657.

Ir3f



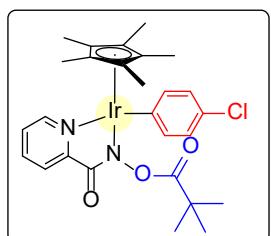
The reaction was conducted with 0.45 mmol of **Ir1c** and 5,5-dimethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborinane. Yellow solid (152 mg, 51%); **m.p.** 174–176 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.33 (d, *J* = 5.8 Hz, 1H), 7.71 (d, *J* = 2.1 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 5.8, 2.3 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 2.44 (s, 3H), 2.33 (s, 3H), 1.58 (s, 15H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 169.1, 165.9, 153.8, 152.3, 150.1, 149.4, 137.7, 128.6, 126.7, 125.7 (q, *J* = 269.1 Hz), 124.7 (q, *J* = 31.3 Hz), 123.6 (q, *J* = 3.9 Hz), 89.8, 21.2, 19.0, 8.9; **¹⁹F NMR** (471 MHz, CD₂Cl₂) δ -62.0; **IR** (cm⁻¹) 2917, 1770, 1646, 1616, 1588, 1451, 1319, 1187, 1073, 954; **HRMS** (ESI) *m/z* calcd. for C₂₆H₂₈F₃IrN₂O₃Na⁺ [M+Na]⁺: 689.1573, found: 689.1580.

Ir3g



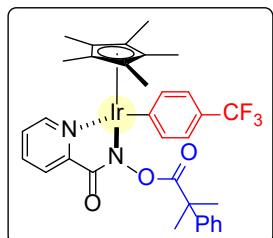
The reaction was conducted with 0.3 mmol of **Ir1b** and 5,5-dimethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborinane. Yellow solid (92.1 mg, 44%); **m.p.** 172–174 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.53 (d, *J* = 5.6 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 1.60 (s, 15H), 1.45 (s, 9H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 175.9, 165.0, 153.2, 153.1, 149.8, 137.7, 137.5, 127.5, 126.0 (q, *J* = 270.0 Hz), 125.8, 124.8 (q, *J* = 31.4 Hz), 123.7 (q, *J* = 3.9 Hz), 91.5, 39.1, 28.0, 9.0; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -62.0; **IR** (cm⁻¹) 2915, 1749, 1647, 1589, 1320, 1095, 1073, 1011, 820; **HRMS** (ESI) *m/z* calcd. for C₂₈H₃₂F₃IrN₂O₃Na⁺ [M+Na]⁺: 717.1886, found: 717.1891.

Ir3h



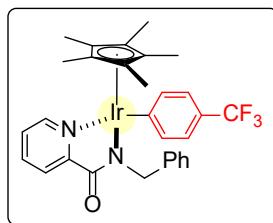
The reaction was conducted with 0.25 mmol of **Ir1b** and 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane. Yellow solid (92.1 mg, 44%); **m.p.** 174–176 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.50 (d, *J* = 5.6 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 15.3 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 1.59 (s, 15H), 1.44 (s, 9H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 176.5, 165.7, 153.1, 149.8, 144.1, 138.5, 137.3, 129.0, 127.6, 127.4, 125.8, 89.8, 39.1, 28.0, 9.0; **IR** (cm⁻¹) 2906, 1748, 1645, 1604, 1465, 1086, 1006, 919, 731; **HRMS** (ESI) *m/z* calcd. for C₂₇H₃₂ClIrN₂O₃Na⁺ [M+Na]⁺: 683.1623, found: 683.1625.

Ir3i



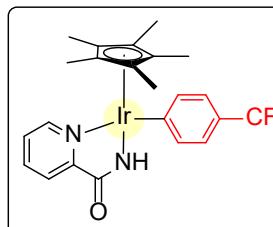
The reaction was conducted with 0.35 mmol of **Ir1d** and 5,5-dimethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborinane. Yellow solid (127 mg, 48%); **m.p.** 181–183 °C (decomp.); **¹H NMR** (400 MHz, CD₂Cl₂) δ 8.51 (d, *J* = 5.5 Hz, 1H), 7.87 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.82 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.42 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 1.86 (s, 3H), 1.80 (s, 3H), 1.44 (s, 15H); **¹³C NMR** (101 MHz, CD₂Cl₂) δ 174.8, 165.2, 153.1, 153.1, 149.7, 144.8, 137.7, 137.5, 128.6, 127.5, 127.2, 127.0, 125.9, 125.7 (q, *J* = 271.5 Hz), 124.8 (q, *J* = 31.4 Hz), 123.6 (d, *J* = 3.7 Hz), 90.0, 46.5, 27.6, 27.0, 8.8; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -62.0; **IR** (cm⁻¹) 2974, 2912, 1754, 1646, 1589, 1320, 1085, 820; **HRMS** (ESI) *m/z* calcd. for C₃₃H₃₄F₃IrN₂O₃Na⁺ [M+Na]⁺: 779.2043, found: 779.2042

Ir3j



The reaction was conducted with 0.35 mmol of **Ir1e** and 5,5-dimethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborinane. Yellow solid (164 mg, 69%); **m.p.** 159–161 °C (decomp.); **¹H NMR** (400 MHz, CD₂Cl₂) δ 8.61 (d, *J* = 5.5 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 6.5 Hz, 1H), 7.27 (d, *J* = 5.6 Hz, 4H), 7.23 – 7.13 (m, 3H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.53 (d, *J* = 15.2 Hz, 1H), 4.58 (d, *J* = 15.2 Hz, 1H), 1.45 (s, 15H); **¹³C NMR** (101 MHz, CD₂Cl₂) δ 171.3, 155.9, 153.3, 149.6, 141.6, 137.2, 137.2, 128.2, 127.6, 127.2, 126.2, 126.0, 125.7 (q, *J* = 271.1 Hz), 124.5 (q, *J* = 31.4 Hz), 123.5 (q, *J* = 3.7 Hz), 89.4, 54.5, 8.9; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -61.9; **IR** (cm⁻¹) 2907, 1619, 1589, 1560, 1384, 1320, 1152, 1096, 1010, 817; **HRMS** (ESI) *m/z* calcd. for C₃₀H₃₁F₃IrN₂O⁺ [M+H]⁺: 685.2012, found: 685.2026.

Ir5



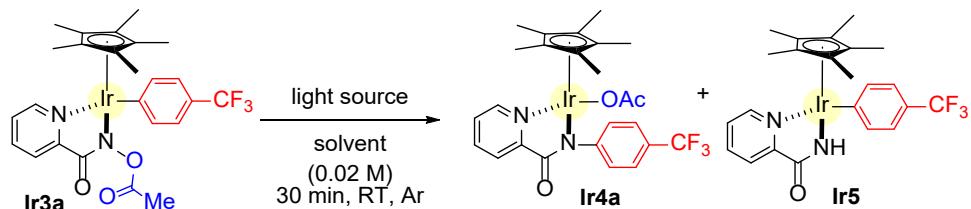
The reaction was conducted with 0.5 mmol of Chloro[(1,2,3,4,5- η)-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl](2-pyridinecarboxamidato- $\kappa N^1,\kappa N^2$) iridium^[5] and 5,5-dimethyl-2-[4-(trifluoromethyl)phenyl]-1,3,2-dioxaborinane. Yellow solid (53.5 mg, 9%); **m.p.** 300–302 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.60 (d, *J* = 5.5 Hz, 1H), 7.78 (d, *J* = 3.8 Hz, 2H), 7.43 (dd, *J* = 9.3, 5.4 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.81 (br, 1H), 1.61 (s, 15H); **¹³C NMR** (101 MHz, CD₂Cl₂) δ 172.3, 155.0, 154.5, 150.1, 138.0, 137.4, 127.4, 125.8, 125.8 (q, *J* = 272.3 Hz), 124.3 (q, *J* = 31.4 Hz), 123.5 (q, *J* = 3.9 Hz), 88.5, 8.9; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -61.9; **IR** (cm⁻¹) 3179, 2916, 1634, 1599, 1585, 1319, 1149, 1111, 1096, 849, 777, 560; **HRMS** (ESI) *m/z* calcd. for C₂₃H₂₄F₃IrN₂O⁺ [M+Na]⁺: 617.1362, found: 617.1369.

3. Procedures for the photoinduced group transposition reactions

3-1. Optimization of reaction conditions

To a pre-dried 4 mL teflon-lined vial equipped with a stir bar were added **Ir3a** (0.01 mmol) and anhydrous solvent (0.02 M, 0.5 mL) under Ar atmosphere. The vial was sealed with a cap, and equipped in a Merck Penn PhD photoreactor M2.^[6] The reaction mixture was irradiated for 30 min (450 nm, 100% intensity) and maintained at room temperature. After completion, the solvent was removed under reduced pressure, and the product yield was determined using ¹H NMR analysis in the presence of 1,1,2-trichloroethane as an internal standard in CD₂Cl₂ (delivered as 0.1 M stock solution in CD₂Cl₂). Detailed reaction optimization conditions are shown in Table S1.

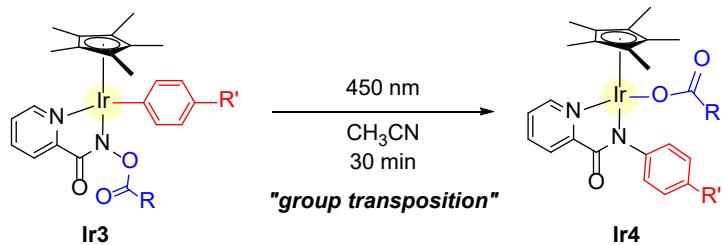
Table S1. Optimization of photoinduced group transposition reaction of **Ir3a**.



Entry	Light source*	Solvent	Ir4a (%)	Ir5 (%)	Remaining Ir3a (%)
1	450 nm	MeCN	87%	<5%	<5%
2	dark, RT, 12 h	MeCN	<5%	<5%	>95%
3	80 °C heating, dark, 16 h	MeCN	8%	<5%	74%
4	450 nm	Acetone	52%	30%	<5%
5	450 nm	MeOH	10%	88%	<5%
6	450 nm	THF	<5%	20%	51%
7	450 nm	EtOAc	<5%	28%	58%
8	450 nm	CH ₂ Cl ₂	<5%	44%	<5%
9	450 nm	benzene	<5%	19%	42%
10	420 nm	MeCN	78%	8%	<5%
11	365 nm	MeCN	77%	9%	<5%
12	456 nm, Kessil LED (50%)	MeCN	70%	17%	<5%
13	450 nm	MeCN (0.04 M)	65%	19%	<5%
14	450 nm	MeCN (0.1 M)	44%	25%	<5%

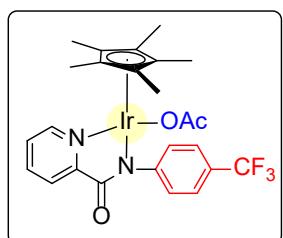
*If otherwise noted, Merck Penn PhD Photoreactor M2 (100% intensity) was used as the light source.

3-2. Procedure for photoinduced group transposition reactions



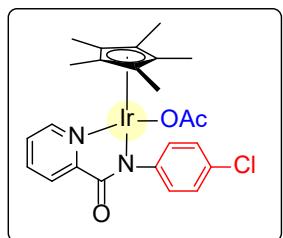
To a pre-dried 8 mL teflon-lined vial equipped with a stir bar were added **Ir3** (0.05 mmol) and anhydrous CH₃CN (0.02 M, 2.5 mL) under Ar atmosphere. The vial was sealed with a cap, and equipped in a Merck Penn PhD photoreactor M2.^[6] The reaction mixture was irradiated for 30 min (450 nm, 100% intensity) and maintained at room temperature. After completion, the solvent was removed under reduced pressure, and **Ir4** was isolated by recrystallization in CH₂Cl₂/n-pentane.

Ir4a



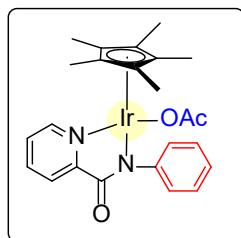
Yellow solid (26.7 mg, 82%); **m.p.** 242–244 °C (decomp.); **¹H NMR** (600 MHz, CD₂Cl₂) δ 9.10 (d, *J* = 4.8 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 1.83 (s, 3H), 1.36 (s, 15H); **¹³C NMR** (101 MHz, CD₂Cl₂) δ 177.2, 169.4, 155.5, 152.6, 152.2, 139.0, 127.7, 126.9, 126.0, 125.9 (q, *J* = 32.0 Hz), 125.5 (q, *J* = 3.9 Hz), 125.2 (q, *J* = 270.6 Hz), 85.6, 23.9, 8.8; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -62.1; **IR** (cm⁻¹) 2973, 1616, 159, 1413, 1365, 1316, 1116, 1104, 949, 844, 752; **HRMS** (ESI) *m/z* calcd. for C₂₃H₂₃F₃IrN₂O⁺ [M–OAc]⁺: 593.1386, found: 593.1389.

Ir4b



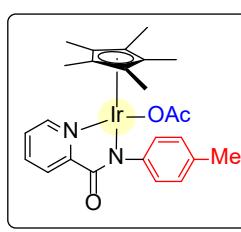
Yellow solid (27.9 mg, 90%); **m.p.** 240–242 °C (decomp.); **¹H NMR** (400 MHz, CD₂Cl₂) δ 9.07 (d, *J* = 5.5 Hz, 1H), 8.01 (d, *J* = 9.5 Hz, 1H), 7.91 (t, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 1.82 (s, 3H), 1.37 (s, 15H); **¹³C NMR** (101 MHz, CD₂Cl₂) δ 177.0, 169.3, 155.7, 152.1, 147.8, 138.8, 129.2, 128.8, 128.4, 126.7, 125.8, 85.5, 23.9, 8.9; **IR** (cm⁻¹) 2962, 1615, 1596, 1484, 1316, 1291, 1171, 831, 752; **HRMS** (ESI) *m/z* calcd. for C₂₂H₂₃ClIrN₂O⁺ [M–OAc]⁺: 559.1123, found: 559.1120.

Ir4c



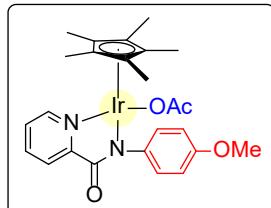
Yellow solid (20.3 mg, 70%); **m.p.** 245–247 °C (decomp.); **¹H NMR** (600 MHz, CD₂Cl₂) δ 9.07 (d, *J* = 5.6 Hz, 1H), 8.02 (d, *J* = 6.9 Hz, 1H), 7.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.50 (d, *J* = 6.8 Hz, 2H), 7.46 (ddd, *J* = 7.3, 5.6, 1.6 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 1.83 (s, 3H), 1.36 (s, 15H); **¹³C NMR** (151 MHz, CD₂Cl₂) δ 177.0, 169.3, 156.2, 152.1, 149.2, 138.7, 128.4, 127.4, 126.5, 125.8, 124.4, 85.5, 24.0, 8.8; **IR** (cm⁻¹) 2911, 1618, 1581, 1489, 1360, 1308, 1290, 1029, 767, 734; **HRMS** (ESI) *m/z* calcd. for C₂₂H₂₄IrN₂O⁺ [M–OAc]⁺: 525.1512, found: 525.1514.

Ir4d



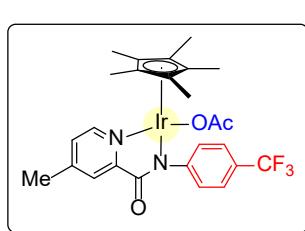
The reaction was conducted for 3h. Yellow solid (26.3 mg, 88%); **m.p.** 231–233 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 9.05 (d, *J* = 5.7 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.90 (td, *J* = 7.6, 1.5 Hz, 1H), 7.45 (ddd, *J* = 7.4, 5.6, 1.7 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 1.82 (s, 3H), 1.36 (s, 15H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 177.0, 169.4, 156.2, 152.0, 146.5, 138.7, 133.9, 129.0, 127.1, 126.4, 125.7, 85.4, 24.0, 21.2, 8.8; **IR** (cm⁻¹) 2912, 1615, 1593, 1507, 1363, 1316, 1289, 1031; **HRMS** (ESI) *m/z* calcd. for C₂₃H₂₆IrN₂O⁺ [M–OAc]⁺: 539.1669, found: 539.1674.

Ir4e



The reaction was conducted for 3h. Yellow solid (16.5 mg, 54%); **m.p.** 242–244 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 9.05 (d, *J* = 6.3 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.95 – 7.86 (m, 1H), 7.48 – 7.43 (m, 1H), 7.43 – 7.38 (m, 2H), 6.94 – 6.86 (m, 2H), 3.82 (s, 3H), 1.82 (s, 3H), 1.37 (s, 15H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 177.0, 169.5, 156.7, 156.2, 152.0, 142.3, 138.7, 128.1, 126.4, 125.7, 113.6, 85.5, 55.8, 24.0, 8.8; **IR** (cm⁻¹) 2919, 1614, 1592, 1504, 1470, 1363, 1314, 1232, 1098; **HRMS** (ESI) *m/z* calcd. for C₂₃H₂₆IrN₂O₂⁺ [M–OAc]⁺: 555.1618, found: 555.1619.

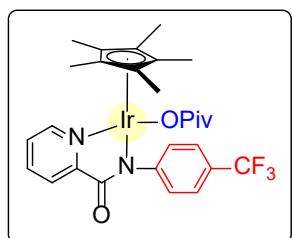
Ir4f



The reaction was conducted in 0.01 M MeCN solution. Yellow solid (25.9 mg, 78%); **m.p.** 230–232 °C (decomp.); **¹H NMR** (400 MHz, CD₂Cl₂) δ 8.91 (d, *J* = 5.7 Hz, 1H), 7.87 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 2.51 (s, 3H), 1.83 (s, 3H), 1.35 (s, 15H); **¹³C NMR** (101 MHz, CD₂Cl₂) δ 176.9, 169.5, 154.9, 152.8, 152.8, 151.5, 127.8, 127.7, 126.7, 125.7 (q, *J* = 32.1 Hz), 125.5 (q, *J* = 4.0 Hz), 125.2 (q, *J* = 270.9 Hz), 85.4,

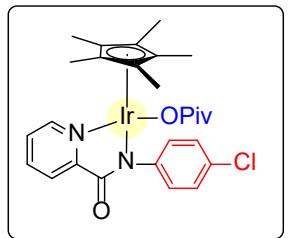
24.0, 21.4, 8.9; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -62.1; **IR** (cm⁻¹) 2922, 1627, 1612, 1591, 1360, 1317, 1156, 1110, 1063; **HRMS** (ESI) *m/z* calcd. for C₂₄H₂₅F₃IrN₂O⁺ [M–OAc]⁺: 607.1543, found: 607.1550.

Ir4g

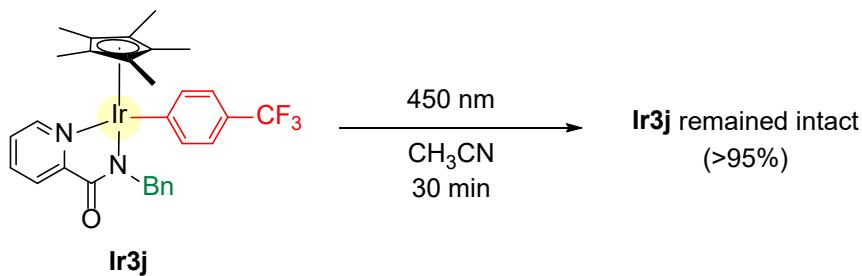


The reaction was conducted in 0.01 M MeCN solution. Yellow solid (22.1 mg, 64%); **m.p.** 250–252 °C (decomp.); **¹H NMR** (400 MHz, CD₂Cl₂) δ 9.04 (d, *J* = 5.5 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 1.38 (s, 15H), 0.85 (s, 9H); **¹³C NMR** (101 MHz, CD₂Cl₂) δ 183.8, 168.9, 155.1, 152.5, 151.6, 138.4, 127.4, 126.1, 125.4 (q, *J* = 32.2 Hz), 125.3, 125.1 (q, *J* = 3.9 Hz), 124.7 (q, *J* = 270.6 Hz), 85.0, 39.1, 28.0, 8.5; **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -62.1; **IR** (cm⁻¹) 2967, 2904, 1615, 1596, 1511, 1361, 1317, 1155, 1110, 1063, 1030; **HRMS** (ESI) *m/z* calcd. for C₂₃H₃₃F₃IrN₂O⁺ [M–OPiv]⁺: 593.1386, found: 593.1421.

Ir4h



The reaction was conducted in 0.005 M MeCN solution. Yellow solid (25.8 mg, 78%); **m.p.** 268–270 °C (decomp.); **¹H NMR** (500 MHz, CD₂Cl₂) δ 9.01 (d, *J* = 5.5 Hz, 1H), 8.01 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.90 (td, *J* = 7.7, 1.5 Hz, 1H), 7.48 (d, *J* = 6.5 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.35 – 7.28 (m, 2H), 1.40 (s, 15H), 0.84 (s, 9H); **¹³C NMR** (126 MHz, CD₂Cl₂) δ 184.2, 169.5, 155.8, 151.9, 148.1, 138.7, 129.3, 128.9, 128.4, 126.4, 125.7, 85.4, 39.5, 28.5, 8.9; **IR** (cm⁻¹) 2946, 1619, 1597, 1564, 1484, 1359, 1317, 1210, 1146, 1083, 1030; **HRMS** (ESI) *m/z* calcd. for C₂₂H₂₃ClIrN₂O⁺ [M–OPiv]⁺: 559.1123, found: 559.1129.



As a control experiment, when an Ir–Ar complex **Ir3j** (0.05 mmol, 34.2 mg) without an N–O bond is subjected to the current photochemical reaction conditions, we could not find any aryl migration outcome, where the starting complex remained intact (>95%, by ¹H NMR analysis with 1,1,2-trichloroethane as an internal standard).

4. Mechanistic experiments

4-1. UV-Vis measurement

UV-Vis spectra were measured using a Shimadzu UV-2600 spectrophotometer. Samples of **Ir3a** and **Ir4a** were prepared in acetonitrile (200 μ M) in a quartz cuvette (optical path length 1cm) for absorption measurements (Figure S1).

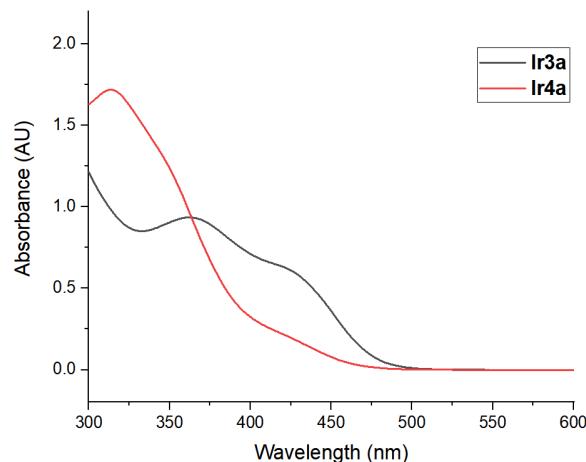


Figure S1. UV-Vis spectra of **Ir3a** and **Ir4a**.

Also, UV-Vis spectra of various $Cp^*\text{Ir}(\text{hydroxamate})(\text{Ar})$ complexes were obtained. When the substituents of the aryl group change (**Ir3a–Ir3e**), we observed redshifts when more electron-withdrawing groups were introduced to the Ir-Ar group (Figure S2 and Table S2). Absorption peaks were analyzed by OriginPro 2019.

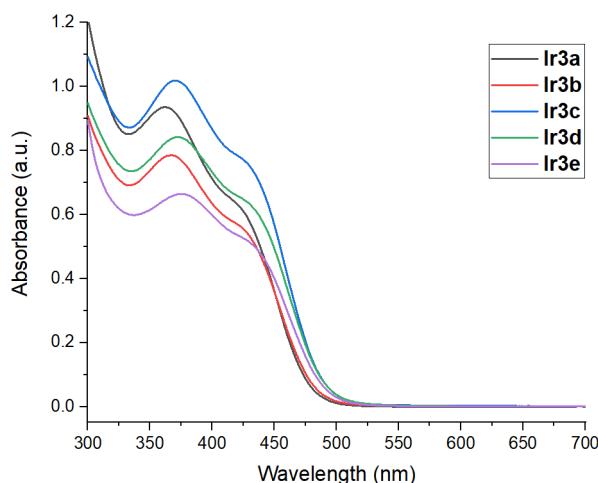
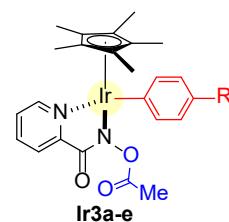


Figure S2. UV-Vis spectra of **Ir3a–Ir3e** (200 μ M MeCN).

Table S2. Two absorption peaks of **Ir3a–Ir3e**.



Entry	λ_{\max} 1	λ_{\max} 2
Ir3a ($R = CF_3$)	361 nm	422 nm
Ir3b ($R = Cl$)	367 nm	423 nm
Ir3c ($R = H$)	369 nm	427 nm
Ir3d ($R = Me$)	371 nm	430 nm
Ir3e ($R = OMe$)	374 nm	428 nm

When changing the OR part of the hydroxamate ligand (**Ir3a** vs **Ir3g**), both complexes showed similar absorption maxima (Figure S3 and Table S3). Finally, when introducing a methyl group at the pyridine part of the hydroxamate ligand (**Ir3a** vs **Ir3f**), we observed a blue shift (Figure S4 and Table S4).

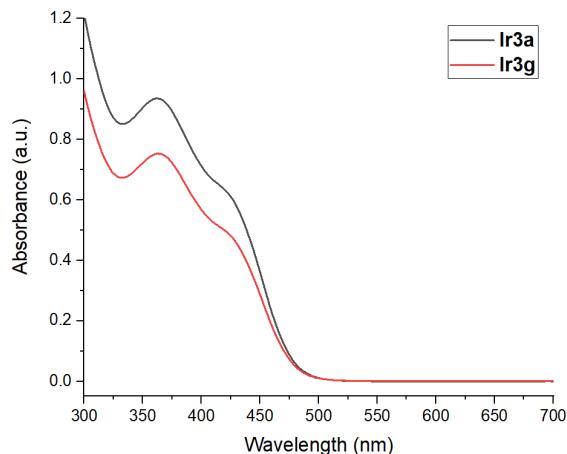
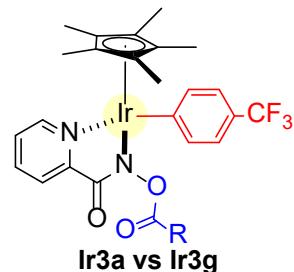


Figure S3. UV–Vis spectra of **Ir3a**,**Ir3g** (200 uM MeCN).

Table S3. Two absorption peaks of **Ir3a**,**Ir3g**.



Entry	λ_{\max} 1	λ_{\max} 2
Ir3a (R = Me)	361 nm	422 nm
Ir3g (R = <i>t</i> Bu)	362 nm	423 nm

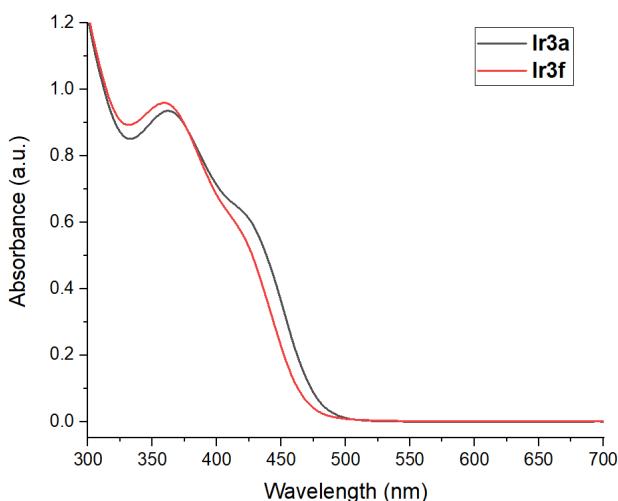
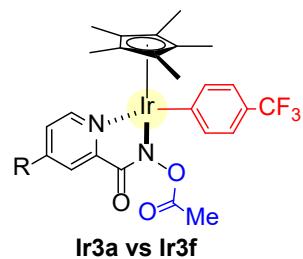


Figure S4. UV–Vis spectra of **Ir3a**,**Ir3f** (200 uM MeCN).

Table S4. Two absorption peaks of **Ir3a**,**Ir3f**.



Entry	λ_{\max} 1	λ_{\max} 2
Ir3a (R = H)	361 nm	422 nm
Ir3f (R = Me)	358 nm	417 nm

Next, the absorption coefficients of **Ir3a**, **Ir4a** and **Ir3j** were calculated at each absorption peak in the visible-light region. For this purpose, we have measured the absorption spectra with different concentrations. A quartz cuvette with a 1 cm pathlength was used (Figures S5–S7).

The absorption coefficient of **Ir3a** was determined as $\varepsilon_{361} = 3358 \text{ cm}^{-1}\text{M}^{-1}$ and $\varepsilon_{422} = 2451 \text{ cm}^{-1}\text{M}^{-1}$.

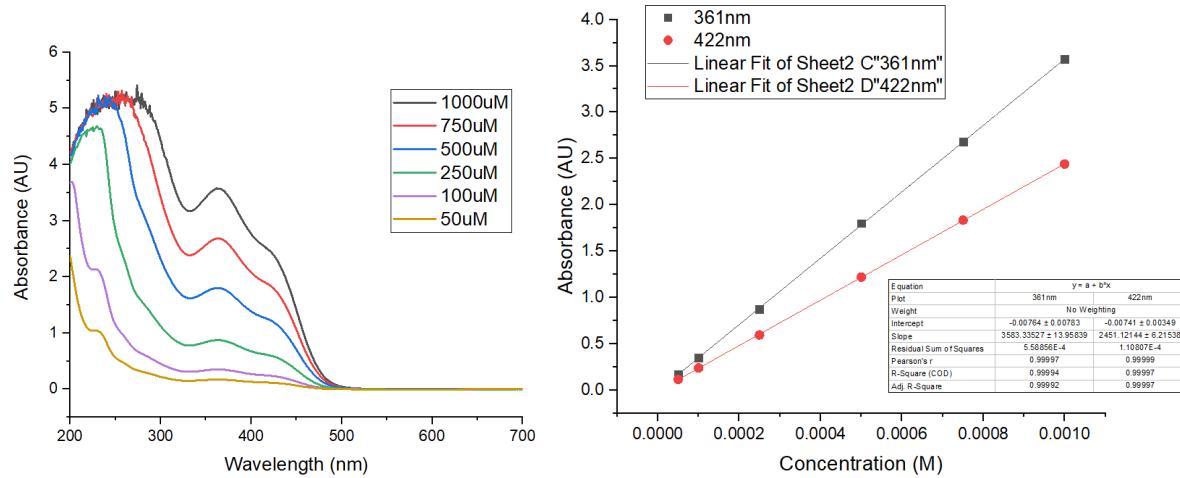


Figure S5. (left) Concentration-dependent UV-Vis spectra of **Ir3a** in MeCN and (right) derivatization of absorption coefficients at 361 nm and 422 nm.

The absorption coefficient of **Ir4a** was determined as $\varepsilon_{313} = 6220 \text{ cm}^{-1}\text{M}^{-1}$, $\varepsilon_{351} = 4362 \text{ cm}^{-1}\text{M}^{-1}$ and $\varepsilon_{427} = 638 \text{ cm}^{-1}\text{M}^{-1}$.

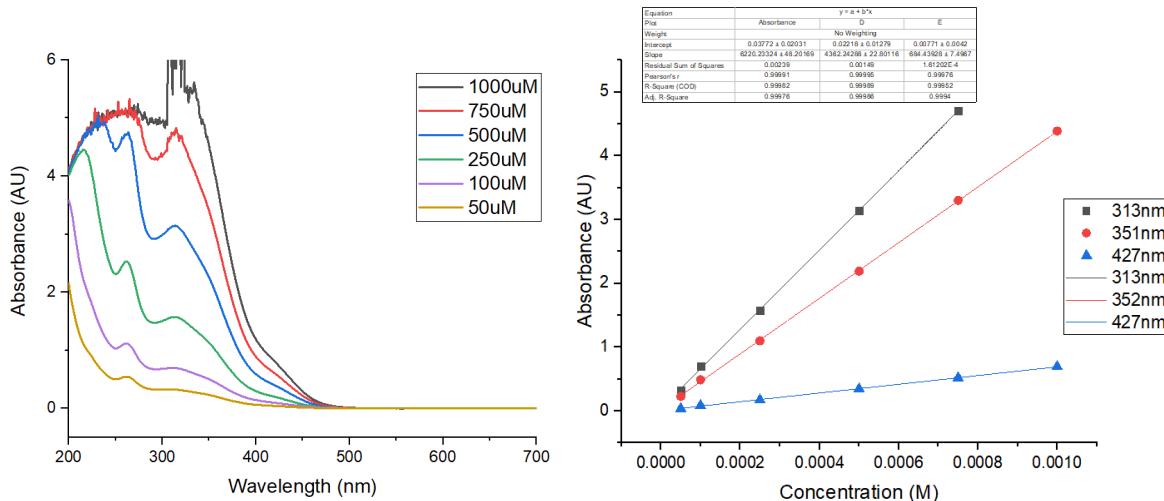


Figure S6. (left) Concentration-dependent UV-Vis spectra of **Ir4a** in MeCN and (right) derivatization of absorption coefficients at 313 nm, 351 nm and 427 nm.

The absorption coefficient of **Ir3j** was determined as $\varepsilon_{363} = 3094 \text{ cm}^{-1}\text{M}^{-1}$ and $\varepsilon_{423} = 2354 \text{ cm}^{-1}\text{M}^{-1}$.

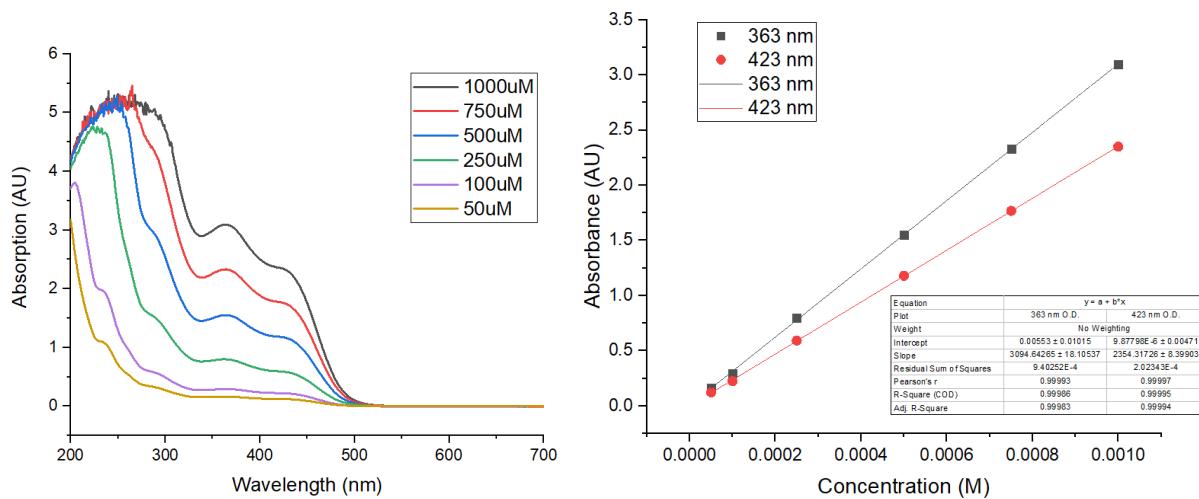


Figure S7. (left) Concentration-dependent UV–Vis spectra of **Ir3j** in MeCN and (right) derivatization of absorption coefficients at 363 and 423 nm.

4-2. Emission and Excitation spectra measurement

- Measurement at 77 K in acetonitrile.

The low-temperature photoluminescence spectrum was collected using Andor SR-750-A-R spectrometer, Andor iVac DR-316B-LDCDD-RES detector, and Changchun New Industries optoelectronics 405 nm laser. **Ir3a** solution in acetonitrile was sampled to an NMR tube, and solidified in a finger dewar at 77 K before measurement. Measurement was conducted with 405 nm excitation with 90% laser intensity, which resulted in a red emission (Figure S8).

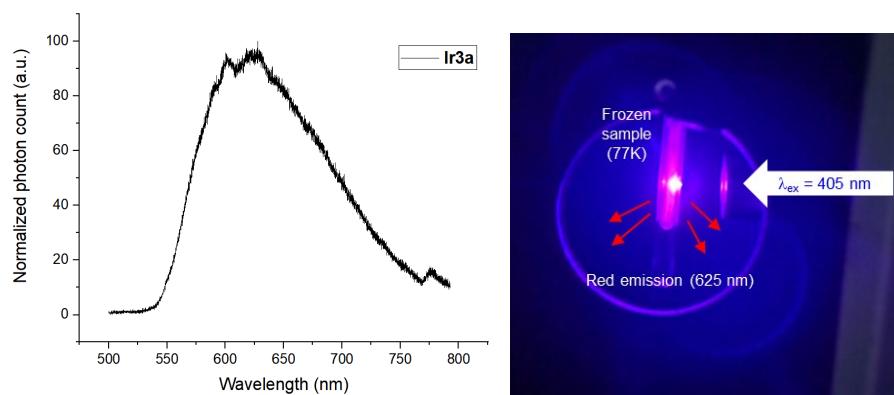


Figure S8. Normalized photoluminescence spectrum of **Ir3a** at 77 K in acetonitrile (left), and a snapshot during measurement (right).

- Measurement at 258.15 K in acetonitrile.

The solution phase emission and excitation spectra were collected using Horiba Fluorolog-QM spectrometer. Solutions of **Ir3a** and **Ir3j** in acetonitrile were sampled to a quartz cuvette and emission spectra were measured at 294.15 K and 258.15 K with 420 nm excitation (Figures S9–S10). To collect excitation spectra, emission at 640 nm was recorded at 258.15 K. Triplet energy of **Ir3a** was estimated via high energy edge approximation (Figure S11).

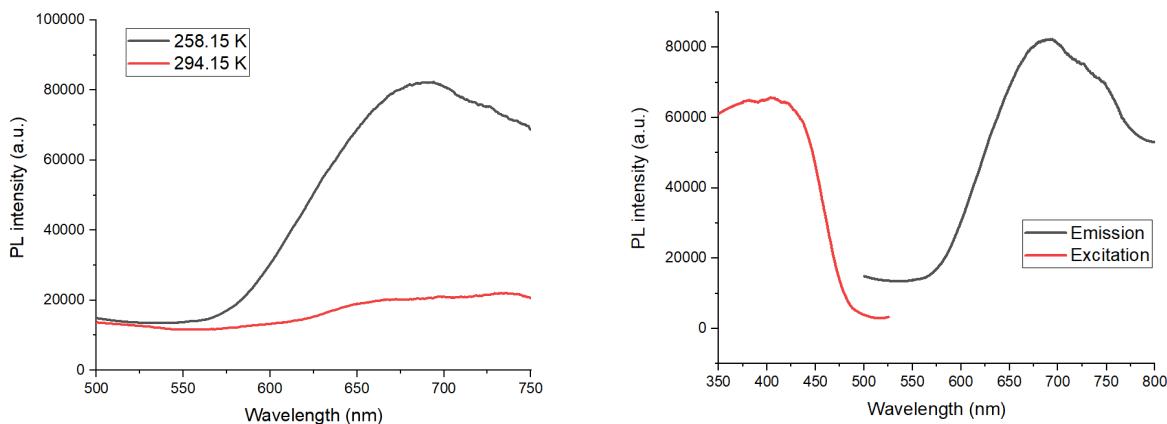


Figure S9. (left) Emission spectra of **Ir3a** at different temperatures and (right) excitation spectrum at 258.15 K in MeCN with $\lambda_{\text{exc}} = 420$ nm, $\lambda_{\text{ems}} = 640$ nm respectively.

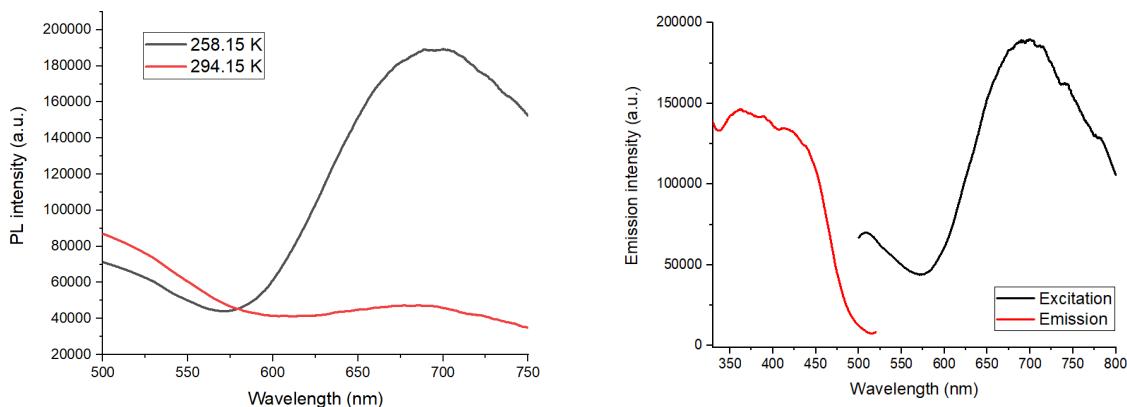


Figure S10. (left) Emission spectra of **Ir3j** at different temperatures and (right) excitation spectrum at 258.15 K in MeCN with $\lambda_{\text{exc}} = 420$ nm, $\lambda_{\text{ems}} = 640$ nm respectively.

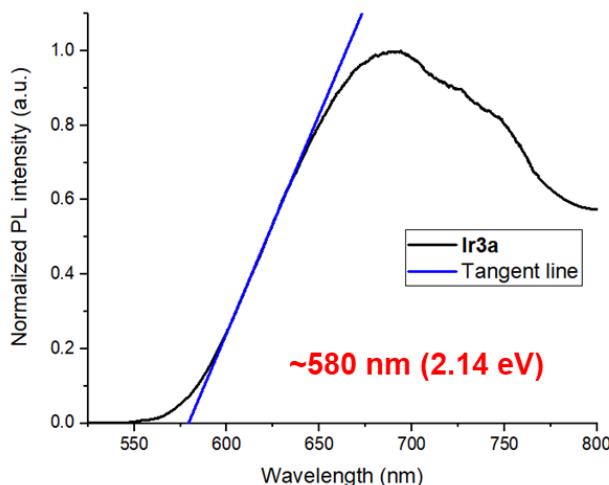


Figure S11. Estimation of triplet energy of **Ir3a** via tangent method.

- Measurement at 77 K in 2-methyl tetrahydrofuran

The phosphorescence spectra of **Ir3a** at 77 K were measured using an intensified charge-coupled device (ICCD, Andor, DH340T). The samples were excited by the 420 nm or 350 nm beam generated from an optical parametric oscillator (Continuum, Horizon I) pumped by a Q-switched Nd:YAG laser (Continuum, Surelite II-10, 355 nm, FWHM of 7 ns).

When photoluminescence was measured with a 420 nm light source at 77 K, we found an emission band at $\lambda_{\text{max}} = 607 \text{ nm}$ (Figure S12). By measuring the photoluminescence with different time delays, we derived the emission lifetime to be 1283 ns (Figure S13).

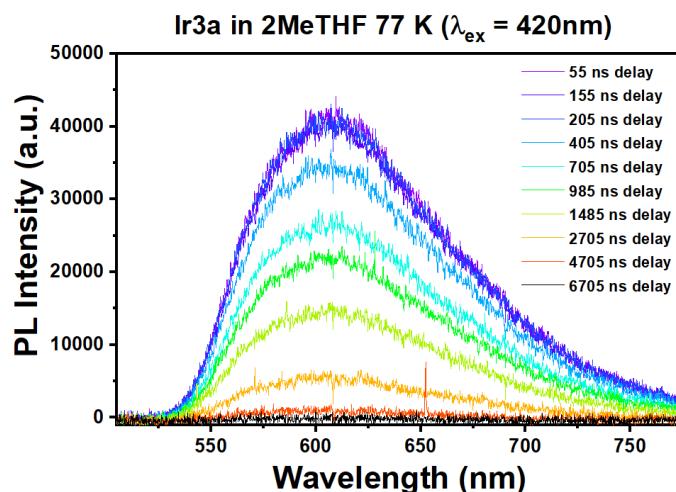


Figure S12. Emission spectra of **Ir3a** at different time delays at 77 K in 2-MeTHF ($\lambda_{\text{exc}} = 420 \text{ nm}$, $\lambda_{\text{ems}} = 607 \text{ nm}$).

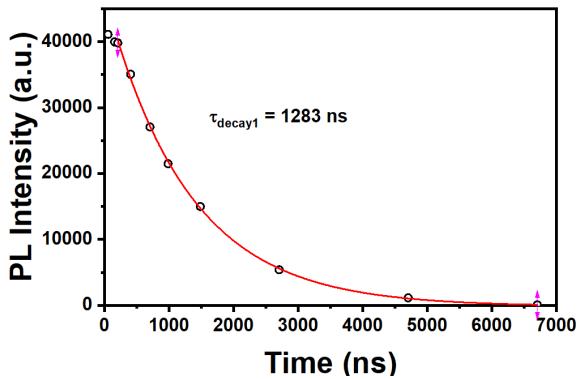


Figure S13. Determination of photoluminescence lifetime of **Ir3a** with $\lambda_{\text{exc}} = 420 \text{ nm}$, $\lambda_{\text{ems}} = 607 \text{ nm}$.

Additionally, when irradiated the sample with a 350 nm laser source, we again observed the emission band at $\lambda_{\text{max}} = 607 \text{ nm}$ (77 K, Figure S14). After the low-temperature measurements, we measured photoluminescence with gradual melting of the sample, we intermittently found a clear red shift of the luminescence peak, where the signal was diminished entirely at room temperature (Figure S15).

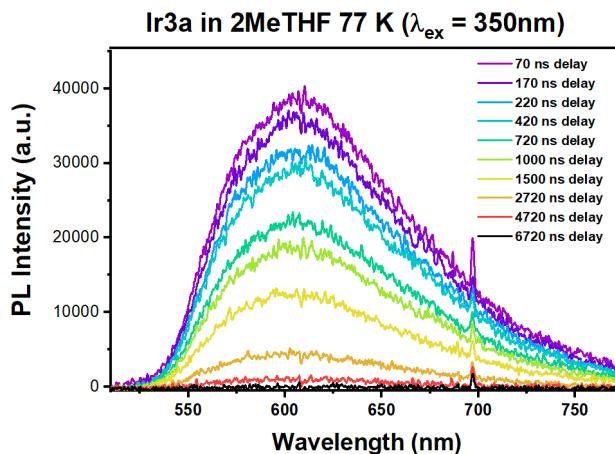


Figure S14. Emission spectra of **Ir3a** at different time delays at 77 K in 2-MeTHF ($\lambda_{\text{exc}} = 350 \text{ nm}$, $\lambda_{\text{ems}} = 607 \text{ nm}$).

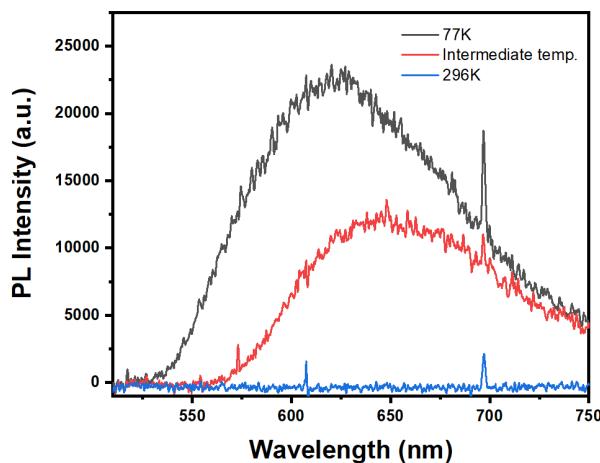
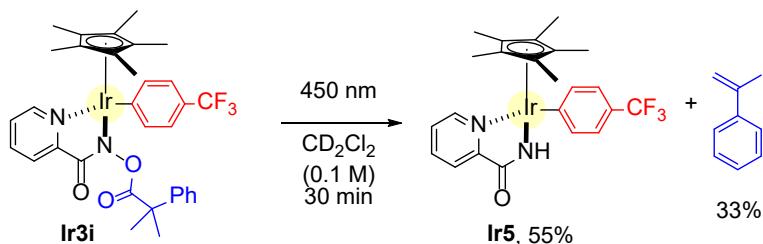


Figure S15. Emission spectra of **Ir3a** with gradual melting of the sample to the room temperature.

4-3. Radical trapping experiments

- Probing radical decarboxylative elimination



To a pre-dried 4 mL teflon-lined vial equipped with a stir bar were added **Ir3i** (0.01 mmol, 7.6 mg) and anhydrous CD₂Cl₂ (0.1 M, 0.1 mL) under Ar atmosphere. The vial was sealed with a cap, and equipped in a Merck Penn PhD photoreactor M2.^[6] The reaction mixture was irradiated for 30 min (450 nm, 100% intensity) and maintained at room temperature. After completion, an internal standard was added (1,1,2-trichloroethane) as 0.1 M stock solution in CD₂Cl₂. Yields of observed products (**Ir5** and α -methylstyrene) were calculated based on ¹H NMR analysis (Figures S16–17).

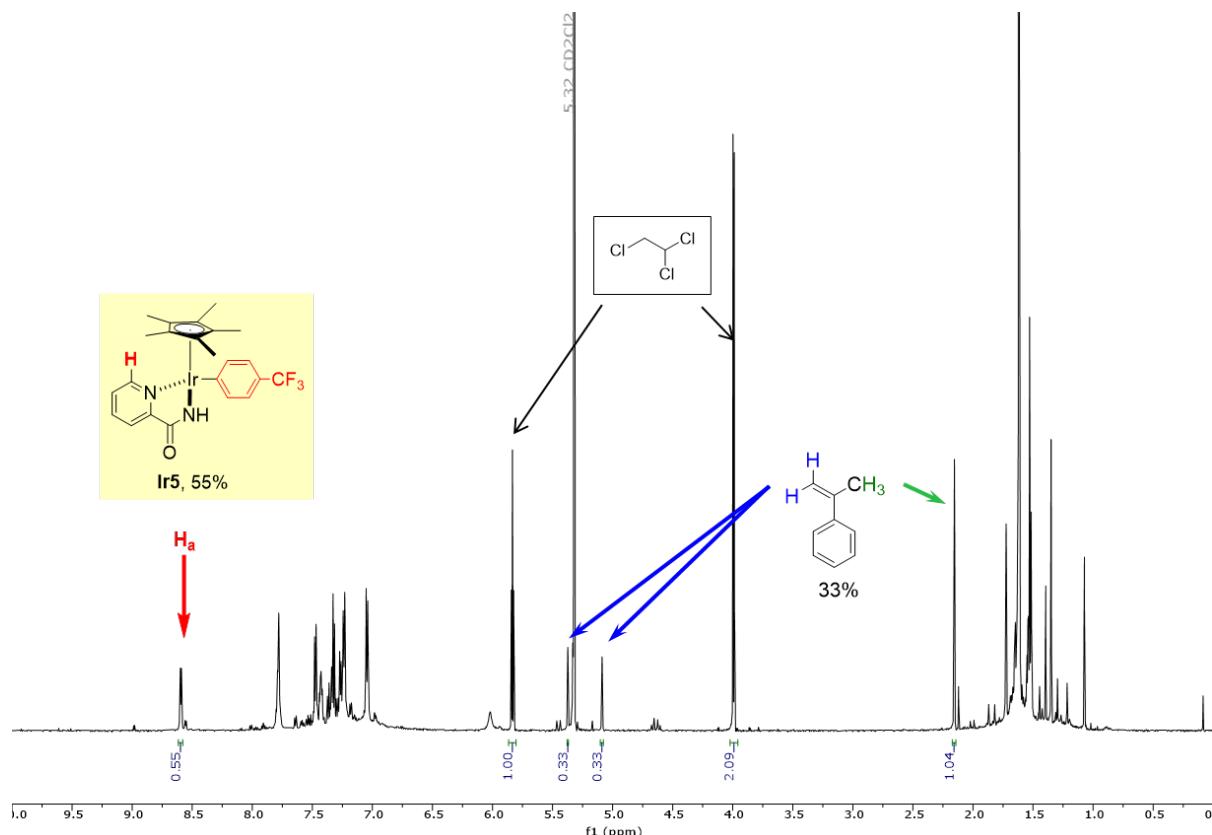


Figure S16. ¹H NMR analysis of the crude mixture of **Ir3i** photolysis (NMR measured in CD₂Cl₂).

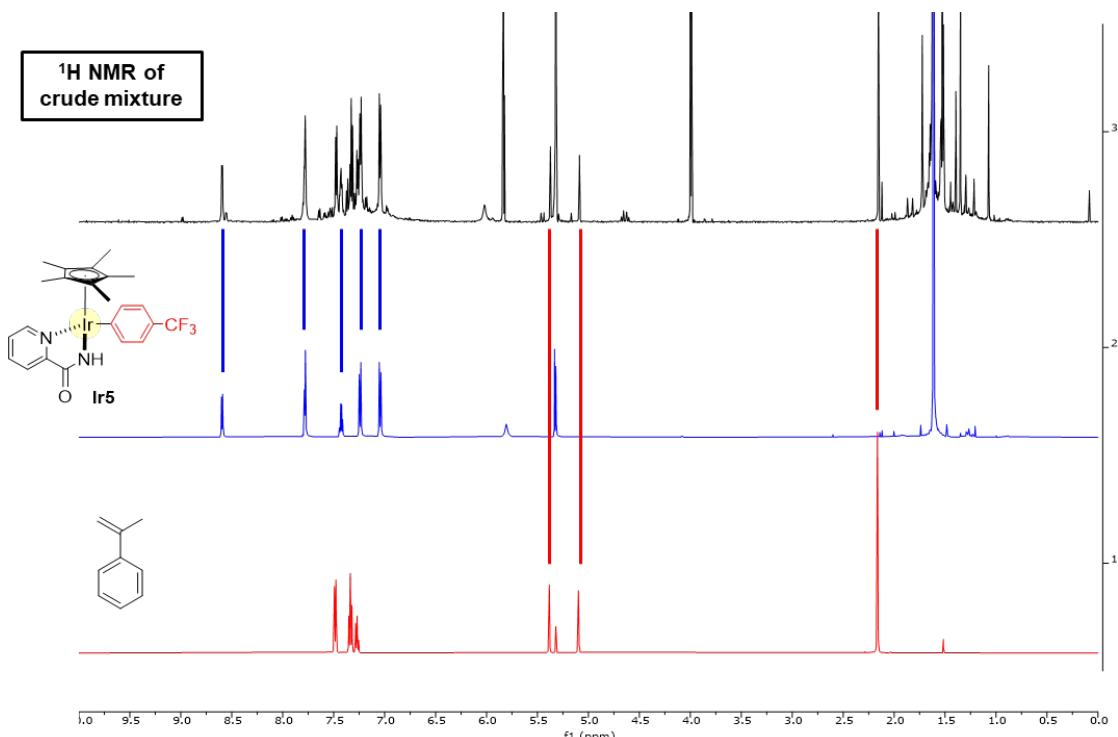
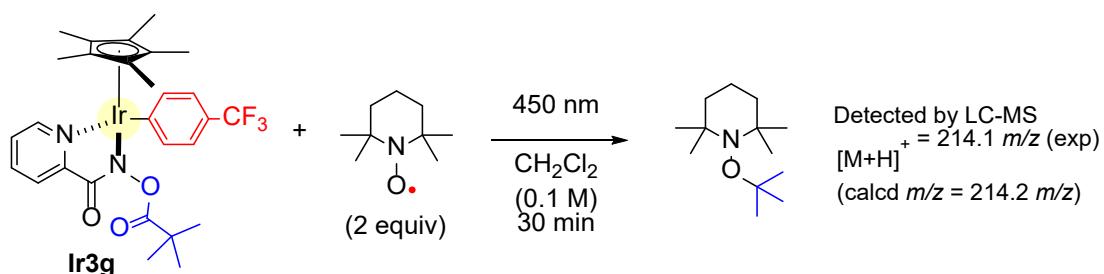


Figure S17. Stacked ¹H NMR spectra of crude mixture, **Ir5**, and α -methyl styrene in CD₂Cl₂.

- Probing radical decarboxylation using TEMPO trap

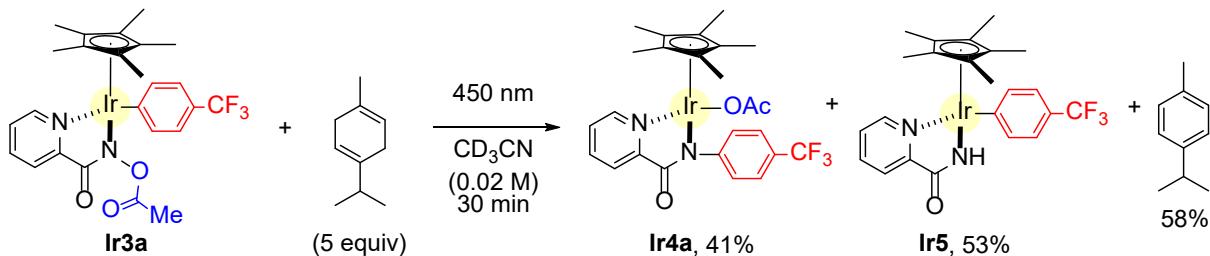


To a pre-dried 4 mL teflon-lined vial equipped with a stir bar were added **Ir3g** (0.01 mmol, 6.9 mg), TEMPO (2 equiv), and anhydrous CH₂Cl₂ (0.1 M, 0.1 mL) under Ar atmosphere. The vial was sealed with a cap, and equipped in a Merck Penn PhD photoreactor M2.^[6] The reaction mixture was irradiated for 30 min (450 nm, 100% intensity) and maintained at room temperature. After completion, the reaction mixture was concentrated, and the crude mixture was analyzed by LC-MS (ESI) with Agilent Poroshell 120 EC-C18 2.7 μ M column. As shown in Figure S18, the *m/z* value of 1-(tert-butoxy)-2,2,6,6-tetramethylpiperidine ($[\text{M}+\text{H}]^+$, calcd *m/z* = 214.2) is observed (exp *m/z* = 214.1).



Figure S18. LC–MS spectrum obtained by TEMPO trapping experiment of **Ir3g**.

- Using γ -terpinene as a radical trap



To a pre-dried 4 mL teflon-lined vial equipped with a stir bar were added **Ir3a** (0.01 mmol, 6.5 mg), γ -terpinene (5 equiv, 8.0 μ L), and anhydrous CD_3CN (0.02 M, 0.5 mL) under Ar atmosphere. The vial was sealed with a cap, and equipped in a Merck Penn PhD photoreactor M2.^[6] The reaction mixture was irradiated for 30 min (450 nm, 100% intensity) and maintained at room temperature. After completion, an internal standard was added (1,1,2-trichloroethane) as 0.1 M stock solution in CD_3CN . Yields of observed products (**Ir4a**, **Ir5**, and *p*-cymene) were calculated based on ^1H NMR analysis (Figures S19–20).

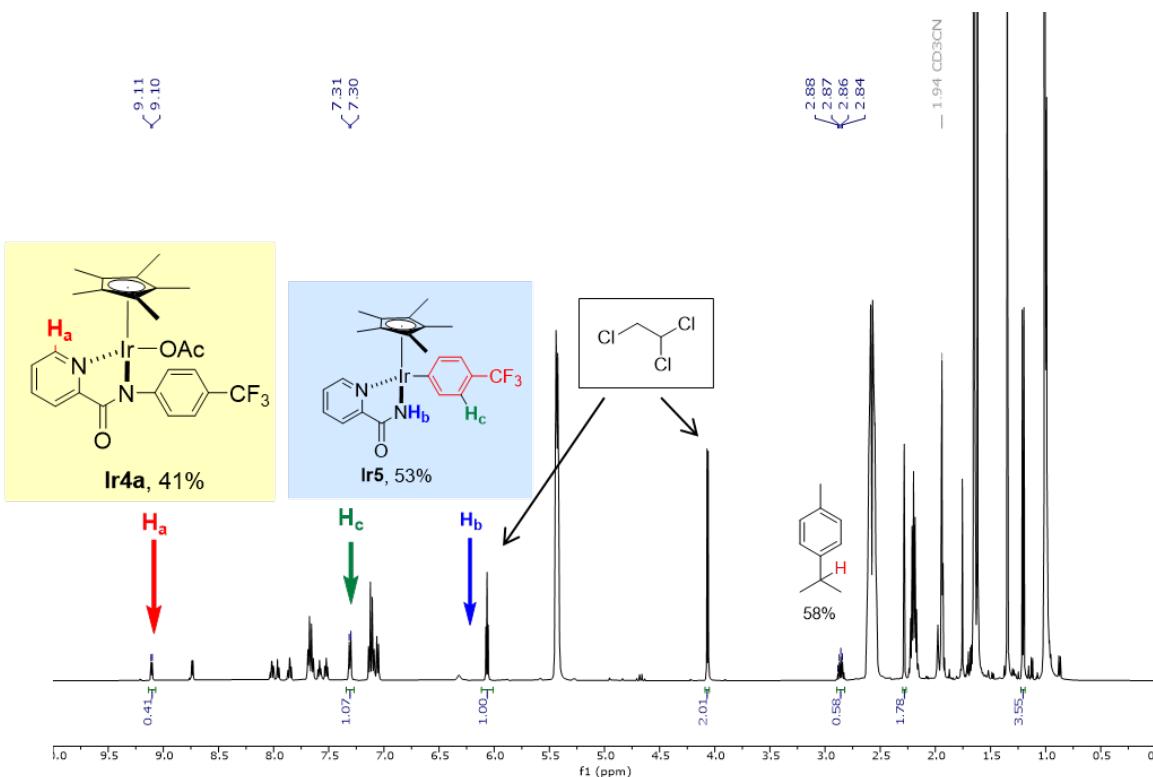


Figure S19. ^1H NMR analysis of the crude mixture from radical trapping experiment with γ -terpinene (NMR measured in CD_3CN).

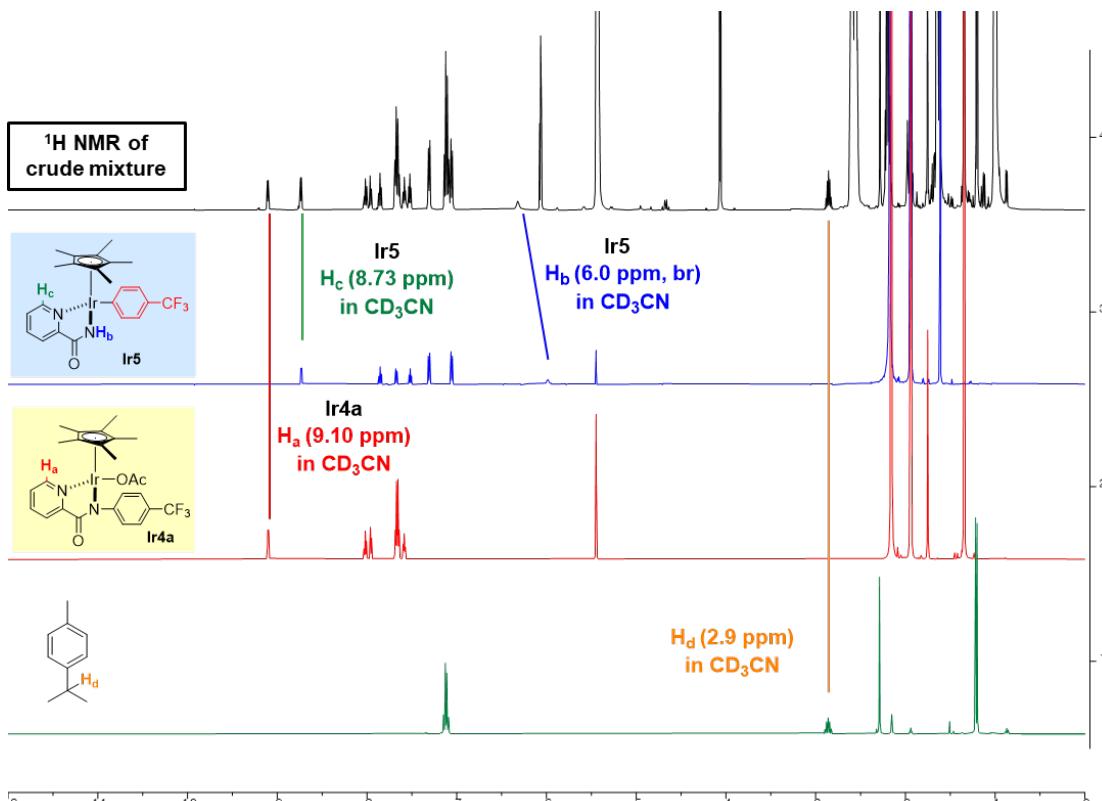
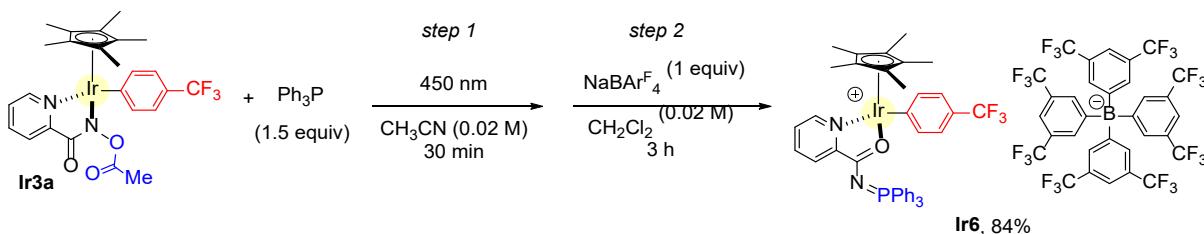


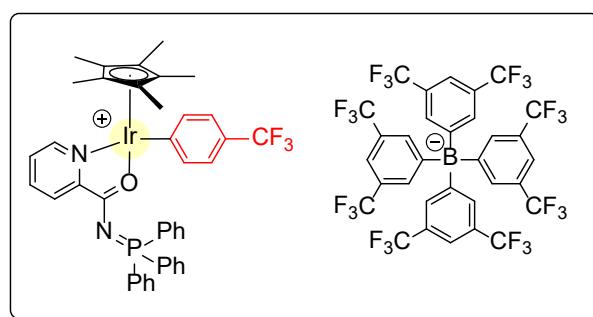
Figure S20. Stacked ^1H NMR spectra of crude mixture, Ir4a, Ir5, and *p*-cymene in CD_3CN .

4-4. Nitrene trapping experiment with triphenylphosphine



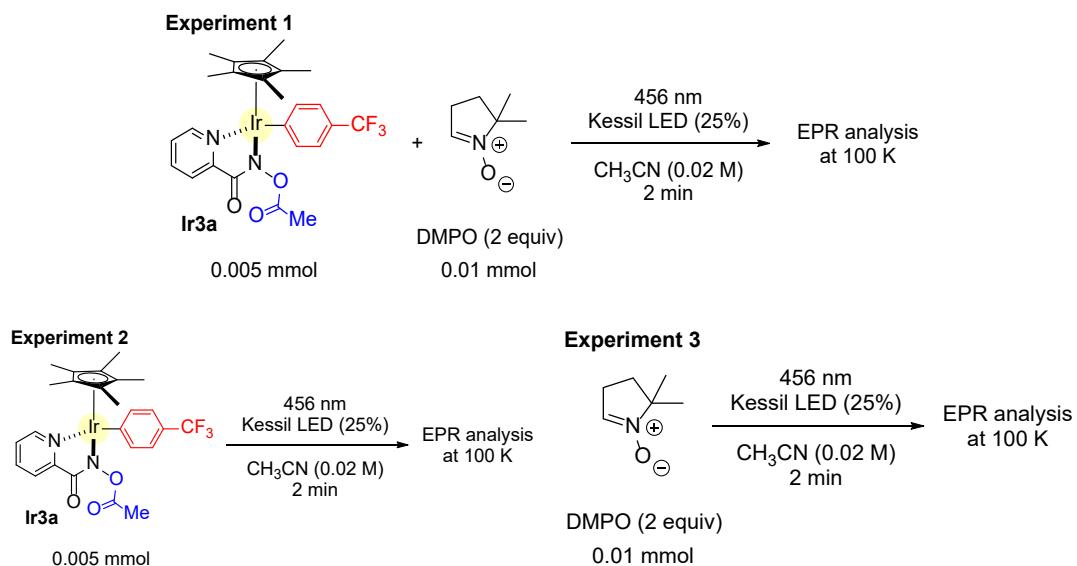
To a pre-dried 4 mL teflon-lined vial equipped with a stir bar were added **Ir3a** (0.05 mmol, 32.6 mg), triphenylphosphine (1.5 equiv, 19.7 mg), and anhydrous CH_3CN (0.02 M, 2.5 mL) under Ar atmosphere. The vial was sealed with a cap, and equipped in a Merck Penn PhD photoreactor M2.^[6] The reaction mixture was irradiated for 30 min (450 nm, 100% intensity) and maintained at room temperature. After completion, the solvent was removed under reduced pressure. To the crude reaction mixture were added sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1 equiv, 44.3 mg) and CH_2Cl_2 (2.5 mL), and the reaction mixture was stirred for 3 h. After completion, the reaction mixture was filtered through a pad of celite with CH_2Cl_2 and purified by recrystallization using a mixture of $\text{CH}_2\text{Cl}_2/n$ -pentane solvent. For structure characterization, crystals were grown with $\text{CH}_2\text{Cl}_2/n$ -pentane solvent mixture for single-crystal X-ray diffraction analysis (see Section 6 for details).

Ir6



Yellow solid (72.1 mg, 84%); **m.p.** 78–80 °C (decomp.); **$^1\text{H NMR}$** (600 MHz, CD_2Cl_2) δ 8.66 (d, $J = 5.5$ Hz, 1H), 8.39 (d, $J = 9.4$ Hz, 1H), 8.00 (td, $J = 7.8, 1.5$ Hz, 1H), 7.80 – 7.75 (m, 9H), 7.74 – 7.73 (m, 8H), 7.73 – 7.71 (m, 1H), 7.62 (td, $J = 7.3, 3.3$ Hz, 6H), 7.56 (s, 4H), 6.94 (d, $J = 8.1$ Hz, 2H), 6.74 (d, $J = 7.9$ Hz, 2H), 1.39 (s, 15H); **$^{13}\text{C NMR}$** (101 MHz, CD_2Cl_2) δ 178.7 (d, $J = 7.4$ Hz), 164.6 – 160.9 (m, BArF_4), 157.6, 152.6 (d, $J = 23.4$ Hz), 149.8 (d, $J = 1.8$ Hz), 138.8, 136.2, 135.7 – 134.8 (m, BArF_4), 134.4 (d, $J = 2.8$ Hz), 133.5 (d, $J = 10.6$ Hz), 130.8, 129.9 (d, $J = 12.9$ Hz), 129.7 – 128.9 (m, BArF_4), 129.3, 125.5 (q, $J = 31.6$ Hz), 125.4 (q, $J = 270.9$ Hz) 125.0 (q, $J = 272.5$ Hz), 124.9 (d, $J = 101.6$ Hz), 124.1 (q, $J = 3.7$ Hz), 119.1 – 116.6 (m, BArF_4), 88.9, 8.7; **$^{19}\text{F NMR}$** (471 MHz, CD_2Cl_2) δ -62.3, -62.9; **$^{31}\text{P NMR}$** (202 MHz, CD_2Cl_2) δ 23.1; **IR** (cm^{-1}) 1540, 1439, 1353, 1323, 1274, 1116, 1012, 886, 745, 712, 526; **HRMS (ESI)** m/z calcd. for $\text{C}_{41}\text{H}_{38}\text{F}_3\text{IrN}_2\text{OP} [\text{M} - \text{BArF}_4]^+$: 855.2303, found: 855.2311.

4-5. EPR (Electron Paramagnetic Resonance) experiment



Under Ar atmosphere, a solution of **Ir3a** (0.005 mmol) and DMPO (5,5-Dimethyl-1-Pyrroline-N-Oxide, 0.01 mmol) was dissolved in 0.25 mL of acetonitrile, and the solution was transferred to a 3 mm EPR tube (Experiment 1). Each **Ir3a** (Experiment 2) and DMPO (0.01 mmol, Experiment 3) solution in acetonitrile was separately sampled in an EPR tube. Each sample was irradiated with a 456 nm Kessil LED lamp (25% intensity) for 2 min at room temperature before being frozen in liquid nitrogen. X-Band EPR spectrum of the frozen sample was collected at 100 K with the following spectrometer settings: g-factor = 2.000, MW frequency = 9.403 GHz, MW power = 2.0 mW, center field = 3359.2 G, sweep width = 200 G, sweep time = 30 s, modulation frequency = 100 kHz, modulation amplitude = 1 G, power attenuation = 25 dB, time constant = 0.01 ms, conversion time = 15 ms, and gain = 30 dB.

To plot the obtained EPR spectra, EasySpin 5.2.35 package^[7] was utilized under MATLAB interface. As summarized in Figure S21, an intense signal was obtained from **experiment 1**, which is the outcome of the irradiation of **Ir3a** and DMPO. In **experiment 2**, where the acetonitrile solution of **Ir3a** was solely irradiated, no signal was detected from the measurement. When irradiating the DMPO solution in acetonitrile (experiment 3), a rhombic signal was found, yet the signal intensity was much lower than that obtained from **experiment 1**. Signals may contain multiple spin systems, as both N-centered radicals and O-centered radicals could be trapped by the DMPO reagent. Hence, we concluded that the photochemically generated open-shell intermediates might be captured via a radical trap DMPO, which provided similar peak patterns to those observed in previous studies.^[8,9]

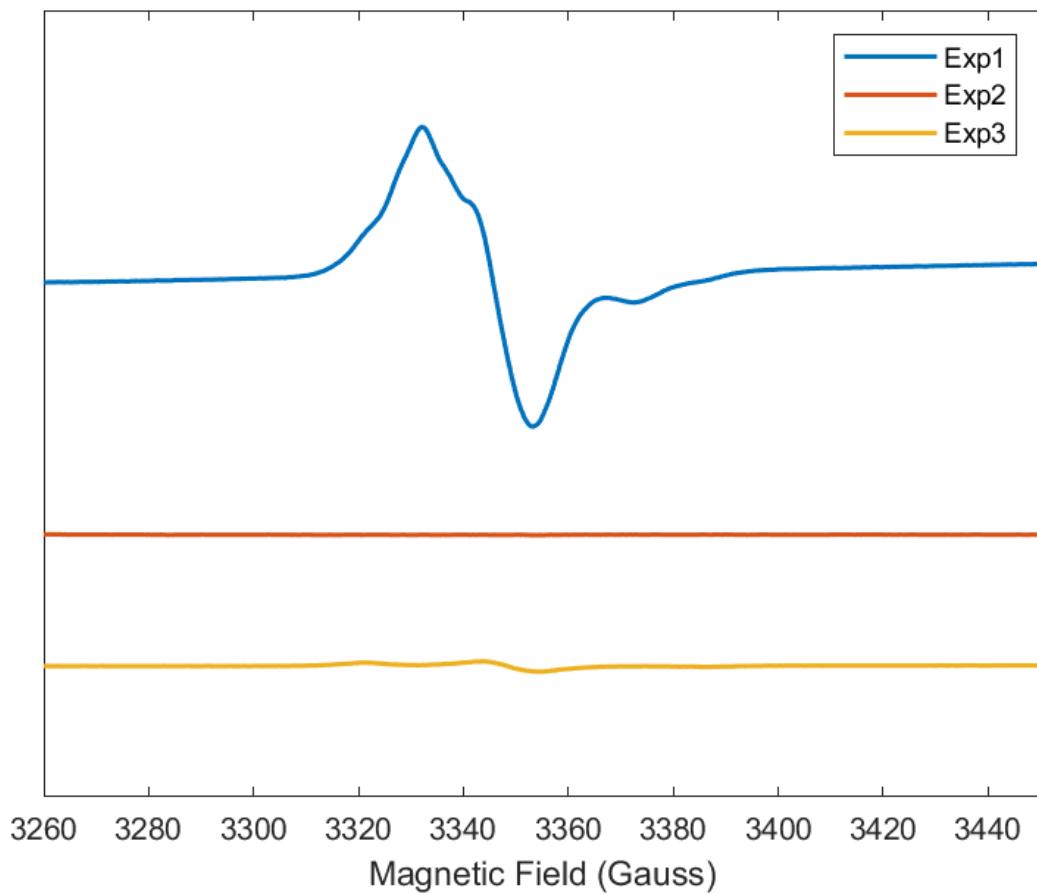
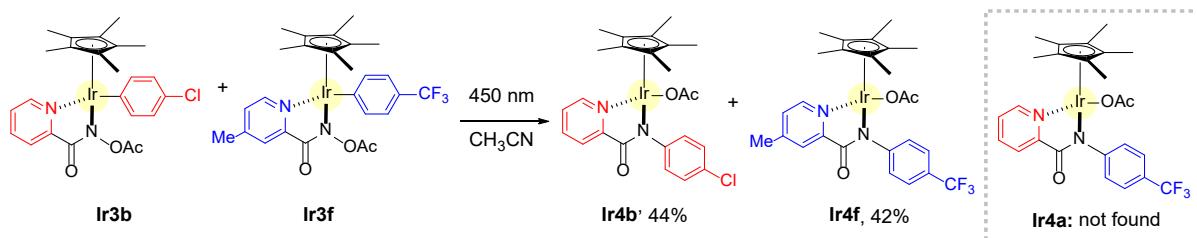


Figure S21. X-Band EPR spectra obtained from experiments 1, 2, and 3.

4-6. Crossover experiments

- Aryl group scrambling experiment



To a pre-dried 8 mL teflon-lined vial equipped with a stir bar were added **Ir3b** (0.025 mmol, 15.5 mg), **Ir3f** (0.025 mmol, 16.6 mg), and anhydrous CH_3CN (0.01 M, 5.0 mL) under Ar atmosphere. The vial was sealed with a cap, and equipped in a Merck Penn PhD photoreactor M2.^[6] The reaction mixture was irradiated for 30 min (450 nm, 100% intensity) and maintained at room temperature. After completion, the solvent was removed under reduced pressure, and yields of observed products (**Ir4b** and **Ir4f**) were calculated based on ^1H NMR analysis with 1,3,5-trimethoxybenzene (0.05 mmol) as an internal standard (Figures S22–23).

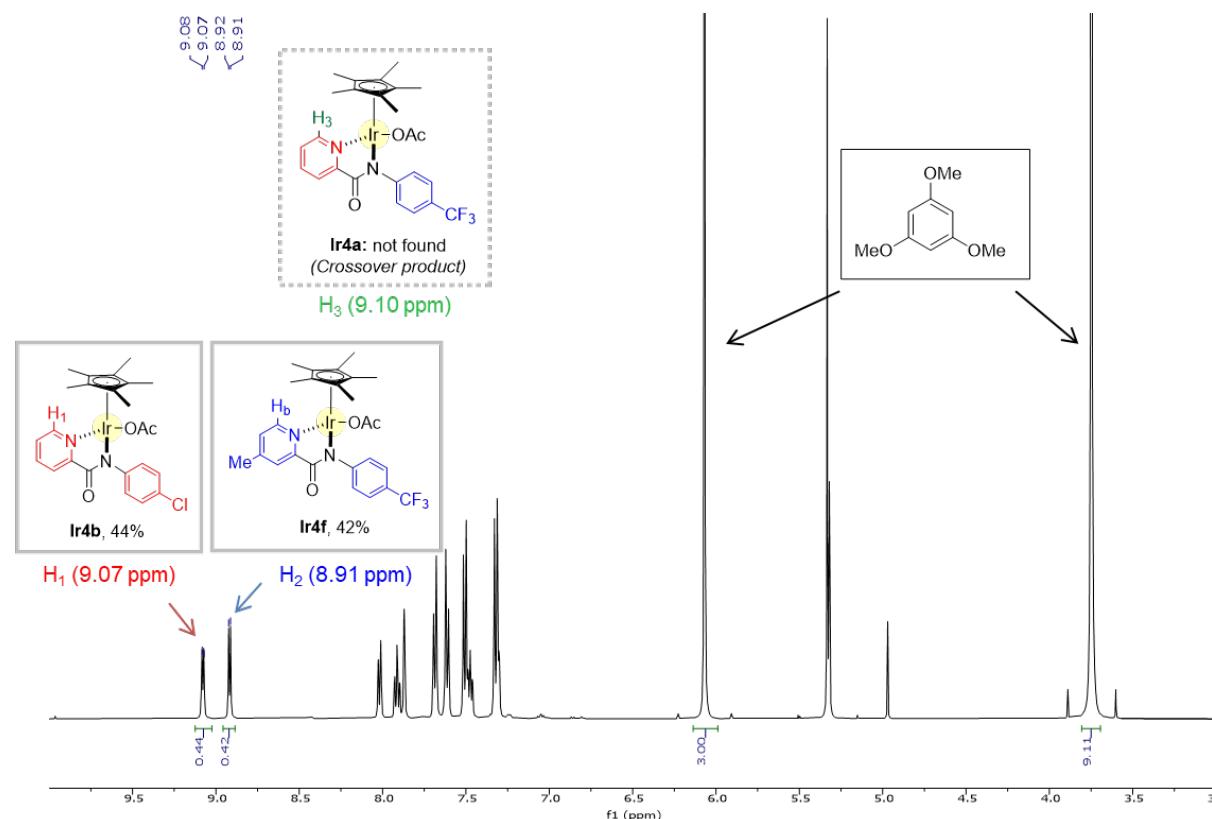


Figure S22. Partial ^1H NMR spectrum obtained from the aryl scrambling crossover experiment.

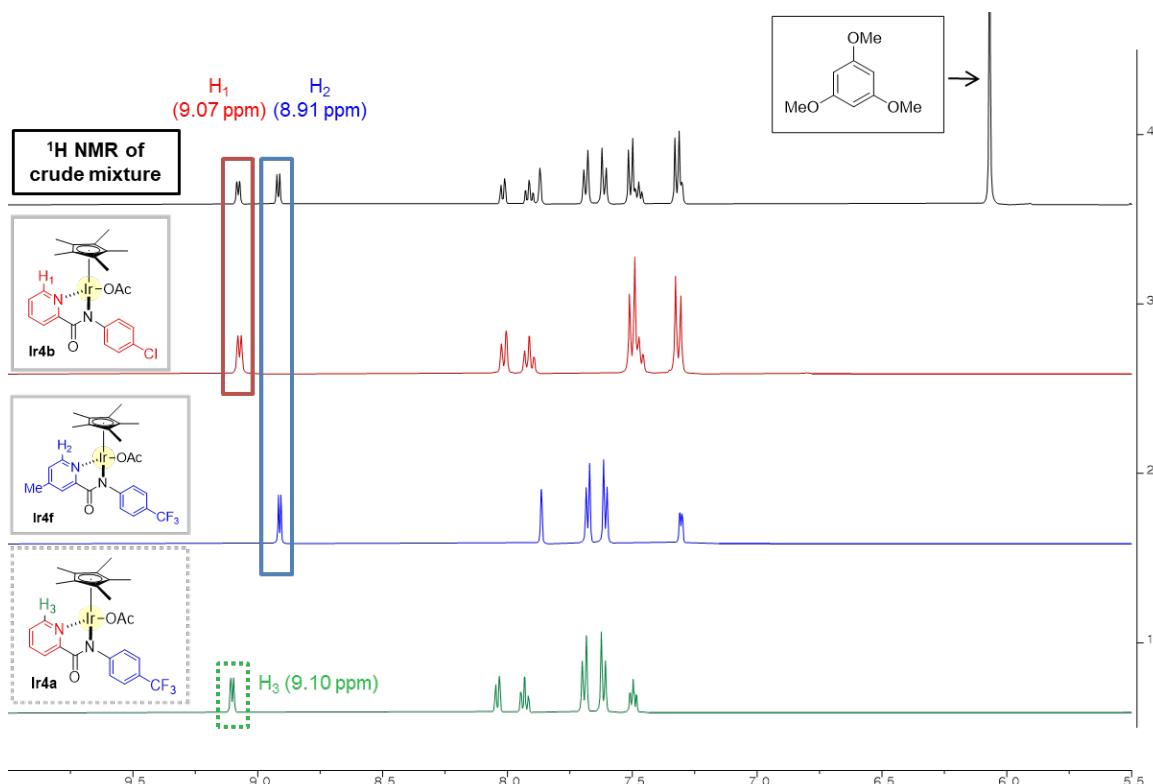


Figure S23. Stacked ¹H NMR spectra of crude mixture, **Ir4b**, **Ir4f**, and **Ir4a** in CD₂Cl₂.

4-7. Quantum yield measurement

The 445 nm Prizmatix[©] Collimated Modular Mic-LED coupled with BLCC-04 LED current controller was used as the light source for the LED-NMR experiment.^[10] The LED source was calibrated using below described 2,4-dinitrobenzaldehyde photoreaction to form nitroso benzoic acid product (Figure S24). Concentration profiles were monitored by ¹H NMR monitoring with 1,3,5-trimethoxybenzene as an internal standard.

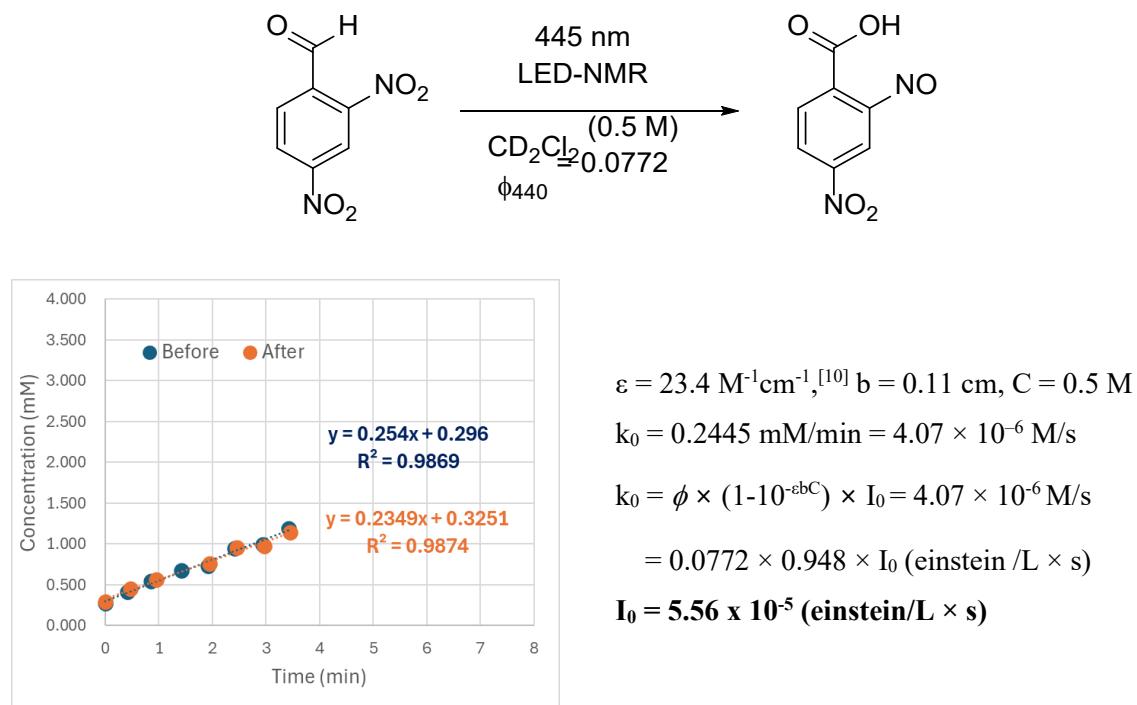
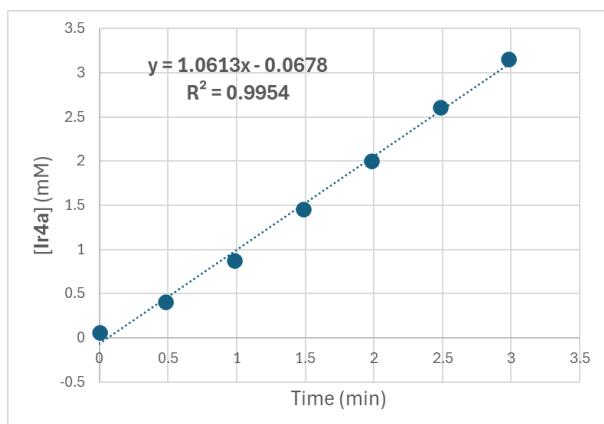
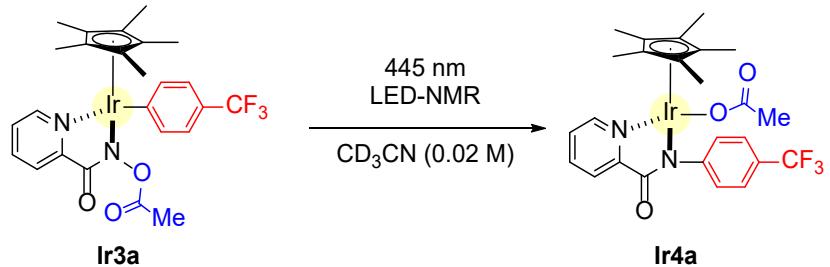


Figure S24. Initial rates of photochemical (445 nm) transformation of 2,4 dinitrobenzaldehyde (0.5 M) conducted before and after the Ir-group transposition reaction.

Ir3a (0.01 mmol, 6.5 mg) and 0.5 mL dry CD₃CN were added to an air-tight PhotoNMR sampling device (NE-397-5-Br, New Era[©]). The optical fiber connected to Mic-LED was placed into the coaxial inner cell, and the whole tube was inserted into the NMR machine. Upon turning on the light source, the ¹H NMR spectroscopic measurements were conducted to monitor the formation of **Ir4a**. LED was turned on and off. Yields were determined based on ¹H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard (Figure S25).



$$\epsilon = 2130 \text{ M}^{-1}\text{cm}^{-1}, b = 0.11 \text{ cm}, C = 0.02 \text{ M}$$

$$k_0 = 1.06 \text{ mM/min} = 1.77 \times 10^{-5} \text{ M/s}$$

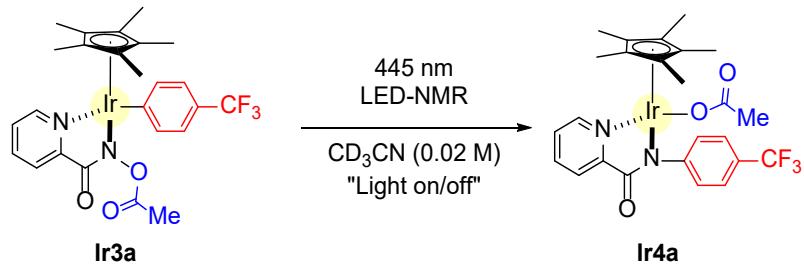
$$k_0 = \phi \times (1 - 10^{-\epsilon b C}) \times I_0 = 1.77 \times 10^{-5} \text{ M/s}$$

$$= \phi \times 1.0 \times 5.56 \times 10^{-5} (\text{einsteins/L} \times \text{s})$$

$$\phi = \mathbf{0.32}$$

Figure S25. Initial rates of photochemical (445 nm) group transposition of **Ir3a** to **Ir4a** (0.5 M) and calculated reaction quantum yield.

4-8. Light on/off experiment



The 445 nm Prizmatix[©] Collimated Modular Mic-LED coupled with BLCC-04 LED current controller was used as the light source for the LED-NMR experiment.^[11,12] **Ir3a** (0.01 mmol, 6.5 mg) and 0.5 mL dry CD₃CN were added to an air-tight PhotoNMR sampling device (NE-397-5-Br, New Era[©]). The optical fiber connected to Mic-LED was placed into the coaxial inner cell, and the whole tube was inserted into the NMR machine. Upon turning on the light source, the ¹H NMR spectroscopic measurements were conducted to monitor the formation of **Ir4a**. LED was turned on and off. Yields were determined based on ¹H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard (Figure S26). Light/dark reaction monitoring indicates that the desired product **Ir4a** is produced only upon photoirradiation conditions.

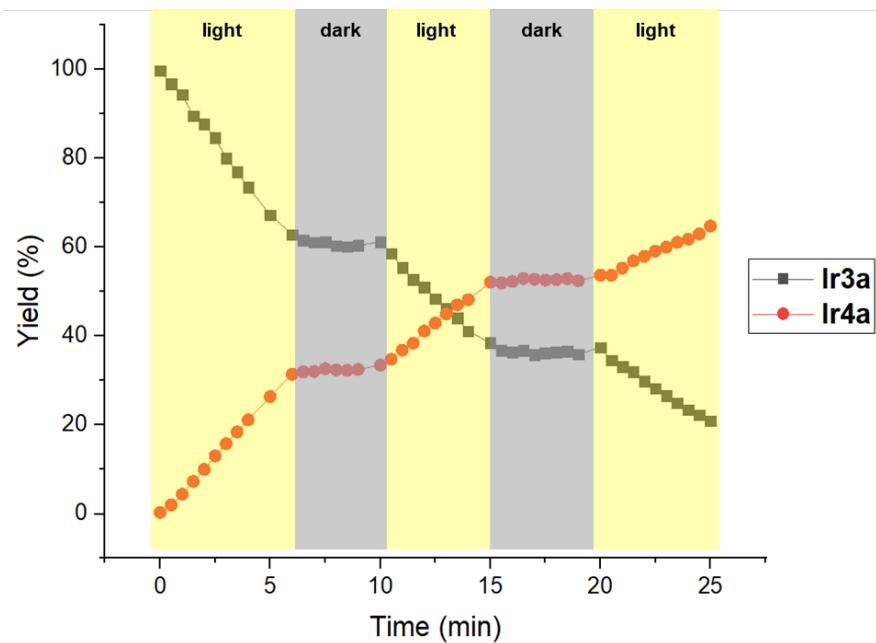


Figure S26. Light on/off reaction monitoring of photoinduced group transposition of **Ir3a**.

5. Transient absorption spectroscopy

A transient absorption spectroscopy system (Ultrafast Systems, Helios) with a Ti:sapphire femtosecond laser system was used to measure the femtosecond time-resolved absorption spectra from **Ir3a** and **Ir3j** samples dissolved in MeCN (1.25 mM). The output pulses at a wavelength of 800 nm from Ti:sapphire amplified laser (Coherent, Astrella, 34 fs) were divided to generate the pump and probe beams. The laser pulses in the pump arm were converted to a pump beam of 400 nm using a tripler (TPH tripler, Minopic Technology, Inc.). The intensity of the excitation beam was adjusted using a continuously variable neutral density filter. The other part of the fundamental laser pulses was directed to a CaF₂ crystal to generate a white light continuum for the probe beam. The white light was then transmitted through the sample cell with a 2 mm optical path, and the transmitted light was detected using a CCD detector installed in the transient absorption measurement system with controlled optical delay.

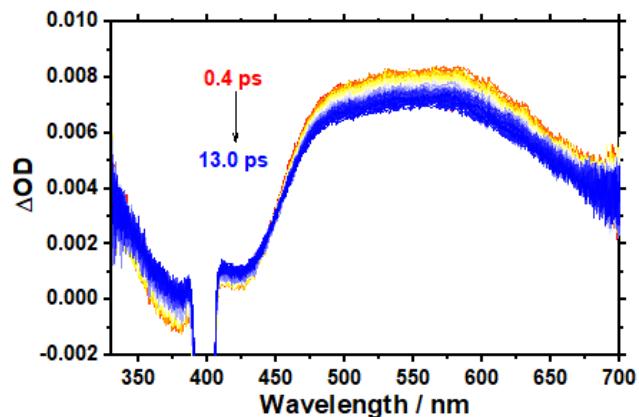


Figure S27. Transient absorption spectra of **Ir3a** in acetonitrile at room temperature after with $\lambda_{\text{exc}} = 400$ nm up to 13 ps.

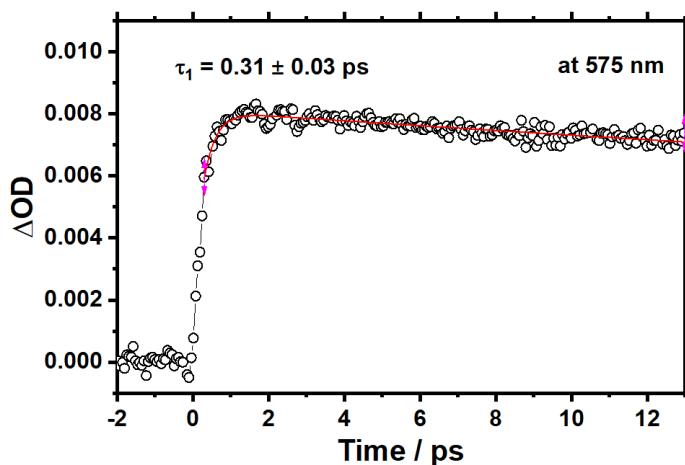


Figure S28. Singe wavelength kinetics and fitting of **Ir3a** in acetonitrile at room temperature after with $\lambda_{\text{exc}} = 400$ nm up to 13 ps.

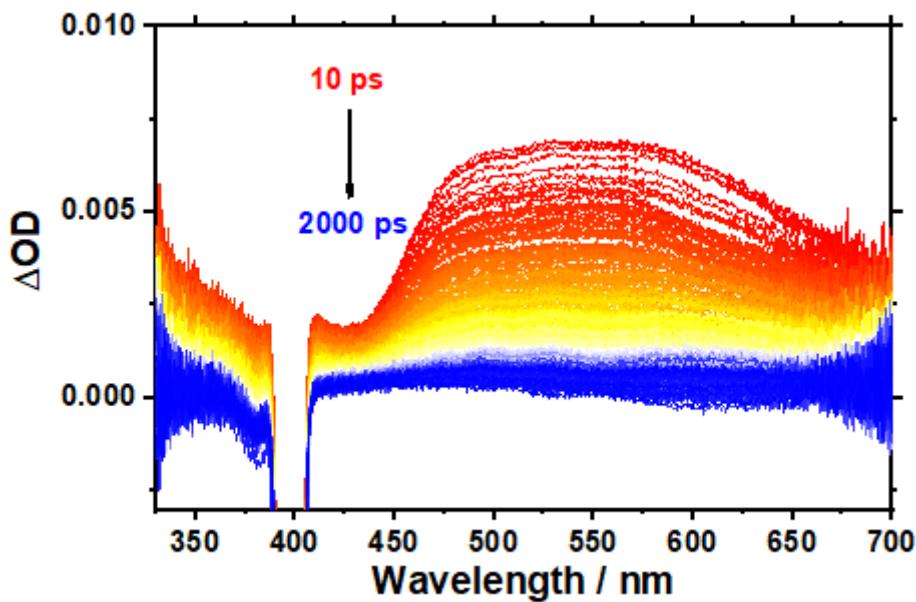


Figure S29. Transient absorption spectra of Ir3a in acetonitrile at room temperature after with $\lambda_{\text{exc}} = 400$ nm up to 2000 ps.

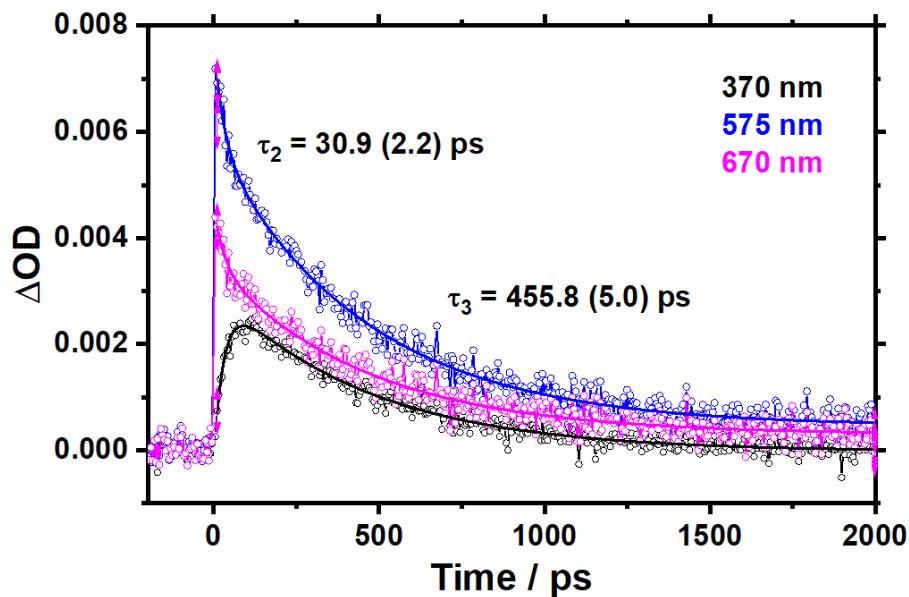


Figure S30. Global fitting analysis of Ir3a in acetonitrile at room temperature after with $\lambda_{\text{exc}} = 400$ nm up to 2000 ps.

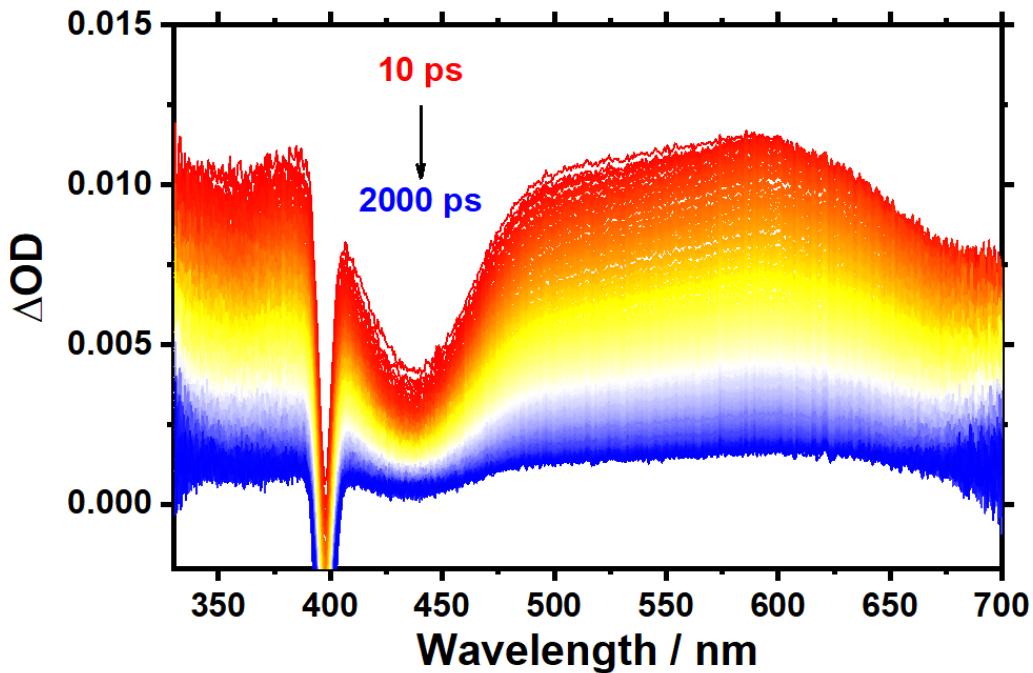


Figure S31. Transient absorption spectra of Ir3j in acetonitrile at room temperature after with $\lambda_{\text{exc}} = 400$ nm up to 2000 ps.

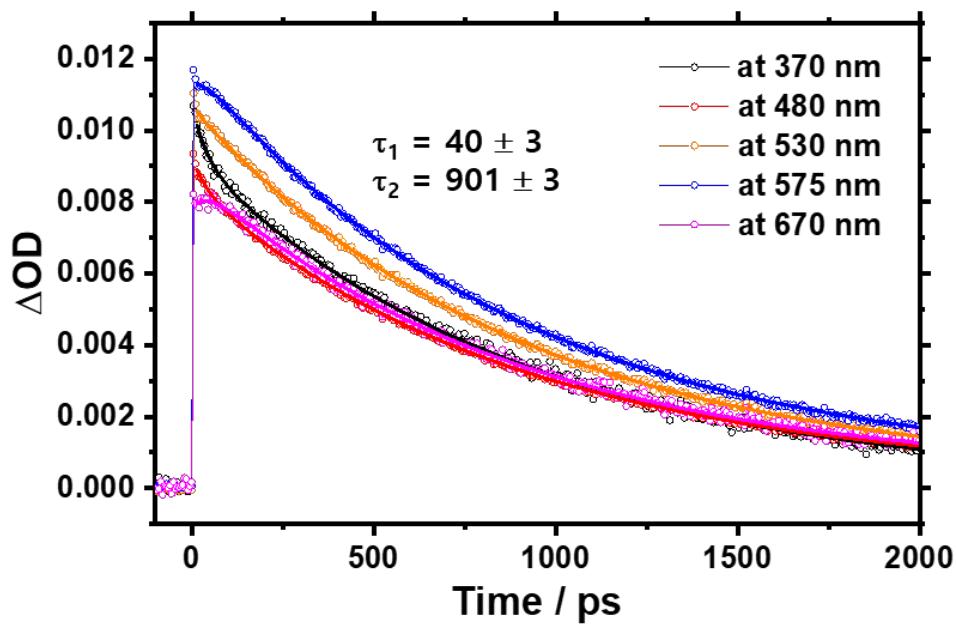


Figure S32. Bi-exponential global fitting analysis of Ir3j in acetonitrile at room temperature after with $\lambda_{\text{exc}} = 400$ nm up to 2000 ps.

6. Computational study

6-1. DFT study

- Computational details

All computational studies were conducted using the Gaussian 16^[13] program package in the density functional theory (DFT) framework,^[14] using High Performance Computing Resources in the Institute for Basic Science (IBS) Research Solution Center. The initial structure of **Ir3a** was derived from the SCXRD analysis, and no simplification was adopted (*vide infra*). The computational level was chosen accordingly with the previous studies describing iridium catalyzed photocatalysis.^[15–17] Geometry optimizations were performed using B3LYP^[18,19] functional with Grimme's D3^[20] dispersion and a mixed basis set of LANL2DZ^[21–23] (Ir) and 6-31G**^[24–28] for all other atoms. Frequency calculations were performed at the same level as that used for geometry optimizations, wherein thermochemistry correction energy (G – E) was acquired. Transition states were verified by one imaginary frequency and confirmed by intrinsic reaction coordinate calculations (IRC).^[29,30] With the optimized geometries of intermediates and transition structures, single-point energy calculations were conducted at B3LYP-D3 functional with a different basis set combination of SDD^[31] (Ir) and 6-311+G**^[27,32–35] for others. The solvent effect was reflected by using the SMD^[36] solvation model and carried out at the same level as single-point calculations (solvent = acetonitrile). Finally, to increase the accuracy of the integration grid, we used the *int = ultrafine* option for all types of calculations. The final solution phase Gibbs free energies were calculated as follows:

$$G_{\text{sol}} = E_{\text{sol}} + (G - E) \quad (1)$$

$$\Delta G(\text{sol}) = \sum G(\text{sol}) \text{ for products} - \sum G(\text{sol}) \text{ for reactants} \quad (2)$$

- Gibbs energy profile on the initial excitation & N-O bond cleavage

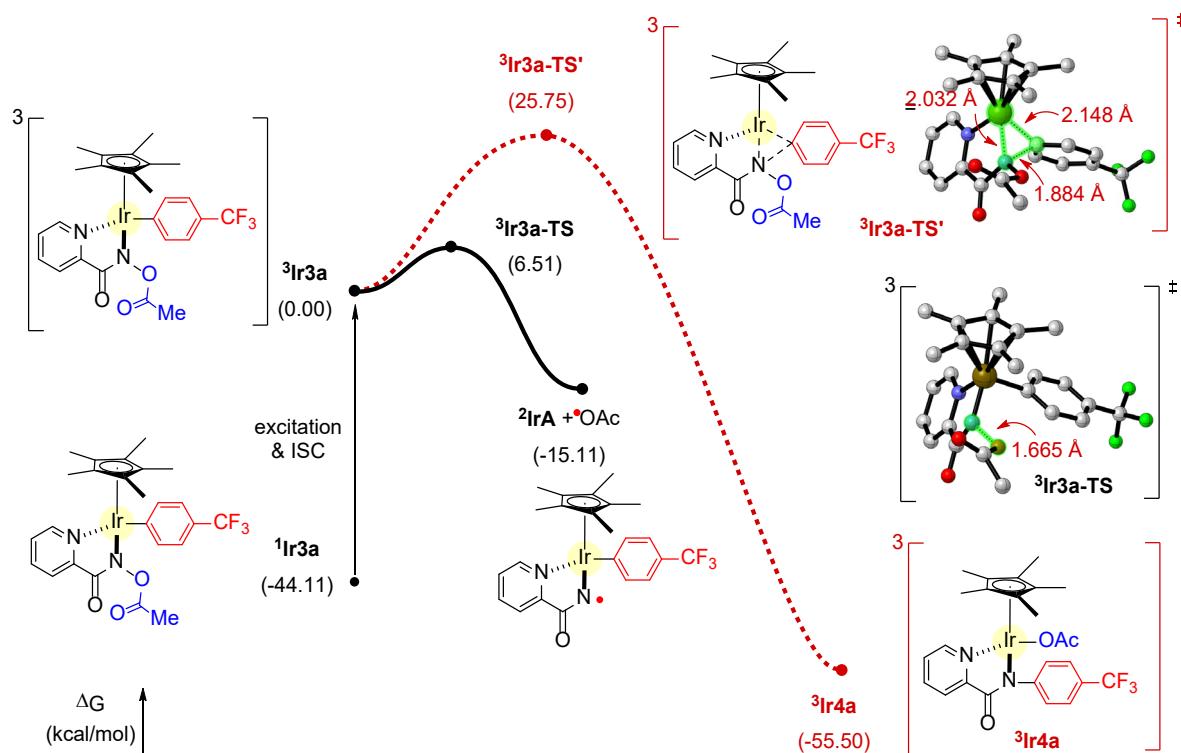


Figure S33. Gibbs energy profile of **Ir3a** photoexcitation and activation.

As shown in Figure S33, upon photoexcitation and intersystem crossing (ISC) of **Ir3a**, it can reach its triplet state $^3\text{Ir3a}$, with a triplet energy of 44.1 kcal/mol. Then, the $\sigma(\text{N}-\text{O})$ bond can undergo a homolytic cleavage by traversing the transition state $^3\text{Ir3a-TS}$ with a 6.5 kcal/mol barrier, which leads to the formation of a radical pair of ^2IrA and acetyloxy radical (-15.1 kcal/mol). Alternatively, $^3\text{Ir3a}$ can undergo a direct C–N bond coupling via photoinduced reductive elimination^[37] to form $^3\text{Ir4a}$, yet, this pathway requires a much higher barrier of 25.8 kcal/mol.

- Gibbs energy profile on the aryl migratory C–N bond formation

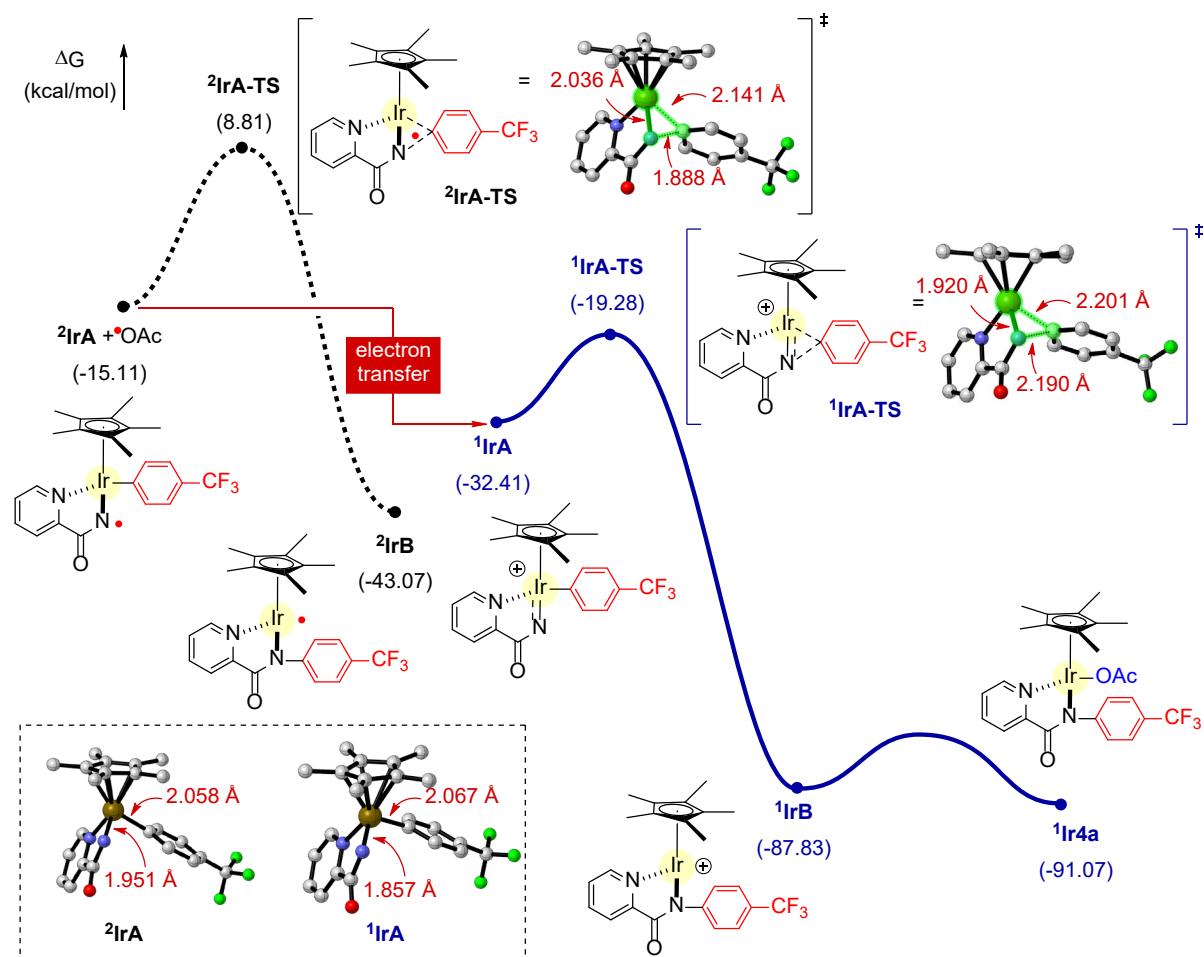


Figure S34. Gibbs energy profile on aryl migratory C–N bond formation pathways from ^2IrA or ^1IrA .

As shown in Figure S34, upon the generation of ^2IrA , we considered the direct C–N bond formation, leading to the formation of ^2IrB via $^2\text{IrA-TS}$. This route requires a barrier of 23.9 kcal/mol, where the original Ir–N bond length is elongated from 1.951 Å (^2IrA) to 2.036 Å ($^2\text{IrA-TS}$). Alternatively, once the electron transfer event takes place to furnish a singlet nitrenoid intermediate ^1IrA , the C–N bond formation barrier is 13.1 kcal/mol, traversing $^1\text{IrA-TS}$, leading to the product complex ^1IrB . During this process, the Ir–N bond length changes from 1.857 Å (^1IrA) to 1.920 Å ($^1\text{IrA-TS}$). The final recombination of acetate gives rise to the intermediate $^1\text{Ir4a}$.

- Computational studies on triphenylphosphine trapping reaction mechanism

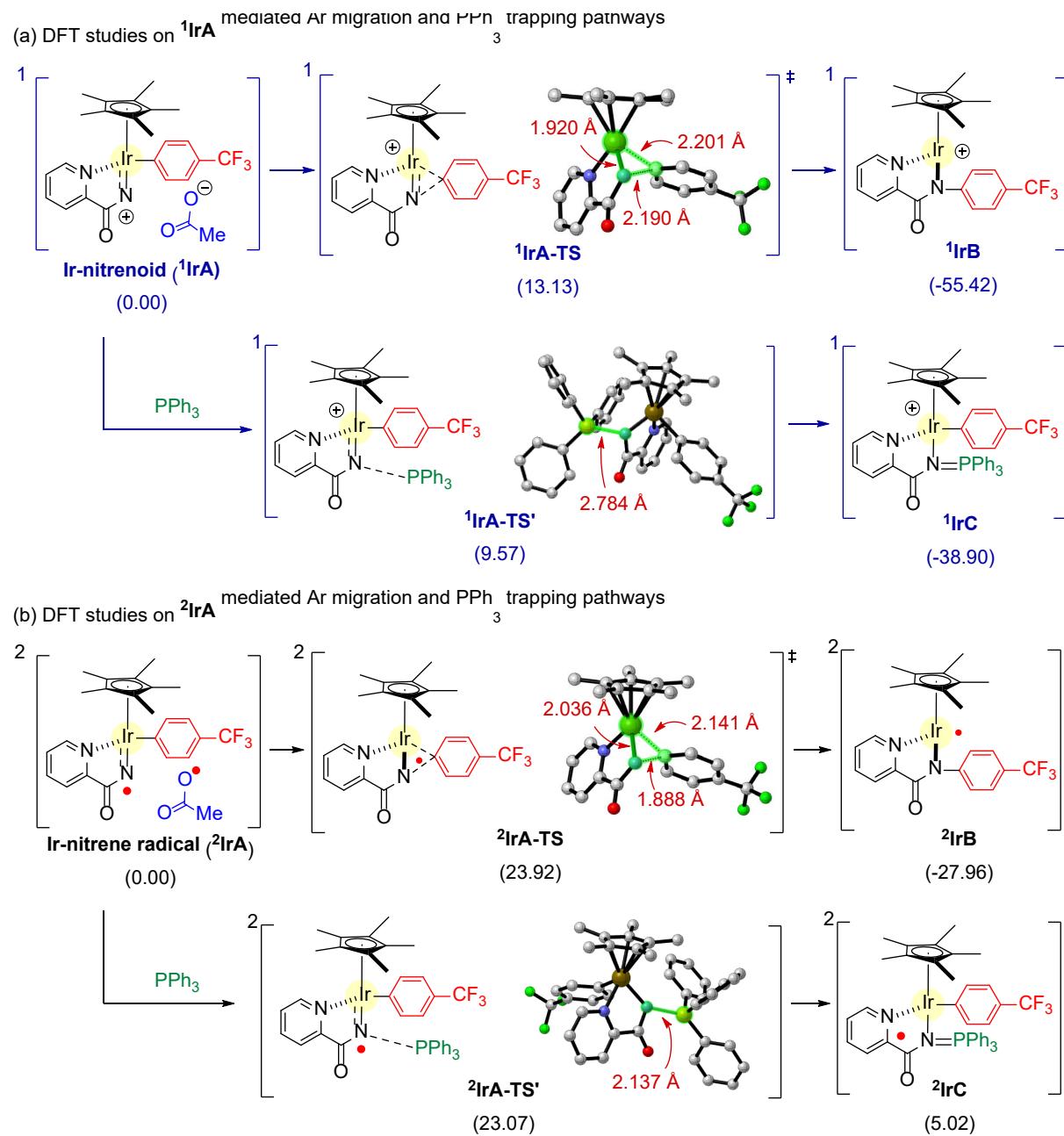


Figure S35. DFT assessment on PPh_3 trapping vs intramolecular C–N bond formation pathways.

As shown in the Figure S35, with Ir-nitrene intermediate ^1IrA , the subsequent P–N bond formation barrier ($^1\text{IrA-TS}'$, 9.6 kcal/mol) is lower than the intramolecular C–N bond formation pathway ($^1\text{IrA-TS}$, 13.1 kcal/mol), which nicely matches with our experimental observations. However, the P–N bond formation step from the ^2IrA intermediate requires a higher barrier of 23.1 kcal/mol, which is almost similar to the Ir–Ar migration barrier (23.9 kcal/mol). At the present stage, the lower P–N bond formation barrier of ^1IrA compared to ^2IrA intermediate is attributed to the more electrophilic nature of ^1IrA than ^2IrA .

- Computational studies on photoinitiated chain propagation mechanism

In addition to the proposed photoinduced group transposition reaction mechanism via the Ir-nitrenoid transfer pathway, we can also consider the photoinitiated, thermal chain propagation mechanism. To briefly evaluate the potential chain propagation pathways to thermally regenerate the reactive intermediates, we evaluated the thermodynamic preference of possible mechanisms.

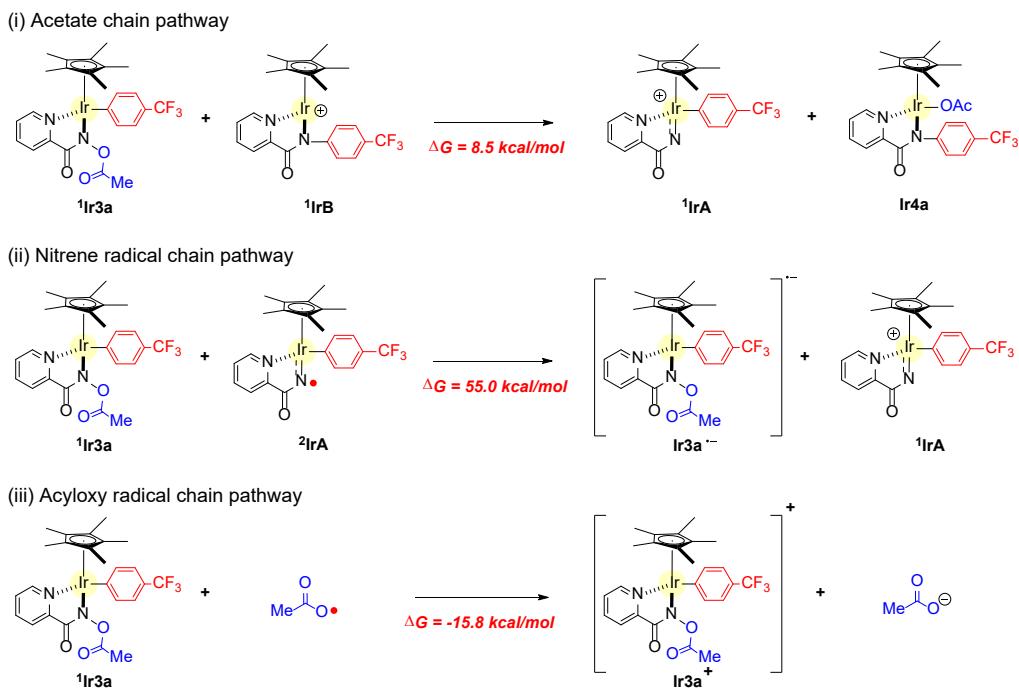


Figure S36. DFT assessment on the thermodynamic preference of potential chain pathways.

When the postulated acetate propagation step was evaluated computationally using **Ir3a** and aryl group-migrated adduct **1IrB** to give **1IrA** and **Ir4a** (Figure S36-i), this process was found to be thermodynamically uphill by 8.5 kcal/mol energy. Additionally, single-electron reduction of **Ir3a** with **2IrA** to form radical anion **Ir3a•⁻** and Ir-nitrenoid **1IrA** was calculated to be highly endergonic by 55.0 kcal/mol (Figure S36-ii). We also considered an acyloxy radical chain pathway, where acyloxy radical can oxidize the **Ir3a** to form a formal Ir(IV) intermediate **Ir3a⁺** (Figure S36-iii). While this process was computed to be exergonic by 15.8 kcal/mol, the following oxidatively induced reductive elimination requires a 31.6 kcal/mol barrier to form **IrD⁺**. Then, subsequent N–O bond cleavage and acetate recombination may give rise to the cationic form of the product complex **Ir4a⁺** (Figure S37).

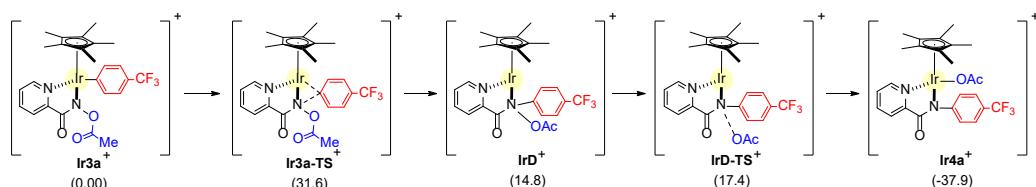


Figure S37. DFT assessment on the potential oxidatively induced reductive elimination pathway.

6-2. TDDFT calculation.

Time-dependent-DFT (TD-DFT) calculations^[38] were conducted using the Gaussian 16^[13] suite of program using DFT optimized structure of **Ir3a** at SMD(acetonitrile)-B3LYP-D3/LANL2DZ|6-31G** levels of theory. For the TD-DFT calculations, 100 eigenstates of the time-dependent Hamiltonian were constructed. The simulated UV–Vis spectrum matches reasonably well with the experimentally obtained spectrum (Figure S38). Transitions at 431 nm and 381 nm are summarized in Table S5.

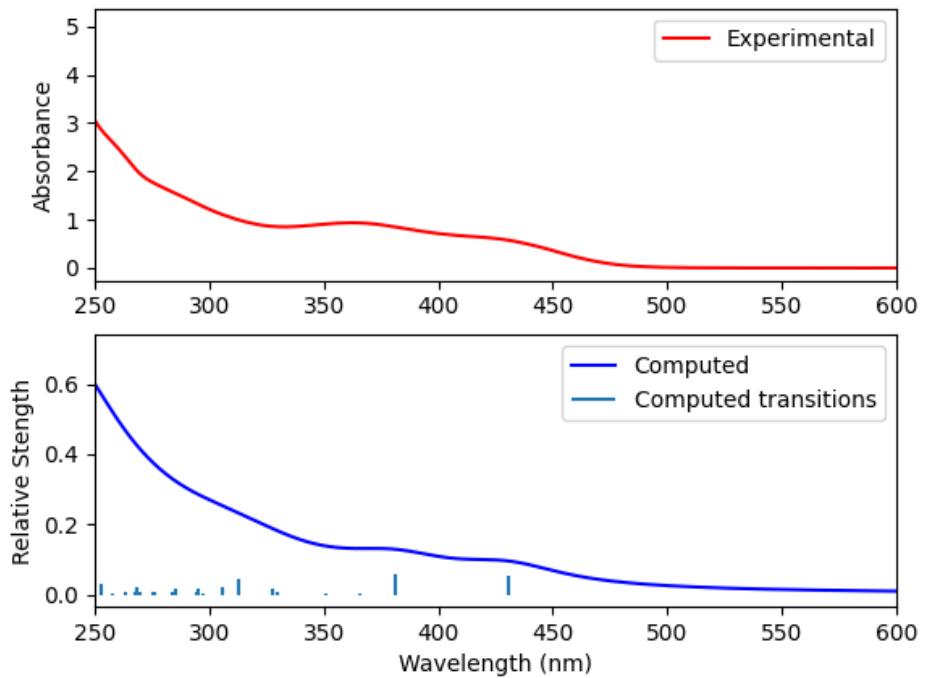
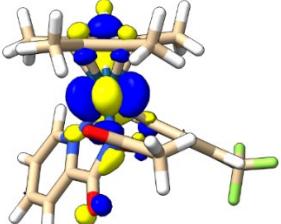
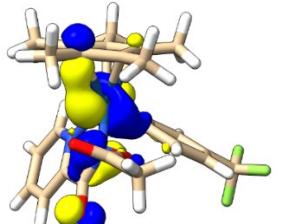
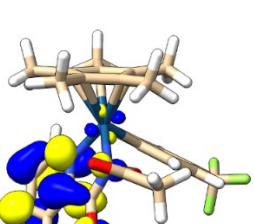


Figure S38. Experimental (upper, red line) and TDDFT simulated (down, blue line) UV–Vis spectrum of **Ir3a**.

Table S5. Frontier orbital transitions result from TDDFT simulation.

Excited State 2: 1.000-?Sym 2.8785 eV 430.73 nm f=0.0531 <S**2>=0.000 128A ->130A 0.17387 129A ->130A 0.68009 128B ->130B 0.17387 129B ->130B 0.68009	Excited State 5: 1.000-?Sym 3.2524 eV 381.21 nm f=0.0590 <S**2>=0.000 128A ->130A 0.67304 129A ->130A -0.16344 128B ->130B 0.67304 129B ->130B -0.16344
 HOMO-1 (#128) 41% Ir(d) character	 HOMO (#129) 36% Ir(d) character
	 LUMO (#130)

6-3. IBO analysis

The intrinsic bond orbital (IBO) analysis^[39] was performed using IBOView software using a DFT-optimized intrinsic reaction coordinate (IRC). A series of geometries were sampled from an IRC calculation. For each sampled geometry, Molden format output was generated based on the results from B3LYP-D3/def2TZVP^[40] levels of theory (*gfninput & IOP(6/7=3)* keywords were used) calculations. Orbitals and energies were reevaluated using the IBO exponent 2 orbital localization method.

- IBO analysis on the N–O bond cleavage TS ($^3\text{Ir3a-TS}$)

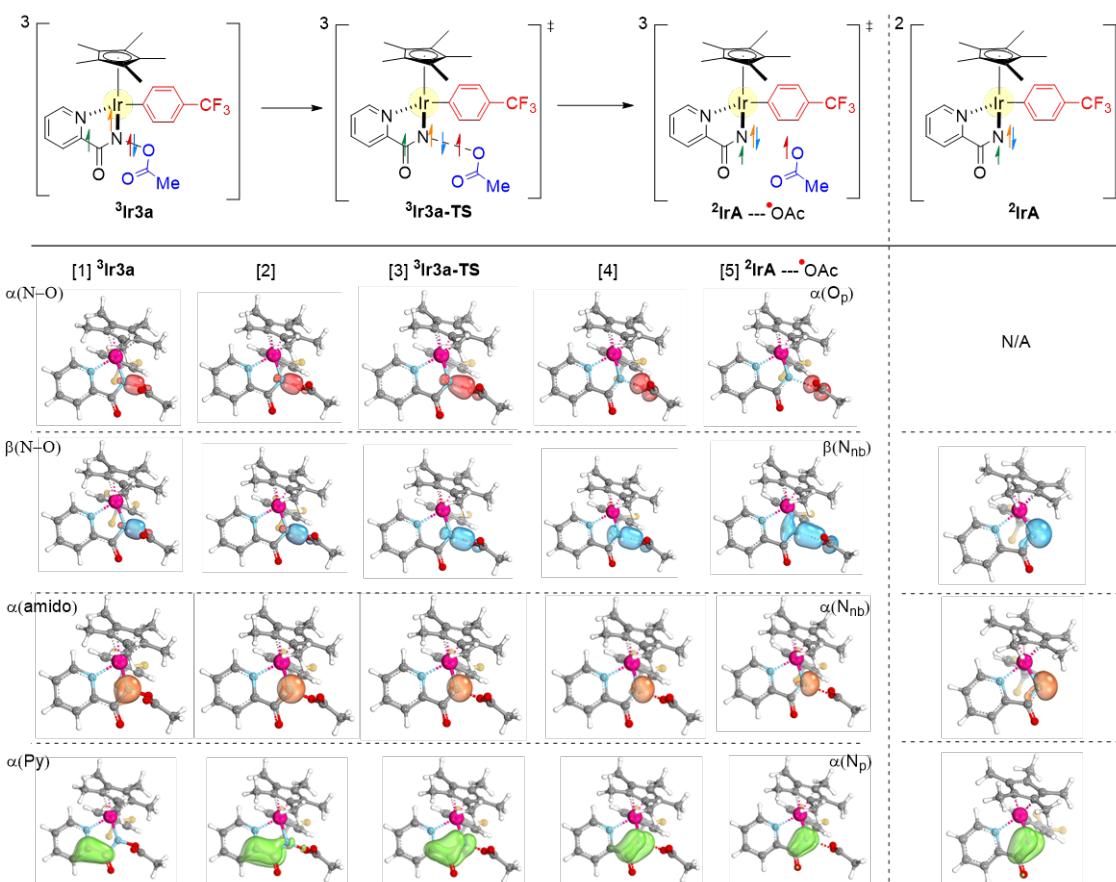


Figure S39. IBO analysis on the IRC trajectory of $^3\text{Ir3a-TS}$.

As summarized in Figure S39, the IBO analysis of $^3\text{Ir3a-TS}$ suggests that the $\sigma(\text{N}-\text{O})$ bond dissociation event shows a homolytic cleavage nature. Following the α - and β -electrons of the $\sigma(\text{N}-\text{O})$ bond, the α -electron (red lobe) moves to the oxygen atom, suggesting the formation of acyloxy radical intermediates. Simultaneously, the β -electron (blue lobe) transfers mainly to the nitrogen atom $\beta(\text{N}_\text{nb})$. Also, when tracking the triplet electron density of $^3\text{Ir3a}$, the $\alpha(\text{N}_\text{amido})$ electron (orange lobe) transforms to $\alpha(\text{N}_\text{nb})$ orbital to make a pair with $\beta(\text{N}_\text{nb})$ orbital. Interestingly, the original $\alpha(\text{Py})$ electron (green lobe) becomes an $\alpha(\text{N}_\text{p})$ orbital, thereby forming an N-centered radical intermediate ^2IrA . Hence, the $\sigma(\text{N}-\text{O})$ bond cleavage event could be assigned as a net homolytic cleavage.

- IBO analysis on the C–N bond formation TS ($^1\text{IrA-TS}$)

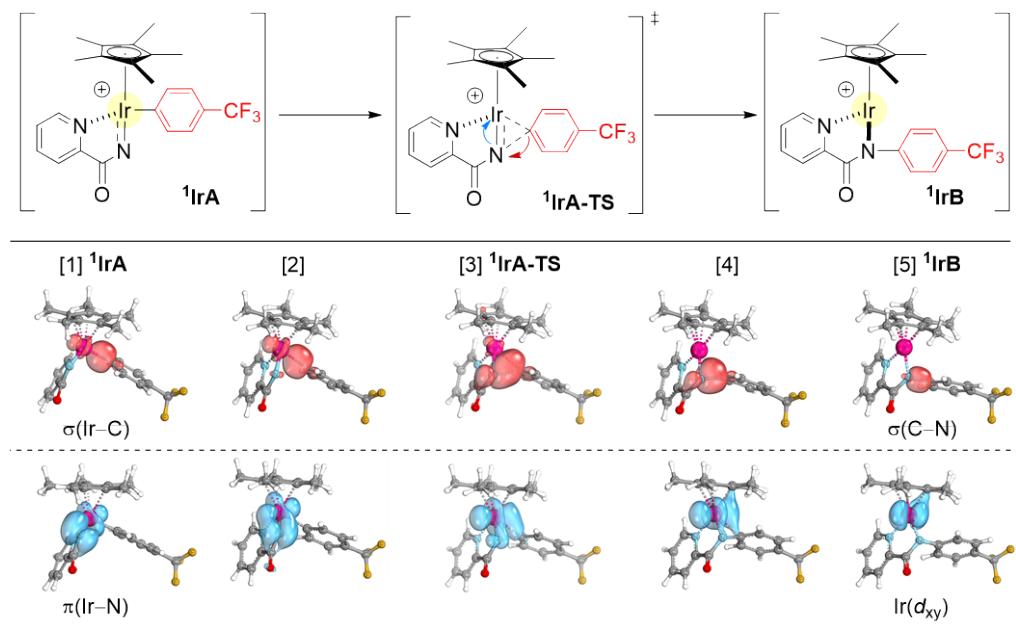


Figure S40. IBO analysis on the IRC trajectory of $^1\text{IrA-TS}$.

As shown in Figure S40, the IBO analysis of $^1\text{IrA-TS}$ indicates that the initial $\sigma(\text{Ir}-\text{C})$ bond is moving to the $\sigma(\text{N}-\text{C})$ bond of ^1IrB (red lobes), and the $\pi(\text{Ir}-\text{N})$ bond becomes the $\text{Ir}(d_{xy})$ orbital (blue lobes). Therefore, this inner-sphere type aryl group transfer could be best explained as the Ir–C migration to an electrophilic Cp^*Ir -acylnitrenoid intermediate.

6-4. Energy components of all DFT optimized geometries

Table S6. Summarized energy components of DFT-optimized structures.

Structure label	E(sol) (SCF/TZ) [eV] SMD(MeCN)-B3LYP- D3/6-311+G**, SDD(Ir)	G-E [eV] B3LYP-D3/6-31G**, LANL2DZ(Ir)	G(sol) [eV]
¹ Ir3a	-46477.817	10.815	-46467.002
³ Ir3a	-46475.798	10.710	-46465.089
³ Ir3a-TS	-46475.487	10.681	-46464.806
² IrA	-40257.975	9.460	-40248.515
OAc radical	-6217.753	0.524	-6217.229
¹ IrA	-40253.389	9.561	-40243.828
OAc ⁻	-6223.222	0.556	-6222.667
¹ IrA-TS	-40252.822	9.564	-40243.258
¹ IrB	-40255.858	9.626	-40246.231
¹ Ir4a	-46479.910	10.872	-46469.038
³ Ir3a-TS'	-46474.718	10.746	-46463.972
³ Ir4a	-46478.229	10.733	-46467.496
² IrA-TS	-40256.964	9.487	-40247.478
² IrB	-40259.255	9.528	-40249.727
Ph ₃ P	-28205.970	6.190	-28199.780
¹ IrA-TS'	-68459.738	16.545	-68443.193
¹ IrC	-68461.979	16.684	-68445.294
² IrA-TS'	-68463.804	16.509	-68447.294
² IrC	-68464.616	16.539	-68448.077
Ir3a ^{•-}	-46479.956	10.654	-46469.302
Ir3a ⁺	-46473.102	10.854	-46462.248
Ir3a-TS ⁺	-46471.687	10.811	-46460.876
IrD ⁺	-46472.395	10.791	-46461.605
IrD-TS ⁺	-46472.238	10.745	-46461.493
Ir4a ⁺	-46474.735	10.845	-46463.890

6-5. Cartesian coordinates of all optimized structures

<hr/> <hr/> ¹Ir3a <hr/> <hr/>			
Charge = 0 Multiplicity = 1			
Cartesian coordinates:			
ATOM	X	Y	Z
Ir	-1.304066	-2.466073	0.650789
C	-1.344654	-4.679735	0.831711
C	-0.668449	-4.115444	1.981603
C	0.501751	-3.432243	1.508432
C	0.637328	-3.684801	0.075289
C	-0.495124	-4.432651	-0.327601
C	1.522634	-2.733464	2.356097
H	1.046426	-2.173279	3.163752
H	2.216286	-3.457071	2.801189
H	2.106460	-2.033702	1.755678
C	1.781339	-3.215201	-0.772208
H	1.593081	-3.399249	-1.832317
H	1.949969	-2.143333	-0.645881
H	2.703716	-3.744288	-0.502075
C	-0.803538	-4.910755	-1.713890
H	-0.236128	-4.360451	-2.466547
H	-0.561038	-5.975476	-1.814039
H	-1.865811	-4.797222	-1.948145
C	-2.534179	-5.592694	0.874964
H	-2.233361	-6.631297	1.063015
H	-3.228023	-5.295013	1.664481
H	-3.082381	-5.579565	-0.071996
C	-1.099010	-4.251389	3.409978
H	-0.690238	-5.173260	3.841026
H	-0.750563	-3.407195	4.008166
H	-2.187132	-4.281673	3.493057
C	-3.510713	-2.394654	-1.481393
C	-4.314884	-1.818749	-2.456809
H	-5.064982	-2.423635	-2.954434
C	-2.398338	-0.380047	-1.124836
C	-4.146028	-0.466233	-2.766658
H	-4.766240	0.008756	-3.520233
C	-3.175714	0.260494	-2.084327
H	-2.988857	1.315193	-2.252232
C	-1.361828	0.376317	-0.341592
O	-1.186994	1.587502	-0.479898
N	-0.717396	-0.486966	0.471343
H	-3.616696	-3.432631	-1.190324
N	-2.560388	-1.693147	-0.833517
O	0.121181	0.162286	1.403575
C	1.375968	0.456852	0.946984
O	1.843310	0.068990	-0.095711
C	-2.731234	-1.859232	1.993258
C	-4.014383	-2.436398	1.981671
C	-2.450325	-0.934285	3.015728
C	-4.967839	-2.129137	2.952192
C	-3.395726	-0.621439	3.991864
C	-4.656693	-1.222353	3.967276
H	-4.277785	-3.151034	1.206470
H	-1.478538	-0.454498	3.053758
H	-5.946883	-2.598013	2.931490
H	-3.154747	0.084176	4.781016
C	-5.692867	-0.845390	4.982578
F	-6.441788	0.211621	4.578798
F	-6.559624	-1.859365	5.225004
F	-5.140291	-0.495024	6.168618
C	2.066212	1.338133	1.958207
H	1.884217	0.982234	2.975222
H	3.134372	1.363731	1.743910
H	1.651887	2.347830	1.878106

<hr/> <hr/> ³Ir3a <hr/> <hr/>			
Charge = 0 Multiplicity = 3			
Cartesian coordinates:			
ATOM	X	Y	Z
Ir	-1.265909	-2.373571	0.698815
C	-1.348300	-4.628528	0.959718
C	-0.541848	-4.045006	2.021003
C	0.609272	-3.441722	1.413837
C	0.567839	-3.706514	-0.012115
C	-0.640304	-4.420612	-0.278708
C	1.745350	-2.778761	2.133647
H	1.391686	-2.214690	2.999239
H	2.463014	-3.529590	2.485131
H	2.273128	-2.090231	1.471867
C	1.605818	-3.289593	-1.009882
H	1.231112	-3.389717	-2.031022
H	1.897625	-2.247045	-0.861436
H	2.503327	-3.914887	-0.920055
C	-1.078245	-4.879573	-1.637707
H	-1.056420	-4.059392	-2.360059
H	-0.408987	-5.667513	-2.000755
H	-2.090491	-5.286819	-1.619845
C	-2.575533	-5.465510	1.165969
H	-2.308239	-6.506489	1.385319
H	-3.172100	-5.084668	1.997400
H	-3.214969	-5.465574	0.279491
C	-0.818226	-4.155633	3.488420
H	-0.436445	-5.108342	3.874992
H	-0.338541	-3.346693	4.043233
H	-1.889029	-4.104670	3.693983
C	-3.390473	-2.267860	-1.522920
C	-4.172228	-1.676609	-2.489045
H	-4.884174	-2.276243	-3.044088

C	-2.326373	-0.210229	-1.012973	C	-0.932272	-4.852352	-1.812091
C	-4.027563	-0.271967	-2.730228	H	-0.337518	-4.309755	-2.548696
H	-4.636508	0.219031	-3.482234	H	-0.736296	-5.923896	-1.937005
C	-3.114397	0.439449	-1.994802	H	-1.986444	-4.679315	-2.045248
H	-2.959441	1.504724	-2.130289	C	-2.685544	-5.515023	0.770153
C	-1.345737	0.450128	-0.223833	H	-2.448840	-6.567370	0.970161
O	-0.990677	1.636929	-0.221671	H	-3.375872	-5.174405	1.545279
N	-0.697415	-0.516773	0.654557	H	-3.210648	-5.477922	-0.188214
H	-3.472520	-3.326271	-1.299424	C	-1.189071	-4.295148	3.317500
N	-2.477238	-1.584389	-0.795683	H	-0.782812	-5.221592	3.741140
O	0.201282	0.065128	1.539071	H	-0.836847	-3.458110	3.922422
C	1.390141	0.478803	0.951834	H	-2.277076	-4.325348	3.398535
O	1.806968	0.036161	-0.086707	C	-3.706113	-2.345730	-1.397372
C	-2.809484	-1.966257	1.996690	C	-4.568734	-1.769524	-2.312519
C	-4.107210	-2.458309	1.801022	H	-5.371280	-2.358666	-2.740445
C	-2.551527	-1.218615	3.158177	C	-2.491010	-0.339900	-1.162781
C	-5.112961	-2.234417	2.742135	C	-4.373430	-0.411762	-2.667334
C	-3.553198	-0.983427	4.097979	H	-5.043532	0.069142	-3.373190
C	-4.835992	-1.499361	3.895502	C	-3.333326	0.292799	-2.100984
H	-4.345642	-3.025088	0.907967	H	-3.128920	1.331755	-2.333861
H	-1.559556	-0.811880	3.329434	C	-1.318556	0.293720	-0.597871
H	-6.109961	-2.633291	2.584805	O	-0.940741	1.457478	-0.818746
H	-3.340754	-0.407407	4.993052	N	-0.590465	-0.628570	0.186321
C	-5.927550	-1.206150	4.882812	H	-3.811636	-3.379478	-1.087165
F	-6.570665	-0.048319	4.597671	N	-2.687732	-1.664168	-0.840175
F	-6.869178	-2.179559	4.900719	O	0.166221	0.229042	1.395737
F	-5.448567	-1.083210	6.143855	C	1.452224	0.431948	1.110250
C	2.036499	1.510207	1.831392	O	2.109605	-0.171700	0.280945
H	1.952722	1.234058	2.885407	C	-2.622529	-1.822678	1.976459
H	3.080116	1.633467	1.543547	C	-3.936214	-2.314303	1.995754
H	1.496430	2.450916	1.686171	C	-2.200508	-1.011628	3.041987

³Ir3a-TS

Charge = 0 Multiplicity = 3

Imaginary frequency: -698.45 cm⁻¹

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.286199	-2.395781	0.510756
C	-1.440843	-4.678342	0.745360
C	-0.749438	-4.158923	1.893956
C	0.455589	-3.511747	1.446841
C	0.573405	-3.738110	0.015682
C	-0.606834	-4.418713	-0.414728
C	1.508066	-2.894507	2.318423
H	1.057979	-2.371589	3.165615
H	2.182839	-3.663854	2.713583
H	2.099959	-2.173123	1.753595
C	1.724478	-3.278761	-0.825228
H	1.505959	-3.374962	-1.890610
H	1.961628	-2.232437	-0.614999
H	2.612855	-3.884467	-0.607268

C	-0.932272	-4.852352	-1.812091
H	-0.337518	-4.309755	-2.548696
H	-0.736296	-5.923896	-1.937005
H	-1.986444	-4.679315	-2.045248
C	-2.685544	-5.515023	0.770153
H	-2.448840	-6.567370	0.970161
H	-3.375872	-5.174405	1.545279
H	-3.210648	-5.477922	-0.188214
C	-1.189071	-4.295148	3.317500
H	-0.782812	-5.221592	3.741140
H	-0.836847	-3.458110	3.922422
H	-2.277076	-4.325348	3.398535
C	-3.706113	-2.345730	-1.397372
C	-4.568734	-1.769524	-2.312519
H	-5.371280	-2.358666	-2.740445
C	-2.491010	-0.339900	-1.162781
C	-4.373430	-0.411762	-2.667334
H	-5.043532	0.069142	-3.373190
C	-3.333326	0.292799	-2.100984
H	-3.128920	1.331755	-2.333861
C	-1.318556	0.293720	-0.597871
O	-0.940741	1.457478	-0.818746
N	-0.590465	-0.628570	0.186321
H	-3.811636	-3.379478	-1.087165
N	-2.687732	-1.664168	-0.840175
O	0.166221	0.229042	1.395737
C	1.452224	0.431948	1.110250
O	2.109605	-0.171700	0.280945
C	-2.622529	-1.822678	1.976459
C	-3.936214	-2.314303	1.995754
C	-2.200508	-1.011628	3.041987
C	-4.799340	-2.027001	3.053860
C	-3.061370	-0.713954	4.097558
C	-4.360060	-1.228703	4.110836
H	-4.300541	-2.934668	1.184215
H	-1.197345	-0.601521	3.040461
H	-5.808328	-2.426677	3.063915
H	-2.723161	-0.089767	4.918646
C	-5.299754	-0.870611	5.225266
F	-5.975511	0.275032	4.968088
F	-6.230474	-1.833109	5.431056
F	-4.646493	-0.682054	6.396037
C	2.012836	1.541413	1.983275
H	1.716960	1.406600	3.026964
H	3.099457	1.558338	1.893396
H	1.596507	2.493121	1.639823

²IrA

Charge = 0 Multiplicity = 2

Cartesian coordinates:

ATOM	X	Y	Z

Ir	-1.462089	-2.506331	0.645206
C	-1.182580	-4.829468	0.315696
C	-1.121283	-4.563466	1.705703
C	-0.038280	-3.616555	1.933832
C	0.641790	-3.418075	0.670783
C	-0.088765	-4.116000	-0.338345
C	0.437891	-3.134012	3.271594
H	-0.406531	-2.907027	3.927147
H	1.063569	-3.887513	3.766323
H	1.025375	-2.219800	3.161739
C	1.853354	-2.554840	0.489215
H	2.245702	-2.628132	-0.527055
H	1.597024	-1.506212	0.677478
H	2.645405	-2.855743	1.182549
C	0.249516	-4.212362	-1.796916
H	0.861321	-3.367093	-2.118154
H	0.801676	-5.135170	-2.016274
H	-0.654377	-4.215972	-2.412994
C	-2.134983	-5.756963	-0.378582
H	-1.700475	-6.758751	-0.484091
H	-3.071448	-5.859491	0.175821
H	-2.372738	-5.401769	-1.385510
C	-1.993805	-5.136805	2.779315
H	-1.486399	-5.974421	3.273371
H	-2.228470	-4.386317	3.536900
H	-2.941143	-5.504676	2.378997
C	-3.878454	-2.506024	-1.286608
C	-4.807523	-1.894183	-2.121262
H	-5.602529	-2.487559	-2.559575
C	-2.759906	-0.485853	-0.966356
C	-4.702944	-0.522244	-2.369376
H	-5.423124	-0.022932	-3.010187
C	-3.662808	0.190368	-1.777818
H	-3.515993	1.255999	-1.915088
C	-1.585808	0.163704	-0.280756
O	-1.420251	1.388511	-0.367486
N	-0.769994	-0.701076	0.386509
H	-3.923522	-3.561889	-1.046570
N	-2.872957	-1.812014	-0.726039
C	-2.835579	-1.931865	2.066760
C	-4.083918	-2.569443	2.172992
C	-2.531256	-0.934953	3.011657
C	-4.987552	-2.244102	3.184101
C	-3.428534	-0.601623	4.025610
C	-4.658011	-1.259263	4.117440
H	-4.353481	-3.348420	1.464316
H	-1.583241	-0.410719	2.944365
H	-5.941003	-2.757796	3.258554
H	-3.175464	0.165831	4.750403
C	-5.649595	-0.861926	5.170109
F	-6.473636	0.127618	4.743501
F	-6.446846	-1.896642	5.532434
F	-5.045491	-0.405168	6.292187

OAc radical

Charge = 0 Multiplicity = 2

Cartesian coordinates:

ATOM	X	Y	Z
O	0.178084	0.099587	1.300394
C	1.364889	0.514115	1.189719
O	2.020206	-0.158703	0.348110
C	1.916704	1.680615	1.946673
H	1.519362	1.683495	2.964770
H	3.007843	1.636422	1.959864
H	1.602500	2.606031	1.452704

¹IrA

Charge = 1 Multiplicity = 1

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.400575	-2.335151	0.663328
C	-1.323268	-4.720647	0.517564
C	-1.151690	-4.429187	1.885652
C	-0.011618	-3.522036	2.023201
C	0.598755	-3.369312	0.732654
C	-0.259151	-4.041838	-0.226994
C	0.537998	-3.025379	3.321927
H	-0.264597	-2.723281	3.998750
H	1.109722	-3.820438	3.814995
H	1.201534	-2.172637	3.168934
C	1.870012	-2.628794	0.457060
H	2.082165	-2.584174	-0.611717
H	1.807129	-1.601158	0.825360
H	2.706968	-3.130188	0.953499
C	0.009067	-4.213875	-1.689910
H	0.609811	-3.394196	-2.086376
H	0.554128	-5.150424	-1.859179
H	-0.919469	-4.262784	-2.263032
C	-2.351741	-5.629610	-0.082687
H	-1.982804	-6.661718	-0.097891
H	-3.280970	-5.622451	0.492147
H	-2.578395	-5.354904	-1.115419
C	-1.950570	-4.956928	3.030800
H	-1.412687	-5.797825	3.485278
H	-2.096827	-4.196682	3.800167
H	-2.931851	-5.313951	2.715735
C	-3.900895	-2.375868	-1.215632
C	-4.809351	-1.779088	-2.087800
H	-5.623901	-2.369587	-2.491883
C	-2.710215	-0.383719	-1.034686
C	-4.658546	-0.431105	-2.417790
H	-5.361707	0.053111	-3.087489

C	-3.585100	0.281331	-1.879030	C	1.888515	-2.931409	0.363268
H	-3.399964	1.327626	-2.096810	H	1.930716	-2.612635	-0.679736
C	-1.490447	0.231447	-0.412392	H	2.185514	-2.090187	0.991232
O	-1.259587	1.423767	-0.457793	H	2.622192	-3.735539	0.499691
N	-0.649877	-0.688307	0.245542	C	-0.140683	-4.463529	-1.594599
H	-3.985150	-3.414442	-0.921582	H	0.507598	-3.725724	-2.070837
N	-2.878300	-1.679723	-0.697656	H	0.352605	-5.440128	-1.663281
C	-2.836434	-2.041876	2.120974	H	-1.067187	-4.516887	-2.170734
C	-4.093004	-2.655806	2.095315	C	-2.675182	-5.398782	0.158021
C	-2.516393	-1.167032	3.169731	H	-2.548095	-6.424957	0.521188
C	-5.031467	-2.386806	3.091054	H	-3.633063	-5.033633	0.537495
C	-3.461383	-0.886462	4.158188	H	-2.724634	-5.449414	-0.931573
C	-4.715341	-1.498224	4.120070	C	-2.283574	-4.289024	3.100778
H	-4.346104	-3.367042	1.316771	H	-1.986626	-5.205755	3.624396
H	-1.545302	-0.685655	3.211858	H	-2.253470	-3.464632	3.813840
H	-6.000518	-2.874200	3.079060	H	-3.314894	-4.409968	2.765497
H	-3.220089	-0.200115	4.962799	C	-3.583109	-2.320366	-1.598170
C	-5.752749	-1.160713	5.162970	C	-4.472310	-1.742731	-2.502247
F	-6.518139	-0.124648	4.761145	H	-5.145561	-2.379192	-3.065514
F	-6.575679	-2.205587	5.391670	C	-2.740976	-0.228242	-1.030234
F	-5.181251	-0.814028	6.333235	C	-4.480494	-0.356091	-2.665178

OAc⁻

Charge = -1 Multiplicity = 1

Cartesian coordinates:

ATOM	X	Y	Z
O	0.079443	0.319169	1.210457
C	1.329091	0.435805	1.129064
O	2.168396	-0.270457	0.515900
C	1.916162	1.663512	1.924753
H	1.647402	1.582415	2.987213
H	3.006790	1.735264	1.833990
H	1.462305	2.595855	1.560856

¹IrA-TS

Charge = 1 Multiplicity = 1

Imaginary frequency: -231.31 cm⁻¹

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.335128	-2.226587	0.565836
C	-1.532626	-4.549372	0.624574
C	-1.356093	-4.056275	1.951654
C	-0.069850	-3.361906	2.029702
C	0.530645	-3.435475	0.732851
C	-0.403513	-4.116062	-0.160934
C	0.602455	-2.881786	3.279192
H	-0.118950	-2.675226	4.069810
H	1.290730	-3.652057	3.645547
H	1.181193	-1.973513	3.097005

C	1.888515	-2.931409	0.363268
H	1.930716	-2.612635	-0.679736
H	2.185514	-2.090187	0.991232
H	2.622192	-3.735539	0.499691
C	-0.140683	-4.463529	-1.594599
H	0.507598	-3.725724	-2.070837
H	0.352605	-5.440128	-1.663281
H	-1.067187	-4.516887	-2.170734
C	-2.675182	-5.398782	0.158021
H	-2.548095	-6.424957	0.521188
H	-3.633063	-5.033633	0.537495
H	-2.724634	-5.449414	-0.931573
C	-2.283574	-4.289024	3.100778
H	-1.986626	-5.205755	3.624396
H	-2.253470	-3.464632	3.813840
H	-3.314894	-4.409968	2.765497
C	-3.583109	-2.320366	-1.598170
C	-4.472310	-1.742731	-2.502247
H	-5.145561	-2.379192	-3.065514
C	-2.740976	-0.228242	-1.030234
C	-4.480494	-0.356091	-2.665178
H	-5.164581	0.112287	-3.365209
C	-3.590904	0.416383	-1.915688
H	-3.530534	1.495772	-2.000593
C	-1.704284	0.468531	-0.197277
O	-1.419804	1.636795	-0.373625
N	-0.993882	-0.342606	0.715351
H	-3.544812	-3.389393	-1.434972
N	-2.734575	-1.568862	-0.876697
C	-2.527575	-1.136850	2.061234
C	-3.918552	-1.206183	1.933831
C	-1.937331	-0.660556	3.234730
C	-4.716367	-0.882697	3.033179
C	-2.742201	-0.336735	4.325329
C	-4.130728	-0.457185	4.226613
H	-4.389436	-1.551188	1.022481
H	-0.866251	-0.518359	3.282720
H	-5.794886	-0.979173	2.966937
H	-2.294596	0.021815	5.245971
C	-5.004895	-0.053092	5.389292
F	-5.316650	1.256589	5.326017
F	-6.162433	-0.746640	5.395412
F	-4.382810	-0.267425	6.566213

¹IrB

Charge = 1 Multiplicity = 1

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.368384	-2.452513	0.472674
C	-1.117655	-4.691572	0.242210
C	-1.352077	-4.312056	1.616163

C	-0.241745	-3.475835	2.067334
C	0.617811	-3.280984	0.944242
C	0.060338	-4.017716	-0.198193
C	-0.031774	-2.978735	3.462688
H	-0.981271	-2.741402	3.945776
H	0.472378	-3.747225	4.059421
H	0.577395	-2.074125	3.478406
C	1.912563	-2.536105	0.928282
H	2.060622	-2.013551	-0.019473
H	1.964667	-1.807260	1.736997
H	2.739390	-3.245905	1.051733
C	0.703436	-4.112769	-1.545122
H	1.170613	-3.167038	-1.827871
H	1.484096	-4.882735	-1.533835
H	-0.018366	-4.378721	-2.319578
C	-1.965201	-5.644175	-0.544262
H	-1.742433	-6.673515	-0.241840
H	-3.031336	-5.475188	-0.372212
H	-1.768904	-5.573084	-1.616099
C	-2.470525	-4.798226	2.478051
H	-2.165689	-5.722767	2.984216
H	-2.728431	-4.066316	3.245707
H	-3.365054	-5.014850	1.891122
C	-3.317166	-2.611711	-1.942426
C	-4.289622	-2.114254	-2.805550
H	-4.657244	-2.740015	-3.610946
C	-3.289659	-0.614232	-0.749582
C	-4.771935	-0.818421	-2.615650
H	-5.531346	-0.410835	-3.274878
C	-4.259901	-0.053937	-1.565425
H	-4.583298	0.959891	-1.357563
C	-2.672496	0.143594	0.392809
O	-3.023400	1.273331	0.678059
N	-1.688231	-0.596050	1.036258
H	-2.915721	-3.610579	-2.050055
N	-2.828464	-1.872184	-0.930109
C	-1.026091	0.004962	2.153329
C	-1.686898	0.131765	3.378531
C	0.305643	0.409163	2.024756
C	-1.004730	0.637942	4.482263
C	0.988370	0.911756	3.130319
C	0.334532	1.016558	4.360766
H	-2.725028	-0.172616	3.460175
H	0.793684	0.324000	1.059608
H	-1.503792	0.728724	5.440589
H	2.024681	1.219618	3.043444
C	1.064520	1.596626	5.546369
F	0.953254	2.939425	5.580631
F	0.573592	1.119150	6.709459
F	2.382525	1.302338	5.500709

¹Ir4a

ATOM	X	Y	Z
Ir	-1.283392	-2.302413	0.675246
C	-1.271681	-4.530342	0.656136
C	-0.831124	-4.075978	1.941187
C	0.359976	-3.272766	1.774392
C	0.673464	-3.254342	0.351986
C	-0.334845	-4.009188	-0.335421
C	1.228575	-2.736405	2.869932
H	0.635518	-2.442015	3.738274
H	1.949382	-3.498090	3.192485
H	1.783116	-1.855223	2.544739
C	1.861247	-2.576397	-0.257436
H	1.693993	-2.352524	-1.312967
H	2.076961	-1.633920	0.249997
H	2.746181	-3.218891	-0.179113
C	-0.404492	-4.278677	-1.807849
H	0.159249	-3.535264	-2.374792
H	0.006962	-5.268340	-2.038034
H	-1.438499	-4.254658	-2.162211
C	-2.424239	-5.453374	0.403061
H	-2.159342	-6.484596	0.665847
H	-3.288542	-5.144556	0.994206
H	-2.710720	-5.447757	-0.651727
C	-1.508905	-4.365148	3.243846
H	-2.585217	-4.466405	3.101047
H	-1.113417	-5.292310	3.675608
C	-3.718856	-2.449795	-1.198998
C	-4.520265	-2.039274	-2.259467
H	-5.371263	-2.646320	-2.548219
C	-2.372823	-0.556553	-1.418677
C	-4.219984	-0.845164	-2.919723
H	-4.832011	-0.505766	-3.749837
C	-3.135460	-0.088711	-2.484567
H	-2.850738	0.859457	-2.926027
C	-1.232896	0.252816	-0.858554
O	-0.923254	1.324984	-1.387701
N	-0.718259	-0.320181	0.258033
H	-3.929496	-3.332472	-0.610649
N	-2.653266	-1.726743	-0.809286
C	0.236433	0.362795	1.036184
C	0.105251	0.337327	2.436696
C	1.327861	1.041289	0.464043
C	1.054048	0.952357	3.244218
C	2.276376	1.653424	1.279090
C	2.150096	1.604950	2.669668
H	-0.752653	-0.170220	2.863875
H	1.414498	1.089648	-0.613498
H	0.952834	0.922294	4.324249
H	3.126144	2.161484	0.835510

C	3.145817	2.304387	3.545384	C	-1.883590	0.295488	-0.173152
F	2.764228	3.570975	3.842226	O	-1.676682	1.512423	-0.168556
F	3.311908	1.665695	4.729789	N	-1.327934	-0.557760	0.894930
F	4.364242	2.393464	2.960651	H	-3.298545	-3.723694	-1.514541
O	-2.635262	-1.395755	2.012832	N	-2.557326	-1.885426	-0.933769
C	-3.771336	-1.986598	2.262077	O	-0.443820	0.153588	1.728245
O	-4.161467	-3.054603	1.776845	C	0.773269	0.446948	1.157892
C	-4.625253	-1.207695	3.253850	O	1.174731	-0.025435	0.124756
H	-4.864305	-0.224023	2.838530	C	-2.568149	-1.482226	1.970298
H	-4.063150	-1.039067	4.177198	C	-3.944496	-1.253747	1.680525
H	-5.544691	-1.753038	3.469552	C	-2.153739	-1.385963	3.328518

³Ir3a-TS'

Charge = 0 Multiplicity = 3
Imaginary frequency: -411.58 cm⁻¹

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.316296	-2.569311	0.605261
C	-1.264152	-4.788715	0.804168
C	-0.575223	-4.203443	1.937509
C	0.555837	-3.469712	1.445106
C	0.623181	-3.651735	0.004902
C	-0.501937	-4.450109	-0.376909
C	1.587618	-2.757275	2.267306
H	1.152379	-2.325317	3.171744
H	2.381998	-3.448499	2.574035
H	2.045063	-1.950226	1.692722
C	1.696774	-3.131602	-0.899023
H	1.383269	-3.175888	-1.944401
H	1.932930	-2.091758	-0.666964
H	2.611286	-3.730440	-0.796023
C	-0.786378	-4.900475	-1.779788
H	-0.812298	-4.056047	-2.473407
H	-0.003530	-5.590119	-2.114684
H	-1.740263	-5.425934	-1.850443
C	-2.435796	-5.720610	0.886133
H	-2.107728	-6.759292	1.022161
H	-3.083310	-5.458519	1.726203
H	-3.044470	-5.680920	-0.020706
C	-0.947310	-4.431531	3.370909
H	-0.683787	-5.455092	3.662935
H	-0.421497	-3.747379	4.038553
H	-2.018989	-4.294890	3.533073
C	-3.328285	-2.661769	-1.727541
C	-4.110762	-2.158947	-2.745760
H	-4.700233	-2.834801	-3.354121
C	-2.596742	-0.501029	-1.110280
C	-4.121887	-0.748007	-2.970380
H	-4.720651	-0.326238	-3.771454
C	-3.378128	0.063004	-2.152496
H	-3.361664	1.142468	-2.256720

C	-1.883590	0.295488	-0.173152
O	-1.676682	1.512423	-0.168556
N	-1.327934	-0.557760	0.894930
H	-3.298545	-3.723694	-1.514541
N	-2.557326	-1.885426	-0.933769
O	-0.443820	0.153588	1.728245
C	0.773269	0.446948	1.157892
O	1.174731	-0.025435	0.124756
C	-2.568149	-1.482226	1.970298
C	-3.944496	-1.253747	1.680525
C	-2.153739	-1.385963	3.328518
C	-4.854096	-1.047589	2.708615
C	-3.068732	-1.182043	4.343470
C	-4.431917	-1.019936	4.042664
H	-4.298528	-1.290824	0.660049
H	-1.100715	-1.477422	3.563408
H	-5.907347	-0.923515	2.479154
H	-2.739979	-1.149942	5.377311
C	-5.405706	-0.741199	5.146591
F	-5.432209	0.572457	5.481169
F	-6.670185	-1.084505	4.809600
F	-5.087683	-1.418497	6.277355
C	1.486269	1.441945	2.034306
H	1.374773	1.186080	3.090696
H	2.538426	1.480539	1.753116
H	1.026648	2.422433	1.876108

³Ir4a

Charge = 0 Multiplicity = 3

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.569916	-2.222742	0.277868
C	-1.587517	-4.437039	0.421758
C	-1.565162	-3.898662	1.766861
C	-0.235967	-3.376342	2.014032
C	0.560390	-3.605674	0.861621
C	-0.305400	-4.131419	-0.166333
C	0.254920	-2.791102	3.301330
H	-0.568438	-2.570330	3.981246
H	0.928338	-3.497180	3.802402
H	0.793520	-1.860997	3.108336
C	1.988783	-3.218430	0.675147
H	2.130657	-2.750381	-0.302471
H	2.304221	-2.502282	1.435979
H	2.647509	-4.095446	0.729980
C	0.150176	-4.528237	-1.539161
H	0.830672	-3.777823	-1.952208
H	0.687677	-5.484338	-1.515534
H	-0.693139	-4.641426	-2.225446
C	-2.677996	-5.262944	-0.192155
H	-2.513027	-6.330381	0.003801

H	-3.656286	-4.995285	0.214665	C	-0.236196	-4.118877	-0.320522
H	-2.718220	-5.125407	-1.275851	C	0.802995	-2.859769	3.077308
C	-2.645484	-4.057755	2.796009	H	0.190762	-2.967074	3.974700
H	-2.506583	-4.990043	3.357010	H	1.752234	-3.378396	3.259858
H	-2.643905	-3.229540	3.506535	H	1.020748	-1.796890	2.939868
H	-3.634443	-4.086042	2.332181	C	1.788271	-2.494807	0.099706
C	-1.745216	-1.646000	-2.738455	H	1.753318	-2.245934	-0.963089
C	-2.317748	-1.104092	-3.883979	H	1.827951	-1.557543	0.659800
H	-1.864332	-1.299549	-4.849647	H	2.720545	-3.042803	0.288347
C	-3.358715	-0.636088	-1.396589	C	-0.085585	-4.316388	-1.799217
C	-3.461258	-0.308629	-3.766905	H	0.465365	-3.491371	-2.255613
H	-3.925782	0.122194	-4.648198	H	0.454232	-5.246328	-2.015702
C	-3.985161	-0.066368	-2.499207	H	-1.057097	-4.377390	-2.297809
H	-4.855412	0.555494	-2.323158	C	-2.185471	-5.844938	0.069030
C	-3.822672	-0.371351	0.004234	H	-1.776196	-6.854513	0.202758
O	-4.824609	0.306319	0.221388	H	-3.120963	-5.785738	0.631104
N	-2.985677	-0.943355	0.937464	H	-2.425187	-5.737273	-0.992469
H	-0.846012	-2.246867	-2.764981	C	-1.726397	-4.850910	3.077891
N	-2.273550	-1.429084	-1.522135	H	-1.166072	-5.641809	3.591211
O	0.675833	-0.167058	1.507617	H	-1.887393	-4.032355	3.783003
C	0.857815	-0.246688	0.287528	H	-2.707020	-5.249342	2.809045
O	0.227681	-1.025450	-0.539353	C	-3.374227	-2.664937	-1.781972
C	-3.236271	-0.732933	2.318663	C	-4.128044	-2.127424	-2.816627
C	-4.511664	-0.915308	2.874542	H	-4.618510	-2.794259	-3.517620
C	-2.152537	-0.398092	3.143265	C	-2.866902	-0.536891	-0.976627
C	-4.692029	-0.789527	4.248497	C	-4.250185	-0.737045	-2.928534
C	-2.341316	-0.273701	4.516573	H	-4.835421	-0.296763	-3.729685
C	-3.607513	-0.477526	5.073512	C	-3.613039	0.063620	-1.986236
H	-5.347053	-1.156505	2.229536	H	-3.662316	1.146875	-1.993814
H	-1.174987	-0.255171	2.690417	C	-2.169069	0.229648	0.105942
H	-5.671583	-0.948597	4.686247	O	-2.172051	1.462890	0.087946
H	-1.502651	-0.026828	5.159035	N	-1.525324	-0.534544	1.062858
C	-3.812568	-0.299411	6.549887	H	-3.270677	-3.733582	-1.642135
F	-4.087758	0.987527	6.871172	N	-2.741270	-1.885065	-0.879859
F	-4.844315	-1.045154	7.011907	C	-2.800904	-1.519411	2.045602
F	-2.711867	-0.649262	7.257068	C	-4.199491	-1.452823	1.801971
C	1.944214	0.590630	-0.388118	C	-2.372544	-1.357665	3.391482
H	2.309148	1.355495	0.298831	C	-5.104897	-1.312128	2.846499
H	2.776385	-0.062202	-0.674157	C	-3.276146	-1.220678	4.429939
H	1.560592	1.051711	-1.302126	C	-4.654918	-1.204904	4.166326

²IrA-TS

Charge = 0 Multiplicity = 2
Imaginary frequency: -483.48 cm⁻¹

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.518412	-2.530585	0.661842
C	-1.206278	-4.801961	0.520184
C	-0.979862	-4.381655	1.866315
C	0.115350	-3.431051	1.872474
C	0.603149	-3.311266	0.514842

²IrB

Charge = 0 Multiplicity = 2

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.366861	-2.434527	0.428847
C	-1.138547	-4.665254	0.264164
C	-1.277157	-4.341222	1.659838
C	-0.183919	-3.469992	2.019688
C	0.665035	-3.314346	0.863901
C	0.063748	-4.041574	-0.230162
C	0.087712	-2.951737	3.400536
H	-0.840396	-2.676772	3.907481
H	0.594830	-3.712991	4.005863
H	0.715152	-2.059899	3.378658
C	1.980744	-2.599883	0.821583
H	2.143241	-2.121605	-0.148003
H	2.036416	-1.827449	1.590477
H	2.806959	-3.302354	0.992430
C	0.645561	-4.199911	-1.602405
H	1.233232	-3.322987	-1.884305
H	1.302672	-5.077834	-1.654632
H	-0.136789	-4.326197	-2.355673
C	-2.028480	-5.609512	-0.489537
H	-1.825953	-6.647200	-0.197881
H	-3.085353	-5.408295	-0.291226
H	-1.867984	-5.540881	-1.568420
C	-2.342392	-4.848860	2.580901
H	-2.031817	-5.790578	3.053879
H	-2.553113	-4.131129	3.377128
H	-3.275417	-5.037544	2.043921
C	-3.202087	-2.540353	-2.004771
C	-4.182110	-2.064222	-2.859278
H	-4.497383	-2.678283	-3.696266
C	-3.303160	-0.591588	-0.722899
C	-4.747765	-0.800858	-2.630590
H	-5.518232	-0.410565	-3.287335
C	-4.292512	-0.062605	-1.542762
H	-4.670498	0.922308	-1.291441
C	-2.761445	0.156228	0.444819
O	-3.183977	1.270941	0.764504
N	-1.756363	-0.551850	1.052049
H	-2.742089	-3.509606	-2.147131
N	-2.757546	-1.824979	-0.940224
C	-1.106307	0.027795	2.169607
C	-1.789734	0.246095	3.372738
C	0.256501	0.341044	2.085860
C	-1.111550	0.740531	4.483125
C	0.936493	0.836004	3.194789
C	0.254319	1.026545	4.400093
H	-2.848445	0.018238	3.424277
H	0.766848	0.179291	1.142624
H	-1.635102	0.893909	5.420738
H	1.994557	1.068010	3.132712
C	0.976238	1.599640	5.584479
F	0.945806	2.954057	5.590849

F	0.431659	1.192723	6.755280
F	2.283004	1.241726	5.599527

Ph₃P

Charge = 0 Multiplicity = 1

Cartesian coordinates:

ATOM	X	Y	Z
P	3.569593	-4.322794	-1.410746
C	1.944118	-4.423297	-0.529688
C	1.092520	-3.310424	-0.629716
C	1.518945	-5.531167	0.219620
C	-0.158259	-3.310404	-0.012407
C	0.271342	-5.526169	0.847077
C	-0.571180	-4.419023	0.730354
H	1.412841	-2.438505	-1.194965
H	2.163572	-6.399400	0.312644
H	-0.806056	-2.442987	-0.103690
H	-0.043118	-6.390660	1.425506
H	-1.541459	-4.417668	1.218934
C	3.127102	-4.970991	-3.087838
C	4.064285	-4.776605	-4.116282
C	1.928281	-5.636713	-3.386471
C	3.818789	-5.249909	-5.405148
C	1.677848	-6.100281	-4.679792
C	2.622210	-5.911702	-5.690641
H	4.991991	-4.250371	-3.904645
H	1.189289	-5.793556	-2.607178
H	4.556418	-5.094771	-6.187595
H	0.744043	-6.612161	-4.896104
H	2.425417	-6.273648	-6.695840
C	4.479684	-5.760989	-0.681353
C	5.204337	-5.527031	0.499301
C	4.486623	-7.052396	-1.230664
C	5.903189	-6.559337	1.124900
C	5.195961	-8.083048	-0.610237
C	5.902420	-7.841012	0.569369
H	5.220650	-4.528852	0.930282
H	3.936596	-7.253396	-2.144469
H	6.454676	-6.361751	2.039893
H	5.193424	-9.077292	-1.048738
H	6.453012	-8.644467	1.050472

¹IrA-TS'

Charge = 1 Multiplicity = 1

Imaginary frequency: -29.13 cm⁻¹

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.145360	-3.543089	-0.001174
C	-2.275755	-5.651500	0.318533

C	-2.694674	-4.731137	1.322887	C	-0.617376	-5.411938	-3.635542
C	-1.513396	-4.333293	2.068465	C	0.049383	-3.830015	-5.345298
C	-0.376644	-5.029478	1.516500	C	-1.656792	-5.856556	-4.449462
C	-0.857268	-5.873654	0.451464	C	-1.000445	-4.271176	-6.151593
C	-1.504963	-3.515221	3.321306	C	-1.854643	-5.284089	-5.709409
H	-2.298136	-2.767018	3.320086	H	-0.469617	-5.850145	-2.656482
H	-1.652839	-4.174449	4.184804	H	0.714664	-3.050861	-5.703399
H	-0.554369	-2.995139	3.451545	H	-2.309028	-6.655311	-4.107091
C	1.012266	-5.015246	2.075733	H	-1.143101	-3.830359	-7.133653
H	1.088693	-5.717773	2.913759	H	-2.662348	-5.632329	-6.345834
H	1.741806	-5.303726	1.319460	C	2.749210	-2.869899	-3.952207
H	1.280742	-4.021291	2.439199	C	2.600566	-1.487453	-4.156189
C	-0.066282	-6.945245	-0.229231	C	3.835086	-3.545338	-4.535728
H	0.959892	-6.639644	-0.428690	C	3.513962	-0.797398	-4.954616
H	-0.028187	-7.826645	0.424143	C	4.742726	-2.848176	-5.330552
H	-0.524123	-7.265035	-1.166878	C	4.581979	-1.475872	-5.543512
C	-3.157715	-6.342684	-0.676638	H	1.797629	-0.944213	-3.672045
H	-4.128352	-5.850081	-0.764779	H	3.970508	-4.609019	-4.368714
H	-2.694945	-6.371722	-1.666471	H	3.397591	0.271596	-5.103865
H	-3.343244	-7.377482	-0.366801	H	5.577258	-3.375474	-5.782643
C	-4.103230	-4.345860	1.656437	H	5.294259	-0.936258	-6.160175
H	-4.518400	-5.038909	2.397374	C	2.386090	-5.176461	-2.215707
H	-4.152671	-3.338548	2.072058	C	2.440709	-6.438678	-2.829482
H	-4.751901	-4.374317	0.777436	C	3.068684	-4.960768	-1.006598
C	-2.845200	-3.085136	-2.570001	C	3.163881	-7.473206	-2.233884
C	-3.172997	-2.382438	-3.725764	C	3.800397	-5.996502	-0.424107
H	-4.055702	-2.664377	-4.287678	C	3.843487	-7.254146	-1.032739
C	-0.935088	-1.783373	-2.272869	H	1.918504	-6.613977	-3.764482
C	-2.361034	-1.322218	-4.134025	H	3.005005	-3.991298	-0.521635
H	-2.611862	-0.748989	-5.020443	H	3.202436	-8.447459	-2.711680
C	-1.224732	-1.011383	-3.386928	H	4.331213	-5.823737	0.507311
H	-0.559972	-0.194705	-3.644669	H	4.408094	-8.060204	-0.574220
C	0.294155	-1.648268	-1.416903				
O	0.995898	-0.654517	-1.413128				
N	0.495826	-2.755600	-0.537926				
H	-3.453916	-3.897963	-2.193685				
N	-1.747754	-2.781446	-1.862545				
C	-1.976366	-1.747044	0.659956				
C	-3.307568	-1.415477	0.383747				
C	-1.193181	-0.851558	1.401456				
C	-3.858296	-0.223866	0.856976				
C	-1.738524	0.344111	1.869266				
C	-3.072470	0.655892	1.602232				
H	-3.932163	-2.085936	-0.197623				
H	-0.150885	-1.074107	1.602869				
H	-4.891819	0.026645	0.641749				
H	-1.123756	1.041125	2.428929				
C	-3.682047	1.911695	2.167521				
F	-4.216290	1.684831	3.389399				
F	-2.765971	2.891846	2.307860				
F	-4.675043	2.380029	1.380532				
P	1.513694	-3.748227	-2.931887				
C	0.258021	-4.403155	-4.079226				

¹IrC

Charge = 1 Multiplicity = 1

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.163738	-2.379546	0.710148
C	-1.196431	-4.572065	0.431708
C	-1.030887	-4.277064	1.825432
C	0.225648	-3.589917	1.976167
C	0.908493	-3.634029	0.681428
C	0.046054	-4.217718	-0.263076
C	0.883581	-3.342794	3.302507
H	0.193766	-2.874298	4.009498
H	1.205450	-4.296471	3.738363
H	1.765339	-2.708573	3.211277
C	2.326664	-3.208411	0.481721
H	2.567570	-3.038382	-0.567073
H	2.551176	-2.293944	1.034206
H	2.993141	-3.991709	0.863621

C	0.313859	-4.504436	-1.708334	C	0.764587	2.543351	-1.692863
H	1.219553	-4.006712	-2.054626	C	0.121331	4.634962	0.050690
H	0.434501	-5.582032	-1.871292	C	0.643159	3.846023	-2.178360
H	-0.514646	-4.170598	-2.342278	C	0.325098	4.889850	-1.309185
C	-2.288734	-5.430568	-0.135046	H	0.053532	3.142441	1.593111
H	-2.115231	-6.477080	0.141383	H	1.026714	1.741801	-2.374359
H	-3.271427	-5.147493	0.249844	H	-0.132546	5.445709	0.725917
H	-2.314861	-5.390968	-1.226601	H	0.805529	4.043013	-3.233288
C	-1.924703	-4.711776	2.943832	H	0.236580	5.903193	-1.688771
H	-1.553522	-5.660384	3.350249	C	1.601100	0.736402	1.893304
H	-1.943477	-3.975118	3.748476	C	1.235575	-0.085135	2.965499
H	-2.951638	-4.861238	2.609133	C	2.649632	1.661718	2.044237
C	-3.308340	-2.438612	-1.557970	C	1.914995	0.009389	4.180298
C	-4.382833	-1.921471	-2.275553	C	3.329536	1.744530	3.258105
H	-4.957400	-2.578537	-2.919047	C	2.963068	0.919778	4.325990
C	-2.848752	-0.358752	-0.642528	H	0.422462	-0.787108	2.842303
C	-4.708358	-0.571071	-2.139202	H	2.916162	2.329133	1.230756
H	-5.554342	-0.148482	-2.671143	H	1.622411	-0.625829	5.010407
C	-3.922408	0.222968	-1.307038	H	4.136101	2.461347	3.374875
H	-4.107313	1.279577	-1.152343	H	3.489453	0.994566	5.272454
C	-1.900850	0.475221	0.166706	<hr/> <hr/> <hr/> <hr/>			
O	-2.153184	1.637153	0.435447	²IrA-TS'			
N	-0.721582	-0.221052	0.446235	<hr/> <hr/> <hr/> <hr/>			
H	-3.046014	-3.485217	-1.612410	Charge = 0 Multiplicity = 2			
N	-2.552381	-1.674168	-0.750298	Imaginary frequency: -45.29 cm ⁻¹			
C	-2.642077	-1.763237	2.011566	Cartesian coordinates:			
C	-3.924257	-2.337393	1.922768				
C	-2.431743	-0.816393	3.026235	ATOM	X	Y	Z
C	-4.941263	-2.002419	2.813434	Ir	-1.403959	-2.572322	0.631436
C	-3.442862	-0.474887	3.926443	C	-1.224406	-4.826349	0.201846
C	-4.699039	-1.070712	3.825396	C	-1.171319	-4.602775	1.609690
H	-4.138971	-3.065703	1.144948	C	0.002347	-3.790805	1.873446
H	-1.478111	-0.310832	3.111418	C	0.708741	-3.627420	0.622532
H	-5.918921	-2.467041	2.733114	C	-0.052236	-4.234395	-0.415554
H	-3.255729	0.254404	4.707872	C	0.532982	-3.514080	3.250624
C	-5.811979	-0.661282	4.749502	H	-0.205282	-2.983662	3.859312
F	-6.550634	0.341867	4.220107	H	0.778380	-4.453433	3.761844
F	-6.659205	-1.686324	4.993657	H	1.441410	-2.911822	3.213992
F	-5.342256	-0.222727	5.938021	C	2.076929	-3.038224	0.493630
P	0.716408	0.596969	0.320926	H	2.324825	-2.800279	-0.539216
C	1.740849	-0.290589	-0.886594	H	2.186919	-2.127691	1.083098
C	1.103052	-0.961626	-1.940640	H	2.815315	-3.762010	0.862474
C	3.139761	-0.195345	-0.861055	C	0.319461	-4.370165	-1.861636
C	1.864762	-1.523475	-2.966265	H	1.048404	-3.614009	-2.154466
C	3.894917	-0.771354	-1.881797	H	0.754015	-5.357100	-2.070615
C	3.258719	-1.431661	-2.936610	H	-0.554935	-4.253693	-2.509419
H	0.021810	-1.046816	-1.949866	C	-2.200033	-5.707623	-0.518193
H	3.641366	0.312962	-0.044447	H	-1.773165	-6.710034	-0.646063
H	1.369948	-2.034928	-3.785980	H	-3.135127	-5.820741	0.036592
H	4.977765	-0.703170	-1.855179	H	-2.431119	-5.325590	-1.516356
H	3.848435	-1.872468	-3.734437	C	-2.039857	-5.210852	2.666862
C	0.559408	2.285200	-0.329158	H	-1.542873	-6.086152	3.104469
C	0.232569	3.338745	0.542184	H	-2.242283	-4.497708	3.468476

H	-3.002228	-5.539559	2.267470	C	2.159179	1.960869	2.186689
C	-4.041432	-2.803526	-0.930762	C	1.589310	-0.162089	3.904386
C	-5.163914	-2.313072	-1.584071	C	2.667860	1.954939	3.485293
H	-5.958150	-2.997547	-1.862162	C	2.383356	0.896293	4.350387
C	-3.098011	-0.682123	-0.824770	H	0.457689	-0.982069	2.267189
C	-5.251946	-0.944097	-1.854315	H	2.381747	2.794284	1.529962
H	-6.124413	-0.533573	-2.353170	H	1.351162	-0.983081	4.573490
C	-4.203257	-0.121154	-1.461156	H	3.285752	2.783056	3.821136
H	-4.190510	0.950883	-1.619190	H	2.772356	0.898518	5.364519
C	-1.921542	0.147508	-0.409009	<hr/> <hr/> <hr/> <hr/>			
O	-1.957704	1.374398	-0.666280	<hr/> <hr/> <hr/> <hr/>			
N	-0.924073	-0.561289	0.141453	²IrC			
H	-3.948327	-3.848823	-0.674111	<hr/> <hr/> <hr/> <hr/>			
N	-3.015882	-2.006982	-0.568883	Charge = 0 Multiplicity = 2			
C	-2.614462	-1.820265	2.125685	Cartesian coordinates:			
C	-3.807920	-2.495547	2.451986	ATOM	X	Y	Z
C	-2.330806	-0.655306	2.861858	Ir	-1.150120	-2.314346	0.769084
C	-4.651962	-2.064539	3.473638	C	-1.179738	-4.503026	0.568452
C	-3.162652	-0.215968	3.891958	C	-0.982656	-4.164720	1.953773
C	-4.324274	-0.922652	4.207988	C	0.292129	-3.517679	2.073575
H	-4.087793	-3.386695	1.896930	C	0.945066	-3.589631	0.768736
H	-1.454908	-0.069143	2.620398	C	0.064174	-4.195849	-0.144466
H	-5.558390	-2.614361	3.708552	C	0.978595	-3.243281	3.379311
H	-2.908300	0.677813	4.453549	H	0.303009	-2.765736	4.094650
C	-5.253196	-0.419414	5.269788	H	1.324911	-4.182525	3.831174
F	-6.191616	0.425386	4.770207	H	1.848921	-2.598155	3.255002
F	-5.930629	-1.427563	5.873616	C	2.357011	-3.159422	0.523688
F	-4.599400	0.263662	6.239903	H	2.566120	-3.011605	-0.536037
P	0.635092	0.897304	0.049885	H	2.581596	-2.222907	1.039846
C	1.787704	-0.068744	-0.998168	H	3.050986	-3.918418	0.907552
C	1.284245	-0.709320	-2.138032	C	0.302980	-4.504133	-1.590774
C	3.167723	-0.096359	-0.748619	H	1.244276	-4.079623	-1.941692
C	2.151276	-1.352959	-3.023525	H	0.334663	-5.588035	-1.757523
C	4.031515	-0.753260	-1.626306	H	-0.496429	-4.100374	-2.221779
C	3.524688	-1.379820	-2.767676	C	-2.290076	-5.373082	0.052786
H	0.214221	-0.712666	-2.317039	H	-2.149001	-6.408691	0.386544
H	3.564306	0.391516	0.136971	H	-3.264444	-5.033613	0.412338
H	1.753355	-1.838600	-3.910086	H	-2.319204	-5.386412	-1.039038
H	5.097834	-0.775066	-1.420101	C	-1.885798	-4.535742	3.089929
H	4.196559	-1.887267	-3.454021	H	-1.575403	-5.501290	3.508638
C	0.968007	2.630834	-0.531316	H	-1.853119	-3.786290	3.883141
C	0.070785	3.613693	-0.074940	H	-2.923943	-4.615977	2.764080
C	1.976001	3.001037	-1.436049	C	-3.046582	-2.440439	-1.661503
C	0.213447	4.940994	-0.471251	C	-4.131066	-2.007902	-2.387527
C	2.105657	4.331384	-1.842756	H	-4.625753	-2.691888	-3.068593
C	1.232827	5.305498	-1.356359	C	-2.747180	-0.306889	-0.692557
H	-0.756701	3.320438	0.562639	C	-4.592354	-0.663990	-2.214597
H	2.668112	2.259745	-1.820356	H	-5.470447	-0.310406	-2.745192
H	-0.482680	5.689973	-0.103994	C	-3.897612	0.162044	-1.364580
H	2.894592	4.604657	-2.538617	H	-4.184768	1.192815	-1.185430
H	1.336735	6.339241	-1.674042	C	-1.936435	0.543668	0.126594
C	1.356280	0.898925	1.728425	O	-2.155167	1.735455	0.370873
C	1.083507	-0.166290	2.604580	N	-0.748147	-0.143126	0.617923

H	-2.698455	-3.462607	-1.736547	Charge = -1 Multiplicity = 2
N	-2.347413	-1.642729	-0.812180	Cartesian coordinates:
C	-2.716403	-1.750657	1.953341	ATOM X Y Z
C	-4.011125	-2.245083	1.704626	Ir -1.326727 -2.467639 0.632164
C	-2.541211	-0.955919	3.099387	C -1.360433 -4.717338 0.744672
C	-5.070458	-1.988043	2.571643	C -0.724959 -4.172764 1.921708
C	-3.594254	-0.693600	3.974649	C 0.465527 -3.487183 1.503871
C	-4.862911	-1.218747	3.719743	C 0.645731 -3.727963 0.071634
H	-4.199241	-2.832789	0.811016	C -0.467968 -4.461264 -0.383049
H	-1.572894	-0.514641	3.305295	C 1.478078 -2.822085 2.390340
H	-6.058275	-2.388588	2.364931	H 0.996165 -2.348556 3.249834
H	-3.433364	-0.084387	4.858802	H 2.215576 -3.543900 2.768977
C	-6.009646	-0.899001	4.627821	H 2.016058 -2.047658 1.839362
F	-6.675638	0.219188	4.243713	C 1.771230 -3.151468 -0.733188
F	-6.927330	-1.897492	4.660309	H 1.674057 -3.399939 -1.793278
F	-5.605532	-0.684321	5.904739	H 1.783586 -2.059965 -0.637643
P	0.679137	0.594508	0.339607	H 2.740300 -3.533215 -0.385968
C	1.641429	-0.280475	-0.945472	C -0.772430 -4.875967 -1.791861
C	0.915495	-0.955400	-1.938877	H -0.022532 -4.500643 -2.491345
C	3.039374	-0.215278	-1.029029	H -0.807392 -5.969326 -1.881783
C	1.588333	-1.546936	-3.009709	H -1.743824 -4.484003 -2.111510
C	3.706303	-0.819950	-2.094103	C -2.562872 -5.615203 0.724396
C	2.981328	-1.483693	-3.087633	H -2.301647 -6.662697 0.935608
H	-0.165036	-1.026289	-1.864261	H -3.300649 -5.297416 1.466688
H	3.612401	0.288804	-0.258644	H -3.051320 -5.593099 -0.254781
H	1.021070	-2.064794	-3.777039	C -1.207856 -4.335939 3.332028
H	4.789950	-0.773877	-2.148007	H -0.823514 -5.267027 3.769024
H	3.501541	-1.950712	-3.918938	H -0.883322 -3.500804 3.956812
C	0.575352	2.308273	-0.268229	H -2.299511 -4.358366 3.371955
C	0.335357	3.351542	0.641652	C -3.575536 -2.493349 -1.464836
C	0.722337	2.596196	-1.631587	C -4.356902 -1.988237 -2.478381
C	0.253686	4.663583	0.190085	H -5.128601 -2.610337 -2.920642
C	0.629971	3.915500	-2.079439	C -2.374288 -0.457055 -1.259790
C	0.399616	4.948417	-1.171926	C -4.140886 -0.632359 -2.912061
H	0.196215	3.131286	1.694024	H -4.748219 -0.200034 -3.701820
H	0.908296	1.800706	-2.344601	C -3.155623 0.101229 -2.286294
H	0.063046	5.464875	0.897487	H -2.940725 1.133614 -2.547193
H	0.741983	4.131806	-3.137687	C -1.334924 0.276358 -0.566245
H	0.331136	5.974379	-1.521933	O -1.104711 1.492566 -0.685199
C	1.682794	0.703394	1.853918	N -0.569351 -0.592899 0.225991
C	1.273427	-0.012546	2.983074	H -3.720200 -3.504231 -1.092685
C	2.814107	1.533791	1.928175	N -2.590832 -1.787829 -0.856693
C	2.000266	0.079376	4.171370	O 0.032903 0.166378 1.297306
C	3.540451	1.617569	3.115011	C 1.323568 0.493129 1.120564
C	3.135598	0.888081	4.236882	O 2.081130 0.069565 0.272998
H	0.388173	-0.631663	2.915624	C -2.657376 -1.788894 1.995050
H	3.104915	2.139170	1.075097	C -3.987027 -2.265085 2.005261
H	1.675639	-0.480264	5.043325	C -2.288569 -0.932035 3.054258
H	4.411971	2.263073	3.169429	C -4.881141 -1.944977 3.024691
H	3.698435	0.961317	5.162869	C -3.173409 -0.605947 4.079649
<hr/>				
Ir3a^{•-}				
<hr/>				
H -4.325721 -2.909559 1.199563				
H -1.287191 -0.517216 3.067378				

H	-5.892328	-2.342462	3.013934	N	-0.724089	-0.430163	0.693911
H	-2.855584	0.041909	4.892098	H	-3.357605	-3.296488	-1.429961
C	-5.438598	-0.735124	5.149506	N	-2.465175	-1.533215	-0.819513
F	-6.132908	0.400533	4.858945	O	0.225575	0.138756	1.536948
F	-6.377057	-1.694124	5.375014	C	1.453127	0.384088	0.909019
F	-4.825964	-0.498408	6.340815	O	1.721755	-0.060806	-0.174138
C	1.714858	1.497069	2.188793	C	-2.829229	-2.003573	1.945439
H	1.368427	1.169265	3.172923	C	-4.102727	-2.525018	1.697423
H	2.797813	1.625985	2.188635	C	-2.618873	-1.224593	3.091784
H	1.225100	2.449446	1.964908	C	-5.157140	-2.270177	2.576123

Ir3a⁺

Charge = 1 Multiplicity = 2

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.216274	-2.334630	0.680269
C	-1.307114	-4.573168	1.123385
C	-0.478768	-3.902831	2.115969
C	0.663636	-3.351296	1.438824
C	0.576934	-3.704726	0.038182
C	-0.652382	-4.435139	-0.145746
C	1.819872	-2.669023	2.102215
H	1.478012	-1.955336	2.854629
H	2.448701	-3.413530	2.602764
H	2.435002	-2.138859	1.375044
C	1.590461	-3.377977	-1.012457
H	1.180948	-3.505653	-2.016249
H	1.943453	-2.348876	-0.915851
H	2.454908	-4.047191	-0.918000
C	-1.111673	-5.016723	-1.447324
H	-1.000883	-4.305358	-2.269636
H	-0.505673	-5.897045	-1.689063
H	-2.152739	-5.341609	-1.402875
C	-2.507343	-5.414926	1.427704
H	-2.191463	-6.428357	1.700462
H	-3.080485	-5.002030	2.258830
H	-3.176683	-5.496332	0.568481
C	-0.698802	-3.917273	3.593974
H	-0.257538	-4.826077	4.020075
H	-0.230276	-3.056573	4.074911
H	-1.761238	-3.903866	3.840531
C	-3.328314	-2.225446	-1.582949
C	-4.142019	-1.593695	-2.518727
H	-4.823930	-2.187442	-3.116966
C	-2.384216	-0.191079	-0.963608
C	-4.066910	-0.207423	-2.664809
H	-4.696385	0.306467	-3.383621
C	-3.167174	0.505888	-1.873190
H	-3.046604	1.581552	-1.936687
C	-1.371923	0.498376	-0.105776
O	-1.137254	1.691972	-0.150436

N	-0.724089	-0.430163	0.693911
H	-3.357605	-3.296488	-1.429961
N	-2.465175	-1.533215	-0.819513
O	0.225575	0.138756	1.536948
C	1.453127	0.384088	0.909019
O	1.721755	-0.060806	-0.174138
C	-2.829229	-2.003573	1.945439
C	-4.102727	-2.525018	1.697423
C	-2.618873	-1.224593	3.091784
C	-5.157140	-2.270177	2.576123
C	-3.672881	-0.962050	3.966643
C	-4.941044	-1.487752	3.710466
H	-4.287980	-3.144831	0.826759
H	-1.638540	-0.809889	3.303391
H	-6.141261	-2.685994	2.387668
H	-3.509801	-0.355881	4.851523
C	-6.091180	-1.160173	4.628736
F	-6.712059	-0.025322	4.240958
F	-7.016162	-2.143263	4.631917
F	-5.673259	-0.976754	5.898136
C	2.297534	1.243983	1.799704
H	2.208966	0.937000	2.844309
H	3.333874	1.198395	1.466861
H	1.934970	2.274314	1.723248

Ir3a-TS⁺

Charge = 1 Multiplicity = 2

Imaginary frequency: -342.08 cm⁻¹

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.344110	-2.543933	0.595838
C	-1.335531	-4.746946	0.879956
C	-0.684870	-4.144340	2.024249
C	0.469275	-3.426357	1.556406
C	0.595949	-3.646527	0.124929
C	-0.523218	-4.447620	-0.281714
C	1.481450	-2.713274	2.399778
H	1.037720	-2.296690	3.306143
H	2.269745	-3.409951	2.707120
H	1.953787	-1.904742	1.839709
C	1.726248	-3.193609	-0.742473
H	1.440864	-3.193437	-1.796252
H	2.046965	-2.183754	-0.484905
H	2.581413	-3.871237	-0.626007
C	-0.737744	-4.965142	-1.672033
H	-0.638508	-4.174517	-2.420230
H	0.016607	-5.727890	-1.894405
H	-1.715445	-5.435709	-1.788115
C	-2.517638	-5.665856	0.939806
H	-2.194957	-6.695427	1.135829
H	-3.205213	-5.370850	1.735326

H	-3.076686	-5.670620	0.001088	H	0.212129	-2.282126	3.535485
C	-1.122100	-4.320865	3.444305	H	1.548043	-3.433526	3.402521
H	-0.855902	-5.329381	3.780952	H	1.539907	-1.966590	2.414680
H	-0.638900	-3.607331	4.111956	C	1.992130	-3.351363	-0.125708
H	-2.202846	-4.203097	3.549477	H	1.919825	-3.133149	-1.193388
C	-3.279462	-2.696013	-1.793084	H	2.380604	-2.461972	0.374858
C	-4.021482	-2.200836	-2.860561	H	2.727863	-4.154920	0.006053
H	-4.570423	-2.893277	-3.489035	C	-0.195786	-5.082206	-1.648517
C	-2.625751	-0.548793	-1.194578	H	0.240083	-4.348370	-2.331287
C	-4.050785	-0.824944	-3.100740	H	0.465731	-5.955878	-1.628033
H	-4.620746	-0.418264	-3.929162	H	-1.151249	-5.411009	-2.062929
C	-3.340920	0.014863	-2.245643	C	-2.646036	-5.609373	0.384037
H	-3.321691	1.092822	-2.360682	H	-2.457078	-6.653233	0.661513
C	-1.873645	0.305519	-0.240843	H	-3.505716	-5.259504	0.959393
O	-1.715250	1.500039	-0.355304	H	-2.918624	-5.594622	-0.673567
N	-1.335889	-0.474003	0.824622	C	-1.932522	-4.178202	3.161455
H	-3.241822	-3.753320	-1.570361	H	-1.619718	-5.010672	3.803342
N	-2.576869	-1.888449	-0.973814	H	-1.826630	-3.254503	3.734239
O	-0.448740	0.274092	1.613518	H	-2.992651	-4.307375	2.935665
C	0.803178	0.449250	1.024833	C	-2.908566	-2.572907	-2.210529
O	1.106101	-0.052234	-0.024290	C	-3.700899	-2.030231	-3.206412
C	-2.516209	-1.270985	1.933555	H	-4.041009	-2.669498	-4.013787
C	-3.908291	-1.093175	1.684941	C	-2.783163	-0.509274	-1.127475
C	-2.056852	-1.182540	3.275964	C	-4.049160	-0.670376	-3.164965
C	-4.796114	-1.003689	2.744532	H	-4.666818	-0.228637	-3.938568
C	-2.956236	-1.089222	4.322480	C	-3.576765	0.092425	-2.105480
C	-4.332454	-1.009922	4.066771	H	-3.798136	1.149291	-2.005395
H	-4.298827	-1.091130	0.676371	C	-2.272952	0.296621	-0.021672
H	-0.994784	-1.214116	3.476651	O	-2.365230	1.480130	0.143906
H	-5.861390	-0.937765	2.551229	N	-1.558398	-0.579040	1.041446
H	-2.599195	-1.079124	5.346720	H	-2.617844	-3.614621	-2.220449
C	-5.300788	-0.845899	5.209219	N	-2.437097	-1.840134	-1.164065
F	-5.467367	0.455894	5.521350	O	-0.354754	0.124951	1.420499
F	-6.514105	-1.347589	4.900210	C	0.509029	0.341957	0.367611
F	-4.857450	-1.474017	6.318355	O	0.248416	0.005004	-0.760441
C	1.626696	1.345979	1.901405	C	-2.389230	-0.658123	2.257868
H	1.534346	1.061887	2.952245	C	-3.699401	-1.131999	2.109613
H	2.666016	1.302735	1.577564	C	-1.884192	-0.329140	3.512813
H	1.255504	2.370683	1.798458	C	-4.498614	-1.290334	3.233906
				C	-2.696755	-0.500303	4.637336
				C	-3.995022	-0.983125	4.502276
				H	-4.084944	-1.399054	1.132296
				H	-0.879941	0.052761	3.623041

IrD⁺

Charge = 1 Multiplicity = 2

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.244662	-2.584638	0.300689
C	-1.432232	-4.776552	0.654190
C	-1.107398	-4.144126	1.914021
C	0.173420	-3.494398	1.759660
C	0.669975	-3.763919	0.436120
C	-0.349624	-4.519715	-0.267788
C	0.906116	-2.750463	2.835343

C	-4.890496	-1.141352	5.706228
F	-5.762121	-0.117746	5.798957
F	-5.614543	-2.278593	5.619207
F	-4.181776	-1.184478	6.851243
C	1.734597	1.052872	0.861661
H	2.111143	0.594640	1.779413
H	2.492544	1.030065	0.079411
H	1.476620	2.092577	1.087317

IrD-TS⁺

Charge = 1 Multiplicity = 2
 Imaginary frequency: -669.95 cm⁻¹
 Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.288651	-2.495598	0.316551
C	-1.506094	-4.704344	0.623779
C	-1.244447	-4.079370	1.904303
C	0.046987	-3.442374	1.823916
C	0.612954	-3.721920	0.523954
C	-0.366445	-4.465320	-0.229659
C	0.760433	-2.736094	2.937451
H	0.068296	-2.432964	3.723313
H	1.511540	-3.396359	3.384860
H	1.268908	-1.839828	2.573722
C	1.972047	-3.323430	0.047286
H	1.977838	-3.125456	-1.026925
H	2.327931	-2.428032	0.561705
H	2.693426	-4.126951	0.244437
C	-0.141085	-5.028552	-1.601226
H	0.306680	-4.289070	-2.271012
H	0.541645	-5.884097	-1.548729
H	-1.069229	-5.388158	-2.051267
C	-2.711610	-5.522353	0.280503
H	-2.541459	-6.575043	0.536718
H	-3.592662	-5.182308	0.828562
H	-2.939596	-5.474561	-0.786846
C	-2.133248	-4.129854	3.106453
H	-1.878184	-4.996403	3.728241
H	-2.028871	-3.232784	3.719086
H	-3.183673	-4.217044	2.822624
C	-2.523467	-2.432237	-2.480479
C	-3.199995	-1.860586	-3.556284
H	-3.353536	-2.446956	-4.455387
C	-2.746572	-0.480284	-1.249359
C	-3.665084	-0.550017	-3.459477
H	-4.196157	-0.085104	-4.282909
C	-3.430660	0.153134	-2.275659
H	-3.759477	1.175648	-2.128795
C	-2.476119	0.237074	0.020583
O	-2.842812	1.342382	0.293539
N	-1.729153	-0.620838	1.031881
H	-2.146796	-3.445229	-2.519747
N	-2.296866	-1.757847	-1.336142
O	-0.390142	0.292674	1.367110
C	0.314927	0.581889	0.261323
O	-0.075071	0.363541	-0.869141
C	-2.427472	-0.639017	2.324130
C	-3.775679	-1.019740	2.301895
C	-1.783770	-0.375410	3.531584
C	-4.474507	-1.150834	3.495296

C	-2.494295	-0.514441	4.725626
C	-3.831446	-0.905361	4.711660
H	-4.269281	-1.238819	1.360900
H	-0.750146	-0.066165	3.547613
H	-5.514559	-1.457051	3.485069
H	-2.000240	-0.320494	5.671023
C	-4.608267	-1.016128	6.000354
F	-5.276118	0.124152	6.264083
F	-5.518648	-2.011189	5.933214
F	-3.794740	-1.264946	7.046591
C	1.652496	1.183815	0.626732
H	2.350700	0.370587	0.852104
H	2.025808	1.748137	-0.228046
H	1.575590	1.823670	1.507496

Ir4a⁺

Charge = 1 Multiplicity = 2

Cartesian coordinates:

ATOM	X	Y	Z
Ir	-1.182384	-2.317154	0.326542
C	-1.833759	-4.424966	0.513631
C	-1.529570	-3.938276	1.842991
C	-0.146429	-3.547769	1.873185
C	0.440096	-3.889924	0.579076
C	-0.584362	-4.435170	-0.242871
C	0.639680	-3.039958	3.040786
H	-0.008761	-2.640361	3.820794
H	1.235621	-3.851406	3.473750
H	1.325326	-2.249842	2.723858
C	1.870846	-3.635252	0.226253
H	2.097054	-3.931396	-0.799010
H	2.094656	-2.569260	0.335947
H	2.528941	-4.196548	0.897547
C	-0.433726	-4.990205	-1.624266
H	0.466803	-4.620146	-2.117853
H	-0.357628	-6.082178	-1.569671
H	-1.297576	-4.753950	-2.249738
C	-3.130213	-5.027643	0.065663
H	-3.141482	-6.104971	0.268521
H	-3.977101	-4.578468	0.588178
H	-3.283638	-4.887762	-1.006724
C	-2.491460	-3.884690	2.985868
H	-2.521531	-4.866284	3.472496
H	-2.197680	-3.143964	3.729801
H	-3.501733	-3.644475	2.649960
C	-1.339753	-1.829336	-2.712374
C	-1.895305	-1.312536	-3.880653
H	-1.417355	-1.515487	-4.832381
C	-2.991910	-0.819888	-1.425674
C	-3.053088	-0.537886	-3.799981
H	-3.505378	-0.127418	-4.696662

C	-3.609558	-0.283381	-2.546537	C	-3.055996	-0.149055	5.014021
H	-4.490505	0.332386	-2.406521	H	-4.964632	-0.834801	2.284699
C	-3.464985	-0.506880	-0.045227	H	-0.684870	-0.465470	2.597361
O	-4.460264	0.157413	0.167626	H	-5.174711	-0.366908	4.709580
N	-2.611511	-1.041592	0.942460	H	-0.908210	0.023729	5.030899
H	-0.437187	-2.426929	-2.720283	C	-3.190262	0.192475	6.478831
N	-1.896012	-1.598133	-1.513721	F	-3.247968	1.526259	6.657570
O	-1.041336	0.909251	-0.240654	F	-4.308003	-0.341866	7.008690
C	0.062871	0.411823	-0.059804	F	-2.133074	-0.266548	7.182095
O	0.296453	-0.866810	0.194566	C	1.341178	1.231738	-0.083010
C	-2.803946	-0.706180	2.289186	H	1.825023	1.182694	0.896825
C	-4.082558	-0.650045	2.881858	H	2.037351	0.811751	-0.814228
C	-1.657914	-0.456602	3.073826	H	1.112359	2.267516	-0.331422
C	-4.197431	-0.382953	4.240561				
C	-1.785940	-0.175597	4.425966				

7. Crystallographic data

Crystallographic data of **Ir3a** (CCDC 2312346).

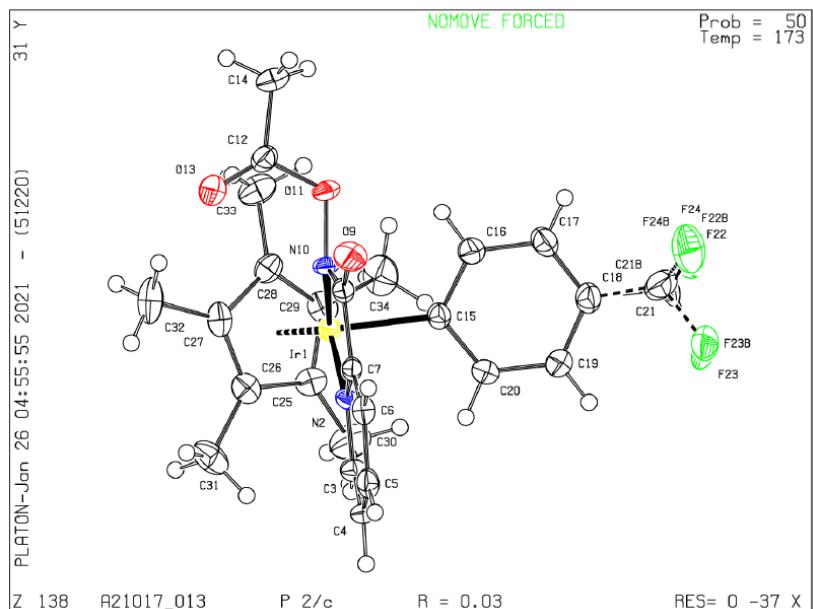


Table S7. Crystal data and structure refinement for **Ir3a**.

Empirical formula	C ₂₅ H ₂₆ F ₃ IrN ₂ O ₃	
Formula weight	651.68	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/c	
Unit cell dimensions	a = 16.7566(8) Å b = 9.7242(4) Å c = 15.4911(7) Å	α = 90° β = 100.1404(15)° γ = 90°
Volume	2484.76(19) Å ³	
Z	4	
Density (calculated)	1.742 Mg/m ³	
Absorption coefficient	5.424 mm ⁻¹	
F(000)	1272	
Crystal size	0.241 x 0.025 x 0.021 mm ³	
Theta range for data collection	2.431 to 27.149°.	
Index ranges	-21<=h<=21, -10<=k<=12, -19<=l<=18	
Reflections collected	38906	
Independent reflections	5491 [R(int) = 0.0663]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.5951	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5491 / 156 / 350	
Goodness-of-fit on F ²	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0575	
R indices (all data)	R1 = 0.0400, wR2 = 0.0596	
Largest diff. peak and hole	1.056 and -2.037 e·Å ⁻³	

Crystallographic data of **Ir3b** (CCDC 2312347).

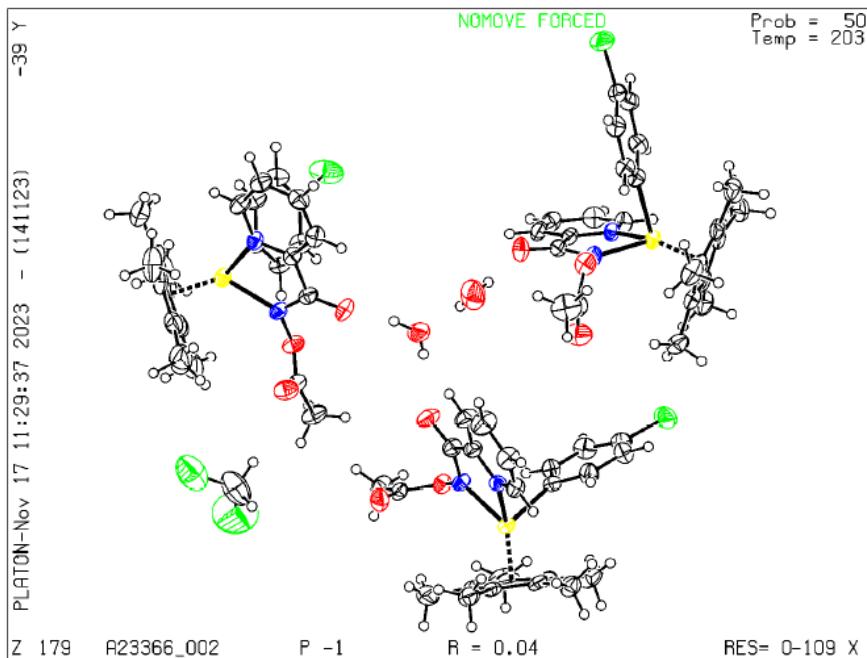


Table S8. Crystal data and structure refinement for **Ir3b**.

Empirical formula	$C_{145} H_{166} Cl_8 Ir_6 N_{12} O_{22}$		
Formula weight	3865.69		
Temperature	203(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	$P\bar{1}$		
Unit cell dimensions	$a = 15.6696(7)$ Å	$\alpha = 61.2031(11)^\circ$	
	$b = 17.3145(7)$ Å	$\beta = 68.1412(14)^\circ$	
	$c = 17.9010(7)$ Å	$\gamma = 71.4772(13)^\circ$	
Volume	$3892.6(3)$ Å ³		
Z	1		
Density (calculated)	1.649 Mg/m ³		
Absorption coefficient	5.311 mm ⁻¹		
F(000)	1894		
Crystal size	$0.133 \times 0.077 \times 0.022$ mm ³		
Theta range for data collection	2.417 to 28.159°.		
Index ranges	$-20 \leq h \leq 20, -22 \leq k \leq 22, -23 \leq l \leq 23$		
Reflections collected	119251		
Independent reflections	18936 [R(int) = 0.1101]		
Completeness to theta = 25.242°	99.8 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7456 and 0.5338		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	18936 / 1 / 913		
Goodness-of-fit on F ²	1.029		
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0747		
R indices (all data)	R1 = 0.0606, wR2 = 0.0856		
Largest diff. peak and hole	1.404 and -0.747 e·Å ⁻³		

Crystallographic data of **Ir3c** (CCDC 2312348).

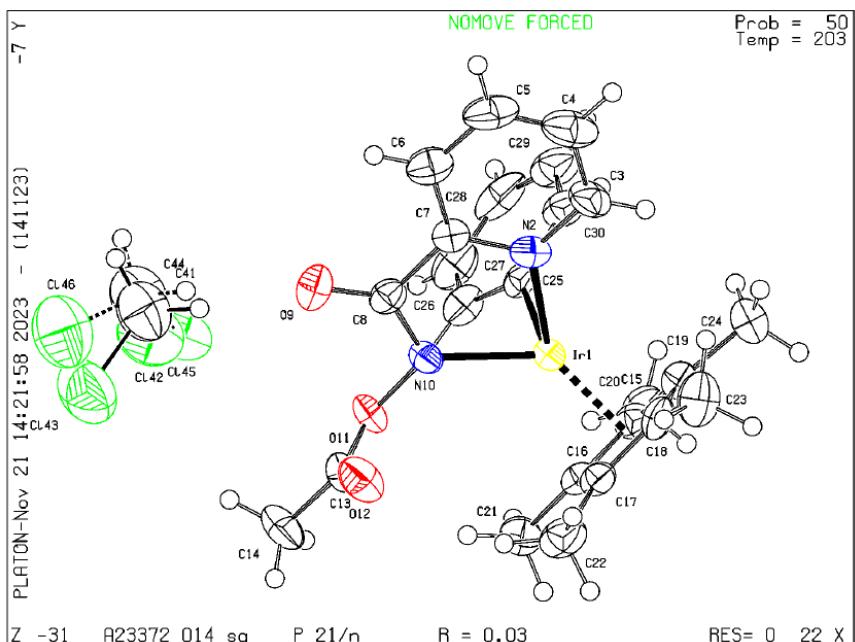


Table S9. Crystal data and structure refinement for **Ir3c**.

Empirical formula	$C_{25} H_{29} Cl_2 Ir N_2 O_3$		
Formula weight	668.60		
Temperature	203(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	$P2_1/n$		
Unit cell dimensions	$a = 11.6167(7)$ Å	$\alpha = 90^\circ$	
	$b = 8.1283(6)$ Å	$\beta = 95.110(2)^\circ$	
	$c = 29.0594(18)$ Å	$\gamma = 90^\circ$	
Volume	$2733.0(3)$ Å ³		
Z	4		
Density (calculated)	1.625 Mg/m ³		
Absorption coefficient	5.108 mm ⁻¹		
F(000)	1312		
Crystal size	$0.174 \times 0.042 \times 0.023$ mm ³		
Theta range for data collection	2.603 to 25.330°.		
Index ranges	$-13 \leq h \leq 13, -9 \leq k \leq 9, -34 \leq l \leq 34$		
Reflections collected	29036		
Independent reflections	4766 [R(int) = 0.1151]		
Completeness to theta = 25.242°	96.0 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7452 and 0.4851		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4766 / 118 / 332		
Goodness-of-fit on F ²	1.088		
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0726		
R indices (all data)	R1 = 0.0558, wR2 = 0.0776		
Largest diff. peak and hole	0.903 and -0.815 e·Å ⁻³		

Crystallographic data of **Ir3d** (CCDC 2312349).

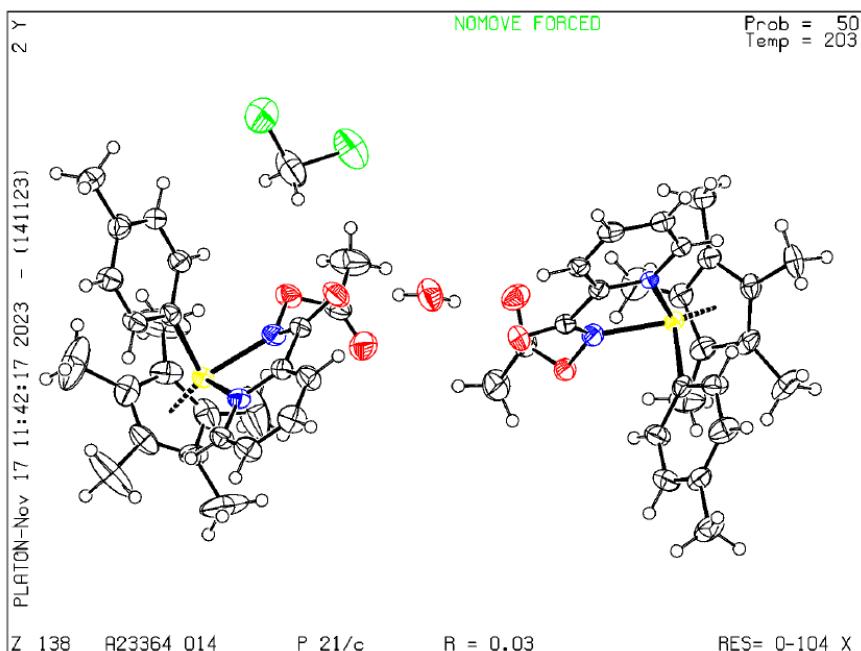


Table S10. Crystal data and structure refinement for **Ir3d**.

Empirical formula	C ₅₁ H ₆₂ Cl ₂ Ir ₂ N ₄ O ₇					
Formula weight	1298.34					
Temperature	203(2) K					
Wavelength	0.71073 Å					
Crystal system	Monoclinic					
Space group	P2 ₁ /c					
Unit cell dimensions	a = 16.7116(5) Å	α = 90°	b = 17.7379(6) Å	β = 94.3734(12)°	c = 17.2896(6) Å	γ = 90°
Volume	5110.2(3) Å ³					
Z	4					
Density (calculated)	1.688 Mg/m ³					
Absorption coefficient	5.361 mm ⁻¹					
F(000)	2560					
Crystal size	0.118 x 0.065 x 0.042 mm ³					
Theta range for data collection	2.576 to 27.102°.					
Index ranges	-19<=h<=21, -22<=k<=22, -17<=l<=22					
Reflections collected	102757					
Independent reflections	11228 [R(int) = 0.0723]					
Completeness to theta = 25.242°	99.8 %					
Absorption correction	Semi-empirical from equivalents					
Max. and min. transmission	0.7455 and 0.4473					
Refinement method	Full-matrix least-squares on F ²					
Data / restraints / parameters	11228 / 0 / 614					
Goodness-of-fit on F ²	1.100					
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0602					
R indices (all data)	R1 = 0.0463, wR2 = 0.0699					
Largest diff. peak and hole	0.831 and -0.870 e·Å ⁻³					

Crystallographic data of **Ir3e** (CCDC 2312350).

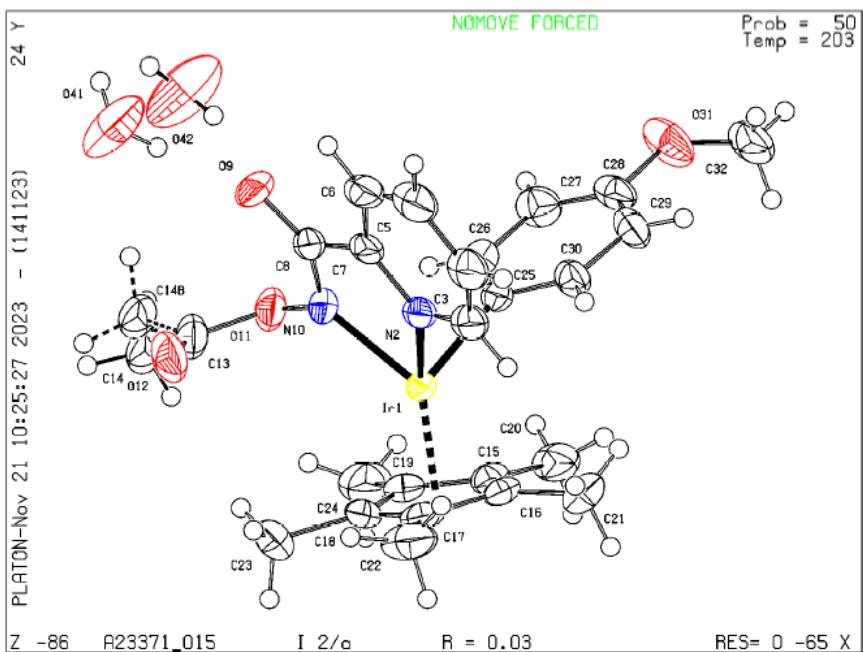


Table S11. Crystal data and structure refinement for **Ir3e**.

Empirical formula	C ₂₅ H ₃₁ IrN ₂ O ₅					
Formula weight	631.72					
Temperature	203(2) K					
Wavelength	0.71073 Å					
Crystal system	Monoclinic					
Space group	I2/a					
Unit cell dimensions	a = 14.8017(6) Å	α = 90°	b = 19.3766(8) Å	β = 110.5971(12)°	c = 18.2350(10) Å	γ = 90°
Volume	4895.6(4) Å ³					
Z	8					
Density (calculated)	1.714 Mg/m ³					
Absorption coefficient	5.492 mm ⁻¹					
F(000)	2496					
Crystal size	0.114 x 0.024 x 0.022 mm ³					
Theta range for data collection	2.548 to 27.188°.					
Index ranges	-18<=h<=19, -21<=k<=24, -23<=l<=23					
Reflections collected	37381					
Independent reflections	5448 [R(int) = 0.0744]					
Completeness to theta = 25.242°	99.9 %					
Absorption correction	Semi-empirical from equivalents					
Max. and min. transmission	0.7455 and 0.4987					
Refinement method	Full-matrix least-squares on F ²					
Data / restraints / parameters	5448 / 55 / 324					
Goodness-of-fit on F ²	1.048					
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0585					
R indices (all data)	R1 = 0.0414, wR2 = 0.0635					
Largest diff. peak and hole	1.223 and -1.995 e·Å ⁻³					

Crystallographic data of **Ir3g** (CCDC 2312351).

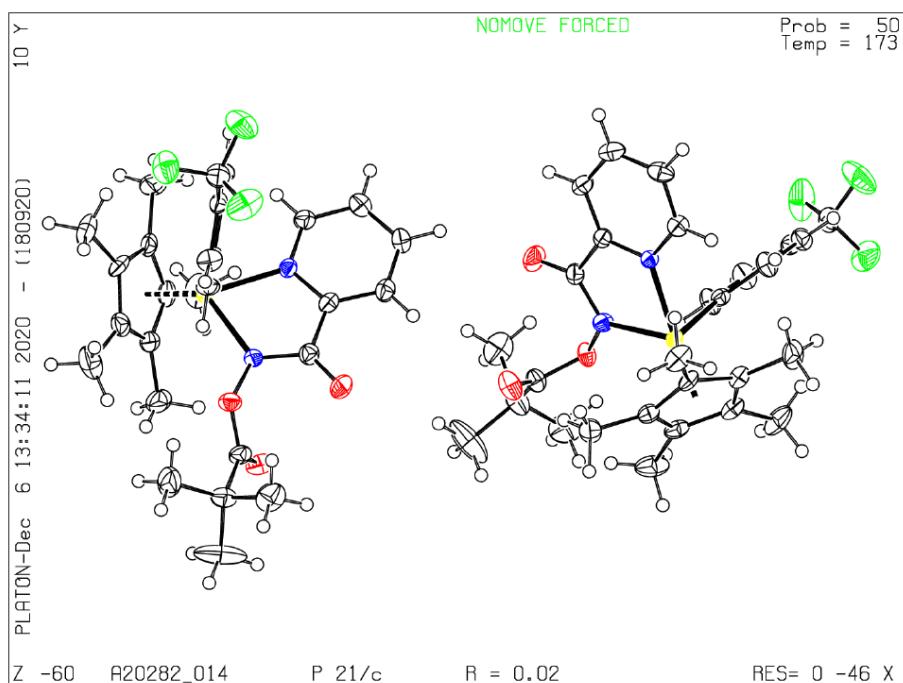


Table S12. Crystal data and structure refinement for **Ir3g**.

Empirical formula	C ₂₈ H ₃₂ N ₂ O ₃ F ₃ Ir		
Formula weight	693.75		
Temperature	173(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2 ₁ /c		
Unit cell dimensions	a = 9.6504(3) Å	α = 90°	b = 15.6395(6) Å
	c = 35.8014(12) Å	β = 90.0482(12)°	γ = 90°
Volume	5403.4(3) Å ³		
Z	8		
Density (calculated)	1.706 Mg/m ³		
Absorption coefficient	4.994 mm ⁻¹		
F(000)	2736		
Crystal size	0.081 x 0.034 x 0.031 mm ³		
Theta range for data collection	2.545 to 27.118°.		
Index ranges	-12<=h<=12, -20<=k<=20, -43<=l<=45		
Reflections collected	82510		
Independent reflections	11860 [R(int) = 0.0367]		
Completeness to theta = 25.242°	99.7 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7455 and 0.6098		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	11860 / 36 / 684		
Goodness-of-fit on F ²	1.214		
Final R indices [$\text{I} > 2\sigma(\text{I})$]	R1 = 0.0238, wR2 = 0.0433		
R indices (all data)	R1 = 0.0253, wR2 = 0.0437		
Largest diff. peak and hole	1.110 and -1.144 e·Å ⁻³		

Crystallographic data of **Ir3h** (CCDC 2312352).

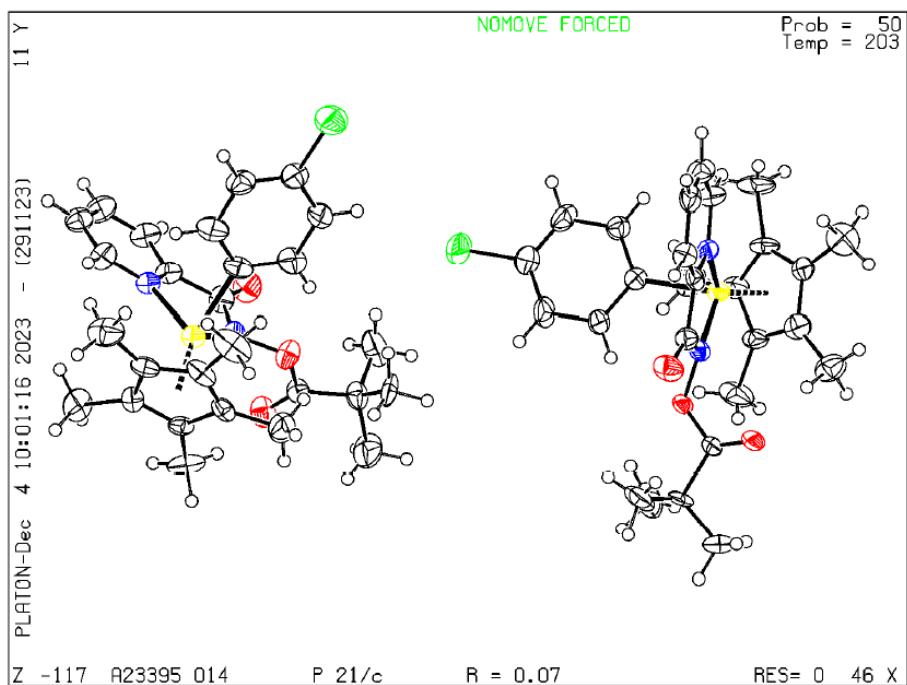


Table S13. Crystal data and structure refinement for **Ir3h**.

Empirical formula	C ₂₇ H ₃₂ ClIrN ₂ O ₃		
Formula weight	660.19		
Temperature	203(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2 ₁ /c		
Unit cell dimensions	a = 9.5643(3) Å	α = 90°	b = 14.8384(4) Å
	c = 36.3130(11) Å	β = 90.0204(19)°	
Volume	5153.5(3) Å ³	γ = 90°	
Z	8		
Density (calculated)	1.702 Mg/m ³		
Absorption coefficient	5.316 mm ⁻¹		
F(000)	2608		
Crystal size	0.124 x 0.036 x 0.032 mm ³		
Theta range for data collection	2.534 to 25.524°.		
Index ranges	-8<=h<=11, -17<=k<=17, -44<=l<=43		
Reflections collected	25831		
Independent reflections	9555 [R(int) = 0.1172]		
Completeness to theta = 25.242°	99.5 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7452 and 0.5669		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	9555 / 646 / 560		
Goodness-of-fit on F ²	1.107		
Final R indices [I>2sigma(I)]	R1 = 0.0729, wR2 = 0.1708		
R indices (all data)	R1 = 0.0856, wR2 = 0.1778		
Largest diff. peak and hole	7.671 and -2.882 e·Å ⁻³		

Crystallographic data of **Ir4a** (CCDC 2312353).

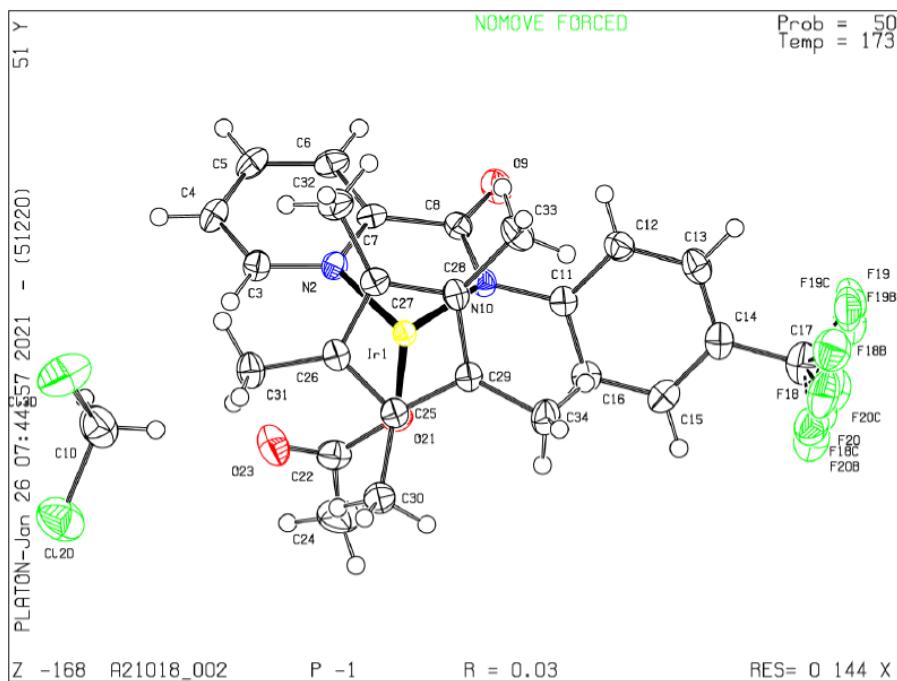


Table S14. Crystal data and structure refinement for **Ir4a**.

Empirical formula	C ₂₆ H ₂₈ Cl ₂ F ₃ IrN ₂ O ₃		
Formula weight	736.60		
Temperature	173(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 8.8585(7) Å	α = 80.066(3)°	b = 12.1308(9) Å
	c = 12.9385(10) Å	β = 76.602(3)°	
Volume	1329.47(18) Å ³	γ = 84.145(3)°	Z
Density (calculated)	1.840 Mg/m ³		Absorption coefficient
Absorption coefficient	5.275 mm ⁻¹		F(000)
F(000)	720		Crystal size
Crystal size	0.162 x 0.081 x 0.024 mm ³		Theta range for data collection
Theta range for data collection	2.568 to 27.158°.		Index ranges
Index ranges	-11≤h≤11, -15≤k≤15, -16≤l≤16		Reflections collected
Reflections collected	31941		Independent reflections
Independent reflections	5859 [R(int) = 0.0550]		Completeness to theta = 25.242°
Completeness to theta = 25.242°	99.8 %		Absorption correction
Absorption correction	Semi-empirical from equivalents		Max. and min. transmission
Max. and min. transmission	0.7455 and 0.5860		Refinement method
Refinement method	Full-matrix least-squares on F ²		Data / restraints / parameters
Data / restraints / parameters	5859 / 223 / 397		Goodness-of-fit on F ²
Goodness-of-fit on F ²	1.092		Final R indices [I>2sigma(I)]
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0523		R indices (all data)
R indices (all data)	R1 = 0.0358, wR2 = 0.0541		Largest diff. peak and hole
Largest diff. peak and hole	0.943 and -1.482 e·Å ⁻³		

Crystallographic data of **Ir4b** (CCDC 2312354).

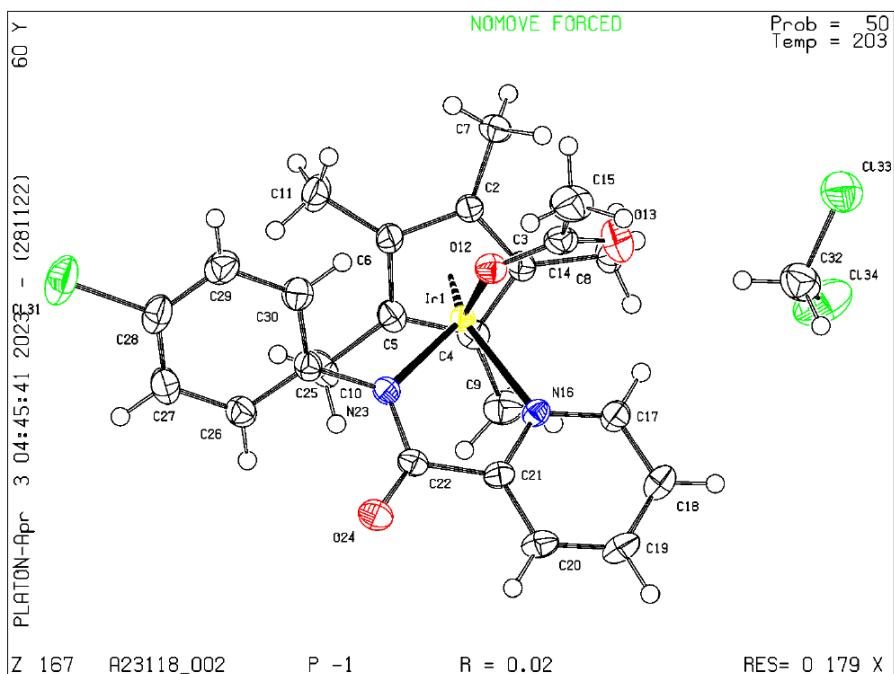


Table S15. Crystal data and structure refinement for **Ir4b**.

Empirical formula	$C_{25} H_{28} Cl_3 Ir N_2 O_3$	
Formula weight	703.04	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.7525(3)$ Å	$\alpha = 80.5035(12)^\circ$
	$b = 12.1009(4)$ Å	$\beta = 75.1201(11)^\circ$
	$c = 12.8589(4)$ Å	$\gamma = 84.3430(12)^\circ$
Volume	1295.96(7) Å ³	
Z	2	
Density (calculated)	1.802 Mg/m ³	
Absorption coefficient	5.490 mm ⁻¹	
F(000)	688	
Crystal size	0.161 x 0.129 x 0.049 mm ³	
Theta range for data collection	2.547 to 28.044°	
Index ranges	$-11 \leq h \leq 11, -15 \leq k \leq 16, -16 \leq l \leq 16$	
Reflections collected	43553	
Independent reflections	6266 [R(int) = 0.0613]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4355	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6266 / 0 / 313	
Goodness-of-fit on F ²	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0196, wR2 = 0.0484	
R indices (all data)	R1 = 0.0203, wR2 = 0.0489	
Largest diff. peak and hole	0.853 and -1.202 e·Å ⁻³	

Crystallographic data of **Ir4c** (CCDC 2312355).

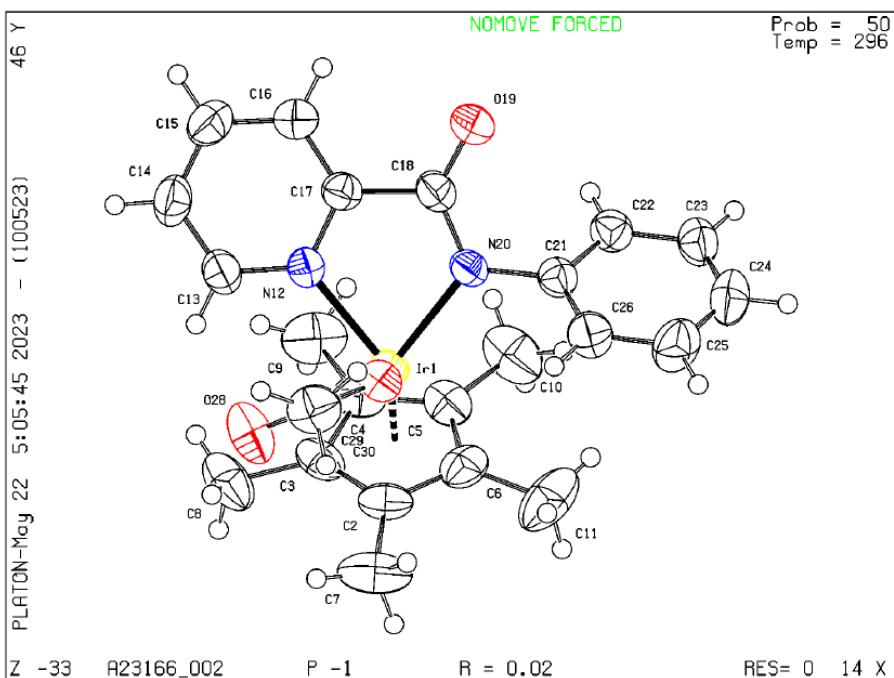


Table S16. Crystal data and structure refinement for **Ir4c**.

Empirical formula	$C_{24} H_{27} Ir N_2 O_3$	
Formula weight	583.67	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.7404(3)$ Å	$\alpha = 92.4255(13)^\circ$
	$b = 8.8429(3)$ Å	$\beta = 100.4762(13)^\circ$
	$c = 15.4080(5)$ Å	$\gamma = 109.2778(12)^\circ$
Volume	$1098.64(6)$ Å ³	
Z	2	
Density (calculated)	1.764 Mg/m ³	
Absorption coefficient	6.104 mm ⁻¹	
F(000)	572	
Crystal size	$0.188 \times 0.091 \times 0.024$ mm ³	
Theta range for data collection	2.604 to 27.056°.	
Index ranges	$-11 \leq h \leq 11, -11 \leq k \leq 11, -19 \leq l \leq 19$	
Reflections collected	33590	
Independent reflections	4819 [R(int) = 0.0561]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.4943	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4819 / 0 / 277	
Goodness-of-fit on F ²	1.032	
Final R indices [$>2\sigma(I)$]	R1 = 0.0218, wR2 = 0.0469	
R indices (all data)	R1 = 0.0270, wR2 = 0.0493	
Largest diff. peak and hole	0.933 and -0.604 e·Å ⁻³	

Crystallographic data of **Ir4d** (CCDC 2312356).

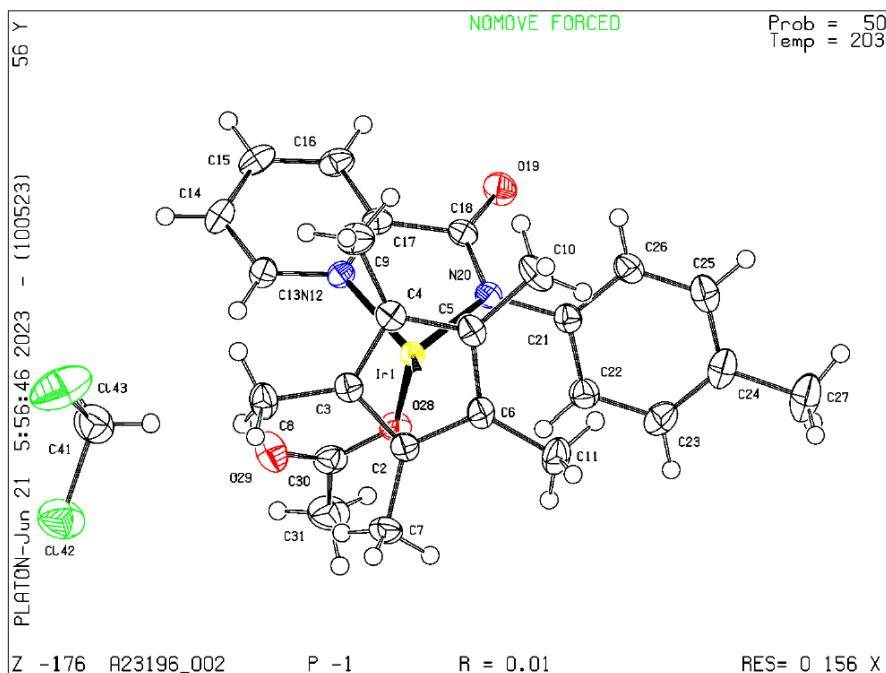


Table S17. Crystal data and structure refinement for **Ir4d**.

Empirical formula	$C_{26} H_{31} Cl_2 Ir N_2 O_3$	
Formula weight	682.63	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.7744(4)$ Å	$\alpha = 80.5195(14)^\circ$
	$b = 12.0623(5)$ Å	$\beta = 76.0098(14)^\circ$
	$c = 12.9086(6)$ Å	$\gamma = 83.9522(14)^\circ$
Volume	$1304.54(10)$ Å ³	
Z	2	
Density (calculated)	1.738 Mg/m ³	
Absorption coefficient	5.352 mm ⁻¹	
F(000)	672	
Crystal size	0.079 x 0.062 x 0.027 mm ³	
Theta range for data collection	2.541 to 27.566°.	
Index ranges	$-11 \leq h \leq 11, -15 \leq k \leq 15, -16 \leq l \leq 16$	
Reflections collected	54352	
Independent reflections	6015 [R(int) = 0.0470]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5606	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6015 / 0 / 314	
Goodness-of-fit on F ²	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0149, wR2 = 0.0348	
R indices (all data)	R1 = 0.0164, wR2 = 0.0358	
Largest diff. peak and hole	0.664 and -0.786 e·Å ⁻³	

Crystallographic data of **Ir4e** (CCDC 2312357).

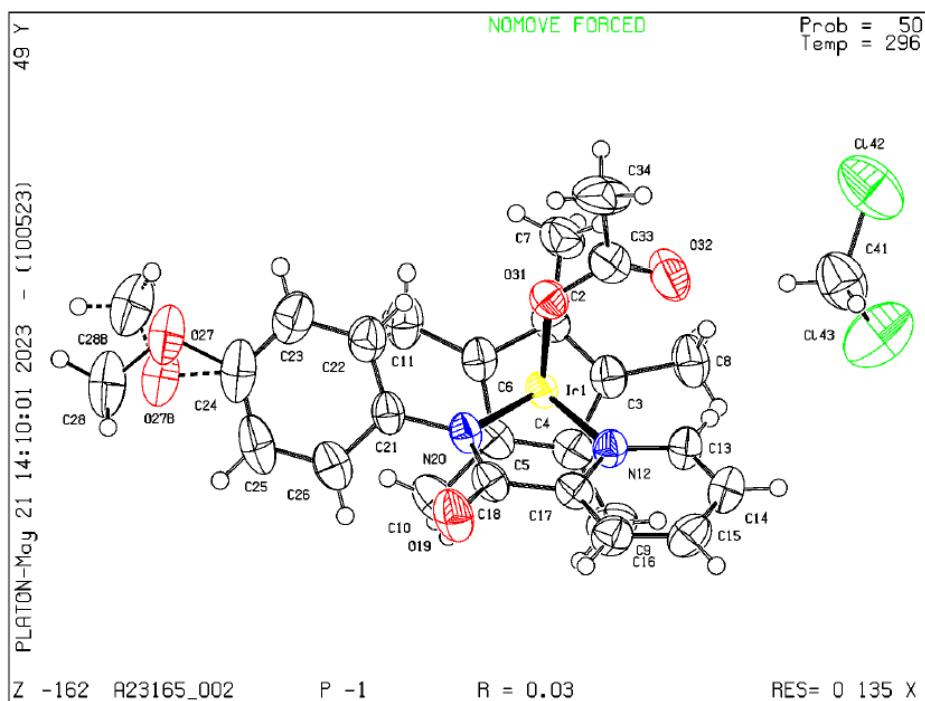


Table S18. Crystal data and structure refinement for **Ir4e**.

Empirical formula	$C_{26} H_{31} Cl_2 Ir N_2 O_4$	
Formula weight	698.63	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.8269(4)$ Å	$\alpha = 79.4453(13)^\circ$
	$b = 12.3763(5)$ Å	$\beta = 75.4257(14)^\circ$
	$c = 13.1384(6)$ Å	$\gamma = 83.0888(14)^\circ$
Volume	$1361.45(10)$ Å ³	
Z	2	
Density (calculated)	1.704 Mg/m ³	
Absorption coefficient	5.133 mm ⁻¹	
F(000)	688	
Crystal size	0.171 x 0.027 x 0.023 mm ³	
Theta range for data collection	2.555 to 27.553°.	
Index ranges	$-11 \leq h \leq 11, -16 \leq k \leq 16, -17 \leq l \leq 17$	
Reflections collected	50374	
Independent reflections	6269 [R(int) = 0.0675]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5345	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6269 / 61 / 343	
Goodness-of-fit on F ²	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0689	
R indices (all data)	R1 = 0.0420, wR2 = 0.0741	
Largest diff. peak and hole	1.179 and -1.127 e·Å ⁻³	

Crystallographic data of **Ir4f**(CCDC 2312358).

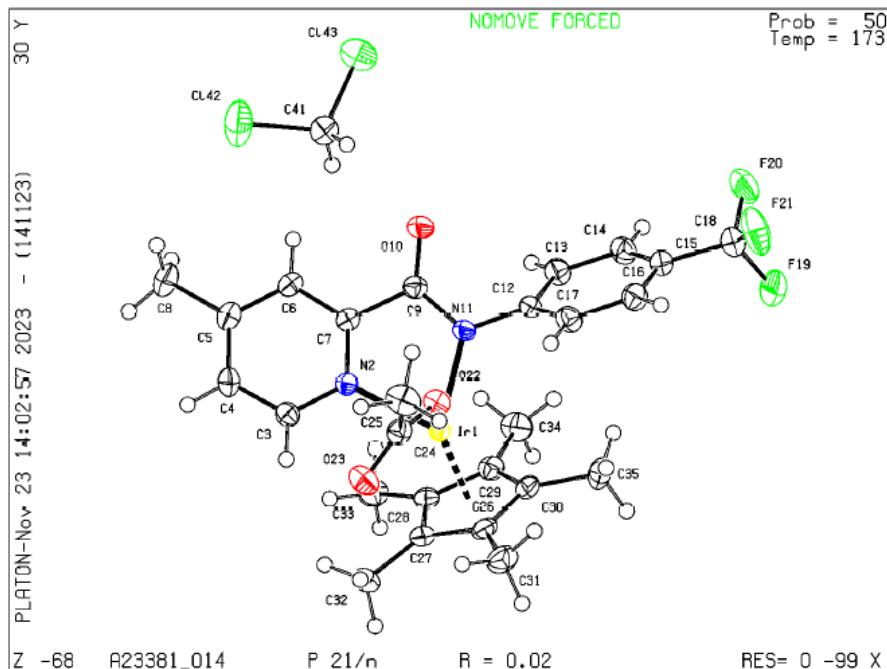


Table S19. Crystal data and structure refinement for **Ir4f**.

Empirical formula	$C_{27} H_{30} Cl_2 F_3 Ir N_2 O_3$	
Formula weight	750.63	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 8.6488(5)$ Å	$\alpha = 90^\circ$
	$b = 12.3574(7)$ Å	$\beta = 95.0025(16)^\circ$
	$c = 25.7383(14)$ Å	$\gamma = 90^\circ$
Volume	$2740.3(3)$ Å ³	
Z	4	
Density (calculated)	1.819 Mg/m ³	
Absorption coefficient	5.120 mm ⁻¹	
F(000)	1472	
Crystal size	$0.172 \times 0.042 \times 0.039$ mm ³	
Theta range for data collection	2.559 to 28.059°.	
Index ranges	$-11 \leq h \leq 11, -16 \leq k \leq 16, -34 \leq l \leq 34$	
Reflections collected	74925	
Independent reflections	6644 [$R(\text{int}) = 0.0610$]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4304	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6644 / 0 / 350	
Goodness-of-fit on F^2	1.053	
Final R indices [$>2\sigma(I)$]	$R_1 = 0.0175, wR_2 = 0.0406$	
R indices (all data)	$R_1 = 0.0223, wR_2 = 0.0428$	
Largest diff. peak and hole	0.586 and -0.565 e·Å ⁻³	

Crystallographic data of **Ir4g** (CCDC 2312359).

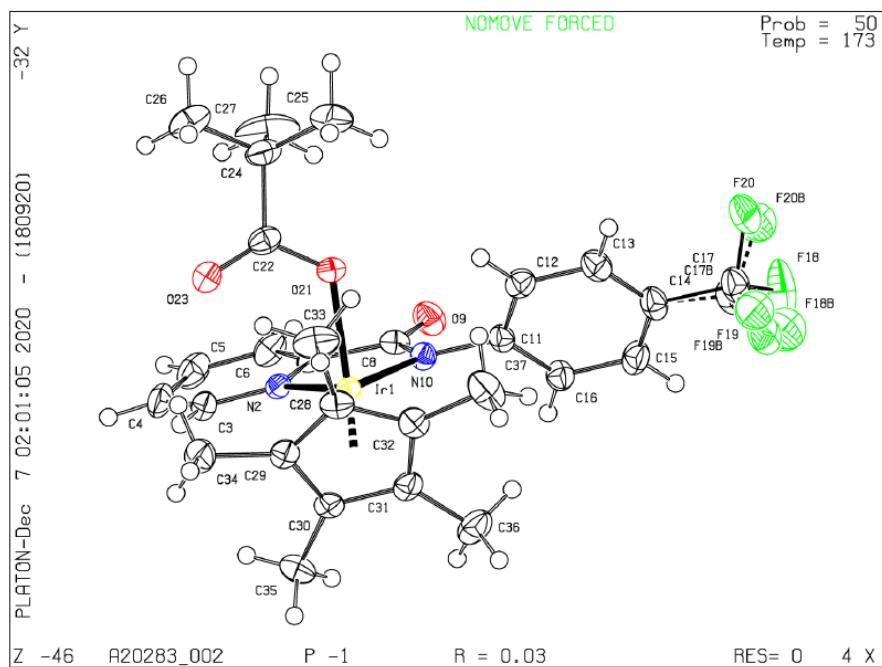


Table S20. Crystal data and structure refinement for **Ir4g**.

Empirical formula	C ₂₈ H ₃₂ N ₂ O ₃ F ₃ Ir					
Formula weight	693.75					
Temperature	173(2) K					
Wavelength	0.71073 Å					
Crystal system	Triclinic					
Space group	P-1					
Unit cell dimensions	a = 8.9385(3) Å	α = 104.2303(15)°	b = 11.7112(4) Å	β = 93.9679(16)°	c = 13.9480(5) Å	γ = 95.1989(15)°
Volume	1403.12(8) Å ³					
Z	2					
Density (calculated)	1.642 Mg/m ³					
Absorption coefficient	4.808 mm ⁻¹					
F(000)	684					
Crystal size	0.085 x 0.032 x 0.027 mm ³					
Theta range for data collection	2.629 to 27.553°.					
Index ranges	-11<=h<=11, -15<=k<=15, -18<=l<=18					
Reflections collected	47078					
Independent reflections	6444 [R(int) = 0.0544]					
Completeness to theta = 25.242°	99.7 %					
Absorption correction	Semi-empirical from equivalents					
Max. and min. transmission	0.7456 and 0.5718					
Refinement method	Full-matrix least-squares on F ²					
Data / restraints / parameters	6444 / 126 / 364					
Goodness-of-fit on F ²	1.146					
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0492					
R indices (all data)	R1 = 0.0373, wR2 = 0.0507					
Largest diff. peak and hole	0.870 and -1.909 e·Å ⁻³					

Crystallographic data of **Ir4h** (CCDC 2312360).

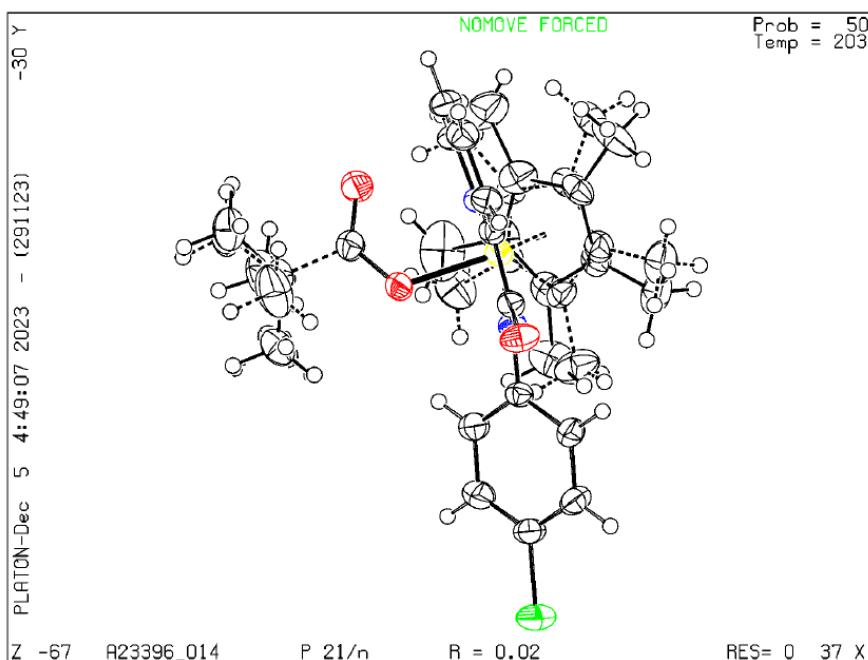


Table S21. Crystal data and structure refinement for **Ir4h**.

Empirical formula	$C_{27}H_{32}ClIrN_2O_3$		
Formula weight	660.19		
Temperature	203(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	$P2_1/n$		
Unit cell dimensions	$a = 9.0746(2)$ Å	$\alpha = 90^\circ$	
	$b = 10.2650(3)$ Å	$\beta = 91.1075(13)^\circ$	
	$c = 28.9794(9)$ Å	$\gamma = 90^\circ$	
Volume	$2698.95(13)$ Å ³		
Z	4		
Density (calculated)	1.625 Mg/m ³		
Absorption coefficient	5.075 mm ⁻¹		
F(000)	1304		
Crystal size	$0.151 \times 0.056 \times 0.042$ mm ³		
Theta range for data collection	2.812 to 28.024°.		
Index ranges	$-11 \leq h \leq 11, -13 \leq k \leq 13, -38 \leq l \leq 29$		
Reflections collected	52508		
Independent reflections	6431 [R(int) = 0.0642]		
Completeness to theta = 25.242°	99.6 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7456 and 0.5021		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	6431 / 354 / 428		
Goodness-of-fit on F ²	1.051		
Final R indices [I>2sigma(I)]	R1 = 0.0213, wR2 = 0.0459		
R indices (all data)	R1 = 0.0315, wR2 = 0.0501		
Largest diff. peak and hole	0.760 and -0.617 e·Å ⁻³		

Crystallographic data of **Ir5** (CCDC 2312361).

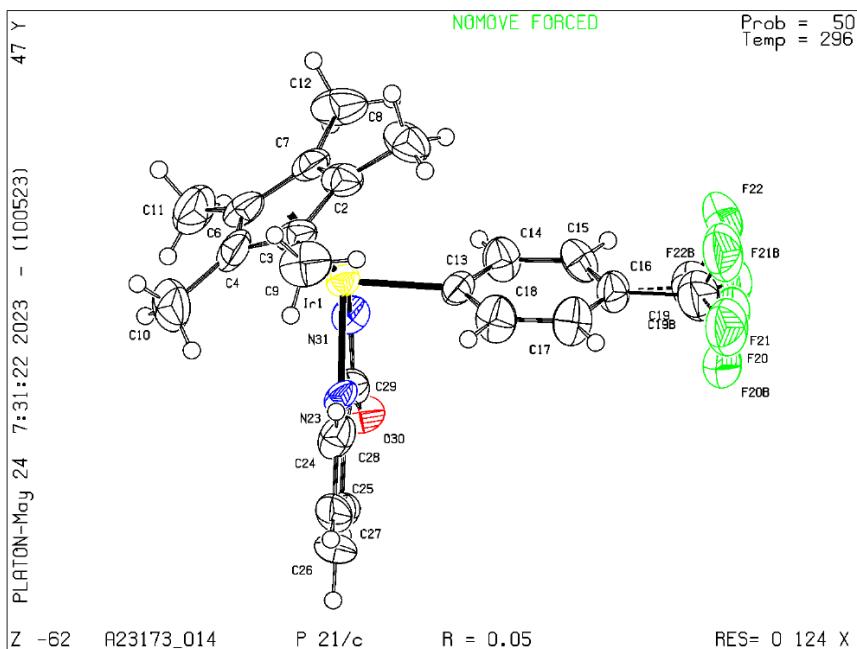


Table S22. Crystal data and structure refinement for **Ir5**.

Empirical formula	C ₂₃ H ₂₄ F ₃ IrN ₂ O					
Formula weight	593.64					
Temperature	296(2) K					
Wavelength	0.71073 Å					
Crystal system	Monoclinic					
Space group	P ₂ ₁ /c					
Unit cell dimensions	a = 12.6385(10) Å	α = 90°	b = 9.9688(7) Å	β = 92.497(2)°	c = 17.3780(13) Å	γ = 90°
Volume	2187.4(3) Å ³					
Z	4					
Density (calculated)	1.803 Mg/m ³					
Absorption coefficient	6.145 mm ⁻¹					
F(000)	1152					
Crystal size	0.056 x 0.039 x 0.017 mm ³					
Theta range for data collection	2.603 to 25.386°.					
Index ranges	-15<=h<=15, -12<=k<=12, -20<=l<=20					
Reflections collected	27855					
Independent reflections	4000 [R(int) = 0.1415]					
Completeness to theta = 25.242°	99.5 %					
Absorption correction	Semi-empirical from equivalents					
Max. and min. transmission	0.7452 and 0.6226					
Refinement method	Full-matrix least-squares on F ²					
Data / restraints / parameters	4000 / 169 / 313					
Goodness-of-fit on F ²	1.005					
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.0654					
R indices (all data)	R1 = 0.1192, wR2 = 0.0823					
Largest diff. peak and hole	0.951 and -0.687 e·Å ⁻³					

Crystallographic data of **Ir6** (CCDC 2312362).

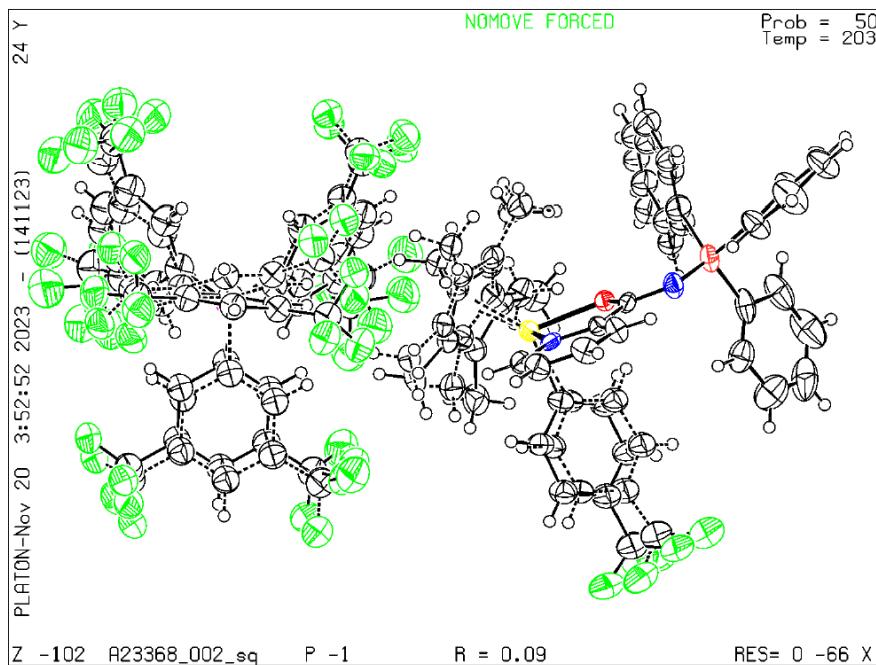
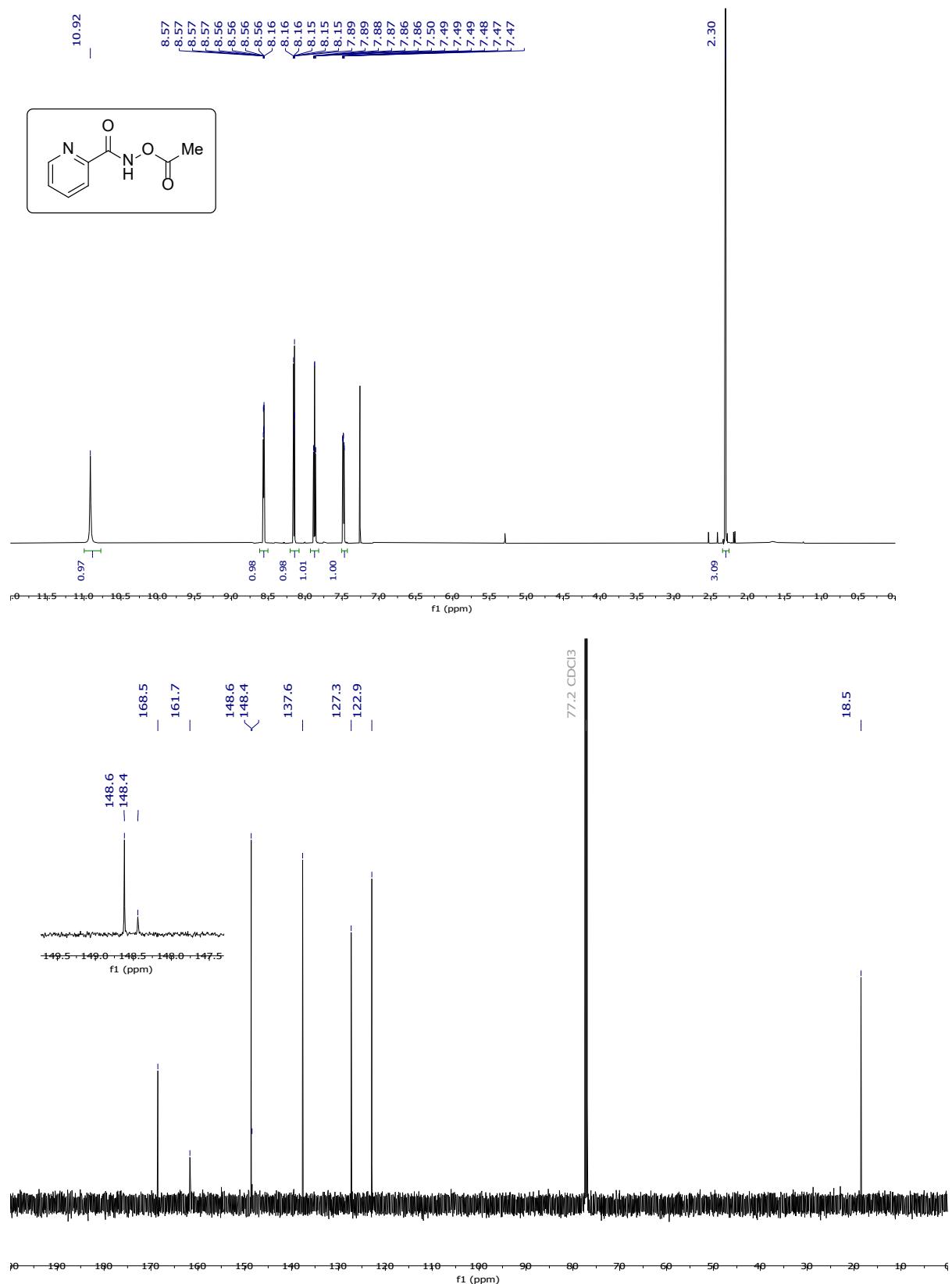


Table S23. Crystal data and structure refinement for **Ir6**.

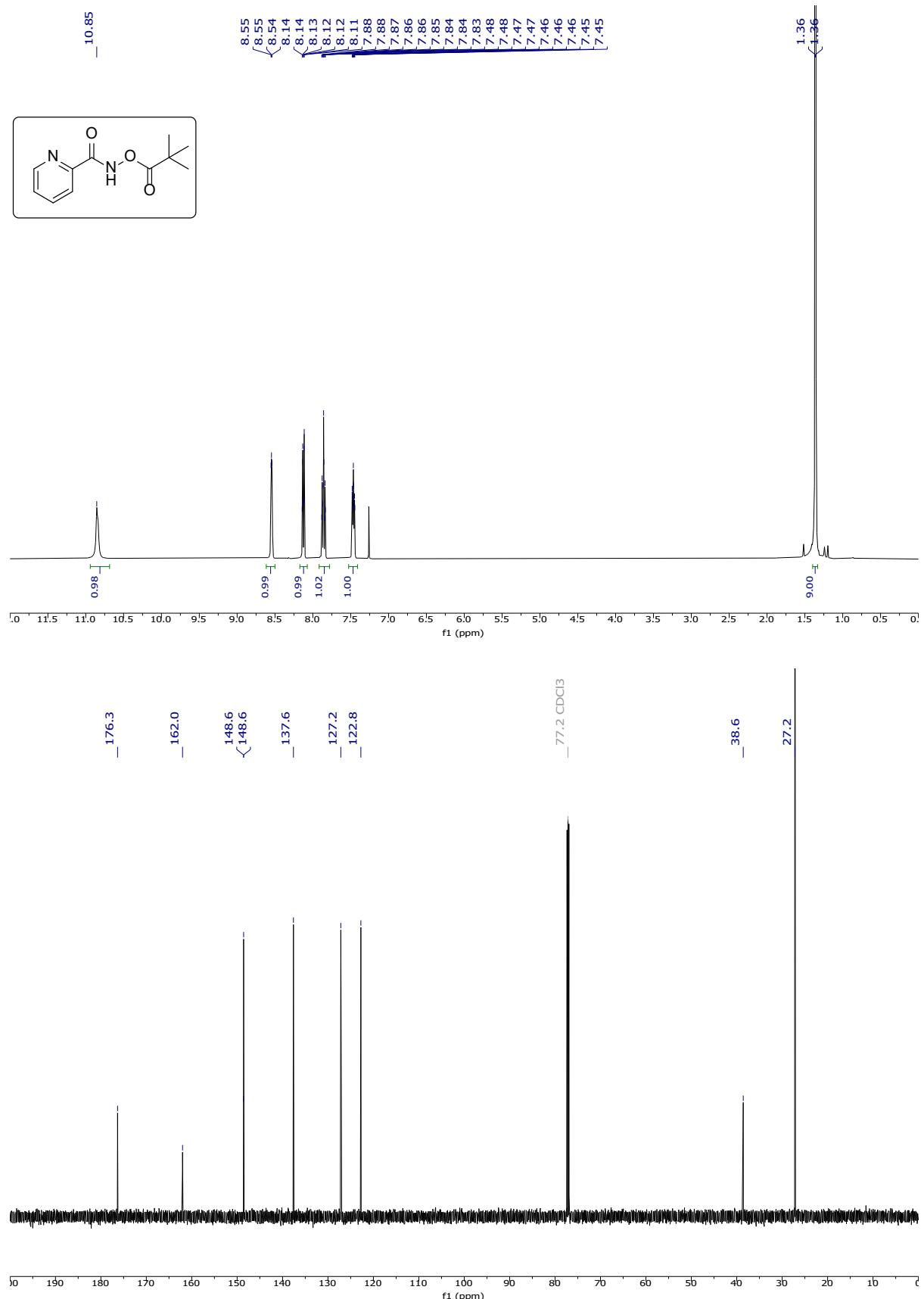
Empirical formula	$C_{73} H_{50} B F_{27} Ir N_2 O P$		
Formula weight	1718.13		
Temperature	203(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	$P\bar{1}$		
Unit cell dimensions	$a = 10.1896(9)$ Å	$\alpha = 62.6343(17)^\circ$	
	$b = 20.3709(18)$ Å	$\beta = 78.1417(17)^\circ$	
	$c = 20.9992(17)$ Å	$\gamma = 82.601(2)^\circ$	
Volume	$3785.5(6)$ Å ³		
Z	2		
Density (calculated)	1.507 Mg/m ³		
Absorption coefficient	1.894 mm ⁻¹		
F(000)	1700		
Crystal size	$0.052 \times 0.037 \times 0.015$ mm ³		
Theta range for data collection	2.481 to 28.083°.		
Index ranges	$-13 \leq h \leq 13, -26 \leq k \leq 26, -27 \leq l \leq 27$		
Reflections collected	177099		
Independent reflections	18057 [R(int) = 0.1037]		
Completeness to theta = 25.242°	99.8 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7456 and 0.6444		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	18057 / 3874 / 1532		
Goodness-of-fit on F ²	1.093		
Final R indices [I>2sigma(I)]	$R_1 = 0.0850, wR_2 = 0.1784$		
R indices (all data)	$R_1 = 0.1164, wR_2 = 0.1953$		
Largest diff. peak and hole	2.327 and -1.786 e·Å ⁻³		

8. ^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectra

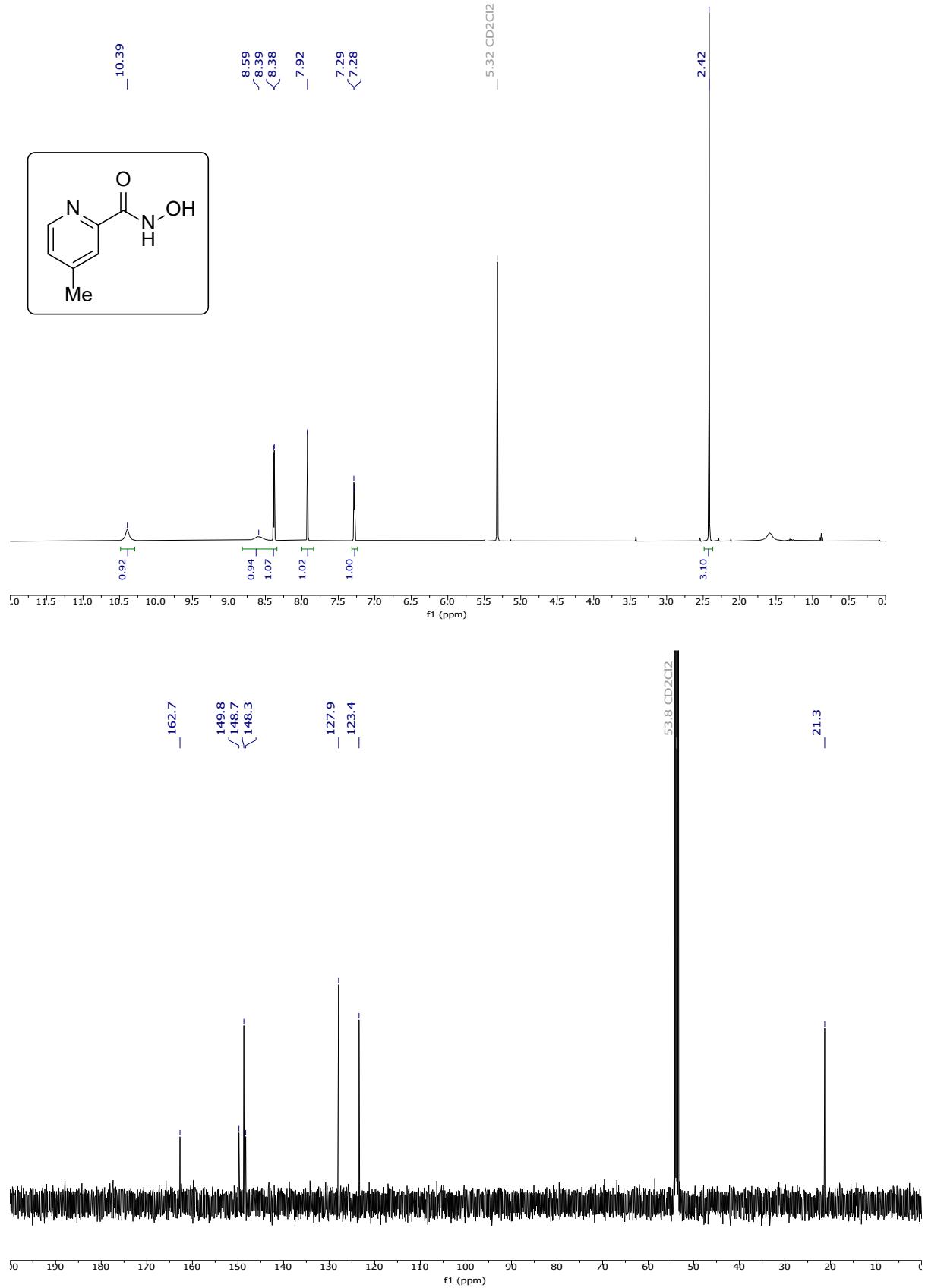
N-Acetoxypicolinamide (L1)



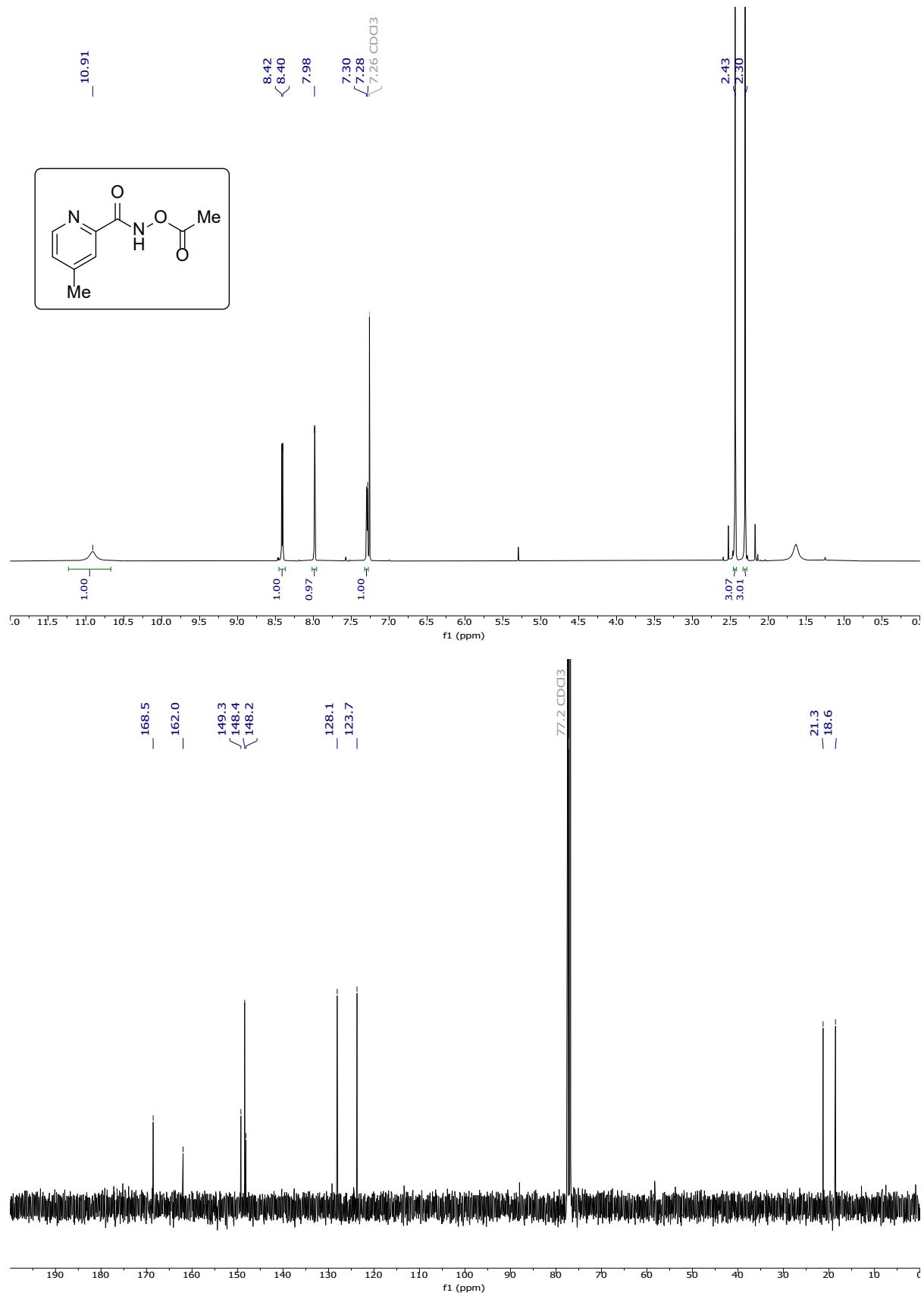
N-(Pivaloyloxy)picolinamide (L2)



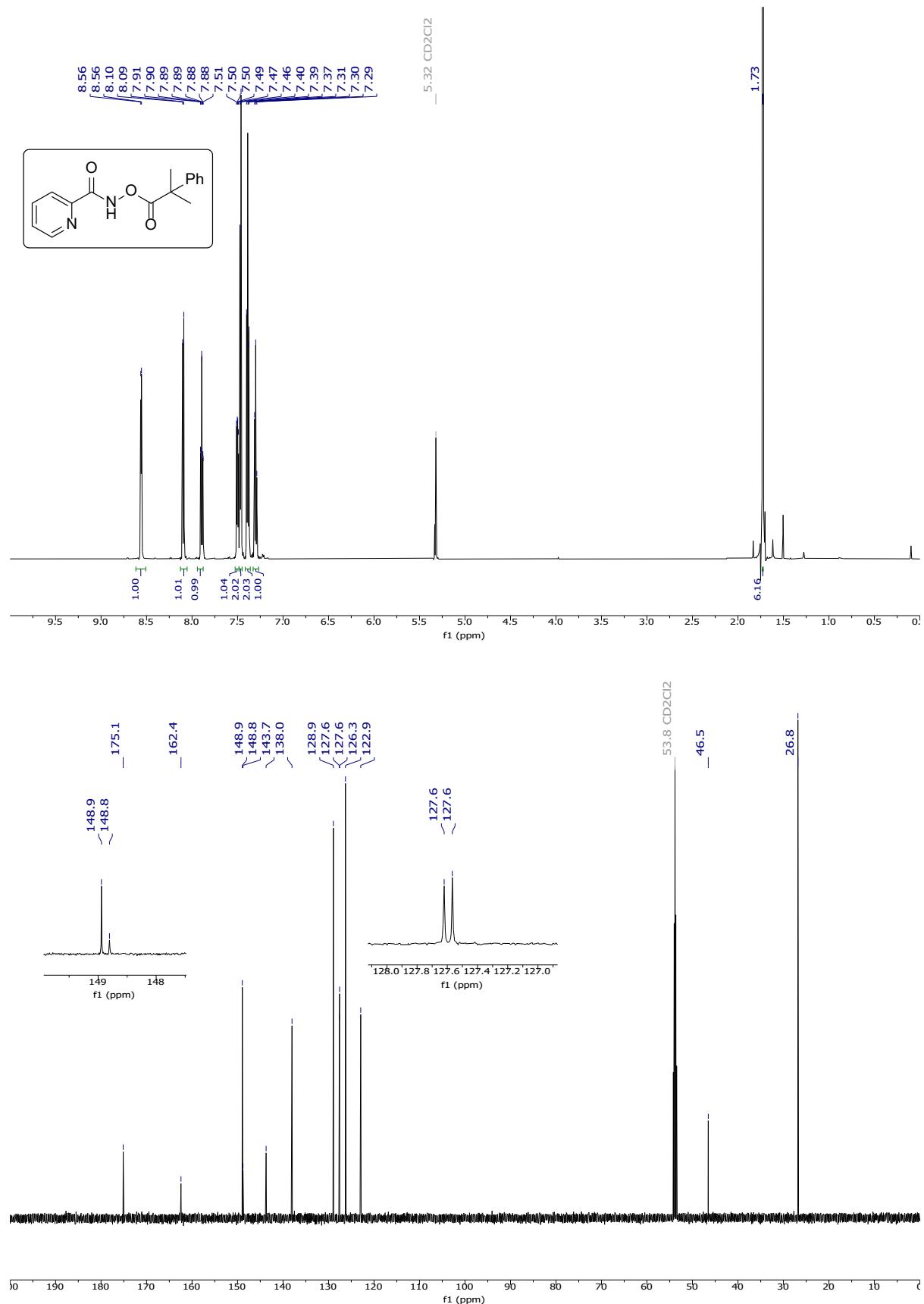
N-Hydroxy-4-methylpicolinamide



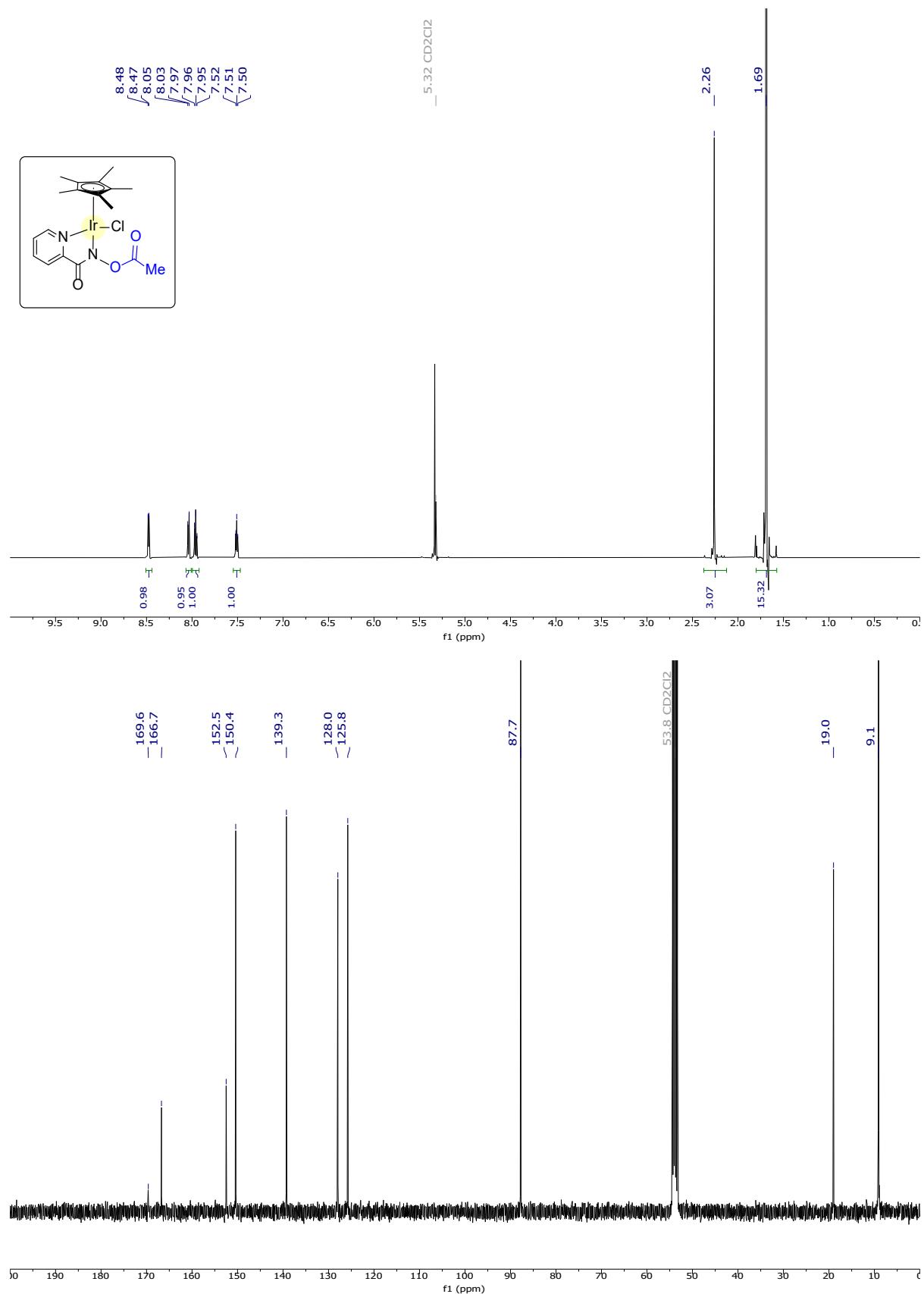
N-Acetoxy-4-methylpicolinamide (L3)



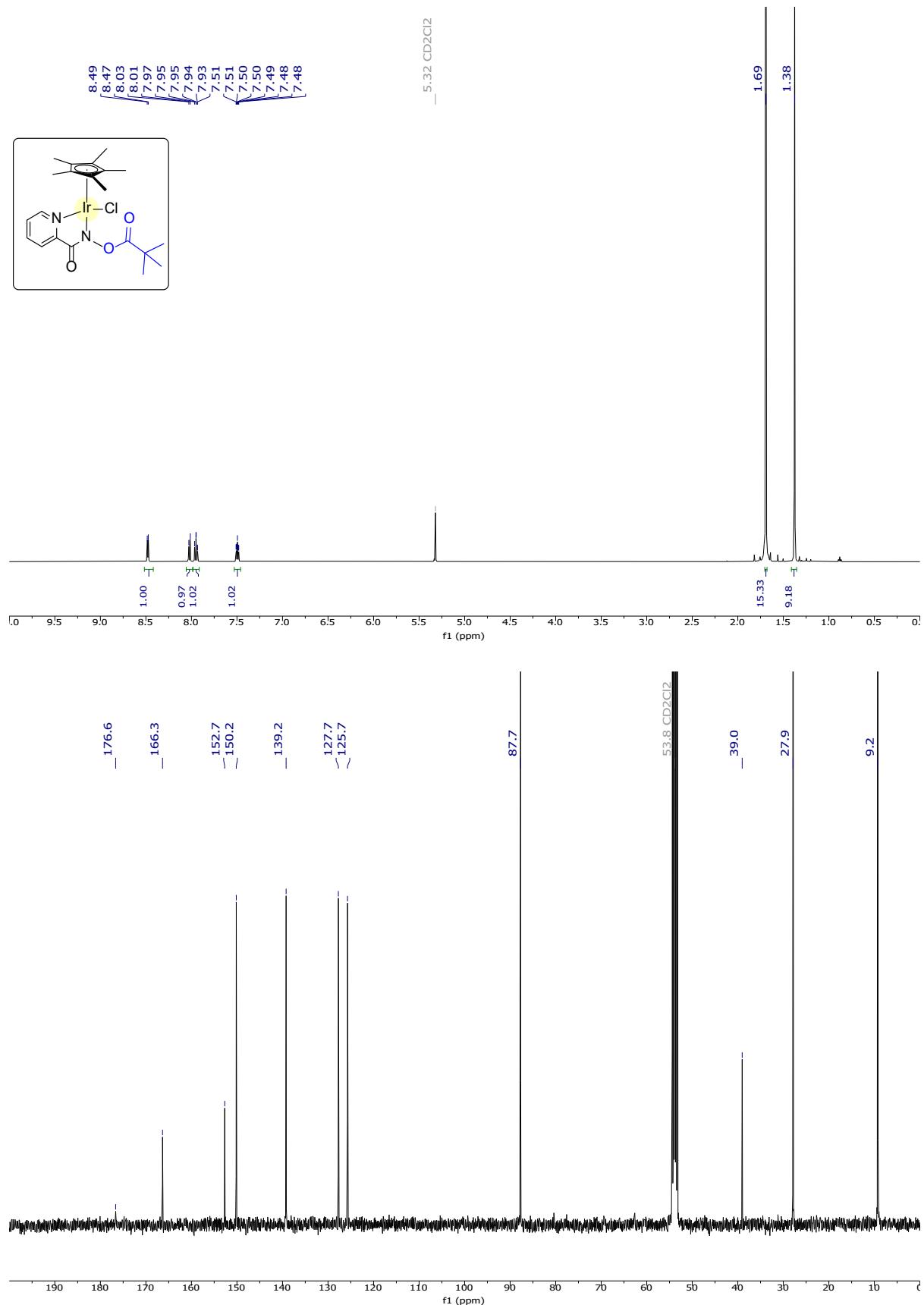
N-{(2-Methyl-2-phenylpropanoyl)oxy}picolinamide (L4)



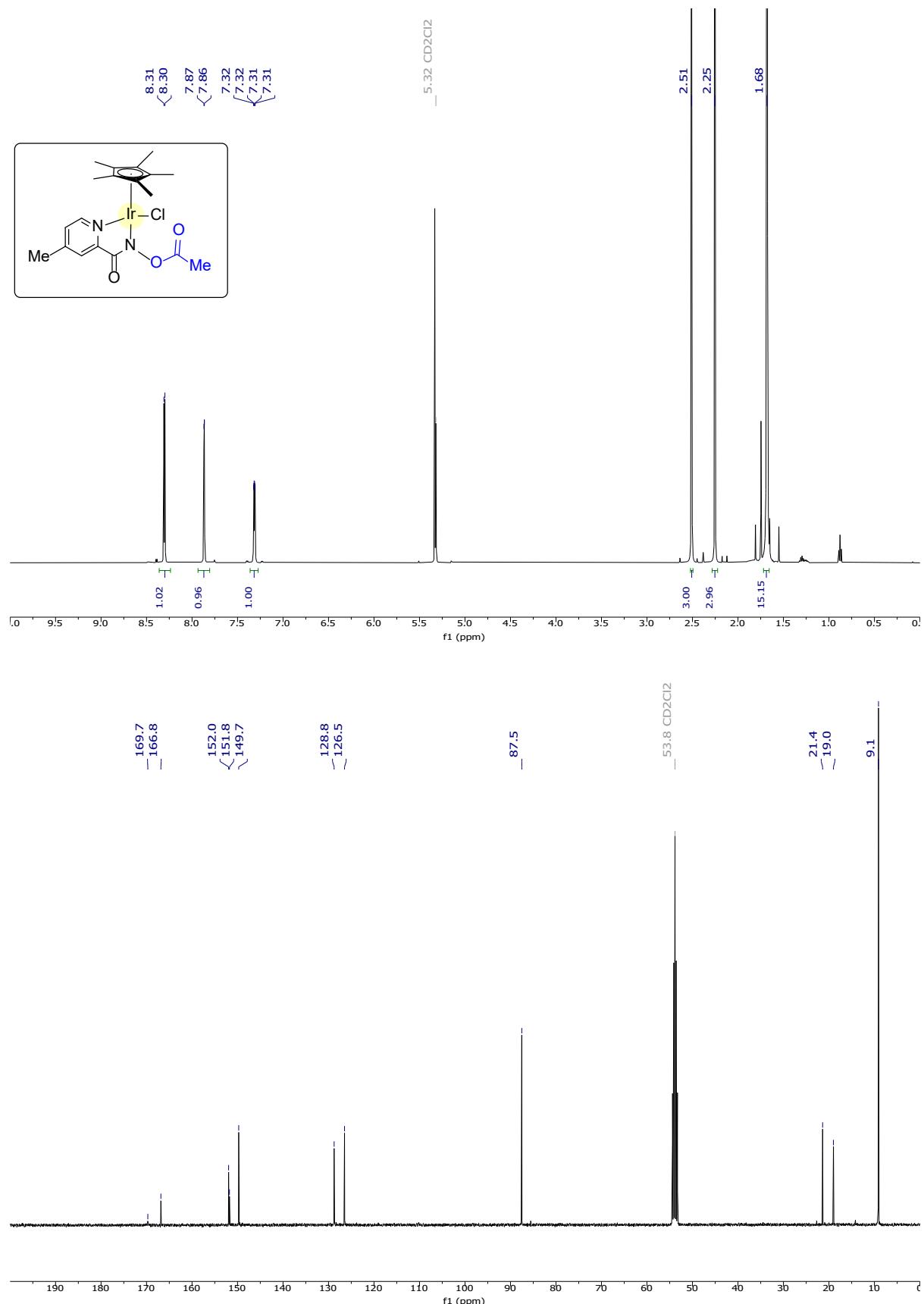
Ir1a



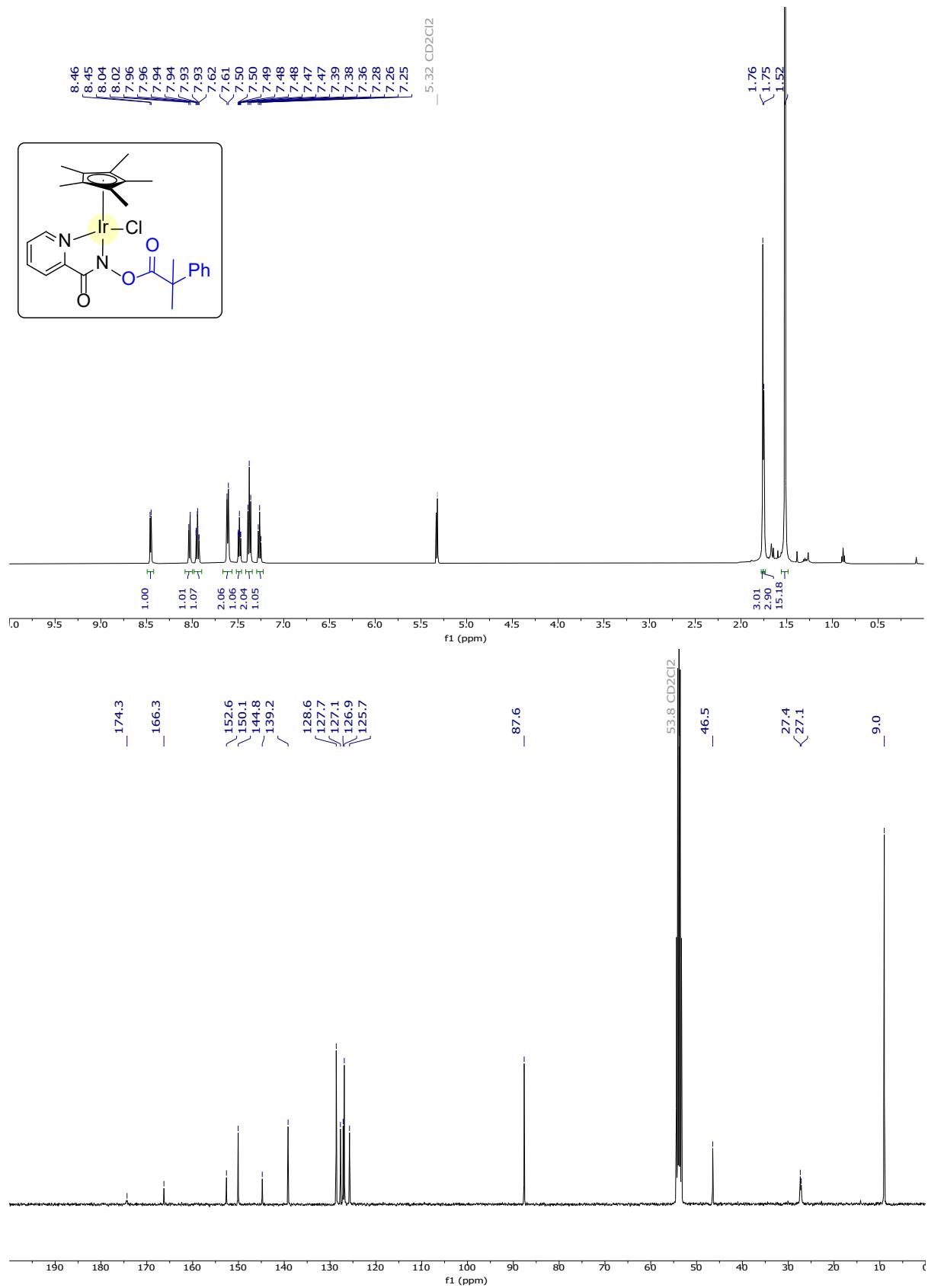
Ir1b



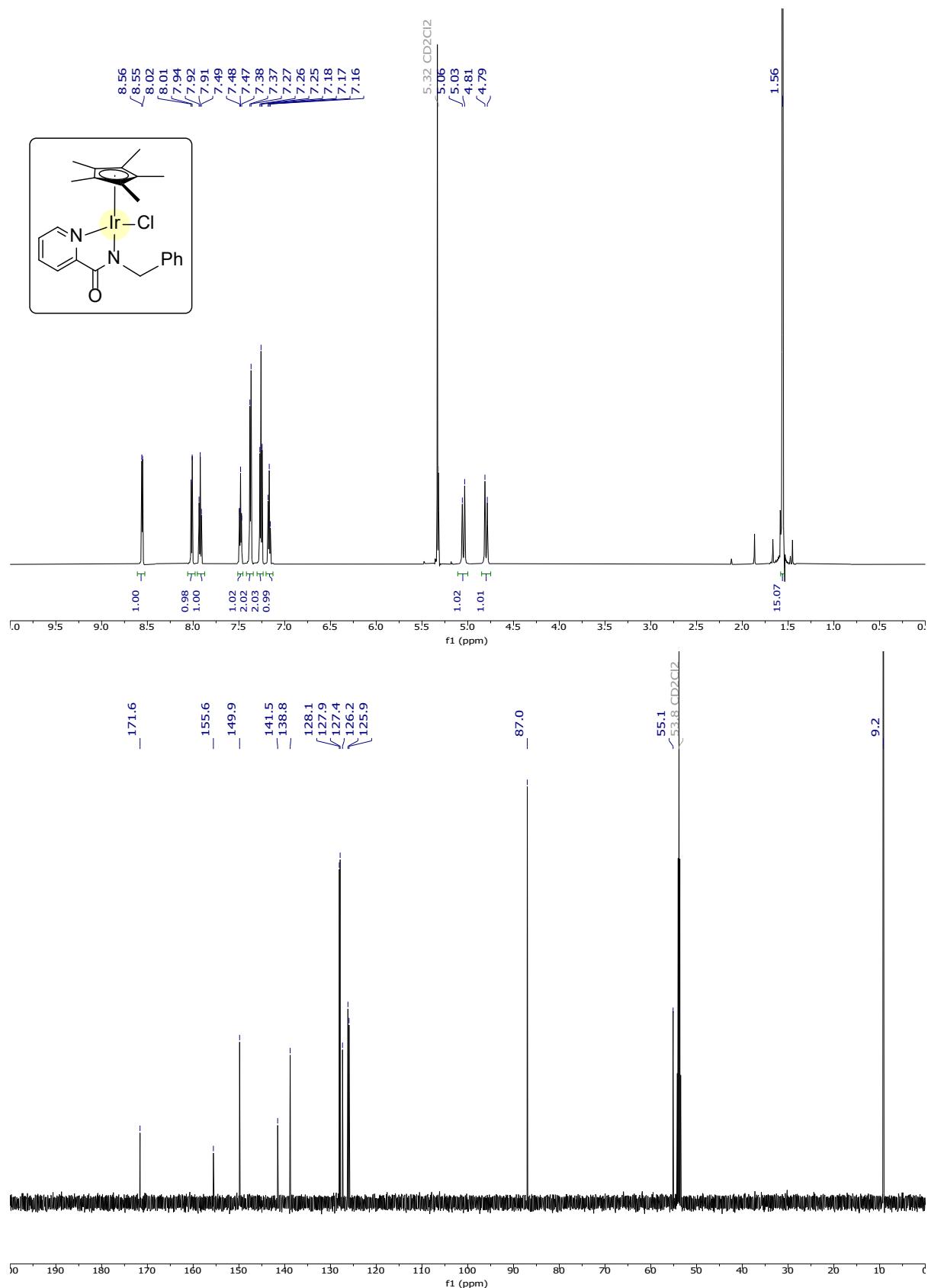
Ir1c



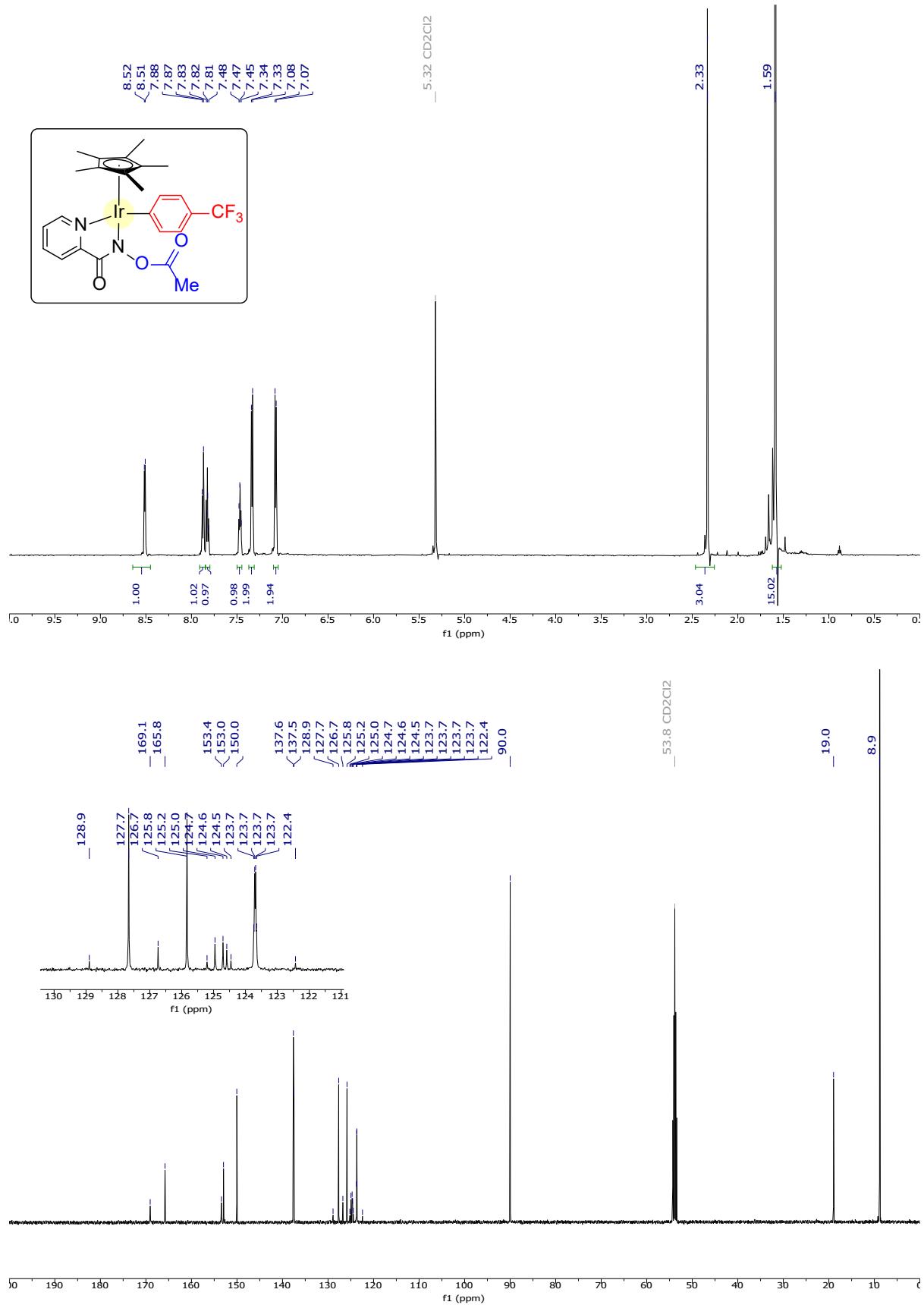
Ir1d

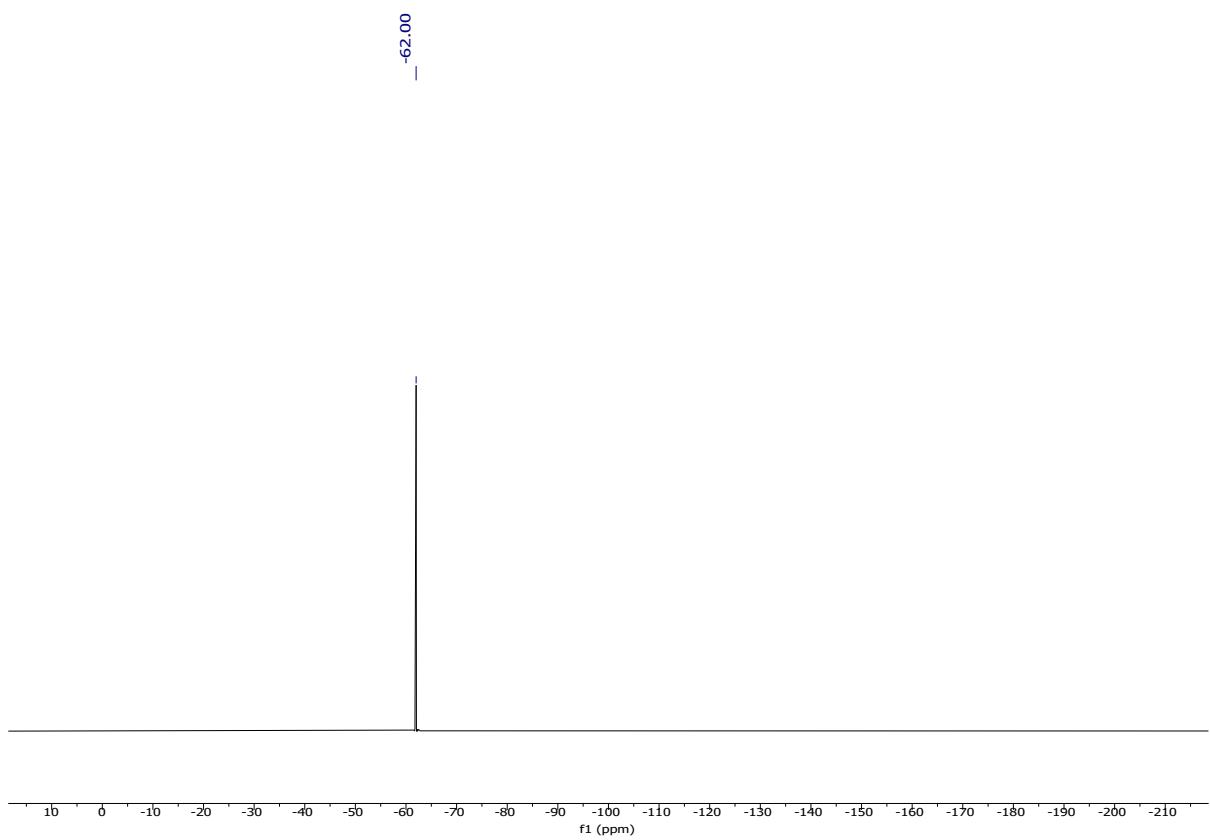


Ir1e

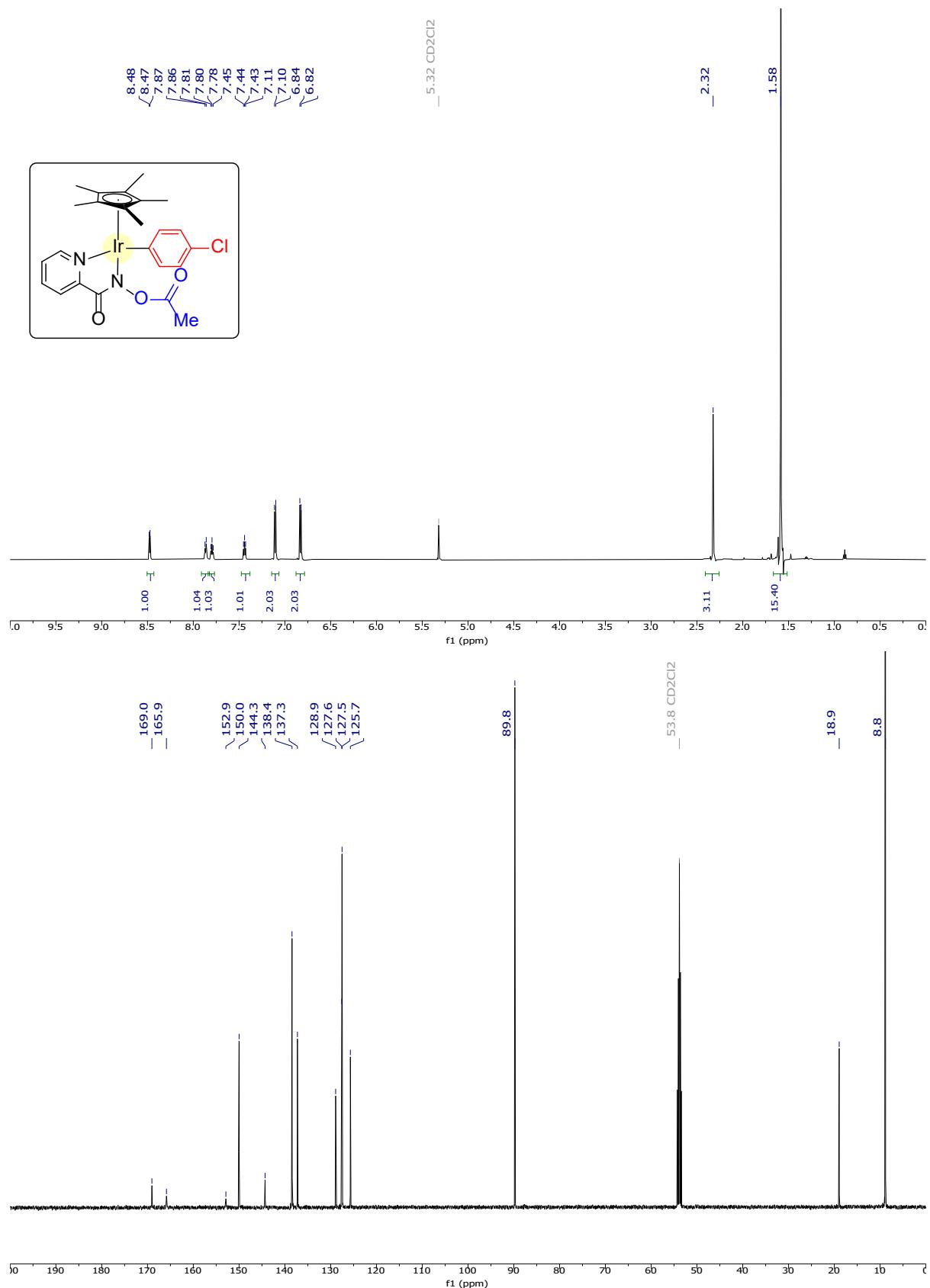


Ir3a

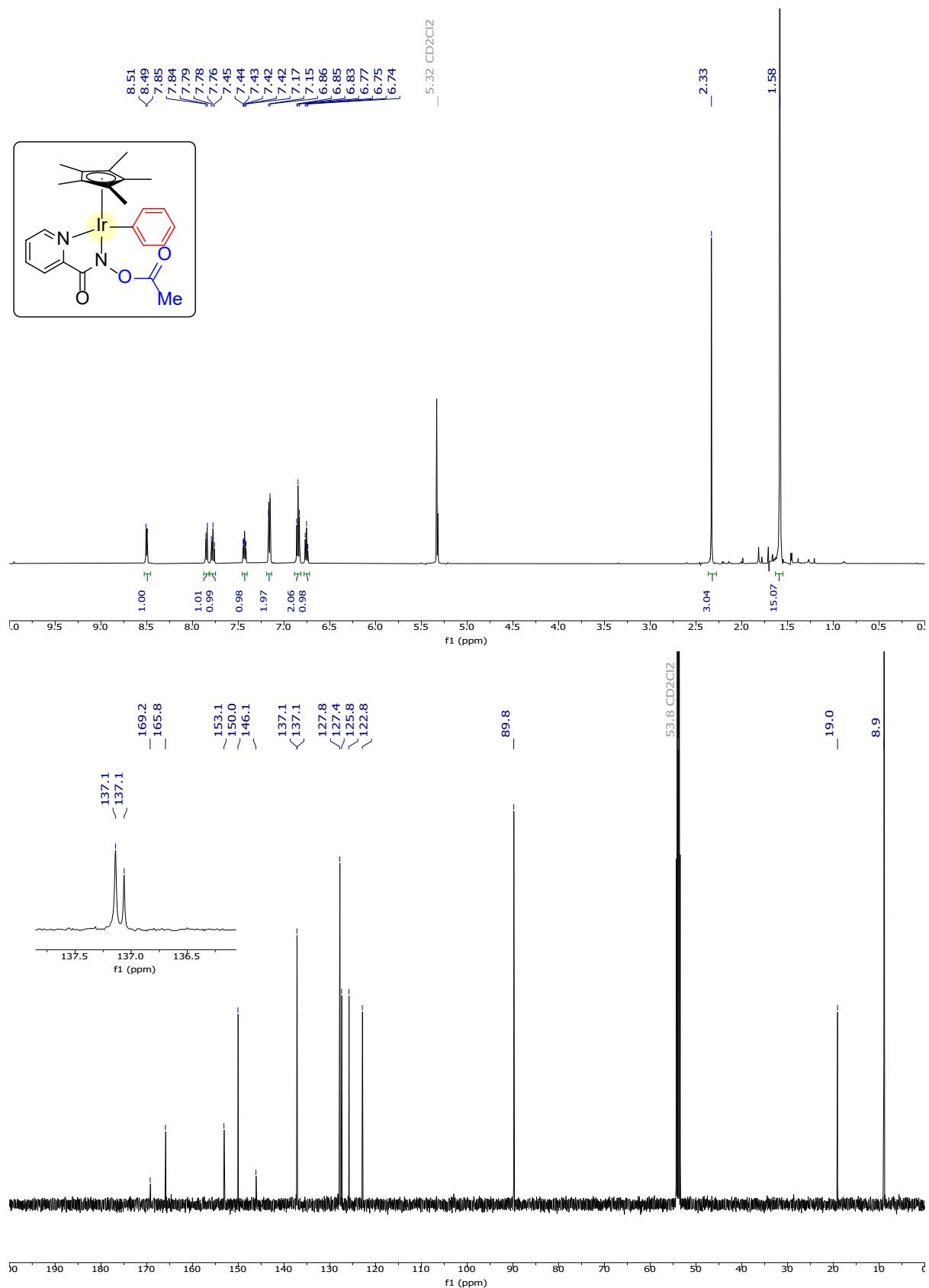




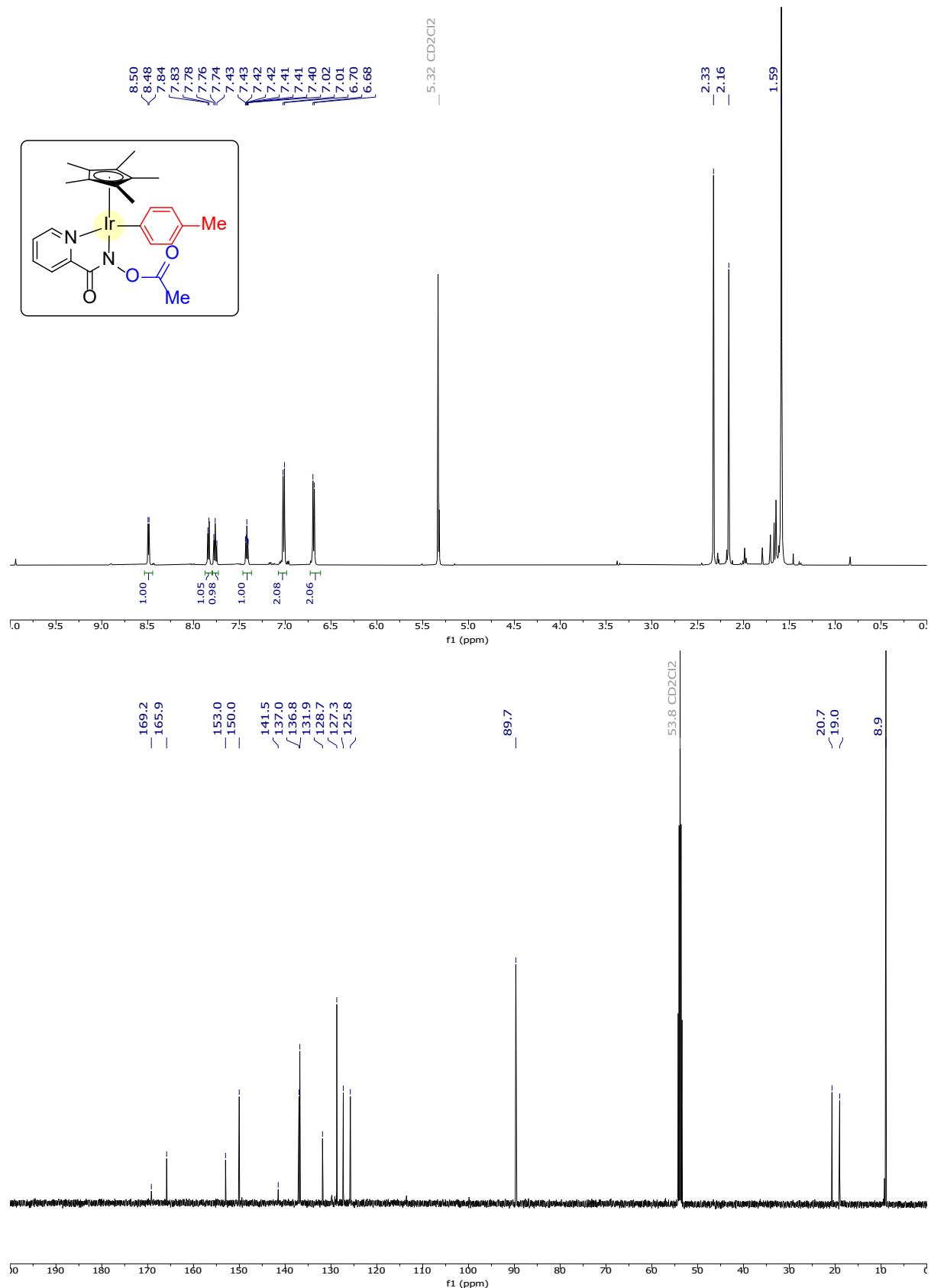
Ir3b



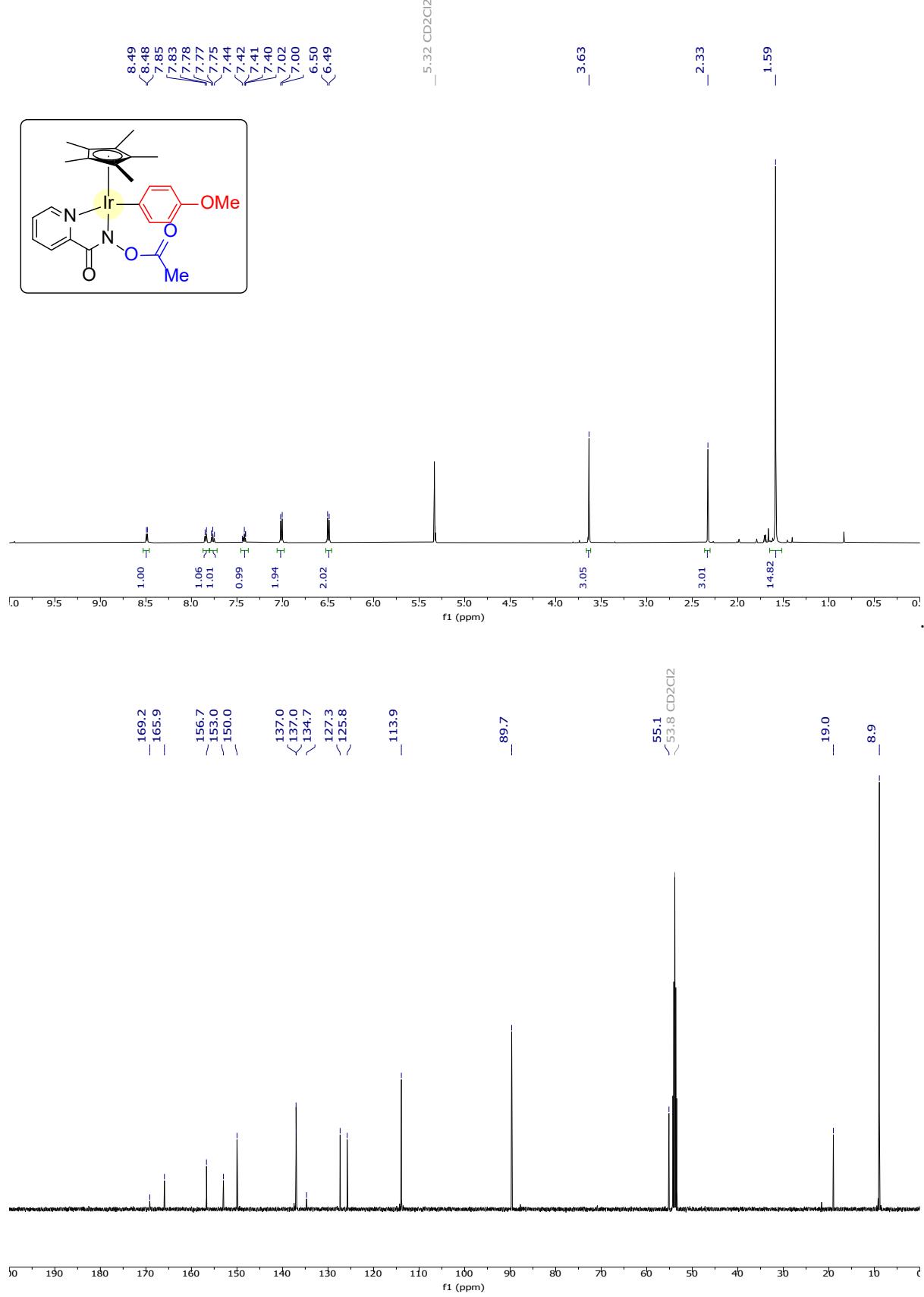
Ir3c



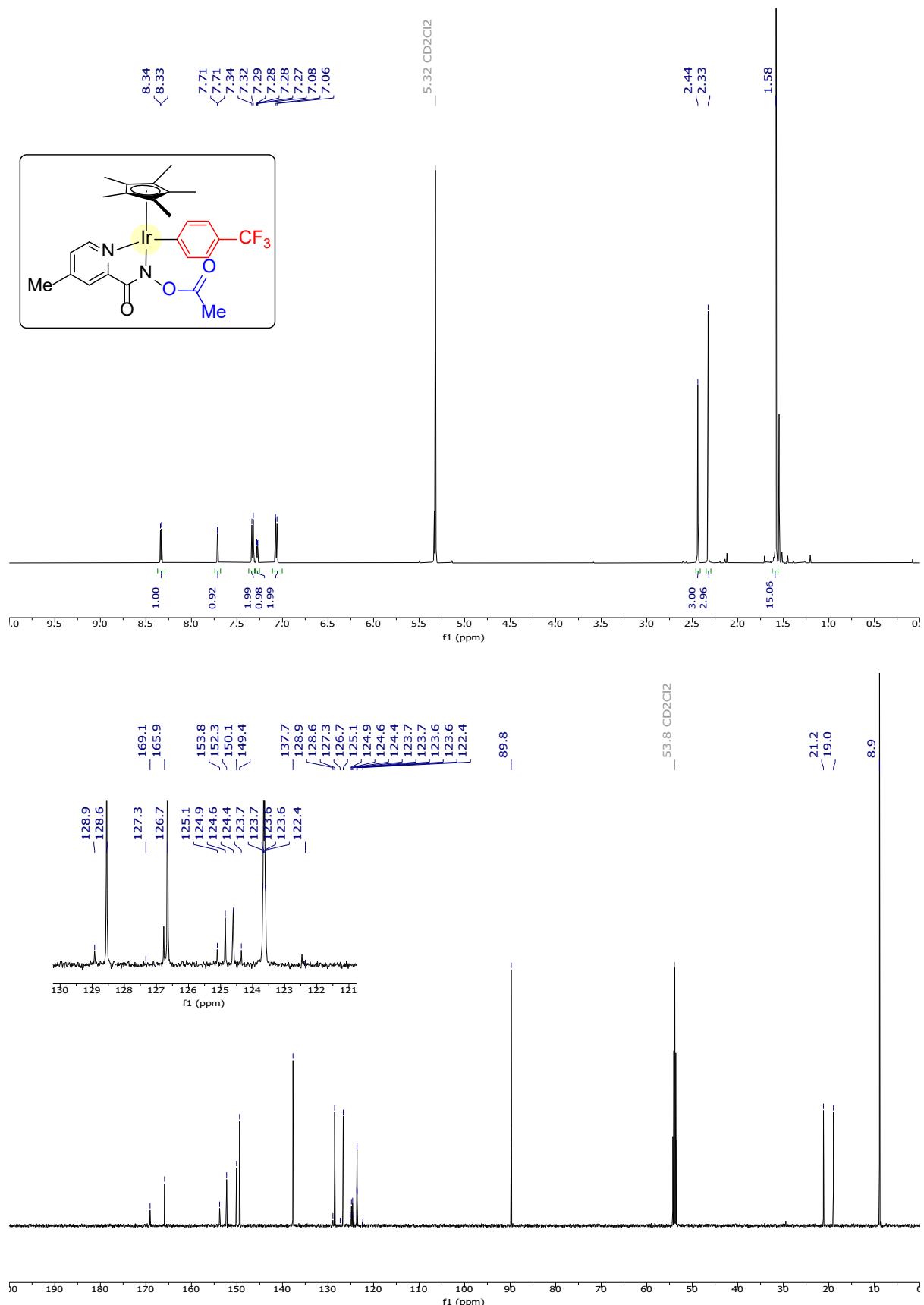
Ir3d

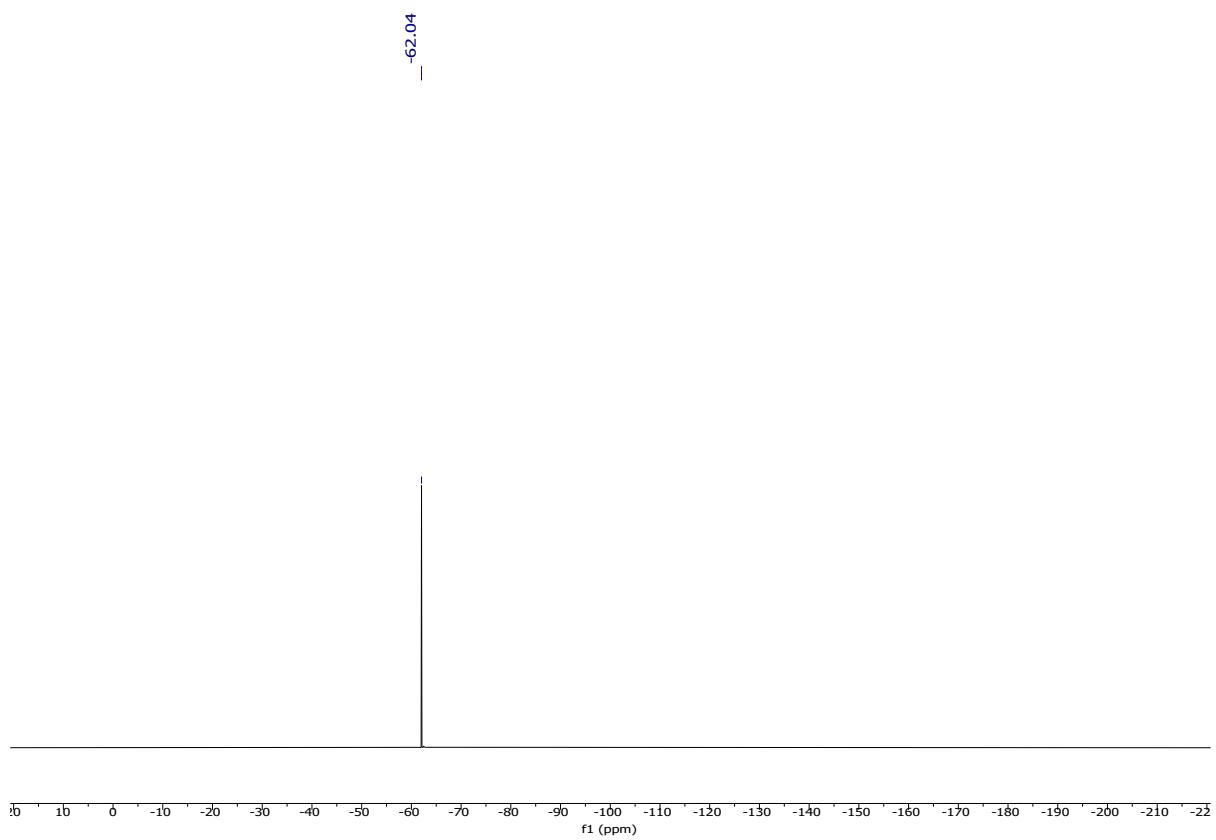


Ir3e

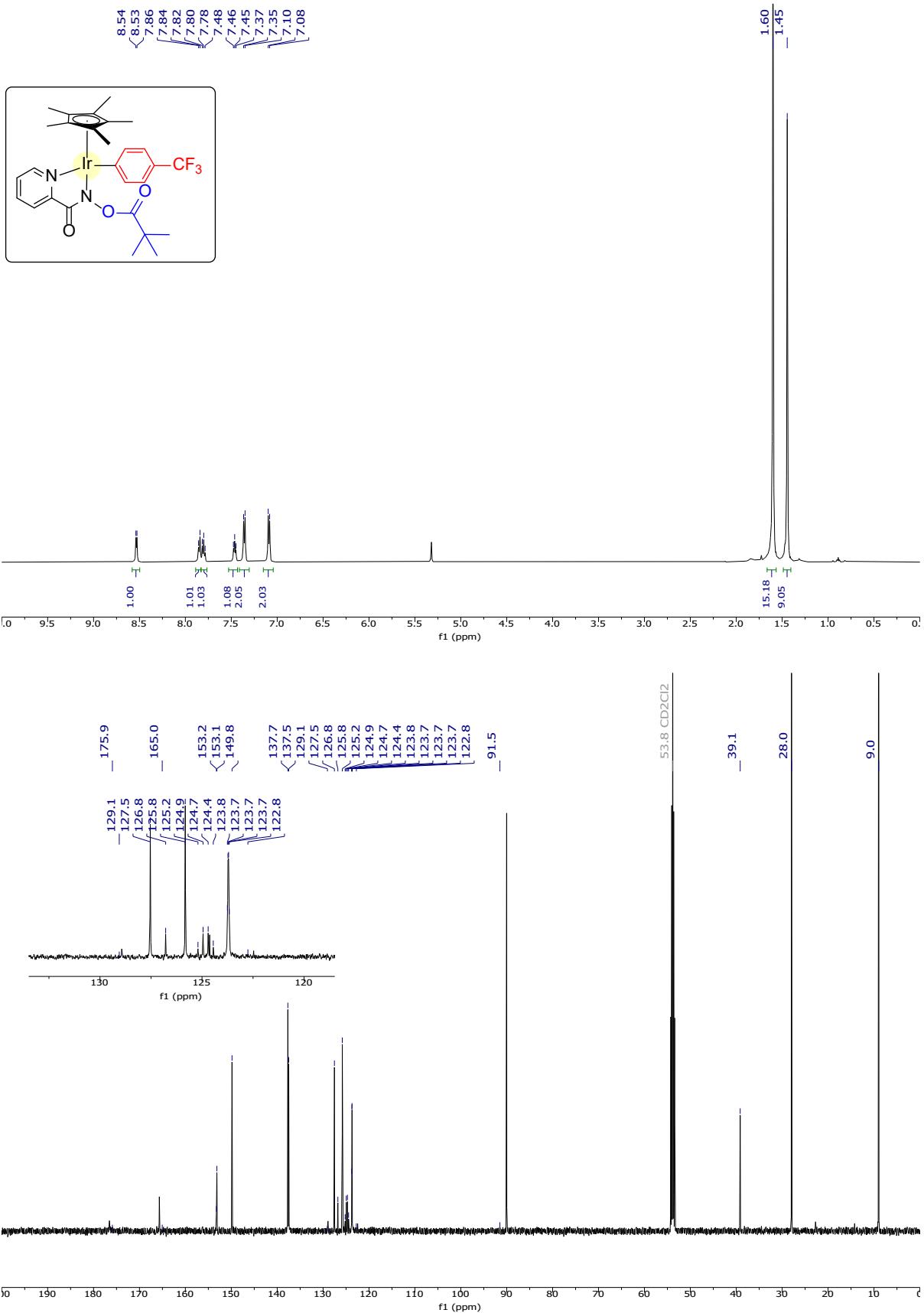


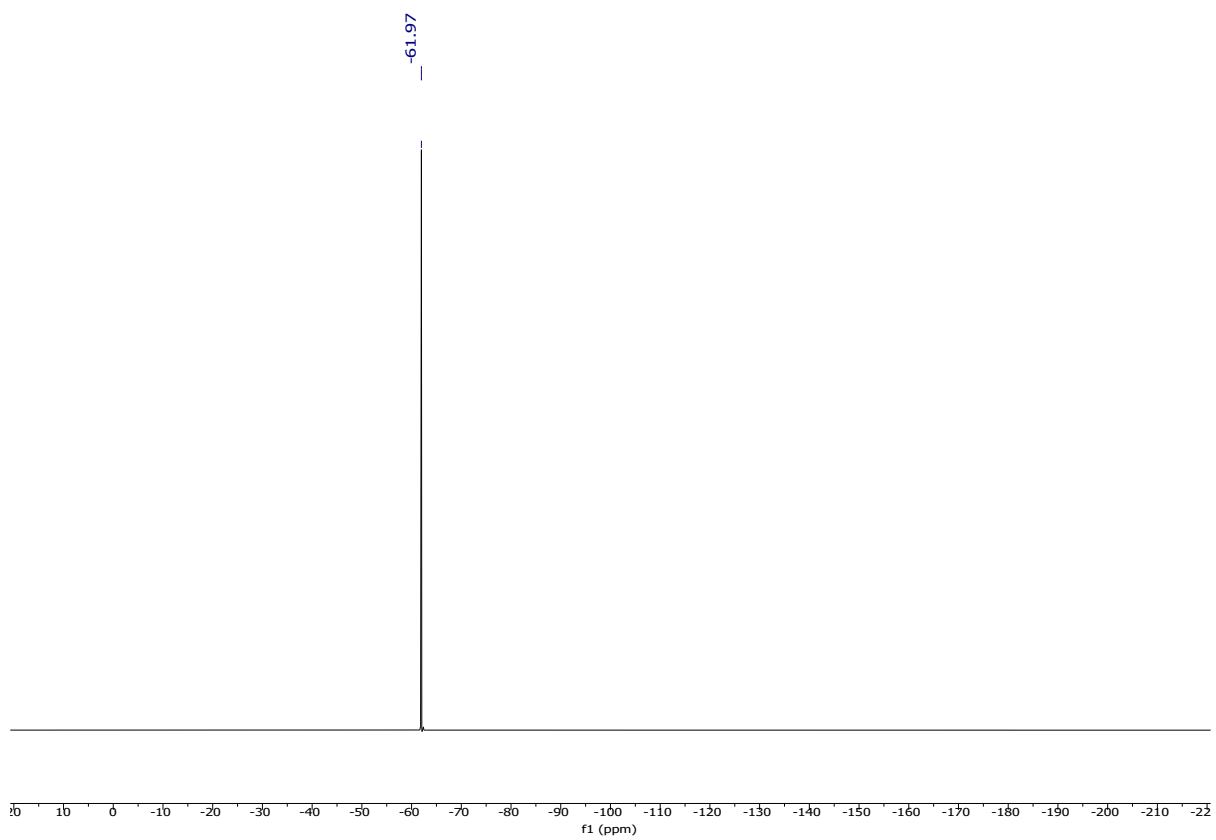
Ir3f



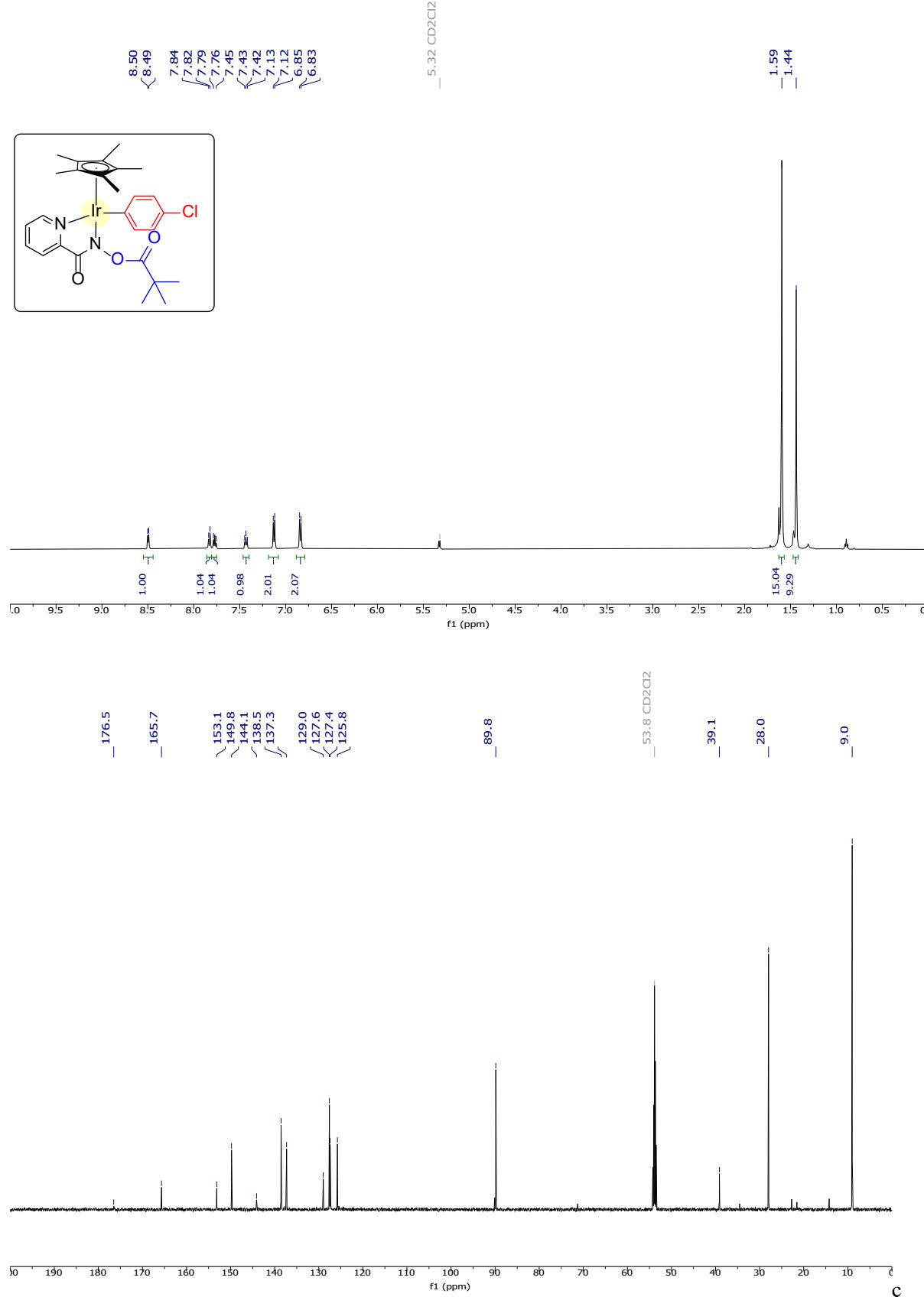


Ir3g

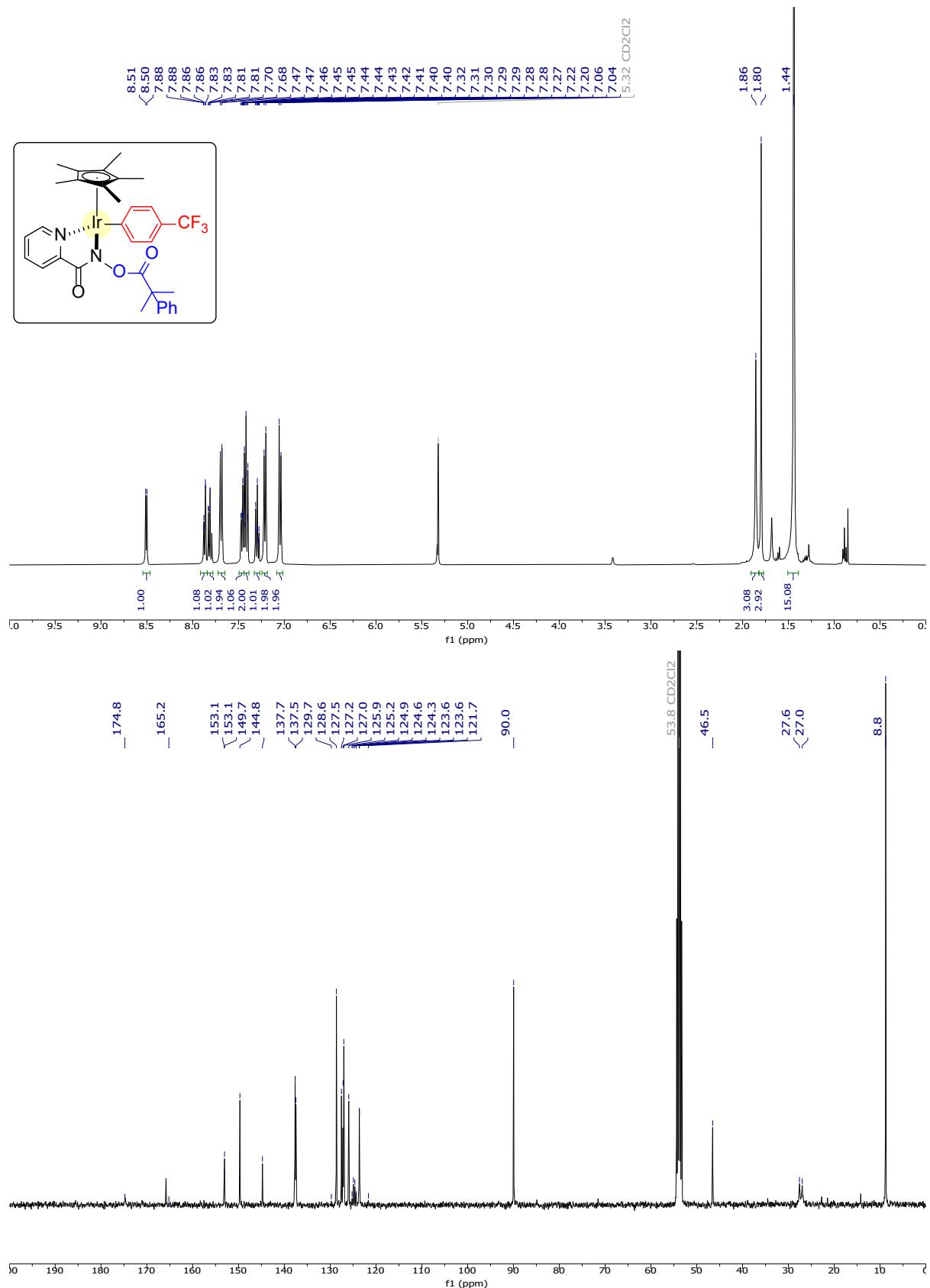


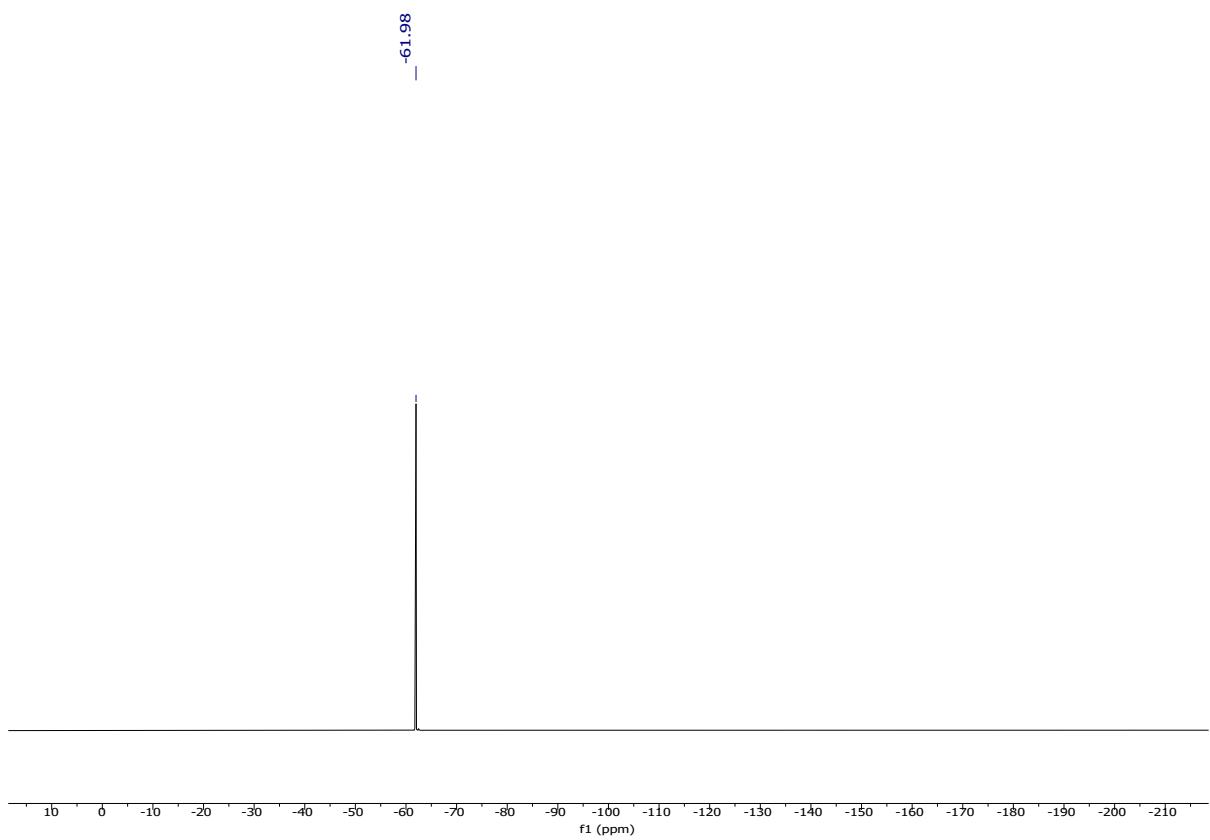


Ir3h



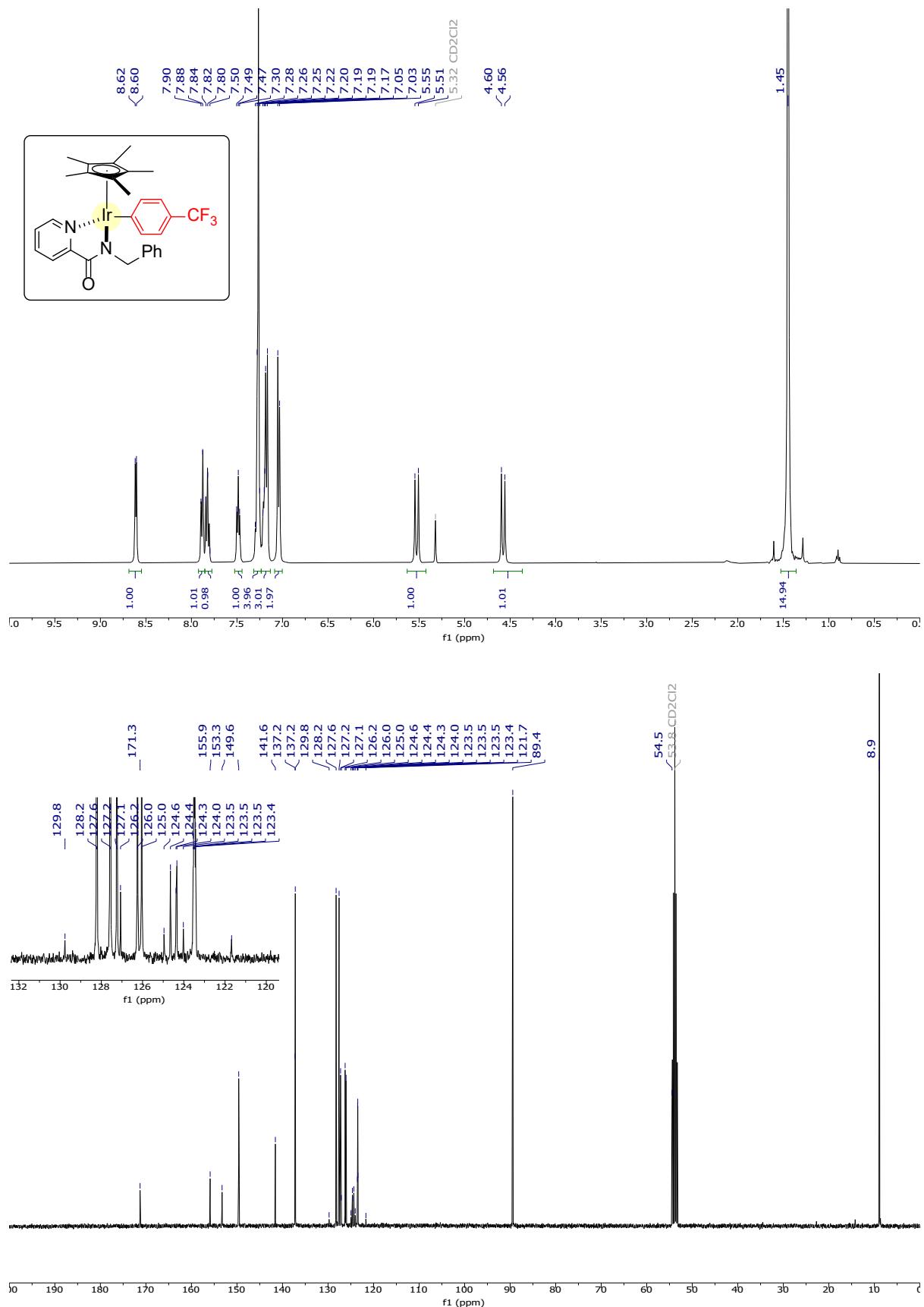
Ir3i

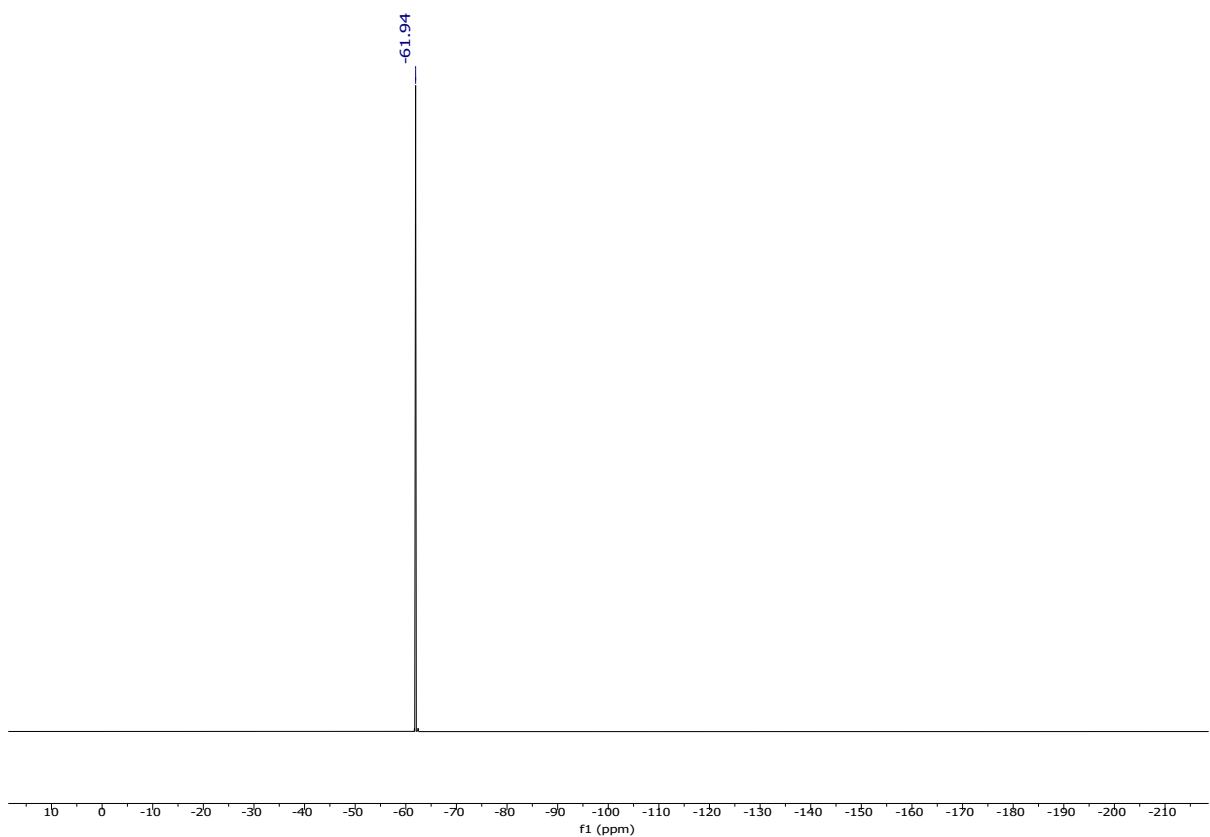




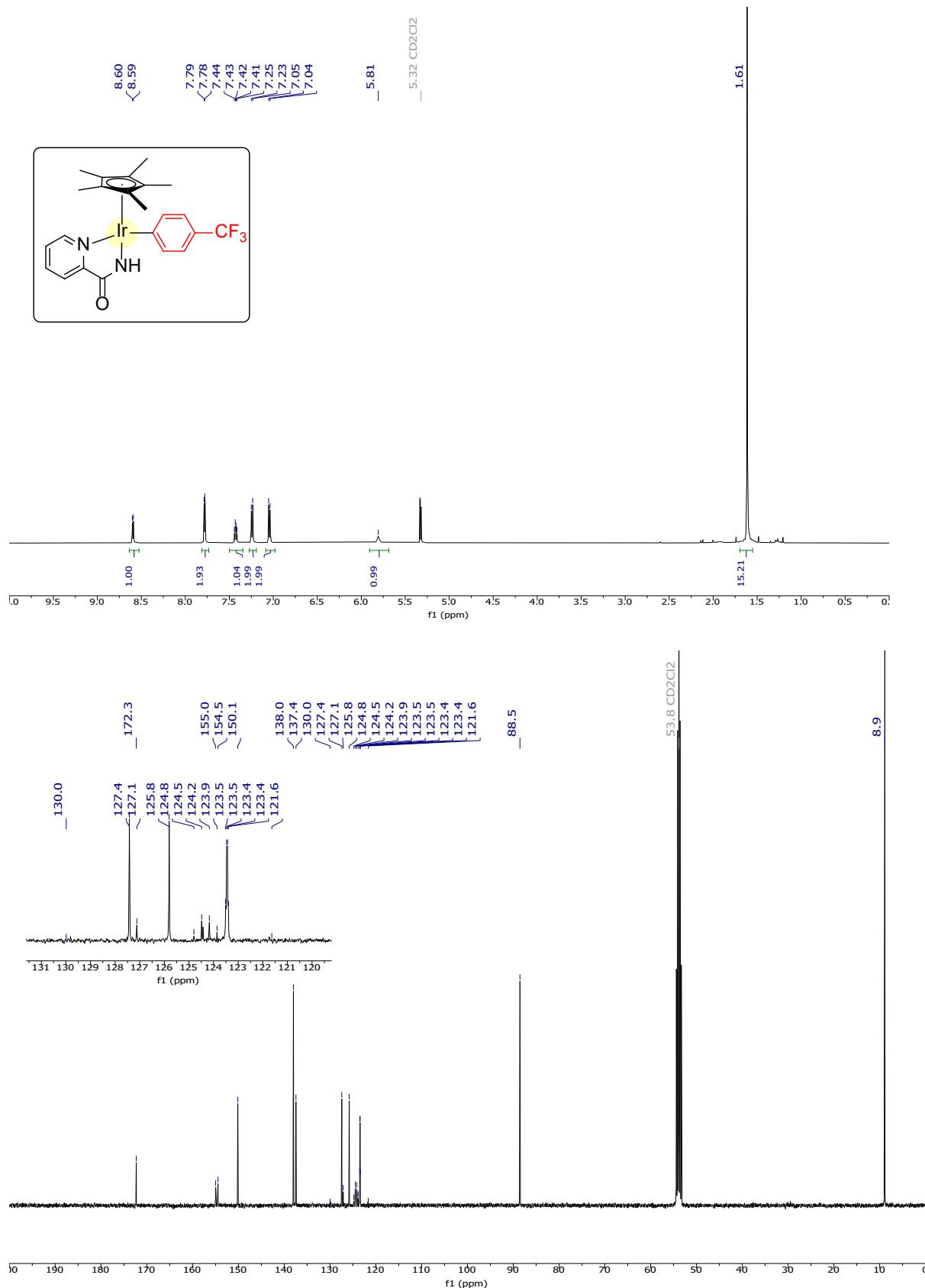
S102

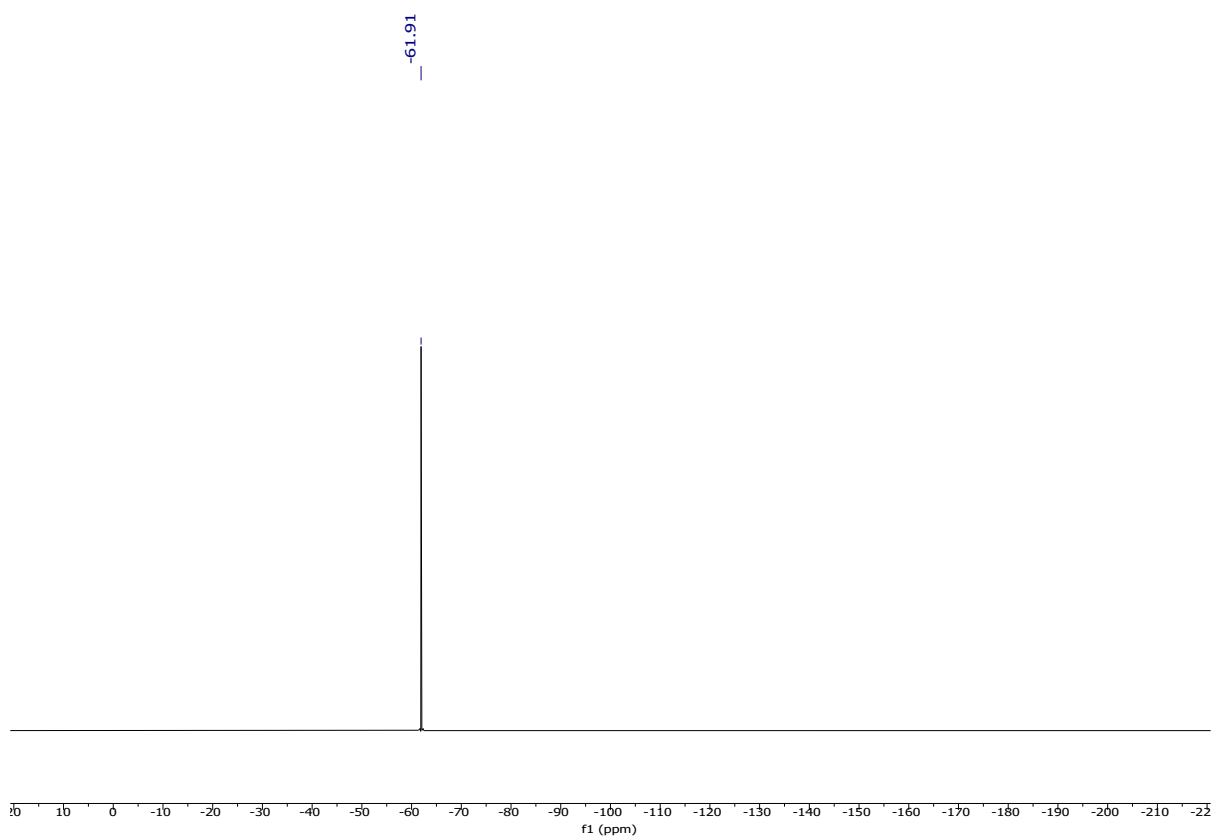
Ir3j

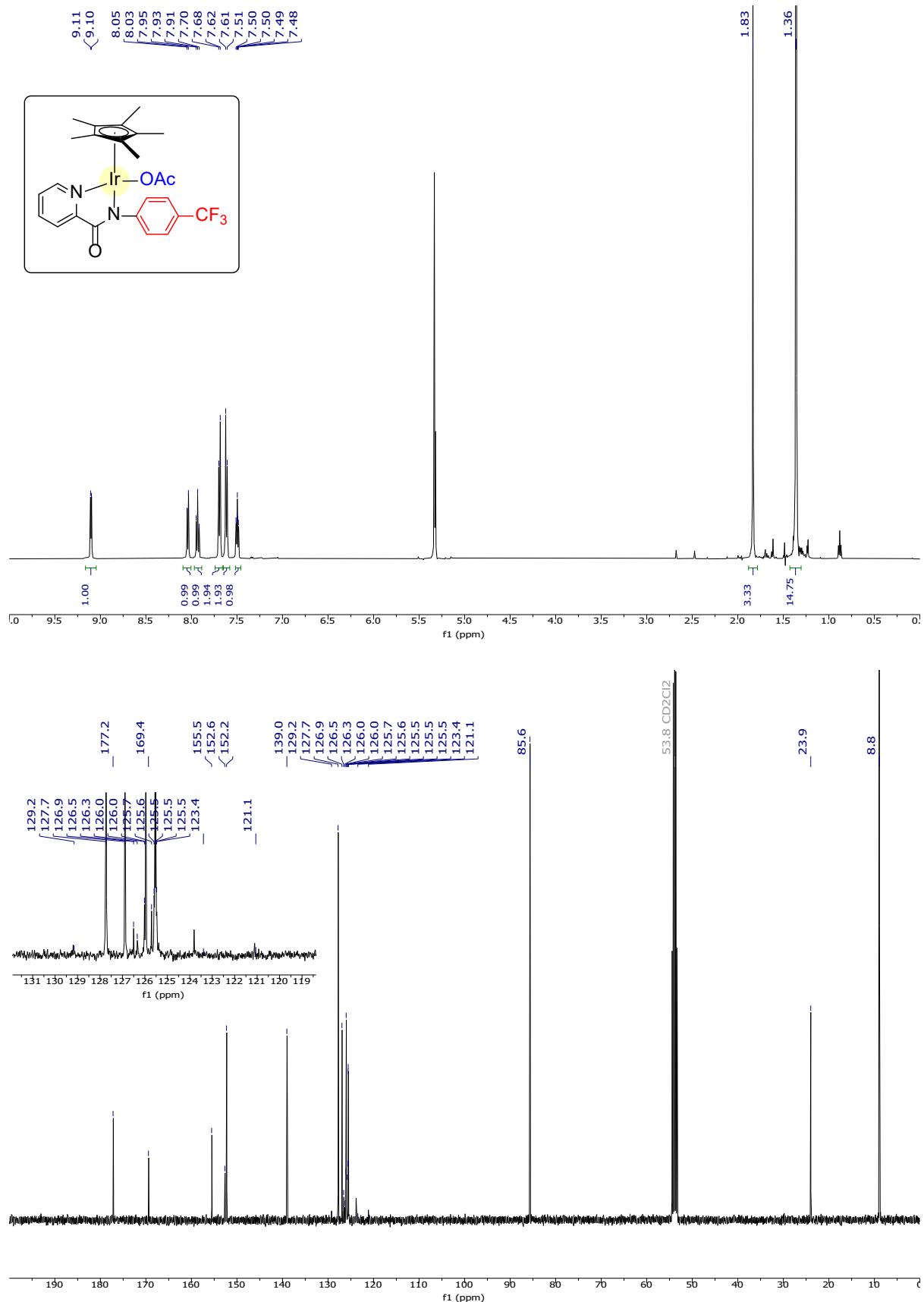


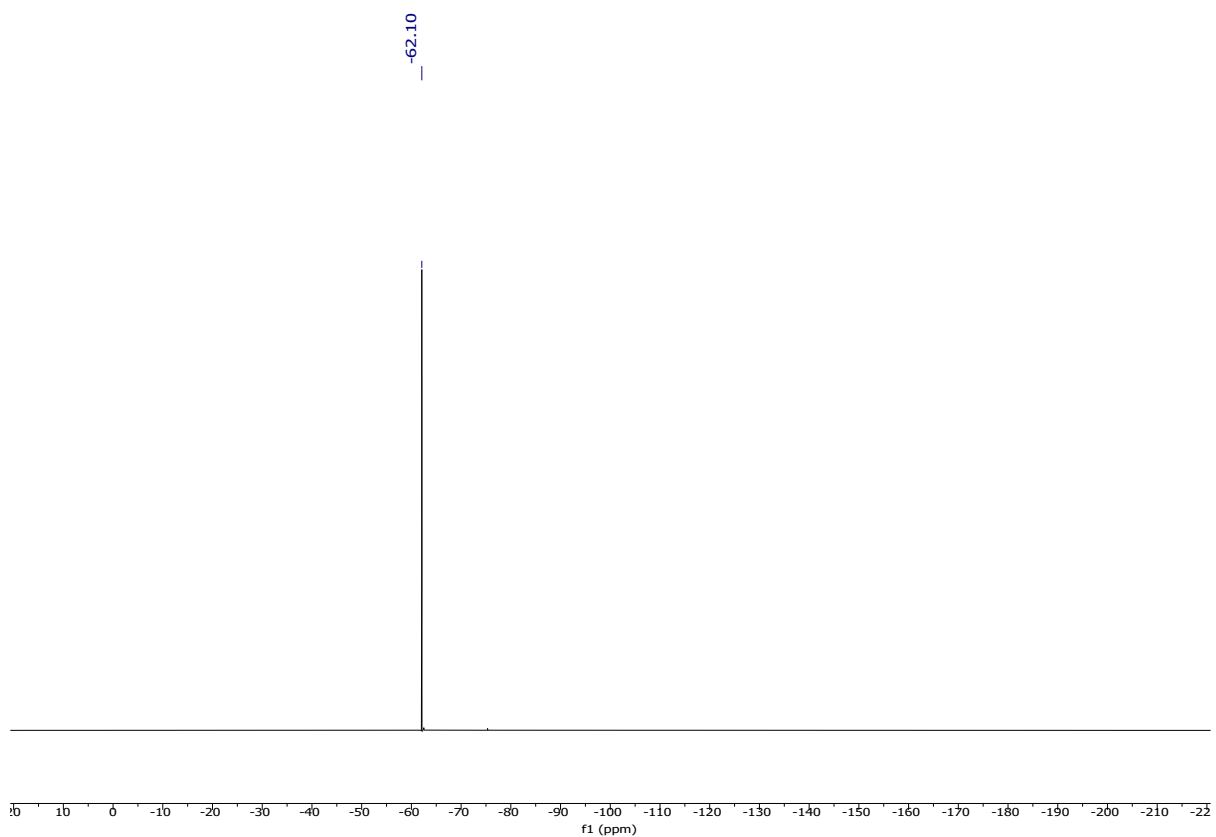


Ir5

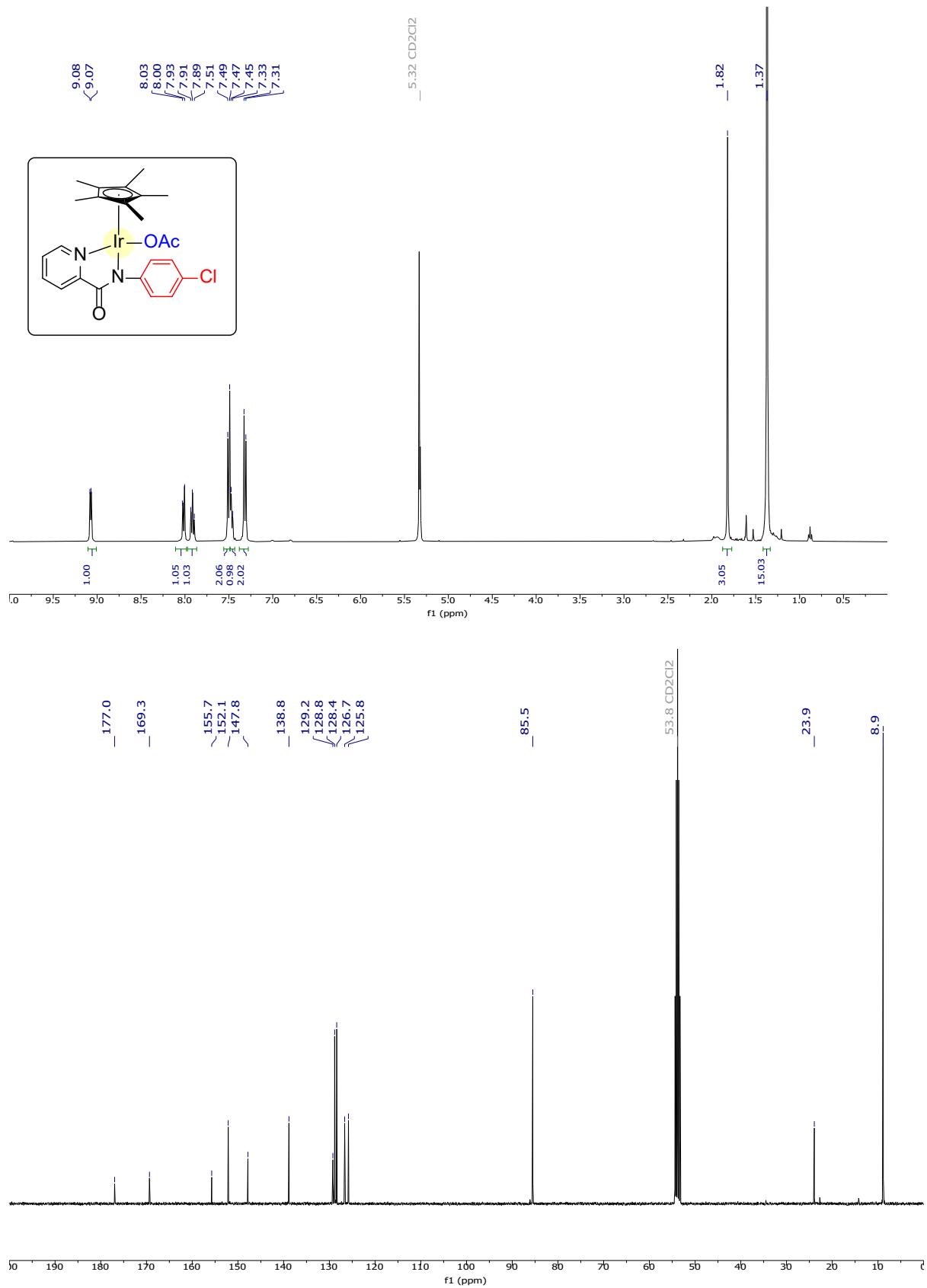




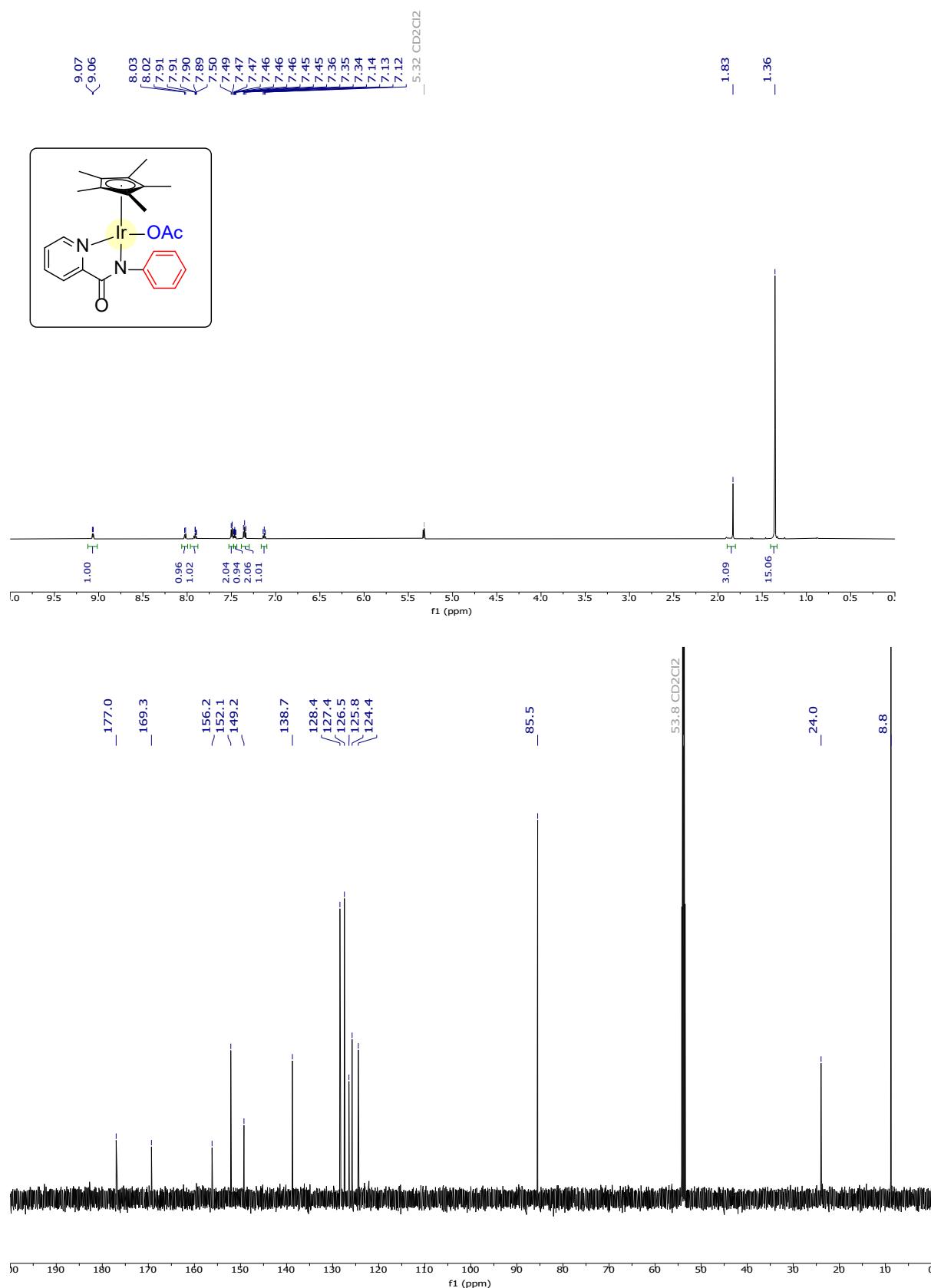
Ir4a



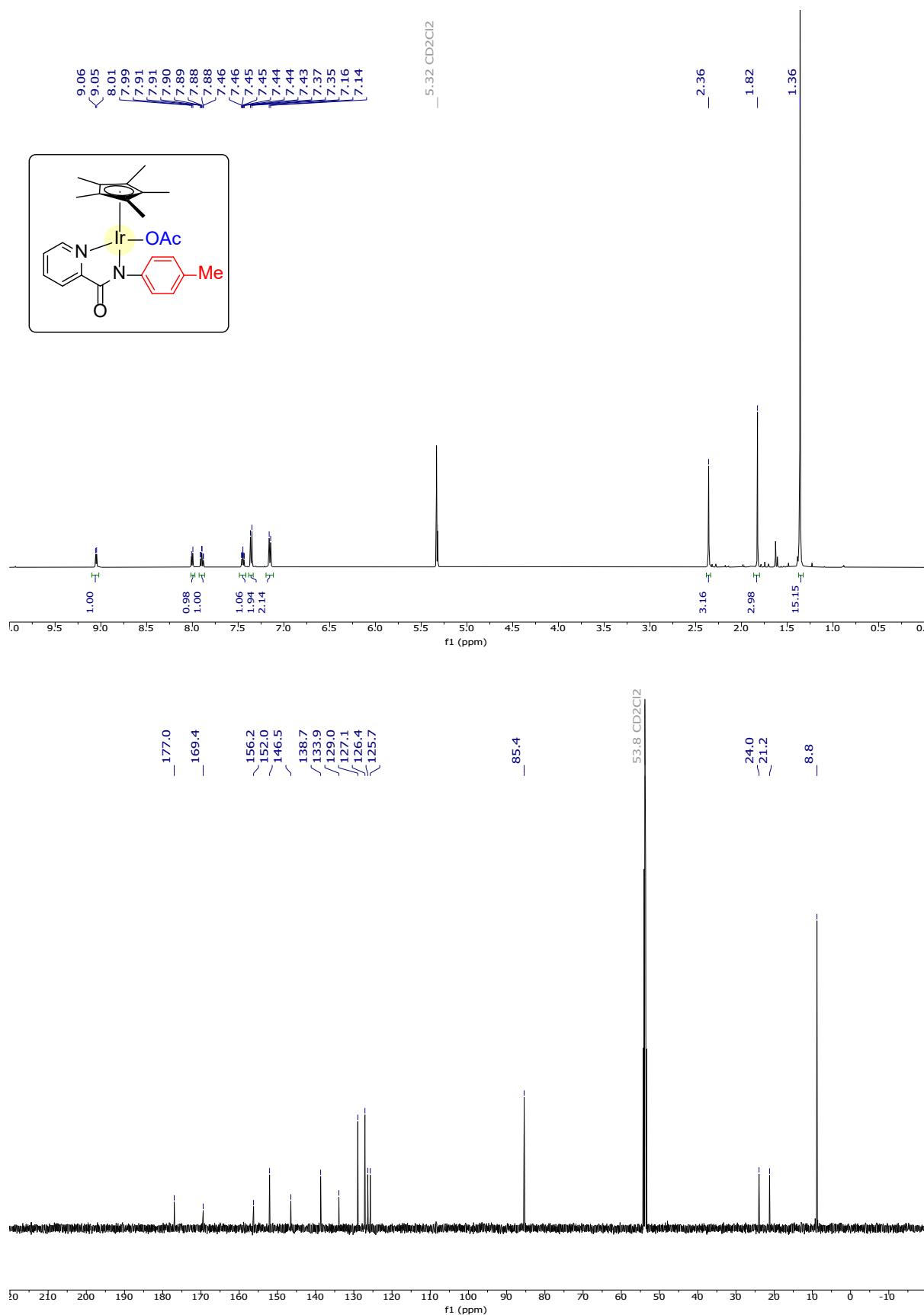
Ir4b



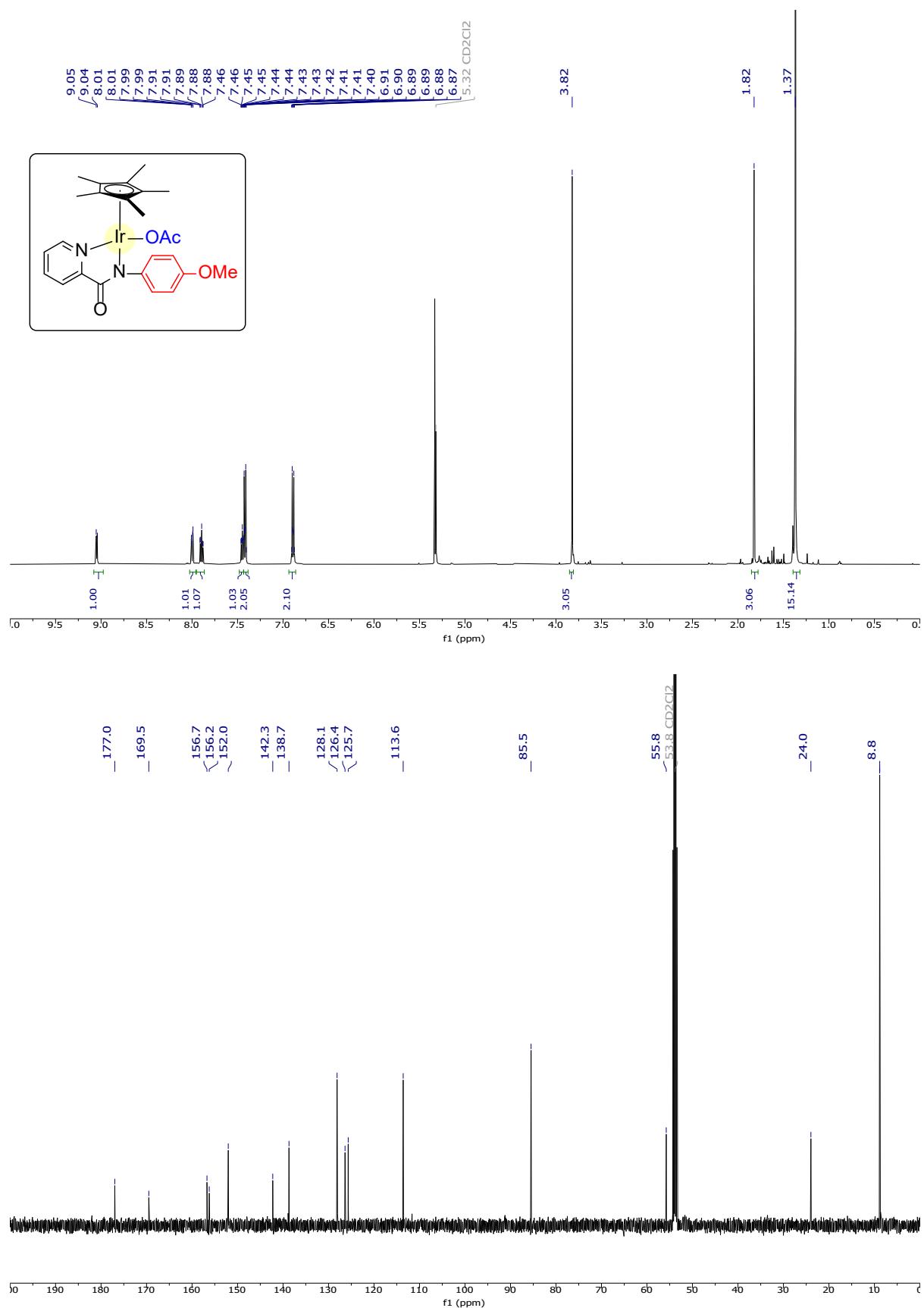
Ir4c



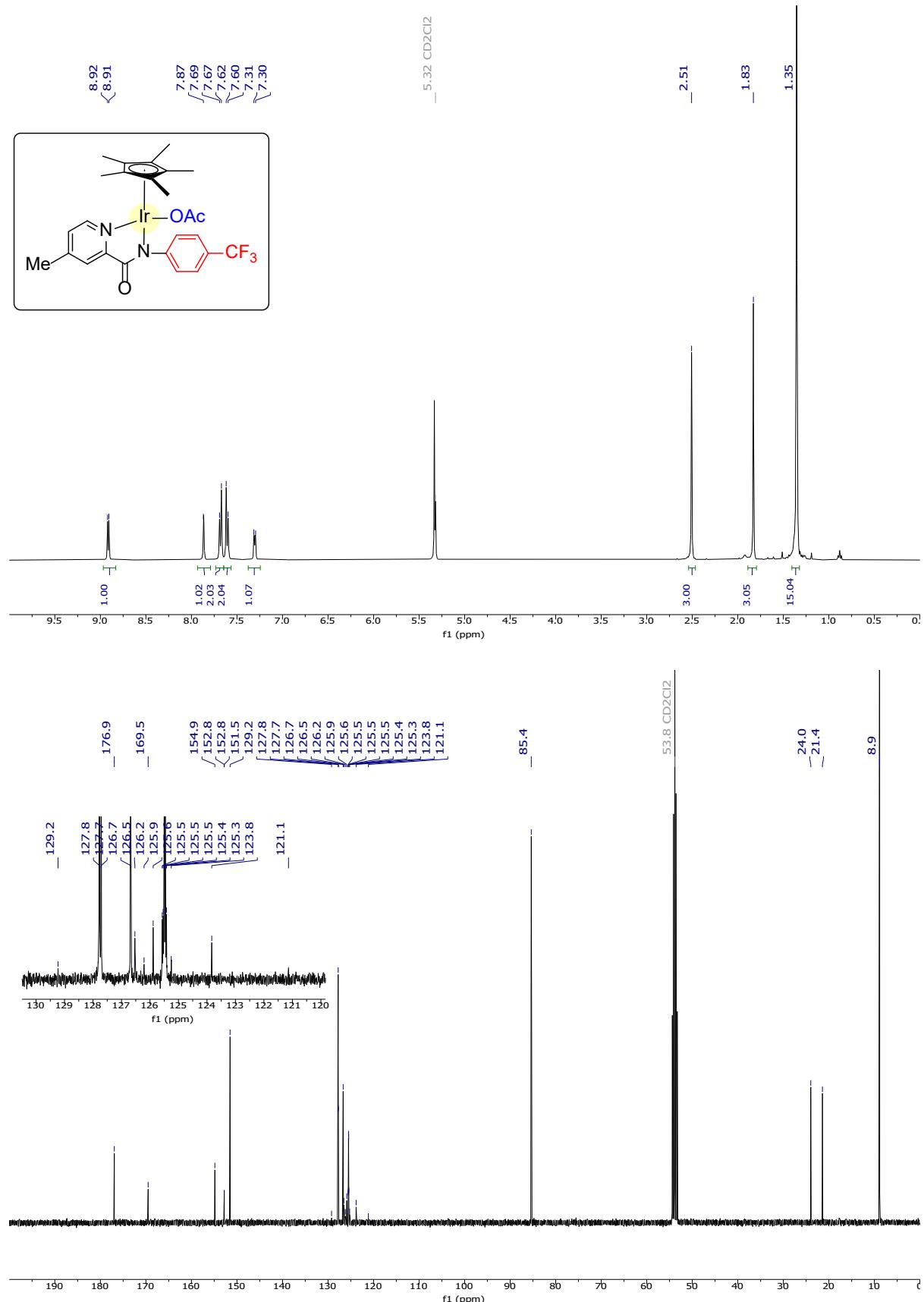
Ir4d

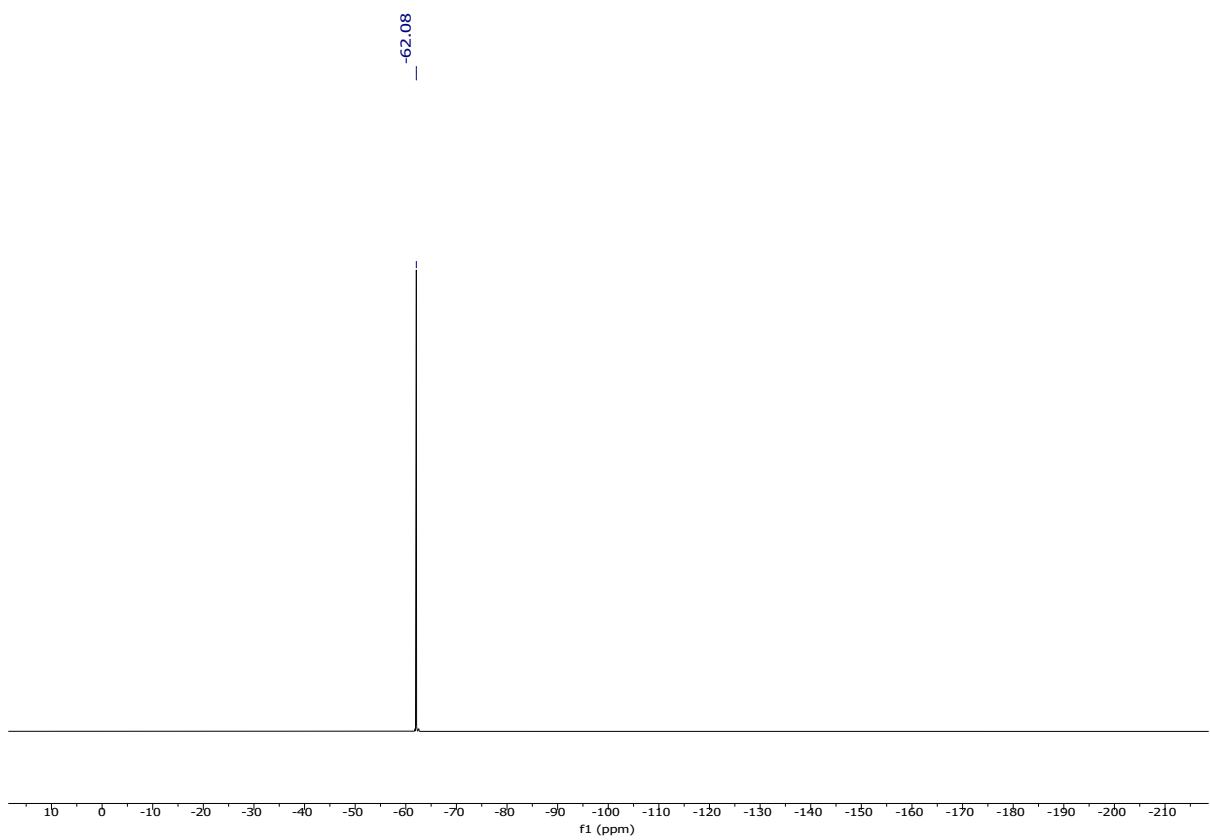


Ir4e

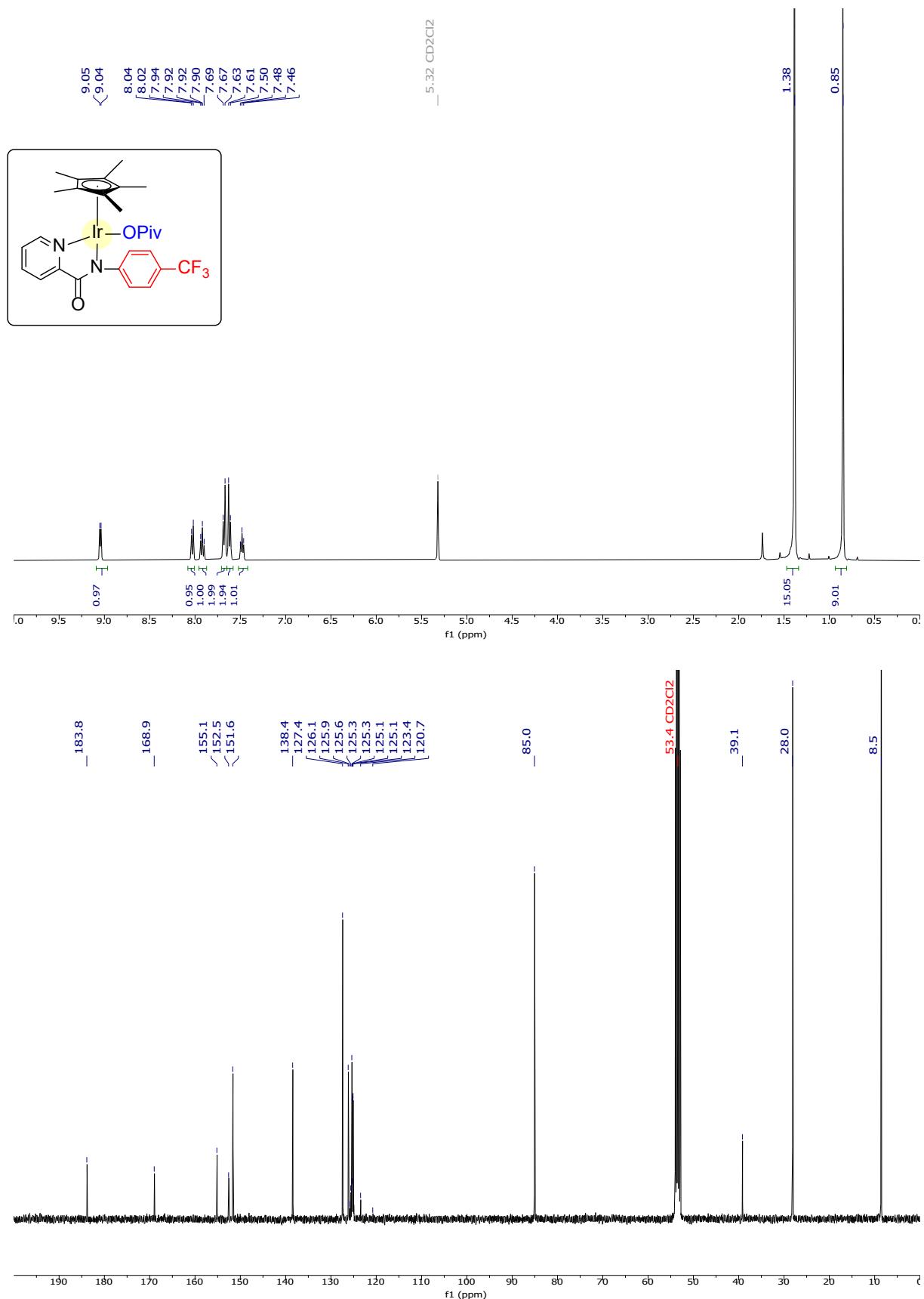


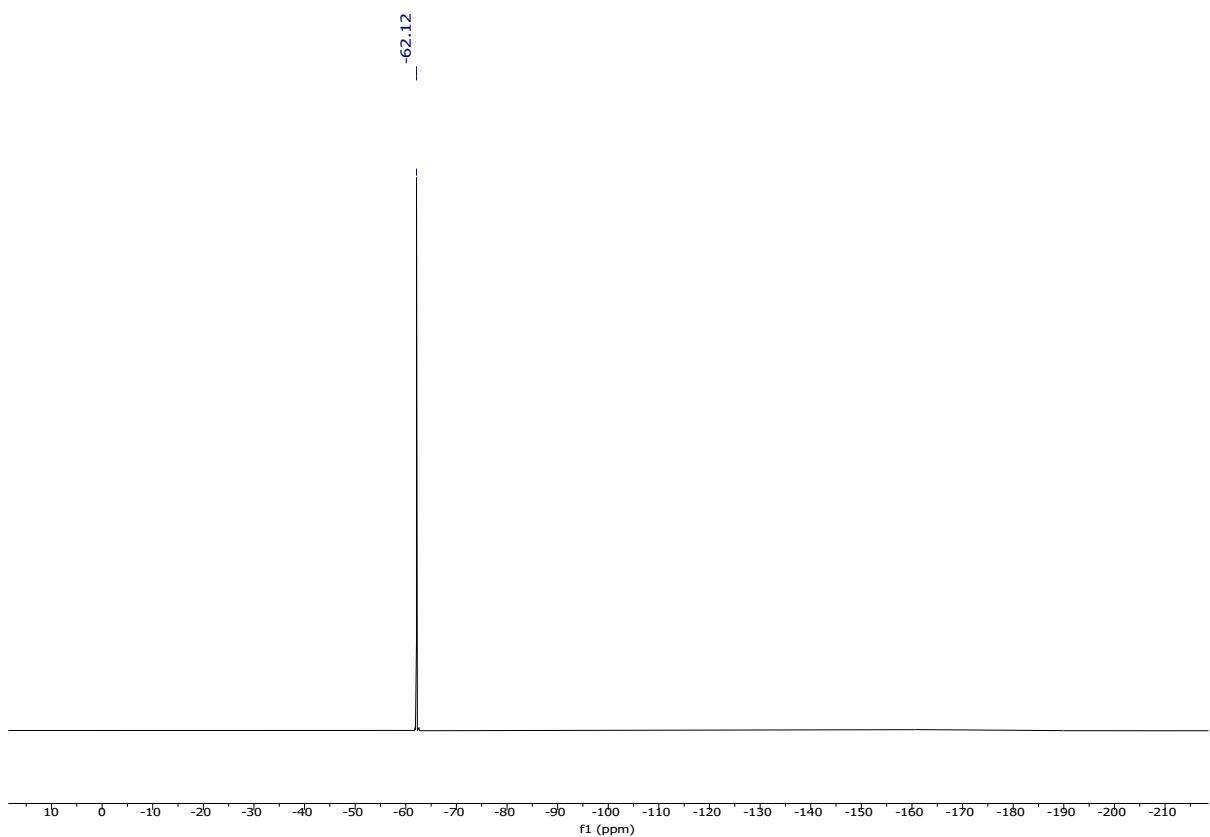
Ir4f



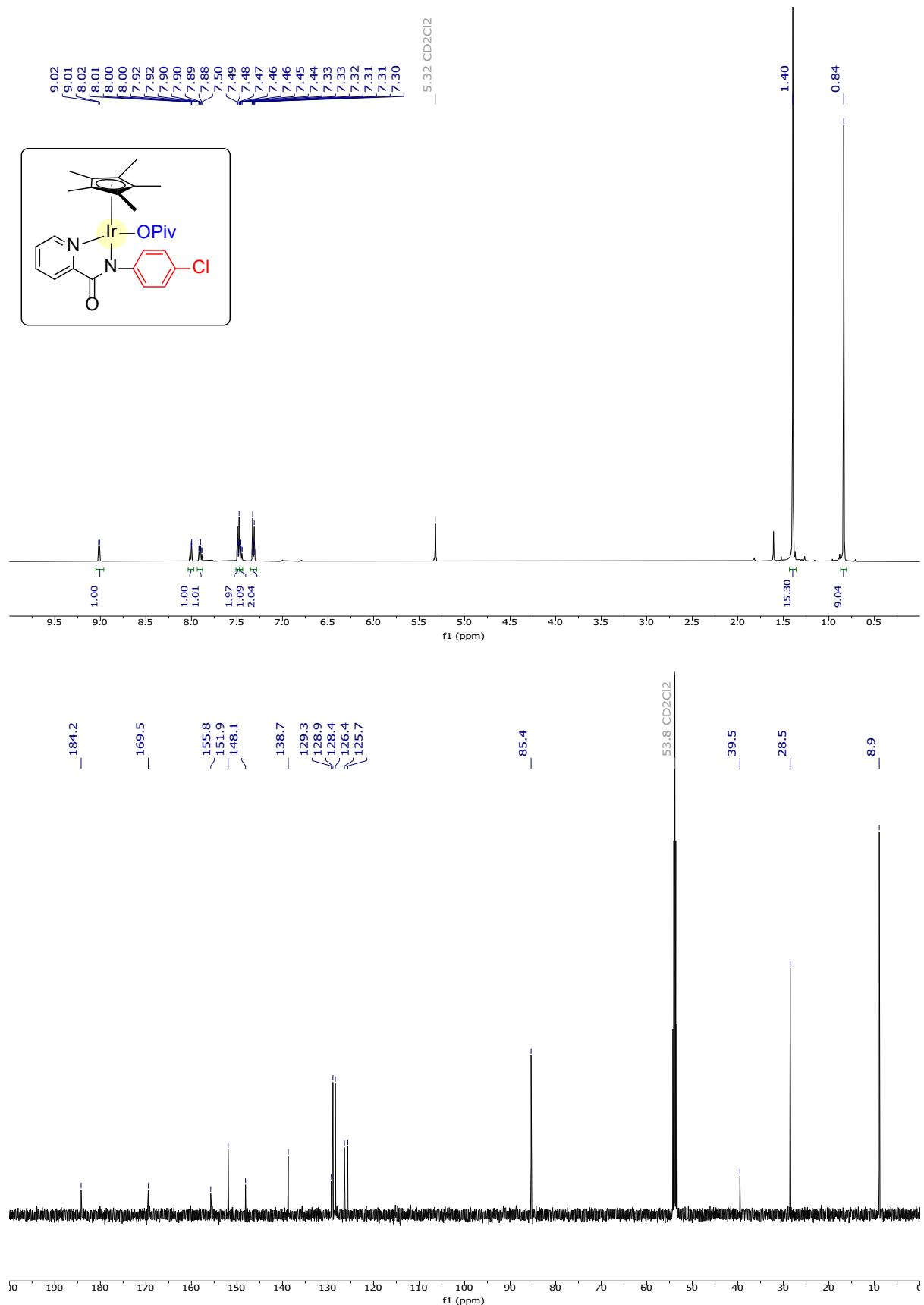


Ir4g

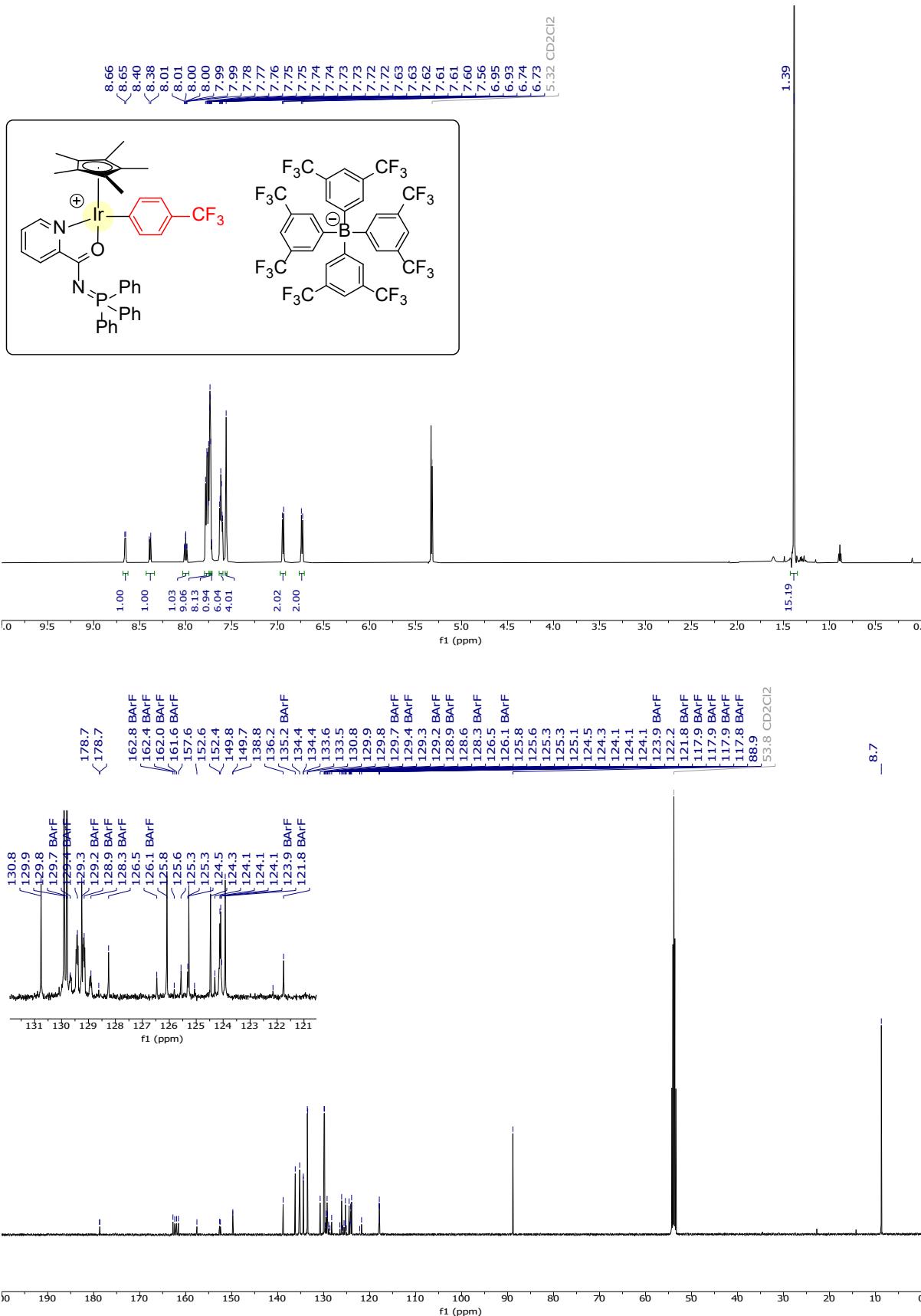


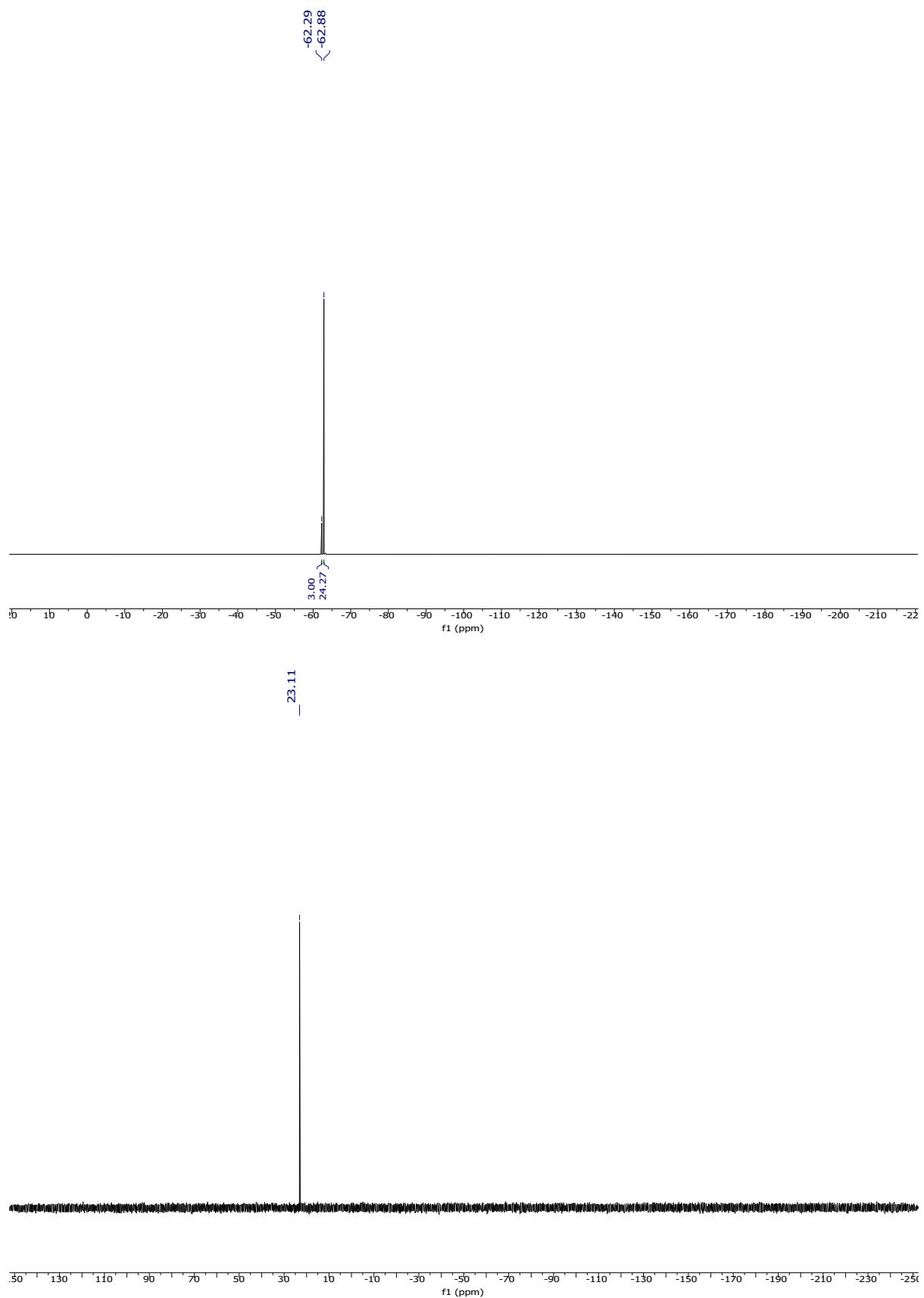


Ir4h



Ir6





9. References

- [1] H. Jung, J. Kweon, J.-M. Suh, M. H. Lim, D. Kim, S. Chang, *Science* **2023**, *381*, 525–532.
- [2] Y. Park, S. Chang, *Nat. Catal.* **2019**, *2*, 219–227.
- [3] Á. M. Martínez, J. Echavarren, I. Alonso, N. Rodríguez, R. Gómez Arrayás, J. C. Carretero, *Chem. Sci.* **2015**, *6*, 5802–5814.
- [4] J. Kim, K. Shin, S. Jin, D. Kim, S. Chang, *J. Am. Chem. Soc.* **2019**, *141*, 4137–4146.
- [5] A. Bucci, S. Dunn, G. Bellachioma, G. Menendez Rodriguez, C. Zuccaccia, C. Nervi, A. Macchioni, *ACS Catal.* **2017**, *7*, 7788–7796.
- [6] C. C. Le, M. K. Wismer, Z.-C. Shi, R. Zhang, D. V. Conway, G. Li, P. Vachal, I. W. Davies, D. W. C. MacMillan, *ACS Cent. Sci.* **2017**, *3*, 647–653.
- [7] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42–55.
- [8] M. J. Davies, *Res. Chem. Intermed.* **1993**, *19*, 669–679.
- [9] M. J. Davies, C. L. Hawkins, *Free Radic. Biol. Med.* **2004**, *36*, 1072–1086.
- [10] Y. Ji, D. A. DiRocco, C. M. Hong, M. K. Wismer, M. Reibarkh, *Org. Lett.* **2018**, *20*, 2156–2159.
- [11] C. Feldmeier, H. Bartling, E. Riedle, R. M. Gschwind, *J. Magn. Reson.* **2013**, *232*, 39–44.
- [12] K. L. Skubi, W. B. Swords, H. Hofstetter, T. P. Yoon, *ChemPhotoChem* **2020**, *4*, 685–690.
- [13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16, Revision C. 01*, Gaussian, Inc., Wallingford CT, **2019**.
- [14] R. G. Parr, Y. Weitao, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, **1994**.
- [15] K. R. Brereton, C. L. Pitman, T. R. Cundari, A. J. M. Miller, *Inorg. Chem.* **2016**, *55*, 12042–12051.
- [16] H. Jung, M. Hong, M. Marchini, M. Villa, P. S. Steinlandt, X. Huang, M. Hemming, E. Meggers, P. Ceroni, J. Park, M.-H. Baik, *Chemical Science* **2021**, *12*, 9673–9681.
- [17] Y. Park, L. Tian, S. Kim, T. P. Pabst, J. Kim, G. D. Scholes, P. J. Chirik, *JACS Au* **2022**, *2*, 407–418.
- [18] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B Condens. Matter* **1988**, *37*, 785–789.
- [19] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- [20] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [21] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270–283.
- [22] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284–298.
- [23] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310.
- [24] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724–728.

- [25] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222.
- [26] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- [27] M. M. Franel, W. J. Pietro, W. J. Hehre, J. S. Binkley, *J. Chem. Phys.* **1982**, *77*, 3654–3665.
- [28] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.* **1982**, *104*, 2797–2803.
- [29] C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1989**, *90*, 2154–2161.
- [30] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523–5527.
- [31] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123–141.
- [32] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–301.
- [33] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.
- [34] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- [35] G. W. Spitznagel, T. Clark, P. von Ragué Schleyer, W. J. Hehre, *J. Comput. Chem.* **1987**, *8*, 1109–1116.
- [36] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [37] J. Kim, D. Kim, S. Chang, *J. Am. Chem. Soc.* **2020**, *142*, 19052–19057.
- [38] E. Runge, E. K. U. Gross, *Phys. Rev. Lett.* **1984**, *52*, 997–1000.
- [39] G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834–4843.
- [40] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.