

## Electronic Supplementary Information

For

# Carbolong Chemistry: Nucleophilic Aromatic Substitution of a Triflate Functionalized Iridapentalene

Jinhua Li, Zhengyu Lu, Yuhui Hua, Dafa Chen\* and Haiping Xia\*

Shenzhen Grubbs Institute and Guangdong Provincial Key Laboratory of Catalysis, Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, People's Republic of China.

E-mail: chendf@sustech.edu.cn; xiahp@sustech.edu.cn

### Contents

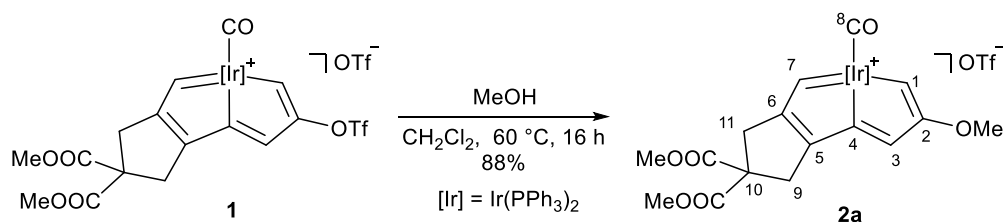
<b>1. General information .....</b>	<b>S2</b>
<b>2. Synthesis and characterization .....</b>	<b>S2</b>
<b>3. NMR spectra.....</b>	<b>S9</b>
<b>4. HRMS spectra .....</b>	<b>S22</b>
<b>5. Crystallographic details.....</b>	<b>S27</b>
<b>6. Theoretical calculations.....</b>	<b>S36</b>
<b>7. The UV-vis absorption spectra of iridacycles 1-5 .....</b>	<b>S37</b>
<b>8. References .....</b>	<b>S38</b>
<b>9. Cartesian coordinates .....</b>	<b>S39</b>

## 1. General information

All syntheses were performed under an N<sub>2</sub> atmosphere using standard Schlenk techniques, unless otherwise stated. Diethyl ether was distilled from sodium/benzophenone and dichloromethane from calcium hydride under N<sub>2</sub> prior to use. The starting material triflate irida-carbolong complex **1** was synthesized according to previously published procedures.<sup>[S1]</sup> Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on silica gel (200-300 mesh or 500-800 mesh) in air. NMR spectroscopic experiments were performed on Bruker AVIII-400 (<sup>1</sup>H, 400.1, <sup>13</sup>C, 100.6, <sup>31</sup>P, 162.0 MHz) spectrometer or a Bruker Ascend III 600 (<sup>1</sup>H, 600.1, <sup>13</sup>C, 150.9, <sup>31</sup>P, 242.9 MHz) spectrometer at room temperature. The <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts (δ) are reported relative to tetramethylsilane, and the <sup>31</sup>P NMR chemical shifts are relative to 85% H<sub>3</sub>PO<sub>4</sub>. The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). **Notes:** The resonances of the *ipso*-, *ortho*- and *meta*-Ph carbon atoms of the PPh<sub>3</sub> ligands in the <sup>13</sup>C NMR spectra are experimentally observed as apparent triplets because of virtual coupling to the two P atoms coordinated to iridium.<sup>[S2]</sup> High-resolution mass spectrometry (HRMS) experiments were performed on a Thermo Scientific Q Exactive instrument. Absorption spectra were recorded on an Agilent Cary 5000 UV-Vis spectrophotometer.

## 2. Synthesis and characterization

### Synthesis and characterization of irida-carbolong complex 2a:

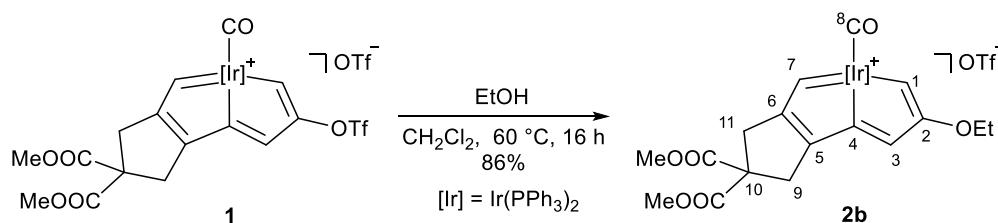


To a mixture of **1** (120 mg, 0.09 mmol) in dichloromethane (3 mL) was added MeOH (0.1 mL) in sealed tube. The reaction mixture was stirred at 60 °C for 16 h to give a red solution. Then the solution was evaporated under vacuum to a volume of approximately 1 mL. Addition of ethyl ether (10 mL) produced a red precipitate, which was collected by ethyl ether (2 × 10 mL) and dried under

vacuum to give **2a** as a red solid. Yield: 96 mg, 88%.

$^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 11.10 (s, 1H, C7H), 9.97 (s, 1H, C1H), 7.86 (d,  $J(\text{PH})$  = 3.1 Hz, 1H, C3H), 7.61-7.17 (30H, Ph), 3.72 (s, 6H,  $\text{COOCH}_3$ ), 3.33 (s, 3H,  $\text{OCH}_3$ ), 3.02 (br, 2H, C9H), 2.39 ppm (br, 2H, C11H);  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = -0.55 ppm (s,  $\text{IrPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ , plus  $^{13}\text{C}$ -dept 135,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC):  $\delta$  = 184.5 (s, C6), 183.1 (s,  $J(\text{PC})$  = 8.7 Hz, C7), 180.2 (s, C2), 174.1 (t,  $J(\text{PC})$  = 8.6 Hz, C8), 173.7 (br, C5), 172.9 (t,  $J(\text{PC})$  = 5.4 Hz, C4), 171.6 (s,  $\text{COOMe}$ ), 157.9 (t,  $J(\text{PC})$  = 10.6 Hz, C1), 151.1 (s, C3), 134.6-126.9 (Ph), 126.9 (q,  $J(\text{FC})$  = 60.1 Hz,  $J(\text{FC})$  = 46.1 Hz,  $\text{SO}_3\text{CF}_3$ ), 64.9 (s, C10), 56.4 (s,  $\text{OCH}_3$ ), 53.5 (s,  $\text{COOCH}_3$ ), 38.8 (s, C11), 38.2 ppm (s, C9); HRMS (ESI):  $m/z$  calcd for  $[\text{C}_{52}\text{H}_{46}\text{IrO}_6\text{P}_2]^+$ , 1021.2393,  $[\text{C}_{52}\text{H}_{46}\text{IrO}_6\text{P}_2]^+$ ; found, 1021.2394.

### Synthesis and characterization of irida-carbolong complex **2b**:

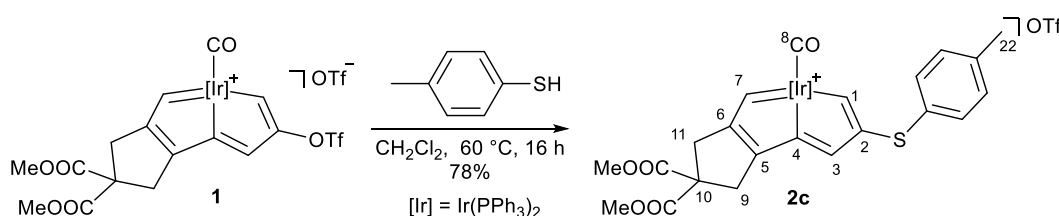


To a mixture of **1** (65 mg, 0.05 mmol) in dichloromethane (2 mL) was added EtOH (0.1 mL) in sealed tube. The reaction mixture was stirred at 60 °C for 16 h to give a red solution. Then the solution was evaporated under vacuum to a volume of approximately 1 mL. Addition of diethylether (10 mL) produced a red precipitate, which was collected by diethylether (2 × 10 mL) and dried under vacuum to give **2b** as a red solid. Yield: 45 mg, 86%.

$^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 10.98 (s, 1H, C7H), 9.94 (s, 1H, C1H), 7.78 (br, 1H, C3H), 7.55-7.14 (30H, Ph), 3.68 (s, 6H,  $\text{COOCH}_3$ ), 3.46 (q,  $J(\text{HH})$  = 6.9 Hz,  $J(\text{HH})$  = 6.6 Hz, 2H,  $\text{CH}_2\text{CH}_3$ ), 2.98 (br, 2H, C9H), 2.35 (br, 2H, C11H), 1.07 ppm (t,  $J(\text{HH})$  = 6.2 Hz, 3H,  $\text{CH}_2\text{CH}_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = -0.51 ppm (s,  $\text{IrPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ , plus  $^{13}\text{C}$ -dept 135,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC):  $\delta$  = 184.2 (s, C6), 182.0 (s,  $J(\text{PC})$  = 8.9 Hz, C7), 179.9 (s, C2), 174.2 (t,  $J(\text{PC})$  = 10.6 Hz, C4), 173.5 (t,  $J(\text{PC})$  = 3.7 Hz, C5), 173.1 (t,  $J(\text{PC})$  = 5.2 Hz, C8), 171.6 (s,  $\text{COOMe}$ ), 159.2 (t,  $J(\text{PC})$  = 10.4 Hz, C1), 151.3 (s, C3), 134.6-126.8 (Ph), 121.1 (q,  $J(\text{FC})$  = 323 Hz,  $J(\text{FC})$  = 320 Hz,  $\text{SO}_3\text{CF}_3$ ), 64.9 (s, C10), 64.8 (s,  $\text{CH}_2\text{CH}_3$ ), 56.4 (s,  $\text{OCH}_3$ ), 53.5 (s,

COOCH<sub>3</sub>), 38.7 (s, C11), 38.2 (s, C9), 30.0 ppm (s, CH<sub>2</sub>CH<sub>3</sub>); HRMS (ESI): m/z calcd for [C<sub>53</sub>H<sub>48</sub>IrO<sub>6</sub>P<sub>2</sub>]<sup>+</sup>, 1035.2550, [C<sub>53</sub>H<sub>48</sub>IrO<sub>6</sub>P<sub>2</sub>]<sup>+</sup>; found, 1035.2532.

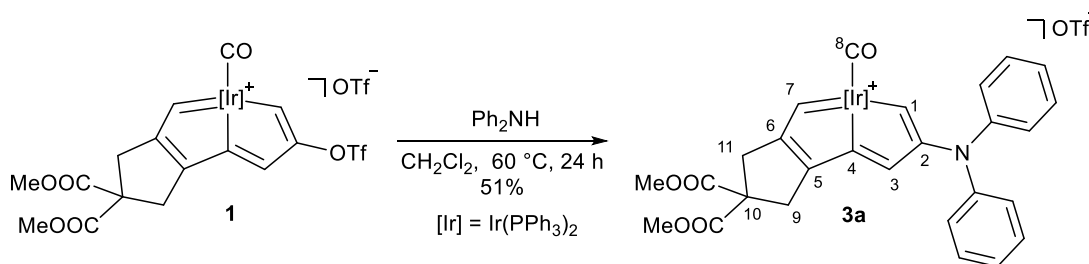
### Synthesis and characterization of irida-carbolong complex **2c**:



To a mixture of **1** (300 mg, 0.23 mmol) and *p*-toluenethiol (145 mg, 1.15 mmol) in sealed tube was added dichloromethane (8 mL). The reaction mixture was stirred at 60 °C for 16 h to give a violet solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography (SiO<sub>2</sub>, 200-300 mesh, elute: dichloromethane/Acetone = 15/1) to give **2c** as a violet solid, which was washed by hexane (2 × 10 mL). Yield: 230 mg, 78%.

<sup>1</sup>H NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 11.19 (s, 1H, C7H), 10.36 (s, 1H, C1H), 7.75 (br, 1H, C3H), 7.75-6.82 (34H, Ph), 3.69 (s, 3H, COOCH<sub>3</sub>), 3.68 (s, 3H, COOCH<sub>3</sub>), 3.03 (br, 2H, C9H), 2.49 (br, 3H, C22H), 2.27 ppm (br, 2H, C11H); <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -0.76 ppm (s, IrPPh<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, plus <sup>13</sup>C-dept 135, <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>1</sup>H-<sup>13</sup>C HMBC): δ = 190.5 (t, *J*(PC) = 9.2 Hz, C7), 185.9 (s, C6), 180.4 (t, *J*(PC) = 10.1 Hz, C1), 177.8 (t, *J*(PC) = 5.2 Hz, C8), 175.4 (br, C5), 173.7 (t, *J*(PC) = 9.2 Hz, C4), 171.5 (s, COOMe), 164.1 (s, C2), 160.8 (br, C3), 140.3-126.9 (Ph), 121.4 (q, *J*(FC) = 319.4 Hz, *J*(FC) = 323.6 Hz, CF<sub>3</sub>SO<sub>3</sub>), 64.6 (s, C10), 53.5 (s, COOCH<sub>3</sub>), 38.7 (s, C9), 38.3 (s, C11), 21.5 ppm (s, C22); HRMS (ESI): m/z calcd for [C<sub>58</sub>H<sub>50</sub>IrSO<sub>5</sub>P<sub>2</sub>]<sup>+</sup>, 1113.2478, [C<sub>58</sub>H<sub>50</sub>IrSO<sub>5</sub>P<sub>2</sub>]<sup>+</sup>; found, 1113.2471.

### Synthesis and characterization of irida-carbolong complex **3a**:

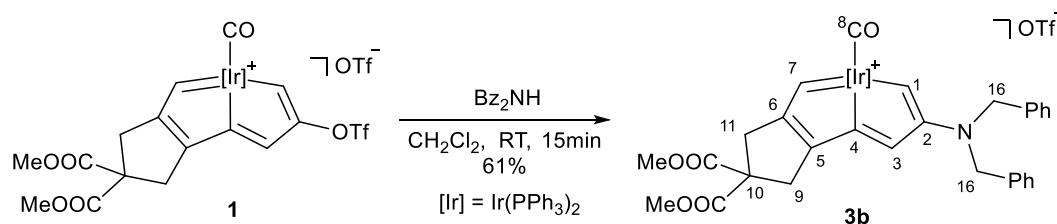


To a mixture of **1** (210 mg, 0.16 mmol) and diphenylamine (135 mg, 0.80 mmol) in sealed tube

was added dichloromethane (8 mL). The reaction mixture was stirred at 60 °C for 24 h to give a green solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography (SiO<sub>2</sub>, 500-800 mesh, elute: dichloromethane/Acetone = 15/1) to give **3a** as blue solid. Yield: 108 mg, 51%.

<sup>1</sup>H NMR (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 10.62 (s, 1H, C7H), 10.24 (s, 1H, C1H), 8.11 (d, *J*(PH) = 3.42 Hz, 1H, C3H), 7.55-6.41 (40H, Ph), 3.68 (s, 6H, COOCH<sub>3</sub>), 2.89 (br, 2H, C9H), 2.29 ppm (br, 2H, C11H); <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -2.27 ppm (s, IrPPh<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, plus <sup>13</sup>C-dept 135, <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>1</sup>H-<sup>13</sup>C HMBC): δ = 181.9 (s, C6), 176.9 (t, *J*(PC) = 9.7 Hz, C7), 174.4 (t, *J*(PC) = 10.2 Hz, C5), 174.2 (t, *J*(PC) = 3.6 Hz, C4), 173.7 (t, *J*(PC) = 5.5 Hz, C8), 172.1 (t, *J*(PC) = 2.3 Hz, C2), 171.6 (s, COOMe), 169.4 (t, *J*(PC) = 9.9 Hz, C1), 151.7 (br, C3), 146.1-125.9 (Ph), 119.6 (q, *J*(FC) = 321.3 Hz, CF<sub>3</sub>SO<sub>3</sub>), 64.6 (s, C10), 53.4 (s, COOCH<sub>3</sub>), 38.6 (s, C9), 38.1 ppm (s, C11); HRMS (ESI): *m/z* calcd for [C<sub>63</sub>H<sub>53</sub>IrNO<sub>5</sub>P<sub>2</sub>]<sup>+</sup>, 1158.3023, [C<sub>63</sub>H<sub>53</sub>IrNO<sub>5</sub>P<sub>2</sub>]<sup>+</sup>; found, 1158.3007.

### Synthesis and characterization of irida-carbolong complex **3b**:

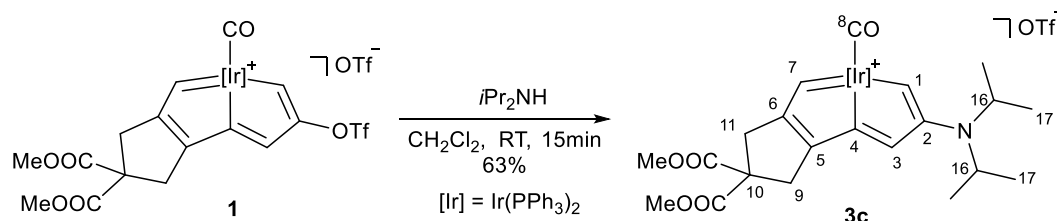


To a dichloromethane (8 mL) solution of **1** (200 mg, 0.16 mmol) was added dibenzylamine (150 mg, 0.80 mmol). The reaction mixture was stirred at RT for 15 min to give a blue solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography (SiO<sub>2</sub>, 500-800 mesh, elute: dichloromethane/Acetone = 18/1) to give **3b** as a blue solid. Yield: 126 mg, 61%.

<sup>1</sup>H NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 10.41 (s, 1H, C7H), 10.08 (s, 1H, C1H), 7.60 (br, 1H, C3H), 7.49-6.99 (40H, Ph), 4.25 (s, 4H, C16H), 3.62 (s, 6H, COOCH<sub>3</sub>), 2.79 (br, 2H, C11H), 2.02 ppm (br, 2H, C11H); <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -1.27 ppm (s, IrPPh<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, plus <sup>13</sup>C-dept 135, <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>1</sup>H-<sup>13</sup>C HMBC): δ = 177.9 (s, C6), 174.9 (t, *J*(PC) = 5.6 Hz, C8), 174.8 (t, *J*(PC) = 9.4 Hz, C4), 173.6 (br, C5), 173.4 (br, C2), 171.7 (s, COOMe),

170.5 (t,  $J(\text{PC}) = 8.8$  Hz, C7), 165.7 (t,  $J(\text{PC}) = 10.8$  Hz, C1), 146.7 (s, C3), 140.6-126.6 (Ph), 121.43 (q,  $J(\text{FC}) = 319.6$  Hz,  $\text{CF}_3\text{SO}_3$ ), 64.6 (s, C10), 56.9 (s, C16), 53.4 (s,  $\text{COOCH}_3$ ), 38.3 (s, C11), 38.0 ppm (s, C9); HRMS (ESI):  $m/z$  calcd for  $[\text{C}_{65}\text{H}_{57}\text{IrNO}_5\text{P}_2]^+$ , 1186.3336,  $[\text{C}_{65}\text{H}_{57}\text{IrNO}_5\text{P}_2]^+$ ; found, 1186.3341.

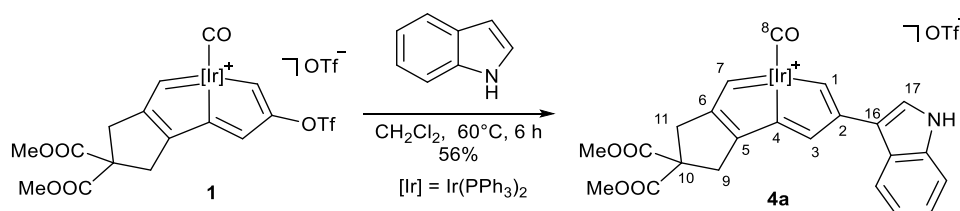
### Synthesis and characterization of irida-carbolong complex 3c:



To a dichloromethane (6 mL) solution of **1** (200 mg, 0.16 mmol) was added diisopropylamine (112  $\mu\text{L}$ , 0.80 mmol). The reaction was stirred at RT for 15 min to give a green solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography ( $\text{SiO}_2$ , 500-800 mesh, elute: dichloromethane/Acetone = 15/1) to give **3c** as a green solid. Yield: 121 mg, 63%.

$^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 10.23$  (s, 1H, C1H), 10.14 (s, 1H, C7H), 7.76 (br, 1H, C3H), 7.47-7.12 (30H, Ph), 3.67 (s, 6H,  $\text{COOCH}_3$ ), 3.44 (m, 2H, C16H), 2.93 (br, 2H, C11H), 2.23 (br, 2H, C9H), 0.89 ppm (d, 12H,  $J(\text{HH}) = 6.77$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = -1.22$  ppm (s,  $\text{IrPPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ , plus  $^{13}\text{C}$ -dept 135,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC):  $\delta = 176.5$  (s, C6), 175.7 (t,  $J(\text{PC}) = 8.9$  Hz, C8), 174.7 (t,  $J(\text{PC}) = 5.4$  Hz, C4), 172.9 (s, C2), 172.5 (t,  $J(\text{PC}) = 3.4$  Hz, C5), 171.9 (s,  $\text{COOMe}$ ), 167.9 (t,  $J(\text{PC}) = 11.6$  Hz, C1), 165.8 (t,  $J(\text{PC}) = 9.2$  Hz, C7), 148.3 (br, C3), 134.3-127.49 (Ph), 121.5 (q,  $J(\text{FC}) = 319.9$  Hz,  $\text{CF}_3\text{SO}_3$ ), 64.8 (s, C10), 53.3 (s,  $\text{COOCH}_3$ ), 48.0 (s, C16), 38.3 (s, C11), 37.8 (s, C9), 20.90 ppm (s, C17); HRMS (ESI):  $m/z$  calcd for  $[\text{C}_{57}\text{H}_{57}\text{IrNO}_5\text{P}_2]^+$ , 1090.3336,  $[\text{C}_{57}\text{H}_{57}\text{IrNO}_5\text{P}_2]^+$ ; found, 1090.3341.

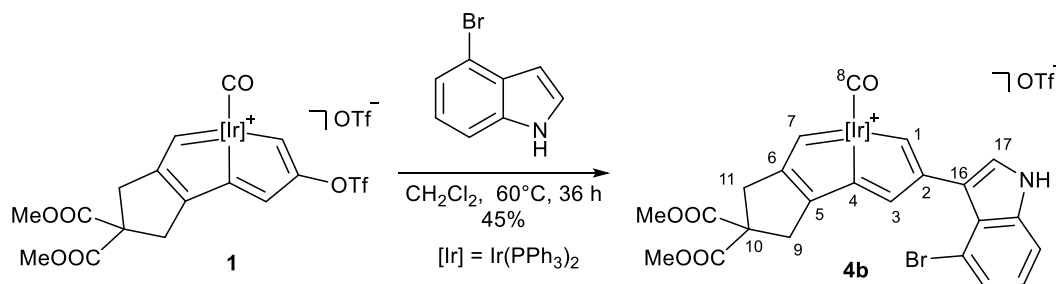
### Synthesis and characterization of irida-carbolong complex 4a:



To a mixture of **1** (300 mg, 0.23 mmol) and indole (136 mg, 1.15 mmol) in sealed tube was added dichloromethane (10 mL). The reaction mixture was stirred at 60 °C for 6 h to give a violet solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography (SiO<sub>2</sub>, 500-800 mesh, elute: dichloromethane/Acetone = 15/1) to give **4a** as a blue solid. Yield: 160 mg, 56%.

<sup>1</sup>H NMR (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 11.66 (s, 1H, C1H), 10.84 (s, 1H, C7H), 9.71(br, 1H, NH), 8.39 (d, *J*(PH) = 2.53 Hz, 1H, C3H), 7.52-6.85 (34H, Ph), 6.70 (d, *J*(HH) = 2.48 Hz, 1H, C17H), 3.71 (s, 6H, COOCH<sub>3</sub>), 3.05 (br, 2H, C9H), 2.41 ppm (br, 2H, C11H); <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -0.29 ppm (s, IrPPh<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, plus <sup>13</sup>C-dept 135, <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>1</sup>H-<sup>13</sup>C HMBC): δ = 190.4 (t, *J*(PC) = 11.4 Hz, C1), 185.1 (s, C6), 182.4 (t, *J*(PC) = 9.0 Hz, C7), 179.2 (t, *J*(PC) = 6.1 Hz, C8), 174.9 (t, *J*(PC) = 10.0 Hz, C5), 174.3 (t, *J*(PC) = 3.0 Hz, C4), 171.7 (s, COOMe), 167.7 (t, *J*(PC) = 3.8 Hz, C2), 163.0 (br, C3), 136.8-127.3 (Ph), 125.3 (d, *J*(PC) = 4.5 Hz, C17), 122.9-115.5 (Ph and CF<sub>3</sub>SO<sub>3</sub>), 112.5 (C16), 64.7 (s, C10), 53.3 (s, COOCH<sub>3</sub>), 38.6 (s, C11), 38.5 ppm (s, C9); HRMS (ESI): *m/z* calcd for [C<sub>59</sub>H<sub>49</sub>IrNO<sub>5</sub>P<sub>2</sub>]<sup>+</sup>, 1106.2710, [C<sub>59</sub>H<sub>49</sub>IrNO<sub>5</sub>P<sub>2</sub>]<sup>+</sup>; found, 1106.2691.

#### Synthesis and characterization of irida-carbolong complex **4b**:

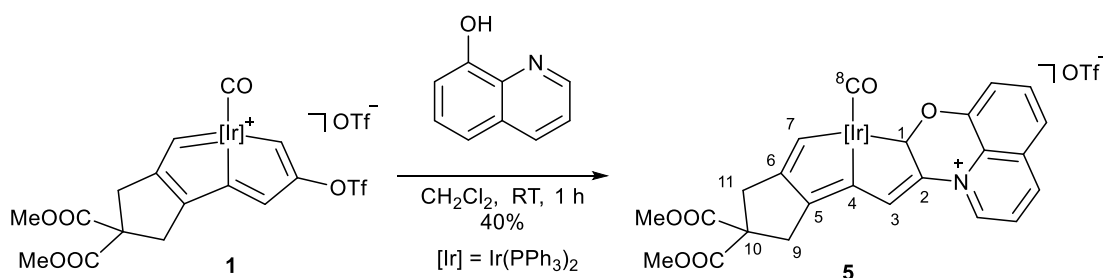


To a solution of **1** (200 mg, 0.16 mmol) in dichloromethane (6 mL) in sealed tube was added 4-bromo-1H-indole (100 μL, 0.80 mmol). The reaction mixture was stirred at 60 °C for 36 h to give a violet solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography (SiO<sub>2</sub>, 500-800 mesh, elute: dichloromethane/Acetone = 15/1) to give **4b** as a violet solid. Yield: 93 mg, 45%.

<sup>1</sup>H NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 11.43 (s, 1H, C1H), 10.86 (s, 1H, C7H), 10.30 (br, 1H, NH), 8.84 (s, 1H, C3H), 7.47-7.16 (33H, Ph), 6.14 (s, 1H, C17H), 3.71 (s, 6H, COOCH<sub>3</sub>), 2.95 (br, 2H, C9H), 2.54 ppm (br, 2H, C11H); <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -1.07 ppm (s, IrPPh<sub>3</sub>);

$^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ , plus  $^{13}\text{C}$ -dept 135,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC):  $\delta$  = 194.9 (t,  $J(\text{PC})$  = 8.9 Hz, C1), 186.2 (s, C6), 182.1 (t,  $J(\text{PC})$  = 10.4 Hz, C7), 175.3 (t,  $J(\text{PC})$  = 5.3 Hz, C8), 174.9 (t,  $J(\text{PC})$  = 3.1 Hz, C5), 174.8 (t,  $J(\text{PC})$  = 10.5 Hz, C4), 171.5 (s, COOMe), 167.9 (s, C3), 165.9 (s, C2), 138.6-122.4 (Ph and  $\text{CF}_3\text{SO}_3$  plus 129.1 (C17)), 116.6 (C16), 64.5 (s, C10), 53.5 (s,  $\text{COOCH}_3$ ), 38.9 (s, C11), 38.1 ppm (s, C9); HRMS (ESI):  $m/z$  calcd for  $[\text{C}_{59}\text{H}_{48}\text{BrIrNO}_5\text{P}_2]^+$ , 1184.1815,  $[\text{C}_{59}\text{H}_{48}\text{BrIrNO}_5\text{P}_2]^+$ ; found, 1184.1790.

### Synthesis and characterization of irida-carbolong complex **5**:



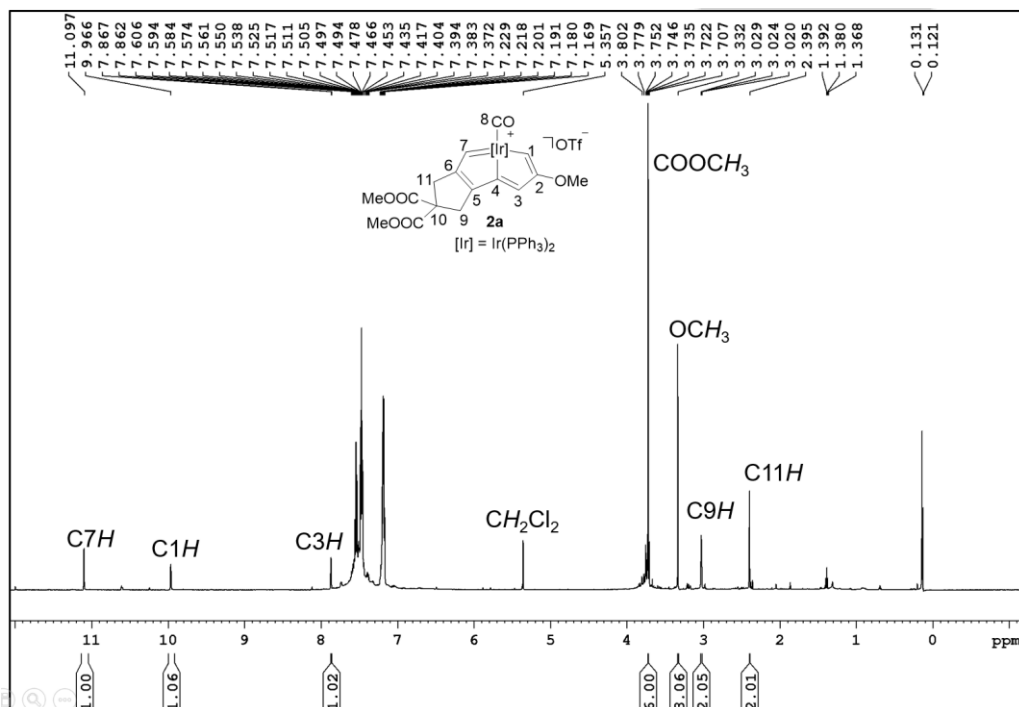
To a mixture of **1** (323 mg, 0.25 mmol) and 8-hydroxyquinoline (180 mg, 1.25 mmol) was added dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 1 h to give a violet solution. Then the solution was evaporated under vacuum to a volume of approximately 2 mL. The residue was purified by column chromatography ( $\text{SiO}_2$ , 200-300 mesh, elute: dichloromethane/Acetone = 10/1) to give **5** as a bluish green solid. Yield: 130 mg, 40%.

$^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.56 (d,  $J(\text{HH})$  = 8.6 Hz, 1H, quinoline-*H*), 8.26 (d,  $J(\text{HH})$  = 6.7 Hz, 1H, quinoline-*H*), 7.75 (t,  $J(\text{HH})$  = 7.7 Hz, 1H, quinoline-*H*), 7.65 (t,  $J(\text{HH})$  = 7.7 Hz, 1H, quinoline-*H*), 7.57 (t,  $J(\text{HH})$  = 7.7 Hz, 1H, quinoline-*H*), 7.52-7.19 (m, 30H, Ph*H*), 7.14 (t,  $J(\text{HH})$  = 7.7 Hz, 1H, quinoline-*H*), 6.99 (br, 1H, C7*H*), 6.59 (s, 1H, C3*H*), 5.98 (d,  $J(\text{PH})$  = 4.3 Hz, 1H, C1*H*), 3.66 (s, 3H,  $\text{COOCH}_3$ ), 3.64 (s, 3H,  $\text{COOCH}_3$ ), 2.83 (d,  $J(\text{HH})$  = 17.7 Hz, 1H, C9*H*), 2.40 (d,  $J(\text{HH})$  = 16.7 Hz, 1H, C11*H*), 2.23 (d,  $J(\text{HH})$  = 17.7 Hz, 1H, C9*H*), 2.83 (d,  $J(\text{HH})$  = 16.7 Hz, 1H, C11*H*);  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 5.04 ppm (d,  $J(\text{PP})$  = 321.37 Hz, Ir $\text{PPh}_3$ ), 2.93 ppm (d,  $J(\text{PP})$  = 321.37 Hz, Ir $\text{PPh}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ , plus  $^{13}\text{C}$ -dept 135,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and  $^1\text{H}$ - $^{13}\text{C}$  HMBC):  $\delta$  = 178.8 (t,  $J(\text{PC})$  = 9.9 Hz, C8), 172.5 (s, COOMe), 172.4 (s, COOMe), 163.7 (s, C6), 159.3 (s, C5), 150.9 (s, quinoline-*C*), 149.6 (t,  $J(\text{PC})$  = 9.4 Hz, C4), 145.3 (t,  $J(\text{PC})$  = 8.3 Hz, C7), 142.9 (s, quinoline-*C*), 139.6 (s, C2), 137.6-118.5 (m, quinoline-*C* and Ph and 134.8 (s, C3) and  $\text{CF}_3\text{SO}_3$ ), 66.5 (t,  $J(\text{PC})$  = 5.8 Hz, C1), 64.5 (s, C10), 53.0 (s,  $\text{COOCH}_3$ ), 52.9 (s,  $\text{COOCH}_3$ ), 37.8 (s,

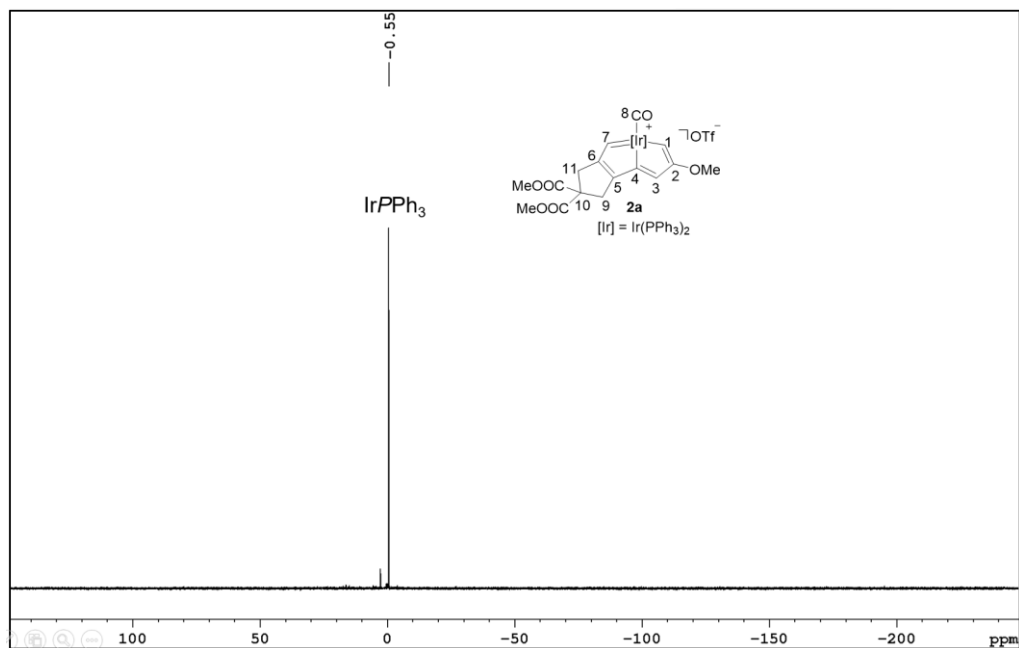


C11), 35.3 ppm (s, C9); HRMS (ESI):  $m/z$  calcd for  $[\text{C}_{60}\text{H}_{49}\text{IrNO}_6\text{P}_2]^+$ , 1134.2659,  $[\text{C}_{60}\text{H}_{49}\text{IrNO}_6\text{P}_2]^+$ ; found, 1134.2657.

### 3. NMR spectra



**Figure S1** The  $^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for complex **2a**.



**Figure S2** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for complex **2a**.

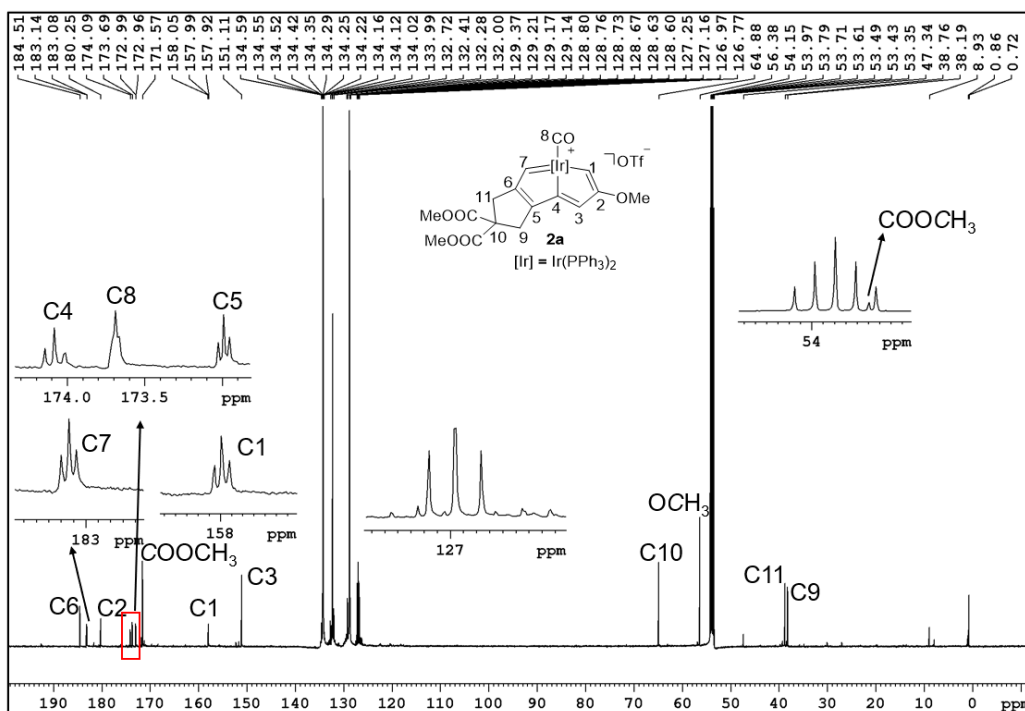


Figure S3 The  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for complex **2a**.

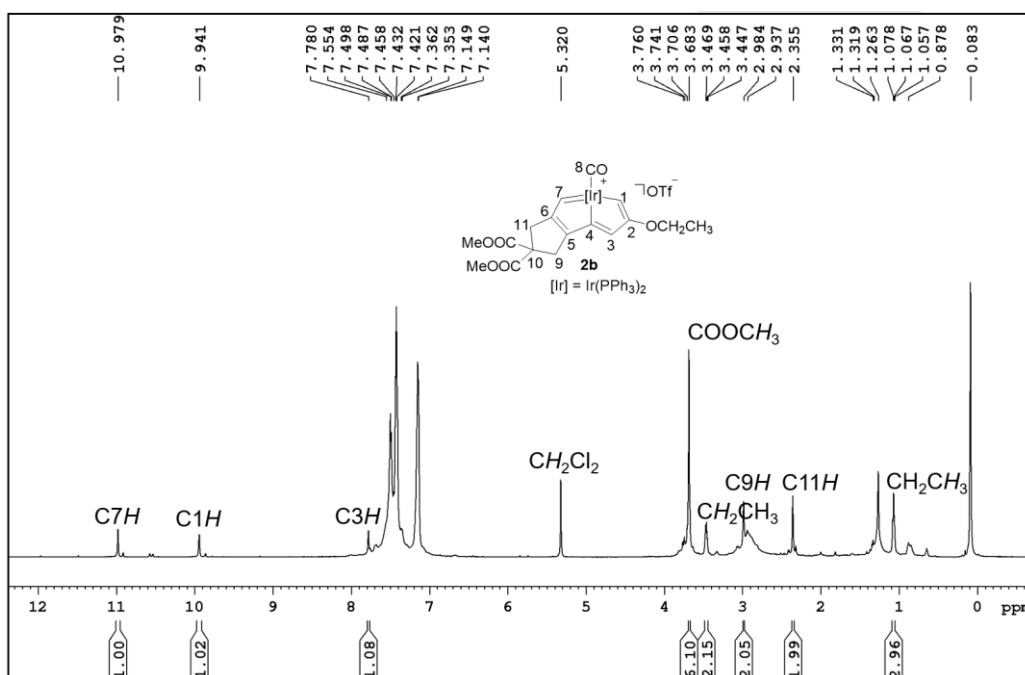
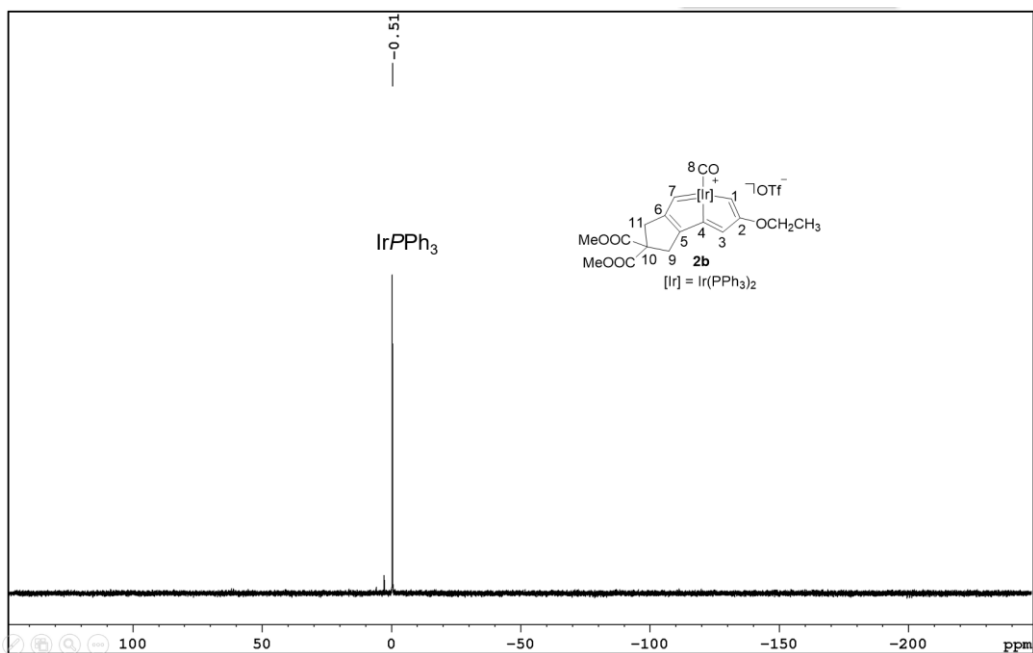
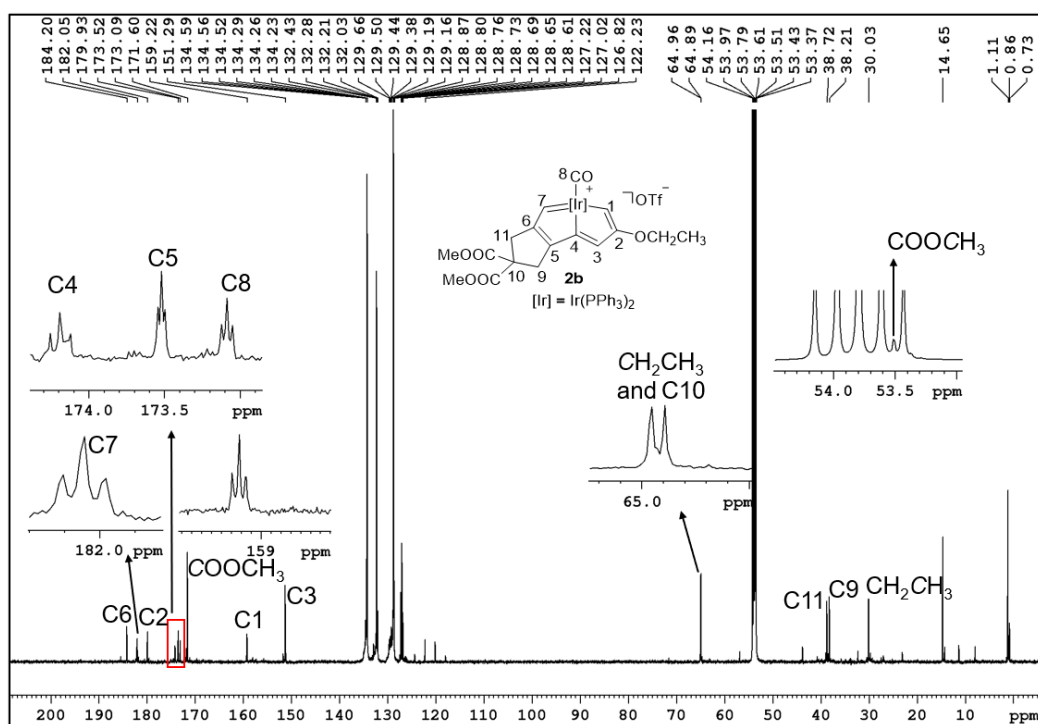


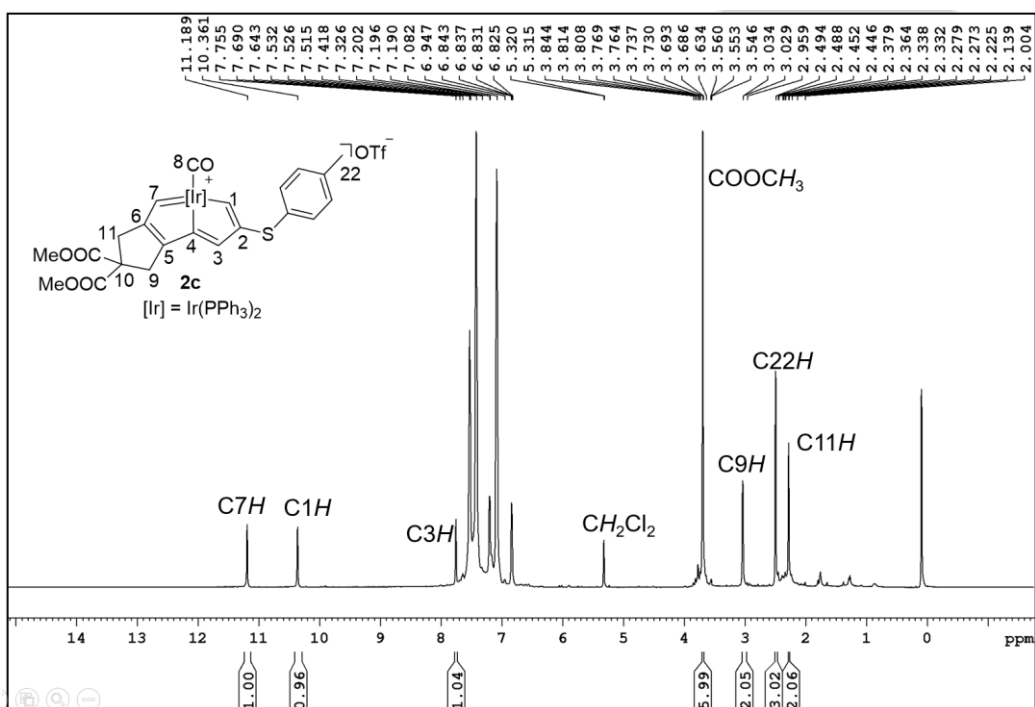
Figure S4 The  $^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **2b**.



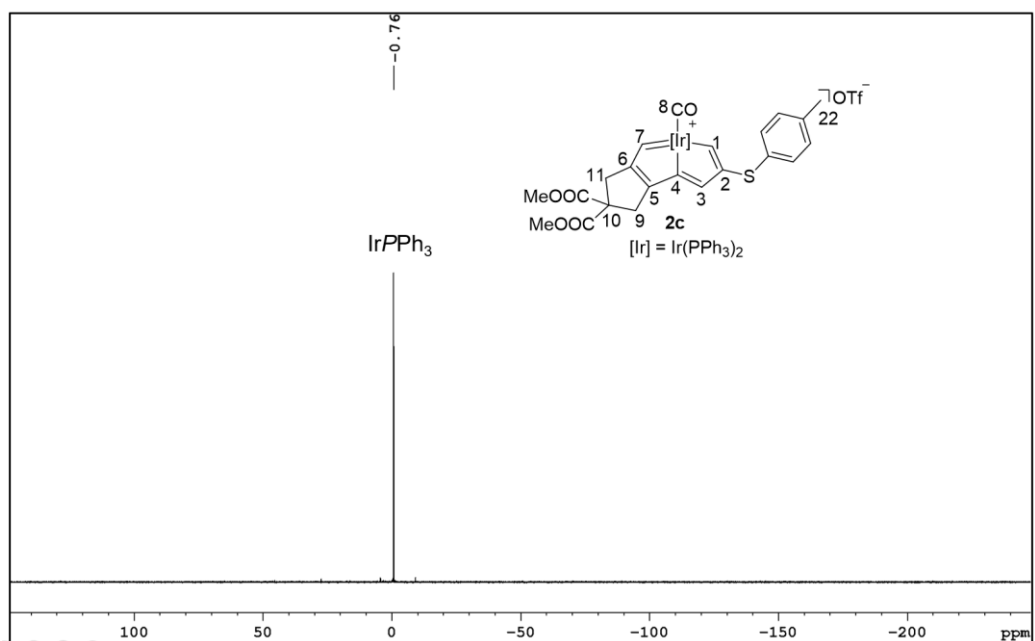
**Figure S5** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **2b**.



**Figure S6** The  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **2b**.

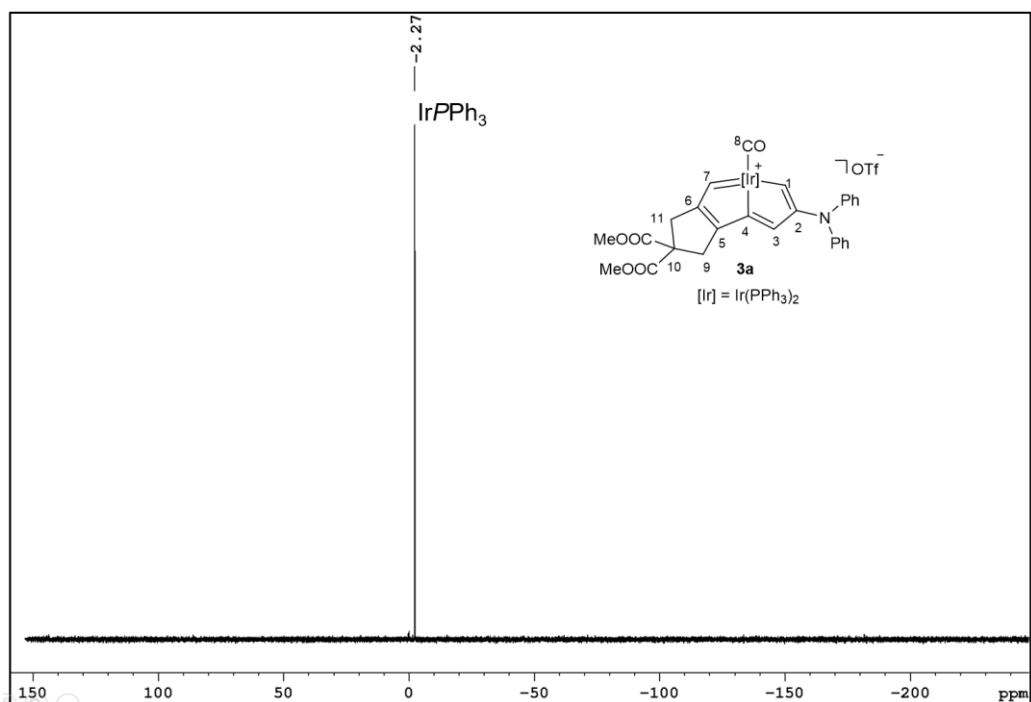


**Figure S7** The  $^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **2c**.

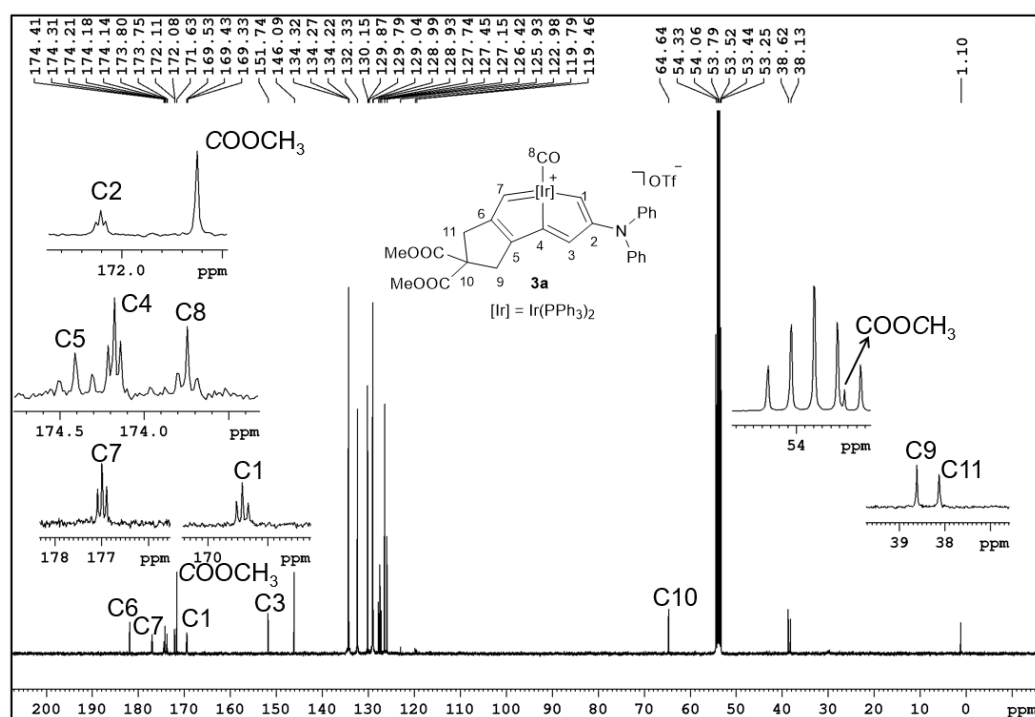


**Figure S8** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **2c**.

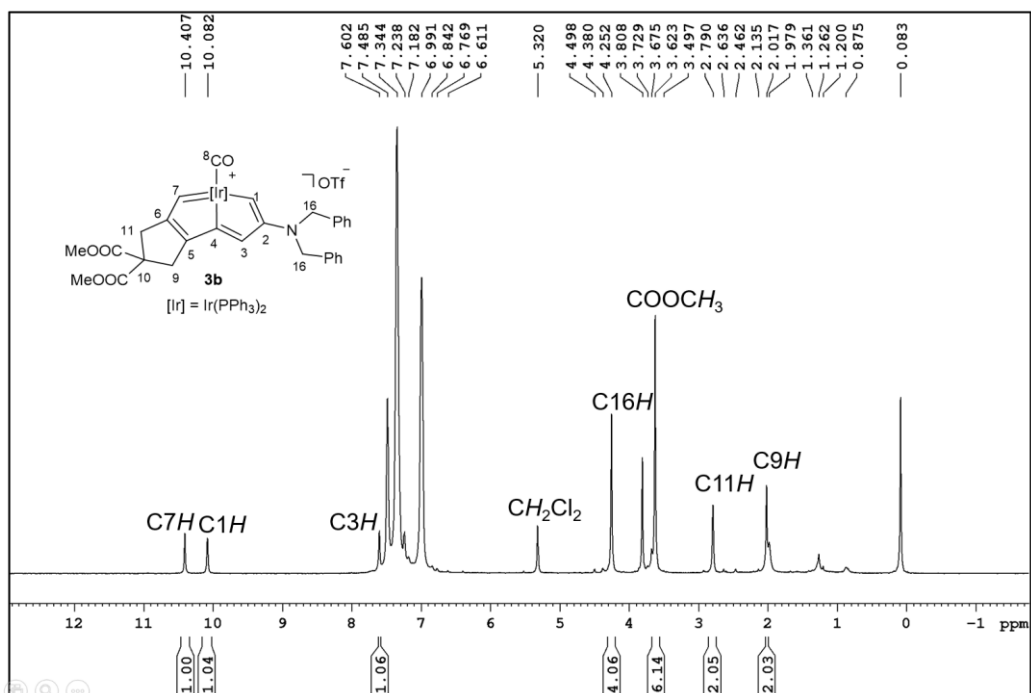




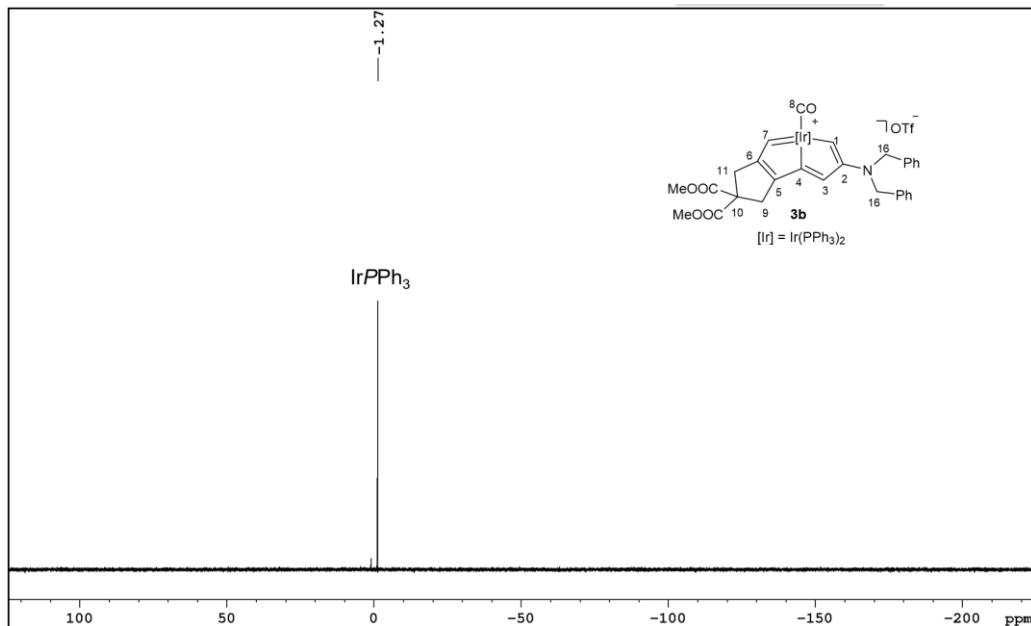
**Figure S11** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3a**.



**Figure S12** The  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3a**.



**Figure S13** The  $^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3b**.



**Figure S14** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3b**.

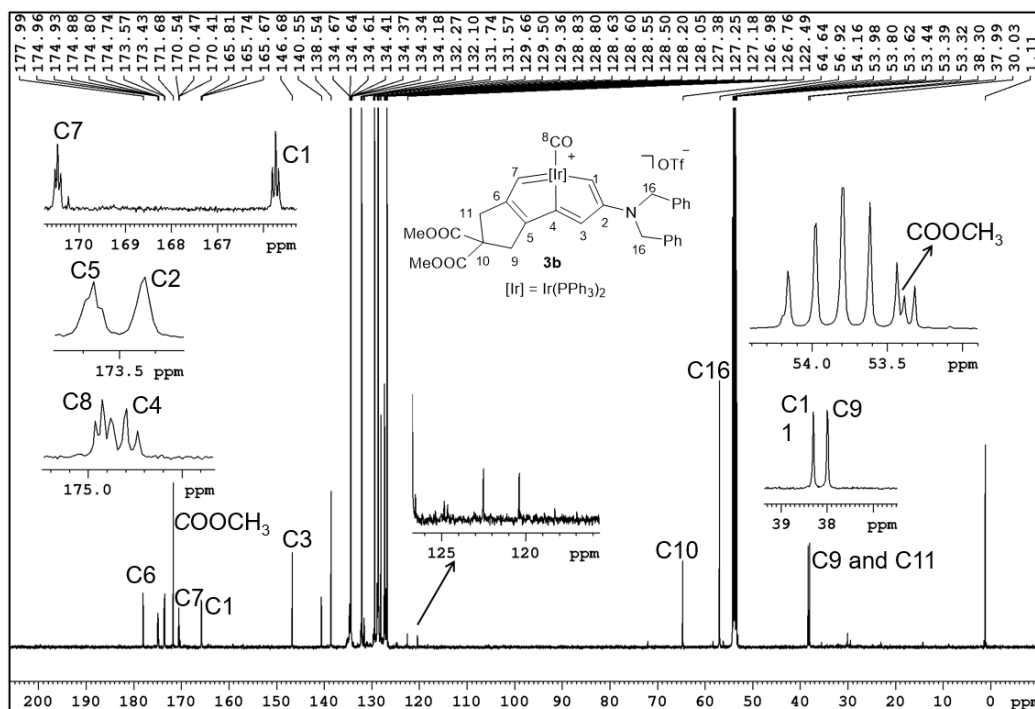


Figure S15 The  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3b**.

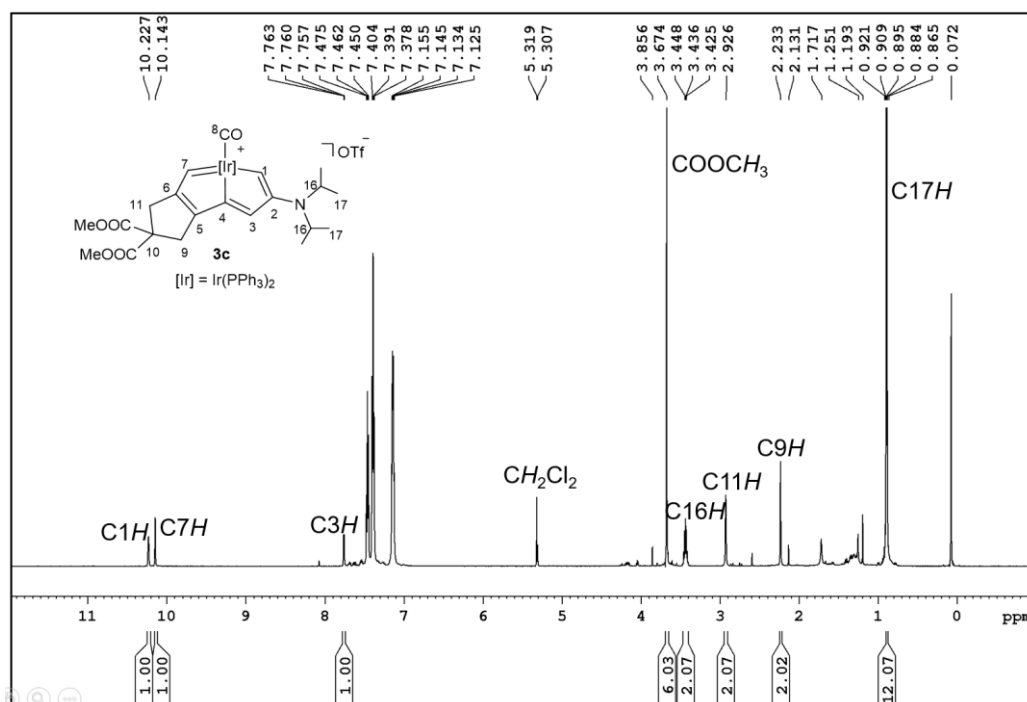
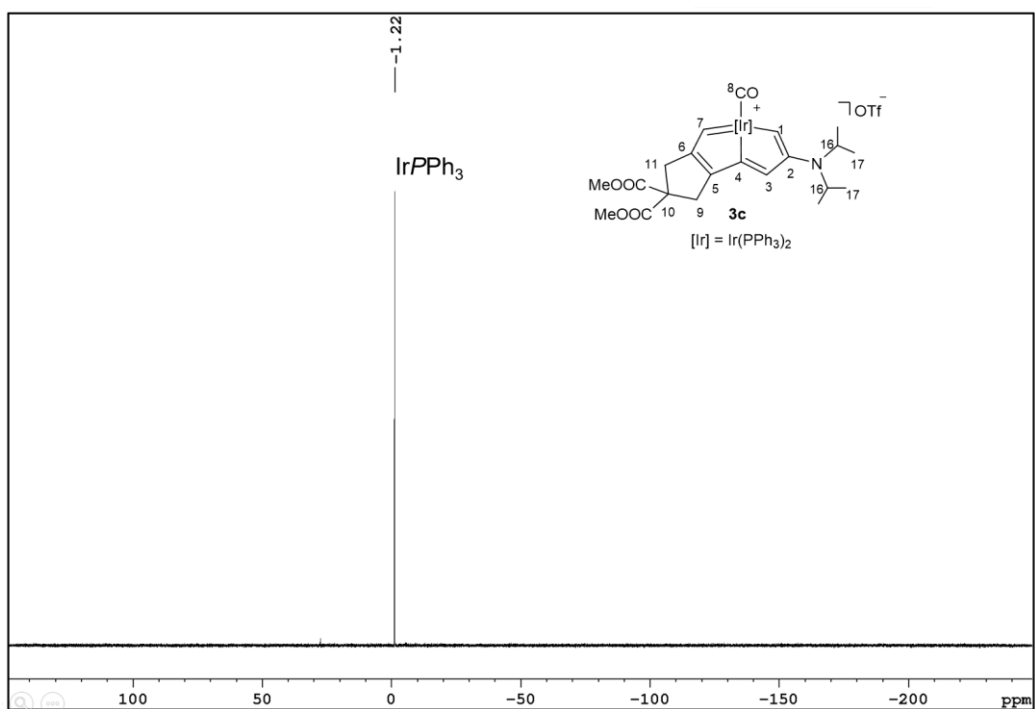
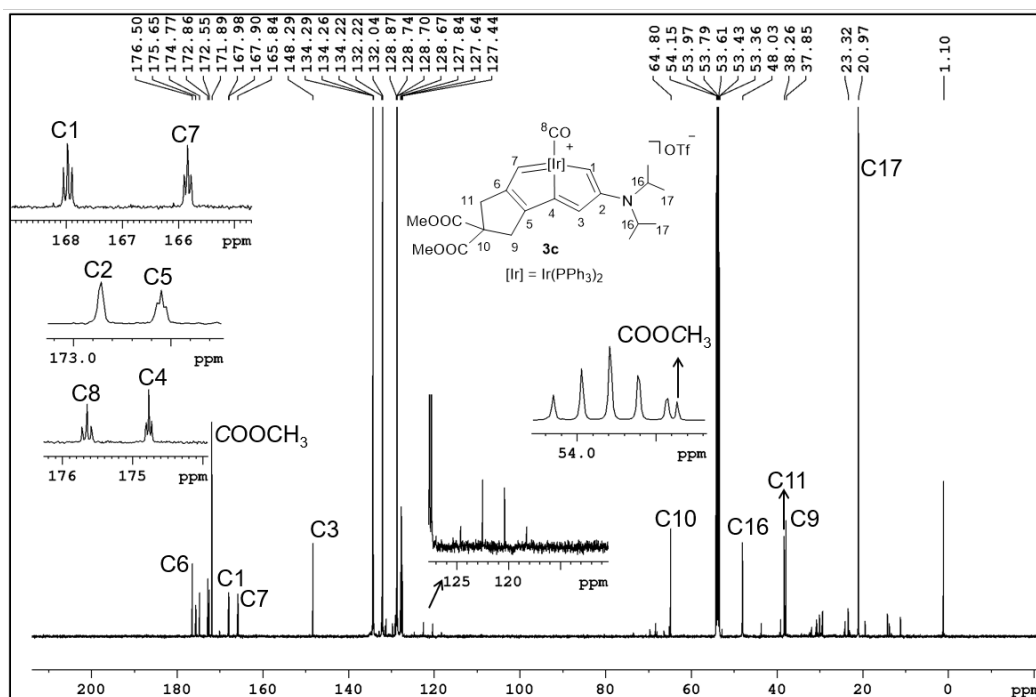


Figure S16 The  $^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3c**.

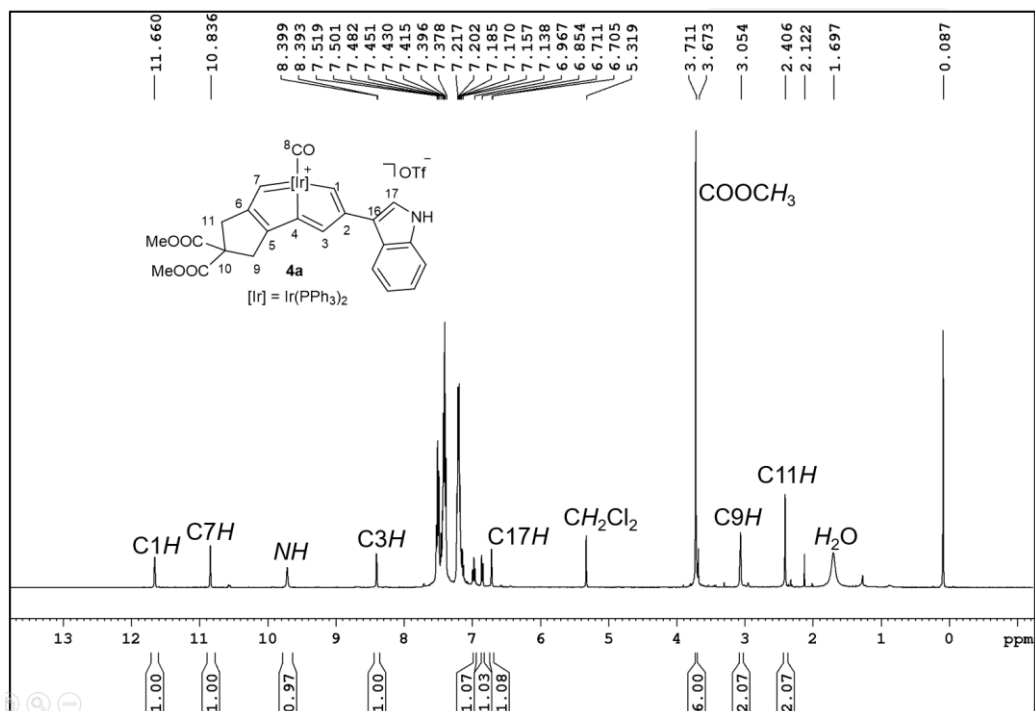




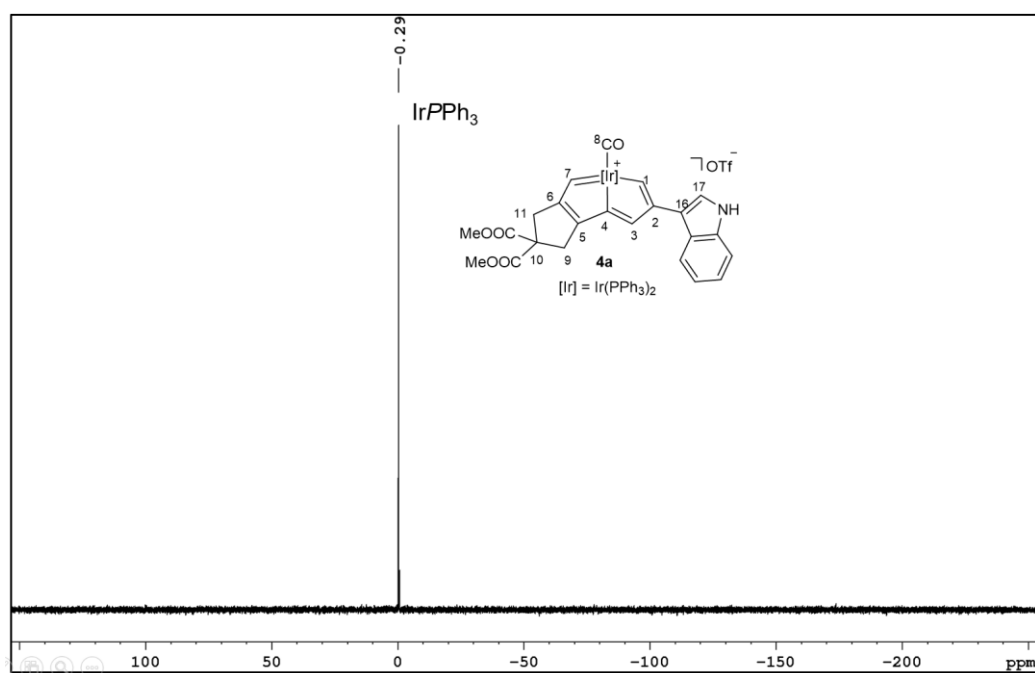
**Figure S17** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3c**.



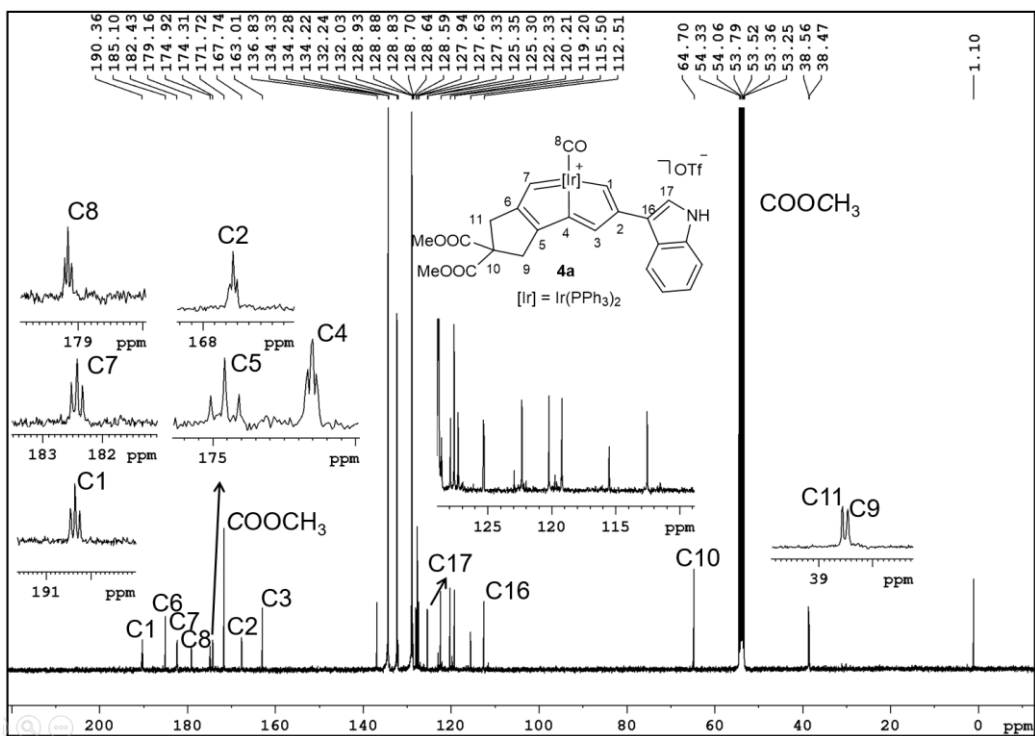
**Figure S18** The  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **3c**.



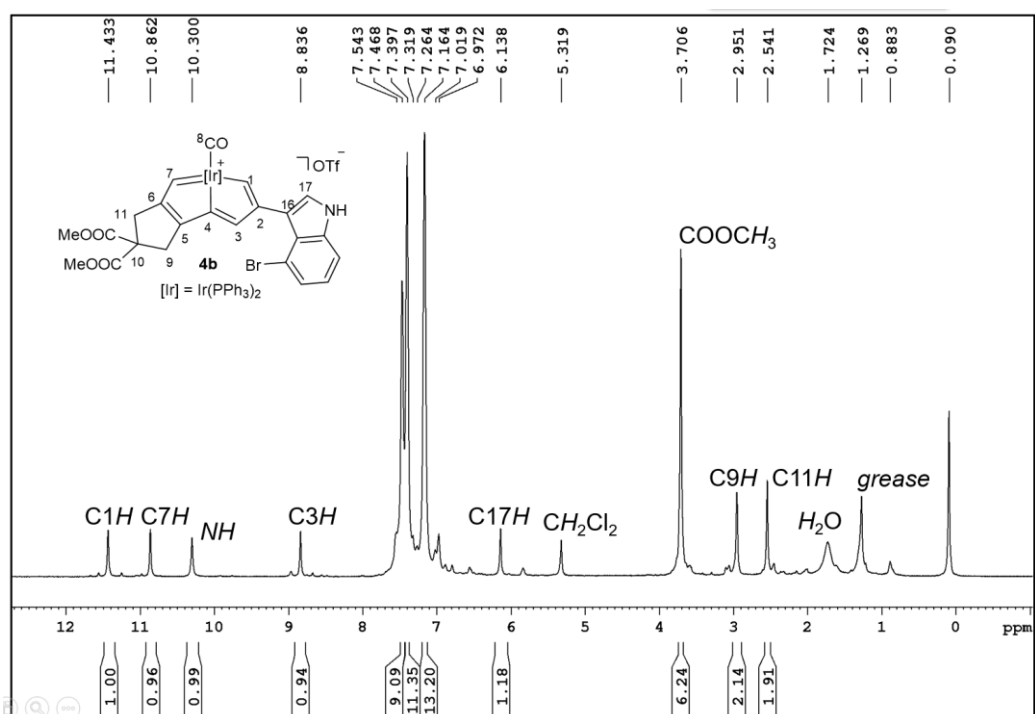
**Figure S19** The  $^1\text{H}$  NMR (400.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **4a**.



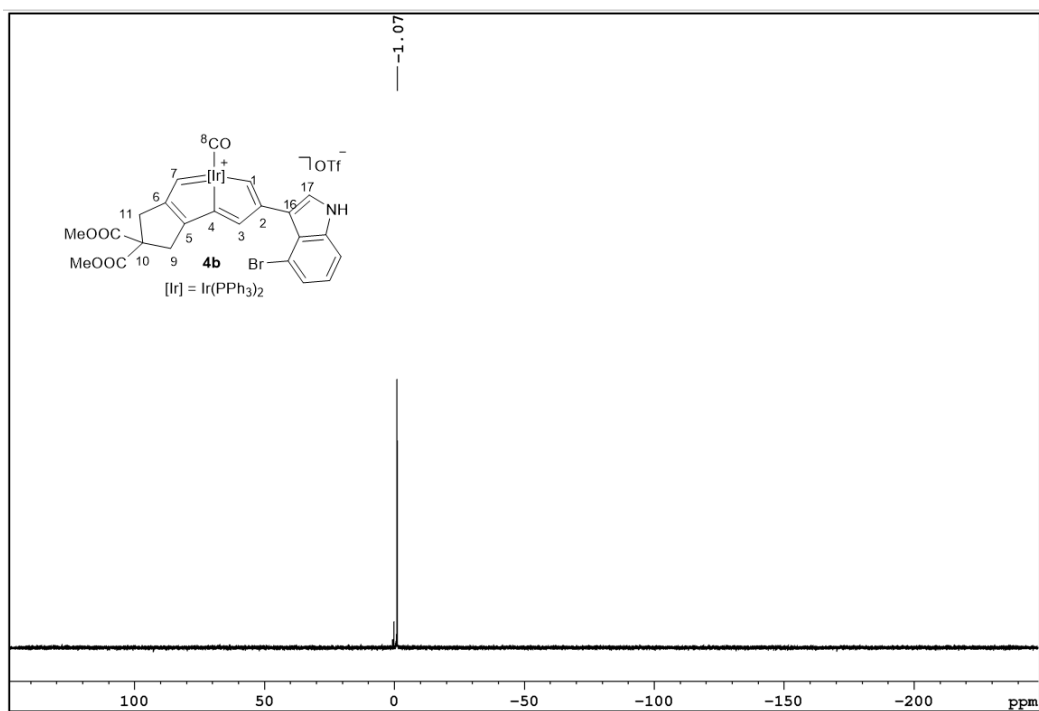
**Figure S20** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **4a**.



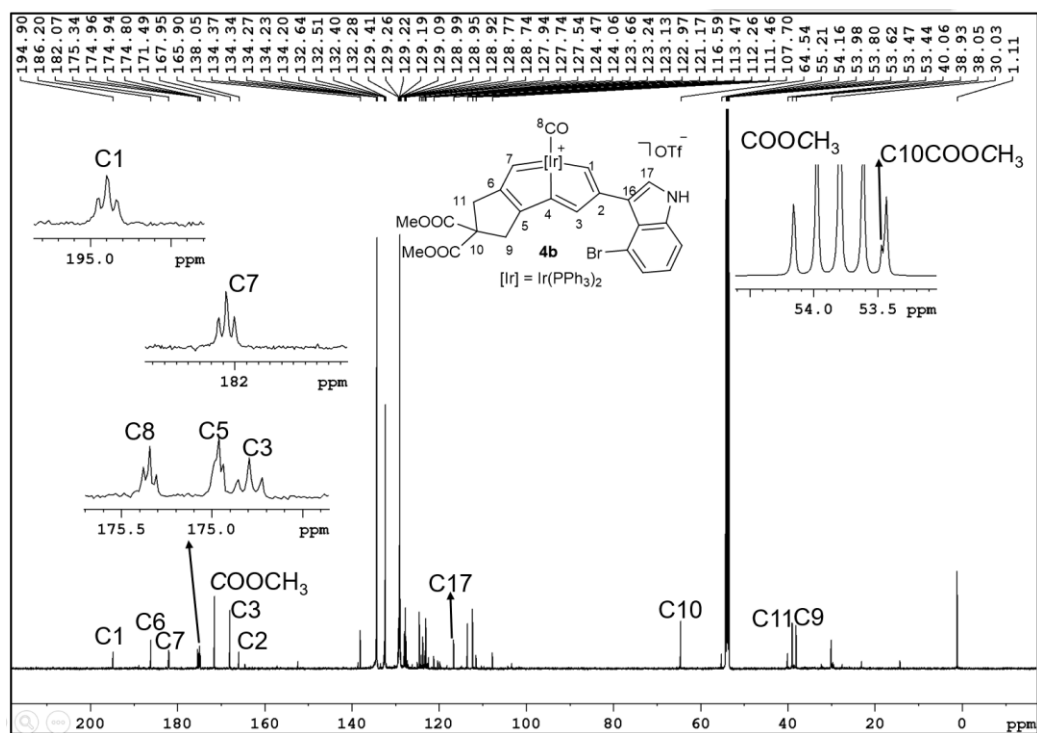
**Figure S21** The  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **4a**.



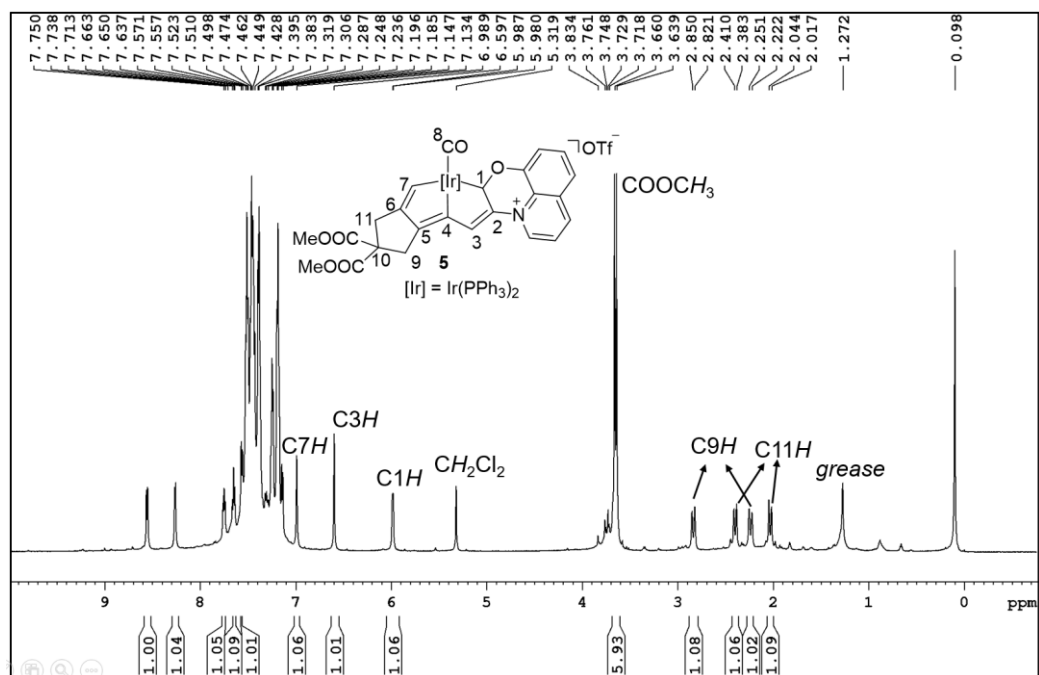
**Figure S22** The  $^1\text{H}$  NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **4b**.



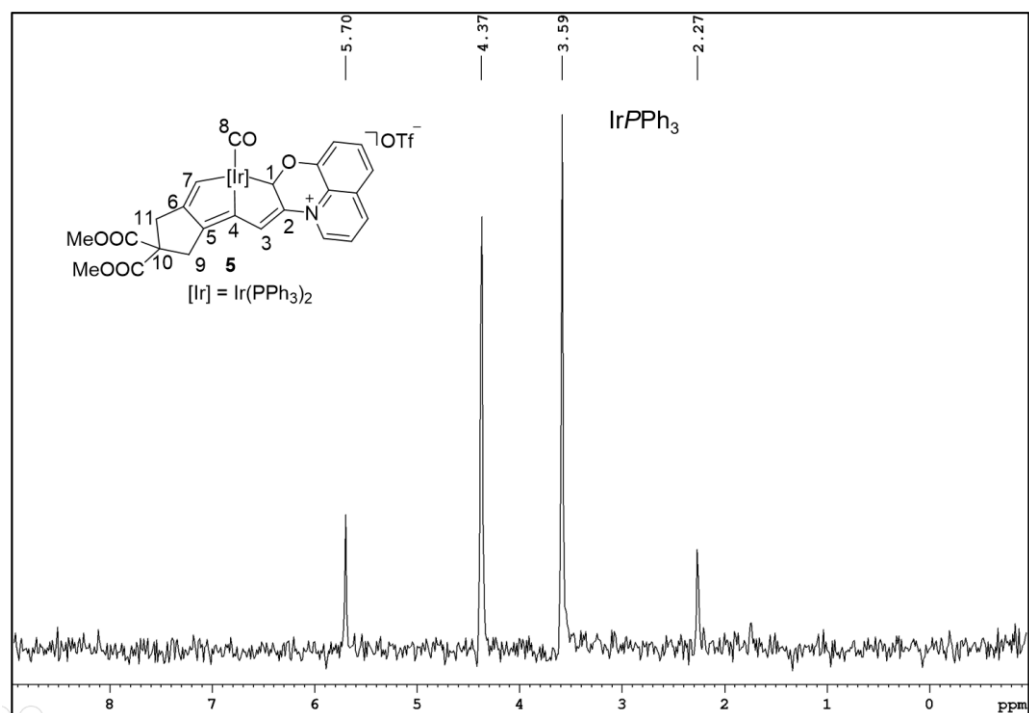
**Figure S23** The  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **4b**.



**Figure S24** The  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for compound **4b**.



**Figure S25** The  $^1H$  NMR (600.1 MHz,  $CD_2Cl_2$ ) spectrum for complex **5**.



**Figure S26** The  $^{31}P\{^1H\}$  NMR (242.9 MHz,  $CD_2Cl_2$ ) spectrum for complex **5**.

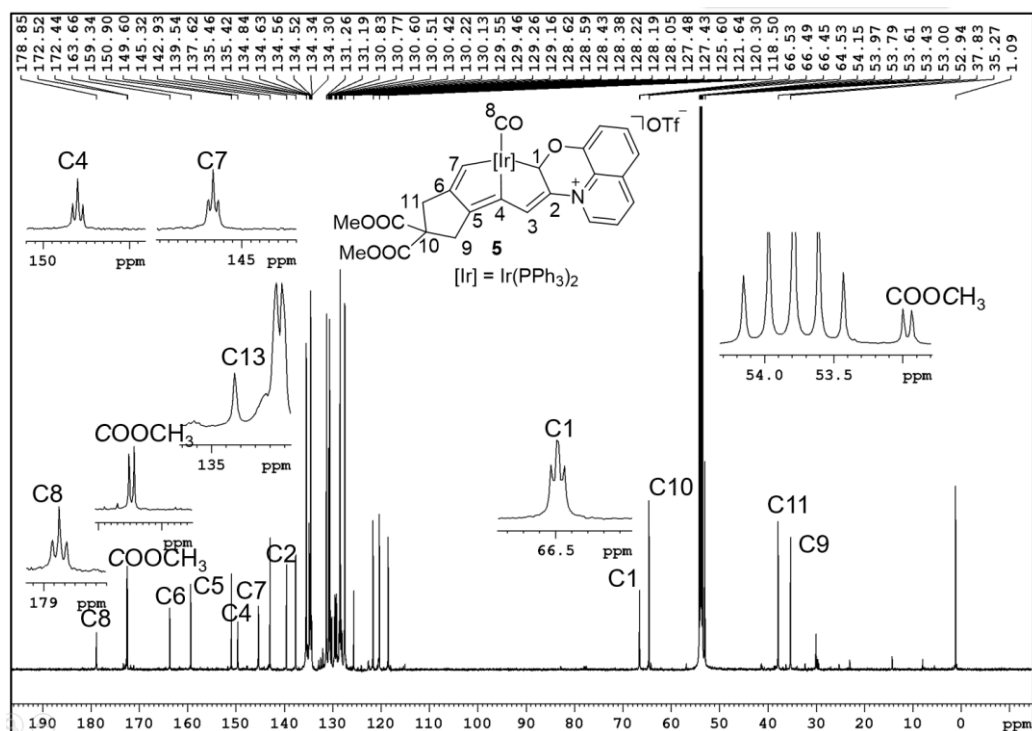


Figure S27 The  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum for complex **5**.

#### 4. HRMS spectra

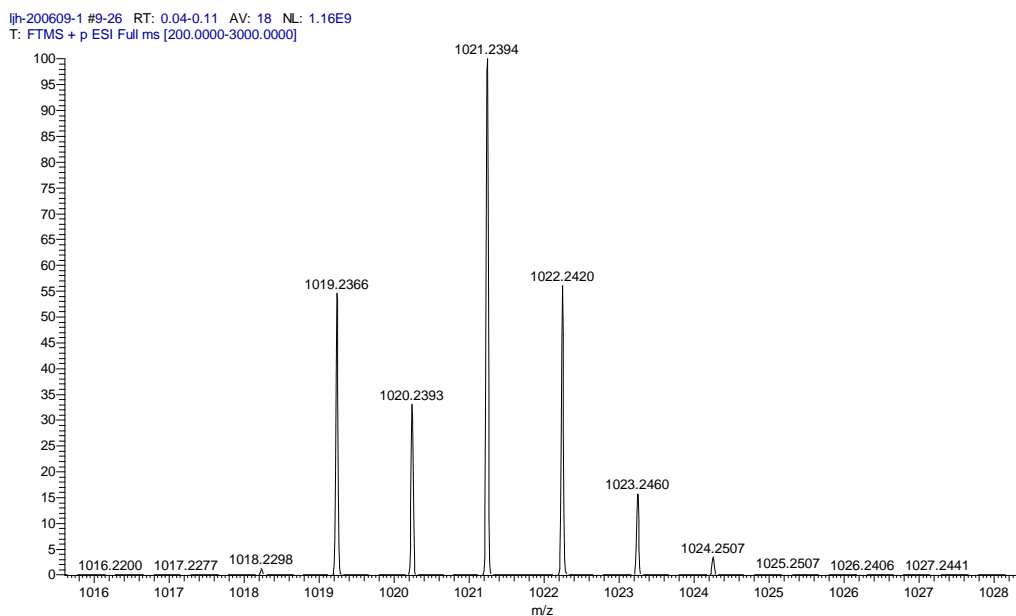
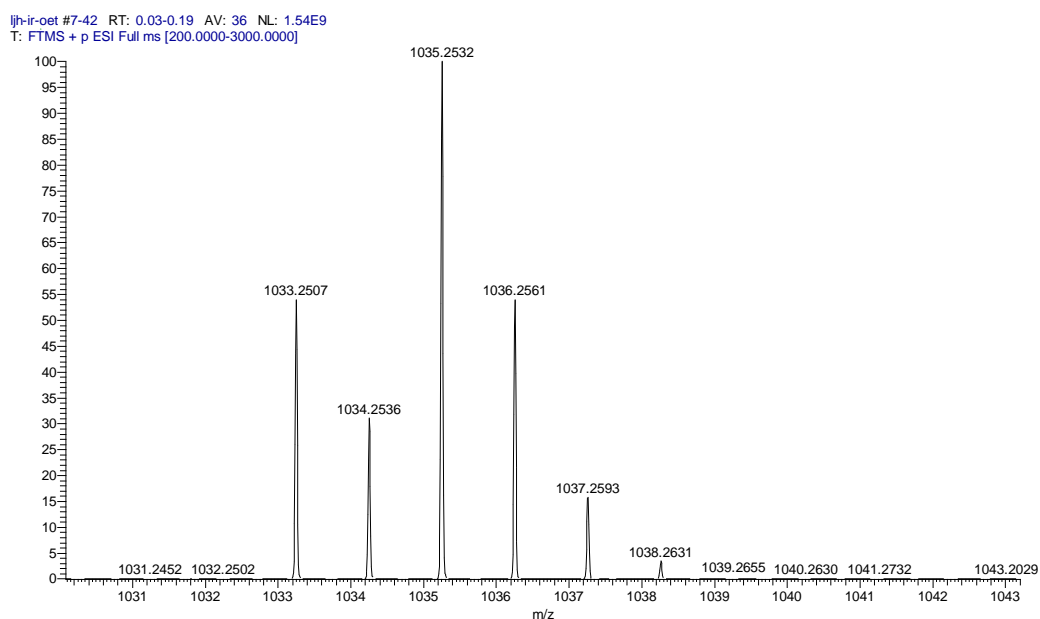
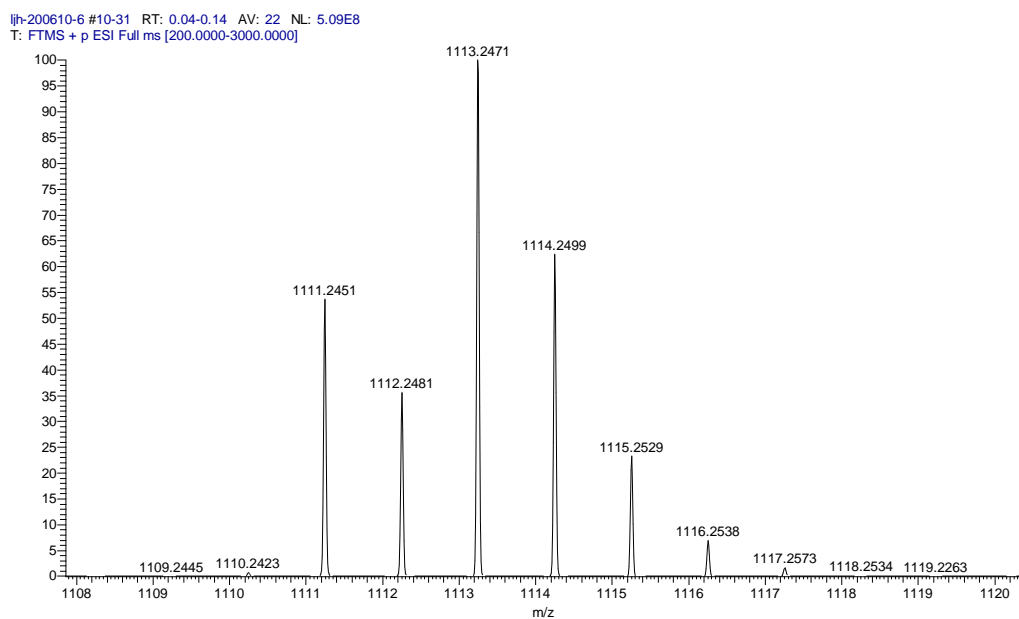


Figure S28 Positive ion ESI-MS spectrum of  $[\mathbf{2a-OTf}]^+ [\text{C}_{52}\text{H}_{46}\text{IrO}_6\text{P}_2]^+$  measured in methanol.

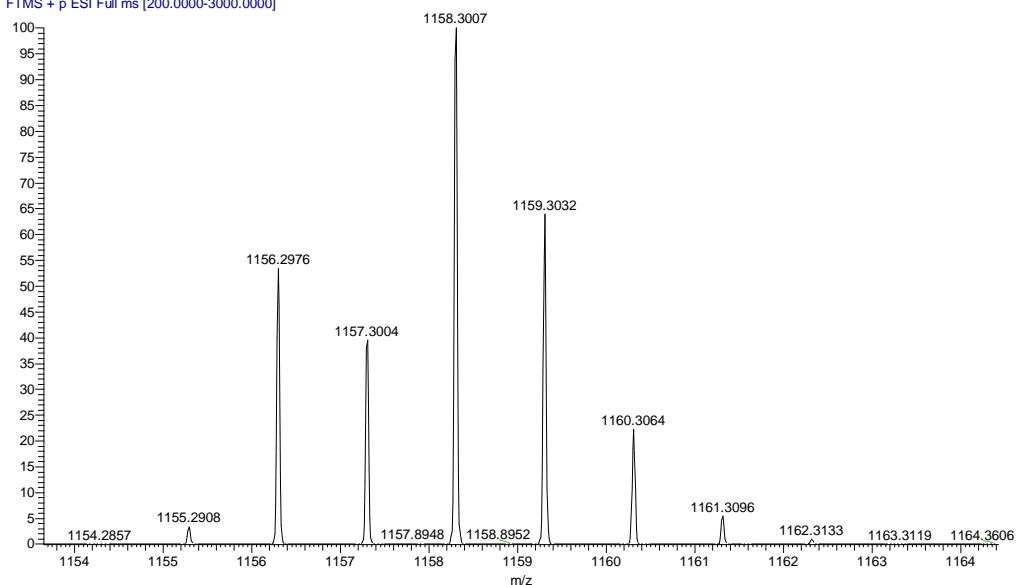


**Figure S29** Positive ion ESI-MS spectrum of  $[2b-OTf]^+ [C_{53}H_{48}IrO_6P_2]^+$  measured in methanol.



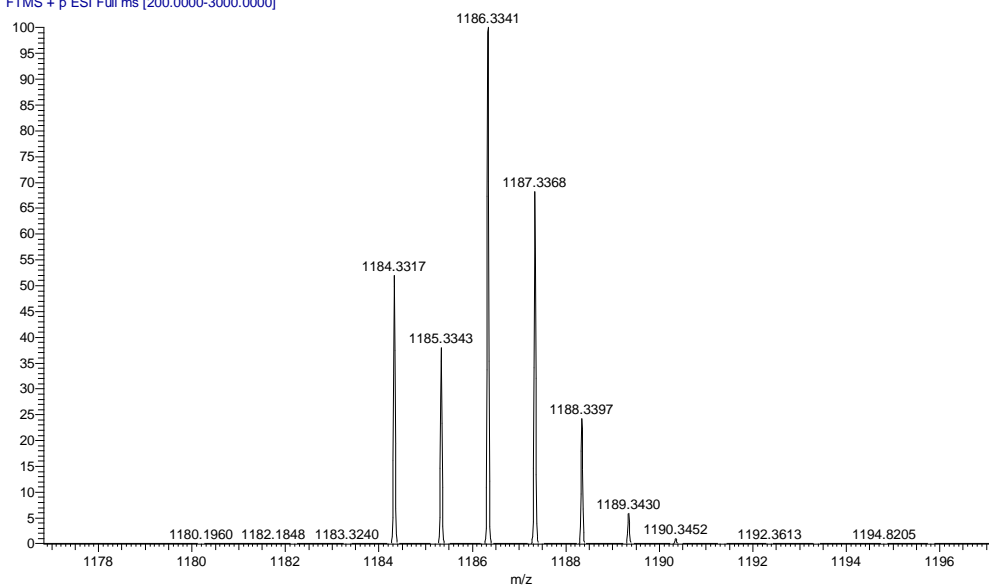
**Figure S30** Positive ion ESI-MS spectrum of  $[2c-OTf]^+ [C_{58}H_{50}IrSO_5P_2]^+$  measured in methanol.

ljh200813-1 #7-29 RT: 0.03-0.13 AV: 23 NL: 1.30E9  
T: FTMS + p ESI Full ms [200.0000-3000.0000]



**Figure S31** Positive ion ESI-MS spectrum of  $[3a-OTf]^+ [C_{63}H_{53}IrNO_5P_2]^+$  measured in methanol.

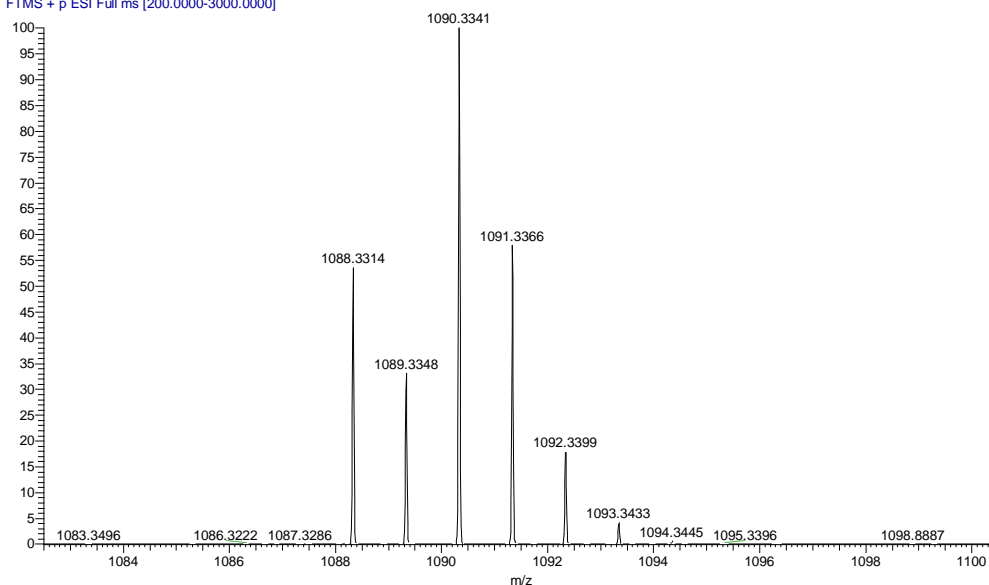
ljh201026-bz #5-36 RT: 0.02-0.16 AV: 32 NL: 1.00E9  
T: FTMS + p ESI Full ms [200.0000-3000.0000]



**Figure S32** Positive ion ESI-MS spectrum of  $[3b-OTf]^+ [C_{65}H_{57}IrNO_5P_2]^+$  measured in methanol.

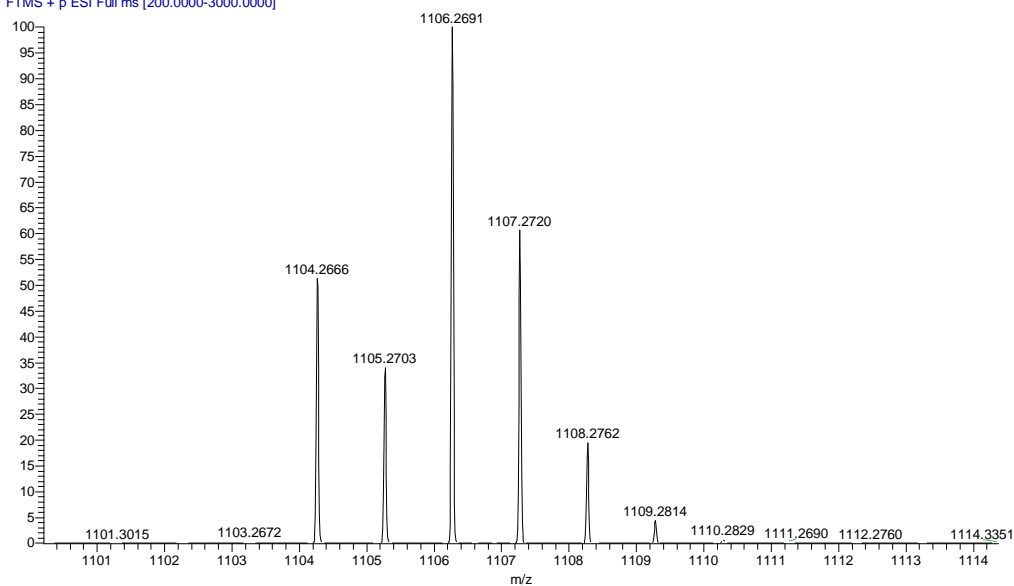


ljh201026-pr #8-34 RT: 0.03-0.15 AV: 27 NL: 1.29E9  
T: FTMS + p ESI Full ms [200.0000-3000.0000]



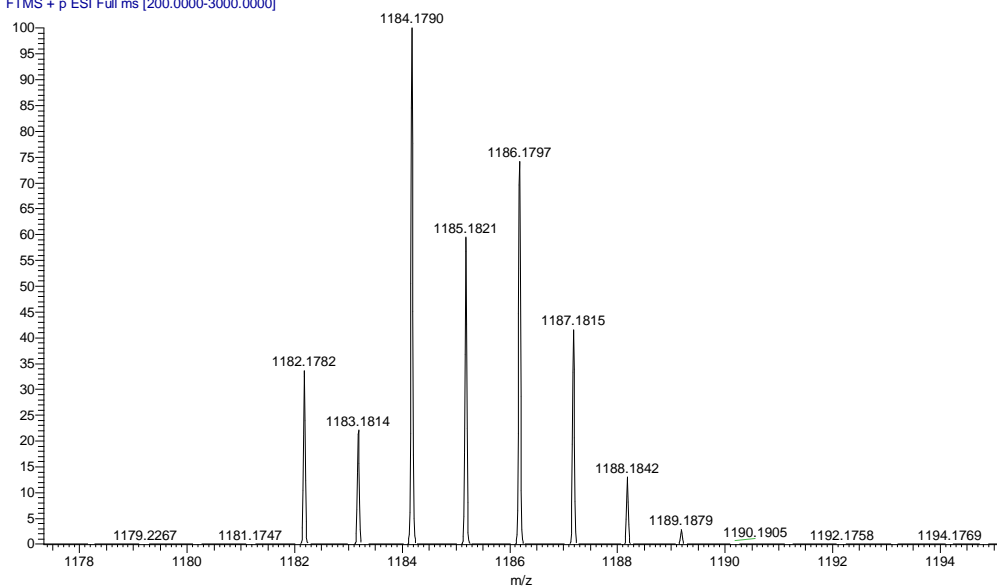
**Figure S33** Positive ion ESI-MS spectrum of  $[3c-OTf]^+ [C_{57}H_{57}IrNO_5P_2]^+$  measured in methanol.

ljh200808-1 #8-29 RT: 0.03-0.13 AV: 22 NL: 1.08E9  
T: FTMS + p ESI Full ms [200.0000-3000.0000]



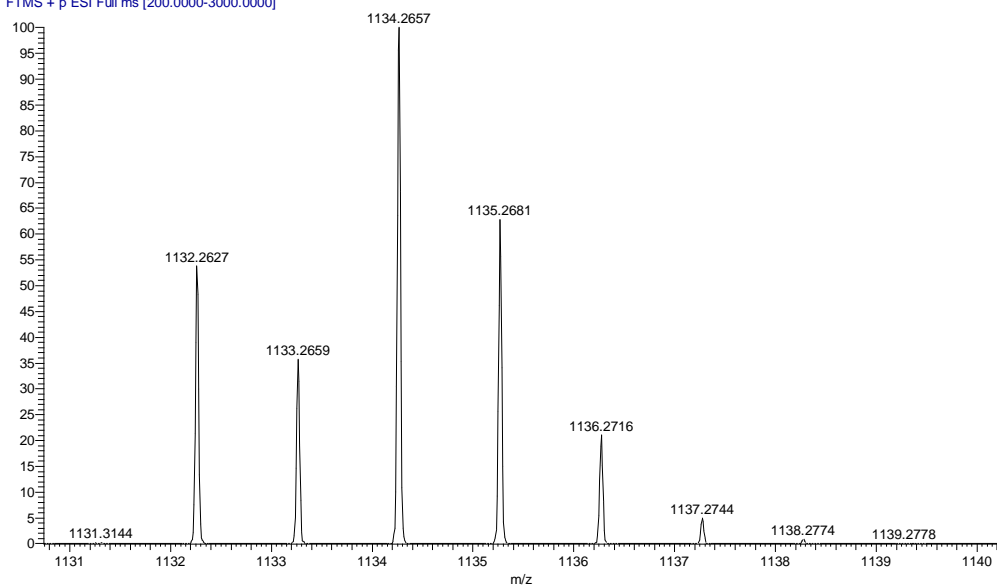
**Figure S34** Positive ion ESI-MS spectrum of  $[4a-OTf]^+ [C_{59}H_{49}IrNO_5P_2]^+$  measured in methanol.

ljh-4br #7-32 RT: 0.03-0.14 AV: 26 NL: 7.49E8  
T: FTMS + p ESI Full ms [200.0000-3000.0000]



**Figure S35** Positive ion ESI-MS spectrum of  $[4b-OTf]^+ [C_{59}H_{48}BrIrNO_5P_2]^+$  measured in methanol.

ljh200604-16-crystal #8-36 RT: 0.03-0.16 AV: 29 NL: 8.42E8  
T: FTMS + p ESI Full ms [200.0000-3000.0000]



**Figure S36** Positive ion ESI-MS spectrum of  $[5-OTf]^+ [C_{60}H_{49}IrNO_6P_2]^+$  measured in methanol.

## 5. Crystallographic details

**Crystallographic details.** Single-crystal X-ray diffraction data were collected on an Bruker PHOTON 100 area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for **2b** and **4a**, and CuK $\alpha$  ( $\lambda = 1.54184$ ) for **2c**, **3a**, **3b**, **4b** and **5**. All the Data were corrected for absorption effects using the multi-scan technique. Using Olex2,<sup>[S3]</sup> the structures were solved with the ShelXT<sup>[S4]</sup> structure solution program using Charge Flipping and refined with the ShelXL<sup>[S5]</sup> refinement package using Least Squares minimization. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. The diffuse electron densities resulting from the residual solvent molecules in complexes **3a**, **3b**, **4a** and **5** were removed from the data set by using the SQUEEZE routine of PLATON. The crystals suitable for X-ray diffraction were grown from the CH<sub>2</sub>Cl<sub>2</sub> solution layered with n-hexane for complexes **2b**, **2c**, **3a**, **3b**, **4a** and **5**; and layered with petroleum ether for **4b**. CCDC-2090490 (**2b**), CCDC-2090498 (**2c**), CCDC-2090504 (**3a**), CCDC-2090503 (**3b**), CCDC-2090505 (**4a**), CCDC-2090509 (**4b**) and CCDC-2090952 (**5**) contain the supplementary crystallographic data for this paper, and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures). For further details on the crystal data, data collection, and refinements, see **Tables S1-S4**.

**Table S1** Crystal data and structure refinement for **2b**  $\cdot$  CH<sub>2</sub>Cl<sub>2</sub> and **2c**  $\cdot$  CH<sub>2</sub>Cl<sub>2</sub>.

	<b>2b</b> $\cdot$ CH <sub>2</sub> Cl <sub>2</sub>	<b>2c</b> $\cdot$ CH <sub>2</sub> Cl <sub>2</sub>
Formula	C <sub>55</sub> H <sub>50</sub> Cl <sub>2</sub> F <sub>3</sub> IrO <sub>9</sub> P <sub>2</sub> S	C <sub>60</sub> H <sub>52</sub> Cl <sub>2</sub> F <sub>3</sub> IrO <sub>8</sub> P <sub>2</sub> S <sub>2</sub>
Mr	1269.05	1347.17
Crystal system	monoclinic	triclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P-1</i>
<i>a</i> [Å]	11.6181(2)	11.8748(9)
<i>b</i> [Å]	14.4247(3)	15.7834(11)
<i>c</i> [Å]	31.3601(8)	16.8217(11)

$\alpha$ [°]	90	66.142(3)
$\beta$ [°]	92.4740(10)	82.914(3)
$\gamma$ [°]	90	83.728(3)
$V$ [Å <sup>3</sup> ]	5250.7(2)	2855.2(4)
$Z$	4	2
$\rho_{\text{calcd}}$ [gcm <sup>-3</sup> ]	1.605	1.567
$\mu$ [mm <sup>-1</sup> ]	2.812	7.140
$F(000)$	2544.0	1352.0
Crystal size [mm <sup>3</sup> ]	0.18 × 0.16 × 0.10	0.12×0.08×0.08
$\theta$ range [°]	2.138 to 27.54	2.883 to 66.752
Reflns collected	51247	107793
Independent reflns	12069	10075
Observed reflns [ $I \geq 2\sigma$ ]	9757	8931
Data/restraints/params	12069/0/661	10075/0/706
GOF on $F^2$	1.040	1.031
$R_1/wR_2$ [ $I \geq 2\sigma(I)$ ]	0.0337 /0.0621	0.0288/0.0735
$R_1/wR_2$ (all data)	0.0508 /0.0691	0.0299/0.0742
Largest peak/hole [e Å <sup>-3</sup> ]	0.81/-0.90	1.19/-1.47

**Table S2** Crystal data and structure refinement for **3a** and **3b**.

	<b>3a</b>	<b>3b</b>
Formula	C <sub>64</sub> H <sub>53</sub> F <sub>3</sub> IrNO <sub>8</sub> P <sub>2</sub> S	C <sub>66</sub> H <sub>57</sub> F <sub>3</sub> IrNO <sub>8</sub> P <sub>2</sub> S
Mr	1307.27	1335.32
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P-1$

$a$ [Å]	12.2983(6)	11.7694(5)
$b$ [Å]	21.2345(11)	14.4795(6)
$c$ [Å]	23.5769(13)	17.2788(7)
$\alpha$ [°]	90	99.712(2)
$\beta$ [°]	95.003(3)	91.494(2)
$\gamma$ [°]	90	95.634(2)
$V$ [Å <sup>3</sup> ]	6133.6(3)	2885.6(2)
$Z$	4	2
$\rho_{\text{calcd}}$ [gcm <sup>-3</sup> ]	1.416	1.537
$\mu$ [mm <sup>-1</sup> ]	5.544	5.905
$F(000)$	2632.0	1348.0
Crystal size [mm <sup>3</sup> ]	0.16 × 0.08 × 0.02	0.26×0.20×0.08
$\theta$ range [°]	2.805 to 64.998	2.597 to 60.000
Reflns collected	39901	30934
Independent reflns	10373	8522
Observed reflns [ $I \geq 2\sigma$ ]	9879	9280
Data/restraints/params	10373/219/779	8522/0/741
GOF on $F^2$	1.079	1.093
$R_1/wR_2$ [ $I \geq 2\sigma(I)$ ]	0.0525 /0.1468	0.0470/0.1233
$R_1/wR_2$ (all data)	0.0641 /0.1537	0.0475/0.1258
Largest peak/hole [e Å <sup>-3</sup> ]	2.27/-1.01	3.79/-1.22

**Table S3** Crystal data and structure refinement for **4a**  $\text{CH}_2\text{Cl}_2$  and **4b**  $\text{CH}_2\text{Cl}_2$ .

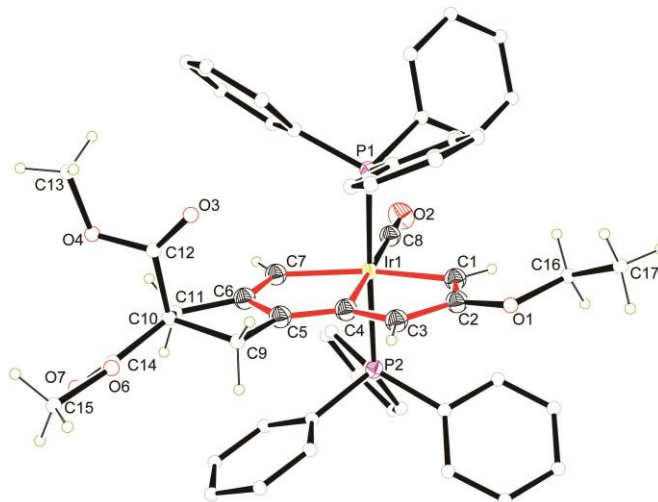
	<b>4a</b> · $\text{CH}_2\text{Cl}_2$	<b>4b</b> · $\text{CH}_2\text{Cl}_2$
Formula	$\text{C}_{61}\text{H}_{51}\text{Cl}_2\text{F}_3\text{IrNO}_8\text{P}_2\text{S}$	$\text{C}_{61}\text{H}_{50}\text{BrCl}_2\text{F}_3\text{IrNO}_8\text{P}_2\text{S}$

Mr	1356.12	1419.03
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	13.3075(4)	12.2728(2)
<i>b</i> [Å]	14.2370(5)	12.9648(2)
<i>c</i> [Å]	14.8738(5)	19.7289(3)
$\alpha$ [°]	87.5740(10)	92.9280(10)
$\beta$ [°]	78.5770(10)	96.0420(10)
$\gamma$ [°]	86.1780(10)	109.1390(10)
<i>V</i> [Å <sup>3</sup> ]	2754.79(16)	2936.90(8)
<i>Z</i>	2	2
$\rho_{\text{calcd}}$ [gcm <sup>-3</sup> ]	1.635	1.605
$\mu$ [mm <sup>-1</sup> ]	2.687	7.425
<i>F</i> (000)	1360.0	1412.0
Crystal size [mm <sup>3</sup> ]	0.18 × 0.10 × 0.06	0.18×0.02×0.02
$\theta$ range [°]	2.284 to 27.573	2.261 to 59.999
Reflns collected	70599	31292
Independent reflns	12678	8612
Observed reflns [ <i>I</i> ≥ 2σ]	9836	9827
Data/restraints/params	12678/36/714	8612/84/723
GOF on <i>F</i> <sup>2</sup>	1.051	1.084
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0510 /0.1258	0.0357/0.0887
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0647 /0.1387	0.0387/0.0901
Largest peak/hole [e Å <sup>-3</sup> ]	2.98/-2.63	1.46/-1.53

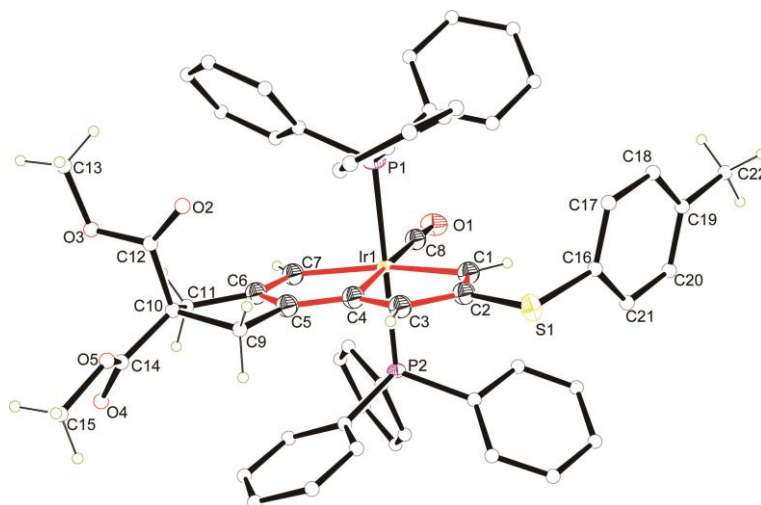
**Table S4** Crystal data and structure refinement for **5**  $\text{CH}_2\text{Cl}_2$ .

	<b>5</b> · $\text{CH}_2\text{Cl}_2$
Formula	$\text{C}_{123}\text{H}_{100}\text{Cl}_2\text{F}_6\text{Ir}_2\text{N}_2\text{O}_{18}\text{P}_4\text{S}_2$
Mr	2651.34
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> [Å]	10.7506 (2)
<i>b</i> [Å]	22.5712(5)
<i>c</i> [Å]	23.8255(5)
$\alpha$ [°]	87.6250(10)
$\beta$ [°]	77.2860(10)
$\gamma$ [°]	81.9300(10)
<i>V</i> [Å <sup>3</sup> ]	5583.4(2)
<i>Z</i>	2
$\rho_{\text{calcd}}$ [gcm <sup>-3</sup> ]	1.577
$\mu$ [mm <sup>-1</sup> ]	6.543
<i>F</i> (000)	2660.0
Crystal size [mm <sup>3</sup> ]	0.24 × 0.16 × 0.08
$\theta$ range [°]	1.977 to 59.999
Reflns collected	203539
Independent reflns	16569
Observed reflns [ <i>I</i> ≥ 2σ]	9689
Data/restraints/params	16569/0/1436
GOF on <i>F</i> <sup>2</sup>	1.167
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0467 /0.1117

$R_1/wR_2$ (all data)	0.0494 / 0.1124
Largest peak/hole [ $e \text{ \AA}^{-3}$ ]	3.00/-2.01



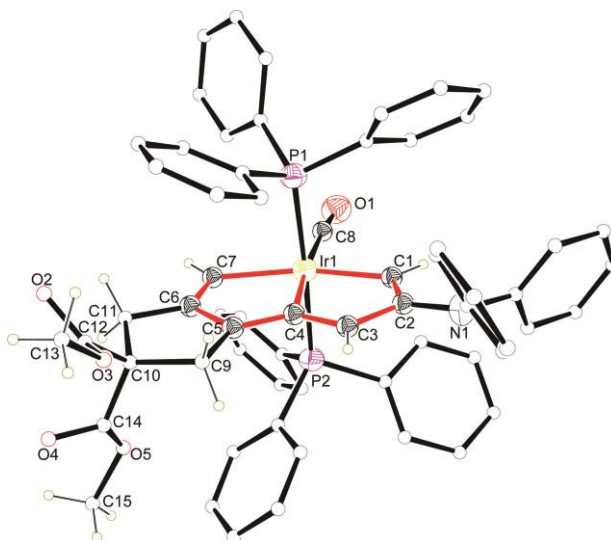
**Figure S37.** X-ray molecular structure for the cation of complex **2b** (ellipsoids are at the 50% probability level, the solvent and hydrogen atoms of phenyl groups are omitted for clarity). Selected bond distances ( $\text{\AA}$ ) and angles (deg): Ir1–C1 2.081(3), Ir1–C4 2.059(3), Ir1–C7 2.056(4), Ir1–C8 1.930(3), C1–C2 1.380(5), C2–C3 1.418(5), C3–C4 1.370(5), C4–C5 1.399(5), C5–C6 1.405(5), C6–C7 1.384(5), C5–C9 1.500(4), C6–C11 1.508(5), C9–C10 1.555(5), C10–C11 1.565(5), C2–O1 1.366(4), C16–O1 1.427(4), C16–C17 1.493(6); C1–Ir1–C7 158.04(13), C1–Ir1–C4 78.39(13), C4–Ir1–C7 79.66(14), Ir1–C1–C2 113.6(2), C1–C2–C3 117.2(3), C2–C3–C4 114.4(3), C3–C4–C5 129.9(3), C4–C5–C6 115.8(3), C5–C6–C7 116.6(3), C6–C7–Ir1 114.0(3).



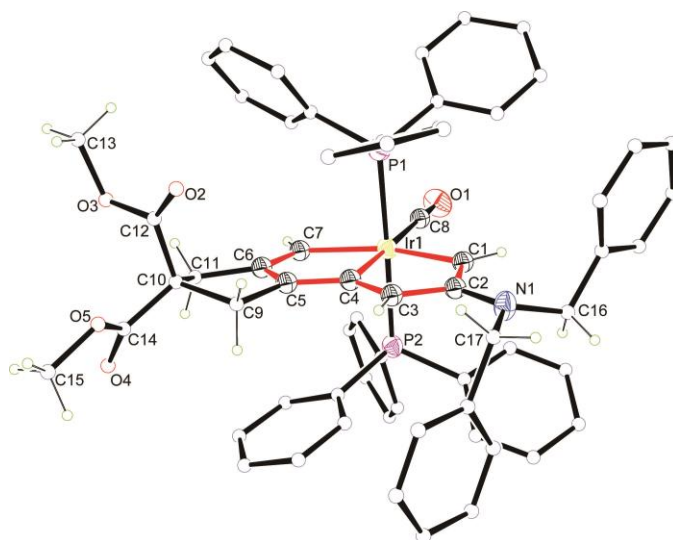
**Figure S38.** X-ray molecular structure for the cation of complex **2c** (ellipsoids are at the 50% probability level, the solvent and hydrogen atoms of phenyl groups are omitted for clarity).



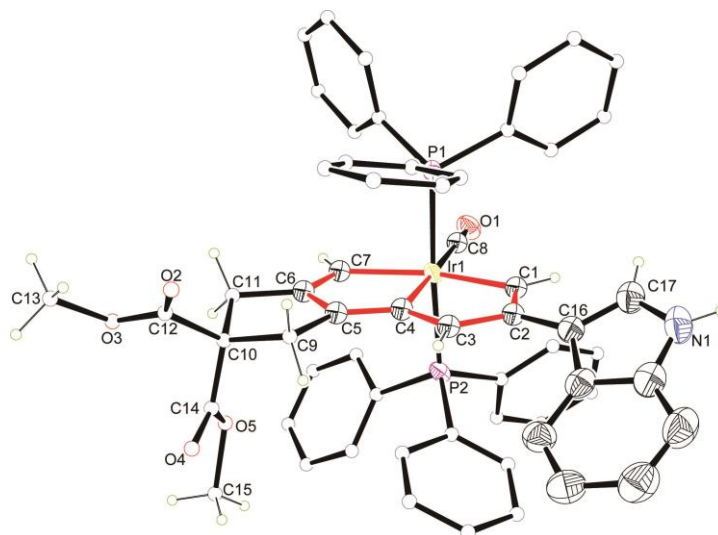
probability level, the solvent and hydrogen atoms of phenyl groups are omitted for clarity). Selected bond distances (Å) and angles (deg): Ir1–C1 2.055(3), Ir1–C4 2.057(3), Ir1–C7 2.059(3), Ir1–C8 1.932(3), C1–C2 1.384 (4), C2–C3 1.413 (4), C3–C4 1.380 (4), C4–C5 1.391 (4), C5–C6 1.397 (4), C6–C7 1.389(4), C5–C9 1.506(4), C6–C11 1.507(4), C9–C10 1.559(4), C10–C11 1.559(4), C2–S1 1.774(3), C16–S1 1.775(3); C1–Ir1–C7 158.06(12), C1–Ir1–C4 78.67(12), C4–Ir1–C7 79.44(12), Ir1–C1–C2 114.6(2), C1–C2–C3 116.4(3), C2–C3–C4 114.7(3), C3–C4–C5 130.4(3), C4–C5–C6 116.1(3), C5–C6–C7 116.6(3), C6–C7–Ir1 113.8(2).



**Figure S39.** X-ray molecular structure for the cation of complex **3a** (ellipsoids are at the 50% probability level, the hydrogen atoms of phenyl groups are omitted for clarity). Selected bond distances (Å) and angles (deg): Ir1–C1 2.048(6), Ir1–C4 2.065(5), Ir1–C7 2.098(6), Ir1–C8 1.931(6), C1–C2 1.396(9), C2–C3 1.443(9), C3–C4 1.371(8), C4–C5 1.392(8), C5–C6 1.421(9), C6–C7 1.374(9), C5–C9 1.498(8), C6–C11 1.509(9), C9–C10 1.578(9), C10–C11 1.555(10), C2–N1 1.399(8); C1–Ir1–C7 156.9(2), C1–Ir1–C4 77.8(2), C4–Ir1–C7 79.1(2), Ir1–C1–C2 116.9(4), C1–C2–C3 113.6(5), C2–C3–C4 115.0(5), C3–C4–C5 128.5(5), C4–C5–C6 115.0(5), C5–C6–C7 117.8(5), C6–C7–Ir1 113.1(4).

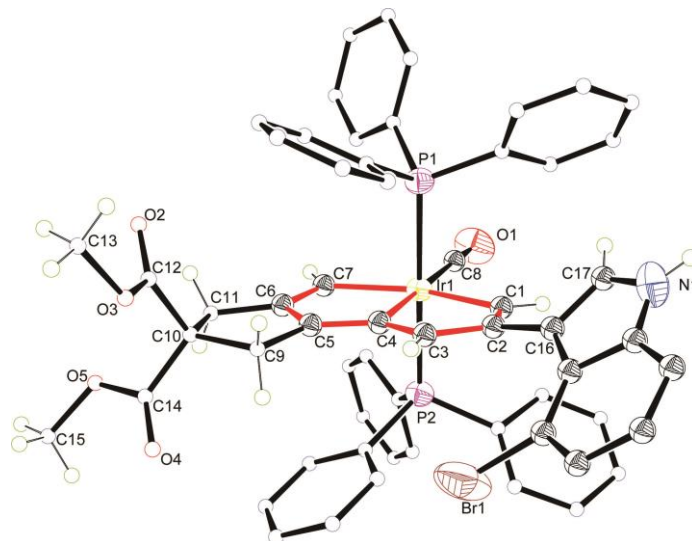


**Figure S40.** X-ray molecular structure for the cation of complex **3b** (ellipsoids are at the 50% probability level, the hydrogen atoms of phenyl groups are omitted for clarity). Selected bond distances (Å) and angles (deg): Ir1–C1 2.048(4), Ir1–C4 2.075(4), Ir1–C7 2.065(5), Ir1–C8 1.975(5), C1–C2 1.411(6), C2–C3 1.415(6), C3–C4 1.375(7), C4–C5 1.392(7), C5–C6 1.398(6), C6–C7 1.377(7), C5–C9 1.509(6), C6–C11 1.509(6), C9–C10 1.558(6), C10–C11 1.553(6), C2–N1 1.374(6), C16–N1 1.467(6), C17–N1 1.463(6); C1–Ir1–C7 157.78(19), C1–Ir1–C4 77.98(18), C4–Ir1–C7 79.97(19), Ir1–C1–C2 116.0(3), C1–C2–C3 114.3(4), C2–C3–C4 115.6(4), C3–C4–C5 131.6(4), C4–C5–C6 116.8(4), C5–C6–C7 117.5(4), C6–C7–Ir1 113.1(3).

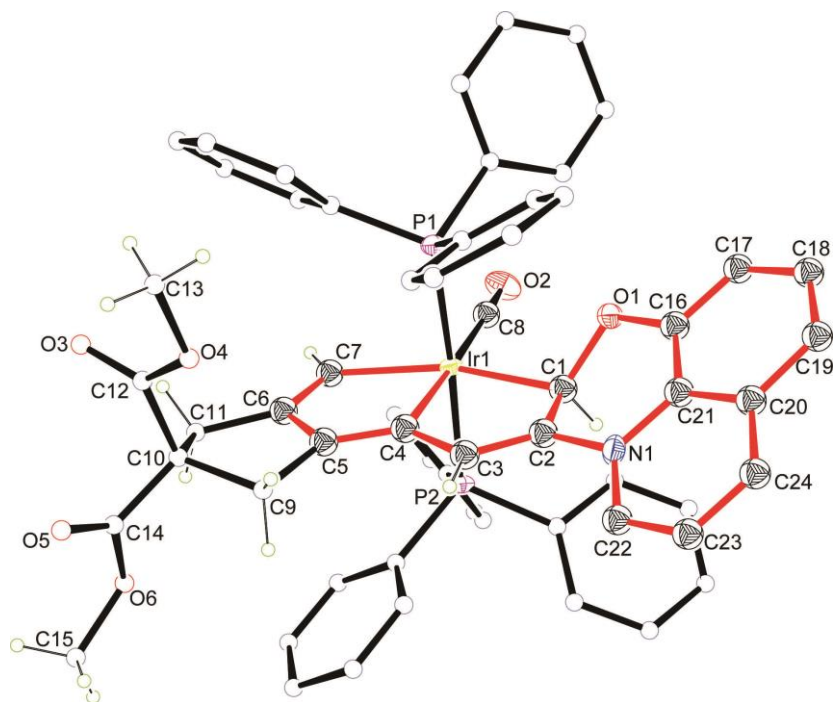


**Figure S41.** X-ray molecular structure for the cation of complex **4a** (ellipsoids are at the 50% probability level, the solvent and hydrogen atoms of phenyl groups in PPh<sub>3</sub> and indole are omitted for

clarity). Selected bond distances (Å) and angles (deg): Ir1–C1 2.074(5), Ir1–C4 2.064(5), Ir1–C7 2.068(6), Ir1–C8 1.947(6), C1–C2 1.399 (8), C2–C3 1.415(8), C3–C4 1.384(8), C4–C5 1.374(8), C5–C6 1.412(9), C6–C7 1.383(9), C5–C9 1.514(9), C6–C11 1.525(9), C9–C10 1.562(11), C10–C11 1.552(11), C2–C16 1.460(8), C16–C17 1.367(9), C17–N1 1.371(9); C1–Ir1–C7 155.8(3), C1–Ir1–C4 77.2(2), C4–Ir1–C7 78.7(2), Ir1–C1–C2 116.7(4), C1–C2–C3 113.7(5), C2–C3–C4 115.8(5), C3–C4–C5 128.5(6), C4–C5–C6 115.9(6), C5–C6–C7 116.1(5), C6–C7–Ir1 114.4(4).



**Figure S42.** X-ray molecular structure for the cation of complex **4b** (ellipsoids are at the 50% probability level, the solvent and hydrogen atoms of phenyl groups in PPh<sub>3</sub> and indole are omitted for clarity). Selected bond distances (Å) and angles (deg): Ir1–C1 2.063(5), Ir1–C4 2.077(4), Ir1–C7 2.072(5), Ir1–C8 1.923(5), C1–C2 1.389 (7), C2–C3 1.409 (7), C3–C4 1.367 (7), C4–C5 1.393 (7), C5–C6 1.404 (7), C6–C7 1.373(7), C5–C9 1.496(7), C6–C11 1.487(7), C9–C10 1.555(8), C10–C11 1.551(8), C2–C16 1.484(7), C16–C17 1.378(8), C17–N1 1.364(7); C1–Ir1–C7 156.12(18), C1–Ir1–C4 77.12(18), C4–Ir1–C7 79.00(18), Ir1–C1–C2 116.8(3), C1–C2–C3 113.6(4), C2–C3–C4 116.7(4), C3–C4–C5 130.7(4), C4–C5–C6 116.2(4), C5–C6–C7 116.8(4), C6–C7–Ir1 114.3(3).

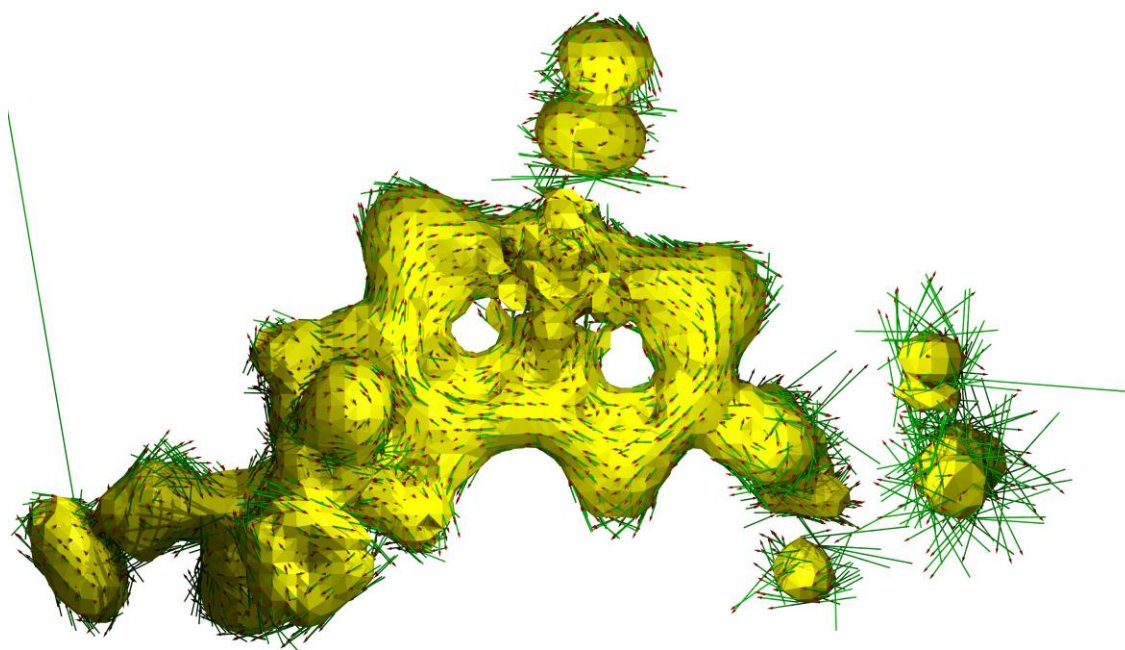


**Figure S43.** X-ray molecular structure for the cation of complex **5** (ellipsoids are at the 50% probability level, the solvent and hydrogen atoms of phenyl groups in PPh<sub>3</sub> and quinoline moieties are omitted for clarity). Selected bond distances (Å) and angles (deg): Ir1–C1 2.178(6), Ir1–C4 2.075(7), Ir1–C7 2.144(6), Ir1–C8 1.907(7), C1–C2 1.499(9), C2–C3 1.341(9), C3–C4 1.436(9), C4–C5 1.355(9), C5–C6 1.442(9), C6–C7 1.365(10), C5–C9 1.496(9), C6–C11 1.513(10), C9–C10 1.547(9), C10–C11 1.566(9), C1–O1 1.469(7), C16–O1 1.356(8), C2–N1 1.435(8); C1–Ir1–C7 158.3(2), C1–Ir1–C4 80.4(5), C4–Ir1–C7 78.1(2), Ir1–C1–C2 106.8(4), C1–C2–C3 122.0(6), C2–C3–C4 115.1(6), C3–C4–C5 128.4(6), C4–C5–C6 116.3(6), C5–C6–C7 116.8(6), C6–C7–Ir1 113.0(4).

## 6. Theoretical calculations

**Computational details.** All optimizations were performed with the Gaussian 09 software package.<sup>[S6]</sup> All structures were optimized by density functional theory (DFT) using the B3LYP functional.<sup>[S7-S9]</sup> Frequency calculations were performed to confirm the calculated structures were minima on the potential energy surface. In the B3LYP calculations, for model complex **1'**, the effective core potentials (ECPs) of Hay and Wadt with a double- $\zeta$  valence basis set (LanL2DZ) were used to describe the Ir, P and S atoms, whereas the standard 6-311++G (d, p) basis set was used for all other atoms.<sup>[S10]</sup> Polarization functions were added for Ir ( $\zeta(f) = 0.938$ ), P ( $\zeta(d) = 0.340$ )<sup>[S11]</sup> and S ( $\zeta(d) =$

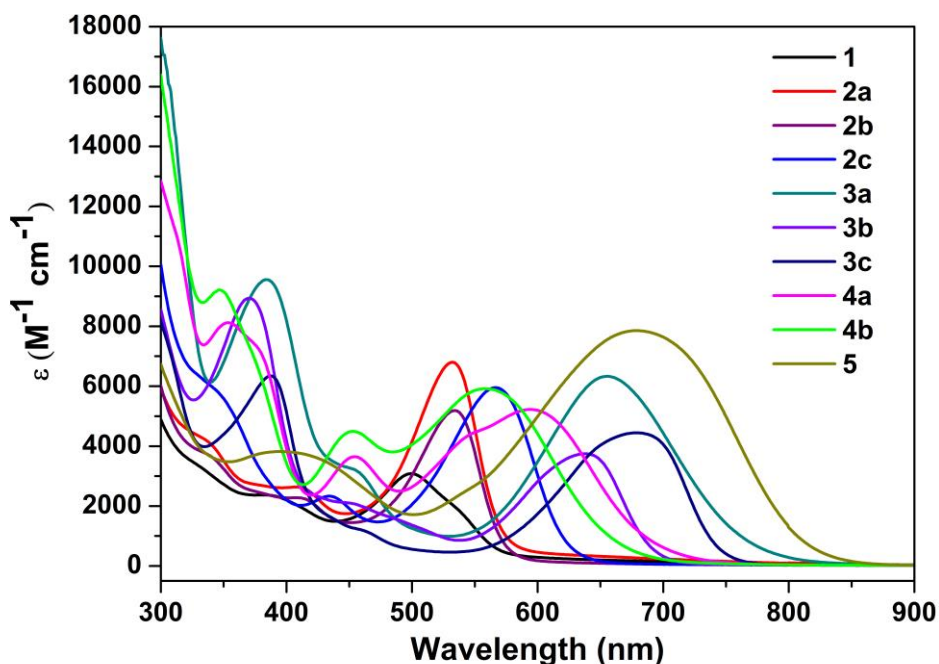
0.421).<sup>[S11]</sup> For model complexes **1-OTf** and **1-OTf'**, the an SDD basis set<sup>[S12]</sup> to describe Ir atom, and the standard 6-31+G(d) basis set was used for all other atoms.<sup>[S10]</sup> Single-point energies were computed on the optimized geometries with the B3LYP functional and the 6-311++G (d, p) basis set for organic atoms and SDD basis set for Os atom. The D3 dispersion correction and PCM (dichloromethane) were also applied to the single-point energy calculations. Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP-GIAO/6-311++G(d, p) level. Anisotropy of the induced current density (AICD) calculations were carried out with the AICD program.<sup>[S13,S14]</sup>



**Figure S44.** AICD isosurfaces of **1'** by  $\pi$  contribution. Current density vectors are plotted onto the AICD isosurface of 0.030 to indicate diatropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

## 7. The UV-vis absorption spectra of iridacycles 1-5

As shown in Figure S45, the absorptions of corresponding nitrogen-containing substituted products **3** are more red-shifted than that of **2** and **4**, which are mainly attributed to the  $n \rightarrow \pi^*$  electron transition from nitrogen atom to the  $\pi$ -conjugated skeleton. In addition, the introduction of a bromide atom in the indole skeleton would render the overlap of the  $\pi$ -conjugation, thus resulting in the blue-shifted absorption for **4b** in comparison with that of **4a**.



**Figure 45.** UV-vis absorption spectra of **1-5**, measured in  $\text{CH}_2\text{Cl}_2$  ( $2.0 \times 10^{-4}$  M) at room temperature.

## 8. Reference

- [S1] (a) J. Wang, J. Li, Y. Zhou, C. Yu, Y. Hua, Y. Yu, R. Li, X. Lin, R. Chen, H. Wu, H. Xia and H.-L. Wang, *J. Am. Chem. Soc.*, 2021, **143**, 7759; (b) J. Li, Q. Zhuo, K. Zhuo, D. Chen and H. Xia, *Acta Chim Sinica*, 2021, **79**, 71.
- [S2] P. S. Beauchamp and R. Marquez, *J. Chem. Educ.*, 1997, **74**, 1483.
- [S3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
- [S4] G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3
- [S5] G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
- [S6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J.

E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01 (Gaussian, Inc., 2009).

[S7] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[S8] B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200–206.

[S9] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

[S10] P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

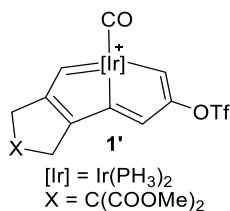
[S11] S. Huzinaga, Gaussian Basis Sets for Molecular Calculations, *Elsevier*, 1984.

[S12] C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comput. Chem.*, 1996, **17**, 49.

[S13] R. Herges and D. Geuenich, *J. Phys. Chem. A*, 2001, **105**, 3214.

[S14] D. Geuenich, K. Hess, F. Kohler and R. Herges, *Chem. Rev.*, 2005, **105**, 3758.

## 9. Cartesian coordinates



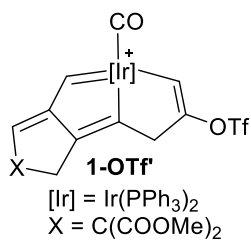
E = -1650.45479955 a.u.

Ir	-0.40231000	1.72921000	-0.03606400
S	-3.94470400	-2.14214000	-0.43361100
O	-3.05388500	-1.48750800	0.86097300
O	-1.37342900	4.65738100	0.05374200
O	3.90472300	0.03833800	1.91217300
C	-2.13931400	0.73432300	0.49731500
H	-3.12792300	1.12666300	0.72435300
O	6.20575700	-1.15349600	-0.92608600
F	-5.83898300	-0.54866200	0.54435400
F	-6.57604800	-2.31733200	-0.48216300
O	4.85320000	-1.98066800	1.61100600



F	-5.73026700	-2.49290000	1.51222700
O	-3.69202400	-3.58906400	-0.49784000
O	4.77186800	-2.66911700	-1.78354100
C	1.58160800	1.98504100	-0.58551700
H	2.11430100	2.91580900	-0.77796800
C	-1.99356600	-0.63427400	0.52257500
O	-3.79887300	-1.24395500	-1.60268700
C	2.30002900	0.80466400	-0.64706900
C	0.24323500	-0.25509000	-0.07905200
C	-1.01448000	3.57799900	0.02020500
C	-0.72165100	-1.19655300	0.22876000
H	-0.55842600	-2.27086100	0.25025000
C	3.76601000	0.51707500	-0.87657900
H	4.42627100	1.22880500	-0.38297100
H	4.00233700	0.52943000	-1.94577700
C	1.59997000	-0.40075500	-0.38927300
C	5.00300200	-1.71427900	-1.08664100
C	3.93878600	-0.93134100	-0.31279600
C	2.52317000	-1.57921300	-0.46538900
H	2.46468600	-2.05984500	-1.44963900
H	2.32209200	-2.35986800	0.27027500
C	4.24703500	-0.87217900	1.19111600
C	7.31118800	-1.78889800	-1.61557200
H	8.18431700	-1.19135900	-1.36787000
H	7.13180800	-1.78887600	-2.69044100
H	7.42848300	-2.81336600	-1.26317300
C	5.15847900	-2.07149000	3.02478300
H	5.81885800	-1.25487800	3.31482100
H	5.65200200	-3.03143100	3.14814200
H	4.23995700	-2.02979800	3.61006400
C	-5.66862400	-1.85170900	0.35965300
P	0.35800500	1.71442000	2.22051800
H	1.69024100	1.25410100	2.39075800
H	0.36927300	2.94733400	2.92296900
H	-0.37894500	0.89084200	3.11066300
P	-1.03373500	1.40661600	-2.31005500
H	-1.66464100	2.48545900	-2.98225100
H	0.02400700	1.10008800	-3.20457300
H	-1.94986900	0.34610400	-2.53068500



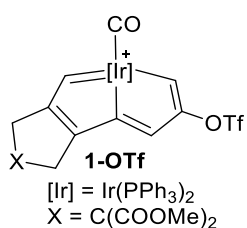


E = -4093.85672165 a.u.

Ir	0.13699200	0.27328700	0.90860100
P	0.95238500	-2.04564000	1.17447800
P	-0.46805600	2.64766900	0.59975800
S	3.71164700	-0.10234600	-3.25686500
O	2.81641800	0.96647900	-2.43526200
O	1.01608100	0.88696600	3.82198700
O	-4.93736700	0.79689700	-2.65444900
C	1.91549100	0.68776400	-0.21468700
H	2.88896700	0.99679500	0.16001900
O	-4.97583300	-3.32602700	-0.81742200
F	5.32708200	0.01326200	-1.14811200
F	6.29535600	-0.55224100	-3.01844400
O	-6.35824900	-0.53212400	-1.50375500
F	5.72824600	1.52425300	-2.66688000
O	3.81705500	0.35266700	-4.63619400
O	-4.76141100	-3.02517200	-3.04705800
C	-1.78939300	-0.26072500	1.27147300
H	-2.36102900	-0.28877400	2.20224300
C	1.76396000	0.55000500	-1.53433300
O	3.34857100	-1.47595800	-2.92504100
C	-0.77886900	-4.09823200	0.31856700
H	-1.16859100	-4.09415800	1.33126400
C	-0.57496600	4.09270900	-3.81572300
H	-0.59504200	4.42551600	-4.84979600
C	0.52557000	4.00791500	-1.65836200
H	1.36567100	4.28568000	-1.03047400
C	1.26280100	-3.94491600	3.22955200
H	2.05490600	-4.35426400	2.61116500
C	-2.50541100	-0.62759300	0.08914500
C	-0.50364800	-0.12134400	-1.07360700
C	2.78900200	-2.21893100	1.11617500
C	0.55044700	-2.80285100	2.81608400
C	0.70501500	0.65674900	2.73673700
C	-1.60065100	2.88822300	-1.98001400
H	-2.41972500	2.28174000	-1.60931300

C	0.26853300	-3.23745600	-0.04588400
C	0.50038200	4.43130900	-2.99049700
H	1.32231400	5.02670500	-3.37796200
C	1.99603600	3.51291700	1.75111100
H	2.39018700	2.53365400	1.51419700
C	-2.11295800	3.06344700	1.33574200
C	3.41649600	-3.30498200	0.48532900
H	2.83664600	-4.03476500	-0.06797000
C	2.83516100	4.45145700	2.35965300
H	3.86275800	4.18172700	2.58694100
C	-1.62617300	3.32218200	-3.30634200
H	-2.46692400	3.05426600	-3.94007100
C	-1.77543000	-0.54665000	-1.17232500
C	1.02878000	6.05665900	2.37573200
H	0.64357400	7.04328500	2.61784600
C	-2.41971100	2.56592800	2.61477700
H	-1.72343000	1.91489300	3.13304400
C	5.57712800	-2.55979100	1.29428000
H	6.65378200	-2.68968500	1.36089600
C	2.35473700	5.72455200	2.67344000
H	3.00615600	6.45262000	3.14876100
C	0.66509400	3.83622000	1.44915000
C	0.75448700	-3.26704500	-1.36458600
H	1.56582400	-2.61465000	-1.66957700
C	-4.64535500	-2.62701900	-1.90548100
C	4.80305500	-3.46883700	0.57074100
H	5.27126500	-4.31310700	0.07228900
C	3.57722900	-1.30796100	1.84078700
H	3.12241400	-0.46186200	2.34452300
C	-0.52624100	3.23489500	-1.14001800
C	0.96370800	-4.56678500	4.44240300
H	1.52457600	-5.44696000	4.74431100
C	4.95877200	-1.47926800	1.93227700
H	5.55079900	-0.76559100	2.49856400
C	-0.45837900	-2.30183400	3.65006800
H	-1.01723100	-1.42010200	3.36592800
C	-0.75611300	-2.92390300	4.86714800
H	-1.53890600	-2.51500300	5.49988000
C	-4.08306400	-1.23052900	-1.56821900
C	-3.61314500	2.91508500	3.24917600
H	-3.82906700	2.52254700	4.23897300
C	0.21157400	-4.15483900	-2.29495000
H	0.60517500	-4.17499400	-3.30749400

C	-2.70846600	-0.96967300	-2.29054900
H	-2.36438800	-1.87993200	-2.79220400
H	-2.83022000	-0.20091500	-3.05864400
C	0.18887800	5.12125600	1.76913600
H	-0.83754200	5.39862800	1.55253400
C	-1.32386500	-4.98094200	-0.61910400
H	-2.12967200	-5.64615600	-0.32144200
C	-5.16334800	-0.19480300	-1.99527800
C	-0.04645700	-4.05791400	5.26614500
H	-0.27364500	-4.53996800	6.21292900
C	-3.02214100	3.93412300	0.71367200
H	-2.80522200	4.35711100	-0.26045900
C	-5.55204500	-4.63815900	-1.03901600
H	-5.74565000	-5.03444000	-0.04336800
H	-4.84414200	-5.26983300	-1.57903300
H	-6.47996200	-4.54274700	-1.60671700
C	-4.52199100	3.76741600	2.61355400
H	-5.45332600	4.03641600	3.10404400
C	-7.46519800	0.35821800	-1.80005100
H	-7.26497700	1.34845700	-1.38571700
H	-8.33018100	-0.09656100	-1.31998700
H	-7.60847300	0.42256900	-2.88042900
C	5.38509800	0.25107000	-2.45945800
C	-4.22163100	4.27596900	1.34784300
H	-4.91587700	4.94578000	0.84802800
C	-0.82977400	-5.01327600	-1.92548700
H	-1.25009100	-5.70403000	-2.65127000
C	-3.80277800	-1.02051000	-0.09122500
H	-4.55937100	-1.14318500	0.67537800
C	0.48257200	0.12398900	-2.18979400
H	0.62615900	-0.77356700	-2.80953600
H	0.12672600	0.90383200	-2.87923700



E = -4093.89854144 a.u.

Ir	0.23962700	0.33821200	0.91032500
P	1.15808500	-1.90974900	1.30169300

P	-0.64704200	2.60920500	0.55170100
S	3.44234600	-0.05679400	-3.49524100
O	2.58871800	1.02501900	-2.62411100
O	1.19523400	1.19748900	3.73267700
O	-4.43011000	0.66352500	-2.14446600
C	1.87327900	0.84602400	-0.30041800
H	2.83785600	1.27428400	-0.03023100
O	-5.23048800	-3.61258100	-1.02656900
F	5.18751100	0.11575500	-1.50164500
F	6.03739100	-0.48538900	-3.41801500
O	-6.13957100	-0.69668400	-1.57801900
F	5.47738100	1.59464800	-3.07612200
O	3.43707300	0.38618600	-4.88026200
O	-4.61620900	-3.18145100	-3.15462200
C	-1.65991700	-0.40688200	1.34158700
H	-2.16516200	-0.44780100	2.30837100
C	1.65020100	0.60137600	-1.63247900
O	3.10091800	-1.42083600	-3.11142300
C	-0.48188900	-4.14316800	0.76365400
H	-0.77920800	-4.08509300	1.80550400
C	-0.74039100	4.02567600	-3.87931100
H	-0.75875100	4.35305800	-4.91523400
C	0.23520000	4.12276700	-1.66282200
H	0.97858100	4.54107700	-0.99300800
C	1.72396100	-3.62292700	3.45865800
H	2.48361100	-4.04298400	2.80729800
C	-2.34692000	-0.91610800	0.24861600
C	-0.43160900	-0.23805700	-0.98851800
C	2.99198800	-2.00275300	1.10497200
C	0.92361300	-2.54998200	3.02283400
C	0.84800600	0.88133400	2.68036300
C	-1.65145500	2.66384000	-2.09145700
H	-2.39076300	1.93992400	-1.76651800
C	0.42092600	0.01956200	-2.04466800
H	0.19688100	-0.18164600	-3.09040800
C	0.45379000	-3.23685400	0.23904900
C	-3.68871900	-1.60354000	0.11924700
H	-4.49171800	-1.10721800	0.67222100
H	-3.63345800	-2.63059500	0.49437000
C	0.21428600	4.53833000	-2.99762100
H	0.94415600	5.26577400	-3.34203900
C	1.72388700	3.79251400	1.59557400
H	2.24381100	2.90379200	1.26018000

C	-2.34197300	2.85335200	1.23998700
C	3.63326900	-3.08997800	0.49038700
H	3.05713000	-3.88598800	0.03235600
C	2.45683900	4.81376400	2.20637100
H	3.52958000	4.69937400	2.33486800
C	-1.67458100	3.09107100	-3.42083200
H	-2.42542500	2.68992600	-4.09601700
C	-1.70421400	-0.82769000	-1.00549800
C	0.43098500	6.10247400	2.47959400
H	-0.08053800	6.99737100	2.82307500
C	-2.59688300	2.41080100	2.55063000
H	-1.82595000	1.90037000	3.11927000
C	5.80116400	-2.17041200	1.06982700
H	6.88565700	-2.23437800	1.05431200
C	1.81243500	5.97093000	2.65117900
H	2.38116100	6.76323300	3.12994900
C	0.33657900	3.91374700	1.42020500
C	0.81829500	-3.33686700	-1.11602000
H	1.53763700	-2.64982000	-1.54876300
C	-4.62855300	-2.88622000	-1.97230100
C	5.02997400	-3.16711800	0.46847000
H	5.50928200	-4.01323400	-0.01619400
C	3.77723200	-1.00287000	1.70517500
H	3.30906000	-0.15573400	2.19545600
C	-0.69827900	3.18196000	-1.19649600
C	1.55533800	-4.16095000	4.73515400
H	2.18296900	-4.98849900	5.05402300
C	5.16985400	-1.08808400	1.69181800
H	5.75939400	-0.30721500	2.16432000
C	-0.04224400	-2.03103600	3.89646200
H	-0.67098900	-1.20414400	3.59357400
C	-0.20798800	-2.56913900	5.17706900
H	-0.95917300	-2.14934100	5.84030700
C	-3.94867300	-1.62204800	-1.43436600
C	-3.83726600	2.63589600	3.14892600
H	-4.01419800	2.29015700	4.16367200
C	0.27048000	-4.33780000	-1.92084100
H	0.57167100	-4.41038700	-2.96227700
C	-2.54208600	-1.43315600	-2.09365900
H	-2.12445100	-2.40650200	-2.38106200
H	-2.58713300	-0.82548600	-3.00059600
C	-0.30324700	5.08360700	1.86810600
H	-1.37430100	5.20616600	1.74679900

C	-1.03409000	-5.13865100	-0.04871100
H	-1.75310100	-5.83557700	0.37311000
C	-4.84673900	-0.41871500	-1.77810400
C	0.58878700	-3.63504800	5.59942400
H	0.46168400	-4.05164600	6.59477000
C	-3.35208500	3.53798800	0.54739400
H	-3.17853500	3.91390600	-0.45430200
C	-5.93377100	-4.79784600	-1.47023500
H	-6.35271100	-5.23583200	-0.56528500
H	-5.23725600	-5.48885900	-1.94987100
H	-6.72532100	-4.52051600	-2.16988000
C	-4.84539900	3.30368900	2.44471700
H	-5.81305800	3.47519600	2.90811400
C	-7.08710700	0.37122500	-1.82435100
H	-6.88303800	1.21191900	-1.15789900
H	-8.06378600	-0.06194300	-1.61351100
H	-7.02194800	0.69300600	-2.86588200
C	5.16279200	0.32502700	-2.81785100
C	-4.59809600	3.75492300	1.14662100
H	-5.36989400	4.28376900	0.59418700
C	-0.65716500	-5.24104200	-1.39016700
H	-1.08070100	-6.01944400	-2.01891600