

## Supporting information

# Selective, Radical-Free Activation of Benzylic C-H Bonds in Methylarenes

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## General experimental details

All air-sensitive manipulations were conducted under an inert atmosphere in an argon-filled Innovative Technology glovebox or by standard Schlenk technique under argon. All glassware was heated in an oven at 120 °C and cooled under vacuum prior to use.

NMR spectra were acquired on a Bruker Avance I (400 MHz) and Bruker Avance III HD (500 MHz) instruments at ambient temperature. Chemical shifts ( $\delta$ ) are reported in ppm and  $^1\text{H}$  NMR spectra are reported relative to the corresponding signals of residual protons in the deuterated solvents:  $\text{C}_6\text{D}_6$   $\delta$  7.16 ppm,  $(\text{CD}_3)_2\text{CO}$   $\delta$  2.05 ppm,  $\text{CF}_3\text{CO}_2\text{D}$  (d-TFA)  $\delta$  11.50 ppm,  $\text{C}_6\text{D}_{12}$   $\delta$  1.38 ppm.  $^{13}\text{C}$  NMR spectra are reported relative to the following signals of deuterated solvents:  $\text{C}_6\text{D}_6$ :  $\delta$  128.06 ppm,  $(\text{CD}_3)_2\text{CO}$  206.26 ppm,  $\text{CF}_3\text{CO}_2\text{D}$  (d-TFA)  $\delta$  116.60 (q) ppm. The splitting patterns are designated as follows: s (singlet), br. s (broad singlet), v. br. s (very broad singlet), d (doublet), br. d (broad doublet), v. br. d (very broad doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), app. t (apparent triplet), q (quartet), m (multiplet), br. m (broad multiplet). New compounds were assigned using HSQC, HMBC and COSY experiments where appropriate or by comparison with known analogues.

Elemental analyses were performed by the Microanalysis Laboratory of the Department of Chemistry, University of Liverpool on a Thermo Flash EA 112 Series instrument.

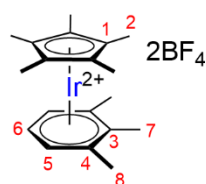
Mass spectrometry analyses were conducted by the EPSRC UK National Mass Spectrometry Facility at Swansea University and by the Microanalysis Laboratory of the Department of Chemistry, University of Liverpool. Samples containing  $[\text{Cp}^*\text{Ir}(\eta^6\text{-arene})][\text{BF}_4]_2$  complexes were sent to Swansea University in vials as solids, whilst  $[\text{Cp}^*\text{Ir}(\eta^4\text{-arene})]$  and  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{H}(\text{Ar})]$  complexes were sealed under argon in vials with Teflon-lined screw caps. High resolution mass spectra (HRMS) were recorded in the positive mode. Electrospray (ESI) and nano-Electrospray (nanoESI) ionization spectra were recorded on the OrbitrapXL; Atmospheric Pressure Ionisation spectra (APCI) were recorded on the Xevo G2S using the Atmospheric Solids Analysis Probe (ASAP).

*n*-Hexane was distilled from sodium benzophenone ketyl still and stored under argon in the glovebox. Anhydrous benzene was purchased from Alfa Aesar and stored under argon in the glovebox. Acetone was purchased from Fisher Scientific and used without further purification. The starting materials  $[\text{Cp}^*\text{IrCl}_2]_2$ ,<sup>[1]</sup>  $[\text{Cp}^*\text{Ir}(\eta^4\text{-arene})]$  (arene = toluene (**1**),<sup>[1]</sup> *o*-xylene,<sup>[2]</sup> *m*-xylene,<sup>[1]</sup> *p*-xylene,<sup>[2]</sup> mesitylene (**11**),<sup>[1]</sup>  $\text{d}_3$ -mesitylene, (**11-d<sub>3</sub>**, 98%-D)<sup>[3]</sup>,  $\text{d}_9$ -mesitylene (**11-d<sub>9</sub>**, 93%-D)<sup>[3]</sup> and hexamethylbenzene<sup>[3]</sup>) were prepared according literature or variations thereof. All other reagents were supplied commercially and used without further purification.

## General procedure for the preparation of $[\text{Cp}^*\text{Ir}(\eta^6\text{-arene})][\text{BF}_4]_2$

$[\text{Cp}^*\text{IrCl}_2]_2$  (50.0 mg, 0.063 mmol) and  $\text{AgBF}_4$  (49.0 mg, 0.252 mmol) were suspended in acetone (1 mL) and stirred for 1 h. The resultant yellow suspension was filtered and the precipitate washed with acetone until the washings became colourless. The combined filtrate and washings were reduced to *ca.* 1 mL and 8 eq. of the appropriate arene was added. The reaction mixture was stirred overnight at room temperature before evaporating to dryness. The residue was then re-dissolved in trifluoroacetic acid and passed through glass wool. Diethyl ether (*ca.* 10 mL) was added to precipitate the product and the solvents were decanted. The solid is then washed with additional amount of  $\text{Et}_2\text{O}$  and subsequently dried under vacuum at 50 °C overnight to afford the product as a white powder. Additional product can be obtained from the decanted solution and washings.

### $[\text{Cp}^*\text{Ir}(\eta^6\text{-1,2,3-trimethylbenzene})][\text{BF}_4]_2$



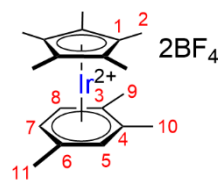
The complex was prepared according to the general procedure using 1,2,3-trimethylbenzene (67.8  $\mu\text{L}$ , 0.502 mmol) to afford  $[\text{Cp}^*\text{Ir}(\eta^6\text{-1,2,3-trimethylbenzene})][\text{BF}_4]_2$  as a white solid (96%, 74.9 mg, 0.121 mmol).

$^1\text{H}$  NMR [500 MHz,  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  7.54-7.49 (m, 3H,  $H_5+H_6$ ), 2.71 (s, 6H,  $H_8$ ), 2.54 (s, 3H,  $H_7$ ), 2.36 (s, 15H,  $H_2$ ).

$^{13}\text{C}$  NMR [126 MHz,  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  114.63 ( $C_4$ ), 113.95 ( $C_3$ ), 105.05 ( $C_1$ ), 99.16 ( $C_5$ ), 97.49 ( $C_6$ ), 17.61 ( $C_8$ ), 13.70 ( $C_7$ ), 9.25 ( $C_2$ ).

HRMS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{}^{191}\text{IrC}_{19}\text{H}_{27}]^{2+}$  223.0859, found 223.0858.

### $[\text{Cp}^*\text{Ir}(\eta^6\text{-1,2,4-trimethylbenzene})][\text{BF}_4]_2$



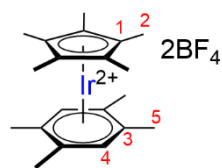
The complex was prepared according to the general procedure using 1,2,4-trimethylbenzene (68.9  $\mu\text{L}$ , 0.502 mmol) to afford  $[\text{Cp}^*\text{Ir}(\eta^6\text{-1,2,4-trimethylbenzene})][\text{BF}_4]_2$  as a white solid (93%, 72.6 mg, 0.117 mmol).

$^1\text{H}$  NMR [500 MHz,  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  7.57 (s, 1H,  $H_5$ ), 7.50-7.47 (m, 2H,  $H_7+H_8$ ), 2.70 (s, 3H,  $H_{11}$ ), 2.64 (s, 6H,  $H_9+H_{10}$ ), 2.37 (s, 15H,  $H_2$ ).

$^{13}\text{C}$  NMR [126 MHz,  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  114.98 ( $C_4$ ), 114.67 ( $C_6$ ), 113.62 ( $C_3$ ), 105.13 ( $C_1$ ), 100.01 ( $C_5$ ), 99.37 ( $C_8$ ), 98.29 ( $C_7$ ), 17.88 ( $C_{11}$ ), 16.62 ( $C_9/C_{10}$ ), 16.28 ( $C_9/C_{10}$ ), 9.25 ( $C_2$ ).

HRMS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{}^{191}\text{IrC}_{19}\text{H}_{27}]^{2+}$  223.0859, found 223.0859.

### [Cp\*Ir( $\eta^6$ -durene)][BF<sub>4</sub>]<sub>2</sub>



The complex was prepared according to the general procedure using durene (68.0 mg, 0.507 mmol) to afford [Cp\*Ir( $\eta^6$ -durene)][BF<sub>4</sub>]<sub>2</sub> as a white solid (94%, 74.9 mg, 0.118 mmol).

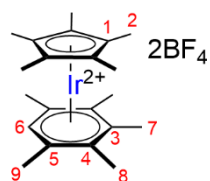
<sup>1</sup>H NMR (400 MHz, d-TFA):  $\delta$  7.13 (br. s, 2H, *H4*), 2.50 (s, 12H, *H5*), 2.22 (s, 15H, *H2*).

<sup>13</sup>C NMR (100 MHz, d-TFA):  $\delta$  115.35 (*C3*), 106.01 (*C1*), 101.61 (*C4*), 17.00 (*C5*), 9.59 (*C2*).

C<sub>20</sub>H<sub>29</sub>B<sub>2</sub>F<sub>8</sub>Ir requires C 37.81, H 4.60. Found: C 37.60, H 4.51%.

HRMS (nanoESI+): *m/z* calculated for [<sup>191</sup>IrC<sub>20</sub>H<sub>29</sub>]<sup>2+</sup> 230.0938, found 230.0934.

### [Cp\*Ir( $\eta^6$ -pentamethylbenzene)][BF<sub>4</sub>]<sub>2</sub>



The complex was prepared according to the general procedure using pentamethylbenzene (74.4 mg, 0.502 mmol) to afford [Cp\*Ir( $\eta^6$ -pentamethylbenzene)][BF<sub>4</sub>]<sub>2</sub> as a white solid (92%, 74.6 mg, 0.115 mmol).

<sup>1</sup>H NMR [500 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  7.52 (s, 1H, *H6*), 2.64 (s, 6H, *H9*), 2.58 (s, 3H, *H7*), 2.54 (s, 6H, *H8*), 2.24 (s, 15H, *H2*).

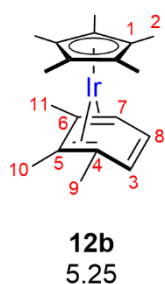
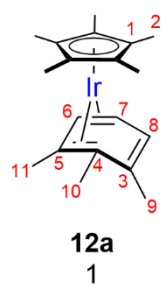
<sup>13</sup>C NMR [126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  112.83 (*C5*), 112.59 (*C3*), 112.32 (*C4*), 103.42 (*C1*), 99.67 (*C6*), 17.59 (*C9*), 15.04 (*C7*), 14.45 (*C8*), 8.37 (*C2*).

HRMS (ESI+): *m/z* calculated for [<sup>191</sup>IrC<sub>21</sub>H<sub>31</sub>]<sup>2+</sup> 237.1016, found 237.1016.

## General procedure for the preparation of [Cp\*Ir( $\eta^4$ -arene)]

In a glovebox, [Cp\*Ir( $\eta^6$ -arene)][BF<sub>4</sub>]<sub>2</sub> (0.077-0.080 mmol) and two eq. of CoCp<sub>2</sub> (0.154-0.161 mmol) were suspended in benzene (1 mL). The resultant mixture was stirred vigorously for 2 h. Hexane (8 mL) was then added, and the yellow/orange suspension was filtered through glass wool. The precipitate was washed with additional hexane until the washings remained colourless. The combined filtrate and washings were evaporated to dryness to afford the product as a residue/oil. Product ratios were calculated from relative integrals in their respective <sup>1</sup>H NMR spectrum.

### [Cp\*Ir( $\eta^4$ -1,2,3-trimethylbenzene)] (12)



Complex **12** was prepared according to the general procedure using [Cp\*Ir( $\eta^6$ -1,2,3-trimethylbenzene)][BF<sub>4</sub>]<sub>2</sub> (50.0 mg, 0.080 mmol) and CoCp<sub>2</sub> (30.4 mg, 0.161 mmol) to afford [Cp\*Ir( $\eta^4$ -1,2,3-trimethylbenzene)] (**12**) as a brown solid (99%, 35.8 mg, 0.080 mmol).

#### Compound **12a**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.54 (d,  $J$  = 4.8 Hz, 1H, *H*6), 5.37 (m, 1H, *H*8), 3.01 (app. t,  $J$  = 4.4 Hz, 1H, *H*7), 2.07 (s, 1H, *H*11), 1.76 (s, 15H, *H*2), 1.61 (d, 3H, *H*9), 1.31 (s, 3H, *H*10).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  140.94 (*C*3), 126.55 (*C*8), 88.61 (*C*1), 79.60 (*C*5), 70.90 (*C*6), 53.32 (*C*4), 44.95 (*C*7), 18.38 (*C*10), 15.76 (*C*9), 15.61 (*C*11), 10.16 (*C*2).

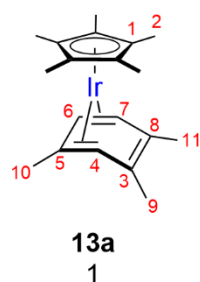
#### Compound **12b**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.66 (dd,  $J$  = 6.2, 4.3 Hz, 1H, *H*8), 5.33 (dd,  $J$  = 6.2, 1.8 Hz, 1H, *H*3), 2.93 (dd,  $J$  = 4.3, 1.8 Hz, 1H, *H*7), 2.01 (s, 1H, *H*11), 1.94 (s, 3H, *H*10), 1.70 (s, 15H, *H*2), 1.35 (s, 3H, *H*9).

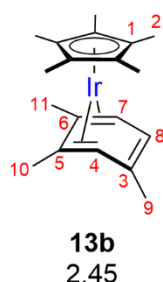
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  134.97 (*C*3), 130.56 (*C*8), 88.23 (*C*1), 79.46 (*C*6), 78.49 (*C*5), 54.24 (*C*4), 51.18 (*C*7), 20.70 (*C*9), 18.88 (*C*11), 13.50 (*C*10), 9.93 (*C*2).

HRMS (ESI<sup>+</sup>):  $m/z$  calculated for [<sup>191</sup>IrC<sub>19</sub>H<sub>26</sub>]<sup>+</sup> 445.1641, found 445.1631.

### [Cp\*Ir( $\eta^4$ -1,2,4-trimethylbenzene)] (**13**)



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Complex **13** was prepared according to the general procedure using [Cp\*Ir( $\eta^6$ -1,2,4-trimethylbenzene)][BF<sub>4</sub>]<sub>2</sub> (50.0 mg, 0.080 mmol) and CoCp<sub>2</sub> (30.4 mg, 0.161 mmol) to afford [Cp\*Ir( $\eta^4$ -1,2,4-trimethylbenzene)] as an orange/brown solid (98%, 35.4 mg, 0.079 mmol).

#### Compound **13a**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.55 (d,  $J$  = 4.7 Hz, 1H, *H*<sub>6</sub>), 3.00 (d,  $J$  = 4.7 Hz, 1H, *H*<sub>7</sub>), 2.83 (s, 1H, *H*<sub>4</sub>), 2.09 (s, 3H, *H*<sub>10</sub>), 1.84 (s, 15H, *H*<sub>2</sub>), 1.55 (d,  $J$  = 1.0 Hz, 3H, *H*<sub>9</sub>), 1.51 (d,  $J$  = 1.0 Hz, 3H, *H*<sub>11</sub>).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  130.59 (*C*<sub>8</sub>), 129.67 (*C*<sub>3</sub>), 88.72 (*C*<sub>1</sub>), 77.99 (*C*<sub>5</sub>), 68.14 (*C*<sub>6</sub>), 54.18 (*C*<sub>4</sub>), 51.54 (*C*<sub>7</sub>), 19.45 (*C*<sub>10</sub>), 16.78 (*C*<sub>9</sub>), 16.66 (*C*<sub>11</sub>), 10.51 (*C*<sub>2</sub>).

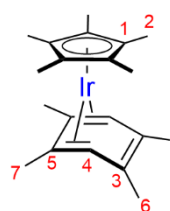
#### Compound **13b**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.18 (m, 1H, *H*<sub>8</sub>), 2.92 (d,  $J$  = 4.4 Hz, 1H, *H*<sub>7</sub>), 2.75 (d,  $J$  = 1.9 Hz, 1H, *H*<sub>4</sub>), 2.04 (s, 3H, *H*<sub>10</sub>), 2.02 (s, 3H, *H*<sub>11</sub>), 1.78 (s, 15H, *H*<sub>2</sub>), 1.61 (d,  $J$  = 1.9 Hz, 3H, *H*<sub>9</sub>).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  139.62 (*C*<sub>3</sub>), 125.02 (*C*<sub>8</sub>), 88.38 (*C*<sub>1</sub>), 78.33 (*C*<sub>5</sub>), 77.65 (*C*<sub>6</sub>), 55.11 (*C*<sub>4</sub>), 44.93 (*C*<sub>7</sub>), 18.35 (*C*<sub>10</sub>), 18.24 (*C*<sub>11</sub>), 18.05 (*C*<sub>9</sub>), 10.27 (*C*<sub>2</sub>).

HRMS (ESI<sup>+</sup>):  $m/z$  calculated for [<sup>191</sup>IrC<sub>19</sub>H<sub>26</sub>]<sup>+</sup> 445.1641, found 445.1635.

### [Cp\*Ir( $\eta^4$ -durene)]



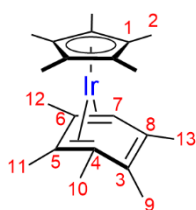
The complex was prepared according to the general procedure using [Cp\*Ir( $\eta^6$ -durene)][BF<sub>4</sub>]<sub>2</sub> (50.0 mg, 0.079 mmol) and CoCp<sub>2</sub> (29.8 mg, 0.158 mmol) to afford [Cp\*Ir( $\eta^4$ -durene)] as a brown solid (98%, 35.8 mg, 0.078 mmol).

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.84 (s, 2H, *H*<sub>4</sub>), 2.03 (s, 6H, *H*<sub>7</sub>), 1.80 (s, 15H, *H*<sub>2</sub>), 1.55 (s, 6H, *H*<sub>6</sub>).

<sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  130.02 (*C*<sub>3</sub>), 88.25 (*C*<sub>1</sub>), 77.32 (*C*<sub>5</sub>), 55.26 (*C*<sub>4</sub>), 18.17 (*C*<sub>7</sub>), 16.81 (*C*<sub>6</sub>), 10.38 (*C*<sub>2</sub>).

HRMS (ASAP):  $m/z$  calculated for [<sup>191</sup>IrC<sub>20</sub>H<sub>28</sub>]<sup>+</sup> 459.1797, found 459.1791.

### [Cp\*Ir( $\eta^4$ -pentamethylbenzene)]



The complex was prepared according to the general procedure using [Cp\*Ir( $\eta^6$ -pentamethylbenzene)][BF<sub>4</sub>]<sub>2</sub> (50.0 mg, 0.077 mmol) and CoCp<sub>2</sub> (29.1 mg, 0.154 mmol) to afford [Cp\*Ir( $\eta^4$ -pentamethylbenzene)] as an orange solid (99%, 36.1 mg, 0.077 mmol).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.77 (s, 1H, *H*7), 2.01 (s, 3H, *H*12), 1.96 (s, 3H, *H*11), 1.73 (s, 15H, *H*2), 1.57 (d, *J* = 1.1 Hz, 3H, *H*13), 1.51 (d, *J* = 1.1 Hz, 3H, *H*9), 1.43 (s, 3H, *H*10).

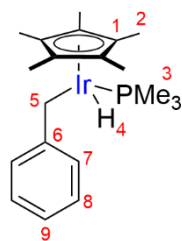
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  131.70 (*C*8), 131.02 (*C*3), 88.35 (*C*1), 78.48 (*C*5), 78.06 (*C*6), 54.49 (*C*4), 54.47 (*C*7), 19.99 (*C*10), 18.67 (*C*12), 17.31 (*C*13), 13.81 (*C*9), 13.48 (*C*11), 9.91 (*C*2).

HRMS (ESI<sup>+</sup>): *m/z* calculated for [<sup>191</sup>IrC<sub>19</sub>H<sub>26</sub>]<sup>+</sup> 473.1954, found 473.1947.

## General procedure for the reaction of [Cp\*Ir( $\eta^4$ -arene)] complexes with PMe<sub>3</sub>

In a glovebox, a 4 mL vial equipped with a Teflon-lined screw cap was charged with a hexane (2 mL) solution of [Cp\*Ir( $\eta^4$ -arene)] (0.044-0.116 mmol) and a stirrer bar. Four eq. of trimethylphosphine (0.181-0.465 mmol) was then added to the reaction mixture. The vial was sealed, taken out from the glovebox, placed into an aluminium heating block and the reaction mixture was stirred at 100 °C for a specified time and then cooled to room temperature. Upon cooling, the mixture was passed through glass wool and the filtrate was dried under vacuum to afford the product as a yellow/brown residue. Product ratios calculated from relative integrals in their respective <sup>1</sup>H NMR spectrum.

### [Cp\*Ir(PMe<sub>3</sub>)(H)(benzyl)] (2a)



Thermolysis of **1** (33.0 mg, 0.079 mmol) was conducted according to the general procedure using PMe<sub>3</sub> (32.6  $\mu$ L, 0.321 mmol) in hexane (2 mL) with a reaction time of 1 h to yield an orange solid (97%, 37.9 mg, 0.076 mmol) as a mixture of products. The complex [Cp\*Ir(PMe<sub>3</sub>)(H)(benzyl)] (**2a**) was identified as the major component (90%) and the remaining species are assigned to the known [Cp\*Ir(PMe<sub>3</sub>)(H)(tolyl)] complexes (10%) identified by their hydride signals.<sup>[4]</sup>

#### Compound **2a**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.53 (d,  $J$  = 8.0 Hz, 2H, *H*7), 7.24 (app. t,  $J$  = 7.8 Hz, 2H, *H*8), 7.24 (t,  $J$  = 7.3 Hz, 1H, *H*9), 3.13 (app. t,  $J$  = 3.1 Hz, 1H, *H*5), 2.98 (dd,  $J$  = 10.9, 3.1 Hz, 1H, *H*5), 1.73 (d,  $J$  = 1.7 Hz, 15H, *H*2), 1.16 (d,  $J_{P-H}$  = 9.6 Hz, 9H, *H*3), -17.31 (d,  $J_{P-H}$  = 36.5 Hz, 1H, *H*4).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  155.82 (d,  $J_{P-C}$  = 3.9 Hz, *C*6), 129.72 (*C*7), 127.48 (*C*8), 122.48 (*C*9), 91.83 (d,  $J_{P-C}$  = 3.6 Hz, *C*1), 19.15 (d,  $J_{P-C}$  = 36.3 Hz, *C*3), 10.12 (*C*2), -7.12 (d,  $J_{P-C}$  = 6.4 Hz, *C*5).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -45.31 (s).

HRMS (ASAP):  $m/z$  calculated for [<sup>191</sup>IrC<sub>20</sub>H<sub>31</sub>P]<sup>+</sup> 493.1769, found 493.1765.



Side products [Cp\*Ir(PMe<sub>3</sub>)(H)(tolyl)]

N.B. The *meta*- and *para*-isomers are not distinguished due to overlapped signals.

[Cp\*Ir(PMe<sub>3</sub>)(H)(*o*-tolyl)]

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.0 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 2.63 (s, 3H), 1.78 (s, 15H), 1.03 (d, *J*<sub>P-H</sub> = 10.0 Hz, 9H), -16.65 (d, *J*<sub>P-H</sub> = 39.0 Hz, 1H).

[Cp\*Ir(PMe<sub>3</sub>)(H)(*m*-tolyl)]

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.64 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H), 1.82 (s, 15H), 1.11 (d, *J*<sub>P-H</sub> = 10.4 Hz, 9H), -17.07 (d, *J*<sub>P-H</sub> = 37.0 Hz, 1H).

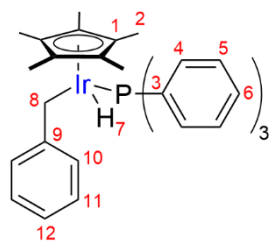
<sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ -41.54 (s).

[Cp\*Ir(PMe<sub>3</sub>)(H)(*p*-tolyl)]

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.63 (d, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.82 (s, 15H), 1.10 (d, *J*<sub>P-H</sub> = 10.0 Hz, 9H), -17.06 (d, *J*<sub>P-H</sub> = 35.0 Hz, 1H).

<sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ -41.63 (s).

### [Cp\*Ir(PPh<sub>3</sub>)(H)(benzyl)] (**2b**)



Complex **2b** was prepared according to the general procedure using four equivalents of triphenylphosphine instead of trimethylphosphine.

Thus, a mixture of **1** (18.6 mg, 0.044 mmol) and PPh<sub>3</sub> (47.4 mg, 0.181 mmol) in hexane (2 mL) was stirred at 100 °C for 1 h. The crude product mixture of [Cp\*Ir(PPh<sub>3</sub>)(H)(benzyl)] and excess PPh<sub>3</sub> was

isolated as a dark brown residue (65.8 mg). The yield of **2b** (96%) was determined by <sup>1</sup>H NMR spectroscopy, using HMDSO (5.0 μL) as an internal standard. Suitable crystals were grown in cold pentane for single crystal XRD analysis. The product contained a trace amount of a second hydride-containing product tentatively identified as [Cp\*Ir(PPh<sub>3</sub>)(H)(tolyl)] by <sup>1</sup>H NMR.

N.B. Phenyl groups of **2b** were not fully assigned due to overlapping signals with free PPh<sub>3</sub> (see its NMR data below).

#### Compound **2b**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.66-7.6 (m, 6H, *H4*), 7.48 (d, *J* = 7.6 Hz, 2H, *H10*), 7.20 (app. t, *J* = 7.6 Hz, 2H, *H11*), 7.09-6.98 (overlapped with PPh<sub>3</sub>, 10H, *H5+H6+H12*), 3.50 (app. t, *J* = 10.6 Hz, 1H, *H8*), 2.75 (dd, *J* = 11.4, 1.1 Hz, 1H, *H8*), 1.49 (d, *J* = 1.6 Hz, 15H, *H2*), -16.39 (d, *J*<sub>P-H</sub> = 34.9 Hz, 1H, *H7*).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  154.22 (d,  $J_{\text{P-C}} = 4.2$  Hz, C9), 135.85 (d,  $J_{\text{P-C}} = 51.7$  Hz, C3), 134.00 (d overlapped with  $\text{PPh}_3$ , C4), 129.99 (C10), 129.35 (d,  $J_{\text{P-C}} = 1.9$  Hz, C5), 127.95 (C6), 127.36 (C11), 122.63 (C12), 93.06 (d,  $J_{\text{P-C}} = 4.1$  Hz, C1), 9.38 (C2), -3.24 (d,  $J_{\text{P-C}} = 5.4$  Hz, C8).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  20.58 (s).

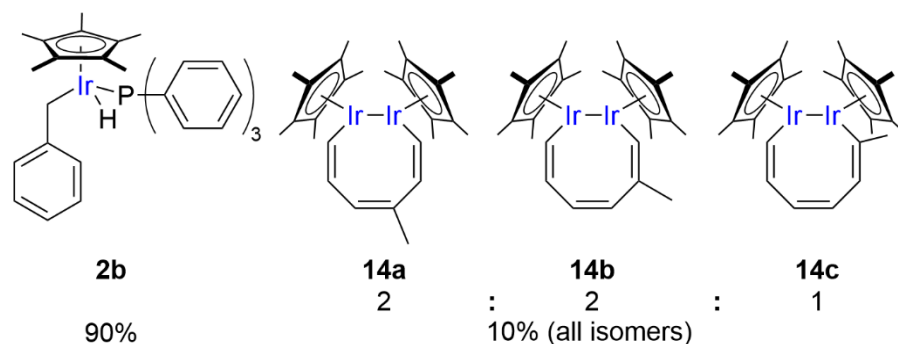
HRMS (ESI+):  $m/z$  calculated for  $[\text{IrC}_{35}\text{H}_{37}\text{P}]^+$  679.2239, found 679.2233.

$\text{PPh}_3$ :  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ): 7.41-7.37 (m), 7.07-7.04 (m).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ): 138.02 (d), 134.19 (d), 128.87 (d), 128.81 (s).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ): -5.29 (s).

### [Cp\*Ir(PPh<sub>3</sub>)(H)(benzyl)] (2b) using one equivalent of PPh<sub>3</sub>



Complex **2b** was prepared according to the general procedure using only one equivalent of triphenylphosphine instead of

trimethylphosphine. Thus, a mixture of **1** (43.1 mg, 0.103 mmol) and  $\text{PPh}_3$  (26.9 mg, 0.103 mmol) in hexane (2 mL) was heated at 100 °C for 1 h. Removal of volatiles *in vacuo* afforded a brown solid (67.1 mg).  $^1\text{H}$  NMR spectrum revealed the product to be a mixture of **2b** (90%) and the known iridacycles **14** (10%)<sup>[1]</sup> as well as residual free  $\text{PPh}_3$ . Product ratios were determined by their respective relative integrals in the  $^1\text{H}$  NMR spectrum.

#### Compound **14a**

$^1\text{H}$  NMR: 5.42 (d,  $J = 6.6$  Hz, 1H), 5.05 (t,  $J = 6.9$  Hz, 1H).

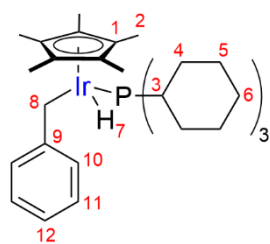
#### Compound **14b**

$^1\text{H}$  NMR: 5.81-5.70 (m, 1H), 5.55 (d,  $J = 8.8$  Hz, 1H), 4.96-4.91 (m, 1H).

#### Compound **14c**

$^1\text{H}$  NMR: 5.81-5.70 (m, 2H), 4.96-4.91 (m, 1H).

### [Cp\*Ir(PCy<sub>3</sub>)(H)(benzyl)] (**2c**)



Complex **2c** was prepared according to the general procedure using four equivalents of tricyclohexylphosphine instead of trimethylphosphine. Thus, a mixture of **1** (20.0 mg, 0.048 mmol) and PCy<sub>3</sub> (54.6 mg, 0.195 mmol) in hexane (2 mL) was stirred at 100 °C for 1 h. The crude product mixture of [Cp\*Ir(PCy<sub>3</sub>)(H)(benzyl)] and residual PCy<sub>3</sub> was isolated as a light brown solid (73.7 mg). The yield of **2c** (94%) was determined by <sup>1</sup>H NMR spectroscopy, using HMDSO (5.0 μL) as an internal standard. The product contained a trace amount of a second hydride-containing product tentatively identified as [Cp\*Ir(PCy<sub>3</sub>)(H)(tolyl)] by <sup>1</sup>H NMR, and tricyclohexylphosphine oxide resulting from impurity in the commercial PCy<sub>3</sub> reagent.

N.B. Cyclohexyl groups of **2c** were not assigned due to overlapping signals with free PCy<sub>3</sub> and OPCy<sub>3</sub> (see their NMR data below).

#### Compound **2c**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.58 (d, *J* = 7.5 Hz, 2H, *H*10), 7.24 (app. t, *J* = 7.6 Hz, 2H, *H*11), 7.02 (app. t, *J* = 7.3 Hz, 1H, *H*12), 3.48 (dd, *J* = 11.9, 8.0 Hz, 1H, *H*8), 2.81 (d, *J* = 12.0 Hz, 1H, *H*8), 1.89-1.09 (m overlapped with PCy<sub>3</sub>, 33H, *H*3-*H*6), 1.75 (d, *J* = 0.9 Hz, 15H, *H*2), -17.87 (d, *J*<sub>P-H</sub> = 35.1 Hz, 1H, *H*7).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>): δ 154.64 (d, *J*<sub>P-C</sub> = 1.7 Hz, *C*9), 130.38 (*C*10), 127.38 (*C*11), 122.74 (*C*12), 92.0 (d, *J*<sub>P-C</sub> = 2.7 Hz, *C*1), 36.10 (d, *J*<sub>P-C</sub> = 28.7 Hz, *C*3), 30.38 (*C*4), 29.50 (*C*5), 27.35 (merged with OPCy<sub>3</sub>, *C*6), 10.82 (*C*2), -8.33 (m, *C*8).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>): δ 15.65 (s).

HRMS (ESI<sup>+</sup>): *m/z* calculated for [<sup>191</sup>IrC<sub>28</sub>H<sub>47</sub>P]<sup>+</sup> (*M* - C<sub>7</sub>H<sub>8</sub>) 605.3021, found 605.3001.

#### PCy<sub>3</sub>

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): 1.89-1.09 (m).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>): 32.26 (d, *J*<sub>P-C</sub> = 18.4 Hz), 31.71 (d, *J*<sub>P-C</sub> = 12.4 Hz), 28.06 (d, *J*<sub>P-C</sub> = 9.1 Hz), 26.99 (s).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>): 9.85 (s).

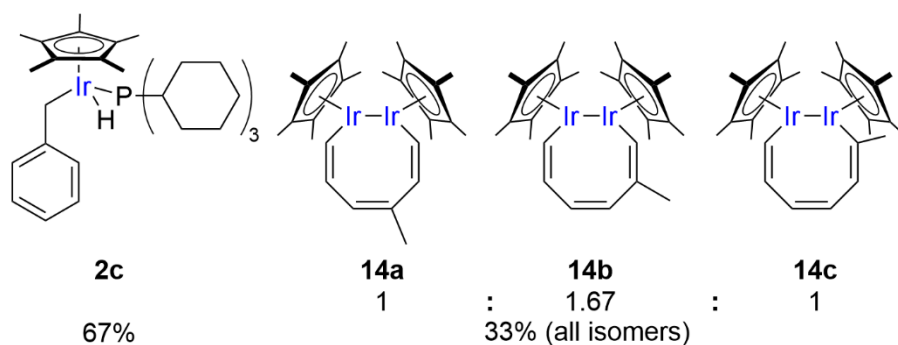
#### OPCy<sub>3</sub>

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): 1.89-1.09 (m).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>): 35.81 (d, *J*<sub>P-C</sub> = 60.8 Hz), 27.30 (d, *J*<sub>P-C</sub> = 10.6 Hz), 26.85 (d, *J*<sub>P-C</sub> = 2.7 Hz), 26.63 (s).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>): 45.36 (s).

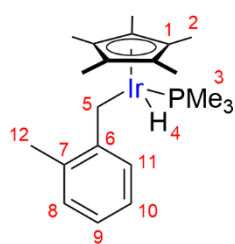
### Attempt of preparation of [Cp\*Ir(PCy<sub>3</sub>)(H)(benzyl)] (**2c**) using one equivalent of PCy<sub>3</sub>



In this experiment, the synthesis of complex **2c** was attempted according to the procedure described above using only one

equivalent of tricyclohexylphosphine. Thus, a mixture of **1** (41.5 mg, 0.099 mmol) and PCy<sub>3</sub> (27.7 mg, 0.099 mmol) in hexane (2 mL) was stirred at 100 °C for 1 h. Removal of volatiles *in vacuo* afforded a brown solid (65.4 mg). <sup>1</sup>H NMR spectrum revealed the product to be a mixture of **2c** (67%) and the known iridacycles **14** (33%)<sup>[1]</sup> as well as residual free PCy<sub>3</sub>. Product ratios were determined by their respective relative integrals in the <sup>1</sup>H NMR spectrum.

### [Cp\*Ir(PMe<sub>3</sub>)(H)(2-methylbenzyl)] (**3**)



Complex **3** was prepared according to the general procedure using [Cp\*Ir( $\eta^4$ -*o*-xylene)] (25.3 mg, 0.058 mmol) and PMe<sub>3</sub> (23.7  $\mu$ L, 0.233 mmol) in hexane (2 mL) with a reaction time of 2 h. The product [Cp\*Ir(PMe<sub>3</sub>)(H)(2-methylbenzyl)] was isolated as a light brown solid (94%, 28.0 mg, 0.055 mmol).

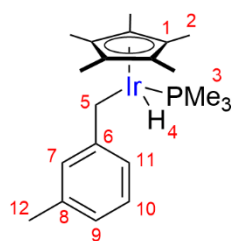
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.41 (d,  $J$  = 7.4 Hz, 1H, *H11*), 7.15-7.13 (m, merged with solvent signal, 3H, *H8+9*), 7.06 (app. t,  $J$  = 7.2 Hz, 1H, *H10*), 2.93 (d,  $J$  = 5.3 Hz, 2H, *H5*), 2.48 (s, 3H, *H12*), 1.72 (d,  $J_{\text{P-H}}$  = 1.5 Hz, 15H, *H2*), 1.09 (d,  $J_{\text{P-H}}$  = 9.7 Hz, 9H, *H3*), -17.48 (d,  $J_{\text{P-H}}$  = 38.0 Hz, 1H, *H4*).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  153.76 (d,  $J_{\text{P-C}}$  = 2.9 Hz, *C6*), 135.47 (*C7*), 130.39 (*C8*), 129.92 (*C11*), 125.13 (*C9*), 122.87 (*C10*), 91.80 (d,  $J_{\text{P-C}}$  = 3.3 Hz, *C1*), 20.20 (*C12*), 19.29 (d,  $J_{\text{P-C}}$  = 36.2 Hz, *C3*), 9.99 (*C2*), -11.55 (d,  $J_{\text{P-C}}$  = 6.5 Hz, *C5*).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -45.85 (s).

HRMS (ESI<sup>+</sup>):  $m/z$  calculated for [<sup>191</sup>IrC<sub>21</sub>H<sub>33</sub>P]<sup>+</sup> 507.1926, found 507.1911.

### [Cp\*Ir(PMe<sub>3</sub>)(H)(3-methylbenzyl)] (**4**)



Complex **4** was prepared according to the general procedure using [Cp\*Ir( $\eta^4$ -*m*-xylene)] (29.0 mg, 0.067 mmol) and PMe<sub>3</sub> (27.3  $\mu$ L, 0.268 mmol) in hexane (2 mL) with a reaction time of 1 h. The product [Cp\*Ir(PMe<sub>3</sub>)(H)(3-methylbenzyl)] was isolated as a brown solid (92%, 31.3 mg, 0.061 mmol).

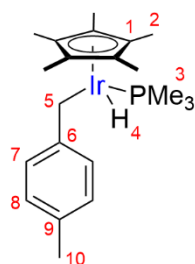
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.39 (s, 1H, *H*7), 7.36 (d, *J* = 8.1 Hz, 1H, *H*11), 7.20 (d, *J* = 7.4 Hz, 1H, *H*10), 6.86 (d, *J* = 7.3 Hz, 1H, *H*9), 3.13 (dd, *J* = 10.8, 8.7 Hz, 1H, *H*5), 3.01 (dd, *J* = 10.8, 2.1 Hz, 1H, *H*5), 2.31 (s, 3H, *H*12), 1.75 (d, *J*<sub>P-H</sub> = 1.1 Hz, 15H, *H*2), 1.17 (d, *J*<sub>P-H</sub> = 9.7 Hz, 9H, *H*3), -17.30 (d, *J*<sub>P-H</sub> = 36.5 Hz, 1H, *H*4).

<sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  155.55 (d, *J*<sub>P-C</sub> = 3.4 Hz, *C*6), 136.08 (*C*8), 130.71 (*C*7), 127.36 (*C*10), 126.92 (*C*11), 123.23 (*C*9), 91.80 (d, *J*<sub>P-C</sub> = 3.5 Hz, *C*1), 21.79 (*C*12), 19.11 (d, *J*<sub>P-C</sub> = 36.4 Hz, *C*3), 10.08 (*C*2), -7.32 (d, *J*<sub>P-C</sub> = 6.6 Hz, *C*5).

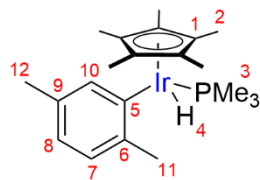
<sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -45.32 (s).

HRMS (ASAP): *m/z* calculated for [<sup>191</sup>IrC<sub>21</sub>H<sub>33</sub>P]<sup>+</sup> 507.1926, found 507.1933.

### [Cp\*Ir(PMe<sub>3</sub>)(H)(4-methylbenzyl)] (**5a**) and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,5-dimethylphenyl)] (**5b**)



**5a**  
2.23



**5b**  
1

Thermolysis of [Cp\*Ir( $\eta^4$ -*p*-xylene)] (50.4 mg, 0.116 mmol) was conducted according to the general procedure using PMe<sub>3</sub> (47.3  $\mu$ L, 0.465 mmol) in hexane (2 mL) with a reaction time of 1 h to yield a brown oil (53.0 mg). According to the <sup>1</sup>H NMR spectrum, the oil contained 65% of [Cp\*Ir(PMe<sub>3</sub>)(H)-(4-methylbenzyl)] (**5a**) and 27%

of [Cp\*Ir(PMe<sub>3</sub>)(H)(2,5-dimethylphenyl)] (**5b**), previously prepared by Bergman.<sup>[5]</sup> Two additional unidentified hydride signals were also noted in the <sup>1</sup>H NMR spectrum (total 8%) which, due to their similar integrals, can be sourced from either one or two species. HRMS shows low abundance *m/z* peaks corresponding to [(Cp\*Ir)<sub>2</sub>(*p*-xylene)]+H<sup>+</sup> so these trace products are tentatively assigned as products of double C-H activation by two iridium centres.

#### Compound **5a**

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.46 (d, *J* = 7.9 Hz, 2H, *H*7), 7.07 (d, *J* = 7.9 Hz, 2H, *H*8), 3.10 (dd, *J* = 10.8, 8.2 Hz, 1H, *H*5), 3.98 (dd, *J* = 10.8, 3.0 Hz, 1H, *H*5), 2.25 (s, 3H, *H*10), 1.75 (m, 15H, *H*2), 1.17 (d, *J*<sub>P-H</sub> = 9.6 Hz, 9H, *H*3), -17.31 (d, *J*<sub>P-H</sub> = 36.6 Hz, 1H, *H*4).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  152.45 (d,  $J_{\text{P-C}} = 3.3$  Hz, C6), 131.00 (C9), 129.68 (C7), 128.16 (C8), 91.78 (d,  $J_{\text{P-C}} = 3.4$  Hz, C1), 21.24 (C10), 19.21 (d,  $J_{\text{P-C}} = 36.3$  Hz, C3), 10.18 (C2), -7.60 (d,  $J_{\text{P-C}} = 6.4$  Hz, C5).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -45.25 (s).

#### Compound **5b**

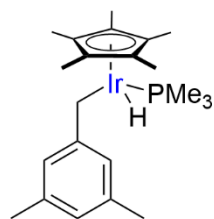
$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.44 (d,  $J = 1.7$  Hz, 1H, H10), 7.30 (d,  $J = 7.5$  Hz, 1H, H7), 6.90 (dd,  $J = 7.5, 1.7$  Hz, 1H, H8), 2.61 (s, 3H, H11), 2.37 (s, 3H, H12), 1.81 (m, 15H, H2), 1.07 (d,  $J_{\text{P-H}} = 10.0$  Hz, 9H, H3), -16.69 (d,  $J_{\text{P-H}} = 39.8$  Hz, 1H, H4).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  155.48 (C6), 144.63 (d,  $J_{\text{P-C}} = 6.8$  Hz, C10), 143.24 (C5), 131.98 (C9), 127.63 (C7), 122.57 (C8), 92.37 (d,  $J_{\text{P-C}} = 3.6$  Hz, C1), 31.69 (C11), 21.09 (C12), 18.84 (d,  $J_{\text{P-C}} = 38.2$  Hz, C3), 10.48 (C2).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -41.75 (s).

HRMS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{}^{191}\text{IrC}_{21}\text{H}_{33}\text{P}]^+$  507.1926, found 507.1921.

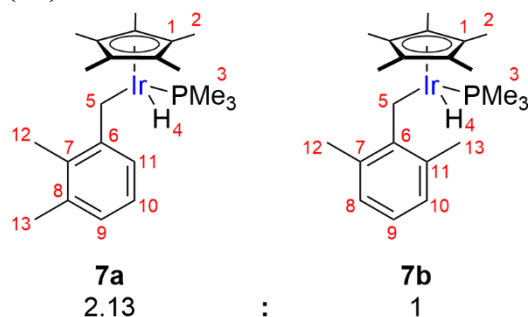
#### [Cp\*Ir(PMe<sub>3</sub>)(H)(3,5-dimethylbenzyl)] (**6**)



Complex **6** was prepared according to the general procedure using **11** (32.0 mg, 0.071 mmol) and  $\text{PMe}_3$  (29.6  $\mu\text{L}$ , 0.286 mmol) in hexane (2 mL) with a reaction time of 1 h. The product [Cp\*Ir(PMe<sub>3</sub>)(H)(3,5-dimethylbenzyl)] was isolated as a light brown solid (91%, 33.9 mg, 0.065 mmol).  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the product agreed

with the literature data.<sup>[3]</sup>

#### [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3-dimethylbenzyl)] (**7a**) and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,6-dimethylbenzyl)] (**7b**)



Thermolysis of **12** (35.5 mg, 0.079 mmol) was conducted according to the general procedure using  $\text{PMe}_3$  (32.3  $\mu\text{L}$ , 0.318 mmol) in hexane (2 mL) with a reaction time of 3 h to give a mixture of [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3-dimethylbenzyl)] and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,6-dimethylbenzyl)] as a dark

brown oil (99%, 41.3 mg, 0.079 mmol).

#### Compound **7a**

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.29 (d,  $J = 7.6$  Hz, 1H, H11), 7.07 (app. t,  $J = 7.5$  Hz, 1H, H10), 6.97 (d,  $J = 7.4$  Hz, 1H, H9), 2.97 (d,  $J = 5.3$ , 2H, H5), 2.36 (s, 3H, H12), 2.28 (s, 3H, H13),

1.73 (dd,  $J = 1.8, 0.6$  Hz, 15H,  $H_2$ ), 1.09 (d,  $J_{P-H} = 9.9$  Hz, 9H,  $H_3$ ), -17.50 (d,  $J_{P-H} = 38.3$  Hz, 1H,  $H_4$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  153.53 (d,  $J_{P-C} = 2.7$  Hz,  $C_6$ ), 136.02 ( $C_8$ ), 133.91 ( $C_7$ ), ~128 (overlapped with solvent signal,  $C_{11}$ ), 124.79 ( $C_9$ ), 124.37 ( $C_{10}$ ), 91.74 (d,  $J_{P-C} = 3.6$  Hz,  $C_1$ ), 21.23 ( $C_{12}$ ), 19.34 (d,  $J_{P-C} = 36.0$  Hz,  $C_3$ ), 15.61 ( $C_{13}$ ), 9.98 ( $C_2$ ), -10.50 (m,  $C_5$ ).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -45.82 (s).

Compound **7b** (Partial assignment)

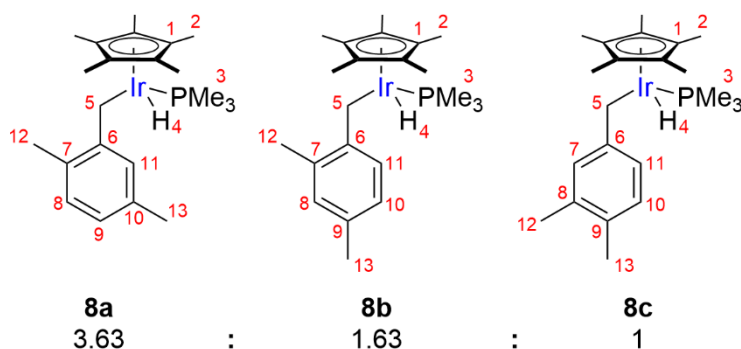
$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.08-7.05 (m, 2H,  $H_8+10$ ), 7.01 (dd,  $J = 8.19, 6.4$  Hz, 1H,  $H_9$ ), 1.65 (br. s, 15H,  $H_2$ ), 1.08 (br. d, 9H,  $H_3$ ), -17.44 (d,  $J_{P-H} = 39.3$  Hz, 1H,  $H_4$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  ~128 (overlapped with solvent signal,  $C_8+C_{10}$ ), 121.83 ( $C_9$ ), 91.80 (d,  $J_{P-C} = 3.7$  Hz,  $C_1$ ), 19.20 (v. br. d,  $J_{P-C} = 32.6$  Hz,  $C_3$ ), 9.93 ( $C_2$ ).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -47.53 (v. br. s).

HRMS (ESI+):  $m/z$  calculated for  $[\text{IrC}_{22}\text{H}_{35}\text{P}]^+$  521.2082, found 521.2071.

**[Cp\*Ir(PMe<sub>3</sub>)(H)(2,5-dimethylbenzyl)] (8a)**, **[Cp\*Ir(PMe<sub>3</sub>)(H)(2,4-dimethylbenzyl)] (8b)**  
and **[Cp\*Ir(PMe<sub>3</sub>)(H)(3,4-dimethylbenzyl)] (8c)**



Thermolysis of **13** (35.0 mg, 0.078 mmol) was conducted according to the general procedure using  $\text{PMe}_3$  (31.8  $\mu\text{L}$ , 0.313 mmol) in hexane (2 mL) with a reaction time of 2 h to give a mixture of  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(2,5\text{-dimethylbenzyl})]$ ,

$[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(2,4\text{-dimethylbenzyl})]$  and  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(3,4\text{-dimethylbenzyl})]$  as a brown oil (94%, 38.4 mg, 0.073 mmol).

Compound **8a**

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.25 (s, 1H,  $H_{11}$ ), 7.08 (d,  $J = 7.6$  Hz, 1H,  $H_8$ ), 6.87 (d,  $J = 7.6$  Hz, 1H,  $H_9$ ), 2.94 (dd,  $J = 5.2, 2.5$  Hz, 2H,  $H_5$ ), 2.47 (s, 3H,  $H_{12}$ ), 2.34 (s, 3H,  $H_{13}$ ), 1.73 (d,  $J = 1.5$  Hz, 15H,  $H_2$ ), 1.10 (d,  $J_{P-H} = 9.7$  Hz, 9H,  $H_3$ ), -17.48 (d,  $J_{P-H} = 38.0$  Hz, 1H,  $H_4$ ).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  153.27 (d,  $J_{P-C} = 3.0$  Hz,  $C_6$ ), 133.47 ( $C_{10}$ ), 132.41 ( $C_7$ ), 131.17 ( $C_{11}$ ), 130.25 ( $C_8$ ), 123.44 ( $C_9$ ), 91.82 ( $C_1$ ), 21.41 ( $C_{13}$ ), 19.78 ( $C_{12}$ ), 19.17 (d,  $J_{P-C} = 36.1$  Hz,  $C_3$ ), 9.96 ( $C_2$ ), -11.68 (m,  $C_5$ ).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -45.78 (s).

### Compound **8b**

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.34 (d,  $J = 7.4$  Hz, 1H, *H11*), 6.97 (s, 1H, *H8*), 6.96 (d,  $J = 7.4$  Hz, 1H, *H10*), 2.92-2.88 (m, 2H, *H5*), 2.49 (s, 3H, *H12*), 2.28 (s, 3H, *H13*), 1.74 (d,  $J = 2.1$  Hz, 15H, *H2*), 1.11 (d,  $J_{\text{P-H}} = 9.8$  Hz, 9H, *H3*), -17.48 (d,  $J_{\text{P-H}} = 38.0$  Hz, 1H, *H4*).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  150.37 (d,  $J_{\text{P-C}} = 3.1$  Hz, *C6*), 135.37 (*C7*), 131.52 (*C9*), 131.26 (*C8*), 130.09 (*C11*), 125.72 (*C10*), 91.85 (*C1*), 21.22 (*C13*), 20.19 (*C12*), 19.17 (d,  $J_{\text{P-C}} = 36.1$  Hz, *C3*), 9.96 (*C2*), -11.90 (m, *C5*).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -45.77 (s).

### Compound **8c**

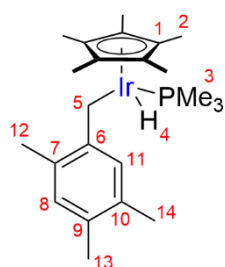
$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.37 (s, 1H, *H7*), 7.32 (d,  $J = 7.5$  Hz, 1H, *H11*), 7.05 (d,  $J = 7.5$  Hz, 1H, *H10*), 3.11 (dd,  $J = 10.9, 8.9$  Hz, 1H, *H5*), 3.02 (dd,  $J = 10.9, 3.1$  Hz, 1H, *H5*), 2.23 (s, 3H, *H12*), 2.16 (s, 3H, *H13*), 1.77 (d,  $J = 1.6$  Hz, 15H, *H2*), 1.18 (d,  $J_{\text{P-H}} = 9.7$  Hz, 9H, *H3*), -17.31 (d,  $J_{\text{P-H}} = 36.6$  Hz, 1H, *H4*).

$^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  152.89 (d,  $J_{\text{P-C}} = 3.2$  Hz, *C6*), 134.51 (*C9*), 131.39 (*C7*), 129.66 (*C8*), 128.83 (*C10*), 127.34 (*C11*), 91.80 (*C1*), 20.10 (*C12*), 19.45 (*C13*), 19.28 (d,  $J_{\text{P-C}} = 36.0$  Hz, *C3*), 10.18 (*C2*), -7.68 (m, *C5*).

$^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -45.14 (s).

HRMS (ESI+):  $m/z$  calculated for  $[\text{}^{191}\text{IrC}_{22}\text{H}_{35}\text{P}]^+$  521.2082, found 521.2075.

### [ $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(2,4,5\text{-trimethylbenzyl})$ ] (**9**)



Complex **9** was prepared according to the general procedure using [ $\text{Cp}^*\text{Ir}(\eta^4\text{-durene})$ ] (40.0 mg, 0.087 mmol) and  $\text{PMe}_3$  (35.9  $\mu\text{L}$ , 0.354 mmol) in hexane (2 mL) with a reaction time of 2 h. The product [ $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(2,4,5\text{-trimethylbenzyl})$ ] was isolated as a yellow oil that can crystallise upon standing (96%, 44.5 mg, 0.083 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.24 (s, 1H, *H11*), 6.95 (s, 1H, *H8*), 2.94 (ddd, ABX,  $J = 10.3, 5.7, 4.6$  Hz, 2H, *H5*), 2.48 (s, 3H, *H12*), 2.26 (s, 3H, *H13/14*), 2.20 (s, 3H, *H13/14*), 1.76 (s, 15H, *H2*), 1.12 (d,  $J_{\text{P-H}} = 9.7$ , 9H, *H3*), -17.50 (d,  $J_{\text{P-H}} = 37.9$  Hz, 1H, *H4*).

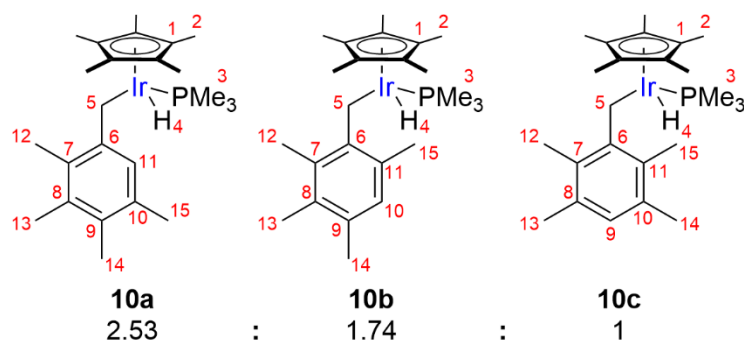
$^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  150.41 (d,  $J_{\text{P-C}} = 2.8$  Hz, *C6*), 132.75 (*C7*), 132.29 (*C11*), 131.84 (*C8*), 131.79 (*C10*), 129.75 (*C9*), 91.83 (d,  $J_{\text{P-C}} = 3.5$  Hz, *C1*), 19.73 (*C12*), 19.50 (*C14*), 19.31 (*C13*), 19.24 (d,  $J_{\text{P-C}} = 36.0$  Hz, *C3*), 10.01 (*C2*), -12.16 (d,  $J_{\text{P-C}} = 6.0$  Hz, *C5*).

$^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -45.89 (s).

HRMS (ASAP):  $m/z$  calculated for  $[\text{}^{191}\text{IrC}_{23}\text{H}_{37}\text{P}]^+$  535.2239, found 535.2234.



[Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,5-tetramethylbenzyl)] (10a), [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,6-tetramethylbenzyl)] (10b) and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,5,6-tetramethylbenzyl)] (10c)



Thermolysis of [Cp\*Ir( $\eta^4$ -penta-methylbenzene)] (34.0 mg, 0.071 mmol) was conducted according to the general procedure using PMe<sub>3</sub> (29.1  $\mu$ L, 0.286 mmol) in hexane (2 mL) with a reaction time of 48 h to

give a mixture of [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,5-tetramethylbenzyl)], [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,6-tetramethylbenzyl)] and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,5,6-tetramethylbenzyl)] as a yellow oil (84%, 33.0 mg, 0.060 mmol).

#### Compound 10a

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.14 (s, 1H, *H*11), 3.02-2.93 (m, 2H, *H*5), 2.42 (s, 3H, *H*12), 2.33 (s, 3H, *H*15), 2.24 (s, 3H, *H*13), 2.17 (s, 3H, *H*14), 1.76 (dd, *J* = 1.8, 0.6 Hz, 15H, *H*2), 1.11 (d, *J*<sub>P-H</sub> = 9.7 Hz, 9H, *H*3), -17.52 (d, *J*<sub>P-H</sub> = 38.0 Hz, 1H, *H*4).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  149.82 (d, *J*<sub>P-C</sub> = 2.7 Hz, *C*6), 134.27 (*C*8), 131.46 (*C*7), 131.11 (*C*10), 130.03 (*C*11), ~128 (overlapped with solvent signal, *C*9), 91.84-91.76 (m, *C*1), 21.01 (*C*15), 19.31 (d, *J*<sub>P-C</sub> = 36.6 Hz, *C*3), 16.65 (*C*13), 16.40 (*C*12), 16.18 (*C*14), 10.01 (*C*2), -10.27--10.33 (m, *C*5).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -45.82 (s).

#### Compound 10b (partial assignment)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.90 (s, 1H, *H*10), 2.29 (s, 3H, *H*13), 2.23 (s, 3H, *H*14), 1.68 (br. s, 15H, *H*2), 1.02 (br. d, 9H, *H*3), -17.46 (d, *J*<sub>P-H</sub> = 39.2 Hz, 1H, *H*4).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  129.56 (*C*10), 128.91 (*C*8), 91.84-91.76 (m, *C*1), 21.04 (*C*13), ~19.50-18.77 (v. br. s, *C*3), 16.28 (*C*14), 9.91 (*C*2).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -48.03 (v. br. s).

#### Compound 10c (partial assignment)

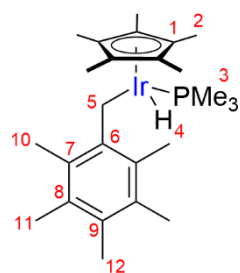
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.81 (s, 1H, *H*9), 2.32 (merged s, 6H, *H*13+*H*14), 1.68 (br. s, 15H, *H*2), 1.02 (br. d, 9H, *H*3), -17.49 (d, *J*<sub>P-H</sub> = 39.5 Hz, 1H, *H*4).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  125.96 (*C*9), 91.84-91.76 (m, *C*1), 21.16 (s, *C*13+*C*14), ~19.50-18.77 (v. br. s, *C*3), 9.86 (*C*2).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -48.03 (v. br. s).

HRMS (ESI<sup>+</sup>): *m/z* calculated for [<sup>191</sup>IrC<sub>24</sub>H<sub>40</sub>P]<sup>+</sup> 549.2395, found 549.2383.

### Thermolysis of [Cp\*Ir( $\eta^4$ -hexamethylbenzene)] at 100 °C



Thermolysis of [Cp\*Ir( $\eta^4$ -hexamethylbenzene)] (33.5 mg, 0.068 mmol) was conducted according to the general procedure using PMe<sub>3</sub> (27.8  $\mu$ L, 0.274 mmol) in hexane (2 mL) with a reaction time of 168 h. Removal of volatiles *in vacuo* afforded a brown oil (37.2 mg). According to the <sup>1</sup>H NMR spectrum, the oil is a mixture of the starting complex (~55%) and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,5,6-pentamethylbenzyl)] (~44%). Product ratios were determined by their respective relative integrals in the <sup>1</sup>H NMR spectrum but, due to significant broadening, only a rough estimate can be established. A minor unidentified hydride species (~1%) is also present. Several additional unidentified species are also noted in trace amounts according to the <sup>31</sup>P NMR spectrum.

[Cp\*Ir( $\eta^4$ -hexamethylbenzene)]

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.96 (s, 6H), 1.66 (s, 15H), 1.54 (s, 6H), 1.42 (s, 6H).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  132.95, 88.53, 79.60, 52.91, 20.09, 14.24, 14.06, 9.64.

[Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,5,6-pentamethylbenzyl)] (partial assignment)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.31 (s, 6H, *H11*), 2.26 (s, 3H, *H12*), 1.67 (br. s, 15H, *H2*), -17.48 (d, *J*<sub>P-H</sub> = 39.2 Hz, 1H, *H4*).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  91.86 (d, *J*<sub>P-C</sub> = 3.4 Hz, *C1*), 17.15 (*C12*), 17.11 (*C11*) 9.87 (*C2*).

<sup>31</sup>P NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -50.96 (v. br. s).

HRMS (ESI+): *m/z* calculated for [<sup>191</sup>IrC<sub>25</sub>H<sub>42</sub>P]<sup>+</sup> 564.2630, found 564.2439 (minor); [<sup>191</sup>IrC<sub>13</sub>H<sub>25</sub>P]<sup>+</sup> (M - C<sub>12</sub>H<sub>17</sub>) 403.1300, found 403.1285 (major).

### Thermolysis of [Cp\*Ir( $\eta^4$ -hexamethylbenzene)] at 150 °C

Thermolysis of [Cp\*Ir( $\eta^4$ -hexamethylbenzene)] (27.8 mg, 0.057 mmol) was conducted according to a modified version of the general procedure. The reaction was conducted at 150 °C using PMe<sub>3</sub> (23.1  $\mu$ L, 0.227 mmol) and *n*-octane (1 mL) in a sealed Schlenk tube with a reaction time of 48 h. Removal of volatiles *in vacuo* afforded a brown residue (26.1 mg). The <sup>1</sup>H NMR spectrum of the residue revealed full consumption of the starting complex and formation of three hydride species as well as free hexamethylbenzene. However, the expected benzylic product [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,5,6-pentamethylbenzyl)] is not observed.

Comparison with literature data and 2D NMR analysis confirms the formation of the known complex  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{H}_2]$ <sup>[6]</sup> as one of the minor hydride species [ $\delta$  1.33 (d,  $J_{\text{P-H}} = 10.0$  Hz, 9H), -17.39 (d,  $J_{\text{P-H}} = 32.2$  Hz)].

$[\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{H}_2]$

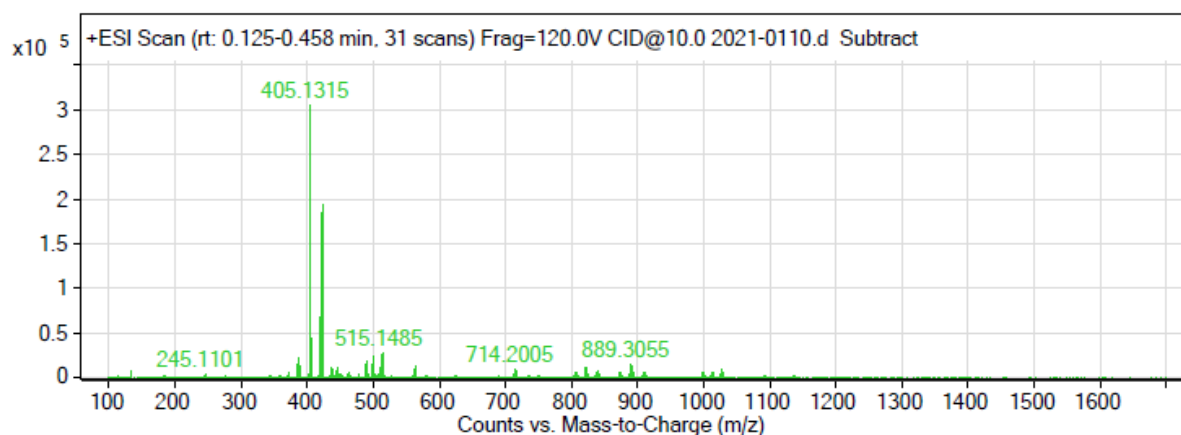
$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.15 (dt,  $J = 2.0, 0.7$  Hz, 15H), 1.33 (d,  $J_{\text{P-H}} = 10.3$  Hz, 9H), -17.42 (d,  $J_{\text{P-H}} = 32.0$  Hz, 1H).

Relative integrals and 2D NMR analysis suggests the major product to possess a  $\{\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{H}\}$  fragment [ $\delta$  1.90 (m, 15H), 1.26 (d,  $J_{\text{P-H}} = 9.6$  Hz, 9H), -17.80 (d,  $J_{\text{P-H}} = 36.4$  Hz, 1H)]. This complex can also be noted in the previous 100 °C reaction.

The final hydride peak [ $\delta$  -12.13 (m)] is substantially downfield relative to previously discussed complexes as well as possessing a complex splitting pattern suggests the structure to be significantly different.

Mass spectrometry analysis of the mixture is dominated by the  $\{\text{Cp}^*\text{Ir}(\text{PMe}_3)\text{H}\}$  fragment as expected, confirming the loss of the bulky hexamethylbenzyl unit. Trace peaks of higher  $m/z$  values are present but no sensible assignments could be made.

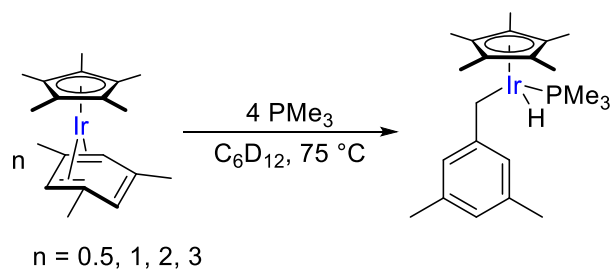
MS (ESI+)



**Figure S1.** ESI+ Mass spectrum of the crude product of thermolysis of  $[\text{Cp}^*\text{Ir}(\eta^4\text{hexamethylbenzene})]$  at 150 °C.

## Kinetic, isotope-labelling and radical studies

### Determination of reaction order on [Cp\*Ir( $\eta^4$ -mesitylene)] (**11**)



In a glovebox, J. Young NMR tube was charged with a 0.025, 0.050, 0.100 or 0.150 M solution of **11** in C<sub>6</sub>D<sub>12</sub> (0.5 mL). HMDSO (5.3 μL) was then added as an internal standard followed by PMe<sub>3</sub> (10.2 μL). The J. Young NMR tube was subsequently sealed, removed from the glovebox and heated in an oil bath at 75 °C. The reaction was monitored periodically by <sup>1</sup>H NMR spectroscopy by cooling the reaction mixture in liquid nitrogen and washing the J. Young NMR tube with DCM to remove external oil prior to each data point collection.

Concentrations of the starting complex and benzylic C-H activation product was quantified by integrating against the internal standard allowing the conversion to be calculated accurately. Experiments were completed in triplicate.

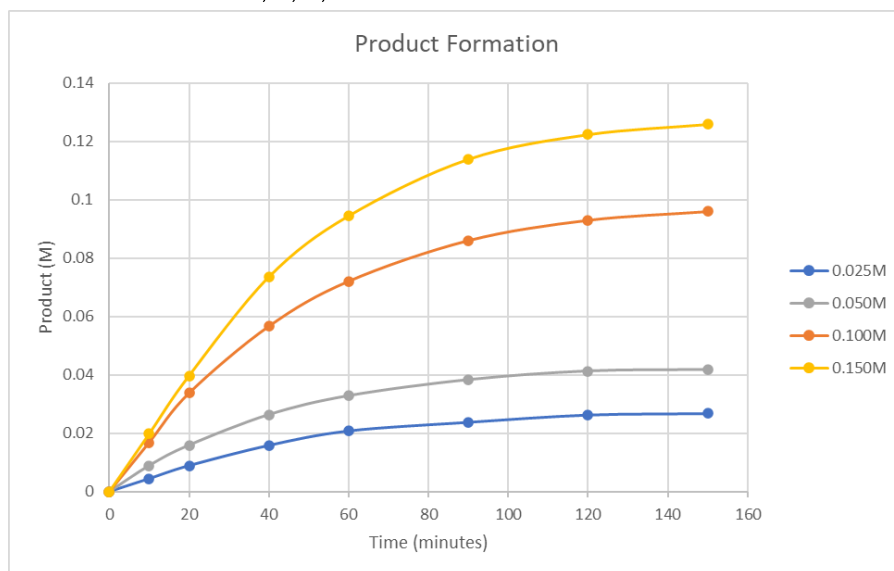
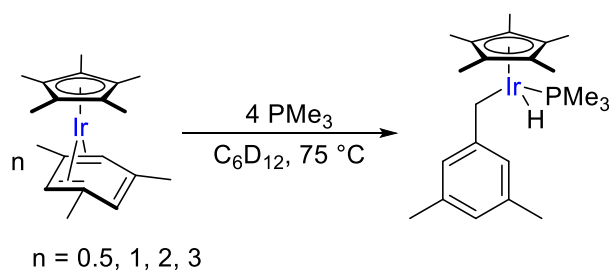
Signals underlined used to determine concentrations.

#### Compound **11**

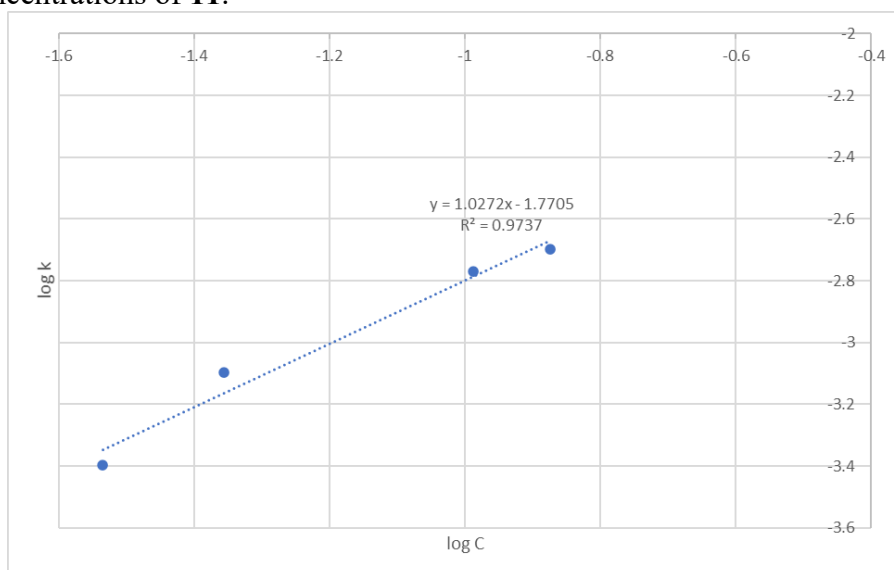
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 5.29 (1H), 4.53 (1H), 2.46 (1H), 2.07 (3H), 1.83 (15H), 1.35 (3H), 1.12 (3H).

#### Compound **6**

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 6.73 (2H), 6.37 (1H), 2.79-2.75 (1H), 2.68-2.65 (1H), 2.13 (6H), 1.77 (15H), 1.33 (d, 9H), -17.70 (d, 1H).



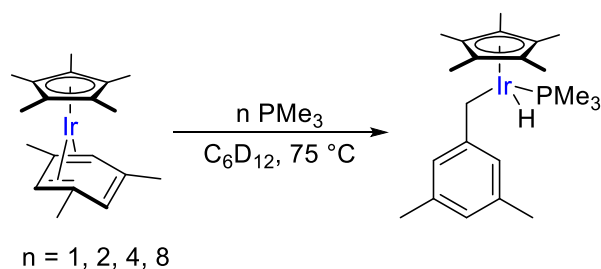
**Figure S2.** Plot of concentration of product **6** (moles) against time (minutes) for varying starting concentrations of **11**.



**Figure S3.** Plot of  $\log(k)$ , where  $k$  = observed rate determined from data points at 10 and 20 minutes, against  $\log(c)$ , where  $c$  = starting concentration of **11**.

Gradient from line of best fit =  $\sim 1$  and thus the reaction is first order with respect to [**11**].

## Determination of reaction order on PMe<sub>3</sub>



In a glovebox, J. Young NMR tube was charged with a 0.050 M solution of **11** in C<sub>6</sub>D<sub>12</sub> (0.5 mL). HMDSO (5.3 μL) was then added as an internal standard followed by 2.5, 5.1, 10.2 or 20.3 μL of PMe<sub>3</sub> (1, 2, 4 or 8 eq., respectively). The J. Young NMR tube was subsequently sealed and heated in an oil bath at 75 °C. The reaction was monitored periodically by <sup>1</sup>H NMR spectroscopy by cooling the reaction mixture in liquid nitrogen and washing the J. Young NMR tube with DCM to remove external oil prior to each data point collection.

Concentrations of the starting complex and benzylic C-H activation product was quantified by integrating against the internal standard allowing the conversion to be calculated accurately. Experiments were completed in triplicate.

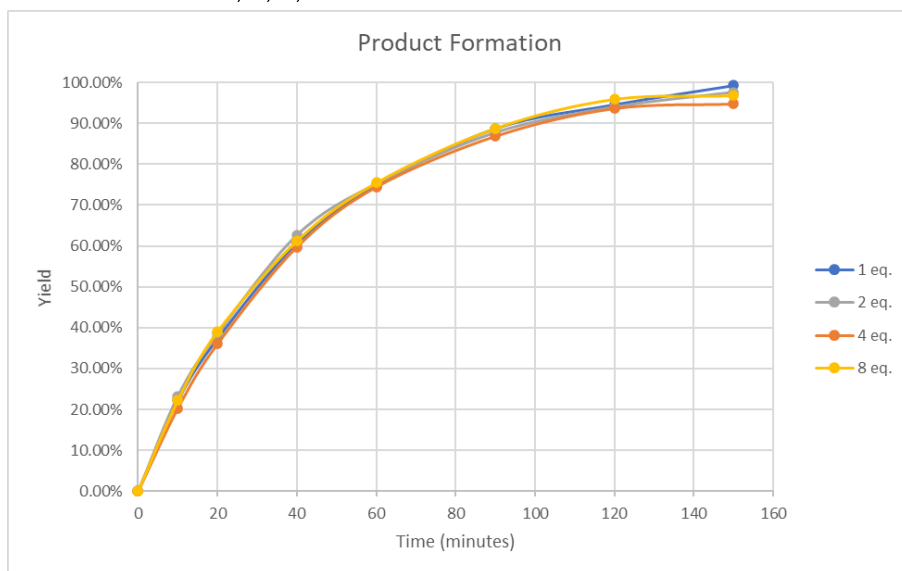
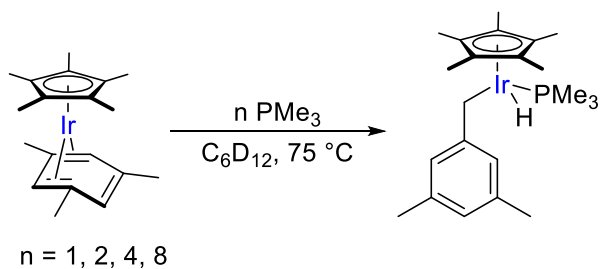
Signals underlined used to determine concentrations.

### Compound **11**

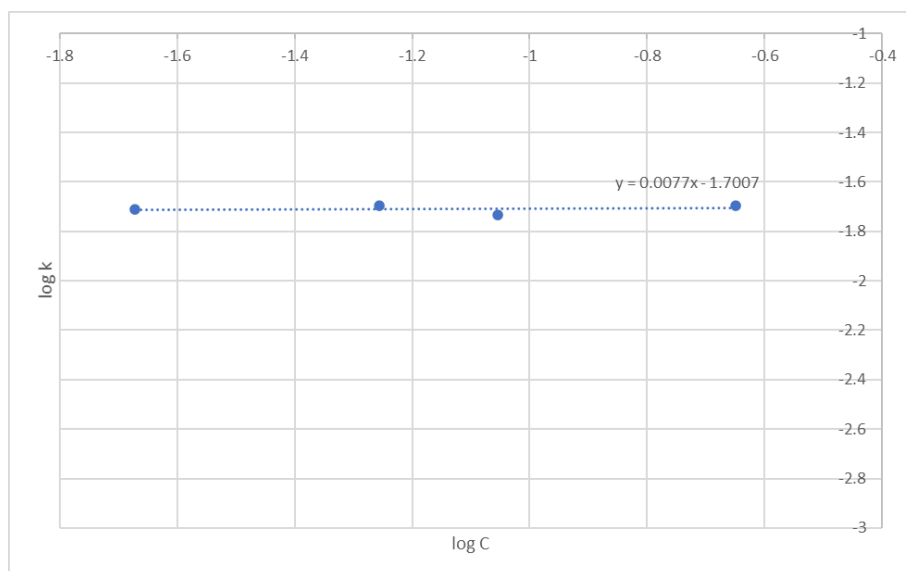
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 5.29 (1H), 4.53 (1H), 2.46 (1H), 2.07 (3H), 1.83 (15H), 1.35 (3H), 1.12 (3H).

### Compound **6**

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 6.73 (2H), 6.37 (1H), 2.79-2.75 (1H), 2.68-2.65 (1H), 2.13 (6H), 1.77 (15H), 1.33 (d, 9H), -17.70 (d, 1H).



**Figure S4.** Plot of concentration of product 6 (NMR yield) against time (minutes) for varying concentrations of  $\text{PMe}_3$ .



**Figure S5.** Plot of  $\log(k)$ , where  $k$  = observed rate determined from data points at 10 and 20 minutes, against  $\log(c)$ , where  $c$  = starting concentration of  $\text{PMe}_3$ . Gradient from line of best fit =  $\sim 0$  and thus the reaction is zero order with respect to  $[\text{PMe}_3]$ .

### Determination of H/D Kinetic Isotope Effects (KIE)

In a glovebox, J. Young NMR tube was charged with a 0.050 M solution of **11-d<sub>3</sub>** or **11-d<sub>9</sub>** in C<sub>6</sub>D<sub>12</sub> (0.5 mL). HMDSO (5.3 μL) was then added as an internal standard followed by PMe<sub>3</sub> (10.2 μL). The J. Young NMR tube was subsequently sealed, removed from the glovebox and heated in an oil bath at 75 °C. The reaction was monitored periodically by <sup>1</sup>H NMR spectroscopy by cooling the reaction mixture in liquid nitrogen and washing the J. Young NMR tube with DCM to remove external oil prior to each data point collection.

Concentrations of the starting complex and benzylic C-H activation product was quantified by integrating against the internal standard allowing the conversion to be calculated accurately. Experiments were completed in triplicate.

Signals underlined used to determine concentrations.

Compound **11-d<sub>3</sub>**

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 2.06 (3H), 1.82 (15H), 1.36 (3H), 1.13 (3H).

Compound **6-d<sub>3</sub>**

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 2.79-2.75 (1H), 2.68-2.64 (1H), 2.14 (6H), 1.76 (15H), 1.32 (d, 9H), -17.69 (d, 1H).

Signals underlined used to determine concentrations.

Compound **11-d<sub>9</sub>**

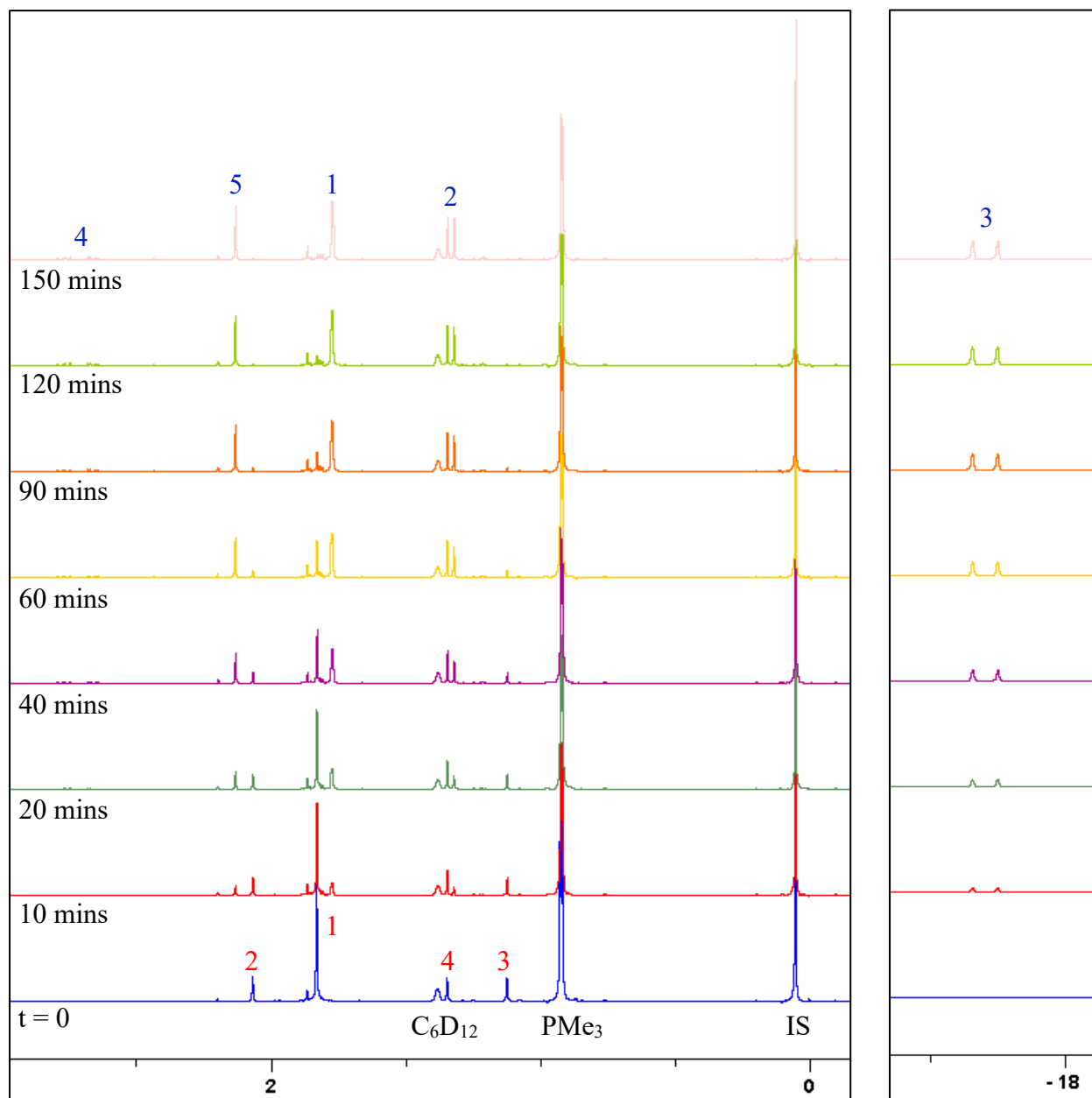
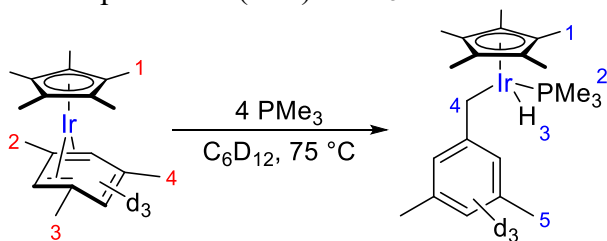
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 5.28 (1H), 4.53 (1H), 2.46 (1H), 1.82 (15H).

Compound **6-d<sub>9</sub>**

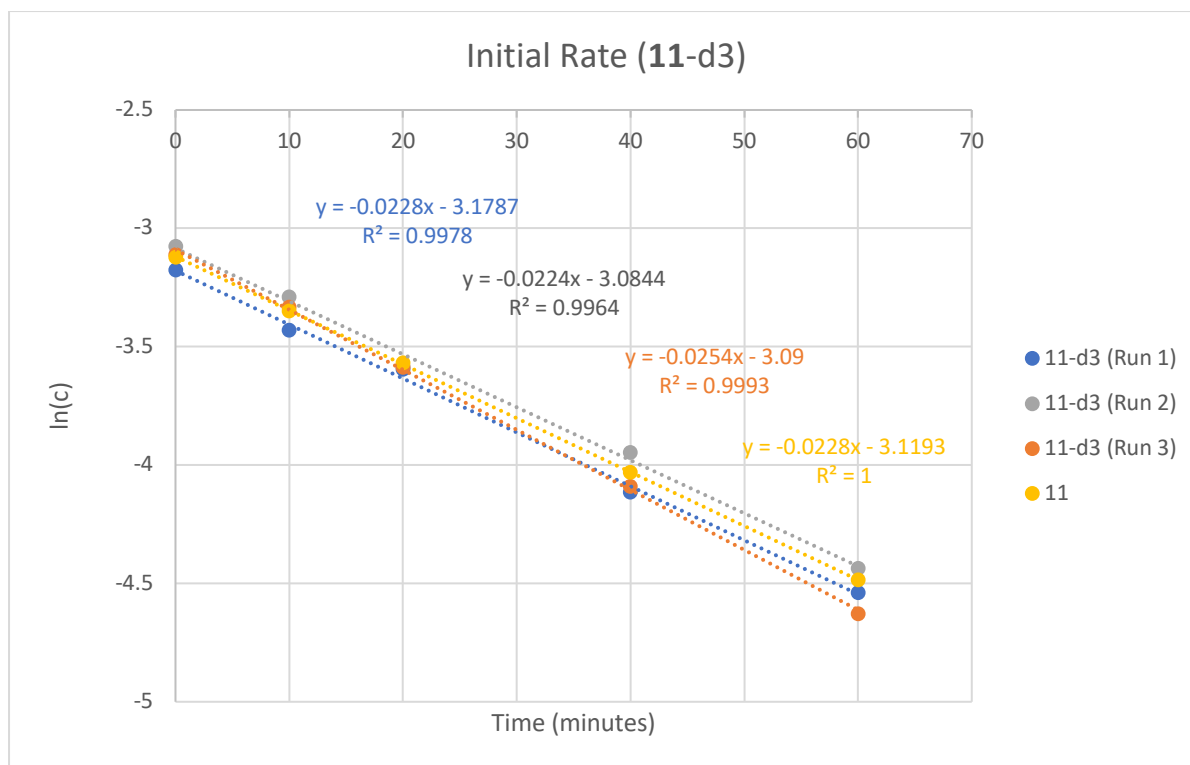
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>12</sub>): δ 6.72 (2H), 6.37 (1H), 1.77 (15H), 1.33 (d, 9H).



Determination of Kinetic Isotope Effects (KIE): **11-d<sub>3</sub>** vs **11**



**Figure S6.** <sup>1</sup>H NMR (400 MHz, 25 °C, C<sub>6</sub>D<sub>12</sub>) spectra of a reaction mixture of thermolysis of **11-d<sub>3</sub>** at 75 °C. The selected hydrogen atoms corresponding to the starting complex **11-d<sub>3</sub>** and the product **6-d<sub>3</sub>** are labelled with the corresponding numbers in red and blue colours, respectively.



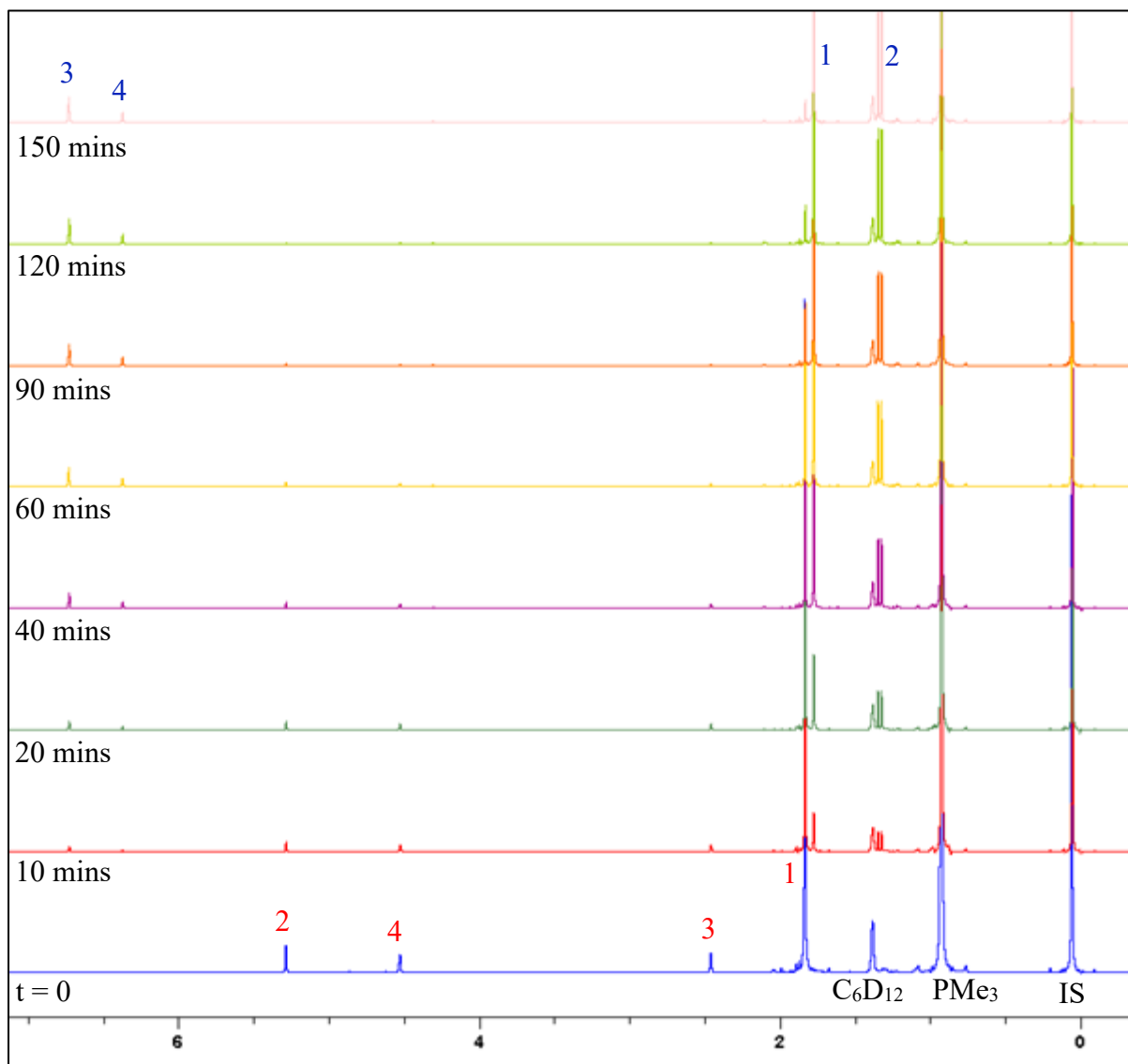
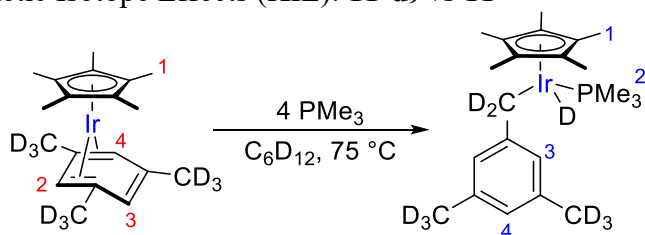
**Figure S7.** Plot of  $\ln(c)$ , where  $c$  = concentration of **11-d<sub>3</sub>** remaining, against time to determine the initial reaction rate. Triplicate results shown.

Using the average reaction rate,  $k_H/k_D$  is determined to be  $1.03 \pm 0.18$  (95% confidence interval).

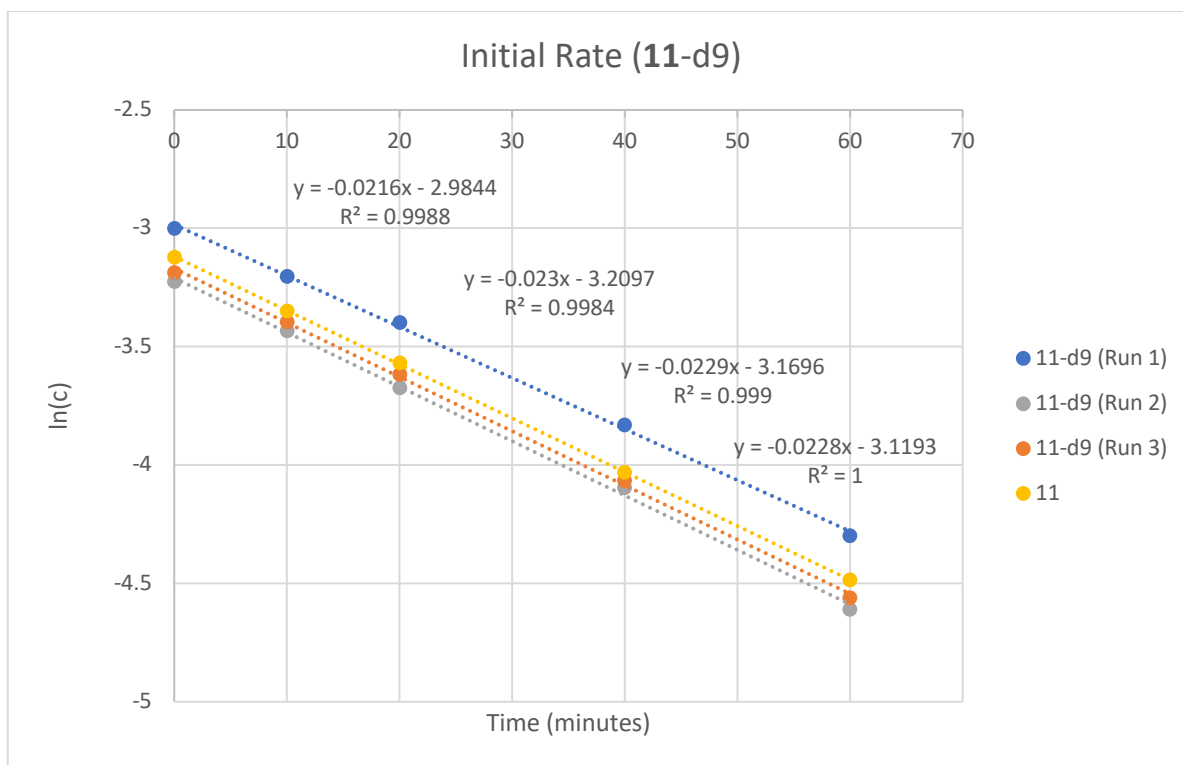
**Table S1.** Concentration-time data for thermolysis **11** (Control), and **11-d<sub>3</sub>** (Run 1, 2 and 3) at 75 °C.

Time (minutes)	Concentration (M)			
	Control	Run 1	Run 2	Run 3
0	0.0441028	0.0416987	0.0461753	0.0446002
10	0.0351496	0.0324139	0.0372221	0.035647
20	0.028186	0.0274399	0.0277715	0.0276886
40	0.0177406	0.0163313	0.0193157	0.0167458
60	0.0112744	0.0106941	0.0118547	0.0097822

Determination of Kinetic Isotope Effects (KIE): **11-d<sub>9</sub>** vs **11**



**Figure S8.**  $^1\text{H}$  NMR (400 MHz, 25 °C,  $\text{C}_6\text{D}_{12}$ ) spectra of a reaction mixture of thermolysis of **11-d<sub>9</sub>** at 75 °C. The selected hydrogen atoms corresponding to the starting complex **11-d<sub>3</sub>** and the product **6-d<sub>9</sub>** are labelled with the corresponding numbers in red and blue colours, respectively.



**Figure S9.** Plot of  $\ln(c)$ , where  $c$  = concentration of **11-d<sub>9</sub>** remaining, against time to determine the initial reaction rate. Triplicate results shown.

Using the average reaction rate,  $k_H/k_D$  is determined to be  $0.99 \pm 0.09$ .

**Table S2.** Concentration-time data for thermolysis **11** (Control), and **11-d<sub>9</sub>** (Run 1, 2 and 3) at 75 °C.

Time (minutes)	Concentration (M)			
	Control	Run 1	Run 2	Run 3
0	0.0441028	0.04974	0.039792	0.0412842
10	0.0351496	0.040621	0.032331	0.0335745
20	0.028186	0.0334916	0.0253674	0.0268596
40	0.0177406	0.0217198	0.0166629	0.0171603
60	0.0112744	0.0135956	0.009948	0.0104454

### **Thermolysis of [Cp\*Ir( $\eta^4$ -mesitylene)] in the presence of PMe<sub>3</sub> and a radical scavenger (TEMPO)**

In a glovebox, a 4 mL vial equipped with a Teflon-lined screw cap was charged with a hexane (2 mL) solution of **11** (28.1 mg, 0.063 mmol). Four eq. of trimethylphosphine (25.5  $\mu$ L, 0.251 mmol), one eq. of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 9.8 mg, 0.063 mmol) and a magnetic stirrer bar were then added into the vial. The vial was removed from the glovebox, placed on a heating block and the reaction mixture was stirred at 100 °C for 1 h. Upon cooling, the vial was transferred into the glovebox and the mixture was passed through glass wool and the filtrate was dried under vacuum to afford a brown residue. HMDSO (5.0  $\mu$ L) was then added as an internal standard and the reaction mixture was analysed by <sup>1</sup>H NMR spectroscopy.

The <sup>1</sup>H NMR spectrum of residue showed full consumption of **11** and formation of the expected product **6** (14%, 0.009 mmol) along with a complex mixture of multiple products. The reduced yield of **6** compared to the reaction in the absence of TEMPO can be rationalised by possible degradation of the product by the TEMPO radical trap, previously observed in hydride-containing complexes,<sup>[7]</sup> or the promotion of unwanted side reactions.

### **Thermolysis of [Cp\*Ir(PMe<sub>3</sub>)(H)(3,5-dimethylbenzyl)] in the presence of TEMPO**

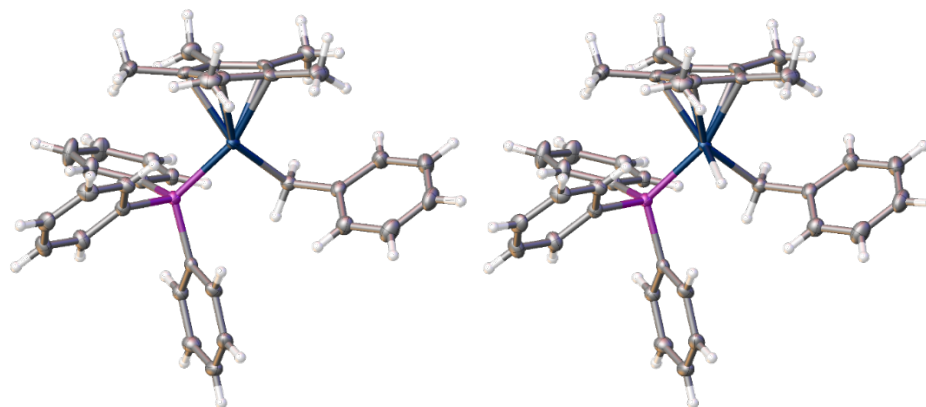
In a glovebox, a 4 mL vial equipped with a Teflon-lined screw cap was charged with a hexane (2 mL) solution of **6** (32.3 mg, 0.062 mmol). One eq. of TEMPO (9.6 mg, 0.062 mmol) and a magnetic stirrer bar were then added into the vial. The vial was removed from the glovebox, placed on a heating block and the reaction mixture was stirred at 100 °C for 1 h. Upon cooling, the mixture was passed through glass wool and the filtrate was dried under vacuum to afford a brown residue. HMDSO (5.0  $\mu$ L) was then added as an internal standard and the reaction mixture was analysed by <sup>1</sup>H NMR spectroscopy.

The <sup>1</sup>H NMR spectrum of the reaction mixture showed 83% conversion of the starting complex **6** (0.017 mmol, 27%). The <sup>31</sup>P NMR spectrum displayed two major signals at  $\delta$  -45.27 and -54.96 ppm, the former corresponding to **6**. The latter signal is not observed when conducting thermolysis of **11** in presence of TEMPO suggesting this new species is derived from degradation of **6**. This also confirms that TEMPO interferes with the formation of **6** from **11** by promoting unwanted side reactions.

Repeating the reaction with added PMe<sub>3</sub> (25.1  $\mu$ L, 0.247 mmol) afforded a similar complex mixture with 69% conversion of **6** (0.019 mmol, 31%).

## Crystallography data

Single crystals of **2b** were mounted on a SuperNova, Dual, AtlasS2 diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2,<sup>[8]</sup> the structure was solved with the SHELXT<sup>[9]</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>[10]</sup> refinement package using Least Squares minimisation.



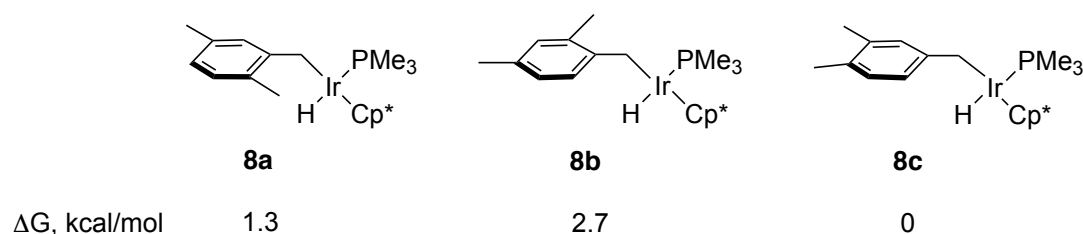
**Figure S10.** Refined structure of **2b** (left) and hydride ligand added for clarity (right).

**Table S3.** Crystal data and structure refinement for compound **2b**

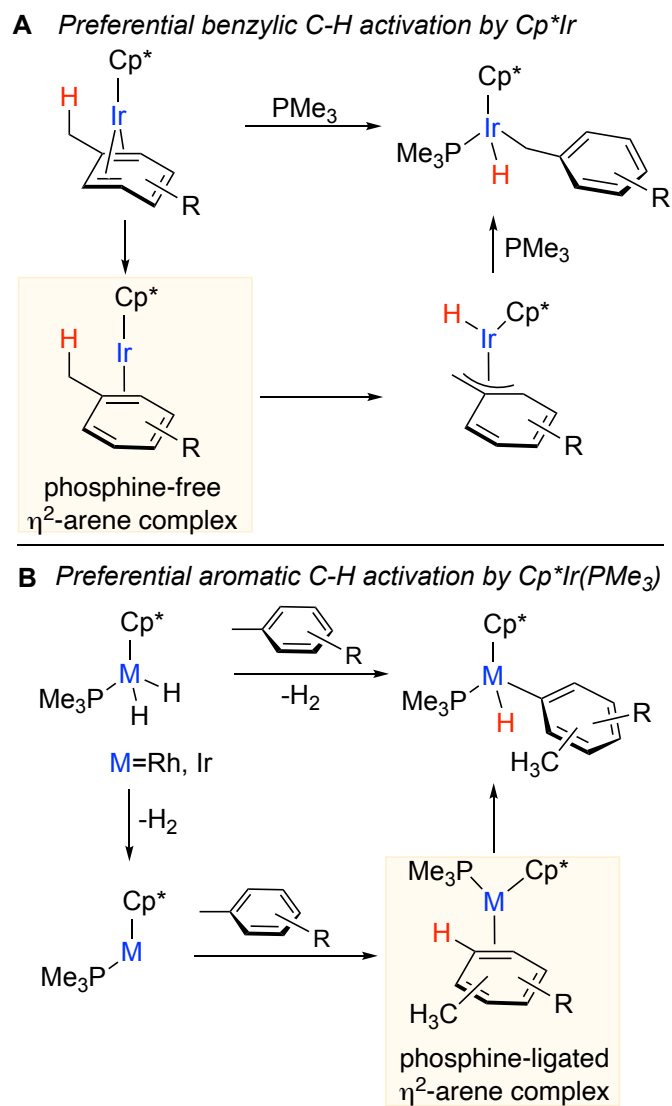
Compound	<b>2b</b>
CCDC	2090576
Formula	C <sub>35</sub> H <sub>37</sub> IrP
<i>M</i>	680.81
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.9650(3)
<i>b</i> /Å	11.3610(3)
<i>c</i> /Å	14.1758(4)
$\alpha$ /°	75.957(2)
$\beta$ /°	68.820(3)
$\gamma$ /°	62.077(3)
<i>V</i> /Å <sup>3</sup>	1449.14(8)
<i>Z</i> , <i>Z'</i>	2, 1
<i>F</i> (000)/e	678
<i>D</i> <sub>calc</sub> /Mg m <sup>-3</sup>	1.560
$\mu$ /mm <sup>-1</sup>	9.585
$\theta$ <sub>max</sub> /°	76.31
Data measured	31991
Unique data	6029
<i>R</i> <sub>int</sub>	0.0249
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (obs. data)	0.0174, 0.0483
<i>S</i>	1.043
Variables	339
<i>E</i> <sub>max</sub> , <i>E</i> <sub>min</sub> /e Å <sup>-3</sup>	1.2, -1.0

## DFT Calculations

All geometry optimizations, analytical frequency calculations and intrinsic reaction path calculations were with the B3LYP<sup>[11]</sup> functional in gas phase and a mixed basis set of LanL2DZ for iridium and 6-31G(d) for other atoms. Stabilities of converged wavefunctions were confirmed by running the “stable” test. Analytical frequency calculations confirmed that all converged minima contained 0 and all converged transition-state geometries contained exactly 1 imaginary frequency. IRCs calculations established all minima connected to each transition-state geometry. Single point energies of all converged geometries were calculated with the M06-L<sup>[12]</sup> functional and mixed basis set of LanL2TZ for the rhodium atom and 6-311+G(d) for the rest of other atoms. The solvent effects were included in single point energy calculations using the conductor polarizable continuum model (CPCM). The free energies were calculated by adding single-point energies calculated at the M06-L/(6-311+G(d)+LANL2TZ) level to thermodynamic corrections calculated in the rigid-rotor/ideal gas/quasi-harmonic approximations.<sup>[13]</sup> The effectiveness of using B3LYP for structure optimization followed by single point energy calculations with the M06 suit of functionals<sup>[14]</sup> and the suitability of B3LYP and M06-L for calculations of barrier heights involving Ir-C and C-C bond formations were reported previously.<sup>[15]</sup> All DFT calculations were performed with Gaussian 09.<sup>[16]</sup>



**Figure S11.** The electronic energies (at B3LYP/(6-31G(d)+LANL2DZ)) of complexes **8a**, **8b** and **8c**.



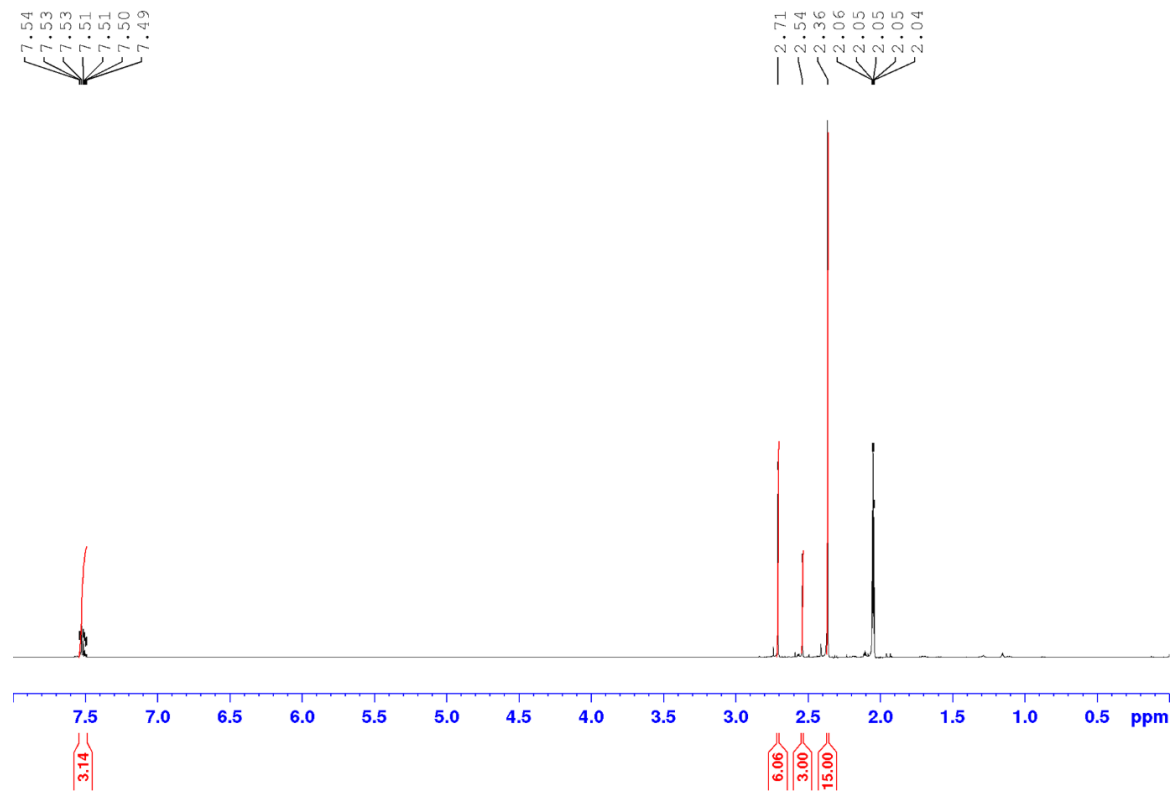
**Figure S12.** Presented benzylic C-H activation by  $\text{Cp}^*\text{Ir}(\eta^2\text{-arene})$  and known aromatic C-H activation by  $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\eta^2\text{-arene})$ .<sup>[5],[17]</sup>



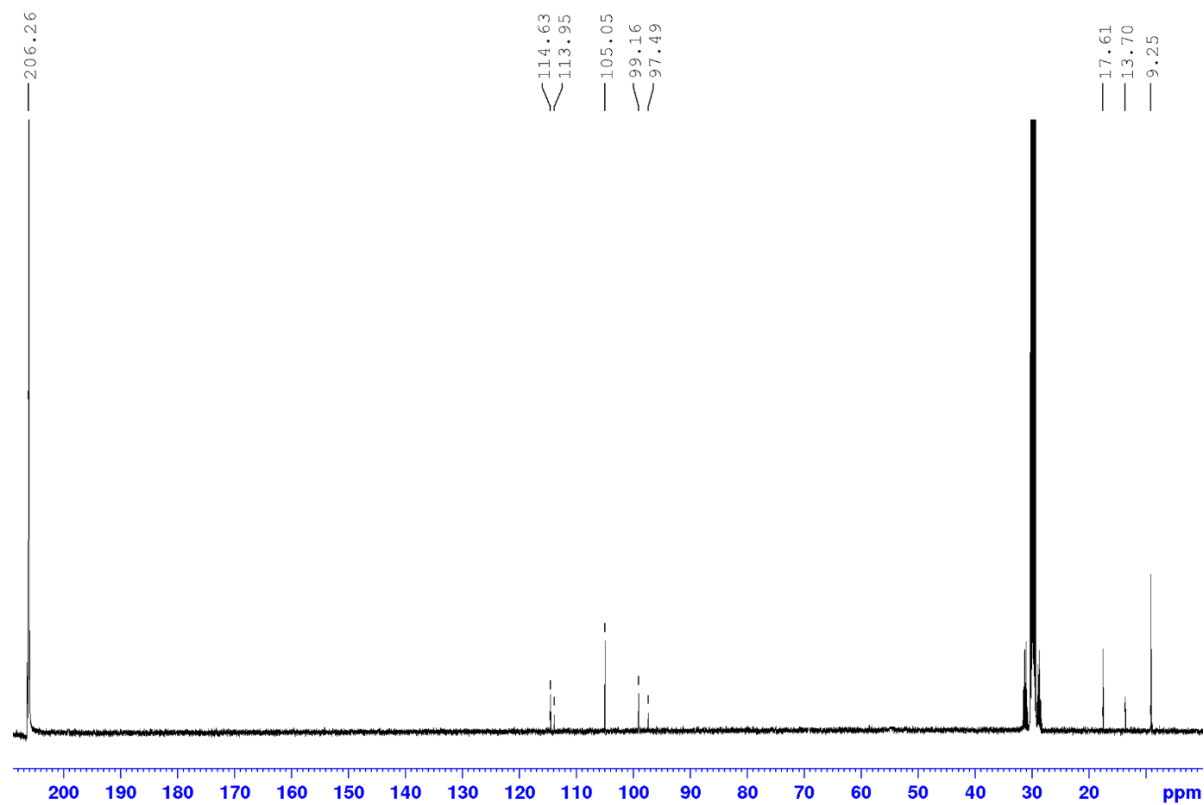
## NMR spectra

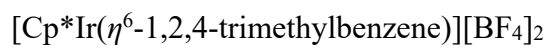
[Cp\*Ir( $\eta^6$ -1,2,3-trimethylbenzene)][BF<sub>4</sub>]<sub>2</sub>

<sup>1</sup>H NMR [500 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]

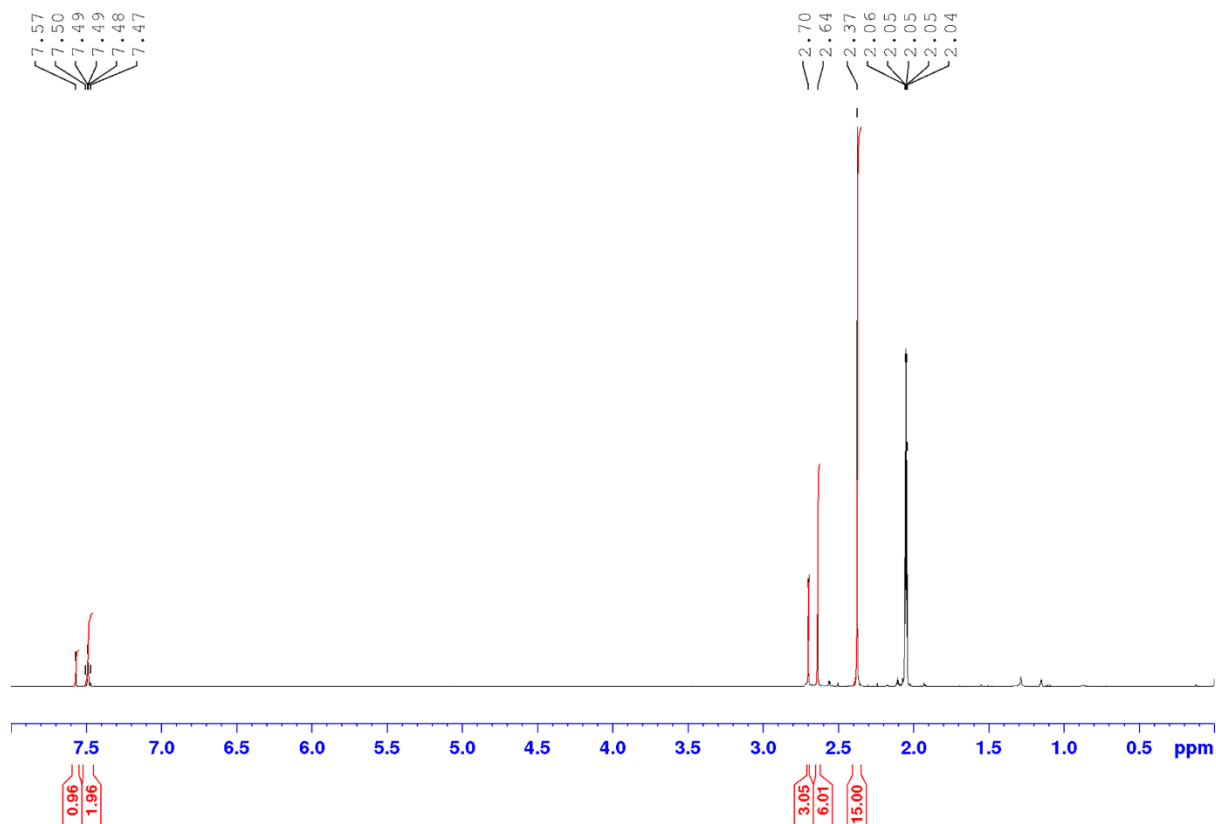


<sup>13</sup>C{<sup>1</sup>H} NMR [126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]

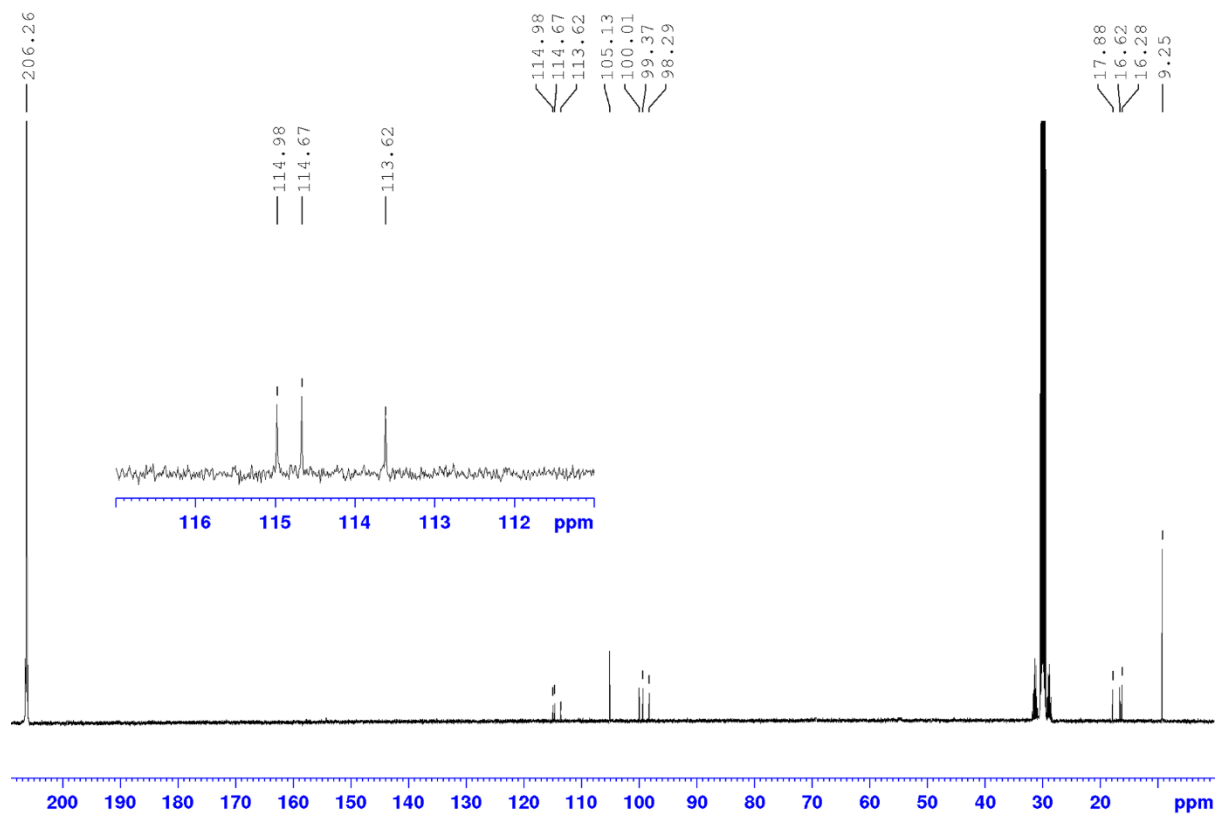


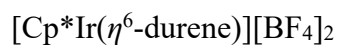


$^1\text{H}$  NMR [500 MHz,  $(\text{CD}_3)_2\text{CO}$ ]

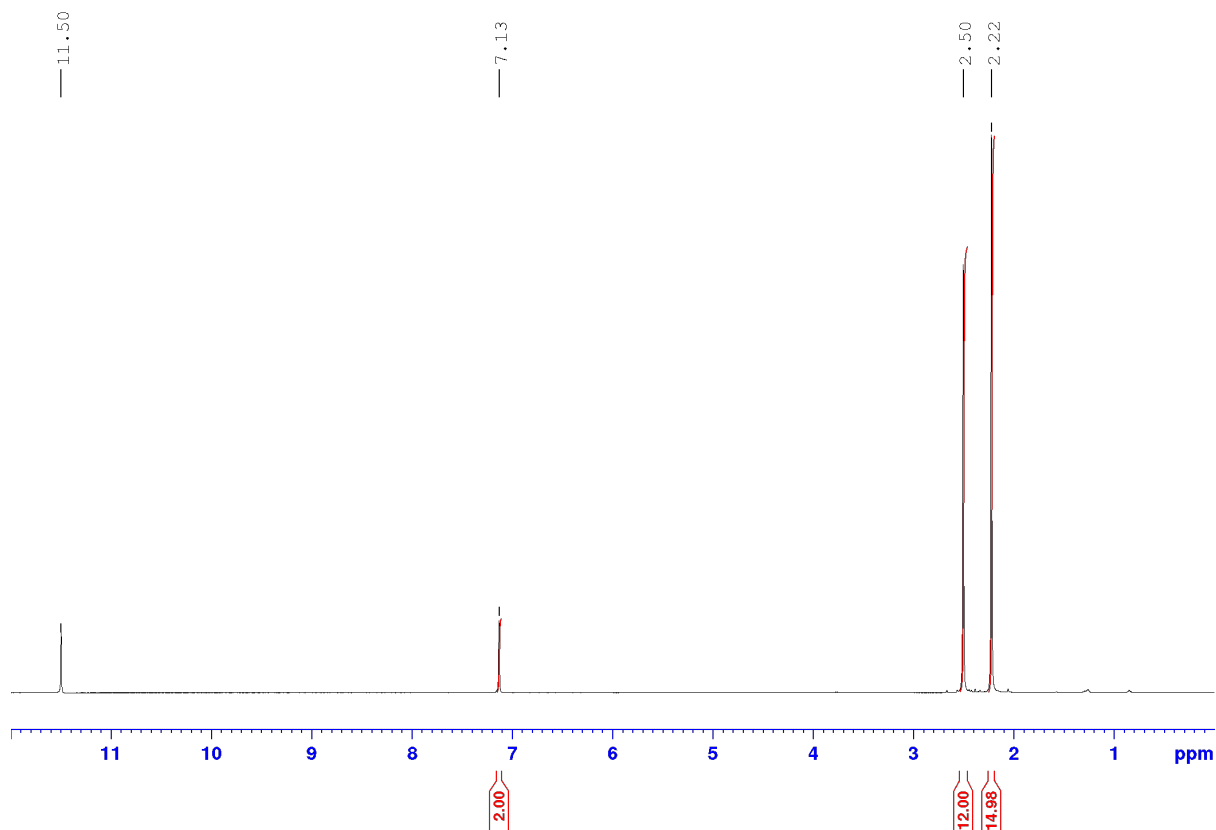


$^{13}\text{C}\{^1\text{H}\}$  NMR [126 MHz,  $(\text{CD}_3)_2\text{CO}$ ]

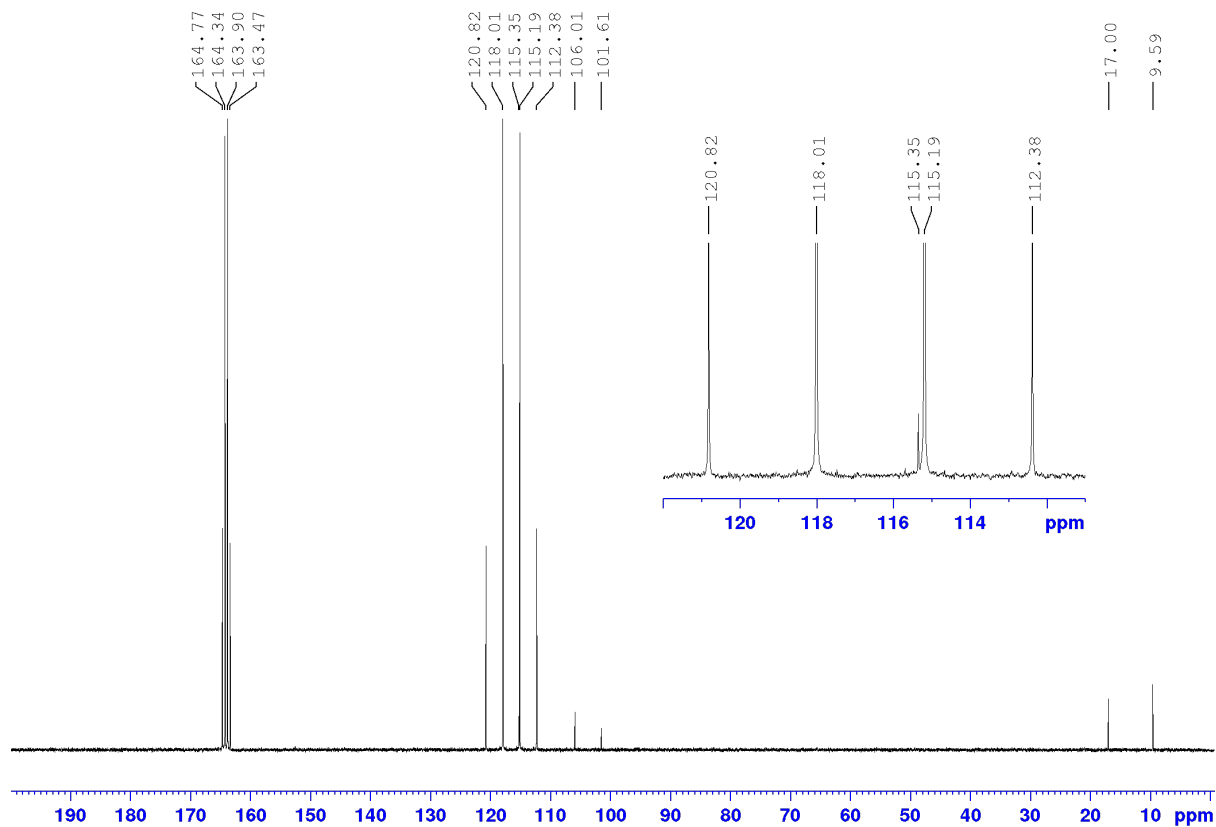


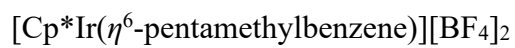


$^1\text{H}$  NMR (400 MHz, d-TFA)

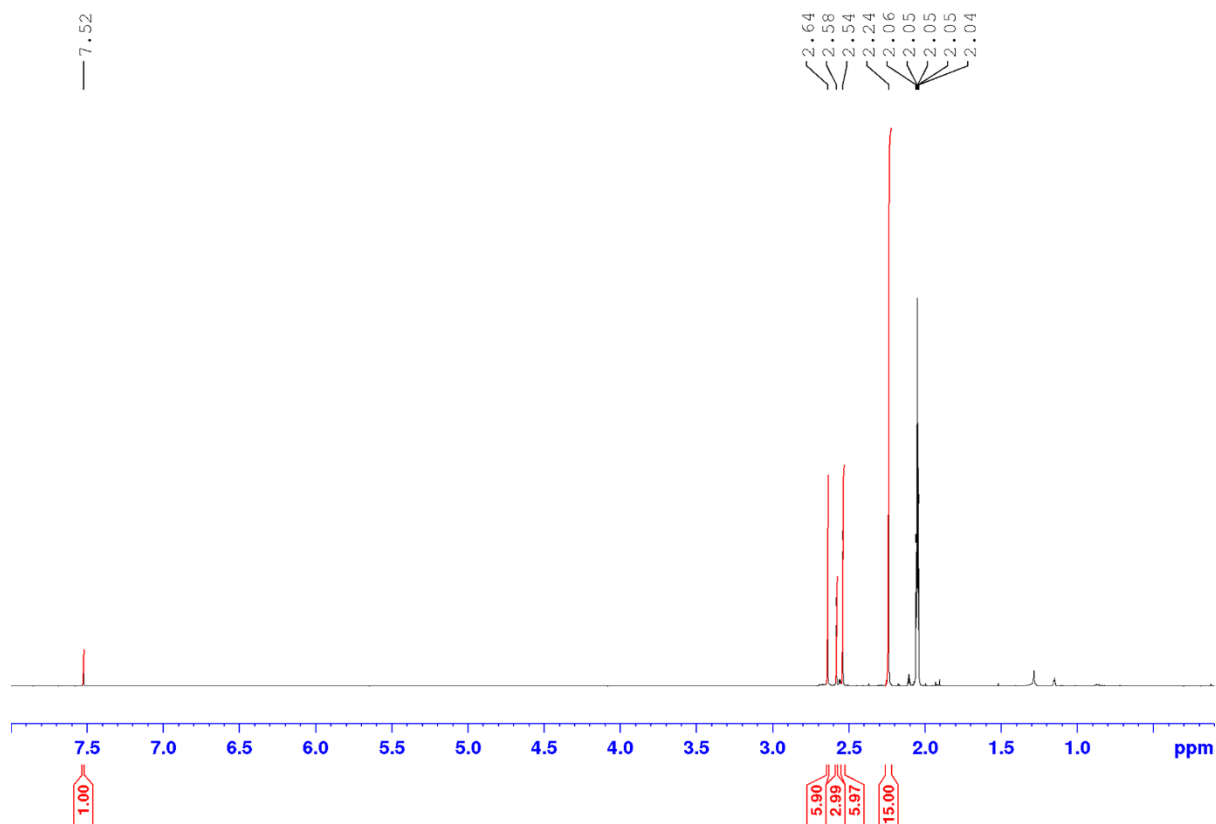


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, d-TFA)

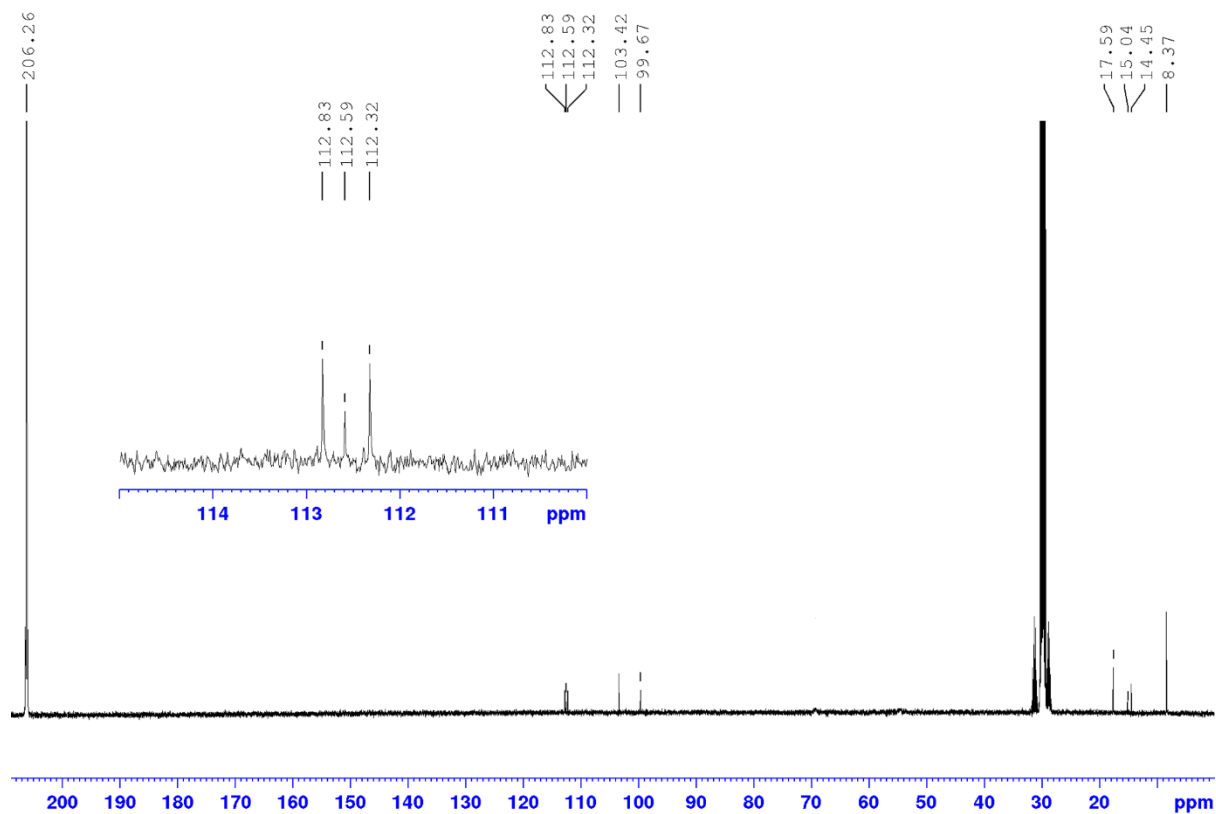




$^1\text{H}$  NMR [500 MHz,  $(\text{CD}_3)_2\text{CO}$ ]

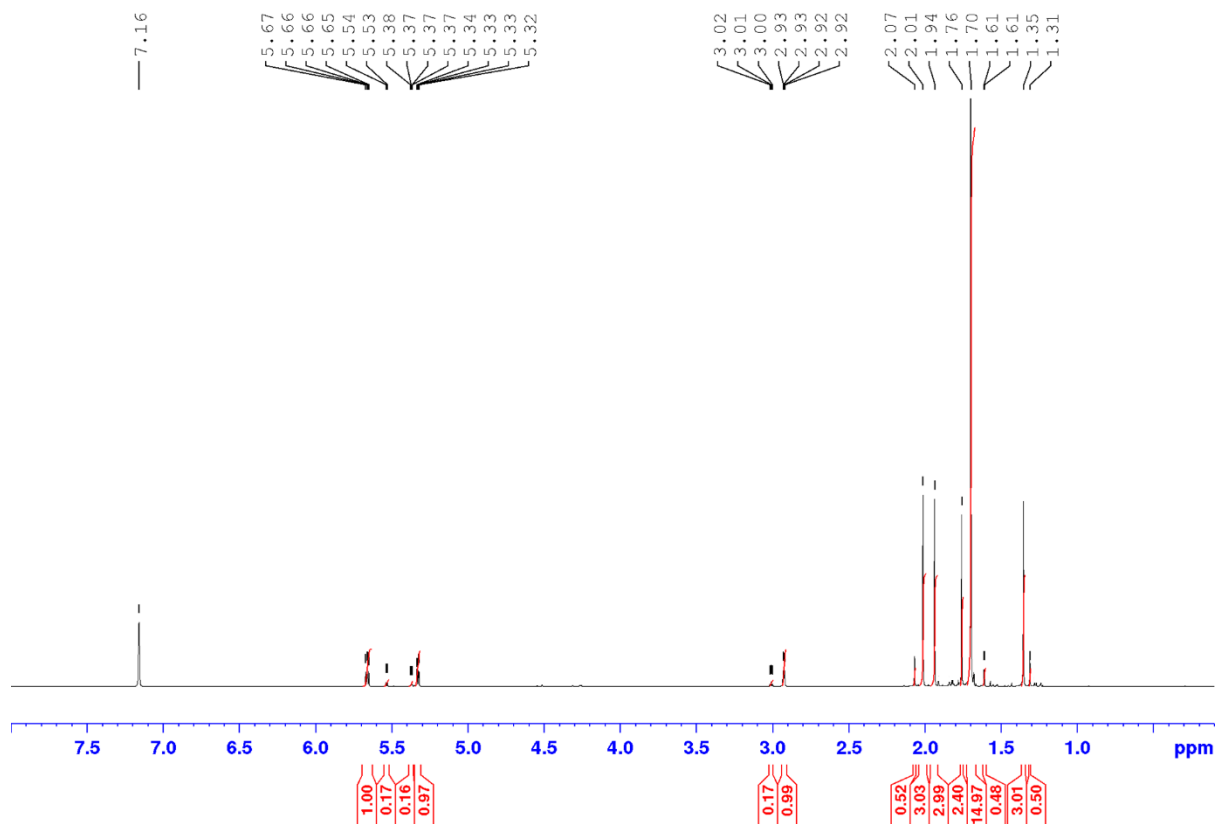


$^{13}\text{C}\{^1\text{H}\}$  NMR [126 MHz,  $(\text{CD}_3)_2\text{CO}$ ]

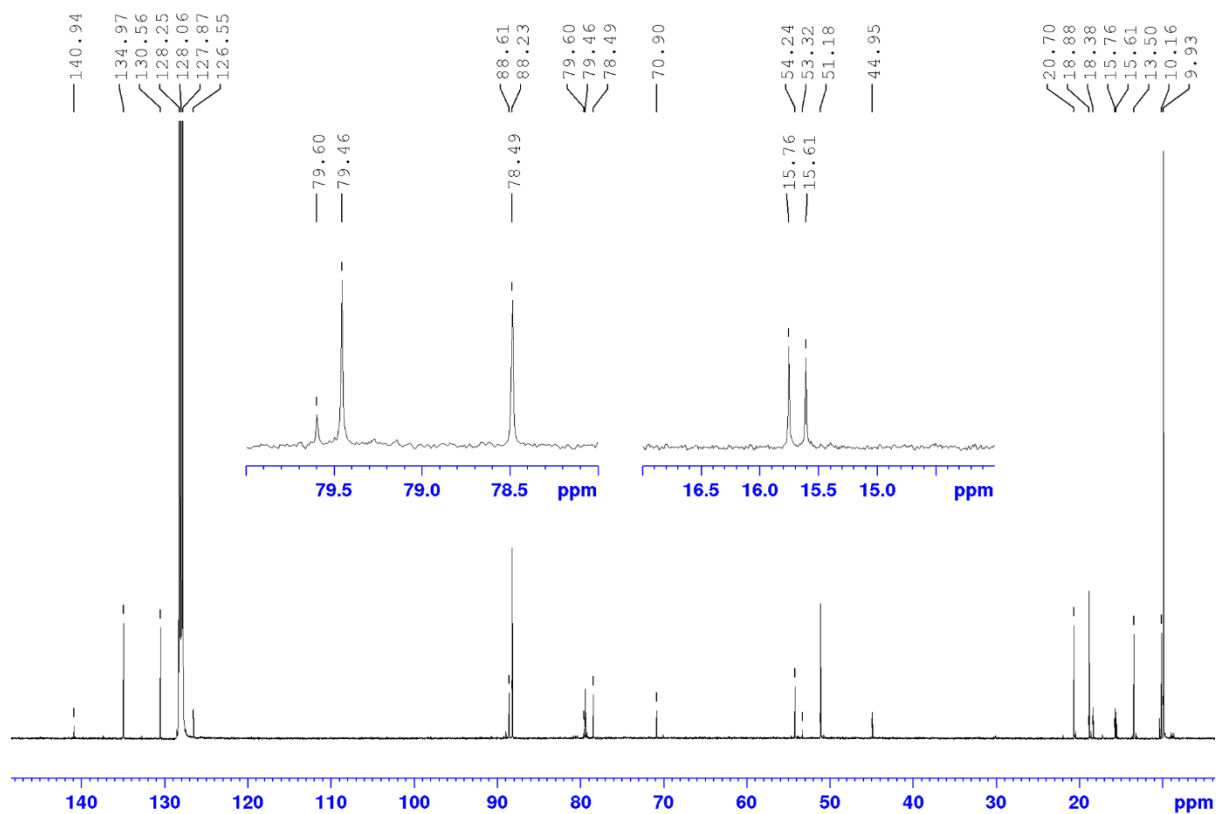


[Cp\*Ir( $\eta^4$ -1,2,3-trimethylbenzene)] (12)

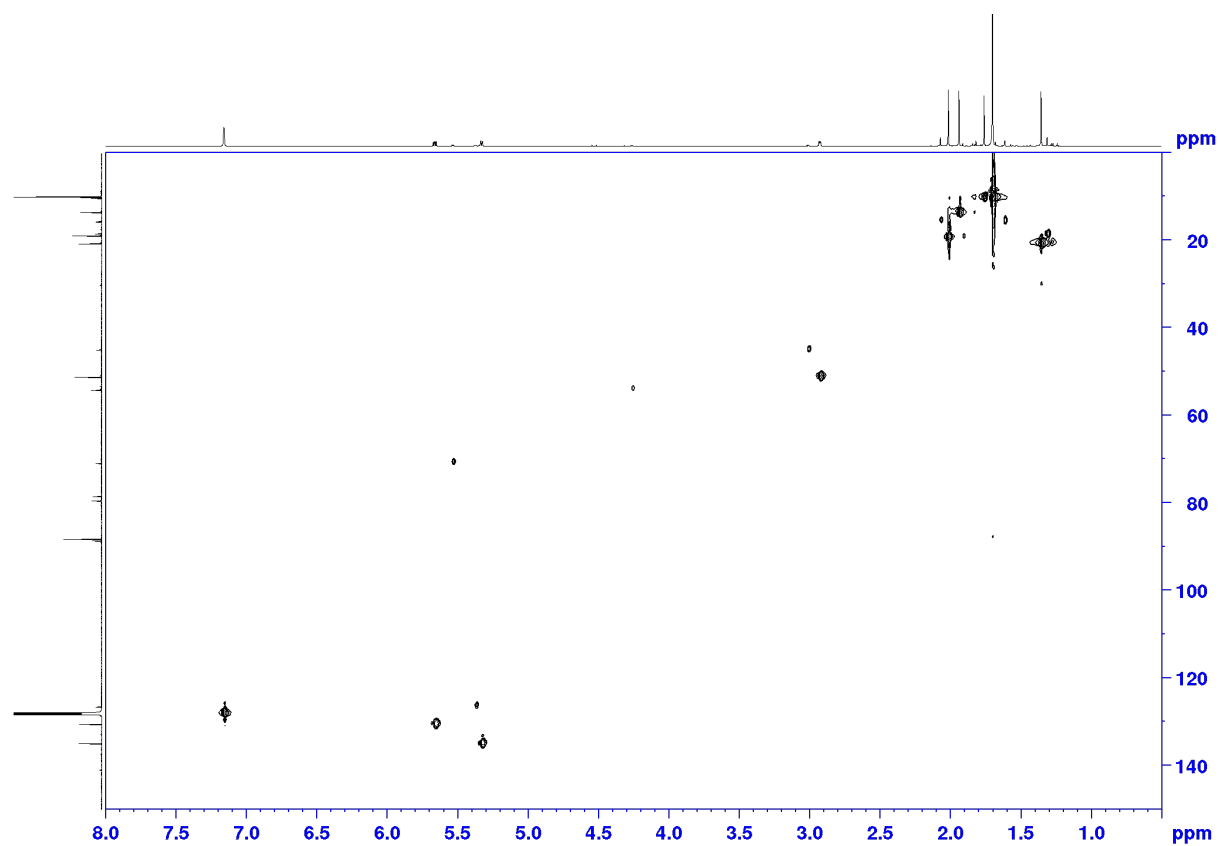
$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )



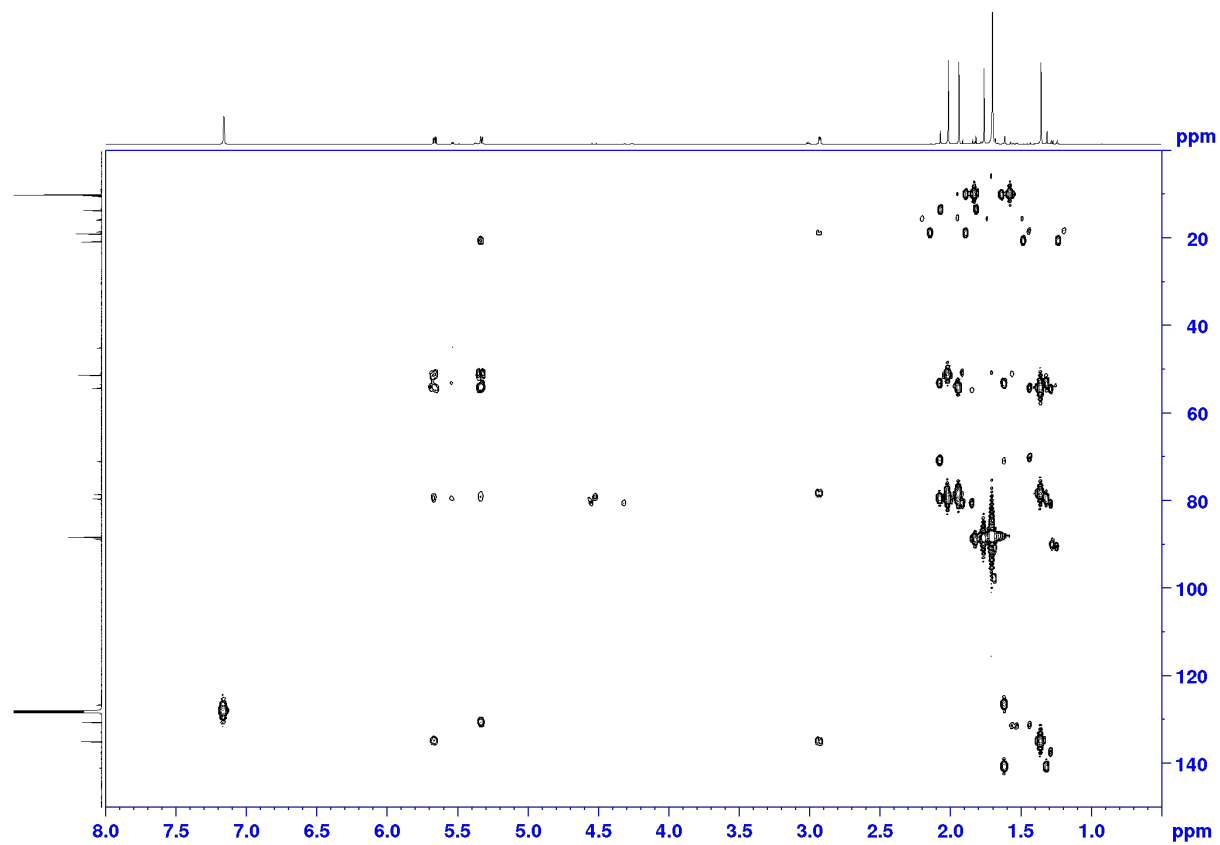
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )



HSQC (500 MHz, C<sub>6</sub>D<sub>6</sub>)

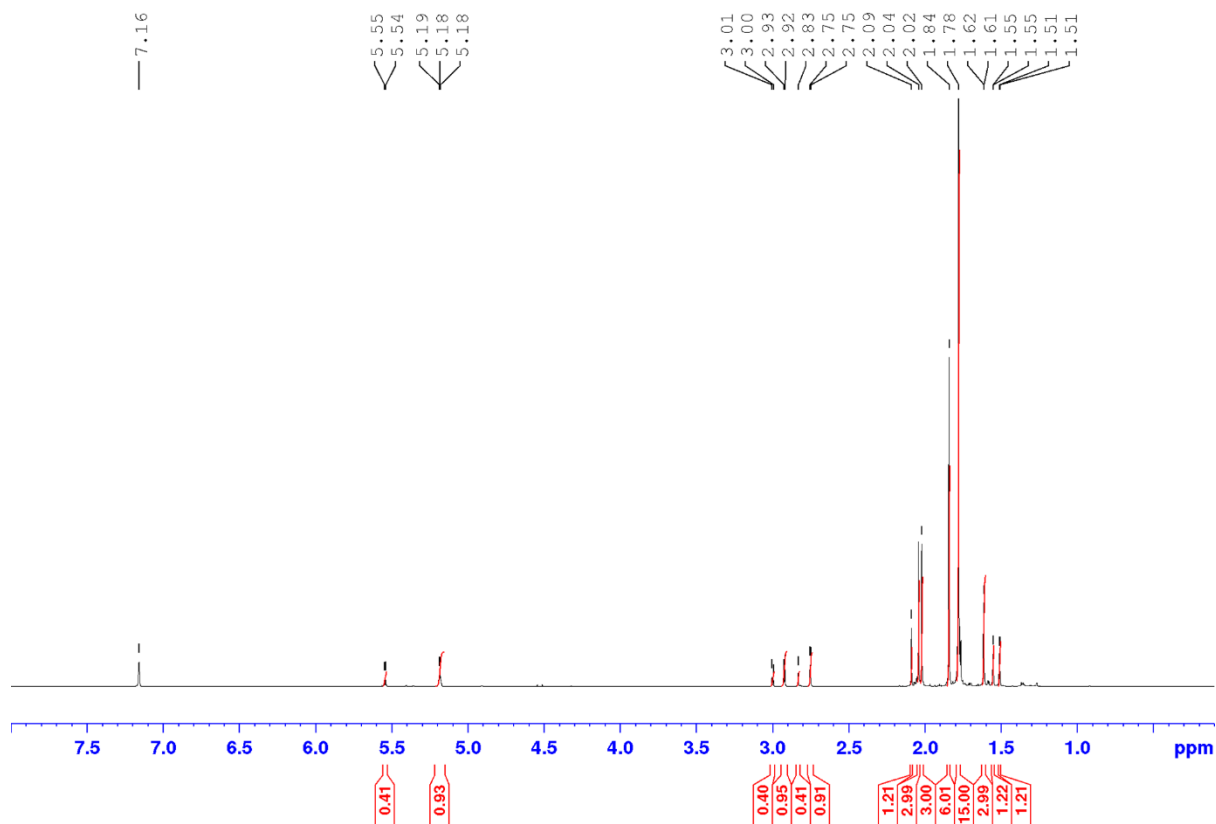


HMBC (500 MHz, C<sub>6</sub>D<sub>6</sub>)

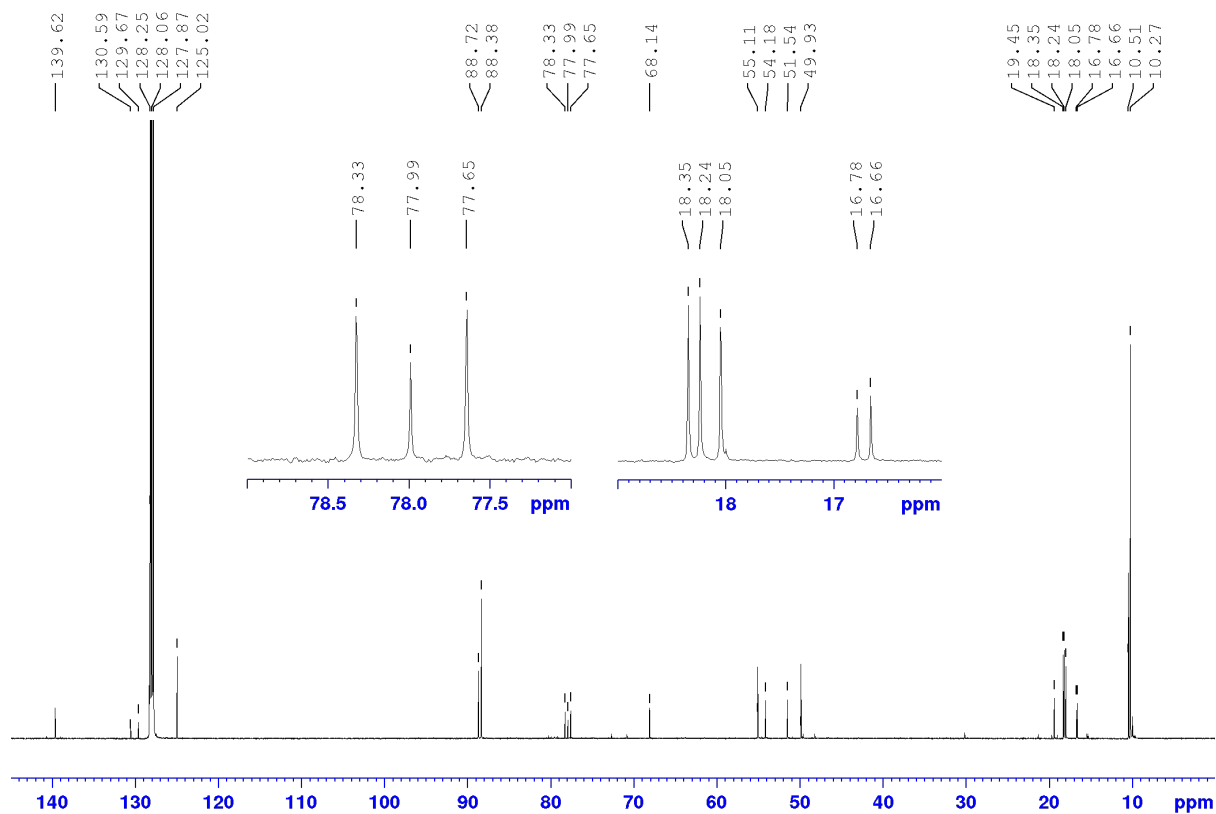


[Cp\*Ir( $\eta^4$ -1,2,4-trimethylbenzene)] (**13**)

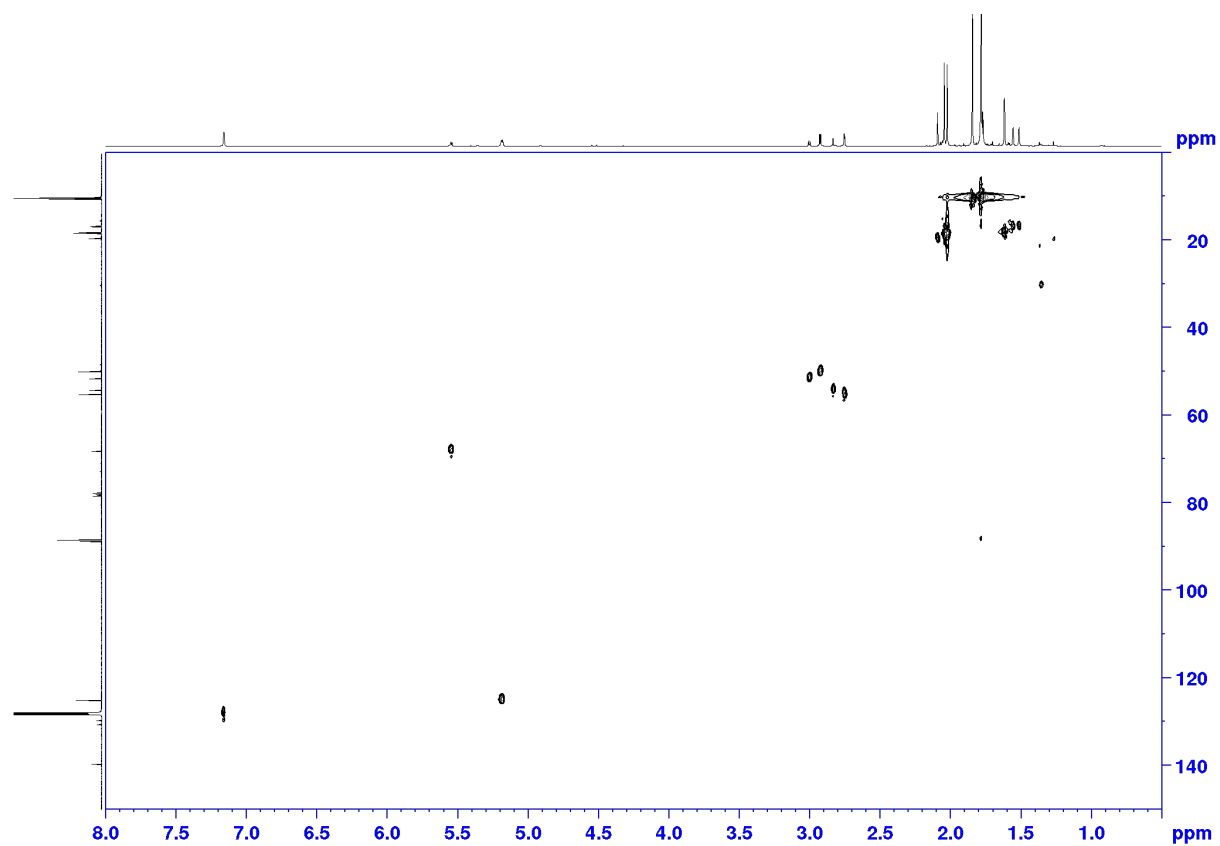
$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )



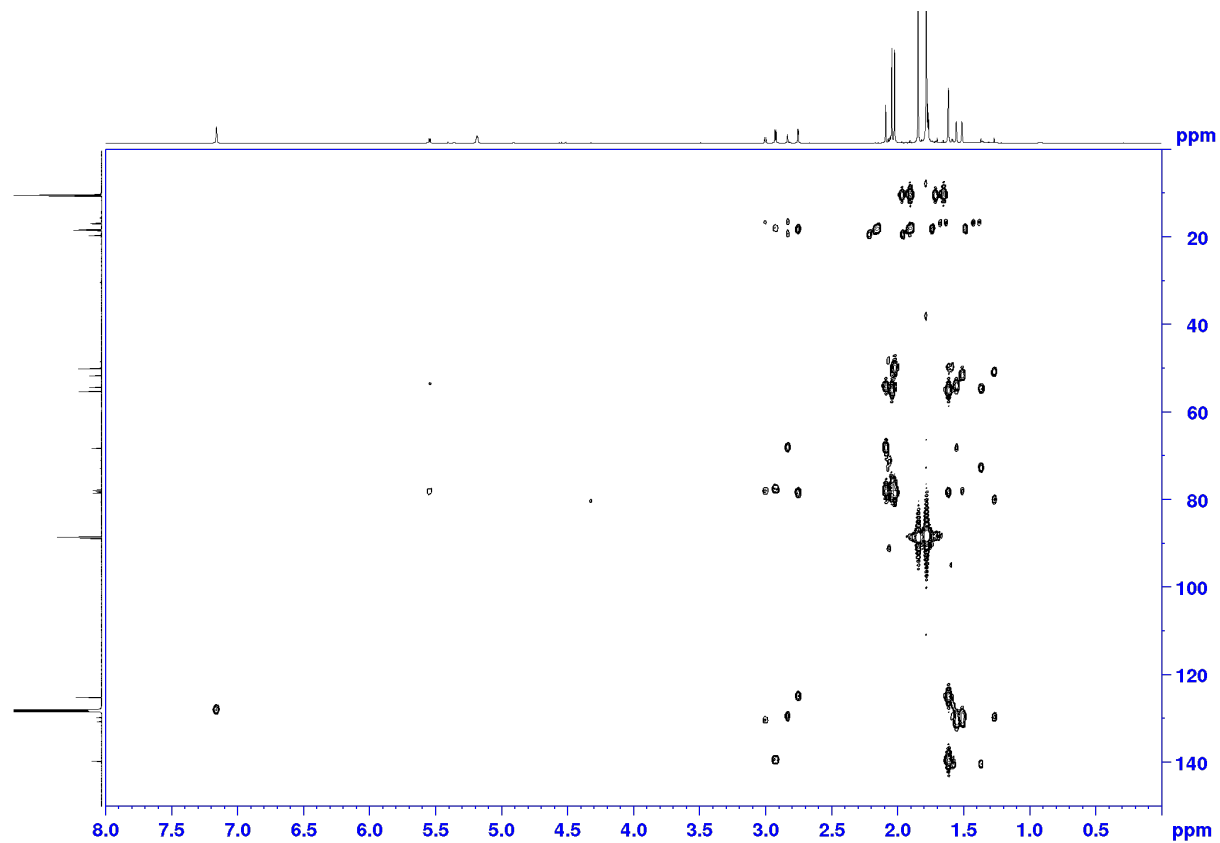
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )



HSQC (500 MHz, C<sub>6</sub>D<sub>6</sub>)



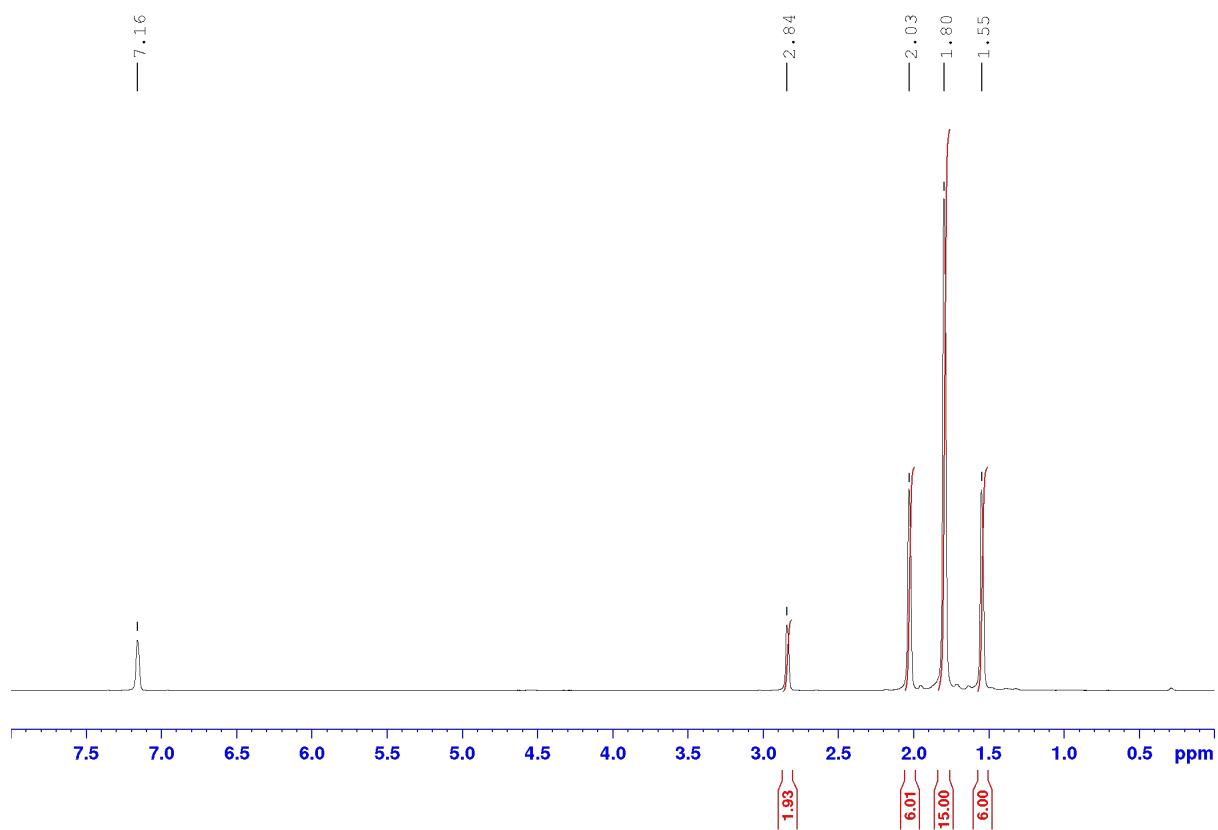
HMBC (500 MHz, C<sub>6</sub>D<sub>6</sub>)



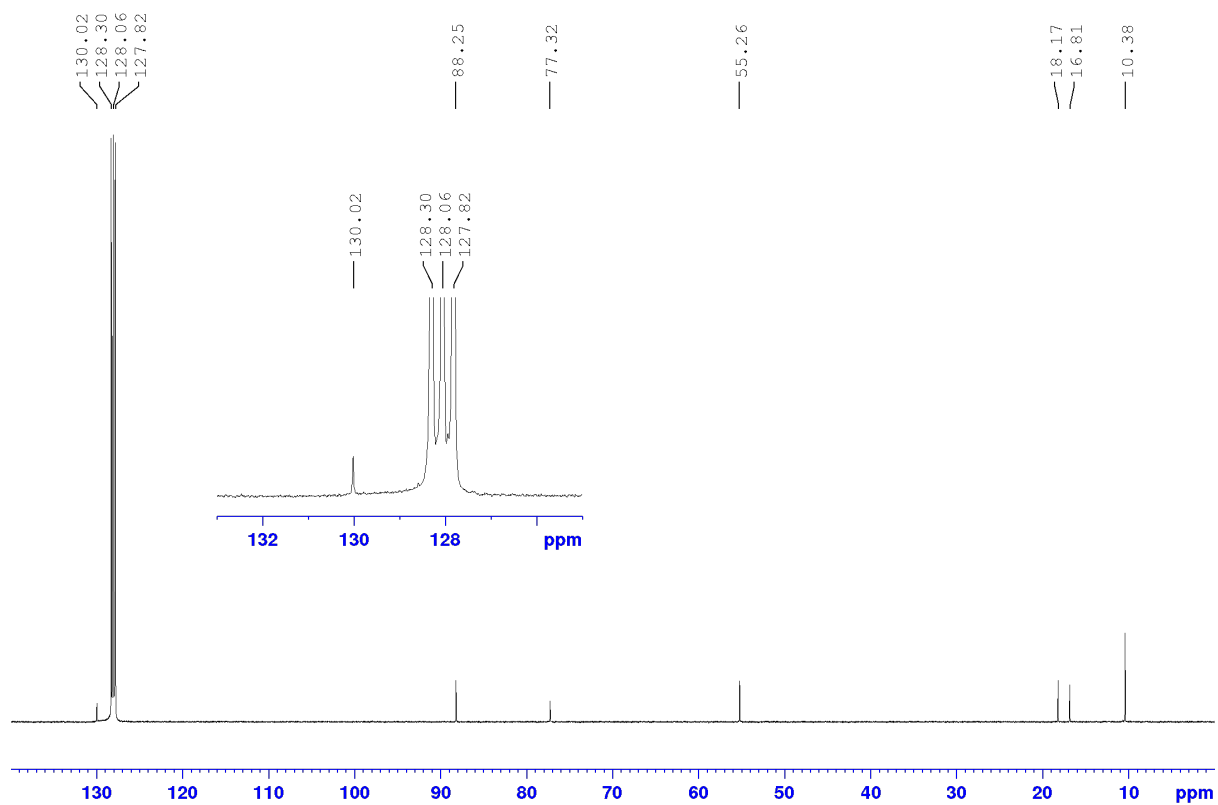
[Cp\*Ir( $\eta^4$ -durene)]



$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )

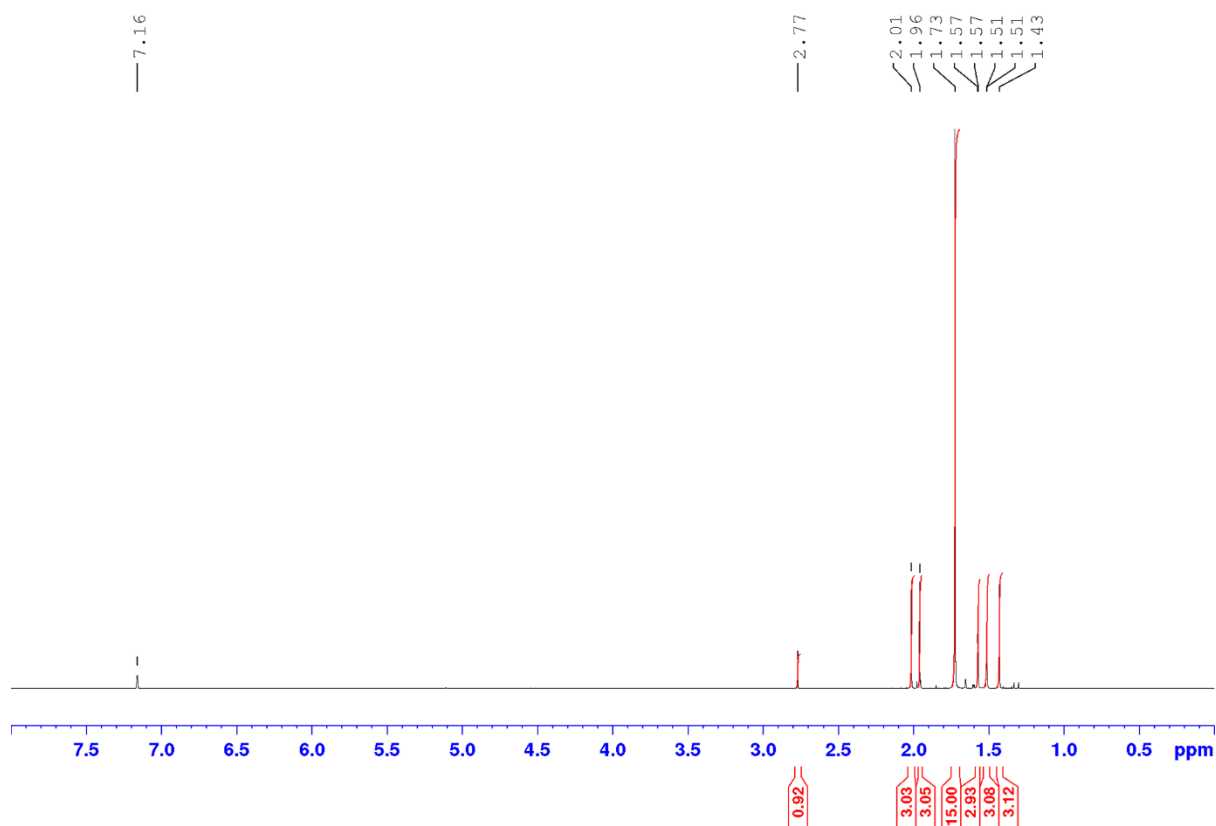


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )

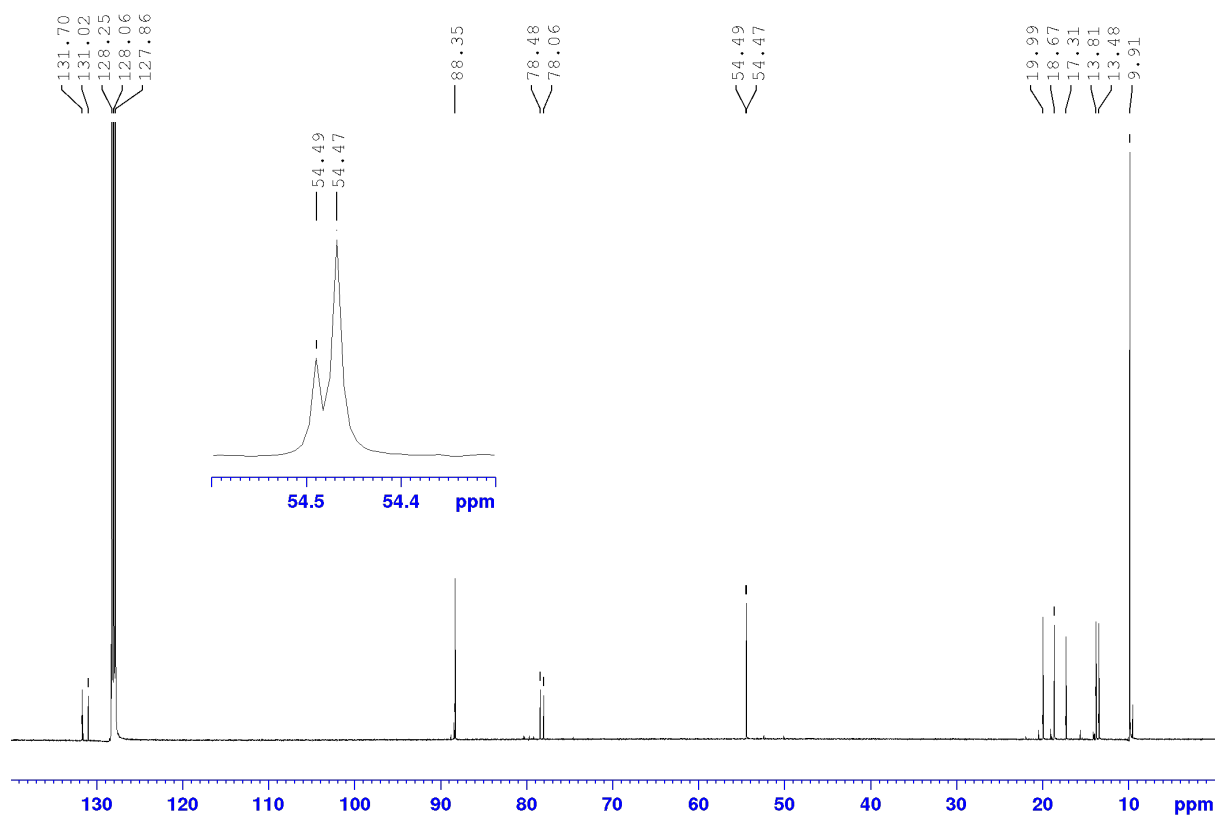


$[\text{Cp}^*\text{Ir}(\eta^4\text{-pentamethylbenzene})]$

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )

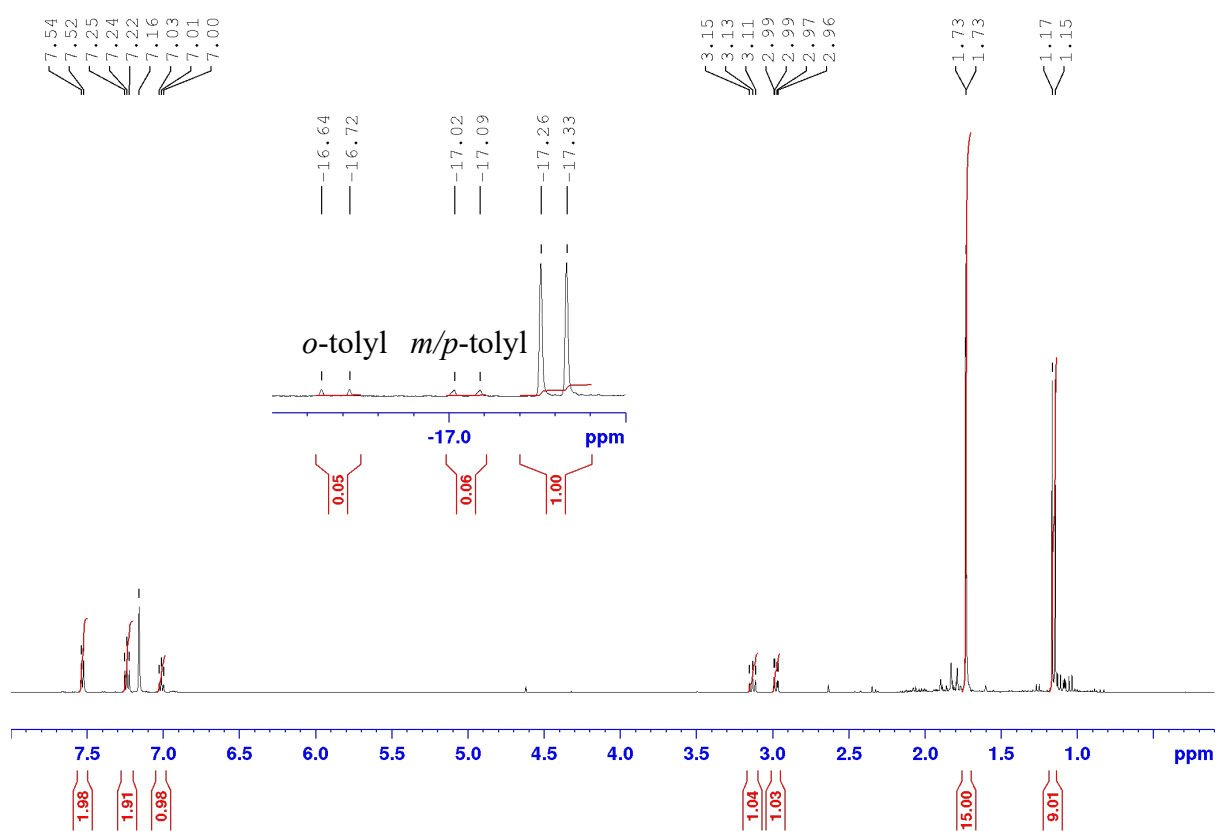


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )

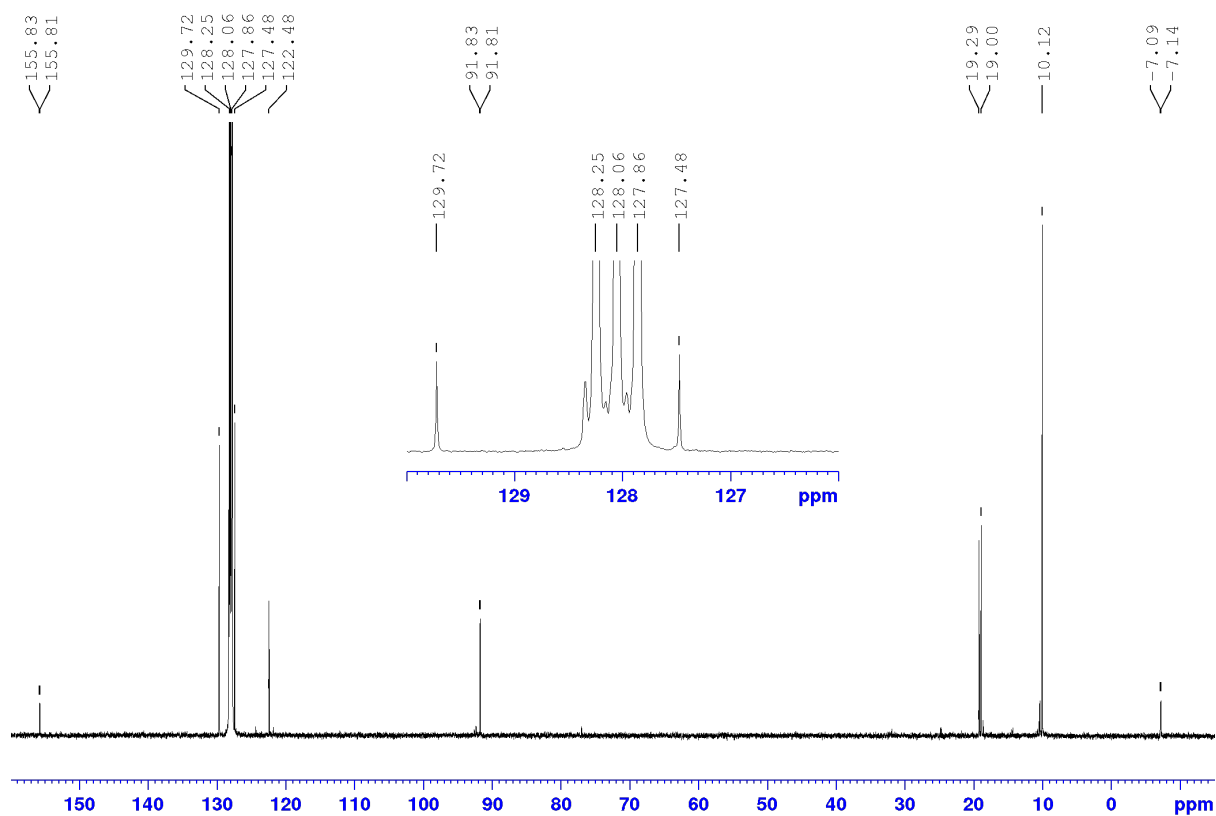


[Cp\*Ir(PMe<sub>3</sub>)(H)(benzyl)] (2a)

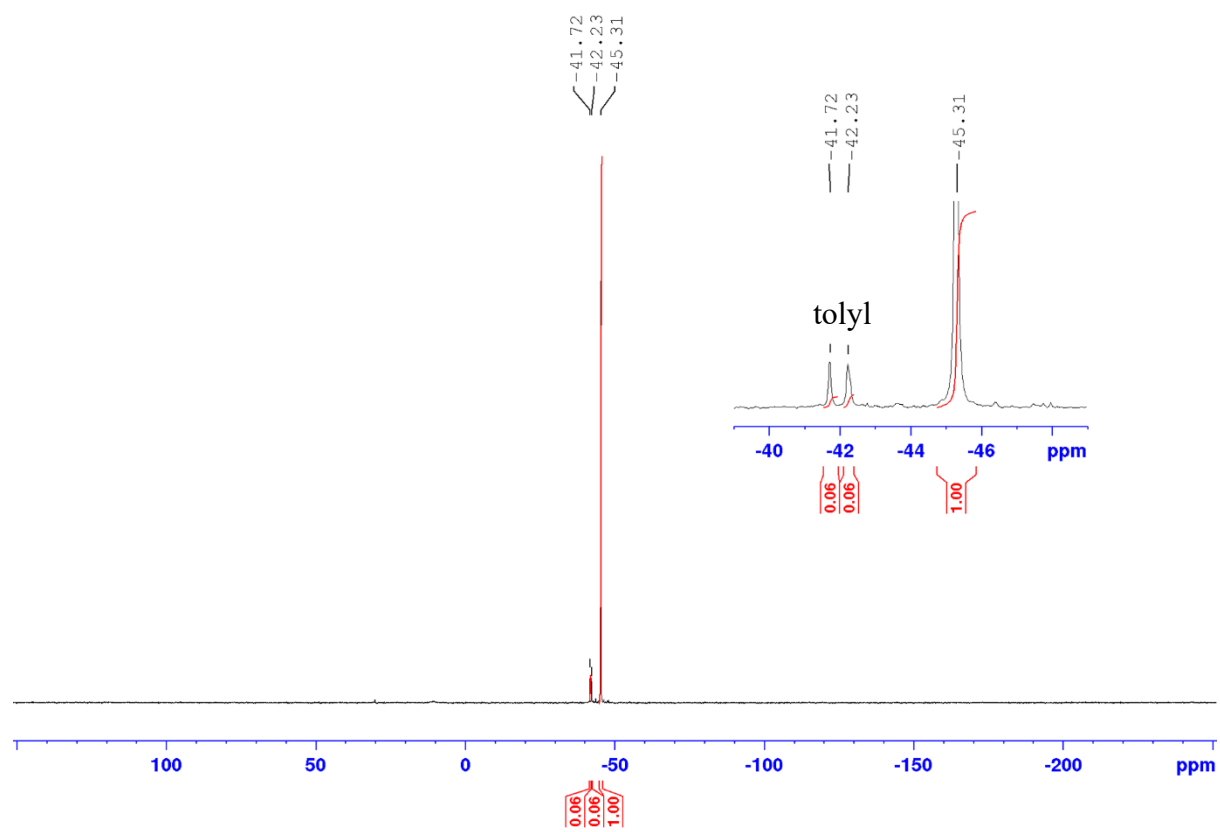
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)

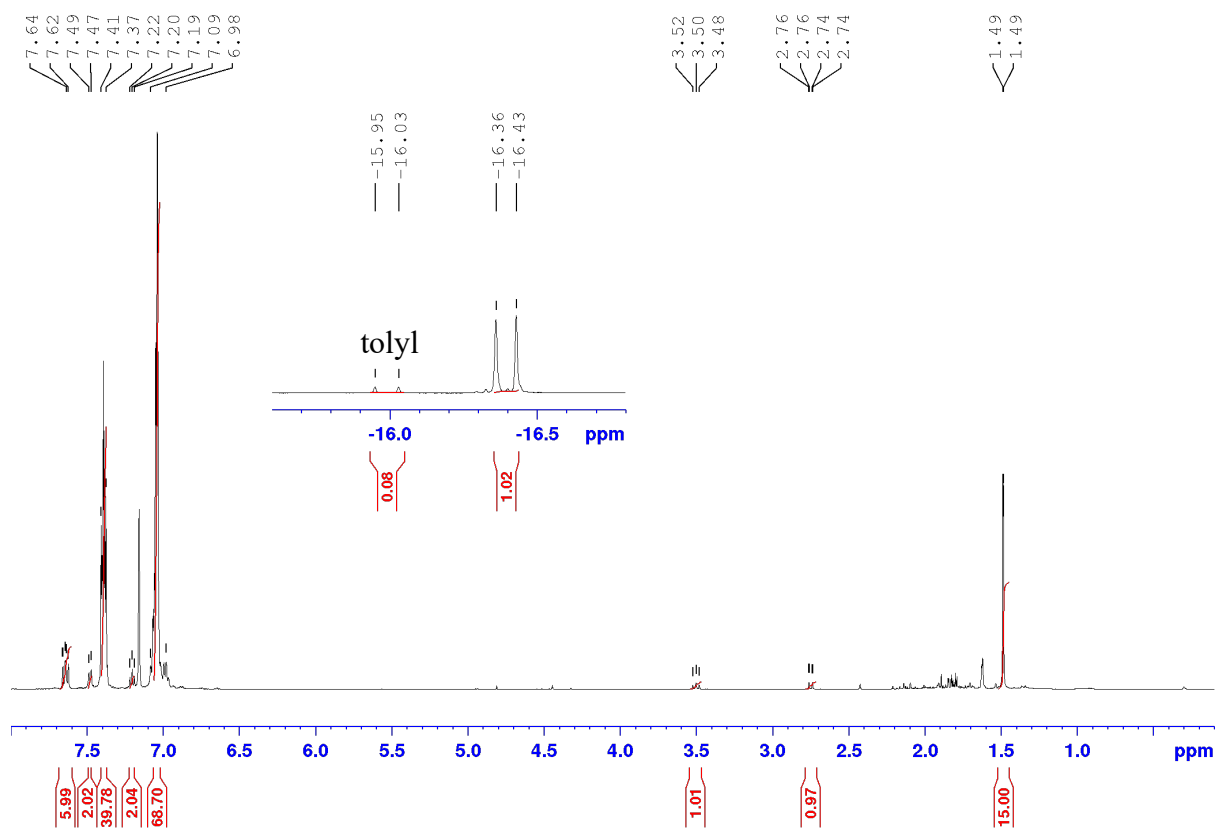


$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

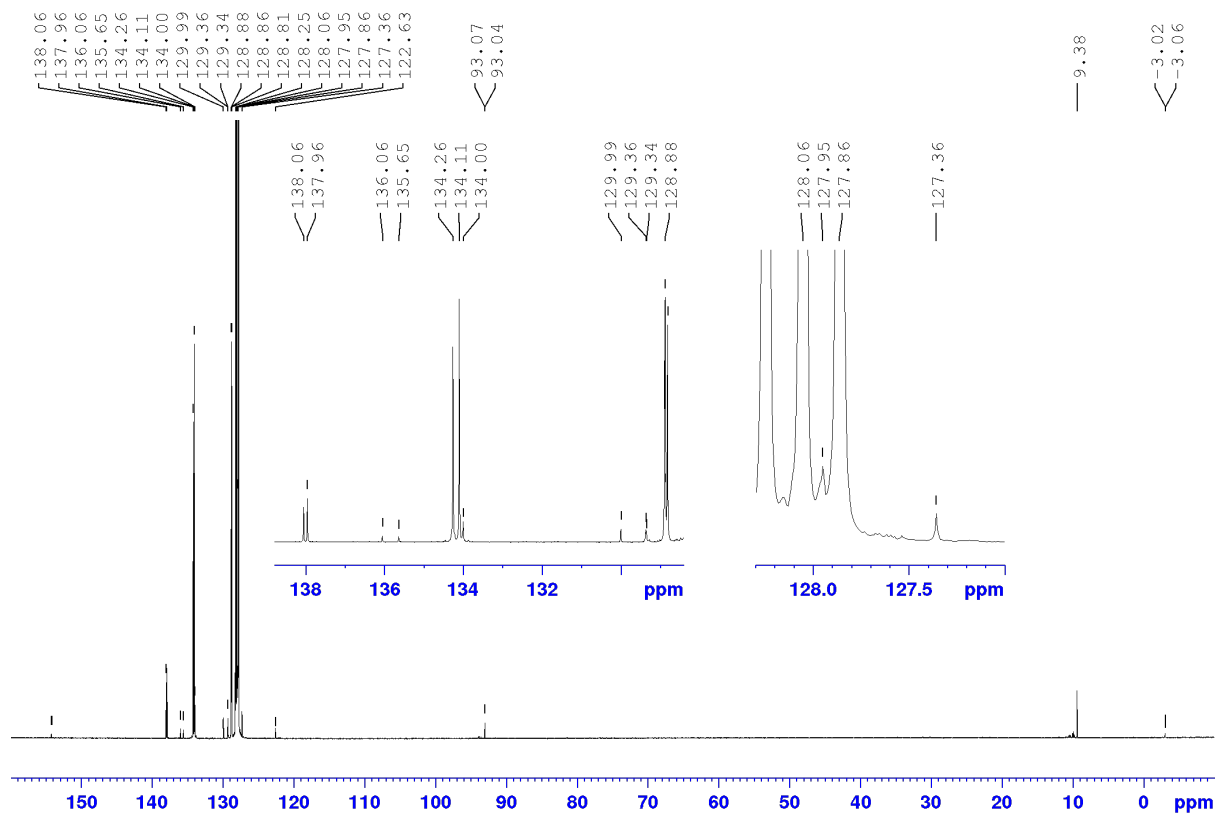


[Cp\*Ir(PPh<sub>3</sub>)(H)(benzyl)] (**2b**) and PPh<sub>3</sub>

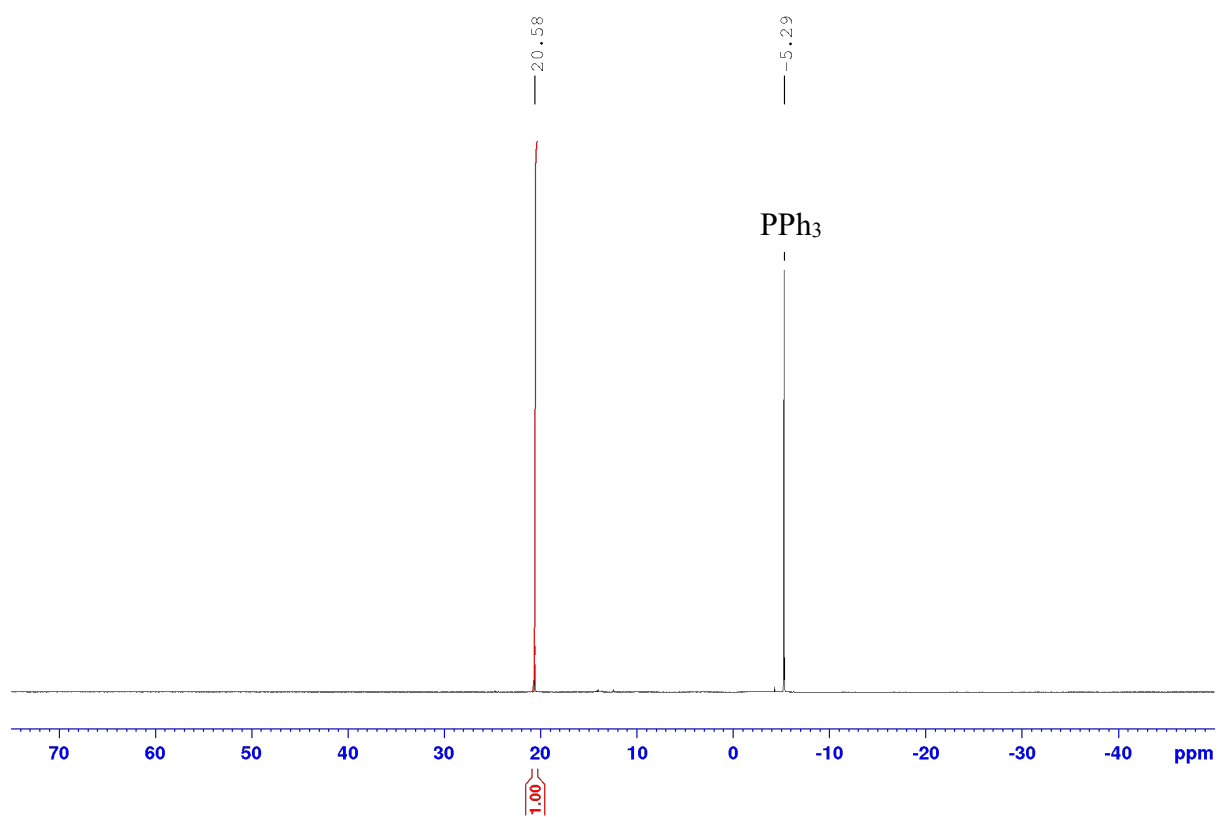
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)

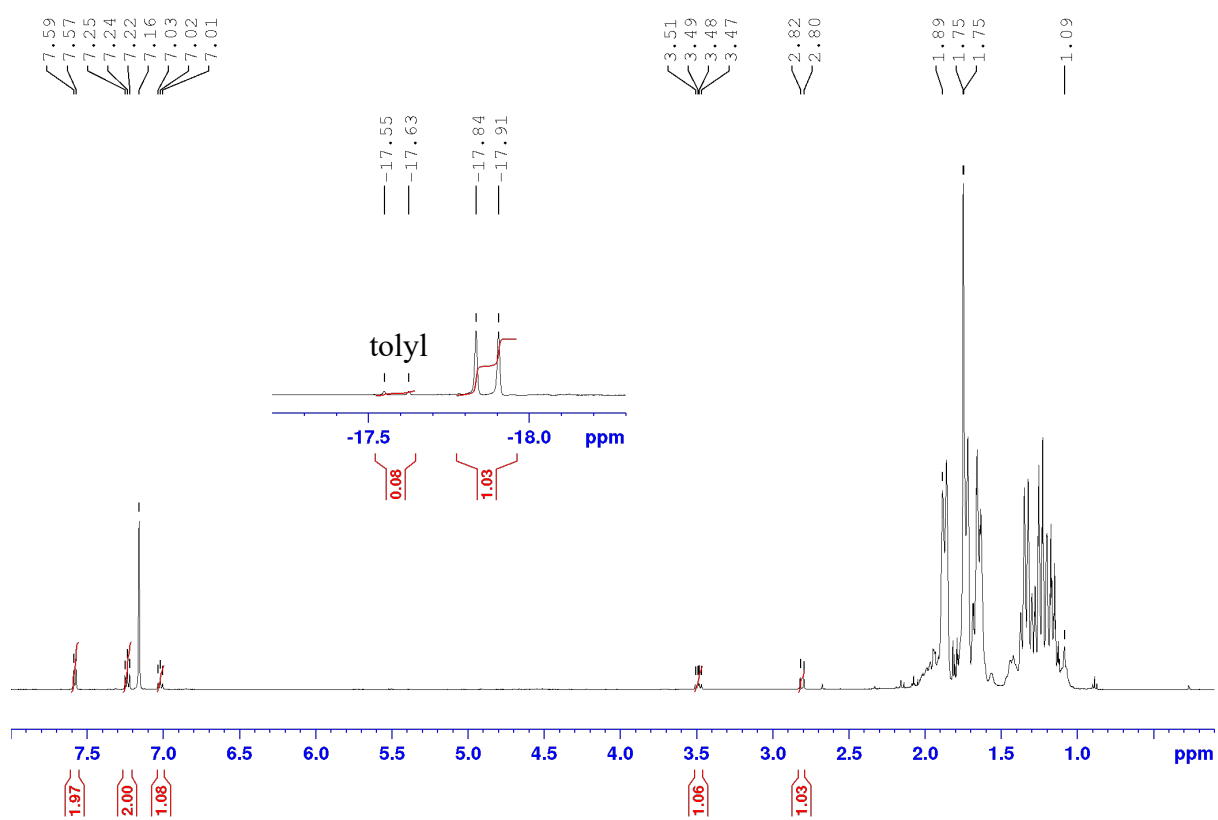


$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

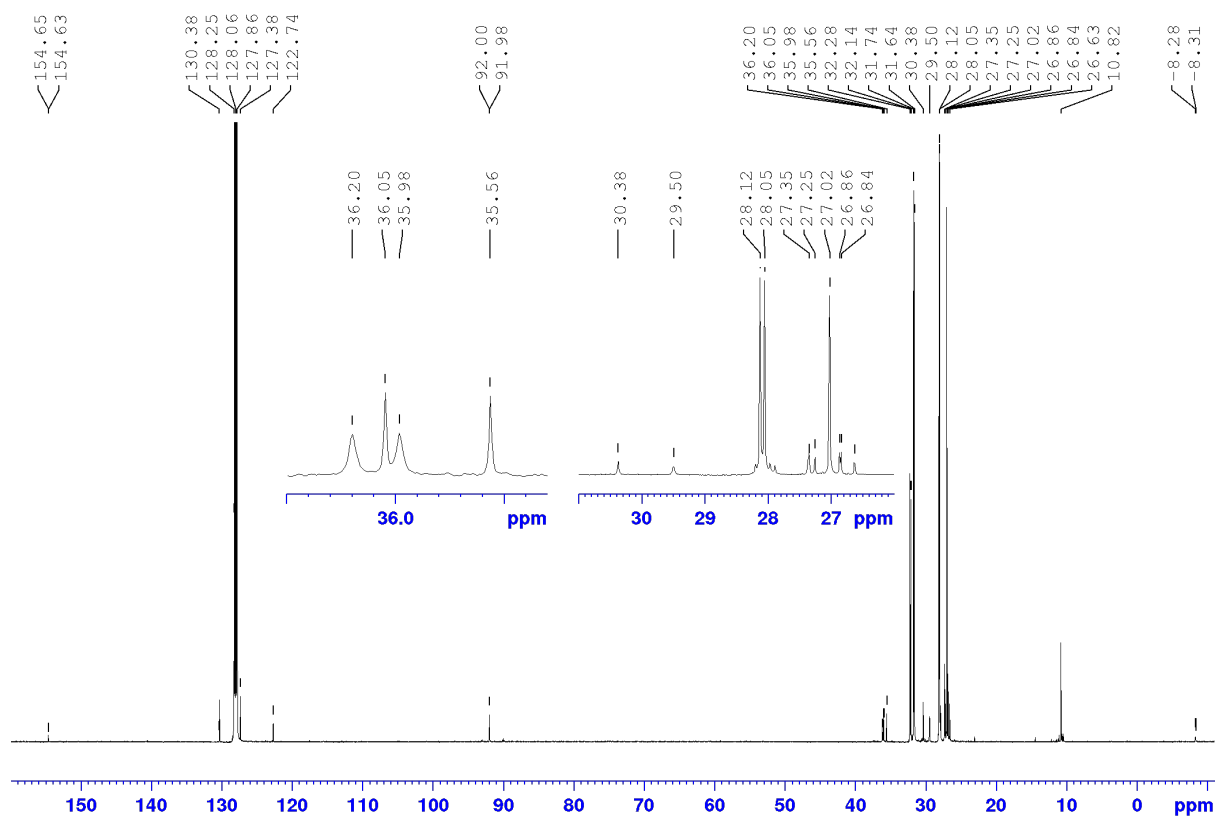


[Cp\*Ir(PCy<sub>3</sub>)(H)(benzyl)] (**2c**) and PCy<sub>3</sub>

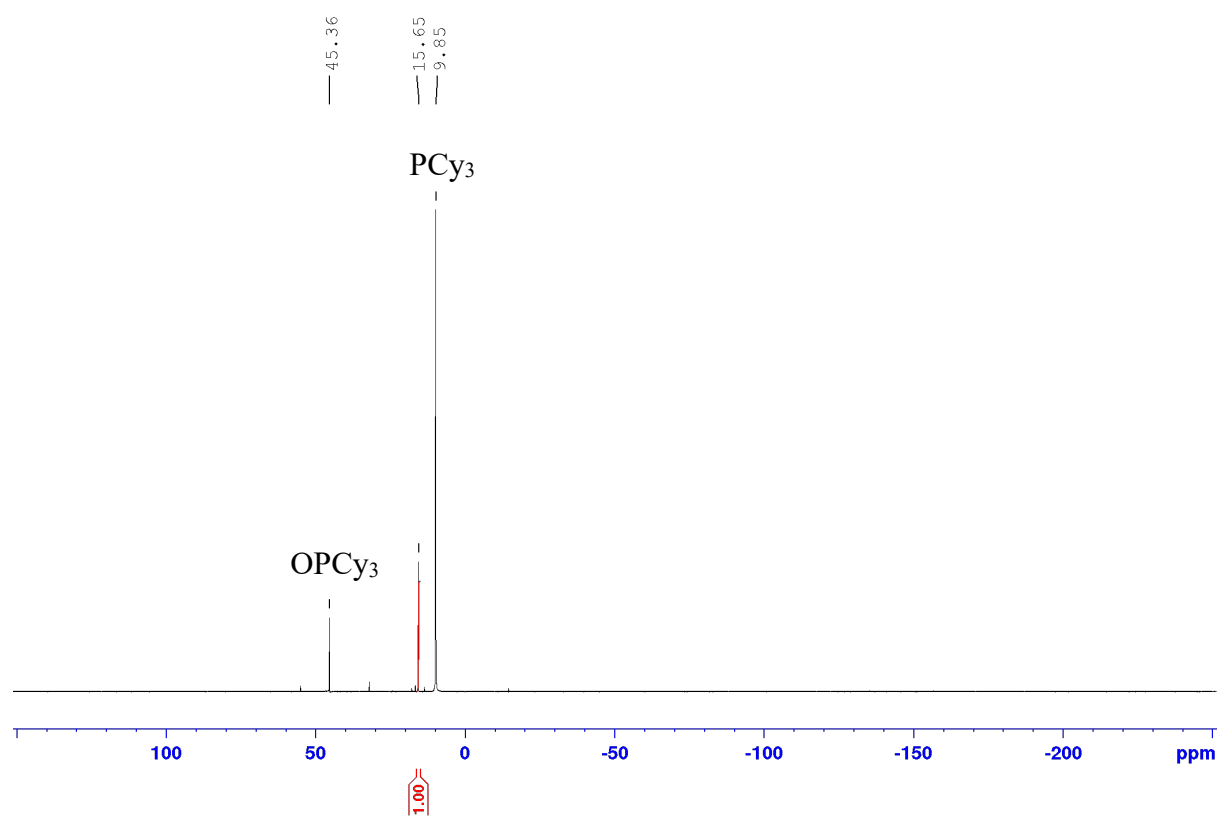
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) Aliphatic region not integrated due to excessive overlapped signals.



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)



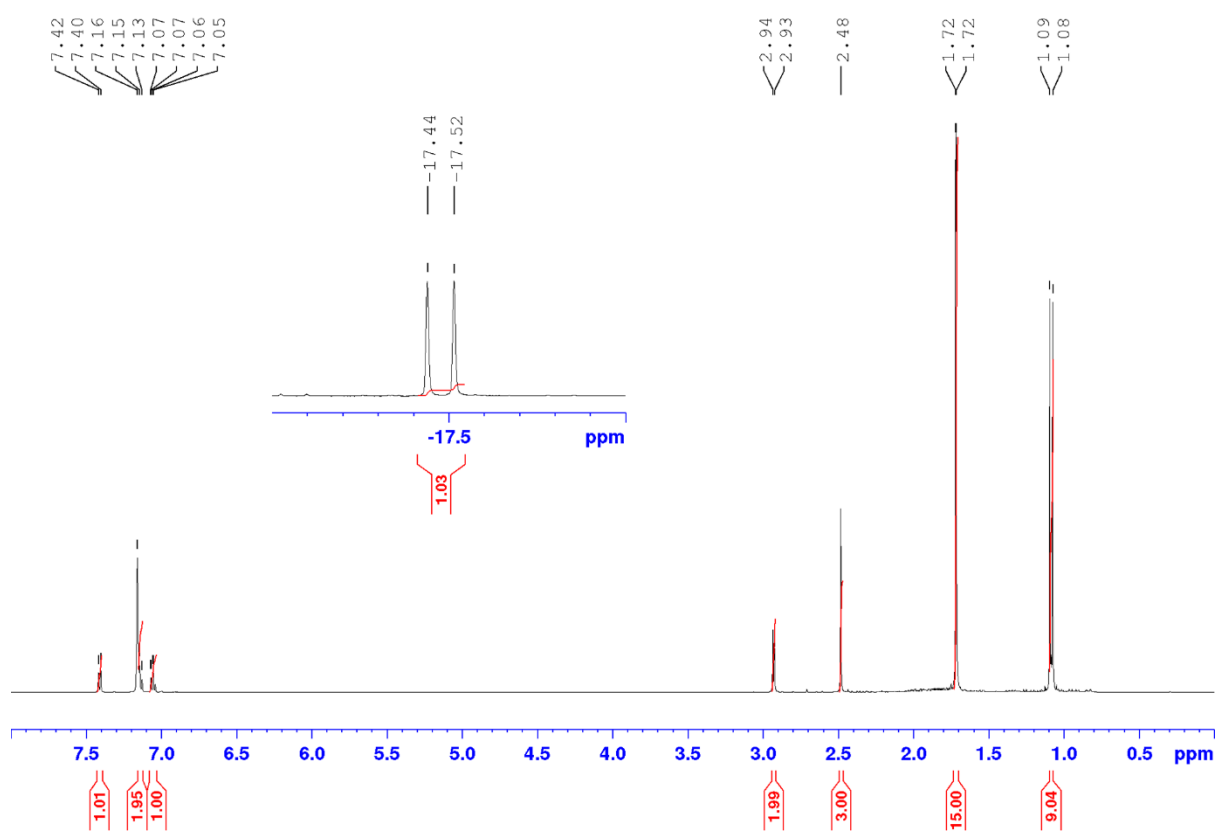
$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )



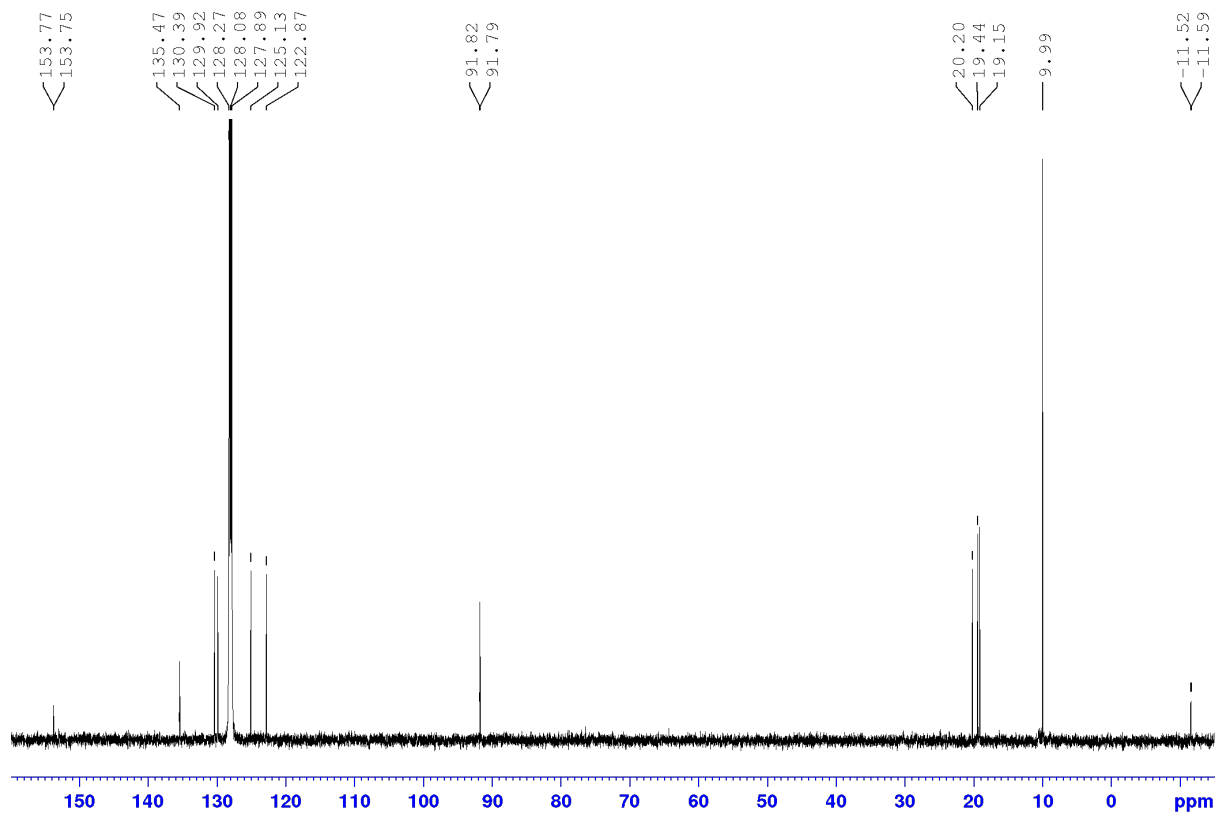


[Cp\*Ir(PMe<sub>3</sub>)(H)(2-methylbenzyl)] (3)

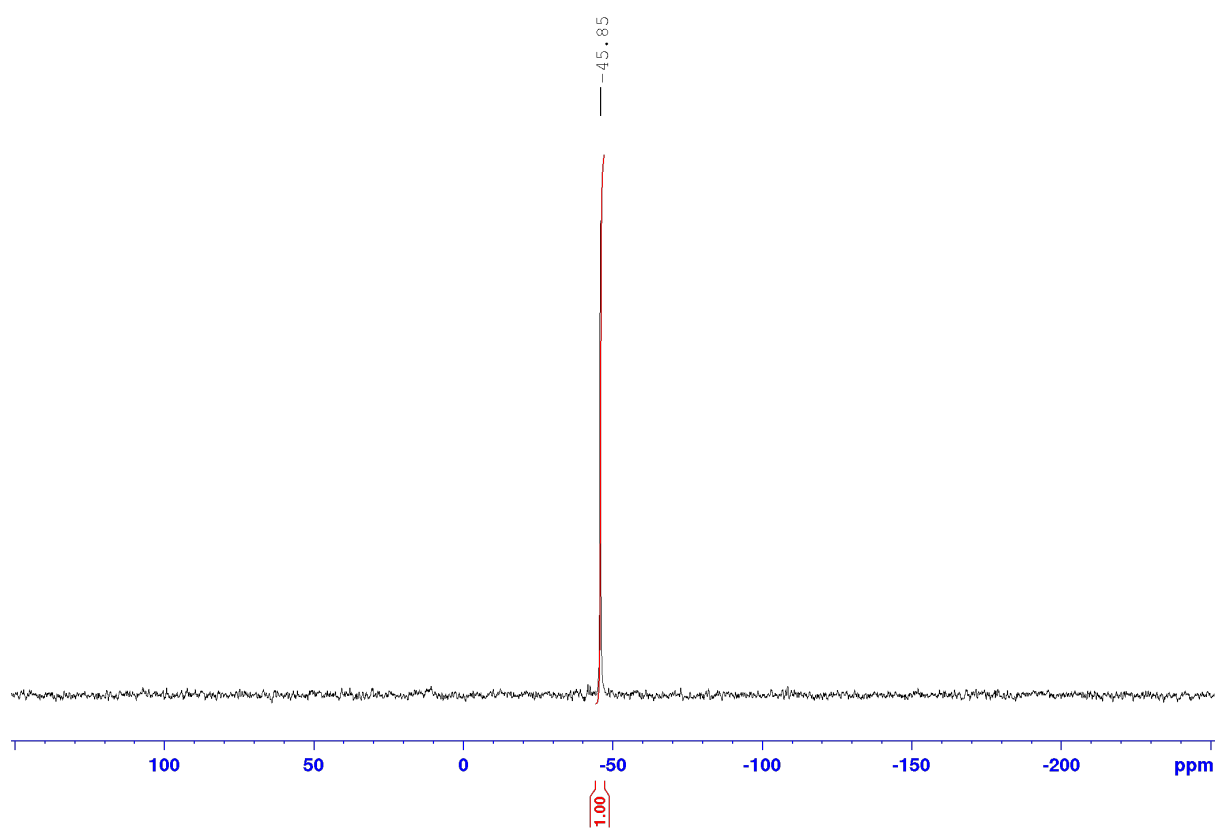
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)

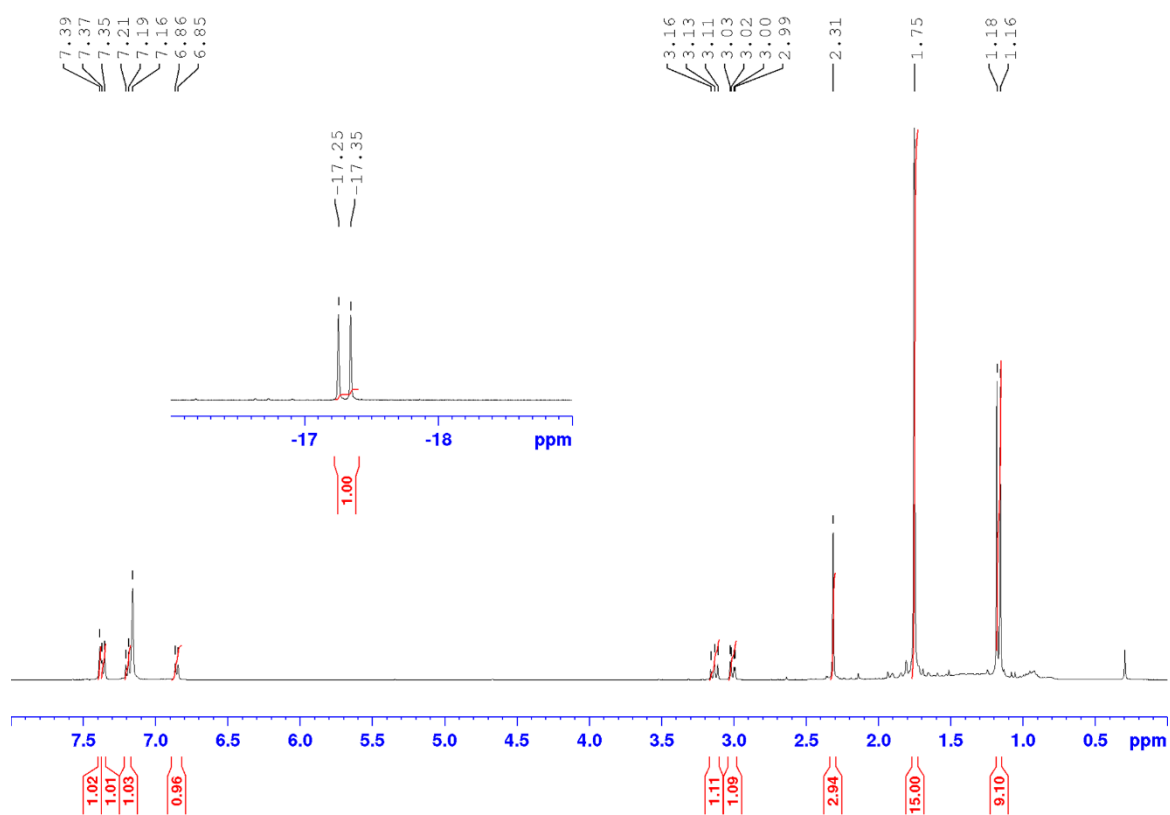


$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

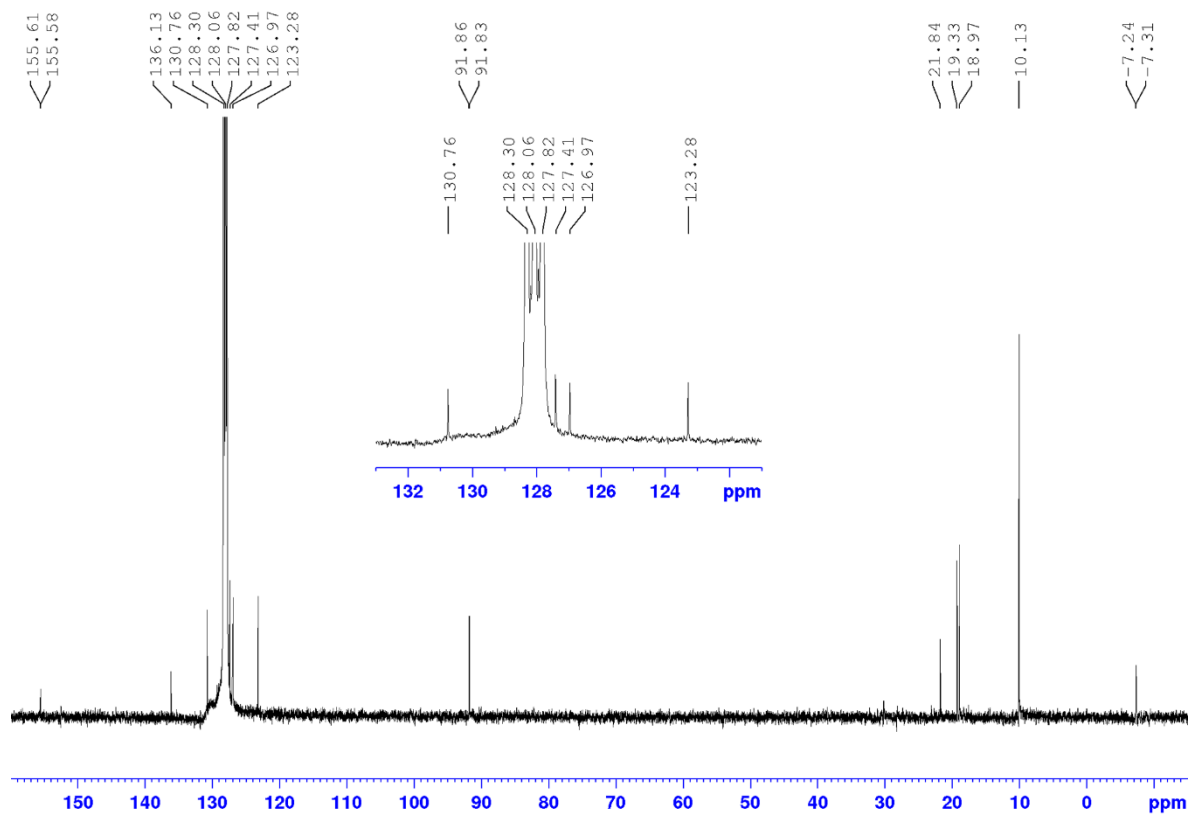


[Cp\*Ir(PMe<sub>3</sub>)(H)(3-methylbenzyl)] (4)

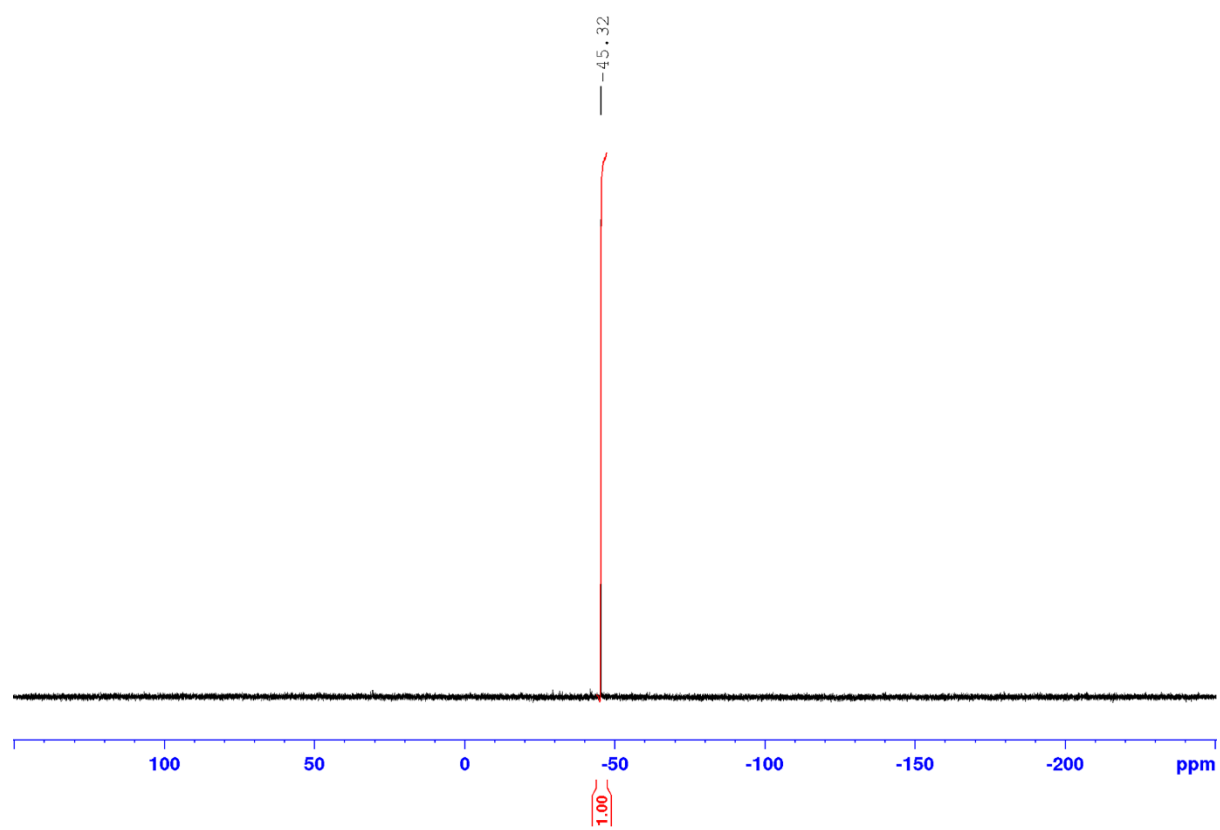
<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>)

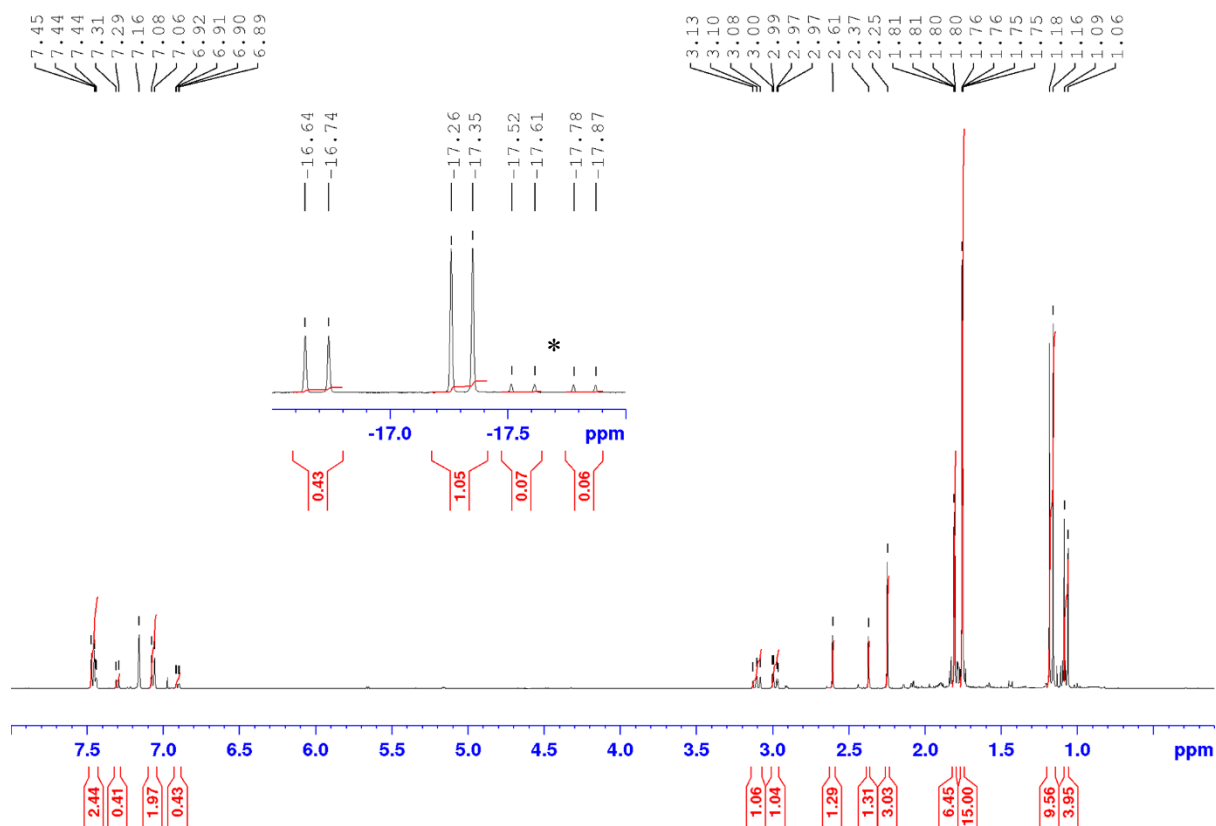


$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ )

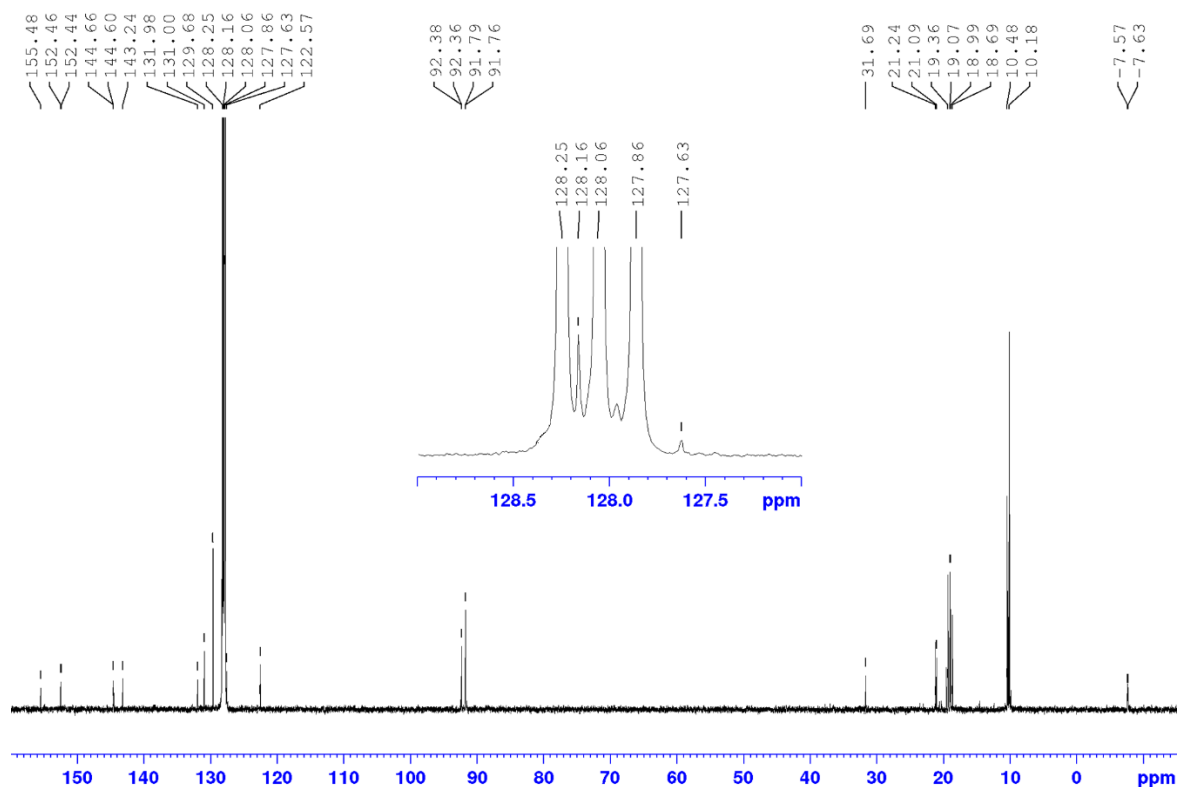


[Cp\*Ir(PMe<sub>3</sub>)(H)(4-methylbenzyl)] (**5a**) and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,5-dimethylphenyl)] (**5b**)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)

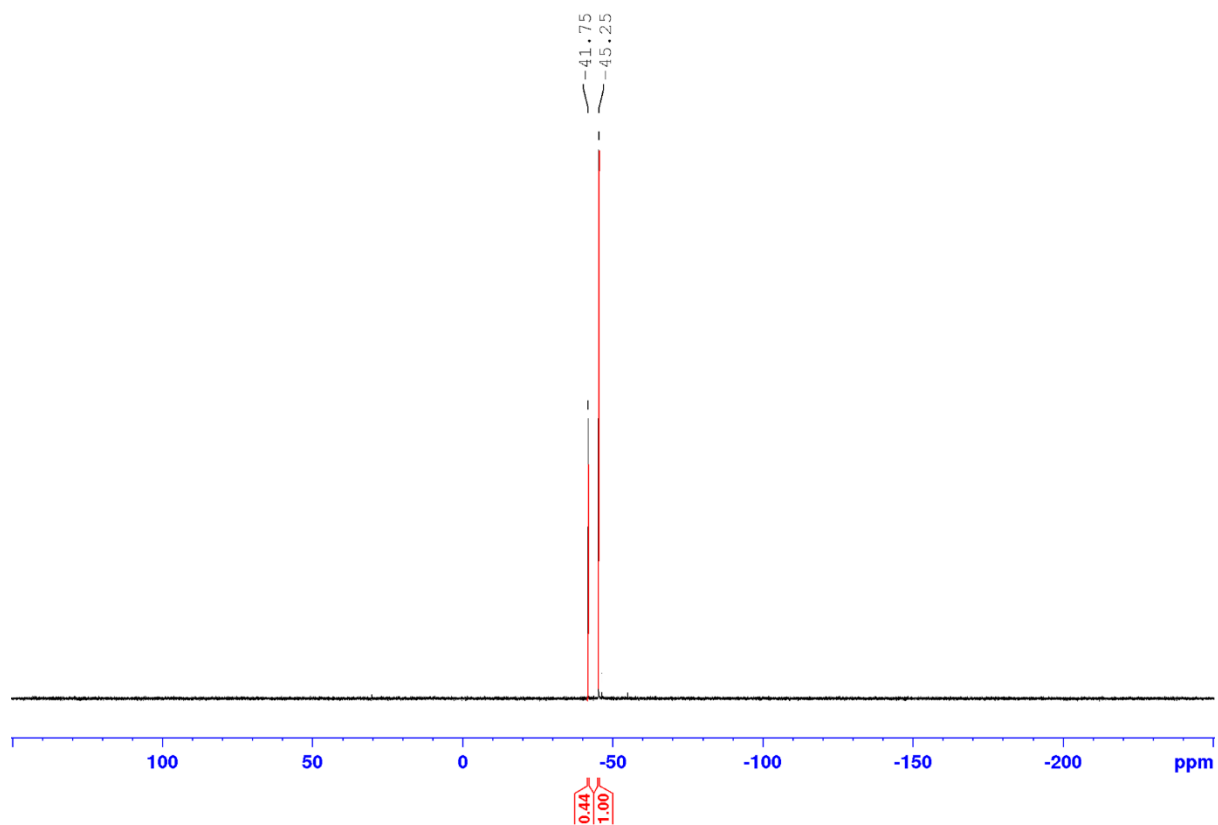


<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)

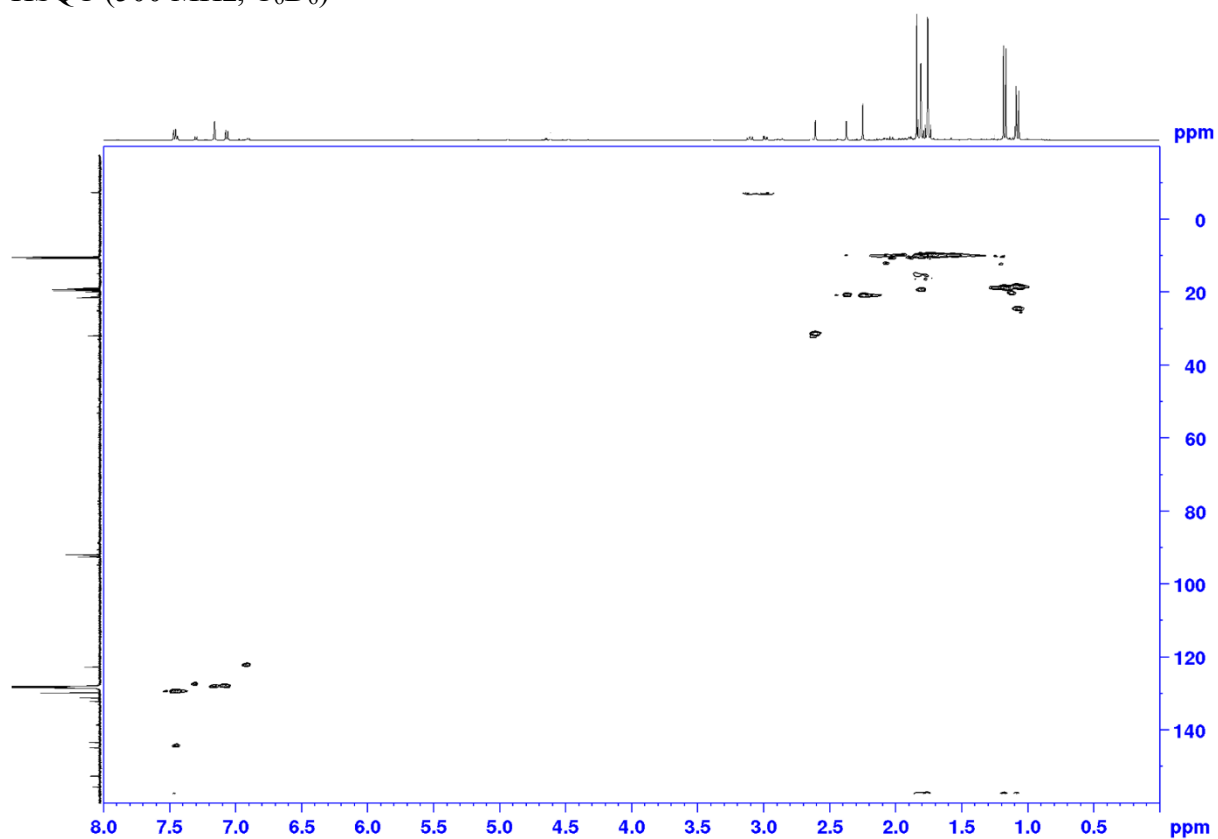


\*Proposed double C-H activation species (see S13)

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

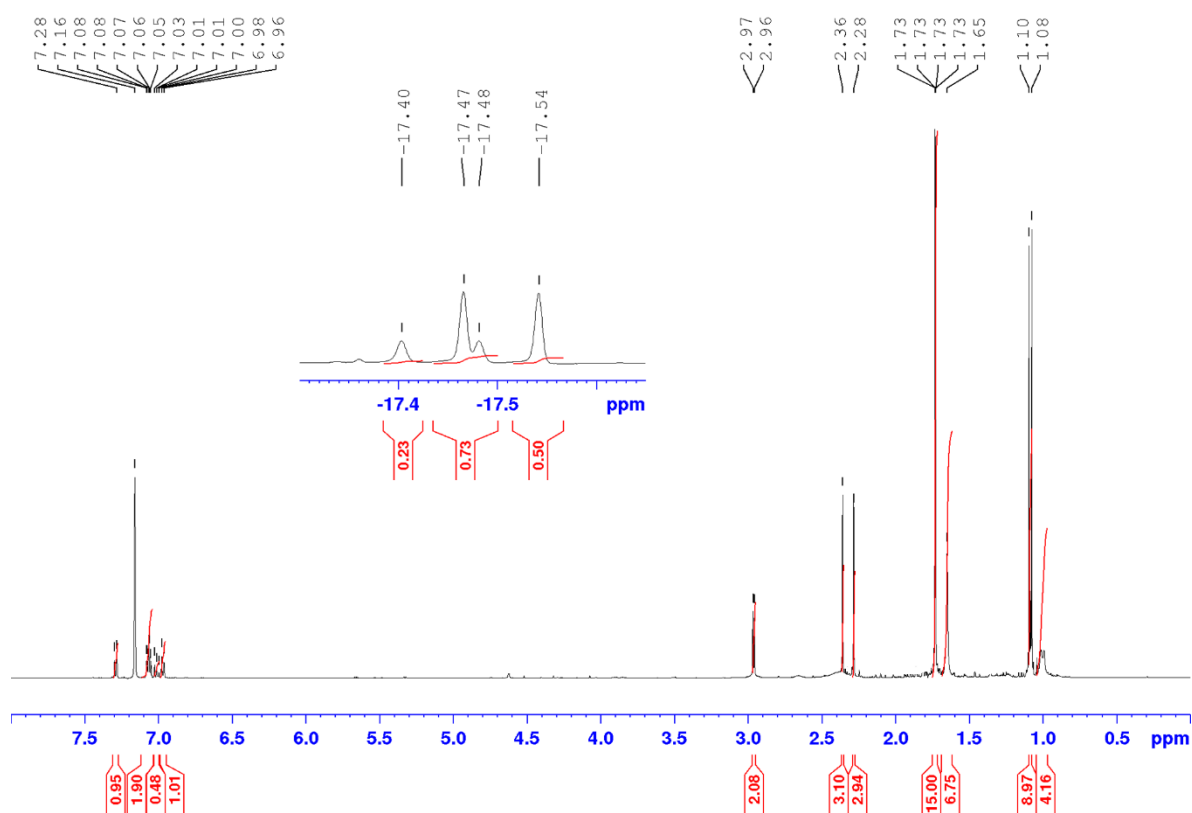


HSQC (500 MHz,  $\text{C}_6\text{D}_6$ )

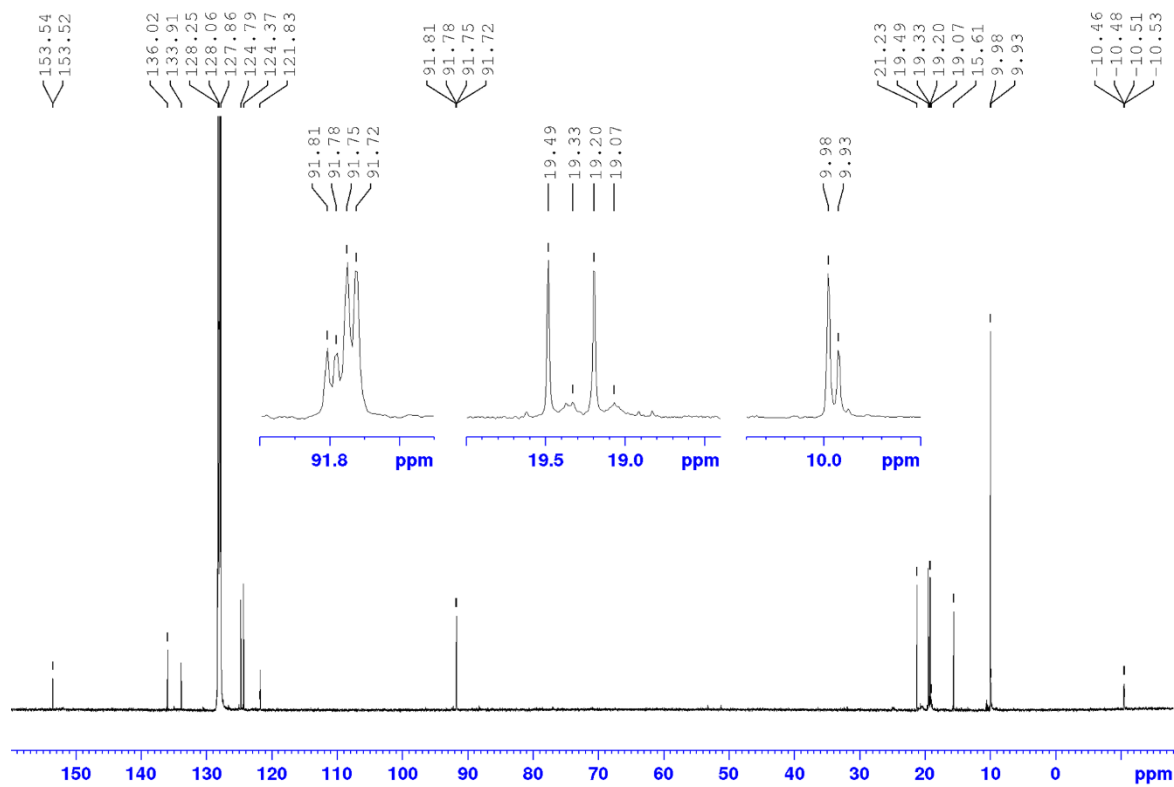


[Cp\*Ir(PMe<sub>3</sub>)(H)(2,3-dimethylbenzyl)] (7a) and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,6-dimethylbenzyl)] (7b)

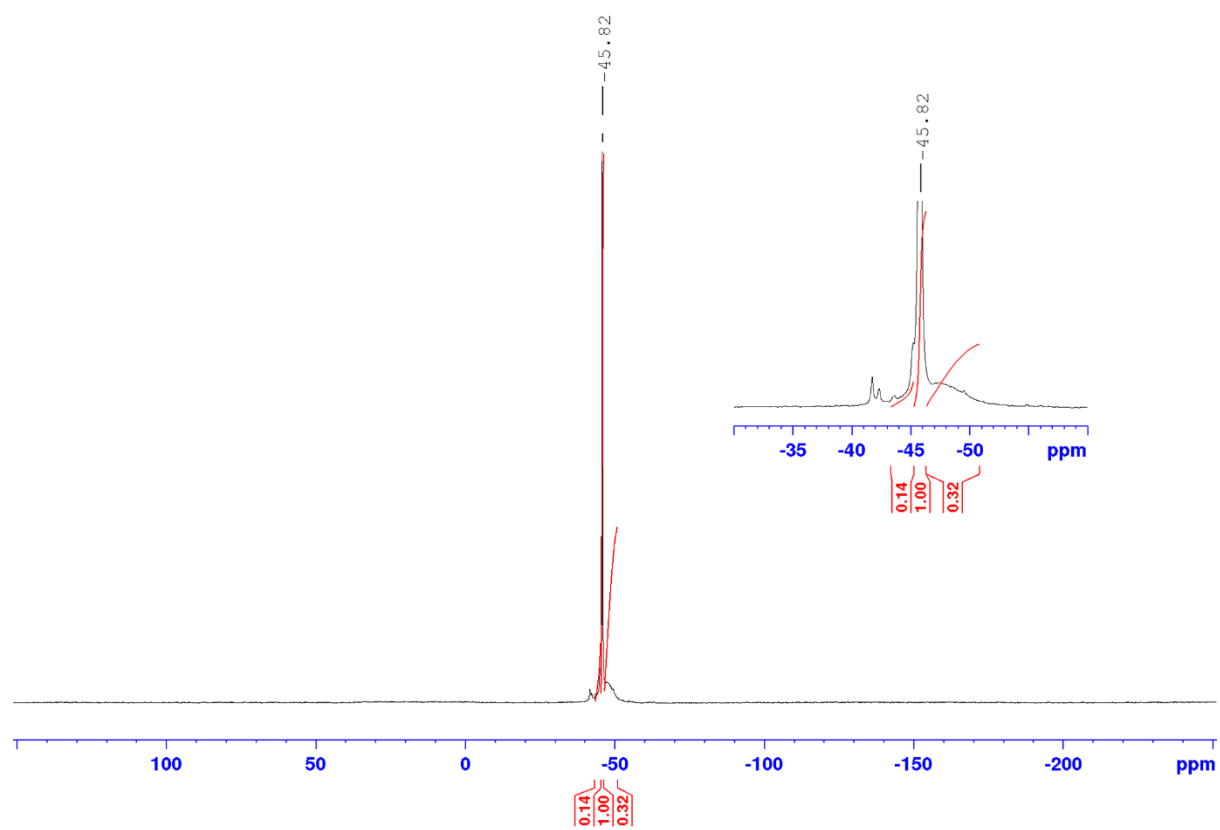
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



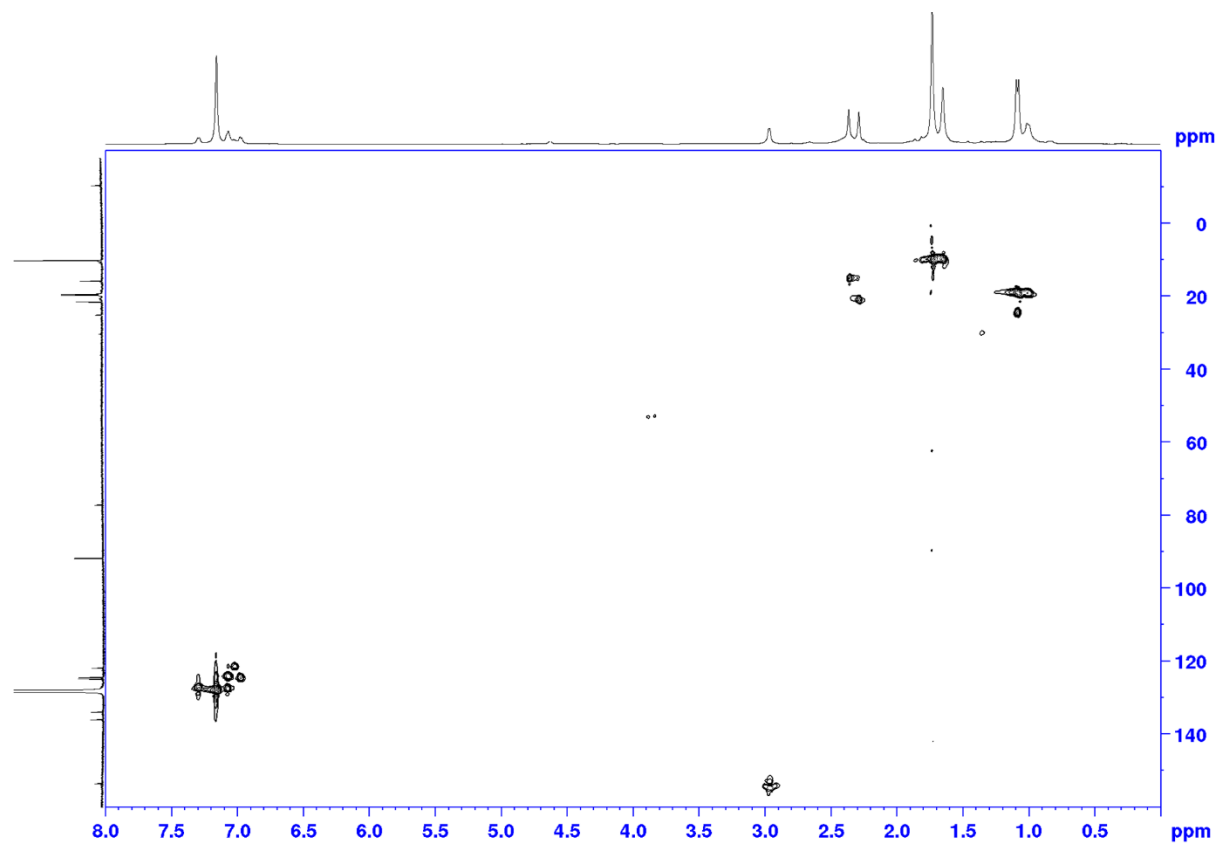
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)



$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

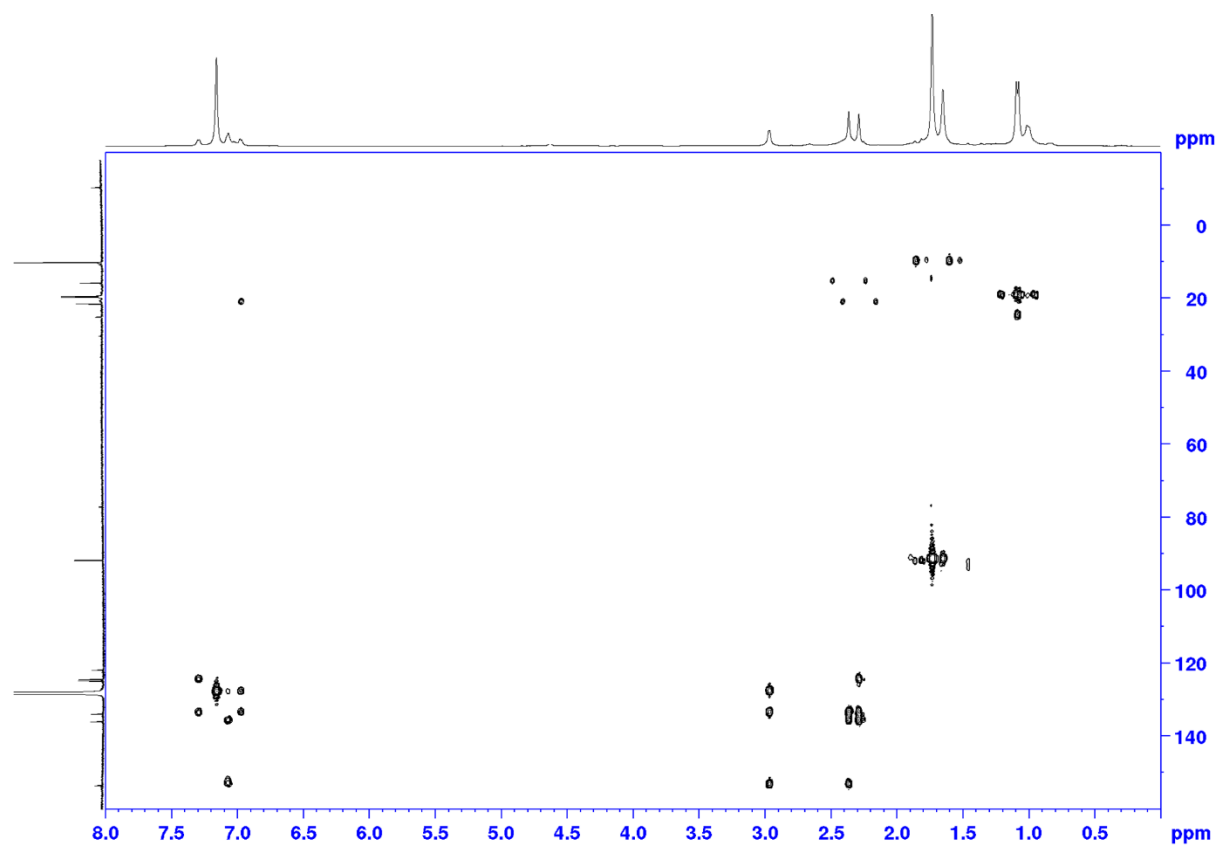


HSQC (500 MHz,  $\text{C}_6\text{D}_6$ )



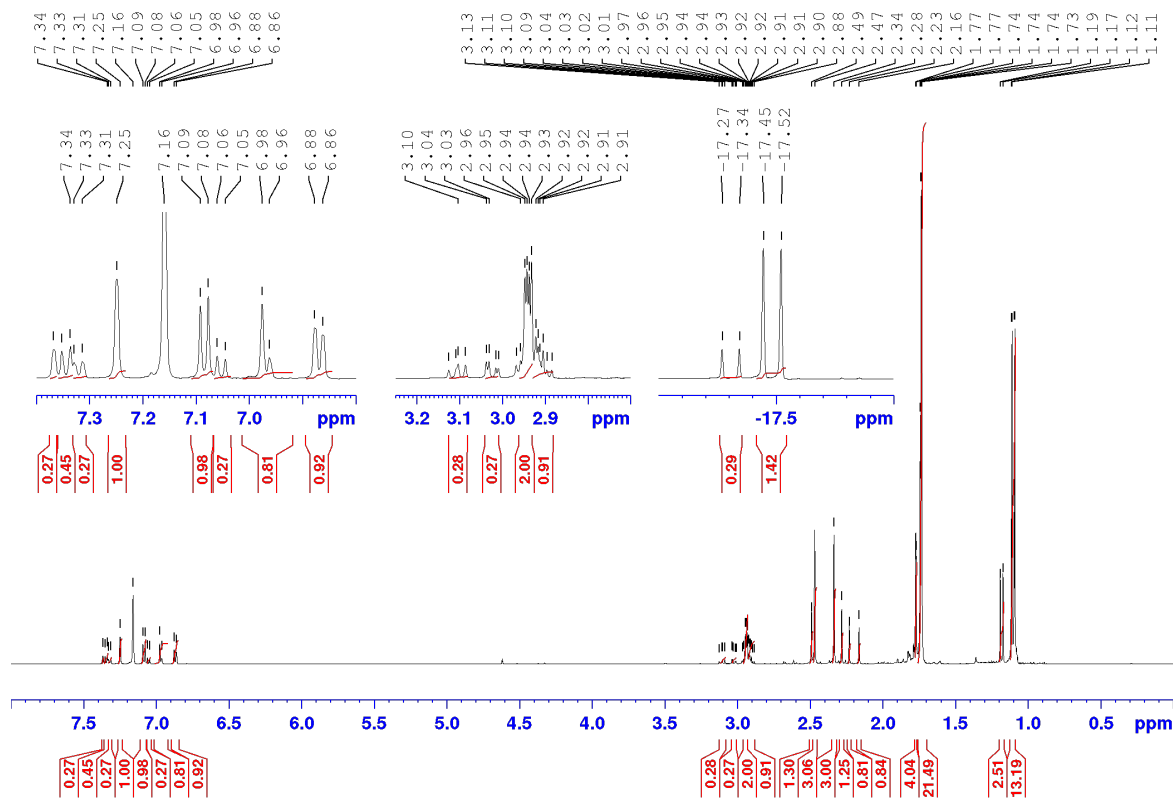


HMBC (500 MHz, C<sub>6</sub>D<sub>6</sub>)

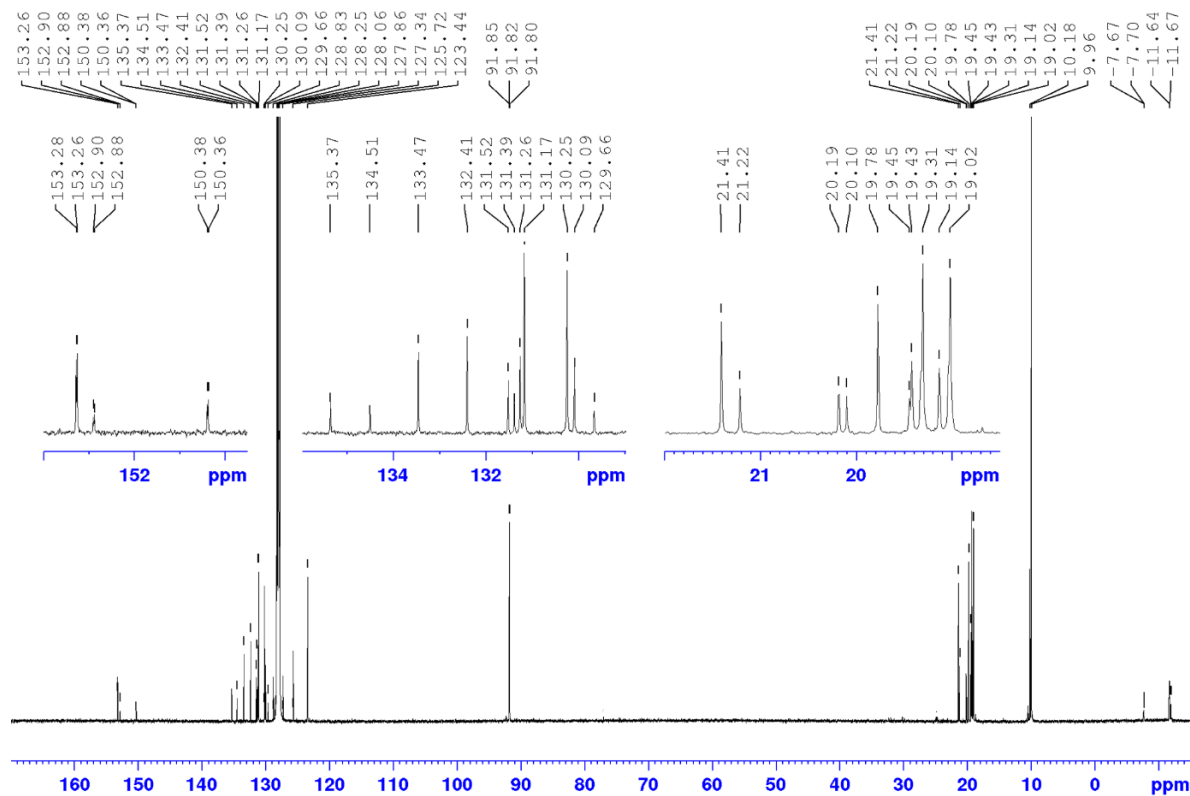


[Cp\*Ir(PMe<sub>3</sub>)(H)(2,5-dimethylbenzyl)] (**8a**), [Cp\*Ir(PMe<sub>3</sub>)(H)(2,4-dimethylbenzyl)] (**8b**)  
and [Cp\*Ir(PMe<sub>3</sub>)(H)(3,4-dimethylbenzyl)] (**8c**)

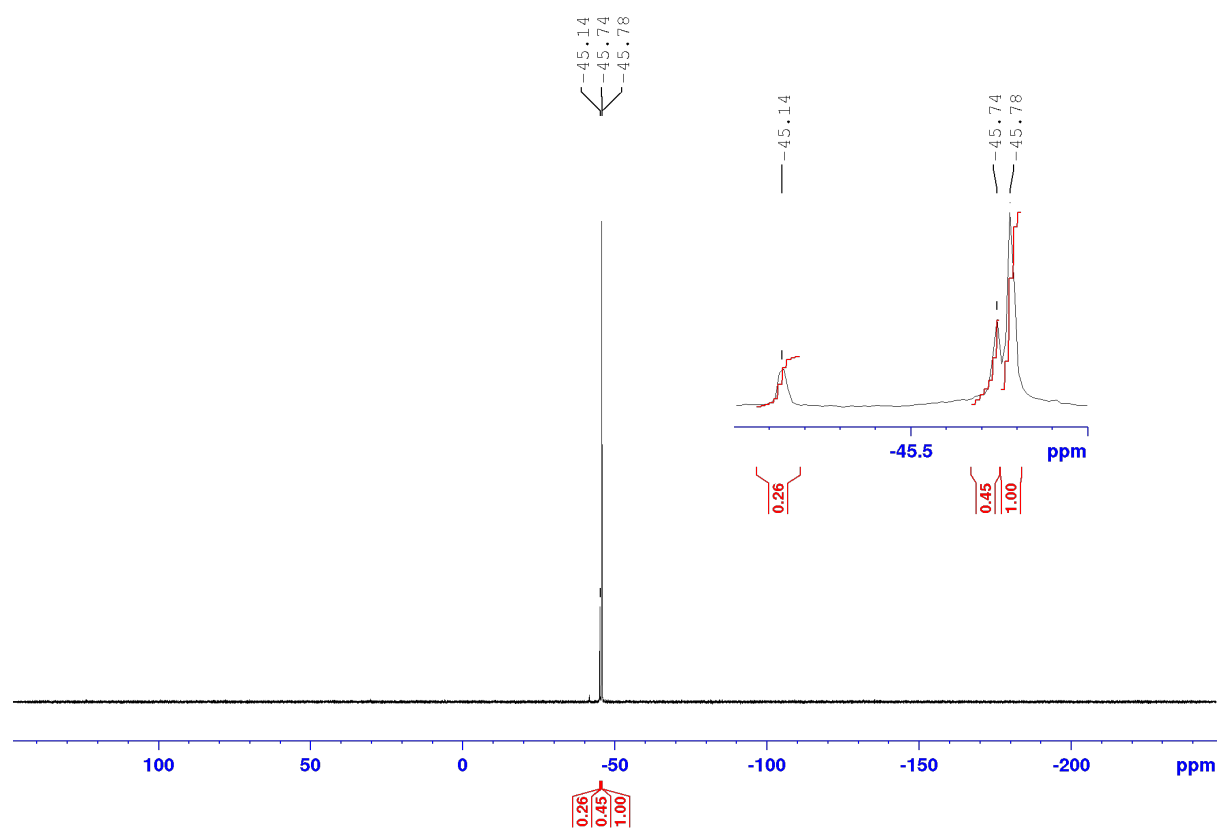
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



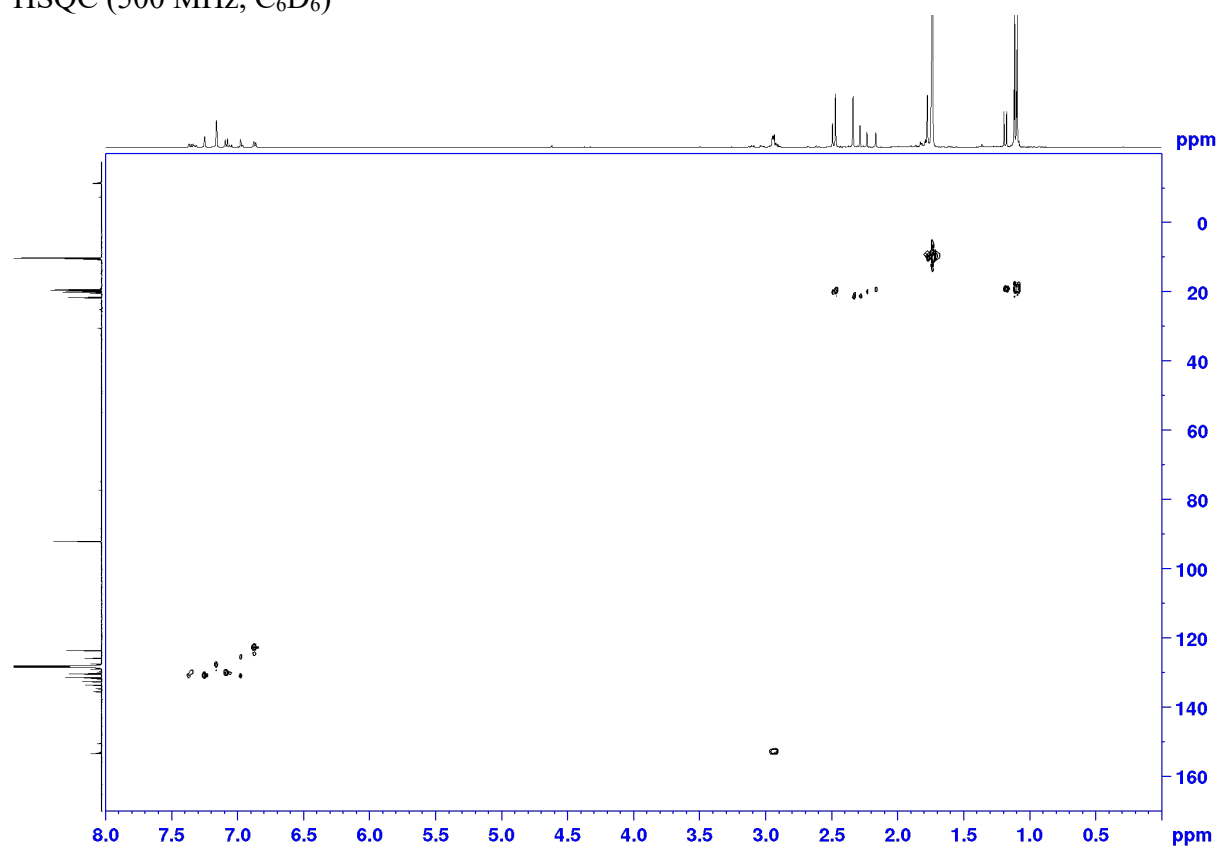
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)



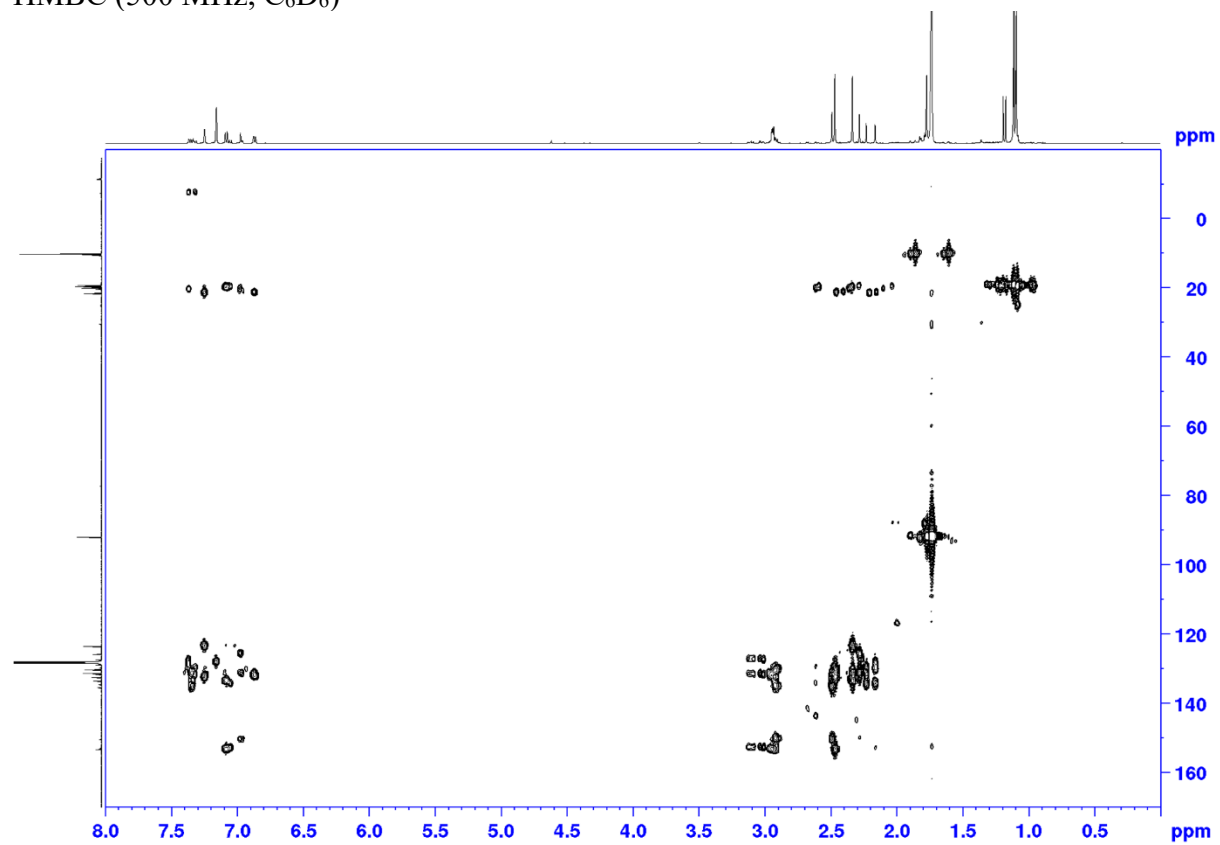
$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )



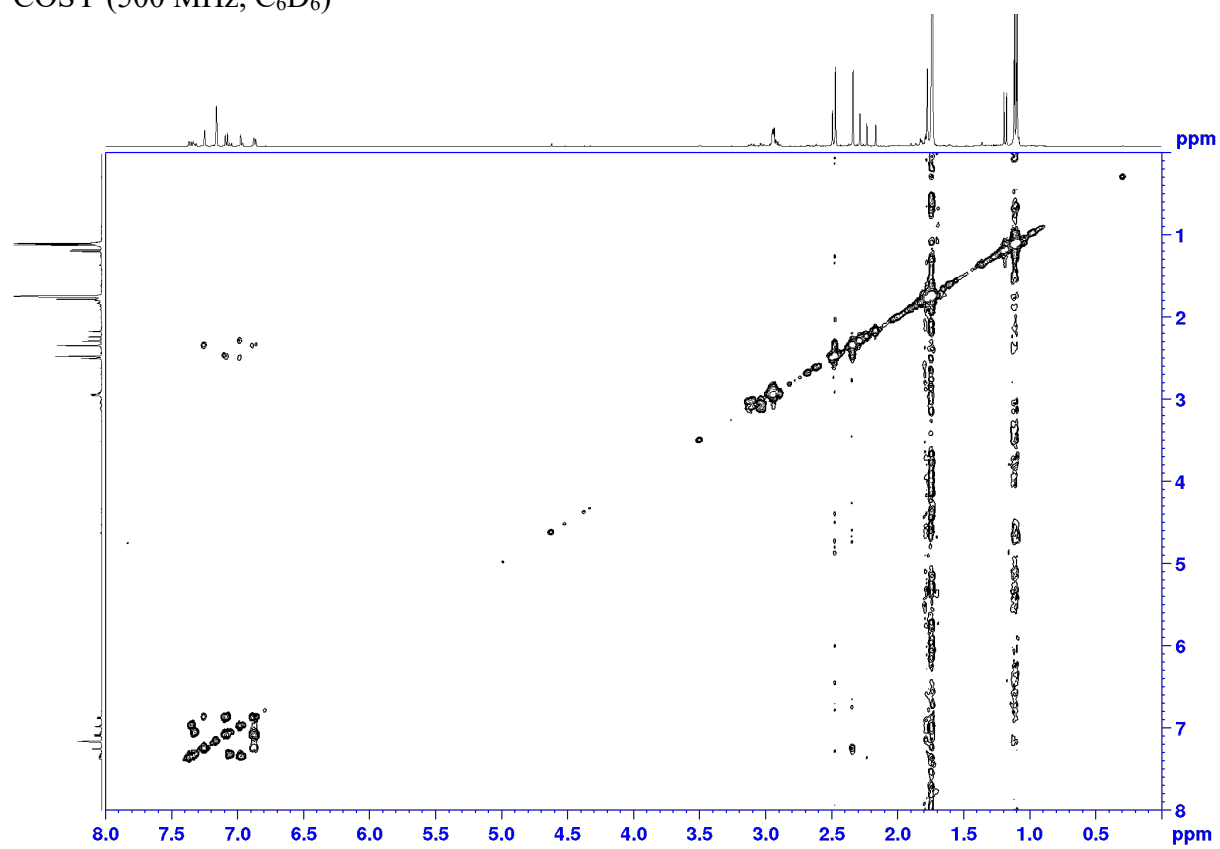
HSQC (500 MHz,  $\text{C}_6\text{D}_6$ )



HMBC (500 MHz, C<sub>6</sub>D<sub>6</sub>)

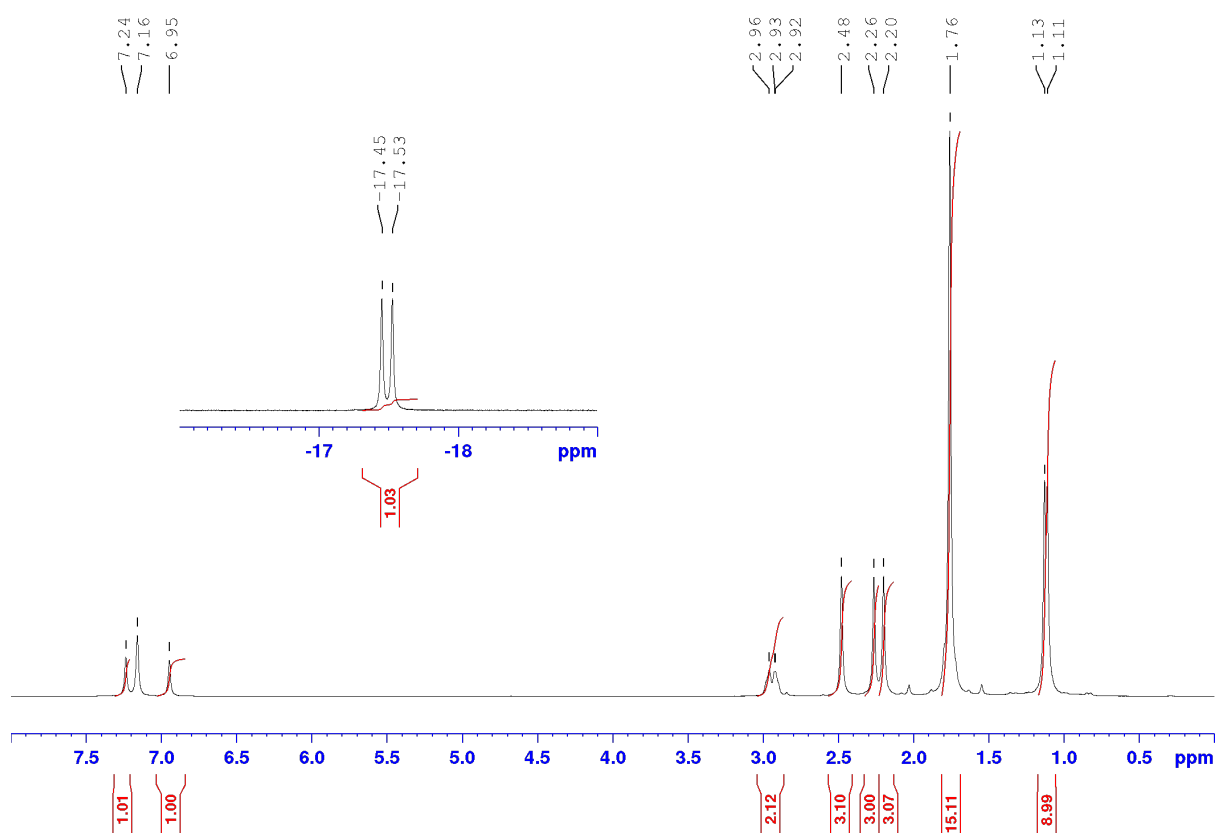


COSY (500 MHz, C<sub>6</sub>D<sub>6</sub>)

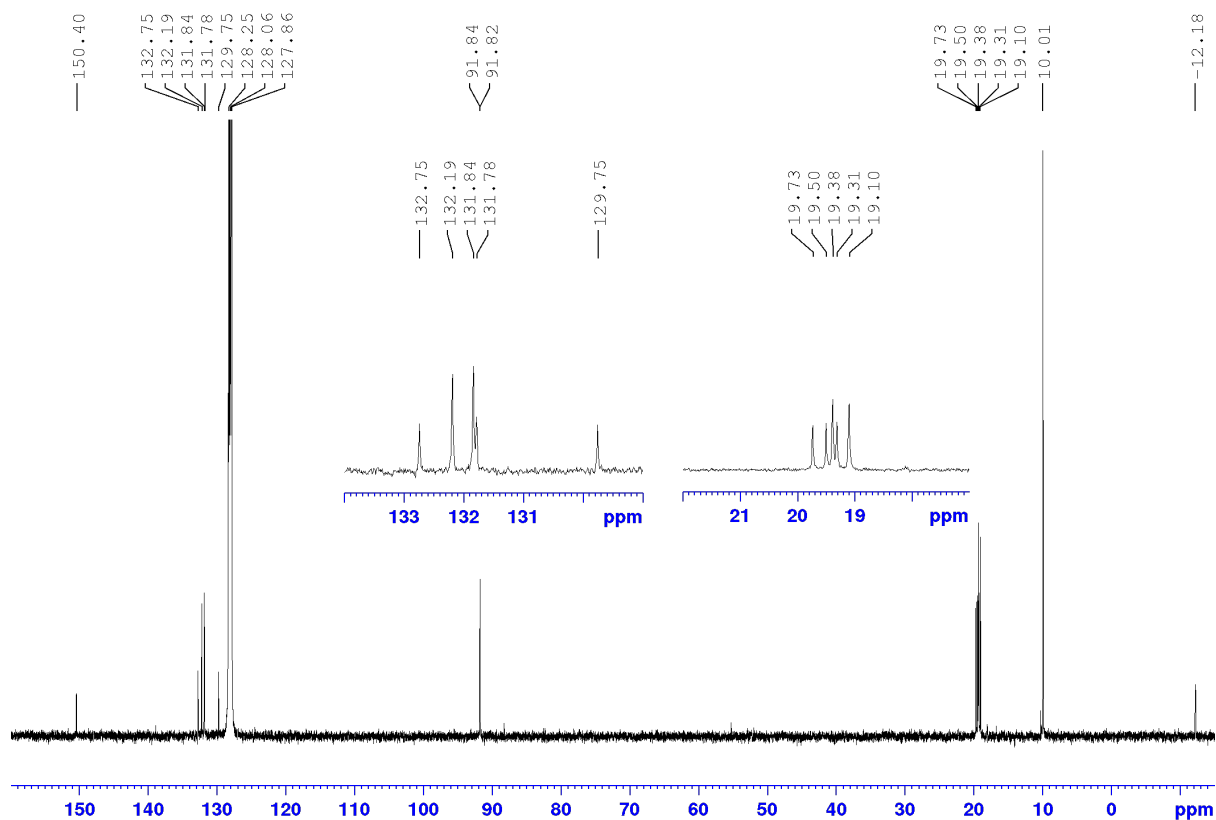


[Cp\*Ir(PMe<sub>3</sub>)(H)(2,4,5-trimethylbenzyl)] (9)

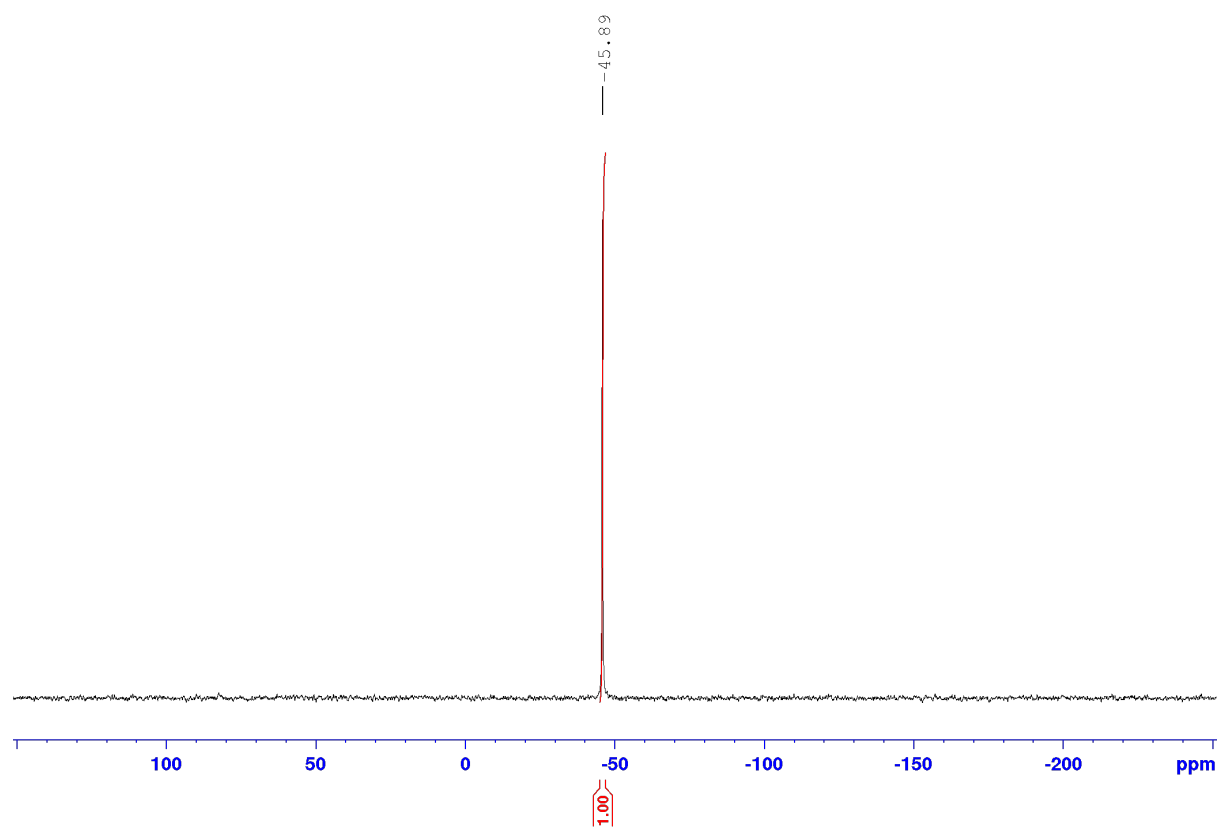
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)

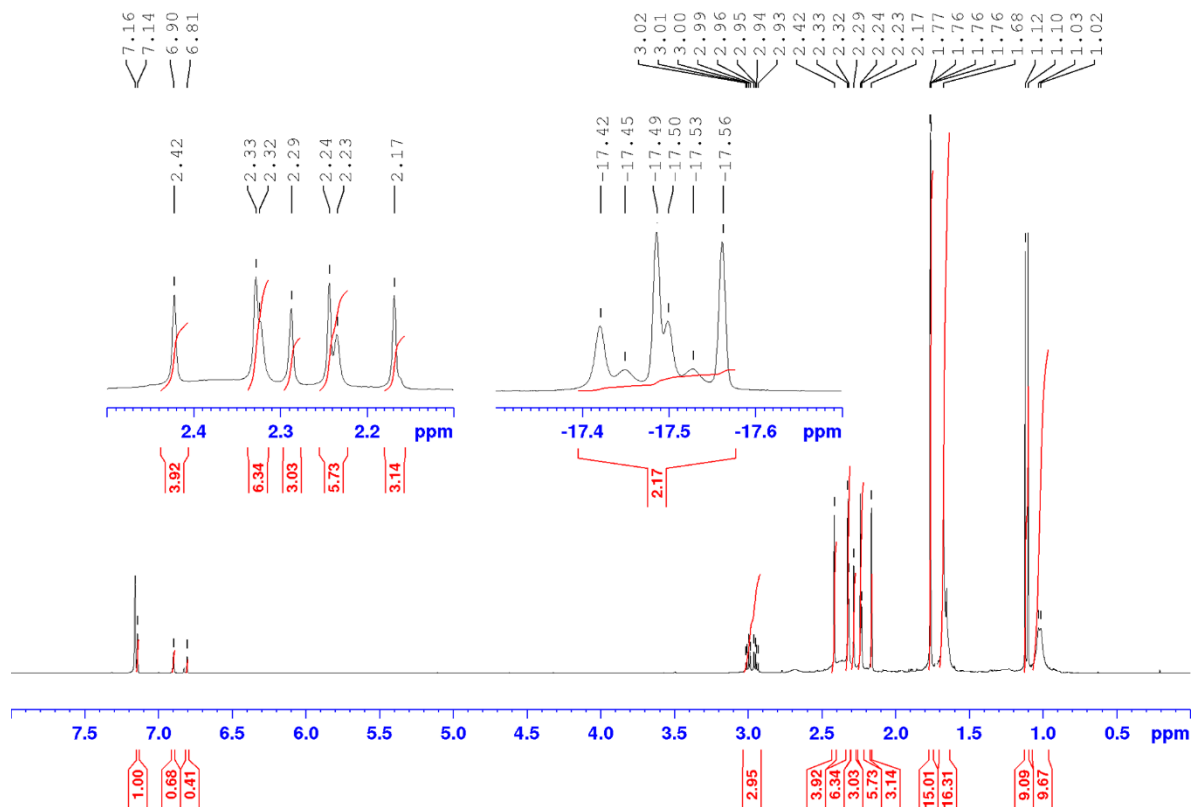


$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

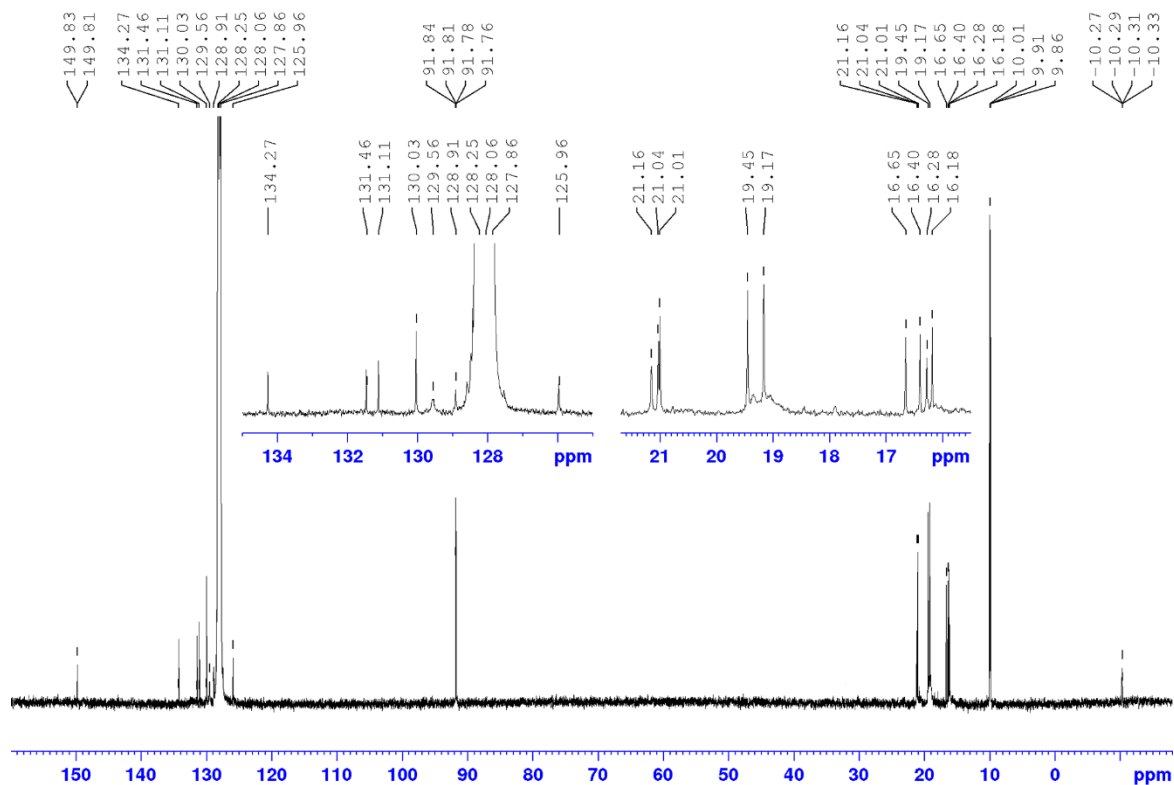


[Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,4,5-tetramethylbenzyl)] (**10a**), [Cp\*Ir(PMe<sub>3</sub>)(H)-(2,3,4,6-tetramethylbenzyl)] (**10b**) and [Cp\*Ir(PMe<sub>3</sub>)(H)(2,3,5,6-tetramethylbenzyl)] (**10c**)

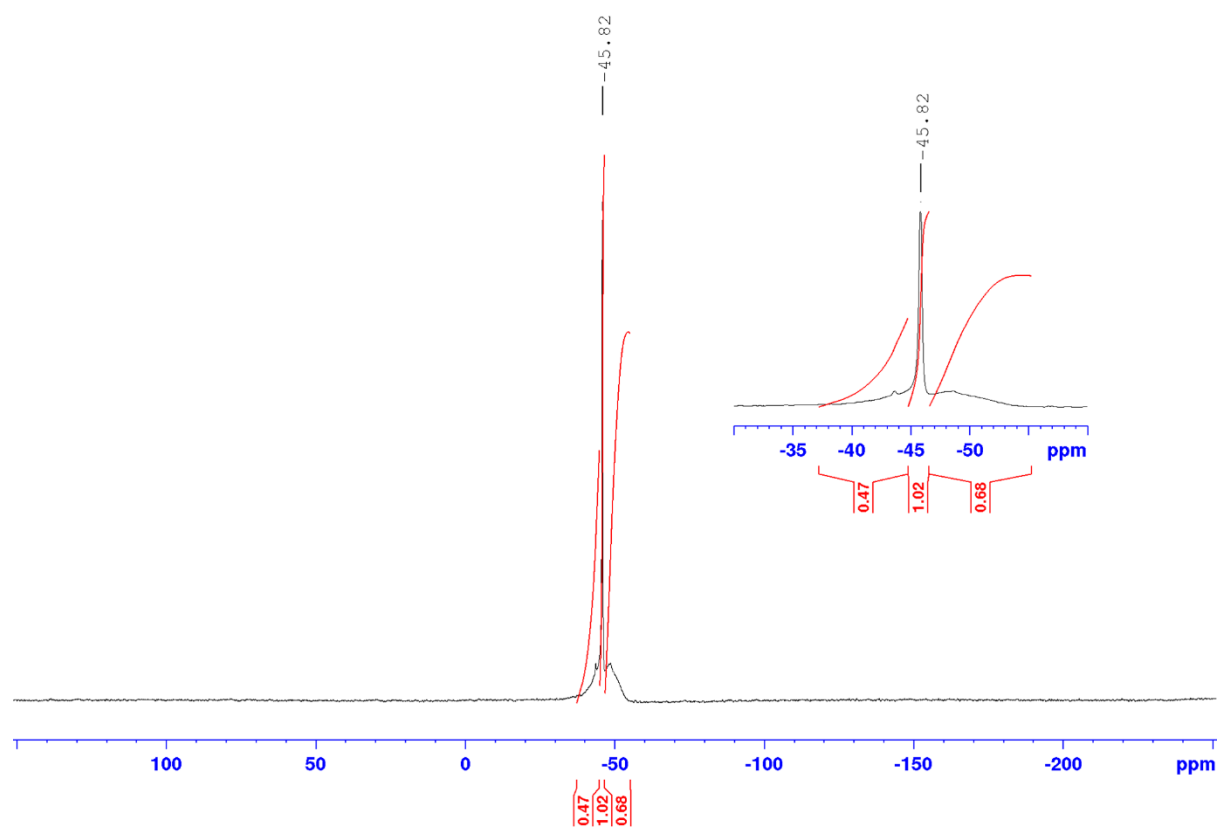
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



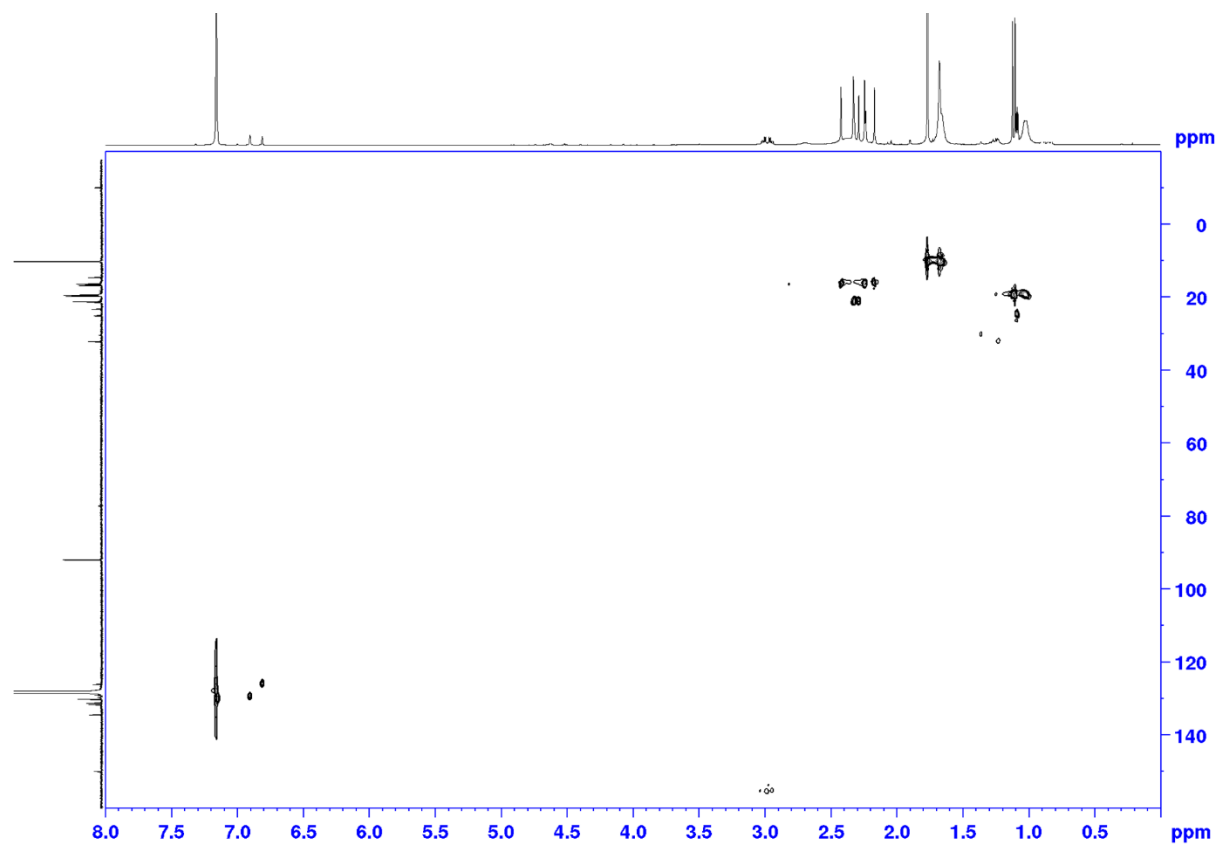
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)



$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

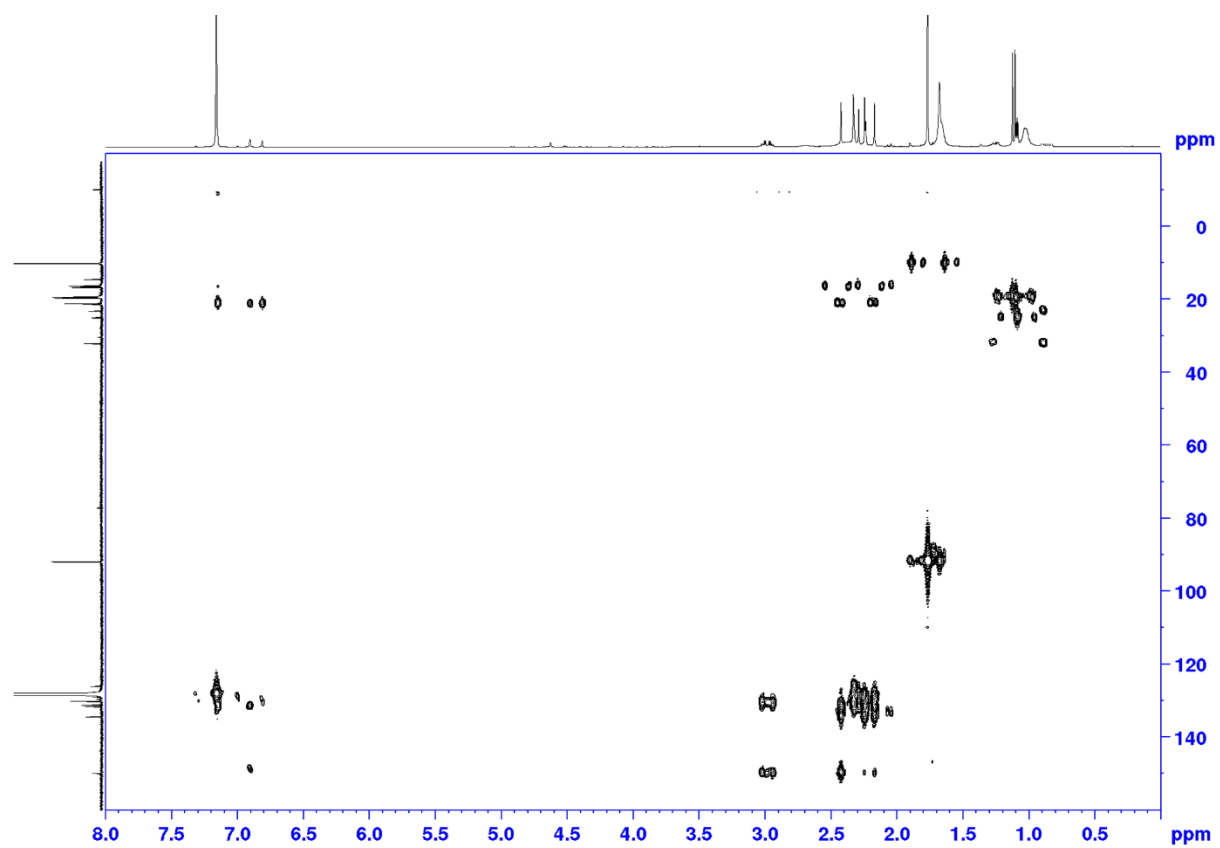


HSQC NMR (500 MHz,  $\text{C}_6\text{D}_6$ )



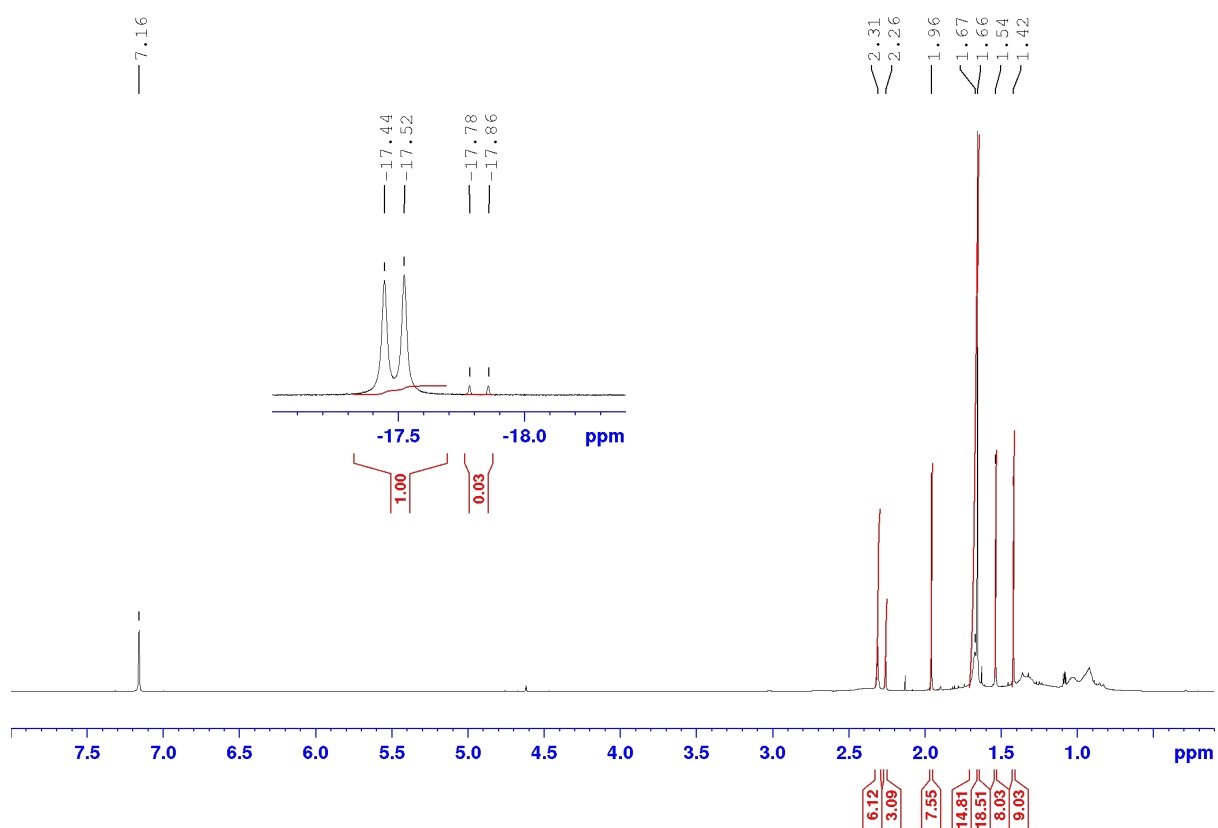


HMBC NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)

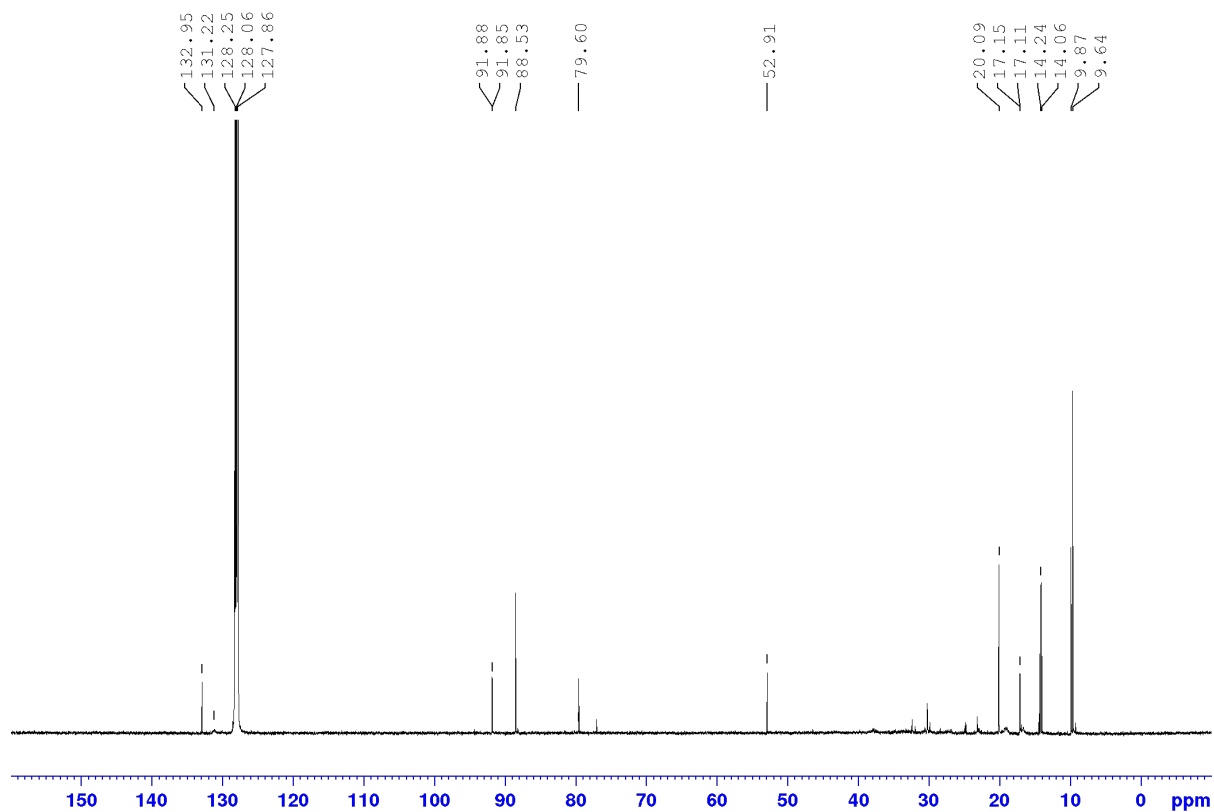


Thermolysis of [Cp\*Ir( $\eta^4$ -hexamethylbenzene)] at 100 °C

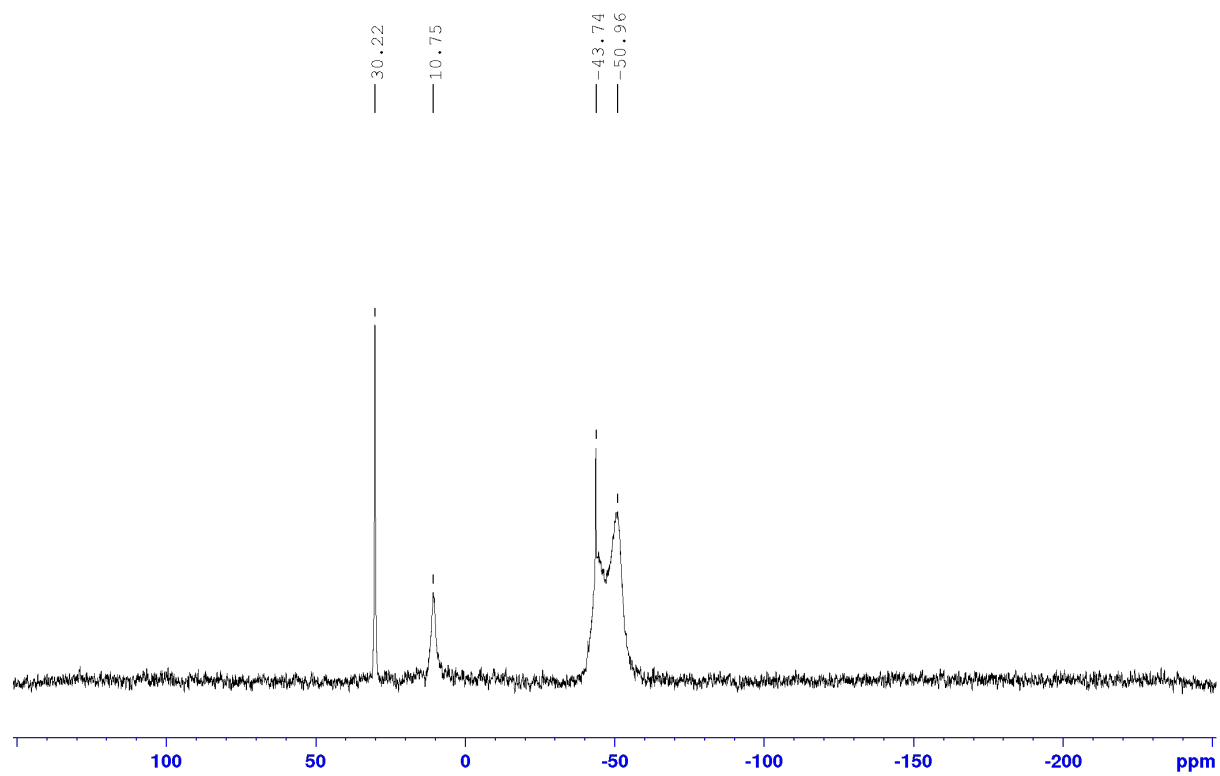
$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )



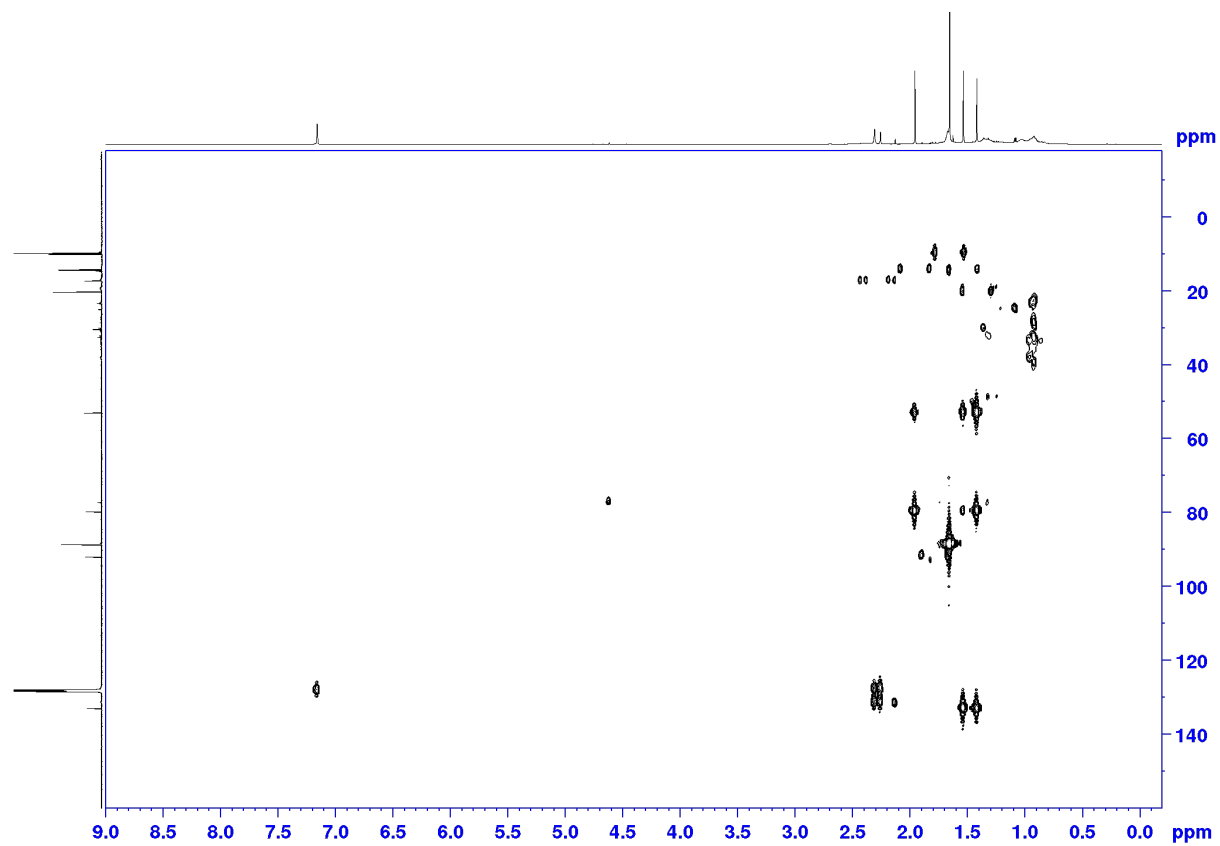
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )



$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )

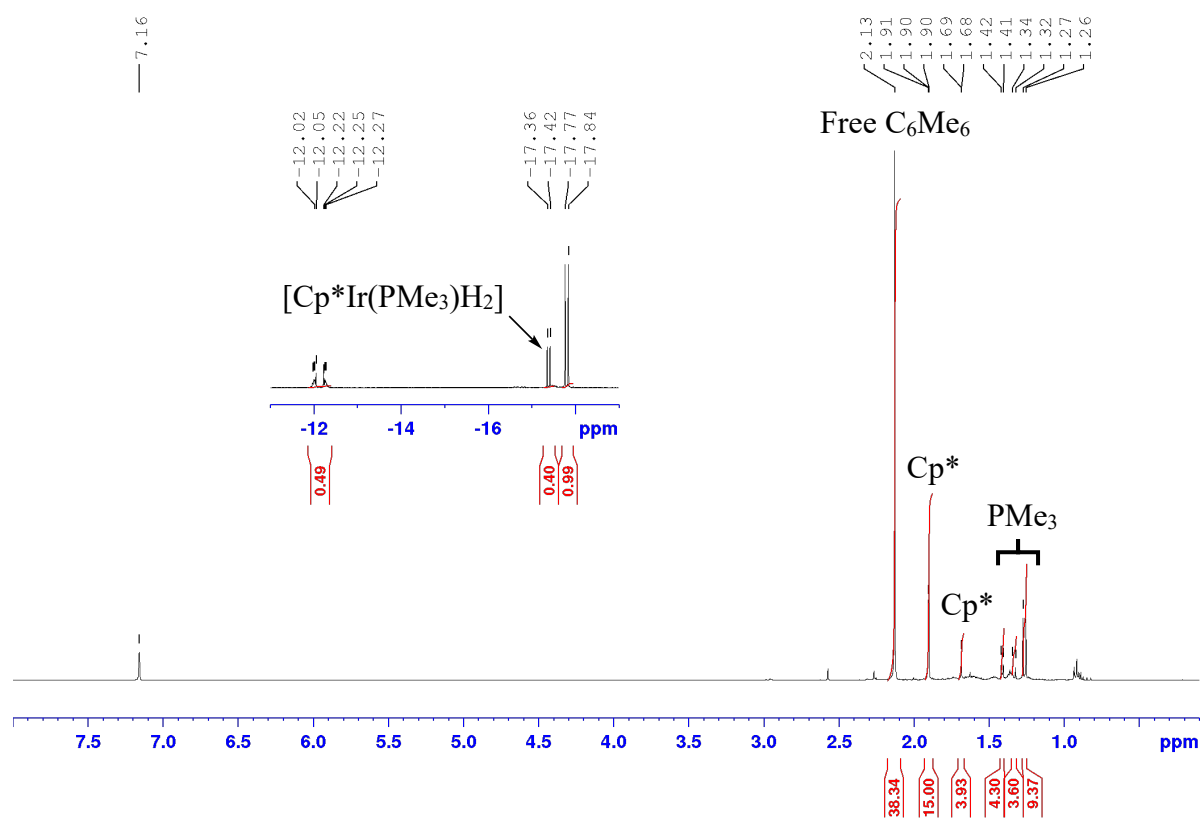


HMBC NMR (500 MHz,  $\text{C}_6\text{D}_6$ )

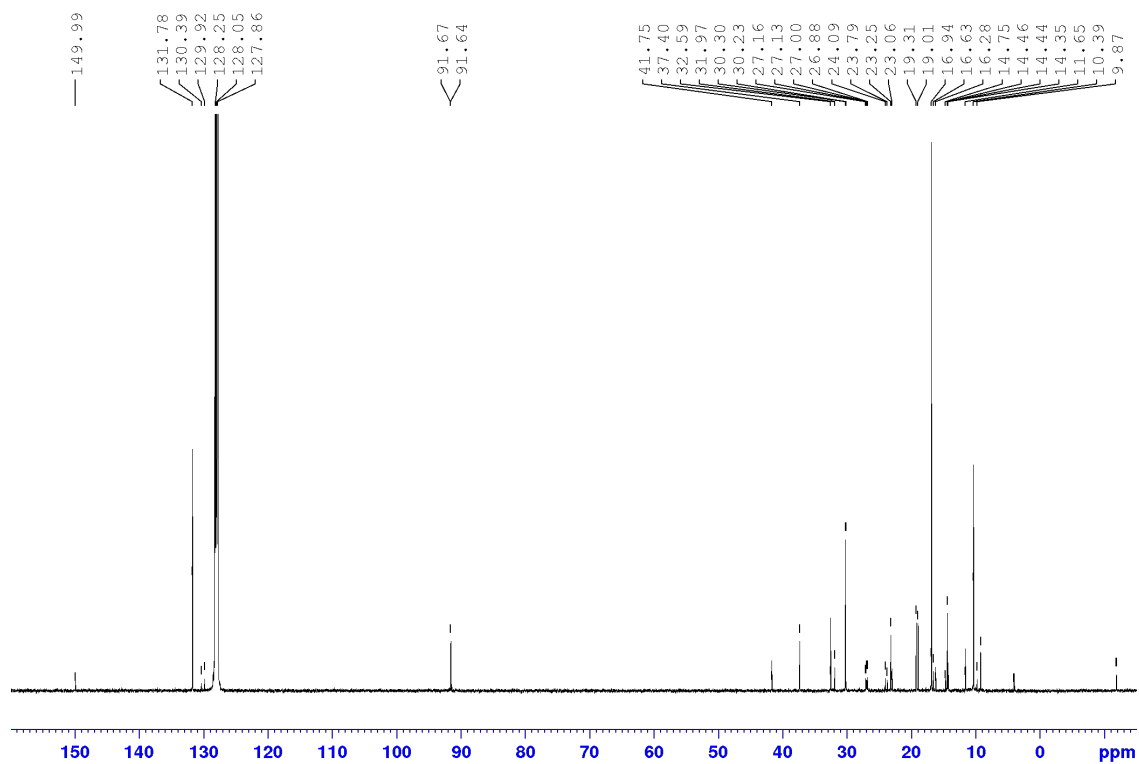


Thermolysis of  $[\text{Cp}^*\text{Ir}(\eta^4\text{-hexamethylbenzene})]$  at 150 °C

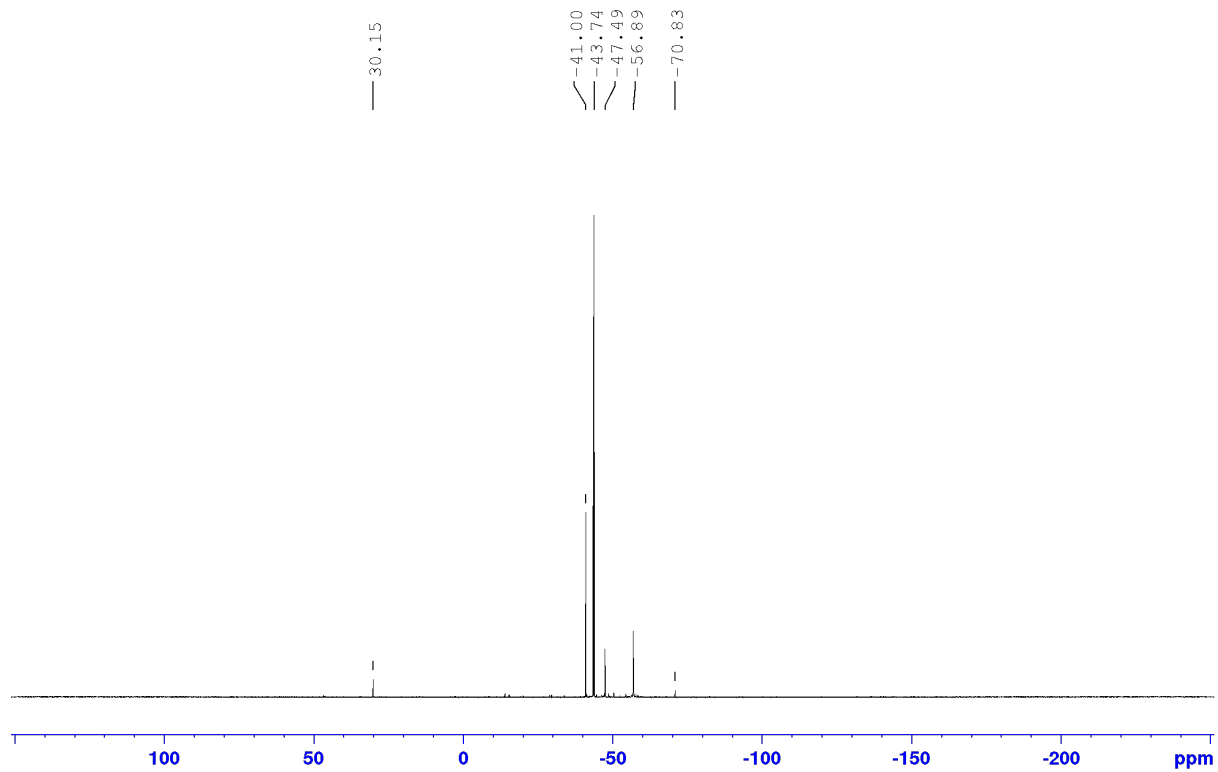
$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )



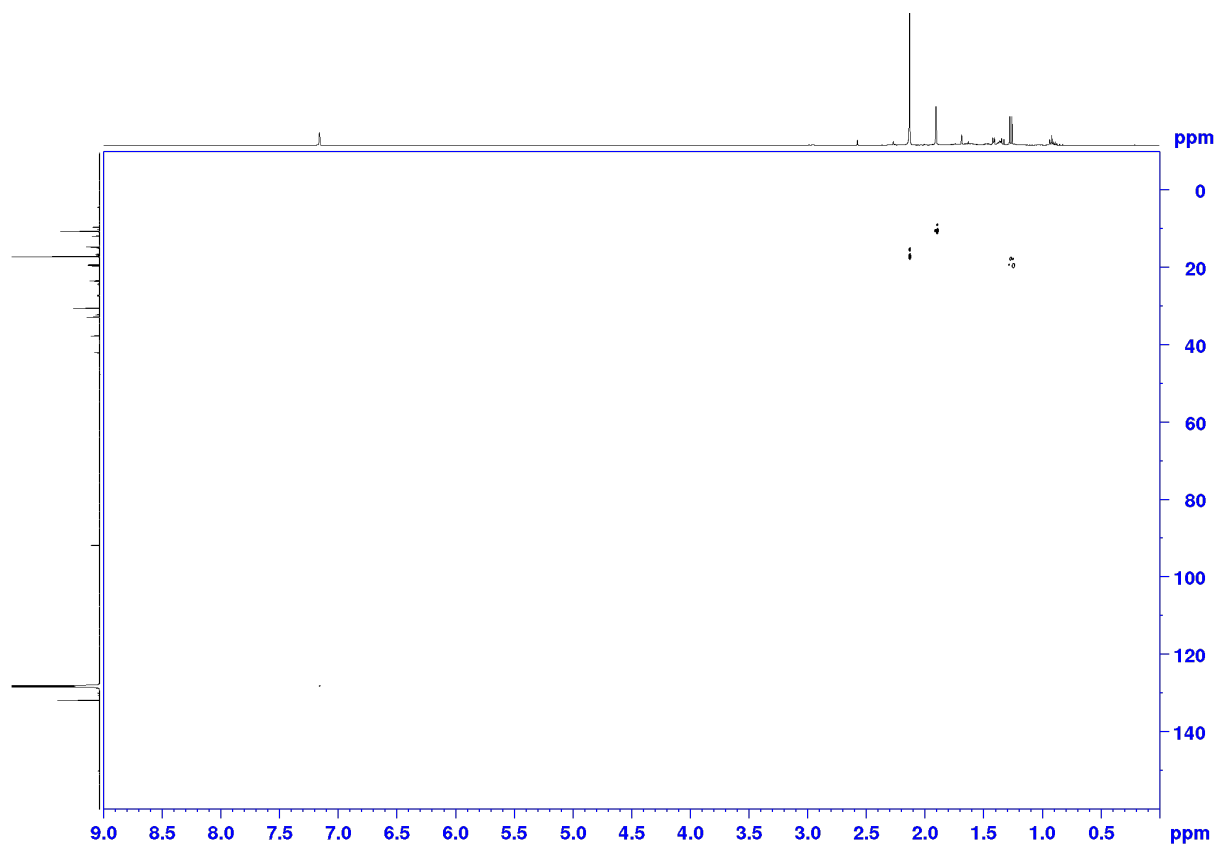
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )



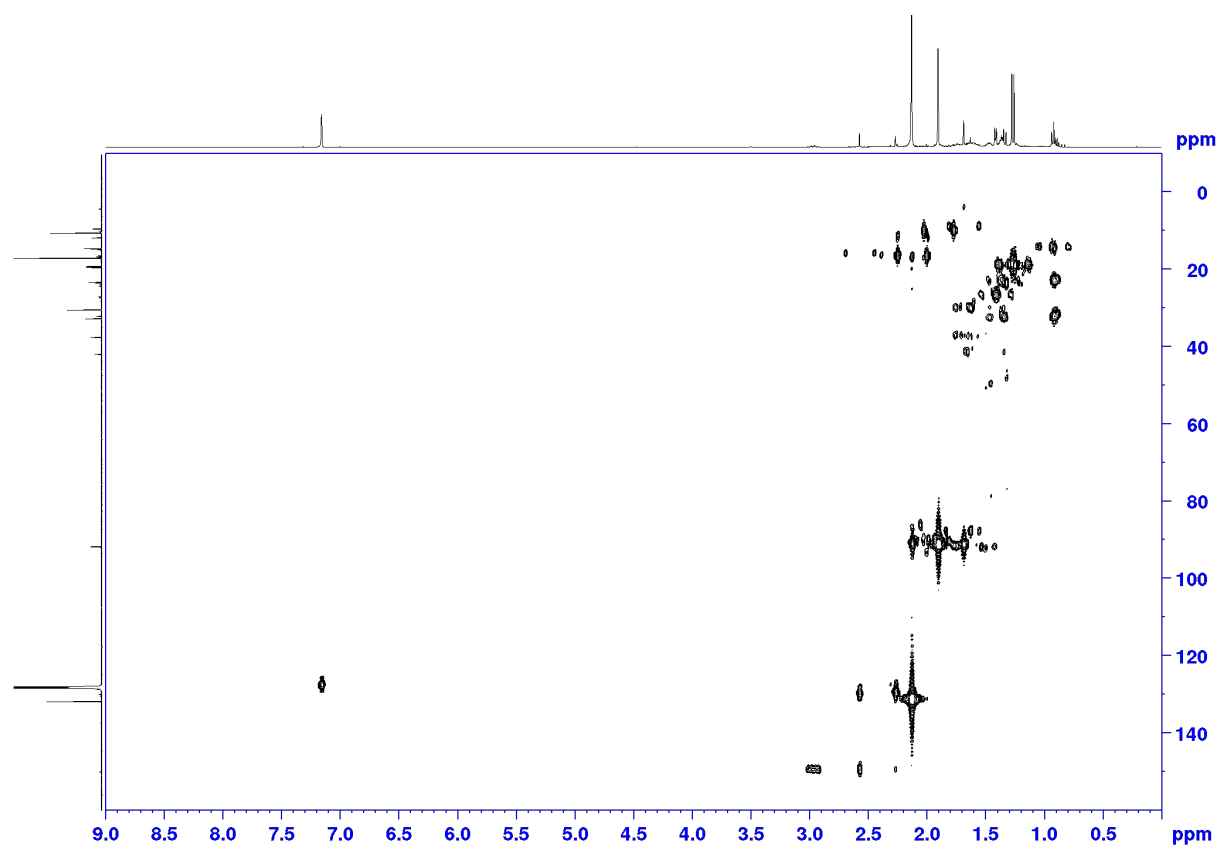
$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ )



HSQC NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)

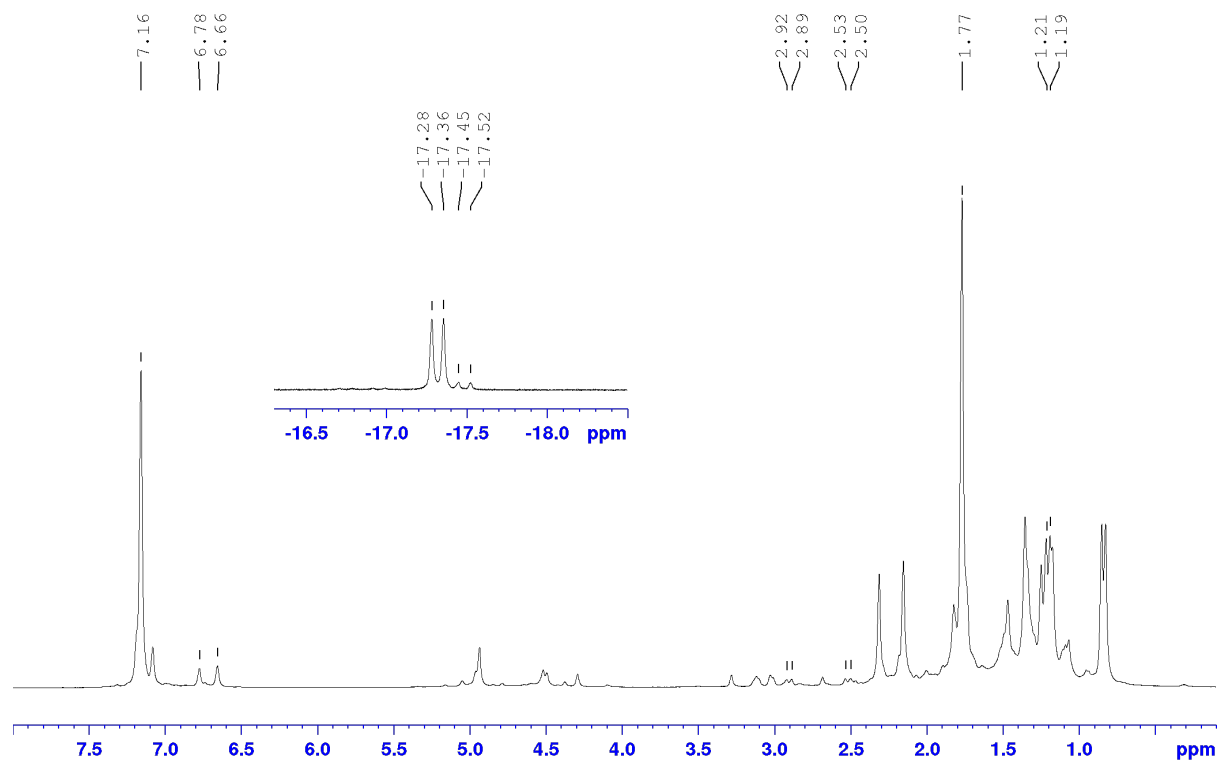


HMBC NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)

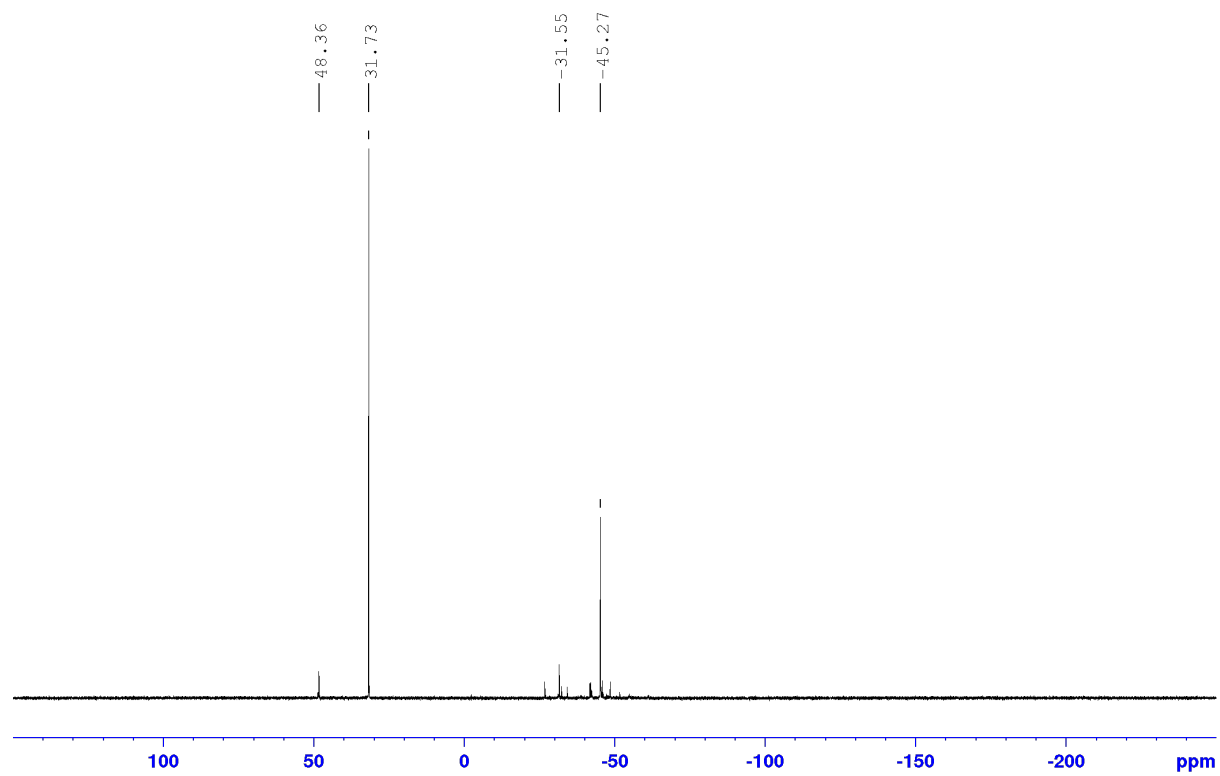


Thermolysis of [Cp\*Ir( $\eta^4$ -mesitylene)] in the presence of PMe<sub>3</sub> and TEMPO

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)

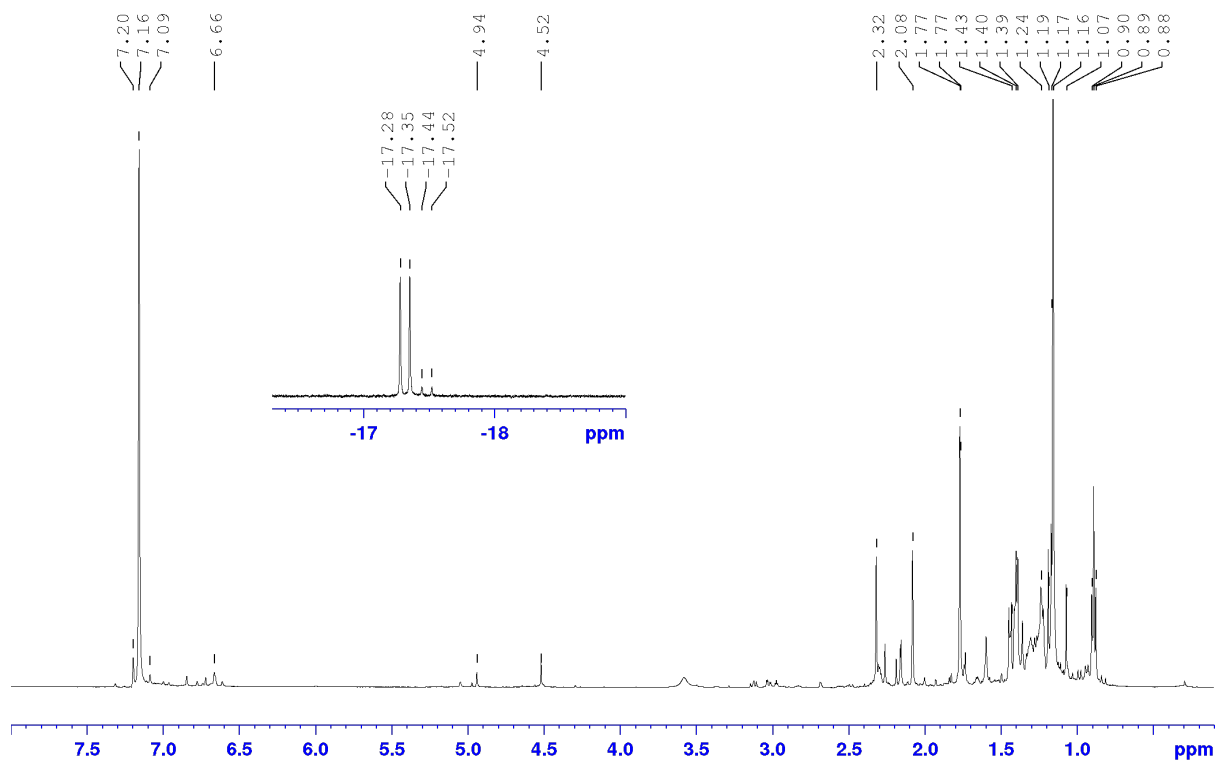


<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>)

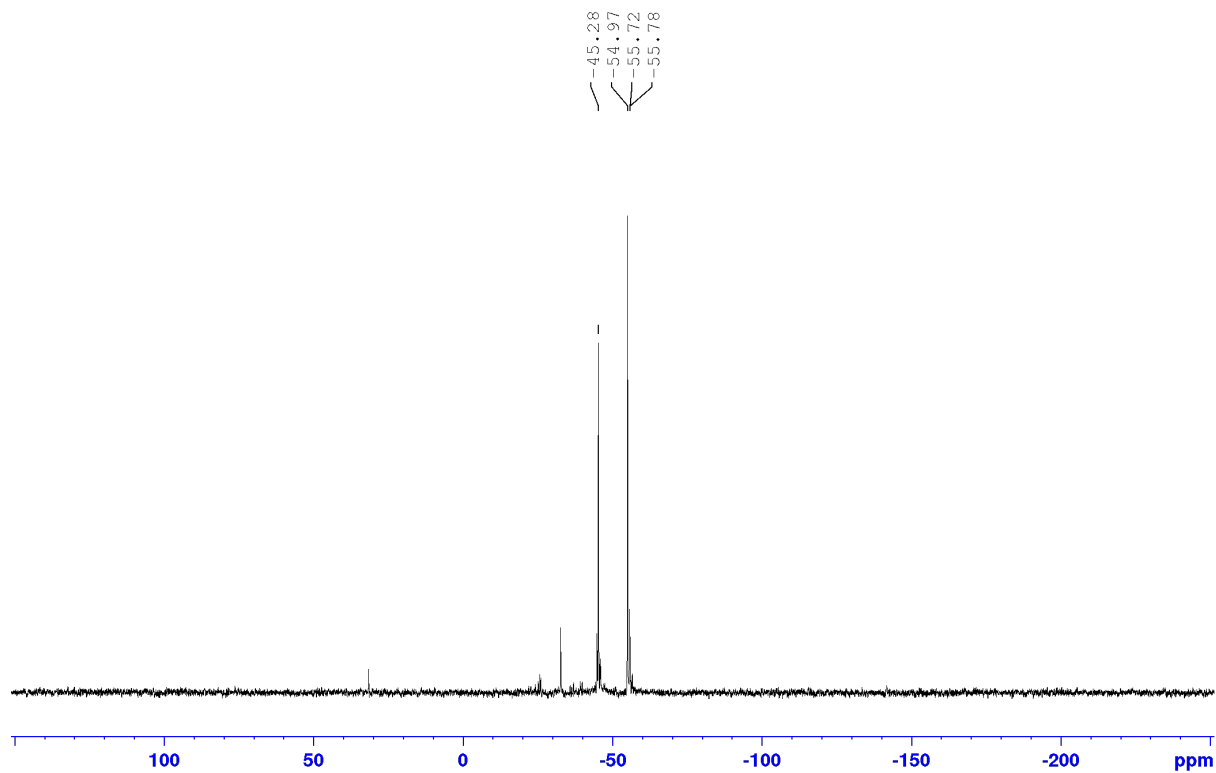


Thermolysis of [Cp\*Ir(PMe<sub>3</sub>)(H)(3,5-dimethylbenzyl)] in the presence TEMPO

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



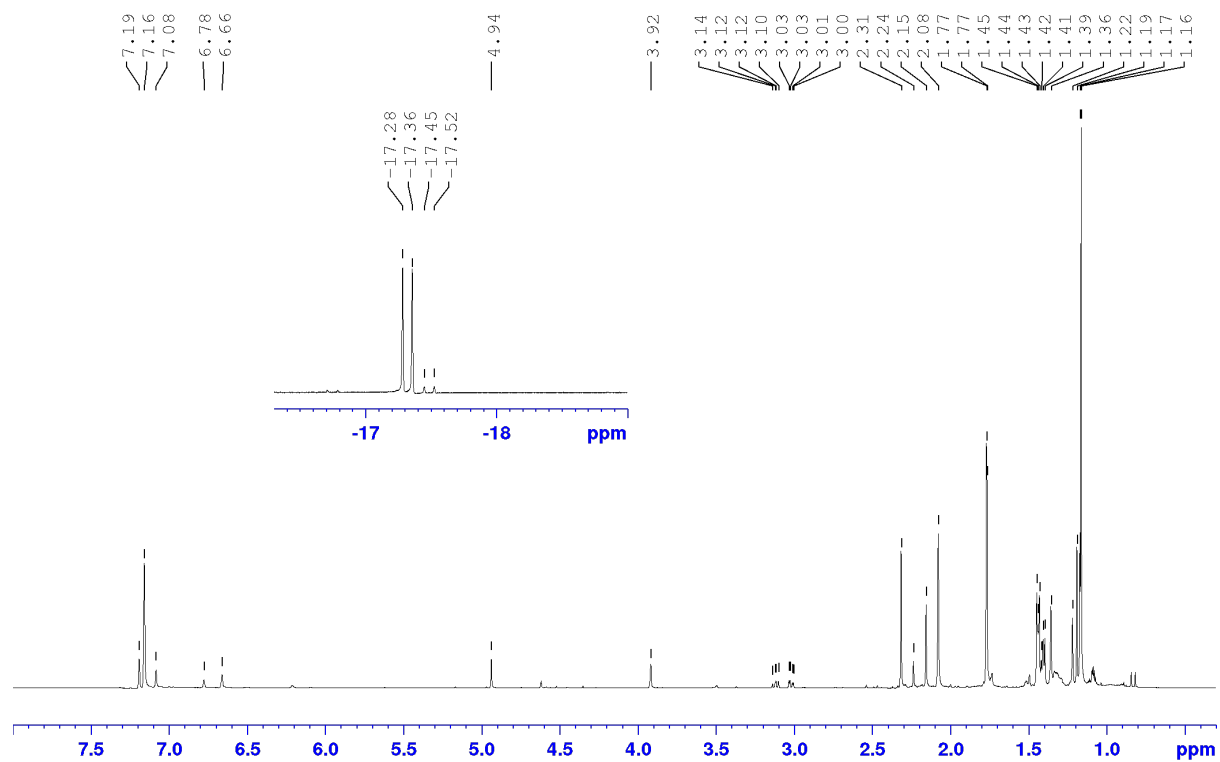
<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>)



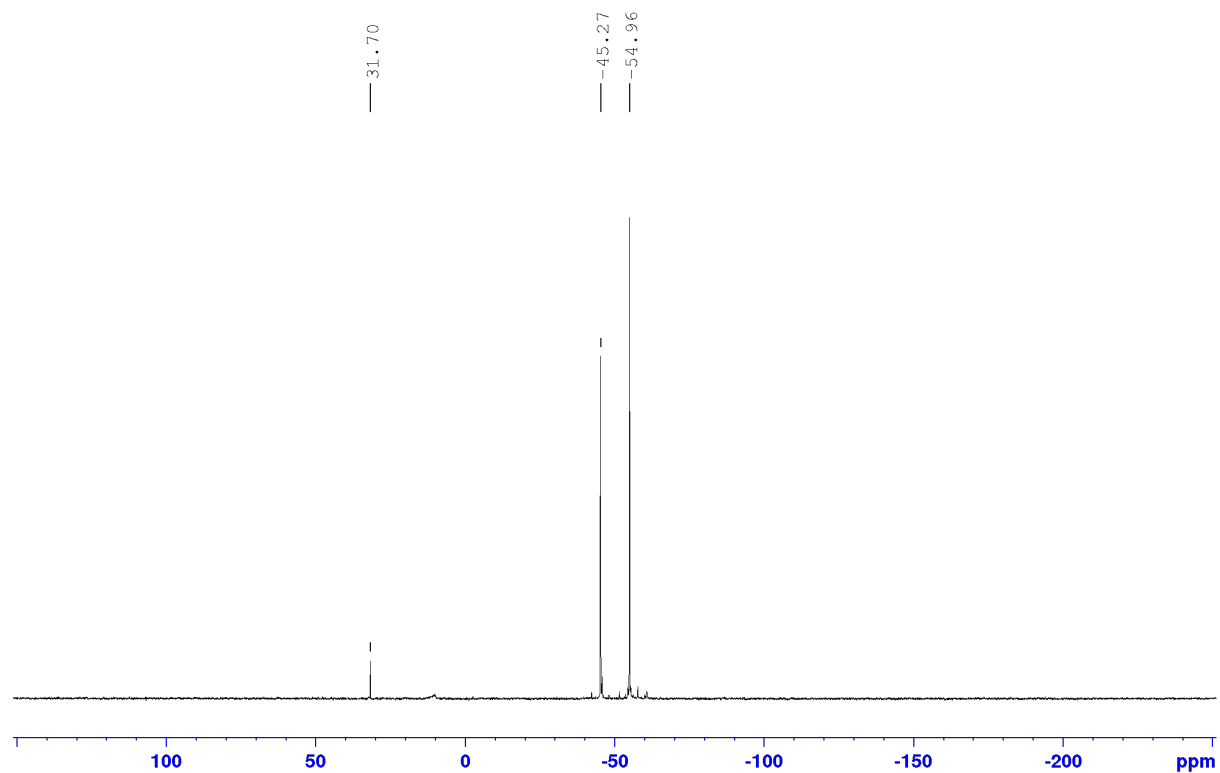


Thermolysis of [Cp\*Ir(PMe<sub>3</sub>)(H)(3,5-dimethylbenzyl)] in the presence PMe<sub>3</sub> and TEMPO

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>)



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