

## Supporting Information

### **Iridium-Induced Regioselective B - H and C - H Activations at Azo-Substituted *m*-Carboranes: Facile Access to Polynuclear Complexes**

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# 1. Experimental Section

## General considerations

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. CH<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub>, Et<sub>2</sub>O was dried over Na, and then distilled under nitrogen atmosphere immediately prior to use. *n*-Butyllithium (1.6 M in *n*-hexane, Acros), *m*-carborane, and other chemicals were used as received from commercial suppliers without further purification. The compounds [Cp\*IrCl<sub>2</sub>]<sub>2</sub><sup>[1]</sup> and *p*-methoxybenzenediazonium tetrafluoroborate<sup>[2]</sup> were prepared following previously reported methods. <sup>1</sup>H (400 MHz) and <sup>13</sup>C{<sup>1</sup>H} (101 MHz) NMR spectra were recorded on Bruker AVANCE I 400 spectrometers. <sup>11</sup>B{<sup>1</sup>H} NMR Spectra (160 MHz) were recorded using a Bruker DMX-500 spectrometer. Proton chemical shifts ( $\delta_{\text{H}} = 7.26$  (CDCl<sub>3</sub>)) and carbon chemical shifts ( $\delta_{\text{C}} = 77.16$  (CDCl<sub>3</sub>)) are reported relative to the solvent residual peak. Coupling constants are expressed in Hertz. Complex multiplets are noted as “m”, triplets are noted as “t” and broad resonances as “br”. IR spectra of solid samples (KBr tablets) in the range of  $\nu = 400\text{-}4000$  cm<sup>-1</sup> were measured with a Nicolet AVATAR-360IR spectrometer. ESI mass spectra were recorded with a Bruker Micro-TOF II using electrospray ionization. Elemental analyses were performed with an Elementar Vario EL III analyzer. X-ray crystallographic data for **1**, **2a**, **2b**, **2c**, **3** and **4** were collected using a Bruker D8 VENTURE system. All unit cell determinations were performed with graphite monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods, using Fourier techniques, and refined on F<sup>2</sup> by a full-matrix least-squares method. Cyclic voltammetry (CV) measurements were carried out at CHI604E electrochemical work-station (Chenhua, Shanghai, China).

**Cyclic Voltammetry.** Cyclic voltammetry measurements were carried out in CH<sub>3</sub>CN solutions with 0.1 M ((*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N)(PF<sub>6</sub>) as supporting electrolyte using a model electrolyte using a model Parstat 2273 (Princeton Applied Research, USA)

potentiostat with a conventional and one-compartment three-electrode cell (5 mL of solution). A glassy carbon (GC) disk electrode with an active surface area of 0.125 cm<sup>2</sup> was used as a working electrode in solution. The electrode was thoroughly polished and rinsed before measurements. A platinum counter electrode and a saturated Ag/AgCl electrode (SCE) reference electrode were applied. The measurements of complexes **2a**, **2b** and **2c** were performed at scan rates of 100 mV s<sup>-1</sup>.

### Synthesis of compound **1**

A suspension of *n*-BuLi (1.6 M in *n*-hexane, 0.625 mL, 1 mmol) was added dropwise to a vigorously stirred solution of *m*-carborane (114 mg, 1 mmol) in Et<sub>2</sub>O (20 mL) at 0 °C for 1 h. The obtained mixture was subsequently stirred at room temperature for an additional 1 h. The suspension was then cooled down to 0 °C and *p*-methoxybenzenediazonium tetrafluoroborate (221 mg, 1 mmol) was added. Thereafter, the obtained mixture was vigorously stirred for an additional 12 h at room temperature. The solvent was removed under vacuum and the residue was purified by column chromatography using silica gel and a mixture of petroleum ether:CH<sub>2</sub>Cl<sub>2</sub>, 8:1 as eluent. Compound **1** (181 mg, 65%) was obtained as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 7.73–6.93 (m, 4 H; Ar-H), 3.87 (s, 3 H; CH<sub>3</sub>-H), 3.03 (s, 1 H; C<sub>cage</sub>-H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 163.5, 145.3, 125.7, 114.4 (Ar-C), 55.8, 53.5 (C<sub>cage</sub>-C), 29.9 (CH<sub>3</sub>-C). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm -4.75–(-5.78) (1 B), -9.74–12.11 (5 B), -13.87 (1 B), -14.91 (1 B), -15.58 (1 B), -16.73 (1 B). IR (KBr disk, cm<sup>-1</sup>): ν (B–H) 2604 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>9</sub>B<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O: C 38.83, H 6.52, N 10.06, found: C 38.80, H 6.52, N 10.04.

### Synthesis of complex **2a**

A sample of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (39.4 mg, 0.05 mmol) was added to a mixture of compound **1** (27.8 mg, 0.1 mmol), NaOAc (24 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The obtained mixture was vigorously stirred for 24 h at room temperature and gradually turned dark

blue. The suspension was then filtered through Celite to obtain a clear solution and the solvent was removed under vacuum. The residue was purified by column chromatography using silica gel and a mixture of petroleum ether:CH<sub>2</sub>Cl<sub>2</sub>, 1:1 as eluent. Complex **2a** (62.7 mg, 98%) was obtained as a dark blue solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 7.76-6.87 (m, 4 H; Ar-H), 3.87 (s, 3 H; CH<sub>3</sub>-H), 2.85 (s, 1 H; C<sub>cage</sub>-H), 1.44 (s, 15 H; Cp\*). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 162.3, 153.9, 125.9, 113.5 (Ar-C), 96.2 (Cp\*-C), 55.9, 53.5 (C<sub>cage</sub>-C), 29.9 (CH<sub>3</sub>-C), 9.06 (Cp\*-CH<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm -4.61–(-6.70) (2 B), -10.76 (2 B), -12.59 (2 B), -14.84 (4 B). IR (KBr, disk): ν (B–H) 2589 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>19</sub>H<sub>32</sub>B<sub>10</sub>ClIrN<sub>2</sub>O: C 35.64, H 5.04, N 4.38, found: C 35.66, H 5.06, N 4.36. ESI-MS: *m/z* = 641.2890 (calcd for [M + H]<sup>+</sup> 641.2899).

### Synthesis of complex **2b**

**Method 1:** A procedure analogous to that introduced for the preparation of **2a** was followed. The reaction of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (39.4 mg, 0.05 mmol) and AgOTf (51 mg, 0.2 mmol) were carried out at room temperature in the dark. Then complex **2a** (27.8 mg, 0.1 mmol) was added to the solution with NaOAc (24 mg, 0.3 mmol). The suspension was vigorously stirred for 24 h at room temperature and with exclusion of light. Complex **2b** was purified by column chromatography using silica gel and a mixture of petroleum ether:CH<sub>2</sub>Cl<sub>2</sub>, 1:1 as eluent. Yield: 78.4 mg (75%) as a dark brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 8.55 (m, *J* = 32.8 Hz, 1 H; Ar-H), 7.18 (t, *J* = 9.2 Hz, 1 H; Ar-H), 6.73 (t, *J* = 16.8 Hz, 1 H; Ar-H), 3.96 (s, 3 H; CH<sub>3</sub>-H), 2.86 (s, 1 H; C<sub>cage</sub>-H), 1.69 (s, 15 H; Cp\*), 1.47 (d, *J* = 4 Hz, 15 H; Cp\*). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 167.5, 162.4, 159.9, 135.9, 115.7, 112.3 (Ar-C), 96.2, 94.4, (Cp\*-C), 55.7, 52.4 (C<sub>cage</sub>-C), 29.8 (CH<sub>3</sub>-C), 10.1, 9.3 (Cp\*-CH<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 0.27–(-5.00) (1 B), -10.29–(-12.85) (6 B), -14.75–(-15.62) (3 B). IR (KBr disk, cm<sup>-1</sup>): ν (B–H) 2591 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>29</sub>H<sub>46</sub>B<sub>10</sub>Cl<sub>2</sub>Ir<sub>2</sub>N<sub>2</sub>O: C 34.76, H 4.63, N 2.80, found: C 34.76, H 4.62, N 2.81. ESI-MS: *m/z* = 1025.3118 (calcd for [M + Na]<sup>+</sup> 1025.3120). **Method 2:** Complex **2b** was prepared following the same procedure as previously described in

method 1, but starting from  $[\text{Cp}^*\text{IrCl}_2]_2$  (78.8 mg, 0.1 mmol) and AgOTf (102 mg, 0.4 mmol) in  $\text{CH}_2\text{Cl}_2$ . Then added compound **1** (27.8 mg, 0.1 mmol) and NaOAc (24 mg, 0.3 mmol) to the mixture solution. Yield: 85.7 mg (82%) as a dark blue solid.

### Synthesis of complex **2c**

**Method 1:** Complex **2c** was prepared following the same procedure as previously described for **2b**, but using a mixture of  $[\text{Cp}^*\text{IrCl}_2]_2$  (78.8 mg, 0.1 mmol) and AgOTf (51 mg, 0.2 mmol) in  $\text{CH}_2\text{Cl}_2$ . Complex **2c** was purified by column chromatography using silica gel and a mixture of  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ , 15:1 as eluent. Yield: 150.1 mg (98%) as a dark brown solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  ppm 8.13 (d,  $J = 9.2$  Hz, 1 H; Ar-H), 7.28 (d,  $J = 2.4$  Hz, 1 H; Ar-H), 6.81 (d,  $J = 9.2$  Hz, 1 H; Ar-H), 4.01 (s, 3 H;  $\text{CH}_3$ -H), 3.08 (s, 1 H;  $\text{C}_{\text{cage}}$ -H), 1.76, 1.75 (d,  $J = 4$  Hz, 30 H;  $\text{Cp}^*$ ), 1.42 (s, 15 H;  $\text{Cp}^*$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  ppm 166.0, 163.1, 158.9, 137.4, 118.0, 112.9 (Ar-C), 97.4, 94.2, 91.7 ( $\text{Cp}^*$ -C), 56.2, 54.9 ( $\text{C}_{\text{cage}}$ -C), 29.8 ( $\text{CH}_3$ -C), 10.2, 10.0, 8.7 ( $\text{Cp}^*$ - $\text{CH}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  ppm  $\delta$  ppm 11.71–(-3.05) (3 B), -10.09–(-13.12) (7 B). IR (KBr, disk):  $\nu$  (B–H) 2580  $\text{cm}^{-1}$ . Elemental analysis calcd (%) for  $\text{C}_{40}\text{H}_{66}\text{B}_{10}\text{Cl}_2\text{F}_3\text{Ir}_3\text{N}_2\text{O}_7\text{S}$ : C 31.37, H 4.34, N 1.83, found: C 31.36, H 4.35, N 1.82. ESI-MS:  $m/z = 1328.3964$  (calcd for  $[\text{M}]^+$  1328.3942).

**Method 2:** Complex **2c** was prepared following the same procedure as described for **2b** (method 2), but using a mixture of  $[\text{Cp}^*\text{IrCl}_2]_2$  (118.2 mg, 0.15 mmol) and AgOTf (102 mg, 0.4 mmol). Yield: 129 mg (84%) as a dark brown solid.

**Method 3:** Complex **2c** was prepared following the same procedure as described for **2b** (method 1), but starting from complex **2b**. Yield: 144 mg (94%) as a dark brown solid.

### Synthesis of compound **3**

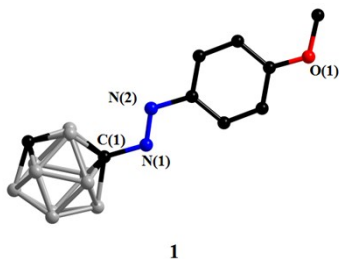
*n*-BuLi (1.6 M in *n*-hexane, 1.25 mL, 2 mmol) was added dropwise to a vigorously stirred solution of *m*-carborane (114 mg, 1 mmol) in  $\text{Et}_2\text{O}$  (20 mL) at 0 °C for 1 h. The obtained mixture was subsequently stirred at room temperature for an additional 1 h. The suspension was then cooled down to 0 °C and *p*-methoxybenzenediazonium tetrafluoroborate (442 mg, 2 mmol). Thereafter, the obtained mixture was vigorously

stirred for an additional 12 h at room temperature. After removal of the solvent under vacuum and the residue was purified by column chromatography using silica gel and a mixture of petroleum ether:CH<sub>2</sub>Cl<sub>2</sub>, 8:1 as eluent. Compound **3** (247 mg, 60%) was obtained as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 7.75-7.72 (d, *J* = 12 Hz, 4 H; Ar-H), 6.96-6.94 (d, *J* = 8 Hz, 4 H; Ar-H), 3.88 (s, 6 H; CH<sub>3</sub>-H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 163.5, 145.3, 125.8, 114.4 (Ar-C), 55.8 (C<sub>cage</sub>-C), 29.9 (CH<sub>3</sub>-C). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm -8.53 (1 B), -10.24–(-15.29) (9 B). IR (KBr, disk): *v* (B–H) 2607 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>16</sub>H<sub>24</sub>B<sub>10</sub>N<sub>4</sub>O<sub>2</sub>: C 46.59, H 5.86, N 13.58, found: C 46.57, H 5.87, N 13.58.

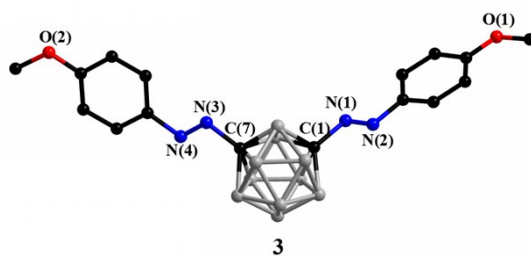
#### Synthesis of complex **4**

A procedure analogous to that introduced for the preparation of **2c** was followed. Compound **3** (41.2 mg, 0.1 mmol) and NaOAc (24 mg, 0.3 mmol) were added to a mixture of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (78.8 mg, 0.1 mmol) and AgOTf (102 mg, 0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The obtained suspension was vigorously stirred for 24 h with exclusion of light. The color turned dark brown from the original orange and a grey precipitate formed. The mixture was filtered through Celite to obtain a clear solution. The solvent was subsequently removed under vacuum and complex **4** was isolated by column chromatography using silica gel and a mixture of CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH, 15:1 as eluent. Yield: 116 mg (93%) as a dark brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 7.51-7.02 (m, 8 H; Ar-H), 3.94 (s, 6 H; CH<sub>3</sub>-H), 1.40 (s, 30 H; Cp\*-H). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, 25 °C): δ ppm 4.61–(-6.13) (2 B), -10.08–(-14.10) (8 B). IR (KBr, disk): *v* (B–H) 2590 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>37</sub>H<sub>52</sub>B<sub>10</sub>ClF<sub>3</sub>Ir<sub>2</sub>N<sub>4</sub>O<sub>5</sub>S: C 35.56, H 4.19, N 4.48, found: C 35.56, H 4.18, N 4.49. ESI-MS: *m/z* = 1103.4012 (calcd for [M]<sup>+</sup> 1103.4002).

## 2. Molecular structure of compounds 1 and 3.



**Fig. S1.** Molecular structure of compound 1. C, N, O and B atoms are represented by black, blue, red and grey spheres, respectively. H atoms have been omitted for clarity.



**Fig S2.** Molecular structure of compound 3. C, N, O and B atoms are represented by black, blue, red and grey spheres, respectively. H atoms have been omitted for clarity.



### 3. Crystallographic data.

**Table S1.** Crystallographic data and structure refinement parameters for **1**, **2a**, **2b** and **2c**.

Complexes	1	2a	2b · 1/2 CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	2c
Empirical formula	C <sub>9</sub> H <sub>18</sub> B <sub>10</sub> N <sub>2</sub> O	C <sub>19</sub> H <sub>32</sub> B <sub>10</sub> ClIrN <sub>2</sub> O	C <sub>32</sub> H <sub>53</sub> B <sub>10</sub> Cl <sub>2</sub> Ir <sub>2</sub> N <sub>2</sub> O	C <sub>40</sub> H <sub>66</sub> B <sub>10</sub> Cl <sub>2</sub> F <sub>3</sub> Ir <sub>3</sub> N <sub>2</sub> O <sub>7</sub> S
<i>M</i> <sub>z</sub>	278.35	640.21	1045.16	1531.60
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1	P-1
<i>a</i> [Å]	20.615(13)	8.7748(16)	8.3378(11)	12.3557(19)
<i>b</i> [Å]	10.897(7)	12.003(2)	12.0979(16)	15.739(2)
<i>c</i> [Å]	13.916(9)	25.147(5)	20.336(3)	16.743(3)
α [°]	90	82.735(3)	75.448(2)	62.772(2)
β [°]	90.229(12)	83.775(3)	79.942(2)	69.902(2)
γ [°]	90	86.970(3)	85.845(2)	89.159(3)
<i>V</i> [Å <sup>3</sup> ]	3126(3)	2609.8(8)	1954.1(4)	2679.0(7)
<i>Z</i>	8	4	2	2
ρ <sub>calc</sub> (g cm <sup>-3</sup> )	1.183	1.629	1.776	1.899
μ (MoKα) [mm <sup>-1</sup> ]	0.065	5.235	6.969	7.628
<i>F</i> (000)	1152	1248	1010	1468
θ range [°]	1.976 - 27.707	1.641 - 26.000	1.740 - 26.998	1.781 - 26.000
limiting indices	-26 ≤ <i>h</i> ≤ 22 -14 ≤ <i>k</i> ≤ 14 -17 ≤ <i>l</i> ≤ 18	-10 ≤ <i>h</i> ≤ 10 -14 ≤ <i>k</i> ≤ 14 -27 ≤ <i>l</i> ≤ 31	-10 ≤ <i>h</i> ≤ 10 -15 ≤ <i>k</i> ≤ 12 -25 ≤ <i>k</i> ≤ 25	-10 ≤ <i>h</i> ≤ 15 -19 ≤ <i>k</i> ≤ 19 -20 ≤ <i>l</i> ≤ 20
Reflections/unique	11275/3650	16844/10059	13592/8432	17332/10332
<i>R</i> (int)	0.0526	0.0485	0.0325	0.0267
Completeness to θ <sup>o</sup> (%)	99.7	98.1	98.6	97.8
Data/restraints/parameter	3650 / 26 / 204	10059 / 97 / 623	8432 / 0 / 458	10322 / 24 / 530
Goodness of fit	1.024	0.988	1.098	1.048
Final <i>R</i> indices [I > 2σ(I)] <sup>a</sup>	R1 = 0.0621, wR2 = 0.1576	R1 = 0.0493, wR2 = 0.1240	R1 = 0.0346, wR2 = 0.1034	R1 = 0.0406, wR2 = 0.1228
<i>R</i> Indices (all data)	R1 = 0.1243, wR2 = 0.1857	R1 = 0.0830, wR2 = 0.1418	R1 = 0.0423, wR2 = 0.1099	R1 = 0.0557, wR2 = 0.1370
Δρ <sub>max,min</sub> / e Å <sup>-3</sup>	0.202, -0.187	1.974, -2.210	2.463, -1.869	1.951, -0.870

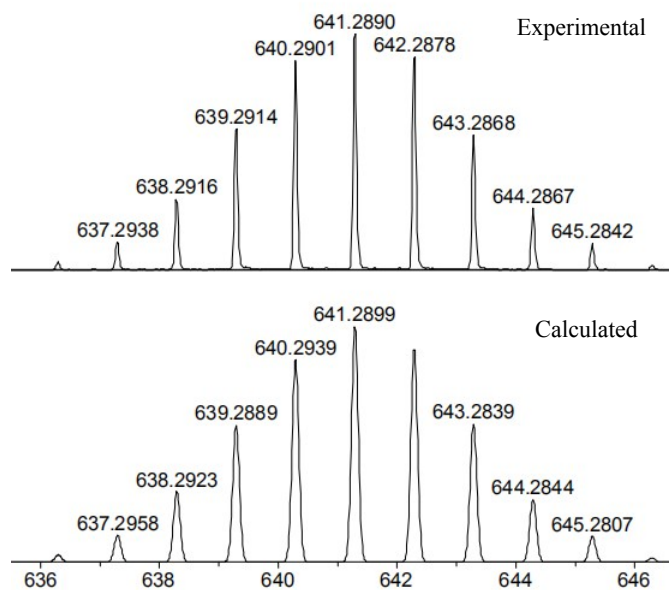
<sup>a</sup>  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ,  $wR_2 = \left[ \frac{\sum (|F_o|^2 - |F_c|^2)^2}{\sum (F_o^2)} \right]^{1/2}$ .

**Table S2.** Crystallographic data and structure refinement parameters for **3** and **4**.

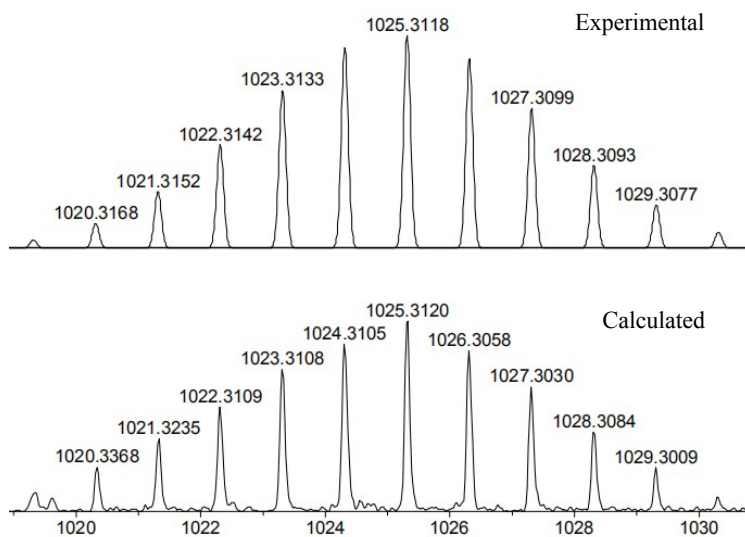
Complexes	<b>3</b>	<b>4</b>
Empirical formula	C <sub>16</sub> H <sub>24</sub> B <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>37</sub> H <sub>52</sub> B <sub>10</sub> ClF <sub>3</sub> Ir <sub>2</sub> N <sub>4</sub> O <sub>5</sub> S
<i>M<sub>r</sub></i>	412.49	1249.83
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 <sub>1</sub> /c
<i>a</i> [Å]	7.334(2)	13.987(3)
<i>b</i> [Å]	7.357(2)	16.285(3)
<i>c</i> [Å]	24.271(8)	20.997(5)
$\alpha$ [°]	86.844(6)	90
$\beta$ [°]	86.080(6)	106.606(4)
$\gamma$ [°]	61.766(5)	90
<i>V</i> [Å <sup>3</sup> ]	1150.8(7)	4583.5(17)
<i>Z</i>	2	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.190	1.811
$\mu$ (MoK $\alpha$ ) [mm <sup>-1</sup> ]	0.071	5.963
<i>F</i> (000)	428	2424
$\theta$ range [°]	0.841 - 25.997	1.609 - 27.169
limiting indices	-9 ≤ <i>h</i> ≤ 8 -9 ≤ <i>k</i> ≤ 6 -29 ≤ <i>l</i> ≤ 29	-17 ≤ <i>h</i> ≤ 14 -20 ≤ <i>k</i> ≤ 20 -26 ≤ <i>l</i> ≤ 26
Reflections/unique	7549/4458	32345/10072
<i>R</i> (int)	0.0358	0.0809
Completeness to $\theta$ ° (%)	98.9	99.5
Data/restraints/parameter	4458 / 30 / 310	10072 / 242 / 649
Goodness of fit	1.047	0.978
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	<i>R</i> 1 = 0.0865, <i>wR</i> 2 = 0.2658	<i>R</i> 1 = 0.0443, <i>wR</i> 2 = 0.0895
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.1512, <i>wR</i> 2 = 0.3298	<i>R</i> 1 = 0.0857, <i>wR</i> 2 = 0.1045
$\Delta\rho_{\text{max,min}}$ / e Å <sup>-3</sup>	0.450, -0.320	1.917, -1.1194

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \left[ \frac{\sum (|F_o|^2 - |F_c|^2)^2}{\sum (F_o^2)} \right]^{1/2}.$$

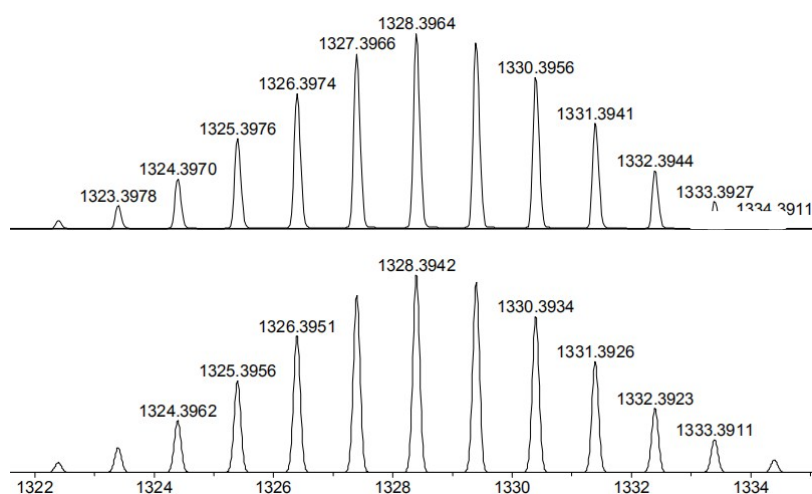
#### 4. ESI Mass Spectra.



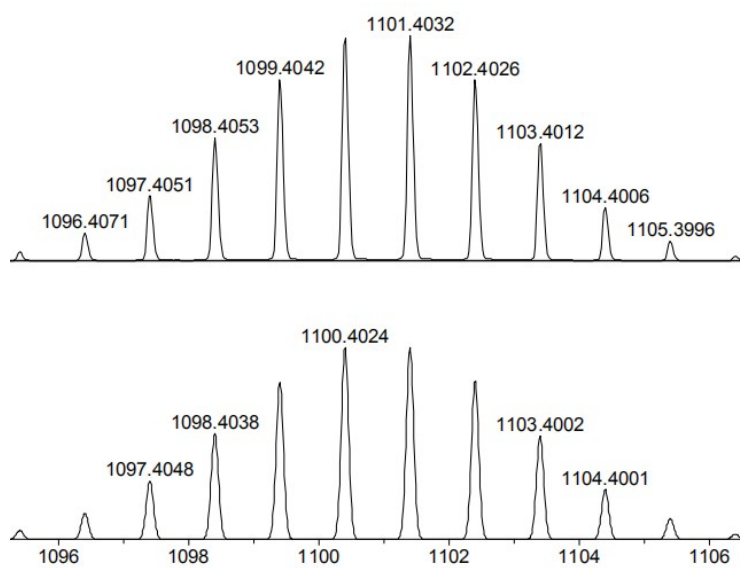
**Fig. S3** Calculated (bottom) and experimental (top) ESI-MS spectra for complex **2a**.



**Fig. S4** Calculated (bottom) and experimental (top) ESI-MS spectra for complex **2b**.



**Fig. S5** Calculated (bottom) and experimental (top) ESI-MS spectra for complex **2c**.



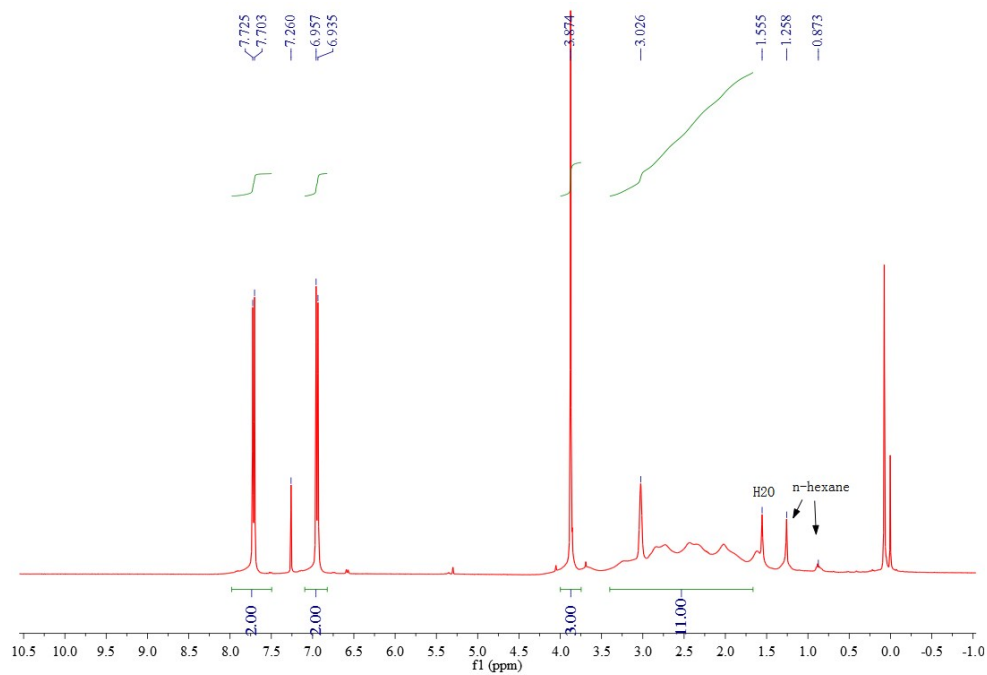
**Fig. S6** Calculated (bottom) and experimental (top) ESI-MS spectra for complex **4**.

## 5. NMR Spectra.

### Compound 1

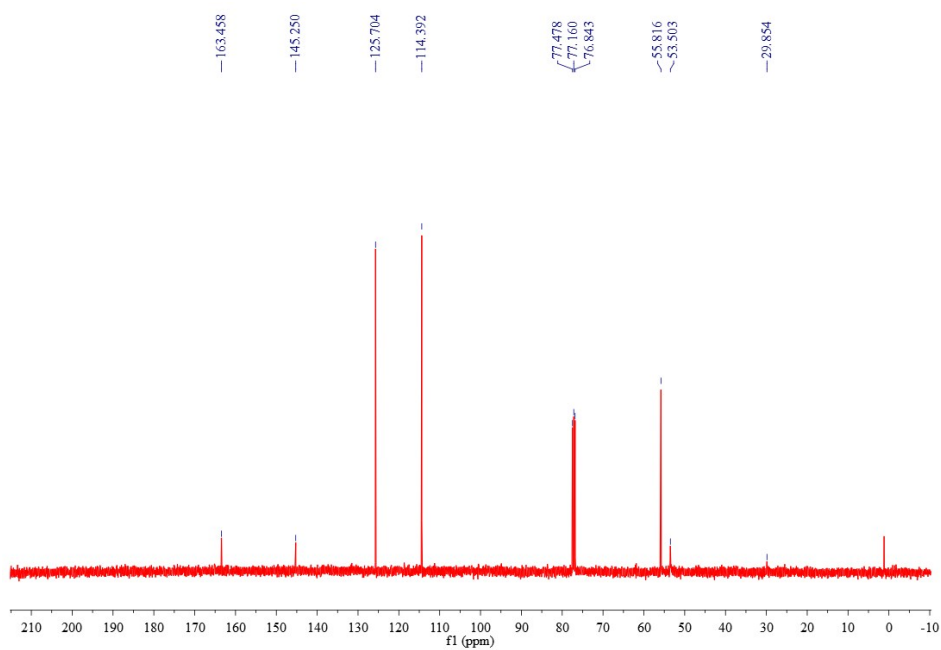
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm 7.73-6.93 (m, 4 H; Ar-H), 3.87 (s, 3 H;  $\text{CH}_3$ -H), 3.03 (s, 1 H;  $\text{C}_{\text{cage}}$ -H).



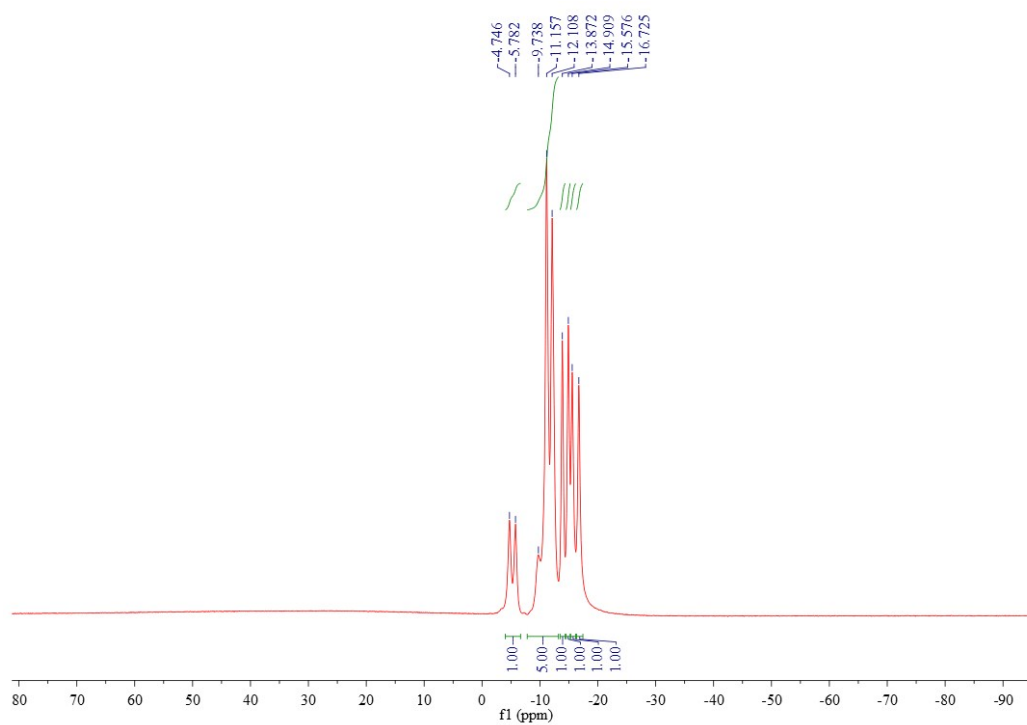
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm 163.5, 145.3, 125.7, 114.4 (Ar-C), 55.8, 53.5 ( $\text{C}_{\text{cage}}$ -C), 29.9 ( $\text{CH}_3$ -C).



$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm -4.75–(-5.78) (1 B), -9.74–12.11 (5 B), -13.87 (1 B), -14.91 (1 B), -15.58 (1 B), -16.73 (1 B).

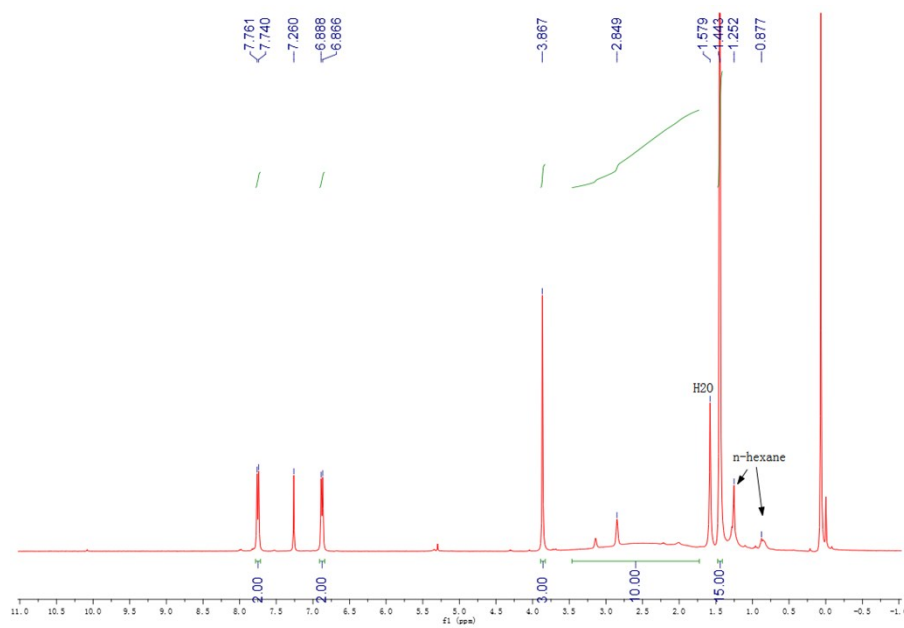


IR (KBr, disk):  $\nu$  (B–H) 2604  $\text{cm}^{-1}$

### Complex 2a

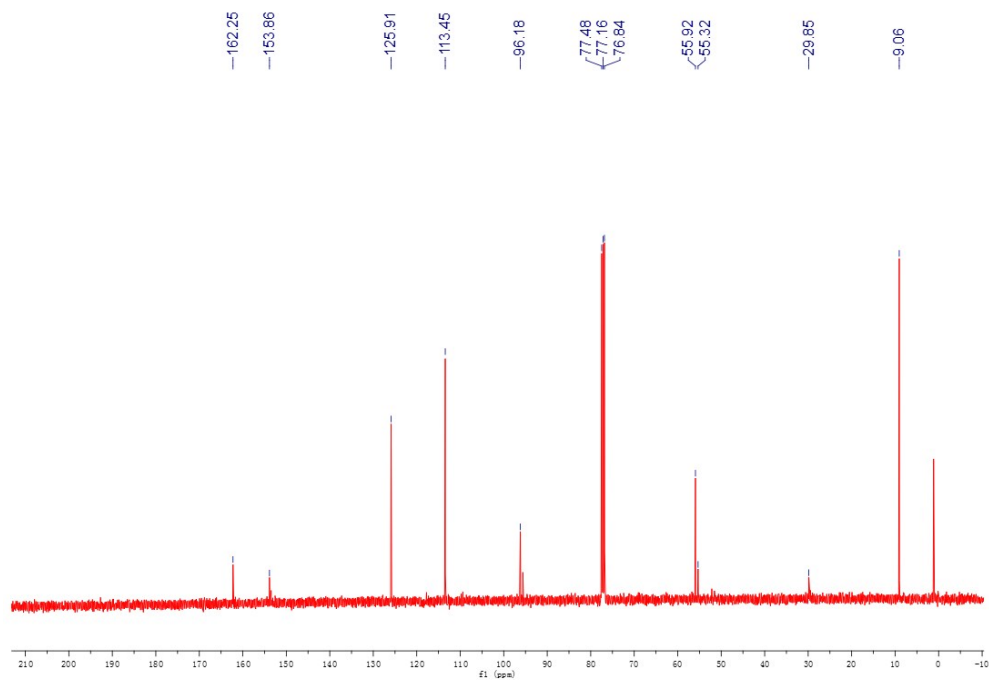
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm 7.76–6.87 (m, 4 H; Ar-H), 3.87 (s, 3 H;  $\text{CH}_3$ -H), 2.85 (s, 1 H;  $\text{C}_{\text{cage}}$ -H), 1.44 (s, 15 H;  $\text{Cp}^*$ )



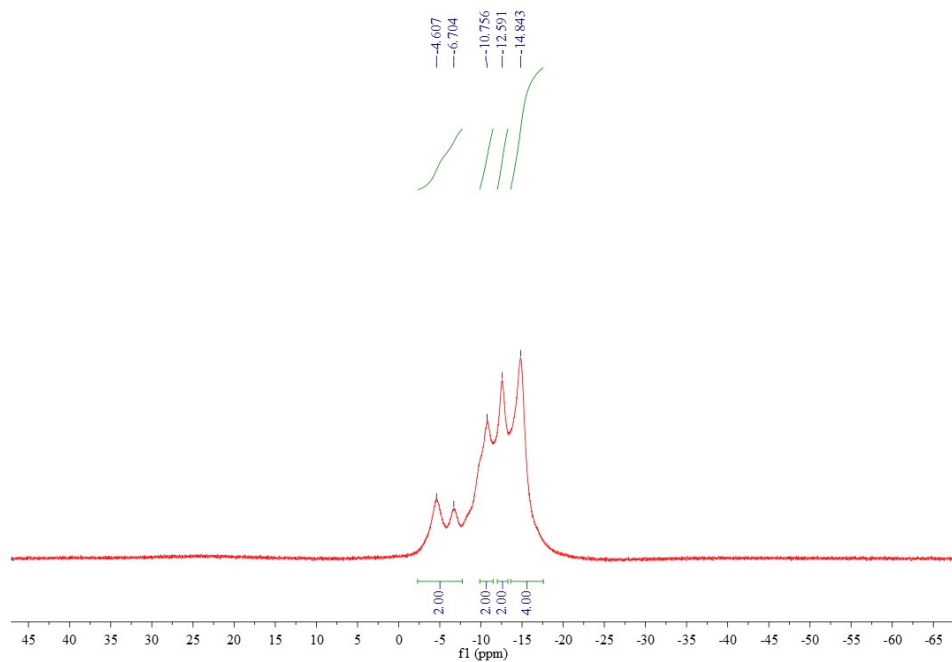
**$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm 162.3, 153.9, 125.9, 113.5 (Ar-C), 96.2 ( $\text{Cp}^*\text{-C}$ ), 55.9, 55.3 ( $\text{C}_{\text{cage-C}}$ ), 29.9 ( $\text{CH}_3\text{-C}$ ), 9.06 ( $\text{Cp}^*\text{-CH}_3$ )

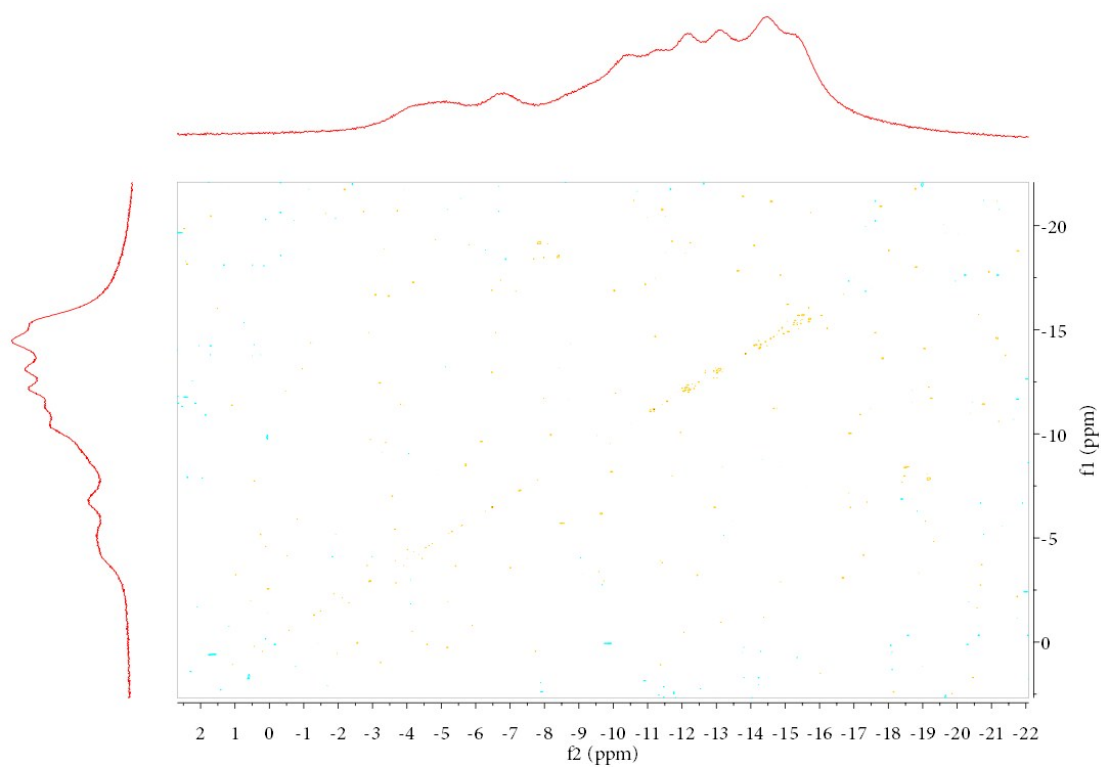


**$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm -4.61–(-6.70) (2 B), -10.76 (2 B), -12.59 (2 B), -14.84 (4 B)



$^{11}\text{B}$ - $^{11}\text{B}$  COSY NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):

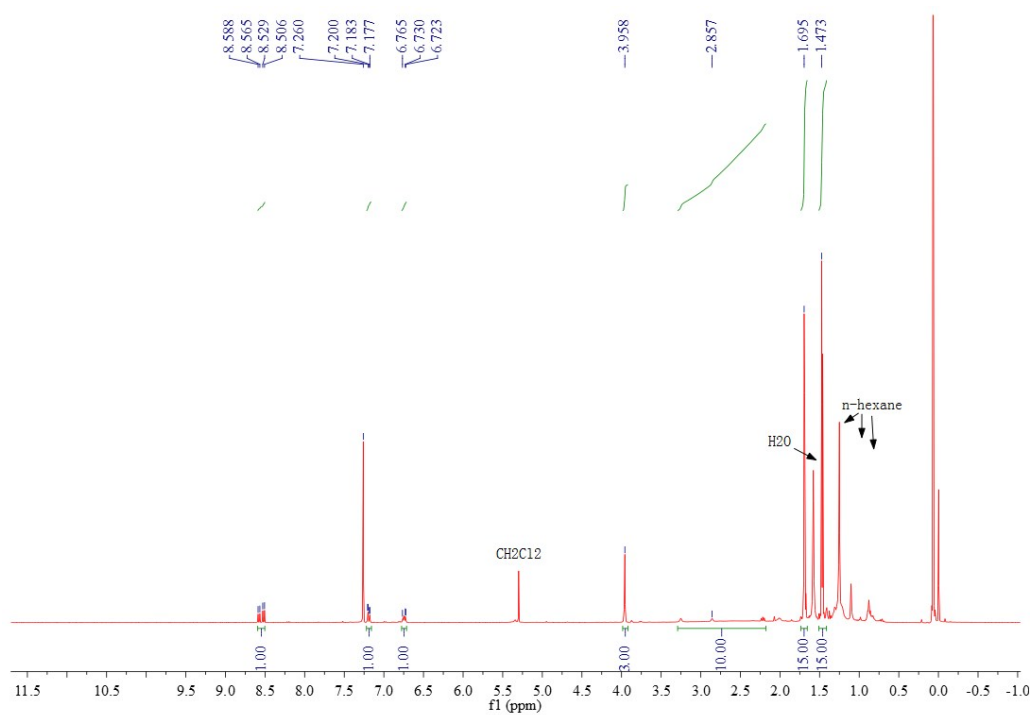


IR (KBr, disk):  $\nu$  (B-H) 2589  $\text{cm}^{-1}$

### Complex 2b

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):

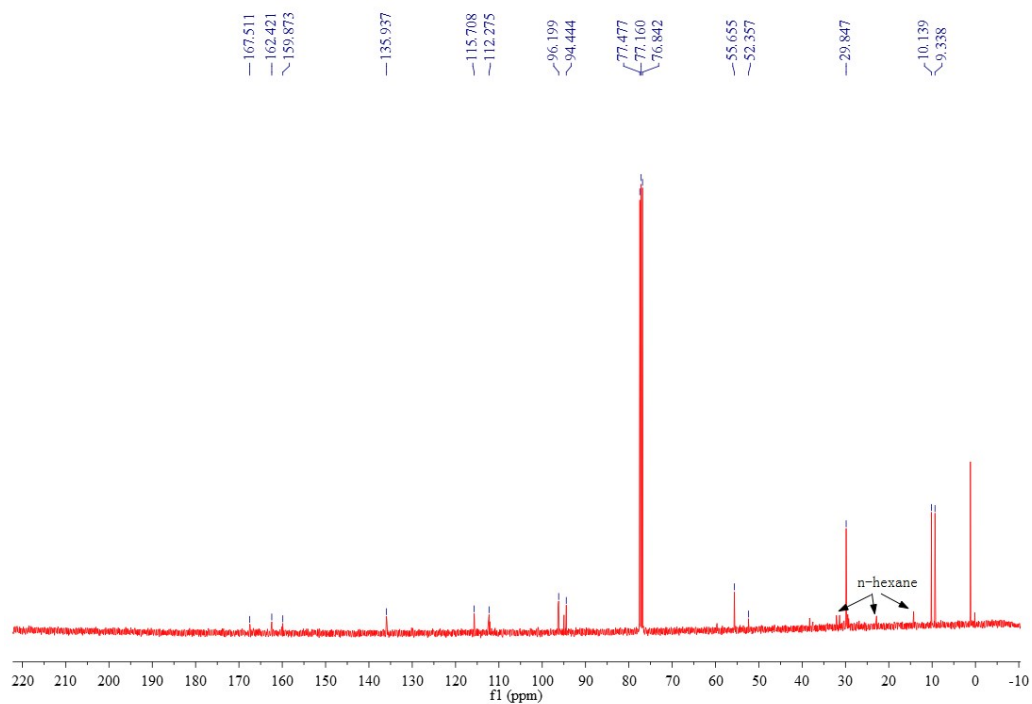
$\delta$  ppm 8.55 (m,  $J = 32.8$  Hz, 1 H; Ar-H), 7.18 (t,  $J = 9.2$  Hz, 1 H; Ar-H), 6.73 (t,  $J = 16.8$  Hz, 1 H; Ar-H), 3.96 (s, 3 H;  $\text{CH}_3$ -H), 2.86 (s, 1 H;  $\text{C}_{\text{cage}}$ -H), 1.69 (s, 15 H;  $\text{Cp}^*$ ), 1.47 (d,  $J = 4$  Hz, 15 H;  $\text{Cp}^*$ )





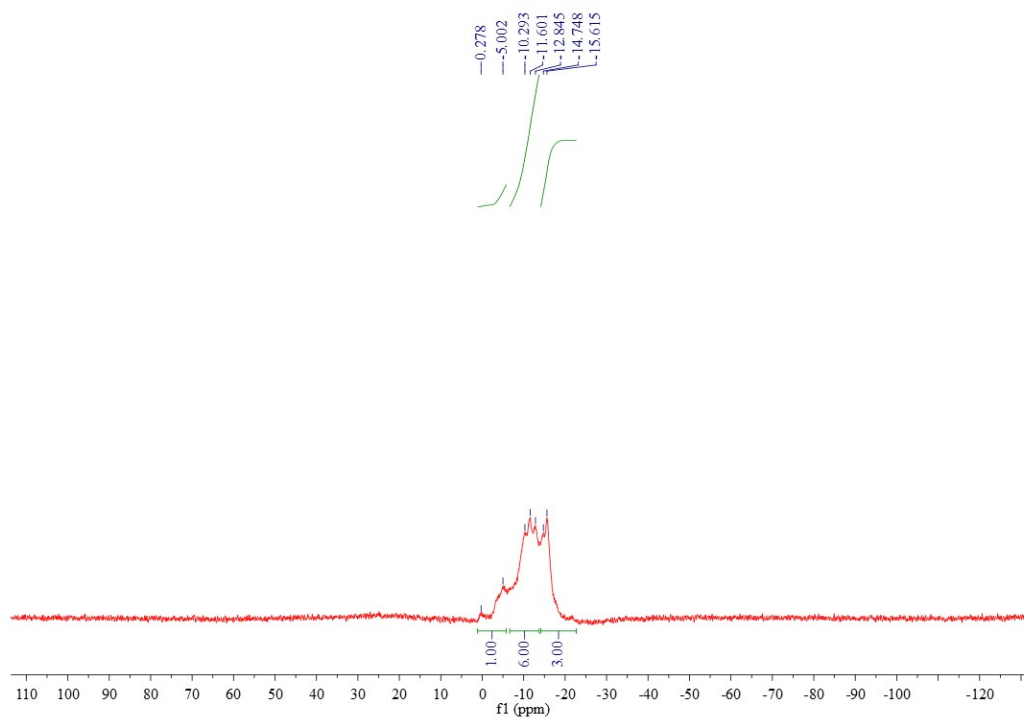
**$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm 167.5, 162.4, 159.9, 135.9, 115.7, 112.3 (Ar-C), 96.2, 94.4, (Cp\*-C), 55.7, 52.4 ( $\text{C}_{\text{cage}}\text{-C}$ ), 29.8 ( $\text{CH}_3\text{-C}$ ), 10.1, 9.3 (Cp\*- $\text{CH}_3$ )



**$^1\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm 0.27–(-5.00) (1 B), -10.29–(-12.85) (6 B), -14.75–(-15.62) (3 B).

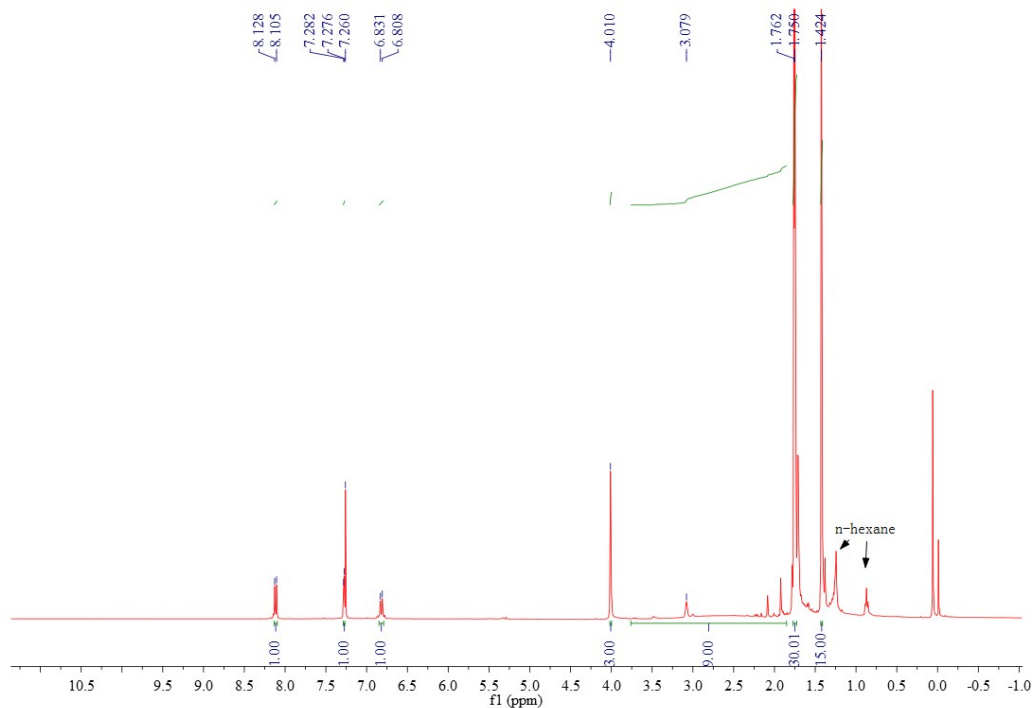


**IR (KBr, disk):**  $\nu$  (B-H) 2591  $\text{cm}^{-1}$

## Complex 2c

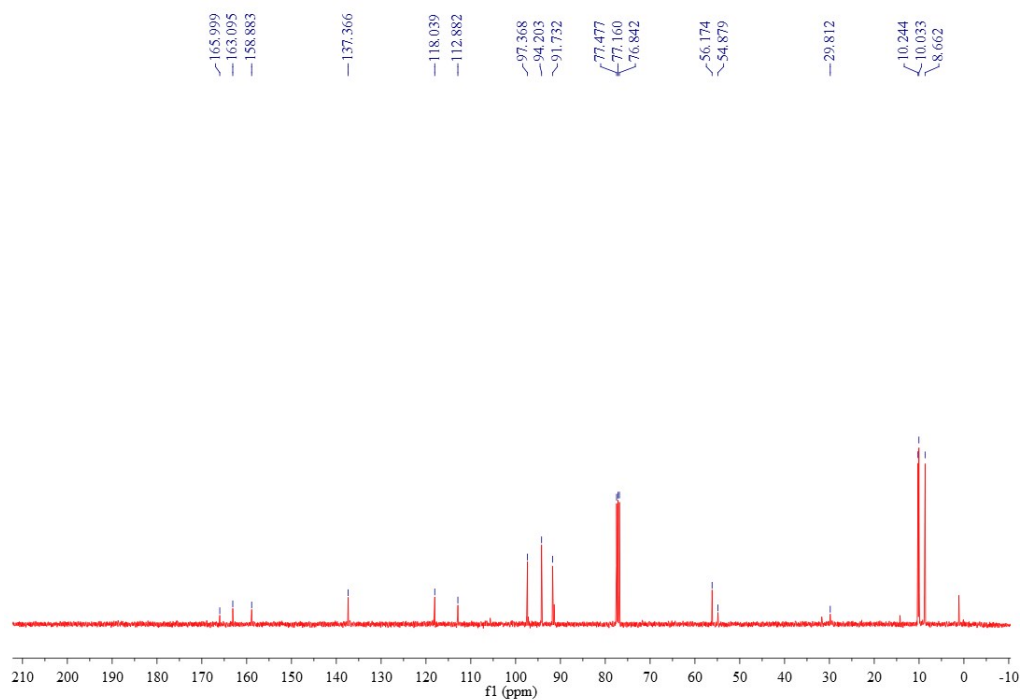
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm 8.13 (d,  $J = 9.2$  Hz, 1 H; Ar-H), 7.28 (d,  $J = 2.4$  Hz, 1 H; Ar-H), 6.81 (d,  $J = 9.2$  Hz, 1 H; Ar-H), 4.01 (s, 3 H;  $\text{CH}_3$ -H), 3.08 (s, 1 H;  $\text{C}_{\text{cage}}$ -H), 1.76, 1.75 (d, 30 H;  $\text{Cp}^*$ ), 1.42 (s, 15 H;  $\text{Cp}^*$ )



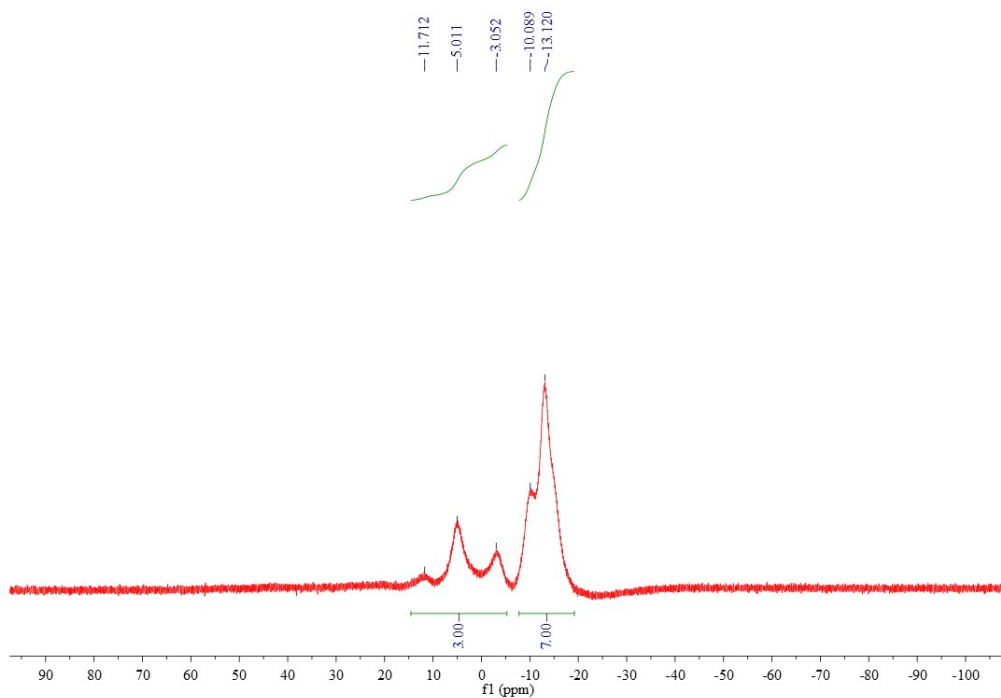
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm 166.0, 163.1, 158.9, 137.4, 118.0, 112.9 (Ar-C), 97.4, 94.2, 91.7 ( $\text{Cp}^*$ -C), 56.2, 54.9 ( $\text{C}_{\text{cage}}$ -C), 29.8 ( $\text{CH}_3$ -C), 10.2, 10.0, 8.7 ( $\text{Cp}^*$ - $\text{CH}_3$ )



**$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm 11.71–(-3.05) (3 B), -10.09–(-13.12) (7 B)

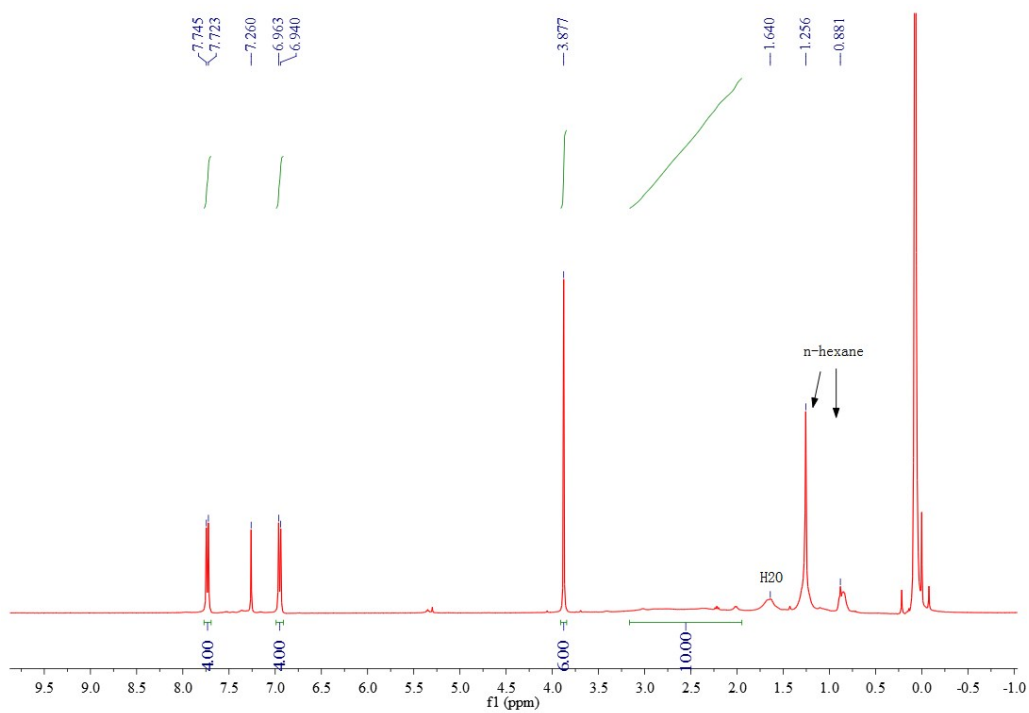


**IR (KBr, disk):**  $\nu$  (B–H) 2580  $\text{cm}^{-1}$ .

### Compound 3

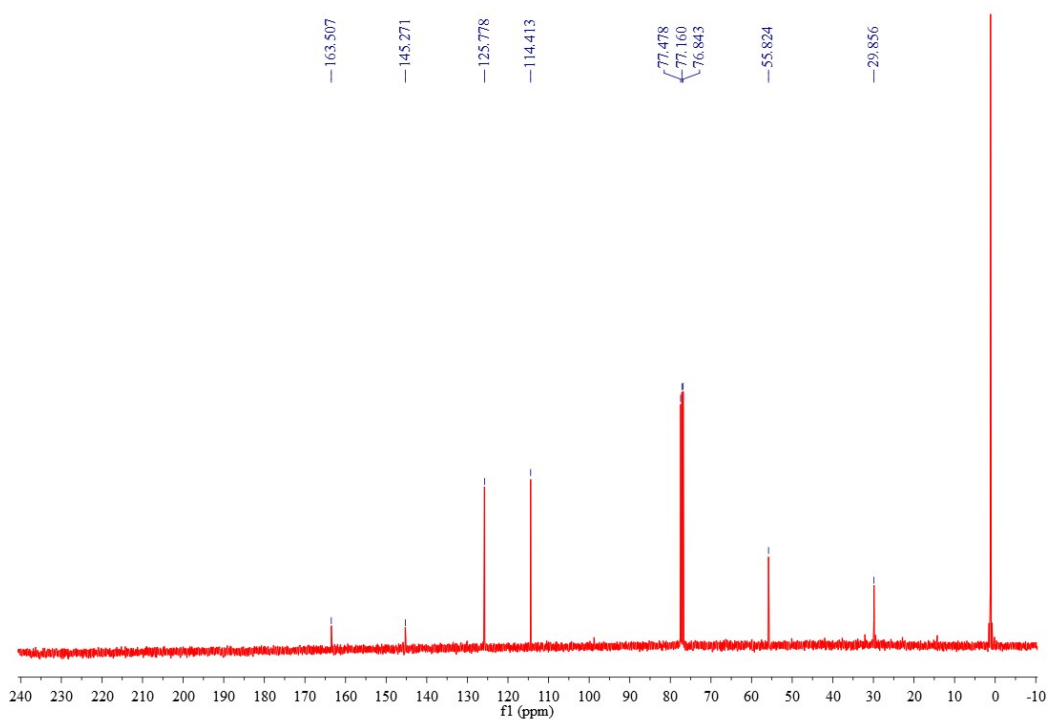
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm 7.75-7.72 (d,  $J = 12$  Hz, 4 H; Ar-H), 6.96-6.94 (d,  $J = 8$  Hz, 4 H; Ar-H), 3.88 (s, 6 H;  $\text{CH}_3$ -H).



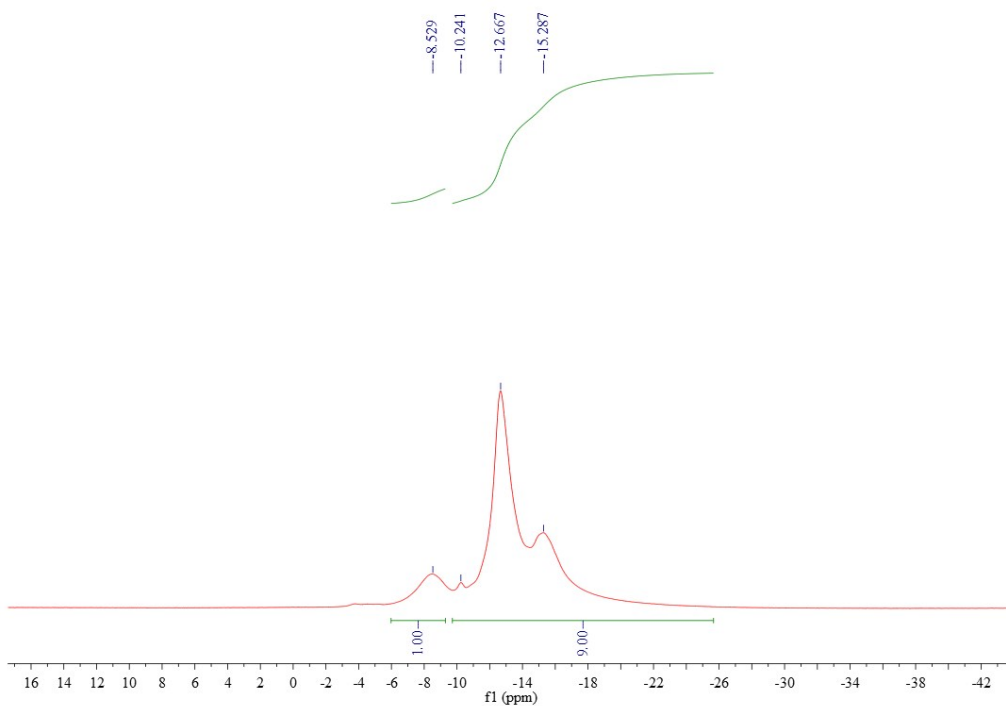
**$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm 163.5, 145.3, 125.8 114.4 (Ar-C), 55.8 ( $\text{C}_{\text{cage}}\text{-C}$ ), 29.9 ( $\text{CH}_3\text{-C}$ ).



**$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):**

$\delta$  ppm -8.53 (1 B), -10.24–(-15.29) (9 B)

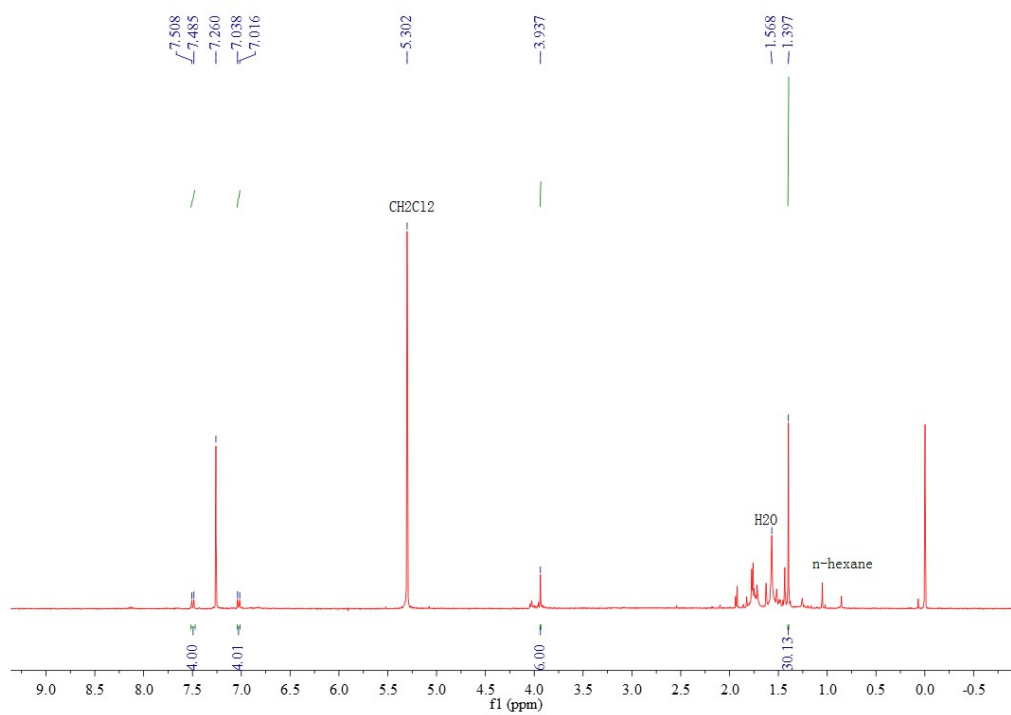


**IR (KBr, disk):**  $\nu$  (B-H) 2607  $\text{cm}^{-1}$

## Complex 4

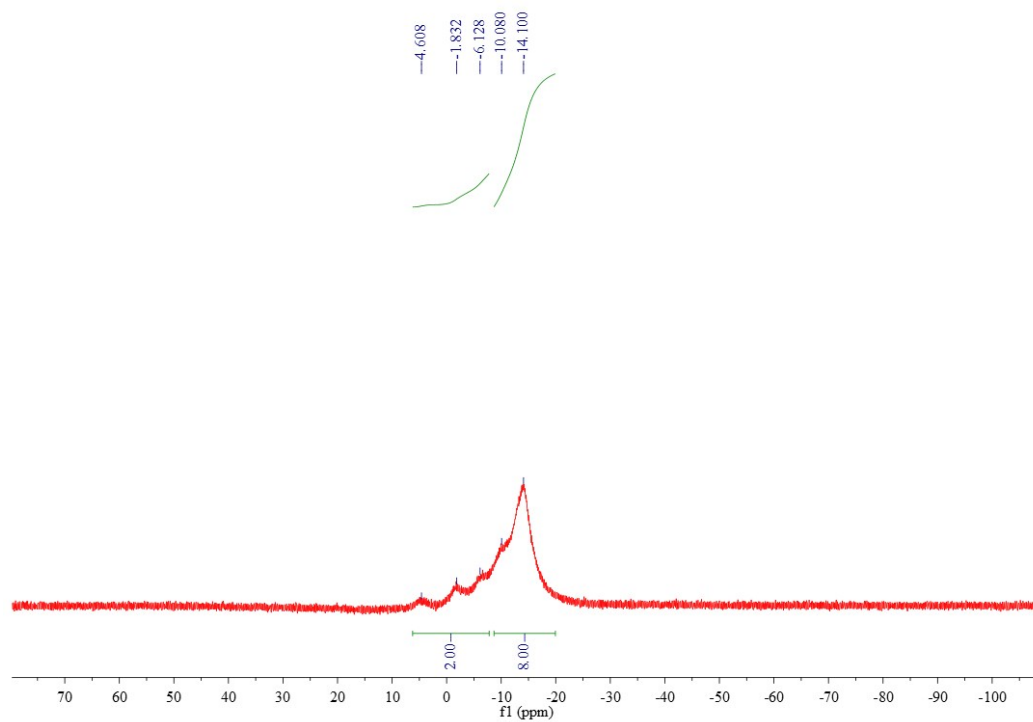
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm 7.51-7.02 (m, 8 H; Ar-H), 3.94 (s, 6 H;  $\text{CH}_3$ -H), 1.40 (s, 30 H;  $\text{Cp}^*$ -H)



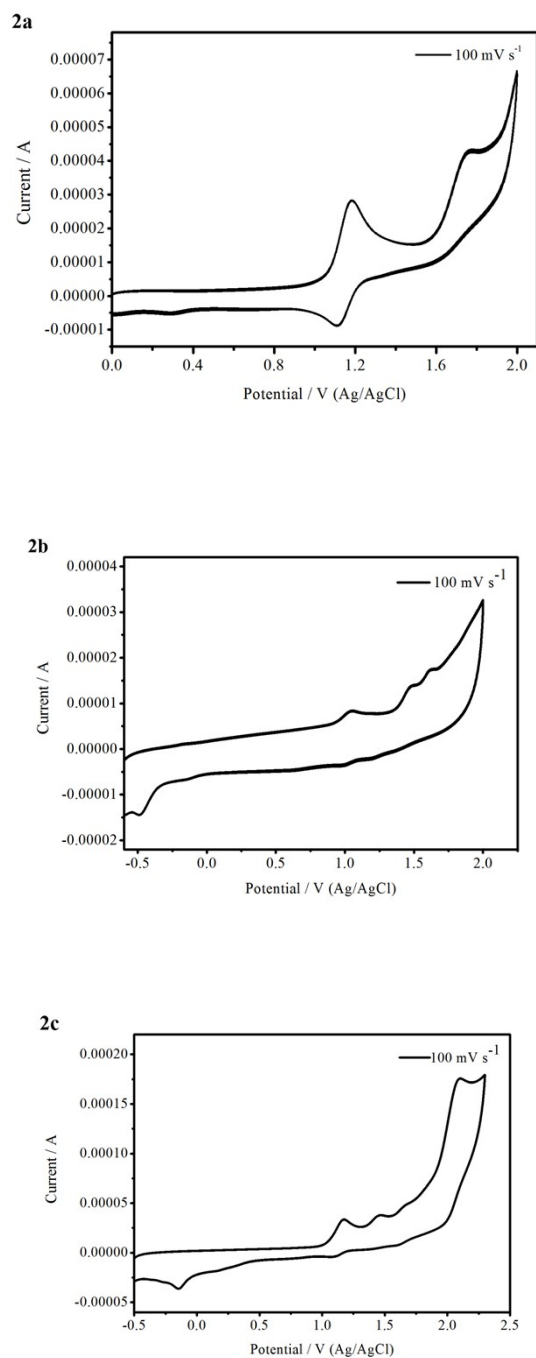
$^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , 25 °C):

$\delta$  ppm 4.61–(-6.13) (2 B), -10.08–(-14.10) (8 B)



IR (KBr, disk):  $\nu$  (B–H) 2590  $\text{cm}^{-1}$ .

## 6. Cyclic Voltammetry.



**Fig. S7** Cyclic voltammograms of complexes **2a**, **2b** and **2c** at a scan rate of 100 mV s<sup>-1</sup>.

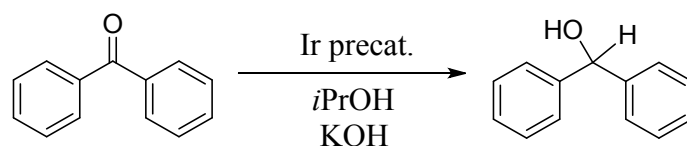
The electrochemical characteristics of solutions of the complexes **2a**, **2b** and **2c** in acetonitril have been studied by cyclic voltammetry (CV) using a glassy carbon (GC) working electrode. All of the cyclic voltammograms exhibit the expected redox

waves in the potential range (Fig. S7), implying Faradaic reaction and pseudocapacitive behavior.

## 7. Catalytic Studies

In an effort to find applications for the obtained polymetallic species, the use of trinuclear complex **2c** as precatalyst for transfer hydrogenation of ketones has been preliminary examined.<sup>[3]</sup> Note that one of the Ir<sup>III</sup> metal ions of **2c** is bound to two chlorido ligands, which exhibit a  $\mu^2$  coordination mode and are linked to other metal centers. We hypothesized that these chlorido ligands may exhibit certain lability, generating vacant sites at the Ir<sup>III</sup>(3) ion to promote hydrogen transfer from *i*PrOH/KOH (for atom numbering see the molecular structure of **2c**).<sup>[4]</sup> Cleavage of Ir(3)–Cl bonds in a first step due to high temperature and harsh reaction conditions is a reasonable activation route for the complex **2c**, considering numerous previous investigations on the field.<sup>[3,4]</sup>

Benzophenone has been selected as substrate for an initial screening. In a typical catalytic experiment, a Schlenck tube was charged with 4 mL of isopropanol. Subsequently, benzophenone (substrate, 0.1 M), KOH (base, 0.05 M) and iridium complex (precatalyst, 5mol% related to substrate) were added. The obtained mixture was heated at reflux. After the reaction time, the flask was cooled to ambient temperature and the crude reaction mixture was filtered. Yields were determined by <sup>1</sup>H NMR spectroscopy. All the experiments were repeated three times to ensure the reproducibility of the method. The collected results are shown in a table.

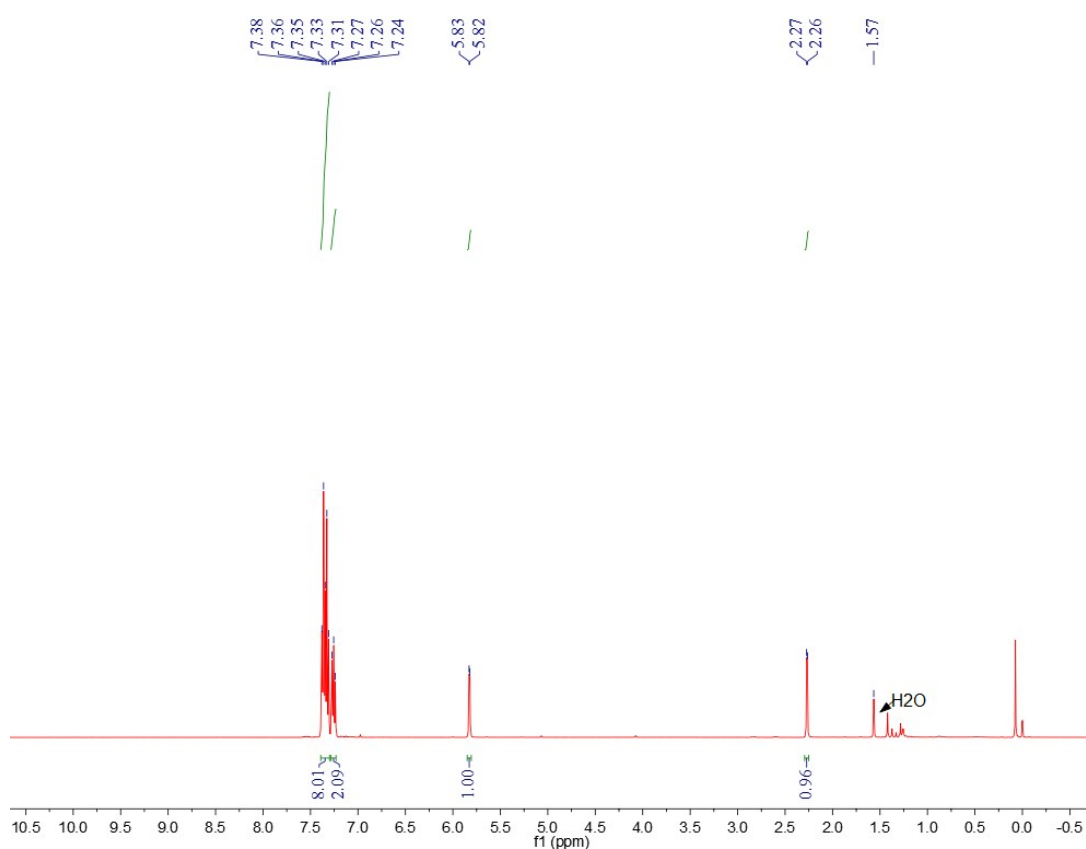


entry	precatalyst	time (h)	conversion (%)
I	–	24	0
II	<b>2c</b>	12	80
III	<b>2c</b>	24	88
IV	<b>2c</b>	48	94
V	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	12	44
VI	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	48	92

The product of the reduction of benzophenone, benzhydrol, has been isolated by column chromatography using silica gel and a CH<sub>2</sub>Cl<sub>2</sub>: hexane mixture 50: 50 to 100: 0. Subsequently, it has been characterized by <sup>1</sup>H NMR spectroscopy (*vide infra*). The application of **2c** in other catalytic processes is currently being investigated.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):**

δ ppm 7.38-7.31 (m, 8 H; Ph-H), 7.27-7.24 (t, 3 H; Ph-H), 5.83 (d, 1 H; OH-H), 2,27 (d, 1 H; CH-H).





## References

- 1 C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228.
- 2 P. Hanson, J. R. Jones, A. B. Taylor, P. H. Walton and A. W. Timms, *J. Chem. Soc. Perkin Trans. 2*, 2002, 1135.
- 3 (a) R. Noyori and T. Ohkuma, *Angew. Chem. Int. Ed.*, 2001, **40**, 40; (b) G. Zassinovich, G. Mestroni and S. Gladiali, *Chem. Rev.* 1992, **92**, 1051.
- 4 R. Corberán, M. Sanaú and E. Peris, *Organometallics*, 2007, **26**, 3492.