

# **Regioselective B-H/C-H Activation and Metal-Metal Bond Formation Induced by Half-Sandwich Metals Complexes at Hydroxy- Substituted o-Carboranes**

Shu-Ting Guo, Peng-Fei Cui, Yang Gao and Guo-Xin Jin\*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Material,  
Collaborative Innovation Center of Chemistry for Energy Materials, Department of  
Chemistry, Fudan University, Shanghai 200433, P. R. China.

\*E-mail: [gxjin@fudan.edu.cn](mailto:gxjin@fudan.edu.cn).

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## Experimental details:

### General Procedures.

All reactions were conducted under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. The materials  $[\text{Cp}^*\text{MCl}_2]_2$  (M = Ir and Rh),<sup>1</sup> (2-pyridine)(*o*-carboranyl)methanol ligand<sup>2</sup> and *o*-carboranylmethanol<sup>3</sup> were prepared according to literature methods. Nondeuterated solvents were dried and distilled under N<sub>2</sub> from appropriate drying agents. All other chemicals were purchased from readily available commercial sources and used without further purification. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE I 400 and AVANCE NEO 400 Spectrometers. Spectra were recorded at room temperature and referenced to the residual protonated solvent for NMR spectra. Proton chemical shift ( $\delta$  H = 7.26 (CDCl<sub>3</sub>)) and ( $\delta$  C = 77.16 (CDCl<sub>3</sub>)) are reported relative to the solvent residual peak. Coupling constants are expressed in Hertz. <sup>11</sup>B NMR (160 MHz) spectra were recorded with a Bruker AVANCE III HD spectrometer. Complex multiplets are noted as “m” and broad resonances as “br”. Elemental analyses were performed on an Elementar Vario EL III analyzer. IR spectra (KBr tablets) in the range 400-4000 cm<sup>-1</sup> were measured on a Nicolet AVATAR-360IR spectrometer. Mass spectra were obtained with a Micro TOF II mass spectrometer using electrospray ionization. X-ray diffraction data were collected on a CCD-Bruker SMART APEX system.

## NMR spectra:

Figure S1.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) of **3**.

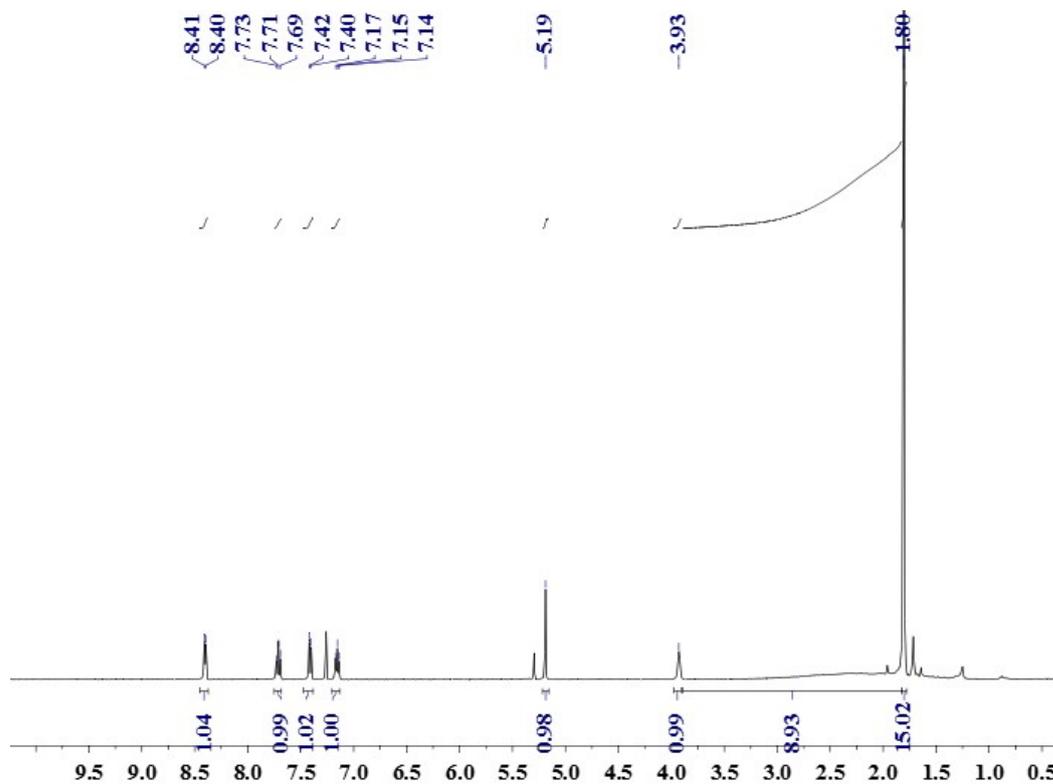


Figure S2.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm) of **3**.

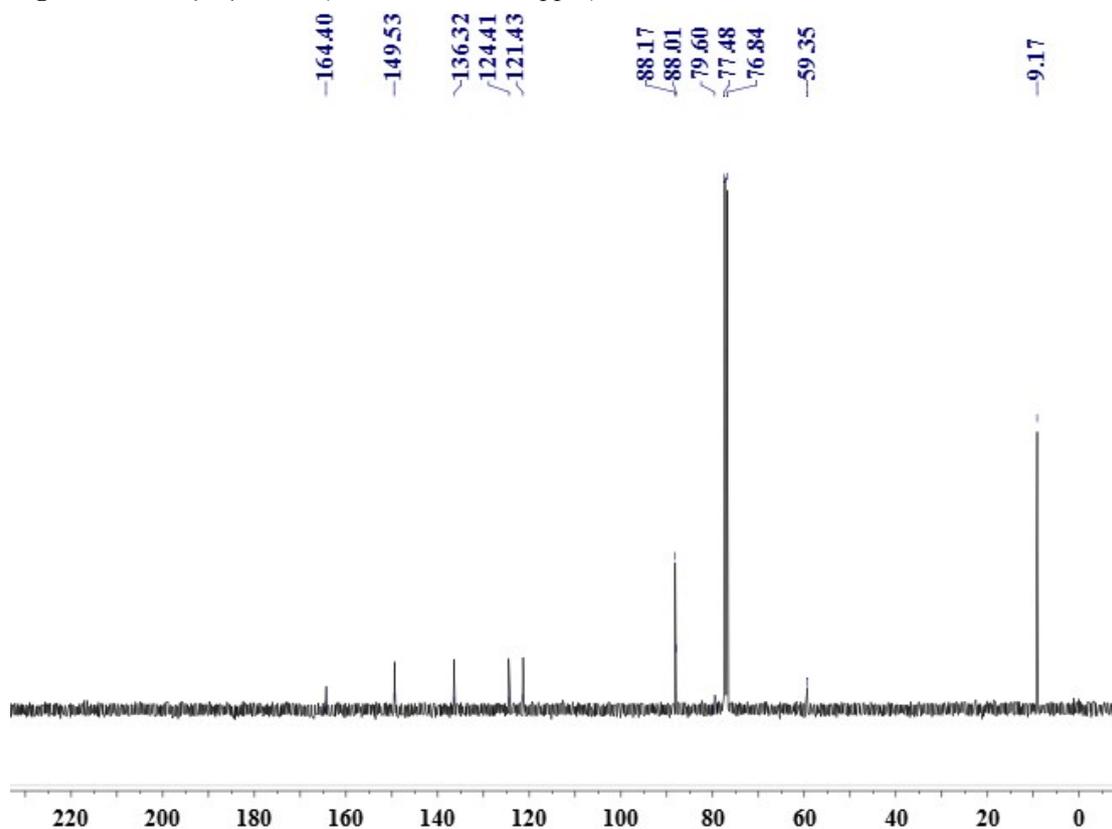


Figure S3:  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm) of **3**.

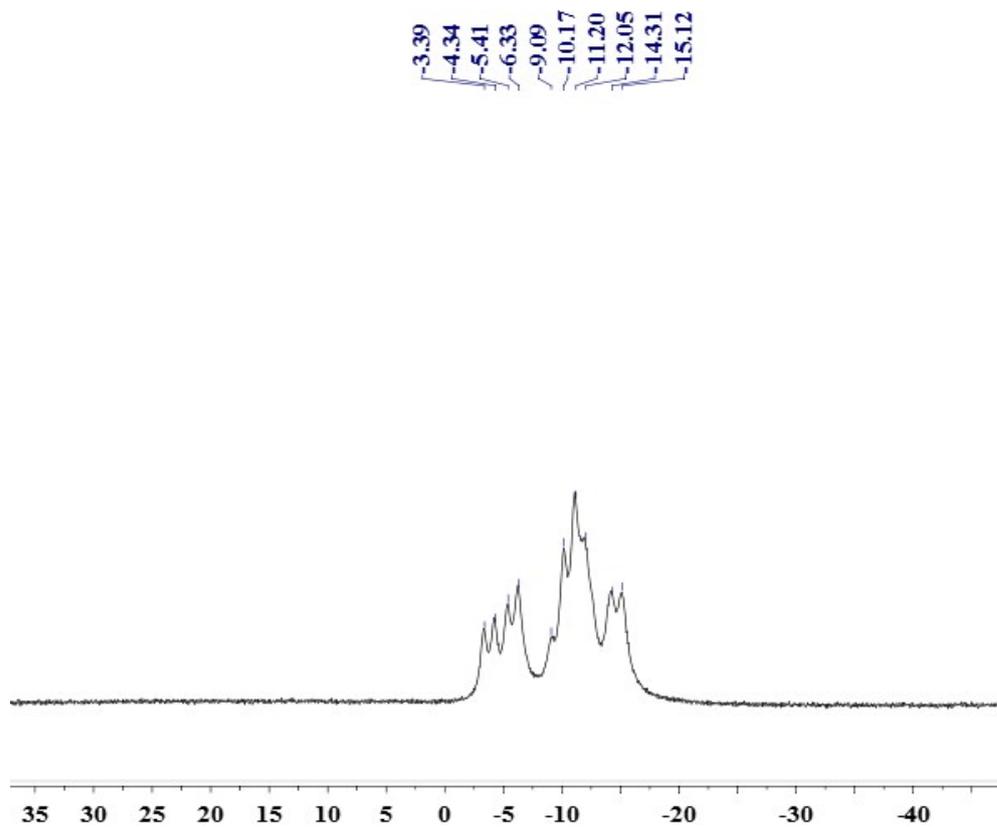


Figure S4.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) of **4**.

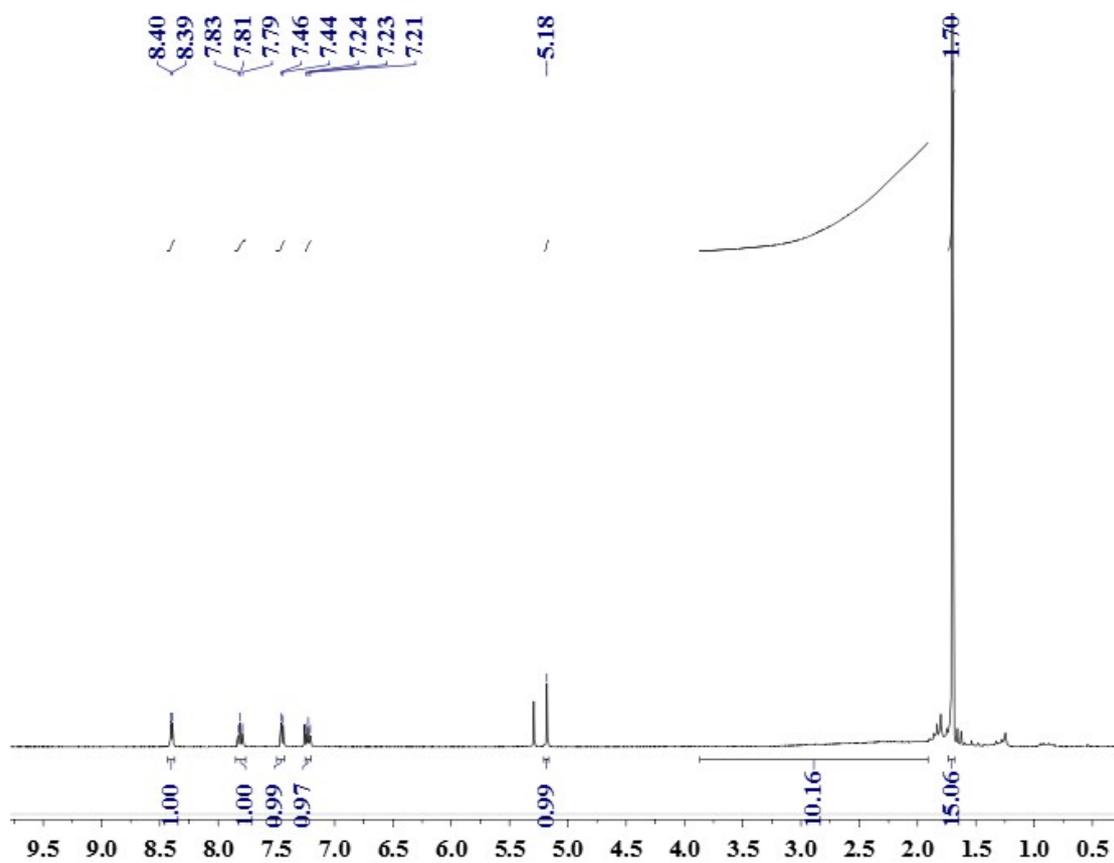


Figure S5.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm) of 4.

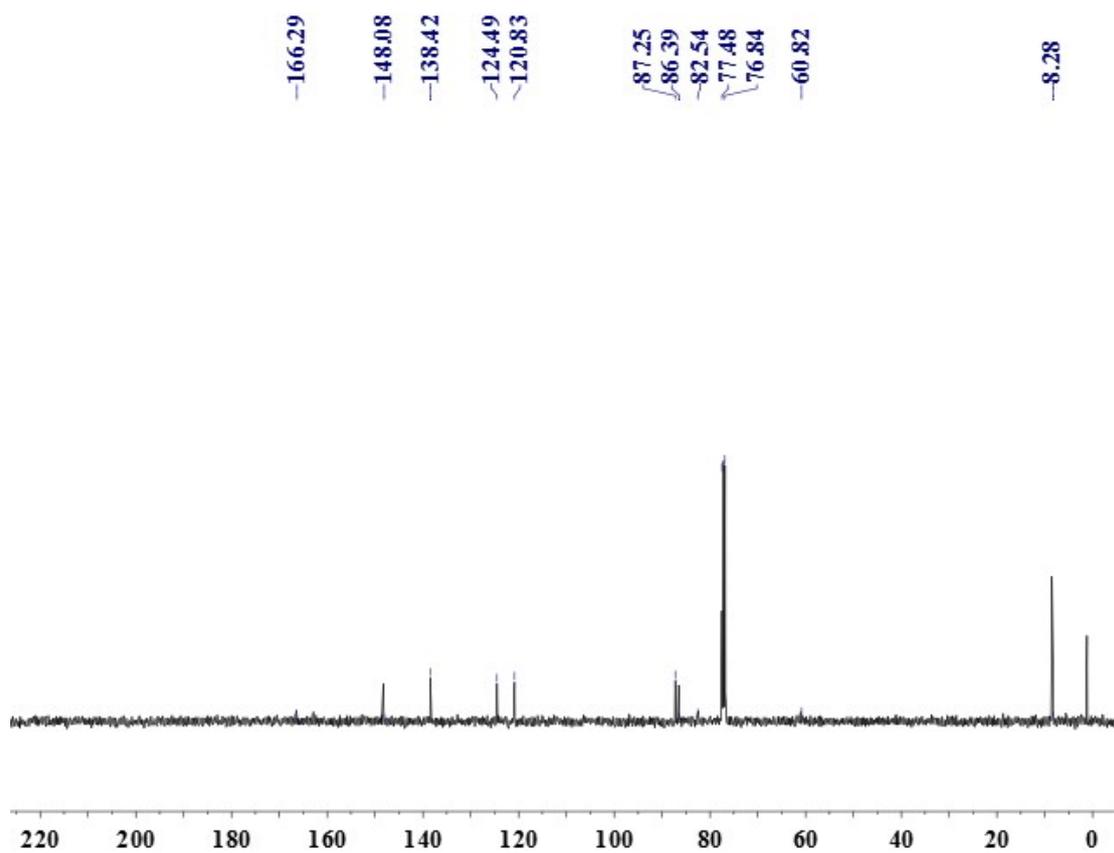


Figure S6.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm) of 4.

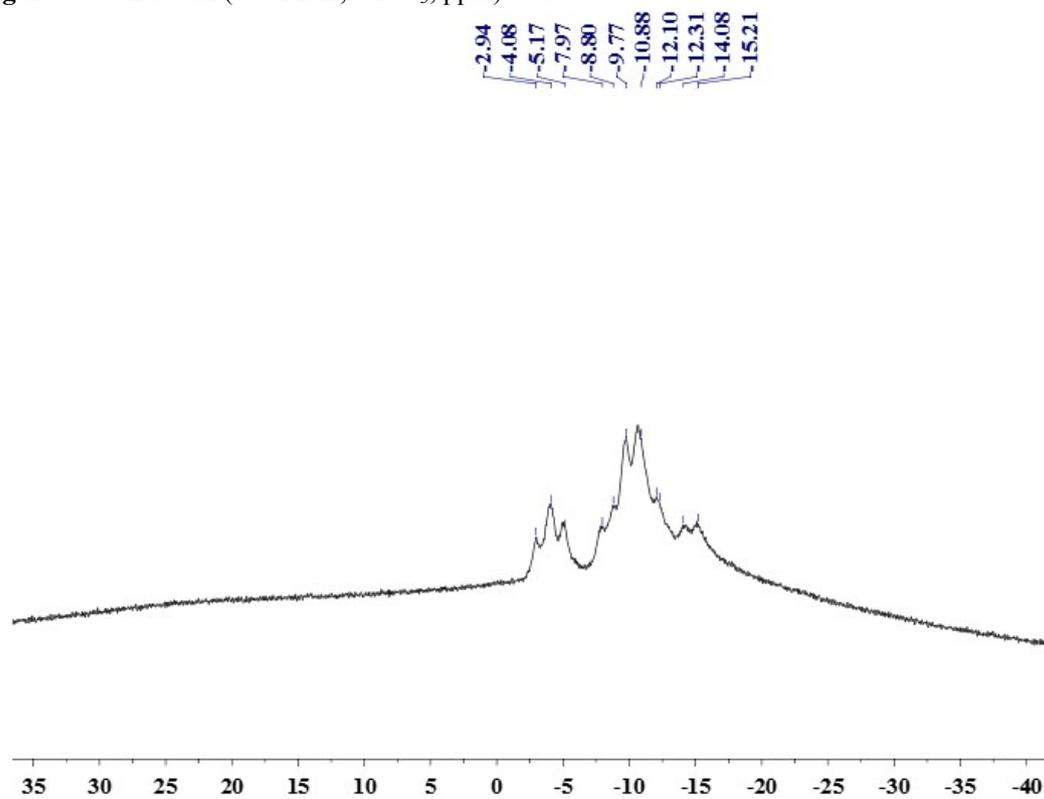


Figure S7.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) of **5**.

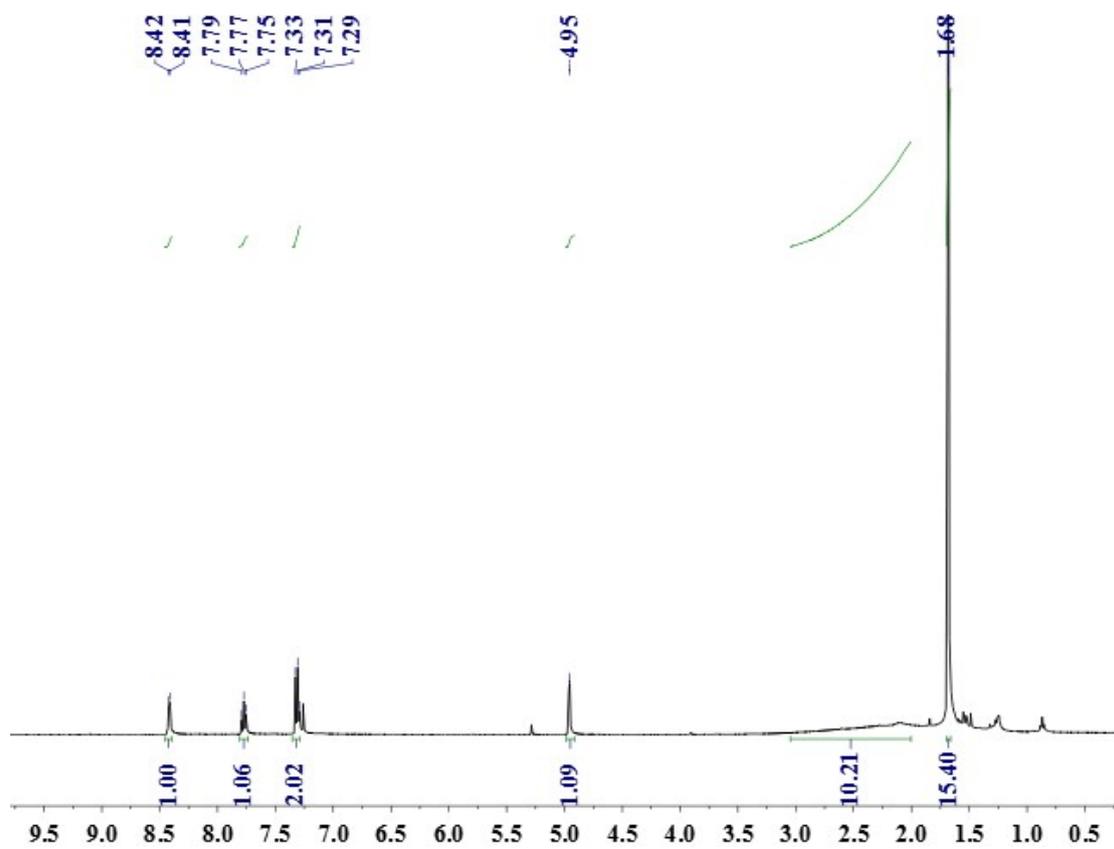


Figure S8.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm) of **5**.

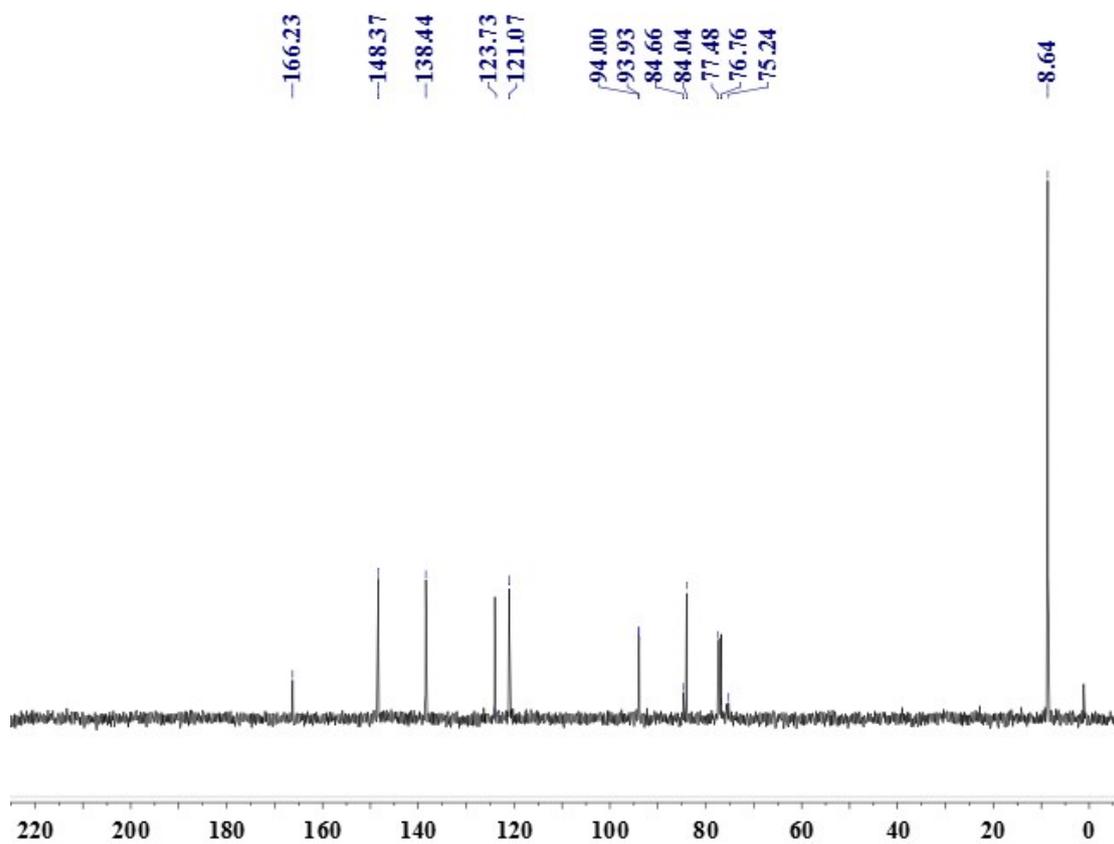


Figure S9.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm) of **5**.

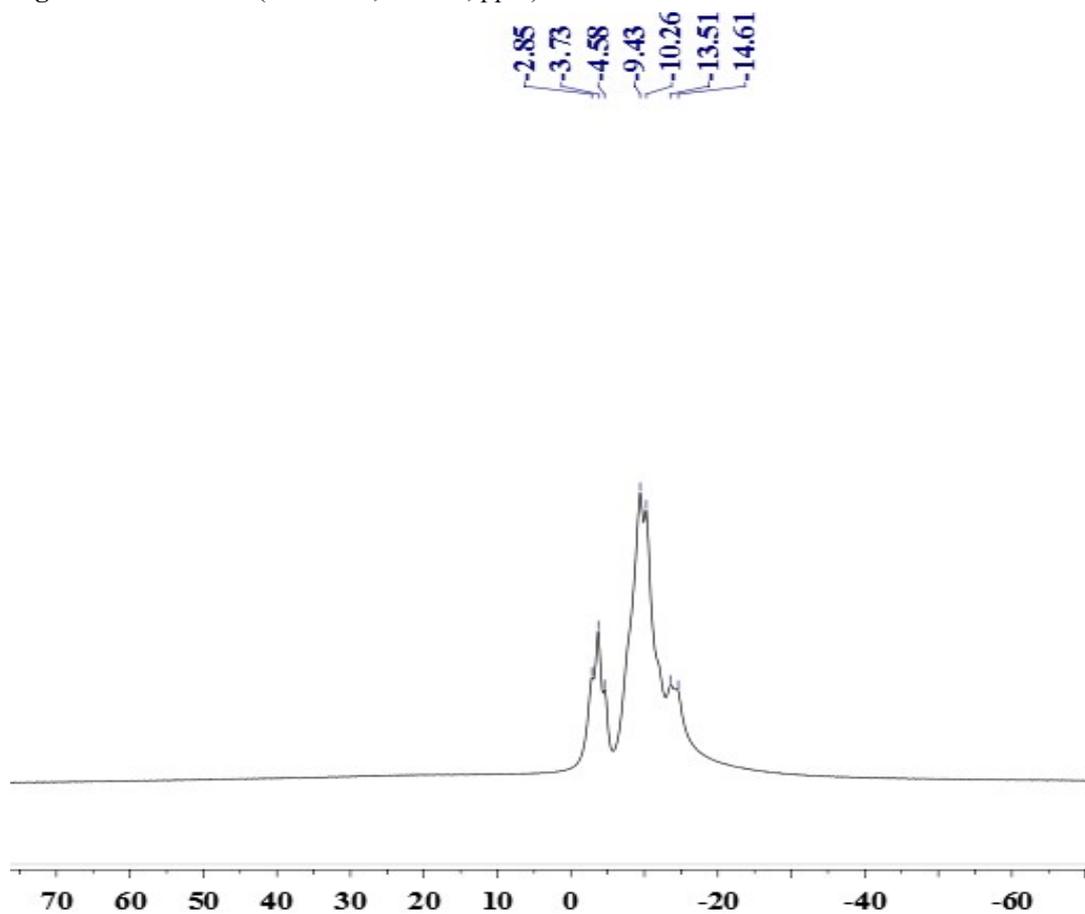


Figure S10.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm) of **6**.

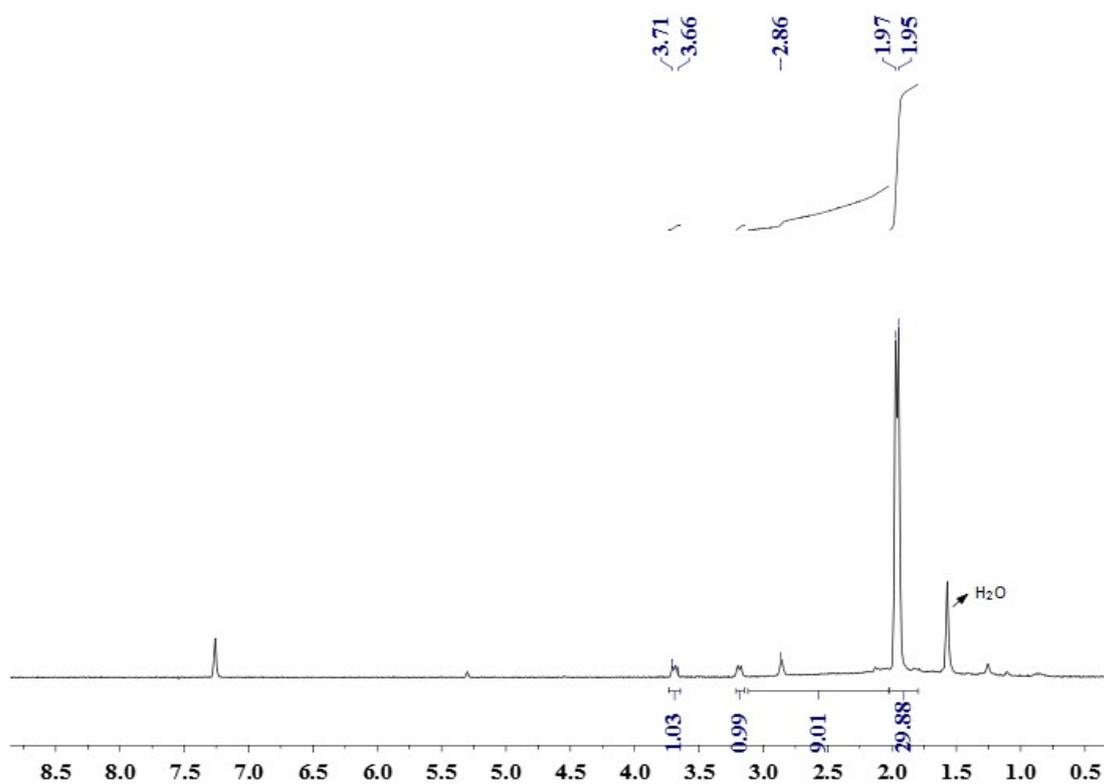


Figure S11.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm) of 6.

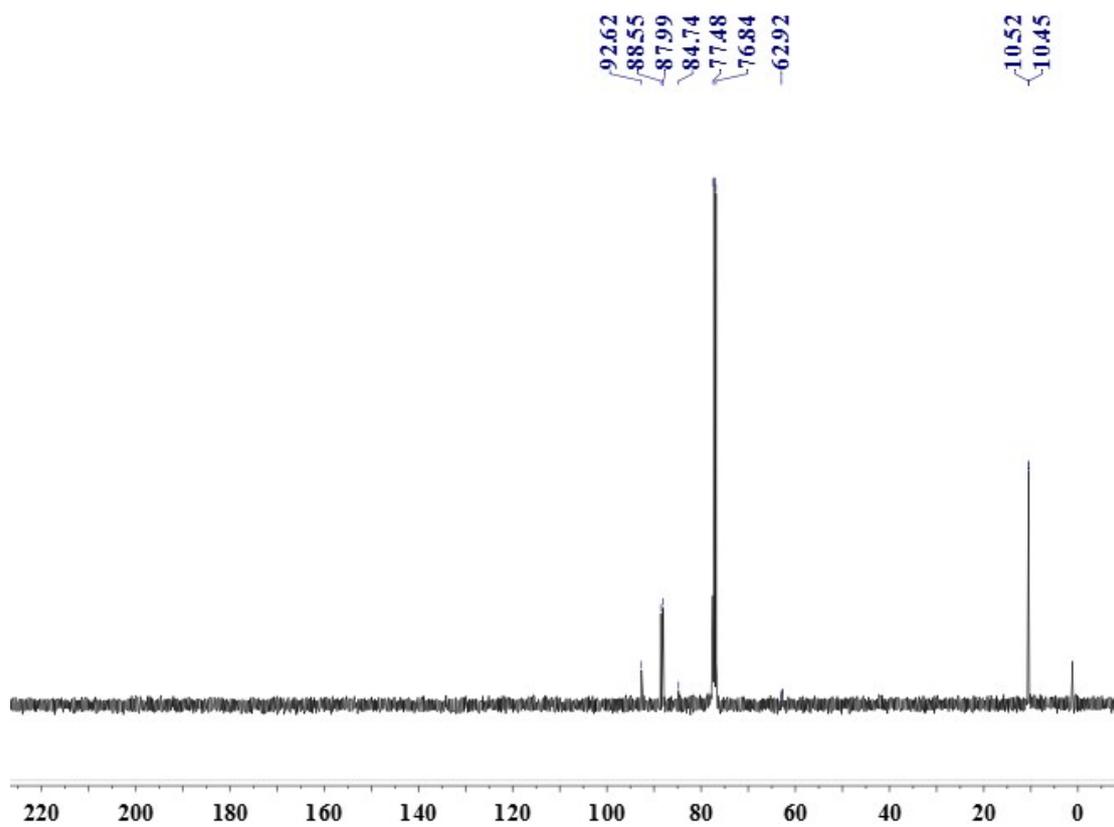
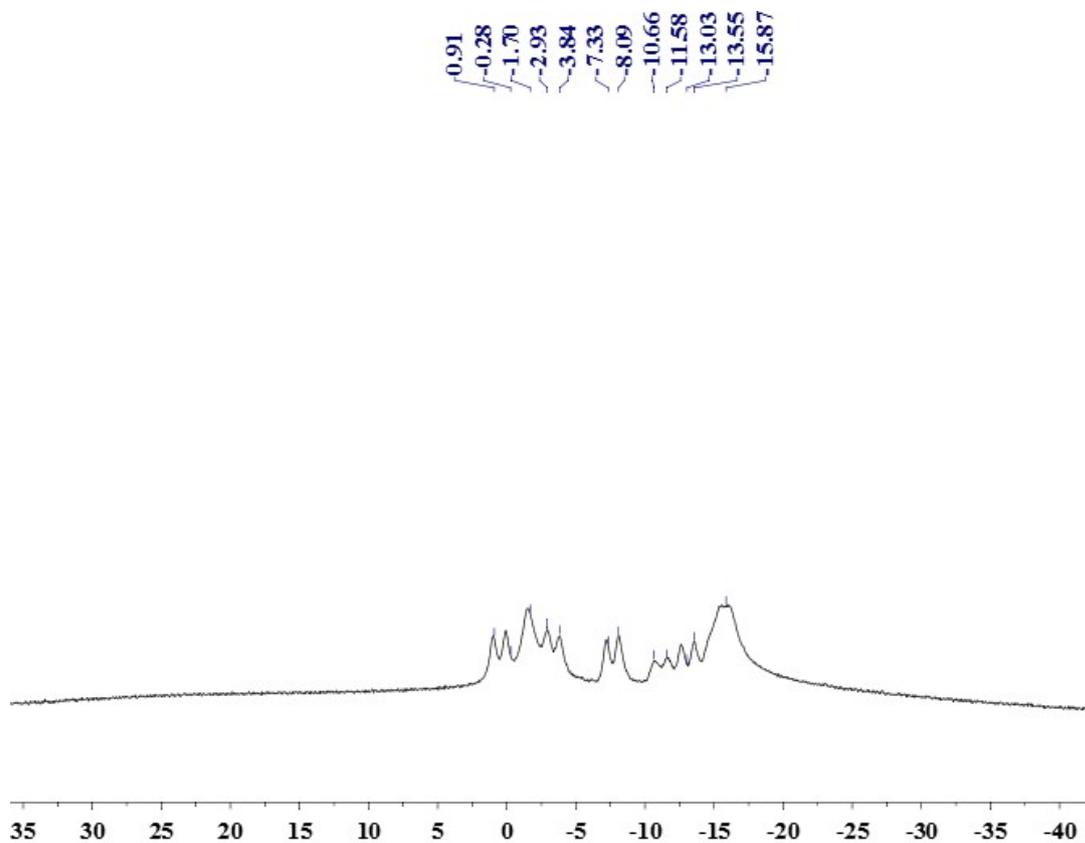
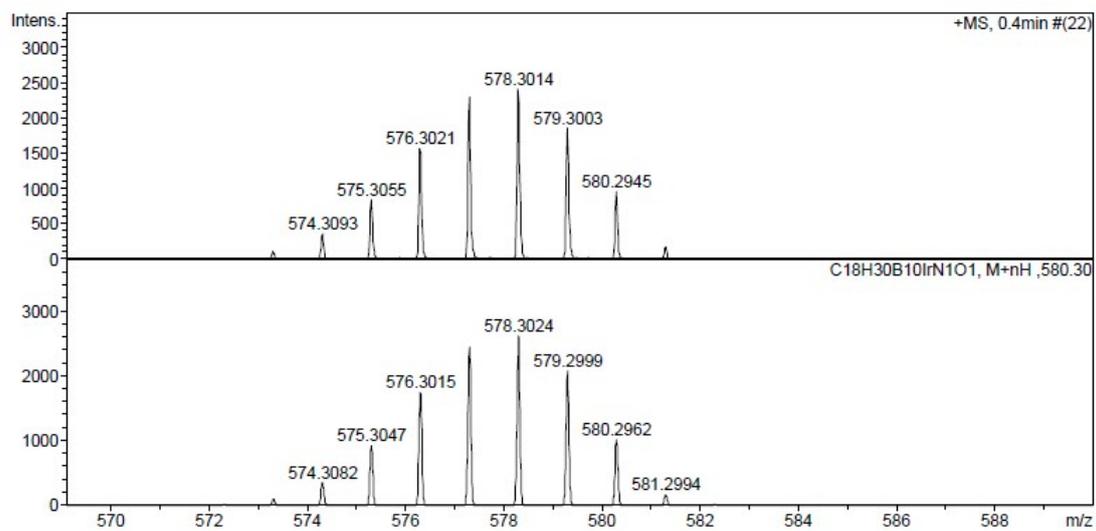


Figure S12.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm) of 6.

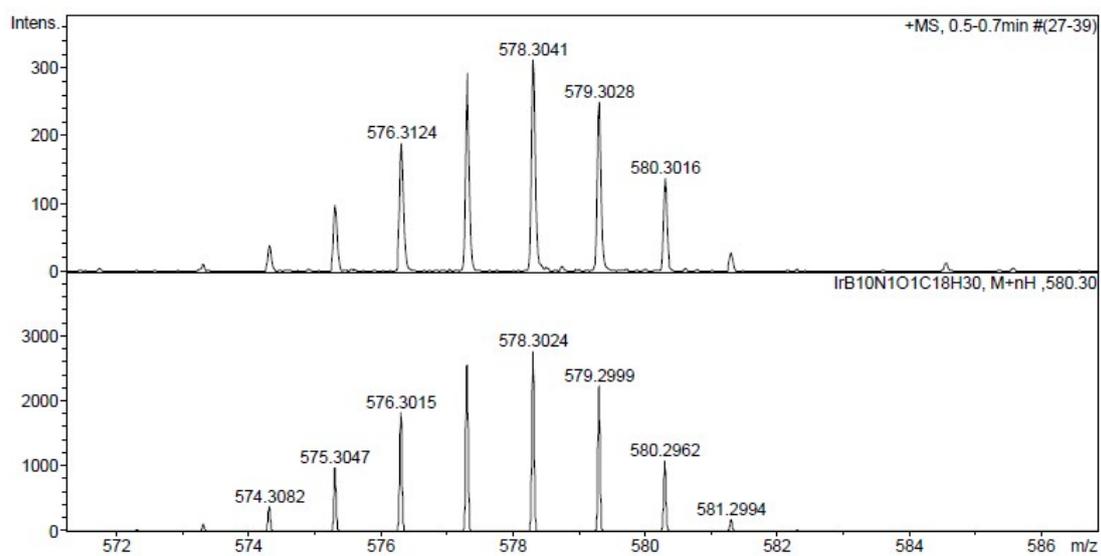


## ESI-MS spectra:

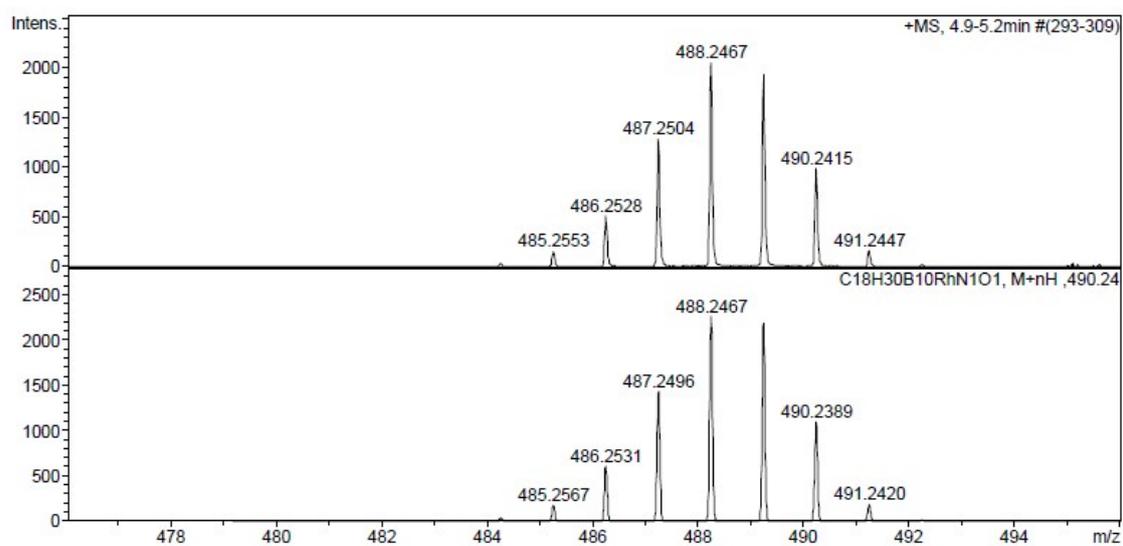
**Figure S13.** Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **3**



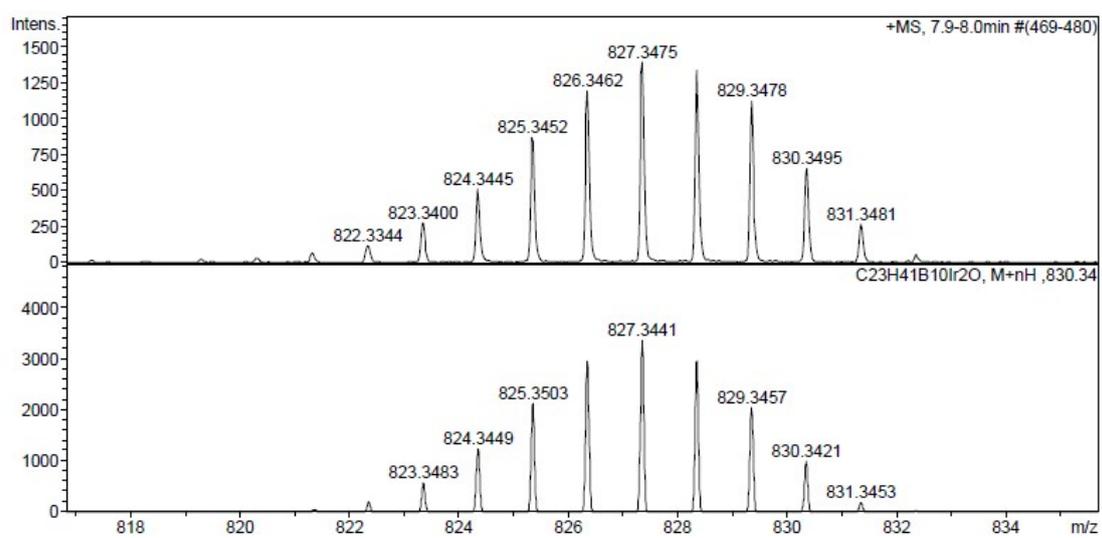
**Figure S14.** Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **4**



**Figure S15.** Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **5**



**Figure S16.** Experimental (top) and theoretical (bottom) ESI-MS spectra of complex **6**.



## X-ray crystallography details:

Single crystals of **3**, **4**, **5** and **6** suitable for X-ray diffraction study were obtained at low temperature. X-ray intensity data of **3**, **4**, **5** and **6** were collected on a CCD-Bruker SMART APEX system.

**Table S1.** Crystal data for complexes **3**, **4**, **5** and **6**.

complex	3	4	5	6
Empirical formula	C18 H30 B10 Ir N O	C18 H32 B10 Ir N O2	C18 H32 B10 N O2 Rh	C23 H41 B10 Ir2 O
Formula weight	576.73	594.74	505.45	826.06
Temperature	173(2) K	203(2) K	173(2) K	203(2) K
Wavelength	1.34138 Å	0.71073 Å	1.34138 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a	10.6487(3) Å	a = 8.7460(19) Å	a = 8.7191(4) Å	a = 11.509(4) Å
b	21.3310(6) Å	b = 18.478(4) Å	b = 18.3682(7) Å	b = 13.941(4) Å
c	11.2665(3) Å	c = 14.961(3) Å	c = 14.9487(6) Å	c = 18.125(6) Å
$\alpha$	90°	a = 90°.	90°	a = 90°.
$\beta$	116.9850(10)°	b = 99.519(3)°.	99.5160(10)°.	b = 90°.
$\gamma$	90°	g = 90°.	90°	g = 90°.
Volume	2280.53(11) Å <sup>3</sup>	2384.5(9) Å <sup>3</sup>	2361.15(17) Å <sup>3</sup>	2907.9(16) Å <sup>3</sup>
Z	4	4	4	4
Density (calculated)	1.680 Mg/m <sup>3</sup>	1.657 Mg/m <sup>3</sup>	1.422 Mg/m <sup>3</sup>	1.887 Mg/m <sup>3</sup>
Absorption coefficient	7.554 mm <sup>-1</sup>	5.616 mm <sup>-1</sup>	4.025 mm <sup>-1</sup>	9.160 mm <sup>-1</sup>
F(000)	1120	1160	1032	1564
Crystal size (mm <sup>3</sup> )	0.670 x 0.160 x 0.160	0.250 x 0.220 x 0.180 mm <sup>3</sup>	0.630 x 0.240 x 0.210	0.350 x 0.210 x 0.120 mm <sup>3</sup>
Theta range for data collection	4.234 to 58.153°.	1.766 to 28.500°.	3.344 to 59.280°.	1.843 to 27.677°.
Index ranges	-13<=h<=13, 24<=k<=27, 14<=l<=14	- 11<=h<=11, - - 24<=k<=21, - 20<=l<=19	-11<=h<=11, 23<=k<=19, 19<=l<=19	- 14<=h<=14, - - 18<=k<=11, - 23<=l<=23
Reflections collected	20599	18145	20049	20797
Independent reflections	4841 [R(int) = 0.0520]	= 6018 [R(int) = 0.0589]	5187 [R(int) = 0.0501]	6736 [R(int) = 0.0466]
Data / restraints / parameters	4841 / 0 / 289	6018 / 12 / 304	5187 / 12 / 304	0.647 and 0.261
Goodness-of-fit on F <sup>2</sup>	1.080	1.043	1.102	6736 / 42 / 335

Final R indices	R1 = 0.0338, wR2 = 0.0809	R1 = 0.0358, wR2 = 0.0921	R1 = 0.0352, wR2 = 1.100	0.0896
[I>2sigma(I)]				
R indices (all data)	R1 = 0.0353, wR2 = 0.0819	R1 = 0.0456, wR2 = 0.0979	R1 = 0.0385, wR2 = 0.0921	R1 = 0.0448, wR2 = 0.1325

$\alpha$ :  $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$  (based on reflections with  $F_o^2 > 2\sigma F^2$ ).  $wR_2 = [\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}]^{1/2}$ ;  
 $w = 1 / [\sigma^2(F_o^2) + (0.095P)^2]$ ;  $P = [\max(F_o^2, 0) + 2F_c^2] / 3(F_o^2 > 2\sigma F^2)$ .

## Reference:

1. C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228.
2. F. D. Salvo, B. Camargo, Y. García, F. Teixidor, C. Viñas, J. G. Planas, M. E. Light and M. B. Hursthouse, *Crystengcomm*, 2011, **13**, 5788-5806.
3. F. A. Gomez, S. E. Johnson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1991, **113**, 5913-5914.