Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and Reactivity of 16-electron Half-Sandwich Iridium Complexes Bearing a Carboranylthioamide Ligand

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1. Experimental details

General Procedures. All experiments were conducted under nitrogen using standard Schlenk techniques. Nondeuterated solvents were distilled under N_2 from appropriate drying agents. The compounds $[Cp^*MCl_2]_2$ (M=Ir and Rh),[1] and *o*-carboranylthioamide ligand[2] were prepared according to literature procedures. All other chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded on Bruker AVANCE I 400 and AVANCE-DMX 500 spectrometers. Spectra were recorded at room temperature unless otherwise noted and referenced to the residual protonated solvent for NMR spectra. Proton chemical shift (δ_H = 7.26 ($CDCl_3$)) and (δ_C = 77.16 ($CDCl_3$)) are reported relative to the solvent residual peak. Coupling constants are expressed in Hertz. Complex multiplets are noted as "m" and broad resonances as "br". Mass spectra were obtained with a Micro TOF II mass spectrometer using electrospray ionization. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm^{-1} were recorded on a Nicolet AVATAR-360IR spectrometer. Elemental analyses were performed with an Elementar Vario EL III analyzer.

2. NMR spectra

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **2.**

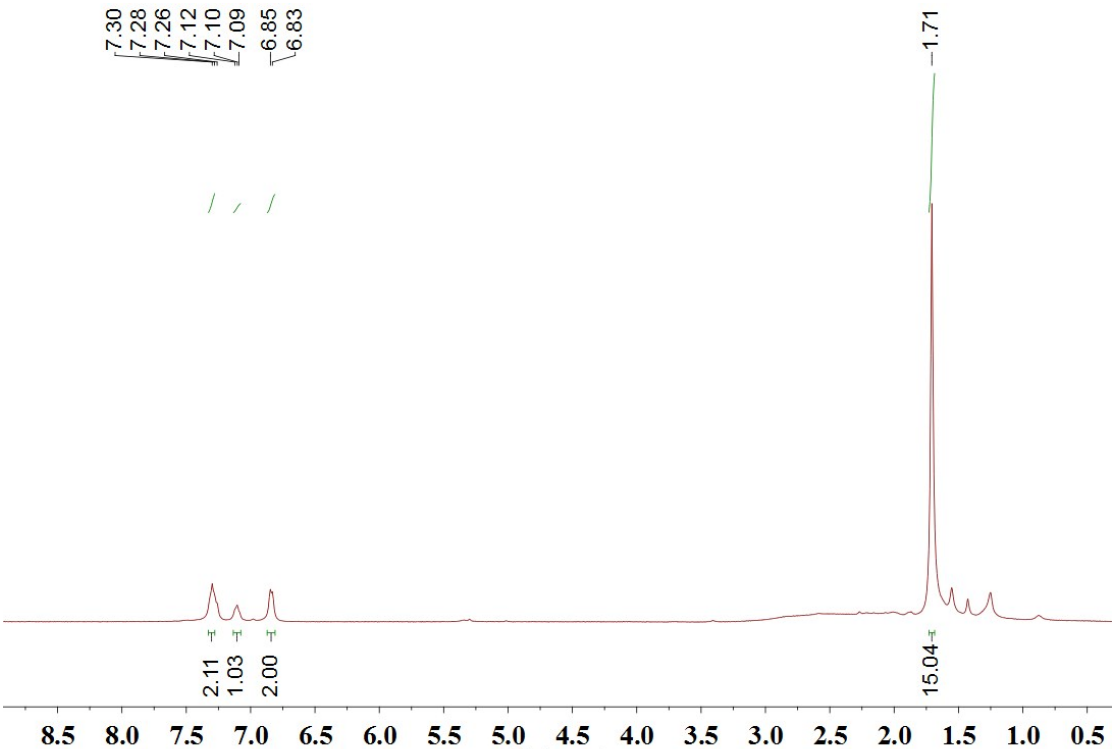


Figure S2. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **2**.

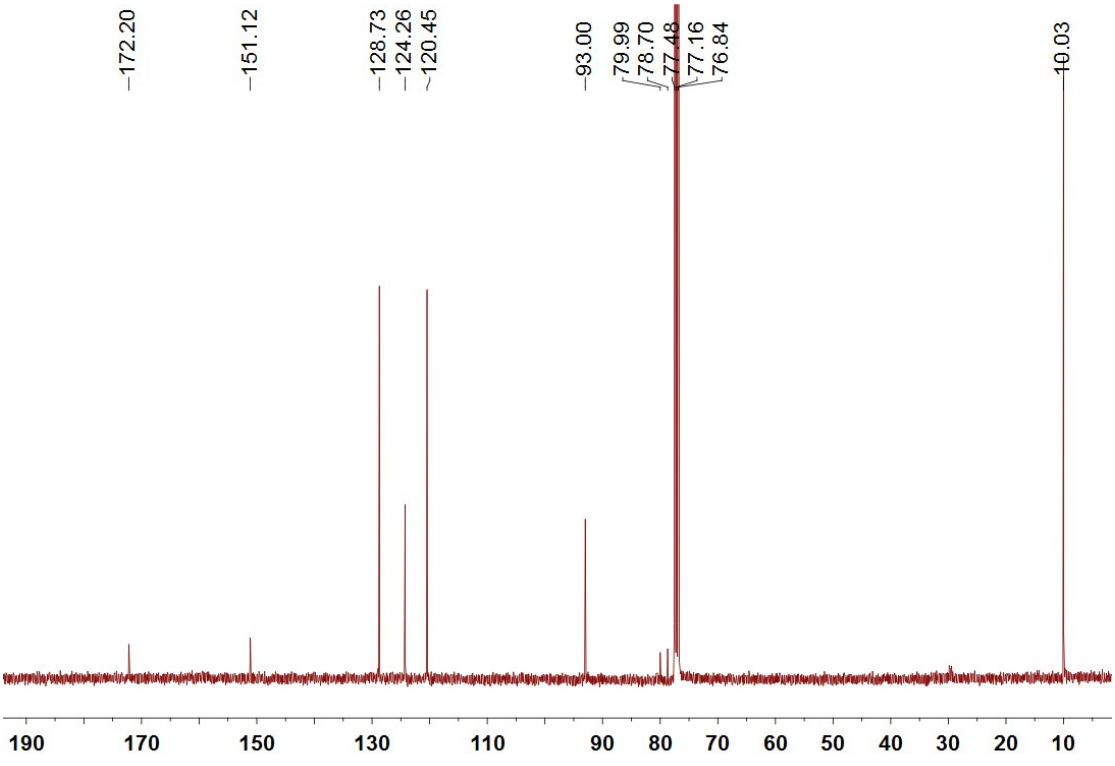


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **3.**

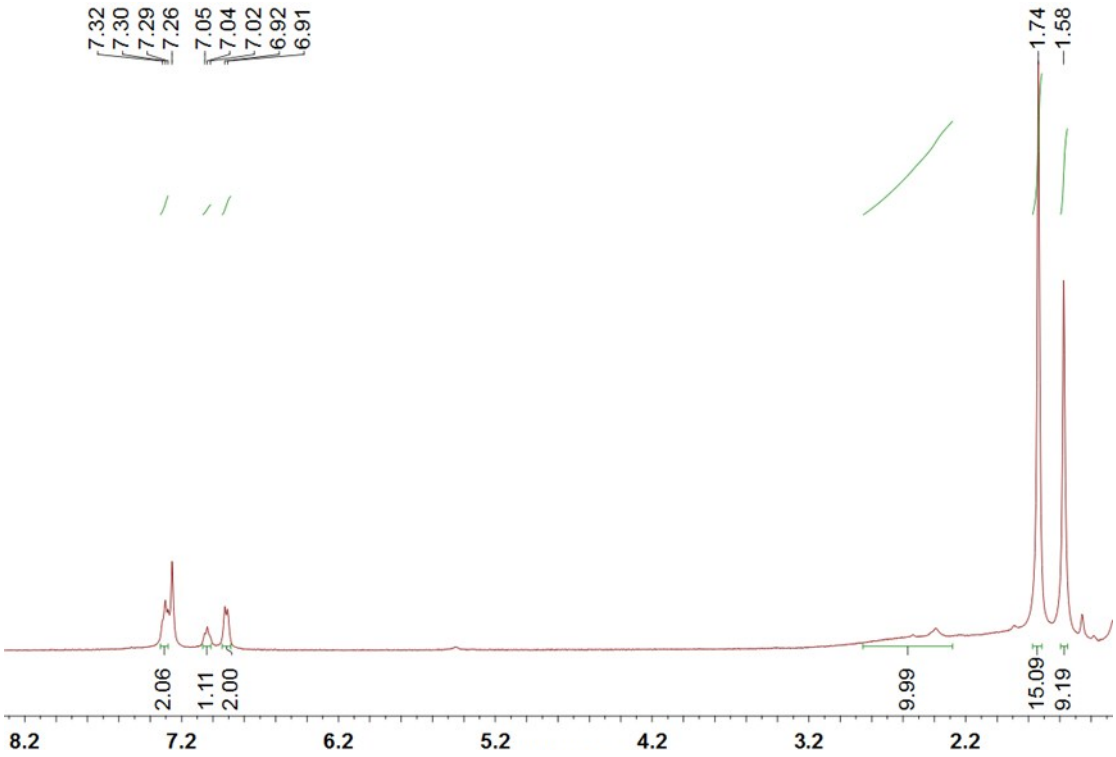


Figure S4. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **3**.

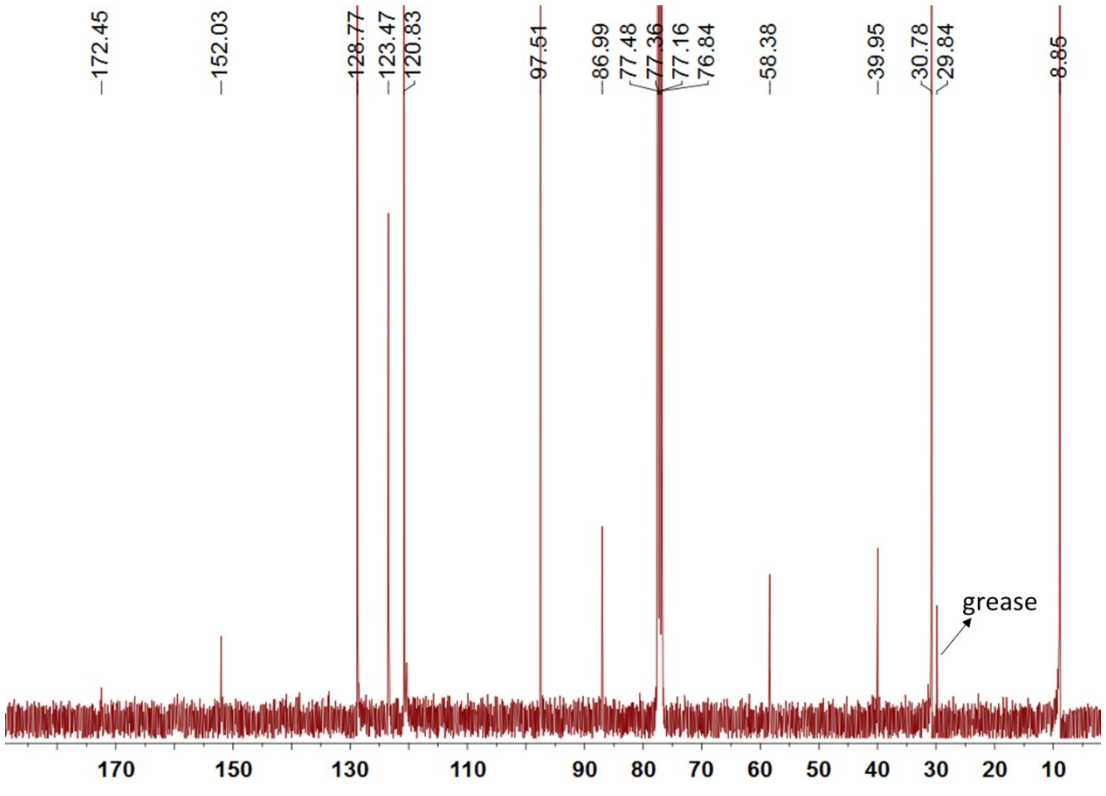


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **4**.

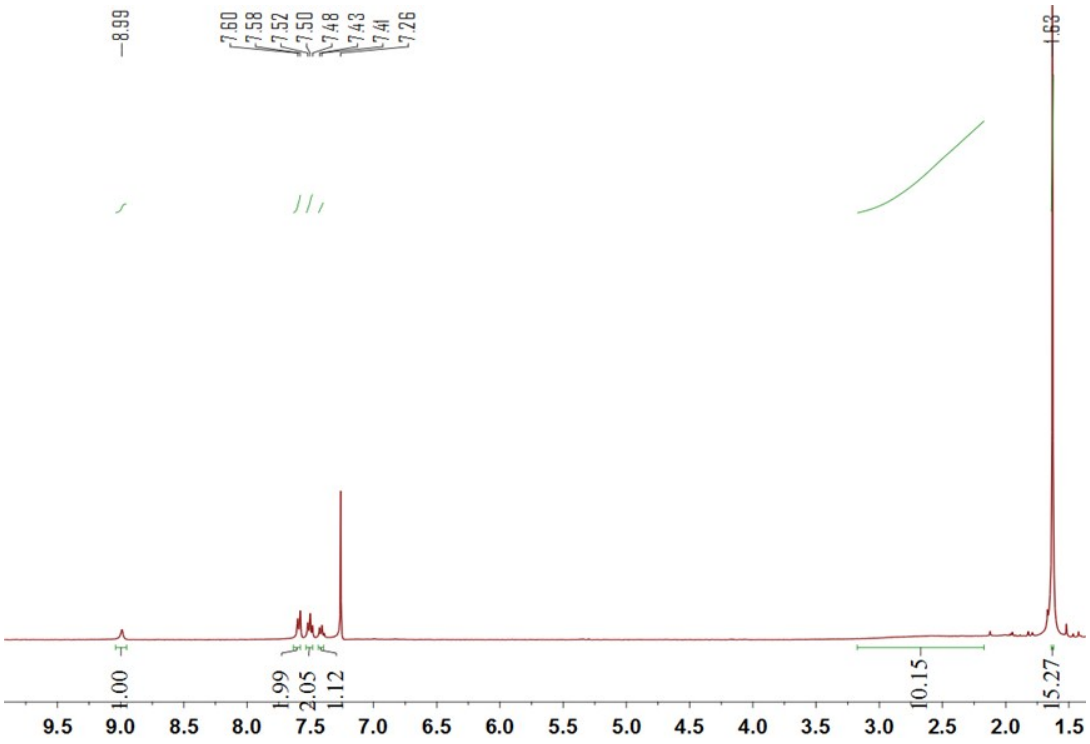


Figure S6. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **4**.

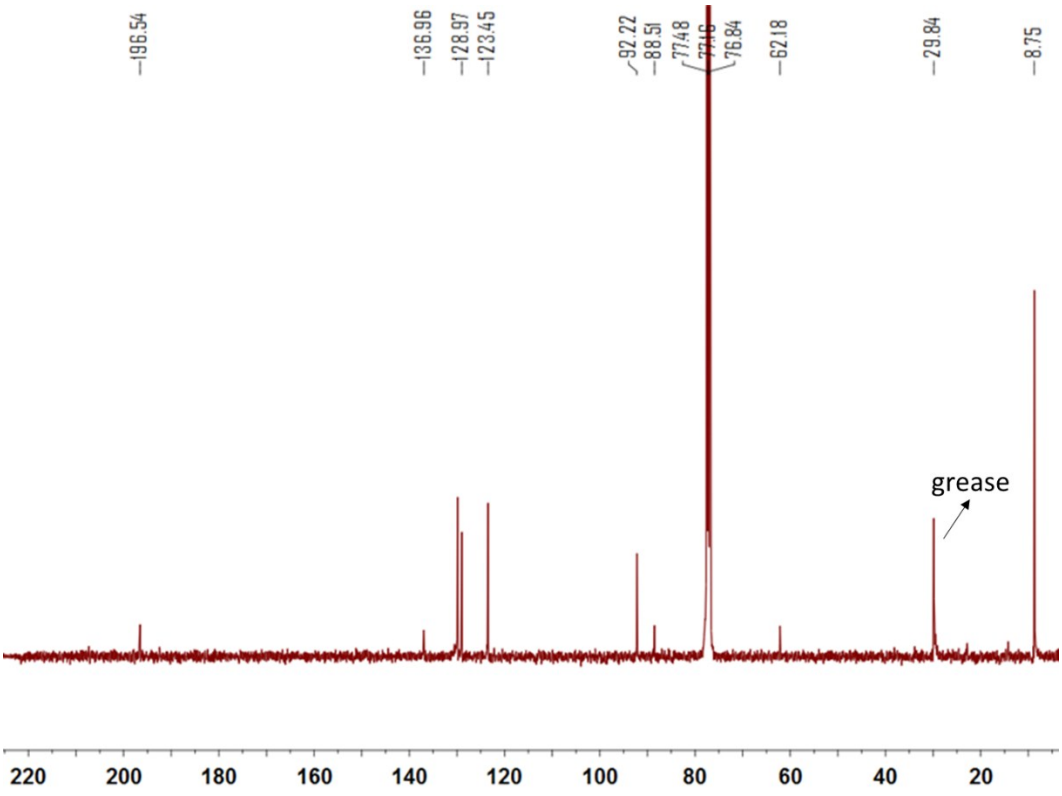


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **5**.

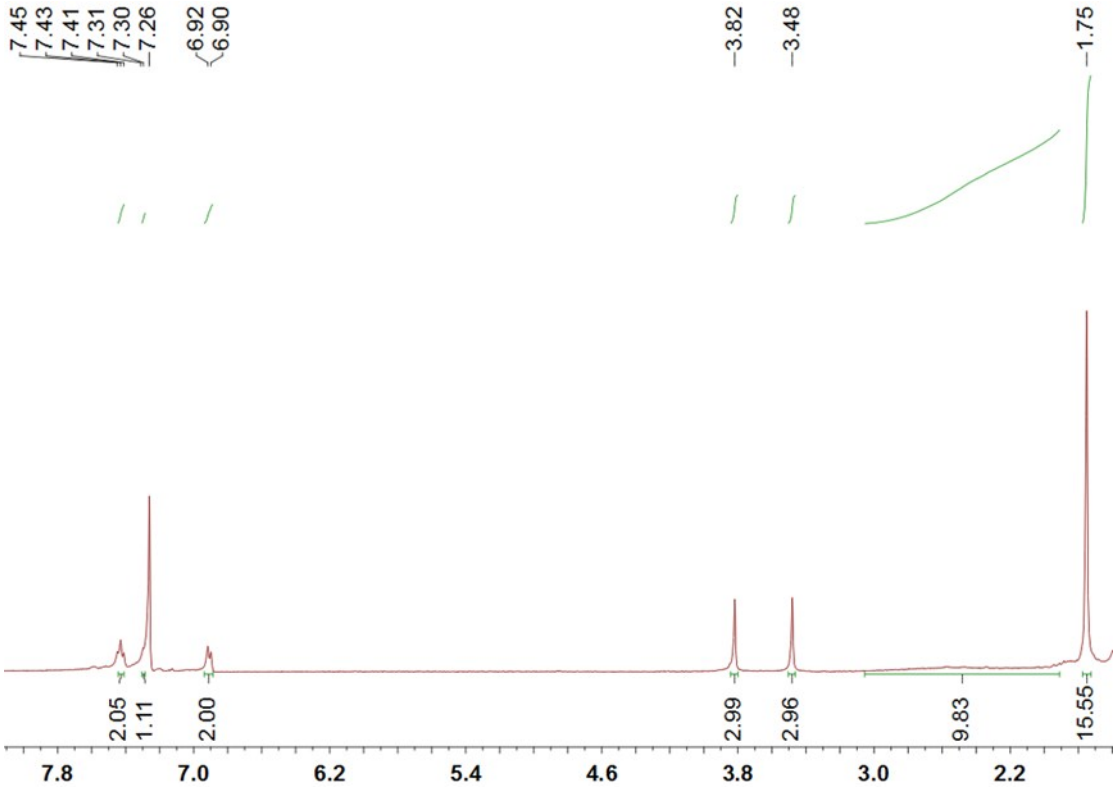


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **6**.

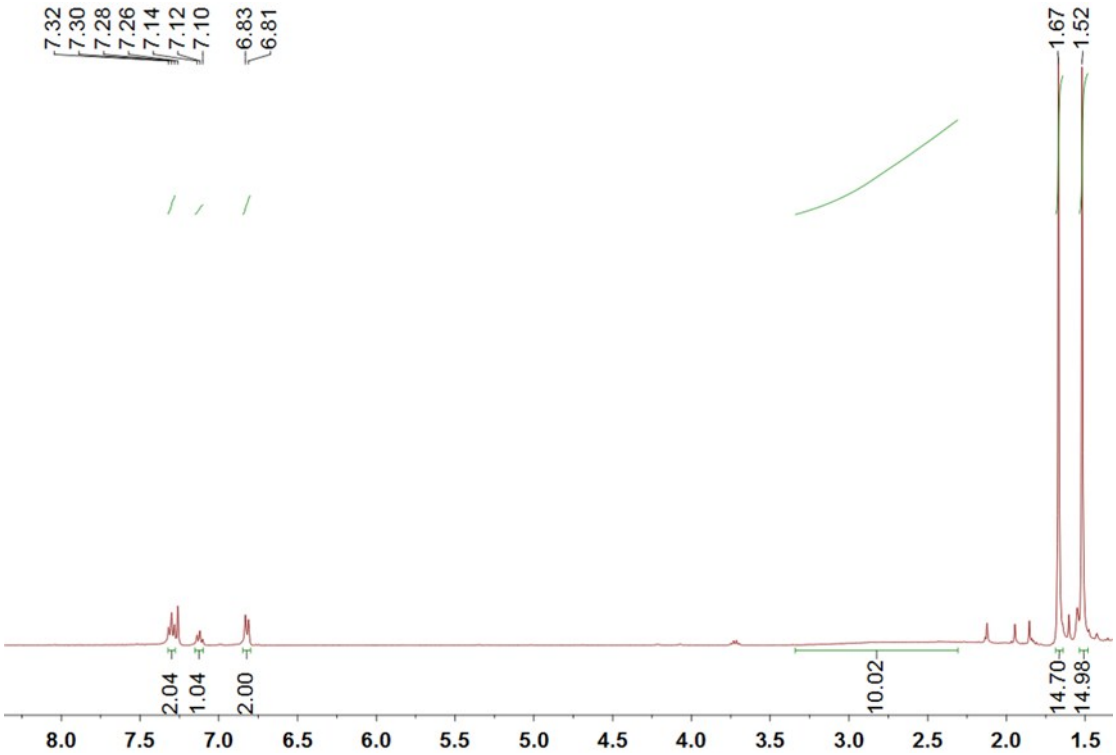


Figure S9. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **6**.

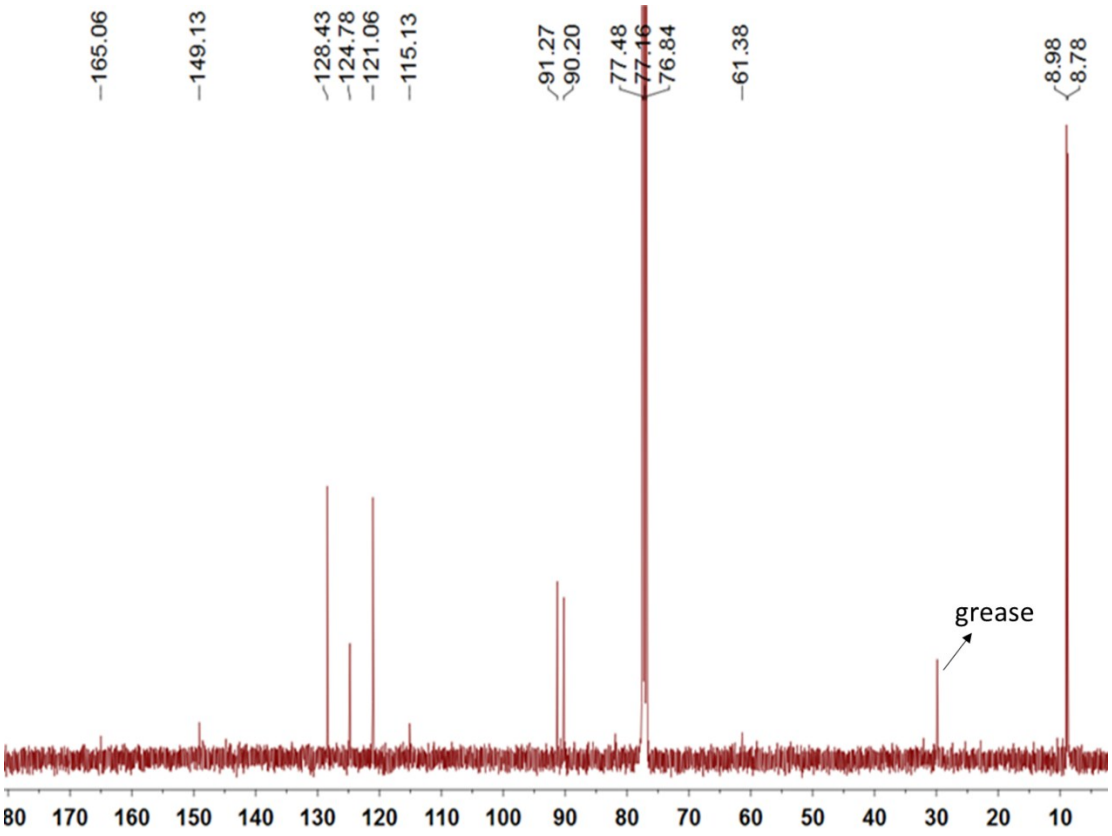


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of **7**.

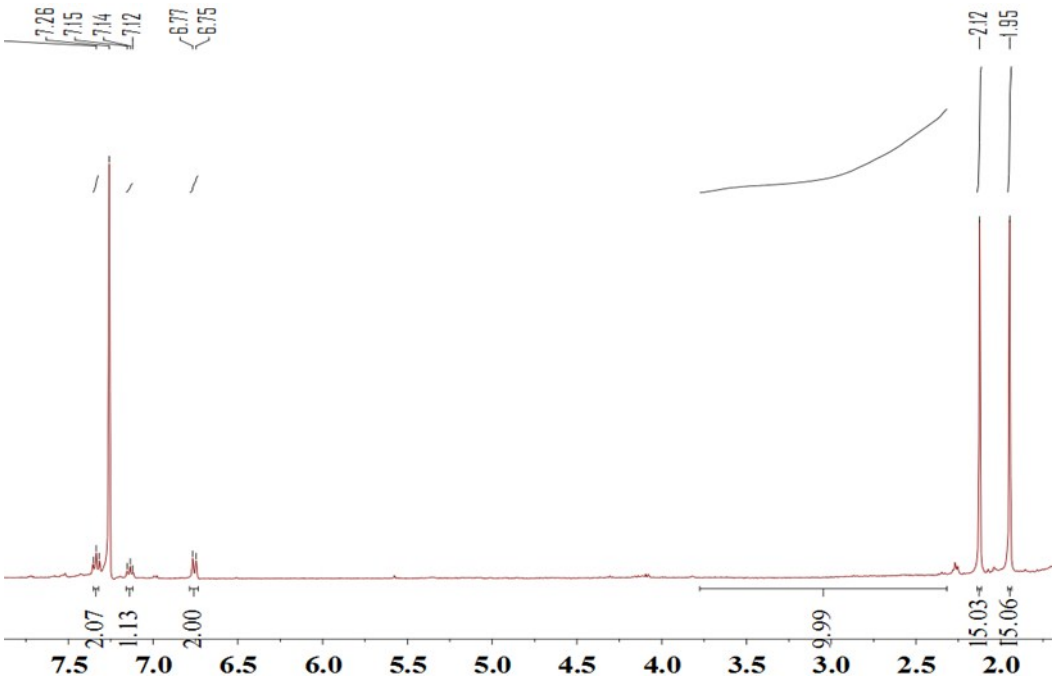


Figure S11. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **7**.

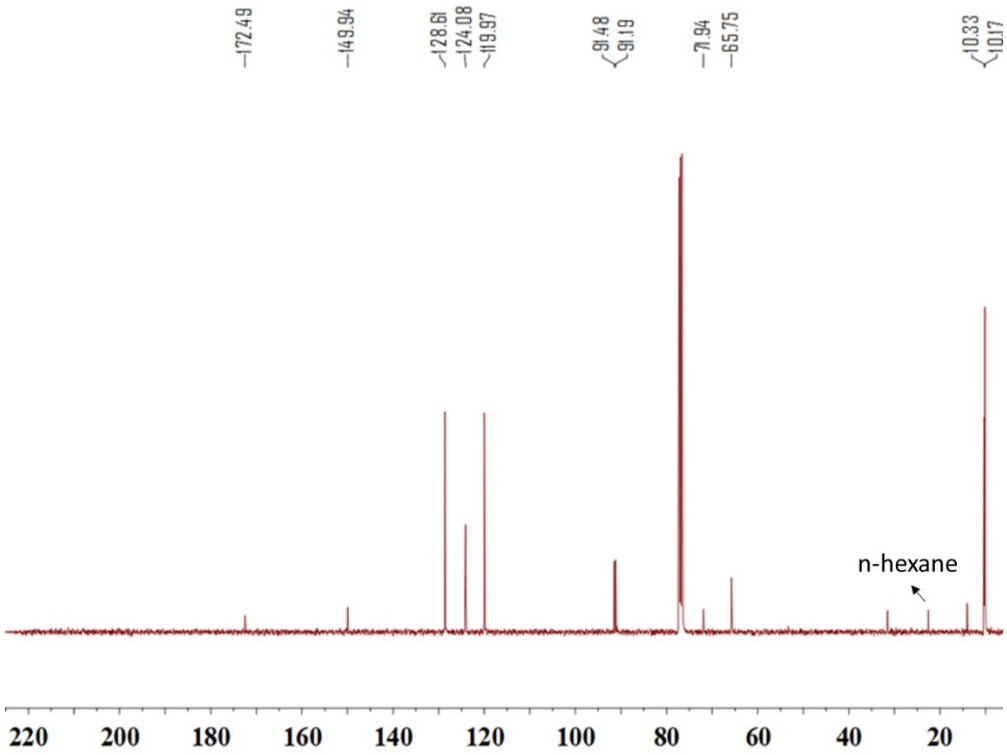


Figure S12. ^{11}H NMR (400 MHz, $CDCl_3$, ppm) of **8**.

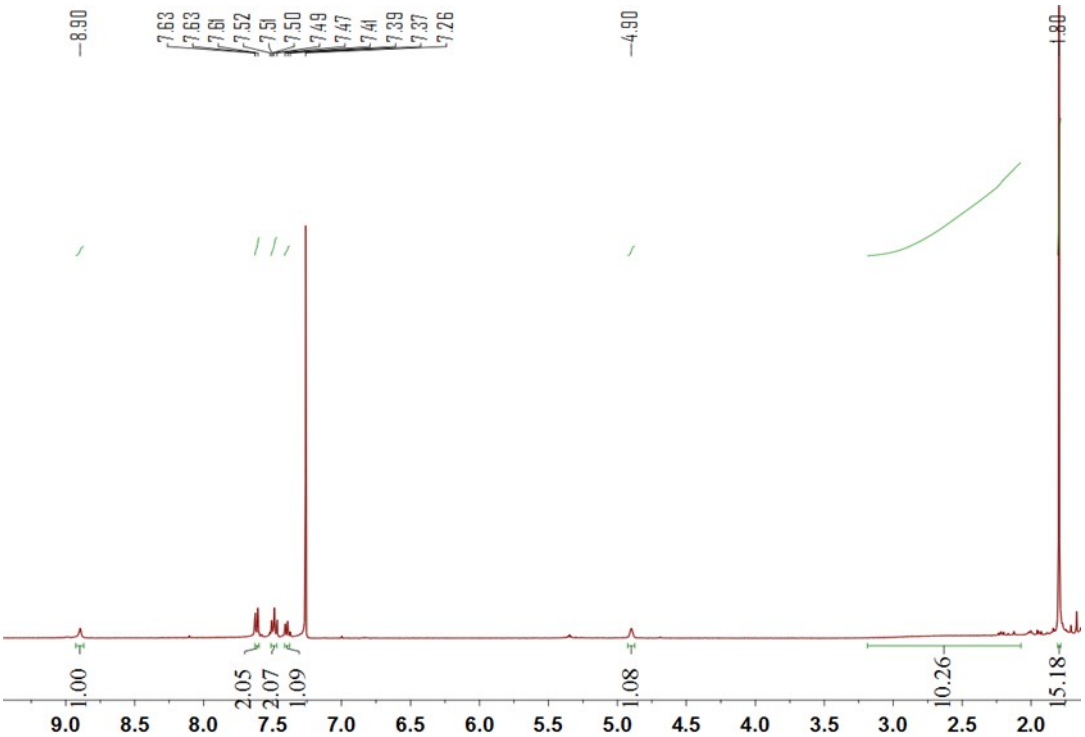
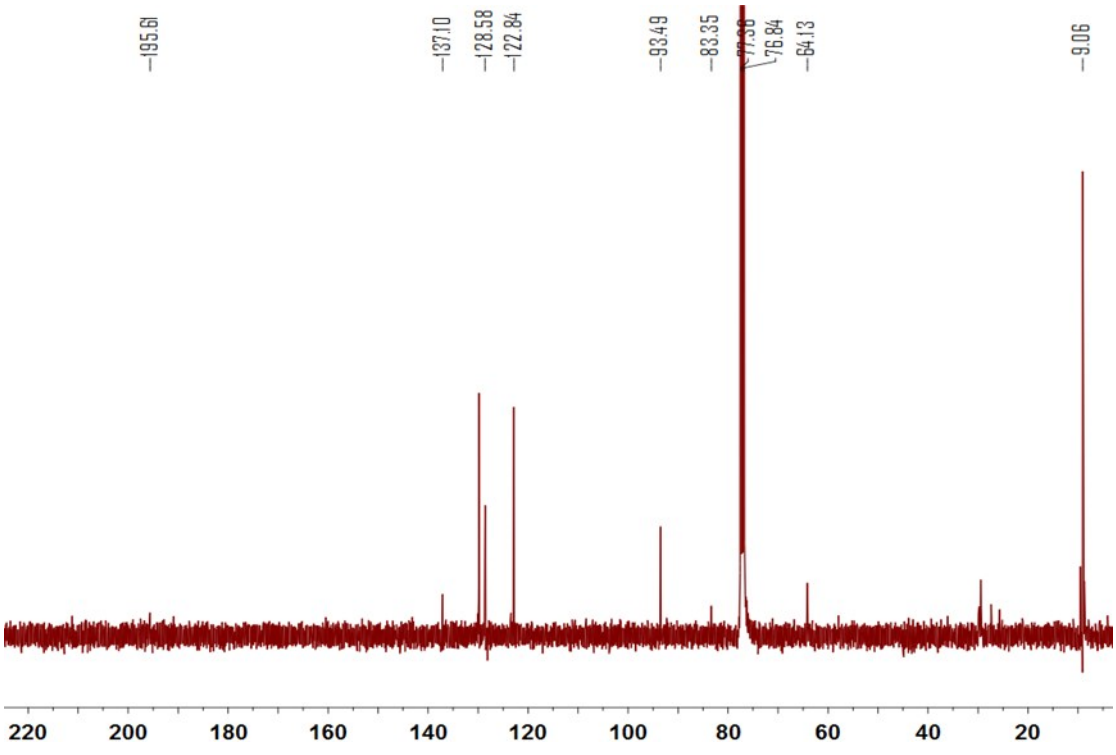


Figure S13. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, ppm) of **8**.



3. ESI-MS spectra

Figure S14. Experimental (top) and Theoretical (bottom) ESI-MS spectra of complex **2**.

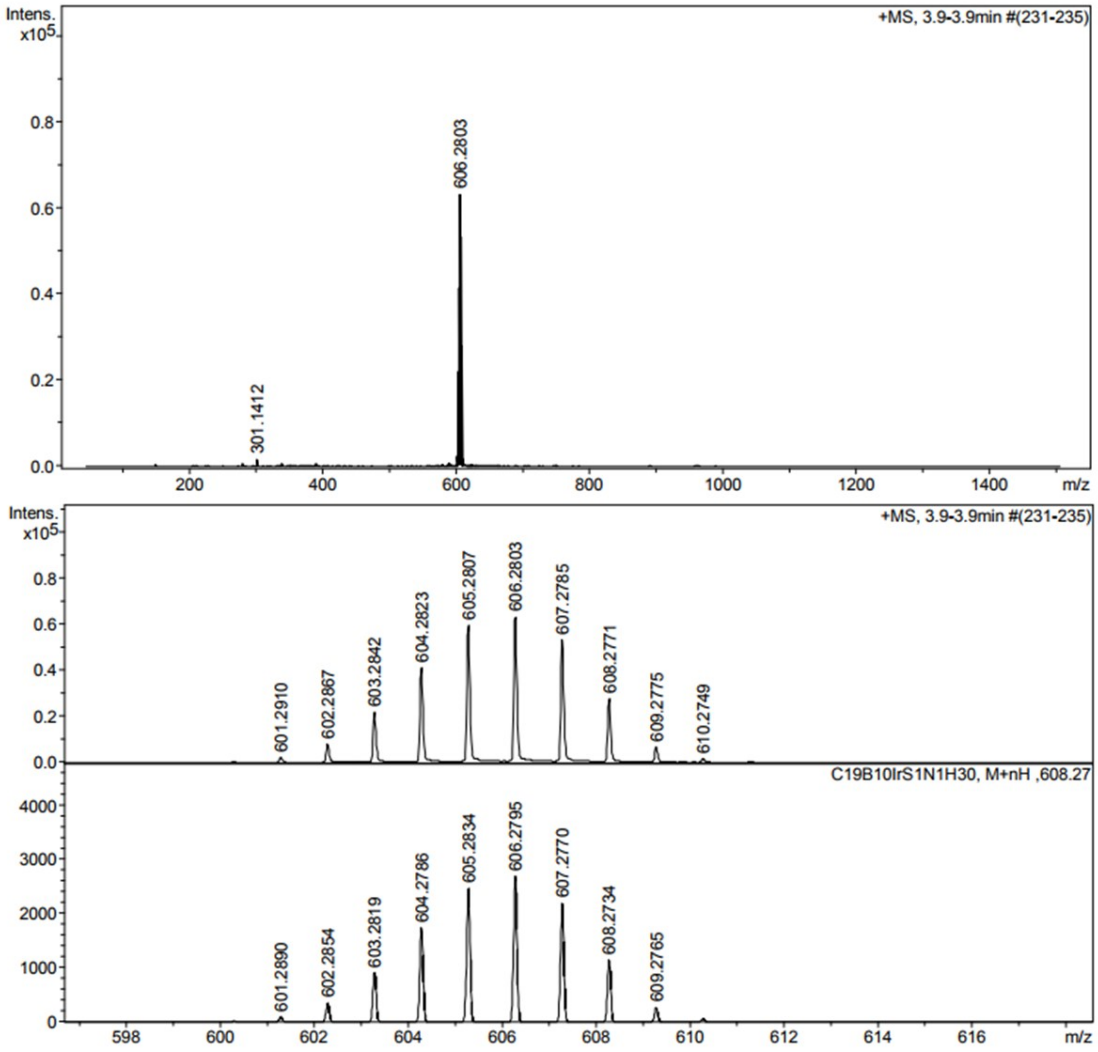


Figure S15. Experimental (top) and Theoretical (bottom) ESI-MS spectra of complex **3**.

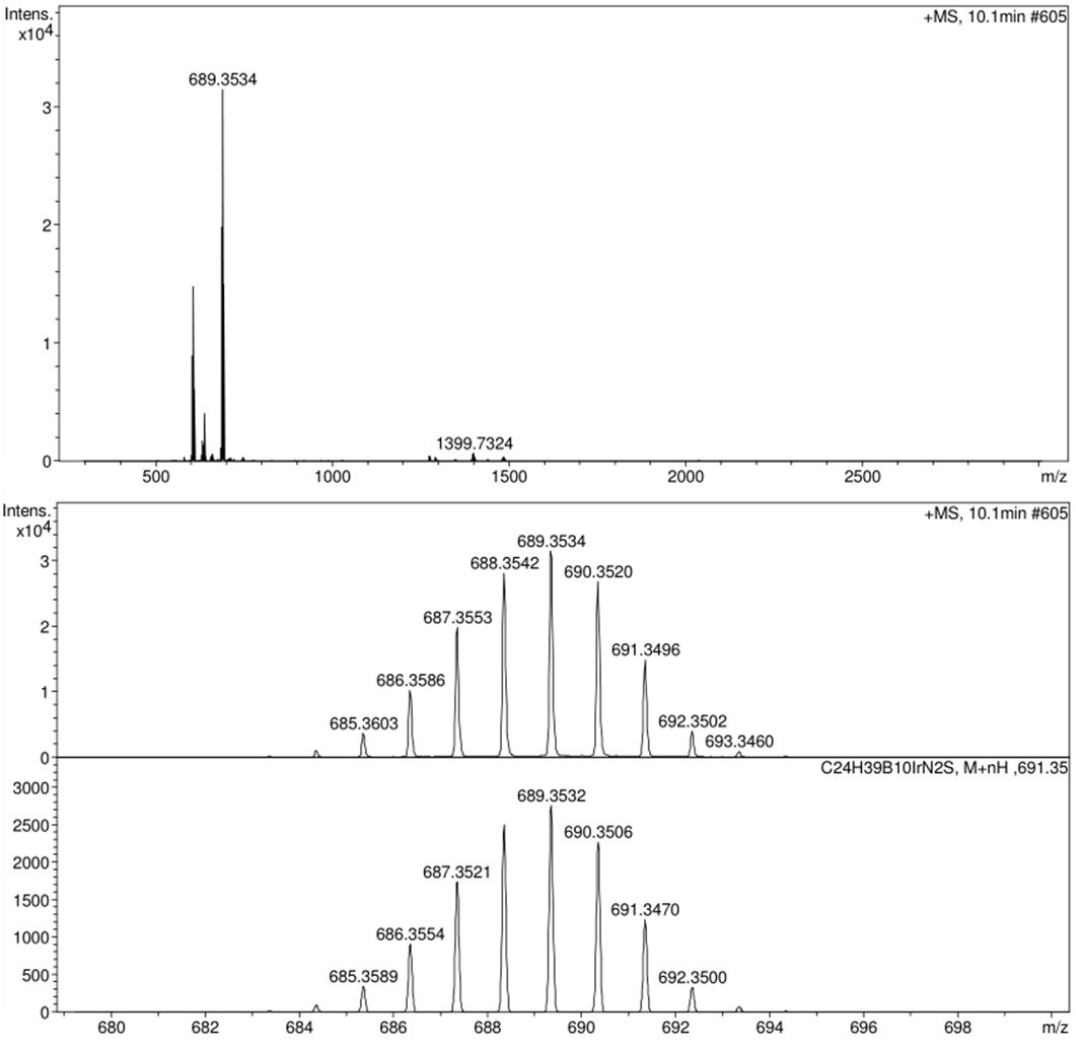


Figure S16. Experimental (top) and Theoretical (bottom) ESI-MS spectra of complex **5**.

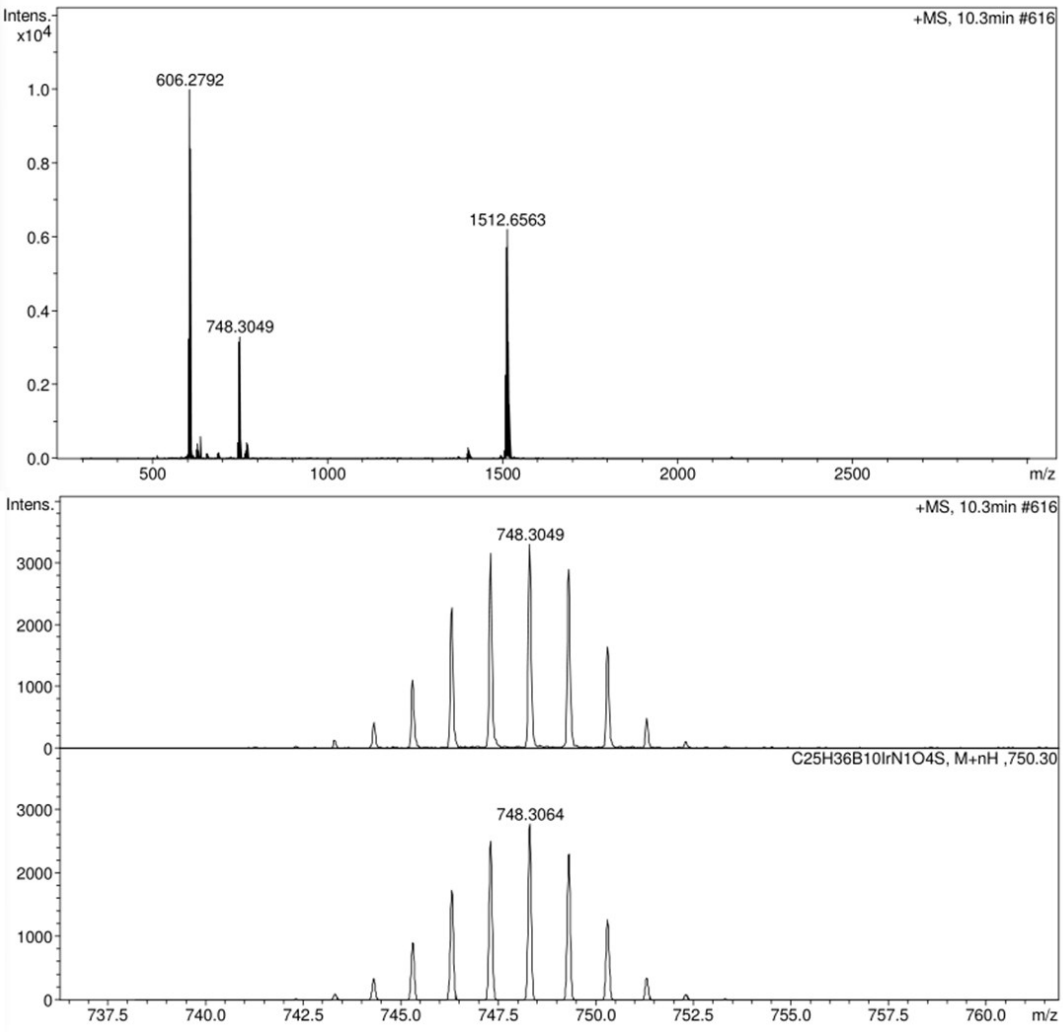
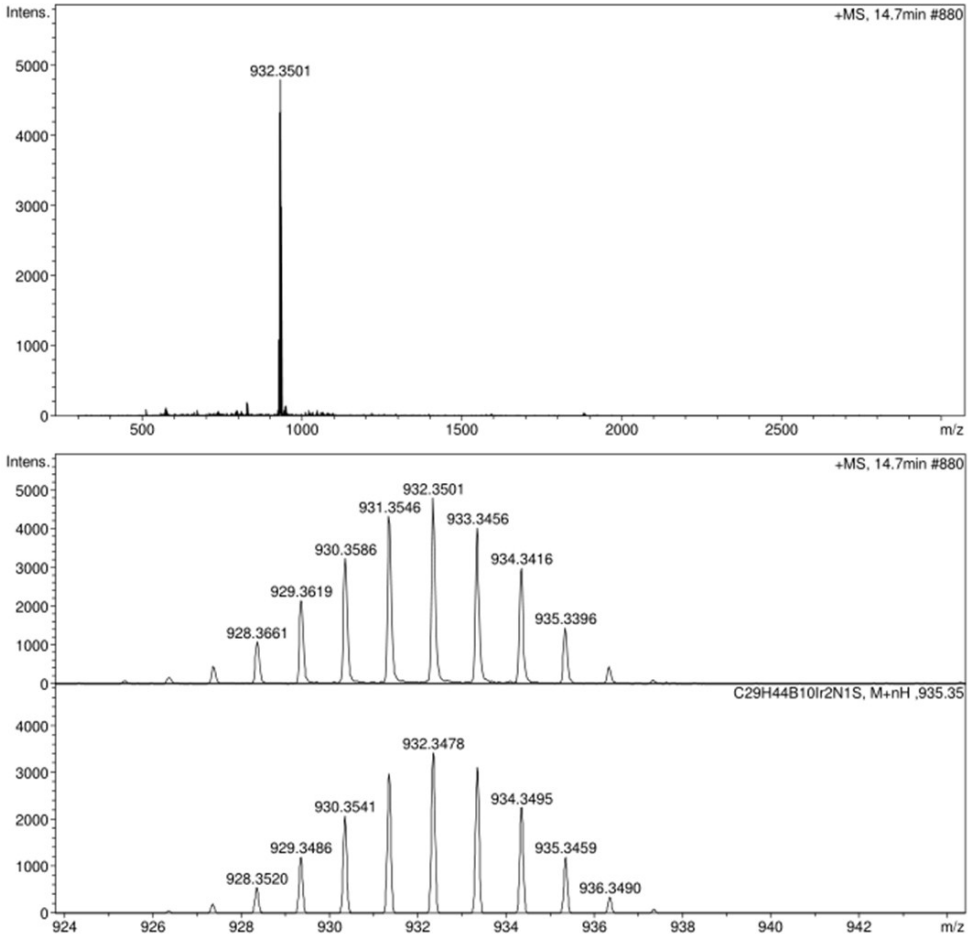


Figure S17. Experimental (top) and Theoretical (bottom) ESI-MS spectra of complex **6**.



4. X-ray crystallography details

X-ray crystallography details: Single crystals of **2**, **3**, **4**, **5**, **7** and **8** suitable for X-ray diffraction study were obtained at room temperature. X-ray intensity data were collected on a CCD-Bruker SMART APEX system.

In asymmetric unit of **2**, 9 ISOR instructions were used to restrain carborane ligand and Cp* fragment so that there were 54 restraints in the data.

In asymmetric unit of **4**, 6 ISOR instructions were used to restrain solvents and Cp* fragments so that there were 36 restraints in the data.

In asymmetric unit of **7**, one *n*-hexane molecule was strongly disordered and could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit it. 3 ISOR instructions were used to restrain Cp* fragments so that there were 19 restraints in the data.

Table S1. Crystal data for complexes **2**, **3** and **4**.

complex	2	3	4
Empirical formula	$C_{20}H_{32}B_{10}C_{l2}IrNS$	$C_{25}H_{40}B_{10}C_{l3}IrN_2S$	$C_{20}H_{32.5}B_{10}Cl_{3.5}IrNS$
Formula weight	689.72	807.30	743.40
Temperature	296(2) K	223(2) K	223(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	$P2_1/n$	P-1
a	9.883(5) Å	12.4951(19) Å	12.2564(10) Å
b	12.408(6) Å	13.980(2) Å	12.9860(11) Å
c	12.678(6) Å	20.222(3) Å	18.7275(15) Å
α	80.594(9)°	90 (3)°	96.0060(10)°
β	67.786(7)°	90.973(3)°	96.1970(10)°
γ	87.367(8)°	90 (3)°	98.6200(10)°
Volume	1419.8(11) $Å^3$	3532.0(9) $Å^3$	2907.6(4) $Å^3$
Z	2	4	4
Density (calculated)	1.613 Mg/m^3	1.518 Mg/m^3	1.698 Mg/m^3
Absorption coefficient	4.976 mm^{-1}	4.086 mm^{-1}	4.999 mm^{-1}
F(000)	672	1592	1448
Crystal size (mm^3)	0.120x0.110x0.100	0.470x0.410x0.350	0.130x0.100x0.090
Theta range for data collection	1.757 to 25.998°.	1.771 to 26.992°.	2.050 to 27.493°
Index ranges	-12<=h<=11, -15<=k<=14, -15<=l<=14	-14<=h<=15, -17<=k<=17, -25<=l<=25	-15<=h<=9, -16<=k<=16, -24<=l<=24
Reflections collected	9338	24085	21412
Independent reflections	5489 [R(int) = 0.0619]	7661 [R(int) = 0.0515]	13102 [R(int) = 0.0409]
Data / restraints / parameters	5489 / 54 / 320	7661 / 13 / 391	13102 / 36 / 667
Goodness-of-fit on F^2	1.004	1.062	1.039
Final R indices [I>2sigma(I)][a]	R1 = 0.0573, wR2 = 0.1115	R1 = 0.0352, wR2 = 0.0953	R1 = 0.0465, wR2 = 0.1057
R indices (all data)	R1 = 0.1164, wR2 = 0.1459	R1 = 0.0543, wR2 = 0.1079	R1 = 0.0874, wR2 = 0.1394

[a] $R1=\sum||F_a| - |F_c||/\sum|F_a|$; $wR_2 = [\sum w(|F_a^2| - |F_a^2|)^2/\sum w|F_a^2|2]^{1/2}$

Table S2. Crystal data for complexes **5**, **7** and **8**.

complex	5	7	8
Empirical formula	$C_{25}H_{36}B_{10}IrNO_4S$	$C_{35}H_{58}B_{10}NRh_2S$	$C_{20}H_{33}B_{10}Cl_3IrNS$
Formula weight	746.91	838.80	726.18
Temperature	173(2) K	296(2) K	173(2) K
Wavelength	1.54178 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$Cmc2_1$	$P2_1/c$
a	10.0392(2) Å	12.9711(17) Å	12.2270(15) Å
b	12.9768(2) Å	24.739(4) Å	26.087(3) Å
c	24.0642(5) Å	24.982(3) Å	9.7410(12) Å
α	90°	90°	90°
β	90°	90°	109.654(2)°
γ	90°	90°	90°
Volume	3135.00(10) $Å^3$	8017(2) $Å^3$	2926.1(6) $Å^3$
Z	4	8	4
Density (calculated)	1.582 Mg/m^3	1.390 Mg/m^3	1.648 Mg/m^3
Absorption coefficient	9.116 mm^{-1}	0.902 mm^{-1}	4.922 mm^{-1}
F(000)	1472	3448	1416
Crystal size (mm^3)	0.180x0.150x0.130	0.250x0.220x0.180	0.230x0.210x0.190
Theta range for data collection	3.870 to 70.023°	1.630 to 27.504°	1.561 to 27.388°
Index ranges	-12<=h<=10, -15<=k<=13, -28<=l<=15	-16<=h<=16, -32<=k<=32, -32<=l<=26	-15<=h<=12, -33<=k<=32, -12<=l<=12
Reflections collected	13147	23445	20620
Independent reflections	5545 [R(int) = 0.0235]	8402 [R(int) = 0.0584]	6589 [R(int) = 0.0653]
Data / restraints / parameters	5545 / 0 / 386	8402 / 19 / 426	6589 / 7 / 337
Goodness-of-fit on F^2	1.112	1.008	1.100
Final R indices [I>2sigma(I)]	R1 = 0.0183, wR2 = 0.0411	R1 = 0.0498, wR2 = 0.1209	R1 = 0.0434, wR2 = 0.0930
R indices (all data)	R1 = 0.0194, wR2 = 0.0423	R1 = 0.011, wR2 = 0.1490	R1 = 0.0730, wR2 = 0.1020

[a] $R1=\sum||F_a| - |F_c||/\sum|F_a|$; $wR_2 = [\sum w(|F_a^2| - |F_a^2|)^2/\sum w|F_a^2|2]^{1/2}$

Figure S18. Molecular of complex **2** (left) and complex **3** (right) with 30% probability ellipsoids. Color code: Ir, red; S, yellow; N, blue; C, black; B, grey.

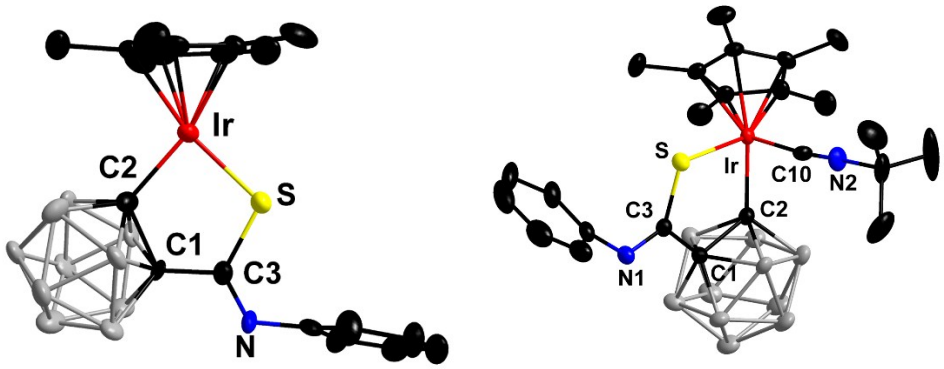


Figure S19. Molecular of complex **4** (left) and complex **5** (right) with 30% probability ellipsoids. Color code: Ir, red; S, yellow; N, blue; C, black; B, grey; Cl, green; O, orange.

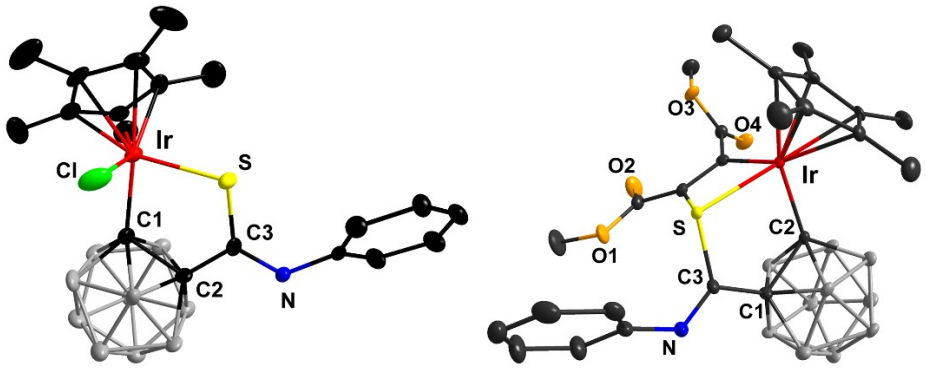
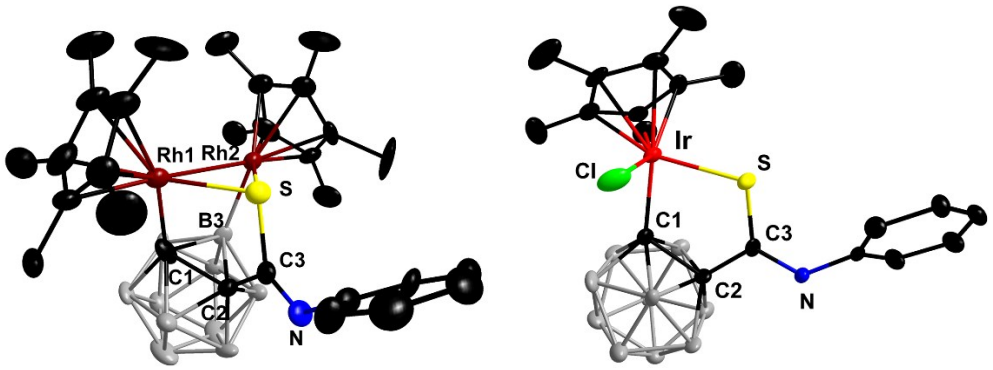


Figure S20. Molecular of complex **7** (left) and complex **8** (right) with 30% probability ellipsoids. Color code: Ir, red; Rh, dark red; S, yellow; N, blue; C, black; B, grey; Cl, green.



5. References

1. C. White, A. Yates, P. M. Maitles, *Inorg. Synth.* 1992, **29**, 228-234.
2. (a) B. Xu, Y.-P. Wang, Z.-J. Yao and G.-X. Jin, *Dalton Trans.* 2015, **44**, 1530-1533; (b) Y.-P. Wang, L. Zhang, Y.-J. Lin, Z.-H. Li and G.-X. Jin, *Chem.- Eur. J.* 2017, **23**, 1814–1819.