Supporting Information

Reactivity of cyclopentadienyl transition metal(II) complexes with borate ligands: structural characterization of the toluene-activated molybdenum complex [Cp*Mo(CO)$_2$(η^3-CH$_2$C$_6$H$_5$)]

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I Spectroscopic details

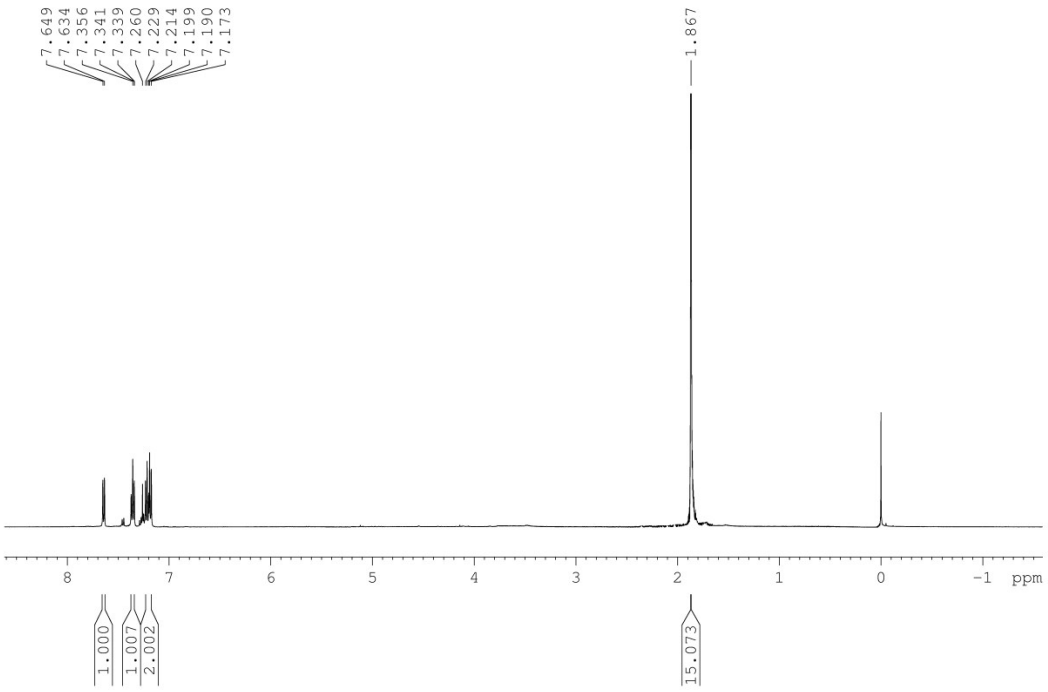


Fig. S1. ^{1}H NMR spectrum of **3** (500 MHz)

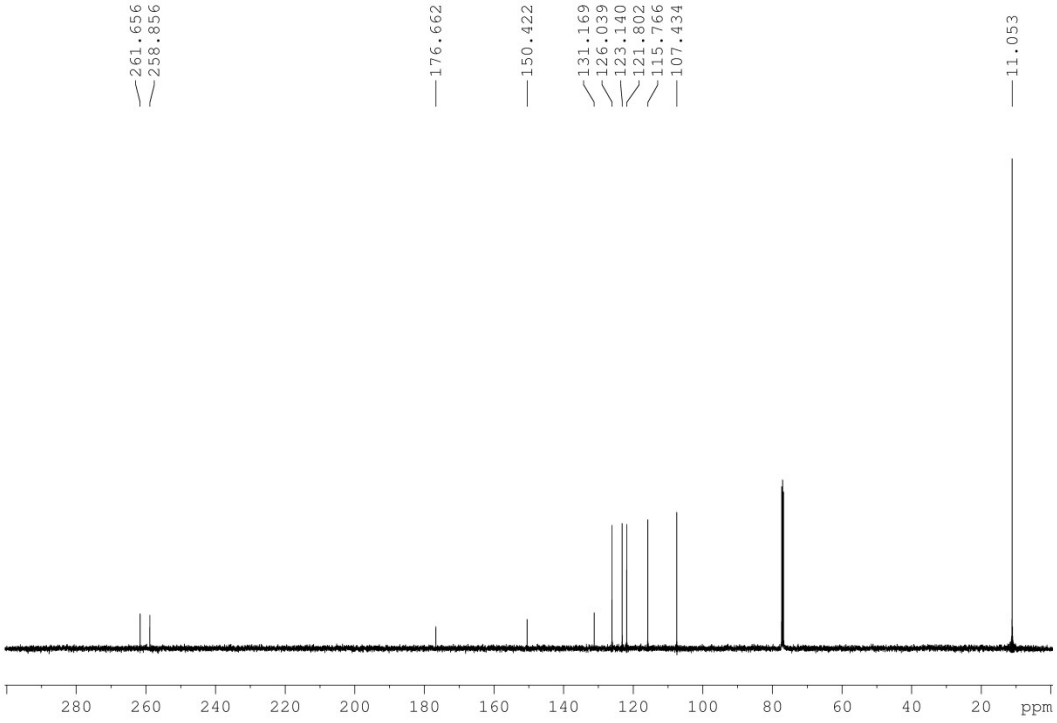


Fig. S2. ^{13}C{^{1}H} NMR spectrum of **3** (125 MHz)

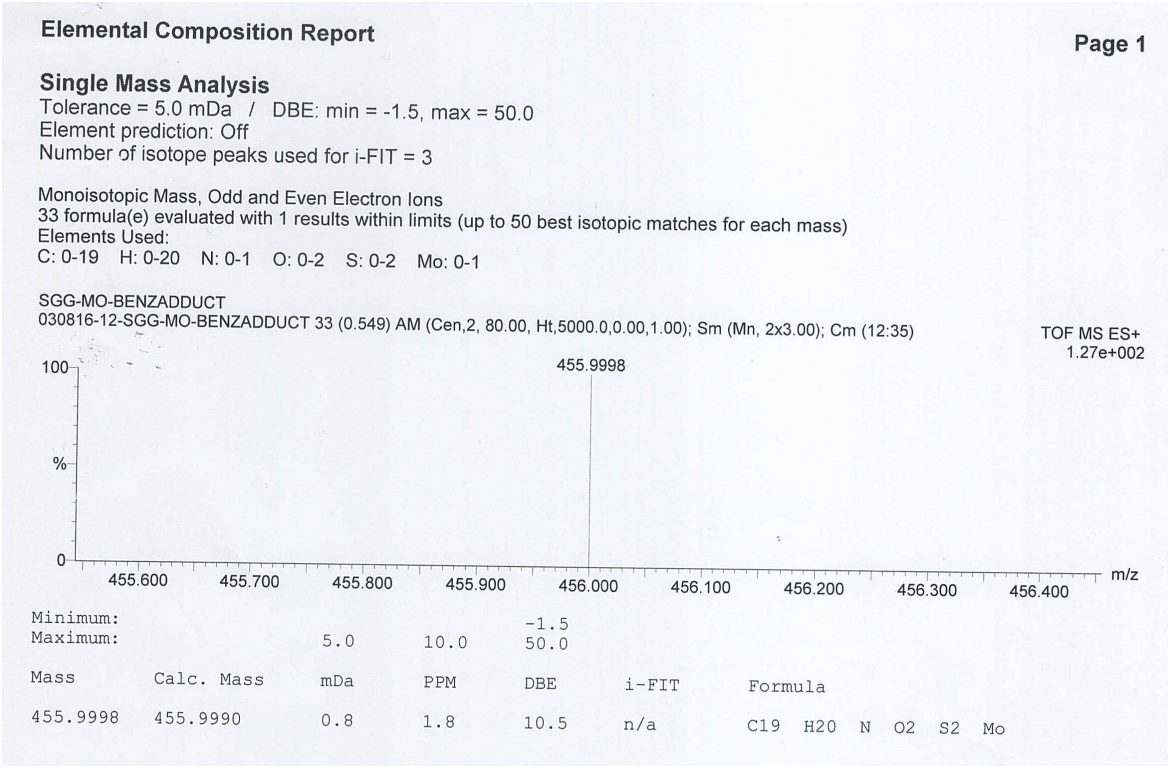


Fig. S3. HRMS spectrum of **3**

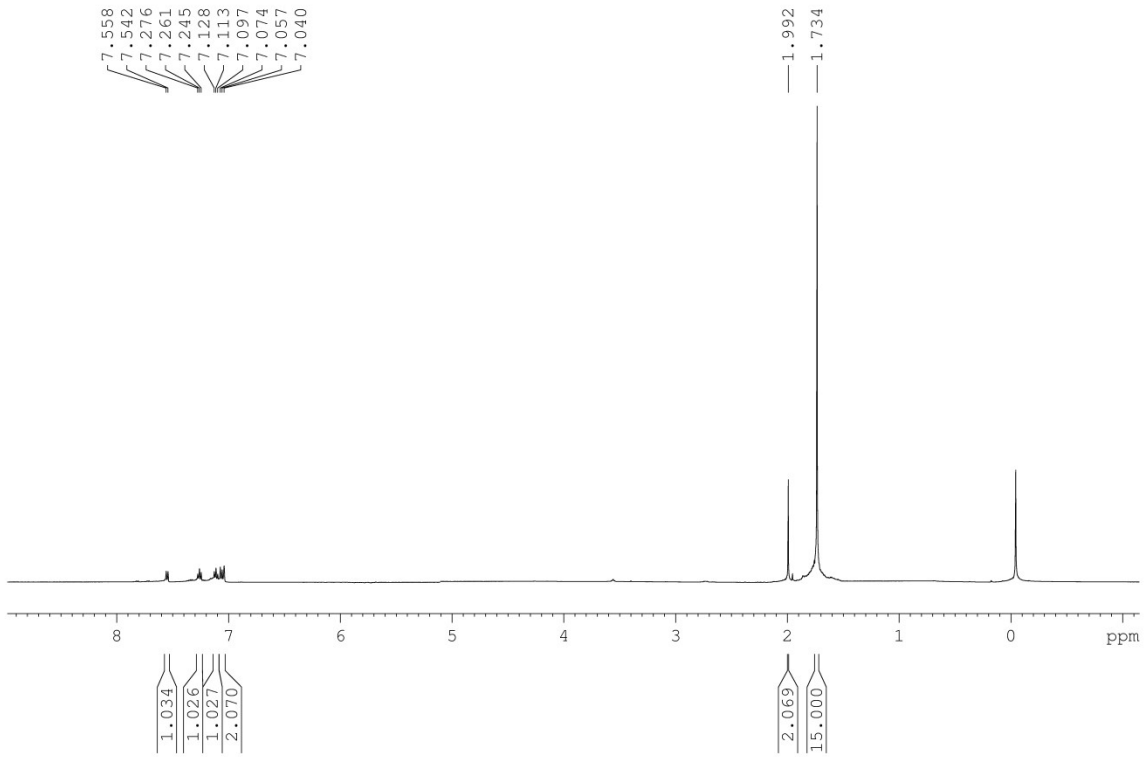


Fig. S4. ^{1}H NMR spectrum of **4** (500 MHz)

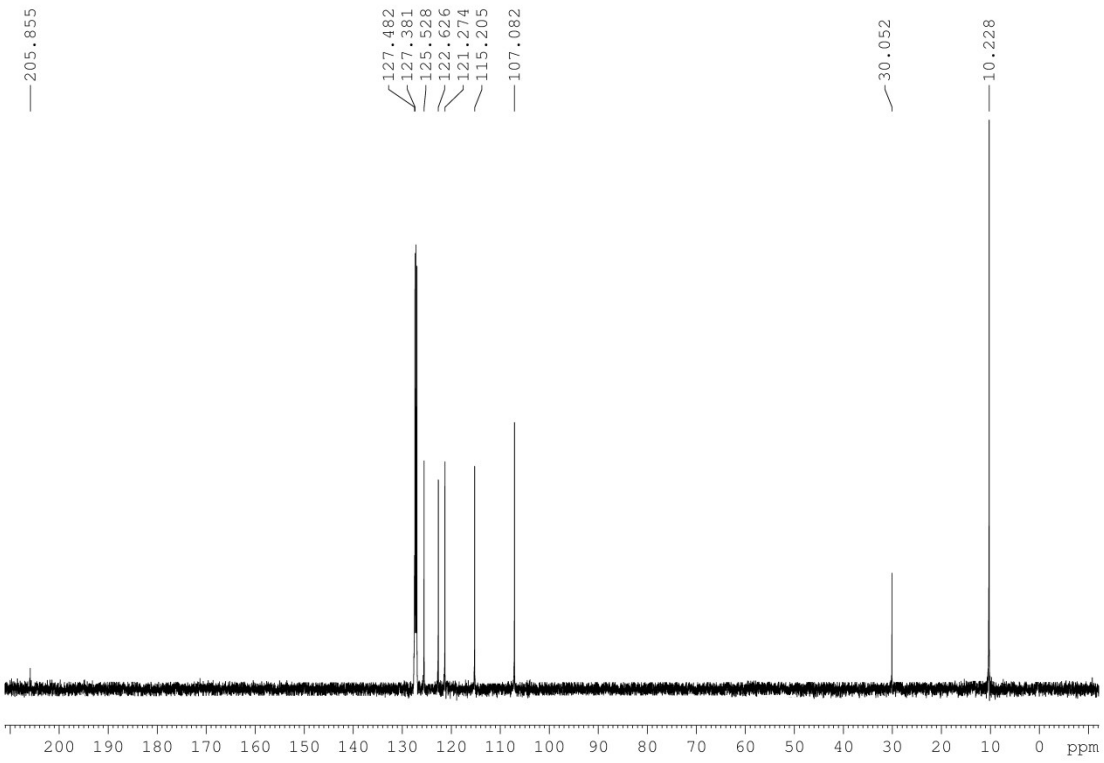


Fig. S5. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (125 MHz)

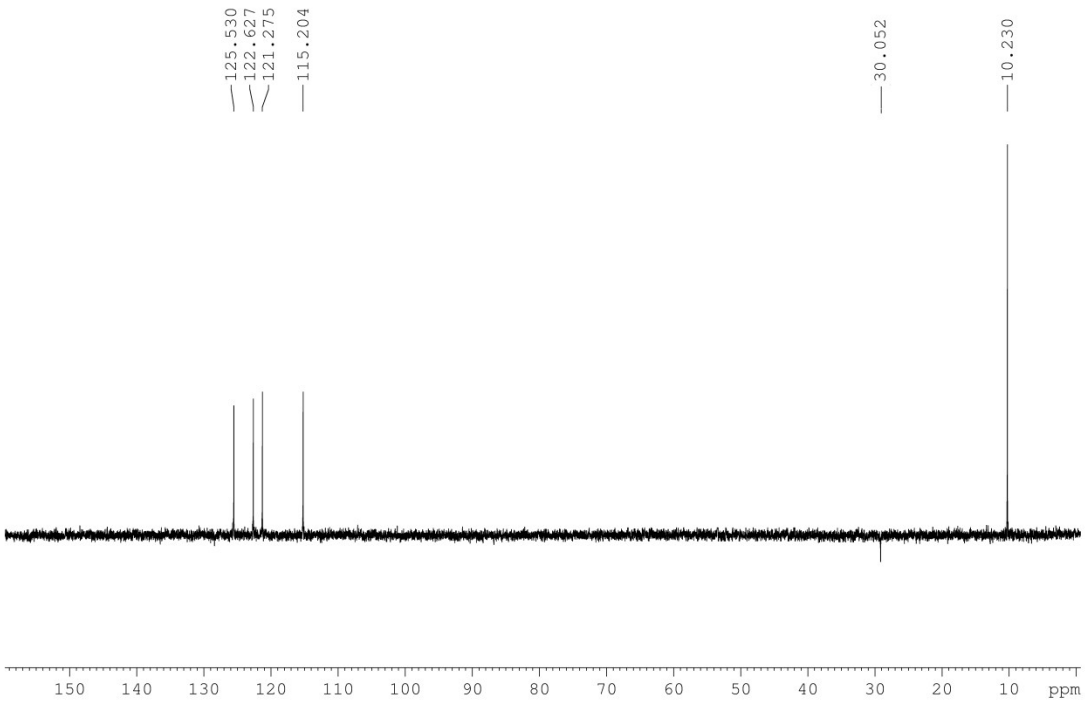


Fig. S6. ^{13}C DEPT NMR spectrum of **4** (125 MHz)

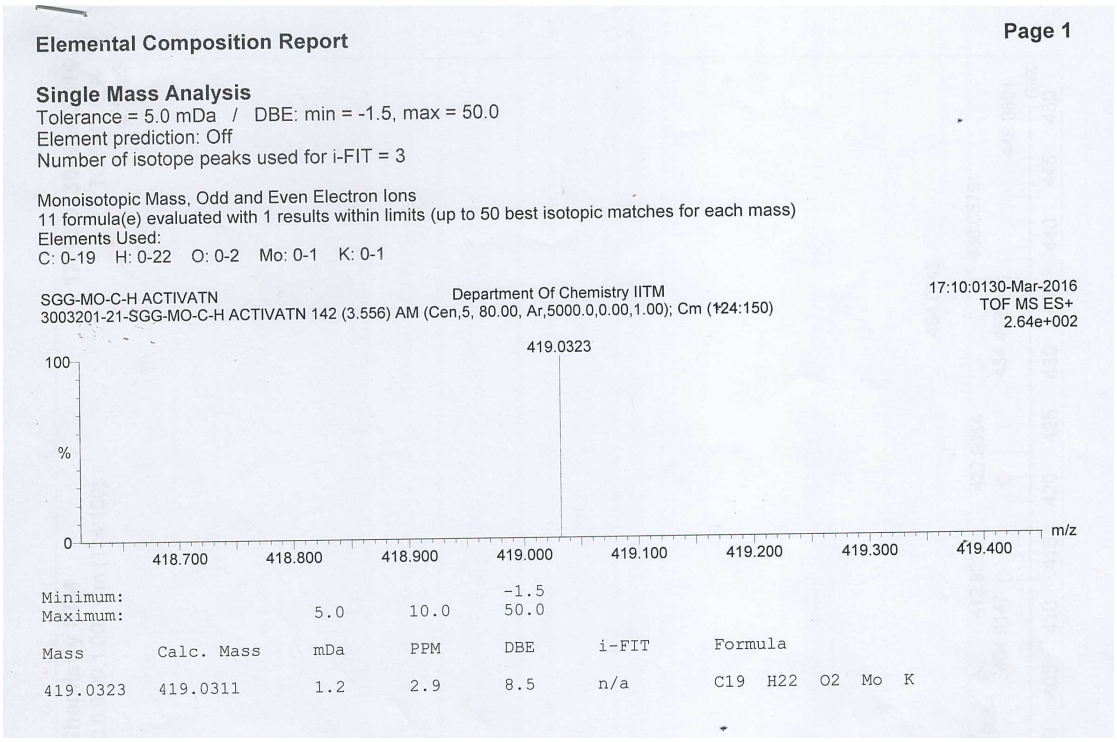


Fig. S7. HRMS spectrum of **4**

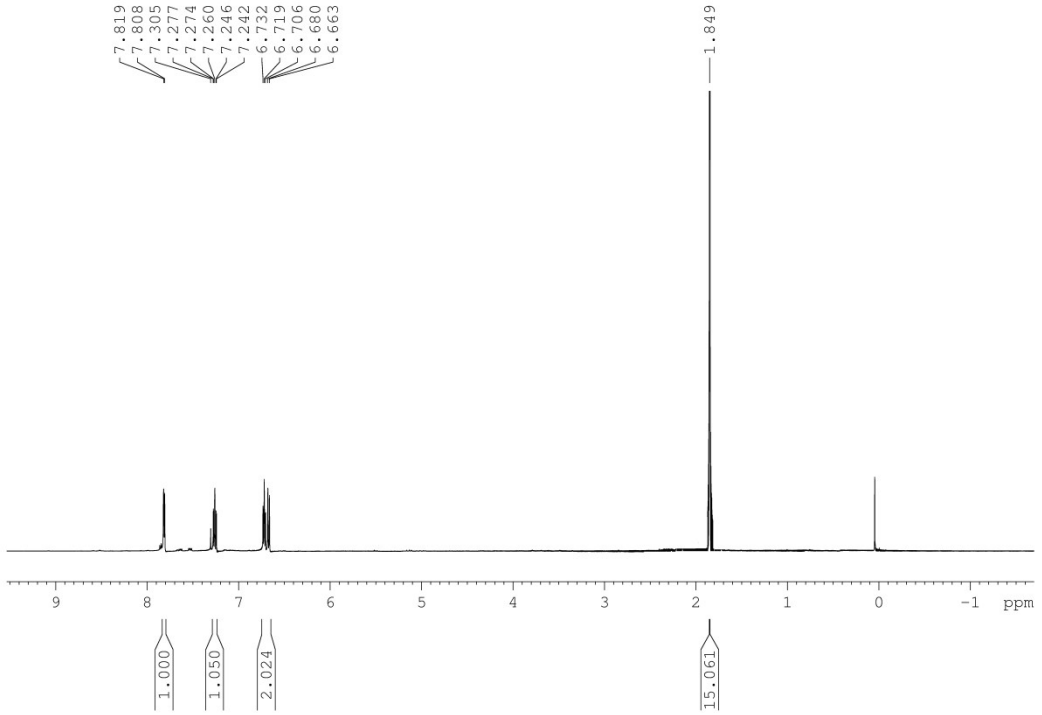


Fig. S8. ^{1}H NMR spectrum of **5** (500 MHz)

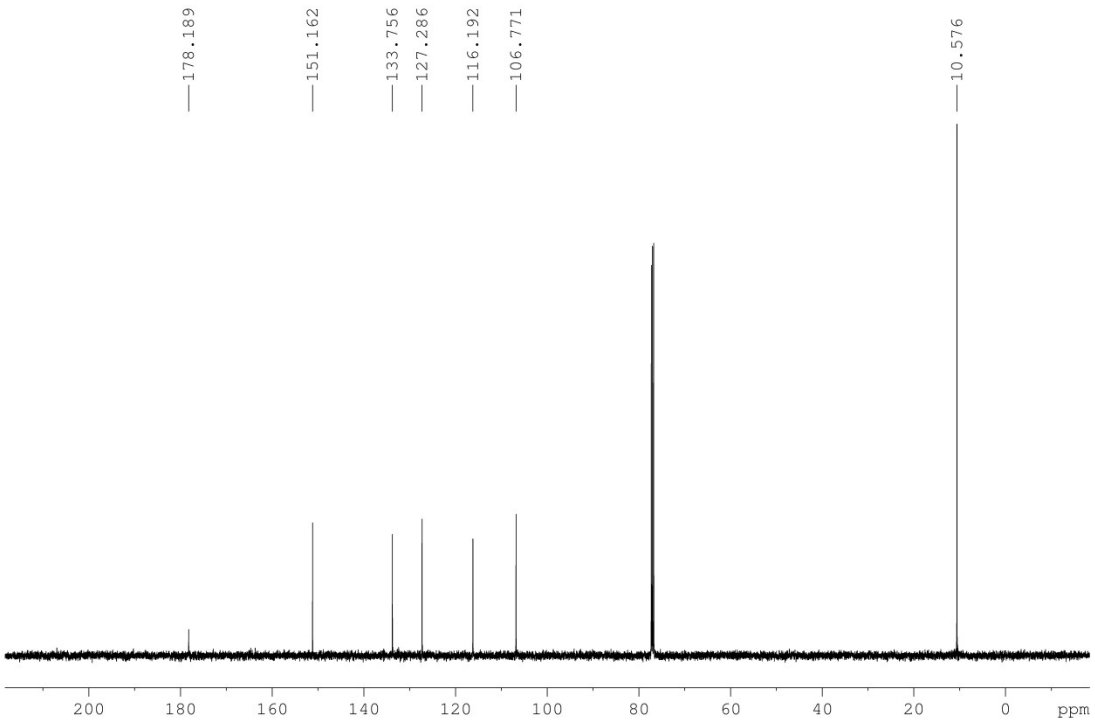


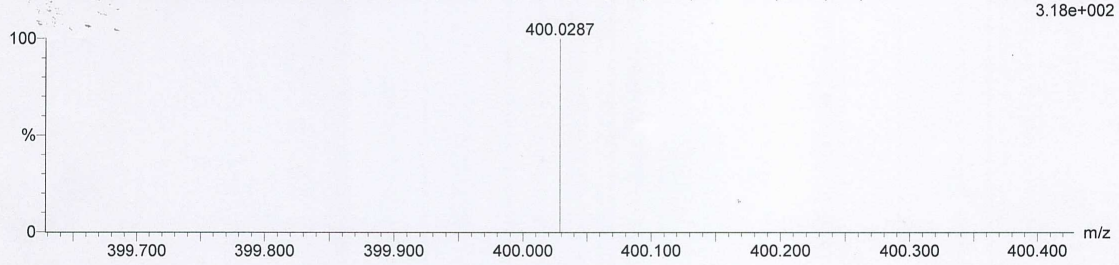
Fig. S9. $^{13}C\{^{1}H\}$ NMR spectrum of **5** (125 MHz)

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-20 N: 0-1 O: 0-2 S: 0-1 Mo: 0-1

SGG-MO-BMPADDUCT
030816-14-SGG-MO-BMPADDUCT 26 (0.654) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:28) TOF MS ES+
3.18e+002



Minimum:		5.0	10.0	-1.5		
Maximum:				50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
400.0287	400.0269	1.8	4.5	8.5	n/a	C17 H20 N O2 S Mo

Fig. S10. HRMS spectrum of **5**

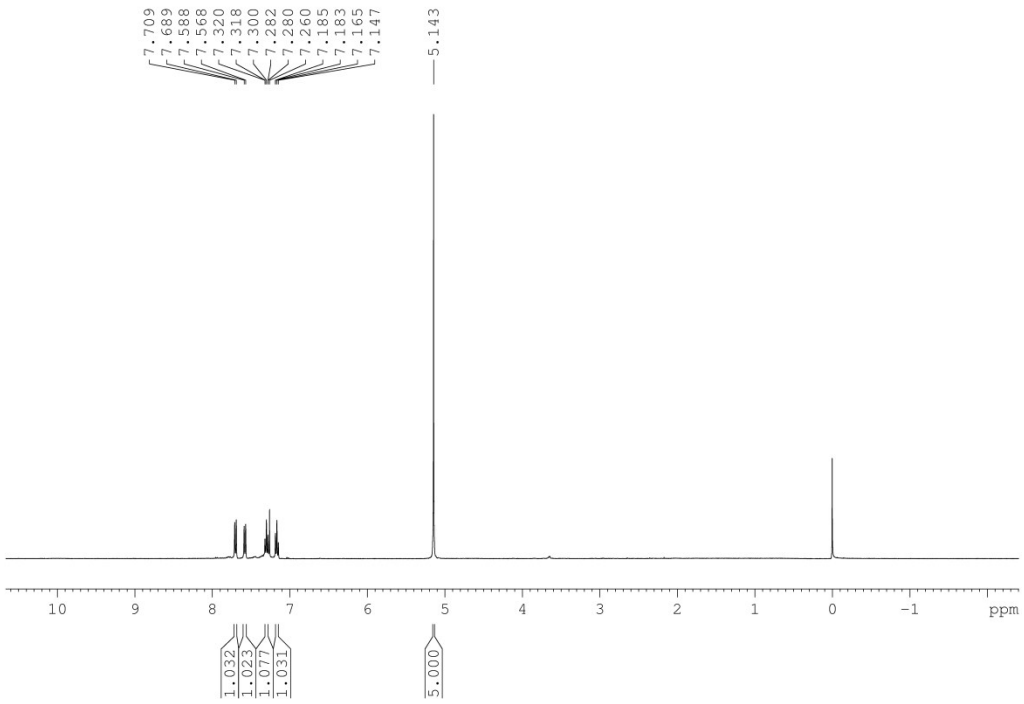


Fig. S11. ^{1}H NMR spectrum of **6** (400 MHz)

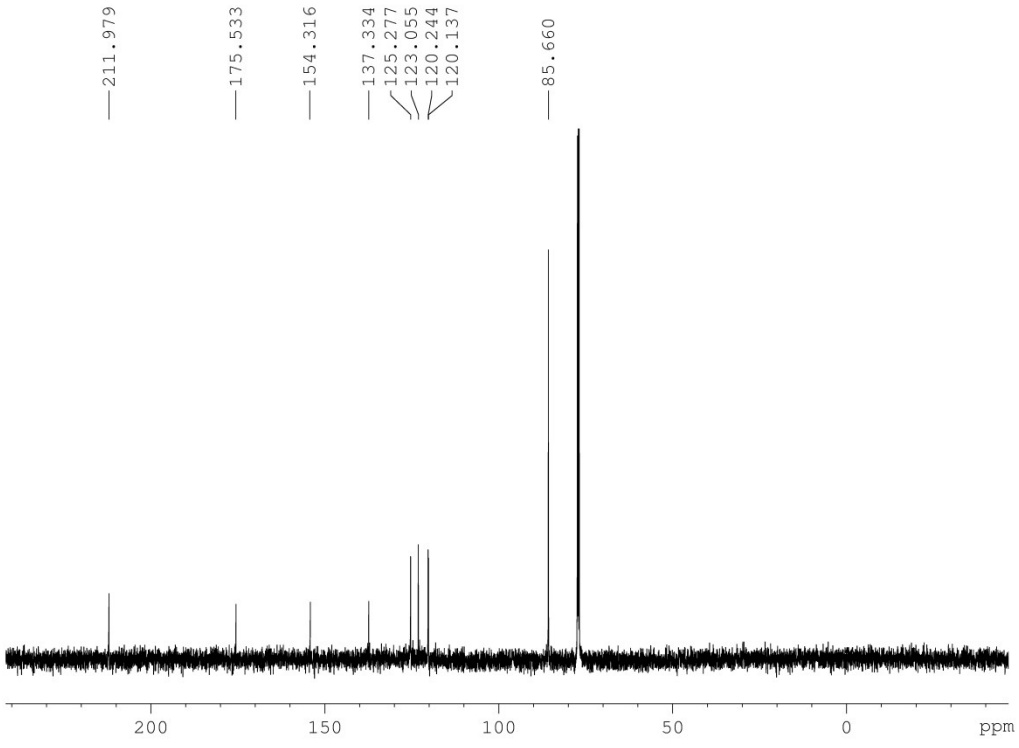


Fig. S12. ^{13}C{^{1}H} NMR spectrum of **6** (100 MHz)

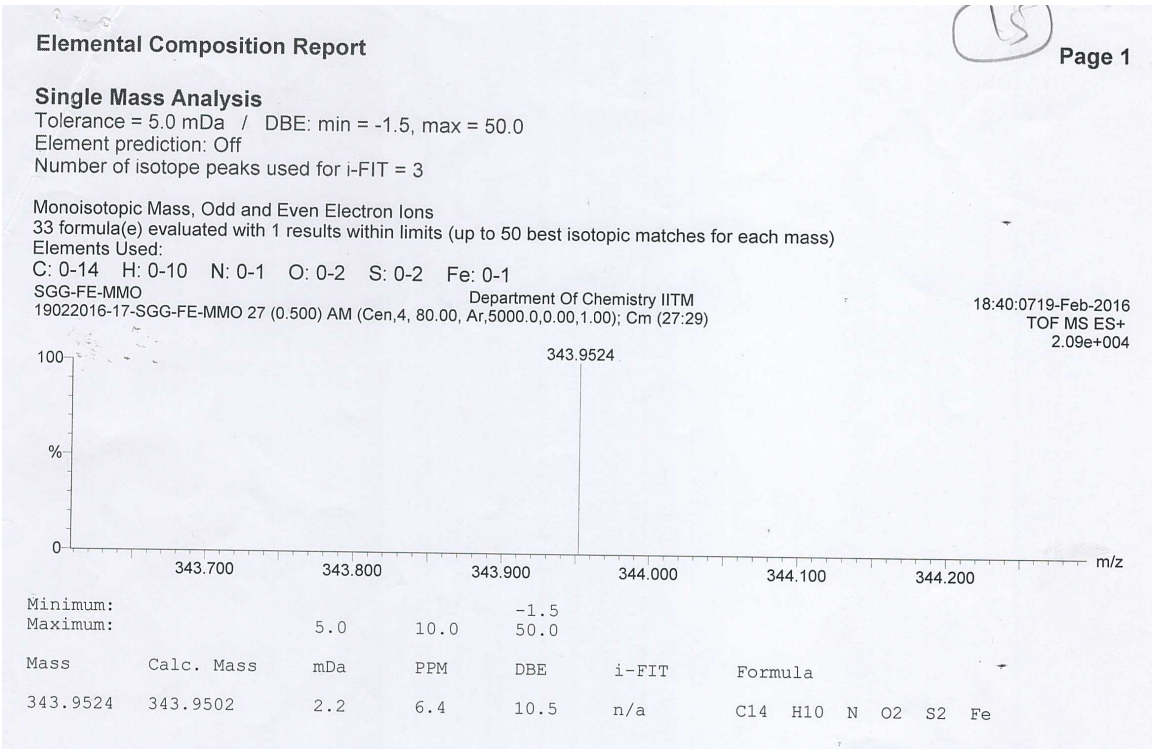


Fig. S13. HRMS spectrum of **6**

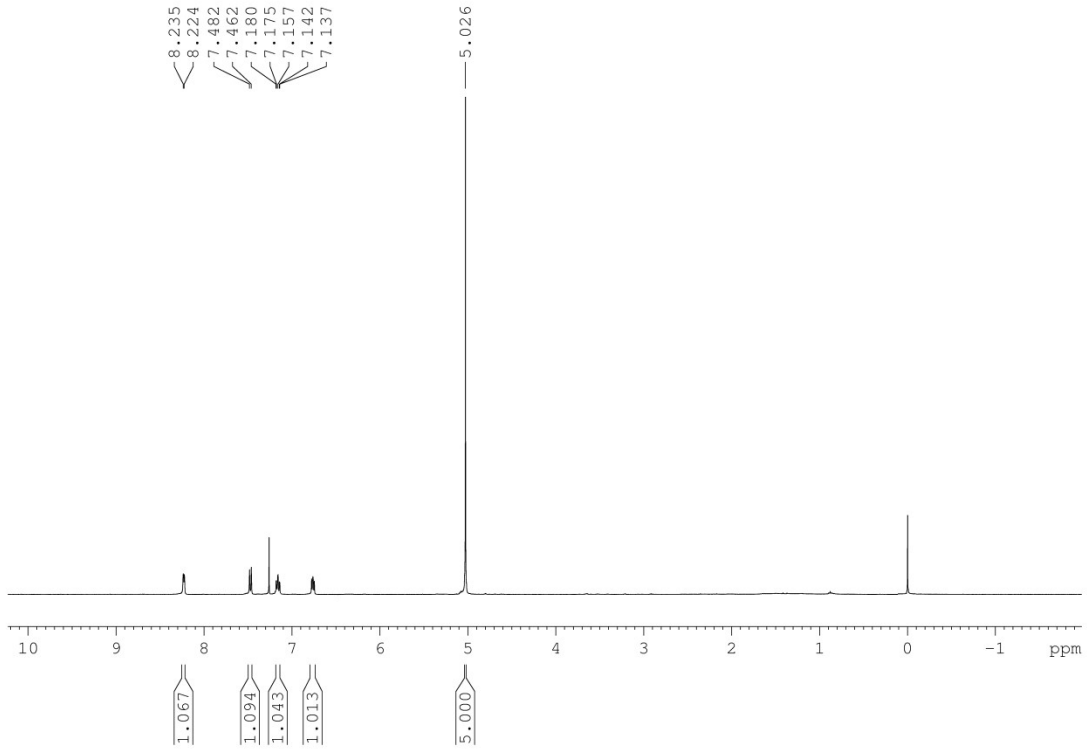


Fig. S14. ^{1}H NMR spectrum of **7** (400 MHz)

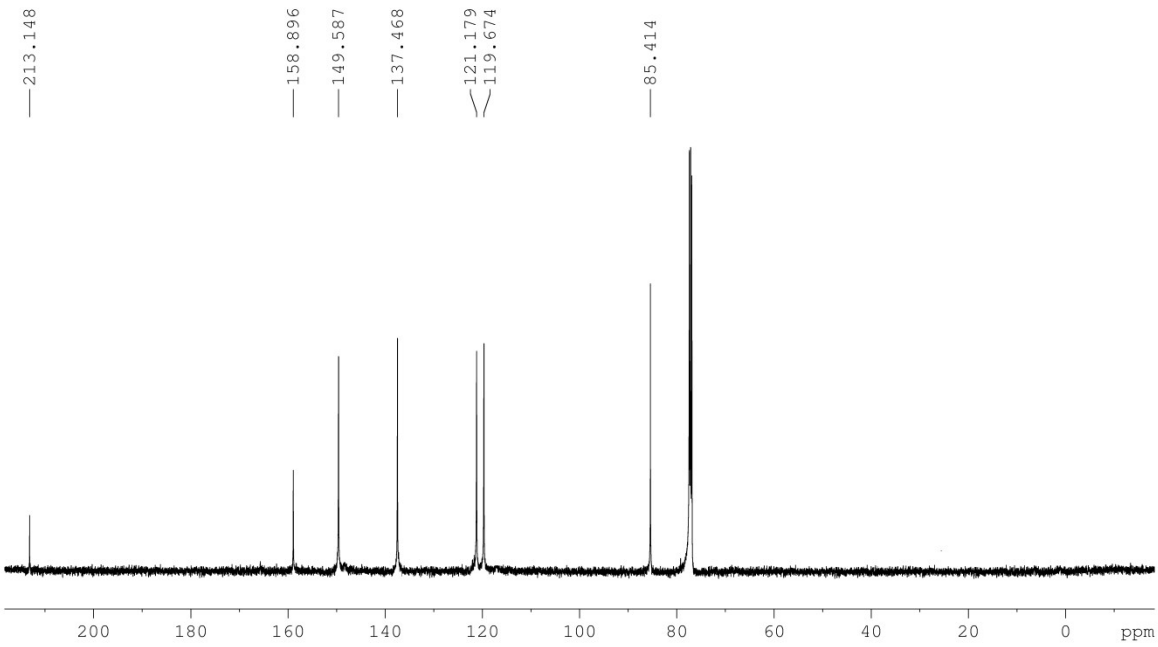


Fig. S15. $^{13}C\{^{1}H\}$ NMR spectrum of **7** (100 MHz)

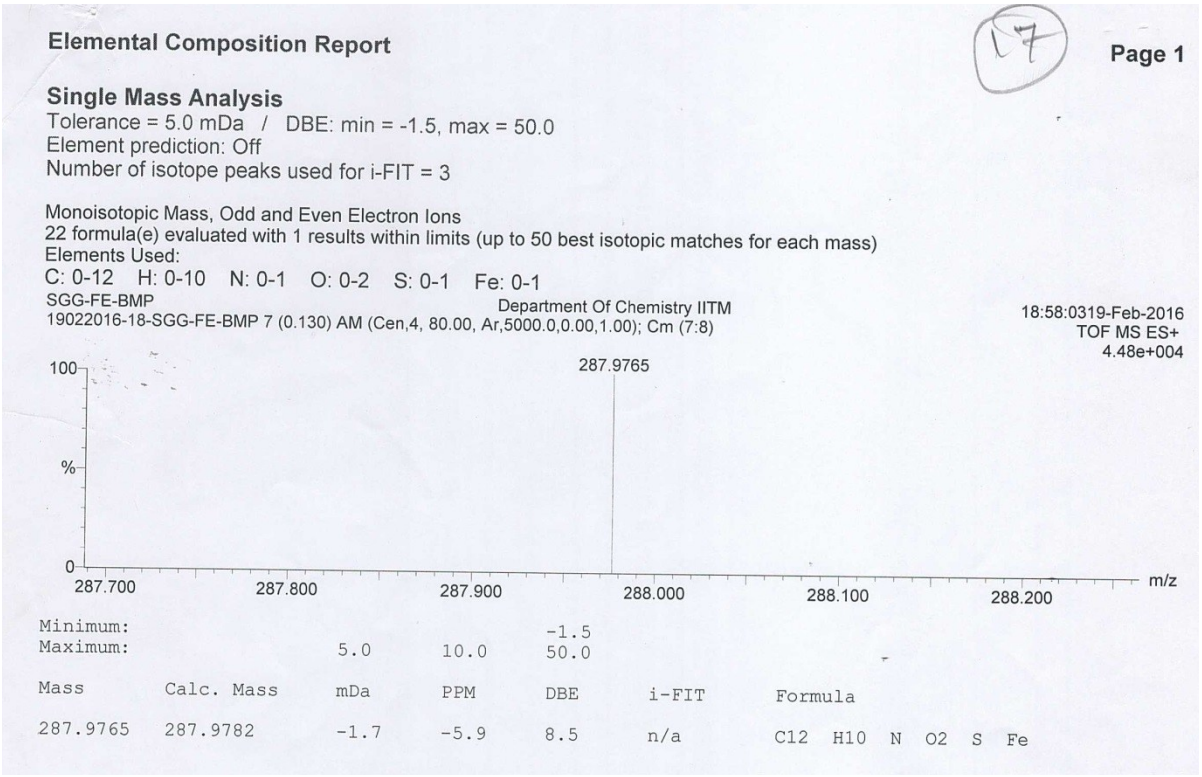


Fig. S16. HRMS spectrum of **7**

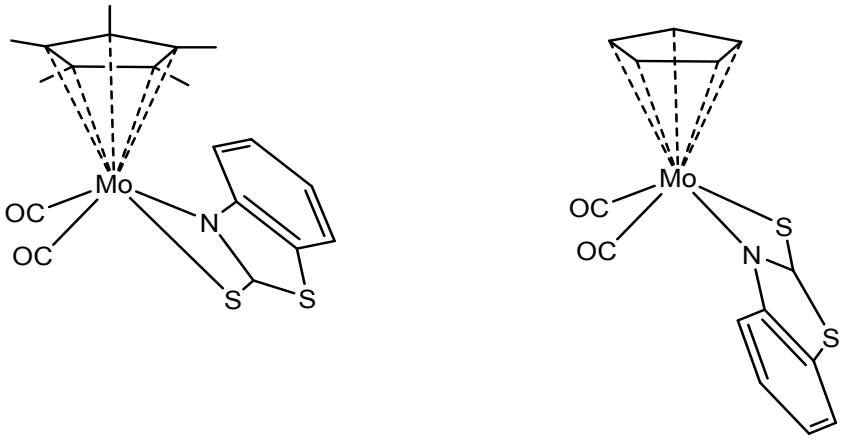
II Supplementary Data

Table S1. Selected bond parameters of **4** and other related Mo-complexes.

Compound	Mo-C_{ipso}	Mo-C_{ortho}	Mo-$C_{methylene}$	Mo-CH_2-Ph	References
Cp*Mo(CO)$_2$(η^3-$CH_2C_6H_5$)	2.370(4)	2.449(5)	2.263(4)	76.2(2)	This work
CpMo(CO)$_2$[η^3-(*p*-$MeC_6H_4CH_2$)]	2.364 (5)	2.480 (6)	2.269 (7)	76.6(2)	1
Cp*Mo(NO)(η^2-$CH_2C_6H_5$)Cl	2.188 (2)	-	2.193 (3)	81.10(4)	2
Cp*Mo(NO)(η^2-$CH_2C_6H_5$)(CH_2SiMe_3)	2.473 (2)	-	2.188 (2)	82.97(12)	3

Table S2. Comparison of bond and torsion angles of **3** and **5** with their Cp analogues **3′** and **5′**.

Compound	Angle of S-Mo-N [°]	Deviation in Mo-C-O angles	Torsion angle	References
3′	64.64	0.76	9.30	4
3	64.51	1.86	-5.07	This work
5′	64.43	0.57	1.25	5
5	64.94	2.54	-8.03	6



Endo

3

Exo

3'

Fig. S17. Conformational comparison of **3** and **3′** (**3′**: Cp analogue **3**).

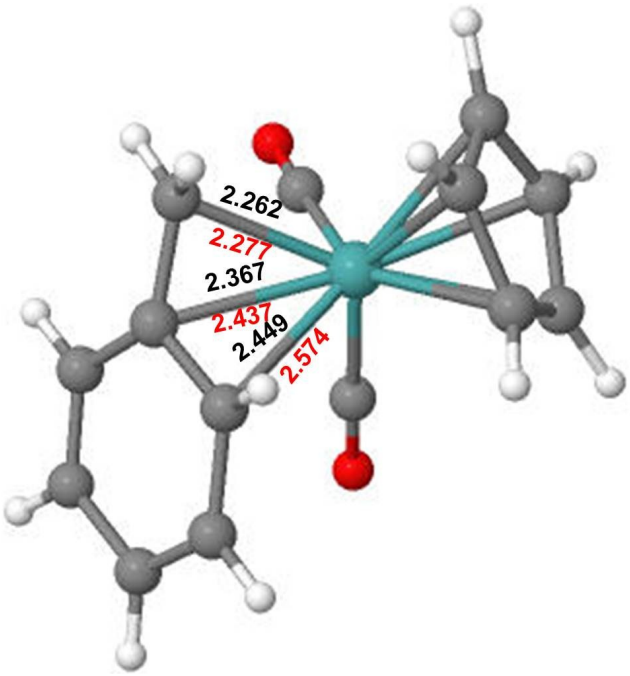


Fig. S18. Selected bond distances (Å) of compound **4**. (Experimental distances shown in black color and calculated distances shown in red color).

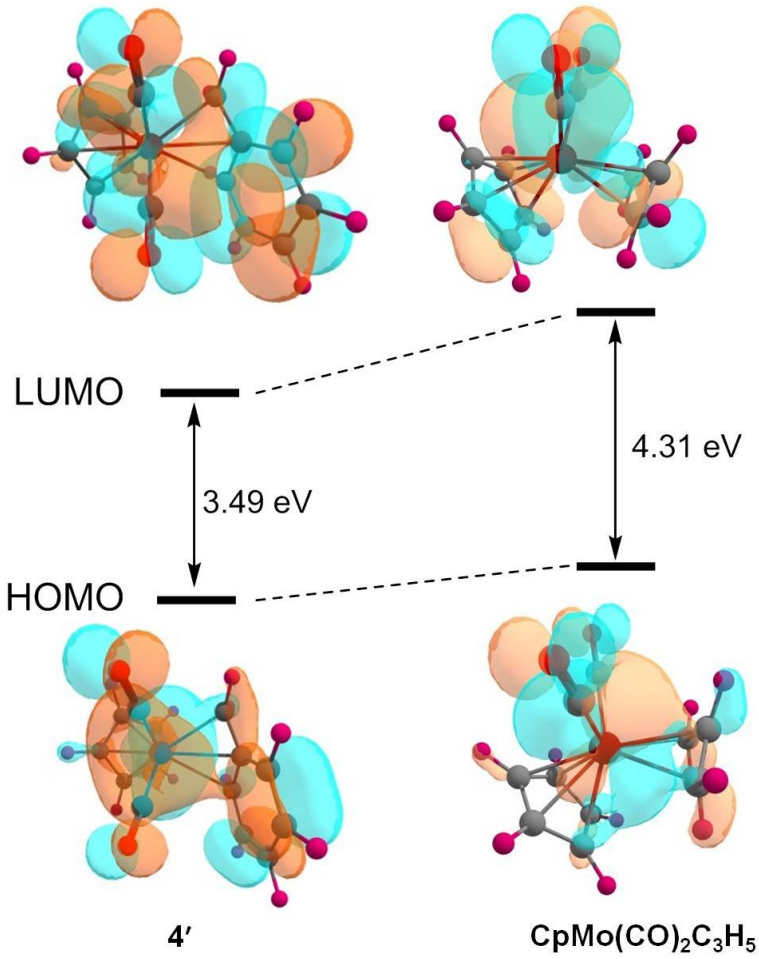


Fig. S19. DFT calculated energies of HOMO-LUMO gaps ($\Delta E = E_{LUMO}-E_{HOMO}$, eV) for compounds **4′** and [**$CpMo(CO)_2C_3H_5$**].

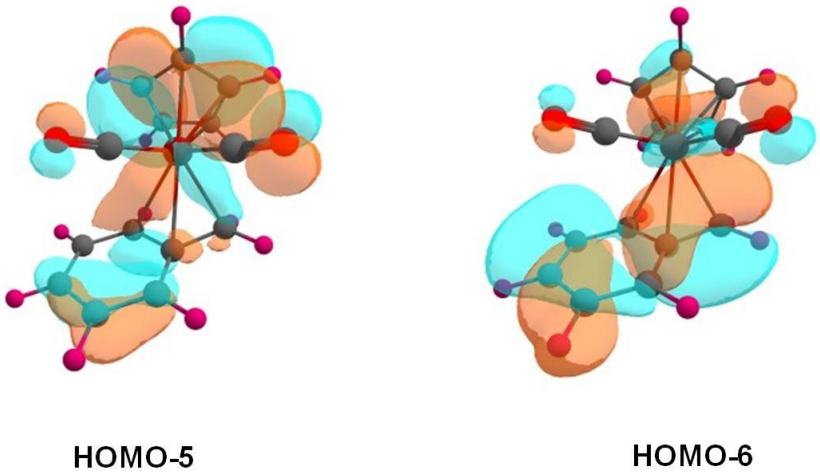


Fig. S20. Selected molecular orbitals of compound **4′**.

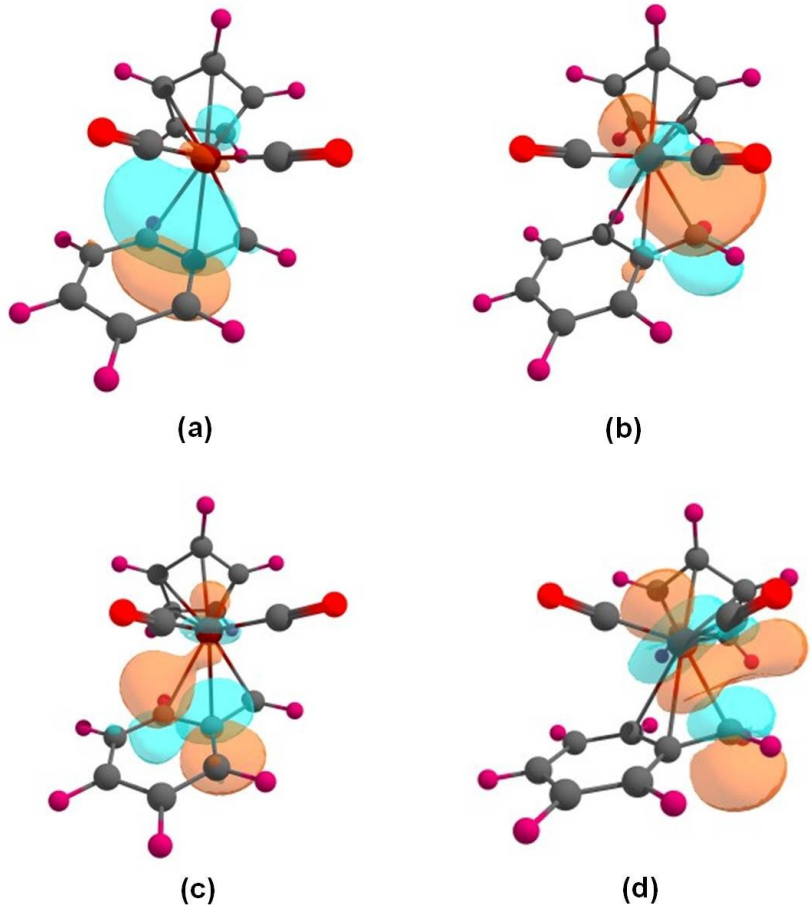


Fig. S21. NBO analysis of **4′**.

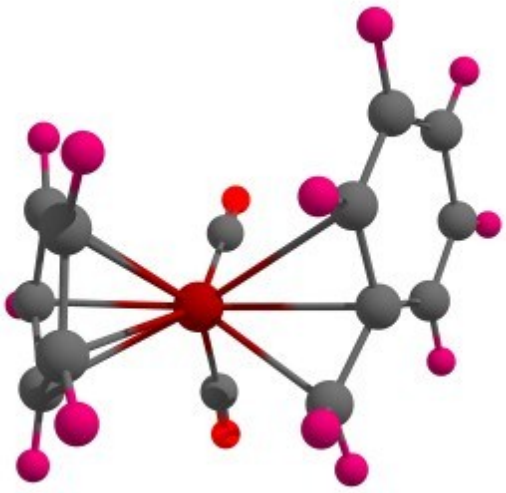


Fig. S22. Optimized geometry of compound **4′**.

Cartesian coordinates for the calculated structure of **4′** (in Å).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.365800	0.398684	-2.060750
2	6	0	1.488469	-0.056915	-1.273377
3	6	0	1.414836	-1.359147	-0.695187
4	6	0	2.435027	-1.812772	0.186906
5	1	0	2.381226	-2.823426	0.582909
6	6	0	3.493574	-0.992966	0.505565
7	1	0	4.276301	-1.340843	1.173557
8	6	0	3.572608	0.311070	-0.050900

9	1	0	4.414928	0.949704	0.200582
10	6	0	2.593045	0.774961	-0.895985
11	1	0	2.649081	1.778393	-1.310277
12	6	0	0.418009	0.496628	1.637414
13	6	0	-0.587234	2.052026	-0.104663
14	6	0	-2.042382	-1.393494	1.151864
15	6	0	-1.895070	-2.004252	-0.126485
16	6	0	-2.415507	-1.118653	-1.102862
17	6	0	-2.898628	0.046555	-0.433407
18	6	0	-2.683939	-0.129143	0.970850
19	8	0	0.979976	0.744695	2.624488
20	8	0	-0.644565	3.216325	-0.152645
21	42	0	-0.595488	0.099200	-0.018444
22	1	0	0.735832	-2.088048	-1.127438
23	1	0	-0.083872	-0.332011	-2.734052
24	1	0	0.446489	1.388132	-2.505557
25	1	0	-1.455637	-2.975605	-0.315565
26	1	0	-2.446884	-1.293674	-2.170537
27	1	0	-1.755436	-1.830821	2.099449
28	1	0	-2.994849	0.549318	1.753757
29	1	0	-3.391633	0.888835	-0.900820

The MOL2 cartesian coordinates for the calculated structure of **4′** (in Å).

C	11.74940000	10.74550000	5.06750000
C	10.88940000	9.61190000	5.03640000
C	9.73290000	9.66650000	5.82330000
C	8.89980000	8.51220000	5.92150000
H	8.11600000	8.54940000	6.42140000
C	9.24000000	7.36640000	5.29410000
H	8.70130000	6.61310000	5.37490000
C	10.41930000	7.31510000	4.51110000
H	10.64440000	6.53060000	4.06570000
C	11.20280000	8.37720000	4.40900000
H	11.98430000	8.31170000	3.91010000
C	11.54880000	8.11800000	7.59830000
C	13.46820000	9.40170000	6.72490000
C	11.13000000	10.45910000	9.43280000
C	10.25980000	11.28300000	8.67210000
C	11.06540000	12.19260000	7.93200000
C	12.43290000	11.95360000	8.25580000
C	12.47080000	10.90470000	9.21880000
O	11.47570000	6.98770000	7.81430000
O	14.54110000	9.01740000	6.47100000
Mo	11.71550000	10.03250000	7.21390000
H	9.32510000	10.46770000	6.06930000

H	11.31960000	11.64810000	5.03830000
H	12.63630000	10.65730000	4.62010000
H	9.19030000	11.25010000	8.67490000
H	10.67080000	12.96920000	7.31070000
H	10.81950000	9.74560000	10.16730000
H	13.33440000	10.55080000	9.74220000
H	13.28110000	12.53000000	7.95030000

III References

1. F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, 1968, **90**, 5418–5422.
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5. N. Begum, S. E. Kabir, G. M. G-Hossain, A. F. M. M-Rahman and E. Rosenberg, *Organometallics*, 2005, **24**, 266–271.
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