

## **SUPPORTING INFORMATION**

### **Cooperative B-H activation Cp\* based $\kappa^2$ -N,S-chelated Ru(II) and Mo(II) complexes**

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## I Spectroscopic Details

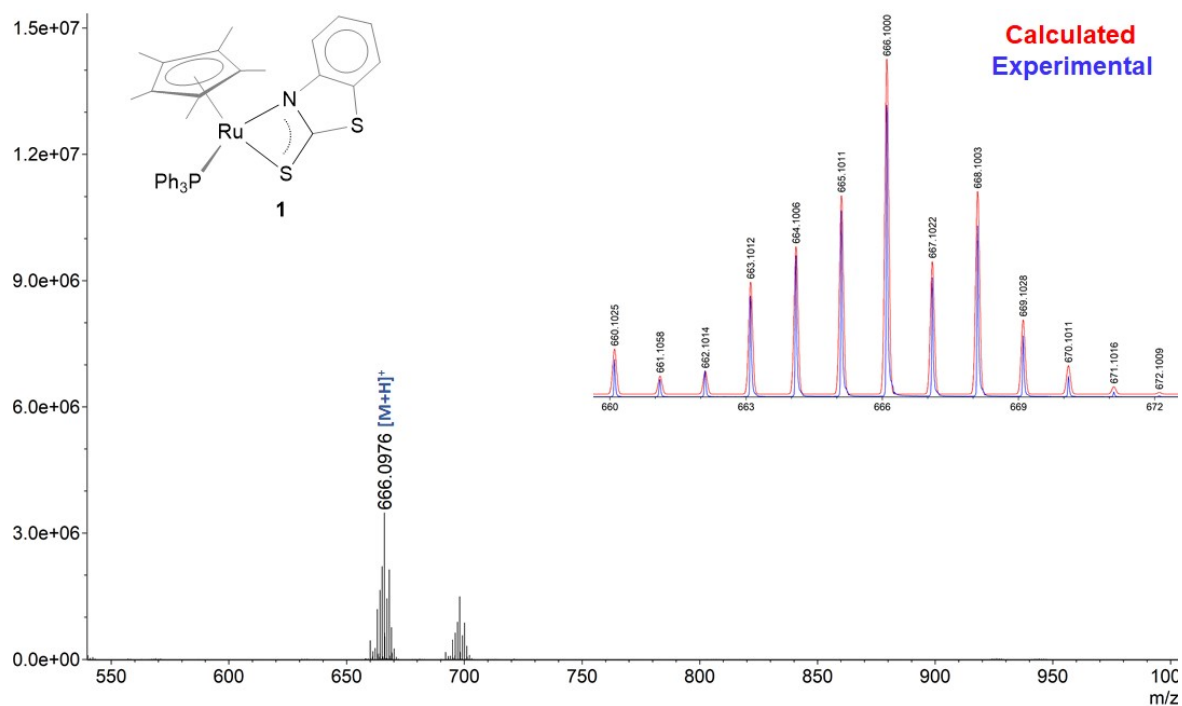


Figure S1. ESI-MS of compound 1

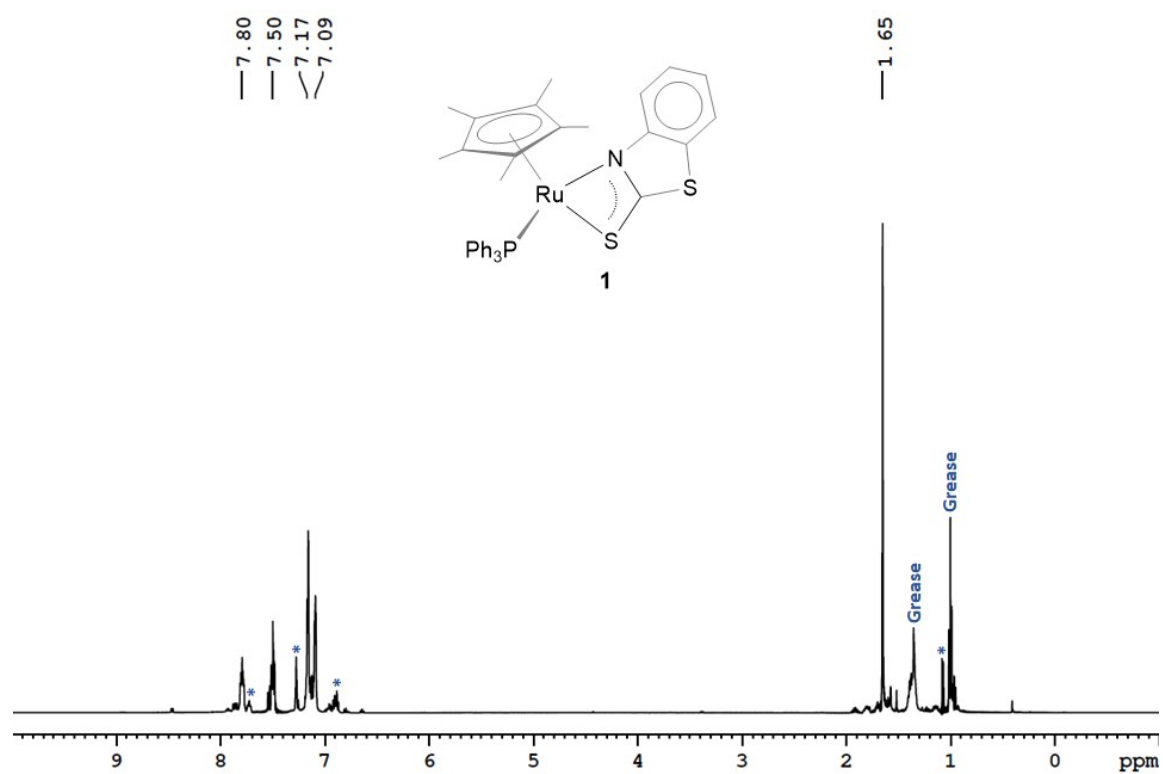
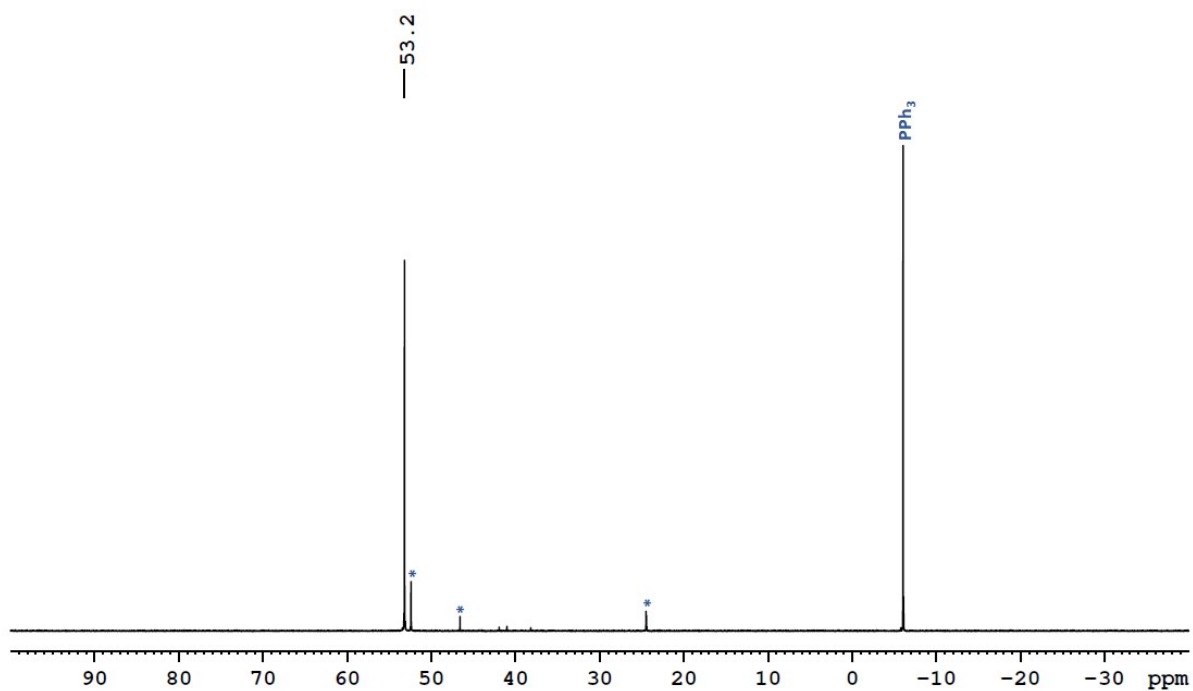
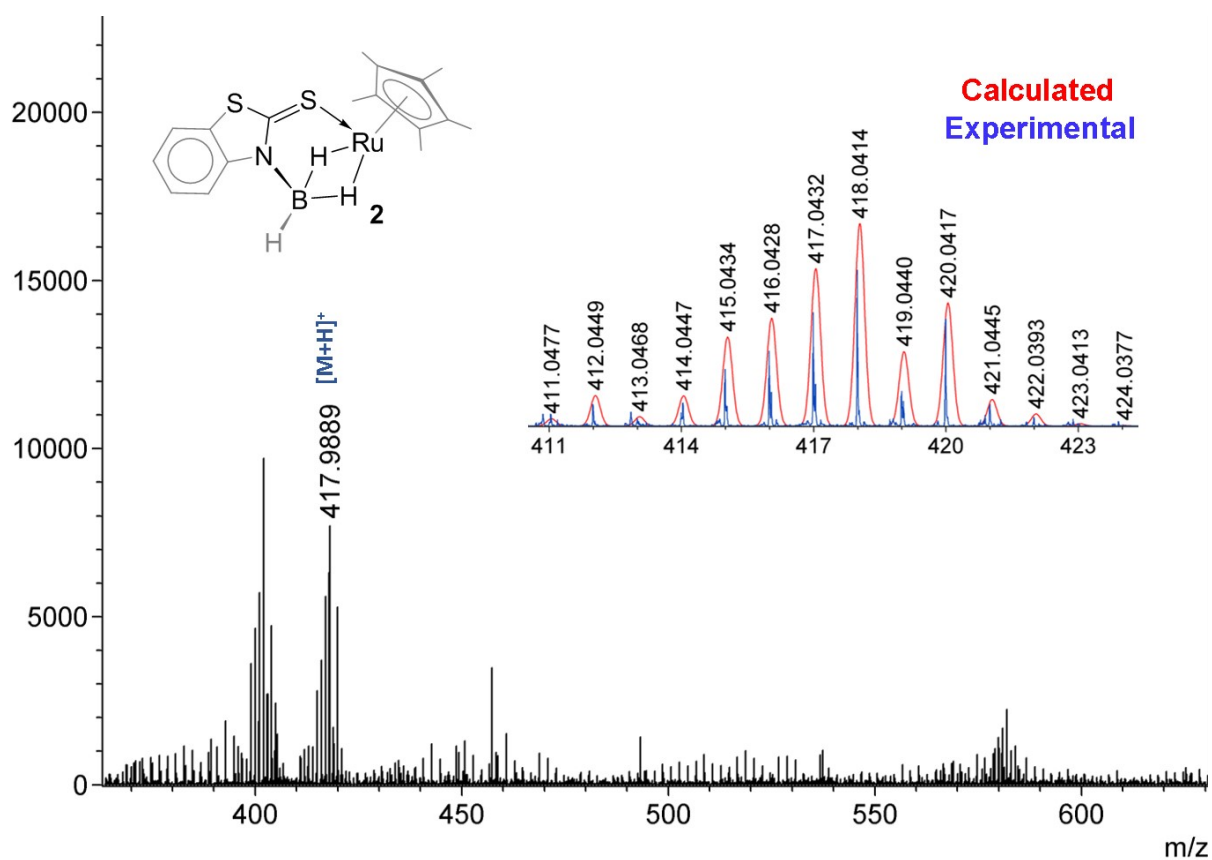


Figure S2. <sup>1</sup>H NMR spectrum of compound 1 (impure) in C<sub>6</sub>D<sub>6</sub> (\* = peaks corresponding to PPh<sub>3</sub> and other impurities)



**Figure S3.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of compound 1 (impure) in C<sub>6</sub>D<sub>6</sub> (\* = peaks corresponding some impurities)



**Figure S4.** ESI-MS of compound 2

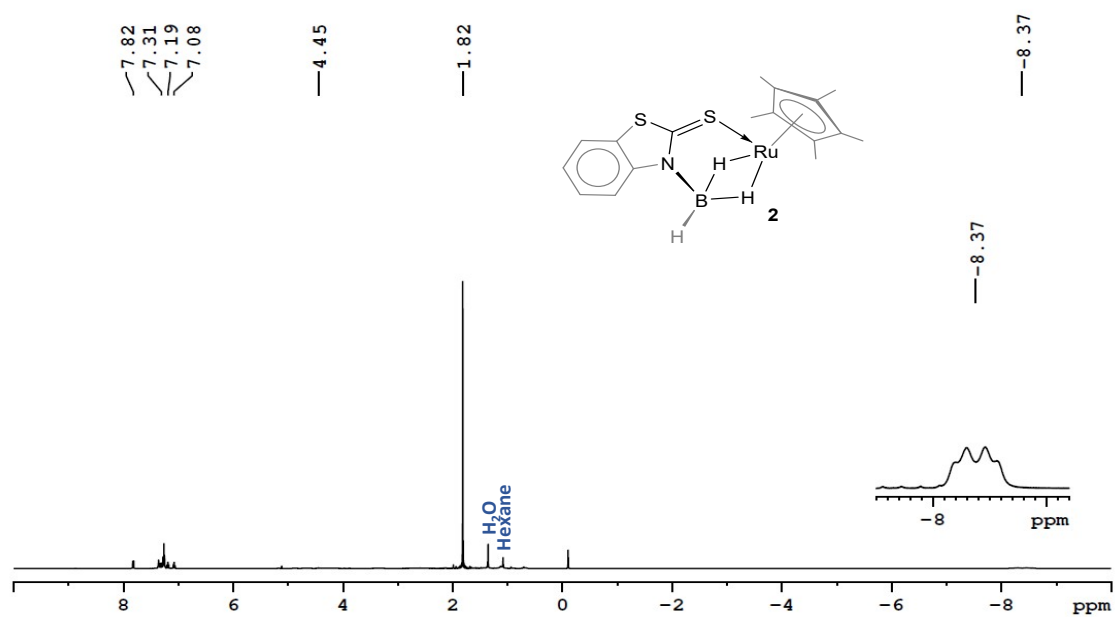


Figure S5.  $^1\text{H}$  NMR spectrum of compound 2 in  $\text{CDCl}_3$

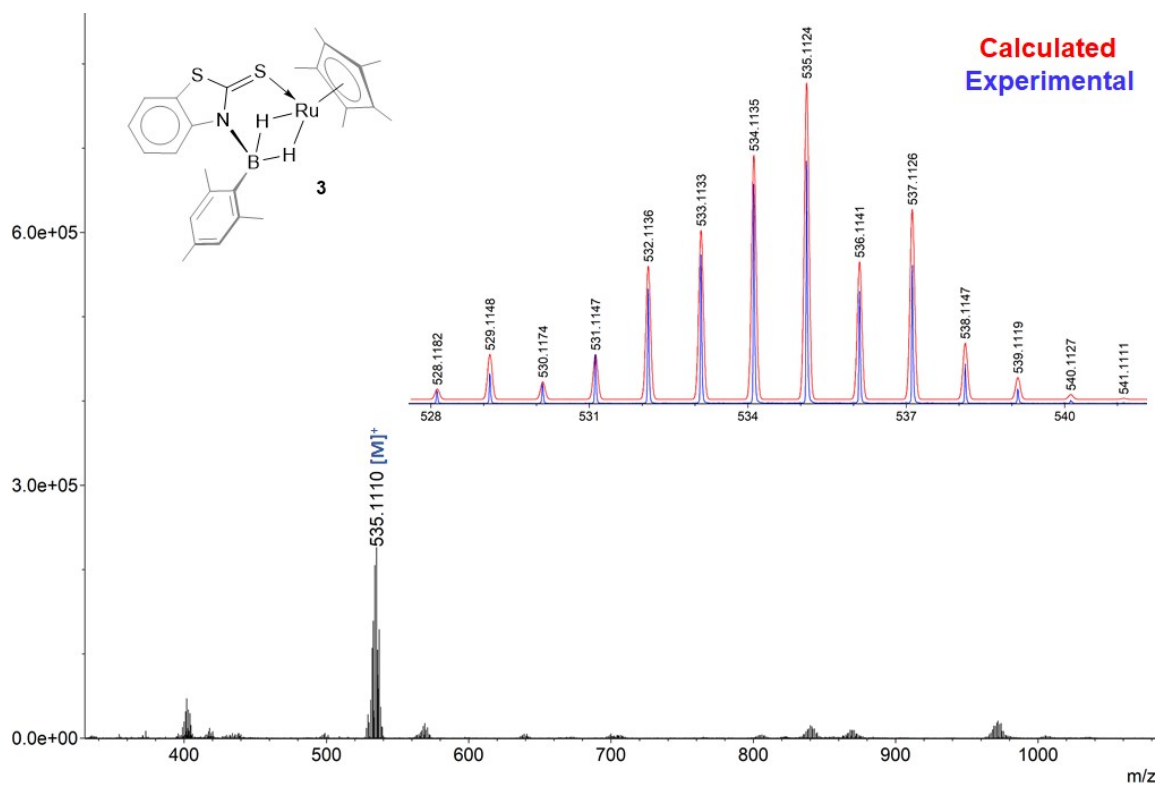
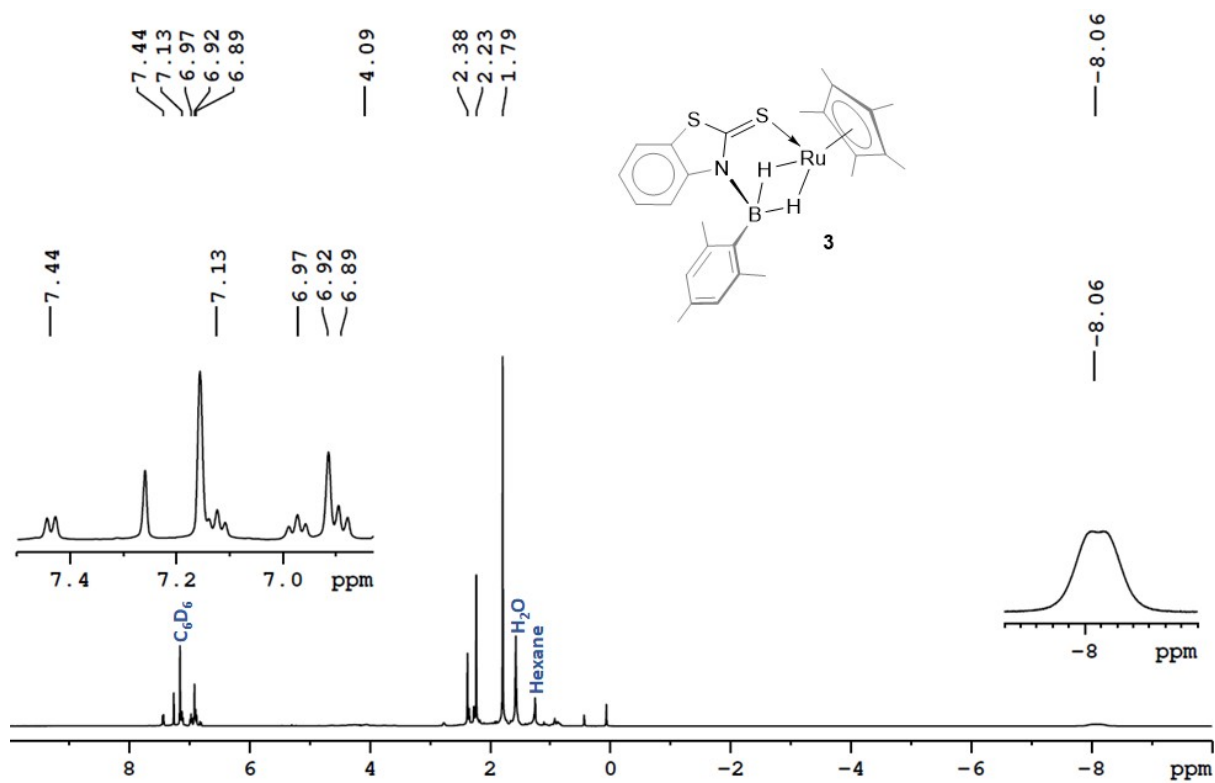
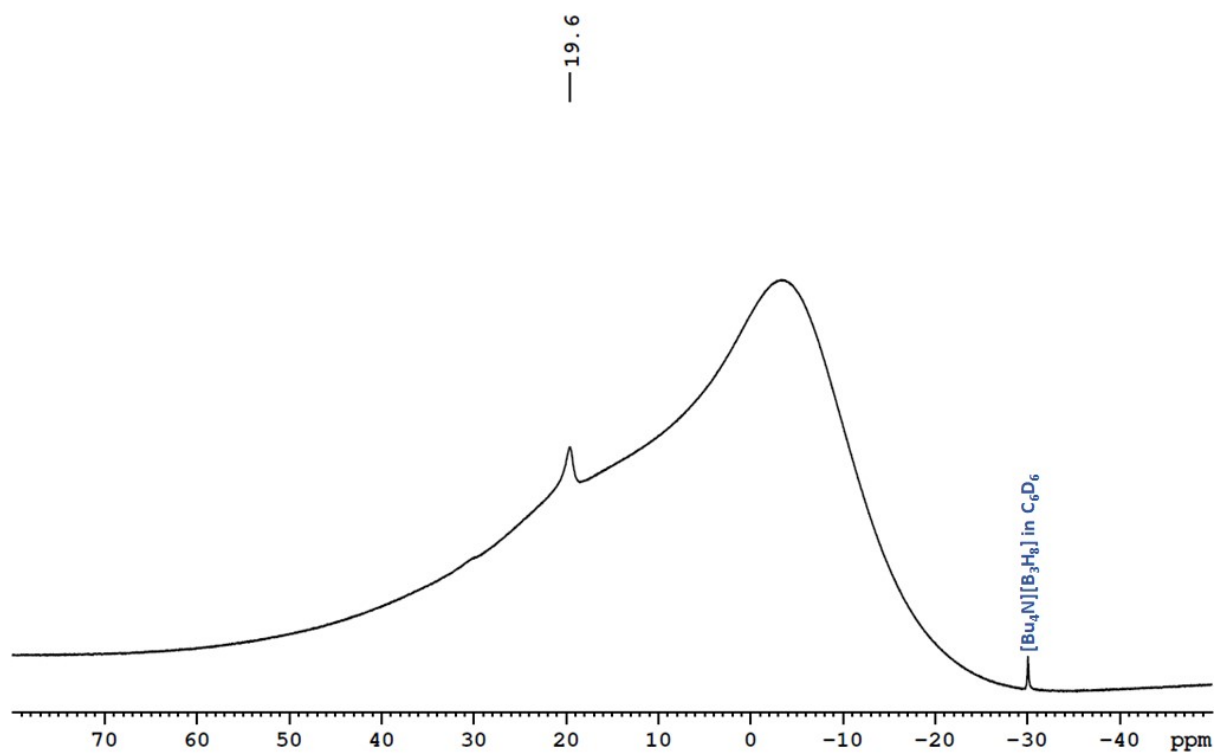


Figure S6. ESI-MS of compound 3



**Figure S7.**  $^1\text{H}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$



**Figure S8.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$

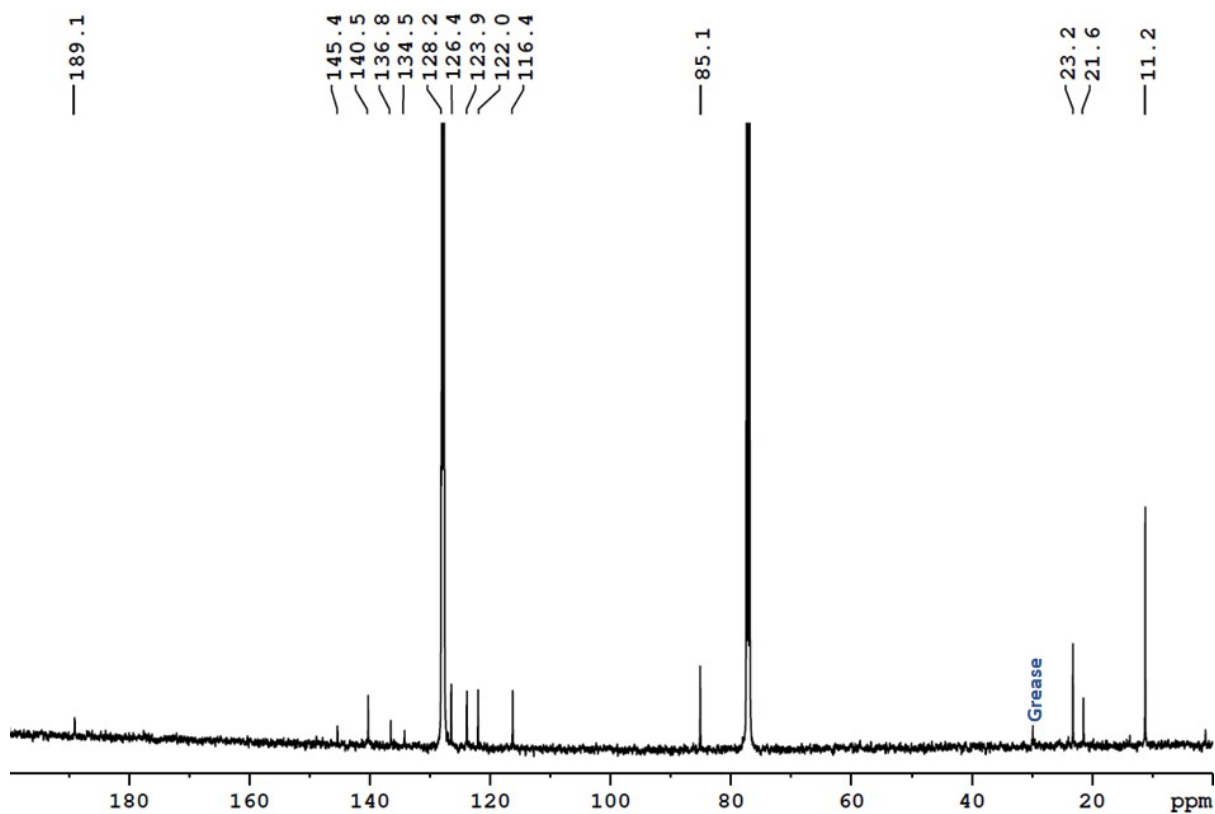


Figure S9.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$

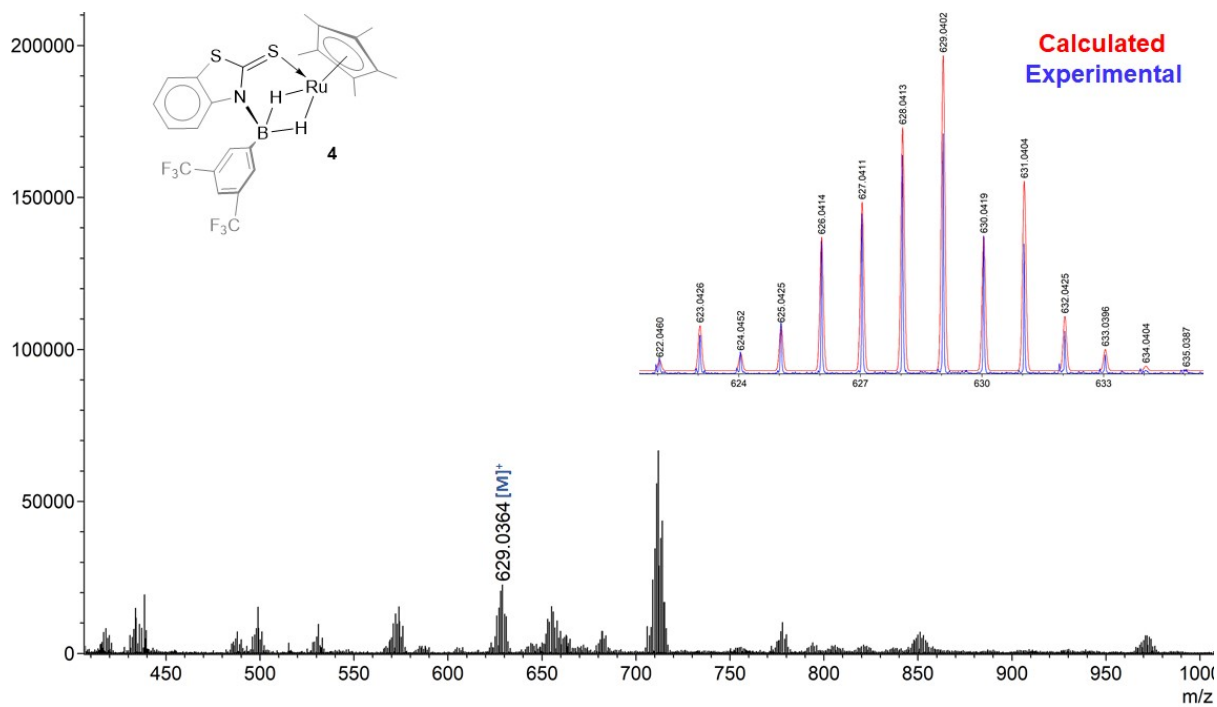
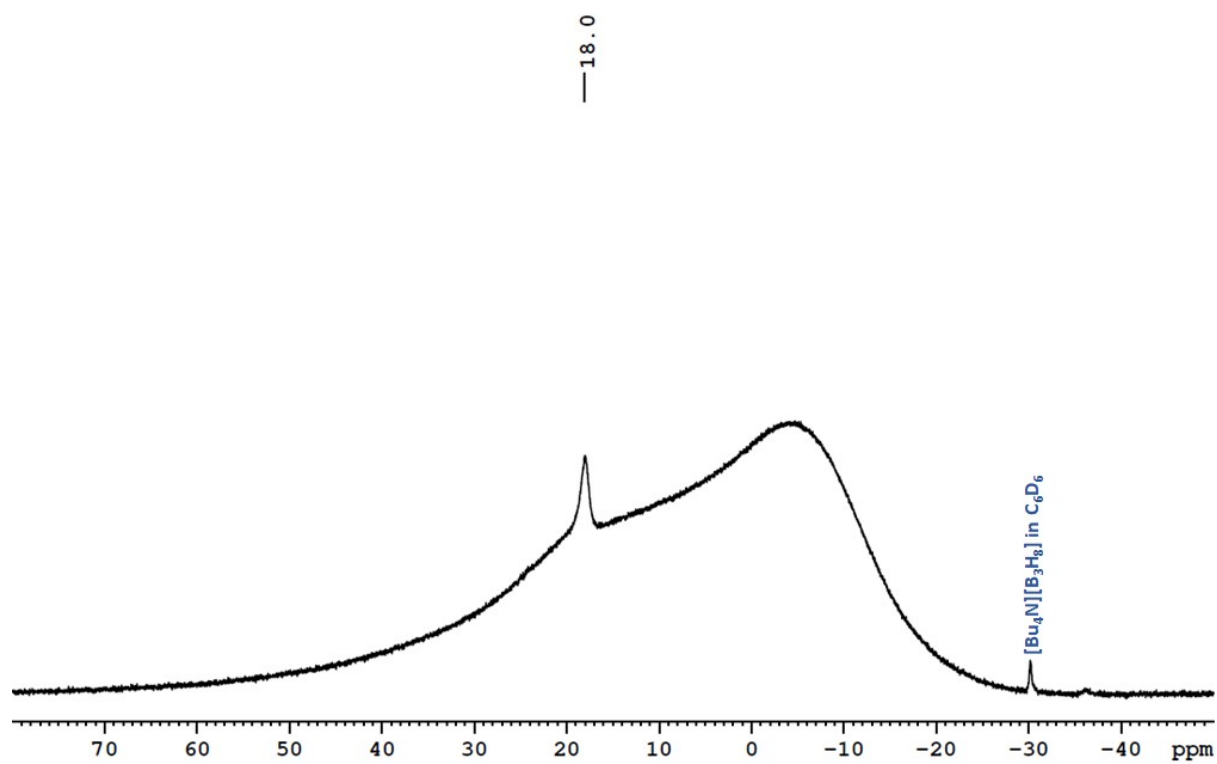
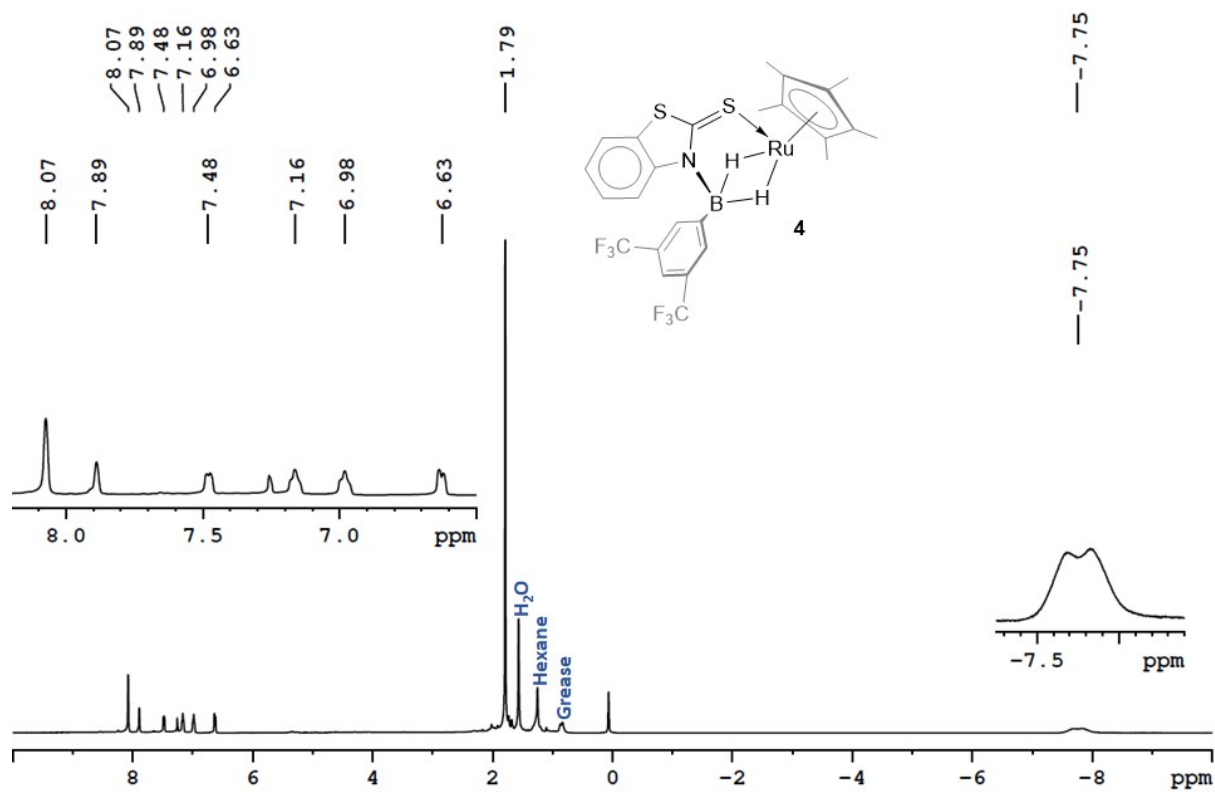
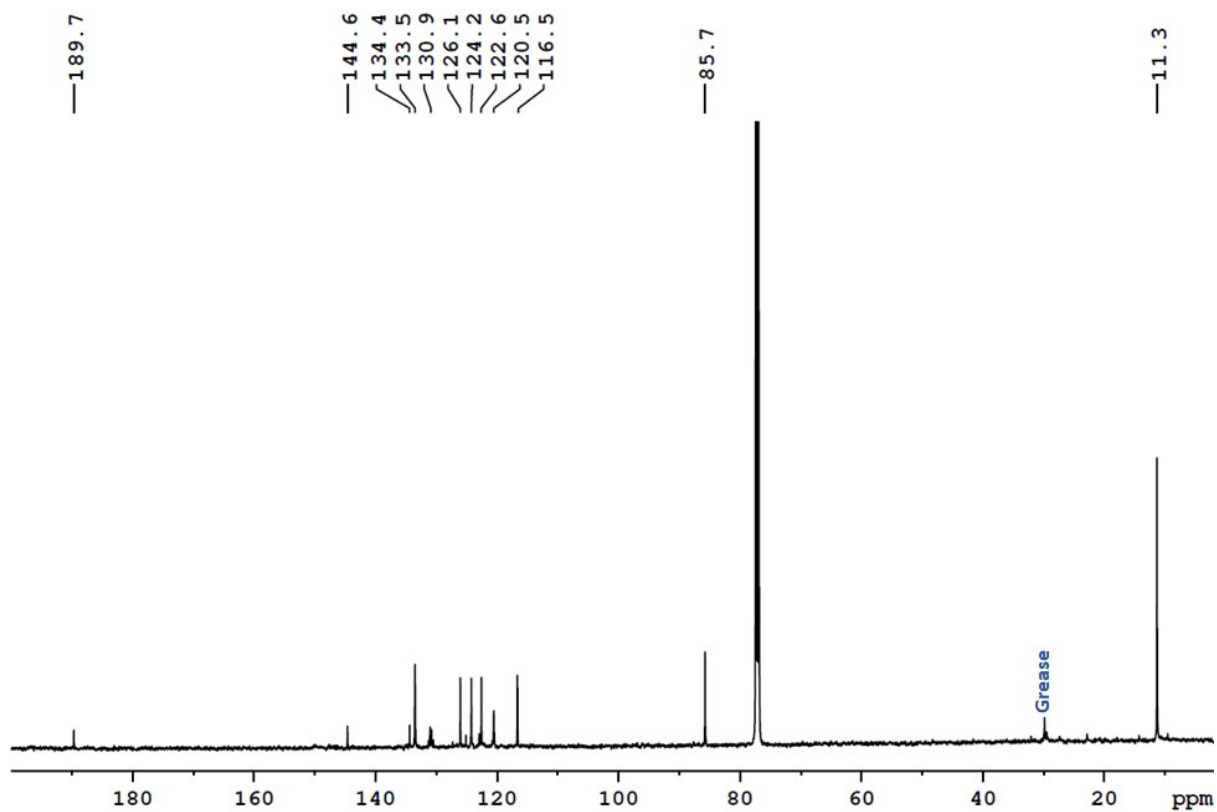


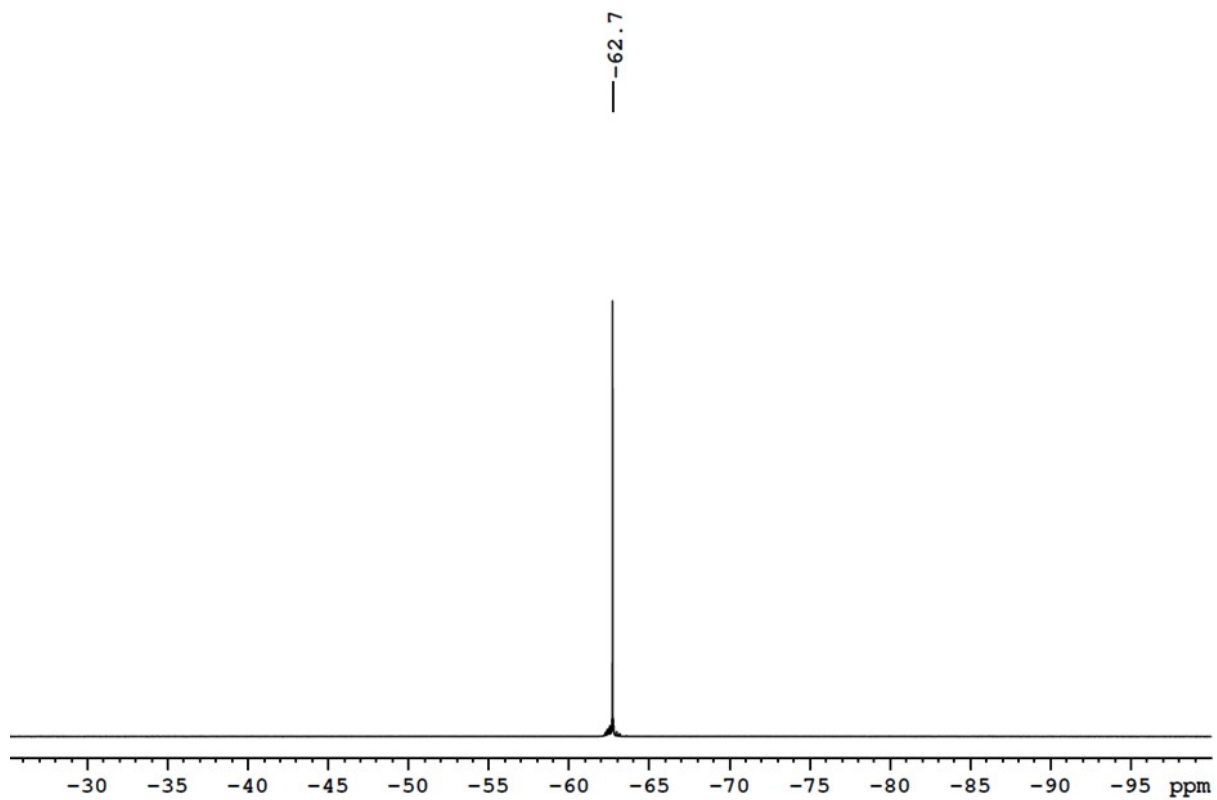
Figure S10. ESI-MS of compound **4**



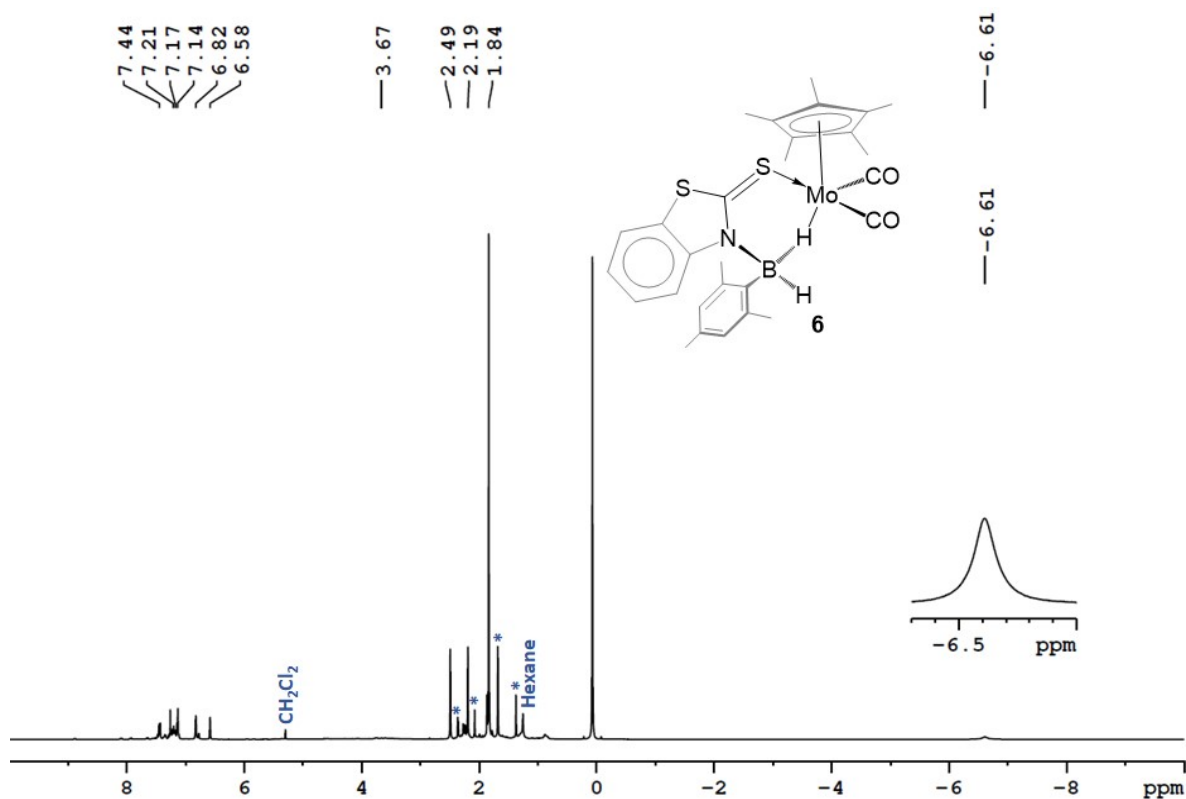




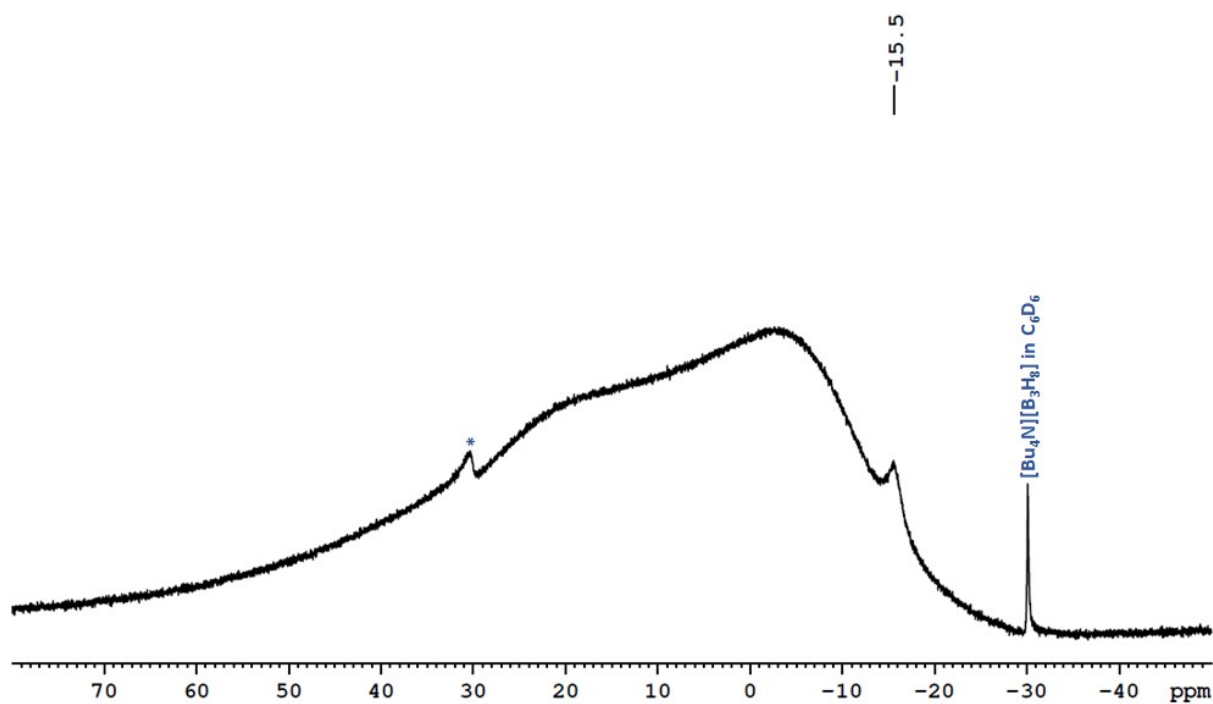
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**Figure S14.**  $^{19}\text{F}$  NMR spectrum of compound **4** in  $\text{C}_6\text{D}_6$



**Figure S15.** <sup>1</sup>H NMR spectrum of compound **6** (impure) in CDCl<sub>3</sub> (\* = peaks corresponding to inseparable impurities)



**Figure S16.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of compound **6** (impure) in CDCl<sub>3</sub> (\* = peak corresponding to an inseparable impurity)

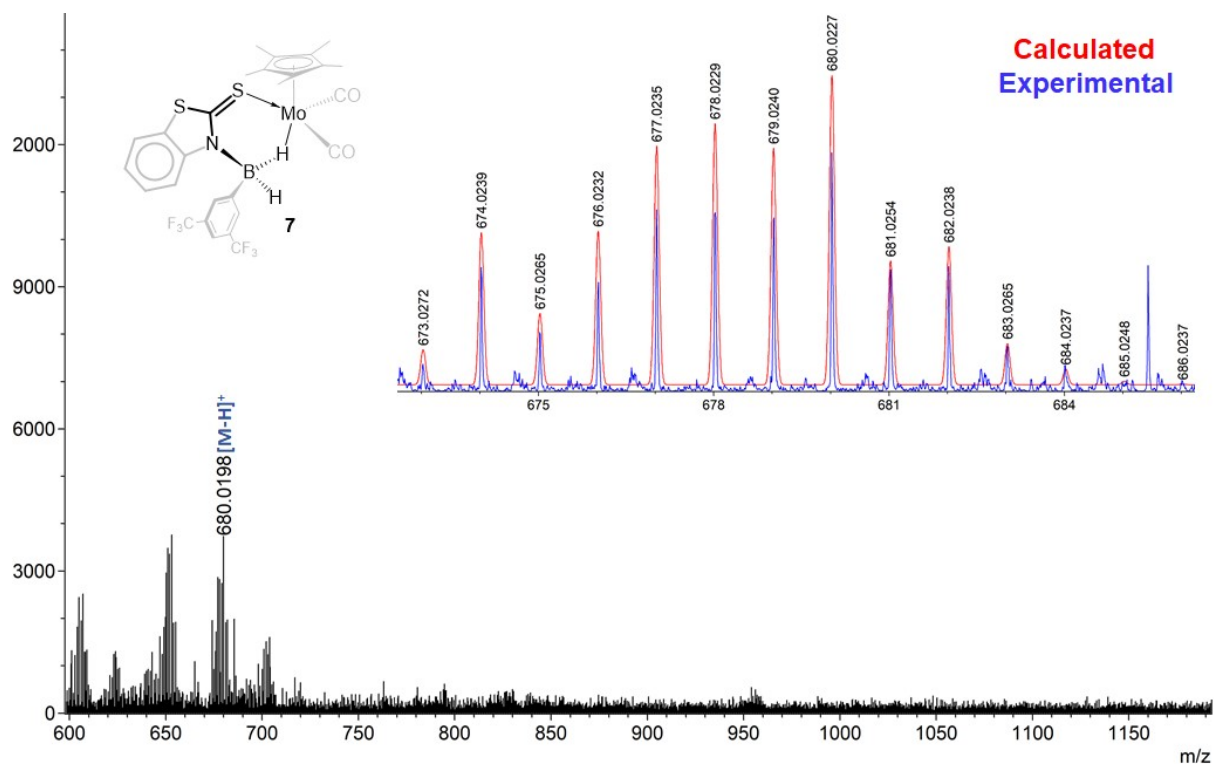


Figure S17. ESI-MS of compound 7

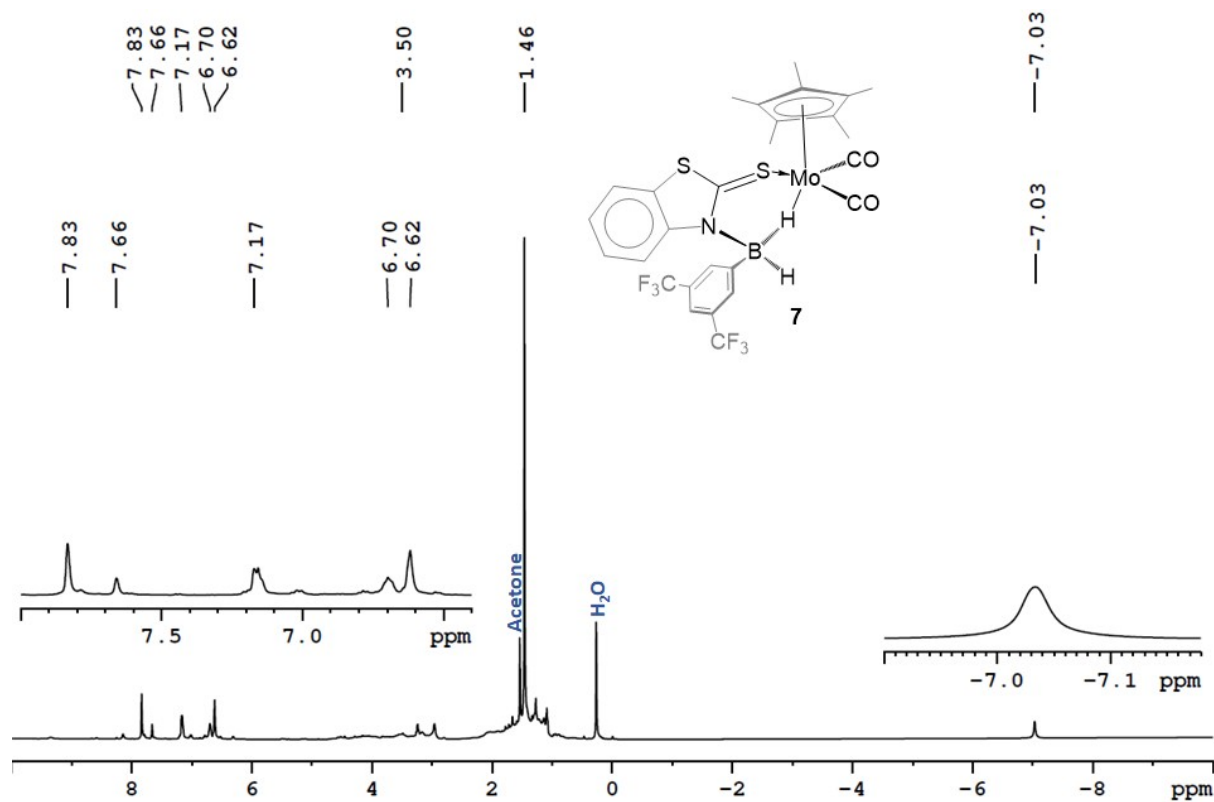


Figure S18.  $^1\text{H}$  NMR spectrum of compound 7 in  $\text{C}_6\text{D}_6$

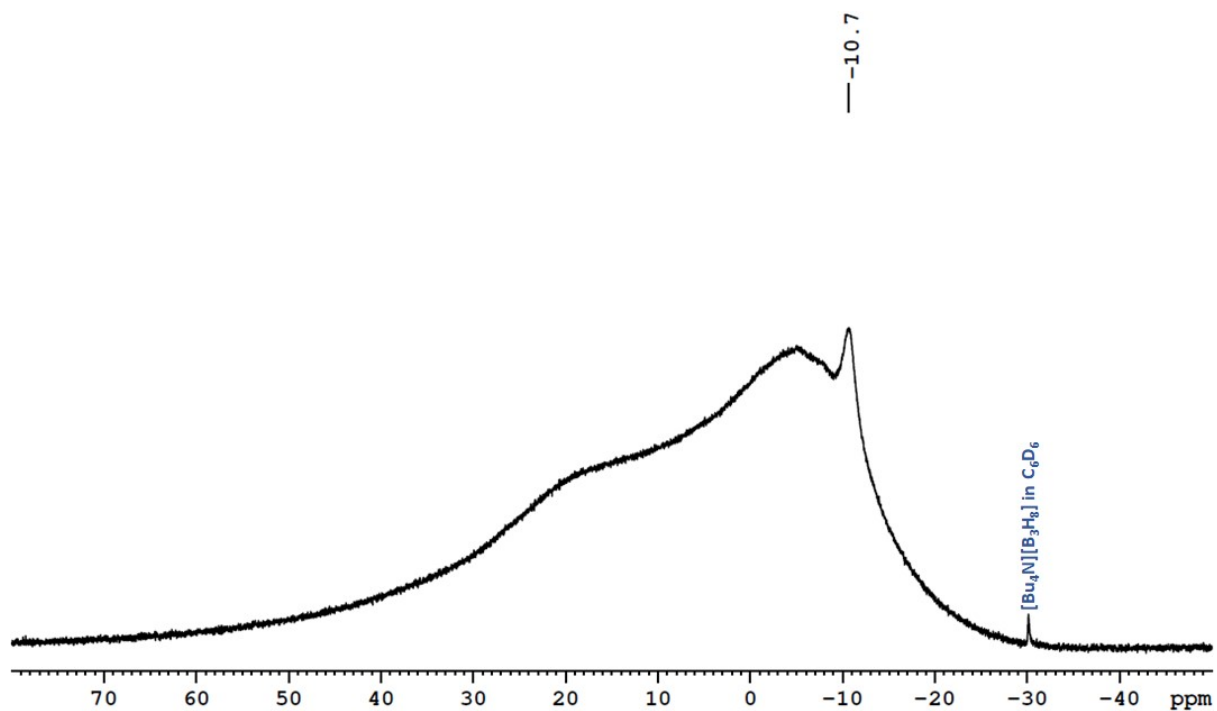


Figure S19.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **7** in  $\text{C}_6\text{D}_6$

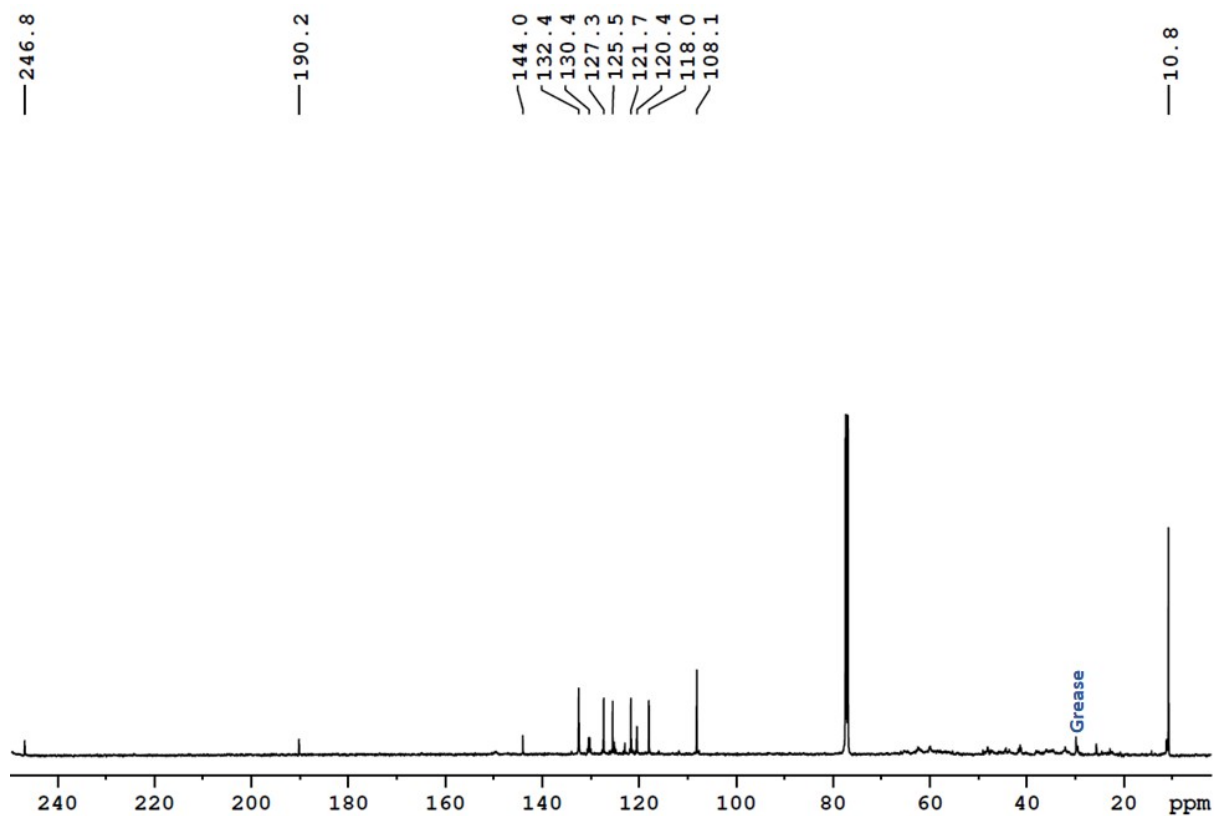
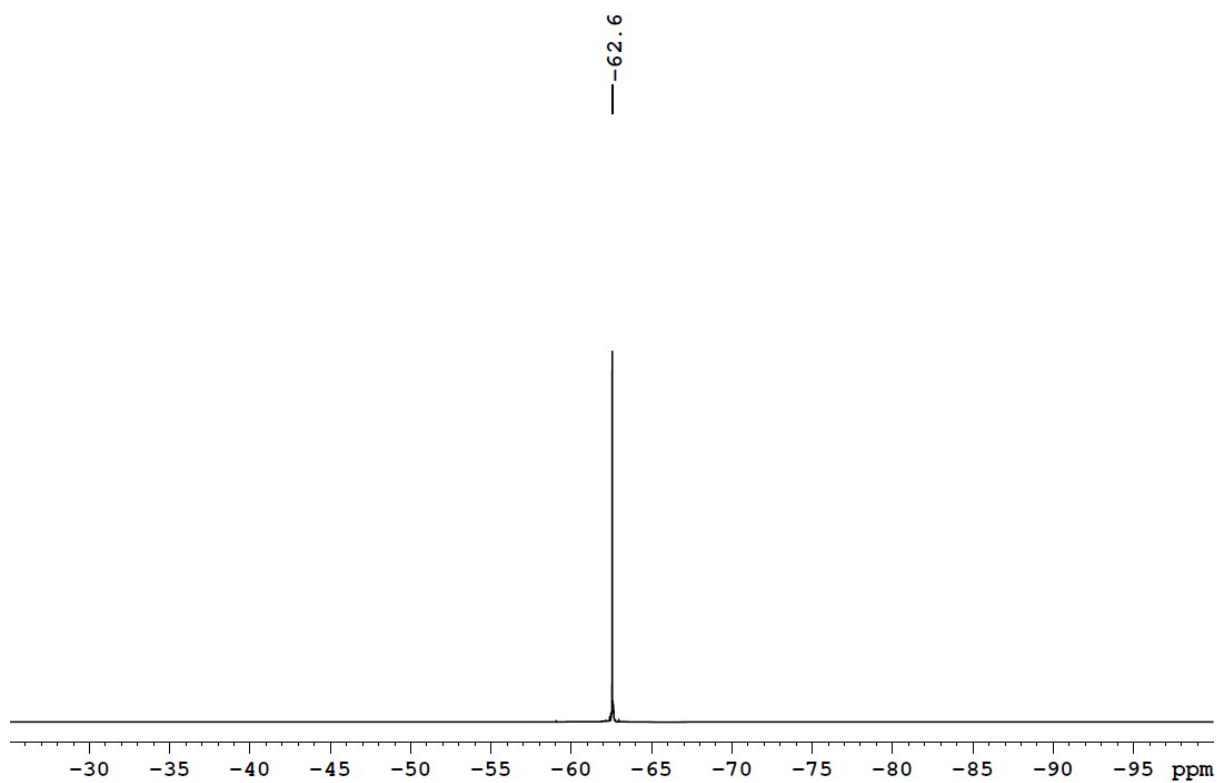
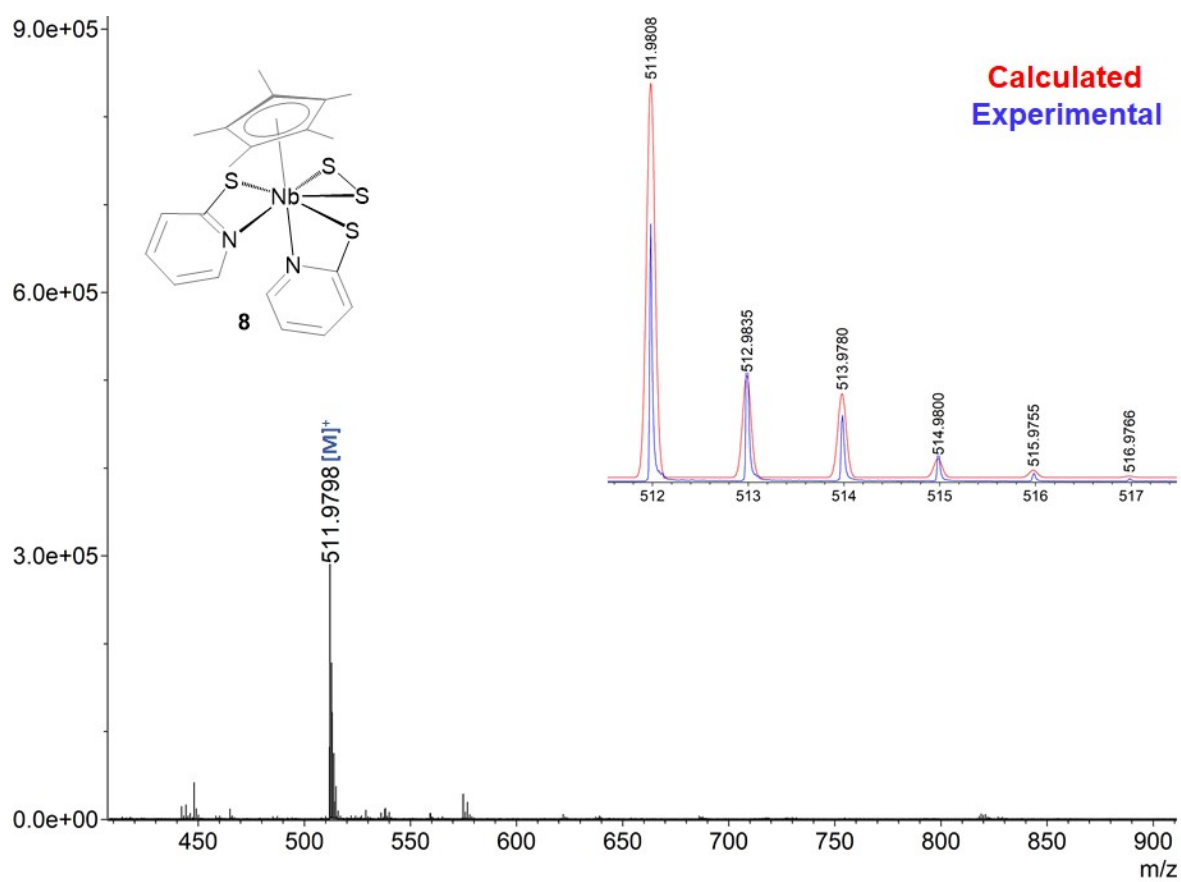


Figure S20.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **7** in  $\text{C}_6\text{D}_6$



**Figure S21.**  $^{19}\text{F}$  NMR spectrum of compound **7** in  $\text{C}_6\text{D}_6$



**Figure S22.** ESI-MS of compound **8**

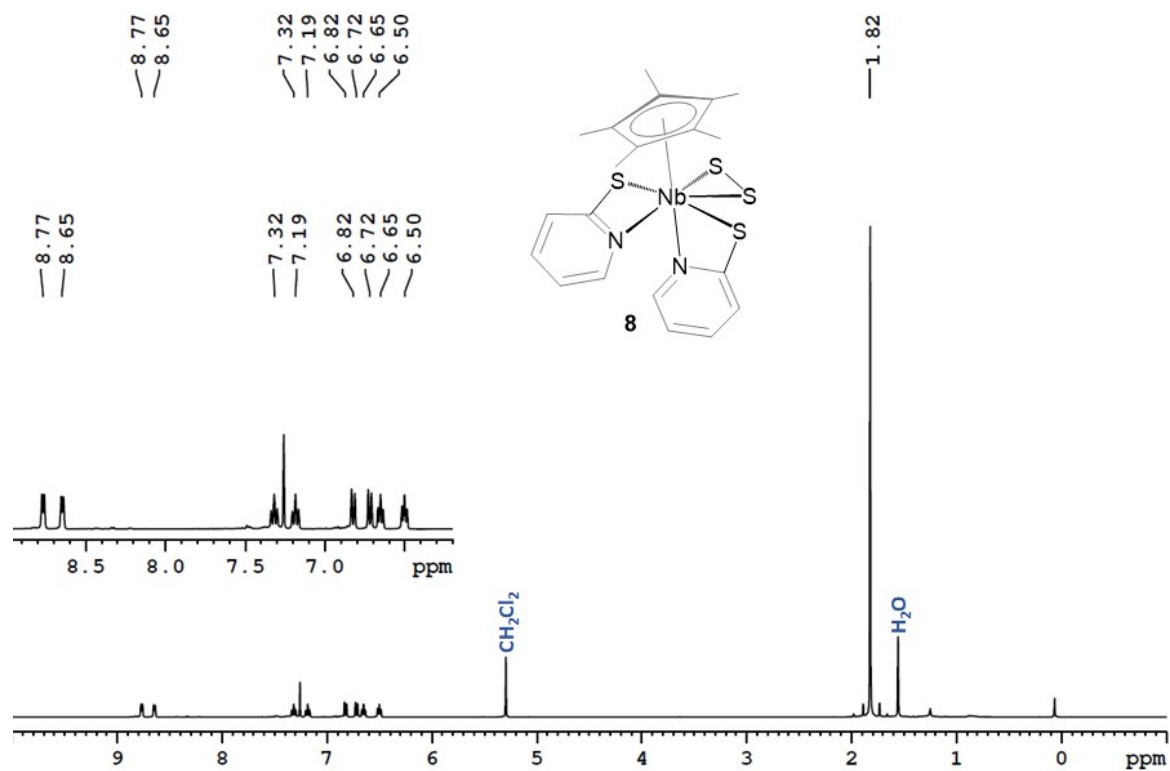


Figure S23.  $^1\text{H}$  NMR spectrum of compound **8** in  $\text{CDCl}_3$

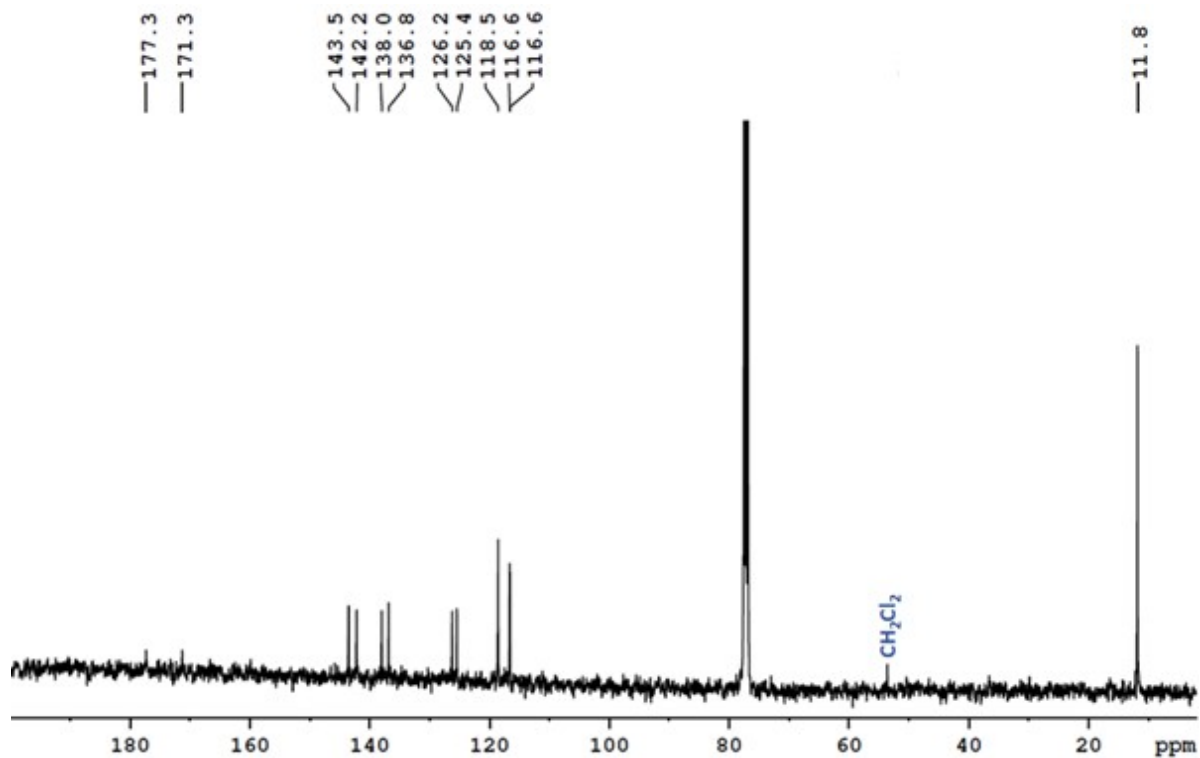


Figure S24.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **8** in  $\text{CDCl}_3$ .

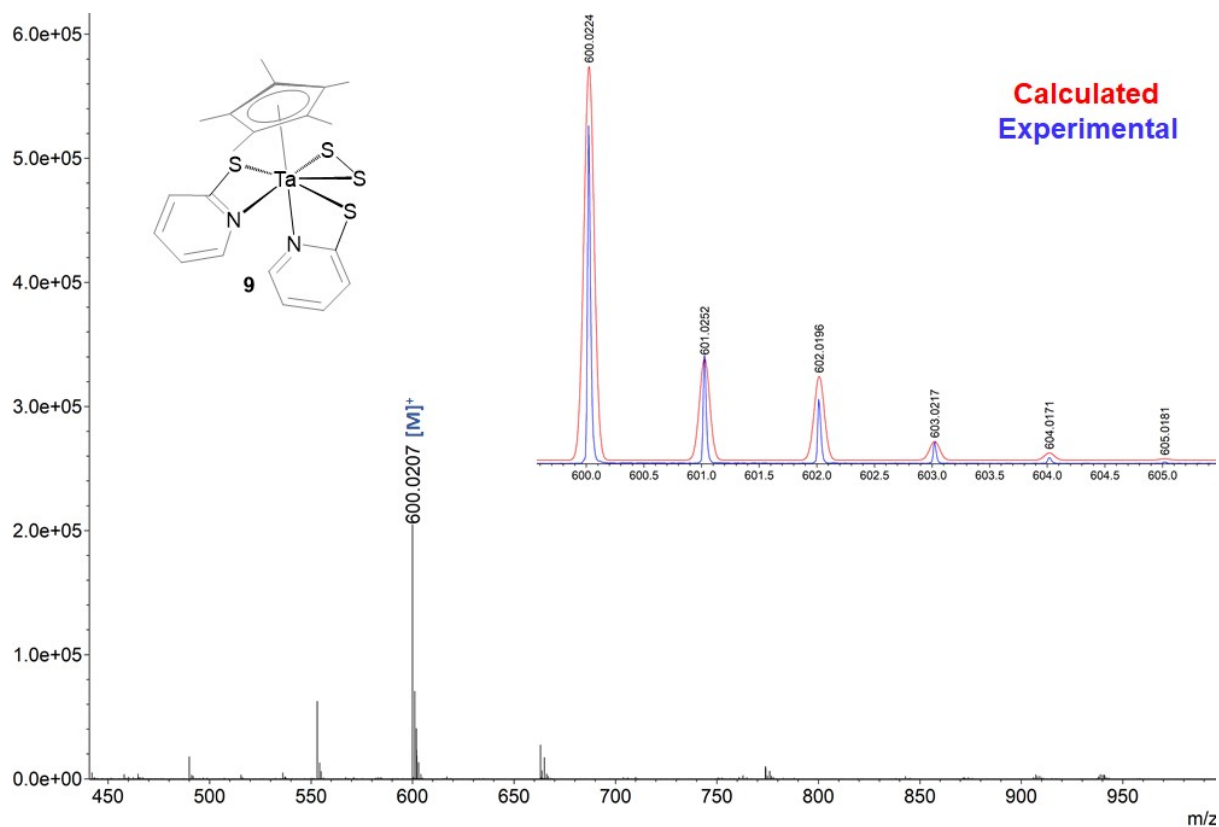


Figure S25. ESI-MS of compound **9**

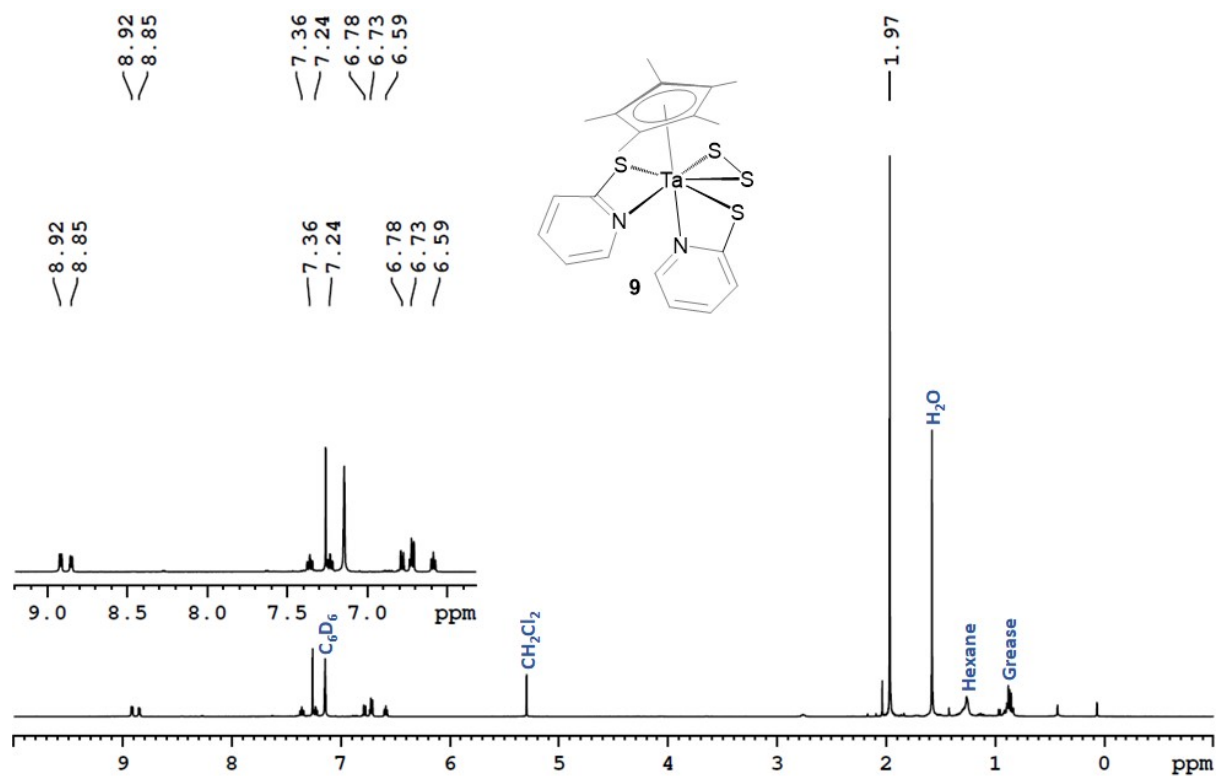


Figure S26.  $^1\text{H}$  NMR spectrum of compound **9** in  $\text{CDCl}_3$



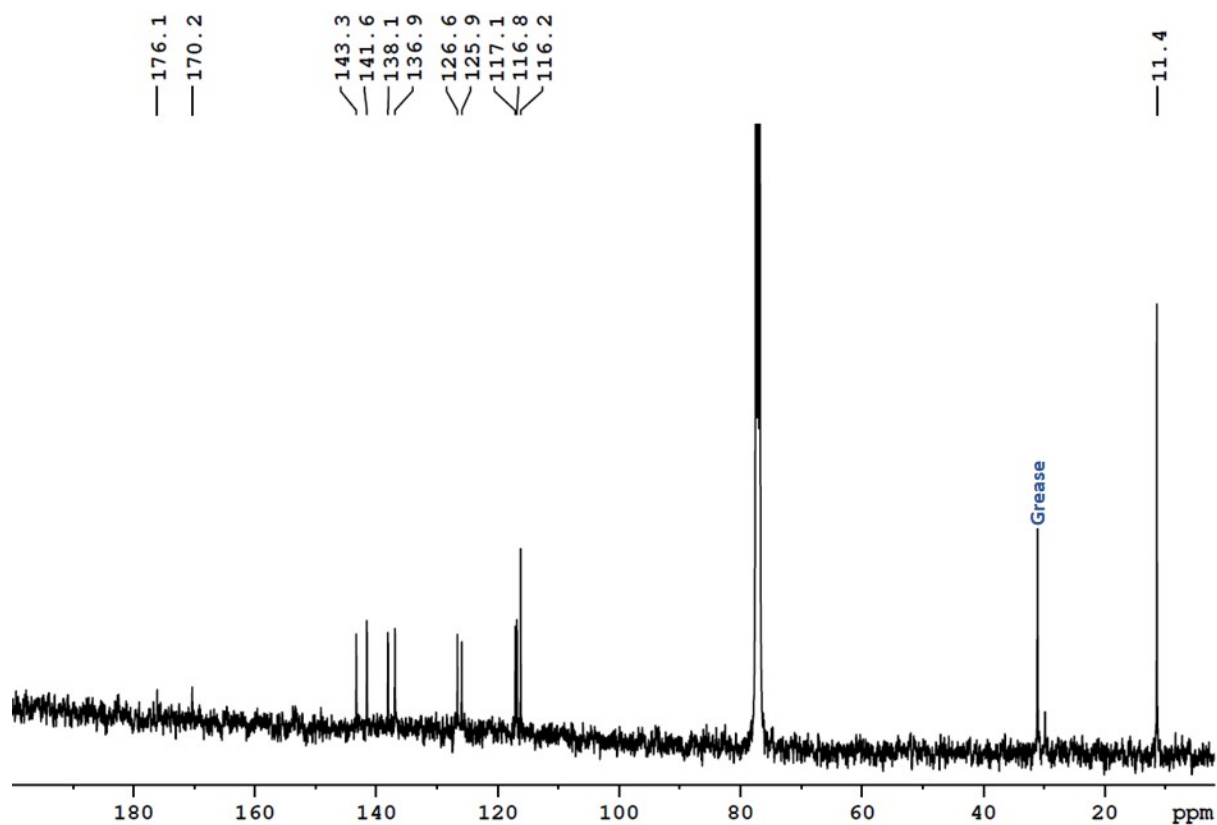


Figure S27.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **9** in  $\text{CDCl}_3$

## II Computational data

**Table S1.** Experimental and DFT calculated (B3LYP/Def2-TZVP) NMR chemical shifts  $\delta$  (ppm) for compounds **3**, **4**, **6** and **7**.

Comp.	<sup>11</sup> B NMR	
	Exp.	Calc.
<b>3</b>	19.6	16.9
<b>4</b>	18	15.8
<b>6</b>	-15.5	-13.6
<b>7</b>	-10.7	-11

**Table S2.** Calculated natural charges (q), natural valence population (Pop) and HOMO–LUMO gaps of complexes **1-3**, **5,6** and **9**.

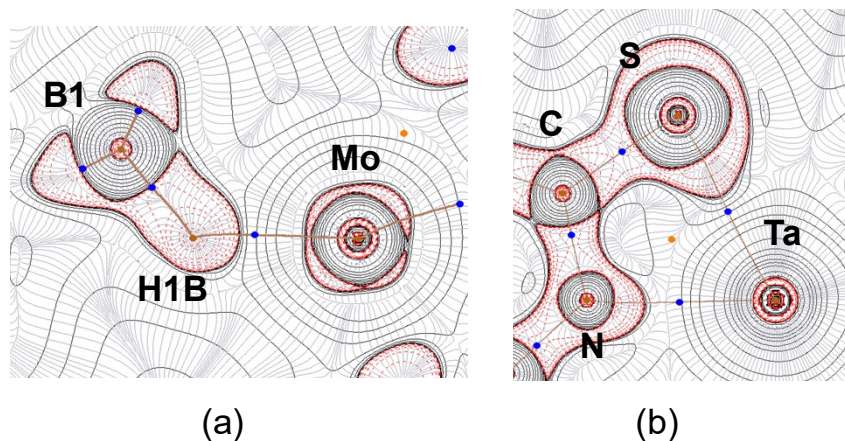
Comp.	q <sub>M</sub>	q <sub>N</sub>	q <sub>B</sub>	Pop(M <sub>val</sub> )	Pop(N <sub>val</sub> )	Pop(B <sub>val</sub> )	$\Delta E_{H-L}$ (eV)
<b>1</b>	-0.725	-0.360		8.707	5.318		2.249
<b>2</b>	-0.754	-0.468	-0.004	8.735	5.441	2.979	2.331
<b>3</b>	-0.755	-0.486	0.261	8.736	5.459	2.708	2.307
<b>5</b>	-0.854	-0.399		6.937	5.364		1.237
<b>6</b>	-1.027	-0.454	0.173	7.037	5.426	2.805	2.014
<b>9</b>	0.006	-0.445		4.853	5.404		1.339

**Table S3.** Selected geometrical parameters and Wiberg bond indices (WBI) of **3** and **6**.

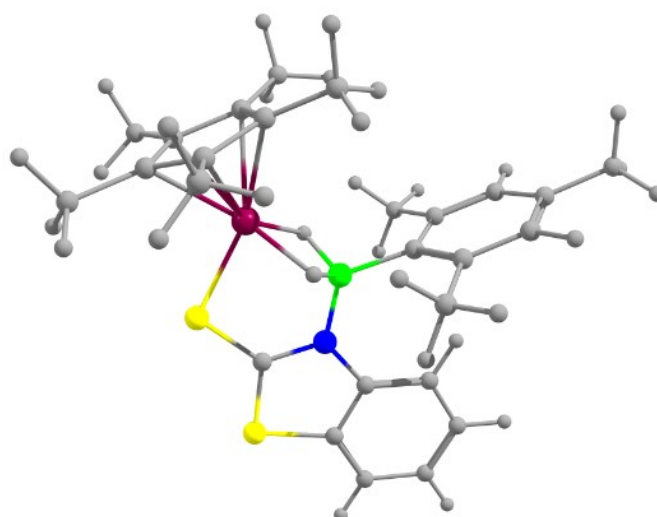
<b>3</b>				<b>6</b>			
	Expt. (Å)	Cal. (Å)	WBI		Expt. (Å)	Cal. (Å)	WBI
Ru1-B1	2.229(10)	2.238	0.455	Mo1-B1	2.768	2.862	0.236
Ru1-H1	1.75(6)	1.767	0.297	Mo1-H1A	2.805	3.034	0.013
Ru1-H2	1.83(7)	1.770	0.293	Mo1-H1B	1.84(6)	1.861	0.326
B1-H1	1.27(6)	1.337	0.561	B1-H1A	1.075	1.262	0.931
B1-H2	1.31(7)	1.340	0.565	B1-H1B	1.23(6)	1.302	0.545

**Table S4.** Topological parameters of **1**, **5** and **9**.

Comp.	Electron density ( $\rho(r)$ )	Total energy density(H(r))	Laplacian of the electron density ( $\nabla^2(r)$ )
<b>1</b>	0.0808	-0.0139	0.313
<b>5</b>	0.1122	-0.0313	0.460
<b>9</b>	0.0652	-0.0133	0.171



**Figure S28.** Contour-line map of the Laplacian of the electron density in the Mo-H-B plane of **6** (a), and Contour-line map of the Laplacian of the electron density in the Ta-N-C-S plane of **9** (b). The solid brown lines are bond paths, whereas the orange and blue spheres indicate the ring and bond-critical points, respectively. Areas of charge concentration [ $\rho(r) < 0$ ] are meant for red lines and areas of charge depletion [ $\rho(r) > 0$ ] are shown by black lines.

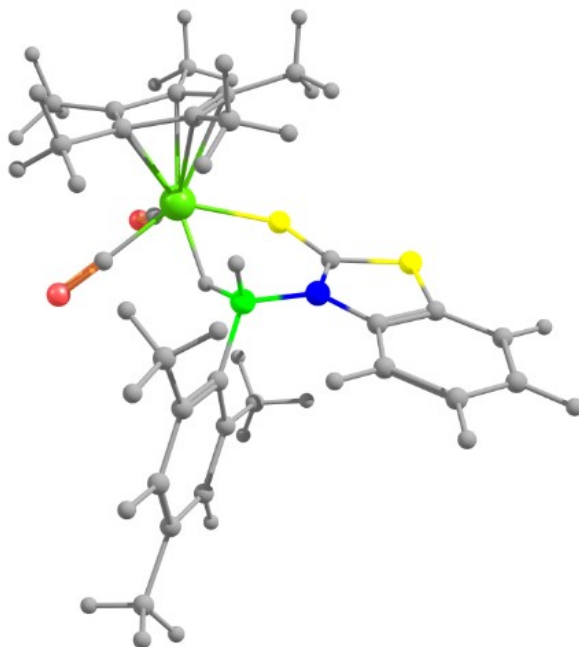


**Figure S29.** Optimized geometry of **3**.

Cartesian coordinates for the calculated structure of **3** (in Å).

Ru	-1.651811000	-0.331053000	-0.002670000	H	-4.291336000	-2.732742000	0.094326000
C	-3.292291000	0.394270000	1.229591000	C	-3.377116000	0.403872000	2.725995000
C	-2.818147000	1.494035000	0.400951000	H	-2.565952000	0.995086000	3.172638000
C	-2.986490000	1.101172000	-0.971177000	H	-3.317322000	-0.611554000	3.140195000
C	-3.584251000	-0.225741000	-1.006726000	H	-4.332222000	0.846966000	3.059196000
C	-3.788323000	-0.647207000	0.362770000	C	-2.342693000	2.828967000	0.889448000
C	-4.470514000	-1.908885000	0.799556000	H	-1.895075000	2.756880000	1.890268000
H	-5.562221000	-1.759518000	0.862765000	H	-3.178894000	3.547431000	0.953433000
H	-4.121324000	-2.236622000	1.788235000	H	-1.582550000	3.257550000	0.222070000

C	-2.701784000	1.954211000	-2.170036000	H	0.278741000	1.305786000	2.721117000
H	-3.599446000	2.529910000	-2.456085000	C	3.149914000	5.408428000	-0.012334000
H	-2.410744000	1.346534000	-3.038168000	H	3.790147000	5.562610000	-0.893306000
H	-1.895293000	2.673316000	-1.972898000	H	3.756587000	5.582986000	0.888295000
C	-4.052067000	-0.946476000	-2.235259000	H	2.369937000	6.188117000	-0.036105000
H	-4.054528000	-2.035226000	-2.088761000	C	2.769679000	-1.479183000	0.004073000
H	-3.407384000	-0.731544000	-3.098766000	C	3.779655000	-0.505773000	0.013050000
H	-5.080082000	-0.644253000	-2.504263000	H	3.522272000	0.551137000	0.015628000
C	1.317674000	1.440540000	-0.000641000	C	5.115662000	-0.912419000	0.019199000
C	1.627304000	2.108725000	1.213492000	H	5.897609000	-0.151182000	0.026266000
C	2.225139000	3.377286000	1.190622000	C	5.466767000	-2.269449000	0.016854000
H	2.460914000	3.867709000	2.140731000	H	6.517503000	-2.563921000	0.021925000
C	2.538815000	4.028260000	-0.007934000	C	4.474421000	-3.250712000	0.008719000
C	2.250772000	3.358492000	-1.202859000	H	4.732804000	-4.310743000	0.007579000
H	2.507739000	3.833514000	-2.155325000	C	3.137461000	-2.845852000	0.002680000
C	1.654029000	2.089432000	-1.218471000	C	0.679793000	-2.461566000	-0.006277000
C	1.414016000	1.423742000	-2.555707000	S	1.719546000	-3.870726000	-0.005554000
H	0.341051000	1.260965000	-2.743908000	S	-1.004980000	-2.536923000	-0.006126000
H	1.895445000	0.434533000	-2.610905000	N	1.372005000	-1.279894000	-0.002495000
H	1.812264000	2.037050000	-3.376482000	B	0.551801000	0.034675000	0.000822000
C	1.356060000	1.466263000	2.555992000	H	-0.269240000	-0.017544000	-1.057468000
H	1.734849000	2.093716000	3.375257000	H	-0.266463000	-0.026787000	1.056894000
H	1.834881000	0.477819000	2.639908000				

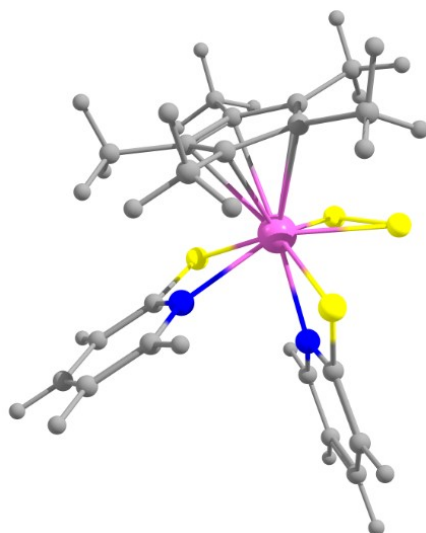


**Figure S30.** Optimized geometry of **6**.

Cartesian coordinates for the calculated structure of **6** (in Å)

C	-3.512141000	-1.297527000	1.226157000	H	-3.385493000	-0.290232000	1.619416000
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C	-4.638527000	-2.059178000	1.537719000	C	3.829439000	-0.711088000	0.284238000
H	-5.395455000	-1.639379000	2.202180000	C	4.785271000	-1.411212000	-0.639137000
C	-4.818025000	-3.347587000	1.009542000	H	5.168285000	-0.736655000	-1.415844000
H	-5.709340000	-3.921988000	1.266880000	H	4.311224000	-2.264756000	-1.143349000
C	-3.864941000	-3.904022000	0.154541000	H	5.652277000	-1.798696000	-0.076593000
H	-3.996657000	-4.905163000	-0.258138000	C	2.637794000	-2.851173000	1.189420000
C	-2.734884000	-3.143857000	-0.156228000	H	3.461215000	-3.352807000	1.725914000
C	-2.548815000	-1.843916000	0.366212000	H	2.585200000	-3.284307000	0.180293000
C	-0.617999000	-2.024828000	-0.850158000	H	1.703237000	-3.099910000	1.709572000
C	-2.060195000	1.368835000	0.076711000	C	1.366470000	-0.671438000	3.149833000
C	-2.453792000	2.285857000	1.091427000	H	0.725837000	-1.543499000	2.962420000
C	-3.422463000	3.264112000	0.825896000	H	0.709690000	0.183895000	3.354935000
H	-3.711510000	3.952245000	1.626995000	H	1.944115000	-0.874566000	4.068404000
C	-4.023563000	3.394266000	-0.430845000	C	2.677603000	2.142491000	2.480334000
C	-3.619381000	2.507896000	-1.433396000	H	1.644079000	2.239580000	2.839615000
H	-4.060673000	2.595241000	-2.431615000	H	2.909484000	3.037905000	1.889345000
C	-2.656804000	1.514357000	-1.205144000	H	3.337494000	2.147675000	3.364997000
C	-2.282645000	0.620791000	-2.366826000	C	4.871166000	1.693891000	0.186328000
H	-1.196637000	0.456043000	-2.431031000	H	5.768798000	1.662838000	0.827784000
H	-2.612809000	1.062980000	-3.317419000	H	4.472494000	2.716475000	0.224201000
H	-2.757818000	-0.371369000	-2.289082000	H	5.193915000	1.503312000	-0.845833000
C	-1.853899000	2.261669000	2.482216000	C	1.486757000	2.215433000	-0.663510000
H	-2.319206000	3.030146000	3.115926000	C	2.523117000	0.637781000	-2.119983000
H	-0.770896000	2.459410000	2.456488000	B	-0.950299000	0.240234000	0.378003000
H	-1.982615000	1.287433000	2.979082000	N	-1.358355000	-1.234748000	-0.054562000
C	-5.036190000	4.479097000	-0.704651000	O	1.327872000	3.351514000	-0.874932000
H	-5.732609000	4.187001000	-1.504065000	O	3.020190000	0.855476000	-3.157613000
H	-4.540936000	5.410603000	-1.026674000	S	0.884034000	-1.659487000	-1.575286000
H	-5.624063000	4.717484000	0.194024000	S	-1.372004000	-3.577197000	-1.162139000
C	2.872424000	-1.372736000	1.144978000	Mo	1.820138000	0.303239000	-0.339719000
C	2.296344000	-0.400155000	2.007740000	H	-0.573713000	0.197774000	1.521902000
C	2.875972000	0.882051000	1.687264000	H	-0.014505000	0.593128000	-0.454911000
C	3.861043000	0.683397000	0.649898000				



**Figure S31.** Optimized geometry of **9**

Cartesian coordinates for the calculated structure of **9** (in Å).

Ta	0.359261000	-0.216715000	-0.110259000	H	2.287869000	2.081819000	-2.480497000
S	-0.475472000	1.152900000	-2.157486000	H	3.969852000	1.878811000	-1.932674000
S	-0.747374000	-1.104704000	2.111027000	H	3.075394000	0.491858000	-2.604195000
S	0.958205000	-1.652328000	-2.040084000	C	1.079294000	1.786354000	2.798983000
S	0.967527000	-2.625164000	-0.208190000	H	0.329557000	2.562487000	2.597436000
N	-1.273558000	1.417864000	0.263724000	H	0.619194000	1.032392000	3.452473000
N	-1.658743000	-1.233731000	-0.288945000	H	1.895550000	2.263719000	3.368134000
C	1.721228000	1.860626000	0.266701000	C	3.885226000	-1.144637000	-0.364293000
C	-1.986841000	-1.570678000	0.987595000	H	4.011621000	-1.960216000	0.356573000
C	-3.189241000	-2.242390000	1.266314000	H	3.544181000	-1.580728000	-1.317180000
H	-3.431897000	-2.505440000	2.296023000	H	4.869840000	-0.678185000	-0.538023000
C	-2.002456000	1.871362000	1.304484000	C	-3.193480000	3.390438000	-0.129366000
H	-1.802328000	1.392450000	2.263966000	H	-3.947440000	4.166545000	-0.278135000
C	2.510994000	1.038674000	-0.602981000	C	-2.966663000	2.860457000	1.152818000
C	-2.459282000	2.918894000	-1.208316000	H	-3.534539000	3.201782000	2.017976000
H	-2.613970000	3.295503000	-2.219818000	C	2.630315000	-1.001775000	2.553531000
C	2.920138000	-0.115678000	0.128423000	H	2.572117000	-2.040876000	2.196576000
C	2.356658000	-0.036247000	1.441823000	H	3.643501000	-0.839223000	2.958935000
C	-4.026507000	-2.572041000	0.205801000	H	1.918413000	-0.889313000	3.381641000
H	-4.961849000	-3.102890000	0.395965000	C	-3.665080000	-2.229521000	-1.107230000
C	-2.468780000	-1.553266000	-1.316652000	H	-4.300135000	-2.484129000	-1.955288000
H	-2.115750000	-1.257512000	-2.304999000	C	1.305489000	3.271923000	-0.019801000
C	1.624147000	1.190599000	1.534731000	H	0.999332000	3.399500000	-1.067194000
C	-1.489210000	1.920959000	-0.984710000	H	0.475374000	3.599166000	0.620293000
C	2.980435000	1.392113000	-1.979887000	H	2.151755000	3.955467000	0.165392000