***SUPPORTING INFORMATION***

# Synthesis, Structure and Bonding of the Tungstaboranes [Cp*W(CO)$_2$B$_3$H$_8$] and [(Cp*W)$_3$(CO)$_2$B$_4$H$_7$]

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## Table of contents

### I. Spectroscopic details



### II. Computational Data

## I. Spectroscopic Details

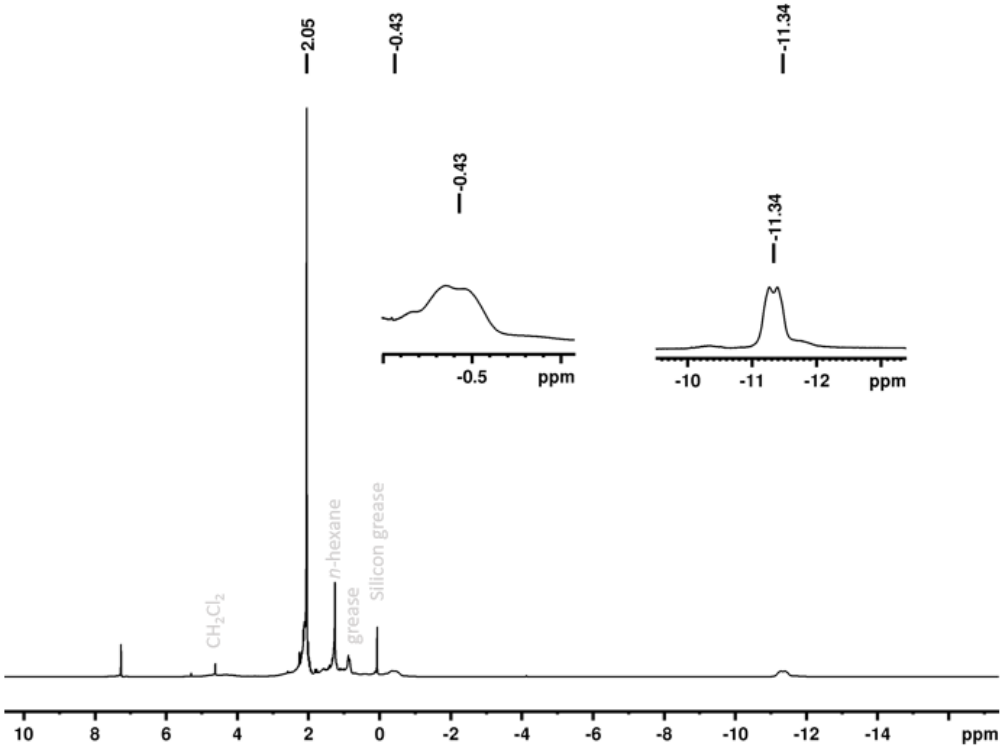


**Figure S1**. $^{1}$H NMR spectrum of **1** in $CDCl_3$.

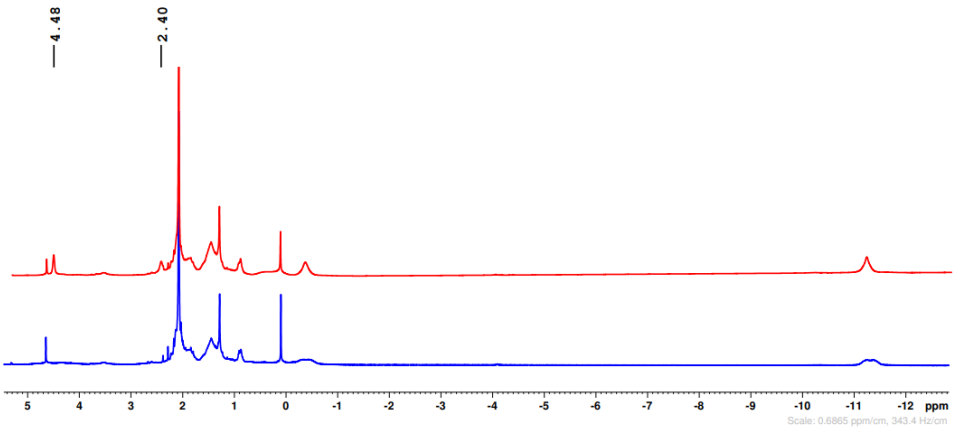


**Figure S2**. Stacked $^{1}$H (bottom; blue) and $^{1}$H{$^{11}$B} NMR (top; red) spectrum of **1** in $CDCl_3$.

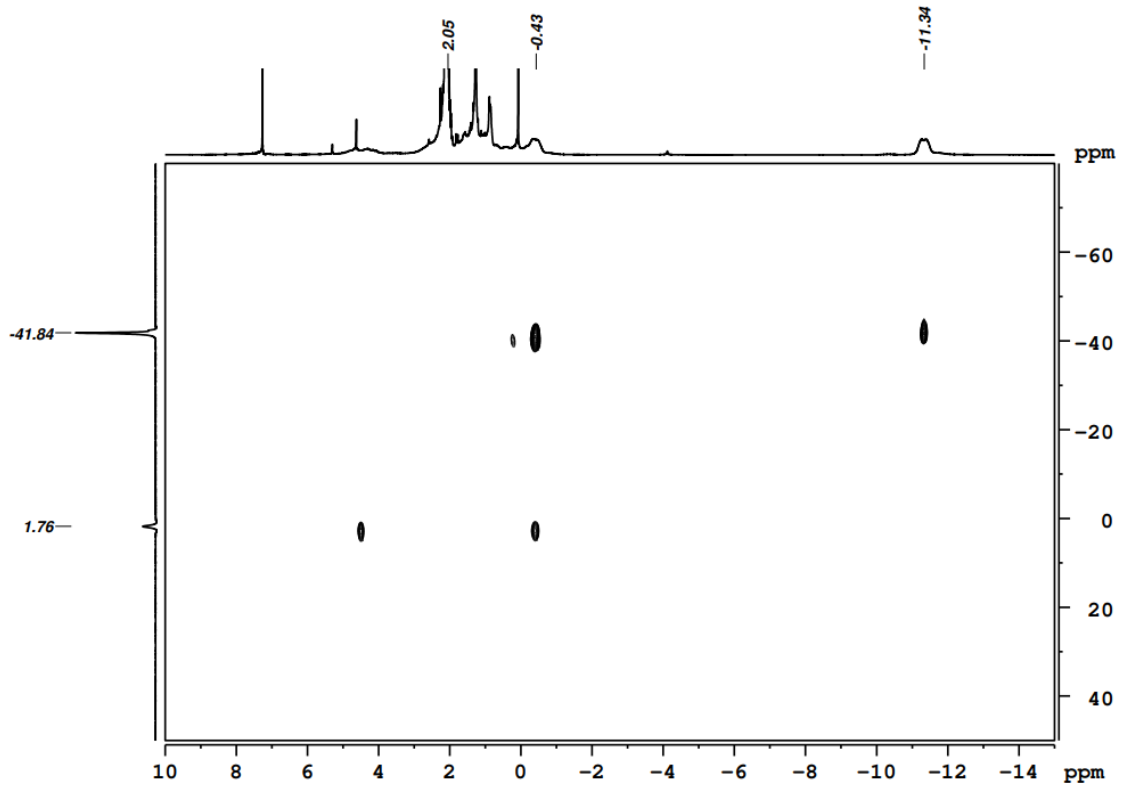


**Figure S3**. $^{1}H$-$^{11}B\{^{1}H\}$ HSQC NMR spectrum of **1** in $CDCl_3$.

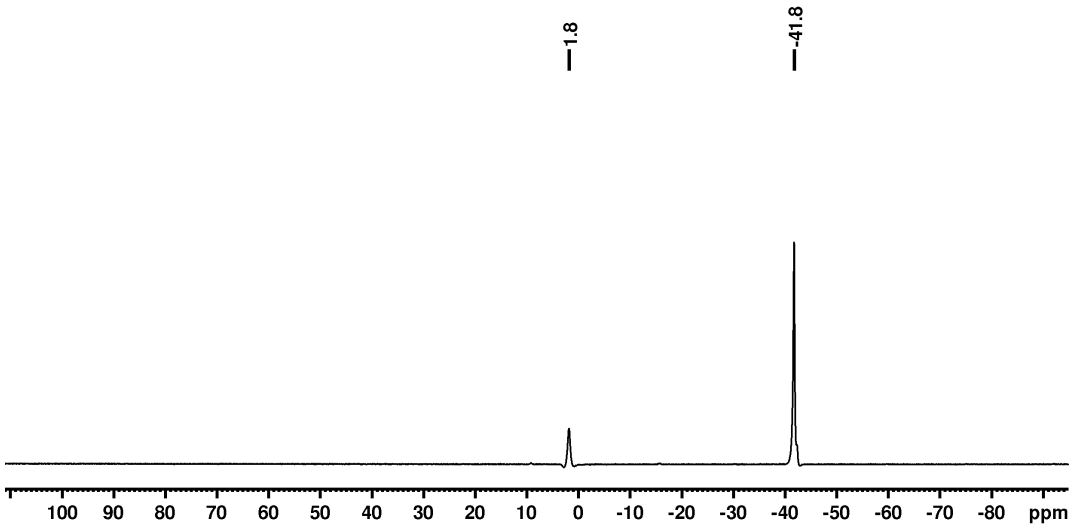


**Figure S4**. $^{11}B\{^{1}H\}$ NMR spectrum of **1** in $C_6D_6$.

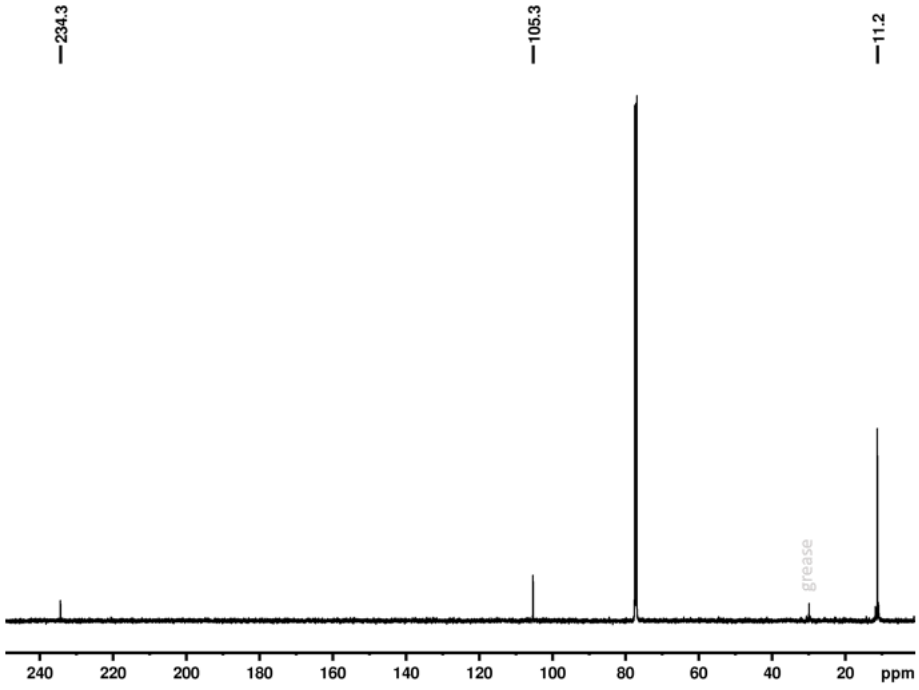


**Figure S5**. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

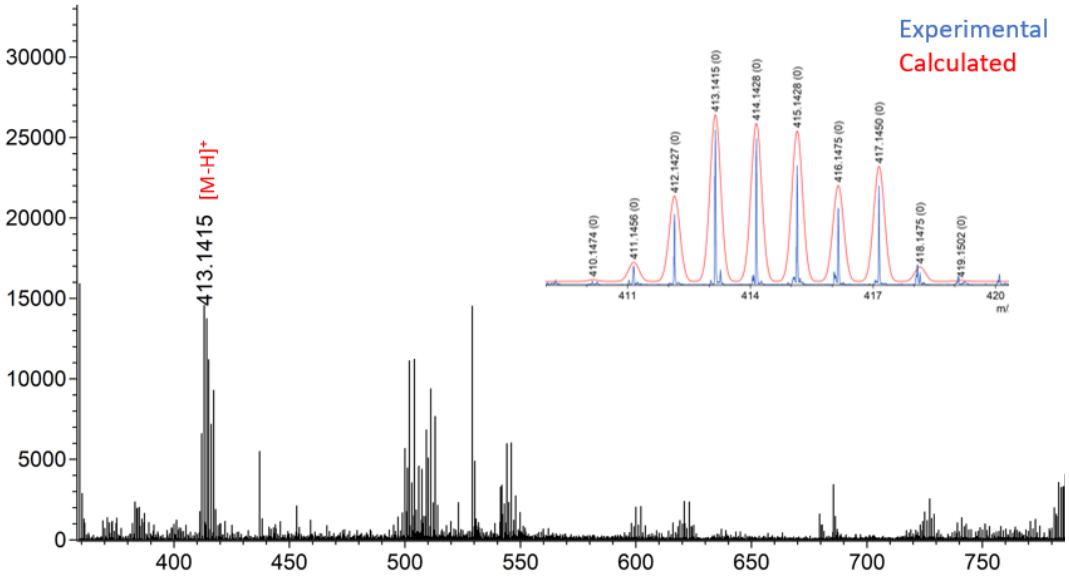


**Figure S6**. ESI-MS spectrum of **1** in $CH_2Cl_2$ and MeOH mixture.

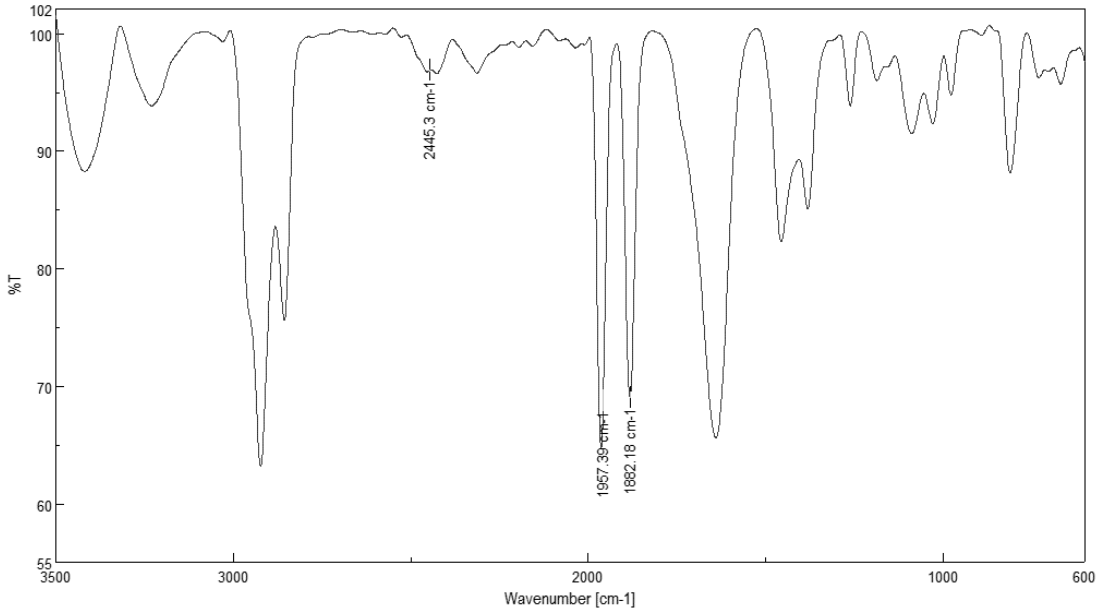


**Figure S7**. IR spectrum of **1** in $CH_2Cl_2$.

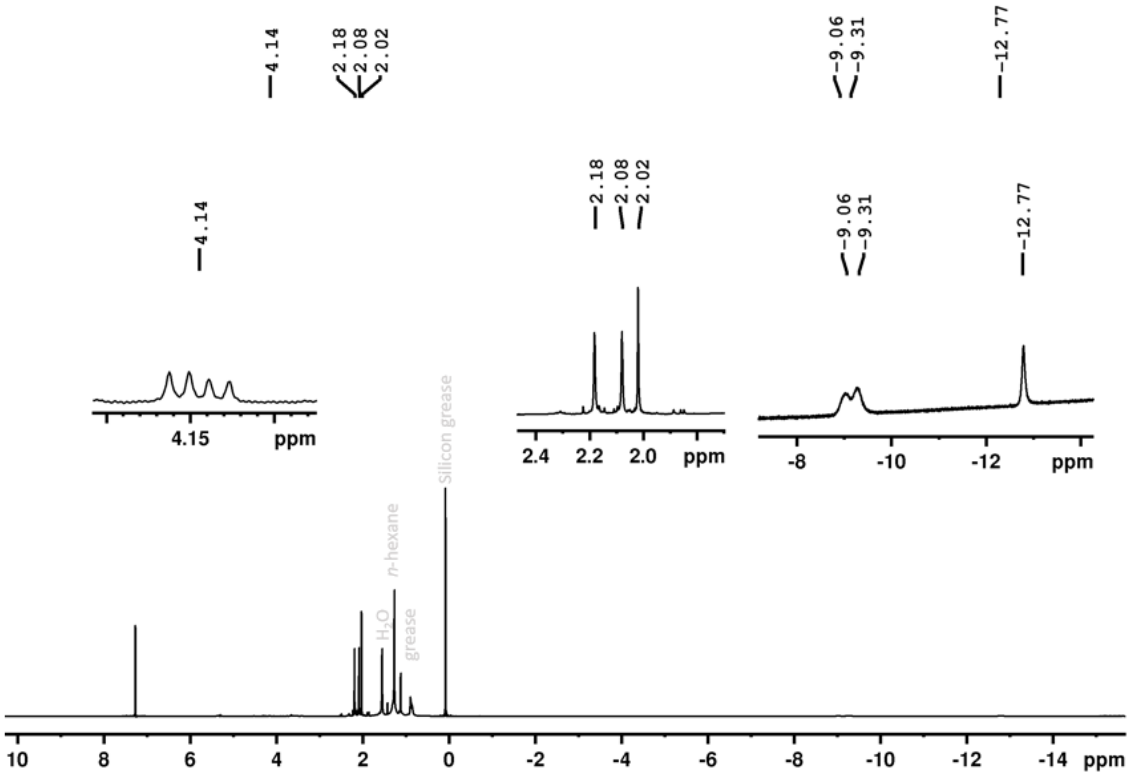


**Figure S8**. $^1$H NMR spectrum of **4** in $CDCl_3$.

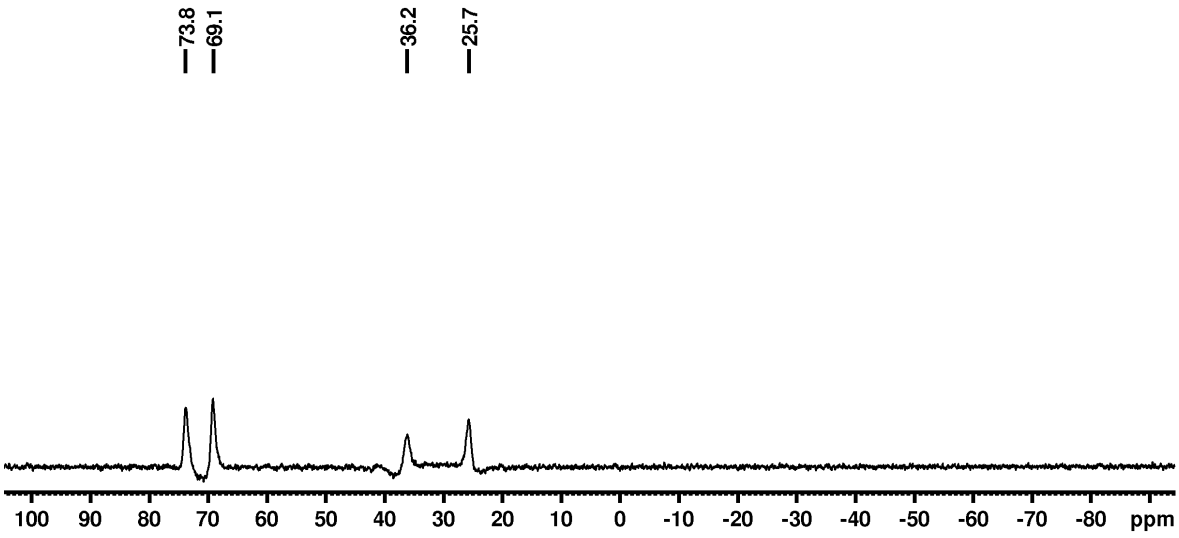


**Figure S9**. $^{11}B\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

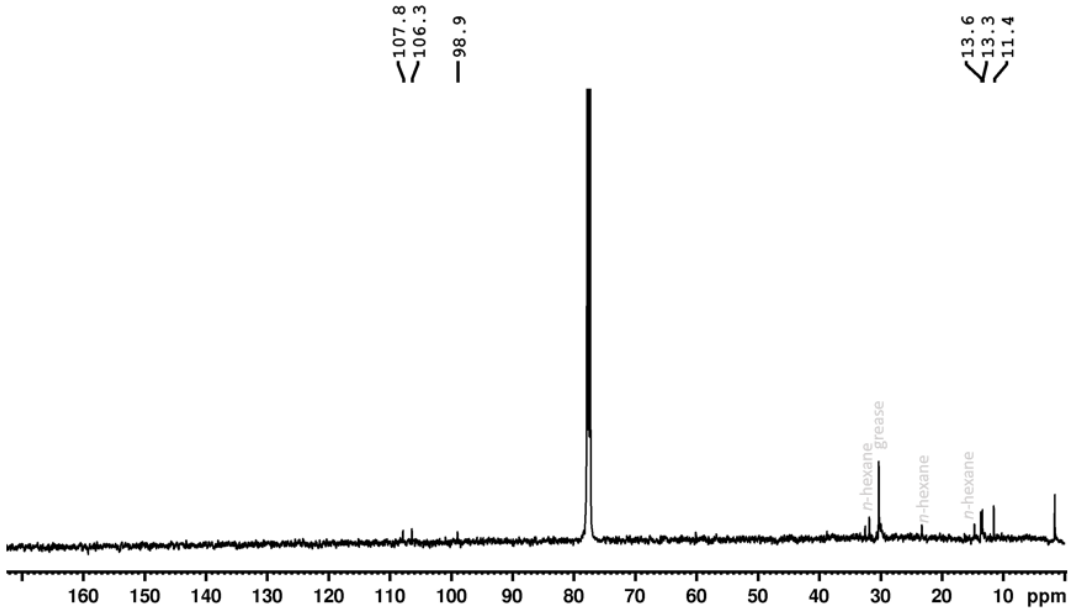


**Figure S10**. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

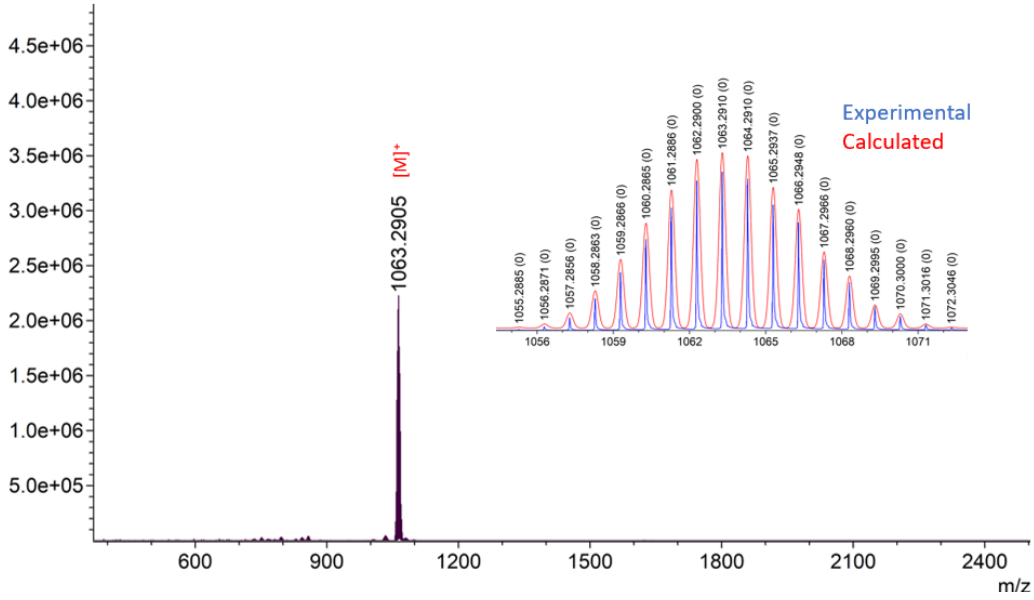


**Figure S11**. ESI-MS spectrum of **4** in $CH_2Cl_2$ and MeOH mixture.

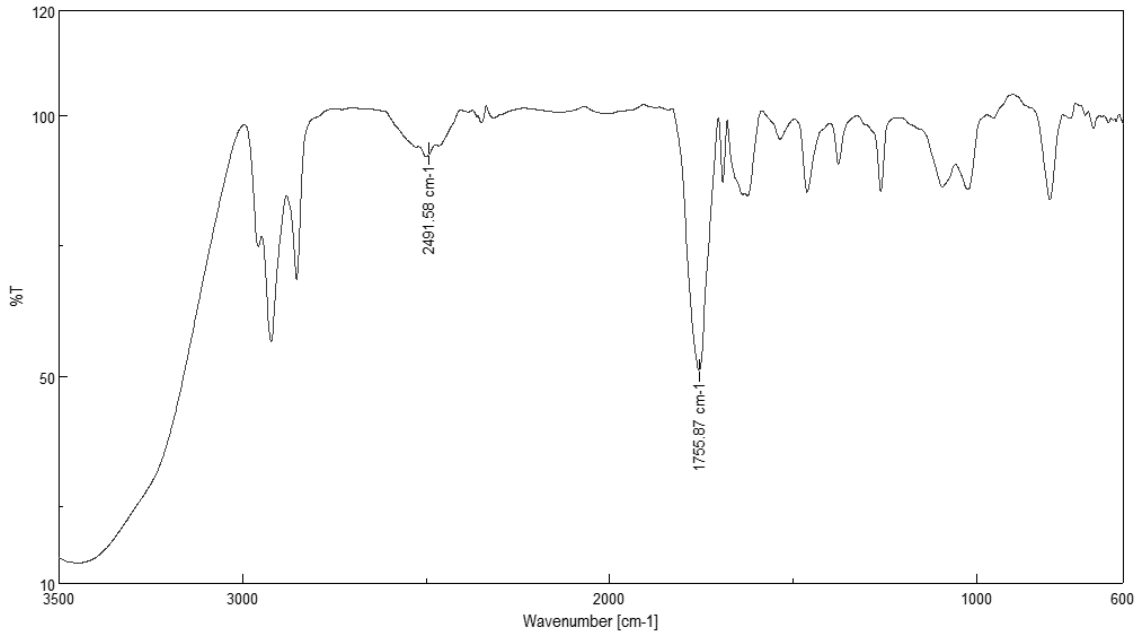


**Figure S12**. IR spectrum of **4** in $CH_2Cl_2$.

## II. Computational Data

**Table S1**. Selected geometrical parameters and Wiberg bond indices (WBI) of **1'-4'.**

| **1'** | | | | **2'** | | | |
|---|---|---|---|---|---|---|---|
| | Expt. | Cal. | WBI | | Expt. | Cal. | WBI |
| W1-B1 | 2.511 | 2.568 | 0.313 | Mo1-B1 | 2.548 | 2.575 | 0.324 |
| W1-B2 | 2.511 | 2.568 | 0.313 | Mo1-B2 | 2.544 | 2.575 | 0.323 |
| B1-B2 | 1.705 | 1.799 | 0.536 | B1-B2 | 1.732 | 1.797 | 0.538 |
| B2-B3 | 1.794 | 1.799 | 0.536 | B2-B3 | 1.777 | 1.797 | 0.538 |
| B1-B3 | 1.802 | 1.723 | 0.739 | B1-B3 | 1.797 | 1.725 | 0.728 |
| **3'** | | | | **4'** | | | |
| | Expt. | Cal. | WBI | | Expt. | Cal. | WBI |
| Cr1-B1 | _ | 2.507 | 0.323 | W1-W2 | 2.961 | 3.048 | 0.391 |
| Cr1-B2 | _ | 2.507 | 0.323 | W1-W3 | 2.948 | 2.938 | 0.545 |
| B1-B2 | _ | 1.792 | 0.542 | W2-W3 | 2.845 | 2.850 | 0.738 |
| B2-B3 | _ | 1.792 | 0.542 | W1-B1 | 2.336 | 2.395 | 0.408 |
| B1-B3 | _ | 1.723 | 0.724 | B1-B2 | 1.714 | 1.743 | 0.442 |

**Table S2**. Experimentally observed and calculated $^{11}$B chemical shifts of **1'-4'**.

| $^{11}$B- NMR value (ppm) | 1' | 2' | 3' | 4' |
|---|---|---|---|---|
| Experimental | 1.8,<br>-41.8 | 1.0,<br>-39.1 | _ | 25.7,<br>36.2,<br>69.1,<br>73.8 |
| Theoretical | -0.8,<br>-47.2, | -0.1,<br>-45.0 | -1.7,<br>-45.6 | 11.4,<br>19.1<br>61.7<br>73.1 |

**Table S3**. Calculated natural charges ($q$), natural valence population (Pop) and HOMO–LUMO gaps of **1'-3'**.

| Cluster | $Q$ | Pop | HOMO (eV) | LUMO (eV) | $\Delta E_{H\text{-}L}$ (eV) |
|---|---|---|---|---|---|
| **1'** | -0.466 (W1) | 6.459 (W1) | -6.046 | -2.278 | 3.768 |
| | -0.379 (B1) | 3.354 (B1) | | | |
| | -0.379 (B2) | 3.354 (B2) | | | |
| | -0.188 (B3) | 3.177 (B3) | | | |
| **2'** | -0.953 (Mo1) | 6.946 (Mo1) | -6.241 | -2.419 | 3.822 |
| | -0.347 (B1) | 3.220 (B1) | | | |
| | -0.347 (B2) | 3.220 (B2) | | | |
| | -0.190 (B3) | 3.179 (B3) | | | |
| **3'** | -1.571 (Cr1) | 7.552 (Cr1) | -6.538 | -2.376 | 4.161 |
| | -0.322 (B1) | 3.296 (B1) | | | |
| | -0.322 (B2) | 3.296 (B2) | | | |
| | -0.195 (B3) | 3.183 (B3) | | | |
| **4'** | -0.349 (W1) | 6.401 (W1) | -4.991 | -2.278 | 2.713 |
| | -0.234 (W2) | 6.202 (W2) | | | |
| | -0.177 (W3) | 6.152 (W3) | | | |
| | -0.213 (B1) | 3.166 (B1) | | | |

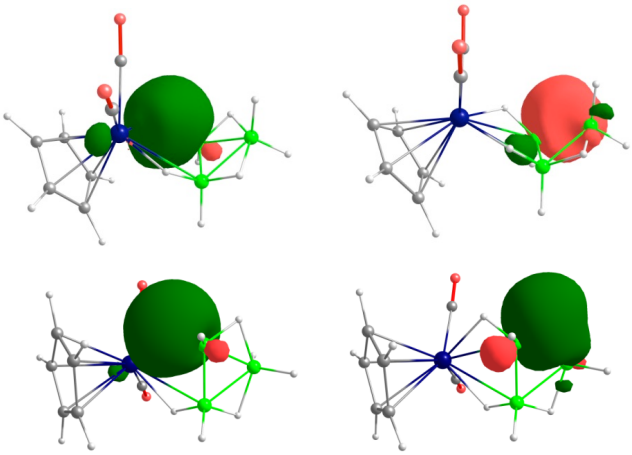

**Figure S13.** Selected natural bonding orbitals of **1'**. Isosurfaces are plotted at an isovalue of ±0.04 $(e/bohr^3)^{1/2}$.

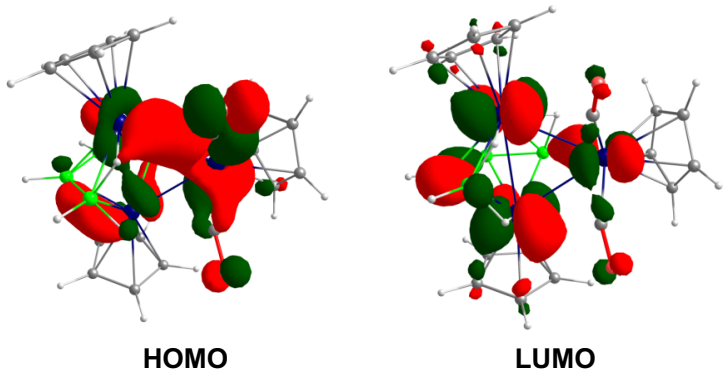


**Figure S14.** Selected molecular orbitals of **4'**. Isosurfaces are plotted at an isovalue of ±0.04 $(e/bohr^3)^{1/2}$.

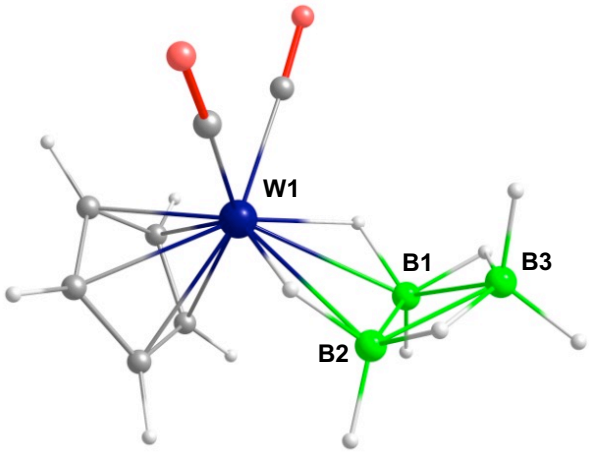


**Figure S15.** Optimized geometry of **1'**.
**Total Energy** = -566.9331 a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.537367000 | 1.485084000 | -1.215974000 | H | -2.807120000 | -1.329289000 | 1.401082000 |
| C | 1.727507000 | -1.584171000 | 0.703579000 | H | -3.684125000 | -0.195172000 | 0.000036000 |
| C | 2.285689000 | 0.539209000 | 0.002952000 | H | -4.063096000 | -2.206852000 | -0.001576000 |
| C | -0.539732000 | 1.483586000 | 1.216365000 | B | -1.728650000 | -1.638429000 | -0.863201000 |
| C | 1.729107000 | -1.581741000 | -0.706303000 | H | -2.807383000 | -1.326635000 | -1.403130000 |
| C | 2.060434000 | -0.275934000 | 1.153267000 | H | -1.101229000 | -0.626680000 | -1.361978000 |
| C | 2.062944000 | -0.272006000 | -1.150633000 | H | -1.355819000 | -2.655613000 | -1.354181000 |
| B | -1.728499000 | -1.640048000 | 0.860338000 | W | 0.032369000 | 0.020101000 | -0.000043000 |
| B | -3.274371000 | -1.314484000 | -0.000784000 | H | 1.481534000 | -2.425457000 | 1.331512000 |
| O | -0.823558000 | 2.346590000 | 1.923695000 | H | 2.180319000 | 0.026883000 | 2.180582000 |
| O | -0.820125000 | 2.348913000 | -1.922677000 | H | 2.624237000 | 1.561882000 | 0.005033000 |
| H | -1.100919000 | -0.629421000 | 1.361143000 | H | 2.184840000 | 0.034439000 | -2.176611000 |
| H | -1.355510000 | -2.658026000 | 1.349561000 | H | 1.484533000 | -2.420904000 | -1.337747000 |

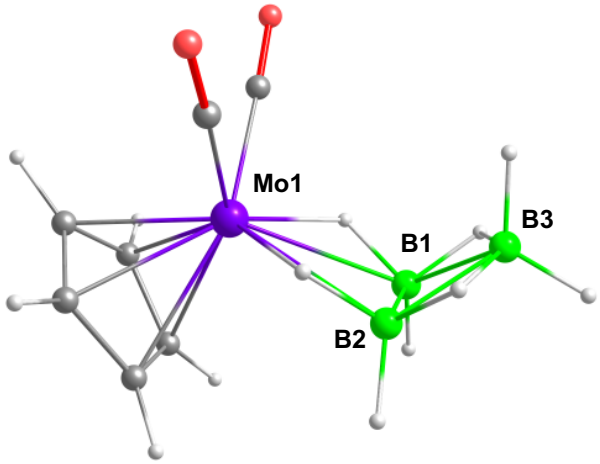


**Figure S16.** Optimized geometry of **2'.**
Total Energy = -568.0540 a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.502748000 | 1.474496000 | 1.221332000 | H | 3.653868000 | -0.085131000 | 0.000317000 |
| C | -1.720322000 | -1.587019000 | -0.703322000 | H | 4.117230000 | -2.077677000 | 0.000167000 |
| C | -2.289754000 | 0.530678000 | -0.001466000 | B | 1.760499000 | -1.605044000 | 0.862088000 |
| C | 0.502564000 | 1.475759000 | -1.220615000 | H | 2.827672000 | -1.262199000 | 1.405278000 |
| C | -1.720928000 | -1.585330000 | 0.705744000 | H | 1.085636000 | -0.624689000 | 1.351620000 |
| C | -2.061078000 | -0.280843000 | -1.150962000 | H | 1.418655000 | -2.634505000 | 1.350884000 |
| C | -2.061979000 | -0.278145000 | 1.150027000 | Mo | -0.044616000 | 0.017195000 | -0.000269000 |
| B | 1.760827000 | -1.603890000 | -0.863191000 | H | -1.470354000 | -2.426293000 | -1.332411000 |
| B | 3.290011000 | -1.220482000 | 0.000241000 | H | -2.181299000 | 0.023278000 | -2.177936000 |
| O | 0.775439000 | 2.336812000 | -1.929016000 | H | -2.628979000 | 1.553309000 | -0.002763000 |
| O | 0.775471000 | 2.334814000 | 1.930718000 | H | -2.182809000 | 0.028417000 | 2.176205000 |
| H | 1.086943000 | -0.622519000 | -1.352368000 | H | -1.471370000 | -2.423084000 | 1.337030000 |
| H | 1.418515000 | -2.632700000 | -1.353075000 | | | | |
| H | 2.828703000 | -1.261890000 | -1.405394000 | | | | |

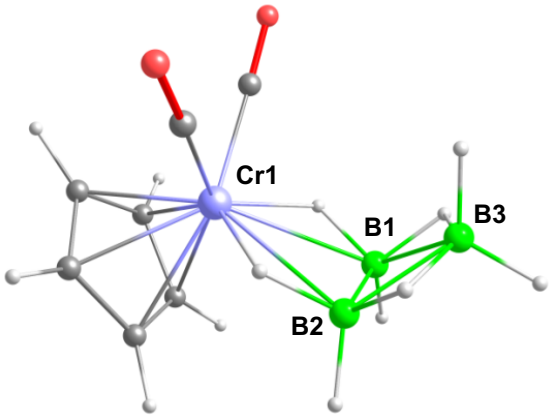


**Figure S17.** Optimized geometry of **3'**.
Total Energy = -1544.2724 a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.344048000 | 1.386210000 | 1.193258000 | H | 2.785397000 | -0.961493000 | -1.410427000 |
| C | -1.494942000 | -1.624363000 | -0.702129000 | H | 3.443479000 | 0.318785000 | 0.000440000 |
| C | -2.211973000 | 0.441923000 | -0.001081000 | H | 4.172067000 | -1.590066000 | -0.001017000 |
| C | 0.342685000 | 1.386749000 | -1.192817000 | B | 1.776046000 | -1.442971000 | 0.860856000 |
| C | -1.495761000 | -1.623069000 | 0.704451000 | H | 2.785427000 | -0.963349000 | 1.409611000 |
| C | -1.928398000 | -0.348791000 | -1.148060000 | H | 0.942205000 | -0.593641000 | 1.307813000 |
| C | -1.929752000 | -0.346746000 | 1.147584000 | H | 1.567044000 | -2.507986000 | 1.349911000 |
| B | 1.776083000 | -1.442035000 | -0.862262000 | Cr | -0.077759000 | 0.010085000 | 0.000149000 |
| B | 3.233842000 | -0.855788000 | -0.000488000 | H | -1.172052000 | -2.438003000 | -1.330604000 |
| O | 0.563225000 | 2.234311000 | -1.927883000 | H | -2.054154000 | -0.047609000 | -2.175294000 |
| O | 0.565550000 | 2.233672000 | 1.928147000 | H | -2.597479000 | 1.448343000 | -0.002169000 |
| H | 0.941768000 | -0.592657000 | -1.307992000 | H | -2.056575000 | -0.043710000 | 2.174143000 |
| H | 1.567139000 | -2.506473000 | -1.352648000 | H | -1.173548000 | -2.435550000 | 1.334780000 |

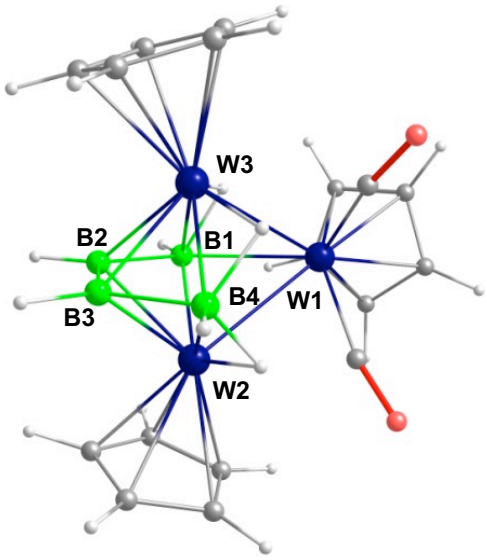


**Figure S18.** Optimized geometry of **4'**.
Total Energy = -1112.7886 a.u.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| B | -0.679232000 | -1.700634000 | 1.628606000 | O | -1.572590000 | 2.306837000 | 2.083058000 |
| B | -0.931405000 | -2.516485000 | 0.109085000 | O | 2.640136000 | 0.626698000 | 2.166879000 |
| H | -1.360634000 | -3.627656000 | 0.080498000 | H | -0.964690000 | -2.324339000 | 2.604040000 |
| B | -0.670655000 | -1.757054000 | -1.408154000 | H | -0.866599000 | 0.759459000 | -1.190346000 |
| H | -0.873830000 | -2.385440000 | -2.397037000 | H | 0.533967000 | -1.272688000 | 1.849794000 |
| B | 0.050933000 | -0.188642000 | -1.576134000 | H | -1.354960000 | -0.565079000 | 1.778066000 |
| H | 0.228353000 | 0.081638000 | -2.724658000 | H | -4.056480000 | -2.142961000 | 0.948966000 |
| C | 2.271139000 | -3.369593000 | 0.351380000 | H | -3.738915000 | -1.967301000 | -1.711785000 |
| C | 2.098636000 | -3.174361000 | -1.043443000 | H | -3.923921000 | 0.354373000 | 1.963383000 |
| C | 2.775453000 | -1.980197000 | -1.411207000 | H | -3.553581000 | 2.054406000 | -0.063493000 |
| C | 3.358610000 | -1.434462000 | -0.240406000 | H | -3.442102000 | 0.620804000 | -2.345967000 |
| C | 3.043138000 | -2.287667000 | 0.849523000 | H | -0.442740000 | 3.504966000 | -2.185741000 |
| C | -3.905730000 | -1.235510000 | 0.389212000 | H | -0.219084000 | 4.495392000 | 0.301381000 |
| C | -3.845329000 | 0.082513000 | 0.923452000 | H | 2.198144000 | 3.826987000 | 1.252191000 |
| C | -3.646711000 | 0.984800000 | -0.151174000 | H | 3.489977000 | 2.435698000 | -0.659182000 |
| C | -3.586679000 | 0.226611000 | -1.353180000 | H | 1.836258000 | 2.198965000 | -2.762922000 |
| C | -3.743647000 | -1.142179000 | -1.020622000 | H | 3.936798000 | -0.528406000 | -0.178732000 |
| C | 0.404982000 | 3.390541000 | -1.529958000 | H | 2.835119000 | -1.568494000 | -2.404613000 |
| C | 0.528677000 | 3.922515000 | -0.222620000 | H | 3.334939000 | -2.127965000 | 1.874603000 |
| C | 1.801515000 | 3.562068000 | 0.286178000 | H | 1.873569000 | -4.187412000 | 0.928902000 |
| C | 2.484470000 | 2.816461000 | -0.726858000 | H | 1.550005000 | -3.819573000 | -1.707758000 |
| C | 1.619848000 | 2.708423000 | -1.838827000 | W | -1.715861000 | -0.424735000 | -0.005505000 |
| C | -0.836041000 | 1.834866000 | 1.301309000 | W | 0.967128000 | -1.384457000 | 0.058688000 |
| C | 1.805421000 | 0.767789000 | 1.350982000 | W | 0.611237000 | 1.532093000 | -0.005865000 |