

## Supporting Information

# Reduction induced S-nucleophilicity in mono-dithiolene molybdenum complexes - *in situ* generation of sulfonium ligands

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# 1 Experimental Details

## 1.1 General Procedures

All measurements were carried out in a dry argon atmosphere using dry degassed solvents. Acetonitrile was freshly distilled from molecular sieves, thf was distilled from sodium/benzophenone, and DCM was freshly distilled from P<sub>2</sub>O<sub>5</sub>. [Mo(CO)<sub>2</sub>(cydt)(dppe)] was synthesized following a published literature method<sup>1</sup>.

## 1.2 Synthesis of [Mo(CO)<sub>2</sub>(CH<sub>2</sub>-cydt)(dppe)] (1<sup>CH<sub>2</sub></sup>)

The synthesis of the title compound is performed under strict exclusion of air and moisture. [Mo<sup>II</sup>(CO)<sub>2</sub>(cydt)(dppe)] (51.5 mg, 0.074 mmol, 1 eq.) is weighted into a Schlenk flask together with an equivalent amount of [Co(Cp\*)<sub>2</sub>] (50 mg, 0.152 mmol, 2.05 eq.). The reaction immediately starts upon addition of 2.5 mL dichloromethane showing a color shift to green which then changes to brown. After 24 hours of stirring at room temperature the colored solution is layered with ca. 10 mL of CH<sub>3</sub>CN. After some days orange single crystals suitable for X-ray analysis were obtained. [Mo(CO)<sub>2</sub>(CH<sub>2</sub>-cydt)(dppe)] · 0.5 CH<sub>2</sub>Cl<sub>2</sub>, 31.3 mg, 0.042 mmol, 56 % yield

<sup>1</sup>H-NMR (300 MHz, THF-d<sub>8</sub>, δ [ppm]): 0.95 (m, 1H, 0.5 · CH<sub>2,cydt</sub>), 1.08 (m, 2H, CH<sub>2,cydt</sub>), 1.31 (m, 1H, 0.5 · CH<sub>2,cydt</sub>), 1.62 (m, 1H, 0.5 · CH<sub>2,cydt</sub>), 1.72 (m, 1H, 0.5 · CH<sub>2,cydt</sub>), 1.79 (m, 1H, 0.5 · CH<sub>2,cydt</sub>), 2.20 (m, 2H, 2 · 0.5 · CH<sub>2</sub>, dppe/cydt), 2.36 (m, 1H, 0.5 · CH<sub>2,methylene</sub>), 2.62 (m, 1H, 0.5 · CH<sub>2,dppe</sub>), 2.77 (m, 1H, 0.5 · CH<sub>2,dppe</sub>), 3.01 (m, 1H, 0.5 · CH<sub>2,methylene</sub>), 3.15 (m, 1H, 0.5 · CH<sub>2,dppe</sub>), 7.10-7.23 (m, 3H, CH), 7.28-7.36 (m, 5H, CH), 7.38-7.50 (m, 8H, CH), 7.85-7.95 (m, 4H, CH).

<sup>13</sup>C-NMR (75.5 MHz, THF-d<sub>8</sub>, δ [ppm]): 24.2 (s, CH<sub>2,cydt</sub>), 24.5 (s, CH<sub>2,cydt</sub>), 25.0 (dd), 28.9 (dd, J<sub>1,C-P</sub> = 24.5 Hz, J<sub>2,C-P</sub> = 19.7 Hz, CH<sub>2,dppe</sub>), 33.9 (s, CH<sub>2,cydt</sub>), 36.3 (s, CH<sub>2,cydt</sub>), 39.1 (d, J<sub>C-P</sub> = 5.6 Hz, CH<sub>2,methylene</sub>), 114.1 (s, C<sub>quart.</sub>, CH<sub>2-S-C=C</sub>), 127.5 (d, J<sub>C-P</sub> = 8.0 Hz, CH), 129.0 (d, J<sub>C-P</sub> = 5.6 Hz, CH), 129.1 (d, J<sub>C-P</sub> = 5.6 Hz, CH), 129.2 (d, J<sub>C-P</sub> = 8.8 Hz, CH), 129.5 (d, J<sub>C-P</sub> = ca. 2.1 Hz, CH), 130.4 (d, J<sub>C-P</sub> = ca. 2.1 Hz, CH), 131.1 (dd, J<sub>1,C-P</sub> = 15.7 Hz, J<sub>2,C-P</sub> = 2.0 Hz, CH), 132.2 (d, J<sub>C-P</sub> = 8.8 Hz, CH), 132.9 (d, J<sub>C-P</sub> = 10.4 Hz, CH), 134.5 (d, J<sub>C-P</sub> = 11.2 Hz, CH), 135.1 (m, CH), 135.6 (m, ipso-C), 136.0 (m, ipso-C), 137.6 (s, ipso-C), 138.2 (s, ipso-C), 152.1 (d, J<sub>C-P</sub> = 4.8 Hz, C<sub>CH<sub>2</sub>-S-C=C</sub>), 221.1 (dd, J<sub>1,C-P</sub> = 8.8 Hz, J<sub>2,C-P</sub> = 6.4 Hz, CO), 233.8 (dd, J<sub>1,C-P</sub> = 25.3 Hz, J<sub>2,C-P</sub> = 13.3 Hz, CO).

<sup>31</sup>P-NMR (121.5 MHz, THF-d<sub>8</sub>, δ [ppm]): 46.6 (d, <sup>1</sup>P-P = 28.4 Hz), 63.9 (d, <sup>1</sup>P-P = 28.4 Hz).

<sup>135</sup>DEPT NMR (75.5 MHz, THF-d<sub>8</sub>, δ [ppm]): 24.2 (neg., CH<sub>2,cydt</sub>), 24.5 (neg., CH<sub>2,cydt</sub>), 25.0 (neg., dd, CH<sub>2,dppe</sub>), 28.9 (neg., dd, CH<sub>2,dppe</sub>), 33.9 (neg., CH<sub>2,cydt</sub>), 36.3 (neg., CH<sub>2,cydt</sub>), 39.1 (neg., d, CH<sub>2,methylene</sub>), 127.5 (pos., d, CH), 129.1 (pos., d, CH), 129.2 (pos., d, CH), 129.5 (pos., d, CH), 130.4 (pos., d, CH<sub>H,ar.</sub>), 131.1 (pos., dd, CH), 132.2 (pos., d, CH), 132.9 (pos., d, CH), 134.5 (pos., d, CH), 135.1 (pos., dd, CH).

HSQC NMR (300 & 75.5 MHz, THF-d<sub>8</sub>, δ [ppm]): 0.95 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) and 24.5 (<sup>13</sup>C, CH<sub>2,cydt</sub>), 1.08 (<sup>1</sup>H, CH<sub>2</sub>) and 24.2 (<sup>13</sup>C, CH<sub>2,cydt</sub>), 1.31 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 24.5 (<sup>13</sup>C, CH<sub>2,cydt</sub>), 1.62 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 36.3 (<sup>13</sup>C, CH<sub>2,cydt</sub>), 1.72 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 36.3 (<sup>13</sup>C, CH<sub>2,cydt</sub>), 1.79 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 33.9 (<sup>13</sup>C, CH<sub>2,cydt</sub>), 2.20 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 28.9 (<sup>13</sup>C, CH<sub>2,dppe</sub>), 2.20 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 33.9 (<sup>13</sup>C, CH<sub>2,cydt</sub>), 2.36 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 39.1 (<sup>13</sup>C, CH<sub>2,methylene</sub>), 2.62 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 25.0 (<sup>13</sup>C, CH<sub>2,dppe</sub>), 2.77 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 25.0 (<sup>13</sup>C, CH<sub>2,dppe</sub>), 3.01 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 39.1 (<sup>13</sup>C, CH<sub>2,methylene</sub>), 3.15 (<sup>1</sup>H, 0.5 · CH<sub>2</sub>) & 28.9 (<sup>13</sup>C, CH<sub>2,dppe</sub>), 7.10-7.23 (<sup>1</sup>H, CH) & 127.5 (<sup>13</sup>C, CH), 7.10-7.23 (<sup>1</sup>H, CH) & 129.3 (<sup>13</sup>C, CH), 7.28-7.36 (<sup>1</sup>H, CH) & 129.0 (<sup>13</sup>C, CH), 7.28-7.36 (<sup>1</sup>H, CH) & 130.4 (<sup>13</sup>C, CH), 7.28-7.36 (<sup>1</sup>H, CH) & 132.2 (<sup>13</sup>C, CH), 7.38-7.50 (<sup>1</sup>H, CH) & 129.2 (<sup>13</sup>C, CH), 7.38-7.50 (<sup>1</sup>H, CH) & 131.1 (<sup>13</sup>C, CH), 7.38-7.50 (<sup>1</sup>H, CH) & 132.9 (<sup>13</sup>C, CH), 7.85-7.95 (<sup>1</sup>H, CH) & 134.5 (<sup>13</sup>C, CH), 7.85-7.95 (<sup>1</sup>H, CH) & 135.1 (<sup>13</sup>C, CH).

IR (KBr):  $\tilde{\nu}$  = 700 cm<sup>-1</sup>, 1094 cm<sup>-1</sup>, 1431 cm<sup>-1</sup>, 1815 cm<sup>-1</sup>, 1929 cm<sup>-1</sup>.

Elemental analysis calcd. for C<sub>35</sub>H<sub>34</sub>MoO<sub>2</sub>P<sub>2</sub>S<sub>2</sub> · 0.5 CH<sub>2</sub>Cl<sub>2</sub>: C: 56.80, H: 4.63, S: 8.54. Found: C: 56.88, H: 4.69, S: 8.43.

## 1.3 Synthesis of 6,7-Dihydro-4H-1,3-dithiol-4,5-thiopyran-2-one (tpydt)

The synthesis of the tpydt precursor ligand follows essentially published routes for 1,3-Dithiol-2-ones.<sup>1-3</sup> Tetrahydro-4H-thiopyran-4-one (5.62 g, 48.4 mmol, 1 eq.) was brominated in  $\alpha$ -position utilising elemental bromine (7.68 g, 48.4 mmol, 1 eq.) under basic conditions (Na<sub>2</sub>CO<sub>3</sub>, 8 g, 57.9 mmol, 1.18 eq.) in DCM. The following workup should be done quickly, as the brominated product appears to be unstable. The interme-

diate product was isolated after typical workup with water and brine and used without further purification. The entire product was then reacted with potassium isopropyl xanthate (9.26 g; 53.24 mmol, 1.1 equiv.) in a 50:50 mixture of acetone and ethanol overnight yielding O-iso-propyl-S-(2-tetrahydro-4H-thiopyranonyl) dithiocarbonate in ca. 98 % yield. The following ring closing step to yield the final product worked best with sulfuric acid added to a solution of the xanthate in ether/dichloromethane overnight. The entire product mixture was then poured onto crushed ice (ca. 400 mL) and extracted with diethylether. Sublimation of the entire product at  $3.2 \cdot 10^{-2}$  mbar and 140 °C yielded colorless crystals suitable for X-ray analysis. Final Yield: 18.5% (1.7 g, 8.93 mmol).

$^1\text{H-NMR}$  (300 MHz,  $\text{CHCl}_3\text{-d}_1$ ,  $\delta$  [ppm]): 2.71-2.79 (m, 2H,  $\text{CH}_2$ ), 2.97 (t,  $J_1 = 5.5$  Hz, 2H,  $\text{CH}_2$ ), 3.46 (t,  $J_1 = 1.9$  Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C NMR}$  (75.5 MHz,  $\text{CHCl}_3\text{-d}_1$ ,  $\delta$  [ppm]): 25.2 (s,  $\text{CH}_2$ ), 25.6 (s,  $\text{CH}_2$ ), 26.8 (s,  $\text{CH}_2$ ), 121.8 (s,  $\text{C}_{\text{quart.}}\text{-S}$ ), 126.4 (s,  $\text{C}_{\text{quart.}}\text{-S}$ ), 189.7 (s,  $\text{C}_{\text{quart.}}\text{=O}$ ).

EI-MS [M]: 190.6 m/z.

Elemental analysis calcd. for  $\text{C}_6\text{H}_6\text{OS}_3$ : C: 37.87, H: 3.18, S: 50.54. Found: C: 37.46, H: 3.49, S: 51.64.

## 1.4 Synthesis of $[\text{Mo}(\text{CO})_2(\text{tpydt})(\text{dppe})]$ (2)

The synthesis and purification of this complex followed the literature procedure<sup>1</sup>.  $[\text{Mo}(\text{CO})_4(\text{dppe})]$  (700 mg, 1.15 mmol, 1 eq.) and **tpydt** (250 mg, 1.31 mmol, 1.1 eq.) were irradiated in a THF solution yielding 252 mg (30.6 %, 0.35 mmol) **2**.

$^1\text{H-NMR}$  (300 MHz, THF- $\text{d}_8$ ,  $\delta$  [ppm]): 2.52 (m, 4H,  $2 \cdot \text{CH}_2, \text{dppe}$ ), 2.74 (t,  $J_1 = 6.05$  Hz, 2H,  $\text{CH}_2, \text{tpydt}$ ), 3.16 (t,  $J_1 = 5.96$  Hz, 2H,  $\text{CH}_2, \text{tpydt}$ ), 3.91 (s, 2H,  $\text{CH}_2, \text{tpydt}$ ), 6.99 (m, 4H, 4  $\text{CH}_{\text{ar}}$ ), 7.26 (m, 6H,  $\text{CH}_{\text{ar}}$ ), 7.40 (m, 6H,  $\text{CH}_{\text{ar}}$ ), 7.50 (m, 4H,  $\text{CH}_{\text{ar}}$ ).

$^{31}\text{P-NMR}$  (121.5 MHz, THF- $\text{d}_8$ ,  $\delta$  [ppm]): 82.59 (s).

$^{13}\text{C-NMR}$  (75.5 MHz, THF- $\text{d}_8$ ,  $\delta$  [ppm]): 27.5 (s,  $\text{CH}_2, \text{tpydt}$ ), 28.5 (t,  $J_{\text{P-C}} = 21.3$  Hz,  $\text{CH}_2, \text{dppe}$ ), 35.6 (s,  $\text{CH}_2, \text{tpydt}$ ), 38.9 (s,  $\text{CH}_2, \text{tpydt}$ ), 128.9 (dt,  $2 \cdot 2 \text{CH}$ ,  $J_{1,\text{P-C}} = 32.3$  Hz,  $J_{2,\text{P-C}} = 5.1$  Hz), 130.7 (d,  $2 \cdot 2 \text{CH}$ ,  $J_{\text{P-C}} = 31.6$  Hz), 133.7 (dt,  $2 \cdot 2 \text{CH}$ ,  $J_{1,\text{P-C}} = 16.9$  Hz,  $J_{2,\text{P-C}} = 5.1$  Hz), 136.2 (m,  $\text{C}_{\text{quart.}}$ ), 138.0 (m,  $\text{C}_{\text{quart.}}$ ), 148.5 (m,  $\text{C}_{\text{quart.}}, \text{C-S}$ ), 153.0 (m,  $\text{C}_{\text{quart.}}, \text{C-S}$ ), 242.9 (t,  $\text{C}_{\text{CO}}$ ,  $^2J_{\text{P-C}} = 30.1$  Hz).

$^{135}\text{DEPT NMR}$  (75.5 MHz, THF- $\text{d}_8$ ,  $\delta$  [ppm]): 27.5 (neg.,  $\text{CH}_2$ ), 28.5 (neg.,  $\text{CH}_2$ ), 35.6 (neg.,  $\text{CH}_2$ ), 38.9 (neg.,  $\text{CH}_2$ ), 128.9 (pos., CH), 130.7 (pos., CH), 133.7 (pos., CH), 136.2 (pos., CH).

HH-COSY NMR (300 MHz, THF- $\text{d}_8$ ,  $\delta$  [ppm]): 2.74 ( $2 \text{ CH}_2, \text{tpydt}$  & 3.16  $\text{CH}_2, \text{tpydt}$ ), 3.16 ( $2 \text{ CH}_2, \text{tpydt}$  & 3.91  $\text{CH}_2, \text{tpydt}$ ), 6.99-7.50 ( $\text{CH}_{\text{ar}}$ ) & 6.99-7.50 ( $\text{CH}_{\text{ar}}$ ).

HSQC NMR (300 und 75.5 MHz, THF- $\text{d}_8$ ,  $\delta$  [ppm]): 2.54 ( $^1\text{H}$ ,  $2 \cdot \text{CH}_2, \text{dppe}$ ) & 28.5 ( $^1\text{H}$ ,  $2 \cdot \text{CH}_2, \text{dppe}$ ), 2.70 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 27.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.08 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 38.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.86 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 35.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 6.99 ( $^1\text{H}$ ,  $\text{CH}_{\text{ar}}$ ) & 133.6 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.26 ( $^1\text{H}$ ,  $\text{CH}_{\text{ar}}$ ) & 128.9 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.26 ( $^1\text{H}$ ,  $\text{CH}_{\text{ar}}$ ) und 130.7 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.40 ( $^1\text{H}$ ,  $\text{CH}_{\text{ar}}$ ) & 128.9 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.40 ( $^1\text{H}$ ,  $\text{CH}_{\text{ar}}$ ) & 130.7 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.50 ( $^1\text{H}$ ,  $\text{CH}_{\text{ar}}$ ) & 133.7 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ).

HMBC NMR (300 and 75.5 MHz, THF- $\text{d}_8$ ,  $\delta$  [ppm]): 2.74 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 35.6 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 2.74 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 153.0 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.16 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 27.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.16 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 148.5 ( $^{13}\text{C}$ , C-S), 3.16 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 153.0 ( $^{13}\text{C}$ , C-S), 3.91 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 27.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.91 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 148.5 ( $^{13}\text{C}$ , C-S), 3.91 ( $^1\text{H}$ ,  $\text{CH}_2, \text{tpydt}$ ) & 153.0 ( $^{13}\text{C}$ , C-S), 6.99-7.50 ( $^1\text{H}$ ,  $\text{CH}_{\text{ar}}$ ) & 128.9-138.0 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ).

IR (KBr):  $\tilde{\nu} = 1434 \text{ cm}^{-1}$ ,  $1877 \text{ cm}^{-1}$ ,  $1957 \text{ cm}^{-1}$ .

TLC Rf-value: 0.47 (*n*-hexan/DCM: 2/3).

Elemental analysis calcd. for  $\text{C}_{33}\text{H}_{30}\text{O}_2\text{P}_2\text{S}_3\text{Mo}$ : C: 55.62, H: 4.24, S: 13.50. Found: C: 55.32, H: 4.36, S: 13.48.

## 1.5 Synthesis of $[\text{Mo}(\text{CO})_2(\text{CH}_2\text{-tpydt})(\text{dppe})]$ ( $2^{\text{CH}_2}$ )

The synthesis of the title compound is performed under strict exclusion of air and moisture.  $[\text{Mo}(\text{CO})_2(\text{tpydt})(\text{dppe})]$  (24.2 mg, 0.033 mmol, 1 eq.) is weighted in a Schlenk flask together with an equivalent amount of  $[\text{Co}(\text{Cp}^*)_2]$  (24.2 mg, 0.07 mmol, 2.2 eq.). The reaction immediately starts upon addition of 2.5 mL dichloromethane showing a color shift to green which then changes to brown. After 24 hours of stirring at room temperature the colored solution is layered with ca. 10 mL of  $\text{CH}_3\text{CN}$ . After some days orange

single crystals suitable for X-ray analysis were obtained.  $[\text{Mo}(\text{CO})_2(\text{CH}_2\text{-tpydt})(\text{dppe})] \cdot 0.5 \text{CH}_2\text{Cl}_2$ , 16.0 mg, 0.021 mmol, 63 % yield.

$^1\text{H-NMR}$  (300 MHz, THF-d<sub>8</sub>,  $\delta$  [ppm]):<sup>1</sup> 1.83-2.12 (br m, 3H,  $\text{CH}_2$ ,tpydt), 2.12-2.55 (br m, 4H,  $\text{CH}_2$ ,tpydt and  $\text{CH}_2$ ,dppe), 2.59-2.87 (br m, 3H,  $\text{CH}_2$ ,tpydt), 3.02 (m, 1H, 0.5 ·  $\text{CH}_2$ ,methylene, major and minor), 3.09-3.26 (br m, 1H,  $\text{CH}_2$ ,tpydt and  $\text{CH}_2$ ,dppe), 7.10-7.25 (m, 4H,  $\text{CH}_{\text{ar}}$ ), 7.28-7.36 (m, 4H,  $\text{CH}_{\text{ar}}$ ), 7.36-7.51 (m, 8H,  $\text{CH}_{\text{ar}}$ ), 7.81-7.94 (m, 4H,  $\text{CH}_{\text{ar}}$ ).

$^{13}\text{C NMR}$  (75.5 MHz, THF-d<sub>8</sub>,  $\delta$  [ppm]): 24.7 (dd<sup>2</sup>,  $\text{CH}_2$ , tpydt), 26.5 (s, minor,  $\text{CH}_2$ ,tpydt), 27.2 (s, major,  $\text{CH}_2$ ,tpydt), 29.0 (pddd<sup>3</sup>,  $J_{1,\text{C-P}} = 19.7 \text{ Hz}$ ,  $J_{2,\text{C-P}} = 6.2 \text{ Hz}$ ,  $\text{CH}_2$ ,dppe), 32.8 (s,  $\text{CH}_2$ ,tpydt), 34.9 (s,  $\text{CH}_2$ ,tpydt), 36.2 (s,  $\text{CH}_2$ ,tpydt), 37.7 (d, minor,  $J_{\text{C-P}} = 6.2 \text{ Hz}$ ,  $\text{CH}_2$ ,methylene), 38.6 (d, major,  $J_{\text{C-P}} = 6.2 \text{ Hz}$ ,  $\text{CH}_2$ ,methylene), 38.8 (s,  $\text{CH}_2$ ,tpydt), 110.5 (s, minor,  $\text{C}_{\text{quart.}}$ , C-S- $\text{CH}_2$ ), 115.2 (s, major,  $\text{C}_{\text{quart.}}$ , C-S- $\text{CH}_2$ ), 127.5 (d, minor,  $J_{\text{C-P}} = 8.6 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 127.6 (d, major,  $J_{\text{C-P}} = 8.6 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 128.9 (m, minor,  $\text{CH}_{\text{ar}}$ ), 129.2 (m, major,  $\text{CH}_{\text{ar}}$ ), 129.6 (d,  $J_{\text{C-P}} = 2.3 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 129.8 (d,  $J_{\text{C-P}} = 2.3 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 130.4 (m, minor,  $\text{CH}_{\text{ar}}$ ), 131.0 (m, major,  $\text{CH}_{\text{ar}}$ ), 131.2 (dd,  $J_{1,\text{C-P}} = 3.9 \text{ Hz}$ ,  $J_{2,\text{C-P}} = 2.3 \text{ Hz}$ ,  $\text{CH}_{\text{H,ar}}$ ), 132.0 (d,  $J_{\text{C-P}} = 2.4 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 132.1 (d,  $J_{\text{C-P}} = 3.1 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 132.7 (d,  $J_{\text{C-P}} = 2.4 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 132.8 (d,  $J_{\text{C-P}} = 3.1 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 134.2 (d, minor,  $J_{\text{C-P}} = 5.5 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 134.3 (d,  $J_{\text{C-P}} = 5.5 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 134.5 (s,  $\text{C}_{\text{quart.}}$ ), 134.6 (s,  $\text{C}_{\text{quart.}}$ ), 134.8 (d, minor,  $J_{\text{C-P}} = 3.9 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 135.0 (d, major,  $J_{\text{C-P}} = 3.9 \text{ Hz}$ ,  $\text{CH}_{\text{ar}}$ ), 135.1 (m,  $\text{C}_{\text{quart.}}$ ), 135.3 (s,  $\text{C}_{\text{quart.}}$ ), 135.5 (m,  $\text{C}_{\text{quart.,ar}}$ ), 135.7 (m,  $\text{C}_{\text{quart.,ar}}$ ), 137.3 (s,  $\text{C}_{\text{quart.,ar}}$ ), 137.9 (s,  $\text{C}_{\text{quart.,ar}}$ ), 148.7 (d, minor,  $^2J_{\text{C-P}} = 4.8 \text{ Hz}$ ,  $\text{C}_{\text{quart.}}$ , C-S), 153.6 (d, major,  $^2J_{\text{C-P}} = 4.7 \text{ Hz}$ ,  $\text{C}_{\text{quart.}}$ , C-S), 220.9 (m, minor, CO), 233.1 (m, major, CO).

$^{31}\text{P NMR}$  (121.5 MHz, THF-d<sub>8</sub>,  $\delta$  [ppm]): 46.7 (d, minor,  $^1P\text{-P} = 28.4 \text{ Hz}$ ), 47.0 (d, major,  $^1P\text{-P} = 28.4 \text{ Hz}$ ), 63.7 (m, minor and major).

$^{135}\text{DEPT NMR}$  (75.5 MHz, THF-d<sub>8</sub>,  $\delta$  [ppm]): 24.7 (neg., dd,  $\text{CH}_2$ ,tpydt); 26.5 (neg., s, minor,  $\text{CH}_2$ ,tpydt), 27.2 (neg., s, major,  $\text{CH}_2$ ,tpydt), 29.0 (neg., m,  $\text{CH}_2$ ,dppe), 32.8 (neg., s,  $\text{CH}_2$ ,tpydt), 34.9 (neg., s,  $\text{CH}_2$ ,tpydt), 36.2 (neg., s,  $\text{CH}_2$ ,tpydt), 37.7 (neg., d, minor,  $\text{CH}_2$ ,Methylene), 38.6 (neg., d, major,  $\text{CH}_2$ ,methylene), 38.8 (neg., s,  $\text{CH}_2$ ,tpydt), 127.5 (pos., d, minor,  $\text{CH}_{\text{ar}}$ ), 127.6 (pos., d, major,  $\text{CH}_{\text{ar}}$ ), 128.9 (pos., m, minor,  $\text{CH}_{\text{ar}}$ ), 129.2 (pos., m, major,  $\text{CH}_{\text{ar}}$ ), 129.6 (pos., d,  $\text{CH}_{\text{ar}}$ ), 129.8 (pos., d,  $\text{CH}_{\text{ar}}$ ), 130.4 (pos., m,  $\text{CH}_{\text{ar}}$ ), 131.0 (pos., m,  $\text{CH}_{\text{ar}}$ ), 131.2 (pos., dd,  $\text{CH}_{\text{ar}}$ ), 132.0 (pos., d,  $\text{CH}_{\text{ar}}$ ), 132.1 (pos., d,  $\text{CH}_{\text{ar}}$ ), 132.7 (pos., d,  $\text{CH}_{\text{ar}}$ ), 132.8 (pos., d,  $\text{CH}_{\text{ar}}$ ), 134.2 (pos., d, minor,  $\text{CH}_{\text{ar}}$ ), 134.3 (pos., d, major,  $\text{CH}_{\text{ar}}$ ), 134.8 (pos., d, minor,  $\text{CH}_{\text{ar}}$ ), 135.0 (pos., d, major,  $\text{CH}_{\text{ar}}$ ).

HSQC NMR (300 und 75.5 MHz, THF-d<sub>8</sub>,  $\delta$  [ppm]): 1.90 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 27.2 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.02 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 26.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.04 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 38.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.06 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 36.2 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.18 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 26.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.27 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 29.0 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,dppe), 2.35 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 27.2 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.35 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 37.7 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,methylene), 2.39 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 38.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,methylene), 2.47 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 36.2 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.61 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 34.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.65 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 24.7 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.66 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 34.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.73 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 34.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.77 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 24.7 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.79 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 34.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.81 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 32.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 2.86 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 32.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 3.02 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 37.7 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,methylene), 3.04 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 38.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,methylene), 3.08 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 29.0 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,dppe), 3.22 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 29.0 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,dppe), 3.24 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 32.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 3.30 ( $^1\text{H}$ ,  $\text{CH}_2$ ) and 32.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,tpydt), 7.18 ( $^1\text{H}$ , CH) and 127.5 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.18 ( $^1\text{H}$ , CH) and 132.0 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.21 ( $^1\text{H}$ , CH) and 129.6 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.33 ( $^1\text{H}$ , CH) and 128.9 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.33 ( $^1\text{H}$ , CH) and 130.4 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.33 ( $^1\text{H}$ , CH) and 132.0 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.44 ( $^1\text{H}$ , CH) and 128.9 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.45 ( $^1\text{H}$ , CH) and 128.9 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.47 ( $^1\text{H}$ , CH) and 131.0 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.87 ( $^1\text{H}$ , CH) and 132.7 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.90 ( $^1\text{H}$ , CH) and 134.3 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ), 7.90 ( $^1\text{H}$ , CH) and 134.2 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{ar}}$ ).

Elemental analysis calcd. for  $\text{C}_{34}\text{H}_{32}\text{MoO}_2\text{P}_2\text{S}_3 \cdot 0.5 \cdot \text{CH}_2\text{Cl}_2$  C: 53.87, H: 4.32, S: 12.50. Found: C: 53.26, H: 4.23, S: 12.29.

<sup>1</sup>Due to the asymmetric character of the used dithiolenes (**tpydt**) two diastereomeric complexes exist. This causes several broad signals in the range from 1.83 to 3.26 ppm which cannot directly be integrated. To certainly assign those peaks though, these signals were identified by HSQC experiments which is mentioned if necessary.

<sup>2</sup>hidden by the signal from THF-d<sub>8</sub>, but clearly assigned by  $^{135}\text{DEPT-NMR}$

<sup>3</sup>merged double doublets of both conformers.

## 1.6 $^{31}\text{P}$ -NMR Signals for $1^{\text{CH}_2}$ and $2^{\text{CH}_2}$

Both initial complexes **1** and **2** show a singlet in the  $^{31}\text{P}$ -NMR due to the relative free rotation and trigonal-prismatic structure. The two respective methenylated complexes, in contrast, are octahedral and hindered in their rotation. Thus, both phosphorous atoms are chemically inequivalent now and exhibit different shifts. Each signal is a doublet peak representing the P-P coupling ( $^2J^{\text{PP}} = 28.4$  Hz). An additional interesting feature with  $2^{\text{CH}_2}$  is related to the additional asymmetry due to the exchange of one  $\text{CH}_2$  group with sulfur in the respective dithiolene. The triplet observed in the room temperature NMR actually consists of two doublets merging at this temperature. Similarly, the apparent doublet at around 63 ppm starts to split into two doublets. The respective temperature dependent NMR-study is shown in Figure S1.

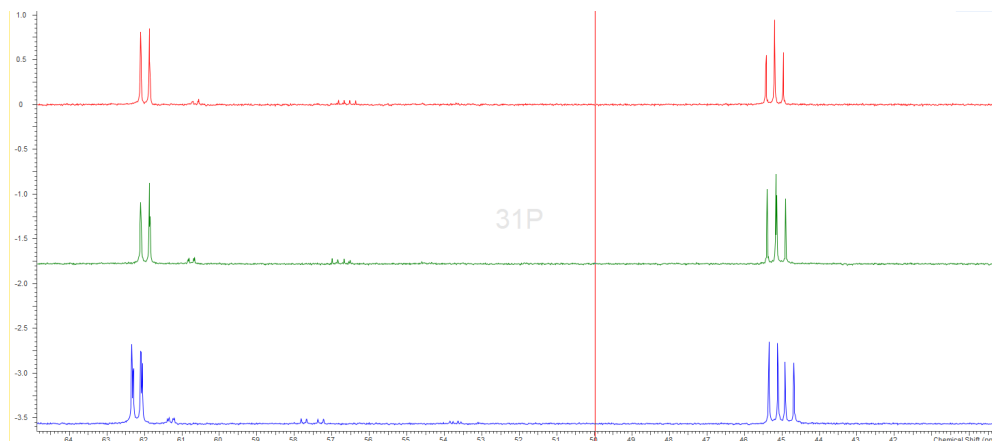


Figure S 1: Temperature dependent  $^{31}\text{P}$ -NMR spectra of  $2^{\text{CH}_2}$ . From top to bottom 338 K, 298 K, 258 K. Especially the spectrum at the lowest measured temperature clearly shows that the former doublet and triplet actually consist of two doublets as explained in the text.

## 1.7 Electrochemistry

The experiments were carried out in a conventional three-electrode cell using a METROHM PGSTAT204 apparatus. Counter electrode and pseudo-reference electrode were platinum rods while a glassy-carbon or platinum disc served (diameter 1.6 mm) as working electrode. Cyclic voltammograms were referenced with Decamethylferrocene ( $\text{DFc}/\text{DFc}^+$ ) and re-calculated to the reference couple  $\text{Fc}/\text{Fc}^+ = 0$  V as internal standard. Tetrabutylammonium hexafluorophosphate (0.1 M) was employed as supporting electrolyte in most cases.

## 1.8 X-ray

Crystals of **tpydt**,  $[\text{Mo}(\text{CO})_2(\text{CH}_2\text{-cydt})(\text{dppe})]$  ( $1^{\text{CH}_2}$ ),  $[\text{Mo}(\text{CO})_2(\text{tpydt})(\text{dppe})]$  (**2**) and  $[\text{Mo}(\text{CO})_2(\text{CH}_2\text{-tpydt})(\text{dppe})]$  ( $2^{\text{CH}_2}$ ) were mounted on a glass fiber in inert paraffin oil. Data were recorded at 170 K on a STOE-IPDS 2 T diffractometer with graphite-monochromated Mo- $\text{K}\alpha$ -radiation ( $\lambda = 0.71073$  Å). The program XArea was used for integration of diffraction profiles; numerical absorption corrections were carried out with the programs X-Shape and X-Red32; all from STOE<sup>©</sup>. The structures were solved by dual space methods (SHELXT-2018) and refined by full-matrix least-squares techniques using the WingX GUI or OLEX<sup>2</sup> and SHELXL-2018.<sup>4-8</sup> All non-hydrogen-atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropically at calculated positions using a riding model with their  $U_{\text{iso}}$  values constrained to 1.2  $U_{\text{eq}}$  of their pivot atoms. The structure of  $1^{\text{CH}_2}$  was refined as inversion twin with  $\text{BASF} = 0.36516$ . Atoms of the dithiolene ligand in compound  $2^{\text{CH}_2}$  are disordered over three locations with regard to a ring pucker and the relative location of the ring sulfur atom. The disorder was modelled with SADI, SIMU and DELU constraints. Occupancies are 41%, 31%, and 28%.

Atoms of the dithiolene ligand in compound **2** are disordered over two locations with regard to ring pucker and the relative location of the ring sulfur atom. The disorder was modelled using SAME, SIMU and DELU constraints and with occupancies of 93% and 7%. One reflex was omitted as clear outlier. The disorder results in a B-alert (PLAT410\_ALERT\_2\_B Short Intra H...H Contact H4A..H5'1) which points to a H-H

contact that involves hydrogen atoms that cannot be present in the same molecule (i.e. it is either one or the other for a specific individual molecule). Another B-alert (PLAT910\_ALERT\_3\_B Missing # of FCF Reflection(s) Below Theta(Min). 11 Note) goes back to relatively weak diffraction of the crystal and beam-stop affection.

The crystal of **tpydt** was a non-merohedral twin and the reflexes of the different domains were separated during integration with X-Area. This led to some reflexes having not been included in the hkl file (for being assigned to a different domain) and an incomplete data set. This is reflected in a completeness of only ca. 50% and a respective A-alert in the checkcif file (PLAT029\_ALERT\_3\_A\_diffn\_measured\_fraction\_theta\_full value Low.).

In all four structures a low bond precision on C-C bonds was observed (PLAT342\_ALERT\_3\_B/C Low Bond Precision on C-C Bonds). This is, however, rather common for the crystal structures of *non-innocent* dithiolenes species.

Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. These data can be obtained free of charge upon quoting the depository numbers CCDC 2080179 (**1<sup>CH2</sup>**), 2094531 (**2<sup>CH2</sup>**), 2094530 (**2**), and 2094532 (**tpydt**) by FAX (+44-1223-336-033), email (deposit@ccdc.cam.ac.uk), or their web interface (at <http://www.ccdc.cam.ac.uk>).

## 1.9 Other Physical Methods

IR spectra were recorded as KBr pellets with an FTIR spectrometer Shimadzu IRAffinity-1. Elemental analyses (C, H, and S) were carried out with an Elementar Vario MICRO elemental analyzer.

## 1.10 Quantum chemical calculations

The ORCA program package, version 4.1.2, was used for all density functional theory calculations.<sup>9</sup> Geometry optimisation started with the single crystal structure data. The BP86 density functional under the resolution of the identity approximation was applied.<sup>10-12</sup> Ahlrich's triple- $\zeta$  basis set def2-TZVP with the effective core potentials for molybdenum was used, except for the carbon and hydrogen atoms where def2-SVP was employed.<sup>13,14</sup> def2/J was chosen as the auxiliary basis set.<sup>15</sup> Dispersion corrections were included according to Grimme's D3zero scheme.<sup>16</sup> Environmental effects were considered with the CPCM model using THF as the solvent.<sup>17</sup> Tight SCF and optimisation convergence criteria as well as a grid size of 7 were chosen in the ORCA nomenclature. The integration accuracy was set to 7.0.

To confirm the geometries obtained as true minima on the potential energy surface, frequency calculations were run with the same setup as for the geometry optimisations except for the omission of the solvent model. From these calculations, the computed IR spectra and the thermodynamic data were extracted.

## 2 Additional Figures

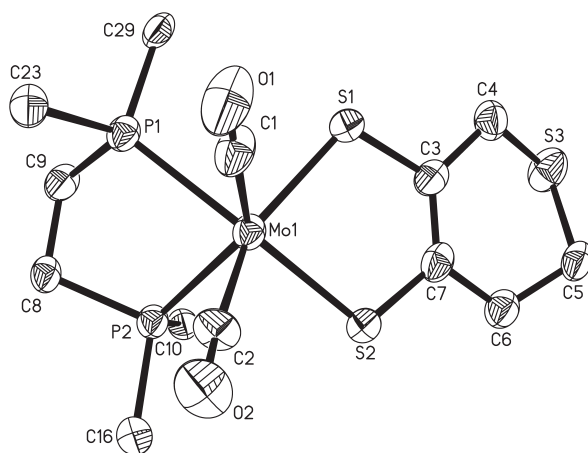


Figure S 2: Molecular structure of  $[\text{Mo}(\text{CO})_2(\text{tpydt})(\text{dppe})]$  (**2**,  $R = 5.59\%$ ,  $R_{\text{int}} = 9.61\%$ ), ellipsoids are shown at the 50% probability level. Phenyl rings, hydrogen atoms and co-crystallized solvent molecules are not shown for clarity reasons.

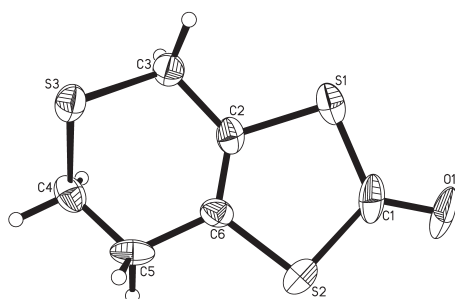


Figure S 3: Molecular structure of 6,7-Dihydro-4H-1,3-dithiol[4,5]thiopyran-2-one (**tpydt**,  $R = 5.23\%$ ,  $R_{\text{int}} = 10.13\%$ ), ellipsoids are shown at the 50% probability level.

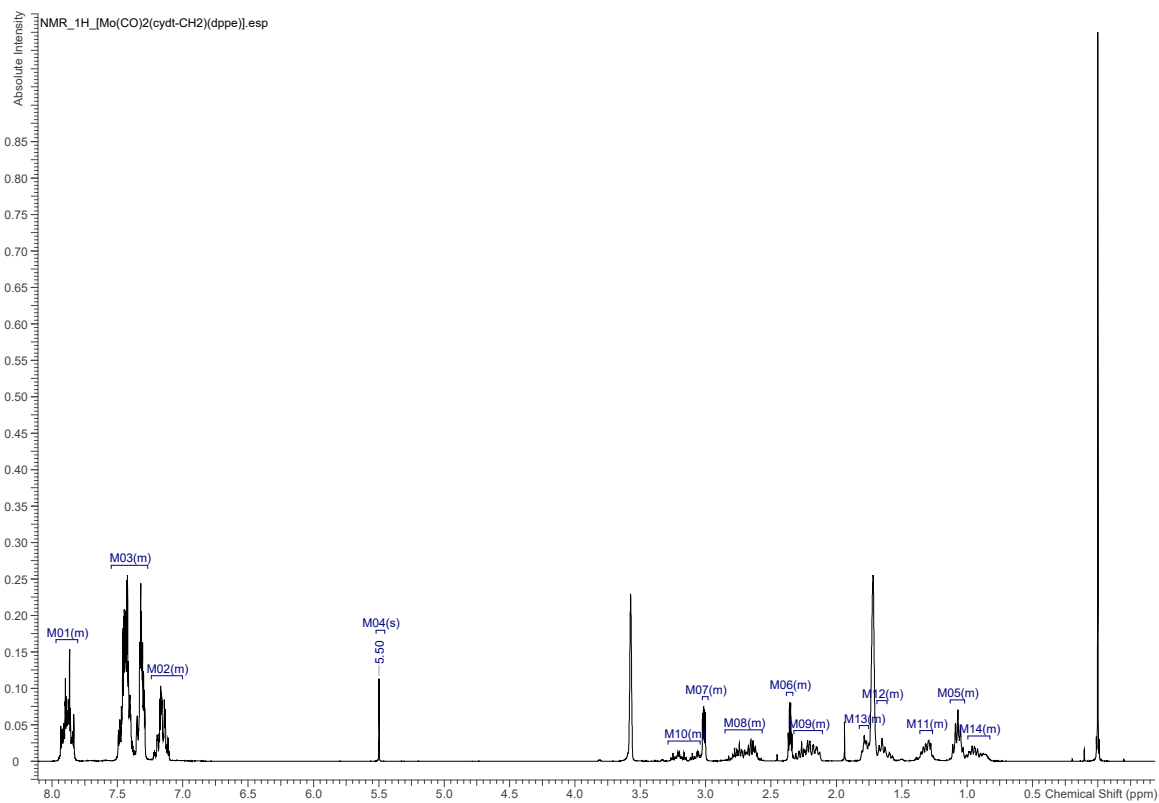


Figure S 4:  $^1\text{H}$ -NMR of  $1\text{CH}_2$  in THF-d8.

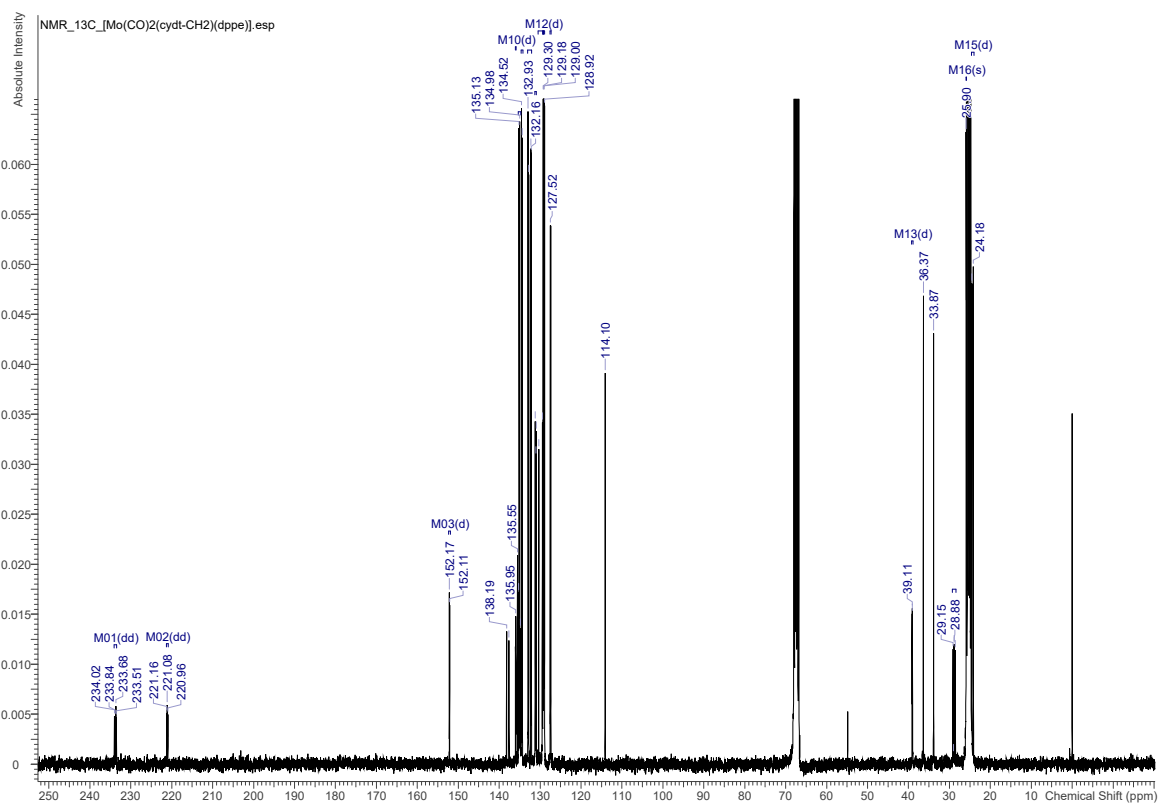


Figure S 5:  $^{13}\text{C}$ -NMR of  $1\text{CH}_2$  in THF-d8.



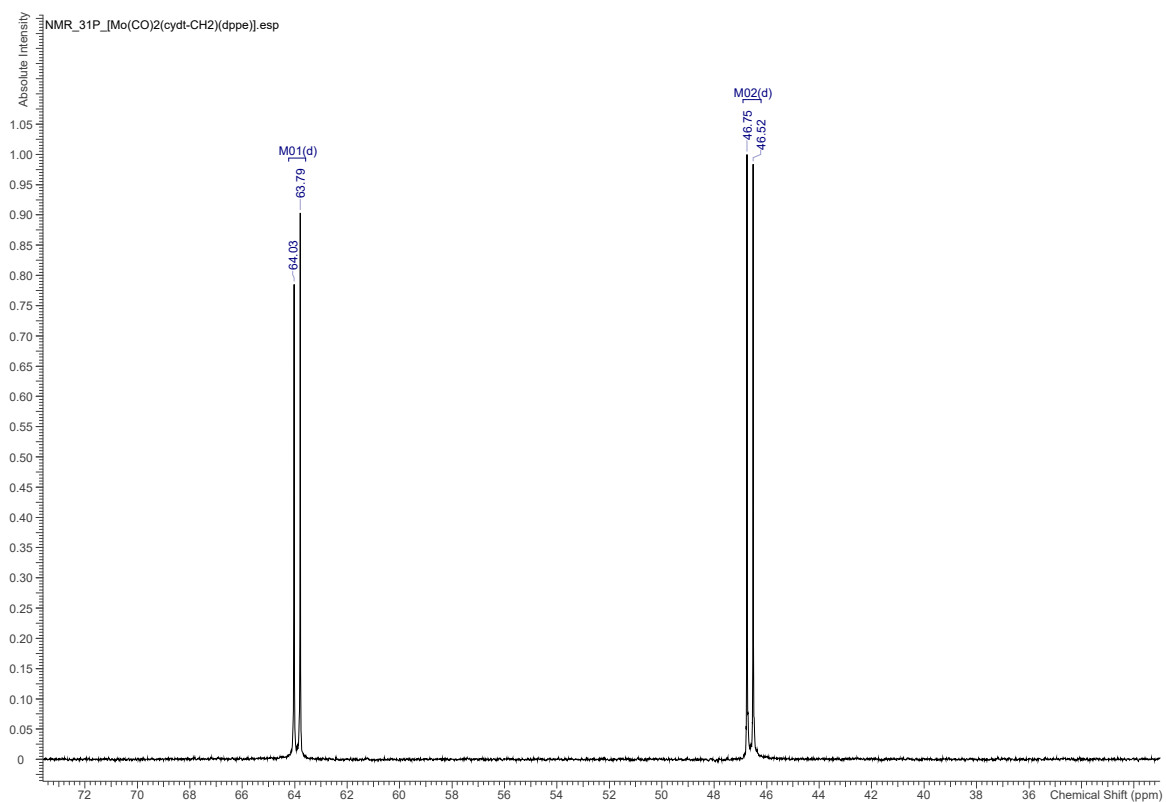


Figure S 6:  $^{31}\text{P}$ -NMR of  $1^{\text{CH}_2}$  in THF-d8.

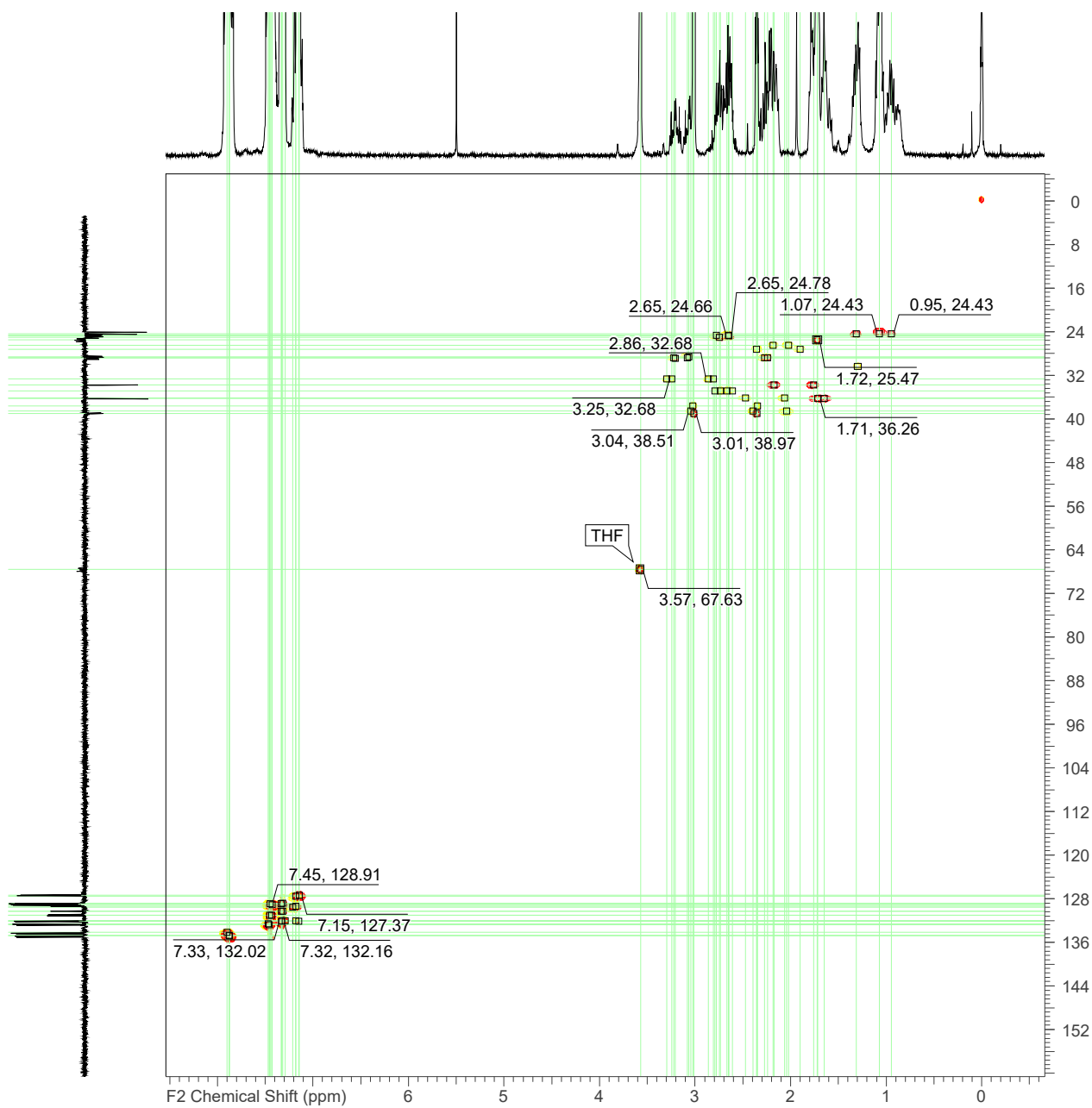


Figure S 7:  $^1\text{H}$ - $^{13}\text{C}$ -HSQC-NMR of  $1^{\text{CH}_2}$  in THF- $d_8$ .

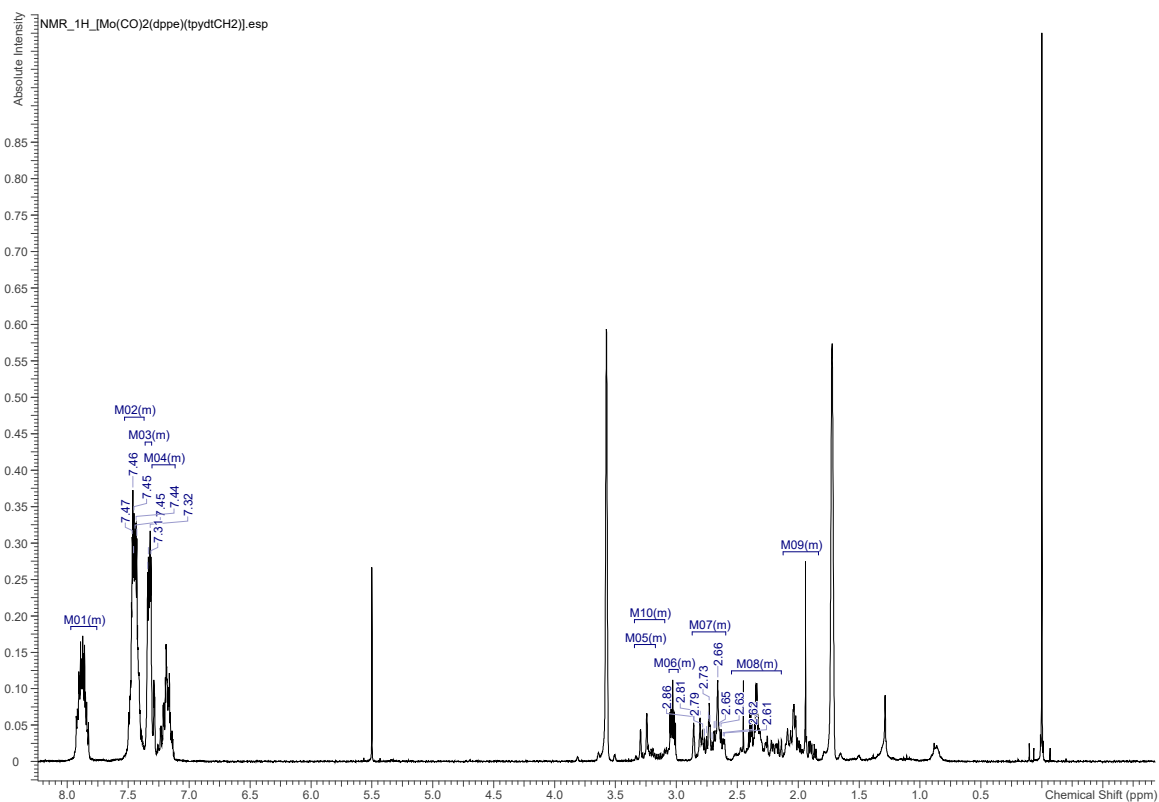


Figure S 8:  $^1\text{H-NMR}$  of  $2^{\text{CH}_2}$  in THF-d8.

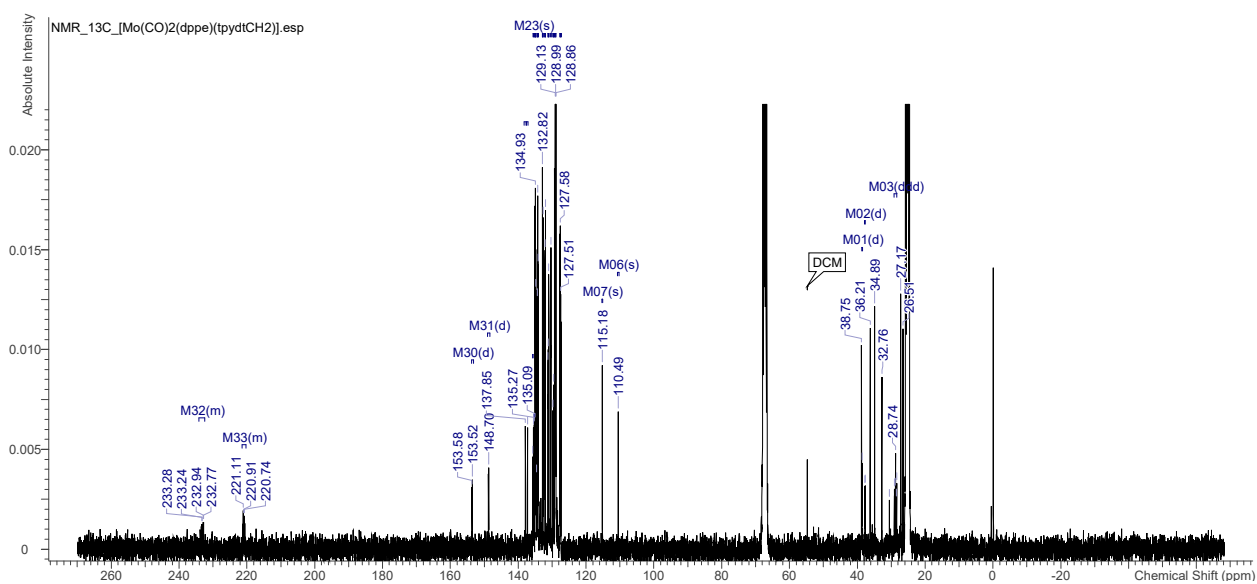


Figure S 9:  $^{13}\text{C-NMR}$  of  $2^{\text{CH}_2}$  in THF-d8.

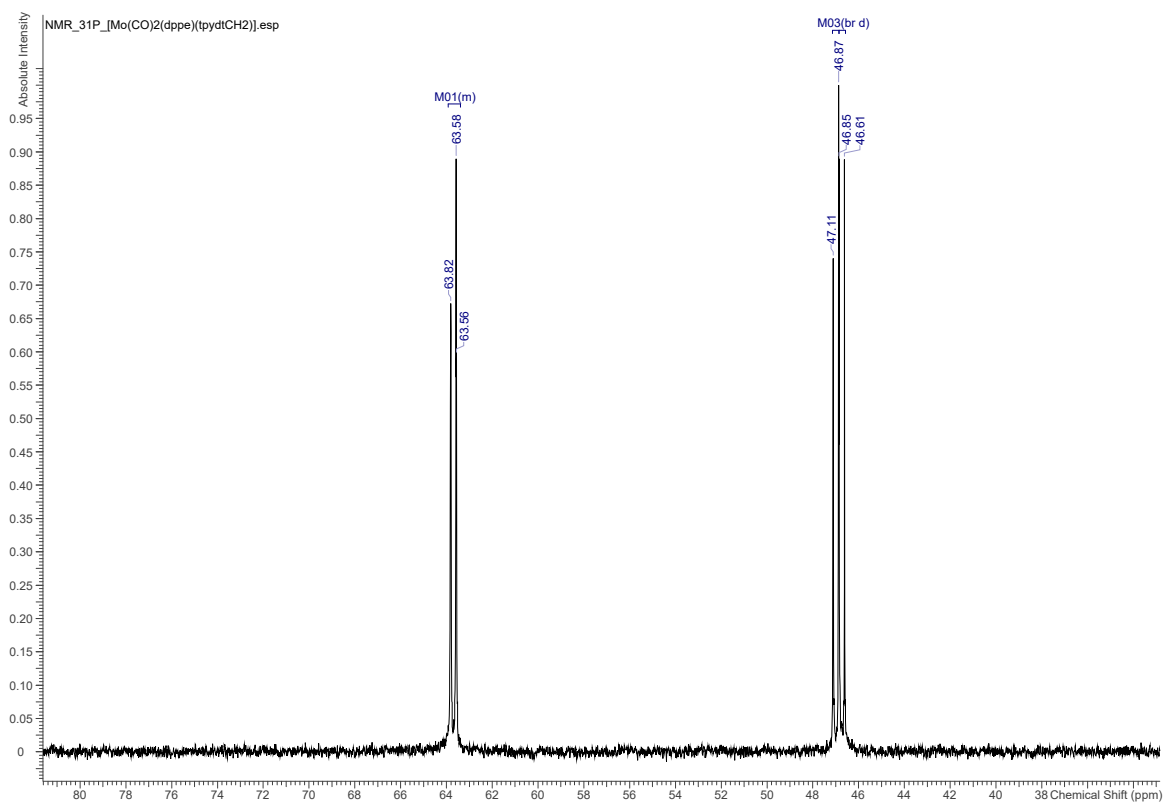


Figure S 10:  $^{31}\text{P}$ -NMR of  $2^{\text{CH}_2}$  in THF-d<sub>8</sub>.

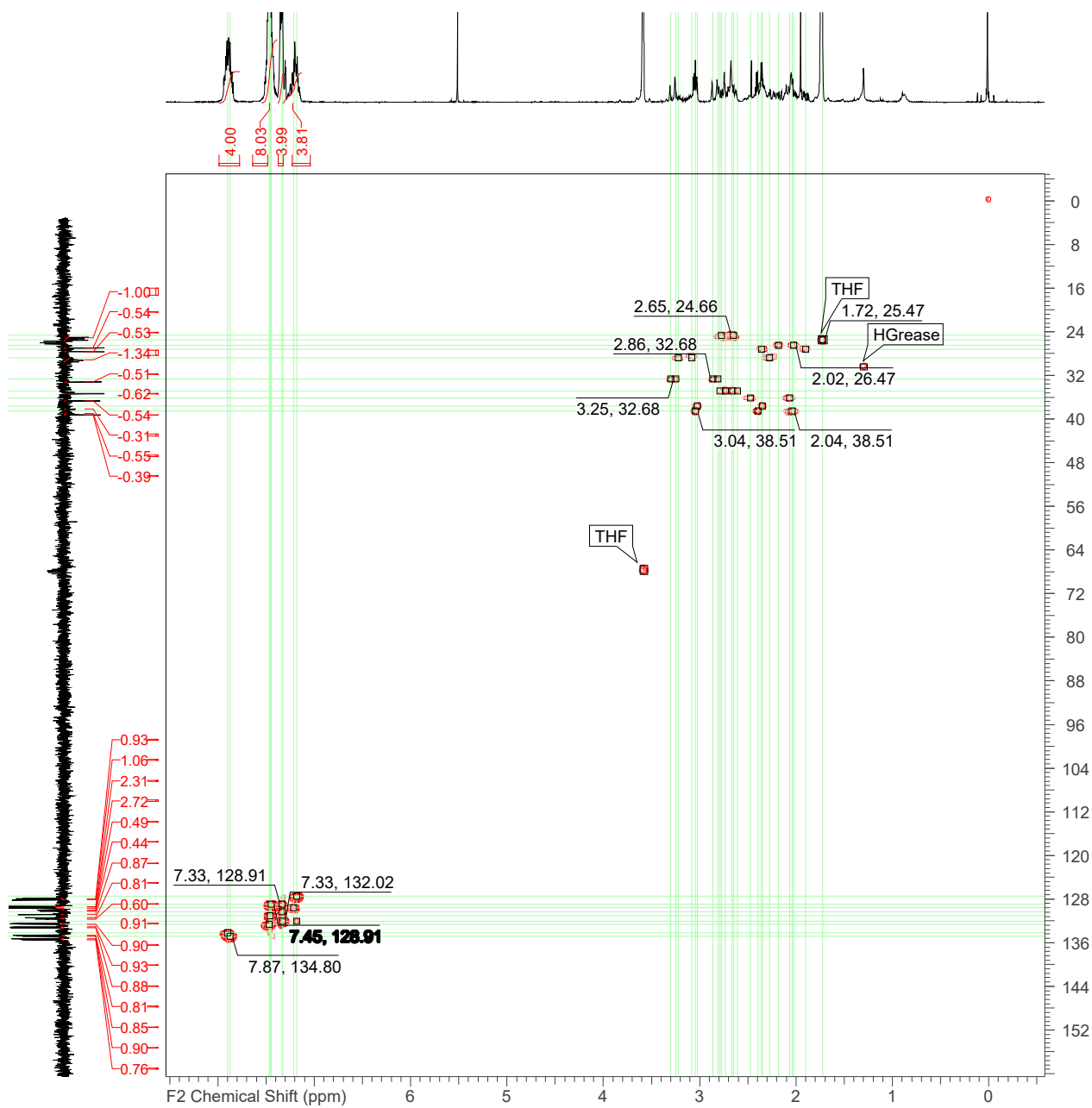


Figure S 11:  $^1\text{H}$ - $^{13}\text{C}$ -HSQC-NMR of  $2^{\text{CH}_2}$  in THF-d<sub>8</sub>.

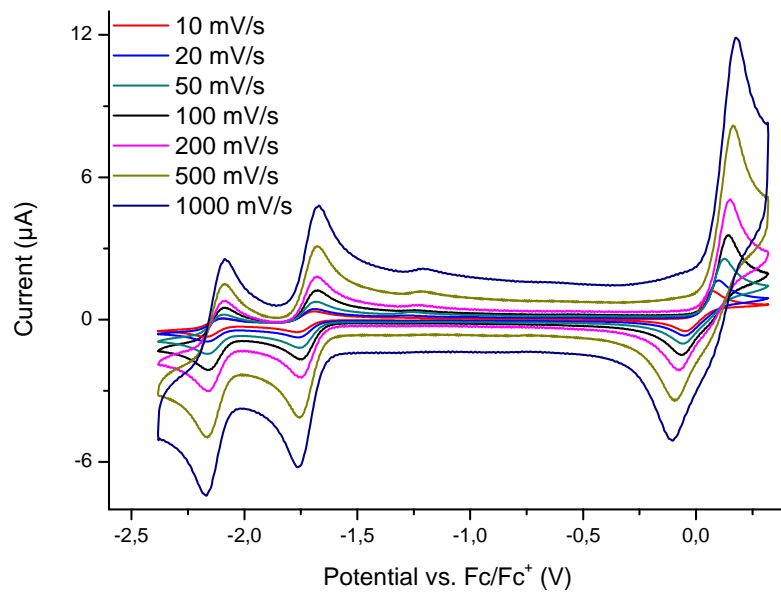


Figure S 12: Scan rate dependent CV's in THF of complex **1** ( $[\text{Mo}(\text{CO})_2(\text{cydt})(\text{dppe})]$ ) (0.32 mM). Electrolyte 0.2 M  $\text{NBu}_4\text{PF}_6$ .

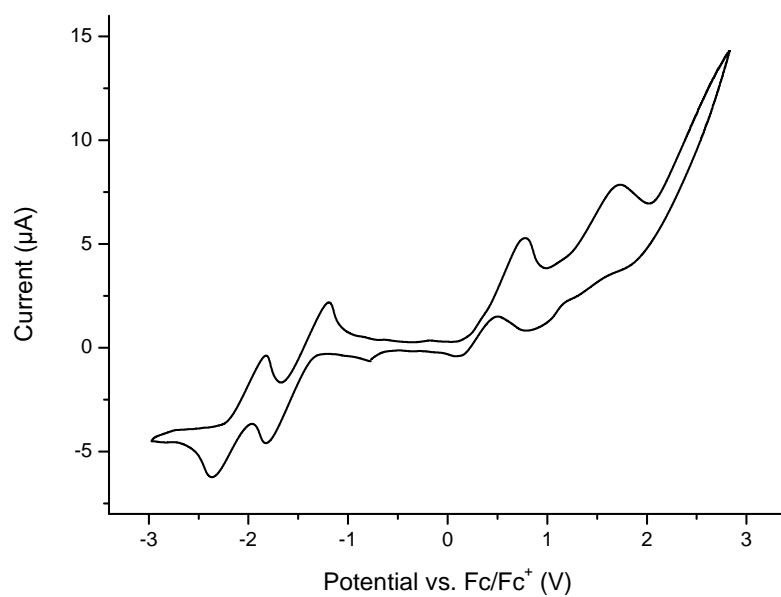


Figure S 13: Cyclic voltammogram of complex **1** ( $[\text{Mo}(\text{CO})_2(\text{cydt})(\text{dppe})]$ ) (3.3 mM) in benzene. Electrolyte 0.165 M  $\text{NHex}_4\text{BF}_4$ ,  $5 \text{ mV s}^{-1}$ .

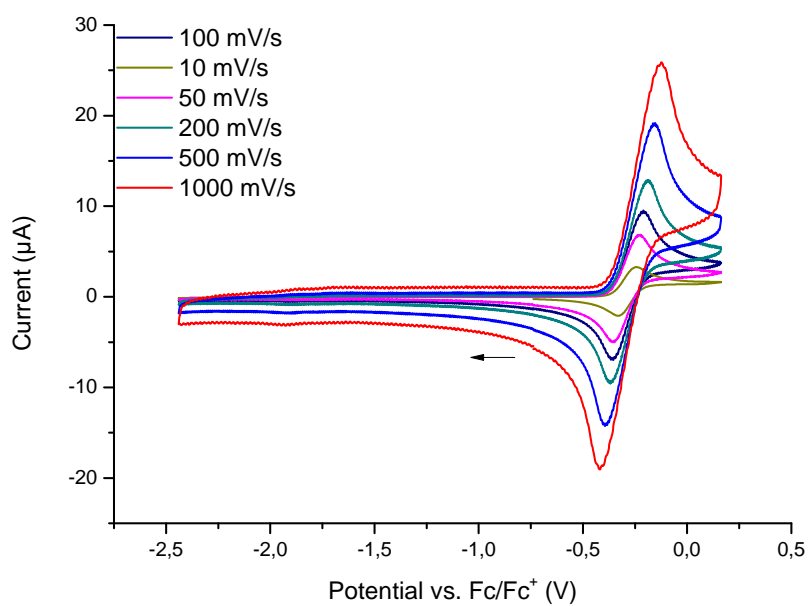


Figure S 14: Cyclic voltammogram of complex  $1^{CH_2}$  ( $[Mo(CO)_2(CH_2-cydt)(dppe)]$ ) in ACN. Electrolyte 0.1 M  $NBu_4PF_6$

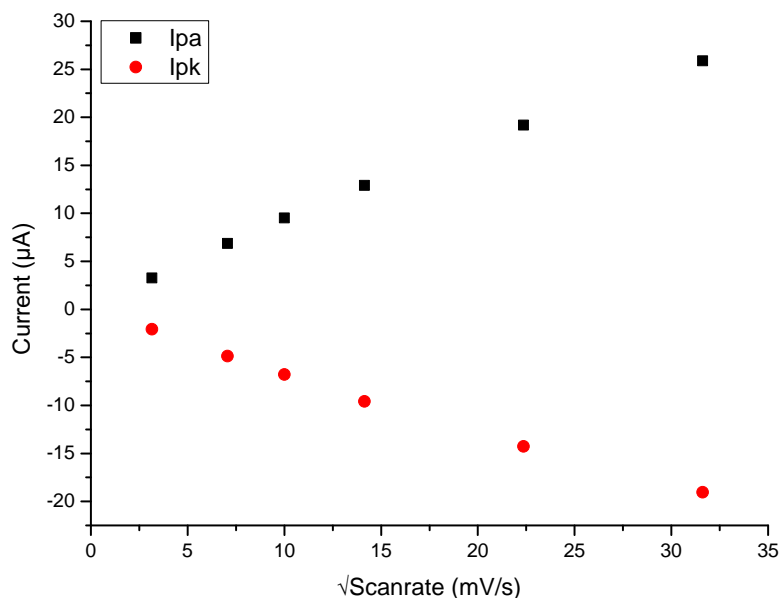


Figure S 15: Plot of the anodic and cathodic peak currents in dependence of the square root of the scan rate. Complex  $1^{CH_2}$  in ACN using 0.1 M  $NBu_4PF_6$ . Data plots are taken from the respective CV measurements in Figure S 14.

### 3 Additional Tables

Table S 1: Selected bond distances and angles of  $[\text{Mo}(\text{CO})_2(\text{cydt}-\text{CH}_2)(\text{dppe})]$  (resolution and accuracy of C-C-bonds at 0.0212 Å) in comparison with the corresponding DFT calculations, the published values of the *King-Bisnette* complex, and the initial complex  $[\text{Mo}(\text{CO})_2(\text{cydt})(\text{dppe})]$  and the corresponding complexes utilising the **tpydt**-ligand. {Mo} represents the  $\{\text{Mo}(\text{CO})_2(\text{dppe})\}$  core.

	{Mo} & cydt <b>1</b>	{Mo} & cydt <b>1<sup>red</sup></b>	{Mo} & CH <sub>2</sub> -cydt <b>1<sup>CH<sub>2</sub></sup></b>			[MoCp(CO) <sub>2</sub> (π-CH <sub>2</sub> SCH <sub>3</sub> )] <b>King-Bisnette</b>	{Mo} & tpydt <b>2</b>	{Mo} & CH <sub>2</sub> -tpydt <b>2<sup>CH<sub>2</sub></sup></b>
	X-ray	DFT Singlet	X-ray	DFT Singlet	Triplet	X-ray	X-ray	X-ray
C=C	1.354(17)	1.370	1.340(2)	1.367	1.376	-	1.350(7)	1.337(10)
C4-S1	1.738(12)	1.776	1.779(15)	1.788	1.772	1.820	1.744(5)	1.793(8)
C9-S2	1.726(13)	1.774	1.751(16)	1.752	1.756	-	1.739(5)	1.760(7)
S1-C3 (CH <sub>2</sub> )	-	-	1.728(14)	1.776	1.786	1.780	-	1.749(7)
Mo1-C3 (CH <sub>2</sub> )	-	-	2.210(12)	2.241	2.247	2.240	-	2.207(6)
C1-O1	1.145(15)	1.210	1.150(2)	1.176	1.178	1.180	1.143(6)	1.150(9)
C2-O2	1.162(16)	1.211	1.189(2)	1.189	1.179	1.200	1.141(6)	1.140(9)
Mo1-S1	2.351(3)	2.536	2.427(4)	2.460	2.908	2.442	2.3617(14)	2.4155(17)
Mo1-S2	2.404(3)	2.601	2.556(4)	2.584	2.457	-	2.3856(14)	2.5504(18)
Mo1-C1	1.973(16)	1.930	1.985(19)	1.974	1.992	1.903	1.979(5)	1.936(7)
Mo1-C2	1.965(14)	1.925	1.926(15)	1.938	1.967	1.918	1.977(4)	1.986(7)
Mo1-P1	2.474(3)	2.392	2.495(4)	2.494	2.530	-	2.4839(14)	2.4918(17)
Mo1-P2	2.491(3)	2.574	2.528(4)	2.547	2.610	-	2.4743(14)	2.5326(17)
Mo-CH <sub>2</sub> -S	-	-	74.97(2)	74.5	91.53	73.5	-	74.3(2)
S1-Mo1-S2	81.54(10)	80.8	81.88(12)	81.4	79.0	-	81.73(5)	81.79(6)
C1-Mo1-C2	76.7(5)	85.5	84.3(6)	85.4	90.3	-	80.3(2)	85.9(3)
P1-Mo1-P2	72.28(10)	77.7	77.499(15)	77.1	76.1	-	76.46(4)	77.49(5)
CH <sub>2</sub> -Mo-S	-	-	43.454(17)	44.1	84.7	44.4	-	44.18(18)



Table S 2: Crystal and Refinement Data for crystallized compounds. {Mo} represents the {Mo(CO)<sub>2</sub>(dppe)} core.

	<b>1<sup>CH2</sup></b> {Mo} & CH <sub>2</sub> -cydt	<b>tpydt</b>	<b>2</b> {Mo} & tpydt	<b>2<sup>CH2</sup></b> {Mo} & CH <sub>2</sub> -tpydt
formular	C <sub>36</sub> H <sub>36</sub> Cl <sub>2</sub> MoO <sub>2</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> OS <sub>3</sub>	C <sub>33</sub> H <sub>30</sub> MoO <sub>2</sub> P <sub>2</sub> S <sub>3</sub>	C <sub>35</sub> H <sub>34</sub> Cl <sub>2</sub> MoO <sub>2</sub> P <sub>2</sub> S <sub>3</sub>
CCDC	2080179	2094532	2094530	2094531
formular wt	793.55	190.29	712.63	811.58
temperature, K	170(2)	170(2)	170(2)	170(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>
<i>a</i> , Å	8.8543(18)	11.986(2)	14.235(3)	8.8426(18)
<i>b</i> , Å	10.246(2)	7.7681(16)	11.186(2)	10.239(2)
<i>c</i> , Å	19.033(4)	16.643(3)	20.632(4)	19.000(4)
$\alpha$ , deg.	90	90	90	90
$\beta$ , deg.	91.12(3)	100.66	108.82(3)	90.96(3)
$\gamma$ , deg.	90	90	90	90
<i>V</i> , Å <sup>3</sup>	1726.4(6)	1522.8	3109.4(12)	1720.1(6)
<i>Z</i>	2	8	4	2
density, mg/cm <sup>3</sup>	1.527	1.660	1.522	1.567
$\mu$ , mm <sup>-1</sup>	0.781	0.894	0.756	0.844
total reflections	13582	6120	35040	19308
indep. reflections	6881	2109	8575	8475
R1 <sup>a</sup> , wR2 <sup>b</sup> ( <i>I</i> >2 $\sigma$ )	0.0718, 0.1603	0.0523, 0.1000	0.0559, 0.1295	0.0492, 0.1333
R1 <sup>a</sup> , wR2 <sup>b</sup> all data	0.1190, 0.1907	0.1170, 0.1163	0.1135, 0.1706	0.0571, 0.1411
Largest diff. peak and hole, e $\cdot$ Å <sup>-3</sup>	1.052/ -1.204	0.312/ -0.327	1.575/ -1.394	1.209/ -2.179
R <sub>int</sub>	0.1091	0.1013	0.0961	0.0493
Goof	1.031	0.991	1.086	1.045

## 4 Selected Results of the DFT calculations

Table S 3: Löwdin Population Analysis for the HOMO and Natural Population Analysis (NPA) Charges

Complex	Charge	Multiplicity	Orbital composition				NPA charges			
			Mo	S1 (trans-CO)	S2 (trans-P)	CO (trans-P)	CO (trans-S)	Mo	S(1)	S(2)
<b>1</b>	0	1	37.3	4.1	7.5	13.2	14.3	-0.73	0.07	-0.06
<b>1<sup>red</sup></b>	-2	1	18.6	21.1	13.8	9.1	2.4	-1.00	-0.32	-0.23
<b>1<sup>CH<sub>2</sub></sup></b>	0	1	23.4	31.7	<1	3.2	9.5	-0.89	-0.18	0.53
<b>1<sup>CH<sub>2</sub></sup></b>	0	3	41.9	12.7	<1	8.2	14.6	-	-	-

Table S 4: Calculated Energies ( $E_h$ ) for all relevant complexes.

complex	Charge	Multiplicity	Thermal energy	Enthalpy	Entropy	Gibbs free enthalpy
<b>[Mo(CO)<sub>2</sub>(cydt)(dppe)]<sup>2-</sup></b>	-2	1	-3011.8306	-3011.8297	0.1077	-3011.9374
<b>[Mo(CO)<sub>2</sub>(cydt)(dppe)]</b>	0	1	-3011.8205	-3011.8196	0.1063	-3011.9258
<b>[Mo(CO)<sub>2</sub>(CH<sub>2</sub>-cydt)(dppe)]</b>	0	1	-3051.0455	-3051.0446	0.1075	-3051.1521
<b>[Mo(CO)<sub>2</sub>(CH<sub>2</sub>-cydt)(dppe)]</b>	0	3	-3050.9932	-3050.9923	0.1106	-3051.1029

Table S 5: Calculated Vibrational Frequencies of [Mo(CO)<sub>2</sub>(CH<sub>2</sub>-cydt)(dppe)] **1<sup>CH<sub>2</sub></sup>**

Spin-Multiplicity: 1						Spin-Multiplicity: 3					
#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
6	20.27	0.166552	0.234563	0.269283	-0.197532	6	16.71	0.135329	0.331138	-0.085507	-0.135519
7	29.24	0.123621	-0.14972	-0.090151	0.305086	7	24.96	0.292851	0.071645	0.46409	-0.268959
8	34.95	0.330062	-0.116552	0.561043	0.041327	8	34.15	0.103984	0.297938	-0.107979	-0.059642
9	41.34	0.40785	-0.432167	0.468846	-0.035564	9	41.03	0.366917	-0.561955	0.225908	-0.009485
10	48.33	0.216296	0.447674	-0.045023	-0.117716	10	44.12	0.783207	0.786082	-0.302875	-0.271199

to be continued

Table S 5: Calculated Vibrational Frequencies - continued from above

#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
11	51.46	0.311984	0.148019	0.138267	0.520534	11	47.96	0.05423	-0.073104	-0.22021	-0.019843
12	53.36	0.288734	0.34408	-0.382914	-0.15401	12	49.6	0.511356	0.175538	0.27102	0.638036
13	57.21	0.114234	-0.006005	0.33543	-0.041045	13	52.27	0.061568	0.082834	0.213492	-0.095542
14	66.94	0.193692	0.111316	0.047509	-0.423135	14	60.25	0.293041	-0.296223	0.008355	-0.453015
15	69.38	0.031735	-0.170578	0.045399	0.024022	15	64.29	0.501472	-0.46651	-0.413724	-0.335667
16	70.33	0.237271	-0.221195	-0.385312	-0.199697	16	68.33	0.284685	0.440286	0.265982	0.141726
17	78.03	0.274561	0.162519	0.173335	0.467015	17	74.17	0.194649	-0.137034	-0.059243	-0.415164
18	90.26	0.166999	0.144001	0.194502	-0.32929	18	81.48	2.902146	-1.008739	-1.04249	-0.8932
19	95.94	1.381704	-0.195493	-1.146845	-0.168023	19	84.75	0.907132	0.604012	0.735851	-0.028725
20	97.97	0.584809	0.274423	0.649717	-0.295582	20	90.83	0.341058	-0.538216	-0.086803	-0.209397
21	100.85	0.605119	-0.599076	-0.241893	0.433261	21	93.81	0.21345	-0.079515	-0.211177	-0.403151
22	108.07	0.325318	-0.515861	-0.242479	-0.020238	22	99.63	1.157978	-1.05575	-0.048494	-0.202531
23	109.71	0.655628	-0.31004	0.546556	-0.510666	23	100.78	0.219339	-0.09051	-0.228723	-0.398538
24	115.51	0.808277	-0.531653	0.256369	0.678156	24	108.01	0.571833	0.384725	-0.029902	0.650327
25	121.78	0.706455	0.810296	-0.167499	0.147712	25	111.27	0.900572	-0.910222	-0.110873	0.244489
26	130.18	1.246113	0.711167	0.815009	-0.275889	26	123.04	0.178153	0.037468	0.338598	-0.2492
27	139.83	0.103527	0.006849	0.294793	-0.128752	27	128.8	0.798632	-0.491768	0.014296	0.746051
28	151.51	1.662558	-0.586725	-0.123816	1.141482	28	137.51	0.128431	-0.103535	-0.256486	0.227873
29	160.82	1.57667	0.305473	0.22398	-1.197159	29	147.48	0.564401	-0.66901	-0.310195	0.143546
30	173.97	1.44273	0.84185	-0.122403	0.847959	30	153.41	0.372521	-0.577045	0.181621	-0.080955
31	188.07	0.147194	0.10046	0.366584	0.052128	31	174.25	0.814311	0.773908	-0.404227	0.227986
32	197.23	0.855457	-0.275021	0.834656	0.288393	32	178.08	0.950334	-0.310579	0.414361	0.825942
33	206.47	0.505967	0.22553	-0.174399	0.651681	33	192.83	2.469246	-0.64949	0.97676	1.045633
34	214.08	1.881806	-1.065583	-0.779674	0.372085	34	205.36	0.248705	0.047968	0.388839	-0.308559
35	223.25	1.60646	-0.913916	-0.418681	0.771962	35	206.14	1.850378	1.107461	0.600331	0.513334
36	227.53	0.116579	-0.285236	-0.185456	0.028723	36	217.82	2.507512	-1.004612	-0.457502	1.135323
37	231.01	1.321951	-0.058872	-1.106827	0.305646	37	227.64	2.410941	0.771369	1.165258	-0.676835
38	248.36	0.234194	-0.19138	0.438764	0.07109	38	246.52	0.768637	-0.42317	0.758455	0.119622
39	262	0.570536	-0.364107	0.522463	0.406195	39	256.54	0.617585	-0.17636	0.512304	0.569233
40	265.52	0.396607	0.475192	0.303439	0.280579	40	262.51	0.027312	0.099578	-0.094398	0.092115
41	279.5	1.349582	-1.087285	-0.09336	-0.398343	41	264.86	1.769665	0.515	1.217934	-0.145176
42	304.83	2.090908	-0.304712	-1.347968	-0.425488	42	283.46	1.390802	-1.146163	-0.275669	-0.033439
43	310.84	1.403534	-0.001962	1.154747	-0.264745	43	302.63	0.47564	0.491154	0.051802	-0.481378
44	319.3	2.34781	1.510717	-0.189413	0.172243	44	313.56	5.23584	2.253753	0.334059	0.211756

to be continued

Table S 5: Calculated Vibrational Frequencies - continued from above

#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
45	336.81	3.504323	-1.842425	0.058461	0.326155	45	329.96	3.090254	-1.441066	-0.762342	0.657585
46	341.06	1.97511	-0.955488	-0.526844	-0.88577	46	331.26	8.276412	2.354649	1.576148	0.497791
47	353.26	7.231203	-2.44568	-0.726182	0.850006	47	336.34	2.266009	-1.297147	0.566438	0.512411
48	361.58	12.978921	-0.750378	-2.341019	-2.633531	48	362.44	12.756615	-1.031936	-2.217391	-2.602864
49	394.01	0.028185	-0.044658	-0.030182	0.158998	49	396.36	0.045121	-0.005821	-0.024538	0.210915
50	395.99	0.357947	0.188997	0.434197	-0.36565	50	396.88	0.394764	-0.098966	-0.423927	0.453051
51	400.9	1.804881	0.881431	0.179087	-0.997942	51	399.82	5.55941	1.658693	0.52271	-1.592144
52	404.3	9.182167	2.231331	0.63701	-1.948729	52	400.37	8.169023	2.013896	0.532531	-1.95695
53	405.3	2.455814	1.11558	0.118085	-1.094235	53	406.07	0.198429	0.315913	0.284337	-0.133342
54	409.82	12.494726	1.698275	0.05844	-3.099544	54	409.6	3.914138	1.598746	0.025616	-1.165115
55	420.79	5.804167	1.762101	-0.189211	1.631982	55	411.31	13.755543	-2.295443	-0.320067	-2.895521
56	429.17	14.21236	1.10521	-0.872425	3.497105	56	419.51	2.828017	-0.093148	-1.663578	0.227703
57	440.5	19.579252	3.292191	2.397846	1.72947	57	431.85	1.091373	0.848485	0.451093	-0.40983
58	447.89	0.234133	0.29953	-0.311759	-0.217306	58	443.83	5.54656	0.273954	-2.056294	1.114973
59	465.46	3.469285	-0.46363	1.657707	0.711575	59	448.43	4.06736	-1.132268	-1.649996	-0.250686
60	474.49	8.509693	-0.907936	-2.216798	1.664677	60	464.83	3.579941	0.340178	1.727127	0.693723
61	484.02	10.35895	-1.487817	-2.802637	0.53905	61	470.34	2.629961	-0.732004	0.780046	-1.218876
62	488.06	36.190421	5.278493	0.871557	-2.751058	62	477.14	4.871203	0.434961	-2.152757	0.21829
63	496.35	1.803621	0.713211	-0.322853	-1.0912	63	483.58	0.705614	0.263334	-0.568416	0.559619
64	502.36	18.29764	2.247973	0.853707	3.537717	64	486.29	44.141885	5.571345	1.060924	-3.4607
65	508.66	20.7083	-3.626533	-0.12572	-2.746043	65	490.95	13.949224	-2.98792	-0.868319	2.065813
66	513.12	40.860167	4.504241	4.462388	0.811836	66	496.68	7.460097	-2.066159	-0.759751	1.616745
67	515.55	44.038064	0.707894	-4.001338	-5.246546	67	504.15	16.106463	-0.313128	3.184398	2.4224
68	528.19	54.542481	-3.492223	-3.719484	-5.339691	68	507.1	37.04066	-5.243754	-1.758223	-2.540149
69	531.44	5.000554	0.158291	-1.743824	1.39089	69	519.13	82.71094	-4.009598	-5.01228	-6.442911
70	583.6	2.169921	0.829636	0.984624	0.71564	70	531.74	6.140693	1.599534	0.85137	1.690371
71	592.65	34.604534	5.156624	2.08198	1.918104	71	575.71	0.265124	0.373651	-0.245401	-0.255515
72	607.05	8.381954	-1.406805	2.238415	1.17998	72	584.95	27.340787	-0.133322	4.896937	1.828393
73	607.66	0.947966	-0.523511	0.817459	-0.075261	73	608.3	0.579491	-0.504854	0.232212	-0.52028
74	609.09	2.26665	0.878577	1.116104	0.499064	74	608.63	2.027215	1.352257	0.295225	-0.333853
75	610.94	1.276343	0.773364	-0.356927	0.742196	75	609.81	0.494811	-0.217594	0.181655	0.643789
76	613.98	11.972871	-0.278234	-3.272737	-1.088415	76	610.91	0.231085	0.278969	0.123394	0.371531
77	635.97	37.037242	-4.443085	-1.291491	3.953263	77	631.5	32.105558	-4.46666	-0.719059	3.411372
78	662.46	21.893115	-4.189578	0.927389	-1.865611	78	649.79	20.87315	-3.954772	0.417496	-2.249138

to be continued

Table S 5: Calculated Vibrational Frequencies - continued from above

#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
79	689.2	6.99192	0.641515	0.86044	2.416614	79	652.66	0.15308	-0.291063	0.051373	0.256365
80	690.78	15.687459	3.341127	-1.310353	-1.6755	80	685.19	3.483428	0.050888	-0.605115	1.764844
81	691.39	16.959457	-3.486906	-0.709368	2.073099	81	688.32	3.763978	-0.35994	0.901367	1.679869
82	693.37	40.351385	4.867387	2.633677	3.118281	82	690.73	31.123745	5.150152	-0.405373	-2.106027
83	698.08	35.778401	-3.516243	-2.219785	4.29965	83	692.85	28.264302	-4.638666	-1.313648	-2.24085
84	700.24	22.97245	2.842174	-1.971898	-3.317547	84	694.78	7.660871	1.78016	1.074031	-1.827117
85	702.39	11.539367	-1.40012	-2.980523	-0.833975	85	697	11.841895	2.289578	2.313032	-1.117859
86	703.99	29.321486	-3.887289	-0.548386	-3.729576	86	698.79	26.013665	-2.226758	1.84599	4.200897
87	730.67	0.962014	-0.877741	-0.183149	-0.397544	87	702.07	26.497633	3.006428	0.201165	4.173554
88	736.12	1.186518	-1.038963	-0.206783	-0.253602	88	716.64	6.674882	-0.875294	-0.242828	-2.418631
89	737.64	10.285973	3.104085	-0.791686	-0.154471	89	735.23	2.97133	1.708134	-0.11921	0.198488
90	741.07	9.030784	-2.689911	1.08162	-0.790733	90	737.53	13.365605	-3.425439	0.649145	-1.100264
91	743.68	6.297684	-0.174272	-0.113159	2.500902	91	742.77	9.326575	-0.230055	1.226008	-2.787571
92	746.63	4.225467	1.501386	-1.171713	-0.773559	92	745.23	3.920433	1.101855	-0.738735	-1.469904
93	783.32	2.393797	-1.291509	-0.849507	-0.06433	93	782.8	1.662341	-0.976637	0.841112	-0.032407
94	799.63	41.513442	-1.733186	1.146804	6.098717	94	790.71	41.719182	-0.228056	1.668469	6.235654
95	805.25	2.704717	-0.742222	-1.438536	-0.290581	95	803.76	2.969455	1.036294	1.375274	-0.064579
96	824.41	2.986085	0.16636	-0.137451	1.714502	96	825.21	1.26749	0.493139	0.914482	-0.43362
97	825.92	1.52832	0.567032	0.996692	-0.461951	97	828.74	1.936928	-0.019552	0.470946	-1.309487
98	840.7	0.319385	0.25239	0.505048	0.024708	98	837.98	0.747802	0.146331	0.828831	0.198567
99	842.1	1.883552	-1.054675	-0.772786	0.417151	99	840.37	1.435871	-0.770733	-0.914432	0.075205
100	850.27	2.236682	1.087012	0.781691	0.666368	100	854.75	1.868226	0.609816	1.067647	0.59706
101	863.32	25.148358	4.98818	0.387214	-0.341299	101	860	16.914294	4.074995	0.412406	0.372328
102	882.88	0.022627	-0.080843	0.076143	0.101458	102	878.13	0.270053	-0.289639	-0.082416	0.423521
103	898.12	0.310946	0.253176	-0.333303	-0.368452	103	896.22	2.02162	0.697404	-0.778115	-0.964254
104	898.53	0.205922	-0.279596	-0.014286	0.357134	104	898.32	0.330585	-0.514718	-0.209336	0.147746
105	919.13	0.171919	0.311	-0.252236	-0.10759	105	915.85	0.37198	0.499399	-0.288208	0.198788
106	920.67	0.875524	0.465225	-0.785369	-0.205635	106	917.8	0.938271	-0.426086	0.840592	0.223893
107	937.38	1.906564	0.767487	0.163041	1.136198	107	940.76	1.051801	0.412369	0.073597	-0.936128
108	943.76	5.3338	1.817143	1.06346	0.949128	108	947.37	4.833742	0.743757	1.057374	1.77835
109	955.02	2.768913	0.848478	-0.200781	1.417281	109	956.62	0.242203	0.137084	-0.47216	-0.021819
110	956.08	3.694501	0.098455	0.536654	-1.843044	110	957.41	0.10552	0.212388	0.202042	-0.139965
111	957.22	0.516519	0.021702	-0.447515	-0.561941	111	961.83	0.307277	0.312703	0.355438	0.288371
112	960.7	6.92316	1.92026	1.797282	-0.074422	112	968.02	0.85897	0.161563	0.912179	0.028238

to be continued

Table S 5: Calculated Vibrational Frequencies - continued from above

#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
113	969.81	0.01344	0.064155	0.064403	0.071947	113	969.7	0.981491	0.352433	0.917269	0.126092
114	971.3	1.049049	-0.480149	-0.894547	0.135249	114	974.12	2.896137	-0.279478	-0.562304	-1.581722
115	980.71	1.392036	-0.510435	-0.715623	0.787004	115	980.48	0.708709	-0.260126	-0.094704	0.795031
116	981.54	0.608471	0.298662	0.702024	0.162586	116	980.65	0.524729	0.313977	0.561081	-0.333671
117	982.65	1.127485	-0.766292	-0.681318	0.275837	117	982.17	1.204156	0.885477	0.647489	0.029062
118	983.13	0.40258	0.317168	-0.281049	-0.472225	118	982.57	0.308754	0.353549	0.201243	-0.378495
119	983.26	2.280089	-0.75466	-1.101951	-0.704472	119	983.47	0.572001	-0.593009	-0.363072	0.297523
120	984.08	0.299081	-0.17573	0.057997	0.514623	120	983.78	1.539115	-0.6234	-0.866719	-0.63189
121	991.16	0.632107	-0.301624	-0.69199	0.249559	121	990.1	0.514942	-0.163084	-0.698741	0.010355
122	993.31	0.241512	-0.311672	-0.265867	0.271454	122	991.22	0.190801	0.178201	-0.342351	0.204552
123	996.01	0.694263	0.486621	0.097843	-0.669246	123	999.86	0.717921	-0.634344	-0.431682	0.359416
124	1011.42	4.071683	-0.923473	-1.548427	-0.906231	124	1012.64	0.633827	0.21878	-0.367237	-0.67164
125	1018.41	2.267241	-0.650093	-1.252593	-0.525004	125	1018.86	7.059717	-1.650887	-2.06947	-0.227119
126	1019.57	3.11497	-1.330212	-1.038553	0.516636	126	1018.92	1.330346	0.570992	-0.267525	-0.965787
127	1020.64	2.20363	0.427342	1.303857	0.566537	127	1020.07	1.738887	-0.197468	1.104974	0.692044
128	1020.92	1.802593	-0.192418	-0.242772	1.30638	128	1020.54	2.595244	-0.26615	-0.374338	1.544111
129	1050.87	1.08488	0.062181	0.895278	0.528669	129	1050.41	1.150271	-0.000885	-1.072493	-0.005317
130	1061.67	6.753036	1.545173	1.995105	-0.620511	130	1063.02	3.305036	-0.88982	-1.258948	0.963486
131	1069.62	3.480456	1.348942	-0.015748	1.288628	131	1069.94	4.069563	0.675422	-1.881148	-0.273226
132	1069.69	5.954492	0.236885	2.24755	0.920271	132	1071.45	12.617167	-1.012472	-3.255352	0.99737
133	1072.86	4.146951	-0.432359	-1.9523	0.385411	133	1072.14	1.613475	0.526256	0.714606	0.908772
134	1077.08	2.911829	-0.461167	-0.893077	1.378974	134	1076.18	1.382302	0.784369	-0.871473	-0.087185
135	1077.36	3.299833	-0.673165	1.679855	-0.157388	135	1076.27	5.777359	-1.272623	-1.128066	1.698604
136	1083.42	13.495585	-2.564035	-0.065665	2.630018	136	1077.66	8.540931	-2.543675	-1.393074	0.360549
137	1085.99	58.935829	-4.601398	-5.937935	-1.582368	137	1085.38	7.069521	-1.913135	-1.829262	-0.251467
138	1089.19	27.920611	-2.860324	-2.537517	3.646939	138	1086.31	24.41262	-2.944232	-3.701848	1.428441
139	1094.53	11.461386	1.421933	2.73365	1.402374	139	1086.78	20.777119	1.403002	3.335127	2.772297
140	1106.02	4.380664	0.794814	0.610453	1.837467	140	1104.37	1.077616	-0.073174	-0.001524	1.0355
141	1112.63	0.82946	-0.286481	-0.855428	0.125029	141	1112.39	4.842594	-0.901684	-1.93215	-0.544387
142	1113.24	4.265328	-1.366717	-1.441919	0.564164	142	1113.58	1.936378	-0.966153	-0.334137	0.944076
143	1145.97	0.046696	0.093747	0.03668	0.191212	143	1145.64	0.205213	-0.006052	0.406472	-0.199892
144	1146.29	0.337862	-0.11716	0.523771	-0.223157	144	1146.23	0.099355	-0.168971	0.217127	-0.153817
145	1147.34	0.134087	-0.127505	0.036625	0.341304	145	1146.31	0.053142	0.077199	-0.192575	0.100483
146	1147.43	0.094458	0.022565	-0.303502	-0.042841	146	1146.85	0.107561	-0.016669	-0.327126	0.016477

to be continued

Table S 5: Calculated Vibrational Frequencies - continued from above

#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
147	1156.06	1.742761	0.545029	1.195674	-0.126757	147	1161.48	1.639209	0.690337	1.076882	-0.054475
148	1162.93	4.625154	1.030967	1.507788	1.135269	148	1164.27	4.772491	-1.169574	-1.487669	-1.091526
149	1167.06	6.520655	-2.269871	-1.168343	0.057583	149	1166.85	5.041599	-1.954398	-1.087051	-0.200617
150	1169.79	1.23727	-0.431346	0.446492	0.922961	150	1169.22	0.28708	-0.304513	-0.335215	0.286326
151	1173.84	1.243174	0.328132	0.328643	-1.013655	151	1172.45	0.966909	0.257404	0.239275	-0.918368
152	1210.11	3.155652	1.696001	0.460152	-0.259795	152	1209.71	1.996186	-1.370966	-0.335039	0.066246
153	1220.3	4.807217	-1.216836	-1.577235	-0.915891	153	1223.6	7.902465	1.407824	2.382104	0.49606
154	1241.67	2.271974	0.583397	0.851052	-1.098786	154	1247.29	0.968032	-0.736537	0.576835	-0.304642
155	1246.46	2.317467	-1.490093	0.106679	-0.29276	155	1247.94	1.611967	-0.258239	0.000349	1.243093
156	1275.01	5.141324	-1.598429	0.95022	-1.29747	156	1275.06	5.84469	-1.146526	2.068682	0.500721
157	1277.09	3.947656	-1.163717	1.52377	0.521097	157	1276.47	3.855589	-1.398908	1.169904	-0.727991
158	1285.62	3.598225	0.634112	-0.579585	1.691215	158	1284	2.915778	0.540085	-0.762942	1.428988
159	1287.06	2.615726	-0.455922	1.481802	0.460571	159	1285.38	2.31573	-0.267733	1.435139	0.429447
160	1297.34	3.142365	-1.032915	-0.802565	-1.196386	160	1299.58	0.36077	0.141726	0.056703	-0.58092
161	1311.59	0.86136	-0.590865	-0.453215	-0.553926	161	1313.34	0.509283	-0.532678	-0.390775	-0.269875
162	1314.56	6.209514	-1.550947	-1.463625	-1.289139	162	1319.94	4.331166	1.130879	1.637931	0.607833
163	1330.3	1.3156	-0.301905	-1.073505	-0.268404	163	1332.19	3.534253	-0.526896	-1.767675	-0.363262
164	1344.07	1.124655	-0.53027	0.495236	0.773441	164	1338.12	1.477184	1.038606	-0.557258	-0.296557
165	1351.59	0.868516	0.385723	-0.41565	-0.739574	165	1350.17	0.643758	0.694286	-0.130305	-0.380454
166	1352.21	0.401932	0.311098	-0.410724	0.369399	166	1351.6	0.238935	-0.199444	0.353148	-0.272844
167	1356.83	1.480142	0.435977	0.861728	0.739926	167	1356.32	0.58387	0.063479	-0.243257	-0.721573
168	1357.67	0.62331	0.716965	0.083422	-0.319864	168	1356.41	3.181627	0.878276	1.412058	0.645254
169	1373.68	5.004282	-0.763832	2.02143	-0.578501	169	1376.04	6.593236	0.178916	2.555329	-0.177534
170	1383.57	2.842506	0.669778	-0.484845	1.469295	170	1380.04	2.731509	1.194874	0.822497	0.792012
171	1390.52	4.799138	2.123551	0.445597	0.30185	171	1389.2	9.711244	-2.294132	0.580051	-2.027744
172	1395.35	6.80681	-0.973536	2.224898	-0.953344	172	1389.37	1.87154	-1.210105	-0.094528	0.63107
173	1410.68	2.786104	1.258049	-0.70174	-0.843195	173	1411.49	2.876044	-1.606908	0.32903	0.430849
174	1416.73	11.721971	1.778241	-2.864107	-0.59726	174	1415.79	12.226149	-1.741097	3.004615	0.408683
175	1417.04	15.620708	2.93668	-2.159592	1.527343	175	1417.35	13.722207	-2.724205	2.397576	-0.743333
176	1420.86	10.992035	0.630301	1.894885	2.646538	176	1419.88	7.096784	-1.083693	-1.943909	-1.464107
177	1421.53	10.70893	-0.335146	-0.196653	-3.249298	177	1420.41	9.166556	-0.403063	-0.045255	-3.000341
178	1423.39	3.751358	-1.174997	-1.457225	0.497229	178	1424.42	5.328839	-1.023908	-2.064504	0.135186
179	1458.72	4.576131	1.559103	0.661687	-1.306713	179	1457.47	11.337477	2.61474	1.451814	-1.546884
180	1459.4	8.47584	-1.689948	-2.367504	-0.121818	180	1460.18	9.777348	1.719368	2.552035	0.555194

to be continued

Table S 5: Calculated Vibrational Frequencies - continued from above

#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
181	1463.36	7.122631	-0.379145	-0.975057	2.455228	181	1461.24	11.994915	-0.002177	-2.615903	-2.269793
182	1463.53	9.083324	0.051553	1.968289	2.281776	182	1461.95	11.270521	-0.28322	-0.454639	3.314153
183	1571.93	37.602824	-3.662055	-2.173973	-4.412031	183	1518.26	23.426923	2.119701	4.304919	-0.633614
184	1575.61	0.72434	0.272822	0.318536	-0.740569	184	1573.15	1.071921	0.247196	0.653769	-0.763807
185	1576.91	1.252977	0.484708	-0.963604	0.299169	185	1575.68	0.855425	-0.591705	0.71083	-0.005527
186	1579.84	2.119976	-0.619341	1.001018	0.856945	186	1576.47	0.275515	-0.316777	-0.296738	-0.295151
187	1580.12	2.954661	1.052461	1.070781	0.836907	187	1578.88	1.664219	-0.379363	-1.226305	-0.128364
188	1592.37	0.392388	-0.503641	0.005195	-0.372434	188	1590.28	3.771794	-1.241598	-1.27047	-0.784942
189	1592.77	0.536512	0.3059	-0.553418	0.369683	189	1591.03	14.55969	-1.507891	1.986785	2.88767
190	1593.59	3.222829	-0.340174	-0.142319	-1.756945	190	1591.85	1.919282	0.261125	-0.084678	1.357912
191	1594.49	0.799963	-0.205169	0.730671	0.473274	191	1592.75	2.836694	-1.062729	0.04279	-1.305937
192	1798.94	785.561976	-3.626557	-14.595683	23.651133	192	1826.39	835.206922	-9.664823	-3.289313	27.036615
193	1894.1	765.521143	10.622767	-22.826066	-11.473827	193	1868.75	1013.6394	7.77541	NaN	NaN
194	2910.61	47.572845	5.752637	0.600581	3.757568	194	2926.03	11.854584	1.699565	-2.678365	1.338815
195	2939.12	12.964323	-2.177099	2.43499	-1.515053	195	2926.98	24.737126	-3.996096	0.374225	-2.937397
196	2949.97	42.307426	5.194307	3.465818	-1.820633	196	2952	40.847146	4.882875	3.780396	-1.647204
197	2959.4	10.680682	-2.308431	-1.600163	1.670721	197	2969.6	21.512933	1.718346	3.917764	1.792022
198	2971.21	39.594639	0.945015	3.684762	5.012396	198	2972.65	9.315874	1.421067	-2.612259	-0.68742
199	2978.87	10.285206	-2.268606	2.152751	0.710137	199	2977.4	17.394916	-0.342311	2.598525	3.244288
200	2986.11	9.387359	1.92126	1.241025	2.038621	200	2984.37	10.201818	2.334105	0.980816	1.947247
201	3002.2	17.163071	-1.493494	-2.755281	2.709423	201	2996.98	15.651929	-2.020866	-1.607428	2.997367
202	3008.17	44.762229	-0.590327	-6.478382	-1.563429	202	3000.13	9.829393	3.010624	-0.874765	0.017988
203	3020.66	7.42105	-2.70391	-0.060425	-0.325992	203	3010.34	48.972078	-0.323191	-6.988639	-0.16293
204	3023.16	32.906316	-5.621709	-0.697079	-0.90376	204	3026.62	29.071591	5.078953	0.971616	1.527019
205	3041.5	1.873562	1.194176	-0.42614	0.515666	205	3037.7	3.249514	1.781437	-0.128431	-0.243928
206	3049.94	2.10984	-0.583232	-0.290483	1.298191	206	3047.68	2.883461	-0.074007	-0.707049	1.542098
207	3095.19	0.266891	-0.011639	0.500013	-0.129393	207	3086.83	0.377386	-0.218323	-0.119759	0.561586
208	3095.62	0.972594	0.248062	0.813395	0.499448	208	3096.08	0.187283	0.194152	0.385734	-0.028228
209	3097.9	0.402989	-0.058825	0.151747	0.613597	209	3097.07	0.901354	-0.075321	-0.124469	-0.938183
210	3097.94	0.196651	0.109526	-0.385792	-0.189263	210	3097.17	1.299184	0.271703	0.854146	0.704128
211	3103.1	0.758662	-0.5647	0.007681	-0.663112	211	3097.73	0.990684	0.398244	-0.672508	-0.616294
212	3104.35	1.827436	0.296903	1.317406	-0.061051	212	3103.78	1.603723	-0.455679	0.365934	-1.123464
213	3106.67	3.362657	1.142247	-1.428236	-0.134424	213	3104.48	2.53844	0.711264	1.39682	0.285372
214	3107.11	3.567799	-1.034873	0.652452	1.439147	214	3105.65	3.161561	-0.495817	1.684032	-0.282425

to be continued



Table S 5: Calculated Vibrational Frequencies - continued from above

#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ	#	freq /cm <sup>-1</sup>	T <sup>2</sup>	TX	TY	TZ
215	3113.43	10.611818	0.656468	-3.128729	0.626036	215	3107.65	4.02042	-1.148677	0.561813	1.544451
216	3113.74	0.761316	0.459873	-0.658724	-0.340463	216	3112.32	7.855803	-1.877081	1.237031	-1.673955
217	3114.16	13.673972	2.324381	-0.472249	2.836936	217	3112.77	6.263462	0.233228	2.489264	-0.112398
218	3114.97	7.225748	0.534769	1.216307	-2.336743	218	3114.07	11.533625	0.851659	-0.312385	-3.272723
219	3119.68	6.063479	-1.545876	1.053493	1.601217	219	3115.16	3.357408	0.039257	1.680846	0.728439
220	3122.19	14.813818	-1.701141	1.505303	3.107089	220	3118.16	6.709294	-2.342217	0.537251	-0.966785
221	3123.01	11.780215	-1.148316	-2.78523	-1.644409	221	3120.3	8.677386	-0.700714	2.809906	0.53927
222	3124.01	14.306782	0.899336	2.31346	2.854099	222	3121.14	8.659738	-2.183342	0.666142	1.857151
223	3126	22.881158	-3.300488	-2.29716	2.590558	223	3122.39	11.118474	-0.664781	-0.922166	-3.134669
224	3126.18	0.60408	-0.620722	0.362506	0.29559	224	3125.43	15.264047	-0.110628	-0.209361	-3.899741
225	3127.13	10.900259	-0.326444	2.226066	-2.416263	225	3125.88	24.947386	1.901263	4.612018	0.24875
226	3131.96	17.615125	-1.610958	-3.782266	-0.845223	226	3126.52	17.572851	-2.767831	-2.254288	2.19776
227	3133.96	3.618133	0.277918	-1.718858	0.765781	227	3127.98	7.967542	0.081891	-2.81253	-0.224741

End of Table

Table S 6: Coordinates for Geometry Optimized Structures **1**CH<sub>2</sub>

Spin-Multiplicity: 1				Spin-Multiplicity: 3			
Element	x	y	z	Element	x	y	z
'Mo'	8.870072	7.409622	5.040581	'Mo'	9.054568	7.340275	4.901722
'S'	10.353091	8.540304	6.645292	'S'	10.531706	8.750428	6.971966
'S'	9.006643	9.715641	3.883088	'S'	9.471296	9.495169	3.797375
'P'	7.04998	6.886663	3.417383	'P'	7.078743	6.918742	3.378796
'P'	6.823366	8.479207	6.115209	'P'	7.059605	8.492399	6.128411
'O'	10.380008	5.408207	3.137169	'O'	10.381014	5.576533	2.661023
'O'	8.794562	4.97834	7.003512	'O'	9.054062	4.860106	6.869764
'C'	9.822191	6.1902	3.814963	'C'	9.926843	6.262698	3.506426
'C'	11.083454	7.646824	5.295485	'C'	11.124407	7.604911	5.736047
'H'	11.611136	8.309656	4.587557	'H'	11.867173	8.067191	5.058877
'H'	11.668889	6.773664	5.629225	'H'	11.565949	6.748633	6.279603
'C'	10.480831	10.258582	6.168384	'C'	10.540212	10.360601	6.230665
'C'	8.77859	5.88531	6.234072	'C'	8.993434	5.753904	6.104671

to be continued

Table S 6: Coordinates for Geometry Optimized Structures - continued from above

Element	x	y	z	Element	x	y	z
'C'	11.274027	11.102123	7.143949	'C'	11.057935	11.411336	7.197509
'H'	10.918376	10.909637	8.181221	'H'	10.555602	11.272011	8.180965
'H'	12.343519	10.783291	7.127446	'H'	12.138638	11.211549	7.385047
'C'	11.168873	12.602463	6.824677	'C'	10.865676	12.85332	6.705113
'H'	11.952381	13.158462	7.380422	'H'	11.50237	13.53673	7.304304
'H'	10.186485	12.978922	7.181172	'H'	9.812691	13.160869	6.875943
'C'	11.277684	12.849572	5.315611	'C'	11.181625	12.959542	5.210611
'H'	11.262377	13.936768	5.091203	'H'	11.100271	14.009255	4.859201
'H'	12.251589	12.459255	4.943224	'H'	12.230799	12.637481	5.024467
'C'	10.128898	12.149695	4.574405	'C'	10.222023	12.068384	4.411777
'H'	10.276201	12.200195	3.474844	'H'	10.511574	12.034049	3.339989
'H'	9.167673	12.676371	4.776305	'H'	9.196783	12.506976	4.432977
'C'	9.944992	10.697731	4.989972	'C'	10.126339	10.647161	4.950036
'C'	5.430075	7.680794	3.897975	'C'	5.557491	7.891406	3.871448
'H'	4.851897	7.902496	2.97921	'H'	5.01146	8.223313	2.96648
'H'	4.870899	6.901258	4.453881	'H'	4.903601	7.179671	4.414404
'C'	5.641496	8.922529	4.764736	'C'	5.930465	9.071974	4.770354
'H'	4.691078	9.289072	5.201115	'H'	5.031838	9.541173	5.219216
'H'	6.114096	9.741604	4.187327	'H'	6.487529	9.845039	4.203299
'C'	7.396239	7.526273	1.735511	'C'	7.394489	7.444836	1.652878
'C'	6.975736	8.811991	1.332215	'C'	7.227189	8.794258	1.268887
'H'	6.374202	9.44339	2.001238	'H'	6.850049	9.537591	1.986243
'C'	7.32967	9.308108	0.065314	'C'	7.551408	9.206152	-0.034388
'H'	6.993328	10.311686	-0.237699	'H'	7.411549	10.259781	-0.321733
'C'	8.108448	8.529806	-0.807894	'C'	8.054087	8.27941	-0.965579
'H'	8.384704	8.920695	-1.799416	'H'	8.309363	8.6045	-1.986073
'C'	8.530959	7.2468	-0.411205	'C'	8.228064	6.935512	-0.587644
'H'	9.136452	6.62805	-1.091505	'H'	8.618374	6.203115	-1.311292
'C'	8.177888	6.747355	0.851834	'C'	7.900316	6.518602	0.712988
'H'	8.506778	5.74015	1.149504	'H'	8.034946	5.464324	0.997313
'C'	6.531102	5.160336	3.078774	'C'	6.428655	5.218768	3.1624
'C'	7.037726	4.088984	3.840178	'C'	7.108551	4.109889	3.703645
'H'	7.79235	4.283072	4.615394	'H'	8.048849	4.266356	4.252013
'C'	6.584606	2.777825	3.607027	'C'	6.589508	2.812442	3.545094

to be continued

Table S 6: Coordinates for Geometry Optimized Structures - continued from above

Element	x	y	z	Element	x	y	z
'H'	6.989488	1.947201	4.205314	'H'	7.129112	1.953497	3.972802
'C'	5.622755	2.531418	2.612717	'C'	5.387167	2.615851	2.844591
'H'	5.268291	1.505123	2.429809	'H'	4.978463	1.600656	2.72324
'C'	5.115843	3.59831	1.845292	'C'	4.707365	3.719086	2.293149
'H'	4.365613	3.408352	1.062091	'H'	3.768289	3.568902	1.738183
'C'	5.569161	4.906466	2.073364	'C'	5.226805	5.013836	2.445474
'H'	5.179015	5.734173	1.460468	'H'	4.695708	5.867712	1.996955
'C'	5.738373	7.498138	7.226227	'C'	5.89006	7.456306	7.10196
'C'	5.613163	6.10785	7.010173	'C'	5.793359	6.073123	6.831234
'H'	6.229329	5.615015	6.243884	'H'	6.466297	5.608107	6.096747
'C'	4.711304	5.346556	7.772688	'C'	4.835907	5.279639	7.485376
'H'	4.624248	4.264193	7.591706	'H'	4.775466	4.20416	7.258269
'C'	3.933188	5.964215	8.767451	'C'	3.965647	5.857155	8.426098
'H'	3.233219	5.366637	9.371818	'H'	3.219493	5.235504	8.944811
'C'	4.0527	7.348683	8.989645	'C'	4.05128	7.234863	8.700468
'H'	3.444687	7.838499	9.76608	'H'	3.3697	7.696102	9.432114
'C'	4.944542	8.114202	8.220501	'C'	5.000791	8.031327	8.039808
'H'	5.023513	9.197489	8.39742	'H'	5.048687	9.108909	8.257117
'C'	7.160552	10.014881	7.03269	'C'	7.291838	9.97854	7.161382
'C'	7.76779	9.907278	8.305377	'C'	7.743686	9.810397	8.491747
'H'	7.948705	8.913927	8.745577	'H'	7.89471	8.797066	8.894823
'C'	8.141667	11.059568	9.012189	'C'	7.990381	10.925768	9.305757
'H'	8.612207	10.96418	10.00266	'H'	8.337216	10.779634	10.340336
'C'	7.919657	12.331512	8.451854	'C'	7.797371	12.225606	8.800818
'H'	8.216721	13.236449	9.003707	'H'	7.994445	13.101428	9.437775
'C'	7.32387	12.442888	7.184276	'C'	7.363285	12.399858	7.475615
'H'	7.156249	13.435192	6.738031	'H'	7.214635	13.412589	7.070345
'C'	6.94401	11.291043	6.473734	'C'	7.118377	11.284652	6.655668
'H'	6.493475	11.398675	5.477689	'H'	6.794296	11.448454	5.618416

End of Table

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