

## Bridging arsolido complexes

Ryan M. Kirk<sup>a</sup> and Anthony F. Hill<sup>\*a</sup>

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### Experimental considerations

**General Precautions:** Unless otherwise stated, reactions were carried out under an atmosphere of commercially purified argon or nitrogen using standard Schlenk techniques. Most complexes in this work are reasonably air and moisture stable and are stated-so in their respective texts, except for precursor **1** and complex **5** which are air sensitive. Caution should be exercised when handling the arsenic-containing materials described herein – in all cases their toxicological properties are unknown and they are therefore regarded as **toxic**. The preparation of **1** generates organotin by-products which are **lipophilic and toxic**. Metal carbonyls are volatile sources of both carbon monoxide and nanoparticulate metal. Benzene (including benzene-*d*<sub>6</sub>) is a known **carcinogen**. The utmost caution should be exercised when distilling and storing flammable solvents over alkali metals. UV-radiation is non-ionising though ocular protection and suitable shielding should still be in place when sources are active; photolysis of metal carbonyls typically liberates one or more equivalents of carbon monoxide which should be vented appropriately.

**Materials:** [Mo(AsC<sub>4</sub>Me<sub>4</sub>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] was prepared from [Mo(SnBu<sub>3</sub>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] and freshly-prepared ClAsC<sub>4</sub>Me<sub>4</sub>.<sup>1</sup> [Au(C<sub>6</sub>F<sub>5</sub>)(THT)] (THT = tetrahydrothiophene) was prepared from [AuCl(THT)] and C<sub>6</sub>F<sub>5</sub>Li in Et<sub>2</sub>O medium at -78 °C and purified by flash chromatography on neutral alumina with Et<sub>2</sub>O eluent;<sup>11</sup> [CpFe(THF)(CO)<sub>2</sub>]PF<sub>6</sub> was prepared from [CpFeBr(CO)<sub>2</sub>] and AgPF<sub>6</sub> in THF solution, purified by extraction into CH<sub>2</sub>Cl<sub>2</sub>, filtration and re-crystallisation from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O;<sup>12</sup> [(μ<sup>3</sup>-HC)Co<sub>3</sub>(CO)<sub>9</sub>] was prepared from [Co<sub>2</sub>(CO)<sub>8</sub>] and CHBr<sub>3</sub> in refluxing THF, purified by flash chromatography on silica gel with petroleum ether eluent.<sup>13</sup> Reagents and materials were obtained from commercial vendors and used as received: [Co<sub>2</sub>(CO)<sub>8</sub>], [Cp<sub>2</sub>ZrCl<sub>2</sub>], [Cr(CO)<sub>6</sub>], [Mo(CO)<sub>6</sub>] (Strem); 2-butyne, C<sub>6</sub>F<sub>5</sub>Br (Oakwood); [Mn(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>4</sub>Me)] (Ethyl Corp.), AgPF<sub>6</sub>, AsCl<sub>3</sub>, CHBr<sub>3</sub>, *cis*-cyclooctene, dicyclopentadiene, *n*-BuLi (2.5 M in hexanes), neutral alumina, silica gel (230–400 mesh), SnBu<sub>3</sub>Cl, tetrahydrothiophene (Sigma-Aldrich); C<sub>6</sub>D<sub>6</sub>, CD<sub>2</sub>Cl<sub>2</sub> (Cambridge Isotopes Laboratories). HPLC-grade solvents were purchased from Merck and re-purified by distillation under nitrogen from an appropriate desiccant: THF, Et<sub>2</sub>O (Na/benzophenone); CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>

(P<sub>2</sub>O<sub>5</sub>); *n*-pentane, *n*-hexane, *n*-heptane, C<sub>6</sub>D<sub>6</sub> (K mirror); CD<sub>2</sub>Cl<sub>2</sub> (CaD<sub>2</sub>). Solvents for chromatography were degassed with nitrogen and used as received from the same vendor without re-purification.

**Instrumentation.** NMR spectra were collected on Bruker Avance 400, 600, 700 or 800 MHz spectrometers (<sup>13</sup>C frequencies of 100.6, 150.9, 176.0 and 201.2 MHz respectively). Spectra are reported in ppm shift downfield from SiMe<sub>4</sub> and referenced to the residual protio-solvent impurity (<sup>1</sup>H: C<sub>6</sub>D<sub>6</sub> 7.16, CD<sub>2</sub>Cl<sub>2</sub> 5.32 ppm) or the solvent signal itself (<sup>13</sup>C: C<sub>6</sub>D<sub>6</sub> 128.0, CD<sub>2</sub>Cl<sub>2</sub> 53.8 ppm); <sup>19</sup>F spectra (376.5 MHz) are externally referenced to neat CFCl<sub>3</sub>. <sup>1</sup>H and <sup>19</sup>F spectra are reported to two decimal places, and <sup>13</sup>C to one decimal place. NMR spectra were processed within the MestReNova software package. We thank Dr Doug Lawes of the ANU for assistance and helpful conversation during acquisition of NMR data.

Solution IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IT spectrometer with polished KBr-window cells and wavenumbers are reported to the nearest whole number. Elemental microanalysis was carried out by the Chemical Analysis Facility at Macquarie University (NSW, Australia) and compositions are reported to two decimal places. Data provided are generally the average of dual analyses.

High-resolution ESI mass spectrometry was carried out in positive-ion mode with acetonitrile matrices by the JMSF service at the Research School of Chemistry, ANU, using a Waters Synapt G2-Si HDMS LC-Q/TOF MS-MS spectrometer. Ion masses are reported to four decimal places and most-abundant isotopic compositions for non-C,H,O elements are listed in the text. We thank Mrs Anitha Jeyasingham for acquisition of this data and helpful conversation.

Photolysis of transition metal carbonyls was carried out in a home-made chamber equipped with a 370 nm UV-LED lamp, magnetic stirrer, argon gas inlet and outlet leading to a ventilated fumehood. A 50 mL quartz-glass Schlenk tube was used for all experiments. Internal temperature is maintained by extraction fan and a supplementary corrugated aluminium mesh heat-sink, though in our experience temperatures never exceeded *ca* 30 °C inside the apparatus. We thank Dr Jamie Hicks of the ANU for kind loan of this equipment.

**Crystallography.** Single crystal X-ray diffraction was performed on either an Agilent Technologies Supernova/EoS2-CCD

<sup>a</sup> Research School of Chemistry, Australian National University, Canberra, ACT.  
Email: a.hill@anu.edu.au.

diffractometer with graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ; compounds **2–6**) at 150 K. Selected crystals were mounted in oil on Nylon loops and fixed under a cold stream of nitrogen. Data were processed using the CrysAlisPRO-CCD and -RED software packages.<sup>2</sup> Absorption corrections are stated for each sample separately. The structures were solved within the Olex2<sup>3</sup> software package with SHELXT<sup>4</sup> using intrinsic phasing and refined with SHELXL<sup>4</sup> using full-matrix least-squares against  $F^2$  in an anisotropic (non-hydrogen atoms only) approximation. All hydrogen atom positions were refined by isotropic approximation in a “riding” model with the  $U_{\text{iso}}(\text{H})$  parameters fixed to 1.2  $U_{\text{eq}}(\text{C}_i)$  (for methyl hydrogens) or 1.5  $U_{\text{eq}}(\text{C}_i)$  (for cyclopentadienyl hydrogens), where  $U_{\text{eq}}(\text{C}_i)$  is the equivalent thermal parameter of the carbon atom to which the corresponding H atom is bonded. Crystal structures were analysed and POV-RAY images rendered within the Mercury 4.3.0 software package.<sup>5</sup> We thank Dr Michael Gardiner of the ANU for helpful discussions during data collection and solution.

**Computational Studies.** Calculations were performed by using the SPARTAN20<sup>®</sup> suite of programs.<sup>6</sup> Geometry optimisation (gas phase) was performed at the DFT level of theory using the exchange functionals  $\omega$ B97X-D of Head-Gordon.<sup>7,8</sup> The Los Alamos effective core potential type basis set (LANL2DZ) of Hay and Wadt<sup>9</sup> was used for elements with  $Z > \text{Kr}$  while Pople 6-31G\* basis sets<sup>10</sup> were used for all other atoms. Frequency calculations were performed for all compounds to confirm that each optimized structure was a local minimum and also to identify vibrational modes of interest. Cartesian atomic coordinates are provided below.

## Synthetic Procedures

**Synthesis of [CrMo( $\mu$ -AsC<sub>4</sub>Me<sub>4</sub>)(CO)<sub>8</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (**2**).** A dilute solution of [Cr(THF)(CO)<sub>5</sub>] was prepared by UV-photolysis of [Cr(CO)<sub>6</sub>] (0.1 g, excess. *Caution*: toxic) in 20 mL THF at ambient temperature: progress was monitored by IR spectroscopy ( $\nu_{\text{CO}}$  2072(w), 1935(vs), 1896(s)  $\text{cm}^{-1}$ ). When complete, the orange solution was transferred to a solution of **1** (0.11 g, 0.25 mmol) in 5 mL THF and the mixture allowed to stir for 15 hours. The mixture was then freed of volatiles (including residual [Cr(CO)<sub>6</sub>]) under reduced pressure and the yellow-brown residue extracted with small portions of petroleum ether and transferred to a chromatography column loaded with neutral alumina (20 x 2.5 cm) and eluted with 9:1 petroleum ether/Et<sub>2</sub>O to remove traces of unreacted/reformed [Cr(CO)<sub>6</sub>]. Eluting with 4:1 petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> provided a yellow band which was collected and freed of volatiles. The residue was re-crystallised from the minimum amount of hot CHCl<sub>3</sub>/*n*-heptane (*ca* 1:9 v/v) cooled to -20 °C overnight under nitrogen. Isolated yield: 0.13 g (72%). The product is readily soluble in polar organic and aromatic solvents, and somewhat soluble in aliphatic hydrocarbons. The solid product is reasonably air stable, however solutions decompose to insoluble green materials overnight.

NMR <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C):  $\delta_{\text{H}} = 4.36$  (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.07 (s, 6 H,  $\alpha$ -CH<sub>3</sub>), 1.73 (s, 6 H,  $\beta$ -CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 176 MHz, 25 °C):  $\delta_{\text{C}} = 223.1$  (CO), 224.7 (CO), 223.8 (CO), 218.3 (CO), 149.4 [C<sup>2,5</sup>(AsC<sub>4</sub>)], 137.5 [C<sup>3,4</sup>(AsC<sub>4</sub>)], 93.2 (C<sub>5</sub>H<sub>5</sub>), 15.0 ( $\alpha$ -CH<sub>3</sub>), 13.7 ( $\beta$ -CH<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>)

$\nu_{\text{CO}}$  2056(m), 2024(s), 1947(vs), 1934(sh), 1917(sh)  $\text{cm}^{-1}$ . IR (*n*-hexane)  $\nu_{\text{CO}}$  2058(s), 2025(vs), 1978(w), 1956(vs), 1939(vs), 1924(vs)  $\text{cm}^{-1}$ . HR-MS (ESI, MeCN, +ve ion) Found  $m/z$  565.8706 (calc. for C<sub>19</sub>H<sub>17</sub>O<sub>6</sub><sup>75</sup>As<sub>1</sub><sup>52</sup>Cr<sub>1</sub><sup>98</sup>Mo<sub>1</sub> [M-2CO]<sup>+</sup>: 565.8704). Analysis Found: C, 40.68; H, 2.70%. Calc. for C<sub>21</sub>H<sub>17</sub>O<sub>8</sub>AsCrMo: C, 40.69; H, 2.76%.

Crystals suitable for diffractometry were grown from cooling a hot hexane solution. *Crystal data* for C<sub>21</sub>H<sub>17</sub>AsCrMoO<sub>8</sub> ( $M_w = 620.21 \text{ gmol}^{-1}$ ): triclinic, space group  $P-1$  (no. 2),  $a = 10.0861(3)$ ,  $b = 10.5319(4)$ ,  $c = 13.2660(5) \text{ \AA}$ ,  $\alpha = 77.541(3)^\circ$ ,  $\beta = 70.581(3)^\circ$ ,  $\gamma = 61.676(3)^\circ$ ,  $V = 1167.06(8) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 150.0(1) \text{ K}$ ,  $\mu(\text{Cu K}\alpha) = 10.200 \text{ mm}^{-1}$ ,  $D_{\text{calc}} = 1.765 \text{ Mgm}^{-3}$ , yellow prism 0.14 x 0.11 x 0.04 mm, 4647 reflections measured ( $9.538^\circ \leq 2\theta \leq 146.11^\circ$ ), 4337 unique, which were used in all calculations. The final  $R_1$  was 0.0273 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0698 (all data) for 293 refined parameters without restraints. CCDC 2145366.

**Synthesis of [MoMn( $\mu$ -AsC<sub>4</sub>Me<sub>4</sub>)(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)] (**3**).** A dilute solution of [Mn(THF)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)] was prepared by UV-photolysis of [Mn(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)] (0.10 mL, 1.38  $\text{g mL}^{-1}$ , excess *ca* 0.6 mmol, *Caution*: toxic) in 20 mL THF at ambient temperature: progress was monitored by IR spectroscopy ( $\nu_{\text{CO}}$  1939(vs), 1841(vs)  $\text{cm}^{-1}$ ). When complete, the purple solution was cannulated to a solution of **1** (0.11g, 0.25 mmol) in THF (5 mL) and allowed to stir for 15 hours. After this time, the mixture was freed of volatiles under reduced pressure to afford a dark brown residue that was extracted with small portions of petroleum ether and transferred to a chromatography column loaded with neutral alumina (20 x 2.5 cm) in petroleum ether. Eluting with the same solvent provided a pale yellow band containing unreacted/reformed [Mn(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)] which was discarded. Eluting with 9:1 petroleum ether/Et<sub>2</sub>O provided a thin orange band of mooted to be the bimetallic bisarsoly complex [Mn<sub>2</sub>{ $\mu$ -(AsC<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>}(CO)<sub>4</sub>( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>] (**8**) discussed in the text (*vide infra*). The formulation reflects the high symmetry indicated by <sup>1</sup>H NMR and IR spectroscopy and elemental composition tentatively suggested by mass spectrometry. Prohibitively low yields prevented further characterisation. Eluting with 1:1 petroleum ether/Et<sub>2</sub>O provided a red-purple band which was collected, freed of volatiles, and crystallised from the minimum amount of hot *n*-heptane cooled to -20 °C overnight under nitrogen. Isolated yield 0.105 g (65%). The product is readily soluble in common organic solvents. The product is sufficiently air stable to permit prompt workup without the need for inert atmosphere, however solutions decompose to insoluble brown materials overnight.

NMR <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C):  $\delta_{\text{H}} = 4.90$  (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.10 [s, 2 H, H<sup>3,4</sup>(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)], 3.94 [s, 2 H, H<sup>2,5</sup>(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)], 2.07 (s, 6 H,  $\alpha$ -CH<sub>3</sub>), 1.79 (s, 9 H, isochronous C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub> &  $\beta$ -CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 176 MHz, 25 °C):  $\delta_{\text{C}} = 235.8$  (CO), 235.7 (CO), 225.0 (CO), 150.2 [C<sup>2,5</sup>(AsC<sub>4</sub>)], 135.9 [C<sup>3,4</sup>(AsC<sub>4</sub>)], 96.4 [C<sup>1</sup>(C<sub>5</sub>H<sub>4</sub>Me)], 92.7 (C<sub>5</sub>H<sub>5</sub>), 82.0 [C<sup>2,5</sup>(C<sub>5</sub>H<sub>4</sub>Me)], 80.1 [C<sup>3,4</sup>(C<sub>5</sub>H<sub>4</sub>Me)], 14.8 ( $\alpha$ -CH<sub>3</sub>), 13.8 (C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 13.6 ( $\beta$ -CH<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{CO}}$  2021(vs), 1944(vs), 1903(s), 1839(s)  $\text{cm}^{-1}$ . IR (*n*-hexane)  $\nu_{\text{CO}}$  2022(s), 1952(vs), 1913(s), 1853(s)  $\text{cm}^{-1}$ . HR-MS (ESI, MeCN, +ve ion) Found  $m/z$  619.9280 (Calc. for C<sub>24</sub>H<sub>24</sub>O<sub>5</sub><sup>75</sup>As<sup>55</sup>Mn<sup>98</sup>Mo [M]<sup>+</sup>: 619.9285); Analysis Found: C, 46.57; H, 4.10%. Calc. for C<sub>24</sub>H<sub>24</sub>O<sub>5</sub>AsMnMo: 46.62% C, 3.91% H.

Crystals suitable for diffractometry were grown from hexane at -20 °C. *Crystal data* for C<sub>24</sub>H<sub>24</sub>AsMnMoO<sub>5</sub> ( $M_w = 618.23 \text{ gmol}^{-1}$ ):

monoclinic, space group  $P2_1/c$  (no. 14),  $a = 14.9876(2)$ ,  $b = 9.27920(10)$ ,  $c = 17.3004(2)$  Å,  $\beta = 96.5650(10)^\circ$ ,  $V = 2390.24(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150.0(1)$  K,  $\mu(\text{Cu K}\alpha) = 10.406$  mm<sup>-1</sup>, red plate 0.13 x 0.08 x 0.05 mm,  $D_{\text{calc}} = 1.718$  Mgm<sup>-3</sup>, 4827 reflections measured ( $10.27^\circ \leq 2\theta \leq 147.26^\circ$ ), 4507 unique which were used in all calculations. The final  $R_1$  was 0.0253 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0611 (all data) for 294 refined parameters without restraints. CCDC 2145365.

**Data for presumed biarsolyl complex**  $[\text{Mn}_2\{\mu\text{-}(\text{AsC}_4\text{Me}_4)_2\}(\text{CO})_4(\eta\text{-C}_5\text{H}_4\text{Me}_4)_2]$ . NMR <sup>1</sup>H ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C)  $\delta_{\text{H}}$  4.11 (s, 2 H,  $\text{C}_5\text{H}_4\text{Me}$ ), 3.95 (s, 2 H,  $\text{C}_5\text{H}_4\text{Me}$ ), 2.09 (s, 6 H,  $\alpha\text{-CH}_3$ ), 1.75 (s.br, 9 H, isochronous  $\text{C}_5\text{H}_4\text{CH}_3$  and  $\beta\text{-CH}_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}}$  1921(vs), 1864(vs) cm<sup>-1</sup>.

**Synthesis of  $[\text{MoAu}(\mu\text{-AsC}_4\text{Me}_4)(\text{C}_6\text{F}_5)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  (4).** To a stirred solution of **1** (0.12 g, 0.28 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added solid  $[\text{Au}(\text{C}_6\text{F}_5)(\text{THT})]$  (0.12 g, 0.26 mmol)<sup>11</sup> and the mixture was then stirred for 15 hours during which time no obvious colour change occurred. The volatiles were removed under reduced pressure and the yellow residue washed with  $\text{Et}_2\text{O}$  (3 x 5 mL) and *n*-pentane (3 x 3 mL) and dried under vacuum. Isolated yield 0.15 g (75%). The product is readily soluble in polar organic and aromatic solvents, poorly soluble in  $\text{Et}_2\text{O}$  and aliphatic hydrocarbons, and is reasonably air stable as a solid.

NMR <sup>1</sup>H ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C):  $\delta_{\text{H}}$  4.70 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 1.84 (s, 6 H,  $\alpha\text{-CH}_3$ ), 1.62 (s, 6 H,  $\beta\text{-CH}_3$ ). <sup>13</sup>C{<sup>1</sup>H} ( $\text{C}_6\text{D}_6$ , 176 MHz, 25 °C):  $\delta_{\text{C}}$  = 232.7 (CO), 223.7 (CO), 149.9 (m.br,  $\text{C}_6\text{F}_5$ ), 148.8 (m.br,  $\text{C}_6\text{F}_5$ ), 142.7 [ $\text{C}^{2,5}(\text{AsC}_4)$ ], 140.4 [ $\text{C}^{3,4}(\text{AsC}_4)$ ], 138.6 (m.br,  $\text{C}_6\text{F}_5$ ), 137.0 (m.br,  $\text{C}_6\text{F}_5$ ), 92.7 ( $\text{C}_5\text{H}_5$ ), 14.8 ( $\alpha\text{-CH}_3$ ), 14.5 ( $\beta\text{-CH}_3$ ). <sup>19</sup>F{<sup>1</sup>H} ( $\text{C}_6\text{D}_6$ , 376 MHz, 25 °C):  $\delta_{\text{F}}$  = -115.9 [m, 2 F,  $\text{F}^{2,6}(\text{C}_6\text{F}_5)$ ], -158.7 [t, <sup>3</sup>J<sub>FF</sub> = 20 Hz, 1 F,  $\text{F}^4(\text{C}_6\text{F}_5)$ ], -162.0 [m, 2 F,  $\text{C}^{3,5}(\text{C}_6\text{F}_5)$ ]. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}}$  2034(vs), 1965(sh), 1949(vs) cm<sup>-1</sup>; HR-MS (ESI, MeCN, +ve ion) revealed many ion fragments with correct isotopic envelopes for the presence of both Mo and gold nuclei, however no chemically-sensible formulae were identified; Analysis Found C, 33.19; H, 2.14%. Calc. for  $\text{C}_{22}\text{H}_{17}\text{O}_3\text{AsAuF}_5\text{Mo}$ : C, 33.36; H, 2.16%.

**Crystal data for  $\text{C}_{22}\text{H}_{17}\text{AsAuF}_5\text{MoO}_3$**  ( $M_w = 792.18$  gmol<sup>-1</sup>): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 23.8893(5)$ ,  $b = 38.4002(3)$ ,  $c = 14.8049(3)$  Å,  $\beta = 136.531(4)^\circ$ ,  $V = 9343.4(6)$  Å<sup>3</sup>,  $Z = 16$ ,  $T = 150.0(1)$  K,  $\mu(\text{Cu K}\alpha) = 18.183$  mm<sup>-1</sup>,  $D_{\text{calc}} = 2.253$  Mgm<sup>-3</sup>, yellow prism, 0.077 x 0.058 x 0.058 mm, 18440 reflections measured ( $10.72^\circ \leq 2\theta \leq 147.18^\circ$ ), 15682 unique which were used in all calculations. The final  $R_1$  was 0.0369 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0840 (all data) for 1181 refined parameters with 60 restraints. CCDC 2145368.

**Synthesis of  $[\text{MoFe}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)_2]\text{PF}_6$  (5).** A solution of **1** (0.12 g, 0.28 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added to a stirred solution of  $[\text{Fe}(\text{THF})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$  (0.095 g, 0.25 mmol)<sup>12</sup> also dissolved in 5 mL of the same solvent. A colour change from orange to a dark yellow-brown took place over several minutes after which the mixture is stirred for 14 hours. After this time, the mixture is filtered through a short plug of diatomaceous earth (2 x 1 cm) and the dark yellow filtrate was freed of volatiles. The solids are washed with toluene (3 x 3 mL) and  $\text{Et}_2\text{O}$  (3 x 3 mL) to remove any neutral species and dried. The crude residue was then crystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  at -20 °C overnight under nitrogen. Isolated yield 0.092 g (61%). The product is readily soluble in polar organic solvents and

may be handled in air as a solid. Solutions however darken overnight. The compound could, however, not be isolated in an analytically pure state. *Note:* the use of  $[\text{Fe}(\text{THF})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$  prepared *in situ* from  $[\text{FeBr}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  and  $\text{AgPF}_6$  in THF gave very low yields of impure product and the formation of  $[\text{Fe}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$  as the major species (by IR and NMR spectroscopy) for reasons which remain presently unclear; it was thus preferable to first isolate  $[\text{Fe}(\text{THF})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$  where this eventuality was not encountered to such an extent.

NMR <sup>1</sup>H ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, 25 °C):  $\delta_{\text{H}}$  = 5.20 (s.br, 5 H, Mo  $\text{C}_5\text{H}_5$ ), 4.85 (s.br, 5 H,  $\text{FeC}_5\text{H}_5$ ), 2.02 (s.br, 6 H,  $\alpha\text{-CH}_3$ ), 1.87 (s.br, 6 H,  $\beta\text{-CH}_3$ ). <sup>13</sup>C{<sup>1</sup>H} ( $\text{CD}_2\text{Cl}_2$ , 176 MHz, 25 °C):  $\delta_{\text{C}}$  = 229.2 (CO), 226.0 (CO), 211.2 (CO), 148.2 [ $\text{C}^{2,5}(\text{AsC}_4)$ ], 139.3 [ $\text{C}^{3,4}(\text{AsC}_4)$ ], 95.1 (Mo $\text{C}_5\text{H}_5$ ), 86.4 (Fe $\text{C}_5\text{H}_5$ ), 15.1 ( $\alpha\text{-CH}_3$ ), 14.2 ( $\beta\text{-CH}_3$ ) ppm; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}}$  2052(vs), 2036(vs), 2004(s), 1980(m), 1947(s) cm<sup>-1</sup> HR-MS (ESI, MeCN, +ve ion) revealed many ion fragments with correct isotopic envelopes for the presence of Mo nuclei, however no chemically-sensible formulae were identified. Analysis Found C, 36.56; H, 3.05%. Calc. for  $\text{C}_{23}\text{H}_{22}\text{O}_5\text{AsF}_6\text{FeMoP}$ : C, 36.83; H, 2.96%.

**Crystal data for  $\text{C}_{23}\text{H}_{22}\text{AsFeMoO}_5\text{F}_6\text{P}$**  ( $M_w = 750.08$  gmol<sup>-1</sup>): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 13.6104(11)$ ,  $b = 14.7837(7)$ ,  $c = 13.7151(12)$  Å,  $\beta = 100.707(8)^\circ$ ,  $V = 2711.6(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150.0(1)$  K,  $\mu(\text{Cu K}\alpha) = 10.674$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.837$  Mgm<sup>-3</sup>, 5784 reflections measured ( $8.82^\circ \leq 2\theta \leq 155.68^\circ$ ), 4066 unique which were used in all calculations. The final  $R_1$  was 0.0743 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.2143 (all data) for 349 refined parameters without restraints. CCDC 2145380.

**Synthesis of  $[\text{MoCo}_3(\mu\text{-AsC}_4\text{Me}_4)(\mu^3\text{-CH})(\text{CO})_{11}(\eta\text{-C}_5\text{H}_5)]$  (6).** A 20 mL Schlenk tube was charged with **1** (0.14 g, 0.33 mmol) and  $[\text{Co}_3(\mu\text{-CH})(\text{CO})_9]$  (0.16 g, 0.36 mmol)<sup>13</sup> under nitrogen. To this was added  $\text{CH}_2\text{Cl}_2$  (10 mL) and the mixture was stirred for 14 hours at ambient temperature. The brown solution is absorbed onto a small quantity of diatomaceous earth by evaporation of the solvent. Once dry, this was transferred to a chromatography column loaded with silica gel (20 x 2.5 cm) in petroleum ether. Eluting with the same solvent provided a purple band of unchanged  $[\text{Co}_3(\mu_3\text{-CH})(\text{CO})_9]$  (isolated *ca* 15 mg). Subsequent elution with 9:1 petroleum ether/ $\text{Et}_2\text{O}$  provided a blue-green band of the known cluster  $[\text{MoCo}_2(\mu_3\text{-CH})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$  which was collected and freed of volatiles *in vacuo*. Isolated yield: *ca* 20 mg (12 %).

The following data may be compared with those reported by Vahrenkamp.<sup>14</sup>  $[\text{MoCo}_2(\mu_3\text{-CH})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ : NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C) <sup>1</sup>H:  $\delta_{\text{H}}$  = 10.78 (s, 1 H,  $\mu^3\text{-CH}$ ), 4.48 (s, 5 H,  $\text{C}_5\text{H}_5$ ). <sup>13</sup>C{<sup>1</sup>H} ( $\text{C}_6\text{D}_6$ , 176 MHz, 25 °C) <sup>1</sup>H:  $\delta_{\text{C}}$  = 251.3 ( $\mu^3\text{-CH}$ ), 208.5 (br, FWHM *ca* 100 Hz, MoCO and CoCO), 90.7 ( $\eta^5\text{-C}_5\text{H}_5$ ) ppm; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}}$  2083(s), 2071(s), 2040(sh), 2028(vs), 2015(vs), 2001(vs) cm<sup>-1</sup>.

Eluting with 9:1 petroleum ether/ $\text{CH}_2\text{Cl}_2$  provides a dark yellow band containing the title compound which was collected and dried *in vacuo* providing a brown residue. Solutions are dark yellow in colour, however repeated drying and prolonged trituration in *n*-pentane gives the product as a red-brown solid which was collected and dried under air. Isolated yield: 95 mg (54%). The product is readily soluble in polar organic and aromatic solvents, and somewhat soluble in  $\text{Et}_2\text{O}$  and aliphatic hydrocarbons. The product is reasonably air stable as a

solid or solution however decomposes to insoluble grey residues over several days.

NMR  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ , 400 MHz, 25 °C):  $\delta_{\text{H}} = 9.75$  (s, 1H,  $\mu^3\text{-CH}$ ), 4.33 (s, 5H,  $\eta^5\text{-C}_5\text{H}_5$ ), 1.99 (s, 6H,  $\alpha\text{-CH}_3$ ), 1.67 (s, 6H,  $\beta\text{-CH}_3$ ); ( $\text{C}_6\text{D}_6$ , 176 MHz, 25 °C):  $\delta_{\text{C}} = 235.5$  ( $\mu^3\text{-CH}$ ), 232.8 (Mo-CO), 224.8 (Mo-CO), 206.8 (br, Co-CO), 147.5 [ $\text{C}^{2,5}(\text{AsC}_4)$ ], 137.7 [ $\text{C}^{3,4}(\text{AsC}_4)$ ], 93.0 ( $\eta^5\text{-C}_5\text{H}_5$ ), 14.7 ( $\alpha\text{-CH}_3$ ), 13.3 ( $\beta\text{-CH}_3$ ) ppm; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}}$  2072(s), 2032(vs), 2011(vs), 1961(s), 1936(s), 1862(m, br)  $\text{cm}^{-1}$ ; HR-MS (ESI, MeCN, +ve ion) found many ion fragments corresponding to the presence of Mo nuclei, however no chemically sensible formulae could be devised; Analysis Found C, 35.51; H, 2.47%. Calc. for  $\text{C}_{25}\text{H}_{18}\text{O}_{11}\text{AsCo}_3\text{Mo}$ : C, 35.66; H, 2.15%.

Crystals suitable for diffractometry were grown by slowly concentrating a solution in  $\text{C}_6\text{D}_6$ . *Crystal data for  $\text{C}_{25}\text{H}_{18}\text{AsCo}_3\text{MoO}_{11}$*  ( $M_w = 842.04$   $\text{g mol}^{-1}$ ): monoclinic, space group  $C2/c$  (no. 15),  $a = 30.0109(4)$ ,  $b = 11.14800(10)$ ,  $c = 17.8024(2)$  Å,  $\beta = 100.5150(10)^\circ$ ,  $V = 5855.98(12)\text{Å}^3$ ,  $Z = 8$ ,  $T = 150.0(1)$  K,  $\mu(\text{Cu K}\alpha) = 18.264$   $\text{mm}^{-1}$ ,  $D_{\text{calc}} = 1.910$   $\text{Mg m}^{-3}$ , red prism, 0.289 x 0.255 x 0.115 mm, 5839 reflections measured ( $8.45^\circ \leq 2\theta \leq 147.21^\circ$ ), 5676 unique which were used in all calculations. The final  $R_1$  was 0.0340 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0877 (all data) for 374 refined parameters without restraints. CCDC 2234994.

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## Computational Results

### 1. $[\text{AsMe}_2]^-$ anion

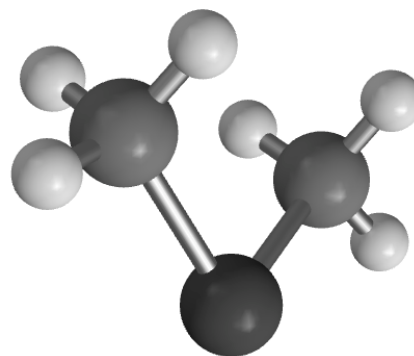


Figure S1. Optimised Geometry (wB97X-D/6-31G\*/Gas Phase)

### Thermodynamic Properties at 298.15 K

Zero Point Energy :	179.64	kJ/mol	(ZPE)
Temperature Correction :	15.83	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	195.48	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2315.361368	au	(Electronic Energy + Enthalpy Correction)
Entropy :	304.07	J/mol•K	
Gibbs Energy :	-2315.395898	au	(Enthalpy - T*Entropy)
$C_v$ :	73.63	J/mol•K	

### Cartesian Coordinates

Atom	x	y	z
As	-1.310589	0.515170	0.020978
C	-0.036944	-0.099581	1.465134
H	0.239195	-1.158670	1.358072
H	-0.523059	0.018440	2.443355
H	0.892135	0.488759	1.483608
C	-0.000526	0.113993	-1.464288
H	0.927264	0.697823	-1.374849
H	-0.462849	0.373924	-2.426263
H	0.275372	-0.949859	-1.505747

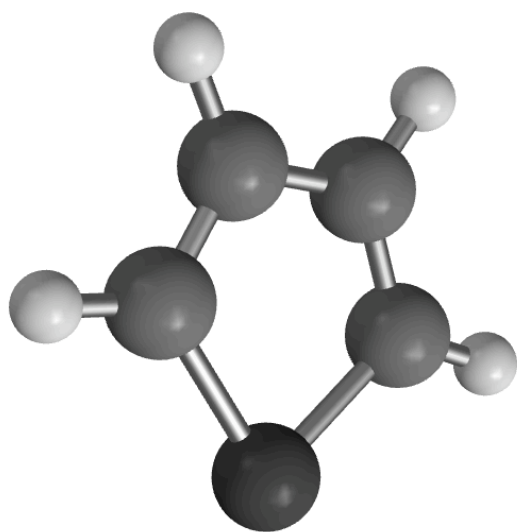
2.  $[\text{AsC}_4\text{H}_4]^-$  anion

Figure S2. Optimised Geometry (wb97X-D/6-31G\*/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	159.74	kJ/mol	(ZPE)
Temperature Correction :	14.45	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	174.19	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2390.359239	au	(Electronic Energy + Enthalpy Correction)
Entropy :	299.11	J/mol•K	
Gibbs Energy :	-2390.393206	au	(Enthalpy - T*Entropy)
$C_v$ :	72.49	J/mol•K	

## Cartesian Coordinates

Atom	x	y	z
As	1.021759	-0.015207	1.669041
C	1.399127	0.019311	-0.180459
H	2.398770	0.040550	-0.611379
C	0.251599	0.018357	-0.950495
H	0.261254	0.036229	-2.042487
C	-0.960806	-0.008028	-0.208574
H	-1.937851	-0.012583	-0.696644
C	-0.797439	-0.028736	1.163696
H	-1.636413	-0.049894	1.857300

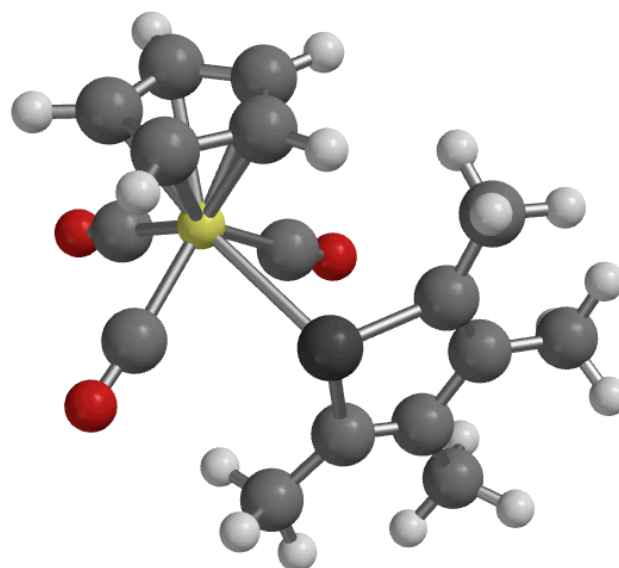
3.  $[\text{Mo}(\text{AsC}_4\text{Me}_4)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ 

Figure S3. Optimised Geometry (wb97X-D/6-31G\*/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	723.46	kJ/mol	(ZPE)
Temperature Correction :	55.53	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	778.99	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3148.289972	au	(Electronic Energy + Enthalpy Correction)
Entropy :	591.53	J/mol•K	
Gibbs Energy :	-3148.357146	au	(Enthalpy - T*Entropy)
$C_v$ :	376.07	J/mol•K	

## Cartesian Coordinates

Atom	x	y	z
Mo	1.579753	-0.795416	-1.222233
As	-0.555769	-1.179455	0.467000
C	-1.861545	1.101063	1.153650
C	-0.124347	-0.258050	2.111099
C	0.938457	-0.755616	3.046850
H	0.842448	-0.331166	4.050451
H	1.938627	-0.496351	2.675983
H	0.908361	-1.845433	3.146726
O	0.961592	2.045956	-0.004194
C	-1.785639	0.265131	0.091817
C	-0.924446	1.731400	3.466609
H	-0.640349	2.749830	3.175411
H	-0.222417	1.403534	4.235381
H	-1.917339	1.794596	3.927767
C	1.162281	0.980519	-0.390847
C	0.510889	-0.347429	-3.308190
H	-0.016297	0.577220	-3.499298
C	0.968458	-2.525721	-2.710924
H	0.840904	-3.543715	-2.369431
O	2.544649	-2.834754	0.958360
C	-0.058502	-1.546103	-2.802035
H	-1.098223	-1.695943	-2.545876
C	2.180321	-2.043492	0.201896
C	-2.601665	0.310409	-1.167697
H	-1.994634	0.625962	-2.026455
H	-3.444747	1.003904	-1.098376
H	-3.017740	-0.674771	-1.409715
O	4.490684	0.307004	-0.775331
C	2.178478	-1.934774	-3.167793
H	3.136135	-2.429132	-3.256773
C	-0.930855	0.816096	2.270854
C	3.420681	-0.093617	-0.923753
C	-2.792629	2.278986	1.265194
H	-3.429461	2.392222	0.385987
H	-2.226541	3.210590	1.383815
H	-3.447784	2.188837	2.139839
C	1.891569	-0.582003	-3.534006
H	2.596642	0.129681	-3.941758

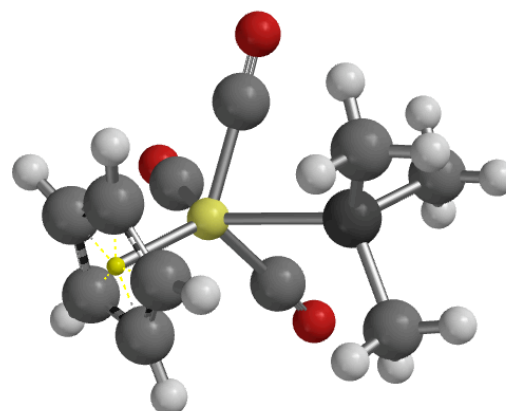
4.  $[\text{Mo}(\text{AsMe}_3)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^+$  cation

Figure S4. Optimised Geometry (wB97X-D/6-31G\*/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	560.73	kJ/mol	(ZPE)
Temperature Correction :	46.75	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	607.48	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2955.889358	au	(Electronic Energy + Enthalpy Correction)
Entropy :	538.11	J/mol•K	
Gibbs Energy :	-2955.950465	au	(Enthalpy - T*Entropy)
$C_v$ :	309.62	J/mol•K	

## Cartesian Coordinates

Atom	x	y	z
Mo	0.171817	1.191789	0.122085
H	-0.903486	3.184849	2.146655
C	-1.259731	2.415797	1.474537
C	-1.478590	1.052658	1.810045
H	-1.668306	3.544304	-0.427258
H	-1.304583	0.597317	2.775621
C	-2.012354	0.404254	0.662274
H	-2.333213	-0.628179	0.613353
C	-2.130430	1.359464	-0.385069
H	-2.536454	1.176800	-1.370765
C	-1.664469	2.606347	0.111506
C	1.381503	2.824424	0.004353
O	2.047803	3.748941	-0.056224
C	0.728293	1.142079	-1.817181
O	0.984814	1.112892	-2.934344
C	1.670177	0.677001	1.372025
O	2.480317	0.374543	2.124880
As	0.596275	-1.345896	-0.372133
C	0.325675	-2.511269	1.154605
H	1.013477	-2.228516	1.954468
H	0.516764	-3.546598	0.861852
H	-0.700722	-2.420871	1.516254
C	-0.551585	-2.086745	-1.749438
H	-0.381422	-1.556027	-2.688767
H	-1.599011	-1.977327	-1.461009
H	-0.321768	-3.146432	-1.885243
C	2.382805	-1.787978	-0.976190
H	3.107694	-1.501207	-0.211580
H	2.600754	-1.245522	-1.898490
H	2.451448	-2.862897	-1.159695

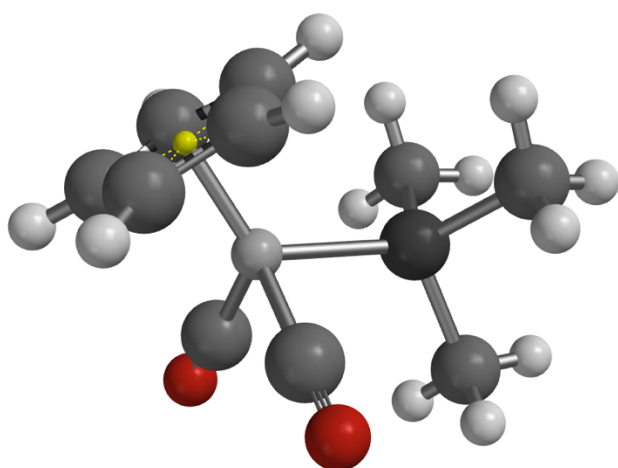
5.  $[\text{Fe}(\text{AsMe}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^+$  cation

Figure S5. Optimised Geometry (wb97X-D/6-31G\*/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	544.43	kJ/mol	(ZPE)
Temperature Correction :	41.03	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	585.46	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-4038.655144	au	(Electronic Energy + Enthalpy Correction)
Entropy :	497.41	J/mol•K	
Gibbs Energy :	-4038.711630	au	(Enthalpy - T*Entropy)
$C_v$ :	270.36	J/mol•K	

## Cartesian Coordinates

Atom	x	y	z
Fe	-0.321186	0.000000	1.060841
H	1.499548	2.179837	1.425237
C	1.295373	1.151607	1.690243
C	1.777071	0.000000	1.018607
H	0.051393	1.340089	3.548829
H	2.403617	0.000000	0.136237
C	1.295373	-1.151607	1.690243
H	1.499548	-2.179837	1.425237
C	0.540608	-0.705675	2.821551
H	0.051393	-1.340089	3.548829
C	0.540608	0.705675	2.821551
C	-1.519266	-1.314865	1.064269
O	-2.254796	-2.187601	1.096213
C	-1.519266	1.314865	1.064269
O	-2.254796	2.187601	1.096213
As	-0.315325	-0.000000	-1.266029
C	0.550435	1.536583	-2.071568
H	0.025594	2.444791	-1.765515
H	0.515416	1.449716	-3.160317
H	1.591996	1.599200	-1.749254
C	0.550435	-1.536583	-2.071568
H	0.025594	-2.444791	-1.765515
H	1.591996	-1.599199	-1.749254
H	0.515416	-1.449716	-3.160317
C	-2.074982	0.000000	-2.077803
H	-2.626113	0.890325	-1.765455
H	-2.626113	-0.890325	-1.765454
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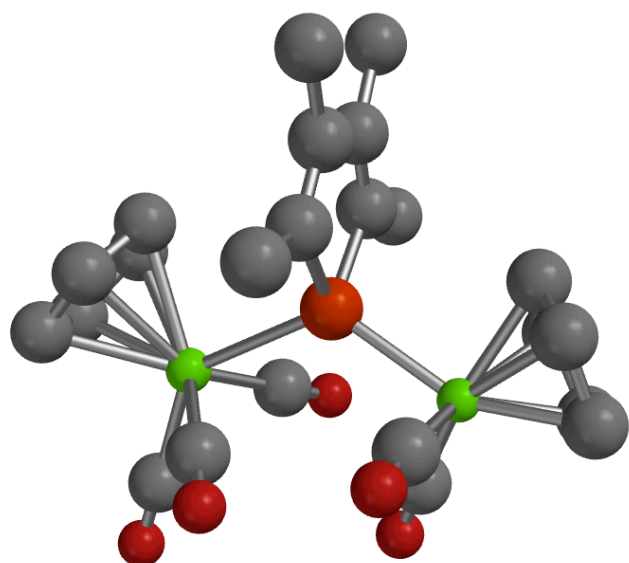
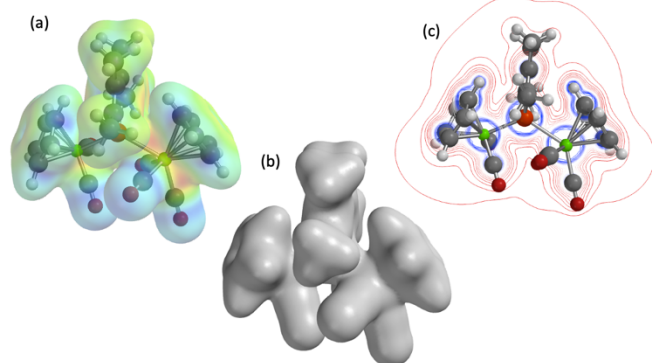
6. [MoFe(AsC<sub>4</sub>Me<sub>4</sub>)(CO)<sub>5</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup> cation

Figure S6. Optimised Geometry (wB97X-D/6-31G\*/LANL2DZ/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	989.15	kJ/mol	(ZPE)
Temperature Correction :	76.69	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1065.84	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-4831.718225	au	(Electronic Energy + Enthalpy Correction)
Entropy :	727.56	J/mol·K	
Gibbs Energy :	-4831.800846	au	(Enthalpy - T*Entropy)
C <sub>v</sub> :	541.67	J/mol·K	

Figure S7. Non-covalent interaction between cyclopentadienyl C-H and arsolyl  $\pi$ -system. (a) Local ionisation potential map. (b) Potential slice. (c) Electron density surface.

## Cartesian Coordinates

Atom	x	y	z
Mo	-0.155563	-2.102731	-1.694870
As	-0.373115	-0.002761	-0.066848
Fe	-2.433099	1.081628	0.464116
C	1.848646	1.447832	0.376827
O	-4.015074	-1.240220	-0.327905
O	-2.648984	2.512251	-2.067664
C	0.685116	-0.345433	1.508625
C	0.364861	-1.425260	2.500356
H	0.713159	-1.172764	3.506014
H	0.836352	-2.375767	2.221166
H	-0.709307	-1.618119	2.563443
O	-1.753369	-3.261216	0.775734
C	-2.525851	1.883982	-1.121386
C	0.900267	1.345634	-0.580516
C	-2.369490	0.979001	2.545622
H	-2.101173	0.120902	3.144106
C	2.808262	0.512530	2.582301
H	3.782745	0.241184	2.159605
H	2.596792	-0.188319	3.391358
H	2.920360	1.510093	3.020906
C	-1.196551	-2.810578	-0.121977
C	-3.681071	1.328467	2.120512
H	-4.580486	0.756730	2.308403
C	1.888558	-3.110512	-1.016872
H	2.007677	-3.620398	-0.070633
C	1.895110	-1.470313	-2.641013
H	2.036571	-0.519405	-3.135868
O	-1.842165	-0.066484	-3.406997
C	2.153726	-1.739848	-1.265155
H	2.505766	-1.023137	-0.537083
C	-1.486651	2.003235	2.095426
H	-0.417480	2.029929	2.251442
C	-3.371860	-0.343422	-0.031739
C	-1.250824	-0.802822	-2.750923
C	-3.607768	2.530981	1.378556
H	-4.438355	3.050538	0.920697
C	0.762070	2.163583	-1.831434
H	0.211665	1.627152	-2.610017
H	1.737419	2.432020	-2.248475
H	0.221251	3.099638	-1.646677
O	-2.249894	-4.011918	-3.115560
C	1.467903	-2.682575	-3.247603
H	1.234598	-2.825747	-4.293931
C	1.741549	0.498517	1.520520
C	-1.500154	-3.320786	-2.598385
C	2.977981	2.442099	0.350668
H	2.976161	3.042633	-0.560542
H	3.950889	1.943814	0.425494
H	2.909842	3.133051	1.198923
C	-2.237989	2.953373	1.374506
H	-1.848444	3.845817	0.903716
C	1.453946	-3.696864	-2.235232
H	1.205475	-4.739213	-2.383738



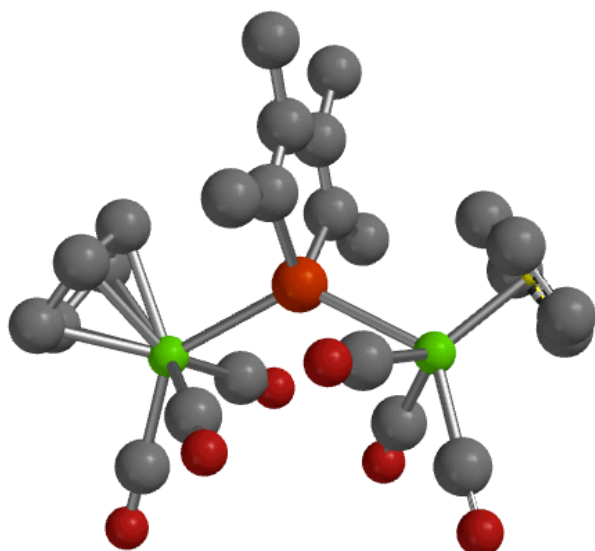
7.  $[\text{Mo}_2(\text{AsC}_4\text{Me}_4)(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]^+$  cation

Figure S8. Optimised Geometry (wb97X-D/6-31G\*/LANL2DZ/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	1005.73	kJ/mol	(ZPE)
Temperature Correction :	82.34	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1088.07	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3748.948326	au	(Electronic Energy + Enthalpy Correction)
Entropy :	762.68	J/mol•K	
Gibbs Energy :	-3749.034935	au	(Enthalpy - T*Entropy)
$C_v$ :	580.03	J/mol•K	

## Cartesian Coordinates

Atom	x	y	z
Mo	0.198768	-1.901171	-2.181910
As	-0.235264	-0.140761	-0.197499
C	1.903556	1.347740	0.490578
C	0.823624	-0.641638	1.335800
C	0.515635	-1.824722	2.208420
H	0.739188	-1.615836	3.259840
H	1.100854	-2.706264	1.921263
H	-0.538508	-2.111771	2.147985
O	-0.628593	-3.928123	0.097017
C	0.953562	1.354633	-0.471597
C	2.886151	0.149819	2.557228
H	3.891164	0.088853	2.124889
H	2.748876	-0.727031	3.192039
H	2.872338	1.037226	3.200664
C	-0.391328	-3.139654	-0.701204
C	2.445897	-2.652960	-1.940441
H	2.752802	-3.342158	-1.165048
C	1.989665	-0.705132	-3.090250
H	1.927227	0.343358	-3.344480
O	-2.080669	-0.063714	-3.362738
C	2.453888	-1.240673	-1.850022
H	2.766504	-0.665363	-0.990055
C	-1.270030	-0.727442	-2.893491
C	0.807162	2.333918	-1.600554
H	0.256278	1.903214	-2.441940
H	1.781804	2.659445	-1.978764
H	0.261742	3.233348	-1.292149
O	-1.642554	-3.960949	-3.727335
C	1.694276	-1.798727	-3.951171
H	1.363454	-1.733462	-4.978839
C	1.840448	0.237638	1.478030
C	-0.986453	-3.213727	-3.162871
C	2.992959	2.379492	0.611173
H	2.897822	3.165599	-0.139540
H	3.985737	1.927137	0.503933
H	2.970014	2.860651	1.595390
C	1.966407	-3.005028	-3.231082
H	1.869682	-4.011412	-3.616858
Mo	-2.600441	0.766145	0.707999
H	-1.523864	-0.232098	3.391684
C	-1.954718	0.655087	2.949615
C	-3.337721	0.981670	2.897710
H	-0.154613	1.806275	2.275248
H	-4.151145	0.386037	3.288840
C	-3.458515	2.265345	2.278524
H	-4.380024	2.806756	2.112333
C	-2.153776	2.736886	1.973554
H	-1.910658	3.684603	1.513119
C	-1.228673	1.743303	2.374827
C	-4.488922	0.718604	-0.019389
O	-5.559621	0.704445	-0.420481
C	-2.430947	1.822520	-1.005508
O	-2.383677	2.543234	-1.896332
C	-2.919808	-1.198717	0.431137
O	-3.144572	-2.319569	0.327798

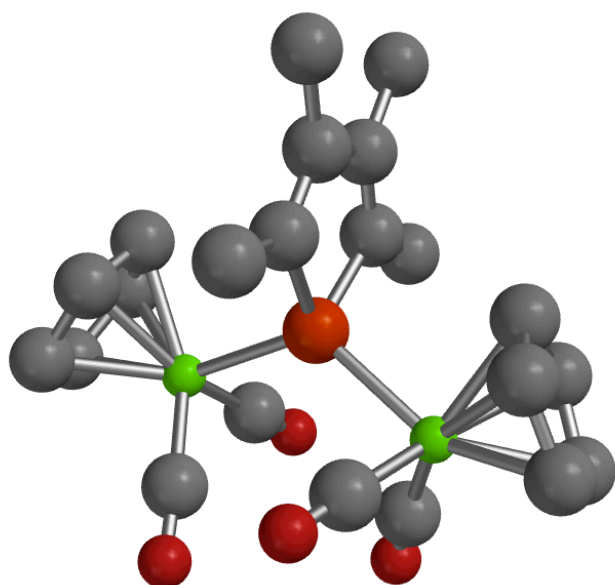
8.  $[\text{Fe}_2(\text{AsC}_4\text{Me}_4)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]^+$  cation

Figure S9. Optimised Geometry (wB97X-D/6-31G\*/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	971.07	kJ/mol	(ZPE)
Temperature Correction :	71.06	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1042.13	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-5914.483525	au	(Electronic Energy + Enthalpy Correction)
Entropy :	690.79	J/mol•K	
Gibbs Energy :	-5914.561970	au	(Enthalpy - T*Entropy)
$C_v$ :	503.93	J/mol•K	

## Cartesian Coordinates

Atom	x	y	z
Fe	2.091732	0.020709	-1.509212
As	0.176058	-0.334143	-0.150940
Fe	-0.772141	-2.462263	0.287941
C	-1.391289	1.798624	0.309545
O	1.833322	-3.765295	0.202020
O	-1.457427	-2.769517	-2.528413
C	0.408304	0.676998	1.467941
C	1.467975	0.347074	2.477344
H	1.163188	0.610124	3.494841
H	2.402524	0.883682	2.270226
H	1.708910	-0.721282	2.472361
O	3.805298	-1.295382	0.445702
C	-1.140820	-2.639597	-1.437166
C	-1.241269	0.861237	-0.652155
C	-1.086184	-2.404683	2.342501
H	-0.365114	-2.118496	3.095053
C	-0.548698	2.747620	2.560740
H	-0.306827	3.742067	2.167501
H	0.142577	2.542676	3.380065
H	-1.559688	2.809979	2.977993
C	3.098452	-0.816023	-0.314451
C	-1.316541	-3.724635	1.850631
H	-0.776311	-4.614339	2.146330
C	3.226488	1.752609	-1.235976
H	3.894424	1.938806	-0.405478
C	1.347290	1.669570	-2.553577
H	0.334467	1.801464	-2.904579
C	1.858102	2.089363	-1.289679
H	1.290046	2.560528	-0.499565
C	-2.016448	-1.542293	1.701224
H	-2.090433	-0.474047	1.846483
C	0.820279	-3.233772	0.212329
C	-2.351681	-3.668836	0.890265
H	-2.749586	-4.505717	0.333120
C	-2.047736	0.672838	-1.903994
H	-1.479621	0.140652	-2.674345
H	-2.372258	1.626238	-2.332814
H	-2.951970	0.081212	-1.713444
O	1.626490	-2.350019	-3.140463
C	2.419785	1.087175	-3.277445
H	2.353608	0.669819	-4.273725
C	-0.466687	1.707250	1.476719
C	1.784572	-1.432653	-2.475678
C	-2.428365	2.888180	0.275185
H	-2.996399	2.884888	-0.656926
H	-1.970934	3.877203	0.388058
H	-3.144302	2.773899	1.097397
C	-2.787278	-2.306772	0.798131
H	-3.576986	-1.932859	0.160875
C	3.580249	1.109961	-2.463106
H	4.558853	0.740179	-2.735387

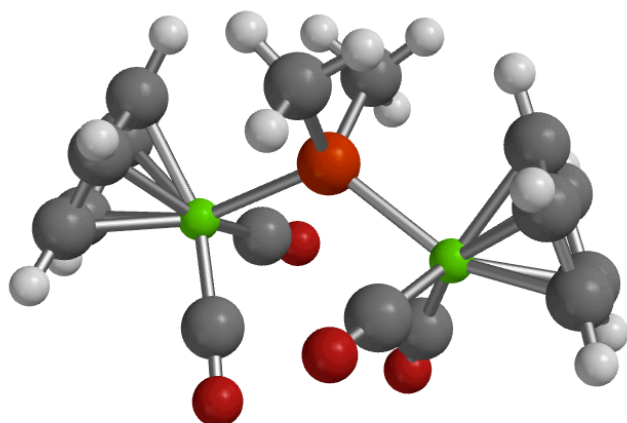
9.  $[\text{Fe}_2(\text{AsMe}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]^+$  cation

Figure S10. Optimised Geometry (wB97X-D/6-31G\*/Gas Phase)

## Thermodynamic Properties at 298.15 K

Zero Point Energy :	713.57	kJ/mol	(ZPE)
Temperature Correction :	57.68	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	771.25	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-5682.407786	au	(Electronic Energy + Enthalpy Correction)
Entropy :	608.40	J/mol·K	
Gibbs Energy :	-5682.476875	au	(Enthalpy - T*Entropy)
$C_v$ :	401.95	J/mol·K	

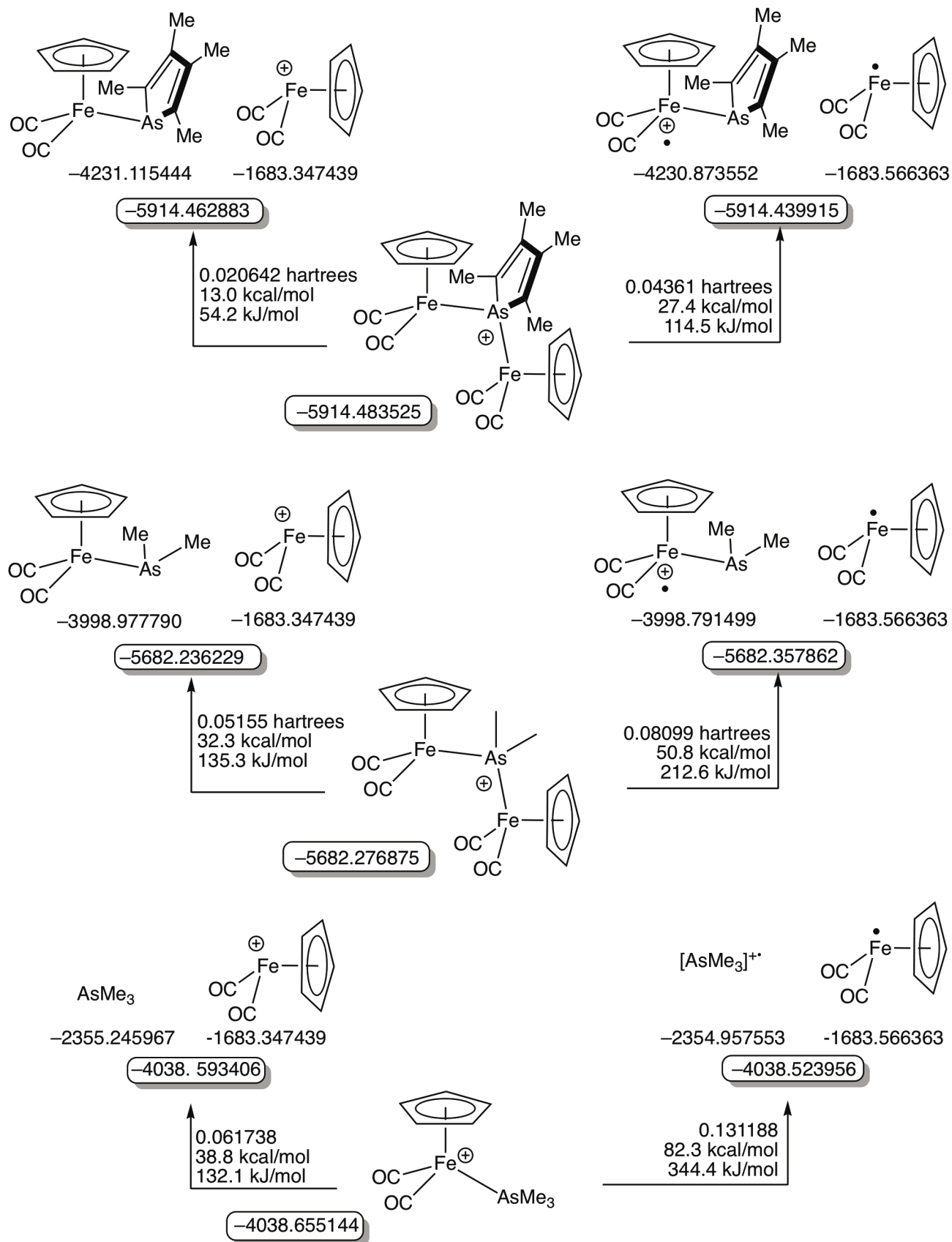
Table S1. Comparison of Infrared data( $\text{cm}^{-1}$ ) for  $[\text{Fe}_2(\mu\text{-AsR}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]^+$ 

	Calculated <sup>a</sup> $\mu\text{-AsMe}_2$	Calculated <sup>a</sup> $\mu\text{-AsC}_4\text{Me}_4$
$\nu(\text{CO})$	2080	2080
	2053	2055
	2043	2045
	2028	2029
Mean:	2051	2052
$\nu_s(\text{FeAs}_2)$	193/197	191
$\nu_{as}(\text{FeAs}_2)$	254	236

<sup>a</sup>Scaling factor = 0.9420; DFT:  $\omega\text{B97X-D/6-31G}^*/\text{gas phase}$ 

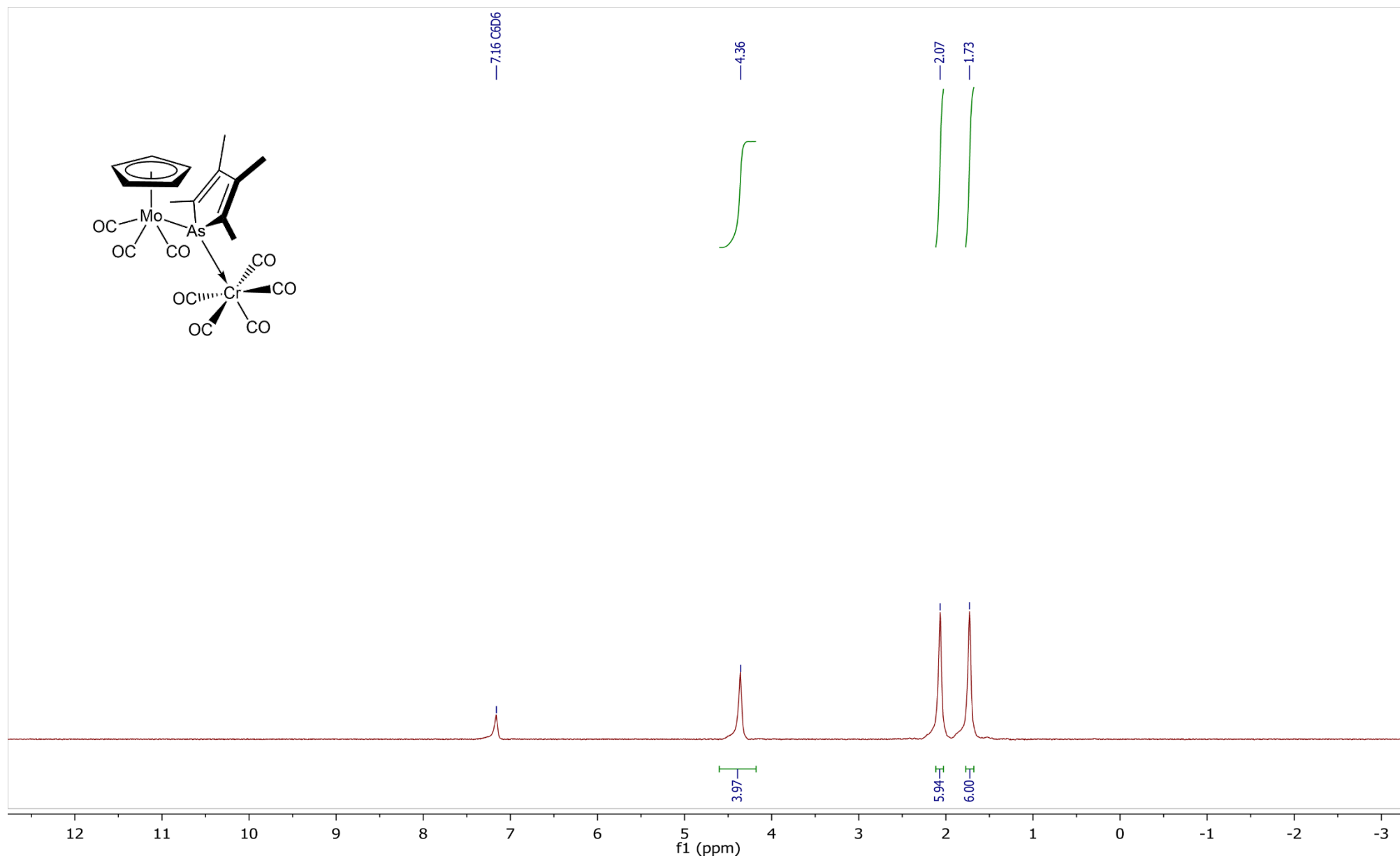
## Cartesian Coordinates

Atom	x	y	z
Fe	-1.719638	1.143289	-0.710497
As	0.193170	-0.242363	-0.397694
Fe	1.136605	-0.615369	1.750318
O	-1.480809	-0.494158	3.023445
O	1.796548	2.221136	1.832025
O	-3.347032	-0.974440	0.454622
C	1.493248	1.118341	1.811122
C	1.463967	-2.670257	1.800964
H	0.759564	-3.444122	1.529778
C	-2.690888	-0.138438	0.033015
C	1.647114	-2.115129	3.103003
H	1.077954	-2.374646	3.986072
C	-2.851570	0.990311	-2.464836
H	-3.508912	0.169893	-2.720646
C	-0.982789	2.316956	-2.270934
H	0.024629	2.695348	-2.369977
C	-1.480722	1.084948	-2.790465
H	-0.916493	0.352537	-3.351010
C	2.423117	-2.064968	0.944666
H	2.565677	-2.283449	-0.104134
C	-0.463147	-0.514935	2.501066
C	2.678342	-1.151557	3.039229
H	3.043614	-0.553615	3.862592
O	-1.323022	2.628196	1.764290
C	-2.065646	2.981762	-1.641199
H	-2.013186	3.944739	-1.150161
C	-1.450789	2.017410	0.805783
C	3.161413	-1.120301	1.691287
H	3.964708	-0.499476	1.317758
C	-3.218830	2.159582	-1.732084
H	-4.201429	2.391274	-1.345708
C	-0.229561	-1.963488	-1.228655
H	-0.991377	-2.473664	-0.633941
H	0.653729	-2.601796	-1.296394
H	-0.622857	-1.803206	-2.235657
C	1.654199	0.380522	-1.541839
H	1.338653	0.451558	-2.585128
H	2.496631	-0.312730	-1.480073
H	1.985818	1.364306	-1.200001

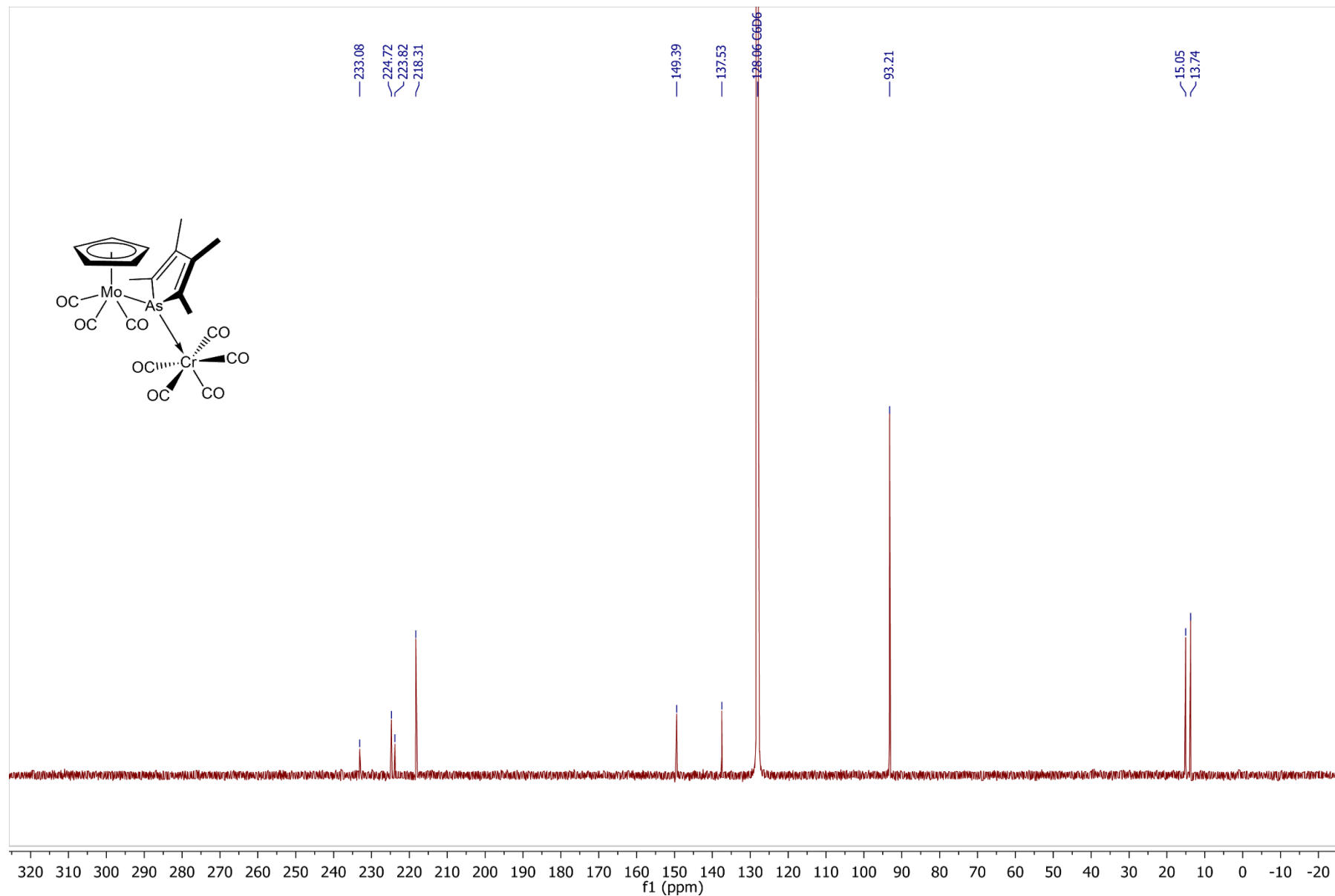


Energies associated with homolytic and heterolytic Fe-As bond cleavage (DFT: $\omega$ B97X-D/6-31G\*) for  $[\text{Fe}(\text{AsMe}_3)(\text{CO})_2(\text{C}_5\text{H}_5)]^+$ ,  $[\text{Fe}_2(\mu\text{-AsMe}_2)(\text{CO})_2(\text{C}_5\text{H}_5)_2]^+$  and  $[\text{Fe}_2(\mu\text{-AsC}_4\text{Me}_9)(\text{CO})_4(\text{C}_5\text{H}_5)_2]^+$ .

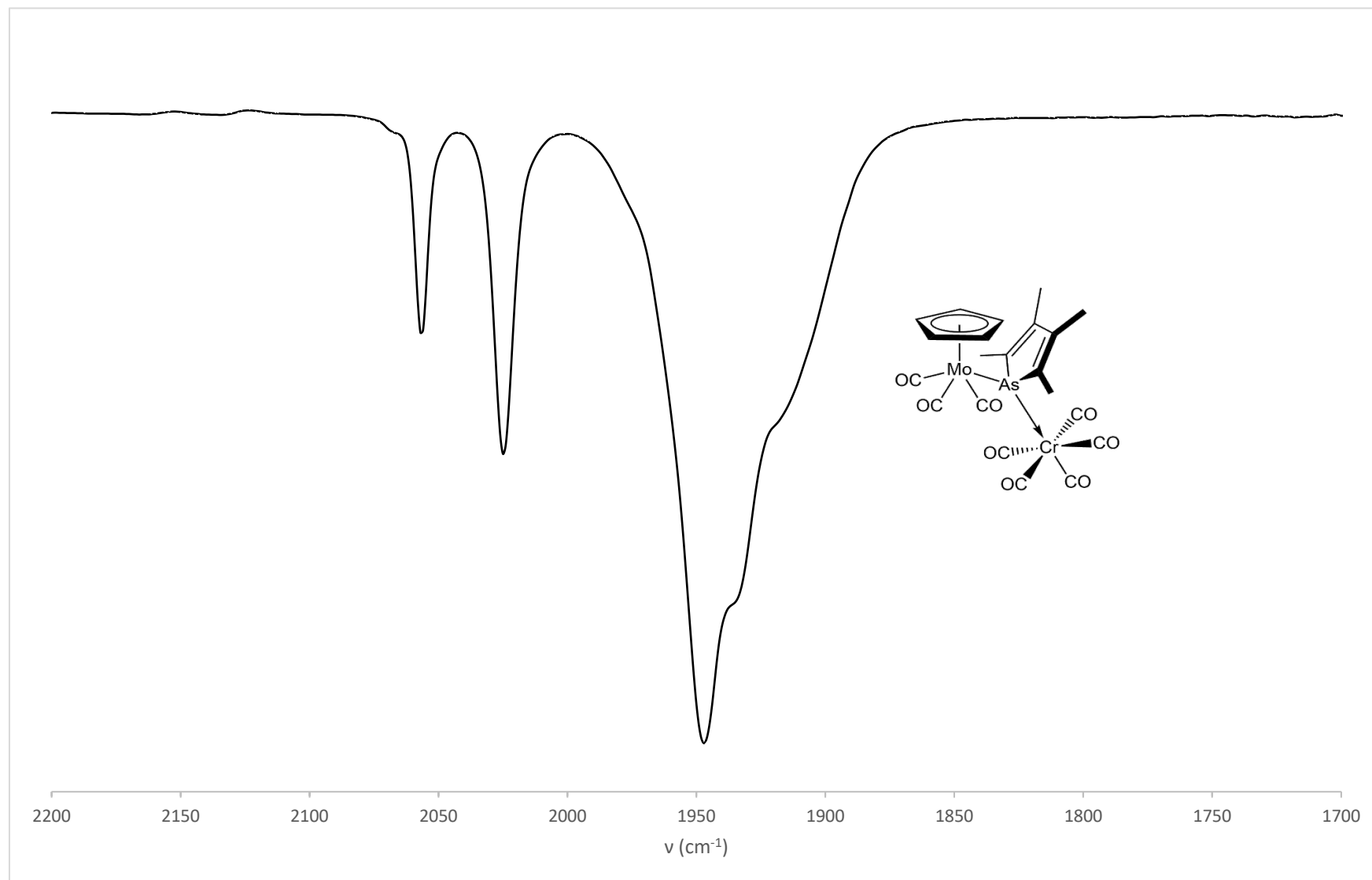




**Figure S11.**  $^1\text{H}$  spectrum of  $[\text{MoCr}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)]$  (2) in  $d_6$ -benzene (278 K, 400 MHz,  $\delta_{\text{H}}$ /ppm).

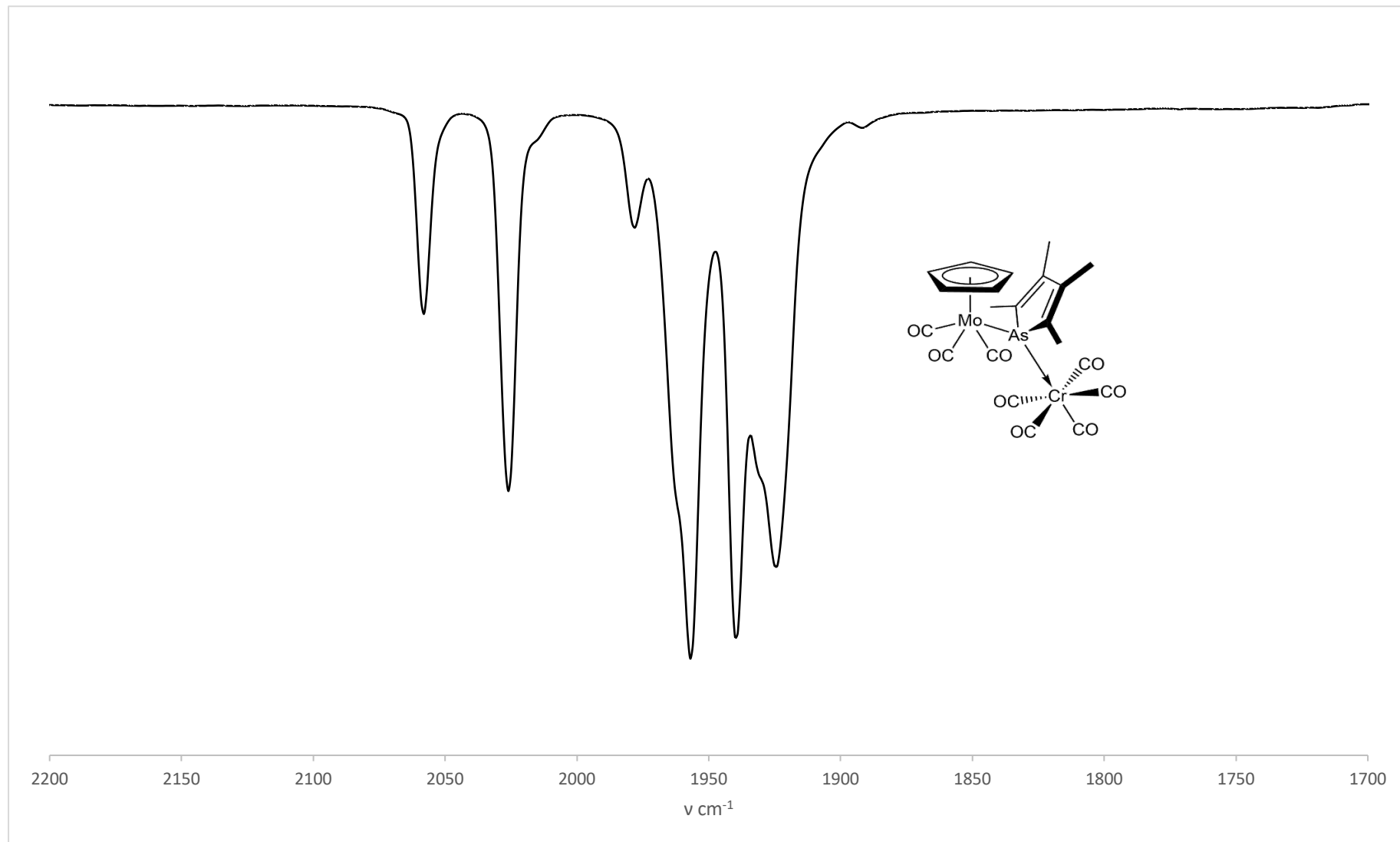


**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of  $[\text{MoCr}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)]$  (2) in  $d_6$ -benzene (278 K, 176.0 MHz,  $\delta_{\text{C}}$ /ppm).

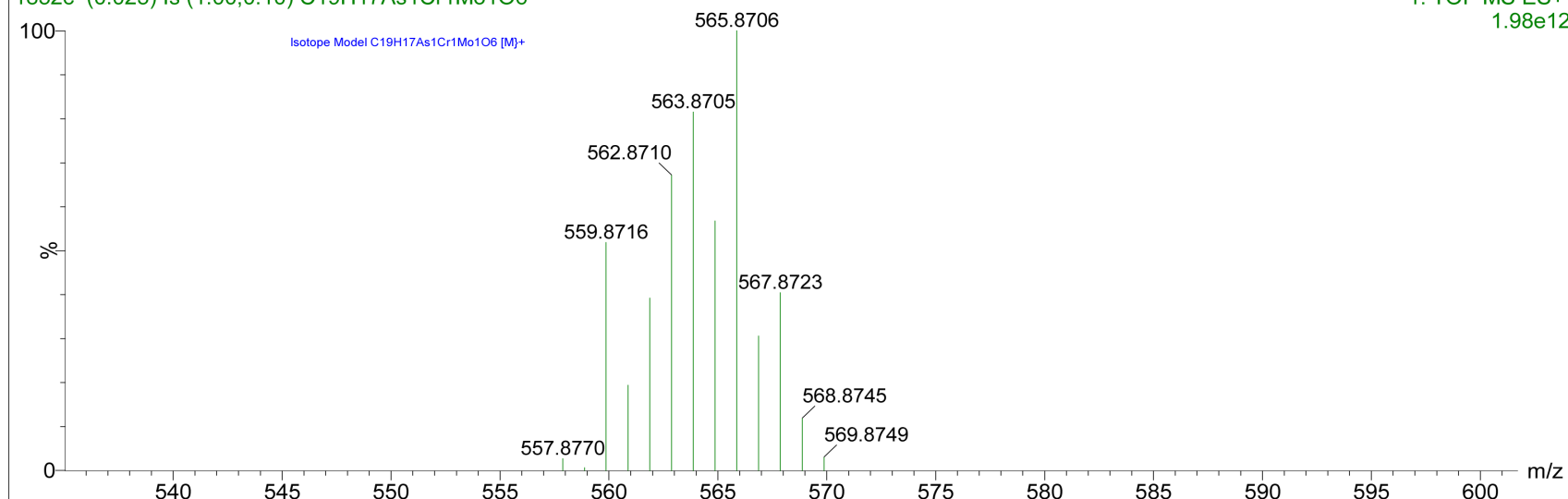


**Figure S13.** Solution infrared spectrum of  $[\text{MoCr}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)]$  (**2**) in dichloromethane.

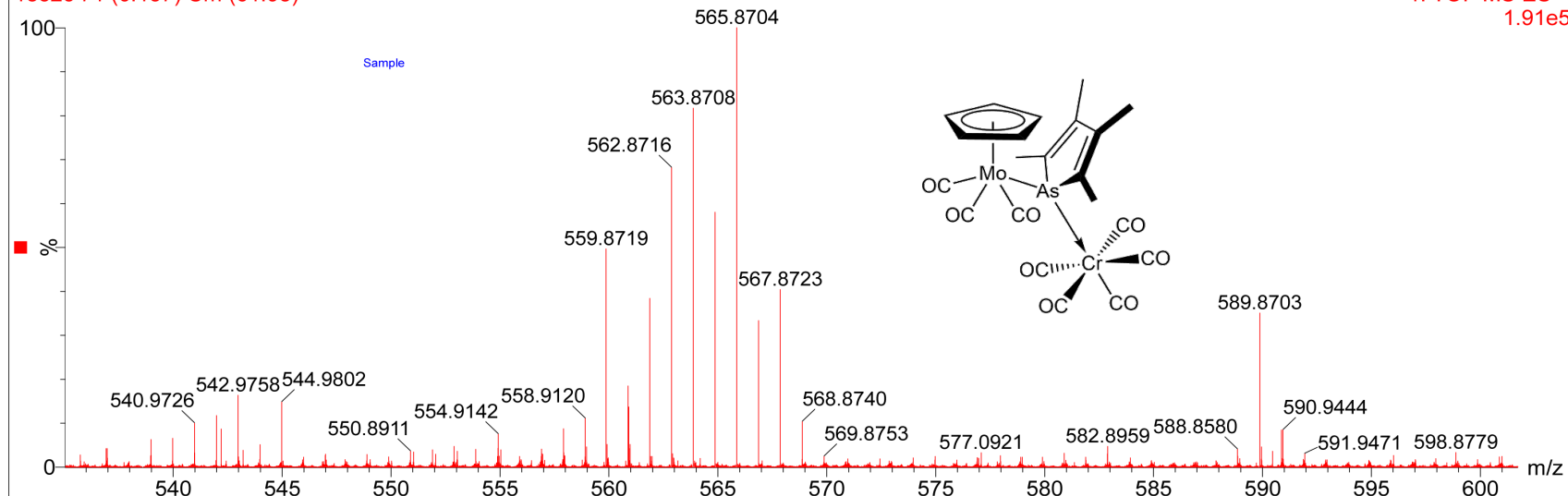


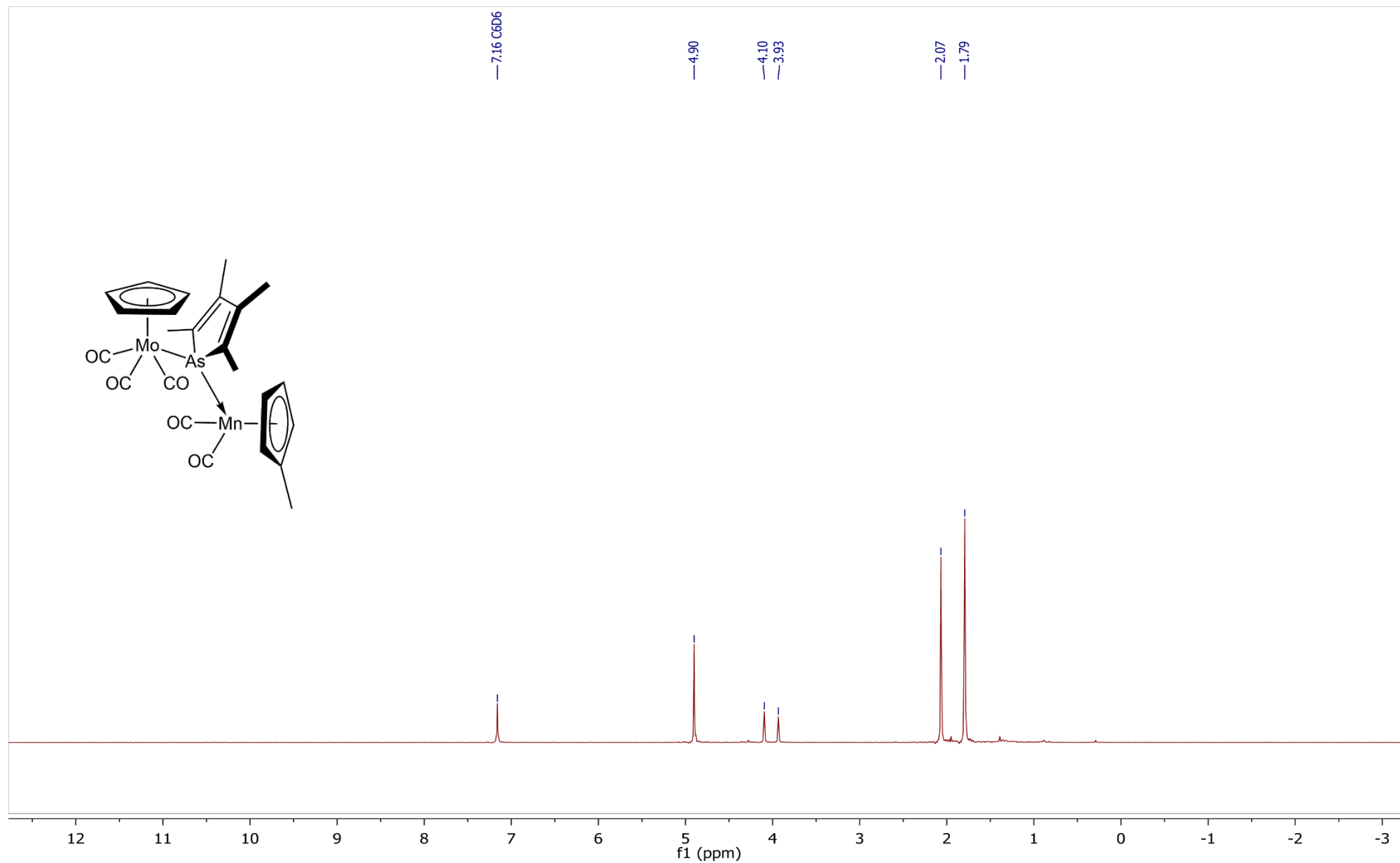


**Figure S14.** Solution infrared spectrum of  $[\text{MoCr}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_8(\eta^5\text{-C}_5\text{H}_5)]$  (**2**) in *n*-hexane.

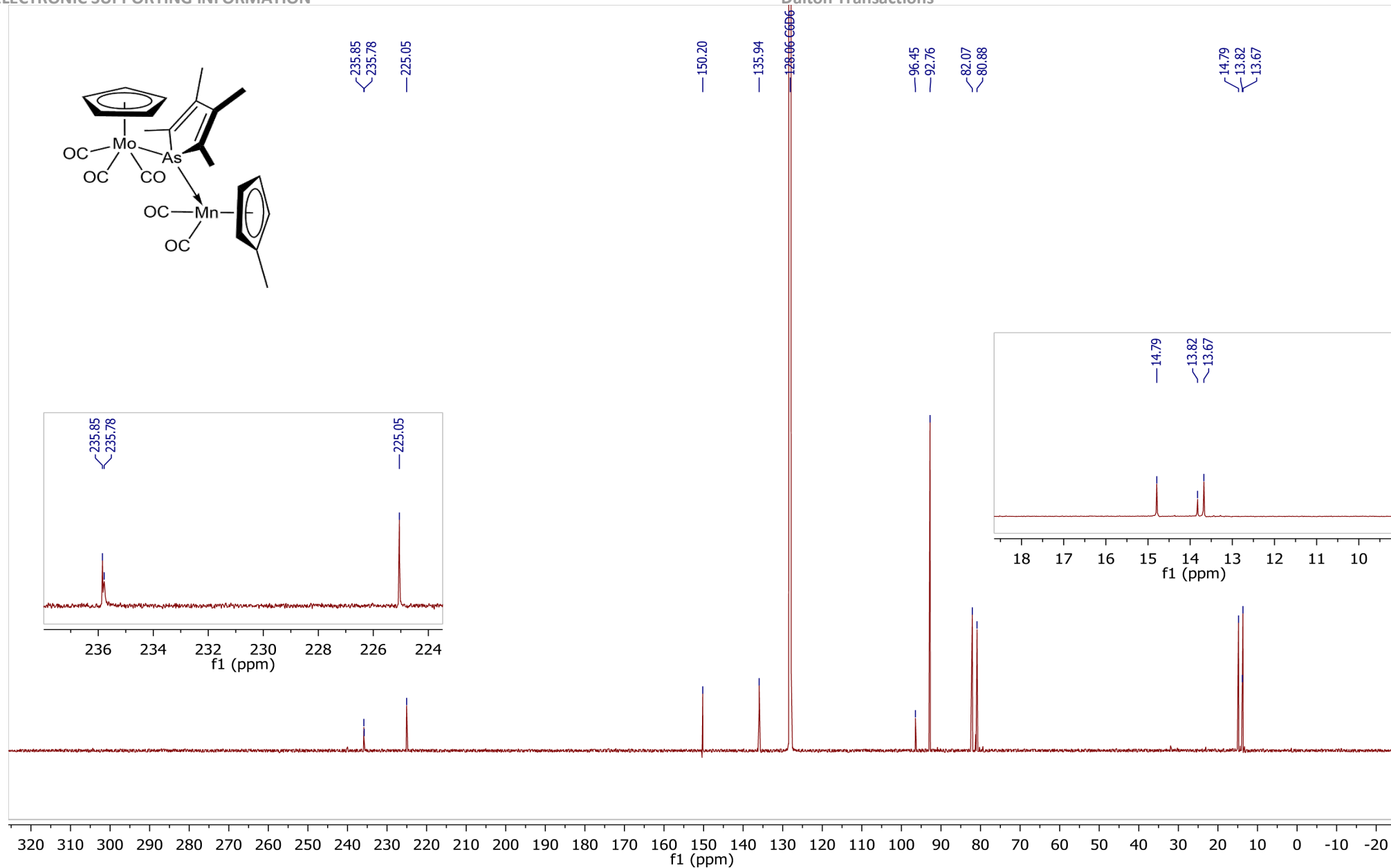
1832c (0.023) Is (1.00,0.10) C<sub>19</sub>H<sub>17</sub>As<sub>1</sub>Cr<sub>1</sub>Mo<sub>1</sub>O<sub>6</sub>1: TOF MS ES+  
1.98e12

1832c 71 (0.157) Cm (61:98)

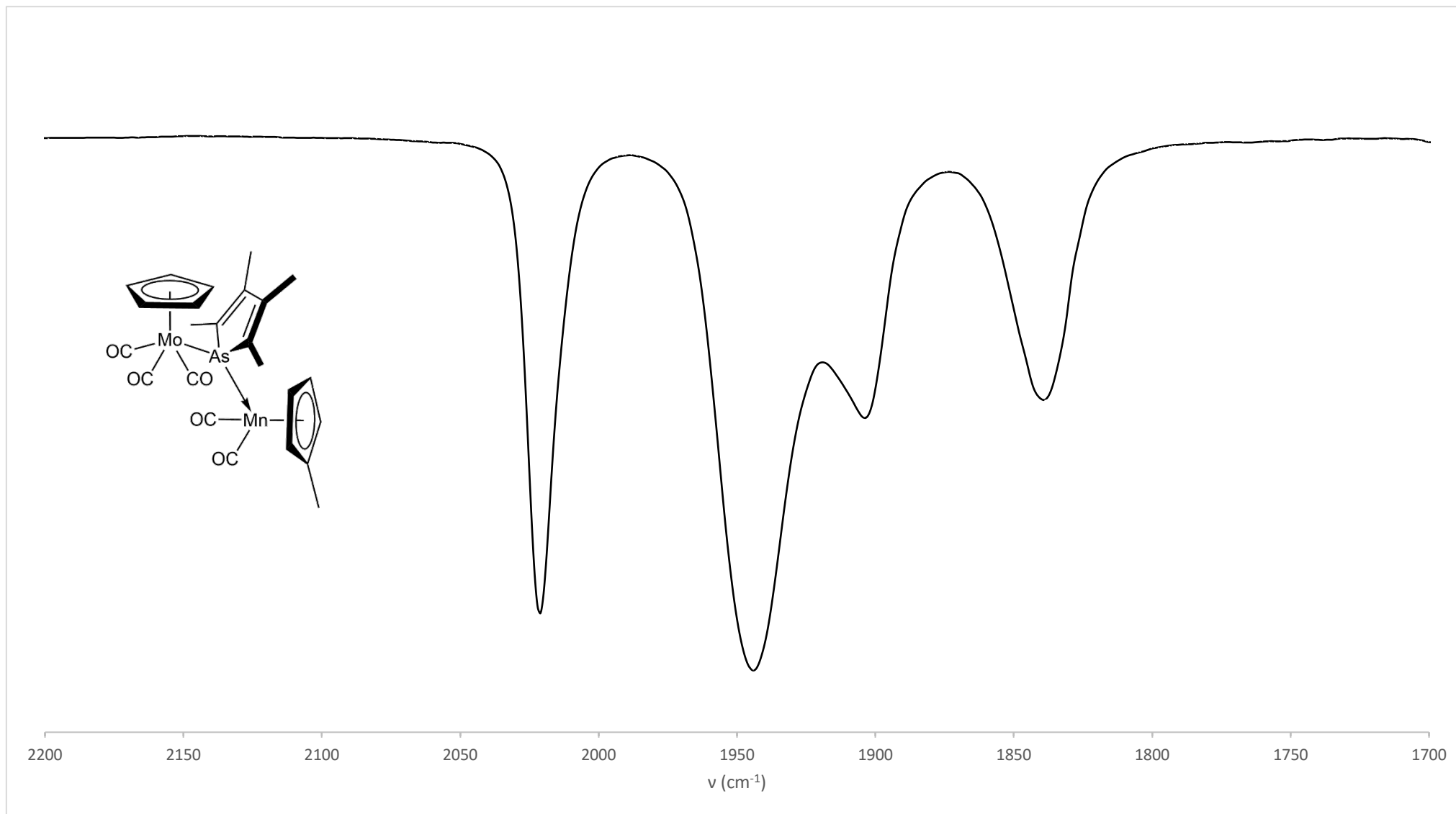
1: TOF MS ES+  
1.91e5**Figure S15.** Electrospray mass spectrometry of [MoCr(μ-AsC<sub>4</sub>Me<sub>4</sub>)(CO)<sub>8</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] (2).



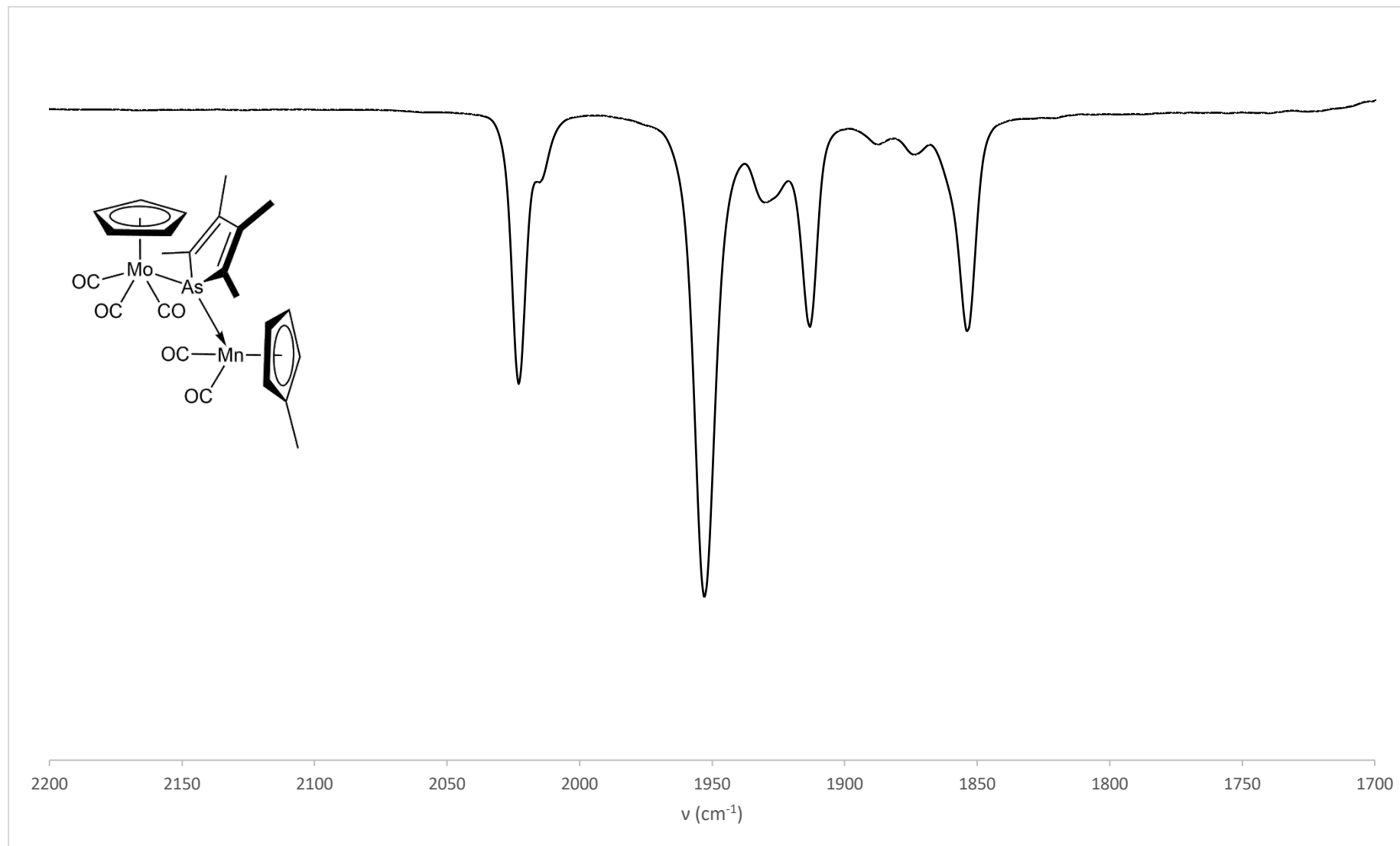
**Figure S16.**  $^1\text{H}$  spectrum of  $[\text{MoMn}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\text{h}5\text{-C}_5\text{H}_4\text{Me})]$  (3) in  $d_6$ -benzene (278 K, 400 MHz,  $\delta_{\text{H}}$ /ppm).



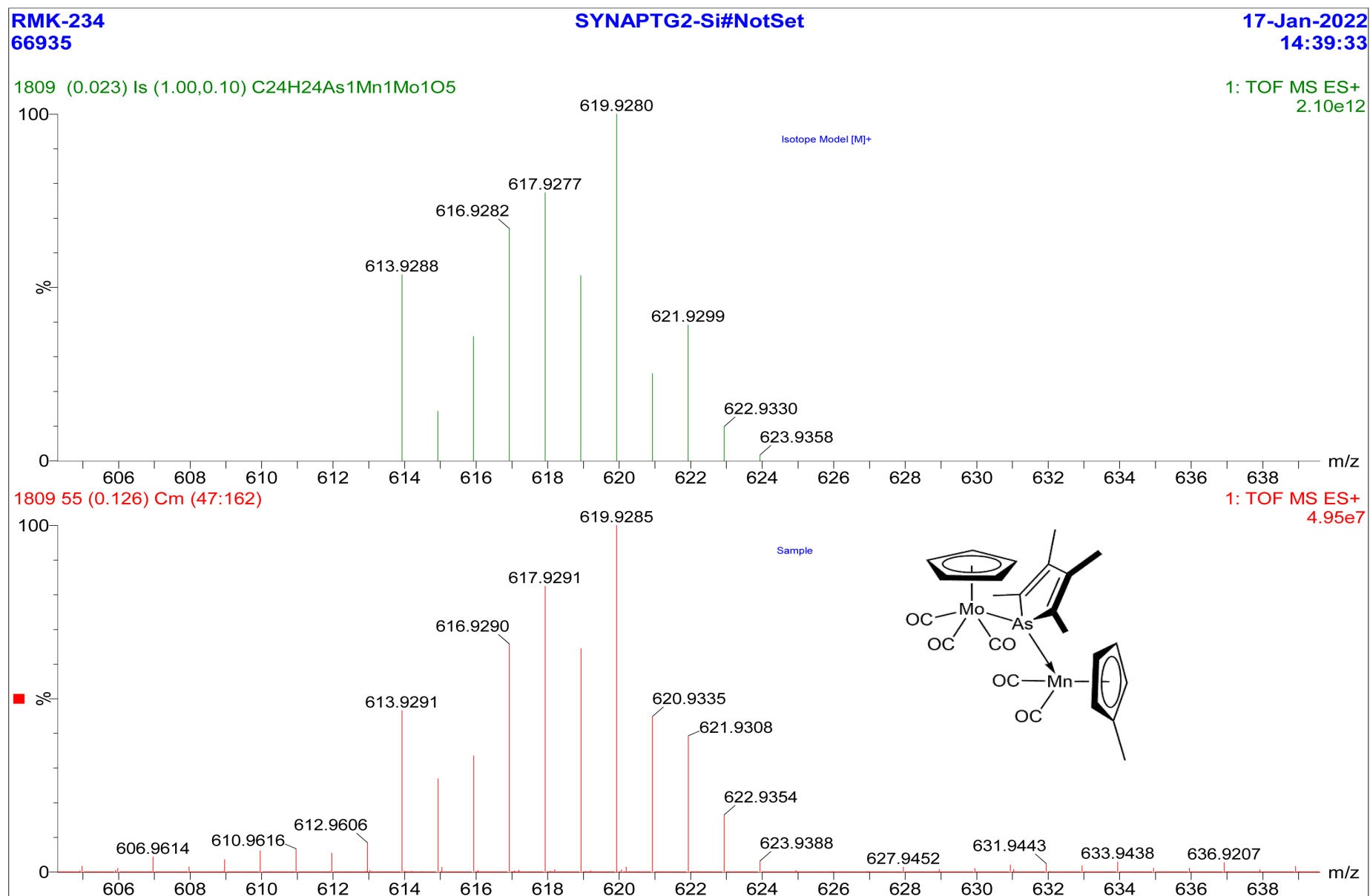
**Figure S17.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of  $[\text{MoMn}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})]$  (**3**) in  $d_6$ -benzene (278 K, 176.0 MHz,  $\delta_{\text{C}}/\text{ppm}$ ).



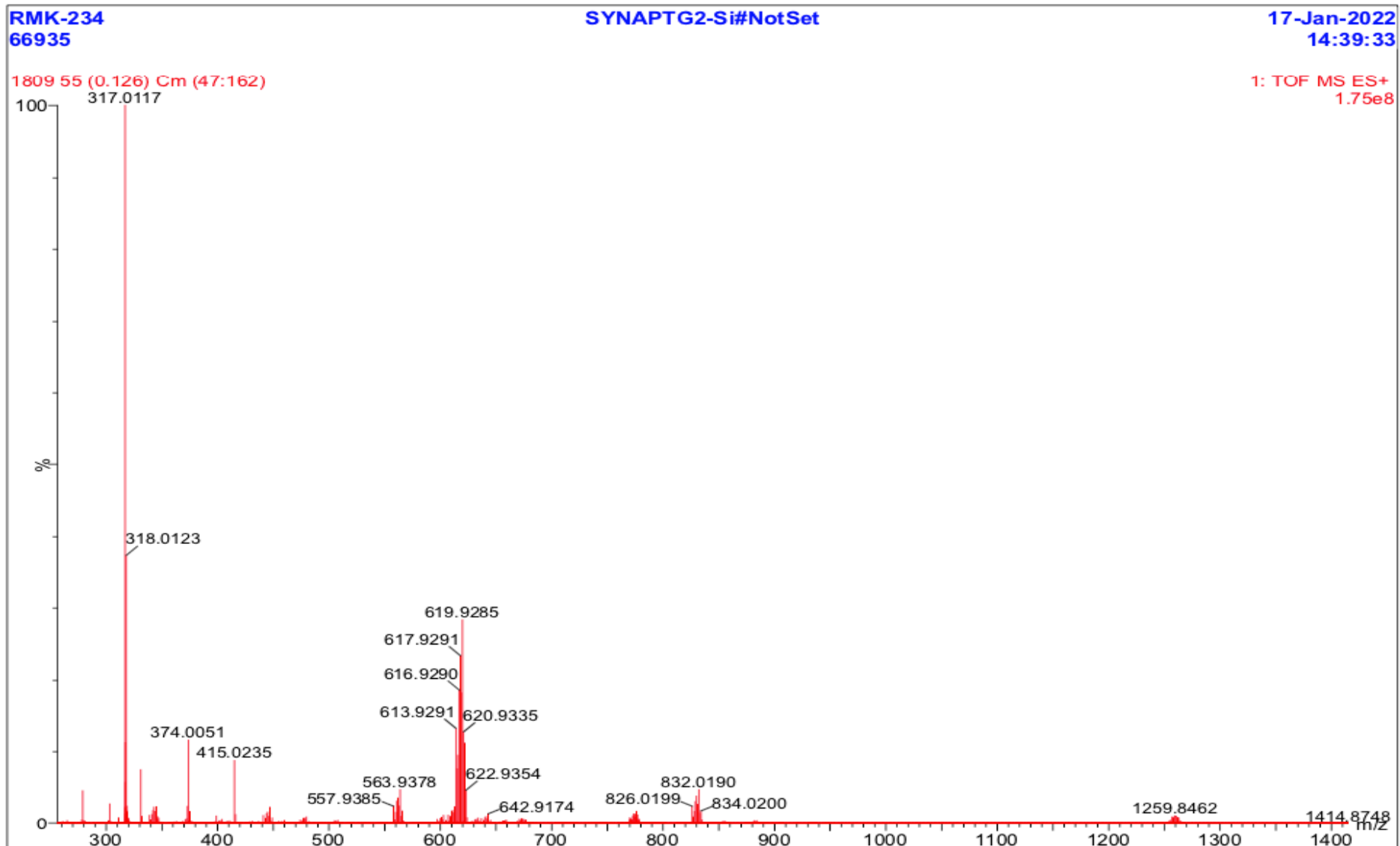
**Figure S18.** Solution infrared spectrum of  $[\text{MoMn}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})]$  (3) in dichloromethane.



**Figure S19.** Solution infrared spectrum of  $[\text{MoMn}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})]$  (3) in *n*-hexane.



**Figure S20a.** Electrospray mass spectrometry of [MoMn( $\mu$ -AsC<sub>4</sub>Me<sub>4</sub>)(CO)<sub>5</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)] (**3**).



**Figure S20b.** Electrospray mass spectrometry of  $[\text{MoMn}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{Me})]$  (**3**) – Full spectrum.



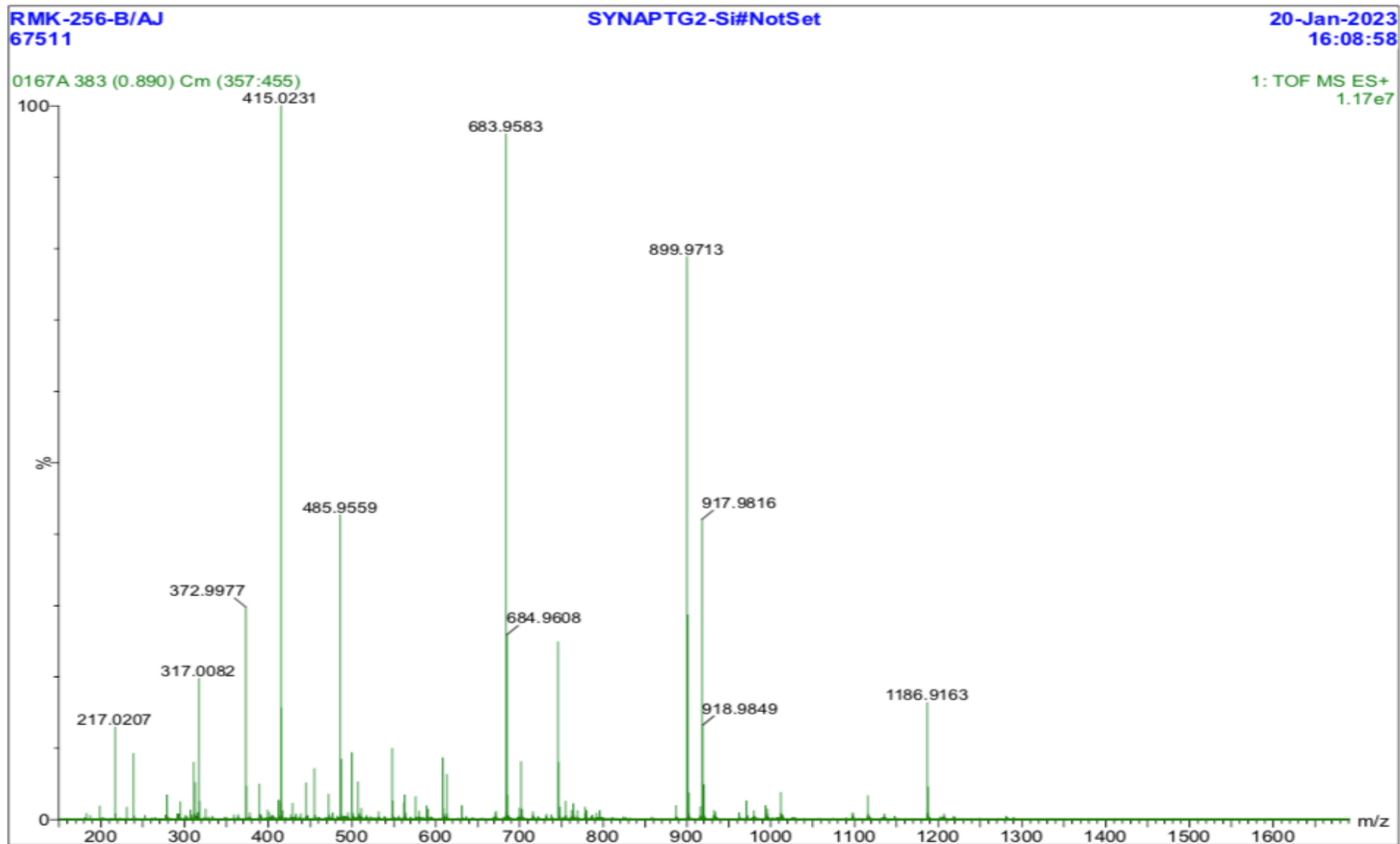
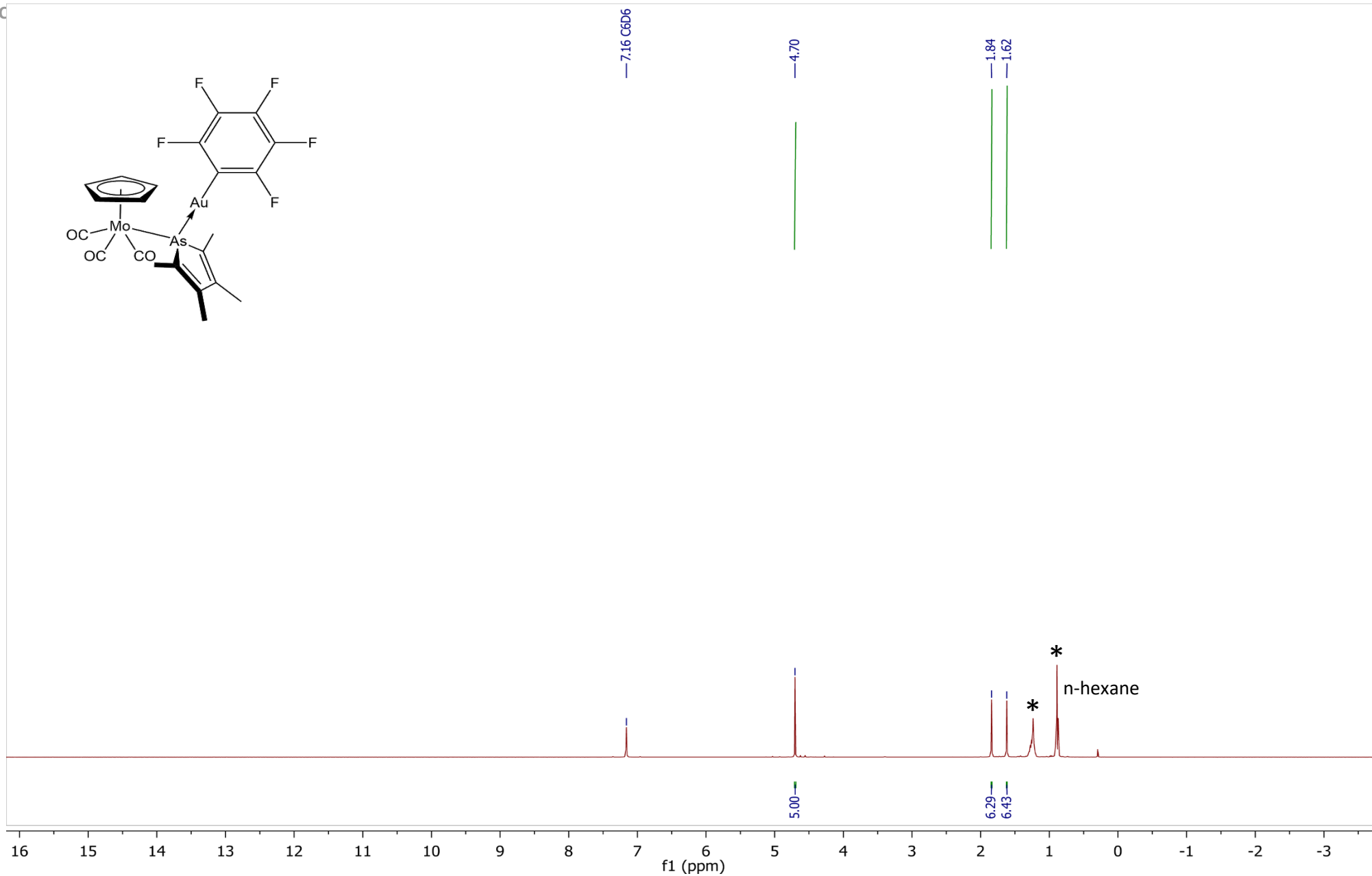
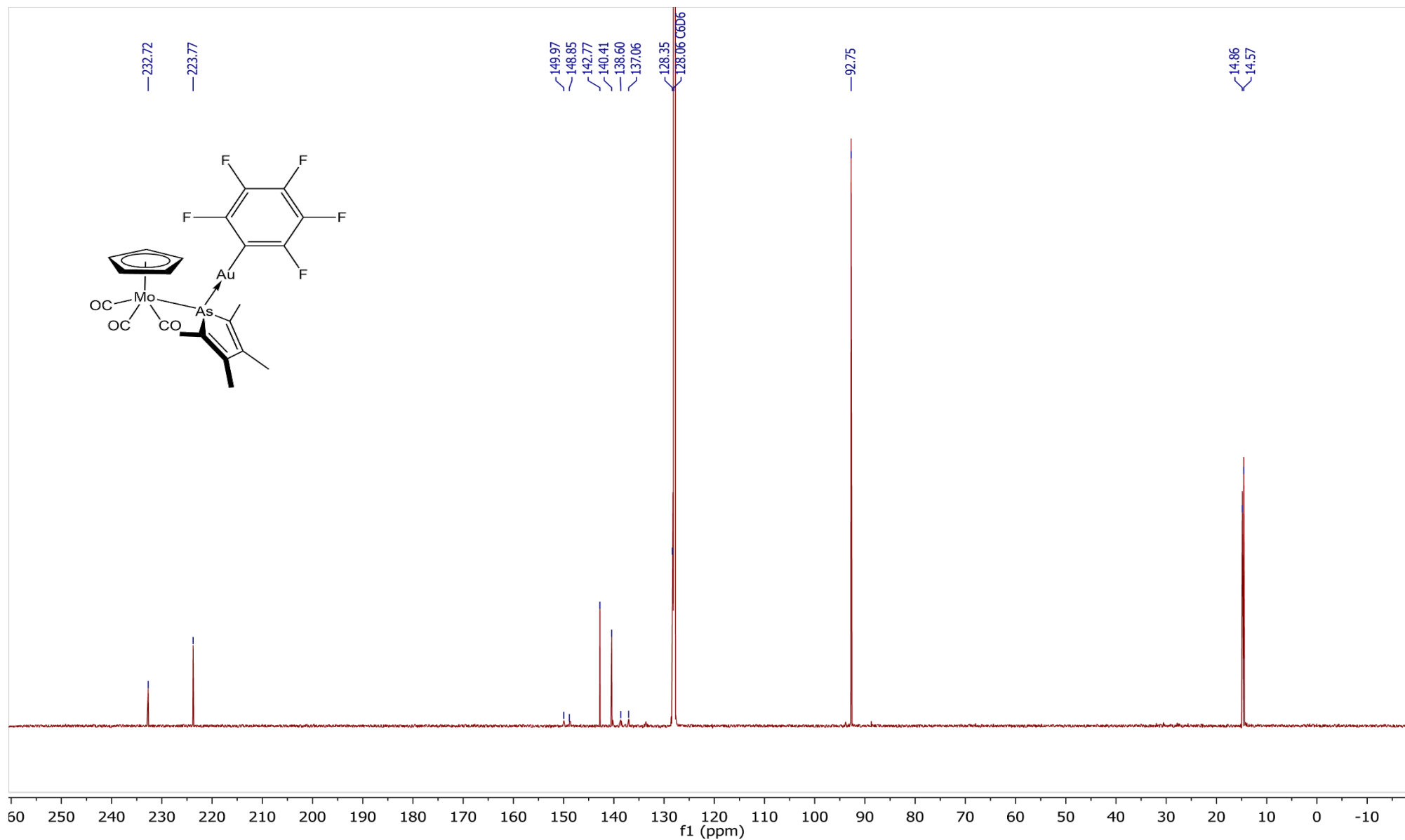
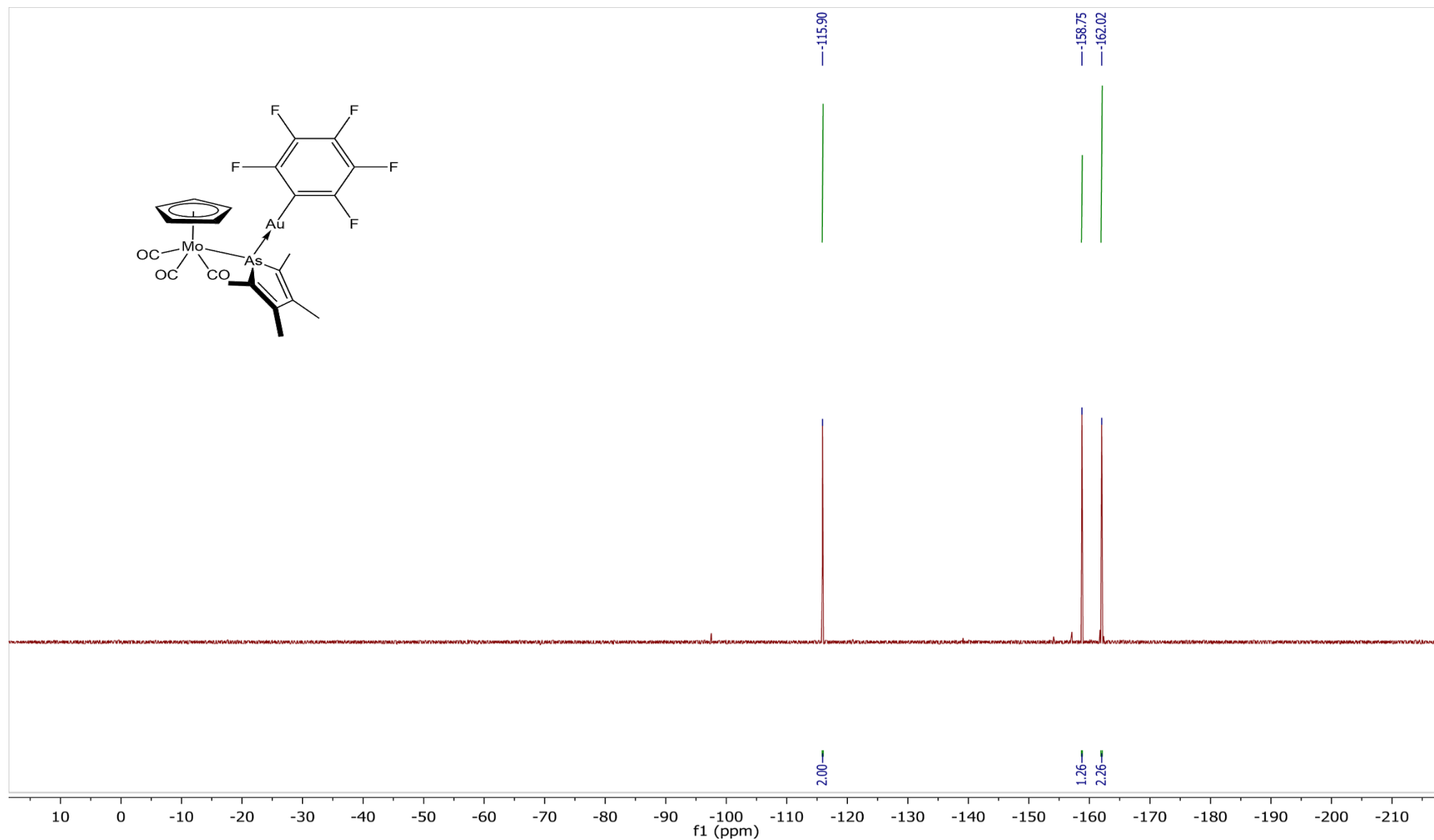


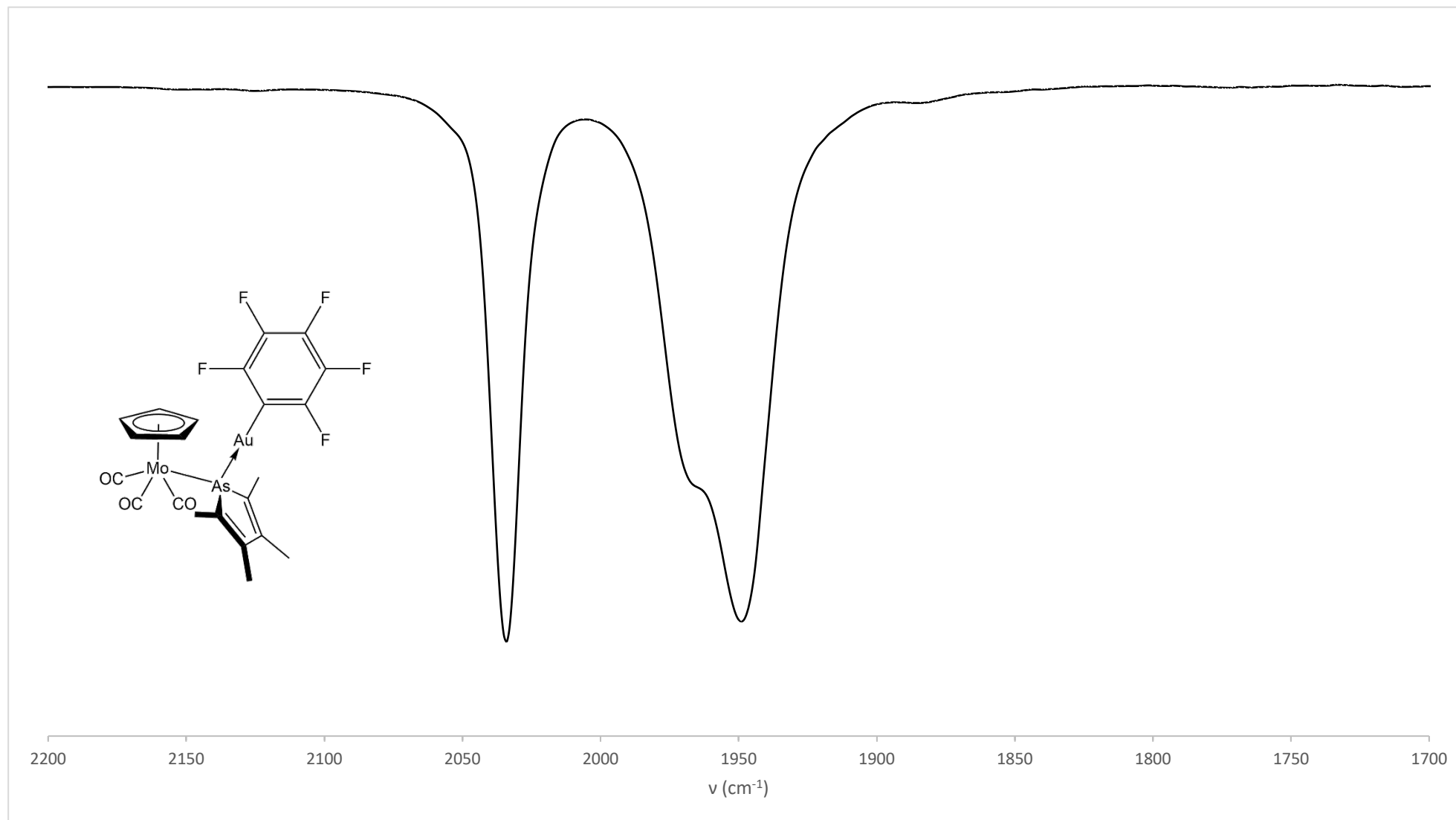
Figure S20c. Electrospray mass spectrometry of side product from **3** synthesis – Full spectrum.



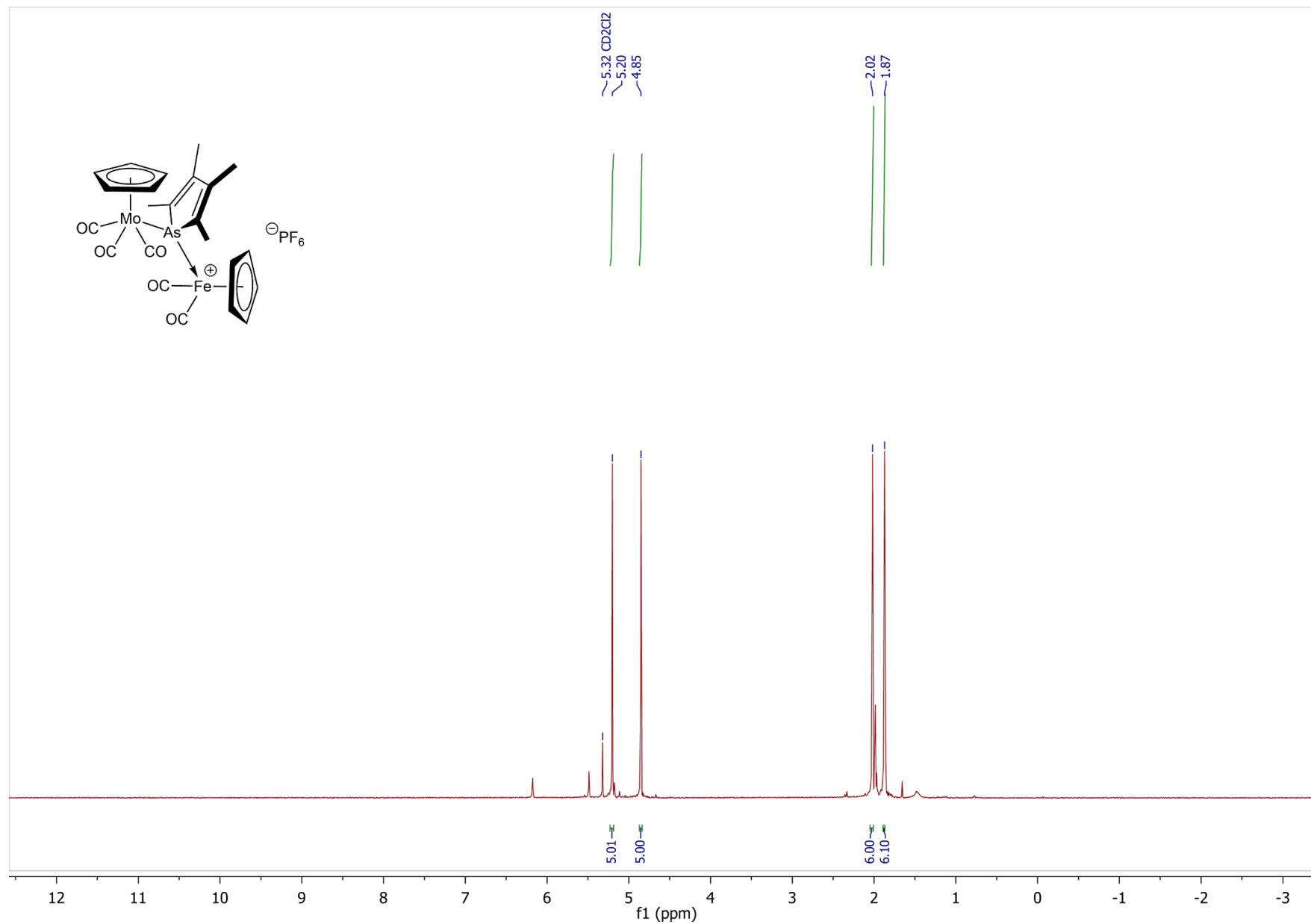




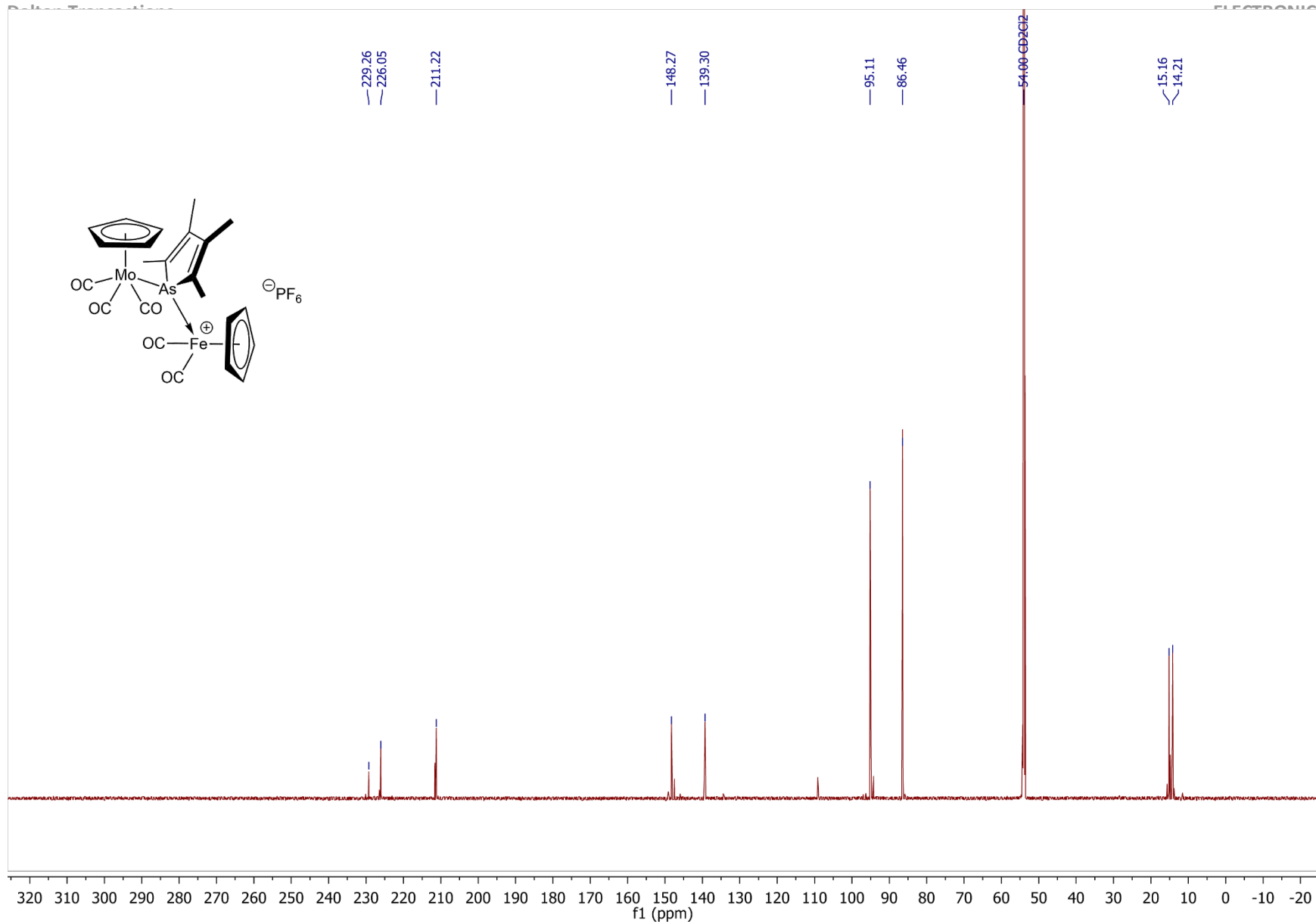
**Figure S23.**  $^{19}\text{F}\{^1\text{H}\}$  spectrum  $[\text{MoAu}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_3(\text{C}_6\text{F}_5)(\eta^5\text{-C}_5\text{H}_5)]$  (4) in  $d_6$ -benzene (278 K, 376.3 MHz,  $\delta_F$ /ppm).



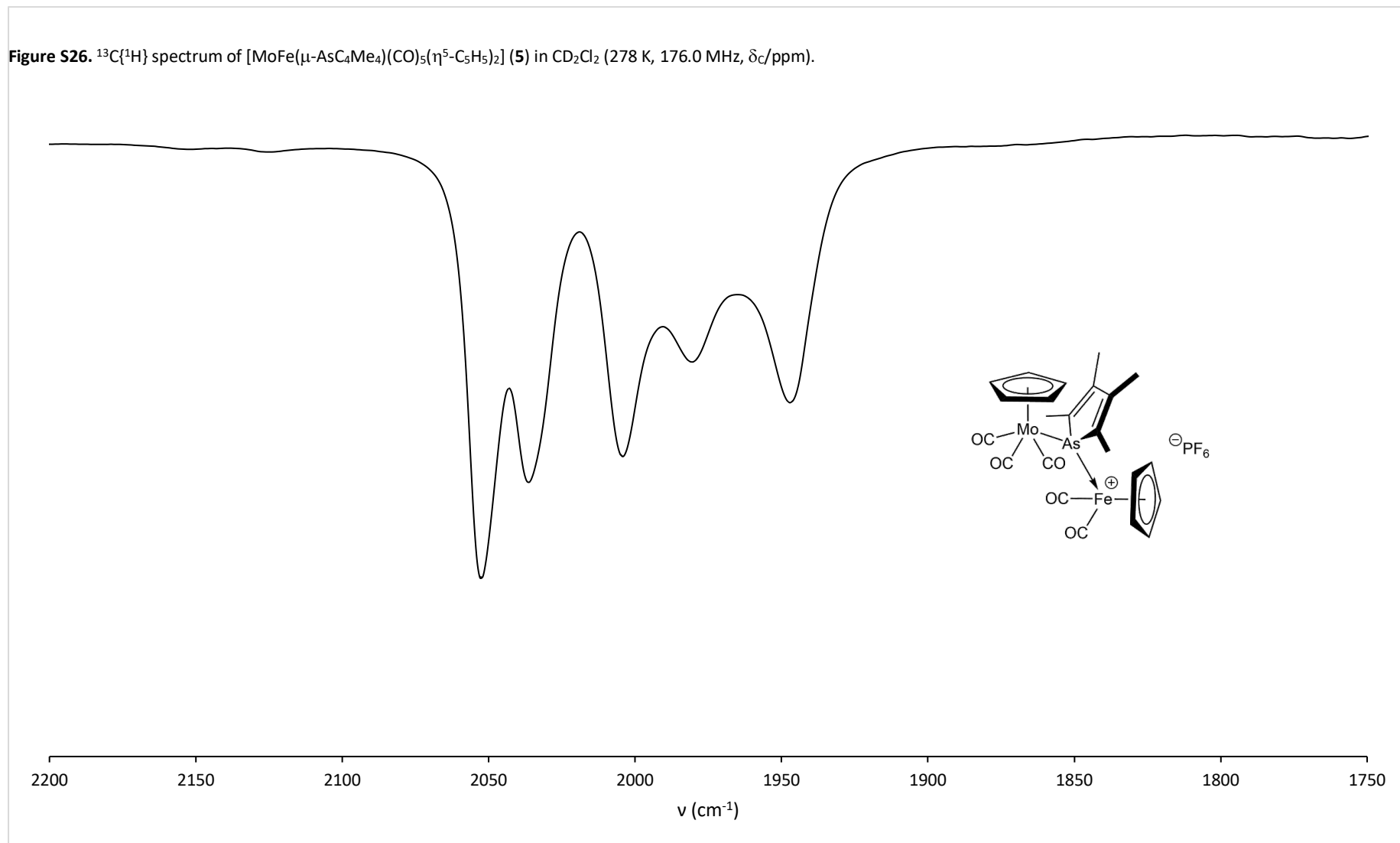
**Figure S24.** Solution infrared spectrum of  $[\text{MoAu}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_3(\text{C}_6\text{F}_5)(\eta^5\text{-C}_5\text{H}_5)]$  (**4**) in dichloromethane.



**Figure S25.**  $^1\text{H}$  spectrum of  $[\text{MoFe}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)_2]$  (5) in  $\text{CD}_2\text{Cl}_2$  (278 K, 400 MHz,  $\delta_{\text{H}}$ /ppm).

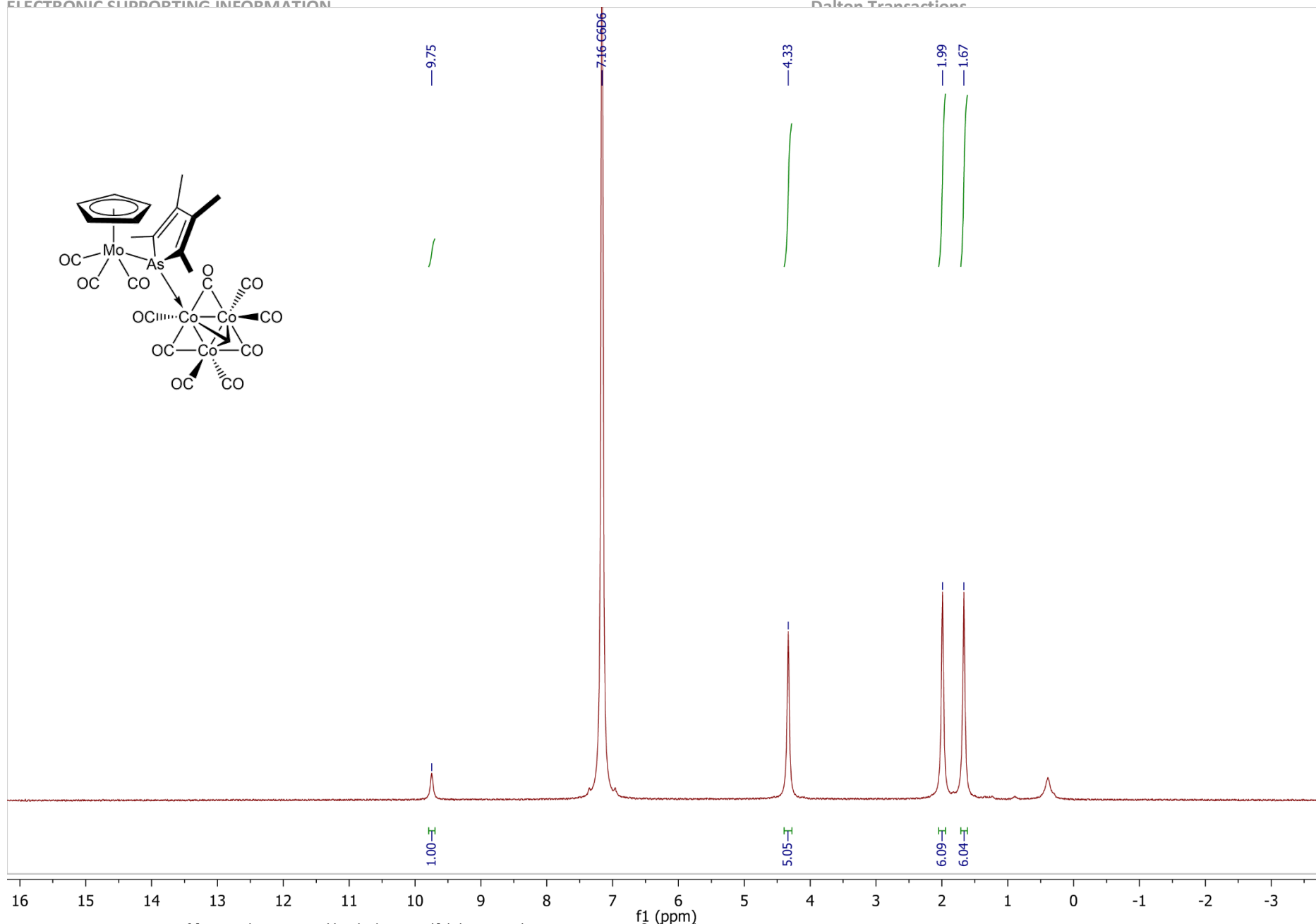


**Figure S26.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of  $[\text{MoFe}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)_2]$  (**5**) in  $\text{CD}_2\text{Cl}_2$  (278 K, 176.0 MHz,  $\delta_c/\text{ppm}$ ).

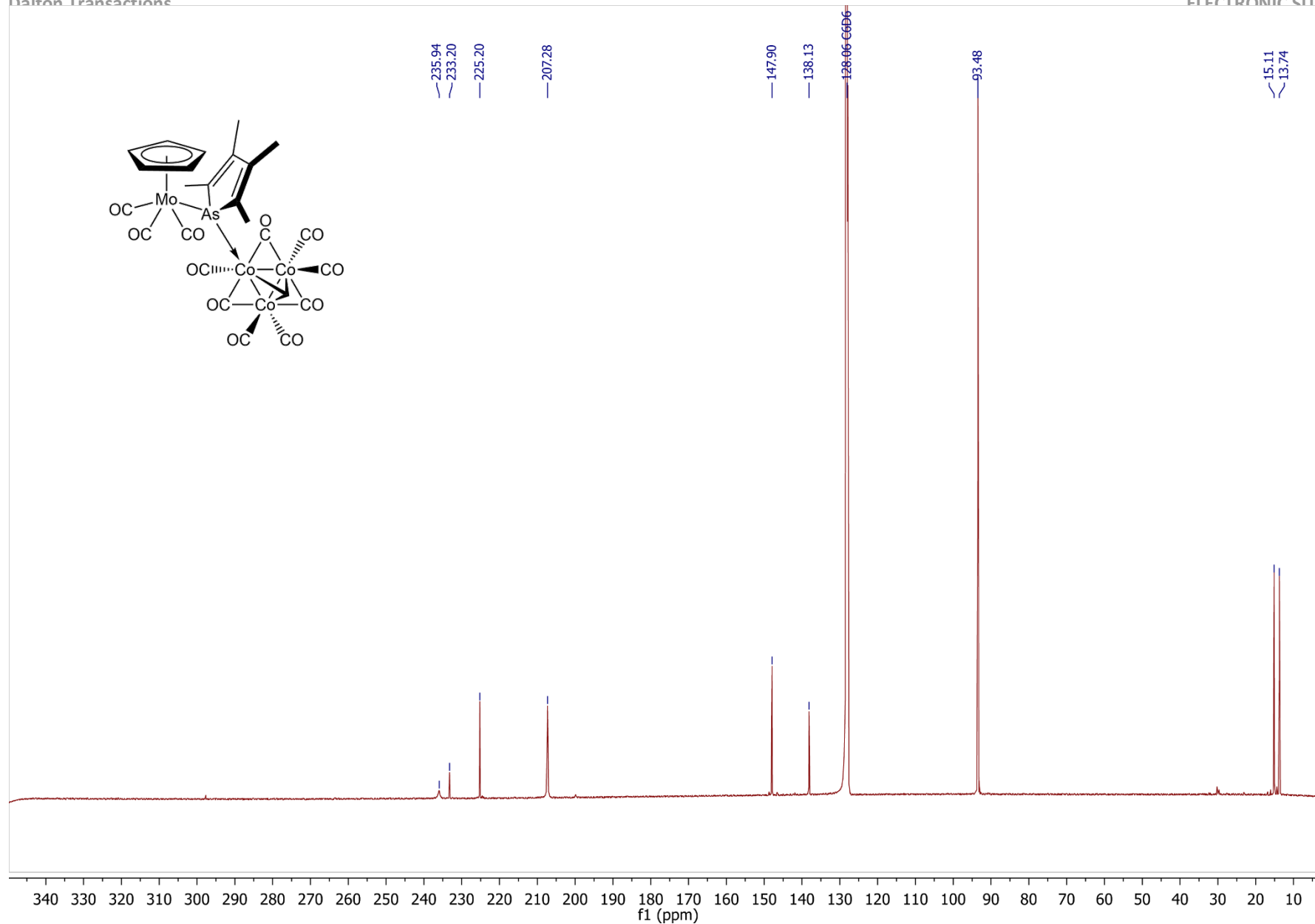




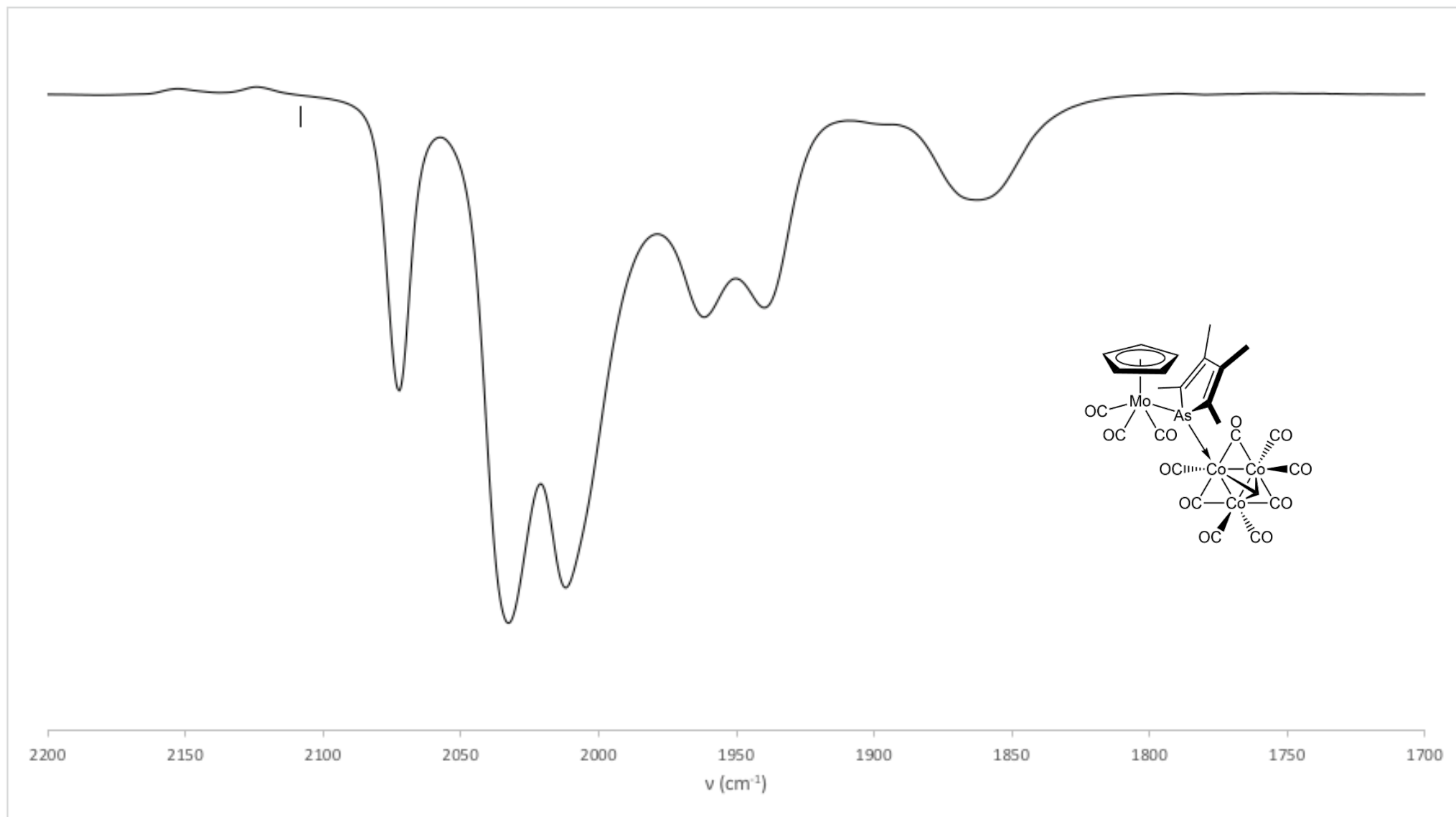
**Figure S27.** Solution infrared spectrum of  $[\text{MoFe}(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)_2]$  (**5**) in dichloromethane.



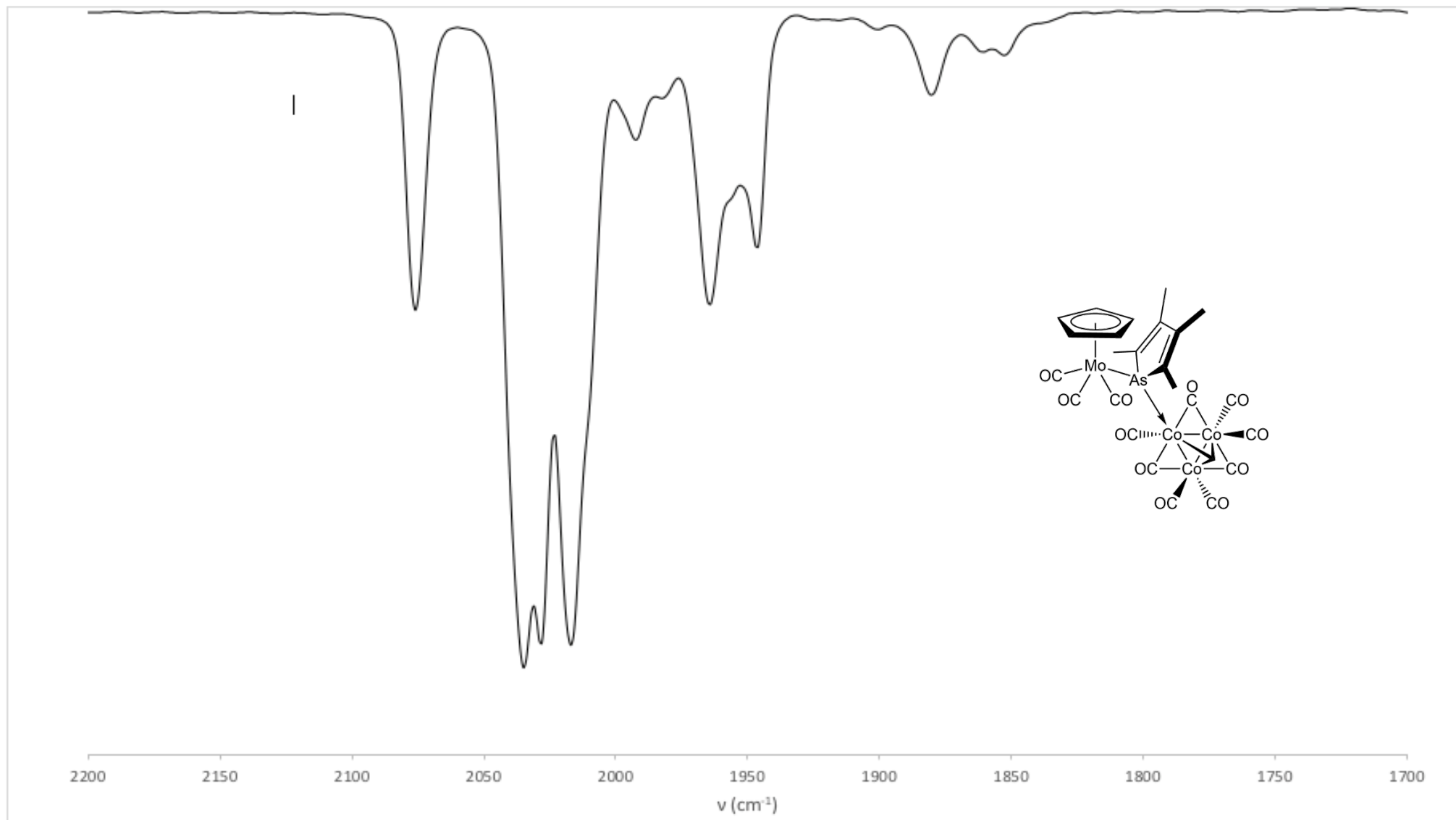
**Figure S28.**  $^1\text{H}$  spectrum of  $[\text{MoCo}_3(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$  (6) in  $\text{C}_6\text{D}_6$  (278 K, 400 MHz,  $\delta_{\text{H}}$ /ppm).



**Figure S29.**  $^{13}\text{C}\{^1\text{H}\}$  spectrum of  $[\text{MoCo}_3(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$  (6) in  $\text{C}_6\text{D}_6$  (278 K, 176.0 MHz,  $\delta_c/\text{ppm}$ ).



**Figure S30.** Solution infrared spectrum of  $[\text{MoCo}_3(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$  (**6**) in dichloromethane.



**Figure S31.** Solution infrared spectrum of  $[\text{MoCo}_3(\mu\text{-AsC}_4\text{Me}_4)(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)]$  (6) in *n*-hexane.

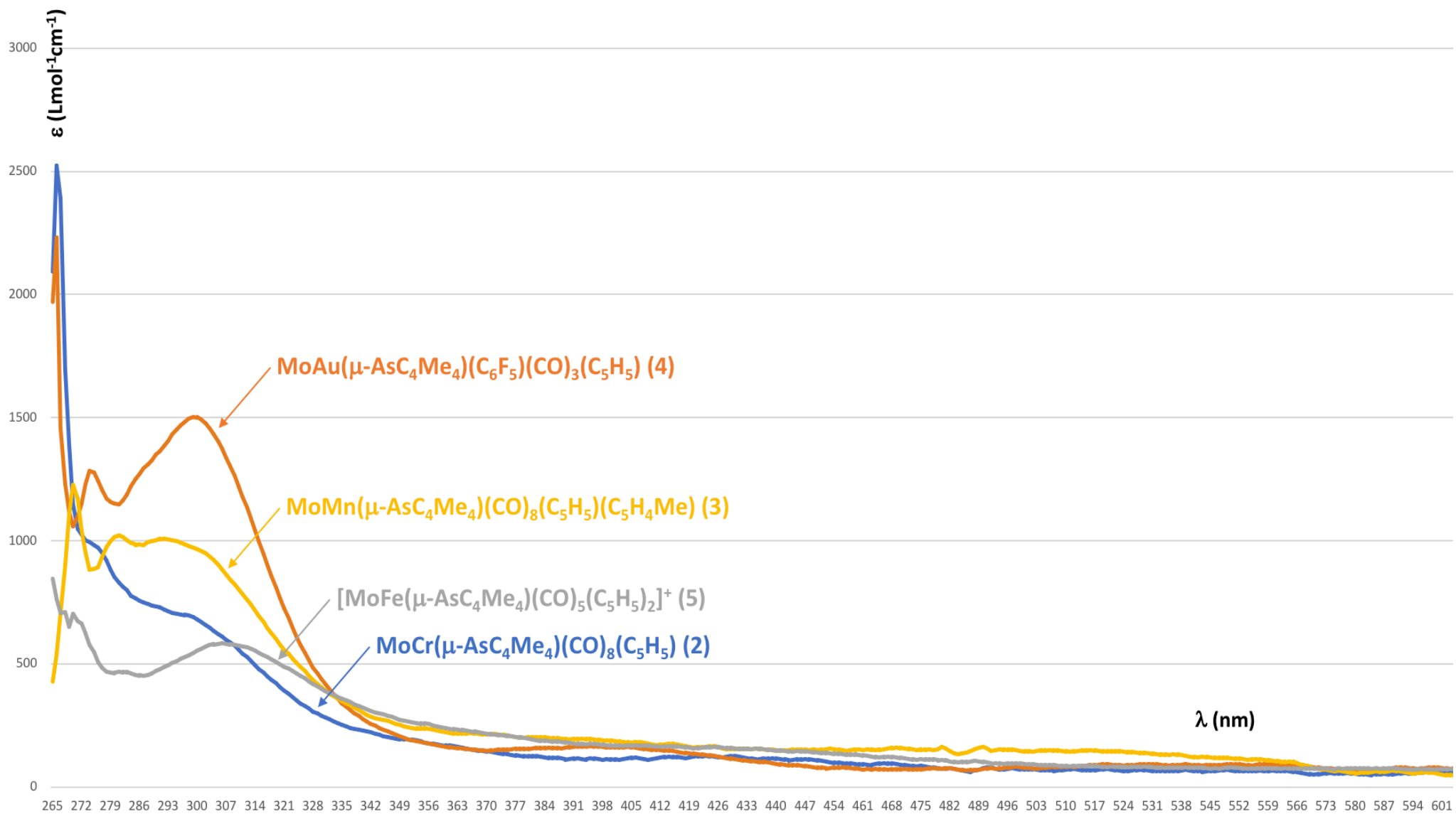


Figure S32. Electronic spectra of (2–5) in dichloromethane ( $\approx 0.0005 \text{ molL}^{-1}$ ).