# Free and Coordinated Biarsolyls

Ryan M. Kirk[a] and Anthony F. HIll*[a]

Received 6th July 2023,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

.

## Experimental considerations

**General Precautions:** Unless otherwise stated, reactions were carried out under an atmosphere of commercially purified argon or nitrogen using standard Schlenk techniques. 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**. Metal carbonyls are volatile sources of both carbon monoxide and nanoparticulate metal. Benzene (including benzene-$d_6$) 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:** Reagents and materials were obtained from commercial vendors and used as received: [$Cp_2ZrCl_2$], 2-butyne, [$Mn(CO)_3(\eta$-$C_5H_4Me)$] (Ethyl Corp.), $AsCl_3$, *n*-BuLi (2.5 M in hexanes), neutral alumina, silica gel (230—400 mesh), $C_6D_6$, $CD_2Cl_2$ (Cambridge Isotopes Laboratories). HPLC-grade solvents were purchased from Merck and re-purified by distillation under nitrogen from an appropriate desiccant: THF, $Et_2O$ (Na/benzophenone); $CH_2Cl_2$, $CHCl_3$ ($P_2O_5$); *n*-pentane, *n*-hexane, *n*-heptane, $C_6D_6$ (K mirror); $CD_2Cl_2$ ($CaD_2$). 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 ($^{13}C$ frequencies of 100.6, 150.9, 176.0 and 201.2 MHz respectively). Spectra are reported in ppm shift downfield from $SiMe_4$ and referenced to the residual protio-solvent impurity ($^1H$: $C_6D_6$ 7.16, $CD_2Cl_2$ 5.32 ppm) or the solvent signal itself ($^{13}C$: $C_6D_6$ 128.0, $CD_2Cl_2$ 53.8 ppm). $^1H$ NMR spectra are reported to two decimal places, and $^{13}C$ 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.

[a] *Research School of Chemistry, Australian National University, Canberra, ACT. Email: a.hill@anu.edu.au.*

Solution IR 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 fume-hood. 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 XCaliber or Supernova/EosS2-CCD diffractometer with graphite monochromated Mo-Kα (λ = 0.71069 Å) or Cu Kα (λ = 1.54184 Å) 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.[1] Absorption corrections are stated for each sample separately. The structures were solved within the Olex2[2] software package with SHELXT[4] using intrinsic phasing and refined with SHELXL[3] 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 $U_{iso}$(H) parameters fixed to 1.2 $U_{eq}(C_i)$ (for methyl hydrogens) or 1.5 $U_{eq}(C_i)$ (for cyclopentadienyl hydrogens), where $U_{eq}(C_i)$ 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.[4]

**Computational Studies.** Calculations were performed by using the *SPARTAN20*® suite of programs.[5] Geometry optimisation (gas phase) was performed at the DFT level of theory using the exchange functionals ωB97X-D of Head-Gordon,[6,7] with the exception of the compounds $AMe_3$, $A_2Me_4$ and $(AC_4H_4)_2$ (A = N, P, As, Sb, Bi) for which the ωB97X functional was used for consistency due to the element bismuth not being implemented in the wB97X-D functional within *SPARTAN20®*. The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt[8] was used for elements with Z > Kr while Pople 6-31G* basis sets[9] 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. The vertical excitation energies of the first 6 excited states were predicted by TD-DFT calculations using the ωB97X-D functional and the 6-31G* basis sets starting from the respective ωB97X-D optimized gas-phase $S_0$ geometry.. Cartesian atomic coordinates are provided below.

**Synthesis of $(AsC_4Me_4)_2$ (4d)** - To a stirred solution of 2.00 g $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ (6.8 mmol) in 50 mL THF cooled to -78 °C was added 5.5 mL *n*-BuLi solution (13.7 mmol; 2.5 M in hexanes). After 30 minutes at low temperature, 1.1 mL 2-butyne (13.8 mmol) was added and the mixture allowed to warm to ambient temperature. A colour change from yellow to deep red was observed. After 3 hours, volatiles were removed under reduced pressure and the crude $[ZrC_4Me_4(\eta^5\text{-}C_5H_5)_2]$ re-dissolved in 50 mL *n*-pentane and cooled to -40 °C. To this was added 0.55 mL $AsCl_3$ (6.6 mmol. **Caution: poison and vesicant**) dropwise causing the red colour to discharge to a pale-yellow suspension. After 15 minutes the suspension was filtered through a short diatomaceous earth plug (5 x 2.5 cm) into a flask cooled to -40 °C under nitrogen, rinsing with small portions of cold *n*-pentane until the washings ran clear. The yellow filtrate was freed of volatioes under reduced pressure at -40 °C leaving $ClAsC_4Me_4$ as a waxy yellow solid, used in the next step without further purification. Crude isolated yield: 1.30 g (5.9 mmol, 89%).

A dilute sodium amalgam was prepared by slow addition of 150 mg freshly cut sodium (6.6 mmol, in *ca* 30 mg pieces. **Caution: flammable**) to *ca* 1 mL of stirred elemental mercury (**caution: toxic, exothermic dissolution**) under argon. The amalgam was then covered with 10 mL THF. The crude $ClAsC_4Me_4$ from the previous step was dissolved in 20 mL THF, of which 10 mL was withdrawn by syringe and transferred to the amalgam. The remaining THF solution of $ClAsC_4Me_4$ was cooled to -78 °C to prolong shelf-life while $Na[AsC_4Me_4]$ was being prepared. The amalgam was rapidly stirred for 90 minutes over which time the colour of the mixture changed to green, and then eventually to an orange-brown with deposition of a fine grey precipitate. The solution of $Na[AsC_4Me_4]$ was then decanted back into the flask containing the remaining $ClAsC_4Me_4$ at -78 °C and allowed to warm to ambient temperature overnight with stirring. After this time, volatiles were removed under reduced pressure and the residue extracted with *n*-hexane and eluted through a short plug of oven-dried neutral alumina (10 x 2.5 cm) under nitrogen with the same solvent. A yellow band was collected under nitrogen and taken to dryness leaving the product as a lemon-yellow solid, which was deemed sufficiently pure by NMR spectroscopy for use as is. Isolated yield: 0.64 g (1.7 mmol, 51%). The product is readily soluble in common organic solvents and is air sensitive both as a solid and solution, reverting to unidentified oily brown residues upon exposure to air.

The following data may be compared with those reported by Theopold.[10] NMR: $^1H$ ($C_6D_6$, 400 MHz, 25 °C) $\delta_H$ 1.91 (s, 6 H, α-C$H_3$), 1.72 (s, 6 H, β-C$H_3$) ppm. $^{13}C\{^1H\}$ ($C_6D_6$, 400 MHz, 25 °C) $\delta_C$ 142.9 (arsole {2,5}-*C*), 139.5 (arsole {3,4}-*C*), 15.5 (α-*C*$H_3$), 14.6 (β-*C*$H_3$) ppm. HR-MS (EI, MeCN, +ve ion) found *m/z* 366.0303 (calc. for $C_{16}H_{24}As_2$ $[M]^+$: 366.0304).

Single crystals were obtained by slow evaporation of $Et_2O$ solution at -30 °C. Data for $C_{16}H_{24}As_2$ ($M_w$ = 366.19 $gmol^{-1}$): yellow plate 0.079 × 0.161 × 0.311 mm, triclinic, space group *P*-1 (no. 2), *a* = 7.9490(3) Å, *b* = 9.1682(4) Å, *c* = 11.5715(5) Å, α = 86.399(4)°, *β* = 87.580(4)°, *γ* = 77.707(4)°, *V* = 821.99(6) $Å^3$, *Z* = 2, multi-scan correction $T_{min}/T_{max}$ = 0.795/1.000, $\mu$(Mo-Kα) = 4.048 $mm^{-1}$, $\rho_{calc}$ = 1.480 $Mgm^{-3}$, 6873 reflections measured (6.914° ≤ 2Θ ≤ 52.736°), 3349 unique ($R_{int}$ = 0.0276, $R_{sigma}$ = 0.0482) which were used in all calculations, *GOF* = 1.055, $D_{min}/D_{max}$ = -0.40/0.56 $eÅ^{-3}$. The final $R_1$ was 0.0309 ($I > 2\sigma(I)$) and $wR_2$ was 0.0662 (all data). CCDC number 2237549.

**Synthesis of $[Mn_2\{\mu\text{-}(AsC_4Me_4)_2\}(CO)_4(\eta^5\text{-}C_5H_4Me)_2]$ (8).** A dilute solution of $[Mn(THF)(CO)_2(\eta^5\text{-}C_5H_4Me)]$ was prepared by UV-photolysis of 0.20 mL $[Mn(CO)_3(\eta^5\text{-}C_5H_4Me)]$ (1.2 mmol. **Caution: toxic**) in 30 mL THF at ambient temperature. Progress is monitored by IR spectroscopy. When the conversion was deemed complete the solution was transferred to a solution of 150 mg $(AsC_4Me_4)_2$ (0.40 mmol) in 5 mL THF and allowed to stir overnight. The resulting orange solution was freed of volatiles under reduced pressure and the residue extracted with portions of petroleum ether. The combined extracts were transferred to a silica gel column (20 x 2.5 cm) made up in petroleum ether. Eluting with the same solvent provided a pale yellow band of unchanged/reformed $[Mn(CO)_3(\eta^5\text{-}C_5H_4Me)]$ which is discarded. Eluting with 9:1 petroleum ether/$Et_2O$ provided a bright orange band which was collected under a stream of nitrogen and dried in vacuo giving an orange-red solid. Isolated yield: 185 mg (0.24 mmol, 61%). No other products were obtained. The product is readily soluble in common organic solvents and is reasonably air stable in the solid state, however solutions exposed to air degrade to insoluble brown residues over several hours.

NMR: $^1H$ ($C_6D_6$, 400 MHz, 25 °C) $\delta_H$ 4.10 (s, 4 H, {2,5}-$\eta^5$-$C_5H_4CH_3$), 3.95 (s, 4 H, {3,4}-$\eta^5$-$C_5H_4CH_3$), 2.09 (s, 12 H, α-C$H_3$), 1.75 (s, 12 H, β-C$H_3$), 1.70 (s, 6 H, $\eta^5$-$C_5H_4CH_3$) ppm. $^{13}C\{^1H\}$ ($C_6D_6$, 176 MHz, 25 °C) $\delta_C$ 232.4 (*C*O), 143.5 (arsole {2,5}-*C*), 139.7 (arsole {3,4}-*C*), 97.3 ({1}-$\eta^5$-$C_5H_4(CH_3)$), 80.1 ({2,5}-$\eta^5$-$C_5H_4(CH_3)$), 79.4 ({3,4}-$\eta^5$-$C_5H_4(CH_3)$), 15.4 (α-C$H_3$), 14.5 (β-C$H_3$), 13.7 ($\eta^5$-$C_5H_4$(C$H_3$)) ppm. IR ($CH_2Cl_2$) $\nu_{CO}$ 1921(vs), 1864(vs) $cm^{-1}$. IR (*n*-hexane) $\nu_{CO}$ 1941(s), 1930(vs), 1877(vs) $cm^{-1}$. HR-MS (ESI, MeCN, +ve ion) found *m/z* 745.9956 (calc. for $C_{32}H_{38}O_4{}^{55}Mn_2{}^{75}As_2$ $[M]^+$: 745.9963). Analysis found 51.61% C, 5.16% H; calc. for $C_{32}H_{38}O_4Mn_2As_2$: 51.50% C, 5.13% H.

Single crystals were obtained from slow evaporation of an NMR solution in $C_6D_6$. $C_{32}H_{38}O_4As_2Mn_2$ ($M_w$ = 746.34 $gmol^{-1}$): orange prism 0.111 × 0.239 × 0.289 mm, monoclinic, space

group *Cc* (no. 9), $a$ = 15.1023(3) Å, $b$ = 10.6207(2) Å, $c$ = 19.3216(5) Å, $\beta$ = 99.683(2)°, $V$ = 3054.97(12) Å$^3$, $Z$ = 4, multi-scan correction $T_{min}/T_{max}$ = 0.830/1.000, $\mu$(Mo-Kα) = 3.012 mm$^{-1}$, $\rho_{calc}$ = 1.623 Mgm$^{-3}$, 32377 reflections measured (6.668° ≤ 2Θ ≤ 65.13°), 9848 unique ($R_{int}$ = 0.0247, $R_{sigma}$ = 0.0281) which were used in all calculations, *GOF* = 1.045, $D_{min}/D_{max}$ = -0.39/0.69 e/Å$^3$. The final $R_1$ was 0.0240 ($I > 2\sigma(I)$) and $wR_2$ was 0.0562 (all data). CCDC number 2239173.

**Crystal Structure Determination of $(AsC_4H_2Ph_2\text{-}2,5)_2$ (4c)** – Crystals were grown by slow evaporation of a chloroform solution at room temperature. $C_{16}H_{12}As_2$ ($M_w$ = 279.18 gmol$^{-1}$): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 21.2484(13) Å, $b$ = 7.16710(10) Å, $c$ = 12.0812(7) Å, β = 140.098(12)°, $V$ = 1180.2(2) Å$^3$, $Z$ = 4, Gaussian correction $T_{min}/T_{max}$ = 0.530/1.000, yellow prism 0.165 x 0.091 x 0.062 mm, $\mu$(Cu Kα) = 2.259 mm$^{-1}$, $\rho_{calc}$ = 1.571 Mgm$^{-3}$, 11117 reflections measured (12.99° ≤ 2Θ ≤ 147.30°), 2383 unique ($R_{int}$ = 0.02204, $R_{sigma}$ = 0.0155) which were used in all calculations, *GOF* = 1.105, $D_{min}/D_{max}$ = -1.97/1.37 eÅ$^{-3}$. The final $R_1$ was 0.0226 ($I > 2\sigma(I)$) and $wR_2$ was 0.0584 (all data) for 154 refined parameters without retraints. CCDC number 2236821.

**Crystal Structure Determination of $(AsC_4Ph_4)_2$ (4g)** - Crystals were grown by evaporation of $CH_2Cl_2$/petroleum ether solution. $C_{56}H_{40}As_2$ ($M_w$ = 862.72 gmol$^{-1}$): triclinic, space group *P*-1 (no. 2), $a$ = 10.03710(10) Å, $b$ = 12.67500(10) Å, $c$ = 17.32020(10) Å, α = 89.7530(10)°, β = 88.1950(10)°, γ = 71.8550(10)°, $V$ = 2092.83(3) Å$^3$, $Z$ = 2, spherical correction $T_{min}/T_{max}$ = 0.819/1.000 , $\mu$(Cu Kα) = 2.259 mm$^{-1}$, $\rho_{calc}$ = 1.369 Mgm$^{-3}$, 80145 reflections measured (7.34° ≤ 2Θ ≤ 156.164°), 8843 unique ($R_{int}$ = 0.0356, $R_{sigma}$ = 0.0178) which were used in all calculations, *GOF* = 1.043, $D_{min}/D_{max}$ = -0.5/1.2 eÅ$^{-3}$. The final $R_1$ was 0.0316 ($I > 2\sigma(I)$) and $wR_2$ was 0.0831 (all data). CCDC number 2244816.

## Notes and references


1 *CrysAlis PRO*, Agilent Technologies Ltd, Yarnton, Oxfordshire, England, 2014.

2 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallog.*, **2009**, *42*, 339-341.

3 (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2015, 71, 3.

4 (a) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457. (b) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.

5 *Spartan 20*® (2020) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.

6 J. D. Chai and M. Head-Gordon, *J Chem Phys.*, 2008, **128**, 084106.

7 J. D. Chai and M. Head-Gordon, *Phys Chem Chem Phys*, 2008, **10**, 6615-6620.

8 (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283. (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299-310. (c) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284-298.

9 W. J. Hehre, R. Ditchfeld and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.

10 S. C. Sendlinger, B. S. Haggerty, A. L. Rheingold and K. H. Theopold, *Chem Ber.*, 1991, **124**, 2453-2456.

11 G. Märkl and H. Hauptmann, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 439-440.


## Computational Results

### 1. *syn*-$[Mn_2\{\mu\text{-}(AsC_4H_4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$

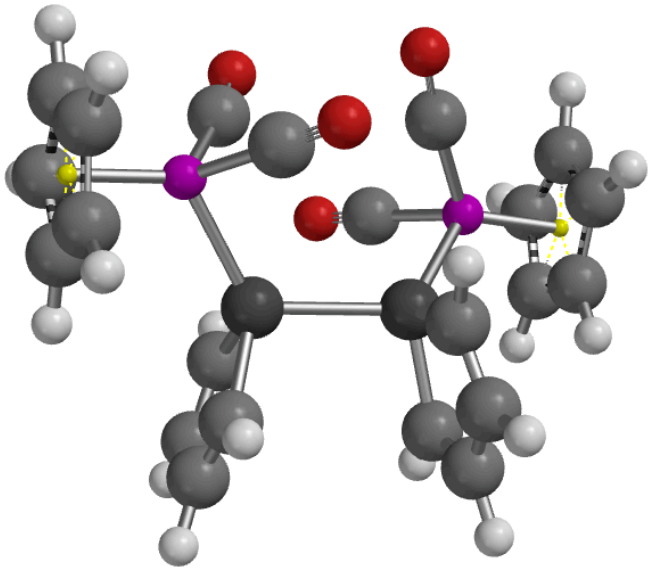


**Figure S1.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

**Thermodynamic Properties at 298.15 K**

| | | | |
|---|---|---|---|
| Zero Point Energy : | 855.04 | kJ/mol | (ZPE) |
| Temperature Correction : | 68.16 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 923.21 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -7922.486760 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 675.17 | J/mol•K | |
| Gibbs Energy : | -7922.563432 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 497.37 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| Mn | -2.508871 | -0.287022 | 1.098676 |
| As | -1.161013 | 0.361740 | -0.649888 |
| As | 1.160383 | -0.359422 | -0.650003 |
| Mn | 2.509109 | 0.287417 | 1.098638 |
| C | 0.953510 | -2.203982 | -1.179246 |
| H | 0.626160 | -2.993209 | -0.513432 |
| C | 1.694912 | 0.009942 | -2.464254 |
| H | 1.941561 | 0.995407 | -2.839861 |
| C | 1.340883 | -2.355752 | -2.456508 |
| H | 1.359372 | -3.317796 | -2.962416 |
| C | 1.746022 | -1.132001 | -3.168394 |
| H | 2.055601 | -1.177654 | -4.209488 |
| C | -1.695554 | -0.007023 | -2.464171 |
| H | -1.942568 | -0.992269 | -2.840144 |
| C | -0.954258 | 2.206453 | -1.178196 |
| H | -0.626974 | 2.995286 | -0.511879 |
| C | -1.340994 | 2.358367 | -2.455647 |
| H | -1.359295 | 3.320638 | -2.961085 |
| C | -1.746227 | 1.134993 | -3.168180 |
| H | -2.055813 | 1.181157 | -4.209225 |
| H | -4.344929 | 0.082481 | 3.272828 |
| C | -4.295897 | -0.033662 | 2.199046 |
| C | -4.342061 | -1.258055 | 1.490537 |
| H | -4.137365 | 2.081111 | 1.462079 |
| H | -4.428246 | -2.241695 | 1.931918 |
| C | -4.260113 | -0.974796 | 0.095195 |
| H | -4.289445 | -1.696345 | -0.709011 |
| C | -4.170979 | 0.437226 | -0.045274 |
| H | -4.093157 | 0.973436 | -0.982843 |
| C | -4.188498 | 1.023949 | 1.242105 |
| H | 4.433046 | 2.238492 | 1.928800 |
| C | 4.344901 | 1.254656 | 1.488096 |
| C | 4.261754 | 0.969027 | 0.093293 |
| H | 4.345216 | -0.081889 | 3.272810 |
| H | 4.292558 | 1.690375 | -0.711050 |
| C | 4.169075 | -0.443101 | -0.044662 |
| H | 4.090068 | -0.981542 | -0.980815 |
| C | 4.185652 | -1.027523 | 1.243704 |
| H | 4.132376 | -2.084293 | 1.464848 |
| C | 4.296045 | 0.031520 | 2.198727 |
| C | 1.645707 | 1.820714 | 1.313590 |
| O | 1.153835 | 2.862826 | 1.442953 |
| C | 1.575125 | -0.577021 | 2.343775 |
| O | 1.089731 | -1.165124 | 3.212763 |
| C | -1.576794 | 0.581128 | 2.342695 |
| O | -1.091997 | 1.171132 | 3.210715 |
| C | -1.642376 | -1.818425 | 1.314794 |
| O | -1.149177 | -2.859873 | 1.444544 |

## 2. *anti*-[$Mn_2\{\mu$-$(AsC_4H_4)_2\}(CO)_4(\eta$-$C_5H_5)_2$]

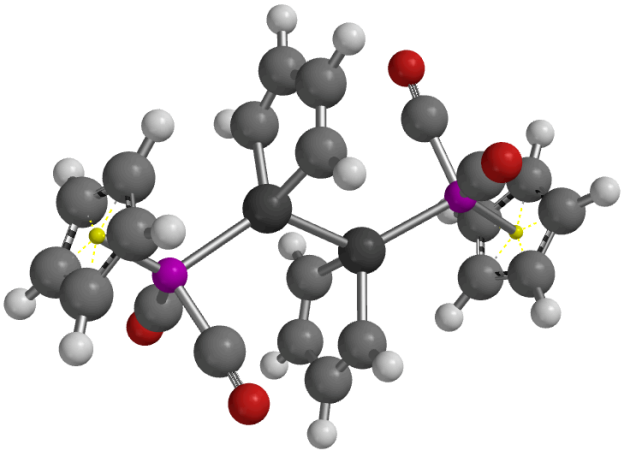


**Figure S2.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 855.47 | kJ/mol | (ZPE) |
| Temperature Correction : | 68.23 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 923.70 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -7922.487889 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 676.34 | J/mol•K | |
| Gibbs Energy : | -7922.564694 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 497.26 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| Mn | 0.497223 | -0.071717 | -3.126273 |
| As | -0.545571 | 0.163176 | -1.082172 |
| As | 0.553779 | -0.031246 | 1.088215 |
| Mn | -0.527805 | -0.247960 | 3.114671 |
| C | 1.941519 | -1.273480 | 0.587728 |
| H | 1.810317 | -2.345665 | 0.507033 |
| C | 1.848814 | 1.373441 | 0.826121 |
| H | 1.641841 | 2.428823 | 0.957228 |
| C | 3.087876 | -0.614035 | 0.351452 |
| H | 4.008869 | -1.110321 | 0.057965 |
| C | 3.038209 | 0.849680 | 0.487409 |
| H | 3.921849 | 1.451478 | 0.295416 |
| C | -1.586622 | 1.736955 | -0.684519 |
| H | -1.203114 | 2.749817 | -0.715195 |
| C | -2.127522 | -0.866792 | -0.687826 |
| H | -2.179952 | -1.948505 | -0.709689 |
| C | -3.148082 | -0.047734 | -0.383676 |
| H | -4.142533 | -0.406141 | -0.131872 |
| C | -2.849824 | 1.392352 | -0.384712 |
| H | -3.620029 | 2.114700 | -0.130120 |
| H | 1.378726 | 1.065859 | -5.606795 |
| C | 0.525278 | 0.606833 | -5.126766 |
| C | -0.509487 | 1.295490 | -4.422613 |
| H | 0.821666 | -1.560184 | -5.555266 |
| H | -0.585816 | 2.363877 | -4.278225 |
| C | -1.436010 | 0.322544 | -3.970341 |
| H | -2.333698 | 0.524632 | -3.398872 |
| C | -0.986453 | -0.959508 | -4.377247 |
| H | -1.485656 | -1.900177 | -4.191964 |
| C | 0.231355 | -0.776835 | -5.099801 |
| H | 2.364502 | -0.238036 | 3.403632 |
| C | 1.441279 | -0.314997 | 3.964760 |
| C | 0.751084 | -1.519292 | 4.257602 |
| H | 0.998683 | 1.814476 | 4.471451 |
| H | 1.061997 | -2.516080 | 3.978347 |
| C | -0.412066 | -1.174024 | 5.010481 |
| H | -1.145182 | -1.866887 | 5.400410 |
| C | -0.433596 | 0.231834 | 5.169241 |
| H | -1.186520 | 0.798156 | 5.700332 |
| C | 0.717666 | 0.771869 | 4.518035 |
| C | -1.661741 | 1.093961 | 2.851227 |
| O | -2.386249 | 1.997229 | 2.810185 |
| C | -1.660023 | -1.498049 | 2.560368 |
| O | -2.391156 | -2.359451 | 2.302989 |
| C | 1.342728 | -1.566705 | -2.683668 |
| O | 1.881957 | -2.574954 | -2.493903 |
| C | 1.880810 | 0.976205 | -2.753903 |
| O | 2.784649 | 1.693084 | -2.644814 |

### Calculated Infrared Absorptions ($\nu_{CO}$/cm$^{-1}$)[a]

| | $\nu_{CO}$ | Intensity |
|---|---|---|
| 1 | 1934 | 152 |
| 2 | 1937 | 1463 |
| 3 | 1976 | 1086 |
| 4 | 1978 | 172 |

[a]Scaling factor = 0.9420; DFT: ωB97X-D/6-31G*/gas phase

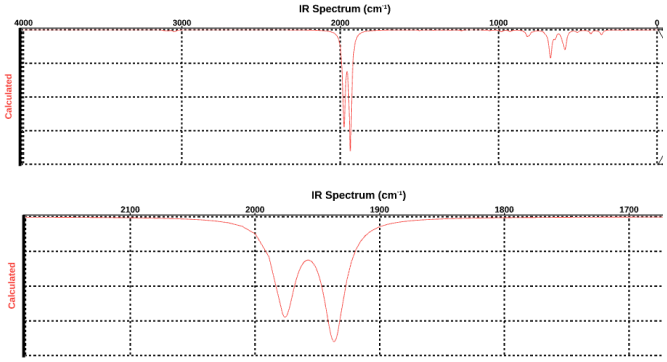



**Figure S3.** Calculated IR spectrum (carbonyl region) (wB97X-D/6-31G*/Gas Phase)

A band at 258 cm$^{-1}$ corresponds primarily to the $\nu_{As-As}$ stretch with negligible IR intensity.

## 3. *anti*-[Mn$_2${μ-(AsC$_4$Me$_4$)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$]

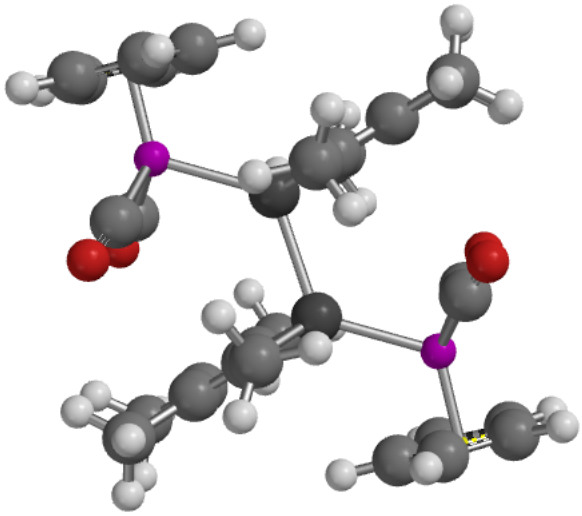


**Figure S4.** Optimised Geometry (wB97X-D/6-311+G(2df,2p)/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 1418.51 | kJ/mol | (ZPE) |
| Temperature Correction : | 96.89 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 1515.40 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -8236.751354 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 855.36 | J/mol•K | |
| Gibbs Energy : | -8236.848488 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 695.56 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| Mn | 0.543779 | 0.094803 | -3.134886 |
| As | -0.562208 | 0.103937 | -1.074604 |
| As | 0.563386 | -0.083483 | 1.079139 |
| Mn | -0.540552 | -0.075460 | 3.140211 |
| C | 1.769271 | -1.524439 | 0.674790 |
| C | 2.011169 | 1.145834 | 0.781386 |
| C | 2.984150 | -1.022078 | 0.405412 |
| C | 3.118573 | 0.456077 | 0.465838 |
| C | -1.771029 | 1.543365 | -0.670950 |
| C | -2.008860 | -1.127118 | -0.780996 |
| C | -3.118150 | -0.439125 | -0.469062 |
| C | -2.986170 | 1.039243 | -0.405441 |
| H | 1.245359 | 1.538223 | -5.514526 |
| C | 0.466076 | 0.928663 | -5.088404 |
| C | -0.653801 | 1.400770 | -4.346150 |
| H | 1.073127 | -1.124372 | -5.680357 |
| H | -0.881748 | 2.427391 | -4.116418 |
| C | -1.429399 | 0.274340 | -3.986384 |
| H | -2.343275 | 0.298444 | -3.414065 |
| C | -0.802895 | -0.887869 | -4.489387 |
| H | -1.161303 | -1.897738 | -4.384426 |
| C | 0.376032 | -0.476430 | -5.176336 |
| H | 2.345966 | -0.288176 | 3.414566 |
| C | 1.432838 | -0.265649 | 3.988263 |
| C | 0.654343 | -1.391804 | 4.342938 |
| H | 1.172457 | 1.904425 | 4.397944 |
| H | 0.878050 | -2.418134 | 4.107169 |
| C | -0.463110 | -0.920606 | 5.089242 |
| H | -1.243441 | -1.530361 | 5.512493 |
| C | -0.368987 | 0.483702 | 5.184578 |
| H | -1.063735 | 1.129836 | 5.693850 |
| C | 0.810286 | 0.895465 | 4.498314 |
| C | -1.553446 | 1.350713 | 2.788641 |
| O | -2.200183 | 2.293723 | 2.662795 |
| C | -1.805660 | -1.240722 | 2.667180 |
| O | -2.621741 | -2.026203 | 2.466091 |
| C | 1.566290 | -1.323375 | -2.778652 |
| O | 2.221431 | -2.260073 | -2.650027 |
| C | 1.800588 | 1.269319 | -2.663647 |
| O | 2.609836 | 2.061728 | -2.462541 |
| C | 1.855532 | 2.626229 | 0.917415 |
| H | 1.706917 | 3.099425 | -0.055686 |
| H | 2.736506 | 3.083378 | 1.369180 |
| H | 0.998019 | 2.876126 | 1.542983 |
| C | 4.442890 | 1.087197 | 0.160121 |
| H | 5.228633 | 0.699958 | 0.811264 |
| H | 4.409766 | 2.167866 | 0.265887 |
| H | 4.736569 | 0.869611 | -0.868569 |
| C | 4.174267 | -1.855318 | 0.037004 |
| H | 4.529827 | -1.588786 | -0.959830 |
| H | 3.934347 | -2.915361 | 0.022850 |
| H | 5.002335 | -1.697124 | 0.730644 |
| C | 1.350972 | -2.959881 | 0.695259 |
| H | 2.119884 | -3.596620 | 1.134728 |
| H | 1.159083 | -3.330995 | -0.313548 |
| H | 0.440009 | -3.095529 | 1.279046 |
| C | -1.351060 | 2.977826 | -0.685556 |
| H | -0.464943 | 3.120798 | -1.304152 |
| H | -1.115197 | 3.332013 | 0.319966 |
| H | -2.136282 | 3.622851 | -1.080934 |
| C | -4.178594 | 1.868513 | -0.036232 |
| H | -4.512795 | 1.620948 | 0.973111 |
| H | -5.017424 | 1.683850 | -0.709751 |
| H | -3.952712 | 2.931151 | -0.050848 |
| C | -4.444052 | -1.073602 | -0.175915 |
| H | -4.397603 | -2.156525 | -0.254472 |
| H | -5.218000 | -0.710300 | -0.854543 |
| H | -4.764849 | -0.833419 | 0.839195 |
| C | -1.854050 | -2.607502 | -0.921547 |
| H | -1.738142 | -3.087199 | 0.052721 |
| H | -0.978331 | -2.856752 | -1.521332 |
| H | -2.721984 | -3.058549 | -1.404320 |

### Calculated Infrared Absorptions ($\nu_{CO}$/cm$^{-1}$)[a]

| $\nu_{CO}$ | Intensity |
|---|---|
| 1913 | 26 |
| 1917 | 1494 |
| 1959 | 1039 |
| 1961 | 208 |

[a]Scaling factor = 0.9420; DFT: ωB97X-D/6-31G*/gas phase

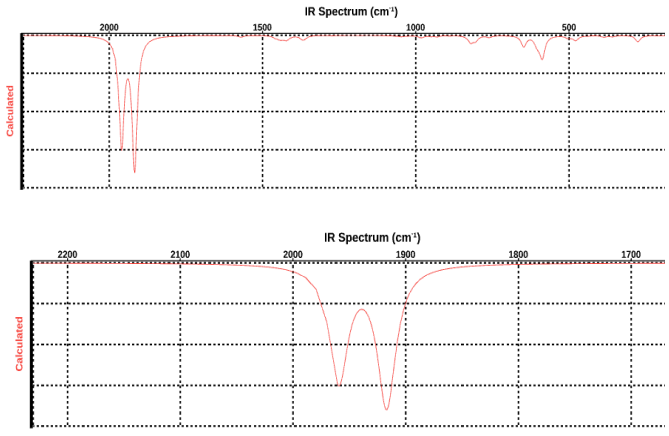



**Figure S5.** Calculated IR spectrum (carbonyl region) (ωB97X-D/6-311+G(2df,2p)/Gas Phase)

A band at 247 cm$^{-1}$ corresponds primarily to the $\nu_{As-As}$ stretch with negligible IR intensity.

Comparison of calculated data for parent and permethylated biarsolyl complexes $[Mn_2\{\mu\text{-}(AsC_4R_4)_2\}(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (R = H, Me, ωB97X-D, 6-31G*)

| Parameter[a] | R = H 6-31G* | R = Me 6-31G* |
|---|---|---|
| Mn–As [Å] | 2.308 | 2.310 |
| As–As [Å] | 2.441 | 2.428 |
| As–$C_\alpha$[a] [Å] | 1.928 | 1.924 |
| $C_\alpha$-$C_\beta$ [Å] | 1.344 | 1.349 |
| $C_\beta$-$C_{\beta'}$ [Å] | 1.470 | 1.488 |
| $C_\alpha$–As–$C_\alpha$ [°] | 87.2 | 88.7 |
| Natural Charge (Mn) | 0.721 | 0.718 |
| Natural Charge (As) | 0.704 | 0.765 |
| Natural Charge ($C_\alpha$) | –0.581 | –0.368 |
| Natural Charge ($C_\beta$) | –0.244 | –0.028 |
| Löwden BO (Mn–As) | 0.98 | 0.97 |
| Löwden BO (As–As) | 0.84 | 0.85 |
| Löwden BO (As–$C_\alpha$) | 0.99 | 0.95 |
| Löwden BO ($C_\alpha$-$C_\beta$) | 1.89 | 1.77 |
| Löwden BO ($C_\beta$-$C_{\beta'}$) | 1.15 | 1.07 |
| LUMO (eV) | –0.34 | 0.19 |
| HOMO (eV) | –7.54 | –7.42 |

[a]Mean values where appropriate.

The only significant geometrical variation upon permethylation involves a contraction (0.013 Å) of the As–As bond which is not however reflected in the negligible change (0.01) in the Mn–As and As–As bond orders.

## 4. *anti*-$(AsC_4Me_4)_2$ – *anti*-4d

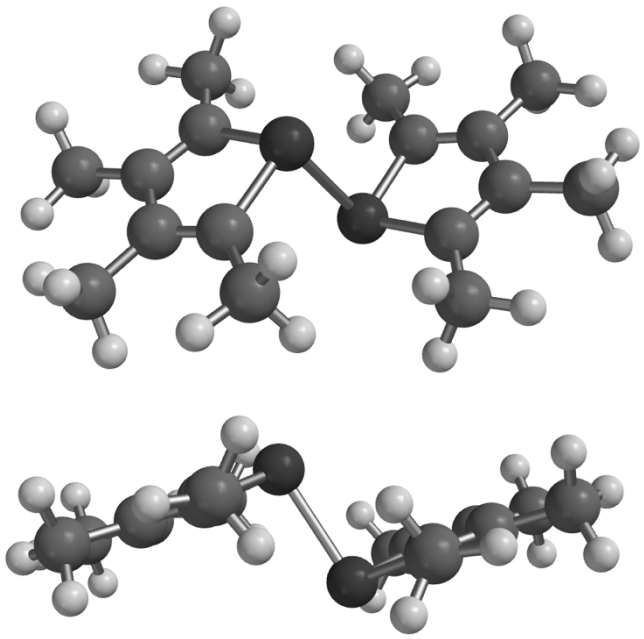


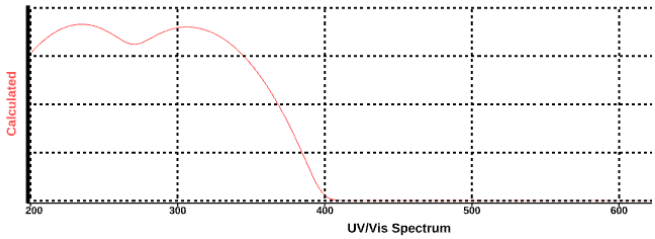
**Figure S6.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 891.38 | kJ/mol | (ZPE) |
| Temperature Correction : | 55.72 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 947.10 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -5094.909823 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 593.01 | J/mol•K | |
| Gibbs Energy : | -5094.977164 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 367.63 | J/mol•K | |

### Allowed Electronic Transitions

| nm ▼ | strength | MO Component | |
|---|---|---|---|
| 227.14 | 0.0021 | HOMO-1 -> LUMO+2 | 58% |
| | | HOMO-2 -> LUMO+1 | 14% |
| 234.90 | 0.3062 | HOMO-3 -> LUMO | 82% |
| 239.55 | 0.0002 | HOMO-4 -> LUMO | 74% |
| 299.66 | 0.1548 | HOMO-2 -> LUMO | 88% |
| 314.64 | 0.0952 | HOMO-1 -> LUMO | 92% |
| 316.46 | 0.0316 | HOMO -> LUMO | 94% |



**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| As | 0.677282 | 1.115309 | 0.051718 |
| As | -0.887022 | -0.715214 | 0.571587 |
| C | -0.166547 | -1.006494 | 2.350992 |
| C | 0.216924 | -2.195957 | -0.002524 |
| C | 0.500505 | 1.074801 | -1.874449 |
| C | -0.718197 | 2.465723 | 0.043657 |
| C | 0.848563 | -2.751960 | 1.055993 |
| C | 0.650129 | -2.084487 | 2.361913 |
| C | -0.382095 | 2.011749 | -2.287939 |
| C | -1.074012 | 2.773225 | -1.224544 |
| C | 1.382721 | 0.226426 | -2.749987 |
| H | 2.152120 | 0.830296 | -3.247788 |
| H | 0.811473 | -0.285689 | -3.533170 |
| H | 1.900217 | -0.542634 | -2.169204 |
| C | 0.188269 | -2.730433 | -1.409231 |
| H | 1.196045 | -2.921326 | -1.796279 |
| H | -0.295051 | -2.027403 | -2.093392 |
| H | -0.370268 | -3.673426 | -1.466502 |
| C | -1.265118 | 3.025902 | 1.324109 |
| H | -0.459404 | 3.359604 | 1.988377 |
| H | -1.837467 | 2.266003 | 1.872746 |
| H | -1.931574 | 3.877923 | 1.160720 |
| C | -0.532191 | -0.102949 | 3.492255 |
| H | -0.164537 | -0.468537 | 4.455731 |
| H | -1.619213 | 0.013011 | 3.575526 |
| H | -0.114148 | 0.902127 | 3.346465 |
| C | -0.664119 | 2.316912 | -3.734540 |
| H | -0.388153 | 3.349264 | -3.982821 |
| H | -1.730878 | 2.207796 | -3.963960 |
| H | -0.107651 | 1.655825 | -4.403114 |
| C | -2.109554 | 3.794632 | -1.614060 |
| H | -2.515737 | 4.322668 | -0.749223 |
| H | -2.950282 | 3.318362 | -2.133747 |
| H | -1.693672 | 4.543381 | -2.298397 |
| C | 1.692949 | -3.994856 | 0.969991 |
| H | 1.772704 | -4.359070 | -0.056911 |
| H | 1.268624 | -4.804405 | 1.576658 |
| H | 2.708417 | -3.815438 | 1.342839 |
| C | 1.357692 | -2.629330 | 3.574373 |
| H | 1.104691 | -3.683117 | 3.740916 |
| H | 1.101352 | -2.081808 | 4.483167 |
| H | 2.446211 | -2.576409 | 3.452050 |

## 5. *gauche*-($AsC_4Me_4$)$_2$ – *gauche*-4d

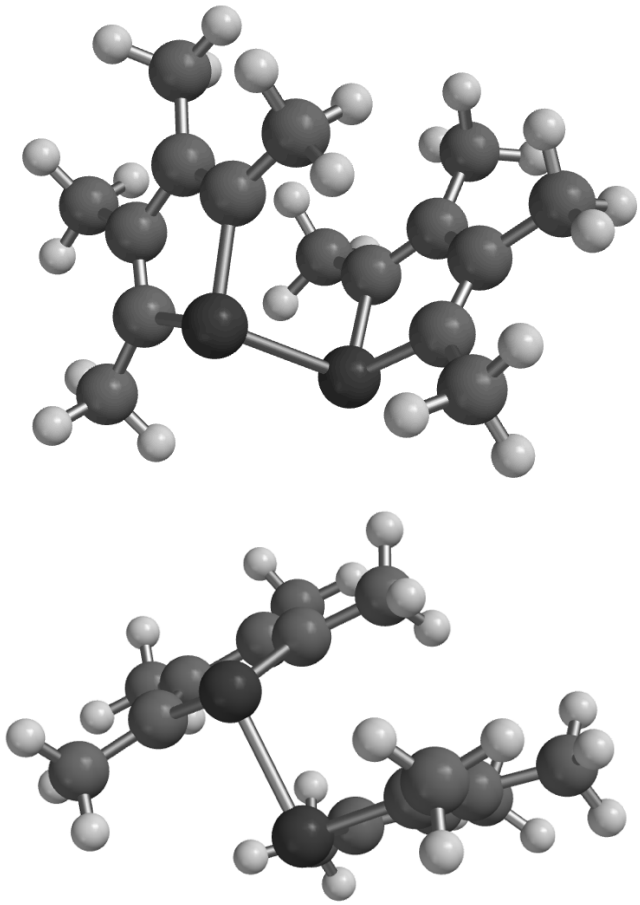


**Figure S7.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

**Thermodynamic Properties at 298.15 K**

| | | | |
|---|---|---|---|
| Zero Point Energy : | 891.77 | kJ/mol | (ZPE) |
| Temperature Correction : | 55.74 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 947.51 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -5094.916203 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 591.39 | J/mol•K | |
| Gibbs Energy : | -5094.983360 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 367.20 | J/mol•K | |

**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| As | 0.790385 | 2.044806 | -0.678101 |
| C | 1.239354 | 2.196565 | 1.202773 |
| C | 0.173551 | 1.858547 | 1.963778 |
| C | -1.016139 | 1.374000 | 1.228795 |
| C | -0.908742 | 1.323900 | -0.117434 |
| As | 2.046325 | -0.041319 | -1.041004 |
| C | 1.015421 | -1.251258 | 0.051526 |
| C | 0.170671 | -1.972878 | -0.717662 |
| C | 0.147313 | -1.636206 | -2.159002 |
| C | 0.972965 | -0.636628 | -2.543924 |
| C | -1.953579 | 0.829417 | -1.077552 |
| H | -2.142156 | -0.240967 | -0.924985 |
| H | -1.637761 | 0.950926 | -2.117042 |
| H | -2.907166 | 1.357527 | -0.954423 |
| C | 2.577063 | 2.709099 | 1.650328 |
| H | 2.765353 | 2.512968 | 2.710496 |
| H | 2.663137 | 3.791465 | 1.492917 |
| H | 3.389484 | 2.239843 | 1.082523 |
| C | 0.128474 | 1.921544 | 3.467116 |
| H | -0.111979 | 0.941137 | 3.896241 |
| H | -0.646449 | 2.618030 | 3.810034 |
| H | 1.077232 | 2.249592 | 3.896136 |
| C | -2.239374 | 0.930119 | 1.985981 |
| H | -2.614133 | 1.718931 | 2.649082 |
| H | -2.019387 | 0.060662 | 2.619006 |
| H | -3.050211 | 0.647751 | 1.310297 |
| C | 1.162627 | -0.058780 | -3.915596 |
| H | 2.136665 | -0.339032 | -4.334976 |
| H | 1.133249 | 1.037550 | -3.888189 |
| H | 0.391290 | -0.387709 | -4.618558 |
| C | 1.194231 | -1.374613 | 1.538617 |
| H | 1.462211 | -2.395808 | 1.836424 |
| H | 1.974449 | -0.704294 | 1.908441 |
| H | 0.268859 | -1.104719 | 2.063480 |
| C | -0.789932 | -2.385240 | -3.068711 |
| H | -0.622493 | -3.466843 | -3.006730 |
| H | -0.672736 | -2.094815 | -4.114554 |
| H | -1.836140 | -2.207095 | -2.789276 |
| C | -0.742604 | -3.040998 | -0.178009 |
| H | -0.642085 | -3.146228 | 0.904723 |
| H | -0.533462 | -4.018365 | -0.630086 |
| H | -1.793781 | -2.810584 | -0.392900 |

## 6. *gauche*-($AsC_4H_2Me_2$-2,5)$_2$ – *gauche*-4b

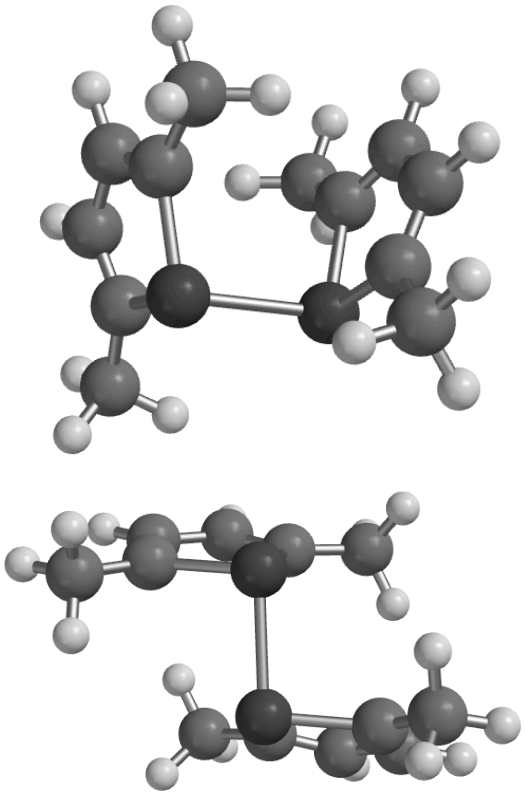


**Figure S8.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

**Thermodynamic Properties at 298.15 K**

| | | | |
|---|---|---|---|
| Zero Point Energy : | 610.85 | kJ/mol | (ZPE) |
| Temperature Correction : | 41.57 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 652.42 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4937.798462 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 501.11 | J/mol•K | |
| Gibbs Energy : | -4937.855368 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 267.78 | J/mol•K | |

**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| As | 0.997868 | 1.068981 | 0.923865 |
| As | -0.376094 | -0.897223 | 1.430840 |
| C | 0.942059 | -2.224501 | 0.894307 |
| C | -1.255927 | -1.220523 | -0.271583 |
| C | 0.913979 | 1.125445 | -1.017681 |
| C | -0.455161 | 2.361133 | 0.930274 |
| C | -0.644583 | -2.244556 | -0.899718 |
| H | -1.007116 | -2.646279 | -1.844577 |
| C | 0.548521 | -2.795076 | -0.262555 |
| H | 1.093306 | -3.620535 | -0.719004 |
| C | 0.045902 | 2.085647 | -1.394742 |
| H | -0.112424 | 2.346943 | -2.439910 |
| C | -0.705462 | 2.753524 | -0.335289 |
| H | -1.434489 | 3.527411 | -0.571778 |
| C | 1.777355 | 0.293642 | -1.911725 |
| H | 2.842213 | 0.451348 | -1.703335 |
| H | 1.597088 | 0.537098 | -2.964584 |
| H | 1.573752 | -0.773409 | -1.764451 |
| C | -2.471393 | -0.482535 | -0.734761 |
| H | -2.825443 | -0.876998 | -1.693710 |
| H | -2.254526 | 0.584564 | -0.860323 |
| H | -3.290883 | -0.562738 | -0.010834 |
| C | -1.111223 | 2.883859 | 2.171098 |
| H | -0.386922 | 3.367797 | 2.836760 |
| H | -1.582222 | 2.075874 | 2.744797 |
| H | -1.886241 | 3.617550 | 1.923843 |
| C | 2.130444 | -2.609316 | 1.720746 |
| H | 2.711390 | -3.395796 | 1.226878 |
| H | 1.831222 | -2.978769 | 2.708701 |
| H | 2.795011 | -1.752560 | 1.888453 |

## 7. *anti*-($AsC_4H_2Me_2$-2,5)$_2$ – *anti*-4b

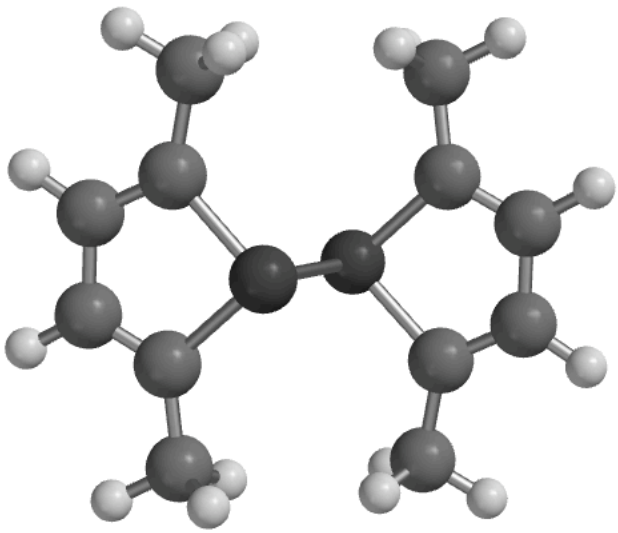


**Figure S9.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

**Thermodynamic Properties at 298.15 K**

| | | | |
|---|---|---|---|
| Zero Point Energy : | 611.43 | kJ/mol | (ZPE) |
| Temperature Correction : | 41.63 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 653.07 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4937.791689 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 500.84 | J/mol•K | |
| Gibbs Energy : | -4937.848564 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 267.41 | J/mol•K | |

**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| As | 0.759888 | 0.927283 | -0.258763 |
| As | -0.771268 | -0.919954 | 0.278745 |
| C | -0.296046 | -1.049562 | 2.168435 |
| C | 0.490877 | -2.378456 | -0.022591 |
| C | 0.327740 | 1.058587 | -2.158234 |
| C | -0.523261 | 2.373304 | 0.016707 |
| C | 0.947540 | -2.828652 | 1.162962 |
| H | 1.600088 | -3.697102 | 1.242724 |
| C | 0.524073 | -2.102978 | 2.352973 |
| H | 0.856090 | -2.414219 | 3.342548 |
| C | -0.489986 | 2.110519 | -2.360587 |
| H | -0.796397 | 2.425533 | -3.357223 |
| C | -0.955109 | 2.823127 | -1.178174 |
| H | -1.618492 | 3.681993 | -1.270467 |
| C | 0.912284 | 0.195487 | -3.235932 |
| H | 0.746046 | 0.642109 | -4.222613 |
| H | 0.454174 | -0.800720 | -3.244684 |
| H | 1.991206 | 0.055035 | -3.106072 |
| C | 0.803029 | -2.987123 | -1.356812 |
| H | 1.314925 | -3.948151 | -1.234020 |
| H | 1.459259 | -2.339056 | -1.949418 |
| H | -0.102543 | -3.160095 | -1.949246 |
| C | -0.893069 | 2.959694 | 1.346075 |
| H | -0.011481 | 3.156906 | 1.966620 |
| H | -1.544524 | 2.284852 | 1.913743 |
| H | -1.432208 | 3.904494 | 1.215358 |
| C | -0.834133 | -0.169398 | 3.256275 |
| H | -0.626252 | -0.600845 | 4.241663 |
| H | -1.917528 | -0.028546 | 3.170619 |
| H | -0.374923 | 0.825933 | 3.229387 |

## 8. *anti*-($AsC_4H_2Ph_2$-2,5)$_2$ – *anti*-4c

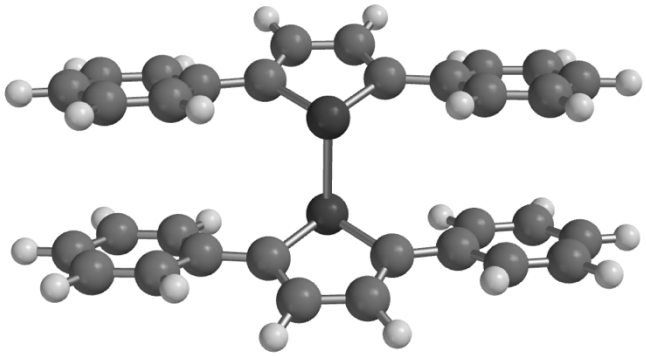


**Figure S10.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| As | 0.859755 | 0.877344 | 0.019662 |
| C | 1.981349 | 0.036574 | 1.380557 |
| C | 2.033469 | 0.042262 | -1.299666 |
| C | 3.051705 | -0.586565 | -0.663574 |
| H | 3.888382 | -1.031596 | -1.197645 |
| C | 3.023782 | -0.589180 | 0.781506 |
| H | 3.840304 | -1.034661 | 1.345555 |
| C | 1.807404 | 0.184046 | 2.832031 |
| C | 1.914762 | 0.193043 | -2.756208 |
| C | 1.251871 | 1.288484 | -3.323803 |
| H | 0.788324 | 2.029228 | -2.677816 |
| C | 2.353034 | -0.760222 | 3.714309 |
| H | 2.851470 | -1.638770 | 3.315153 |
| C | 2.488335 | -0.752361 | -3.619370 |
| H | 2.967090 | -1.634088 | -3.203424 |
| C | 1.118295 | 1.274990 | 3.376627 |
| H | 0.675624 | 2.014958 | 2.715303 |
| C | 1.002037 | 1.431453 | 4.751723 |
| H | 0.455291 | 2.280674 | 5.149206 |
| C | 2.433041 | -0.587072 | -4.996866 |
| H | 2.886844 | -1.330564 | -5.645904 |
| C | 1.187988 | 1.448072 | -4.701972 |
| H | 0.661536 | 2.301148 | -5.118201 |
| C | 1.573454 | 0.502096 | 5.614827 |
| H | 1.479863 | 0.624406 | 6.689598 |
| C | 1.786044 | 0.517012 | -5.545029 |
| H | 1.732385 | 0.641456 | -6.622298 |
| C | 2.246009 | -0.597675 | 5.089117 |
| H | 2.679044 | -1.340029 | 5.753500 |
| As | -0.860444 | -0.877936 | -0.020411 |
| C | -1.982719 | -0.036775 | -1.380492 |
| C | -2.033572 | -0.043534 | 1.299817 |
| C | -3.052341 | 0.585126 | 0.664357 |
| H | -3.889059 | 1.029105 | 1.199244 |
| C | -3.025085 | 0.588383 | -0.780716 |
| H | -3.841627 | 1.034362 | -1.344361 |
| C | -1.808967 | -0.182619 | -2.832183 |
| C | -1.914364 | -0.195204 | 2.756227 |
| C | -1.249104 | -1.289645 | 3.323010 |
| H | -0.784432 | -2.029261 | 2.676543 |
| C | -2.353720 | 0.763166 | -3.713441 |
| H | -2.852223 | 1.641316 | -3.313541 |
| C | -2.489000 | 0.748772 | 3.620221 |
| H | -2.970740 | 1.629541 | 3.205669 |
| C | -1.120682 | -1.273587 | -3.378018 |
| H | -0.677482 | -2.013792 | -2.717284 |
| C | -1.004797 | -1.428677 | -4.753392 |
| H | -0.457974 | -2.277433 | -5.151785 |
| C | -2.431870 | 0.583163 | 4.997605 |
| H | -2.886543 | 1.325505 | 5.647384 |
| C | -1.183440 | -1.449409 | 4.701079 |
| H | -0.653887 | -2.300999 | 5.116395 |
| C | -1.575455 | -0.497834 | -5.615444 |
| H | -1.482297 | -0.619350 | -6.690320 |
| C | -1.782421 | -0.519812 | 5.544930 |
| H | -1.728305 | -0.644720 | 6.622121 |
| C | -2.246543 | 0.602116 | -5.088443 |
| H | -2.679398 | 1.345574 | -5.751668 |

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 1145.08 | kJ/mol | (ZPE) |
| Temperature Correction : | 67.45 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 1212.53 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -5704.292445 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 666.80 | J/mol•K | |
| Gibbs Energy : | -5704.368167 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 502.78 | J/mol•K | |

## 9. *anti*-($AsC_4H_4)_2$ – *anti*-4f (ωB97X-D)

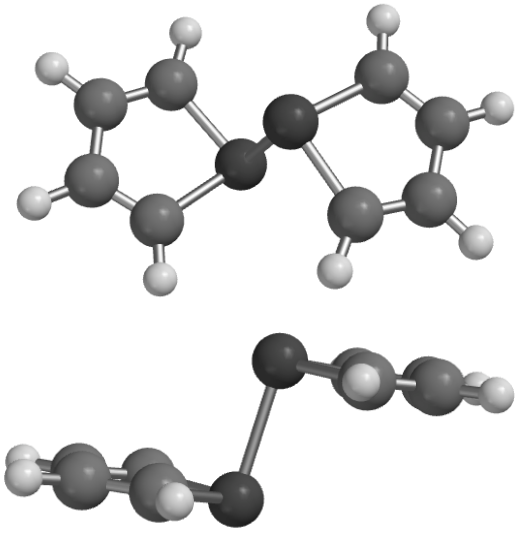


**Figure S11.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 330.68 | kJ/mol | (ZPE) |
| Temperature Correction : | 26.61 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 357.29 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4780.672030 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 399.10 | J/mol•K | |
| Gibbs Energy : | -4780.717352 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 166.97 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| As | 0.755804 | 0.949893 | -0.156645 |
| As | -0.845250 | -0.847512 | 0.352853 |
| C | -0.278878 | -1.050673 | 2.195486 |
| H | -0.664681 | -0.460800 | 3.019400 |
| C | 0.425237 | -2.257390 | -0.036851 |
| H | 0.617249 | -2.647807 | -1.030141 |
| C | 0.339833 | 0.982472 | -2.049307 |
| H | 0.791644 | 0.323136 | -2.782072 |
| C | -0.542246 | 2.379906 | 0.001002 |
| H | -0.813389 | 2.857904 | 0.935821 |
| C | 0.975729 | -2.744673 | 1.092513 |
| H | 1.674893 | -3.578357 | 1.103772 |
| C | 0.585528 | -2.076344 | 2.331716 |
| H | 0.985716 | -2.398520 | 3.290340 |
| C | -0.503101 | 1.991649 | -2.346722 |
| H | -0.816647 | 2.226932 | -3.360932 |
| C | -0.995931 | 2.763111 | -1.208390 |
| H | -1.691510 | 3.587072 | -1.351844 |

## 10. *gauche*-($AsC_4H_4)_2$ – *gauche*-4f (ωB97X-D)

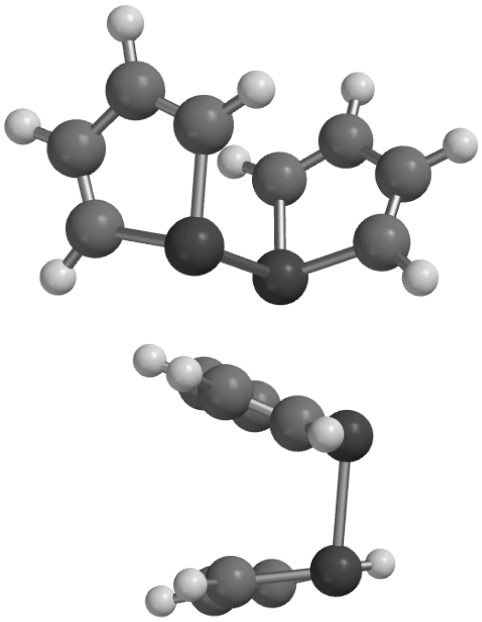


**Figure S12.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 330.82 | kJ/mol | (ZPE) |
| Temperature Correction : | 26.63 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 357.45 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4780.671957 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 399.47 | J/mol•K | |
| Gibbs Energy : | -4780.717320 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 167.10 | J/mol•K | |

**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| As | 0.871286 | 1.234907 | 1.314455 |
| As | -0.356890 | -0.840464 | 1.788410 |
| C | 1.062317 | -2.042959 | 1.248539 |
| H | 1.925952 | -2.284469 | 1.857666 |
| C | -1.142988 | -1.207823 | 0.065715 |
| H | -2.055458 | -0.748136 | -0.294295 |
| C | 1.051848 | 1.136005 | -0.603322 |
| H | 1.818628 | 0.563637 | -1.111175 |
| C | -0.692106 | 2.328643 | 0.979775 |
| H | -1.324247 | 2.747952 | 1.754185 |
| C | -0.458859 | -2.171140 | -0.579788 |
| H | -0.767466 | -2.580608 | -1.538705 |
| C | 0.766394 | -2.631710 | 0.073827 |
| H | 1.388160 | -3.399109 | -0.381485 |
| C | 0.160236 | 1.941101 | -1.211095 |
| H | 0.131877 | 2.093921 | -2.287311 |
| C | -0.808263 | 2.599657 | -0.334468 |
| H | -1.570419 | 3.260596 | -0.740928 |

## 11. *gauche*-$(AsC_4Ph_4)_2$ – *gauche*-4g

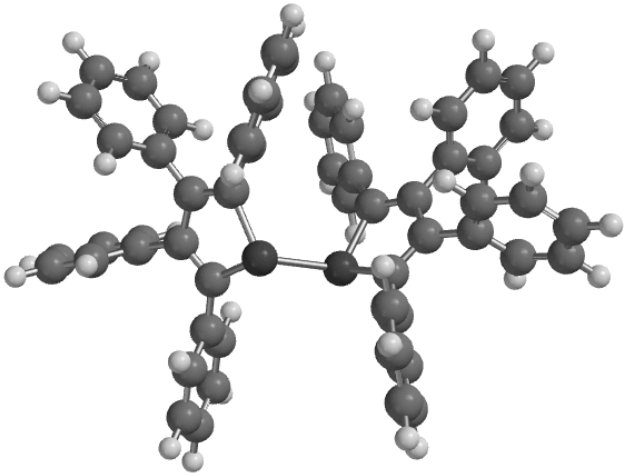


**Figure S13.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| As | -0.148187 | 1.685245 | 0.676565 |
| As | -0.863860 | -0.466774 | 1.553292 |
| C | 0.522978 | -0.927168 | 2.860046 |
| C | -0.235699 | -1.991755 | 0.510593 |
| C | 0.511888 | 1.601588 | -1.154163 |
| C | -1.791778 | 2.454889 | -0.069186 |
| C | 0.663899 | -2.692898 | 1.237279 |
| C | 1.065360 | -2.114350 | 2.527630 |
| C | -0.356150 | 2.233554 | -1.976404 |
| C | -1.606735 | 2.718822 | -1.374498 |
| C | 1.841816 | 1.092725 | -1.524150 |
| C | 4.358333 | 0.126215 | -2.293831 |
| C | 1.953311 | 0.045777 | -2.447315 |
| C | 3.009917 | 1.654661 | -0.993388 |
| C | 4.259088 | 1.172972 | -1.381928 |
| C | 3.201655 | -0.439610 | -2.824542 |
| H | 1.045877 | -0.371475 | -2.863333 |
| H | 2.948057 | 2.467741 | -0.280639 |
| H | 5.169123 | 1.608104 | -0.975039 |
| H | 3.277894 | -1.259116 | -3.537961 |
| H | 5.331583 | -0.250679 | -2.603390 |
| C | -0.099704 | 2.474603 | -3.415983 |
| C | 0.363567 | 2.946243 | -6.125347 |
| C | 0.532179 | 3.647689 | -3.827881 |
| C | -0.497385 | 1.537310 | -4.368811 |
| C | -0.266049 | 1.772709 | -5.718672 |
| C | 0.759987 | 3.883000 | -5.178657 |
| H | 0.861312 | 4.370458 | -3.093960 |
| H | -0.998301 | 0.628372 | -4.042063 |
| H | -0.583396 | 1.037703 | -6.457088 |
| H | 1.254625 | 4.799943 | -5.496149 |
| H | 0.537872 | 3.132050 | -7.181847 |
| C | -2.563642 | 3.494114 | -2.205869 |
| C | -4.388177 | 4.984286 | -3.706101 |
| C | -2.418104 | 4.879497 | -2.316397 |
| C | -3.620111 | 2.860678 | -2.861271 |
| C | -4.530902 | 3.603879 | -3.609815 |
| C | -3.326559 | 5.621564 | -3.060130 |
| H | -1.586890 | 5.373407 | -1.805823 |
| H | -3.722832 | 1.779782 | -2.786944 |
| H | -5.355882 | 3.110928 | -4.121410 |
| H | -3.202711 | 6.699690 | -3.142436 |
| H | -5.098341 | 5.573056 | -4.275678 |
| C | -2.952296 | 2.891650 | 0.726060 |
| C | -5.152105 | 3.767141 | 2.220097 |
| C | -2.828294 | 3.966695 | 1.613652 |
| C | -4.196212 | 2.269517 | 0.588812 |
| C | -5.287627 | 2.703197 | 1.334612 |
| C | -3.920826 | 4.399204 | 2.354869 |
| H | -1.866990 | 4.464714 | 1.712276 |
| H | -4.316968 | 1.450213 | -0.114305 |
| H | -6.254533 | 2.213043 | 1.231920 |
| H | -3.811151 | 5.235259 | 3.036345 |
| H | -6.001382 | 4.102897 | 2.807250 |
| C | -0.794721 | -2.380351 | -0.793007 |
| C | -1.817702 | -3.131101 | -3.290032 |
| C | -2.169318 | -2.566104 | -0.968344 |

| Atom | x | y | z (continued) |
|---|---|---|---|
| C | 0.061302 | -2.587981 | -1.882776 |
| C | -0.446195 | -2.951372 | -3.123313 |
| C | -2.675009 | -2.944467 | -2.209940 |
| H | -2.846680 | -2.419766 | -0.130346 |
| H | 1.128344 | -2.469350 | -1.727808 |
| H | 0.235316 | -3.103871 | -3.956870 |
| H | -3.742074 | -3.097199 | -2.339726 |
| H | -2.209911 | -3.425179 | -4.260136 |
| C | 0.776638 | -0.194946 | 4.115505 |
| C | 1.234059 | 1.181745 | 6.508630 |
| C | -0.221166 | -0.114816 | 5.091570 |
| C | 2.012077 | 0.411331 | 4.358295 |
| C | 2.235607 | 1.099283 | 5.547605 |
| C | 0.006986 | 0.569843 | 6.279030 |
| H | -1.173885 | -0.597834 | 4.909986 |
| H | 2.801966 | 0.339058 | 3.618985 |
| H | 3.194139 | 1.577457 | 5.729033 |
| H | -0.780181 | 0.622967 | 7.024326 |
| H | 1.401508 | 1.725181 | 7.432968 |
| C | 2.005775 | -2.861766 | 3.401133 |
| C | 3.746576 | -4.218975 | 5.106083 |
| C | 1.508502 | -3.756307 | 4.347823 |
| C | 3.380750 | -2.660064 | 3.303046 |
| C | 4.253407 | -3.346781 | 4.147711 |
| C | 2.373619 | -4.425673 | 5.203709 |
| H | 0.438903 | -3.922325 | 4.421084 |
| H | 3.767799 | -1.963261 | 2.564364 |
| H | 5.324976 | -3.193445 | 4.067516 |
| H | 1.970445 | -5.105184 | 5.948351 |
| H | 4.417642 | -4.740204 | 5.780998 |
| C | 1.246760 | -3.987112 | 0.808817 |
| C | 2.381576 | -6.414371 | 0.041878 |
| C | 0.553081 | -5.180342 | 1.007970 |
| C | 2.508154 | -4.014402 | 0.216408 |
| C | 3.074353 | -5.223722 | -0.165397 |
| C | 1.122715 | -6.390739 | 0.626162 |
| H | -0.434847 | -5.166355 | 1.465772 |
| H | 3.044698 | -3.076265 | 0.064938 |
| H | 4.069337 | -5.239846 | -0.609858 |
| H | 0.581247 | -7.321264 | 0.785755 |
| H | 2.832459 | -7.357084 | -0.246793 |

## 12. $(NC_4Me_4)_2$ ωB97X-D

See reference 11 for experimentally determined approximate but non-crystallographic $D_{2d}$ geometry.

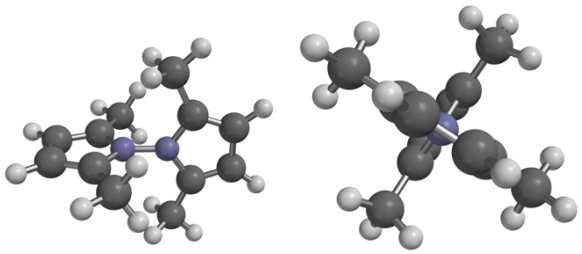


**Figure S14.** Optimised Geometry (ωB97X-D/6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 642.14 | kJ/mol | (ZPE) |
| Temperature Correction : | 36.10 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 678.24 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -575.948163 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 454.64 | J/mol•K | |
| Gibbs Energy : | -575.999792 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 236.08 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| N | -0.403198 | 0.139227 | 0.534366 |
| C | -0.051072 | -0.071434 | 1.854852 |
| C | -1.112538 | 0.357852 | 2.607327 |
| C | -2.122089 | 0.837443 | 1.720048 |
| C | -1.665513 | 0.695300 | 0.436073 |
| N | 0.398900 | -0.149132 | -0.534689 |
| C | 0.409866 | -1.359766 | -1.202487 |
| C | 1.341617 | -1.237894 | -2.199851 |
| C | 1.901892 | 0.072695 | -2.129036 |
| C | 1.305295 | 0.736017 | -1.089308 |
| C | -2.267249 | 1.016576 | -0.889824 |
| H | -2.361973 | 0.126097 | -1.522275 |
| H | -1.664047 | 1.743021 | -1.447125 |
| H | -3.263867 | 1.440474 | -0.745873 |
| C | 1.269279 | -0.661678 | 2.217227 |
| H | 1.399950 | -1.663714 | 1.791780 |
| H | 1.348923 | -0.739900 | 3.304018 |
| H | 2.103514 | -0.048677 | 1.856274 |
| C | 1.474656 | 2.111729 | -0.539470 |

| Atom | x | y | z |
|---|---|---|---|
| H | 2.236965 | 2.643746 | -1.113451 |
| H | 1.786804 | 2.095858 | 0.511460 |
| H | 0.543923 | 2.689122 | -0.588831 |
| C | -0.480997 | -2.481097 | -0.787262 |
| H | -0.334468 | -3.331248 | -1.457573 |
| H | -0.270933 | -2.812863 | 0.236459 |
| H | -1.539109 | -2.196203 | -0.821611 |
| H | 1.597451 | -2.012612 | -2.909829 |
| H | -3.085157 | 1.244250 | 1.996828 |
| H | -1.160943 | 0.331073 | 3.687408 |
| H | 2.664117 | 0.485739 | -2.775624 |

## 13. $(PC_4Me_4)_2$ ωB97X-D

NB: $(PC_4Ph_4)_2$ adopts a gauche geometry in the solid state.[12] The permethylated $(PC_4Me_4)_2$[13] has not been structurally characterised.

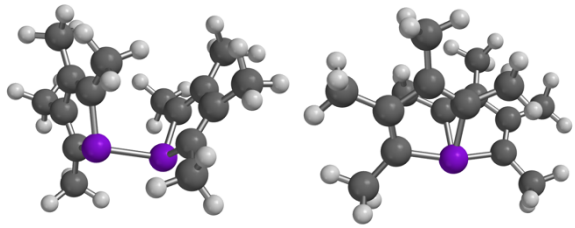


**Figure S15.** Optimised Geometry (ωB97X-D/6-31G*/Gas Phase)

**Thermodynamic Properties at 298.15 K**

| | | | |
|---|---|---|---|
| Zero Point Energy : | 897.13 | kJ/mol | (ZPE) |
| Temperature Correction : | 53.83 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 950.96 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -1306.268333 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 574.22 | J/mol•K | |
| Gibbs Energy : | -1306.333541 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 360.05 | J/mol•K | |

**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| P | 0.691528 | 1.816533 | -0.530255 |
| C | 1.216429 | 2.092026 | 1.183485 |
| C | 0.152000 | 1.951113 | 2.011530 |
| C | -1.081355 | 1.493533 | 1.343092 |
| C | -0.956950 | 1.296088 | 0.007889 |
| P | 1.768470 | -0.071843 | -0.958935 |
| C | 0.908501 | -1.327107 | 0.021231 |
| C | 0.183635 | -2.126187 | -0.799319 |
| C | 0.184892 | -1.711072 | -2.215765 |
| C | 0.905165 | -0.590598 | -2.469119 |
| C | -1.997300 | 0.781683 | -0.944224 |
| H | -2.020190 | -0.315259 | -0.929304 |
| H | -1.781028 | 1.083064 | -1.972990 |
| H | -3.000575 | 1.144228 | -0.694540 |
| C | 2.611958 | 2.524541 | 1.526686 |
| H | 2.826827 | 2.405419 | 2.592778 |
| H | 2.781310 | 3.576702 | 1.267493 |
| H | 3.352085 | 1.934127 | 0.973552 |
| C | 0.150974 | 2.211456 | 3.491997 |
| H | -0.173730 | 1.324280 | 4.049287 |
| H | -0.543124 | 3.021067 | 3.748954 |
| H | 1.138467 | 2.496314 | 3.861005 |
| C | -2.332918 | 1.246089 | 2.138939 |
| H | -2.621508 | 2.130303 | 2.719768 |
| H | -2.188455 | 0.427532 | 2.855558 |
| H | -3.175270 | 0.975024 | 1.498242 |
| C | 1.112955 | 0.107337 | -3.781226 |
| H | 2.098313 | -0.121020 | -4.205117 |
| H | 1.060760 | 1.195824 | -3.658621 |
| H | 0.358307 | -0.176987 | -4.520358 |
| C | 1.065903 | -1.438842 | 1.509857 |
| H | 1.077451 | -2.480910 | 1.847158 |
| H | 1.993002 | -0.968003 | 1.849361 |
| H | 0.241577 | -0.925107 | 2.020733 |
| C | -0.579778 | -2.511652 | -3.232487 |
| H | -0.183265 | -3.531411 | -3.311128 |
| H | -0.535499 | -2.064703 | -4.227768 |
| H | -1.635980 | -2.601160 | -2.950770 |
| C | -0.606136 | -3.328910 | -0.361831 |
| H | -0.460945 | -3.547660 | 0.698600 |
| H | -0.325677 | -4.222336 | -0.932359 |
| H | -1.680825 | -3.173515 | -0.521078 |

## 14. $(SbC_4Me_4)_2$ ωB97X-D

Only a single bistibolyl has been structurally characterised, viz. *anti*-[$(SbC_4Me_2H_2$-2,5$)_2$.14

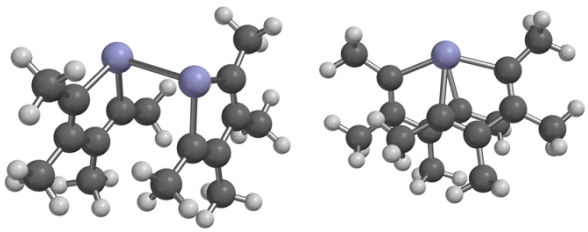


**Figure S16.** Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sb)/Gas Phase)

**Thermodynamic Properties at 298.15 K**

| | | | |
|---|---|---|---|
| Zero Point Energy : | 887.55 | kJ/mol | (ZPE) |
| Temperature Correction : | 56.38 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 943.93 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -634.402058 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 602.15 | J/mol•K | |
| Gibbs Energy : | -634.470439 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 371.18 | J/mol•K | |

**Cartesian Coordinates**

| Atom | x | y | z |
|---|---|---|---|
| Sb | 0.892104 | 2.364096 | -0.805937 |
| C | 1.257800 | 2.362788 | 1.300449 |
| C | 0.193335 | 1.850211 | 1.959571 |
| C | -0.955705 | 1.338049 | 1.163083 |
| C | -0.896095 | 1.402138 | -0.185560 |
| Sb | 2.375758 | -0.060133 | -1.169321 |
| C | 1.113854 | -1.251523 | 0.055303 |
| C | 0.188740 | -1.886772 | -0.698335 |
| C | 0.140956 | -1.615858 | -2.161826 |
| C | 1.031156 | -0.741989 | -2.685135 |
| C | -1.943669 | 0.891395 | -1.137721 |
| H | -2.252300 | -0.129367 | -0.880627 |
| H | -1.573451 | 0.859067 | -2.165960 |
| H | -2.842904 | 1.521375 | -1.128899 |
| C | 2.520362 | 2.925768 | 1.890188 |
| H | 2.628646 | 2.713144 | 2.958502 |
| H | 2.563565 | 4.015332 | 1.765723 |
| H | 3.406194 | 2.517548 | 1.388222 |
| C | 0.108633 | 1.739813 | 3.462733 |
| H | 0.023202 | 0.692805 | 3.778528 |
| H | -0.773639 | 2.263478 | 3.849041 |
| H | 0.981824 | 2.164119 | 3.960606 |
| C | -2.129204 | 0.734056 | 1.895853 |
| H | -2.591157 | 1.457926 | 2.577981 |
| H | -1.824431 | -0.125878 | 2.505599 |
| H | -2.904065 | 0.391760 | 1.207168 |
| C | 1.160687 | -0.307557 | -4.118659 |
| H | 2.077067 | -0.706134 | -4.572252 |
| H | 1.222769 | 0.785195 | -4.195134 |
| H | 0.319792 | -0.626714 | -4.742344 |
| C | 1.262339 | -1.372764 | 1.548521 |
| H | 1.645734 | -2.358487 | 1.842351 |
| H | 1.943329 | -0.617474 | 1.949979 |
| H | 0.299329 | -1.227445 | 2.054046 |
| C | -0.926865 | -2.314666 | -2.967518 |
| H | -0.844126 | -3.403735 | -2.874697 |
| H | -0.873976 | -2.072981 | -4.030156 |
| H | -1.928664 | -2.038858 | -2.615689 |
| C | -0.821008 | -2.840902 | -0.108373 |
| H | -0.688383 | -2.954078 | 0.969407 |
| H | -0.738694 | -3.838374 | -0.556977 |
| H | -1.848837 | -2.498374 | -0.281731 |

## 15. *gauche*-$(AsC_4H_4)_2$ – 4f ωB97X-D

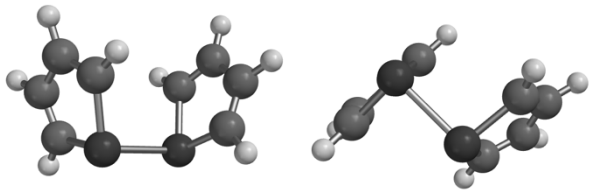


**Figure S17.** Optimised Geometry (ωB97X-D/6-31G*/Gas Phase)

**Thermodynamic Properties at 298.15 K**
(ωB97X-D/6-31G*/Gas Phase)

| | | | |
|---|---|---|---|
| Zero Point Energy : | 330.82 | kJ/mol | (ZPE) |
| Temperature Correction : | 26.63 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 357.45 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4780.671957 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 399.47 | J/mol•K | |
| Gibbs Energy : | -4780.717320 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 167.10 | J/mol•K | |

**Calculated electronic transitions**[a]

| nm ▼ | strength | | MO Component | |
|---|---|---|---|---|
| 217.68 | 0.0415 | | HOMO-1 -> LUMO+1 | 92% |
| 223.40 | 0.0618 | | HOMO -> LUMO+1 | 62% |
| | | | HOMO-4 -> LUMO | 18% |
| 269.52 | 0.0015 | | HOMO-3 -> LUMO | 94% |
| 286.62 | 0.1925 | | HOMO-1 -> LUMO | 54% |
| | | | HOMO-2 -> LUMO | 37% |
| 295.45 | 0.0755 | | HOMO-2 -> LUMO | 57% |
| | | | HOMO-1 -> LUMO | 38% |
| 312.48 | 0.0046 | | HOMO -> LUMO | 95% |

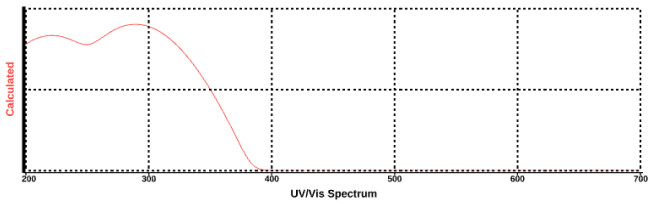



**Figure S18.** Calculated electronic spectrum (TD-DFT: ωB97X-D/6-31G*/Gas Phase)

**Cartesian Coordinates** (ωB97X-D/6-31G*/Gas Phase)

| Atom | x | y | z |
|---|---|---|---|
| As | 0.871286 | 1.234907 | 1.314455 |
| As | -0.356890 | -0.840464 | 1.788410 |
| C | 1.062317 | -2.042959 | 1.248539 |
| H | 1.925952 | -2.284469 | 1.857666 |
| C | -1.142988 | -1.207823 | 0.065715 |
| H | -2.055458 | -0.748136 | -0.294295 |
| C | 1.051848 | 1.136005 | -0.603322 |
| H | 1.818628 | 0.563637 | -1.111175 |
| C | -0.692106 | 2.328643 | 0.979775 |
| H | -1.324247 | 2.747952 | 1.754185 |
| C | -0.458859 | -2.171140 | -0.579788 |
| H | -0.767466 | -2.580608 | -1.538705 |
| C | 0.766394 | -2.631710 | 0.073827 |
| H | 1.388160 | -3.399109 | -0.381485 |
| C | 0.160236 | 1.941101 | -1.211095 |
| H | 0.131877 | 2.093921 | -2.287311 |
| C | -0.808263 | 2.599657 | -0.334468 |
| H | -1.570419 | 3.260596 | -0.740928 |

## 16. *anti*-$(AsC_4H_4)_2$ – *anti*-4f

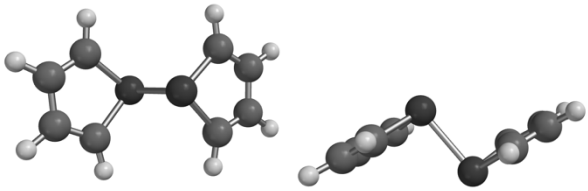


**Figure S19.** Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

**Thermodynamic Properties at 298.15 K**

| | | | |
|---|---|---|---|
| Zero Point Energy : | 330.68 | kJ/mol | (ZPE) |
| Temperature Correction : | 26.61 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 357.29 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4780.672030 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 399.10 | J/mol•K | |
| Gibbs Energy : | -4780.717352 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 166.97 | J/mol•K | |

**Calculated electronic transitions**[a]

The pale yellow colour of biarsolyls most likely arises from the HOMO (As lone-pair) →LUMO (ring-based π*) UV transition having an absorption that tail slightly into the visible region.

| nm ▼ | strength | | MO Component | |
|---|---|---|---|---|
| 218.01 | 0.0001 | | HOMO -> LUMO+1 | 72% |
| | | | HOMO-4 -> LUMO | 23% |
| 232.58 | 0.2521 | | HOMO-3 -> LUMO | 82% |
| 238.28 | 0.0002 | | HOMO-4 -> LUMO | 71% |
| | | | HOMO -> LUMO+1 | 22% |
| 283.80 | 0.0011 | | HOMO-2 -> LUMO | 93% |
| 294.37 | 0.0225 | | HOMO-1 -> LUMO | 94% |
| 309.05 | 0.1707 | | HOMO -> LUMO | 90% |

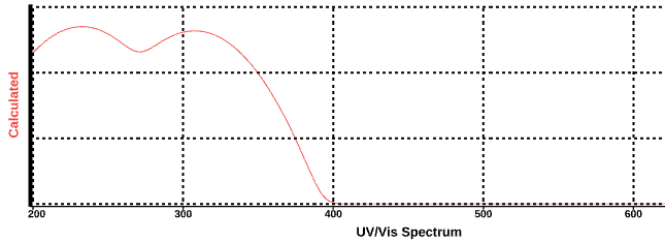



**Figure S20.** Calculated electronic spectrum (TD-DFT: ωB97X-D/6-31G*/Gas Phase)

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| As | 0.755804 | 0.949893 | -0.156645 |
| As | -0.845250 | -0.847512 | 0.352853 |
| C | -0.278878 | -1.050673 | 2.195486 |
| H | -0.664681 | -0.460800 | 3.019400 |
| C | 0.425237 | -2.257390 | -0.036851 |
| H | 0.617249 | -2.647807 | -1.030141 |
| C | 0.339833 | 0.982472 | -2.049307 |
| H | 0.791644 | 0.323136 | -2.782072 |
| C | -0.542246 | 2.379906 | 0.001002 |
| H | -0.813389 | 2.857904 | 0.935821 |
| C | 0.975729 | -2.744673 | 1.092513 |
| H | 1.674893 | -3.578357 | 1.103772 |
| C | 0.585528 | -2.076344 | 2.331716 |
| H | 0.985716 | -2.398520 | 3.290340 |
| C | -0.503101 | 1.991649 | -2.346722 |
| H | -0.816647 | 2.226932 | -3.360932 |
| C | -0.995931 | 2.763111 | -1.208390 |
| H | -1.691510 | 3.587072 | -1.351844 |

## 17. *gauche*-$(PC_4H_4)_2$ ωB97X

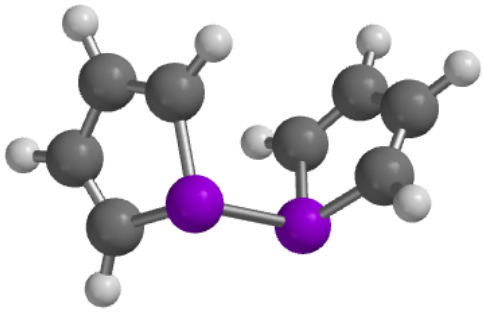


**Figure S21.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 358.80 | kJ/mol | (ZPE) |
| Temperature Correction : | 23.36 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 382.16 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -992.030057 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 366.38 | J/mol•K | |
| Gibbs Energy : | -992.071664 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 145.28 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| P | 0.922470 | -0.615100 | 1.380263 |
| C | 2.164400 | 0.685630 | 1.147803 |
| C | 2.742511 | 0.547433 | -0.070891 |
| C | 2.138774 | -0.502151 | -0.914235 |
| C | 1.109801 | -1.166762 | -0.333947 |
| P | -0.922470 | 0.615100 | 1.380263 |
| C | -1.109801 | 1.166762 | -0.333947 |
| C | -2.138774 | 0.502151 | -0.914235 |
| C | -2.742511 | -0.547433 | -0.070891 |
| C | -2.164400 | -0.685630 | 1.147803 |
| H | -2.508195 | 0.676357 | -1.930945 |
| H | -0.482477 | 1.950890 | -0.773418 |
| H | -3.581924 | -1.139609 | -0.452939 |
| H | -2.425028 | -1.388905 | 1.948308 |
| H | 0.482477 | -1.950890 | -0.773418 |
| H | 2.508195 | -0.676357 | -1.930945 |
| H | 3.581924 | 1.139609 | -0.452939 |
| H | 2.425028 | 1.388905 | 1.948308 |

## 18. *gauche*-($AsC_4H_4$)$_2$ *gauche*-4f ωB97X

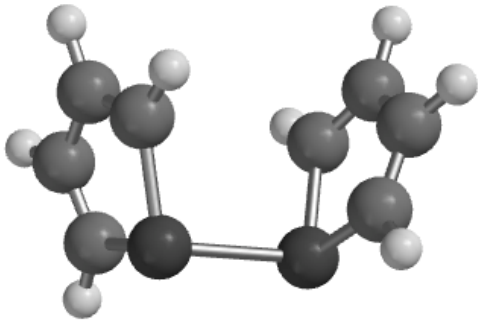


**Figure S22.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 353.21 | kJ/mol | (ZPE) |
| Temperature Correction : | 25.41 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 378.62 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4780.630247 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 392.75 | J/mol•K | |
| Gibbs Energy : | -4780.674848 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 157.53 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| As | 1.041139 | -0.640225 | 1.547147 |
| C | 2.211787 | 0.848761 | 1.159053 |
| C | 2.676224 | 0.774496 | -0.101165 |
| C | 2.126485 | -0.310247 | -0.920320 |
| C | 1.218639 | -1.097290 | -0.316424 |
| As | -1.041532 | 0.641528 | 1.546036 |
| C | -1.217065 | 1.095835 | -0.318371 |
| C | -2.125332 | 0.308758 | -0.921563 |
| C | -2.676158 | -0.774659 | -0.101406 |
| C | -2.212585 | -0.847407 | 1.159242 |
| H | -2.435012 | 0.437877 | -1.956941 |
| H | -0.708810 | 1.928878 | -0.791608 |
| H | -3.409967 | -1.467601 | -0.508978 |
| H | -2.530485 | -1.583238 | 1.890557 |
| H | 0.711297 | -1.931408 | -0.788730 |
| H | 2.435513 | -0.439433 | -1.955916 |
| H | 3.408458 | 1.468536 | -0.509717 |
| H | 2.527404 | 1.586838 | 1.889104 |

## 19. *gauche*-($SbC_4H_4$)$_2$ ωB97X

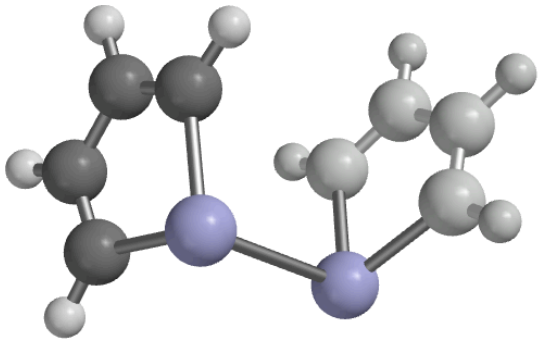


**Figure S23.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 347.46 | kJ/mol | (ZPE) |
| Temperature Correction : | 26.68 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 374.14 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -320.149525 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 408.63 | J/mol•K | |
| Gibbs Energy : | -320.195928 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 164.07 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| Sb | 1.210827 | 0.722209 | -1.733591 |
| C | 2.393133 | -0.988759 | -1.227309 |
| C | 2.699310 | -0.982050 | 0.081816 |
| C | 2.140295 | 0.078231 | 0.934394 |
| C | 1.338355 | 1.000014 | 0.375811 |
| Sb | -1.222298 | -0.734683 | -1.730158 |
| C | -1.352962 | -1.009556 | 0.379926 |
| C | -2.144783 | -0.078191 | 0.937778 |
| C | -2.689796 | 0.989074 | 0.084768 |
| C | -2.384397 | 0.990465 | -1.224634 |
| H | -2.375378 | -0.076877 | 2.003197 |
| H | -0.896787 | -1.816469 | 0.944311 |
| H | -3.319100 | 1.757653 | 0.533812 |
| H | -2.755293 | 1.743275 | -1.913560 |
| H | 0.870558 | 1.800367 | 0.939698 |
| H | 2.370130 | 0.080068 | 1.999817 |
| H | 3.341131 | -1.740264 | 0.530728 |
| H | 2.777053 | -1.734510 | -1.916804 |

## 20. *gauche*-($BiC_4H_4$)$_2$ ωB97X

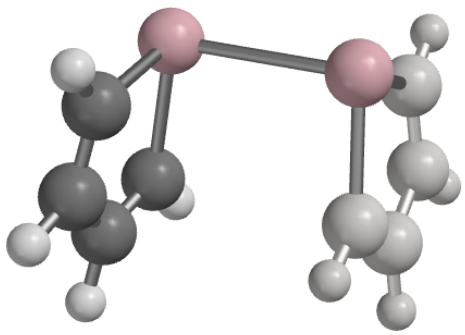


**Figure S24.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 344.36 | kJ/mol | (ZPE) |
| Temperature Correction : | 27.33 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 371.69 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -320.210798 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 421.07 | J/mol•K | |
| Gibbs Energy : | -320.258615 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 167.42 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| Bi | 0.521307 | 2.172210 | -0.660680 |
| C | 0.959587 | 2.297194 | 1.499042 |
| C | -0.064963 | 1.817068 | 2.222386 |
| C | -1.232797 | 1.242008 | 1.534163 |
| C | -1.250861 | 1.192007 | 0.193230 |
| Bi | 2.115852 | -0.306202 | -0.937199 |
| C | 0.692495 | -1.583408 | 0.144144 |
| C | -0.139526 | -2.209182 | -0.702634 |
| C | -0.063323 | -1.913808 | -2.143526 |
| C | 0.842545 | -1.028905 | -2.591320 |
| H | -0.891611 | -2.916573 | -0.350723 |
| H | 0.672226 | -1.742896 | 1.218484 |
| H | -0.757269 | -2.419166 | -2.816621 |
| H | 0.942132 | -0.783394 | -3.644875 |
| H | -2.073241 | 0.762453 | -0.371341 |
| H | -2.052269 | 0.845342 | 2.134607 |
| H | -0.058690 | 1.835764 | 3.313134 |
| H | 1.838405 | 2.739489 | 1.959728 |

## 21. $D_{2d}$-($NC_4H_4$)$_2$ ωB97X

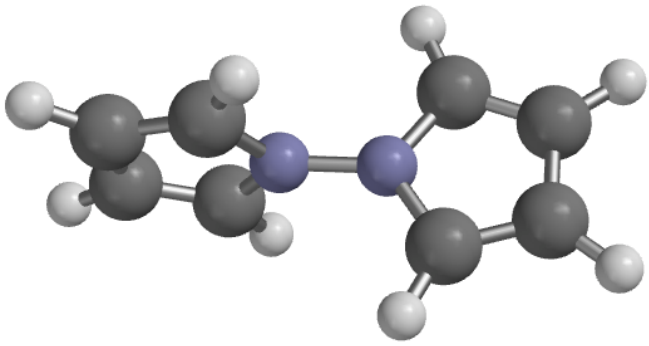


**Figure S25.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 387.46 | kJ/mol | (ZPE) |
| Temperature Correction : | 20.26 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 407.71 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -418.835918 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 345.50 | J/mol•K | |
| Gibbs Energy : | -418.875153 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 125.22 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| N | 0.678260 | -0.092133 | -0.002882 |
| C | 1.562762 | 0.619365 | 0.772711 |
| C | 2.817663 | 0.150977 | 0.490352 |
| C | 2.684430 | -0.878858 | -0.487905 |
| C | 1.352349 | -1.008277 | -0.775249 |
| N | -0.679145 | 0.086214 | -0.004581 |
| C | -1.350423 | 1.005972 | -0.775125 |
| C | -2.682646 | 0.881522 | -0.486411 |
| C | -2.818638 | -0.148300 | 0.491583 |
| C | -1.565309 | -0.621715 | 0.772464 |
| H | -3.480562 | 1.463999 | -0.927487 |
| H | -0.803981 | 1.650280 | -1.449374 |
| H | -3.740054 | -0.499044 | 0.936991 |
| H | -1.205278 | -1.387505 | 1.444980 |
| H | 0.807631 | -1.654425 | -1.449112 |
| H | 3.484068 | -1.458029 | -0.930226 |
| H | 3.738248 | 0.505296 | 0.934651 |
| H | 1.200625 | 1.384661 | 1.444620 |

## 22. *gauche*-$P_2Me_4$ ωB97X

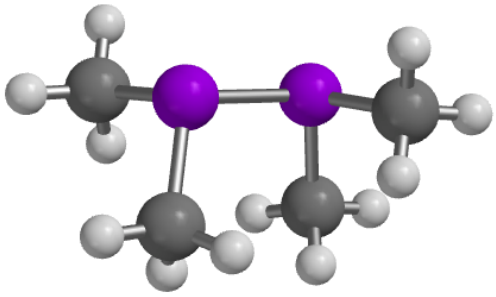


**Figure S26.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 408.73 | kJ/mol | (ZPE) |
| Temperature Correction : | 26.30 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 435.04 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -842.117097 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 378.67 | J/mol•K | |
| Gibbs Energy : | -842.160098 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 147.80 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| P | 0.503820 | 0.976037 | -0.914639 |
| P | -0.503820 | -0.976037 | -0.914639 |
| C | -0.988418 | 2.073103 | -0.855733 |
| H | -0.665135 | 3.117711 | -0.799234 |
| H | -1.641003 | 1.868371 | 0.001138 |
| H | -1.568699 | 1.950415 | -1.775037 |
| C | 1.120627 | 1.197845 | 0.820515 |
| H | 1.596523 | 2.181008 | 0.901763 |
| H | 1.883993 | 0.446195 | 1.047908 |
| H | 0.327474 | 1.135020 | 1.573318 |
| C | -1.120627 | -1.197845 | 0.820515 |
| H | -1.883993 | -0.446195 | 1.047908 |
| H | -0.327474 | -1.135020 | 1.573318 |
| H | -1.596523 | -2.181008 | 0.901763 |
| C | 0.988418 | -2.073103 | -0.855733 |
| H | 1.568699 | -1.950415 | -1.775037 |
| H | 0.665135 | -3.117711 | -0.799234 |
| H | 1.641003 | -1.868371 | 0.001138 |

## 23. *gauche*-$As_2Me_4$ ωB97X

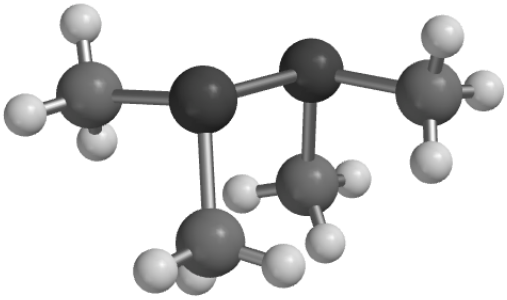


**Figure S27.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 399.95 | kJ/mol | (ZPE) |
| Temperature Correction : | 27.91 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 427.86 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4630.720200 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 408.67 | J/mol•K | |
| Gibbs Energy : | -4630.766608 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 158.59 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| As | 0.458883 | 1.127018 | -1.021374 |
| As | -0.459264 | -1.127839 | -1.021412 |
| C | -1.268178 | 2.070484 | -0.885962 |
| H | -1.081114 | 3.140983 | -0.759518 |
| H | -1.868397 | 1.717569 | -0.041591 |
| H | -1.834430 | 1.927275 | -1.810272 |
| C | 1.004084 | 1.340618 | 0.862260 |
| H | 1.377345 | 2.359929 | 1.001577 |
| H | 1.819380 | 0.649052 | 1.096139 |
| H | 0.177972 | 1.170401 | 1.558225 |
| C | -1.004291 | -1.340793 | 0.862363 |
| H | -1.819329 | -0.648955 | 1.096358 |
| H | -0.178011 | -1.170742 | 1.558171 |
| H | -1.377868 | -2.359974 | 1.001807 |
| C | 1.268366 | -2.070289 | -0.885883 |
| H | 1.834628 | -1.927208 | -1.810209 |
| H | 1.081813 | -3.140826 | -0.759011 |
| H | 1.868412 | -1.716703 | -0.041665 |

## 24. $Sb_2Me_4$ ωB97X

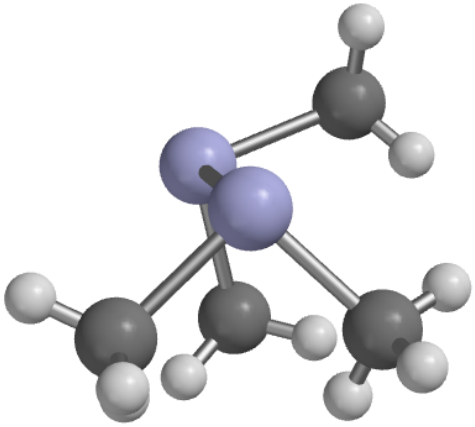


**Figure S28.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 367.41 | kJ/mol | (ZPE) |
| Temperature Correction : | 29.40 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 396.81 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -170.285338 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 427.93 | J/mol•K | |
| Gibbs Energy : | -170.333933 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 173.03 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| Sb | 1.364215 | -0.425307 | -1.248471 |
| Sb | -1.362367 | 0.424388 | -1.247238 |
| C | 2.140686 | 1.566659 | -0.838381 |
| H | 3.212939 | 1.504867 | -0.632856 |
| H | 1.640775 | 2.004302 | 0.030168 |
| H | 1.990026 | 2.218310 | -1.703155 |
| C | 1.421000 | -1.064050 | 0.829110 |
| H | 2.424363 | -1.420085 | 1.078895 |
| H | 0.714520 | -1.883754 | 0.989328 |
| H | 1.162596 | -0.235711 | 1.493568 |
| C | -1.419739 | 1.063812 | 0.830077 |
| H | -0.709727 | 1.879917 | 0.992104 |
| H | -1.169646 | 0.233856 | 1.495414 |
| H | -2.422142 | 1.426474 | 1.074426 |
| C | -2.141118 | -1.566631 | -0.837071 |
| H | -1.991231 | -2.216091 | -1.703844 |
| H | -3.213354 | -1.503468 | -0.632114 |
| H | -1.641797 | -2.007489 | 0.030041 |

## 25. $Bi_2Me_4$ ωB97X

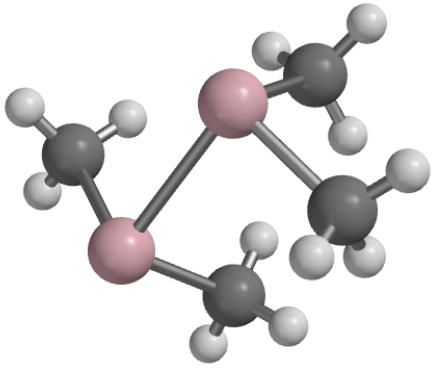


**Figure S29.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 387.70 | kJ/mol | (ZPE) |
| Temperature Correction : | 29.23 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 416.93 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -170.312258 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 436.93 | J/mol•K | |
| Gibbs Energy : | -170.361874 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 170.98 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| Bi | 1.434230 | -0.348986 | -1.315824 |
| Bi | -1.440327 | 0.350378 | -1.318568 |
| C | 2.074130 | 1.740573 | -0.817177 |
| H | 3.141076 | 1.750180 | -0.578888 |
| H | 1.517981 | 2.117055 | 0.045706 |
| H | 1.898930 | 2.405242 | -1.667261 |
| C | 1.492290 | -1.033330 | 0.818735 |
| H | 2.518694 | -1.303582 | 1.083550 |
| H | 0.858236 | -1.914757 | 0.948016 |
| H | 1.148416 | -0.240124 | 1.486573 |
| C | -1.495416 | 1.034048 | 0.816849 |
| H | -0.854612 | 1.911540 | 0.946088 |
| H | -1.152048 | 0.238339 | 1.481626 |
| H | -2.519489 | 1.305491 | 1.086749 |
| C | -2.070390 | -1.741438 | -0.816318 |
| H | -1.899476 | -2.404024 | -1.669814 |
| H | -3.137711 | -1.751986 | -0.578065 |
| H | -1.514513 | -2.114620 | 0.048023 |

## 26. $H_2As–AsH_2$ ωB97X

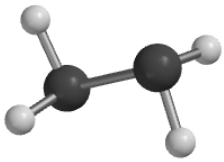


**Figure S30.** Optimised Geometry (wB97X /6-31G*/Gas Phase)

### Thermodynamic Properties at 298.15 K

| | | | |
|---|---|---|---|
| Zero Point Energy : | 78.41 | kJ/mol | (ZPE) |
| Temperature Correction : | 14.25 | kJ/mol | (vibration + gas law + rotation + translation) |
| Enthalpy Correction : | 92.66 | kJ/mol | (ZPE + temperature correction) |
| Enthalpy : | -4473.674454 | au | (Electronic Energy + Enthalpy Correction) |
| Entropy : | 292.85 | J/mol•K | |
| Gibbs Energy : | -4473.707710 | au | (Enthalpy - T*Entropy) |
| $C_v$ : | 60.79 | J/mol•K | |

### Cartesian Coordinates

| Atom | x | y | z |
|---|---|---|---|
| As | 1.179997 | -0.346111 | 0.063470 |
| H | 1.579029 | 0.747796 | 1.053885 |
| H | 1.510898 | 0.564450 | -1.117355 |
| As | -1.179997 | 0.346111 | 0.063470 |
| H | -1.579029 | -0.747796 | 1.053885 |
| H | -1.510898 | -0.564450 | -1.117355 |

Illustrative Effect of Dispersion Correction for *gauche*-$(AsC_4Me_4)_2$

| Parameter[a] | ωB97X 6-31G* | ωB97X-D 6-31G* |
|---|---|---|
| As–As [Å] | 2.446 | 2.462 |
| As–$C_\alpha$[a] [Å] | 1.934 | 1.871 |
| $C_\alpha$-$C_\beta$ [Å] | 1.351 | 1.352 |
| $C_\beta$-$C_{\beta'}$ [Å] | 1.488 | 1.480 |
| $C_\alpha$-As-As-$C_\alpha$ [°] | 9.37 | 21.68 |
| | 167.76 | 154.46 |
| $C_\alpha$–As–$C_\alpha$ [°] | 87.18 | 87.19 |
| Natural Charge (As) | 0.664 | 0.674 |
| Natural Charge ($C_\alpha$) | –0.340 | –0.337 |
| Natural Charge ($C_\beta$) | –0.570 | –0.055 |
| Löwden BO (As–As) | 1.01 | 0.98 |
| Löwden BO (As–$C_\alpha$) | 0.97 | 1.02 |
| Löwden BO ($C_\alpha$-$C_\beta$) | 1.78 | 1.76 |
| Löwden BO ($C_\beta$-$C_{\beta'}$) | 1.08 | 1.09 |
| Dipole (Deb) | 1.80 | 2.10 |
| LUMO (eV) | 0.88 | 0.46 |
| HOMO (eV) | –7.74 | –7.27 |
| $\nu_{(AsAs)}$ ($cm^{-1}$, uncorrected) | | 219 |

[a]Mean values where appropriate

**General observations:** Inclusion of the dispersion correction results in a modest lengthening of the As–As bond and contraction of As–C bonds with negligible effect on remaining C–C bonds. A negligible increase in the positive charge of the heavy atoms of the AsC4 ring (0.03 - 0.01) is noted while very modest decrease in As–As bond order (0.03) is absorbed by a comparable increase in bonding between arsenic and carbon. Taken together, the very small magnitude of these changes would appear to make it acceptable to omit the dispersion correction so as to allow the same functional (ωB97X) to be employed for (and within) the complete series $(AC_4H_4)_2$ (A = N, P, As, Sb, Bi).

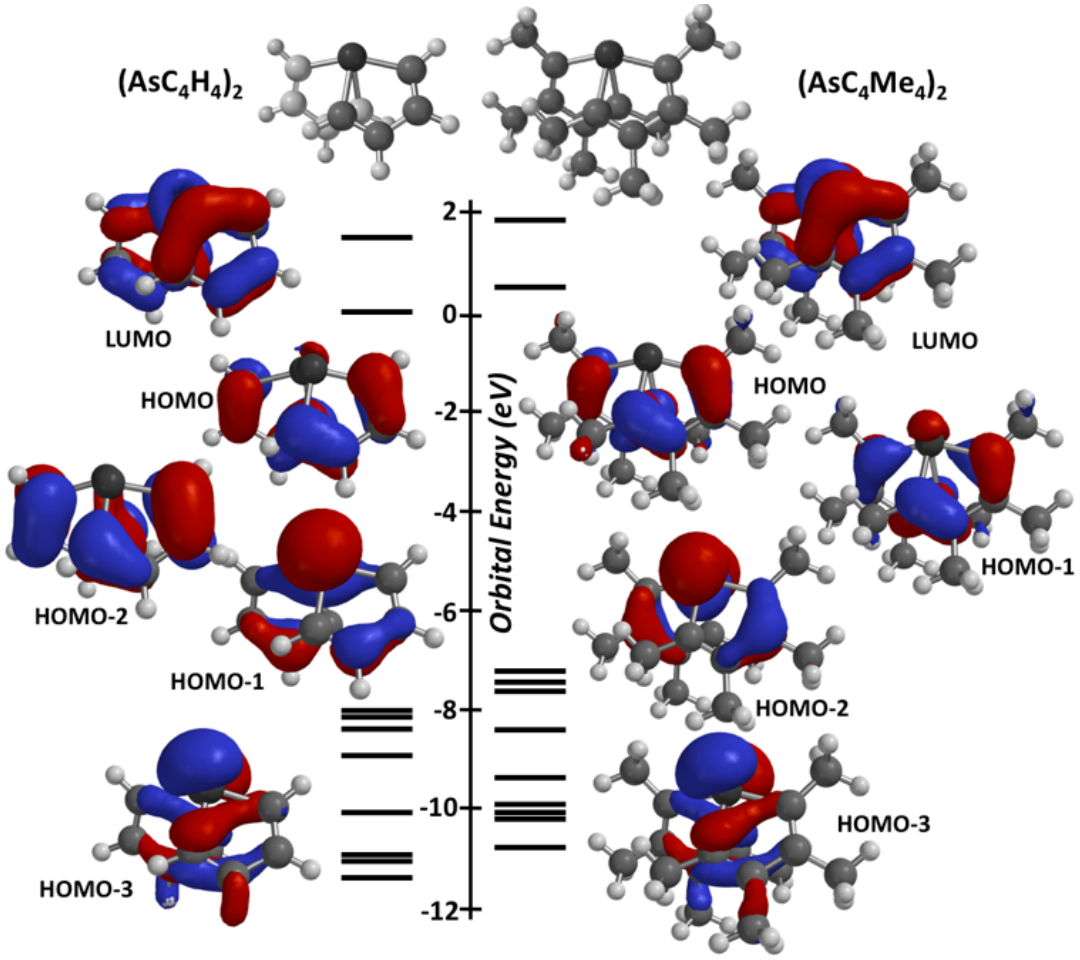



**Figure S31.** Comparison of the energies and topologies of the frontier orbitals of $(AsC_4H_4)_2$ *vs* $(AsC_4Me_4)_2$. Other than raising the energies of all orbitals, permethylation has little effect on the topologies of the orbitals. Accordingly, similar bonding to a transition metal may be anticipated with the proviso that the permethylated derivative will be a stronger donor and poorer acceptor ligand.

Comparison of Basis Set Selection for *anti*-$(AC_4H_4)_2$ (A = As, P; ωB97X-D))

| **Parameter**[a] | **6-31G*** | **6-311+G**** | **6-311+G(3df,2p)** | **6-31G*** | **6-31G*** | **6-311+G**** | **6-311+G(3df,2p)** |
|---|---|---|---|---|---|---|---|
| **E =** | **As** | **As** | **As** | **P** *(gauche)* | **P***(anti)* | **P** | **P** |
| E–E [Å] | 2.460 | 2.460 | 2.460 | 2.211 | 2.232 | 2.241 | 2.259 |
| E–$C_\alpha$[a] [Å] | 1.938 | 1.936 | 1.936 | 1.806 | 1.811 | 1.810 | 1.795 |
| $C_\alpha$-$C_\beta$ [Å] | 1.348 | 1.345 | 1.345 | 1.352 | 1.352 | 1.349 | 1.348 |
| $C_\beta$-$C_{\beta'}$ [Å] | 1.461 | 1.460 | 1.460 | 1.458 | 1.457 | 1.455 | 1.452 |
| $C_\alpha$-E-E-$C_\alpha$ [°] | 101.0 | 94.4 | 93.9 | 68.3 | 88.6 | 89.1 | 88.4 |
| | 173.1 | 179.8 | 179.8 | 161.82 | 179.9 | 179.9 | 179.8 |
| $C_\alpha$–E–$C_\alpha$ [°] | 85.6 | 85.5 | 85.5 | 90.5 | 89.9 | 89.7 | 90.1 |
| LUMO (eV) | –0.03 | –0.40 | –0.40 | 0.12 | 0.09 | –0.30 | –0.24 |
| HOMO (eV) | –8.05 | –8.29 | –8.27 | –8.17 | –8.01 | –8.31 | –8.22 |
| $\nu_{(EE)}$ ($cm^{-1}$, uncorrected[b]) | 241 | 241 | 249 | 328 | 322 | 320 | 325 |

[a]Mean values where appropriate. [b]For recommended scaling factors see https://cccbdb.nist.gov/vibscalejust.asp.

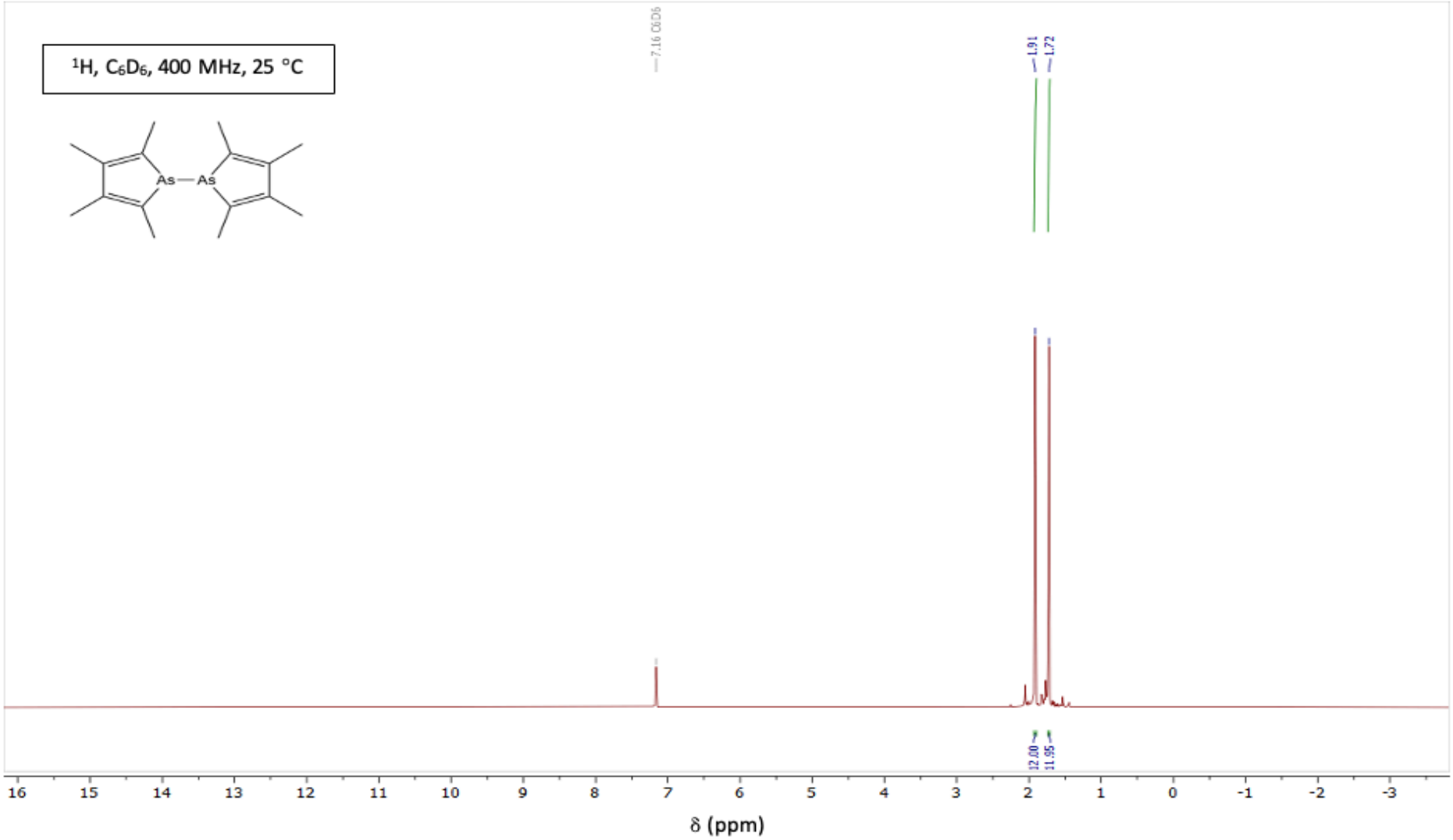



**Figure S32.** $^{1}H$ NMR Spectrum of $(AsC_4Me_4)_2$ ($C_6D_6$, 400 MHz, 25 °C)

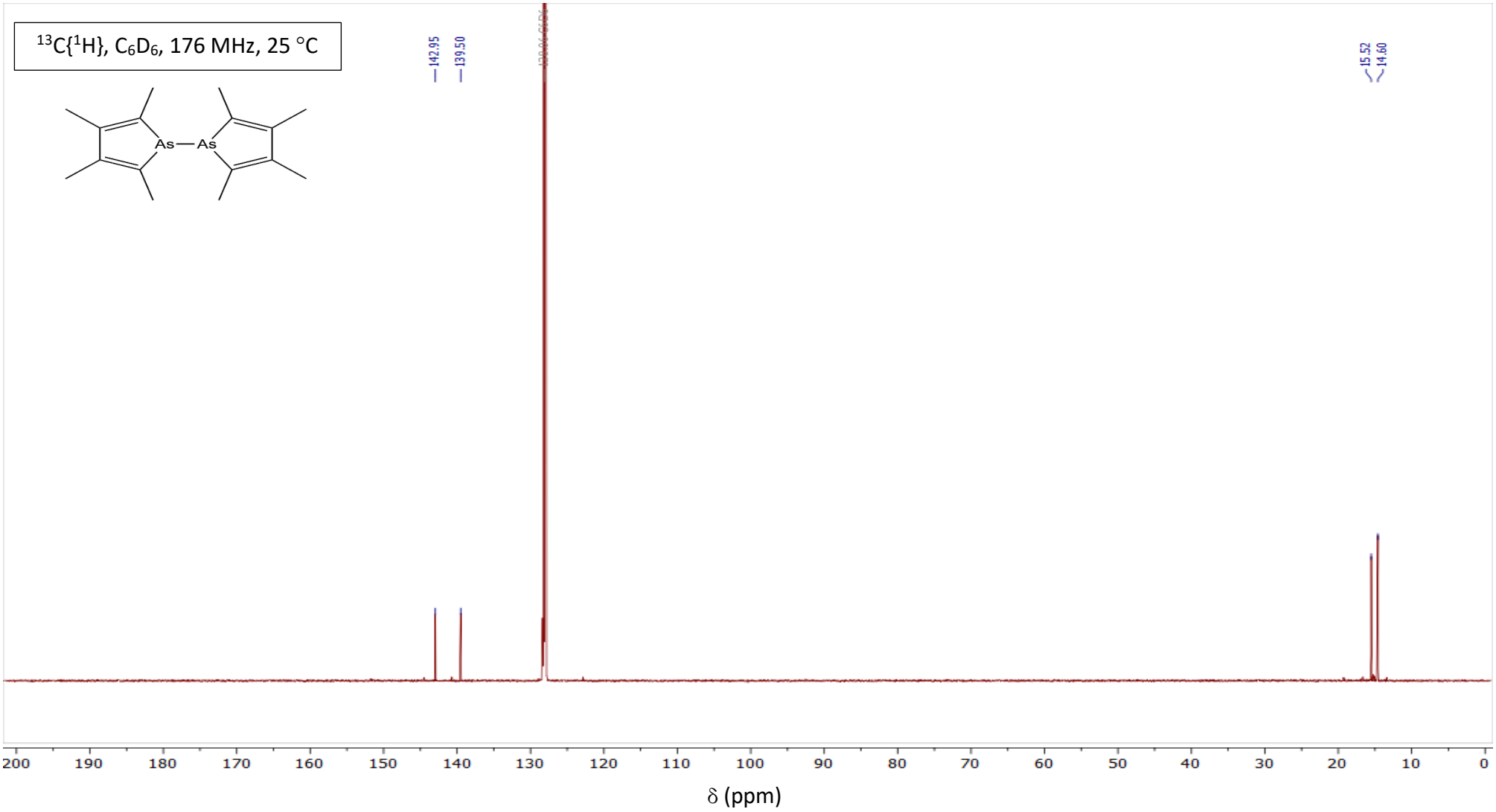



**Figure S33.** $^{13}C\{^{1}H\}$ NMR Spectrum of $(AsC_4Me_4)_2$ ($C_6D_6$, 176 MHz, 25 °C)

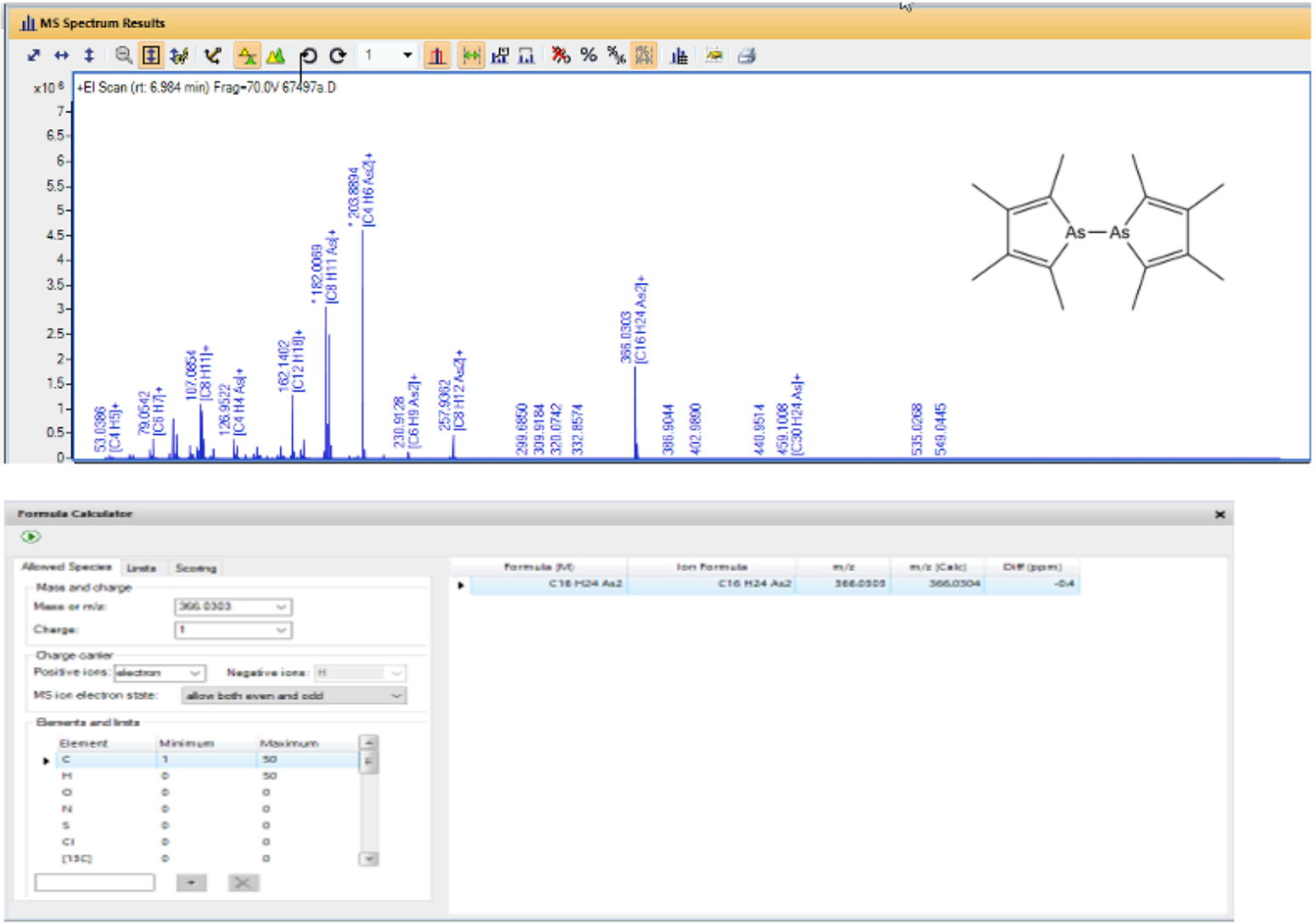



**Figure S34.** ESI-MS of $(AsC_4Me_4)_2$

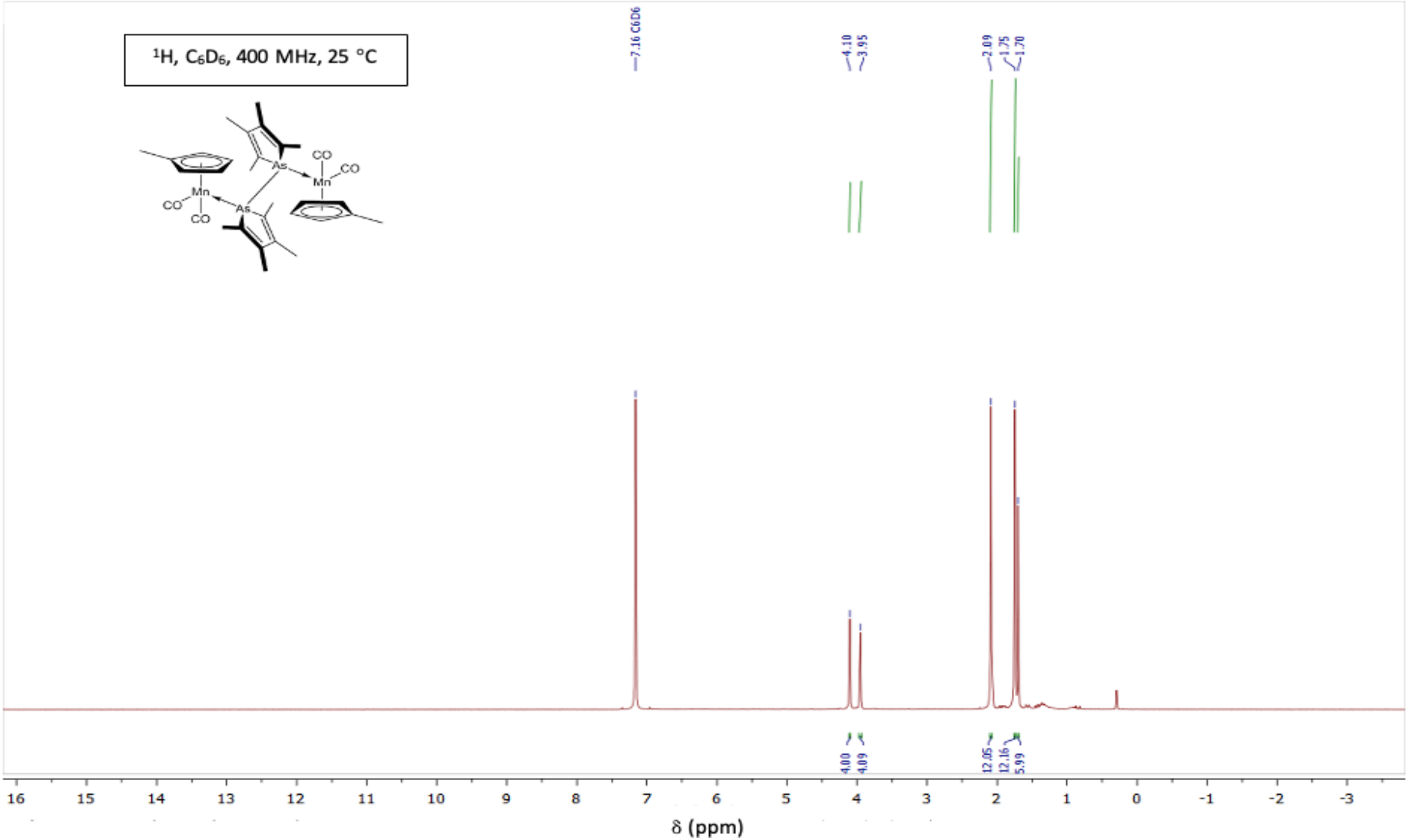



**Figure S35.** $^{1}H$ NMR Spectrum of $[Mn_2\{(AsC_4Me_4)_2\}(CO)_4(\eta\text{-}C_5H_4Me)_2]$ ($C_6D_6$, 400 MHz, 25 °C)

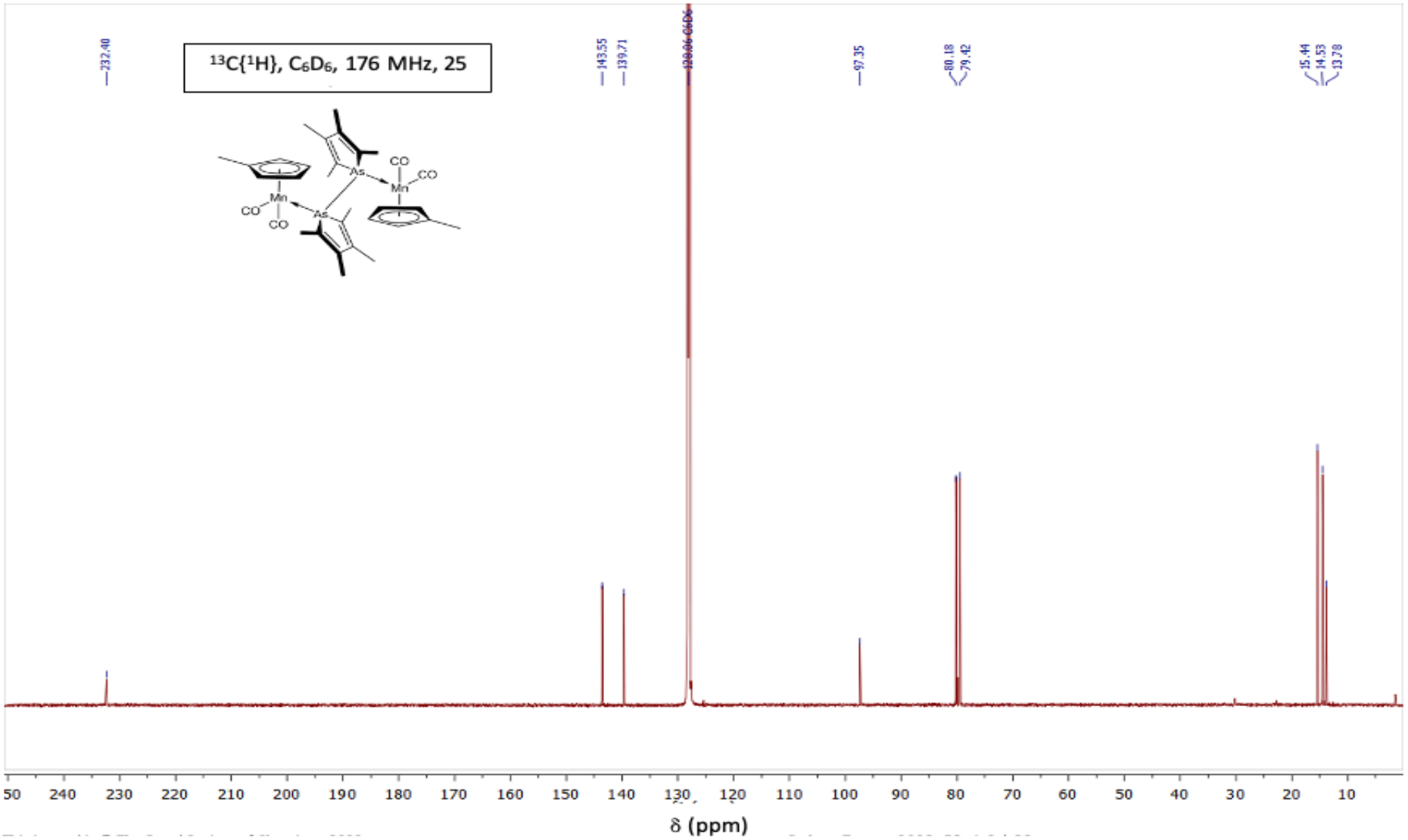



**Figure S36.** $^{13}C\{^{1}H\}$ NMR Spectrum of $[Mn_2\{(AsC_4Me_4)_2\}(CO)_4(\eta\text{-}C_5H_4Me)_2]$ ($C_6D_6$, 176 MHz, 25 °C)

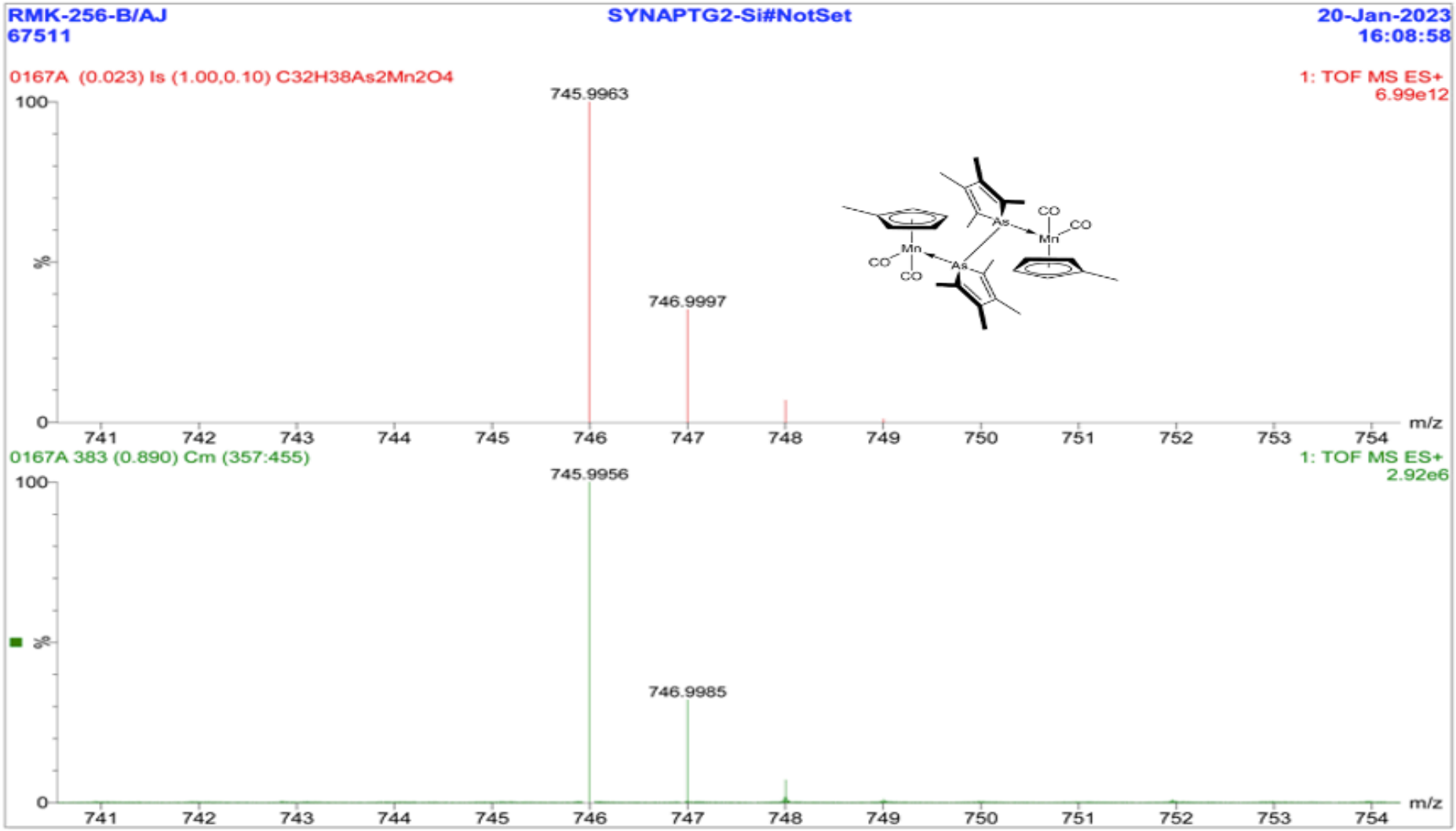



**Figure S37.** ESI-MS of $[Mn_2\{(AsC_4Me_4)_2\}(CO)_4(\eta\text{-}C_5H_4Me)_2]$

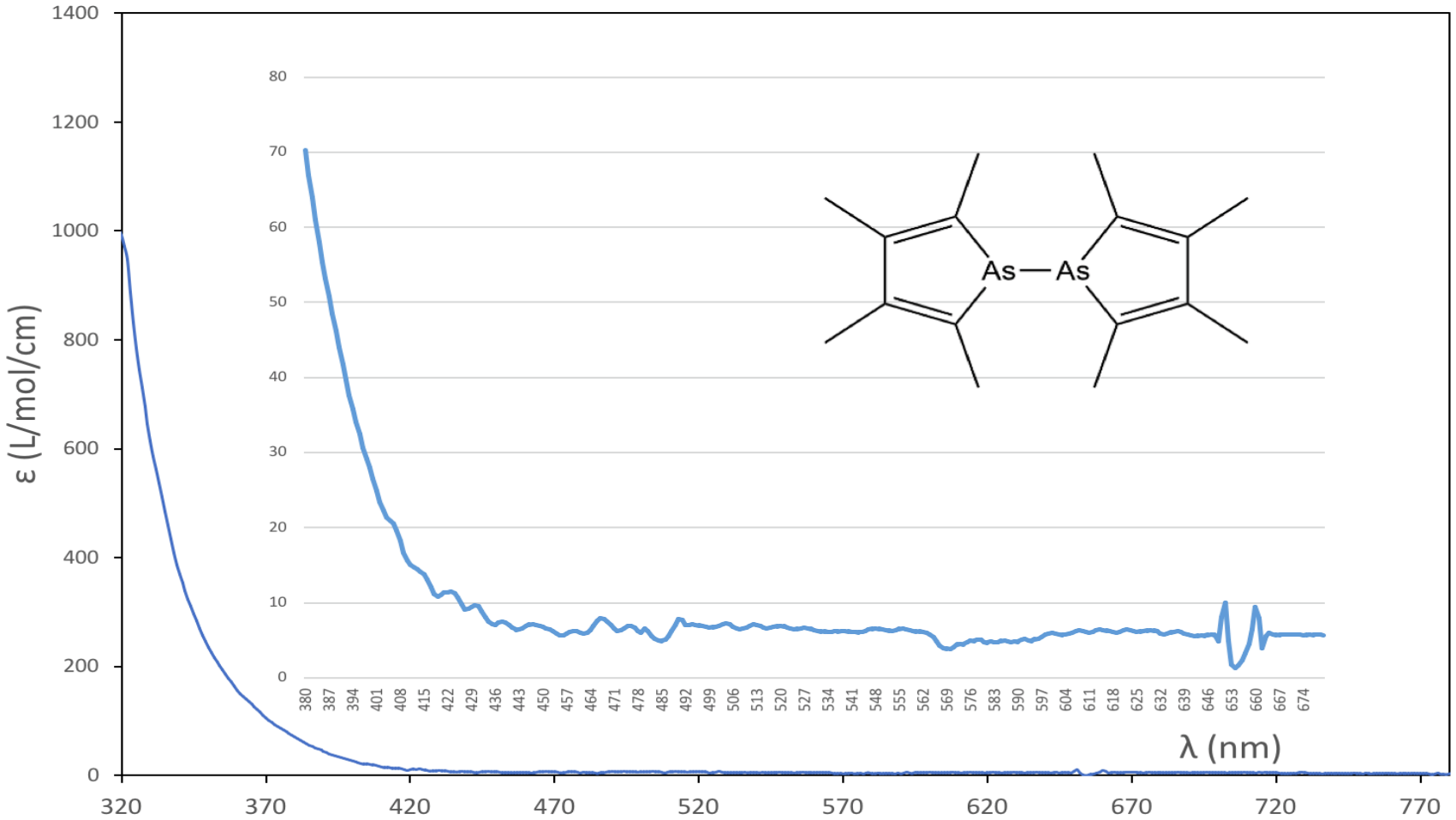



**Figure S38.** Electronic spectrum of $(AsC_4Me_4)_2$ in hexane (2.7 mmol/L).