Electronic Supporting Information for *σ–Arsolido complexes* by Ryan M. Kirk and Anthony F. Hill

Crystal and Refinement Parameters

Parameter	2a	2b	2c	2d	2e	3a	endo-6	$ClAsC_4Me_2{}^tBu_2$
Empirical Formula	$C_{36}H_{25}AsMoO_3 \cdot C_6H_6$	$C_{36}H_{25}AsO_3W \cdot C_6H_6$	$C_{16}H_{17}AsMoO_3$	$C_{16}H_{17}AsO_3W$	$C_{17}H_{21}AsMoO_3Si$	$C_{35}H_{25}AsFeO_2$	$C_{16}H_{24}As_2Cl_2$	$C_{14}H_{24}AsCl$
M_w/gmol^{-1}	754.53	842.44	428.15	516.06	472.29	608.32	437.09	302.70
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space Group (No.)	*P*bca (#16)	*P*bca (#16)	*P*–1 (#2)	$P2_1/c$ (#14)	$P2_12_12_1$ (#19)	C2/c (#15)	$P2_1/n$ (#14)	*P*–1 (#2)
a/Å	18.87950(10)	18.88750(10)	7.6134(2)	7.66960(10)	6.65790(10)	20.34180(10)	14.355(4)	9.0412(3)
b/Å	15.39100(10)	15.38100(10)	7.7893(2)	28.8296(3)	13.0043(2)	15.50870(10)	9.7741(6)	11.8621(4)
c/Å	23.5717(2)	23.5386(2)	14.8554(6)	7.74520(10)	22.3782(5)	17.76510(10)	20.102(5)	14.5361(5)
α/deg	90	90	78.829(3)	90	90	90	90	80.871(3)
β/deg	90	90	88.971(3)	106.6740(10)	90	91.4300(10)	141.48(5)	81.879(3)
γ/deg	90	90	72.297(2)	90	90	90	90	77.842(3)
V/Å^3	6849.33(8)	6838.17(8)	822.56(5)	1640.54(4)	1937.53(6)	5602.70(6)	1756.7(14)	1495.27(9)
Z	8	8	2	4	4	8	4	4
Crystal Dimensions/mm	0.197/0.093/0.062	0.283/0.119/0.043	0.193/0.165/0.095	0.179/0.126/0.056	0.414/0.077/0.066	0.222/0.159/0.105	0.37/0.261/0.222	0.321/
Crystal Description	Yellow prism	Yellow prism	Orange prism	Orange plate	Orange needle	Orange prism	Colourless prism	Yellow needle
D_{calc}/Mgm^{-3}	1.463	1.637	1.729	2.089	1.619	1.442	1.653	1.345
μ/mm^{-1}	Cu: 4.508	Cu: 7.639	Cu: 8.814	Cu: 15.349	Cu: 8.116	Cu: 5.863	Mo: 4.098	Cu: 4.495
Total reflections	45669	27682	9139	28908	7373	34915	12271	15607
Unique reflections	6909	6869	9139	3293	3665	5650	5547	5973
R_{int}	0.0241	0.0247	0.0441	0.0231	0.0269	0.0178	0.0320	0.0312
GOF on F^2	1.032	1.037	1.114	1.224	1.036	1.033	1.036	1.028
R_1,	0.0272	0,0247	0.0391	0.0203	0.0264	0.0195	0.0377	0.0285
ωR_2	0.0746	0.0636	0.1121	0.0488	0.0617	0.0525	0.0811	0.0722
Largest diff. peak /eÅ^{-1}	-0.65	-0.68	-0.95	-0.77	-0.45	-0.21	-0.70	0.50
Largest diff. hole/eÅ^{-1}	0.60	0.69	0.59	0.81	0.40	0.26	0.89	0.36
Refined parameters	424	424	195	194	214	418	189	305
CCDC	2145356	2145353	2145355	2145363	2145352	2145354	2145384	2359530

Goodness-of-fit S = $[\Sigma\omega(Fo^2\text{-}Fc^2)^2/(n\text{-}p)]^{1/2}$, where n is the number of reflections and p the number of parameters. $R_1 = \Sigma \| Fo | - | Fc \| / \Sigma | Fo |$, $\omega R_2 = [\Sigma[\omega(Fo^2 - Fc^2)^2]/\Sigma[\omega(Fo^2)^2]]^{1/2}$

Selected Spectra

1 Cl–AsC$_4$Ph$_4$

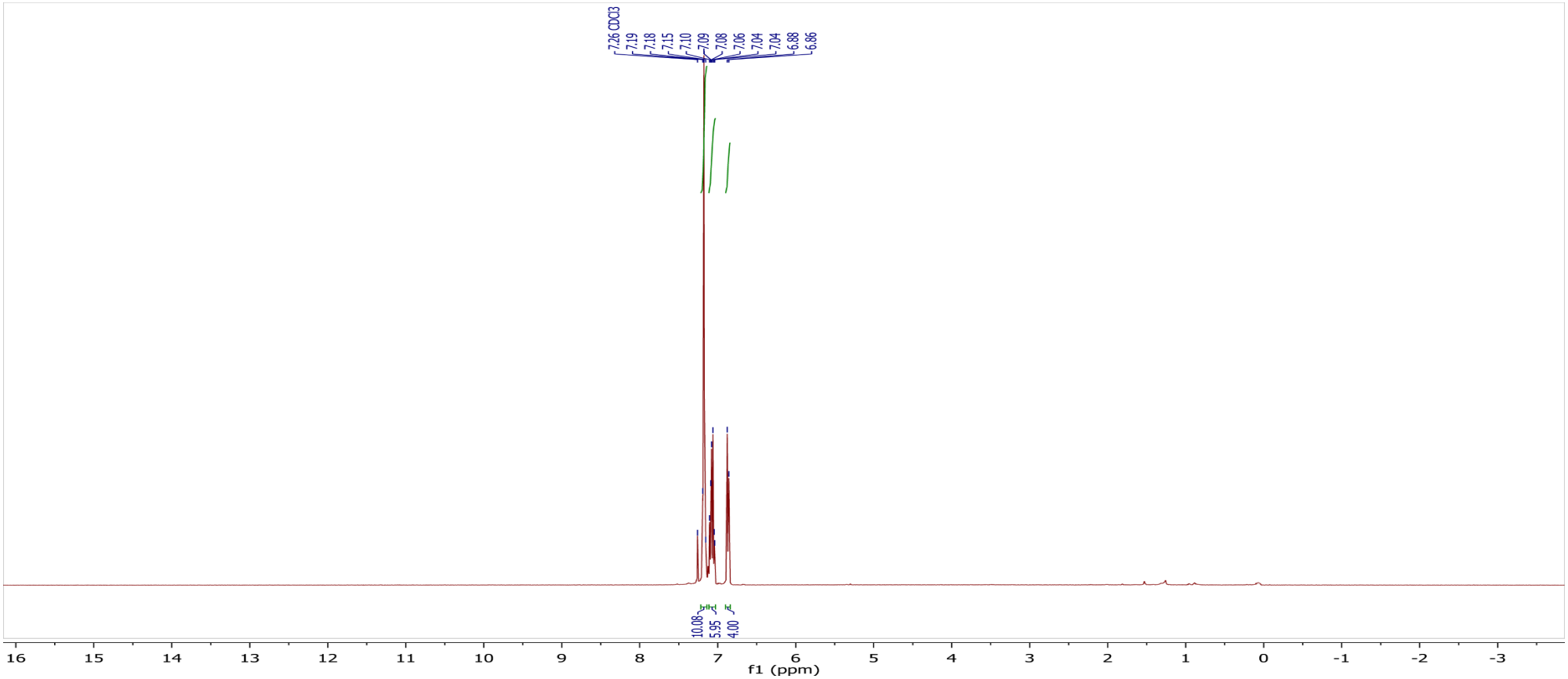

Figure S1. ^{1}H NMR Spectrum ($CDCl_3$, 295 K, 400 MHz, δ) of $ClAsC_4Ph_4$

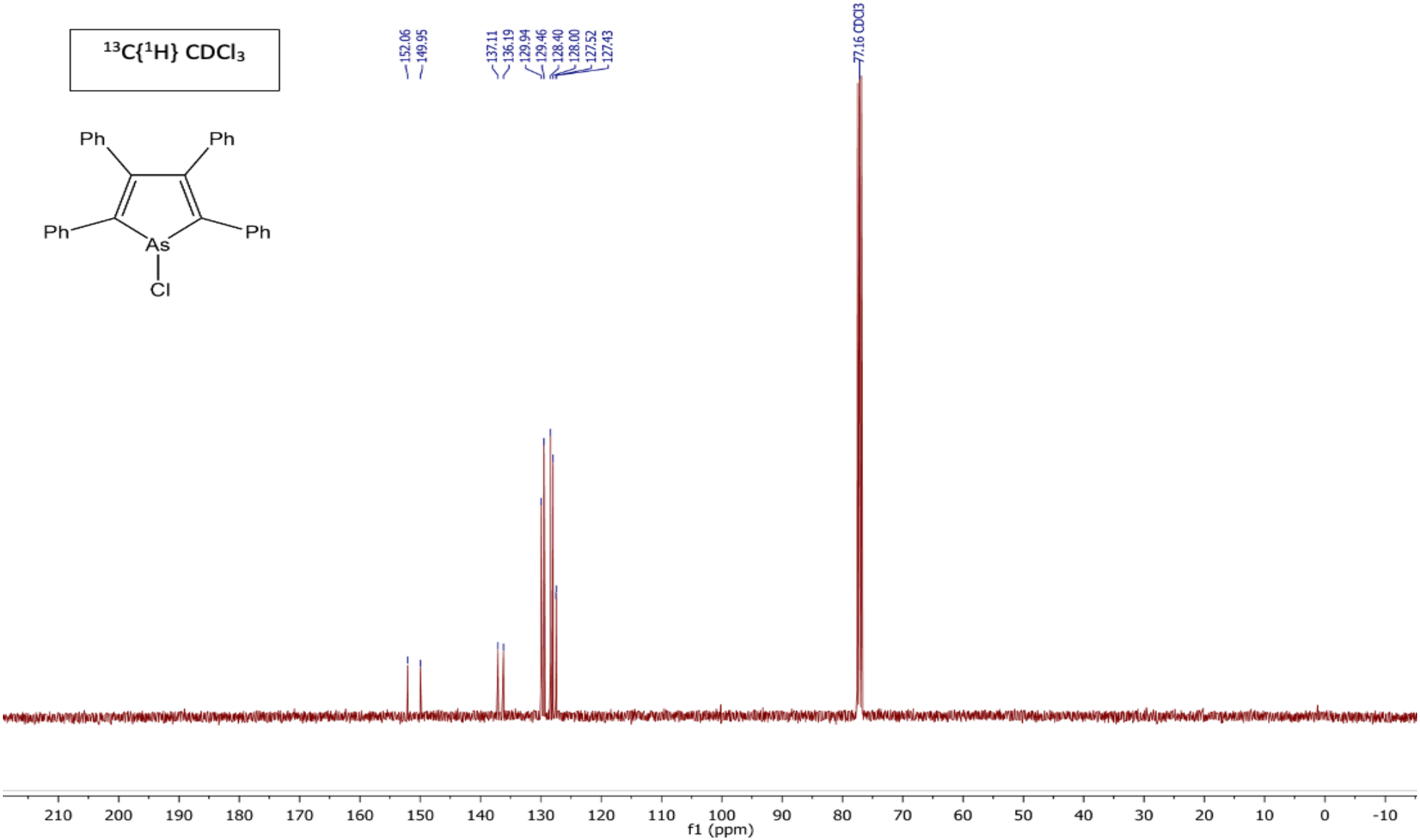

Figure S2. $^{13}C\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 295 K, 101 MHz, δ) of $ClAsC_4Ph_4$

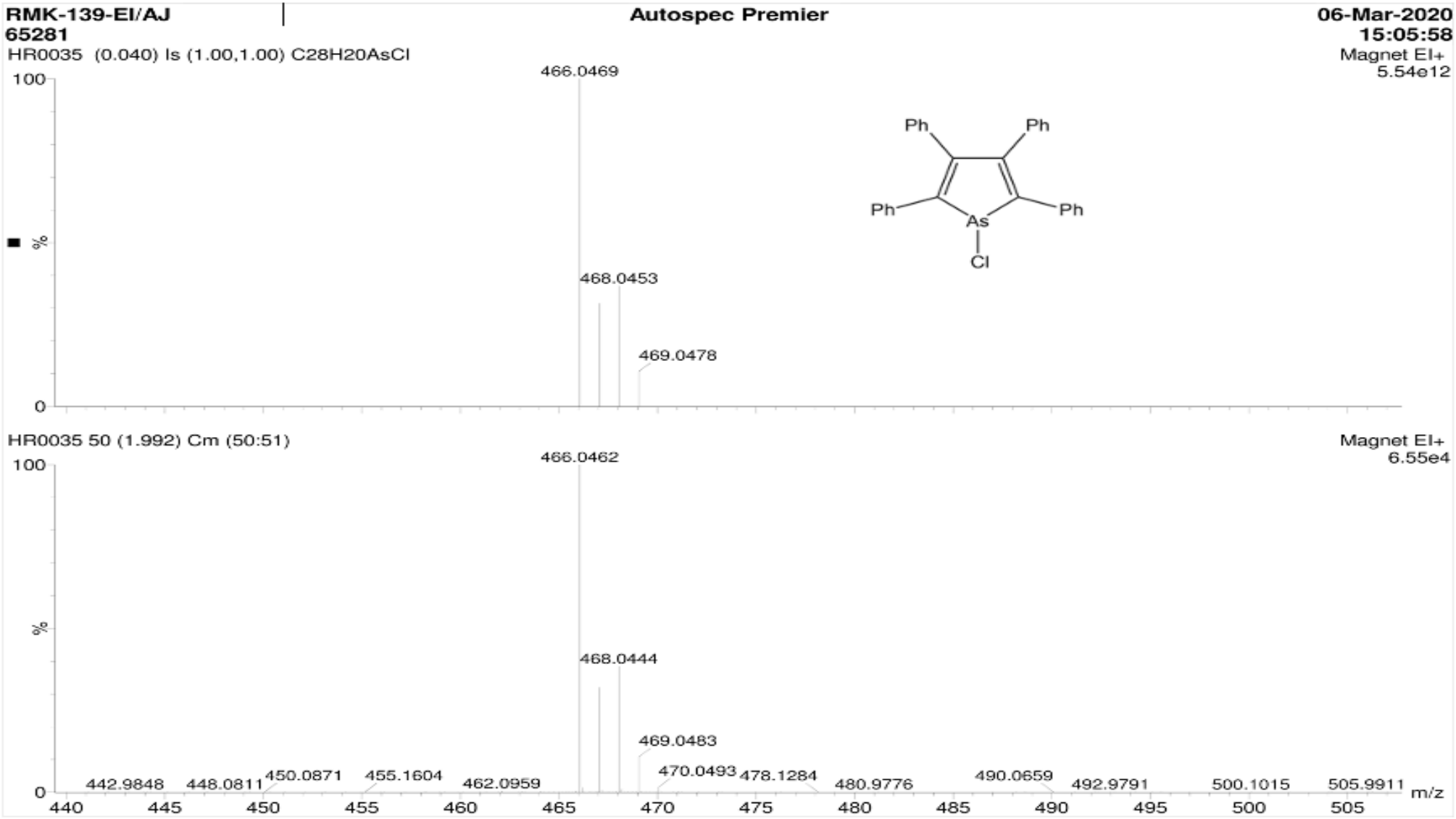

Figure S3. High Resolution Mass Spectrum (ESI-MS. MeCN) of $ClAsC_4Ph_4$

2 $[Mo(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (2a)

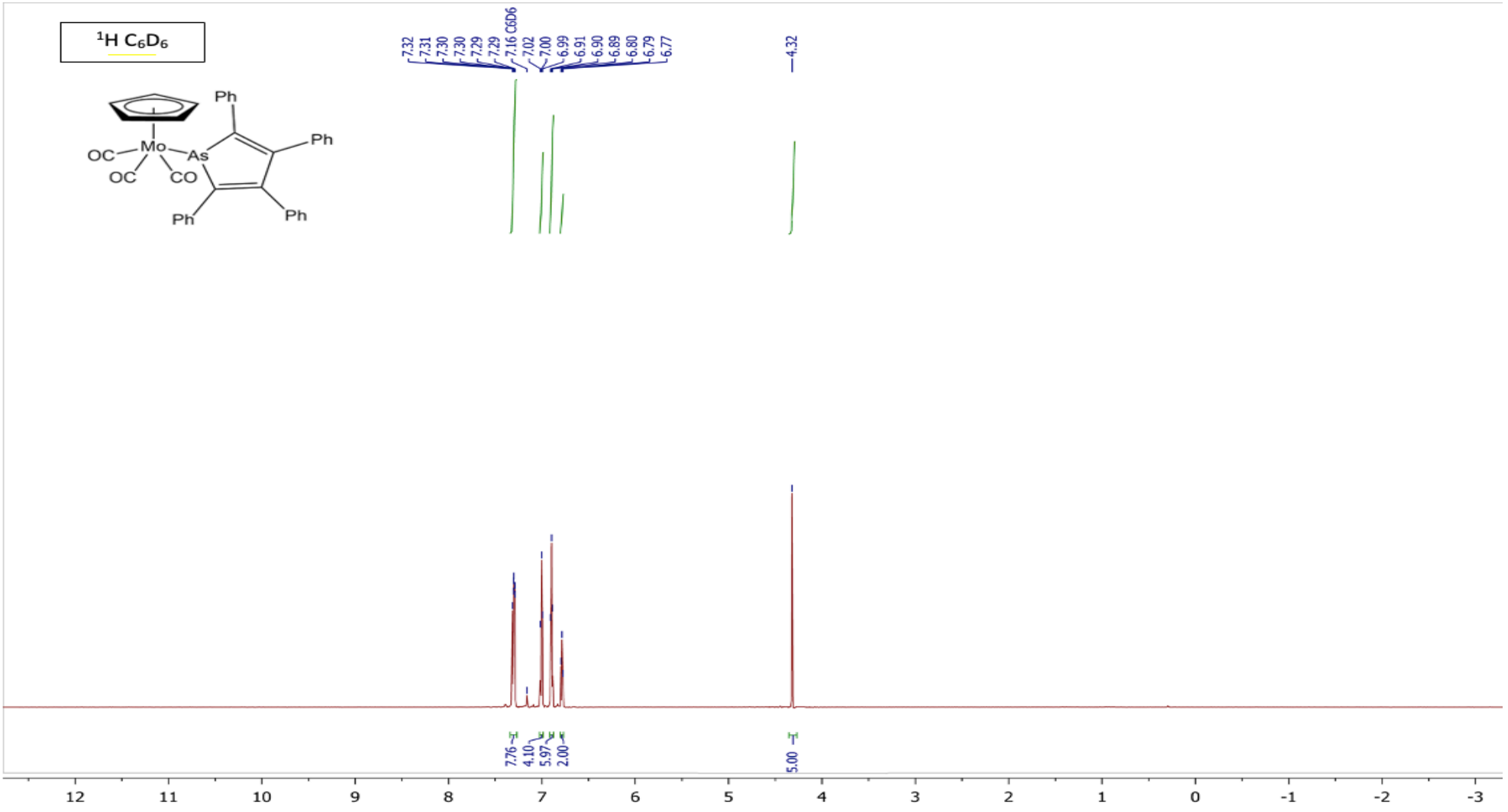

Figure S4. ^1H NMR Spectrum ($CDCl_3$, 295 K, 400 MHz, δ) of $[Mo(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2a**)

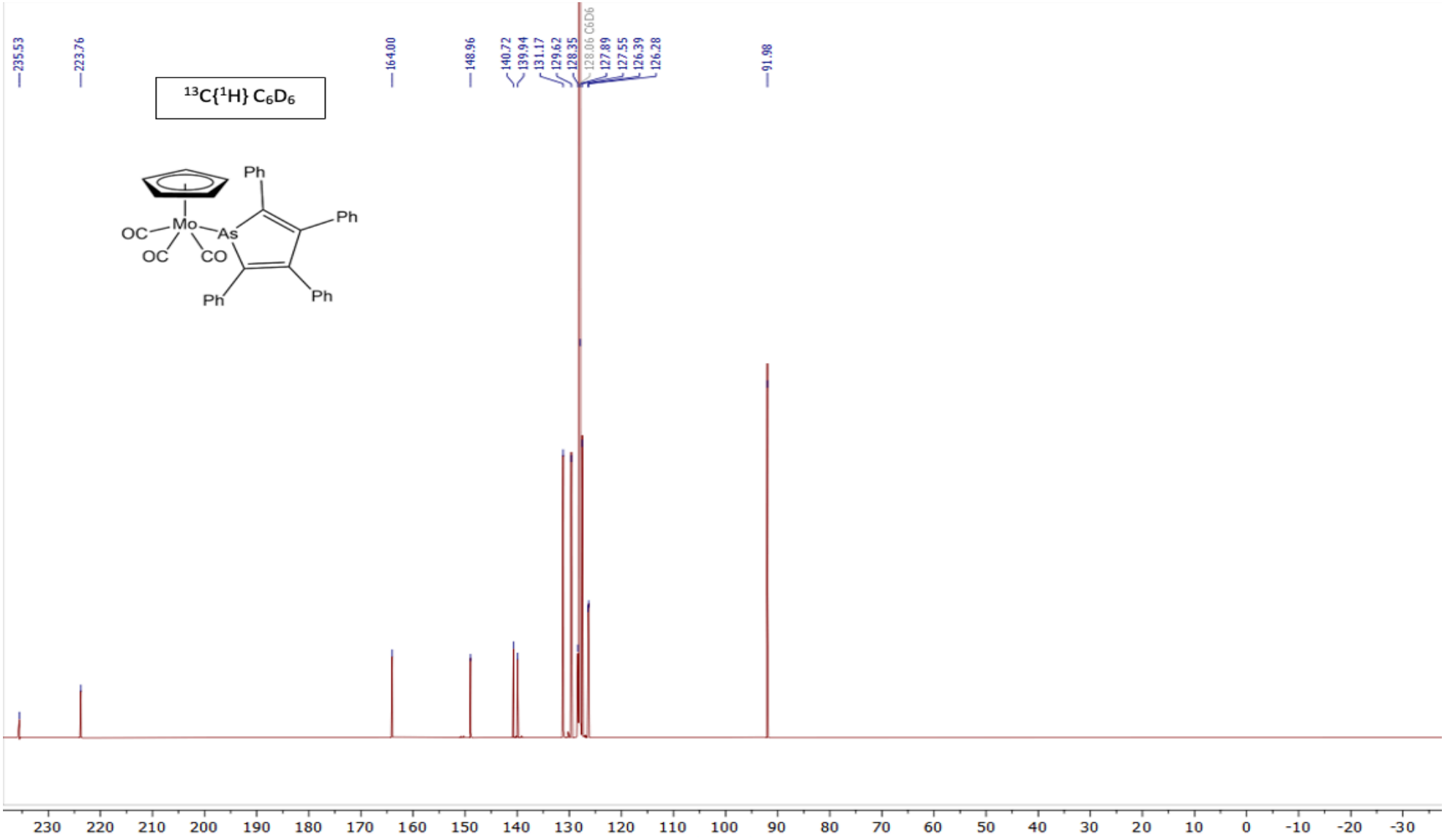

Figure S5. $^{13}C\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 295 K, 201 MHz, δ) of $[Mo(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2a**)

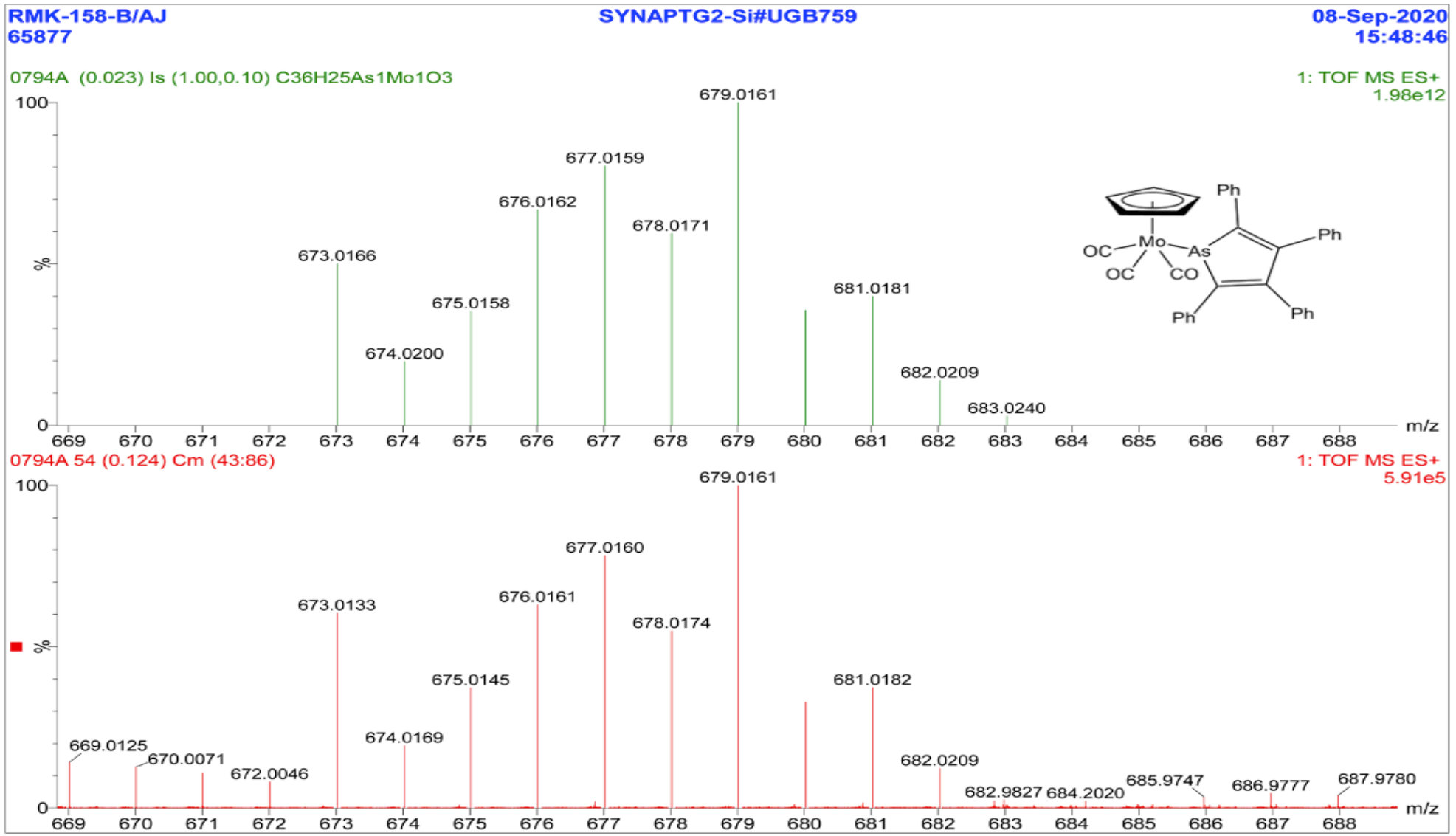

Figure S6. High Resolution Mass Spectrum (ESI-MS, MeCN) of $[Mo(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2a**)

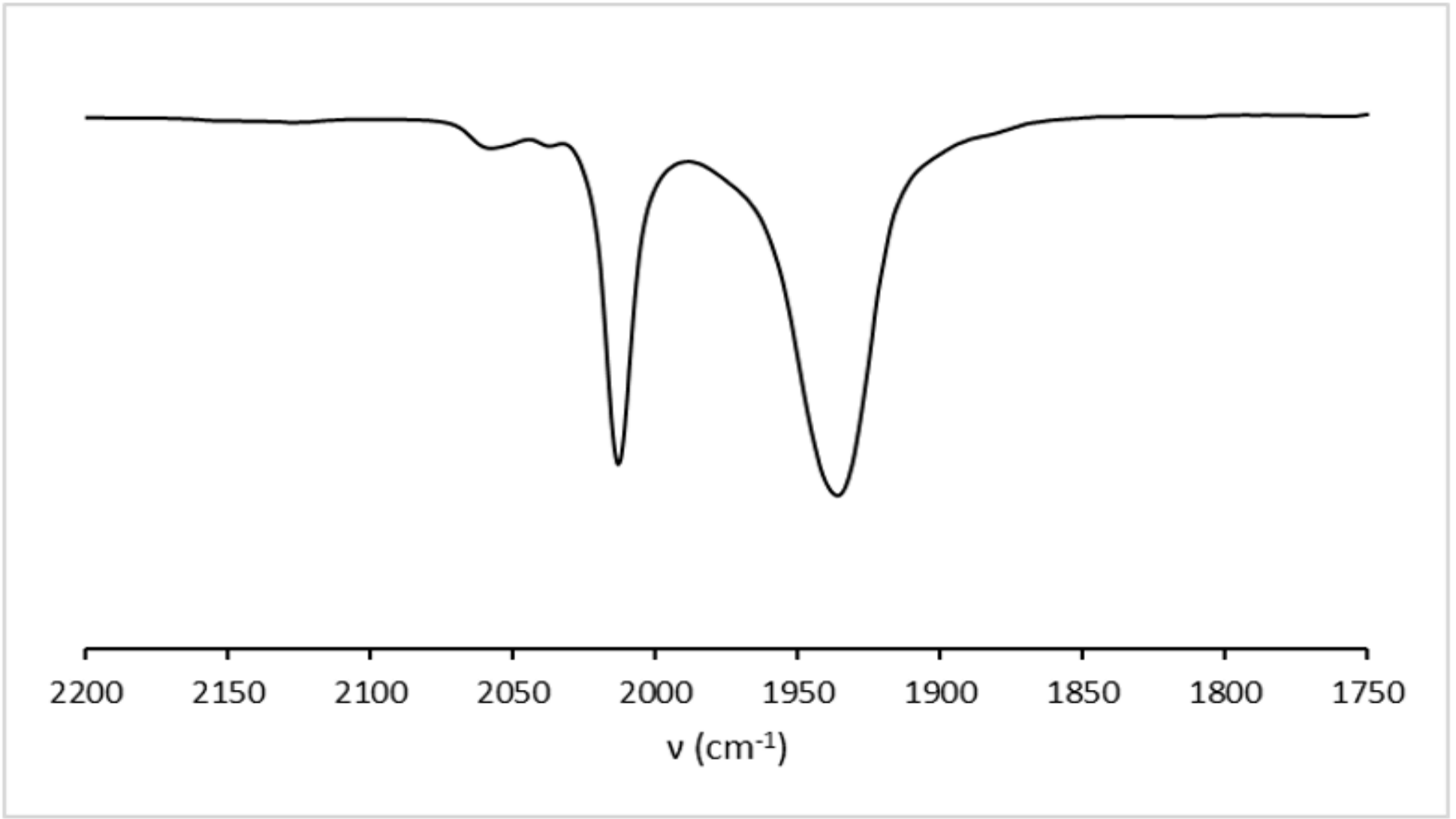

Figure S7. IR Spectrum (CH_2Cl_2, 295 K, ν cm^{-1}) of $[Mo(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2a**)

3 $[W(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (2b)

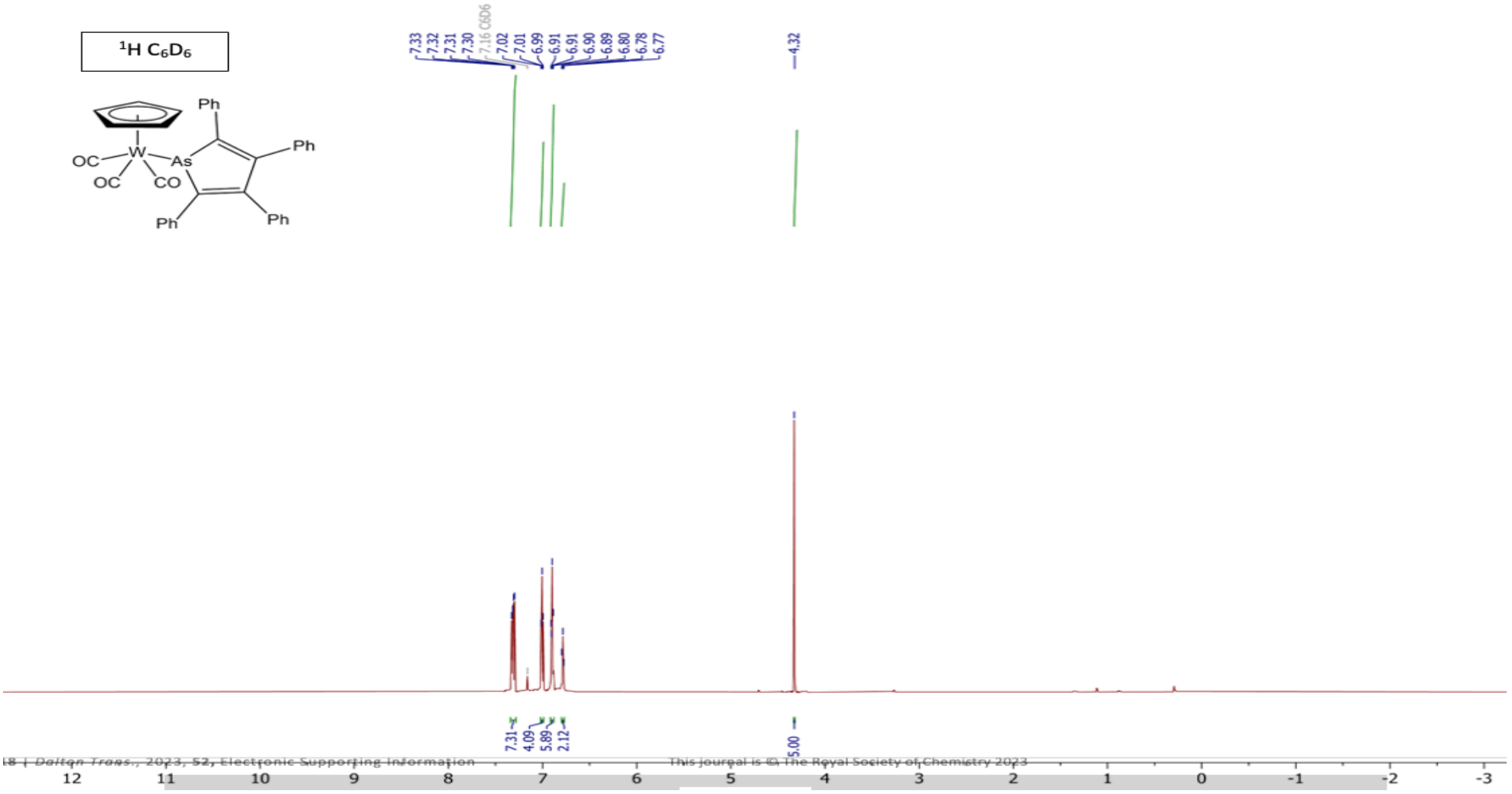

Figure S8. ^1H NMR Spectrum ($CDCl_3$, 295 K, 400 MHz, δ) of $[W(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2b**)

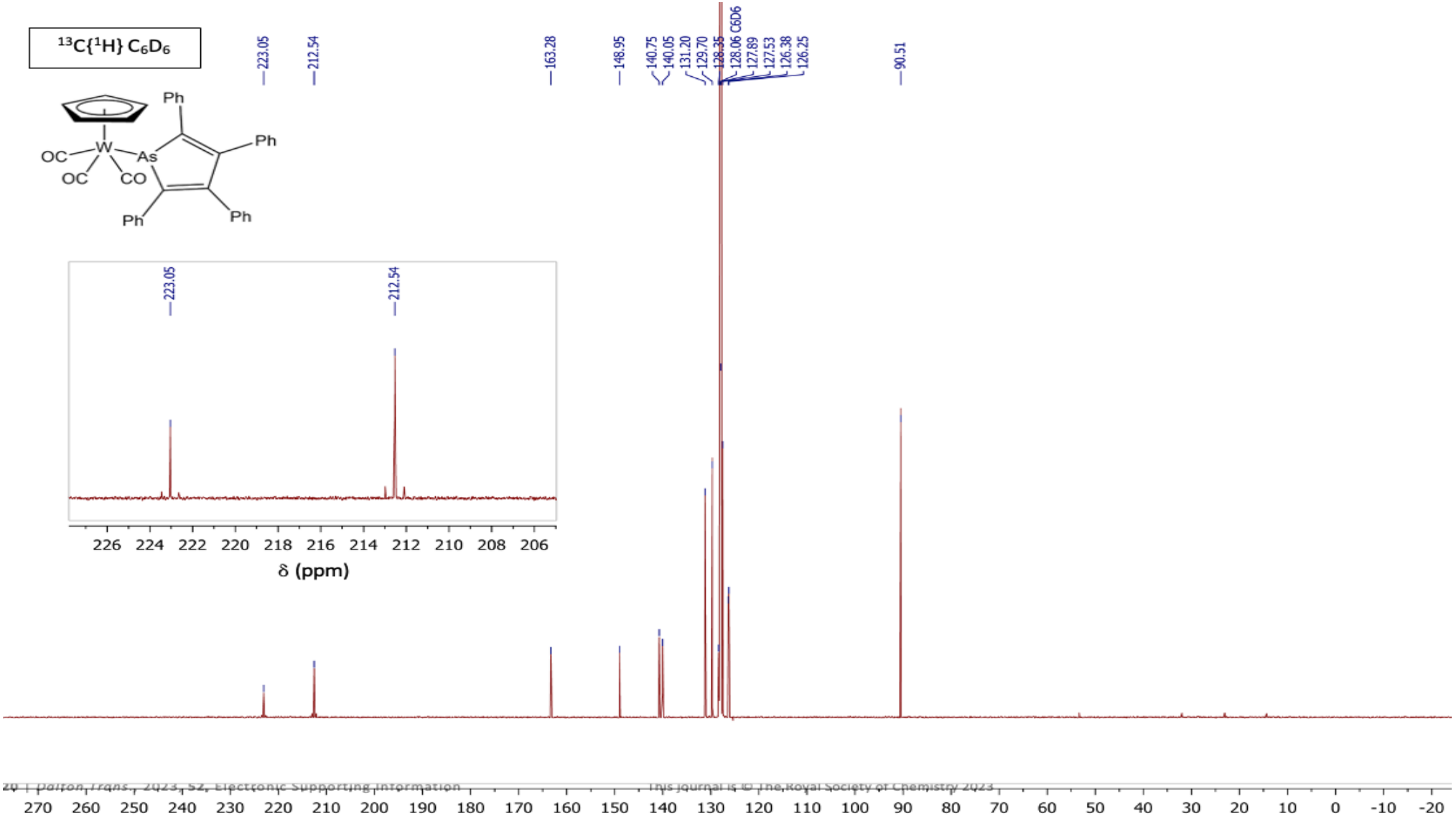

Figure S9. $^{13}C\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 295 K, 201 MHz, δ) of $[W(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2b**)

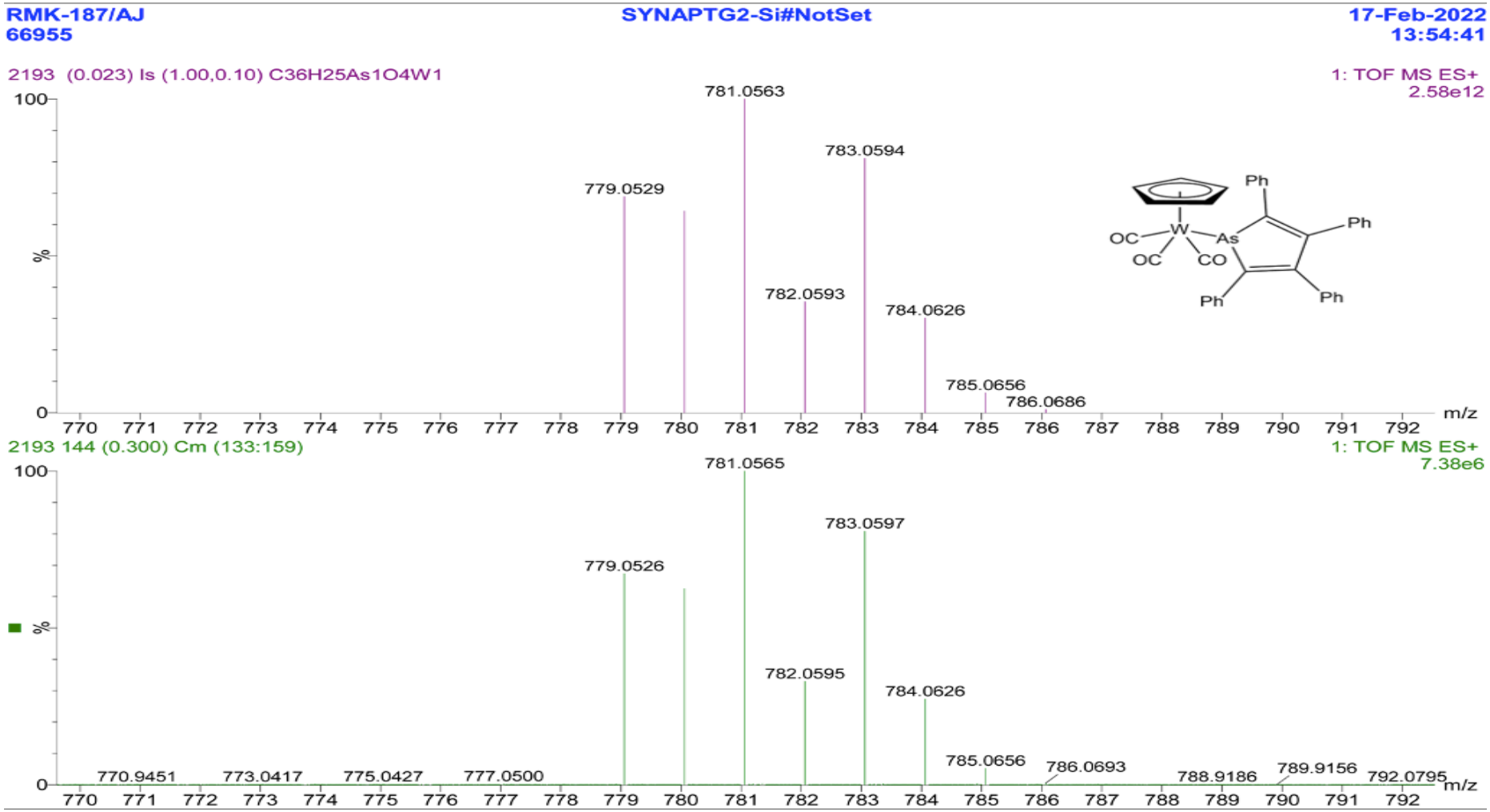

Figure S10. High Resolution Mass Spectrum (ESI-MS, MeCN) of $[W(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2b**)

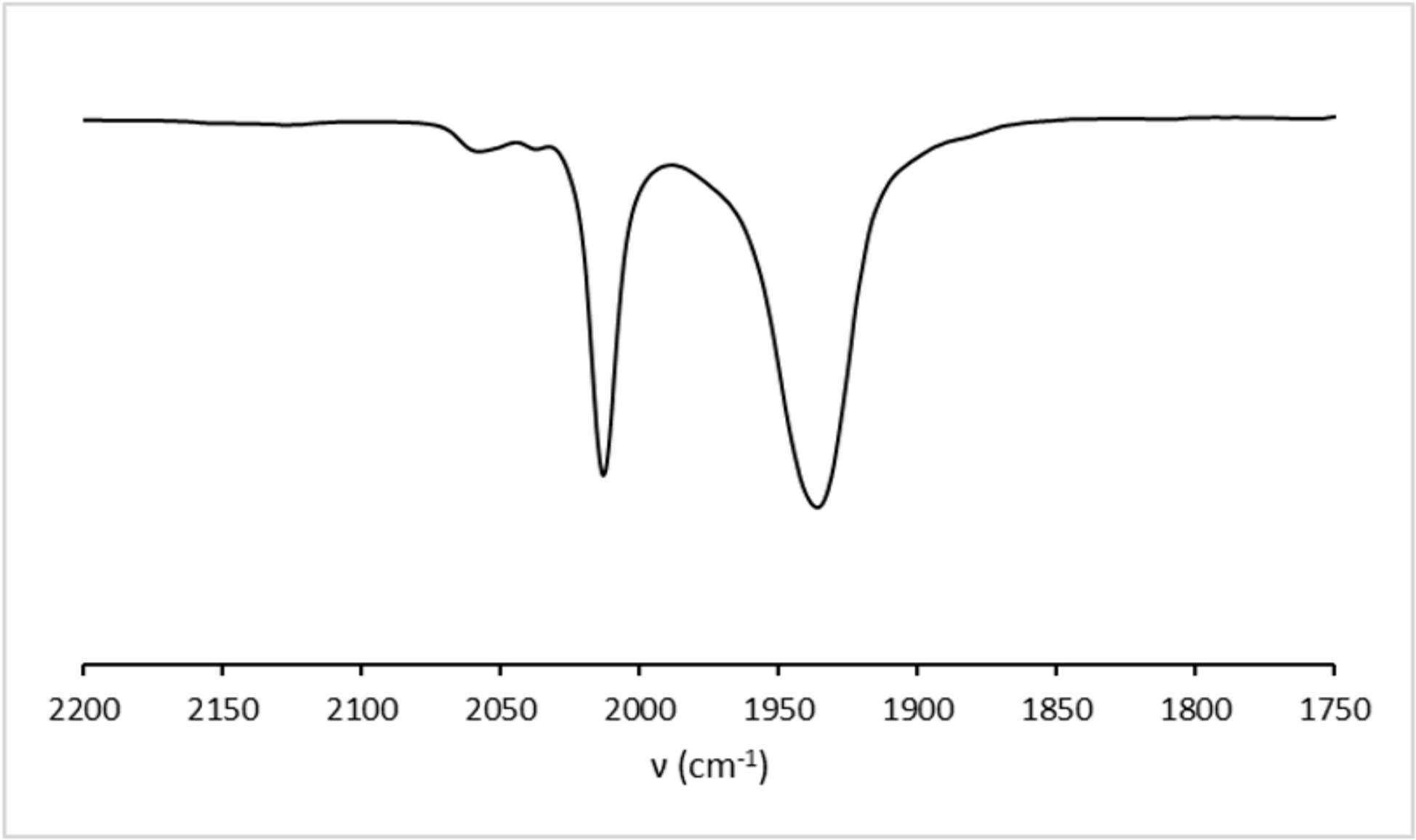

Figure S11. IR Spectrum (CH_2Cl_2, 295 K, ν cm^{-1}) of [W(AsC_4Ph_4)(CO)$_3$(η^5-C_5H_5)] (**2b**)

4 [Fe(AsC$_4$Ph$_4$)(CO)$_2$(η^5-C$_5$H$_5$)] (3)

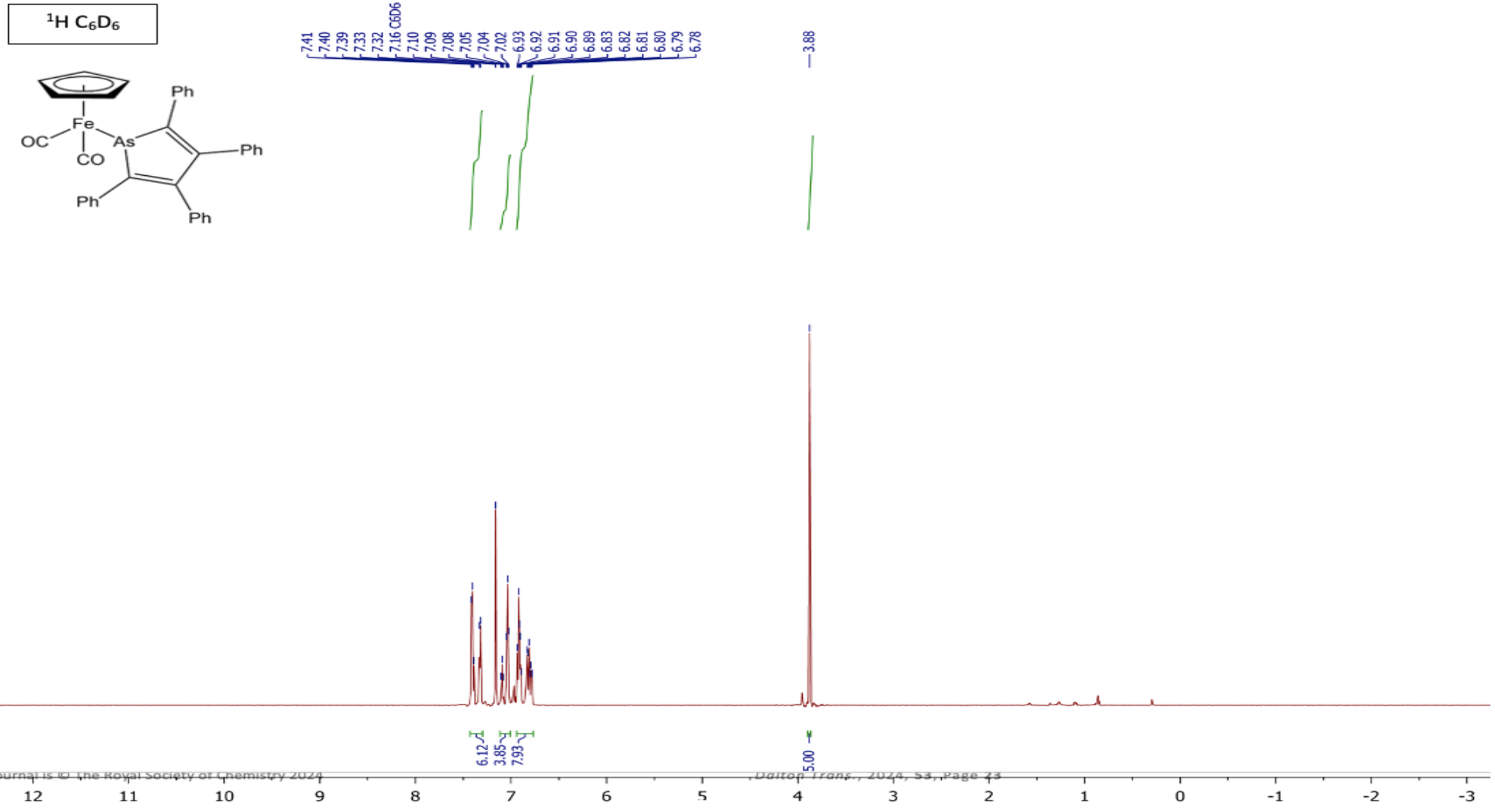

Figure S12. ^{1}H NMR Spectrum ($CDCl_3$, 295 K, 400 MHz, δ) of [Fe(AsC$_4$Ph$_4$)(CO)$_2$(η^5-C$_5$H$_5$)] (**3a**)

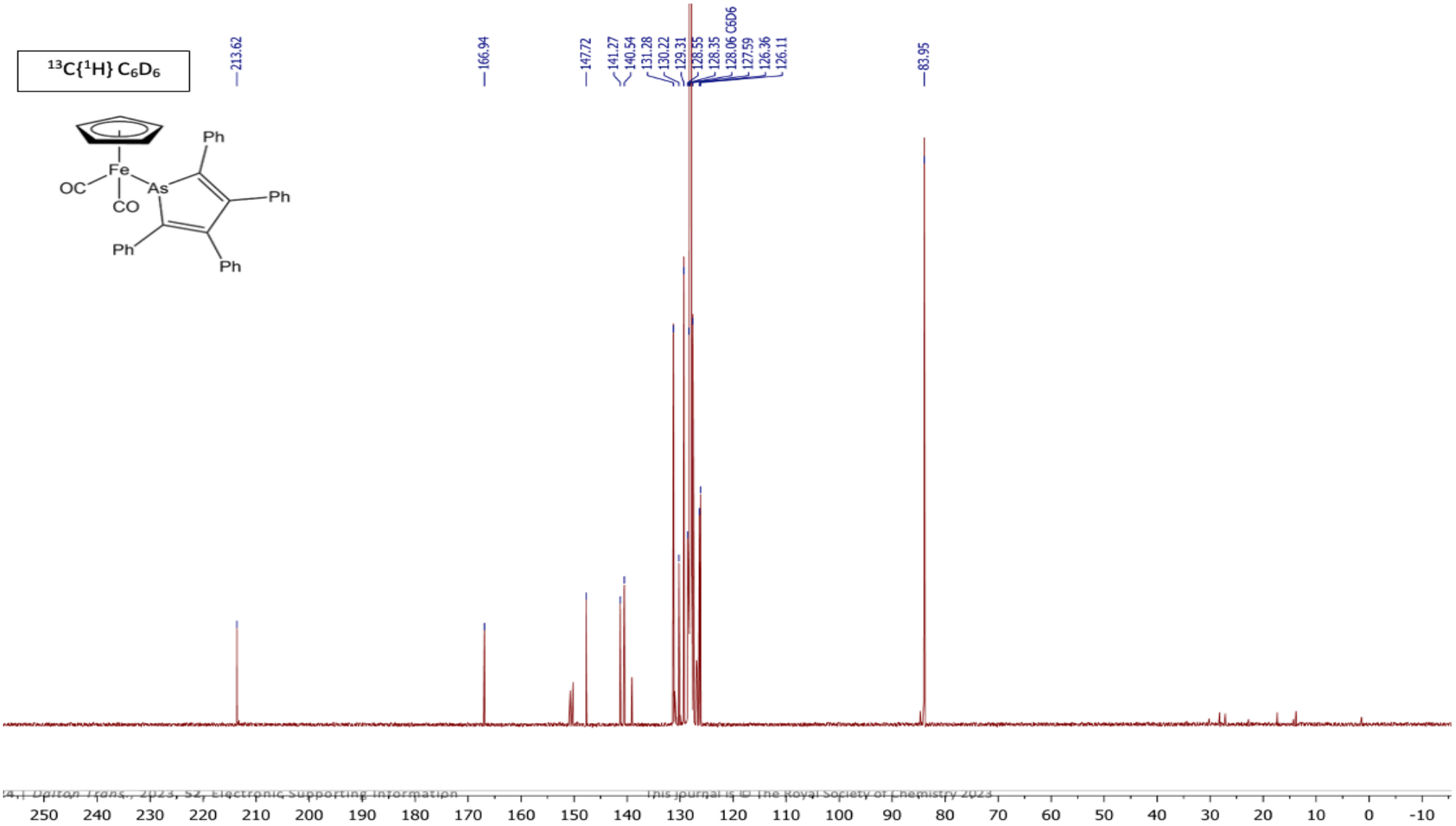

Figure S13. $^{13}C\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 295 K, 101 MHz, δ) of $[Fe(AsC_4Ph_4)(CO)_2(\eta^5\text{-}C_5H_5)]$ (3a)

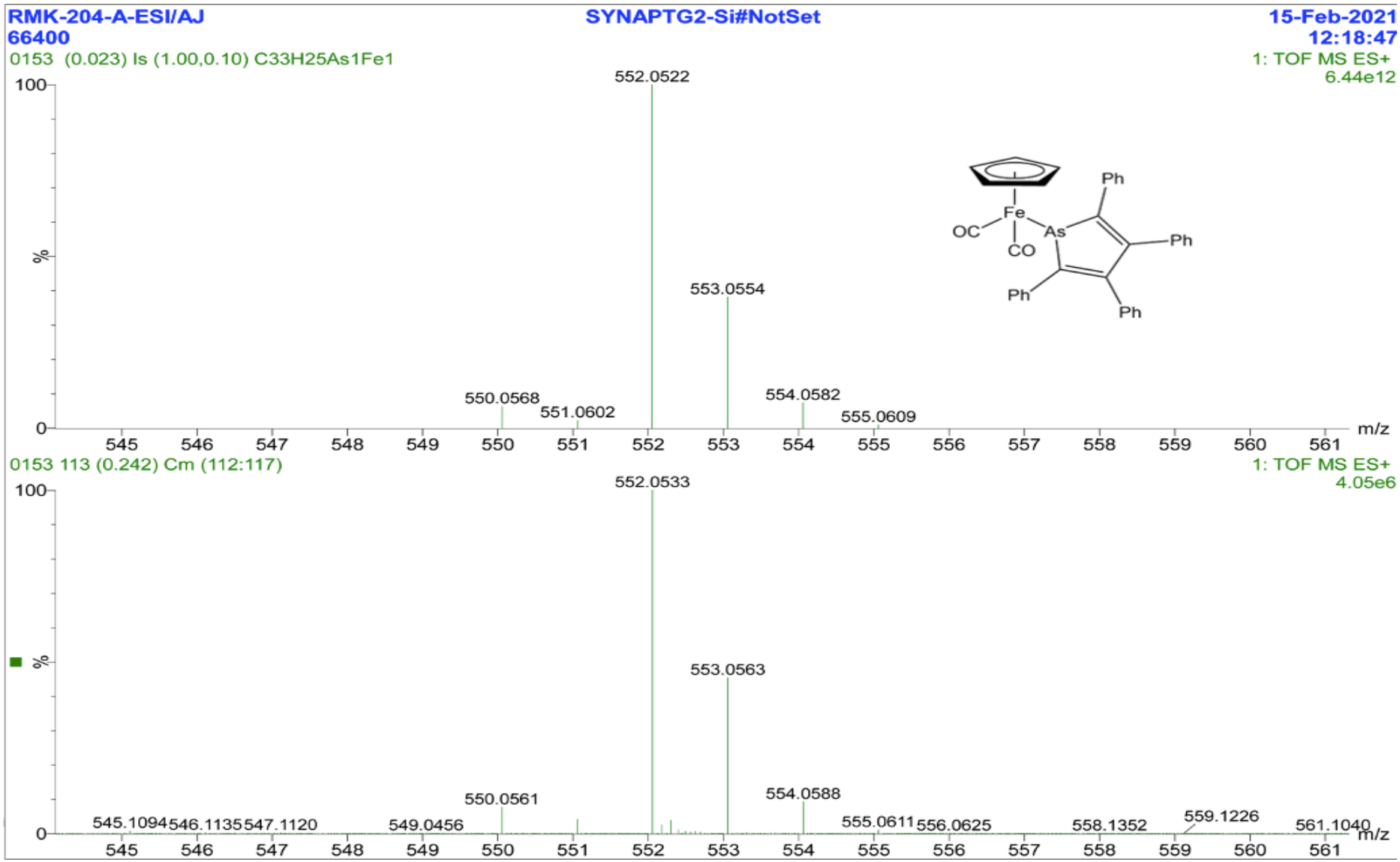

Figure S14. High Resolution Mass Spectrum (ESI-MS, MeCN) of $[Fe(AsC_4Ph_4)(CO)_2(\eta^5\text{-}C_5H_5)]$ (**3a**)

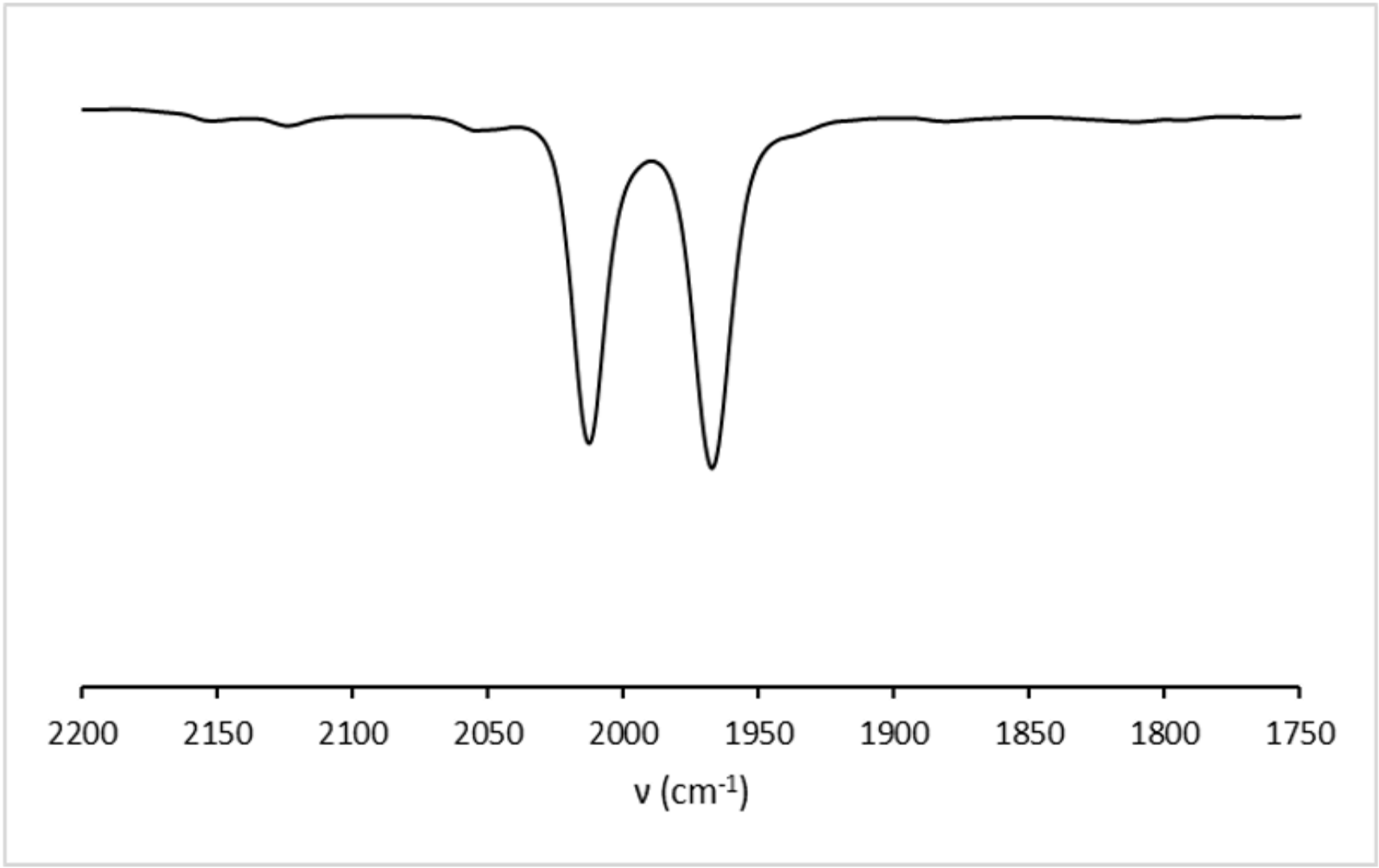

Figure S15. IR Spectrum (CH_2Cl_2, 295 K, ν cm^{-1}) of [$Fe(AsC_4Ph_4)(CO)_2(\eta^5\text{-}C_5H_5)$] (**3a**)

5 [Mo(AsC$_4$Me$_4$)(CO)$_3$(η^5-C$_5$H$_5$)] (2c)

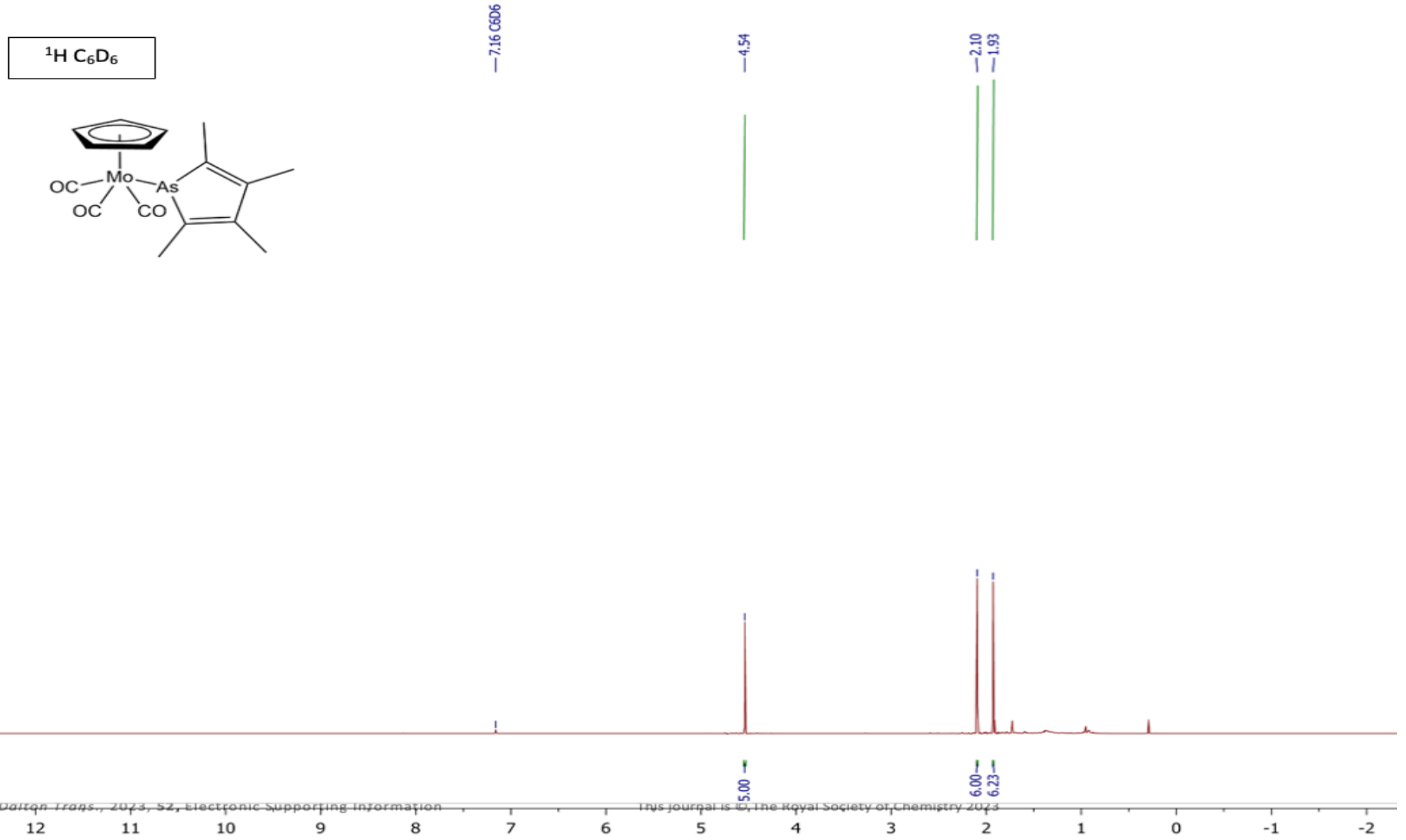

Figure S16. ^{1}H NMR Spectrum (CDCl$_3$, 295 K, 400 MHz, δ) of [Mo(AsC$_4$Me$_4$)(CO)$_3$(η^5-C$_5$H$_5$)] (**2c**)

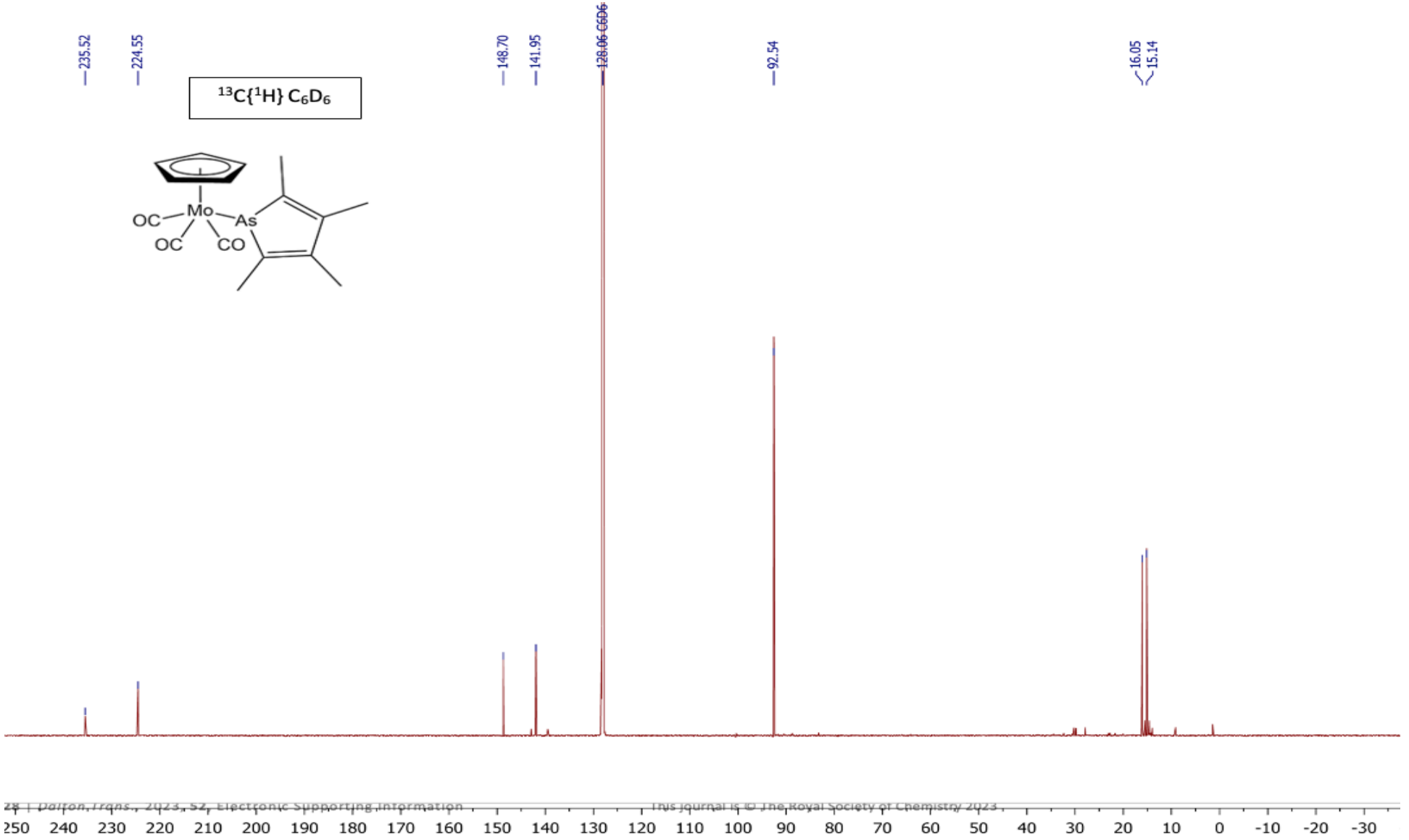

Figure S17. $^{13}C\{^{1}H\}$ NMR Spectrum (C_6D_6, 295 K, 202 MHz, δ) of $[Mo(AsC_4Me_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2c**)

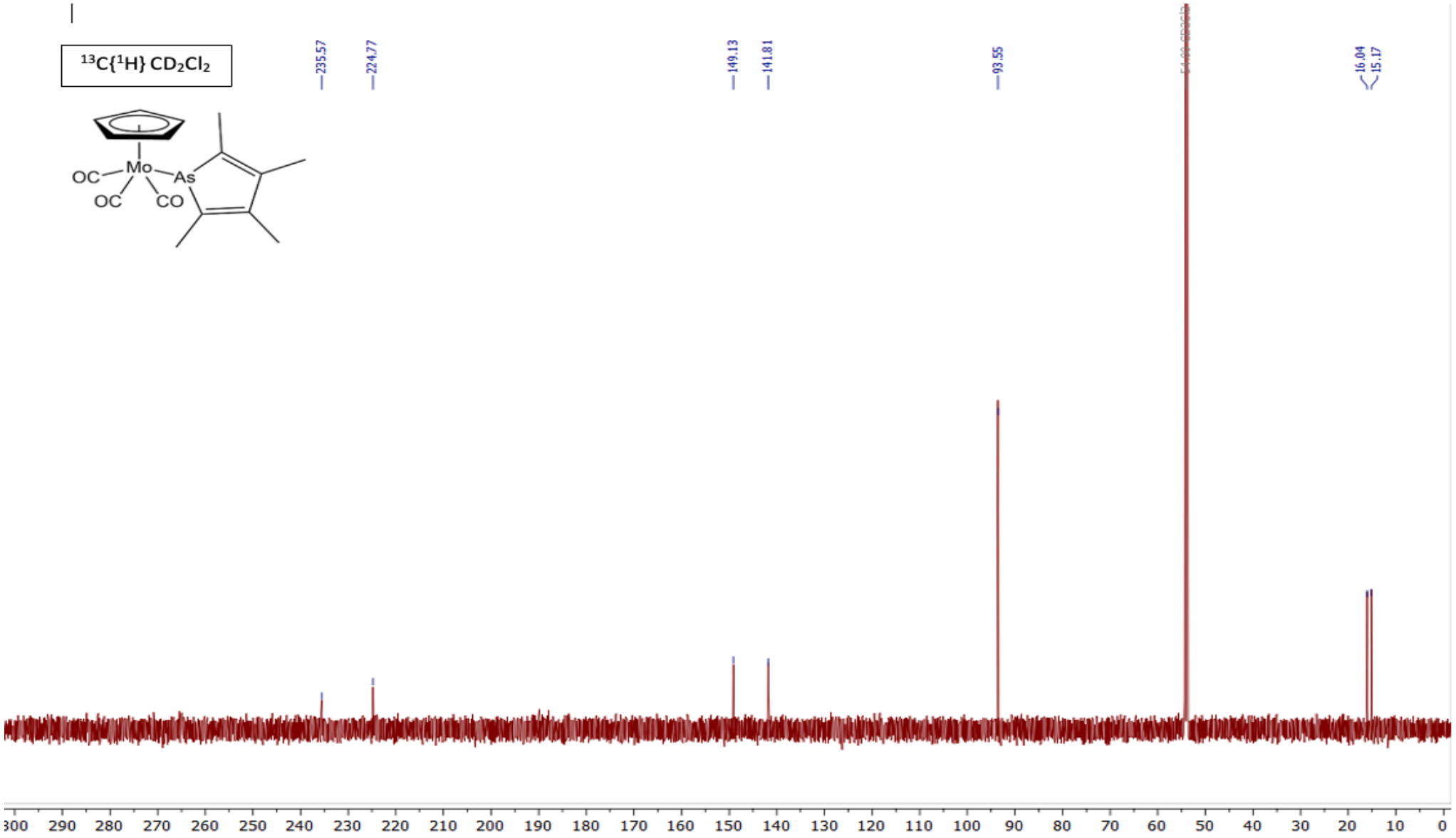

Figure S18. $^{13}C\{^{1}H\}$ NMR Spectrum (CD_2Cl_2, 295 K, 101 MHz, δ) of $[Mo(AsC_4Me_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2c**)

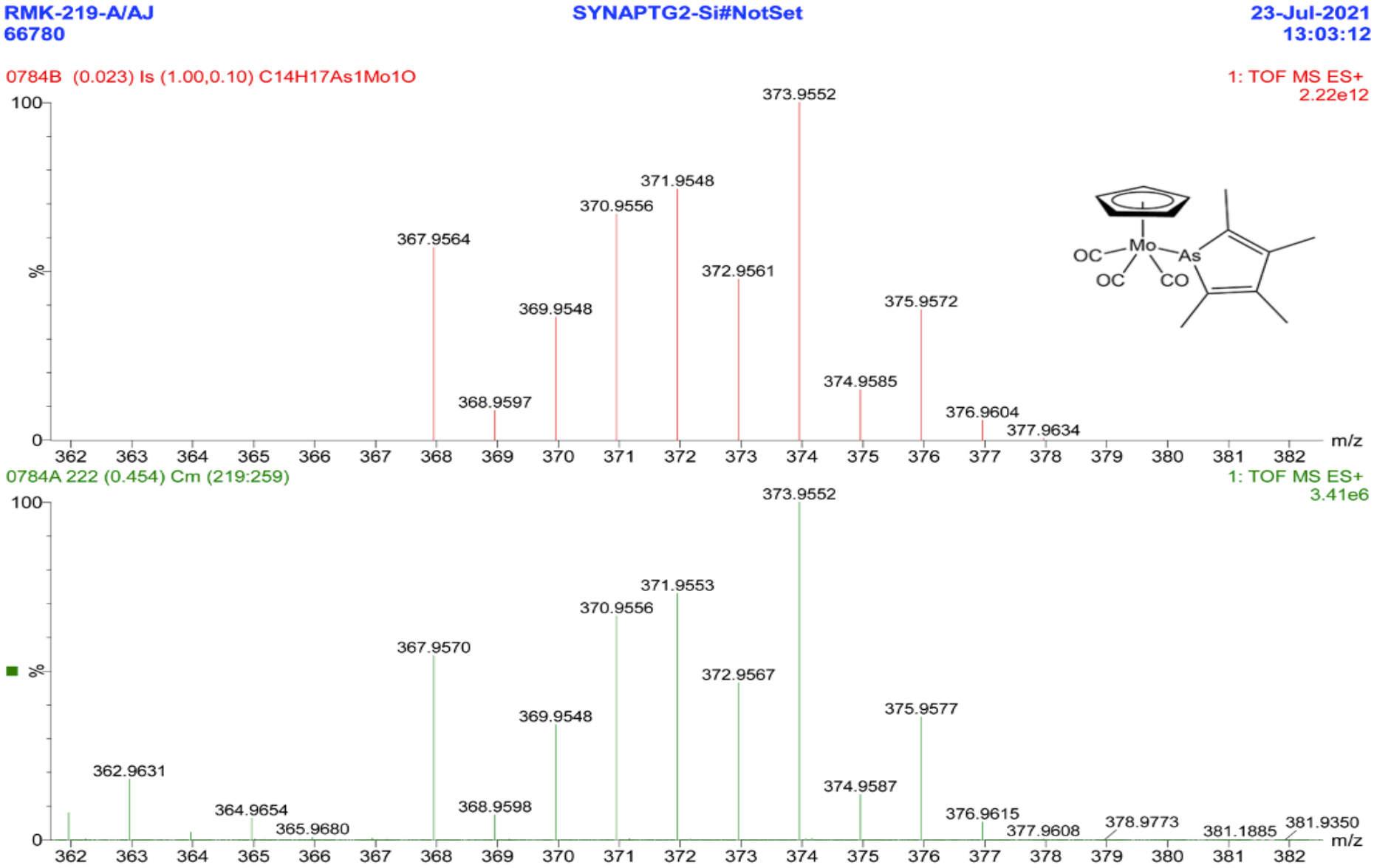

Figure S19. High Resolution Mass Spectrum (ESI-MS, MeCN) of $[Mo(AsC_4Me_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2c**)

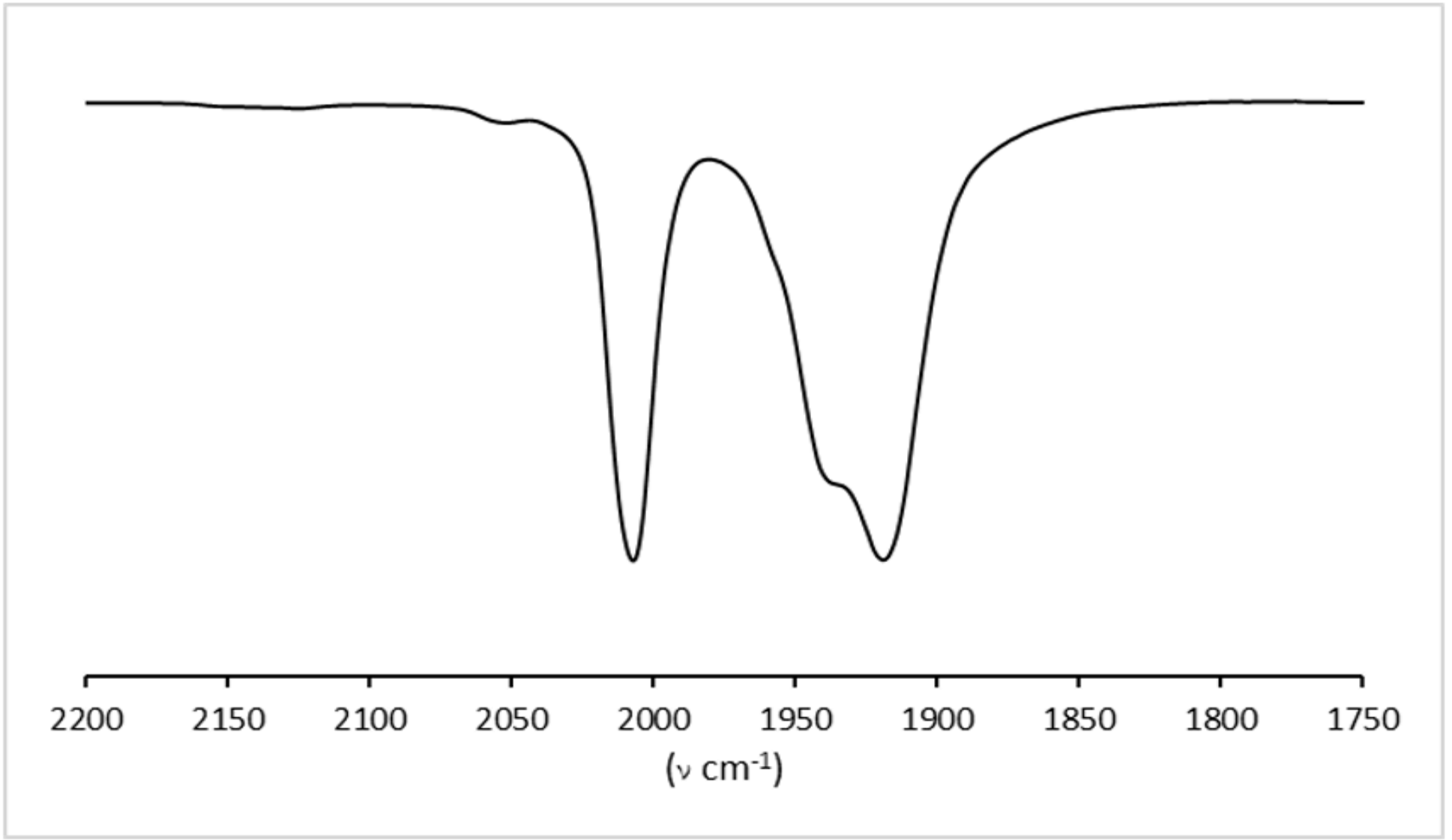

Figure S20. IR Spectrum (CH_2Cl_2, 295 K, ν cm^{-1}) of [Mo(AsC_4Me_4)(CO)$_3$(η^5-C_5H_5)] (**2c**)

6 [W(AsC$_4$Me$_4$)(CO)$_3$(η^5-C$_5$H$_5$)] (2d)

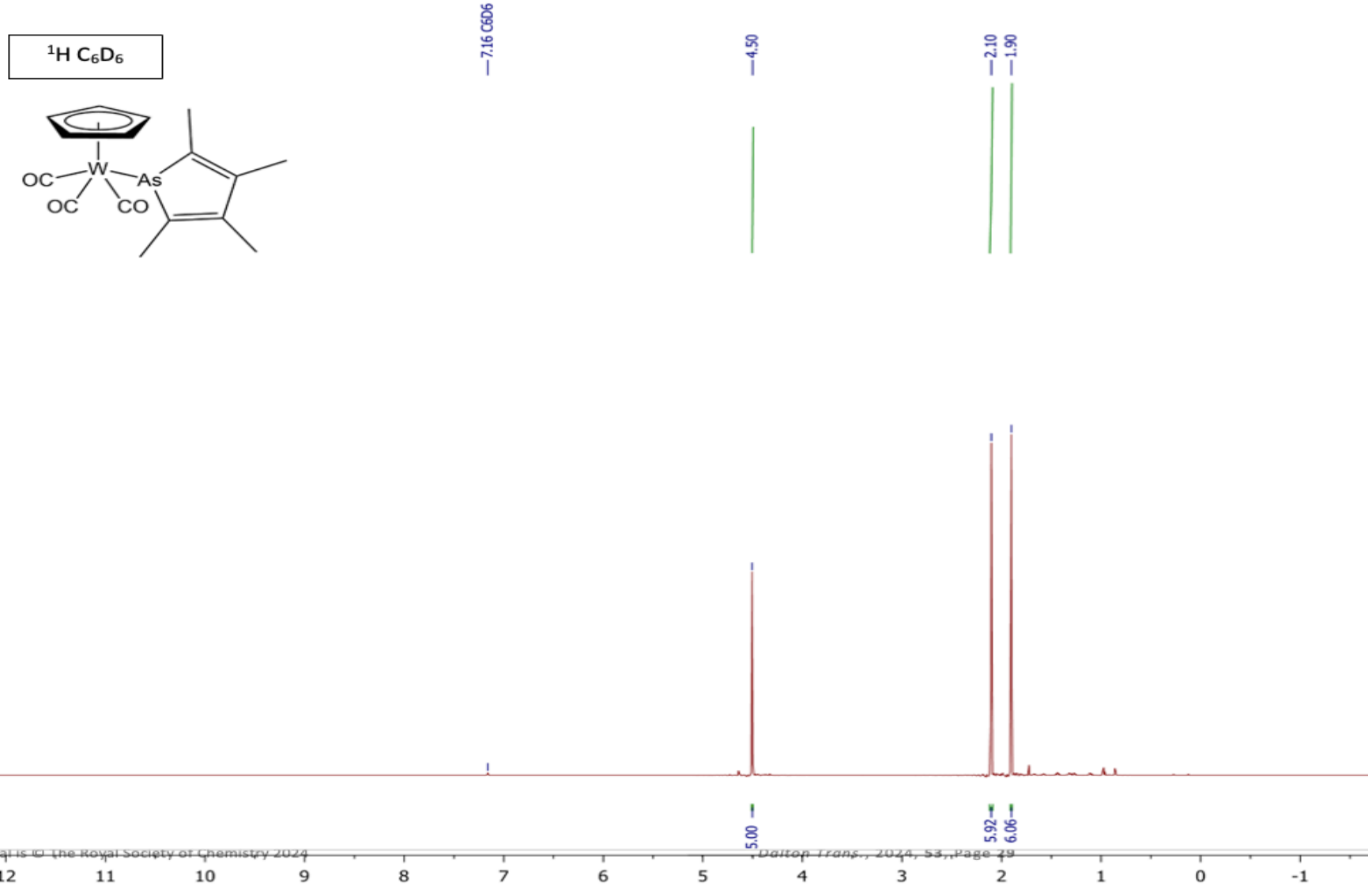

Figure S21. ^{1}H NMR Spectrum ($CDCl_3$, 295 K, 400 MHz, δ) of [W(AsC$_4$Me$_4$)(CO)$_3$(η^5-C$_5$H$_5$)] (**2d**)

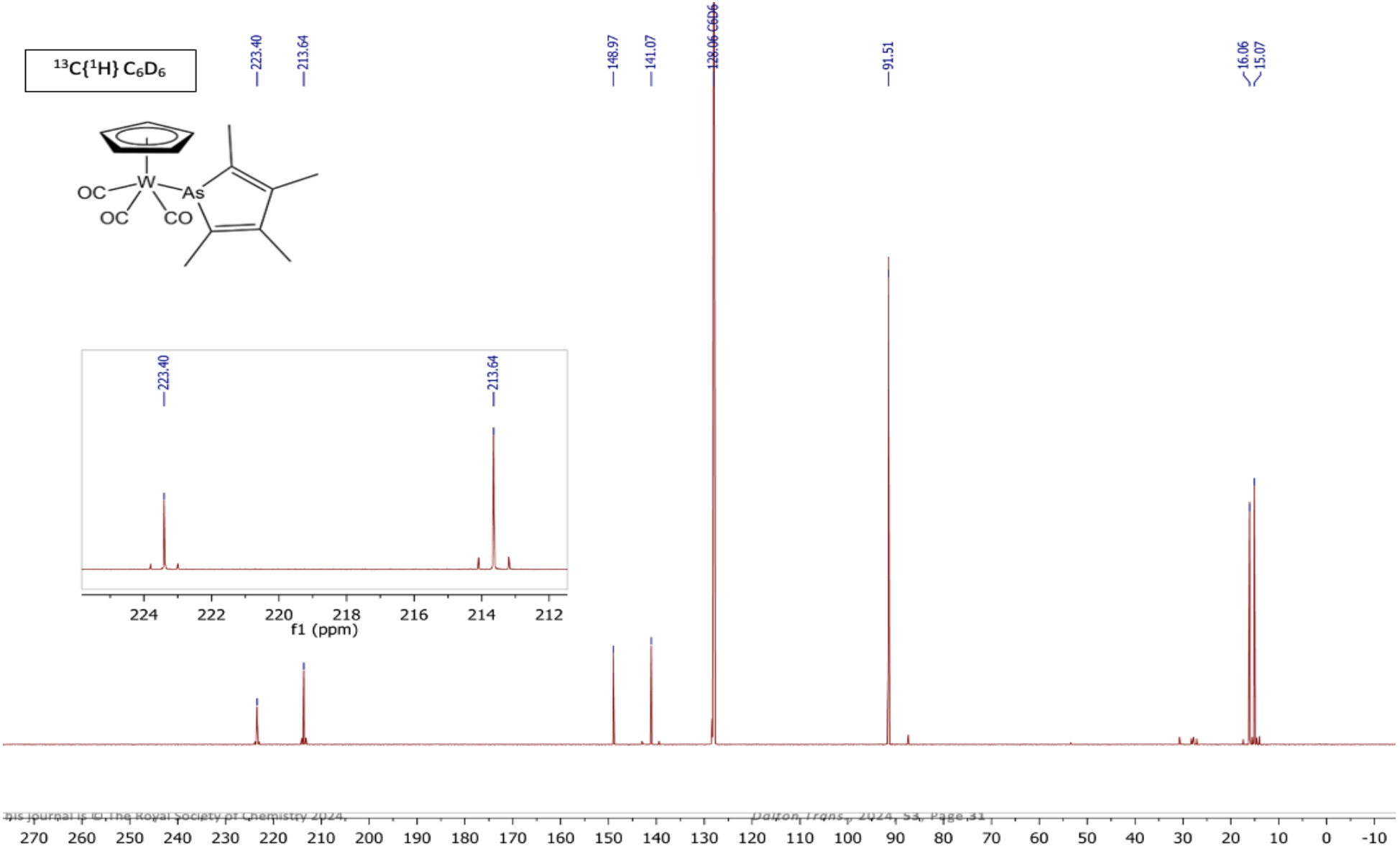

Figure S22. $^{13}C\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 295 K, 202 MHz, δ) of $[W(AsC_4Me_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2d**)

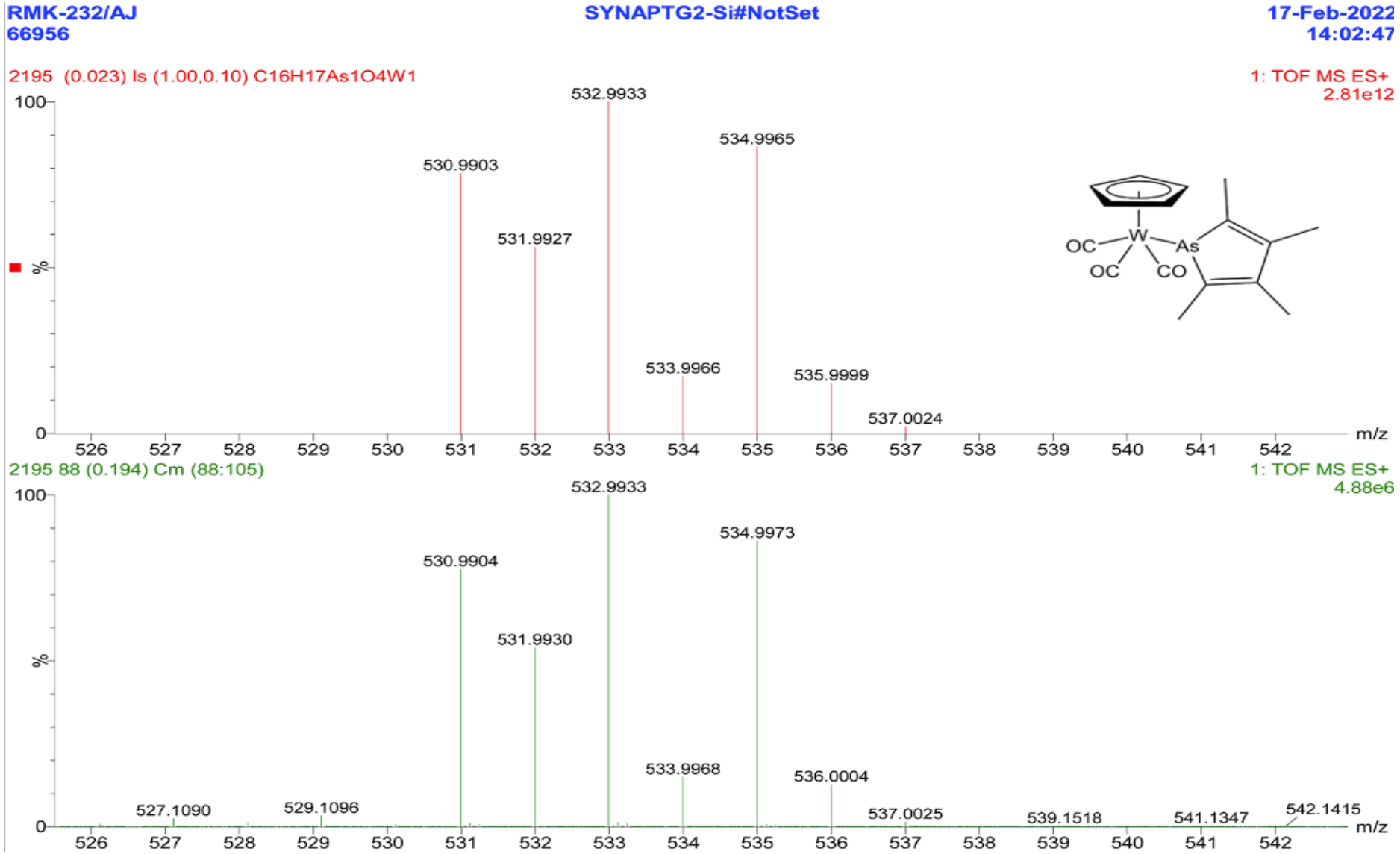

Figure S23. High Resolution Mass Spectrum (ESI-MS. MeCN) of $[W(AsC_4Me_4)(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2d**)

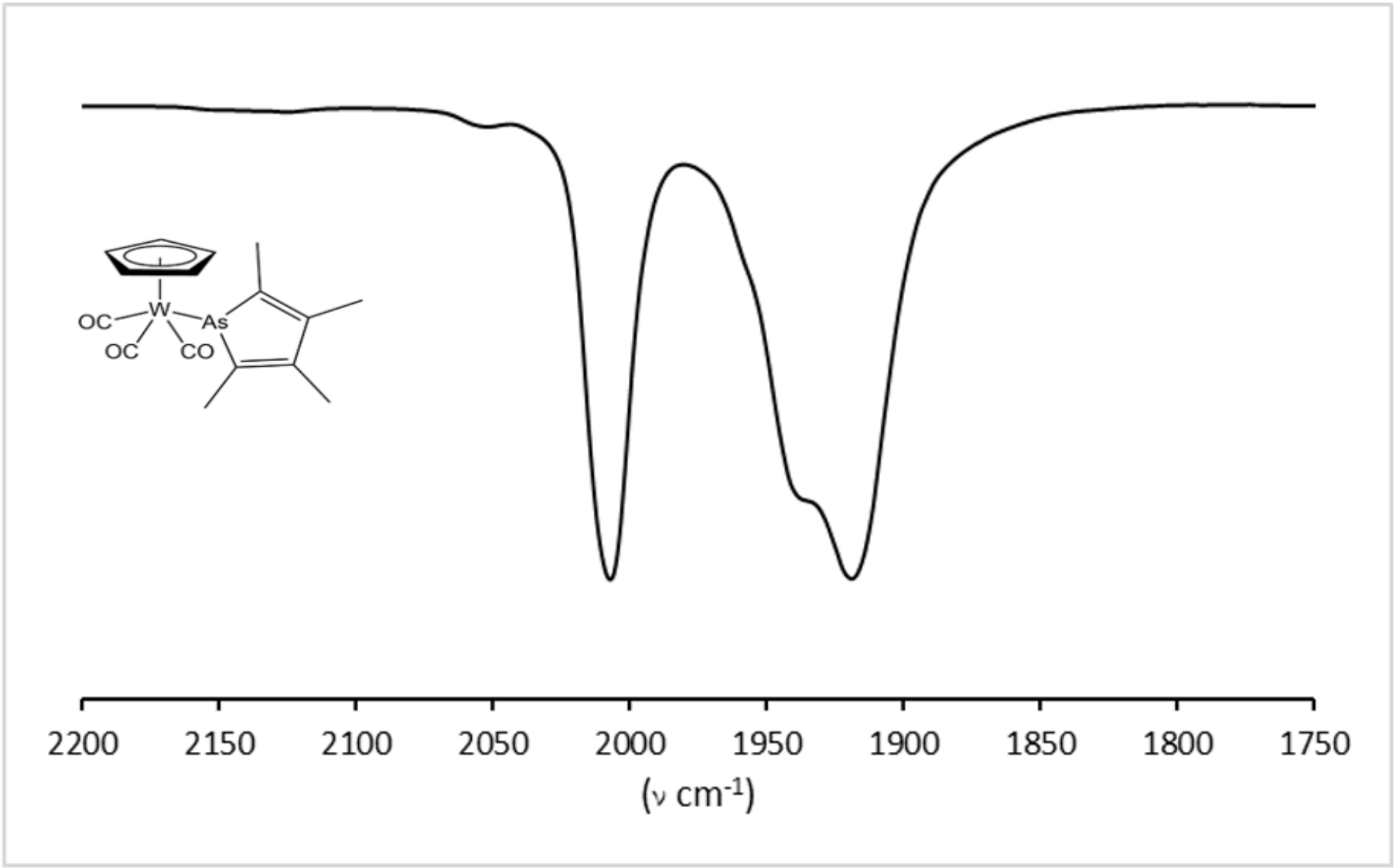

Figure S24. IR Spectrum (CH_2Cl_2, 295 K, ν cm^{-1}) of [$W(AsC_4Me_4)(CO)_3(\eta^5\text{-}C_5H_5)$] (**2d**)

7 [Mo{($AsC_4H(SiMe_3)Me_2$}$(CO)_3(\eta^5\text{-}C_5H_5)$] (2e)

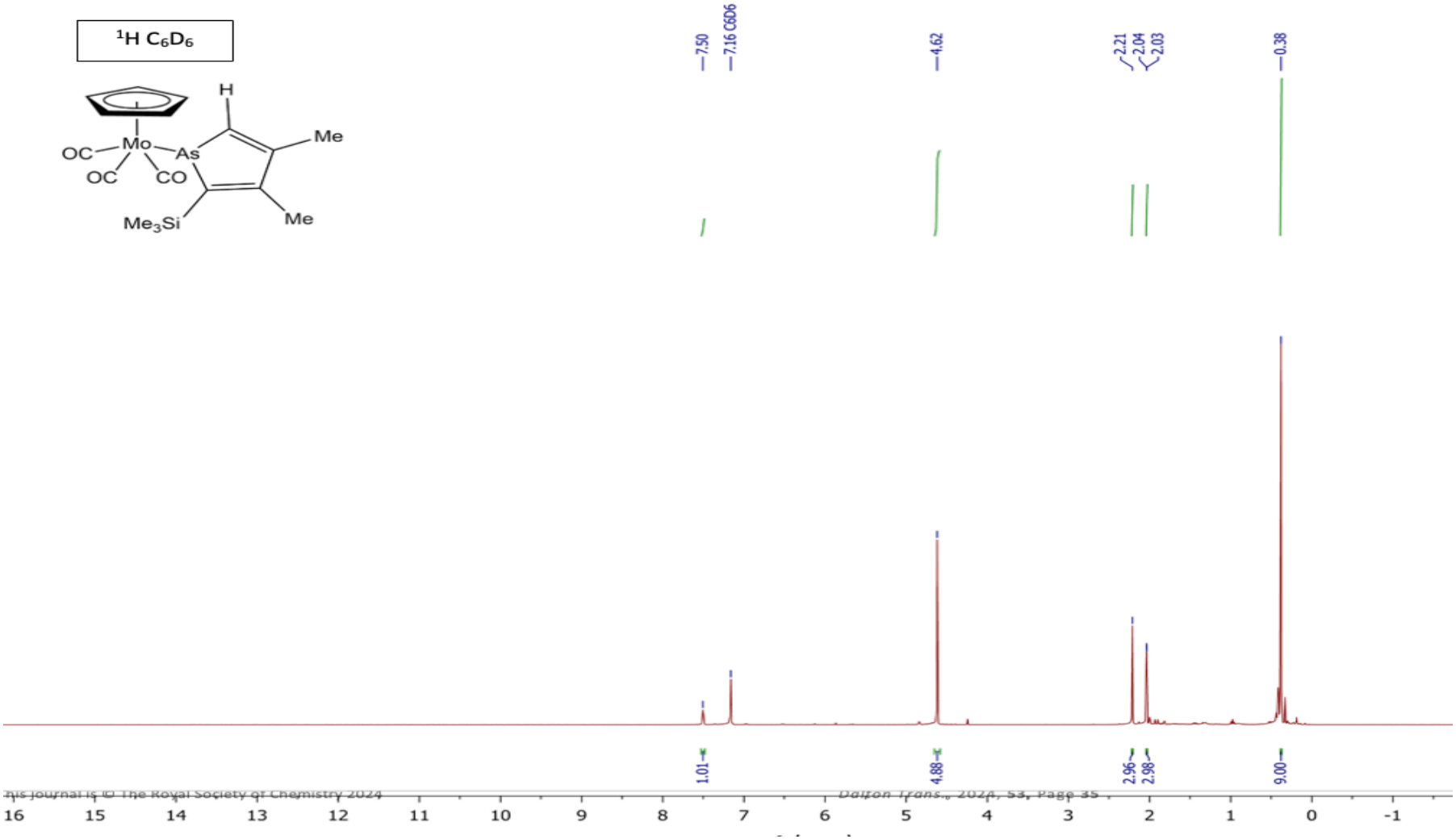

Figure S25. ^1H NMR Spectrum ($CDCl_3$, 295 K, 400 MHz, δ) of [[Mo($AsC_4H(SiMe_3)Me_2$}$(CO)_3(\eta^5\text{-}C_5H_5)$] (**2e**)

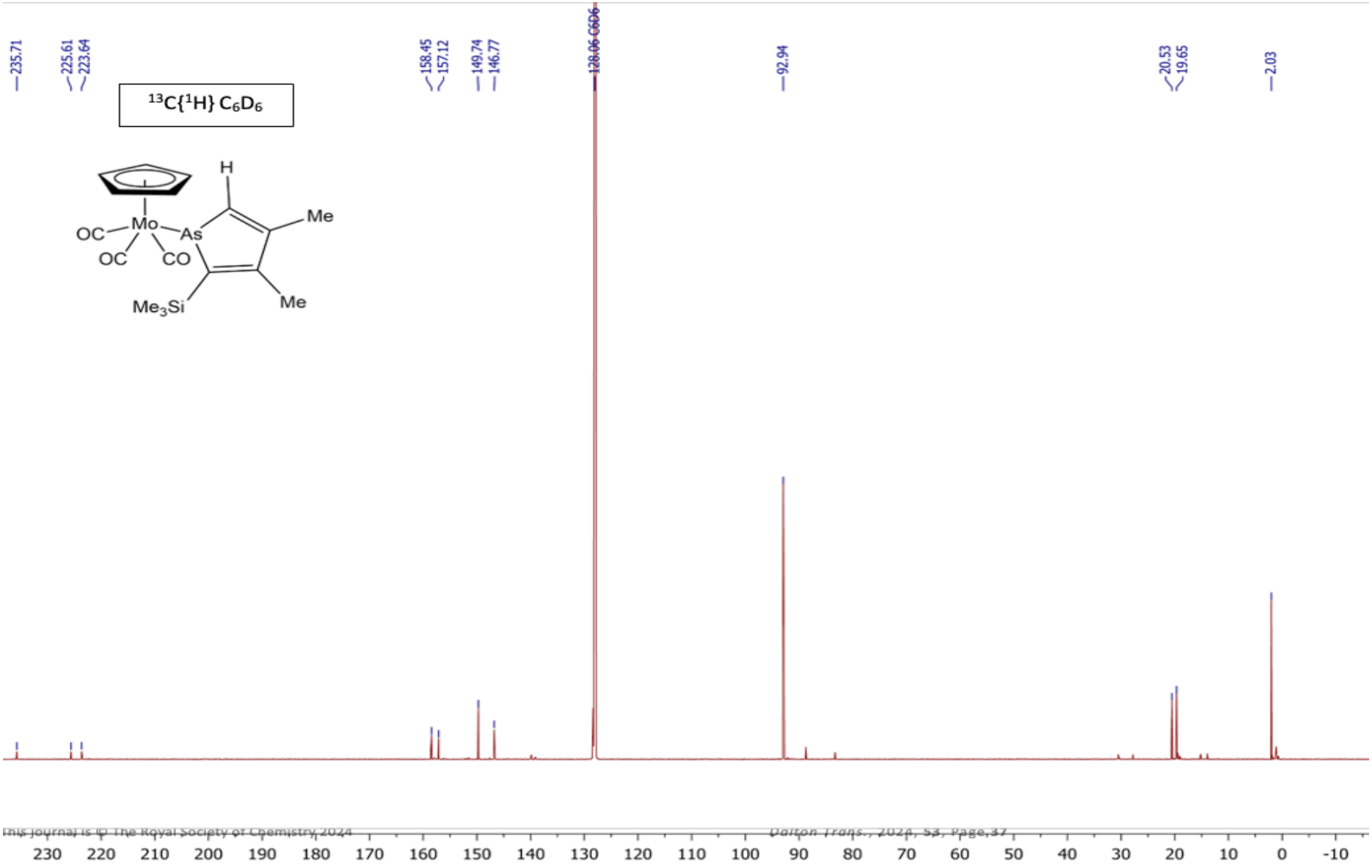

Figure S26. $^{13}C\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 295 K, 201 MHz, δ) of $[Mo(AsC_4H(SiMe_3)Me_2\}(CO)_3(\eta^5\text{-}C_5H_5)]$ (**2e**)

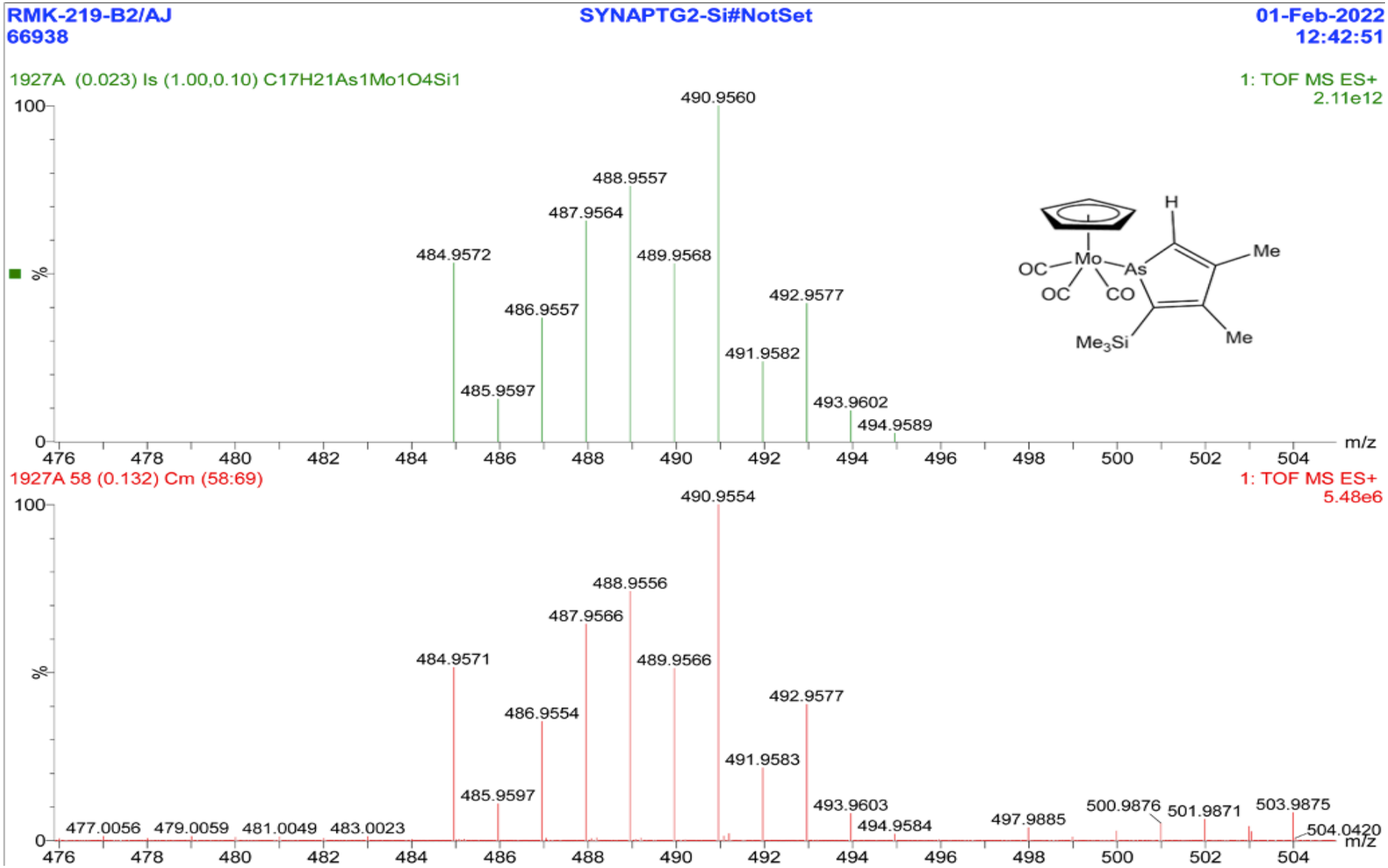

Figure S27. High Resolution Mass Spectrum (ESI-MS, MeCN) of [Mo(AsC$_4$H(SiMe$_3$)Me$_2$}(CO)$_3$(η^5-C$_5$H$_5$)] (**2e**)

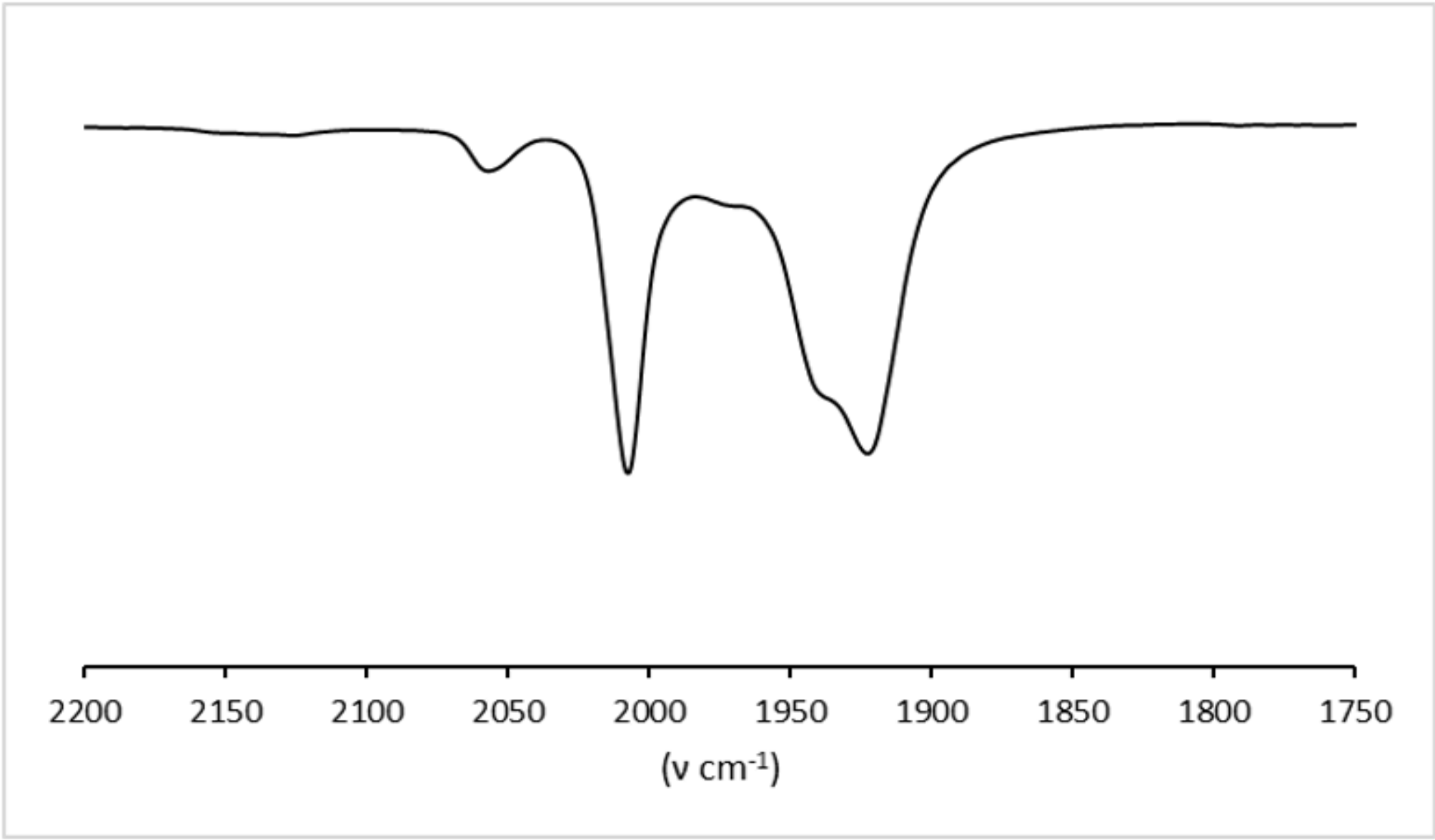

Figure S28. IR Spectrum (CH_2Cl_2, 295 K, ν cm^{-1}) of [Mo{($AsC_4H(SiMe_3)Me_2$}$(CO)_3(\eta^5$-$C_5H_5)$] (**2e**)

Computational Results

1 $ClAsC_4H_4$

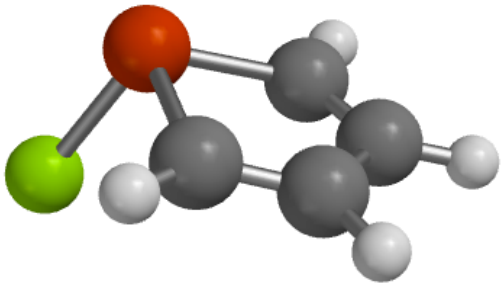

Figure S29. Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	167.25	kJ/mol	(ZPE)
Temperature Correction :	18.06	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	185.30	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2850.524466	au	(Electronic Energy + Enthalpy Correction)
Entropy :	333.02	J/mol•K	
Gibbs Energy :	-2850.562283	au	(Enthalpy - T*Entropy)
C_v :	94.85	J/mol•K	

Lowest energy vibrational mode = 103 cm^{-1}
Second lowest energy vibrational mode = 141 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
C	-1.214422	0.410129	0.470971
H	-2.193693	0.610954	0.888618
C	-0.102814	0.182371	1.184290
H	-0.082448	0.162395	2.271260
C	1.127707	-0.065592	0.406025
H	2.067300	-0.275805	0.911072
C	0.998766	-0.026161	-0.927506
H	1.803474	-0.183186	-1.635672
As	-0.790084	0.554125	-1.421325
Cl	-1.613785	-1.369229	-2.147734

2 $(ClAsC_4H_4)_2$ (As···As)

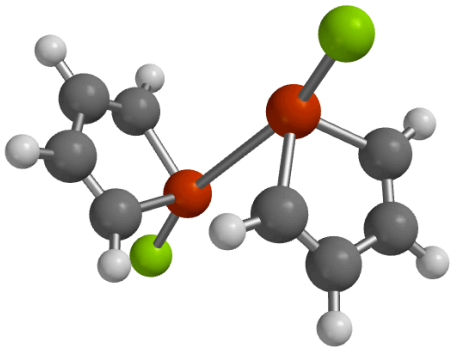

Figure S30. Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	335.53	kJ/mol	(ZPE)
Temperature Correction :	33.66	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	369.19	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-5701.057207	au	(Electronic Energy + Enthalpy Correction)
Entropy :	456.44	J/mol•K	
Gibbs Energy :	-5701.109040	au	(Enthalpy - T*Entropy)
C_v :	214.58	J/mol•K	

Lowest energy vibrational mode = 9 cm^{-1}
Second lowest energy vibrational mode = 11 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
C	0.147606	-1.207825	2.655079
H	-0.401921	-1.002494	3.565766
C	1.481564	-1.163195	2.531536
H	2.150925	-0.928836	3.355488
C	2.020317	-1.464646	1.190990
H	3.092887	-1.460401	1.012888
C	1.114949	-1.748350	0.243859
H	1.340844	-1.985632	-0.788593
Cl	-1.384265	-3.547962	1.090448
As	-0.684452	-1.453248	0.916248
As	-0.092777	1.872847	-0.080926
C	-1.882203	2.113302	-0.800230
H	-2.682449	2.618020	-0.272611
C	0.320606	0.994762	-1.766366
H	1.298267	0.603461	-2.019902
C	-2.019892	1.440712	-1.951315
H	-2.963749	1.354098	-2.483740
C	-0.794405	0.819495	-2.489432
H	-0.820626	0.267362	-3.425778
Cl	0.758773	3.878529	-0.483409

3 $(ClAsC_4H_4)_2$ (Cycloaddition)

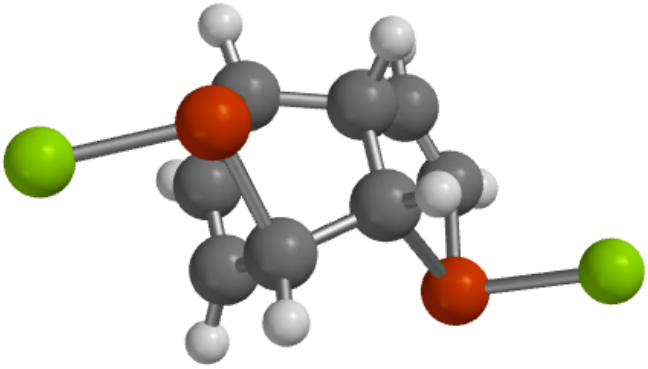

Figure S31. Optimised Geometry (wB97X-D/6-31G*/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	349.95	kJ/mol	(ZPE)
Temperature Correction :	30.68	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	380.62	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-5701.109099	au	(Electronic Energy + Enthalpy Correction)
Entropy :	434.97	J/mol•K	
Gibbs Energy :	-5701.158494	au	(Enthalpy - T*Entropy)
C_v :	194.27	J/mol•K	

Lowest energy vibrational mode = 54 cm^{-1}
Second lowest energy vibrational mode = 77 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
C	0.679893	-1.597326	-0.310837
C	1.512302	-0.916877	0.482351
C	0.759713	-0.087121	1.496517
As	-0.763156	-1.272186	2.060219
C	-0.763742	-1.355639	0.050911
H	0.976422	-2.209700	-1.154765
H	2.593297	-0.899750	0.398115
H	1.355925	0.343922	2.300217
H	-1.491632	-2.028414	-0.402808
C	-1.086685	0.163961	-0.192079
C	-0.087800	0.960460	0.712094
As	1.068223	2.083527	-0.470627
C	0.006675	1.460504	-1.962597
C	-0.926875	0.569302	-1.628639
H	-2.124858	0.354892	0.111351
H	-0.613249	1.639777	1.388470
H	0.183177	1.789196	-2.981634
Cl	0.262223	-3.145395	2.609937
H	-1.580165	0.106683	-2.367879
Cl	0.040312	4.040183	-0.138317

4 $(ClAsC_4H_4)_2$ Cycloaddition Transition State

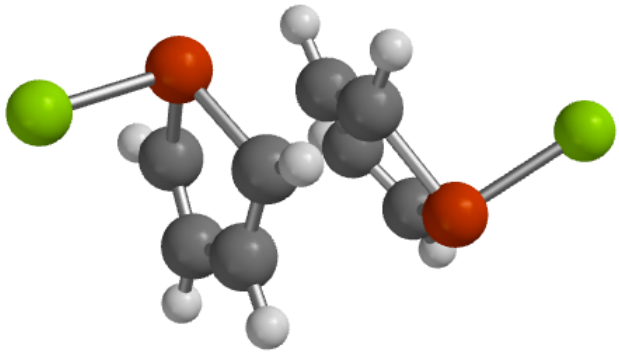

Figure S32. Transition State Geometry (wB97X-D/6-31G*/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	336.81	kJ/mol	(ZPE)
Temperature Correction :	33.23	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	370.04	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-5701.032067	au	(Electronic Energy + Enthalpy Correction)
Entropy :	453.33	J/mol•K	
Gibbs Energy :	-5701.083547	au	(Enthalpy - T*Entropy)
C_v :	202.66	J/mol•K	

Imaginary vibrational mode = –471 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
C	0.496201	-1.856201	-0.140047
C	1.539168	-1.061021	0.388269
C	1.143794	-0.199430	1.406344
As	-0.530838	-0.846554	2.208893
C	-0.719672	-1.714936	0.483525
H	0.642605	-2.474208	-1.020543
H	2.551615	-1.080515	-0.005052
H	1.861177	0.379495	1.981181
H	-1.614162	-2.249416	0.187521
C	-1.225758	0.745760	-0.040163
C	-0.043498	1.310913	0.450693
As	1.145795	1.796500	-1.052057
C	-0.269807	1.132902	-2.201373
C	-1.303023	0.639916	-1.494967
H	-2.147612	0.740437	0.534539
H	-0.062043	1.959038	1.321799
H	-0.234840	1.161882	-3.285749
Cl	0.331675	-2.586241	3.335602
H	-2.194210	0.227909	-1.965557
Cl	0.633433	3.973771	-1.092859

5 $ClAsC_4Me_4$

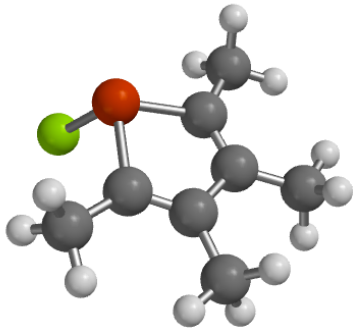

Figure S33. Optimised Geometry (ωB97X-D/6-31G*/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	447.19	kJ/mol	(ZPE)
Temperature Correction :	32.52	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	479.71	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3007.647586	au	(Electronic Energy + Enthalpy Correction)
Entropy :	436.43	J/mol•K	
Gibbs Energy :	-3007.697147	au	(Enthalpy - T*Entropy)
C_v :	195.46	J/mol•K	

Lowest energy vibrational mode = 67 cm^{-1}
Second lowest energy vibrational mode = 80 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
C	-0.357332	-0.436614	-0.643901
C	0.746507	0.410401	-0.085735
C	0.487496	1.023812	1.084376
As	-1.372400	0.749429	1.573052
C	-1.485228	-0.498365	0.089242
Cl	-1.094884	-0.694004	3.243952
C	-2.742115	-1.274360	-0.162454
H	-2.650245	-1.955521	-1.013180
H	-3.591755	-0.608922	-0.357818
H	-3.001438	-1.876792	0.716586
C	-0.134992	-1.150875	-1.949481
H	0.723336	-1.829735	-1.888367
H	0.077310	-0.437313	-2.754408
H	-1.004061	-1.738583	-2.249905
C	2.045356	0.499689	-0.840454
H	2.765452	1.152587	-0.344410
H	1.886828	0.889564	-1.852757
H	2.507438	-0.488751	-0.946459
C	1.375927	1.893039	1.920818
H	2.405522	1.916446	1.552485
H	1.403473	1.528510	2.954704
H	1.009805	2.926358	1.954113

6 $ClAsMe_2$

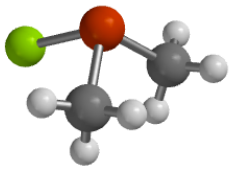

Figure S34. Optimised Geometry (ωB97X-D/6-31G*/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	189.27	kJ/mol	(ZPE)
Temperature Correction :	18.90	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	208.18	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2775.592285	au	(Electronic Energy + Enthalpy Correction)
Entropy :	336.39	J/mol•K	
Gibbs Energy :	-2775.630485	au	(Enthalpy - T*Entropy)
C_v :	93.30	J/mol•K	

Lowest energy vibrational mode = 156 cm^{-1}
Second lowest energy vibrational mode = 174 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
As	-0.932598	0.000000	-0.712949
C	-0.049361	1.464467	0.257488
H	1.029012	1.301345	0.319294
H	-0.471646	1.507142	1.267394
H	-0.248224	2.412030	-0.247923
C	-0.049361	-1.464467	0.257488
H	1.029012	-1.301345	0.319294
H	-0.248224	-2.412030	-0.247924
H	-0.471645	-1.507143	1.267394
Cl	0.413035	-0.000000	-2.479556

7 $ClSnMe_3$

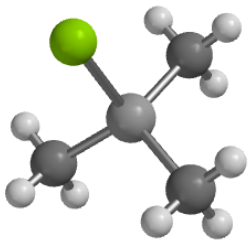

Figure S35. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	274.84	kJ/mol	(ZPE)
Temperature Correction :	24.45	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	299.29	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-583.201444	au	(Electronic Energy + Enthalpy Correction)
Entropy :	381.17	J/mol•K	
Gibbs Energy :	-583.244729	au	(Enthalpy - T*Entropy)
C_v :	136.59	J/mol•K	

Lowest energy vibrational mode = 67 cm^{-1}
Second lowest energy vibrational mode = 73 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Sn	0.000126	0.000000	-0.371213
C	-2.055428	-0.000000	0.188221
H	-2.555778	0.886846	-0.209595
H	-2.158908	0.000002	1.278015
H	-2.555777	-0.886848	-0.209592
C	1.028080	1.780599	0.185786
H	0.513580	2.656616	-0.217879
H	2.048349	1.767516	-0.206650
H	1.074429	1.874226	1.275479
C	1.028080	-1.780599	0.185785
H	2.048348	-1.767517	-0.206652
H	0.513579	-2.656616	-0.217878
H	1.074431	-1.874225	1.275478
Cl	-0.003110	0.000001	-2.749304

8 [Cr(SnMe$_3$)(CO)$_3$(η^5-C$_5$H$_5$)]

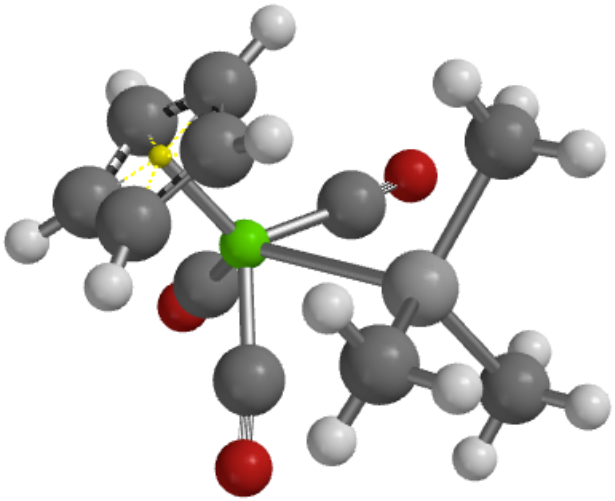

Figure S36. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	554.83	kJ/mol	(ZPE)
Temperature Correction :	46.37	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	601.20	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1700.667694	au	(Electronic Energy + Enthalpy Correction)
Entropy :	535.52	J/mol•K	
Gibbs Energy :	-1700.728508	au	(Enthalpy - T*Entropy)
C_v :	312.02	J/mol•K	

Lowest energy vibrational mode = 28 cm^{-1}
Second lowest energy vibrational mode = 60 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Cr	-0.272743	-0.000014	1.255699
C	-1.538776	0.000060	2.581570
O	-2.310636	0.000101	3.439096
C	-1.158116	-1.512193	0.724946
O	-1.681719	-2.516742	0.478606
C	-1.158379	1.512161	0.724641
O	-1.682157	2.516676	0.478105
Sn	-0.488979	-0.000017	-1.488995
C	0.511049	1.752513	-2.235553
H	1.572035	1.756434	-1.967894
H	0.050349	2.655662	-1.825983
H	0.438795	1.797928	-3.326633
C	0.510921	-1.752629	-2.235535
H	0.049911	-2.655731	-1.826367
H	1.571741	-1.756839	-1.967477
H	0.439104	-1.797831	-3.326591
C	-2.528265	0.000055	-2.144562
H	-3.047795	-0.887495	-1.771975
H	-2.587433	0.000130	-3.237385
H	-3.047787	0.887563	-1.771843
H	1.691111	-2.175670	1.081718
C	1.586597	-1.149400	1.406285
C	1.186191	-0.712955	2.692541
H	2.242253	0.000175	-0.393088
H	0.933351	-1.349098	3.529477
C	1.186138	0.712849	2.692642
H	0.933251	1.348856	3.529670
C	1.586507	1.149501	1.406447
H	1.690932	2.175836	1.082046
C	1.839815	0.000115	0.610604

9 [Mo(SnMe$_3$)(CO)$_3$(η^5-C$_5$H$_5$)]

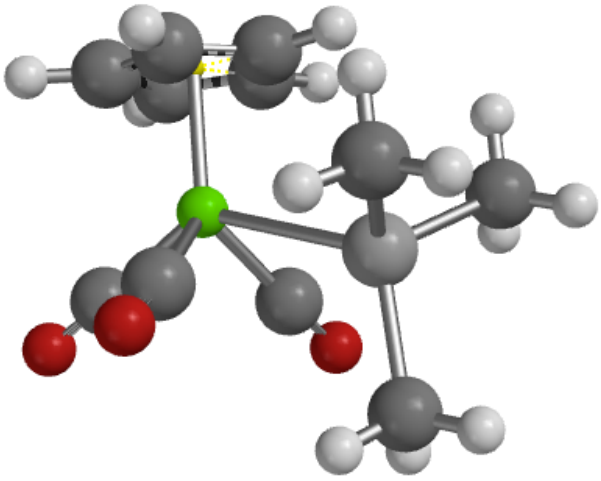

Figure S37. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	549.63	kJ/mol	(ZPE)
Temperature Correction :	47.42	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	597.06	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-723.831153	au	(Electronic Energy + Enthalpy Correction)
Entropy :	544.12	J/mol•K	
Gibbs Energy :	-723.892943	au	(Enthalpy - T*Entropy)
C_v :	318.00	J/mol•K	

Lowest energy vibrational mode = 32 cm^{-1}
Second lowest energy vibrational mode = 56 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Mo	-0.282954	0.000380	1.316435
C	-1.642859	-0.000607	2.776956
O	-2.409169	-0.001090	3.636962
C	-1.341065	-1.578753	0.754040
O	-1.909444	-2.549658	0.477357
C	-1.342100	1.579274	0.757658
O	-1.911161	2.550120	0.482460
Sn	-0.567954	-0.000275	-1.531915
C	0.416574	1.759935	-2.284121
H	1.478225	1.770442	-2.017132
H	-0.050922	2.656876	-1.866783
H	0.339368	1.809307	-3.375447
C	0.415332	-1.761419	-2.283534
H	-0.052719	-2.657942	-1.865919
H	1.476988	-1.772408	-2.016537
H	0.338089	-1.811142	-3.374885
C	-2.612423	0.000401	-2.176936
H	-3.130232	-0.886418	-1.800153
H	-2.677213	0.000219	-3.269843
H	-3.129439	0.887804	-1.800452
H	1.873930	-2.179074	1.080895
C	1.783452	-1.151897	1.407129
C	1.456799	-0.715615	2.715590
H	2.313265	0.000377	-0.435933
H	1.268429	-1.352886	3.568526
C	1.456637	0.716627	2.715567
H	1.268054	1.353674	3.568620
C	1.783145	1.153004	1.407087
H	1.873311	2.180181	1.080736
C	1.981619	0.000563	0.593252

10 [W(SnMe$_3$)(CO)$_3$(η^5-C$_5$H$_5$)]

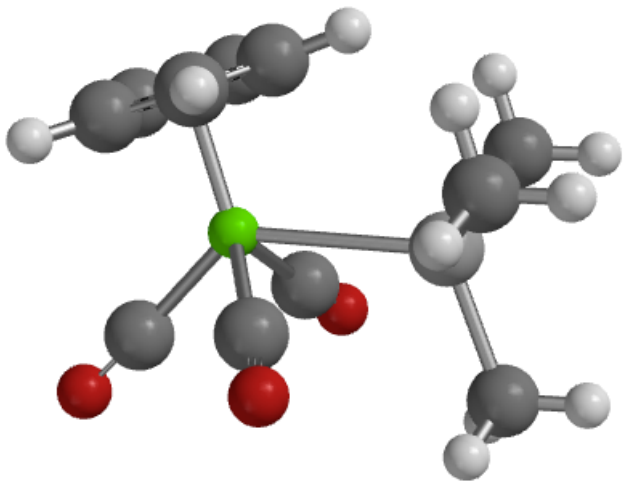

Figure S38. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	550.53	kJ/mol	(ZPE)
Temperature Correction :	47.16	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	597.69	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-724.129041	au	(Electronic Energy + Enthalpy Correction)
Entropy :	545.37	J/mol•K	
Gibbs Energy :	-724.190972	au	(Enthalpy - T*Entropy)
C_v :	316.94	J/mol•K	

Lowest energy vibrational mode = 39 cm^{-1}
Second lowest energy vibrational mode = 57 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
W	-0.207096	-0.000398	1.327863
C	-1.509122	0.002826	2.829148
O	-2.241269	0.004321	3.722088
C	-1.280972	-1.582580	0.825033
O	-1.857709	-2.555817	0.563059
C	-1.280490	1.582572	0.826715
O	-1.856079	2.556293	0.565732
Sn	-0.649096	0.000008	-1.506005
C	0.298271	1.756691	-2.318752
H	1.372232	1.767042	-2.106501
H	-0.145359	2.657277	-1.883951
H	0.166990	1.800441	-3.404822
C	0.299583	-1.756073	-2.318664
H	-0.143224	-2.656937	-1.883736
H	1.373547	-1.765665	-2.106647
H	0.168171	-1.800037	-3.404620
C	-2.725804	-0.001057	-2.035403
H	-3.218911	-0.888514	-1.628101
H	-2.855271	-0.000922	-3.122443
H	-3.220008	0.885617	-1.627721
H	1.931158	-2.180055	1.002378
C	1.854537	-1.153449	1.333106
C	1.574934	-0.717276	2.655898
H	2.306437	0.000346	-0.529443
H	1.418825	-1.353032	3.516128
C	1.575183	0.715595	2.656309
H	1.419308	1.350939	3.516883
C	1.854851	1.152583	1.333810
H	1.931589	2.179446	1.003868
C	2.025375	-0.000185	0.514495

11 $[Fe(SnMe_3)(CO)_2(\eta^5\text{-}C_5H_5)]$

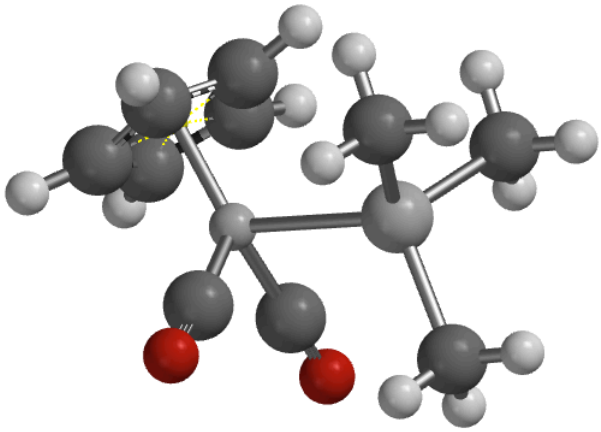

Figure S39. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	531.54	kJ/mol	(ZPE)
Temperature Correction :	42.05	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	573.59	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-1806.577079	au	(Electronic Energy + Enthalpy Correction)
Entropy :	506.41	J/mol•K	
Gibbs Energy :	-1806.634587	au	(Enthalpy - T*Entropy)
C_v :	280.93	J/mol•K	

Lowest energy vibrational mode = 26 cm^{-1}
Second lowest energy vibrational mode = 49 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Fe	-0.375640	-0.000326	1.193390
C	-1.538268	-1.280760	1.010304
O	-2.280812	-2.161528	0.937643
C	-1.538693	1.281143	1.009627
O	-2.281028	2.162076	0.936593
Sn	-0.330006	-0.000030	-1.367172
C	0.719426	1.753017	-2.053814
H	1.750568	1.771981	-1.685314
H	0.217036	2.658781	-1.699055
H	0.751708	1.789699	-3.147589
C	0.719450	-1.752925	-2.054168
H	0.217062	-2.658774	-1.699624
H	1.750584	-1.771961	-1.685649
H	0.751755	-1.789365	-3.147950
C	-2.297198	0.000038	-2.233433
H	-2.857288	-0.886030	-1.918384
H	-2.246405	0.000163	-3.326938
H	-2.857305	0.886022	-1.918179
H	1.424682	-2.177273	1.461057
C	1.251108	-1.149433	1.747792
C	0.541281	-0.706455	2.908067
H	2.311441	-0.000273	0.150954
H	0.075854	-1.343198	3.647717
C	0.541046	0.706374	2.907795
H	0.075381	1.343222	3.647204
C	1.250774	1.149120	1.747339
H	1.424036	2.176896	1.460184
C	1.703245	-0.000202	1.045462

12 [Ru(SnMe$_3$)(CO)$_2$(η^5-C$_5$H$_5$)]

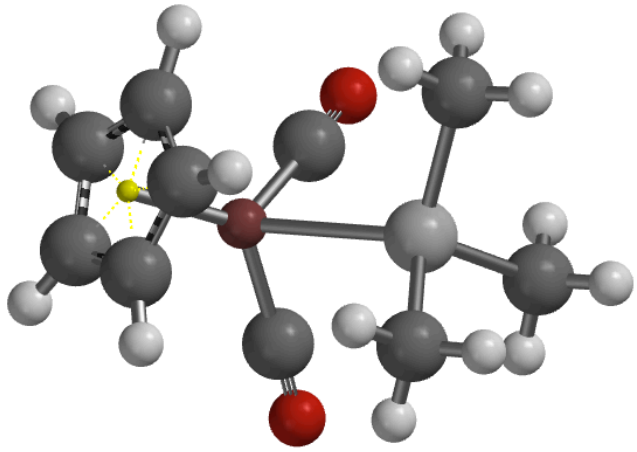

Figure S40. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	528.46	kJ/mol	(ZPE)
Temperature Correction :	42.78	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	571.24	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-636.905428	au	(Electronic Energy + Enthalpy Correction)
Entropy :	513.69	J/mol•K	
Gibbs Energy :	-636.963762	au	(Enthalpy - T*Entropy)
C_v :	284.76	J/mol•K	

Lowest energy vibrational mode = 22 cm^{-1}
Second lowest energy vibrational mode = 42 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Ru	-0.446528	-0.051369	1.223490
C	-1.607756	-1.526097	1.068400
O	-2.303769	-2.444176	1.006808
C	-1.877219	1.158033	1.064567
O	-2.731208	1.930252	0.986815
Sn	-0.427423	-0.039500	-1.437271
C	0.336201	1.856765	-2.121800
H	1.345270	2.035656	-1.736082
H	-0.307751	2.670877	-1.774305
H	0.377671	1.895926	-3.215436
C	0.881453	-1.604282	-2.133908
H	0.513979	-2.580779	-1.802691
H	1.894615	-1.472833	-1.740051
H	0.940322	-1.613319	-3.227418
C	-2.380253	-0.342102	-2.287205
H	-2.792244	-1.306080	-1.972775
H	-2.341579	-0.326174	-3.381316
H	-3.067212	0.443881	-1.957812
H	1.895275	-1.938562	1.369994
C	1.582132	-0.963957	1.717398
C	0.926483	-0.680994	2.960662
H	2.345087	0.405642	0.119756
H	0.628223	-1.412960	3.698451
C	0.727781	0.715637	3.046278
H	0.254143	1.243506	3.862162
C	1.259829	1.310356	1.853720
H	1.283075	2.367059	1.626257
C	1.819865	0.274642	1.055771

13 [Os(SnMe$_3$)(CO)$_2$(η^5-C$_5$H$_5$)]

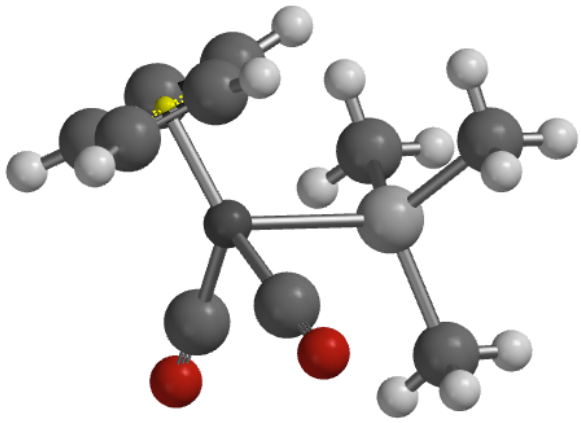

Figure S41. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	529.36	kJ/mol	(ZPE)
Temperature Correction :	42.54	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	571.89	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-634.085987	au	(Electronic Energy + Enthalpy Correction)
Entropy :	515.77	J/mol•K	
Gibbs Energy :	-634.144557	au	(Enthalpy - T*Entropy)
C_v :	283.24	J/mol•K	

Lowest energy vibrational mode = 17 cm^{-1}
Second lowest energy vibrational mode = 31 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Os	-0.383764	0.012006	1.258763
C	-1.683186	-1.342028	1.203385
O	-2.456913	-2.203463	1.182041
C	-1.707427	1.337000	1.161628
O	-2.502290	2.178451	1.120733
Sn	-0.506497	-0.032301	-1.423056
C	0.580515	1.666230	-2.190744
H	1.631695	1.633492	-1.883103
H	0.146926	2.596492	-1.809836
H	0.550436	1.698232	-3.284941
C	0.435356	-1.818207	-2.183115
H	-0.064159	-2.709610	-1.790571
H	1.490345	-1.866068	-1.891663
H	0.384833	-1.852068	-3.276560
C	-2.520959	0.037784	-2.171566
H	-3.088782	-0.832305	-1.826998
H	-2.536412	0.044264	-3.266382
H	-3.032154	0.938036	-1.816387
H	1.582173	-2.214688	1.782035
C	1.479461	-1.147517	1.916723
C	0.936153	-0.491223	3.073016
H	2.374509	-0.316463	0.041035
H	0.550958	-0.979556	3.956446
C	1.006318	0.910340	2.851034
H	0.673250	1.675067	3.538572
C	1.587453	1.131575	1.558202
H	1.795304	2.091634	1.108505
C	1.894275	-0.145175	0.994369

14 [Mo(AsMe$_2$)(CO)$_3$(η^5-C$_5$H$_5$)]

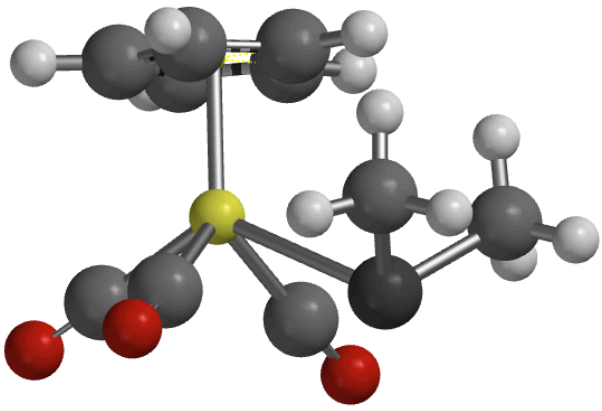

Figure S42. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	464.59	kJ/mol	(ZPE)
Temperature Correction :	42.02	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	506.61	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2916.218991	au	(Electronic Energy + Enthalpy Correction)
Entropy :	506.70	J/mol•K	
Gibbs Energy :	-2916.276531	au	(Enthalpy - T*Entropy)
C_v :	275.14	J/mol•K	

Lowest energy vibrational mode = 26 cm^{-1}
Second lowest energy vibrational mode = 66 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Mo	0.591734	0.923651	-0.047227
H	-0.593538	2.817329	2.018511
C	-0.926000	2.054383	1.328051
C	-1.073993	0.672915	1.623890
H	-1.356945	3.208079	-0.545231
H	-0.863139	0.196913	2.571766
C	-1.568391	0.027850	0.459572
H	-1.806818	-1.021913	0.374459
C	-1.726299	1.002687	-0.560291
H	-2.096739	0.818865	-1.559487
C	-1.330404	2.258721	-0.028181
C	1.770329	2.526992	-0.162746
O	2.429077	3.470154	-0.220330
C	1.190832	0.779742	-1.940250
O	1.473714	0.721347	-3.057710
C	2.098632	0.335942	1.112865
O	2.930238	0.010855	1.844172
As	1.311521	-1.696554	-0.634217
C	0.665480	-2.628472	0.993895
H	1.286634	-2.338078	1.845124
H	0.792248	-3.703632	0.829157
H	-0.382412	-2.433146	1.232945
C	-0.176791	-2.233396	-1.830527
H	-0.091132	-1.692106	-2.776190
H	-1.171161	-2.065131	-1.410615
H	-0.061572	-3.302689	-2.037112

15 $[Mo\{As(CHCH_2)_2\}(CO)_3(\eta^5\text{-}C_5H_5)]$

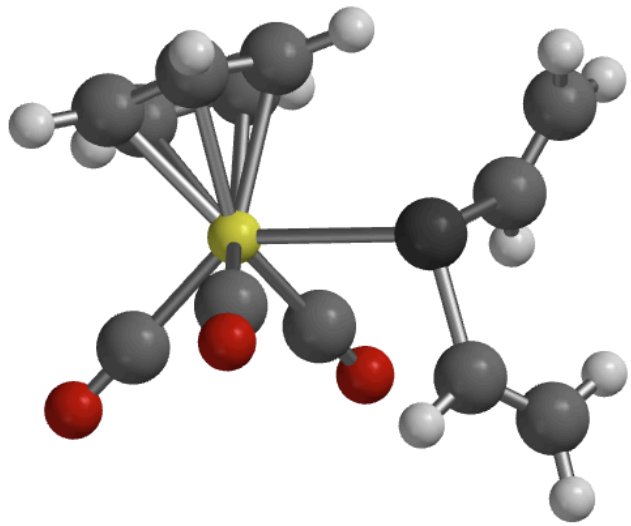

Figure S43. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Cartesian Coordinates

Atom	x	y	z
Mo	1.117263	-0.339540	-0.542466
As	-0.835660	-0.508115	1.392242
C	-3.314748	0.545850	0.384700
C	-0.080931	0.436396	2.913069
O	0.748534	2.596625	0.523169
C	-2.083453	0.864911	0.785801
C	0.882789	1.501105	0.187562
C	-0.277244	-0.018595	-2.440435
H	-0.839366	0.893527	-2.586851
C	0.284815	-2.162361	-1.802551
H	0.216202	-3.163486	-1.399633
O	2.247235	-2.128023	1.779910
C	-0.745325	-1.183077	-1.773028
H	-1.726180	-1.301406	-1.333752
C	1.839214	-1.440677	0.947005
O	4.106388	0.648800	-0.600061
C	1.397777	-1.603643	-2.486225
H	2.328730	-2.108201	-2.705817
C	-0.635486	1.474835	3.537720
C	3.012243	0.291058	-0.565209
C	1.046238	-0.273429	-2.883162
H	1.665799	0.403447	-3.455656
H	-1.762542	1.906389	0.767706
H	-4.016324	1.297821	0.029025
H	-0.177058	1.912510	4.421653
H	0.847427	0.011569	3.293945
H	-3.679304	-0.480310	0.406098
H	-1.567033	1.926021	3.205245

Thermodynamic Properties at 298.15 K

Zero Point Energy :	492.13	kJ/mol	(ZPE)
Temperature Correction :	44.93	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	537.06	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2992.334863	au	(Electronic Energy + Enthalpy Correction)
Entropy :	524.69	J/mol•K	
Gibbs Energy :	-2992.394446	au	(Enthalpy - T*Entropy)
C_v :	298.81	J/mol•K	

Lowest energy vibrational mode = 42 cm^{-1}
Second lowest energy vibrational mode = 52 cm^{-1}.

16 $[Mo(AsC_4H_4)(CO)_3(\eta^5\text{-}C_5H_5)]$

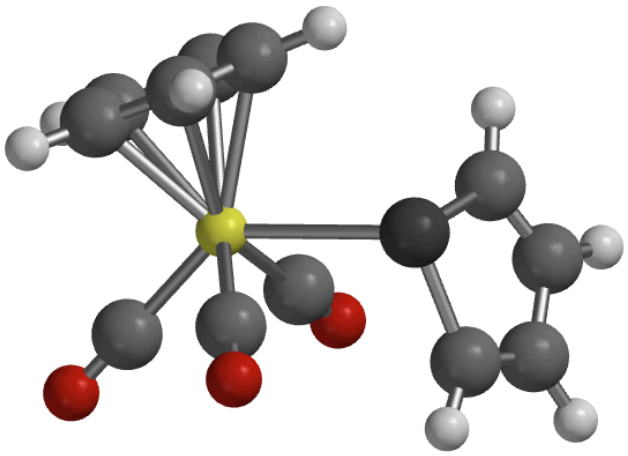

Figure S44. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	442.23	kJ/mol	(ZPE)
Temperature Correction :	41.12	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	483.36	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2991.170688	au	(Electronic Energy + Enthalpy Correction)
Entropy :	498.53	J/mol•K	
Gibbs Energy :	-2991.227301	au	(Enthalpy - T*Entropy)
C_v :	276.28	J/mol•K	

Lowest energy vibrational mode = 38 cm^{-1}
Second lowest energy vibrational mode = 60 cm^{-1}.

Atom	x	y	z
Mo	0.936393	-0.309970	-0.422687
As	-1.214781	-0.719838	1.215598
C	-2.473021	1.571954	1.953172
C	-0.798846	0.157575	2.876872
O	0.354460	2.557208	0.759047
C	-2.393442	0.763854	0.874001
C	0.544085	1.488240	0.381760
C	-0.149035	0.128167	-2.499296
H	-0.678028	1.053287	-2.682926
C	0.312141	-2.049795	-1.895348
H	0.185989	-3.066254	-1.548935
O	1.891949	-2.211699	1.889985
C	-0.714229	-1.066835	-1.981086
H	-1.752986	-1.213601	-1.717782
C	1.539494	-1.486797	1.065447
O	3.859939	0.788637	-0.024453
C	1.517817	-1.462227	-2.364968
H	2.473620	-1.958225	-2.461166
C	-1.583443	1.240205	3.061423
C	2.788197	0.389413	-0.156693
C	1.229477	-0.109658	-2.735159
H	1.931724	0.598178	-3.154112
H	-3.002151	0.874247	-0.017455
H	-3.148259	2.422366	2.015099
H	-1.567225	1.843967	3.965705
H	-0.089840	-0.222399	3.603959

17 [Mo(AsC$_4$Me$_4$)(CO)$_3$(η^5-C$_5$H$_5$)]

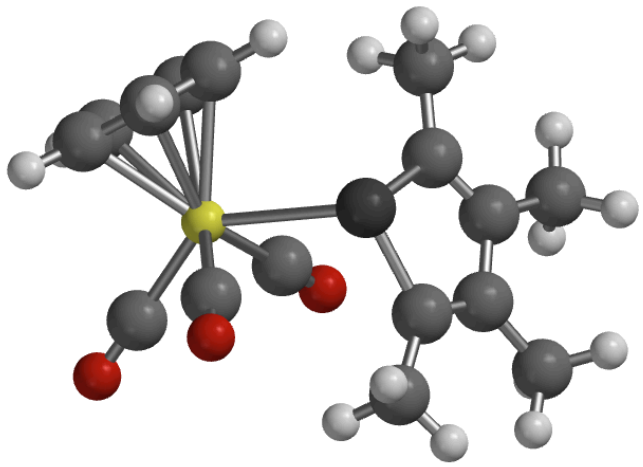

Figure S45. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

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	

Lowest energy vibrational mode = 38 cm^{-1}
Second lowest energy vibrational mode = 45 cm^{-1}.

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

18 $[Mo(AsC_4Ph_4)(CO)_3(\eta^5\text{-}C_5H_5)]$

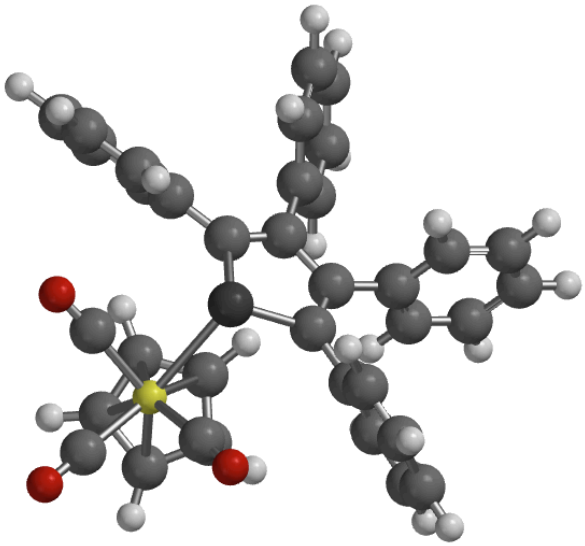

Figure S46. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	1254.94	kJ/mol	(ZPE)
Temperature Correction :	81.75	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1336.68	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3914.778925	au	(Electronic Energy + Enthalpy Correction)
Entropy :	759.12	J/mol•K	
Gibbs Energy :	-3914.865130	au	(Enthalpy - T*Entropy)
C_v :	611.46	J/mol•K	

Lowest energy vibrational mode = 13 cm^{-1}
Second lowest energy vibrational mode = 23 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Mo	2.119157	-1.612060	-2.191997
As	0.019336	-2.065547	-0.497249
C	-1.200738	0.293206	0.139898
C	0.530228	-1.073326	1.077284
O	3.210423	-3.676791	-0.065181
C	-1.165951	-0.595380	-0.894856
C	2.769281	-2.934896	-0.824163
C	3.213218	0.266030	-1.238207
H	3.715822	0.187993	-0.283991
C	1.575654	0.590838	-2.831943
H	0.622240	0.814417	-3.290607
O	-0.065635	-3.008232	-3.989186
C	1.855696	0.626724	-1.436923
H	1.150265	0.882405	-0.659905
C	0.703435	-2.513231	-3.291546
O	3.841881	-3.561680	-3.968452
C	2.765192	0.200031	-3.502176
H	2.891458	0.102217	-4.571899
C	-0.248078	0.033651	1.228457
C	3.203901	-2.860965	-3.315592
C	3.779070	-0.009531	-2.511667
H	4.805627	-0.290433	-2.703905
C	-1.971173	-0.531084	-2.127745
C	-3.444865	-0.416686	-4.518906
C	-2.088263	0.669091	-2.845439
C	-2.611047	-1.669079	-2.632969
C	-3.340682	-1.612576	-3.815358
C	-2.816361	0.725140	-4.027171
H	-1.612118	1.566136	-2.459991
H	-2.538146	-2.606931	-2.089357
H	-3.826665	-2.509082	-4.188466
H	-2.894172	1.665363	-4.565420
H	-4.012560	-0.373527	-5.443548
C	-2.180016	1.410844	0.222724
C	-4.059961	3.486817	0.338822
C	-3.549735	1.133043	0.228525
C	-1.766185	2.744826	0.276249
C	-2.698216	3.775498	0.332372
C	-4.483102	2.161721	0.286592
H	-3.878096	0.099086	0.178519
H	-0.705583	2.977427	0.266586
H	-2.359119	4.806582	0.370349
H	-5.543542	1.927370	0.289440
H	-4.787892	4.291422	0.384346
C	-0.224278	0.892605	2.447360
C	-0.214721	2.498401	4.742559
C	-1.068185	0.601997	3.520566
C	0.622149	1.999880	2.538621
C	0.629512	2.798287	3.677442
C	-1.063477	1.398074	4.661353
H	-1.729612	-0.257005	3.455709
H	1.278747	2.239535	1.705103
H	1.294337	3.655435	3.732386
H	-1.723658	1.157342	5.489343

Atom	x	y	z
H	-0.211150	3.120198	5.632881
C	1.540299	-1.572590	2.028120
C	3.498146	-2.559780	3.783676
C	1.452204	-2.870546	2.545570
C	2.630631	-0.779420	2.406177
C	3.599134	-1.267320	3.276466
C	2.420002	-3.358913	3.415384
H	0.611691	-3.498186	2.262064
H	2.711953	0.230480	2.016580
H	4.435955	-0.635003	3.558966
H	2.331283	-4.368565	3.805291
H	4.255054	-2.941746	4.462034

19 $[Mo(SnMe_3)(CO)_3(\eta^5\text{-}C_5H_5)]/ClAsMe_2$-TS

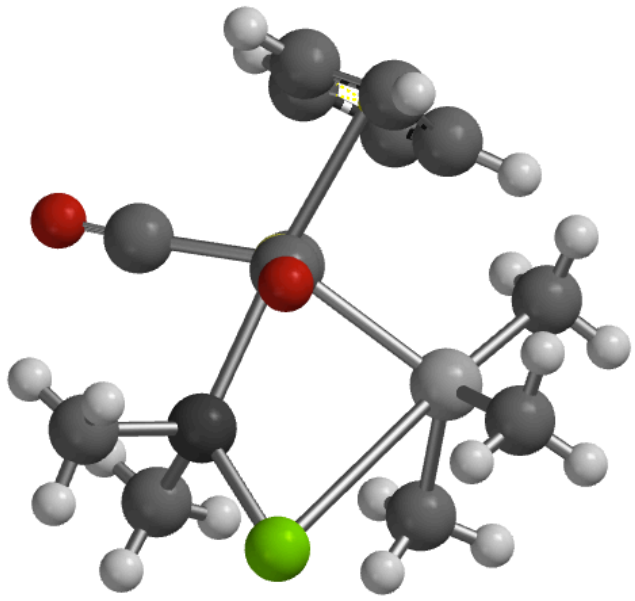

Figure S47. Transition State Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	739.65	kJ/mol	(ZPE)
Temperature Correction :	65.18	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	804.83	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3499.378387	au	(Electronic Energy + Enthalpy Correction)
Entropy :	669.29	J/mol•K	
Gibbs Energy :	-3499.454391	au	(Enthalpy - T*Entropy)
C_v :	431.03	J/mol•K	

Imaginary vibrational mode = –38 cm^{-1}

Cartesian Coordinates

Atom	x	y	z
Mo	0.390524	1.023497	-0.037267
C	-0.173038	2.722118	-0.895542
O	-0.418329	3.719178	-1.427077
C	0.960521	0.590160	-1.914523
O	1.277039	0.337005	-2.997754
C	-0.287345	1.186371	1.952748
O	-0.764864	1.227550	2.994378
As	-2.125846	0.740228	-0.352349
Sn	0.242250	-1.850685	-0.266198
Cl	-3.302838	-0.844442	0.680284
C	-1.072479	-2.678697	-1.757356
H	-0.898282	-2.212684	-2.732316
H	-2.126999	-2.573953	-1.490408
H	-0.853803	-3.747197	-1.857887
C	2.196385	-2.552415	-0.853368
H	2.518050	-2.080291	-1.786745
H	2.157197	-3.634792	-1.018101
H	2.950976	-2.354175	-0.086642
C	-0.201594	-2.695551	1.662880
H	-0.210392	-3.789526	1.604079
H	-1.177127	-2.356738	2.019205
H	0.557796	-2.392083	2.389777
C	-3.232111	2.222905	0.263896
H	-2.897117	3.137289	-0.234563
H	-3.101767	2.334180	1.342769
H	-4.283094	2.032726	0.035900
C	-2.813592	0.499974	-2.153025
H	-2.395012	-0.410616	-2.582633
H	-2.481115	1.360982	-2.741689
H	-3.903864	0.448185	-2.145576
H	2.768686	2.714977	-0.305984
C	2.496622	2.014779	0.474293
C	2.663620	0.601299	0.412479
H	2.208183	3.361561	2.238716
H	3.089311	0.044558	-0.411958
C	2.554590	0.107930	1.748757
H	2.622962	-0.936879	2.028845
C	2.432992	1.197245	2.633866
H	2.274997	1.130550	3.702370
C	2.357907	2.355478	1.863720

20 [Mo(SnMe$_3$)(CO)$_3$(η^5-C$_5$H$_5$)]/ClAsC$_4$H$_4$-TS

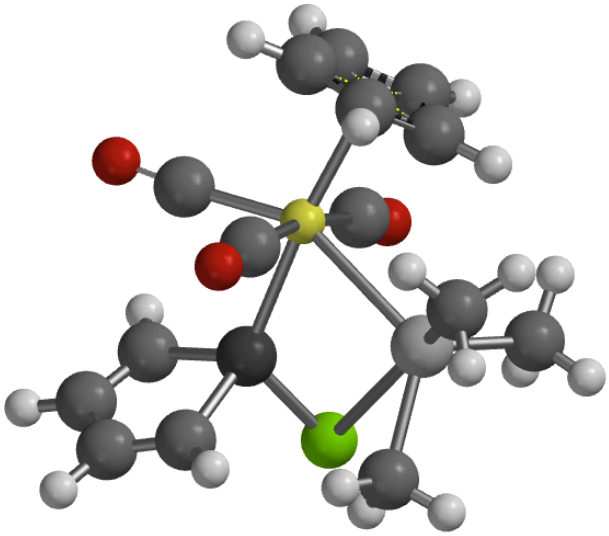

Figure S48. Transition State Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	714.83	kJ/mol	(ZPE)
Temperature Correction :	64.97	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	779.81	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3574.282808	au	(Electronic Energy + Enthalpy Correction)
Entropy :	665.17	J/mol•K	
Gibbs Energy :	-3574.358344	au	(Enthalpy - T*Entropy)
C_v :	435.53	J/mol•K	

Imaginary vibrational mode = –220 cm^{-1}

Cartesian Coordinates

Atom	x	y	z
Mo	0.431800	1.037260	-0.225242
C	-0.491687	2.807530	-0.243067
O	-0.938027	3.867383	-0.163751
C	0.747466	0.807440	-2.289351
O	0.810702	0.650746	-3.423607
C	-0.104802	1.007964	1.737120
O	-0.486535	0.955676	2.824458
As	-1.845866	0.386145	-0.928572
Sn	0.430294	-1.817086	0.345517
Cl	-2.151216	-1.189836	-2.484938
C	1.450276	-2.764743	-1.298059
H	2.399911	-2.262802	-1.507731
H	0.833444	-2.725398	-2.200494
H	1.656711	-3.814968	-1.063468
C	1.544941	-2.184959	2.162075
H	1.089468	-3.023595	2.699301
H	1.542707	-1.316861	2.827608
H	2.584928	-2.447087	1.940938
C	-1.393351	-2.917708	0.696231
H	-1.110840	-3.973662	0.781469
H	-2.126954	-2.831850	-0.108545
H	-1.857370	-2.624087	1.643521
C	-3.257428	-0.034445	0.319323
H	-3.183371	-0.789115	1.090106
C	-3.014987	1.732711	-1.681841
H	-2.755076	2.358324	-2.526670
H	2.571927	3.293863	-1.188312
C	2.614623	2.429185	-0.537916
C	3.068051	1.148645	-0.886934
H	2.160018	3.329274	1.485272
H	3.308164	0.804041	-1.883361
C	2.953375	0.330059	0.255416
H	3.278564	-0.700232	0.323492
C	2.691470	1.194903	1.391902
H	2.599545	0.863441	2.417288
C	2.454303	2.460414	0.910655
C	-4.143208	1.792582	-0.967112
H	-4.941529	2.501552	-1.168257
C	-4.268894	0.824689	0.145749
H	-5.151547	0.834607	0.779786

21 [Mo(AsMe$_2$)(CO)$_2$(η^5-C$_5$H$_5$)]

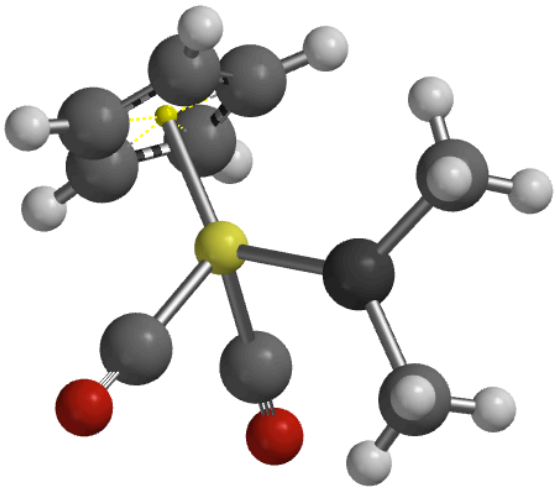

Figure S49. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	441.47	kJ/mol	(ZPE)
Temperature Correction :	37.45	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	478.92	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2802.914242	au	(Electronic Energy + Enthalpy Correction)
Entropy :	475.67	J/mol•K	
Gibbs Energy :	-2802.968259	au	(Enthalpy - T*Entropy)
C_v :	242.77	J/mol•K	

Lowest energy vibrational mode = 31 cm^{-1}
Second lowest energy vibrational mode = 39 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Mo	-0.266022	-0.139570	-0.746565
H	0.255819	-0.967182	-3.631605
C	0.808698	-0.793092	-2.719330
C	1.122724	-1.764909	-1.725810
H	1.348113	1.374265	-2.857454
H	0.839329	-2.808334	-1.743476
C	1.918091	-1.138087	-0.727409
H	2.326003	-1.618035	0.152073
C	2.085443	0.222464	-1.089957
H	2.641919	0.966652	-0.536250
C	1.392841	0.441308	-2.312430
C	-1.572868	1.168002	-1.430481
O	-2.330174	1.930402	-1.861703
C	-1.857104	-1.299964	-0.769916
O	-2.780550	-1.997719	-0.810420
As	-0.620249	0.476030	1.476360
C	0.677418	0.688812	2.928462
H	0.644238	1.710720	3.317534
H	1.677818	0.480137	2.543891
H	0.449890	-0.004430	3.743445
C	-2.273211	0.889297	2.431999
H	-3.106013	0.809946	1.730746
H	-2.233240	1.903596	2.839123
H	-2.420295	0.183284	3.254381

22 [Mo(AsMe$_2$)(CO)$_2$(η^5-C$_5$H$_5$)]

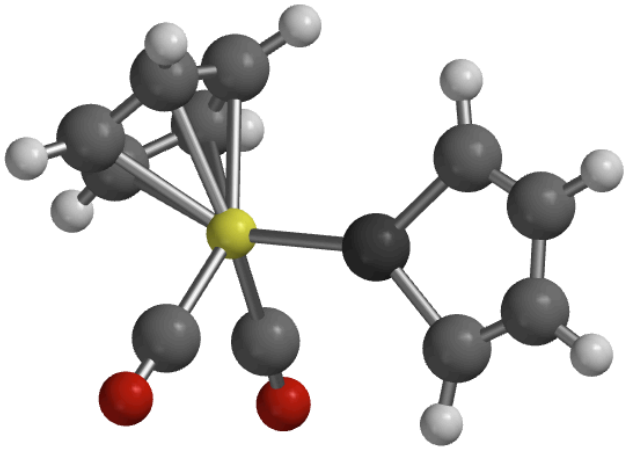

Figure S50. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	420.21	kJ/mol	(ZPE)
Temperature Correction :	36.66	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	456.87	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2877.855673	au	(Electronic Energy + Enthalpy Correction)
Entropy :	469.67	J/mol•K	
Gibbs Energy :	-2877.909009	au	(Enthalpy - T*Entropy)
C_v :	243.72	J/mol•K	

Lowest energy vibrational mode = 30 cm^{-1}
Second lowest energy vibrational mode = 36 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Mo	-0.579156	0.914442	-0.025200
As	1.206221	-0.587323	0.286935
C	2.707180	-2.814865	0.343927
C	2.923266	-0.564441	1.126203
O	-0.255446	2.151022	2.828544
C	1.502756	-2.434844	-0.123225
C	-0.351824	1.684952	1.774830
C	-2.827326	0.372737	0.252758
H	-3.232125	0.141800	1.228416
C	-1.936388	0.135317	-1.855574
H	-1.501763	-0.293679	-2.748430
C	-2.313841	-0.572406	-0.684479
H	-2.242423	-1.641461	-0.536549
O	1.226450	3.365345	-0.767516
C	-2.207593	1.513593	-1.644241
H	-2.032206	2.308618	-2.356437
C	3.491690	-1.781060	1.034554
C	0.578774	2.450309	-0.487831
C	-2.775687	1.665116	-0.350286
H	-3.124945	2.588781	0.089289
H	0.807247	-3.073530	-0.654118
H	3.102365	-3.820797	0.228936
H	4.473103	-2.012678	1.439649
H	3.361672	0.305055	1.599848

23 [Mo{$AsC_4(SiMe_3)_2Me_2$}Me_2}$(CO)_2(\eta^5$-$C_5H_5)$]

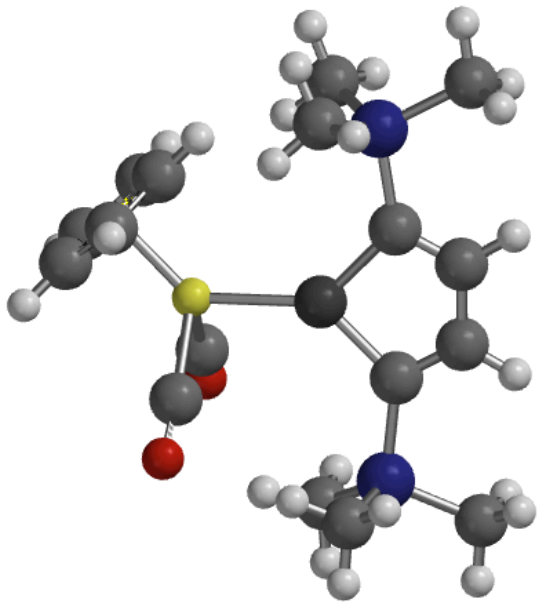

Figure S51. Optimised Geometry (ωB97X-D/6-31G*/LANL2Dζ(Sn)/Gas Phase)

Thermodynamic Properties at 298.15 K

Zero Point Energy :	934.43	kJ/mol	(ZPE)
Temperature Correction :	69.29	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	1003.71	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-3694.919842	au	(Electronic Energy + Enthalpy Correction)
Entropy :	686.12	J/mol•K	
Gibbs Energy :	-3694.997757	au	(Enthalpy - T*Entropy)
C_v :	482.21	J/mol•K	

Lowest energy vibrational mode = 20 cm^{-1}
Second lowest energy vibrational mode = 34 cm^{-1}.

Cartesian Coordinates

Atom	x	y	z
Mo	-2.149672	0.211180	-0.211425
C	-2.482677	1.204683	1.465968
O	-2.731607	1.752951	2.451965
C	-2.063489	2.024163	-0.953952
O	-2.079529	3.089951	-1.410017
H	-5.032149	-0.426306	0.699023
C	-4.320312	-0.773550	-0.037779
C	-3.365367	-1.811800	0.149437
H	-4.769270	0.518408	-1.796712
H	-3.237793	-2.399521	1.048658
C	-2.623276	-1.946026	-1.055017
H	-1.859642	-2.684556	-1.250102
C	-3.128495	-0.990033	-1.988056
H	-2.791207	-0.853437	-3.006608
C	-4.181965	-0.274390	-1.353986
As	0.176151	0.128050	0.154081
C	1.525493	1.406771	0.675811
C	1.499499	-1.279072	0.167208
C	2.669338	-0.720791	0.554328
H	3.588349	-1.294900	0.662253
C	2.683230	0.720533	0.822018
H	3.616364	1.199080	1.113882
Si	1.234061	-3.069771	-0.290868
Si	1.392712	3.275908	0.819106
C	1.340977	4.009818	-0.913960
H	0.451461	3.678799	-1.459445
H	2.224860	3.716929	-1.491323
H	1.313745	5.104919	-0.868857
C	-0.132429	3.797997	1.785123
H	-1.045993	3.656063	1.200608
H	-0.066944	4.862806	2.038037
H	-0.240103	3.237509	2.719228
C	2.939536	3.887694	1.710163
H	2.896037	4.976086	1.832462
H	3.852197	3.657087	1.149197
H	3.032444	3.443306	2.707272
C	0.749955	-3.153784	-2.114030
H	0.327524	-4.128864	-2.383022
H	1.634597	-2.990158	-2.739575
H	0.022779	-2.378886	-2.379922
C	-0.098722	-3.807216	0.822306
H	-0.449127	-4.777097	0.450944
H	-0.960806	-3.139339	0.911834
H	0.300860	-3.957362	1.831517
C	2.841598	-4.019627	-0.040332
H	2.708332	-5.074137	-0.308170
H	3.173483	-3.981854	1.003086
H	3.645760	-3.618360	-0.667085