Electronic Supporting information for:

Arsinocarbyne Reactivity

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1 [W(≡CAsMe$_2$)(CO)$_2$(Tp)]

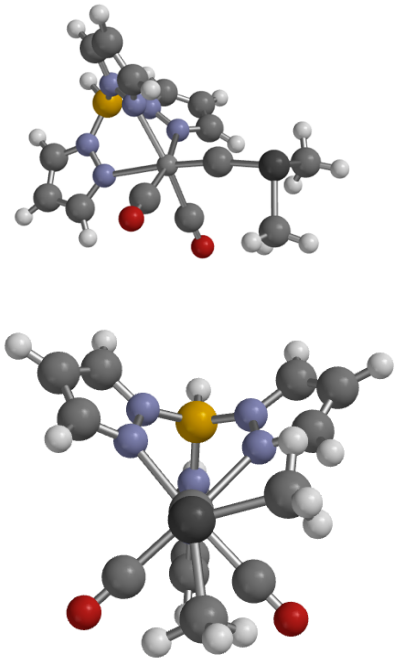

Figure S1. Optimised Geometry for [W(≡CAsMe$_2$)(CO)$_2$(Tp)]

Thermodynamic Properties at 298.15 K

Zero Point Energy:	748.90 kJ/mol (ZPE)
Temperature Correction: (vibration + gas law + rotation + translation)	57.91 kJ/mol
Enthalpy Correction: (ZPE + temperature correction)	806.81 kJ/mol
Enthalpy: (Electronic Energy + Enthalpy Correction)	-3349.891257 au
Entropy:	618.54 J/mol.K
Gibbs Energy: (Enthalpy - T*Entropy)	-3349.961497 au
C_V:	403.94 J/mol.K

Cartesian Coordinates for [W(≡CAsMe$_2$)(CO)$_2$(Tp)]

Atom	x	y	z
W	-0.721020	-0.300532	-0.277070
O	-2.818635	-2.662858	-0.373757
O	-3.029818	1.837638	-0.469724
N	-0.844148	-0.281819	2.070263
N	0.283735	-0.206030	2.809075
N	0.826213	1.239580	0.183316
N	1.695247	1.112487	1.209183
N	1.004398	-1.635536	0.217192
N	1.851113	-1.375599	1.237247
C	-0.787960	-0.321046	-2.078205
C	-2.054545	-1.797945	-0.325074
C	-2.192022	1.044307	-0.381573
C	-1.865968	-0.339172	2.924552
C	-1.401453	-0.299987	4.242395
H	-1.981019	-0.328666	5.151938
C	-0.025852	-0.214744	4.116717
C	1.100151	2.397495	-0.420172
C	2.164832	3.037069	0.218989
H	2.617184	3.983731	-0.032110
C	2.507997	2.181573	1.251005
C	1.427641	-2.757852	-0.366042
C	2.568389	-3.239824	0.280678
H	3.141605	-4.122618	0.044066
C	2.798342	-2.327293	1.294920
B	1.663309	-0.129351	2.124793
H	2.538289	-0.064035	2.949019
H	-2.877094	-0.404497	2.547764
H	0.753995	-0.159036	4.861973
H	3.269110	2.256325	2.013413
H	0.518684	2.699797	-1.278879
H	3.565308	-2.285055	2.054022
H	0.891066	-3.150244	-1.217451
As	-1.082093	-0.334661	-3.974931
C	-3.047319	-0.119941	-3.875888
H	-3.436825	0.120251	-4.869137
H	-3.316229	0.673948	-3.174648
H	-3.489453	-1.060889	-3.539413
C	-0.623600	1.570204	-4.244977
H	0.451224	1.700094	-4.093723
H	-1.170867	2.201946	-3.540555
H	-0.871912	1.862786	-5.269191

2 $[W(\equiv CAsMe_3)(CO)_2(Tp)]^+$

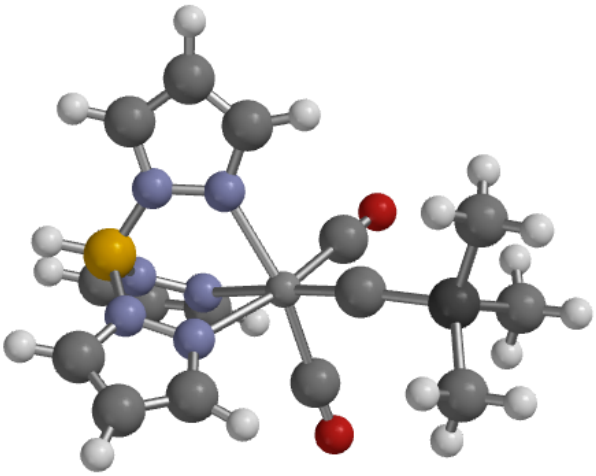

Figure S2. Optimised Geometry for $[W(\equiv CAsMe_3)(CO)_2(Tp)]^+$

Thermodynamic Properties at 298.15 K

Zero Point Energy:	846.67 kJ/mol (ZPE)
Temperature Correction: (vibration + gas law + rotation + translation)	62.37 kJ/mol
Enthalpy Correction: (ZPE + temperature correction)	909.04 kJ/mol
Enthalpy: (Electronic Energy + Enthalpy Correction)	-3389.545056 au
Entropy:	647.54 J/mol·K
Gibbs Energy: (Enthalpy - T*Entropy)	-3389.618591 au
C_V:	428.70 J/mol·K

Cartesian Coordinates for $[W(\equiv CAsMe_3)(CO)_2(Tp)]^+$

Atom	x	y	z
W	0.304336	-0.042469	0.505579
As	1.847023	2.988664	-0.795235
N	-1.871317	0.013471	0.188125
N	-0.836544	-2.515181	-1.042959
N	0.166456	-1.608402	-1.032795
N	-0.290166	-1.800363	1.844801
N	-2.599002	-1.112248	0.012932
O	0.105720	1.744763	3.120896
N	-1.238802	-2.670510	1.422408
C	0.952382	1.425136	-0.326446
O	3.315008	-0.788951	1.182234
C	2.219566	-0.534074	0.948771
C	0.961568	-1.892034	-2.070778
C	0.468160	-2.991690	-2.769336
H	0.882544	-3.459031	-3.648712
C	0.171933	1.081490	2.185250
C	-0.587170	-3.360680	3.426316
H	-0.491781	-3.926872	4.339411
C	-2.723735	1.043342	0.138185
C	-0.673935	-3.356386	-2.075538
C	-3.892394	-0.793262	-0.146542
C	-4.021117	0.584284	-0.078223
H	-4.924468	1.166853	-0.167058
C	0.107754	-2.212216	3.054459
C	2.441404	2.911471	-2.625475
H	3.198495	2.130489	-2.720238
H	2.864918	3.875347	-2.916734
H	1.588252	2.671355	-3.263003
C	-1.431122	-3.613612	2.357063
C	3.379662	3.231961	0.347009
H	3.035814	3.317144	1.379972
H	3.921324	4.135445	0.058274
H	4.030299	2.360141	0.253297
B	-1.923352	-2.497351	0.050000
H	-2.727647	-3.368257	-0.134139
H	-2.355443	2.051236	0.261146
H	-4.630361	-1.567881	-0.293219
H	-1.379557	-4.156833	-2.241804
H	1.840119	-1.291221	-2.254212
H	0.869458	-1.663019	3.590251
H	-2.155275	-4.399118	2.197921
C	0.684944	4.511887	-0.595030
H	1.225165	5.425481	-0.853590
H	0.346868	4.561514	0.442084
H	-0.175984	4.390187	-1.255318

3 *syn*-[W(≡CAsMe$_2$AuCl)(CO)$_2$(Tp)]

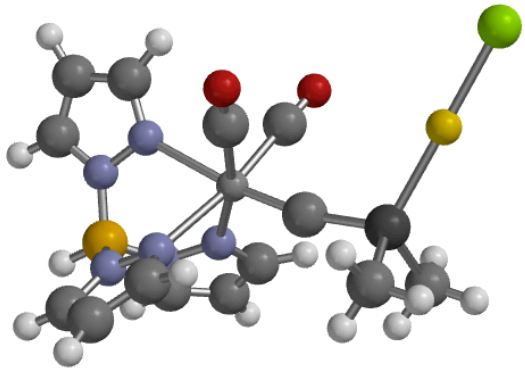

Figure S3. Optimised Geometry for [W(≡CAsMe$_2$AuCl)(CO)$_2$(Tp)]-syn conformer

Thermodynamic Properties at 298.15 K

Zero Point Energy:	755.55 kJ/mol (ZPE)
Temperature Correction: (vibration + gas law + rotation + translation)	65.07 kJ/mol
Enthalpy Correction: (ZPE + temperature correction)	820.62 kJ/mol
Enthalpy: (Electronic Energy + Enthalpy Correction)	-3945.607947 au
Entropy:	676.53 J/mol·K
Gibbs Energy: (Enthalpy - T*Entropy)	-3945.684773 au
C_V:	450.51 J/mol•K

Cartesian Coordinates for *syn*-[W(≡CAsMe$_2$AuCl)(CO)$_2$(Tp)]

Atom	x	y	z
W	-0.355696	-0.545461	0.440716
Au	-2.983419	-4.294219	-1.370855
As	-1.852657	-2.439971	-2.327970
Cl	-4.089387	-6.108891	-0.416309
O	0.349113	-3.442829	1.503254
N	0.336718	2.536300	0.445624
O	-3.287934	-0.803136	1.600690
N	-0.570482	1.627948	0.024469
N	0.312819	0.315164	2.501038
C	-2.216392	-0.713421	1.189534
N	1.763475	-0.062940	-0.021948
N	1.102262	1.411549	2.551132
N	2.354720	1.073546	0.406451
C	0.071061	-0.049955	3.761507
C	-1.520511	2.298263	-0.631189
C	0.711022	0.817873	4.649049
H	0.706670	0.785462	5.727338
C	-0.039116	3.766058	0.057331
C	1.354371	1.730880	3.831403
C	-1.228781	3.663397	-0.642357
H	-1.801293	4.460189	-1.090700
C	2.681312	-0.748420	-0.707025
C	3.889164	-0.048926	-0.730050
H	4.814739	-0.339763	-1.201628
C	3.632962	1.102148	-0.005292
B	1.574824	2.099216	1.254224
C	0.088333	-2.386965	1.127068
C	-0.993083	-1.354080	-1.035443
H	2.267117	3.048432	1.510066
H	2.419979	-1.702176	-1.141541
H	4.267170	1.938216	0.249445
H	1.972545	2.584206	4.068788
H	-0.546685	-0.914052	3.962903
H	-2.356112	1.761001	-1.055202
H	0.565308	4.624457	0.310297
C	-2.958387	-1.175163	-3.309065
H	-2.344834	-0.344524	-3.665468
H	-3.736837	-0.804583	-2.639286
H	-3.426406	-1.687744	-4.152682
C	-0.428598	-2.855595	-3.585562
H	0.295869	-3.502480	-3.087246
H	0.057100	-1.933840	-3.913534
H	-0.852042	-3.385172	-4.441976

4 *anti*-[W(≡CAsMe$_2$AuCl)(CO)$_2$(Tp)]

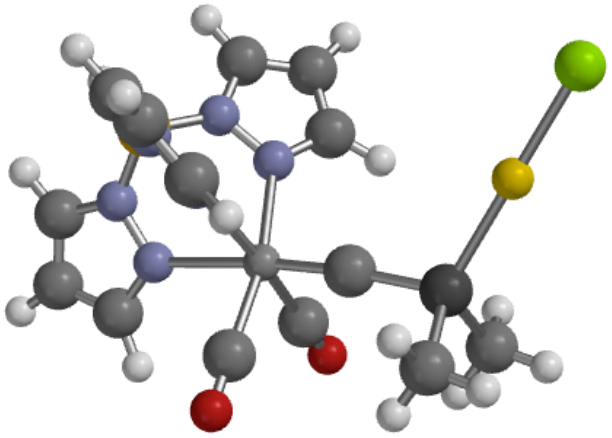

Figure S4. Optimised Geometry for [W(≡CAsMe$_2$AuCl)(CO)$_2$(Tp)]-anti conformer

Thermodynamic Properties at 298.15 K

Zero Point Energy:	755.59 kJ/mol (ZPE)
Temperature Correction: (vibration + gas law + rotation + translation)	65.04 kJ/mol
Enthalpy Correction: (ZPE + temperature correction)	820.63 kJ/mol
Enthalpy: (Electronic Energy + Enthalpy Correction)	-3945.609658 au
Entropy:	676.55 J/mol•K
Gibbs Energy: (Enthalpy - T*Entropy)	-3945.686487 au
C_V:	442.16 J/mol·K

Cartesian Coordinates for *anti*-[W(≡CAsMe$_2$AuCl)(CO)$_2$(Tp)]

Atom	x	y	z
W	-0.331180	-0.488710	0.443959
Au	-1.431563	-1.286857	-4.573369
As	-1.766736	-2.279336	-2.442968
Cl	-1.106149	-0.314726	-6.667272
O	0.360380	-3.363707	1.571028
N	0.370413	2.587171	0.309808
O	-3.253975	-0.716399	1.636528
N	-0.536552	1.660309	-0.071315
N	0.371746	0.458493	2.456710
C	-2.184171	-0.627264	1.215184
N	1.777331	-0.029459	-0.074226
N	1.167104	1.550759	2.449865
N	2.380689	1.120610	0.299787
C	0.152646	0.143981	3.735433
C	-1.466470	2.293774	-0.790061
C	0.814387	1.040959	4.576160
H	0.830152	1.051668	5.654822
C	0.013281	3.791619	-0.166397
C	1.446284	1.918122	3.710779
C	-1.163930	3.653240	-0.879988
H	-1.717971	4.421399	-1.396103
C	2.667699	-0.725859	-0.784811
C	3.868557	-0.021262	-0.879069
H	4.770959	-0.315578	-1.391654
C	3.637718	1.146362	-0.172619
B	1.618624	2.183670	1.116952
C	0.111329	-2.309284	1.175589
C	-0.970506	-1.311485	-1.021706
H	2.317874	3.139640	1.323444
H	2.391717	-1.686959	-1.192750
H	4.276079	1.993874	0.028251
H	2.072211	2.777284	3.902320
H	-0.466968	-0.706945	3.982005
H	-2.291774	1.736714	-1.208281
H	0.623575	4.658933	0.037060
C	-1.062134	-4.077013	-2.208845
H	-1.228651	-4.407692	-1.181177
H	0.007644	-4.065077	-2.424916
H	-1.562523	-4.749927	-2.909005
C	-3.619038	-2.443504	-1.872413
H	-4.070464	-1.449694	-1.867798
H	-3.662061	-2.872411	-0.868754
H	-4.155584	-3.079432	-2.580192

5 [WAu(μ-CAsMe$_2$)Cl(CO)$_2$(Tp)]

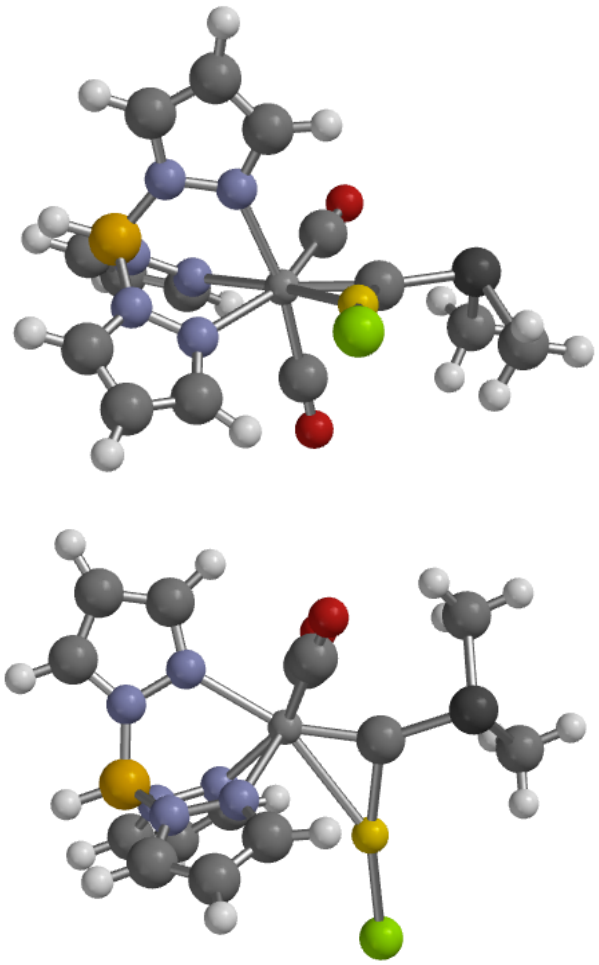

Figure S5. Optimised Geometry for [WAu(μ-CAsMe$_2$)Cl(CO)$_2$(Tp)]

Thermodynamic Properties at 298.15 K

Zero Point Energy:	755.66 kJ/mol (ZPE)
Temperature Correction:	64.89 kJ/mol
(vibration + gas law + rotation + translation)	
Enthalpy Correction:	820.55 kJ/mol
(ZPE + temperature correction)	
Enthalpy:	-3945.614859 au
(Electronic Energy + Enthalpy Correction)	
Entropy:	672.93 J/mol·K
Gibbs Energy:	-3945.691276 au
(Enthalpy - T*Entropy)	
C_V:	450.00 J/mol·K

Cartesian Coordinates for [WAu(μ-CAsMe$_2$)Cl(CO)$_2$(Tp)]

Atom	x	y	z
W	-0.285361	-0.406648	-0.004344
Au	0.182494	-0.596491	-2.776530
As	-2.729835	-2.275425	-2.087869
Cl	1.541936	-0.116568	-4.616140
O	0.576361	-3.314424	0.851896
N	0.189552	2.689239	0.280351
O	-3.202918	-0.643144	1.165749
N	-0.557897	1.766260	-0.361493
N	0.033020	0.257551	2.127371
C	-2.136518	-0.576496	0.736293
N	1.851049	0.196040	-0.120610
N	0.700357	1.407137	2.377335
N	2.282246	1.345996	0.448322
C	-0.314493	-0.262590	3.307865
C	-1.411656	2.425560	-1.147197
C	0.129767	0.557881	4.343771
H	0.005890	0.409674	5.404962
C	-0.187910	3.921867	-0.100722
C	0.771607	1.604372	3.702698
C	-1.216540	3.802309	-1.017733
H	-1.744149	4.594669	-1.524723
C	2.912203	-0.380743	-0.694308
C	4.048358	0.402810	-0.499745
H	5.048992	0.211273	-0.853249
C	3.599904	1.487392	0.233395
B	1.312900	2.249890	1.231707
C	0.250704	-2.252975	0.538739
C	-1.218355	-1.266760	-1.404511
H	1.888459	3.202931	1.683400
H	2.797900	-1.311607	-1.230625
H	4.122840	2.349731	0.619495
H	1.283037	2.470778	4.095299
H	-0.862352	-1.193311	3.346286
H	-2.104824	1.874080	-1.765735
H	0.306792	4.791733	0.305012
C	-1.786257	-3.337574	-3.453336
H	-0.874105	-3.781999	-3.047933
H	-1.530352	-2.702982	-4.305379
H	-2.460121	-4.129418	-3.793759
C	-2.783856	-3.668551	-0.690662
H	-3.148624	-3.243604	0.246738
H	-1.797981	-4.112020	-0.536235
H	-3.482264	-4.445840	-1.013845

6 [W(μ-CAuClAsMe$_2$)(CO)$_2$(Tp)]-TS

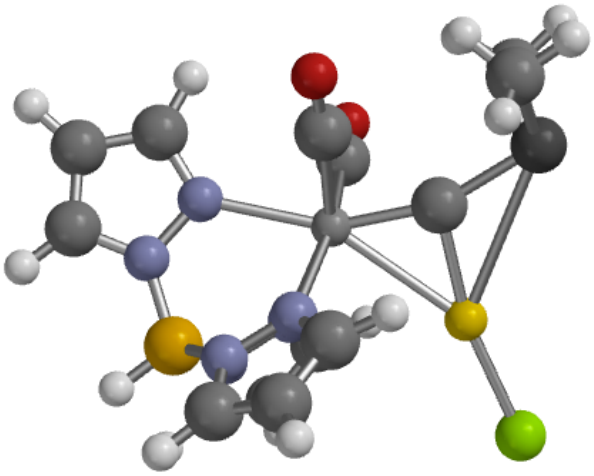

Figure S6. Optimised Geometry for [WAu(μ-CAsMe)Cl(CO)$_2$(Tp)]

Thermodynamic Properties at 298.15 K

Zero Point Energy:	755.78 kJ/mol (ZPE)
Temperature Correction: (vibration + gas law + rotation + translation)	64.95 kJ/mol
Enthalpy Correction: (ZPE + temperature correction)	820.73 kJ/mol
Enthalpy: (Electronic Energy + Enthalpy Correction)	-3945.606617 au
Entropy:	672.49 J/mol·K
Gibbs Energy: (Enthalpy - T*Entropy)	-3945.682985 au
C_V:	441.55 J/mol·K
Single imaginary frequency	i35 cm^{-1}

Cartesian Coordinates for [W(μ-CAuClAsMe$_2$)(CO)$_2$(Tp)]-TS

Atom	x	y	z
W	-0.122823	-0.489274	-0.216582
As	-2.191647	-2.334581	-2.800698
O	0.754743	-3.454947	0.415604
N	0.345555	2.565689	0.371903
O	-3.015095	-0.879526	0.974535
N	-0.394844	1.707693	-0.362547
N	0.157599	-0.027587	1.987154
C	-1.969971	-0.759005	0.506362
N	2.020479	0.121512	-0.203342
N	0.800384	1.101787	2.361989
N	2.435435	1.209782	0.486064
C	-0.207484	-0.663434	3.104976
C	-1.220303	2.441469	-1.112791
C	0.200637	0.059809	4.224792
H	0.055260	-0.190694	5.263962
C	-0.010114	3.830403	0.085517
C	0.839872	1.171941	3.701621
C	-1.015952	3.800190	-0.863630
H	-1.520489	4.638217	-1.318400
C	3.103306	-0.418251	-0.773716
C	4.236776	0.327678	-0.455595
H	5.251466	0.153974	-0.777167
C	3.763752	1.349863	0.348518
B	1.441699	2.043632	1.313757
C	0.422769	-2.376689	0.180672
C	-0.983970	-1.225839	-1.723625
H	2.000660	2.954058	1.863420
H	-1.899467	1.953015	-1.796166
H	-0.742455	-1.600440	3.043869
H	1.325390	2.005659	4.187131
H	4.275808	2.168250	0.832882
H	3.006647	-1.296628	-1.395524
H	0.481381	4.657613	0.575619
Au	0.467602	-0.383308	-2.965484
Cl	1.867922	0.325589	-4.696547
C	-3.933234	-1.911134	-1.971006
H	-3.981354	-2.191784	-0.917986
H	-4.697116	-2.464753	-2.526003
H	-4.140862	-0.842500	-2.075134
C	-1.849035	-4.026113	-1.843311
H	-0.820012	-4.344345	-2.026767
H	-2.526355	-4.787631	-2.240506
H	-2.012560	-3.919359	-0.767822

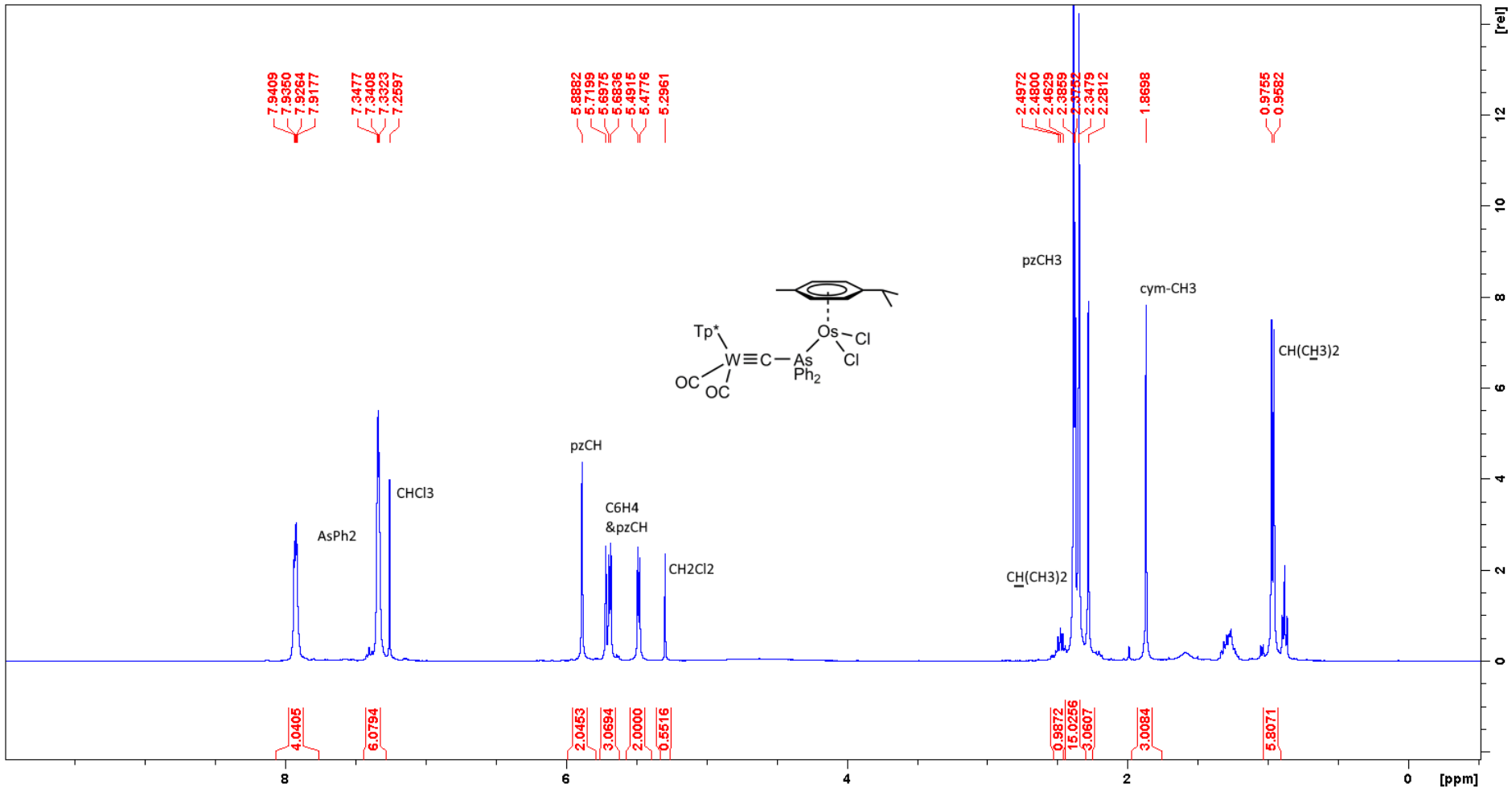

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C, δ) of [W{≡CAsPh_2OsCl_2(*p*-cymene)}$(CO)_2$(Tp*)] (**2**).

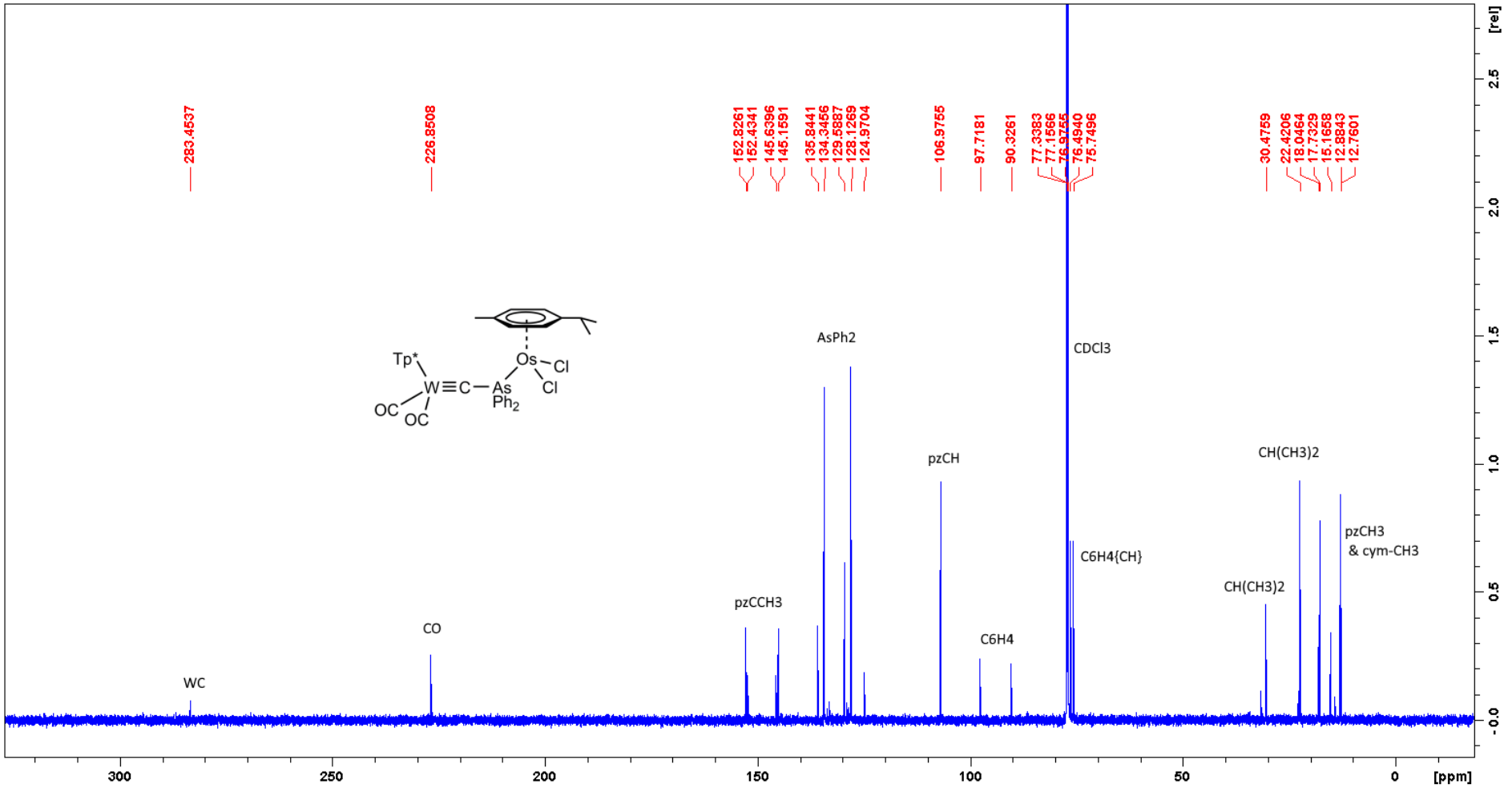

Figure S8. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 25˚C, δ) of [W{≡CAsPh_2OsCl_2(*p*-cymene)}$(CO)_2$(Tp*)] (**2**).

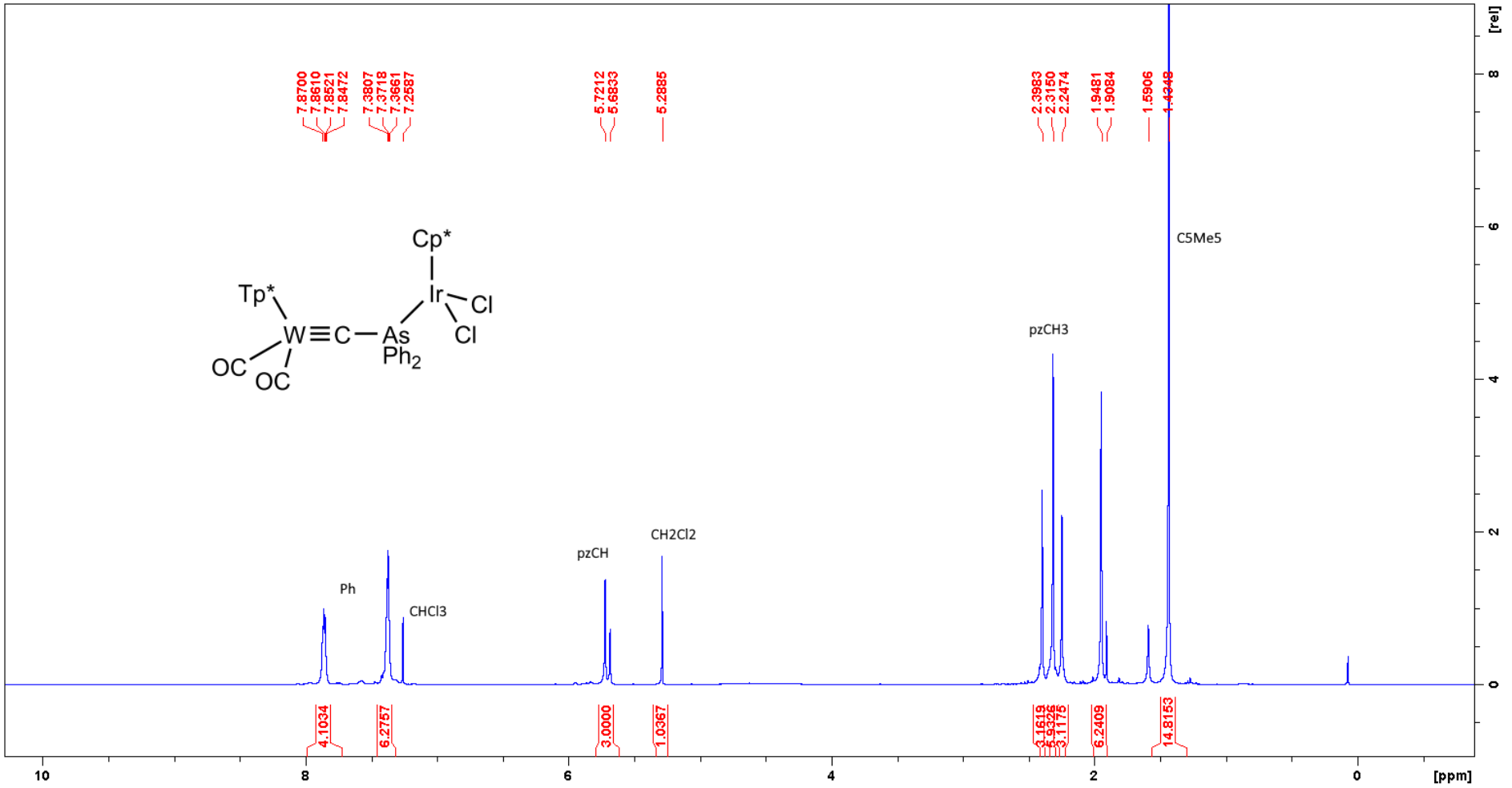

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C, δ) of [W(≡CAsPh_2IrCl_2Cp*)$(CO)_2$(Tp*)] (**3**).

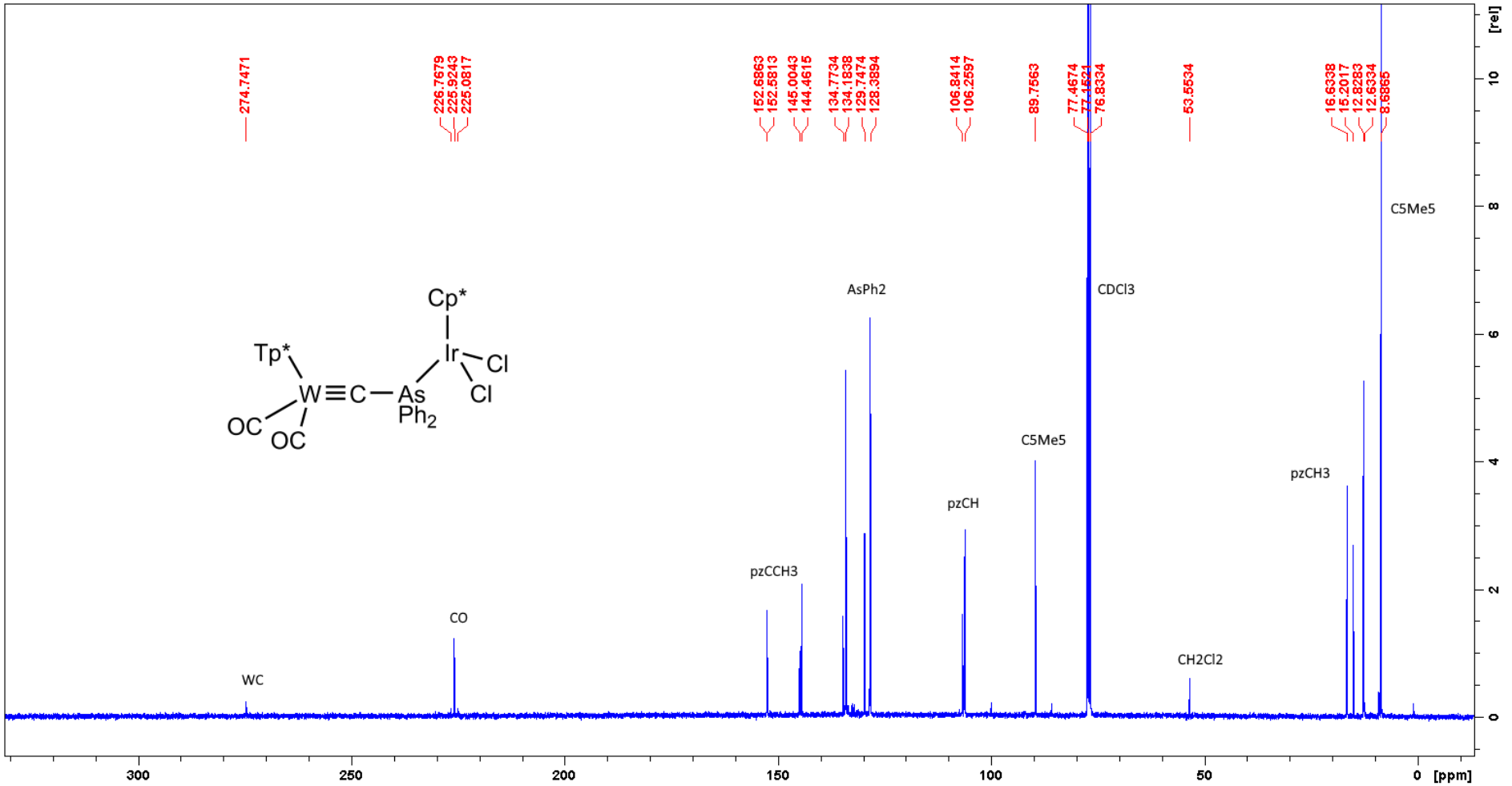

Figure S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 25˚C, δ) of [W(≡CAsPh_2IrCl_2Cp*)$(CO)_2$(Tp*)] (**3**).

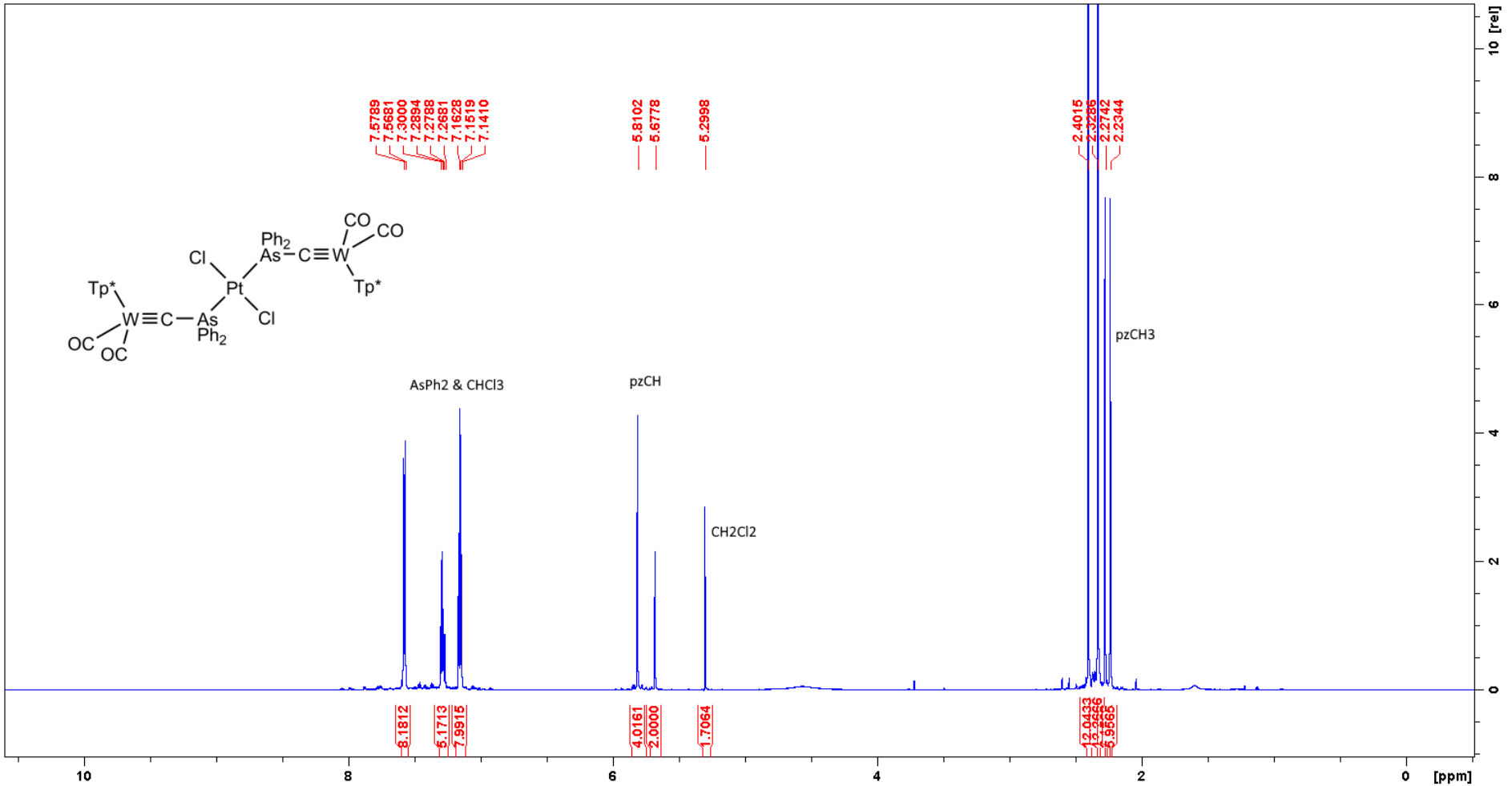

Figure S11. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of [*trans*-{(Tp*)(CO)$_2$W≡CAsPh$_2$}$_2$PtCl$_2$] (**4a**).

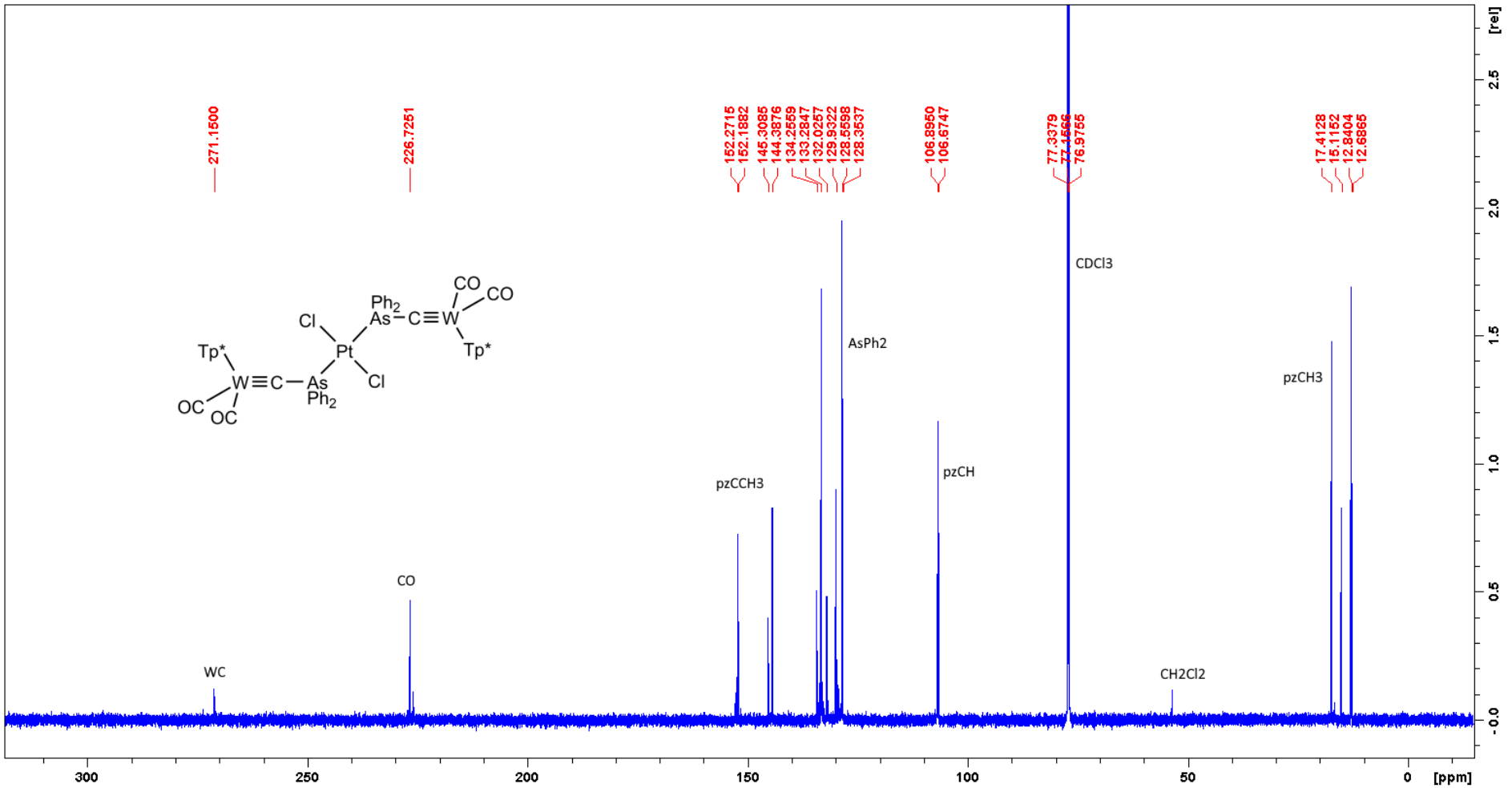

Figure S12. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 25˚C, δ) of [*trans*-{(Tp*)$(CO)_2$W≡CAsPh_2}$_2$PtCl_2] (**4a**).

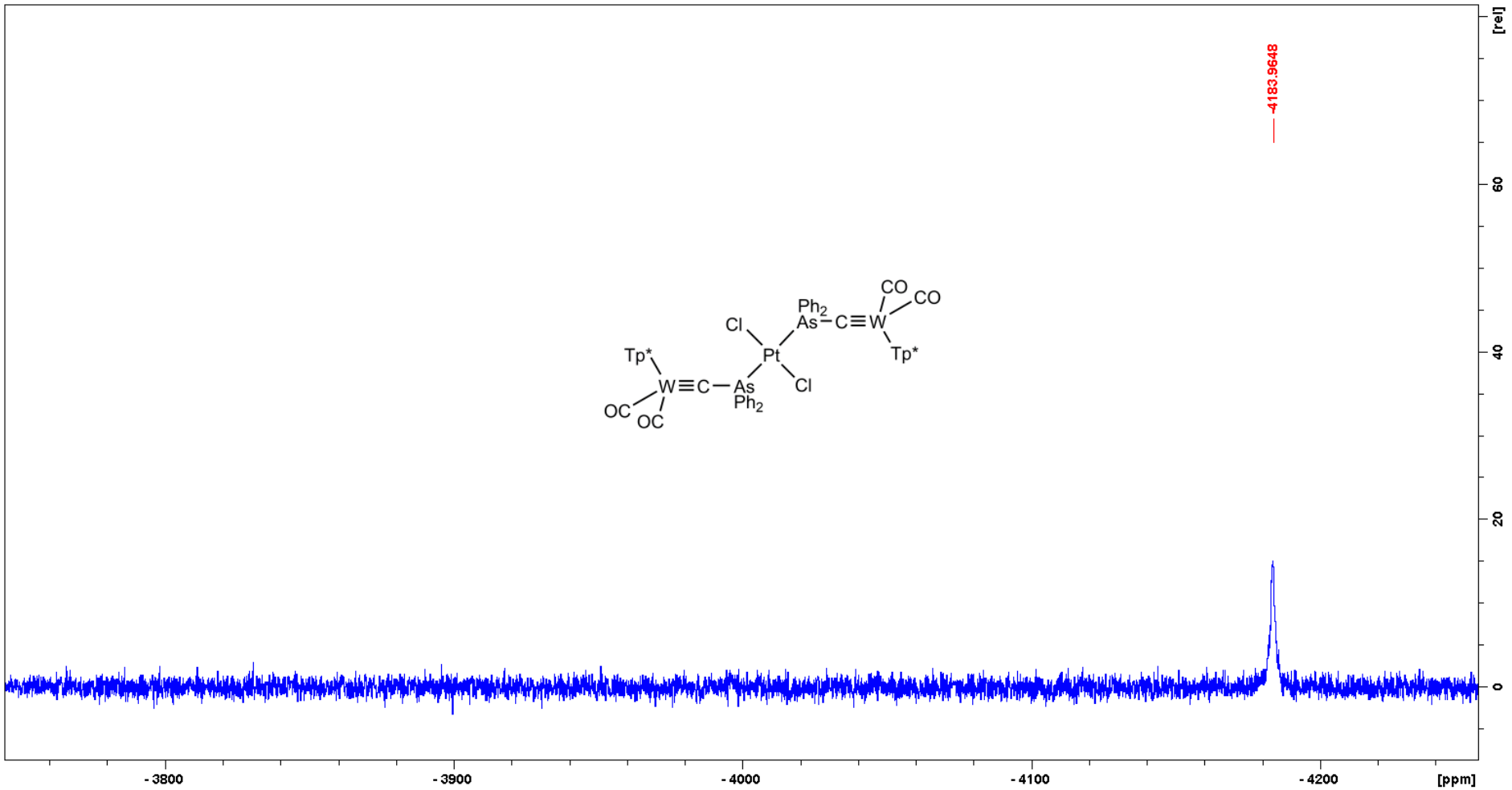

Figure S13. $^{195}Pt\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 25˚C, δ) of [*trans*-{(Tp*)$(CO)_2$W≡CAsPh_2}$_2$PtCl_2] (**4a**).

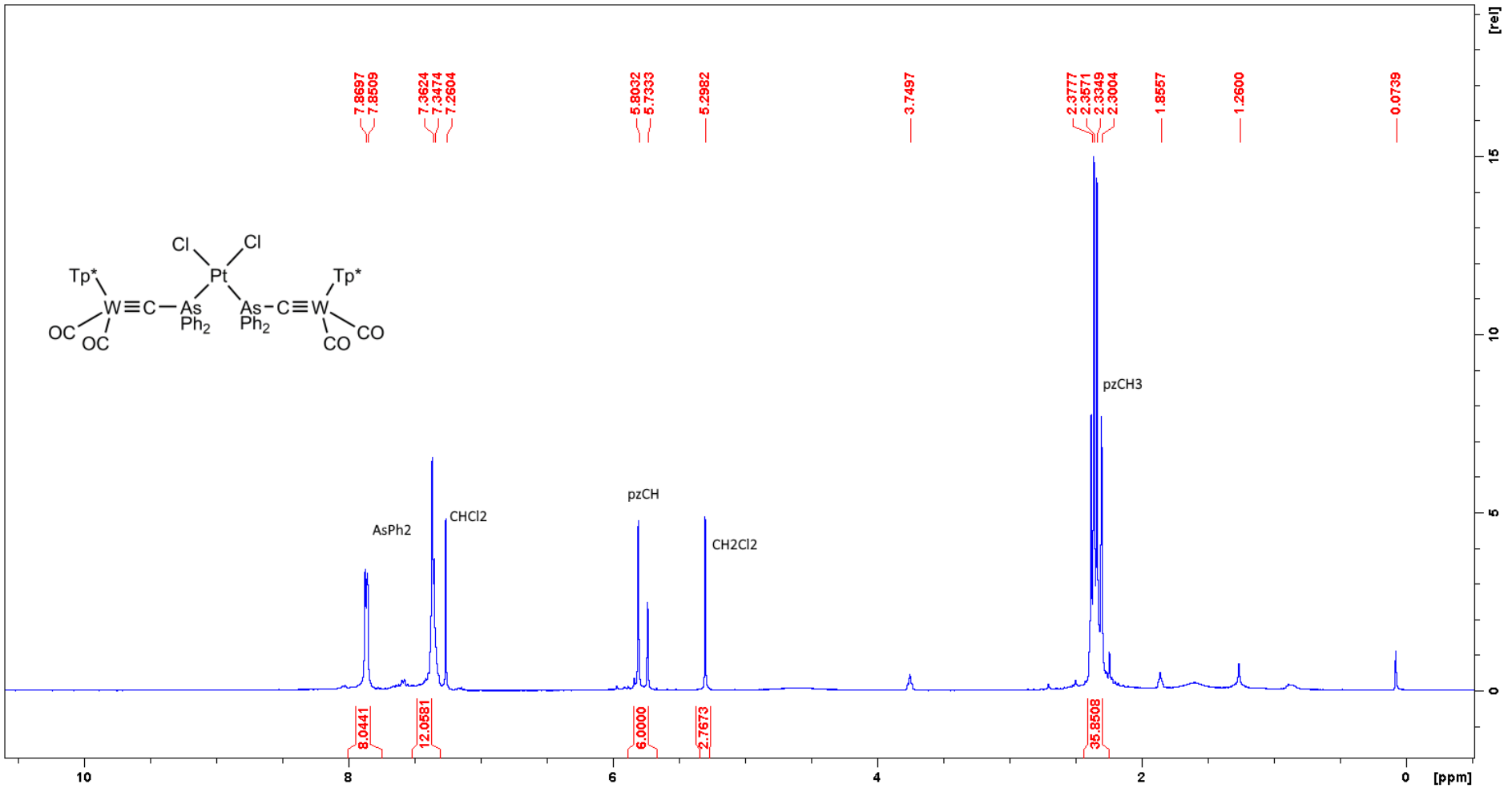

Figure S14. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of [*cis*-{(Tp*)(CO)$_2$W≡CAsPh$_2$}$_2$PtCl$_2$] (**4b**).

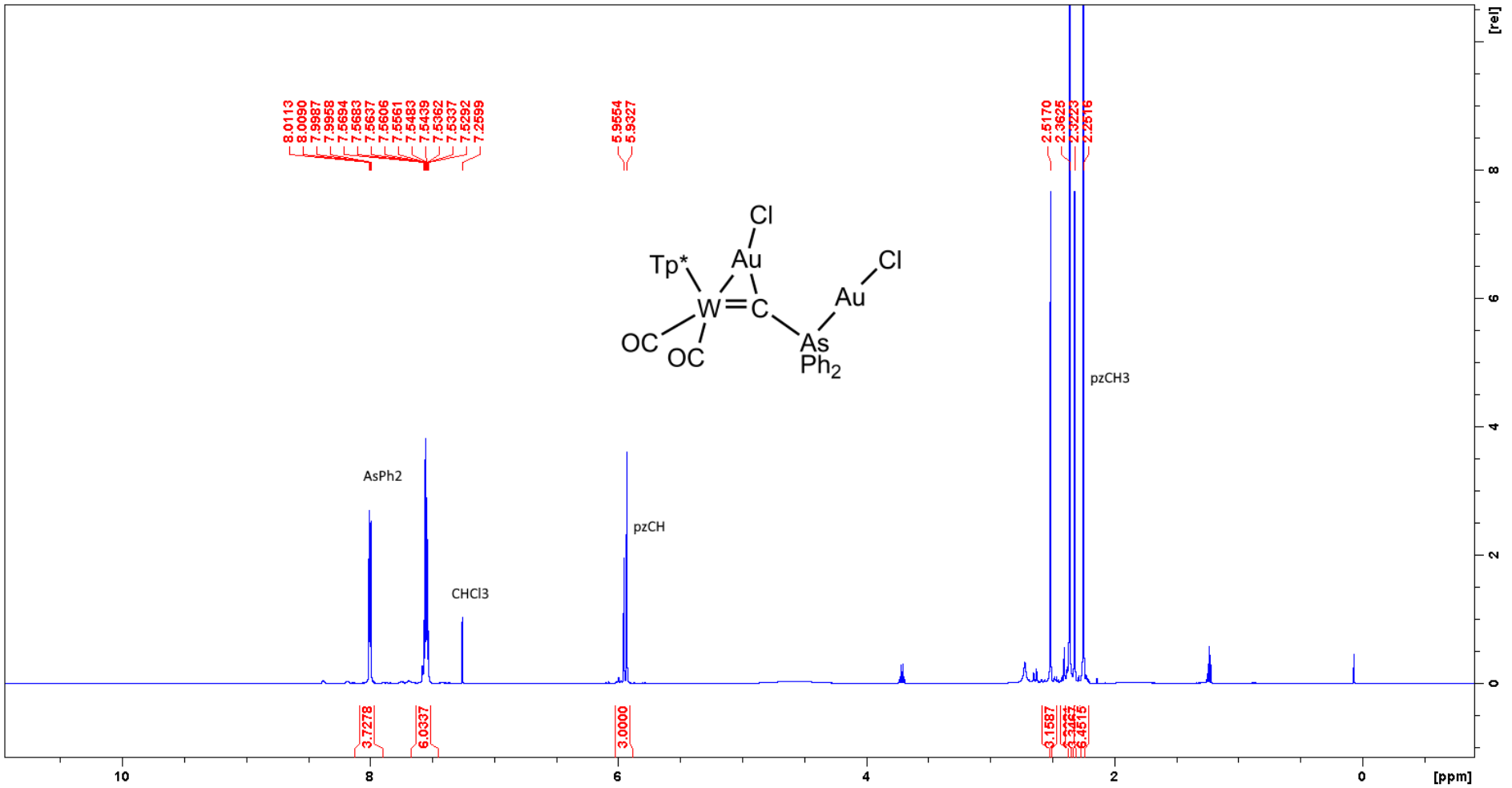

Figure S15. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ˚C, δ) of [WAu(μ-CAsPh_2{AuCl})Cl$(CO)_2$(Tp*)] (**5**).

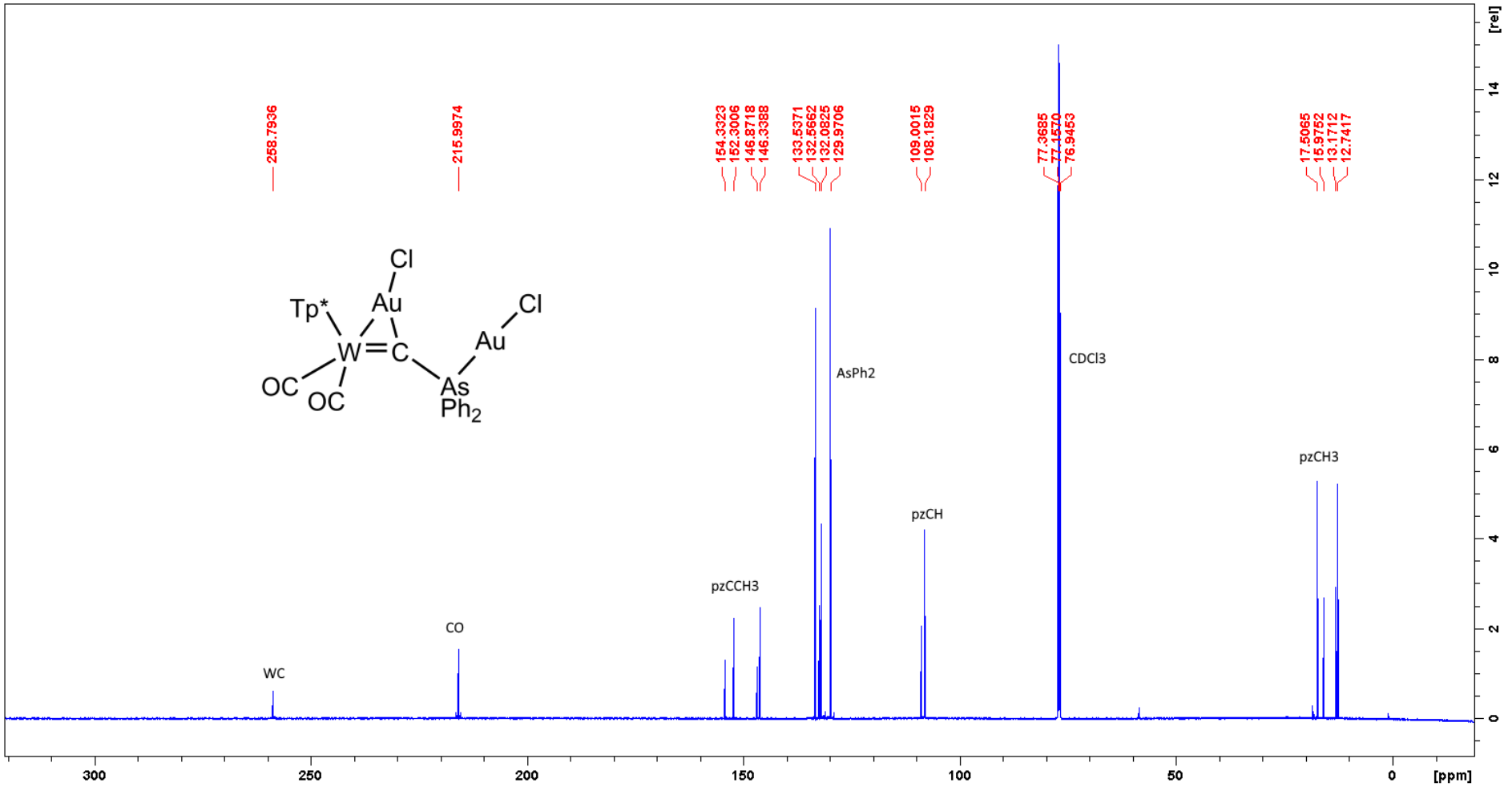

Figure S16. $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 25˚C, δ) of [WAu(μ-$CAsPh_2${AuCl})Cl$(CO)_2$(Tp*)] (**5**).

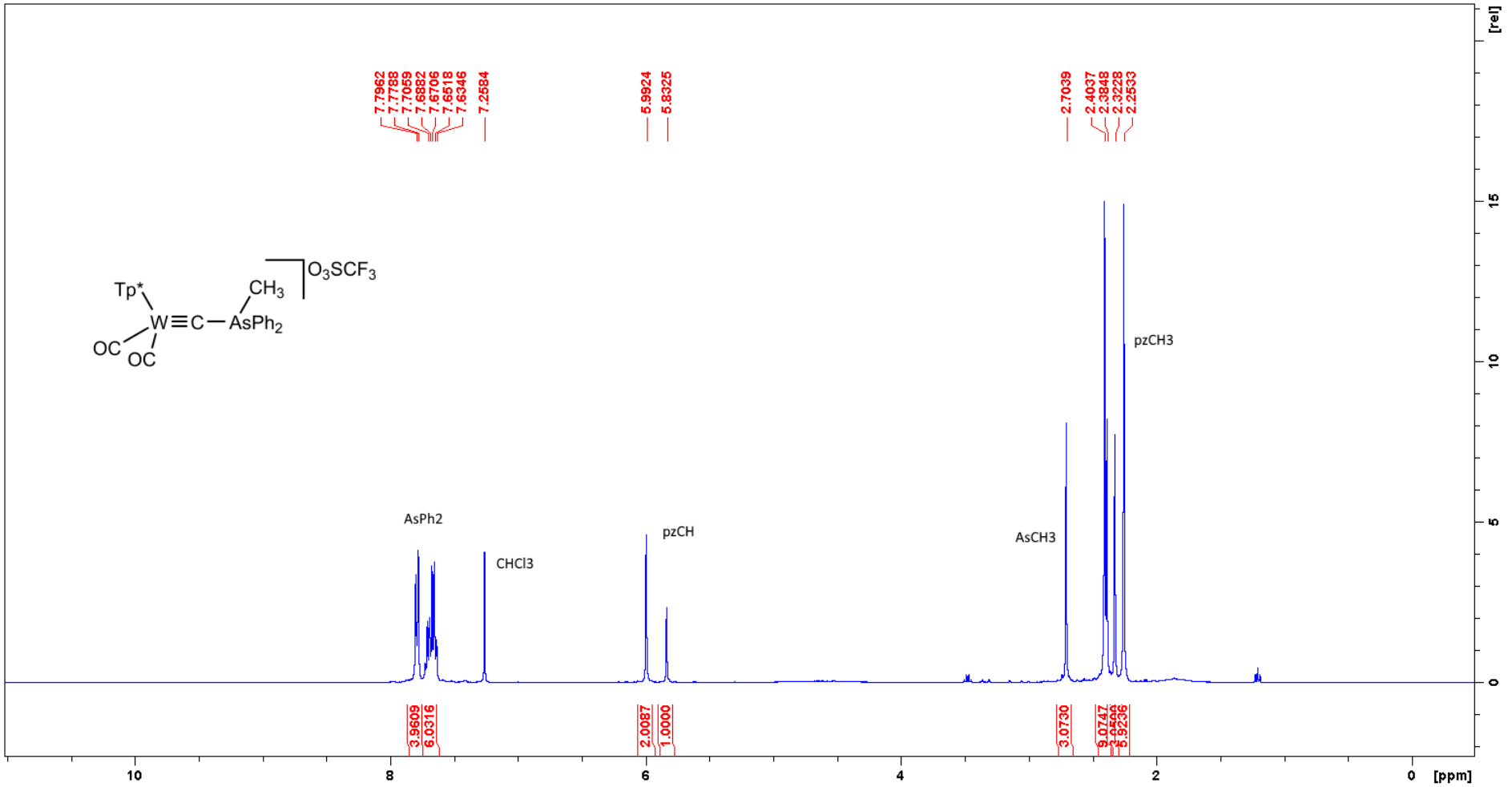

Figure S17. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ˚C, δ) of $[W(\equiv CAsPh_2Me)(CO)_2(Tp^*)]O_3SCF_3$ [**6**]O_3SCF_3.

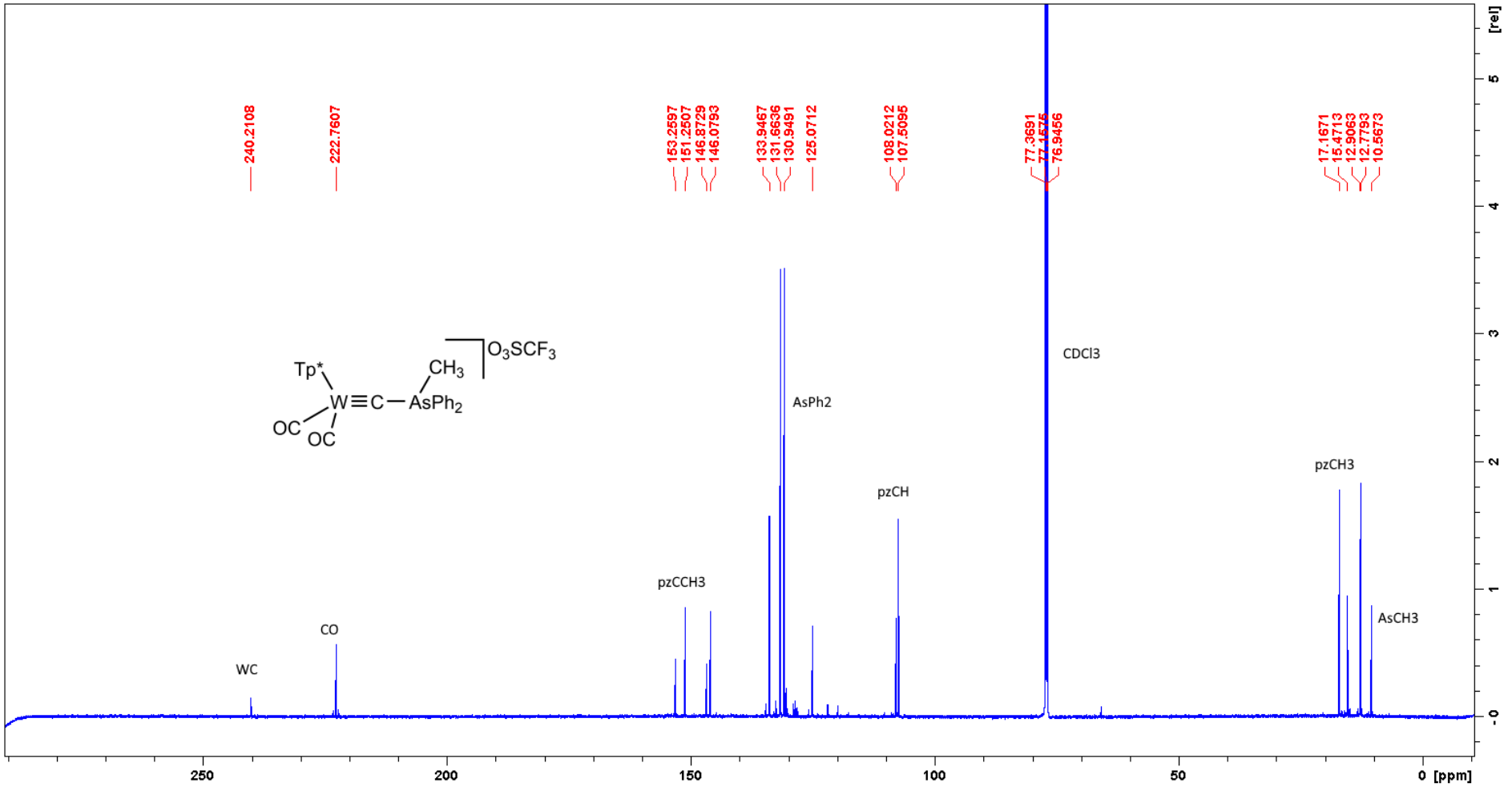

Figure S18. $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 25˚C, δ) of $[W(\equiv CAsPh_2Me)(CO)_2(Tp^*)]O_3SCF_3$ [**6**]O_3SCF_3.

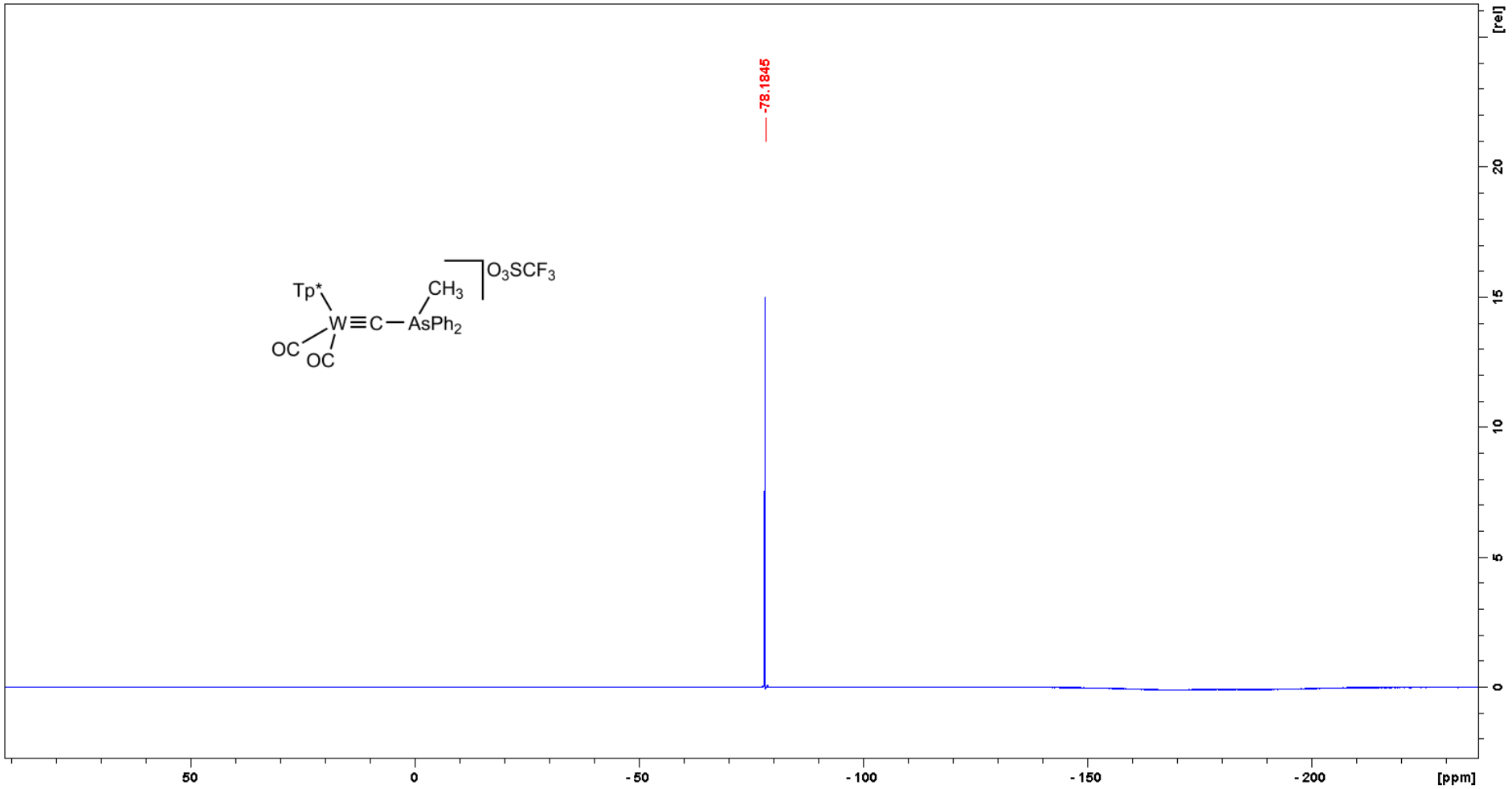

Figure S19. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 25˚C, δ) of $[W(\equiv CAsPh_2Me)(CO)_2(Tp^*)]O_3SCF_3$ [**6**]O_3SCF_3.

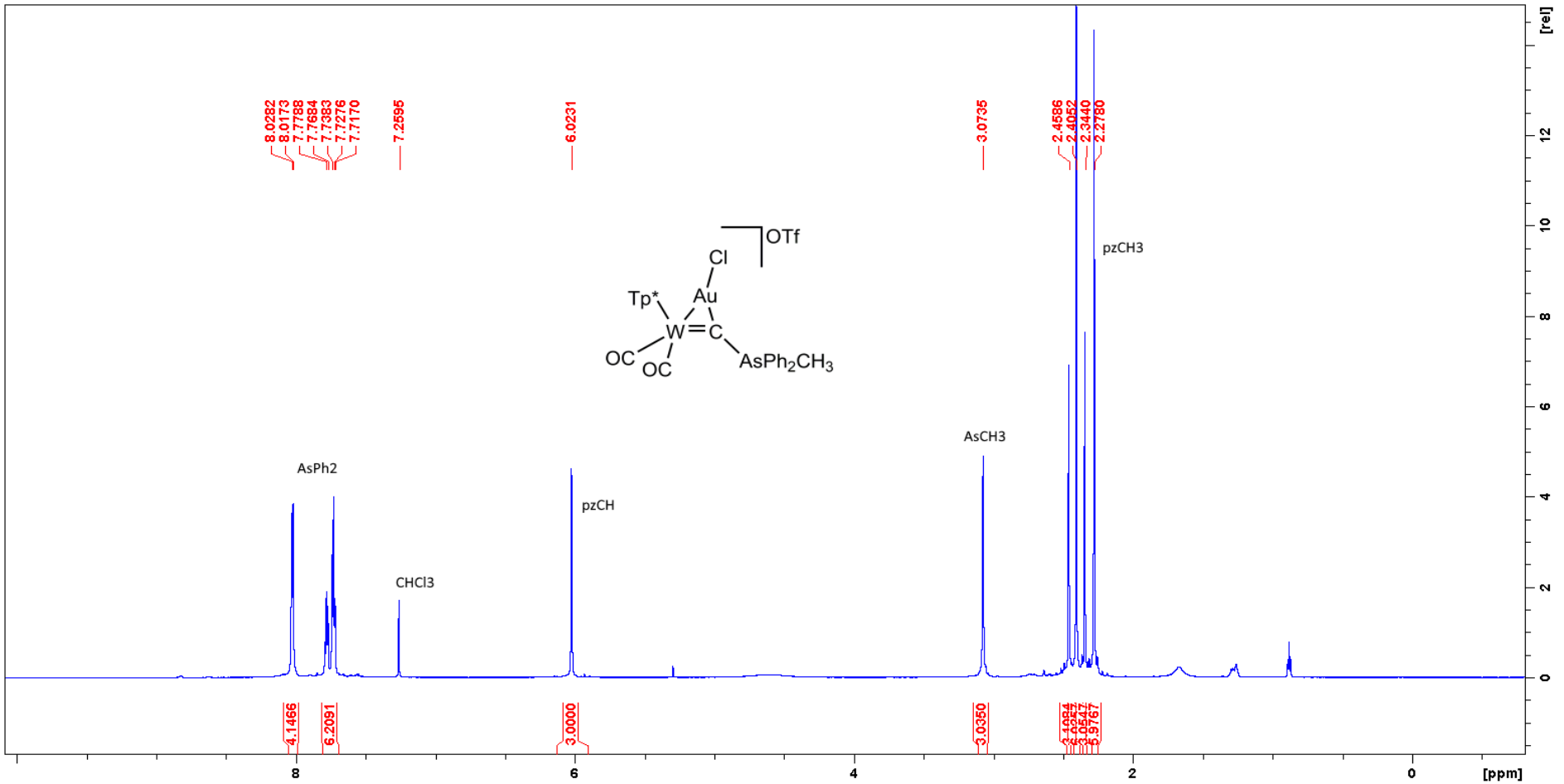

Figure S20. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of [WAu(μ-CAsPh$_2$Me)Cl(CO)$_2$(Tp*)]O_3SCF_3 [**7**]O_3SCF_3.

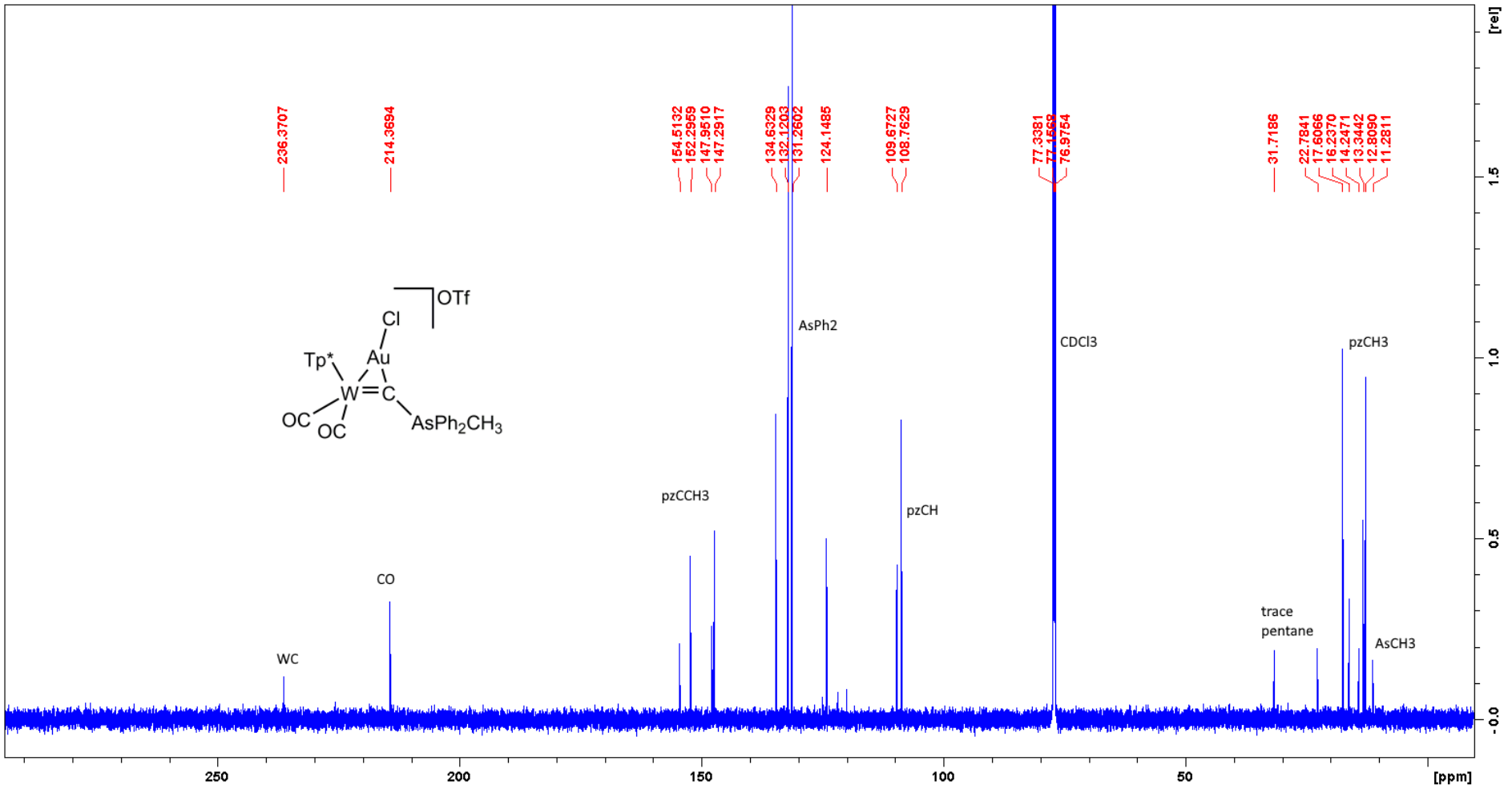

Figure S21. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 25˚C, δ) of $[WAu(\mu\text{-}CAsPh_2Me)Cl(CO)_2(Tp^*)]O_3SCF_3$ [**7**]O_3SCF_3.

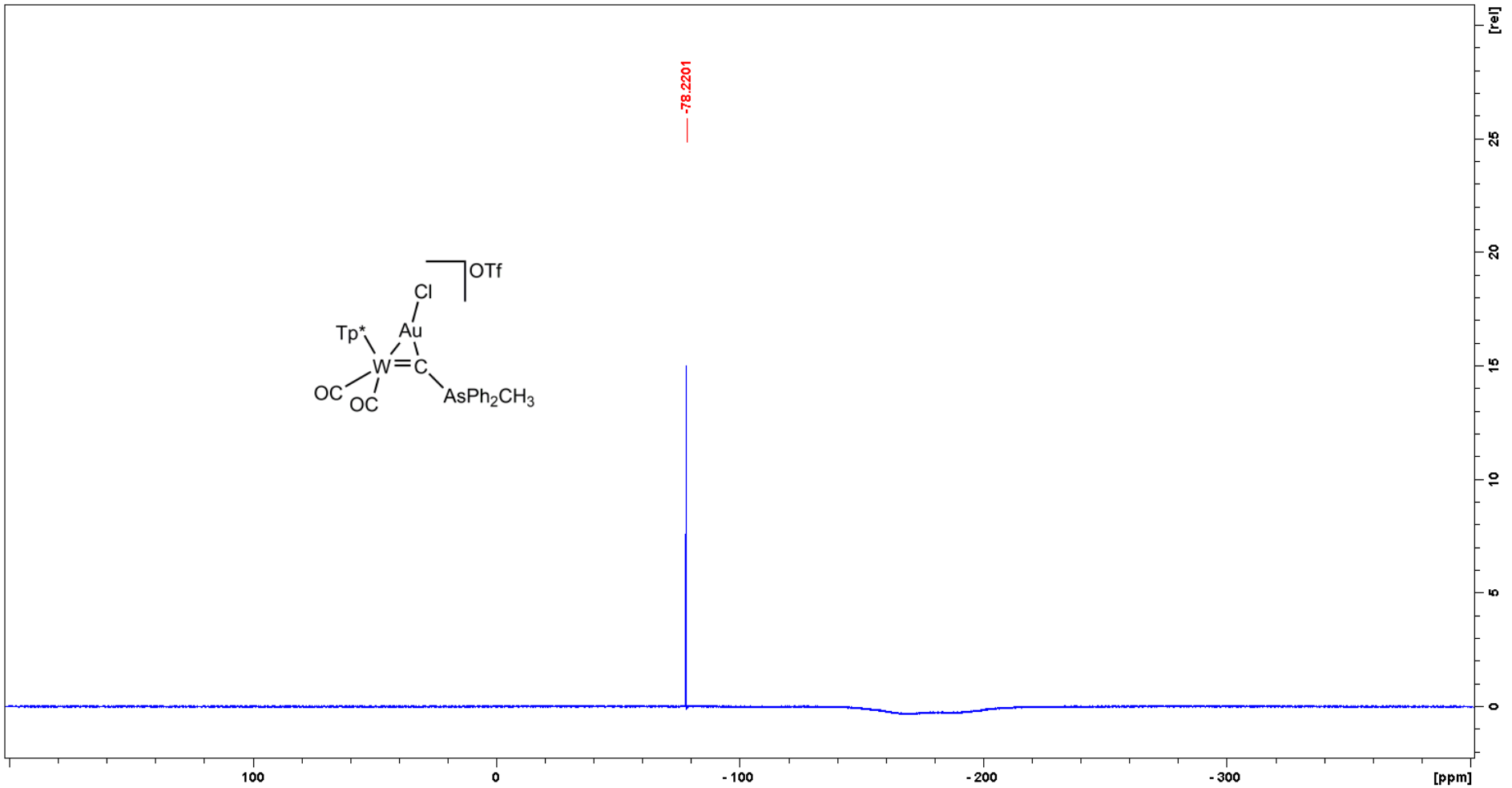

Figure S22. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 25˚C, δ) [WAu(μ-CAsPh_2Me)Cl$(CO)_2$(Tp*)]O_3SCF_3 [**7**]O_3SCF_3.

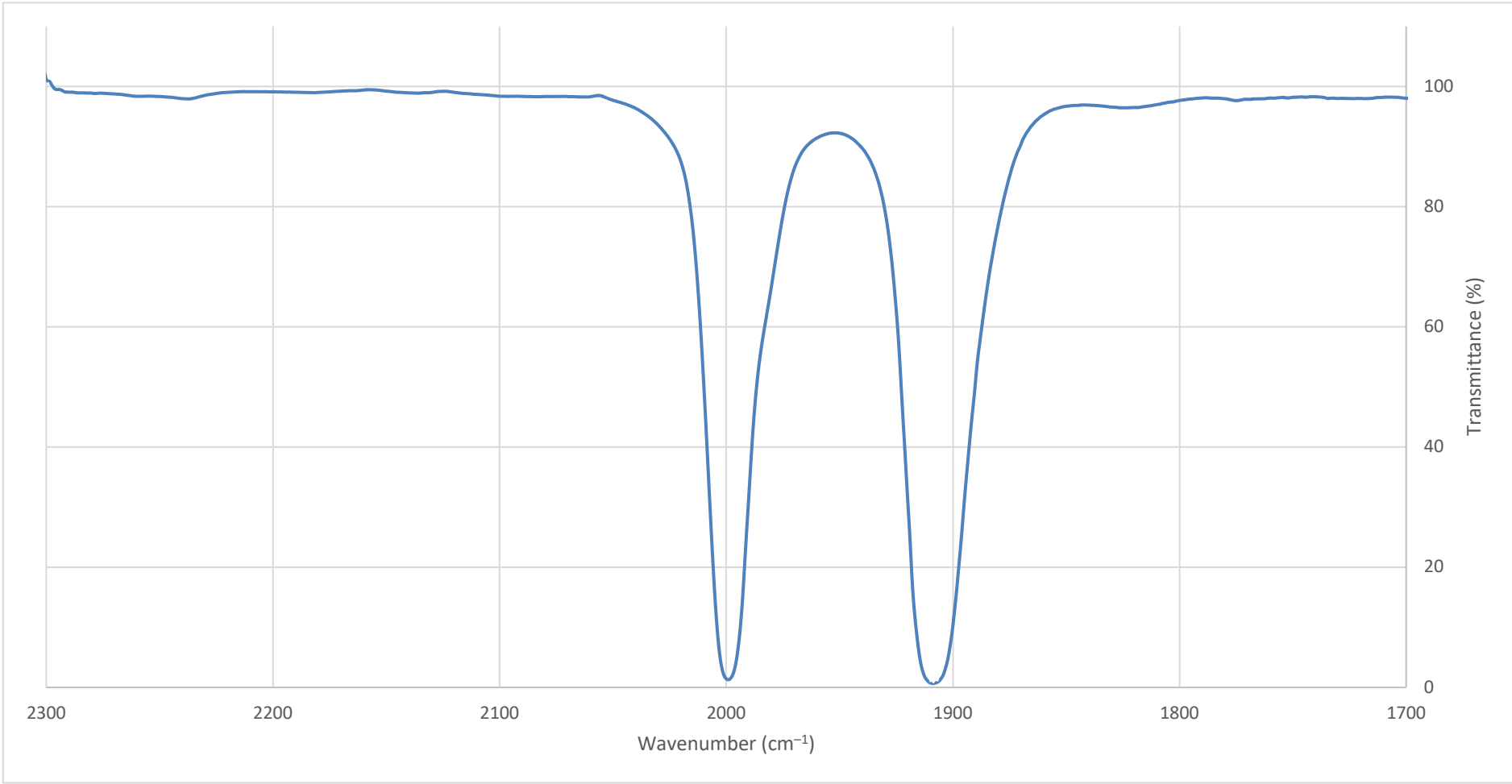

Figure S23. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [W{≡CAsPh_2OsCl_2(*p*-cymene)}$(CO)_2$(Tp*)] (**2**).

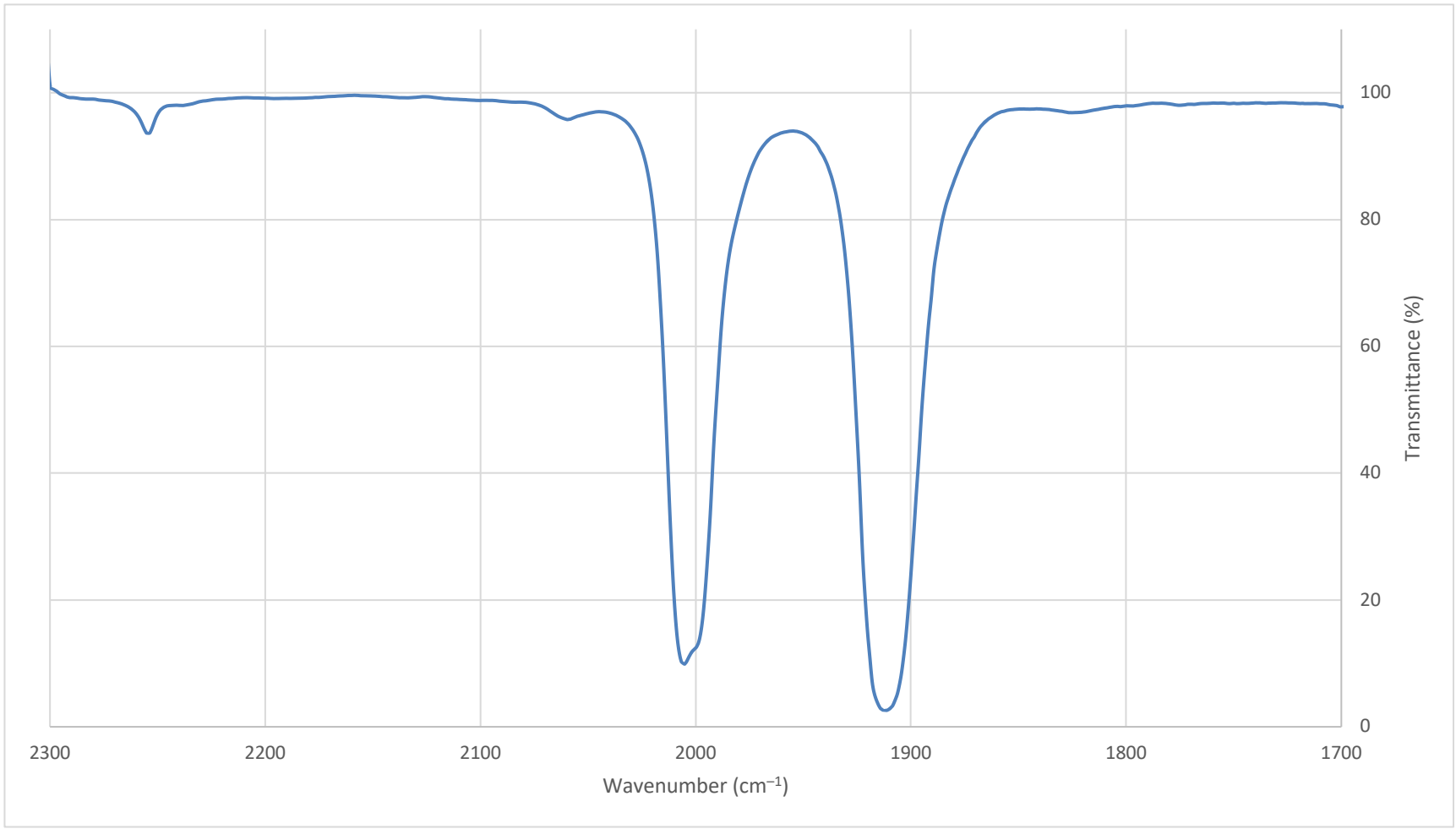

Figure S24. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [W(≡CAsPh_2IrCl_2Cp*)$(CO)_2$(Tp*)] (**3**).

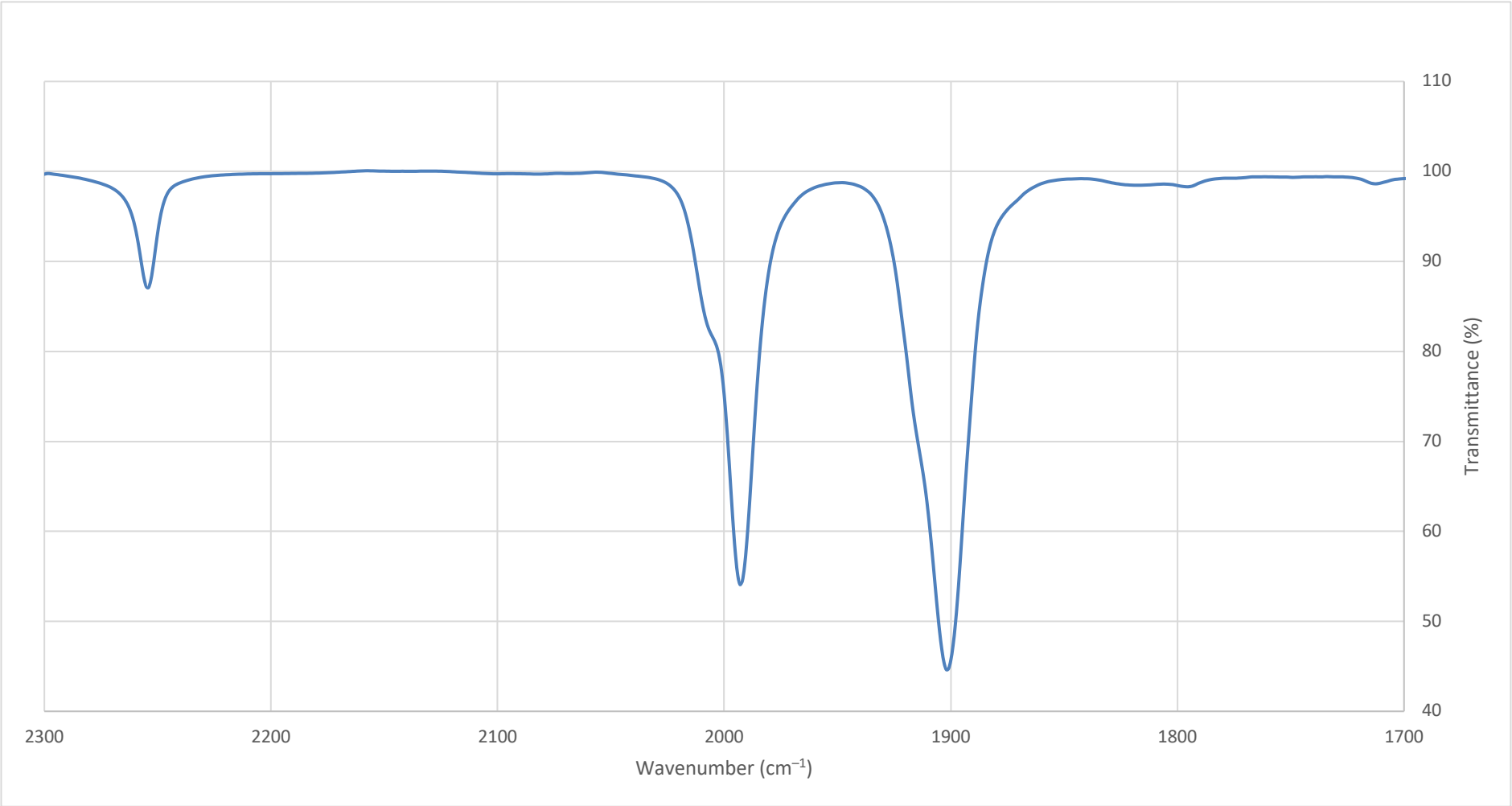

Figure S25. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [*trans*-{(Tp*)$(CO)_2W{\equiv}CAsPh_2$}$_2PtCl_2$] (**4a**).

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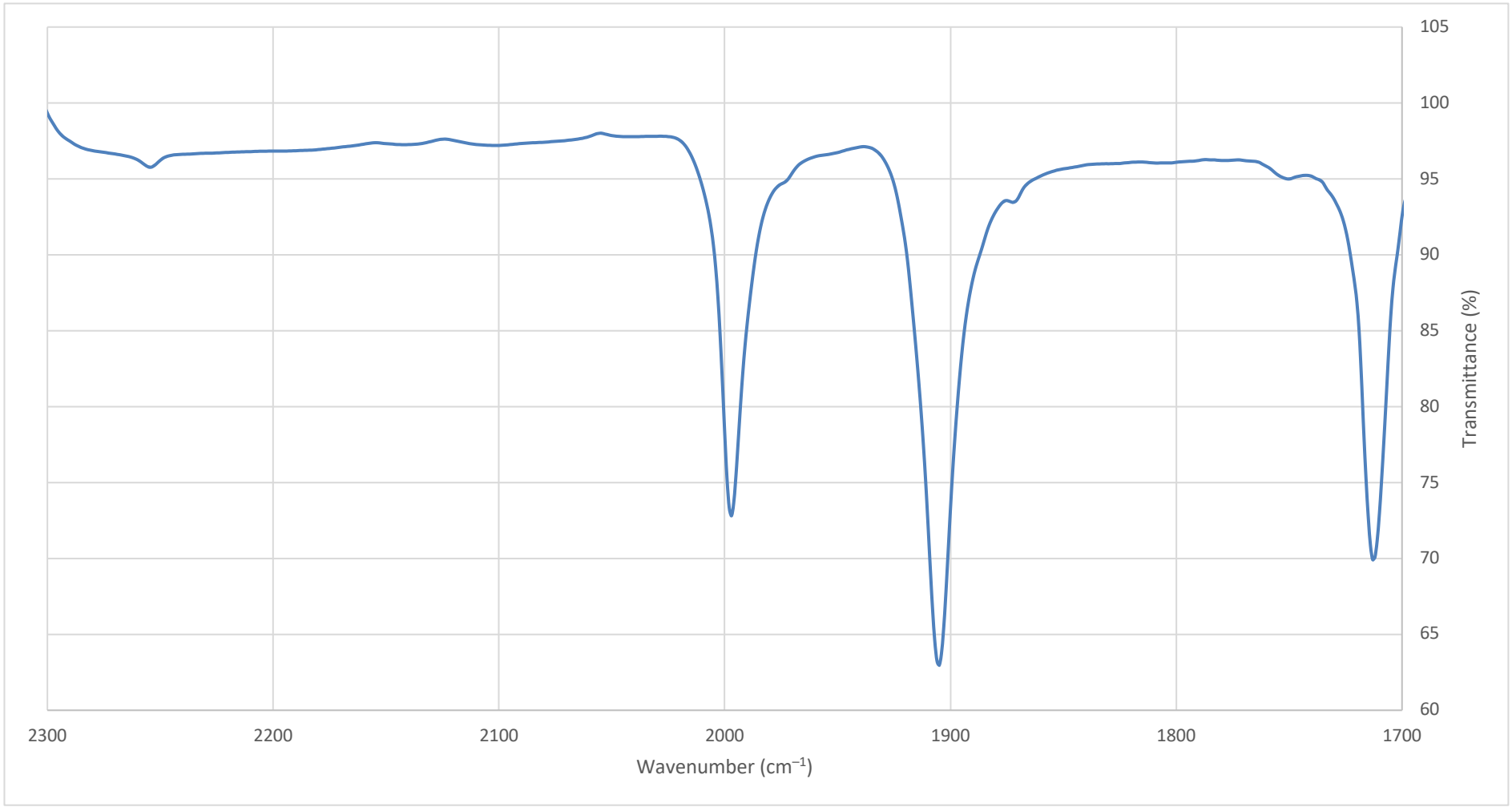

Figure S26. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [*cis*-{(Tp*)$(CO)_2$W≡CAsPh_2}$_2$$PtCl_2$] (**4b**).

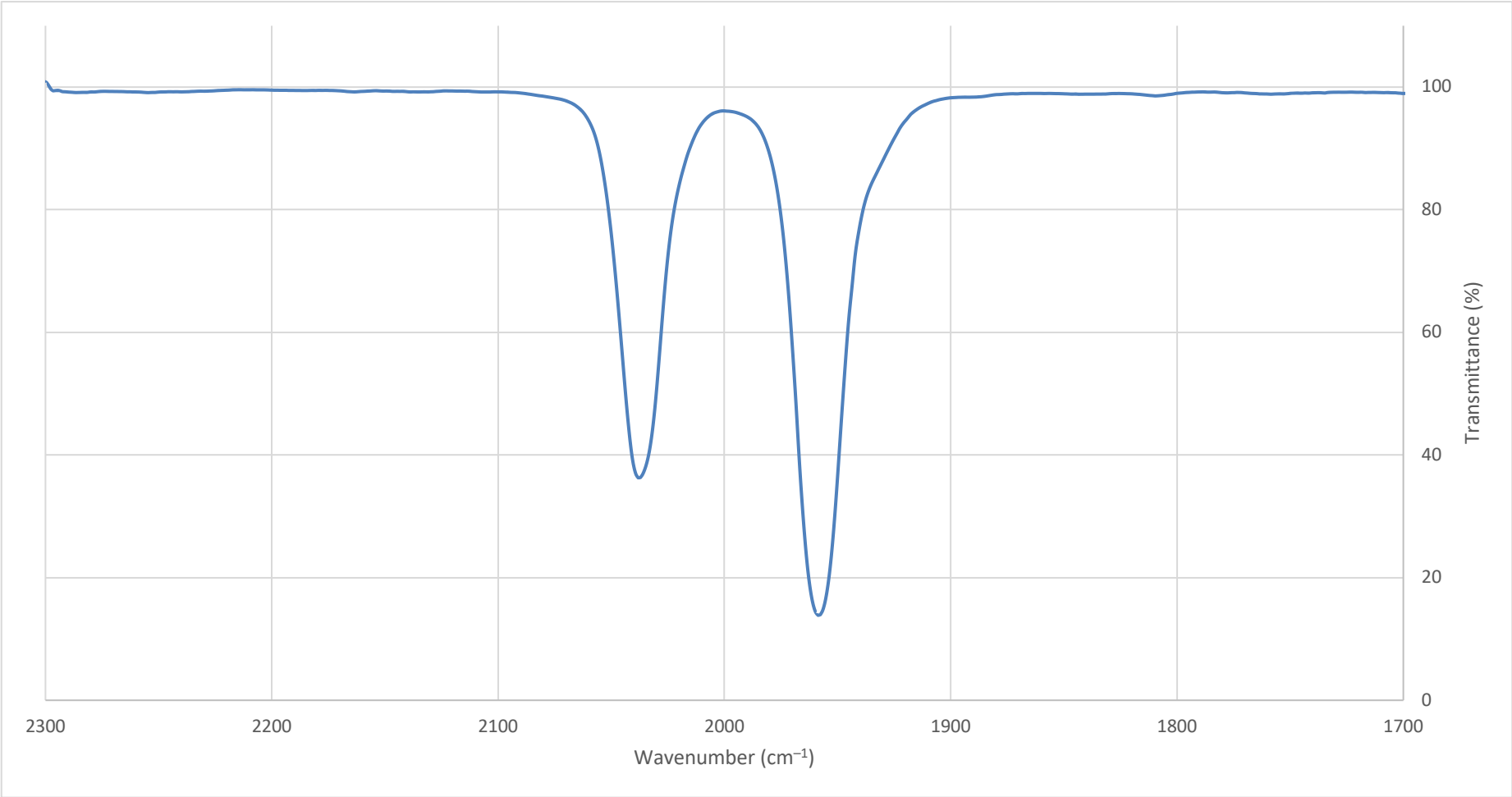

Figure S27. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [WAu(μ-CAsPh$_2${AuCl})Cl(CO)$_2$(Tp*)] (**5**).

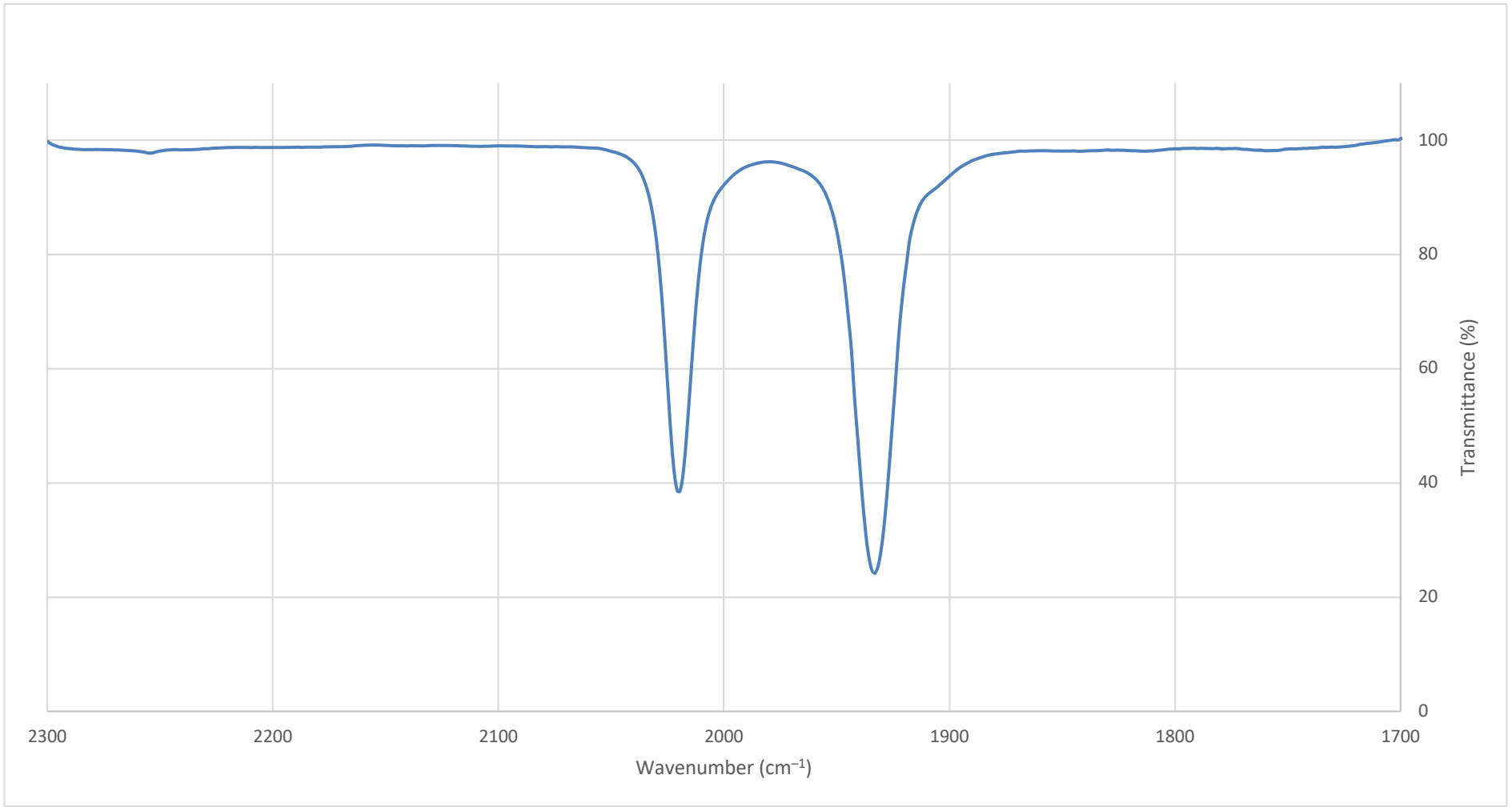

Figure S28. Infrared spectrum (CH_2Cl_2, cm^{-1}) of $[W(\equiv CAsPh_2Me)(CO)_2(Tp^*)]O_3SCF_3$ [**6**]O_3SCF_3.

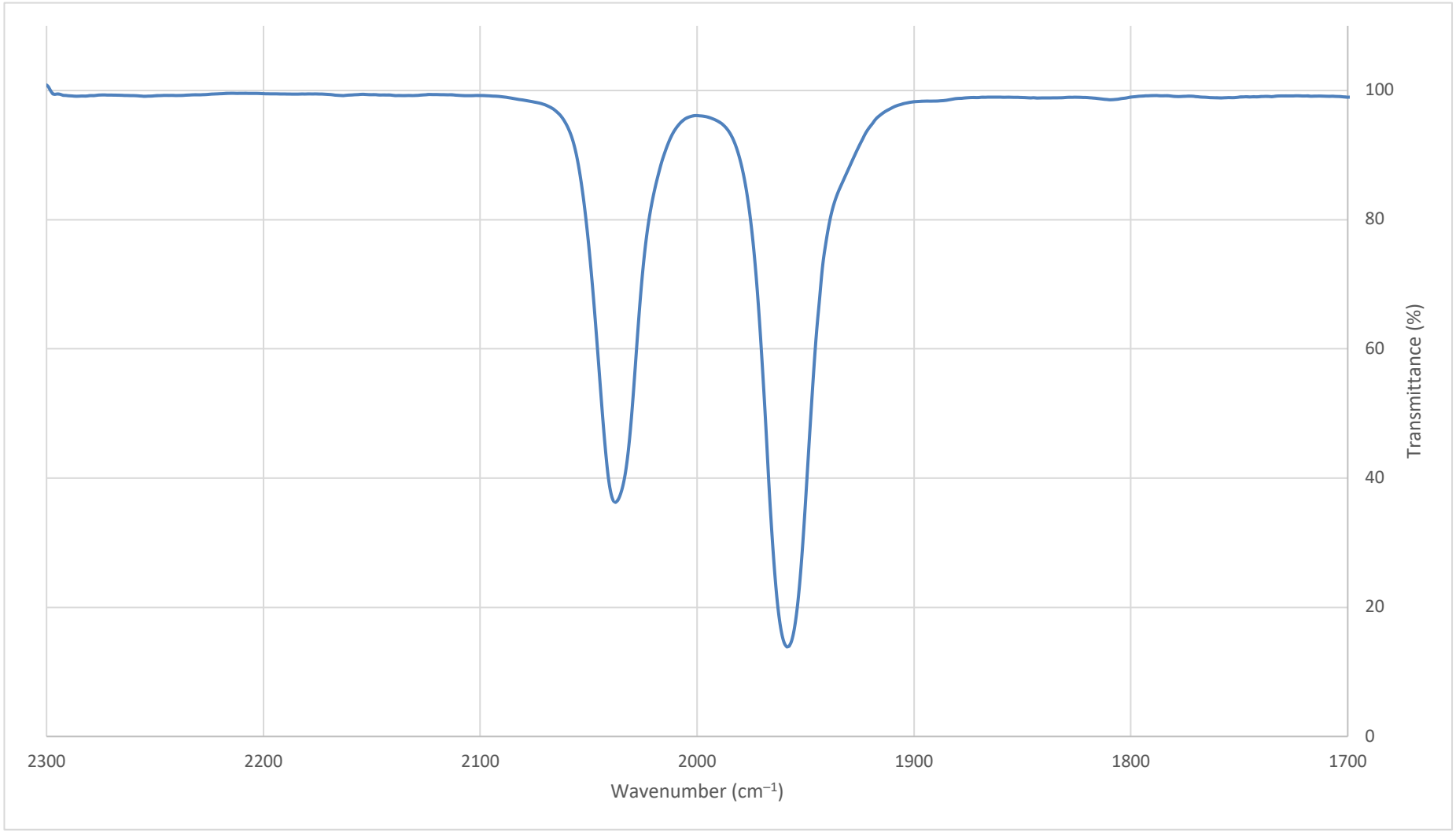

Figure S29. Infrared spectrum (CH_2Cl_2, cm^{-1}) of $[WAu(\mu\text{-}CAsPh_2Me)Cl(CO)_2(Tp^*)]O_3SCF_3$ [**7**]O_3SCF_3.