Dalton Transactions

Electronic Supporting information for:

Non-palindromic Anthracen-diyl Bis(alkylidynes)

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Author Contributions

AFH was responsible for funding acquisition and project administration. BJF and SSW were responsible for conducting the experiments and characterisation of the products.

All authors, listed alphabetically, contributed to the preparation of the original manuscript and subsequent drafts.

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Cartesian Coordinates

1. $[Tm(CO)_2W{\equiv}CC(C_6H_4)_2CC{\equiv}W(CO)_2Tp]$ (5d)

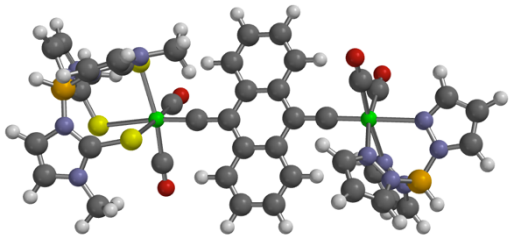

Figure S1. Optimised Geometry of **5d**

Atom	x	y	z
W	-3.277594	-1.978401	0.172277
W	3.542165	4.270937	-0.972450
S	-1.579119	-3.893164	0.773741
S	-5.292282	-3.839049	0.195591
S	-3.765777	-1.639312	2.690565
O	-5.439118	0.223861	-0.467362
N	-6.975540	-3.297114	2.241518
O	-3.080668	-2.723407	-2.881791
N	3.549862	4.388941	-3.205042
C	-3.170319	-2.450892	-1.760280
N	4.689758	4.428200	-3.928853
N	-5.246197	-4.428712	2.929171
C	2.184702	3.093844	-0.729976
C	0.162445	-1.188033	-2.003320
H	-0.596909	-1.946803	-1.858127
C	-2.532715	-5.330192	0.873856
C	0.110608	-0.007115	-1.202039
N	5.298253	5.770932	-1.290375
C	-1.920737	1.582865	1.555778
H	-2.701342	0.840031	1.679071
N	5.200047	2.841816	-1.438864
N	6.119484	3.081253	-2.399136
C	-2.674759	-2.738178	3.459161
C	-1.890500	2.690628	2.352492
H	-2.661829	2.836529	3.103049
O	4.032080	4.157153	2.144421
C	2.152422	0.748713	-2.345593
H	2.922124	1.500567	-2.482583
C	0.117866	3.479610	1.267903
H	0.906863	4.214868	1.157780
C	-6.060711	-4.186604	4.018693
H	-5.791487	-4.536406	5.002190
C	-0.915153	1.363169	0.564392
C	2.232817	5.767515	-0.745941
C	-7.132958	-3.480276	3.600021
H	-7.989536	-3.099318	4.132284
C	-5.816049	-3.868226	1.837874
C	5.468142	1.638510	-0.929937
C	-0.924365	0.203525	-0.254668
C	6.961152	2.037361	-2.491433
C	-7.851939	-2.520464	1.382560
H	-8.181706	-3.126406	0.537213
H	-7.319896	-1.645331	1.003109
H	-8.713910	-2.203692	1.971456
C	1.138160	0.973699	-1.364274
C	3.858470	4.215060	1.002537
C	3.018558	4.432211	-5.382148
H	2.448188	4.443207	-6.297693
C	7.104255	6.570867	-2.271553
C	-0.857416	3.654049	2.205817
H	-0.845352	4.533654	2.842424
C	6.581343	1.082464	-1.564181
H	7.040966	0.124723	-1.377070
N	6.191362	5.585187	-2.286810
C	6.802578	7.433376	-1.232074
H	7.332815	8.326658	-0.940902
C	-4.650097	-0.587635	-0.227366
C	1.138415	2.137696	-0.552825
C	0.125876	2.332287	0.418336
C	5.658629	6.882656	-0.647696
C	4.394371	4.457595	-5.239493
N	-2.821572	-4.057111	3.699925
N	-2.547450	-6.268399	-0.101401
N	-1.473498	-2.363028	3.947740
N	-3.342219	-5.767436	1.862723
C	-0.891133	-1.043559	3.760695
H	-0.714878	-0.870384	2.695751
H	0.051900	-1.003041	4.306990
H	-1.570093	-0.275148	4.131844
C	-1.686996	-4.504802	4.349383
H	-1.581886	-5.538156	4.638068
C	-1.856157	-6.144817	-1.373028
H	-2.217837	-5.264084	-1.907496
H	-2.059238	-7.041796	-1.959673
H	-0.782407	-6.042279	-1.208790
C	-3.871546	-6.986105	1.485358

Atom	x	y	z
H	-4.555148	-7.518398	2.126890
O	1.463303	6.620423	-0.617386
C	-0.841838	-3.459886	4.496132
H	0.135864	-3.389196	4.944706
C	-3.384092	-7.301990	0.265419
H	-3.544891	-8.159581	-0.367756
C	2.158737	-0.386564	-3.102063
H	2.939352	-0.539242	-3.841558
B	6.065464	4.375849	-3.234978
H	6.950789	4.386673	-4.050140
B	-3.854492	-5.074228	3.150746
H	-3.989056	-5.937074	3.991039
C	1.153132	-1.373094	-2.922938
H	1.174171	-2.279193	-3.521130
C	2.535427	4.388988	-4.071865
C	-1.964026	-0.764970	-0.081039
H	7.768092	2.052008	-3.209039
H	4.840807	1.240391	-0.145708
H	1.520622	4.351422	-3.703225
H	5.185241	4.493613	-5.973960
H	7.900480	6.587382	-3.001098
H	5.078278	7.225332	0.197437

2. $[Tm(CO)_2W{\equiv}CC(C_6H_4)_2CC{\equiv}W(CO)_2Tp]^+$ $[5d]^+$

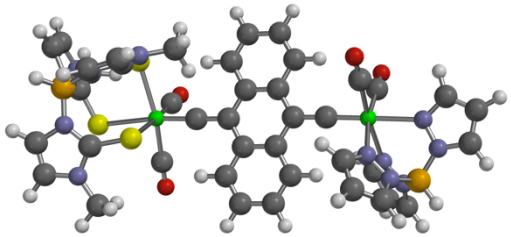

Figure S2. Optimised Geometry of $[5d]^+$

Atom	x	y	z
W	-3.010650	-1.915829	0.640315
W	3.420586	4.503556	-1.325056
S	-1.578261	-4.095704	0.824970
S	-5.226175	-3.314431	0.168667
S	-3.411994	-1.986993	3.117338
O	-4.950663	0.570955	0.507240
N	-6.945497	-2.981673	2.244639
O	-2.733033	-2.211243	-2.502062
N	3.533788	4.225757	-3.514361
C	-2.874227	-2.100667	-1.366407
N	4.710785	4.201752	-4.180262
N	-5.409612	-4.455062	2.712424
C	2.156018	3.256837	-0.875001
C	0.611582	-1.361522	-1.246261
H	-0.070003	-2.152450	-0.950865
C	-2.730760	-5.365608	0.571063
C	0.442559	-0.066816	-0.705925
N	5.048272	6.038635	-1.810056
C	-1.716260	1.812426	1.785867
H	-2.394303	1.023160	2.090205
N	5.181946	3.157683	-1.412401
N	6.137569	3.278442	-2.360449
C	-2.622678	-3.420592	3.703444
C	-1.803545	3.058399	2.362096
H	-2.565150	3.254611	3.109821
O	3.752107	5.144058	1.762560
C	2.403773	0.653406	-1.973271
H	3.098401	1.435923	-2.257981
C	0.073504	3.825384	1.057909
H	0.769548	4.607446	0.778114
C	-6.249578	-4.351028	3.803575
H	-6.092872	-4.947612	4.687950
C	-0.730494	1.532738	0.813690
C	1.979795	5.913901	-1.439498
C	-7.203025	-3.434884	3.520563
H	-8.041219	-3.077069	4.096564
C	-5.846343	-3.602631	1.762300
C	5.522064	2.119527	-0.642826
C	-0.650210	0.234889	0.187600
C	7.069457	2.327275	-2.188142
C	-7.708857	-1.963891	1.537060
H	-8.071458	-2.359801	0.587677
H	-7.081631	-1.092259	1.344772
H	-8.553719	-1.675925	2.164323
C	1.362633	0.954661	-1.062419
C	3.643598	4.921666	0.638379
C	3.119560	3.891478	-5.690852
H	2.602007	3.732711	-6.623992
C	6.845501	6.802145	-2.831960
C	-0.907166	4.075919	1.988375
H	-0.984399	5.059395	2.439986
C	6.713941	1.553803	-1.095902
H	7.245416	0.710222	-0.684428
N	6.016526	5.753767	-2.711473
C	6.412518	7.809702	-1.985548
H	6.852505	8.783728	-1.840855
C	-4.255640	-0.346531	0.555234
C	1.232107	2.272654	-0.497287
C	0.193590	2.550823	0.456455

C	5.280870	7.279235	-1.368240
C	4.484794	4.006032	-5.489332
N	-3.011970	-4.704700	3.608586
N	-2.790312	-6.090016	-0.567472
N	-1.472096	-3.387147	4.405216
N	-3.679248	-5.840206	1.404372
C	-0.699646	-2.183820	4.671125
H	-0.455604	-1.693625	3.726601
H	0.216134	-2.471484	5.187778
H	-1.274659	-1.495643	5.293798
C	-2.077336	-5.486085	4.260175
H	-2.184618	-6.557433	4.313895
C	-1.937208	-5.894304	-1.728670
H	-2.044377	-4.874103	-2.101019
H	-2.248753	-6.597985	-2.500931
H	-0.894132	-6.074632	-1.464495
C	-4.339833	-6.871951	0.766394
H	-5.145228	-7.402267	1.248417
O	1.137580	6.696293	-1.495972
C	-1.115792	-4.673585	4.753636
H	-0.230501	-4.885842	5.331258
C	-3.793929	-7.030508	-0.459508
H	-4.015584	-7.724617	-1.253933
C	2.540069	-0.613151	-2.489909
H	3.346386	-0.828669	-3.183455
B	6.044571	4.388077	-3.427718
H	6.972441	4.325309	-4.187765
B	-4.157719	-5.369905	2.800862
H	-4.487922	-6.357754	3.412573
C	1.641830	-1.629876	-2.117335
H	1.760543	-2.631406	-2.518559
C	2.567070	4.041114	-4.419041
C	-1.630387	-0.713053	0.438570
H	7.919678	2.271445	-2.851751
H	4.889059	1.838395	0.186332
H	1.533895	4.025651	-4.103624
H	5.310881	3.962646	-6.183547
H	7.685295	6.758446	-3.509781
H	4.623528	7.721909	-0.633162

3. $HC{\equiv}CC(C_6H_4)_2CC{\equiv}CH$

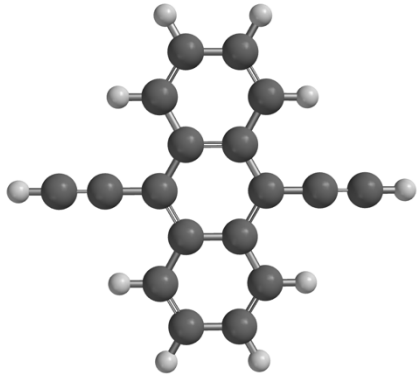

Figure S3. Optimised Geometry of $HC{\equiv}CC(C_6H_4)_2CC{\equiv}CH$

Atom	x	y	z
H	-4.599999	0.000000	1.247802
C	-3.656169	0.000000	0.711167
H	-2.475481	0.000000	2.485324
C	-2.480614	0.000000	1.400575
C	-2.480614	0.000000	-1.400575
C	-1.226785	0.000000	0.715336
C	-3.656169	0.000000	-0.711167
C	-1.226785	0.000000	-0.715336
C	0.000000	0.000000	1.412881
H	-4.599999	0.000000	-1.247802
H	-2.475481	0.000000	-2.485324
C	1.226785	0.000000	0.715336
C	2.480614	0.000000	1.400575
C	1.226785	0.000000	-0.715336
H	2.475481	0.000000	-2.485324
C	0.000000	0.000000	-1.412881
C	3.656169	0.000000	0.711167
H	2.475481	0.000000	2.485324
H	4.599999	0.000000	1.247802
C	3.656169	0.000000	-0.711167
H	4.599999	0.000000	-1.247802
C	2.480614	0.000000	-1.400575
C	0.000000	0.000000	-2.843566
H	0.000000	0.000000	-5.117870
C	0.000000	0.000000	-4.051019
C	0.000000	0.000000	2.843566
H	0.000000	0.000000	5.117870
C	0.000000	0.000000	4.051019

4. $HC(C_6H_4)_2CH$

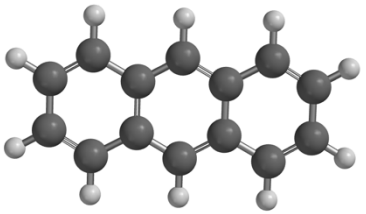

Figure S4. Optimised Geometry of $HC(C_6H_4)_2CH$

Atom	x	y	z
H	-4.594978	0.000199	1.245822
C	-3.648684	0.000080	0.713206
H	-2.470576	0.000249	2.490833
C	-2.473995	0.000117	1.403842
C	-2.473995	-0.000117	-1.403842
C	-1.218674	0.000022	0.717527
C	-3.648684	-0.000080	-0.713206
C	-1.218674	-0.000022	-0.717527

C	0.000000	0.000000	1.398638
H	-4.594978	-0.000199	-1.245822
H	0.000000	0.000000	-2.486697
H	-2.470576	-0.000249	-2.490833
C	1.218674	-0.000022	0.717527
H	0.000000	0.000000	2.486697
C	2.473995	-0.000117	1.403842
C	1.218674	0.000022	-0.717527
H	2.470576	0.000249	-2.490833
C	0.000000	0.000000	-1.398638
C	3.648684	-0.000080	0.713206
H	2.470576	-0.000249	2.490833
H	4.594978	-0.000199	1.245822
C	3.648684	0.000080	-0.713206
H	4.594978	0.000199	-1.245822
C	2.473995	0.000117	-1.403842

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Selected Spectra

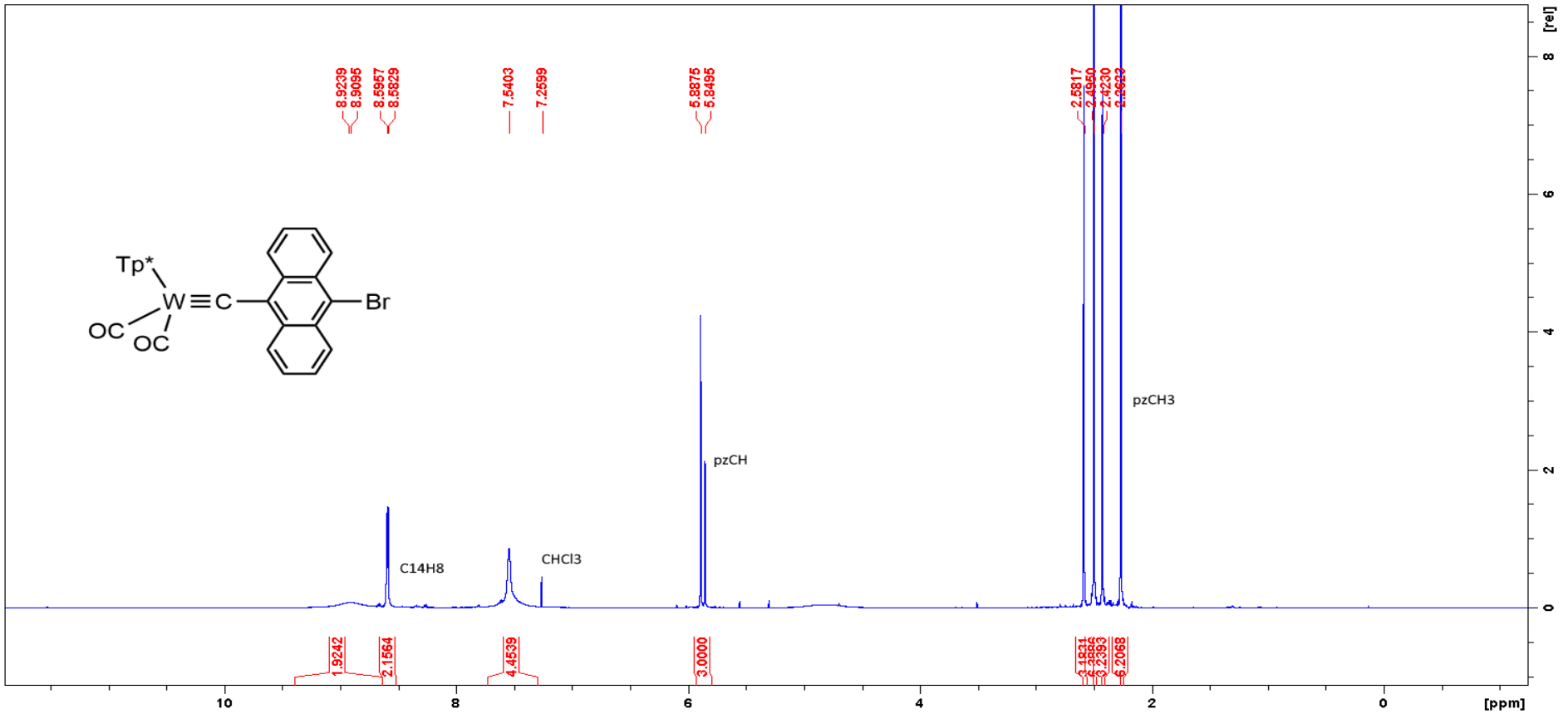

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1a**).

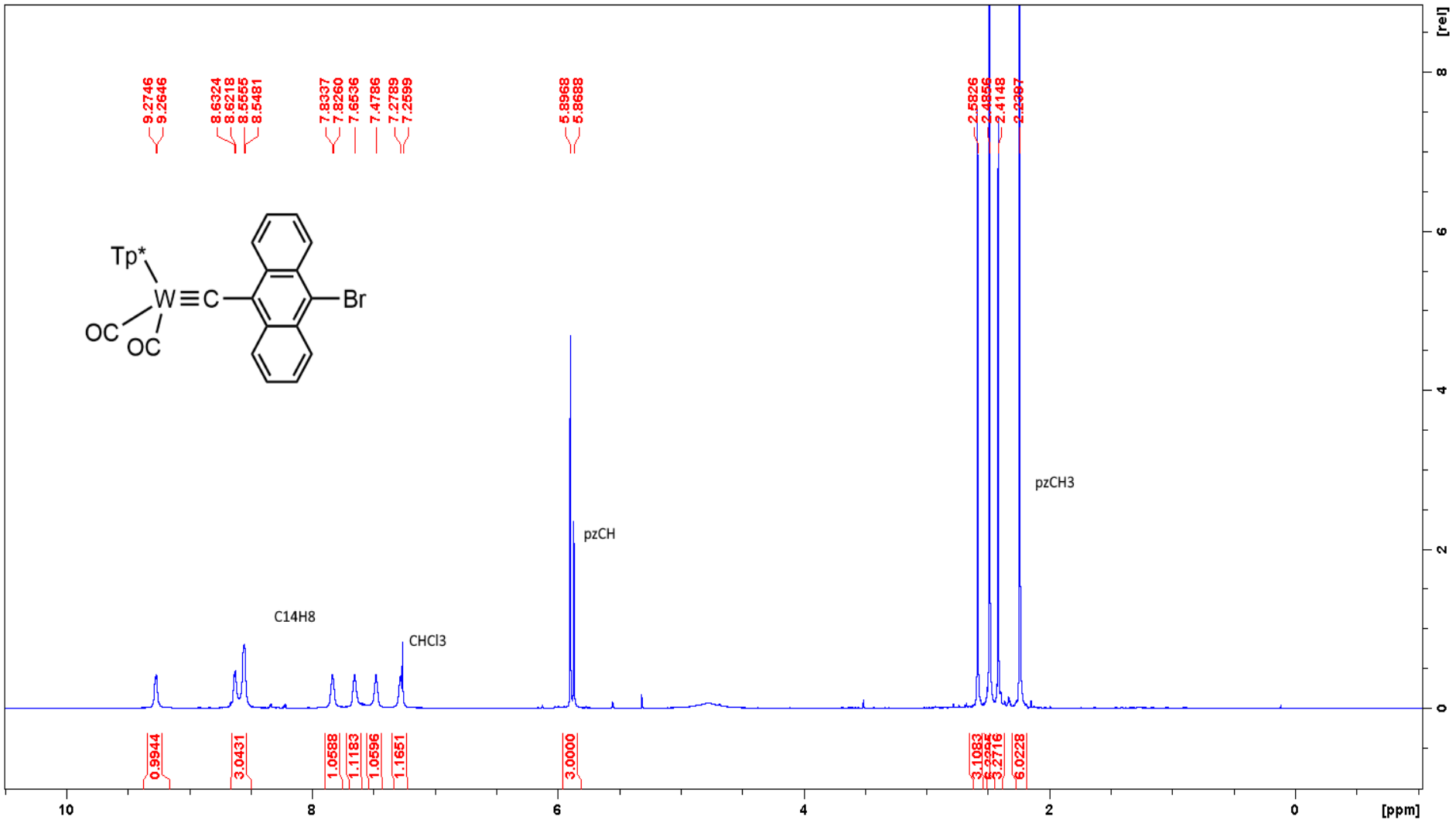

Figure S6. ^{1}H NMR (700 MHz, $CDCl_3$, –40 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1a**).

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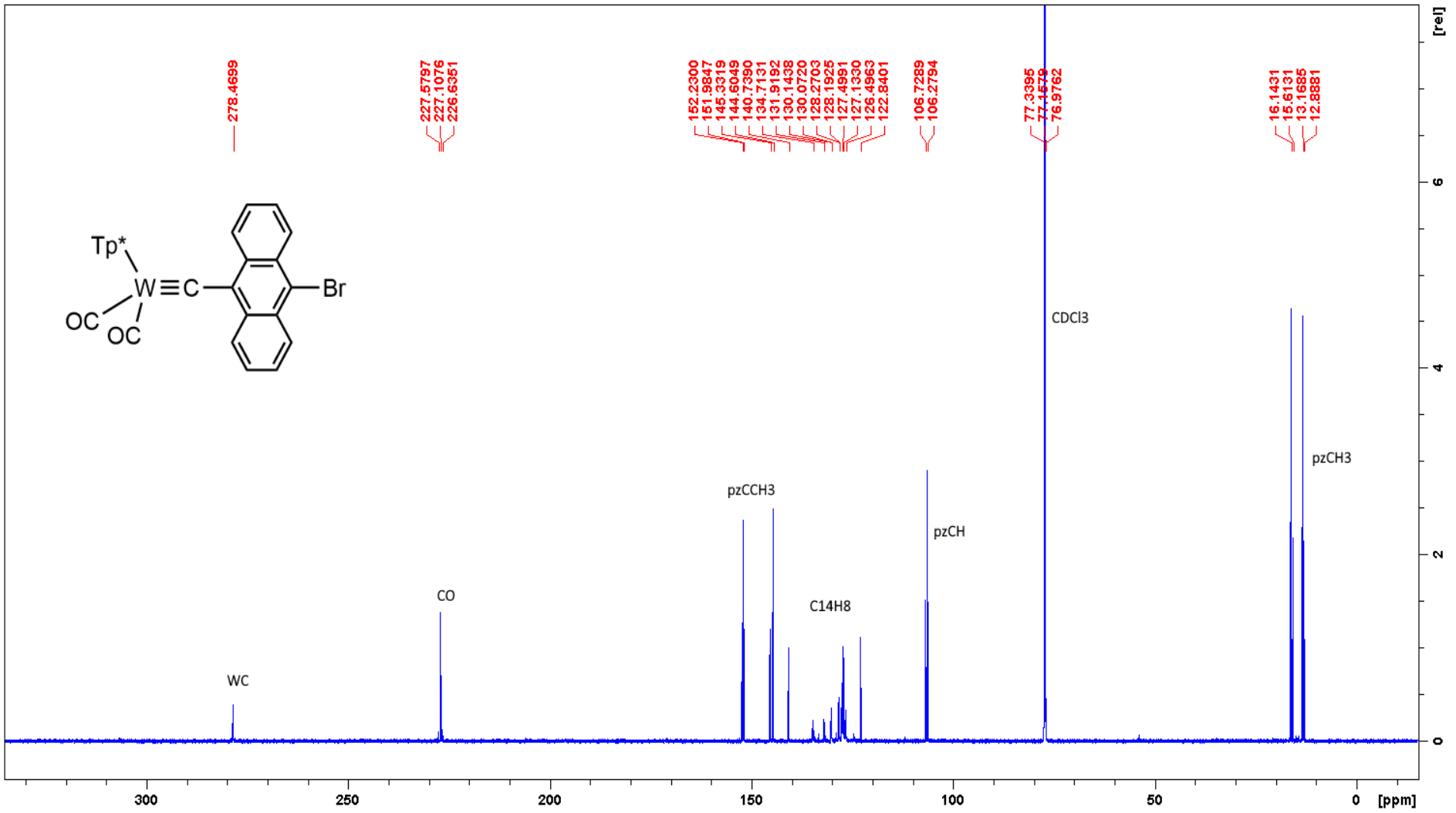

Figure S7. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, –40 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1a**).

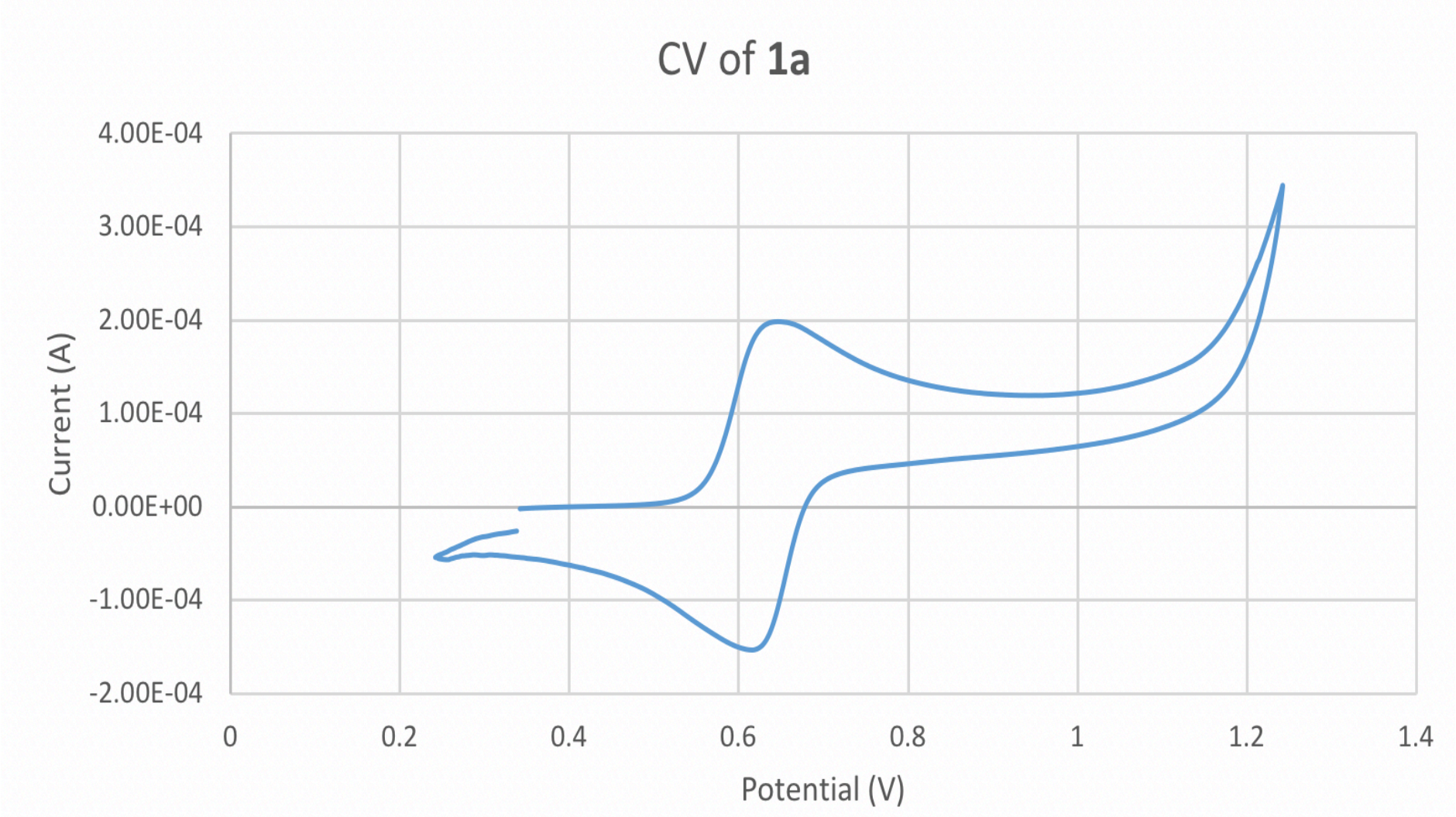

Figure S8. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1a**).

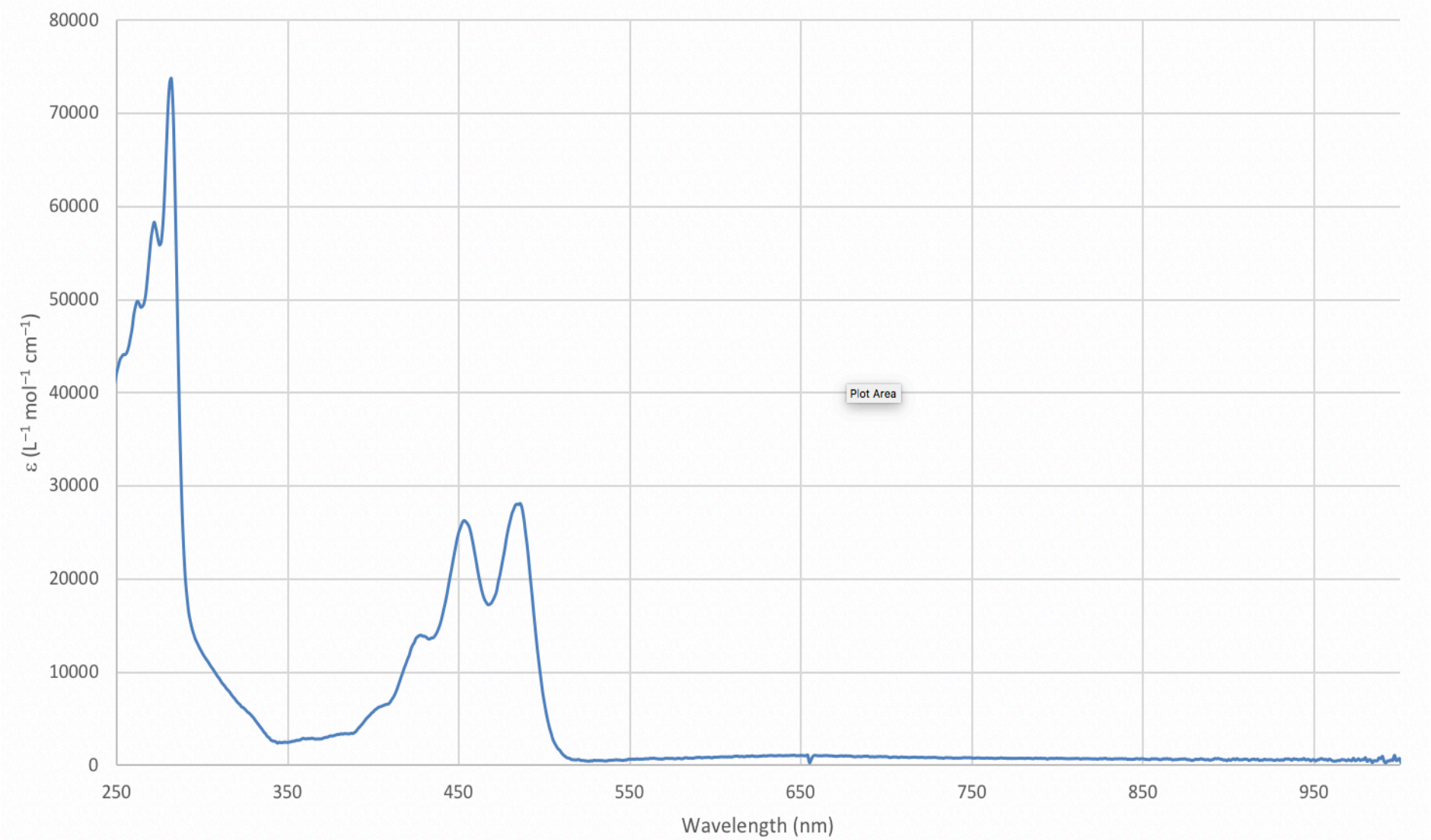

Figure S9b. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1a**).

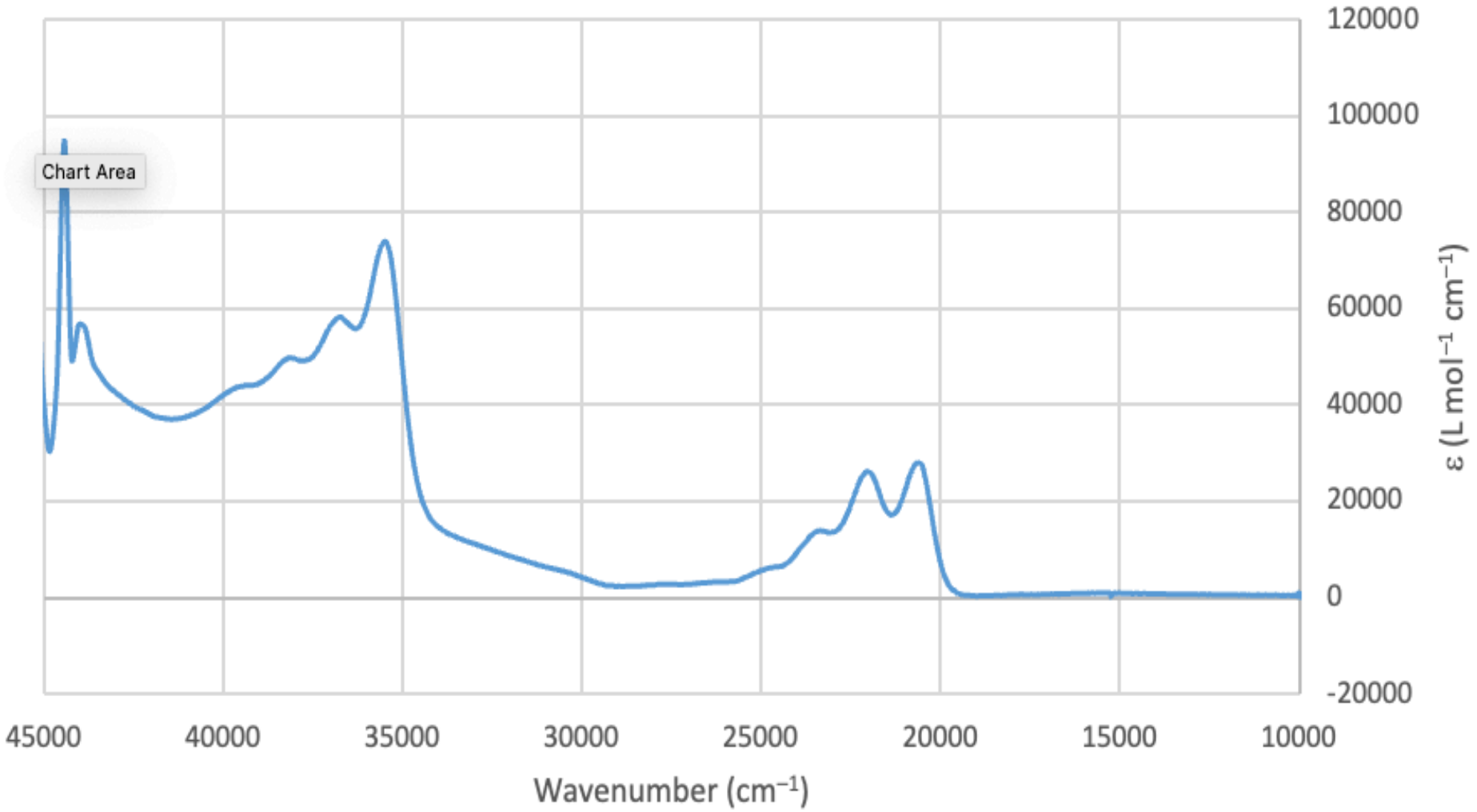

Figure S9b. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1a**).

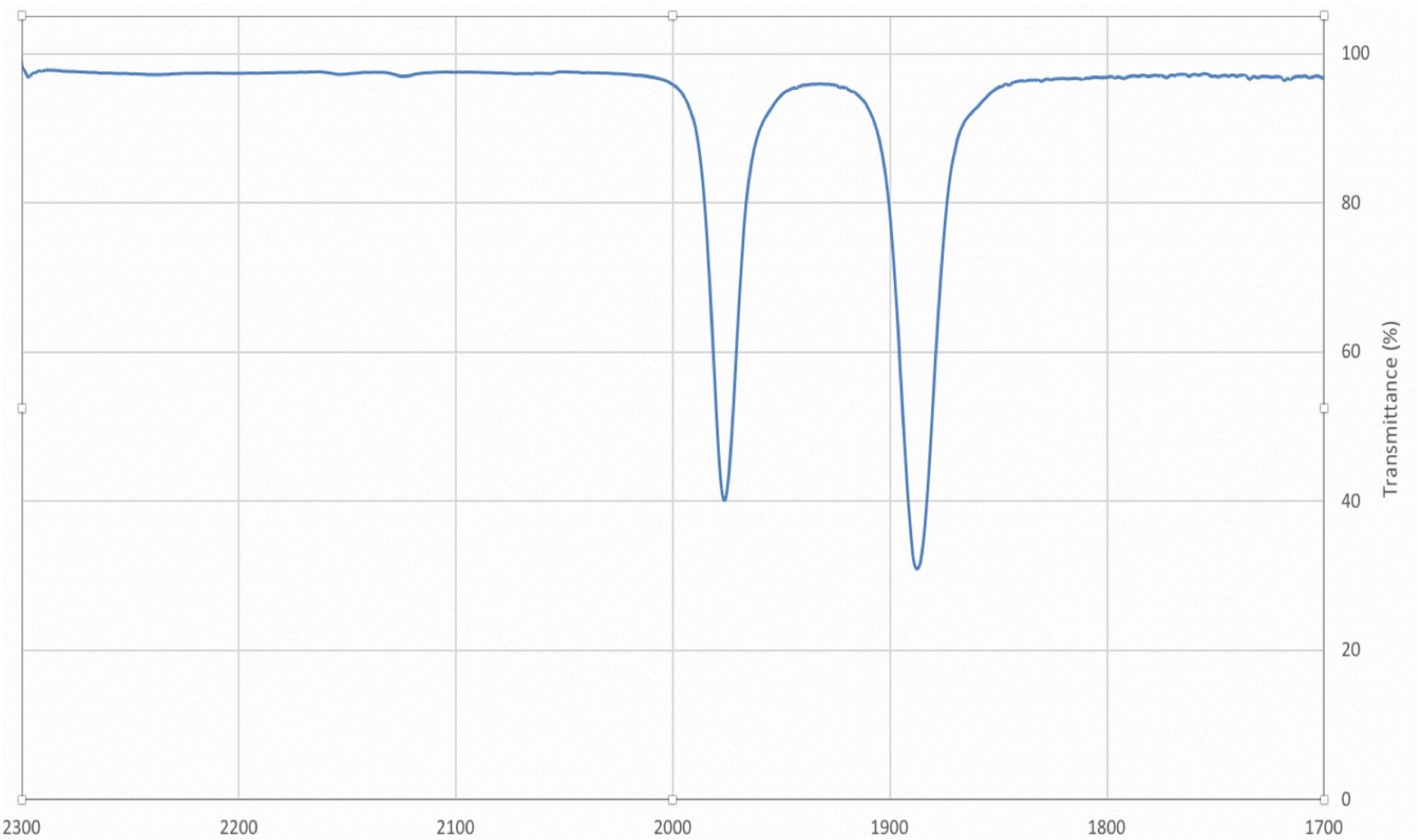

Figure S10. Infrared spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1a**).

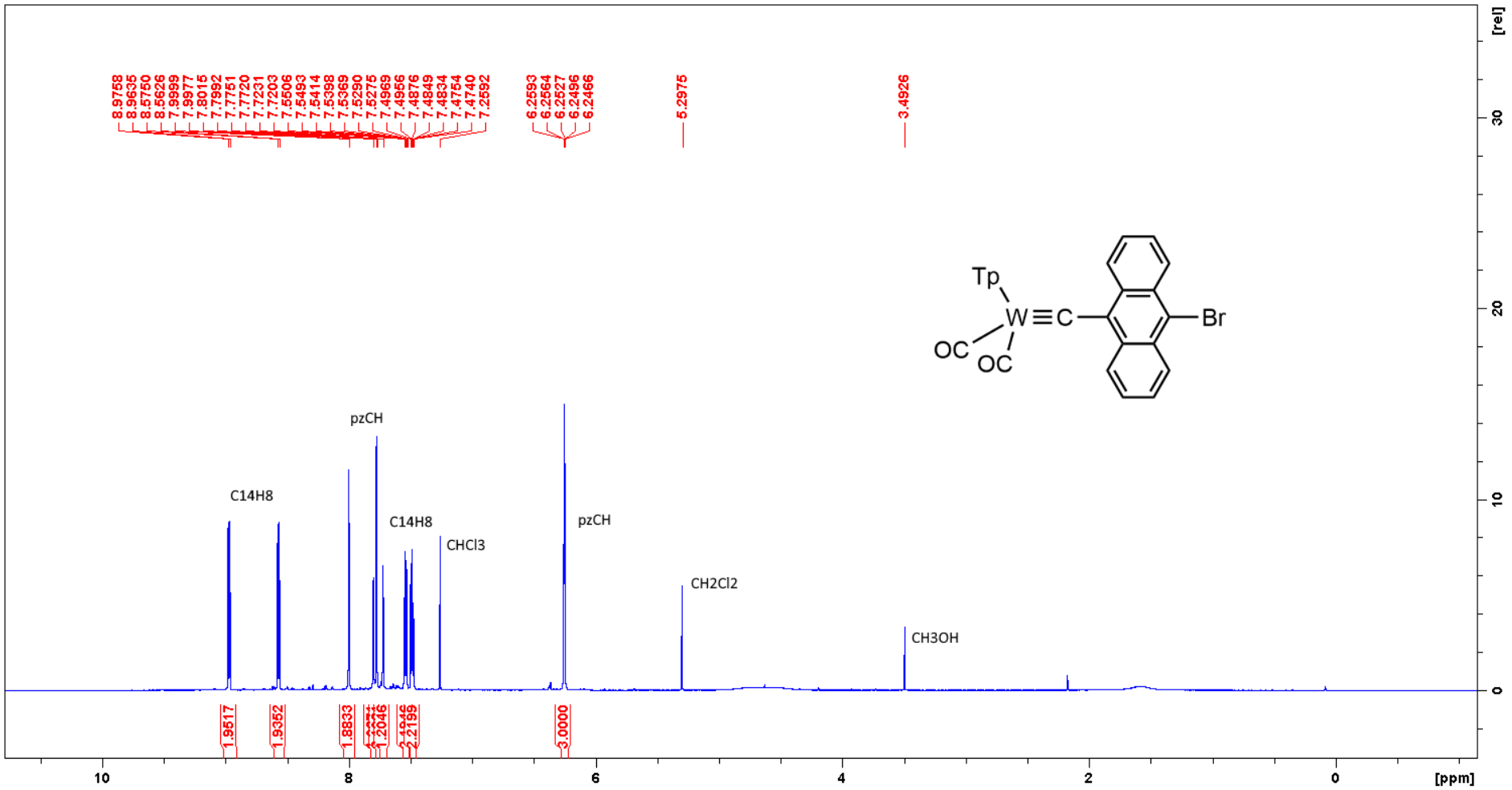

Figure S11. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp*)] (**1b**).

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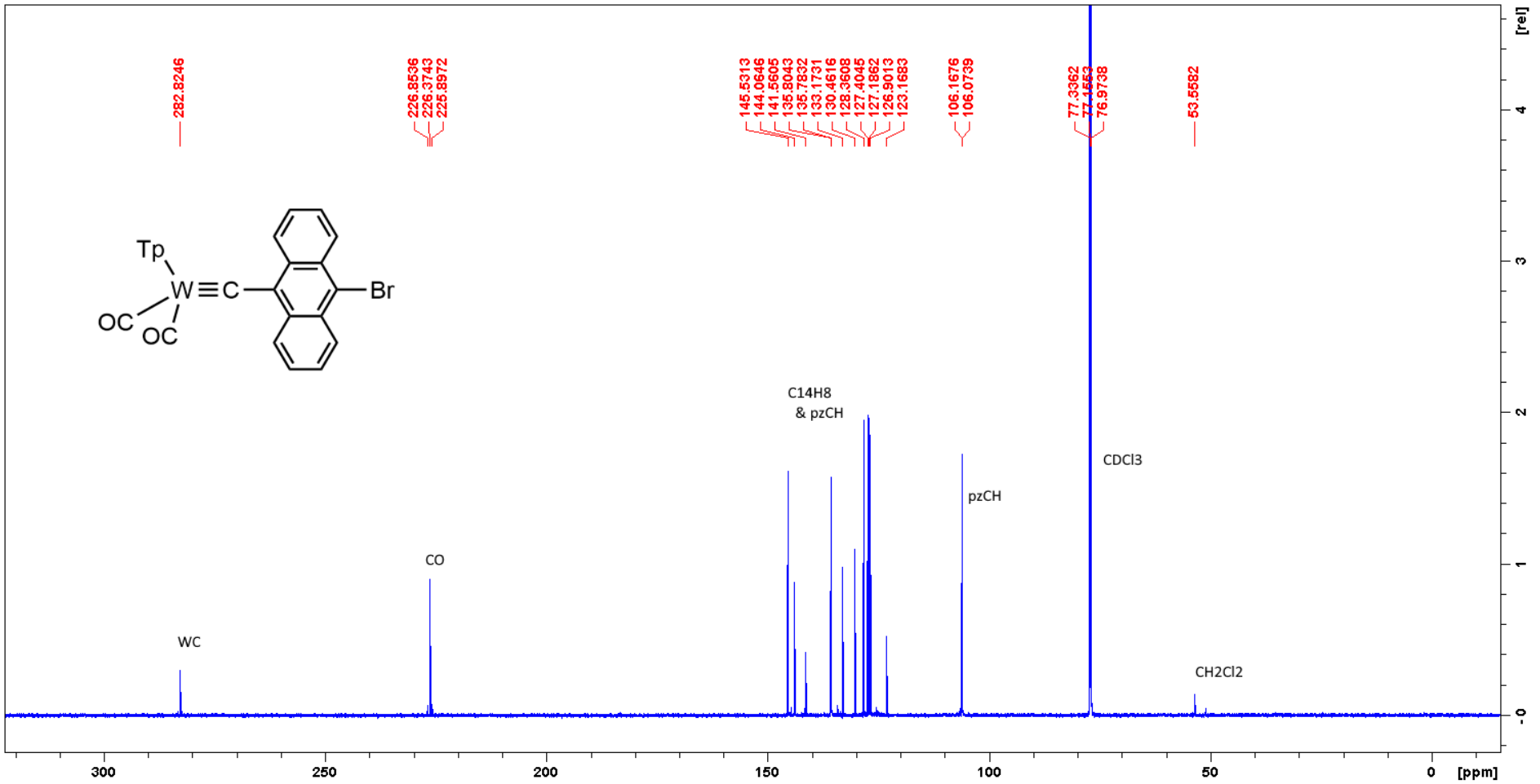

Figure S12. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 25 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp)] (**1b**).

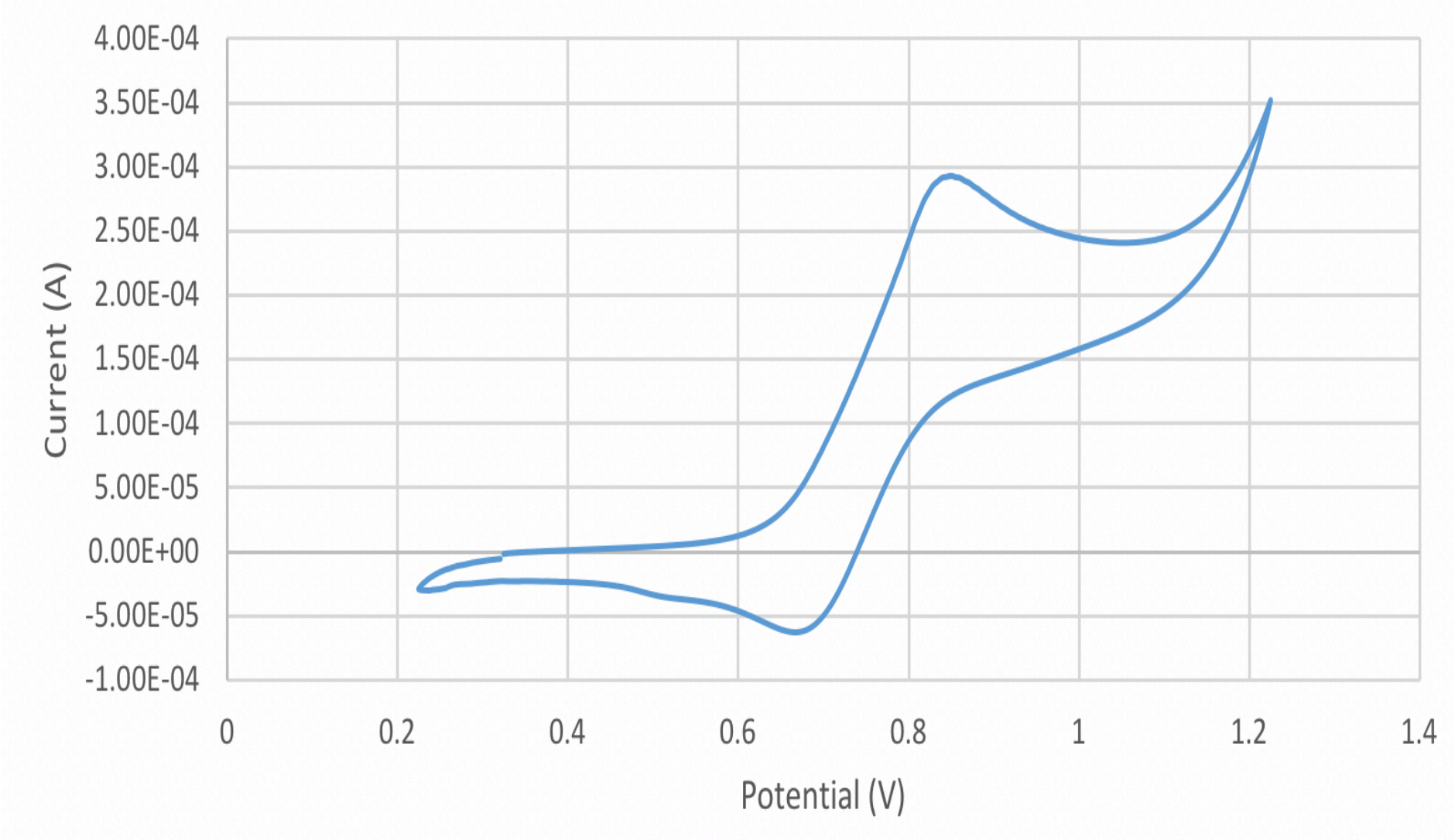

Figure S13. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp)] (**1b**).

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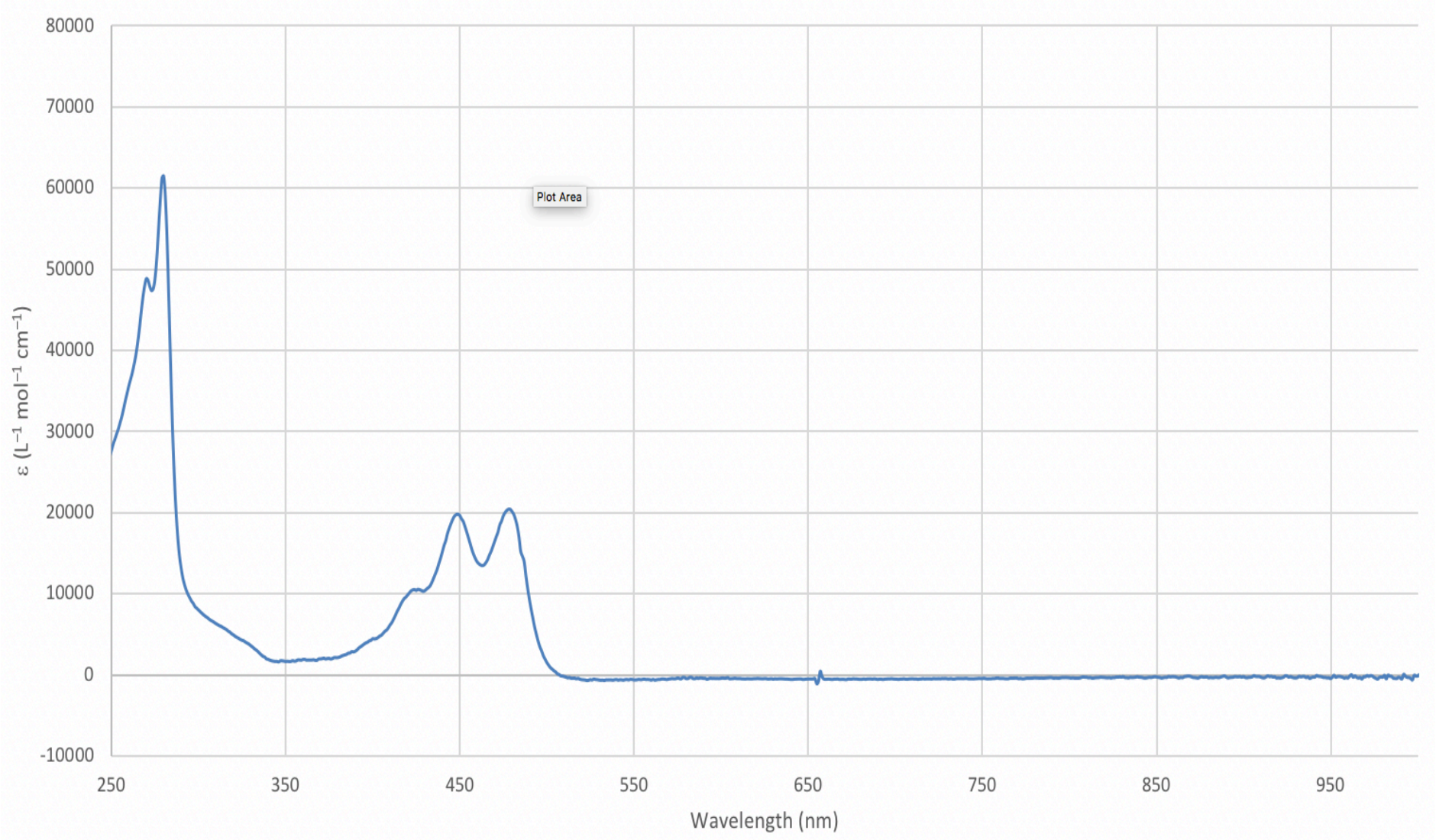

Figure S14a. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp)] (**1b**).

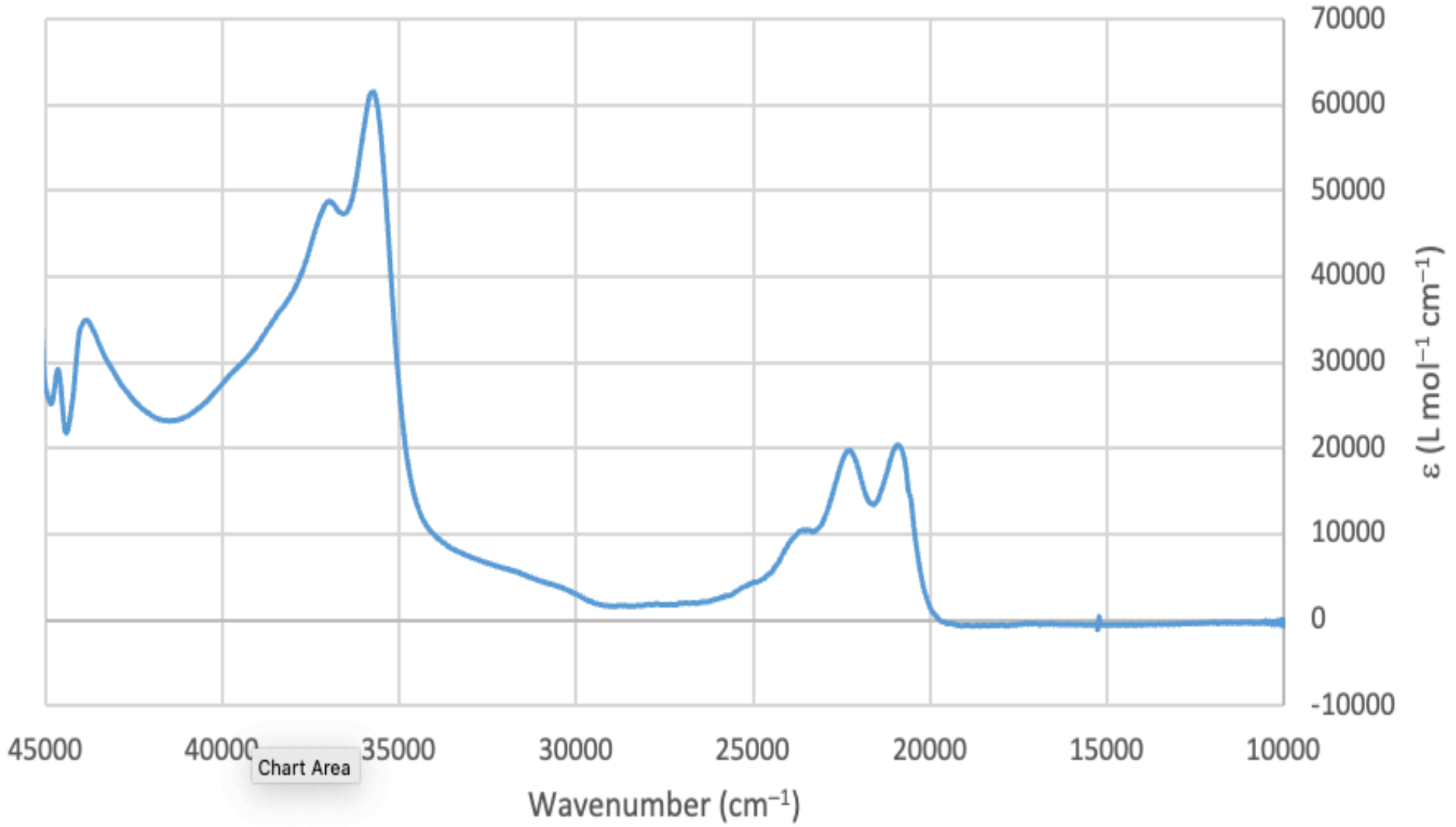

Figure S14b. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp)] (**1b**).

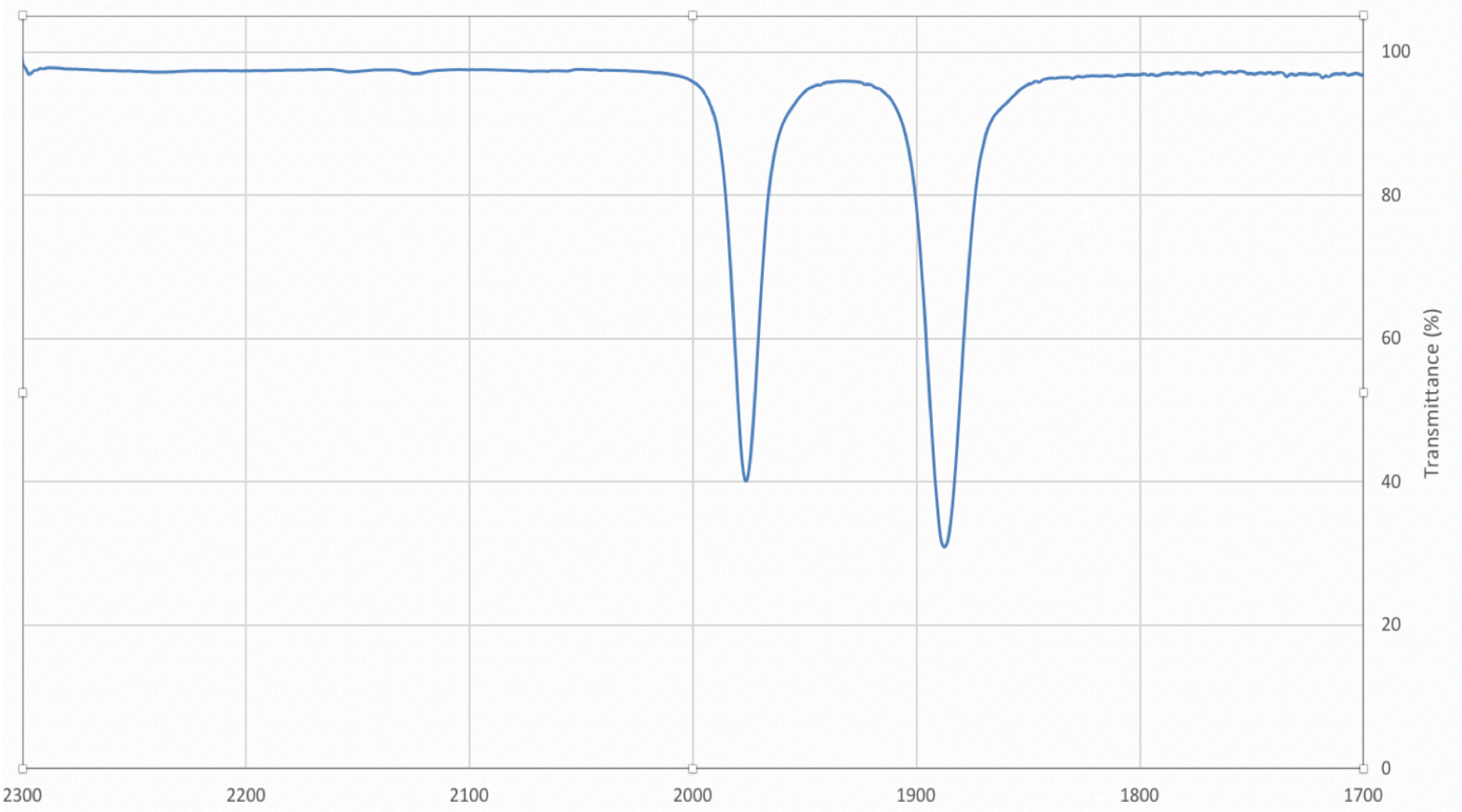

Figure S15. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tp)] (**1b**).

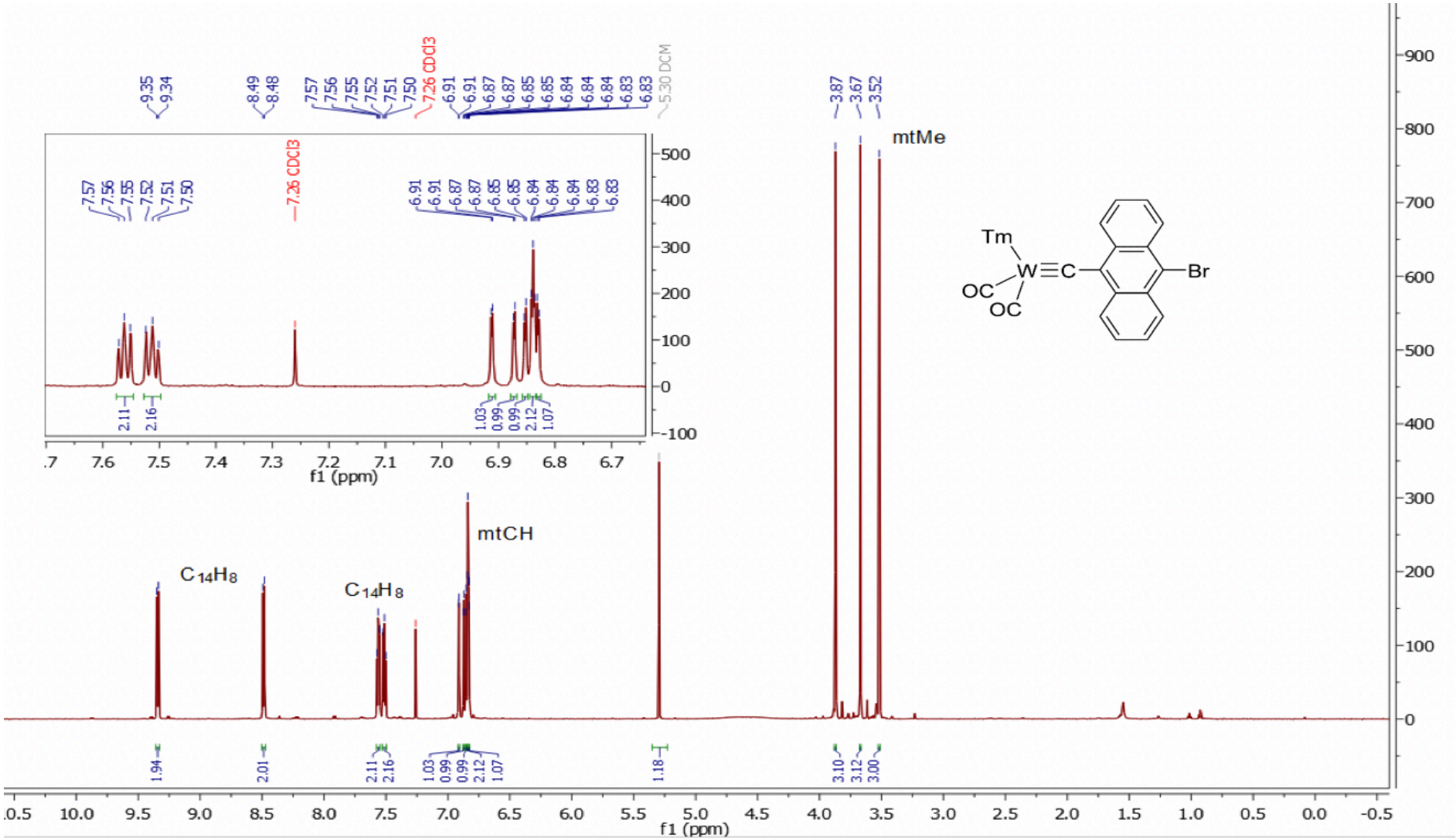

Figure S16. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tm)] (**1c**).

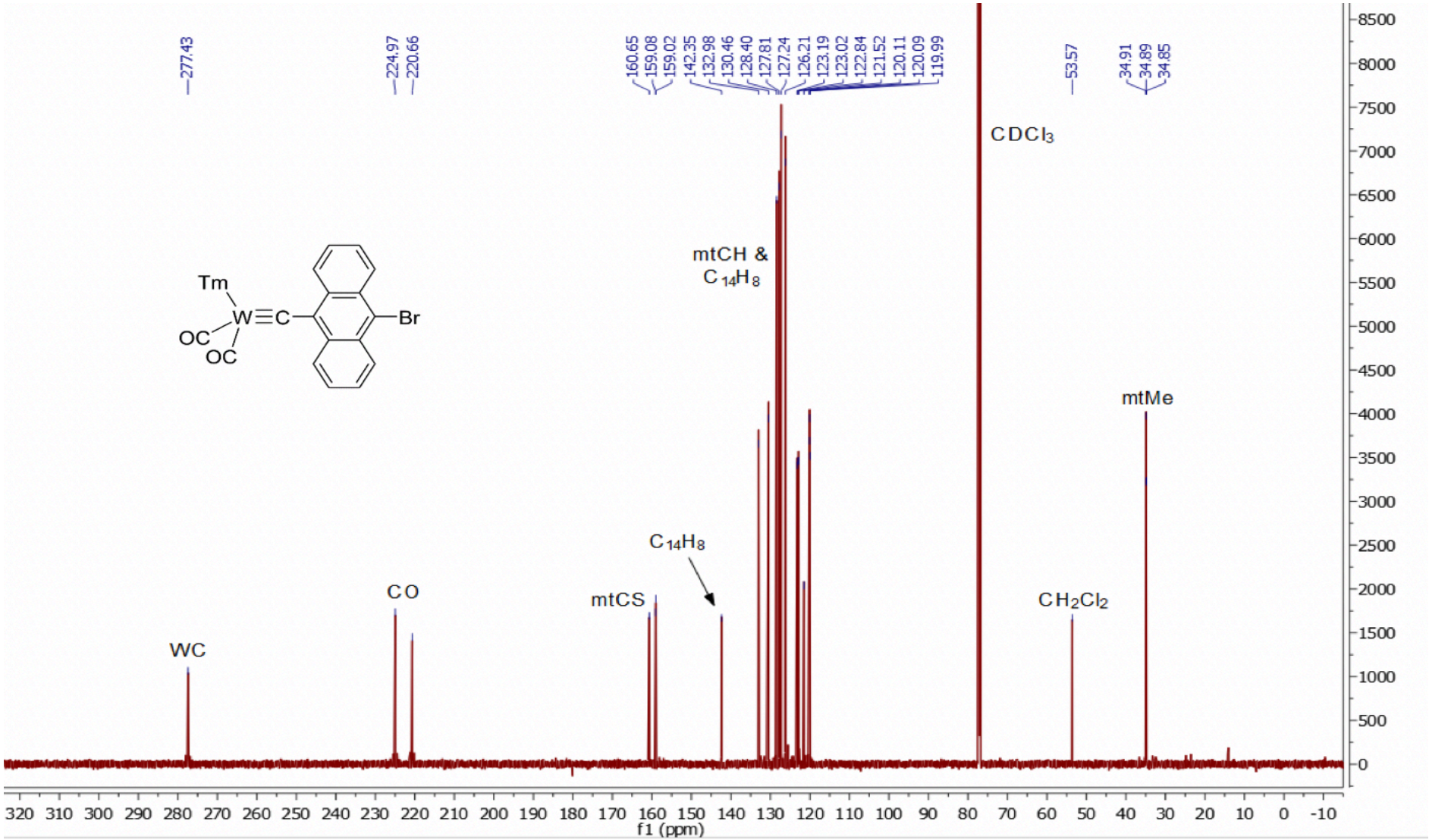

Figure S17. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, 25 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tm)] (**1c**).

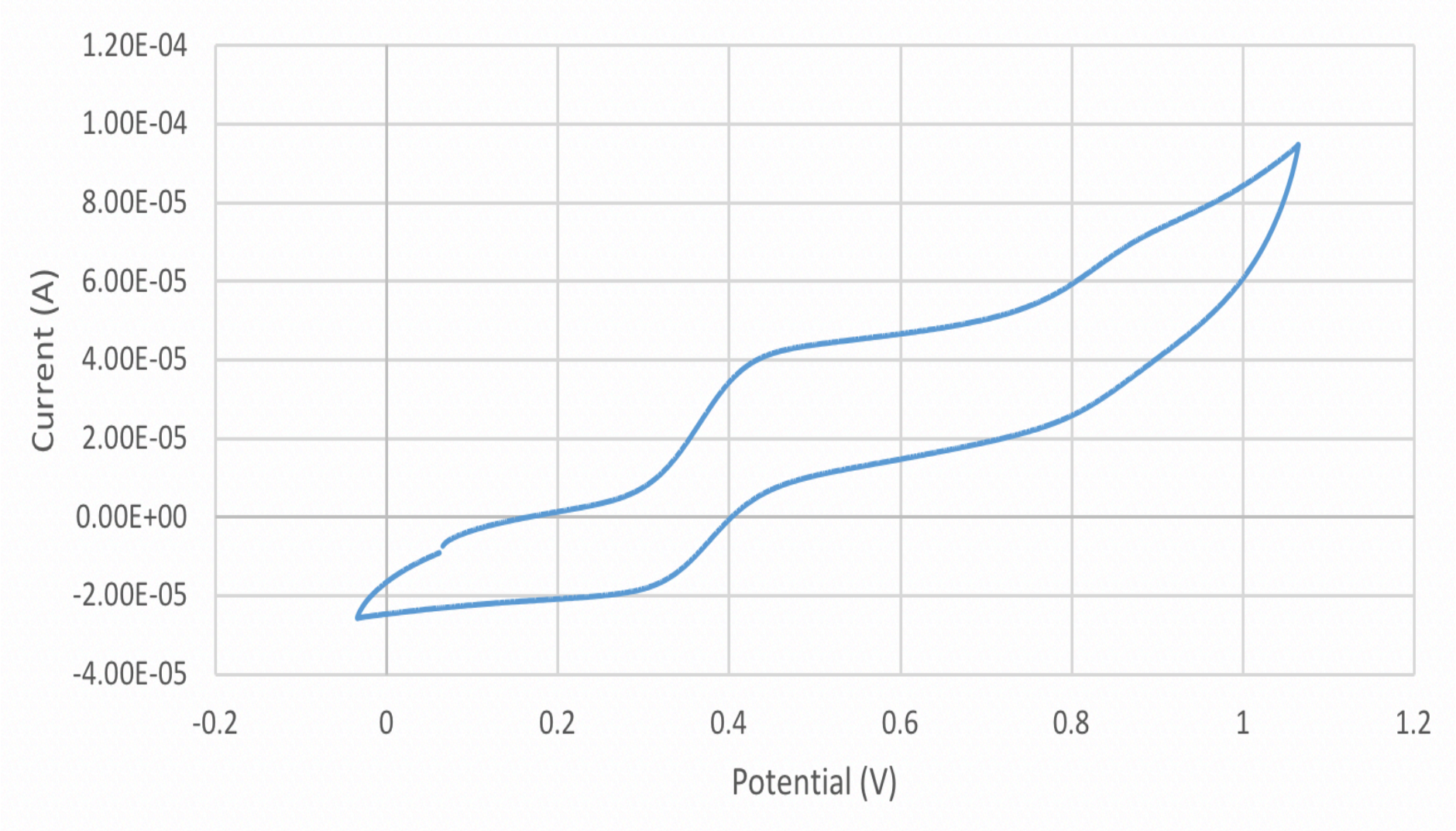

Figure S18. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tm)] (**1c**).

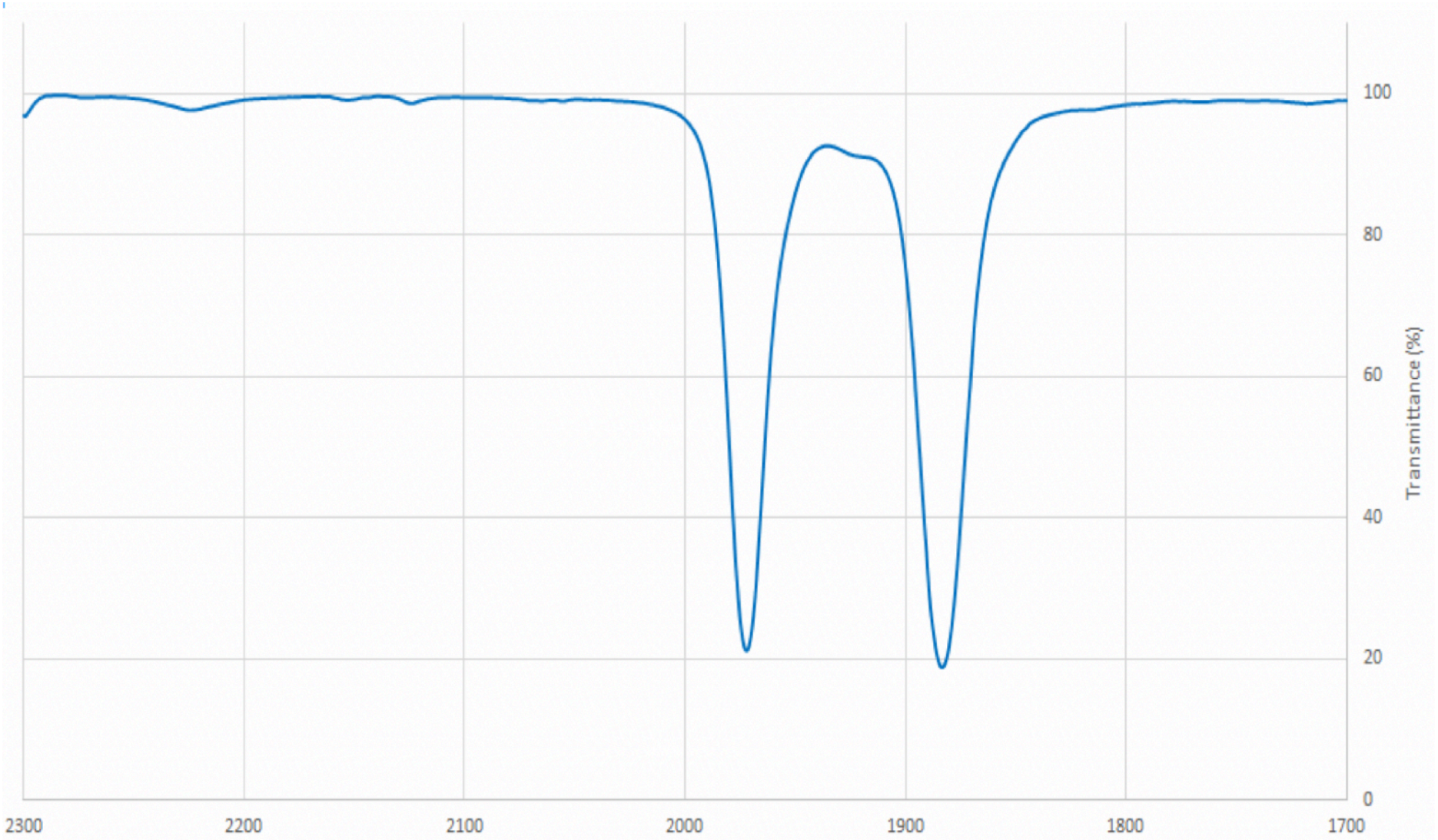

Figure S19. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tm)] (**1c**).

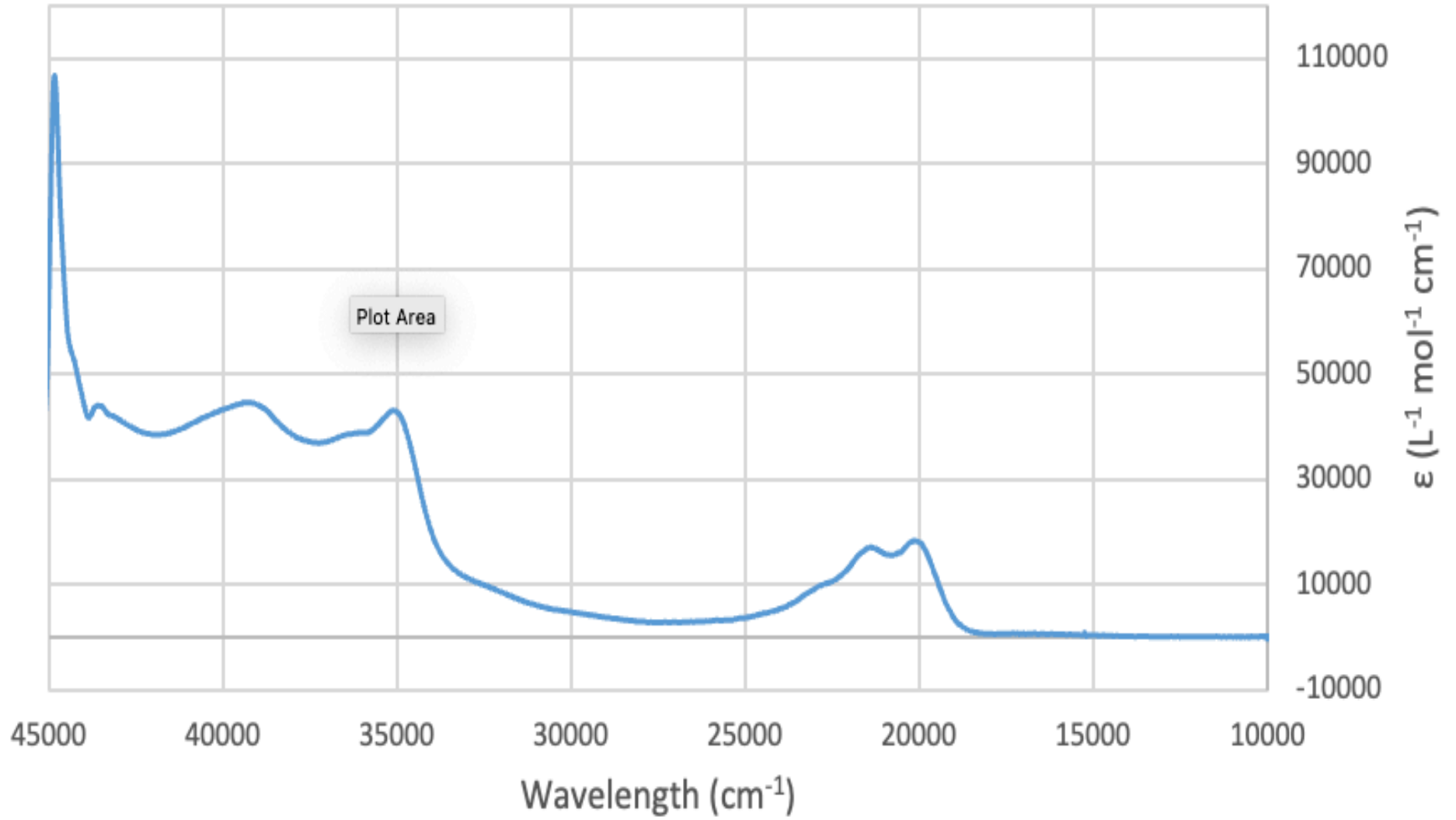

Figure S20a. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tm)] (**1c**).

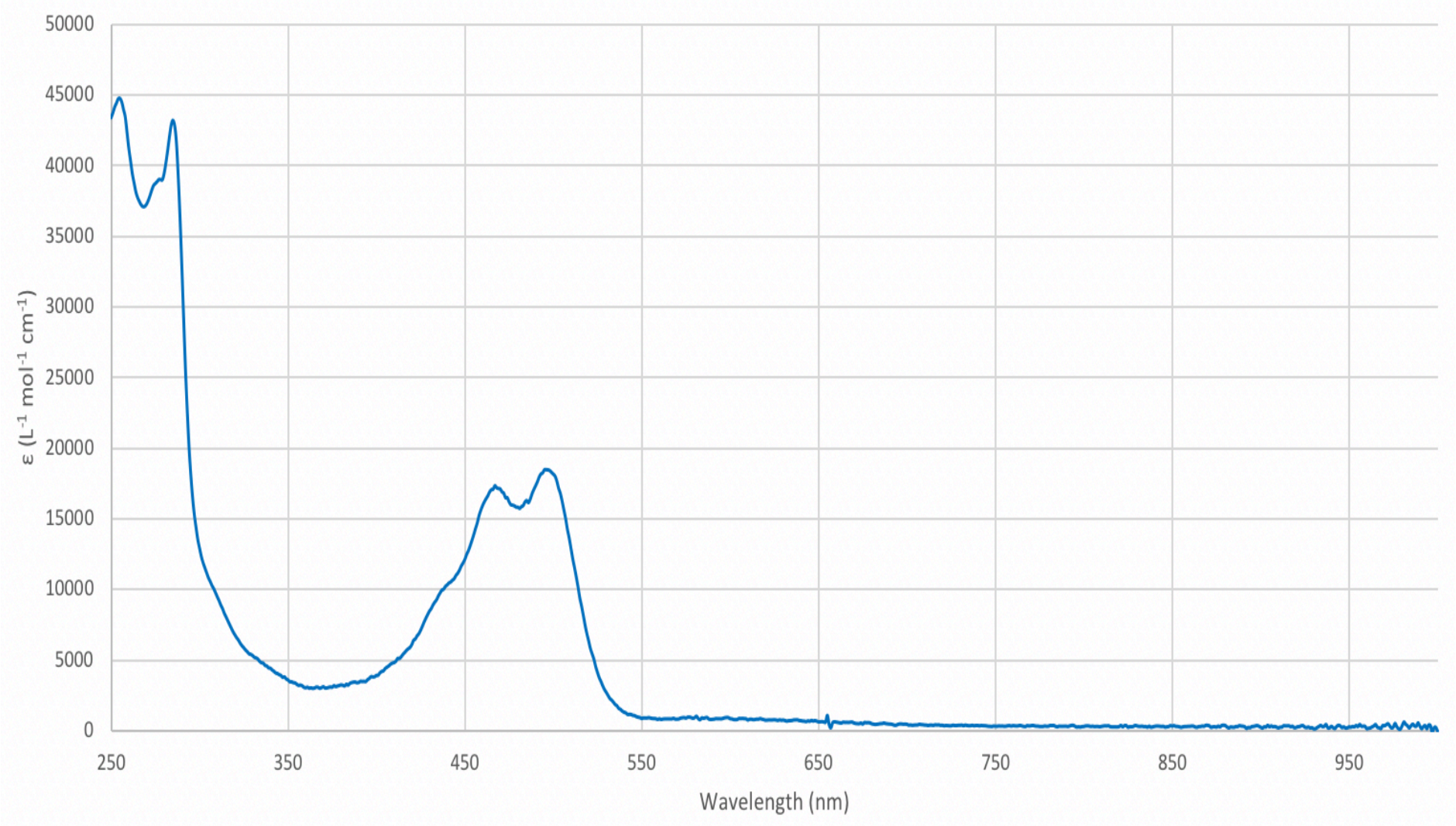

Figure S20b. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CBr}(CO)$_2$(Tm)] (**1c**).

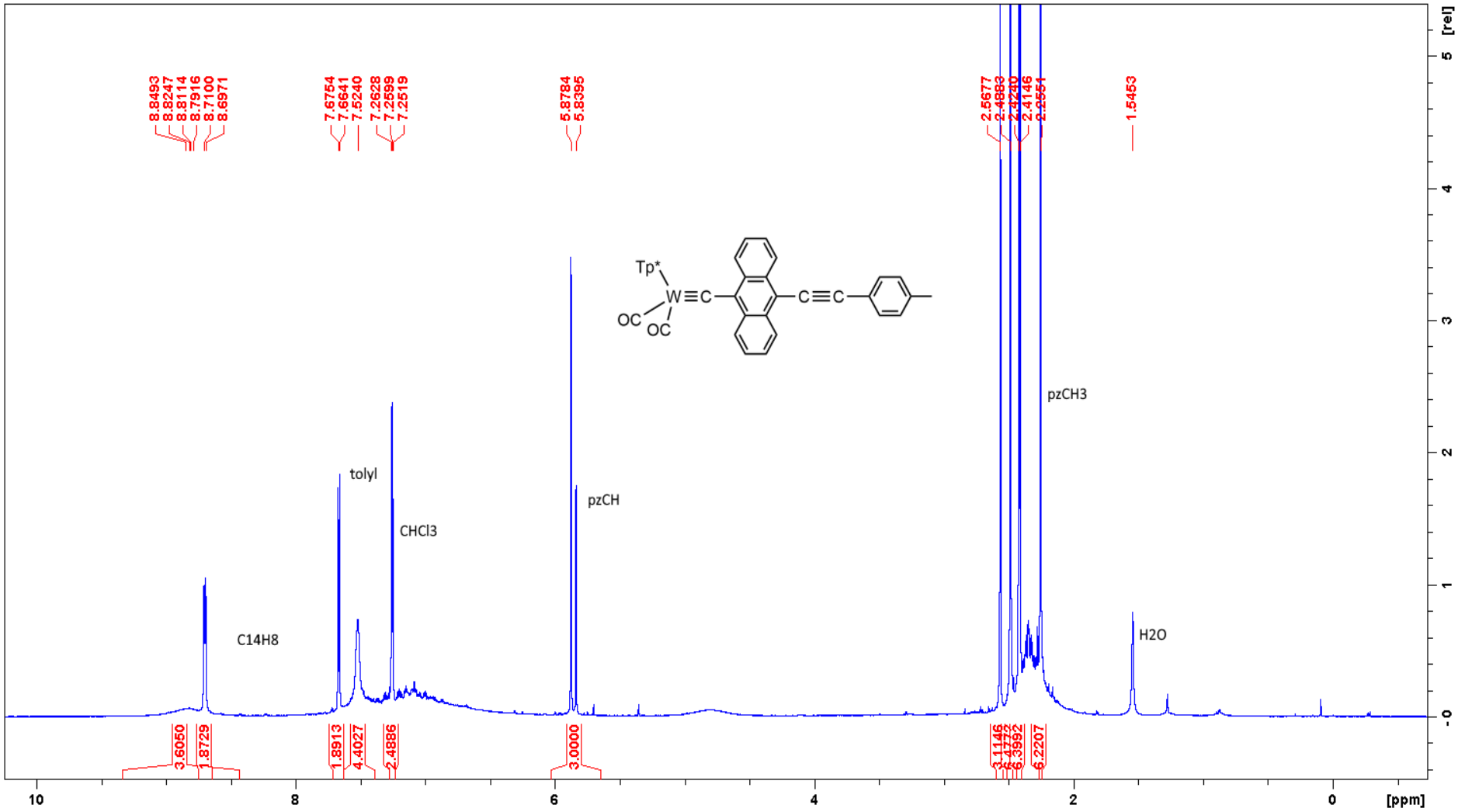

Figure S21. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CC≡C$C_6H_4CH_3$-4)(CO)$_2$(Tp*)] (**2**).

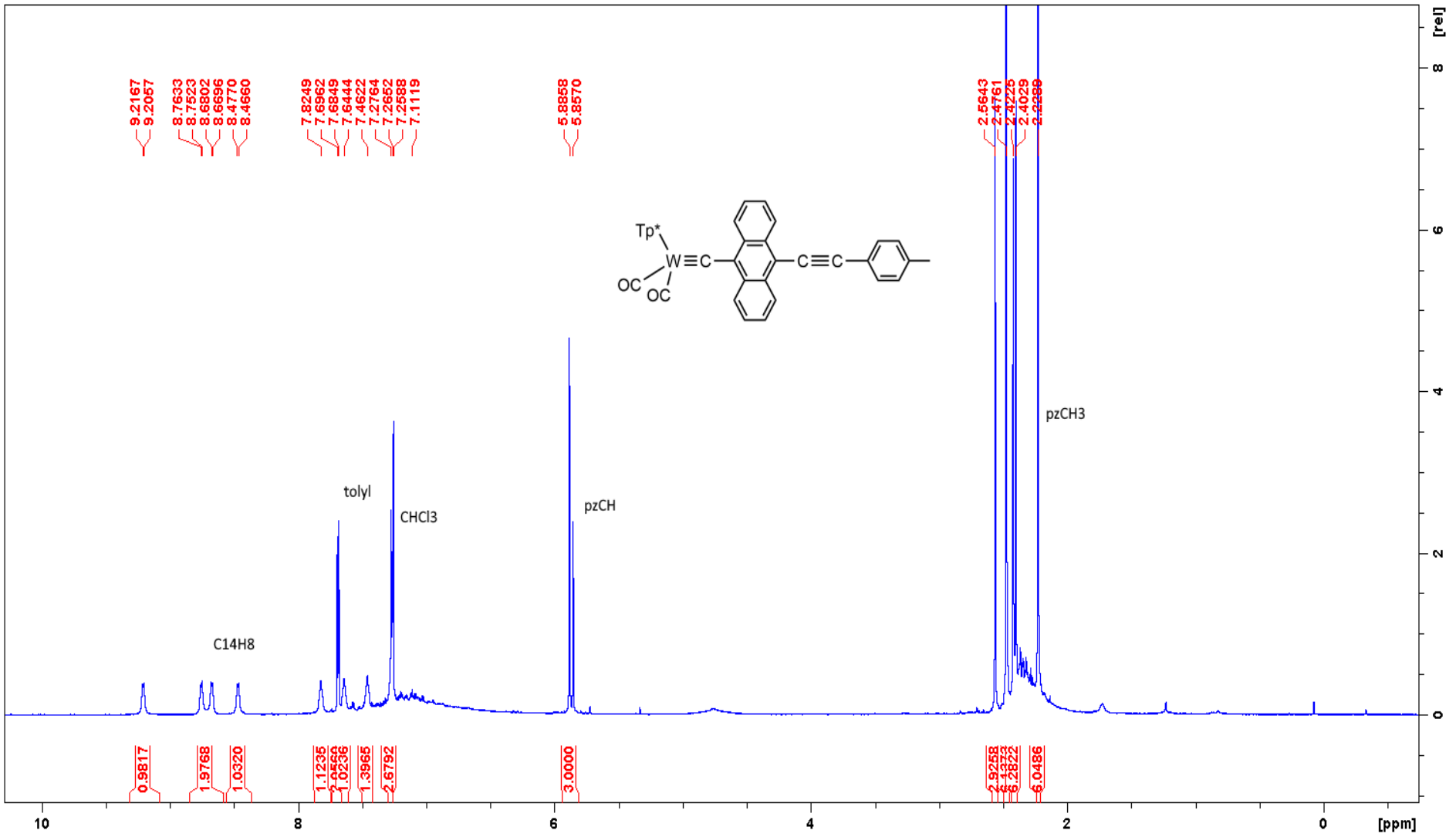

Figure S22. ^{1}H NMR (700 MHz, $CDCl_3$, –40 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CC≡CC$_6$H$_4$CH$_3$-4)(CO)$_2$(Tp*)] (**2**).

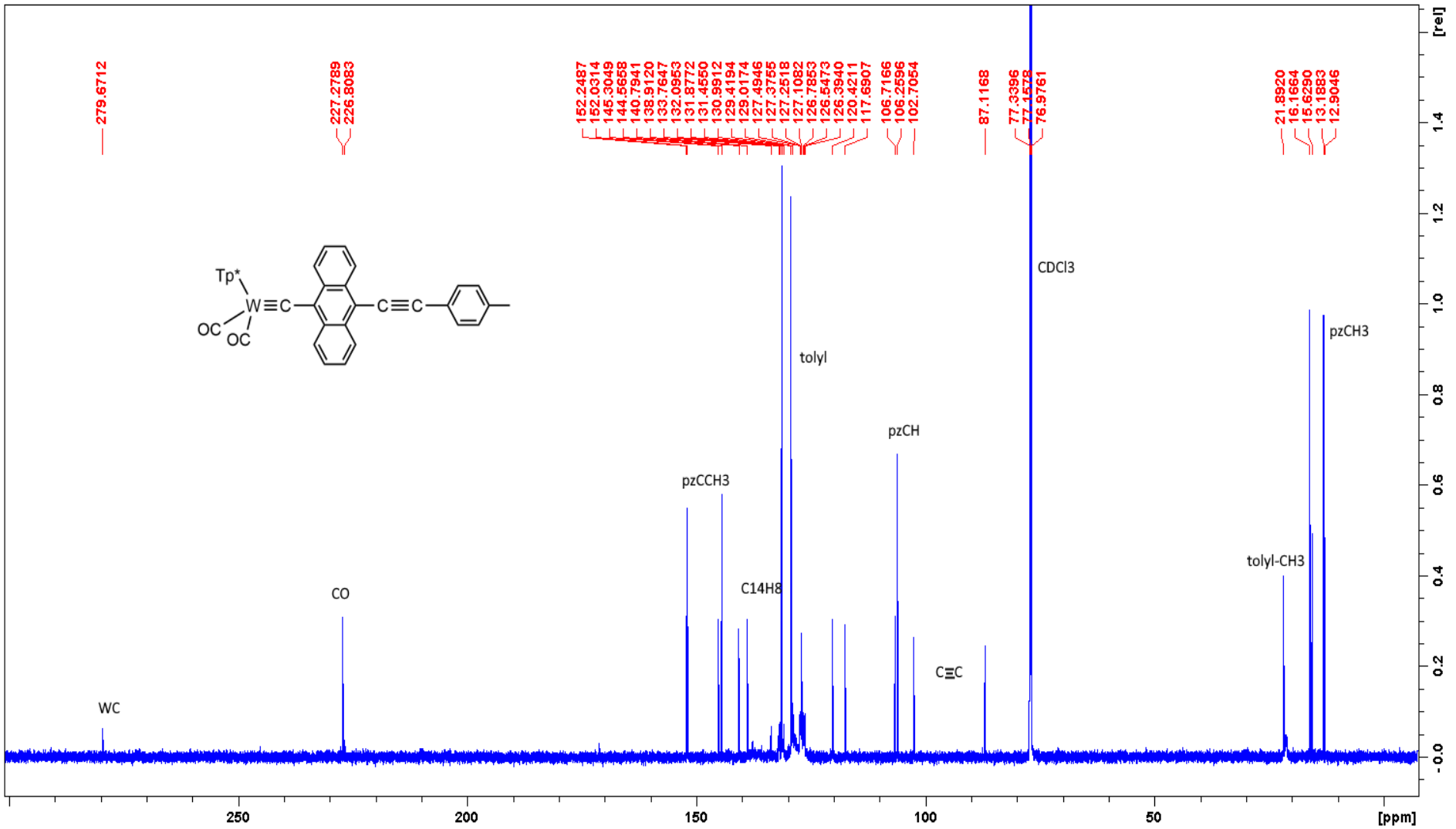

Figure S23. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, –40 ˚C, δ) of [W{≡CC(C_6H_4)$_2$CC≡C$C_6H_4CH_3$-4)$(CO)_2$(Tp*)] (**2**).

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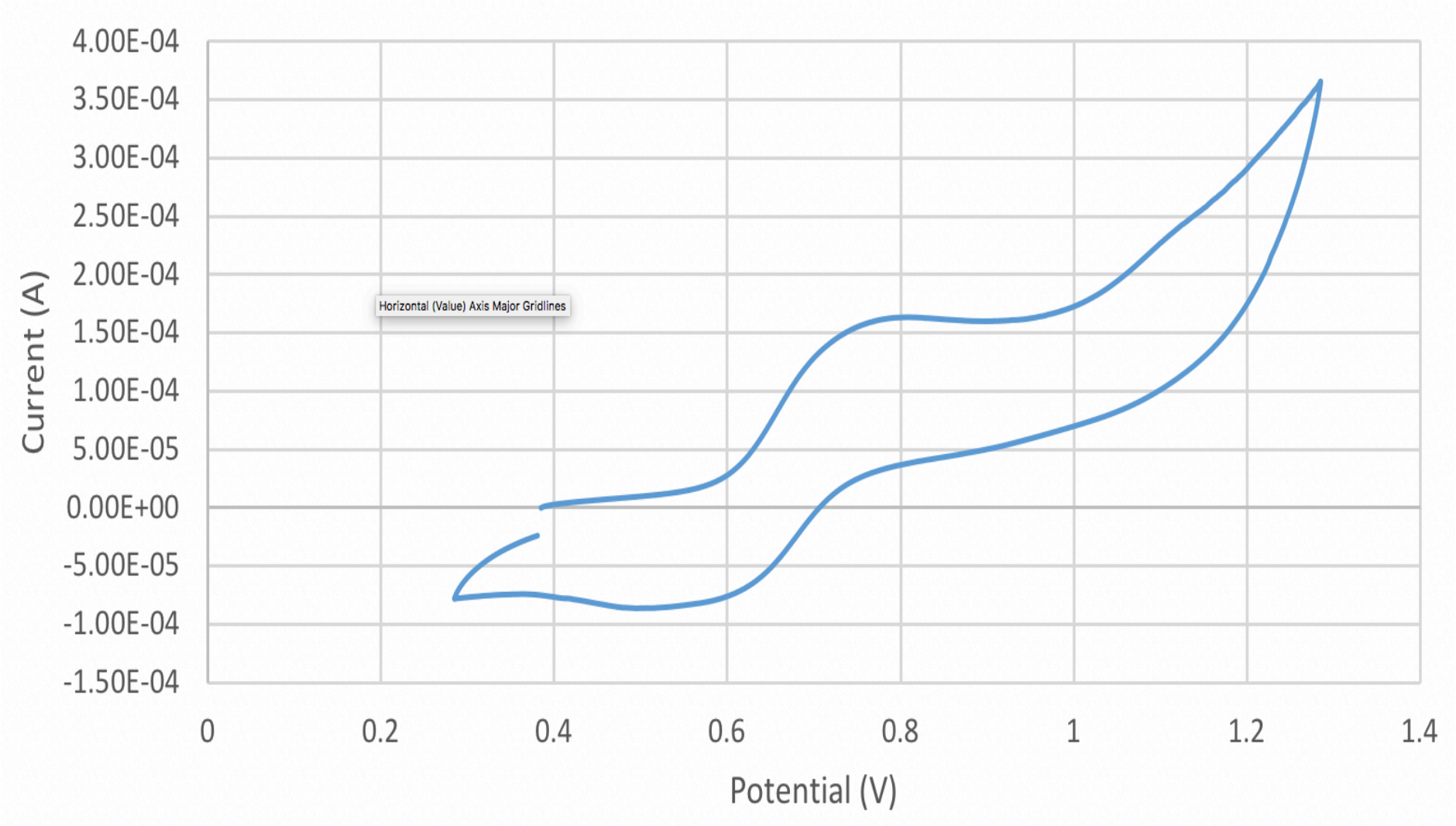

Figure S24. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [W{≡CC(C_6H_4)$_2$CC≡C$C_6H_4CH_3$-4)$(CO)_2$(Tp*)] (**2**).

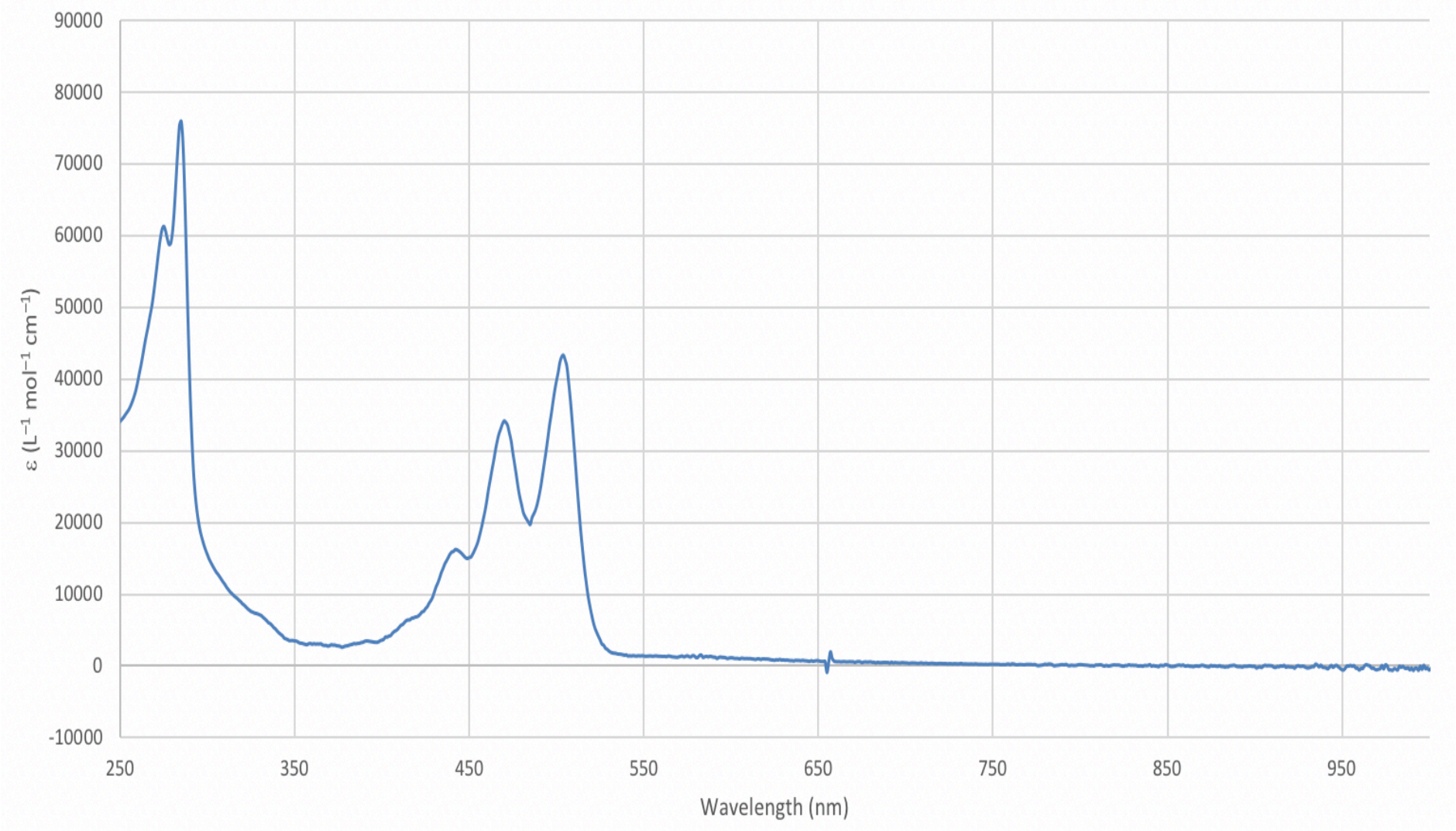

Figure S25a. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CC≡C$C_6H_4CH_3$-4)(CO)$_2$(Tp*)] (**2**).

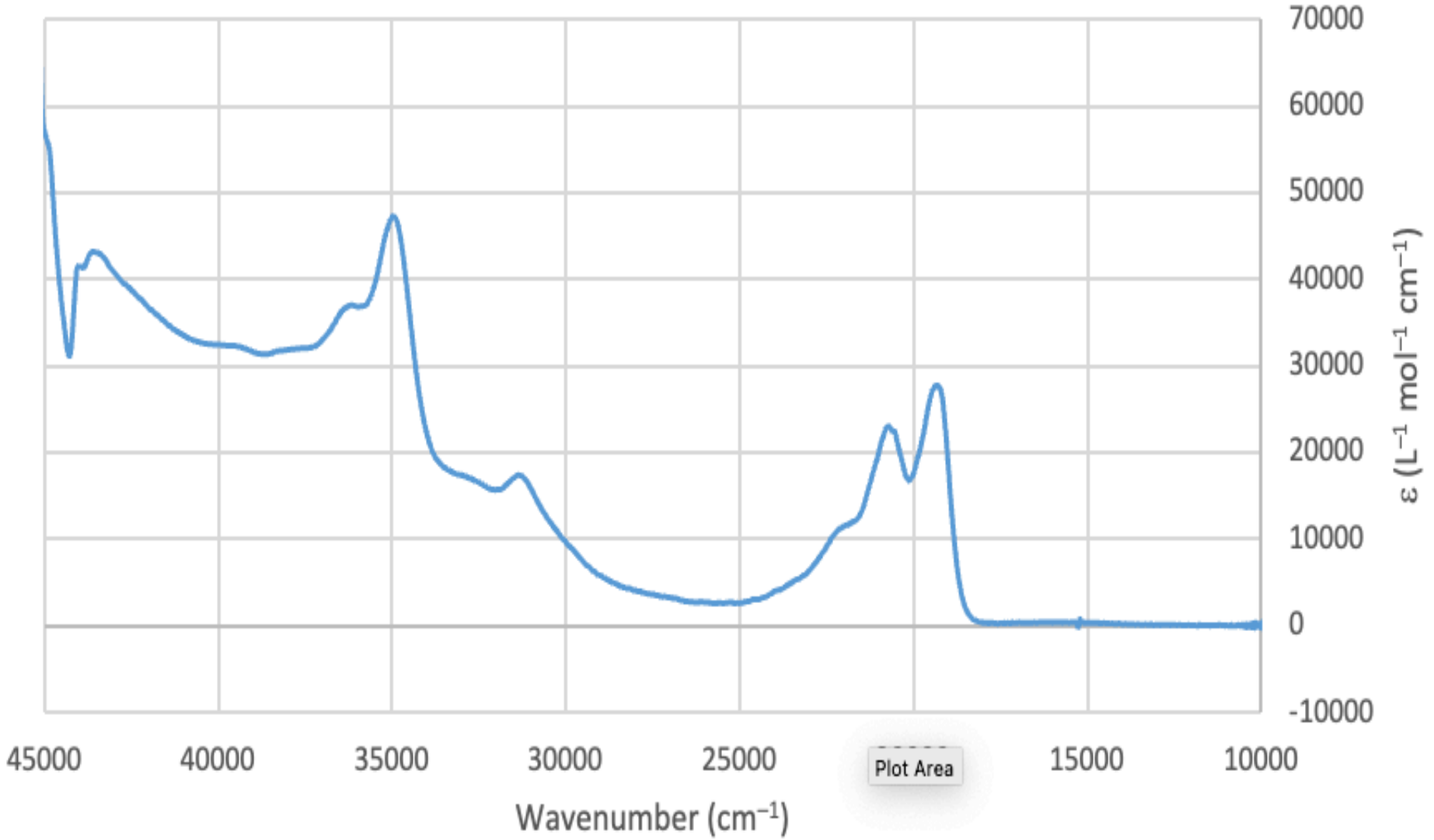

Figure S25b. Electronic spectrum (CH_2Cl_2) of [W{≡CC(C_6H_4)$_2$CC≡C$C_6H_4CH_3$-4)$(CO)_2$(Tp*)] (**2**).

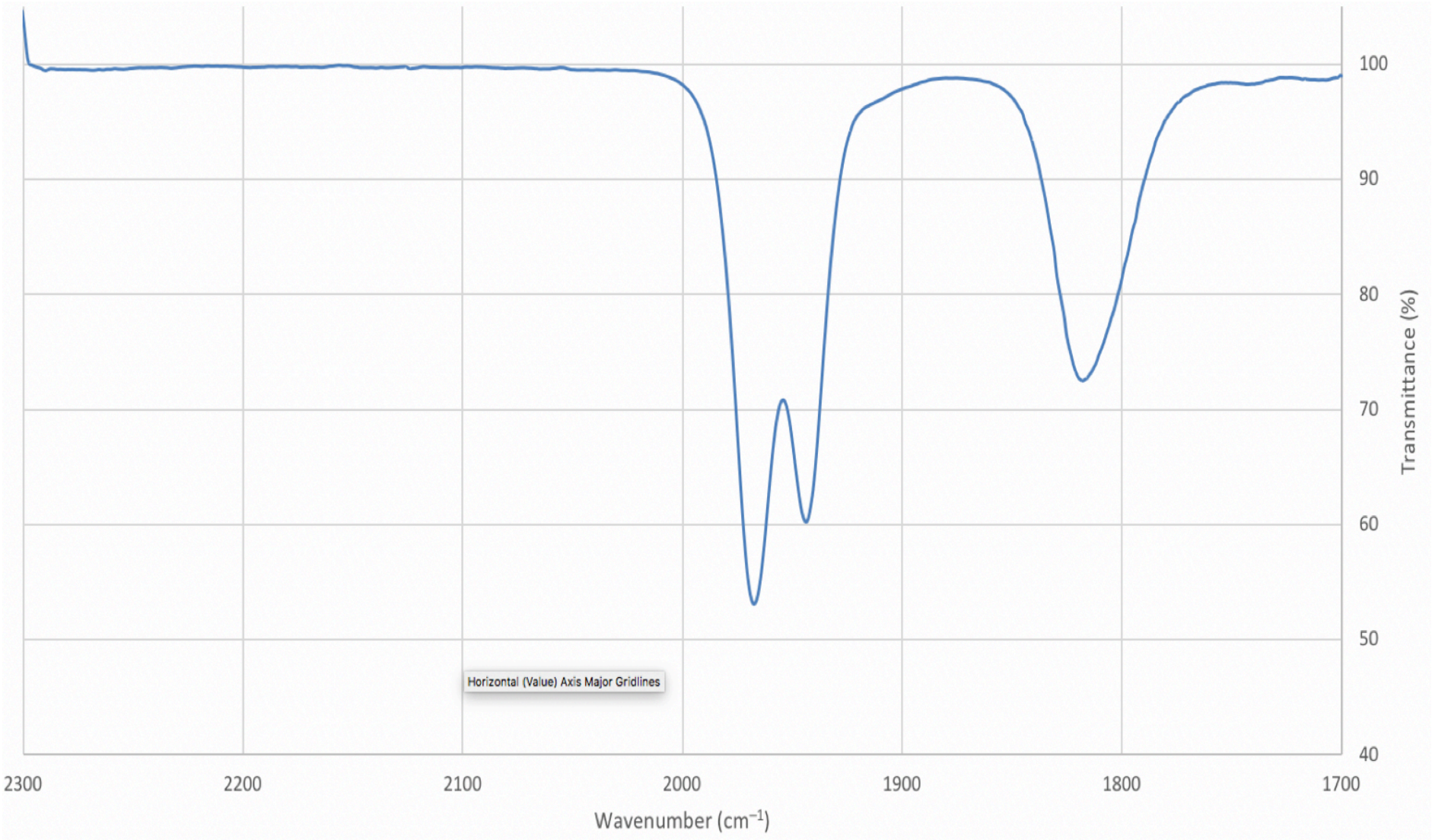

Figure S26. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [W{≡CC(C_6H_4)$_2$CC≡CC$_6$H$_4$CH$_3$-4)(CO)$_2$(Tp*)] (**2**).

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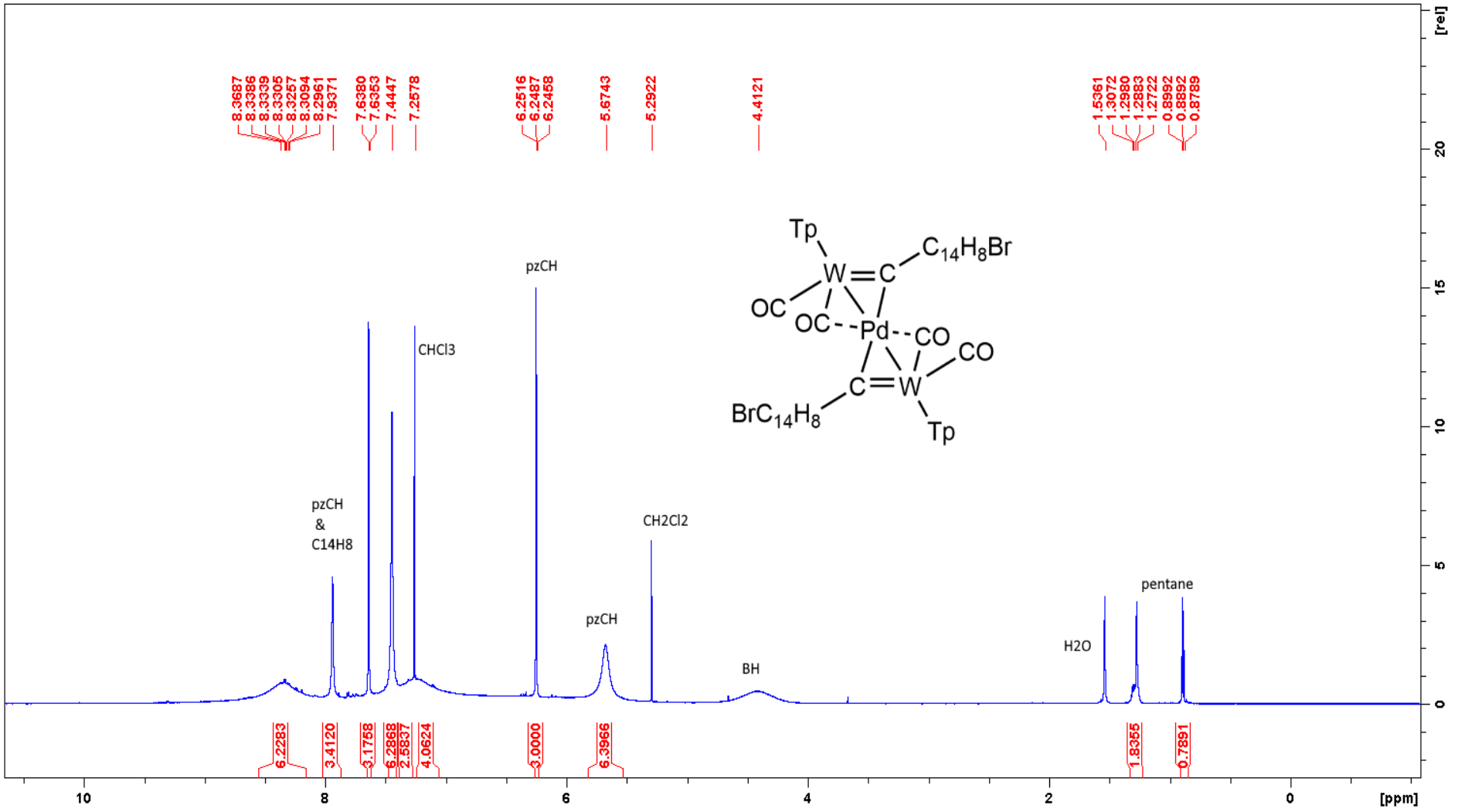

Figure S27. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**3a**).

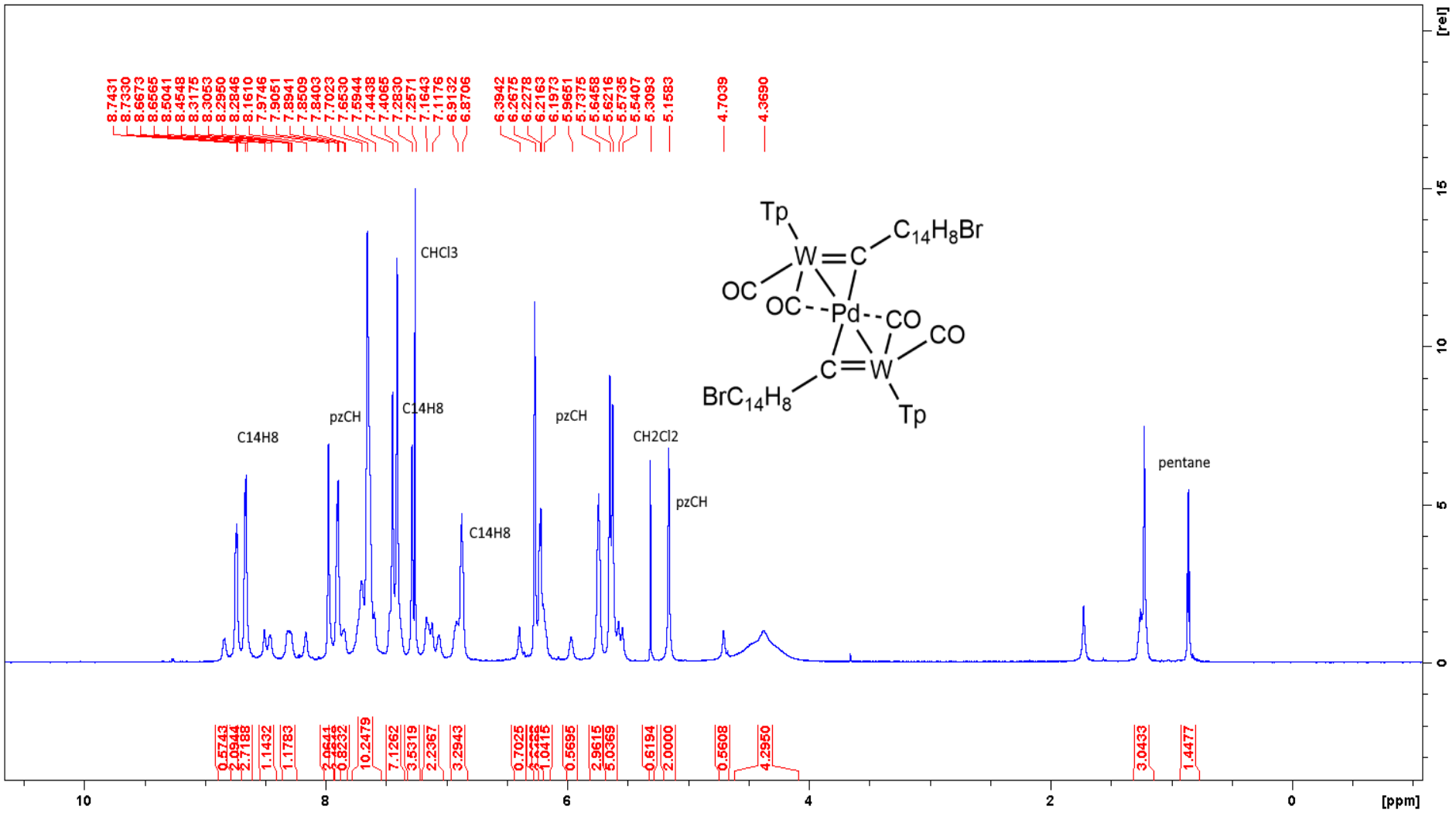

Figure S28. ^{1}H NMR (700 MHz, $CDCl_3$, –50 ˚C, δ) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**3a**).

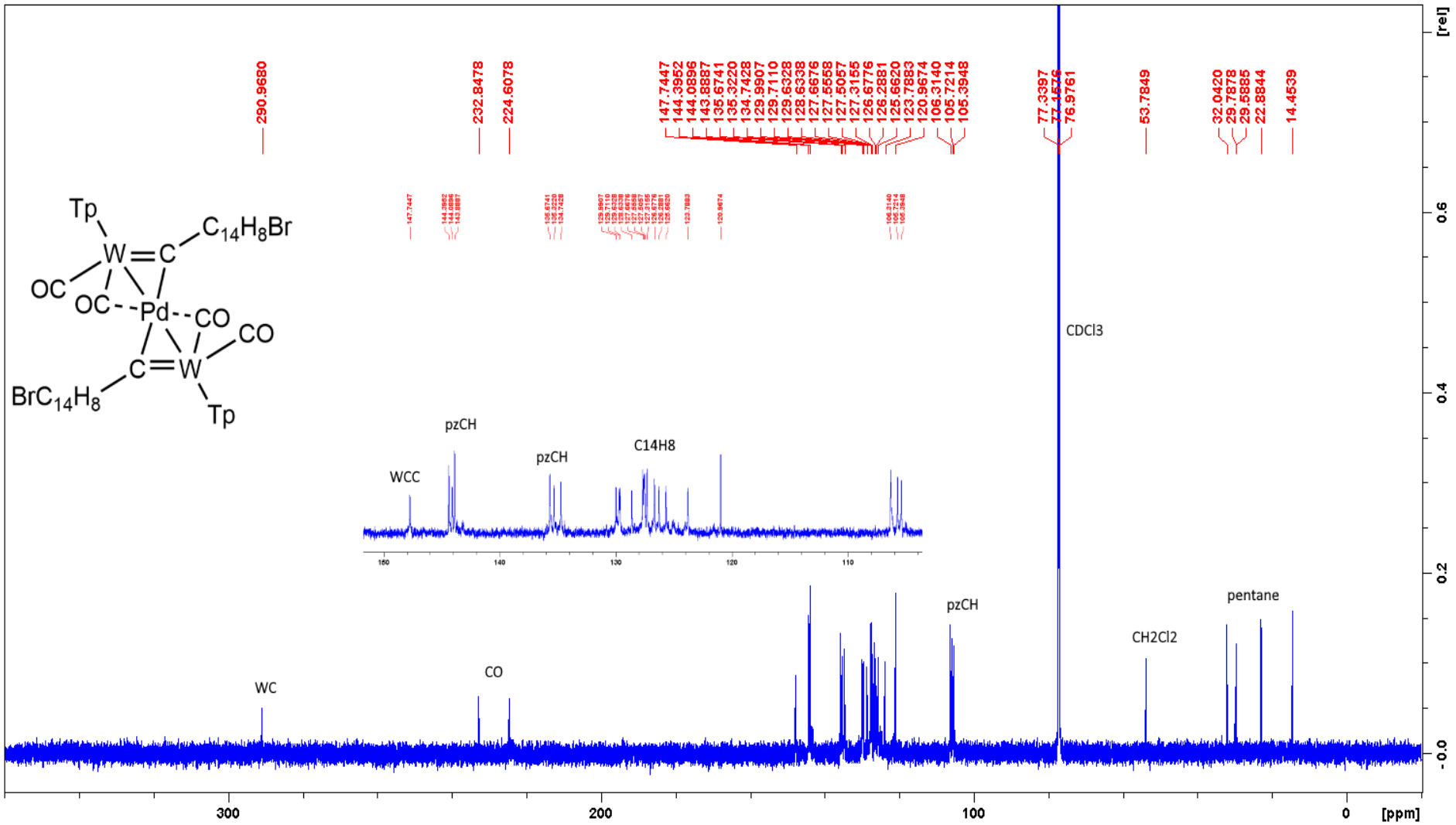

Figure S29. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, –50 ˚C, δ) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**3a**).

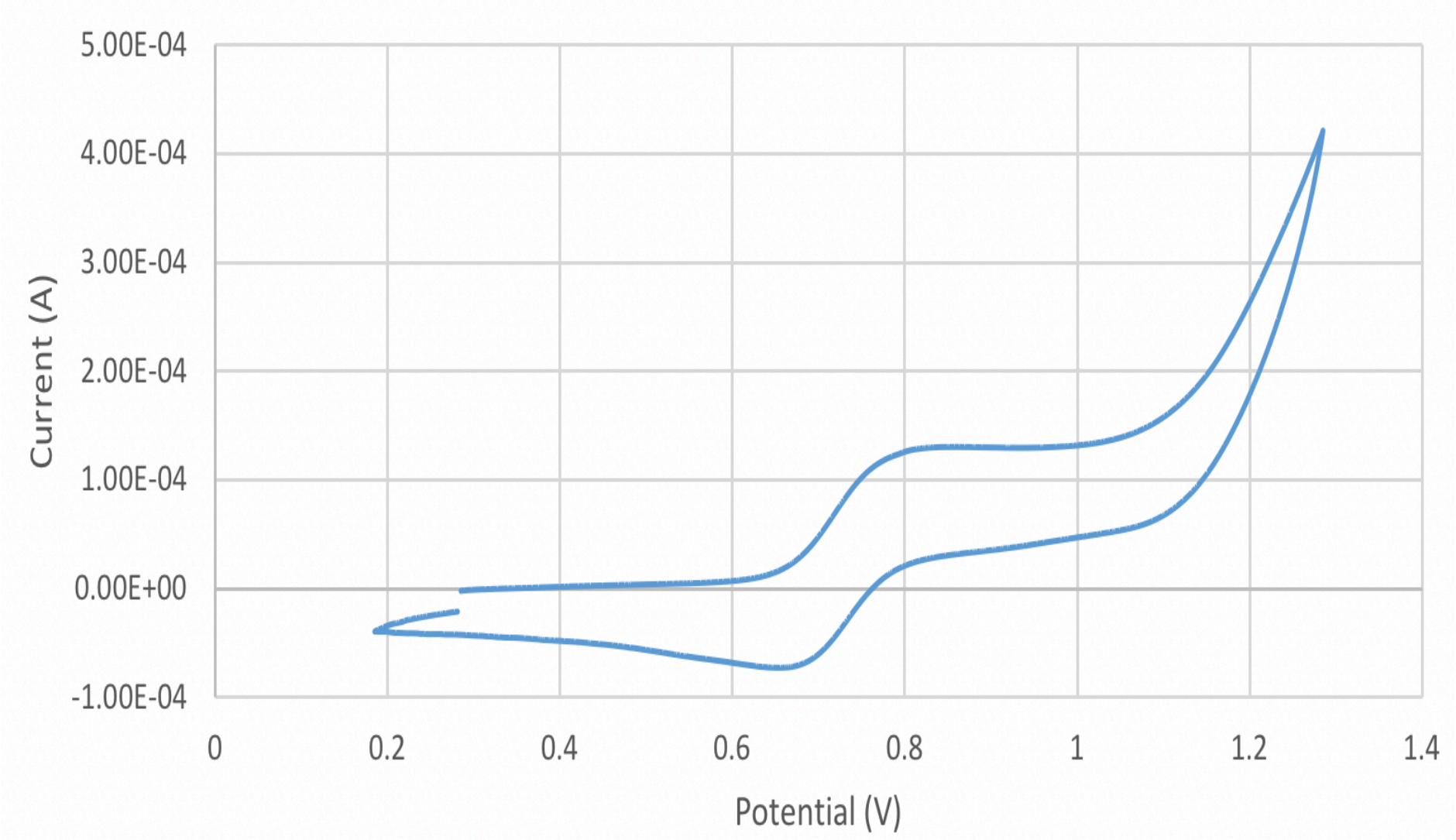

Figure S30. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [$W_2Pd\{\mu$-$CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2$] (**3a**).

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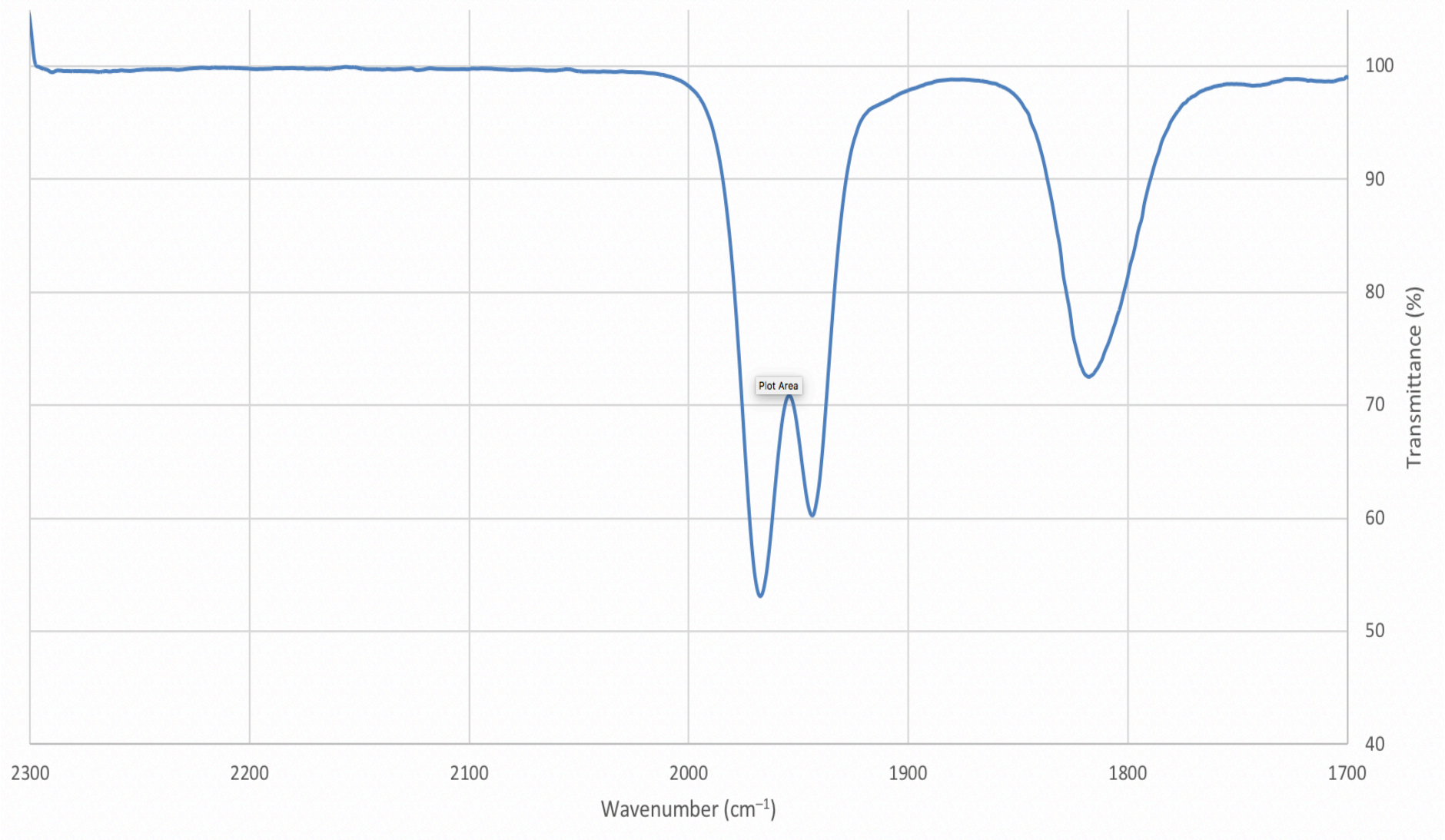

Figure S31. Infrared spectrum (CH_2Cl_2, cm^{-1}) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**3a**).

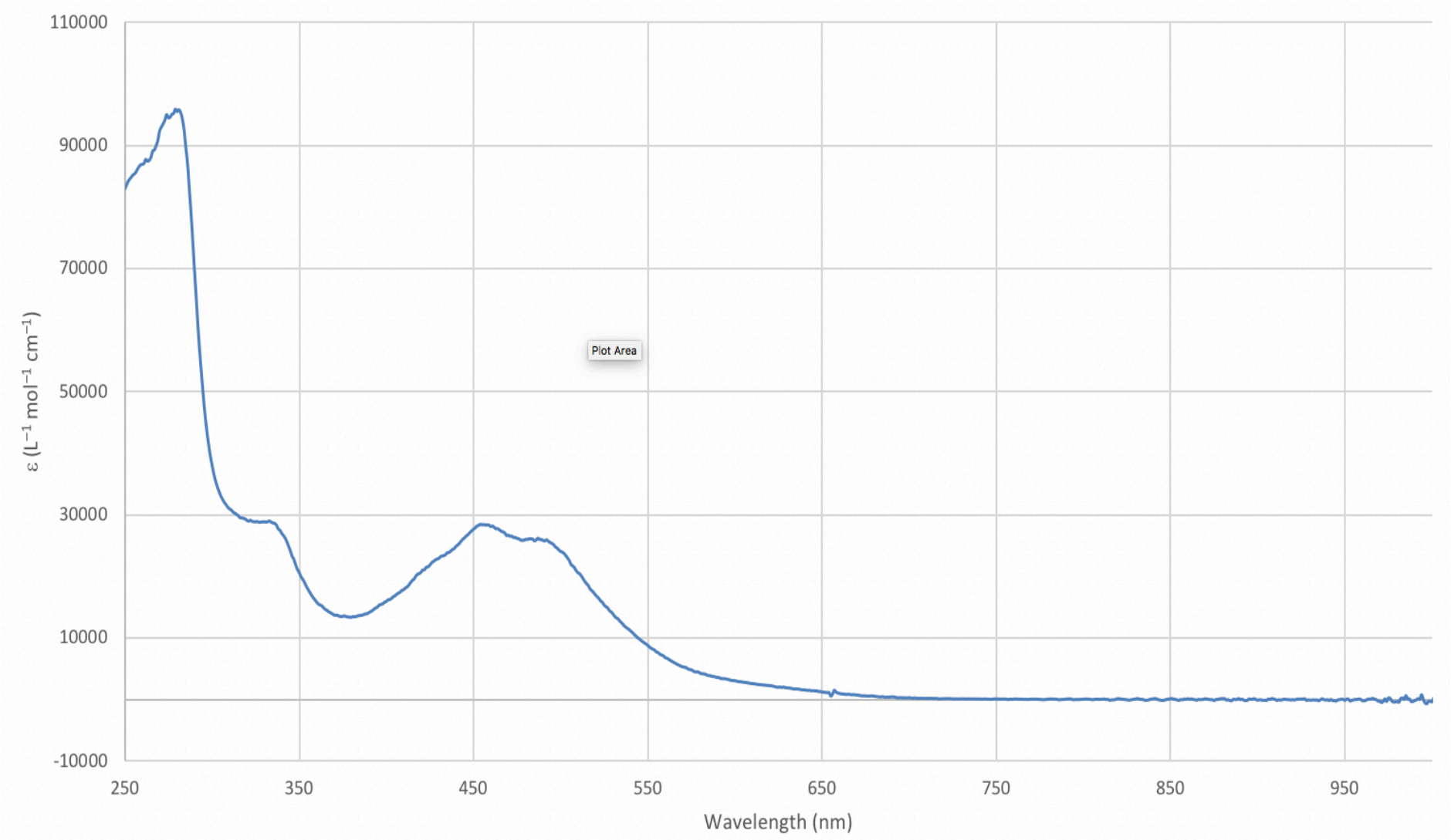

Figure S32a. Electronic spectrum (CH_2Cl_2) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**3a**).

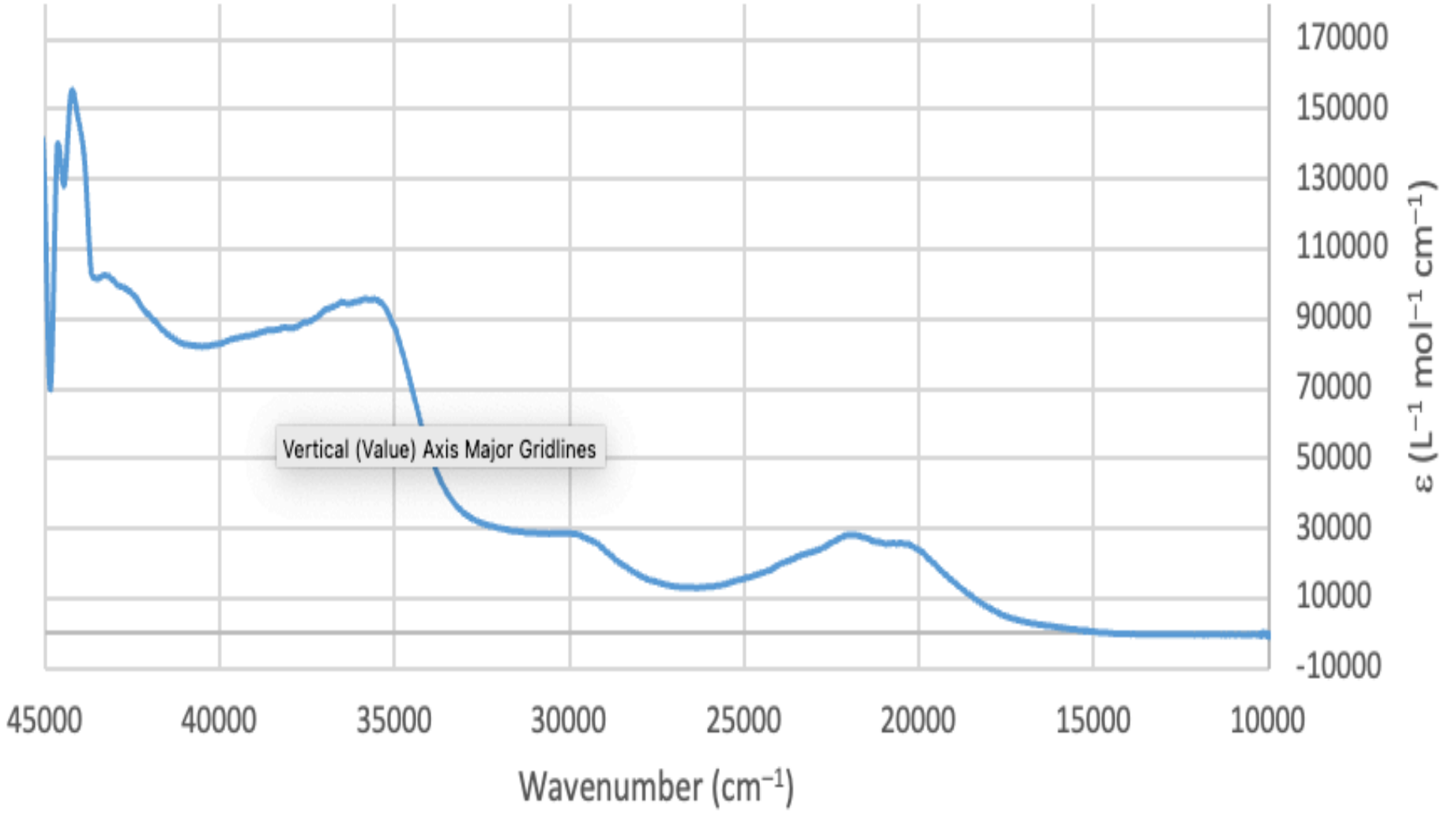

Figure S32a. Electronic spectrum (CH_2Cl_2) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**3a**).

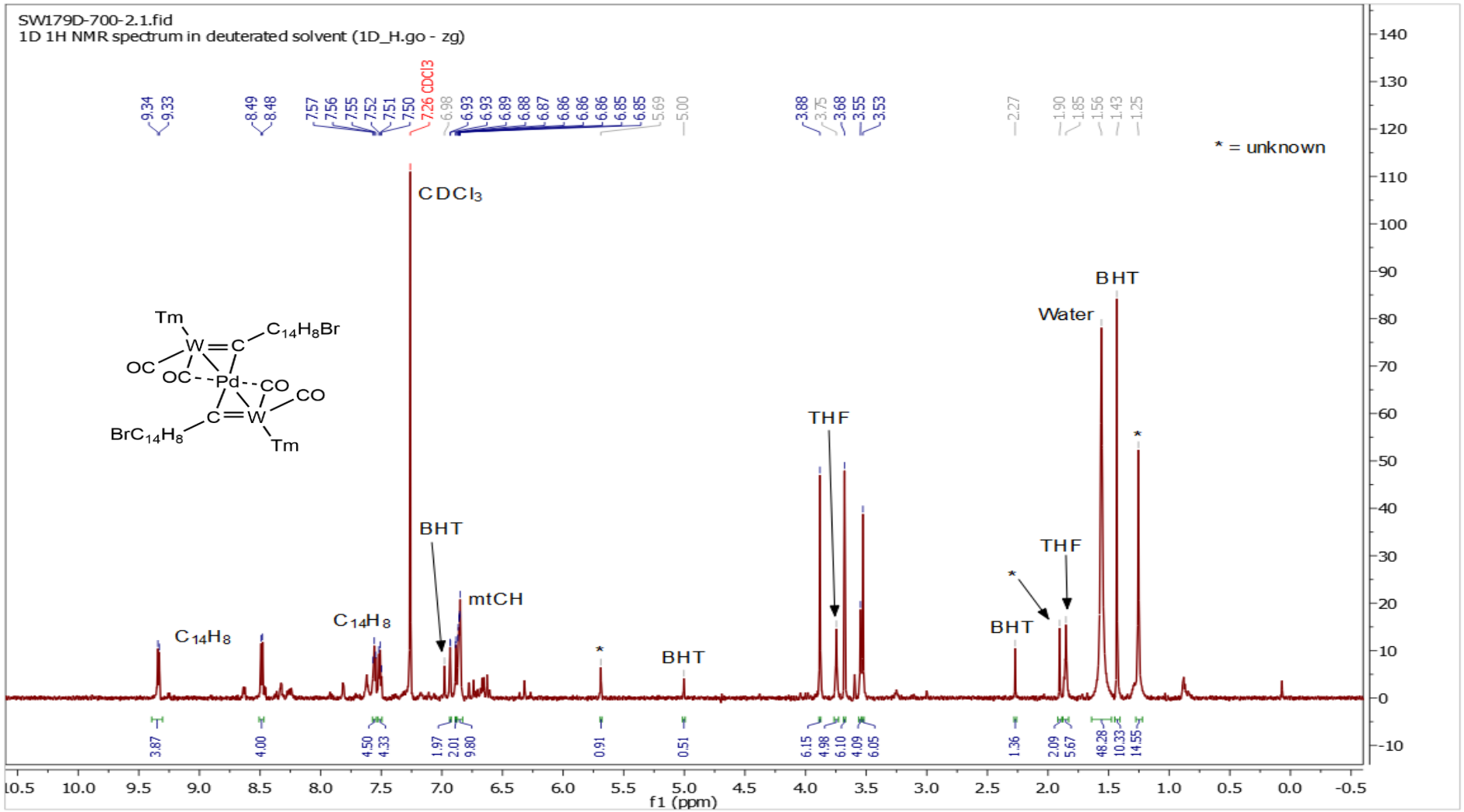

Figure S33. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**3b**)

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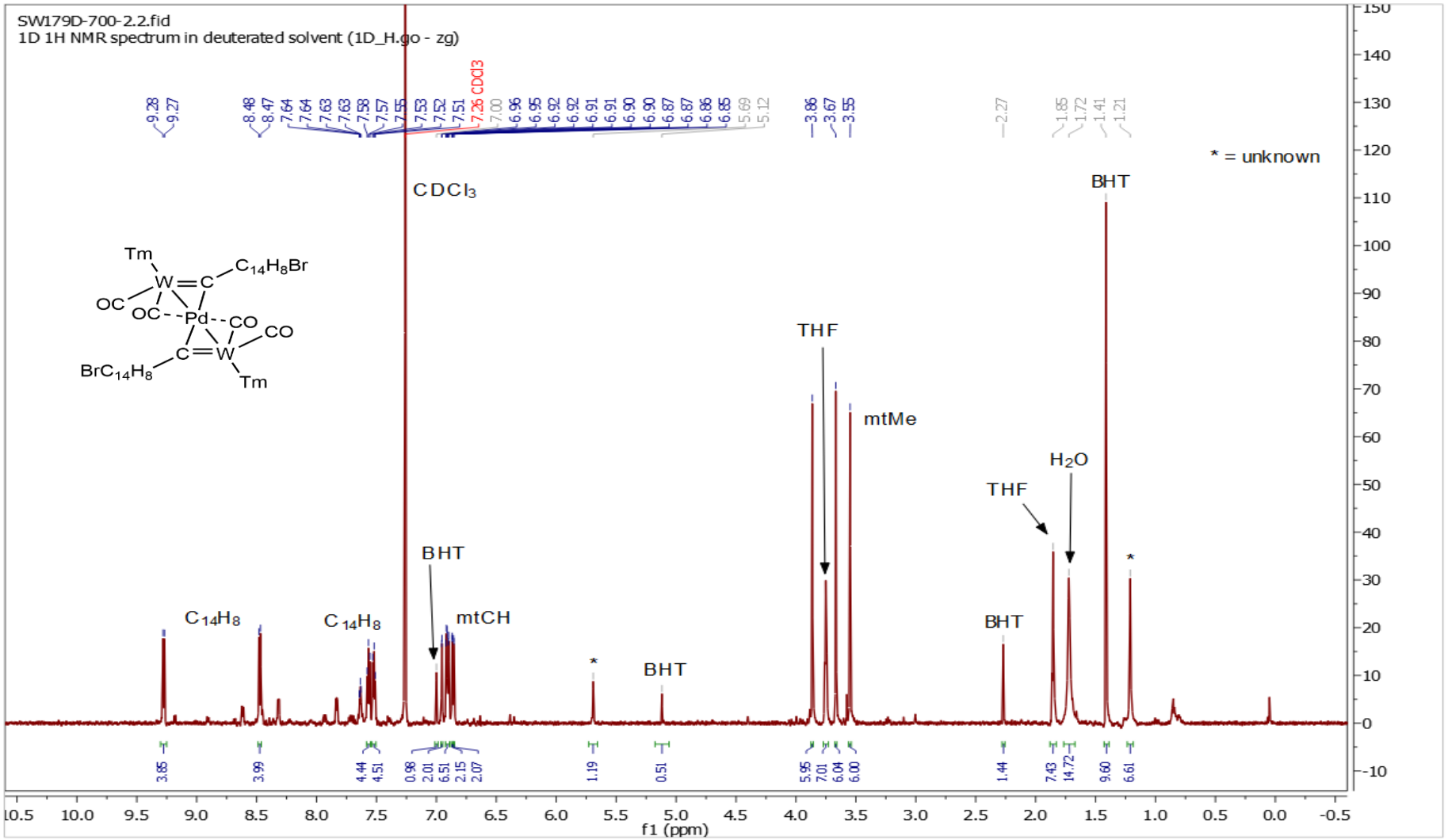

Figure S34. ^{1}H NMR (700 MHz, $CDCl_3$, –40 ˚C, δ) $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**3b**).

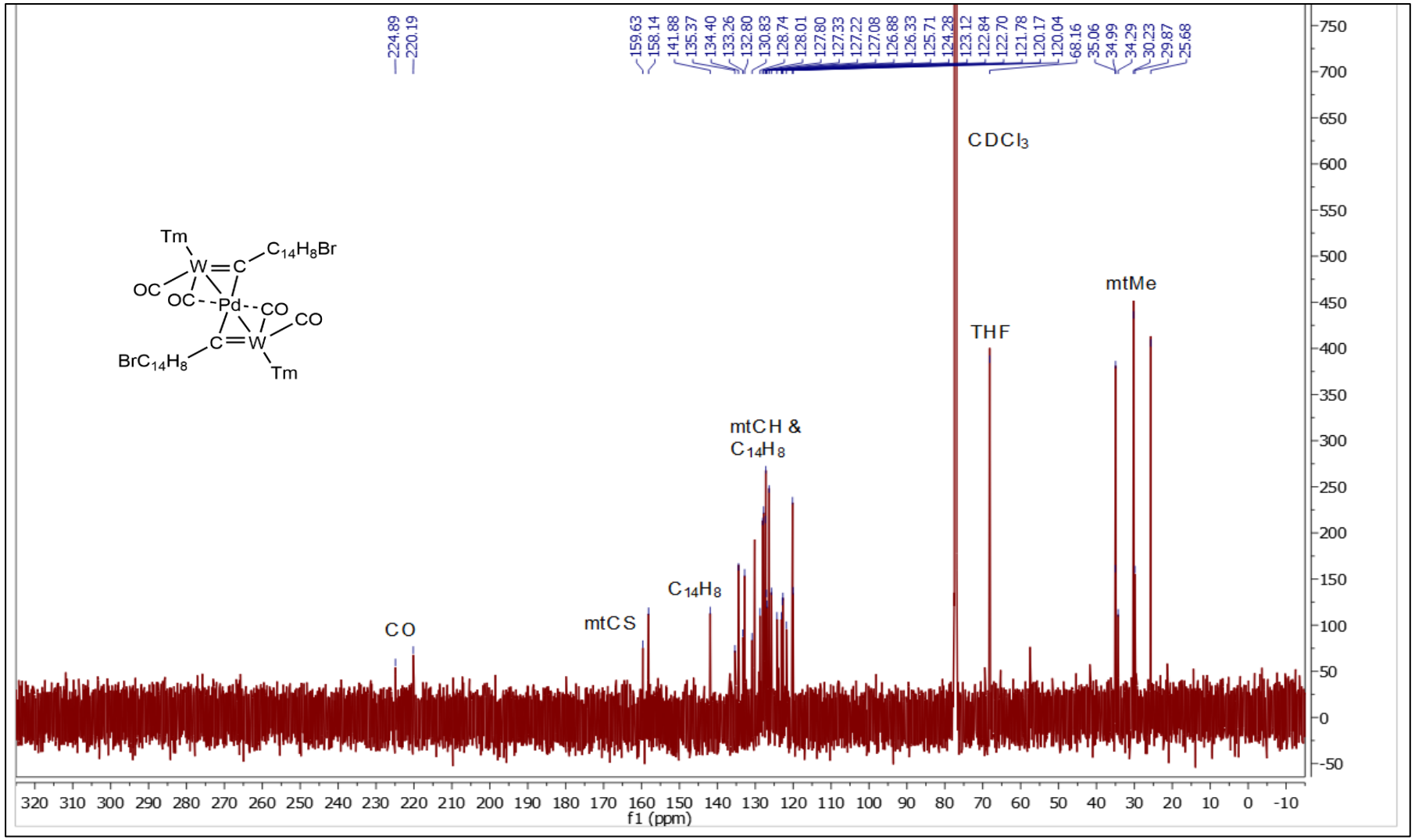

Figure S35. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, –40 °C, δ) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**3b**).

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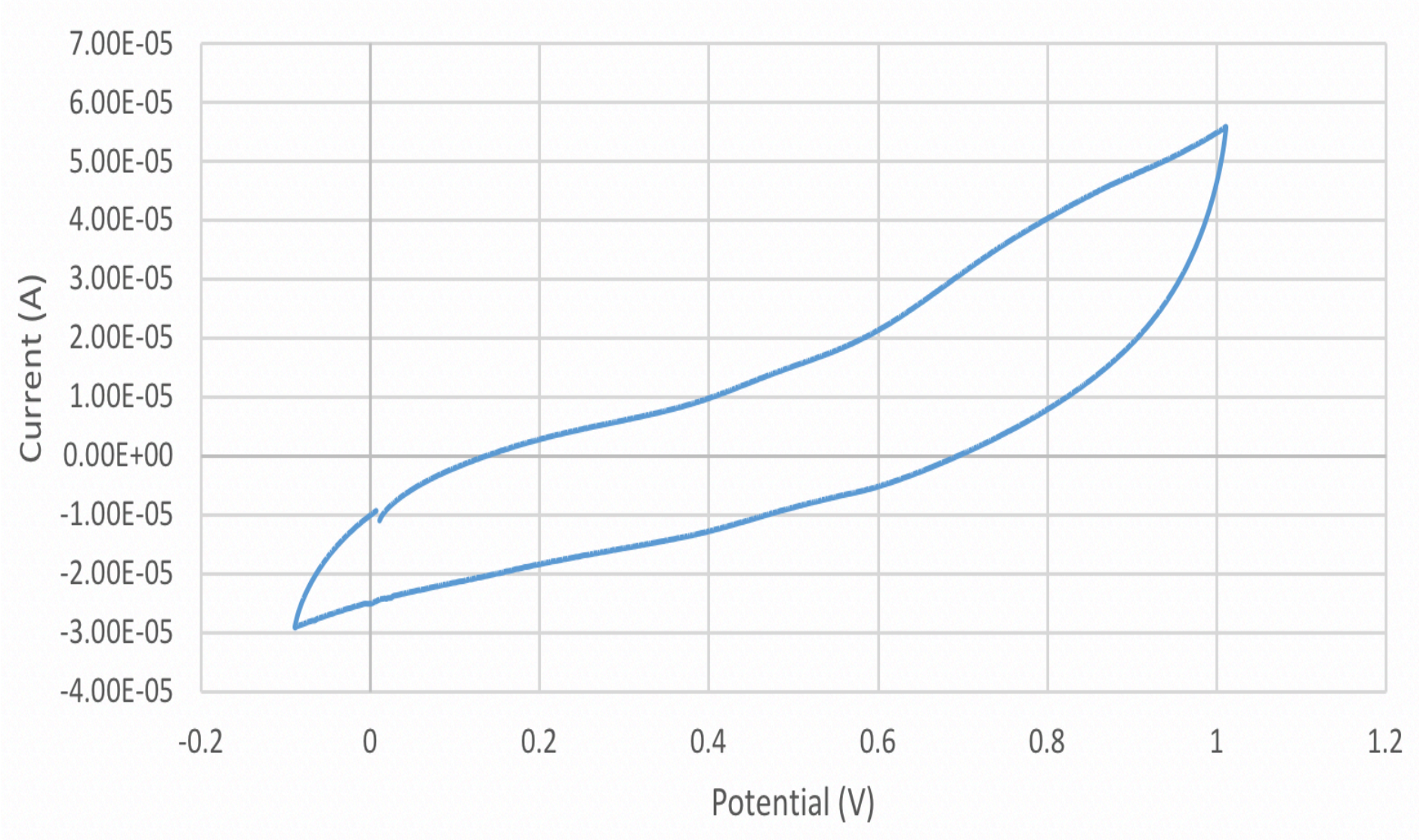

Figure S36. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [$W_2Pd\{\mu$-$CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2$] v (**3b**).

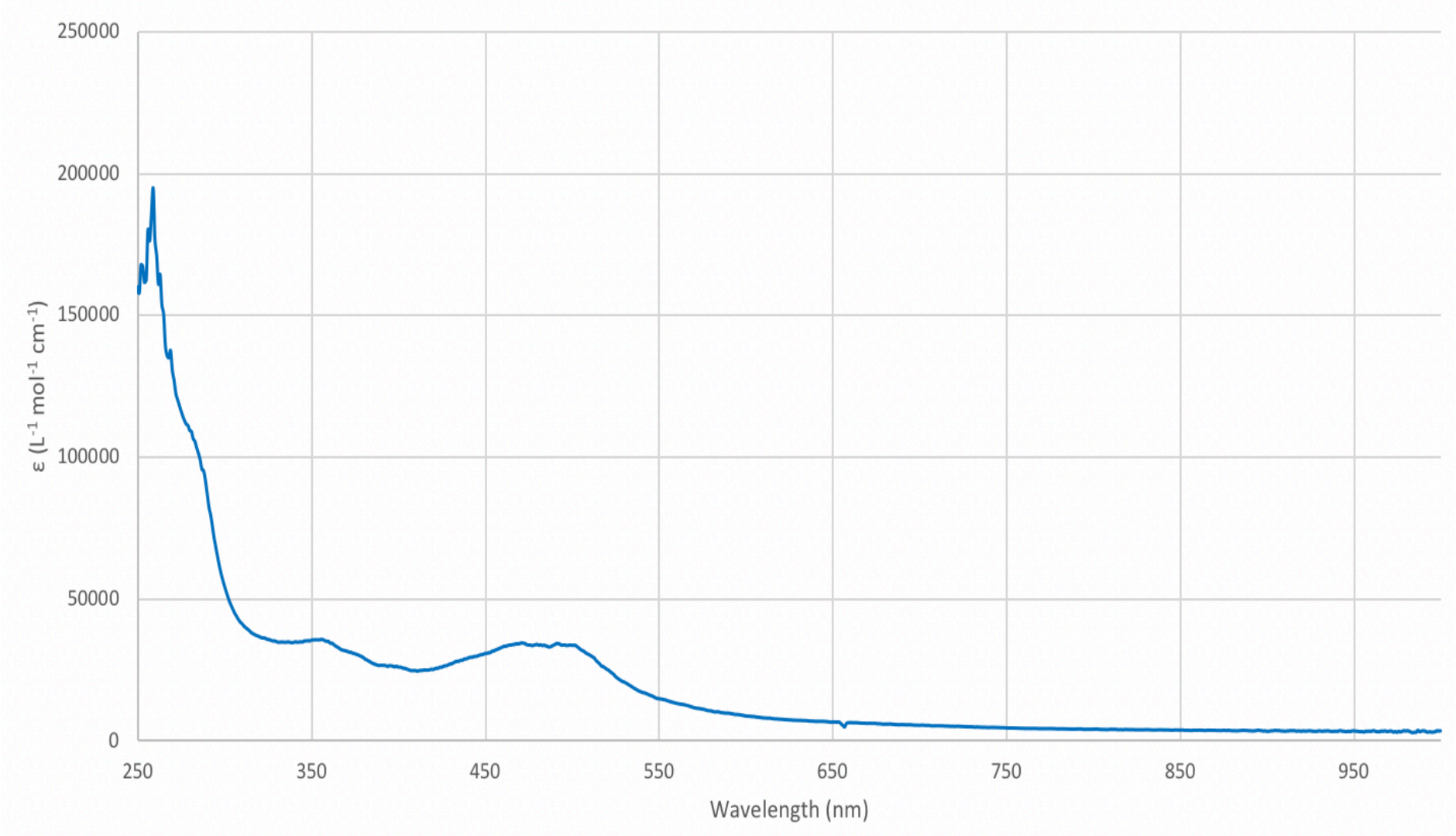

Figure S37. Electronic spectrum (CH_2Cl_2) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**3b**).

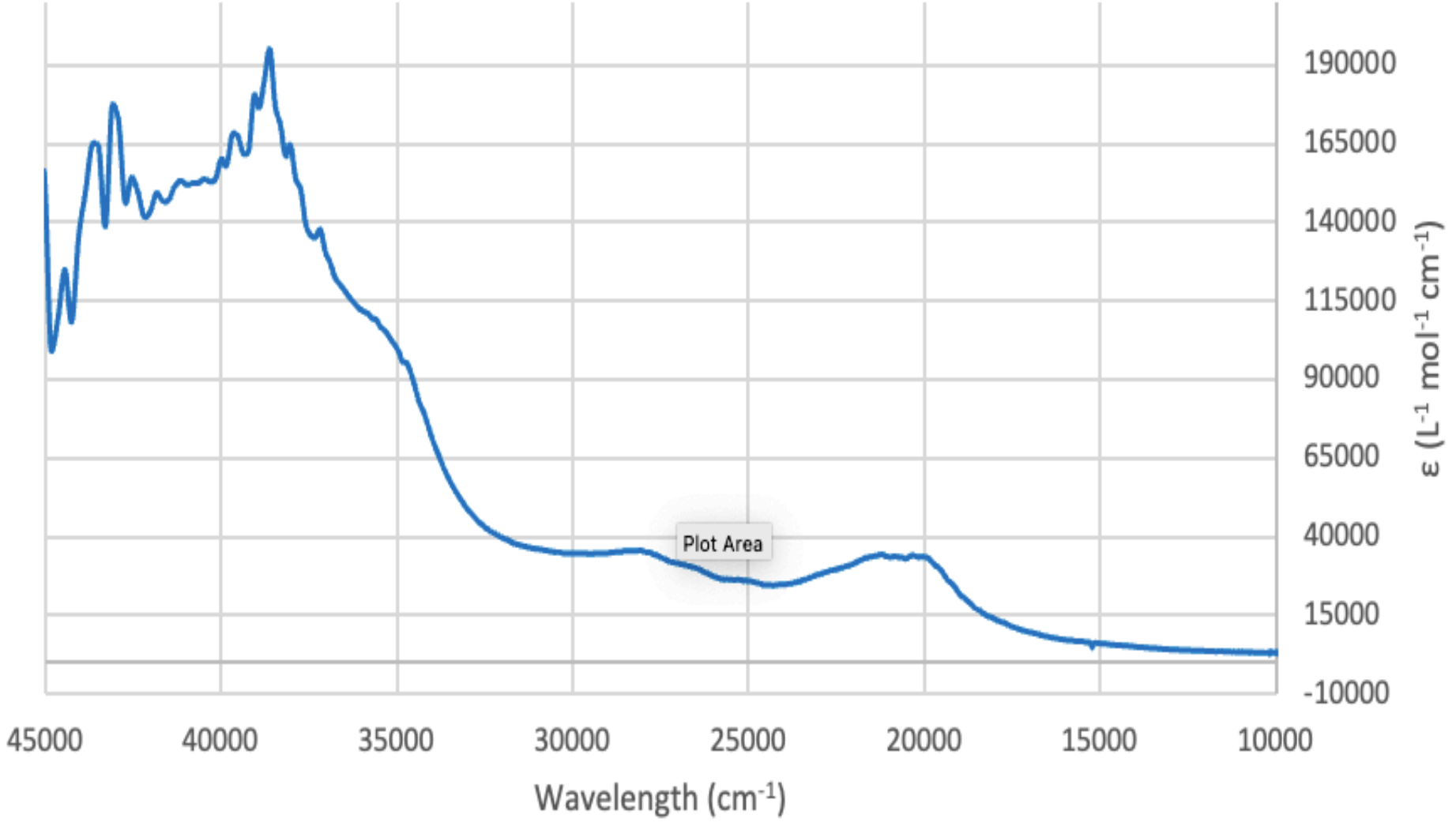

Figure S37. Electronic spectrum (CH_2Cl_2) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**3b**).

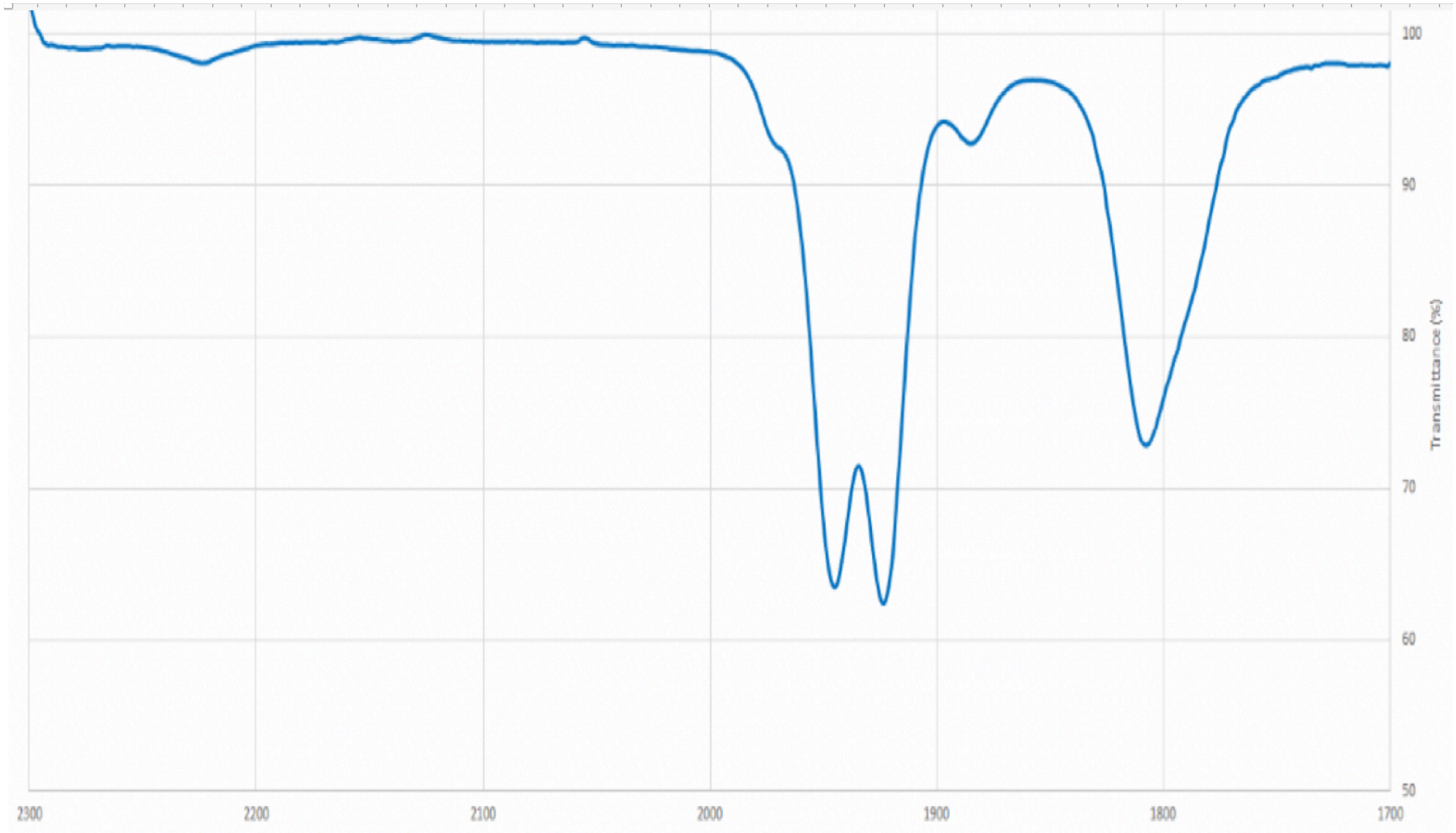

Figure S38. Infrared spectrum (CH_2Cl_2, cm^{-1}) of $[W_2Pd\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**3b**).

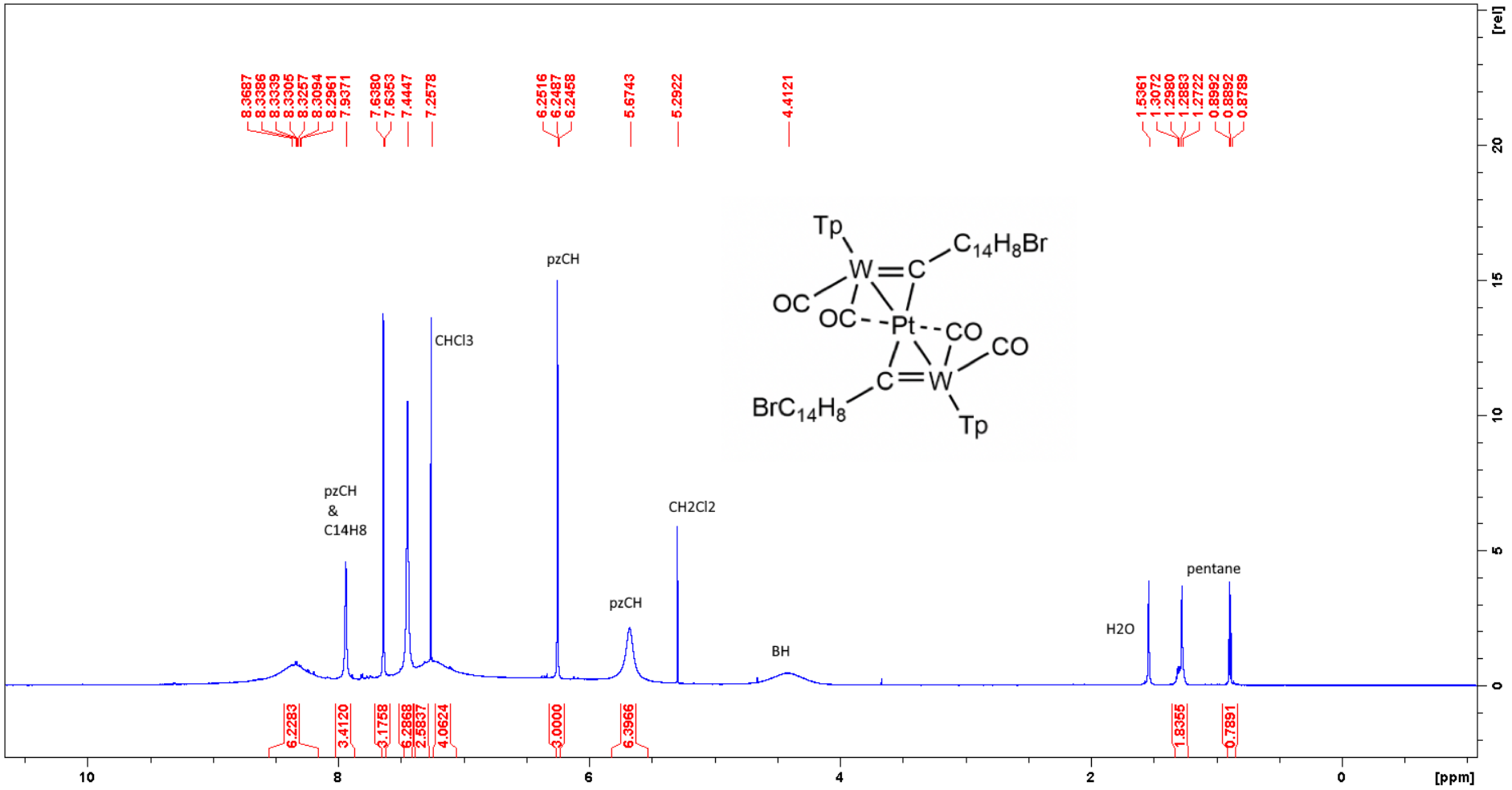

Figure S39. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**4a**).

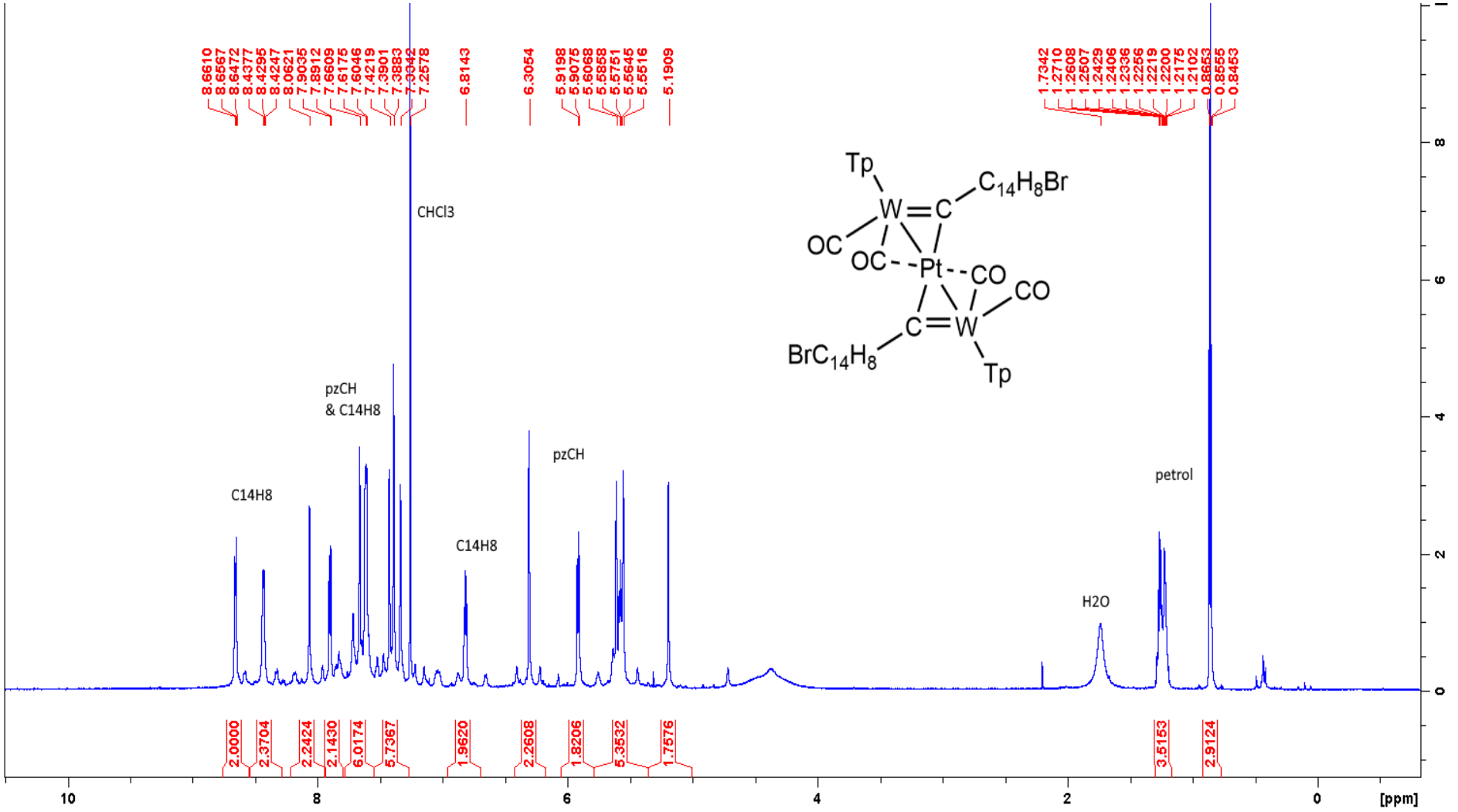

Figure S40. ^{1}H NMR (700 MHz, $CDCl_3$, –40 ˚C, δ) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**4a**).

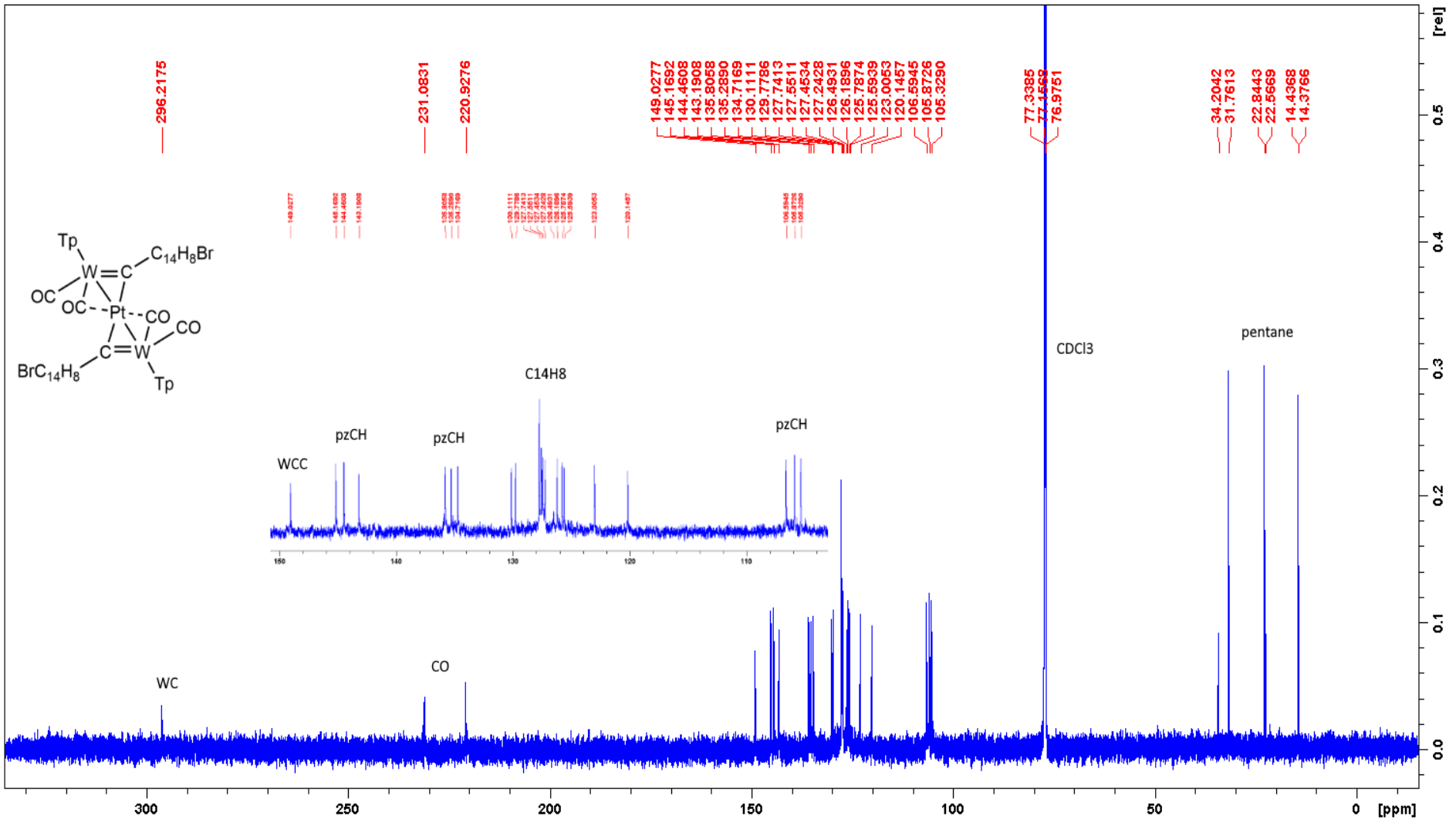

Figure S41. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, –40 ˚C, δ) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**4a**).

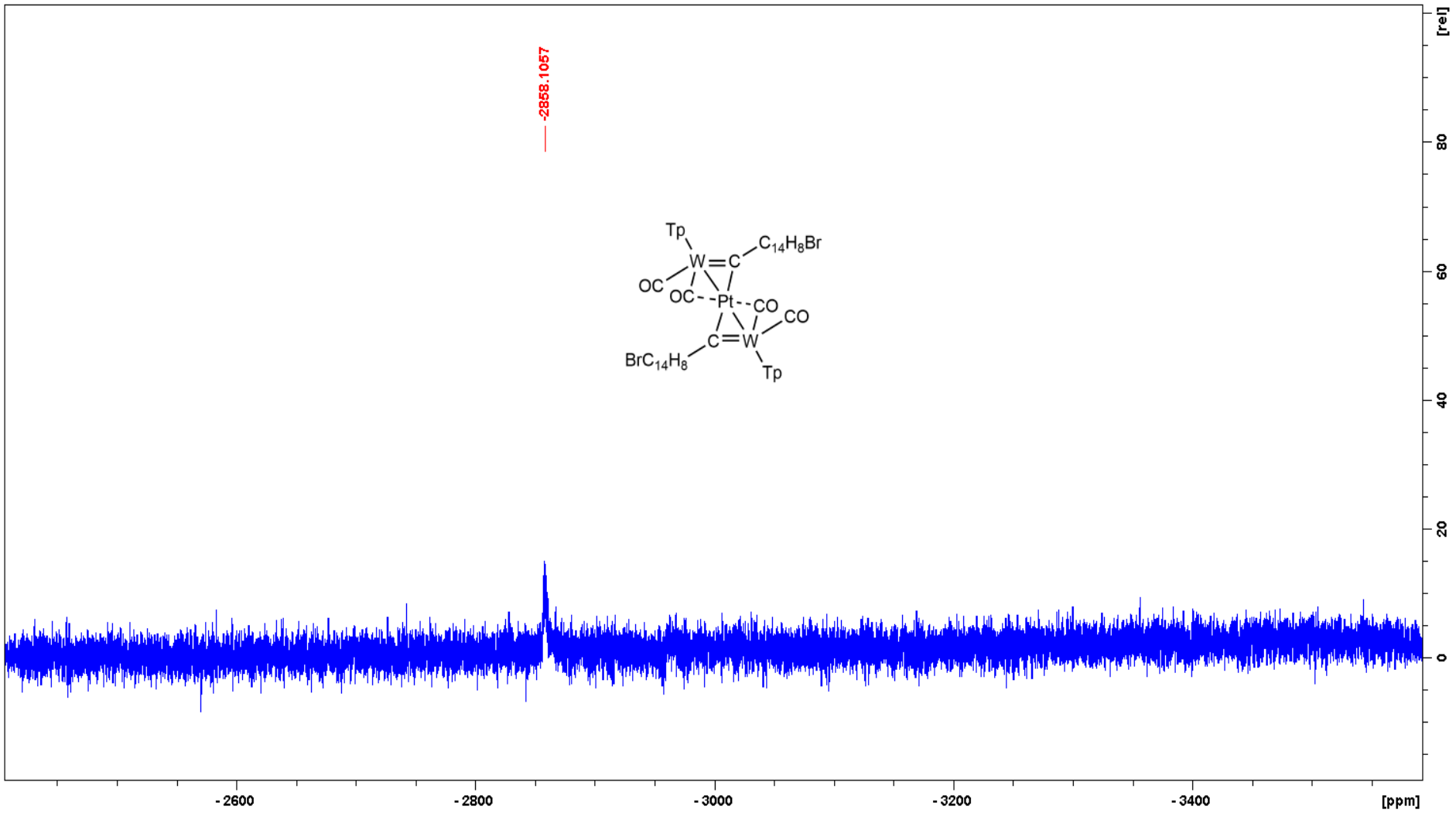

Figure S42. ^{195}Pt NMR (150 MHz, $CDCl_3$, –40 ˚C, δ) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**4a**).

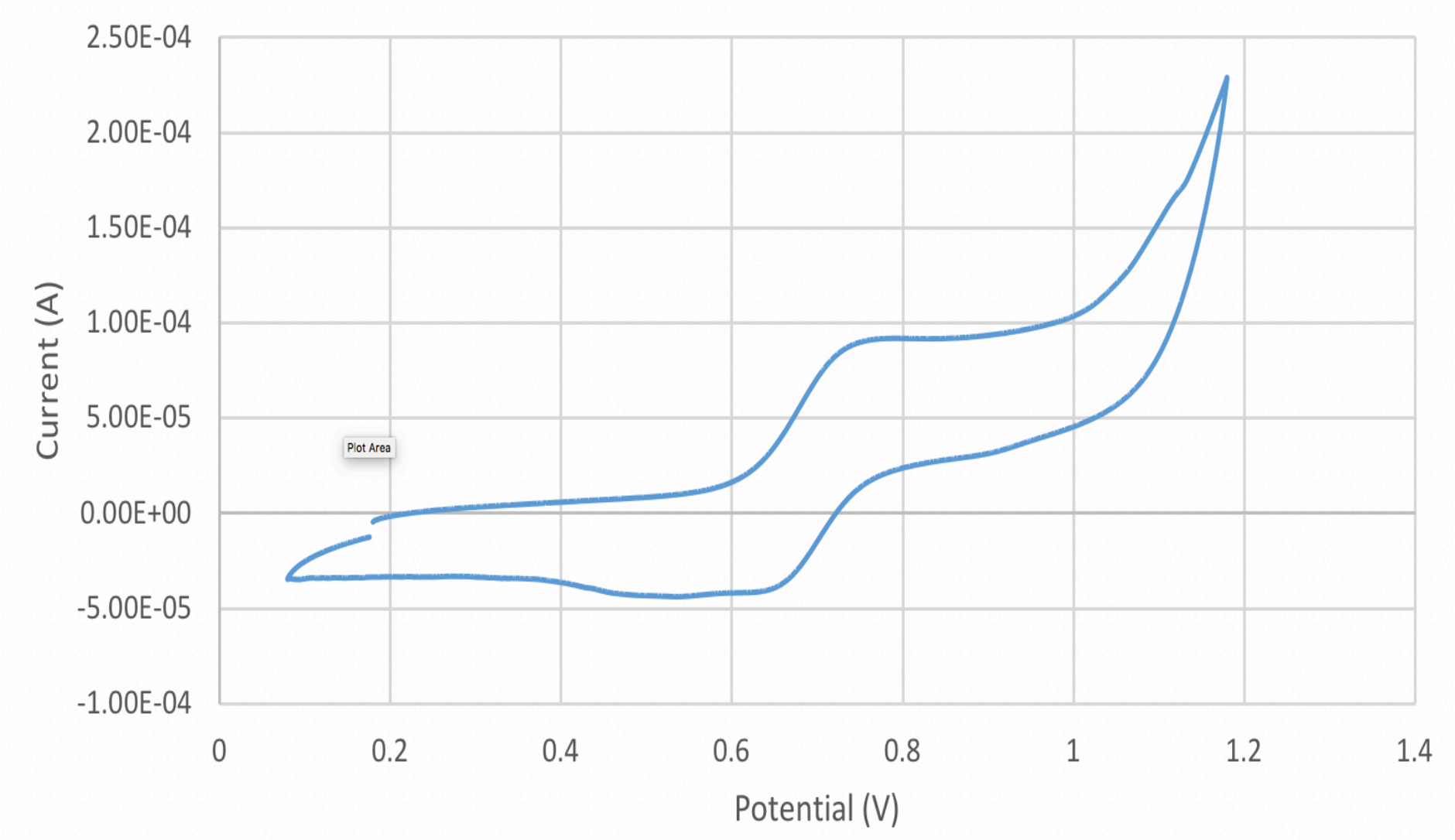

Figure S43. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [$W_2Pt(\mu\text{-}CC_{14}H_8Br)_2(CO)_4(Tp)_2$] (**4a**).

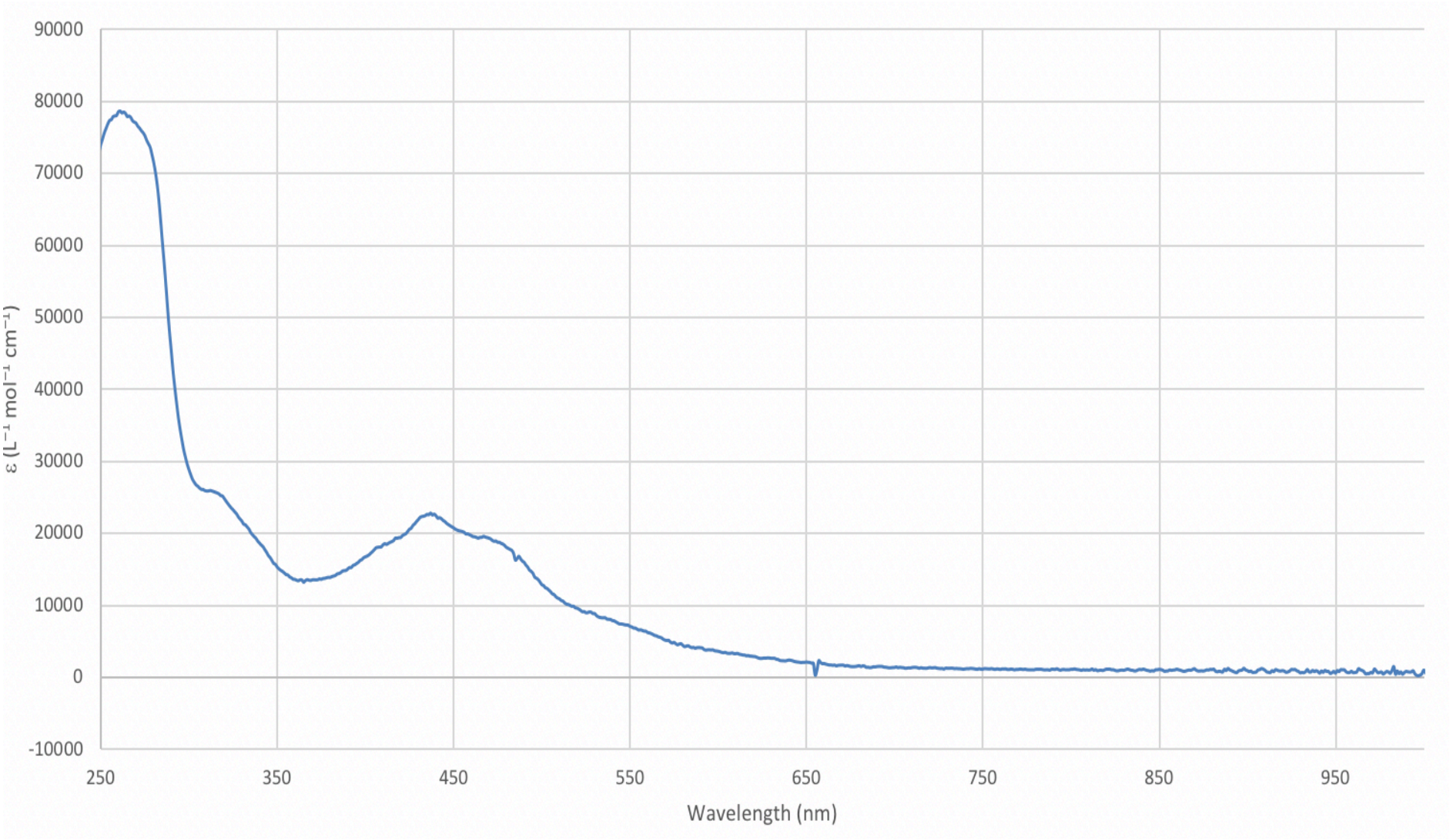

Figure S44. Electronic spectrum (CH_2Cl_2) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**4a**).

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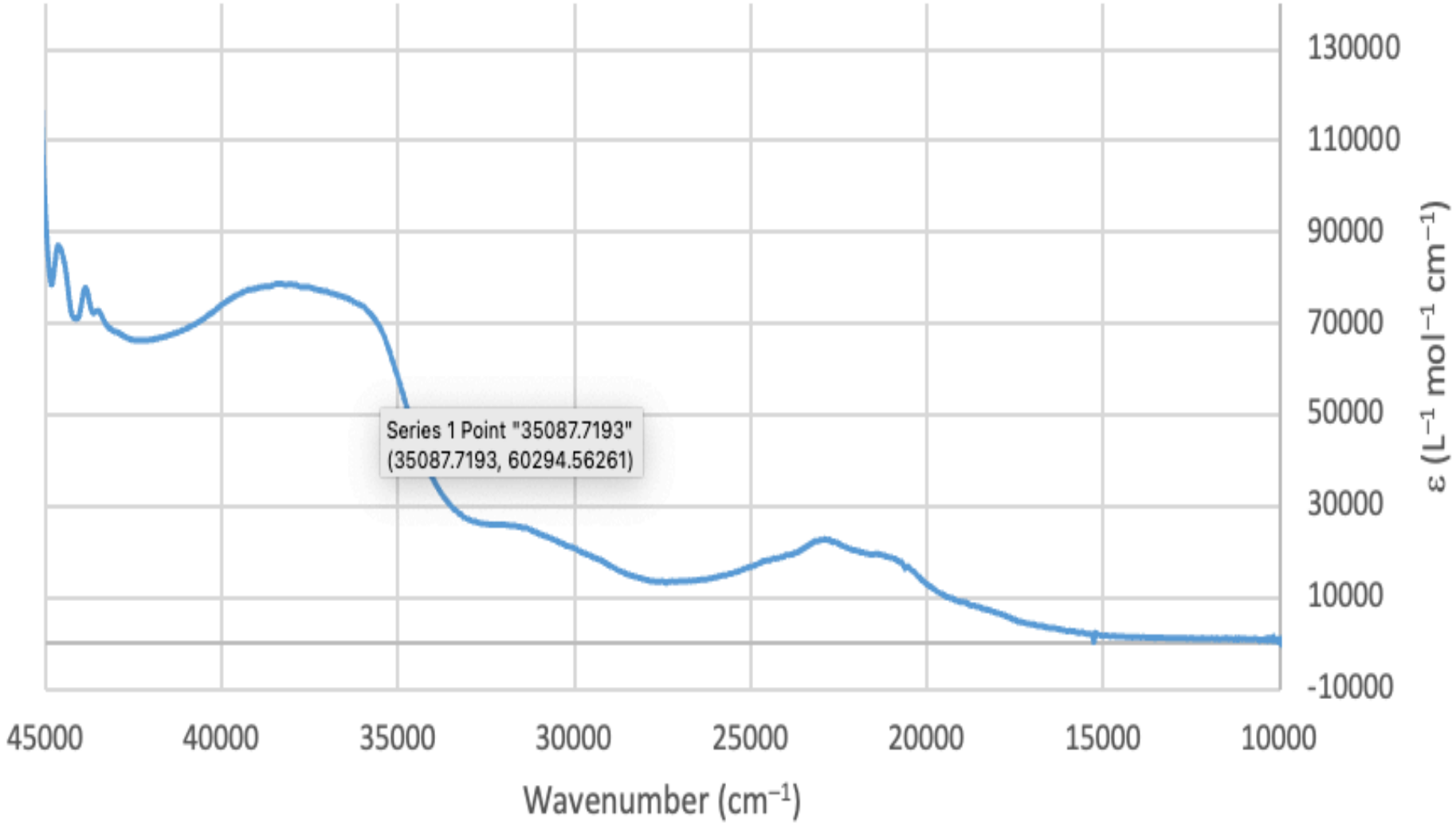

Figure S44. Electronic spectrum (CH_2Cl_2) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**4a**).

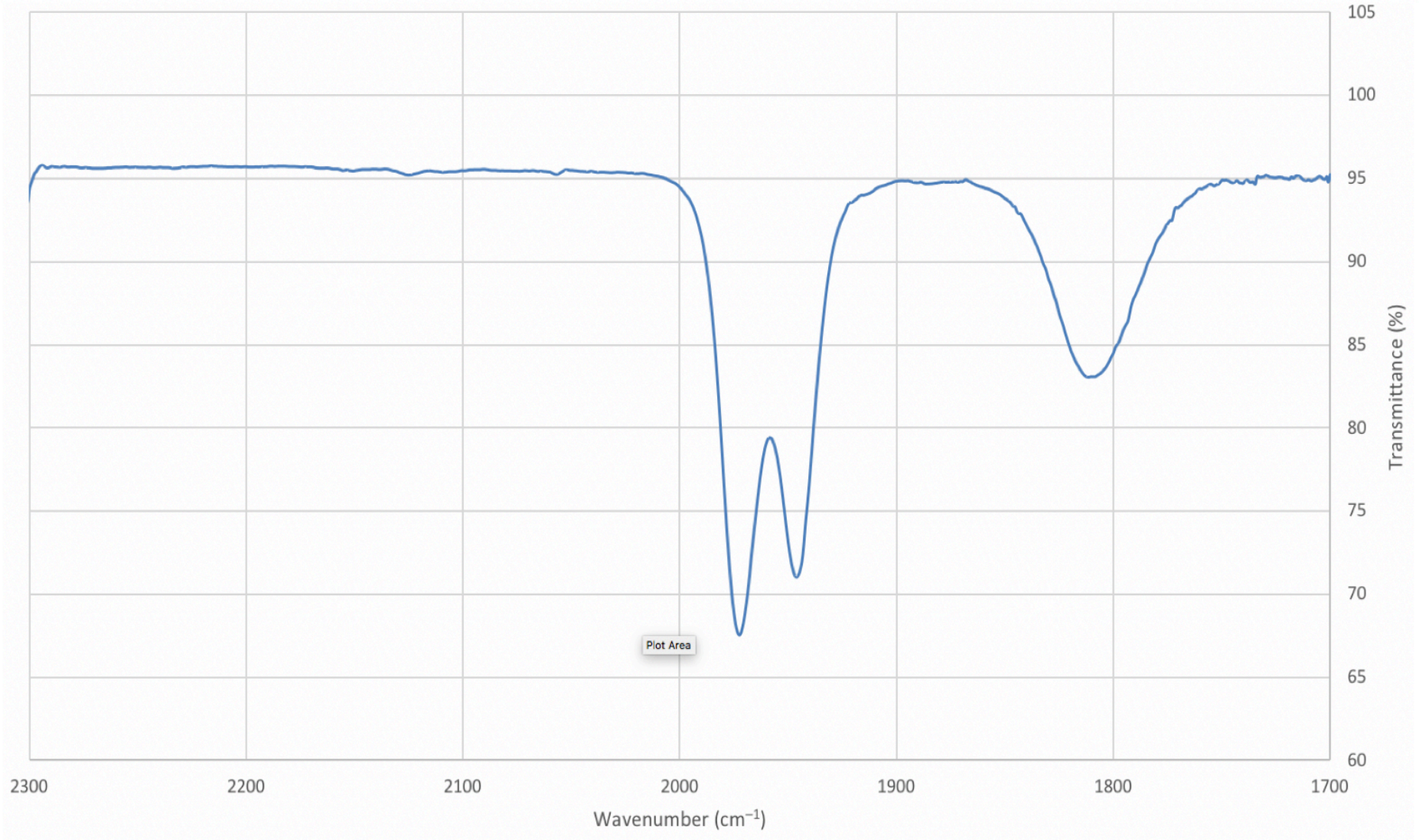

Figure S45. Infrared spectrum (CH_2Cl_2, cm^{-1}) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tp)_2]$ (**4a**).

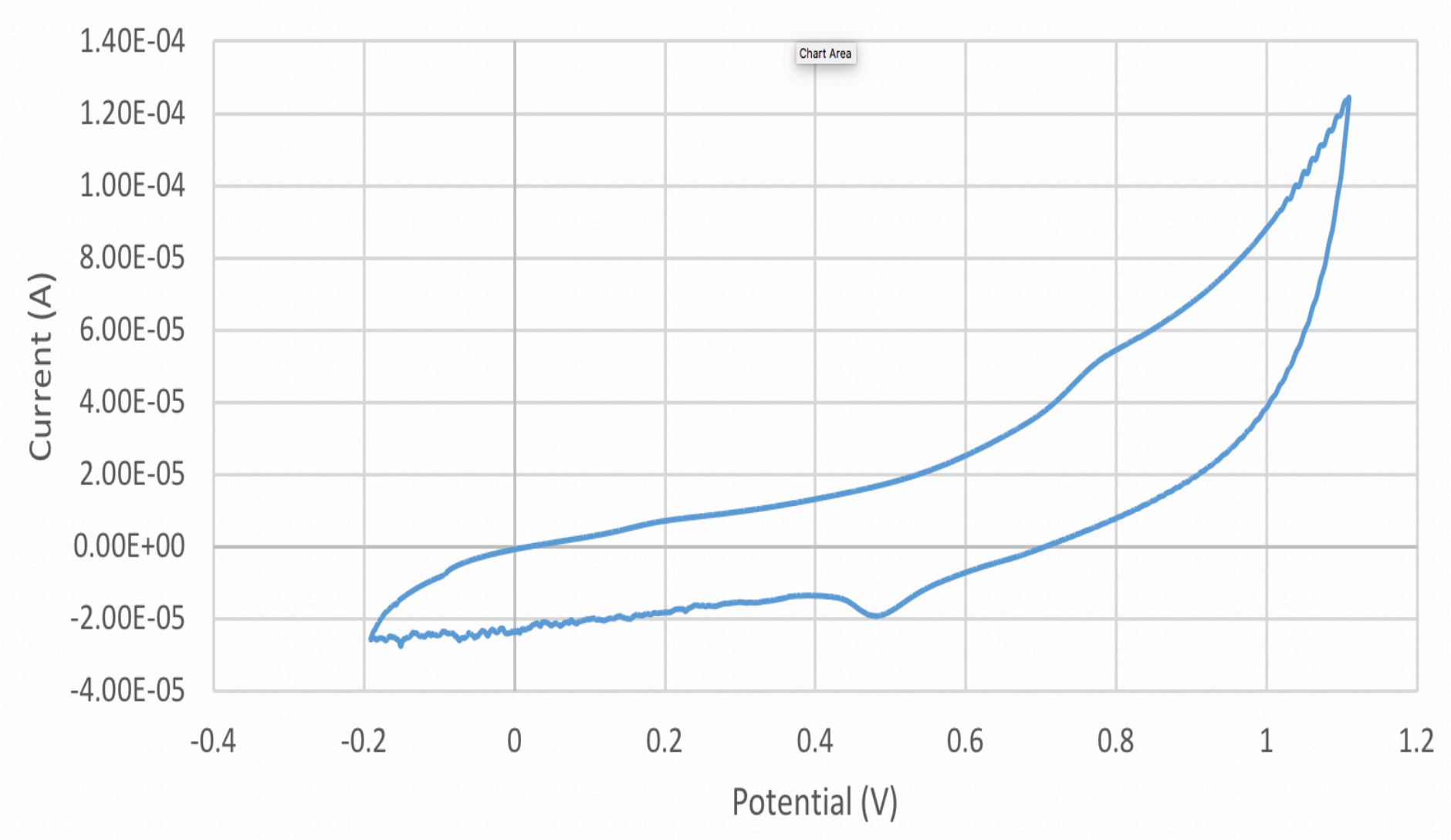

Figure S46. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [$W_2Pt\{\mu$-$CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2$] (**4b**).

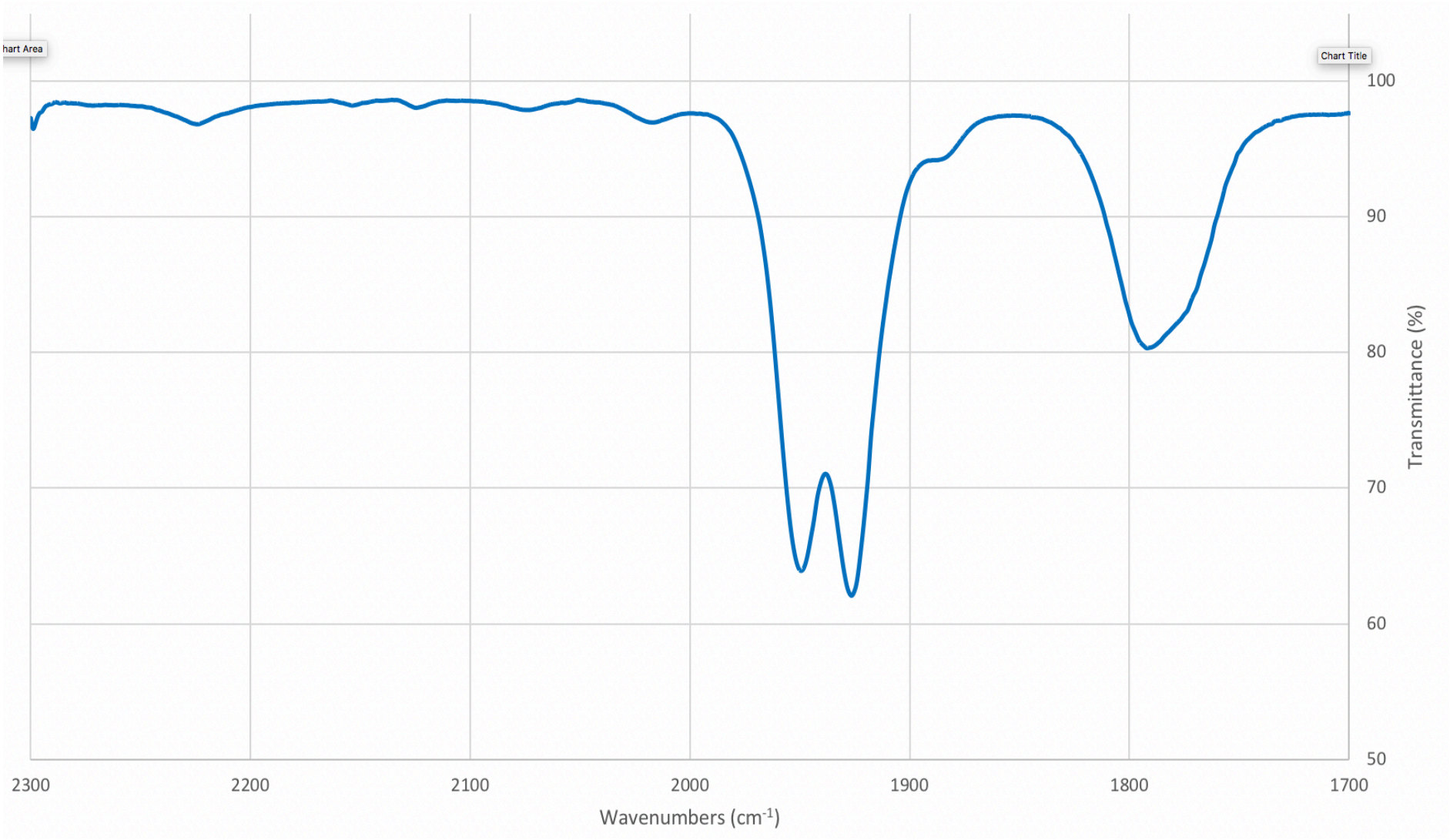

Figure S47. Infrared spectrum (CH_2Cl_2, cm^{-1}) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**4b**).

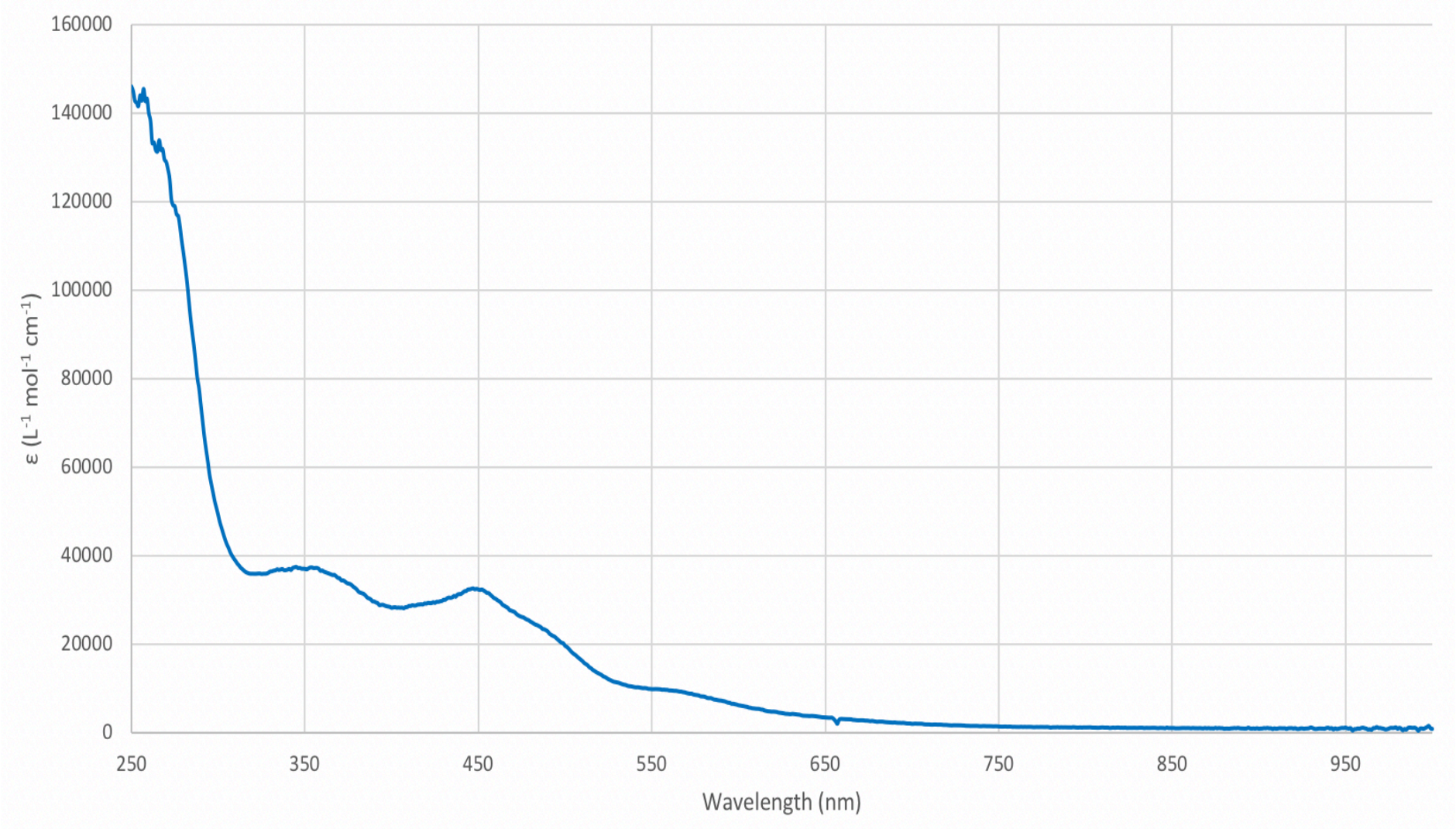

Figure S48a. Electronic spectrum (CH_2Cl_2) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**4b**).

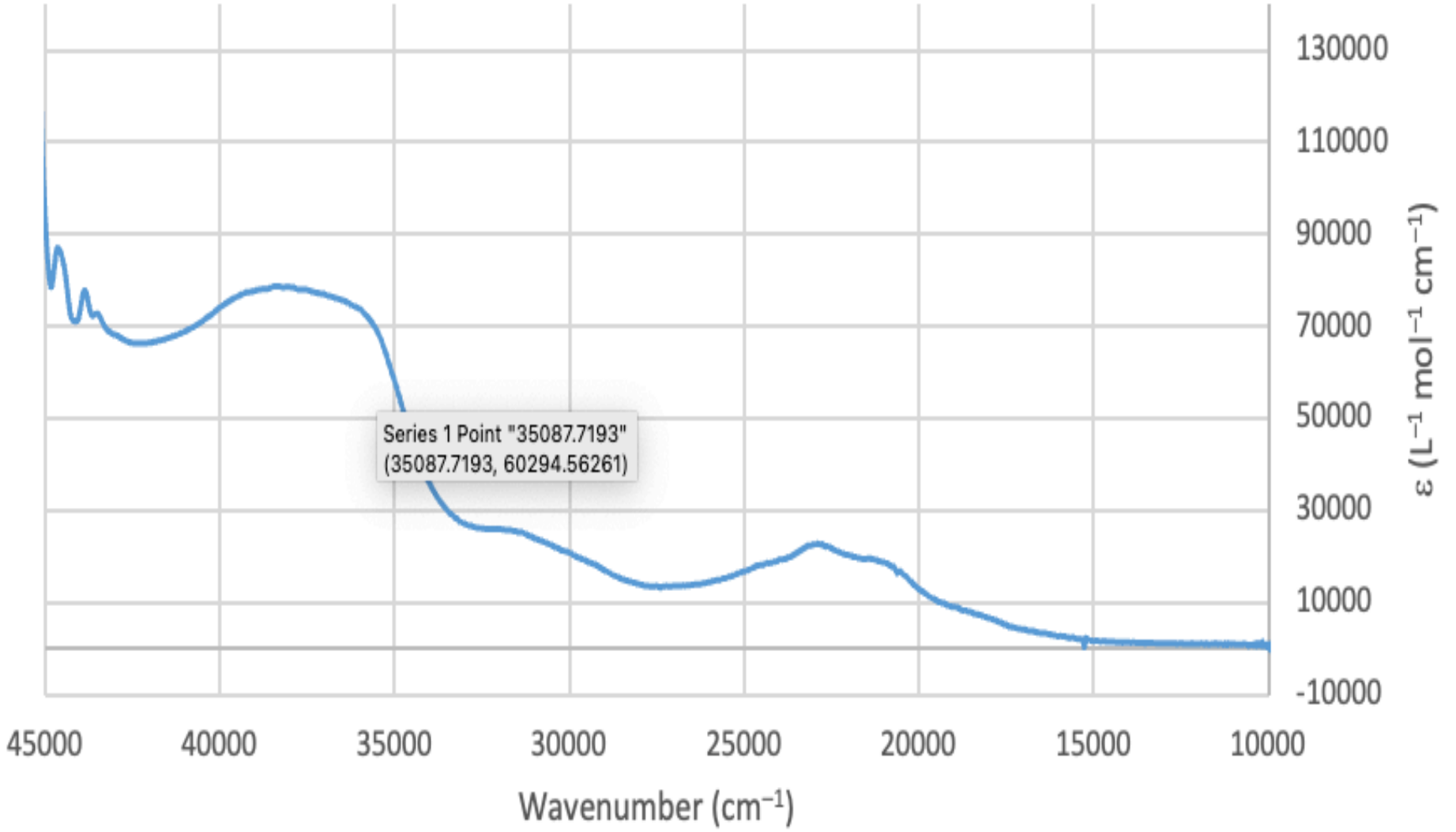

Figure S48b. Electronic spectrum (CH_2Cl_2) of $[W_2Pt\{\mu\text{-}CC(C_6H_4)_2CBr\}_2(CO)_4(Tm)_2]$ (**4b**).

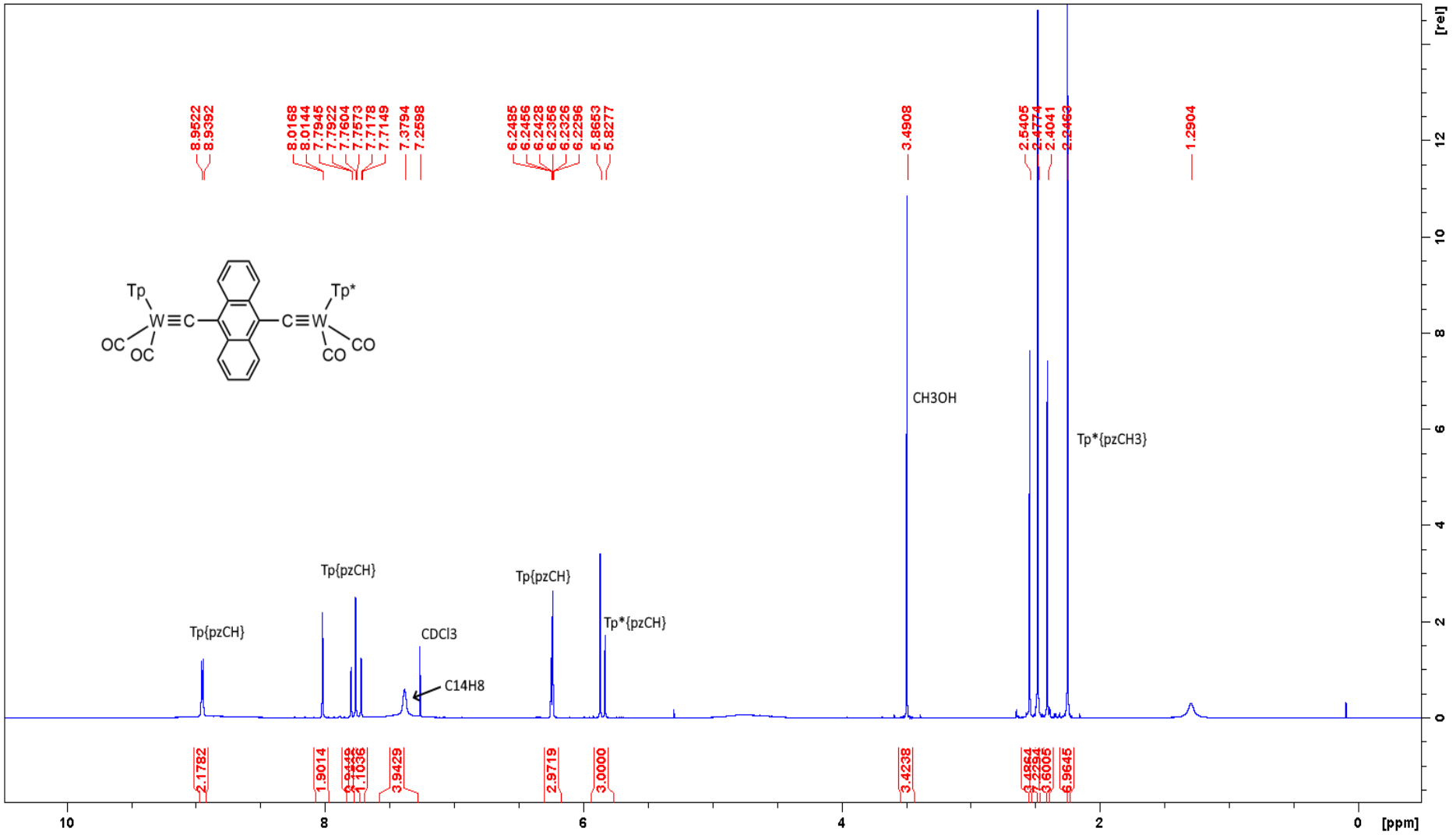

Figure S49. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of [(Tp)(CO)$_2$W{≡CC(C_6H_4)$_2$CC≡}W(CO)$_2$(Tp*)] (**5b**).

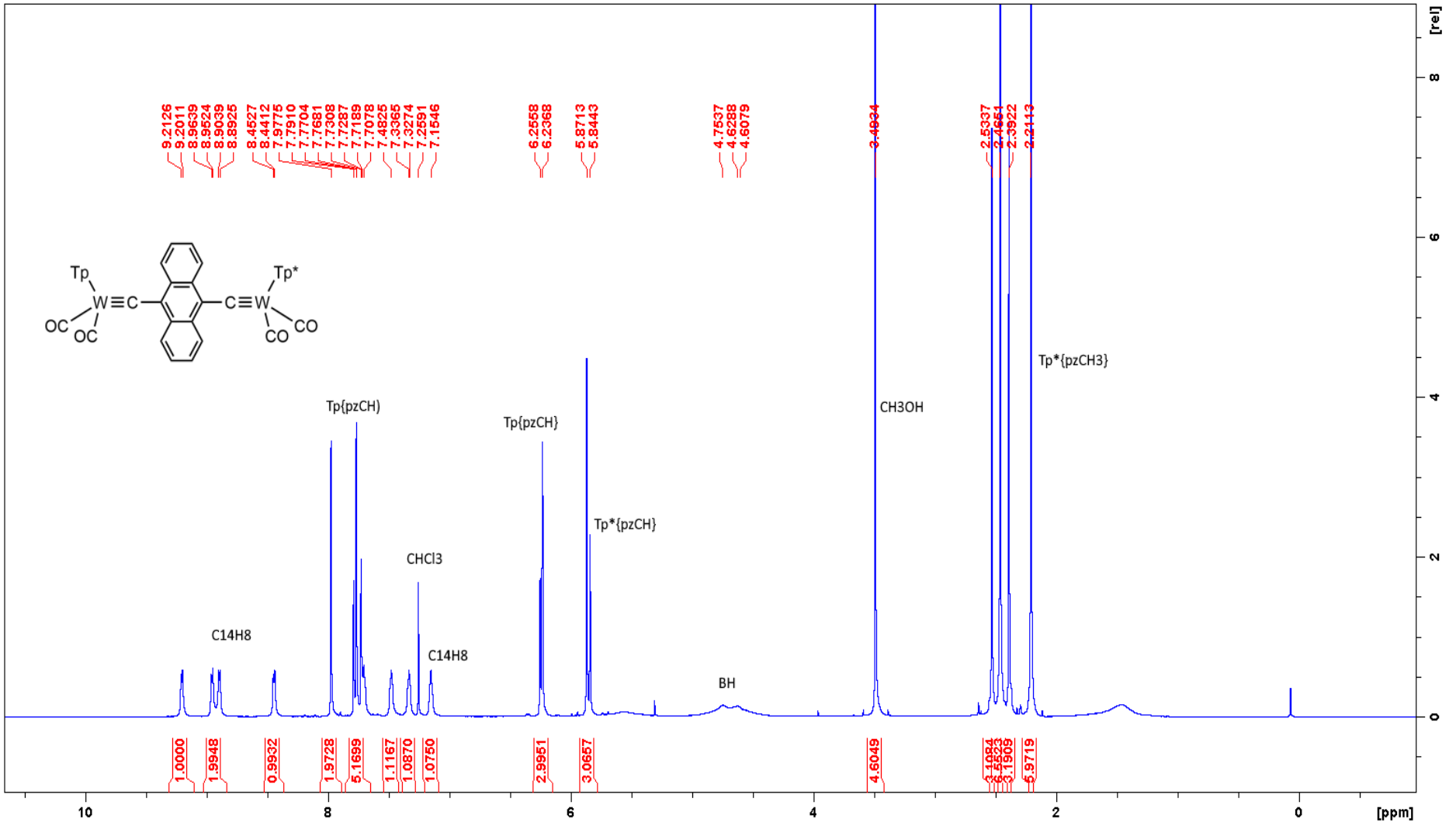

Figure S50. ^{1}H NMR (700 MHz, $CDCl_3$, –40 ˚C, δ) of [(Tp)(CO)$_2$W{≡CC(C_6H_4)$_2$CC≡}W(CO)$_2$(Tp*)] (**5b**).

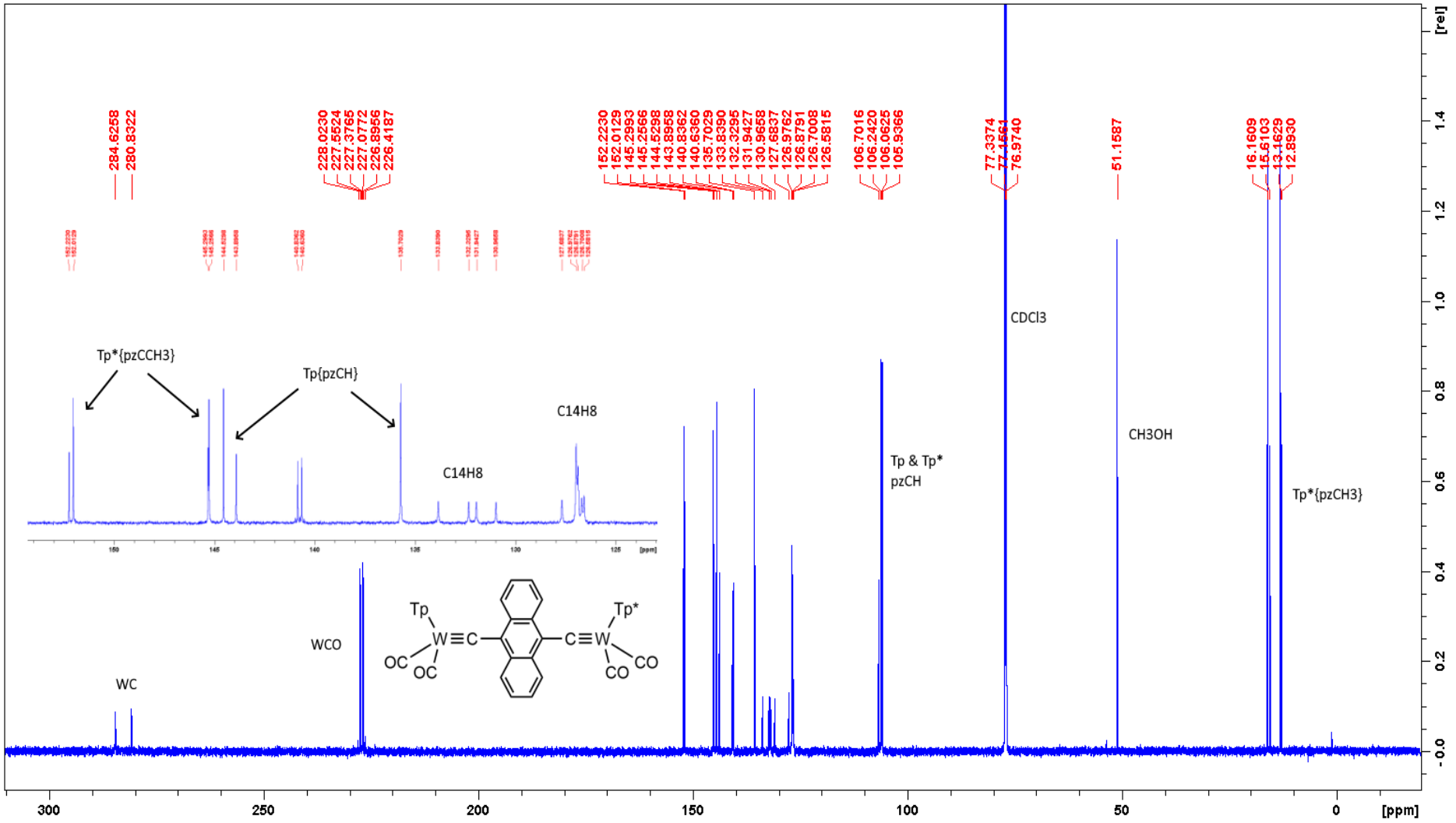

Figure S51. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, –40 ˚C, δ) of $[(Tp)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}W(CO)_2(Tp^*)]$ (**5b**).

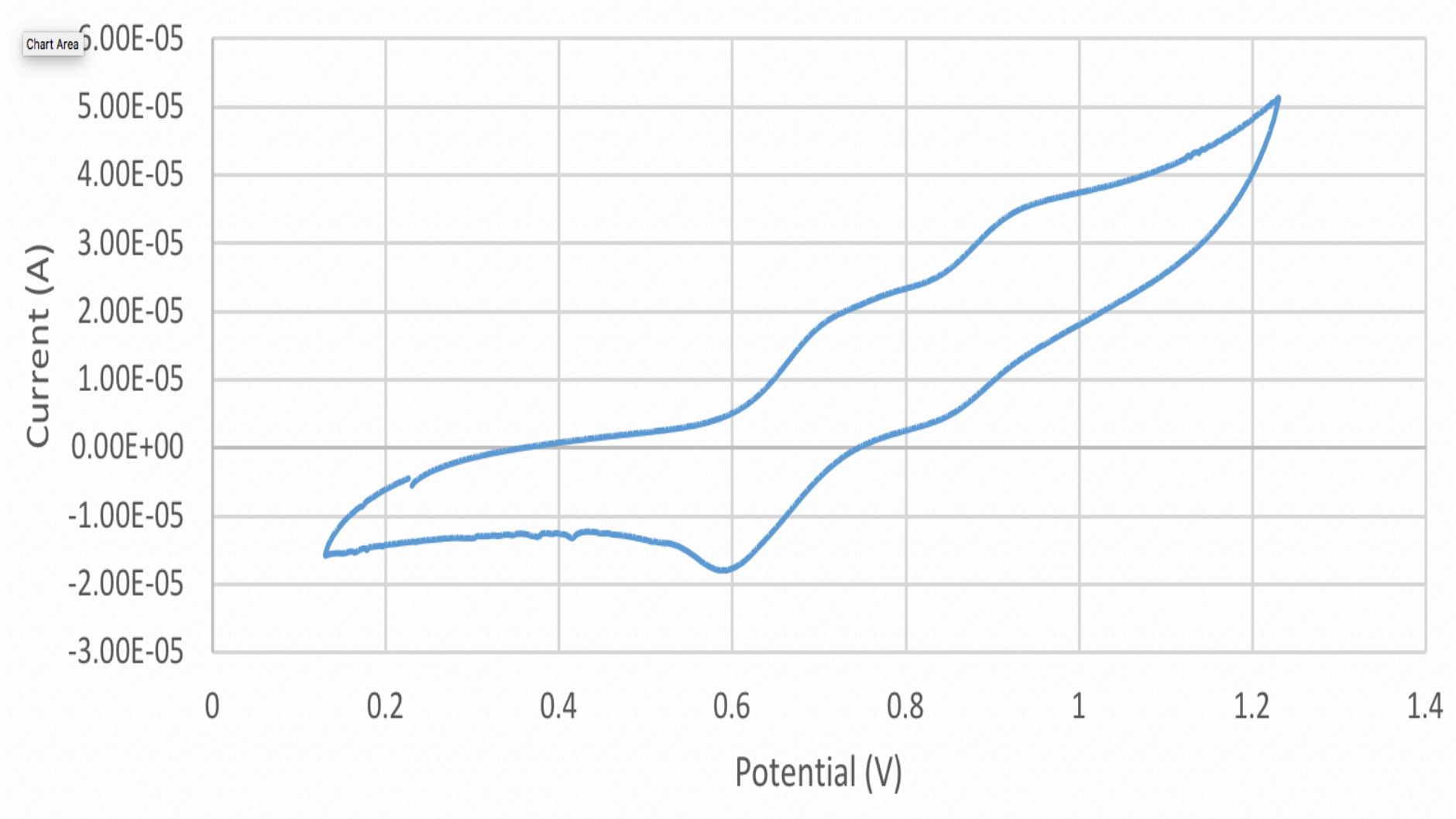

Figure S52. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [(Tp)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5b**).

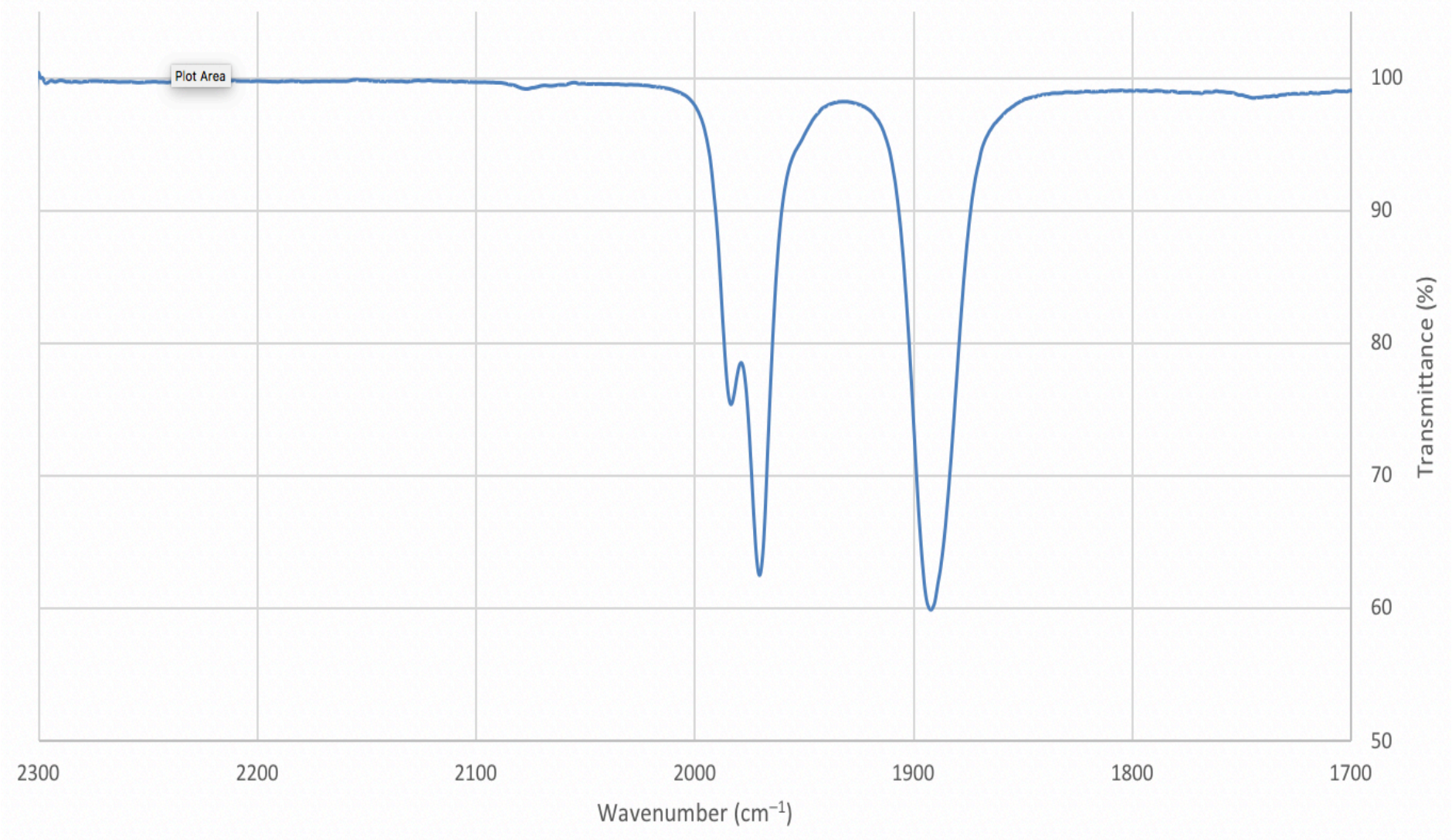

Figure 53. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [(Tp)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5b**).

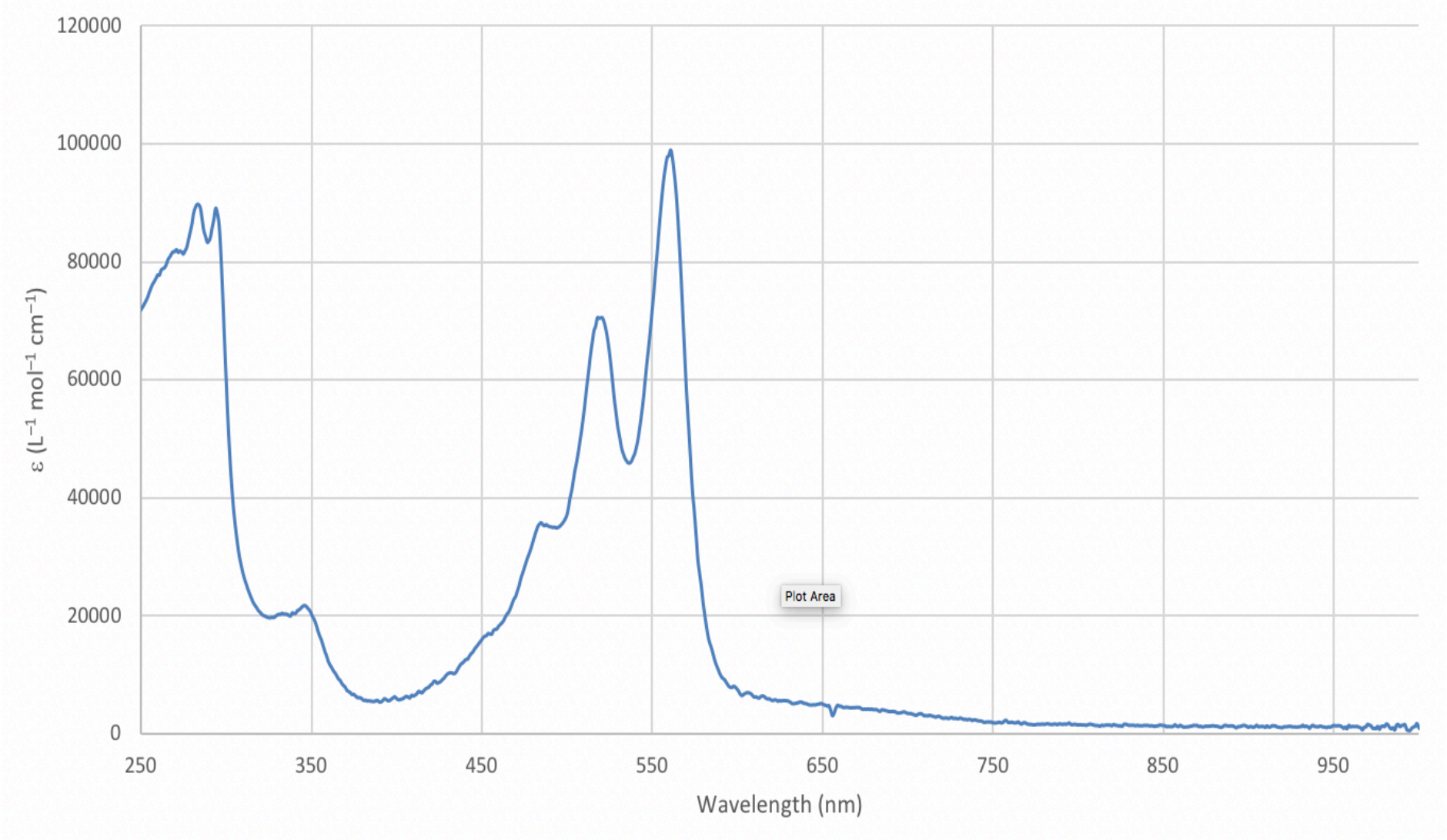

Figure S54a. Electronic spectrum (CH_2Cl_2) of [(Tp)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5b**).

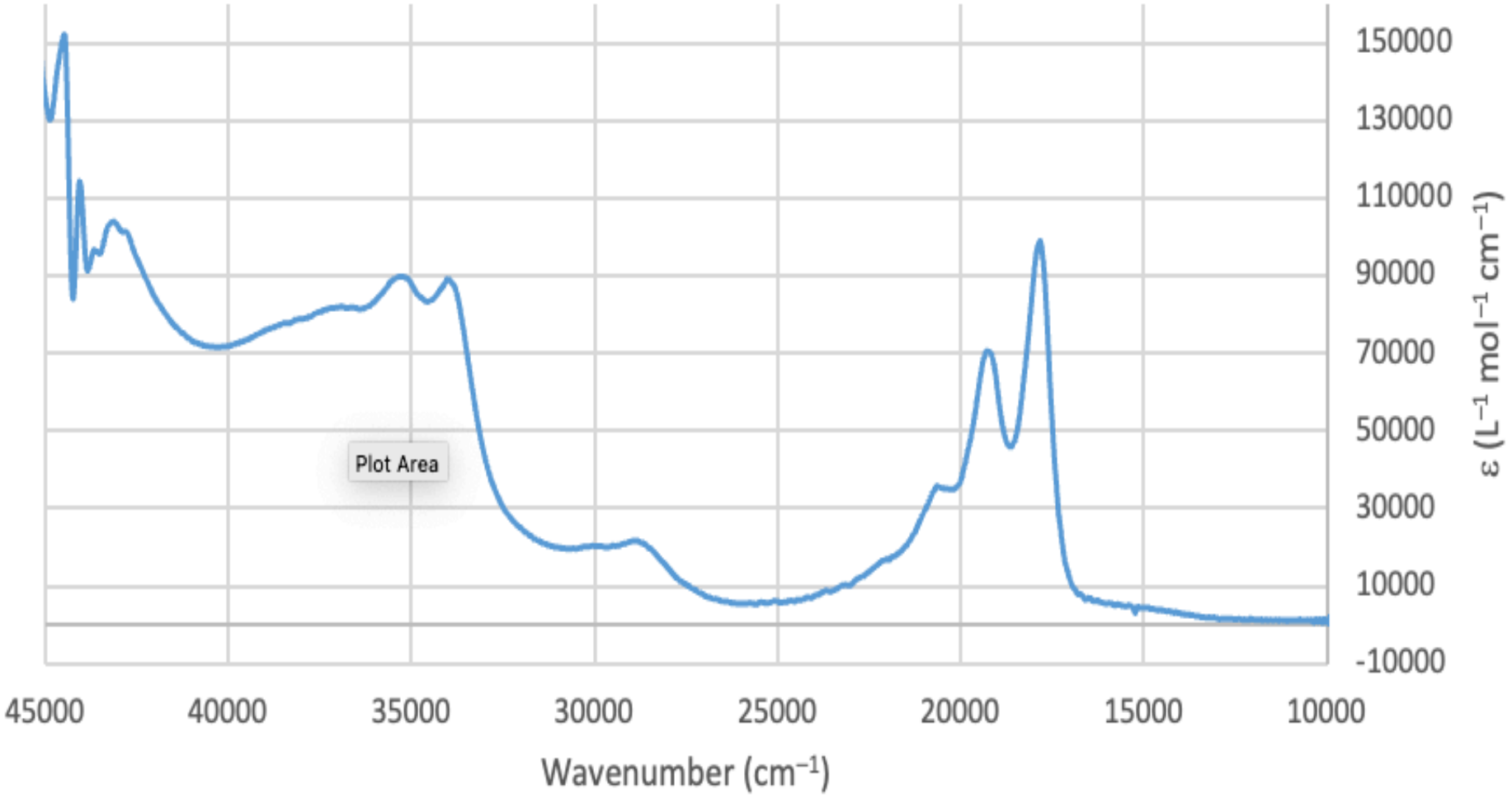

Figure S54. Electronic spectrum (CH_2Cl_2) of [(Tp)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5b**).

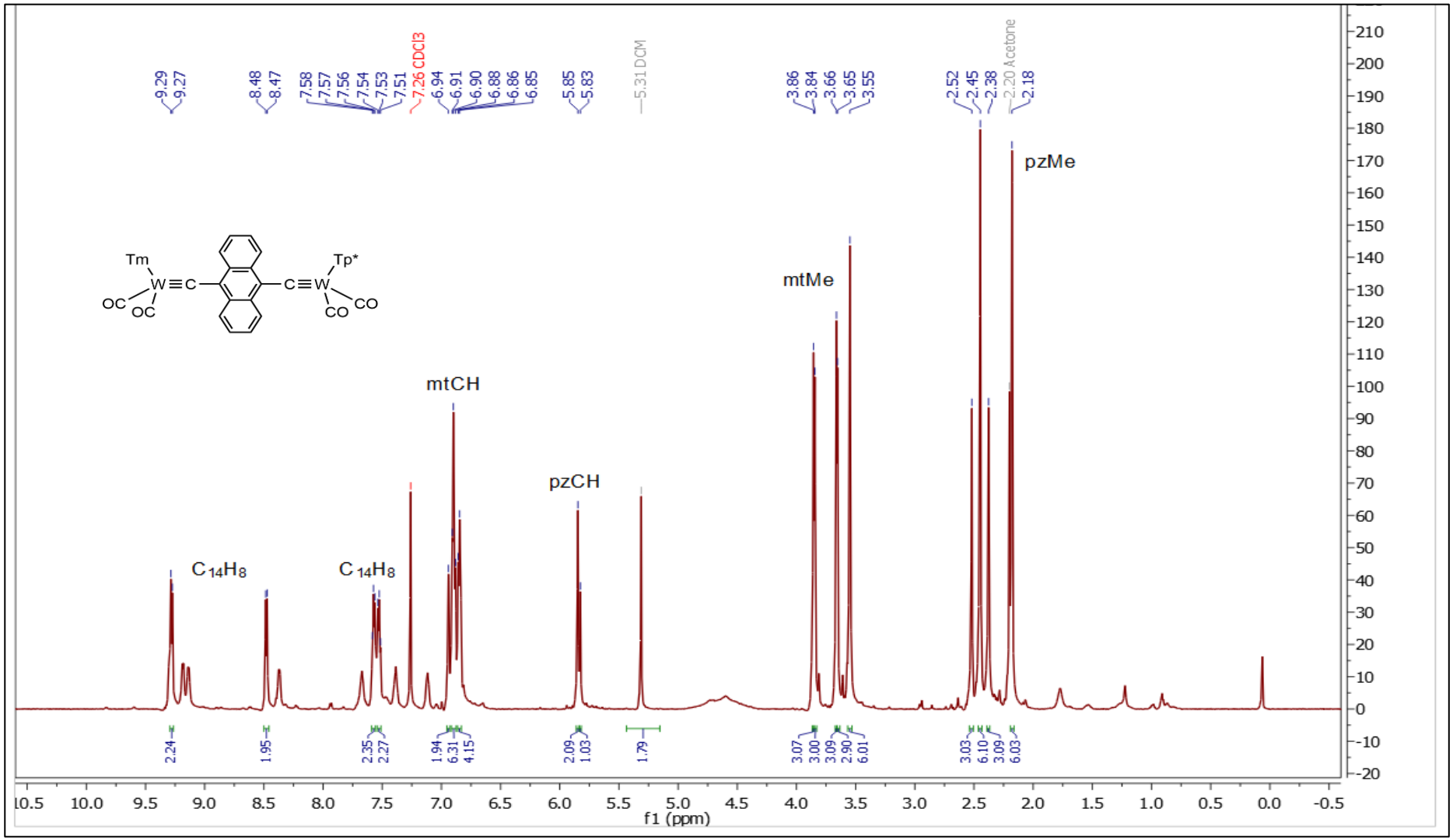

Figure S55. ^{1}H NMR (700 MHz, $CDCl_3$, -20 ˚C, δ) of $[(Tm)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}W(CO)_2(Tp^*)]$ (**5c**).

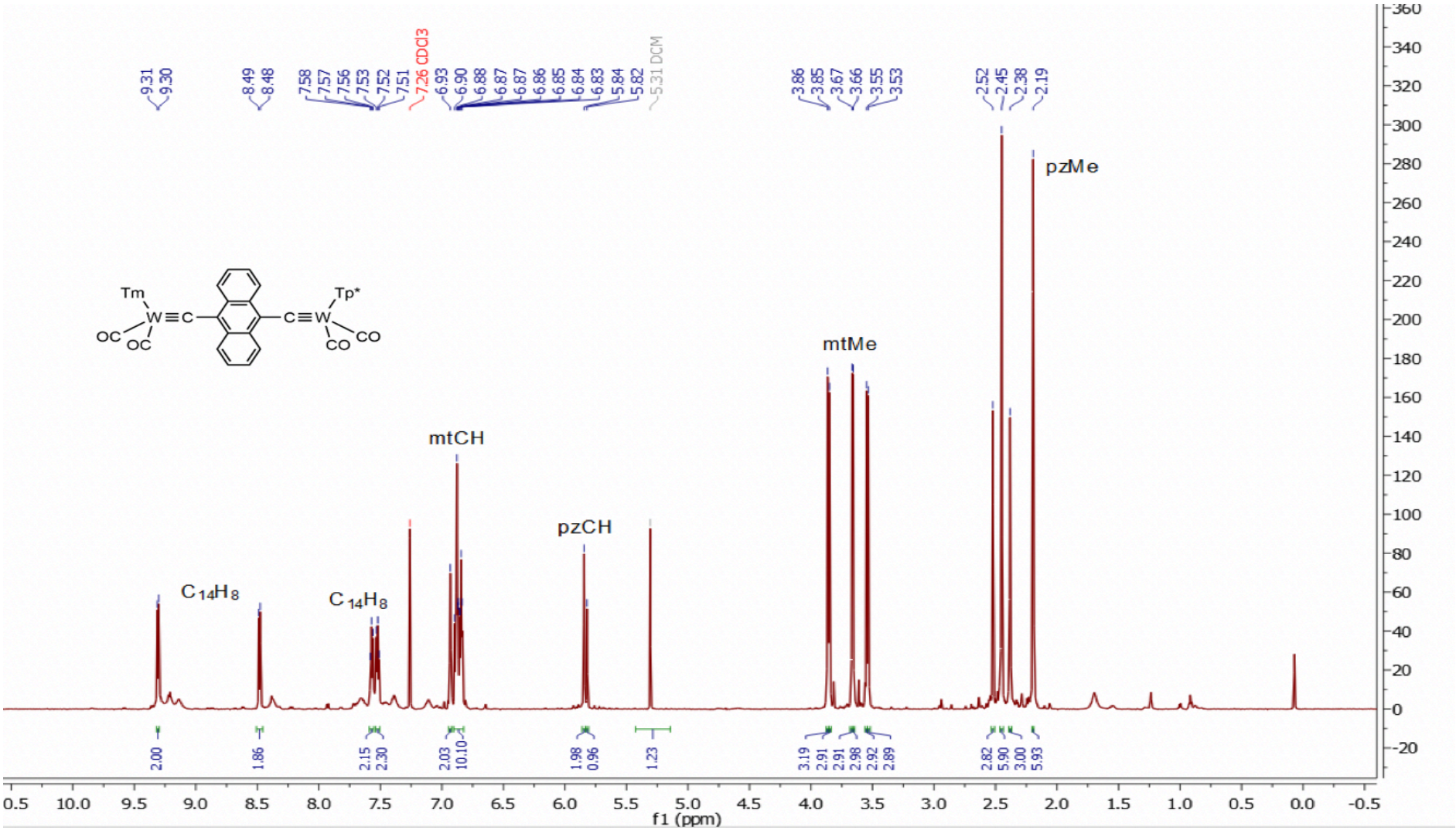

Figure S56. ^{1}H NMR (700 MHz, $CDCl_3$, –40 ˚C, δ) of [(Tm)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5c**).

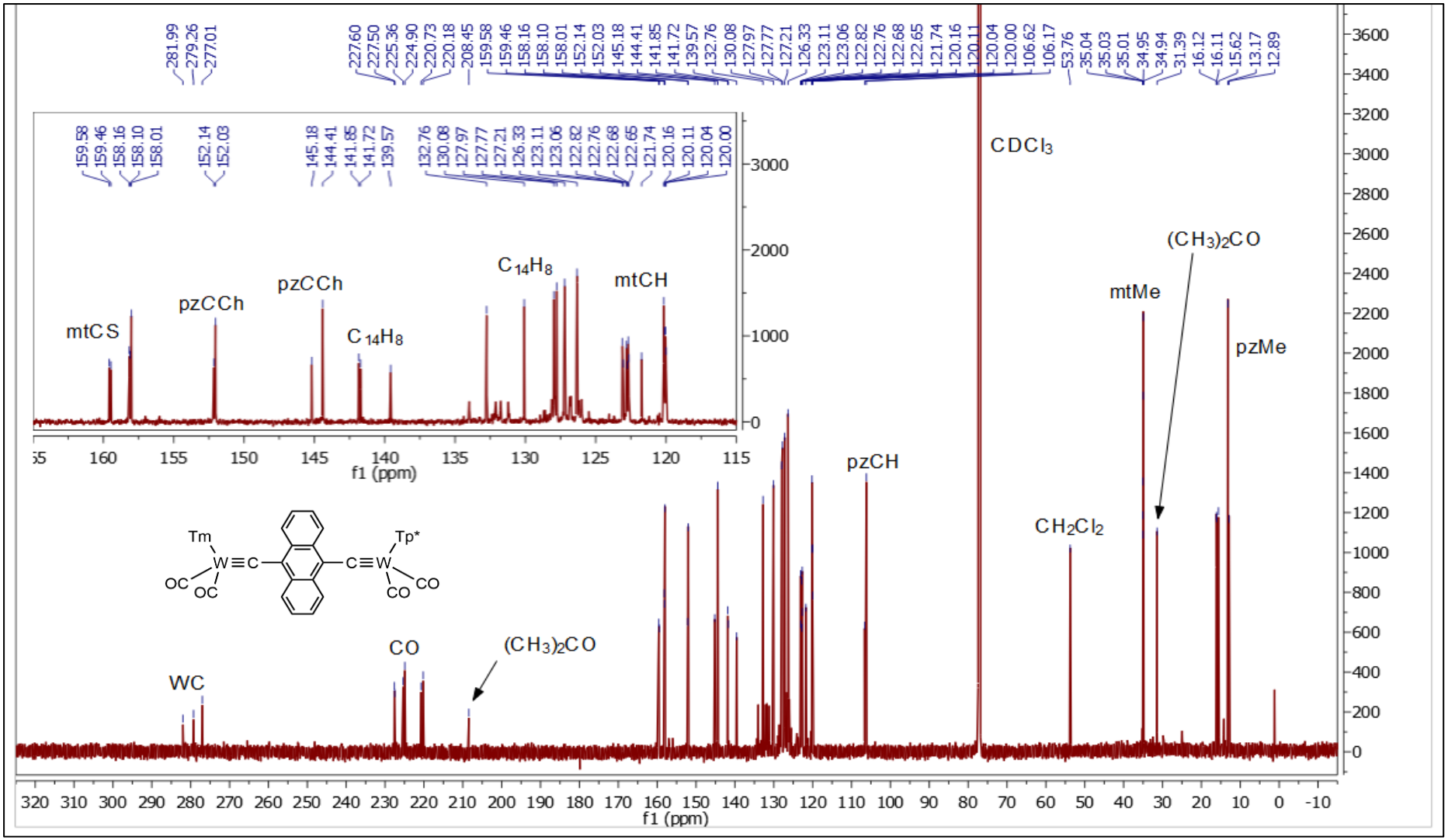

Figure S57. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, –40 ˚C, δ) of $[(Tm)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}W(CO)_2(Tp^*)]$ (**5c**).

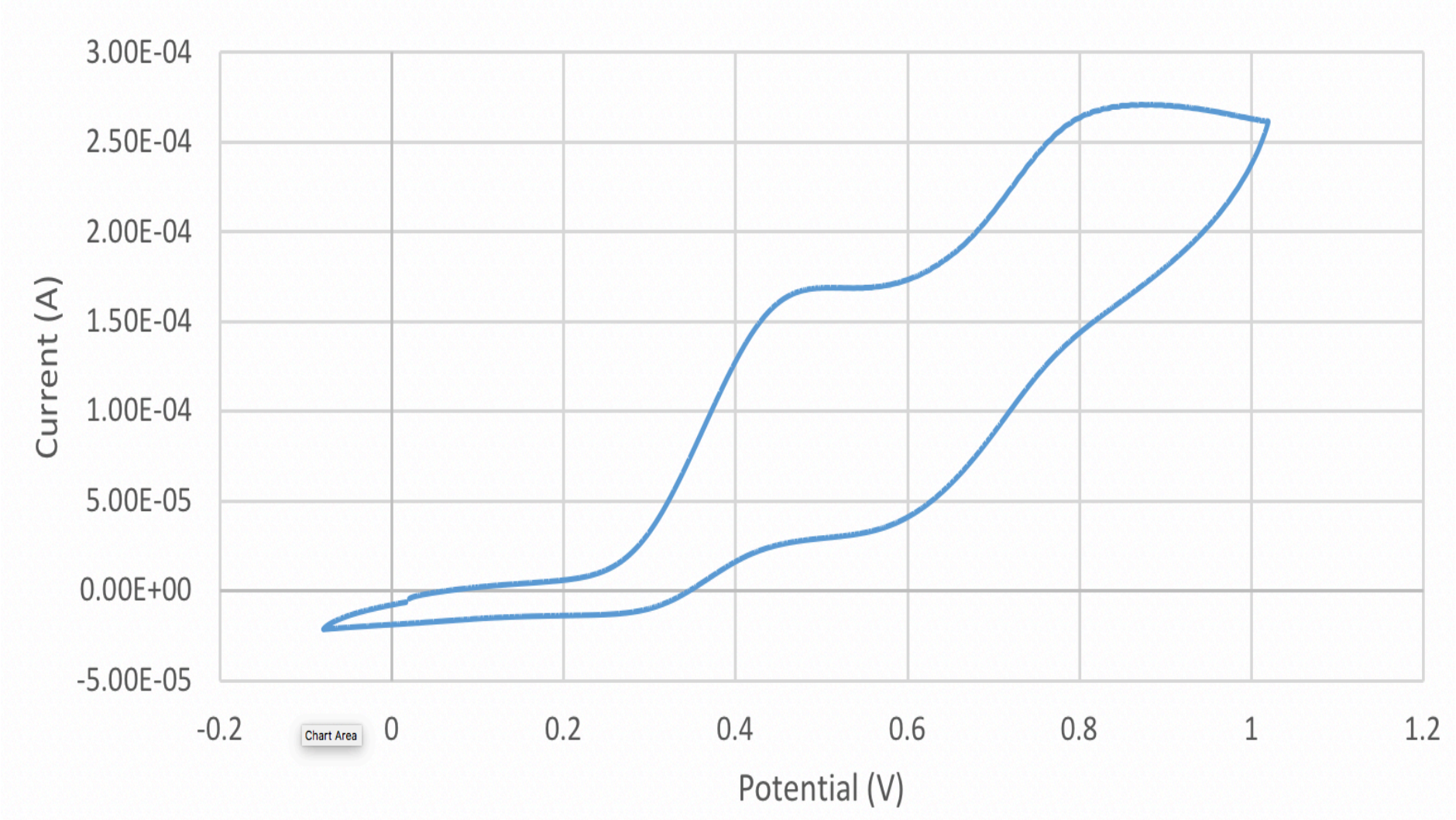

Figure S58. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [(Tm)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5c**).

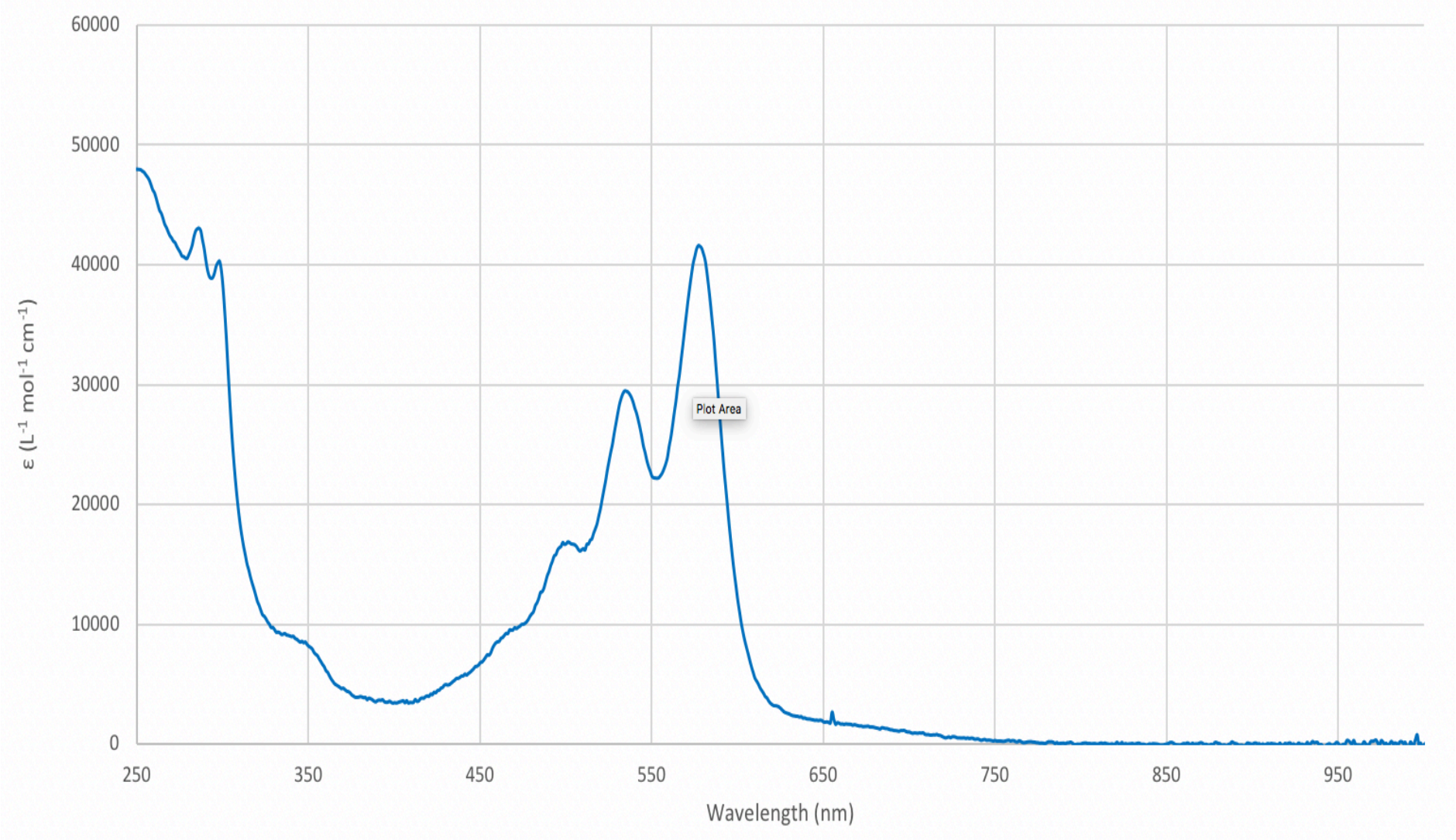

Figure S59a. Electronic spectrum (CH_2Cl_2) of [(Tm)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5c**).

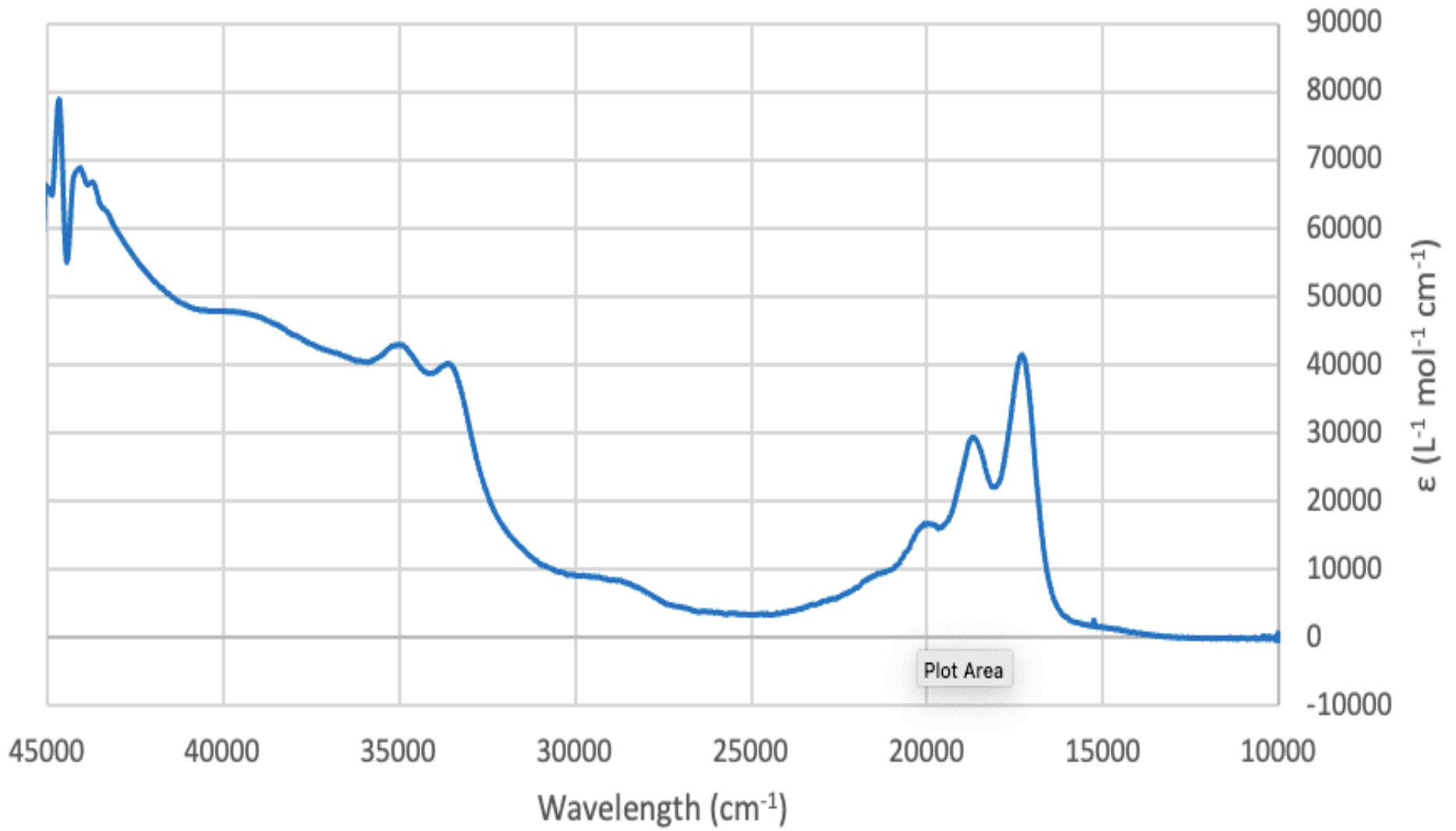

Figure S59b. Electronic spectrum (CH_2Cl_2) of [(Tm)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5c**).

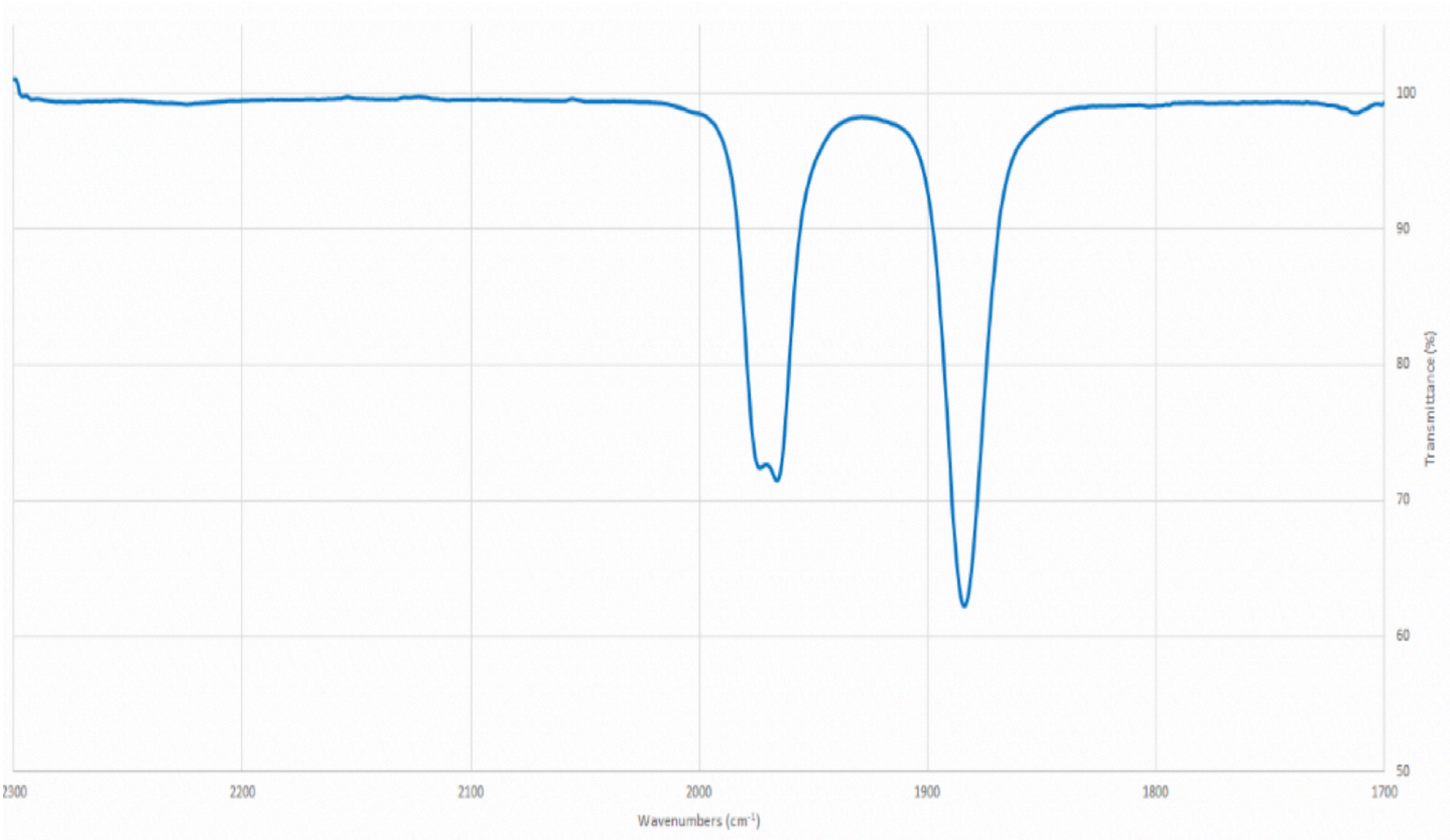

Figure S60. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [(Tm)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}W$(CO)_2$(Tp*)] (**5c**).

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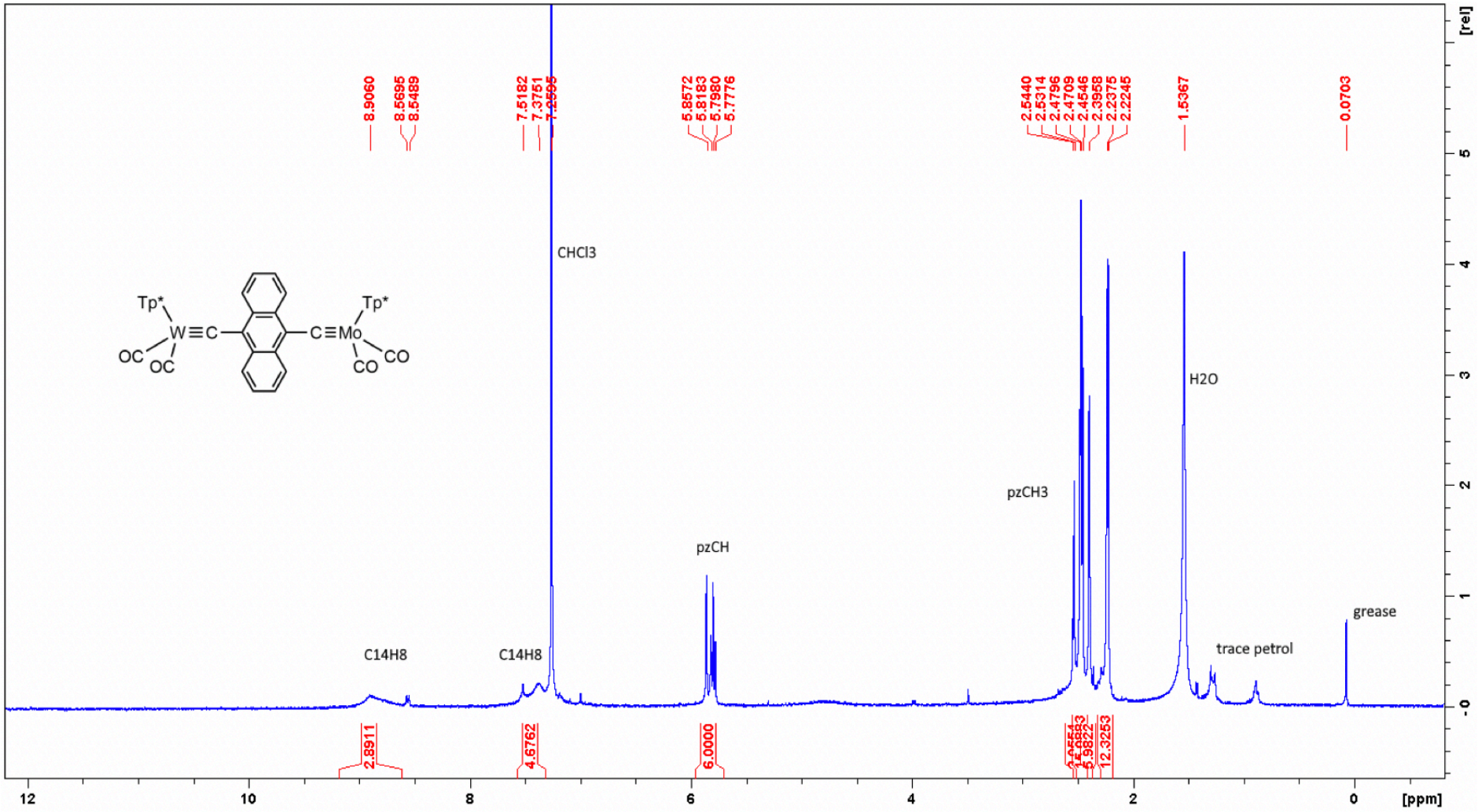

Figure 61. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C, δ) of [(Tp*)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6a**).

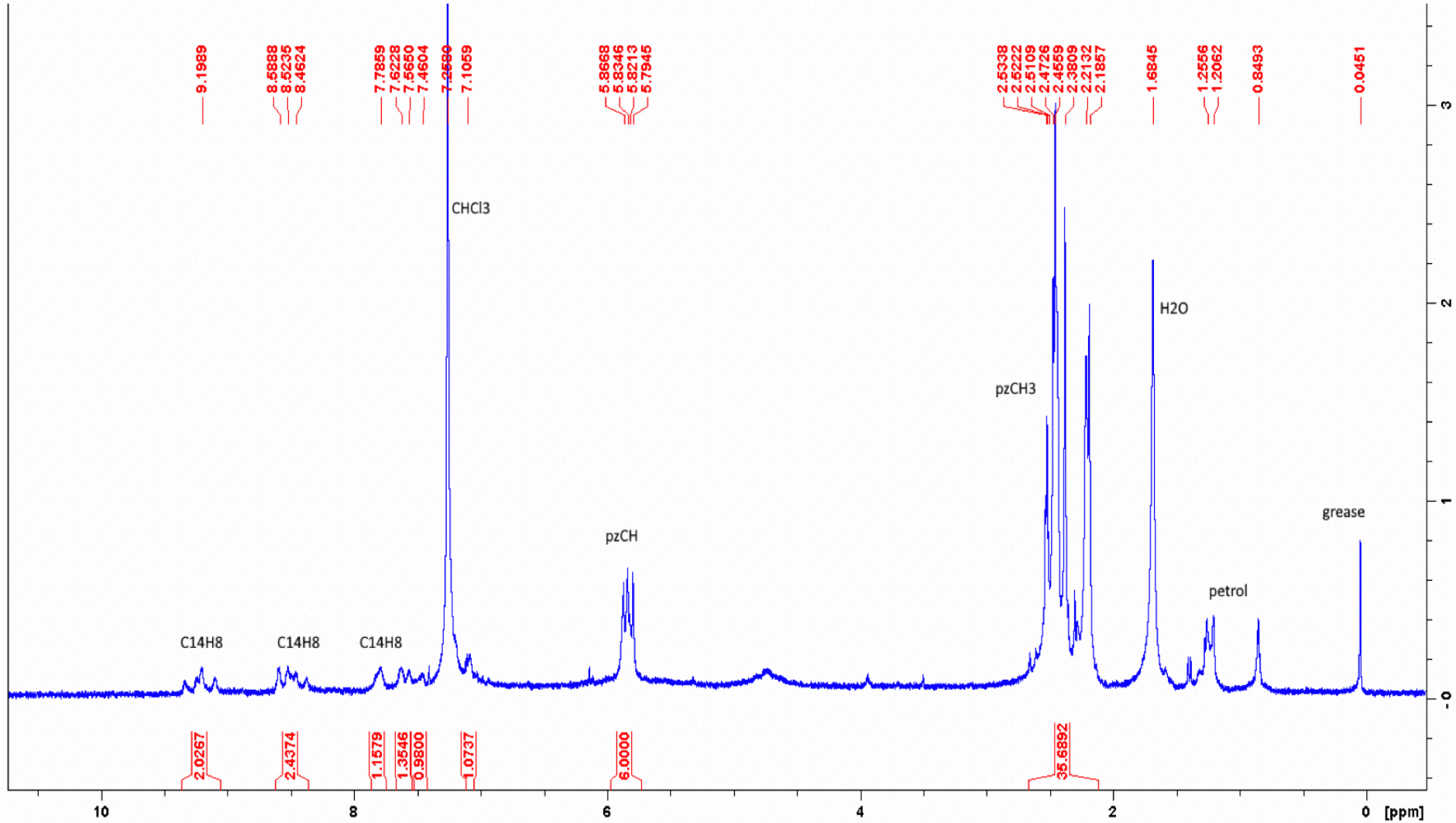

Figure 62. ^{1}H NMR (700 MHz, $CDCl_3$, -50 ˚C, δ) of [(Tp*)(CO)$_2$W{≡CC(C$_6$H$_4$)$_2$CC≡}Mo(CO)$_2$(Tp*)] (**6a**). Poor date due to onset of crystallization.

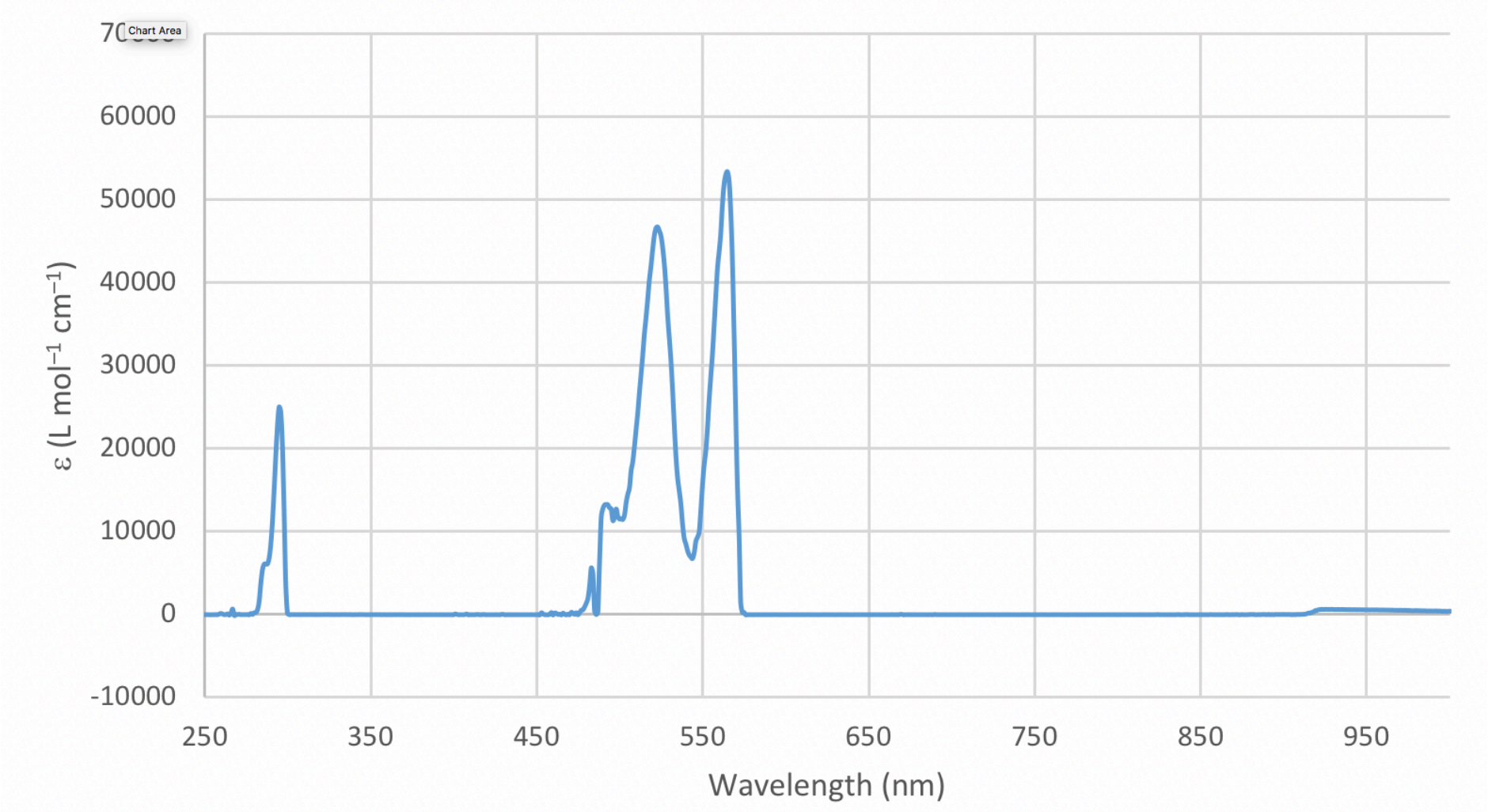

Figure S63a. Electronic spectrum (CH_2Cl_2, cm^{-1}) of [(Tp*)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6a**). Poor data quality due to extremely low solubility.

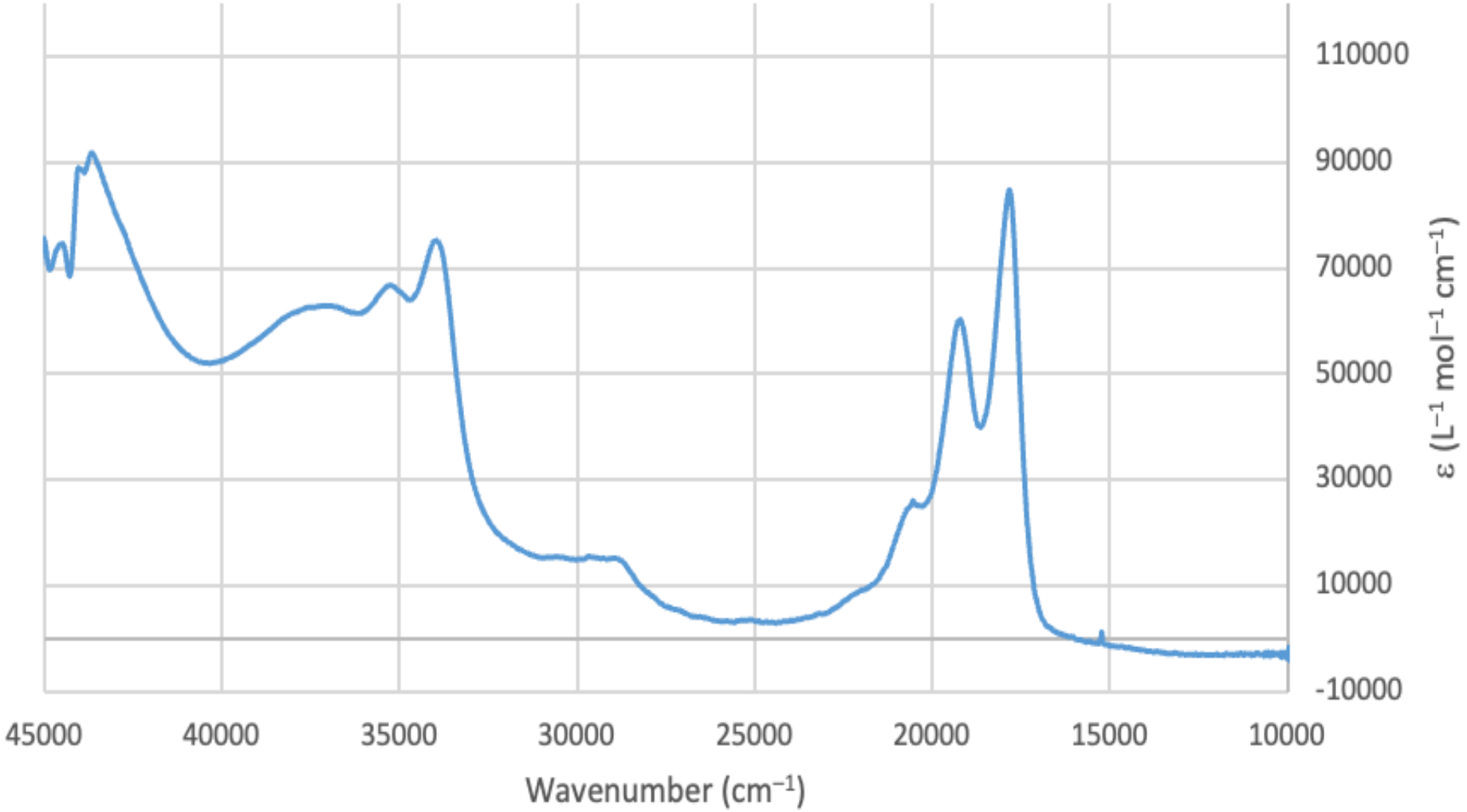

Figure S63b. Electronic spectrum (CH_2Cl_2, cm^{-1}) of [(Tp*)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6a**).

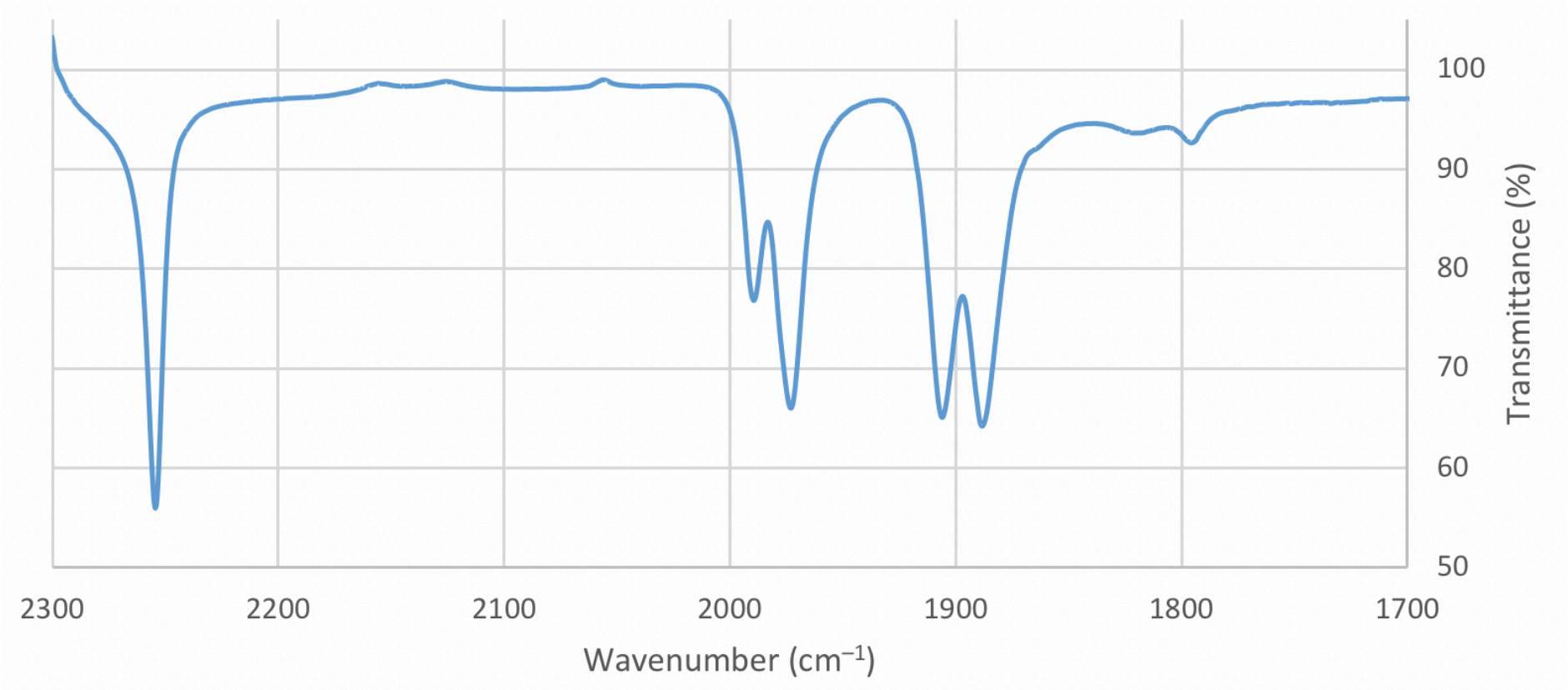

Figure S64. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [(Tp*)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6a**).

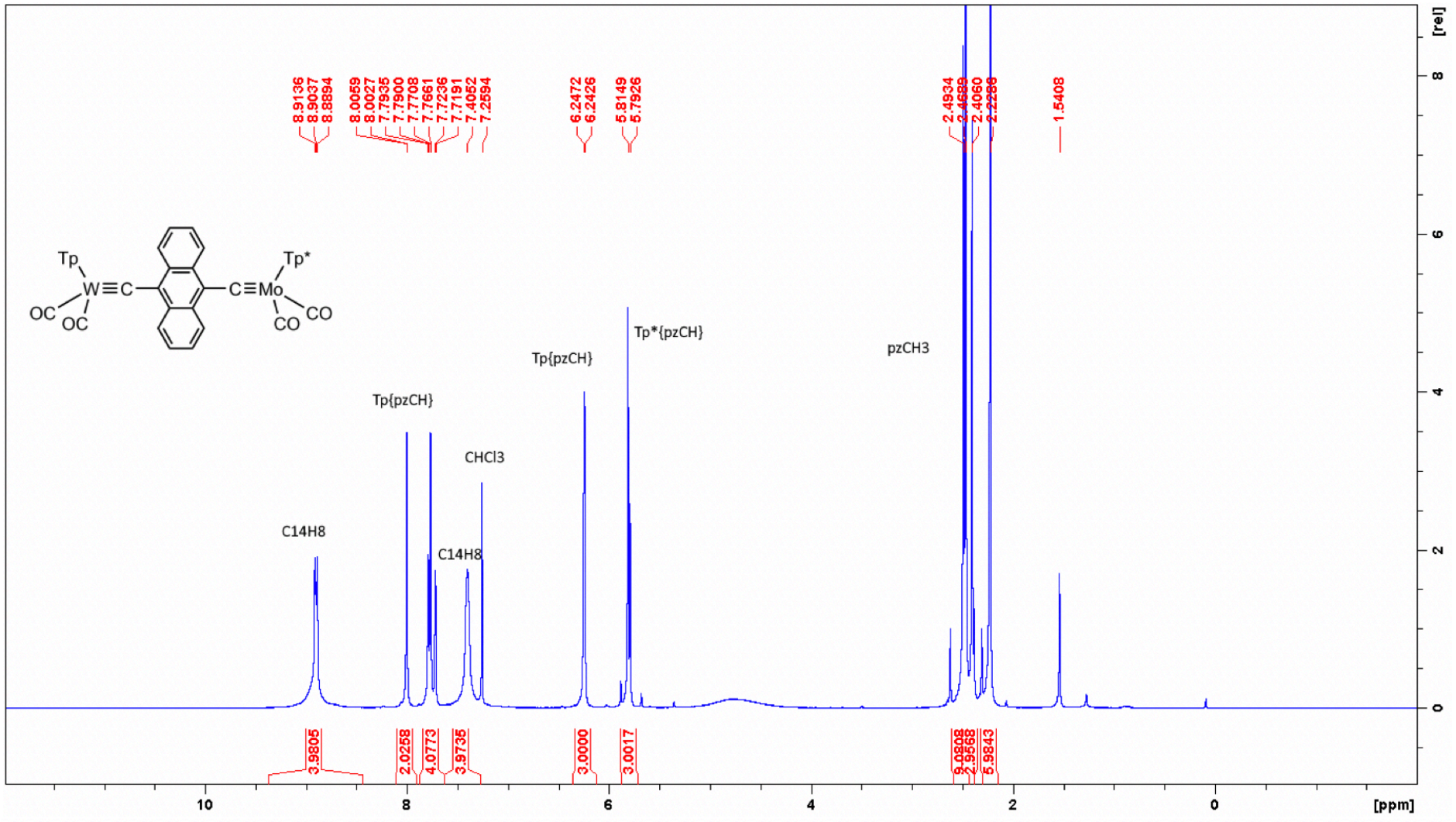

Figure S65. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of $[(Tp)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}Mo(CO)_2(Tp^*)]$ (**6b**).

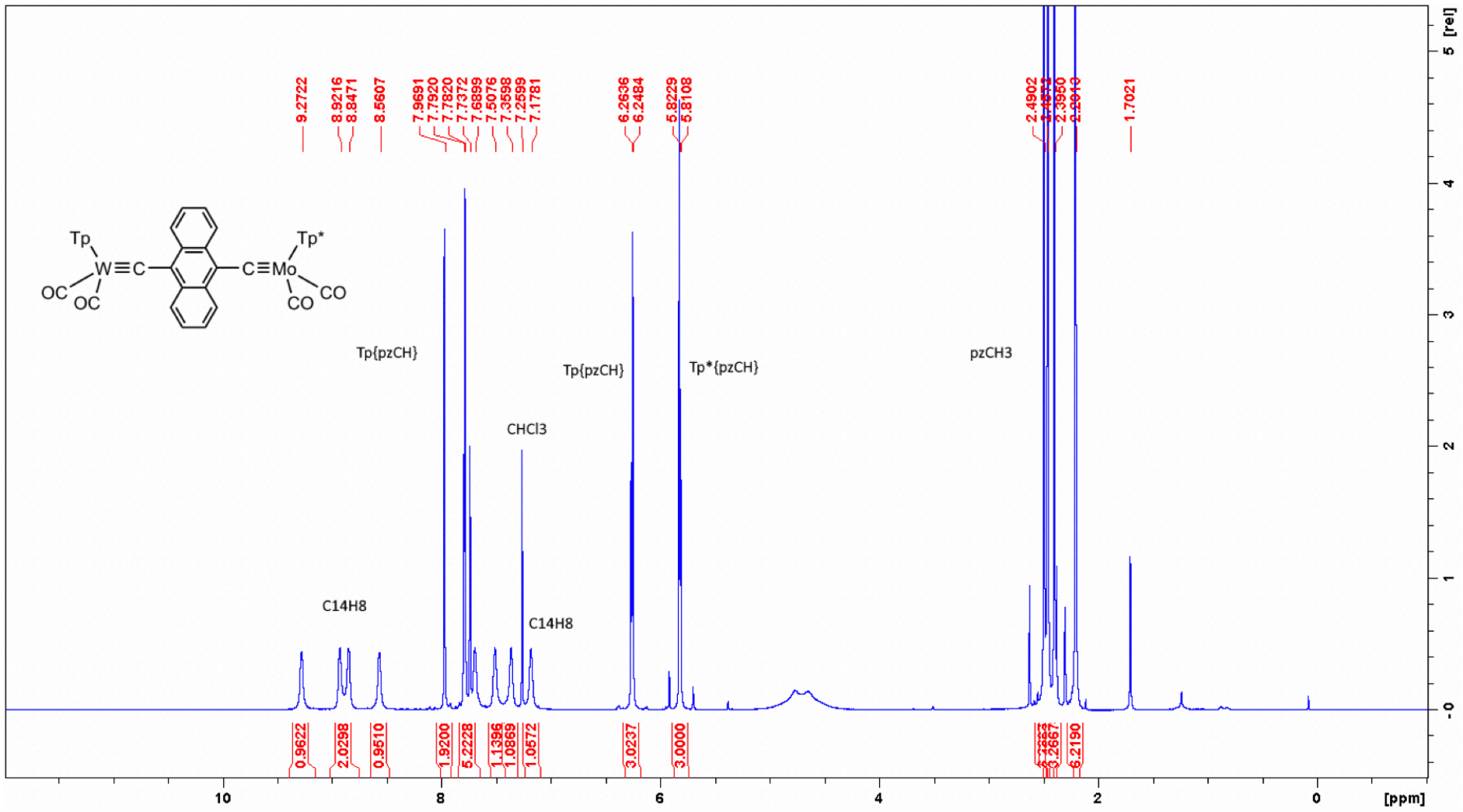

Figure S66. ^{1}H NMR (700 MHz, $CDCl_3$, -40 ˚C, δ) of $[(Tp)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}Mo(CO)_2(Tp^*)]$ (**6b**).

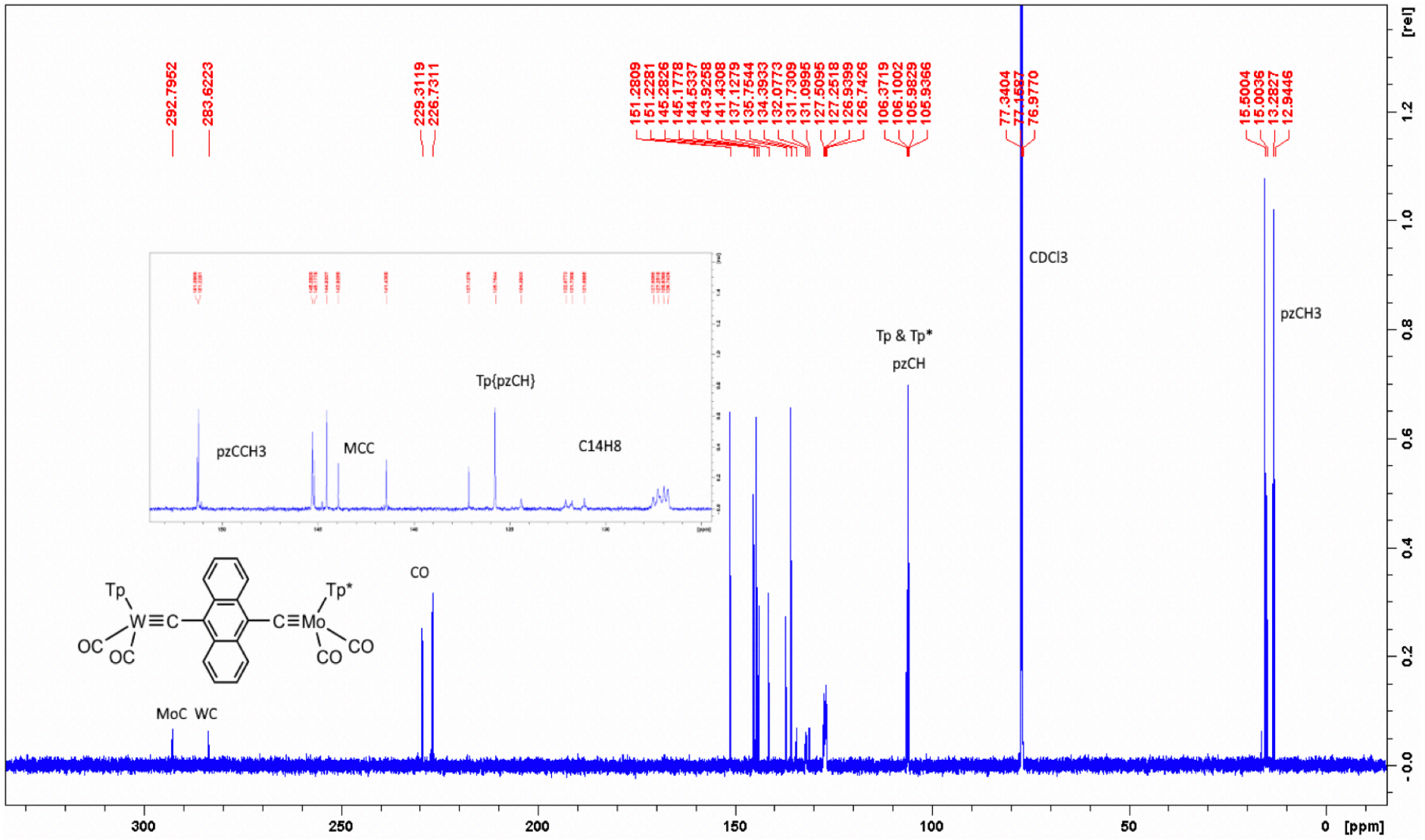

Figure S67. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, -40 ˚C, δ) of $[(Tp)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}Mo(CO)_2(Tp^*)]$ (**6b**).

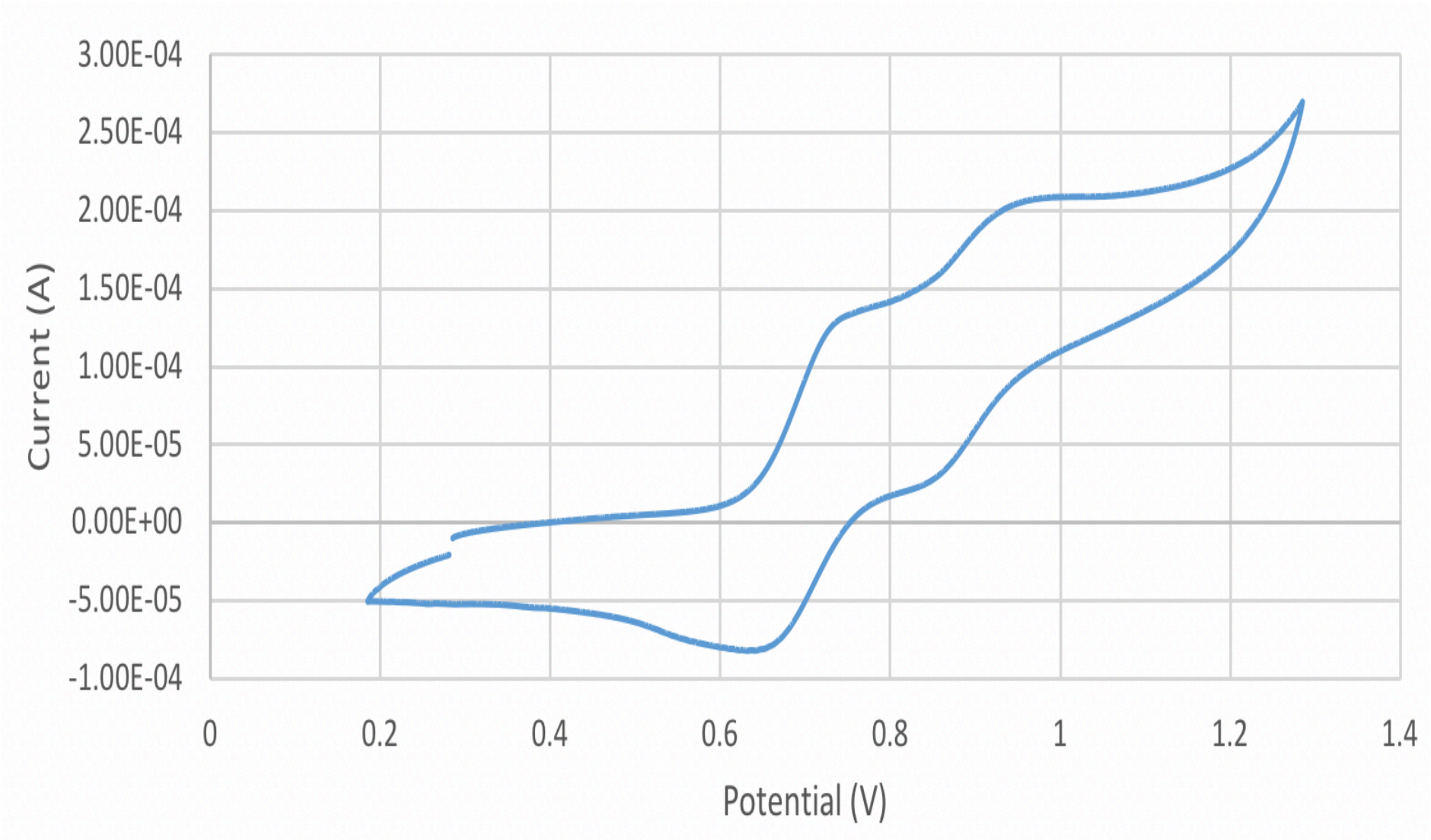

Figure S68. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [(Tp)$(CO)_2$W{≡CC(C_6H_4)$_2$CC≡}Mo$(CO)_2$(Tp*)] (**6b**).

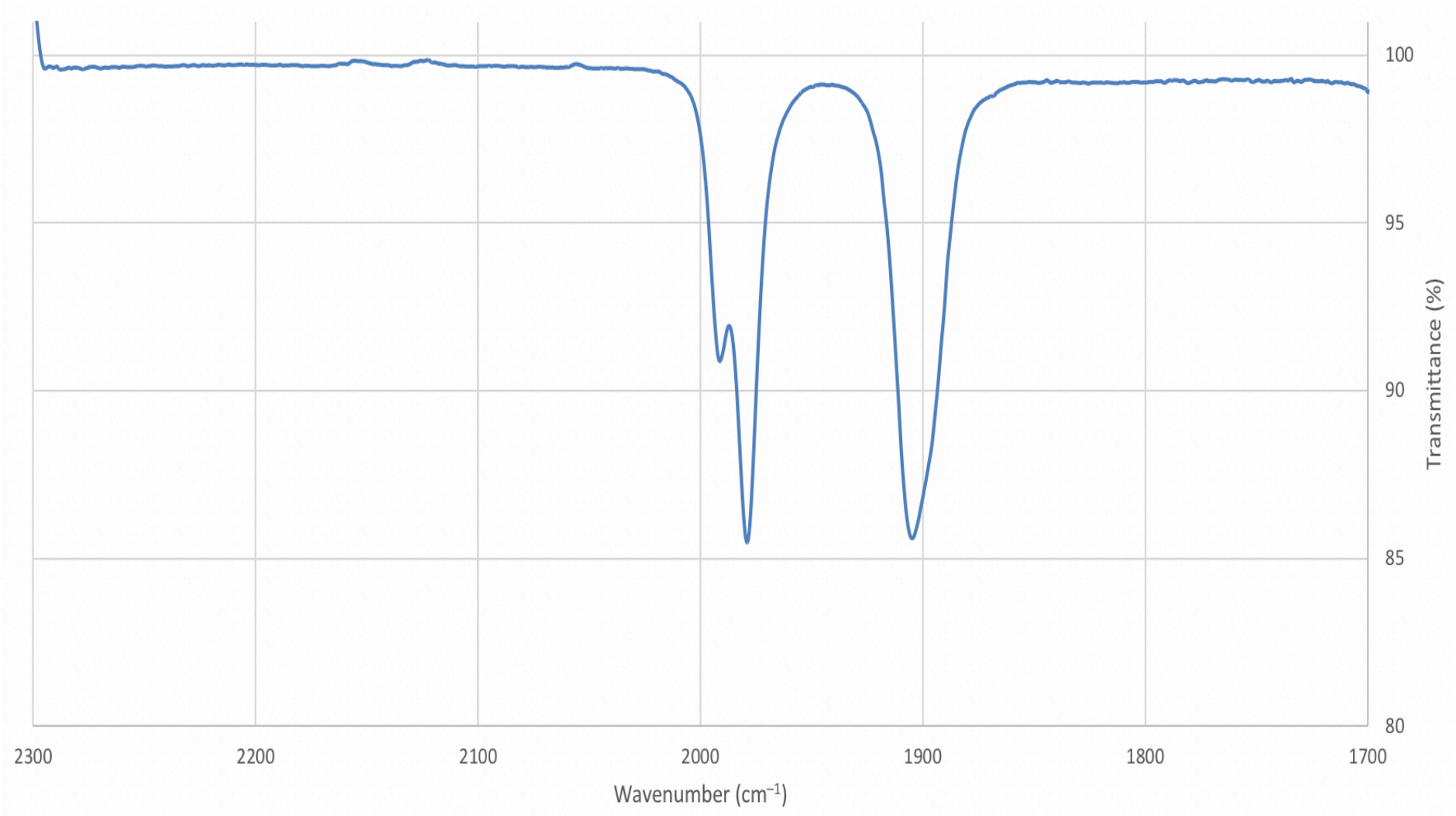

Figure S69. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [(Tp)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6b**).

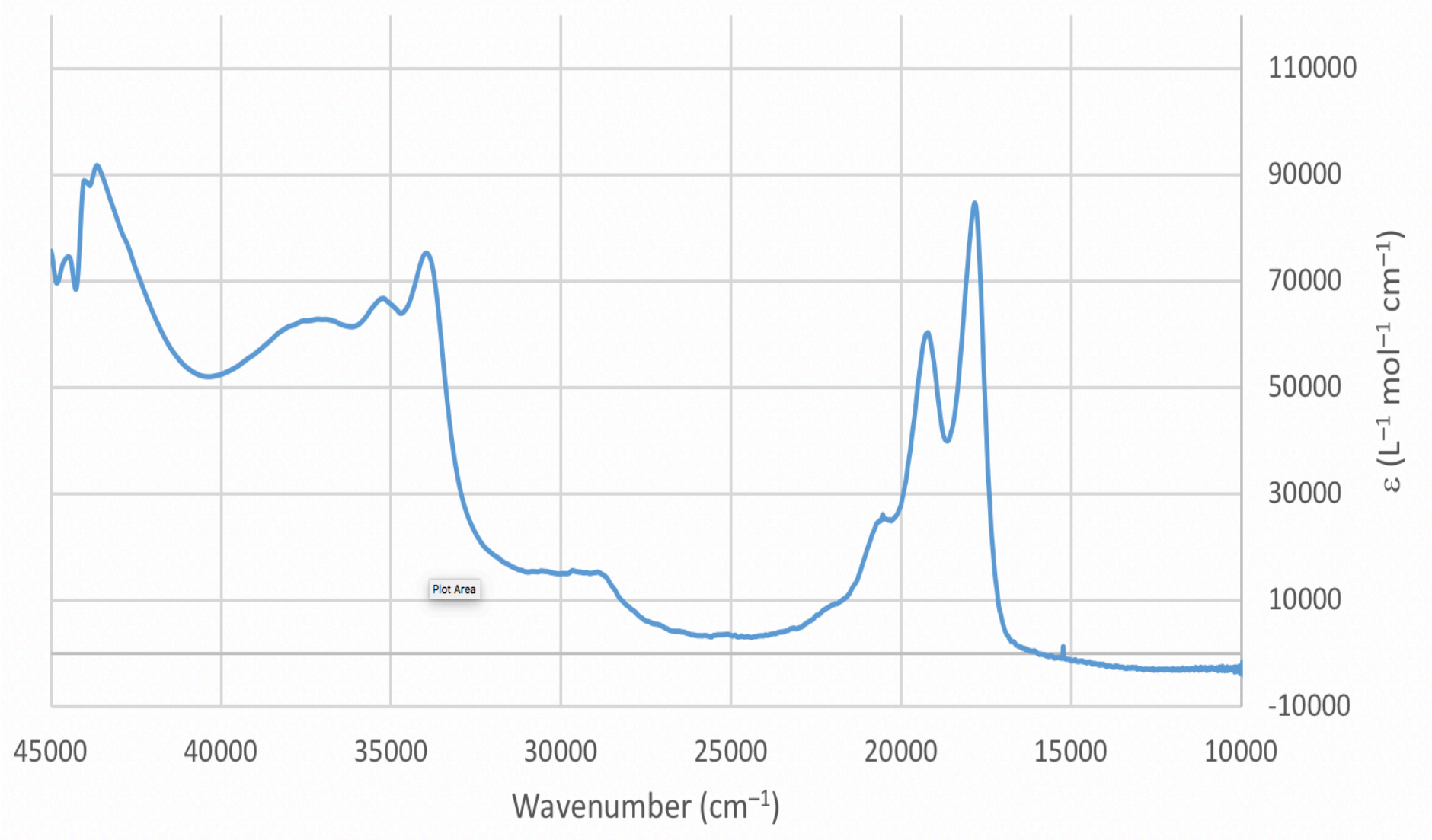

Figure S70a. Electronic spectrum (CH_2Cl_2, cm^{-1}) of [(Tp)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6b**).

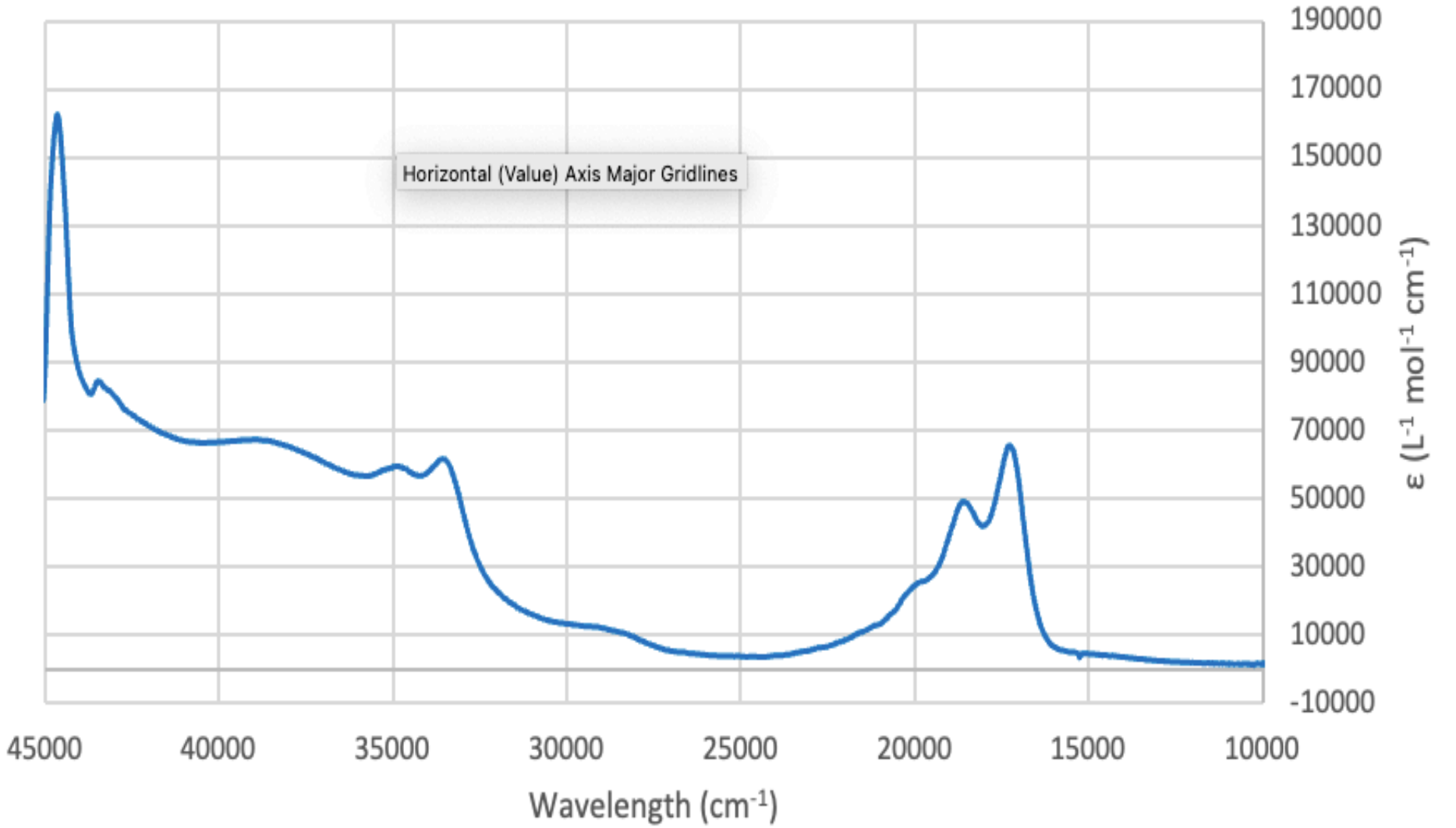

Figure S70b. Electronic spectrum (CH_2Cl_2, cm^{-1}) of [(Tp)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6b**).

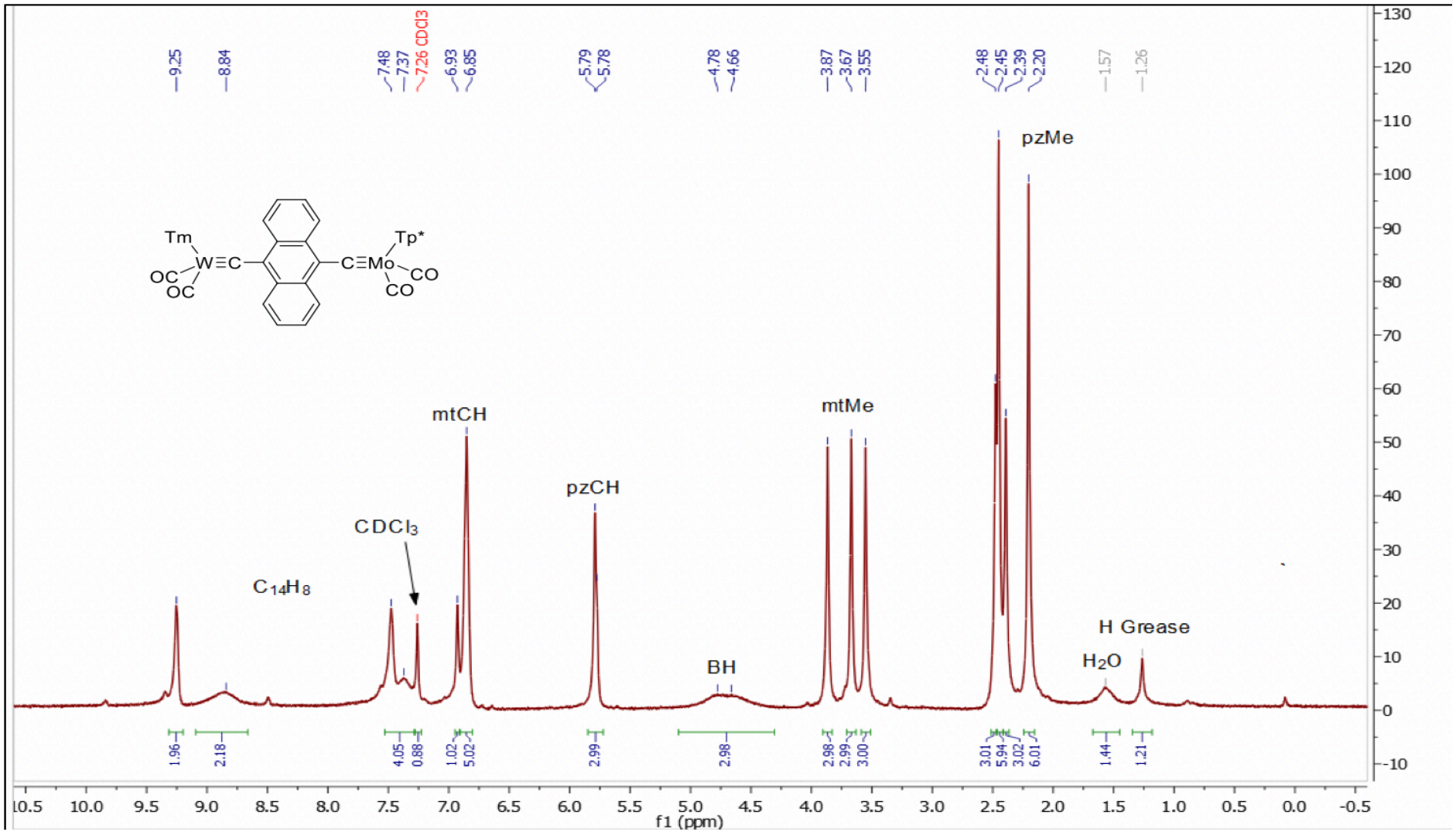

Figure S71. ^{1}H NMR (700 MHz, $CDCl_3$, 25 ˚C, δ) of $[(Tm)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}Mo(CO)_2(Tp^*)]$ (**6c**).

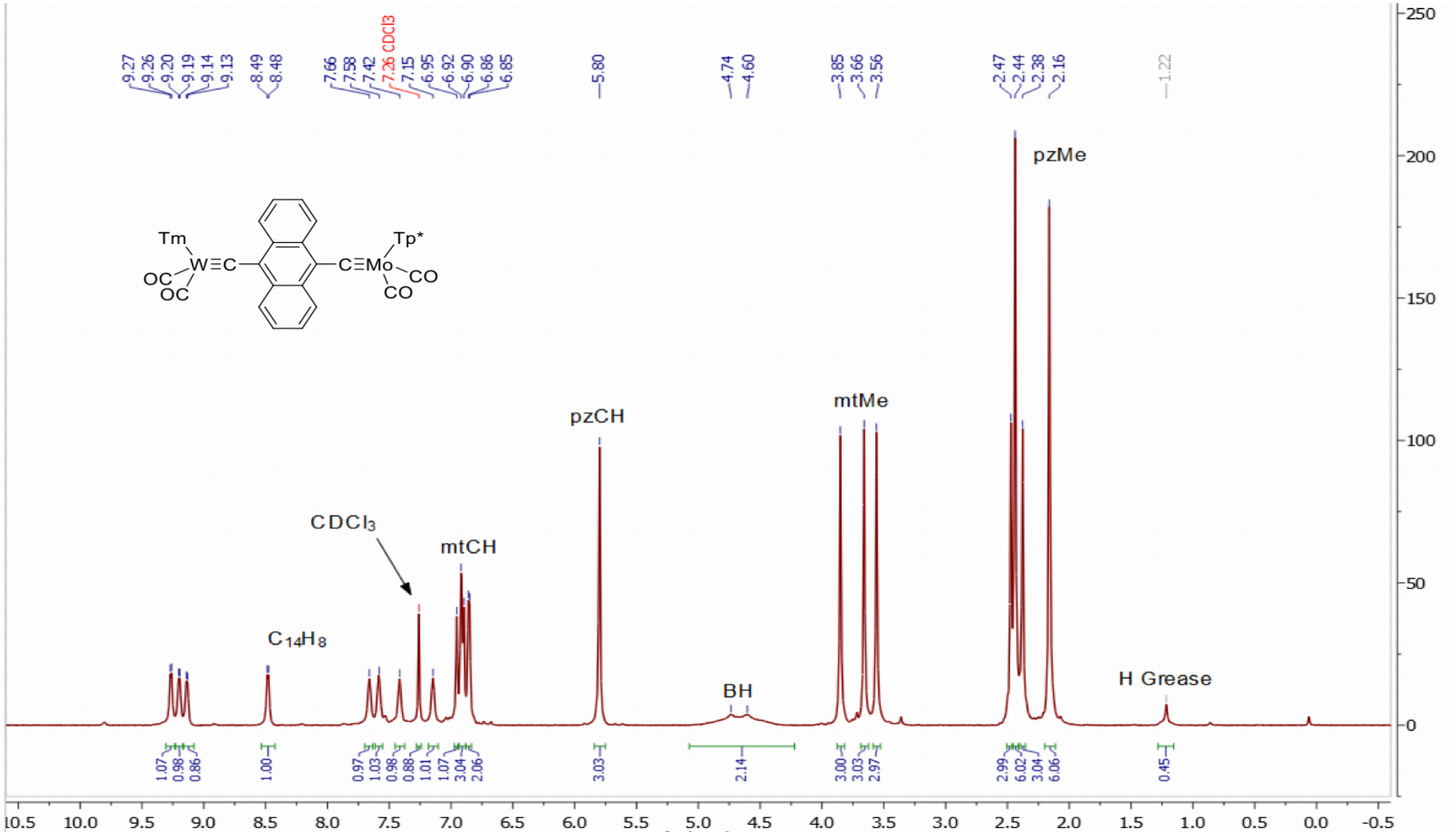

Figure 72. ^{1}H NMR (700 MHz, $CDCl_3$, -50 ˚C, δ) of $[(Tm)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}Mo(CO)_2(Tp^*)]$ (**6c**).

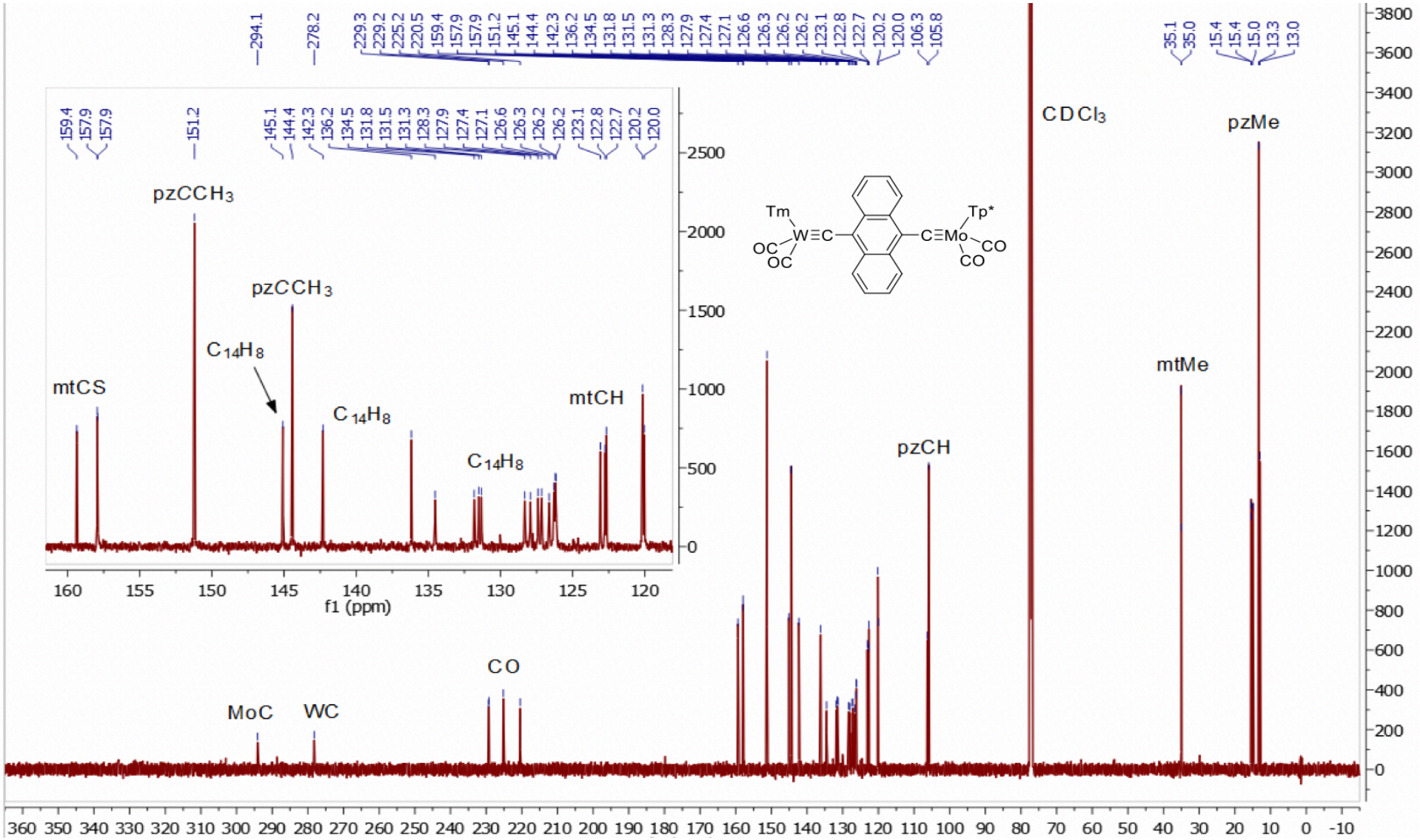

Figure 73. $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$, -50 ˚C, δ) of $[(Tm)(CO)_2W\{\equiv CC(C_6H_4)_2CC\equiv\}Mo(CO)_2(Tp^*)]$ (**6c**).

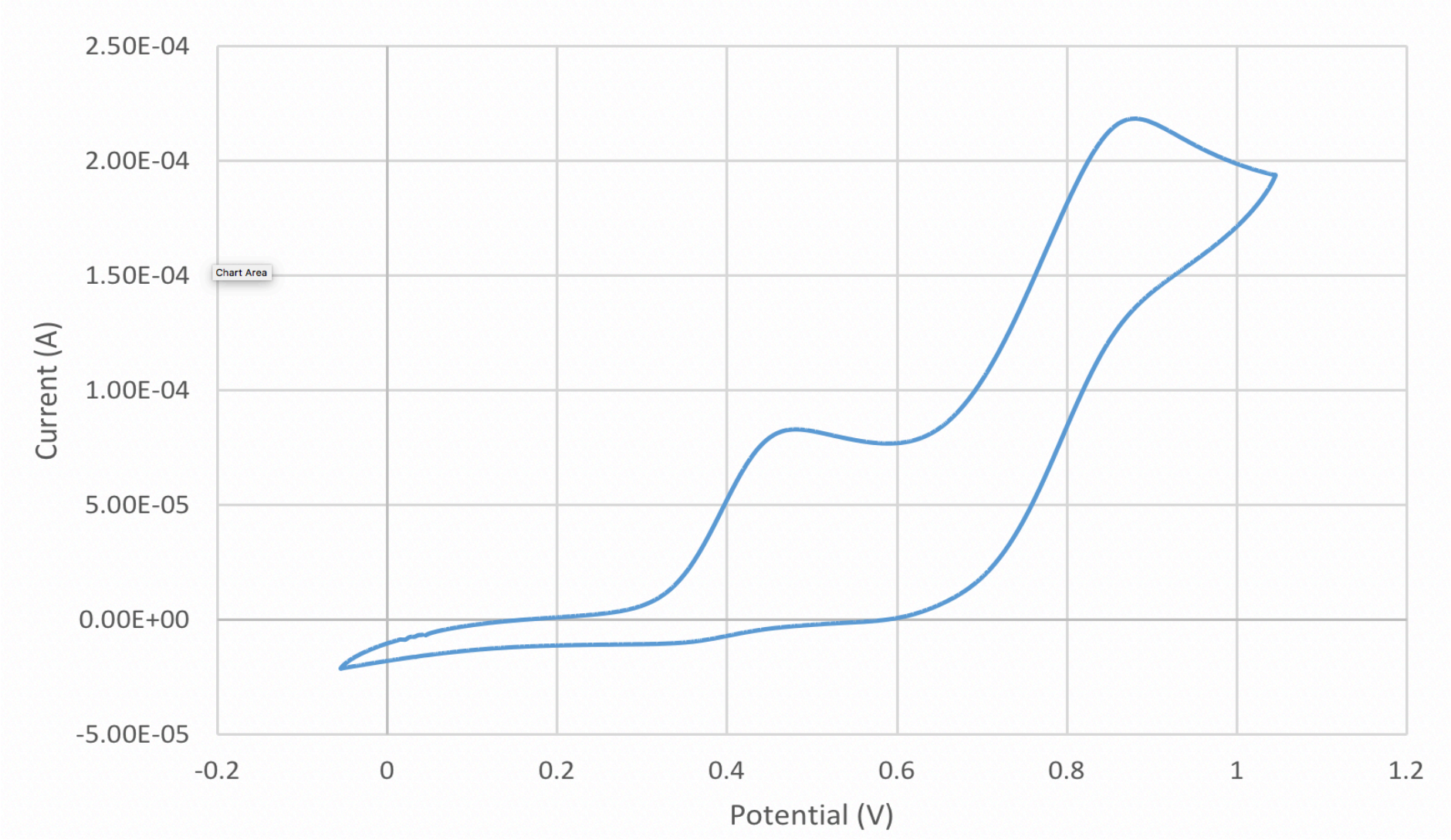

Figure S74. Cyclic Voltammogram (CH_2Cl_2/[NBu_4][PF_6] 0.1 M) at 25 ˚C at 100 mV s^{-1} of [(Tm)$(CO)_2$W{≡CC(C_6H_4)$_2$CC≡}Mo$(CO)_2$(Tp*)] (**6c**).

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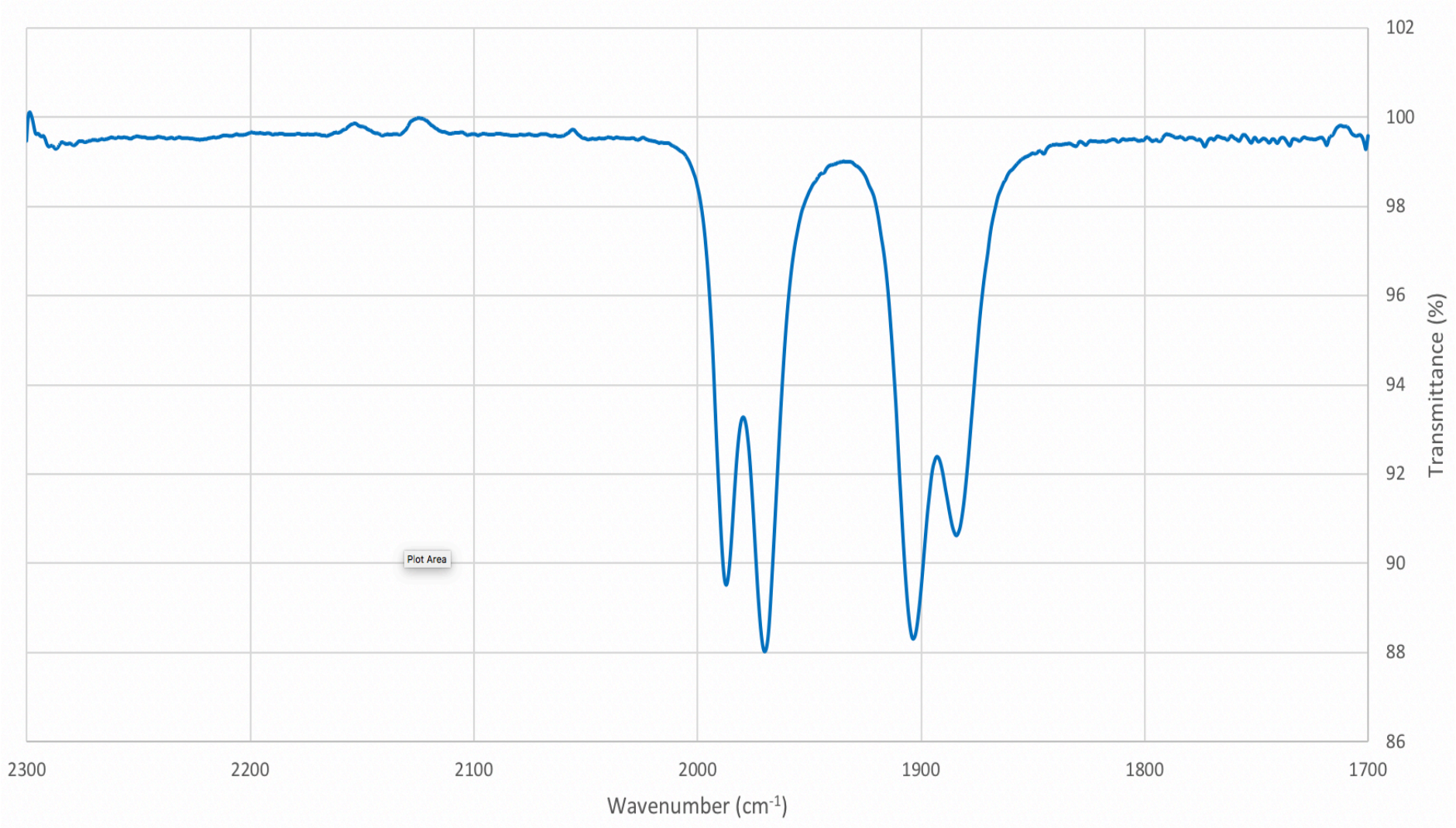

Figure S75. Infrared spectrum (CH_2Cl_2, cm^{-1}) of [(Tm)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6c**).

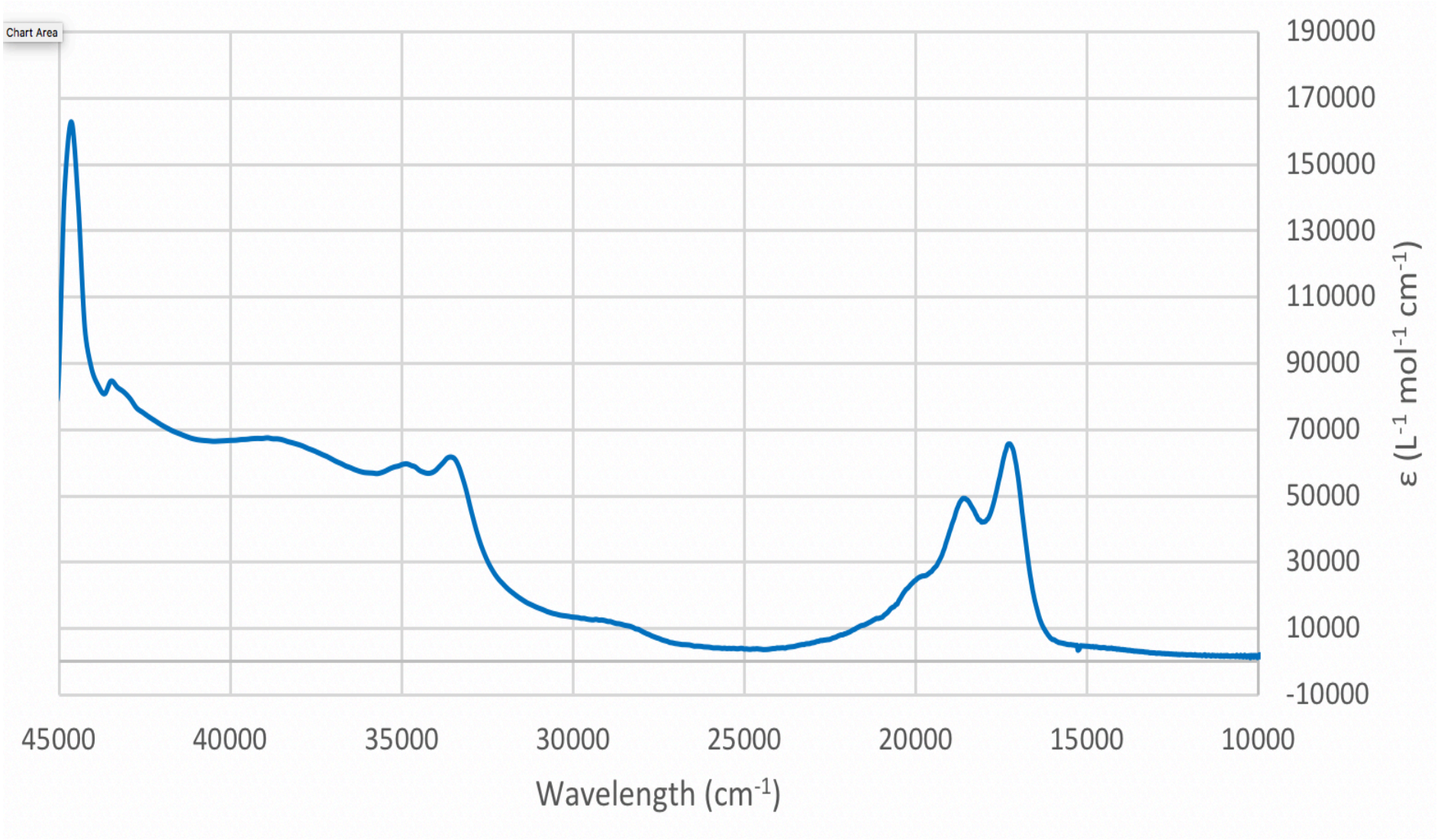

Figure S76. Electronic spectrum (CH_2Cl_2, cm^{-1}) of [(Tm)$(CO)_2$W{≡CC$(C_6H_4)_2$CC≡}Mo$(CO)_2$(Tp*)] (**6c**).

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