Supporting Information

Aerobic C-H Acetoxylation of 8-Methylquinoline in Pd^{II} – Pyridinecarboxylic Acids Systems: Some Structure – Reactivity Relationships

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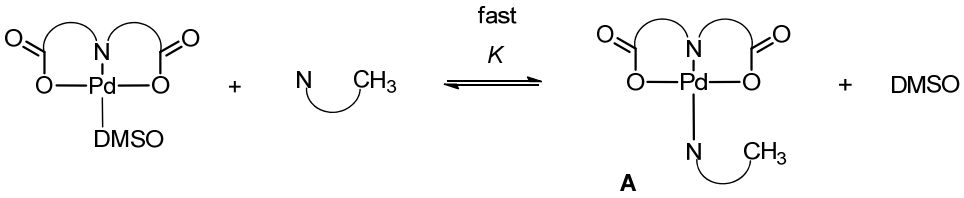
General

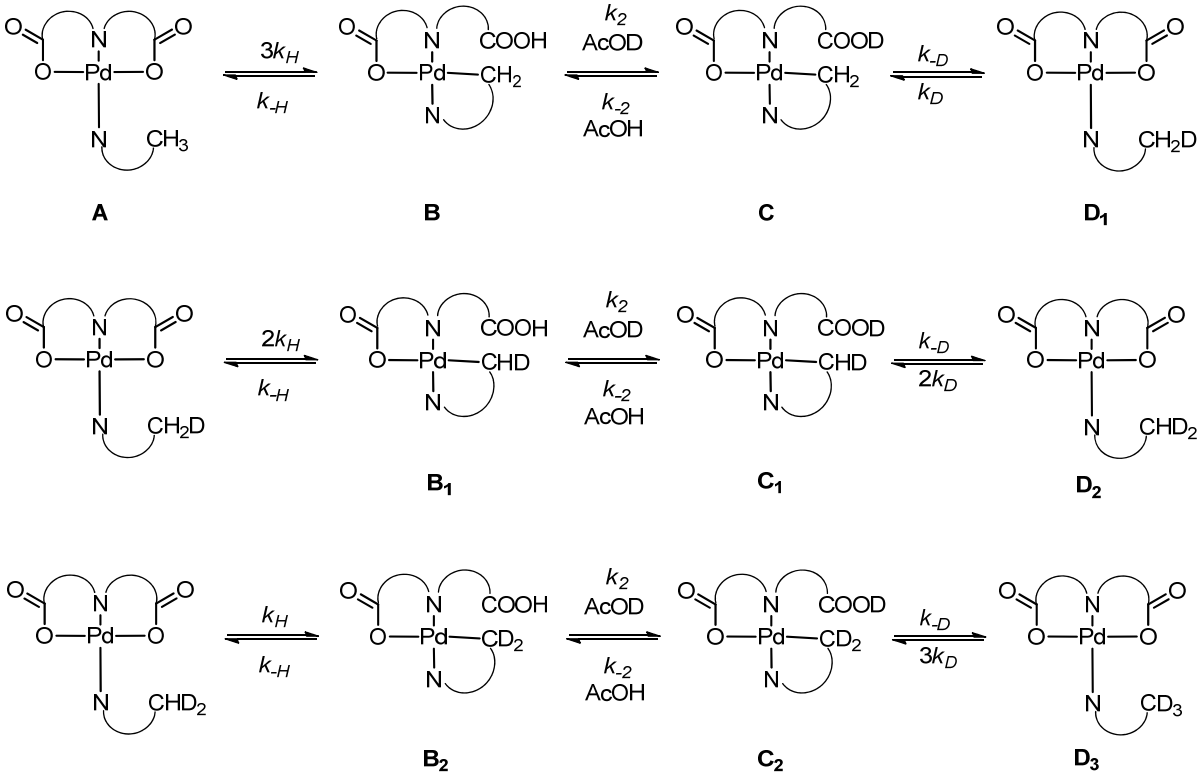
1. Kinetics data modeling: curve fitting.

The scheme below was used to model the kinetics for the C-H activation of 8-methylquinoline by complexes **5**, **6** and **7**. We assumed that i) each batch of the NMR solvent, acetic acid-d_4, is characterized by some individual ratio of [CD_3COOD] and [CD_3COOH] and that ii) these solvent concentrations remained constant during the reaction, that is the substrate concentration was much lower than any of the values [CD_3COOD] and [CD_3COOH], iii) the equilibration between intermediates **B** and **C** was "instanteneous" in the time scale of the C-H/C-D cleavage and C-Pd cleavage reaction rates; iv) the ligand exchange between free and coordinated 8-methylquinoline is much faster than the C-H/C-D cleavage/formation:



(S0)

The C-H activation kinetics model.



The signals of the isotopologues **B** – $\mathbf{B_2}$ as well as **A,** $\mathbf{D_1}$ – $\mathbf{D_3}$ could not be

resolved. The integral intensity of the three following signals was monitored as a function of time: i) one originating from the methyl group of free 8-methylquinoline, ii) one from the methyl group of the palladium - coordinated substrate (**A**+$\mathbf{D_1}$+$\mathbf{D_2}$) and iii) one from the cyclometallated substrate methylene group (**B**+$\mathbf{B_1}$+**C**+$\mathbf{C_1}$). The total integral intensity of these three signals, [H_{total}] was determined.

The experimentally determined relative [H_{total}] vs. time for 1 : 1 mixtures of 8-methylquinoline and complex **5**, **6** or **7** at 60 ^{o}C in AcOH solution.

Time, h	Complex **5**	Complex **6**	Complex **7**
0	3.00	3.00	3.00
0.17	2.03		
0.33	1.58		
0.50	1.47		
1.00	1.29	2.50	2.80
2.00	1.24	2.13	2.70
3.00	1.13	1.94	2.52

The best least square curve-fitting of the total integral intensity [H_{total}] was performed using the model in the Scheme above and the numerical integration of the corresponding kinetics equations below. All the reactions considered were assumed to follow (pseudo)first order kinetics.

The following algorithm was used:

1) The reaction period was split into N = 50 – 60 relatively short intervals Δt ~30 s (in the beginning of a reaction) – 300 s (in the end of the reaction).
2) The concentrations of the species present before the reaction started, [free 8-Me-quinoline-d_0]$_0$, [**A**]$_0$, [**B**+**C**]$_0$, were determined based on the NMR integration of the reaction mixtures before heating.

3) Let's define, $[\text{free 8-Me-quinoline-}d_0]_i + [\mathbf{A}]_i = [\mathbf{A'}]_i$,

$[\text{free 8-Me-quinoline-}d_n]_i + [\mathbf{D_n}]_i = [\mathbf{D_n'}]_i$, ($n$ = 1, 2, 3)

According to equation (S0), when the DMSO : Me-quinoline ratio is 1:1, $[\mathbf{A}]_i = \frac{\sqrt{K}}{1+\sqrt{K}}\ [\mathbf{A'}]_i \approx [\mathbf{A'}]_i/2$ since $K \approx 1$ for all three substrates **5**, **6** and **7**.

Similarly, $[\mathbf{D_n}]_i = \frac{\sqrt{K}}{1+\sqrt{K}}\ [\mathbf{D_n'}]_i \approx 0.5[\mathbf{D_n'}]_i/2$

In other words, in our experiments only ~50% of 8-methylquinoline was bound to the Pd(II) center in the form of complexes **A**, $\mathbf{D_1}$, $\mathbf{D_2}$ and $\mathbf{D_3}$.

4) For each subsequent ith+1 moment of time (i = 0, … N) the current concentrations $[\mathbf{A'}]_{i+1}$, $[\mathbf{B+C}]_{i+1}$, $[\mathbf{B_1+C_1}]_{i+1}$, $[\mathbf{B_2+C_2}]_{i+1}$, $[\mathbf{D_1'}]_{i+1}$, $[\mathbf{D_2'}]_{i+1}$, $[\mathbf{D_3'}]_{i+1}$ were found using the appropriate equations, e.g., (S1) - (S7):

$$[\mathbf{A'}]_{i+1} = [\mathbf{A'}]_i + \Delta t(k_{-H}[\mathbf{B+C}]_i/(1+K_2) - 3/2k_H[\mathbf{A'}]_i) \quad (S1)$$

$$[\mathbf{B+C}]_{i+1} = [\mathbf{B+C}]_i + \Delta t(3/2k_H[\mathbf{A'}]_i + k_D/2[\mathbf{D_1'}]_i - k_{-H}[\mathbf{B+C}]_i/(1+K_2) - k_{-D}[\mathbf{B+C}]_i[K_2/(1+K_2)]) \quad (S2)$$

$$[\mathbf{D_1'}]_{i+1} = [\mathbf{D_1'}]_i + \Delta t(k_{-D}[\mathbf{B+C}]_i[K_2/(1+K_2)] + k_{-H}[\mathbf{B_1+C_1}]_i/(1+K_2) - 2/2k_H[\mathbf{D_1'}]_i - k_D/2[\mathbf{D_1'}]_i) \quad (S3)$$

$$[\mathbf{B_1+C_1}]_{i+1} = [\mathbf{B_1+C_1}]_i + \Delta t(2k_H/2[\mathbf{D_1'}]_i + 2k_D/2[\mathbf{D_2'}]_i - k_{-H}[\mathbf{B_1+C_1}]_i/(1+K_2) - k_{-D}[\mathbf{B_1+C_1}]_i[K_2/(1+K_2)]) \quad (S4)$$

$$[\mathbf{D_2'}]_{i+1} = [\mathbf{D_2'}]_i + \Delta t(k_{-D}[\mathbf{B_1+C_1}]_i[K_2/(1+K_2)] + k_{-H}[\mathbf{B_2+C_2}]_i/(1+K_2) - k_H/2[\mathbf{D_2'}]_i - 2k_D/2[\mathbf{D_2'}]_i) \quad (S5)$$

$$[\mathbf{B_2+C_2}]_{i+1} = [\mathbf{B_2+C_2}]_i + \Delta t(k_H/2[\mathbf{D_2'}]_i + 3k_D/2[\mathbf{D_3'}]_i - k_{-H}[\mathbf{B_2+C_2}]_i/(1+K_2) - k_{-D}[\mathbf{B_2+C_2}]_i[K_2/(1+K_2)]) \quad (S6)$$

$$[\mathbf{D_3'}]_{i+1} = [\mathbf{D_3'}]_i + \Delta t(k_{-D}[\mathbf{B_2+C_2}]_i[K_2/(1+K_2)] - 3k_D/2[\mathbf{D_3'}]_i) \quad (S7)$$

The [**B**] and [**C**] were calculated using the relationships $[\mathbf{B}] = [\mathbf{B+C}]/(1+K_2)$ and $[\mathbf{C}] = [\mathbf{B+C}][K_2/(1+K_2)]$.

5) The total concentrations of all protium in the groups originating from the substrate CH_3 fragment, $[H_{total}]$, were calculated and compared to the experimental values.

6) The sum of squares of the deviations of the calculated and the experimentally determined values from the previous step was minimized by varying the rate constants k_H, k_{-H}, k_D, k_{-D} and $K_2 = k_2/k_{-2}$.

7) The value of $K_2 = 10.1$ found from curve-fitting for **5** was used for **6** and **7**.

The k_H values found are given below.

Calculated first order rate constants k_H and the Gibbs activation energies for the C-H activation of 8-methylquinoline with complexes **5**, **6** and **7** in CD_3COOD solution at 60 ^oC.

Complex	k_H, s^{-1}	$\Delta G^{\#}$, kcal/mol
5	$(2.8\pm0.1)\times10^{-3}$	23.5
6	$(1.23\pm0.1)\times10^{-4}$	25.6
7	$(4.7\pm0.1)\times10^{-5}$	26.2

2. Computational details. Theoretical calculations in this work have been performed using density functional theory (DFT) method,[1] specifically functional PBE,[2] and LACVP relativistic basis set with two polarization functions implemented in the Jaguar program[3] package. Full geometry optimization has been performed without constraints on symmetry. For all species under investigation frequency analysis has been carried out. All energy minima have been checked for the absence of imaginary frequencies. All transition states possessed just one imaginary frequency. Using the method of Intrinsic Reaction Coordinate, reactants, products and the corresponding transition states were proven to be connected by a single minimal energy reaction path.

The solvation of all complexes in Scheme 6 in CH_3COOH solvent was modeled using a Poisson-Boltzmann continuum solvation model (PBF).[3]

DFT-optimized geometries for complexes 8, 11, 19, 20, TS1, TS2 for gas phase and CH_3COOH solutions

Drawings are given for all metal complexes with geometry optimized in MeCN solution.

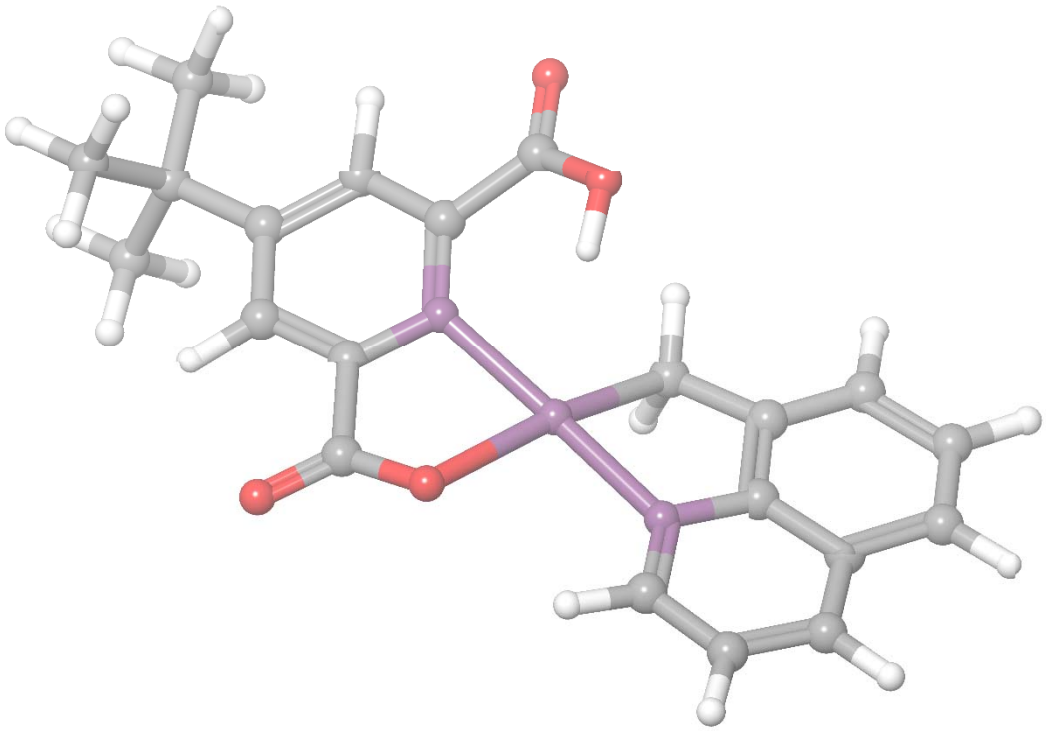
Total Gibbs energy (Gtot) for 298K is given in Hartrees (1 Hartree = 627.51 kcal/mol).

Reaction Gibbs energies in kcal/mol were calculated as

$627.51*[\Sigma(Gtot)_{products} - \Sigma(Gtot)_{reactants}]$

Complex 8, acetic acid solution

Title: Pd_CH2_8_quinolyl_HRIbupda_b_acoh



Total Gibbs free energy, Gtot (Htot - T*S): -1347.782032 hartrees

O1	3.0332742265	2.5218051495	-2.7585555873
C2	4.3517168531	1.8335677870	-0.3327733361
C3	3.0004256014	1.5702708498	-0.5641195361
C4	4.9373071537	1.5768677452	0.9238989065
O5	1.0475128441	1.7821942452	-1.9443911396
N6	2.1989252673	1.0383383247	0.4029545654
C7	2.3338452503	1.9809661712	-1.8819567469
C8	4.0599850905	1.1363558032	1.9307418627
C9	2.7065083125	0.9006633396	1.6552380222
H10	4.9139479944	2.2559489819	-1.1710245128
H12	4.3851074388	0.9889812394	2.9621230215
C13	1.7983453726	0.6524167478	2.8393472000
O14	0.4888751190	0.9234196650	2.6733968067
O15	2.2381675262	0.3205791558	3.9346691897
C16	-3.8692243411	-0.9705611038	-2.2088541863
C17	-3.3298575515	-1.5871692637	-1.0452456571
Pd18	0.4543502830	0.3176619577	-0.4645218349
C19	-3.1120301313	-0.0401411637	-2.9089281807
C20	-2.0041730100	-1.2152840390	-0.6588561205
C21	-4.0256327807	-2.5128618901	-0.2141768697
C22	-1.8170720523	0.3024981765	-2.4506635111

C23	-1.3543499112	-1.7671882697	0.4751981187
N24	-1.2908972952	-0.2599659066	-1.3560707302
C25	-3.4114716278	-3.0142660957	0.9259624857
C26	0.0829232497	-1.3748429578	0.6633700263
C27	-2.0807399674	-2.6488520033	1.2734318117
H28	-4.8819286567	-1.2309061733	-2.5377328935
H29	-3.4995717377	0.4502093114	-3.8061603093
H30	-5.0502370709	-2.8010649823	-0.4746059534
H31	-1.1952222552	1.0436678478	-2.9621811373
H32	-3.9557128989	-3.7112343269	1.5729439178
H33	0.7518078324	-2.0875327241	0.1365229683
H34	0.3768007052	-1.3450496763	1.7235038916
H35	-1.6192998207	-3.0795037908	2.1700485921
H36	0.2858866593	1.0574302190	1.7034496882
C36	6.4296961587	1.8295074764	1.1669240408
C39	6.7252941689	3.3322026510	0.9236861102
H40	6.4799171823	3.6392724287	-0.1059539964
H41	6.1487077353	3.9667653907	1.6181015010
H42	7.7983409230	3.5287790043	1.0881813118
C42	7.2481444662	0.9705728089	0.1680689761
H43	7.0080480363	1.2170502005	-0.8789044116
H44	8.3258527764	1.1524585171	0.3189548175
H45	7.0564643241	-0.1049811672	0.3200433091
C45	6.8521506074	1.4642102342	2.6036230464
H46	7.9338122239	1.6403521985	2.7219439564
H47	6.3330064570	2.0805189715	3.3580539531
H48	6.6608642132	0.4016735193	2.8296980765

Complex 8, gas phase

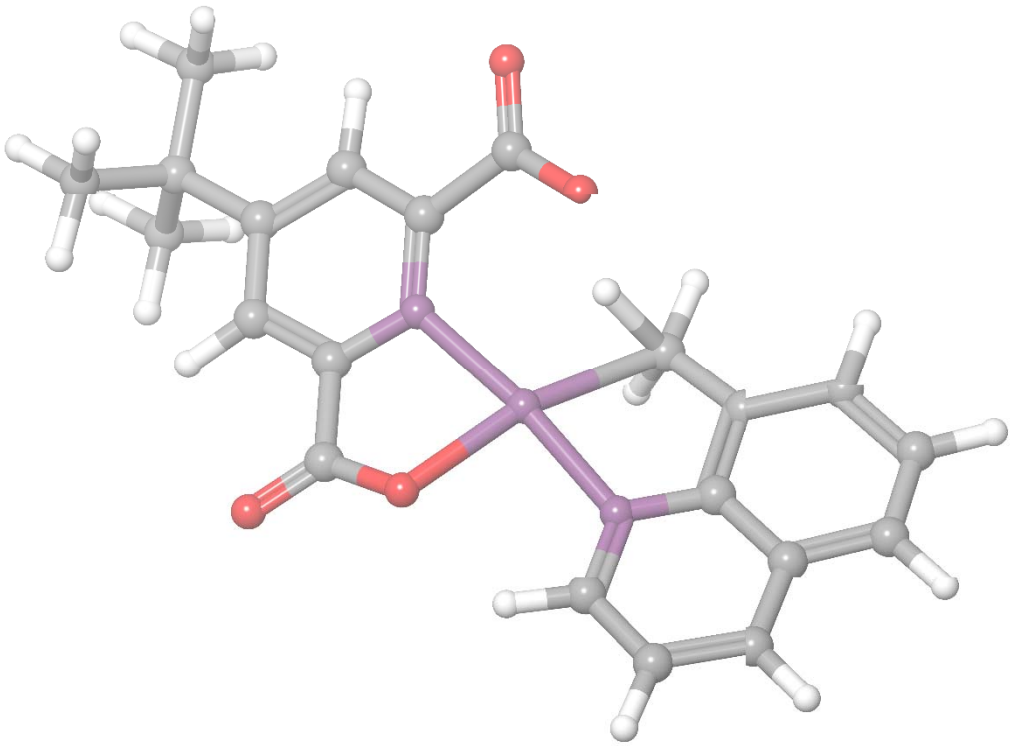
Total Gibbs free energy, Gtot (Htot - T*S): -1347.758185 hartrees

O1	2.8915163284	2.5203121809	-2.6963678598
C2	4.2986356783	1.8497686213	-0.3581847775
C3	2.9433334191	1.5634420852	-0.5148459941
C4	4.9565938139	1.6125957388	0.8625123580
O5	0.9500943890	1.7119682885	-1.8304001030
N6	2.1990516965	1.0213246974	0.4935811476
C7	2.2318606710	1.9598861507	-1.8131506081
C8	4.1462156096	1.1475911417	1.9122646729
C9	2.7837344234	0.8828189351	1.7123941195
H10	4.7889903832	2.2789643026	-1.2370176555
H12	4.5232306002	0.9936627697	2.9247365027
C13	1.9673879098	0.5830711201	2.9539767474
O14	0.6370800832	0.7949731718	2.8748547801
O15	2.5024310147	0.2615832555	4.0044693691
C16	-3.7155712943	-0.9501396963	-2.4578475271
C17	-3.3044423376	-1.5723759755	-1.2470657351
Pd18	0.4182203748	0.3082442567	-0.3330905730
C19	-2.8941838668	-0.0132242157	-3.0673046756
C20	-2.0292050005	-1.1985796298	-0.7192027977
C21	-4.0772363734	-2.5075567676	-0.5037390938
C22	-1.6578964196	0.3332474863	-2.4724825151
C23	-1.4922118214	-1.7522264467	0.4714384170
N24	-1.2555511814	-0.2386302456	-1.3332911109
C25	-3.5809737208	-3.0122432529	0.6896163335
C26	-0.0884107647	-1.3438566612	0.8263341574
C27	-2.2979539863	-2.6430875745	1.1767127882
H28	-4.6844396459	-1.2132484041	-2.8951811097
H29	-3.1878462338	0.4777969490	-3.9981811829
H30	-5.0648163573	-2.8010191038	-0.8725304795
H31	-0.9740118615	1.0776615407	-2.8933434567
H32	-4.1851493420	-3.7165399138	1.2698465840
H33	0.6324692437	-2.0926460357	0.4409671554
H34	0.0528476289	-1.2643792551	1.9140664572
H35	-1.9319862754	-3.0763767144	2.1132847723
H36	0.3723942273	0.9279684220	1.9231878753
C36	6.4562092903	1.8941379693	1.0120748080
C39	6.7293678836	3.3782797680	0.6605485475
H40	6.4264142045	3.6212181058	-0.3704289617
H41	6.1882310075	4.0549554999	1.3423190681
H42	7.8077572092	3.5905215008	0.7525732874

C42	7.2239821862	0.9799201499	0.0237591250
H43	6.9163828922	1.1571824497	-1.0194933607
H44	8.3070040882	1.1763108164	0.0956339558
H45	7.0532174722	-0.0850488289	0.2527712750
C45	6.9581367419	1.6202422139	2.4423237582
H46	8.0385712757	1.8299900626	2.5008849376
H47	6.4551248589	2.2622736334	3.1847896442
H48	6.8078344210	0.5679645023	2.7352267992

TS1, acetic acid solution

Title: Pd_tBupda_H_CH2_8_quinolyl_b_CH_activation_TS_acoh - TS Guess



Total Gibbs free energy, Gtot (Htot - T*S): -1347.755728 hartrees

O1	2.8192466290	2.4776330897	-2.7883118028
C2	4.1946686339	2.1757673155	-0.2572771776
C3	2.8623337259	1.8384389407	-0.4703057596
C4	4.7510072575	2.0901464134	1.0374875061
O5	0.9051448887	1.7536049193	-1.8455857846
N6	2.0589238971	1.3958023765	0.5395965079
C7	2.1970609008	2.0324843166	-1.8156252771
C8	3.8658053444	1.7258354604	2.0664187399
C9	2.5237490187	1.3916639519	1.8097806694
H10	4.7662487097	2.5099330515	-1.1287965717
H12	4.1682723092	1.6976648746	3.1143722618
C13	1.5881527820	1.1485636425	3.0141488676
O14	0.3389799703	0.9091221340	2.7755393074
O15	2.1032088621	1.2675948312	4.1459872322
C16	-3.7741857771	-0.8953637432	-2.3325658654
C17	-3.3630827832	-1.4270508677	-1.0785585553
Pd18	0.3079115990	0.6440870872	-0.2294131292
C19	-2.9726114351	0.0292971525	-2.9863804724
C20	-2.1121863007	-0.9784240848	-0.5393608322
C21	-4.1286335286	-2.3598097253	-0.3210406657
C22	-1.7624617469	0.4480576303	-2.3876907267

C23	-1.6020589915	-1.4855414463	0.6889378638
N24	-1.3618757069	-0.0303848033	-1.2024146122
C25	-3.6531270800	-2.8123033991	0.9011170918
C26	-0.2094181038	-1.1066904322	1.1012502485
C27	-2.3936280402	-2.3839803549	1.4004883399
H28	-4.7235524652	-1.2244474079	-2.7706476127
H29	-3.2561850005	0.4512947662	-3.9548806073
H30	-5.0954844715	-2.6956433731	-0.7115528167
H31	-1.0995490781	1.1764944478	-2.8640283893
H32	-4.2460974437	-3.5195282294	1.4904036881
H33	0.5478660431	-1.6155042739	0.4719986778
H34	0.0093123873	-1.4472781073	2.1298188195
H35	-2.0279453862	-2.7824729403	2.3539703617
H36	0.0405663771	0.1073567997	1.6122114366
C36	6.2335610026	2.4065361281	1.2718879438
C39	6.5392958586	3.8345368415	0.7528388764
H40	6.3393399275	3.9367656385	-0.3266819260
H41	5.9374677672	4.5886669441	1.2864329228
H42	7.6051892378	4.0659258303	0.9181547745
C42	7.0817846627	1.3786314024	0.4776311664
H43	6.8674824079	1.4181535657	-0.6036309850
H44	8.1548345529	1.5949482255	0.6178514129
H45	6.8905172482	0.3504812191	0.8277478473
C45	6.6151803645	2.3248181687	2.7633539862
H46	7.6868668530	2.5568969356	2.8799200594
H47	6.0494176008	3.0501967299	3.3725817410
H48	6.4465016790	1.3161804414	3.1776046765

TS1, gas phase

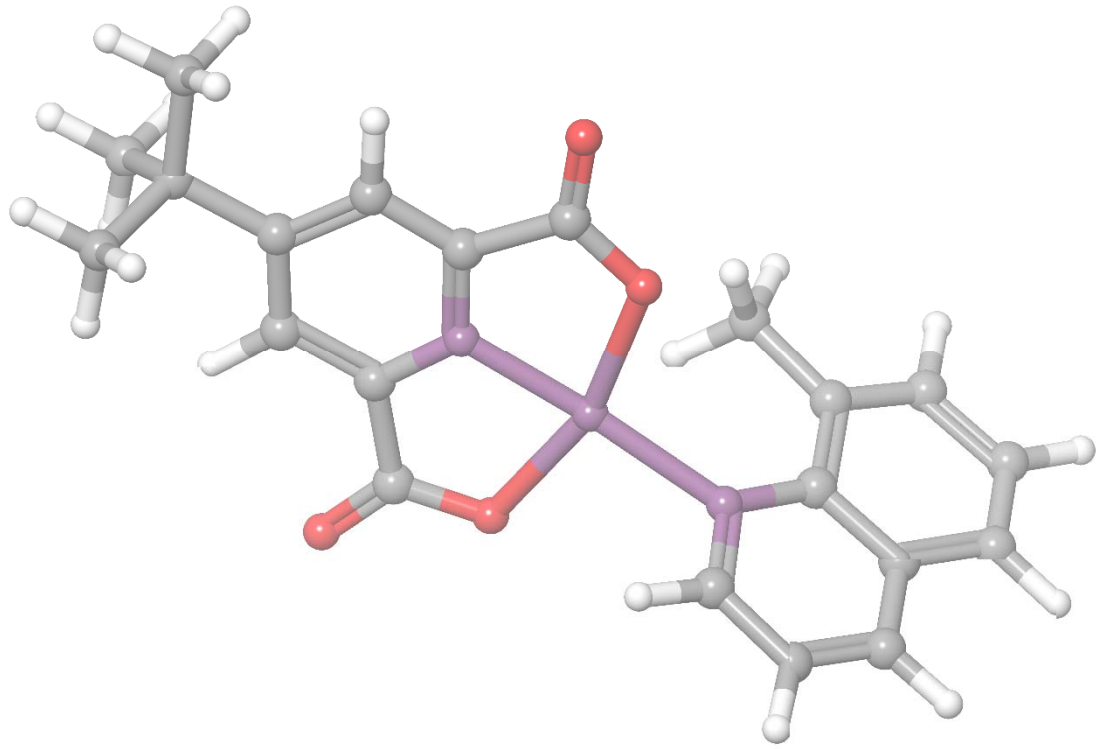
Total Gibbs free energy, Gtot (Htot - T*S): -1347.724169 hartrees

O1	2.8776003824	2.2938608950	-2.8476495071
C2	4.2304314529	2.1918595124	-0.2751234355
C3	2.9423659039	1.7278804691	-0.5099849158
C4	4.7663722321	2.1630039318	1.0310326971
O5	1.0200547192	1.4531236704	-1.8999050397
N6	2.1609315254	1.2339508872	0.4909291258
C7	2.2940285837	1.8374182768	-1.8663422853
C8	3.9124390649	1.6911423763	2.0393217477
C9	2.6033606464	1.2530449224	1.7652331452
H10	4.7755609964	2.5798207873	-1.1407153542
H12	4.1895501654	1.6508147895	3.0953456527
C13	1.6722050965	0.9257149111	2.9674415531
O14	0.4153794630	0.8876980474	2.7062893264
O15	2.2512189847	0.8057511913	4.0642788461
C16	-3.8448076937	-0.6246576105	-2.2800687348
C17	-3.5044857935	-1.1833376833	-1.0190141249
Pd18	0.4020574348	0.4845816989	-0.2427361105
C19	-2.9284705163	0.1621443477	-2.9581121655
C20	-2.1973140647	-0.9068565609	-0.4951933373
C21	-4.3946792552	-1.9779672801	-0.2446303711
C22	-1.6689187165	0.4194568732	-2.3742883903
C23	-1.7670995773	-1.4546457926	0.7482385743
N24	-1.3284611075	-0.0877338328	-1.1839039130
C25	-3.9885323704	-2.4673168398	0.9856195649
C26	-0.3519524439	-1.2434352682	1.1929239285
C27	-2.6817382613	-2.2129932686	1.4737194764
H28	-4.8355691202	-0.8225827519	-2.7013059356
H29	-3.1610661823	0.6013260883	-3.9309503876
H30	-5.3991181784	-2.1786113392	-0.6294977528
H31	-0.9105055924	1.0457333854	-2.8543183502
H32	-4.6762553057	-3.0664573279	1.5894872978
H33	0.3663611954	-1.7812984734	0.5439251539
H34	-0.1835465505	-1.6317834935	2.2116280462
H35	-2.3771253245	-2.6302204699	2.4388379986
H36	-0.0382883683	-0.1138969158	1.5643802013
C36	6.1950455552	2.6571426939	1.2943288502
C39	6.3024604372	4.1384230906	0.8517609646
H40	6.0783257854	4.2667580230	-0.2196802331
H41	5.6067590392	4.7747476320	1.4232097069
H42	7.3268889183	4.5082341738	1.0269212509

C42	7.1792707839	1.7976372502	0.4619419048
H43	6.9678480191	1.8598760122	-0.6180198453
H44	8.2125422635	2.1485944507	0.6232946419
H45	7.1281944136	0.7368367177	0.7582500373
C45	6.5781556216	2.5542707621	2.7831145102
H46	7.6119193762	2.9107071407	2.9228006891
H47	5.9237316248	3.1728544858	3.4192394656
H48	6.5305689447	1.5153162313	3.1488930334

Complex 19, acetic acid solution

Title: Pd_8_Me_quinoline_tBupda_acoh



Total Gibbs free energy, Gtot (Htot - T*S): -1347.790144 hartrees

O1	3.5000262505	0.6601082435	-3.0348394278
C2	4.5728561651	1.6905679103	-0.4211772102
C3	3.2904197542	1.2235935805	-0.7055894861
C4	4.8916249087	2.1517852717	0.8824089896
O5	1.4954988810	0.3420432978	-2.0378603977
N6	2.3625412604	1.2162288356	0.2712353932
C7	2.7674211409	0.7112041699	-2.0382591925
C8	3.8694175341	2.1167358254	1.8590779288
C9	2.5973738552	1.6424635068	1.5241329463
H10	5.3057887342	1.6895185722	-1.2343093747
H12	4.0290780491	2.4564119594	2.8857711141
C13	1.3800632669	1.5558383334	2.4325404536
O14	0.2766192039	1.1077719222	1.8500898621
O15	1.4456506280	1.8903602001	3.6221696183
C16	-4.0009371285	-0.0660415476	-1.7319349941
C17	-3.5127468402	-1.0914646385	-0.8778772017
Pd18	0.5804911928	0.5902933400	-0.1706630081
C19	-3.1778214428	0.9883511991	-2.0833791979
C20	-2.1556001837	-1.0140076339	-0.3792174325
C21	-4.3461999500	-2.1882593775	-0.5199221633
C22	-1.8684975349	1.0135362479	-1.5629524242

C23	-1.6594746029	-2.0686052279	0.4647317390
N24	-1.3707781602	0.0718170738	-0.7437422883
C25	-3.8567029598	-3.1888948300	0.2982233388
C26	-0.2618677046	-2.1024411305	1.0319898534
C27	-2.5247419759	-3.1187477348	0.7728596388
H28	-5.0298253885	-0.1311267107	-2.1052179735
H29	-3.5096465645	1.7949932460	-2.7433893377
H30	-5.3699437998	-2.2185156437	-0.9100071656
H31	-1.1918917236	1.8338934380	-1.8181352938
H32	-4.4864072968	-4.0387908603	0.5794447588
H33	0.5100399721	-1.9800486348	0.2489621816
H34	-0.0820840504	-3.0675819231	1.5323401919
H35	-2.1488596800	-3.9263009334	1.4123286524
H36	-0.1043162604	-1.3006497826	1.7753986735
C36	6.3041490963	2.6779160502	1.1810422542
C39	6.5796844752	3.9004817043	0.2661512823
H40	6.5236793756	3.6378698012	-0.8035229412
H41	5.8561701889	4.7107793599	0.4584506826
H42	7.5930199908	4.2901445191	0.4641090513
C42	7.3355775638	1.5607486263	0.8760053308
H43	7.3006059337	1.2388865955	-0.1785506372
H44	8.3539715676	1.9341477672	1.0789609471
H45	7.1613180345	0.6752636007	1.5112732958
C45	6.4628323689	3.1111627926	2.6523009404
H46	7.4907921411	3.4759527970	2.8155166996
H47	5.7737621849	3.9314350983	2.9193357888
H48	6.2930915942	2.2720240662	3.3491547289

Complex 19, gas phase

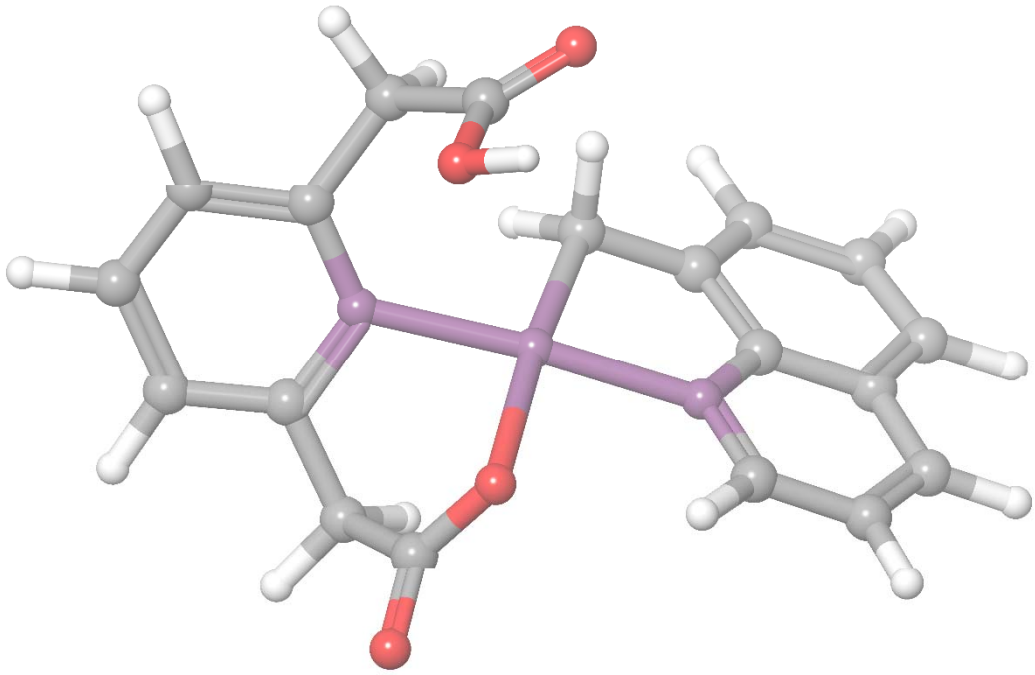
Total Gibbs free energy, Gtot (Htot - T*S): -1347.762765 hartrees

O1	3.4471055623	1.2006055848	-3.1246142840
C2	4.5190766199	1.9280148319	-0.4228355613
C3	3.2852725507	1.3626179967	-0.7369784364
C4	4.8434075437	2.2325089746	0.9230717343
O5	1.5230682656	0.5206676925	-2.1337336920
N6	2.4120607113	1.1088803835	0.2564687911
C7	2.7577926349	1.0133343952	-2.1226795313
C8	3.8770573573	1.9439237183	1.9120701649
C9	2.6500500675	1.3809196024	1.5486136644
H10	5.2027812543	2.1269323865	-1.2530547620
H12	4.0351271040	2.1499515324	2.9729298278
C13	1.4824543751	1.0419850106	2.4669252950
O14	0.4064223615	0.5820579785	1.8406065082
O15	1.5762693617	1.2023795445	3.6841134947
C16	-3.8896351955	0.0533342037	-1.7854317341
C17	-3.5612822898	-0.8600014223	-0.7498363275
Pd18	0.6821445526	0.3923615031	-0.2365767223
C19	-2.8927401107	0.7849249200	-2.4011221703
C20	-2.1810262347	-0.9862423988	-0.3389787491
C21	-4.5640780783	-1.6606684617	-0.1392780042
C22	-1.5725288582	0.6532264728	-1.9257520060
C23	-1.8231235866	-1.9970247921	0.6172060638
N24	-1.2297620979	-0.1586389524	-0.9128577575
C25	-4.2124864816	-2.5889977339	0.8203679241
C26	-0.4026367598	-2.2962328706	1.0174157436
C27	-2.8522690938	-2.7601597132	1.1670241864
H28	-4.9359221731	0.1482031672	-2.0944522134
H29	-3.1003477675	1.4718846380	-3.2245331983
H30	-5.6038176324	-1.5345571928	-0.4571139334
H31	-0.7513134330	1.2204399029	-2.3742817821
H32	-4.9748002157	-3.2132942922	1.2955537026
H33	0.2800330066	-2.2846534375	0.1504037799
H34	-0.3463870492	-3.2908273907	1.4871666990
H35	-2.5848160935	-3.5365818615	1.8914237459
H36	-0.0304379413	-1.5480503481	1.7382883094
C36	6.2016510207	2.8724868717	1.2508206587
C39	6.2955685061	4.2386886785	0.5242002780
H40	6.2073130744	4.1314740517	-0.5690222445
H41	5.5016330413	4.9244856573	0.8632736337
H42	7.2692687168	4.7107544293	0.7382100784

C42	7.3336752775	1.9400379975	0.7508000564
H43	7.2789637790	1.7675377171	-0.3361193111
H44	8.3150438826	2.3936721834	0.9689858547
H45	7.2915366106	0.9593098020	1.2528448829
C45	6.3854788693	3.1028931992	2.7631806288
H46	7.3722887078	3.5575412928	2.9485873638
H47	5.6240158289	3.7874226164	3.1727416831
H48	6.3439555949	2.1579329739	3.3298892941

Complex 11, acetic acid solution

Title: Pd Hpdaa _8 CH2 quinolyl CO trans AcOH



Total Gibbs free energy, Gtot (Htot - T*S): -1269.318179 hartrees

C1	-4.3416700942	-1.4926488736	0.9117847614
C2	-4.3636531826	-2.1961532981	2.1172998083
H3	-5.2675308682	-1.2342512204	0.3891166063
C4	-3.1113642615	-1.1022273482	0.3544530120
C5	-3.1467453267	-2.5243074733	2.7266436886
H6	-5.3144853571	-2.4930197526	2.5729638008
N7	-1.9330912493	-1.3774070237	0.9940192907
C8	-3.0572810385	-0.4127674839	-0.9811034545
Pd9	-0.2561191930	-0.6952526000	-0.0421921029
C10	-1.9385629187	-2.1059980097	2.1473067413
H11	-3.1220742423	-3.0900784466	3.6630129592
C12	-0.6310567960	-2.4126352407	2.8437163010
H13	-2.4901182903	0.5347935314	-0.8904728014
H14	-4.0767252148	-0.1800376371	-1.3244832708
C15	-2.3415345352	-1.2791817834	-2.0786305652
O16	-2.9558456723	-1.5377915241	-3.1308847751
O17	-1.1281427609	-1.6566330662	-1.8004549333
C18	0.4824276878	-3.1121373361	2.0608151927
H19	-0.8459907654	-3.0578011787	3.7152270706
H20	-0.1885479893	-1.4906391667	3.2555578699
O21	1.6727376368	-2.9523770532	2.3137493697

O22	0.0298147749	-3.9901143545	1.1348533874
N23	1.2760525992	0.1077365240	-1.1238225576
C24	1.9870977222	1.0955573014	-0.4708018423
C25	1.5467870256	-0.1784807480	-2.4022176392
C26	3.0011547355	1.8504800899	-1.1425741732
C27	1.6246059030	1.3320945360	0.8816961491
C28	2.5586900451	0.5058345245	-3.1195363320
H29	0.9239922092	-0.9529874393	-2.8595656991
H30	2.7444653410	0.2306880606	-4.1623520266
C31	2.2547719973	2.3854651585	1.5414853551
C32	3.6359266542	2.8996734550	-0.4191711943
C33	3.2800793052	1.5154276360	-2.4985691653
H34	4.0560611270	2.0665307085	-3.0426118680
H35	4.4091687943	3.4989215247	-0.9131522402
C36	3.2526941867	3.1627647036	0.8896105097
C37	0.6242481745	0.3769439834	1.4840056359
H38	3.7311000943	3.9805112997	1.4391022533
H39	-0.1218404587	0.8928007289	2.1165238314
H40	1.9908656403	2.6119749532	2.5816363174
H41	1.1612976083	-0.3657157590	2.1044910074
H42	0.8226956609	-4.3982726911	0.7076117172

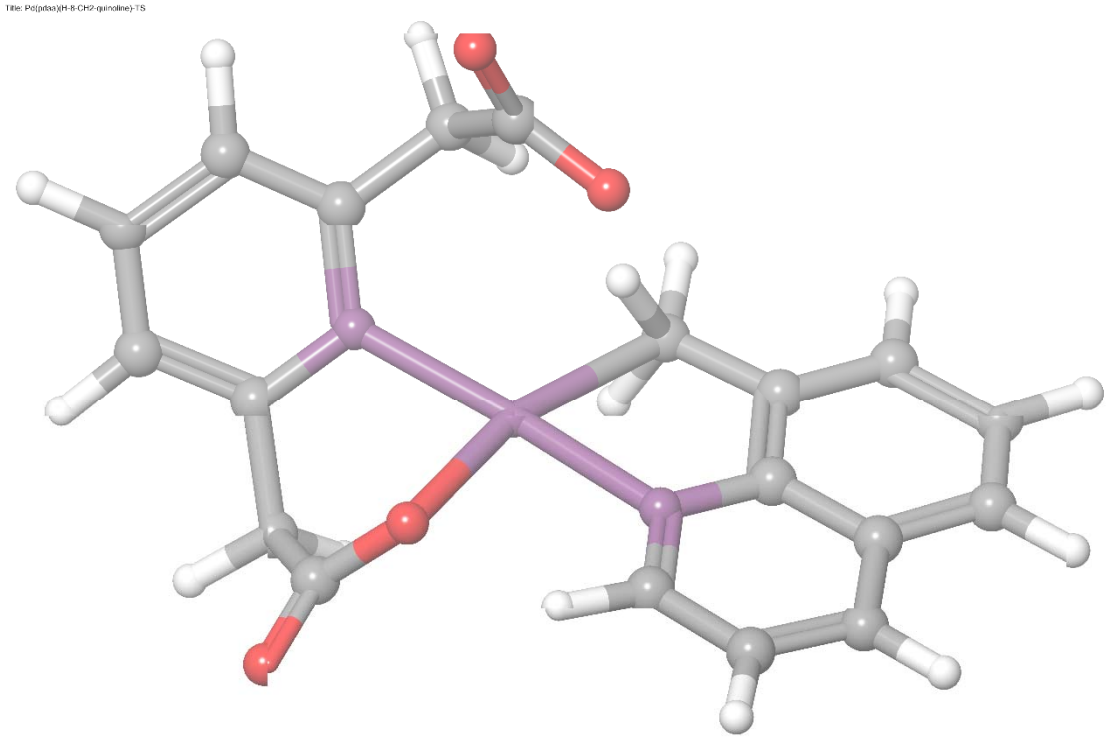
Complex 11, gas phase

Total Gibbs free energy, Gtot (Htot - T*S): -1269.288420 hartrees

C1	-4.1642078191	-2.0267473222	0.7726157042
C2	-3.9936992589	-2.8047061548	1.9178574619
H3	-5.1358312057	-1.9476936763	0.2794080020
C4	-3.0713060842	-1.3263231572	0.2336146894
C5	-2.7202885432	-2.9036619031	2.4874254334
H6	-4.8394434701	-3.3439859737	2.3549058641
N7	-1.8387229481	-1.4040812032	0.8256163000
C8	-3.1920829364	-0.5386391908	-1.0299473122
Pd9	-0.3437694070	-0.3830862903	-0.1886989264
C10	-1.6507899047	-2.2062195888	1.9081260103
H11	-2.5307505587	-3.5306724773	3.3616578379
C12	-0.2424264027	-2.3587547250	2.4526727796
H13	-2.8160035725	0.4894660133	-0.8690791037
H14	-4.2406595057	-0.4880379773	-1.3550599082
C15	-2.3436601700	-1.1521970128	-2.2192516128
O16	-2.9241929021	-1.4011458618	-3.2775837731
O17	-1.0735847567	-1.3202433291	-1.9708428559
C18	0.1876883981	-3.8204140028	2.5009064059
H19	-0.1818961065	-1.9321562731	3.4686164494
H20	0.4510260102	-1.8284638802	1.7825048841
O21	0.7796383675	-4.4185524718	1.6212574539
O22	-0.1816326575	-4.4086147378	3.6820604301
N23	1.1430974768	0.5248561373	-1.2248509070
C24	2.0095346718	1.2769758237	-0.4604214609
C25	1.3709624038	0.3422259040	-2.5278946446
C26	3.1887428793	1.8527388402	-1.0280986858
C27	1.6772583598	1.4024947126	0.9153780413
C28	2.5042716037	0.9067932737	-3.1611120699
H29	0.6323805646	-0.2791208640	-3.0475703273
H30	2.6535975215	0.7332008205	-4.2296493003
C31	2.5855685682	2.0735999916	1.7308325075
C32	4.0719600250	2.5476815685	-0.1562103811
C33	3.4086643521	1.6520767147	-2.4197670785
H34	4.2994568723	2.0812783783	-2.8904473509
H35	4.9892233211	2.9864195141	-0.5611664377
C36	3.7736671441	2.6390588226	1.1955172857
C37	0.3572387989	0.8167397256	1.3443777040
H38	4.4628354207	3.1611246525	1.8666960305
H39	-0.4122496980	1.6131081768	1.3918886429
H40	2.3745892753	2.1779208323	2.8005242365

H41	0.4169434481	0.3623991879	2.3476914909
H42	0.1110726363	-5.3423959381	3.6014868166

TS2, acetic acid solution



Total Gibbs free energy, Gtot (Htot - T*S): -1269.279719 hartrees

C1	-1.3092286603	2.4062406117	-3.7807998715
C2	-1.4434621610	3.6996064367	-3.2653084903
H3	-1.6106791810	2.1665076494	-4.8038073439
C4	-0.7942686034	1.3900228417	-2.9659680420
C5	-0.9977161737	3.9537705805	-1.9685758616
H6	-1.8734752166	4.5011773349	-3.8743044343
N7	-0.4149781226	1.6385475623	-1.6763661457
C8	-0.6894839967	-0.0208686203	-3.4769833000
C9	-0.4576743496	2.9164919906	-1.1862422202
H10	-1.0507098453	4.9570616957	-1.5378581925
C11	0.0828090010	3.2149412849	0.1791869598
H12	0.3110462236	-0.4321076069	-3.2459450351
H13	-0.8376287484	-0.0514516456	-4.5658303549
C14	-1.7450751273	-0.9222999535	-2.8157666661
O15	-2.5106755072	-1.6322736988	-3.4743814075
O16	-1.8051707306	-0.8759320697	-1.4977443526
C17	-0.8620185113	2.7216612267	1.3305354558
H18	0.1819169241	4.3056455981	0.2791268008
H19	1.0840791869	2.7696053927	0.2830834307
O20	-1.8257829320	3.4517247417	1.6312795262
O21	-0.5566694781	1.5825710203	1.8579008902

C22	-0.2066276683	-4.0898807483	2.3177395192
C23	0.8007520433	-3.1021835806	2.4878255124
Pd24	-0.2479911413	-0.0768634431	-0.4558001201
C25	-1.1878338890	-3.9111541461	1.3570159062
C26	0.7652067796	-1.9446875879	1.6385278931
C27	1.8219032665	-3.1924719917	3.4751952502
C28	-1.1687637107	-2.7490210589	0.5542808717
C29	1.7387128226	-0.9151009318	1.7659172569
N30	-0.2309347809	-1.8050368918	0.6901728009
C31	2.7514877189	-2.1737550511	3.6073778409
C32	1.6603244755	0.2530013668	0.8275288056
C33	2.7070418032	-1.0384490289	2.7573411552
H34	-0.1974277173	-4.9805820821	2.9551454659
H35	0.6009622909	0.8375111827	1.0840277409
H36	-1.9825041062	-4.6455142186	1.2018601031
H37	1.8449816061	-4.0681134233	4.1324159216
H38	-1.9189852443	-2.5656402191	-0.2201846146
H39	3.5293148854	-2.2366496012	4.3748580431
H40	1.9878687785	-0.0290476158	-0.1979599377
H41	2.3271308310	1.0847753535	1.1106568644
H42	3.4496990508	-0.2430583995	2.8813984823

TS2, gas phase

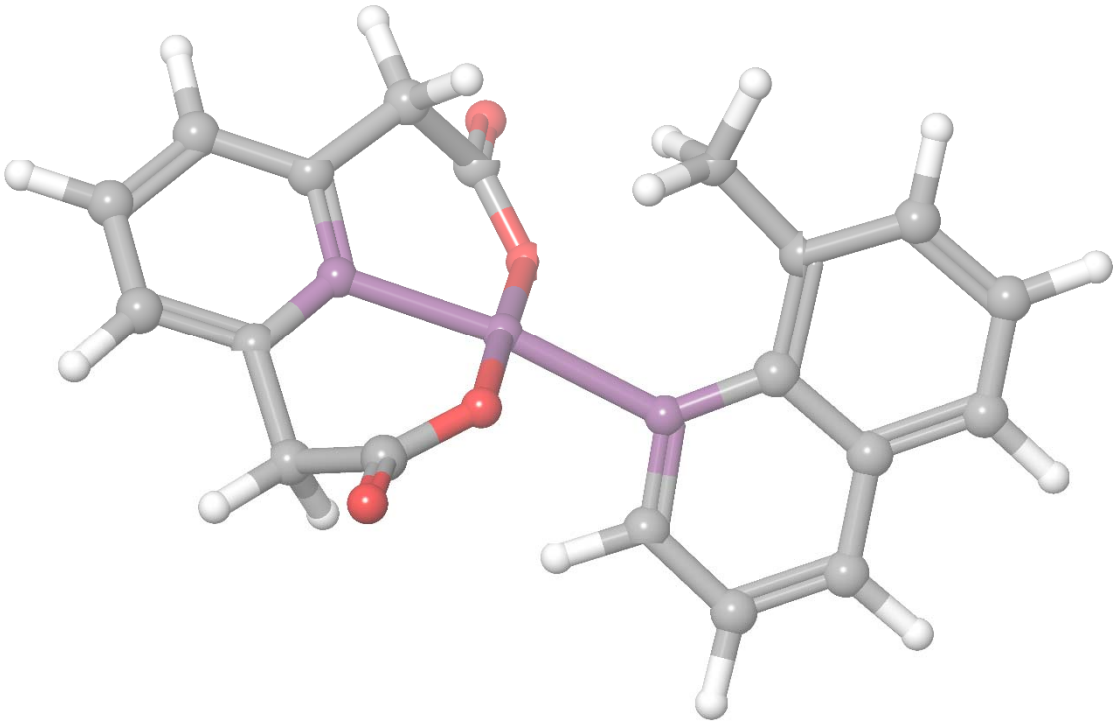
Total Gibbs free energy, Gtot (Htot - T*S): -1269.244655 hartrees

C1	-1.2205868719	2.4089721249	-3.8117117782
C2	-1.3650785227	3.7011778425	-3.2934816519
H3	-1.4794906611	2.1763088050	-4.8469875440
C4	-0.7551807482	1.3843197268	-2.9801855293
C5	-0.9867863193	3.9450763835	-1.9765985893
H6	-1.7544579626	4.5101087691	-3.9188054264
N7	-0.4239914025	1.6299280225	-1.6771709670
C8	-0.6505553319	-0.0280829466	-3.4820959803
C9	-0.4821079882	2.9033351939	-1.1714829632
H10	-1.0612446961	4.9431290705	-1.5392762737
C11	-0.0106550672	3.1882723273	0.2123762349
H12	0.3450720722	-0.4408441922	-3.2339084609
H13	-0.7865950405	-0.0663073899	-4.5719286124
C14	-1.7167854748	-0.9369338089	-2.8345593322
O15	-2.4728024314	-1.6422989673	-3.4968382925
O16	-1.7769375860	-0.8955776563	-1.5115174389
C17	-0.9751775989	2.6126049825	1.3542287375
H18	0.0339835462	4.2774953622	0.3505116995
H19	1.0037538670	2.7787111315	0.3462897295
O20	-1.9069254677	3.3429842409	1.7026912305
O21	-0.6555932856	1.4326583617	1.7705168766
C22	-0.2232341066	-4.0236816313	2.3507183752
C23	0.8206739315	-3.0701601624	2.4853694557
Pd24	-0.2633218508	-0.0497426350	-0.4539733062
C25	-1.2257755926	-3.8205297982	1.4197163865
C26	0.7977496739	-1.9159935160	1.6300865165
C27	1.8636275467	-3.1953184778	3.4436665322
C28	-1.1919103139	-2.6669796500	0.6062508557
C29	1.8075180702	-0.9150562272	1.7367902540
N30	-0.2181515862	-1.7572372286	0.7063367356
C31	2.8310302182	-2.2109673927	3.5482821114
C32	1.7306011891	0.2808271337	0.8405709999
C33	2.7981355886	-1.0772099407	2.7003041011
H34	-0.2233801793	-4.9079701248	2.9958920003
H35	0.6921549292	0.8371044946	1.1053431456
H36	-2.0470576890	-4.5299207605	1.2958469315
H37	1.8738051740	-4.0696254749	4.1015747369
H38	-1.9490240962	-2.4606272515	-0.1573655753
H39	3.6270238199	-2.3006256363	4.2932142596
H40	1.9708149164	0.0141414605	-0.2144371180

H41	2.4521961730	1.0693630277	1.1094804664
H42	3.5668622137	-0.3045352935	2.8039987371

Complex 20, acetic acid solution

Title: Pd(pdaa)(N-8-Me-quinoline)



Total Gibbs free energy, Gtot (Htot - T*S): -1269.325140 hartrees

C1	-4.3961128073	0.4589169624	-1.6840433014
C2	-5.1051580069	-0.7043955542	-1.3712994204
H3	-4.8757483838	1.2954067012	-2.1990824777
C4	-3.0445575136	0.5625310815	-1.3222216172
C5	-4.4459426943	-1.7532382320	-0.7214099237
H6	-6.1632070418	-0.7956706511	-1.6366052643
N7	-2.4218262522	-0.4726747047	-0.6949933477
C8	-2.2346159791	1.7937699325	-1.6088708027
Pd9	-0.4444758170	-0.3318789245	-0.2215120358
C10	-3.0859221938	-1.6257823282	-0.4042501850
H11	-4.9670572082	-2.6803068533	-0.4686045653
C12	-2.3144841234	-2.7461274446	0.2355669279
H13	-1.9133438873	2.2434949604	-0.6489005062
H14	-2.8484938378	2.5322916847	-2.1441106545
C15	-0.9687613226	1.5170669188	-2.4539253932
O16	-0.8031024186	2.1044354787	-3.5314695499
O17	-0.0833899968	0.6752881681	-1.9699995521
C18	-1.6142797269	-2.3567680876	1.5562978267
H19	-1.5329068315	-3.0872678569	-0.4721538296
H20	-2.9829143659	-3.5956077385	0.4374450624
O21	-1.8411769567	-2.9943440181	2.5926481836

O22	-0.7631235627	-1.3562425796	1.5190674416
N23	1.6278408707	-0.4831944729	0.2046245059
C24	2.6056868805	0.4719014829	0.4464626228
C25	1.9674311183	-1.7808751810	0.1425394200
C26	3.9851740372	0.0437837861	0.5656259972
C27	2.2988155686	1.8678136053	0.6086838281
C28	3.2849641544	-2.2588962097	0.2807716362
H29	1.1502476311	-2.4853707148	-0.0305365574
H30	3.4746553486	-3.3335943028	0.2196338598
C31	3.3576464538	2.7506720094	0.8203946008
C32	5.0194031341	0.9970226667	0.7789880661
C33	4.2964897192	-1.3376347429	0.4791340125
H34	5.3408140329	-1.6530357767	0.5792746327
H35	6.0528578847	0.6413545161	0.8559151703
C36	4.7091962769	2.3385319434	0.8914083923
C37	0.9029901683	2.4309466756	0.5652603306
H38	5.4966595113	3.0831501941	1.0522148050
H39	0.8859298717	3.4362520598	1.0146401392
H40	3.1235256136	3.8140686781	0.9416138641
H41	0.1790150767	1.7962606836	1.1054980942
H42	0.5536849013	2.5179539953	-0.4761061298

Complex 20, gas phase

Total Gibbs free energy, Gtot (Htot - T*S): -1269.293290 hartrees

C1	-4.2554213750	0.4995322527	-1.8764065914
C2	-5.0192928199	-0.6380661622	-1.6027138507
H3	-4.6706770859	1.3425879798	-2.4332009405
C4	-2.9316678261	0.5742523167	-1.4154254352
C5	-4.4414984509	-1.6961418292	-0.8955897109
H6	-6.0572332506	-0.7015291875	-1.9428087434
N7	-2.3868496351	-0.4723814212	-0.7357095274
C8	-2.0765373925	1.7820570979	-1.6458800521
Pd9	-0.4501824951	-0.3740428919	-0.1094381489
C10	-3.1019209148	-1.6049025377	-0.4854676052
H11	-5.0043302758	-2.6046753152	-0.6708017132
C12	-2.4072576811	-2.7378550504	0.2080900255
H13	-1.8351159530	2.2332371300	-0.6645037154
H14	-2.6240471051	2.5276123044	-2.2392345032
C15	-0.7287632715	1.4939742012	-2.3791431460
O16	-0.4718118592	2.0856292205	-3.4269204166
O17	0.0954969542	0.6485473292	-1.7976679467
C18	-1.7791405735	-2.3784821705	1.5881279235
H19	-1.5868687906	-3.0927435264	-0.4454397468
H20	-3.1058699692	-3.5712198992	0.3663104739
O21	-2.0997345525	-3.0175422338	2.5889038853
O22	-0.8819242662	-1.4149023647	1.5948497056
N23	1.5893509331	-0.5151572526	0.4106159433
C24	2.5552036890	0.4747812761	0.4492904511
C25	1.9565786891	-1.8036119155	0.3977719783
C26	3.9467432932	0.1054002038	0.3236814514
C27	2.2163177623	1.8518785121	0.6698568714
C28	3.2981783174	-2.2298558124	0.3257262870
H29	1.1405072654	-2.5283772516	0.4416831556
H30	3.5222792983	-3.2986859760	0.3086930250
C31	3.2499064495	2.7861123983	0.6647157567
C32	4.9531460943	1.1088139512	0.3090685800
C33	4.2882311043	-1.2699023613	0.2484819931
H34	5.3425378311	-1.5488036818	0.1511272351
H35	5.9978674674	0.8036881768	0.1938383351
C36	4.6047158595	2.4359231149	0.4610780225
C37	0.8140743928	2.3232207883	0.9526203399
H38	5.3707004230	3.2166769521	0.4548774308
H39	0.8388445790	3.3057062369	1.4499739706
H40	2.9955858280	3.8366129610	0.8408946873

H41	0.2594451536	1.6200224734	1.5956023842
H42	0.2504084446	2.4313759269	0.0129418190

3. Crystal structure determination for 12

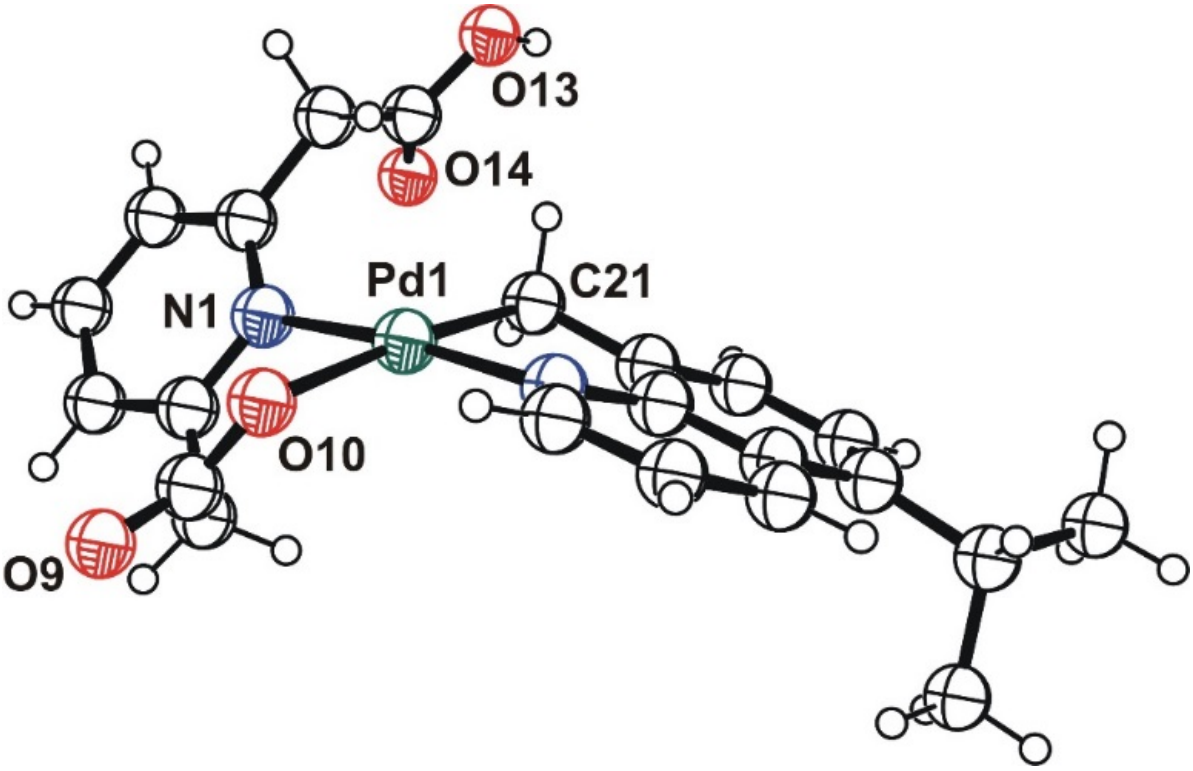


Fig. S1. ORTEP drawing with 50% probability ellipsoids for **12**. The conformer with a facial arrangement of the ligand donor atoms.

A colorless prism of $2[C_{22}H_{22}N_2O_4Pd]\cdot C_4H_{10}O\cdot\sim 4C_2H_4O_2$, approximate dimensions 0.16× 0.255× 0.33 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 100(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ= 0.71073 Å) . The detector was placed at a distance of 5.000 cm from the crystal.

A total of 2730 frames were collected with a scan width of -0.30° an exposure time of 25 sec/frame using Apex2 (Bruker, 2010). The total data collection time was 23.5 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 30216 reflections to a maximum θ angle of 25.00°, of which 10144 were independent (completeness = 99.9%, R_{int} = 2.88%, R_{sig} = 2.88%) and 8301 were greater than 2σ(I). The final cell dimensions of a = 13.4534(17) Å, b = 15.2917(19) Å, c = 15.3176(19) Å, α = 111.3499(19)°, β = 92.9602(19)°, γ = 98.317(2)°, V = 2885.4(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 16576 reflections with 2.2 < θ < 28.3° using Apex2 software. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 2008). The minimum and maximum transmission coefficients were 0.771 and 0.895.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 2008) and SHELXL-97 (Sheldrick, 2008) software in the space group *P-1* with Z = 2 for the formula unit $2[C_{22}H_{22}N_2O_4Pd]\cdot C_4H_{10}O\cdot\sim 4C_2H_4O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 815 variables converged at R_1 = 5.99 % for the observed data and wR_2 = 12.74 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 1.408 $\bar{e}/Å^3$ and the largest

hole was -0.877 $\bar{e}/Å^3$. On the basis of the final model, the calculated density was 1.478 g/cm^3 and F(000), 1324 $\bar{e}$.

Comments:

Disorder: substantial - 1 of 2 symmetrically independent Pd-complexes shows whole-molecule-disorder assuming 2 alternative orientations in about 2:1 ratio; of 4 CH_3COOH molecules one is also disordered in 2 orientation and one shows much more complex disorder around the inversion center and was approximately modeled with a group of carbon atoms with variable occupation factor
s.

- H-atoms: constrained geometry as riding on attached atom (A)
$U_{iso}(H)=1.5U_{iso}(A)$ for CH_3 and $1.2U_{iso}(A)$ for other groups

- Residual density: near heavy atoms and near disordered groups
- Structure quality: good to average due to substantial disorder

Table 1. Crystal data and structure refinement for UM#2004.

X-ray lab book No.		2004
Crystal ID		Vedern/Wang wdy-1 in HAc Et2O 100K
Empirical formula		$2[C_{22}H_{22}N_2O_4Pd]\cdot C_4H_{10}O\cdot\sim 4C_2H_4O_2$
Formula weight		1283.96
Temperature		100(2) K
Wavelength		0.71073 Å
Crystal size		0.33× 0.255× 0.16 mm^3
Crystal habit		colorless prism
Crystal system		Triclinic
Space group		P-1
Unit cell dimensions		a = 13.4534(17) Å α = 111.3499(19)°
		b = 15.2917(19) Å β = 92.9602(19)°
		c = 15.3176(19) Å γ = 98.317(2)°
Volume		2885.4(6) $Å^3$
Z		2
Density, ρ_{calc}		1.478 g/cm^3
Absorption coefficient, μ		0.696 mm^{-1}
F(000)		1324 $\bar{e}$
Diffractometer		Bruker Smart Apex II CCD area detector
Radiation source		fine-focus sealed tube, MoKα
Detector distance		5.000 cm
Data collection method		ω and scans
Total frames		2730
Frame size		512 pixels
Frame width		-0.30°
Exposure per frame		25 sec
Total measurement time		23.5 hours
θ range for data collection		2.17 to 25.00°
Index ranges		$-15 \le h \le 15$, $-18 \le k \le 18$, $-18 \le l \le 18$
Reflections collected		30216
Independent reflections		10144
Observed reflection, I>2σ(I)		8301
Coverage of independent reflections		99.9 %
Variation in check reflections		0 %
Absorption correction		Semi-empirical from equivalents SADABS (Sheldrick, 2008)
Max. and min. transmission		0.895 and 0.771
Structure solution technique		direct
Structure solution program		SHELXS-97 (Sheldrick, 2008)
Refinement technique		Full-matrix least-squares on F^2
Refinement program		SHELXL-97 (Sheldrick, 2008)
Function minimized		$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters		10144 / 563 / 815
Goodness-of-fit on F^2		1.239
Δ/σ_{max}		0.001
Final R indices:	R_1, I>2σ(I)	0.0599
	wR_2, all data	0.1274
	R_{int}	0.0288
	R_{sig}	0.0288
Weighting scheme		$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 18P]$, $P = [\max(F_o^2, 0) + 2F_o^2]/3$
Largest diff. peak and hole		1.408 and -0.877 $\bar{e}/Å^3$

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table 2. Atomic coordinates and equivalent* isotropic atomic displacement parameters ($Å^2$) for UM#2004.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Pd1	0.41086(4)	0.50046(4)	0.25414(3)	0.04056(16)
N1A	0.4375(4)	0.5627(4)	0.3985(3)	0.0480(15)
C2A	0.3546(5)	0.5657(6)	0.4441(4)	0.054(2)
C3A	0.3609(6)	0.6065(6)	0.5421(4)	0.066(2)
C4A	0.4532(6)	0.6463(7)	0.5937(5)	0.072(3)
C5A	0.5384(6)	0.6455(6)	0.5486(4)	0.065(2)
C6A	0.5295(5)	0.6031(5)	0.4503(4)	0.052(2)
C7A	0.2553(5)	0.5177(6)	0.3861(5)	0.060(2)
C8A	0.2535(5)	0.4127(6)	0.3336(5)	0.063(2)
O9A	0.1895(4)	0.3556(5)	0.3506(4)	0.086(2)
O10A	0.3181(3)	0.3848(4)	0.2768(3)	0.0544(14)
C11A	0.6236(5)	0.5990(5)	0.4013(5)	0.056(2)
C12A	0.6656(5)	0.6908(6)	0.3911(5)	0.059(2)
O13A	0.7388(4)	0.6793(4)	0.3345(3)	0.0648(16)
O14A	0.6380(4)	0.7656(4)	0.4291(4)	0.0683(17)
N15A	0.3708(4)	0.4446(4)	0.1129(3)	0.0389(13)
C16A	0.3230(5)	0.3582(5)	0.0627(4)	0.0457(17)
C17A	0.2849(5)	0.3317(5)	-0.0326(4)	0.0528(19)
C18A	0.2949(5)	0.3984(5)	-0.0731(4)	0.0502(19)
C19A	0.3452(4)	0.4914(5)	-0.0218(4)	0.0422(16)
C20A	0.3863(4)	0.5123(4)	0.0724(4)	0.0375(14)
C22A	0.4412(5)	0.6004(4)	0.1304(4)	0.0395(15)
C23A	0.4543(5)	0.6716(5)	0.0948(4)	0.0479(17)
C24A	0.4119(5)	0.6546(5)	0.0031(4)	0.0503(18)
C25A	0.3587(5)	0.5689(5)	-0.0551(4)	0.0488(18)
C26A	0.3042(5)	0.5545(7)	-0.1505(5)	0.064(2)
C27A	0.1954(6)	0.5689(10)	-0.1397(7)	0.102(4)
C28A	0.3566(6)	0.6210(7)	-0.1955(5)	0.068(2)
C21A	0.4860(5)	0.6092(5)	0.2259(4)	0.0446(16)
Pd2	0.9518(5)	0.0695(4)	0.7907(5)	0.0412(6)
N1B	0.8884(11)	0.0941(10)	0.6636(10)	0.038(2)
C2B	0.9632(13)	0.1488(15)	0.6406(11)	0.049(3)
C3B	0.9594(16)	0.1464(15)	0.5484(11)	0.051(3)
C4B	0.8900(16)	0.0788(14)	0.4802(11)	0.053(3)
C5B	0.8226(16)	0.0163(14)	0.5027(11)	0.053(3)
C6B	0.8302(18)	0.0188(13)	0.5950(11)	0.049(3)
C7B	1.0540(12)	0.2017(11)	0.7108(15)	0.055(2)
C8B	1.1276(11)	0.1377(14)	0.7184(16)	0.041(3)
O9B	1.1018(12)	0.0713(10)	0.7481(11)	0.040(2)

O10B	1.2205(11)	0.1604(12)	0.7104(16)	0.042(2)
C11B	0.7584(13)	-0.0484(11)	0.6223(15)	0.054(2)
C12B	0.7950(9)	-0.1357(9)	0.6219(8)	0.048(3)
O13B	0.7491(13)	-0.1673(11)	0.6829(11)	0.051(2)
O14B	0.8568(11)	-0.1746(11)	0.5741(10)	0.069(2)
N15B	1.0020(11)	0.0905(18)	0.9239(10)	0.038(2)
C16B	1.0962(12)	0.093(2)	0.9533(12)	0.046(3)
C17B	1.1273(12)	0.118(2)	1.0502(12)	0.047(3)
C18B	1.0610(11)	0.1508(18)	1.1147(11)	0.046(3)
C19B	0.9597(10)	0.148(2)	1.0865(8)	0.041(2)
C20B	0.9313(11)	0.114(2)	0.9872(9)	0.037(2)
C22B	0.8330(11)	0.104(2)	0.9484(10)	0.038(3)
C23B	0.7643(11)	0.1439(15)	1.0086(9)	0.043(3)
C24B	0.7891(11)	0.1770(13)	1.1071(9)	0.046(2)
C25B	0.8829(11)	0.1814(12)	1.1469(8)	0.044(2)
C26B	0.9083(12)	0.2158(12)	1.2541(8)	0.052(2)
C27B	0.9106(17)	0.1318(13)	1.2836(13)	0.068(3)
C28B	0.8353(16)	0.2791(13)	1.3075(12)	0.061(3)
C21B	0.812(2)	0.0603(18)	0.8405(19)	0.052(3)
Pd2X	0.9344(3)	0.0911(3)	0.7996(3)	0.0412(6)
N1X	0.8963(7)	0.0600(6)	0.6535(6)	0.038(2)
C2X	0.9579(10)	0.1200(9)	0.6242(7)	0.049(3)
C3X	0.9462(10)	0.1082(9)	0.5292(7)	0.051(3)
C4X	0.8733(10)	0.0378(9)	0.4684(7)	0.053(3)
C5X	0.8136(10)	-0.0228(9)	0.4993(7)	0.053(3)
C6X	0.8256(11)	-0.0098(8)	0.5944(7)	0.049(3)
C7X	1.0322(9)	0.2021(8)	0.6945(9)	0.055(2)
C8X	1.1156(8)	0.1654(8)	0.7339(9)	0.041(3)
O9X	1.0941(7)	0.1024(6)	0.7690(6)	0.040(2)
O10X	1.2065(7)	0.1906(7)	0.7228(9)	0.042(2)
C11X	0.7632(8)	-0.0774(8)	0.6290(9)	0.054(2)
C12X	0.8214(7)	-0.1461(6)	0.6449(5)	0.048(3)
O13X	0.7700(8)	-0.2014(7)	0.6836(7)	0.051(2)
O14X	0.9056(7)	-0.1533(7)	0.6265(7)	0.069(2)
N15X	0.9814(7)	0.1117(10)	0.9357(6)	0.038(2)
C16X	1.0735(8)	0.1131(12)	0.9699(8)	0.046(3)
C17X	1.0984(8)	0.1318(12)	1.0668(8)	0.047(3)
C18X	1.0237(7)	0.1429(11)	1.1252(7)	0.046(3)
C19X	0.9244(7)	0.1404(12)	1.0913(6)	0.041(2)
C20X	0.9047(7)	0.1251(14)	0.9938(6)	0.037(2)
C22X	0.8097(7)	0.1199(12)	0.9505(7)	0.038(3)
C23X	0.7297(8)	0.1198(9)	1.0034(6)	0.043(3)
C24X	0.7464(8)	0.1351(9)	1.0996(6)	0.046(2)
C25X	0.8389(7)	0.1458(8)	1.1450(6)	0.044(2)

C26X	0.8567(9)	0.1687(8)	1.2512(6)	0.052(2)
C27X	0.7605(9)	0.1443(10)	1.2912(9)	0.068(3)
C28X	0.9004(10)	0.2748(8)	1.3021(8)	0.061(3)
C21X	0.8010(13)	0.0967(11)	0.8457(12)	0.052(3)
O1C	0.1465(5)	0.5522(5)	0.1895(5)	0.0857(19)
C11C	0.1773(9)	0.6448(9)	0.1801(9)	0.105(4)
C12C	0.2330(9)	0.7120(8)	0.2704(9)	0.102(4)
C21C	0.0938(7)	0.4804(8)	0.1048(7)	0.087(3)
C22C	0.0694(7)	0.3899(8)	0.1186(7)	0.086(3)
O1D	0.3437(9)	0.0878(8)	0.7375(8)	0.103(3)
O2D	0.3137(8)	0.1119(7)	0.8867(7)	0.089(3)
C1D	0.3566(15)	0.0760(11)	0.8206(13)	0.088(4)
C2D	0.4363(16)	0.0190(15)	0.8185(13)	0.124(5)
O3D	0.4929(18)	0.090(2)	0.8586(17)	0.103(3)
O4D	0.3386(18)	0.120(2)	0.8285(19)	0.089(3)
C3D	0.417(2)	0.100(3)	0.804(2)	0.088(4)
C4D	0.450(3)	0.092(3)	0.711(2)	0.124(5)
O1E	0.9415(6)	0.6275(7)	0.5197(6)	0.136(3)
O2E	0.8348(5)	0.5153(5)	0.4159(4)	0.0837(19)
C1E	0.9157(6)	0.5655(7)	0.4369(6)	0.068(2)
C2E	0.9923(7)	0.5651(8)	0.3704(7)	0.089(3)
O1F	0.3499(8)	0.1192(7)	0.0500(7)	0.149(4)
O2F	0.5110(7)	0.1423(7)	0.0597(7)	0.125(3)
C1F	0.4372(8)	0.1385(8)	0.0983(8)	0.085(3)
C2F	0.4305(11)	0.1503(11)	0.1950(9)	0.134(5)
C1G	0.474(2)	1.006(3)	0.489(3)	0.132(5)
C2G	0.617(3)	1.152(2)	0.536(2)	0.132(5)
C3G	0.430(3)	0.849(3)	0.521(3)	0.132(5)
C4G	0.448(2)	0.787(2)	0.456(2)	0.132(5)
C5G	0.451(2)	0.906(2)	0.425(2)	0.132(5)
C6G	0.500(3)	0.886(2)	0.596(3)	0.132(5)
C7G	0.447(3)	0.935(3)	0.549(3)	0.132(5)
C8G	0.681(3)	1.162(3)	0.464(3)	0.132(5)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Bond lengths (Å) and angles (°) for UM#2004.

Pd1-C21A	2.014(6)	Pd1-N15A	2.025(5)
Pd1-N1A	2.052(5)	Pd1-O10A	2.159(4)
N1A-C2A	1.344(7)	N1A-C6A	1.365(7)
C2A-C3A	1.393(8)	C2A-C7A	1.493(8)
C3A-C4A	1.365(9)	C3A-H3A	0.9500
C4A-C5A	1.368(9)	C4A-H4A	0.9500
C5A-C6A	1.396(8)	C5A-H5A	0.9500
C6A-C11A	1.502(8)	C7A-C8A	1.508(10)
C7A-H7A1	0.9900	C7A-H7A2	0.9900
C8A-O9A	1.241(7)	C8A-O10A	1.269(8)
C11A-C12A	1.501(9)	C11A-H11A	0.9900
C11A-H11B	0.9900	C12A-O14A	1.203(8)
C12A-O13A	1.334(8)	O13A-H13A	0.8400
N15A-C16A	1.310(7)	N15A-C20A	1.384(7)
C16A-C17A	1.411(8)	C16A-H16A	0.9500
C17A-C18A	1.370(9)	C17A-H17A	0.9500
C18A-C19A	1.396(8)	C18A-H18A	0.9500
C19A-C20A	1.422(7)	C19A-C25A	1.445(8)
C20A-C22A	1.387(8)	C22A-C23A	1.379(8)
C22A-C21A	1.505(8)	C23A-C24A	1.404(8)
C23A-H23A	0.9500	C24A-C25A	1.355(9)
C24A-H24A	0.9500	C25A-C26A	1.527(8)
C26A-C27A	1.520(10)	C26A-C28A	1.536(9)
C26A-H26A	1.0000	C27A-H27A	0.9800
C27A-H27B	0.9800	C27A-H27C	0.9800
C28A-H28A	0.9800	C28A-H28B	0.9800
C28A-H28C	0.9800	C21A-H21A	0.9900
C21A-H21B	0.9900	Pd2-N15B	2.010(16)
Pd2-C21B	2.07(3)	Pd2-O9B	2.152(17)
Pd2-N1B	2.261(16)	N1B-C6B	1.348(10)
N1B-C2B	1.358(10)	C2B-C3B	1.398(11)
C2B-C7B	1.499(11)	C3B-C4B	1.365(12)
C3B-H3B	0.9500	C4B-C5B	1.370(12)
C4B-H4B	0.9500	C5B-C6B	1.398(11)
C5B-H5B	0.9500	C6B-C11B	1.494(11)
C7B-C8B	1.518(12)	C7B-H7C	0.9900
C7B-H7D	0.9900	C8B-O9B	1.269(10)
C8B-O10B	1.272(10)	C11B-C12B	1.487(12)
C11B-H11C	0.9900	C11B-H11D	0.9900
C12B-O14B	1.212(11)	C12B-O13B	1.339(10)
O13B-H13B	0.8400	N15B-C16B	1.312(11)
N15B-C20B	1.384(10)	C16B-C17B	1.415(11)

C16B-H16B	0.9500	C17B-C18B	1.371(12)
C17B-H17B	0.9500	C18B-C19B	1.398(11)
C18B-H18B	0.9500	C19B-C20B	1.428(10)
C19B-C25B	1.446(11)	C20B-C22B	1.386(11)
C22B-C23B	1.383(11)	C22B-C21B	1.53(3)
C23B-C24B	1.410(11)	C23B-H23C	0.9500
C24B-C25B	1.355(12)	C24B-H24C	0.9500
C25B-C26B	1.532(11)	C26B-C27B	1.513(13)
C26B-C28B	1.534(12)	C26B-H26C	1.0000
C27B-H27D	0.9800	C27B-H27E	0.9800
C27B-H27F	0.9800	C28B-H28D	0.9800
C28B-H28E	0.9800	C28B-H28F	0.9800
C21B-H21C	0.9900	C21B-H21D	0.9900
Pd2X-C21X	1.965(18)	Pd2X-N15X	2.044(10)
Pd2X-N1X	2.129(10)	Pd2X-O9X	2.218(10)
N1X-C6X	1.333(9)	N1X-C2X	1.359(9)
C2X-C3X	1.398(10)	C2X-C7X	1.509(10)
C3X-C4X	1.363(11)	C3X-H3X	0.9500
C4X-C5X	1.369(11)	C4X-H4X	0.9500
C5X-C6X	1.393(10)	C5X-H5X	0.9500
C6X-C11X	1.499(10)	C7X-C8X	1.517(11)
C7X-H7E	0.9900	C7X-H7F	0.9900
C8X-O10X	1.267(9)	C8X-O9X	1.271(9)
C11X-C12X	1.476(11)	C11X-H11E	0.9900
C11X-H11F	0.9900	C12X-O14X	1.193(10)
C12X-O13X	1.335(9)	O13X-H13X	0.8400
N15X-C16X	1.314(9)	N15X-C20X	1.386(9)
C16X-C17X	1.417(10)	C16X-H16X	0.9500
C17X-C18X	1.367(11)	C17X-H17X	0.9500
C18X-C19X	1.398(10)	C18X-H18X	0.9500
C19X-C20X	1.428(9)	C19X-C25X	1.444(10)
C20X-C22X	1.388(9)	C22X-C23X	1.381(10)
C22X-C21X	1.507(19)	C23X-C24X	1.407(10)
C23X-H23X	0.9500	C24X-C25X	1.351(11)
C24X-H24X	0.9500	C25X-C26X	1.533(10)
C26X-C27X	1.516(12)	C26X-C28X	1.530(11)
C26X-H26X	1.0000	C27X-H27G	0.9800
C27X-H27H	0.9800	C27X-H27I	0.9800
C28X-H28G	0.9800	C28X-H28H	0.9800
C28X-H28I	0.9800	C21X-H21E	0.9900
C21X-H21F	0.9900	O1C-C21C	1.427(11)
O1C-C11C	1.477(12)	C11C-C12C	1.472(15)
C11C-H11G	0.9900	C11C-H11H	0.9900
C12C-H12A	0.9800	C12C-H12B	0.9800

C12C-H12C	0.9800	C21C-C22C	1.469(14)
C21C-H21G	0.9900	C21C-H21H	0.9900
C22C-H22E	0.9800	C22C-H22F	0.9800
C22C-H22G	0.9800	O1D-C1D	1.36(2)
O1D-H1D	0.8400	O2D-C1D	1.187(19)
C1D-C2D	1.47(2)	C2D-H2D1	0.9800
C2D-H2D2	0.9800	C2D-H2D3	0.9800
O3D-C3D	1.35(2)	O3D-H3D	0.8400
O4D-C3D	1.19(2)	C3D-C4D	1.47(2)
C4D-H4D1	0.9800	C4D-H4D2	0.9800
C4D-H4D3	0.9800	O1E-C1E	1.270(11)
O1E-H1E	0.8400	O2E-C1E	1.191(10)
C1E-C2E	1.485(11)	C2E-H2E1	0.9800
C2E-H2E2	0.9800	C2E-H2E3	0.9800
O1F-C1F	1.291(12)	O1F-H1F	0.8400
O2F-C1F	1.186(12)	C1F-C2F	1.434(15)
C2F-H2F1	0.9800	C2F-H2F2	0.9800
C2F-H2F3	0.9800	C1G-C1G#1	0.83(5)
C1G-C5G	1.46(5)	C1G-C7G#1	1.55(5)
C1G-C5G#1	1.66(5)	C1G-C7G	1.67(6)
C2G-C3G#1	1.05(4)	C2G-C4G#1	1.35(4)
C2G-C5G#1	1.47(4)	C2G-C8G	1.49(5)
C2G-C7G#1	1.58(5)	C3G-C2G#1	1.05(4)
C3G-C4G	1.16(4)	C3G-C7G	1.21(5)
C3G-C6G	1.34(4)	C3G-C8G#1	1.52(5)
C3G-C5G	1.98(5)	C4G-C2G#1	1.35(4)
C4G-C5G	2.04(5)	C5G-C2G#1	1.47(4)
C5G-C1G#1	1.66(5)	C5G-C7G	1.78(5)
C6G-C7G	1.45(5)	C7G-C1G#1	1.55(5)
C7G-C2G#1	1.58(5)	C8G-C3G#1	1.52(5)

C21A-Pd1-N15A	82.9(2)	C21A-Pd1-N1A	97.4(2)
N15A-Pd1-N1A	173.9(2)	C21A-Pd1-O10A	174.7(2)
N15A-Pd1-O10A	93.63(18)	N1A-Pd1-O10A	85.60(19)
C2A-N1A-C6A	118.5(5)	C2A-N1A-Pd1	115.2(4)
C6A-N1A-Pd1	126.2(4)	N1A-C2A-C3A	121.6(6)
N1A-C2A-C7A	117.4(5)	C3A-C2A-C7A	120.8(6)
C4A-C3A-C2A	119.6(6)	C4A-C3A-H3A	120.2
C2A-C3A-H3A	120.2	C3A-C4A-C5A	119.7(6)
C3A-C4A-H4A	120.2	C5A-C4A-H4A	120.2
C4A-C5A-C6A	119.2(6)	C4A-C5A-H5A	120.4
C6A-C5A-H5A	120.4	N1A-C6A-C5A	121.3(6)
N1A-C6A-C11A	119.6(5)	C5A-C6A-C11A	119.1(6)
C2A-C7A-C8A	111.4(6)	C2A-C7A-H7A1	109.3

C8A-C7A-H7A1	109.3	C2A-C7A-H7A2	109.3
C8A-C7A-H7A2	109.3	H7A1-C7A-H7A2	108.0
O9A-C8A-O10A	121.9(8)	O9A-C8A-C7A	117.8(7)
O10A-C8A-C7A	120.3(6)	C8A-O10A-Pd1	112.9(5)
C12A-C11A-C6A	113.6(6)	C12A-C11A-H11A	108.8
C6A-C11A-H11A	108.8	C12A-C11A-H11B	108.8
C6A-C11A-H11B	108.8	H11A-C11A-H11B	107.7
O14A-C12A-O13A	123.7(7)	O14A-C12A-C11A	125.0(6)
O13A-C12A-C11A	111.3(7)	C12A-O13A-H13A	109.5
C16A-N15A-C20A	120.1(5)	C16A-N15A-Pd1	126.7(4)
C20A-N15A-Pd1	112.7(4)	N15A-C16A-C17A	121.6(6)
N15A-C16A-H16A	119.2	C17A-C16A-H16A	119.2
C18A-C17A-C16A	119.5(6)	C18A-C17A-H17A	120.3
C16A-C17A-H17A	120.3	C17A-C18A-C19A	120.5(6)
C17A-C18A-H18A	119.7	C19A-C18A-H18A	119.7
C18A-C19A-C20A	117.2(5)	C18A-C19A-C25A	126.1(5)
C20A-C19A-C25A	116.7(5)	N15A-C20A-C22A	115.6(5)
N15A-C20A-C19A	120.9(5)	C22A-C20A-C19A	123.5(5)
C23A-C22A-C20A	117.8(5)	C23A-C22A-C21A	125.1(6)
C20A-C22A-C21A	117.1(5)	C22A-C23A-C24A	120.4(6)
C22A-C23A-H23A	119.8	C24A-C23A-H23A	119.8
C25A-C24A-C23A	122.9(6)	C25A-C24A-H24A	118.5
C23A-C24A-H24A	118.5	C24A-C25A-C19A	118.7(5)
C24A-C25A-C26A	122.0(6)	C19A-C25A-C26A	119.0(6)
C27A-C26A-C25A	109.8(6)	C27A-C26A-C28A	109.8(7)
C25A-C26A-C28A	112.8(6)	C27A-C26A-H26A	108.1
C25A-C26A-H26A	108.1	C28A-C26A-H26A	108.1
C26A-C27A-H27A	109.5	C26A-C27A-H27B	109.5
H27A-C27A-H27B	109.5	C26A-C27A-H27C	109.5
H27A-C27A-H27C	109.5	H27B-C27A-H27C	109.5
C26A-C28A-H28A	109.5	C26A-C28A-H28B	109.5
H28A-C28A-H28B	109.5	C26A-C28A-H28C	109.5
H28A-C28A-H28C	109.5	H28B-C28A-H28C	109.5
C22A-C21A-Pd1	107.1(4)	C22A-C21A-H21A	110.3
Pd1-C21A-H21A	110.3	C22A-C21A-H21B	110.3
Pd1-C21A-H21B	110.3	H21A-C21A-H21B	108.5
N15B-Pd2-C21B	82.7(9)	N15B-Pd2-O9B	92.5(6)
C21B-Pd2-O9B	174.0(9)	N15B-Pd2-N1B	161.8(8)
C21B-Pd2-N1B	92.6(9)	O9B-Pd2-N1B	93.1(6)
C6B-N1B-C2B	119.7(11)	C6B-N1B-Pd2	117.0(11)
C2B-N1B-Pd2	107.4(9)	N1B-C2B-C3B	119.2(10)
N1B-C2B-C7B	119.5(11)	C3B-C2B-C7B	120.9(12)
C4B-C3B-C2B	119.3(11)	C4B-C3B-H3B	120.4
C2B-C3B-H3B	120.4	C3B-C4B-C5B	120.3(11)

C3B-C4B-H4B	119.8	C5B-C4B-H4B	119.8
C4B-C5B-C6B	119.0(11)	C4B-C5B-H5B	120.5
C6B-C5B-H5B	120.5	N1B-C6B-C5B	119.2(10)
N1B-C6B-C11B	118.8(11)	C5B-C6B-C11B	120.7(11)
C2B-C7B-C8B	112.9(12)	C2B-C7B-H7C	109.0
C8B-C7B-H7C	109.0	C2B-C7B-H7D	109.0
C8B-C7B-H7D	109.0	H7C-C7B-H7D	107.8
O9B-C8B-O10B	118.8(12)	O9B-C8B-C7B	120.6(12)
O10B-C8B-C7B	119.5(12)	C8B-O9B-Pd2	112.3(10)
C12B-C11B-C6B	115.9(12)	C12B-C11B-H11C	108.3
C6B-C11B-H11C	108.3	C12B-C11B-H11D	108.3
C6B-C11B-H11D	108.3	H11C-C11B-H11D	107.4
O14B-C12B-O13B	123.5(13)	O14B-C12B-C11B	126.6(12)
O13B-C12B-C11B	109.9(11)	C12B-O13B-H13B	109.5
C16B-N15B-C20B	120.8(11)	C16B-N15B-Pd2	124.4(10)
C20B-N15B-Pd2	114.3(9)	N15B-C16B-C17B	120.7(12)
N15B-C16B-H16B	119.7	C17B-C16B-H16B	119.7
C18B-C17B-C16B	119.2(12)	C18B-C17B-H17B	120.4
C16B-C17B-H17B	120.4	C17B-C18B-C19B	121.5(11)
C17B-C18B-H18B	119.2	C19B-C18B-H18B	119.2
C18B-C19B-C20B	116.0(10)	C18B-C19B-C25B	127.0(10)
C20B-C19B-C25B	116.8(9)	N15B-C20B-C22B	116.1(10)
N15B-C20B-C19B	121.2(10)	C22B-C20B-C19B	122.7(10)
C23B-C22B-C20B	117.8(11)	C23B-C22B-C21B	124.8(15)
C20B-C22B-C21B	117.0(14)	C22B-C23B-C24B	120.2(12)
C22B-C23B-H23C	119.9	C24B-C23B-H23C	119.9
C25B-C24B-C23B	122.3(11)	C25B-C24B-H24C	118.9
C23B-C24B-H24C	118.9	C24B-C25B-C19B	119.1(9)
C24B-C25B-C26B	121.7(10)	C19B-C25B-C26B	119.1(10)
C27B-C26B-C25B	110.3(12)	C27B-C26B-C28B	111.4(12)
C25B-C26B-C28B	112.0(10)	C27B-C26B-H26C	107.7
C25B-C26B-H26C	107.7	C28B-C26B-H26C	107.7
C26B-C27B-H27D	109.5	C26B-C27B-H27E	109.5
H27D-C27B-H27E	109.5	C26B-C27B-H27F	109.5
H27D-C27B-H27F	109.5	H27E-C27B-H27F	109.5
C26B-C28B-H28D	109.5	C26B-C28B-H28E	109.5
H28D-C28B-H28E	109.5	C26B-C28B-H28F	109.5
H28D-C28B-H28F	109.5	H28E-C28B-H28F	109.5
C22B-C21B-Pd2	105.9(16)	C22B-C21B-H21C	110.6
Pd2-C21B-H21C	110.6	C22B-C21B-H21D	110.6
Pd2-C21B-H21D	110.6	H21C-C21B-H21D	108.7
C21X-Pd2X-N15X	83.4(5)	C21X-Pd2X-N1X	101.2(6)
N15X-Pd2X-N1X	174.1(4)	C21X-Pd2X-O9X	171.2(6)
N15X-Pd2X-O9X	89.6(4)	N1X-Pd2X-O9X	86.1(3)

C6X-N1X-C2X	122.1(7)	C6X-N1X-Pd2X	127.2(6)
C2X-N1X-Pd2X	110.6(6)	N1X-C2X-C3X	118.8(8)
N1X-C2X-C7X	120.4(8)	C3X-C2X-C7X	120.7(8)
C4X-C3X-C2X	119.6(8)	C4X-C3X-H3X	120.2
C2X-C3X-H3X	120.2	C3X-C4X-C5X	120.4(9)
C3X-C4X-H4X	119.8	C5X-C4X-H4X	119.8
C4X-C5X-C6X	119.3(9)	C4X-C5X-H5X	120.3
C6X-C5X-H5X	120.3	N1X-C6X-C5X	119.7(8)
N1X-C6X-C11X	120.1(8)	C5X-C6X-C11X	120.1(8)
C2X-C7X-C8X	110.3(9)	C2X-C7X-H7E	109.6
C8X-C7X-H7E	109.6	C2X-C7X-H7F	109.6
C8X-C7X-H7F	109.6	H7E-C7X-H7F	108.1
O10X-C8X-O9X	119.9(9)	O10X-C8X-C7X	119.3(9)
O9X-C8X-C7X	120.4(8)	C8X-O9X-Pd2X	110.7(7)
C12X-C11X-C6X	112.1(9)	C12X-C11X-H11E	109.2
C6X-C11X-H11E	109.2	C12X-C11X-H11F	109.2
C6X-C11X-H11F	109.2	H11E-C11X-H11F	107.9
O14X-C12X-O13X	121.7(10)	O14X-C12X-C11X	125.3(9)
O13X-C12X-C11X	113.0(8)	C12X-O13X-H13X	109.5
C16X-N15X-C20X	120.2(8)	C16X-N15X-Pd2X	126.5(7)
C20X-N15X-Pd2X	113.3(6)	N15X-C16X-C17X	121.6(9)
N15X-C16X-H16X	119.2	C17X-C16X-H16X	119.2
C18X-C17X-C16X	119.4(9)	C18X-C17X-H17X	120.3
C16X-C17X-H17X	120.3	C17X-C18X-C19X	120.7(8)
C17X-C18X-H18X	119.6	C19X-C18X-H18X	119.6
C18X-C19X-C20X	117.3(7)	C18X-C19X-C25X	125.4(8)
C20X-C19X-C25X	117.2(7)	N15X-C20X-C22X	115.8(7)
N15X-C20X-C19X	120.7(7)	C22X-C20X-C19X	123.5(8)
C23X-C22X-C20X	116.9(9)	C23X-C22X-C21X	125.5(10)
C20X-C22X-C21X	116.6(10)	C22X-C23X-C24X	120.7(9)
C22X-C23X-H23X	119.6	C24X-C23X-H23X	119.6
C25X-C24X-C23X	123.4(9)	C25X-C24X-H24X	118.3
C23X-C24X-H24X	118.3	C24X-C25X-C19X	118.0(7)
C24X-C25X-C26X	122.7(8)	C19X-C25X-C26X	119.2(8)
C27X-C26X-C28X	109.5(9)	C27X-C26X-C25X	112.2(9)
C28X-C26X-C25X	109.2(8)	C27X-C26X-H26X	108.6
C28X-C26X-H26X	108.6	C25X-C26X-H26X	108.6
C26X-C27X-H27G	109.5	C26X-C27X-H27H	109.5
H27G-C27X-H27H	109.5	C26X-C27X-H27I	109.5
H27G-C27X-H27I	109.5	H27H-C27X-H27I	109.5
C26X-C28X-H28G	109.5	C26X-C28X-H28H	109.5
H28G-C28X-H28H	109.5	C26X-C28X-H28I	109.5
H28G-C28X-H28I	109.5	H28H-C28X-H28I	109.5
C22X-C21X-Pd2X	110.7(10)	C22X-C21X-H21E	109.5

Pd2X-C21X-H21E	109.5	C22X-C21X-H21F	109.5
Pd2X-C21X-H21F	109.5	H21E-C21X-H21F	108.1
C21C-O1C-C11C	112.8(8)	C12C-C11C-O1C	107.9(10)
C12C-C11C-H11G	110.1	O1C-C11C-H11G	110.1
C12C-C11C-H11H	110.1	O1C-C11C-H11H	110.1
H11G-C11C-H11H	108.4	C11C-C12C-H12A	109.5
C11C-C12C-H12B	109.5	H12A-C12C-H12B	109.5
C11C-C12C-H12C	109.5	H12A-C12C-H12C	109.5
H12B-C12C-H12C	109.5	O1C-C21C-C22C	109.5(8)
O1C-C21C-H21G	109.8	C22C-C21C-H21G	109.8
O1C-C21C-H21H	109.8	C22C-C21C-H21H	109.8
H21G-C21C-H21H	108.2	C21C-C22C-H22E	109.5
C21C-C22C-H22F	109.5	H22E-C22C-H22F	109.5
C21C-C22C-H22G	109.5	H22E-C22C-H22G	109.5
H22F-C22C-H22G	109.5	C1D-O1D-H1D	109.5
O2D-C1D-O1D	124.1(16)	O2D-C1D-C2D	125.6(17)
O1D-C1D-C2D	110.1(16)	C1D-C2D-H2D1	109.5
C1D-C2D-H2D2	109.5	H2D1-C2D-H2D2	109.5
C1D-C2D-H2D3	109.5	H2D1-C2D-H2D3	109.5
H2D2-C2D-H2D3	109.5	C3D-O3D-H3D	109.5
O4D-C3D-O3D	125(2)	O4D-C3D-C4D	125(2)
O3D-C3D-C4D	110(2)	C3D-C4D-H4D1	109.5
C3D-C4D-H4D2	109.5	H4D1-C4D-H4D2	109.5
C3D-C4D-H4D3	109.5	H4D1-C4D-H4D3	109.5
H4D2-C4D-H4D3	109.5	C1E-O1E-H1E	109.5
O2E-C1E-O1E	121.2(8)	O2E-C1E-C2E	124.5(9)
O1E-C1E-C2E	114.3(8)	C1E-C2E-H2E1	109.5
C1E-C2E-H2E2	109.5	H2E1-C2E-H2E2	109.5
C1E-C2E-H2E3	109.5	H2E1-C2E-H2E3	109.5
H2E2-C2E-H2E3	109.5	C1F-O1F-H1F	109.5
O2F-C1F-O1F	118.8(12)	O2F-C1F-C2F	128.2(12)
O1F-C1F-C2F	113.0(12)	C1F-C2F-H2F1	109.5
C1F-C2F-H2F2	109.5	H2F1-C2F-H2F2	109.5
C1F-C2F-H2F3	109.5	H2F1-C2F-H2F3	109.5
H2F2-C2F-H2F3	109.5		

Symmetry transformation codes: #1 -x+1,-y+2,-z+1

4. ^{1}H and ^{13}C NMR spectra

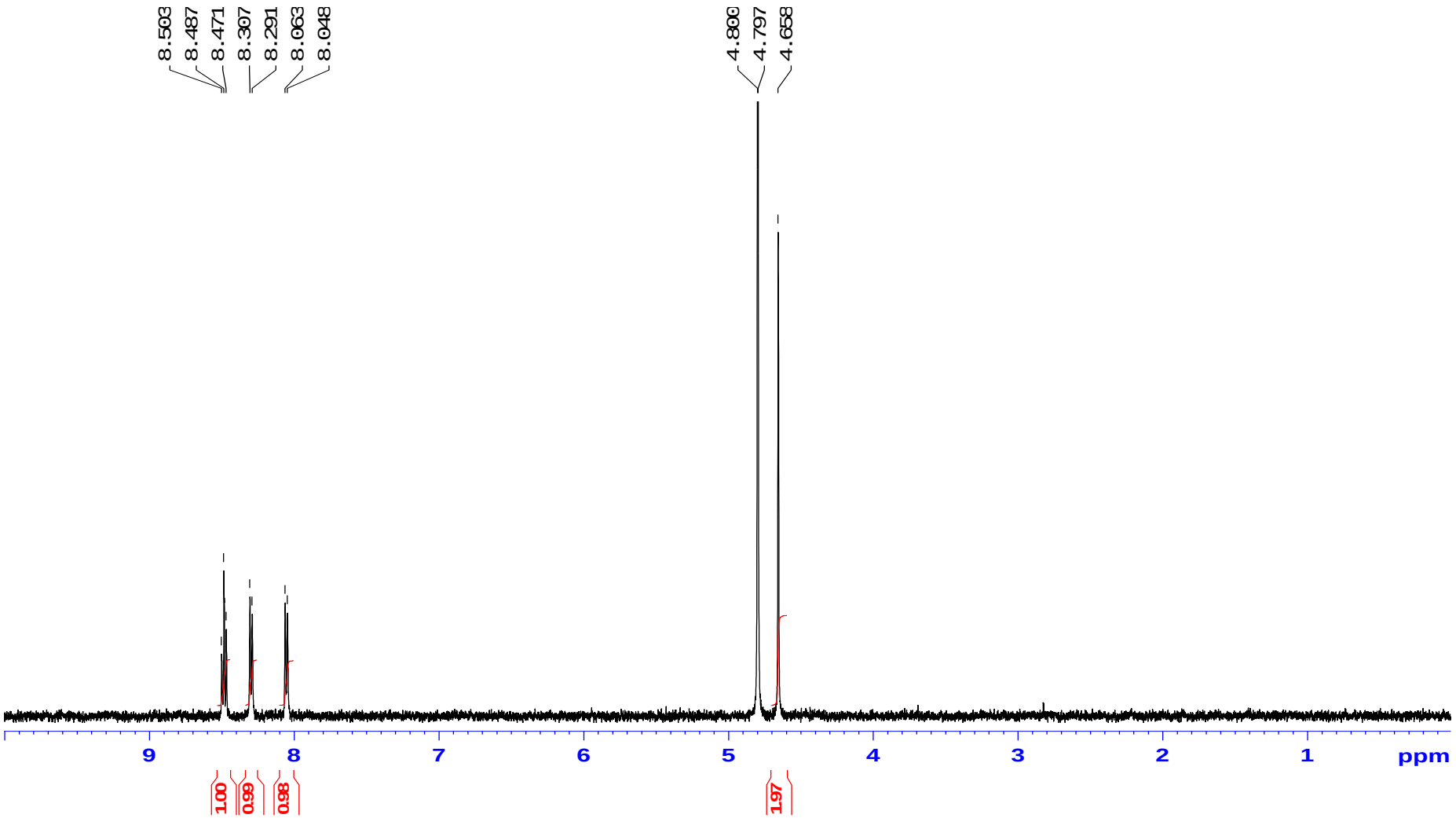


Figure S2 ^{1}H NMR spectrum of 6-(sulfomethyl)pyridine-2-carboxylic acid, lithium salt **2** in D_2O.

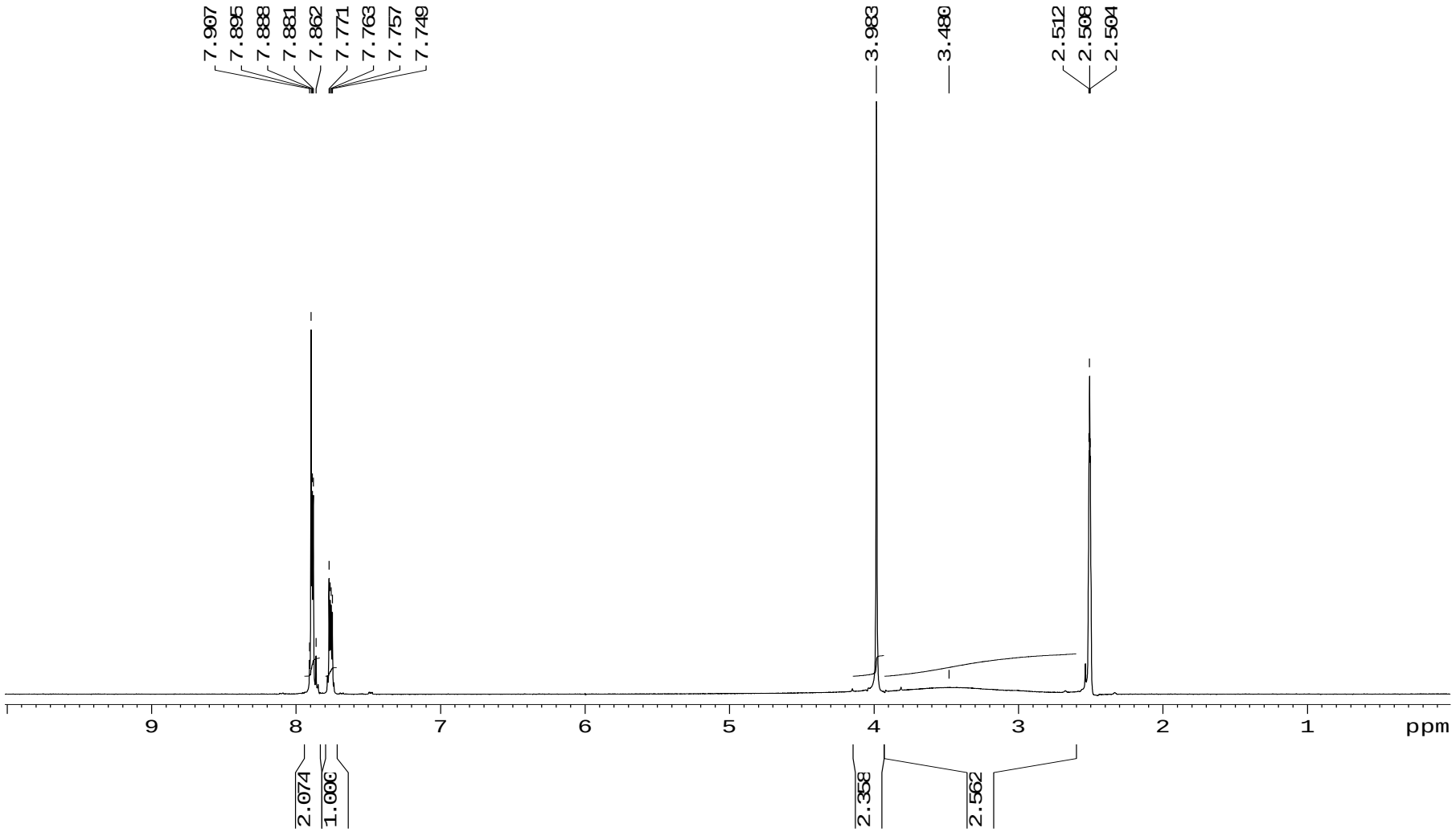


Figure S3. [1]H NMR spectrum of 6-(sulfomethyl)pyridine-2-carboxylic acid, lithium salt **2** in d_6-DMSO.

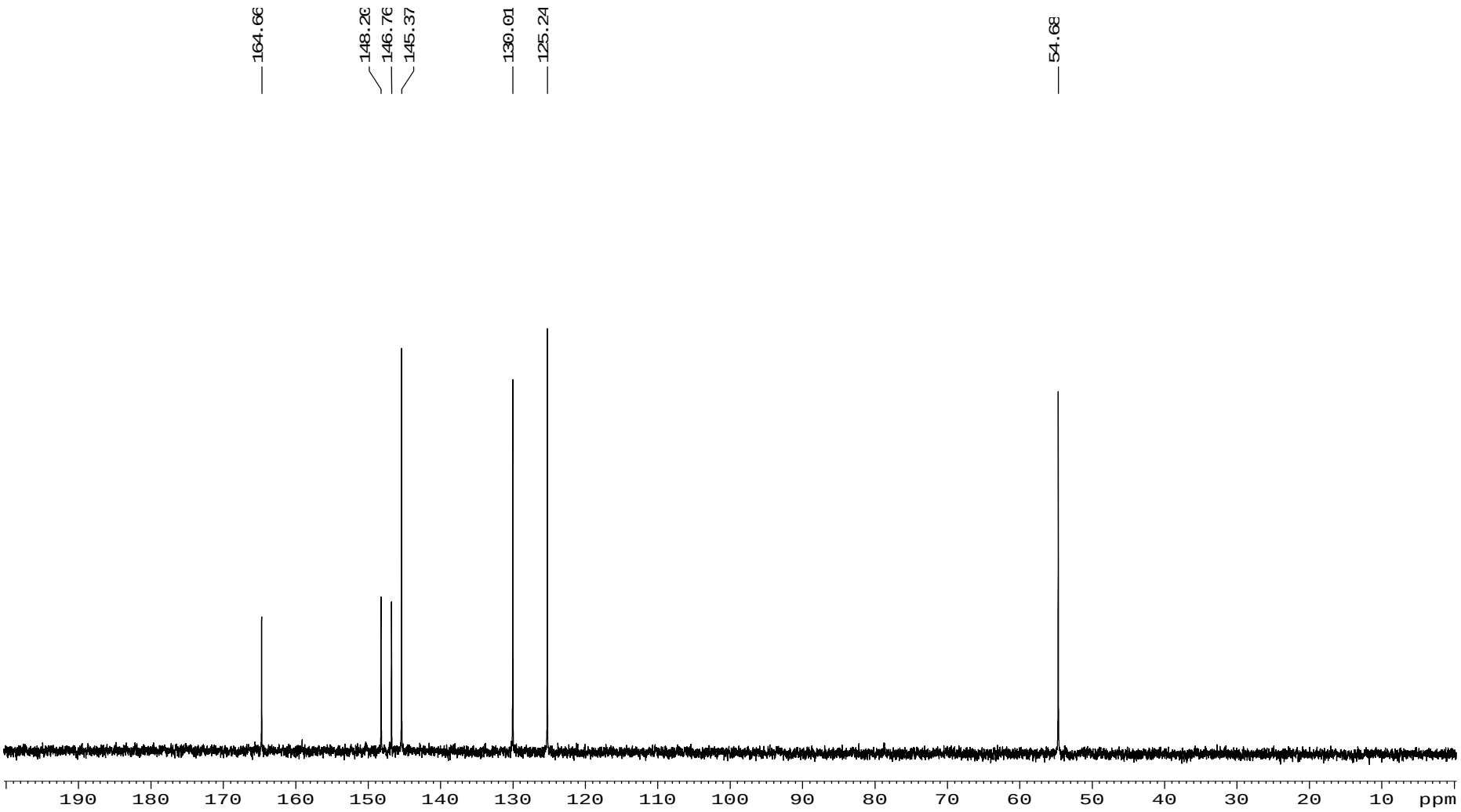


Figure S4. ^{13}C NMR spectrum of 6-(sulfomethyl)pyridine-2-carboxylic acid, Lithium salt **2** in D_2O.

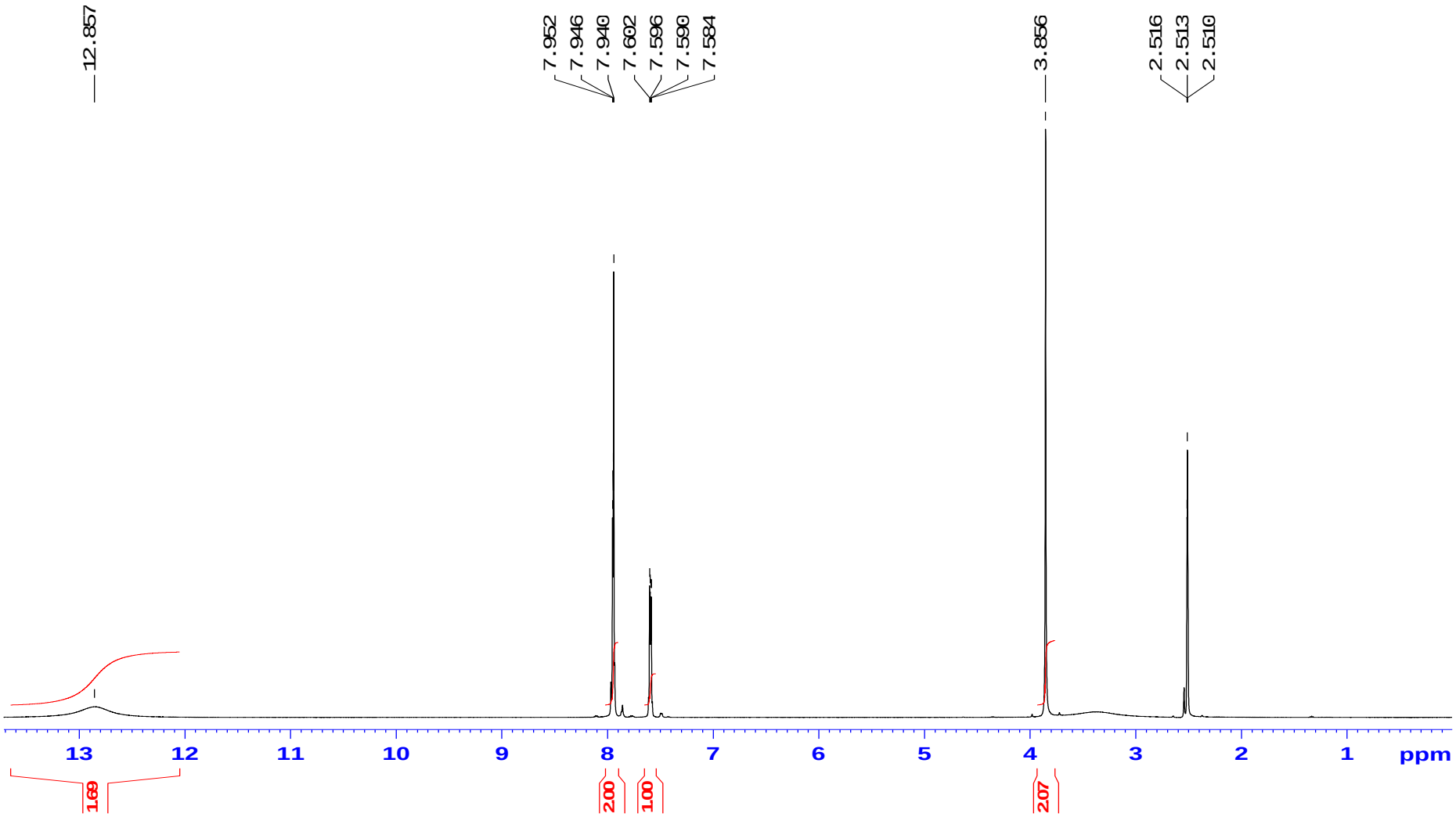


Figure S5. ^{1}H NMR spectrum of 6-(carboxymethyl)pyridine-2-carboxylic acid **3** in d_6-DMSO.

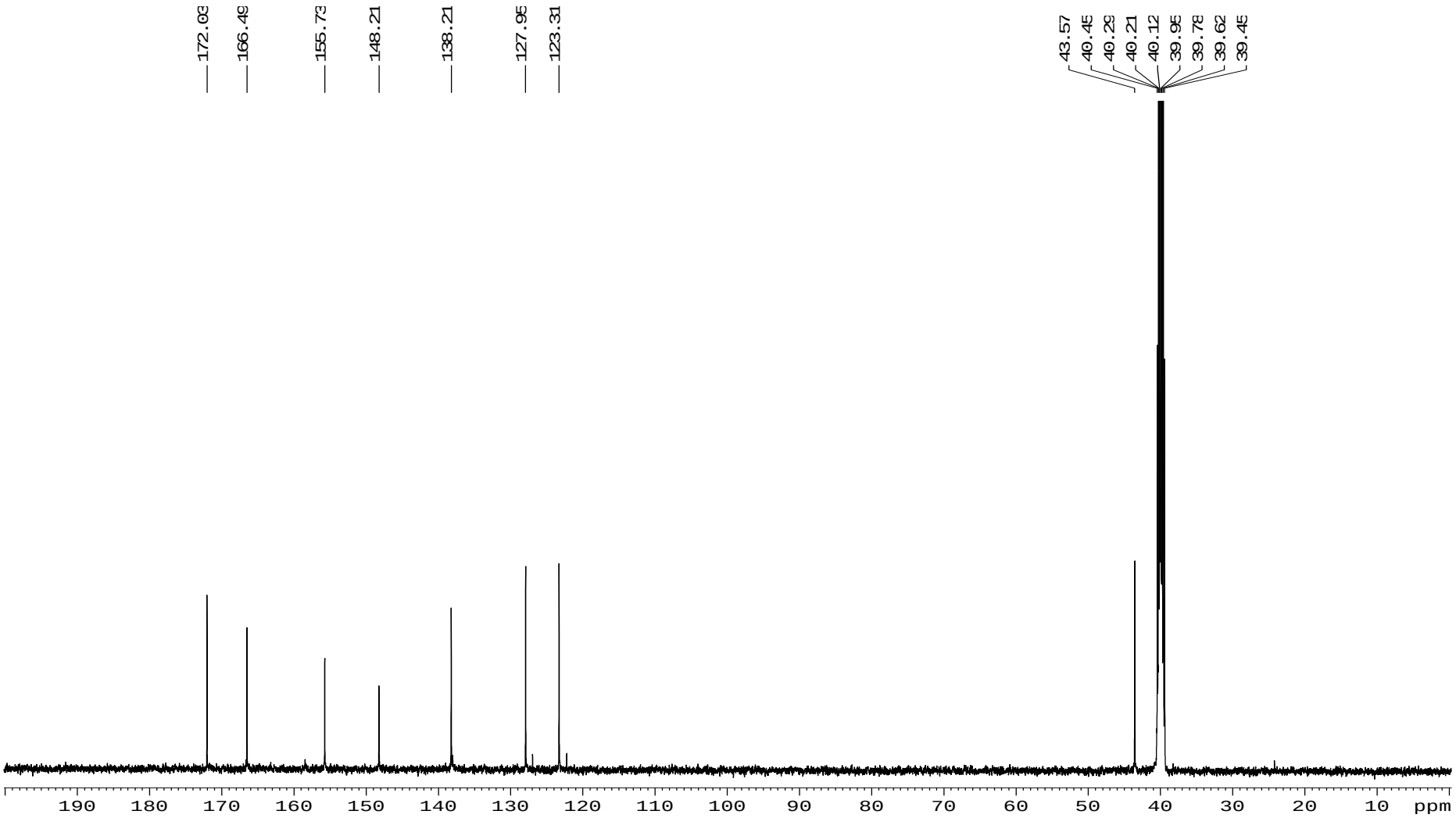


Figure S6. ^{13}C NMR spectrum of 6-(carboxymethyl)pyridine-2-carboxylic acid **3** in d_6-DMSO.

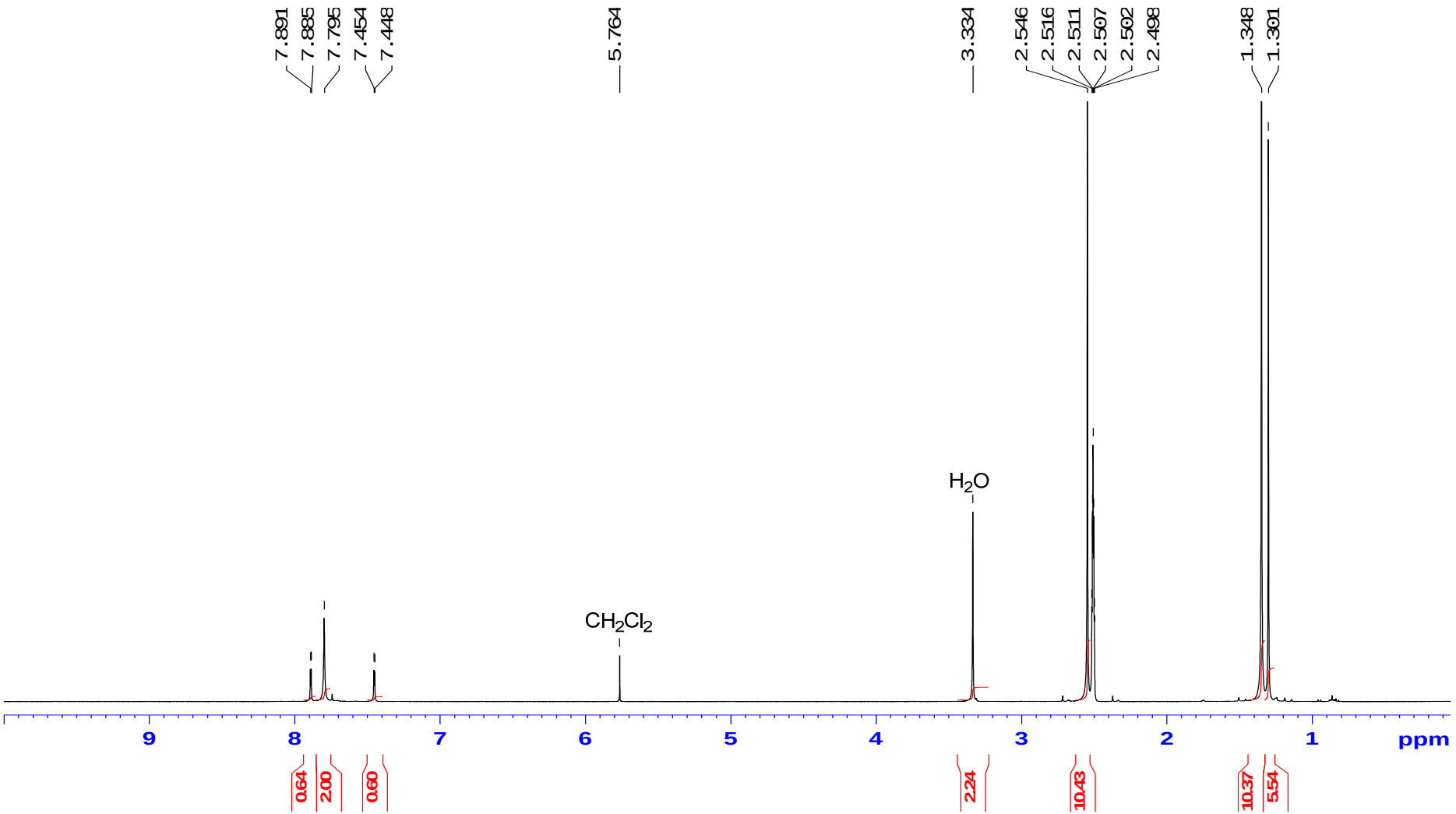


Figure S7. ^{1}H NMR spectrum of **5** in d_6-DMSO.

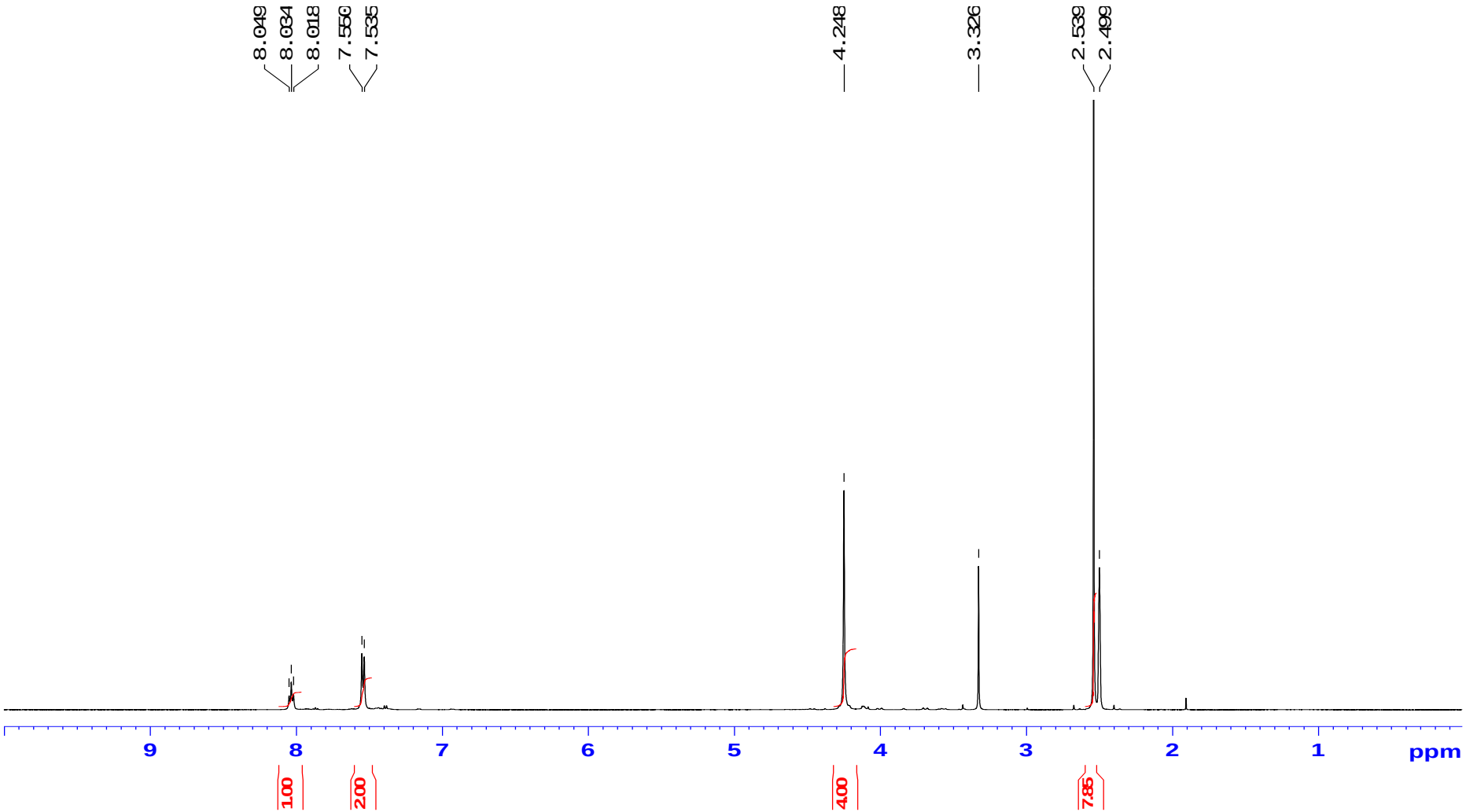


Figure S8. ^{1}H NMR spectrum of **7** in d_6-DMSO.

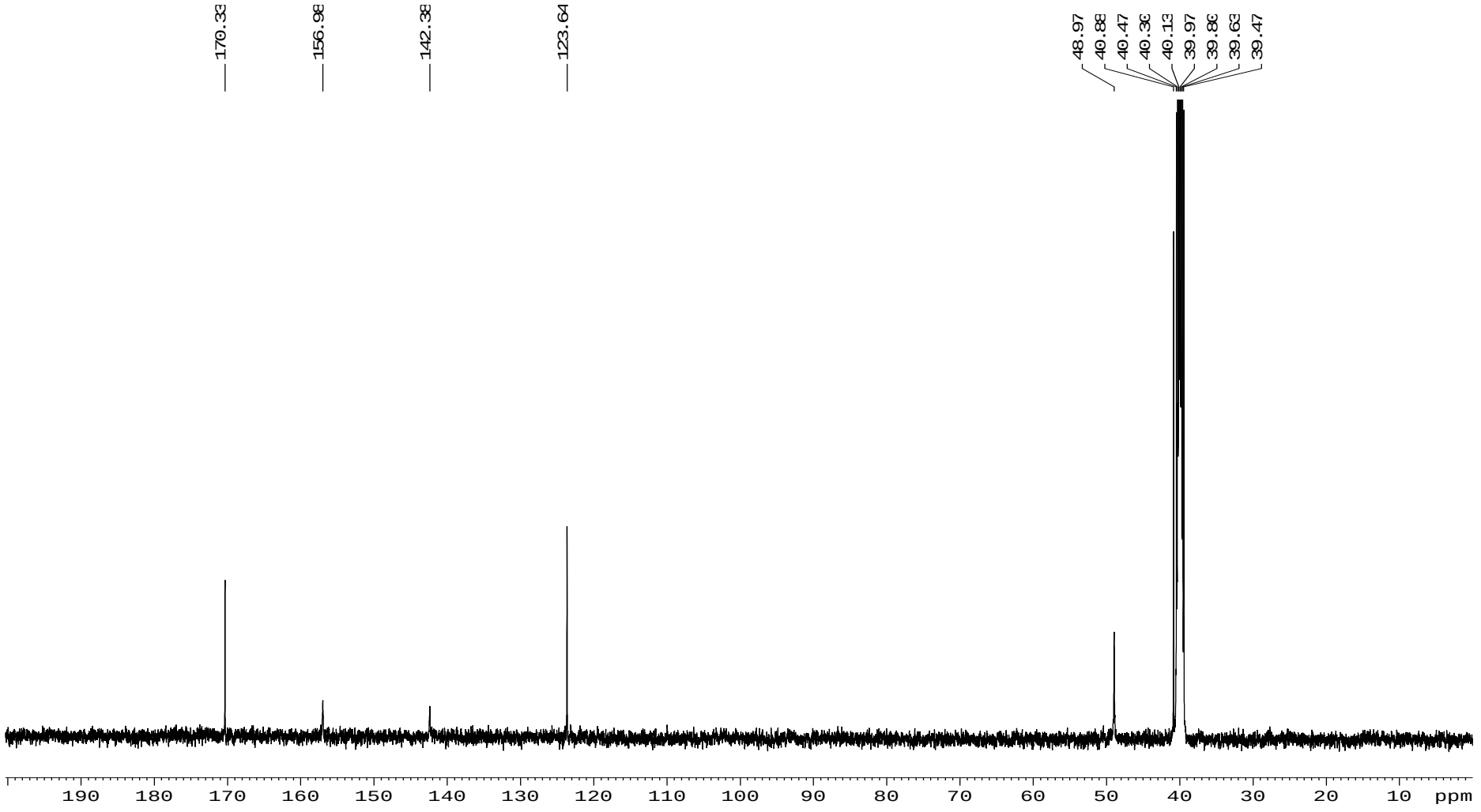


Figure S9. ^{13}C NMR spectrum of **7** in d_6-DMSO.

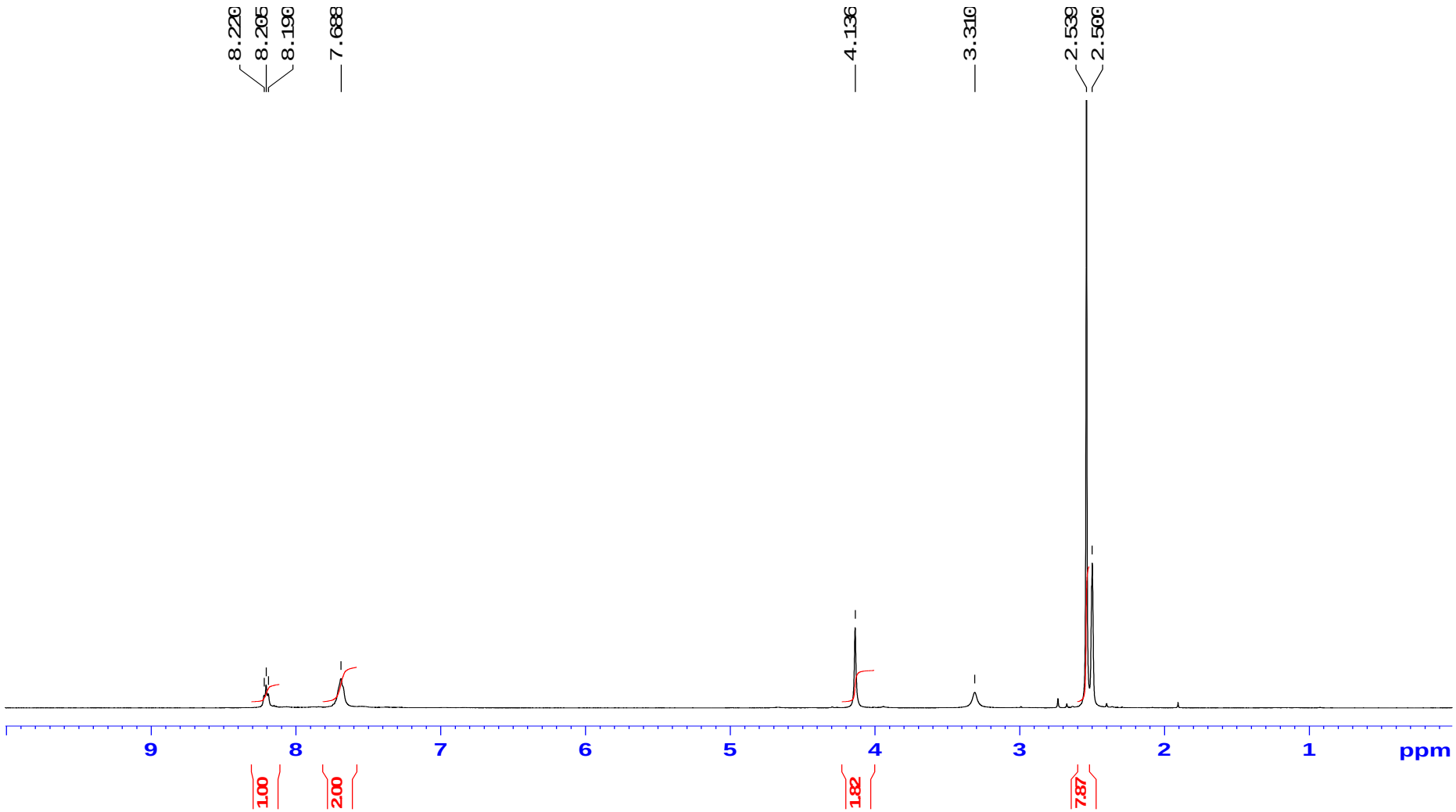


Figure S10. ^{1}H NMR spectrum of **6** in d_6-DMSO.

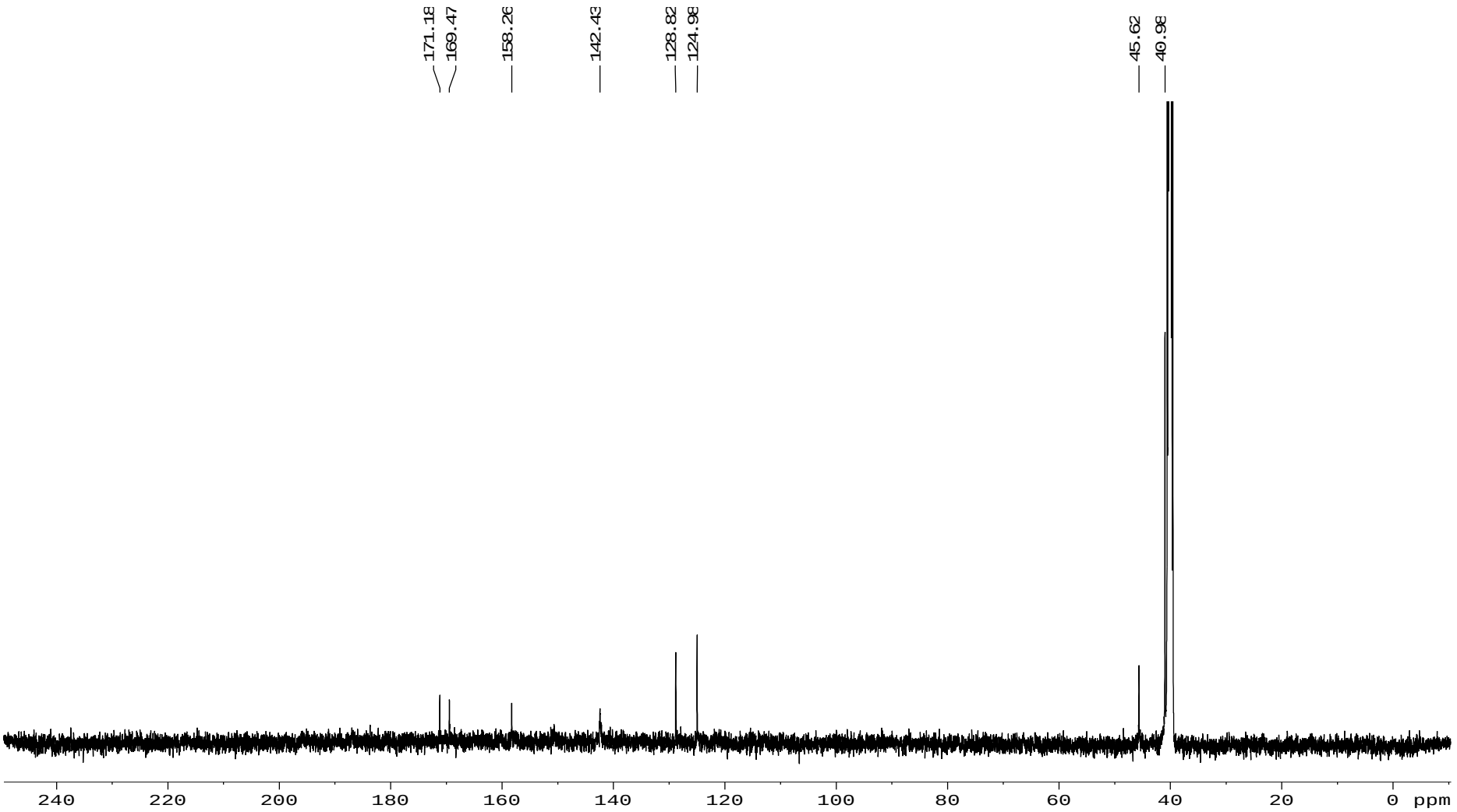


Figure S11. ^{13}C NMR spectrum of **6** in d_6-DMSO.

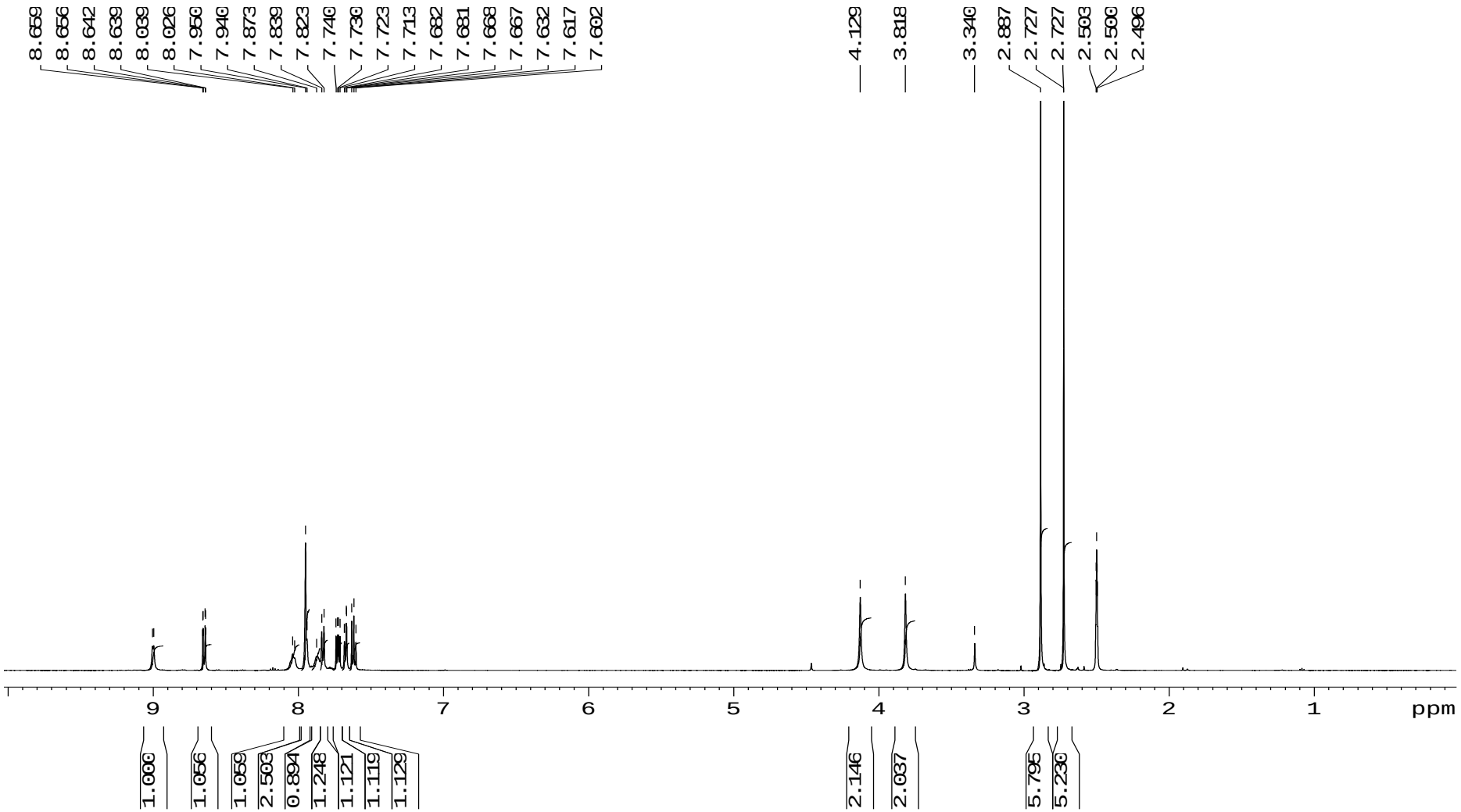


Figure S12. ^{1}H NMR spectrum of **9** in d_6-DMSO.

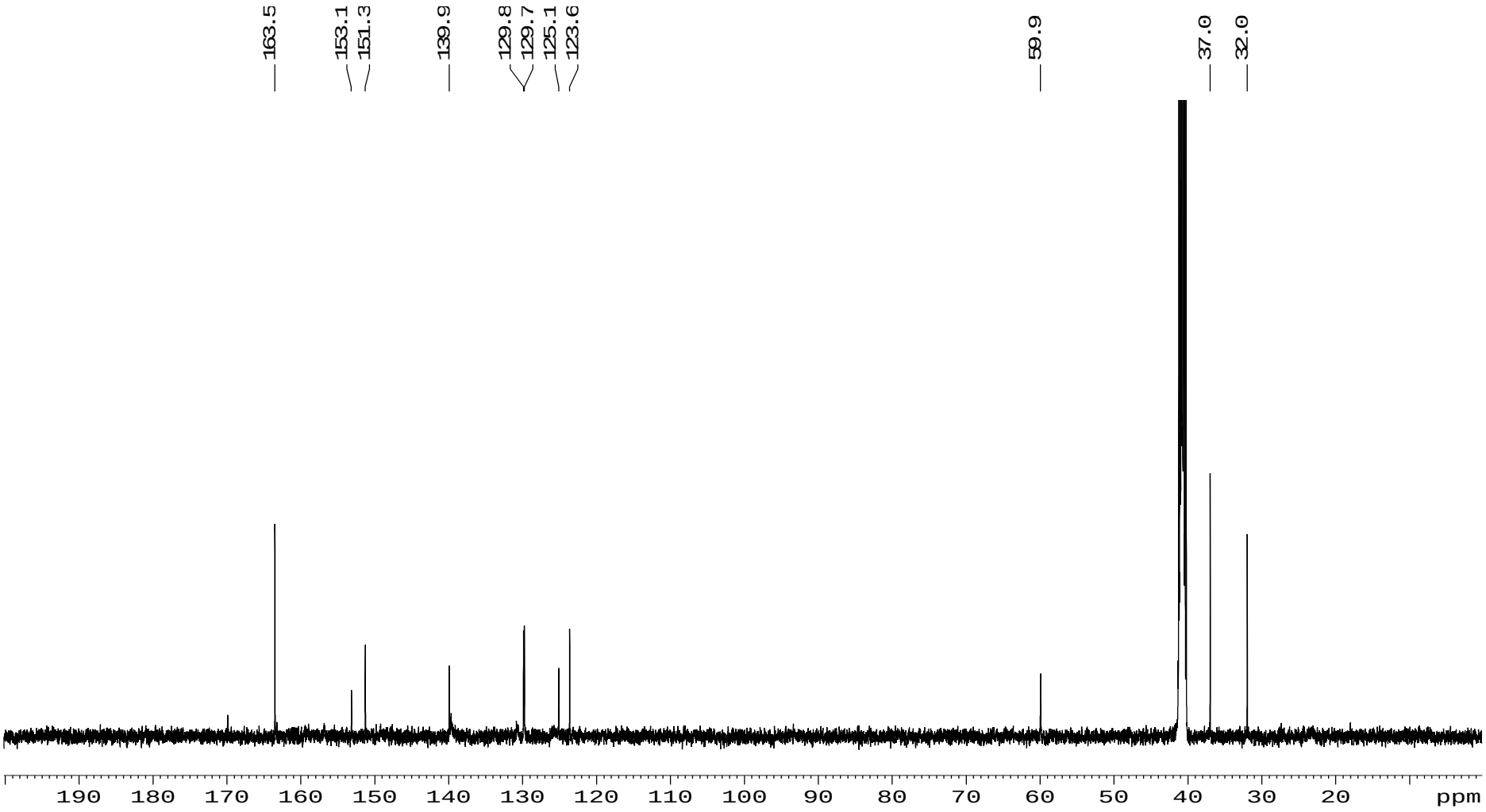


Figure S13. ^{13}C NMR spectrum of **9** in d_6-DMSO.

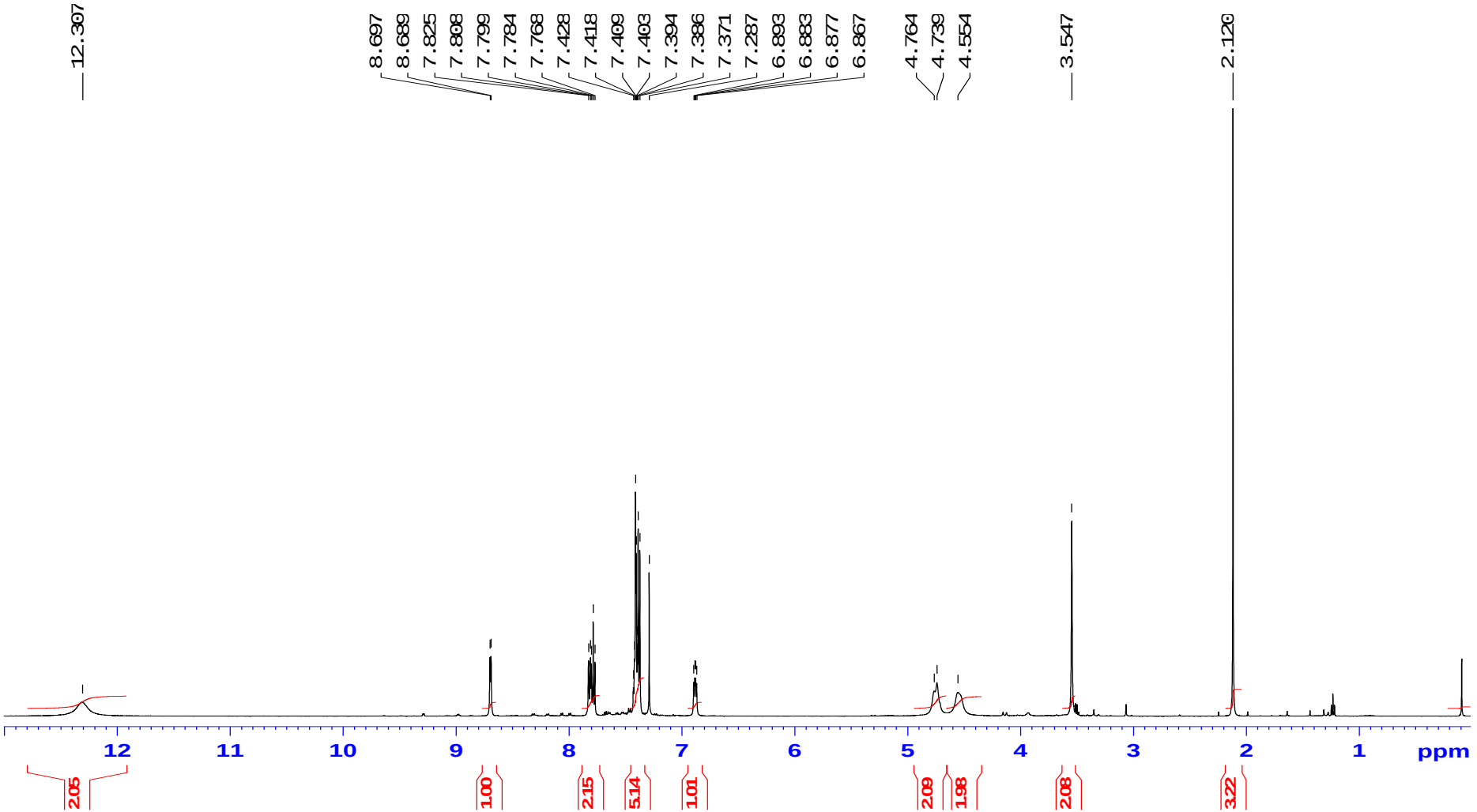


Figure S14. ^{1}H NMR spectrum of **11** in $CDCl_3$.

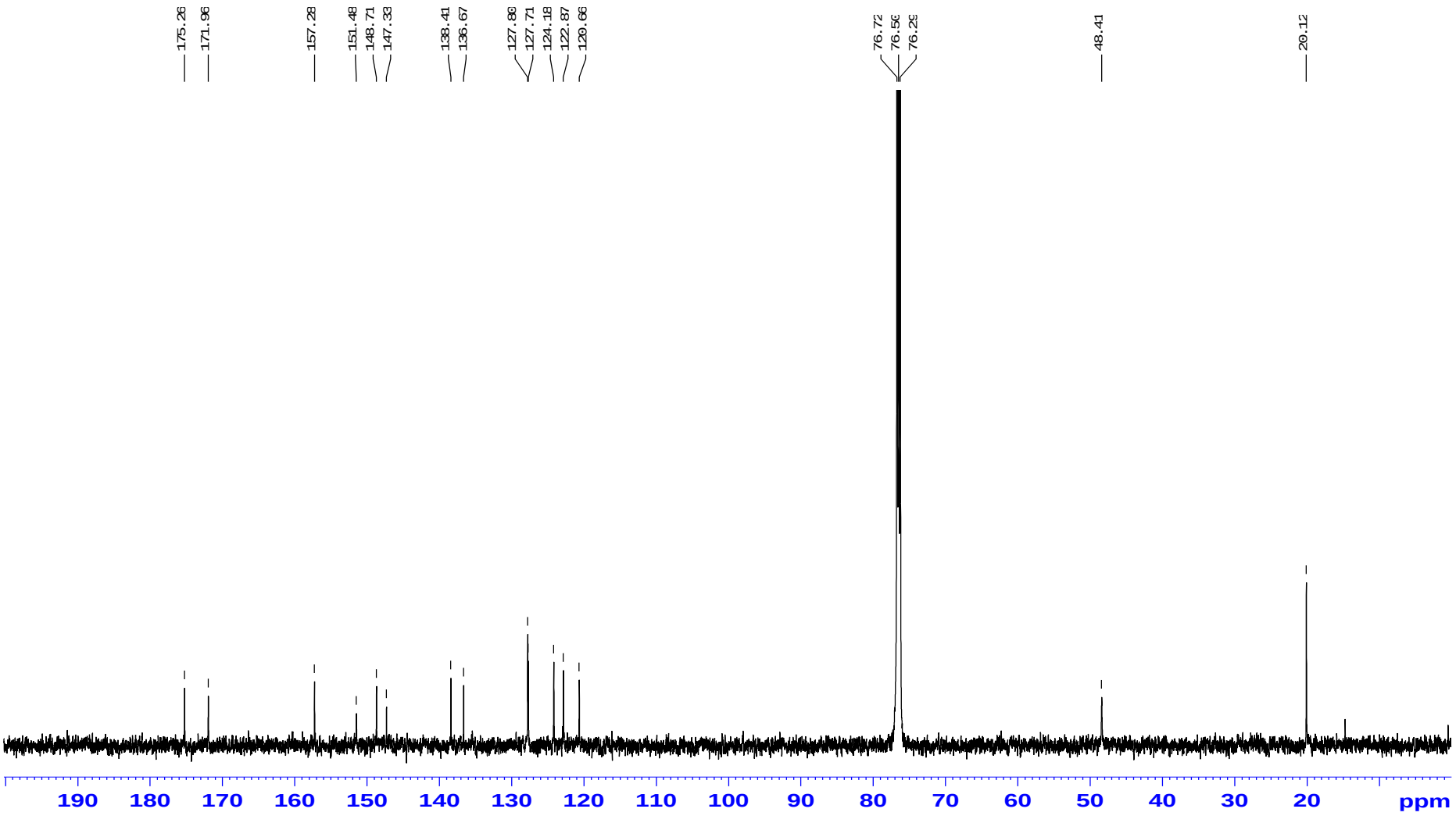


Figure S15. ^{13}C NMR spectrum of **11** in $CDCl_3$.

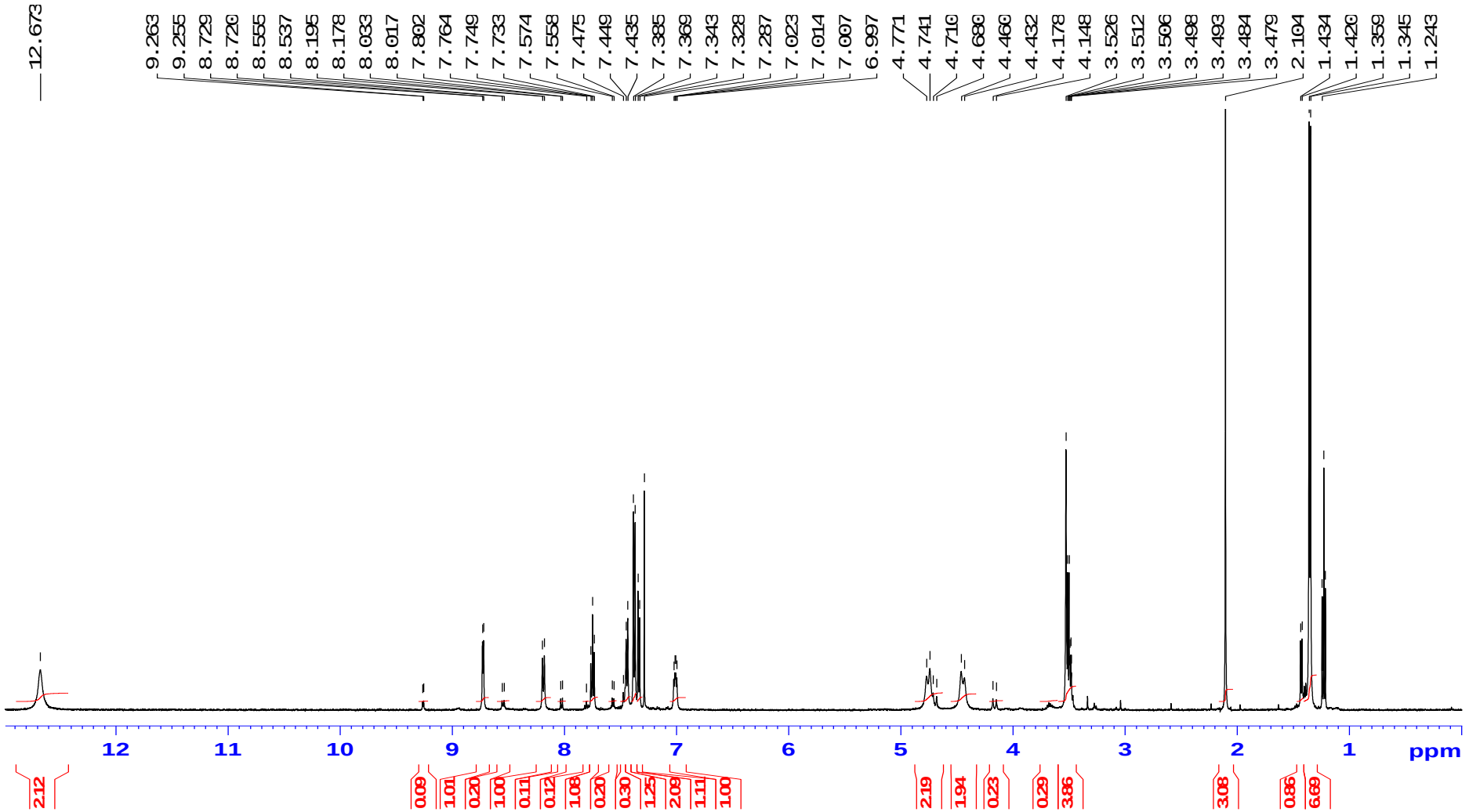


Figure S16. ^{1}H NMR spectrum of **12** in $CDCl_3$.

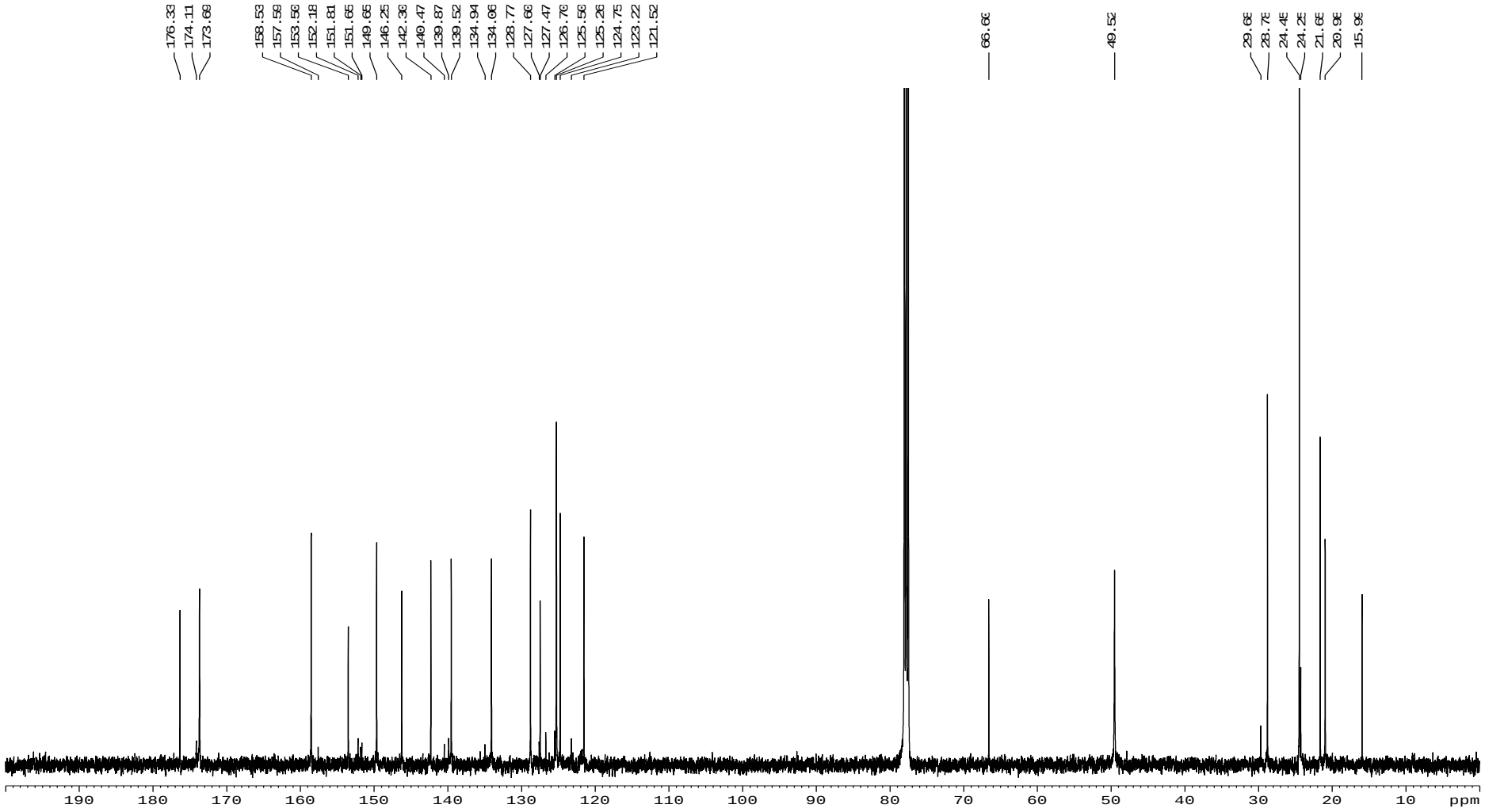


Figure S17. ^{13}C NMR spectrum of **12** in $CDCl_3$.

5. References

1. Parr, R.G.; Yang, W. *Density-functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
2. Perdew, J.P. ; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865-8.
3. Jaguar, version 7.9, Schrödinger, LLC, New York, NY, 2012.