Polycyclic Aromatic Hydrocarbons by Ring-Closing Metathesis

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Supporting Information

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Computational Method

Density functional calculations were performed using Gaussian 03[1]. The B3LYP functional together with standard 6-31G(d) basis set (Cartesian d functions) was used. Standard cut-off values were used in geometry optimizations. Stationary points were subjected to frequency calculations and assigned as minima (all real frequencies); this also provided G298. Use of molecular symmetry was deliberately avoided. No scaling factor was used for frequencies in the thermodynamic functions evaluations and no attempt was made to treat any low frequency vibrations as internal rotations.

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[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr. ; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Revision B.02; Gaussian, Inc.: Pittsburgh PA, 2003.

COMPUTATIONAL DATA

I. Cartesian coordinates of the optimized geometry of 2,2'-divinylbiphenyl (**1**)
(sum of electronic and vibrational energies: -617.890203 Hartrees)

H	2.006477	0.281705	−1.414163
C	1.407688	1.067770	−0.963037
C	−0.135811	3.068146	0.177597
C	0.212914	0.716628	−0.314281
C	1.823824	2.393524	−1.053128
C	1.044132	3.399900	−0.479438
C	−0.581226	1.736780	0.268264
C	−0.212914	−0.716628	−0.314281
H	2.750712	2.638468	−1.564655
H	1.362384	4.437813	−0.530228
C	−1.823824	1.411437	0.995974
H	−0.716869	3.848695	0.659986
C	−1.044132	−3.399900	−0.479438
C	0.581226	−1.736780	0.268264
C	−1.407688	−1.067770	−0.963037
C	−1.823824	−2.393524	−1.053128
C	0.135811	−3.068146	0.177597
C	1.823824	−1.411437	0.995974
H	−2.006477	−0.281705	−1.414163
H	−2.750712	−2.638468	−1.564655
H	0.716869	−3.848695	0.659986
H	−1.362384	−4.437813	−0.530228
C	2.863843	−2.233305	1.187098
H	3.730020	−1.914799	1.759503
H	1.882017	−0.403406	1.400664
H	2.900169	−3.238498	0.774614
H	−1.882017	0.403406	1.400664
H	−3.730020	1.914799	1.759503
C	−2.863843	2.233305	1.187098
H	−2.900169	3.238498	0.774614

II. Cartesian coordinates of the optimized geometry of phenanthrene
(Sum of electronic and thermal tree energies: -539.377988 Hartrees)

C	0.000000	0.679837	2.093973
C	0.000000	1.423261	0.866407
C	0.000000	2.883347	−1.529271
C	0.000000	0.728956	−0.381170
C	0.000000	2.837414	0.878927
C	0.000000	3.561914	−0.296591
C	0.000000	1.500490	−1.566729
C	0.000000	−0.728956	−0.381170

H	0.000000	3.348698	1.838952
H	0.000000	4.648179	-0.271179
H	0.000000	1.007400	-2.532916
H	0.000000	3.446553	-2.458631
C	0.000000	-3.561914	-0.296591
C	0.000000	-1.423261	0.866407
C	0.000000	-1.500490	-1.566729
C	0.000000	-2.883347	-1.529271
C	0.000000	-2.837414	0.878927
C	0.000000	-0.679837	2.093973
H	0.000000	-1.007400	-2.532916
H	0.000000	-3.446553	-2.458631
H	0.000000	-3.348698	1.838952
H	0.000000	-4.648179	-0.271179
H	0.000000	-1.232561	3.030491
H	0.000000	1.232561	3.030491

III. Cartesian coordinates of the optimized geometry of ethylene
(Sum of Electronic and Thermal Free Energies: -78.557102 Hartrees)

C	0.000000	0.000000	0.665512
C	0.000000	0.000000	-0.665512
H	0.000000	0.923548	-1.239447
H	0.000000	-0.923548	1.239447
H	0.000000	-0.923548	-1.239447
H	0.000000	0.923548	1.239447

IV. Cartesian coordinates of the optimized geometry of trans, trans cyclodimer, twisted conformation
(Sum of Electronic and Thermal Free Energies: -1078.668519 Hartrees)

C	-2.898223	2.775355	2.236638
C	-3.928854	2.574205	1.318191
C	-3.879603	1.479884	0.455401
C	-1.838053	1.873183	2.292516
C	-1.775291	0.762555	1.435644
C	-2.812186	0.569732	0.485280
C	-2.812178	-0.569700	-0.485332
C	-1.775226	-0.762591	-1.435625
C	-3.879634	-1.479806	-0.455493
C	-1.837972	-1.873251	-2.292454
C	-3.928868	-2.574156	-1.318251
C	-2.898179	-2.775379	-2.236615
C	-0.646424	0.184032	-1.520537
C	0.646256	-0.183294	-1.520499
C	1.775108	-0.763157	1.435320
C	1.837962	-1.874051	2.291854

C	1.775165	0.763143	-1.435347
C	2.812119	-0.569831	0.485166
C	2.898302	-2.775997	2.235867
C	2.812130	0.569848	-0.485142
C	1.838030	1.874034	-2.291886
C	3.879718	-1.479788	0.455191
C	3.929046	-2.574361	1.317644
C	3.879711	1.479826	-0.455126
C	2.898347	2.776003	-2.235856
C	3.929053	2.574394	-1.317584
C	-0.646501	-0.184090	1.520603
C	0.646176	0.183254	1.520426
H	-0.891716	-1.242913	1.448166
H	0.891238	1.242101	1.447844
H	-0.891633	1.242846	-1.447956
H	0.891355	-1.242144	-1.448068
H	-2.924851	3.623450	2.915719
H	-4.764789	3.266802	1.268546
H	-4.669228	1.333579	-0.277101
H	-1.049994	2.004761	3.028960
H	-4.669305	-1.333442	0.276946
H	-1.049875	-2.004885	-3.028849
H	-4.764839	-3.266716	-1.268647
H	-2.924782	-3.623504	-2.915658
H	1.049827	-2.005997	3.028152
H	2.924984	-3.624302	2.914682
H	1.049920	2.005954	-3.028216
H	4.669423	-1.333118	-0.277148
H	4.765120	-3.266785	1.267914
H	4.669386	1.333180	0.277252
H	2.925046	3.624306	-2.914674
H	4.765108	3.266840	-1.267821

V. Cartesian coordinates of the optimized geometry of trans, trans cyclodimer, chair conformation
(sum of electronic and thermal free energies: -1078.656176 Hartrees)

C	-3.600020	2.840076	0.892715
C	-2.722804	2.996408	1.965168
C	-1.788177	1.999444	2.237592
C	-3.535893	1.687441	0.110171
C	-1.710779	0.835670	1.459164
C	-2.602808	0.669005	0.366466
C	-2.659691	-0.567289	-0.486926
C	-1.578942	-1.153459	-1.209372
C	-3.916998	-1.197237	-0.553274
C	-1.816537	-2.355969	-1.905670

C	-0.651806	-0.161543	1.687473
C	0.651643	0.161402	1.687329
C	-4.133293	-2.366941	-1.276560
C	-3.068309	-2.957012	-1.956216
C	1.579003	1.153517	-1.209343
C	1.710660	-0.835754	1.459074
C	2.602783	-0.669002	0.366479
C	2.659720	0.567315	-0.486869
C	1.788042	-1.999551	2.237483
C	2.722727	-2.996462	1.965115
C	1.816626	2.356043	-1.905603
C	3.917032	1.197248	-0.553163
C	3.600042	-2.840051	0.892741
C	3.535934	-1.687399	0.110237
C	4.133363	2.366962	-1.276420
C	3.068406	2.957077	-1.956085
H	-0.933331	-1.210507	1.612914
H	0.933081	1.210366	1.612459
C	-0.197161	-0.641647	-1.273696
C	0.197221	0.641702	-1.273746
H	0.565942	-1.417038	-1.316976
H	-0.565866	1.417099	-1.317212
H	-4.331375	3.610086	0.662135
H	-2.765928	3.886107	2.587735
H	-1.107583	2.105649	3.078124
H	-4.210859	1.574794	-0.734079
H	-4.737736	-0.761988	0.009844
H	-0.983692	-2.811125	-2.436554
H	-5.120173	-2.821521	-1.290308
H	-3.208847	-3.878014	-2.515513
H	1.107378	-2.105793	3.077955
H	2.765852	-3.886182	2.587652
H	0.983807	2.811224	-2.436504
H	4.737758	0.761977	0.009956
H	4.331467	-3.610014	0.662229
H	4.210986	-1.574687	-0.733935
H	5.120256	2.821514	-1.290149
H	3.208978	3.878090	-2.515353

VI. Cartesian coordinates of the optimized geometry of the trans, cis cyclodimer (Sum of electronic and thermal free energies: -1078.631007 Hartrees)

C	-4.777718	-1.900430	0.065236
C	-4.133281	-2.911119	0.774050
C	-2.768761	-2.803248	0.988358
C	-4.037312	-0.809175	-0.367740
C	-1.984195	-1.698480	0.569420

C	−2.652127	−0.644492	−0.121775
C	−2.141192	0.674755	−0.640708
C	−2.932958	1.794172	−0.304084
C	−1.057422	0.887336	−1.532014
C	−2.737251	3.052482	−0.862899
C	−0.908990	2.154192	−2.129512
C	−1.734618	3.226501	−1.815744
C	−0.545828	−1.940591	0.856608
C	0.030141	−0.097499	−1.705418
C	0.579261	−1.273895	1.186589
C	1.290320	0.333403	−1.525983
C	0.937805	0.119381	1.487175
C	0.135495	0.956918	2.272381
C	0.592331	2.212512	2.674589
C	1.866040	2.642642	2.303449
C	2.670029	1.828395	1.500731
C	2.220309	0.576579	1.071798
C	3.020583	−0.246616	0.107110
C	2.505476	−0.444944	−1.202542
C	4.222300	−0.862254	0.468088
C	3.183413	−1.282966	−2.090539
C	4.899924	−1.687114	−0.435180
C	4.373976	−1.907260	−1.707612
H	−0.202949	−1.157182	−1.756788
H	1.412981	1.401723	−1.354823
H	−0.360667	−3.013546	0.802392
H	1.445757	−1.930250	1.252226
H	−5.838359	−1.962076	−0.162497
H	−4.675657	−3.781909	1.131984
H	−2.260651	−3.608641	1.512373
H	−4.539956	−0.041249	−0.945951
H	−3.728342	1.660282	0.422959
H	−3.375142	3.881381	−0.568289
H	−0.112044	2.283899	−2.855893
H	−1.587421	4.188229	−2.299883
H	−0.839125	0.601465	2.594389
H	−0.040988	2.846260	3.289572
H	2.231418	3.614046	2.625861
H	3.648003	2.177982	1.179175
H	4.615395	−0.713062	1.470713
H	2.787401	−1.425748	−3.092469
H	5.831128	−2.162777	−0.139099
H	4.894715	−2.553946	−2.408953

VII. Cartesian coordinates of the optimized geometry of the cis, cis cyclodimer
(Sum of electronic and thermal free energies: -1078.653050 Hartrees)

C	2.698870	−3.551784	0.116734
C	3.639906	−2.805145	0.822089
C	3.594528	−1.411584	0.762387
C	2.611027	−0.748660	0.018096
C	1.645350	−1.504255	−0.693539
C	1.720773	−2.903344	−0.638019
C	2.611244	0.748057	−0.017829
C	3.595098	1.410467	−0.762137
C	3.640995	2.803997	−0.822112
C	2.700093	3.551079	−0.117061
C	1.721668	2.903150	0.637724
C	1.645752	1.504130	0.693591
C	−0.672367	0.790001	1.556123
C	−0.672606	−0.790131	−1.556214
C	−1.645790	−1.504152	−0.693374
C	−1.645364	1.504266	0.693338
C	−1.721549	−2.903168	−0.637226
C	−2.699952	−3.551051	0.117629
C	−3.640989	−2.803940	0.822466
C	−3.595216	−1.410413	0.762258
C	−2.611378	−0.748049	0.017902
C	−2.611136	0.748656	−0.018191
C	−3.594586	1.411551	−0.762555
C	−3.639823	2.805114	−0.822483
C	−2.698679	3.551760	−0.117294
C	−1.720634	2.903343	0.637561
H	−1.137445	−0.089626	−2.250187
H	−1.137215	0.089365	2.249960
C	0.672473	0.790108	1.556335
H	1.137220	0.089591	2.250362
C	0.672230	−0.790003	−1.556196
H	1.136972	−0.089379	−2.250125
H	2.730811	−4.637919	0.138556
H	4.409796	−3.299888	1.408161
H	4.326478	−0.820088	1.306428
H	1.028411	−3.492274	−1.228055
H	4.326911	0.818563	−1.305912
H	4.411135	3.298392	−1.408149
H	2.732344	4.637200	−0.139173
H	1.029379	3.492562	1.227367
H	−1.029148	−3.492631	−1.226674
H	−2.732084	−4.637172	0.139955
H	−4.411129	−3.298305	1.408528
H	−4.327102	−0.818485	1.305909

H	-4.326607	0.820043	-1.306489
H	-4.409679	3.299841	-1.408615
H	-2.730478	4.637895	-0.139310
H	-1.028188	3.492322	1.227442

VIII. Cartesian coordinates of the optimized geometry of 2,4',6',2"-Tetravinyl-[1,1';3',1"]terphenyl
(Sum of electronic and thermal free energies: -1003.602832 Hartrees)

H	-3.087192	1.286892	-1.860557
C	-3.366264	0.351649	-1.383979
C	-4.061933	-2.044058	-0.177678
C	-2.503627	-0.198102	-0.420799
C	-4.549878	-0.283651	-1.749263
C	-4.898791	-1.490889	-1.140478
C	-2.853363	-1.427589	0.194925
C	-1.219186	0.504781	-0.125421
H	-5.195682	0.161860	-2.501077
H	-5.826403	-1.991777	-1.404596
C	-1.997148	-2.032952	1.233465
H	-4.357151	-2.961361	0.323178
C	1.284983	1.799334	0.249559
C	-1.179357	1.856073	0.306920
C	-0.008333	-0.164586	-0.338065
C	1.237508	0.445253	-0.159121
C	0.071191	2.456961	0.495322
C	-2.417852	2.598605	0.614422
H	-0.035820	-1.195742	-0.676762
C	2.471933	-0.336499	-0.486047
H	0.101342	3.464034	0.898730
C	2.576654	2.478549	0.464155
C	-2.569749	3.928405	0.569537
H	-3.513217	4.393136	0.840216
H	-3.274814	1.990043	0.894862
H	-1.340221	-1.348522	1.764785
H	-1.297793	-3.684515	2.349889
C	-1.950059	-3.331774	1.556681
H	-2.535589	-4.087793	1.039667
C	2.785012	3.801529	0.465166
H	1.993174	4.520662	0.271515
H	3.429942	1.822188	0.620870
H	3.773582	4.210940	0.650410
C	4.692298	-1.835071	-1.363471
C	2.939270	-1.422026	0.298964
C	3.145763	-0.017210	-1.674406
C	4.248011	-0.747773	-2.114949
C	4.038563	-2.161143	-0.179741

C	2.386991	-1.846172	1.601812
H	2.777540	0.814423	-2.268971
H	4.743392	-0.477170	-3.043386
H	4.392550	-3.003529	0.410099
H	5.541816	-2.425668	-1.695652
H	1.423599	-0.097248	2.362749
C	1.699849	-1.135505	2.505929
H	2.641319	-2.873667	1.864244
H	1.404712	-1.591680	3.446998

IX. Cartesian coordinates of the optimized geometry of dibenzo[a,j]anthracene
(Sum of electronic and thermal free energies: -846.579650 Hartrees)

C	3.657935	1.726702	0.000076
C	3.721080	0.289039	0.000041
C	3.861671	-2.511450	-0.000069
C	2.516187	-0.474142	0.000002
C	4.968523	-0.373328	0.000005
C	5.045187	-1.753654	-0.000028
C	2.627865	-1.882430	-0.000059
C	1.231975	0.226346	0.000015
H	5.875703	0.226636	0.000025
H	6.011877	-2.249636	-0.000033
H	1.734266	-2.497334	-0.000067
H	3.911777	-3.596944	-0.000100
C	-1.224391	1.660753	-0.000001
C	1.224390	1.660752	0.000001
C	0.000000	-0.440471	0.000000
C	-1.231976	0.226347	-0.000015
C	0.000000	2.335501	0.000000
C	2.468737	2.380951	0.000027
H	0.000000	-1.522572	0.000000
C	-2.516187	-0.474141	-0.000002
H	0.000000	3.423755	0.000000
C	-2.468737	2.380950	-0.000026
H	2.433671	3.467695	0.000024
H	4.593322	2.281180	0.000133
C	-5.045188	-1.753654	0.000029
C	-2.627865	-1.882430	0.000058
C	-3.721080	0.289039	-0.000041
C	-4.968523	-0.373328	-0.000005
C	-3.861671	-2.511450	0.000069
H	-1.734266	-2.497335	0.000067
C	-3.657934	1.726702	-0.000076
H	-5.875703	0.226636	-0.000024
H	-3.911776	-3.596944	0.000100
H	-6.011877	-2.249636	0.000034

H	-2.433670	3.467694	-0.000025
H	-4.593322	2.281180	-0.000133

X. XYZ File of the Optimized Geometry of 2,2',5',2"-tetravinyl-[1,1',4',1"] terphenyl (Sum of Electronic and Thermal Free Energies: -1003.598483 Hartrees)

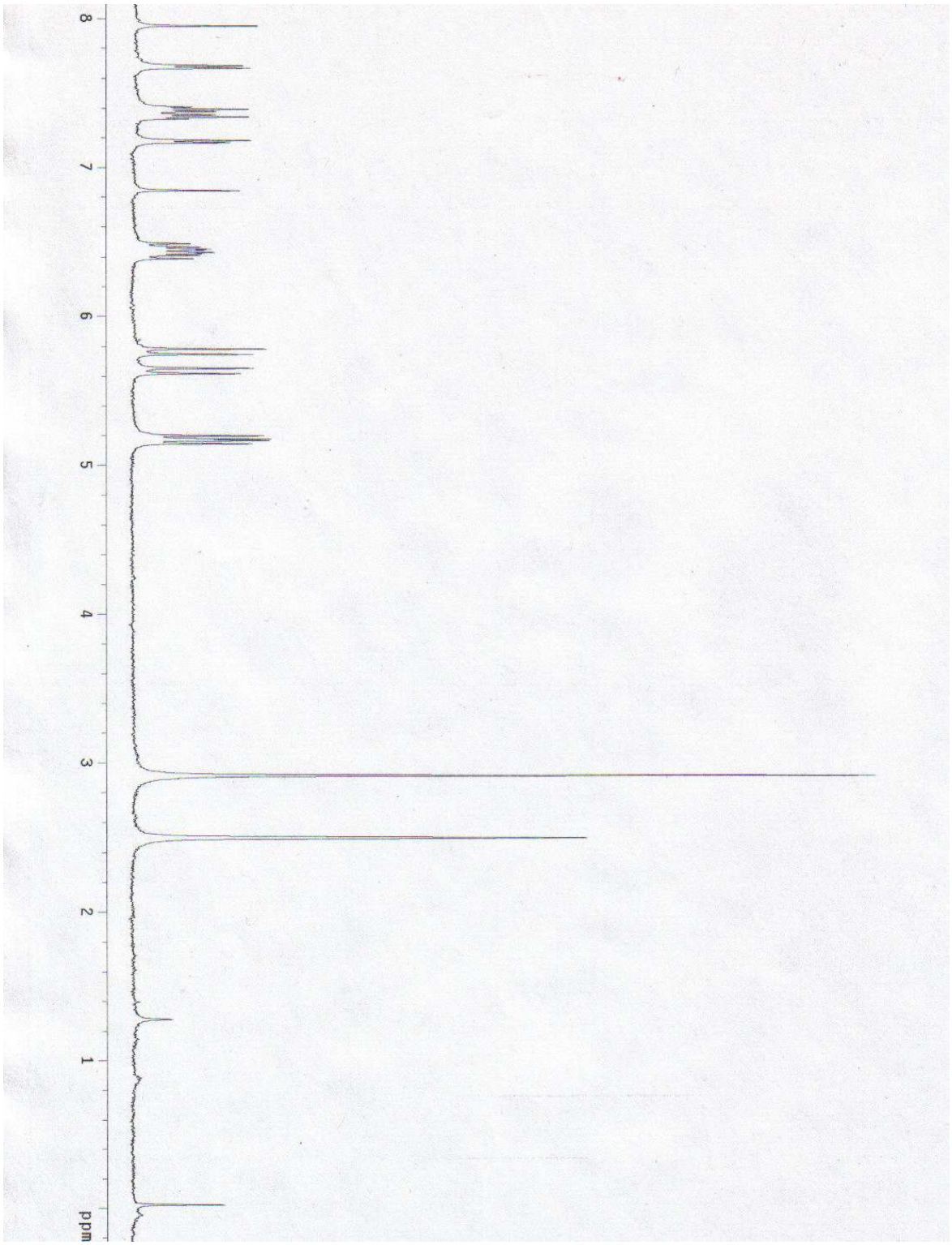
C	-0.769083	-0.892410	-0.841867
C	0.629531	-1.034929	-0.824417
C	-1.471364	0.054621	-0.094089
C	1.361564	-0.170672	0.027722
C	-0.740190	0.930355	0.745241
C	0.659200	0.783544	0.767101
C	-2.951399	0.141834	-0.313345
C	-5.674274	0.361496	-1.004975
C	-4.757056	1.292913	-1.491162
C	-3.412311	1.170326	-1.147792
C	2.840062	-0.266548	0.245377
C	3.343059	-1.368764	0.952956
C	4.698341	-1.481199	1.248868
C	5.580395	-0.482346	0.828252
C	3.727775	0.754404	-0.172530
C	5.097127	0.613823	0.123063
C	-5.231355	-0.667955	-0.181506
C	-3.880049	-0.801451	0.196349
C	-3.567899	-1.921643	1.106827
C	-1.300131	1.971713	1.626564
C	1.192199	-2.057676	-1.726282
C	3.233098	1.919097	-0.932045
C	-2.511614	-2.106902	1.909375
C	2.433584	-2.174198	-2.217149
C	3.827668	3.115613	-1.022826
C	-2.554003	2.139689	2.068814
H	-1.342026	-1.546630	-1.494373
H	1.231356	1.438087	1.420033
H	-6.726242	0.432924	-1.267859
H	-5.080737	2.101112	-2.141319
H	-2.689321	1.882533	-1.535824
H	2.651180	-2.142455	1.273659
H	5.065175	-2.343306	1.799314
H	6.643251	-0.564285	1.039817
H	5.791519	1.370189	-0.231005
H	-5.947859	-1.393225	0.197259
H	-4.355936	-2.674703	1.142363
H	-0.547942	2.673401	1.988279
H	0.452795	-2.784368	-2.064202
H	2.288629	1.773030	-1.451627
H	-1.683551	-1.411975	1.979260

H	−2.461662	−2.986804	2.544947
H	3.239474	−1.492725	−1.972314
H	2.671003	−2.979723	−2.906587
H	4.748940	3.355302	−0.497847
H	3.395542	3.909434	−1.624813
H	−3.377145	1.489984	1.797740
H	−2.783702	2.957791	2.745955

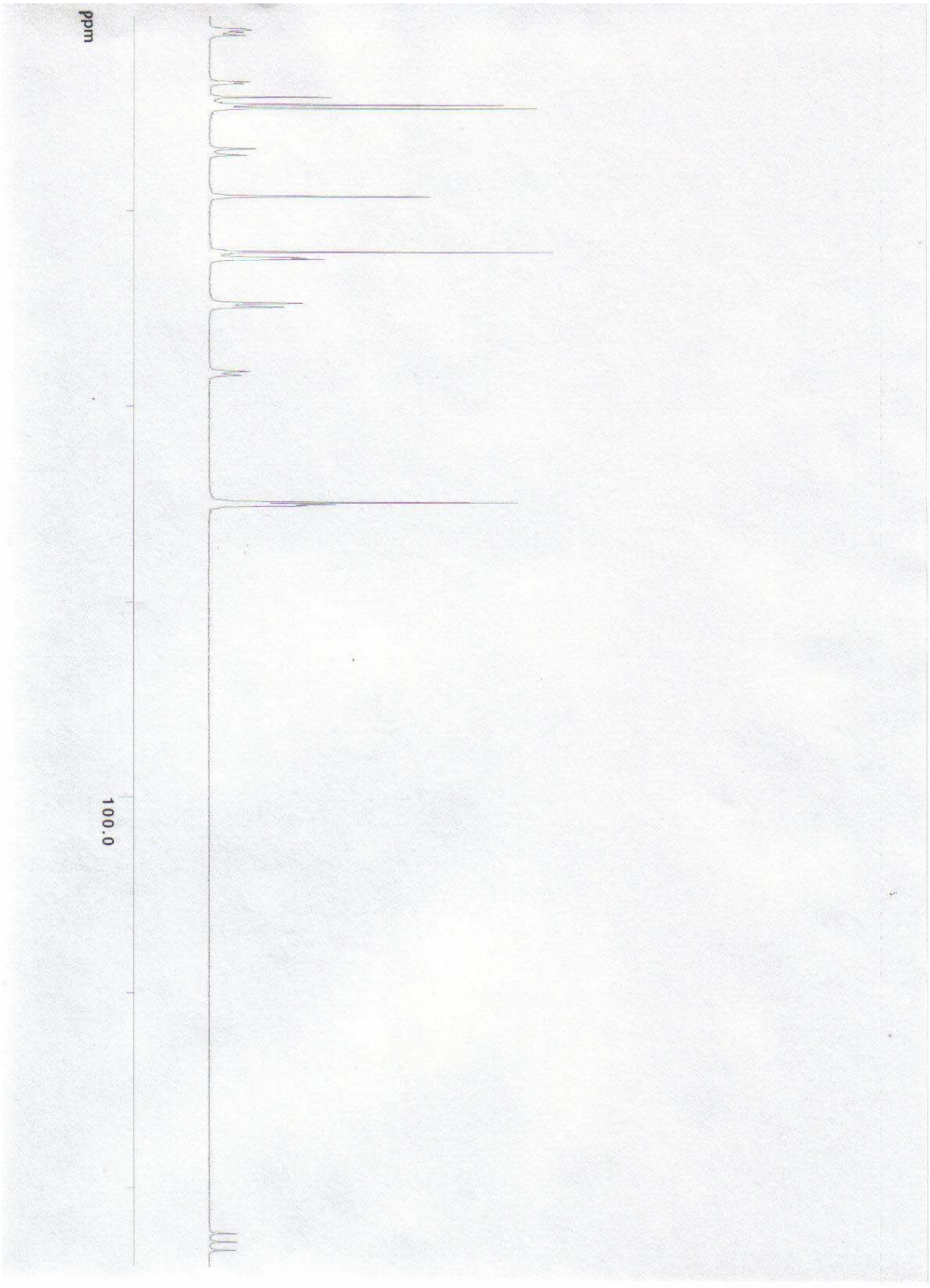
XI. Cartesian coordinates of the optimized geometry of dibenzo[a,h]anthracene (Sum of electronic and thermal free energies: -846.580025 Hartrees)

C	−1.275960	−4.983795	0.000000
C	−1.242580	−3.571884	0.000000
C	−0.109465	−5.726114	0.000000
C	0.013575	−2.896916	0.000000
C	1.131269	−5.065991	0.000000
C	1.187284	−3.682066	0.000000
C	0.033266	−1.435411	0.000000
C	−1.210163	−0.720051	0.000000
C	−1.210163	0.681086	0.000000
C	−0.033318	1.435399	0.000000
C	1.210105	−0.681116	0.000000
C	1.210105	0.720021	0.000000
C	−0.013598	2.896934	0.000000
C	−1.187269	3.682158	0.000000
C	−1.131196	5.066081	0.000000
C	0.109564	5.726147	0.000000
C	1.242580	3.571863	0.000000
C	1.276021	4.983773	0.000000
C	−2.462995	−2.809587	0.000000
C	2.447831	1.451879	0.000000
C	−2.447890	−1.451940	0.000000
C	2.462967	2.809525	0.000000
H	−2.243040	−5.481554	0.000000
H	−0.150791	−6.811858	0.000000
H	2.052926	−5.641618	0.000000
H	2.159870	−3.201368	0.000000
H	−2.175660	1.177369	0.000000
H	2.175597	−1.177426	0.000000
H	−2.159879	3.201524	0.000000
H	−2.052824	5.641752	0.000000
H	0.150939	6.811889	0.000000
H	2.243122	5.481491	0.000000
H	−3.405987	−3.351019	0.000000
H	3.377976	0.888637	0.000000
H	−3.378046	−0.888714	0.000000
H	3.405973	3.350934	0.000000

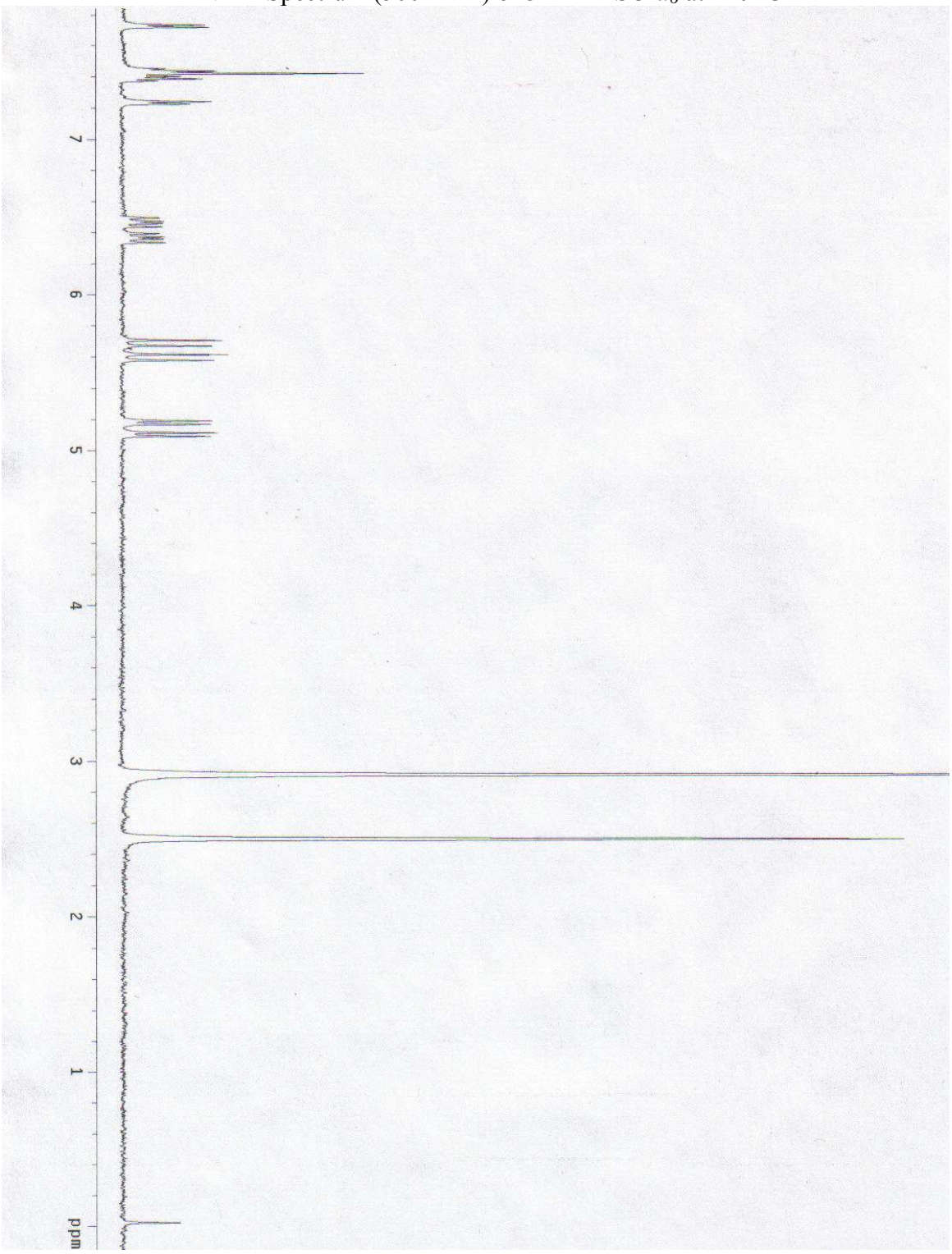
^{1}H NMR Spectrum (500 MHz) of **2** in DMSO-d_6 at 110 ^{o}C



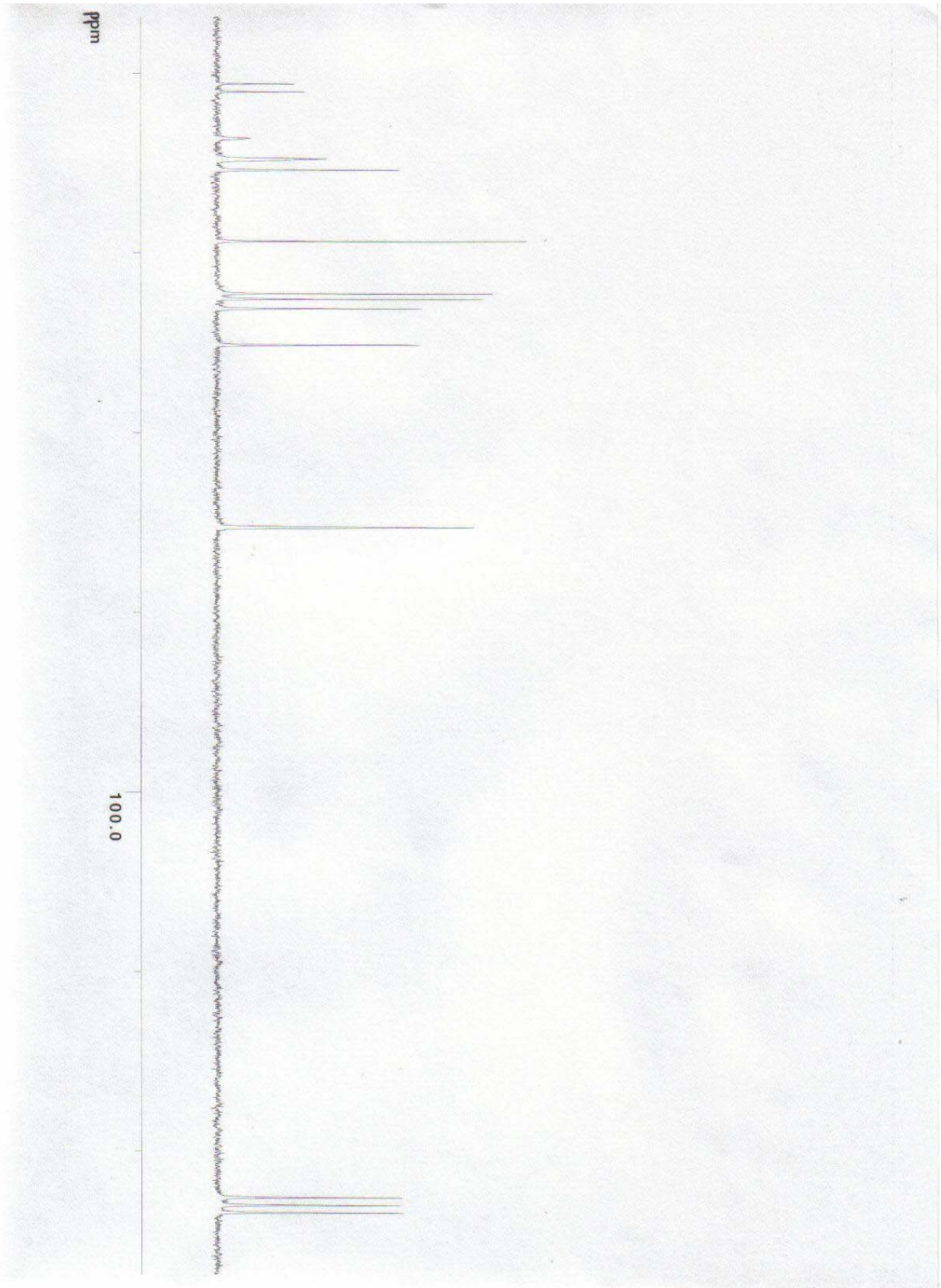
^{13}C NMR Spectrum (300 MHz) of **2** in $CDCl_3$



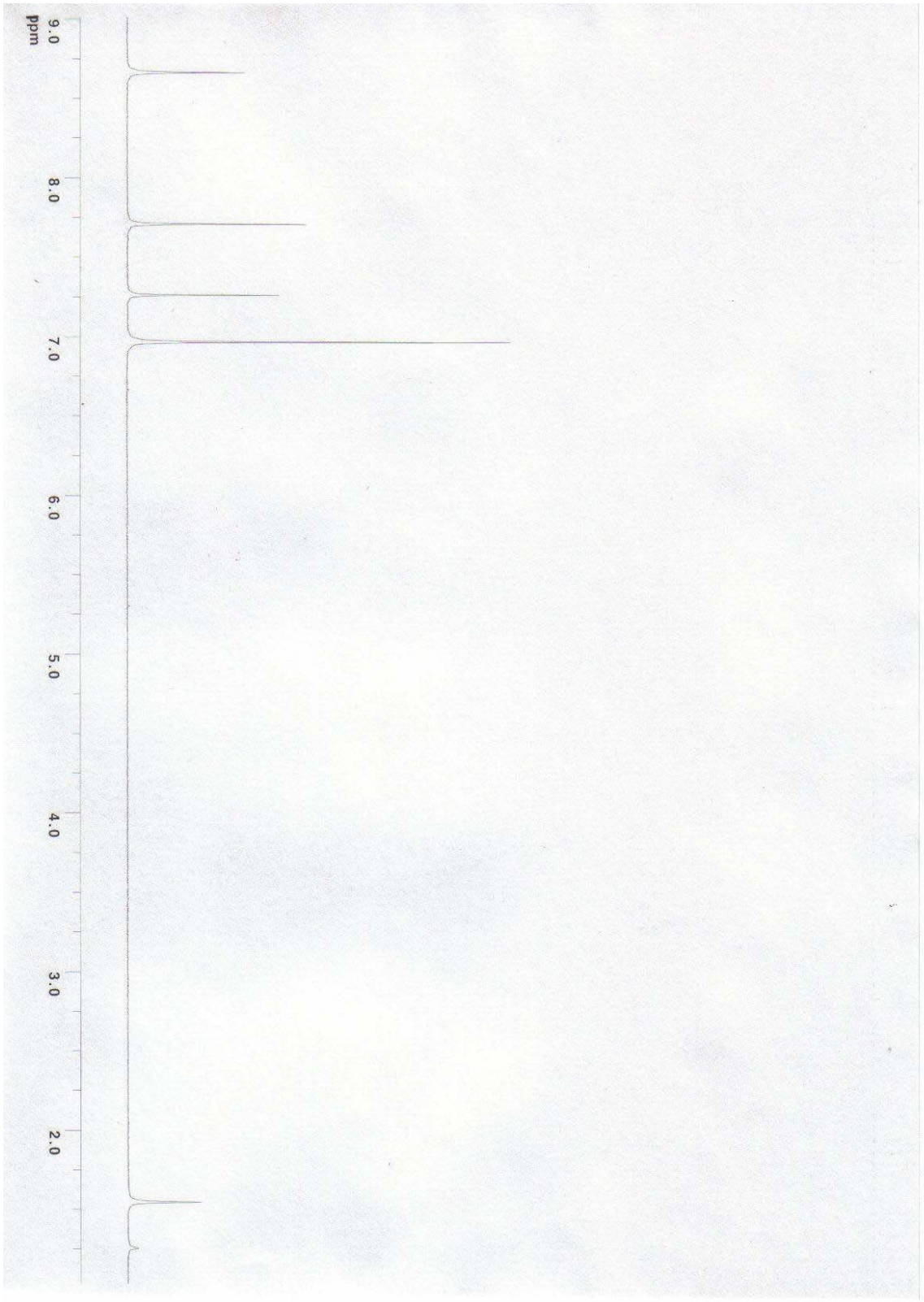
^{1}H NMR Spectrum (500 MHz) of **3** in DMSO-d_6 at 110 ^{o}C



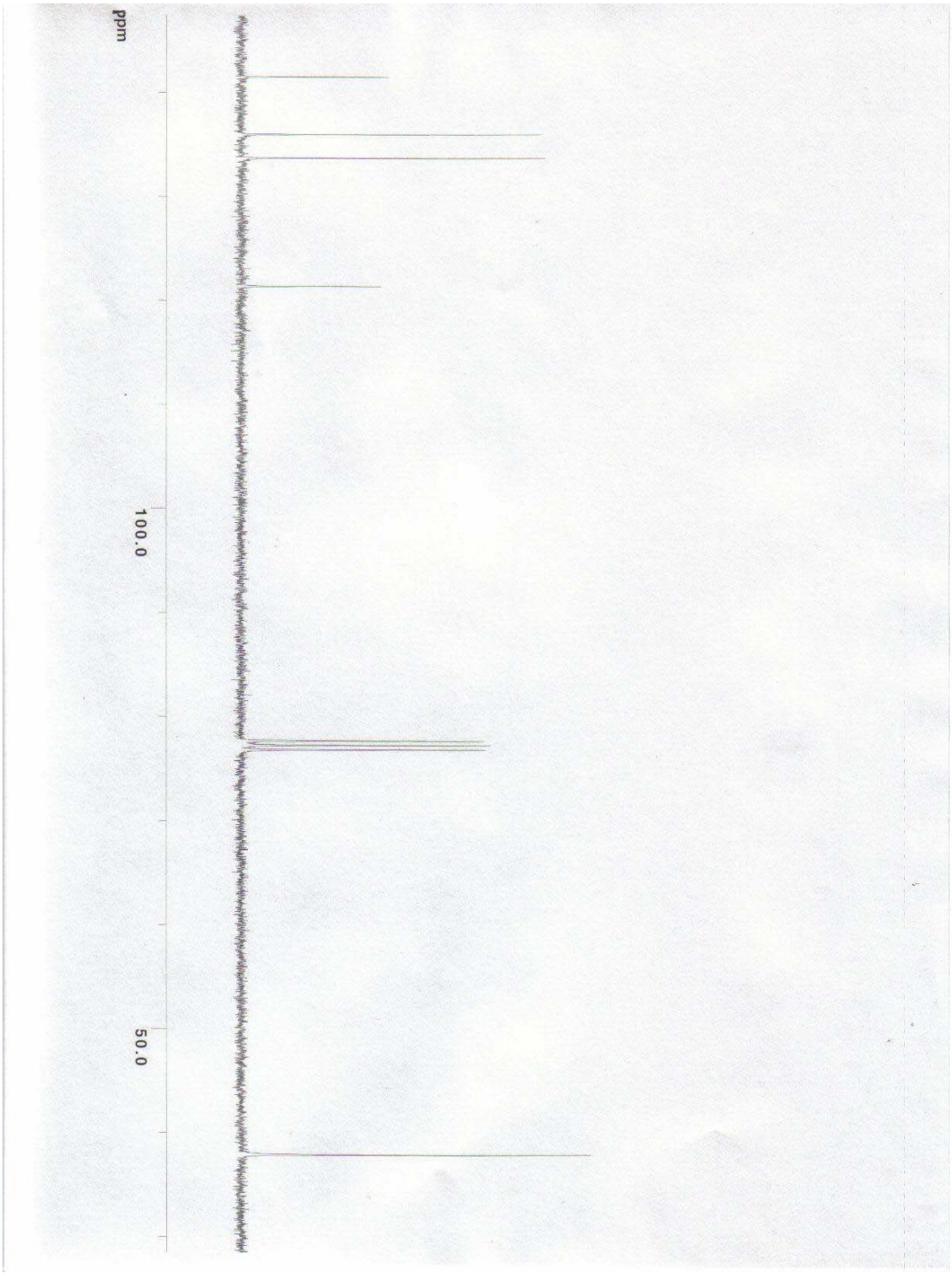
^{13}C NMR Spectrum (300 MHz) of **3** in $CDCl_3$



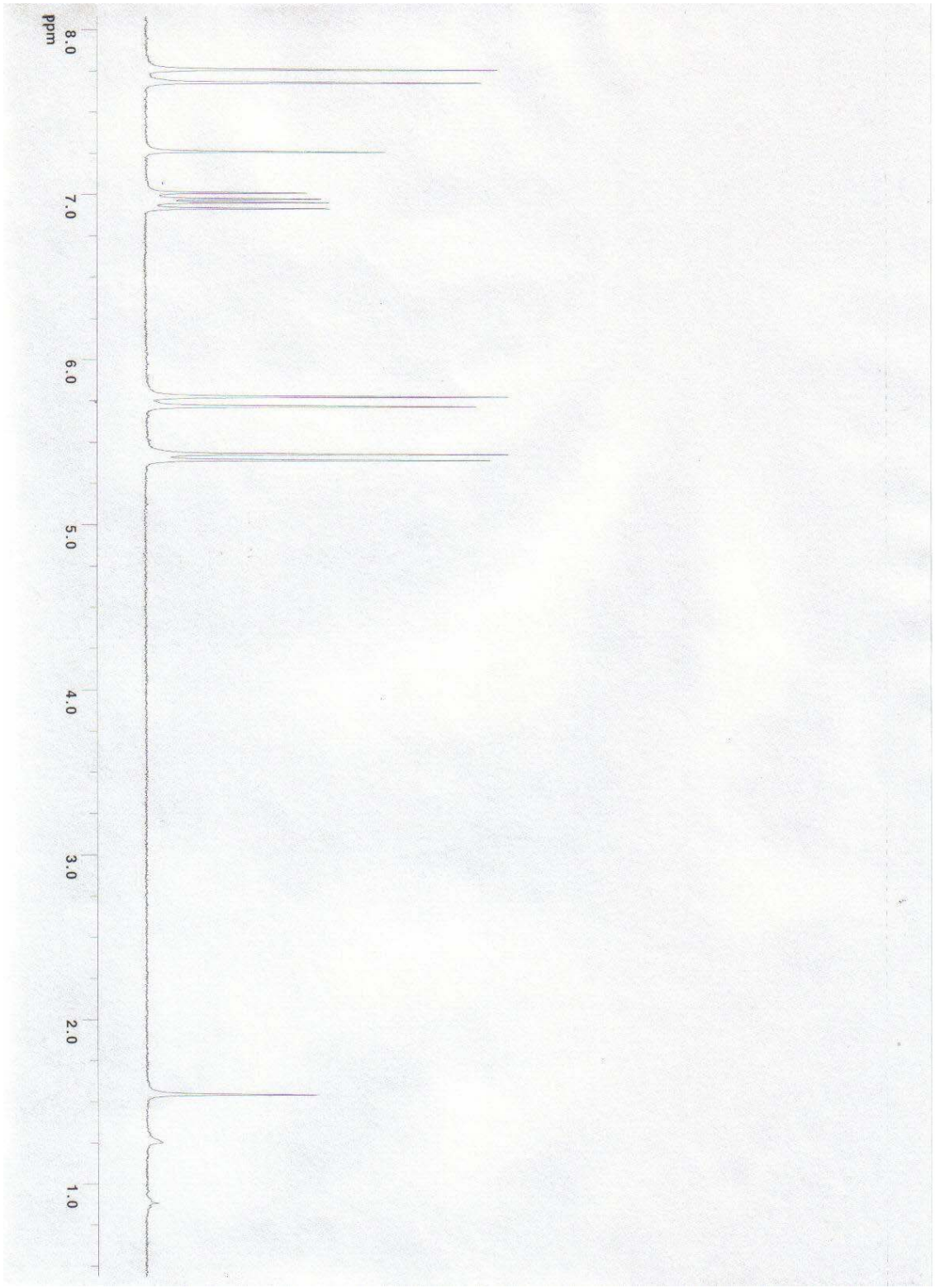
^{1}H NMR Spectrum (300 MHz) of **7** in $CDCl_3$



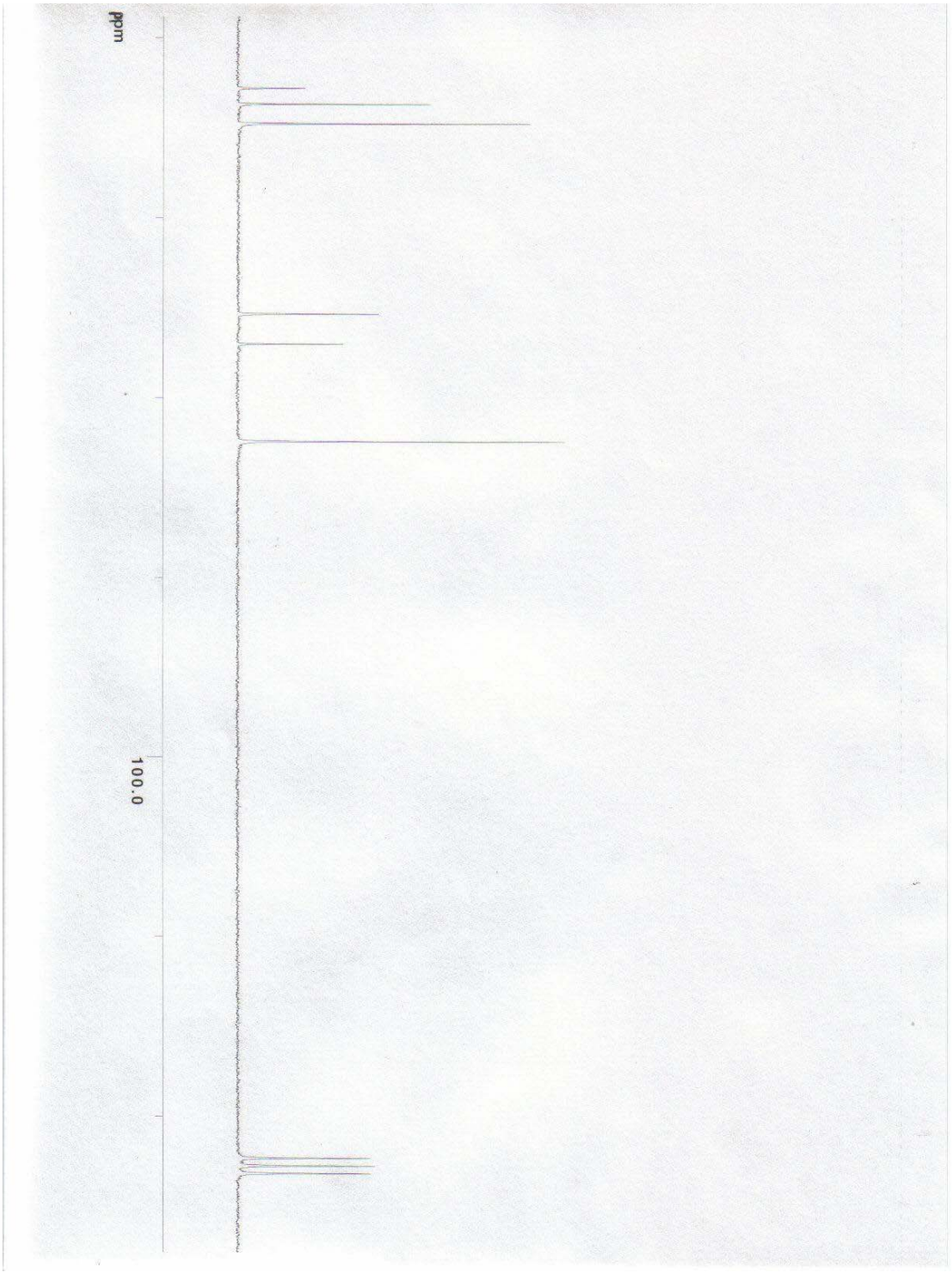
^{13}C NMR Spectrum (300 MHz) of **7** in $CDCl_3$



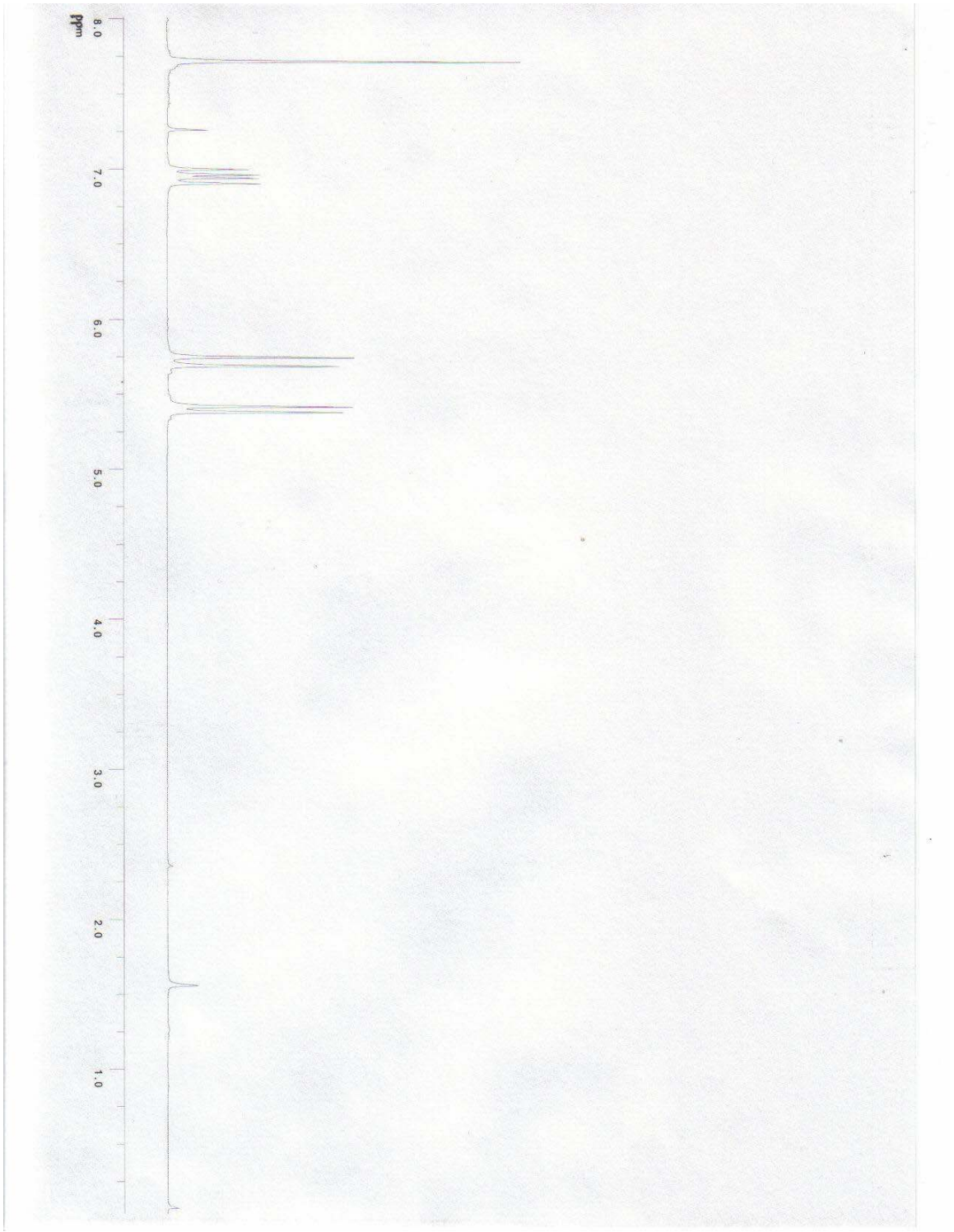
^{1}H NMR Spectrum (300 MHz) of **9** in $CDCl_3$



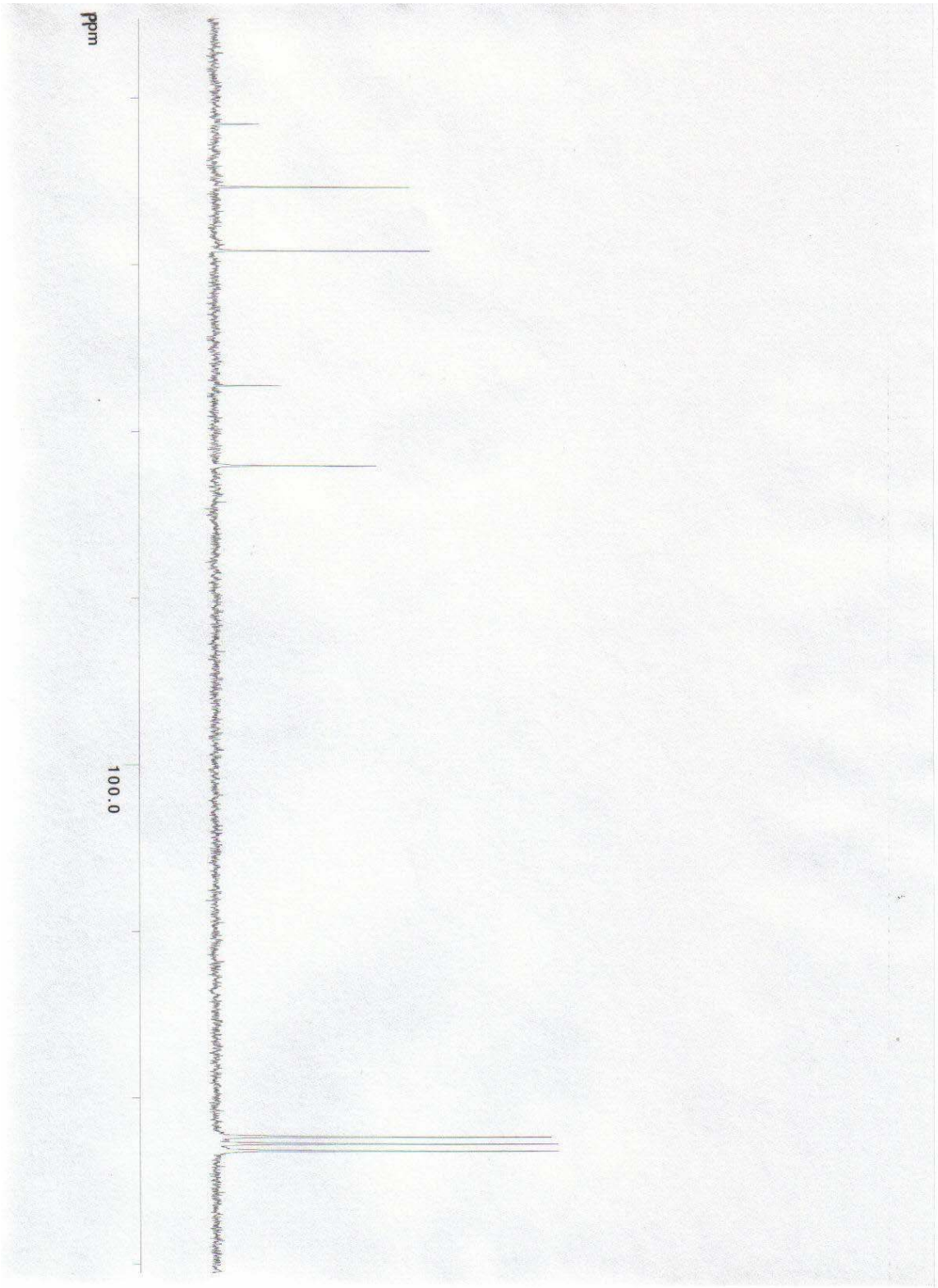
^{13}C NMR Spectrum (300 MHz) of **9** in $CDCl_3$



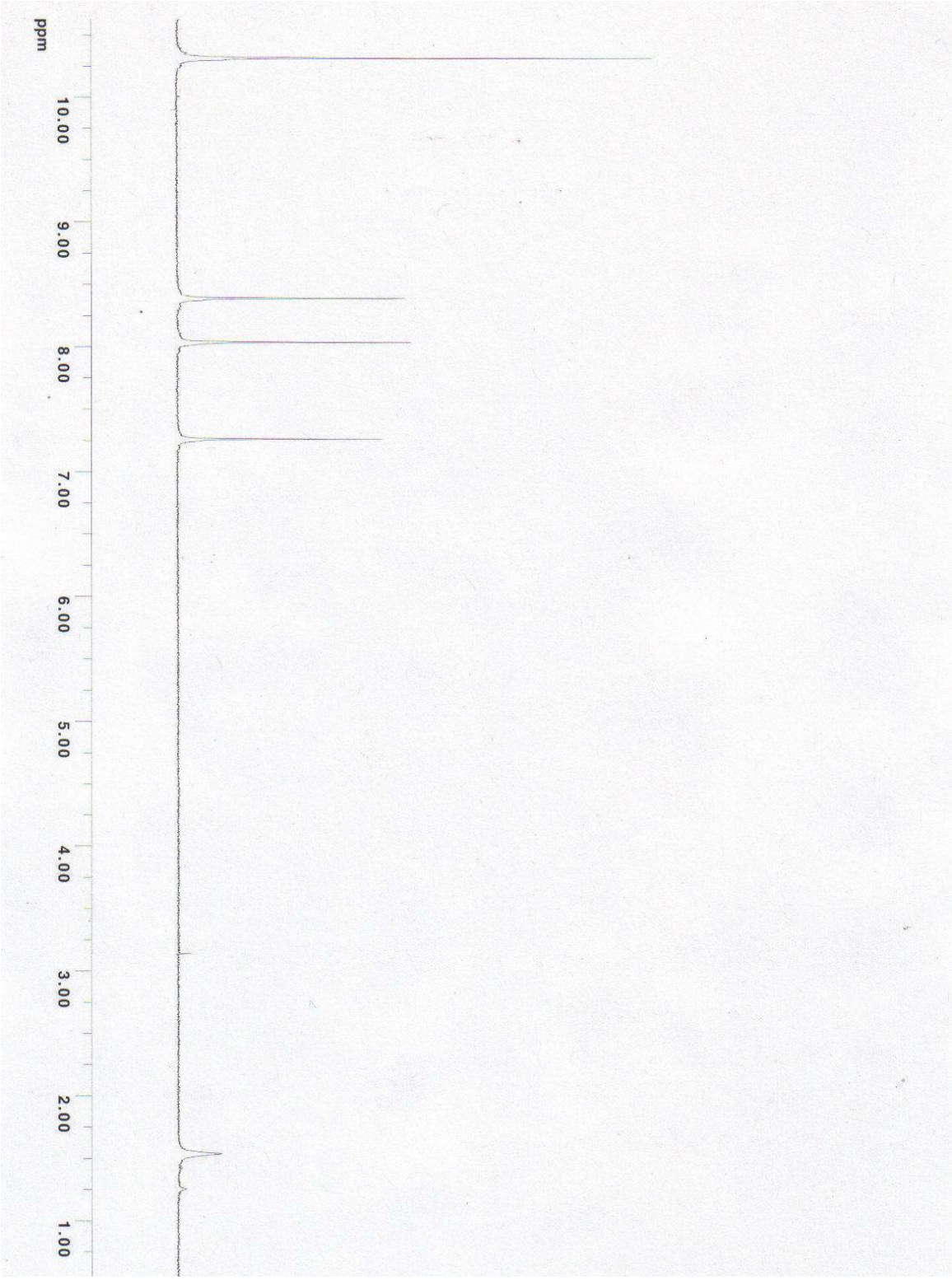
^{1}H NMR Spectrum (300 MHz) of **12** in $CDCl_3$



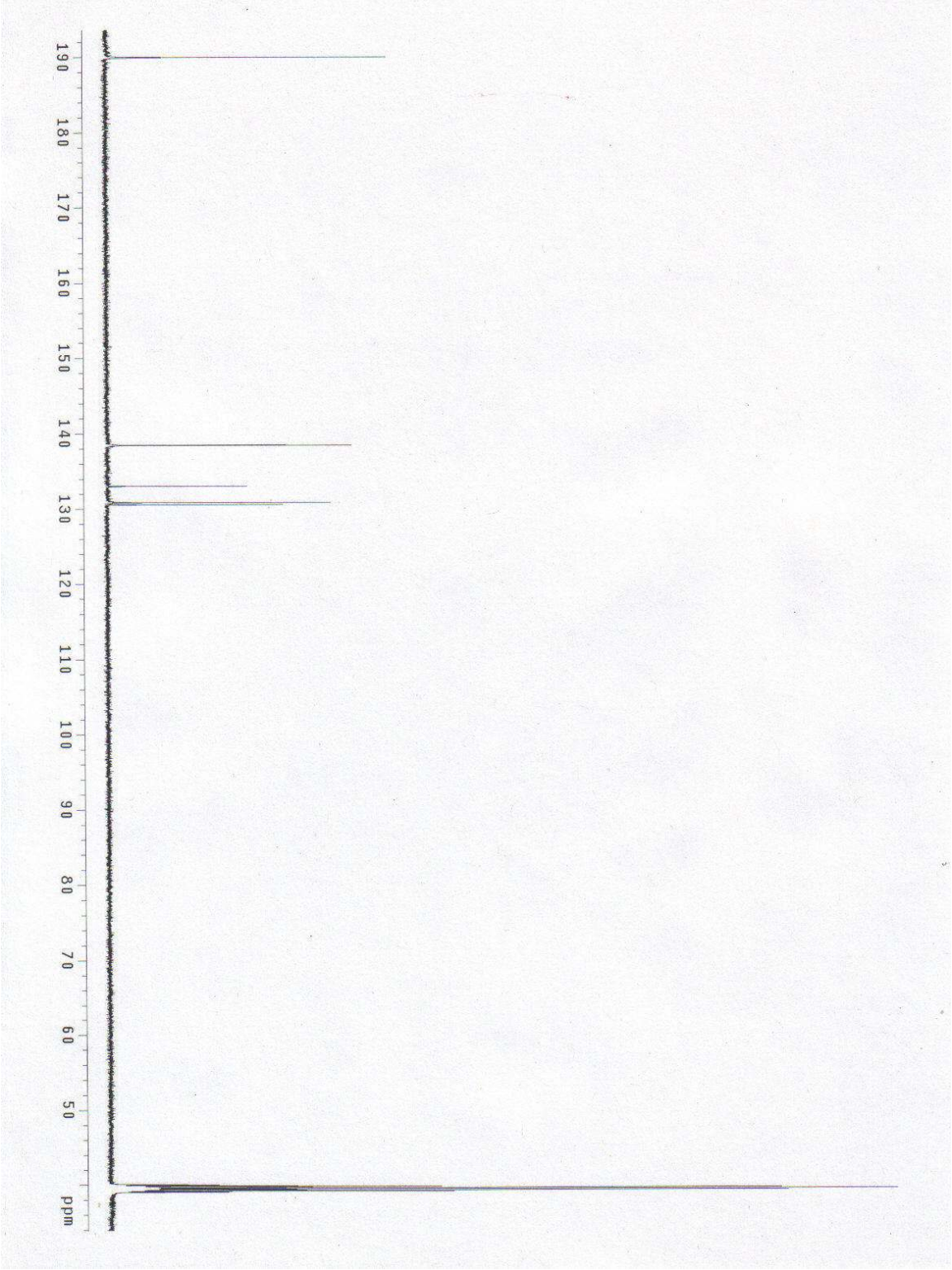
^{13}C NMR Spectrum (300 MHz) of **12** in $CDCl_3$



^{1}H NMR Spectrum (300 MHz) of **8** in $CDCl_3$



^{13}C NMR Spectrum (500 MHz) of **8** in DMSO-d_6 at 60 ^{o}C



Rotational Barriers of Compound 2 and 3

Rotational barriers were calculated from the coalescence temperature:[2]

$$\Delta G^{\ddagger}_{C} = 4.58\ T_C\ (10.32 + \log T_C / k_C)$$

where $\Delta G^{\ddagger}_{C}$ is the activation energy at coalescence, T_C is the coalescence temperature and k_C is the chemical-shift difference in Hz at the stopped exchange limit multiplied by 2.22.

Coalescence of the two peaks (6.838 and 6.812 ppm for **2** and 7.267 and 7.239 ppm for **3)** at room temperature using a 500 MHz spectrometer occurred at 55 ^{o}C for both cmpounds.

The calculated $\Delta G^{\ddagger}_{C}$ 17 kcal/mol for both **2** and **3**.

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[2] Nelson, J. H. *Nuclear Magnetic Resonance Spectroscopy*; Pearson Education: New Jersey, 2003.

General Experimental Details

All reactions were performed under inert atmosphere of nitrogen using conventional vacuum line techniques. Catalysts were dispensed in a glove box under argon. N-Bromosuccinimide was recrystallized from water prior to use. Tetrahydrofuran and diethyl ether were dispensed in a glove box from commercially available cylinders of anhydrous solvent (< 50 ppm H_2O) using a custom delivery system, dried over 4 Å molecular sieves, and tested using a drop of benzophenone ketyl radical solution. Dichloromethane was dried over 4 Å molecular sieves and distilled from calcium hydride. Carbon disulfide was purified[13] by washing 250 mL carbon disulfide with 10 mL bromine for 3 h, followed by water extraction and washing with KOH. Copper turnings were added to the CS_2, to remove trace bromine. The CS_2 was then distilled from anhydrous $CaCl_2$ onto 4 Å molecular sieves. Melting points are uncorrected.

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[3]Armarego, W. L. F.; Perrin, D. D. *"Purification of Laboratory Chemicals", 4th Ed.*; Butterworth-Heinemann: Woburn, MA, 1998.