Electronic Supplementary Information

for

Decomposition of benzoylthioureas into benzamides and thiobenzamides under solvent-free condition using iodine-alumina as catalyst and its mechanistic study by density functional theory†

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Table of contents

Computational Details:

The geometries were fully optimized by density functional calculation in spin restricted shell wavefunction manner.[1, 2] The hybrid functional B3LYP[3,4] containing Becke's gradient corrected exchange functional containing 20% of Hartree-Fock exchange[3] and correlation functional of Lee, Yang and Paar (LYP) was used for the calculations.[4] The method formulated Mayer was utilized for the bonding analysis.[5-7] All the calculations were performed using ORCA version 2.8.[8]

References:

1. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev. B* **1964**, *136*, 864−871.

2. Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev. A* **1965**, *140*, 1133−1138.

3. Becke, A. D. Density Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

4. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula Into A Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785−789.

5. Mayer, I. Charge, Bond Order and Valence in the AB Initio SCF Theory. *Chem. Phys. Lett.* **1983***, 97*, 270 – 274.

6. Mayer, I. Bond Order and Valence: Relations to Mulliken's Population Analysis. *Int. J. Quant. Chem.* **1984**, *26*, 151 – 154.

7. Mayer, I. Bond Orders and Valences in the SCF Theory: A Comment. *Theor.Chim.Acta* **1985**, *67*, 315 – 322.

8. Neese, F. The ORCA Program System. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.

Table S1. Energies of the reactants in atomic unit.

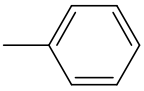
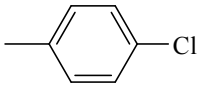
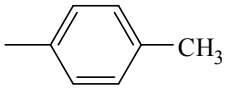
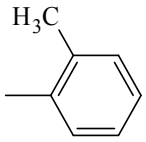
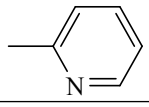
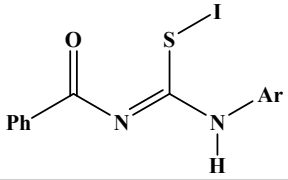
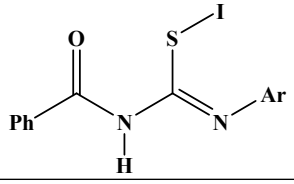
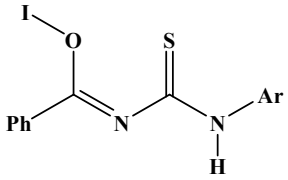
Reactant (1)	Aryl	Energy (a. u.)
Unsubstituted benzoylthiourea		-1123.411205
p-Chlorinated benzoylthiourea		-1582.968024
p-Methylated benzoylthiourea		-1162.712156
o-Methylated benzoylthiourea		-1162.710573
o-Pyridinated benzoylthiourea		-1139.46178

Table S2. Relative energies of different intermediates for unsubstituted benzoylthiourea

Intermediates	Structure	Relative Energy (kcal)
A		0.0
B		0.5
C		35.2

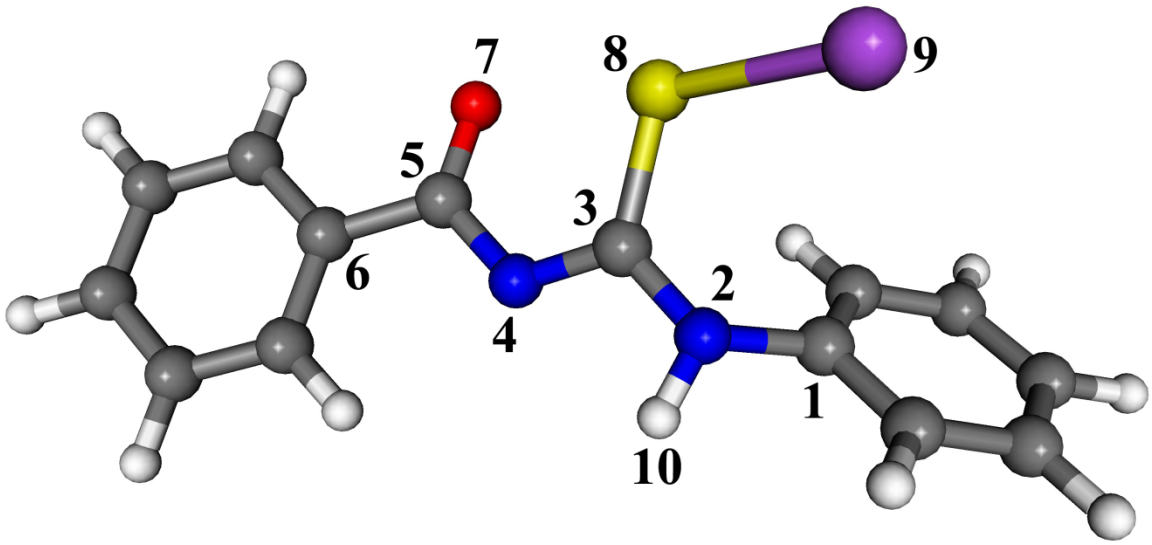


Figure S1: Optimized structure of **A**.

Table S3. Mayer bond order for selected bonds (atom numbering is shown in Figure S1) for unsubstituted benzoylthiourea.

Intermediates	Mayer Bond Order				
	C1 – N2	**N2 – C3**	**C3 – N4**	**N4 – C5**	**C5 – C6**
A	0.9092	1.1663	1.5143	1.3996	0.9238
B	1.1027	1.8061	0.9953	1.1750	0.9085
C	1.0134	1.1414	1.0373	1.9322	0.9493

Table S4. Optimized geometries of different structures for the reactions of unsubstituted benzoylthiourea.

Intermediate: A				**Intermediate: B**			
C	1.825388	1.656687	-0.113115	C	1.773448	1.763068	0.153771
C	2.180248	1.543514	1.230365	C	2.370377	1.362660	1.355911
C	3.431136	1.981007	1.649612	C	3.681977	1.724276	1.634968
C	4.320574	2.553893	0.745960	C	4.417828	2.477722	0.724942
C	3.952738	2.685269	-0.590191	C	3.821532	2.887976	-0.465572
C	2.712065	2.234046	-1.021894	C	2.503324	2.553956	-0.741347
N	0.531827	1.290528	-0.585917	N	0.425562	1.520349	-0.126563
C	-0.352877	0.386952	-0.089801	C	-0.238388	0.451281	-0.022222
S	0.126777	-1.233822	0.534860	S	0.266126	-1.282438	0.274063
N	-1.616852	0.716750	-0.149769	N	-1.629410	0.572980	-0.221800
C	-2.528904	-0.138942	0.400535	C	-2.578451	-0.259753	0.324179
O	-2.184571	-1.087232	1.125114	O	-2.257937	-1.215519	1.017795
I	2.359521	-1.727870	-0.543068	I	2.381843	-1.483864	-1.010339
C	-3.963344	0.132226	0.124131	C	-4.004172	0.076871	0.034559
C	-4.928530	-0.730479	0.655440	C	-4.976967	-0.434099	0.898745

C	-6.275803	-0.506244	0.409576	C	-6.319816	-0.159288	0.679852
C	-6.671824	0.582017	-0.365911	C	-6.704894	0.618103	-0.410058
C	-5.715999	1.444584	-0.896000	C	-5.742958	1.116800	-1.283367
C	-4.365948	1.223045	-0.653233	C	-4.396721	0.849624	-1.063188
H	0.041019	2.027916	-1.077497	H	-1.898094	1.502759	-0.514451
H	1.486249	1.117728	1.942828	H	1.801617	0.779159	2.068259
H	3.704870	1.882660	2.693024	H	4.131512	1.411970	2.569985
H	5.291202	2.897561	1.080645	H	5.442364	2.750839	0.944967
H	4.637153	3.129282	-1.302696	H	4.381804	3.484368	-1.176116
H	2.431892	2.310481	-2.065768	H	2.025188	2.886168	-1.654025
H	-4.603692	-1.570630	1.255535	H	-4.661213	-1.044793	1.734734
H	-7.018833	-1.177870	0.821993	H	-7.067543	-0.553057	1.357162
H	-7.724196	0.756938	-0.556836	H	-7.753393	0.829845	-0.582256
H	-6.024160	2.291517	-1.497361	H	-6.041264	1.707208	-2.141073
H	-3.614881	1.888023	-1.056137	H	-3.662981	1.216529	-1.770515
Intermediate: C				**Molecule: Unsubstituted benzoylthiourea**			
C	-3.958192	0.392674	-0.058268	C	2.949691	-0.432390	-0.129428
C	-4.590548	-0.677780	0.580337	C	3.792556	0.617932	0.242064
C	-5.929737	-0.941639	0.307628	C	5.165468	0.398668	0.313910
C	-6.652859	-0.164677	-0.589709	C	5.716933	-0.840858	0.013505
C	-6.020220	0.900447	-1.226351	C	4.875350	-1.883816	-0.366233
C	-4.687500	1.176503	-0.964847	C	3.506108	-1.683510	-0.434778
N	-2.605411	0.750771	0.116219	N	1.543474	-0.343065	-0.237328
C	-1.623650	0.335611	0.963301	C	0.634537	0.613330	0.118371
S	-1.727488	-0.777482	2.199508	S	0.923878	2.158383	0.634960
N	-0.473263	1.103012	0.756170	N	-0.671396	0.075613	0.034433
C	0.661975	0.660972	0.389745	C	-1.813922	0.715853	-0.453590
O	0.847582	-0.673137	0.186958	O	-1.774837	1.720101	-1.125444
I	1.695676	-1.348910	-1.571445	C	-3.100939	0.015808	-0.124752
C	1.827417	1.569558	0.286890	C	-4.174946	0.194757	-1.000943
C	3.111829	1.111657	0.598059	C	-5.397309	-0.410745	-0.744094
C	4.193324	1.982119	0.548079	C	-5.565608	-1.188575	0.399390
C	4.005553	3.310034	0.176702	C	-4.507816	-1.354349	1.287478
C	2.727810	3.771716	-0.130948	C	-3.278345	-0.758015	1.026047
C	1.642365	2.909073	-0.068338	H	1.133393	-1.156384	-0.675153
H	-2.310269	1.513525	-0.478869	H	-0.797921	-0.862796	0.385137
H	-4.039620	-1.282789	1.282153	H	3.375660	1.587258	0.460682
H	-6.408104	-1.774410	0.809203	H	5.808546	1.221064	0.603580
H	-7.694126	-0.383025	-0.791484	H	6.787456	-0.994889	0.070443
H	-6.564868	1.520074	-1.928666	H	5.284633	-2.857211	-0.607768
H	-4.203000	2.009382	-1.464243	H	2.857389	-2.504200	-0.724527
H	3.257248	0.083792	0.903889	H	-4.033054	0.817149	-1.875133
H	5.182880	1.623947	0.803991	H	-6.222399	-0.272266	-1.432513
H	4.851714	3.985152	0.132137	H	-6.521780	-1.655482	0.602448
H	2.578104	4.805635	-0.417017	H	-4.641632	-1.938673	2.189794
H	0.644279	3.262653	-0.291037	H	-2.476665	-0.863111	1.748086

Table S5. Relative energies of different intermediates for *p*-chlorinated molecule.

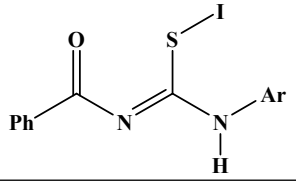
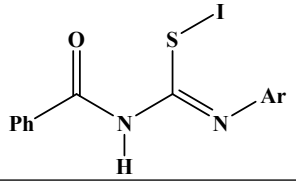
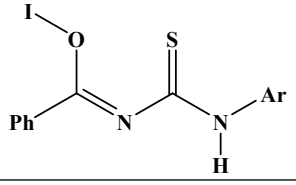
Intermediates	Structure	Relative Energy (kcal)
A_p-Cl		0.2
B_p-Cl		0.0
C_p-Cl		35.0

Table S6. Mayer bond order for selected bonds (atom numbering is shown in Figure S1) for *p*-chlorinated molecule.

Intermediates	Mayer Bond Order				
	C1 – N2	**N2 – C3**	**C3 – N4**	**N4 – C5**	**C5 – C6**
A_p-Cl	0.9138	1.1550	1.5238	1.3918	0.9254
B_p-Cl	1.1197	1.7945	1.0017	1.1714	0.9103
C_p-Cl	1.0194	1.1321	1.0436	1.9265	0.9495

Table S7. Optimized geometries of different structures for the reactions of *p*-chlorinated molecule.

Intermediate: A_p-Cl				**Intermediate: B_p-Cl**			
C	1.822528	1.654431	-0.120252	C	1.772450	1.760920	0.148740
C	2.173378	1.546810	1.224753	C	2.371517	1.361042	1.349803
C	3.419574	1.981791	1.656881	C	3.681747	1.718316	1.637233
C	4.301845	2.548592	0.746520	C	4.402146	2.472706	0.720618
C	3.956544	2.682927	-0.592403	C	3.822615	2.892444	-0.470942
C	2.717330	2.228731	-1.022492	C	2.505021	2.555010	-0.741089
N	0.533275	1.288435	-0.598183	N	0.426455	1.521095	-0.133022

C	-0.352730	0.385914	-0.096909	C	-0.240409	0.453178	-0.021894
S	0.129178	-1.233244	0.529922	S	0.263657	-1.277766	0.285278
N	-1.614531	0.718332	-0.152236	N	-1.629515	0.576425	-0.221072
C	-2.527248	-0.137918	0.400076	C	-2.579149	-0.255949	0.327646
O	-2.179808	-1.084916	1.124032	O	-2.256115	-1.208406	1.024238
I	2.360873	-1.726855	-0.549443	I	2.378733	-1.488296	-1.000088
Cl	5.877869	3.111243	1.297930	Cl	6.071588	2.917914	1.079790
C	-3.961283	0.132813	0.125560	C	-4.004278	0.078087	0.036430
C	-4.925560	-0.730729	0.657453	C	-4.977468	-0.435736	0.898611
C	-6.273037	-0.506448	0.413382	C	-6.320342	-0.163002	0.677797
C	-6.670109	0.582481	-0.360710	C	-6.704904	0.615177	-0.411764
C	-5.715253	1.445838	-0.891313	C	-5.742509	1.116786	-1.282949
C	-4.364928	1.224361	-0.650482	C	-4.396253	0.851623	-1.061045
H	0.042760	2.025025	-1.091280	H	-1.898337	1.506127	-0.514064
H	1.479297	1.124245	1.938797	H	1.807984	0.774973	2.063812
H	3.696337	1.891797	2.698589	H	4.139532	1.410312	2.567589
H	4.651627	3.125399	-1.292922	H	4.390997	3.490065	-1.171158
H	2.448859	2.304517	-2.069196	H	2.032408	2.891117	-1.654870
H	-4.599995	-1.571334	1.256509	H	-4.662123	-1.046678	1.734563
H	-7.015492	-1.178448	0.826127	H	-7.068454	-0.558909	1.353371
H	-7.722736	0.757363	-0.550098	H	-7.753444	0.825363	-0.585440
H	-6.024455	2.293253	-1.491390	H	-6.040520	1.707776	-2.140314
H	-3.614675	1.890122	-1.053588	H	-3.662432	1.220785	-1.767109

Intermediate: C_p-Cl

C	-3.959021	0.395473	-0.066264
C	-4.586023	-0.686883	0.557403
C	-5.927730	-0.951740	0.303104
C	-6.646439	-0.149585	-0.569996
C	-6.038003	0.928584	-1.200948
C	-4.702217	1.193971	-0.947473
N	-2.606091	0.748810	0.098937
C	-1.618529	0.320612	0.935946
S	-1.723850	-0.808226	2.157609
N	-0.471037	1.088850	0.729687
C	0.671398	0.648627	0.381803
O	0.864866	-0.685764	0.195688
I	1.759849	-1.377707	-1.532386
Cl	-8.348213	-0.495568	-0.884722
C	1.831877	1.563391	0.282522
C	3.113385	1.120188	0.625630
C	4.189490	1.997421	0.579962
C	3.999457	3.316996	0.180968
C	2.724608	3.763923	-0.158766
C	1.644116	2.894910	-0.100080
H	-2.313448	1.520357	-0.485827

H	-4.029905	-1.307287	1.241651	
H	-6.408828	-1.790026	0.788868	
H	-6.601387	1.554233	-1.879988	
H	-4.230355	2.037980	-1.439140	
H	3.260310	0.099200	0.952926	
H	5.176473	1.651252	0.860873	
H	4.841644	3.997251	0.139911	
H	2.573304	4.791297	-0.466510	
H	0.648092	3.237356	-0.347812	

Table S8. Relative energies of different intermediates for *p*-methylated molecule.

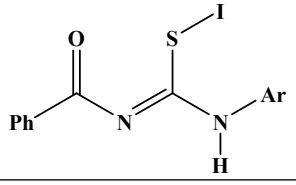
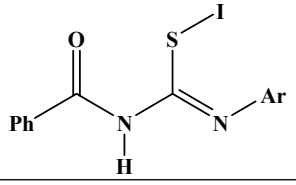
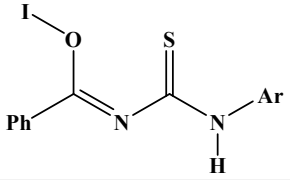
Intermediates	Structure	Relative Energy (kcal)
A_p-Me		0.0
B_p-Me		0.7
C_p-Me		35.5

Table S9. Mayer bond order for selected bonds (atom numbering is shown in Figure S1) for p-methylated molecule.

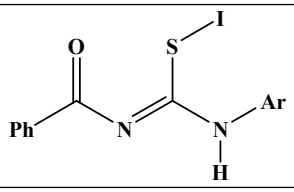
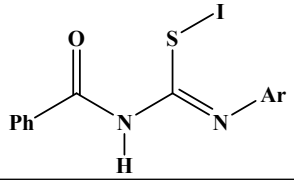
Intermediates	Mayer Bond Order				
	C1 – N2	**N2 – C3**	**C3 – N4**	**N4 – C5**	**C5 – C6**
A_p-Me	0.9047	1.1728	1.5131	1.4038	0.9261
B_p-Me	1.1200	1.8032	0.9944	1.1719	0.9076
C_p-Me	1.0081	1.1453	1.0359	1.9327	0.9498

Table S10. Optimized geometries of different structures for the reactions of *p*-methylated molecule.

Intermediate: A_p-Me				**Intermediate: B_p-Me**			
C	-1.677487	-1.402628	-0.288339	C	-1.699272	-1.506725	-0.112000
C	-2.075350	-1.333081	1.045216	C	-2.289624	-1.278393	1.135151
C	-3.374379	-1.676479	1.395620	C	-3.626578	-1.592531	1.342467
C	-4.296453	-2.119010	0.444101	C	-4.418006	-2.128007	0.325353
C	-3.869911	-2.208388	-0.882968	C	-3.813811	-2.361443	-0.914853
C	-2.579991	-1.849808	-1.250730	C	-2.473977	-2.080323	-1.127448
N	-0.337588	-1.133362	-0.694046	N	-0.335280	-1.315604	-0.348352
C	0.593475	-0.316839	-0.140589	C	0.409483	-0.346119	-0.031418
S	0.213196	1.303546	0.551867	S	0.038966	1.322718	0.619290
N	1.833796	-0.731004	-0.186956	N	1.789318	-0.532944	-0.262492
C	2.785787	0.029221	0.429070	C	2.793422	0.076110	0.453322
O	2.488124	0.958166	1.198689	O	2.542043	0.889938	1.332054
I	-1.931912	2.020855	-0.578434	I	-2.035485	1.956396	-0.594653
C	-5.711158	-2.463066	0.833776	C	-5.866709	-2.473579	0.558068
C	4.206023	-0.321021	0.166144	C	4.191018	-0.322660	0.108259
C	5.212855	0.453702	0.752521	C	5.182420	-0.095118	1.067066
C	6.548066	0.155702	0.518847	C	6.500207	-0.444362	0.806450
C	6.890274	-0.920242	-0.298128	C	6.842792	-1.013976	-0.417667
C	5.892680	-1.695641	-0.883045	C	5.863719	-1.228134	-1.383136
C	4.554665	-1.399295	-0.653526	C	4.541949	-0.885484	-1.123136
H	0.111997	-1.888918	-1.197266	H	1.984329	-1.402621	-0.740235
H	-1.375946	-1.013677	1.806514	H	-1.699452	-0.863687	1.942122
H	-3.670817	-1.611518	2.436615	H	-4.063639	-1.409556	2.318065
H	-4.559017	-2.555418	-1.644549	H	-4.400169	-2.785490	-1.723112
H	-2.273050	-1.902659	-2.288706	H	-2.010605	-2.285293	-2.084480
H	4.929507	1.285516	1.384462	H	4.900561	0.357505	2.008715
H	7.323495	0.760258	0.973143	H	7.261791	-0.270690	1.556894
H	7.933099	-1.153298	-0.478846	H	7.871738	-1.285152	-0.621155
H	6.158807	-2.533244	-1.516718	H	6.129926	-1.656021	-2.341759
H	3.771159	-1.995964	-1.099224	H	3.797988	-1.028971	-1.897553
H	-6.148301	-3.190512	0.147262	H	-6.497260	-2.121425	-0.262072
H	-5.756649	-2.878752	1.842102	H	-6.008921	-3.556248	0.633985
H	-6.348148	-1.573196	0.818383	H	-6.237457	-2.027087	1.481742
Intermediate: C_p-Me				**Molecule: *p*-methylated molecule**			
C	-3.630985	0.459116	0.065498	C	2.946087	-0.438003	-0.117920
C	-4.255524	-0.621548	0.689704	C	3.792480	0.610120	0.249585
C	-5.610107	-0.853452	0.467056	C	5.164177	0.390731	0.317553
C	-6.379354	-0.043583	-0.366020	C	5.738921	-0.844510	0.018847
C	-5.736355	1.030635	-0.989718	C	4.878023	-1.880718	-0.352321
C	-4.390586	1.279524	-0.780827	C	3.508043	-1.685615	-0.418546
N	-2.265359	0.791666	0.191833	N	1.538823	-0.350133	-0.222610

C	-1.263854	0.350655	0.999561	C	0.631054	0.601268	0.142321
S	-1.343960	-0.784986	2.217870	S	0.920227	2.141054	0.677389
N	-0.110393	1.109479	0.773418	N	-0.676787	0.065751	0.051078
C	1.009571	0.660628	0.370234	C	-1.812408	0.708108	-0.447266
O	1.174030	-0.671638	0.139395	O	-1.765188	1.710248	-1.122159
I	1.977044	-1.326257	-1.647983	C	-3.104903	0.014225	-0.125069
C	-7.850735	-0.295329	-0.575293	C	-4.170678	0.190955	-1.011715
C	2.183070	1.557619	0.254662	C	-5.397272	-0.409028	-0.761919
C	3.468950	1.080622	0.528601	C	-5.578265	-1.178964	0.385065
C	4.558910	1.939823	0.468200	C	-4.528773	-1.342353	1.283488
C	4.377995	3.275720	0.122952	C	-3.295077	-0.751603	1.028998
C	3.098890	3.756481	-0.147605	H	1.128639	-1.160716	-0.665465
C	2.005382	2.904846	-0.074285	H	-0.808516	-0.868972	0.409542
H	-1.981596	1.562931	-0.397756	C	7.232146	-1.044507	0.062387
H	-3.688515	-1.263880	1.344158	H	3.378881	1.580049	0.472688
H	-6.074458	-1.699470	0.961748	H	5.802651	1.217678	0.608612
H	-6.297036	1.684766	-1.648843	H	5.283374	-2.857904	-0.589489
H	-3.919322	2.121970	-1.277330	H	2.864073	-2.512918	-0.700541
H	3.609595	0.046268	0.814307	H	-4.018928	0.807422	-1.888460
H	5.549890	1.566535	0.695507	H	-6.215808	-0.272343	-1.458514
H	5.230542	3.942128	0.070019	H	-6.537715	-1.641503	0.582659
H	2.954408	4.796631	-0.413178	H	-4.672404	-1.920453	2.188311
H	1.006561	3.273115	-0.268060	H	-2.499923	-0.854791	1.758528
H	-8.139014	-1.282937	-0.212586	H	7.700893	-0.720713	-0.872550
H	-8.458747	0.441373	-0.041536	H	7.688216	-0.468245	0.869621
H	-8.120204	-0.233395	-1.632474	H	7.489297	-2.094698	0.209991

Table S11. Relative energies of different intermediates for *o*-methylated molecule.

Intermediates	Structure	Relative Energy (kcal)
A_o-Me		0.0
B_o-Me		0.31

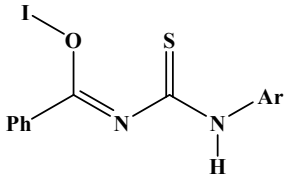
C_o-Me		36.3

Table S12. Mayer bond order for selected bonds (atom numbering is shown in Figure S1) for *o*-methylated molecule.

Intermediates	Mayer Bond Order				
	C1 – N2	**N2 – C3**	**C3 – N4**	**N4 – C5**	**C5 – C6**
A_o- Me	0.9585	1.1536	1.5098	1.4015	0.9236
B_o-Me	1.1379	1.7861	0.9979	1.1722	0.9090
C_o-Me	0.9087	1.1397	1.0361	1.9337	0.9413

Table S13. Optimized geometries of different structures for the reactions of *o*-methylated molecule.

Intermediate: A_o-Me				**Intermediate: B_o-Me**			
C	1.753064	1.523065	0.224158	C	1.758459	1.501277	0.436002
C	2.015887	1.276031	1.570415	C	2.242150	1.060957	1.673652
C	3.257389	1.591698	2.105354	C	3.548975	1.332111	2.053943
C	4.226391	2.182273	1.302174	C	4.385552	2.045027	1.202155
C	3.946470	2.450708	-0.033171	C	3.899279	2.494232	-0.022358
C	2.713999	2.127685	-0.600389	C	2.586801	2.251612	-0.421596
N	0.464404	1.259010	-0.329349	N	0.411324	1.344484	0.090649
C	-0.447659	0.317863	0.022377	C	-0.302511	0.303778	0.113739
S	-0.010588	-1.381494	0.433210	S	0.126590	-1.461619	0.331126
N	-1.705209	0.677979	-0.016708	N	-1.680588	0.491734	-0.122461
C	-2.640781	-0.224901	0.400369	C	-2.674973	-0.325733	0.364001
O	-2.325162	-1.271001	0.992272	O	-2.408890	-1.319685	1.026217
I	2.249504	-1.763008	-0.640519	I	2.267925	-1.666901	-0.908918
C	2.432134	2.395987	-2.054320	C	2.069658	2.739869	-1.746425
C	-4.066088	0.111339	0.148247	C	-4.078366	0.074190	0.048595
C	-5.055450	-0.794876	0.545967	C	-5.093526	-0.426318	0.869072
C	-6.394534	-0.510165	0.318663	C	-6.418633	-0.095438	0.621457
C	-6.758211	0.682285	-0.304402	C	-6.743585	0.727562	-0.454504
C	-5.778209	1.588544	-0.700925	C	-5.739300	1.216473	-1.284660
C	-4.436459	1.306923	-0.476206	C	-4.410461	0.893671	-1.035057
H	-0.002113	2.066051	-0.727573	H	-1.905724	1.444542	-0.375445
H	1.250716	0.833255	2.194725	H	1.582794	0.514172	2.335578
H	3.459803	1.386250	3.149134	H	3.909869	0.988289	3.015560
H	5.195992	2.435681	1.712743	H	5.407798	2.257503	1.490141

H	4.703895	2.910403	-0.657801	H	4.549924	3.057605	-0.682328
H	-4.755707	-1.715751	1.028843	H	-4.824422	-1.073541	1.693868
H	-7.156408	-1.215632	0.627302	H	-7.199458	-0.481277	1.265091
H	-7.804171	0.904382	-0.480955	H	-7.778313	0.982252	-0.649752
H	-6.061312	2.516043	-1.183796	H	-5.991215	1.842289	-2.132092
H	-3.666904	2.004548	-0.775990	H	-3.643085	1.253451	-1.709495
H	1.655403	3.156950	-2.189020	H	1.136674	3.295504	-1.621144
H	3.328089	2.755435	-2.560734	H	2.799373	3.387562	-2.234494
H	2.089682	1.490434	-2.560967	H	1.854164	1.905174	-2.420206
Intermediate: C_o-Me				**Molecule: *o*-methylated molecule**			
C	-3.791126	0.088872	-0.003309	C	2.946656	-0.446125	-0.186477
C	-4.146684	-1.228191	0.290474	C	3.772451	0.657706	0.032950
C	-5.459661	-1.647949	0.119405	C	5.151745	0.492620	0.088372
C	-6.420767	-0.765068	-0.358356	C	5.718849	-0.761739	-0.091012
C	-6.058302	0.542395	-0.662239	C	4.892563	-1.855944	-0.325803
C	-4.751044	0.996436	-0.491289	C	3.507083	-1.727914	-0.377125
N	-2.455301	0.546896	0.117119	N	1.535644	-0.350520	-0.270618
C	-1.492122	0.258645	1.035034	C	0.637986	0.550545	0.228788
S	-1.610504	-0.745900	2.357012	S	0.942269	1.993683	0.978877
N	-0.364881	1.057884	0.828180	N	-0.675554	0.044239	0.075441
C	0.769274	0.653435	0.420774	C	-1.806758	0.761072	-0.321773
O	0.974814	-0.672356	0.180282	O	-1.750892	1.845068	-0.854502
I	1.772920	-1.294761	-1.623088	C	-3.105436	0.044388	-0.084931
C	-4.392790	2.426279	-0.811591	C	-4.176672	0.350843	-0.928629
C	1.915474	1.585898	0.316640	C	-5.408490	-0.263844	-0.749521
C	3.216121	1.141585	0.574715	C	-5.588909	-1.179299	0.285076
C	4.280214	2.033379	0.525392	C	-4.533517	-1.473997	1.142388
C	4.058319	3.369799	0.207756	C	-3.294825	-0.868166	0.957233
C	2.764127	3.817859	-0.047020	H	1.109556	-1.104836	-0.788671
C	1.696595	2.933251	0.014560	H	-0.815934	-0.929672	0.302559
H	-2.203101	1.301870	-0.505356	C	2.644890	-2.941595	-0.622277
H	-3.397535	-1.909858	0.661551	H	3.329989	1.631728	0.165608
H	-5.725662	-2.670711	0.356508	H	5.779415	1.357645	0.264081
H	-7.445497	-1.088924	-0.493409	H	6.793551	-0.891579	-0.049659
H	-6.805748	1.234122	-1.033978	H	5.330530	-2.837408	-0.468851
H	3.388641	0.106581	0.839701	H	-4.024986	1.078501	-1.715626
H	5.282922	1.684886	0.740271	H	-6.231238	-0.025319	-1.412748
H	4.890671	4.061918	0.164131	H	-6.552258	-1.653481	0.428949
H	2.587691	4.858407	-0.290937	H	-4.676792	-2.167287	1.962527
H	0.686262	3.275556	-0.167067	H	-2.494868	-1.077082	1.658134
H	-3.933841	2.929867	0.043666	H	1.927377	-3.105360	0.187868
H	-3.692694	2.501497	-1.652576	H	2.078133	-2.870795	-1.558551
H	-5.283571	2.988731	-1.090865	H	3.261517	-3.836622	-0.697653

Table S14. Relative energies of different intermediates for *o*-pyridinated molecule.

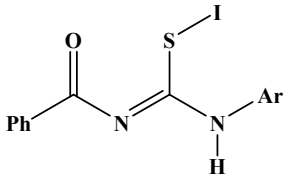
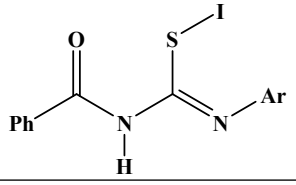
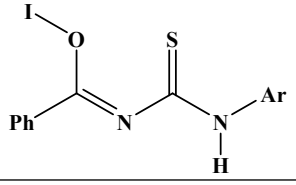
Intermediates	Structure	Relative Energy (kcal)
A_o-Py		0.0
B_o-Py		3.12
C_o-Py		32.8

Table S15. Mayer bond order for selected bonds (atom numbering is shown in Figure S1) for *o*-pyridinated molecule.

Intermediates	Mayer Bond Order				
	C1 – N2	**N2 – C3**	**C3 – N4**	**N4 – C5**	**C5 – C6**
A_o-Py	1.0052	1.1535	1.5311	1.3810	0.9264
B_o-Py	1.0588	1.8130	1.0024	1.1710	0.9111
C_o-Py	1.0440	1.1511	1.0501	1.9346	0.9517

Table S16. Optimized geometries of different structures for the reactions of *o*-pyridinated molecule.

Intermediate: A_o-Py				**Intermediate: B_o-Py**			
C	1.860826	1.667231	-0.067557	C	1.769888	1.782946	0.084348
C	2.400519	1.311722	1.170874	C	2.321998	1.547748	1.351952
C	3.630293	1.848833	1.515764	C	3.632005	1.933086	1.581322
C	4.273244	2.717829	0.639753	C	4.353408	2.529095	0.551505
C	3.633073	3.025712	-0.553438	C	3.708464	2.728200	-0.664239
N	2.452509	2.516363	-0.905293	N	2.442121	2.386203	-0.898450
N	0.593891	1.250042	-0.524871	N	0.422276	1.525464	-0.166058
C	-0.315433	0.373772	-0.016763	C	-0.241720	0.466337	-0.007599
S	0.133047	-1.249975	0.631514	S	0.263540	-1.256365	0.357664

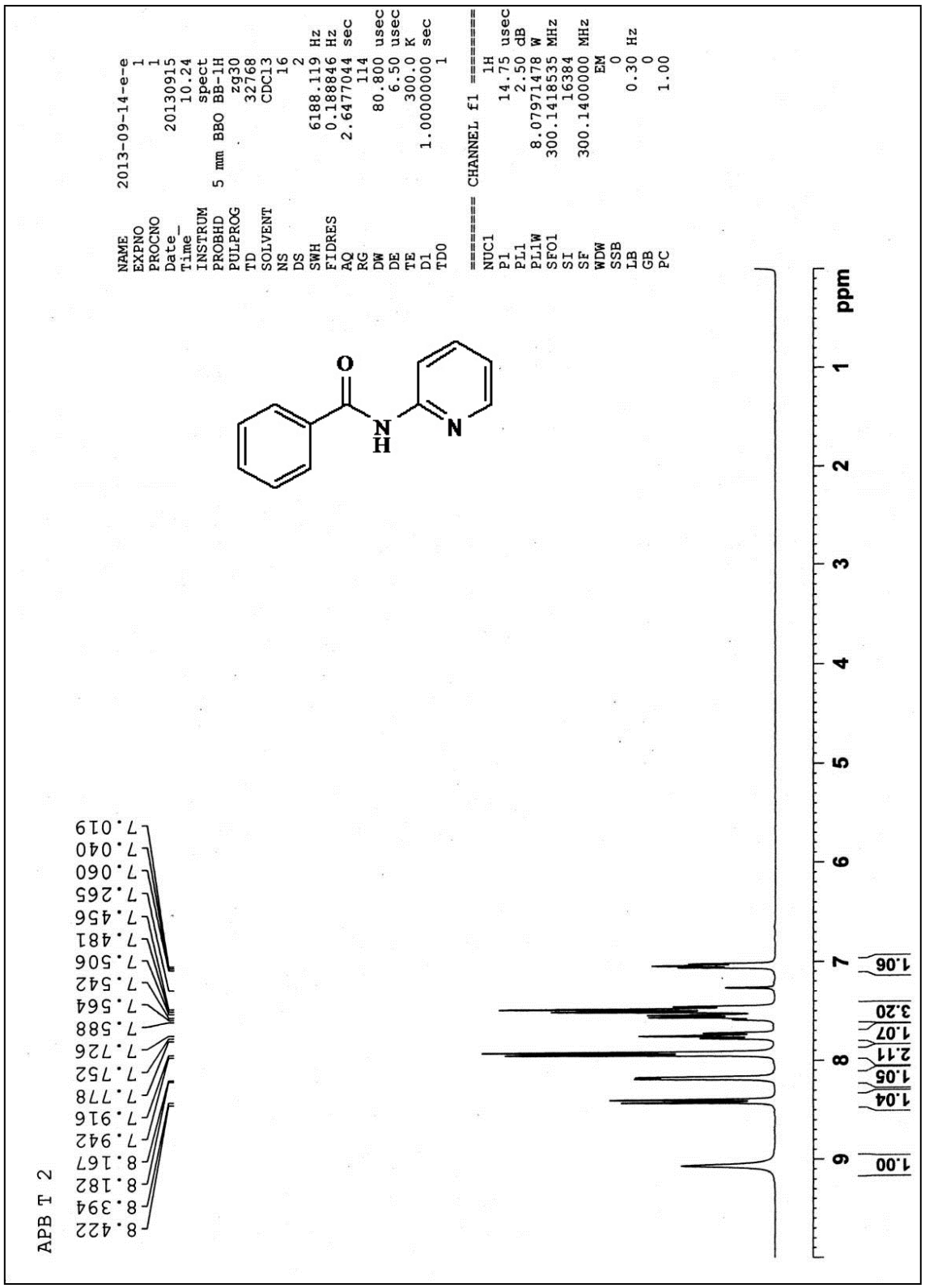
N	-1.568794	0.722764	-0.091752	N	-1.634193	0.585444	-0.183508
C	-2.500394	-0.112423	0.465643	C	-2.579990	-0.244311	0.371377
O	-2.172827	-1.035898	1.227962	O	-2.253665	-1.189199	1.077180
I	2.308667	-1.816129	-0.520196	I	2.433547	-1.494734	-0.822925
C	-3.924378	0.155970	0.146304	C	-4.006111	0.082105	0.076731
C	-4.905735	-0.697081	0.664184	C	-4.976717	-0.403884	0.957837
C	-6.244774	-0.474561	0.376648	C	-6.320138	-0.137867	0.732356
C	-6.616205	0.602547	-0.426402	C	-6.707709	0.603971	-0.381332
C	-5.644346	1.455466	-0.942704	C	-5.747783	1.076891	-1.271046
C	-4.302065	1.235429	-0.659378	C	-4.400752	0.820136	-1.043791
H	0.171550	1.934644	-1.141887	H	-1.905049	1.502649	-0.511666
H	1.875394	0.648091	1.841949	H	1.730074	1.076908	2.125429
H	4.079176	1.591730	2.467232	H	4.086126	1.764057	2.550574
H	5.234513	3.152949	0.877531	H	5.380785	2.840740	0.686745
H	4.079919	3.714007	-1.263382	H	4.229919	3.198046	-1.492679
H	-4.599930	-1.528335	1.286300	H	-4.659158	-0.987724	1.812101
H	-7.000665	-1.138560	0.777764	H	-7.066379	-0.510945	1.422882
H	-7.662364	0.776232	-0.649530	H	-7.756774	0.808060	-0.559164
H	-5.933709	2.293675	-1.565154	H	-6.047913	1.638892	-2.146887
H	-3.538819	1.893101	-1.051242	H	-3.669238	1.166897	-1.763557
Intermediate: C_o-Py				**Molecule: *o*-Pyridinated molecule**			
C	-3.910190	0.357729	-0.114161	C	2.956043	-0.388682	-0.095565
C	-4.626836	-0.547679	0.673987	C	3.806238	0.649655	0.293236
C	-5.951927	-0.782280	0.334472	C	5.164266	0.370454	0.366196
C	-6.518845	-0.129725	-0.754600	C	5.633228	-0.899587	0.049706
C	-5.715039	0.749120	-1.471280	C	4.700740	-1.856483	-0.333935
N	-4.442954	0.991871	-1.165241	N	3.394172	-1.615211	-0.404178
N	-2.566180	0.716974	0.074653	N	1.558285	-0.306162	-0.217149
C	-1.619665	0.376682	0.992030	C	0.647478	0.687284	0.020321
S	-1.775092	-0.639830	2.303765	S	0.957888	2.277428	0.363606
N	-0.459280	1.119730	0.782965	N	-0.652187	0.152919	-0.020702
C	0.666206	0.666876	0.403676	C	-1.822680	0.775758	-0.476291
O	0.827745	-0.669517	0.191243	O	-1.826871	1.795275	-1.123408
I	1.641036	-1.353059	-1.580302	C	-3.081327	0.031332	-0.134608
C	1.843314	1.559205	0.298734	C	-4.183408	0.209813	-0.975633
C	3.124657	1.078995	0.587445	C	-5.382082	-0.436355	-0.706737
C	4.217183	1.935617	0.537772	C	-5.498504	-1.255728	0.413944
C	4.042663	3.271548	0.189416	C	-4.412574	-1.422395	1.267389
C	2.767684	3.755062	-0.095875	C	-3.206745	-0.784842	0.993650
C	1.671470	2.906227	-0.034227	H	1.198628	-1.185520	-0.569191
H	-2.278564	1.401214	-0.615611	H	-0.753216	-0.808162	0.272275
H	-4.152736	-1.032930	1.511850	H	3.408131	1.626940	0.511684
H	-6.536829	-1.477315	0.925151	H	5.851994	1.152422	0.664867
H	-7.548743	-0.294054	-1.042700	H	6.686429	-1.144150	0.093548
H	-6.104720	1.284523	-2.330909	H	5.010585	-2.862260	-0.597276

H	3.259815	0.044854	0.876358	H	-4.081541	0.863188	-1.832657
H	5.204822	1.560467	0.776098	H	-6.228908	-0.298042	-1.368208
H	4.897255	3.935961	0.145549	H	-6.436138	-1.754959	0.626394
H	2.628440	4.795149	-0.364148	H	-4.505888	-2.040462	2.152174
H	0.675561	3.275901	-0.240202	H	-2.382926	-0.893698	1.689737

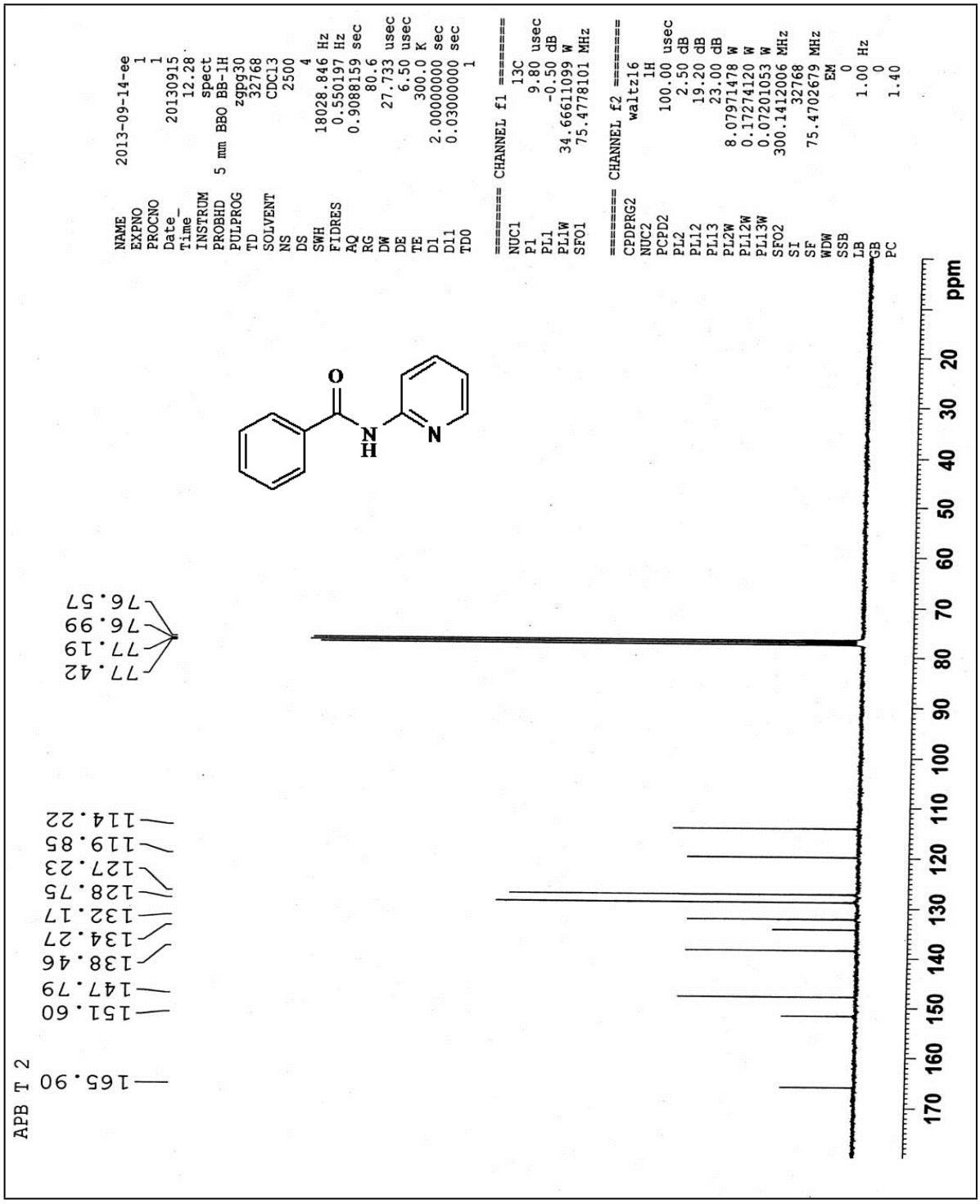
General procedure for the synthesis of *N*-substituted benzamides (2)/benzothioamides (3) from benzoylthioureas (1): Iodine-alumina (0.71 mmol of iodine adsorbed on 1.8g of neutral alumina, i.e. 20 mol%) was added to *N*-substituted-*N*′-benzoylthioureas (1 mmol) and the mixture was ground thoroughly using a motor pestle. The mixture was stirred for 30 sec until they were mixed thoroughly. The reaction mixture was then irradiated without any solvent in microwave for 10-20 min at 100^{o}C using irradiation power of 100 W. The reaction progress was monitored by TLC. After the reaction was complete, the mixture was allowed to cool to room temperature and then poured into cold water. The product was purified by silica gel column chromatography (EtOAc/hexane) to give the corresponding amide. The structures of the products were confirmed by comparison of their mps, TLC, IR, ^{1}H and ^{13}C NMR data with authentic samples obtained commercially or prepared by literature method. The residue of the catalyst was washed with water and dried under vacuum to afford the catalyst, which was used in subsequent runs.

^{1}H NMR and ^{13}C NMR SPECTRA

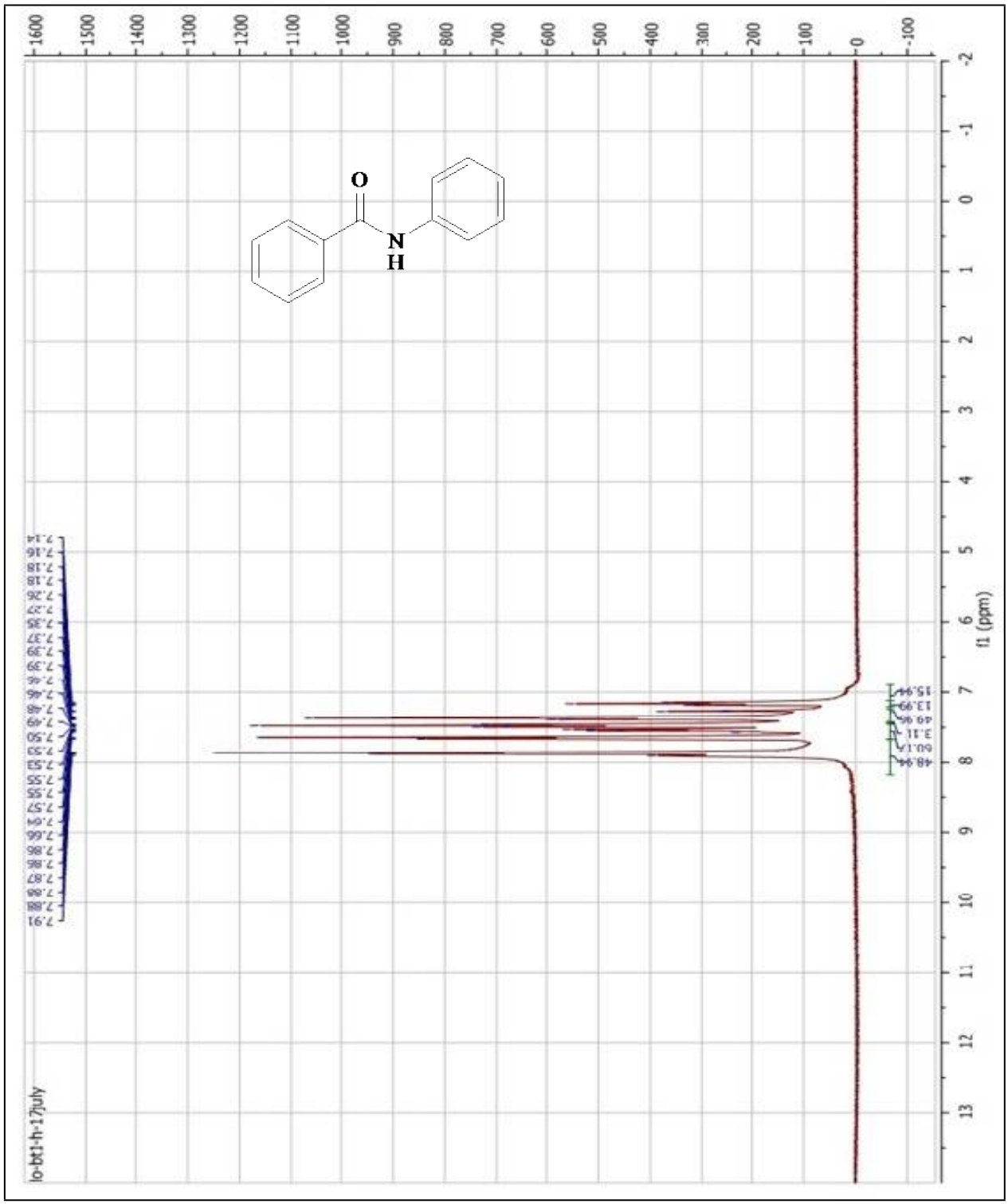
^{1}H NMR Spectrum of *N*-(pyridin-2-yl)benzamide(2a):



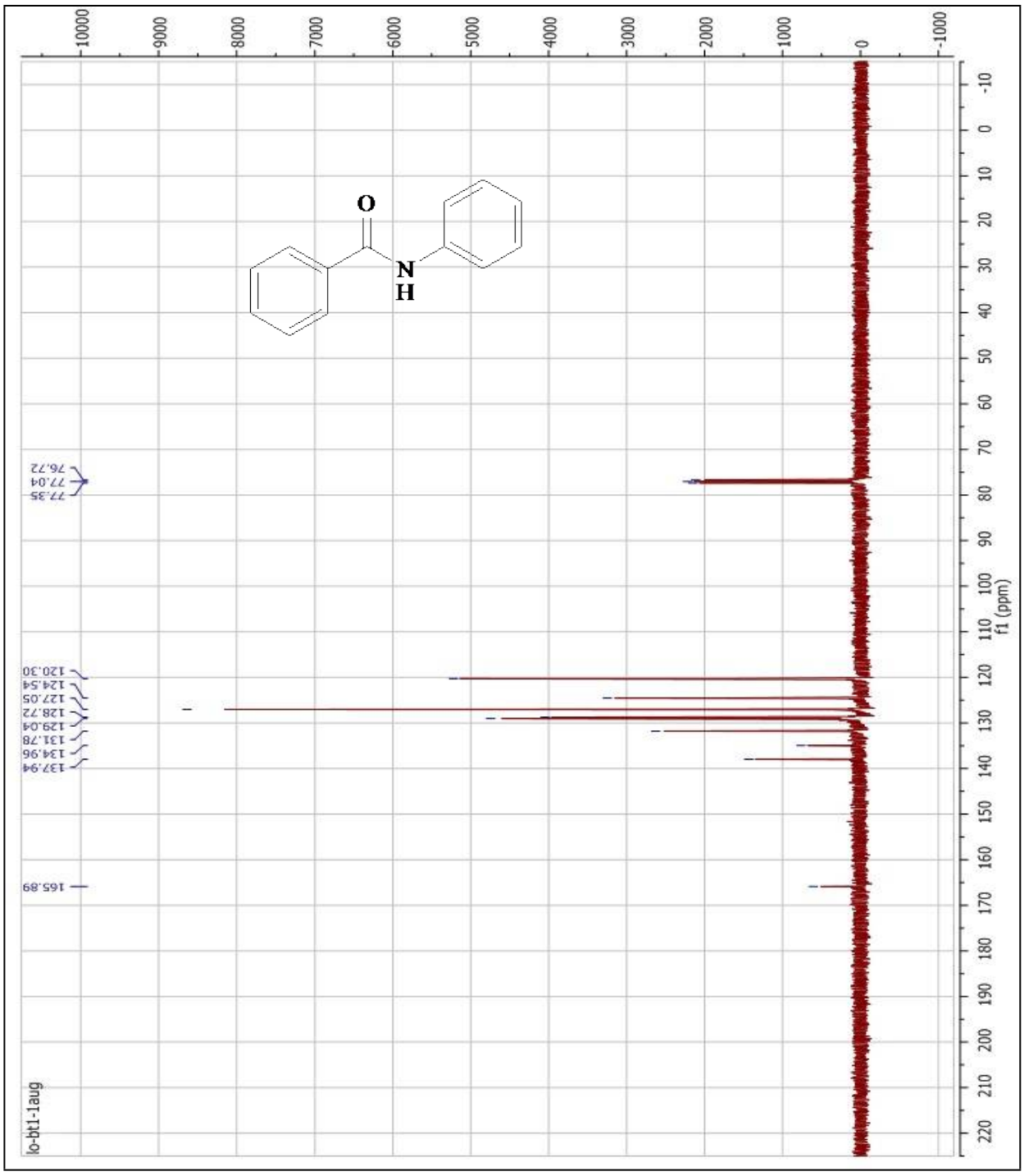
^{13}C NMR Spectrum of *N*-(pyridin-2-yl)benzamide(2a):



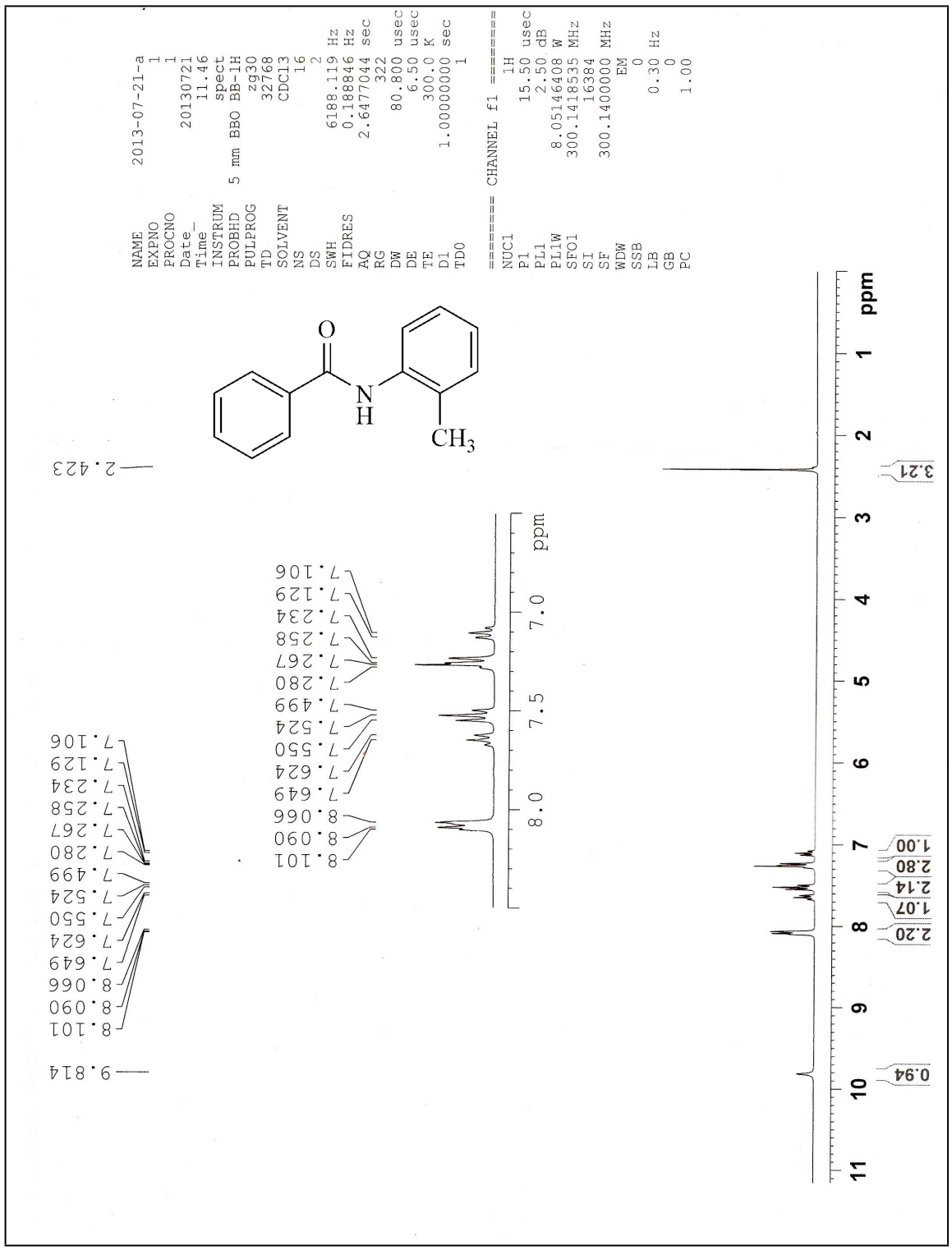
^{1}H NMR Spectrum of *N*-phenylbenzamide(2b):



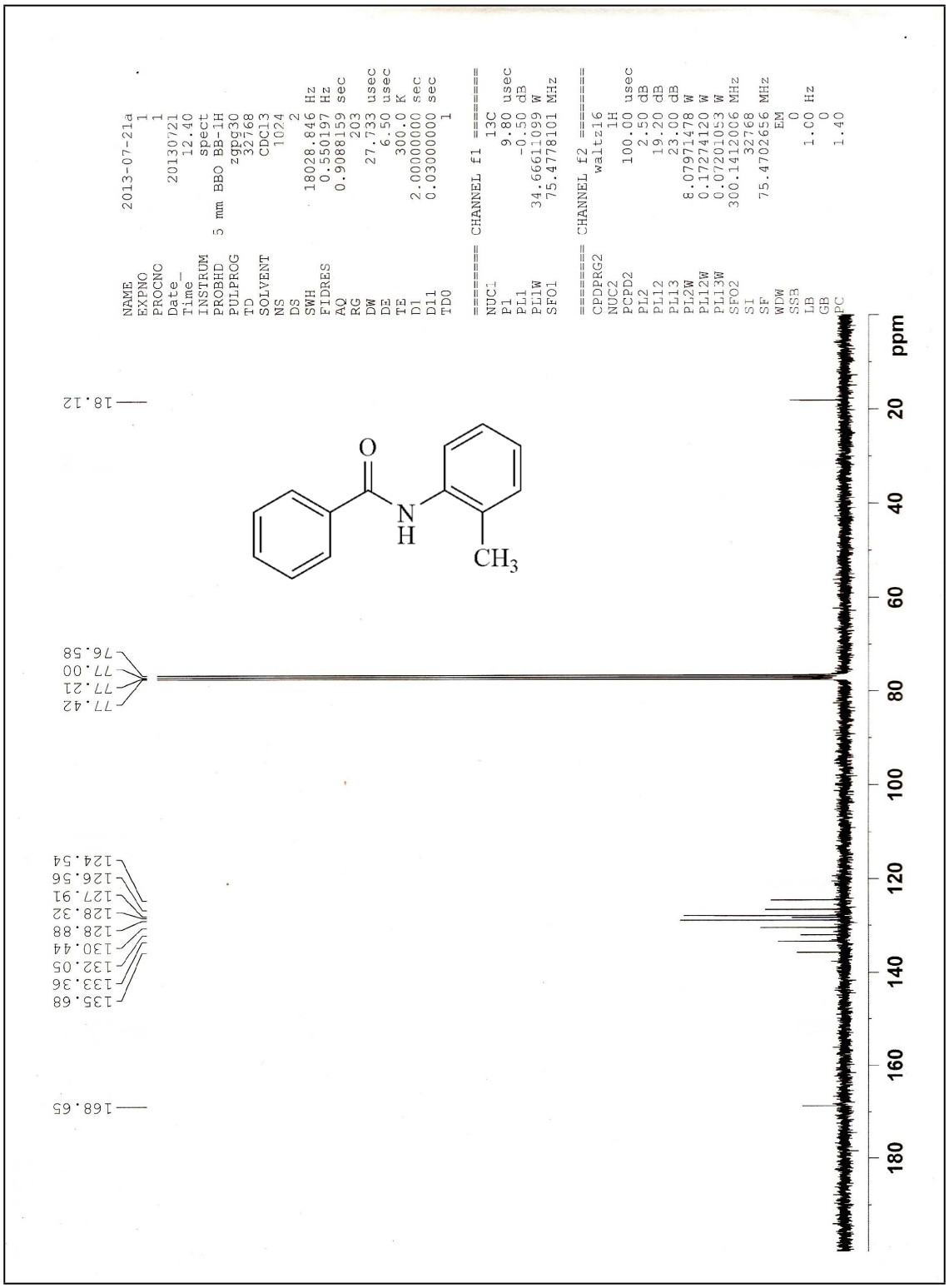
^{13}C NMR Spectrum of *N*-phenylbenzamide(2b):



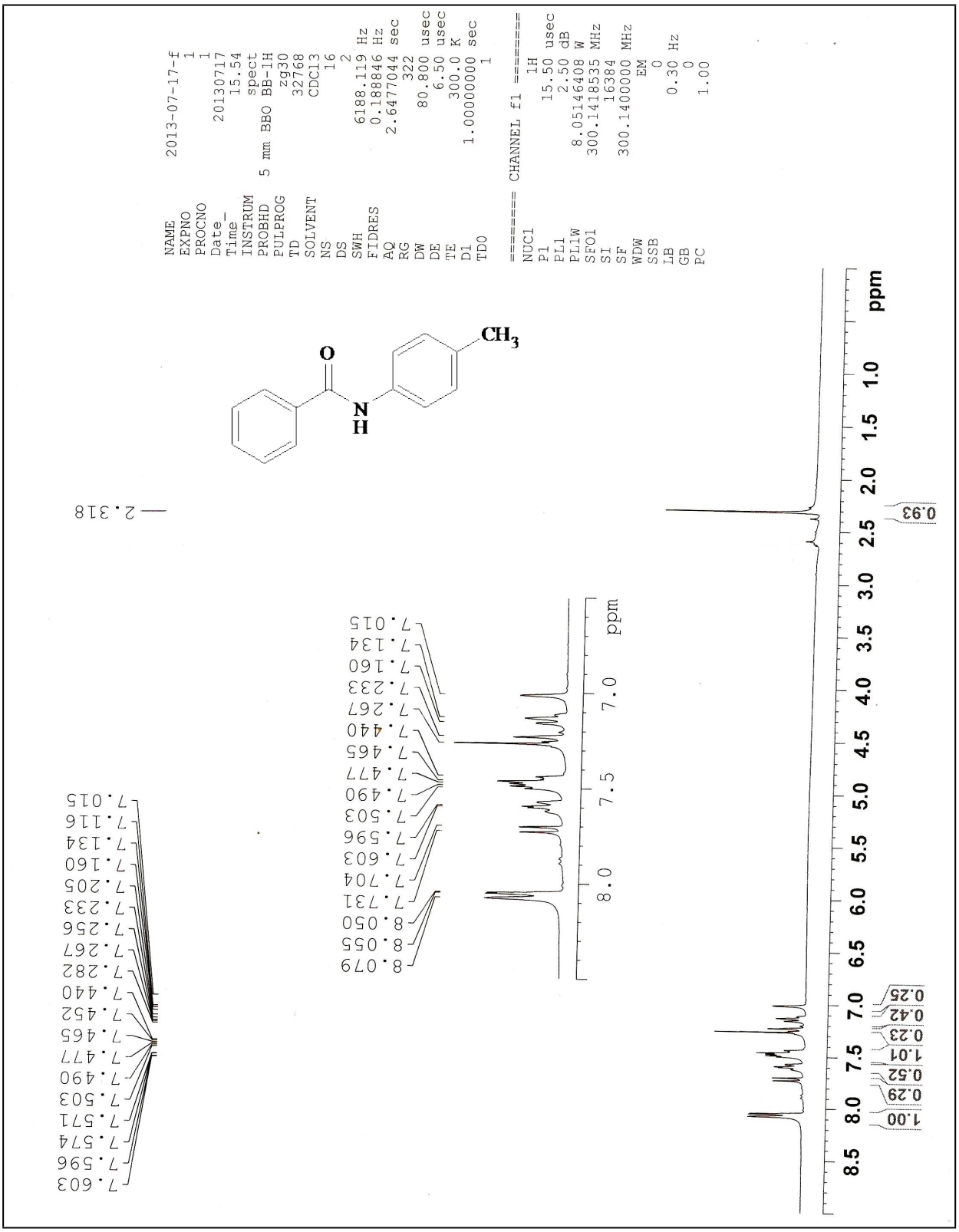
^{1}H NMR Spectrum of *N*-(*o*-tolyl)benzamide(2c):



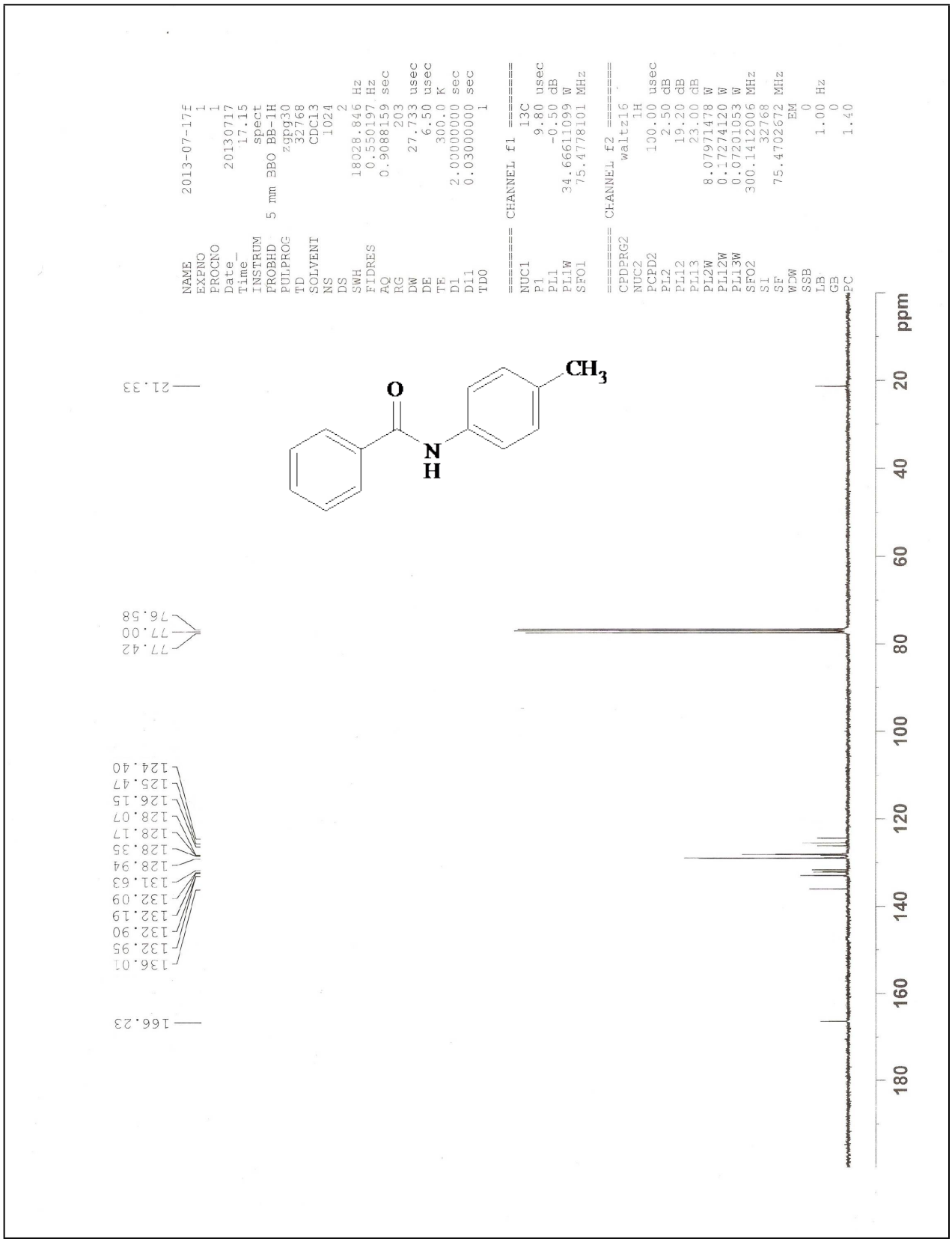
^{13}C NMR Spectrum of *N*-(*o*-tolyl)benzamide(2c):



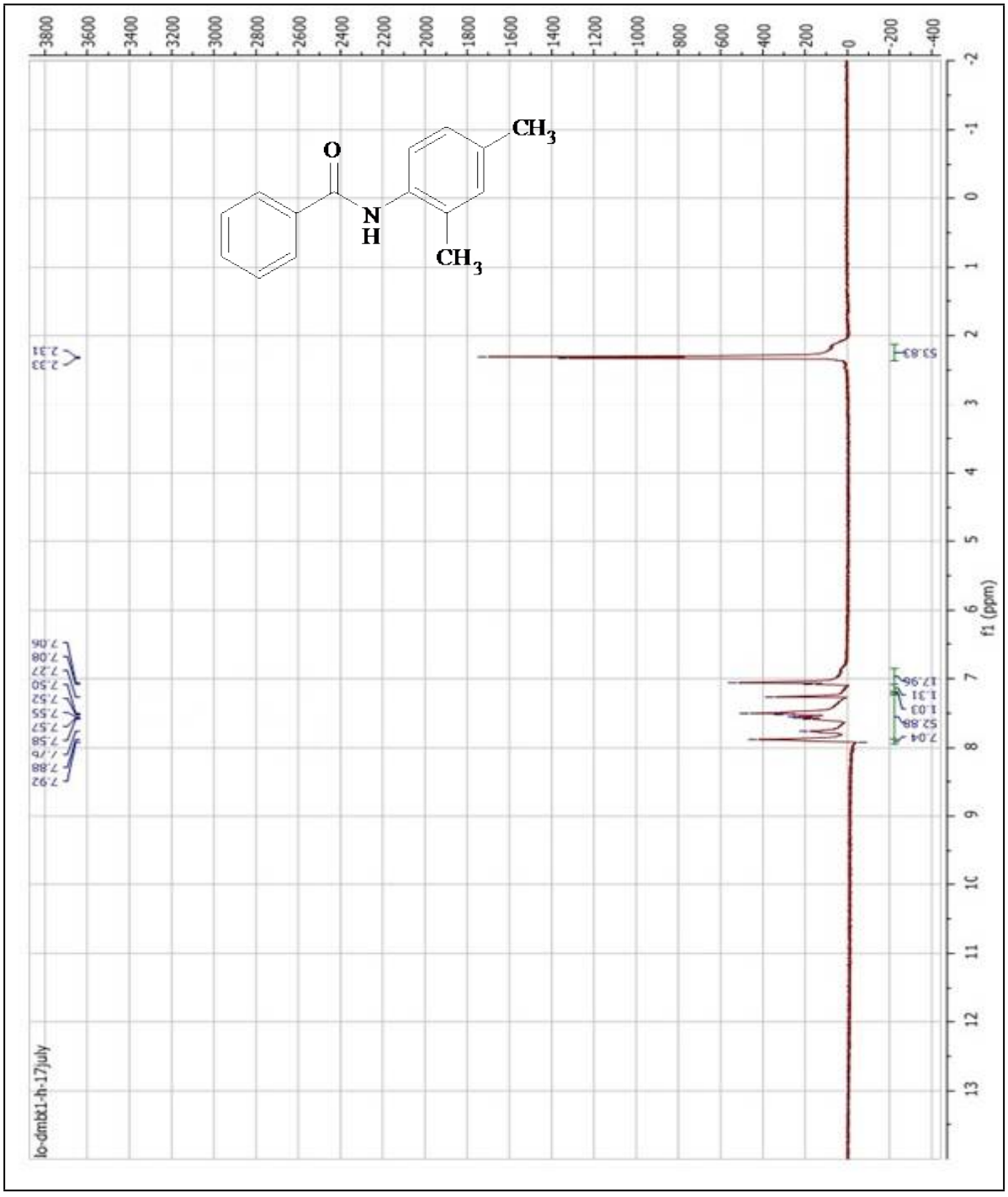
^{1}H NMR Spectrum of *N*-(*p*-tolyl)benzamide(2d):



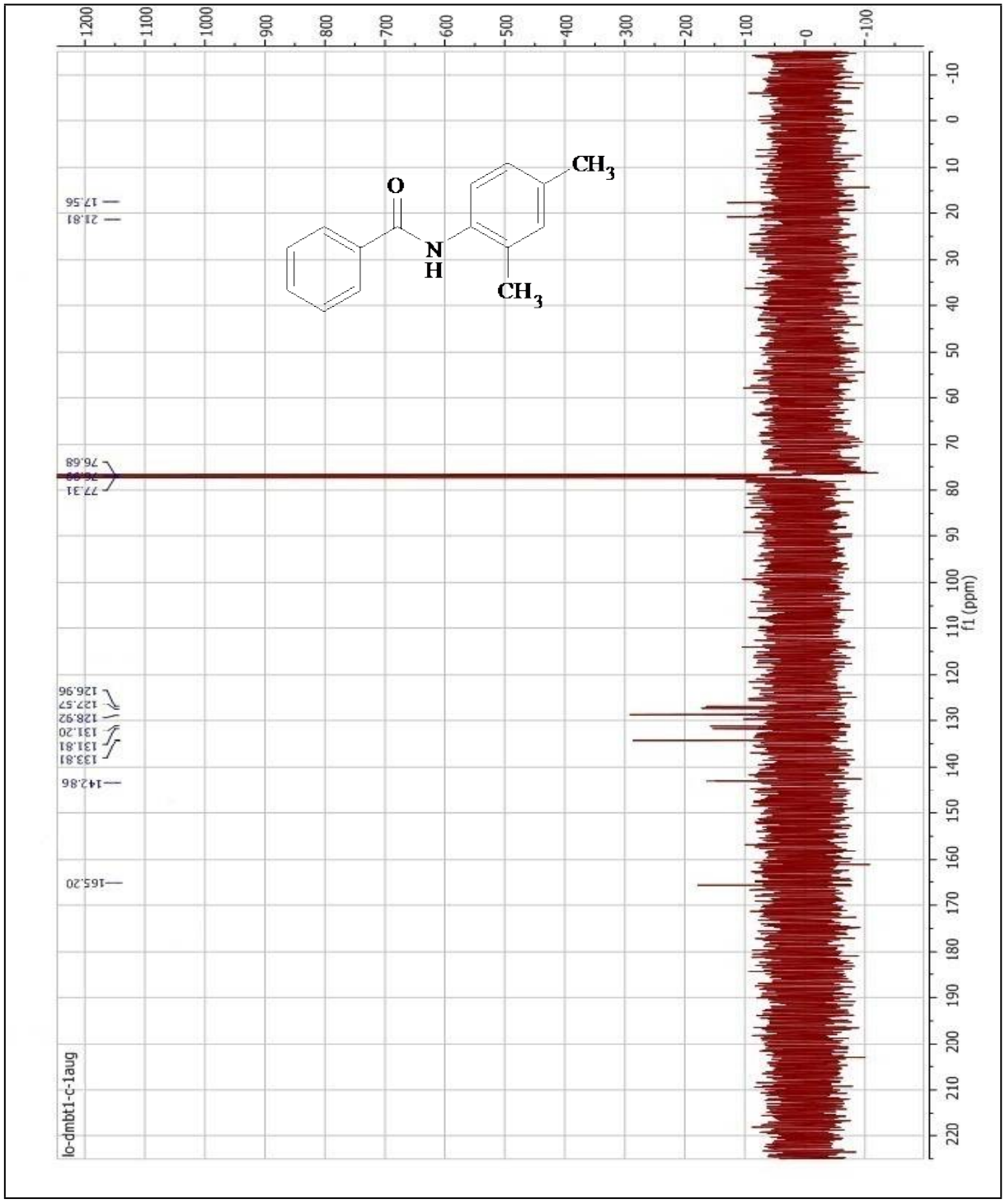
^{13}C NMR Spectrum of *N*-(*p*-tolyl)benzamide(2d):



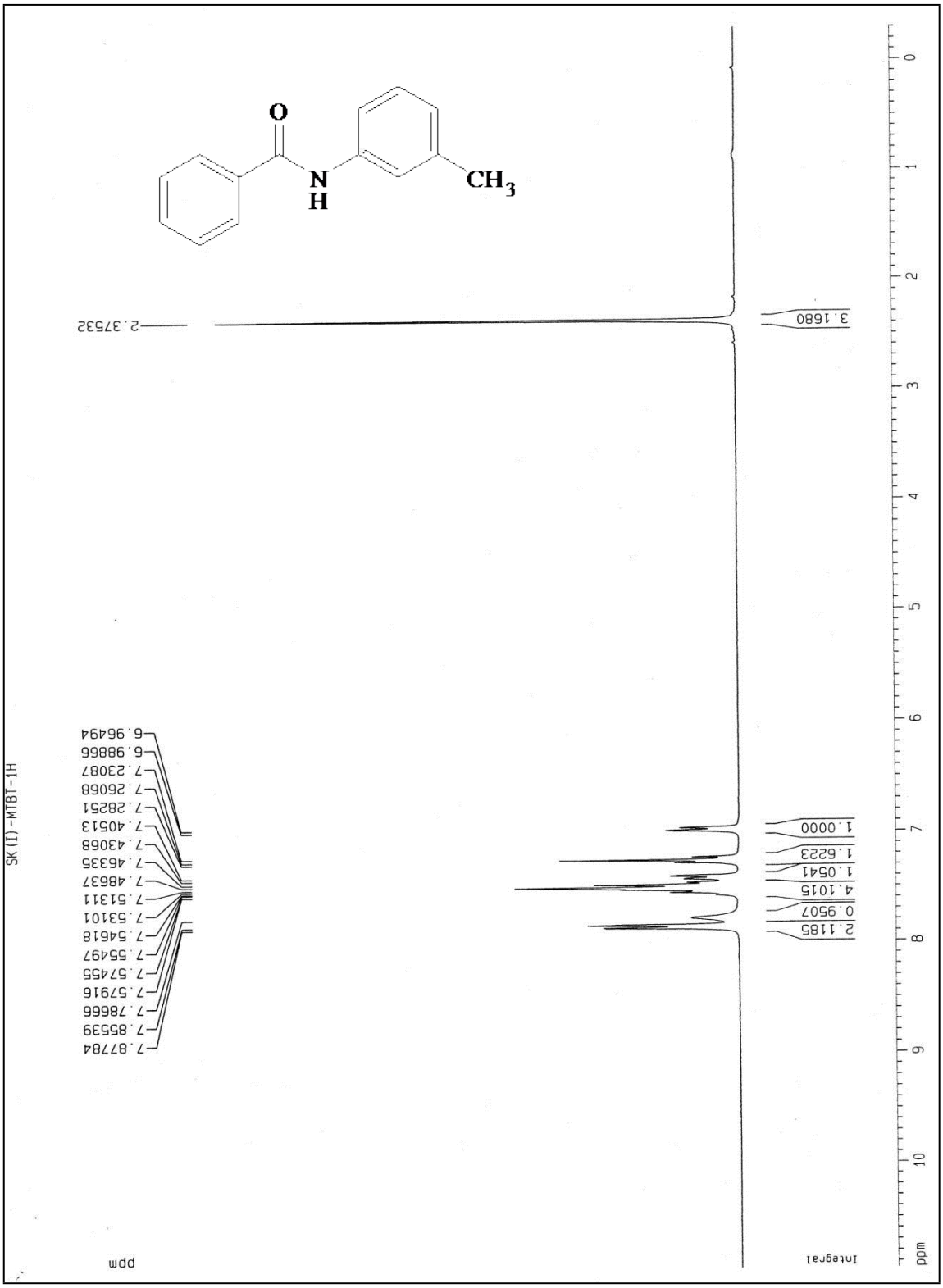
^{1}H NMR Spectrum of *N*-(2, 4-dimethylphenyl)benzamide(2e):



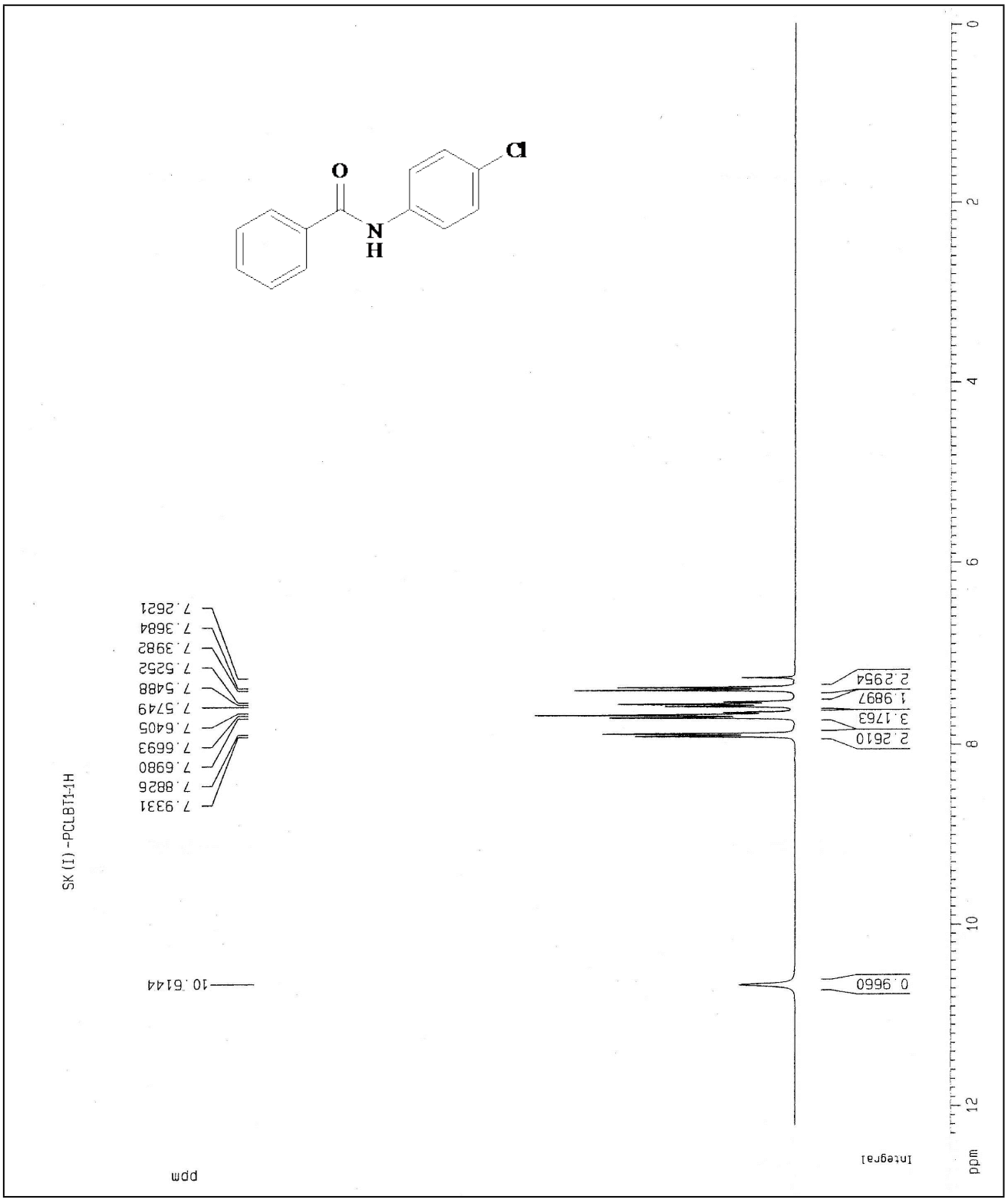
^{13}C NMR Spectrum of *N*-(2, 4-dimethylphenyl)benzamide(2e):



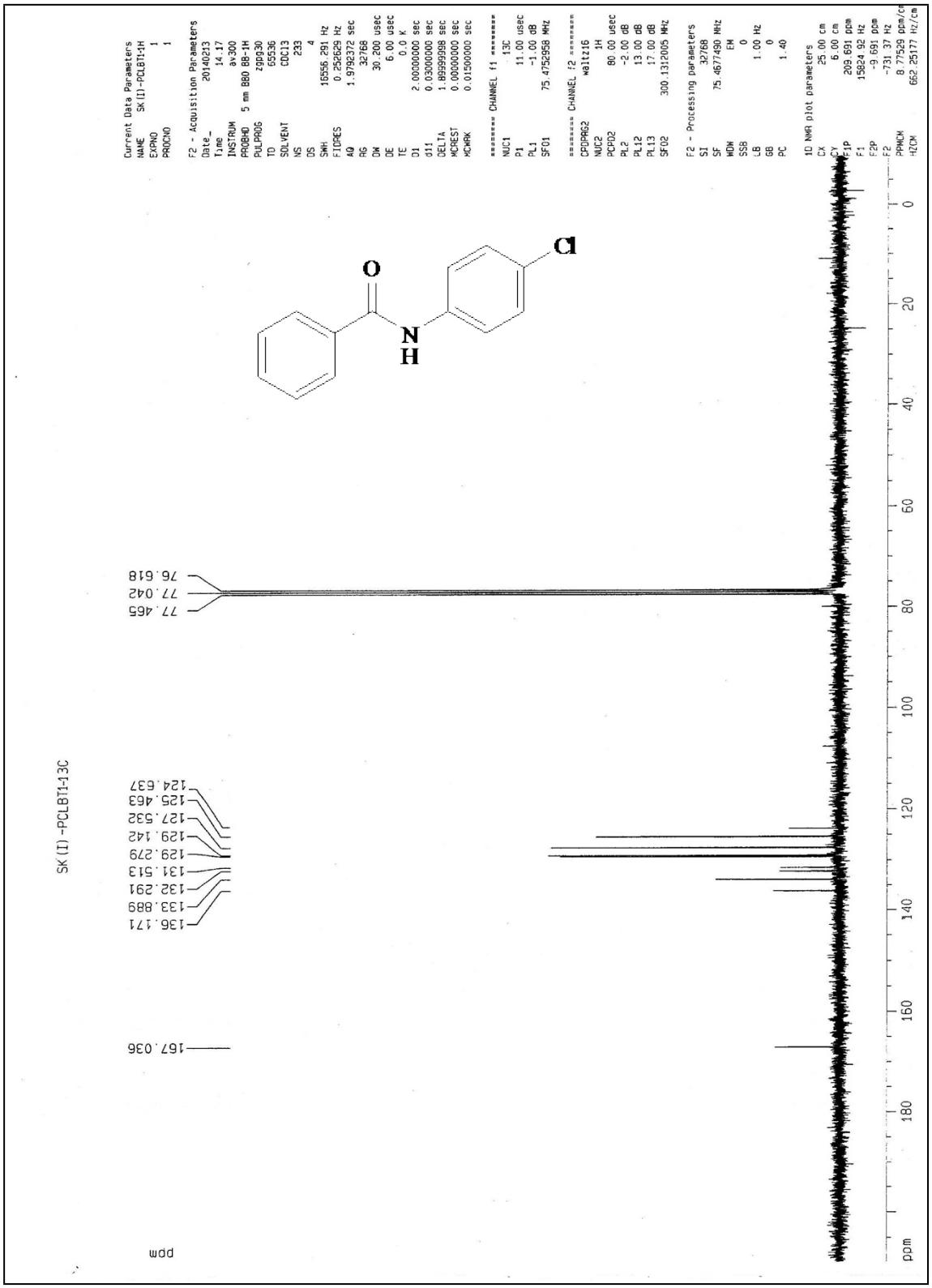
^{1}H NMR Spectrum of *N*-(*m*-tolyl)benzamide(2f):



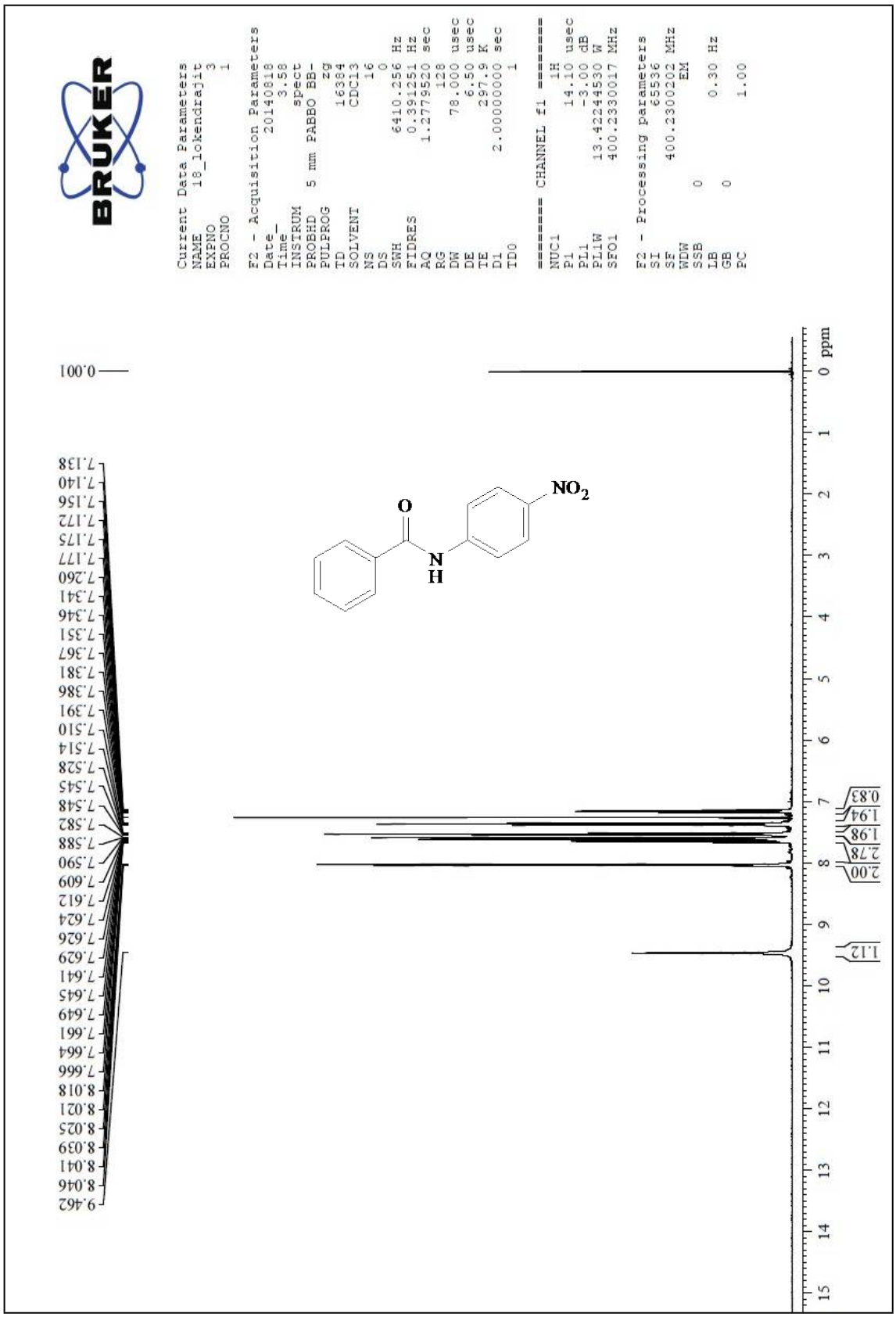
^{1}H NMR Spectrum of *N*-(4-chlorophenyl)benzamide(2g):



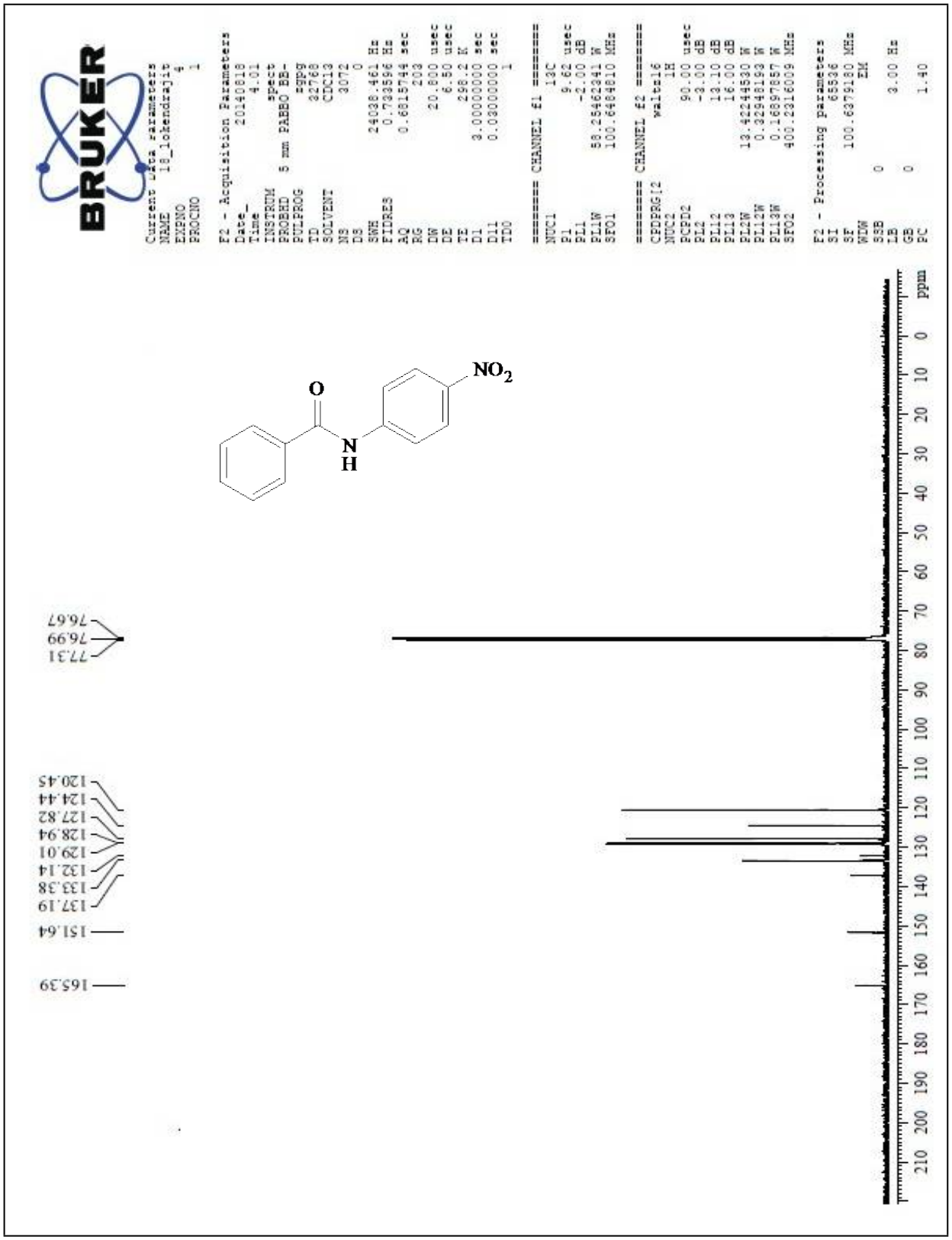
^{13}C NMR Spectrum of *N*-(4-chlorophenyl)benzamide(2g):



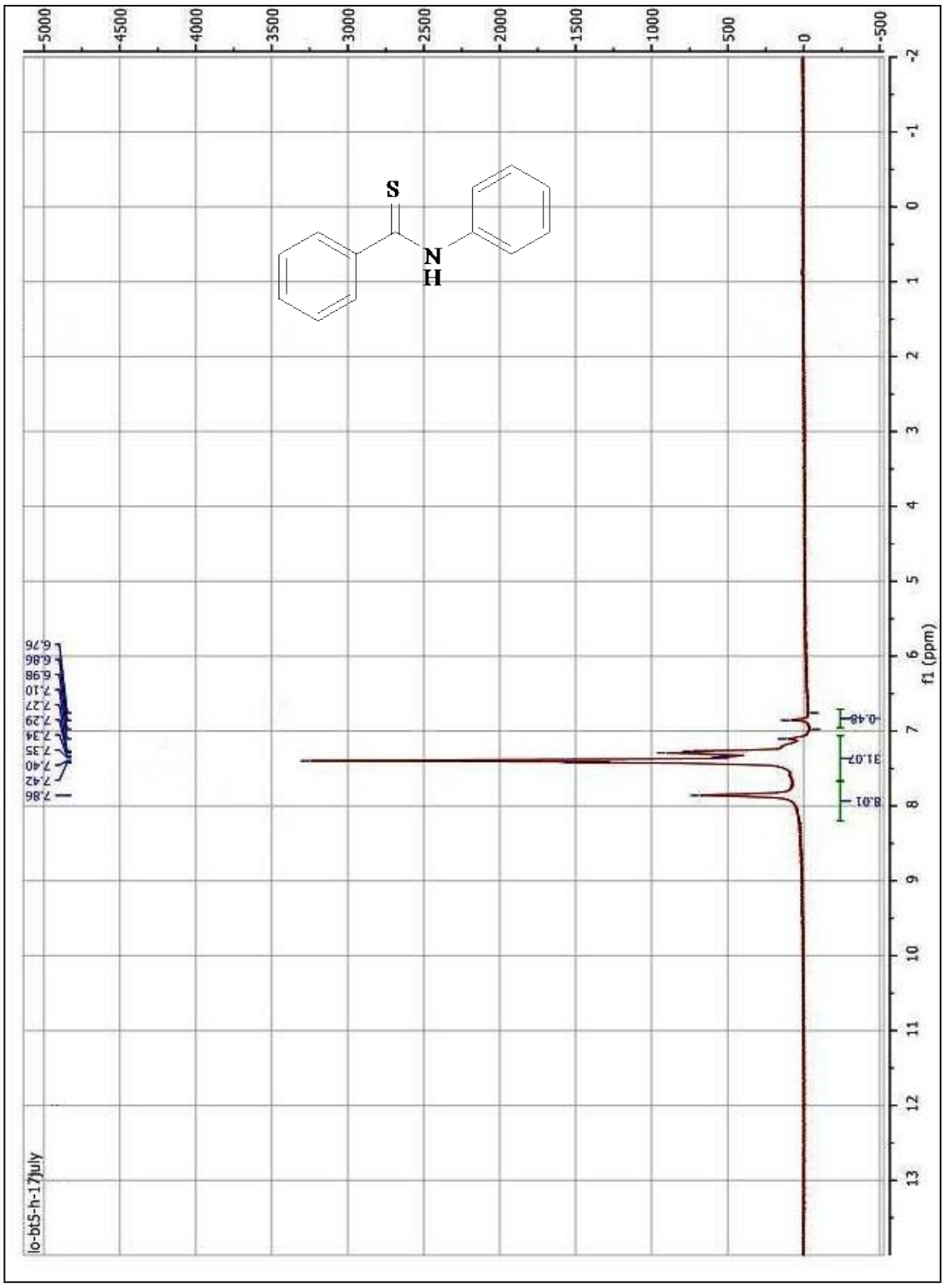
^{1}H NMR Spectrum of *N*-(4-nitrophenyl)benzamide(2h):



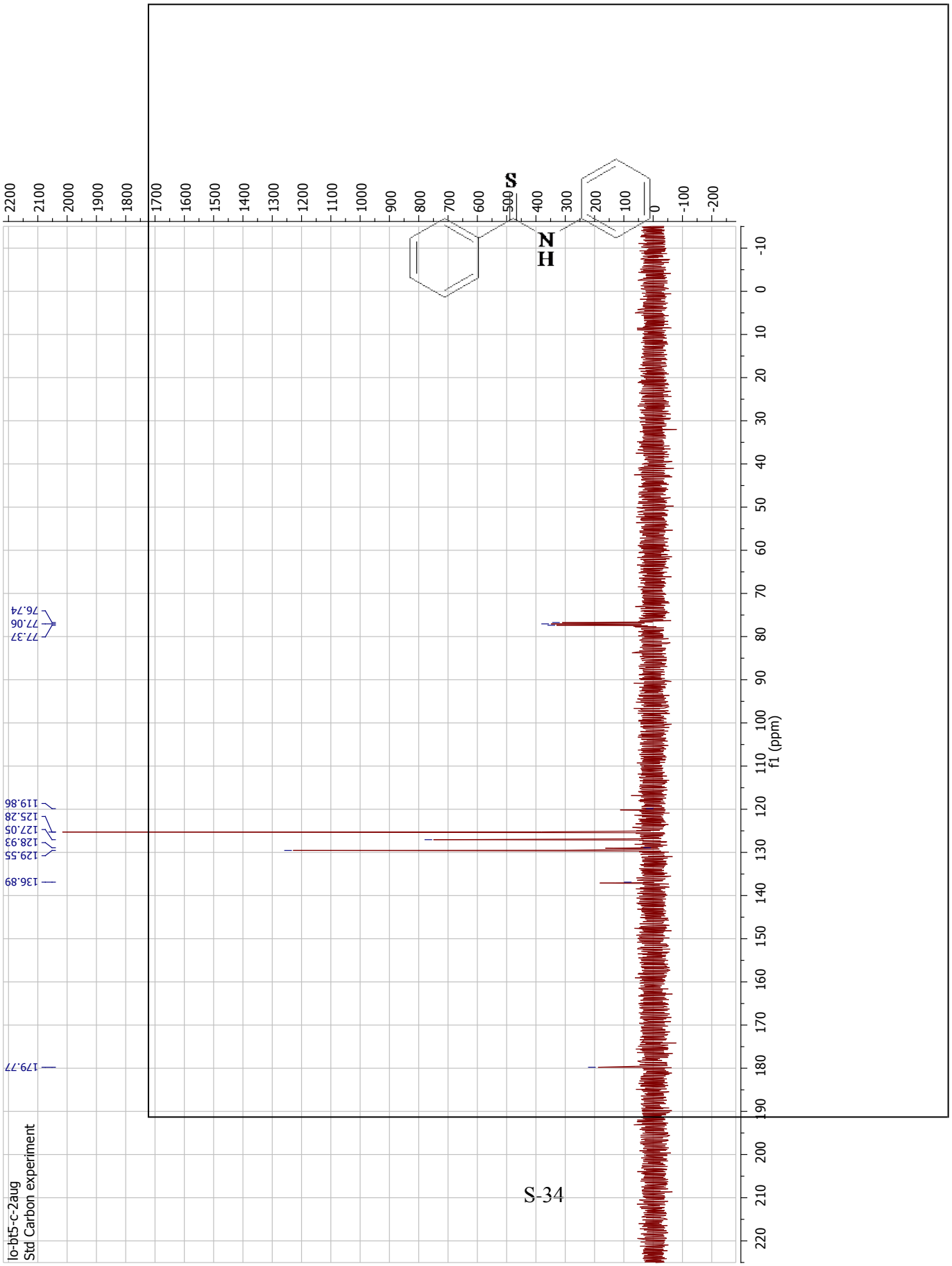
^{13}C NMR Spectrum of *N*-(4-nitrophenyl)benzamide(2h):



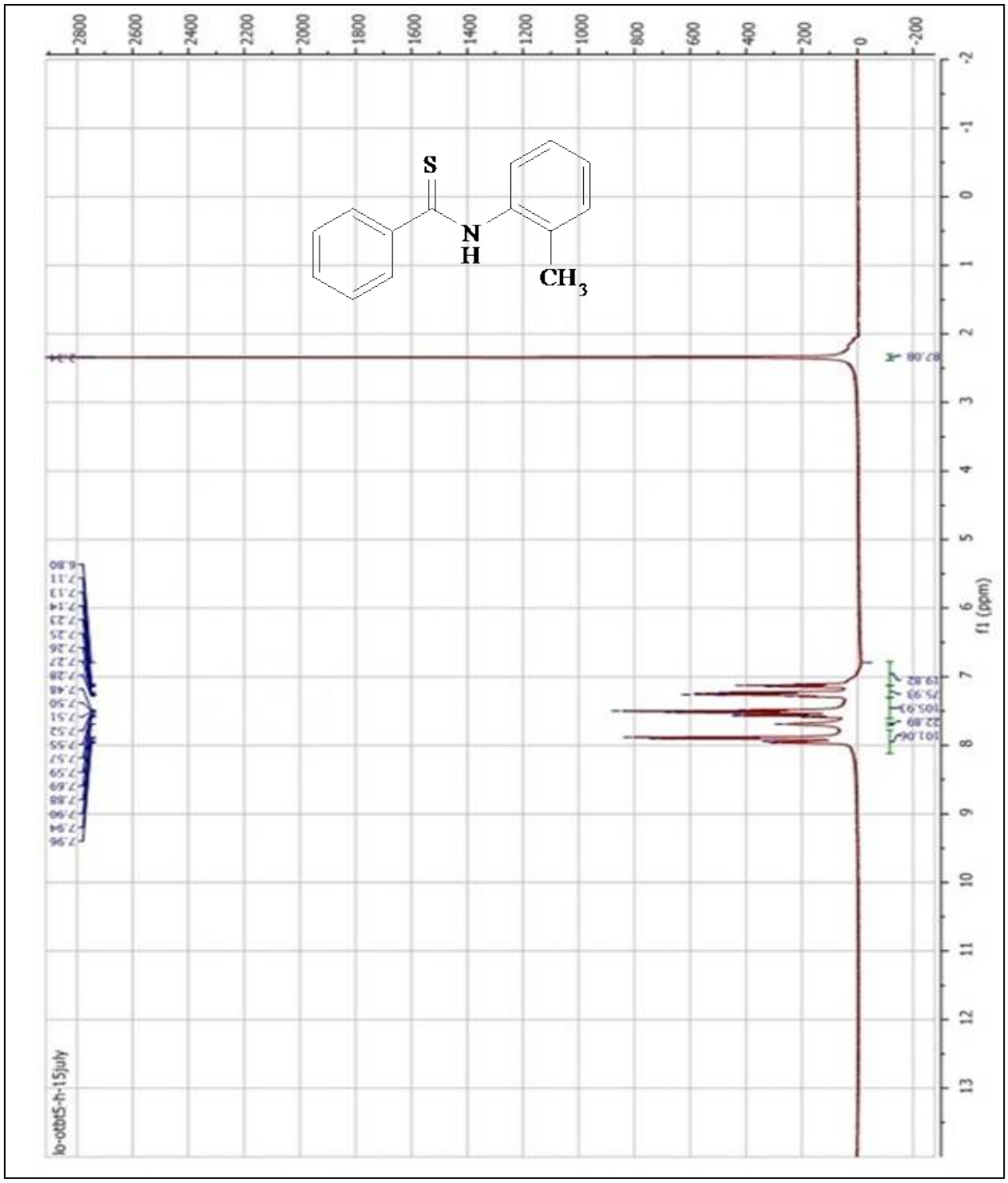
^{1}H NMR Spectrum of *N*-Phenylbenzothioamide(3b):



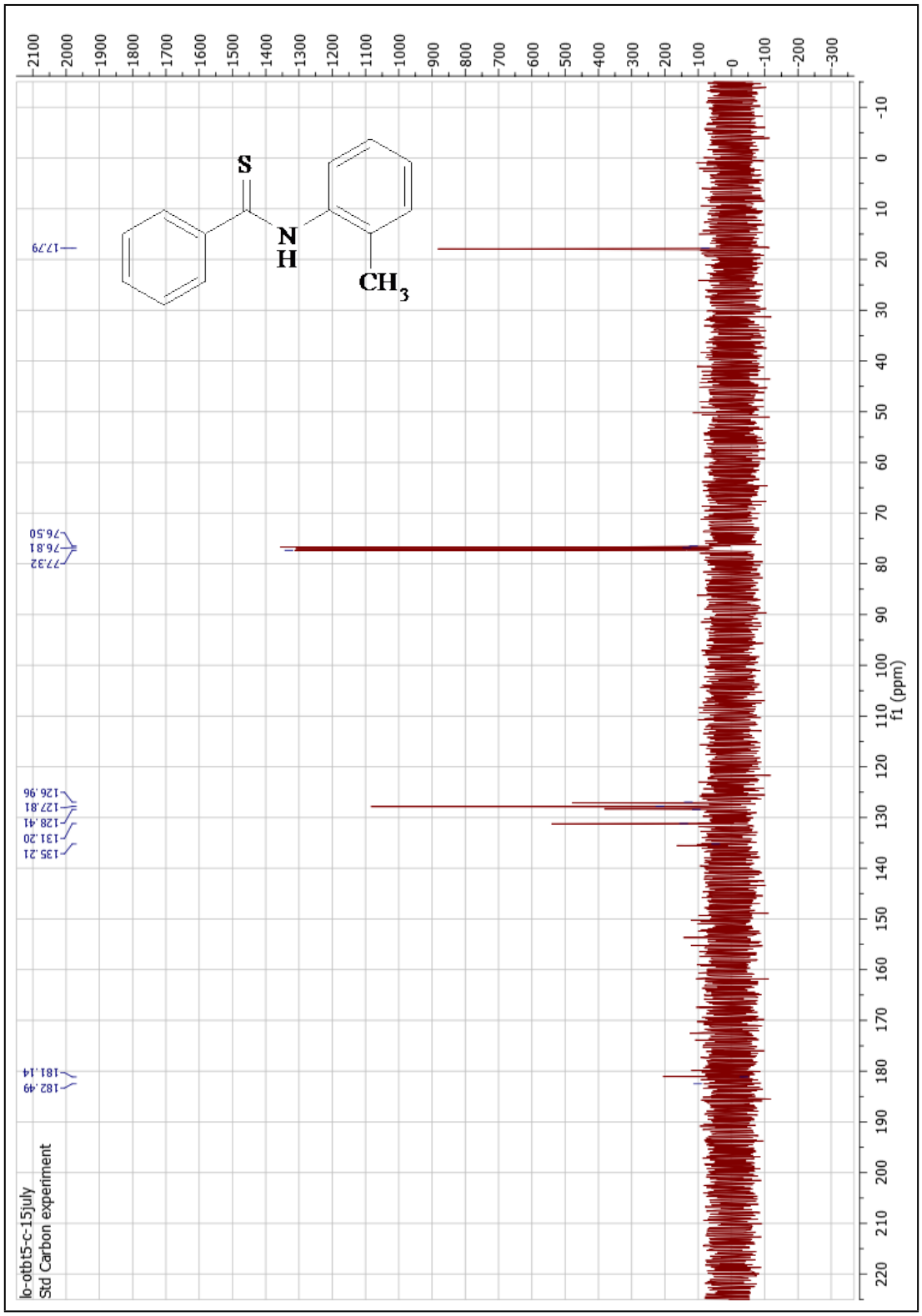
^{13}C NMR Spectrum of *N*-Phenylbenzothioamide(3b):



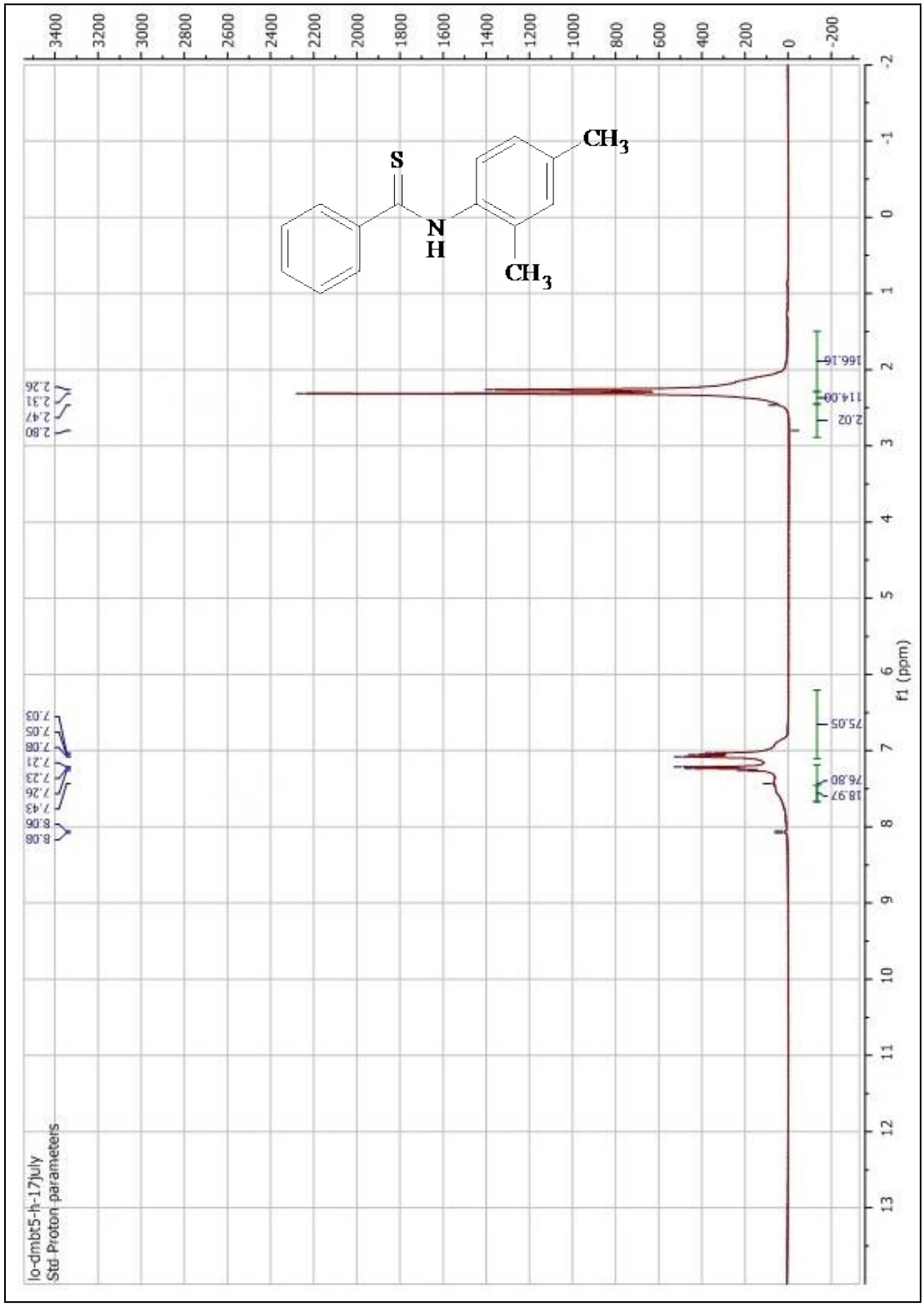
^{1}H NMR Spectrum of *N*-(*o*-tolyl)thiobenzamide(3c):



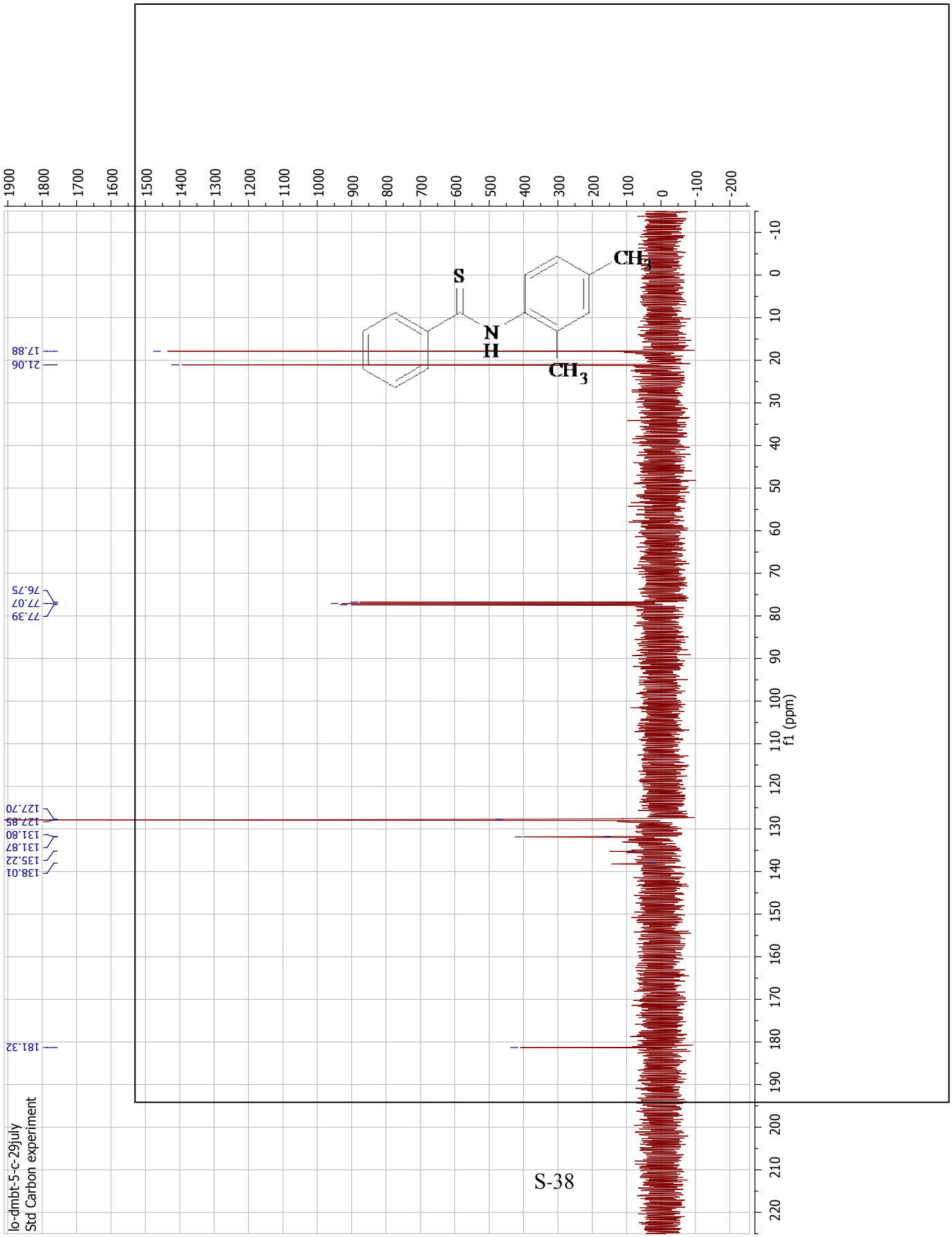
^{13}C NMR Spectrum of *N*-(*o*-tolyl)thiobenzamide(3c):



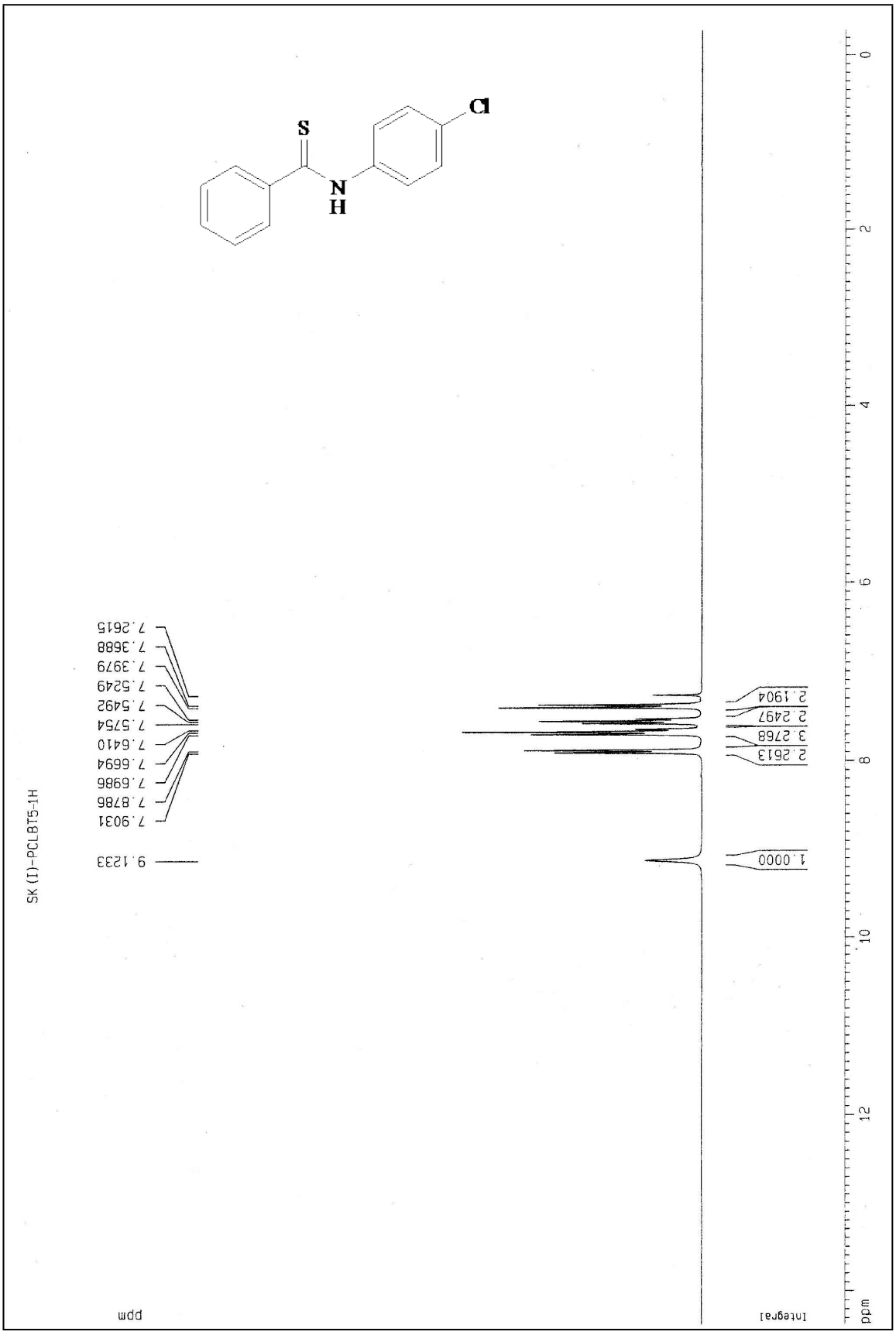
^{1}H NMR Spectrum of *N*-(2, 4-dimethylphenyl)thiobenzamide(3e):



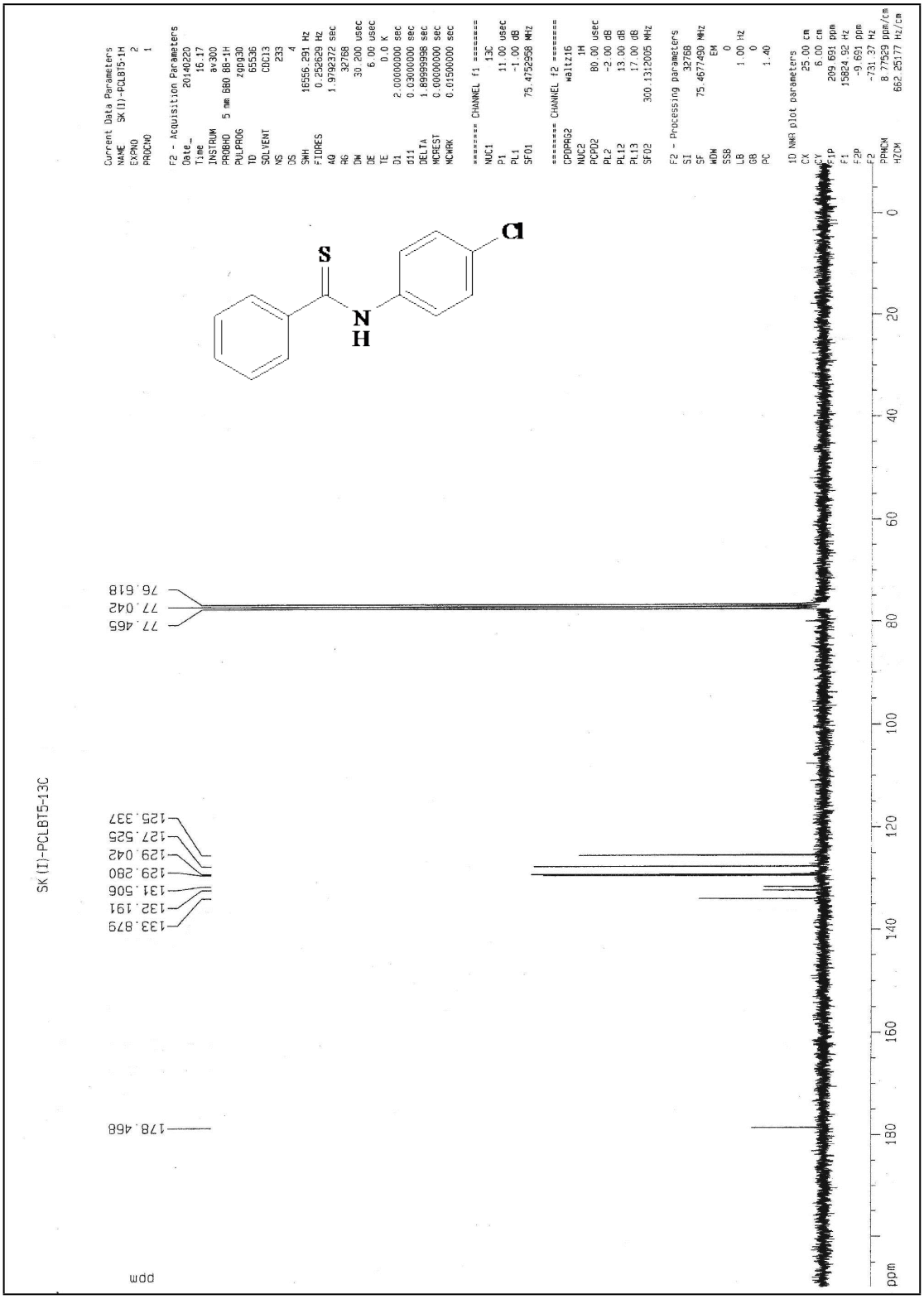
^{13}C NMR Spectrum of *N*-(2, 4-dimethylphenyl)thiobenzamide(3e):



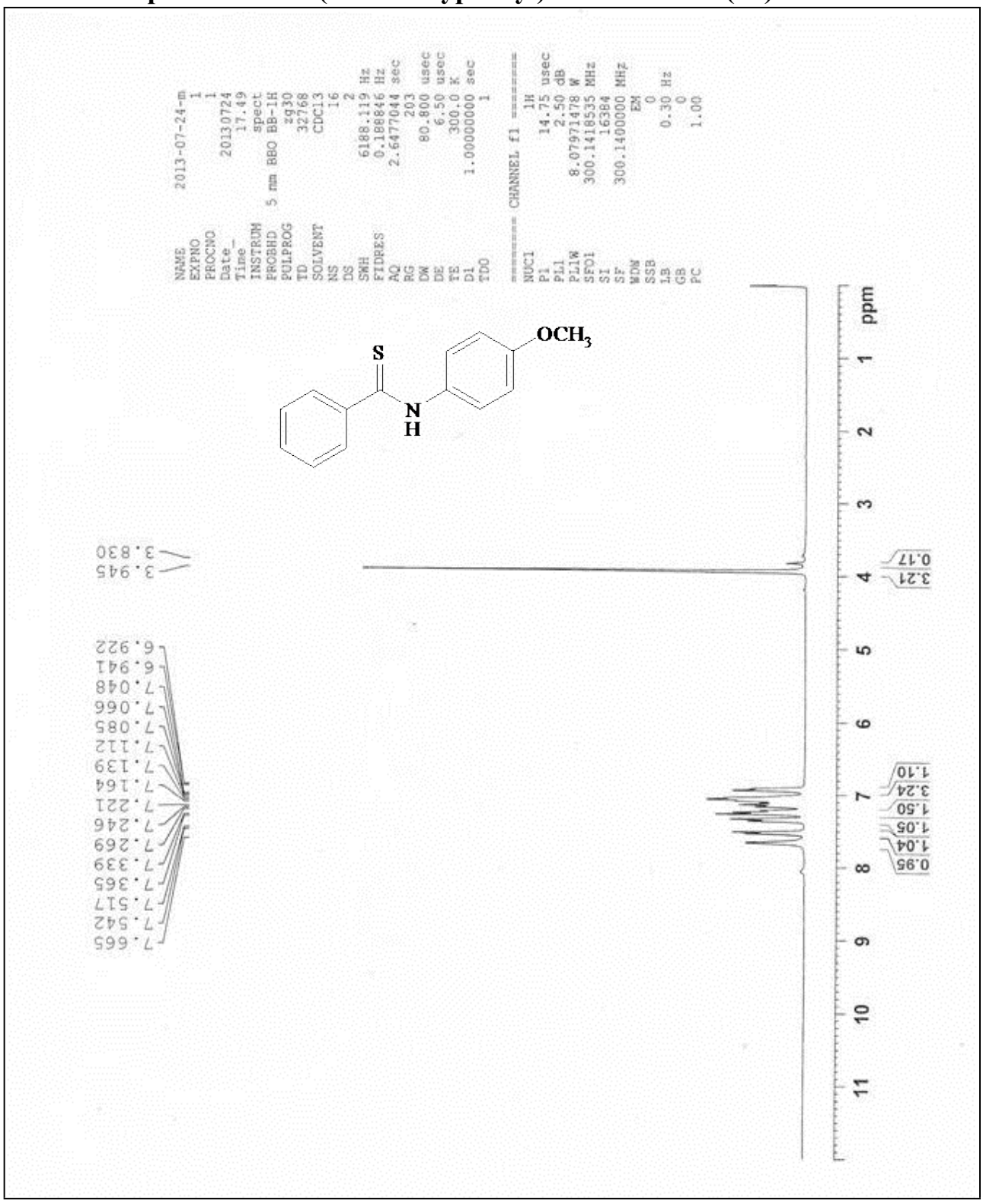
^{1}H NMR Spectrum of *N*-(4-chlorophenyl)thiobenzamide(3g):



^{13}C NMR Spectrum of *N*-(4-chlorophenyl)thiobenzamide(3g):



^{1}H NMR Spectrum of *N*-(4-methoxyphenyl)thiobenzamide(3k):



^{13}C NMR Spectrum of *N*-(4-methoxyphenyl)thiobenzamide(3k):