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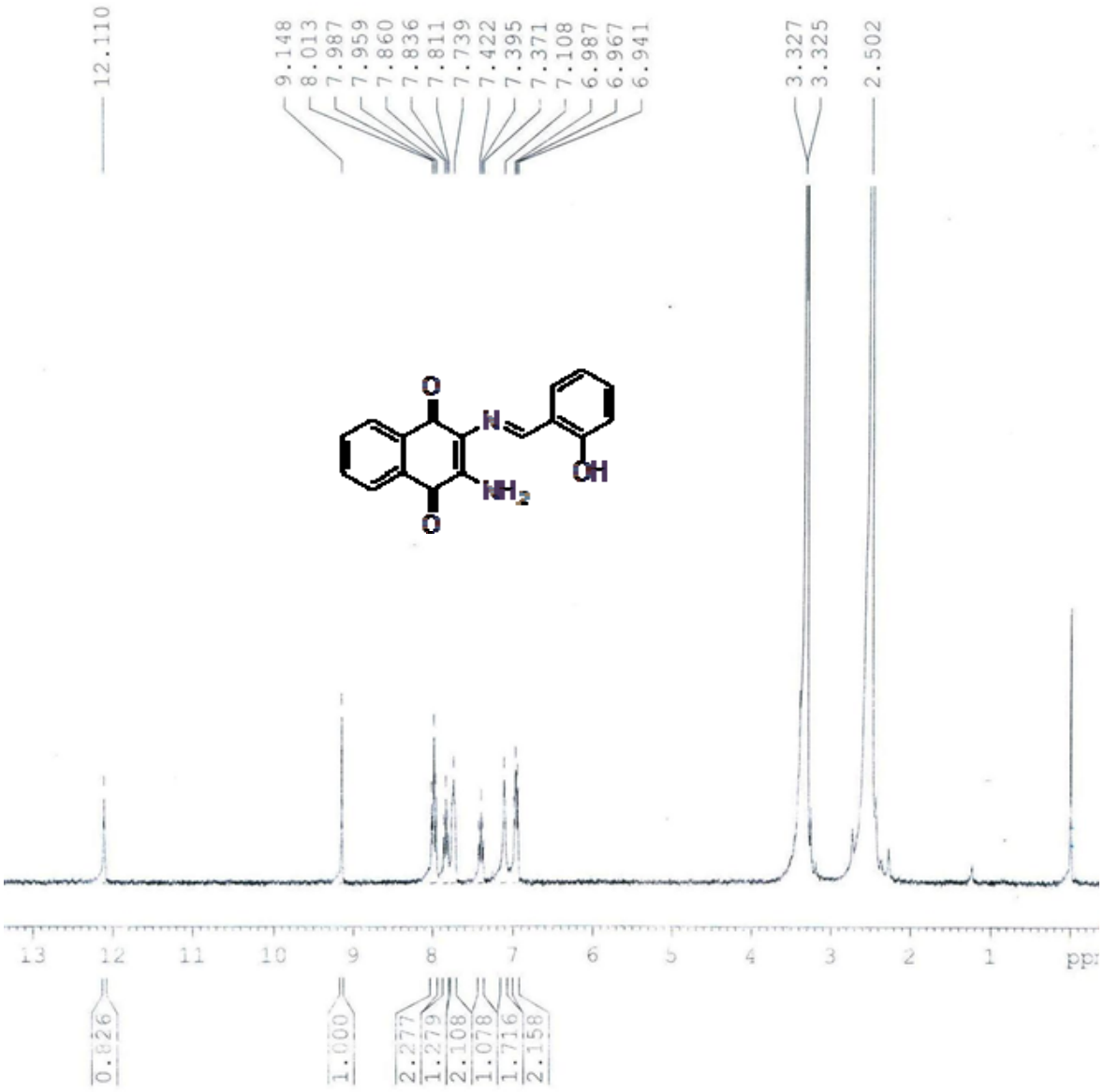
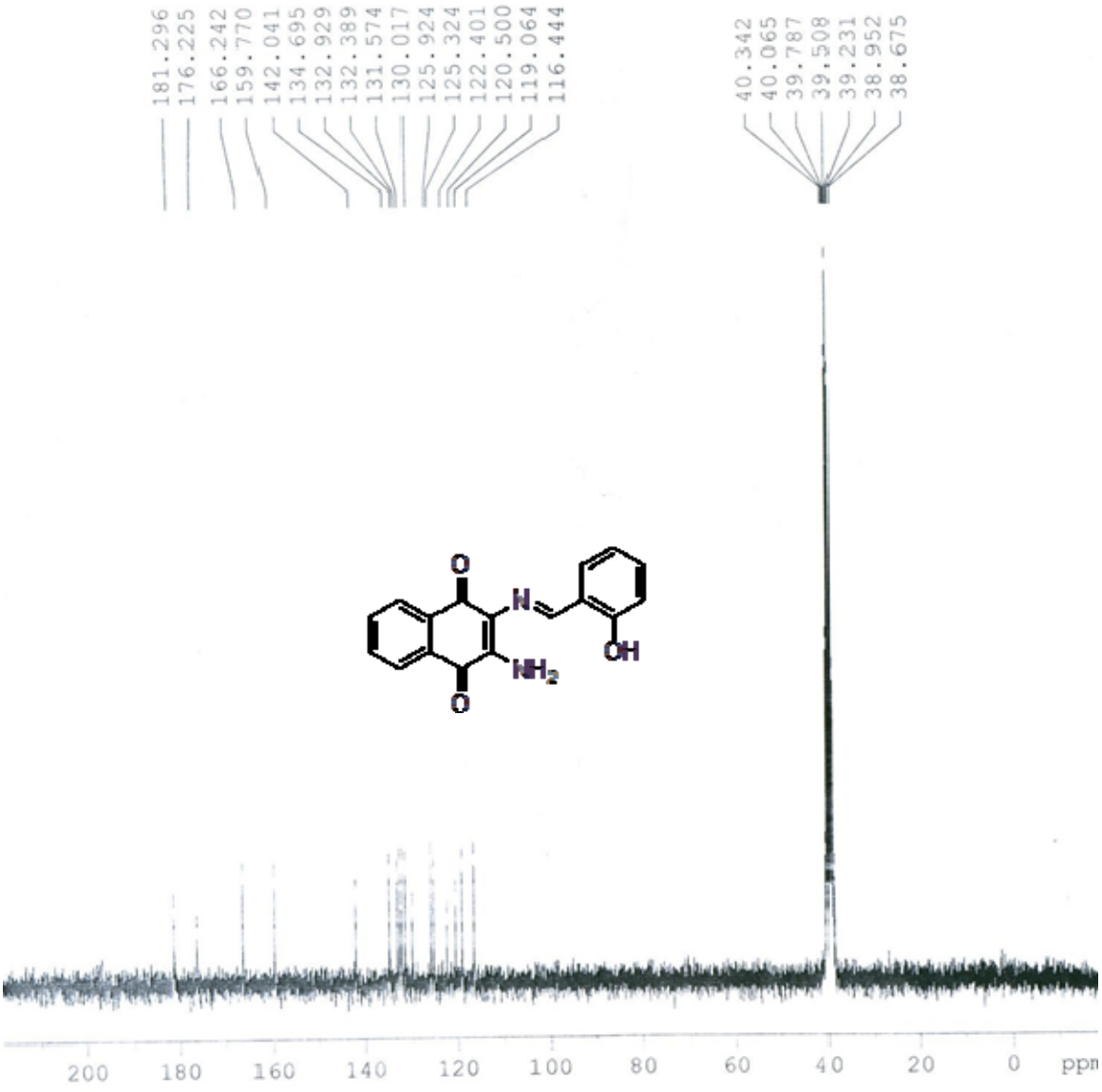
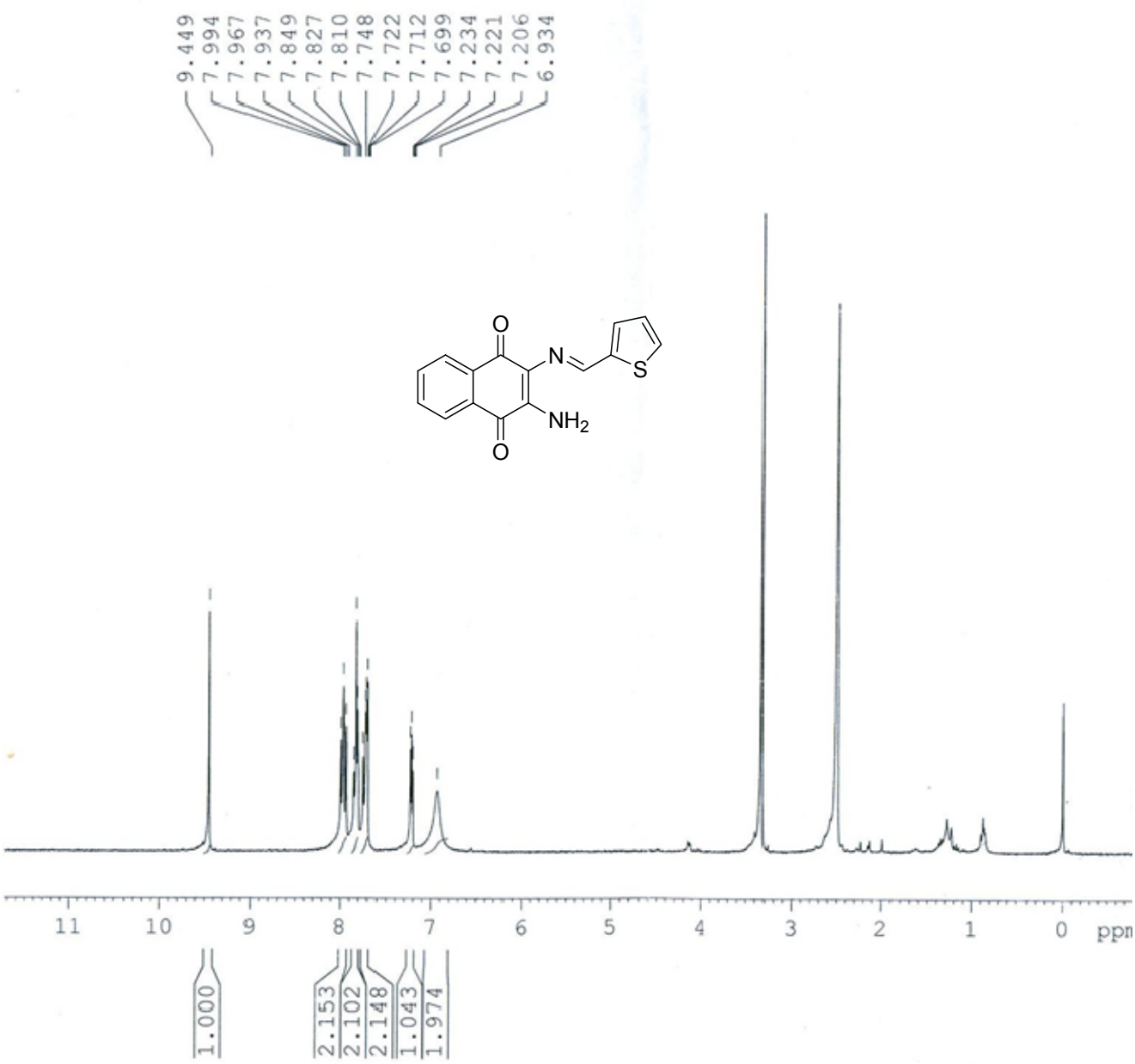


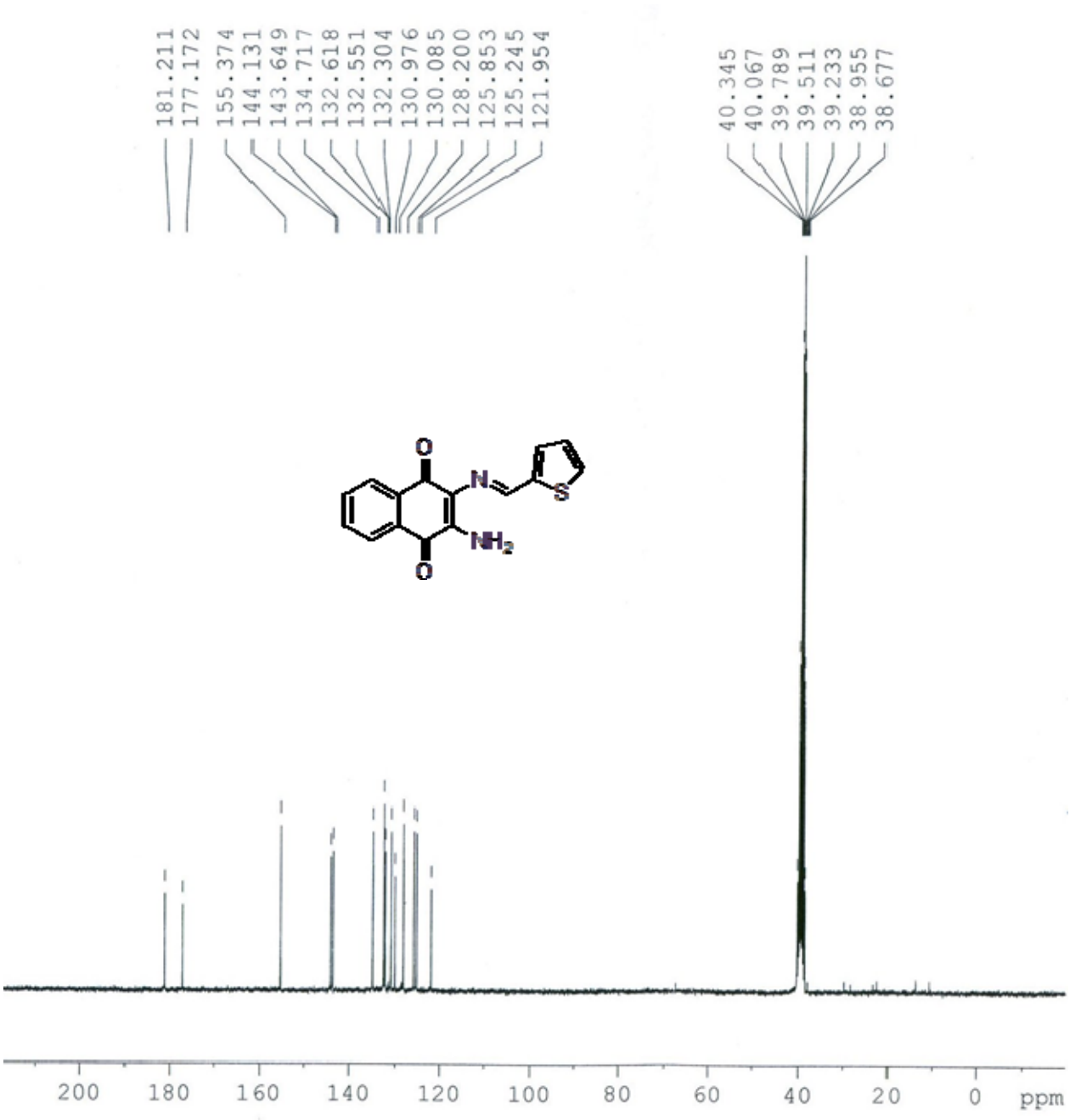
^{1}H NMR spectrum of 3a



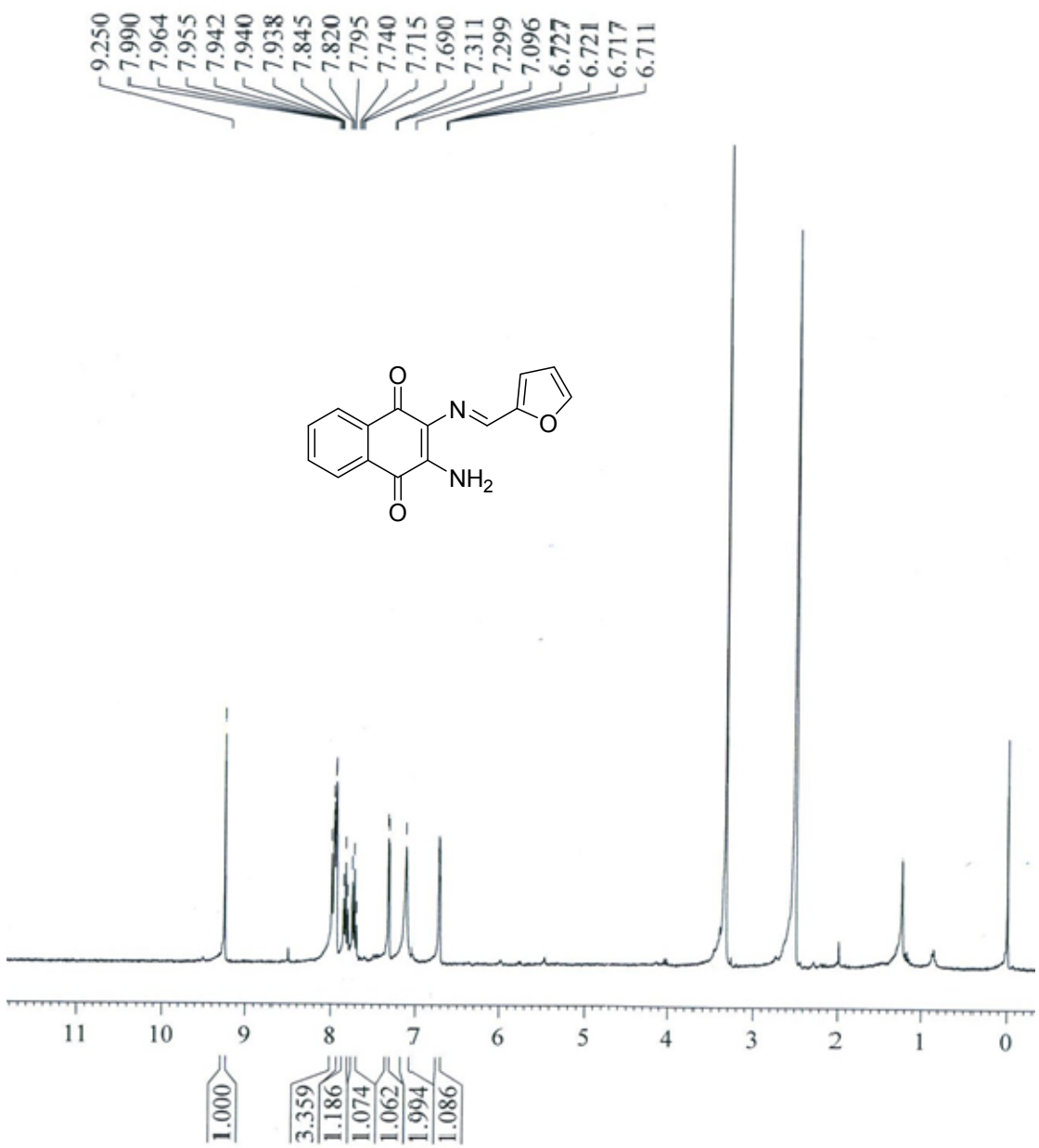
^{13}C NMR spectrum of 3a



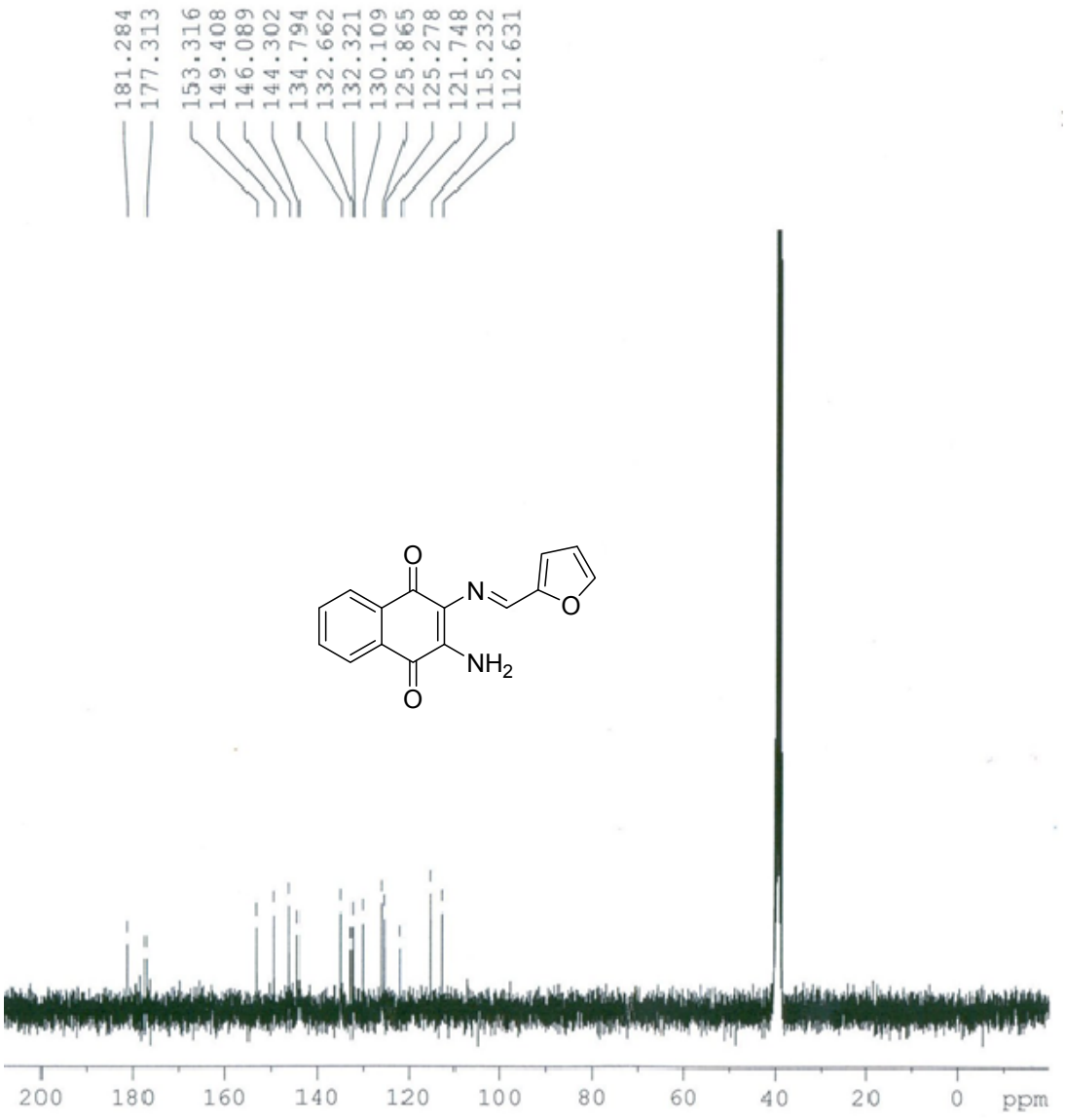
^{1}H NMR spectrum of 3b



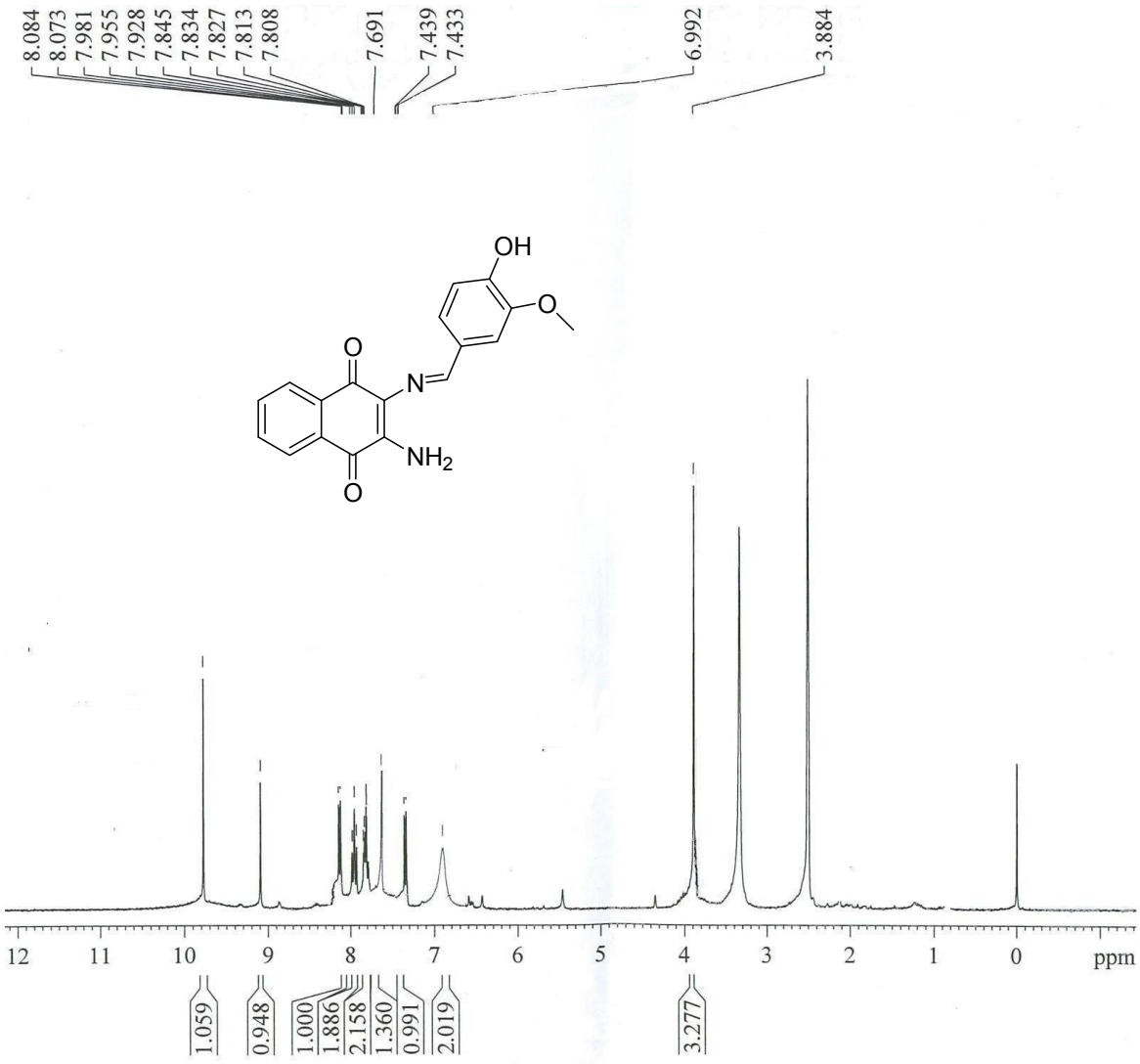
^{13}C NMR spectrum of 3b



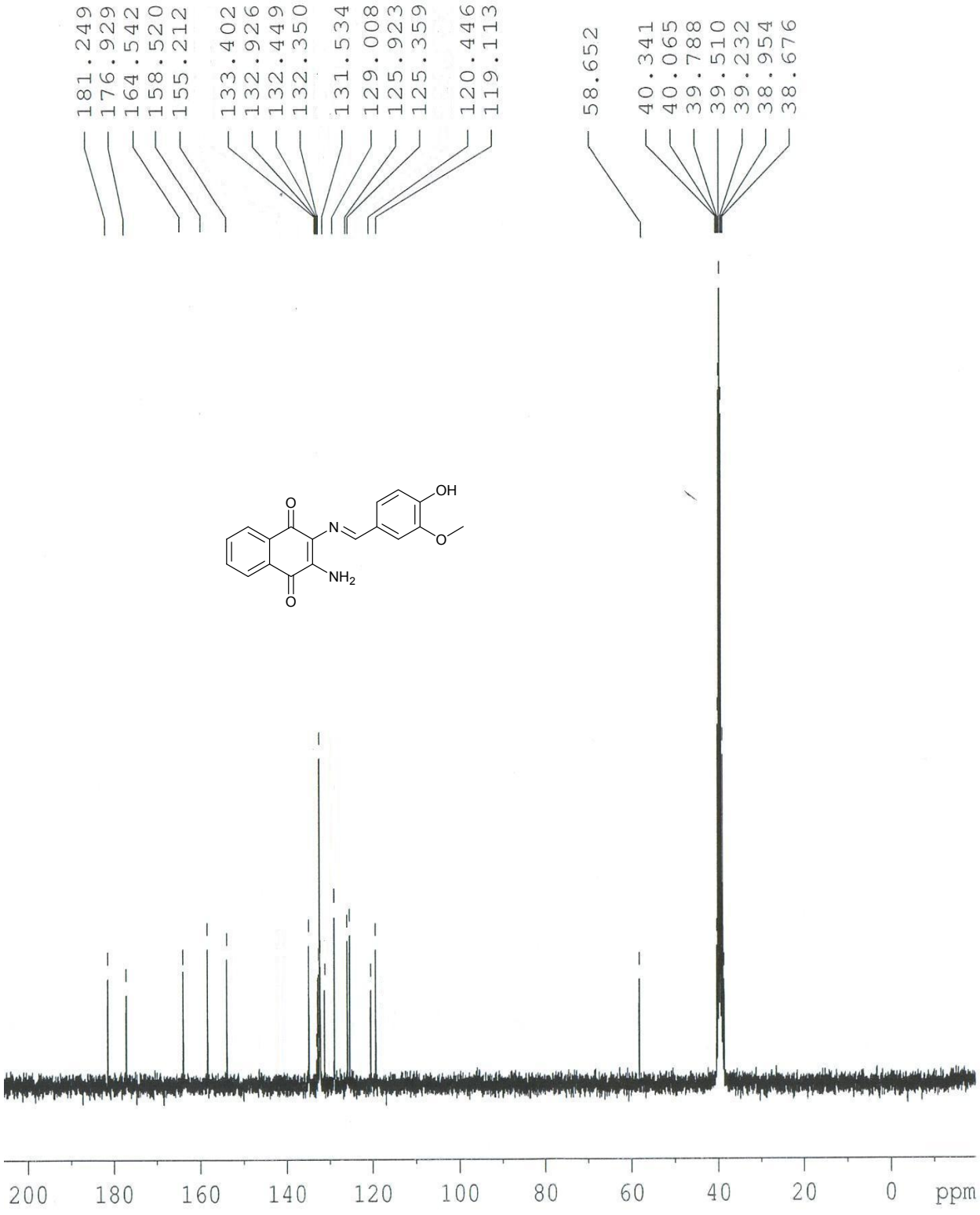
^{1}H NMR spectrum of 3c

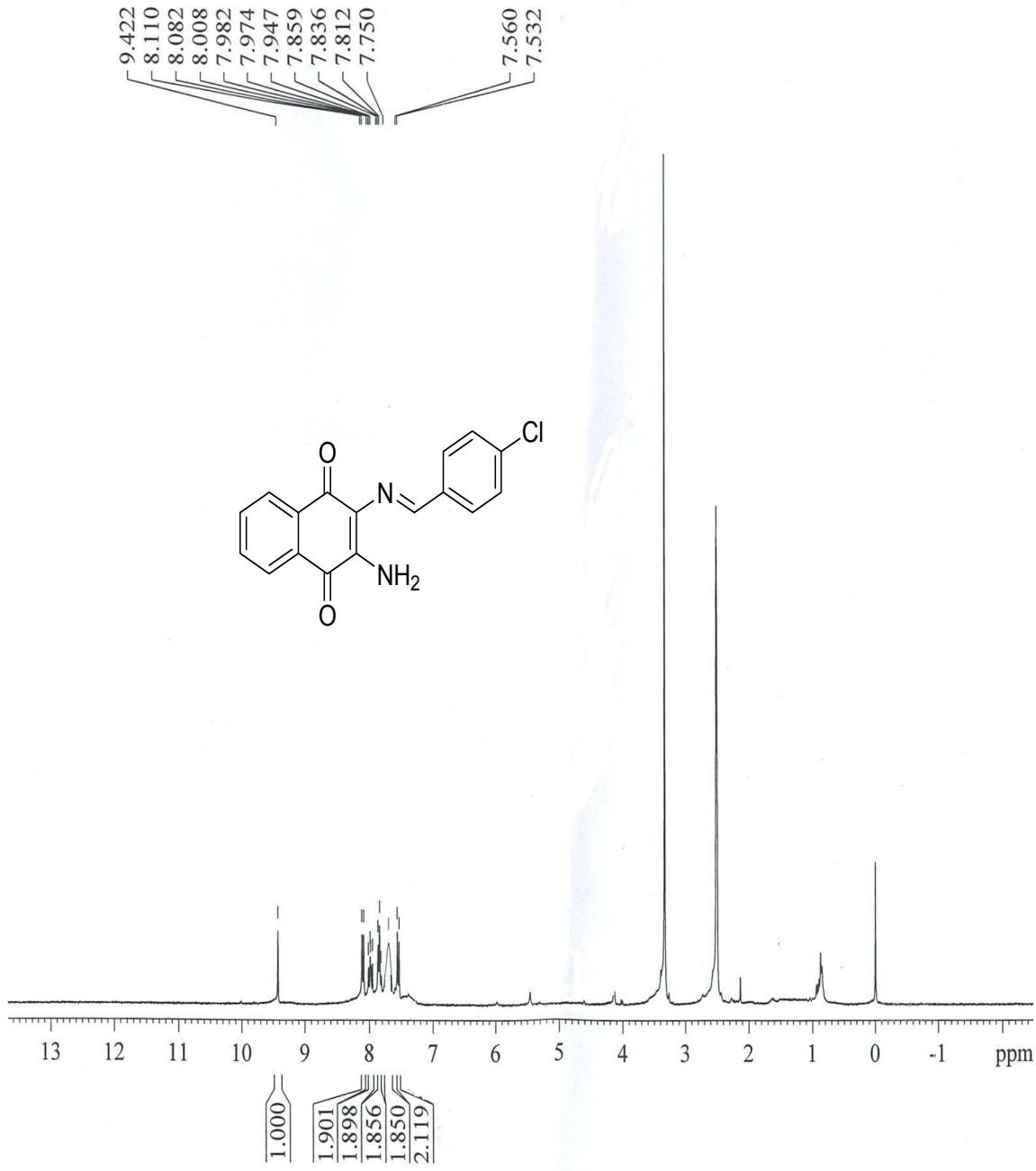


^{13}C NMR spectrum of 3c

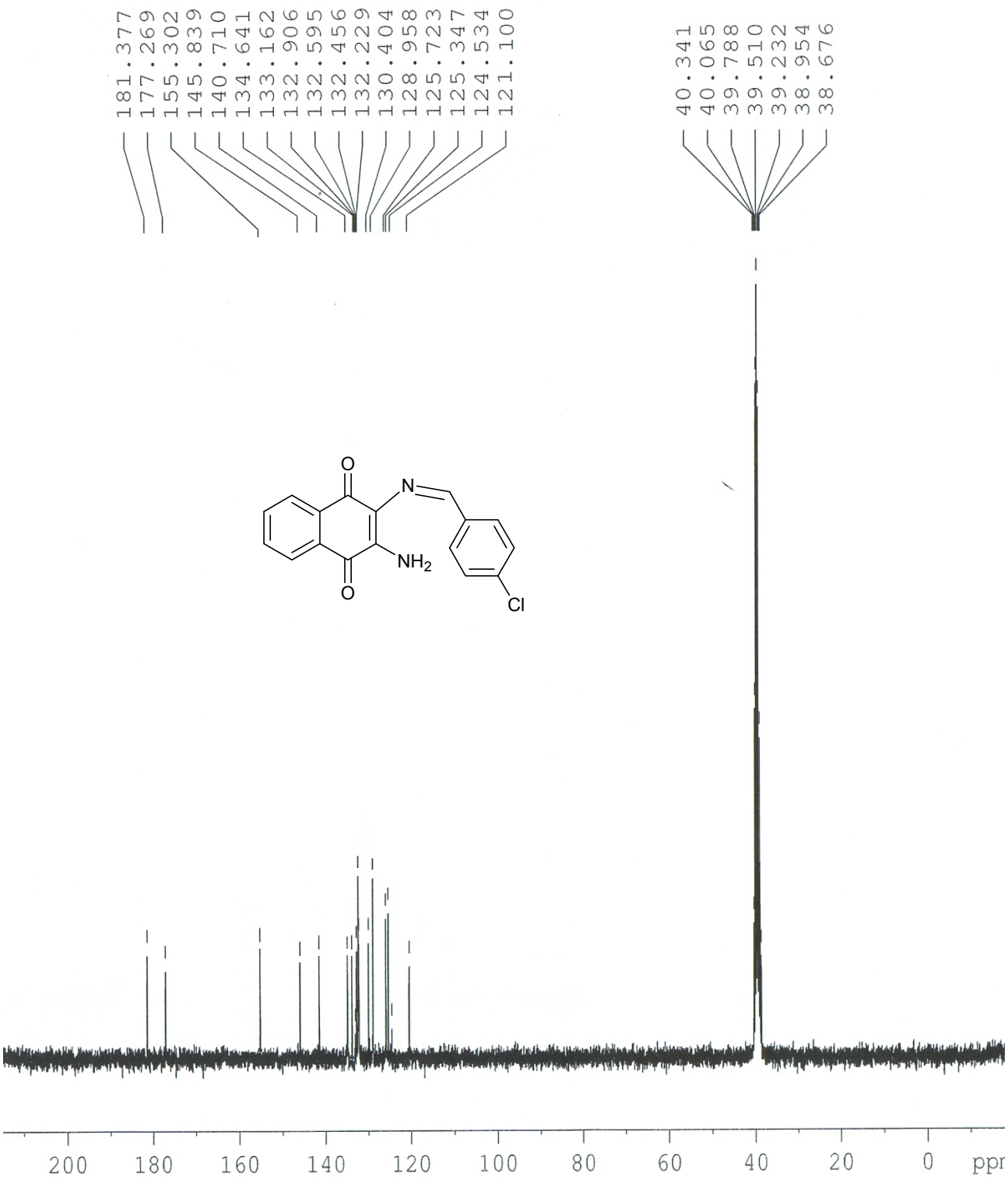


^{1}H NMR spectrum of 3d

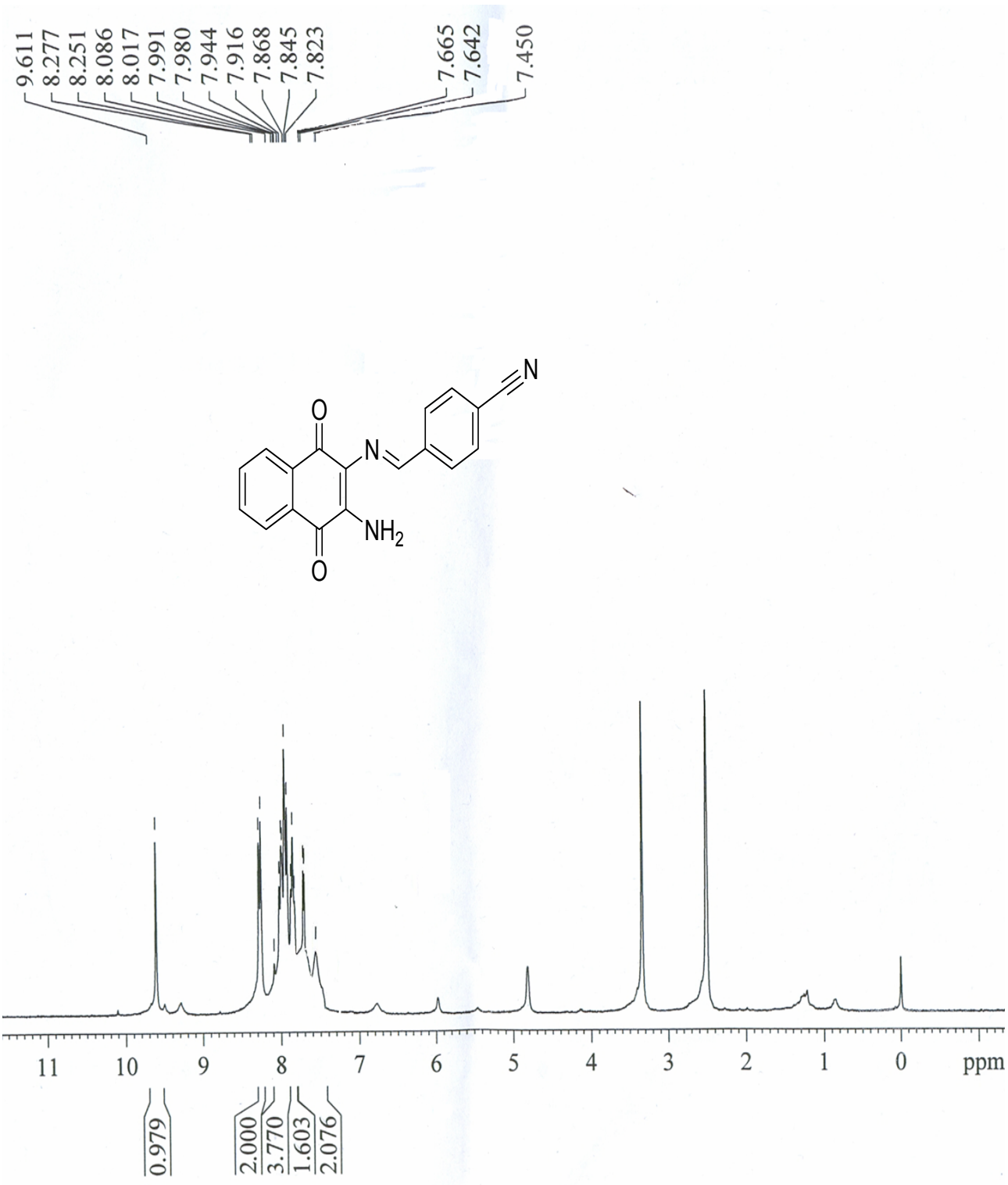




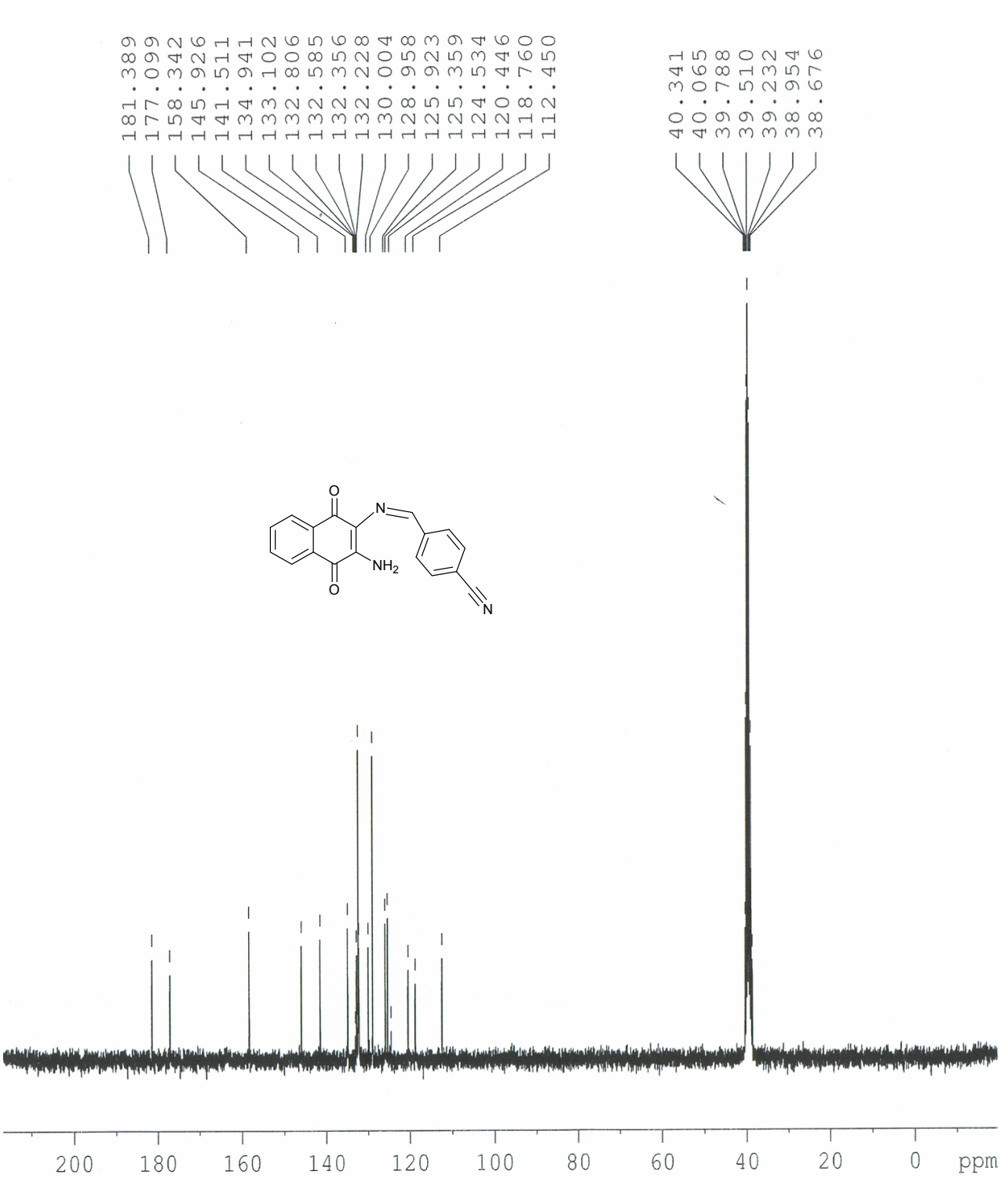
^{1}H NMR spectrum of 3e



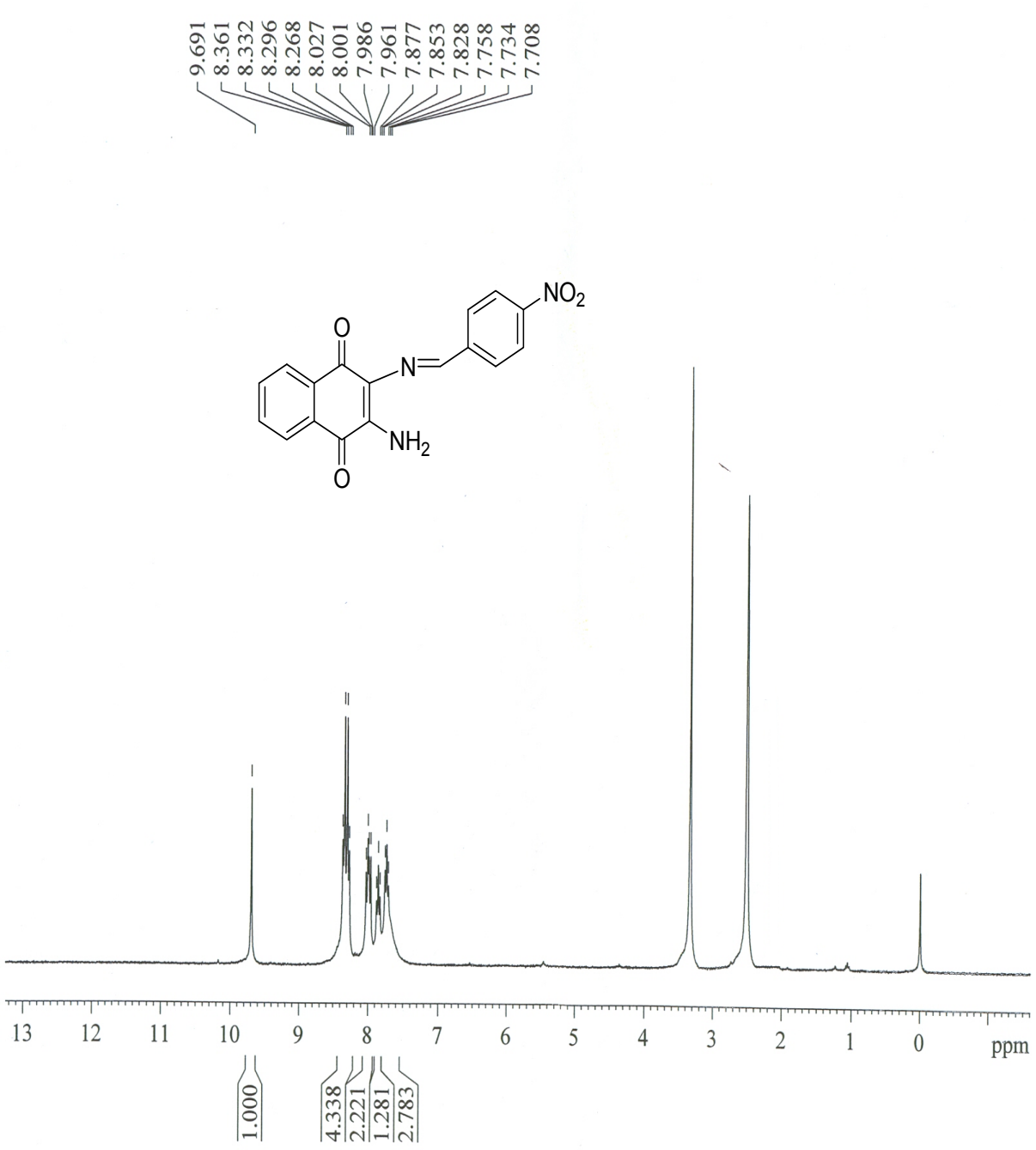
^{13}C NMR spectrum of 3e



^{1}H NMR spectrum of 3f

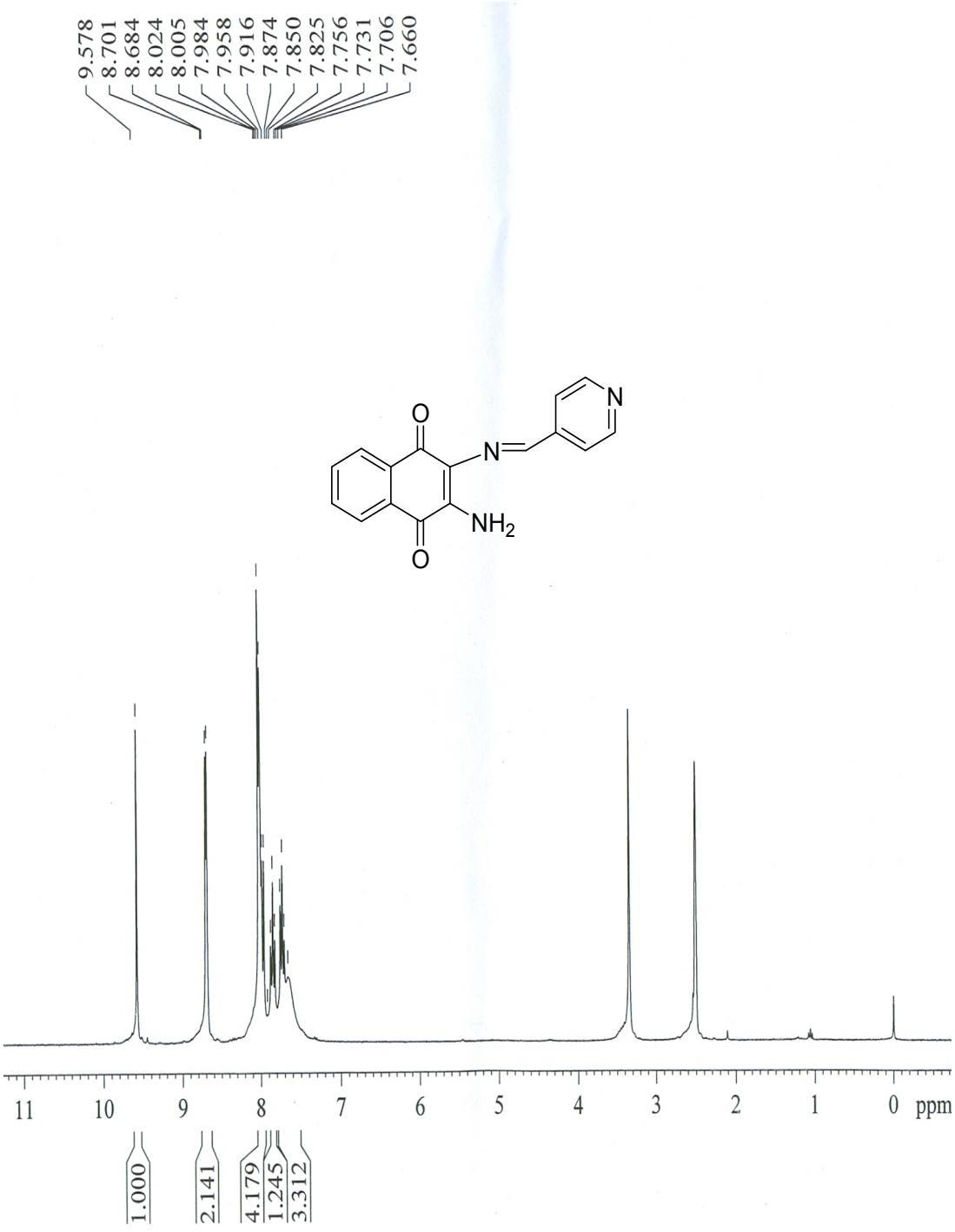


^{13}C NMR spectrum of 3f

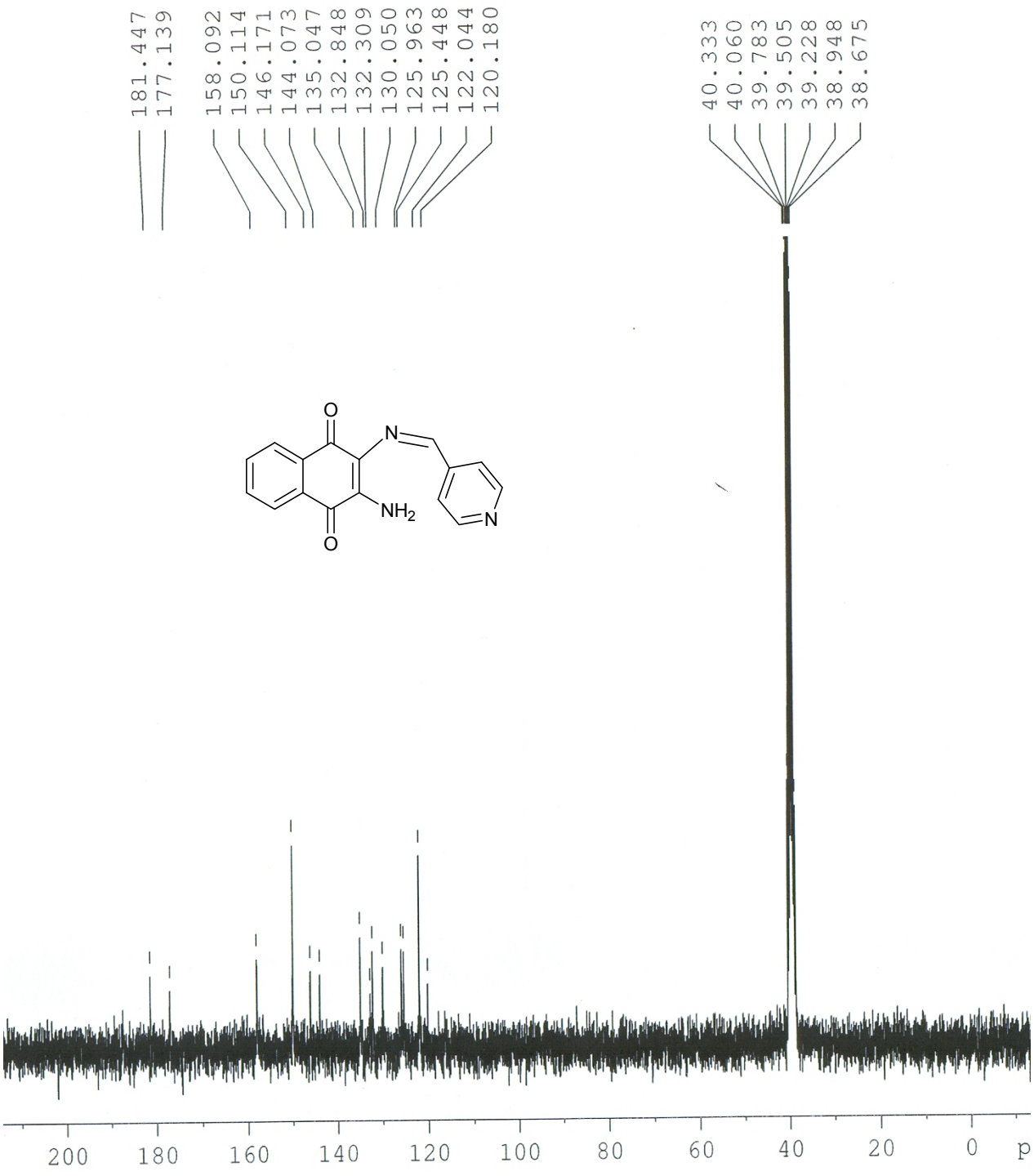


^{1}H NMR spectrum of 3g

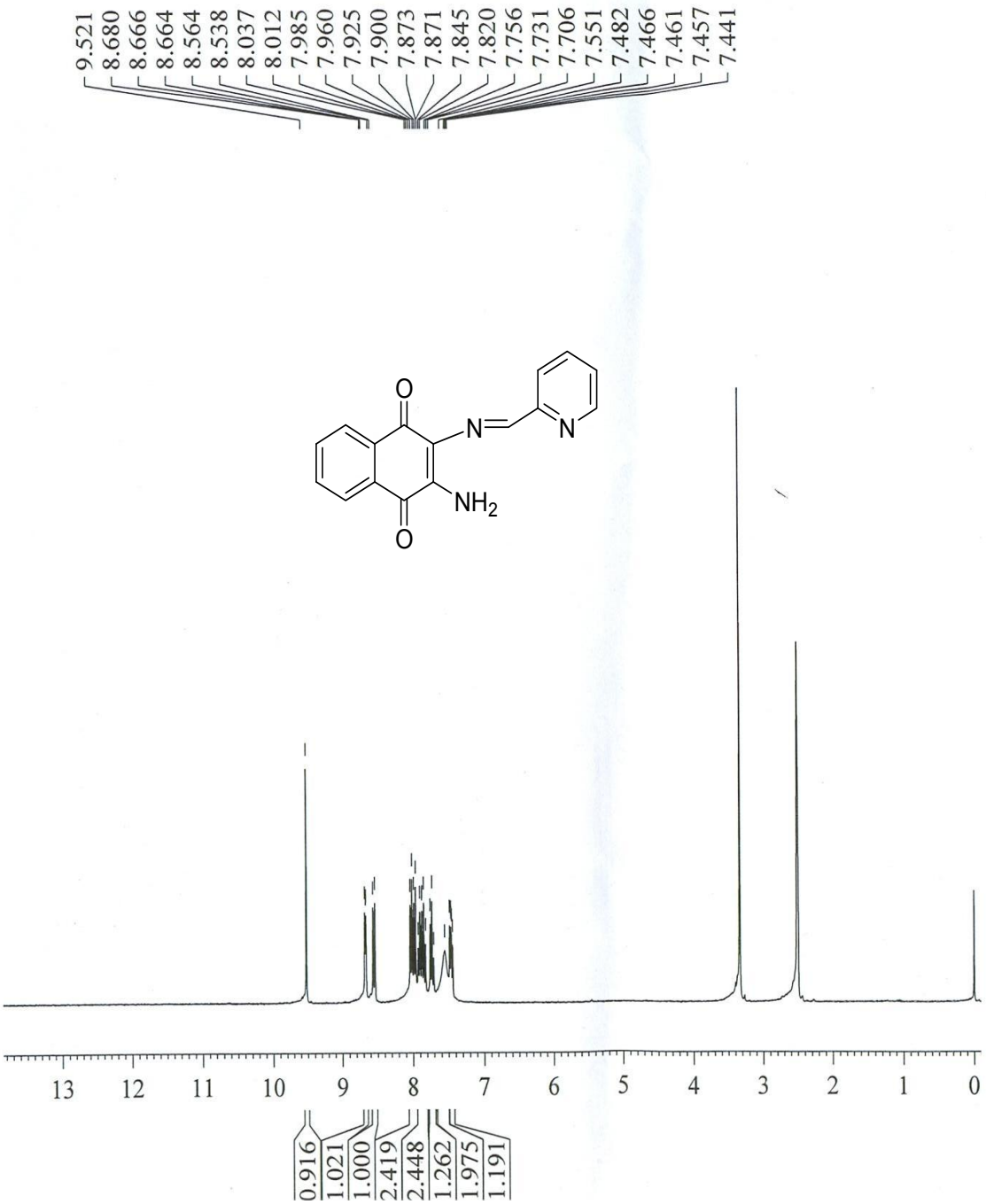
^{13}C NMR spectrum of 3g



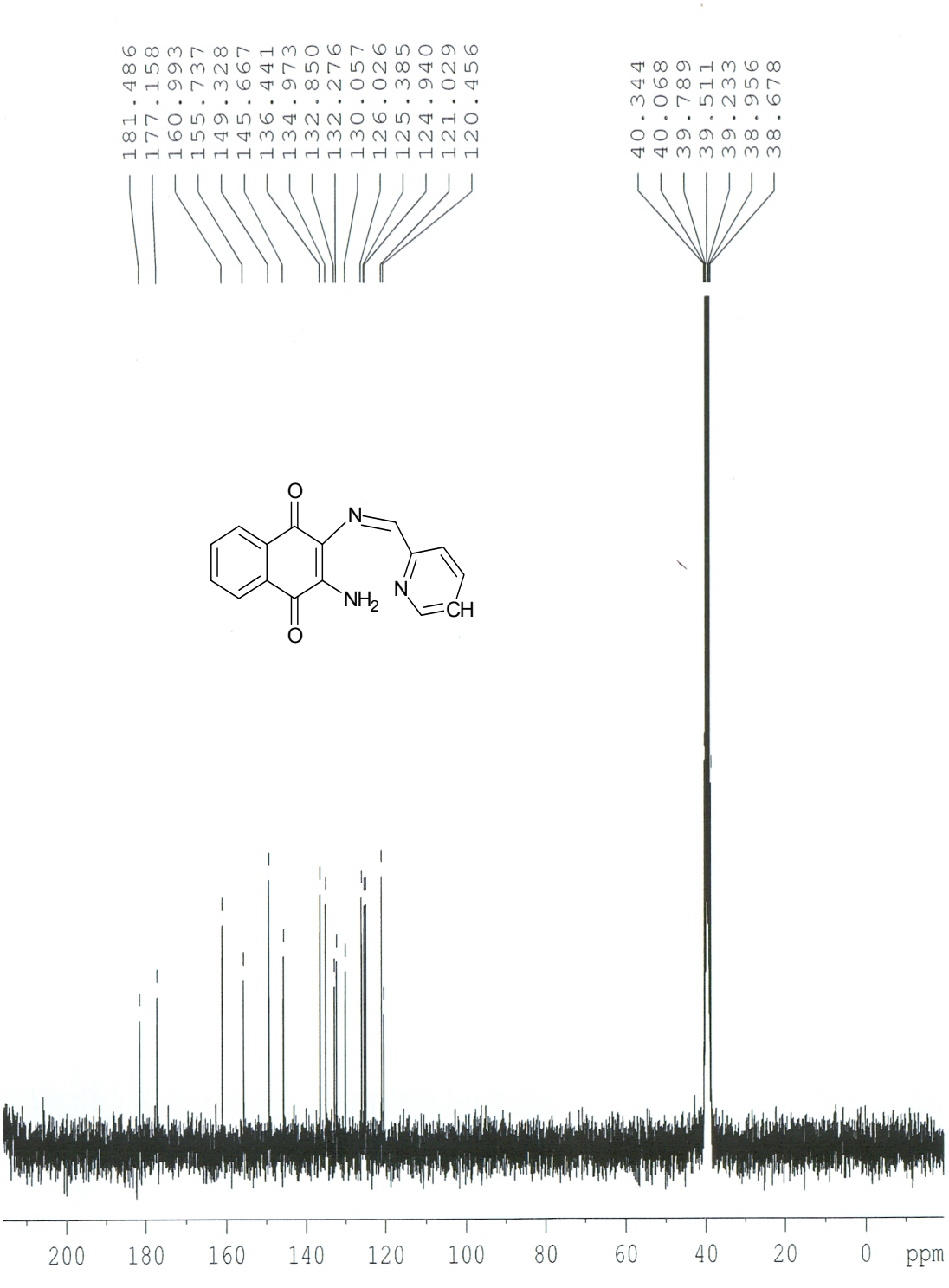
^{1}H NMR spectrum of 3h



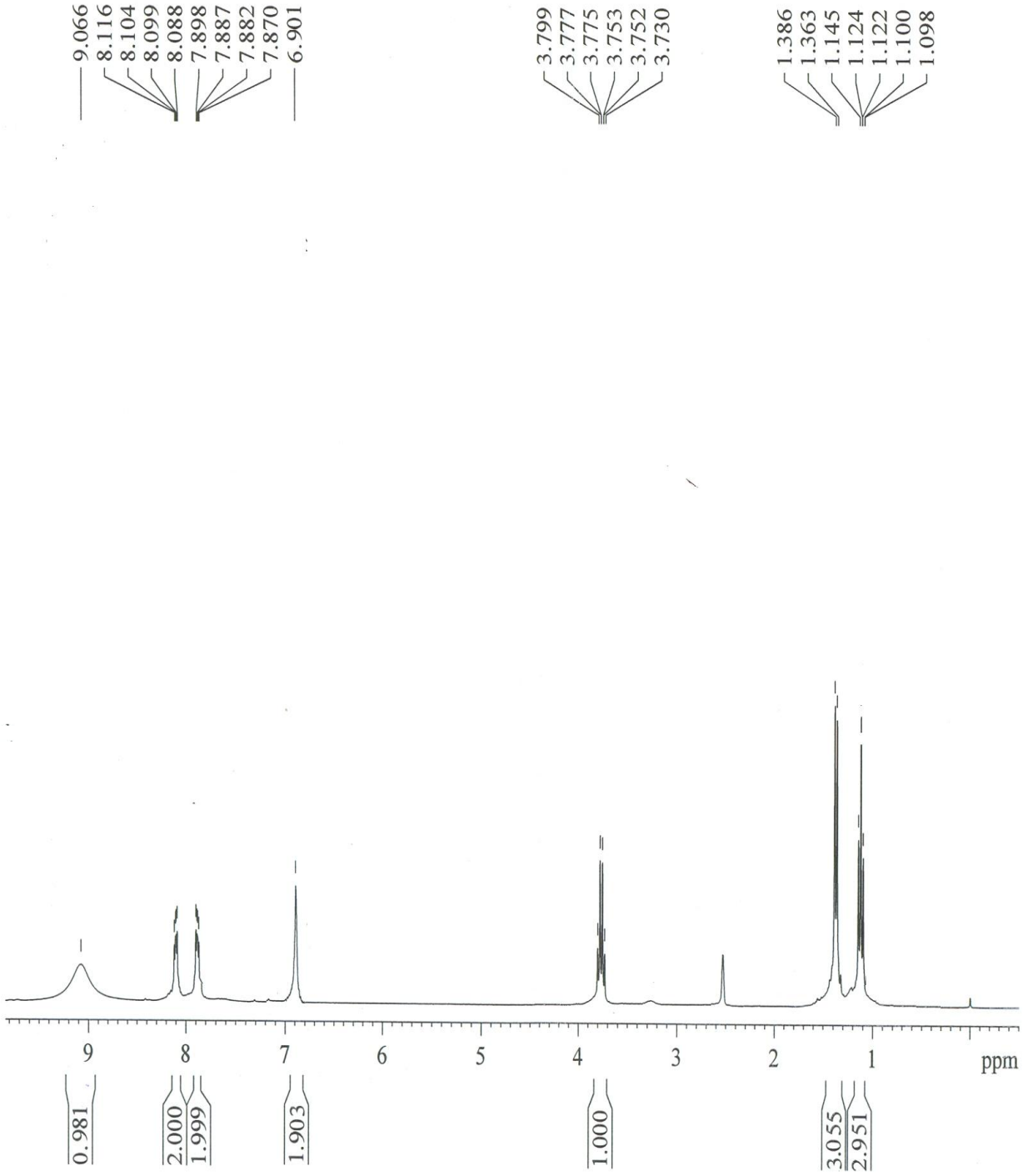
^{13}C NMR spectrum of 3h



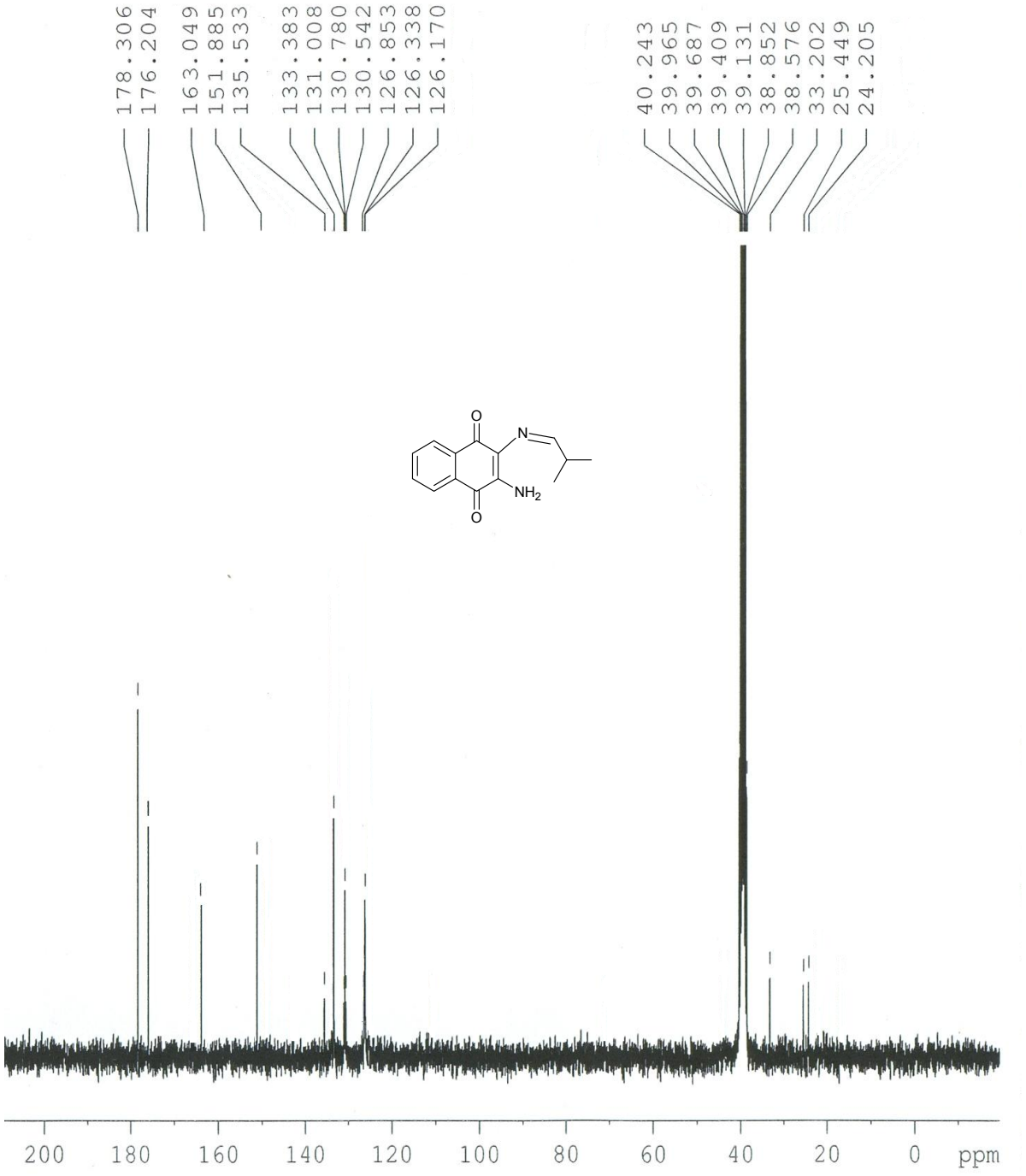
^{1}H NMR spectrum of 3i



^{13}C NMR spectrum of 3i



^{1}H NMR spectrum of 3j



^{13}C NMR spectrum of 3j

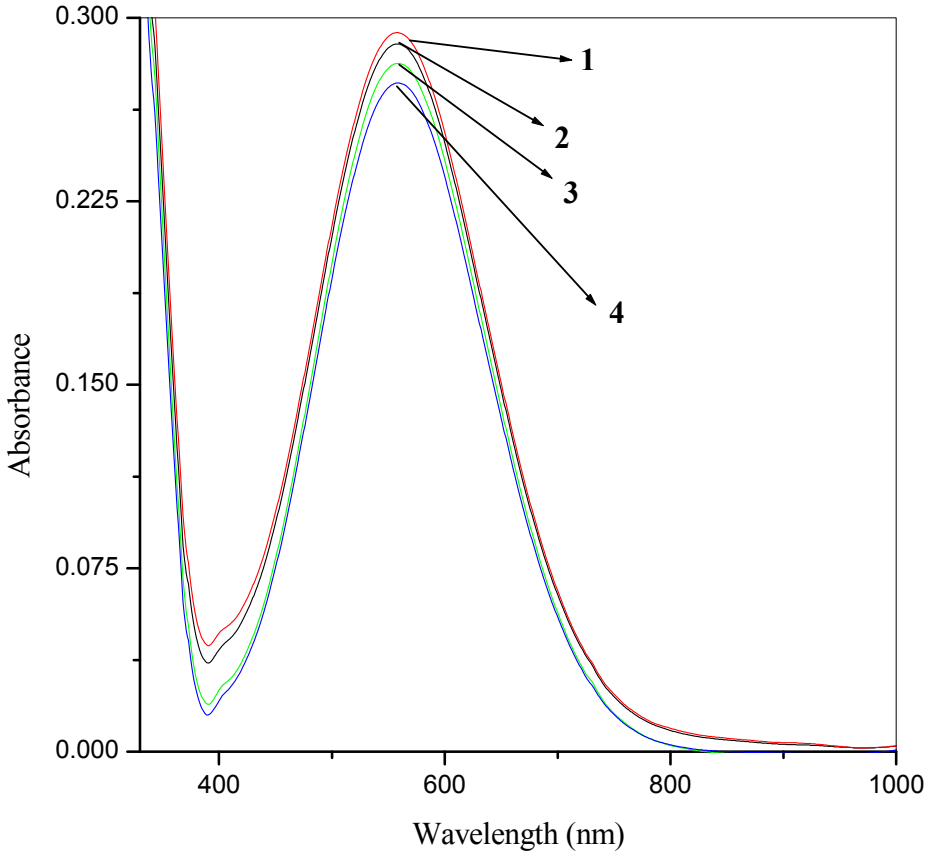


Figure. 1S. Concentration variation spectra for the HMB-DANQ system in ethanol at 298 K. [A] = 2.5 x 10^{-5} M; [D]: 1) 1.25, 2) 1.00, 3) 0.75, 4) 0.50, 5) 0.25 x10^{-3}M.

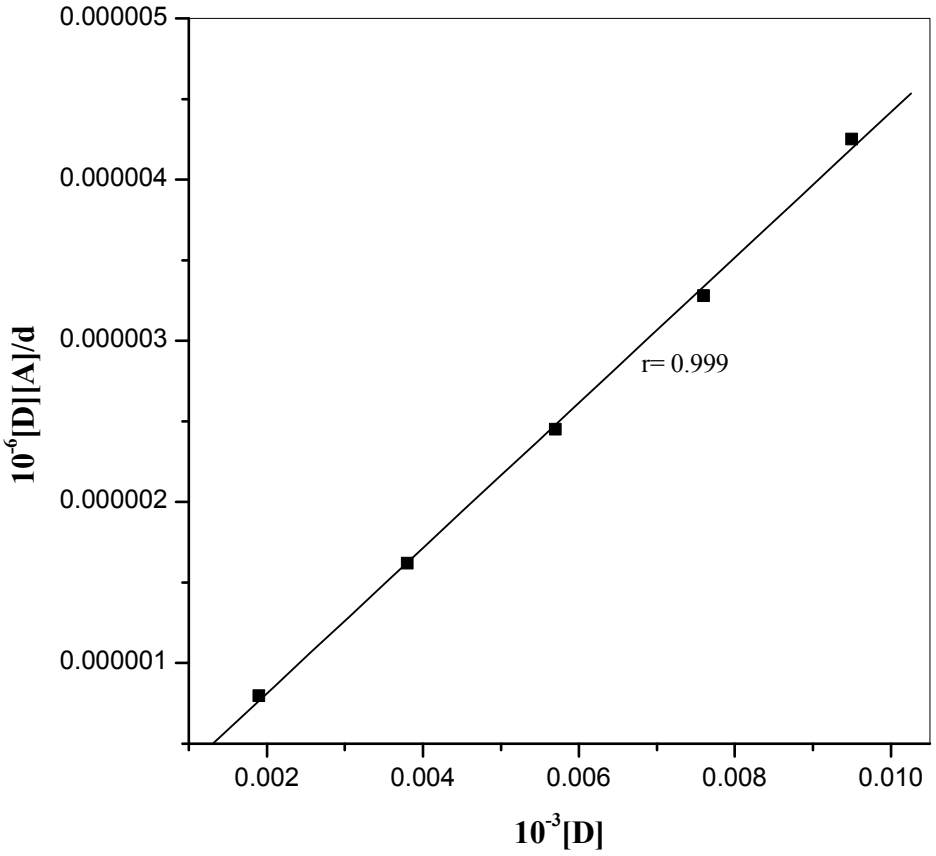


Figure 2S. Scott linear plot for HMB-DANQ system in ethanol at 298 K.

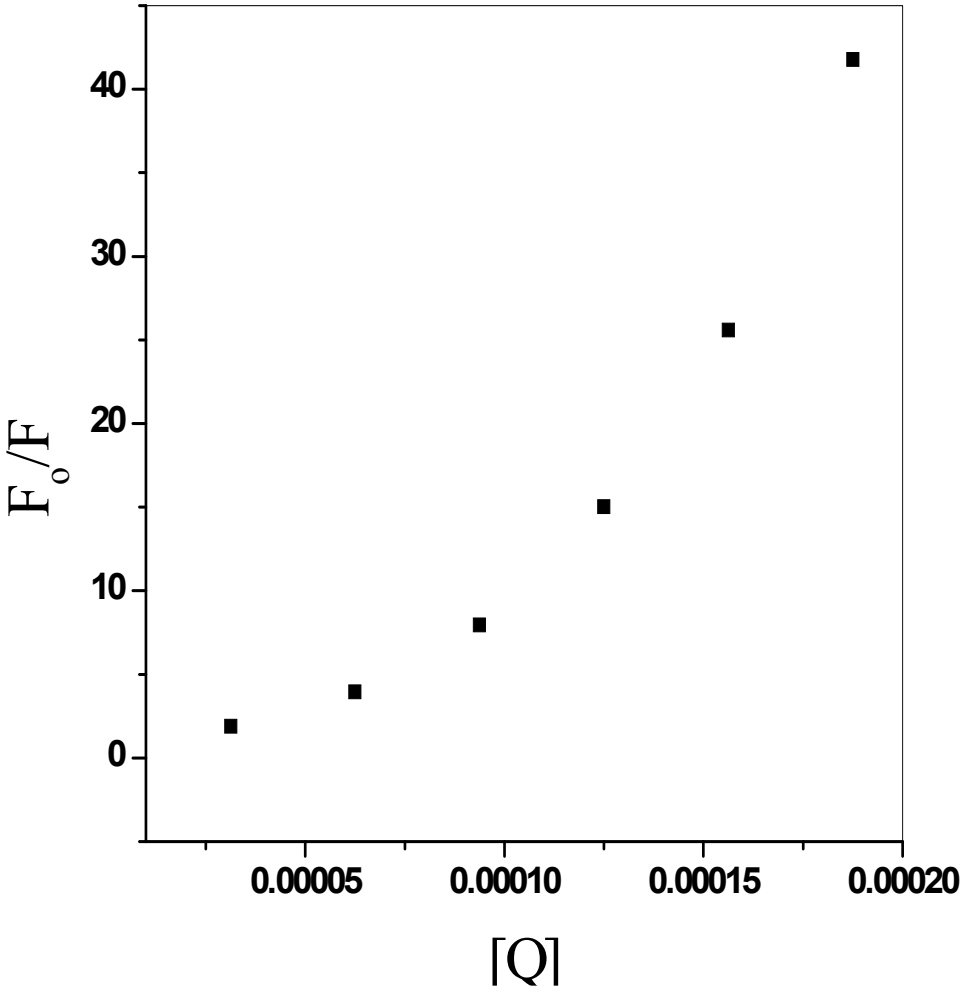


Figure 3S. Stern-Volmer plot for the fluoresence quenching of HMB with DCNQ in chloroform at 298 K

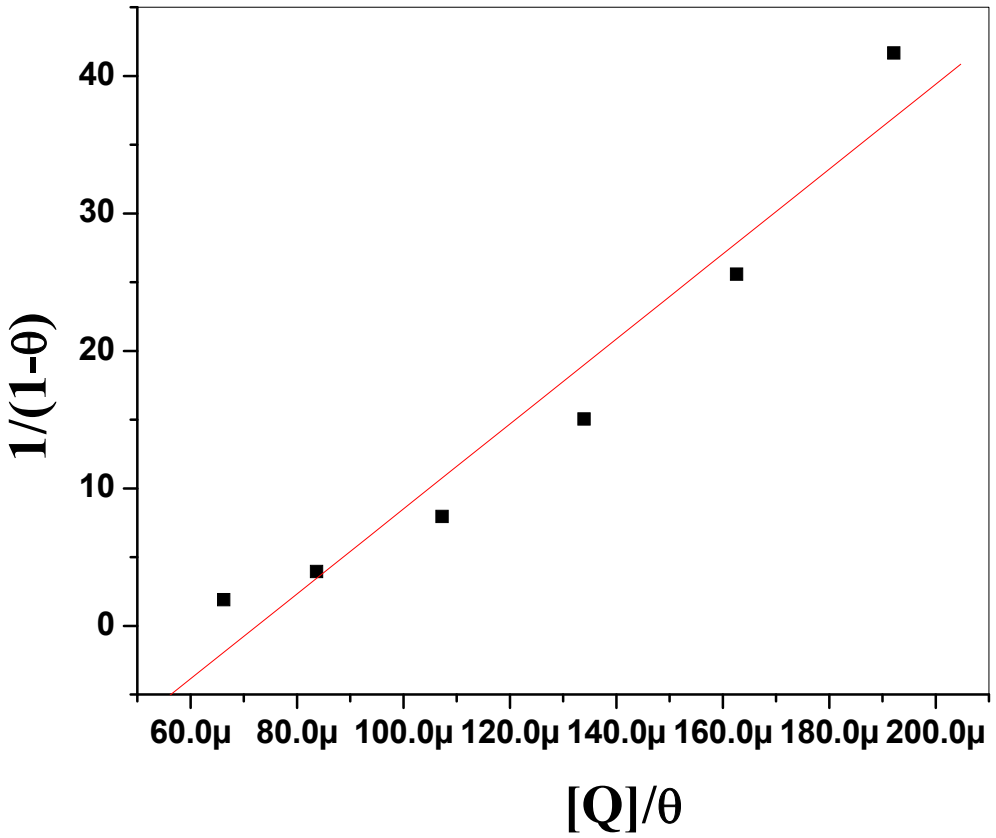


Figure 4S. Ward linear plot for HMB- DANQ in chloroform at298 K

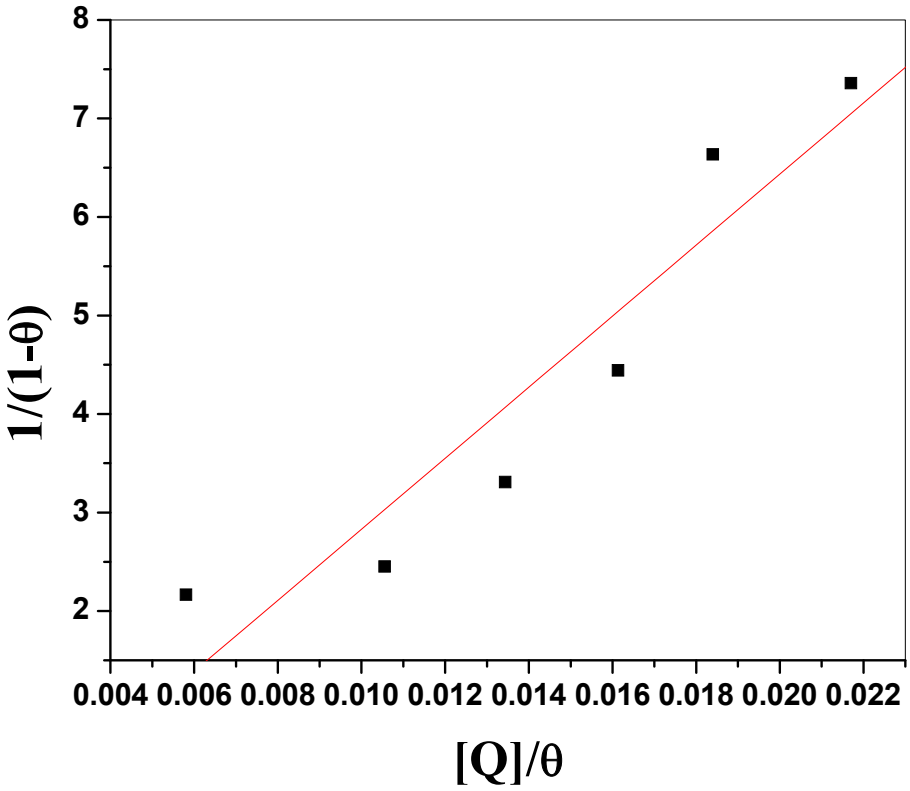


Figure 5S. Ward linear plot for HMB- 3g in chloroform at298 K

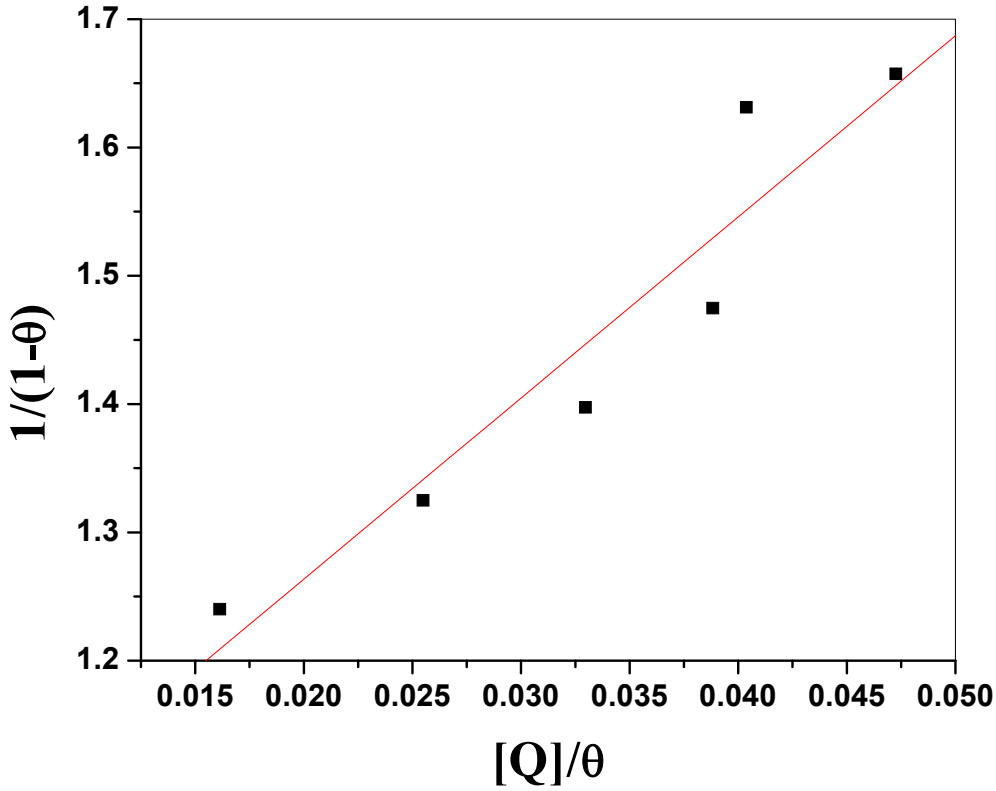
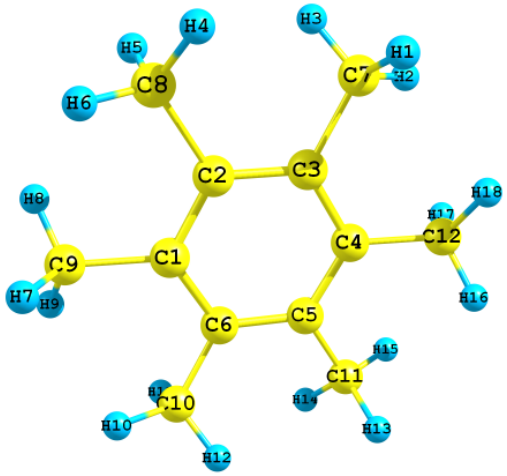


Figure 6S. Ward linear plot for HMB- 3i in chloroform at298 K

Hexamethylbenzene



Z - Matrix

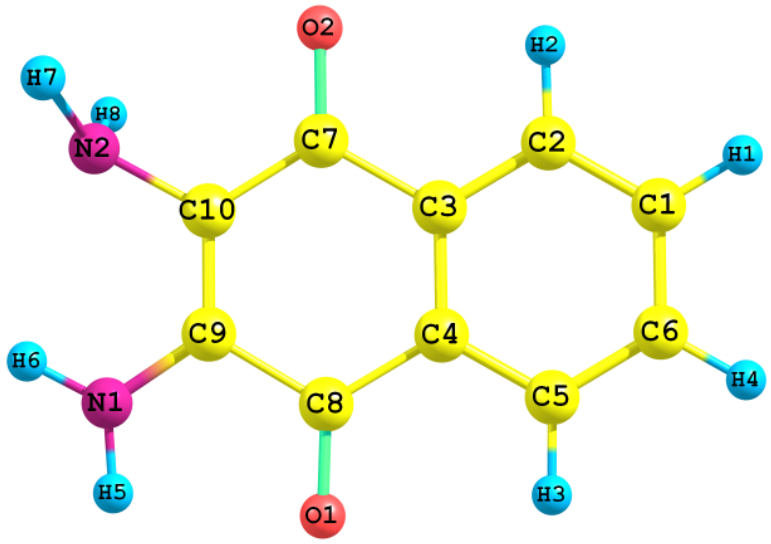
1	C					
2	C	C(1)	1.3989			
3	C	C(2)	1.3989	C(1)	119.9788	
4	C	C(3)	1.3989	C(2)	119.9788	C(1) -2.9031
5	C	C(4)	1.3989	C(3)	119.9787	C(2) 2.9031
6	C	C(5)	1.3989	C(4)	119.9788	C(3) -2.9031
7	C	C(3)	1.5174	C(2)	120.0035	C(1) 175.7201
8	H	C(7)	1.0859	C(3)	112.1176	C(2) 90.6886
9	H	C(7)	1.0781	C(3)	111.4463	C(2) -148.7959
10	H	C(7)	1.0781	C(3)	111.4462	C(2) -29.8269
11	C	C(2)	1.5174	C(1)	120.0034	C(6) -175.7201
12	H	C(11)	1.0781	C(2)	111.4462	C(1) 148.7959
13	H	C(11)	1.0859	C(2)	112.1176	C(1) -90.6886
14	H	C(11)	1.0781	C(2)	111.4463	C(1) 29.8269
15	C	C(1)	1.5174	C(6)	120.0035	C(5) 175.7201
16	H	C(15)	1.0859	C(1)	112.1176	C(6) 90.6886
17	H	C(15)	1.0781	C(1)	111.4462	C(6) -148.7959
18	H	C(15)	1.0781	C(1)	111.4462	C(6) -29.8269
19	C	C(6)	1.5174	C(5)	120.0035	C(4) -175.7201
20	H	C(19)	1.0781	C(6)	111.4463	C(5) 148.7959
21	H	C(19)	1.0859	C(6)	112.1176	C(5) -90.6886
22	H	C(19)	1.0781	C(6)	111.4462	C(5) 29.8269
23	C	C(5)	1.5174	C(4)	120.0034	C(3) 175.7201
24	H	C(23)	1.0859	C(5)	112.1176	C(4) 90.6886
25	H	C(23)	1.0781	C(5)	111.4462	C(4) -148.7959
26	H	C(23)	1.0781	C(5)	111.4463	C(4) -29.8269
27	C	C(4)	1.5174	C(3)	120.0035	C(2) -175.7201
28	H	C(27)	1.0781	C(4)	111.4462	C(3) 148.7959
29	H	C(27)	1.0859	C(4)	112.1176	C(3) -90.6886
30	H	C(27)	1.0781	C(4)	111.4462	C(3) 29.8269

Cartesian coordinates

S.No.	Atom	X	Y	Z
1	C	0.0000	0.0000	0.0000
2	C	0.0000	1.3989	0.0000
3	C	1.2118	2.0979	0.0000
4	C	2.4220	1.3989	0.0614
5	C	2.4220	0.0000	0.0614
6	C	1.2102	-0.6990	0.0614
7	C	1.2142	3.6121	-0.0981
8	H	1.1895	4.0852	0.8791
9	H	2.0920	3.9726	-0.6099
10	H	0.3636	3.9726	-0.6537
11	C	-1.3137	2.1577	0.0316
12	H	-1.2134	3.0981	0.5492
13	H	-1.6858	2.3726	-0.9657
14	H	-2.0781	1.6009	0.5492
15	C	-1.3104	-0.7588	-0.0981
16	H	-1.7325	-0.9737	0.8791
17	H	-2.0476	-0.2020	-0.6537
18	H	-1.1840	-1.6992	-0.6099
19	C	1.2077	-2.2132	0.1594
20	H	0.3300	-2.5736	0.6713
21	H	1.2325	-2.6863	-0.8177
22	H	2.0584	-2.5736	0.7151
23	C	3.7356	-0.7588	0.0298
24	H	4.1077	-0.9737	1.0271
25	H	3.6353	-1.6992	-0.4878
26	H	4.5001	-0.2020	-0.4878
27	C	3.7324	2.1577	0.1594
28	H	4.4696	1.6009	0.7151
29	H	4.1545	2.3726	-0.8177
30	H	3.6060	3.0981	0.6713

Energy = -464.8056953 a.u.

2,3-Diaminonaphthaquinone



Z - Matrix

1	C						
2	C	C(1)	1.3872				
3	C	C(2)	1.3848	C(1)	119.9446		
4	C	C(3)	1.3944	C(2)	119.6942	C(1)	0.0000
5	C	C(4)	1.3873	C(3)	120.2863	C(2)	0.0000
6	C	C(5)	1.3855	C(4)	119.7789	C(3)	0.0000
7	H	C(1)	1.0702	C(2)	119.7329	C(3)	180.0000
8	H	C(2)	1.0682	C(1)	121.2679	C(6)	-180.0000
9	C	C(3)	1.4893	C(2)	119.8571	C(1)	-180.0000
10	C	C(4)	1.4727	C(3)	119.8568	C(2)	180.0000
11	H	C(5)	1.0687	C(4)	119.1232	C(3)	-180.0000
12	H	C(6)	1.0700	C(5)	119.8845	C(4)	180.0000
13	C	C(10)	1.4958	C(4)	118.4040	C(3)	0.0053
14	C	C(13)	1.3489	C(10)	121.0204	C(4)	-0.0129
15	O	C(10)	1.2206	C(4)	122.6424	C(3)	179.9821
16	O	C(9)	1.2285	C(3)	120.2222	C(2)	-0.0040
17	N	C(13)	1.3458	C(10)	115.2003	C(4)	179.9910
18	H	N(17)	0.9879	C(13)	120.1616	C(10)	-0.0078
19	H	N(17)	0.9882	C(13)	118.5492	C(10)	-179.9783
20	N	C(14)	1.4227	C(13)	118.7434	C(10)	-179.9902
21	H	N(20)	0.9972	C(14)	113.8615	C(13)	116.3289
22	H	N(20)	0.9972	C(14)	113.8577	C(13)	-116.5359

Cartesian coordinates

S.No.	Atom	X	Y	Z
1	C	0.0000	0.0000	0.0000
2	C	0.0000	1.3872	0.0000
3	C	1.1999	2.0784	0.0000
4	C	2.4031	1.3736	0.0000
5	C	2.4012	-0.0137	0.0000
6	C	1.1978	-0.7002	0.0000
7	H	-0.9293	-0.5308	0.0000
8	H	-0.9130	1.9416	0.0000
9	C	1.1977	3.5677	0.0000
10	C	3.6812	2.1051	-0.0000
11	H	3.3342	-0.5350	0.0000
12	H	1.1944	-1.7702	-0.0000
13	C	3.6452	3.6005	0.0001
14	C	2.4728	4.2676	-0.0000
15	O	4.7631	1.5401	0.0003
16	O	0.1352	4.1844	-0.0001
17	N	4.8488	4.2026	0.0003
18	H	5.6749	3.6608	0.0005
19	H	4.8828	5.1902	0.0007
20	N	2.4952	5.6902	-0.0001
21	H	2.0971	6.0998	-0.8176
22	H	2.0940	6.0999	0.8157

Energy = -641.8533439 a.u.

Table S1: Energy gap (ΔE = HOMO-LUMO) for DANQ and imines (3a–j)

S.NO	Compound	HOMO (eV)	LUMO (eV)	ΔE	
				Intra [a]	Inter [b]
1	DANQ	-8.8653	0.4446	9.3099	8.5316
2	3a	-7.6957	0.4092	8.1049	8.4962
3	3b	-8.1308	0.6587	8.7895	8.7457
4	3c	-7.8034	0.2419	8.0453	8.3289
5	3d	-7.6608	0.2440	7.9048	8.3310
6	3e	-8.0504	0.0329	8.0833	8.1199
7	3f	-8.6584	0.2019	8.8603	8.2889
8	3g	-8.5112	-0.1379	8.3733 `	7.9491
9	3h	-8.4606	0.2712	8.7318	8.3582
10	3i	-9.3607	0.5540	9.9147	8.6410
11	3j	-8.2900	0.3360	8.6260	8.4230

a – Intra molecular charge transfer within the molecule (DANQ and 3a-3j).

b – Inter molecular charge transfer transition between the corresponding compound and HMB

Determination of K_f value by Ward method :

The experimental results indicated that the quenching efficiency increased with increasing concentration of the electron acceptors (Fig. 4). The fraction of acceptors bound to HMB (θ) was determined by using the following equation.

$$\theta = F_0 - F / F_0 \quad \text{..... (1)}$$

Where, F and F_0 denote the fluorescence intensities of HMB in the presence of acceptor and in the absence of acceptor, respectively. From the resulting values of θ, the association constant K_f for HMB–DANQ and HMB–imine systems was computed using the method described by Ward [24]. It has been shown that for equivalent and independent binding sites:

$$1 / (1 - \theta) K_f = [Q_T] / \theta - n [D_T] \quad \text{.....(2)}$$

where n is the number of binding sites, $[Q_T]$ is the total acceptor concentration and $[D_T]$ is the total donor concentration. The plot $1/(1- \theta)$ versus $[Q_T] / \theta$ is linear indicating that under the experimental conditions all the binding sites are equivalent and independent. The value of K_f obtained, from the plots, for HMB –DANQ , HMB – 3g and HMB – 3i systems are found to be 3.08955×10^5, 3.6064×10^2 and 14.1108 mol L^{-1}, respectively.

Solvent Effect on Intramolecular CT Transition[1-3]

The intramolecular CT transition between the amine moiety and the quinone of DANQ is highly solvent dependent. With an aim to investigate the effect of solvent on the abosrption maxium of this transition quantitatively, the electronic spectrum of DANQ was recorded in ten different solvents belonging to various types and the data obtained are analyzed using the technique of correlation analysis. The following is the regression equation obtained for the correlation of λ_{max} versus relative permittivity of the medium.

$$\lambda_{max} = 0.49\pm0.1\ \varepsilon_r - 251\pm57$$

$$(N = 10;\ r = 0.85)$$

Such a poor correlation obtained may be due to the fact that single solvent parameter is not sufficient enough to explain completely the observed solvent dependence of λ_{max}. Therefore, in order to obtain a deeper insight into the various solute–solvent interactions, which influence electronic spectra, we have tried to adopt the solvatochromic comparison method developed by Kamlet and Taft. The following regression equation was obtained for the correlation of the absorption maximum with the Kamlet–Taft's solvatochromic parameters α (hydrogen bond donor, HBD, acidity), β (hydrogen bond acceptor, HBA, basicity) and π^* (dipolarity/polarizability).

$$\lambda_{max} = 474\pm8 + 0.15\pm0.07\ \alpha + 0.51\pm0.10\ \beta + 0.73\pm0.12\ \pi^*$$

$$(N = 10;\ 100R^2 = 95\%;\ P\alpha = 11\%;\ P\beta = 37\%;\ P\pi^* = 52\%)$$

The absorption maximum of DANQ studied show a good correlation with the solvent with an explained variance of 95%. Such a good correlation indicated the existence of both specific and non-specific solute–solvent interactions. The contributions of each of these solvatochromic parameters to λ_{max} are also calculated and are listed in the above equation. The results indicated that the contribution of solvent dipolarity/polarizability parameter to the solvent effect was found to dominant and it alone accounts for 52% of the observed solvent effect. The sign of the coefficient of this term is positive indicating an increase in λ_{max} with an increase in polarity of the medium. The solvent H-bond acceptor basicity also substantially contributed to the observed solvent effect.

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