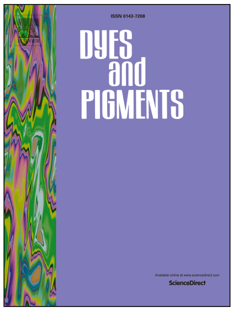

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Graphical Abstract

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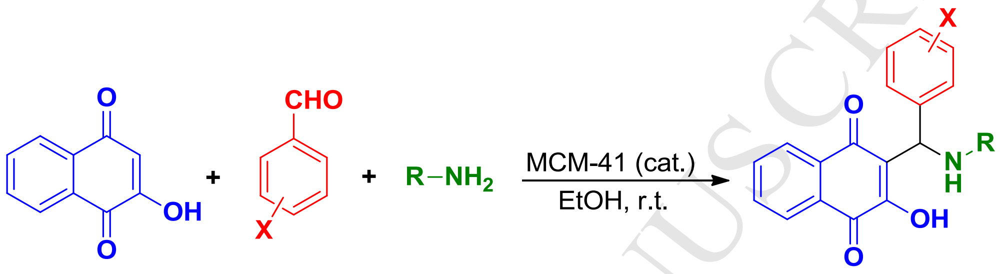

Synthesis of 2-hydroxy-1,4-naphthoquinone derivatives via a three-component reaction catalyzed by nanoporous MCM-41

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Abstract

A one-pot procedure for synthesis of hydroxyl naphthalene-1,4-dione derivatives via a three-component reaction of 2- hydroxynaphthalene-1,4-dione, aromatic aldehydes and heterocyclic or carbocyclic amines is developed. MCM-41 nanoporous catalyst is effective, easy recovery, reusable and makes work-up easy. This approach is clean and environmentally friendly. The structures of the new compounds were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

Keywords: Naphthoquinone pigment, 2-Hydroxynaphthalene-1,4-dione, Nanoporous MCM-41, Environmentally friendly, Multicomponent reaction, One-pot synthesis.

1. Introduction

Multicomponent reactions (MCRs) are an important class of convergent organic reactions, in which three or more starting materials react together to form a unique product [1,2]. They have recently received special interest, because of the ability of the formation of multi-bonds in a one-pot reaction with high atom efficiency and mild and environmentally benign conditions [3]. Due to this important ability, researches on MCRs have received a rapidly increasing attention in both academic and industrial researches [4].

On the other hand, in recent years, the use of heterogeneous catalysts has been widely studied; because, they are easily removable from the reaction media by simple filtration after completion of the reaction and in many cases they are reusable [5]. In order to overcome the lower reaction rate of heterogeneous catalysts compared to homogeneous ones, the use of high surface area materials such as nanoporous MCMs, SBAs, and zeolites have been widely investigated [6-9].

Molecules with the napthoquinone structure constitute one of the most interesting classes of compounds in organic chemistry. They may possess different biological properties, industrial applications (such as pigments) and can be used as potential intermediates in the synthesis of heterocycles [10]. A series of related naphthoquinone pigments from streptocarpus dunnii have been isolated and characterized (Fig. 1) [11,12].

Fig. 1.

2-Hydroxy-1,4-naphthoquinone (HNQ; Lawsone) exists in the leaves of henna as the principal natural dye (1.0–1.4%). Henna (Lawsonia inermis, also called mignonette tree) is a flowering plant, which has been used since the Bronze Age to dye hair, skin (including body art), fingernails, leather, silk and wool. In various festivals and celebrations, it is used as a natural colorant [13,14].

Herein, we wish to report an easy and efficient methodology for the one-pot synthesis of hydroxyl naphthalene-1,4-dione derivatives **4a-t** from 2-hydroxynaphthalene-1,4-dione **1**, aromatic aldehydes **2** and heterocyclic or carbocyclic amines **3** in the presence of MCM-41 as an efficient heterogonous catalyst at room temperature in short reaction times, high yields and simple work-up procedure (Scheme 1).

Scheme 1.

2. Experimental

2.1. General

All chemicals were purchased from Merck or Aldrich and have been used as received, except for liquid aldehydes, which have been freshly distilled prior to use. MCM-41 was synthesized according to the literature [15]. Analytical thin layer chromatography (TLC) for monitoring reactions was performed using Merck 0.2 mm silica gel 60 F-254 Al-plates. Melting points were determined using an Electrothermal 9100 apparatus and uncorrected. FT-IR spectra were recorded as KBr pellets on a Shimadzu FT-IR- 8400S spectrometer. BET apparatus was a Micromeritics ASAP 2020, USA. ^{1}H NMR spectra were obtained using Bruker DRX-500 Avance spectrometer at 500.13 MHz. ^{13}C NMR spectra were obtained using Bruker DRX-400 Avance spectrometer at 100.63 MHz or Bruker DRX-500 Avance spectrometer at 125.76 MHz. Microanalysis of the products was carried out by a CHN analyzer (Perkine Elmer Series II, 2400).

2.2. General procedure for the preparation of MCM-41

To 42 mL deionized water in a 500 mL beaker, 2.7 g diethylamine was added at ambient temperature and stirred. Then, 1.47 g cetyltributylammonium bromide (CTAB) was gradually added to the above mixture until a clear solution was obtained. Tetraethyl orthosilicate (2.1 g) was added drop-wise to the solution and the pH was fixed at 8.5 by addition of 1 M HCl solution. After 2 h, the resulting solid product was filtered and washed several times with deionized water, and dried at 45 °C for 12 h. The obtained MCM-41 was calcined at 550 °C for 5 h to remove all the surfactant [7]. FT-IR spectra showed the characteristic peak of Si-O-Si at 1100 cm^{-1}, while the broad peak around 3413 cm^{-1} belongs to the terminal silanol groups of MCM-41. A sample of the prepared MCM-41 was investigated by SEM and BET tests. According to the SEM micrograph, the particle sizes were around 35 nm in diameter. The adsorption/desorption isotherms of the synthesized MCM-41 were recorded by BET apparatus and the BET surface area was measured as 1261 m^2g^{-1}, while BJH adsorption average pore width (4 V/A) was measured as 2.3 nm. These confirm the nanoporous structure of the synthesized MCM-41.

2.3. General procedure for the preparation of 2-hydroxyl naphthalene-1,4-diones **4**

A mixture of 2-hydroxynaphthalene-1,4-dione (1 mmol), amine (1 mmol), aldehyde (1 mmol), MCM-41 (5 mg) was stirred in EtOH (3 mL) at room temperature for appropriate time (as indicated in Table 4). After completion of the reaction, as indicated by TLC, the mixture was diluted with CH_2Cl_2 and the catalyst was separated by filtration. The solvent was evaporated under reduced pressure. The structures of all known products were determined on the basis of their analytical and/or spectral data comparing with the literature data. The spectral data of the new products are as following.

2.4. Characterization of the new compounds

Despite of heating the samples in $CDCl_3$ prior to ^{13}C NMR measurement, the low solubility of such compounds makes it difficult to receive a clean ^{13}C NMR spectrum (please see also section 2.2 in ref. 14). As a result, although the following data have been carefully taken from the spectra, wherever possible, they could be inaccurate.

2.4.1. 2-((2,4-Dichlorophenyl)(phenylamino)methyl)-3-hydroxynaphthalene-1,4-dione (**4d**)

Yellow powder (yield 90%); mp 147 °C. IR (KBr) (ν_{max}/cm^{-1}): 3338 (br, OH and NH), 3095 (Ar), 1676 (C=O). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.13 (1H, s, CH), 6.50-6.53 (3H, m, H-Ar), 6.91-6.97 (2H, m, H-Ar), 6.97-6.99 (1H, dd, J = 10.0, 2.1 Hz, H-Ar), 7.12-7.14 (1H, m, H-Ar), 7.45-7.54 (3H, m, H-Ar), 7.83-7.84 (2H, m, H-Ar). Anal. Calcd. for $C_{23}H_{15}Cl_2NO_3$: C, 65.11; H, 3.56; N, 3.30%. Found: C, 65.19; H, 3.53; N, 3.11%.

2.4.2. 2-((4-Chlorophenyl)(p-tolylamino)methyl)-3-hydroxynaphthalene-1,4-dione (**4o**)

Orange powder (yield 90%); mp 147 °C. IR (KBr) (ν_{max}/cm^{-1}): 3369 (br, OH and NH), 3084 (Ar), 2920 (CH_3), 1670 (C=O). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.04 (3H, s, CH_3), 5.97 (1H, s, CH), 6.53 (2H, d, J = 8.1 Hz, H-Ar), 6.80 (2H, d, J = 8.0 Hz, H-Ar), 7.09 (2H, d, J = 8.2

Hz, H-Ar), 7.32 (2H, d, *J* = 8.2 Hz, H-Ar), 7.48-7.70 (2H, m, H-Ar), 7.87 (2H, d, *J* = 7.5 Hz, H-Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.0, 54.4, 116.0 (2C), 120.9, 126.8 (2C), 127.1 (2C), 127.6, 129.5 (2C), 129.8 (2C), 130.4 (2C), 130.5, 132.8, 133.6, 134.3, 137.3, 143.8, 181.4, 184.2. Anal. Calcd. for $C_{24}H_{18}ClNO_3$: C, 71.38; H, 4.49; N, 3.47%. Found: C, 71.31; H, 4.43; N, 3.53%.

2.4.3. 2-((Benzylamino)(2,4-dichlorophenyl)methyl)-3-hydroxynaphthalene-1,4-dione (**4t**)

Orange powder (yield 90%); mp 158 °C. IR (KBr) (ν_{max}/cm^{-1}): 3440 (br, OH and NH), 3064 (Ar), 1674 (CO), 1591 (CO). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.86 (1H, d, *J* = 7.7 Hz, CH_2), 4.11 (1H, d, *J* = 7.7 Hz, CH_2), 5.96 (1H, s, CH), 6.96-6.99 (1H, dd, *J* = 10.0, 2.1 Hz, H-Ar), 7.18-7.22 (4H, m, H-Ar), 7.25-7.28 (2H, m, H-Ar), 7.40-7.44 (1H, m, H-Ar), 7.49-7.52 (2H, m, H-Ar), 7.85-7.87 (2H, m, H-Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 50.8, 56.2, 125.6, 126.0, 126.2, 127.1, 127.8, 128.0, 128.9, 129.0 (2C), 129.3, 129.7 (2C), 131.3, 131.3, 131.8, 133.0, 133.6, 134.3, 135.1, 135.6, 181.9, 184.4. Anal. Calcd. for $C_{24}H_{17}Cl_2NO_3$: C, 65.77; H, 3.91; N, 3.20%. Found: C, 65.73; H, 3.91; N, 3.23%.

3. Results and discussion

To optimize the reaction conditions, the reaction of 2-hydroxy-1,4-naphthoquinone **1**, benzaldehyde and aniline as model reactants (1.0 mmol each) was studied at room temperature (Table 1). Different solvents and catalysts were screened in the model reaction. After screening a number of catalysts such as $InCl_3$, $ZnCl_2$, *p*-TSA, MCM-41, and MCM-41-SO_3H, it has been found that mesoporous catalysts MCM-41 and MCM-41-SO_3H promote the reaction in very good yields, while other catalysts formed the product in lower yields. MCM-41 has been used for further investigations, due to its more mildness and easier preparation method in comparison to MCM-41-SO_3H.

Table 1.

In order to examine the rule of different solvents on the yield of hydroxyl naphthalene-1,4-dione derivatives, we investigated the model reaction in various solvents such as CH_3CN, acetone, H_2O and EtOH (96%) and also under solvent-free condition at room temperature. It was found that the best results were obtained in EtOH in the presence of MCM-41 (Table 2).

Table 2.

In order to optimize the amount of the catalyst loading, the model reaction was also studied in the presence of less amounts of MCM-41 at room temperature (Table 3). The best results were obtained when 5 mg of the catalyst was used. It is notable that by using excess amounts of the catalyst, the yield of the desired product was decreased.

Table 3.

After developing the optimized reaction conditions, a variety of aromatic aldehydes and amines were employed under similar circumstances to evaluate the substrate scope of this methodology. The results are summarized in Table 4. The aromatic aldehydes carrying both electron-withdrawing and electron-releasing substituents were converted to their corresponding 2-hydroxyl naphthalene-1,4-diones derivatives in high yields.

In addition, due to various biological properties of polyfunctionalized heterocyclic compounds, a few 2-hydroxy-1,4-naphtoqionin derivatives were also synthesized by starting from heterocyclic amines such as 2-aminopyridine, 2-aminobenzimidazole and benzyl amine in high yields under the same reaction conditions (Table 4, entries 16-20).

Table 4.

The reusability of the catalyst was also investigated in the model reaction. After each run, the filtered catalyst was washed several times with acetone and ethanol, and dried in an oven at 80°C for 5 h [15] and re-used in consecutive runs. The results of catalyst recyclability have been summarized in Fig. 2. As it is shown, after 4 consecutive runs the catalyst remained still intact.

Fig. 2.

4. Conclusions

In summary, we have developed a simple, efficient and green methodology for the synthesis of hydroxyl naphthalene-1,4-dione derivatives under heterogeneous catalysis conditions. The simple experimental procedure at room temperature, short reaction times, high yields, simple work-up, easy recovery and reusability of the catalyst and environmentally acceptable solvent are the advantages of the present method.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at www.elsevier.com/locate/dyepig.

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Captions

Fig. 1. Examples of naphthoquinone pigments.

Scheme 1. Synthesis of hydroxyl naphthalene-1,4-dione derivatives **4a-t**.

Table 1. Screening of different catalysts in the model reaction.

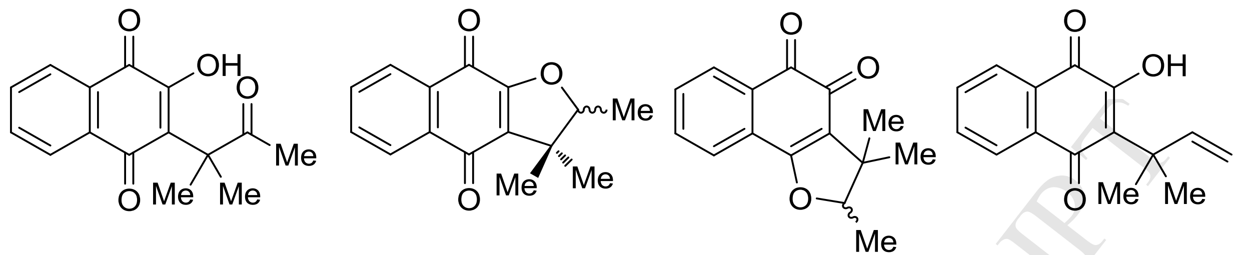
Table 2. Screening of the different solvents in the model reaction.

Table 3. Optimization of the amount of the catalyst loading in the model reaction.

Table 4. Synthesis of 2-hydroxy(aryl(arylamino)methyl)naphthalene-1,4-diones **4a-t.**

Fig. 2. Reusability study of the catalyst in the model reaction.

Fig. 1.



streptocarpone α-dunnione dunnione dunniol

Scheme 1.

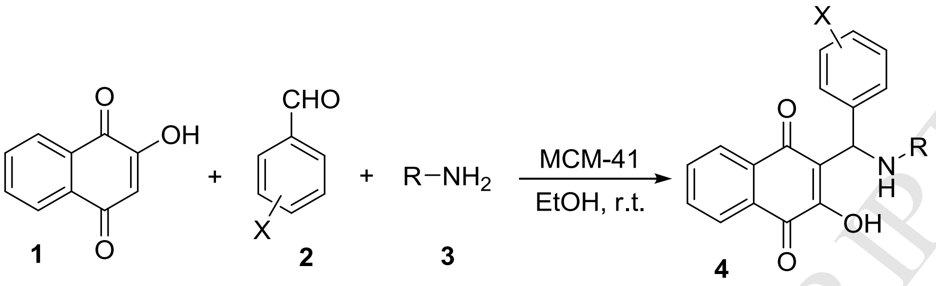
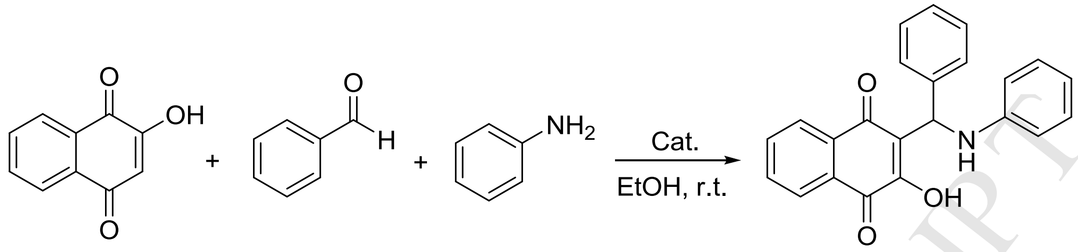


Table 1.



Entry	Catalyst	Catalyst loading (mg)	Time (h)	Yield[a] (%)
1	$InCl_3$	30	6	20
2	$ZnCl_2$	30	6	40
3	*p*-TSA	30	6	30
4	MCM-41	30	3	90
5	MCM-41-SO_3H	30	3	90

[a] Isolated yield.

Table 2.

Entry	Solvent	Time	Yield[a] (%)
1	CH_3CN	10 h	32
2	CH_3COCH_3	12 h	27
3	H_2O	8 h	70
4	EtOH (96%)	80 min	90
5	-	48 h	Trace

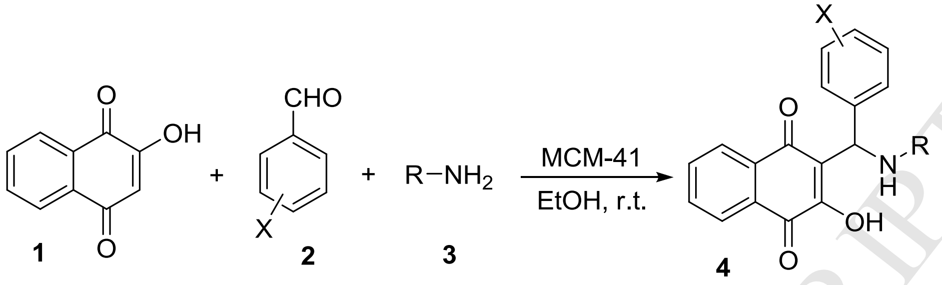
[a] Isolated yield.

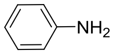
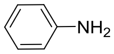
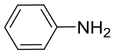
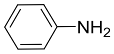
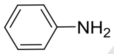
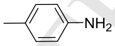
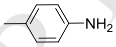
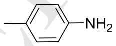
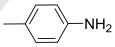
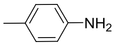
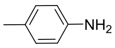
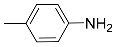
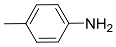
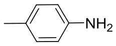
Table 3.

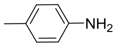
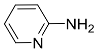
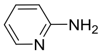
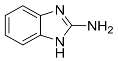
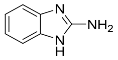
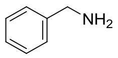
Entry	Catalyst loading (mg)	Time (min)	Yield[a] (%)
1	5	80	95
2	10	100	88
3	20	80	90
4	30	180	90

[a] Isolated yield.

Table 4.

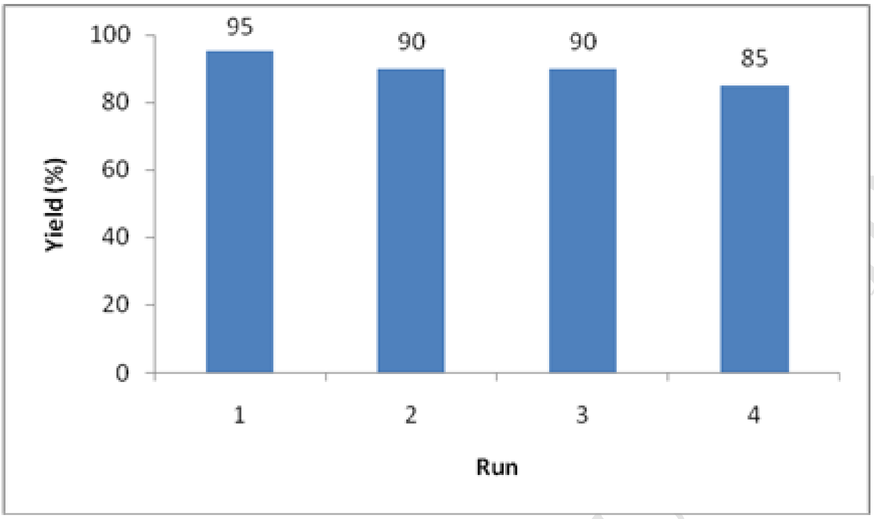


Entry	Product	X	Amine	Time (min)	Yield[a] (%)	Mp (°C)	
						Obsd.	Lit.
1	**4a**	H		80	95	148	143-145 [14]
2	**4b**	4-Me		150	95	145	145-148 [14]
3	**4c**	4-NO_2		25	95	145	145-148 [14]
4	**4d**	2,4-*di*-Cl		180	90	147	-
5	**4e**	4-OH		120	90	175	185-190 [14]
6	**4f**	H		120	90	146	147-150 [14]
7	**4g**	4-OMe		175	90	145	144-147 [14]
8	**4h**	4-Me		125	95	146	146-149 [14]
9	**4i**	4-OH		180	95	150	149-152 [14]
10	**4j**	4-NO_2		60	95	150	141-144 [14]
11	**4k**	4-Br		210	95	154	147-150 [14]
12	**4l**	2,4-*di*-Cl		185	90	148	144-147 [14]
13	**4m**	2-Cl		70	90	144	149-152 [14]
14	**4n**	3-NO_2		70	95	148	144-147 [14]

15	**4o**	4-Cl		95	90	147	-
16	**4p**	H		60	90	145	145-148 [14]
17	**4q**	4-NO_2		20	95	150	148-151 [14]
18	**4r**	H		125	90	150	155-151 [14]
19	**4s**	4-NO_2		70	99	154	150-153 [14]
20	**4t**	2,4-*di*-Cl		60	90	158	-

[a] Isolated yield.

Fig. 2.



Highlights

- A green procedure was developed for the one-pot synthesis of naphthalene-1,4-diones.
- The multicomponent reaction gave good to excellent yields from simple precursors.
- The protocol includes important aspects like easy workup procedure and high atom economy.
- An efficient and reusable nanocatalyst was introduced.

Supplementary data

Synthesis of 2-hydroxy-1,4-naphthoquinone derivatives via a three-component reaction catalyzed by nanoporous MCM-41

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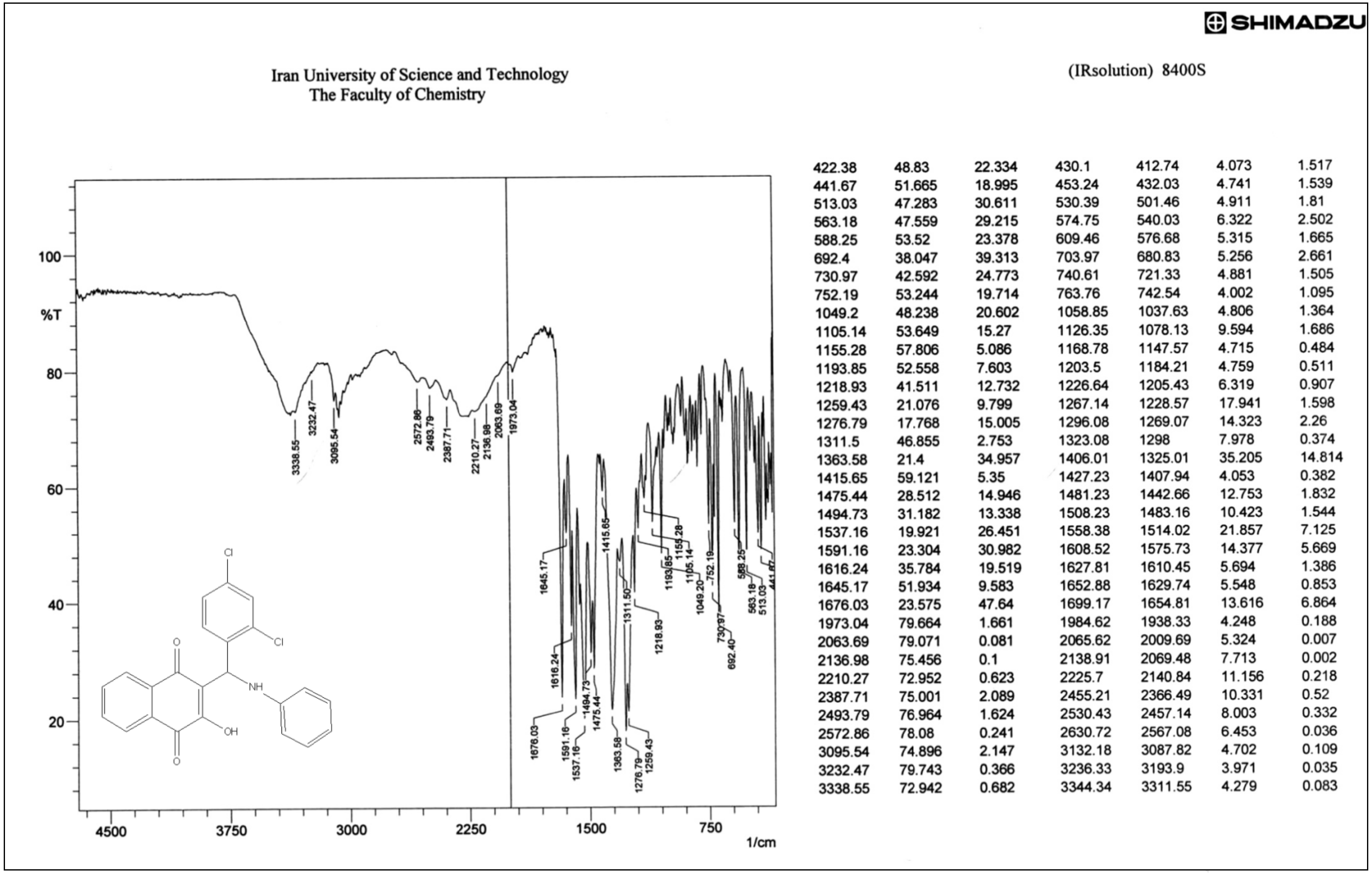
[2] Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran.

E-mail: naimi@iust.ac.ir ; Fax: +98-21-77491204

Supplementary data

Characterization of the new compounds (**4d, 4o** and **4t**)

FT-IR spectrum of **4d**



SHIMADZU

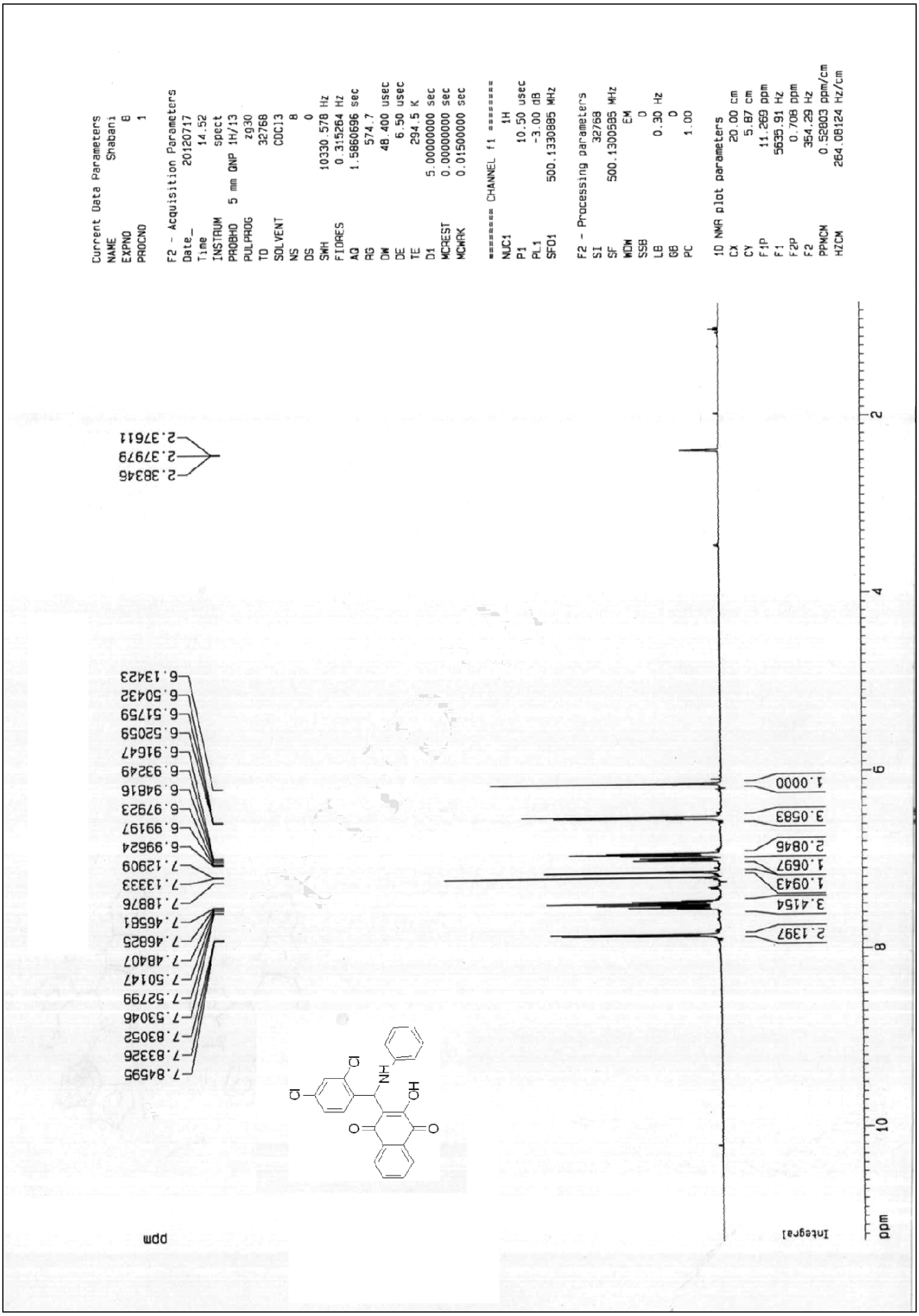
Iran University of Science and Technology
The Faculty of Chemistry

(IRsolution) 8400S

422.38	48.83	22.334	430.1	412.74	4.073	1.517
441.67	51.665	18.995	453.24	432.03	4.741	1.539
513.03	47.283	30.611	530.39	501.46	4.911	1.81
563.18	47.559	29.215	574.75	540.03	6.322	2.502
588.25	53.52	23.378	609.46	576.68	5.315	1.665
692.4	38.047	39.313	703.97	680.83	5.256	2.661
730.97	42.592	24.773	740.61	721.33	4.881	1.505
752.19	53.244	19.714	763.76	742.54	4.002	1.095
1049.2	48.238	20.602	1058.85	1037.63	4.806	1.364
1105.14	53.649	15.27	1126.35	1078.13	9.594	1.686
1155.28	57.806	5.086	1168.78	1147.57	4.715	0.484
1193.85	52.558	7.603	1203.5	1184.21	4.759	0.511
1218.93	41.511	12.732	1226.64	1205.43	6.319	0.907
1259.43	21.076	9.799	1267.14	1228.57	17.941	1.598
1276.79	17.768	15.005	1296.08	1269.07	14.323	2.26
1311.5	46.855	2.753	1323.08	1298	7.978	0.374
1363.58	21.4	34.957	1406.01	1325.01	35.205	14.814
1415.65	59.121	5.35	1427.23	1407.94	4.053	0.382
1475.44	28.512	14.946	1481.23	1442.66	12.753	1.832
1494.73	31.182	13.338	1508.23	1483.16	10.423	1.544
1537.16	19.921	26.451	1558.38	1514.02	21.857	7.125
1591.16	23.304	30.982	1608.52	1575.73	14.377	5.669
1616.24	35.784	19.519	1627.81	1610.45	5.694	1.386
1645.17	51.934	9.583	1652.88	1629.74	5.548	0.853
1676.03	23.575	47.64	1699.17	1654.81	13.616	6.864
1973.04	79.664	1.661	1984.62	1938.33	4.248	0.188
2063.69	79.071	0.081	2065.62	2009.69	5.324	0.007
2136.98	75.456	0.1	2138.91	2069.48	7.713	0.002
2210.27	72.952	0.623	2225.7	2140.84	11.156	0.218
2387.71	75.001	2.089	2455.21	2366.49	10.331	0.52
2493.79	76.964	1.624	2530.43	2457.14	8.003	0.332
2572.86	78.08	0.241	2630.72	2567.08	6.453	0.036
3095.54	74.896	2.147	3132.18	3087.82	4.702	0.109
3232.47	79.743	0.366	3236.33	3193.9	3.971	0.035
3338.55	72.942	0.682	3344.34	3311.55	4.279	0.083

Supplementary data

^{1}H NMR spectrum of **4d**



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PROCNO              1

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SOLVENT         CDCl3
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FIDRES       0.315264 Hz
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RG              574.7
DW             48.400 usec
DE               6.50 usec
TE              294.5 K
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MCREST     0.00000000 sec
MCWRK      0.01500000 sec

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PL1             -3.00 dB
SFO1      500.1330885 MHz

F2 - Processing parameters
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SF        500.1300585 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
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PC               1.00

1D NMR plot parameters
CX              20.00 cm
CY               5.87 cm
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F1            5635.91 Hz
F2P             0.708 ppm
F2             354.29 Hz
PPMCM         0.52803 ppm/cm
HZCM        264.08124 Hz/cm
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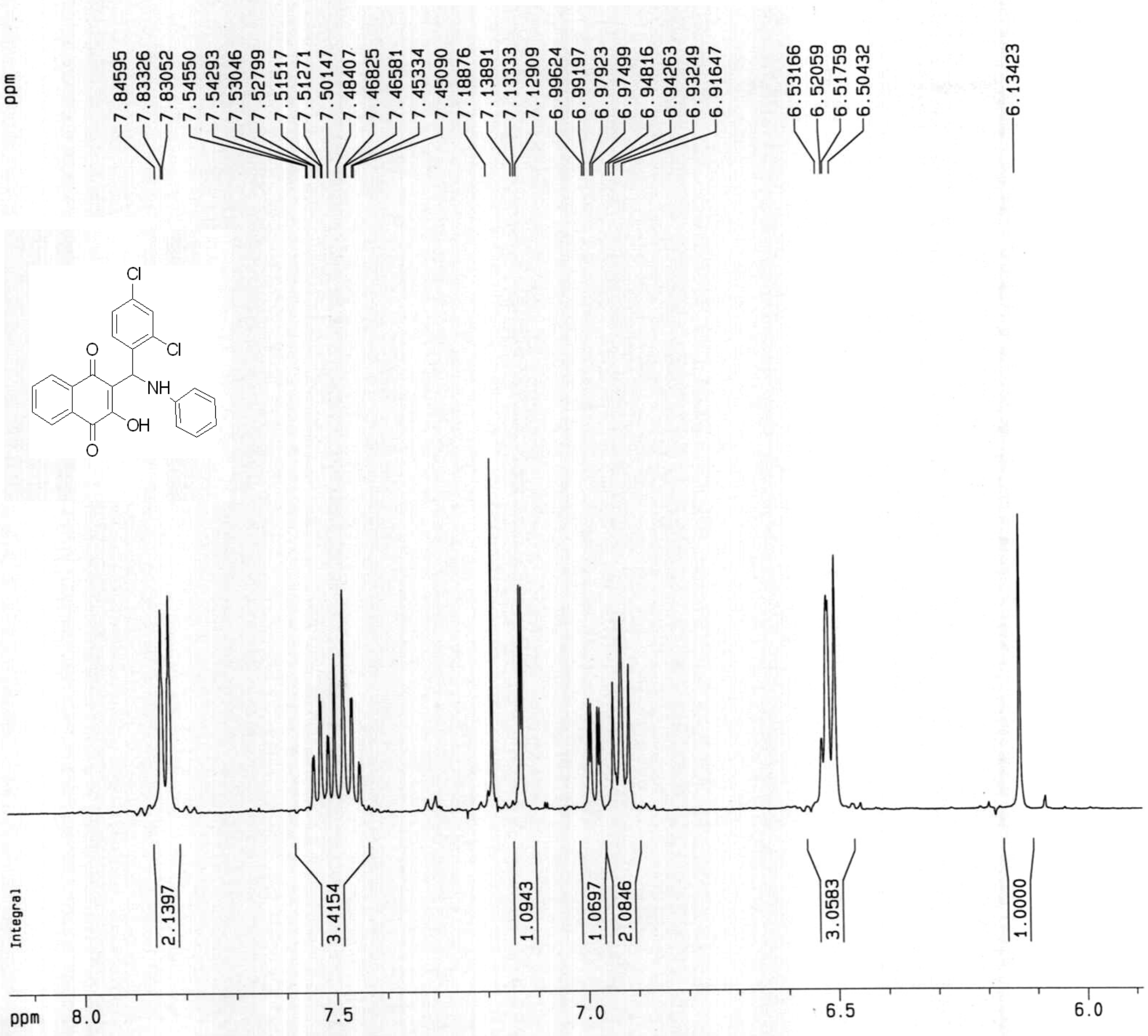
Supplementary data

Expanded ^{1}H NMR spectrum of **4d**



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Current Data Parameters
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EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
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NS                     8
DS                     0
SWH          10330.578 Hz
FIDRES        0.315264 Hz
AQ           1.5860696 sec
RG                 574.7
DW              48.400 usec
DE                6.50 usec
TE               294.5 K
D1          5.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
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PL1                -3.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
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SSB                    0
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GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  5.87 cm
F1P                8.151 ppm
F1               4076.52 Hz
F2P                5.888 ppm
F2               2944.69 Hz
PPMCM            0.11315 ppm/cm
HZCM            56.59164 Hz/cm
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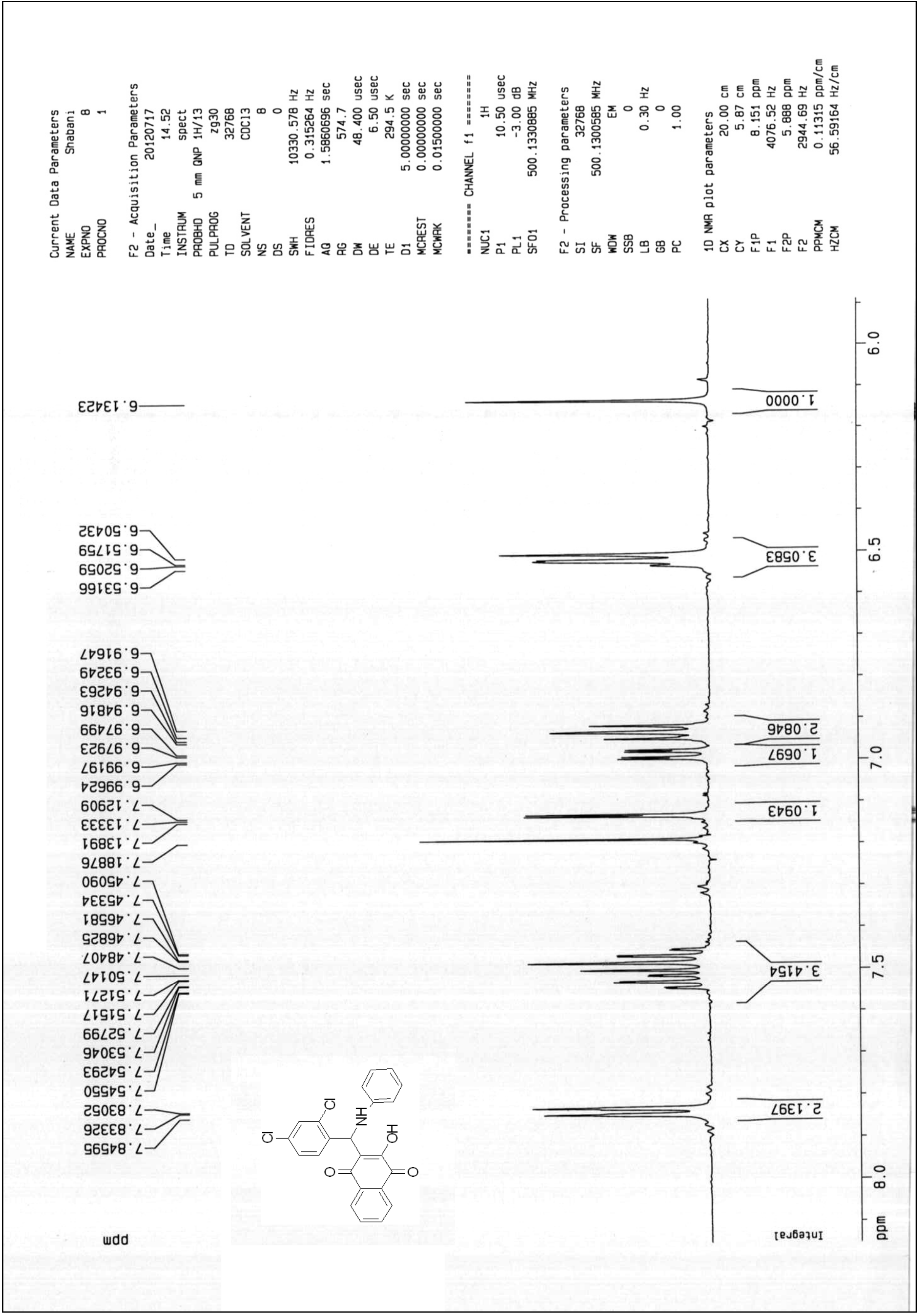
Supplementary data

Expanded ^{1}H NMR spectrum of **4d**



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Current Data Parameters
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EXPNO                 8
PROCNO                1

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PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
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FIDRES        0.315264 Hz
AQ           1.5860696 sec
RG                574.7
DW               48.400 usec
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TE                294.5 K
D1          5.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

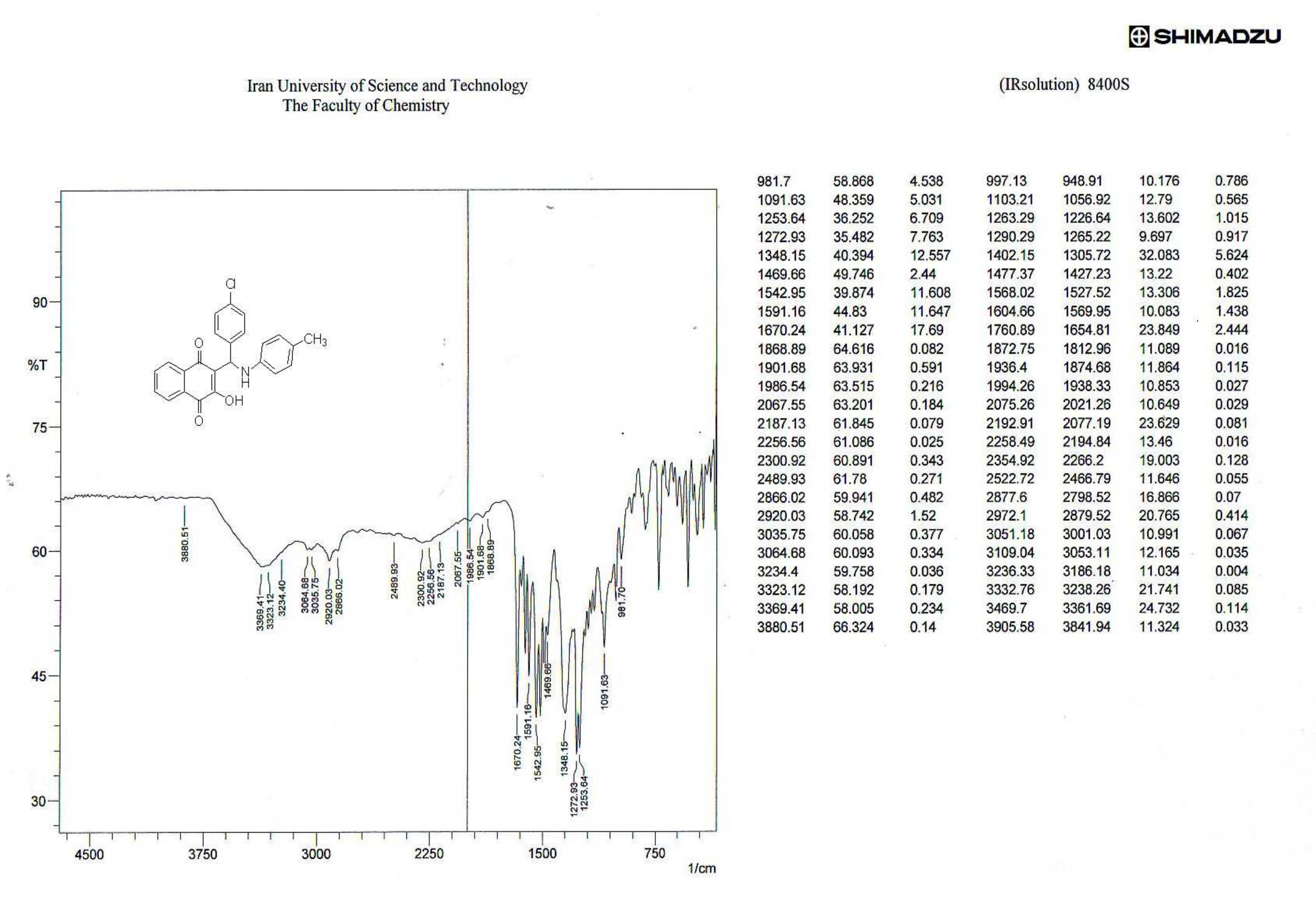
======== CHANNEL f1 ========
NUC1                 1H
P1                10.50 usec
PL1               -3.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300585 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                 5.87 cm
F1P               8.151 ppm
F1              4076.52 Hz
F2P               5.888 ppm
F2              2944.69 Hz
PPMCM           0.11315 ppm/cm
HZCM           56.59164 Hz/cm
```

Supplementary data

FT-IR spectrum of **4o**



981.7	58.868	4.538	997.13	948.91	10.176	0.786
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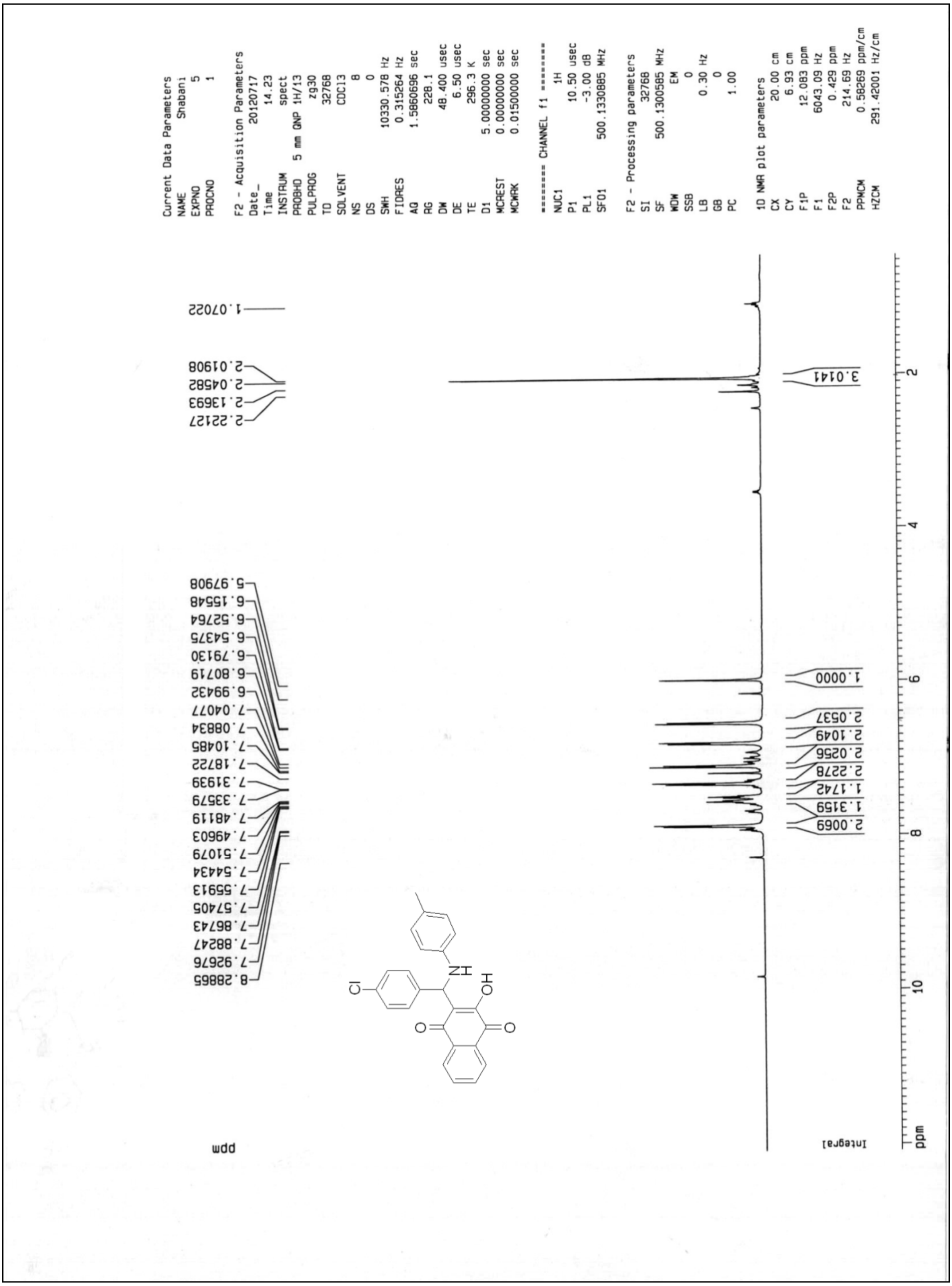
1253.64	36.252	6.709	1263.29	1226.64	13.602	1.015
1272.93	35.482	7.763	1290.29	1265.22	9.697	0.917
1348.15	40.394	12.557	1402.15	1305.72	32.083	5.624
1469.66	49.746	2.44	1477.37	1427.23	13.22	0.402
1542.95	39.874	11.608	1568.02	1527.52	13.306	1.825
1591.16	44.83	11.647	1604.66	1569.95	10.083	1.438
1670.24	41.127	17.69	1760.89	1654.81	23.849	2.444
1868.89	64.616	0.082	1872.75	1812.96	11.089	0.016
1901.68	63.931	0.591	1936.4	1874.68	11.864	0.115
1986.54	63.515	0.216	1994.26	1938.33	10.853	0.027
2067.55	63.201	0.184	2075.26	2021.26	10.649	0.029
2187.13	61.845	0.079	2192.91	2077.19	23.629	0.081
2256.56	61.086	0.025	2258.49	2194.84	13.46	0.016
2300.92	60.891	0.343	2354.92	2266.2	19.003	0.128
2489.93	61.78	0.271	2522.72	2466.79	11.646	0.055
2866.02	59.941	0.482	2877.6	2798.52	16.866	0.07
2920.03	58.742	1.52	2972.1	2879.52	20.765	0.414
3035.75	60.058	0.377	3051.18	3001.03	10.991	0.067
3064.68	60.093	0.334	3109.04	3053.11	12.165	0.035
3234.4	59.758	0.036	3236.33	3186.18	11.034	0.004
3323.12	58.192	0.179	3332.76	3238.26	21.741	0.085
3369.41	58.005	0.234	3469.7	3361.69	24.732	0.114
3880.51	66.324	0.14	3905.58	3841.94	11.324	0.033

Supplementary data

^{1}H NMR spectrum of **4o**



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TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH          10330.578 Hz
FIDRES        0.315264 Hz
AQ           1.5860696 sec
RG                228.1
DW               48.400 usec
DE                 6.50 usec
TE                296.3 K
D1          5.00000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                10.50 usec
PL1               -3.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300585 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                 6.93 cm
F1P              12.083 ppm
F1              6043.09 Hz
F2P               0.429 ppm
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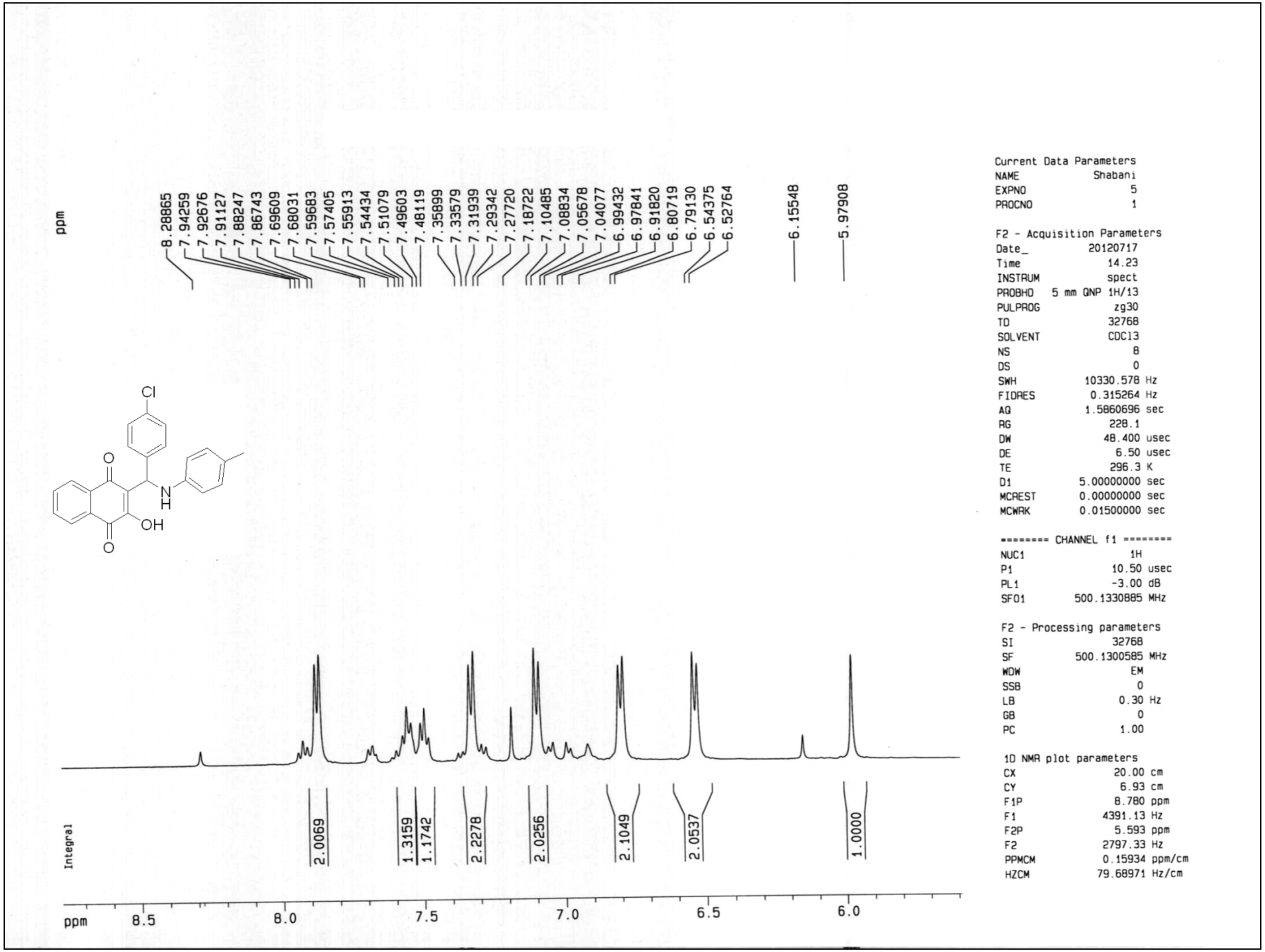
Supplementary data

Expanded ^{1}H NMR spectrum of **4o**



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Current Data Parameters
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EXPNO                  5
PROCNO                 1

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PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10330.578 Hz
FIDRES         0.315264 Hz
AQ            1.5860696 sec
RG                 228.1
DW               48.400 usec
DE                 6.50 usec
TE                296.3 K
D1           5.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.50 usec
PL1                -3.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300585 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  6.93 cm
F1P                8.780 ppm
F1               4391.13 Hz
F2P                5.593 ppm
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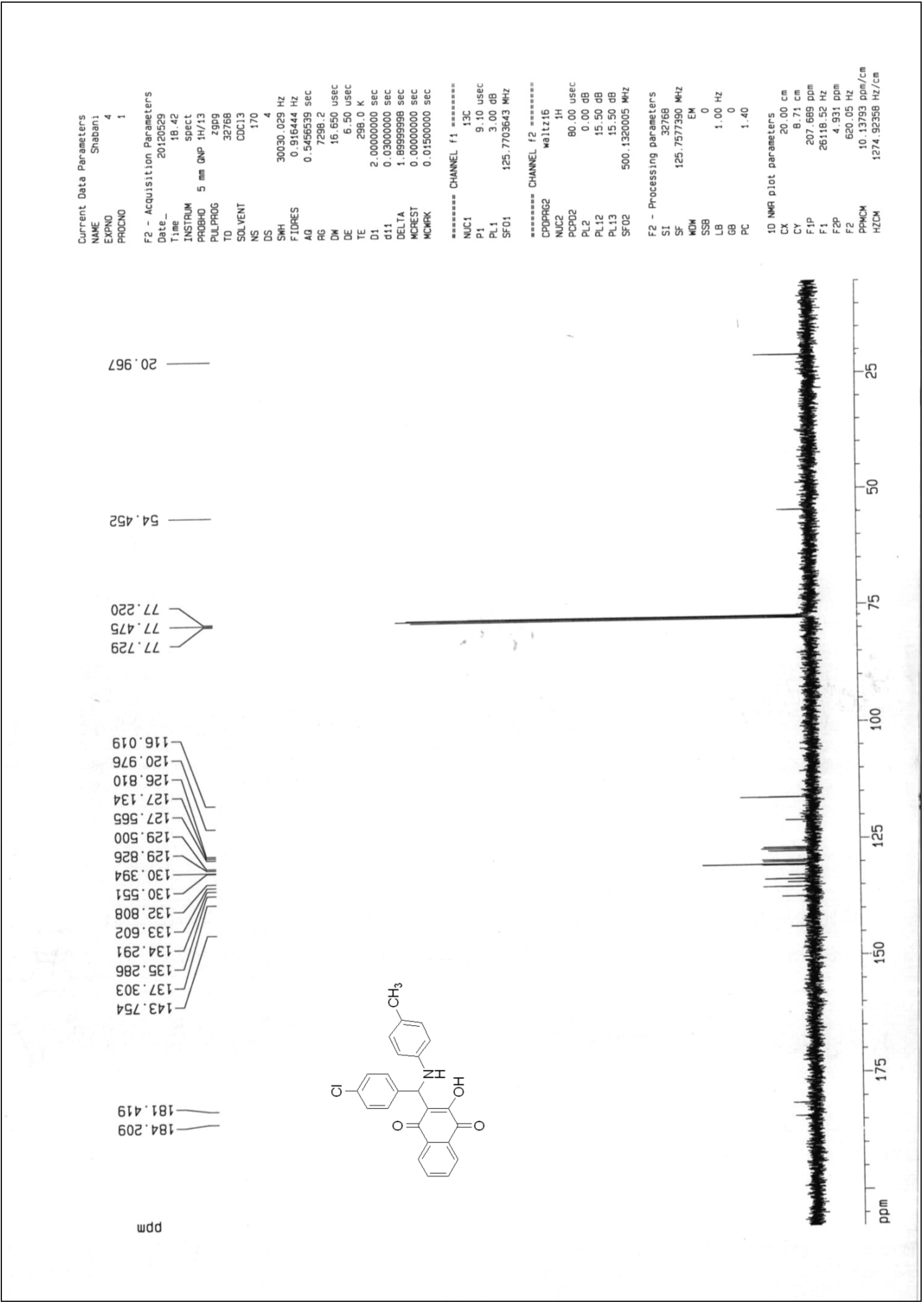
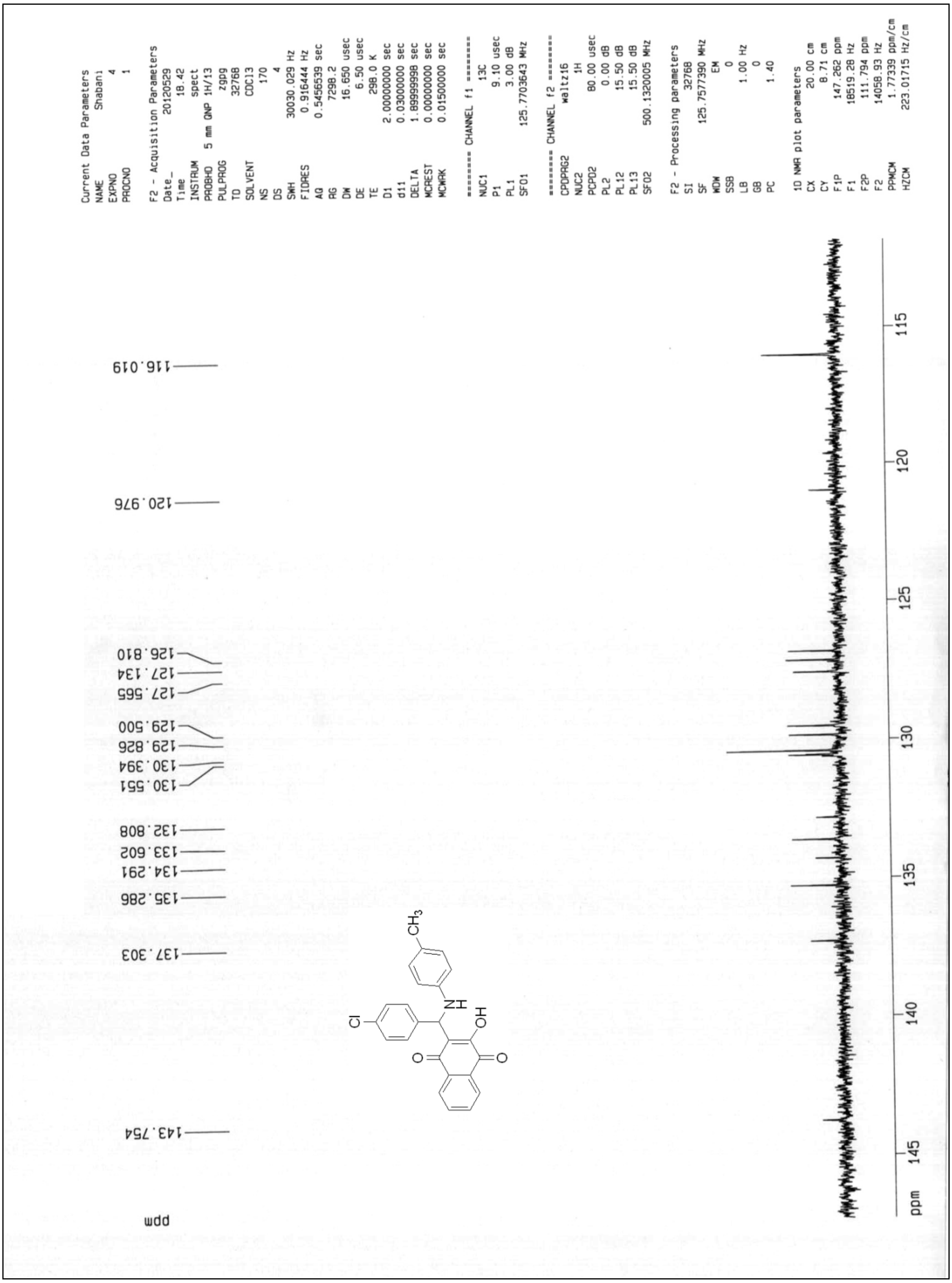
Supplementary data

^{13}C NMR spectrum of **4o**



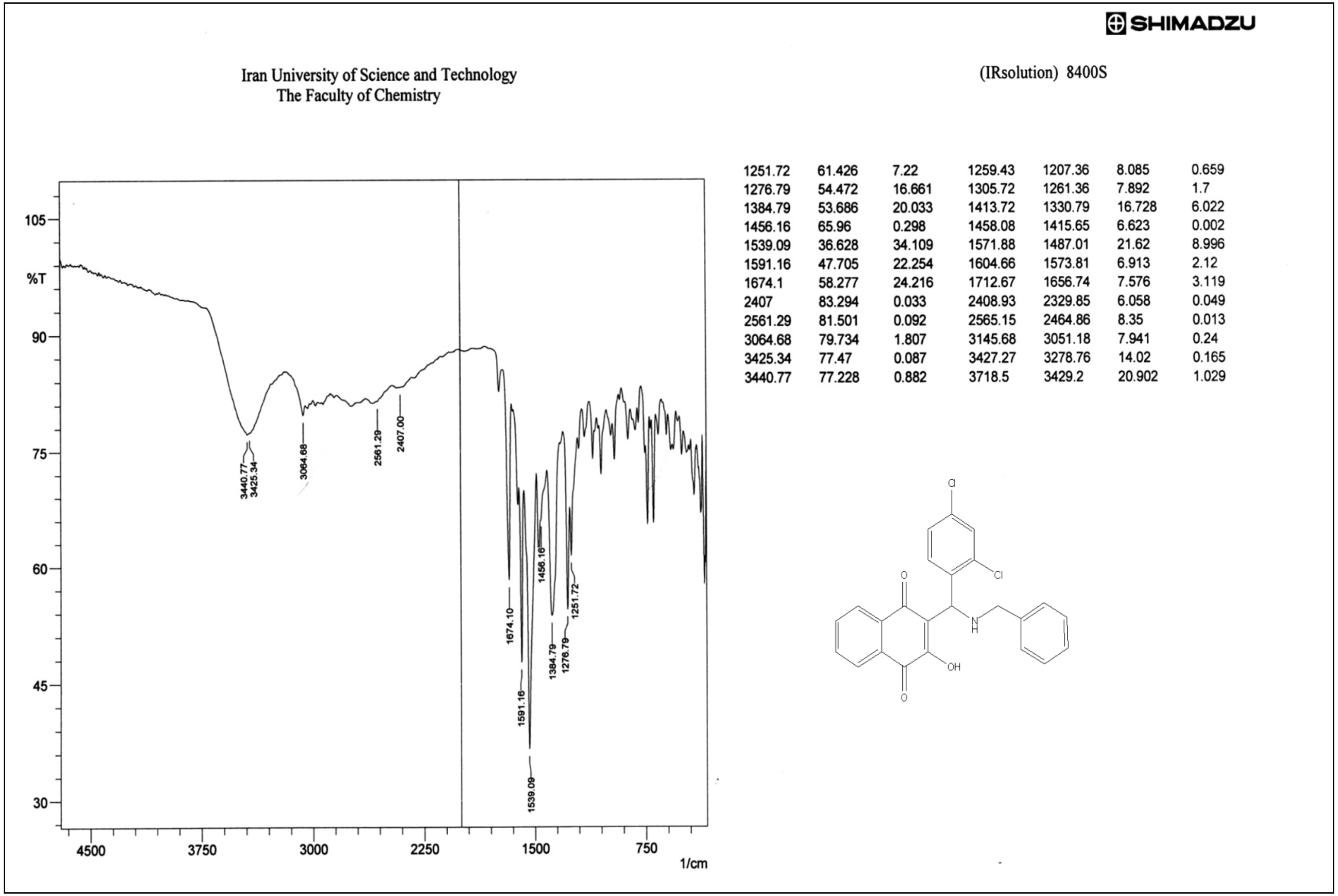
Supplementary data

Expanded ^{13}C NMR spectrum of **4o**



Supplementary data

FT-IR spectrum of **4t**



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The Faculty of Chemistry

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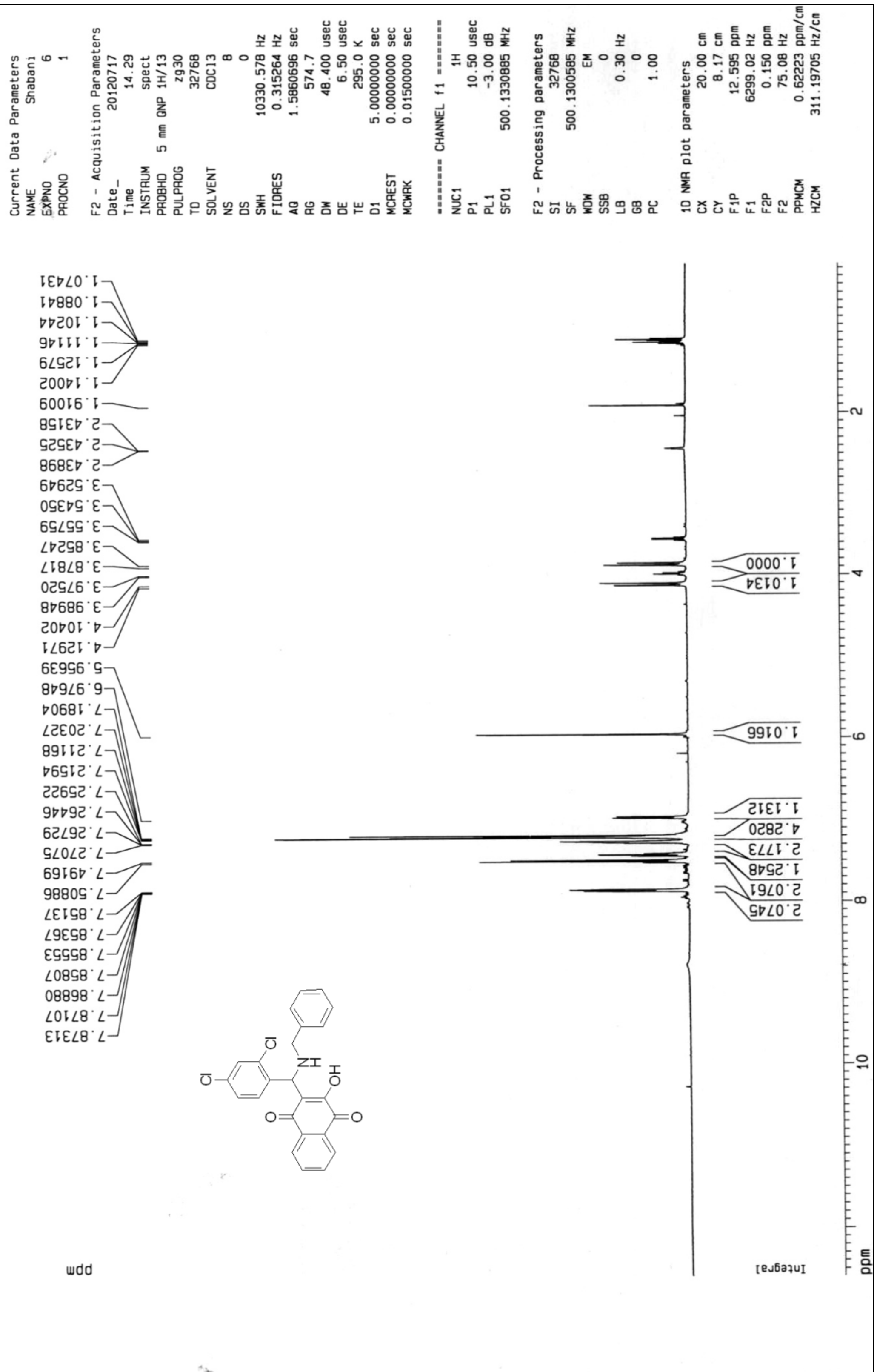
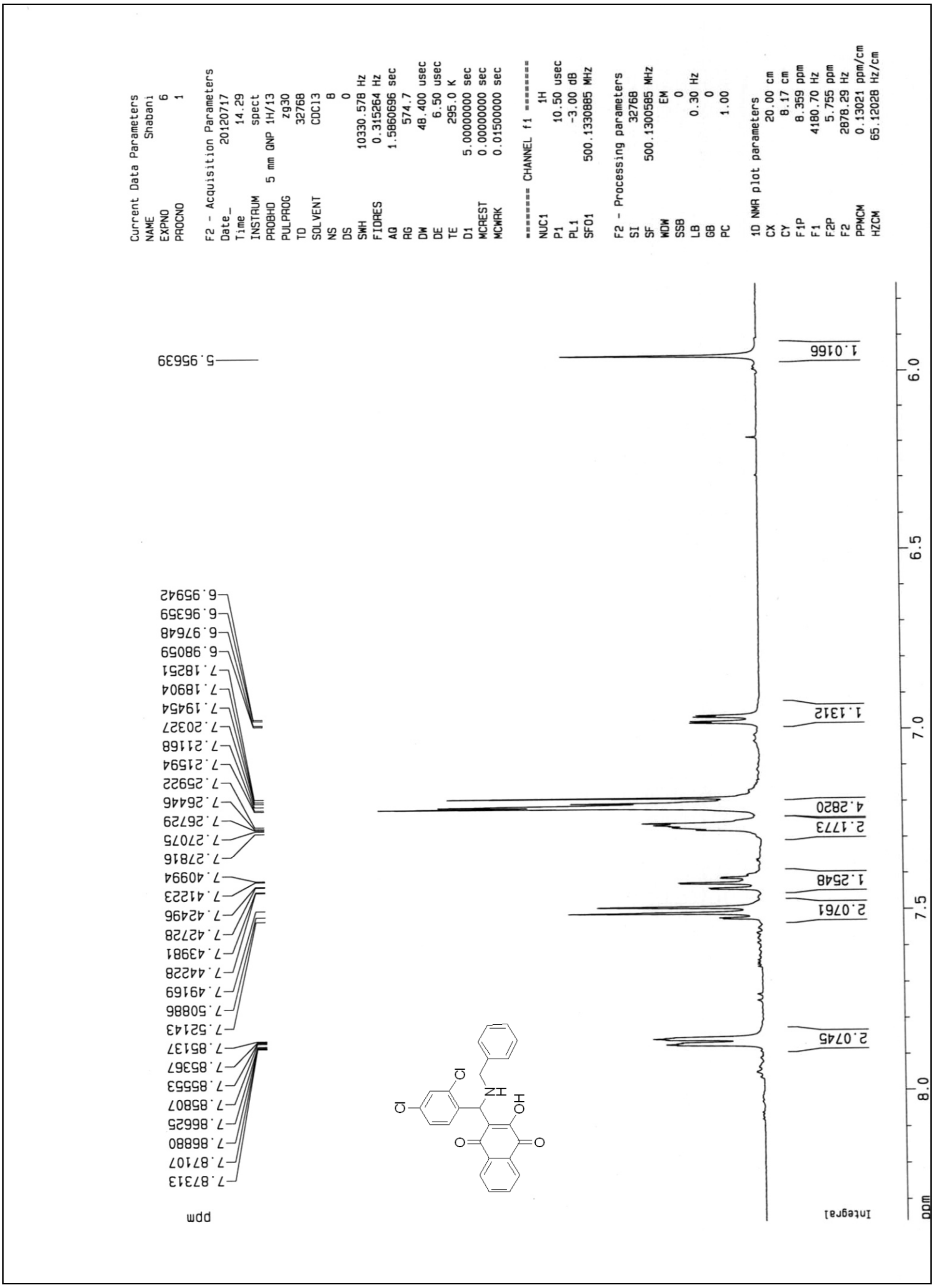
1251.72	61.426	7.22	1259.43	1207.36	8.085	0.659
1276.79	54.472	16.661	1305.72	1261.36	7.892	1.7
1384.79	53.686	20.033	1413.72	1330.79	16.728	6.022
1456.16	65.96	0.298	1458.08	1415.65	6.623	0.002
1539.09	36.628	34.109	1571.88	1487.01	21.62	8.996
1591.16	47.705	22.254	1604.66	1573.81	6.913	2.12
1674.1	58.277	24.216	1712.67	1656.74	7.576	3.119
2407	83.294	0.033	2408.93	2329.85	6.058	0.049
2561.29	81.501	0.092	2565.15	2464.86	8.35	0.013
3064.68	79.734	1.807	3145.68	3051.18	7.941	0.24
3425.34	77.47	0.087	3427.27	3278.76	14.02	0.165
3440.77	77.228	0.882	3718.5	3429.2	20.902	1.029

^{1}H NMR spectrum of **4t**



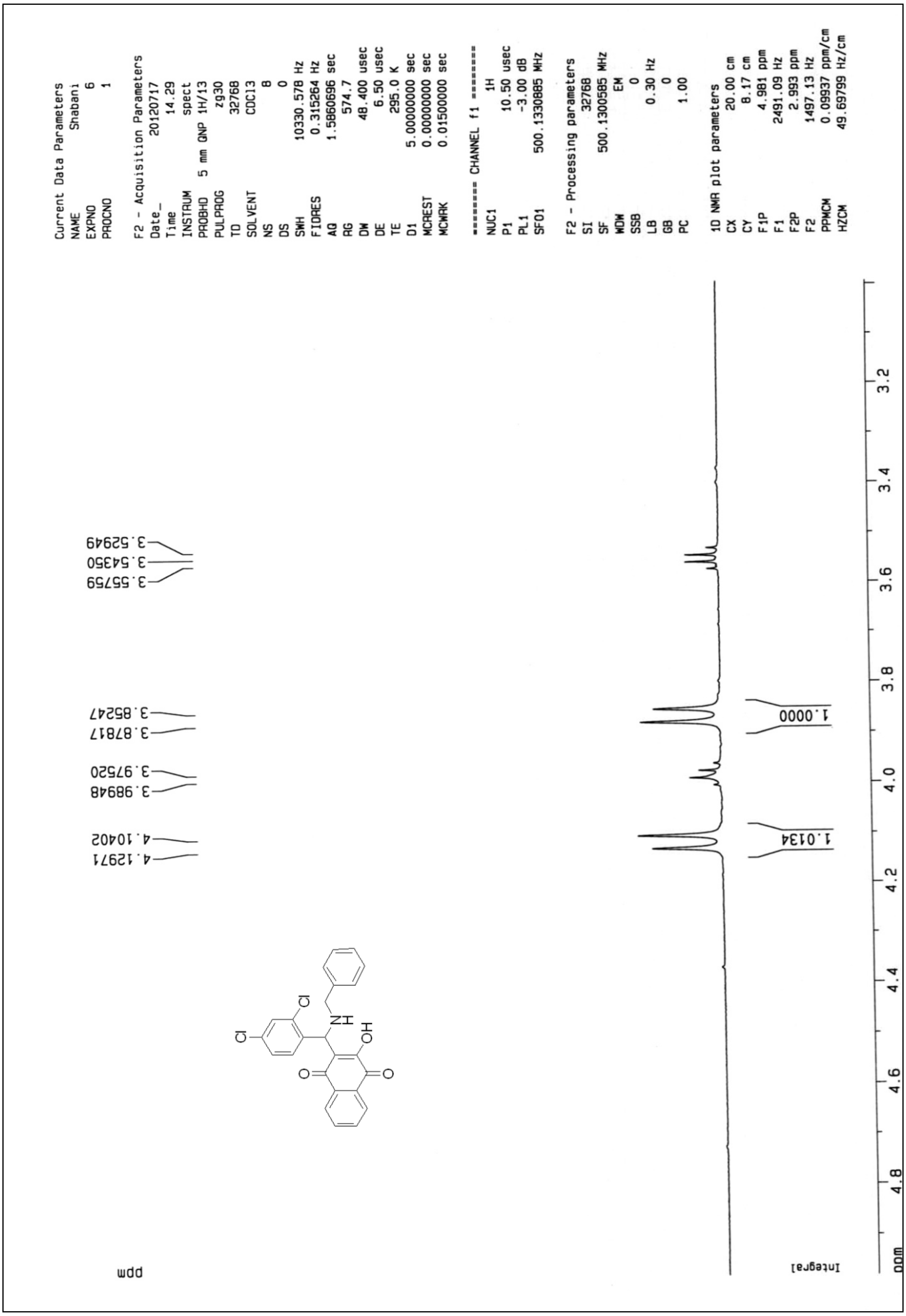
Supplementary data

Expanded ^{1}H NMR spectrum of **4t**



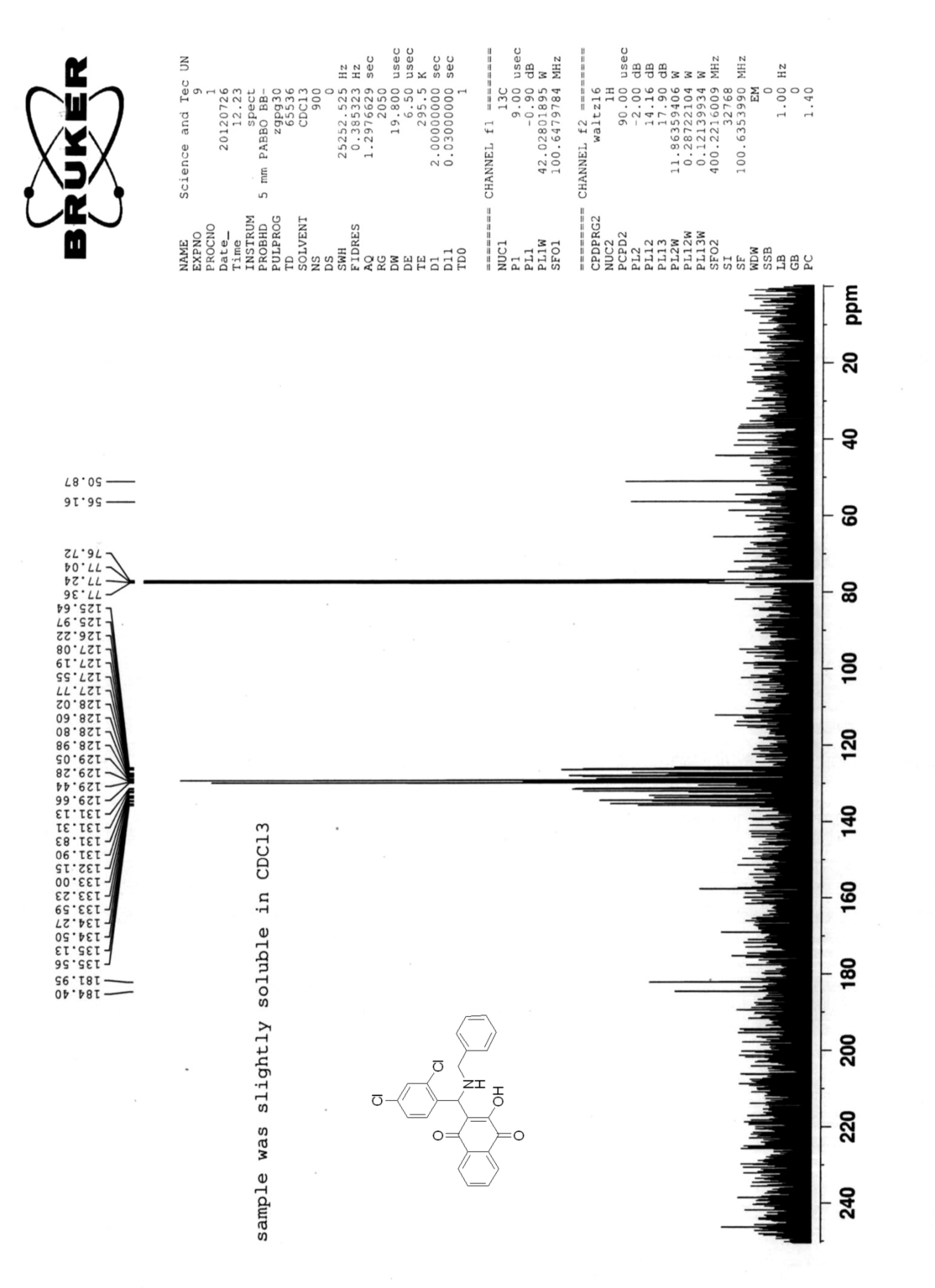
Supplementary data

Expanded ^{1}H NMR spectrum of **4t**



Supplementary data

^{13}C NMR spectrum of **4t**



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FIDRES          0.385323 Hz
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RG                     2050
DW               19.800 usec
DE                 6.50 usec
TE                 295.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                       1

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NUC1                    13C
P1                 9.00 usec
PL1                -0.90 dB
PL1W        42.02801895 W
SFO1        100.6479784 MHz

======== CHANNEL f2 ========
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NUC2                     1H
PCPD2             90.00 usec
PL2                -2.00 dB
PL12               14.16 dB
PL13               17.90 dB
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PL12W        0.28722104 W
PL13W        0.12139934 W
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SSB                       0
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GB                        0
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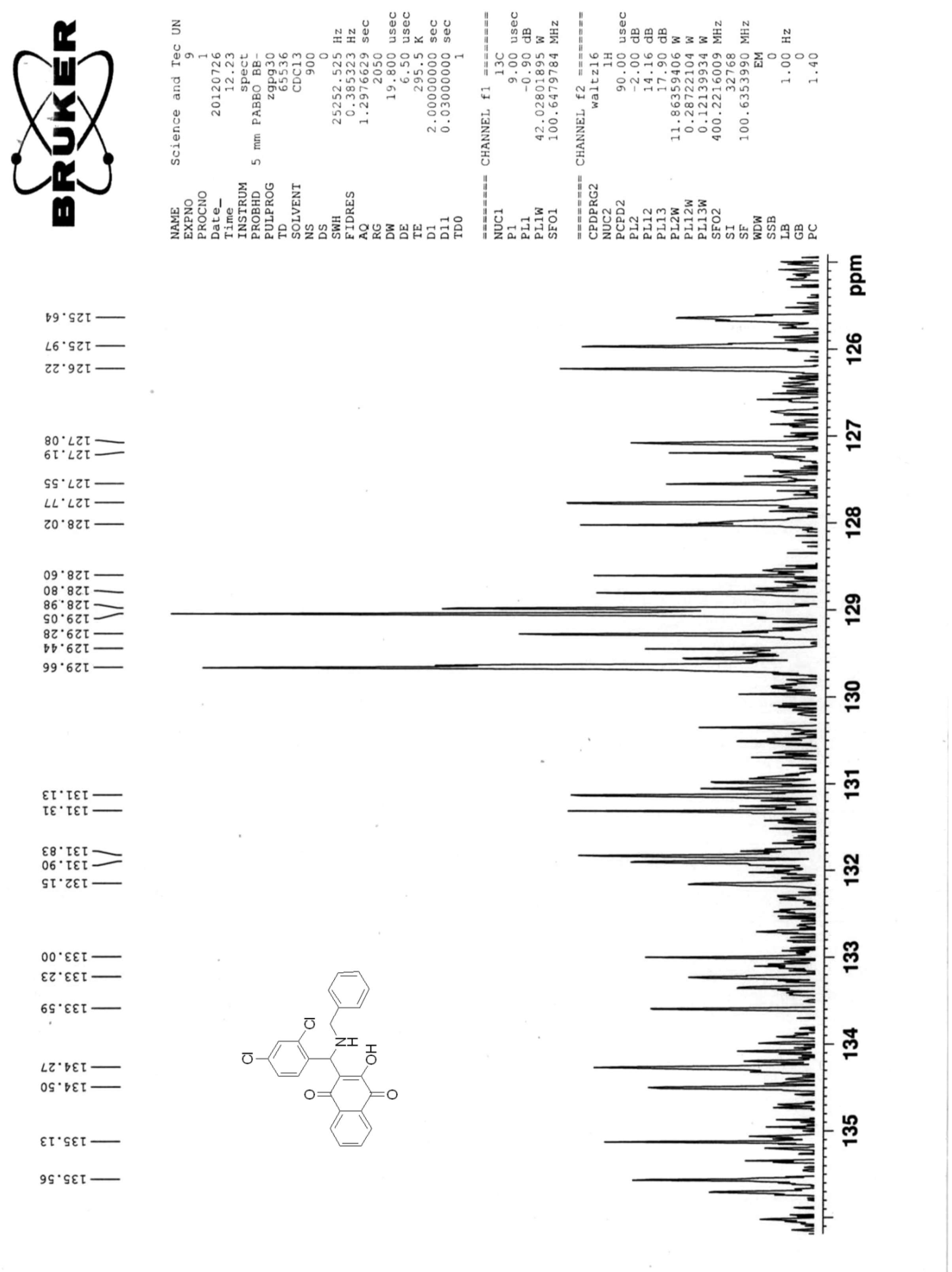
Supplementary data

Expanded ^{13}C NMR spectrum of **4t**



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PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        900
DS                          0
SWH                 25252.525 Hz
FIDRES               0.385323 Hz
AQ                  1.2976629 sec
RG                       2050
DW                     19.800 usec
DE                       6.50 usec
TE                      295.5 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
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PL1                     -0.90 dB
PL1W              42.02801895 W
SFO1              100.6479784 MHz

======== CHANNEL f2 ========
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PL2                     -2.00 dB
PL12                    14.16 dB
PL13                    17.90 dB
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PL12W              0.28722104 W
PL13W              0.12139934 W
SFO2              400.2216009 MHz
SI                      32768
SF                100.6353990 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
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