SUPPORTING INFORMATION

Hyperaromatic Stabilization of Arenium ions: A remarkable *cis*-stereo-selectivity of nucleophilic trapping by water of β-hydroxyarenium ions.

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Table S1 First order rate constants for the dehydration of *trans*-benzene-1,2-dihydrodiol in aqueous perchloric acid at 25° C.

$[HClO_4]$ (M)	0.47	0.94	1.88	2.82	3.76	4.70	5.17
$10^3 k_{obs}$ (s^{-1})	0.142	0.454	1.96	5.65	21.0	86.0	145.0

Table S2 First order rate constants for the dehydration of *cis*- and *trans*-phenanthrene-9,10dihydrodiols in aqueous perchloric acid at 25° C.

$[HClO_4]$ (M)	$10^4 k_{obs}$ (s^{-1}) *cis*	$[HClO_4]$ (M)	$10^4 k_{obs}$ (s^{-1})*trans*
2.0	0.43	4.00	0.070
3.0	1.89	5.00	0.51
4.00	5.04	6.00	2.07
5.00	44.4	7.00	14.2
6.00	230.0	8.00	129.0

Table S3 First order rate constants for the dehydration of *cis*- and *trans*-1,2-naphthalene dihydrodipols in aqueous perchloric acid at 25° C.

$[HClO_4]$ (M)	$10^3 k_{obs}$ (s^{-1}) *cis*	$[HClO_4]$ (M)	$10^4 k_{obs}$ (s^{-1})*trans*
0.152	0.275	1.41	0.012
0.227	0.457	2.35	0.510
0.378	0.854	2.82	0.712
0.471	1.12	3.29	1.70
0.571	1.49	3.77	0.93
0.759	2.30	4.23	6.10
0.933	3.35	4.71	12.1
		5.17	26.0
		5.60	57.7
		5.65	53.0
		6.12	120.0
		6.59	289.0
		7.53	1120.0

Table S4 First order rate constants for the dehydration of *cis*- and *trans*-1,2-dimethoxydihydro naphthalenes in aqueous perchloric acid at 25° C.

$[HClO_4]$ (M)	$10^4 k_{obs}$ (s^{-1}) *cis*	$[HClO_4]$ (M)	$10^4 k_{obs}$ (s^{-1})*trans*
0.18	0.38	2.82	0.491
0.37	1.08	3.76	4.03
0.56	1.85	4.70	17.1
0.75	3.13	5.17	38.9
0.95	4.58	5.76	275.0

Table S5 First order rate constants for the dehydration of *cis*- and *trans*- acenaphthylene dihydrodiols in aqueous perchloric acid at 25° C.

$[HClO_4]$ (M)	$10^5 k_{obs}$ (s^{-1}) *cis*	$10^5 k_{obs}$ (s^{-1})*trans*
5.0	0.45	0.27
6.0	2.75	2.11
7.0	23.50	20.60

Table S6 Ratios of *cis* to *trans* dihydrodiols formed in the solvolysis of acenaphthylene *cis*-6,7-chlorohydrin in the presence of sodium azide at 25° C.[a]

$[NaN_3]$ (M)	% *cis* Dihydrodiol[b]	% *trans* dihydrodiol[b]	[*cis*-dihydrodiol] / [*trans*-dihydrodiol]
0[c]	70.3	29.7	2.36
0.03	59.5	26.4	2.26
0.05	51.6	22.9	2.25
0.10	29.6	12.9	2.29
0.20	24.1	10.0	2.41
0.30	15.0	6.4	2.36
0.40	12.0	5.2	2.34
0.50	10.8	4.6	2.33

[a]Measurements at 285nm; [chloroohydrin] = 5.0×10^{-4} M. [b]Other products are *cis* and *trans* acenaphthylene-6,7-dihydro azidoalcohols. [c]In acetate buffer p*H* 4.36.

Table S7 Ratios of *cis* to *trans* dihydrodiols formed in the solvolysis of acenaphthhylene *trans*-6,7-bromohydrin in the presence of sodium azide at 25° C[a].

$[NaN_3]$ (M)	% *cis* dihydrodiol[b]	% *trans* dihydrodiol[b]	[*cis*-dihydrodiol] / [*trans*-dihydrodiol]
0[c]	71.3	28.7	2.48
0.03	44.5	18.4	2.42
0.05	42.2	13.7	2.42
0.10	19.5	12.9	2.29
0.20	19.5	8.2	2.39
0.30	14.1	8.2	2.42
0.40	11.6	4.9	2.35
0.50	10.3	4.4	2.37

[a]Measurements at 285nm; [chloroohydrin] = 5.0×10^{-3} M. [b]Other products are *cis* and *trans* acenaphthylene-6,7-dihydro azidoalcohols. [c]In acetate buffer p*H* 4.36.

Table S8 HPLC measurements of fractions of reactants for solvolyses of acenaphthylene *cis*-6,7-chlorohydrin and *trans*-6,7-bromohydrin in aqueous solution at 25° C.[a]

Time (secs)	% *cis* chlorohydrin[b]	Time (secs)	% *trans* bromohydrin[c]
0	100	0	97.7
600	91.7	360	59.6
1800	82.1	560	40.3
2400	78.1	850	24.1
3000	72.5	1140	13.2
3600	67.8	1430	7.3
5100	54.9	1740	4.9
6600	43.5	2100	2.0
10500	28.6		
15000	0.0		

[a]Measurements at 285 nm. [b]Initial substrate concentration 1.0×10^{-3}M. [b]Initial substrate concentration 5.0×10^{-4}M

Table S9 HPLC measurements of fractions of cis and trans 6,7-dihydrodiols of acenaphthylene and acenaphthenone for reaction of the *cis* isomer in 6 M $HClO_4$ at 25 °C.

Time(mins)	% *cis* dihydrodiol	% *trans* dihydrodiol	%acenaphthenone
0	100.0	0	0
1.0	98.4	0	1.6
5.0	94.7	2.9	2.4
9.0	93.8	3.8	2.4
13.0	89.1	5.0	5.9
17.0	84.5	6.4	9.1
30.0	66.3	13.8	19.9
60.0	44.8	25.3	29.9
90.0	36.5	25.6	37.8
120.0	30.5	28.3	41.2
150.0	20.5	31.3	48.2
180.0	14.0	30.9	55.1
270.0	9.7	26.7	60.6
300.0	8.7	27.0	64.3

Table S10 HPLC measurements of fractions of *cis*- and *trans*-6,7-dihydrodiols of acenaphthylene and acenaphthenone for reaction of the *trans* isomer in 6 M $HClO_4$ at 25 °C.

Time(mins)	% *cis* dihydrodiol	% *trans* dihydrodiol	%acenaphthenone
0	9.5	90.5	0
1.0	9.8	89.9	0.3
5.0	10.5	88.9	0.6
10.0	11.1	87.9	1.0
15.0	12.3	86.2	1.5
20.0	12,7	85.1	2.2
25.0	13.4	84.7	1.9
30.0	13.8	84.3	1.9
60.0	14.8	79.5	5.8
90.0	16.9	75.3	7.8
120.0	19.0	69.1	11.9
150.0	21.0	70.2	8.8
180.0	19.6	61.9	18.5
210.0	19.5	61.8	18.8
240.0	19.8	62.2	18.0
270.0	17.5	54.4	28.1
300.0	17.4	54.6	28.0

Table S11 HPLC measurements of fractions of *cis*- and *trans*-6,7-dihydrodiols of acenaphthylene and acenaphthenone for reaction of the *cis* isomer in 5 M $HClO_4$ at 25 °C.

Time(mins)	% *cis* dihydrodiol	% *trans* dihydrodiol	%acenaphthenone
0	100.0	0	0
5	96.4	2.9	0.7
30	94.5	2.6	3.0
60	89.4	4.6	6.0
180	77.2	10.6	12.1
360	64.2	17.8	18.0
540	55.2	23.8	21
720	46.3	29.7	24.1
1065	28.7	41.7	29.6
1125	28.5	42.7	28.8
1305	24.3	43.8	31,9
1505	21.2	45.0	33.8
1650	18.8	42.6	38.6
1830	16.9	42.9	40.2
2455	13.6	41.6	44.8
2940	12.6	38.7	48.7

Table S12 HPLC measurements of fractions of *cis*- and *trans*-6,7-dihydrodiols of acenaphthylene and acenaphthenone for reaction of the *trans* isomer in 5 M $HClO_4$ at 25 °C.

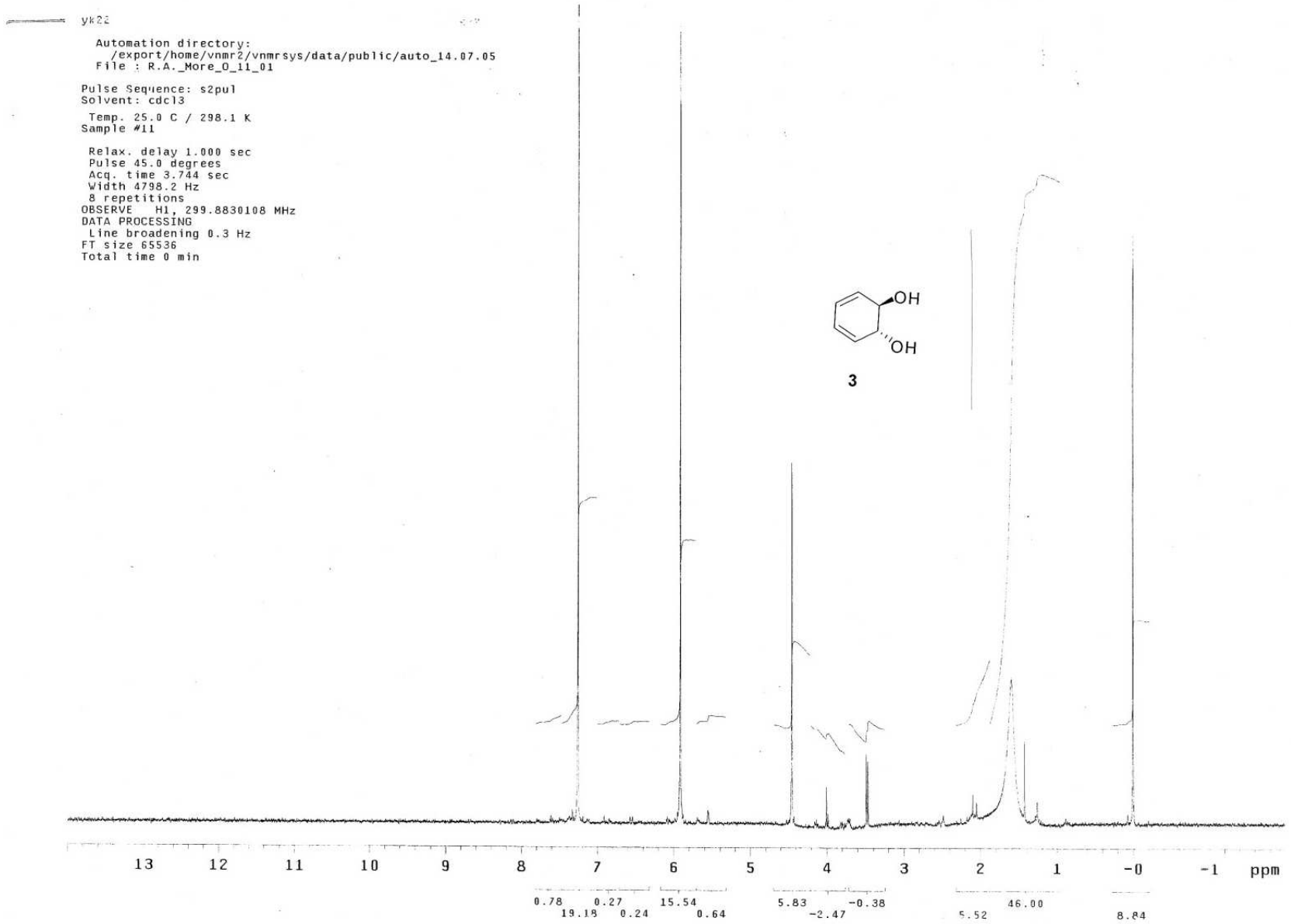
Time(mins)	% *cis* dihydrodiol	% *trans* dihydrodiol	%acenaphthenone
0	6.8	93.20	0.0
5	6.5	93.5	0.0
30	9.3	90.5	0.2
60	11.1	88.4	0.6
180	14.5	84.4	1.1
360	16.4	80.0	3.6
540	17.3	73.7	9.0
720	18.7	69.7	11.5
1065	18.6	64.4	17.0
1125	18.7	64.2	17.1
1305	20.1	61.9	18.0
1505	19.0	60.0	21.1
1650	18.2	55.7	26.1
1830	17.8	54.4	27.8
2455	16.2	49.2	34.7
2940	14.3	43.4	42.4

Table S13 Rate constants from acid-catalyzed equilibration of *cis* and *trans* acenaphthylene dihydrodiols and conversion to acenaphthenone at 25° C based on Scheme 7

$[HClO_4]$ (M)	Reactant	$10^5 k_a$ sec^{-1})	$10^5 k_b$ (sec^{-1})	$10^5 k_c$ (min^{-1})	$10^5 k_d$ (sec^{-1})
6 M	*Cis*	9.90	4.28	10.53	1.98
	Trans	9.10	4.20	4.72	0.95
5 M	*Cis*	1.28	0.38	0.77	0.14_5
	Trans	2.71	1.05	0.87	0.14_5

NMR Spectra

Spectra were recorded on 300 , 400 or 500 MHz NMR spectrometers.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OH
3
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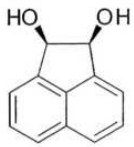
19.18 0.24 0.64 -2.47 5.52 8.84



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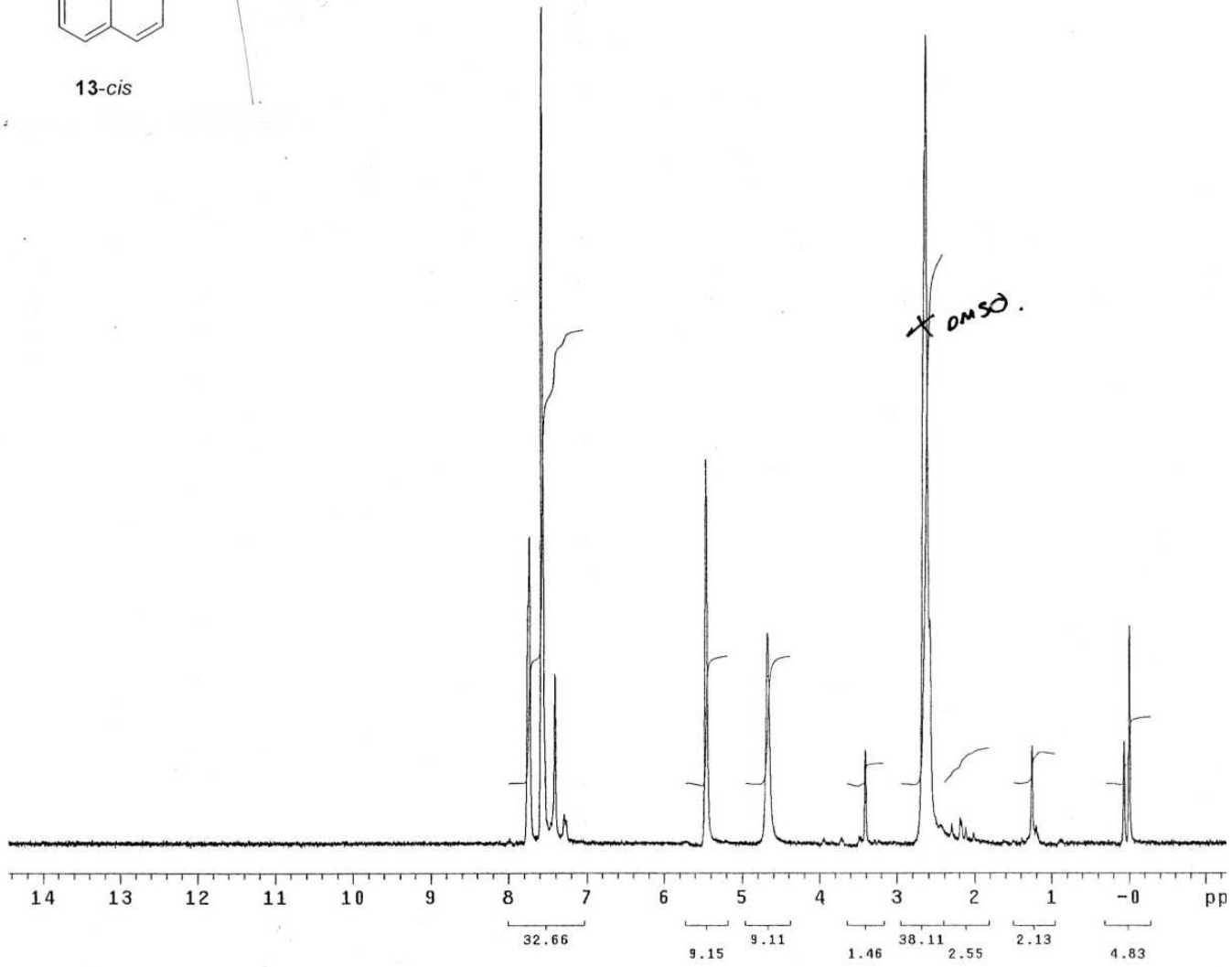

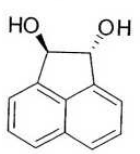

13-*trans*

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 Total time 1 minute
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DL - 65

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Pulse Sequence: s2pul
Solvent: cdcl3

Temp. 25.0 C / 298.1 K
Sample #10

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Pulse 45.0 degrees
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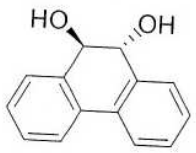

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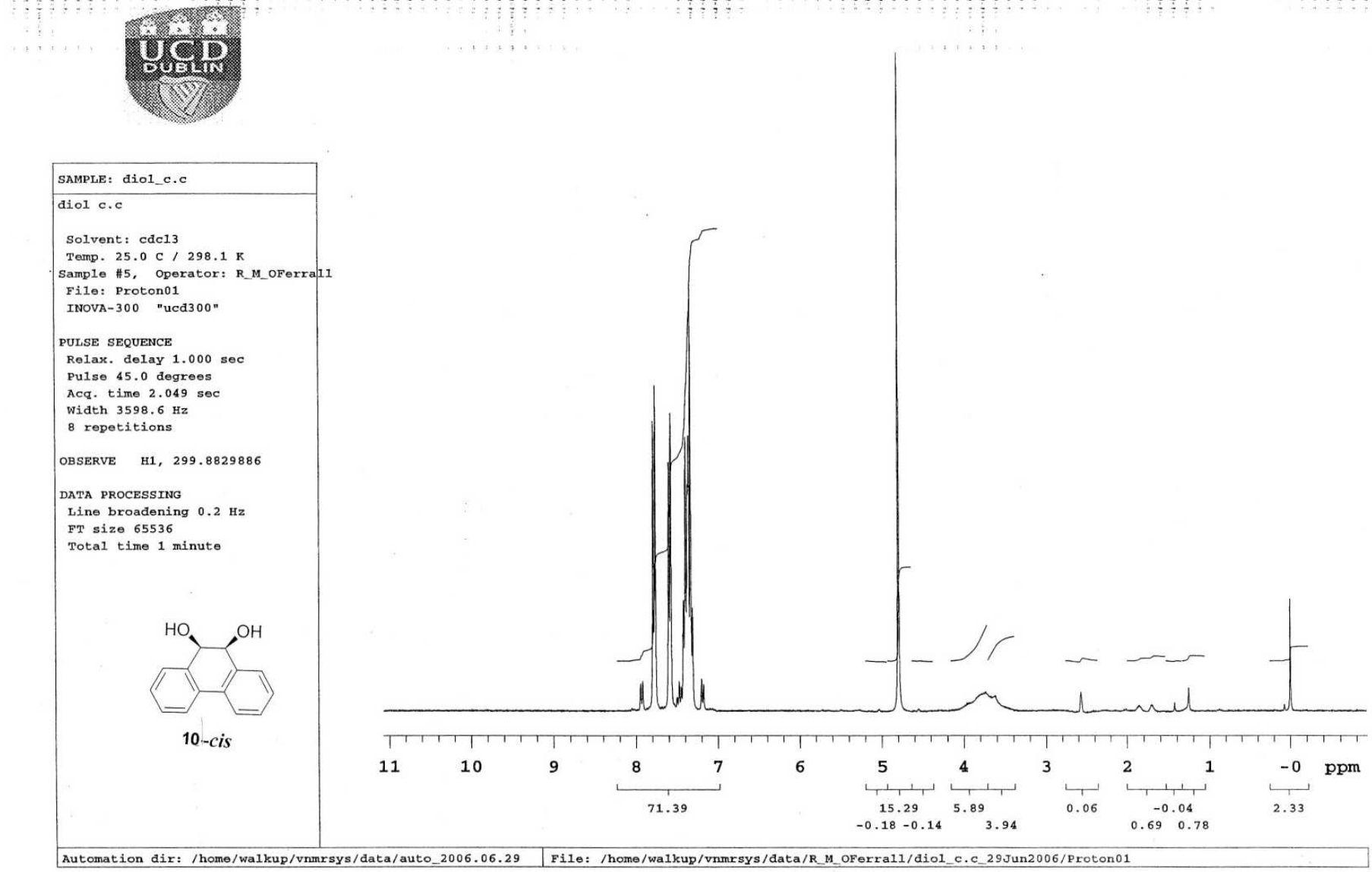
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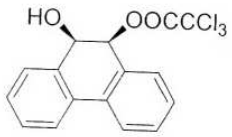

21

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mono solid

Solvent: cdcl3
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PULSE SEQUENCE
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Pulse 45.0 degrees
Acq. time 2.049 sec
Width 4798.2 Hz
8 repetitions

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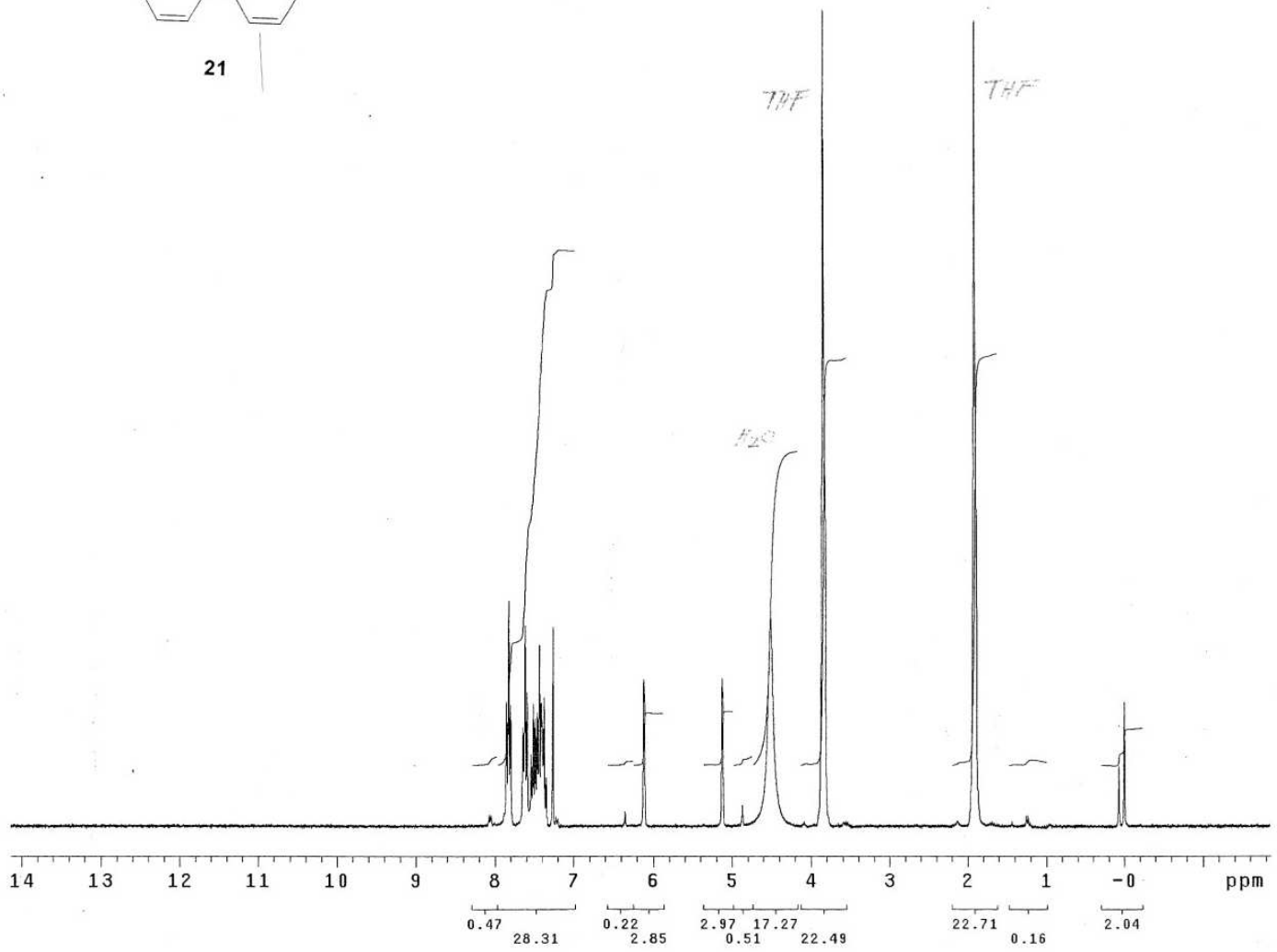
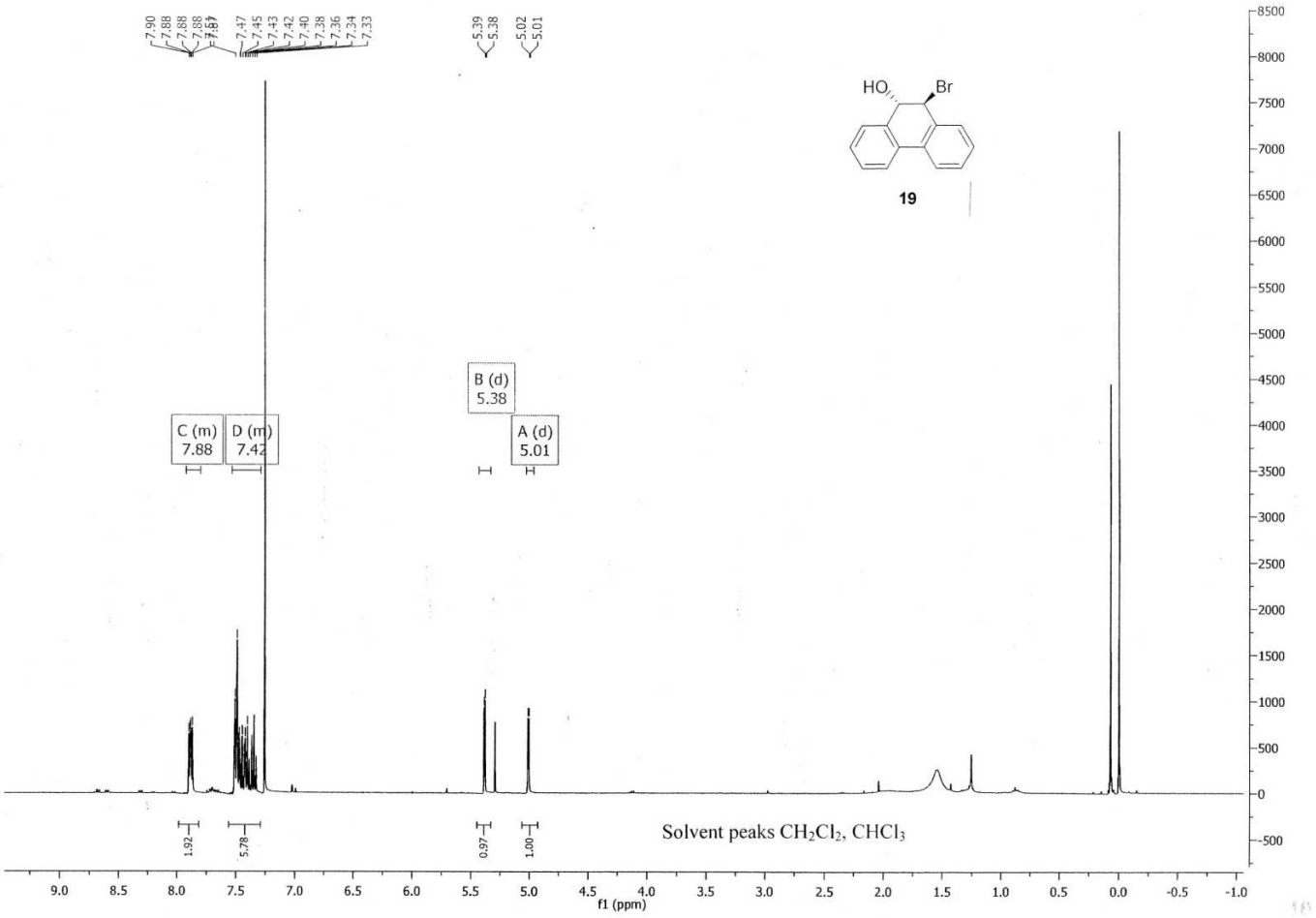
FT size 65536
Total time 1 minute

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7.33
5.39
5.38
5.02
5.01
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Br
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C (m)
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D (m)
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A (d)
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f1 (ppm)

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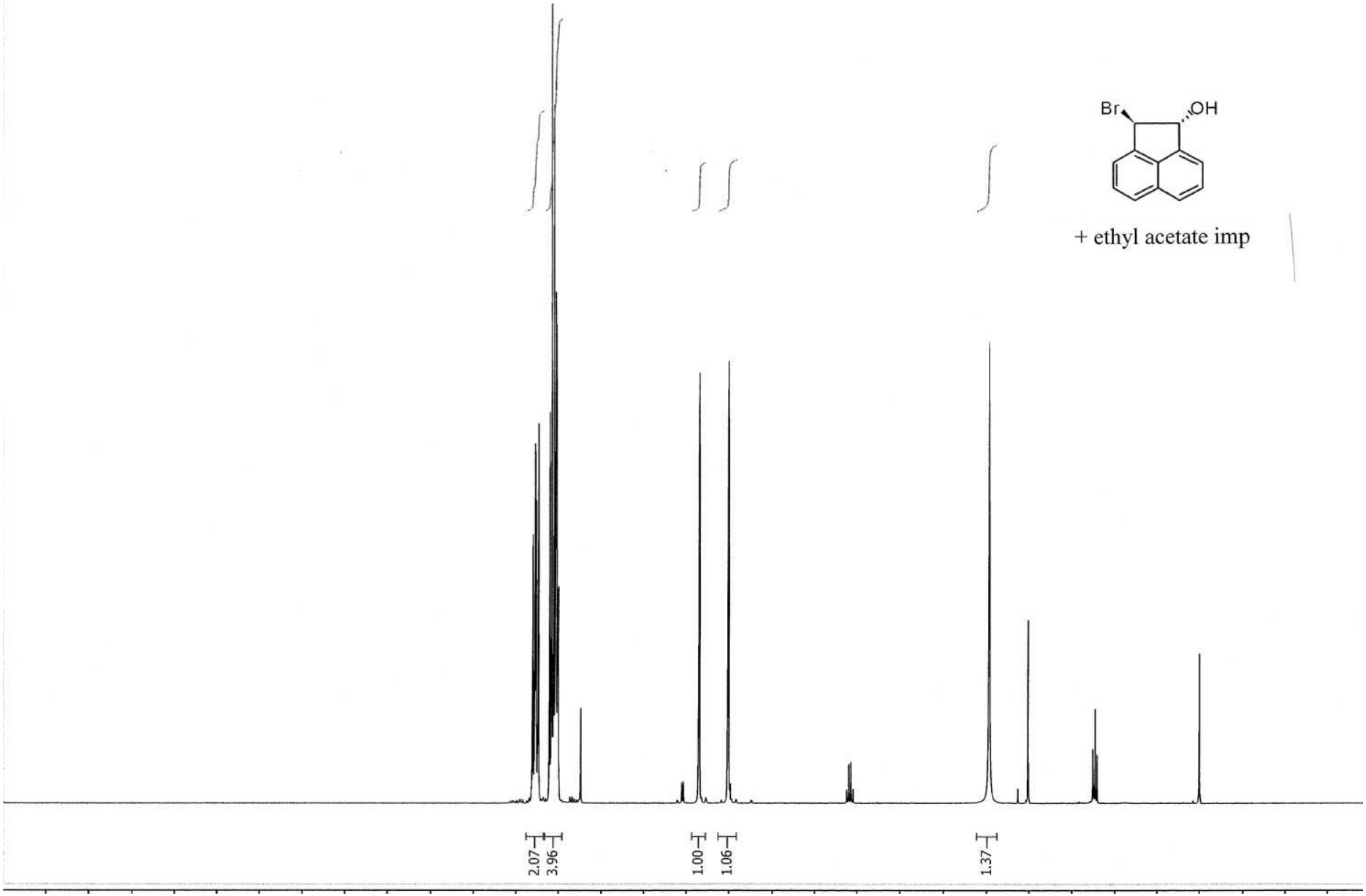

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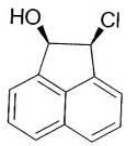

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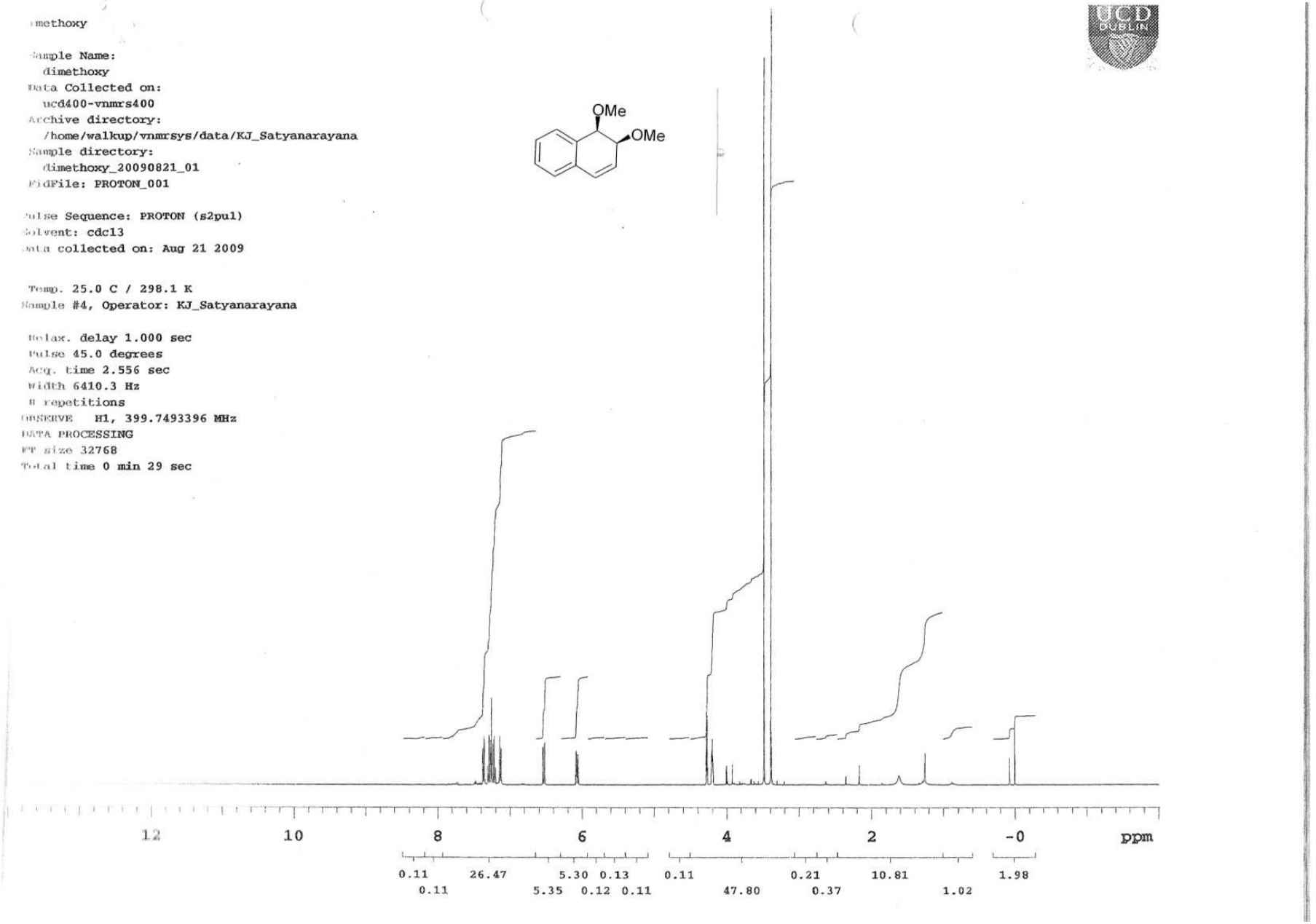
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OMe
OMe
UCD
DUBLIN
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8
6
4
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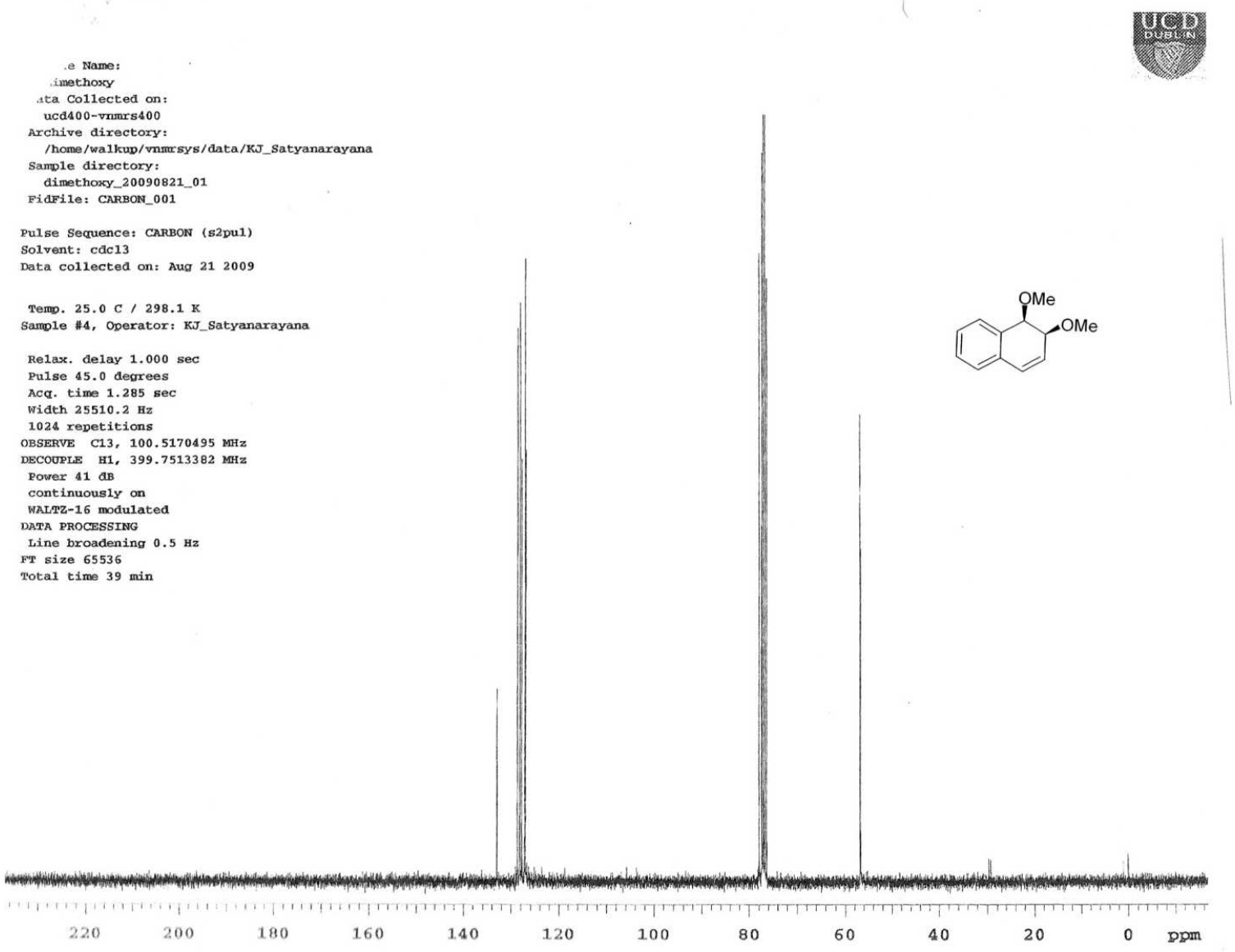
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continuously on
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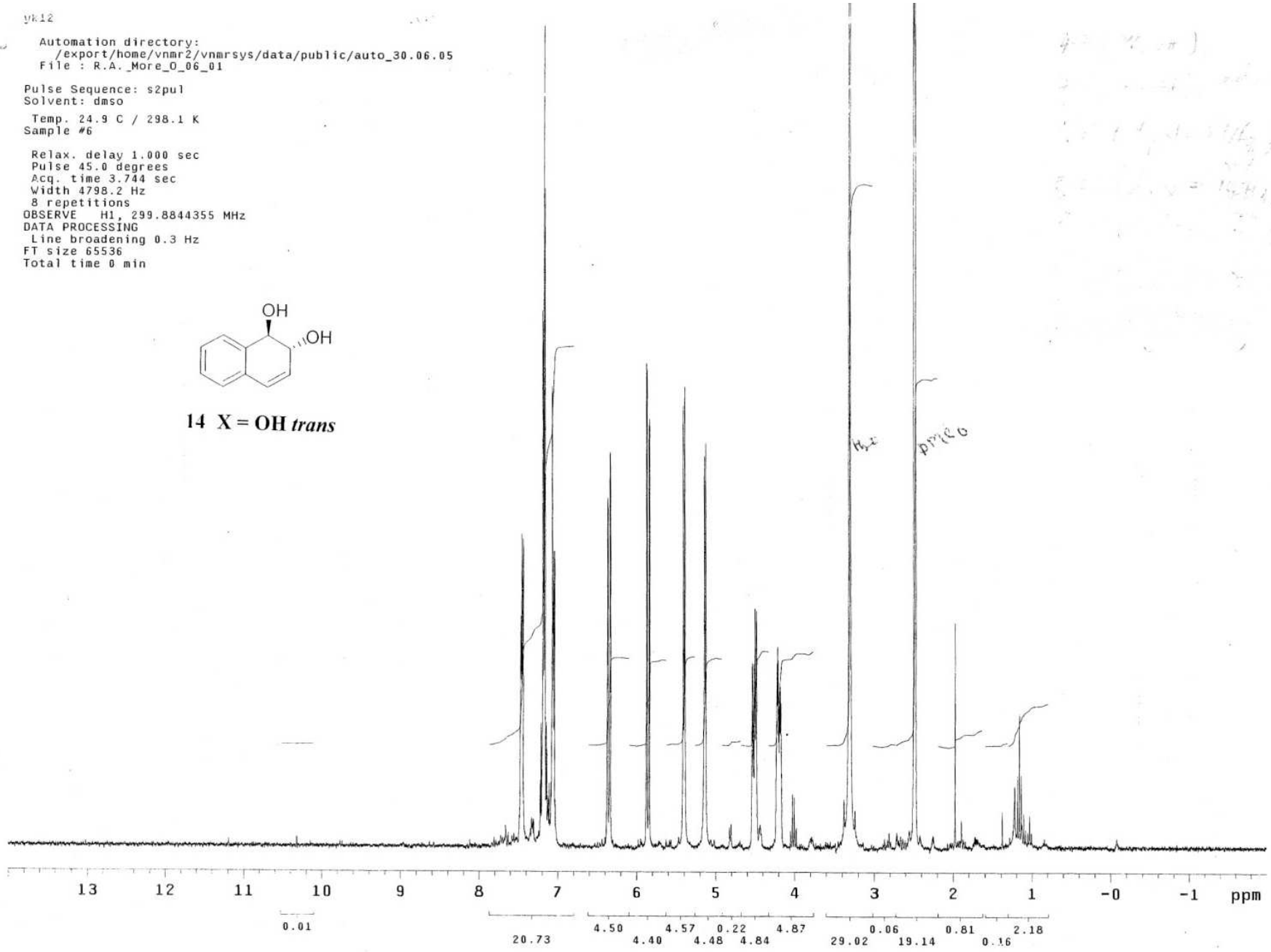
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Pulse 45.0 degrees
Acq. time 3.744 sec
Width 4798.2 Hz
8 repetitions
OBSERVE H1, 299.8844355 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
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OH
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12
11
10
9
8
7
6
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4
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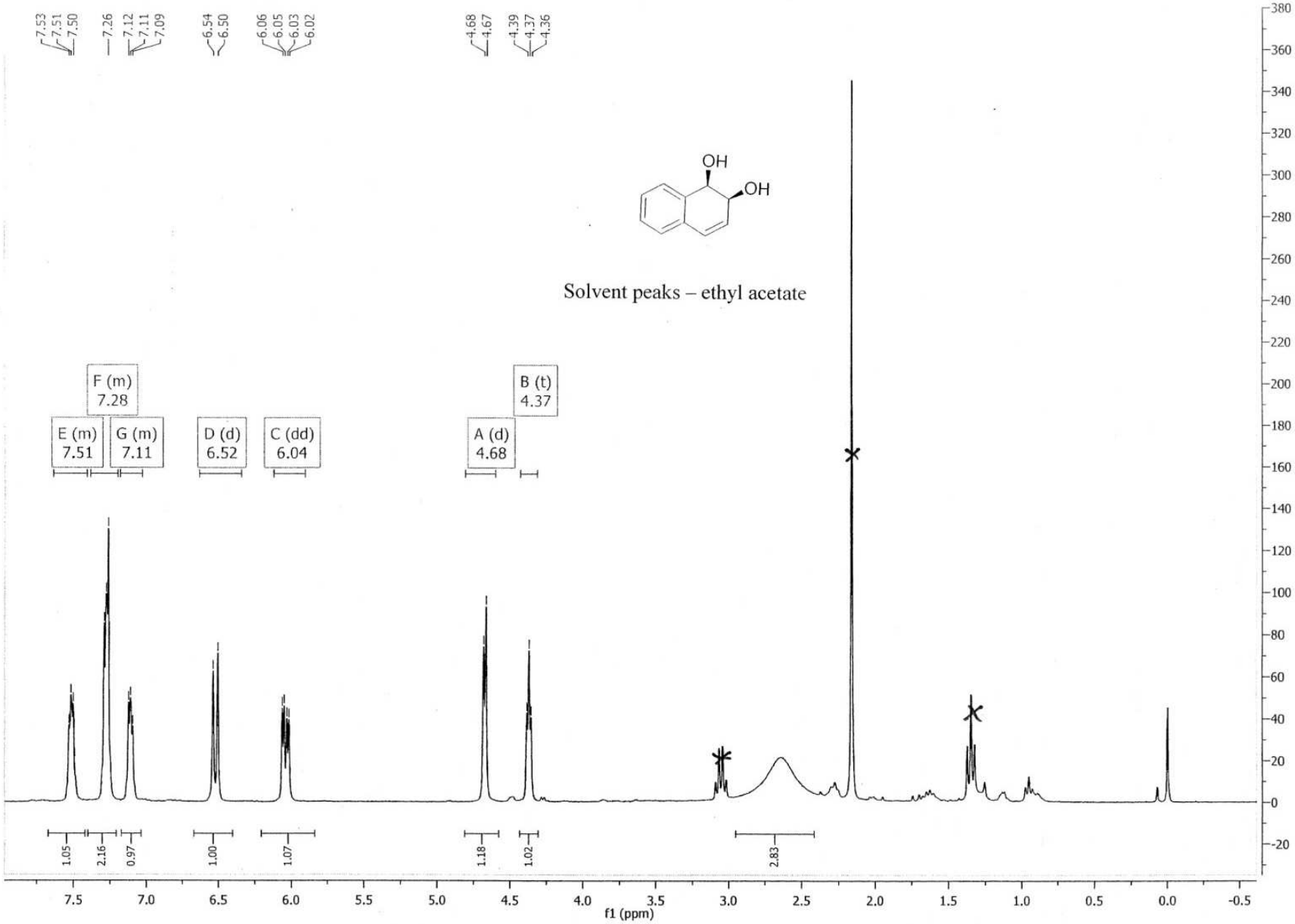
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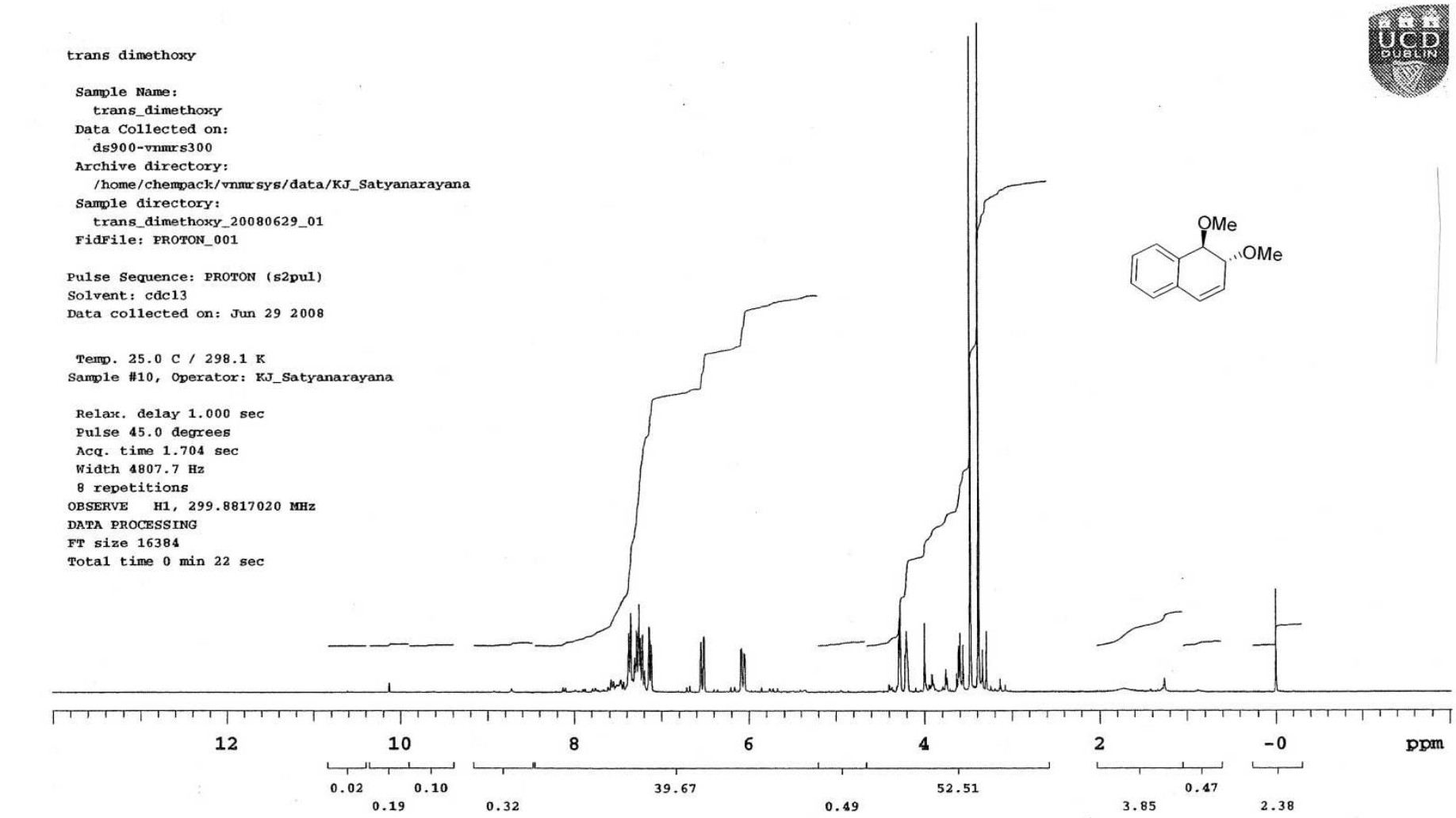
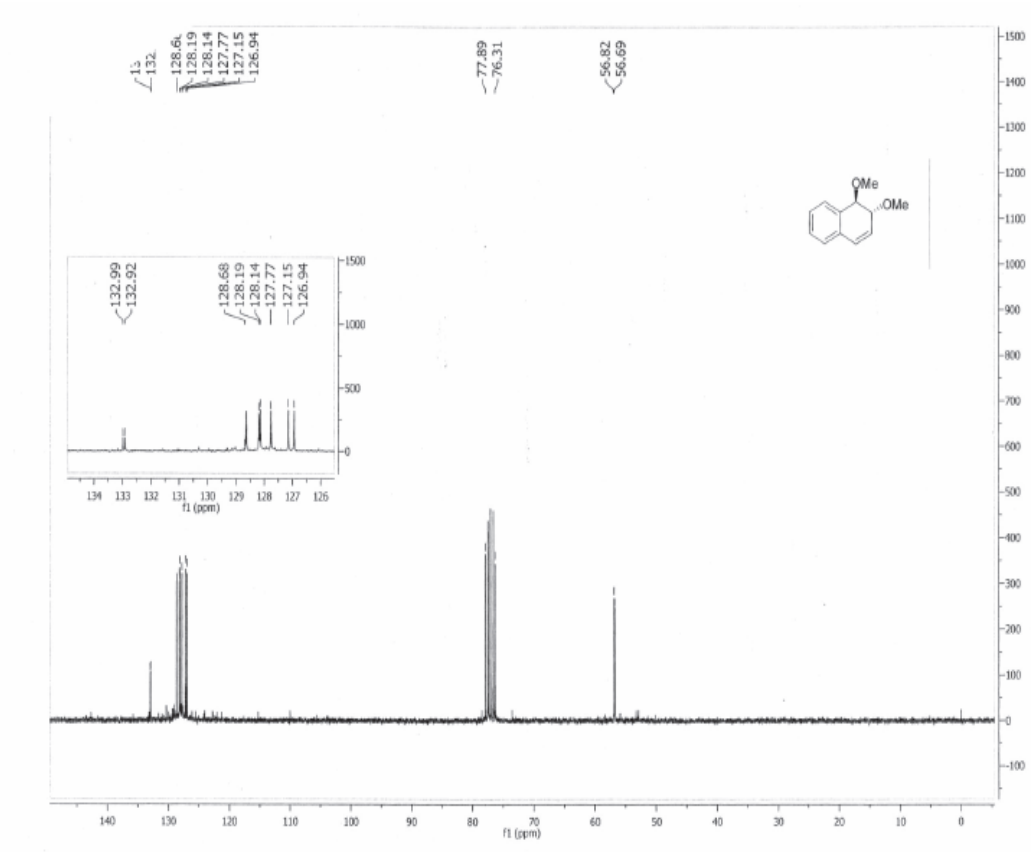
4.36
OH
OH
Solvent peaks – ethyl acetate
F (m)
7.28
E (m)
7.51
G (m)
7.11
D (d)
6.52
C (dd)
6.04
B (t)
4.37
A (d)
4.68
1.05
2.16
0.97
1.00
1.07
1.18
1.02
2.83
f1 (ppm)


trans dimethoxy
Sample Name:
trans_dimethoxy
Data Collected on:
ds900-vnmrs300
Archive directory:
/home/chempack/vnmrsys/data/KJ_Satyanarayana
Sample directory:
trans_dimethoxy_20080629_01
FidFile: PROTON_001
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 29 2008
Temp. 25.0 C / 298.1 K
Sample #10, Operator: KJ_Satyanarayana
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.704 sec
Width 4807.7 Hz
8 repetitions
OBSERVE H1, 299.8817020 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 22 sec
OMe
OMe
12
10
8
6
4
2
-0
ppm
0.02
0.10
39.67
52.51
0.47
0.19
0.32
0.49
3.85
2.38


132.99
132.92
128.68
128.19
128.14
127.77
127.15
126.94
77.89
76.31
56.82
56.69
OMe
OMe
f1 (ppm)