Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting information

Effective Oxidation of Benzylic and Alkane C-H Bond Catalyzed by Sodium *O*-Iodobenzenesulfonate with Oxone as a Terminal Oxidant under the Phase-Transfer Conditions

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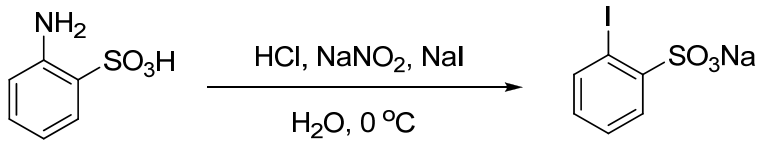
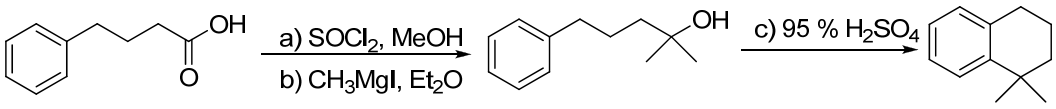
TABLE OF CONTENTS

Preparation of sodium 2-iodobenzenesulfonate (1b) [S1]



To a stirred suspension of 2-aminobenzenesulfonic acid (5.0 g, 28.9 mmol) and crushed-ice (20 g) in concentrated HCl (10 mL) was added $NaNO_2$ (2.09 g, 30.3 mmol) in water (10 mL) slowly at 0 °C, and stirred for 20~30 min at below 5 °C. A solution of NaI (4.76 g, 31.76 mmol) in water (10 mL) was then added slowly with stirring at 0 °C. After addition was complete, stirring was continued at 0 °C for 1 h, at room temperature for 1 h and at 50 °C for 12 h to remove all N_2. The mixture was than refrigerated, and the insoluble component was separated. After the solid was treated with boiling EtOH (some Et_2O added), the mixture was allowed to cool to separate the insoluble solid. The solid was washed with cold EtOH and Et_2O to isolate **1b** (4.92 g, 17.3 mmol, 60 % yield). ^{1}H NMR (D_2O, 400 MHz) δ 8.10 (d, J = 8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 7.8 Hz,1H); ^{13}C NMR (D_2O, 100 MHz) δ 144.76, 142.08, 132.40, 128.45, 128.30, 90.93**.**

Preparation of 1,1-dimethyltetralin [S2]

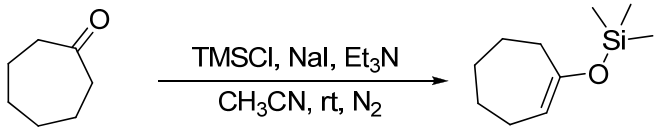


a) To a solution of commercial 4-phenylbutanoic acid (3.28 g, 20 mmol) in MeOH (100 mL) was added $SOCl_2$ (7.5 mL, 100 mmol) dropwise in ice bath. When the addition was complete, the mixture was heated to reflux for 2h. The excess $SOCl_2$ was removed by distillation, the residue was diluted with water (50 mL), extracted by EtOAc (50 mL×3), washed with saturated $NaHCO_3$ (20 mL) and brine (10 mL), dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, the residue was purified by column chromatography to give a colorless oil (3.35g, 94 % yield).

b) 2M CH_3MgI (20 mL, 40 mmol) was added dropwise to the 100 mL flask containing the methyl 4-phenylbutanoate (3.35 g, 18.8 mmol) in dry Et_2O (20 mL) at 0 °C. Then the mixture was stirred overnight at room temperature. The resulting suspension was poured into saturated NH_4Cl (40 mL) slowly, extracted with EtOAc (50 mL×3), combined the organic layer and washed with brine (10 mL), dried over anhydrous $MgSO_4$, solvent was removed *in vacuo*, no further purification was needed (slight yellow liquid). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.28-7.31 (m, 2H), 7.18-7.21 (m, 3H), 2.64 (t, J = 7.8 Hz, 2H), 1.67-1.75 (m, 2H), 1.50-1.54 (m, 2H), 1.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 142.38, 128.35, 128.25, 125.69, 70.90, 43.41, 36.27, 29.17, 26.24.

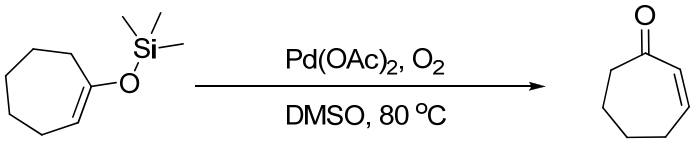
c) The crude 1,1-dimethyl-4-phenylbutanol (3.15 g, 17.7 mmol) was added slowly to 90% solution of H_2SO_4 (30 mL) in ice bath, the yellow slurry was stirred for another 30 min at 0 °C before the petroleum (40 mL) was added. Then the mixture was extracted by hexane (50 mL×4), washed the combined organic layer with brine (20 mL), dried over $MgSO_4$, removed solvent, then the residue was purified by column chromatography to give a colorless oil (2.8 g, 99 %). Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.35 (d, J = 7.8 Hz, 1H), 7.14-7.18 (m, 1H), 7.05-7.11 (m, 2H), 2.78 (t, J = 6.2 Hz, 2H), 1.80-1.86 (m, 2H), 1.67-1.70 (m, 2H), 1.31 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 145.76, 136.11, 129.01, 126.61, 125.76, 125.21, 39.26, 33.79, 31.85, 30.73, 19.68.

Preparation of cycloheptenyloxytrimethylsilane[S3]



To the mixture of cycloheptanone (5.6 g, 50 mmol) and pre-dried NaI (9 g, 60 mmol) in acetonitrile (50 mL) was added Et_3N (8.7 mL, 60 mmol) and then TMSCl (7.6 mL, 60 mmol). The color of the mixture changed to brownish immediately and white solid precipitated from the mixture. After the reaction was complete indicated by GC, the resulting mixture was diluted by cold pentane (50 mL) and cold water (50 mL). The mixture was extracted by cold pentane (50 mL×3), washed with ice water (50 mL×2). Then the aqueous layer was extracted by cold pentane again (50 mL), the combined organic layer was dried with $MgSO_4$. The solvent was removed under reduced pressure to afford the crude cycloheptenyloxytrimethylsilane (9 g) which was used without further purification. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.01 (t, J = 6.2 Hz, 1H), 2.20-2.23 (m, 2H), 1.96-2.00 (m, 2H), 1.65-1.70 (m, 2H), 1.48-1.58 (m, 4H), 0.16 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.98, 108.72, 35.50, 31.57, 27.78, 25.34, 25.21, 0.25.

Preparation of cyclohept-2-enone[S4]

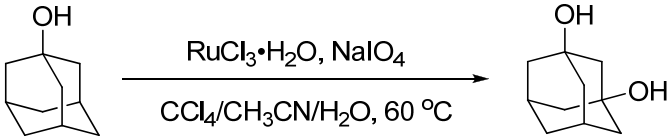


To the mixture of the $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) in DMSO (20 mL) under O_2 atmosphere was added cycloheptenyloxytrimethylsilane (184 mg, 1 mmol). The mixture was heated to 80 °C with vigorous stirring. After the reaction was complete indicated by GC, saturated $NaHCO_3$ (10 mL) was added to the mixture. Then the mixture was extracted by Et_2O (40 mL×3), dried with $MgSO_4$. The solvent was evaporated off in vacuo and the residue was purified by column chromatography to give the cyclohept-2-enone (82 mg, 75%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.52-6.58 (m, 1H), 5.96-5.99 (d, J = 12 Hz, 1H), 2.57-2.59 (m, 2H), 2.41-2.44 (m, 2H), 1.77-1.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.26, 146.35, 132.46, 43.46, 30.16, 26.06, 21.65.

Preparation of cyclohepta-2,6-dienone, cyclooct-2-enone, cycloocta-2,7-dienone[S5]

The cyclohepta-2,6-dienone, cyclooct-2-enone and cycloocta-2,6-dienone were prepared following the procedure reported by K. C. Nicolaou et al. The solution of ketone (1 mmol) in flurobenzene : DMSO (2:1, 0.1 M) was added IBX (1.3 equiv per C-C bond to be oxidized). The solution was heated to 55-75 oC for compounds in which one degree of unsaturation was introduced and 80 oC when higher conjugated system was desired. The reaction was monitored by GC until the complete consumption of starting material was observed. The mixture was diluted with Et2O and washed with NaHCO3, water and brine. Removal of solvent in vacuo led to the crude product which could be purified by flash column chromatography. See manuscript for NMR information.

Preparation of adamantane-1,3-diol[S6]



A mixture of 1-adamantanol (5.9 g, 33 mmol), sodium metaperiodate (16 g, 74.8 mmol), ruthenium chloride hydrate (160 mg, 0.66 mmol), acetonitrile (30 mL), carbon tetrachloride (20 mL) and water (30 mL) was stirred vigorously at 60 oC for 8 h. After being cooled, the reaction mixture was poured into aq. Sodium thiosulfate-sodium hydrogen carbonate, and extracted with chloroform. The extract was washed with brine, and evaperated to give a slight yellow solid (4.5 g, 81%), which was purified by column chromotography to give the white solid adamantane-1,3-diol. White solid; mp 298-300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.49 (s, 2H), 2.12 (s, 2H), 1.46-1.90 (m, 10H), 1.37 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 68.49, 53.21, 44.01, 34.67, 30.62.

Reference

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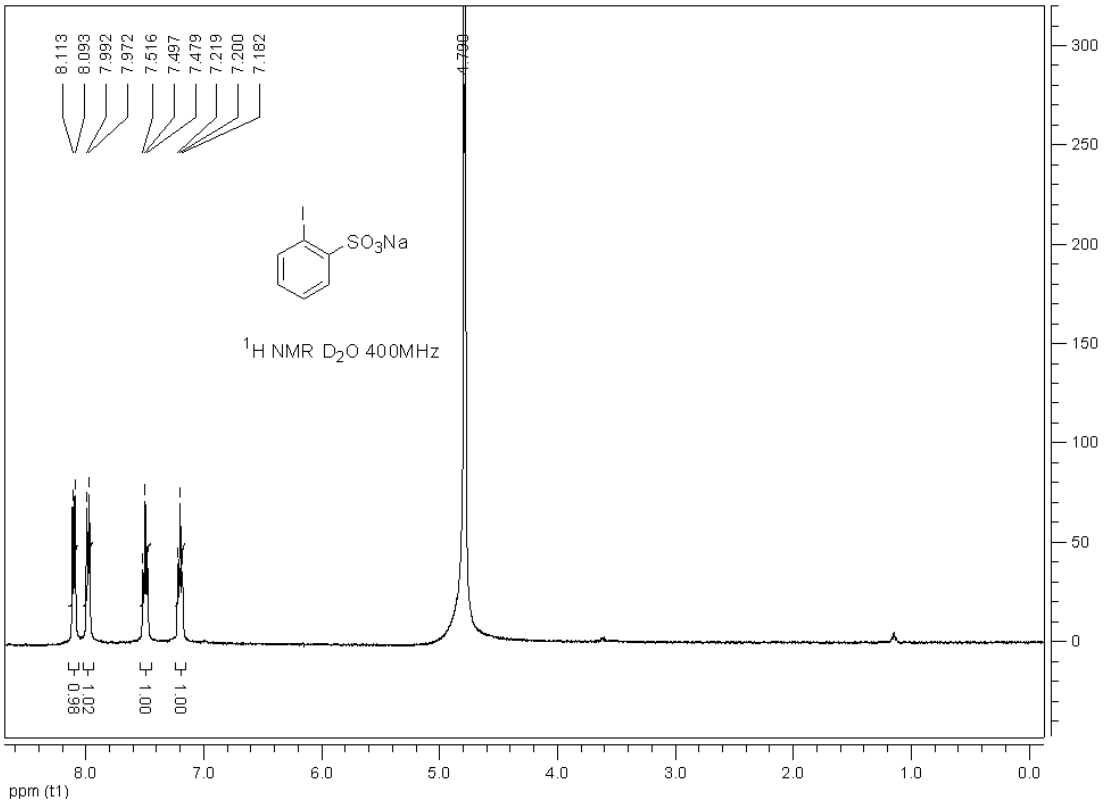
S3 a) R. Rathore, J. K. Kochi, *J. Org. Chem*. 1996, *61*, 636. b) P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron* 1987, *43*, 2075.

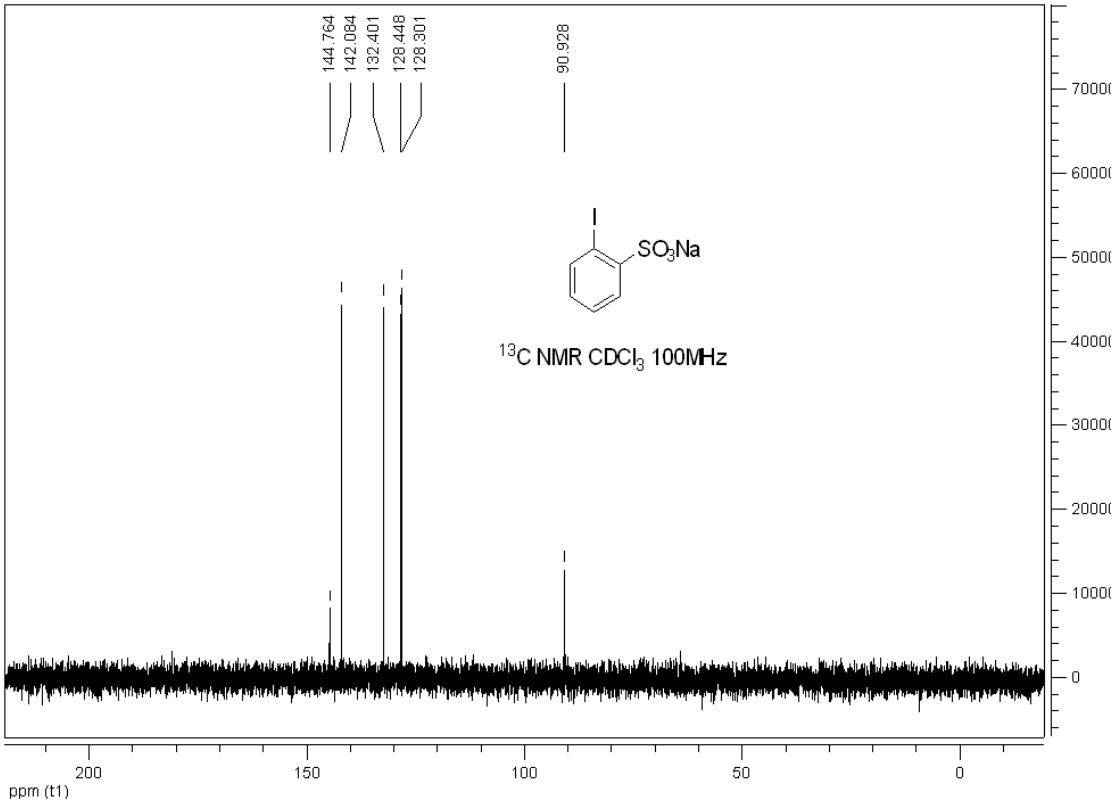
S4 R. C. Larock, T. R. Hightower, *Tetrahedron Lett*. 1995, *36*, 2423-2426.

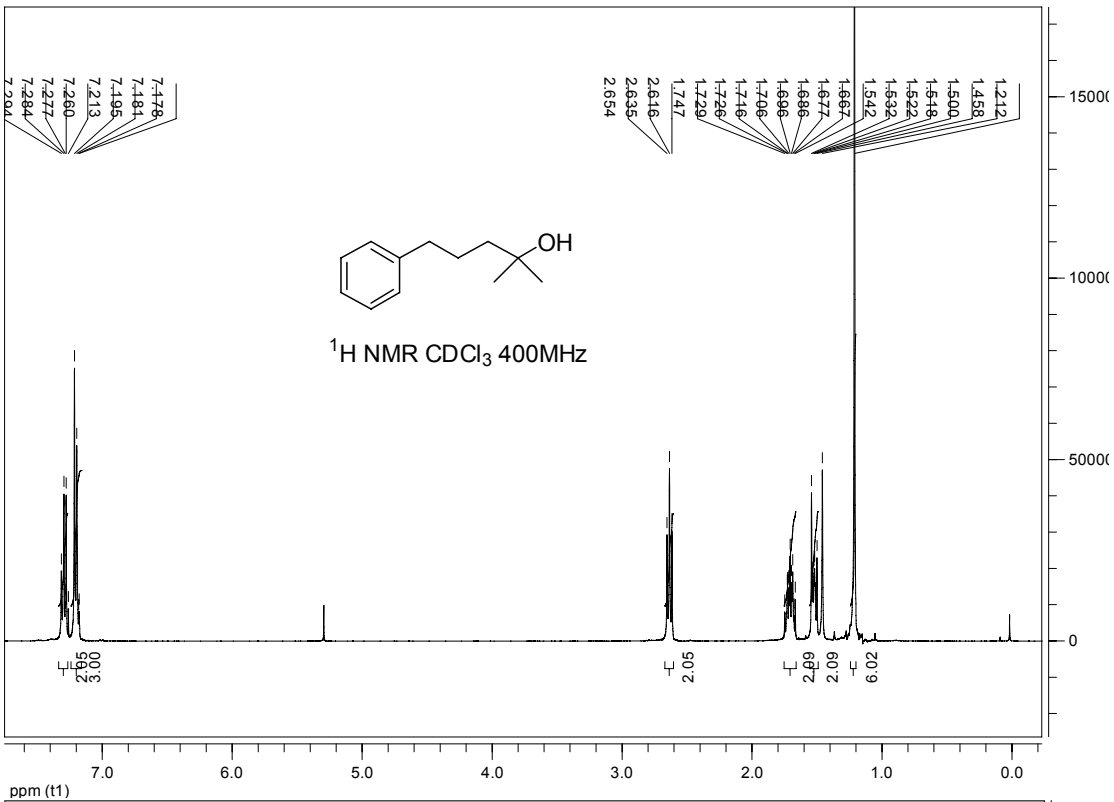
S5 K. C. Nicolaou, Y.-L. Zhong, P. S. Baran, *J. Am. Chem. Soc.* 2000, *122,* 7596-7597.

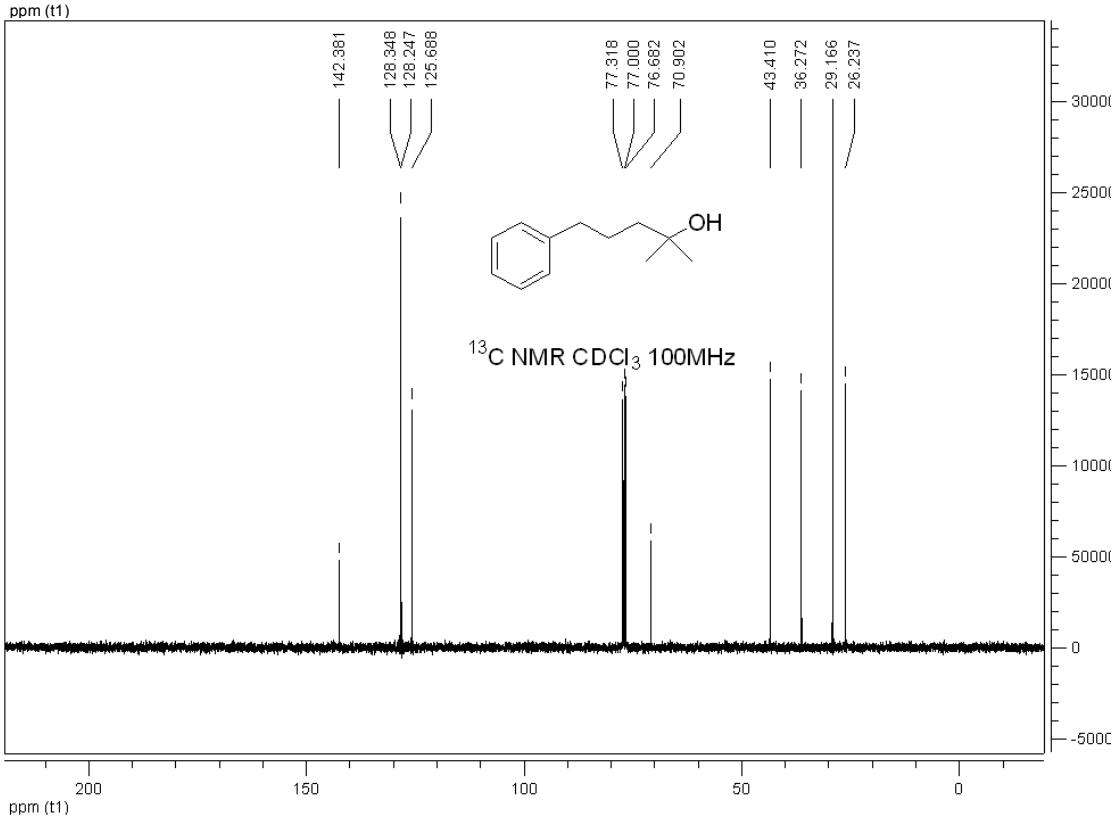
S6 O. Muraoka, Y.-L. Wang, M. Okumura, S. Nishiura, G. Tanabe, T. Momose, *Syn. Commun*. 1996, *26*, 1555-1562.

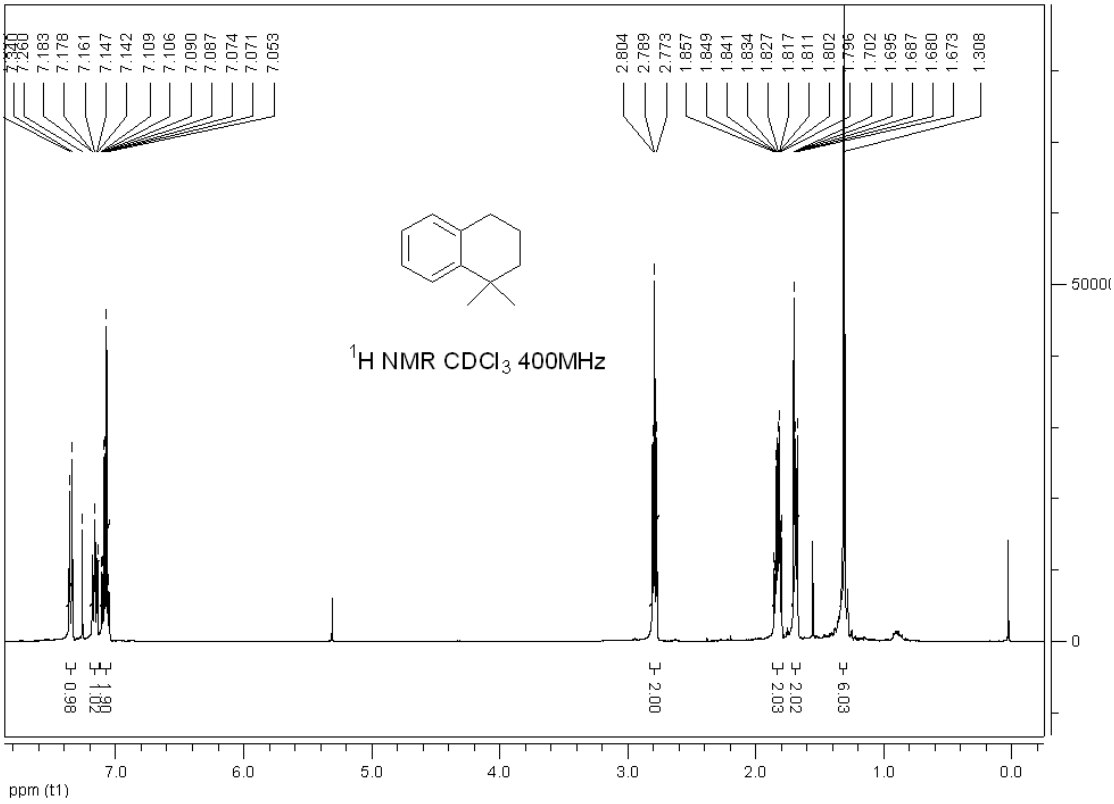
Characterizations







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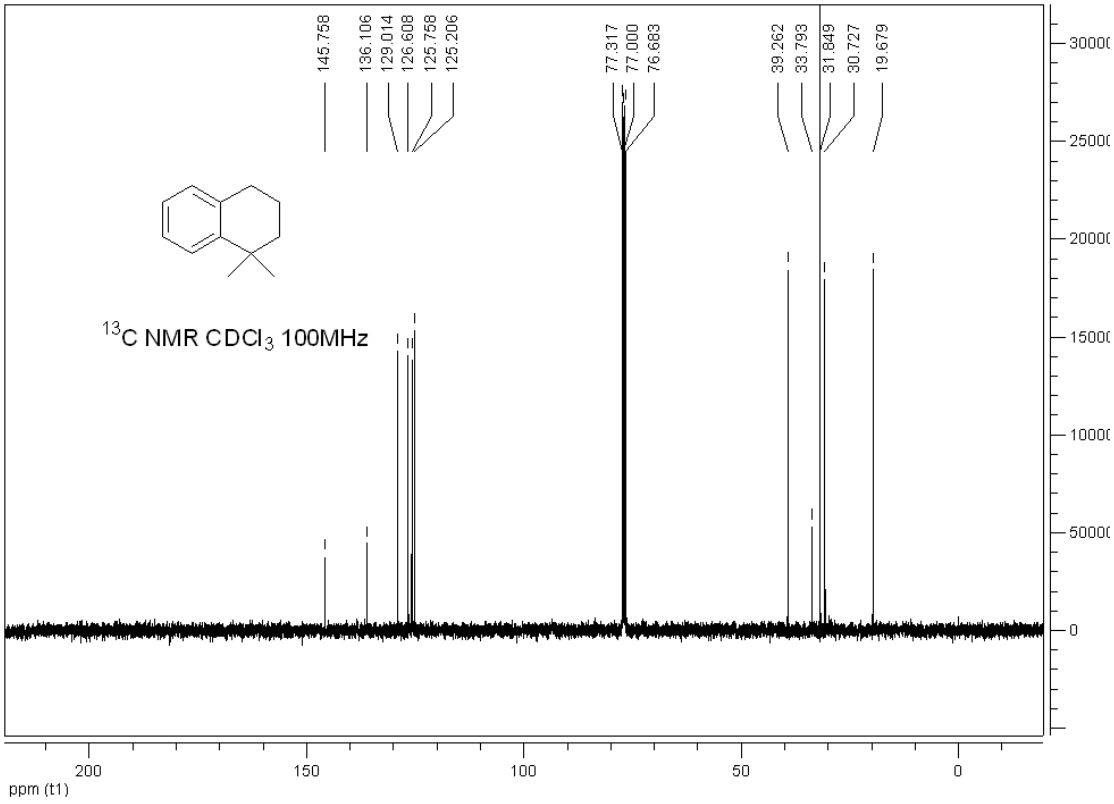
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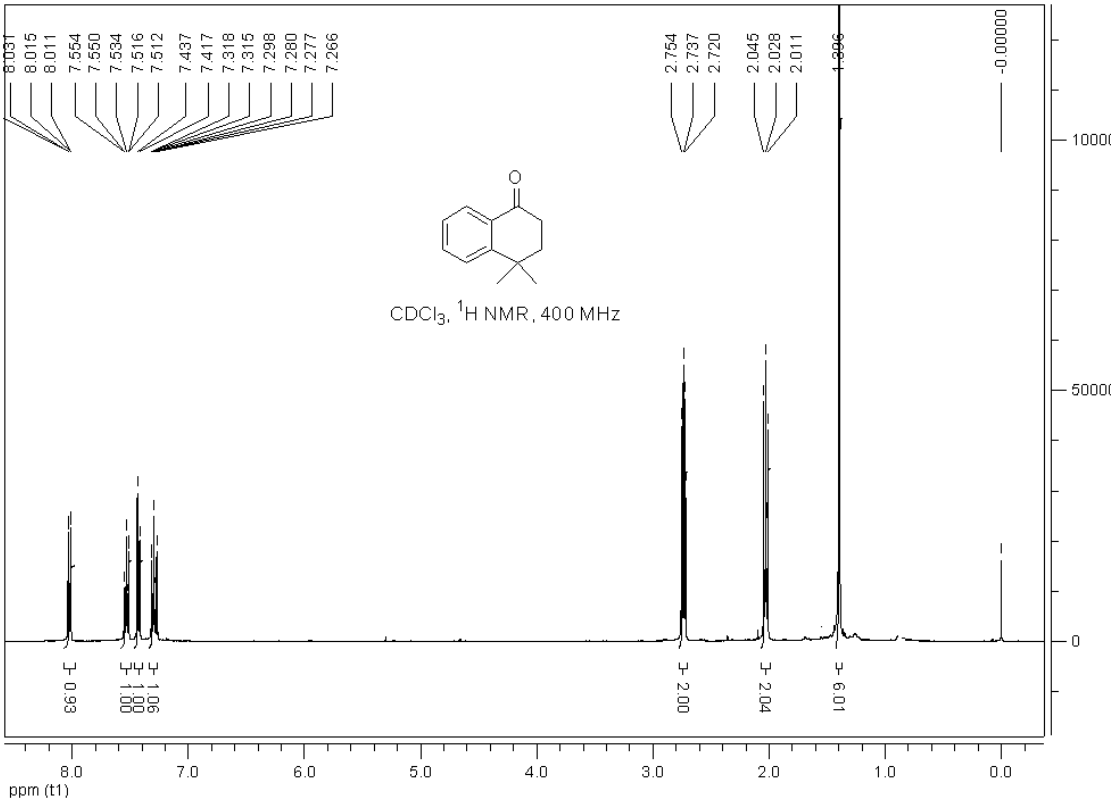
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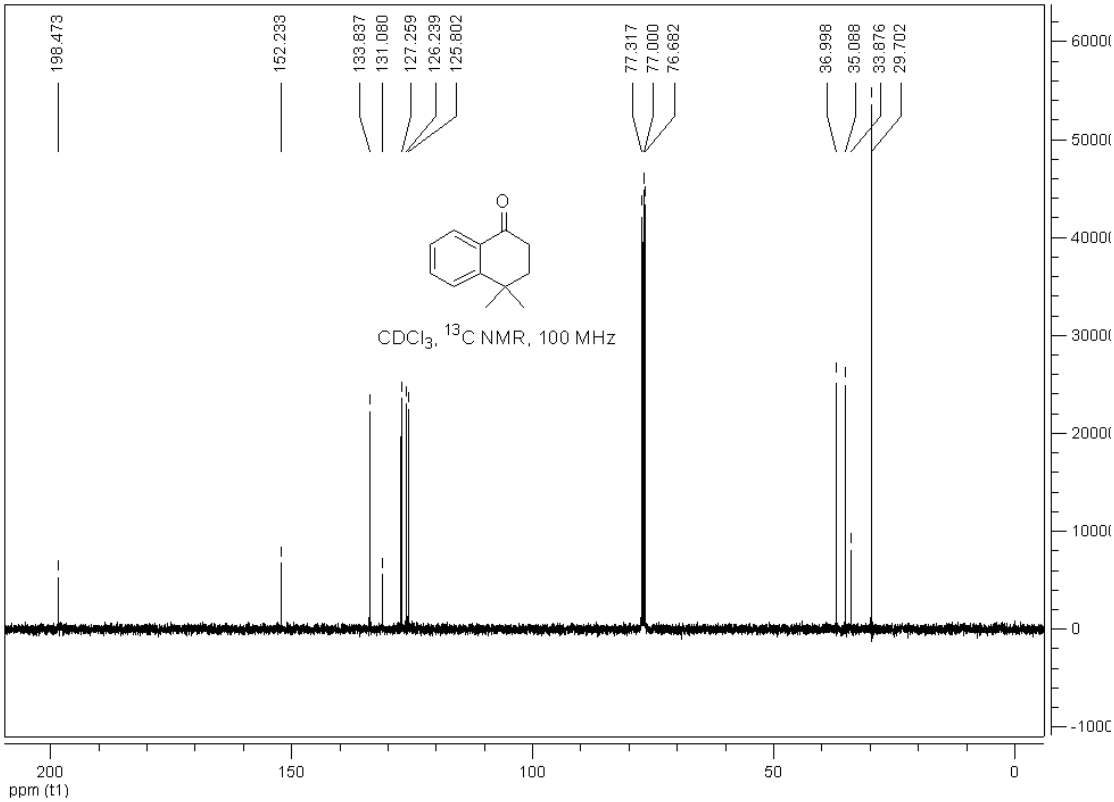
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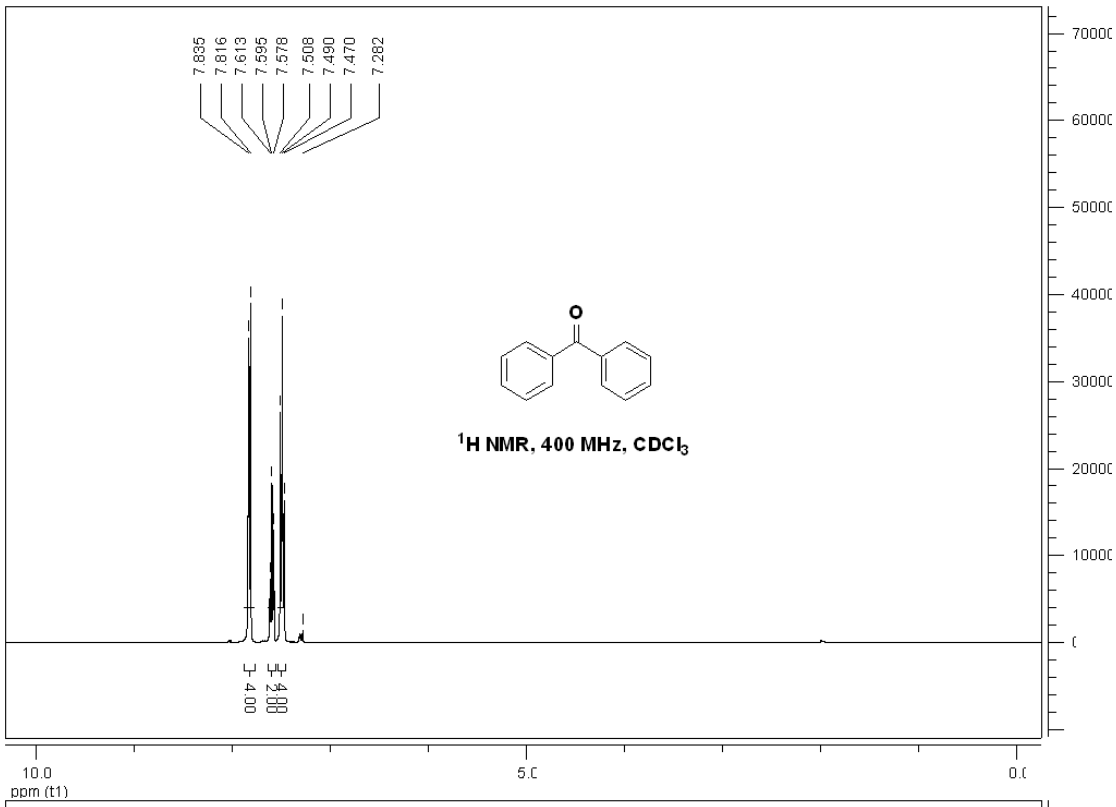

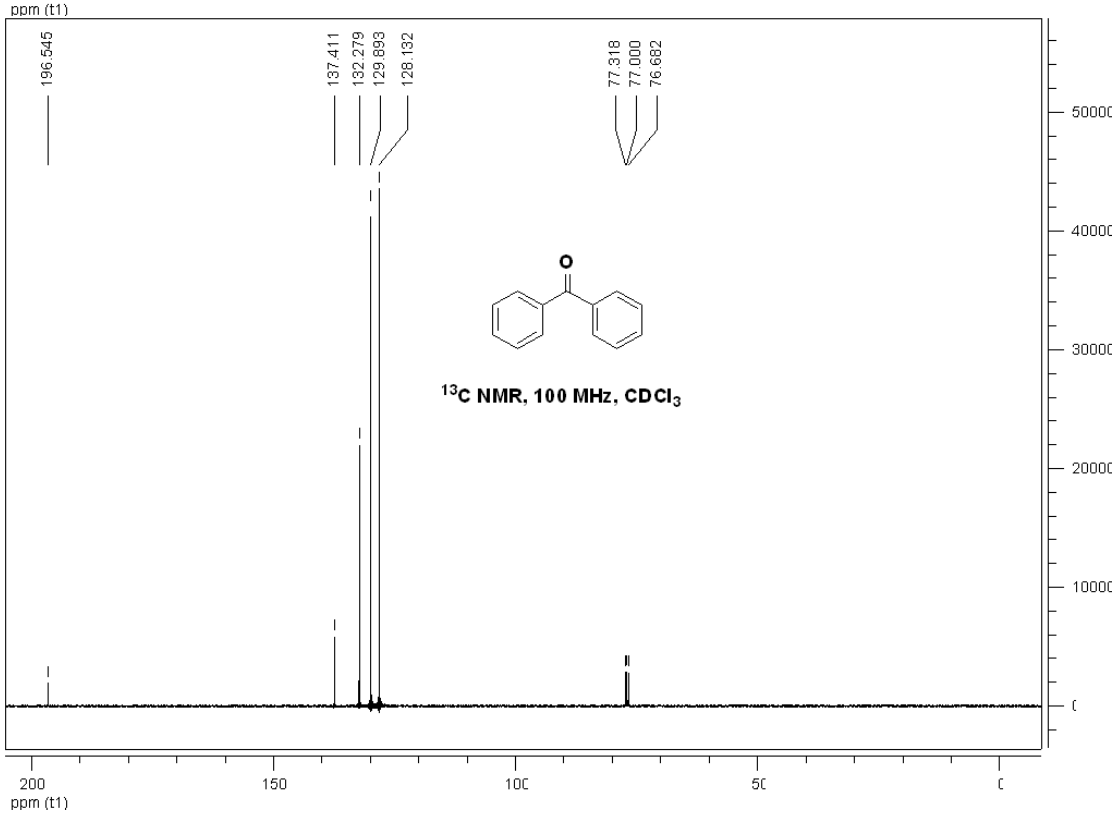

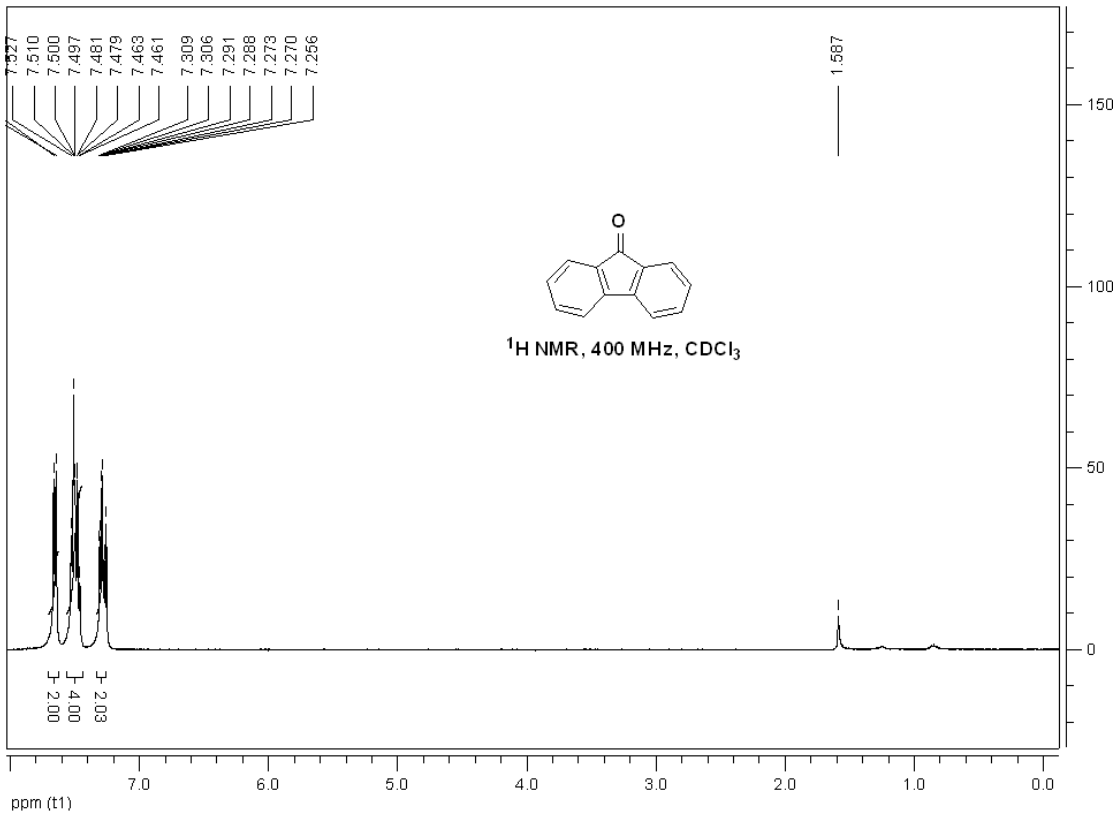

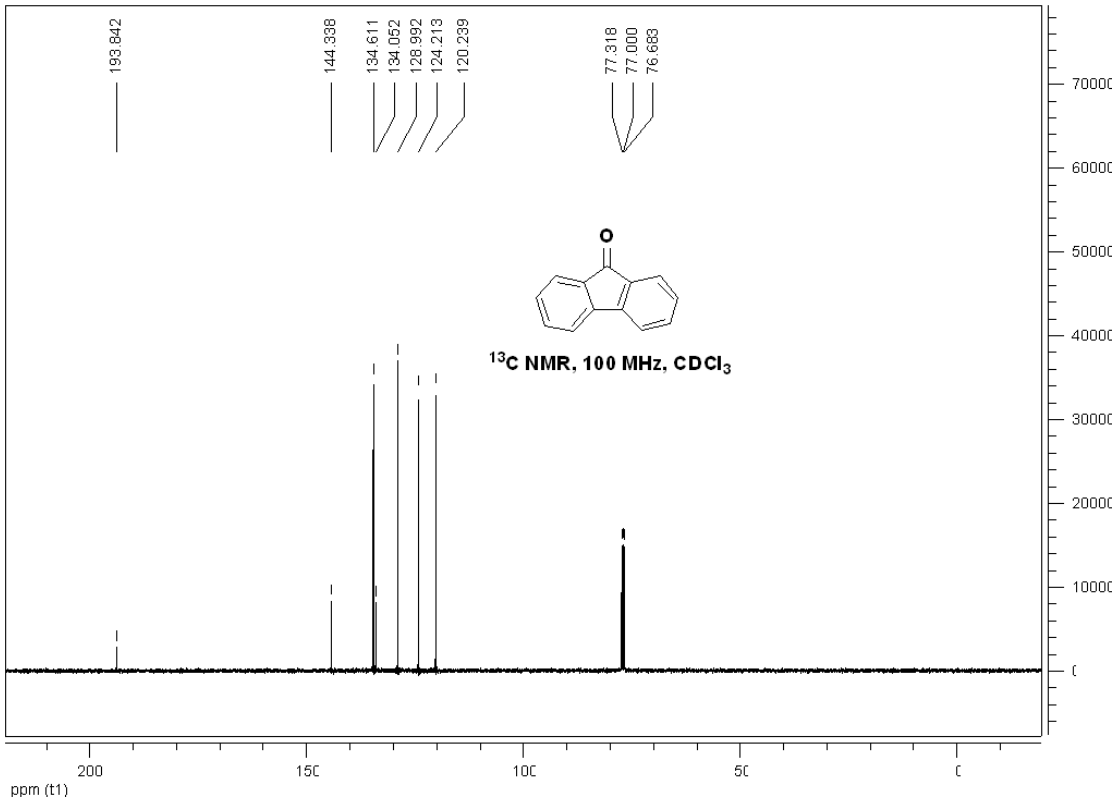

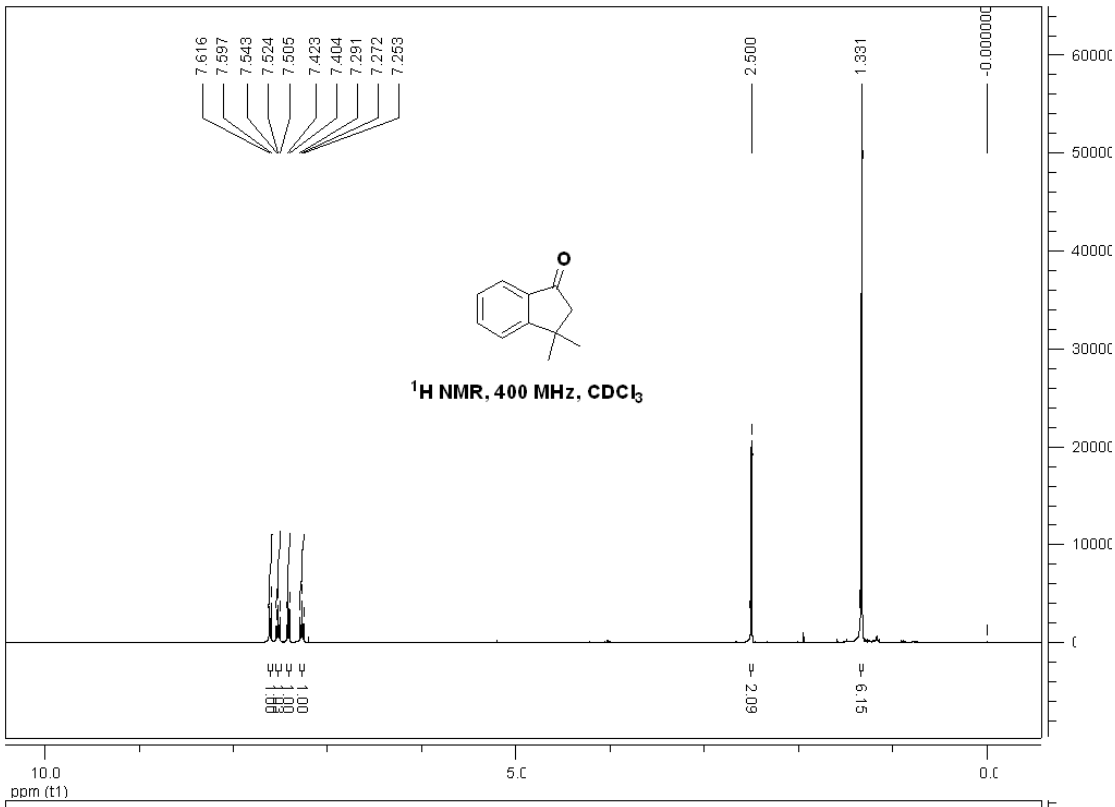

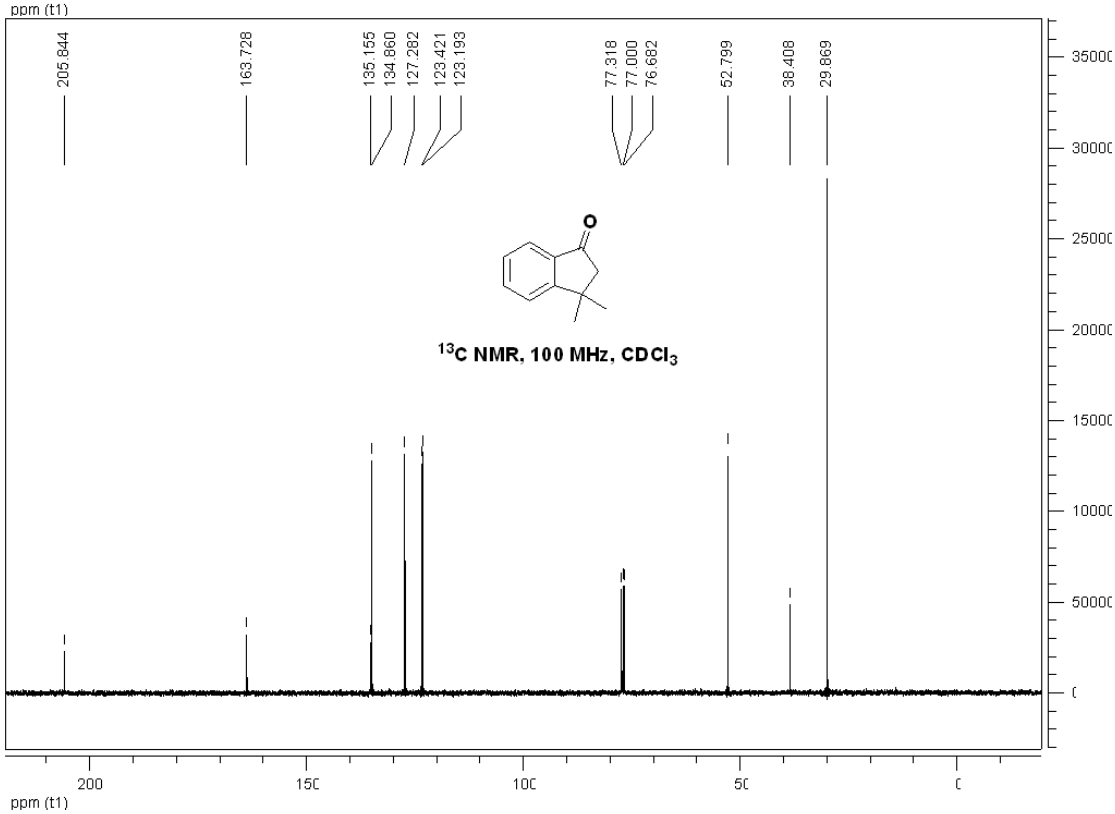

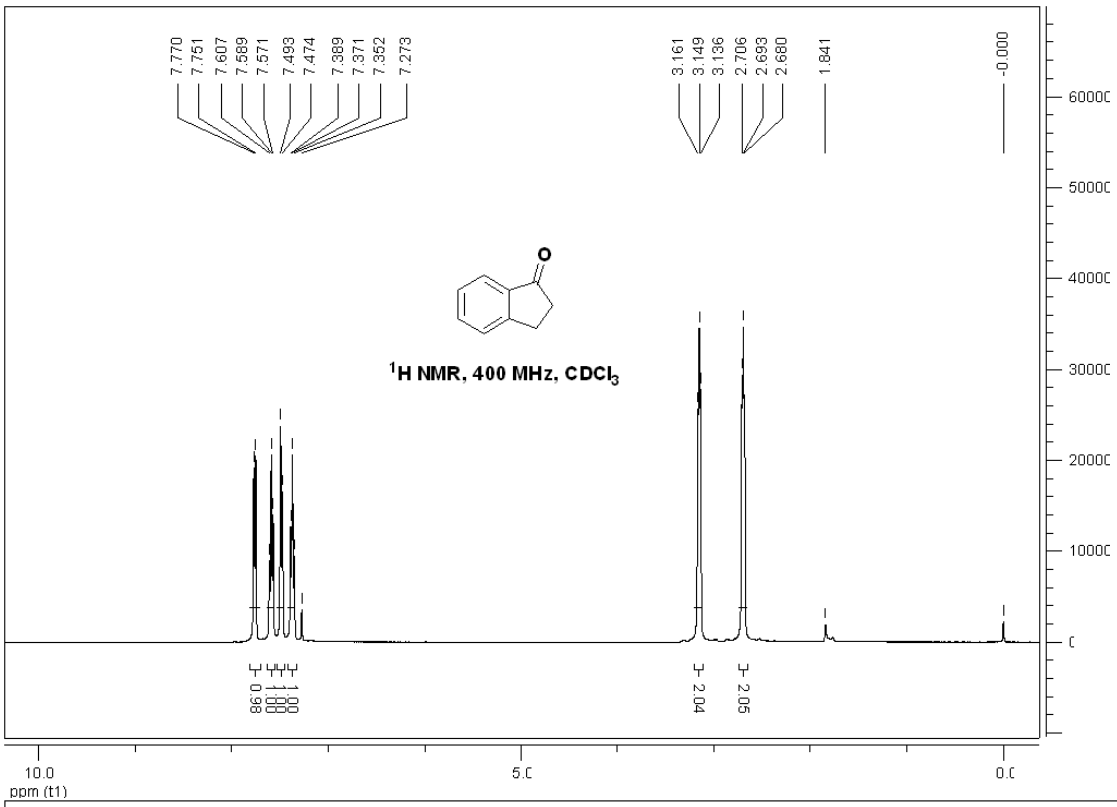

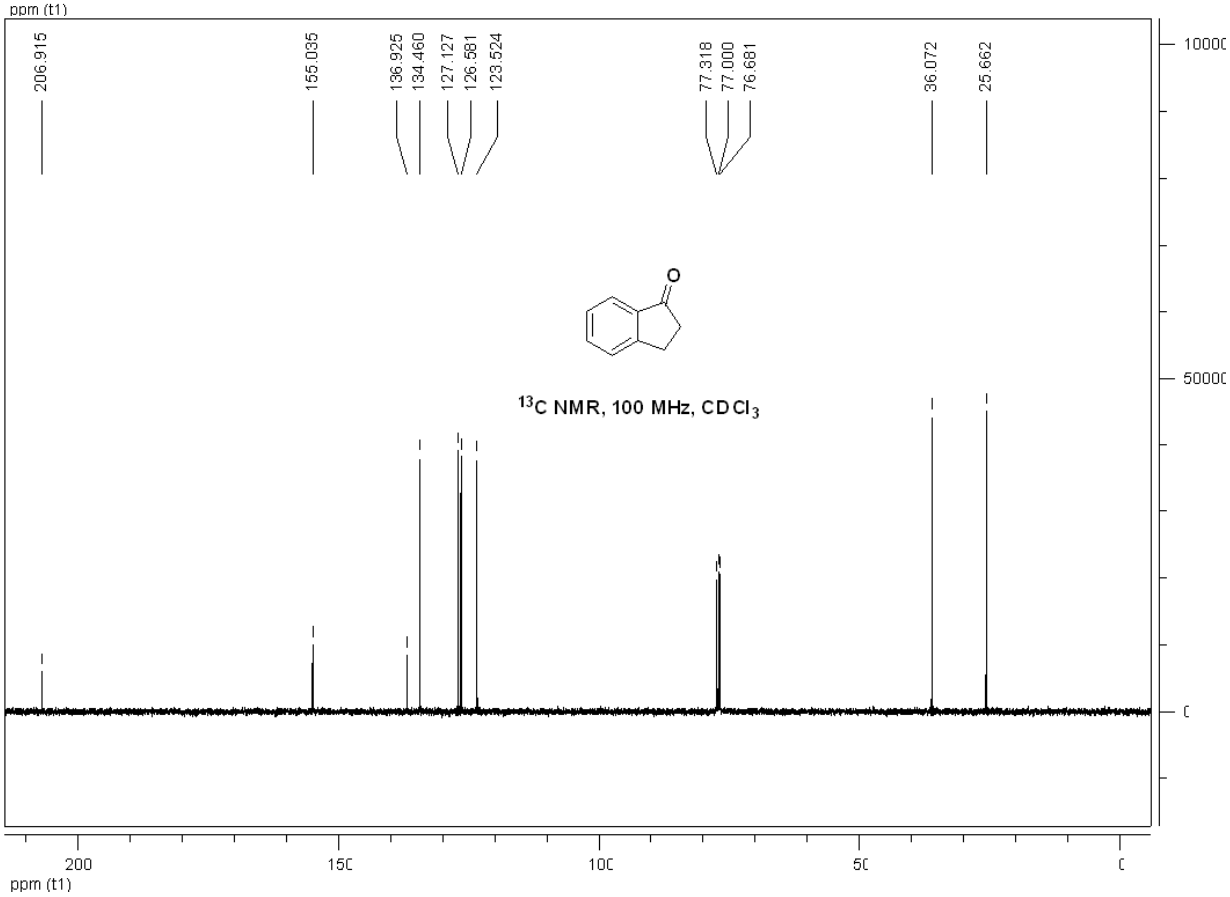

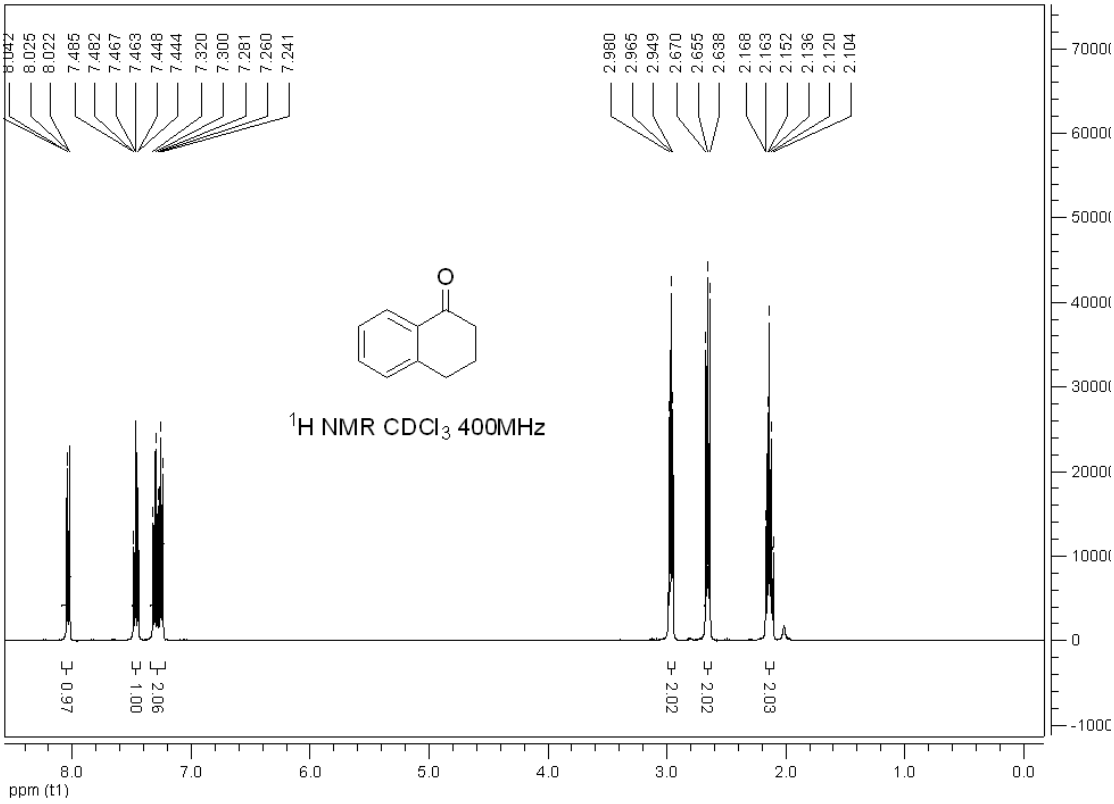

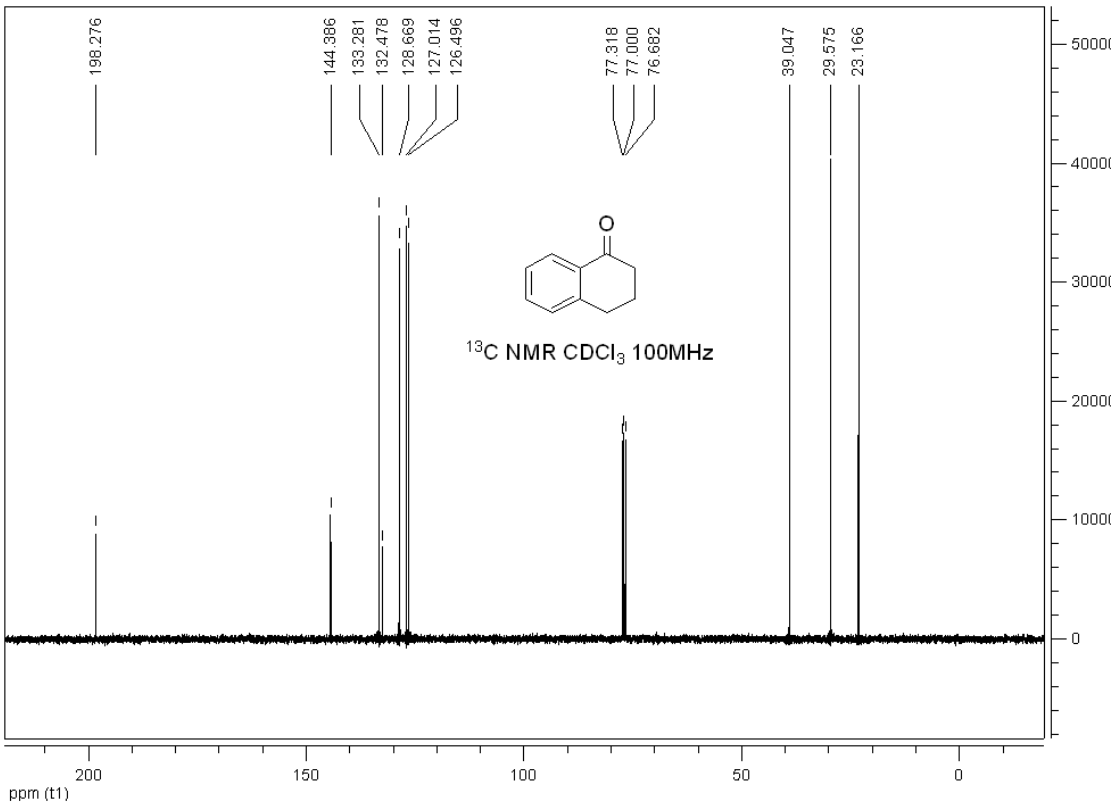

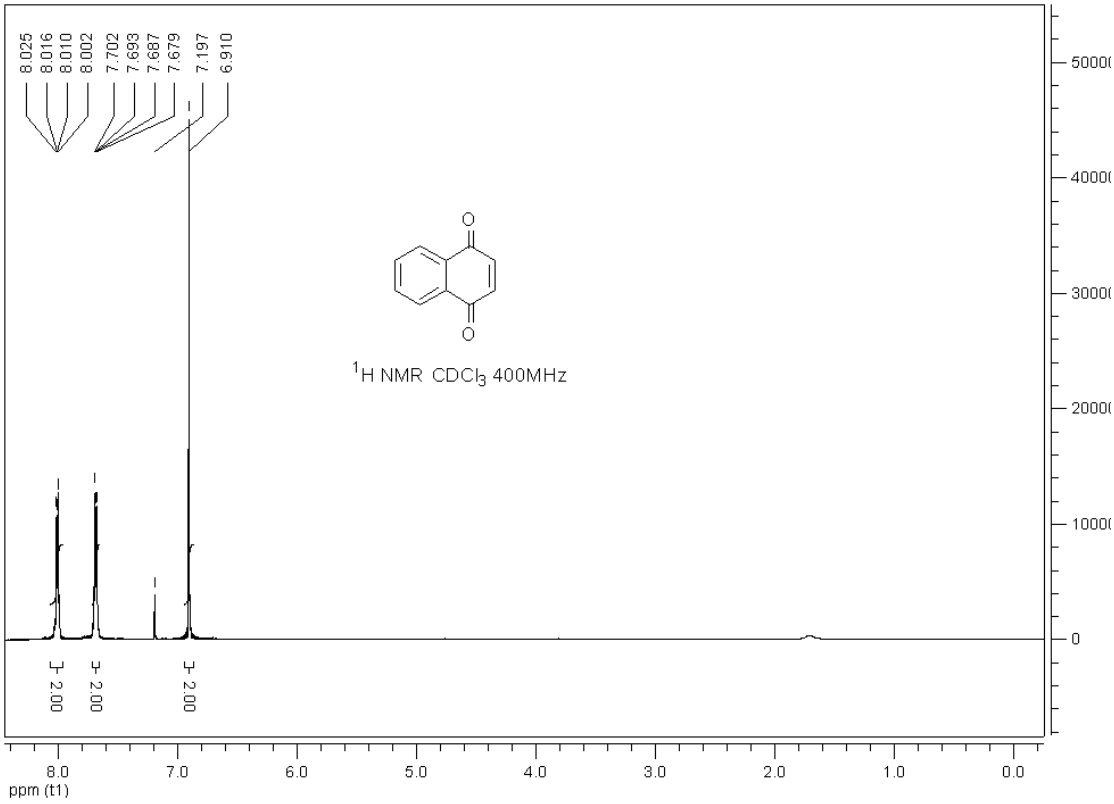

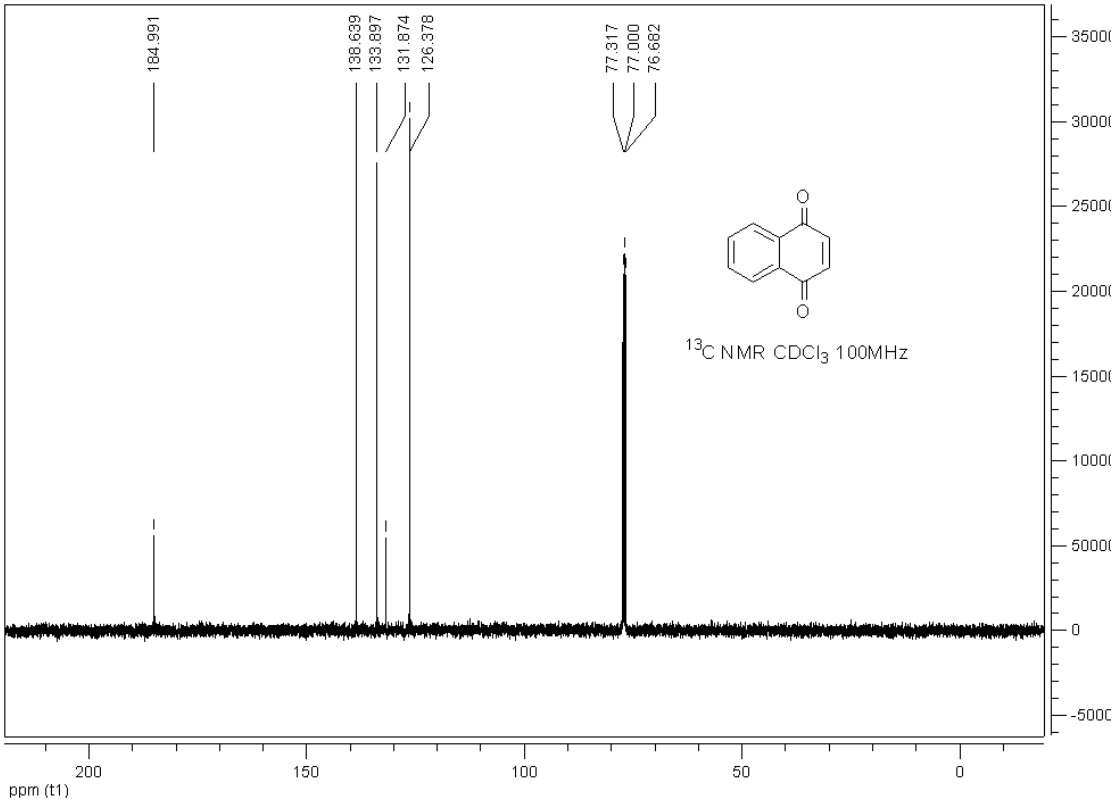

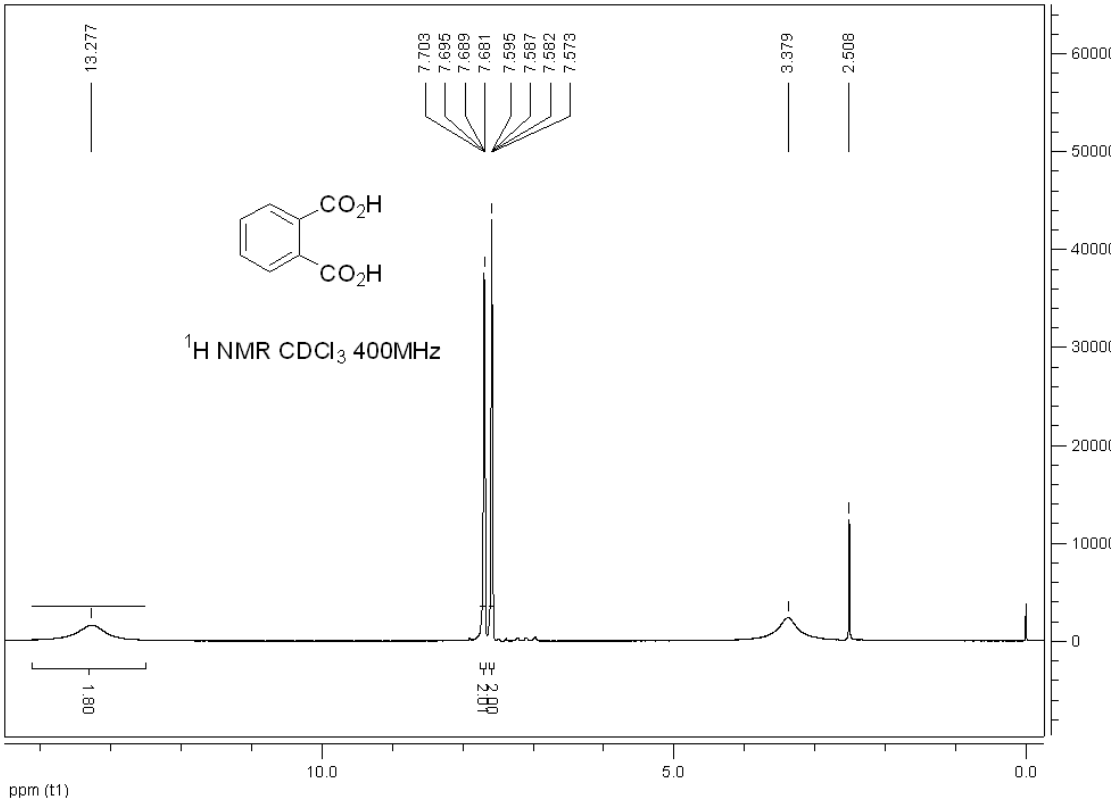

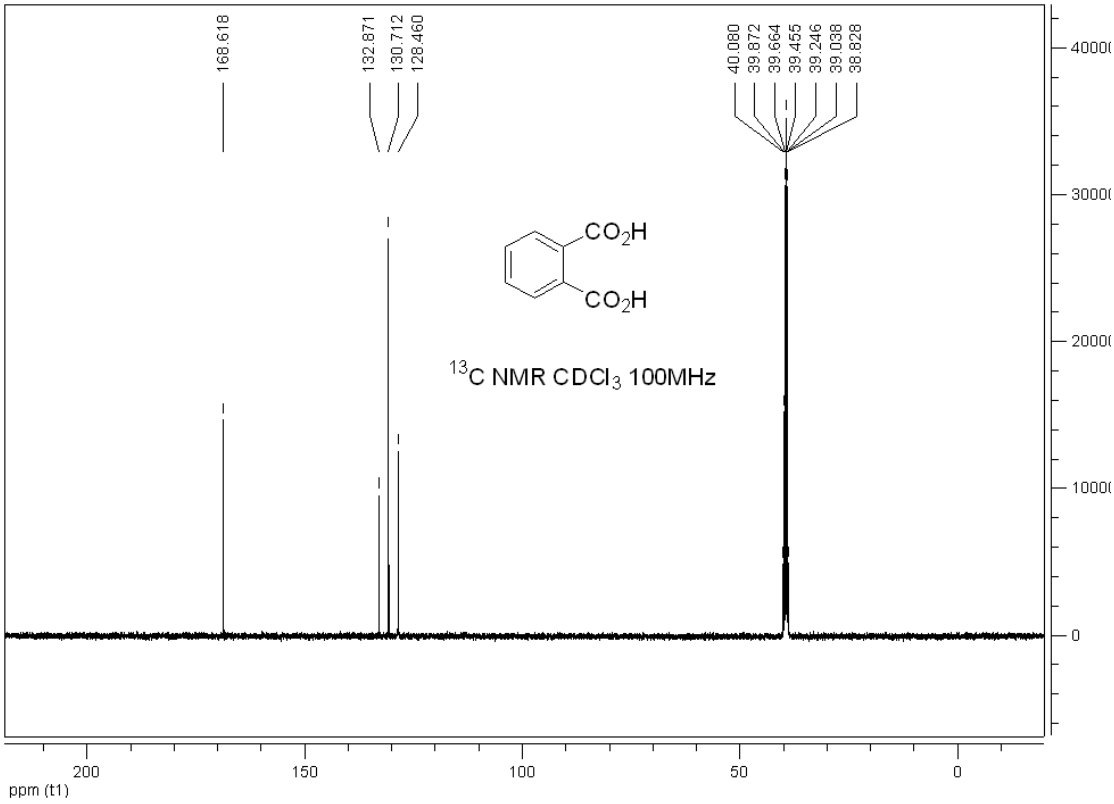

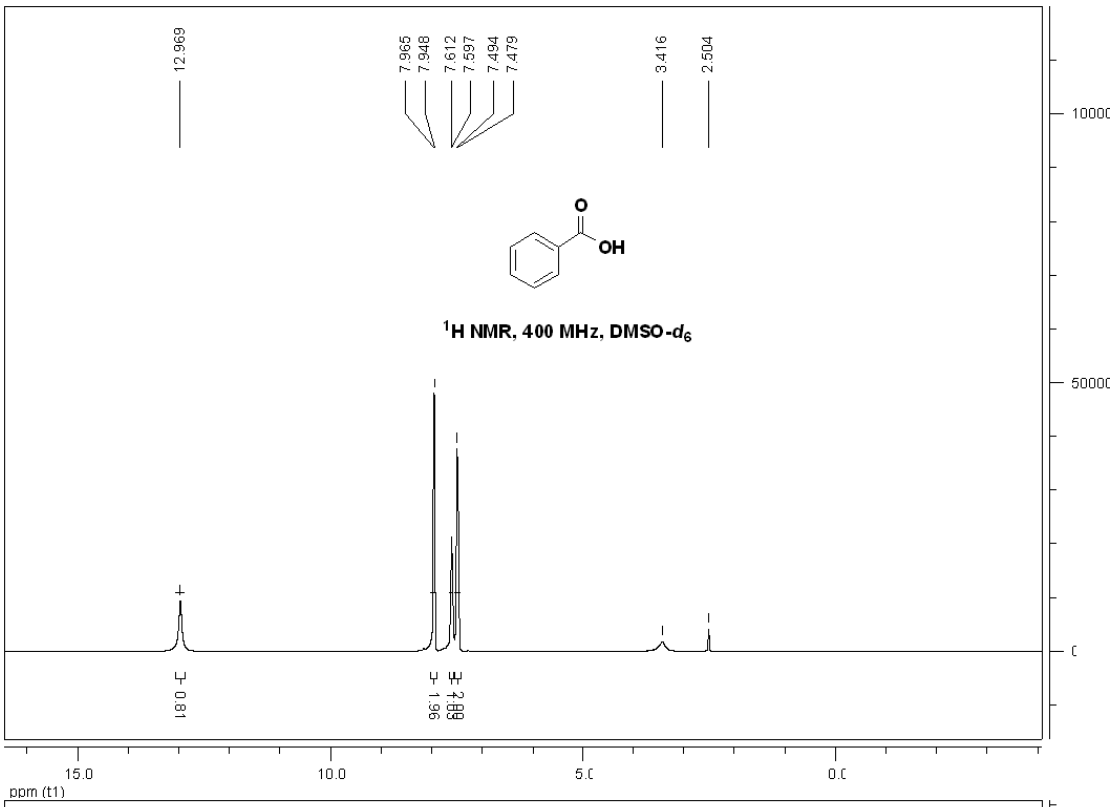

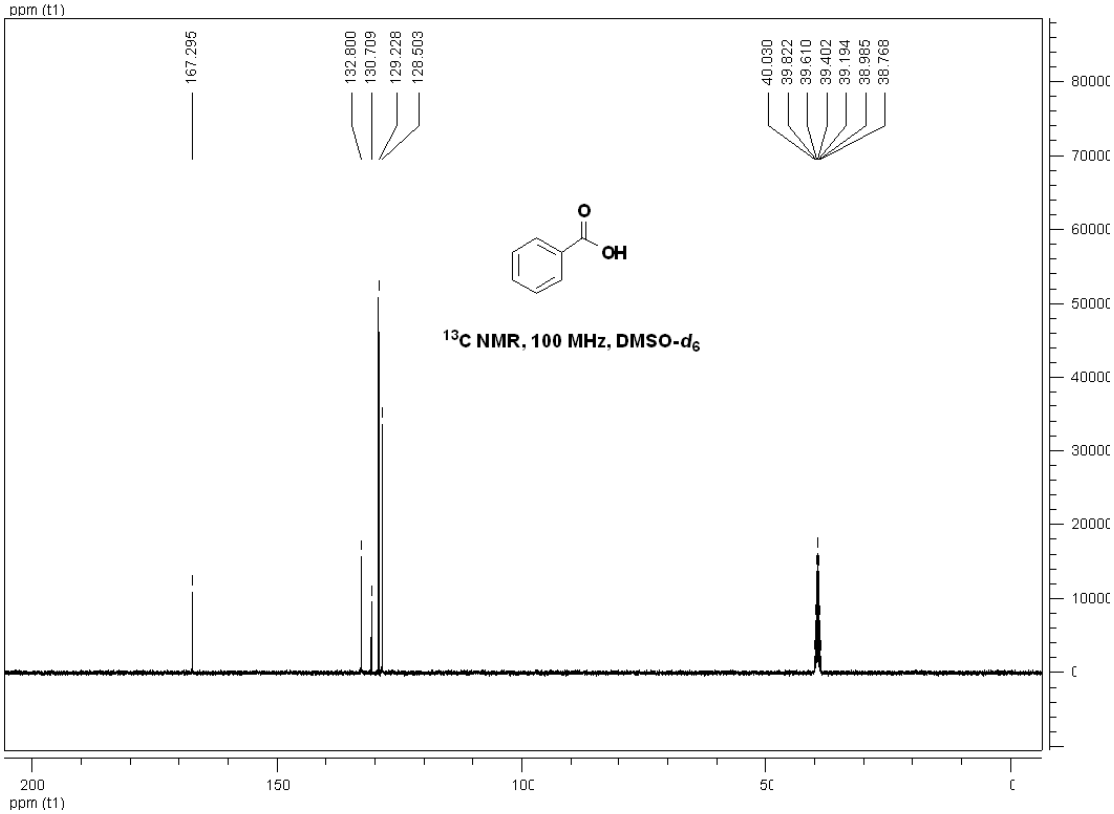

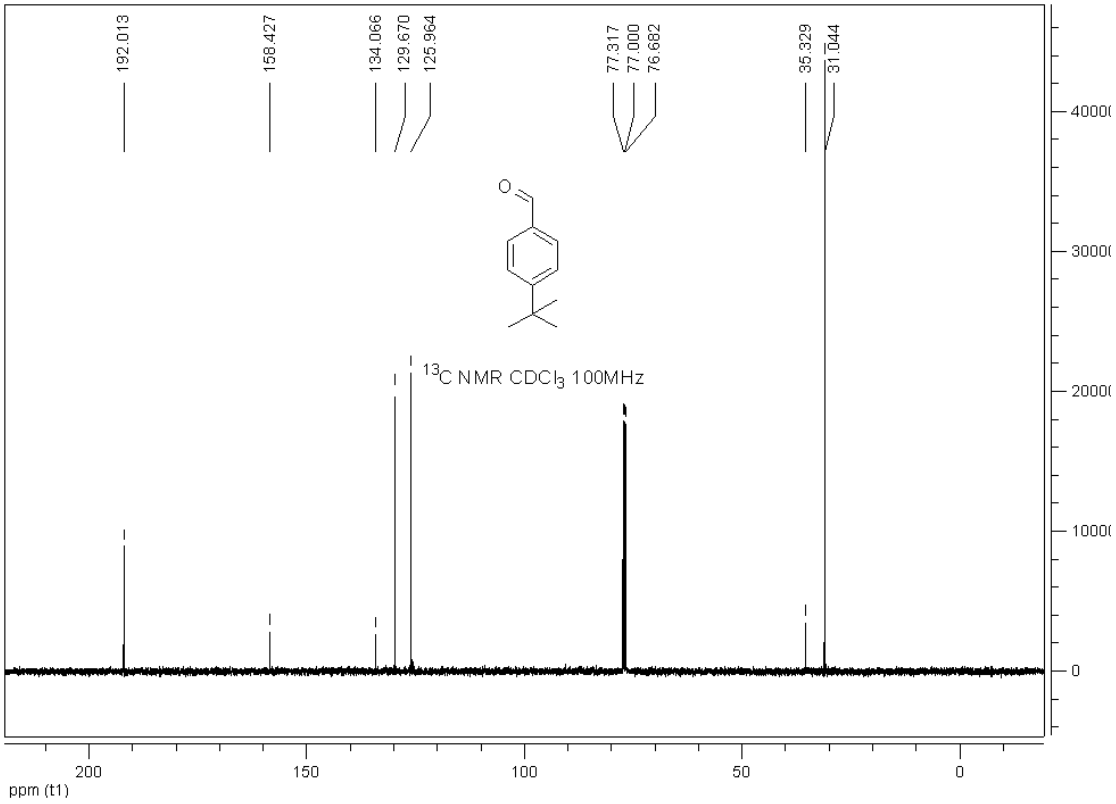
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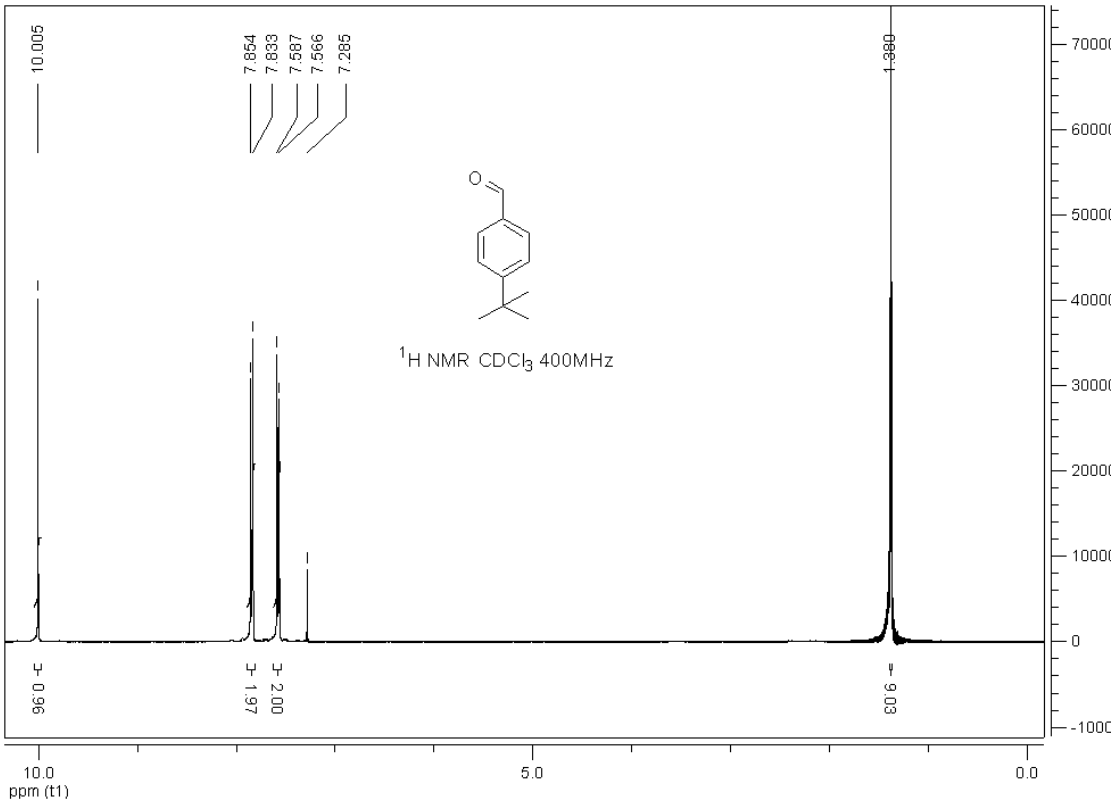
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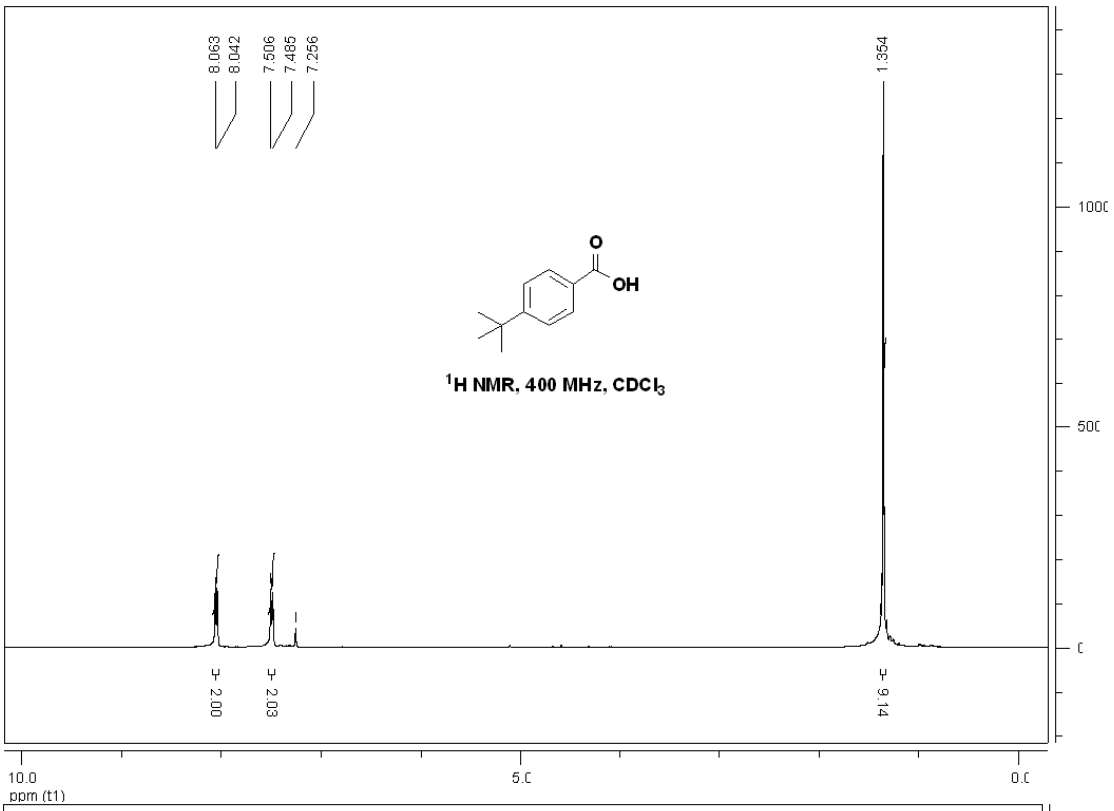
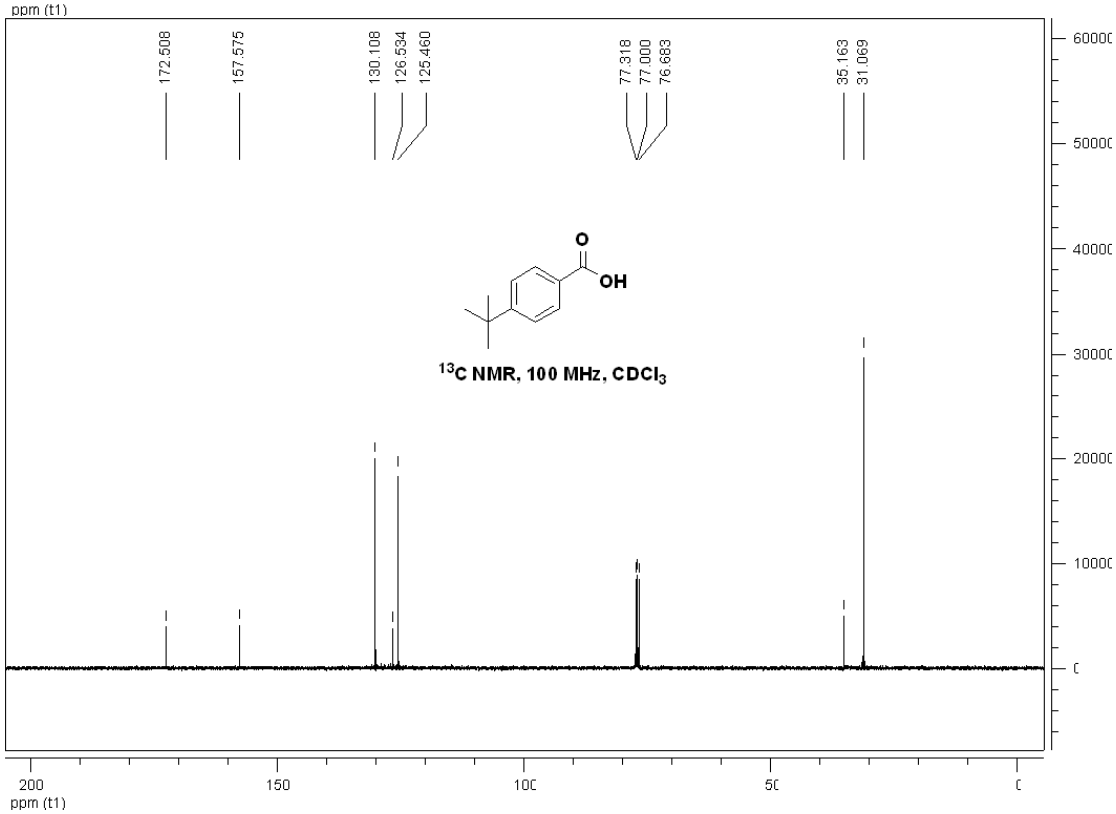
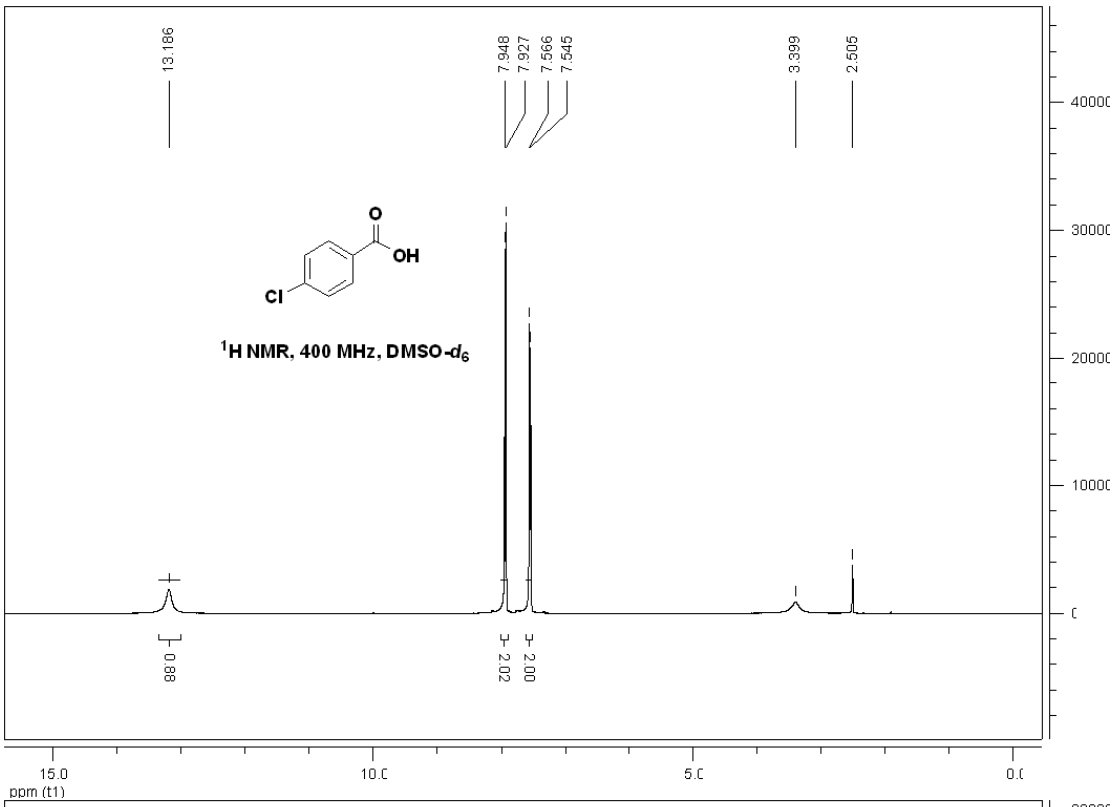
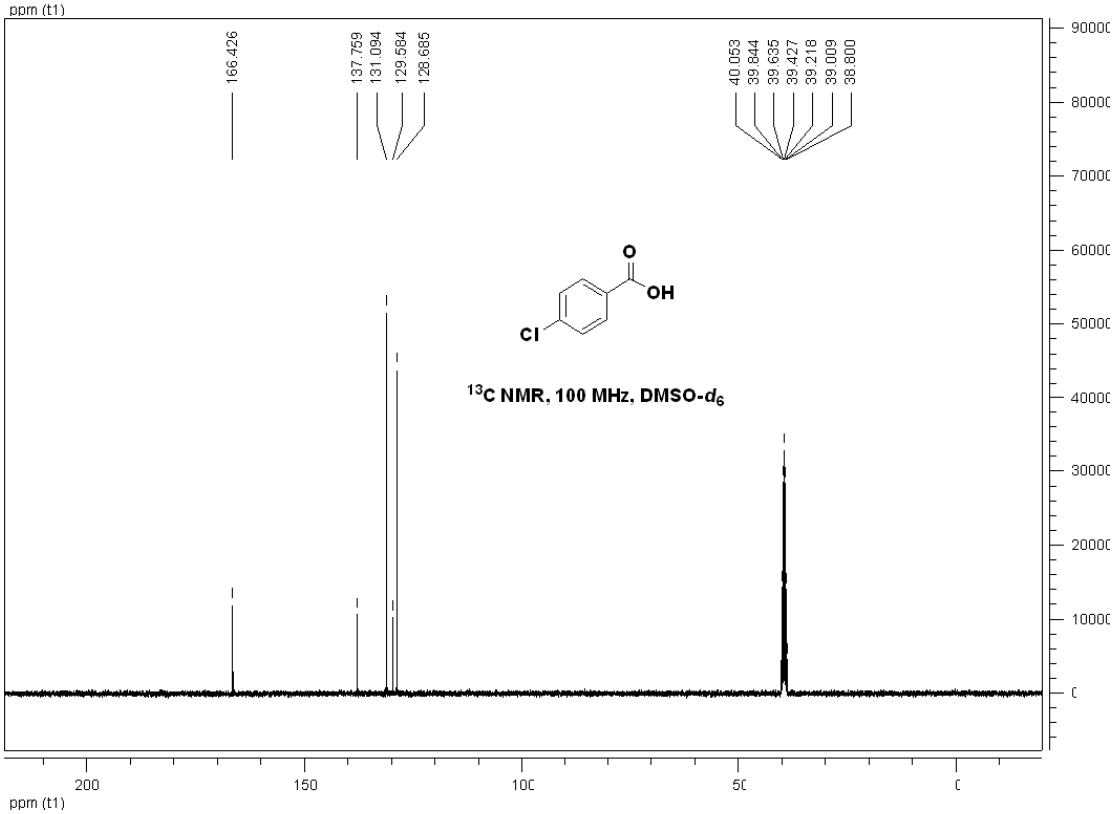
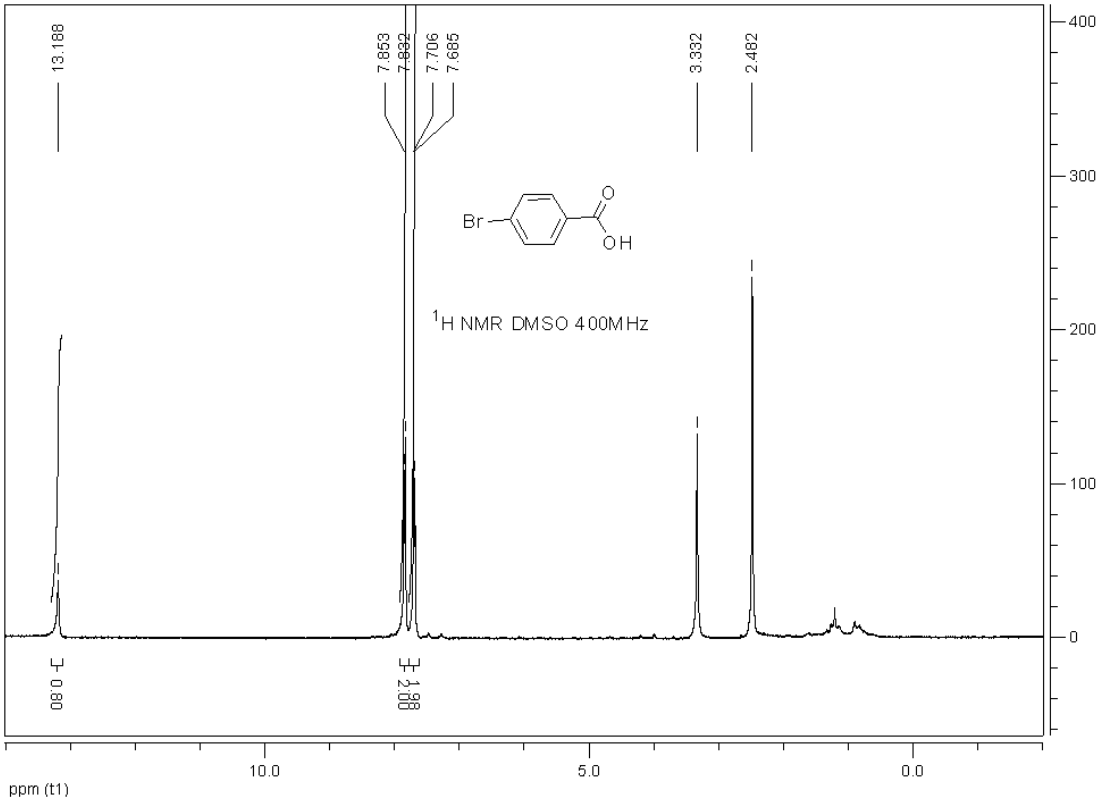
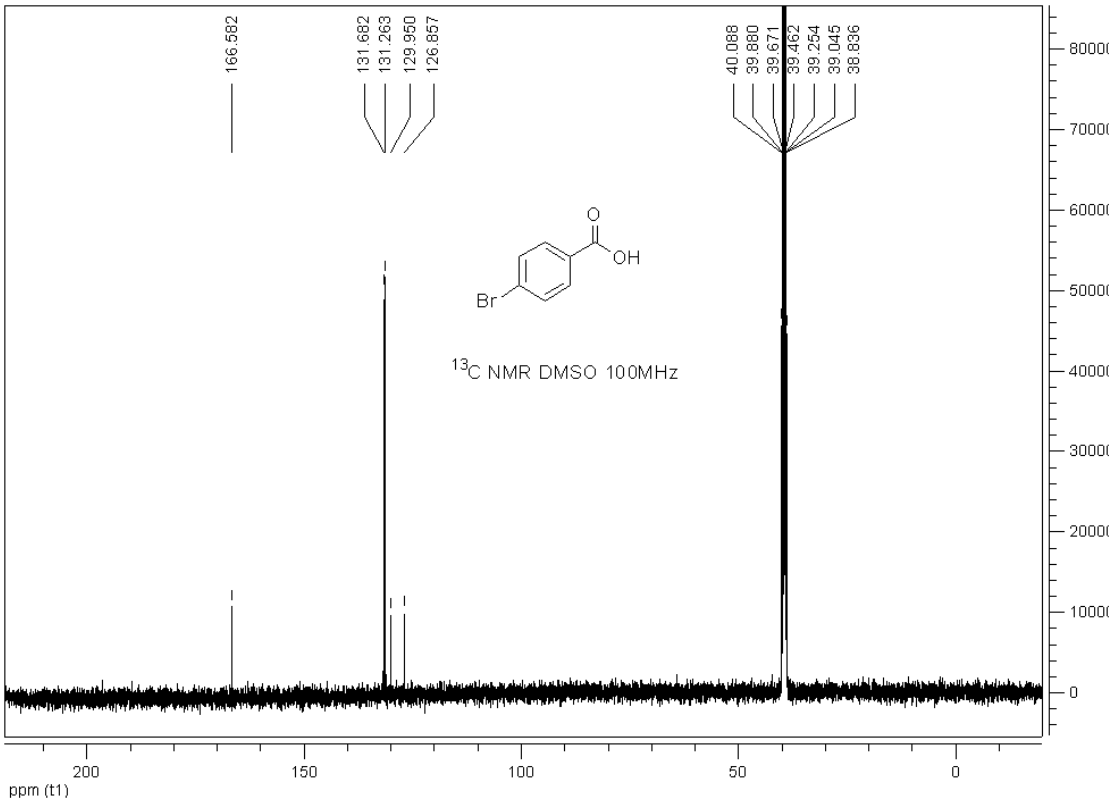


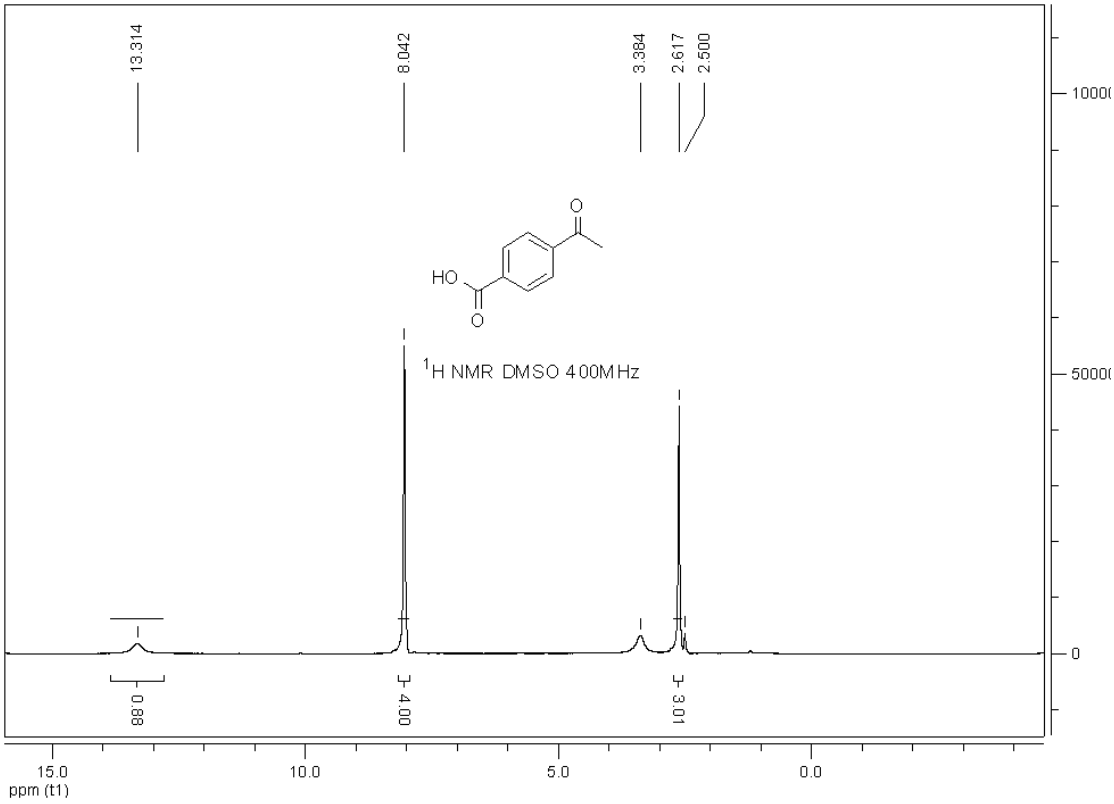


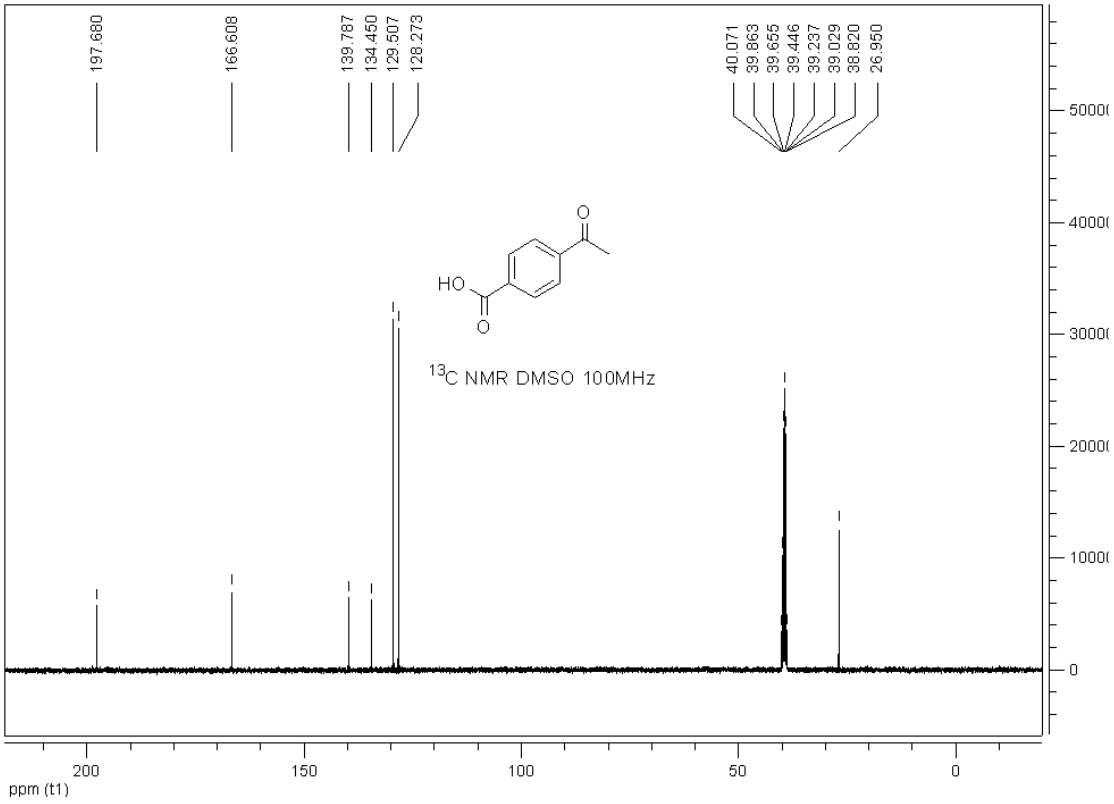


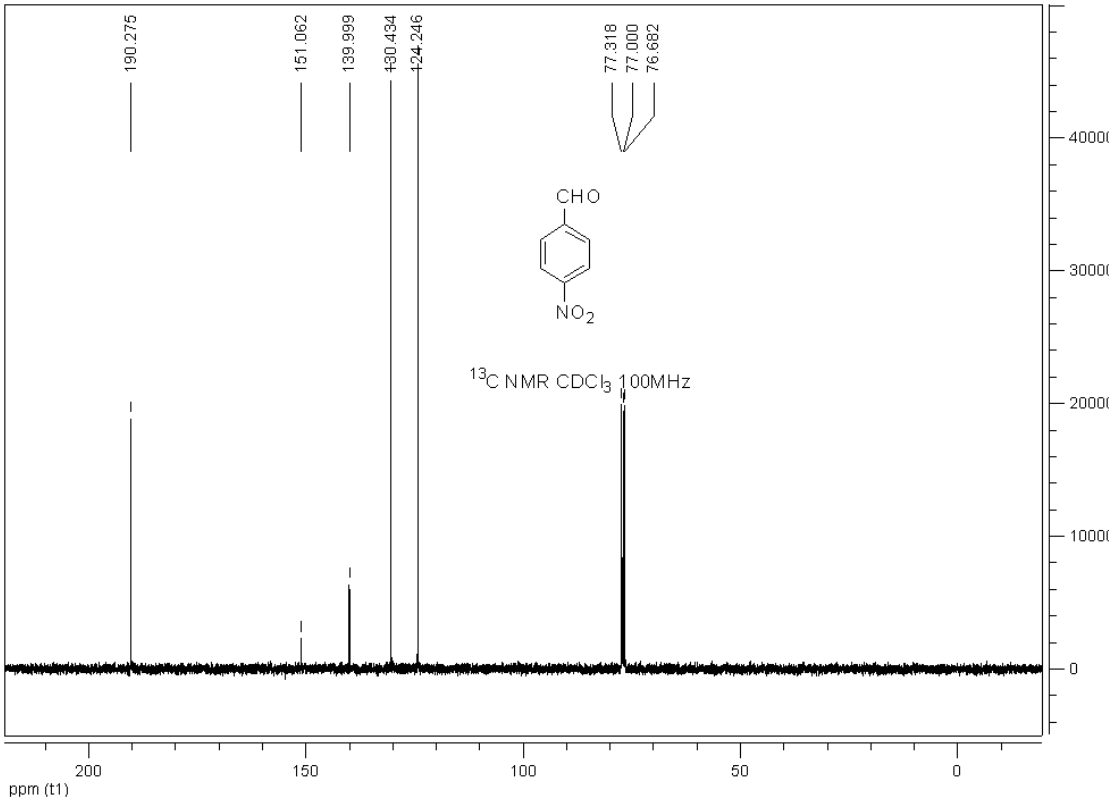


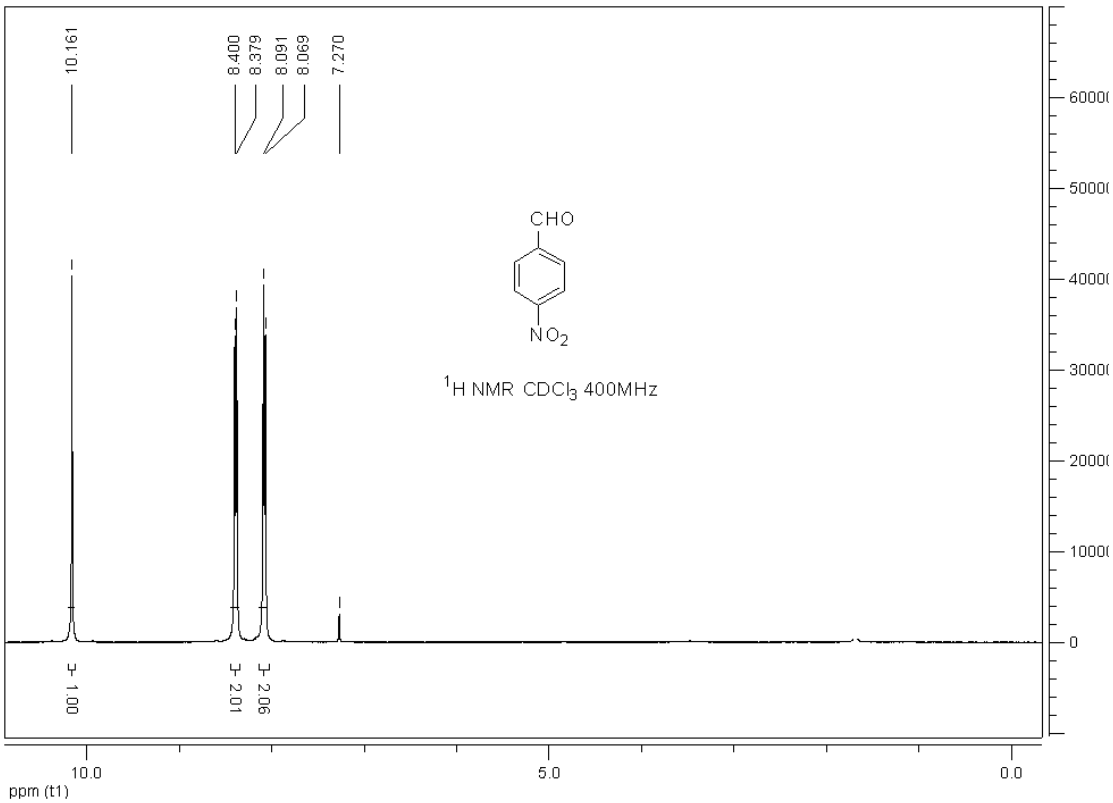


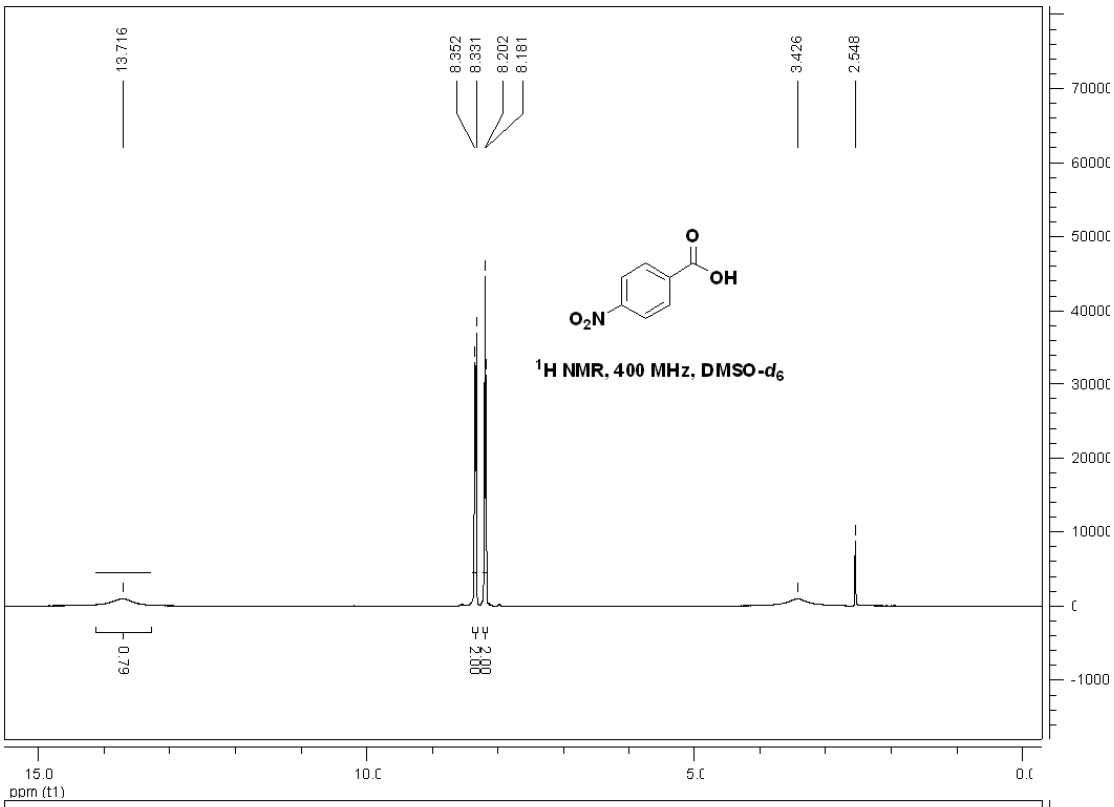


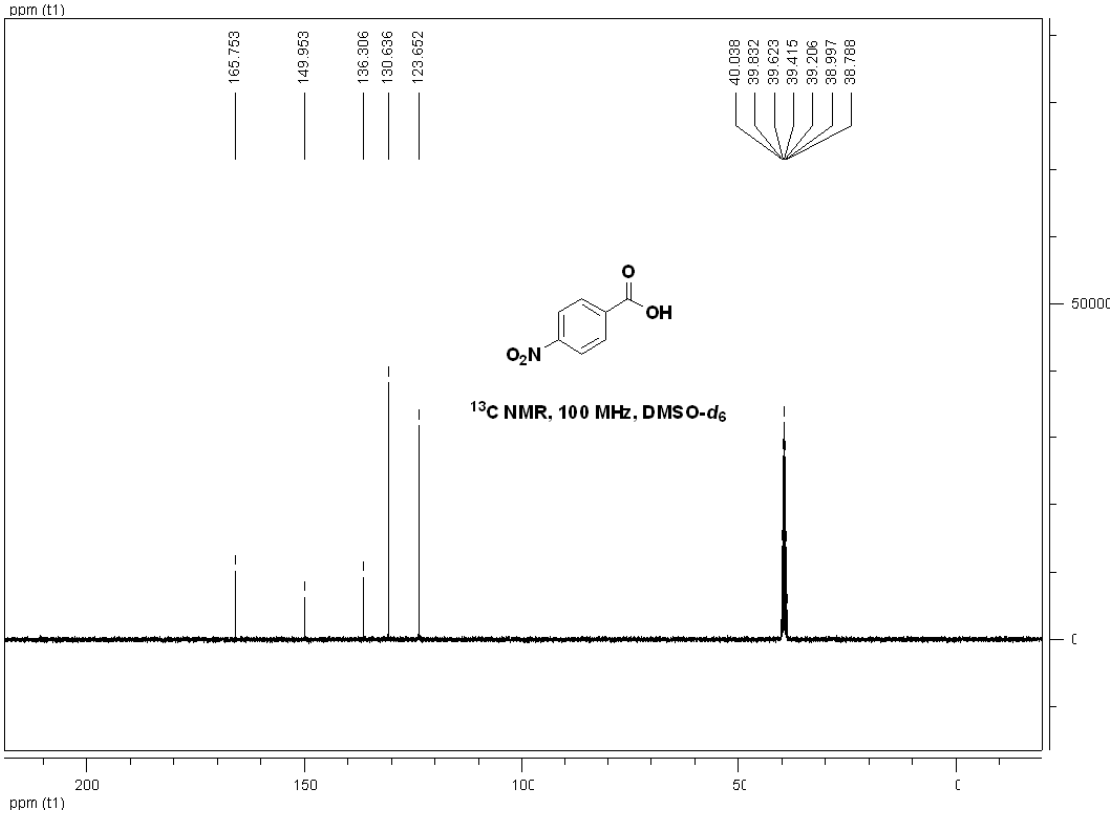


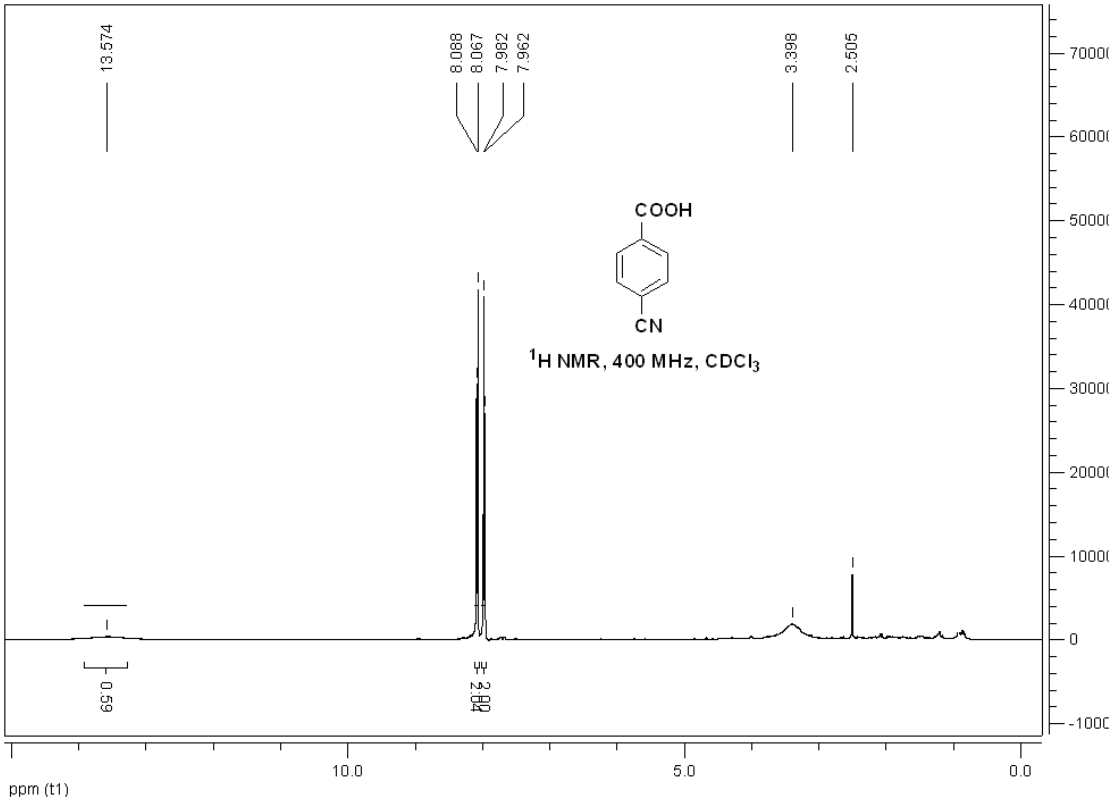


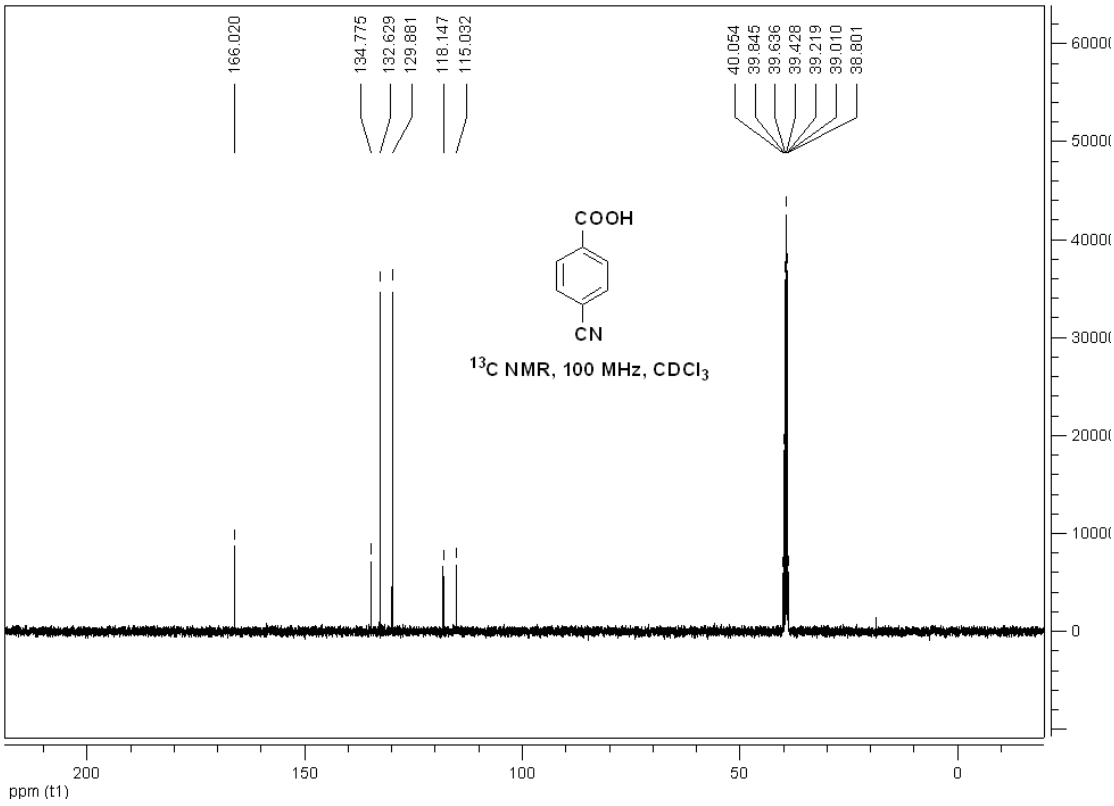


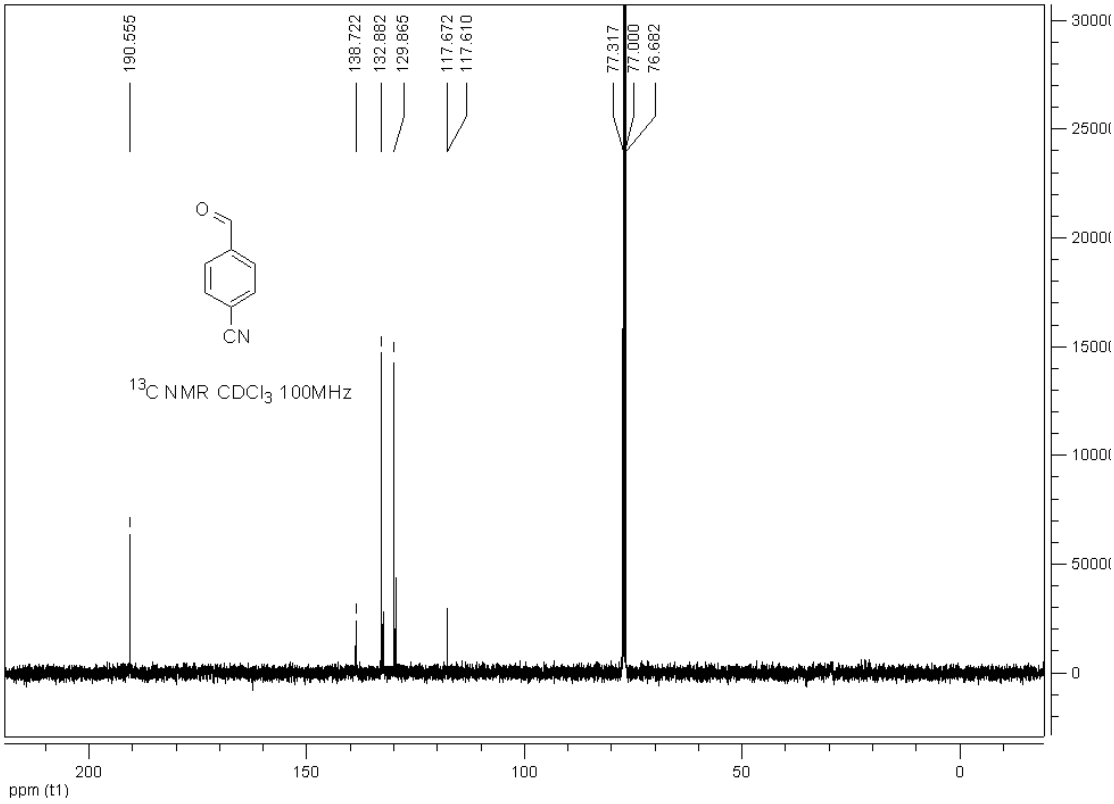


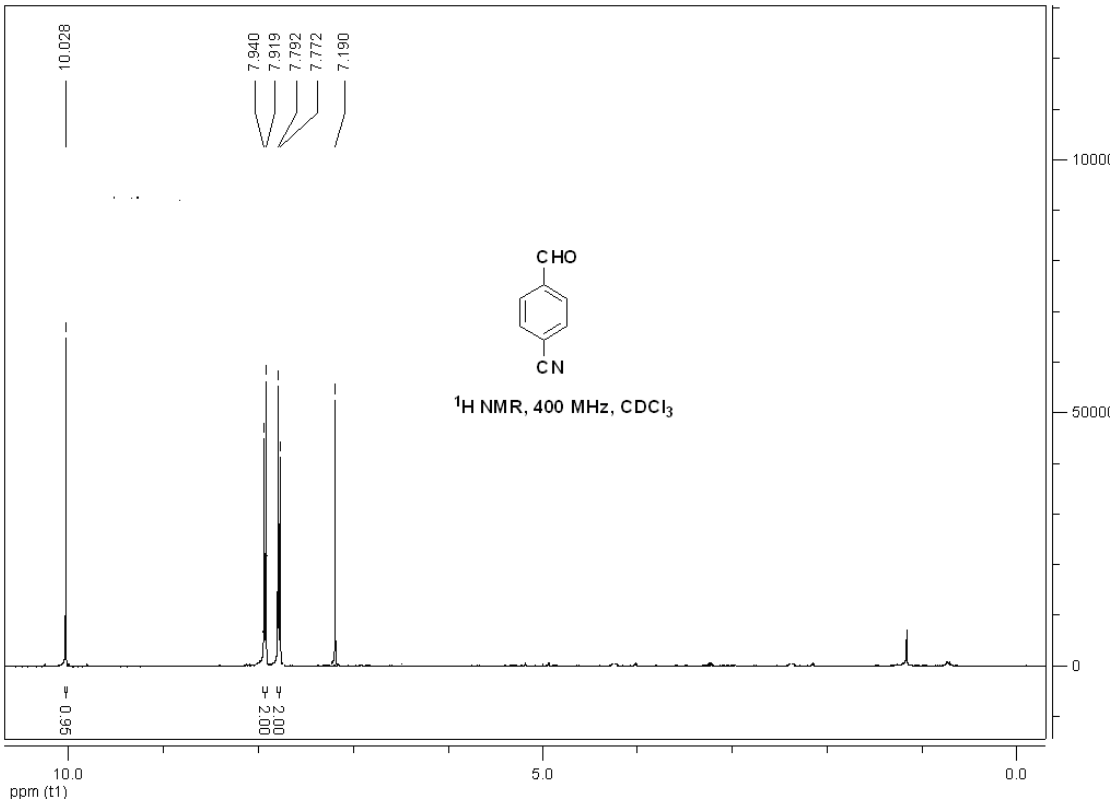

13.716
8.352
8.331
8.202
8.181
3.426
2.548
O
OH
O2N
1H NMR, 400 MHz, DMSO-d6
0.79
2.00
ppm (t1)

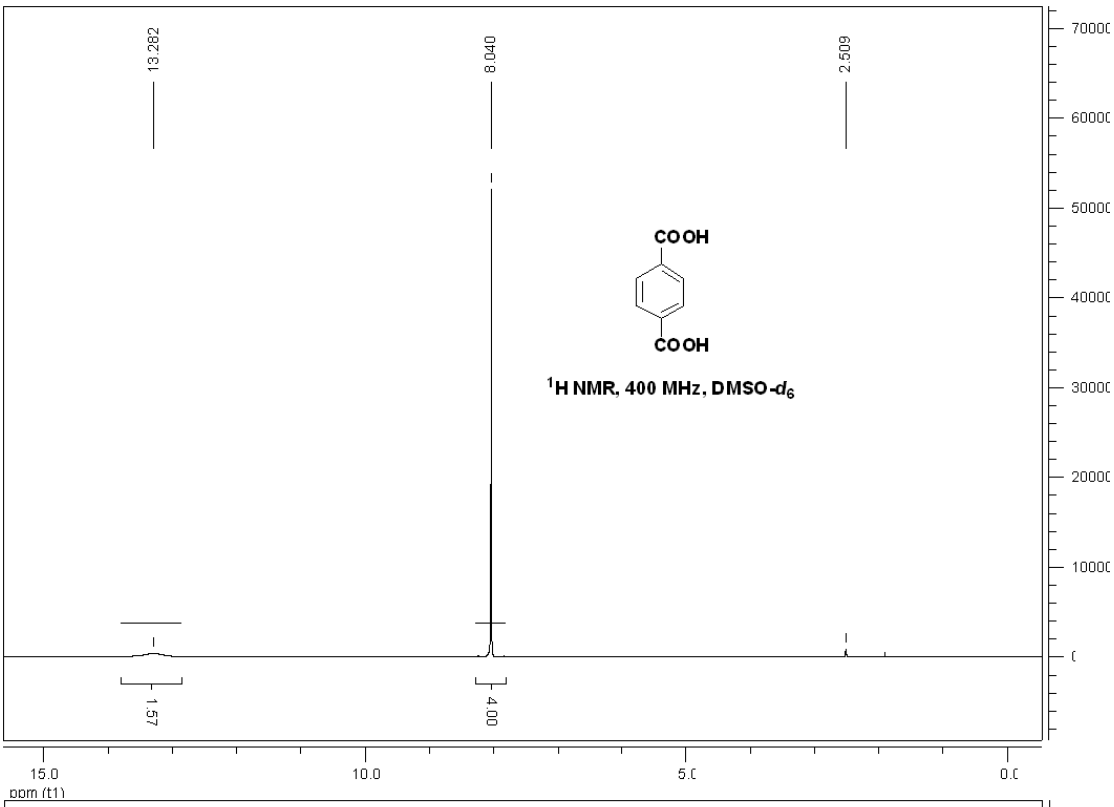

165.753
149.953
136.306
130.636
123.652
40.038
39.832
39.623
39.415
39.206
38.997
38.788
O
OH
O2N
13C NMR, 100 MHz, DMSO-d6
ppm (t1)

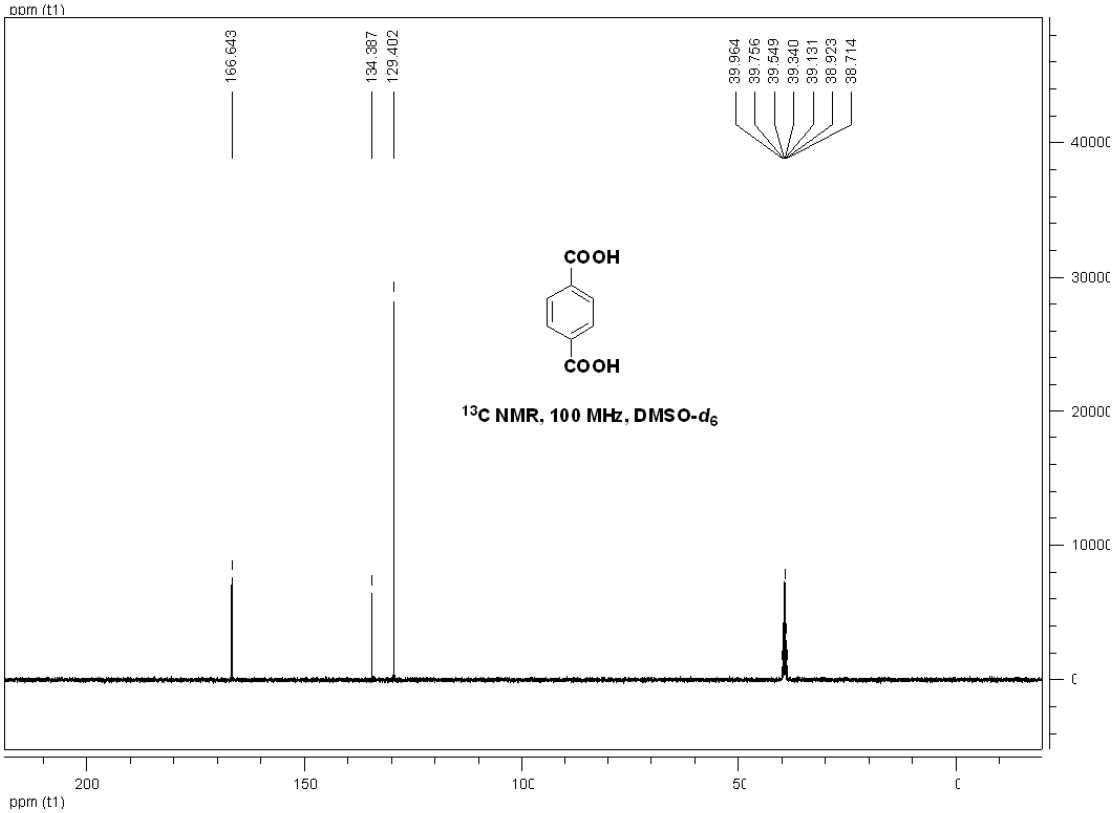


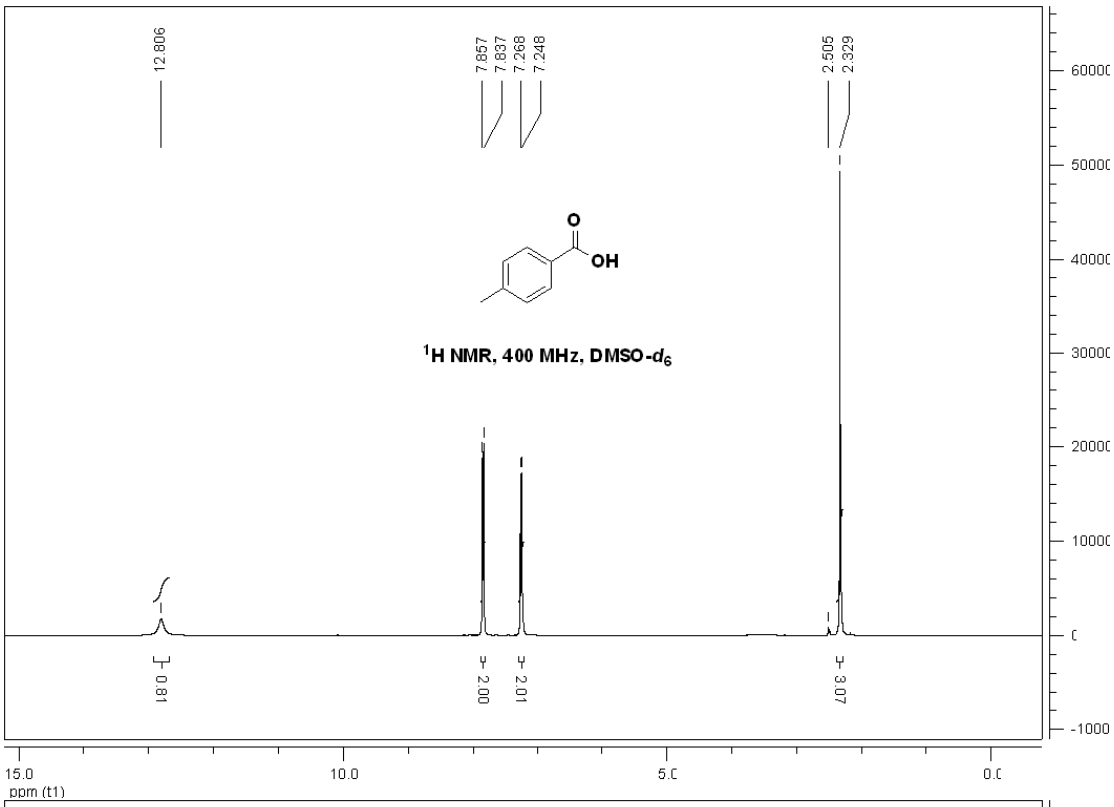


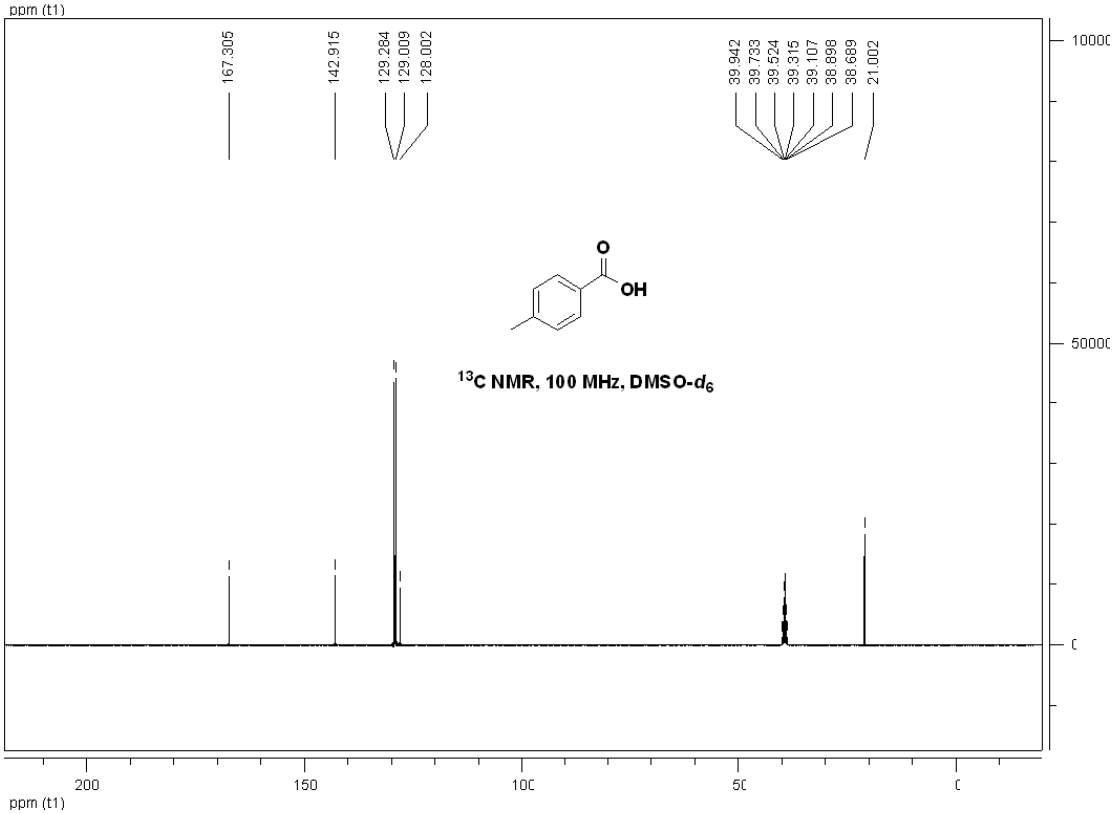


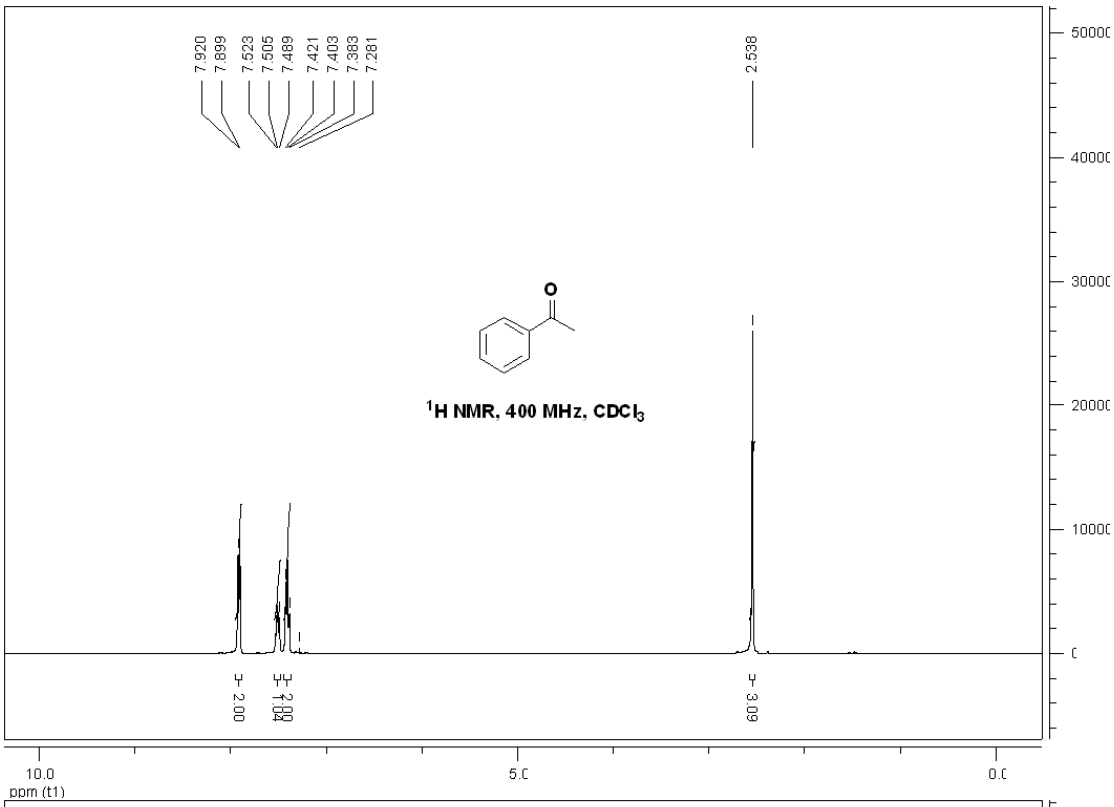


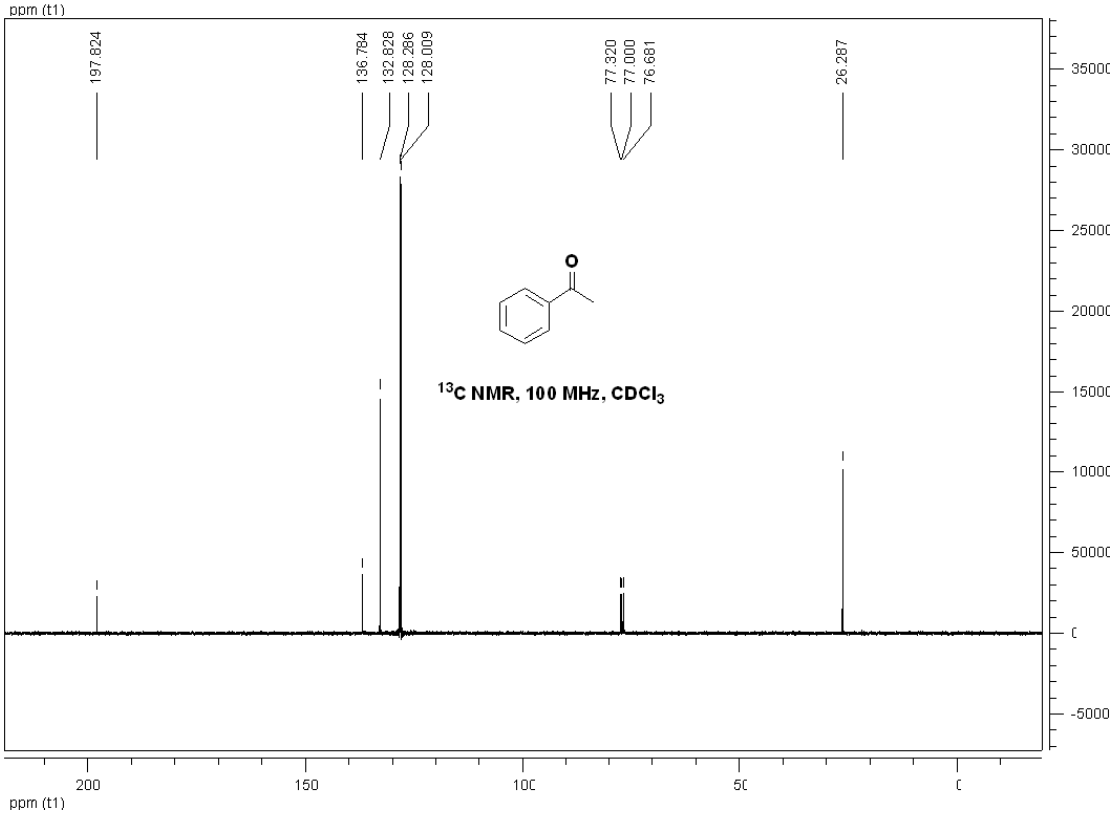

13.282
8.040
2.509
COOH
COOH
^{1}H NMR, 400 MHz, DMSO-d_6
1.57
4.00
ppm (t1)

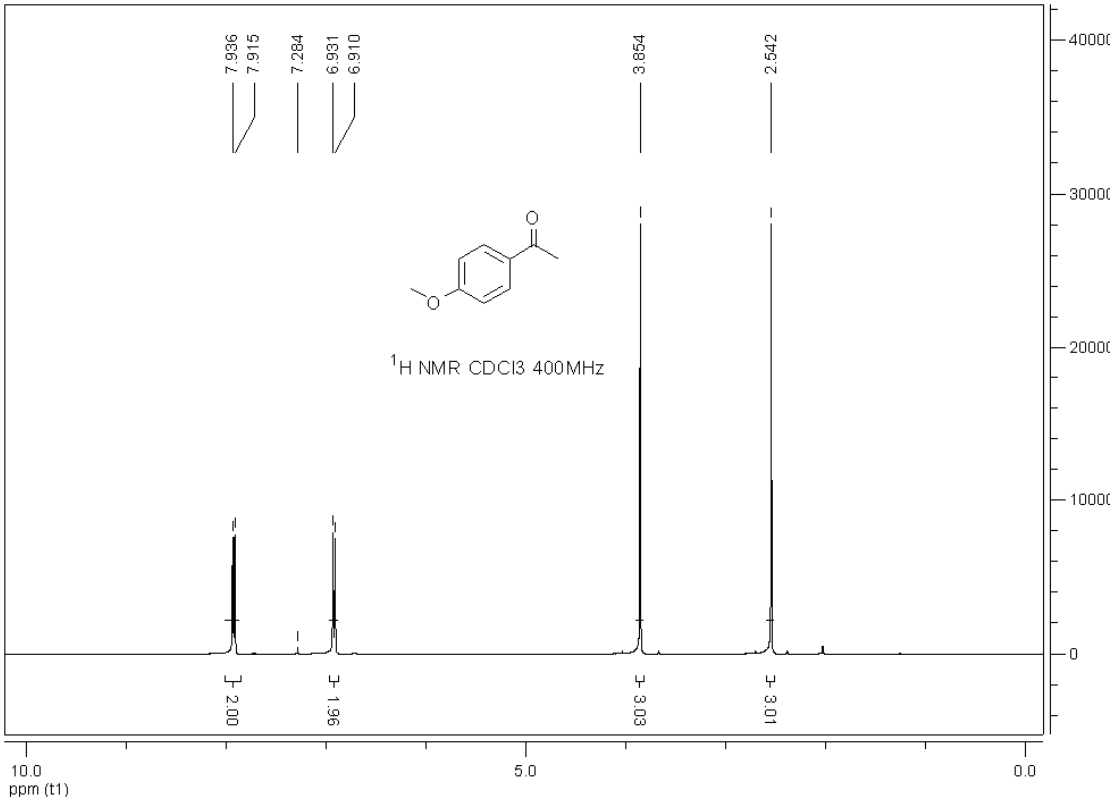

166.643
134.387
129.402
39.964
39.756
39.549
39.340
39.131
38.923
38.714
COOH
COOH
^{13}C NMR, 100 MHz, DMSO-d_6
ppm (t1)

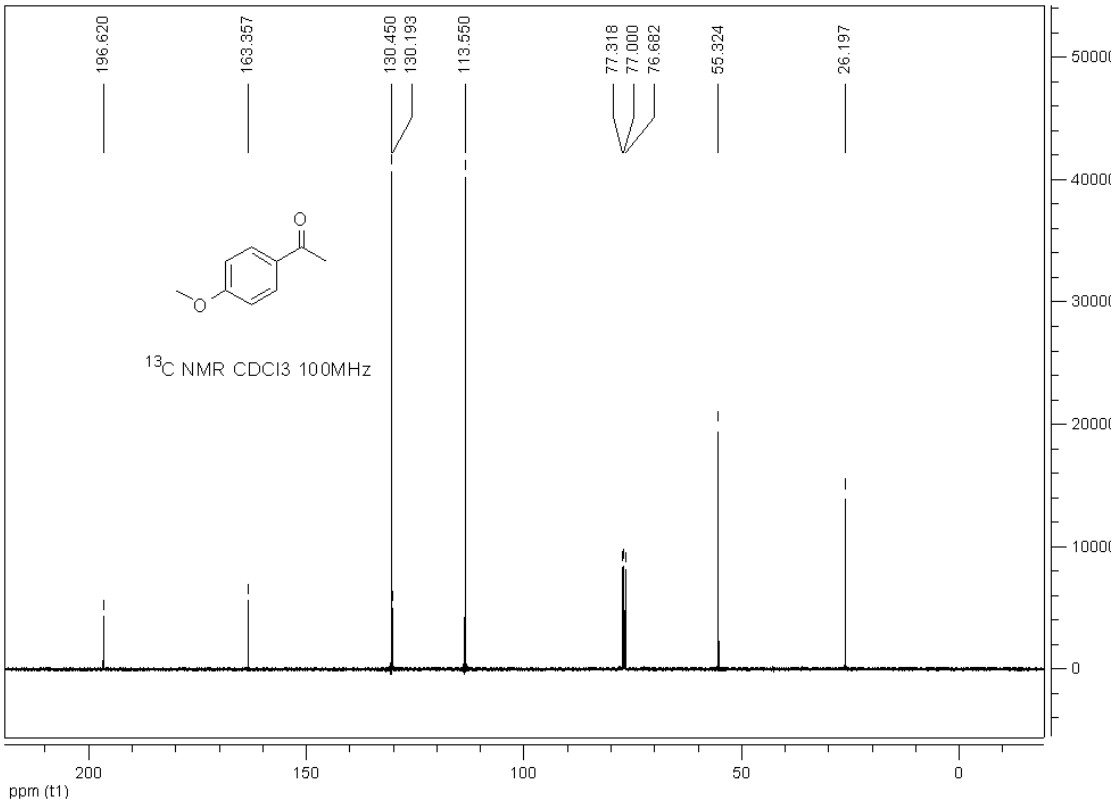

12.806
7.857
7.837
7.268
7.248
2.505
2.329
O
OH
^{1}H NMR, 400 MHz, DMSO-d_6
0.81
2.00
2.01
3.07
15.0
10.0
5.0
0.0
ppm (t1)

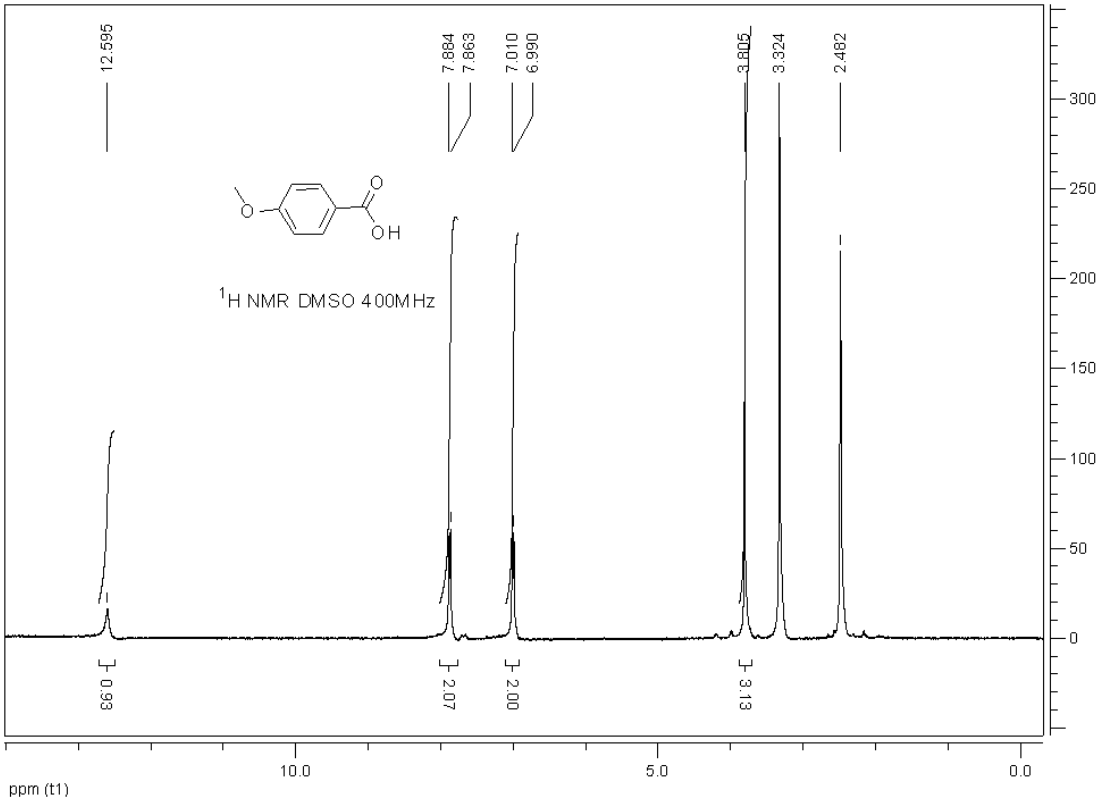

167.305
142.915
129.284
129.009
128.002
39.942
39.733
39.524
39.315
39.107
38.898
38.689
21.002
O
OH
^{13}C NMR, 100 MHz, DMSO-d_6
200
150
100
50
0
ppm (t1)

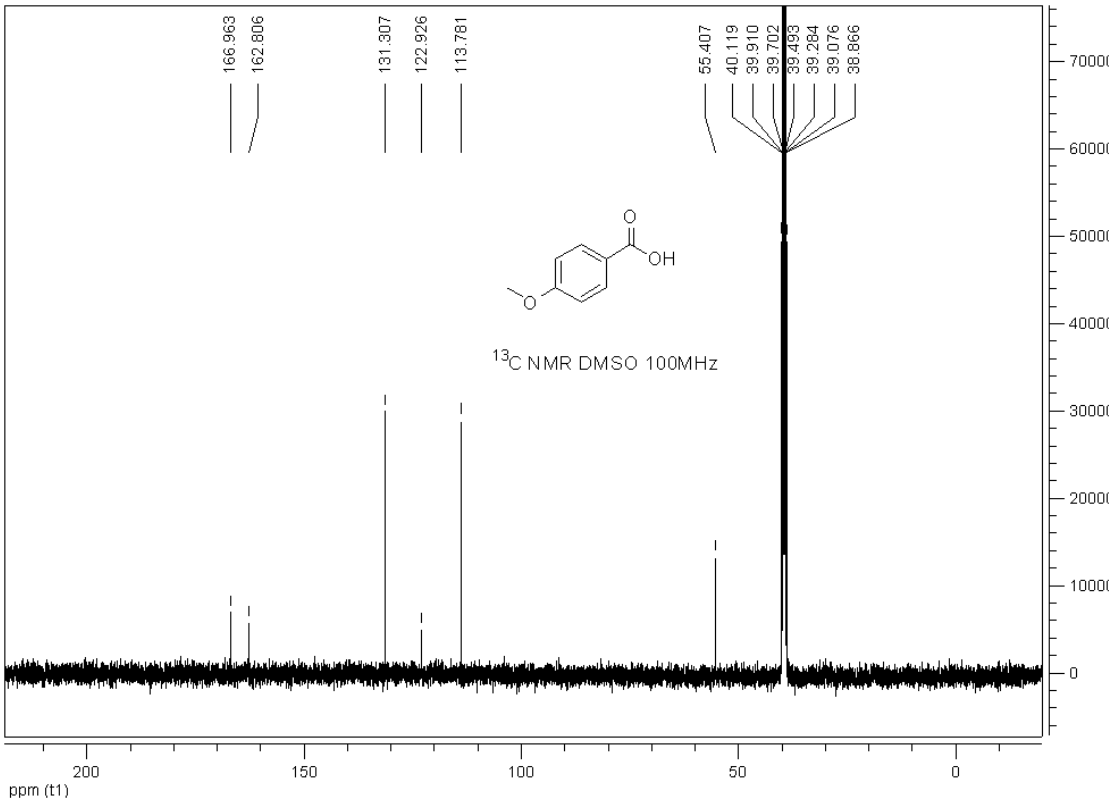

7.920
7.899
7.523
7.505
7.489
7.421
7.403
7.383
7.281
2.538
O
^{1}H NMR, 400 MHz, CDCl$_3$
2.00
2.04
3.09
10.0
5.0
0.0
ppm (t1)

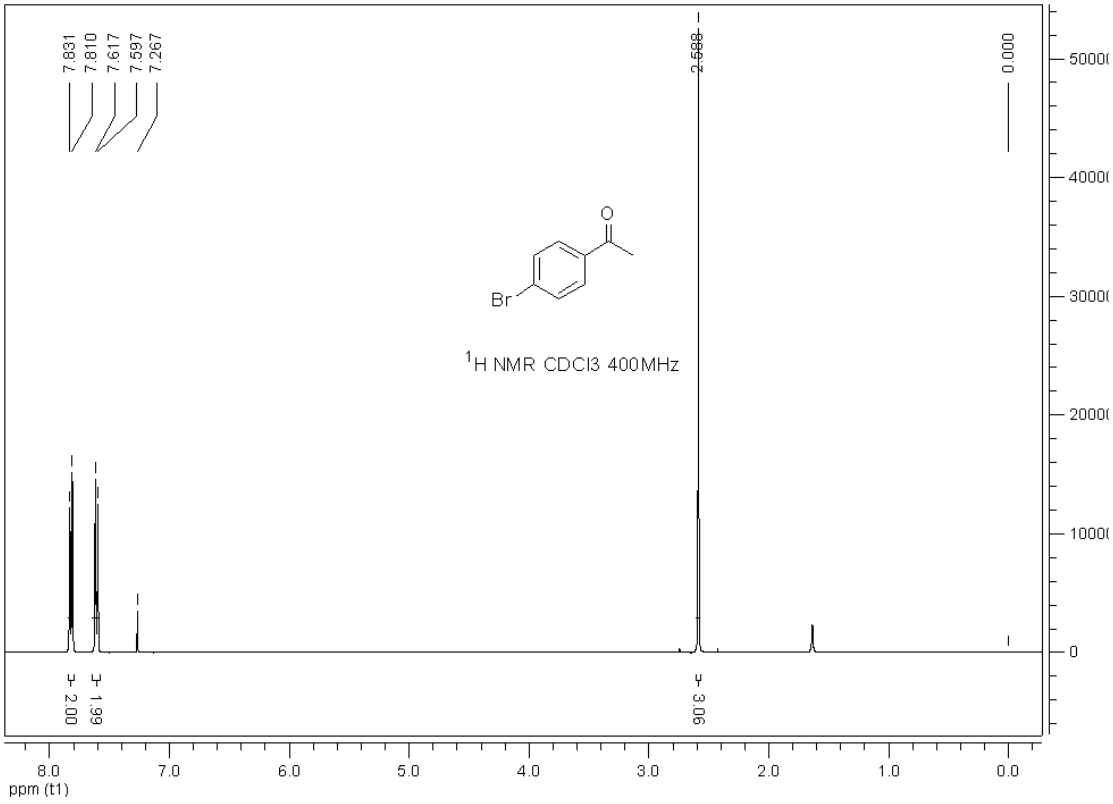

197.824
136.784
132.828
128.286
128.009
77.320
77.000
76.681
26.287
O
^{13}C NMR, 100 MHz, CDCl$_3$
200
150
100
50
0
ppm (t1)

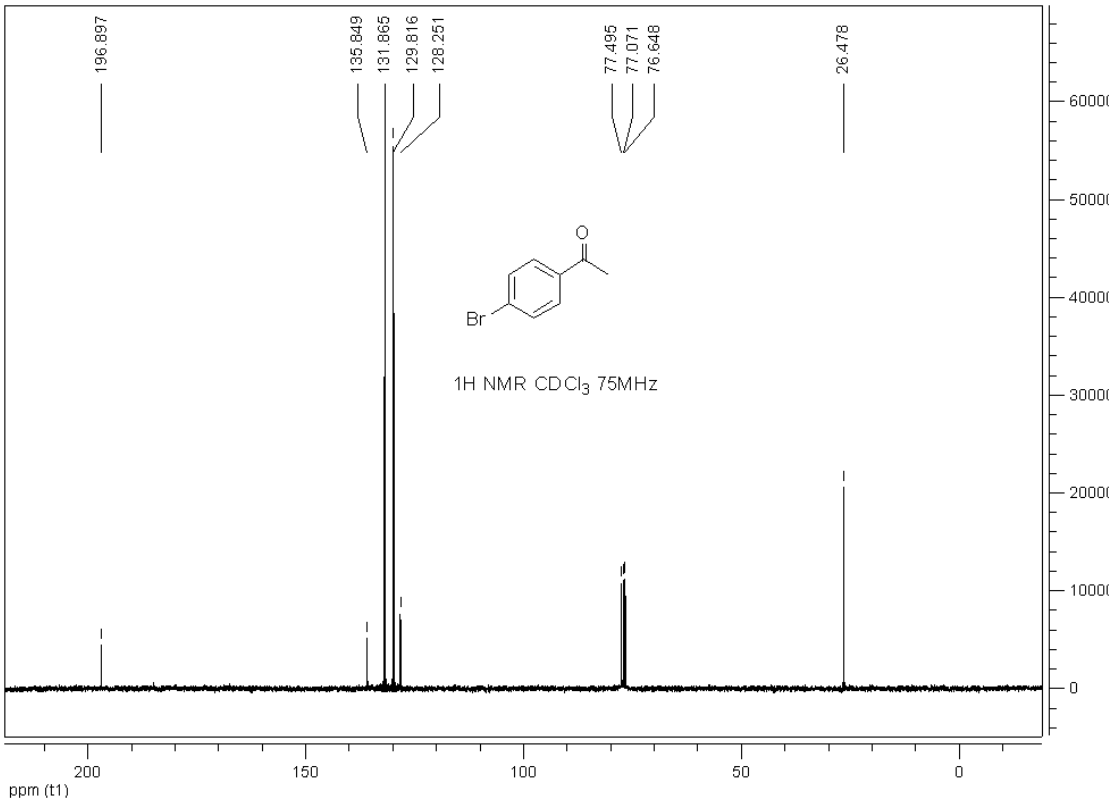


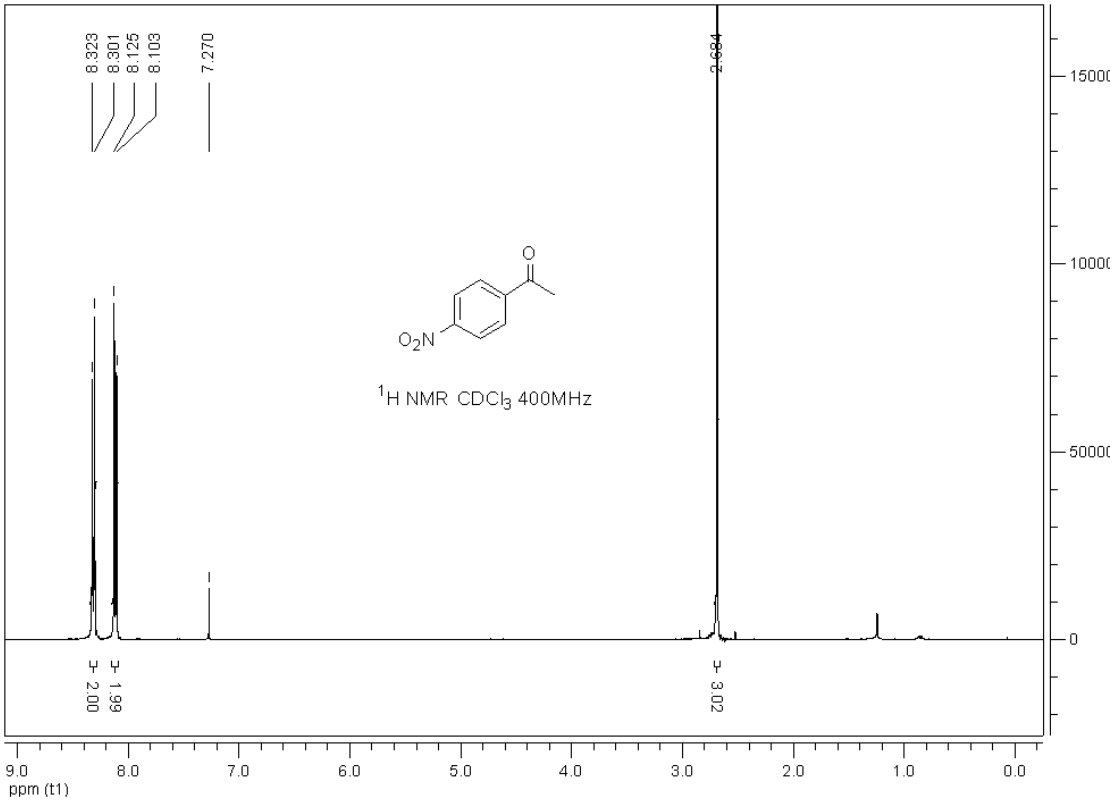


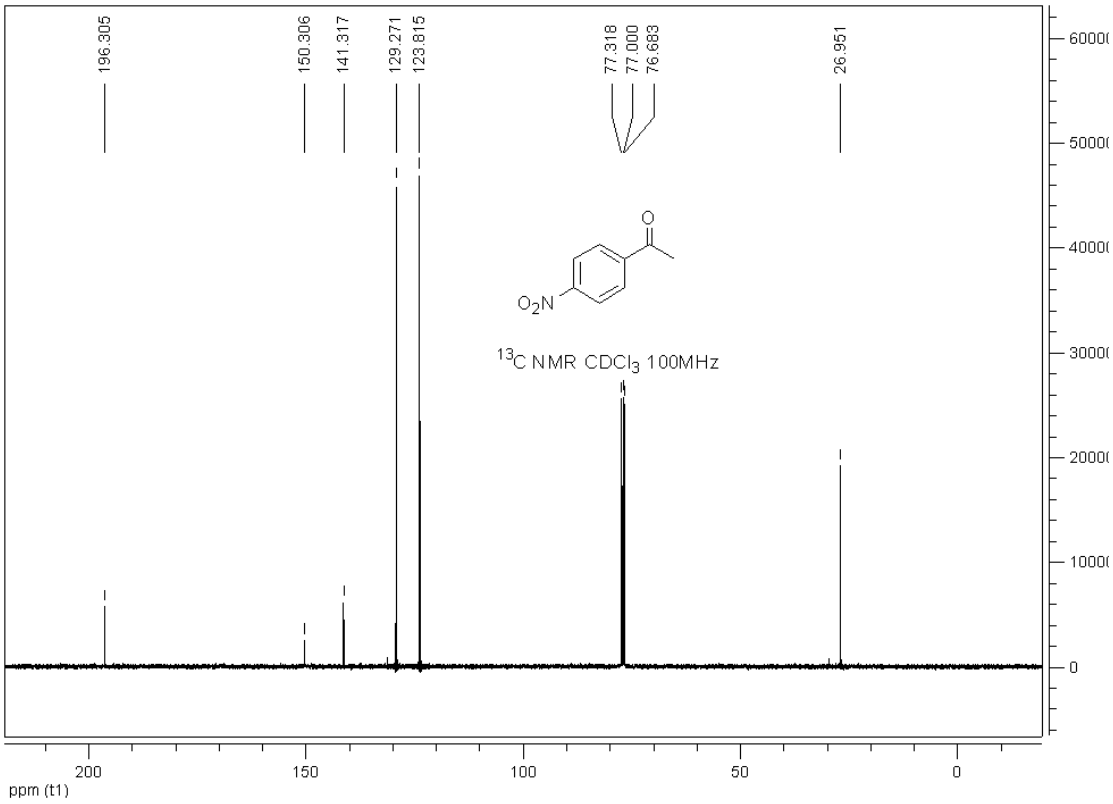


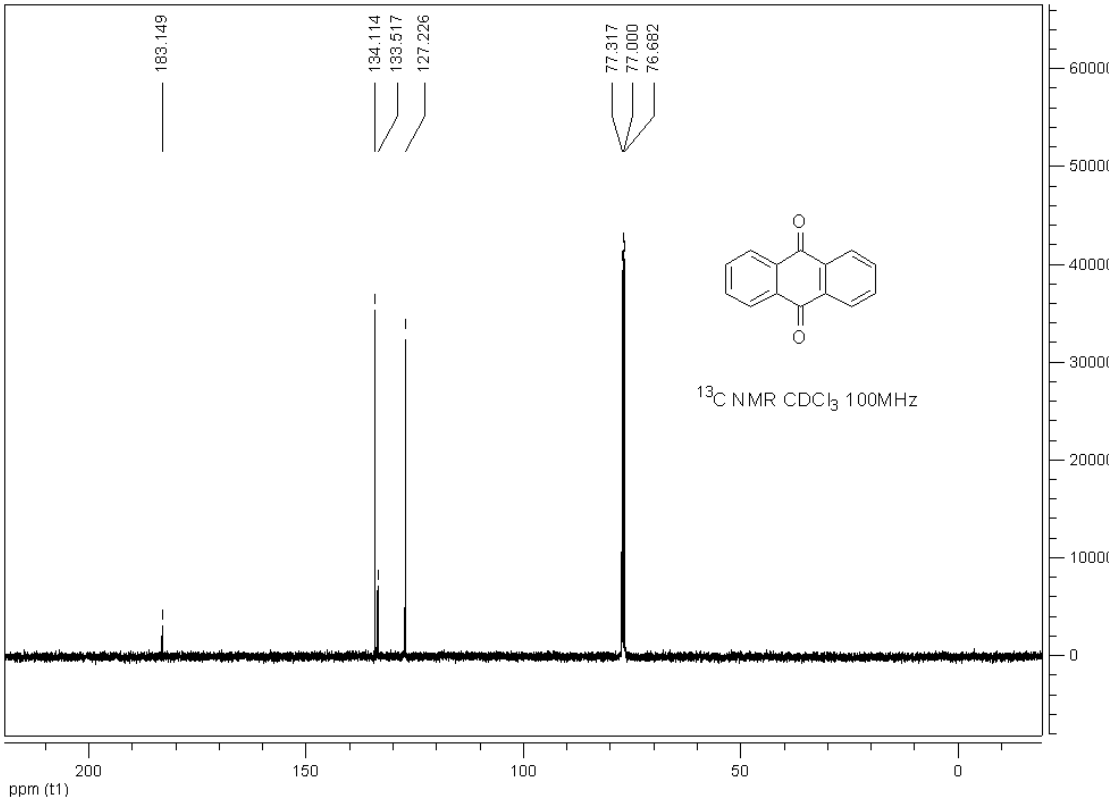


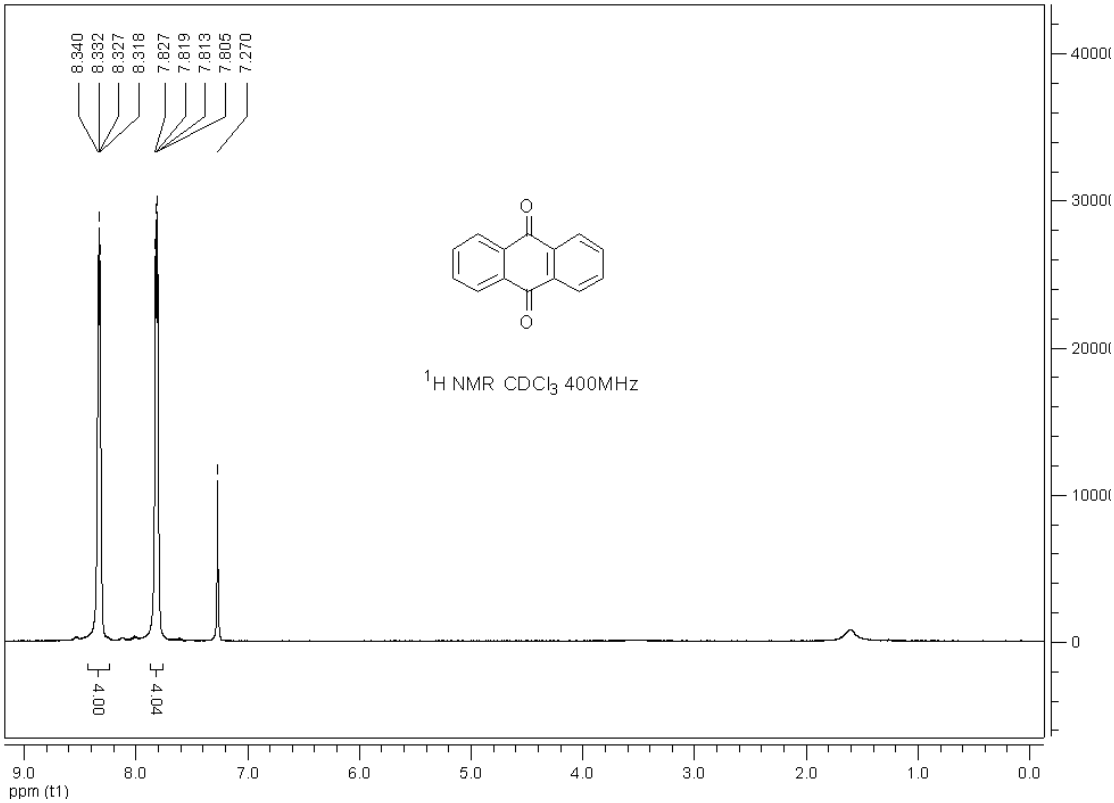


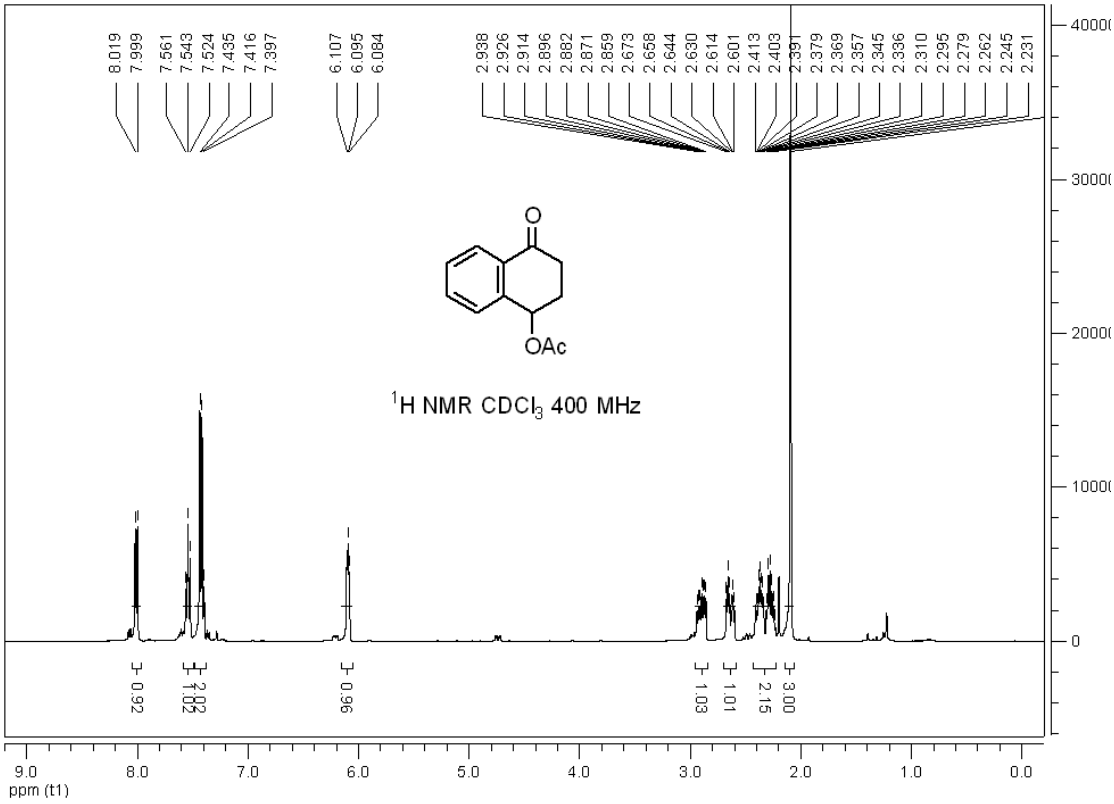


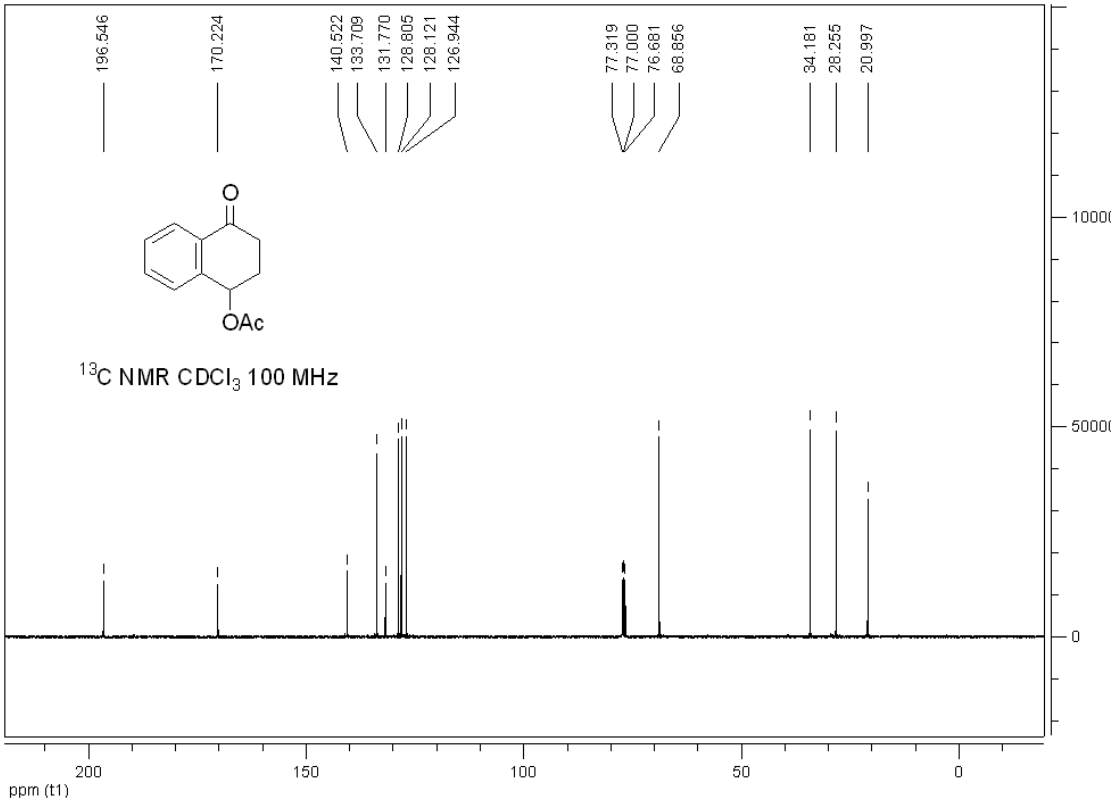


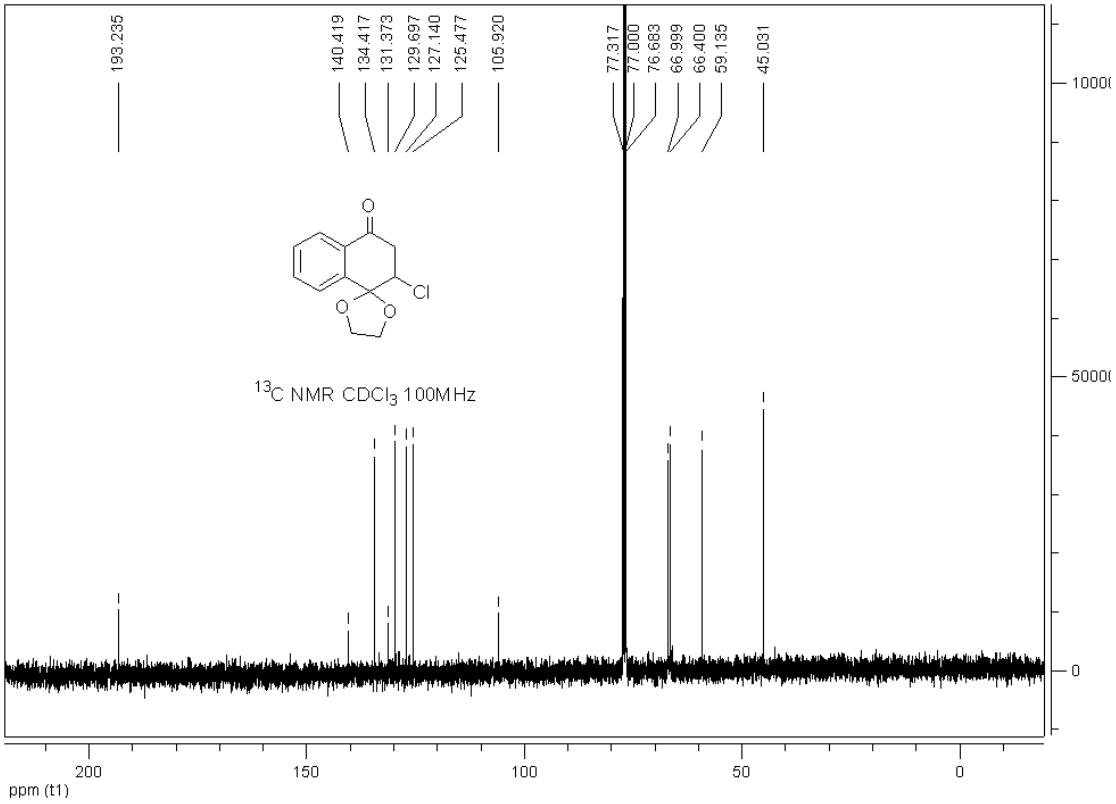


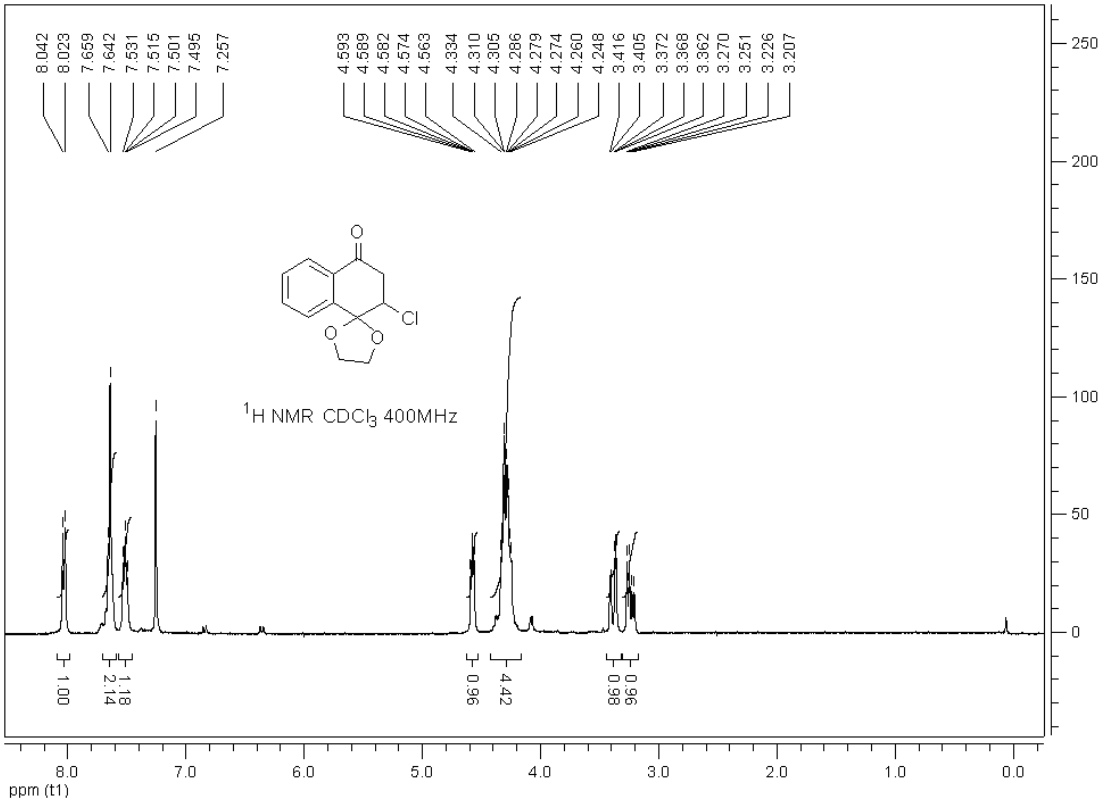


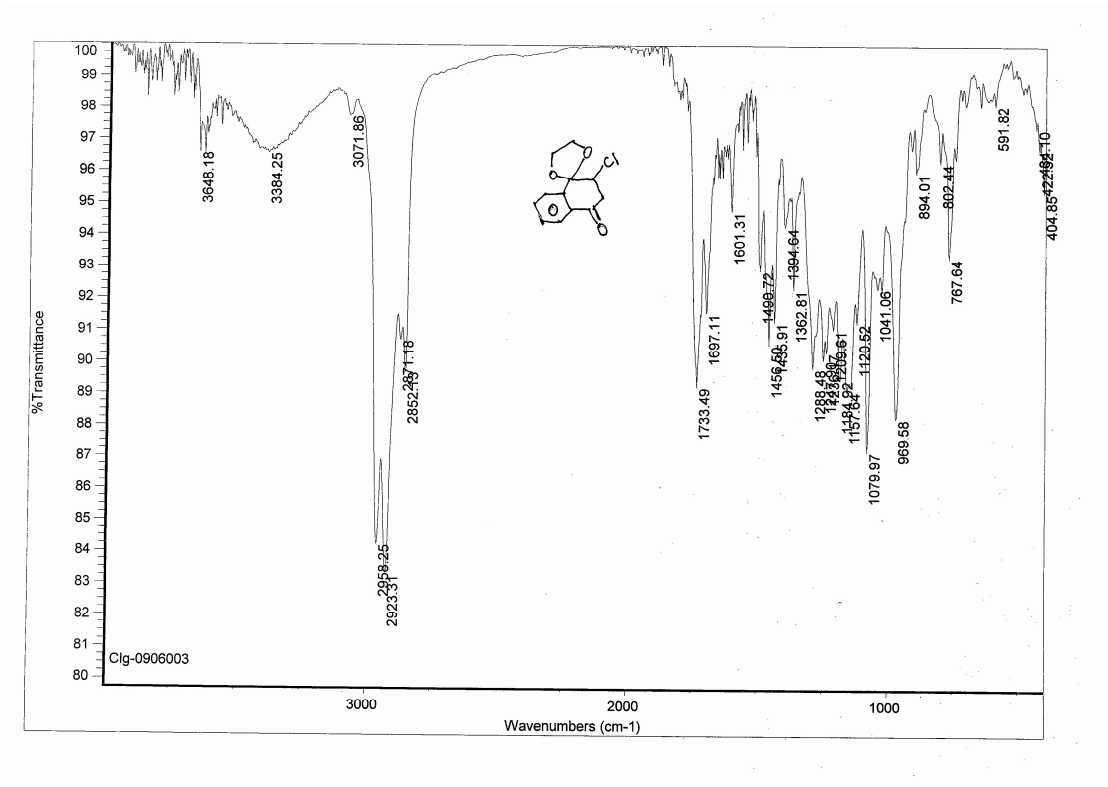




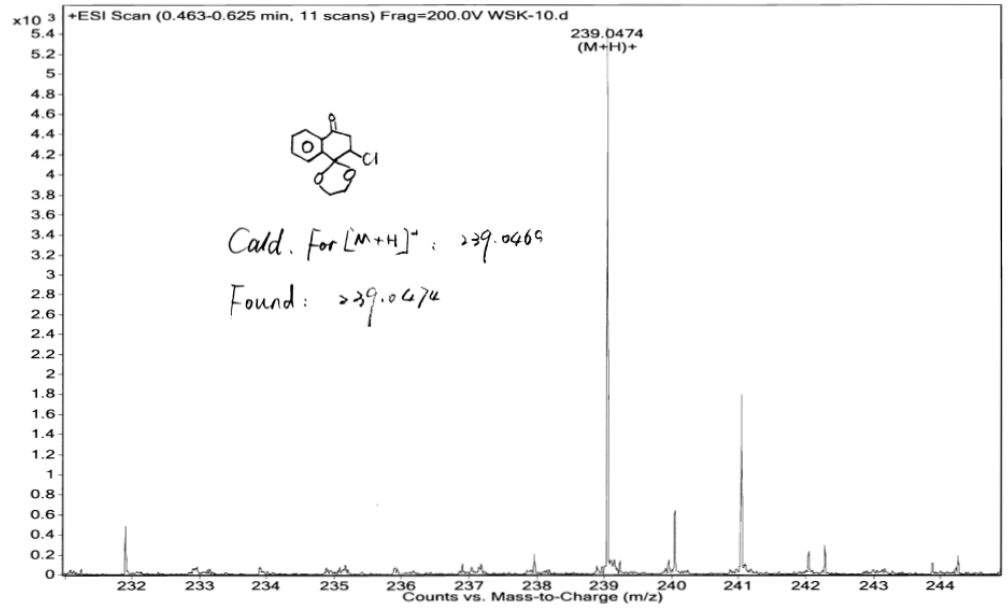


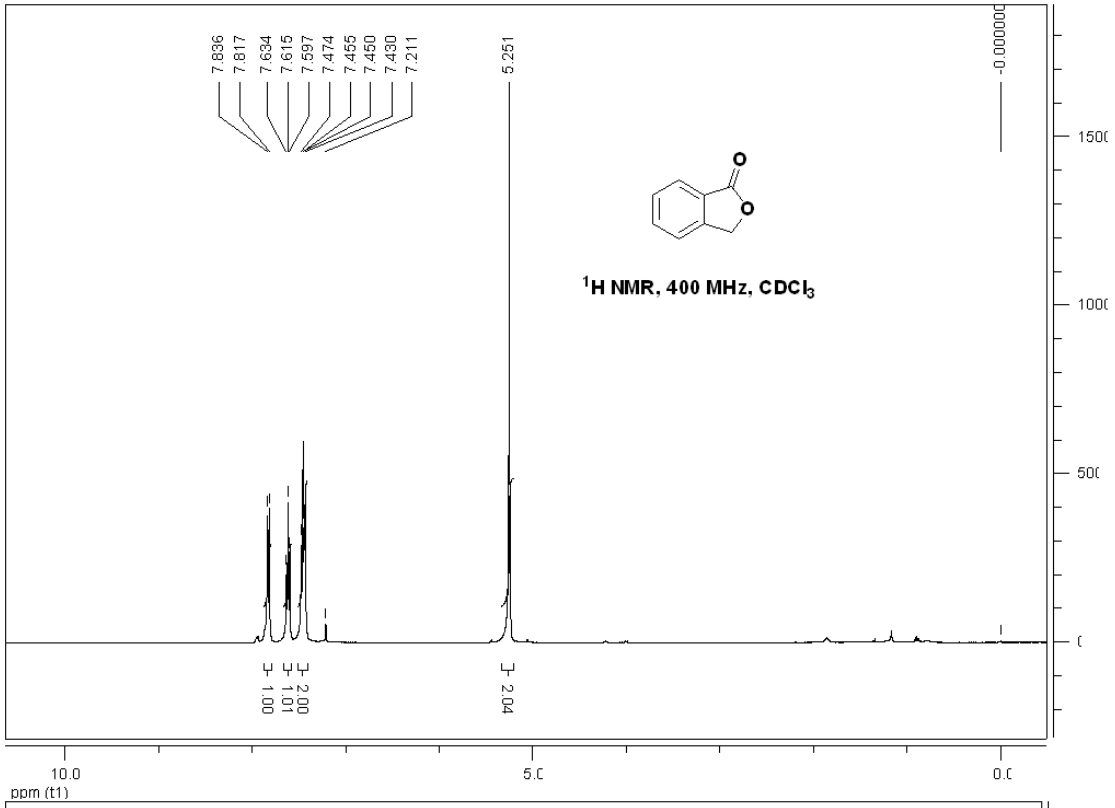


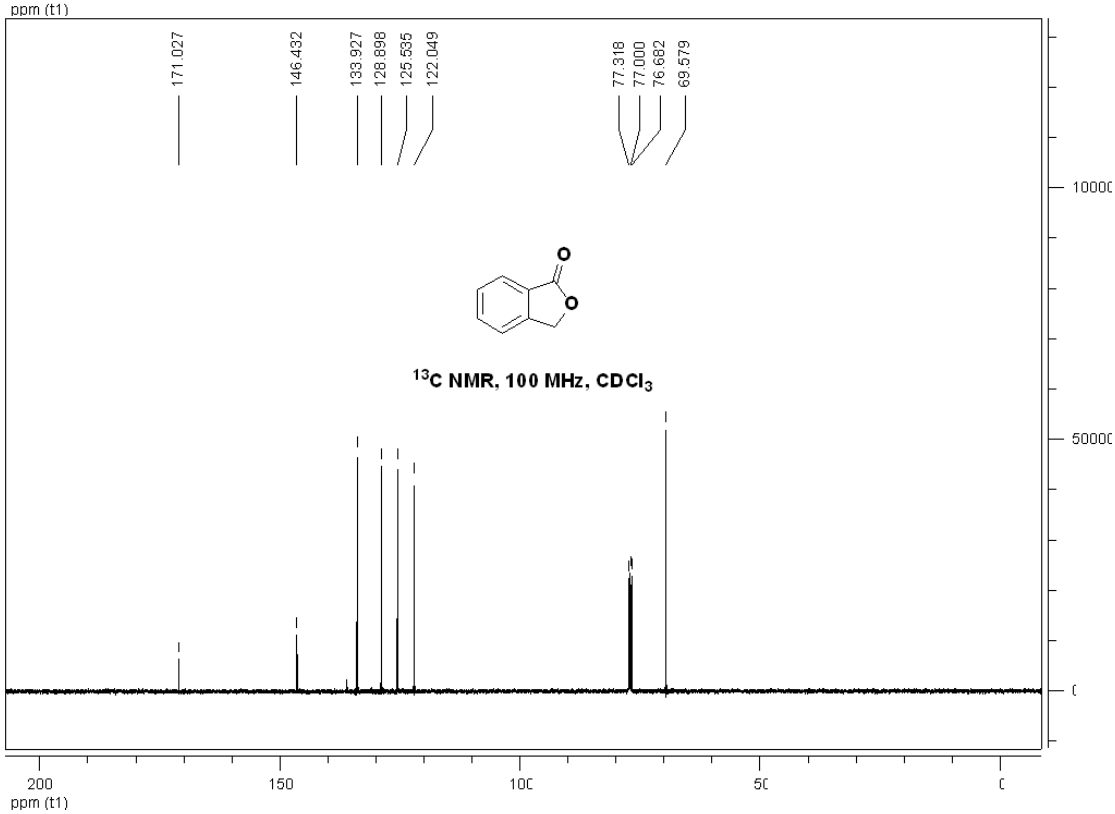


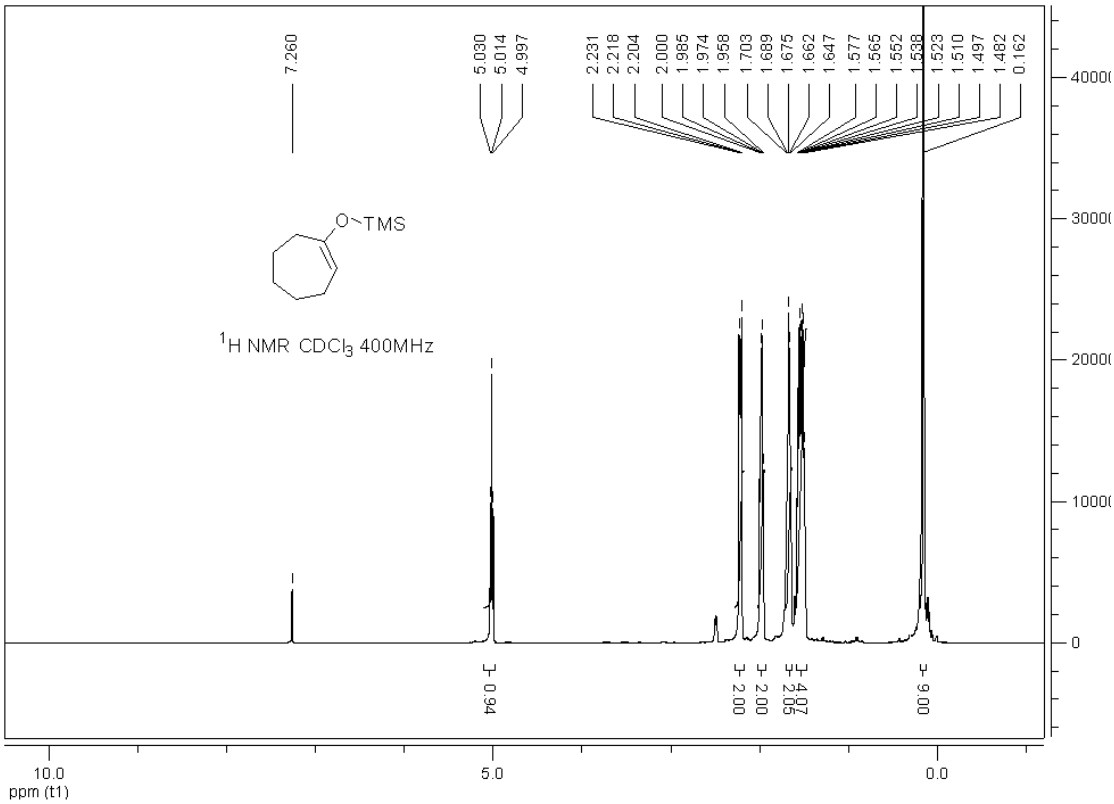


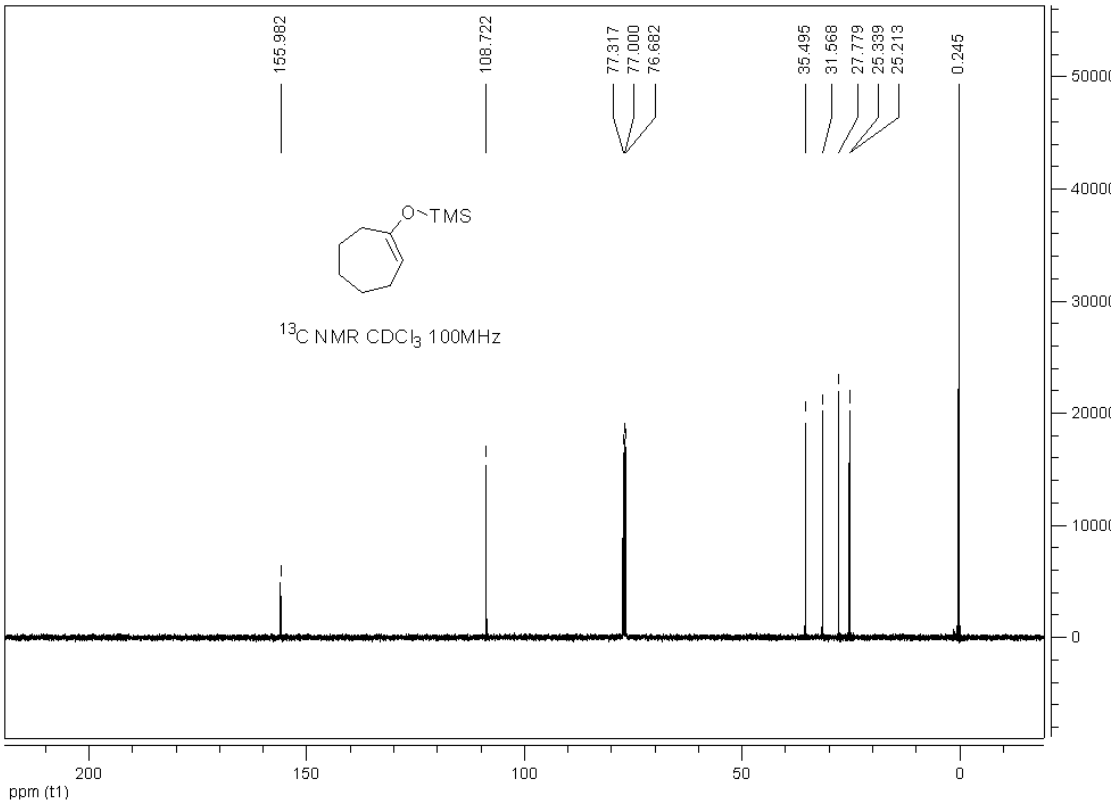
Sample Name	LC/MS	**Position**	Vial 3	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
Data Filename	WSK-10.d	**ACQ Method**		**Comment**		**Acquired Time**	1/13/2010 3:19:01 PM

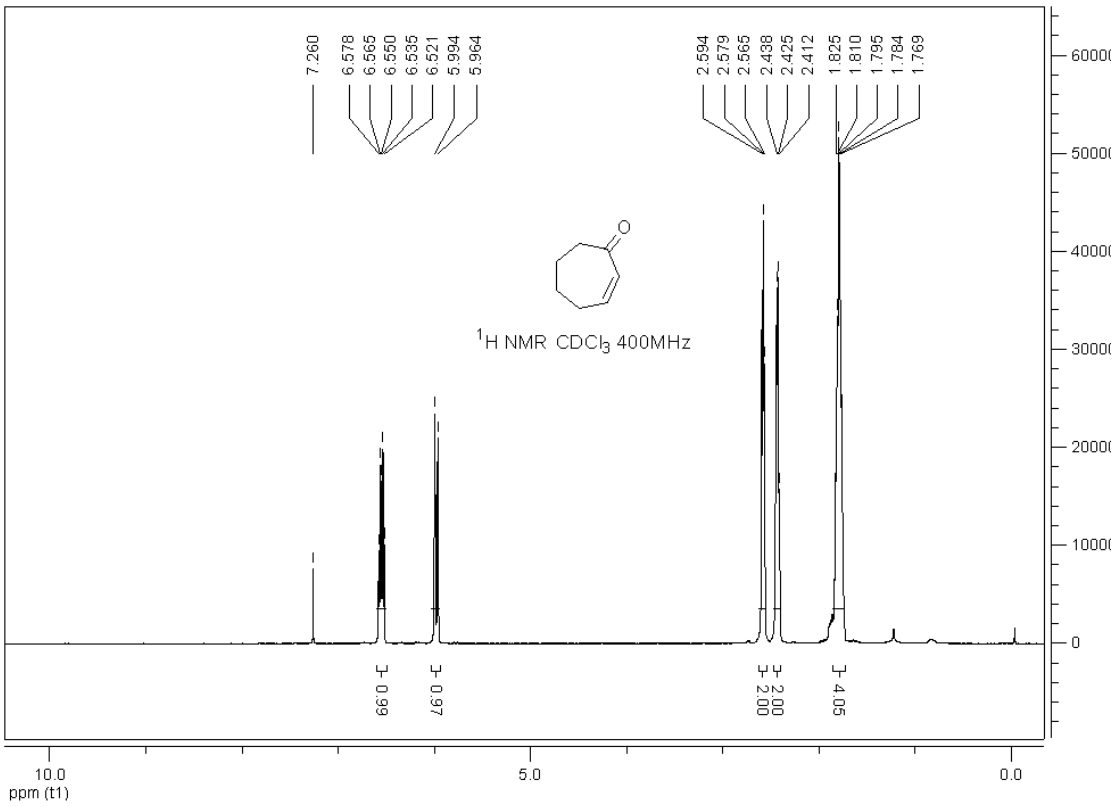


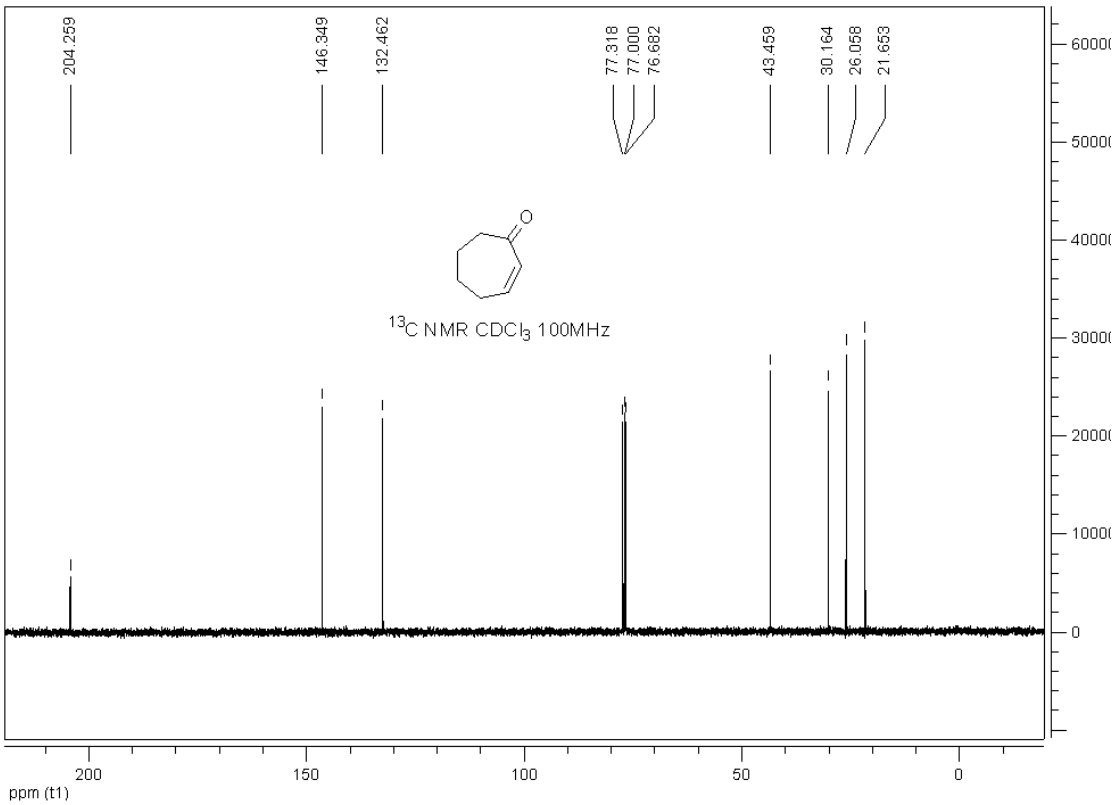


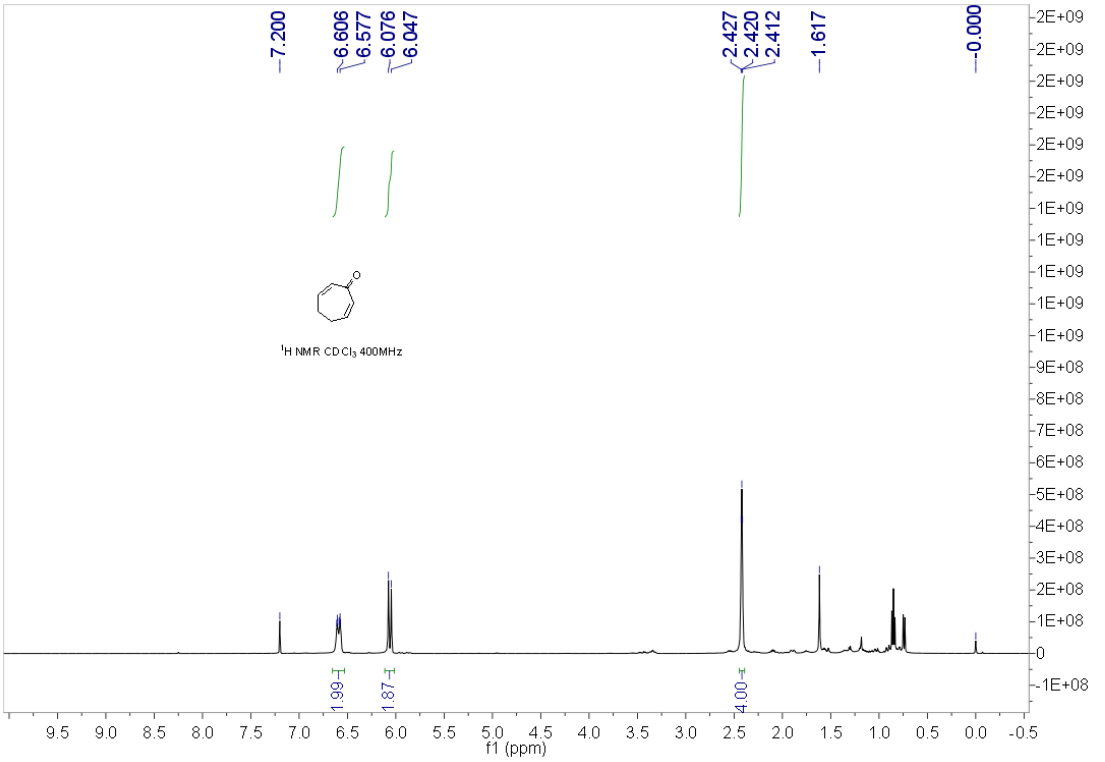


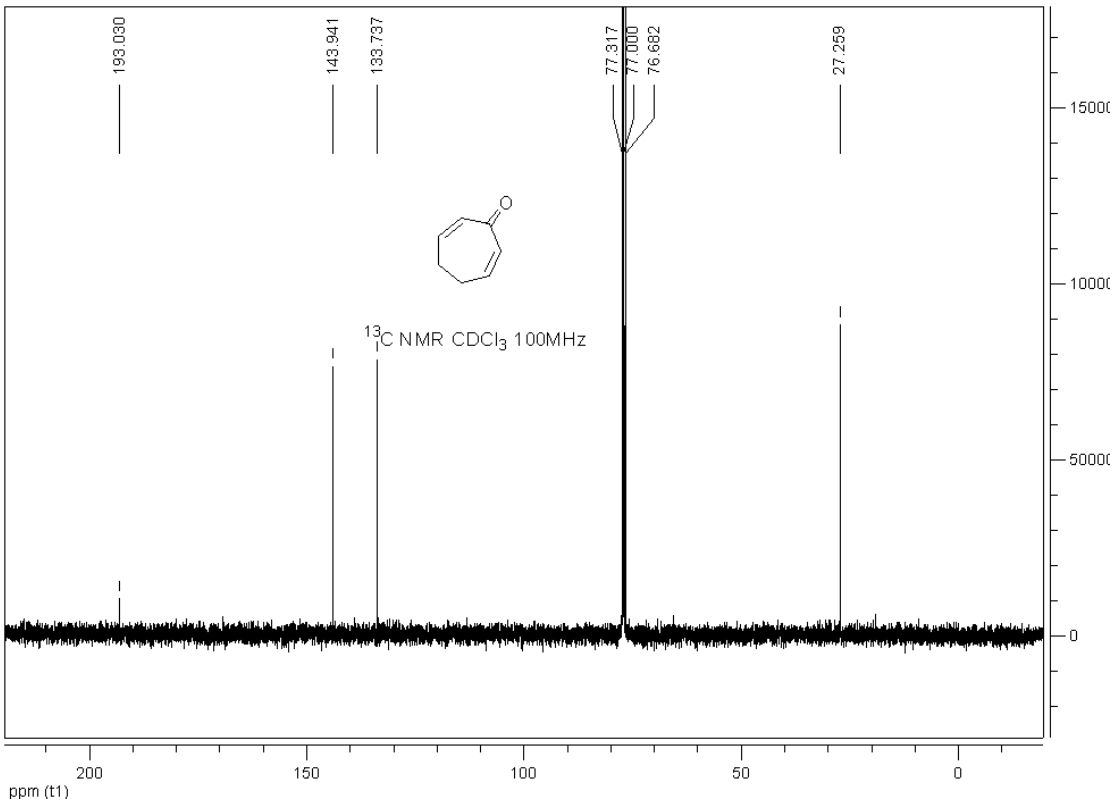


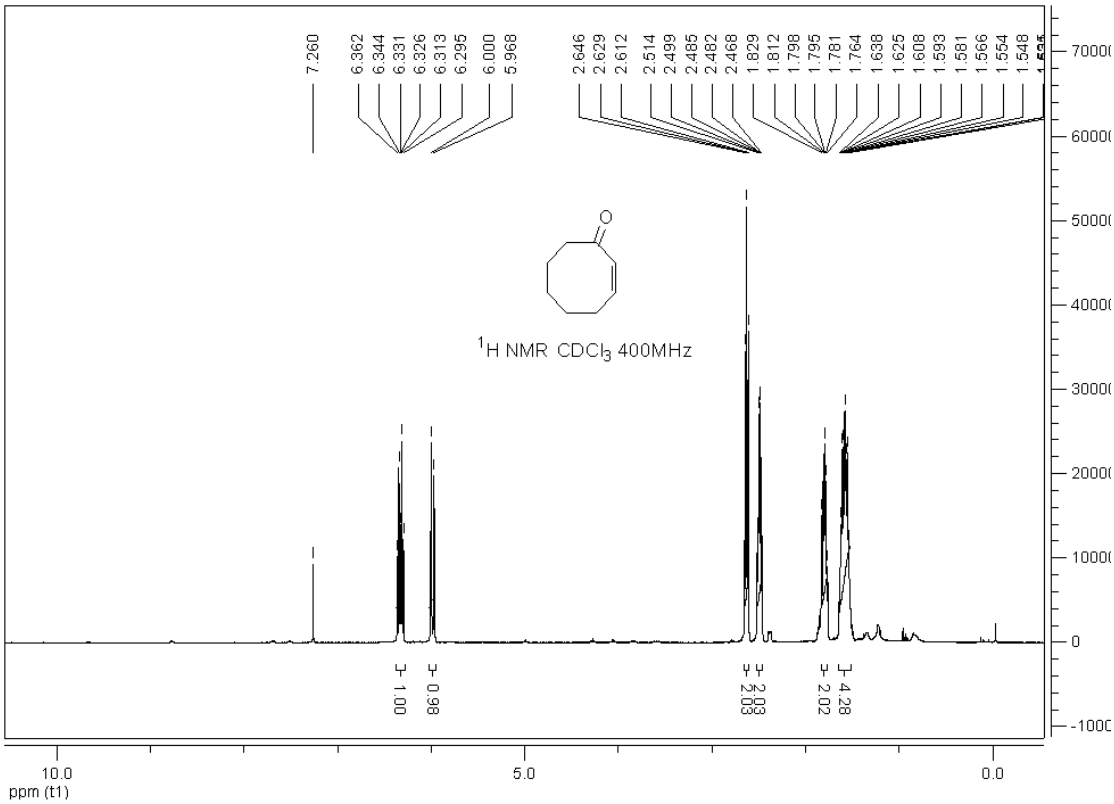


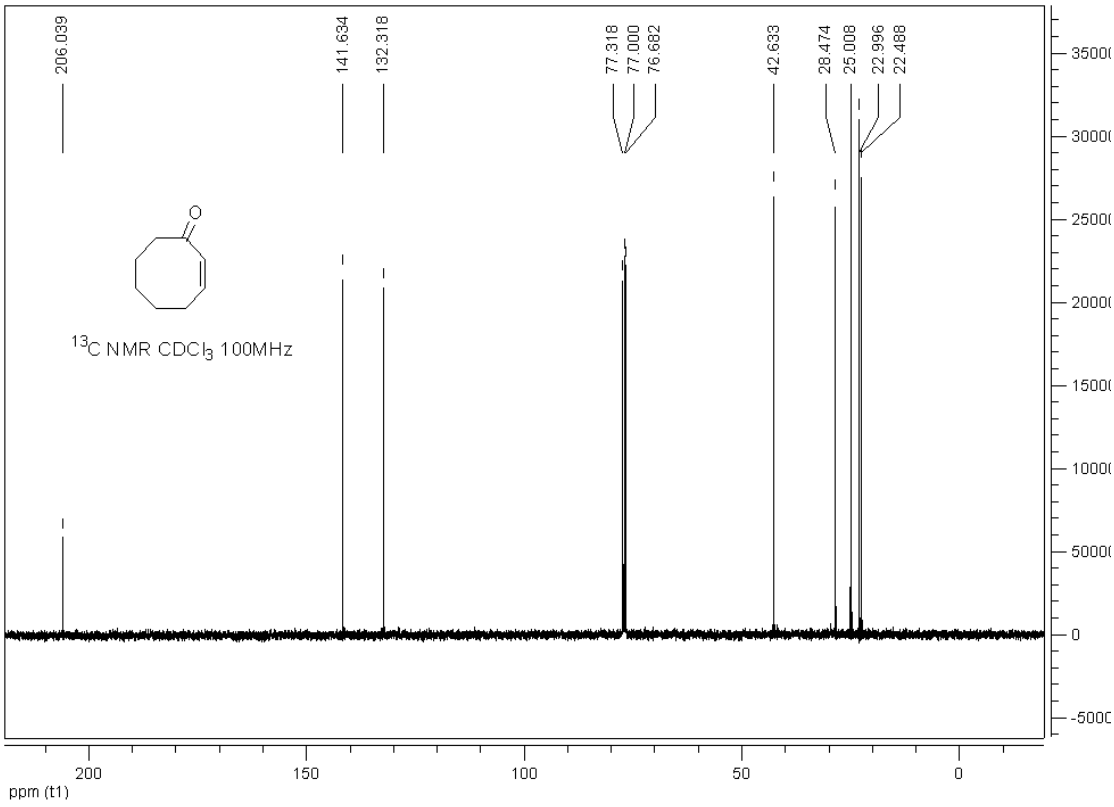

7.260
6.578
6.565
6.550
6.535
6.521
5.994
5.964
2.594
2.579
2.565
2.438
2.425
2.412
1.825
1.810
1.795
1.784
1.769
O
^{1}H NMR CDCl$_3$ 400MHz
0.99
0.97
2.00
2.00
4.05
10.0
5.0
0.0
ppm (t1)

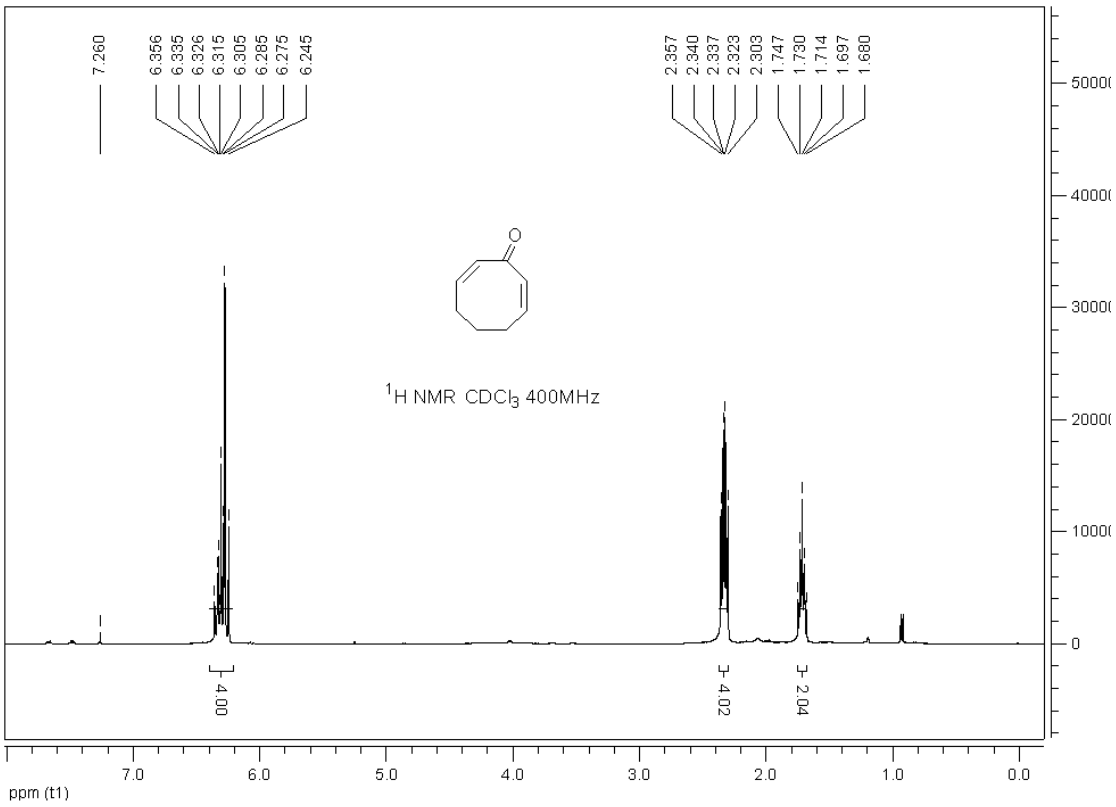

204.259
146.349
132.462
77.318
77.000
76.682
43.459
30.164
26.058
21.653
O
^{13}C NMR CDCl$_3$ 100MHz
200
150
100
50
0
ppm (t1)

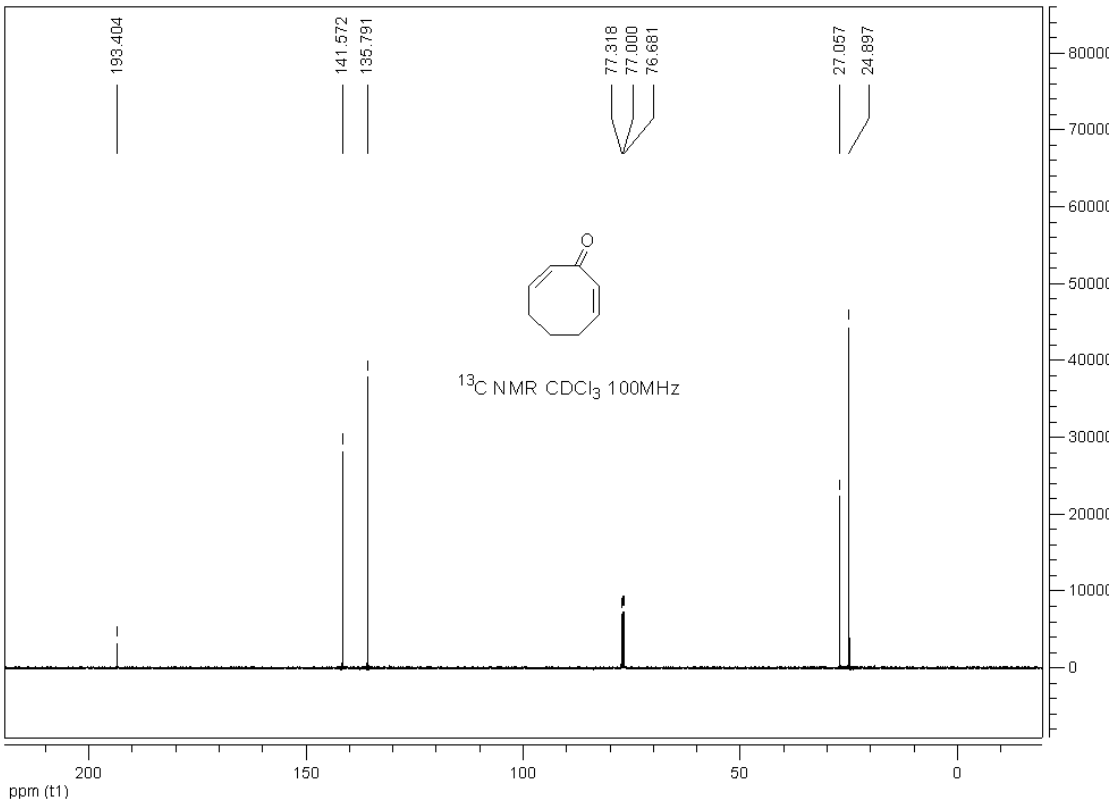


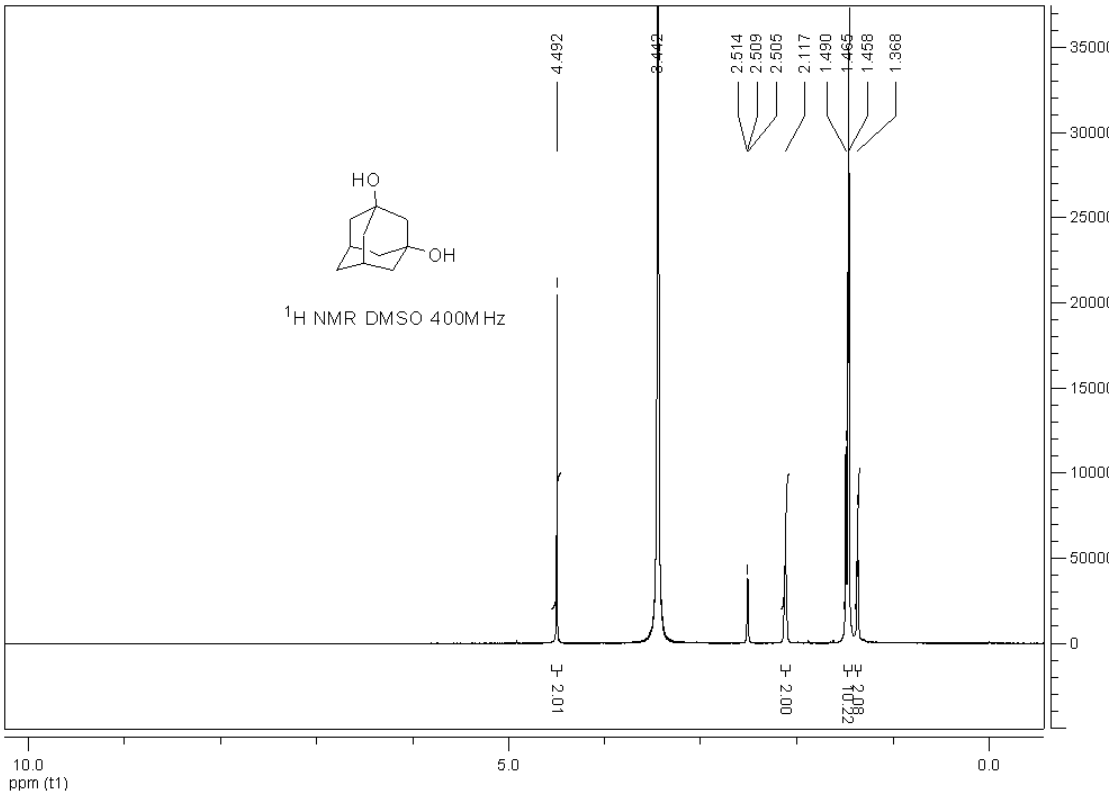


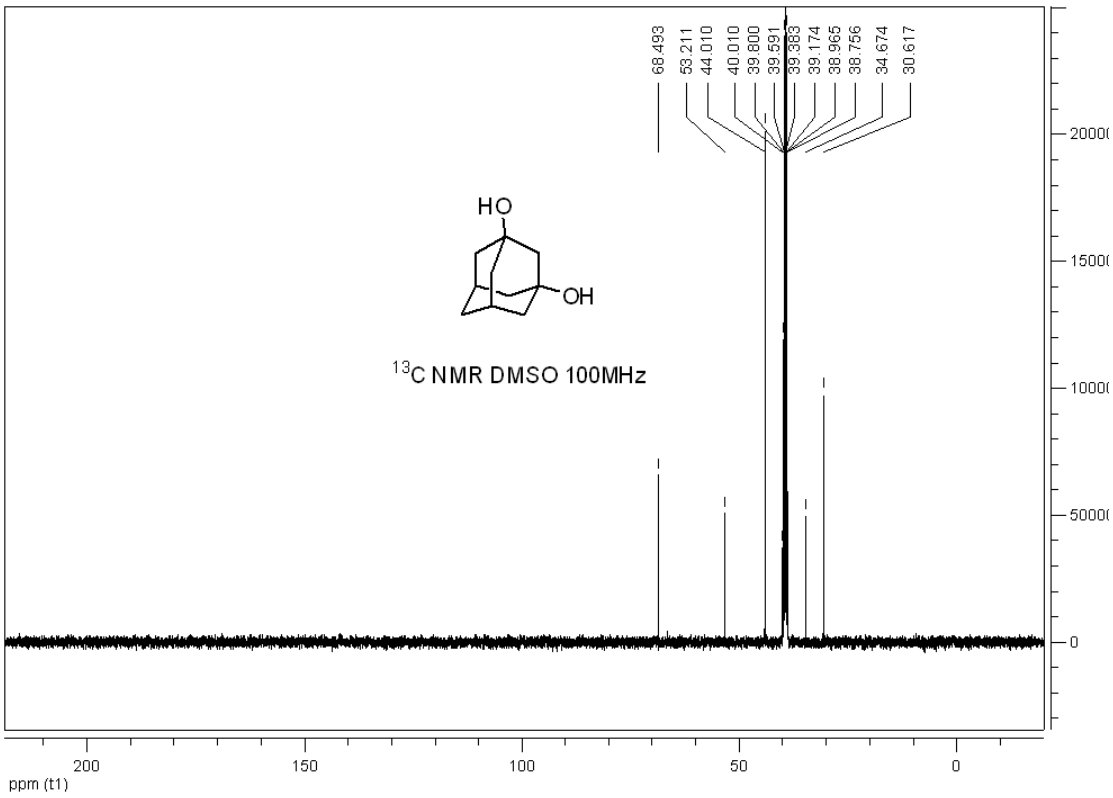


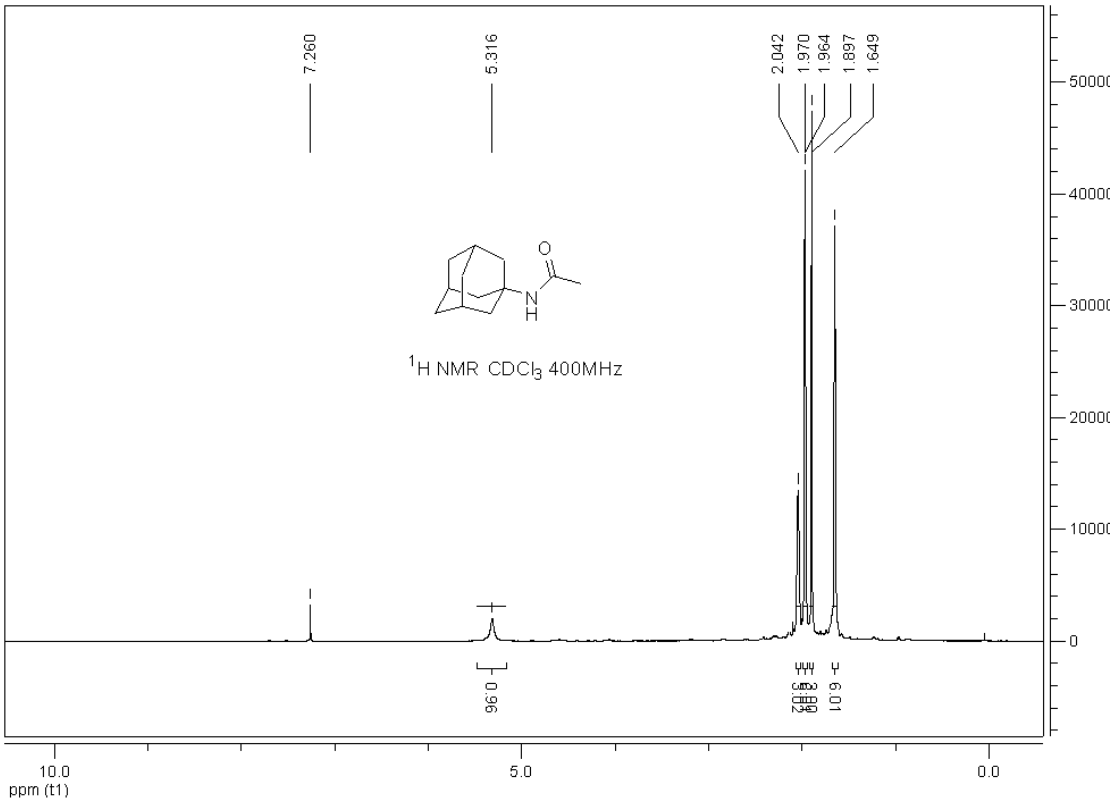


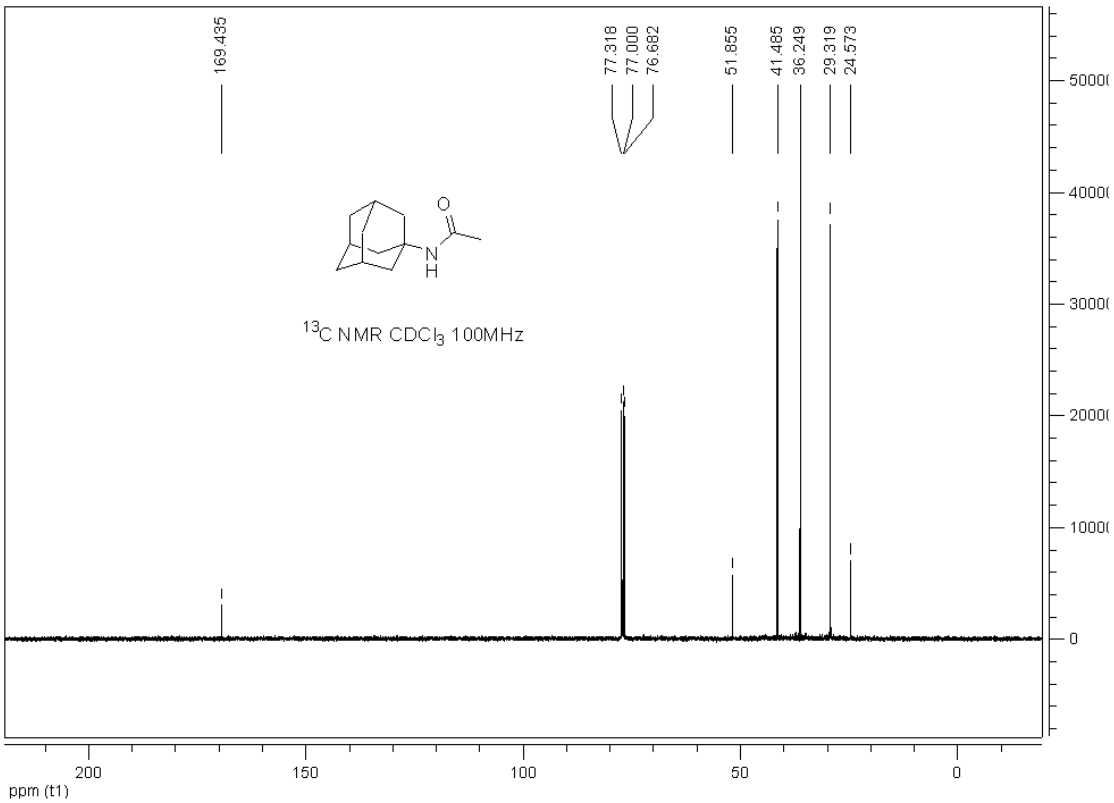

7.260
6.356
6.335
6.326
6.315
6.305
6.285
6.275
6.245
2.357
2.340
2.337
2.323
2.303
1.747
1.730
1.714
1.697
1.680
O
^{1}H NMR CDCl$_3$ 400MHz
4.00
4.02
2.04
ppm (t1)

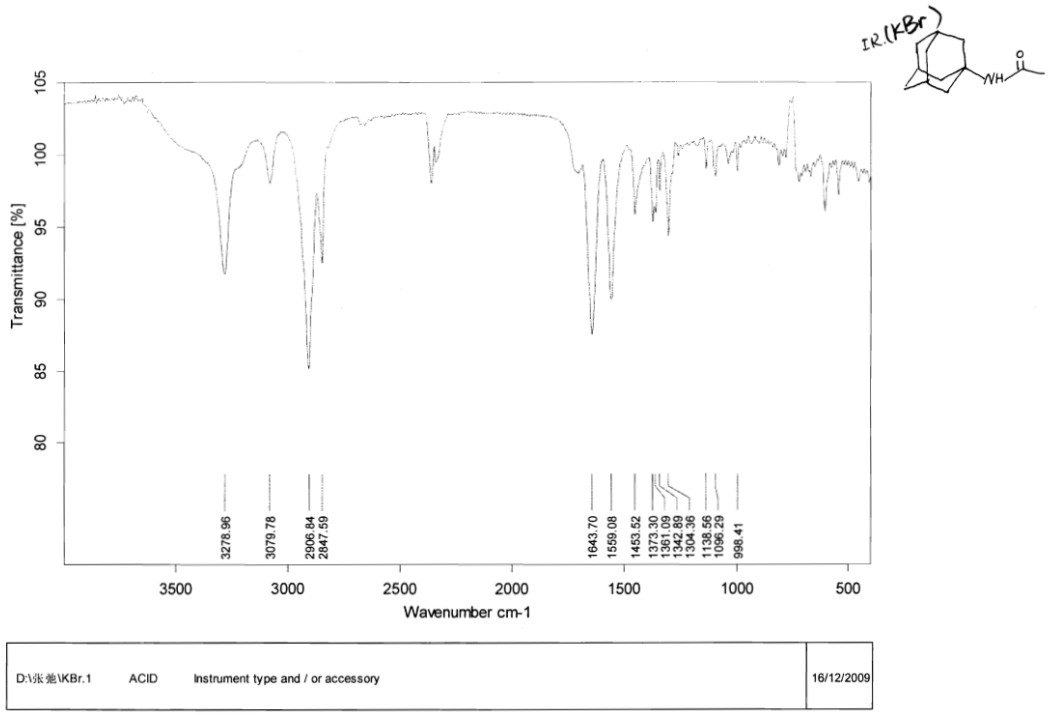

193.404
141.572
135.791
77.318
77.000
76.681
27.057
24.897
O
^{13}C NMR CDCl$_3$ 100MHz
ppm (t1)

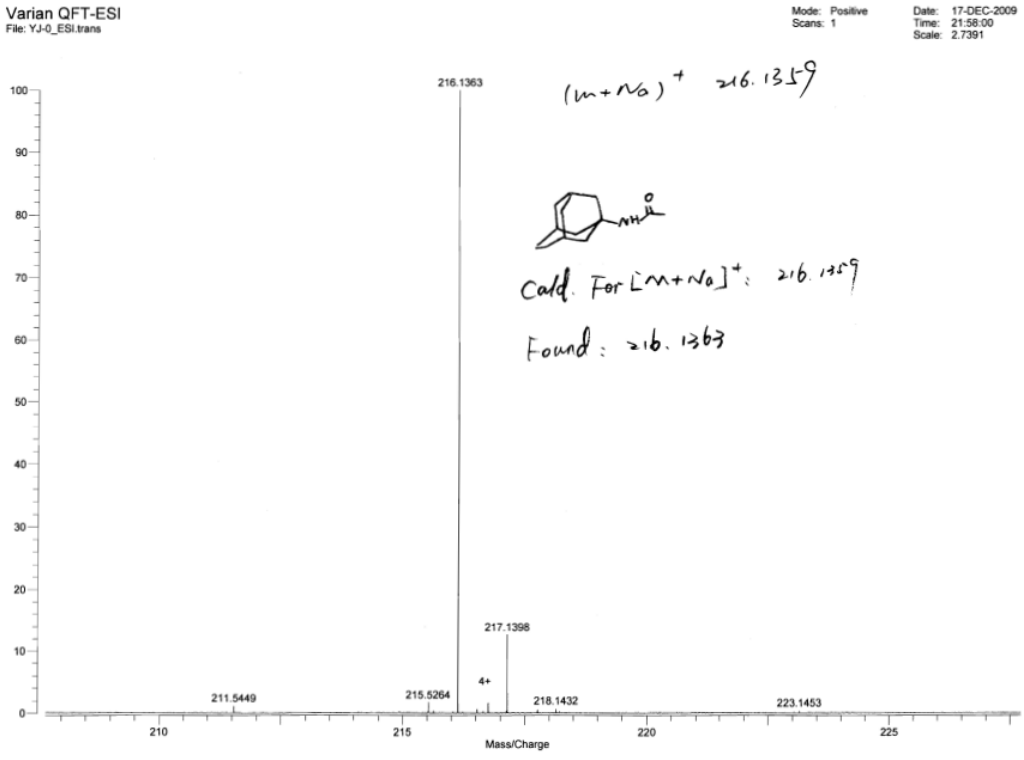









IR (KBr)
NH
O
Transmittance [%]
105
100
95
90
85
80
3278.96
3079.78
2906.84
2847.59
1643.70
1559.08
1453.52
1373.30
1361.09
1342.89
1304.36
1138.56
1096.29
998.41
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
D:\张弛\KBr.1
ACID
Instrument type and / or accessory
16/12/2009


Varian QFT-ESI
File: YJ-0_ESI.trans
Mode: Positive
Scans: 1
Date: 17-DEC-2009
Time: 21:58:00
Scale: 2.7391
216.1363
(m+Na)+ 216.1359
NH
O
Cald. For [m+Na]+: 216.1359
Found: 216.1363
100
90
80
70
60
50
40
30
20
10
0
217.1398
4+
211.5449
215.5264
218.1432
223.1453
210
215
220
225
Mass/Charge