# Nanoporous iron(III) porphyrin frameworks: An efficient catalyst for [4+2] cycloaddition reactions of unactivated aldehydes with a diene

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## Electronic Supplementary Information

### I. Synthesis of 5,10,15,20-*tetrakis*(4-cyanophenyl)porphyrin [$(CN)_4TPPH_2$]

In a 500 mL two necked round bottom flask, dried dichloromethane (300 mL) was added and it was purged with argon for 30 minutes. Freshly distilled pyrrole (0.330 mL, 4.5 mmol), followed by *p*-cyanobenzaldehyde (0.60 g, 4.5 mmol) was added into it under inert atmosphere. After 10 minutes, $BF_3 \cdot (OC_2H_5)_2$ (0.04 mL, 0.3 mmol) was added by using gas tight syringe in the reaction mixture and it was covered with an aluminium foil. The color of the reaction mixture was changed from yellow to orange to wine red. The reaction mixture was stirred on a magnetic stirrer for four hours at room temperature. Then DDQ (0.816 g, 3.6 mmol) was added and the reaction mixture was immediately turned to dark purple. The reaction mixture was further stirred for 1 hour then one equivalent of triethylamine (0.025 mL, 0.33 mmol) was added to it and the reaction mixture was stirred for 5 minutes at room temperature. The excess of solvent was removed by using rotary evaporator. The purple compound was washed with methanol (75 mL). It was dried in air then under vacuum. The crude product was dissolved in dichloromethane and was loaded on a column (2.5 cm x 30 cm) packed with silica gel 60-120 mesh in hexane and the desired compound was eluted with 50% dichloromethane-hexane and solvent was evaporated to get solid product. Yield= 0.268 g (33%).. $^1$H NMR ($CDCl_3$, 300 MHz): δ (ppm) -2.86(s,2H,NH), 8.12(*m*-4-cyanophenyl), 8.33(d, 8H, J= 7.8, *o*-4-cyanophenyl) 8.83(s, 8H, β-pyrrole) . ESI-MS: m/z calcd for $C_{48}H_{27}N_8$, 715.2352 $[M+H]^+$; found, 715.2351 $[M+H]^+$. UV-Vis (λ; nm; $CH_2Cl_2$ solution): 420 (2,05,918), 452 (8,696), 514 (10,002), 548 (4,248), 588(3,676), 645 (2,125).

### II. Synthesis of 5,10,15,20-tetrakis (4-cyanophenyl) porphyrinato iron(III)chloride [$(CN)_4TPPFe(III)Cl$]

In a 250 mL two necked round bottom flask, 70 mL of dried DMF was degassed with dry argon for 30 minutes. It was heated up to 110-120°C and to this hot DMF solvent, solid $(CN)_4TPPH_2$ (0.100 g, 0.139 mmol) was added and after 10 minutes 2,4,6-collidine (100 µL,

0.91 mmol) was added into the reaction mixture and the solution was refluxed continuously. To this refluxing solution, ferrous chloride tetrahydrate (0.275 g, 1.38 mmol) (dissolved in pre-degassed DMF (10mL)) was added slowly in five batches of 2 mL each. The refluxing was continued and the progress of the reaction was monitored by TLC and the reaction was over in 15 minutes. It was cooled down to room temperature and dichloromethane (50 mL) was added and it was passed through a separating funnel containing distilled water (400 mL) without shaking it. It was further washed with brine solution (5 x 400 mL) and organic layer was dried over anhydrous sodium sulphate (25 g) for few hours. The organic layer was evaporated to dryness under reduced pressure.

The crude product was dissolved in minimum volume of dichloromethane and was loaded on a column (2.5 x 30 cm) packed with basic alumina in hexane. The desired product was eluted from the column by dichloromethane and HCl gas was purged for 5-10 seconds. The solution was evaporated to dryness under reduced pressure and pure product was obtained. The iron insertion into the porphyrin ligand was almost quantitative. Yield = 95 mg (90%). ESI-MS: m/z calcd for $C_{48}H_{24}FeN_8$, 768.1473 $[M\text{-}Cl]^+$, found, 768.1498 $[M\text{-}Cl]^+$. UV-Vis ($\lambda$; nm; $CH_2Cl_2$ solution): 373 (92,385), 417 (1,85,776), 510 (23,520).

**III. Characteristic data of polymeric catalysts:**

1. **Table S1.** Solubility and stability of compound **1**.X

| Media | Solubility | Stability |
|---|---|---|
| Dichloromethane | Insoluble | Stable |
| Acetonitrile | Insoluble | Stable |
| Toluene | Insoluble | Stable |
| THF | Insoluble | Stable |
| Methanol | Insoluble | Stable |
| Acetone | Insoluble | Stable |
| m-Cresol | Insoluble | Stable |
| DMSO | Insoluble | Stable |
| Hexane | Insoluble | Stable |
| Water | Insoluble | Stable |
| Air | - | Stable |

Solubility and stability of the polymer was tested at room temperature for the corresponding media for one month.

**2.** FT IR spectroscopy

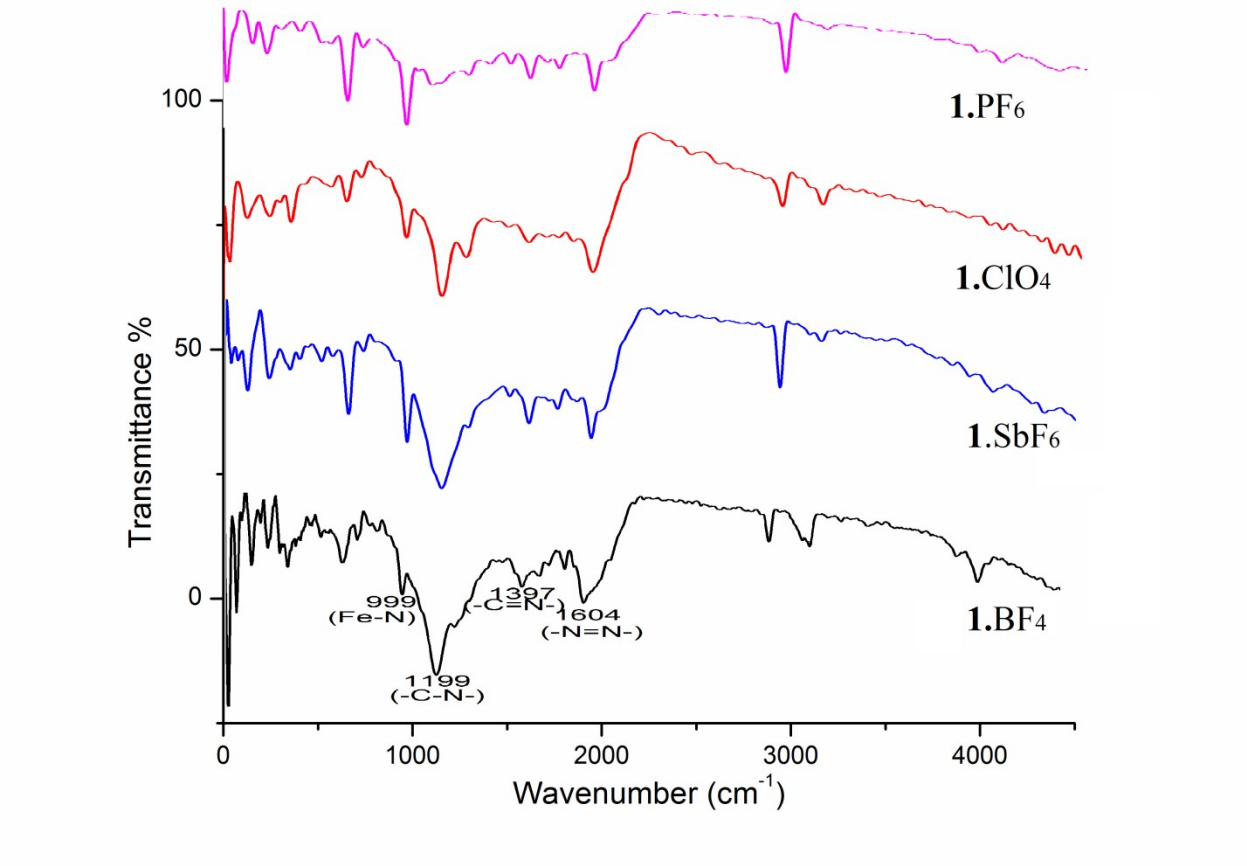



**Figure S1:** FT-IR spectra of compound **1**.X (where X= $BF_4$, $SbF_6$, $ClO_4$, $PF_6$). The peak at 999 $cm^{-1}$ indicates the vibration band due to N–Fe bond while peaks at 1604, 1397 & 1199 $cm^{-1}$ originate from –N=N-, -C=N- and –C-N- stretching of the tetrazine moiety in the respective sample.

**Table S2.** Assignment of FT-IR peaks of tetrazine linked iron(III)porphyrin

| **Peak ($cm^{-1}$)** | **Assignment and notes** |
|---|---|
| 1604 | -N=N- stretching frequency in tetrazine |
| 1588 | C=C stretching of the pyrrole rings |
| 1504 | C=C vibrational mode of phenyl rings |
| 1397 | tetrazine ring stretching (-C=N-) |
| 1199 | C-N stretching |
| 999 | Fe-N Stretching |
| 858 | C-H perylene wag |
| 803 | C-H out of plane bending of phenyl rings |
| 736 | |

### 3. Solid state UV-Visible spectra of compound 1

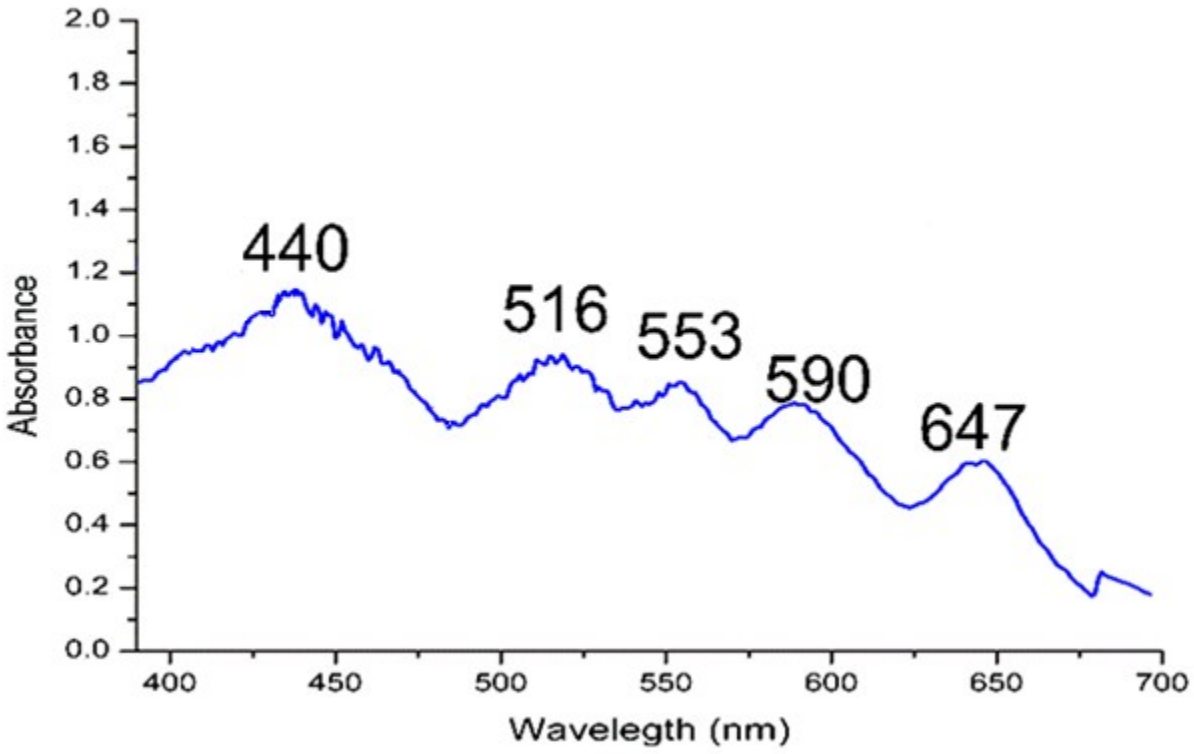



**Figure S2:** Solid state UV-Visible spectra of compound **1.**$BF_4$.

## 4. EDX

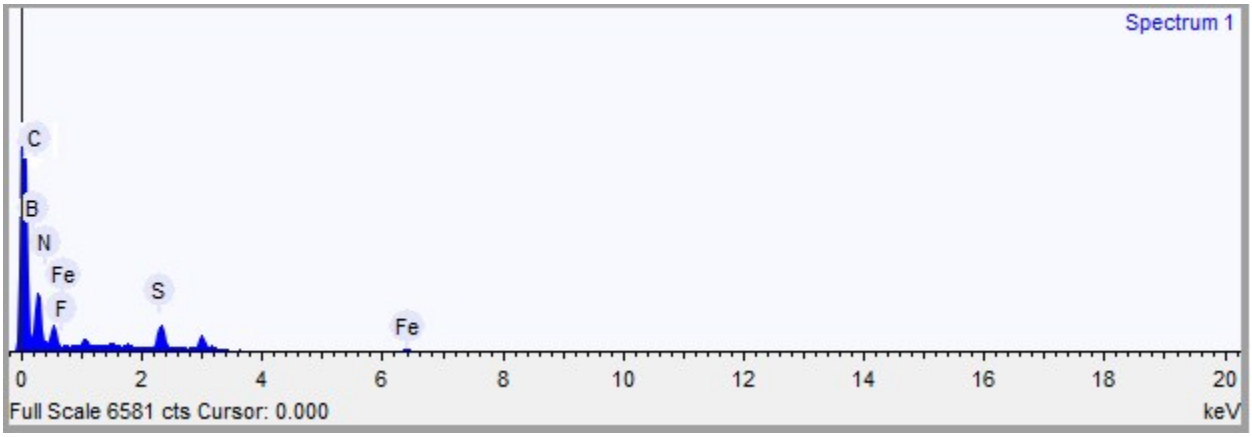



**Figure S3:** EDX for the compound **1**.$BF_4$

5. **$N_2$ physisorption study and pore size distribution analysis**

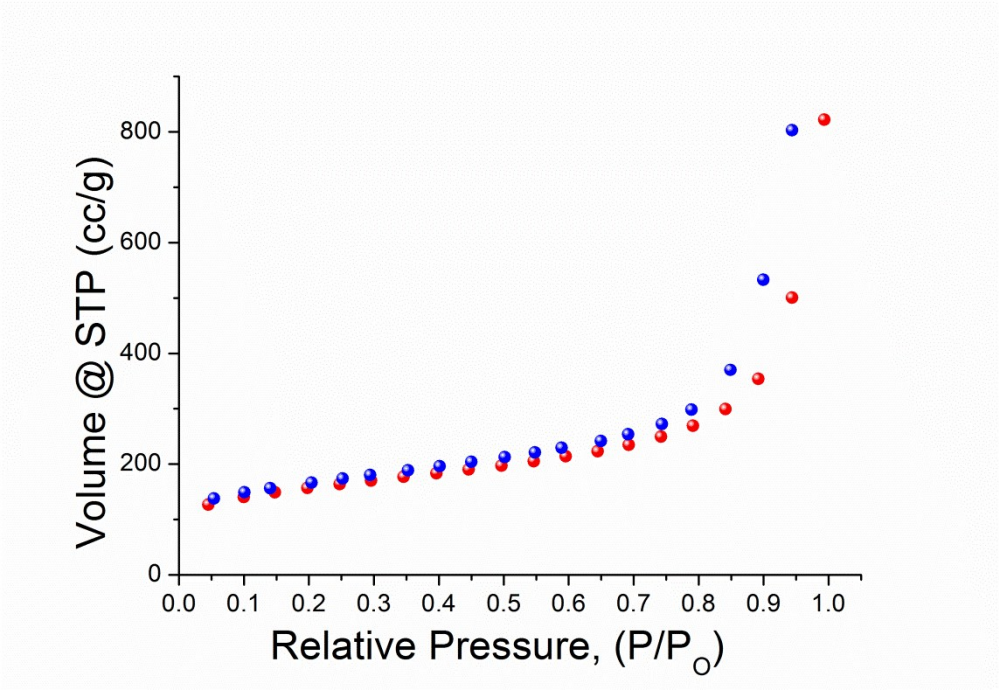



**Figure S4:** $N_2$ gas absorption study for compound **1.**Cl.

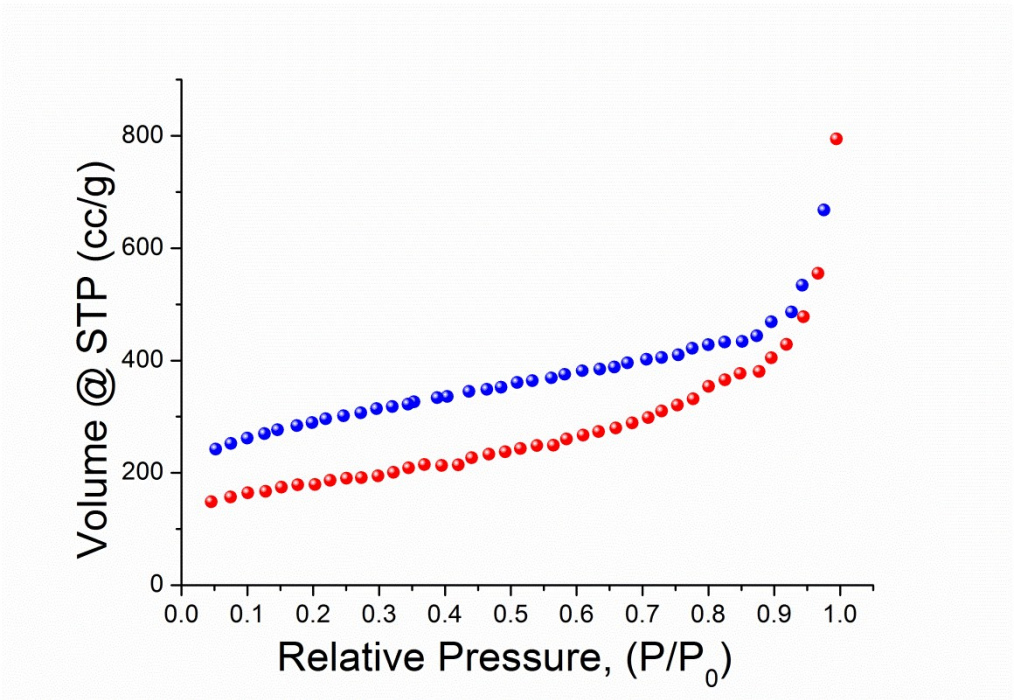



**Figure S5:** $N_2$ gas absorption study for compound **1.**$SbF_6$.

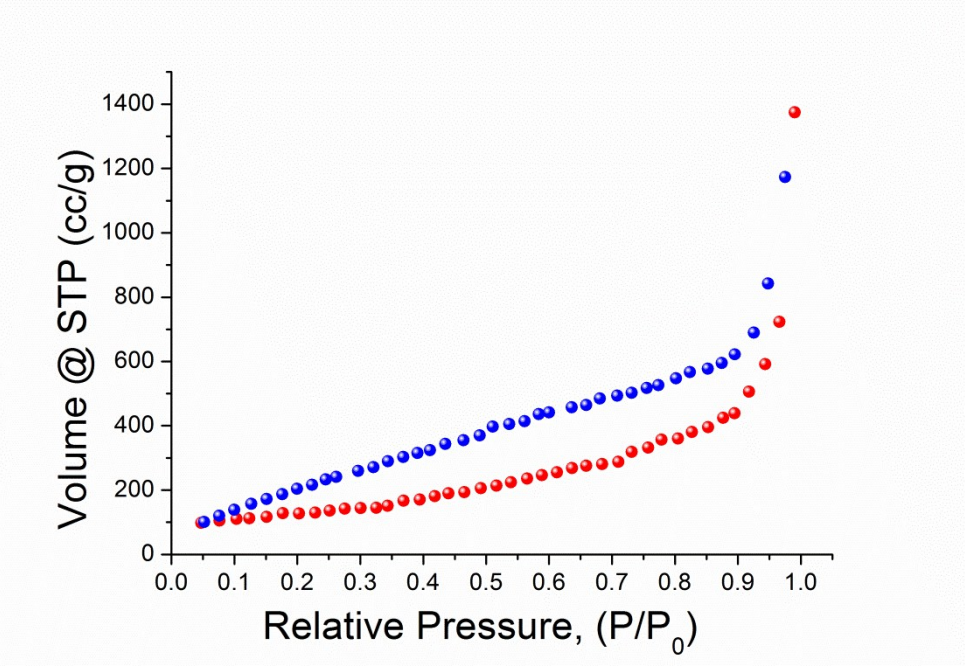



**Figure S6:** $N_2$ gas absorption study for compound **1.**$ClO_4$.

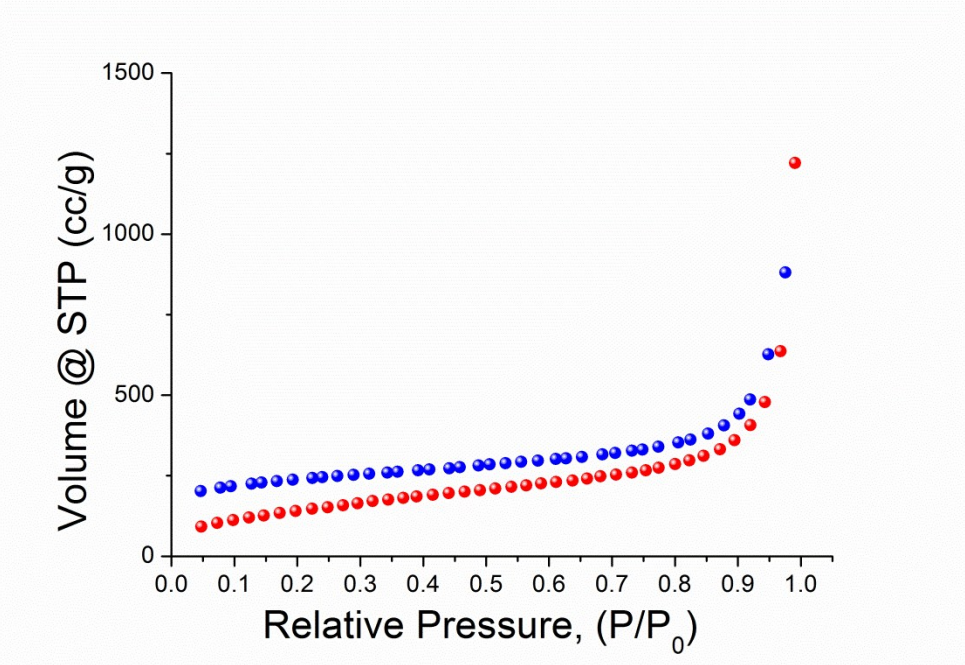



**Figure S7:** $N_2$ gas absorption study for compound **1.**$PF_6$.

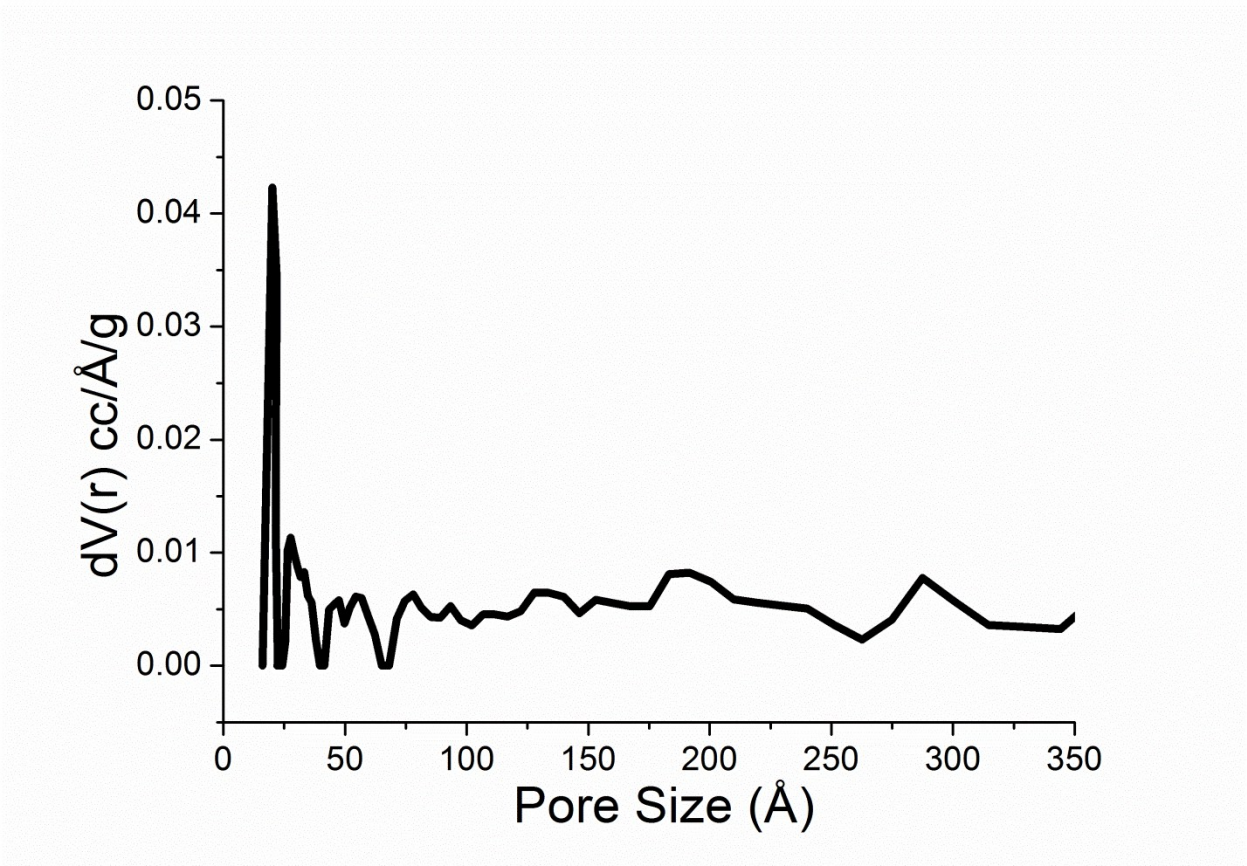


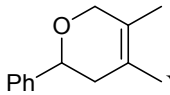

**Figure S8:** Pore size distribution by NLDFT.

**Table S3:** Optimization of reaction condition for the hDA reaction of 4-methyl benzaldehyde and 2,3-dimethyl-1,3-butadiene in the presence of catalyst **1**.$BF_4$ (1 mol%).

| Entry. No. | Number of eq. of 2,3-dimethyl-1,3-butadiene w.r.t. 4-methyl benzaldehyde | Reaction time (h) | Temperature (ºC) | Solvents | Product Yield (%) |
|---|---|---|---|---|---|
| 1 | 1 | 12 | 90 | Toluene | 20 |
| 2 | 2 | 12 | 90 | Toluene | 52 |
| 3 | 3 | 12 | 90 | Toluene | 70 |
| 4 | 4 | 2 | 90 | Toluene | 40 |
| 5 | 4 | 4 | 90 | Toluene | 60 |
| 6 | 4 | 6 | 90 | Toluene | 74 |
| 7 | 4 | 8 | 90 | Toluene | 84 |
| 8 | 4 | 48 | r.t. (22) | Toluene | <5 |
| 9 | 4 | 48 | 40 | Toluene | 10 |
| 10 | 4 | 48 | 65 | Toluene | 40 |
| 11 | 4 | 48 | 90 | Ethanol | <1 |
| 12 | 4 | 48 | 90 | Methanol | <1 |
| 13 | 4 | 48 | 90 | Water | <1 |
| 14 | 4 | 48 | 90 | Dichloromethane | <1 |

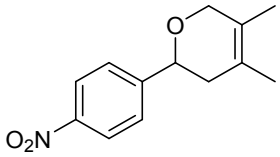
**Characterization data of pyran derivatives:**

1. **4, 5-Dimethyl-2-phenyl-3,6-dihydro-2H-pyran [IIIaa]**



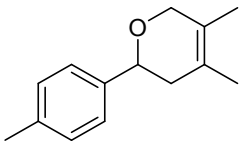
Yield = 94 %, yellow oil. Thin layer chromatography: $R_f$ = 0.58 (hexane/ethyl acetate = 10/1) $^1$H NMR ($CDCl_3$) δ 7.29–7.27 (m, 4H), 7.24–7.21 (m, 1H), 4.49 (dd, 1H), 4.12 (d, 1H), 4.06 (d,1H), 2.28–2.24 (m,1H), 2.09 (d,1H), 1.68 (s, 3H), 1.62 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 142.6, 128.3, 127.3, 125.8, 124.5, 123.8, 77.06, 70.3, 38.5, 18.3, 13.8; ESI-Mass found 211.1064, Calcd for $C_{13}H_{15}O$: $[M+Na]^+$ (211.1099).

2. **4, 5-Dimethyl-2-(4-nitrophenyl)-3,6-dihydro-2H-pyran [IIIba]**



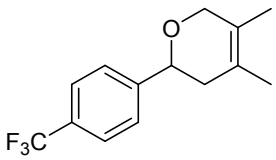
Yield = 87 %, yellow. Thin layer chromatography: $R_f$ = 0.28 (hexane/ethyl acetate = 20/1) $^1$H NMR ($CDCl_3$) δ 8.24 (d, 2H), 7.59 (d, 2H), 4.64 (dd, 1H), 4.16 (d, 1H), 4.13 (d, 1H), 2.17–2.13 (m,1H), 2.98-2.93(d, 1H), 1.67 (s, 3H), 1.57 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 149.1, 125.6, 125.3, 123.7, 122.9, 122.5, 122.2, 76.4, 69.1, 37.3, 17.2, 12.8; ESI-Mass found 256.0957, Calcd for $C_{13}H_{15}NO_3$: $[M+Na]^+$ (256.0950).

3. **4, 5-Dimethyl-2-(p-tolyl)-3,6-dihydro-2H-pyran [IIIca]**



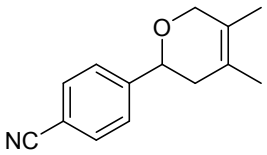
Yield = 95 %, colorless oil. Thin layer chromatography: $R_f$ = 0.42 (hexane/ethyl acetate = 40/1) $^1$H NMR ($CDCl_3$) δ 7.24 (d, 2H), 7.16 (d, 2H), 4.52 (dd, 1H), 4.20 (d, 1H), 4.11 (d, 1H), 2.33 (s, 3H), 2.31 (m,1H), 2.06 (d, 1H), 1.67 (s, 3H), 1.58 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 139.6, 136.9, 129.0, 125.8, 124.5, 123.8, 77.4, 76.2, 70.3, 38.5, 18.3, 13.8; ESI-Mass found 225.1264, Calcd for $C_{14}H_{18}O$: $[M+Na]^+$(225.1255).

4. **4, 5-Dimethyl-2-(4-(trifluoromethyl) phenyl)-3,6-dihydro-2H-pyran [IIIda]**



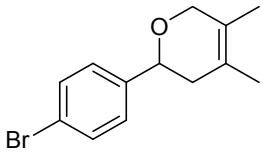
Yield = 90 %, white. Thin layer chromatography: $R_f$ = 0.40 (hexane/ethyl acetate = 10/1) $^1$H NMR ($CDCl_3$) δ 7.64 (d, 2H), 7.52 (d, 1H), 4.64 (dd, 1H),4.22 (d, 1H), 4.17 (d, 1H), 2.20 (m,1H), 2.15 (d, 1H), 1.72 (s, 3H), 1.62 (s, 3H);$^{13}$C NMR ($CDCl_3$) δ 145.6, 128.6, 126.9, 124.9, 124.5, 124.2, 123.6, 75.9, 69.1, 37.4, 17.4, 12.8 ESI-Mass found 279.0977, Calcd for $C_{14}H_{14}OF_3$ : $[M+Na]^+$ 279.0973

**5. 4-(4,5-Dimethyl-3,6-dihydro-2H-pyran-2-yl)benzonitrile [IIIea]**



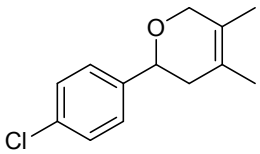
Yield = 64 %, white. Thin layer chromatography: $R_f$ = 0.32 (hexane/ethyl acetate = 40/1) $^1$H NMR ($CDCl_3$) δ 7.58 (d, 2H), 7.42 (d, 2H), 4.54 (dd, 1H), 4.16 (d, 1H), 4.07 (d, 1H), 2.17–2.12 (m,1H), 2.10 (d, 1H), 1.74 (s, 3H), 1.62 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 148.1, 132.1, 126.3, 124.6, 123.3, 111.06, 77.4, 70.1, 38.3, 18.2, 13.8; ESI-Mass found 236.1058, Calcd for $C_{14}H_{15}NO$: $[M+Na]^+$ (236.1051).

**6. 2-(4-Bromophenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran [IIIfa]**



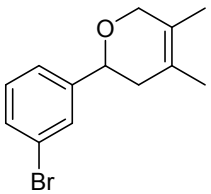
Yield = 90 %, white. Thin layer chromatography: $R_f$ = 0.60 (hexane/ethyl acetate = 20/1) $^1$H NMR ($CDCl_3$) δ 7.67-7.60 (d, 2H), 7.42-7.37 (d, 2H), 4.45 (dd, 1H), 4.09 (d, 1H), 4.04 (d, 1H), 2.15–2.10 (m,1H), 2.02 (d, 1H), 1.65 (s, 3H), 1.51 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 141.7, 131.4, 128.9, 124.5, 123.5, 121.1, 77.1, 70.2, 38.4, 18.3, 13.8; ESI-Mass found 289.0195, Calcd for $C_{13}H_{15}BrO$: $[M+Na]^+$(289.0204).

**7. 2-(4-Chlorophenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran [IIIga]**



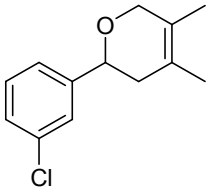
Yield: 90%, colorless liquid. TLC: $R_f$ = 0.35 (hexane/ethyl acetate = 20/1). $^1$H NMR ($CDCl_3$) δ 7.61–7.47 (m, 4H), 4.59 (dd, 1H), 4.19 (d, 1H), 4.14 (d, 1H), 2.23–2.20 (m, 1H), 2.17-2.13 (d, 1H), 1.69 (s, 3H), 1.60 (s, 3H); $^{13}$C NMR (CDCl3) δ 133.0, 128.4, 127.2, 124.6, 121.1, 77.1, 70.2, 38.4, 18.3, 13.8; ESI-Mass found 245.0702, Calcd for $C_{13}H_{15}ClO$: $[M+Na]^+$(245.0709).

**8. 2-(3-Bromophenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran [IIIha]**



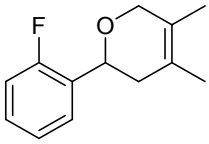
Yield = 91 %, colorless liquid. Thin layer chromatography: $R_f$ = 0.58 (hexane/ethyl acetate = 10/1) $^1$H NMR ($CDCl_3$) δ 7.40–7.28 (m, 2H), 7.16–7.13 (m, 1H), 7.09-7.04 (m, 1H), 4.50 (dd, 1H), 4.20 (d, 1H), 3.98 (d, 1H), 2.17–2.13 (m,1H), 2.12-2.09 (d, 1H), 1.64 (s, 3H), 1.58 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 145.0, 130.3, 128.9, 124.5, 124.3, 123.5, 77.4, 70.2, 38.4, 18.3, 13.8; ESI-Mass found 289.0196, Calcd for $C_{13}H_{15}BrO$: $[M+Na]^+$(289.0204).

**9. 2-(3-Chlorophenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran [IIIia]**



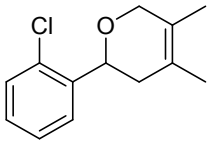

Yield = 90 %, colorless liqiud. Thin layer chromatography: $R_f$ = 0.38 (hexane/ethyl acetate = 10/1) $^1$H NMR ($CDCl_3$) δ 7.31–7.27 (m, 2H), 7.24–7.221 (m, 1H), 7.18-7.10 (m, 1H), 4.46 (dd, 1H), 4.21 (d, 1H), 4.05 (d, 1H), 2.15–2.09 (m,1H), 2.03 (d, 1H), 1.68 (s, 3H), 1.59 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 144.7, 129.4, 126.0, 124.5, 123.8, 122.3, 77.4, 70.2, 38.4, 18.3, 13.8; ESI-Mass found 245.0701, Calcd for $C_{13}H_{15}ClO$: $[M+Na]^+$(245.0709).

**10. 2-(2-Fluorophenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran [IIIja]**



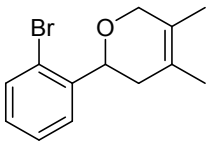

Yield = 90 %, colorless liqiud. Thin layer chromatography: $R_f$ = 0.24 (hexane/ethyl acetate = 10/1) $^1$H NMR ($CDCl_3$) δ 7.51–7.49 (m, 2H), 7.18–7.13 (m, 1H),, 7.04-6.99 (m, 1H), 4.87 (dd, 1H), 4.25 (d, 1H), 4.14 (d, 1H), 2.35–2.30 (m,1H), 2.14 (d, 1H), 1.68 (s, 3H), 1.60 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 157.3, 128.5, 127.1, 126.6, 124.3, 123.8, 76.4, 70.2, 38.5, 18.2, 13.8; ESI-Mass found 229.0996, Calcd for $C_{13}H_{15}FO$: $[M+Na]^+$(229.1005).

**11. 2-(2-Chlorophenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran [IIIka]**



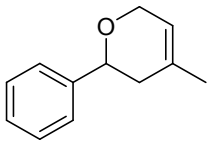

Yield = 92 %, colorless liqiud. Thin layer chromatography: $R_f$ = 0.35 (hexane/ethyl acetate = 10/1) $^1$H NMR ($CDCl_3$) δ 7.63–7.60 (m, 2H), 7.36–7.28 (m, 1H), 7.22-7.20 (m, 1H), 4.96 (dd, 1H), 4.29 (d, 1H), 4.15 (d, 1H), 2.32–2.28 (m,1H), 2.13 (d, 1H), 1.72 (s, 3H), 1.64 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 188.7, 139.4, 129.5, 126.1, 125.9, 123.3, 122.9, 76.3, 69.3, 35.9, 17.3, 12.8; ESI-Mass found 245.0704, Calcd for $C_{13}H_{15}ClO$: $[M+Na]^+$(245.0709).

**12. 2-(2-Bromophenyl)-4,5-dimethyl-3,6-dihydro-2H-pyran [IIIla]**



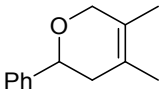

Yield = 92 %, colorless liqiud. Thin layer chromatography: $R_f$ = 0.48 (hexane/ethyl acetate = 10/1) $^1$H NMR ($CDCl_3$) δ 7.61–7.58 (m, 2H), 7.38–7.33 (m, 1H), 7.17-7.14 (m, 1H), 4.90 (dd, 1H), 4.25 (d, 1H), 4.19 (d, 1H), 2.35 (m,1H), 2.29 (d, 1H), 1.72 (s, 3H), 1.63 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 141.0, 131.3, 127.6, 126.7, 126.2, 123.3, 122.8, 76.4, 69.3, 35.9, 17.2, 12.8; ESI-Mass found 289.0199, Calcd for $C_{13}H_{15}BrO$: $[M+Na]^+$(289.0204).

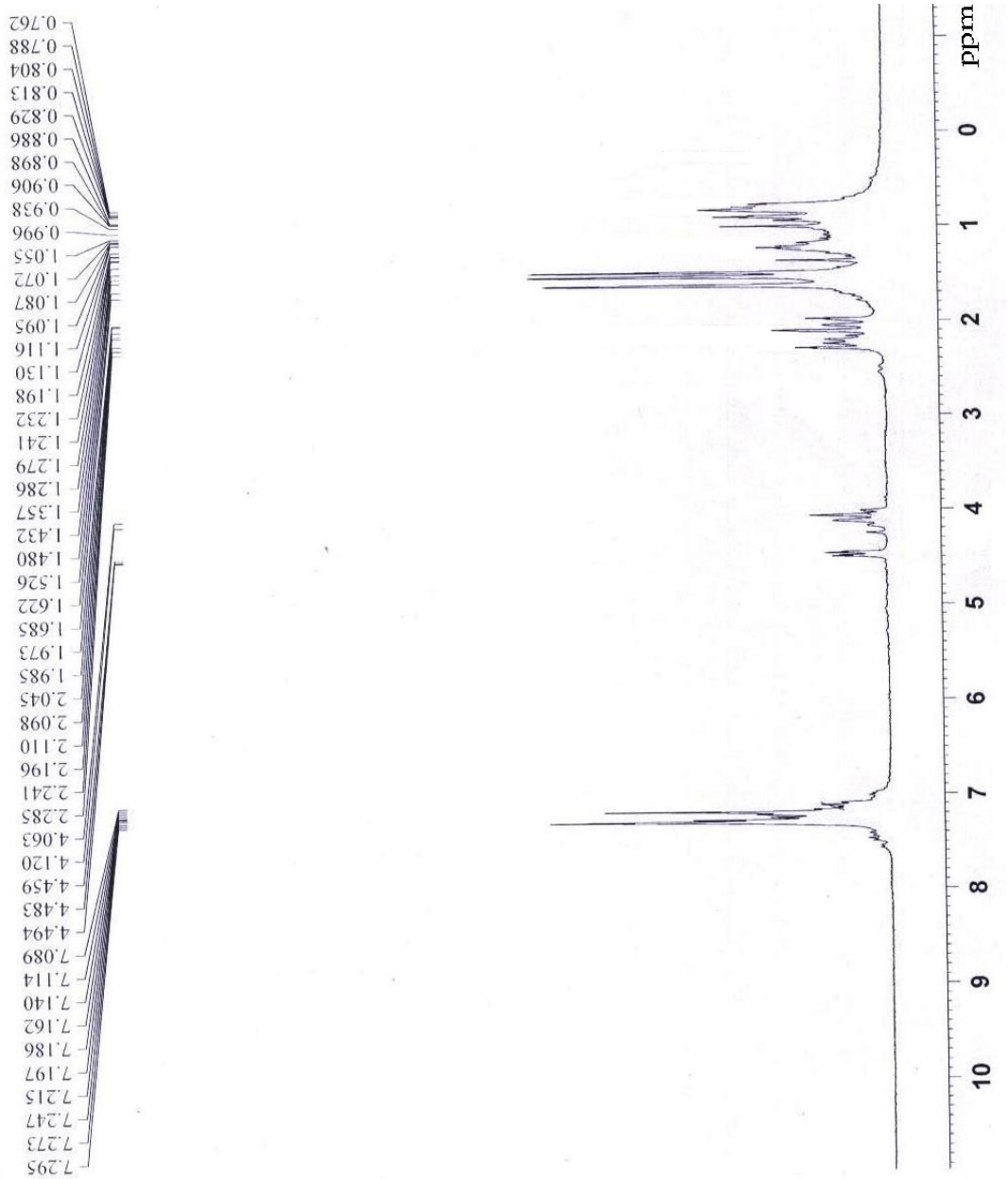
**13. 4 -Methyl-2-phenyl-3,6-dihydro-2H-pyran [IIIac]**

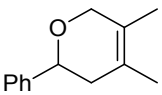


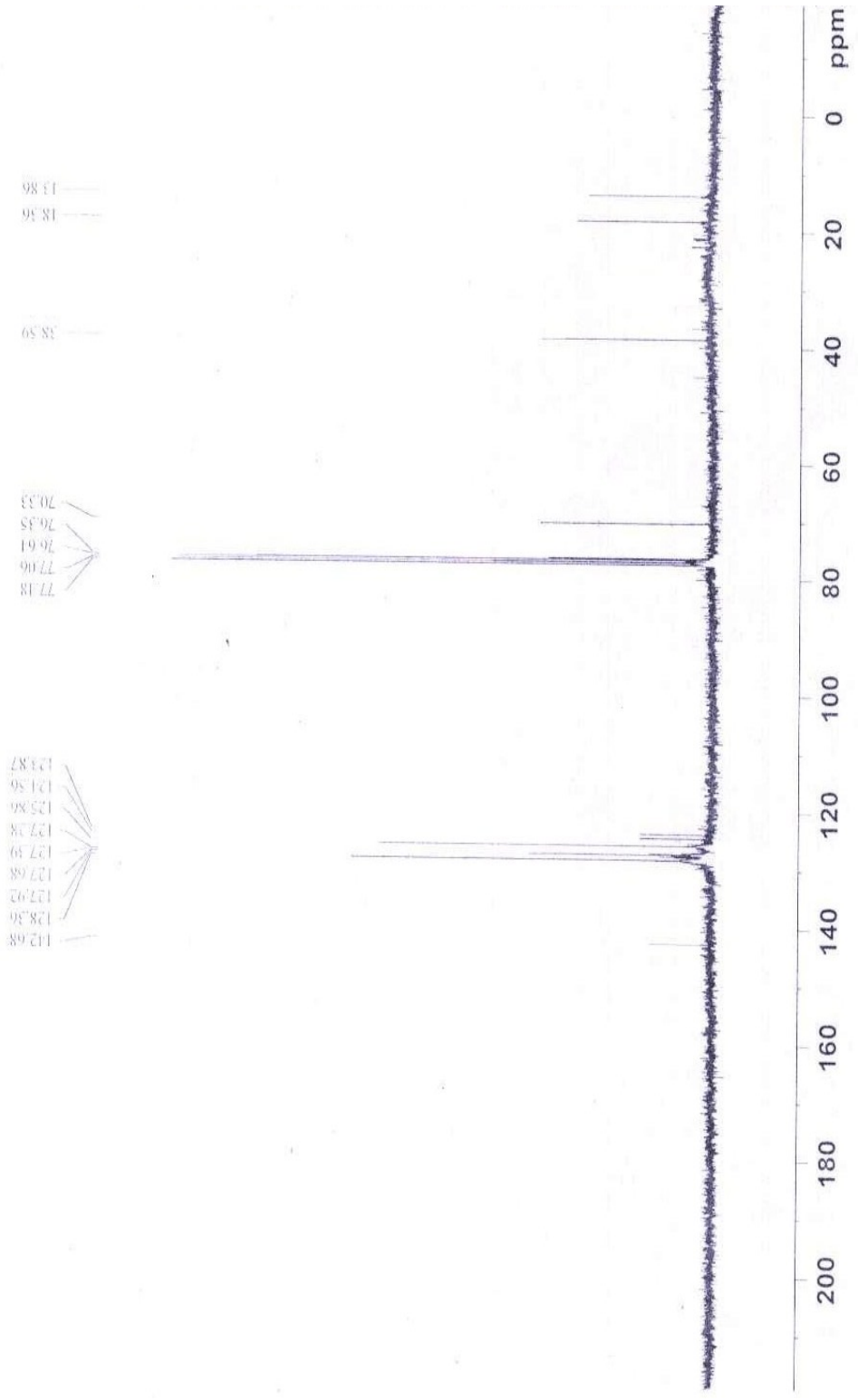
Yield: 85%, colorless oil. TLC: $R_f$ = 0.40 (hexane/ethyl acetate = 20/1). $^1$H NMR ($CDCl_3$) δ 7.38-7.34 (m, 4H), 7.27–7.26 (m, 1H), 5.50 (s, 1H), 4.56 (dd, 1H), 4.18–4.08 (m, 2H), 2.35–2.29 (m,1H), 2.11 (d, 1H), 1.78 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ 142.4, 128.3, 127.4, 125.9, 123.8, 77.4, 66.4, 38.4, 22.8 ; ESI-Mass found 197.0946, Calcd for $C_{12}H_{14}O$:$[M+Na]^+$(197.0942).

**$^{1}$H NMR and $^{13}$C NMR Spectra of Products**

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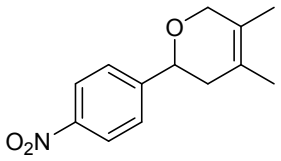
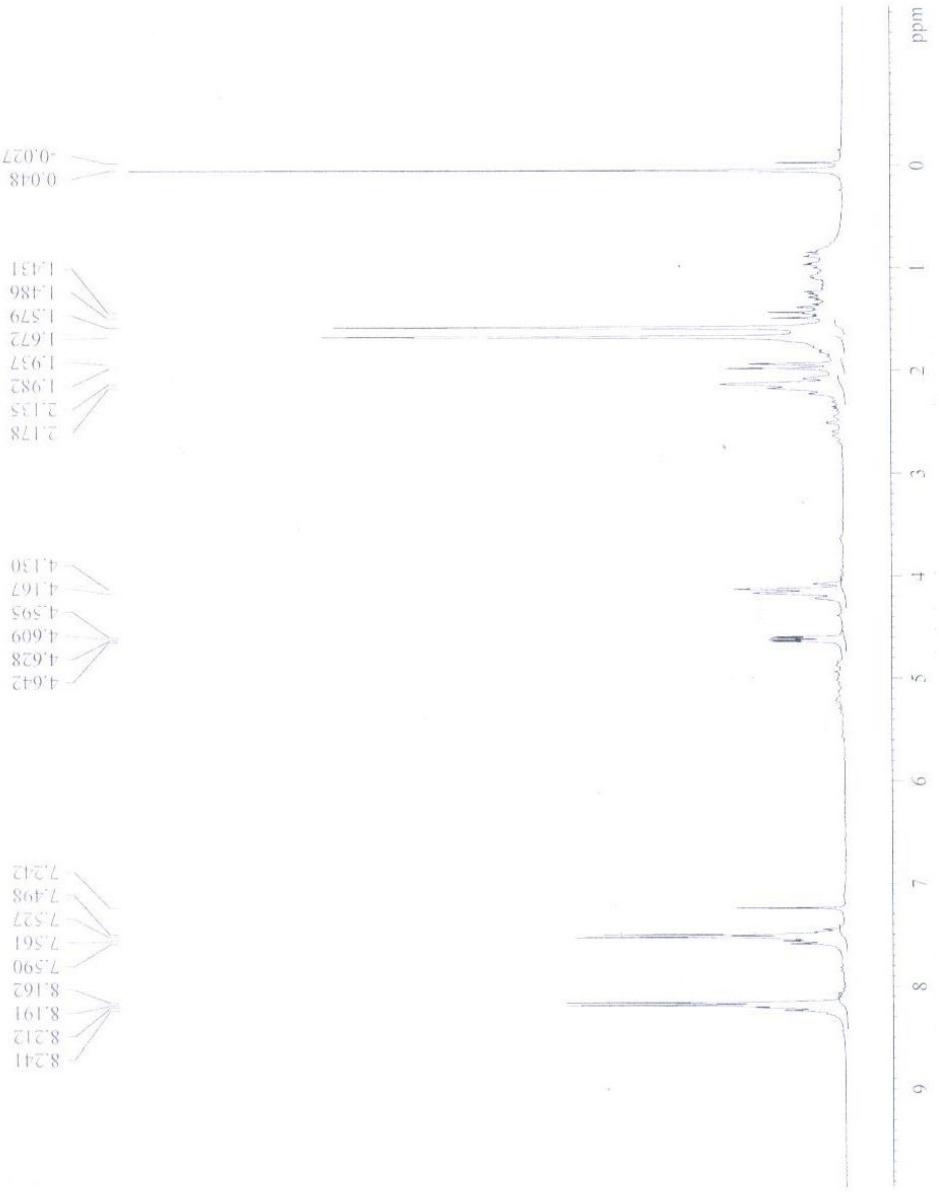
38.59
70.33
76.35
76.61
77.06
77.18
123.87
124.56
125.86
127.38
127.39
127.68
127.92
128.36
142.68
ppm
0
20
40
60
80
100
120
140
160
180
200


O
O2N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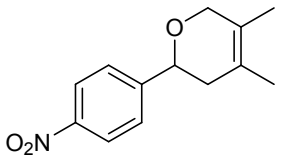
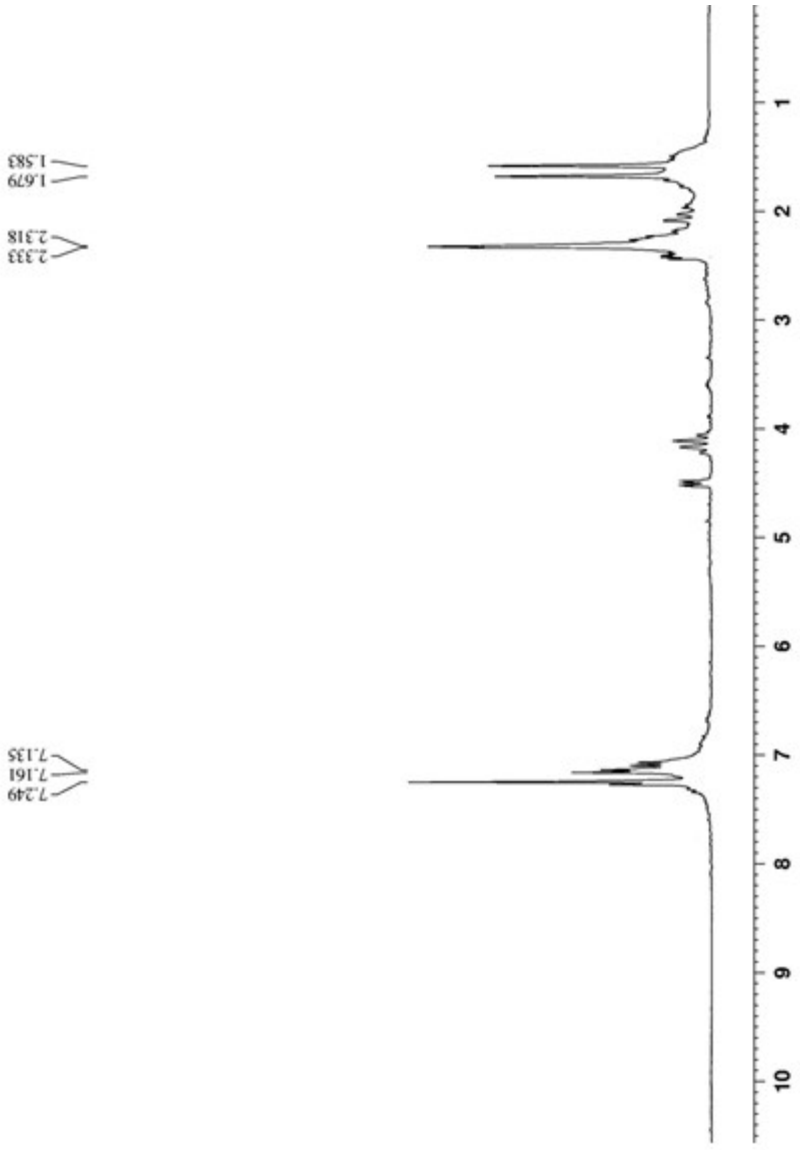
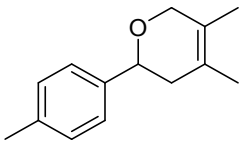
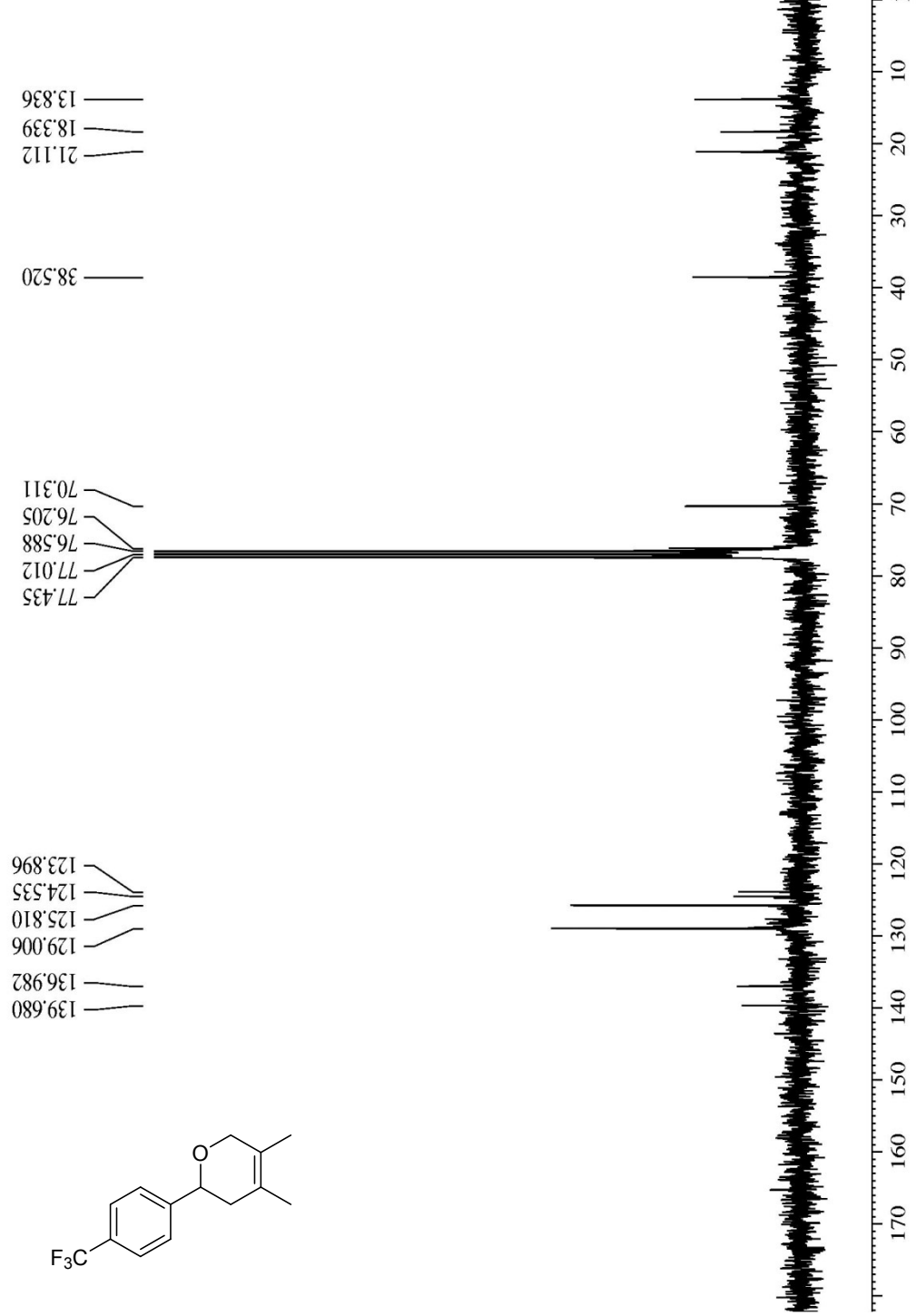
0.018
1.431
1.486
1.579
1.672
1.937
1.982
2.135
2.178
4.130
4.167
4.595
4.609
4.628
4.642
7.242
7.498
7.527
7.561
7.590
8.162
8.191
8.212
8.241
ppm


O
O2N

149.144
125.670
125.373
123.705
122.902
122.580
122.273
76.444
76.020
75.597
74.162
69.108
37.393
17.289
12.816
O


1.583
1.679
2.318
2.333
7.135
7.161
7.249
1
2
3
4
5
6
7
8
9
10


O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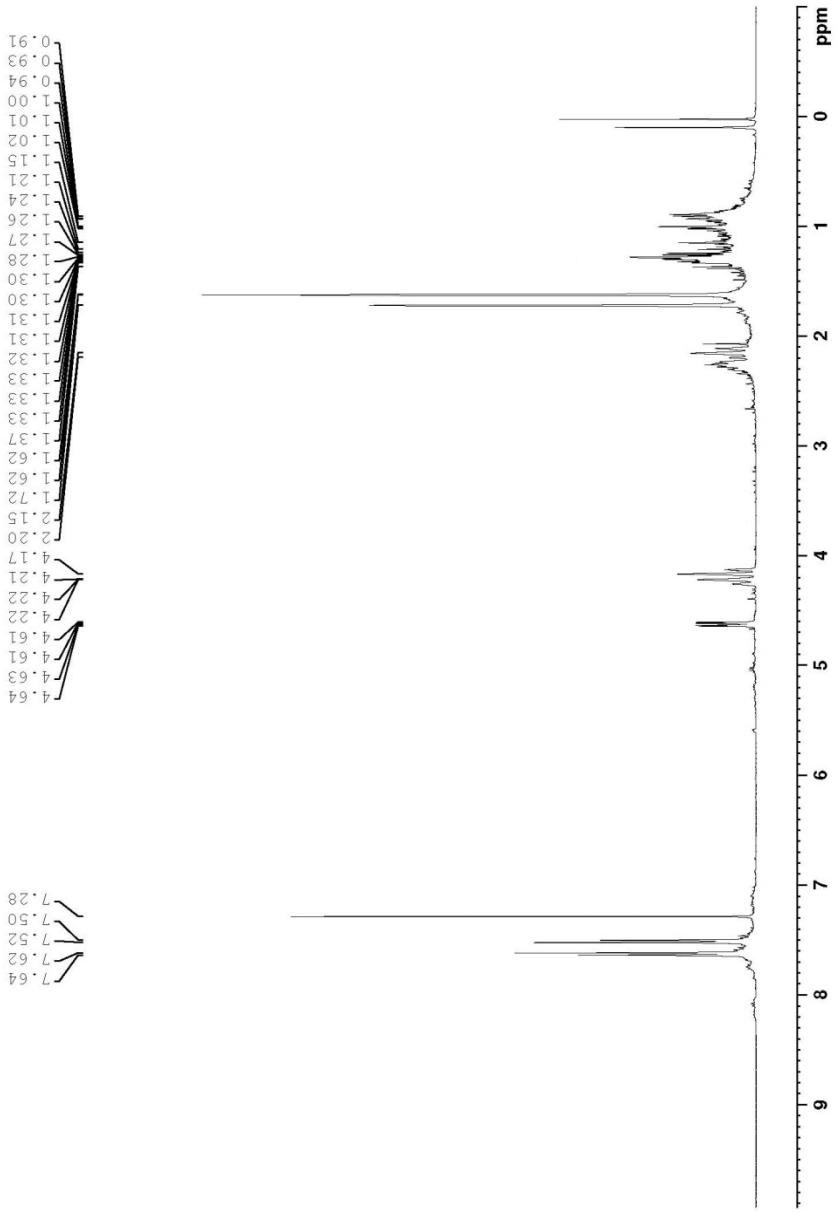
21.112
38.520
70.311
76.205
76.588
77.012
77.435
123.896
124.535
125.810
129.006
136.982
139.680
O
F3C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0.93
0.94
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1.02
1.15
1.21
1.24
1.26
1.27
1.28
1.30
1.30
1.31
1.31
1.32
1.33
1.33
1.33
1.37
1.62
1.62
1.72
2.15
2.20
4.17
4.21
4.22
4.22
4.61
4.61
4.63
4.64
7.28
7.50
7.52
7.62
7.64
ppm
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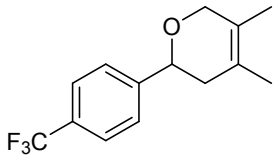
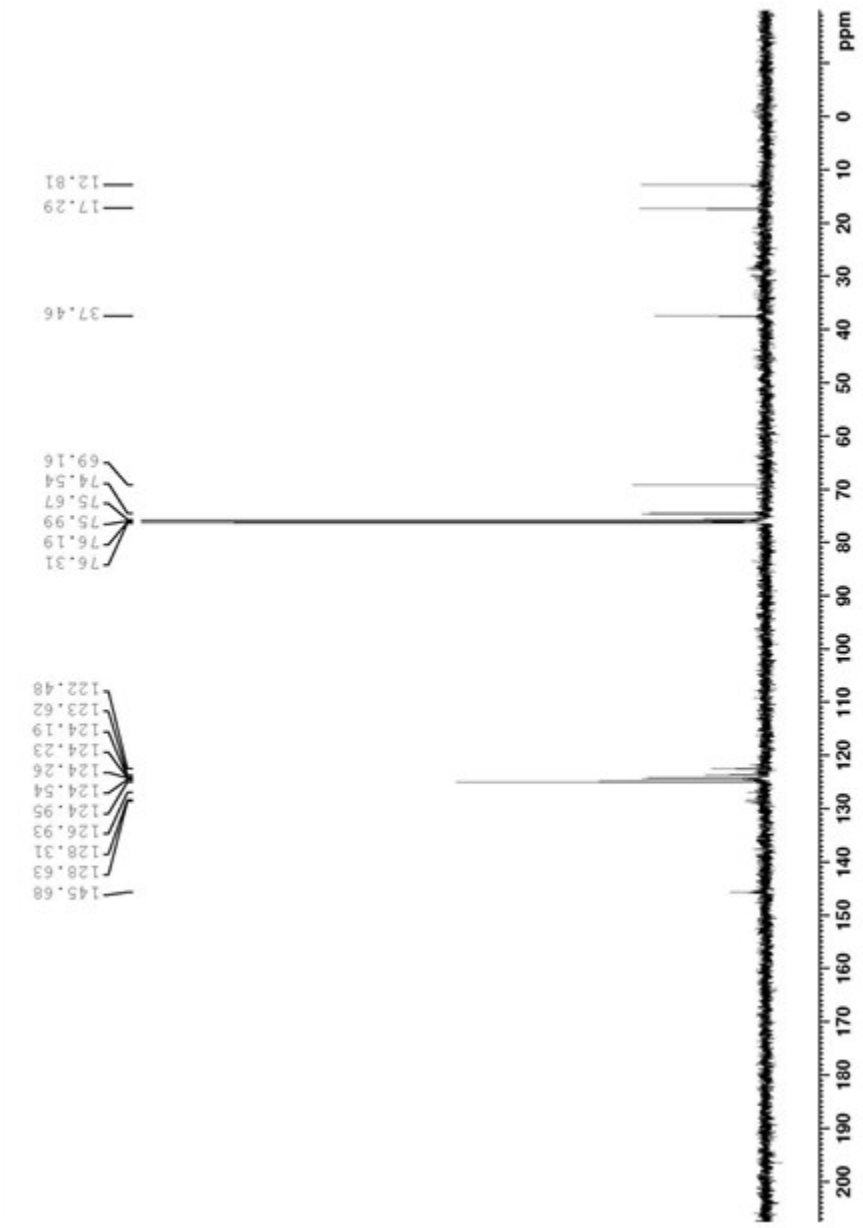
1
2
3
4
5
6
7
8
9


O
F3C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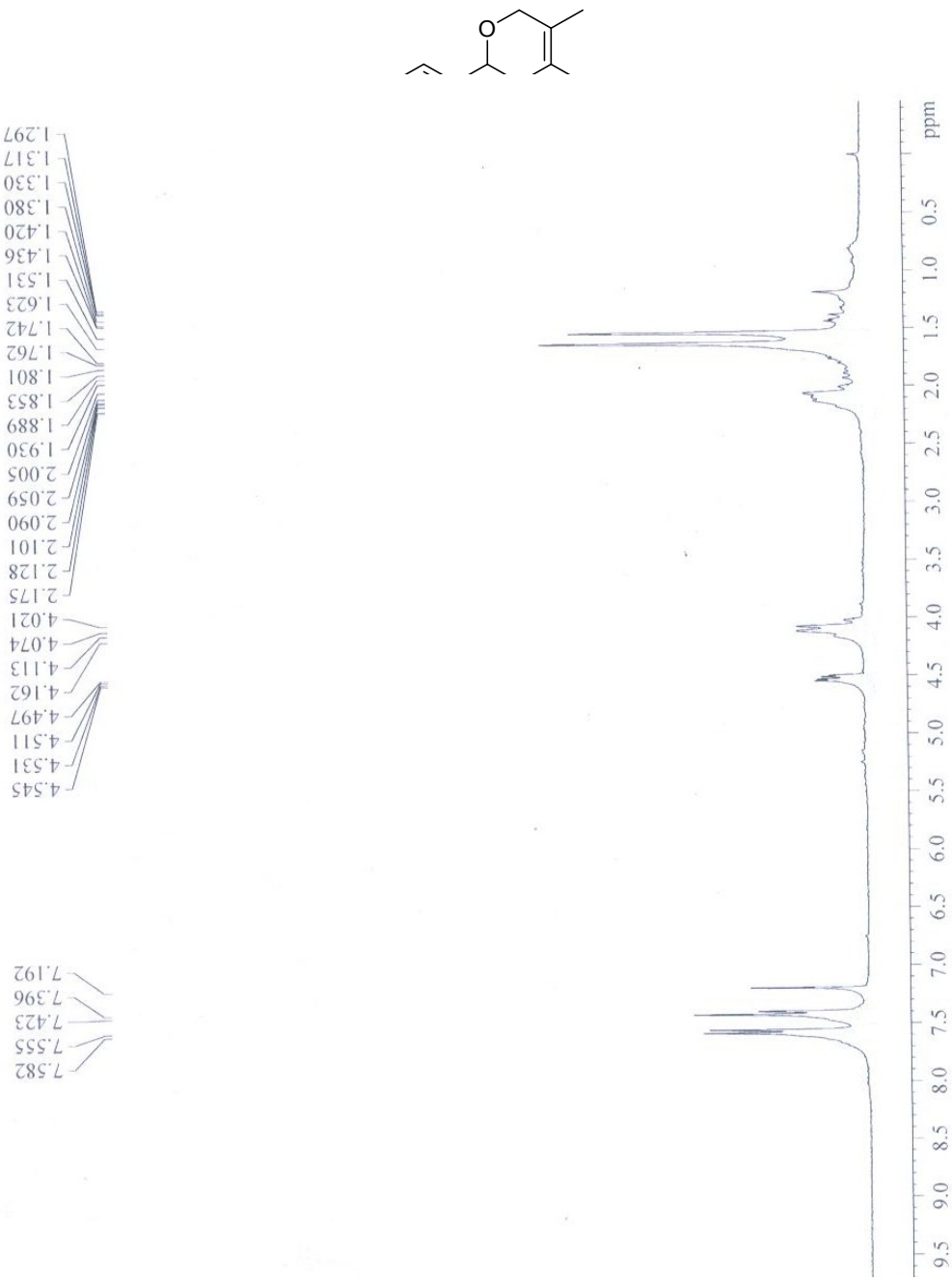
37.46
69.16
74.54
75.67
75.99
76.19
76.31
122.48
123.62
124.19
124.23
124.26
124.54
124.95
126.93
128.31
128.63
145.68
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


O
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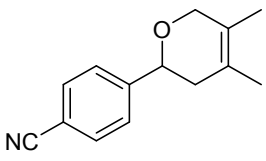
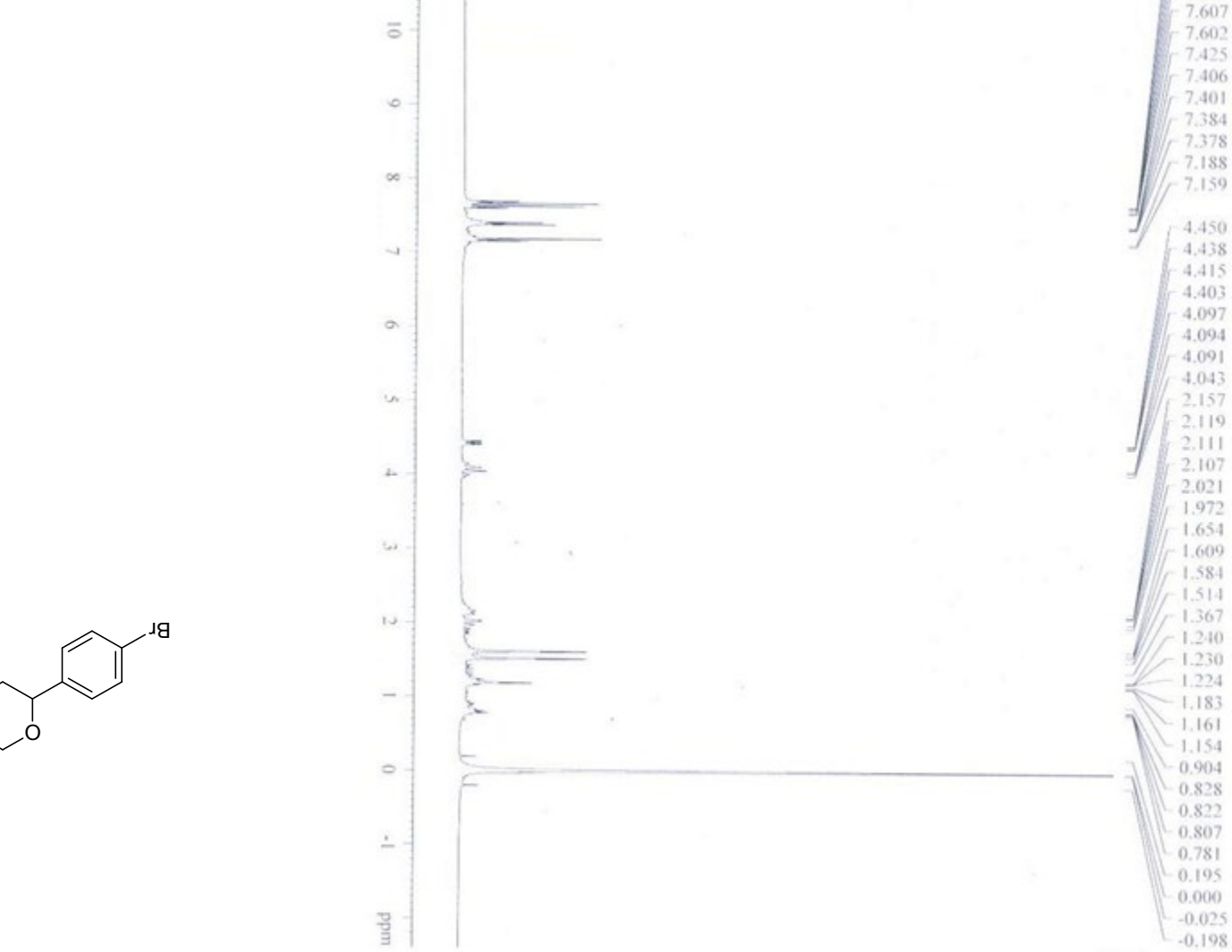
1.317
1.330
1.380
1.420
1.436
1.531
1.623
1.742
1.762
1.801
1.853
1.889
1.930
2.005
2.059
2.090
2.101
2.128
2.175
4.021
4.074
4.113
4.162
4.497
4.511
4.531
4.545
7.192
7.396
7.423
7.555
7.582
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


O
NC




148.10

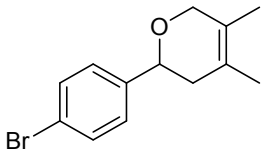
132.19
126.34
124.69
123.33
118.89

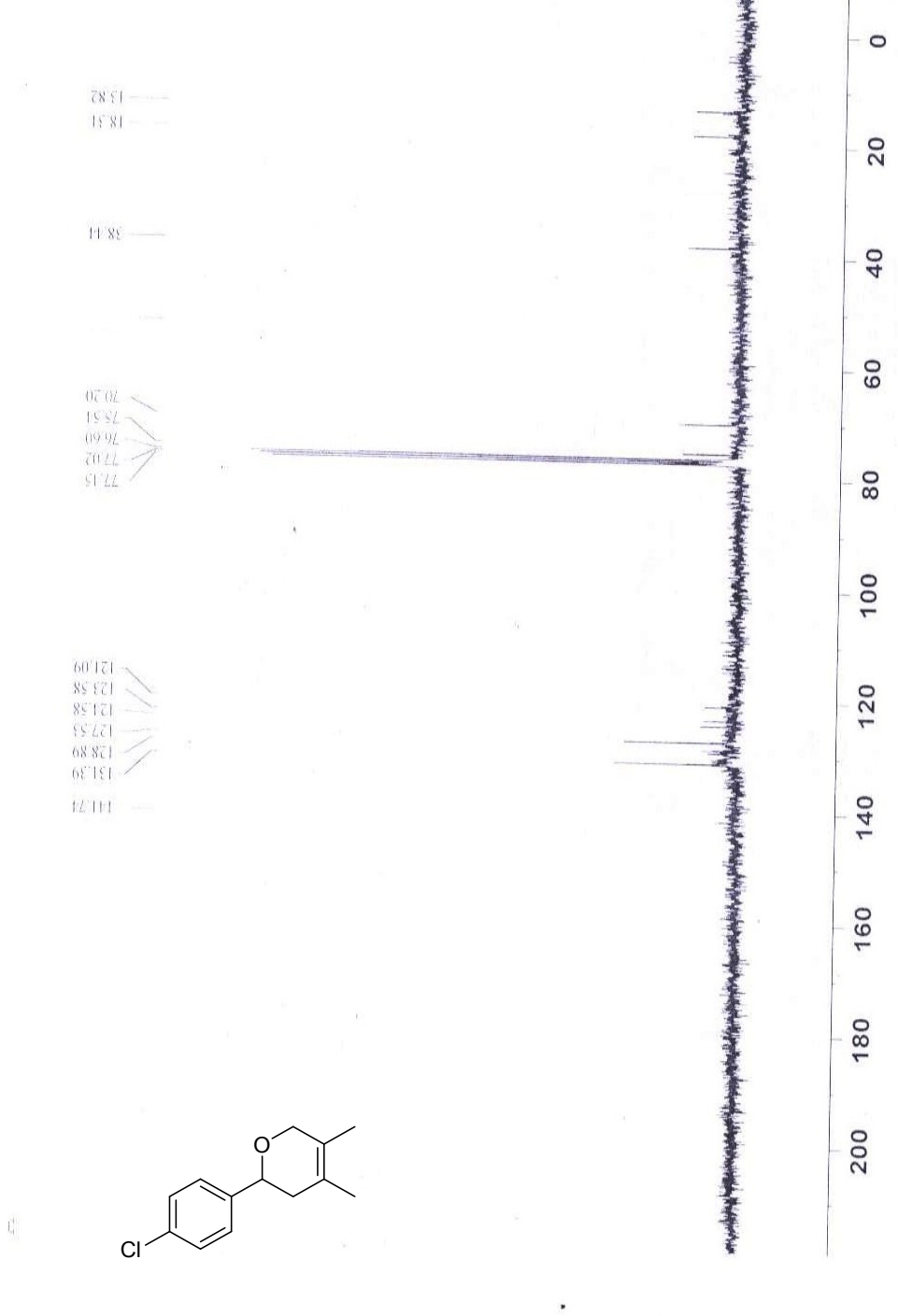
111.06

77.43
77.21
77.01
76.58
75.35
70.12

38.35

18.28
13.80


O
Br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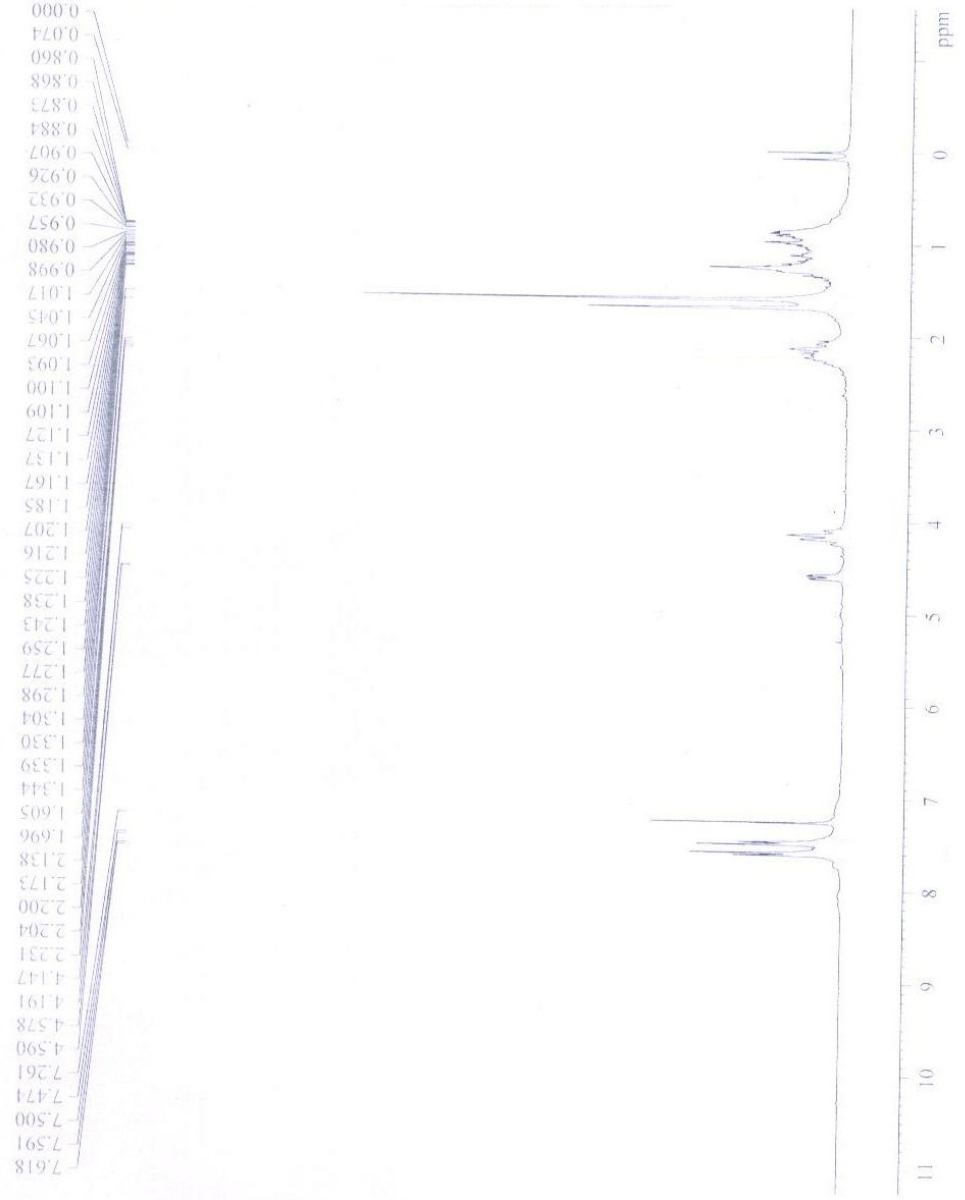
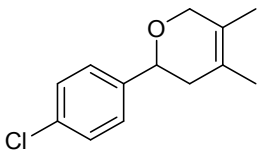
38.11
70.20
75.51
76.69
77.02
77.15
121.09
123.58
124.58
127.55
128.89
131.39
141.74
0
20
40
60
80
100
120
140
160
180
200
O
Cl

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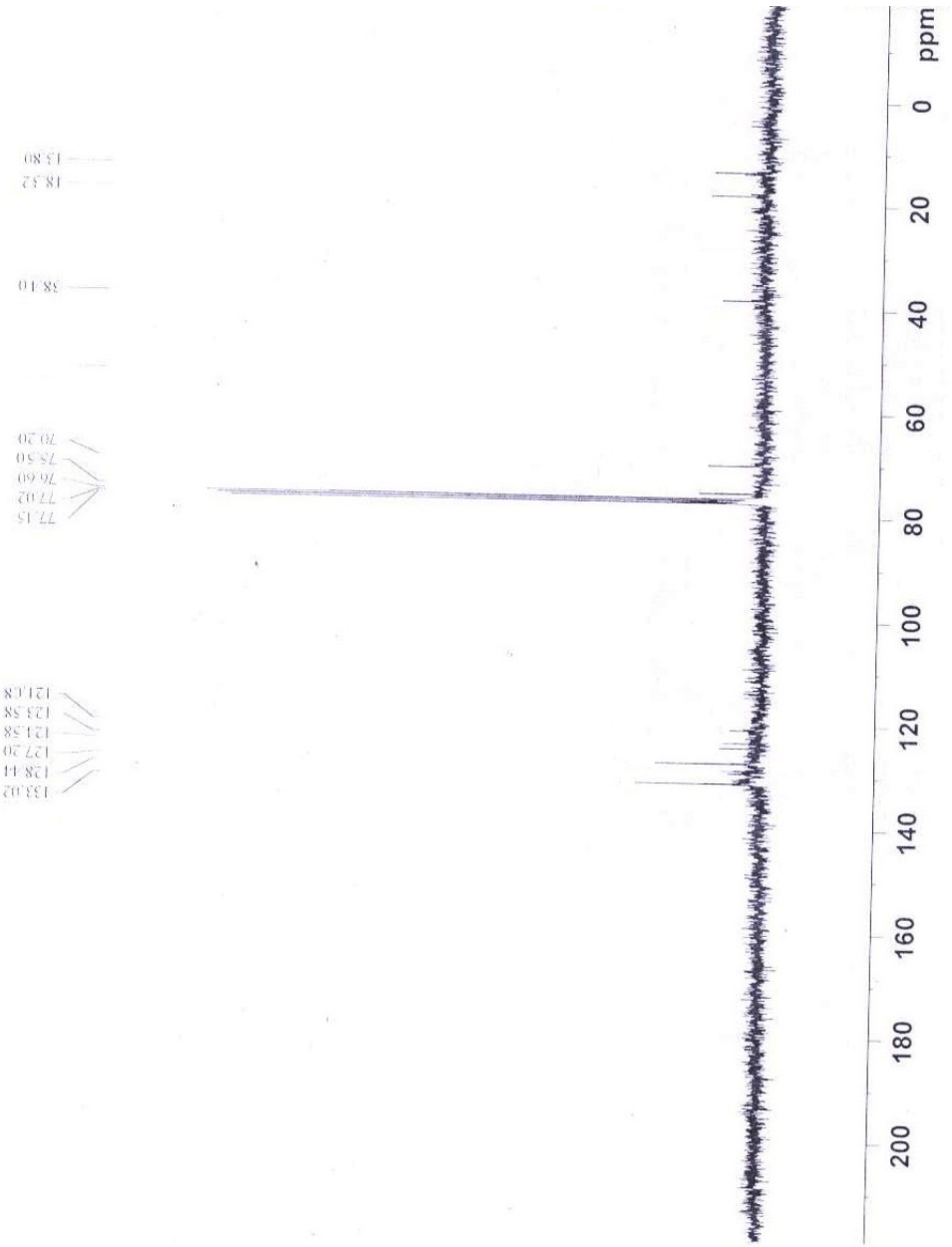
Cl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76.60
77.02
77.15
121.68
123.58
124.58
127.20
128.14
133.02
ppm
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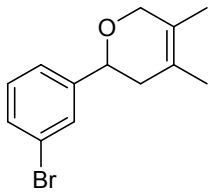
20
40
60
80
100
120
140
160
180
200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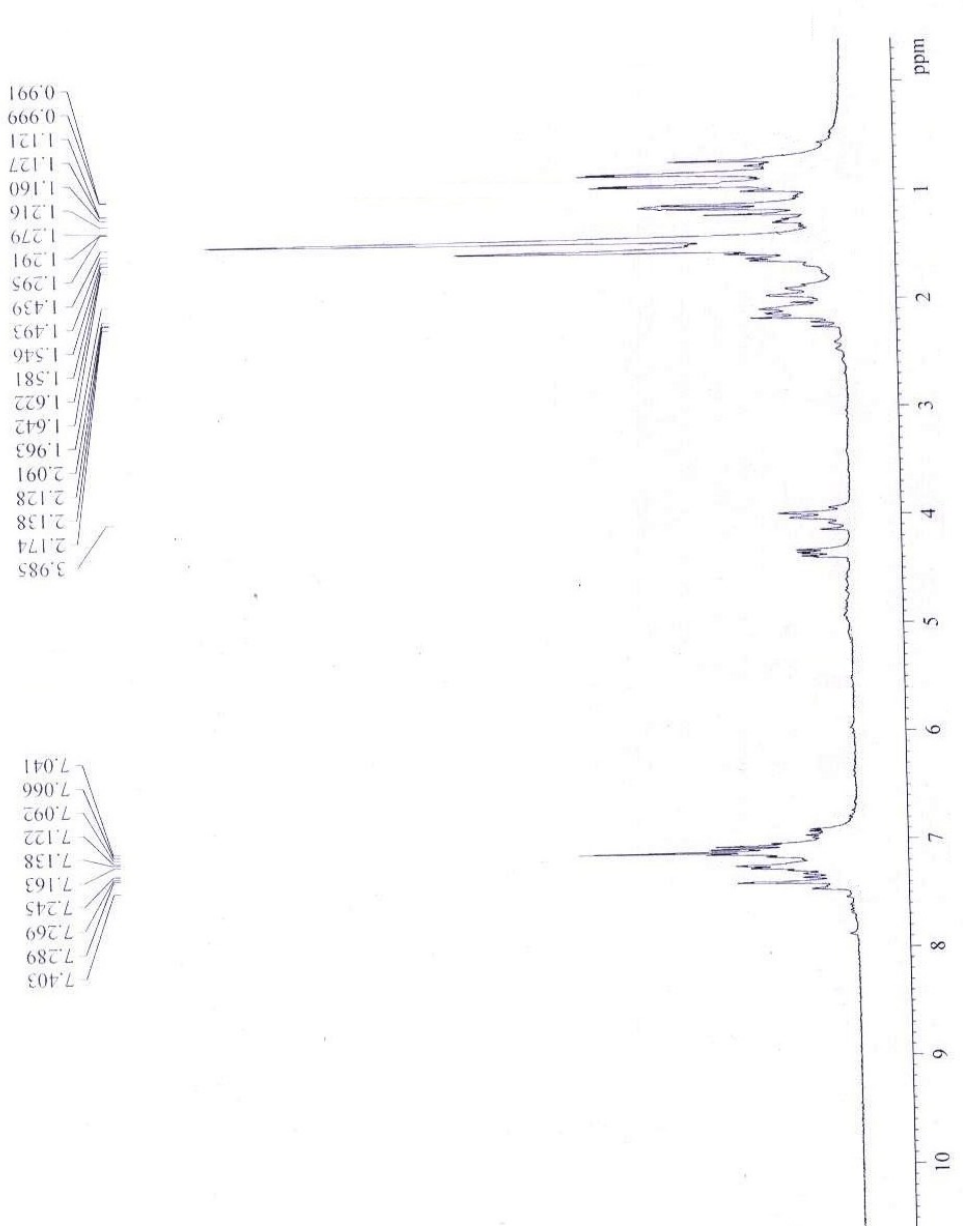
Br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1.295
1.439
1.493
1.546
1.581
1.622
1.642
1.963
2.091
2.128
2.138
2.174
3.985
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7.066
7.092
7.122
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7.245
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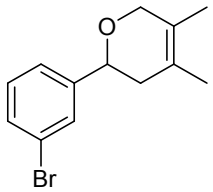
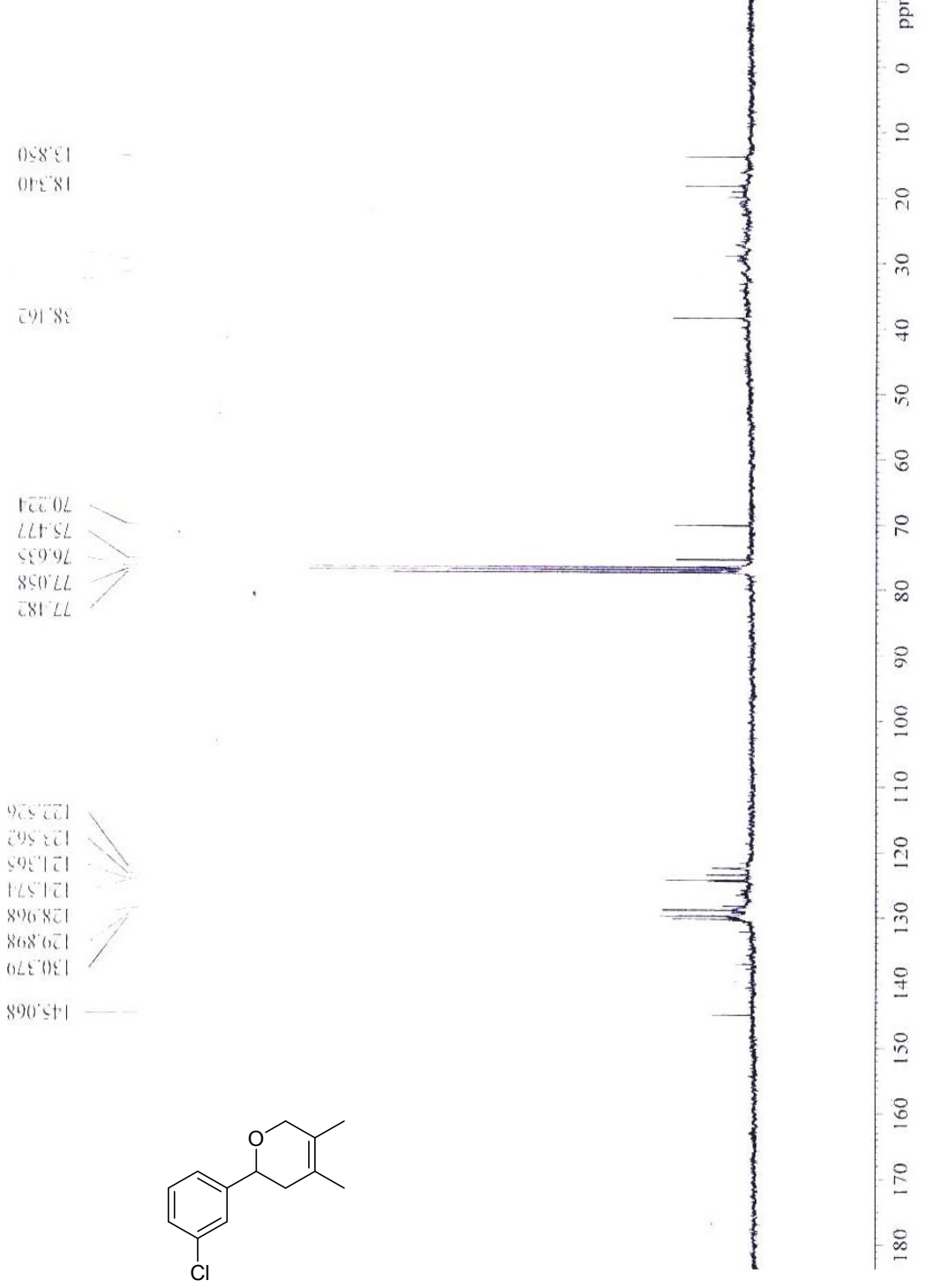
7.403
ppm


O
Br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38.162
70.224
75.477
76.635
77.058
77.482
122.526
123.562
125.365
125.574
128.968
129.898
130.379
145.068
ppm
0
10
20
30
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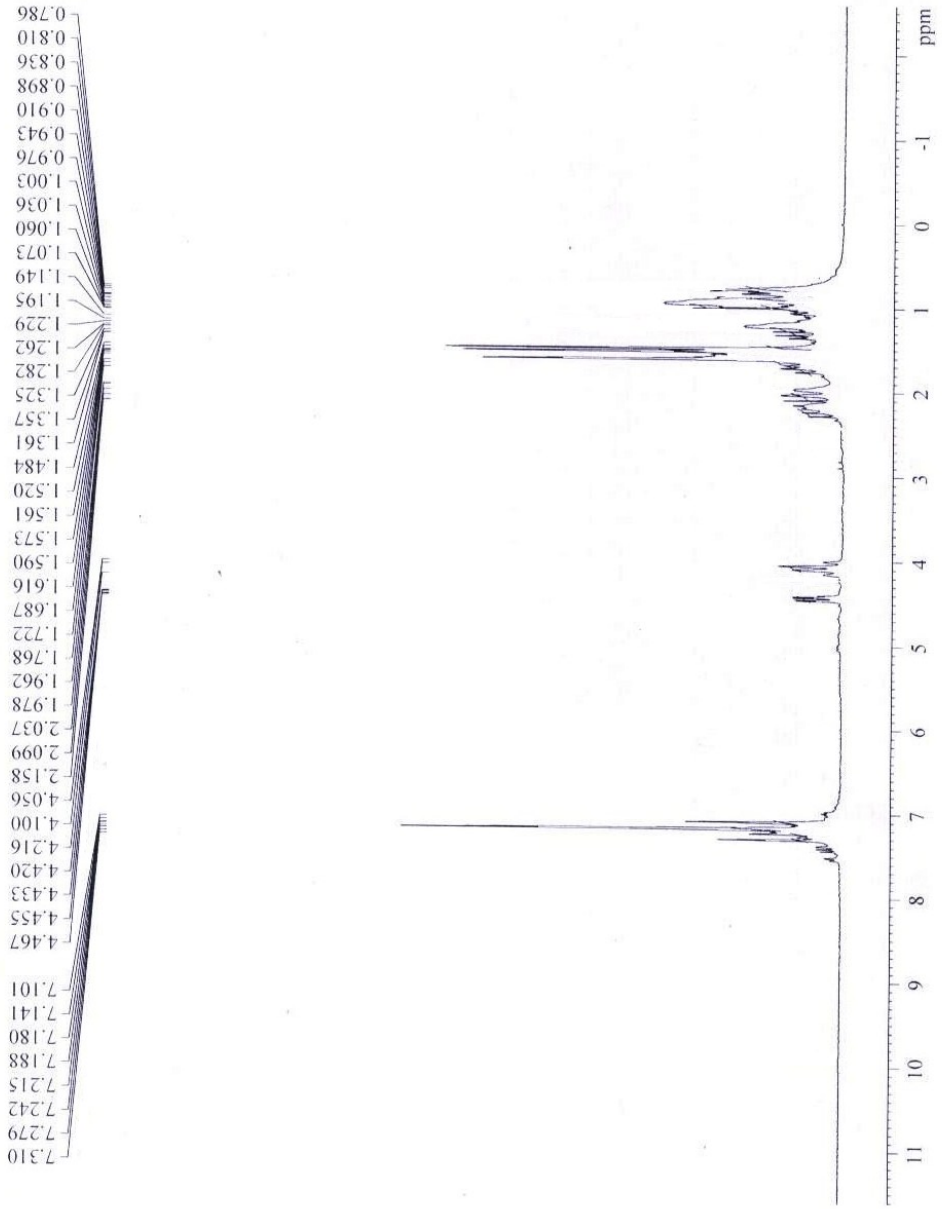
50
60
70
80
90
100
110
120
130
140
150
160
170
180
O
Cl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0.810
0.836
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1.060
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1.149
1.195
1.229
1.262
1.282
1.325
1.357
1.361
1.484
1.520
1.561
1.573
1.590
1.616
1.687
1.722
1.768
1.962
1.978
2.037
2.099
2.158
4.056
4.100
4.216
4.420
4.433
4.455
4.467
7.101
7.141
7.180
7.188
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7.310
ppm
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10
9
8
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6
5
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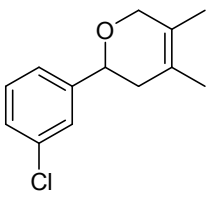
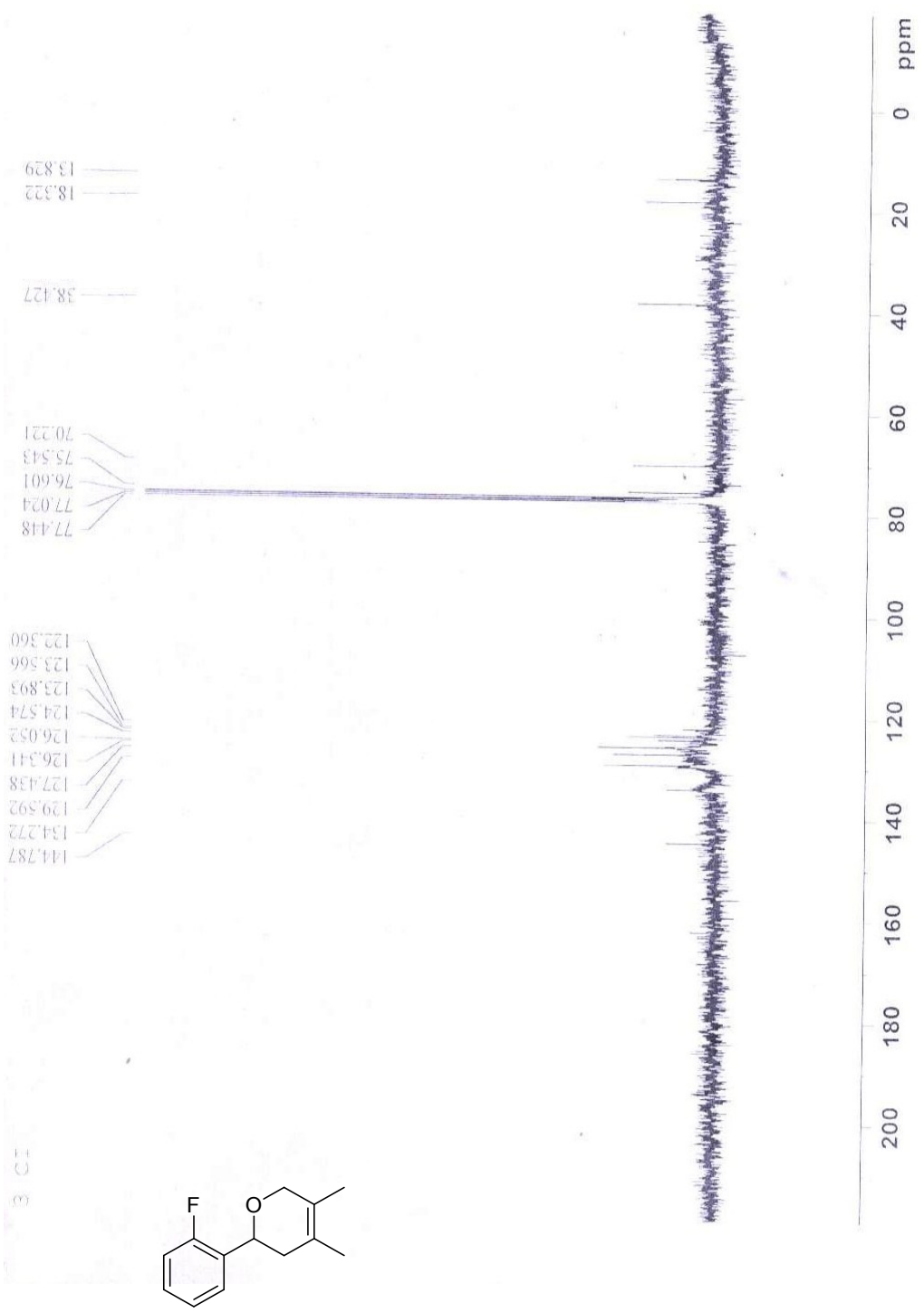

O
Cl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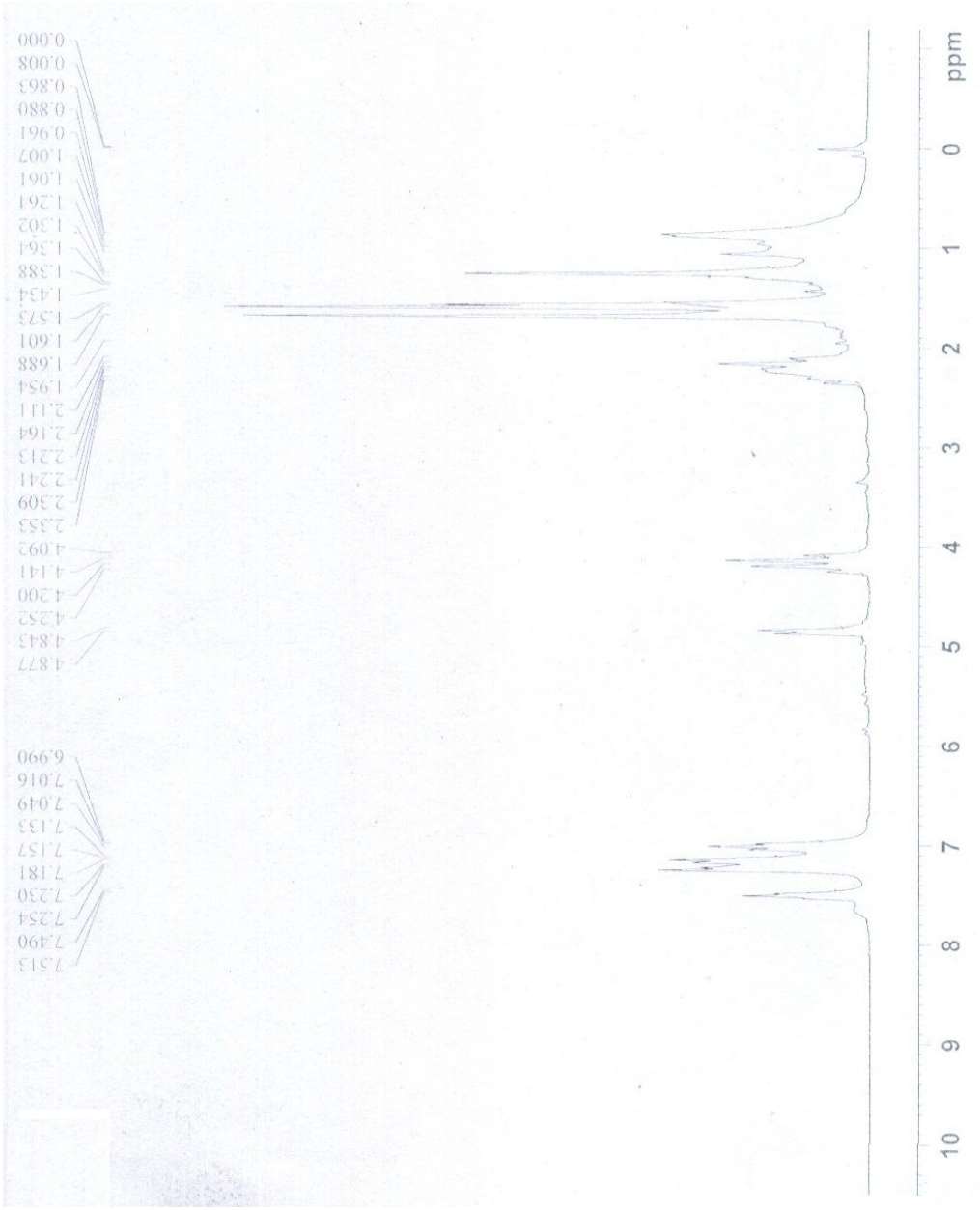
75.543
76.601
77.024
77.448
122.360
123.566
123.893
124.574
126.052
126.341
127.438
129.592
134.272
144.787
ppm
0
20
40
60
80
100
120
140
160
180
200
F
O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0.880
0.961
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1.261
1.302
1.361
1.388
1.434
1.573
1.601
1.688
1.954
2.111
2.164
2.213
2.241
2.309
2.353
4.092
4.141
4.200
4.252
4.843
4.877
6.990
7.016
7.049
7.133
7.157
7.181
7.230
7.254
7.490
7.513
ppm
0
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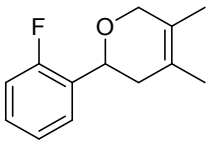
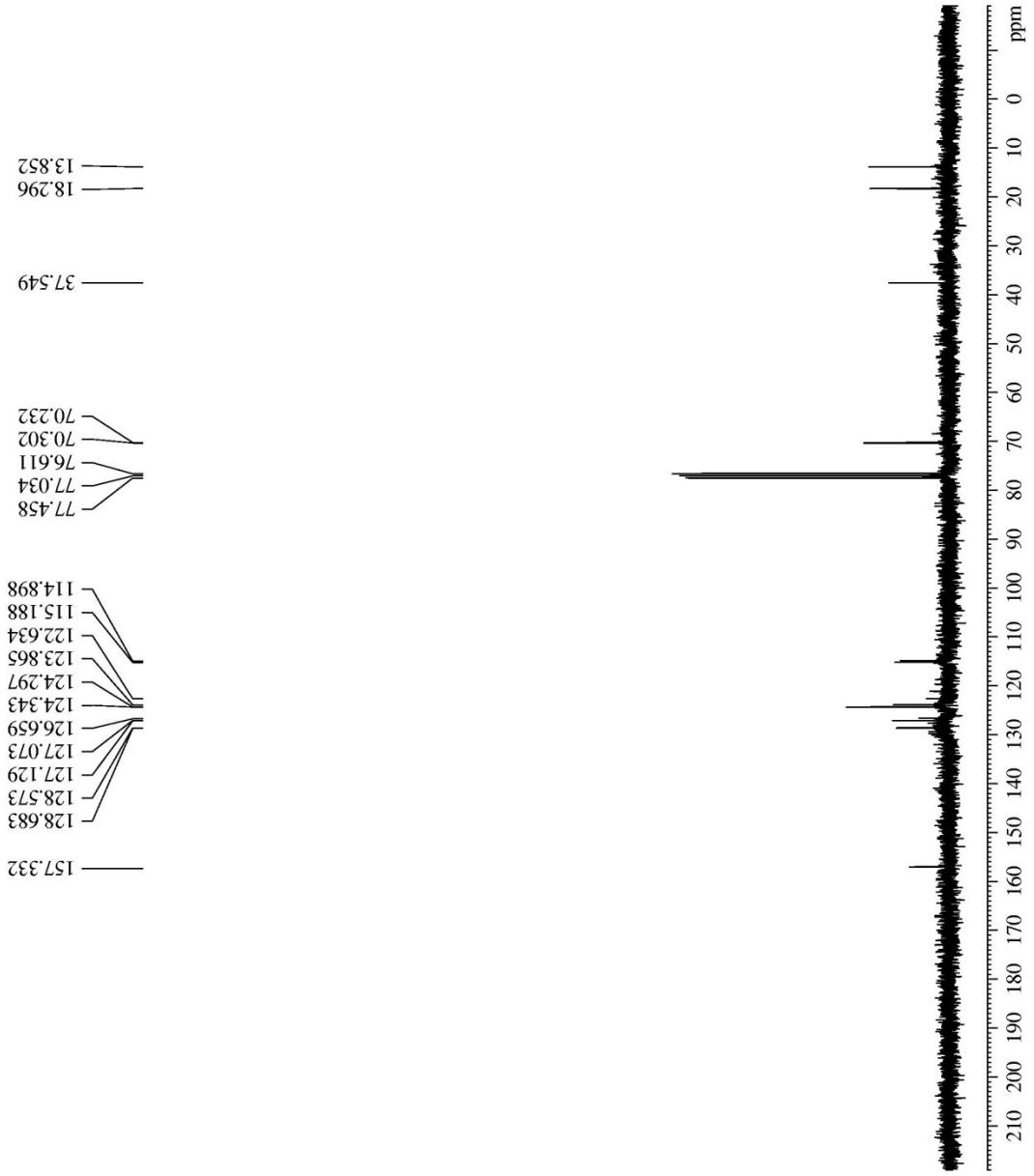
2
3
4
5
6
7
8
9
10


F
O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70.302
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77.034
77.458
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115.188
122.634
123.865
124.297
124.343
126.659
127.073
127.129
128.573
128.683
157.332
ppm
0
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30
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60
70
80
90
100
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120
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140
150
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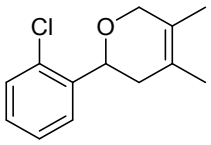
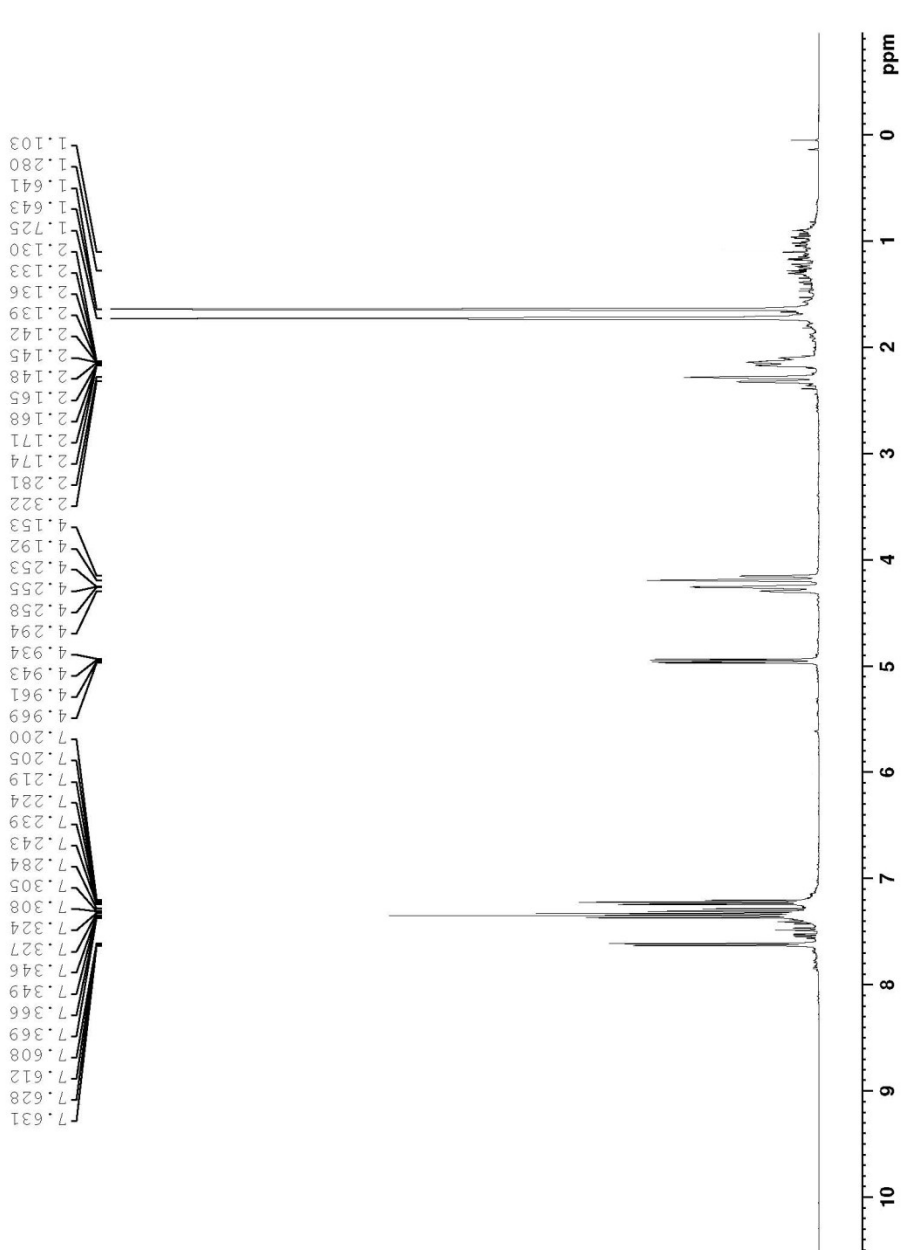
170
180
190
200
210


Cl
O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1.641
1.643
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2.133
2.136
2.139
2.142
2.145
2.148
2.165
2.168
2.171
2.174
2.281
2.322
4.153
4.192
4.253
4.255
4.258
4.294
4.934
4.943
4.961
4.969
7.200
7.205
7.219
7.224
7.239
7.243
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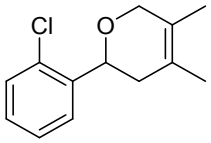
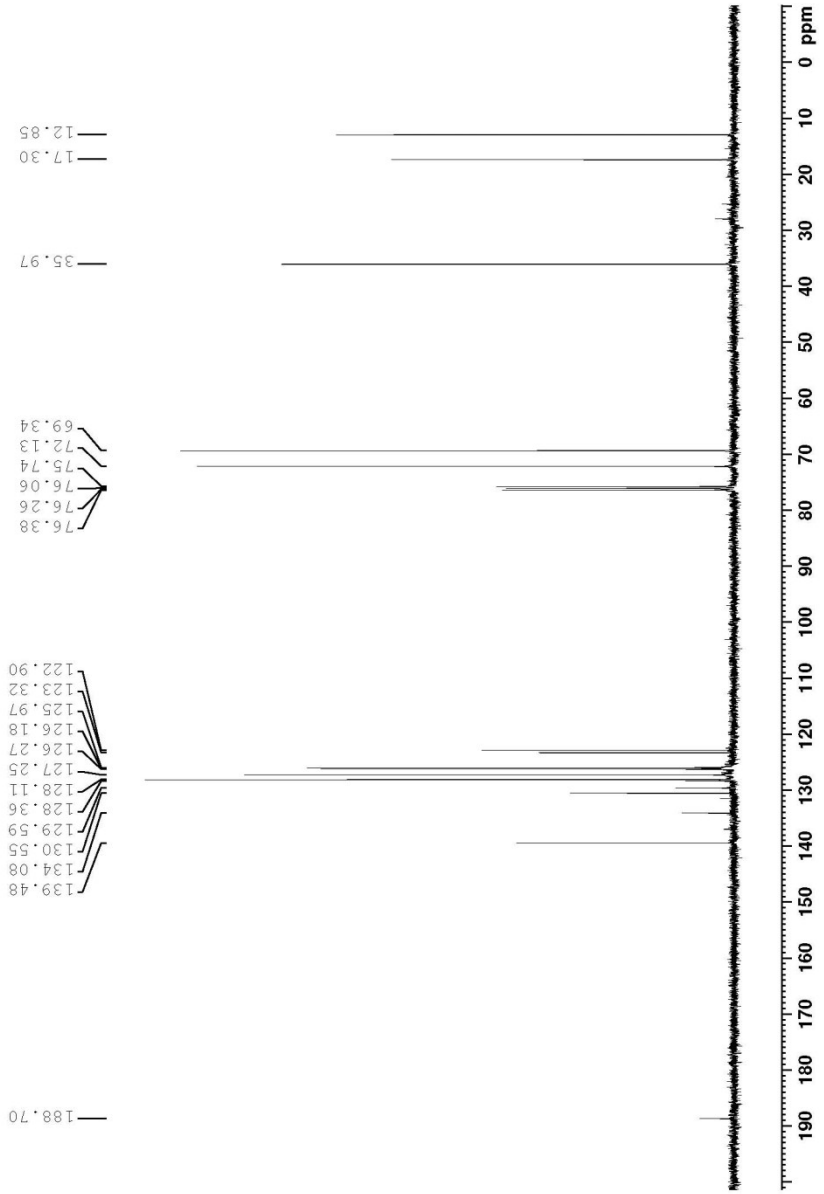
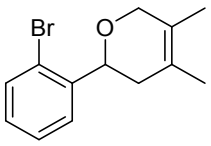
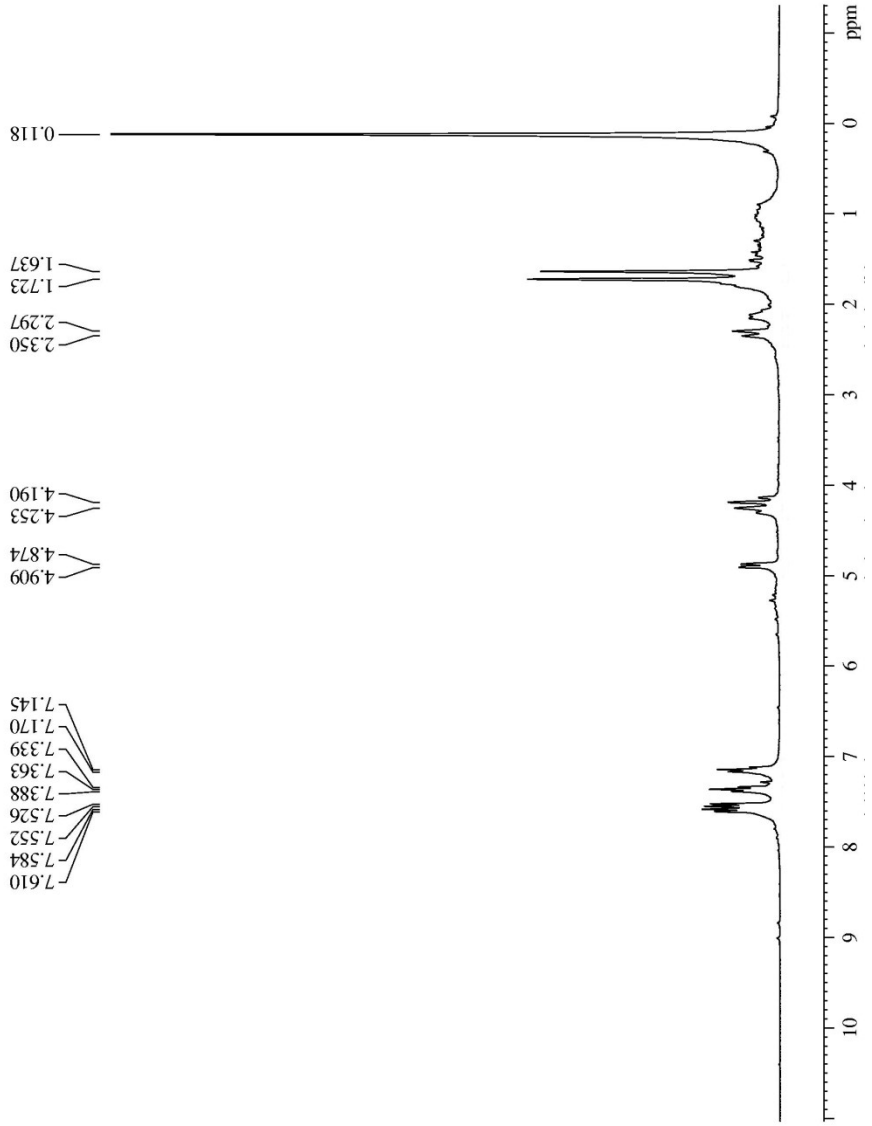
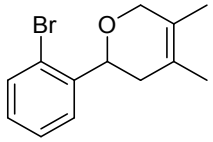
7.308
7.324
7.327
7.346
7.349
7.366
7.369
7.608
7.612
7.628
7.631
ppm
0
1
2
3
4
5
6
7
8
9
10

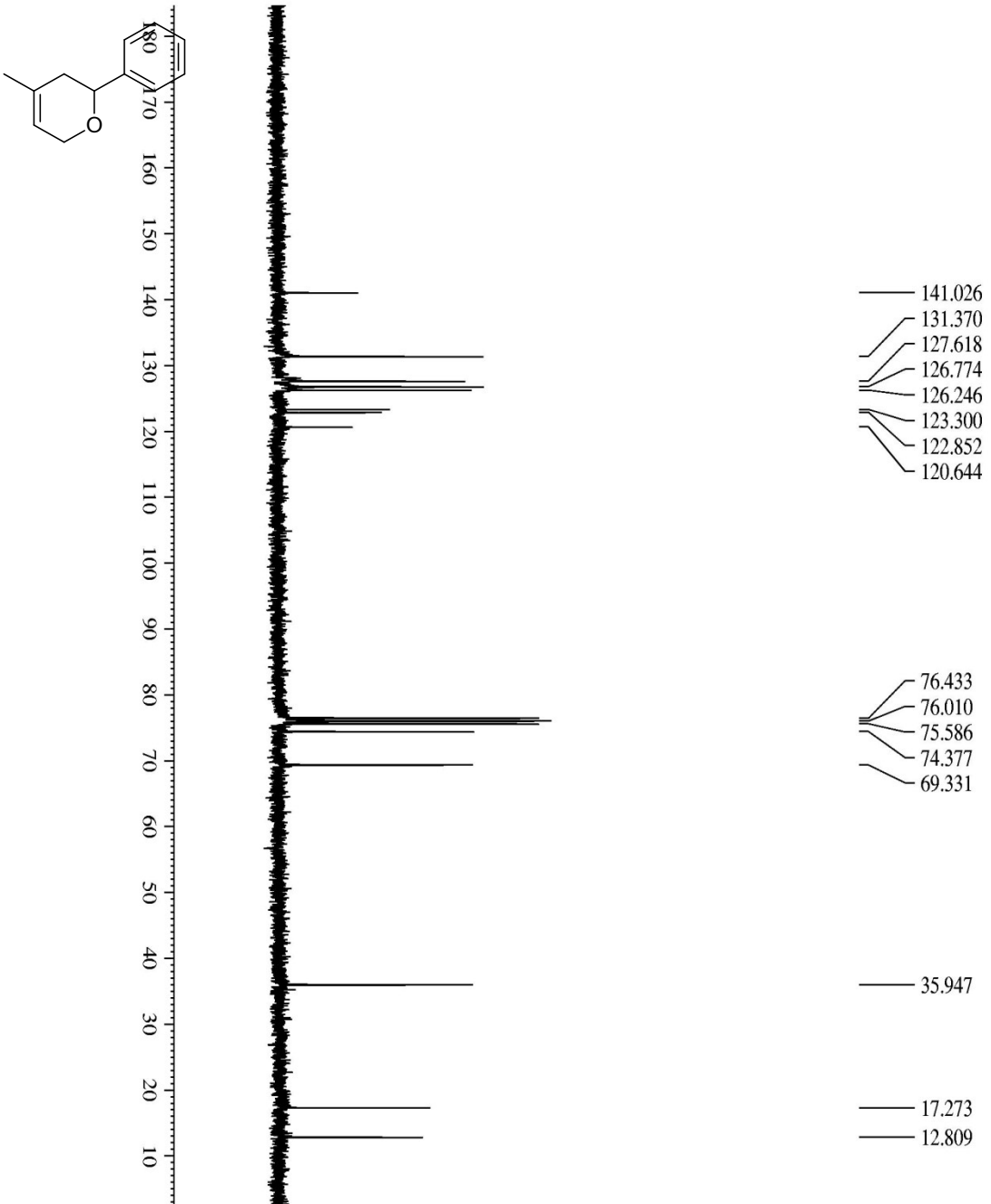

Cl
O

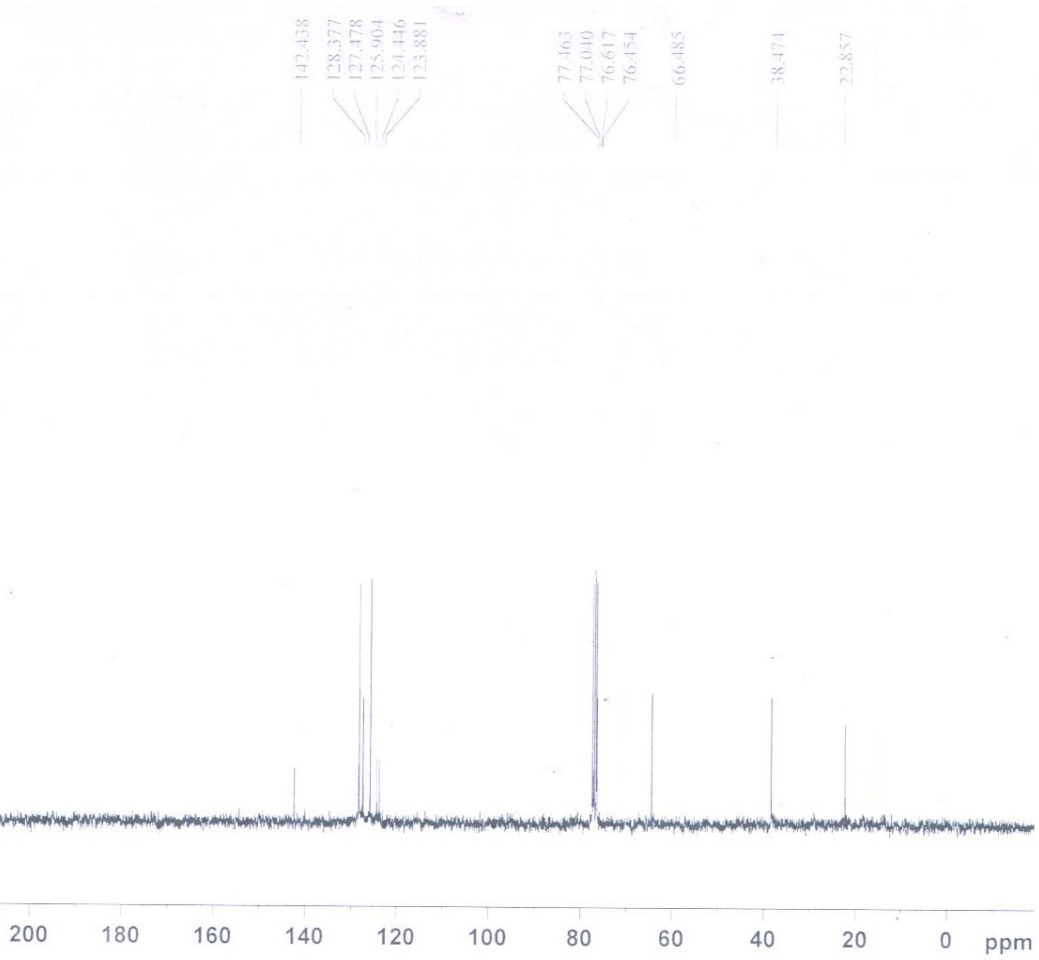

12.85
17.30
35.97
69.34
72.13
75.74
76.06
76.26
76.38
122.90
123.32
125.97
126.18
126.27
127.25
128.11
128.36
129.59
130.55
134.08
139.48
188.70
0 ppm


Br
O


0.118
1.637
1.723
2.297
2.350
4.190
4.253
4.874
4.909
7.145
7.170
7.339
7.363
7.388
7.526
7.552
7.584
7.610
ppm
0
1
2
3
4
5
6
7
8
9
10


Br
O


O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
141.026
131.370
127.618
126.774
126.246
123.300
122.852
120.644
76.433
76.010
75.586
74.377
69.331
35.947
17.273
12.809


142.438
128.377
127.478
125.904
121.446
123.881
77.463
77.040
76.617
76.454
66.485
38.471
22.857
200
180
160
140
120
100
80
60
40
20
0
ppm