Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information For

Heterogeneous Copper-Catalyzed Hydroxylation of Aryl Iodides under Air Condition

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I. General information

All reactions were carried out under air. Urea (A. R. grade) was purchased from Shantou Xilong Chemical Factory (Guangdong, China). $Cu(NO_3)_2\cdot 3H_2O$ was obtained from Sinopharm Chemical Reagent Co. Ltd. Sodium hydroxide, potassium hydroxide, dimethyl sulfoxide, petroleum ether, ethyl acetate were purchased from Beijing Chemical Reagent Company. Cesium hydroxide solution (50 wt%) and all other reagents were provided by Aldrich Alfa Chemical Company. All of the chemicals were analytical grade and used without further purification.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 HD or Brucker Fourier 300 spectrometer in $CDCl_3$ with TMS as an internal standard. Chemical shifts for protons are referenced to tetramethylsilane (TMS, ^{1}H NMR: 0.00 ppm), chemical shifts for carbons are referenced to the residual solvent peaks ($CDCl_3$, ^{13}C NMR: 77.16 ppm). FT-IR spectra were recorded on Bruker Tensor 27 spectrometer with a resolution of 1 cm^{-1} and 32 scans. Powder X-ray diffraction patterns (XRD) were recorded on Rigaku D/max-2500 X-ray diffractometer using CuKa radiation (λ= 0.15406 nm). The tube voltage was 40 kV and current was 200 mA. Gas chromatography was operated on Agilent 6820 equipped with a FID detector and a PEG-20M capillary column (30 m×0.25 mm×0.25 μm). Pore volumes and Brunauer–Emmett–Teller (BET) surface areas were measured on a Micromeritics ASAP 2020 sorptometer by using nitrogen adsorption at 77 K. Thermogravimetrical analysis (TGA) was studied using Netzsch STA 409 PC under an N_2 flow of 60 mL/min at a heating rate of 10 K/min up to 1173 K. X-ray photoelectron spectroscopy data (XPS) were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The content of the Cu in the catalyst was analyzed by ICP-AES (PROFILE. SPEC, Leeman).

II. Preparation of the catalyst Cu-g-C_3N_4

The catalyst Cu-g-C_3N_4 was prepared according to the procedures in our previous work [S1]. Typically, 12.0 g of urea dissolved in 100 mL of distilled water was heated with desired amount of $Cu(NO_3)_2 \cdot 3H_2O$, and stirred at 353 K for 1 h. The mixed solution was then heated at 373 K to remove water. The resulting mixtures were then heated at a rate of 3.0 K/min to reach a temperature of 573 K, and tempered at this temperature for 2 h in a flowing-nitrogen atmosphere. The mixture was then continuously heated to 823 K over 1.5 h, and tempered at this temperature for 4 h. This was followed by cooling the sample naturally to room temperature with nitrogen gas. The final powder was collected and labeled as Cu-g-C_3N_4. The Copper content in the Cu-g-C_3N_4 determined by ICP-AES was 2.7 mmol/g (Cu 17.2 wt%).

III. Procedures for the synthesis of phenol from iodobenzene (Table 1)

A teflotion-lined stainless steel reactor of 15 mL was used. In the experiment, iodobenzene (1.0 mmol), suitable amounts of DMSO, water, base, and Cu-g-C_3N_4 were loaded into the reactor. The reactor was placed in an oil bath of desired temperature and the reaction mixture was stirred. The reaction mixture was cooled to room temperature after a desired reaction time. The reaction mixture was carefully acidified with dilute aqueous HCl, and then 10 mL ethyl acetate was added. After centrifuged, the reaction mother liquid was analyzed by gas chromatography (Agilent 6820) equipped with a FID detector and a PEG-20M capillary column (30 m×0.25 mm×0.25 μm). An internal standard 1, 4-dioxane was used to quantify the generated phenol. GC-MS analysis indicated that phenol was the only product under the reaction conditions. In the experiments to test the reusability of the catalyst, the Cu-g-C_3N_4 was separated by centrifugation and reused in the next run without any further treatment.

IV. General procedures for synthesis of phenols from aryl iodides (Table 2)

A mixture of aryl iodides (1.0 mmol), Cu-g-C_3N_4 (4 mol%) and NaOH (4.0 mmol) was stirred in DMSO aqueous solutions at 120°C for the desired reaction time. The reaction mixture was cooled to room temperature, carefully acidified with dilute aqueous HCl. The resulting mixture was filtered and extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/petroleum ether mixtures) or by crystallization.

V. The effect of solvent

Table S1 The effect of solvent [a]

Entry	*Solvents [b]*	*Yields [c]*
1	**CH_3CN/H_2O(1.5/1.5)**	**0**
2	**H_2O**	**0**
3	**DMF**	**0**
4	**Glycol**	**4.5**
5	**DMSO**	**14.6**
6	**DMSO/H_2O(2.0/1.0)**	**58.5**
7	**Dioxane**	**0**
8	**Dioxane/H_2O(1.5/1.5)**	**0**

[a] All reactions were performed using 1.0 mmol of iodobenzene, 8 mol% Cu-C_3N_4, 120°C, 12 h; [b] 3 mL solvent; [c] GC yield based on the added iodobenzene.

VI. Characterization of the catalyst

XRD patterns of g-C_3N_4 and the catalyst Cu-g-C_3N_4 are shown in Figure S1. Both the samples showed similar diffraction peaks, though the diffraction peaks of the catalyst Cu-g-C_3N_4 are not as strong as that of pure g-C_3N_4. The strong peak at 27.5° represents the stacking of the conjugated interlayers, which is indexed for graphitic materials as the (002) peak. Another peak at 12.9° corresponds to in-plane ordering of tri-s-triazine units, which form 1D melon strands. The two diffraction peaks are in good agreement with that of g-C_3N_4 reported in literature [S2]. No diffraction peaks of copper species are observed in Figure S1, The presence of the copper species in Cu-g-C_3N_4 is confirmed by XPS analysis.

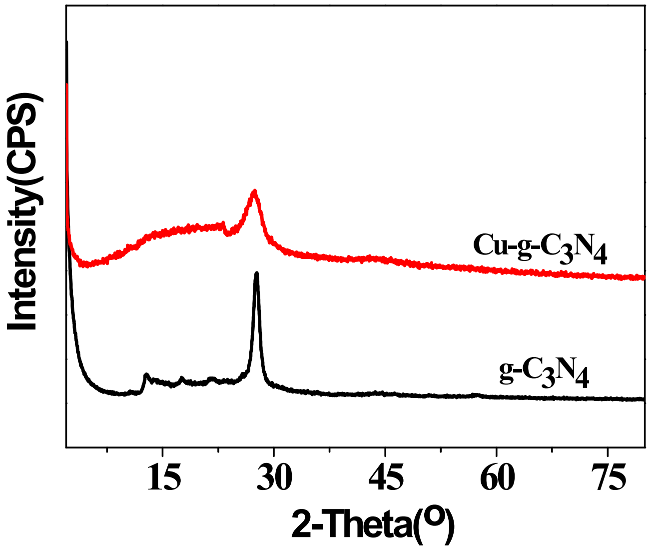


Figure S1. The XRD patterns of the samples.

Figure S2 shows the XPS spectra of the catalyst Cu-g-C_3N_4. As indicated in Figure S2a, the main elements on the surface of the sample are C, N, O and Cu. The photoelectron peaks of these elements appear at binding energies of 287.7 eV (C1s), 398.4 eV (N1s), 532.2 eV (O1s) and 932.3 eV (Cu2p), respectively. Figure S2b shows the high resolution Cu2p XPS spectrum of the sample: two main peaks located at about 952.5 eV and 932.3 eV [S3] corresponds to Cu2p1/2 and Cu2p3/2, which confirms that the existence of Cu^+ species.

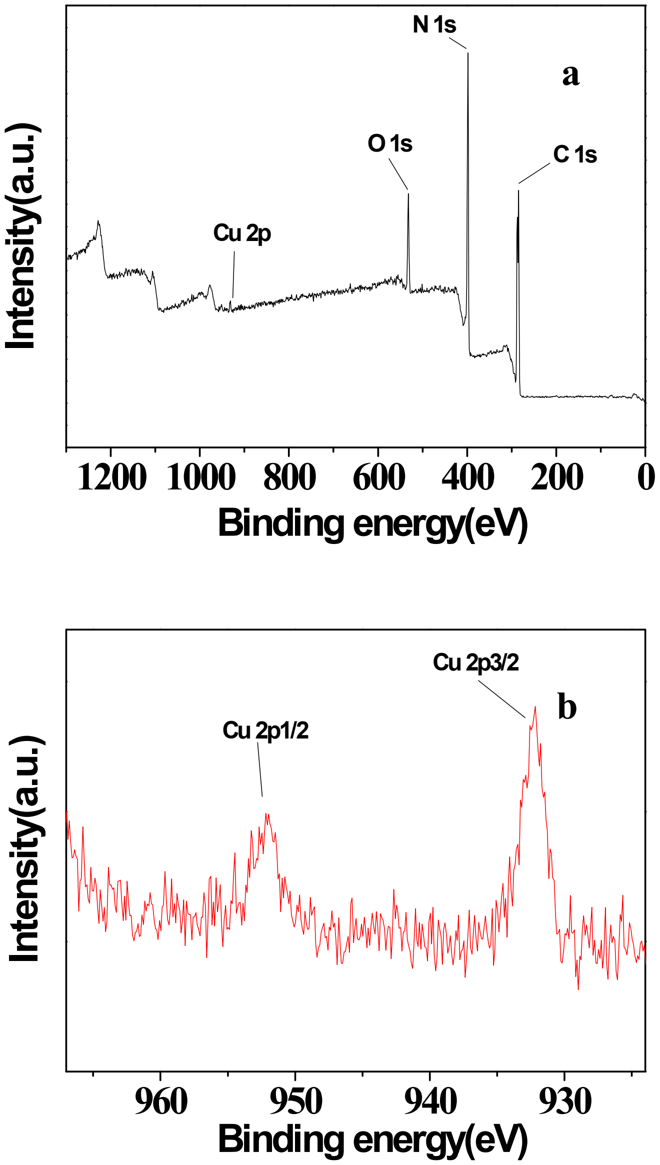


Figure S2 The XPS patterns of the catalyst Cu-g-C_3N_4

Figure S3 shows the FT-IR spectra of g-C_3N_4 and the catalyst Cu-g-C_3N_4. Several bands in the 1200-1650 cm^{-1} region corresponding to the typical stretching modes of CN heterocycles are clearly seen for the two samples. The characteristic mode of the triazine units (C_6N_7) at 810 cm^{-1} is also observed [S1], indicating the presence of typical structure of g-C_3N_4.

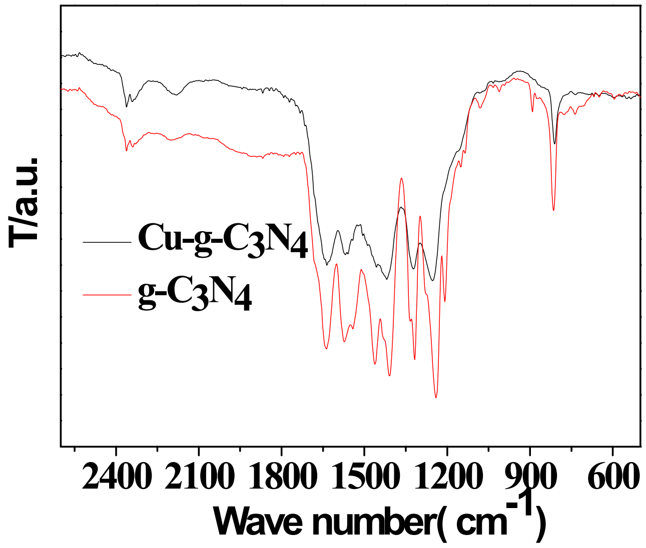


Figure S3 The FT-IR spectra of g-C_3N_4 and Cu-g-C_3N_4

Figure S4 shows the N_2 adsorption-desorption isotherm. The catalyst Cu-g-C_3N_4 had a BET surface area of 31.9 m^2/g, and a pore volume of 0.059 $cm^3 \cdot g^{-1}$. The BET surface area of pure g-C_3N_4 was 96.6 m^2/g[S2]. The decrease in the BET surface area of Cu-g-C_3N_4 should be attributed to the loading of copper.

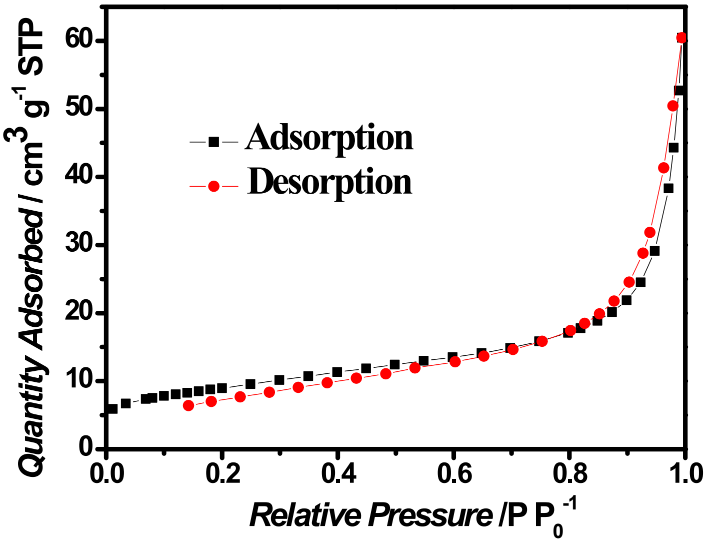


Figure **S4** Nitrogen adsorption-desorption isotherm of Cu-g-C_3N_4

Figure S5 demonstrates the results of thermogravimetrical analysis of Cu-g-C_3N_4. It was showed that the catalyst Cu-g-C_3N_4 can bear high temperature up to 600°C. The weight loss of the sample at high temperature is mainly due to the decomposition of carbon nitride matrix.

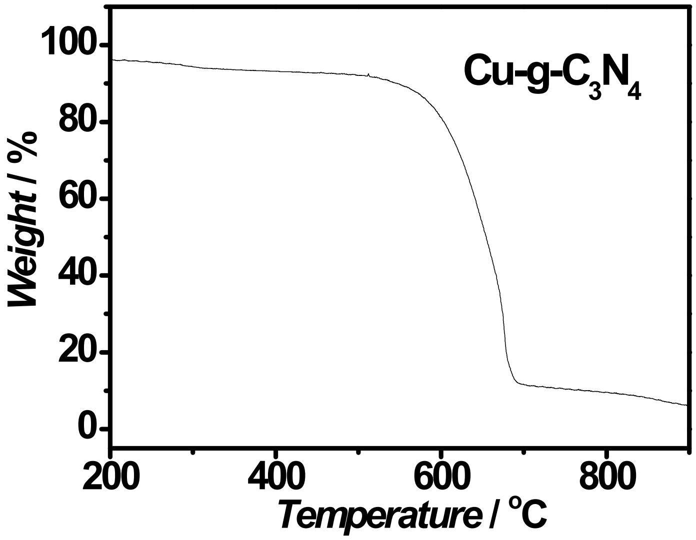


Figure **S5** Thermogravimetric analysis of Cu-g-C_3N_4 under N_2 flow.

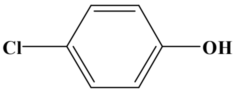
VII. References

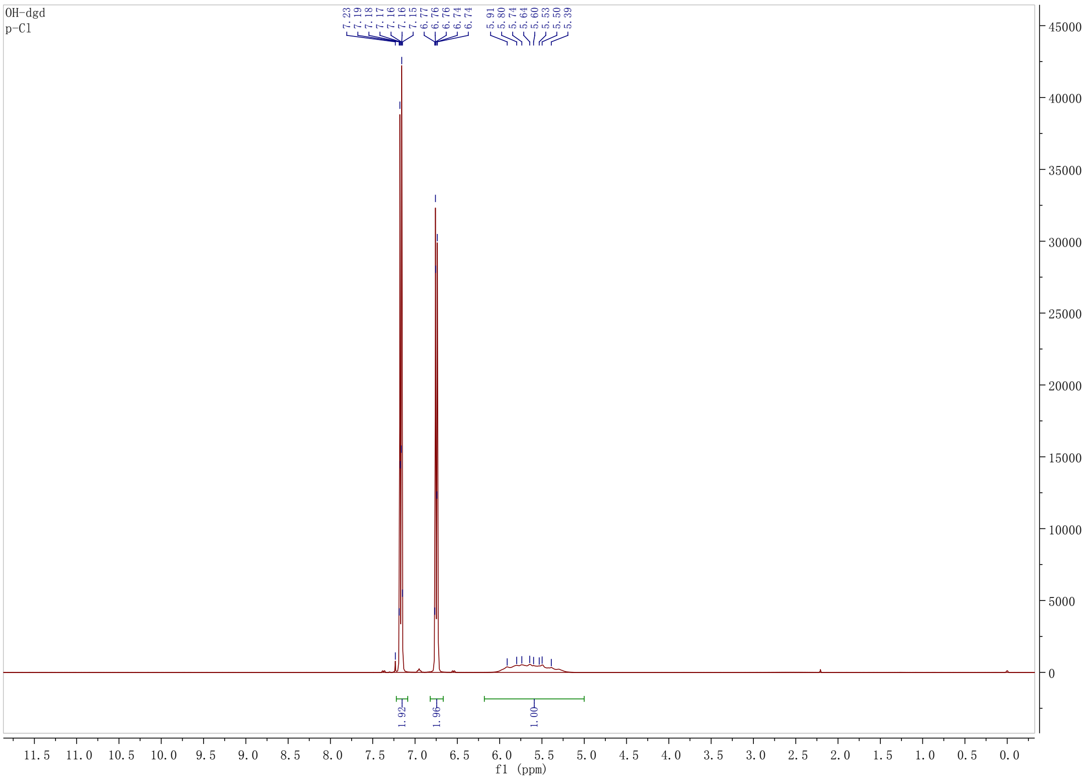
[S1] G. D. Ding, W. T. Wang, T. Jiang, B. X. Han, H. L. Fan, G. Y. Yang, *Chemcatchem* **2013**, *5*, 192.

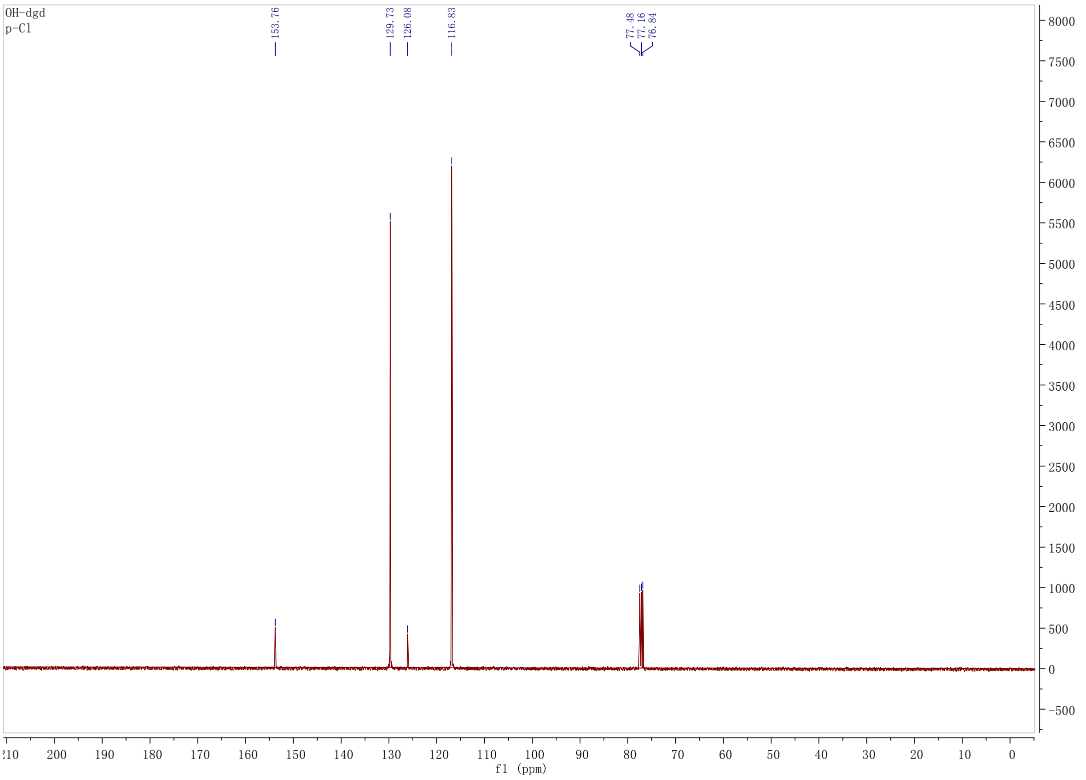
[S2] F. Dong, L.W. Wu, Y.J. Sun, M. Fu, Z.B. Wu, S.C. Lee, *J. Mater. Chem.* **2011**, *21*, 15171.

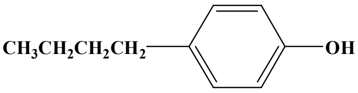
[S3] (a) J. G. Jolley, G. G. Geesey, M. R. Haukins, R. B. Write, P. L. Wichlacz, *Appl. Surf. Sci.* **1989**, *37*, 469; (b) S. W. Gaarenstroom, N. J. Winograd, *Chem. Phys.* **1977**, *67*, 3500; (c) J. C. Klein, A. Proctor, D. M. Hercules, J. F. Black *Anal. Chem.* **1983**, *55*, 2055.

VIII. Copies of ^{1}H NMR and ^{13}C NMR Spectra





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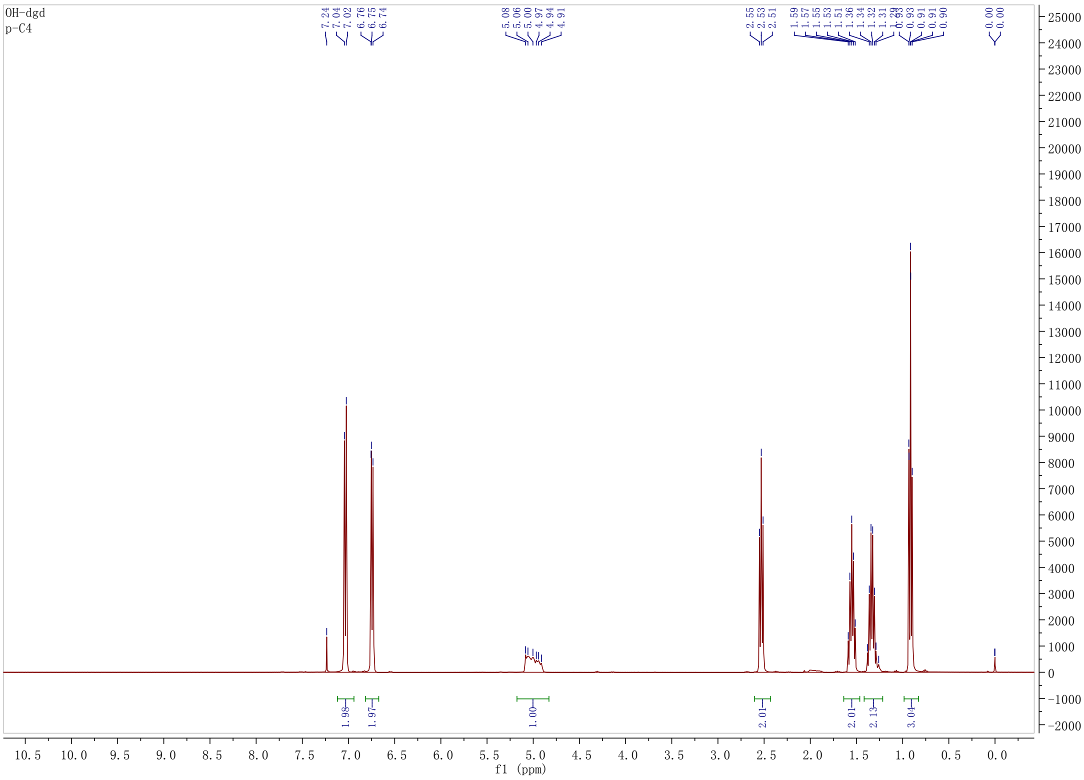
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7.04
7.02
6.76
6.75
6.74
5.08
5.06
5.00
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4.94
4.91
2.55
2.53
2.51
1.59
1.57
1.55
1.53
1.51
1.36
1.34
1.32
1.31
1.29
0.93
0.93
0.91
0.91
0.90
0.00
0.00
1.98
1.97
1.00
2.01
2.01
2.13
3.04
10.5 10.0 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 0.0
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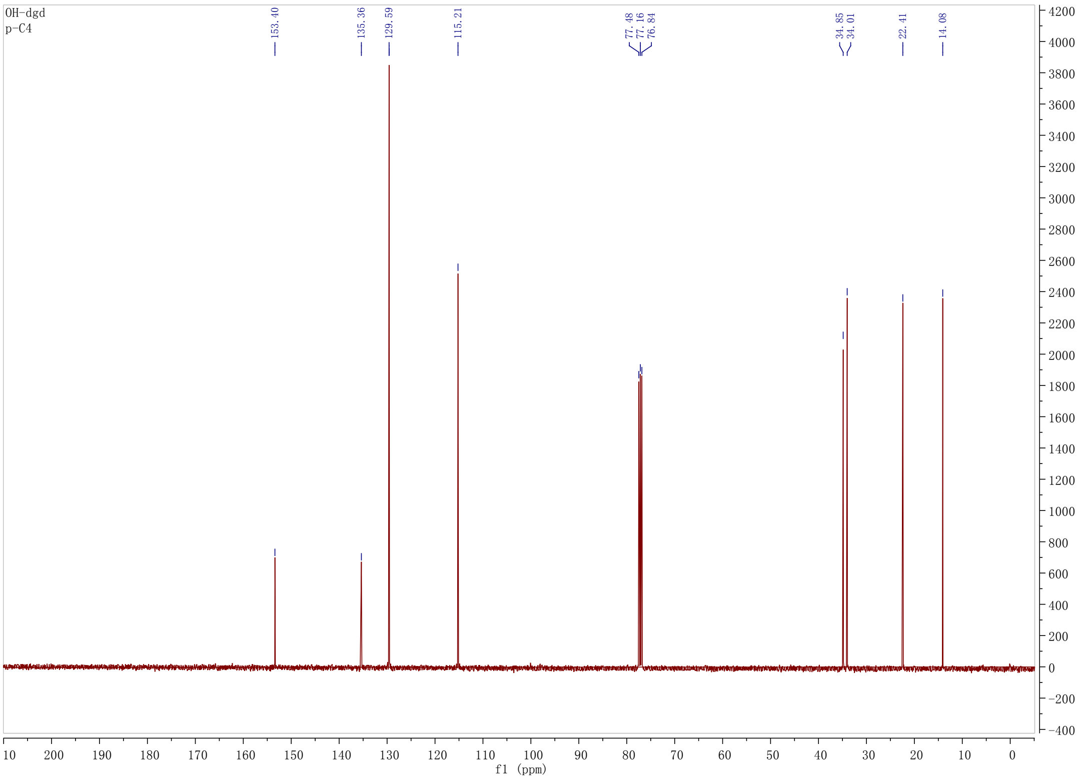
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115.21
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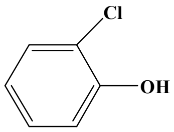
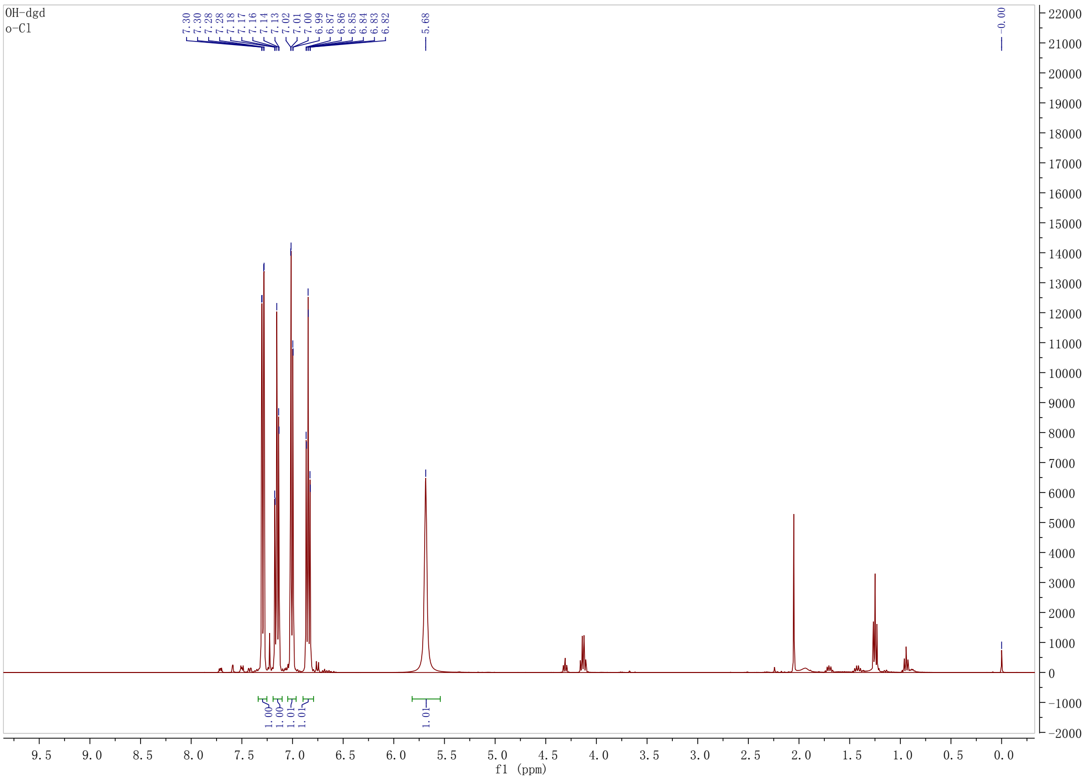
77.16
76.84
34.85
34.01
22.41
14.08
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
4200 4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 −200 −400


Cl
OH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7.30
7.28
7.28
7.18
7.17
7.16
7.14
7.13
7.02
7.01
7.00
6.99
6.87
6.86
6.85
6.84
6.83
6.82
5.68
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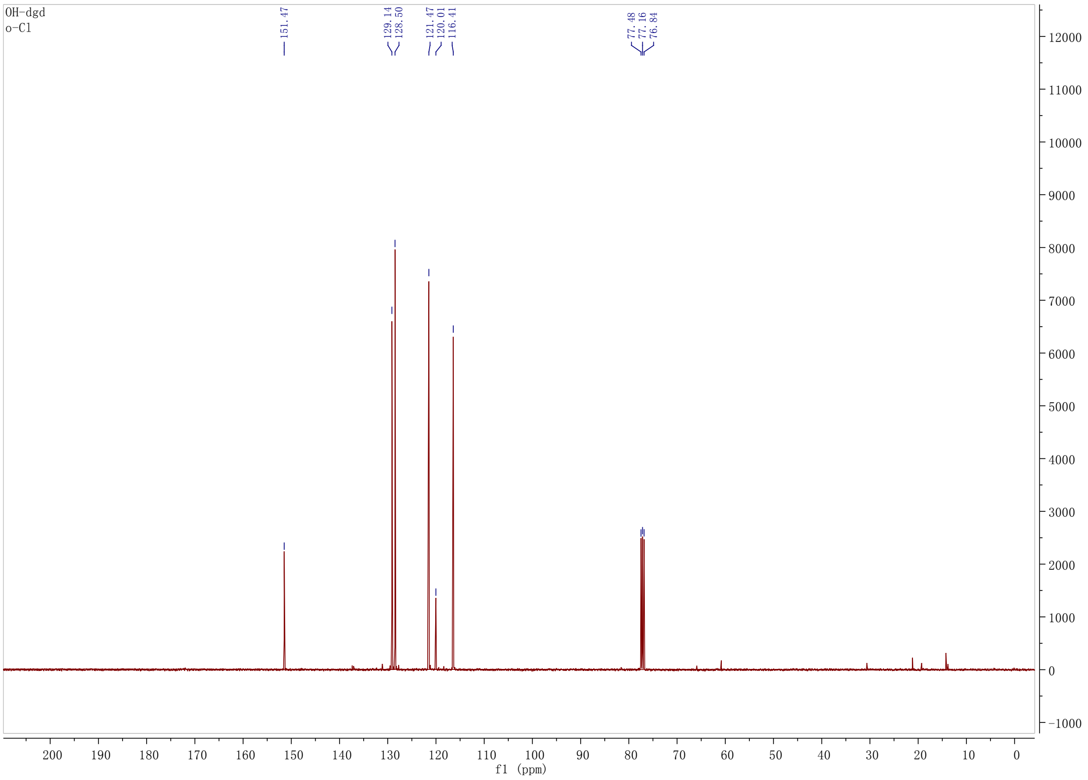
1.00
1.00
1.01
1.01
1.01
f1 (ppm)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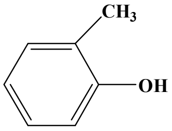
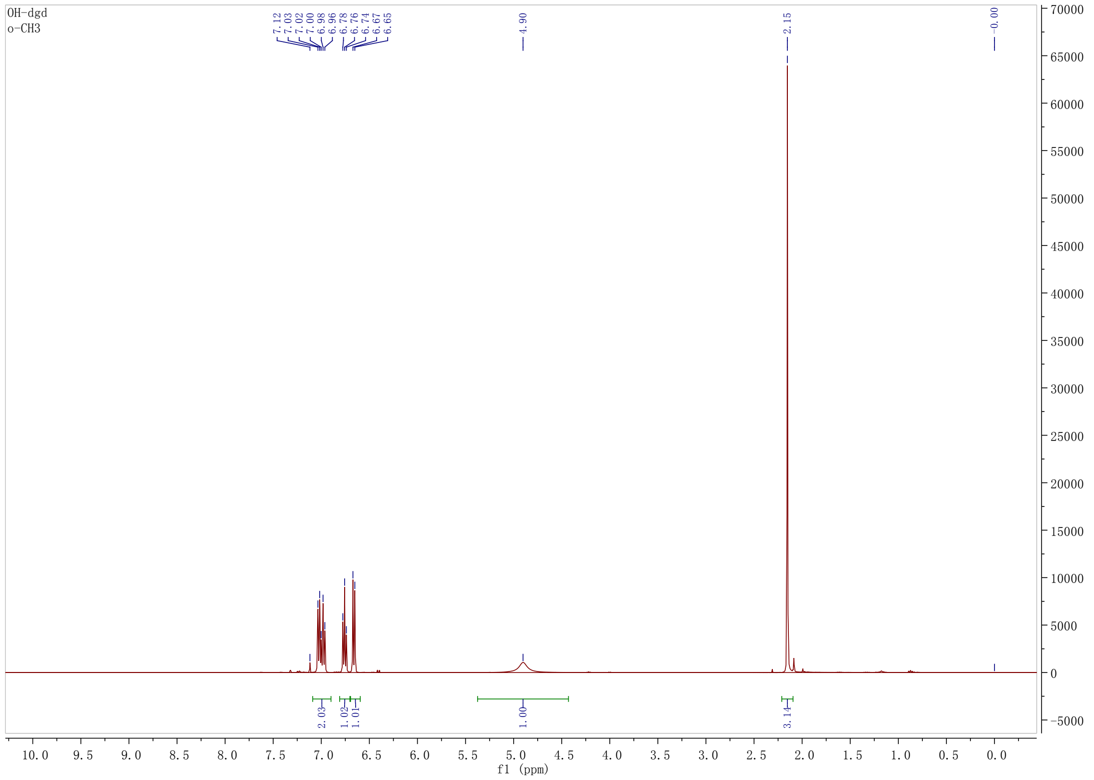

CH3
OH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7.02
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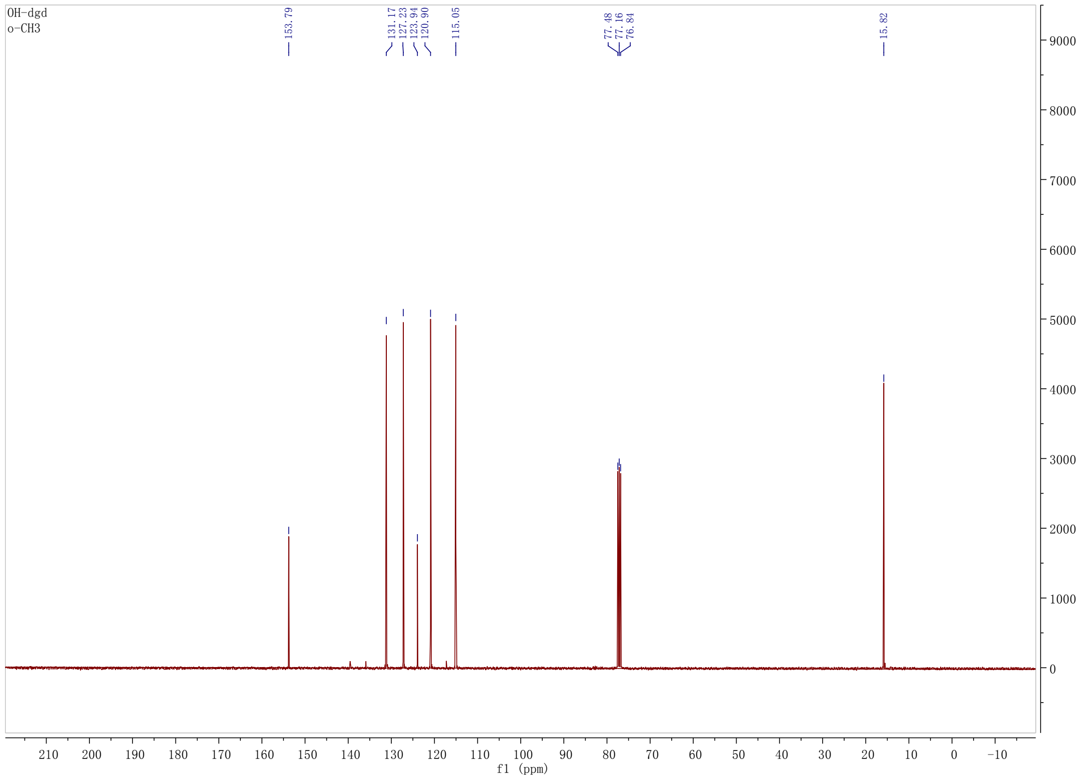
2.03
1.02
1.01
1.00
3.14
f1 (ppm)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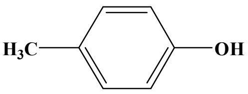
f1 (ppm)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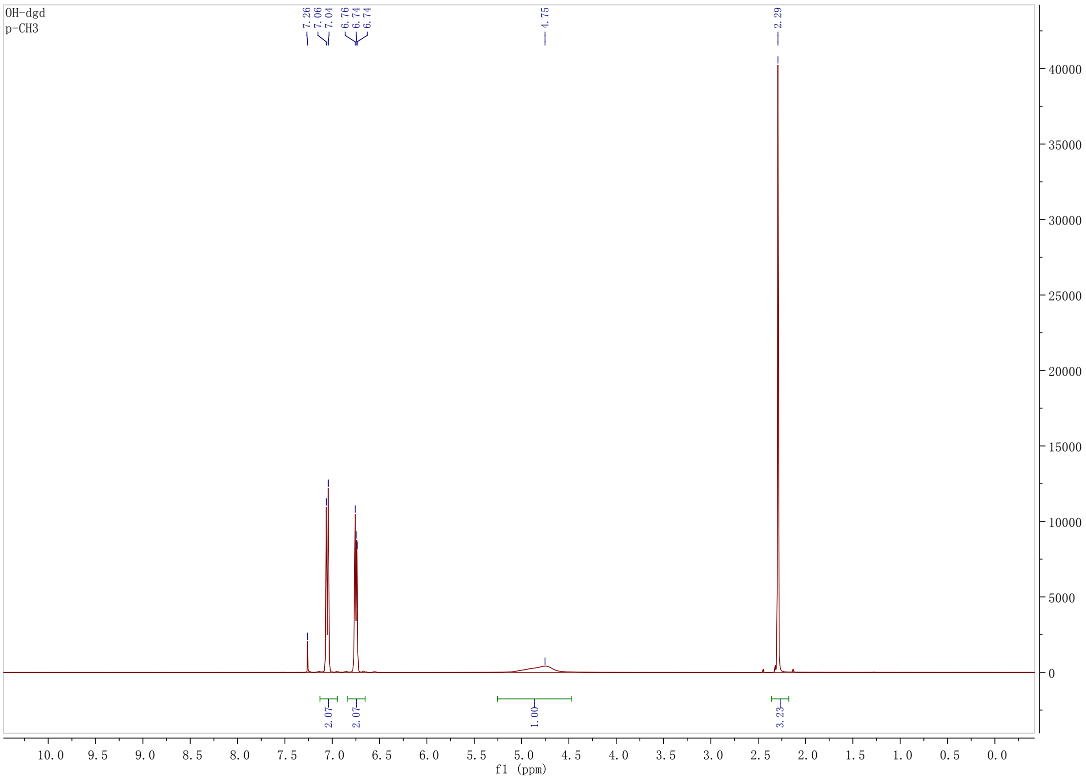
OH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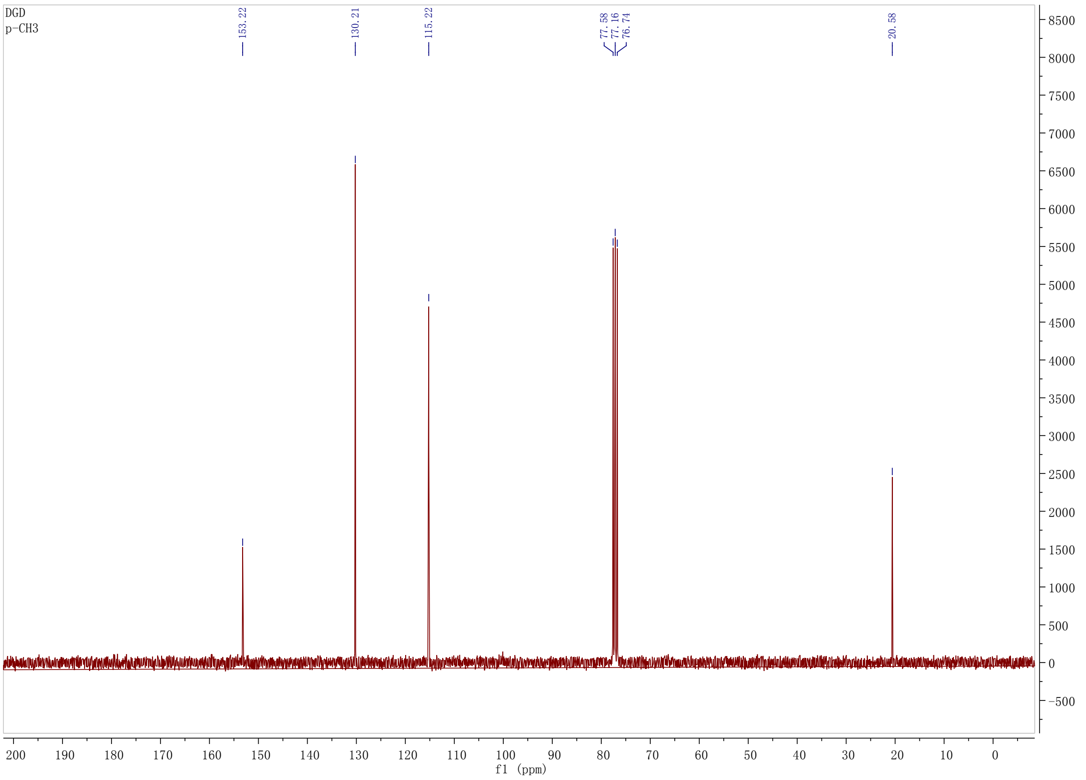
2.07
1.00
3.23
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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76.74
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8000
7500
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6500
6000
5500
5000
4500
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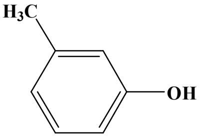
f1 (ppm)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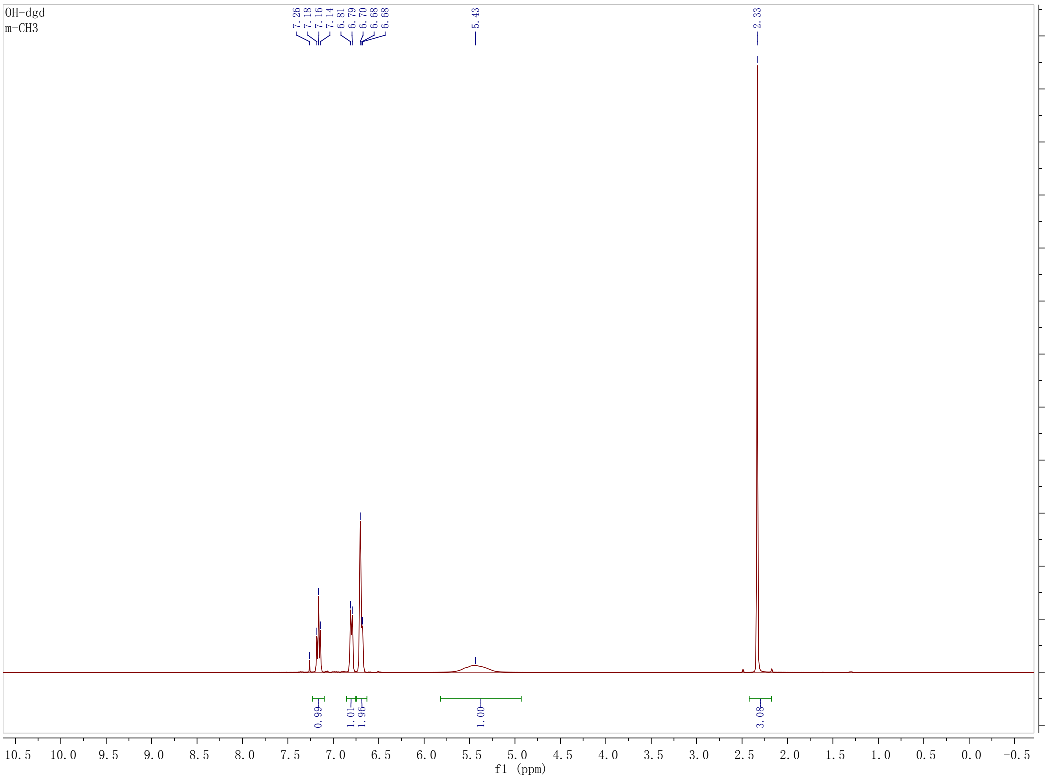
OH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7.14
6.81
6.79
6.70
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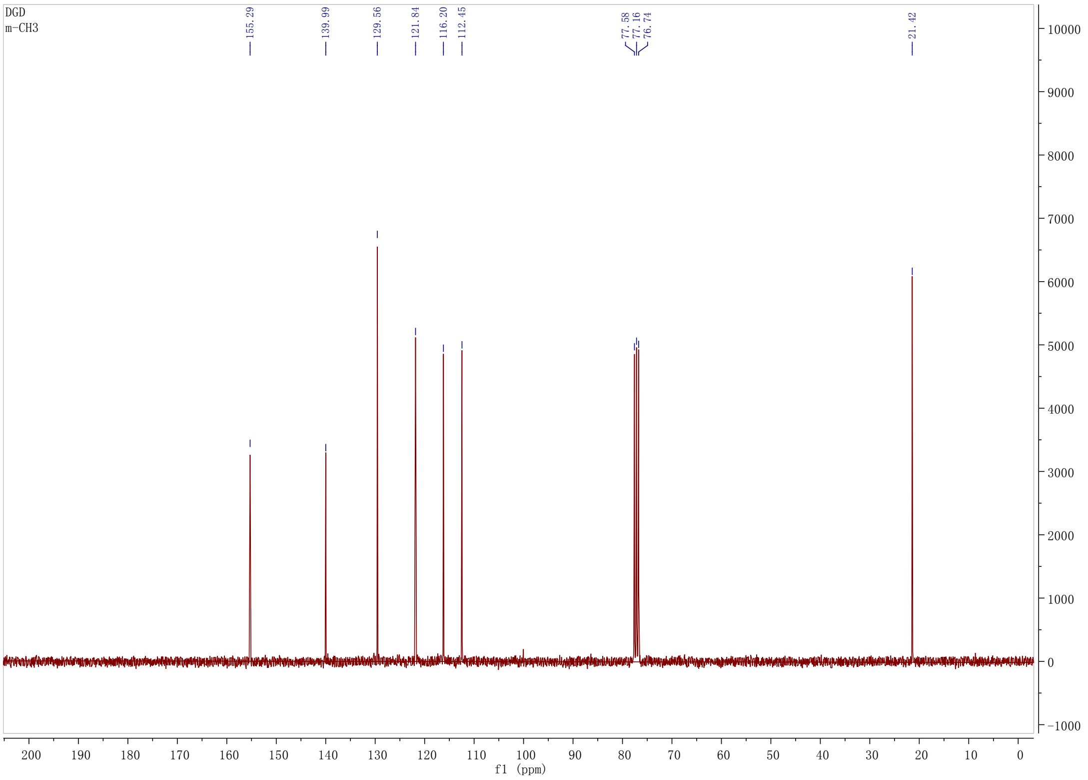
6.68
5.43
2.33
0.99
1.01
1.96
1.00
3.08
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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77.16
76.74
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10000
9000
8000
7000
6000
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4000
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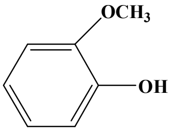
0
−1000
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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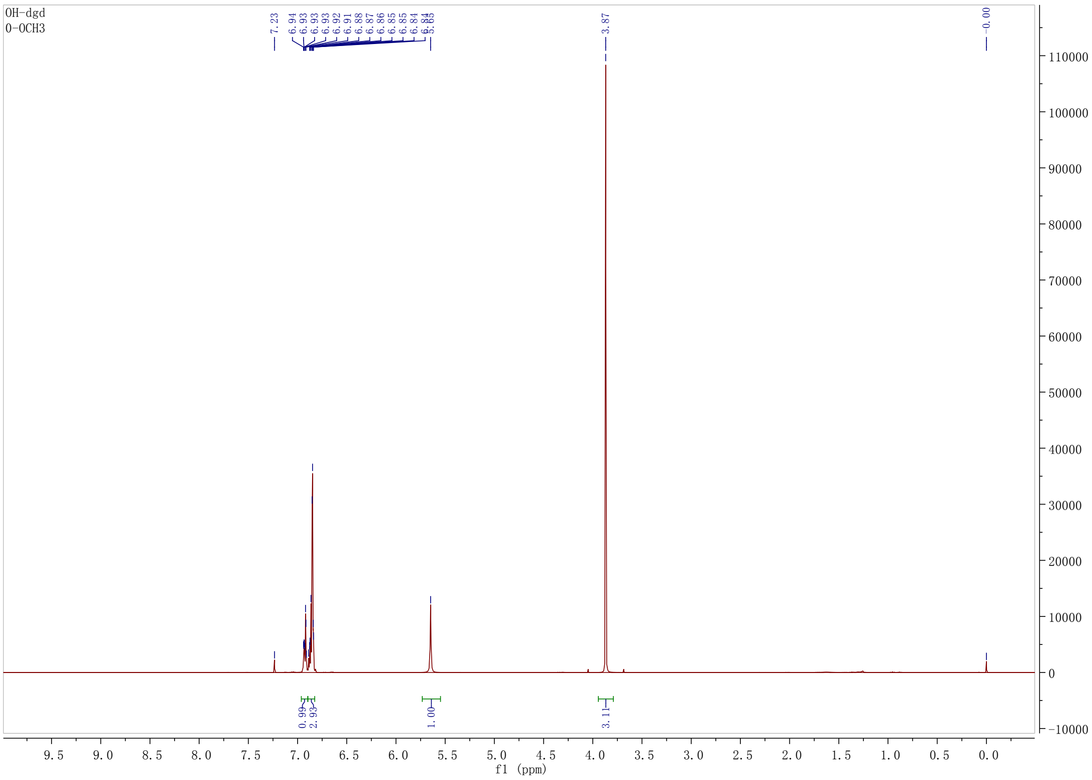
OH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6.85
6.85
6.84
6.84
5.65
3.87
-0.00
0.99
2.93
1.00
3.11
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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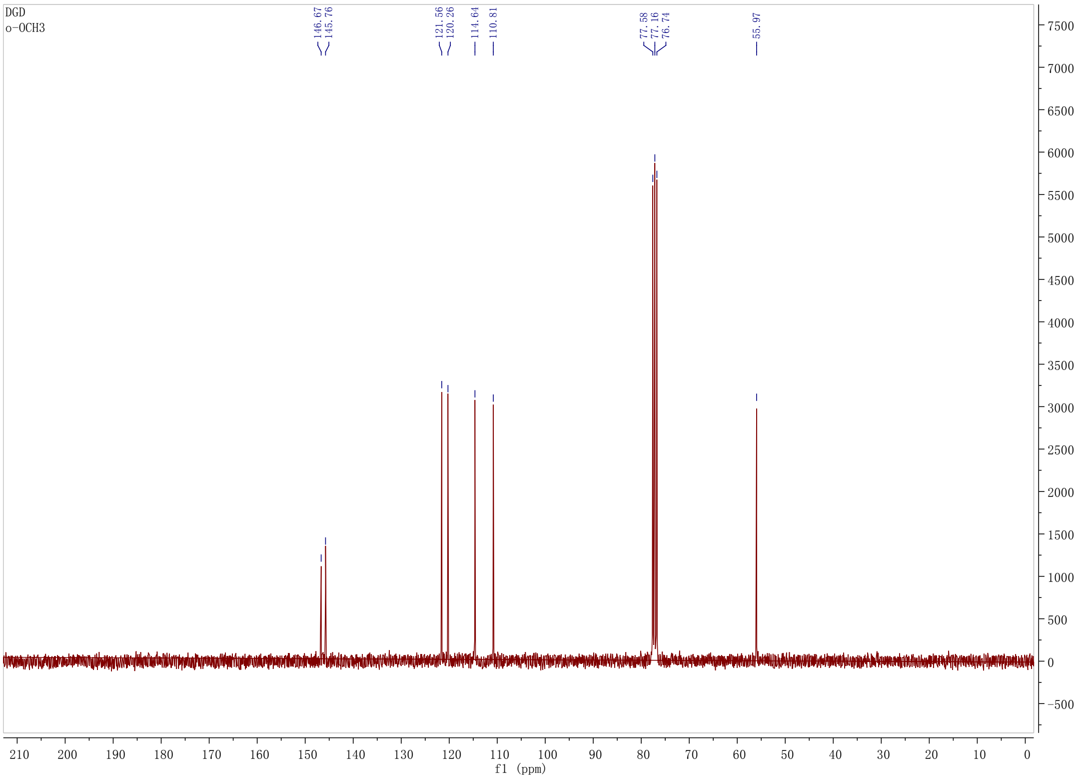
f1 (ppm)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7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
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90
80
70
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50
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30
20
10
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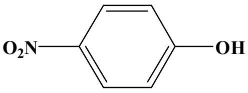
f1 (ppm)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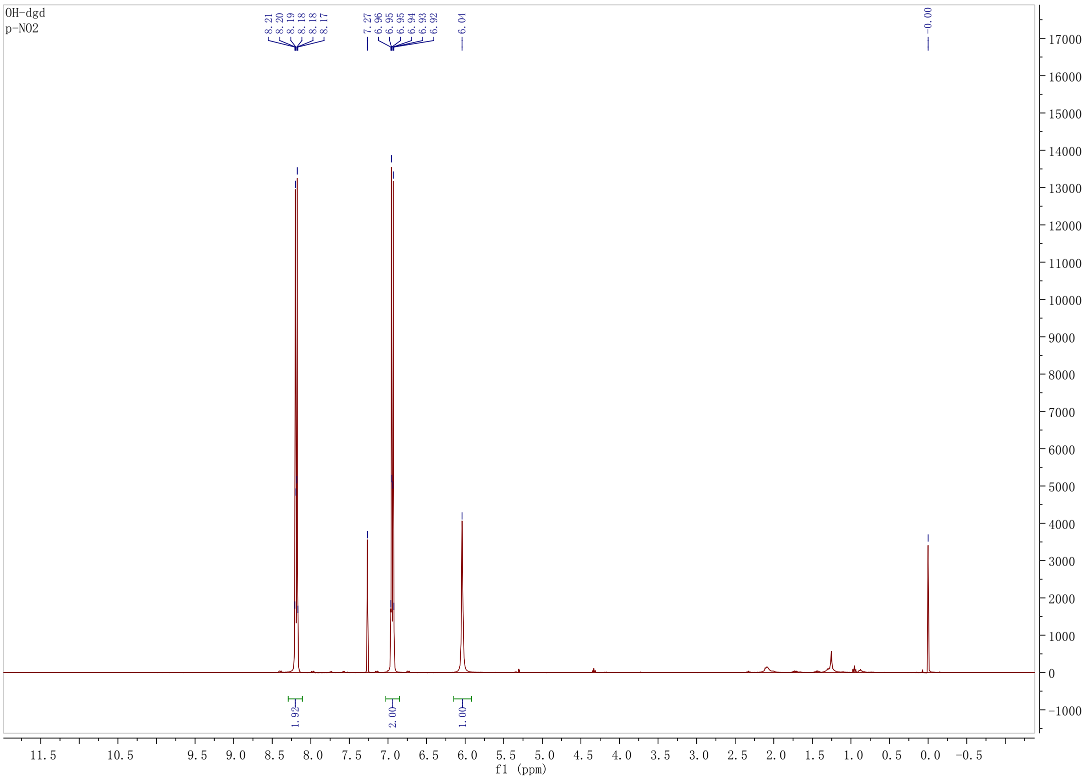
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8.21
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8.19
8.18
8.18
8.17
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6.96
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6.95
6.94
6.93
6.92
6.04
-0.00
1.92
2.00
1.00
11.5 10.5 9.5 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 0.0 -0.5
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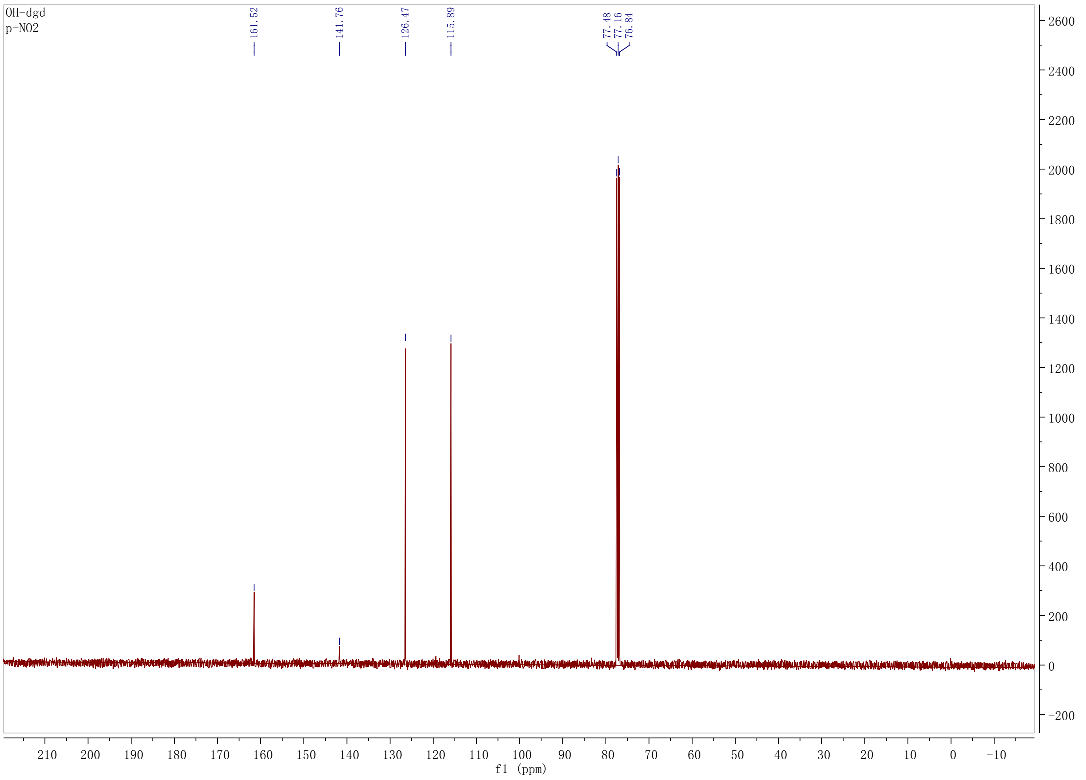
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77.16
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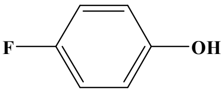
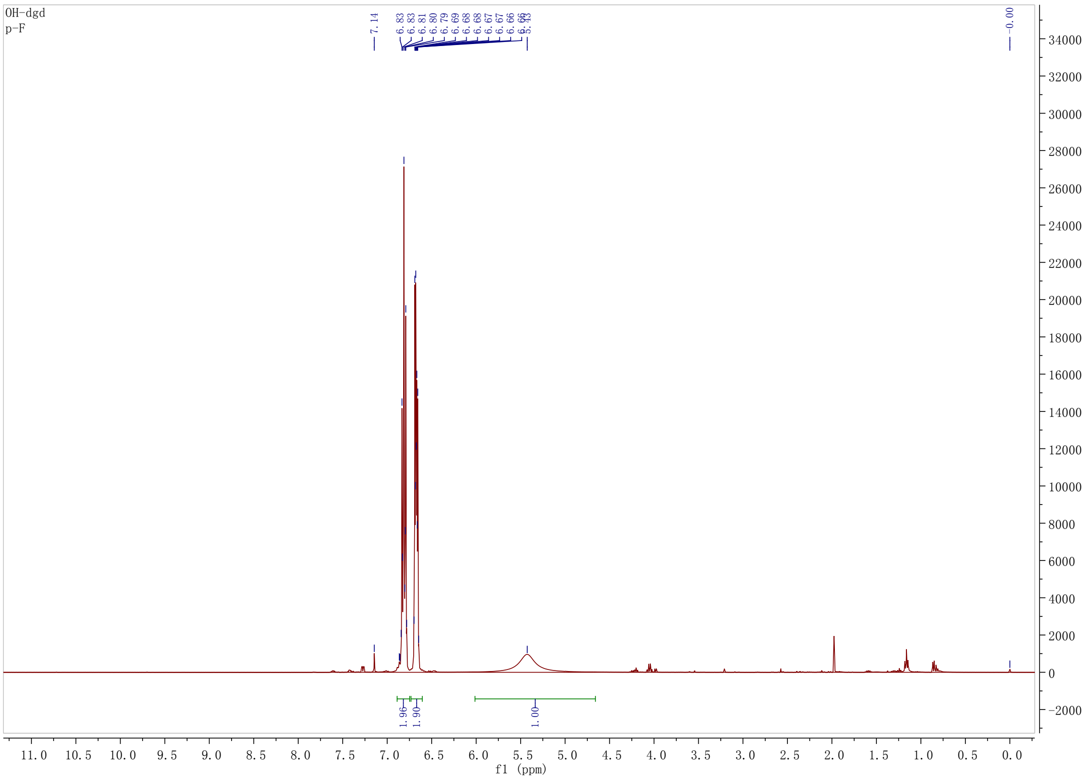
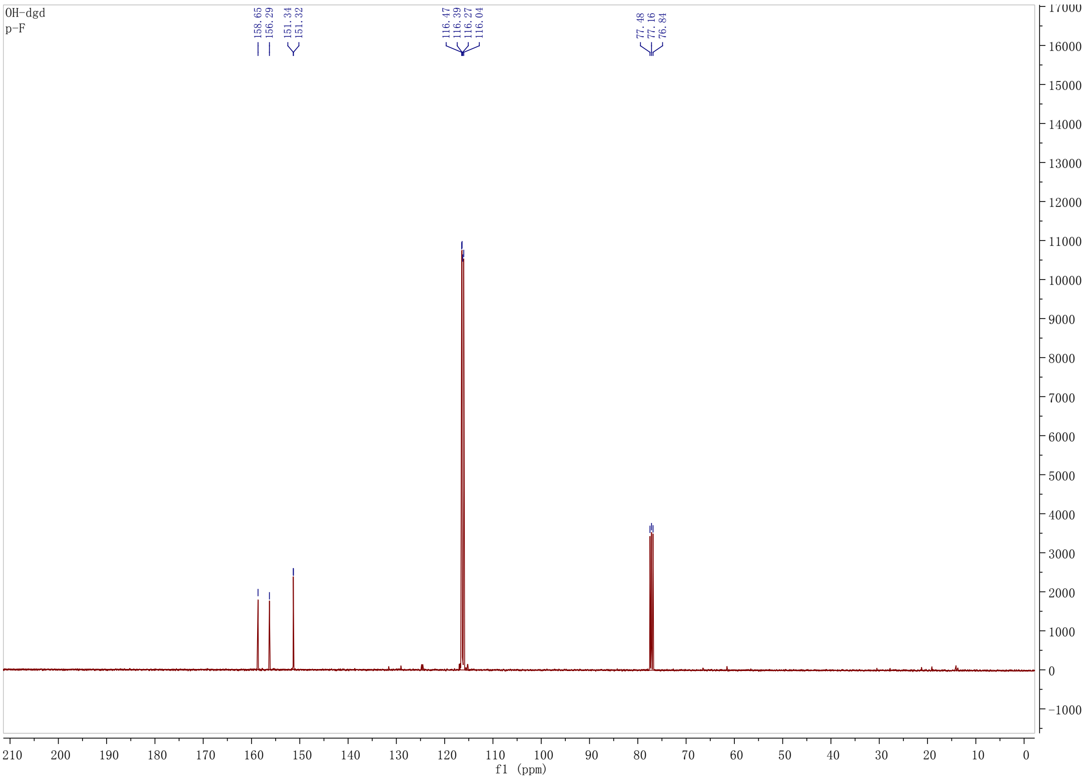
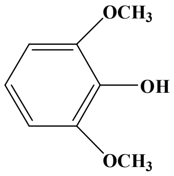
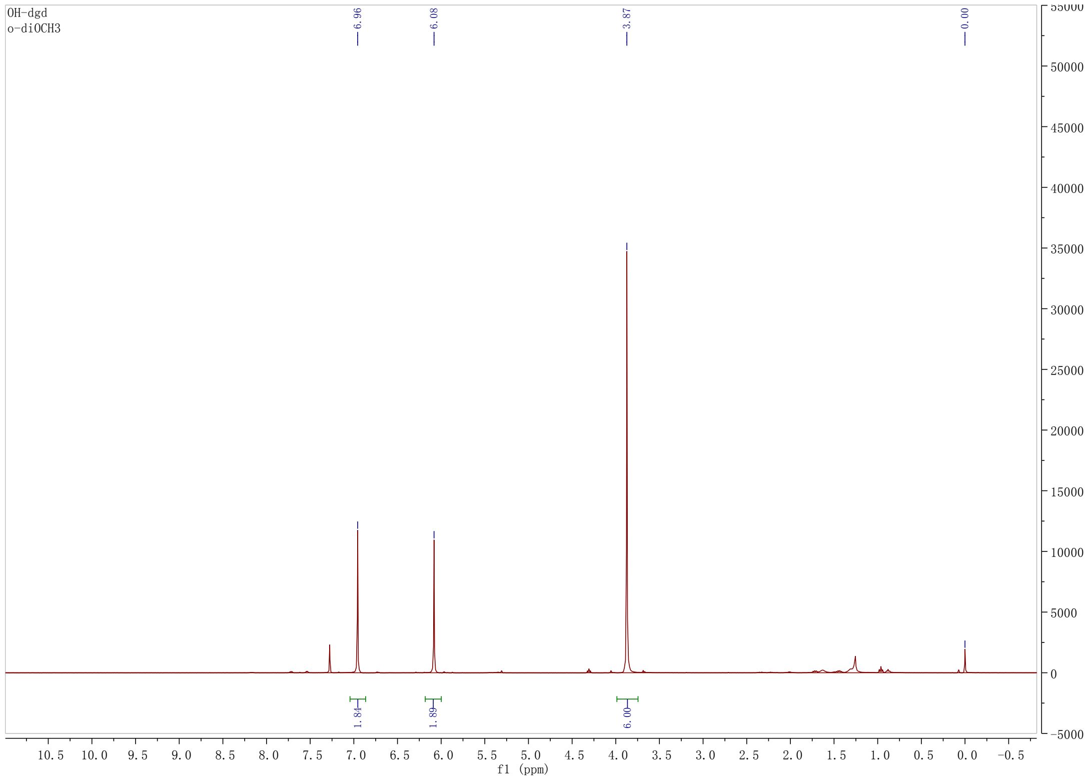
f1 (ppm)
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

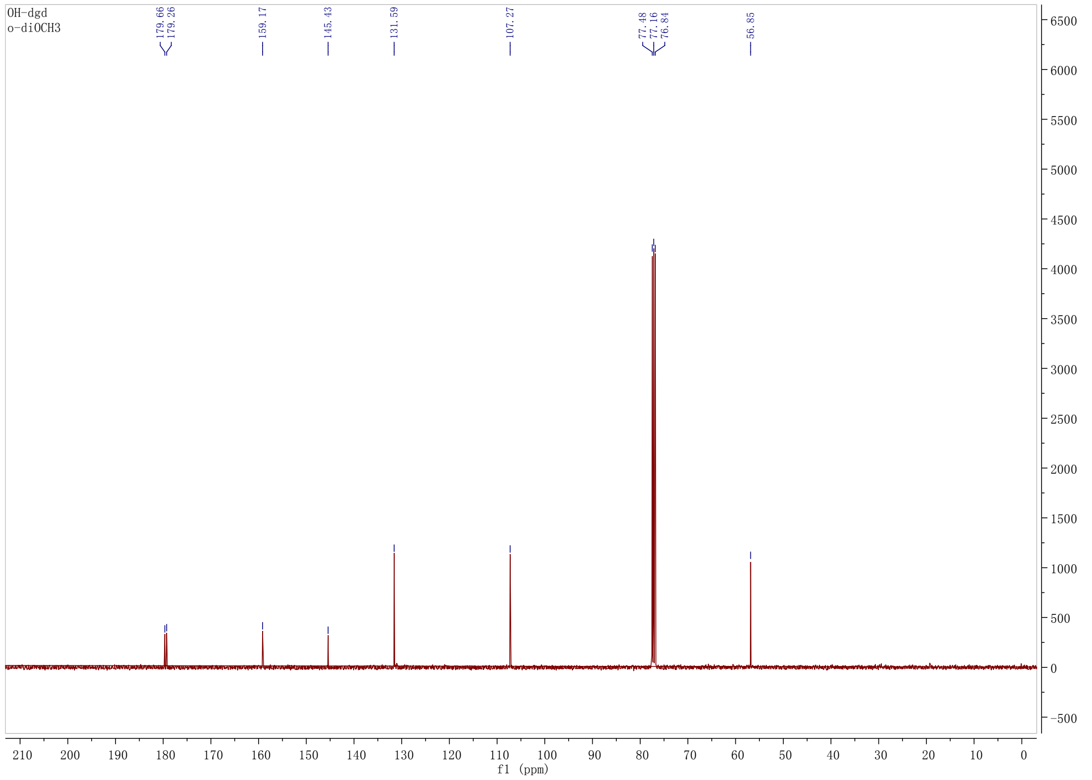

F
OH

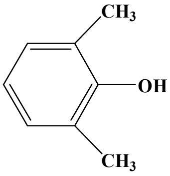

OH-dgd
p-F
7.14
6.83
6.83
6.81
6.80
6.79
6.69
6.68
6.68
6.67
6.66
6.66
5.43
-0.00
1.96
1.90
1.00
f1 (ppm)

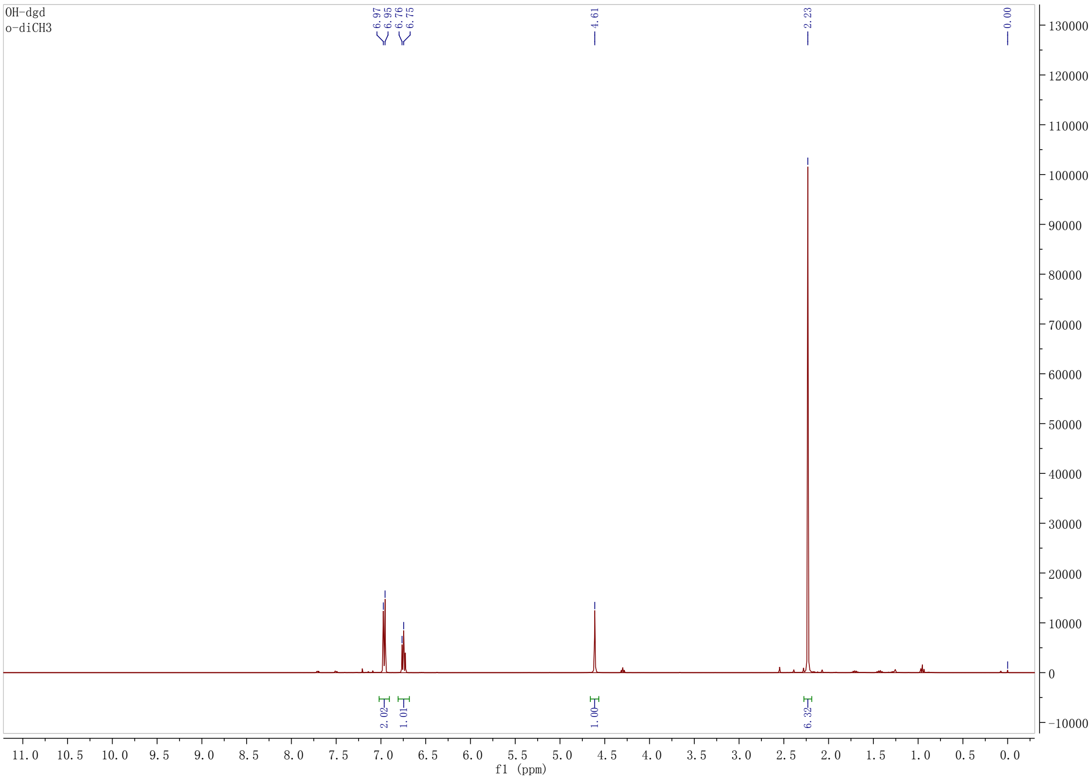

OH-dgd
p-F
158.65
156.29
151.34
151.32
116.47
116.39
116.27
116.04
77.48
77.16
76.84
f1 (ppm)

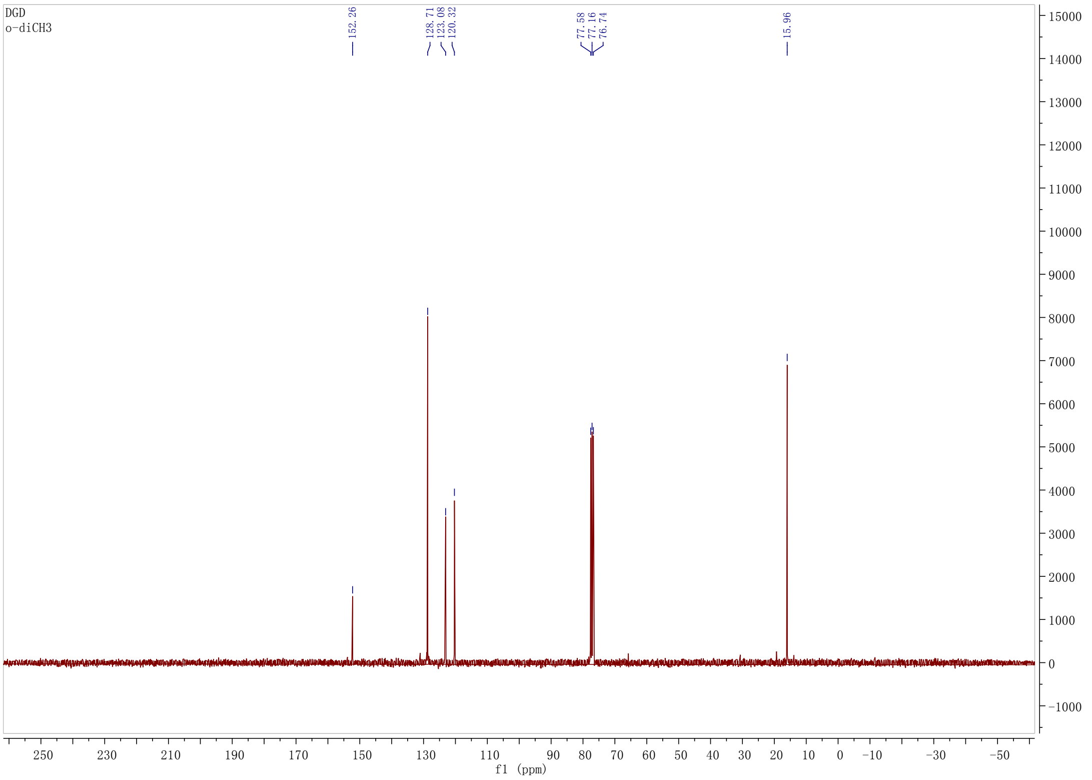

OCH3
OH
OCH3

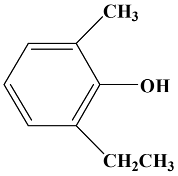

OH-dgd
o-diOCH3
6.96
6.08
3.87
0.00
1.84
1.89
6.00
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

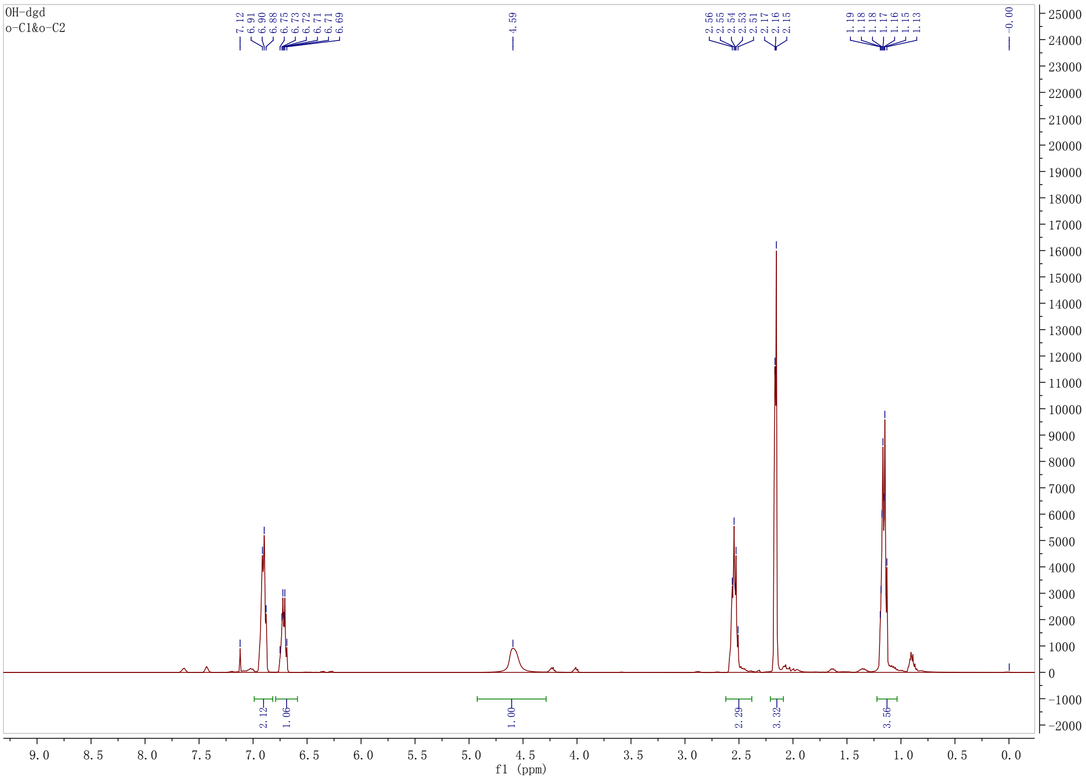

OH-dgd
o-diOCH3
179.66
179.26
159.17
145.43
131.59
107.27
77.48
77.16
76.84
56.85
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

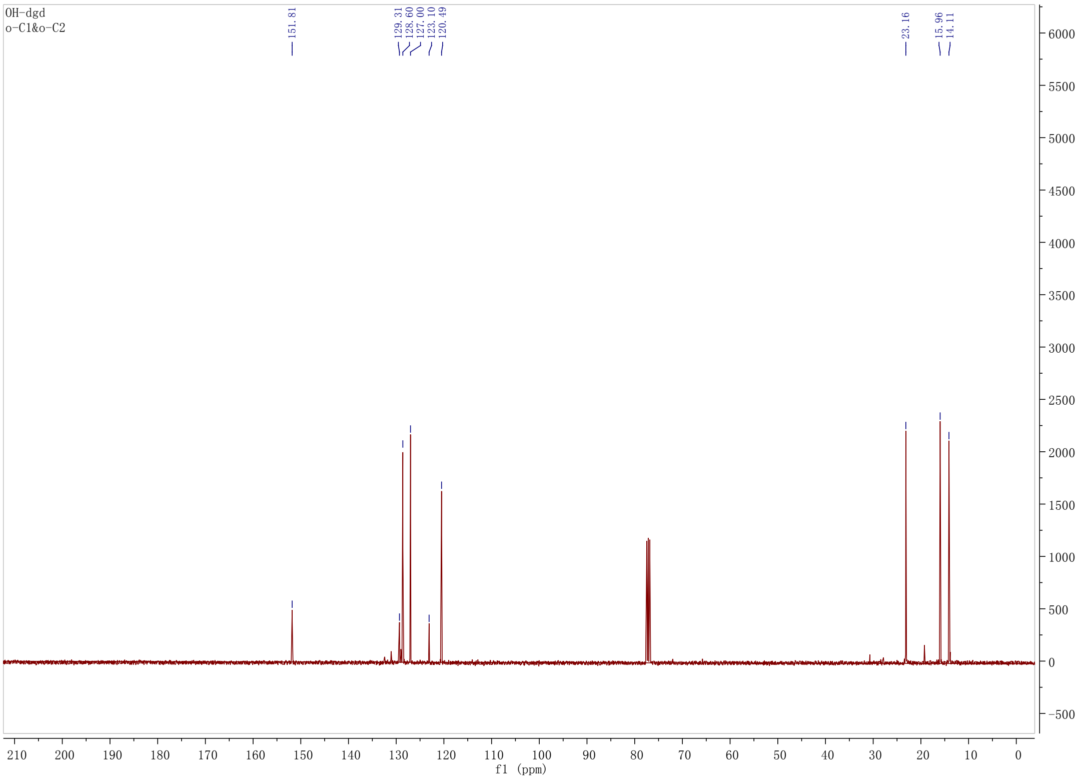

CH3
OH
CH3

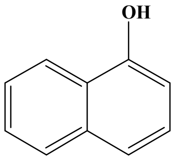

OH-dgd
o-diCH3
6.97
6.95
6.76
6.75
4.61
2.23
0.00
2.02
1.01
1.00
6.32
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
130000 120000 110000 100000 90000 80000 70000 60000 50000 40000 30000 20000 10000 0 −10000

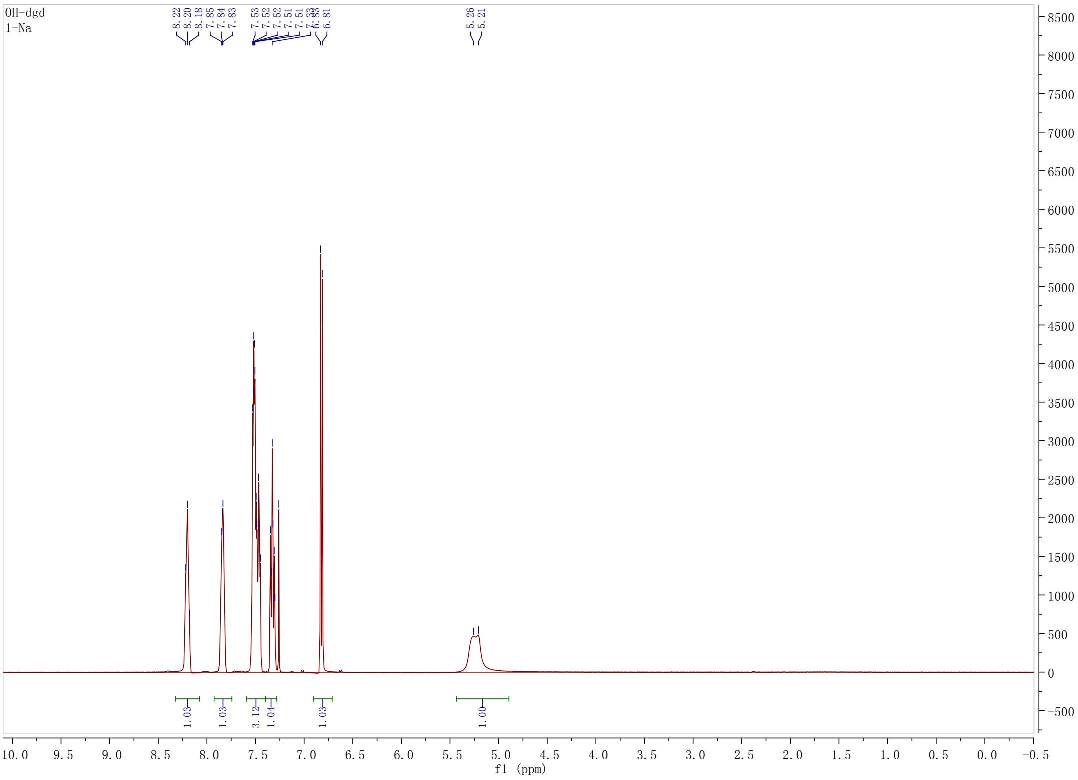

DGD
o-diCH3
152.26
128.71
123.08
120.32
77.58
77.16
76.74
15.96
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 −10 −30 −50
f1 (ppm)
15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000

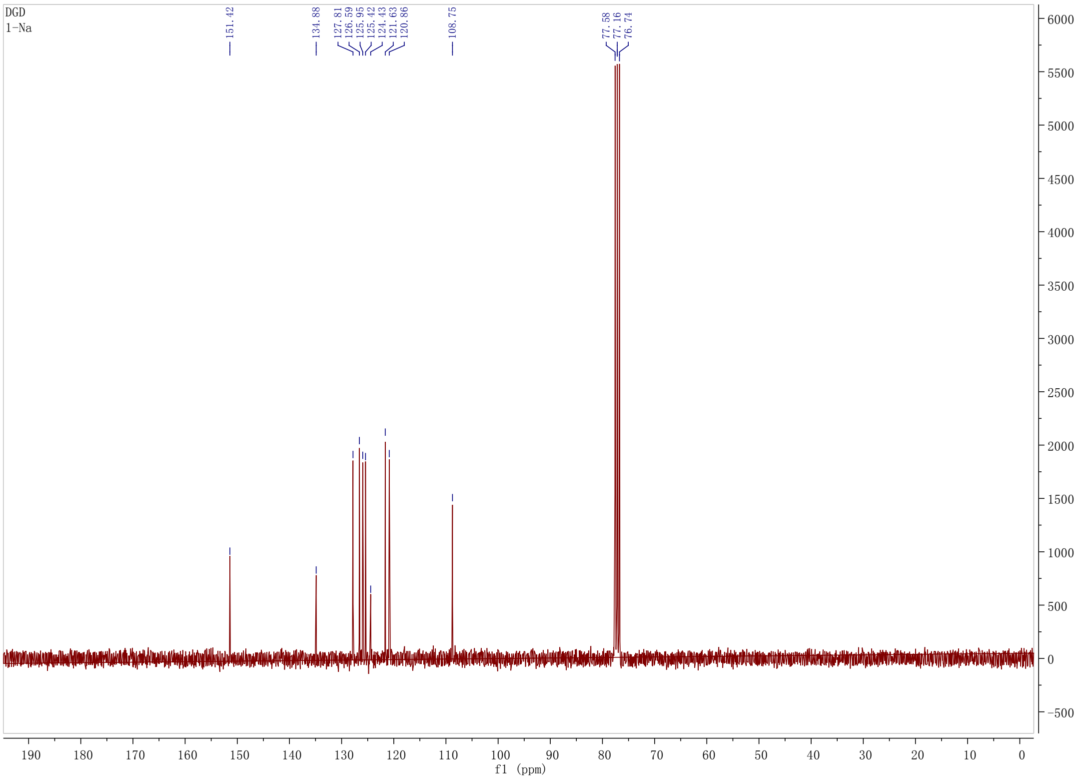

CH_3
OH
CH_2CH_3

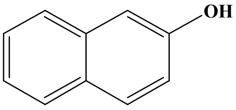

OH-dgd
o-C1&o-C2
7.12
6.91
6.90
6.88
6.75
6.73
6.72
6.71
6.71
6.69
4.59
2.56
2.55
2.54
2.53
2.51
2.17
2.16
2.15
1.19
1.18
1.18
1.17
1.16
1.15
1.13
-0.00
2.12
1.06
1.00
2.29
3.32
3.56
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

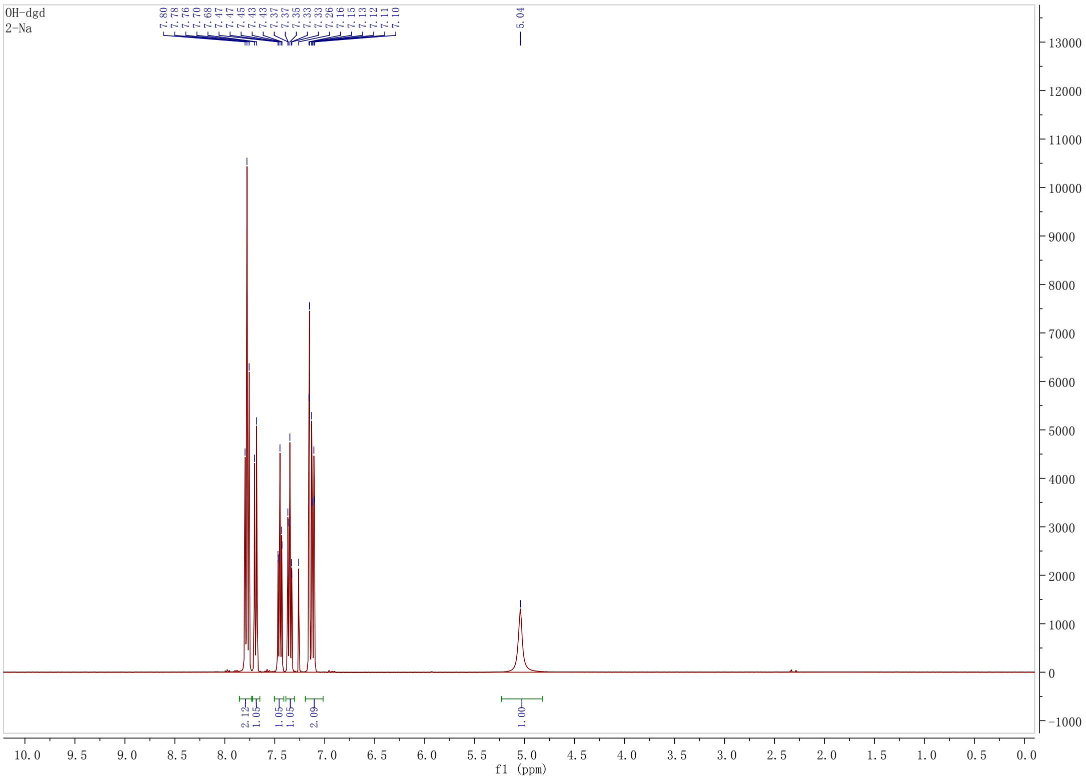

OH-dgd
o-C1&o-C2
151.81
129.31
128.60
127.00
123.10
120.49
23.16
15.96
14.11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

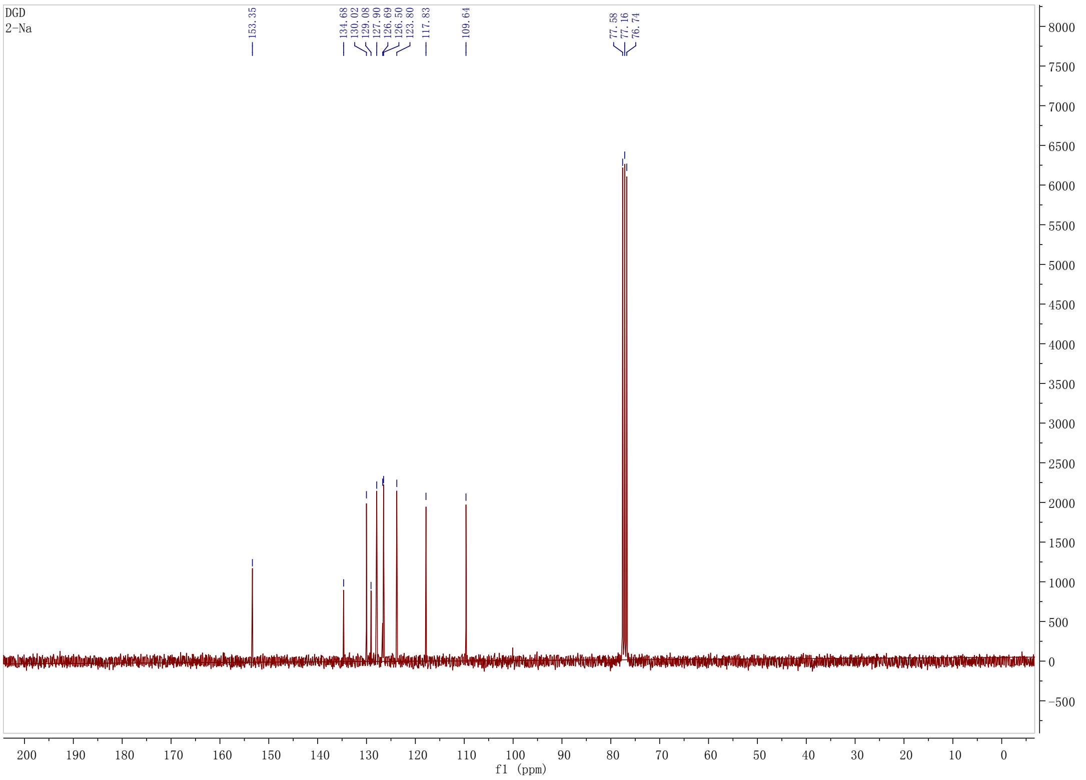

OH

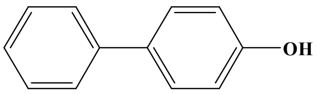

OH-dgd
1-Na
8.22
8.20
8.18
7.85
7.84
7.83
7.53
7.52
7.52
7.51
7.51
7.33
6.83
6.81
5.26
5.21
1.03
1.03
3.12
1.04
1.03
1.00
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

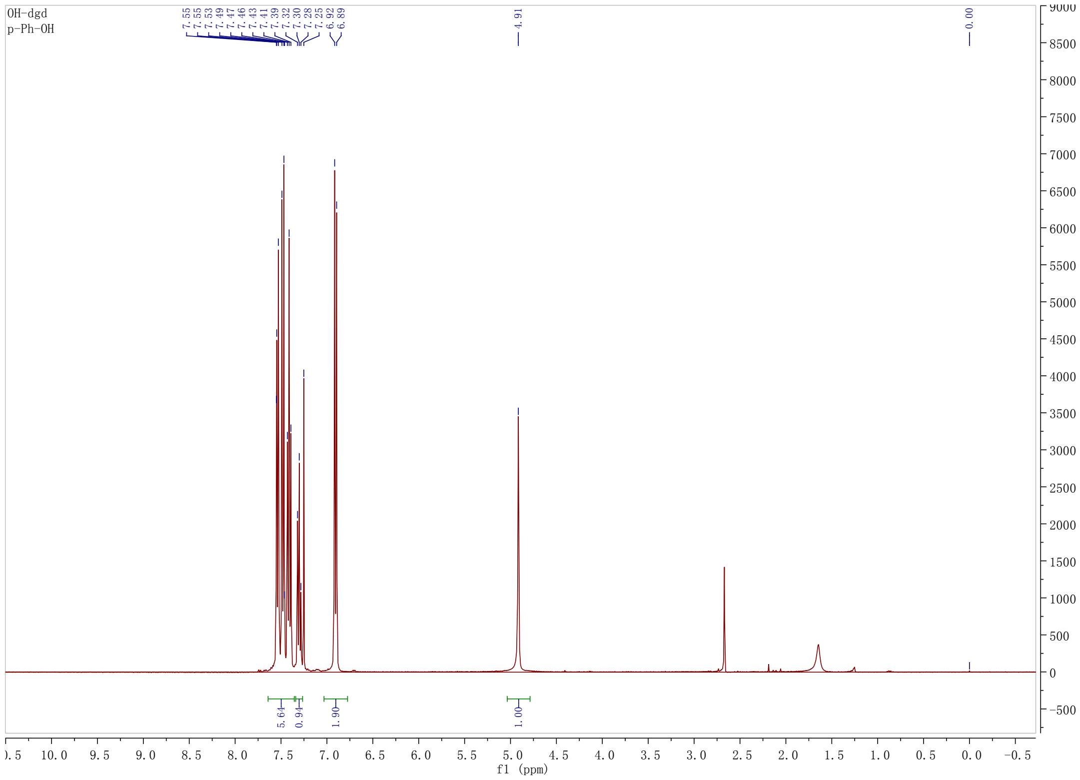

DGD
1-Na
151.42
134.88
127.81
126.59
125.95
125.42
124.43
121.63
120.86
108.75
77.58
77.16
76.74
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

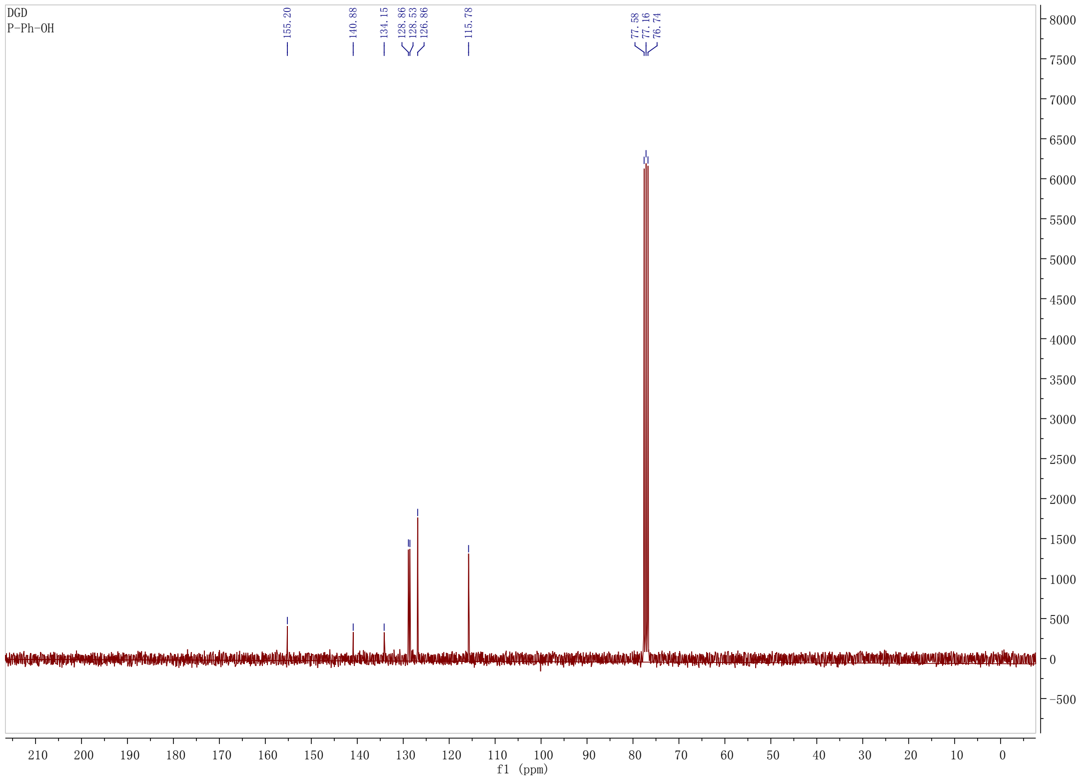

OH


OH-dgd
2-Na
7.80
7.78
7.76
7.70
7.68
7.47
7.45
7.43
7.43
7.37
7.37
7.35
7.33
7.33
7.26
7.16
7.15
7.13
7.12
7.11
7.10
5.04
2.12
1.05
1.05
1.05
2.09
1.00
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
10.0
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
0.0
f1 (ppm)


DGD
2-Na
153.35
134.68
130.02
129.08
127.90
126.69
126.50
123.80
117.83
109.64
77.58
77.16
76.74
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH


OH-dgd
p-Ph-OH
7.55
7.55
7.53
7.49
7.47
7.46
7.43
7.41
7.39
7.32
7.30
7.28
7.25
6.92
6.89
4.91
0.00
5.64
0.94
1.90
1.00
f1 (ppm)


DGD
P-Ph-OH
155.20
140.88
134.15
128.86
128.53
126.86
115.78
77.58
77.16
76.74
f1 (ppm)