Microwave-assisted copper-catalyzed hydroxylation of aryl halides in water

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Supplementary Information

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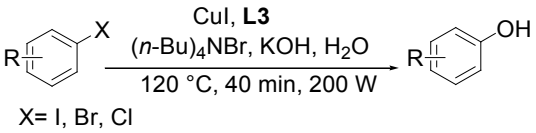
1. General information

All reagents were purchased from commercial suppliers and used without further purification. A CEM Discover microwave synthesizer was used in the standard configuration as delivered, including proprietary software. All experiments were carried out in sealed microwave process vials (10 mL). The temperature of the reaction mixture inside the vessel was monitored using a calibrated infrared temperature control under the reaction vessel. After completion of the reaction, the vial was cooled down to 25 °C via air jet cooling before opening. Column chromatography was carried out with silica gel (200-300 mesh). Thin layer chromatography was carried out using Merck silica gel GF254 plates. All products were characterized by NMR. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz (Bruker DPX) with $CDCl_3$, DMSO-d_6 and D_2O as solvent. Chemical shifts are reported in ppm using TMS as internal standard. Gas chromatography - mass spectra (GC/MS) were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973N mass detector (EI) and a HP5-MS 30 m x 0.25 mm capillary apolar column (Stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 μm). GC/MS method: Initial temperature: 150 °C; Initial time: 1 min; Ramp: about 15°C/min until 250 °C then 20 min.

2. General procedure for the catalytic reactions



In a 10 mL glass tube aryl halide (1.0 mmol), $CuCl_2$ (0.1 mmol), L3 (0.1 mmol), (n-Bu)$_4$NBr (0.1 mmol) and KOH (2.0 equiv) and 3.0 mL water were placed. The vessel was then sealed with a septum and placed into the microwave cavity. Initial microwave irradiation of 200 W by using a CEM Discover microwave synthesiser was used and the temperature being ramped from rt to the desired temperature of 120 °C. Once this was reached, the reaction mixture was held at this temperature for 40 min. The reaction mixture was stirred continuously during the reaction. After allowing the mixture to cool to rt, the reaction vessel was opened and the contents were acidified with 2 M hydrochloric acid to pH 5–7. The aqueous layer was extracted with ethyl acetate (3X15 mL). The organic washings were combined, dried over $MgSO_4$, and then ethyl acetate was removed in vacuo. The residue was purified by silica-gel column chromatography to afford the corresponding product. All the products were confirmed by NMR and MS spectroscopic analysis.

MTT ASSAY MEHTODS

Yellow-coloured MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) is reduced by the mitochondria of living cells to form a purple-coloured (formazan) crystalline derivative. These crystals can be solubilised by the addition of dimethyl sulphoxide (DMSO) and their concentration determined spectrophotometrically, as detailed below.

The human erythroleukemic cell line, K562, and the human nasopharyngeal carcinorma cell line, CNE2, were employed to determine the anticancer ability of synthesized chemicals. Each cell line was seeded in 96-well plates at a density of 9000 cells per well in RPMI 1640 medium for 24 h. The next day, 2,3-dihydroxy-1,4-naphthoquinone solutions, ranging in concentrations from 10^{-10} to 10^{-4} M were added to the culture medium. MTT reagent (5 mg/ml) was added to each sample after 48 hrs of treatment. The cells were incubated for 4 h and the absorbance of samples (A_{550}) was determined using a plate reader. Experiments were repeated 6 times in 8 replicates.

3. Experimental procedures and characterization data

Phenol[1]

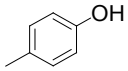
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.32 (m, 2H), 6.99-7.02 (m, 1H), 6.91 (d, *J* = 8 Hz, 2H), 5.73 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ =155.3, 129.8, 121.0, 115.5.

MS (EI, m/z): 94 [M^+].

***p*-Cresol**[1]



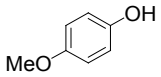
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.09 (d, *J* = 6 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.64 (s, 1H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 130.2, 115.3,115.2, 20.5.

MS (EI, m/z): 108 [M^+].

4-Methoxyphenol[1]



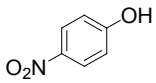
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.81 (d, *J* = 3.2 Hz, 4H), 5.09 (s, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 149.5, 116.2, 115.0, 55.9.

MS (EI, m/z): 124 [M^+].

4-Nitrophenol[1]



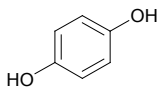
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). Yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 9.2 Hz, 2H), 6.96 (d, *J* = 9.2Hz, 2H), 6.49 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6, 139.9, 126.3, 115.8.

MS (EI, m/z): 139 [M^+].

Hydroquinone[2]



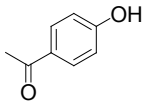
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.62 (s, 2H), 6.59 (s, 4H).

^{13}C NMR (100 MHz, DMSO-d_6) δ = 150.2, 116.1.

MS (EI, m/z): 110 [M^+].

4-Hydroxyacetophenone[1]



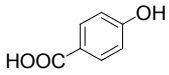
Purification by flash chromatography (petroleum ether/ethyl acetate 5:1). White solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ =10.32 (s, 1H), 7.83-7.84 (m, 2H), 6.85 (d, *J* = 7.2 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ = 196.4, 162.5, 131.2, 129.1, 115.6, 26.7.

MS (EI, m/z): 136 [M^+].

4-Hydroxybenzoic acid[1]



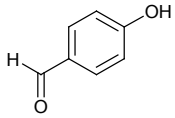
Purification by flash chromatography (petroleum ether/ethyl acetate 3:1). White solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.42 (br, 1H), 10.21 (s, 1H), 7.81 (d, *J* = 9.2 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ = 167.6, 162.1, 132.0, 121.9, 115.6.

MS (EI, m/z): 138 [M^+].

4-Hydroxybenzaldehyde[1]



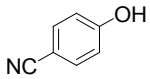
Purification by flash chromatography (petroleum ether/ethyl acetate 5:1). White yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 10.59 (s, 1H), 9.79 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ =191.4, 163.7, 132.6, 128.9, 116.3.

MS (EI, M/Z): 122 [M^+].

4-Hydroxybenzonitrile[3]



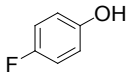
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4, 134.4, 119.3, 116.5, 102.8.

MS (EI, m/z): 119 [M^+].

4-Fluorophenol[4]



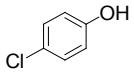
Purification by flash chromatography (petroleum ether/ethyl acetate 6:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.93-6.98 (m, 2H), 6.80-6.84 (m, 2H), 6.20 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7, 156.3, 151.1, 116.5, 116.4, 116.3, 116.0.

MS (EI, m/z): 112 [M^+].

4-Chlorophenol[1]



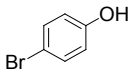
Purification by flash chromatography (petroleum ether/ethyl acetate 6:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.32 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.0, 129.6, 125.8, 116.7.

MS (EI, m/z): 128 [M^+].

4-Bromophenol[1]



Purification by flash chromatography (petroleum ether/ethyl acetate 6:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.12 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.5, 132.5, 117.2, 113.0.

MS (EI, m/z): 173 [M^+].

***o*-Cresol**[4]

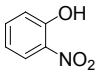
Purification by flash chromatography (petroleum ether/ethyl acetate 5:1).White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12-7.19 (m, 2H), 6.90-6.92 (m, 1H), 6.80-6.83 (m, 1H), 4.92-4.93 (m, 1H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.7, 131.2, 127.2, 123.9, 120.9, 115.1, 15.8.

MS (EI, m/z): 108 [M^+].

***o*-Nitrophenol**[5]



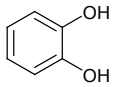
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). Yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.60 (s, 1H), 8.12-8.14 (m, 1H), 7.60-7.61 (m, 1H), 7.02-7.19 (m, 1H), 7.01 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.1, 137.5, 130.3, 125.1, 120.2, 120.0.

MS (EI, m/z): 139 [M^+].

Catechol[1]



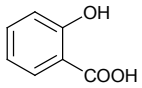
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.89-6.92 (m, 2H), 6.83-6.86 (m, 2H), 5.34 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5 121.3, 115.5.

MS (EI, M/Z): 110 [M^+].

2-Hydroxybenzoic acid



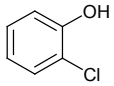
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.63 (br-s, 1H), 11.34 (br-s, 1H), 7.79-7.81 (m, 1H), 7.49-7.52 (m, 1H), 6.91-6.96 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ = 172.3, 161.6, 136.1, 130.7, 119.6, 117.5, 113.4.

MS (EI, m/z): 138 [M^+].

2-Chlorophenol[1]



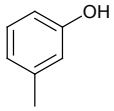
Purification by flash chromatography (petroleum ether/ethyl acetate 6:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.59-6.67 (m, 1H), 6.43-6.59 (m, 2H), 6.39-6.43 (m, 1H), 4.46 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.5, 137.0, 120.0, 117.0, 114.9, 114.8.

MS (EI, m/z): 128 [M^+].

***m*-Methylphenol**[4]



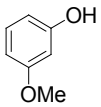
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16-7.18 (m, 1H), 6.67-6.83 (m, 3H), 5.63 (s, 1H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.3, 139.4, 129.5, 121.8, 116.2, 112.4, 21.4.

MS (EI, m/z): 108 [M^+].

***m*-Methoxyphenol**[4]



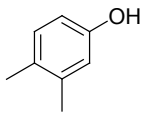
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15-7.19 (m, 1H), 6.47-6.56 (m, 3H), 6.05 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8, 156.7, 130.3, 108.1, 106.6, 101.7, 55.4.

MS (EI, m/z): 124 [M^+].

3,4-Dimethylphenol[6]



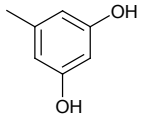
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White soild.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (d, J = 6.4 Hz, 1H), 6.34-6.71 (m, 2H), 5.40 (s, 1H), 2.25 (d, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.4, 138.0, 130.6, 128.8, 116.7, 112.5, 19.9, 18.8.

MS (EI, m/z): 122 [M^+].

3, 5-Dihydroxytoluene[7]



Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White soild.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.04 (s, 2H), 6.02-6.03 (m, 1H), 8.50 (s, 2H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ = 158.7, 139.6, 107.5, 100.2, 21.7.

MS (EI, m/z): 124 [M^+].

3-Hydroxypyridine[8]

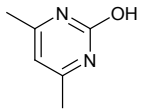
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White oil.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.90 (s, 1H), 8.03-8.16 (m, 1H), 8.02 (d, J = 1.6 Hz, 1H), 7.16-7.19 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ = 154.2, 140.7, 138.5, 124.6, 122.5.

MS (EI, m/z): 95 [M^+].

4,6-Dimethylpyrimidin-2-ol



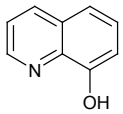
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White soild.

^{1}H NMR (400 MHz, D_2O) δ = 6.65 (s, 1H), 4.71 (s, 1H), 2.45-2.48 (m, 6H).

^{13}C NMR (100 MHz, D_2O) δ = 170.7, 148.9, 106.8, 19.7.

MS (EI, m/z): 124 [M^+].

8-Hydroxyquinoline[9]



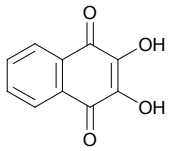
Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.82 (d, J = 1.2 Hz, 1H), 8.1 (br s, 1H), 8.16-8.81 (m, 1H), 7.45-7.51 (m, 2H), 7.34-7.44 (m, 1H), 7.22-7.24 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.3, 147.9, 138.4, 136.2, 128.6, 127.8, 121.8, 117.9, 110.2.

MS (EI, m/z): 145 [M^+].

2,3-Dihydroxy-1,4-naphthoquinone[10]



Purification by flash chromatography (petroleum ether/ethyl acetate 4:1). Yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (s, 2H), 7.83 (d, *J* = 6 Hz, 2H), 7.79 (d, *J* = 6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.4, 135.5, 133.7, 127.6, 127.0.

MS (EI, m/z): 190 [M^+].

4. References

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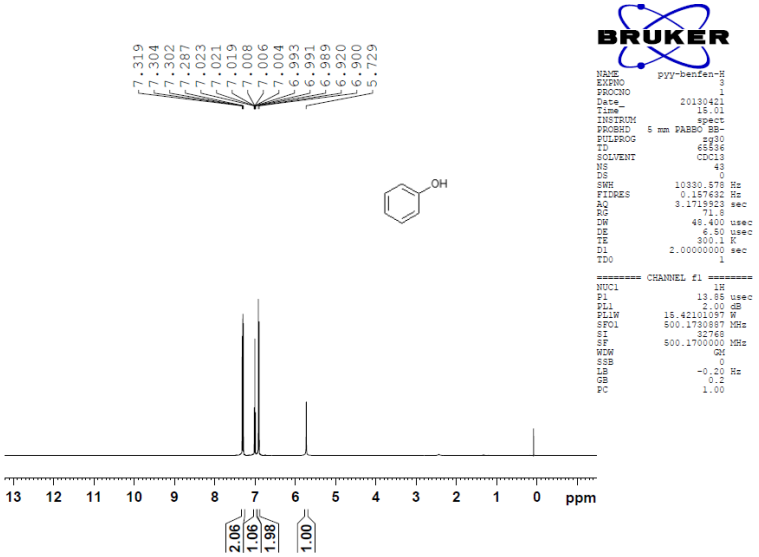
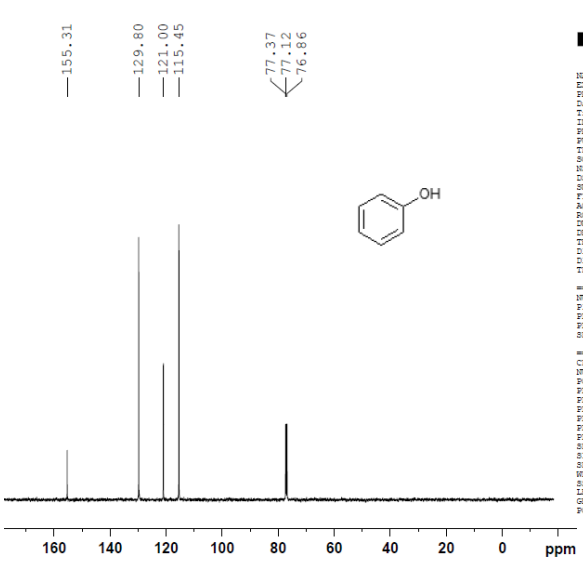
5. ^{1}H NMR and ^{13}C NMR spectra for the products

Phenol

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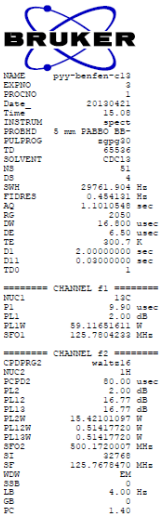
ppm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FIDRES 0.454191 Hz
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RG 2050
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DE 6.50 usec
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D11 0.03000000 sec
TD0 1
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PL1 2.00 dB
PL1W 59.11681611 W
SFO1 125.7804233 MHz
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PCPD2 80.00 usec
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PL12 16.77 dB
PL13 16.77 dB
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PL13W 0.51417720 W
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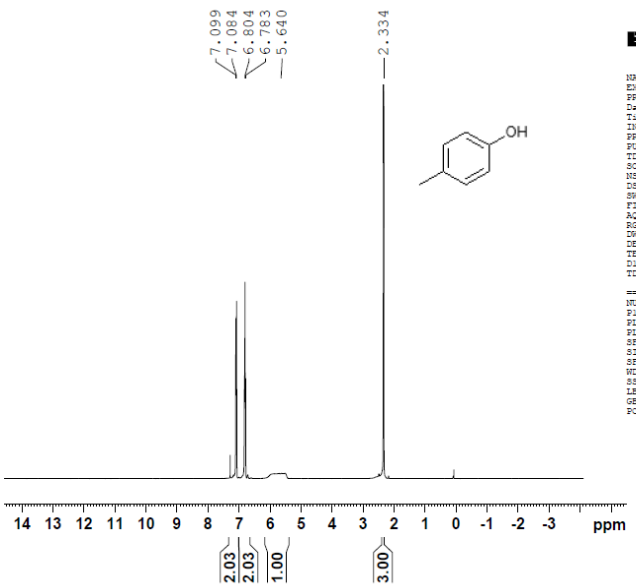
***p*-Cresol**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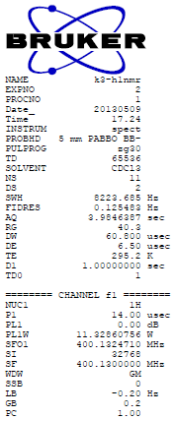
2.03
1.00
3.00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TE 295.2 K
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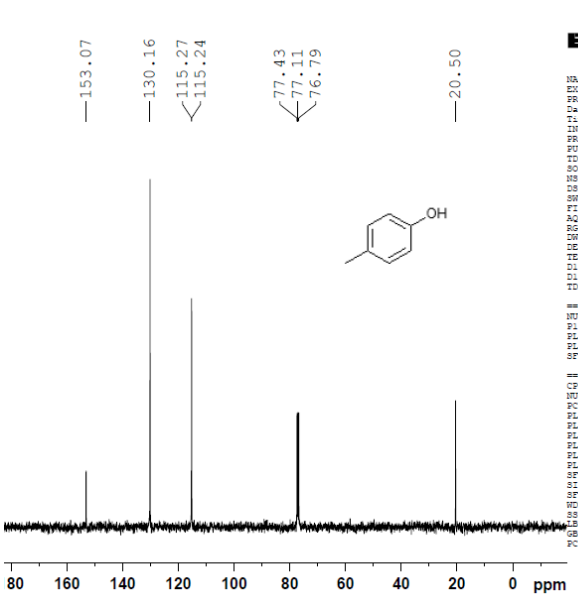
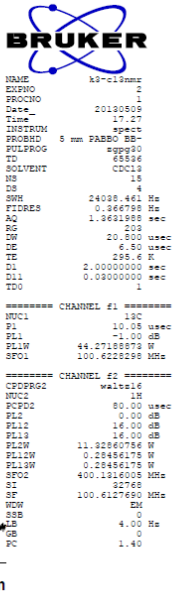
PC 1.00





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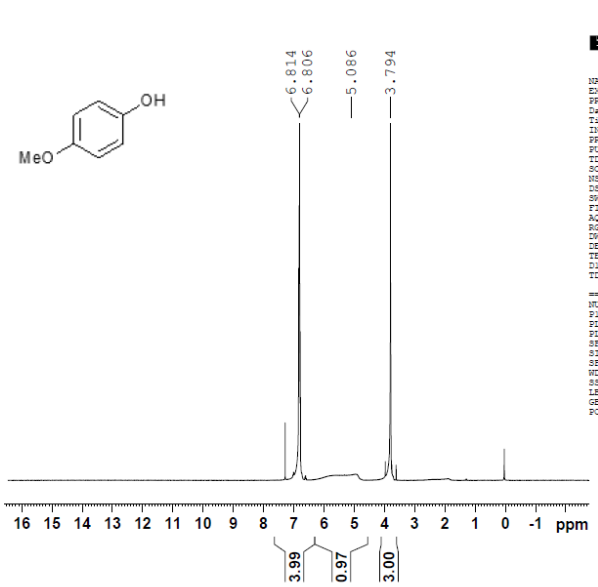

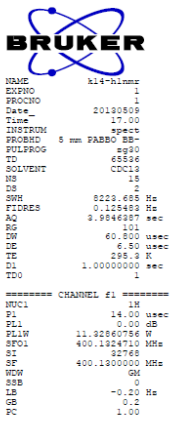

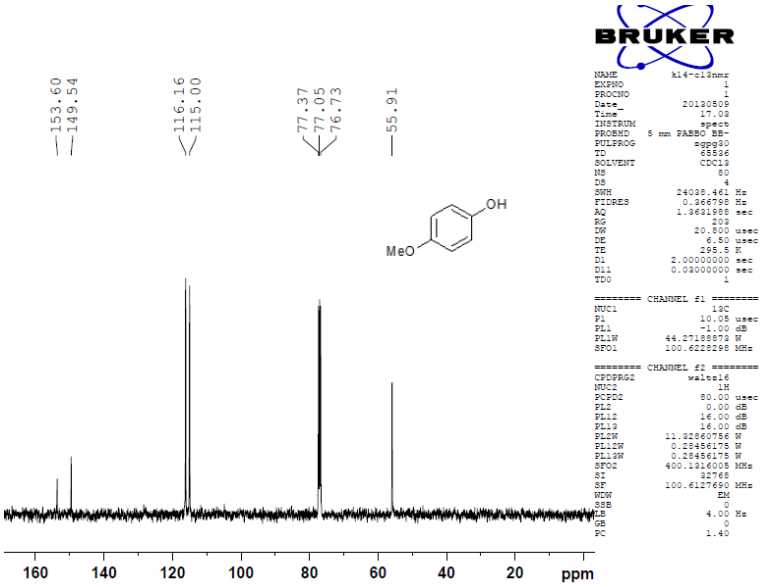

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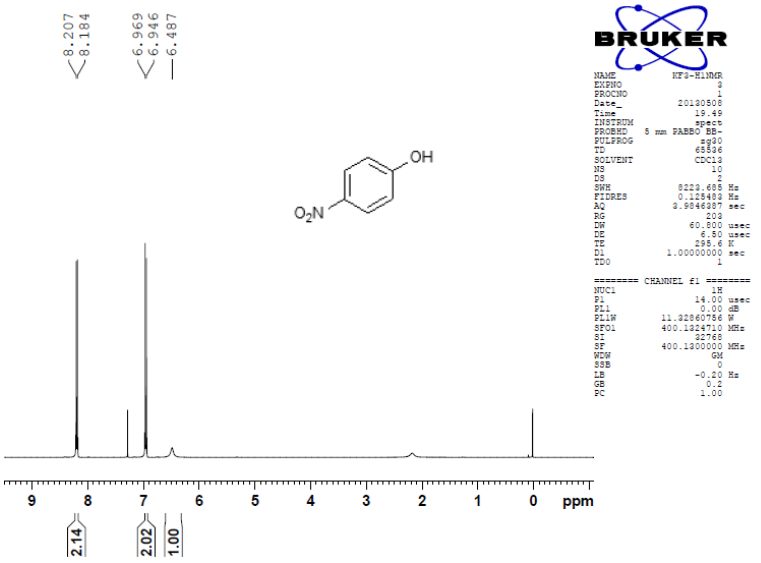
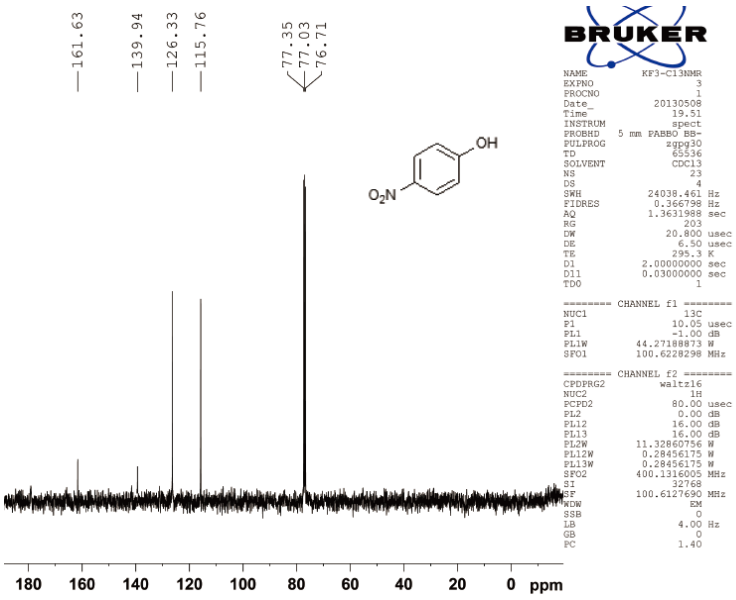
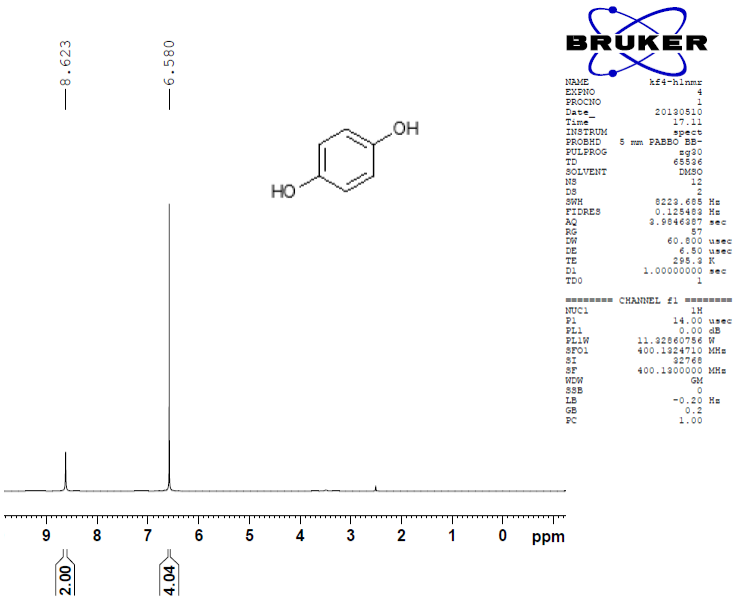
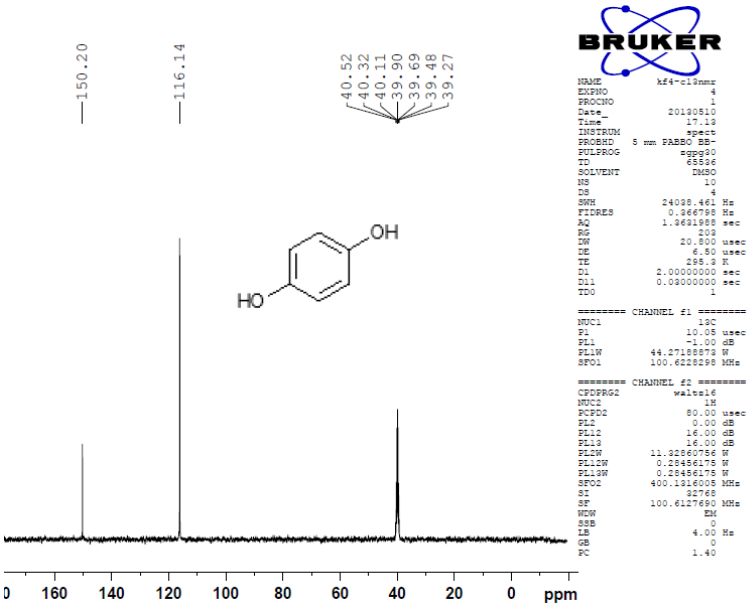




Hydroquinone





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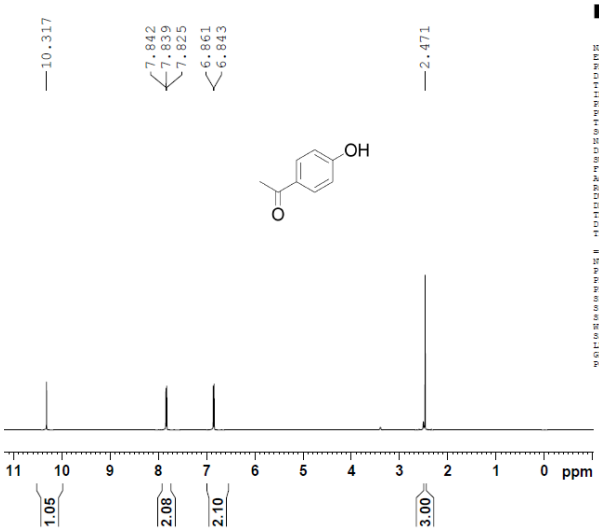

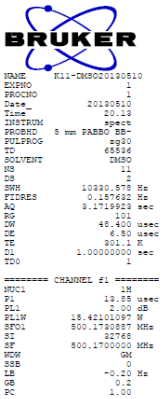

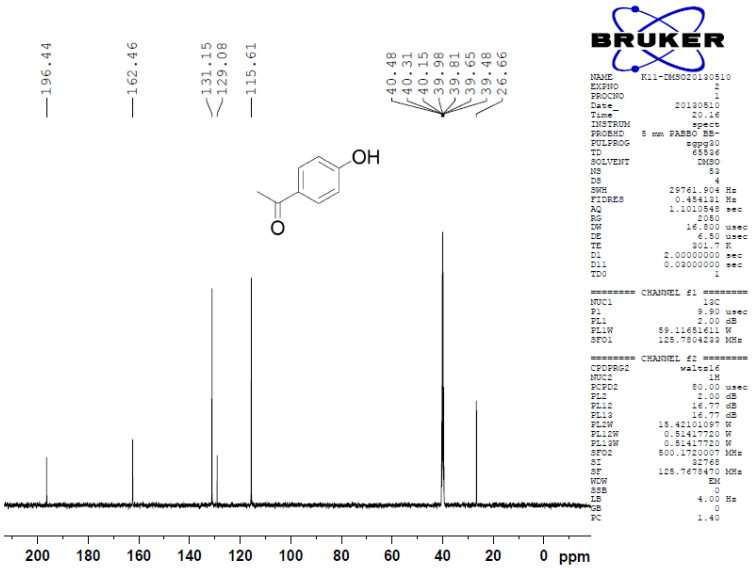

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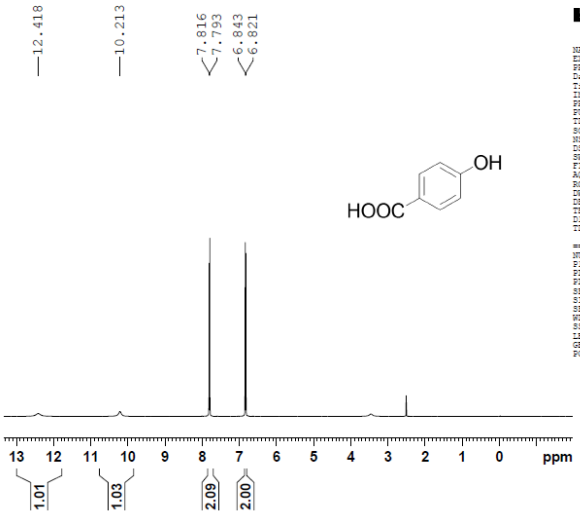

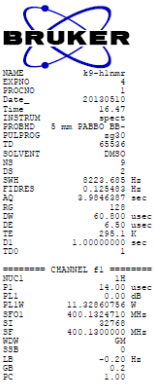

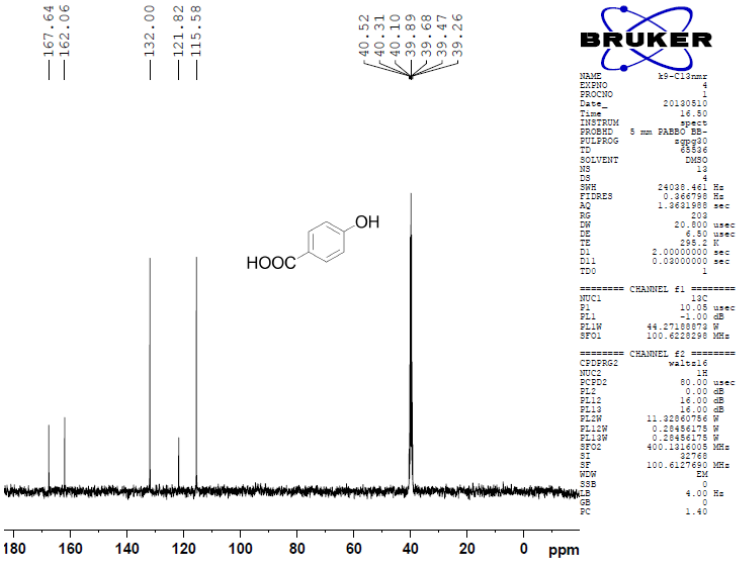

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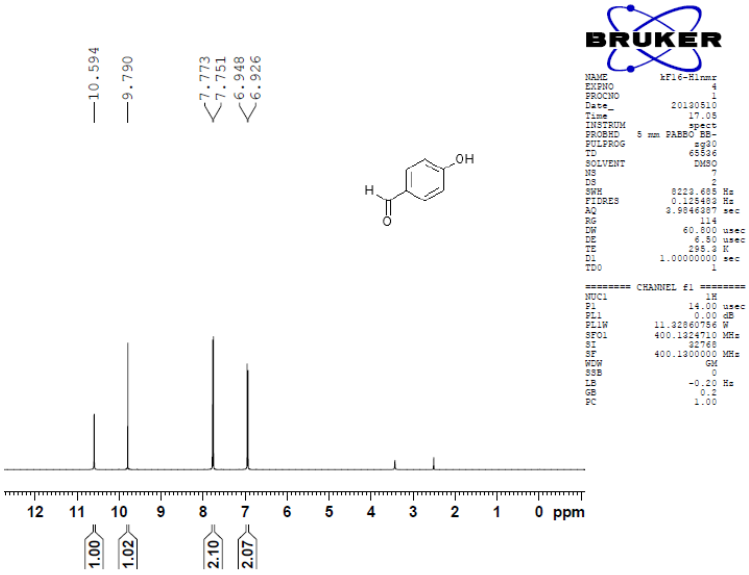

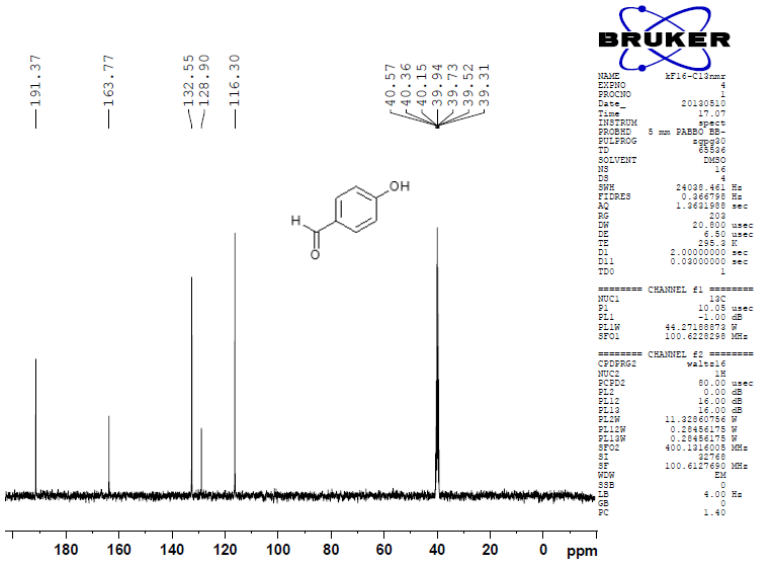

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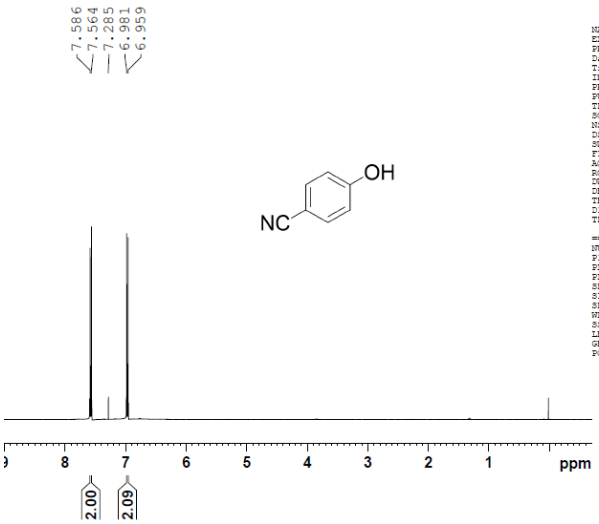

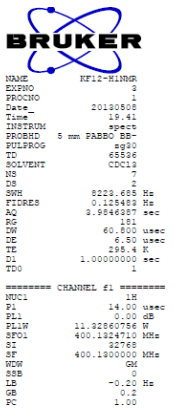

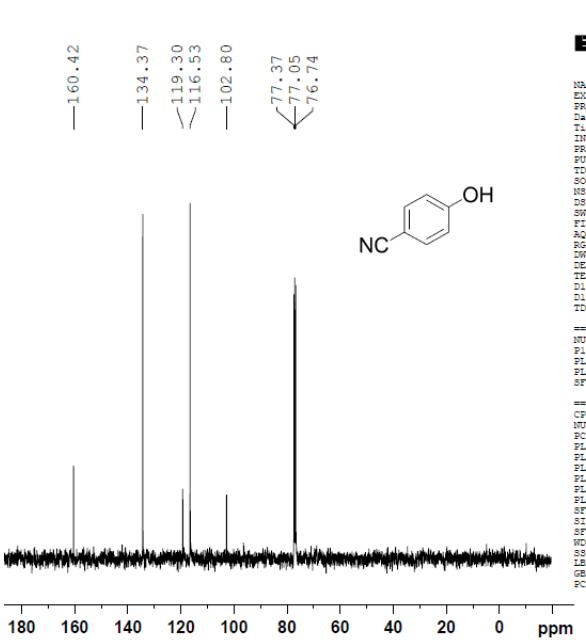

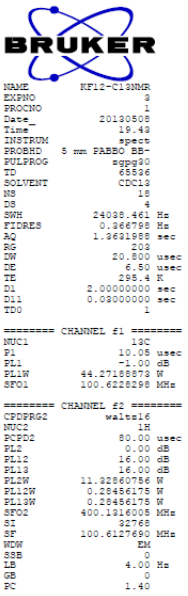

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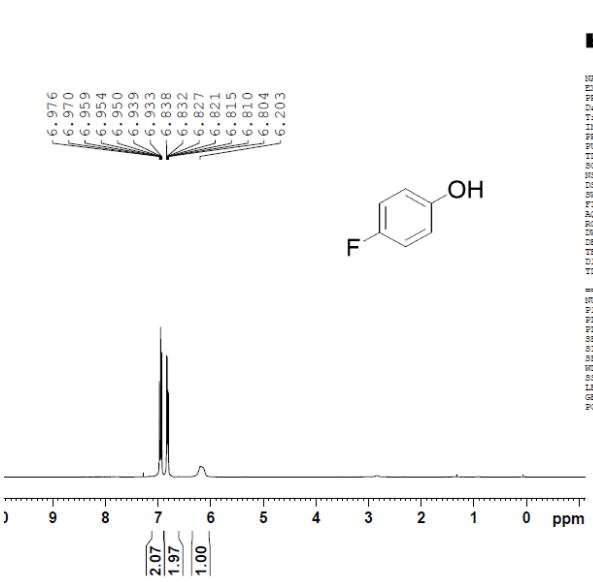

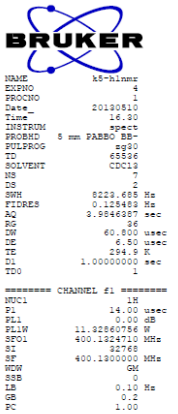

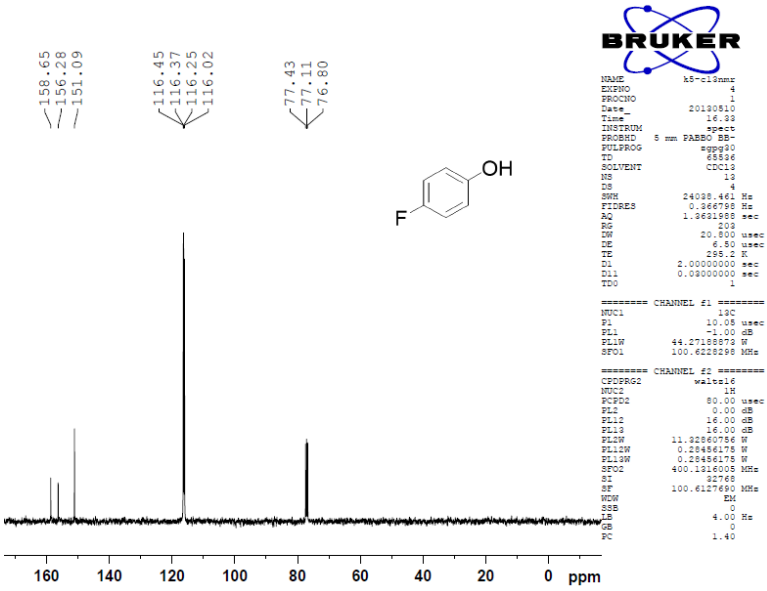

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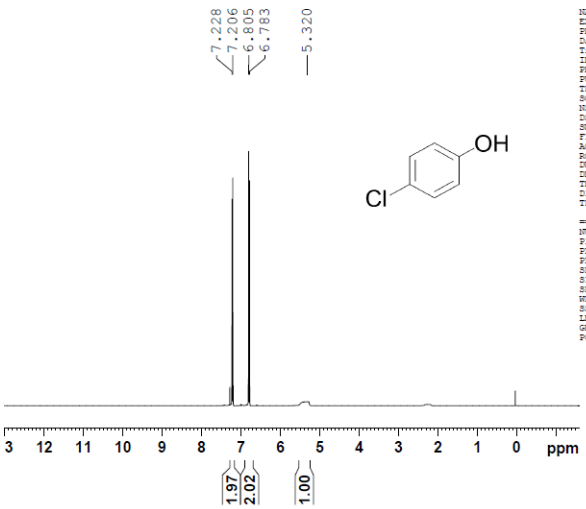

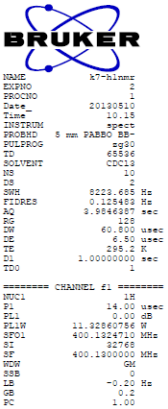

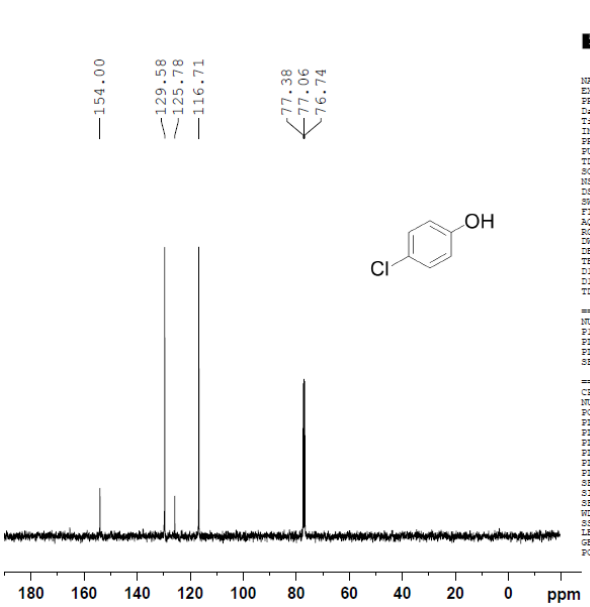


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SOLVENT                  CDCl3
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FIDRES              0.366798 Hz
AQ                  1.3691988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                     295.3 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.05 usec
PL1                     -1.00 dB
PL1W              44.27188873 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
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PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   16.00 dB
PL13                   16.00 dB
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PL12W              0.28456175 W
PL13W              0.28456175 W
SFO2              400.1316005 MHz
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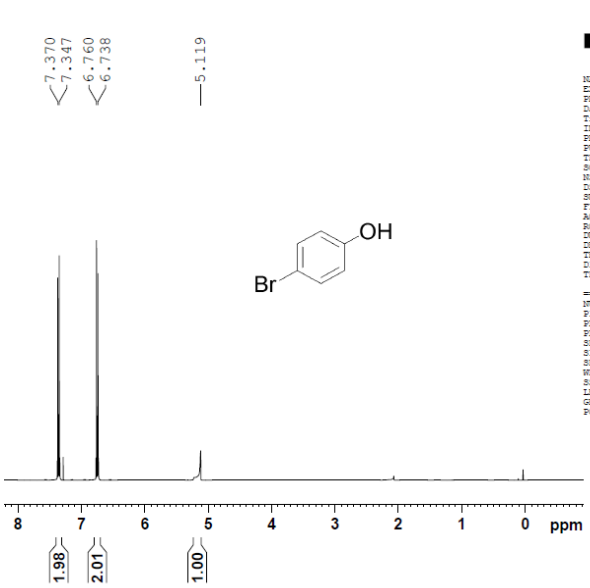
GB                           0
PC                      1.40
```

4-Bromophenol

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TD                       65536
SOLVENT                  CDCl3
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FIDRES              0.125488 Hz
AQ                  3.9846987 sec
RG                         144
DW                    60.800 usec
DE                     6.50 usec
TE                     295.5 K
D1                1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
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P1                      14.00 usec
PL1                      0.00 dB
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SFO1              400.1324710 MHz
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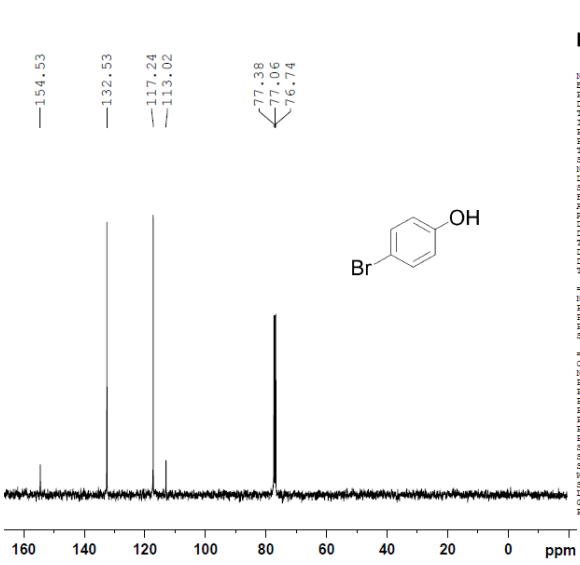
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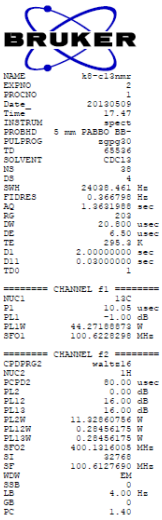
ppm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FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 295.9 K
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D11 0.03000000 sec
TD0 1
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NUC1 13C
P1 10.05 usec
PL1 -1.00 dB
PL1W 44.27188873 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
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NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.00 dB
PL13 16.00 dB
PL2W 11.92560786 W
PL12W 0.28456175 W
PL13W 0.28456175 W
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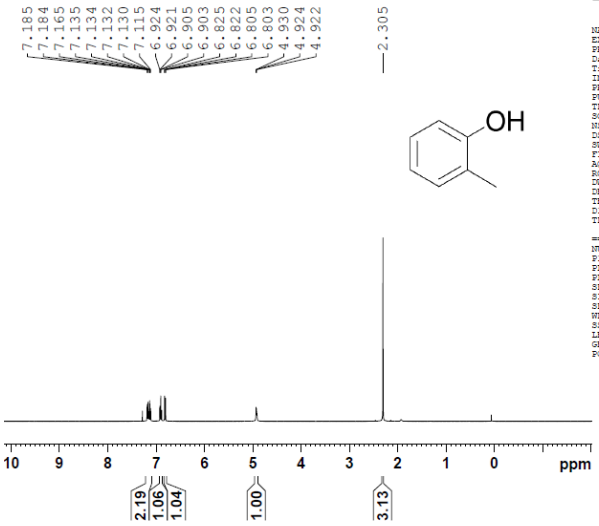
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.40

***o*-Cresol**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6.822
6.805
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4.930
4.924
4.922
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OH
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5
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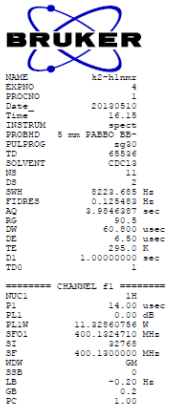
1.04
1.00
3.13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FIDRES 0.125489 Hz
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RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 11.92560756 W
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SF 400.1300000 MHz
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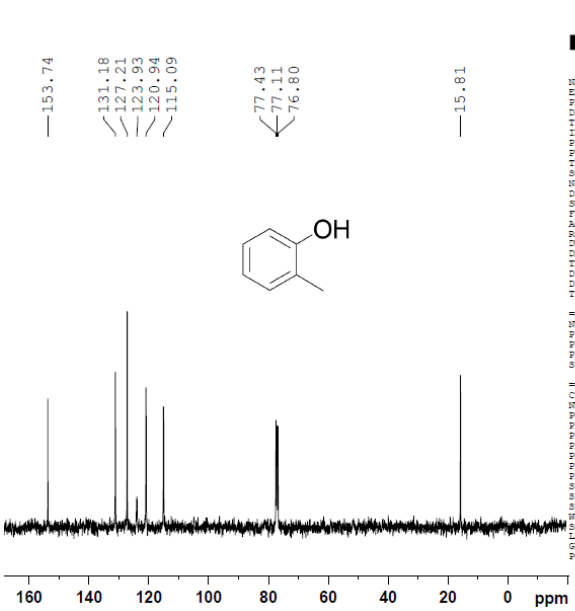
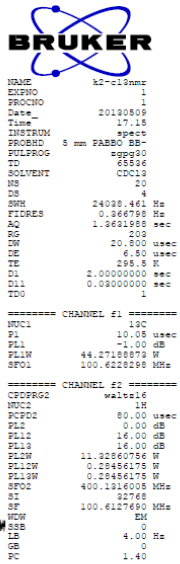
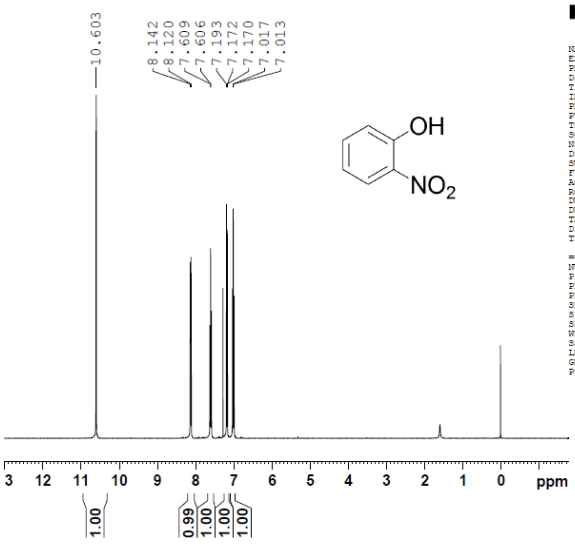
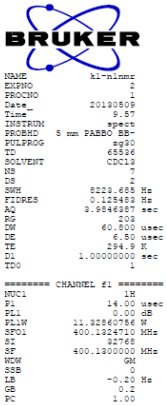
PC 1.00

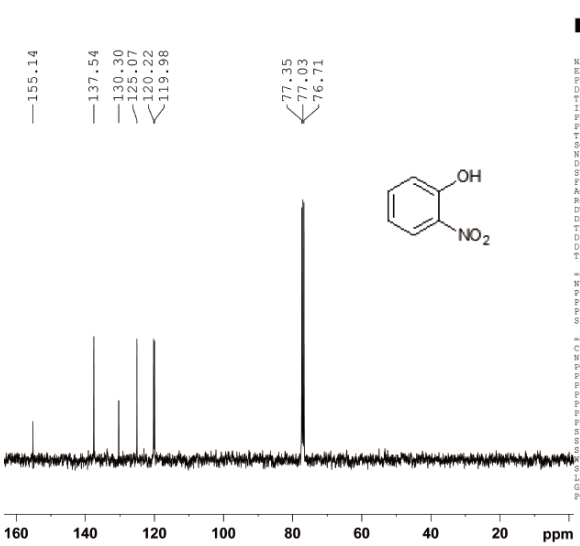


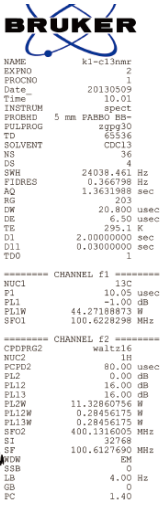


***o*-Nitrophenol**

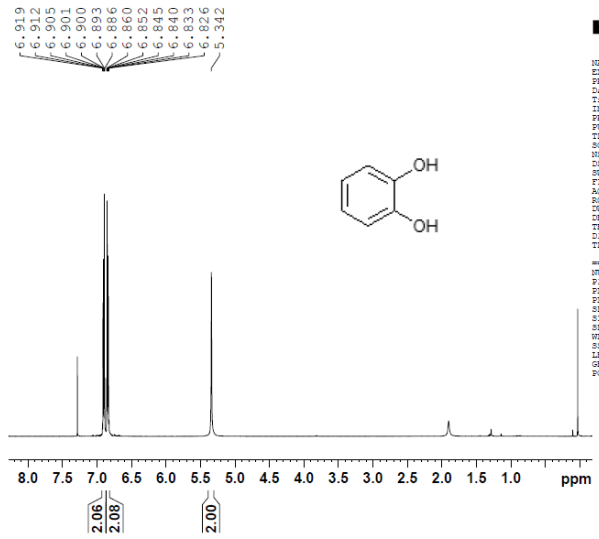


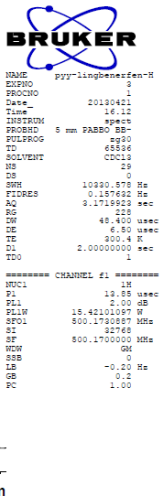


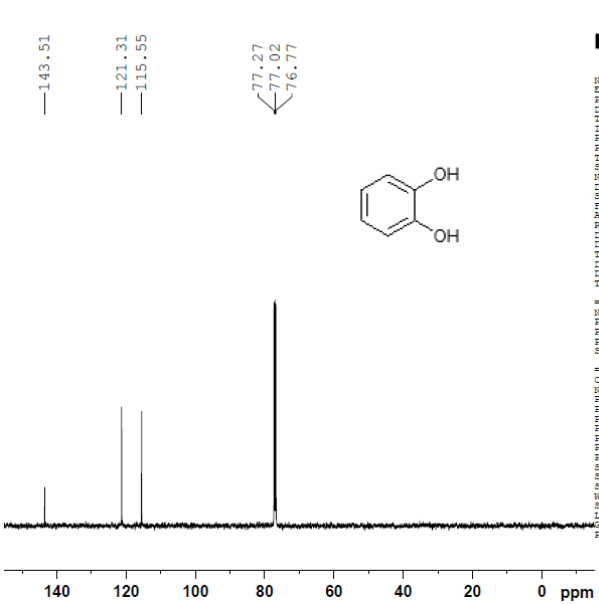

155.14
137.54
130.30
125.07
120.22
119.98
77.35
77.03
76.71
OH
NO2
160
140
120
100
80
60
40
20
ppm

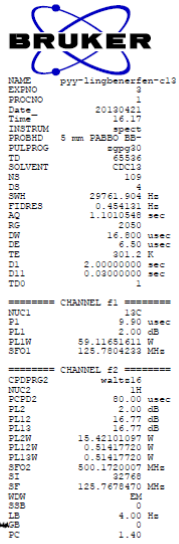

BRUKER
NAME k1-c13nmr
EXPNO 2
PROCNO 1
Date_ 20130509
Time 10.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 36
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.05 usec
PL1 -1.00 dB
PL1W 44.27188873 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.00 dB
PL13 16.00 dB
PL2W 11.32860756 W
PL12W 0.28456175 W
PL13W 0.28456175 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.40

Catechol

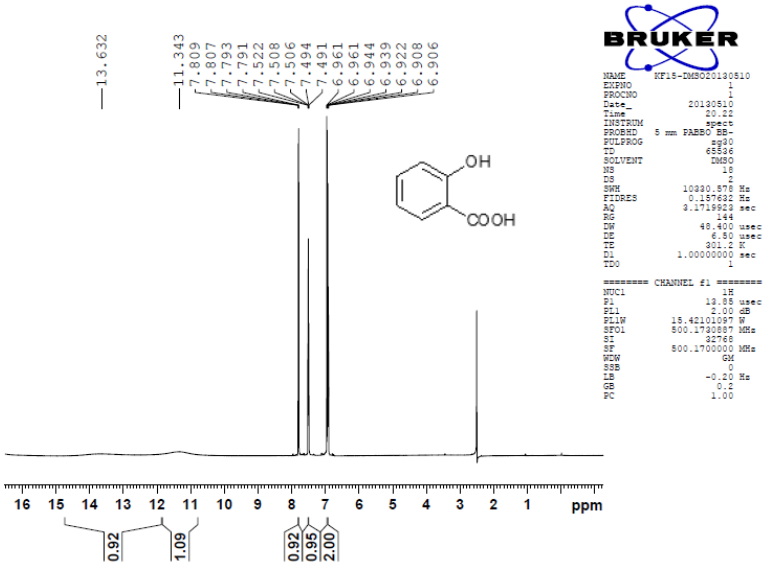

6.919
6.912
6.905
6.901
6.900
6.893
6.886
6.860
6.852
6.845
6.840
6.833
6.826
5.342
OH
OH
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
2.06
2.08
2.00

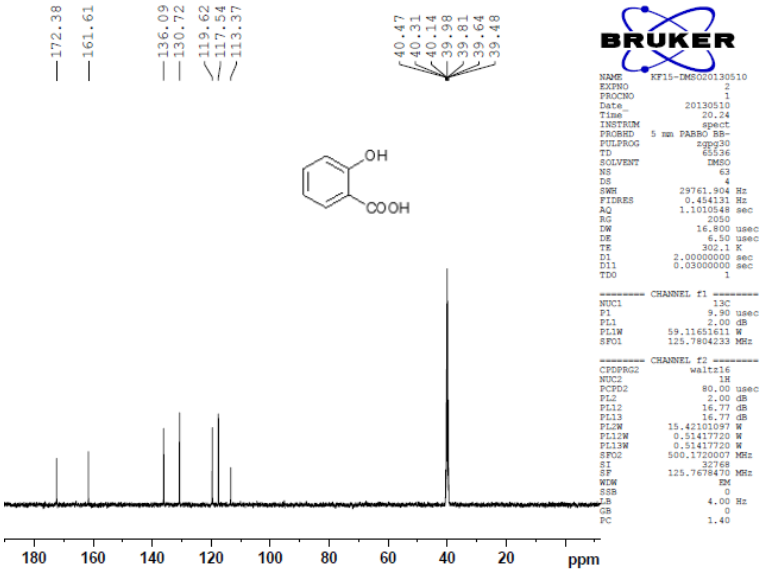

BRUKER
NAME pyy-lingbenerfen-H
EXPNO 3
PROCNO 1
Date_ 20130421
Time 16.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 29
DS 2
SWH 10330.578 Hz
FIDRES 0.157692 Hz
AQ 3.1719929 sec
RG 228
DW 48.400 usec
DE 6.50 usec
TE 300.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.85 usec
PL1 2.00 dB
PL1W 15.42101097 W
SFO1 500.1730867 MHz
SI 32768
SF 500.1700000 MHz
WDW GM
SSB 0
LB -0.20 Hz
GB 0.2
PC 1.00


143.51
121.31
115.55
77.27
77.02
76.77
OH
OH
140
120
100
80
60
40
20
0
ppm

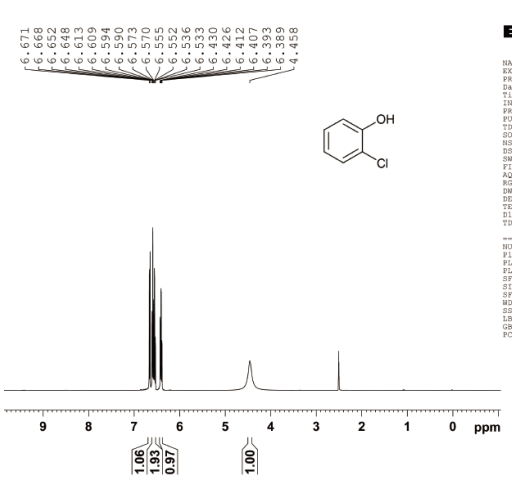

BRUKER
NAME pyy-lingbenerfen-c13
EXPNO 3
PROCNO 1
Date_ 20130421
Time 16.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 109
DS 4
SWH 29761.904 Hz
FIDRES 0.454191 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 301.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 2.00 dB
PL1W 59.11651611 W
SFO1 125.7804233 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 16.77 dB
PL13 16.77 dB
PL1W 15.42101097 W
PL12W 0.51417720 W
PL13W 0.51417720 W
SFO2 500.1720007 MHz
SI 32768
SF 125.7678470 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.40

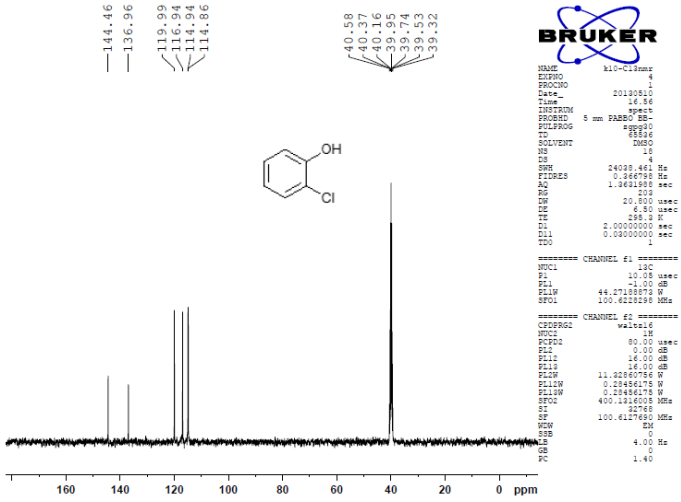
2-Hydroxybenzoic acid





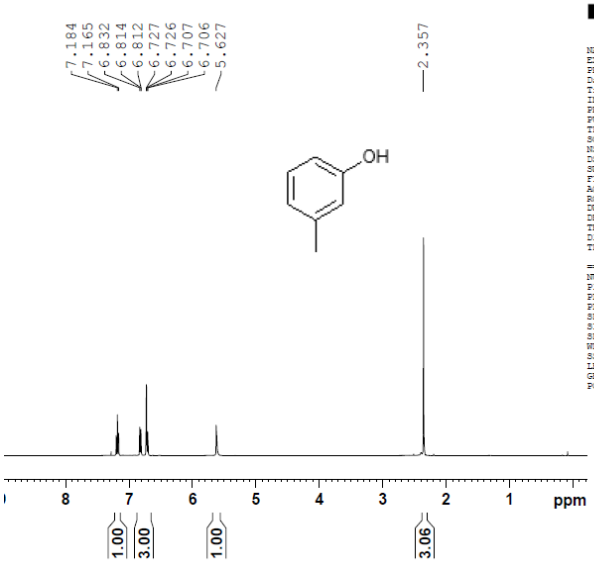
2-Chlorophenol



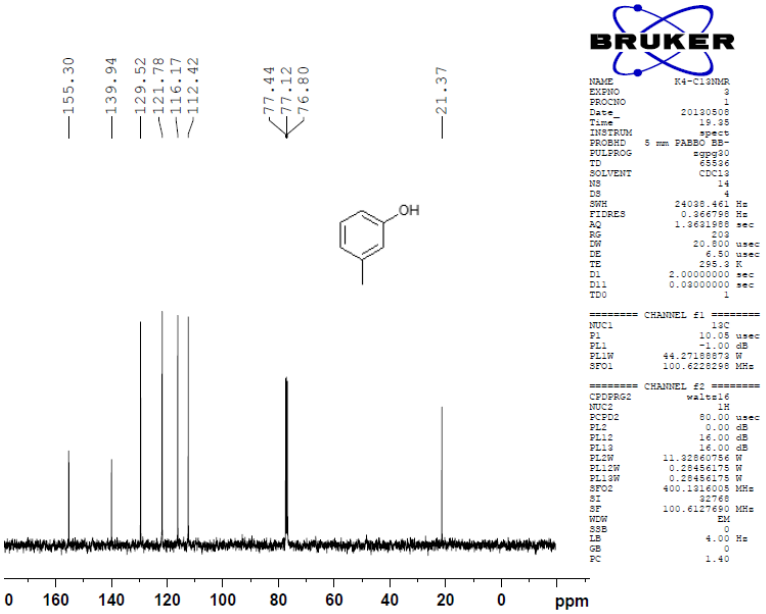


BRUKER
NAME k10-C13nmr
EXPNO 4
PROCNO 1
Date_ 20130510
Time 16.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 10
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 202
DW 20.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.05 usec
PL1 -1.00 dB
PL1W 44.27188873 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL11 16.00 dB
PL13 16.00 dB
PL2W 11.92660756 W
PL12W 0.29456175 W
PL13W 0.29456175 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.40

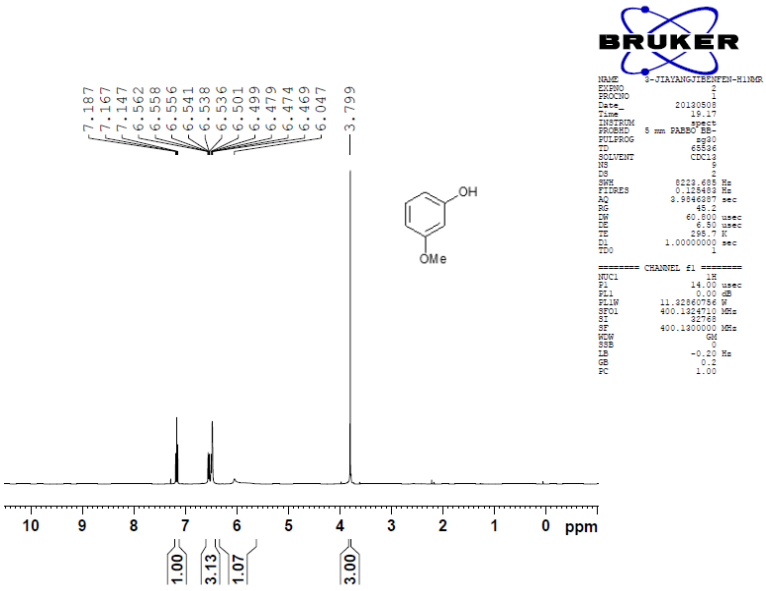
***m*-Methylphenol**

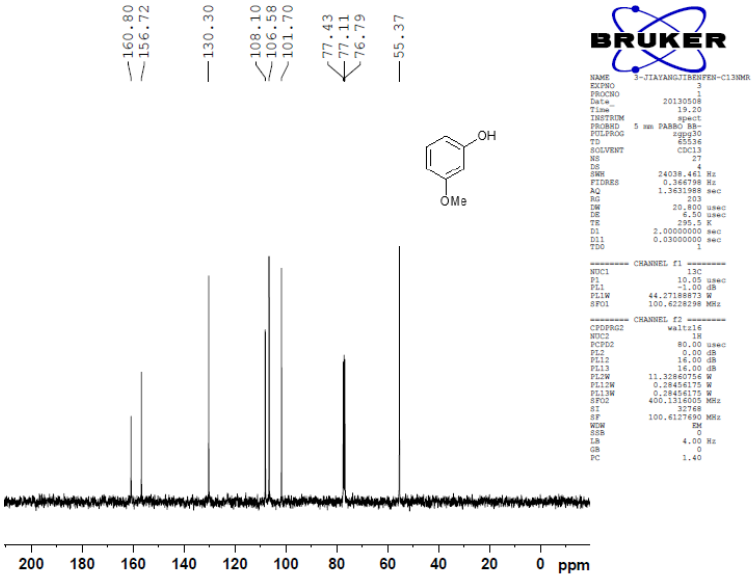


BRUKER
NAME K4-H1NMR
EXPNO 3
PROCNO 1
Date_ 20130508
Time 19.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 8223.685 Hz
FIDRES 0.125459 Hz
AQ 3.9846387 sec
RG 45.2
DW 60.800 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 11.92560756 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW GM
SSB 0
LB -0.20 Hz
GB 0.2
PC 1.00

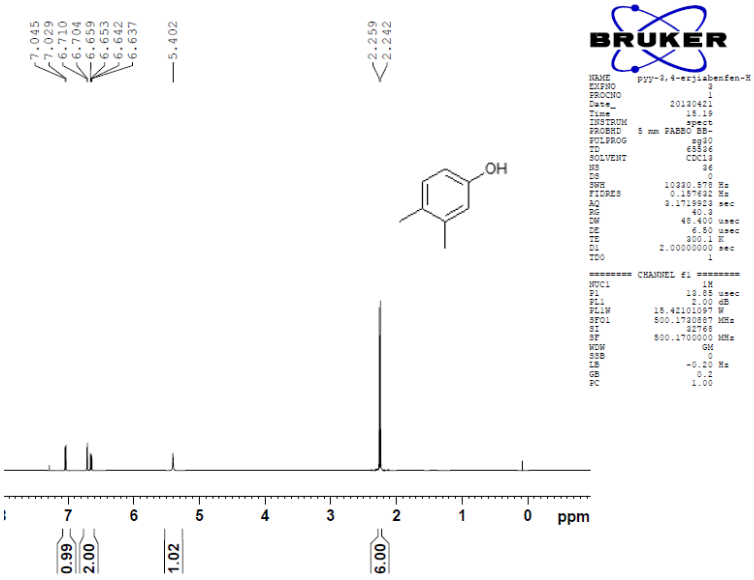


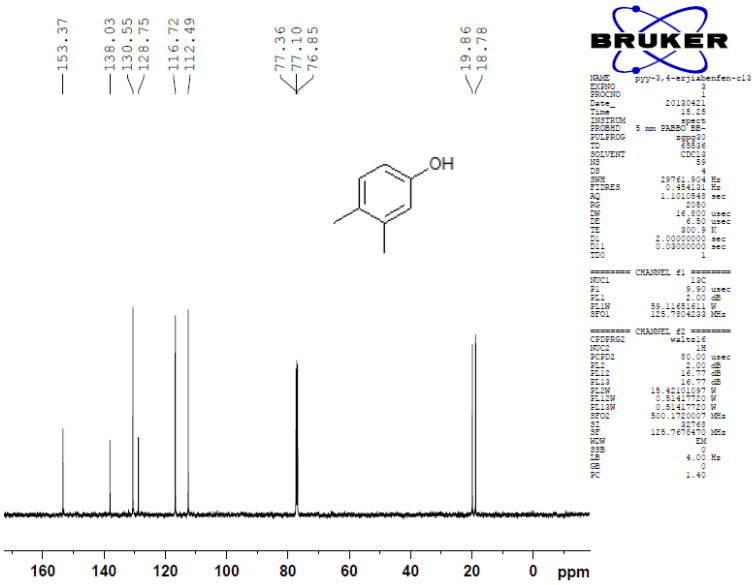
***m*-Methoxyphenol**





3,4-Dimethylphenol



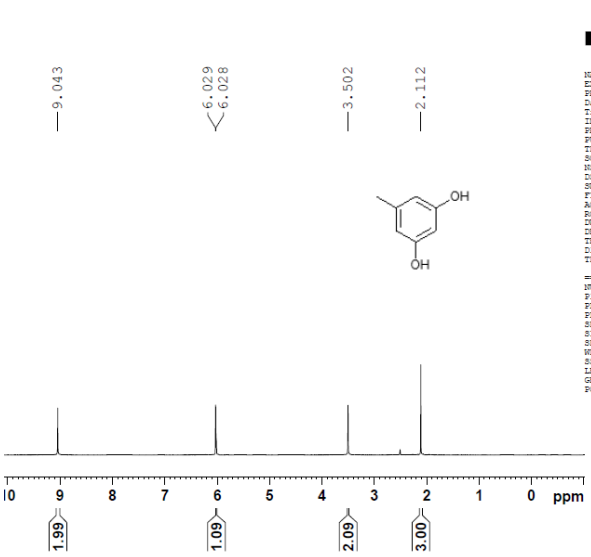


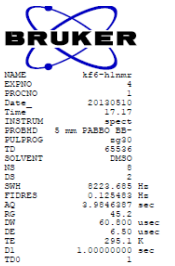

```
NAME          pyy-3,4-erjiabenfen-c13
EXPNO                               9
PROCNO                              1
Date_                        20190421
Time                            18.28
INSTRUM                        spect
PROBHD     5 mm PABBO BB-
PULPROG                     zgpg30
TD                               65536
SOLVENT                        CDCl3
NS                                 59
DS                                  4
SWH                        29761.904 Hz
FIDRES                      0.454191 Hz
AQ                          1.1010548 sec
RG                               2050
DW                             16.800 usec
DE                              6.50 usec
TE                             300.9 K
D1                          2.0000000 sec
D11                         0.03000000 sec
TD0                                 1

======== CHANNEL f1 ========
NUC1                              13C
P1                               9.90 usec
PL1                              2.00 dB
PL1W                      59.11658411 W
SFO1                     125.7804299 MHz

======== CHANNEL f2 ========
CPDPRG2                     waltz16
NUC2                              1H
PCPD2                           80.00 usec
PL2                              2.00 dB
PL12                            16.77 dB
PL13                            16.77 dB
PL2W                      15.42101097 W
PL12W                      0.51417720 W
PL13W                      0.51417720 W
SFO2                     500.1720007 MHz
SI                              32768
SF                       125.7675470 MHz
WDW                                EM
SSB                                 0
LB                               4.00 Hz
GB                                  0
PC                               1.40
```

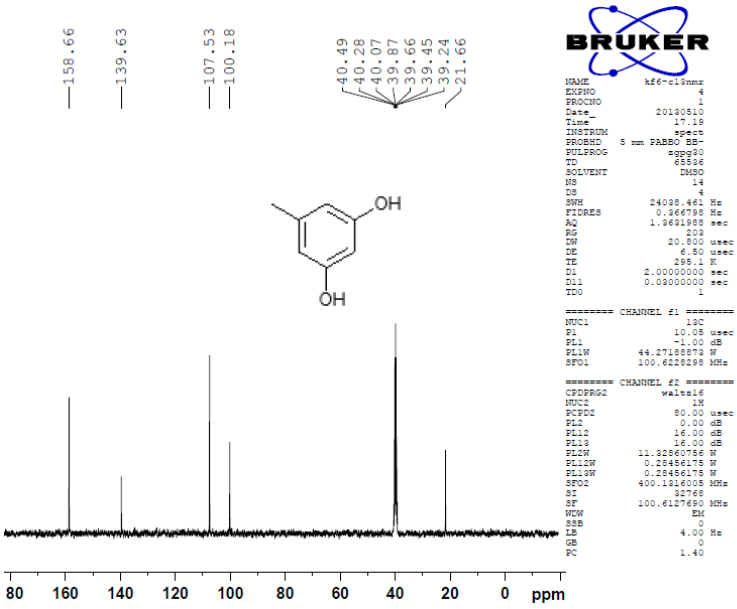
3, 5-Dihydroxytoluene



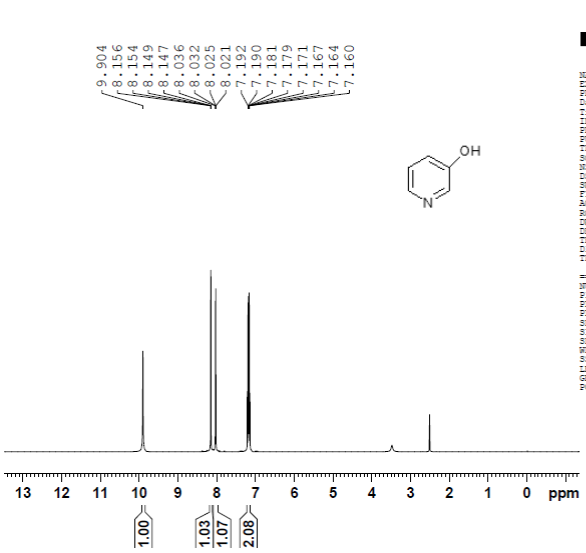


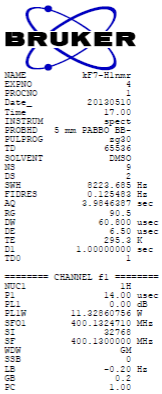

```
NAME                  hf6-hlnmr
EXPNO                         4
PROCNO                        1
Date_                  20190810
Time                      17.17
INSTRUM                   spect
PROBHD     5 mm PABBO BB-
PULPROG                   zg30
TD                         65536
SOLVENT                    DMSO
NS                            8
DS                            2
SWH                    8223.685 Hz
FIDRES                 0.125469 Hz
AQ                     3.9846987 sec
RG                          45.2
DW                        60.800 usec
DE                         6.50 usec
TE                        295.1 K
D1                     1.0000000 sec
TD0                           1

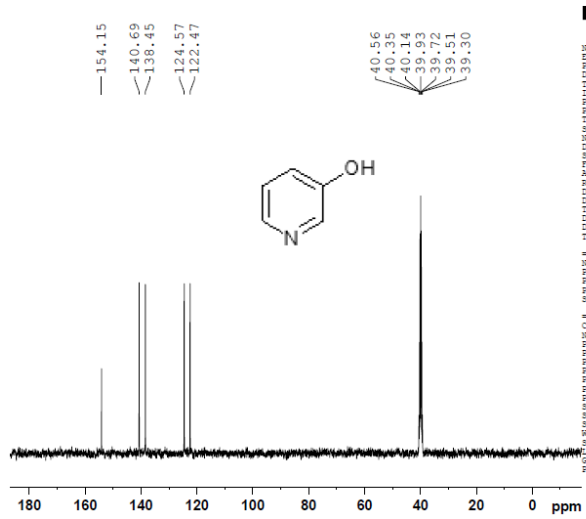
======== CHANNEL f1 ========
NUC1                          1H
P1                          14.00 usec
PL1                          0.00 dB
PL1W                  11.92860756 W
SFO1                  400.1324710 MHz
SI                         32768
SF                    400.1300000 MHz
WDW                           GM
SSB                            0
LB                         -0.20 Hz
GB                            0.2
PC                           1.00
```

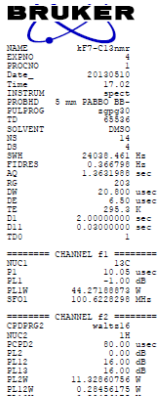


3-Hydroxypyridine

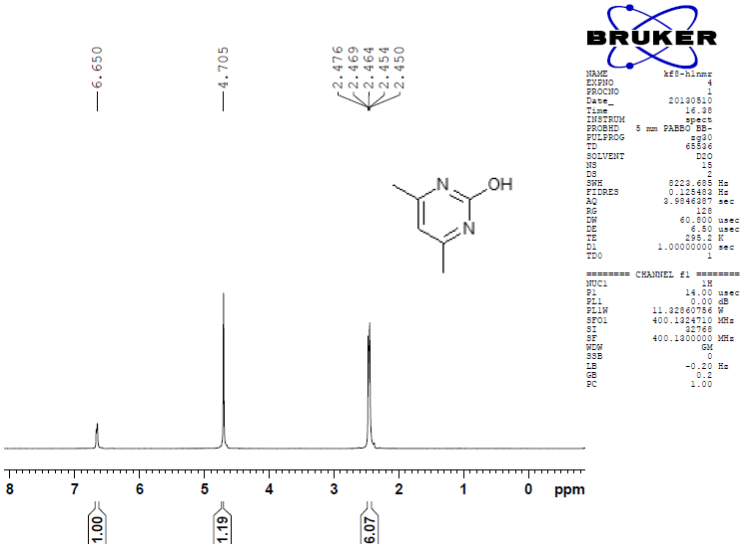


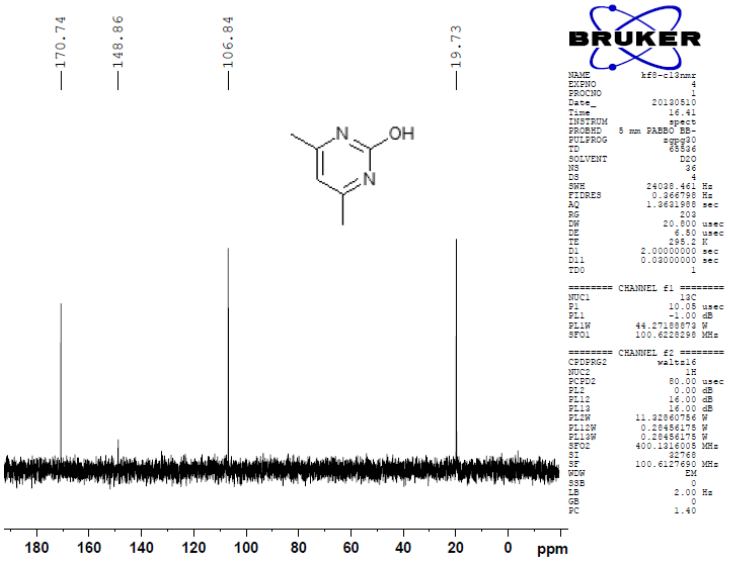




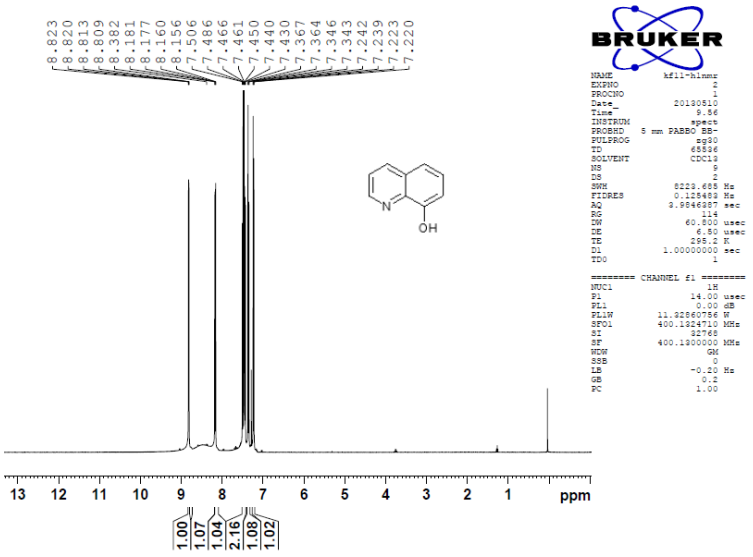


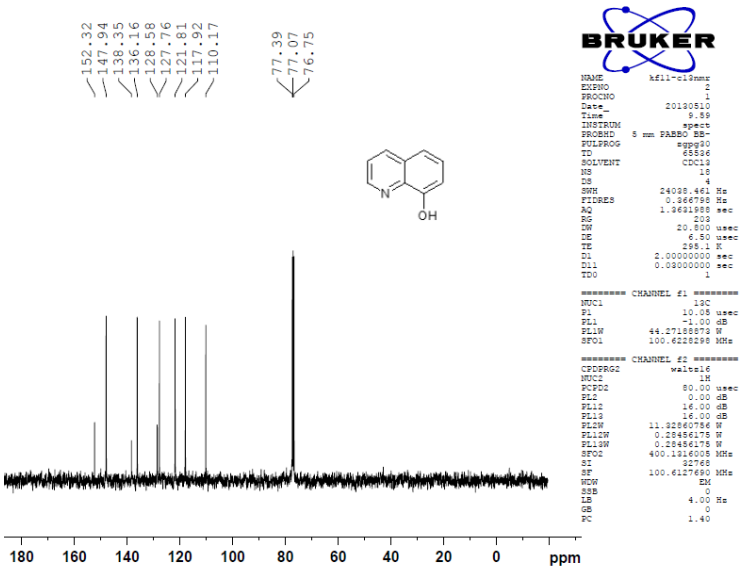
4,6-Dimethylpyrimidin-2-ol



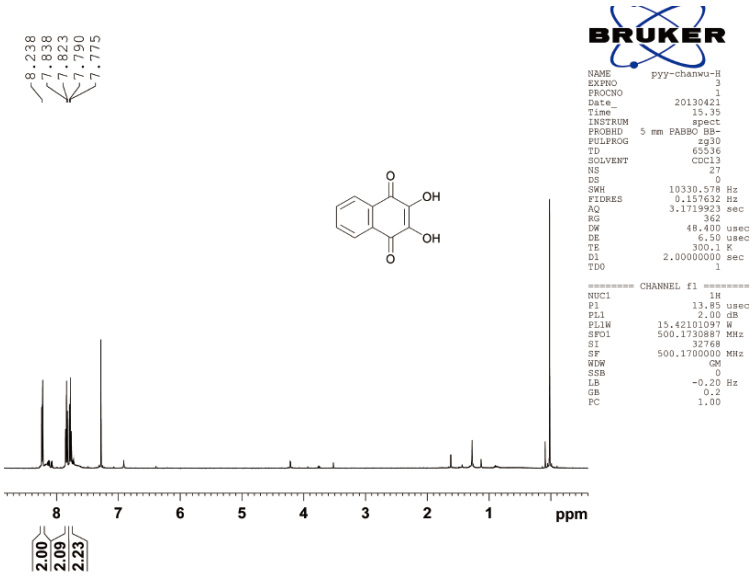


8-Hydroxyquinoline



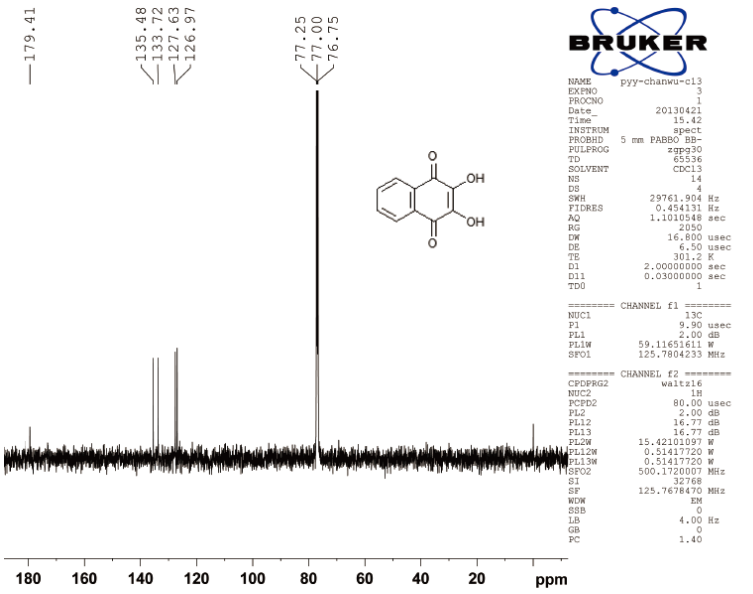


2,3-Dihydroxy-1,4-naphthoquinone




```
NAME          pyy-chanwu-H
EXPNO                    3
PROCNO                   1
Date_             20130421
Time                 15.35
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      27
DS                       0
SWH           10330.578 Hz
FIDRES            0.157632 Hz
AQ            3.1719923 sec
RG                     362
DW                48.400 usec
DE                 6.50 usec
TE                300.1 K
D1            2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.85 usec
PL1                 2.00 dB
PL1W        15.42101097 W
SFO1        500.1730887 MHz
SI                   32768
SF          500.1700000 MHz
WDW                    QM
SSB                     0
LB                 -0.20 Hz
GB                    0.2
PC                   1.00
```




```
NAME       pyy-chanwu-c13
EXPNO                   3
PROCNO                  1
Date_            20130421
Time                15.42
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    14
DS                     4
SWH           29761.904 Hz
FIDRES            0.454131 Hz
AQ            1.1010548 sec
RG                  2050
DW                16.800 usec
DE                 6.50 usec
TE                301.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.90 usec
PL1                2.00 dB
PL1W        59.11651611 W
SFO1        125.7804233 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                2.00 dB
PL12              16.77 dB
PL13              16.77 dB
PL2W        15.42101097 W
PL12W        0.51417720 W
PL13W        0.51417720 W
SFO2        500.1720007 MHz
SI                   32768
SF          125.7678470 MHz
WDW                    EM
SSB                     0
LB                 4.00 Hz
GB                      0
PC                   1.40
```