

**SUPPORTING INFORMATION**

**Title:** Nano-CuO-Catalyzed Ullmann Coupling of Phenols with Aryl Halides under Ligand-Free Conditions

**Author(s):** Jintang Zhang, Zuhui Zhang, Ye Wang, Xiaoqi Zheng,\* Zhiyong Wang\*

**Ref. No.:** O200800637

General information and experiment procedure

Detail table of optimization

Characterization data of products

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of products and nano copper oxide characterization

### **General information and experiment procedure**

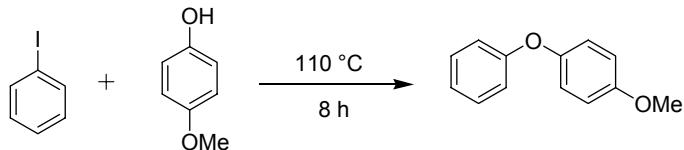
**General.** All reactions were performed under a pure and dry nitrogen atmosphere in oven-dried glassware. DMSO was distilled from CaH<sub>2</sub> under nitrogen and stored on activated 4 Å molecular sieves. Cs<sub>2</sub>CO<sub>3</sub> was ground to fine powder before use. Cs<sub>2</sub>CO<sub>3</sub> and all aryl halides and phenols were purchased from Sinopharm Chemical Reagent Co., Ltd, except for 2-ethylphenol, 2-tert-butylphenol, 4-bromobenzonitrile which were from Alfa Aesar. The solids substrates were purified by recrystallization while liquid substrates were purified by distillation under vacuum.

**Preparation of CuO nanoparticles:** Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O (3.624 g, 15 mmol) was dissolved in 50 mL of distilled water in the air with stirring, and then the pH value of the solution was rapidly adjusted to 10 with Na<sub>2</sub>CO<sub>3</sub> solution (1 M). The resultant solution was then aged together with mother liquor at room temperature for 12 h. The final product was collected by filtration, washed with deionized water, dried at 60 °C for 24 h, and then calcined at 350 °C for 24 h.

**General procedure for the coupling of phenols with aryl halides:** To an oven-dried and cooled under nitrogen tube, a magnetic stirring bar, nano-CuO (4.0 mg, 0.05 mmol), Cs<sub>2</sub>CO<sub>3</sub> (326 mg, 1 mmol) and phenol (0.5 mmol) were added. And the tube was sealed with a septum, following three cycles of evacuation and back-filling with dry and pure nitrogen. Then, 0.5 mL of DMSO and aryl halide (0.75 mmol) were injected with syringe. The tube was sealed and heated to 110 °C under nitrogen, and stirred at that temperature, until the phenol was consumed as determined by TLC. The reaction mixture was allowed to cool to room temperature, diluted with water and extracted with ethyl acetate for three times. The combined organic extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure, the crude mixture was then purified by column chromatography over silica gel to afford product with high purity. The product was characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS.

## Detail table of optimization

Table 1. Coupling of 4-methoxyphenol and iodobenzene under different conditions



Entry	Copper sources	Base	Solvent	Method <sup>[a]</sup>	Yield (%) <sup>[b]</sup>
1	Cu(OAc) <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	A	22
2	CuSO <sub>4</sub>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	A	28
3	none	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	B	n.d. <sup>[c]</sup>
4	CuO powder	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	A	24, (46) <sup>[d]</sup>
5	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	A	44, (n.d.) <sup>[e]</sup>
6	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMF	A	21
7	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	Dioxane	A	12
8	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	A	< 5
9	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	NMP	A	trace
10	nano CuO	KOH	DMSO	A	43
11	nano CuO	K <sub>2</sub> CO <sub>3</sub>	DMSO	A	41
12	nano CuO	K <sub>3</sub> PO <sub>4</sub>	DMSO	A	25
13	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	C	62, (83) <sup>[f]</sup>
14	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	D	43
15	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	E	42
16	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	F	53
17	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	G	60
18	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	C	46 <sup>[g]</sup>
19	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	C	40 <sup>[h]</sup>
20	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	C	12 <sup>[i]</sup>
21	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	C	41 <sup>[j]</sup>
22	nano CuO	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	C	61 <sup>[k]</sup>

[a]. Method A: the ratio of Phenol (1 mmol in 1 M solution) / Iodobenzene / Base/ Nano-CuO = 1.0 / 1.1 / 1.5 / 0.1. Method B: the ratio of Phenol (1 mmol in 1 M solution) / Iodobenzene / Base/ Nano-CuO = 1.0 / 1.1 / 1.5 / 0. Method C: the ratio of Phenol (1 mmol in 1M solution) / Iodobenzene / Base/ Nano-CuO = 1.0 / 1.5 / 2.0 / 0.1. Method D: the ratio of Phenol (1 mmol in 1 M solution) / Iodobenzene / Base/ Nano-CuO = 1.5 / 1.0 / 2.0 / 0.1. Method E: the ratio of Phenol (1 mmol in 1 M solution) / Iodobenzene / Base/ Nano-CuO = 1.0 / 1.1 / 1.5 / 0.025. Method F: the ratio of Phenol (1 mmol in 1 M solution) / Iodobenzene / Base/ Nano-CuO = 1.0 / 1.1 / 1.5 / 0.05. Method G: the ratio of Phenol (1 mmol in 1 M solution) / Iodobenzene / Base/ Nano-CuO = 1.0 / 1.1 / 1.5 / 0.2. [b]. Isolated yield. [d]. The reaction was carried out with Method C for 24 h. [c]. n.d. = not detected. [e]. In the air. [f]. Prolonging the reaction time to 18 h. [g]. concentration = 2 M. [h]. concentration = 0.25 M. [i]. 90 °C for 23 h. [j]. 100 °C. [k]. 120 °C.

## Characterization data of products

### Oxydibenzene

IR (film  $\text{cm}^{-1}$ ): 3040, 2925, 1586, 1487, 1238, 1162, 866, 749, 691.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.36-7.30 (m, 4 H), 7.12-7.07 (m, 2 H), 7.03-7.00 (m, 4 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 157.4, 129.9, 123.4, 119.0.

HRMS: calcd for  $\text{C}_{12}\text{H}_{10}\text{O}$ : 170.0732, found 170.0730.

### 1-methyl-2-phenoxybenzene

IR (film  $\text{cm}^{-1}$ ): 3037, 2925, 1584, 1487, 1239, 1209, 1112, 873, 749, 690.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.32-7.24 (m, 3 H), 7.19-7.14 (m, 1 H), 7.08-7.01 (m, 2 H), 6.92-6.89 (d, 2 H), 2.24 (s, 3 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 158.1, 154.6, 131.6, 130.2, 129.8, 127.3, 124.1, 122.5, 119.9, 117.5, 16.3.

HRMS: calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$ : 184.0888, found 184.0885.

### 1-ethyl-2-phenoxybenzene

IR (film  $\text{cm}^{-1}$ ): 3036, 2967, 2931, 2874, 1582, 1486, 1452, 1236, 874, 749, 691.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.32-7.27 (m, 3 H), 7.19-7.01 (m, 3 H), 6.93-6.88 (m, 3 H), 2.65 (q,  $J = 7.5$  Hz, 2 H), 1.20 (t,  $J = 7.5$  Hz, 3 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 158.3, 154.4, 136.0, 130.0, 129.8, 127.2, 124.2, 122.5, 119.9, 117.7, 23.4, 14.6.

HRMS: calcd for  $\text{C}_{14}\text{H}_{14}\text{O}$ : 198.1045, found 198.1046.

### 1-methyl-3-phenoxybenzene

IR (film  $\text{cm}^{-1}$ ): 3039, 2922, 2863, 1586, 1487, 1462, 1256, 1216, 1162, 1143, 936, 759, 691.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.35-7.30 (m, 2 H), 7.23-7.18 (m, 1 H), 7.11-7.06 (m, 1 H), 7.01-6.99 (m, 2 H), 6.92-6.90 (m, 1 H), 6.83-6.80 (m, 2 H), 2.32 (s, 3 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 157.5, 157.4, 140.1, 129.8, 129.6, 124.2, 123.2, 119.7, 119.0, 116.1, 21.5.

HRMS: calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$ : 184.0888, found 184.0889.

### 1-methyl-4-phenoxybenzene

IR (film  $\text{cm}^{-1}$ ): 3061, 3033, 2923, 2864, 1591, 1506, 1488, 1240, 1164, 870, 834, 758, 692.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.32-7.27 (m, 2 H), 7.14-7.11 (m, 2 H), 7.08-7.03 (m, 1 H), 6.97 (d,  $J = 8.1$  Hz, 2 H), 6.91 (d,  $J = 8.1$  Hz, 2 H), 2.33 (s, 3 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 158.0, 154.9, 133.0, 130.4, 129.8, 122.9, 119.3, 118.5, 20.8.

HRMS: calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$ : 184.0888, found 184.0883.

### 1-methoxy-4-phenoxybenzene

IR (film  $\text{cm}^{-1}$ ): 3042, 3002, 2953, 2836, 1591, 1505, 1489, 1226, 1036, 841, 758, 691.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.32-7.26 (m, 2 H), 7.06-6.86 (m, 7 H), 3.80 (s, 3 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 158.7, 156.1, 150.3, 129.7, 122.6, 120.9, 117.8, 115.0, 55.8.

HRMS: calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_2$ : 200.0837, found 200.0835.

### 1-nitro-2-phenoxybenzene

IR (film  $\text{cm}^{-1}$ ): 3072, 1589, 1528, 1482, 1353, 1246, 1196, 1162, 882, 747, 692.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.95-7.92 (m, 1 H), 7.52-7.46 (m, 1 H), 7.40-7.35 (m, 2 H), 7.21-7.16 (m, 2 H), 7.06-6.99 (m, 3 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 155.9, 150.8, 141.5, 134.2, 130.2, 125.8, 124.7, 123.2, 120.6, 119.3.

HRMS: calcd for  $\text{C}_{12}\text{H}_9\text{NO}_3$ : 215.0582, found 215.0582.

### 1-nitro-4-phenoxybenzene

IR (film  $\text{cm}^{-1}$ ): 2924, 1581, 1507, 1486, 1341, 1247, 1194, 1162, 1100, 874, 844, 749.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 8.21-8.18 (m, 2 H), 7.46-7.41 (m, 2 H), 7.28-7.26 (m, 1 H), 7.10-7.08 (m, 2 H), 7.03-7.00 (m, 2 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 163.5, 154.9, 142.8, 138.8, 130.4, 126.0, 125.5, 120.6, 117.2.

HRMS: calcd for  $\text{C}_{12}\text{H}_9\text{NO}_3$ : 215.0582, found 215.0584.

### 1-phenoxy naphthalene

IR (film  $\text{cm}^{-1}$ ): 3057, 1593, 1576, 1488, 1461, 1393, 1261, 1236, 1212, 1079, 1044, 1016, 773, 691.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 8.22-8.19 (m, 1 H), 7.88-7.85 (m, 1 H), 7.63-7.60 (m, 1 H), 7.52-7.45 (m, 3 H), 7.40-7.31 (m, 3 H), 7.13-7.03 (m, 3 H), 6.96-6.94 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 158.0, 153.2, 135.1, 129.9, 127.9, 127.1, 126.7, 126.1, 125.9, 123.5, 123.3, 122.3, 118.7, 113.6

HRMS: calcd for  $\text{C}_{16}\text{H}_{12}\text{O}$ : 220.0888, found 220.0887.

### 4-phenoxybenzonitrile

IR (film  $\text{cm}^{-1}$ ): 3067, 2227, 1608, 1587, 1503, 1487, 1248, 1198, 1167, 871, 841, 769, 691.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.60-7.57 (m, 2 H), 7.43-7.38 (m, 2 H), 7.25-7.20 (m, 1 H), 7.06 (d,  $J = 8.4$  Hz, 2 H), 7.00 (d,  $J = 8.4$  Hz, 2 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 161.7, 154.9, 134.2, 130.3, 125.2, 120.4, 118.9, 118.0, 105.9.

HRMS: calcd for C<sub>13</sub>H<sub>9</sub>NO: 195.0684, found 195.0685.

#### **1-chloro-4-phenoxybenzene**

IR (film cm<sup>-1</sup>): 3068, 2926, 1584, 1483, 1240, 1090, 755, 691.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.37-7.25 (m, 4 H), 7.14-7.09 (m, 1 H), 7.01-6.92 (m, 4 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 157.1, 156.1, 130.1, 129.9, 128.4, 123.8, 120.2, 119.1.

HRMS: calcd for C<sub>12</sub>H<sub>9</sub>ClO: 204.0342, found 204.0341.

#### **1-tert-butyl-4-phenoxybenzene**

IR (film cm<sup>-1</sup>): 2962, 2869, 1591, 1509, 1489, 1240, 873, 839, 753, 692.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.35-7.29 (m, 4 H), 7.09-7.04 (m, 1 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 2 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 157.8, 154.9, 146.3, 129.8, 126.7, 123.1, 118.8, 118.6, 34.5, 31.7.

HRMS: calcd for C<sub>16</sub>H<sub>18</sub>O: 226.3138, found 226.3135.

#### **1-tert-butyl-2-phenoxybenzene**

IR (film cm<sup>-1</sup>): 2959, 2870, 1594, 1486, 1441, 1229, 751, 692.

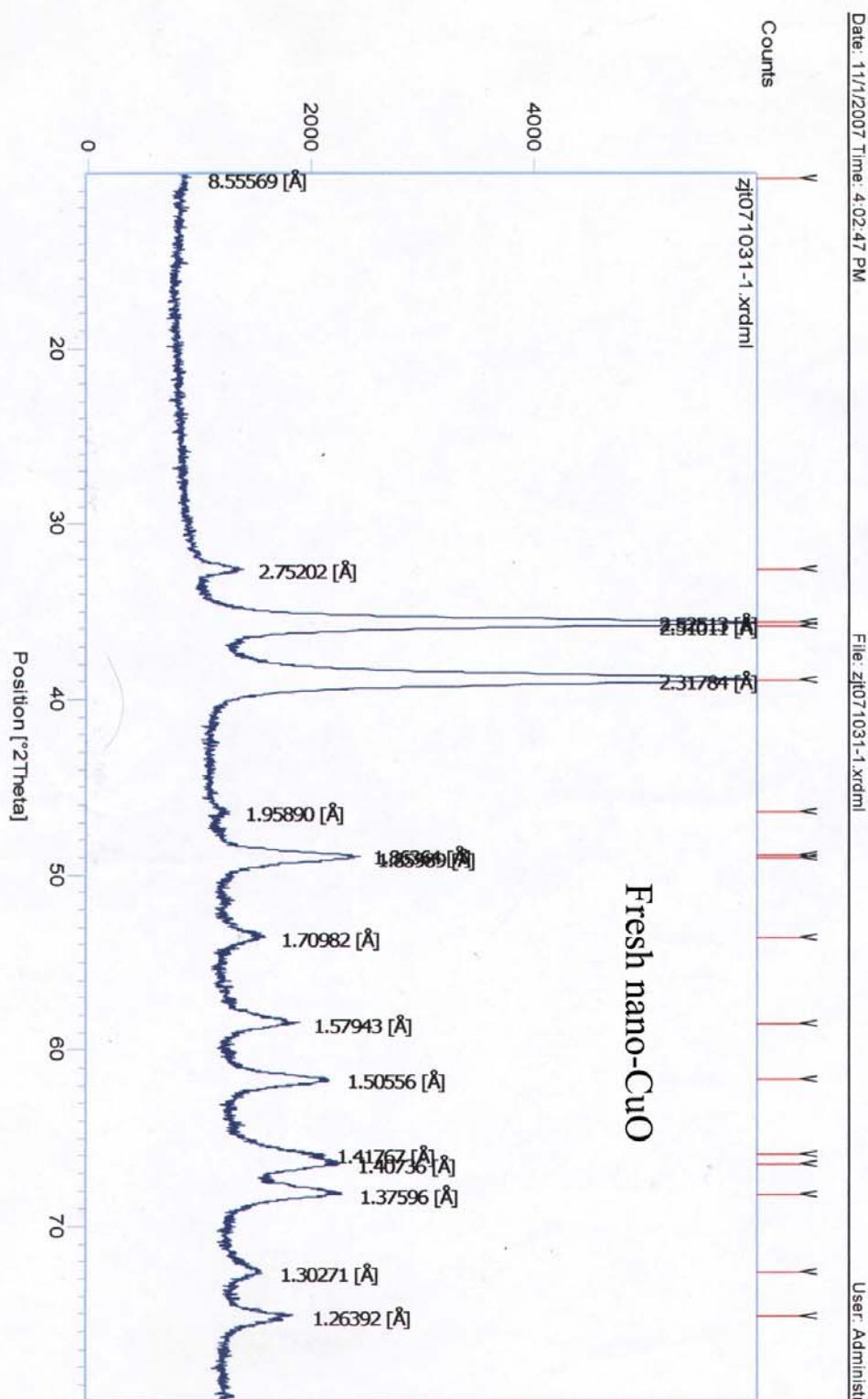
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.41-7.39 (m, 1 H), 7.34-7.29 (m, 2 H), 7.15-7.02 (m, 3 H), 6.99-6.96 (m, 2 H), 6.83-6.81 (m, 1 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 157.9, 156.0, 141.1, 129.8, 127.3, 127.2, 123.3, 122.8, 120.3, 118.8, 34.9, 30.3.

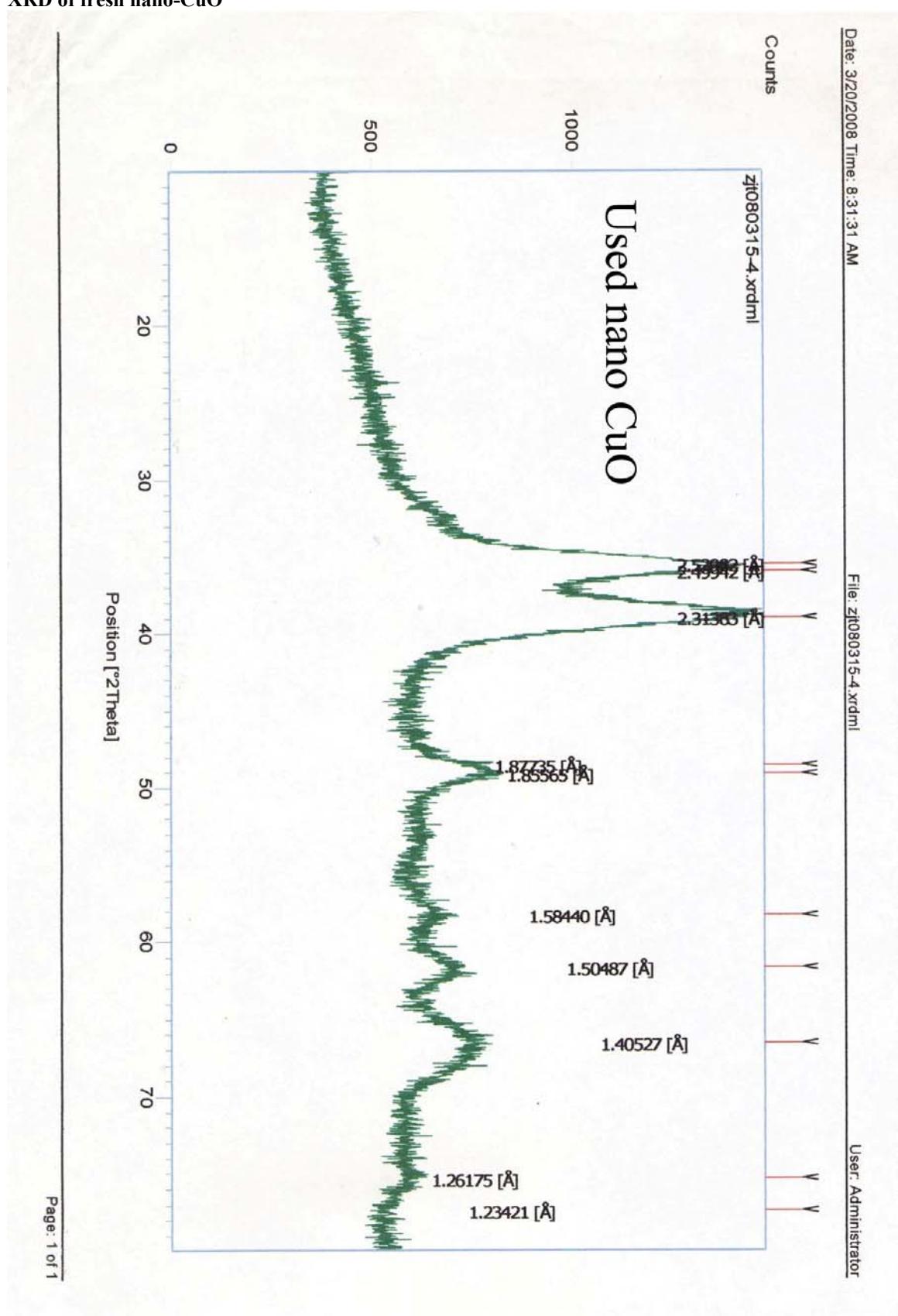
HRMS: calcd for C<sub>16</sub>H<sub>18</sub>O: 226.3138, found 226.3140.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of products and nano copper oxide characterization

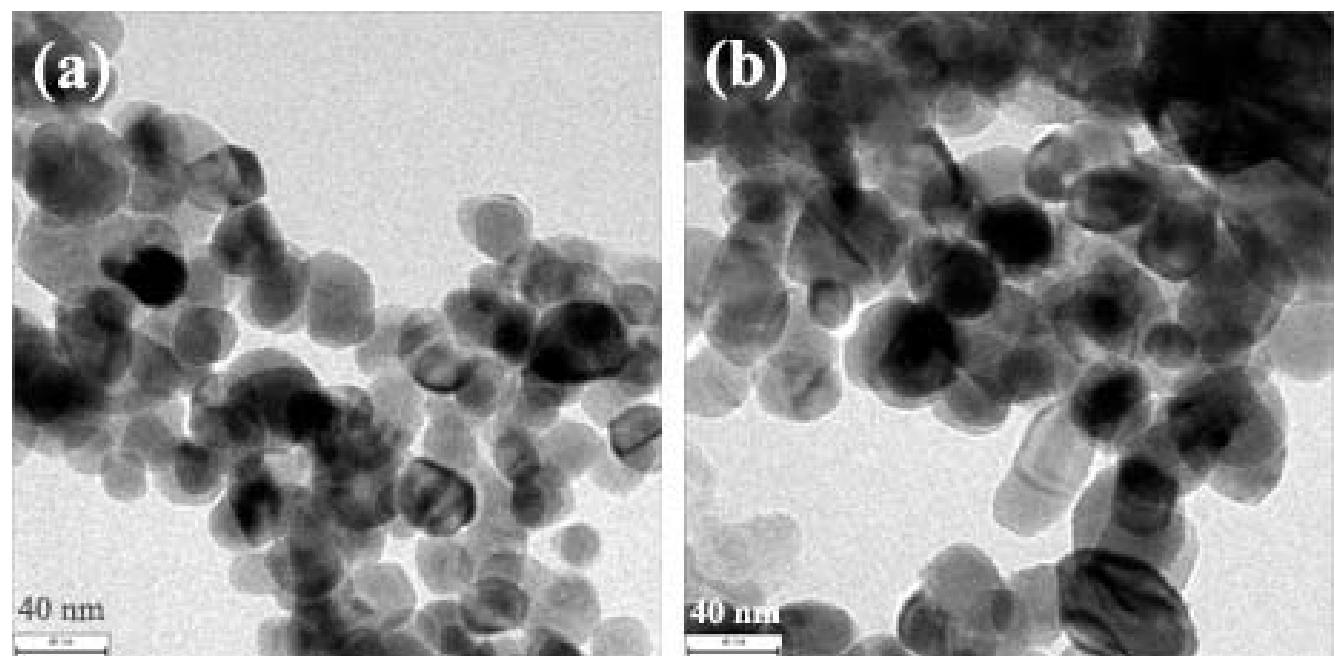
XRD of fresh nano-CuO



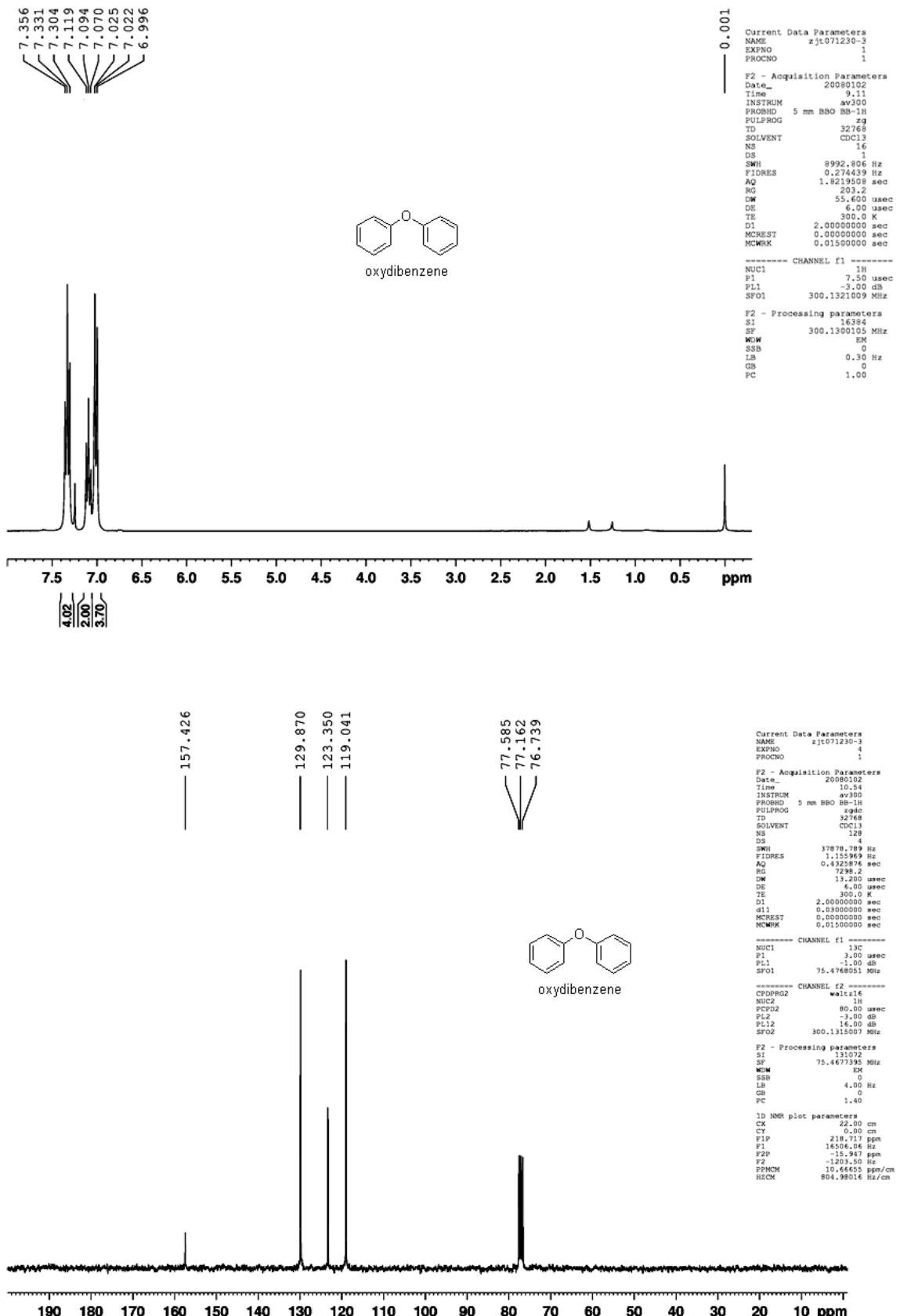
### XRD of fresh nano-CuO



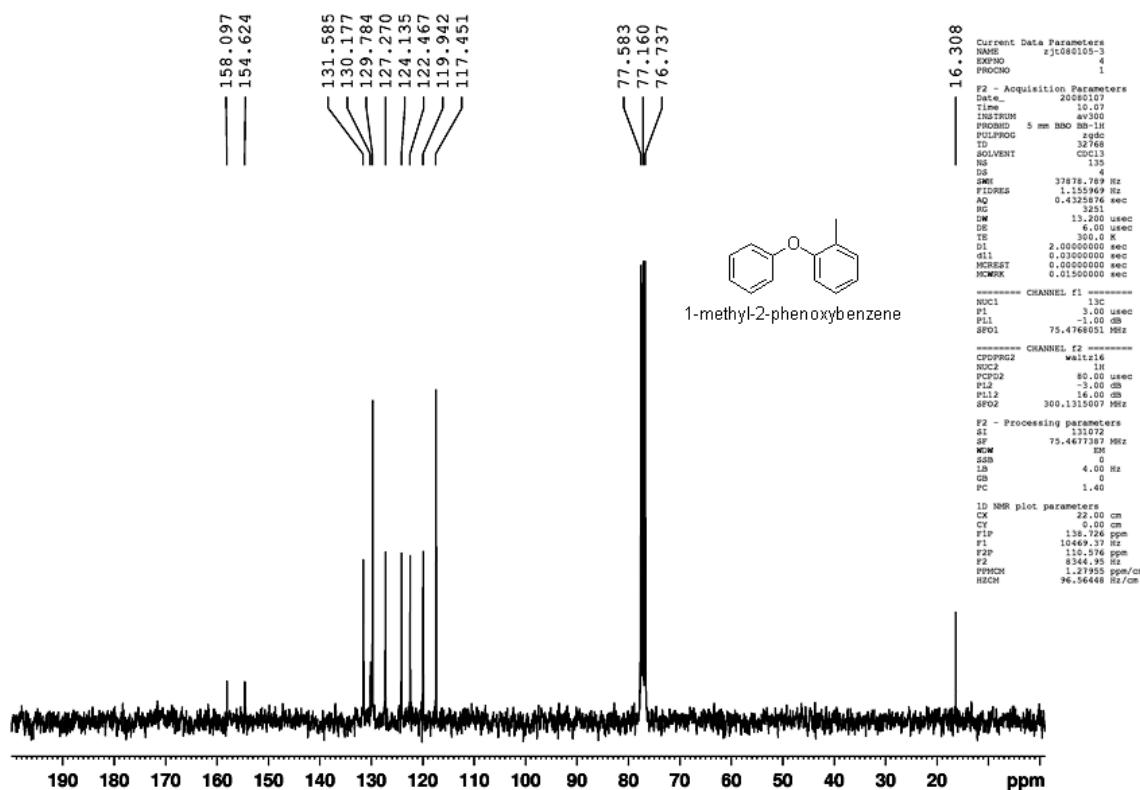
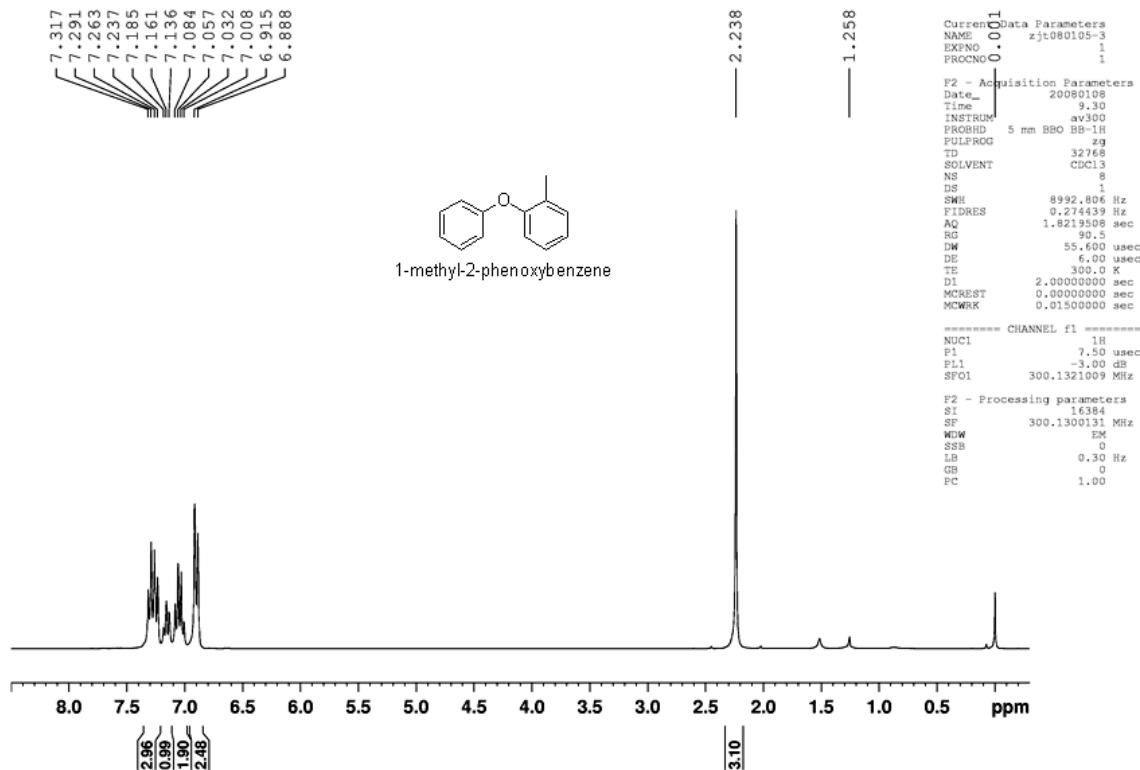
HRTEM images of. (a) fresh nano CuO particles and (b) nano-CuO particles after the fifth cycle.



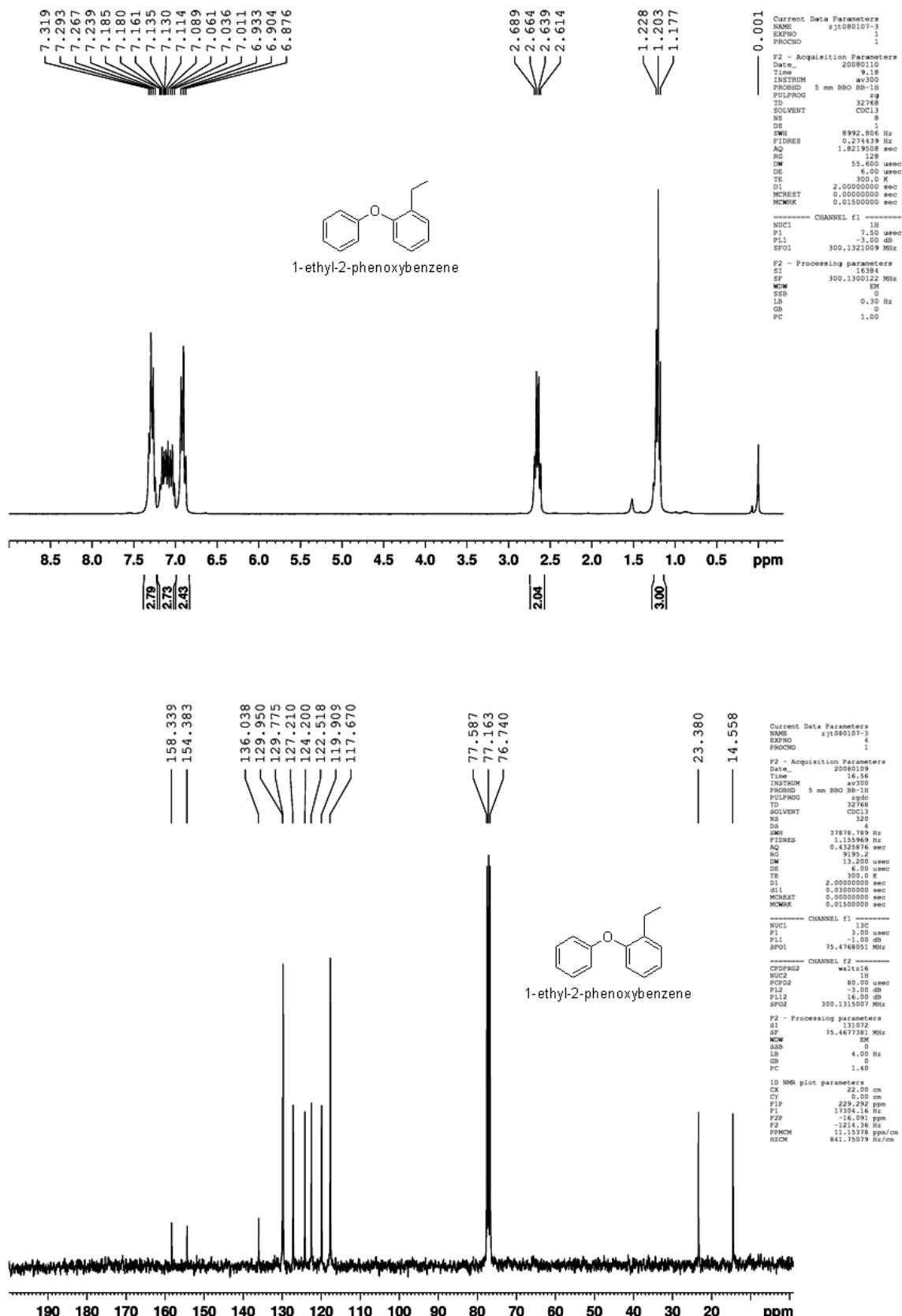
## Oxydibenzene



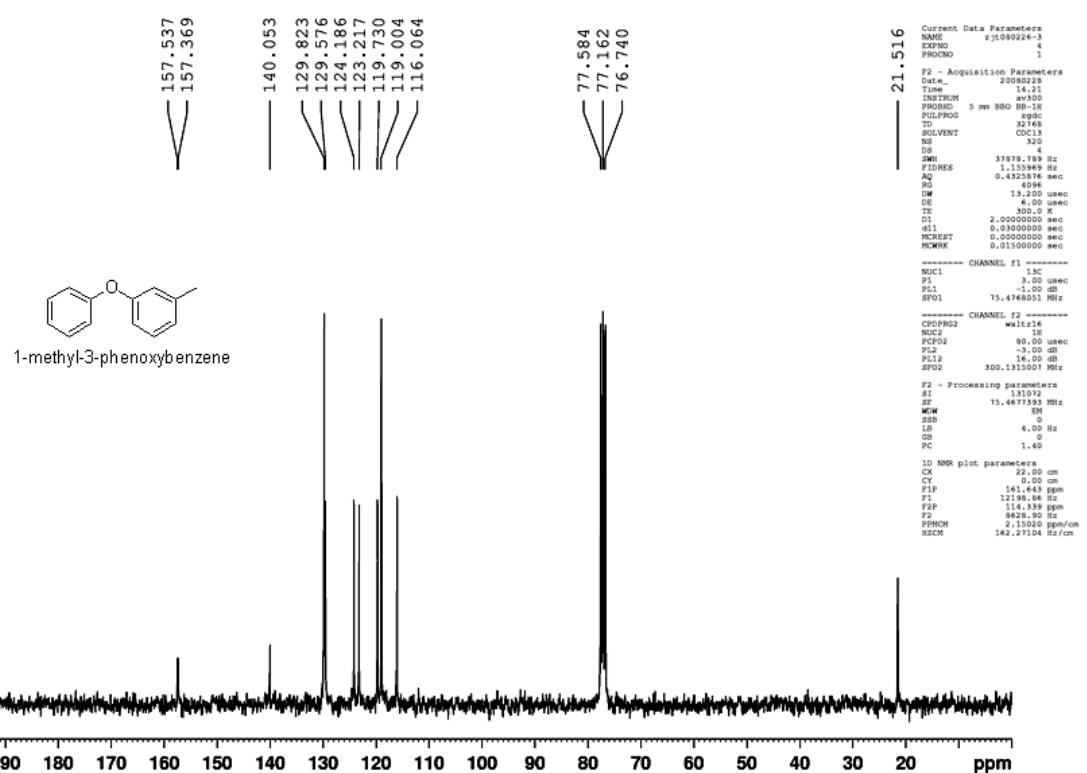
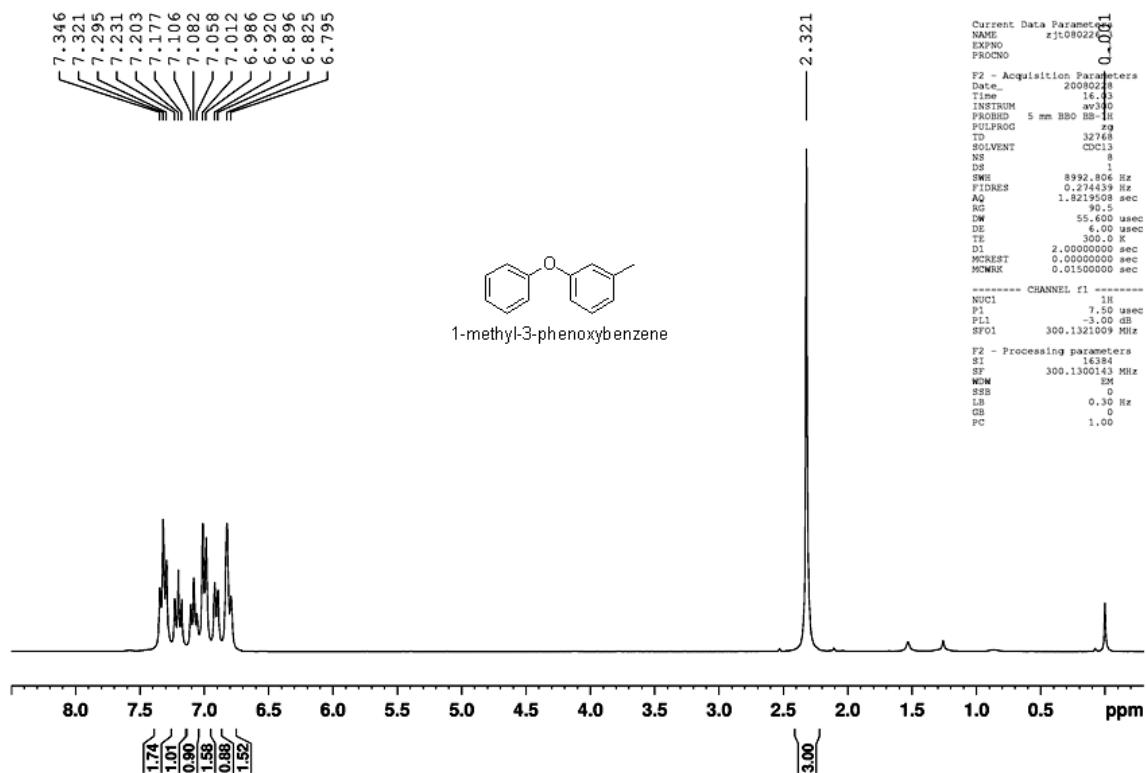
### 1-methyl-2-phenoxybenzene



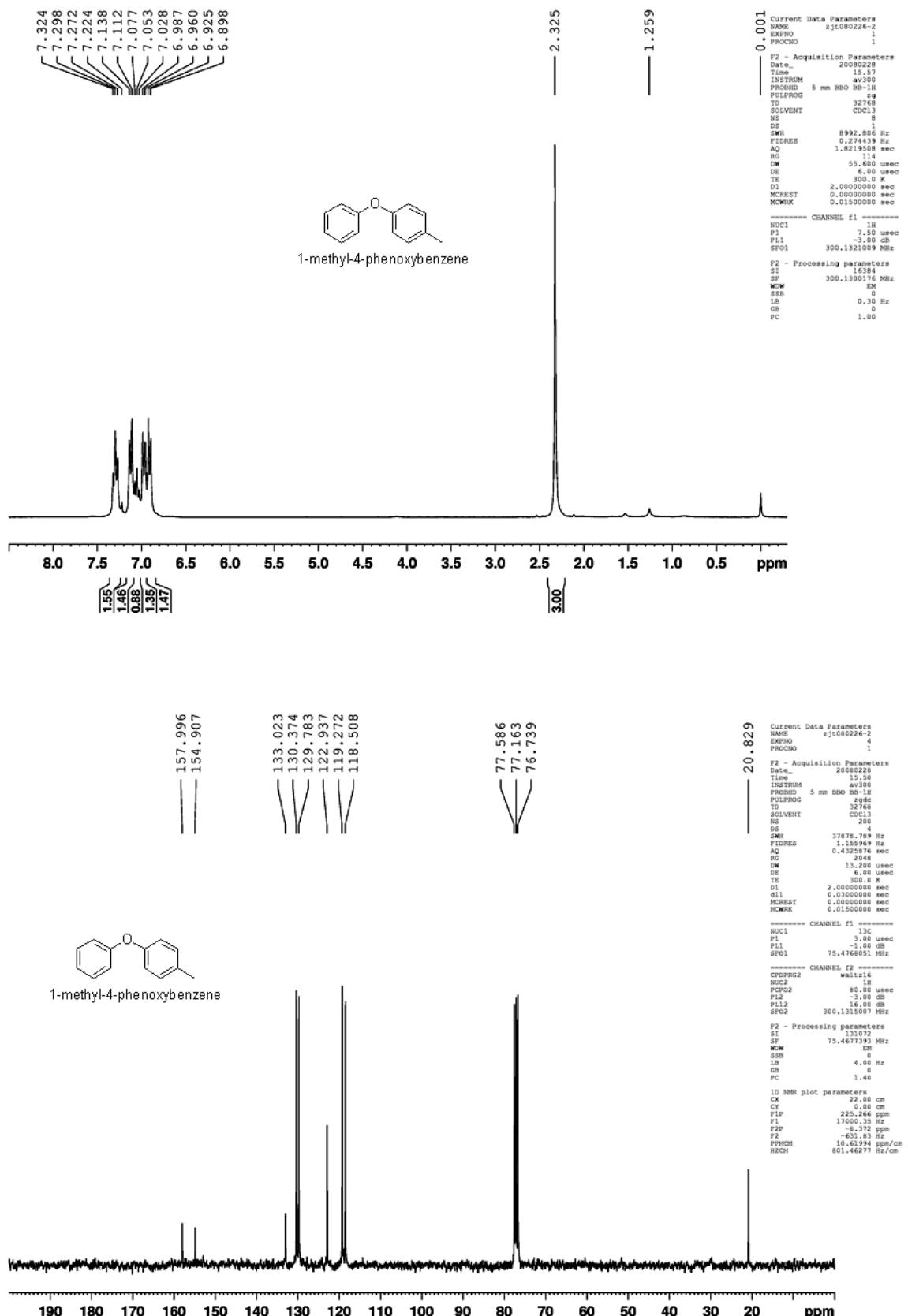
1-ethyl-2-phenoxybenzene



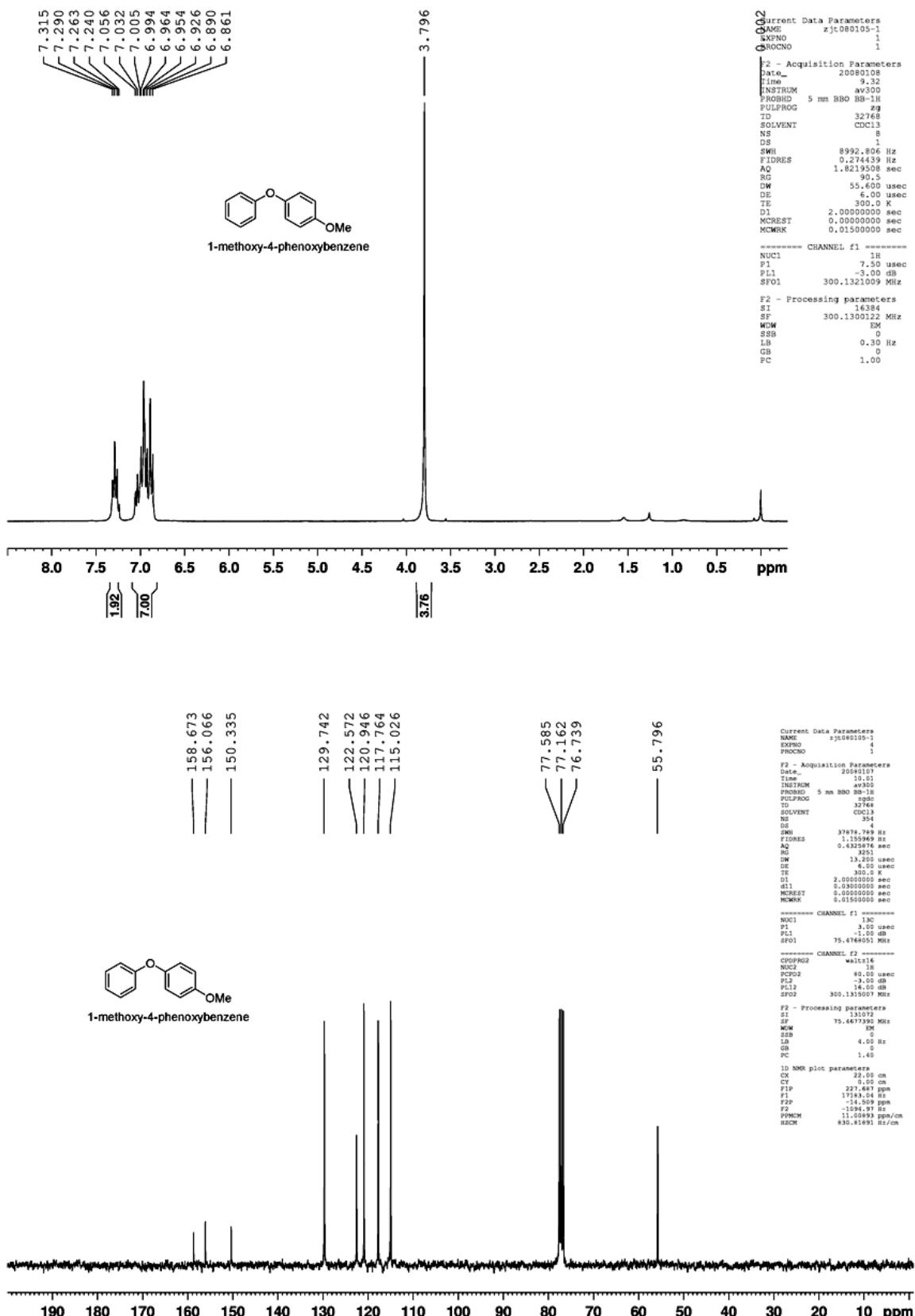
### 1-methyl-3-phenoxybenzene



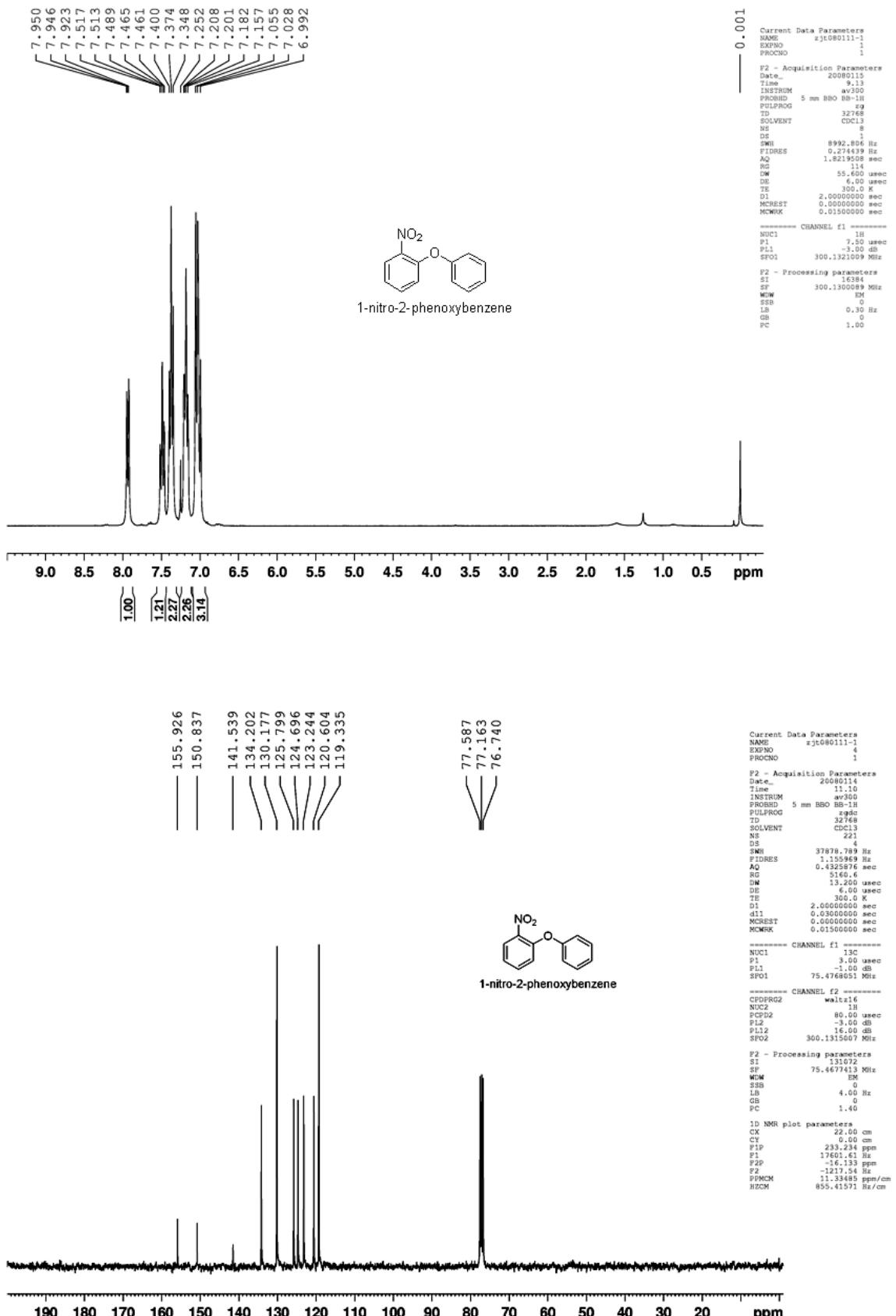
1-methyl-4-phenoxybenzene



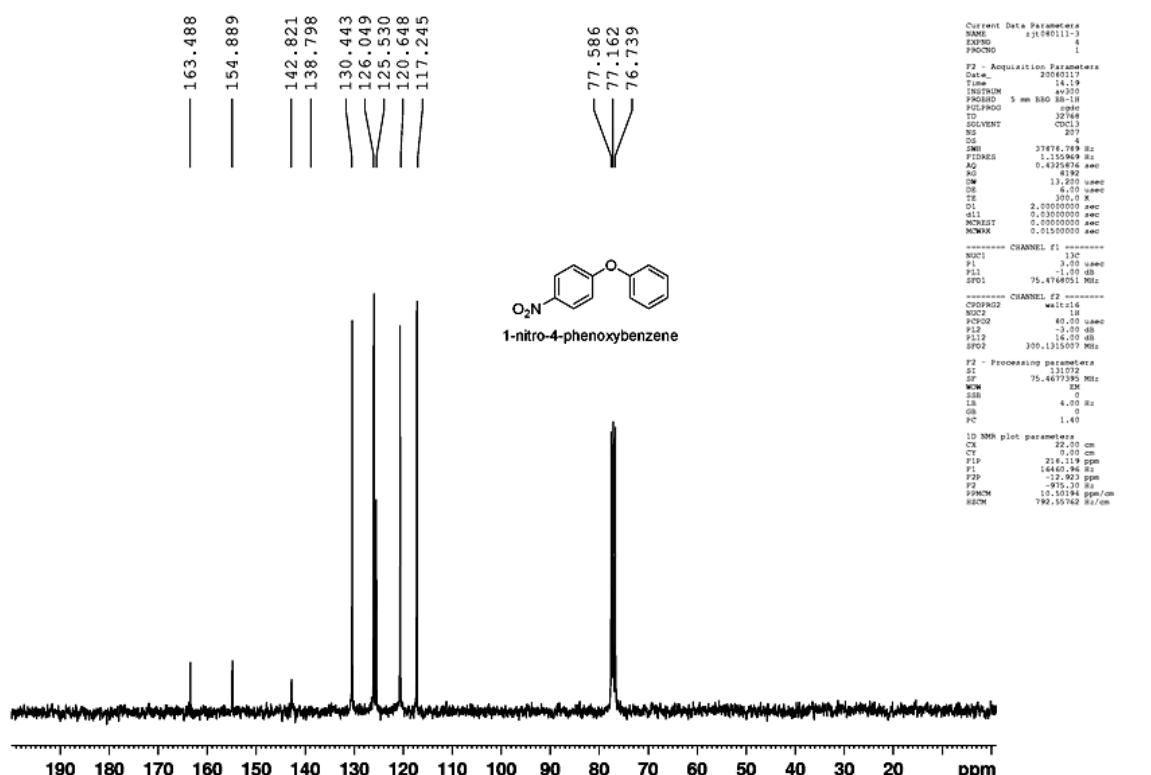
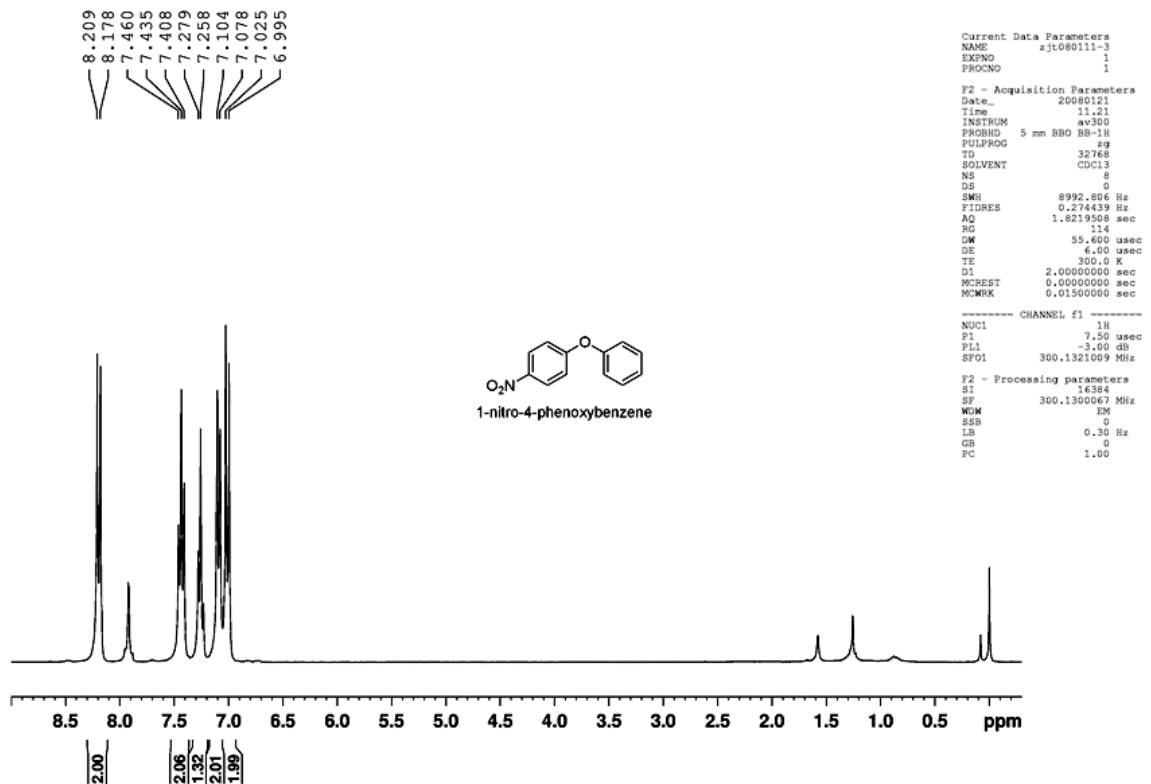
### 1-methoxy-4-phenoxybenzene



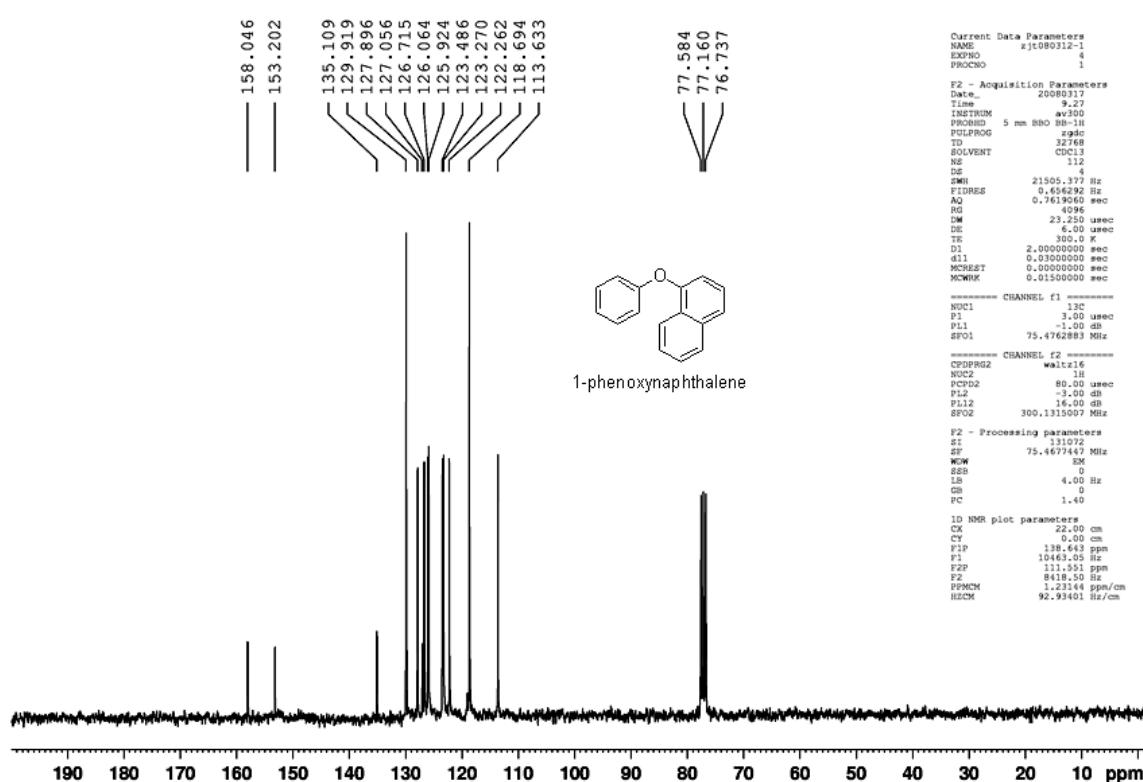
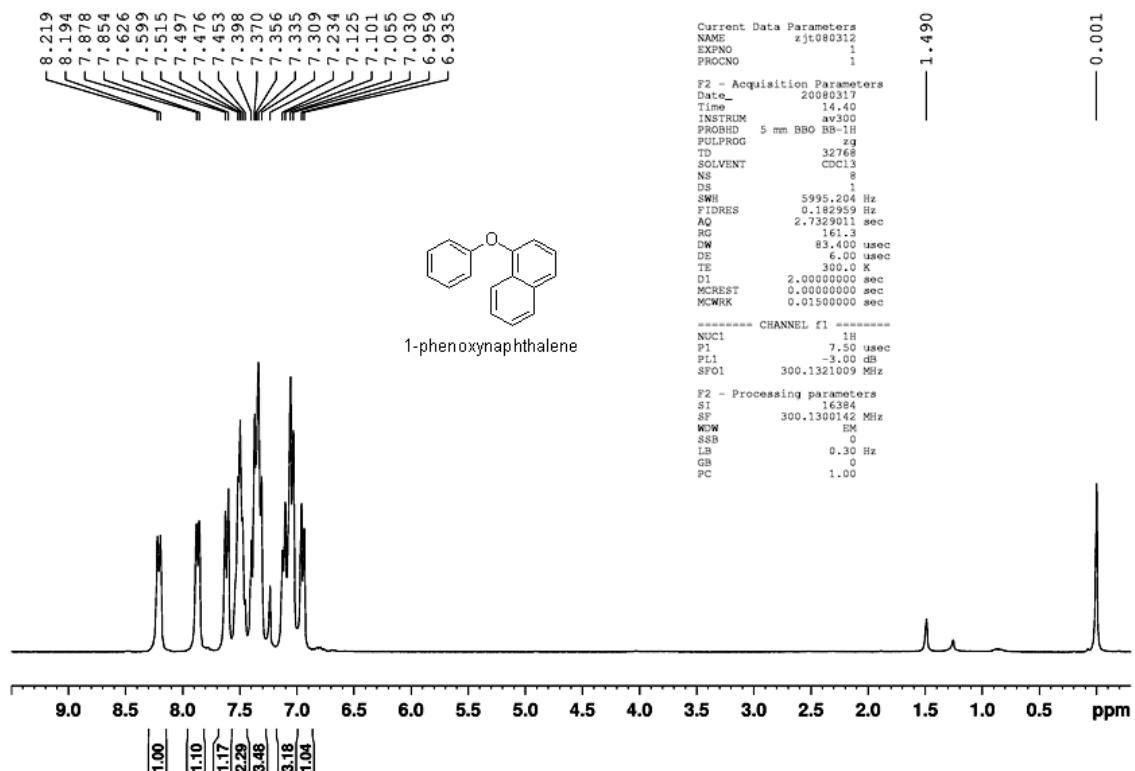
### 1-nitro-2-phenoxybenzene



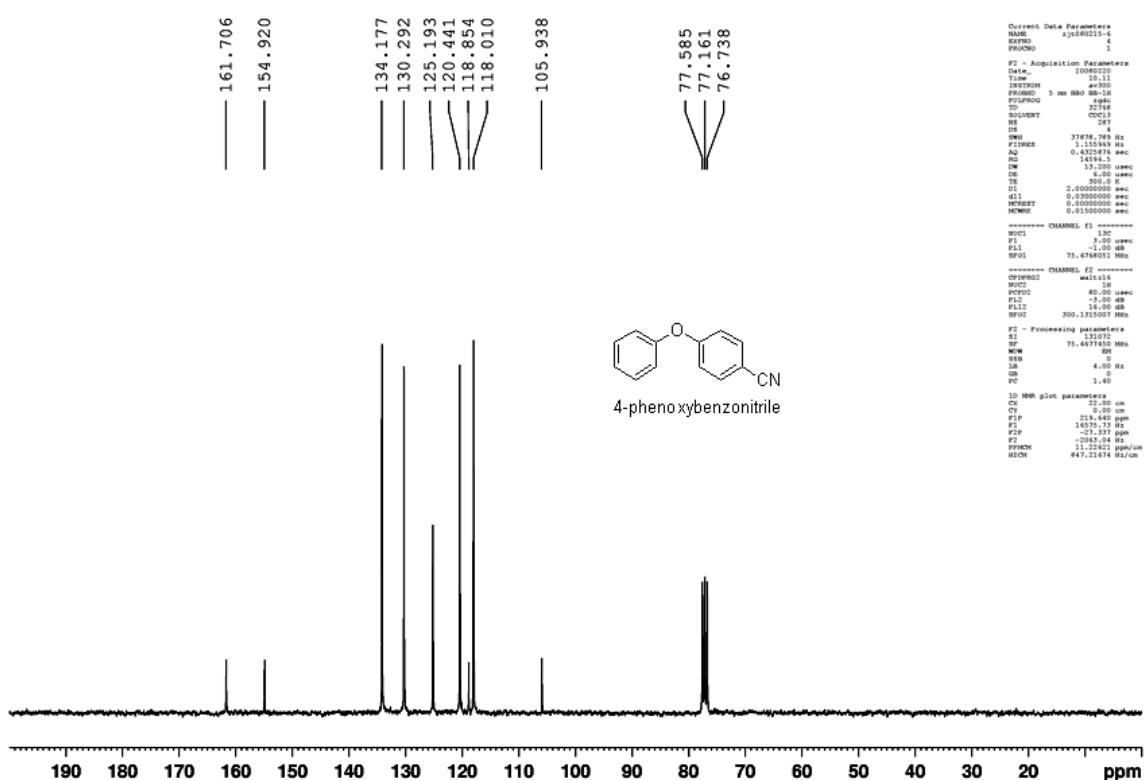
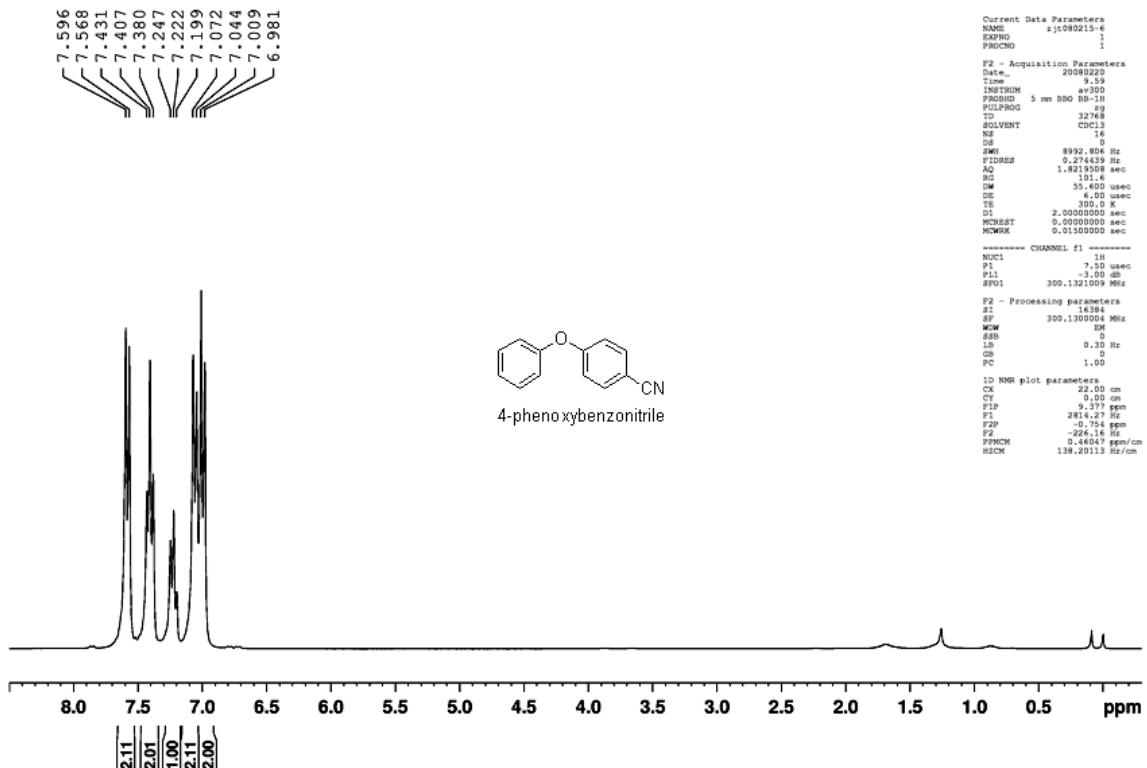
1-nitro-4-phenoxybenzene



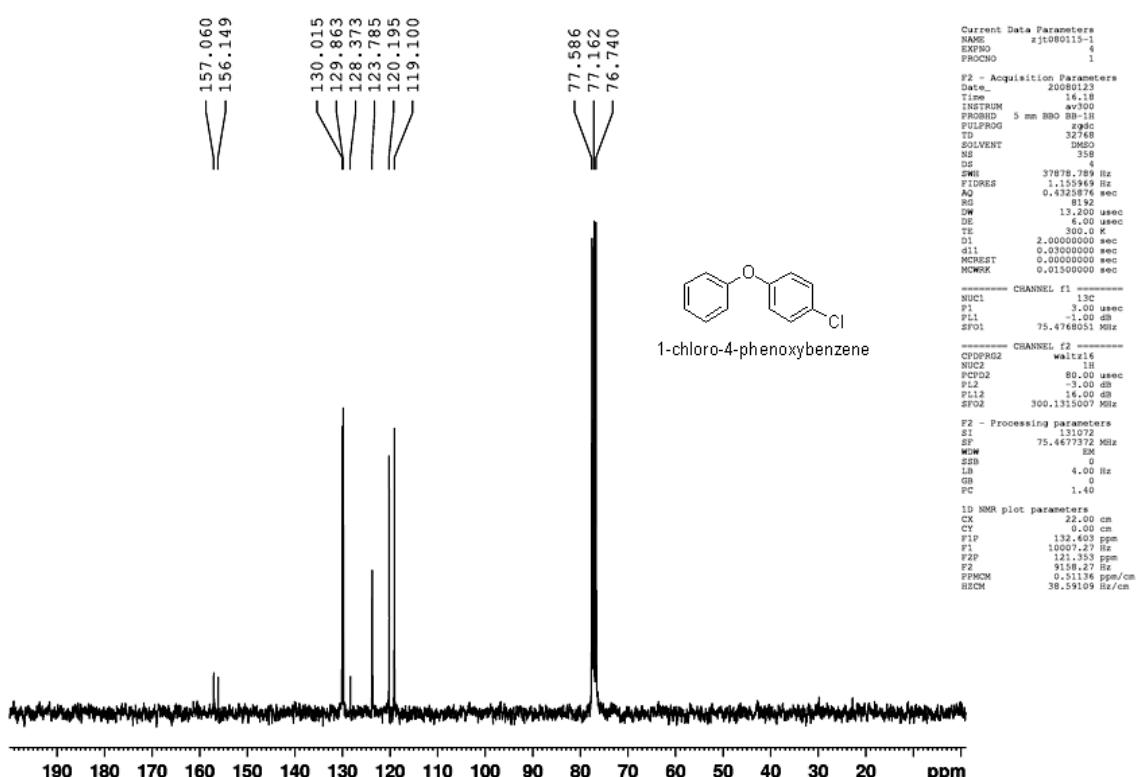
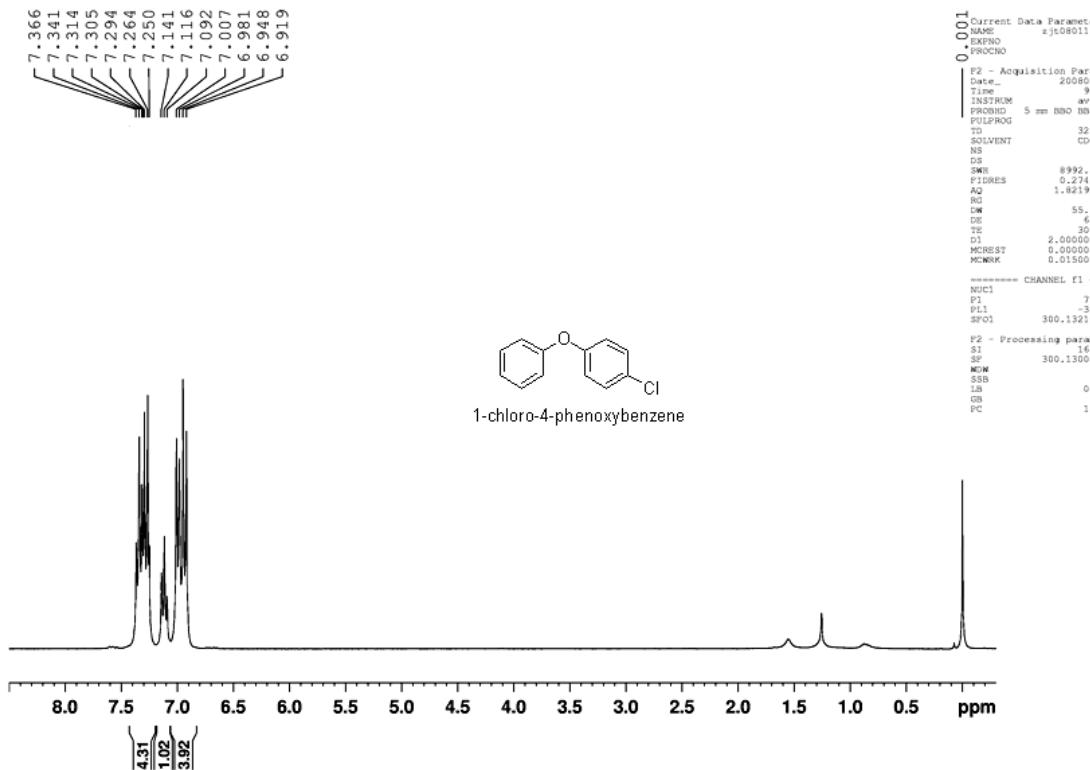
## 1-phenoxynaphthalene



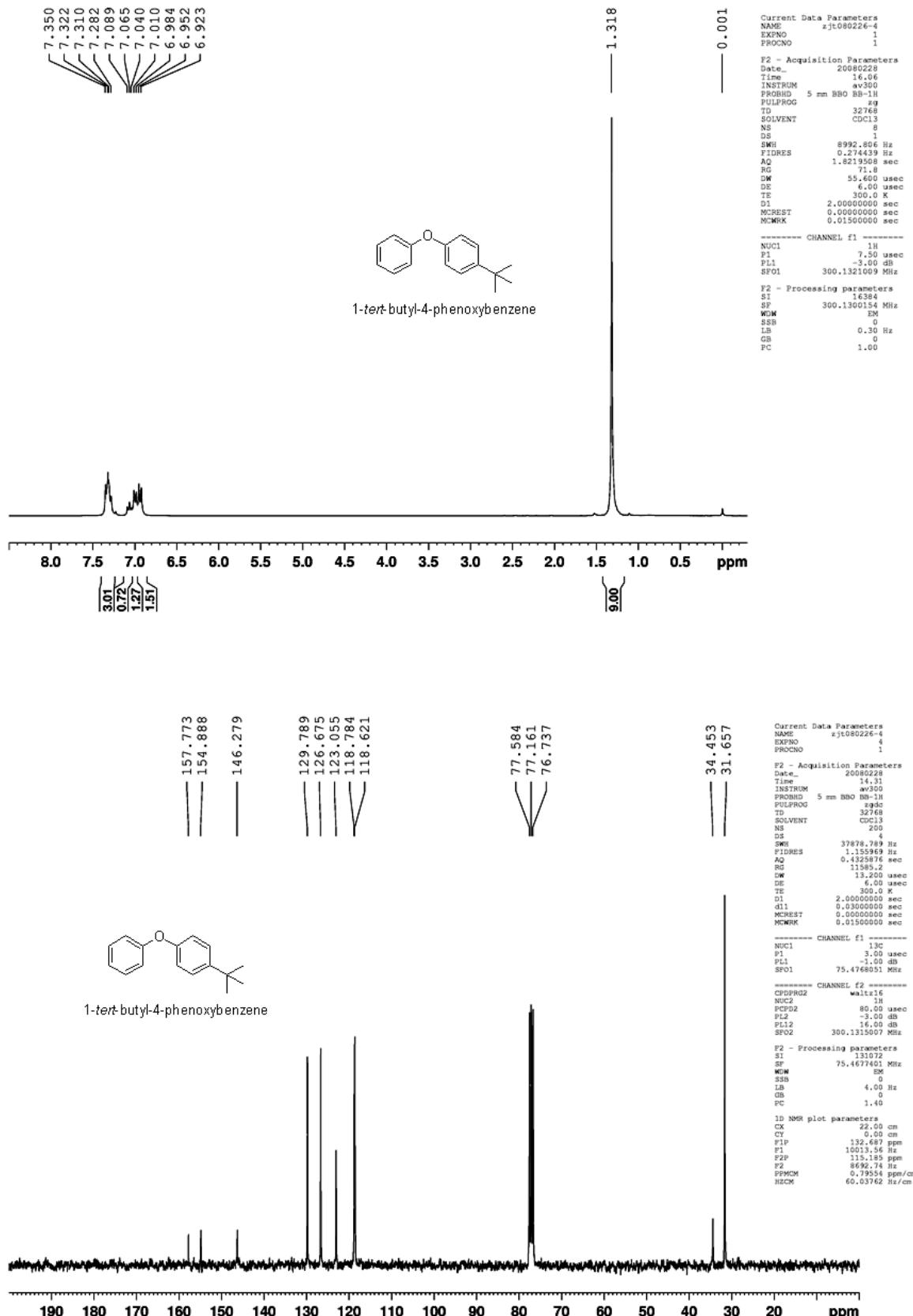
## 4-phenoxybenzonitrile



### 1-chloro-4-phenoxybenzene



1-tert-butyl-4-phenoxybenzene



### 1-tert-butyl-2-phenoxybenzene

