

Supporting Information for:

Preparation of Carbon Nanotube-Supported α - Fe_2O_3 @CuO Nanocomposite: A Highly Efficient and Magnetically Separable Catalyst 5 in Cross-Coupling of Aryl Halides with Phenols

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Experimental

All reagents were purchased from commercial suppliers and used without further purification. Multi wall carbon nanotubes used in this work incorporate 3.06 wt% of OH with an external diameter 10-20 nm, internal diameter 5-10 nm and approximate length of 30 micrometres. All experiments were carried out under argon. Catalysts were characterized using spectroscopic techniques (FTIR, XRD, BET, BJH, ICP, VSM, SEM and TEM). FT-IR spectra were obtained over the region 400-4000 cm^{-1} with NICOLET IR100 FT-IR with spectroscopic grade KBr. Powder XRD spectrum was recorded at r.t by a Philips X'pert 1710 diffractometer using Cu $K\alpha$ ($\lambda = 1.54056 \text{ \AA}$) in Bragg-Brentano geometry (θ -2 θ). The BET specific surface area, pore volume and average pore size were determined by physical adsorption of N_2 at -196°C in an automatic volumetric system using Belsorp instrument. ICP analysis was accomplished using a VISTA-PRO, CCD simultaneous ICP analyser. Magnetic properties of catalyst were obtained by homemade VSM. SEM image was observed using SEM (Philips XL 30 and S-4160) with gold coating equipped with energy dispersive X-ray spectroscopy (EDX). TEM measurements were carried out at 120 kV (Philips, model CM120). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance (DRX 500 MHz) and Bruker Ultrashield (400 MHz) in pure deuterated CDCl_3 solvent with tetramethylsilane (TMS) as internal standards.

Preparation of carbon nanotube-supported $\alpha\text{-Fe}_2\text{O}_3$

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.00 g, 3.6 mmol) was dissolved into 10 mL distilled water and then multiwall carbon nanotubes (0.200 g) were added into solution. The complex was sonicated for 5 min, and then hydrogen peroxide (30 mL, 30%) was dripped slowly into the above complex with vigorous stirring and refluxed at 353 K for 4 h. The black complex was collected by decantation, washed with distilled water, and subsequently treated in an oven at 393 K for 12 h. This resulting nanocomposite ($\text{CNT}@\text{Fe}(\text{OH})_{3.x}\text{H}_2\text{O}$) was then exposed to argon atmosphere at 450 $^\circ\text{C}$ giving rise to a carbon nanotube-supported $\alpha\text{-Fe}_2\text{O}_3$ compound.

Synthesis of Carbon nanotube-supported α -Fe₂O₃@CuO nanoparticles

To a magnetically stirred mixture of Cu(OAc)₂.H₂O (0.4 g, 2.2 mmol) in deionized water (100 mL), carbon nanotube-supported α -Fe₂O₃ (0.4 g) was added and then the solution was heated to 100 °C. After hydrolysis and crystallization for 5 h, the black precipitate formed in the solution was magnetically decanted, washed repeatedly with distilled water and absolute ethanol, and dried in air at room temperature.

Recyclability test of Catalyst

Upon completion of the first reaction between iodobenzene and phenol to afford a quantitative yield of the corresponding aryl ether (92% yield), the catalyst was recovered by external magnet, washed with 10 H₂O and ethanol and oven dried at 80 °C overnight. A new reaction was then performed with fresh solvent and reactants under identical conditions.

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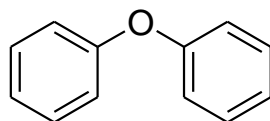
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Spectroscopic data of products:

Diphenyl ether. Following the general procedure using phenol (94 mg, 1mmol) and iodobenzene (0.05 mL, 0.5 mmol) provided 156.6 mg (92% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



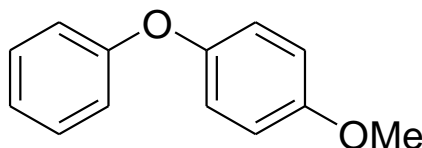
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^1H NMR (CDCl_3 , 500 MHz) δ 7.05 (d, $J=7.75$ Hz, 4H), 7.13 (t, $J=7.35$, 2H), 7.37 (t, $J=7.55$ Hz, 4H),

^{13}C NMR (CDCl_3 , 125 MHz) δ 118.9, 123.2, 129.7, 157.3

All spectral data correspond to those given in the literature

10 4-Methoxyphenyl phenyl ether. Following the general procedure using 4-Methoxyphenol (124 mg, 1mmol) and iodobenzene (0.05 mL, 0.5mmol) provided 180 mg (90% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.

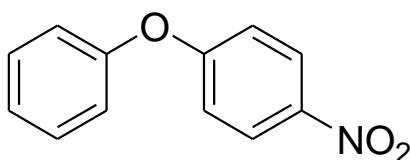


15 ^1H NMR (CDCl_3 , 400 MHz) δ 3.73 (s, 3H), 6.78-6.82 (m, 2H), 6.85-6.92 (m, 4H), 6.96 (t, $J=7.32$ Hz, 1H), 7.22 (t, $J=7.32$ Hz, 2H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 55.8, 114.9, 115.0, 117.7, 121.0, 122.4, 129.6, 129.8, 155.8;

All spectral data correspond to those given in the literature

20 4-Nitrophenyl phenyl ether. Following the general procedure using 4-Nitrophenol (139mg, 1mmol) and iodobenzene (0.05 mL, 0.5 mmol) provided 157 mg (73% yield) of the coupling product as a yellow solid after purification by flash chromatography (8:2 pentane/DCM) of the crude oil.



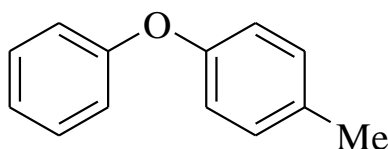
^1H NMR (CDCl_3 , 400 MHz) δ 6.89-6.93 (m, 2H), 7 (d, $J=7.84$ Hz, 2H), 7.17 (t, $J=7.56$ Hz, 1H), 7.34 (t, $J=7.6$ Hz, 2H), 8.10 (d, $J=9.36$ Hz, 2H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 117.1, 120.6, 125.5, 126, 130.4, 142.6, 154.7, 163.4;

All spectral data correspond to those given in the literature

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4-Methylphenyl phenyl ether. Following the general procedure using 4-Methylphenol (100 mg, 1 mmol) and iodobenzene (0.05 mL, 0.5 mmol) provided 175 mg (95% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



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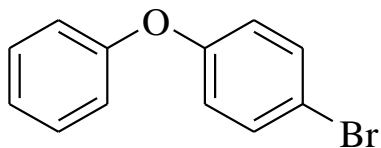
^1H NMR (CDCl_3 , 400 MHz): $\delta=2.26$ (s, 3H), 6.84 (d, $J=8.56$ Hz, 2H), 6.91 (d, $J=8.56$ Hz, 2H), 6.99 (t, $J=7.56$ Hz, 1H), 7.06 (d, $J=8.1$ Hz, 2H), 7.24 (t, $J=7.56$ Hz, 2H),

^{13}C NMR (CDCl_3 , 100 MHz): $\delta=20.7$, 118.3, 119.1, 122.8, 129.7, 130.2, 132.9, 154.7, 157.8

All spectral data correspond to those given in the literature

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4-Bromophenyl phenyl ether. Following the general procedure using 4-Bromophenol (173 mg, 1 mmol) and iodobenzene (0.05 mL, 0.5 mmol) provided 149 mg (60% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



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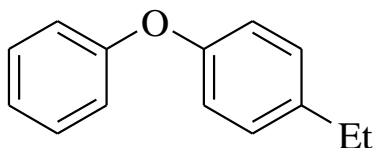
^1H NMR (CDCl_3 , 400 MHz): $\delta=6.79$ -6.83 (m, 2H), 6.93 (d, $J=7.56$ Hz, 2H), 7.05 (t, $J=7.56$ Hz, 1H), 7.27 (t, $J=7.57$ Hz, 2H), 7.33-7.37 (m, 2H),

^{13}C NMR (CDCl_3 , 100 MHz): $\delta=115.6$, 119.0, 120.4, 123.7, 129.9, 130.2, 132.7, 156.6, 156.7

All spectral data correspond to those given in the literature

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4-Ethylphenyl phenyl ether. Following the general procedure using 4-Ethylphenol (122 mg, 1 mmol) and iodobenzene (0.05 mL, 0.5 mmol) provided 178 mg (90% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



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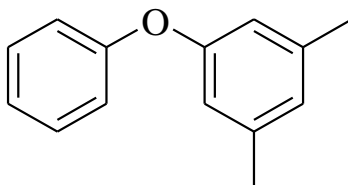
^1H NMR (CDCl_3 , 400 MHz): δ = 1.16 (t, J =7.56 Hz, 3H), 2.56(q, J =7.56 Hz, 2H), 6.87 (d, J =8.32 Hz, 2H), 6.91 (d, J =7.84 Hz, 2H), 7.00 (t, J =7.32 Hz, 1H), 7.09 (d, J = 8.56 Hz, 2H), 7.27 (t, J = 7.32 Hz, 2H),

^{13}C NMR (CDCl_3 , 100 MHz): δ = 15.8, 28.2, 118.4, 119.1, 122.8, 129.0, 129.7, 139.3, 154.9, 157.76.

10 All spectral data correspond to those given in the literature

3,5-Dimethylphenyl phenyl ether. Following the general procedure using 3,5-Dimethylphenol (122 mg, 1 mmol) and iodobenzene (0.05 mL, 0.5 mmol) provided 168 mg (85% yield) of the coupling product as a colorless oil after purification by flash chromatography (pentane) of the crude oil.

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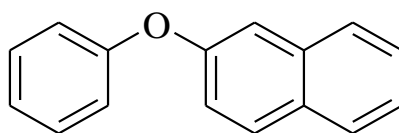
^1H NMR (CDCl_3 , 400 MHz) δ = 2.20 (s, 6H), 6.56 (s, 2H), 6.67 (s, 1H), 6.92 (d, J =7.56 Hz, 2H), 7.01 (t, J =7.32 Hz, 1H), 7.23-7.27 (m, 2H),

^{13}C NMR (CDCl_3 , 100 MHz) δ = 21.3, 116.6, 118.9, 123, 124.9, 129.7, 139.6, 157.1, 157.4

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2-Naphthyl phenyl ether. Following the general procedure using 2-naphthol (144 mg, 1mmol) and iodobenzene (0.05 mL, 0.5 mmol) provided 209 mg (95% yield) of the coupling product as a Pale yellow colored solid after purification by flash chromatography (pentane) of the crude oil.

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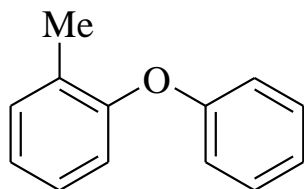


^1H NMR (CDCl_3 , 400 MHz) δ = 7 (d, J = 7.56, 2H), 7.06 (t, J = 7.56 Hz, 1H), 7.17-7.39 (m, 6H), 7.62 (d, J = 7.8 Hz, 1H), 7.73-7.77 (m, 2H),

^{13}C NMR (CDCl_3 , 100 MHz): = 114.1, 119.2, 120.0, 123.5, 124.7, 126.5, 127.1, 127.8, 129.8, 129.9, 130.2, 134.3, 155.1, 157.2.

All spectral data correspond to those given in the literature

10 2-Methylphenyl phenyl ether. Following the general procedure using Phenol (94 mg, 1 mmol) and 2-iodotoluene (0.064 mL, 0.5 mmol) provided 129 mg (70% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



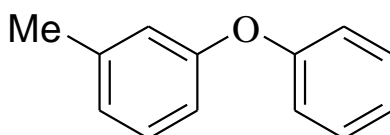
^1H NMR (CDCl_3 , 400 MHz) δ = 2.17 (s, 3H), 6.82-6.84 (m, 3H), 6.95-7.01 (m, 2H), 7.1 (t, J = 6.28 Hz, 1H), 7.17-7.24 (m, 3H);

^{13}C NMR (CDCl_3 , 100 MHz) δ = 16.2, 117.3, 119.8, 122.3, 124.0, 127.1, 129.7, 131.5, 131.46, 154.6, 157.8;

All spectral data correspond to those given in the literature

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3-Methylphenyl phenyl ether. Following the general procedure using phenol (94 mg, 1 mmol) and 3-bromotoluene (0.06 mL, 0.5 mmol) provided 133 mg (72% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil



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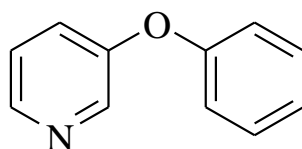
^1H NMR (CDCl_3 , 500 MHz) δ 2.35 (s, 3H), 6.78-6.85(m, 2H), 6.90-6.94 (m, 1H), 7.00-7.03 (m, 2H), 7.11 (t, $J=7.4$ Hz, 1H), 7.22 (t, $J=7.85$ Hz, 1H), 7.33-7.37 (m, 2H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 21.5, 116.0, 119.0, 119.7, 123.2, 124.2, 129.6, 129.8, 140.1, 154.3, 157.5;

5 All spectral data correspond to those given in the literature

3-Pyridine phenyl ether. Following the general procedure using phenol (94 mg, 1 mmol) and 3-iodopyridine (102 mg, 0.5 mmol) provided 128 mg (75% yield) of the coupling product as a colorless oil after purification by flash chromatography (pentane) of the crude oil

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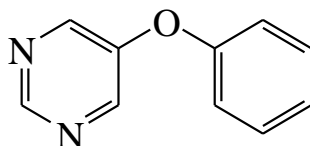
^1H NMR (CDCl_3 , 500 MHz) δ 7.03 (d, $J=8.4$ Hz, 2H), 7.16 (t, $J=7.4$, 1H), 7.22-7.30 (m, 2H), 7.38 (t, $J=8.3$, 2H), 8.37 (br s, 1H), 8.42 (brs, 1H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 119, 121.3, 124, 125, 130, 141, 144, 157.3, 157.5;

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5-Pyrimidine phenyl ether. Following the general procedure using phenol (94 mg, 1 mmol) and 5-bromopyrimidine (79 mg, 0.5 mmol) provided 129 mg (75% yield) of the coupling product as a white solid crystal after purification by flash chromatography (pentane) of the crude oil

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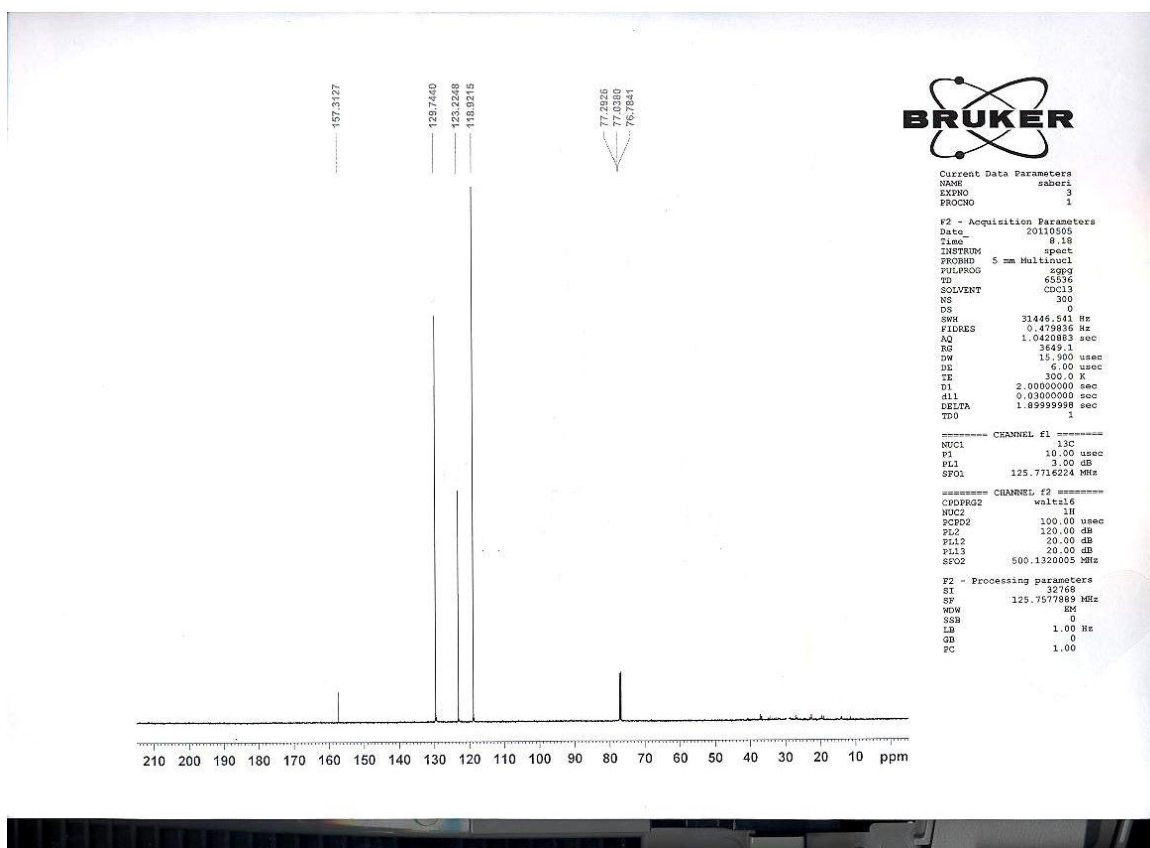
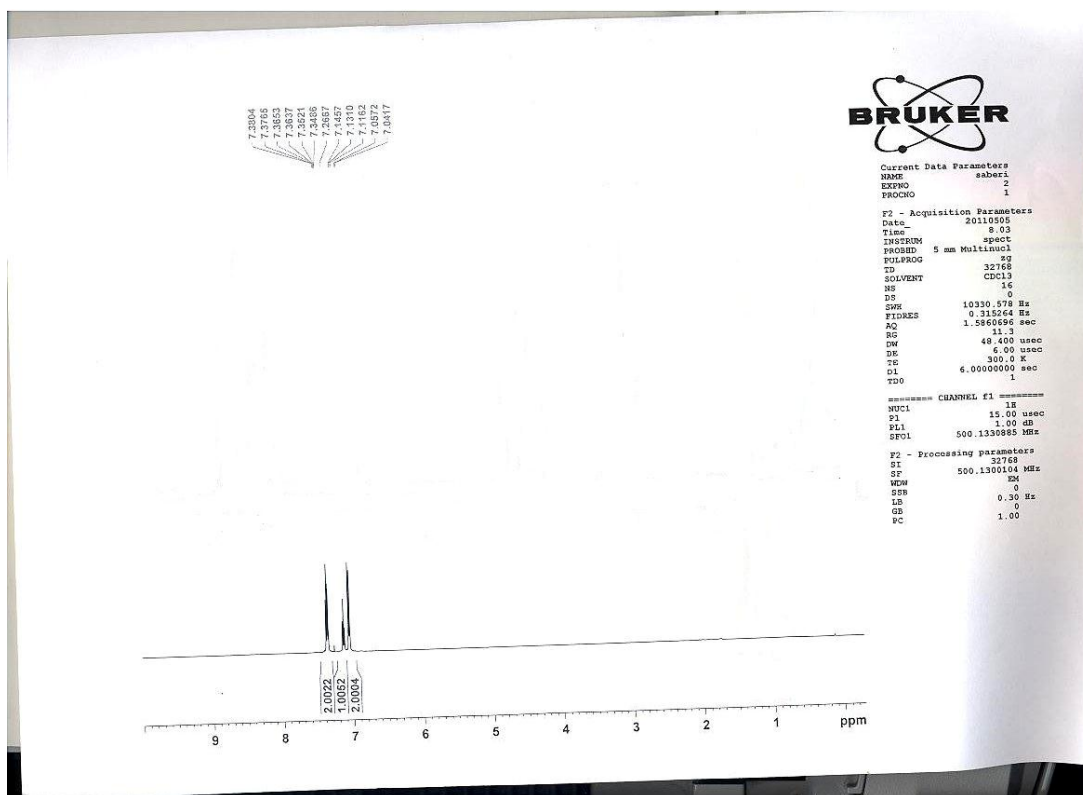


^1H NMR (CDCl_3 , 500 MHz) δ 7.06 (t, $J=8.35$ Hz, 2H), 7.41-7.44 (m, 3H), 8.48(s, 2H), 8.97 (s, 1H);

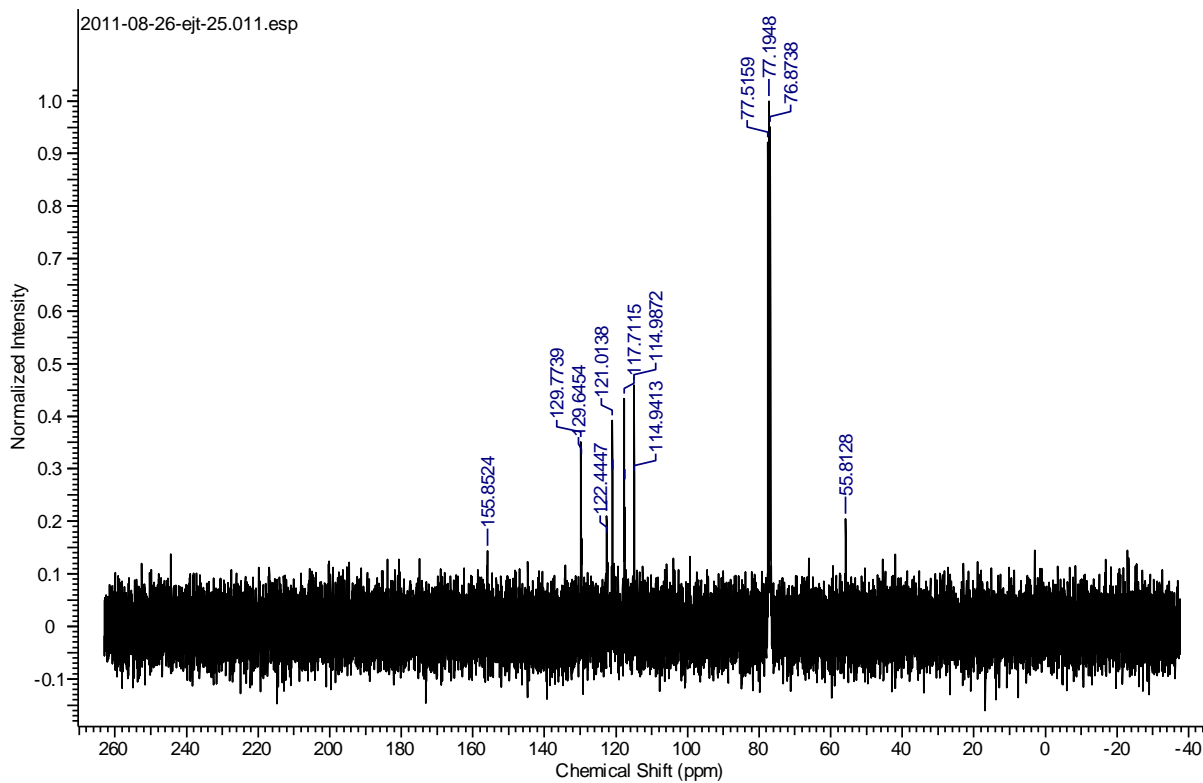
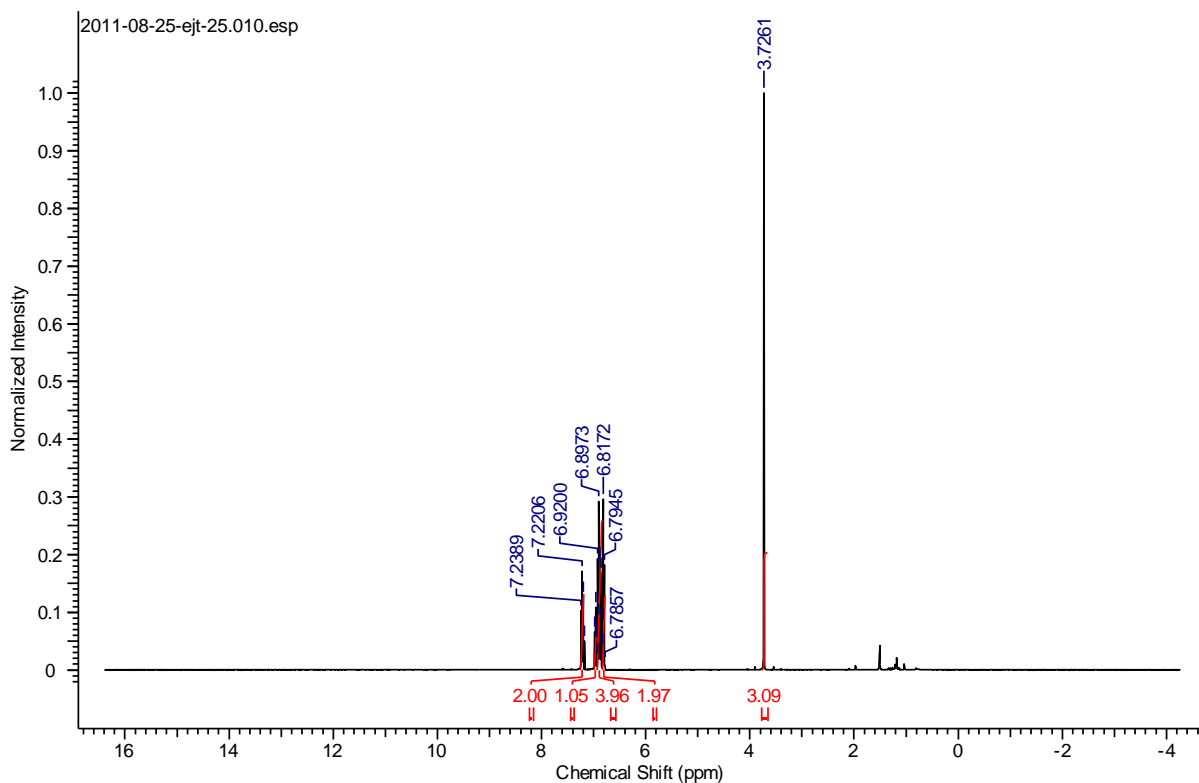
^{13}C NMR (CDCl_3 , 125 MHz) δ 119.1, 123.2, 130.3, 144.4, 147.0, 153.2, 175.2;

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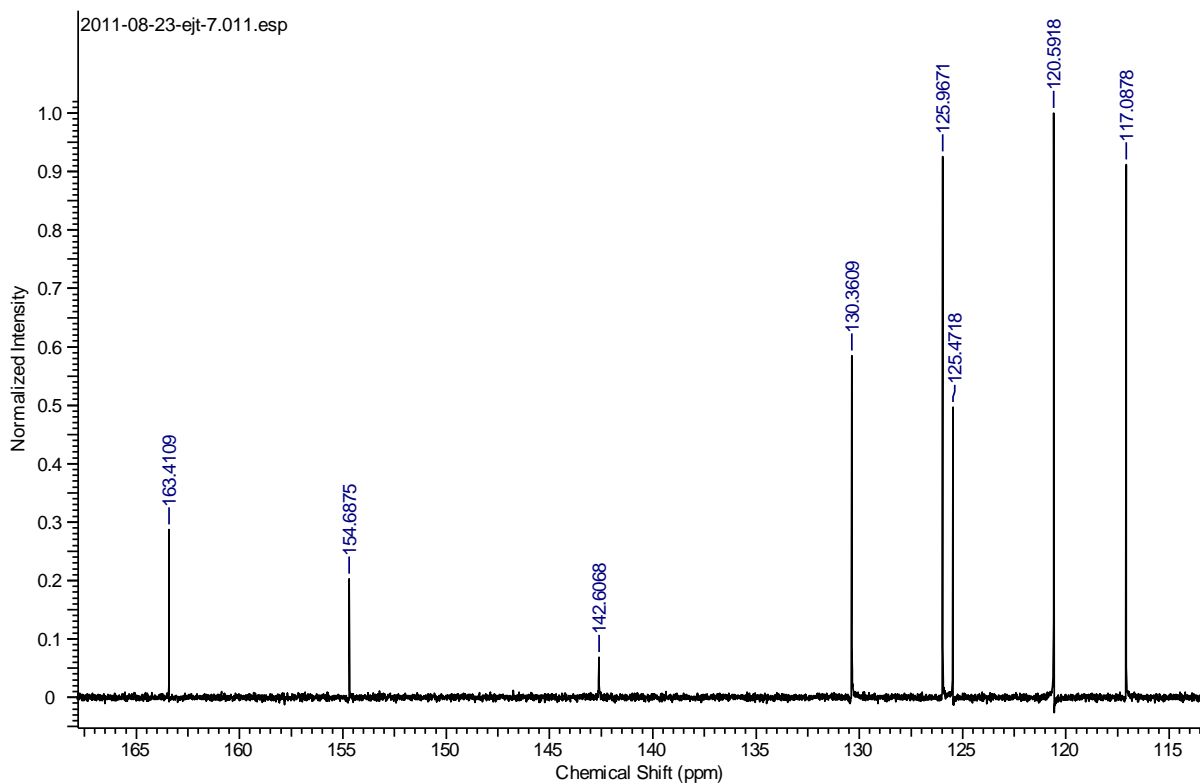
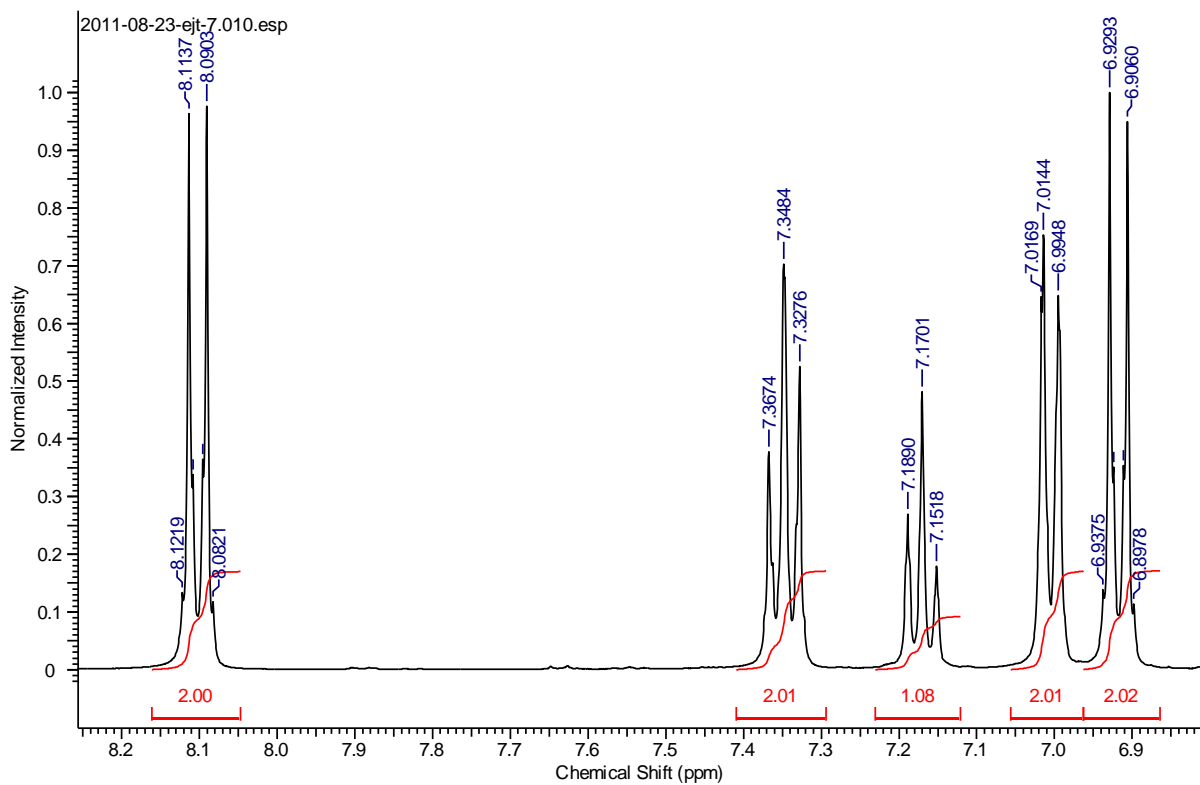
Diphenyl ether



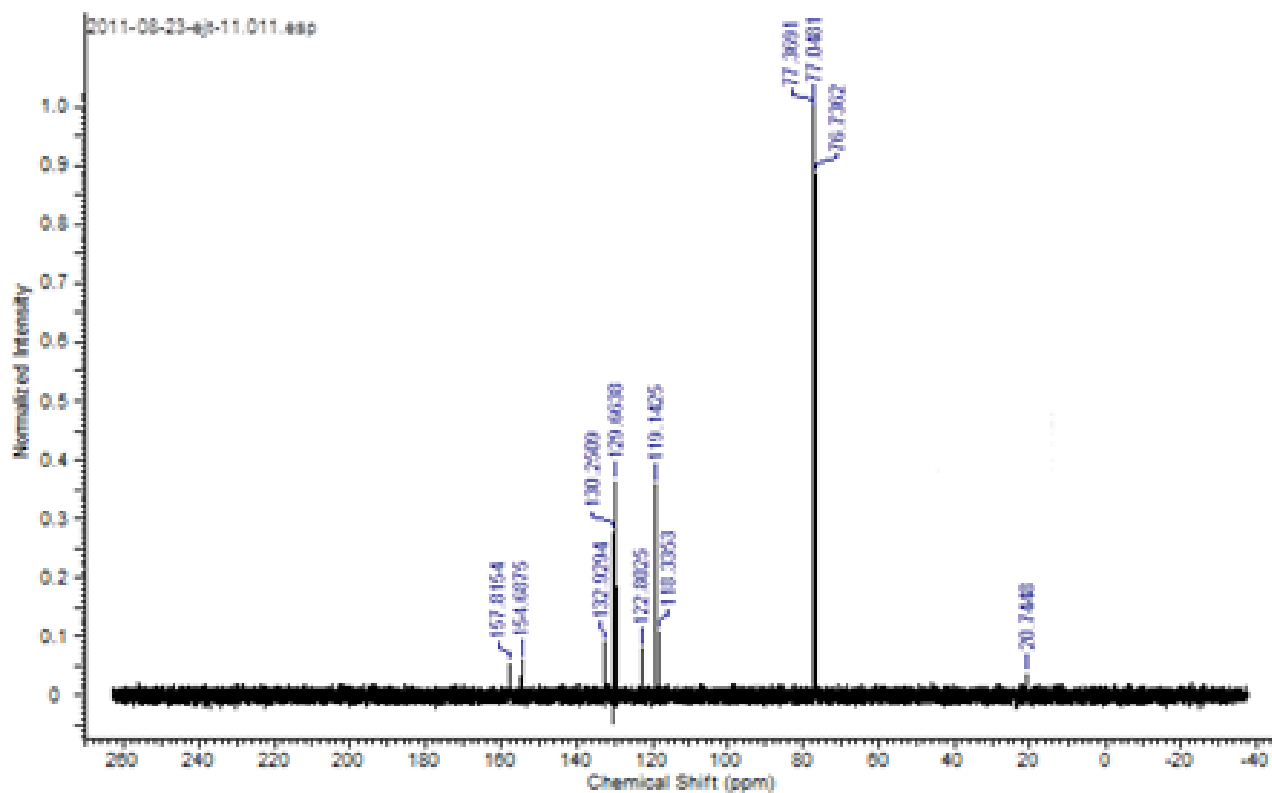
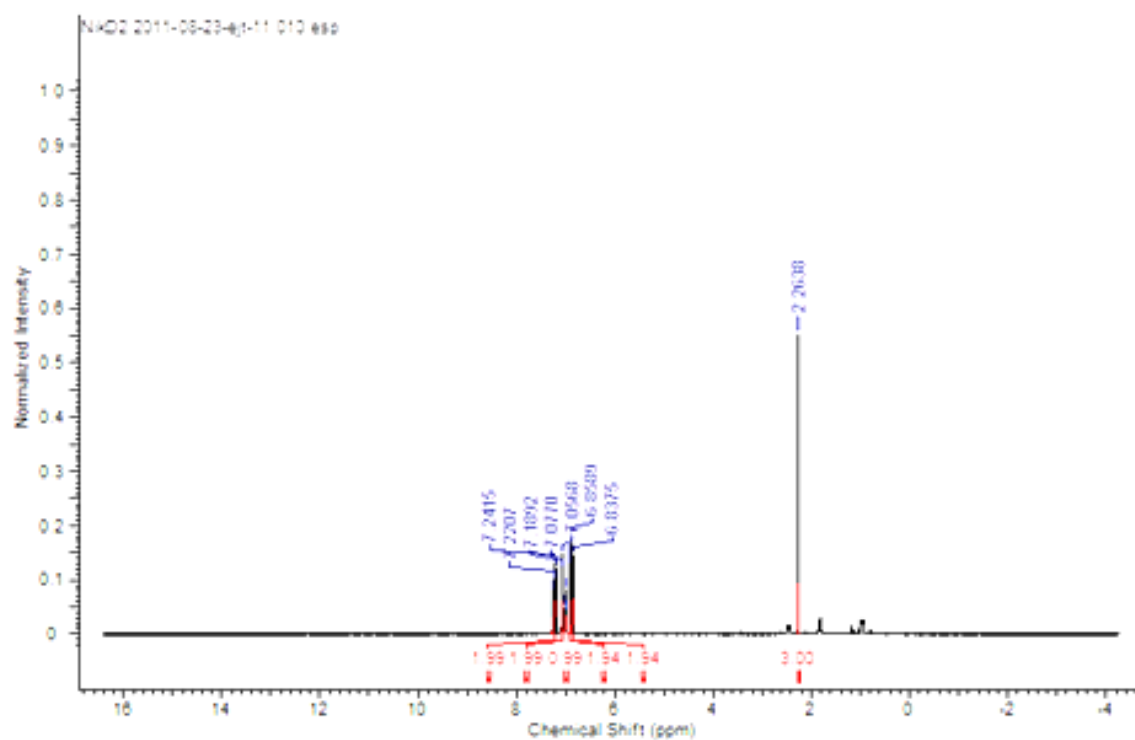
4-Methoxyphenyl phenyl ether



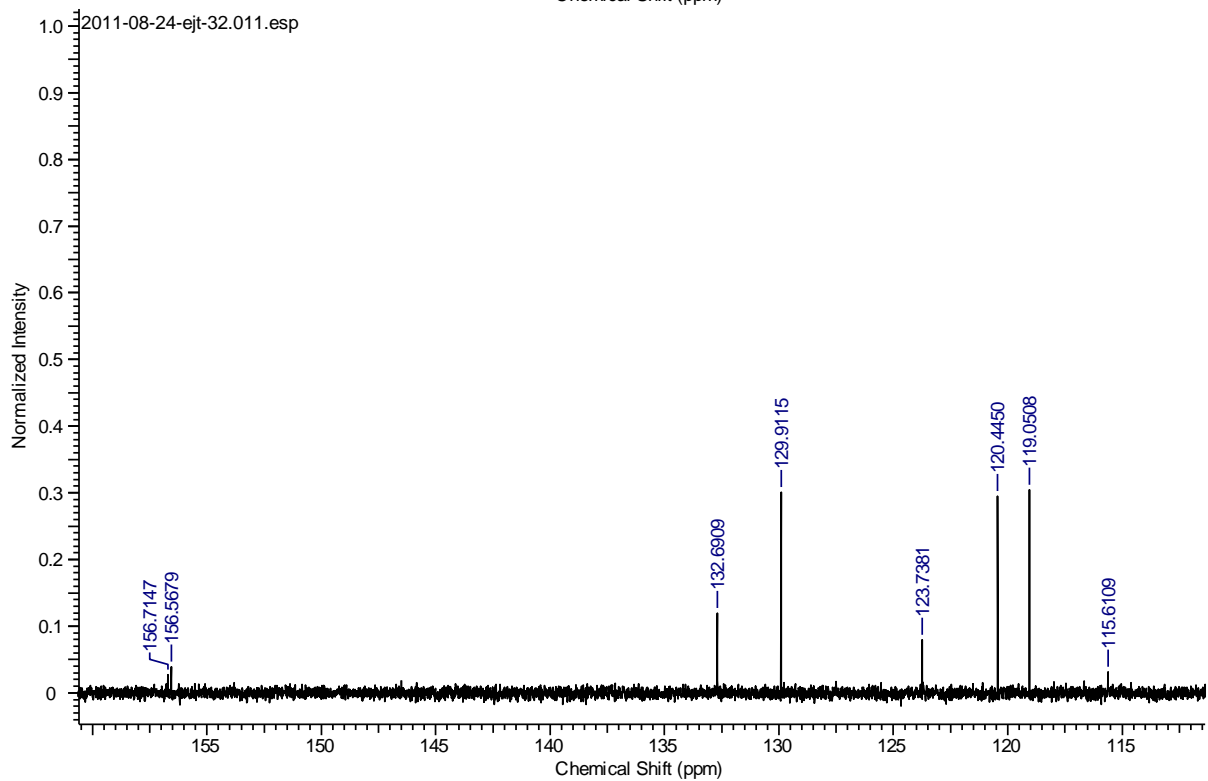
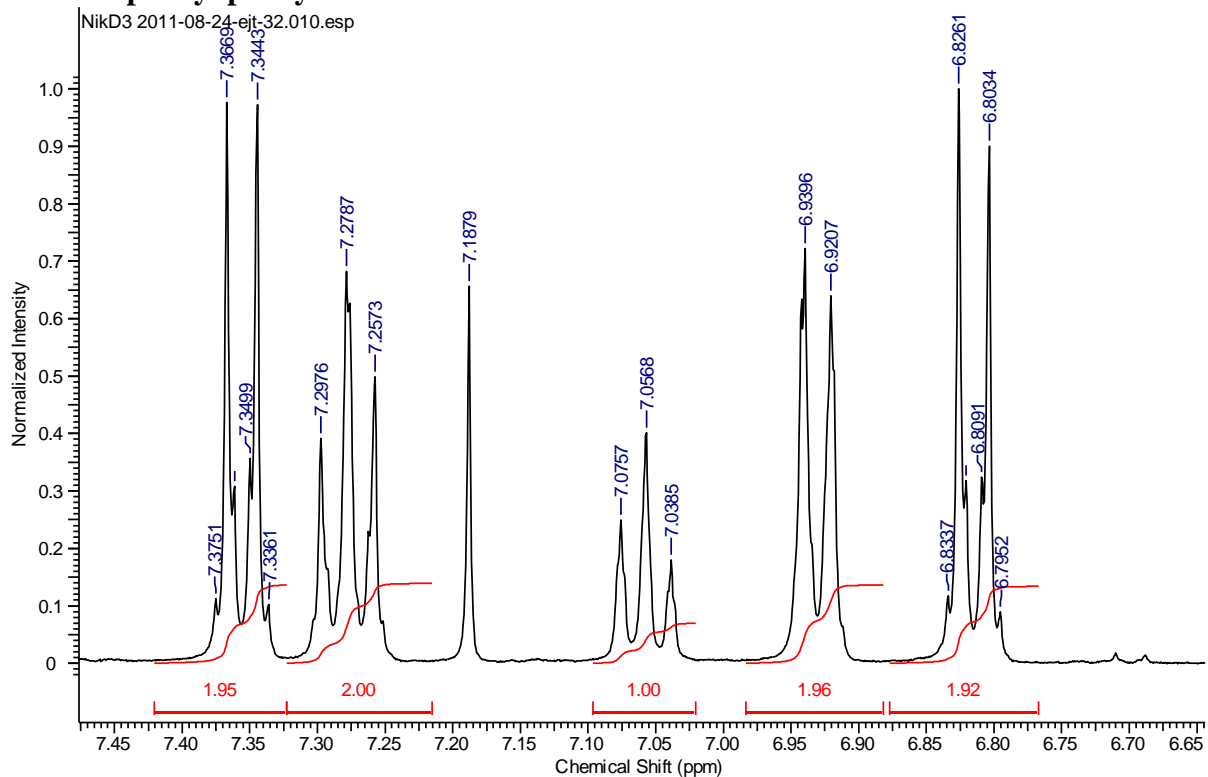
4-Nitrophenyl phenyl ether



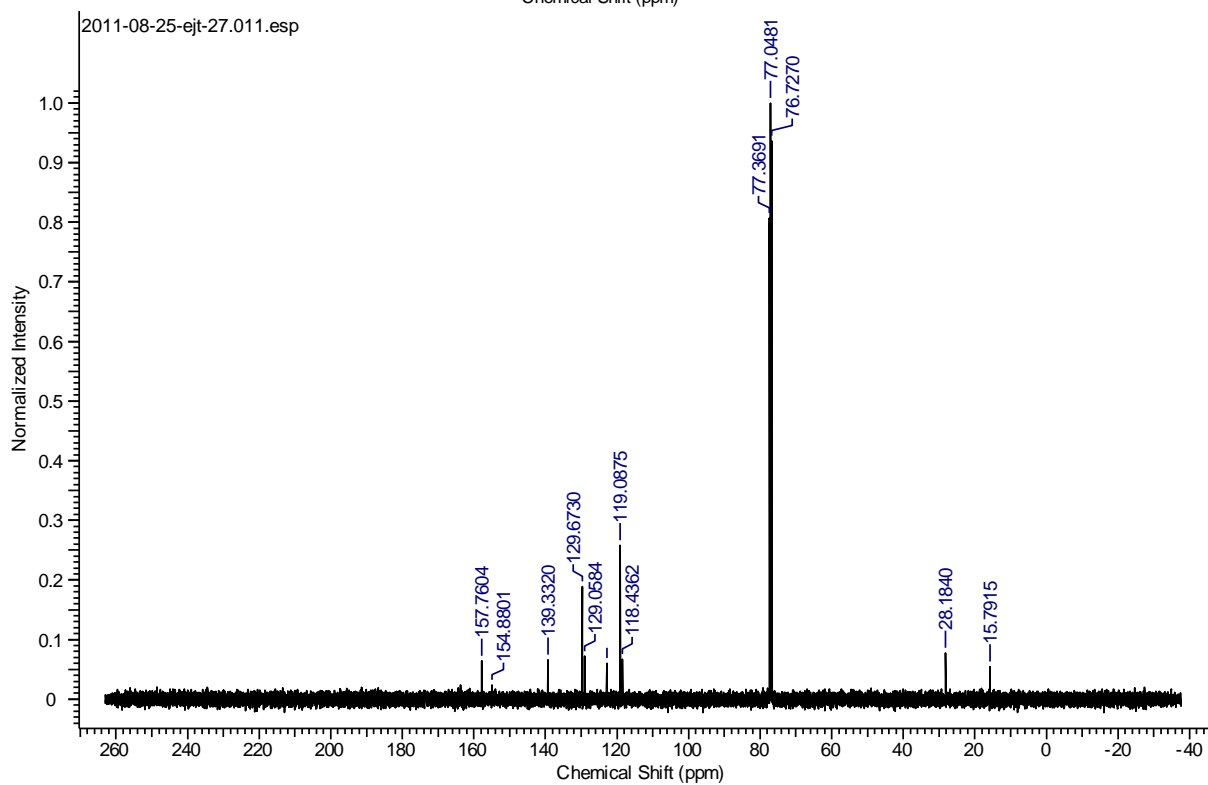
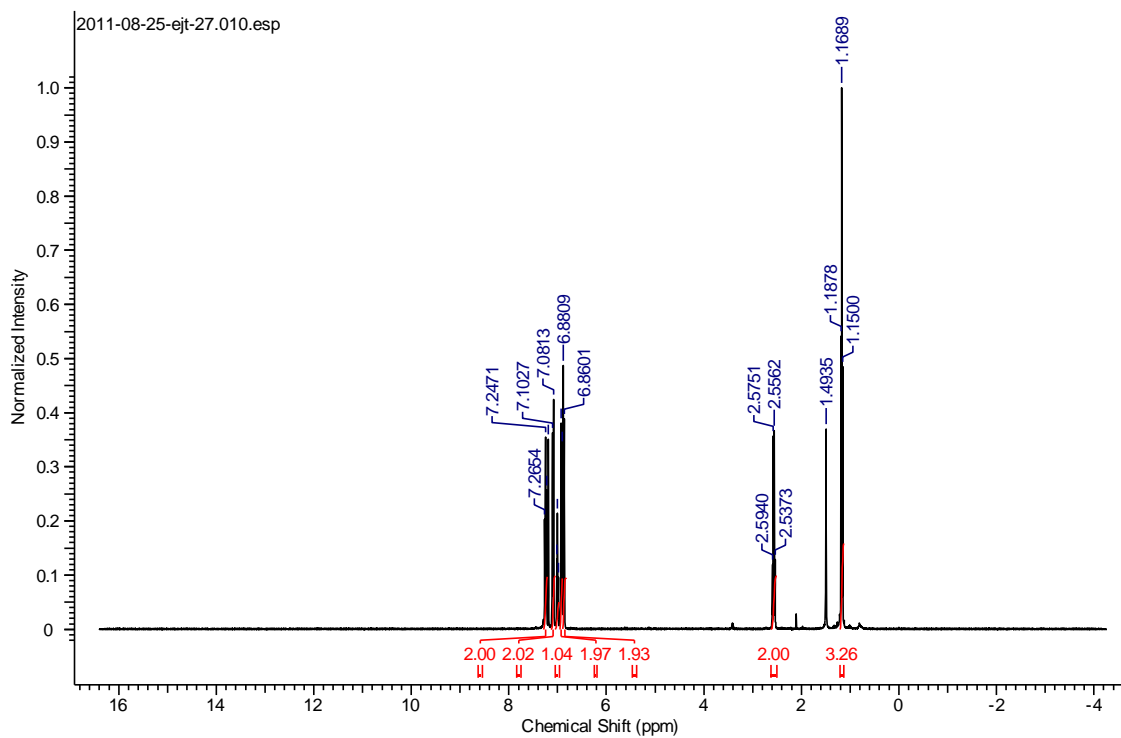
4-Methylphenyl phenyl ether



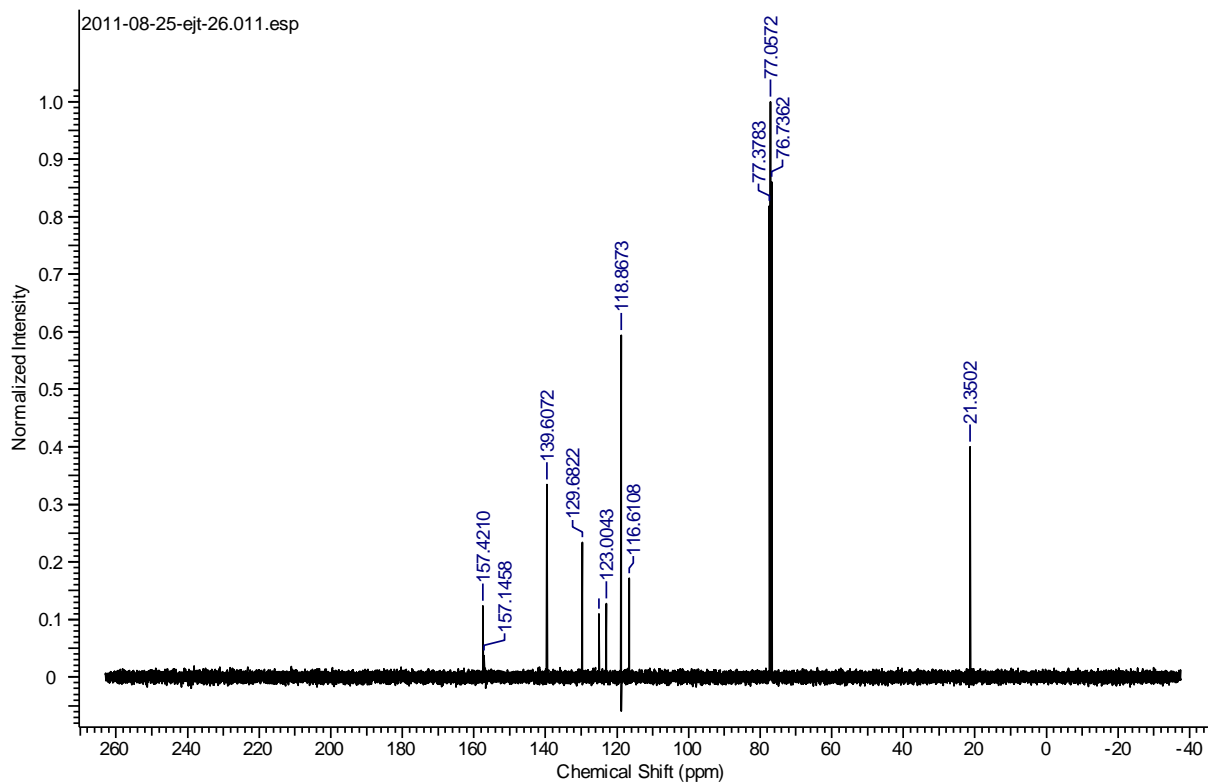
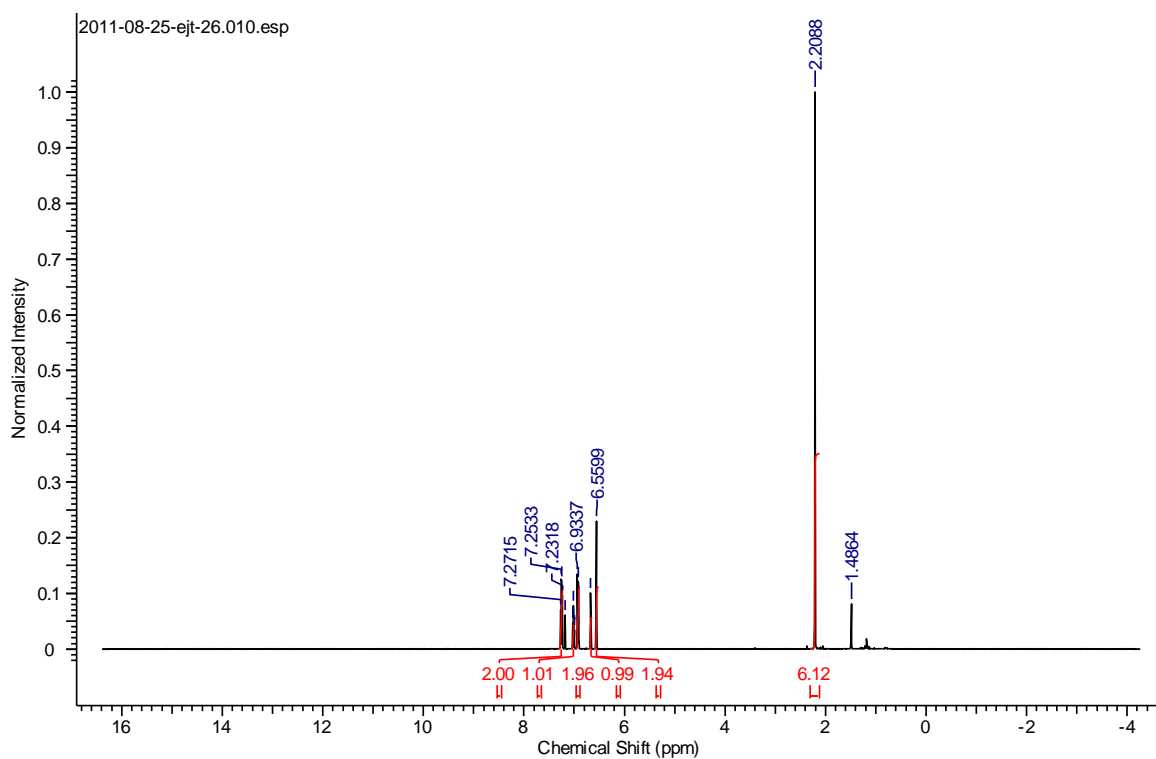
4-Bromophenyl phenyl ether



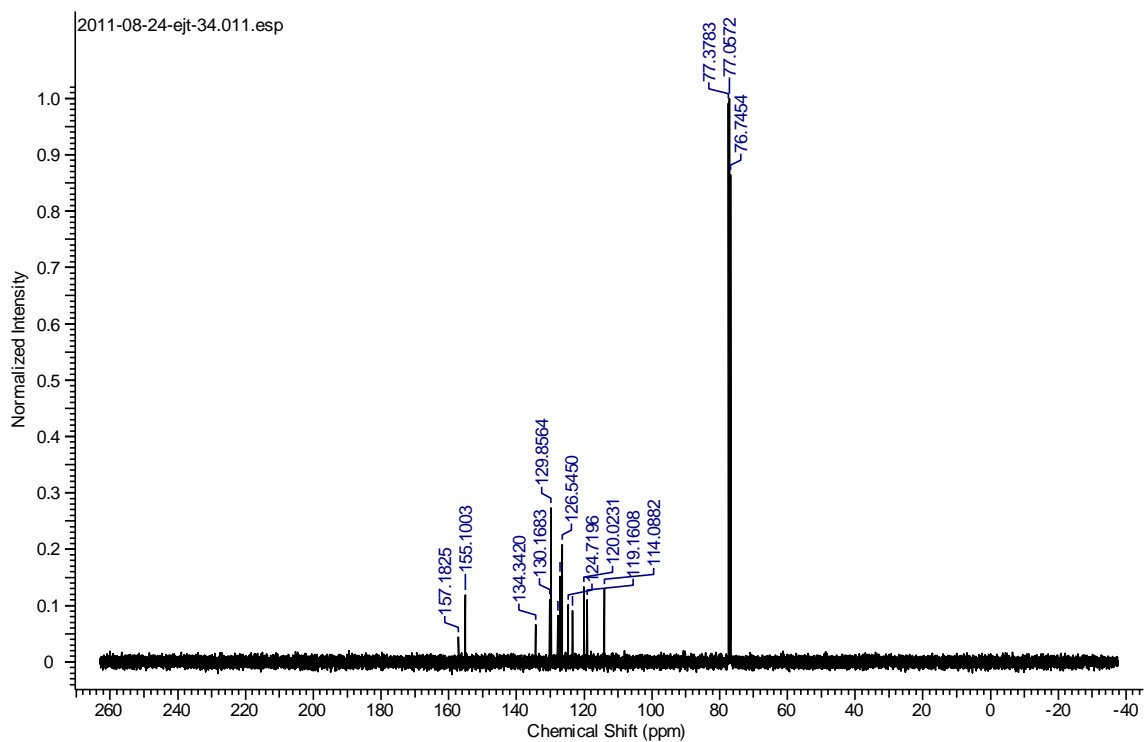
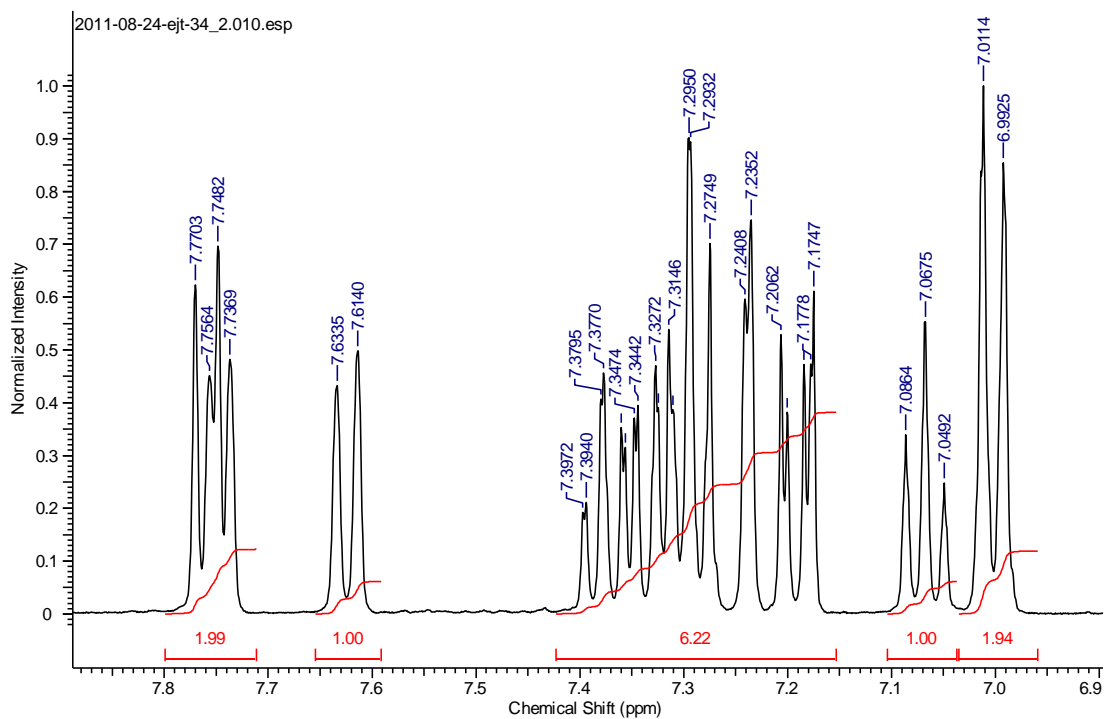
4-Ethylphenyl phenyl ether



3,5-Dimethylphenyl phenyl ether



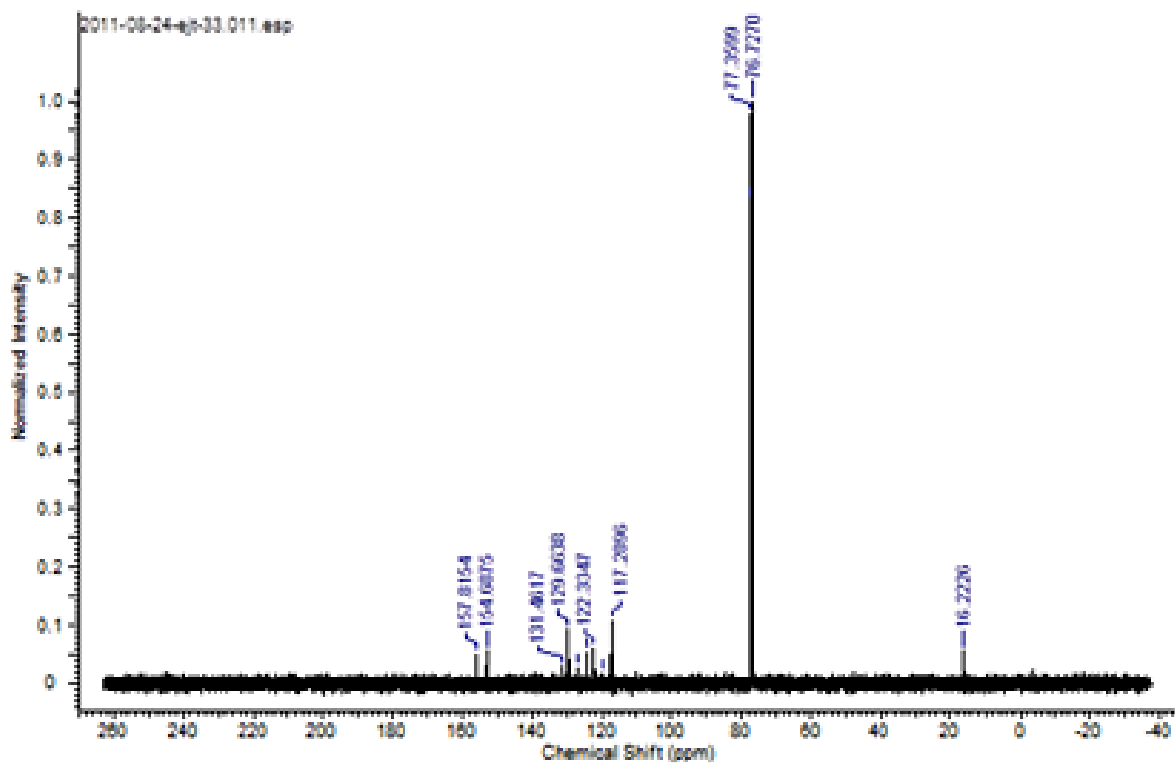
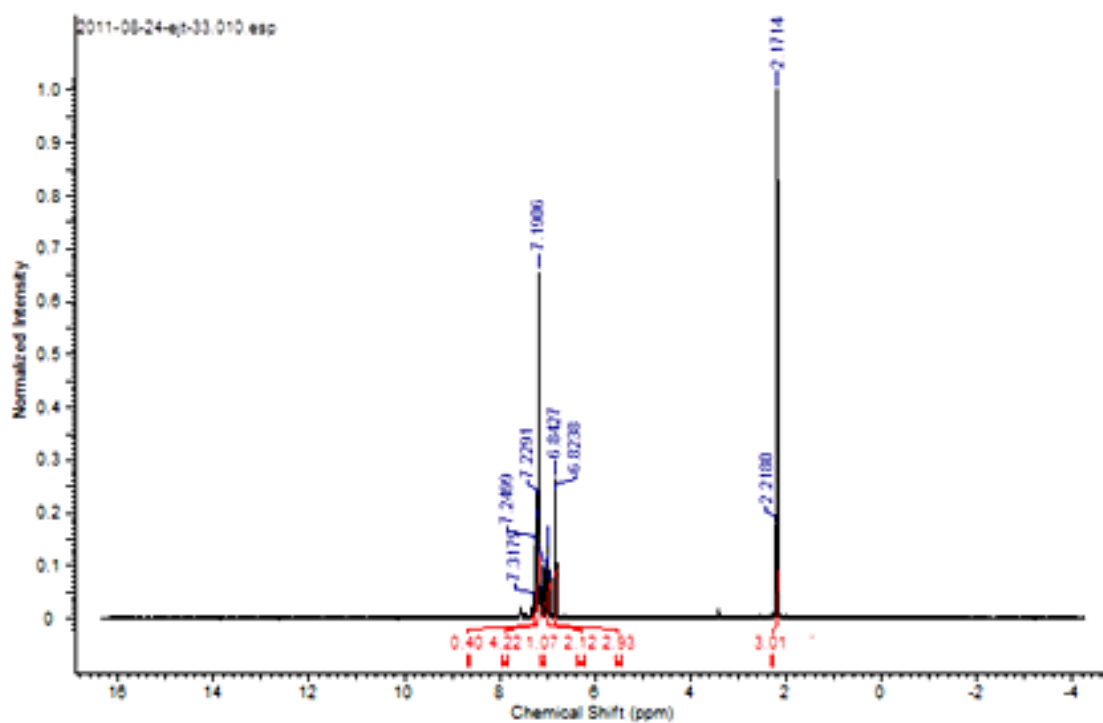
2-Naphthyl phenyl ether



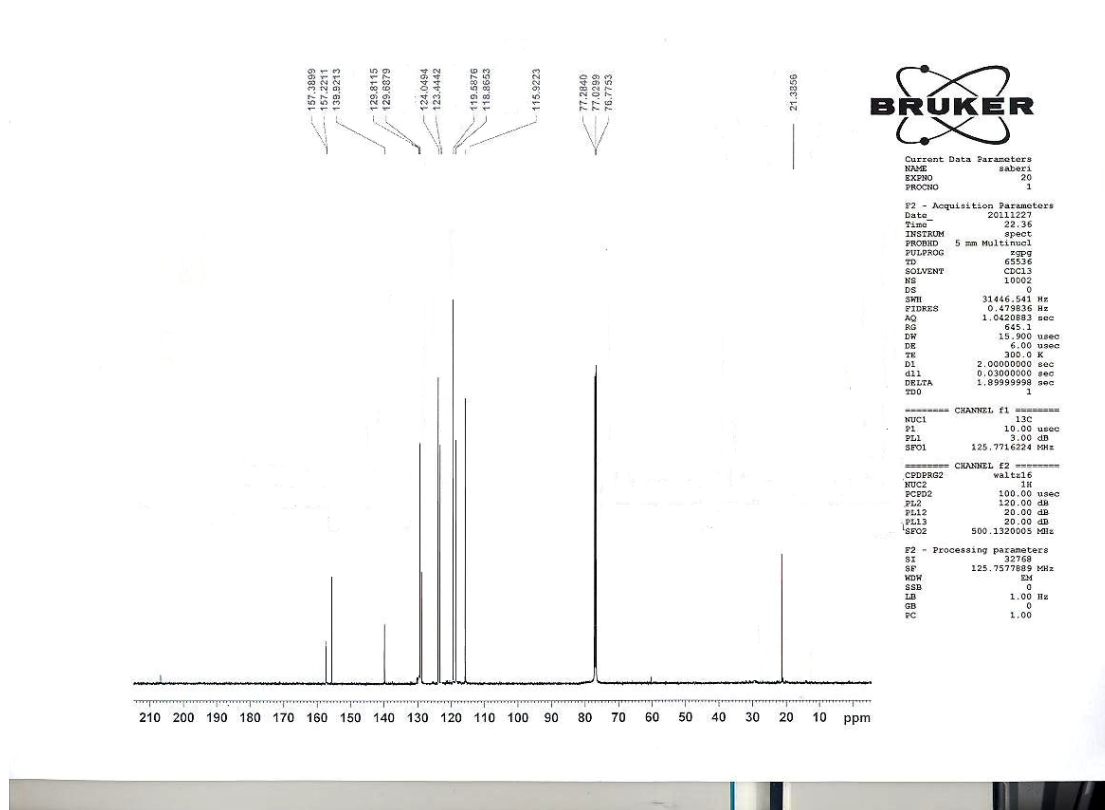
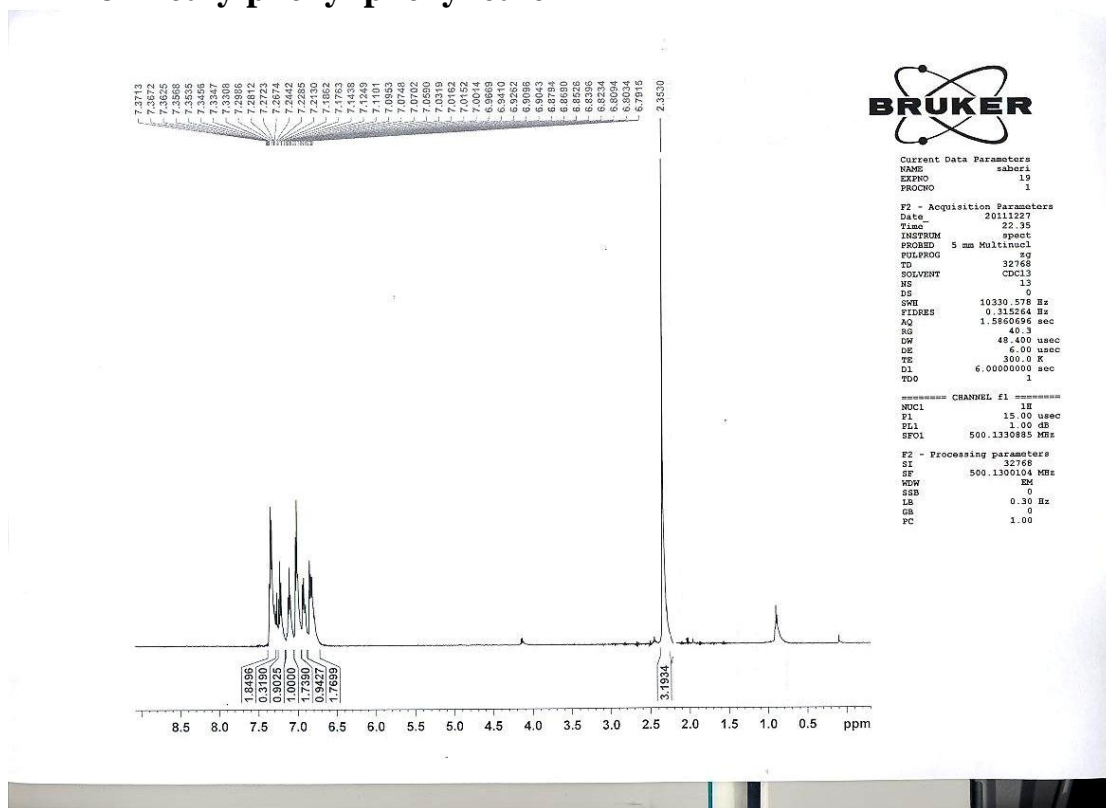
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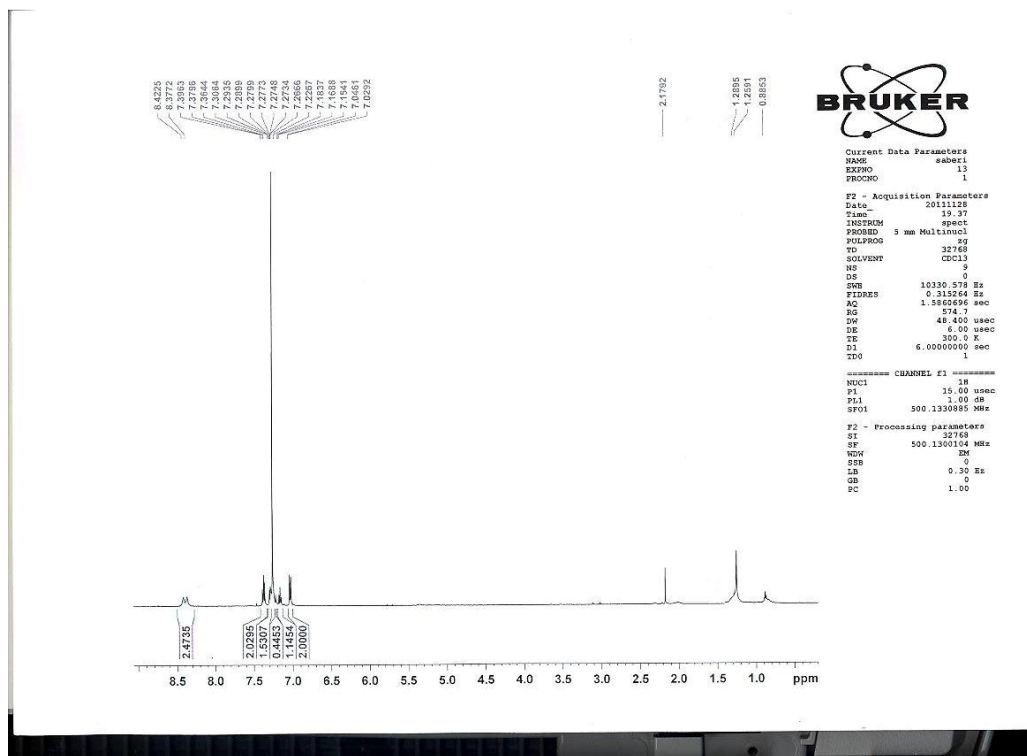
2-Methylphenyl phenyl ether



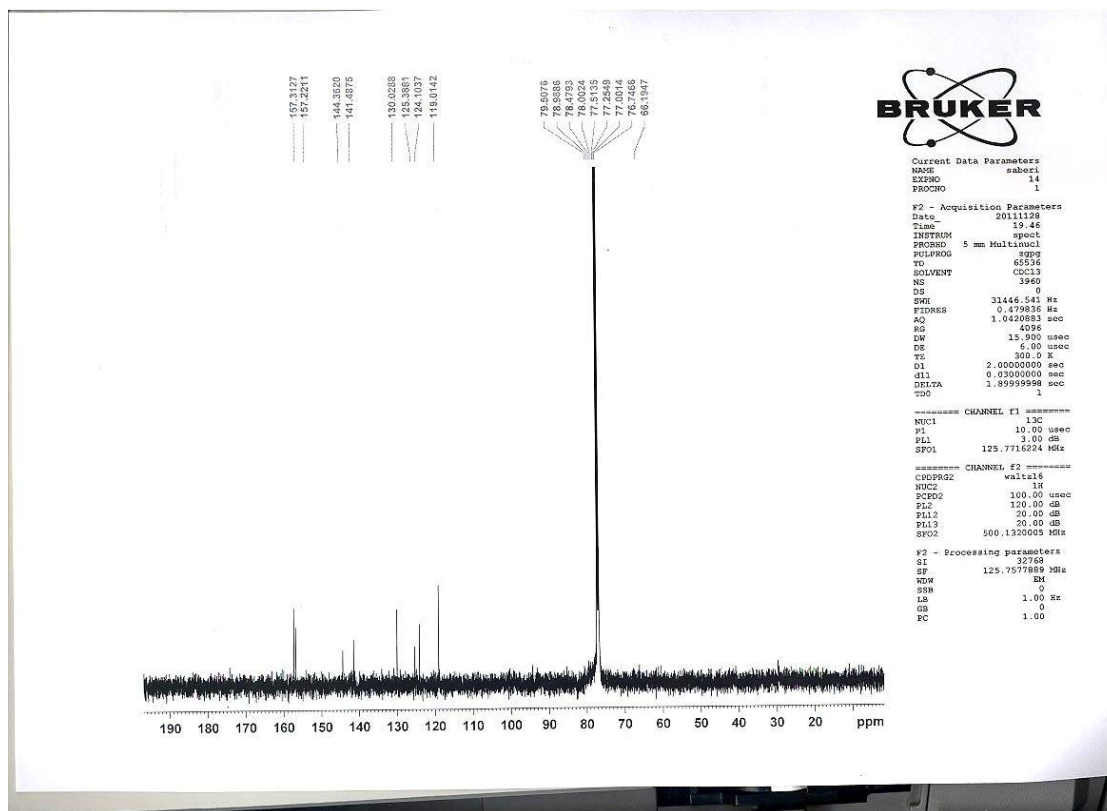
3-Methylphenyl phenyl ether



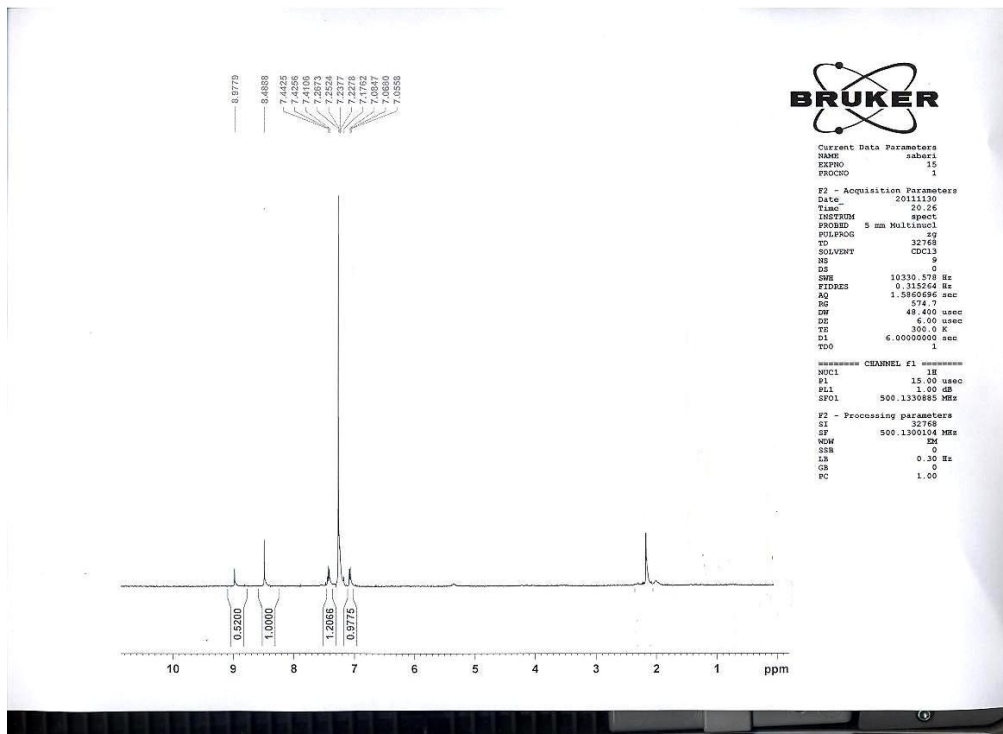
3-Pyridine phenyl ether



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5-Pyrimidine phenyl ether



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