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Supporting Information

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Iron-Catalyzed C-O Cross-Coupling of Phenols with Aryl Iodides

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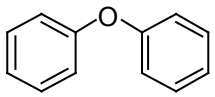
General information: All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out under argon. Flash chromatography was carried out with Merck silica gel 60 (63-200 mesh). Analytical TLC was performed with Merck silica gel 60 F_{254} plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (300 or 400 MHz and 75 or 100 MHz, respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz. IR spectra were recorded on a Perkin-Elmer FT/IR 1760 as KBr pellets. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus and are uncorrected. Mass spectra were acquired on a Varian MAT 212 spectrometer (CI, 100 eV and EI, 70 eV) and HRMS were recorded on a Finnigan MAT 95 spectrometer.

General procedure for *O*-arylation of phenols: A sealable tube equipped with a magnetic stir bar was charged with phenol (1.0 equiv), Cs_2CO_3 (2.0 equiv) and $FeCl_3$ (0.1 equiv). The aperture of the tube was then covered with a rubber septum, and an argon atmosphere was established. Aryl halide (1.5 equiv), 2,2,6,6-tetramethyl-3,5-heptanedione (0.2 equiv) and DMF (1 mL/mmol of phenol) were added via syringe. The

septum was then replaced by a teflon-coated screw cap, and the reaction vessel was placed in a 135 °C oil bath. After stirring at this temperature for 20 h, the heterogeneous mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was directly filtered through a pad of celite and concentrated to yield the product, which was purified by silica gel chromatography to yield the corresponding diaryl ether. The identity and purity of the product was confirmed by ^{1}H and ^{13}C NMR spectroscopic analysis.

Diphenyl ether[1] (3a). Following the general procedure using phenol (100 mg, 1.08 mmol) and iodobenzene (0.18 mL, 1.60 mmol) provided 155 mg (85% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.97-7.02 (m, 4H), 7.04-7.10 (m, 2H), 7.28-7.34 (m, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 118.9 (CH), 123.2 (CH), 129.8 (CH), 157.2 (C).

All spectral data correspond to those given in the literature.

4-Phenylphenyl phenyl ether[2] (3b). Following the general procedure using 4-phenylphenol (100 mg, 0.59 mmol) and iodobenzene (0.10 mL, 0.88 mmol) provided 138 mg (95% yield) of the coupling product as a white solid after purification by flash chromatography (pentane) of the crude oil.

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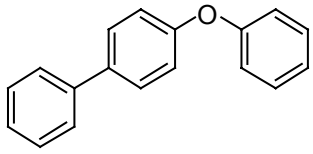
[1] D. Ma, Q. Cai, *Org. Lett.* **2003**, *5*, 3799-3802.

[2] N. F. Mc Kinley, D. F. O´Shea, *J. Org. Chem.* **2004**, *69*, 5087-5092.



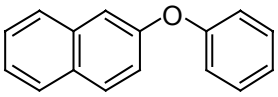
M.p. : 68-69 °C (lit.[2] 67-68 °C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.03-7.13 (m, 5H), 7.28-7.36 (m, 4H), 7.41 (br t, 1H, J = 7.4 Hz), 7.51-7.57 (m, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 119.0 (CH), 119.1 (CH), 123.4 (CH), 126.9 (CH), 127.0 (CH), 128.4 (CH), 128.8 (CH), 129.8 (CH), 136.3 (C), 140.5 (C), 156.8 (C), 157.1 (C).

All spectral data correspond to those given in the literature.

2-Naphthyl phenyl ether[3] (3c). Following the general procedure using 2-naphtol (100 mg, 0.69 mmol) and iodobenzene (0.12 mL, 1.04 mmol) provided 140 mg (92% yield) of the coupling product as a white solid after purification by flash chromatography (pentane) of the crude oil.



M.p. : 45-46 °C (lit.[3] 45-46 °C)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.04-7.15 (m, 3H), 7.22-7.46 (m, 6H), 7.67 (br d, 1H, J = 7.7 Hz), 7.78-7.82 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 114.1 (CH), 118.9 (CH), 119.2 (CH), 120.0 (CH), 123.5 (CH), 124.7 (CH), 126.6 (CH), 127.2 (CH), 127.8 (CH), 129.8 (CH), 129.9 (CH), 130.2 (C), 134.4 (C), 155.1 (C), 157.2 (C).

All spectral data correspond to those given in the literature.

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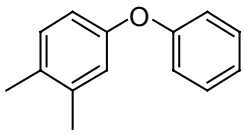
[3] Z. Liu, R. C. Larock, *J. Org. Chem.* **2006**, *71*, 3198-3209.

3,4-Dimethylphenyl phenyl ether (3d). Following the general procedure using 3,4-dimethylphenol (100 mg, 0.82 mmol) and iodobenzene (0.14 mL, 1.23 mmol) provided 149 mg (92% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



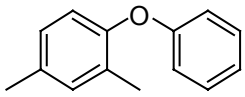
^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.23 (br s, 6H), 6.75 (dd, J = 8.2 Hz, 2.5 Hz, 1H), 6.82 (br d, J = 2.2 Hz, 1H), 6.94-6.99 (m, 2H), 7.02-7.09 (m, 2H), 7.23-7.33 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.2 (CH_3), 20.1 (CH_3), 116.5 (CH), 118.3 (CH), 120.5 (CH), 122.7 (CH), 129.6 (CH), 130.6 (CH), 131.6 (C), 138.1 (C), 154.8 (C), 157.8 (C).

MS (EI) *m/z* (%) 198 (M^+, 100), 183 (14), 105 (21).

HRMS calc. for $C_{14}H_{14}O$ 198.10447, found 198.10446.

2,4-Dimethylphenyl phenyl ether (3e). Following the general procedure using 2,4-dimethylphenol (100 mg, 0.82 mmol) and iodobenzene (0.14 mL, 1.23 mmol) provided 155 mg (95% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



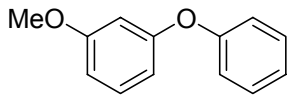
^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.31 (s, 3H), 6.79-6.89 (m, 2H), 6.93-7.07 (m, 4H), 7.21-7.30 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 16.1 (CH_3), 20.8 (CH_3), 116.8 (CH), 120.2 (CH), 122.0 (CH), 127.7 (CH), 129.6 (CH), 129.9 (C), 132.1 (C), 133.7 (C), 151.9(C), 158.4 (C).

MS (EI) *m/z* (%) 198 (M^+, 100), 183 (16), 105 (28).

HRMS calc. for $C_{14}H_{14}O$ 198.10447, found 198.10446.

3-Methoxyphenyl phenyl ether[4] (3f). Following the general procedure using 3-methoxyphenol (0.087 mL, 0.78 mmol) and iodobenzene (0.11 mL, 1.17 mmol) provided 155 mg (99% yield) of the coupling product as a yellowish oil after purification by flash chromatography (pentane) of the crude oil.

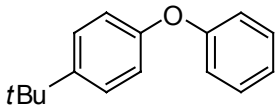


^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 3H), 6.46-6.54 (m, 3H), 6.89-6.97 (m, 3H), 7.06-7.23 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 55.4 (CH_3), 104.9 (CH), 108.9 (CH), 111.0 (CH), 119.1 (2CH), 123.4 (CH), 129.8 (2CH), 130.2 (CH), 157.1 (C), 158.6 (C), 161.1 (C).

All spectral data correspond to those given in the literature.

4-^{t}Butylphenyl phenyl ether[5] (3g). Following the general procedure using 4-tertbutylphenol (100 mg, 0.66 mmol) and iodobenzene (0.09 mL, 0.99 mmol) provided 142 mg (95% yield) of the coupling product as a colorless oil after purification by flash chromatography (pentane) of the crude oil.



^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 9H), 7.00-7.07 (m, 3H), 7.10-7.15 (m, 2H), 7.32-7.42 (m, 4H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 31.5 ($3CH_3$), 34.3 (C), 118.5 (2CH), 118.6 (2CH), 122.9 (CH), 126.6 (2CH), 129.7 (2CH), 146.1 (C), 154.7 (C), 157.6 (C).

All spectral data correspond to those given in the literature.

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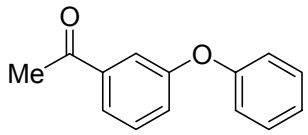
[4] Z. Liu, R. C. Larock, *Org. Lett.* **2004**. *6*, 99-102.

[5] A. Ouali, J.-F. Spindler, M. Taillefer, *Adv. Synth. Catal.* **2006**, *348*, 499-505.

3'-Phenoxyacetophenone[6] (3h). Following the general procedure using 3'-hydroxyacetophenone (100 mg, 0.73 mmol) and iodobenzene (0.10 mL, 1.10 mmol) provided 114 mg (74% yield) of the coupling product as a yellowish oil after purification by flash chromatography (8:2 pentane/ethyl acetate) of the crude oil.



^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.59 (s, 3H), 7.01-7.06 (m, 2H), 7.13-7.19 (m, 1H), 7.22 (ddd, J = 9.5 Hz, 2.7 Hz, 1.0 Hz, 1H), 7.28 (m, 3H), 7.60 (m, 1H), 7.68-7.72 (m, 1H).

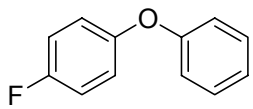
^{13}C-NMR (75 MHz, $CDCl_3$) δ 26.7 (CH3), 118.1 (CH), 119.1 (CH), 123.1 (CH), 123.3 (CH), 123.8 (CH), 129.9 (4CH), 138.9 (C), 156.6 (C), 157.8 (C), 197.4 (C).

IR (cm^{-1}) 1687.

MS (EI) *m/z* (%) 212 (M^+, 77), 197 (100), 169 (16), 141 (33).

HRMS calc. for $C_{14}H_{12}O_2$ 212.08373, found 212.08373.

4-Fluorophenyl phenyl ether[7] (3i). Following the general procedure using 4-fluorophenol (100 mg, 0.89 mmol) and iodobenzene (0.13 mL, 1.34 mmol) provided 141 mg (84% yield) of the coupling product as a yellowish oil after purification by flash chromatography (pentane) of the crude oil. Alternatively, following the general procedure using phenol (100 mg, 1.08 mmol) and 4-fluoroiodobenzene (0.19 mL, 1.60 mmol) provided 158 mg (78% yield) of the coupling product as a yellowish oil after purification by flash chromatography (pentane) of the crude oil.



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[6] H. I. Pérez, H. Luna, N. Manjarrez, A. Solis, *Tetrahedron: Asymmetry* **2001**, *12*, 1709-1712.

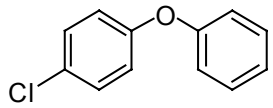
[7] Y. Luo, J. X. Wu, R. X. Ren, *Synlett* **2003**, 1734-1736.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.94-7.09 (m, 6H), 7.28-7.33 (m, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 116.3 (d, J = 23.0 Hz, 2CH), 118.3 (2CH), 120.5 (d, J = 8.4 Hz, 2CH), 123.1 (CH), 129.7 (CH), 129.8 (CH), 152.8 (d, J = 2.2 Hz, C), 157.6 (d, J = 7.7 Hz, C), 159.6 (C).

All spectral data correspond to those given in the literature.

4-Chlorophenyl phenyl ether[8] (3j). Following the general procedure using 4-chlorophenol (100 mg, 0.89 mmol) and iodobenzene (0.15 mL, 1.34 mmol) provided 145 mg (87% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil. Alternatively, following the general procedure using phenol (100 mg, 1.08 mmol) and 4-chloroiodobenzene (386 mg, 1.60 mmol) provided 198 mg (90% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.89-7.01 (m, 4H), 7.08-7.14 (m, 1H), 7.22-7.36 (m, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 119.0 (CH), 120.1 (CH), 123. 7 (CH), 128.2 (C), 129.7 (CH), 129.9 (CH), 156.0 (C), 156.9 (C).

All spectral data correspond to those given in the literature.

4-Nitrophenyl phenyl ether[4] (3k). Following the general procedure using phenol (100 mg, 1.08 mmol) and 1-iodo-4-nitrobenzene (398 mg, 1.60 mmol) provided 184 mg (80% yield) of the coupling product as a yellow solid after purification by flash chromatography (8:2 pentane/DCM) of the crude oil.

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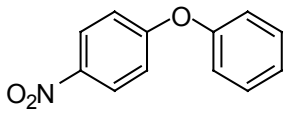
[8] H. Rao, Y. Jin, H. Fu, Y. Jiang, Y. Zhao, *Chem. Eur. J.* **2006**, *12*, 3636-3646.



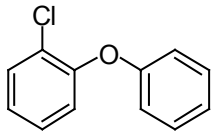
M.p. : 56-57 °C (lit.[4] 58-59 °C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.98-7.03 (m, 2H), 7.07-7.10 (m, 2H), 7.23-7.28 (m, 1H), 7.40-7.46 (m, 2H), 8.16-8.21 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 117.1 (CH), 120.5 (CH), 125.4 (CH), 125.9 (CH), 130.3 (CH), 142.6 (C), 154.6 (C), 163.3 (C).

All spectral data correspond to those given in the literature.

2-Chlorophenyl phenyl ether (3l). Following the general procedure using phenol (100 mg, 1.08 mmol) and 1-chloro-2-iodobenzene (0.20 mL, 1.60 mmol) provided 109 mg (50% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.

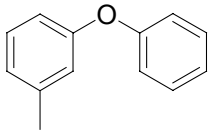


^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.94-7.00 (m, 3H), 7.04-7.12 (m, 2H), 7.17-7.23 (m, 1H), 7.28-7.35 (m, 2H), 7.45 (dt, J = 7.9 Hz, 1.5 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 117.9 (CH), 120.9 (CH), 123.4 (CH), 124.7 (CH), 125.9 (C), 127.9 (CH), 129.8 (CH), 130.8 (CH), 152.5 (C), 157.0 (C).

All spectral data correspond to those of the commercial chemical (CAS Number: 2689-07-8)

3-Methylphenyl phenyl ether[1] (3n). Following the general procedure using phenol (100 mg, 1.08 mmol) and 3-iodotoluene (0.21 mL, 1.60 mmol) provided 177 mg (90% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.

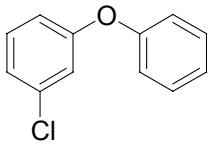


^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 6.78-6.85 (m, 2H), 6.90 (br d, J = 7.7 Hz, 1H), 6.97-7.01 (m, 2H), 7.07 (tt, J = 7.4 Hz, 1.1 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.28-7.33 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.6 (CH_3), 115.9 (CH), 118.9 (CH), 119.6 (CH), 123.1 (CH), 124.1 (CH), 129.4 (CH), 129.7 (CH), 139.9 (C), 157.1 (C), 157.3 (C).

All spectral data correspond to those given in the literature.

3-Chlorophenyl phenyl ether (3o). Following the general procedure using phenol (100 mg, 1.08 mmol) and 1-chloro-3-iodobenzene (0.24 mL, 1.60 mmol) provided 190 mg (87% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.

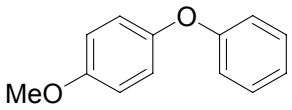


^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.87 (ddd, J = 8.2 Hz, 2.5 Hz, 1.0 Hz, 1H), 6.97-7.06 (m, 4H), 7.13 (tt, J = 7.4 Hz, 1.1 Hz, 1H), 7.17 (t, J = 8.2 Hz, 1H), 7.32-7.37 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 116.7 (CH), 118.8 (CH), 119.4 (CH), 123.2 (CH), 124.0 (CH), 129.9 (CH), 130.5 (CH), 135.0 (C), 156.3 (C), 158.3 (C).

All spectral data correspond to those of the commercial chemical (CAS Number: 6452-49-9).

4-Methoxyphenyl phenyl ether[1] (3p). Following the general procedure using phenol (100 mg, 1.08 mmol) and 4-iodoanisole (378 mg 1.60 mmol) provided 168 mg (78% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.

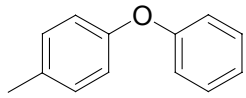


^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.85-7.05 (m, 7H), 7.24-7.32 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 55.7 (CH_3), 114.9 (CH), 117.6 (CH), 120.9 (CH), 122.5 (CH), 129.6 (CH), 150.2 (C), 155.9 (C), 158.6 (C).

All spectral data correspond to those given in the literature.

4-Methylphenyl phenyl ether[1] (3q). Following the general procedure using phenol (100 mg, 1.08 mmol) and 4-iodotoluene (349 mg 1.60 mmol) provided 172 mg (87% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.



^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 6.88-6.93 (m, 2H), 6.95-6.99 (m, 2H), 7.02-7.07 (m, 1H), 7.10-7.14 (m, 2H), 7.26-7.33 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.7 (CH_3), 118.4 (CH), 119.2 (CH), 122.8 (CH), 129.7 (CH), 130.3 (CH), 132.9 (C), 154.8 (C), 157.9 (C).

All spectral data correspond to those given in the literature.

(4-Phenoxy)benzoic acid ethylester[9] (3r). Following the general procedure using phenol (100 mg, 1.08 mmol) and ethyl-4-iodobenzoate (0.27 mL, 1.60 mmol) provided 212 mg (78% yield) of the coupling product as a colorless liquid after purification by flash chromatography (8:2 pentane/DCM) of the crude oil.

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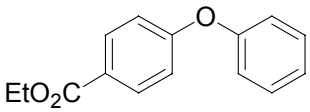
[9] J. A. Campo, M. Cano, J. V. Heras, M. C. Lagunas, J. Perles, E. Pinilla, M. R. Torres, *Helv. Chim. Acta* **2001**, *84*, 2316-2329.

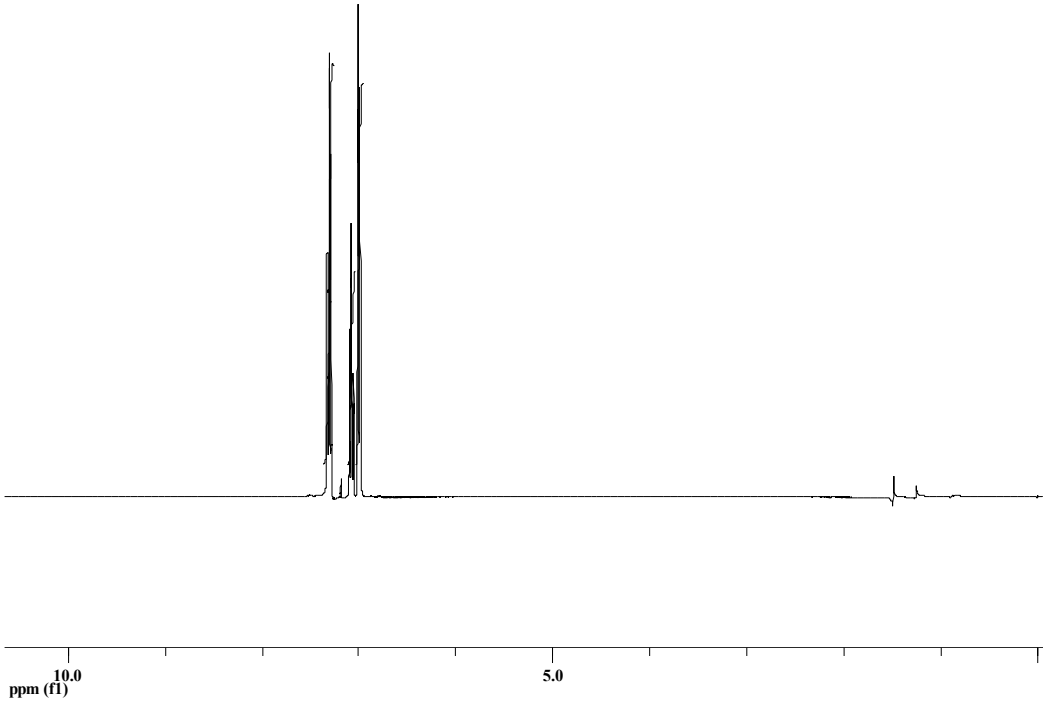


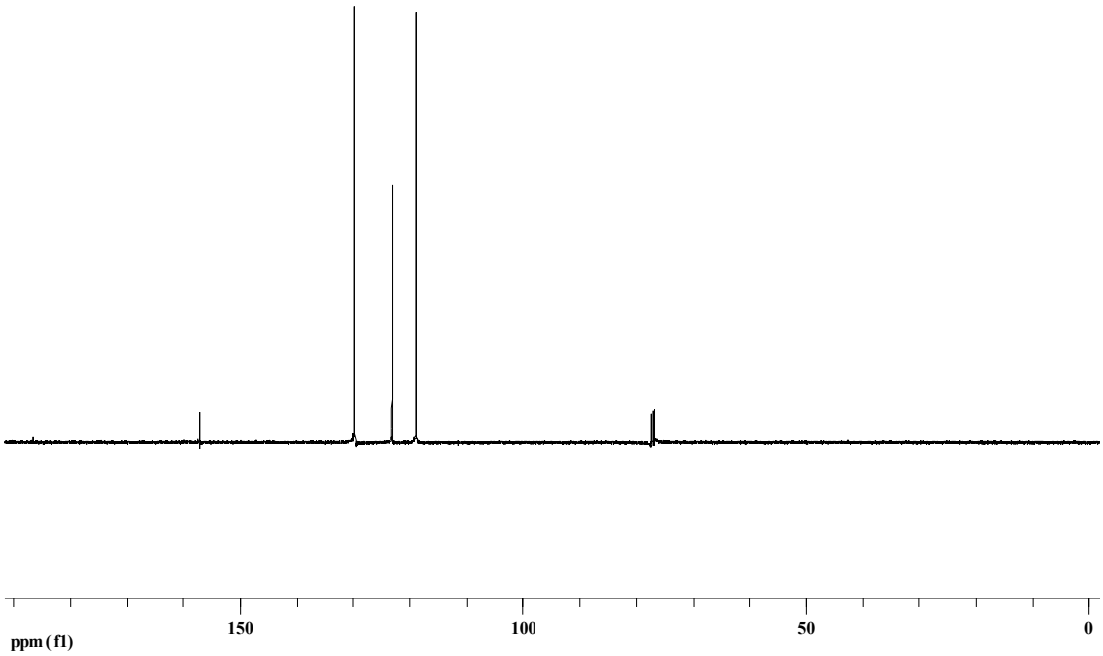
^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J = 7.1 Hz, 3H), 4.35 (q, J = 7.1 Hz, 2H), 6.96-7.00 (m, 2H), 7.04-7.07 (m,2H), 7.15-7.20 (m, 1H), 7.34-7.40 (m, 2H), 7.99-8.03 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.5 (CH_3), 60.9 (CH_2), 124.4 (CH), 124.8 (C=O), 130.0 (CH), 131.6 (CH), 155.6 (C), 161.6 (C), 166.0 (C).

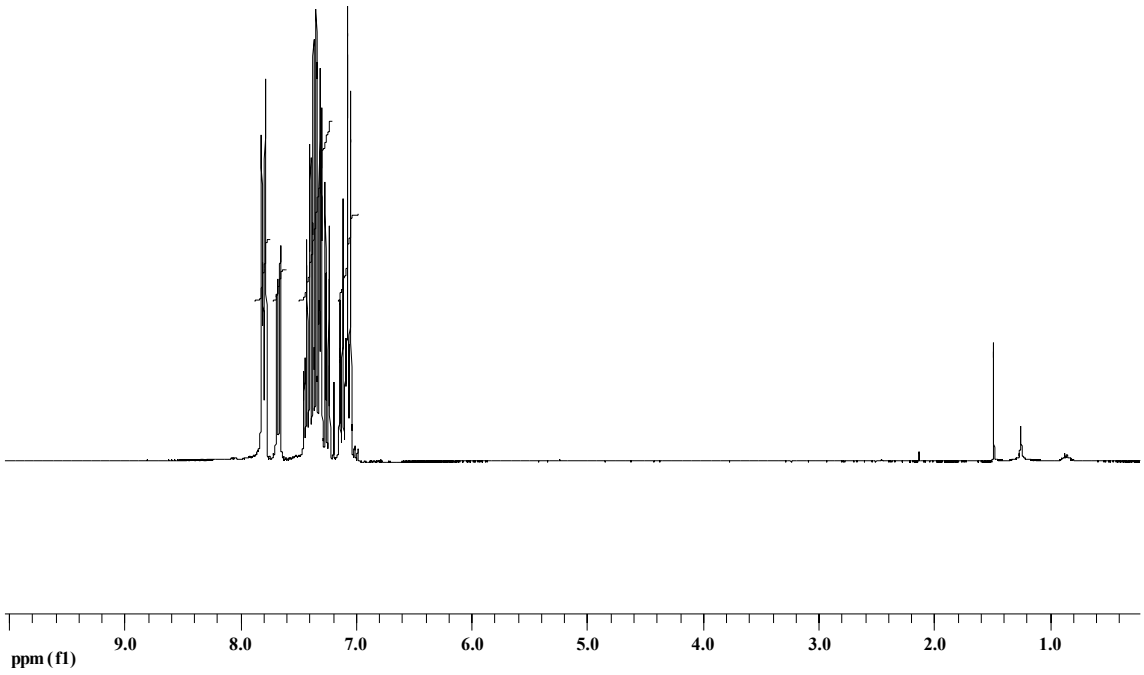
All spectral data correspond to those given in the literature.

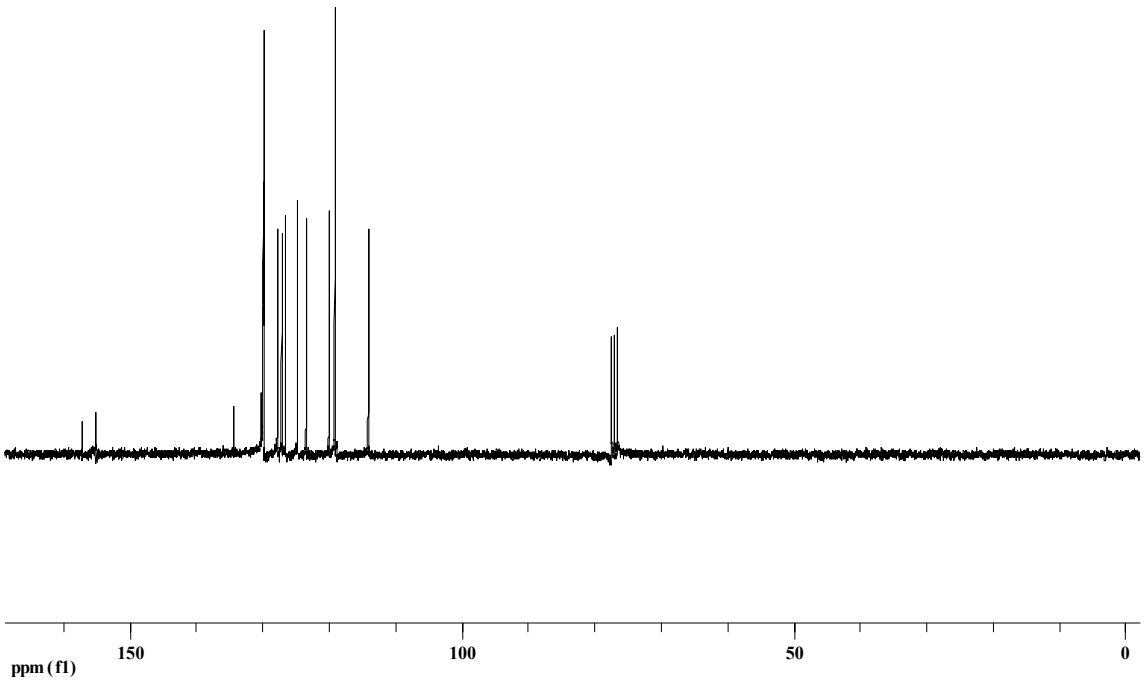
Diphenyl ether (3a)



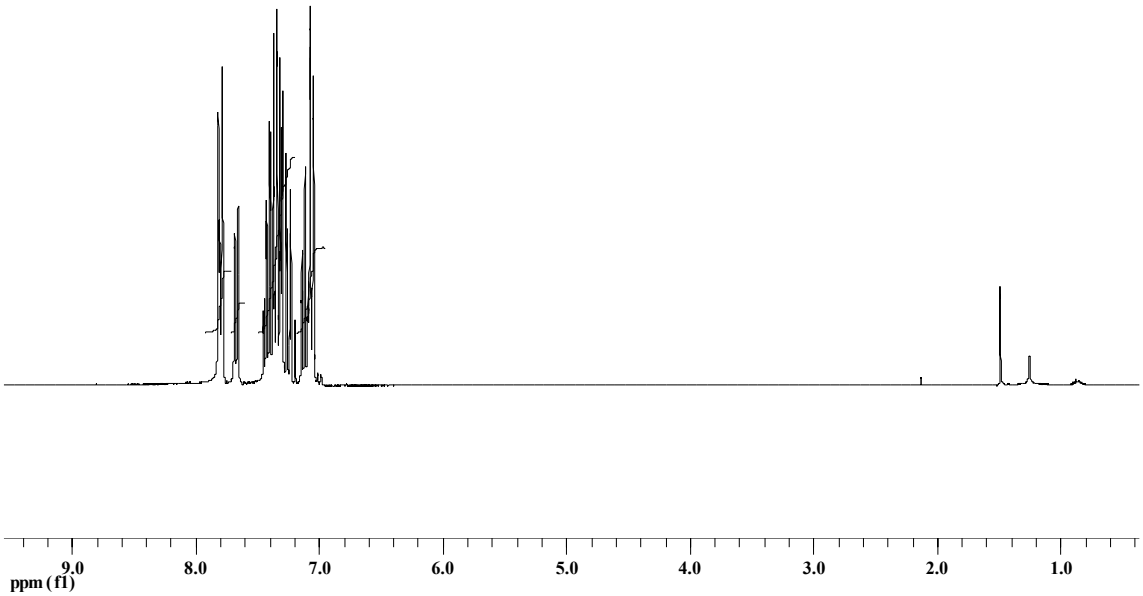


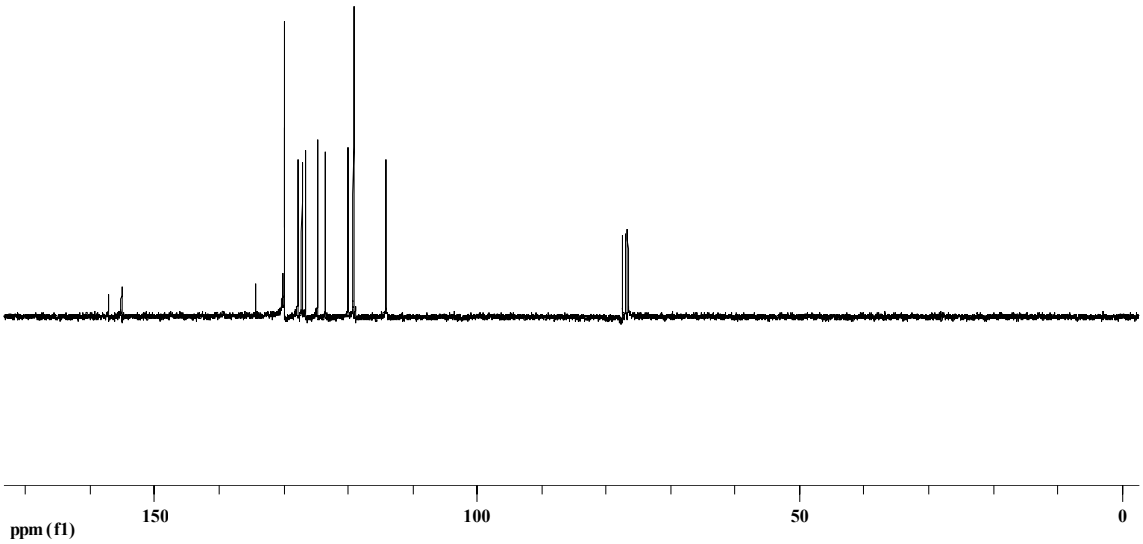
4-phenylphenyl phenyl ether (3b)



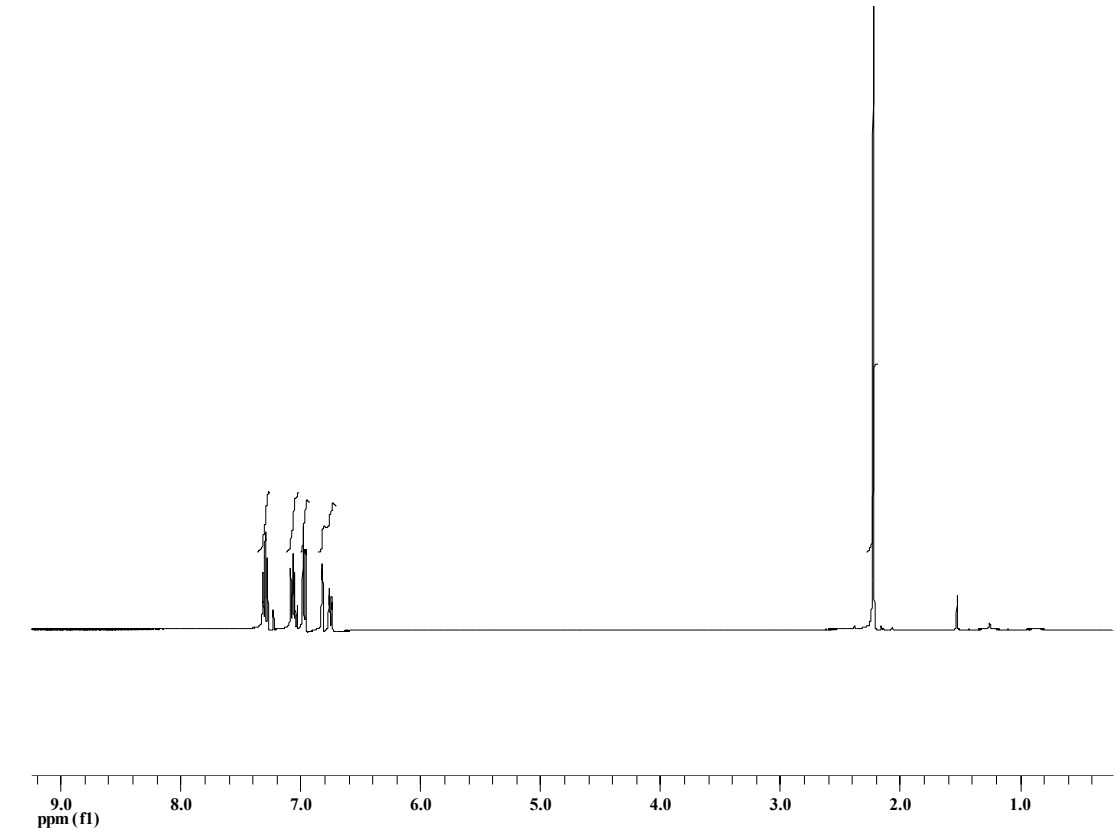


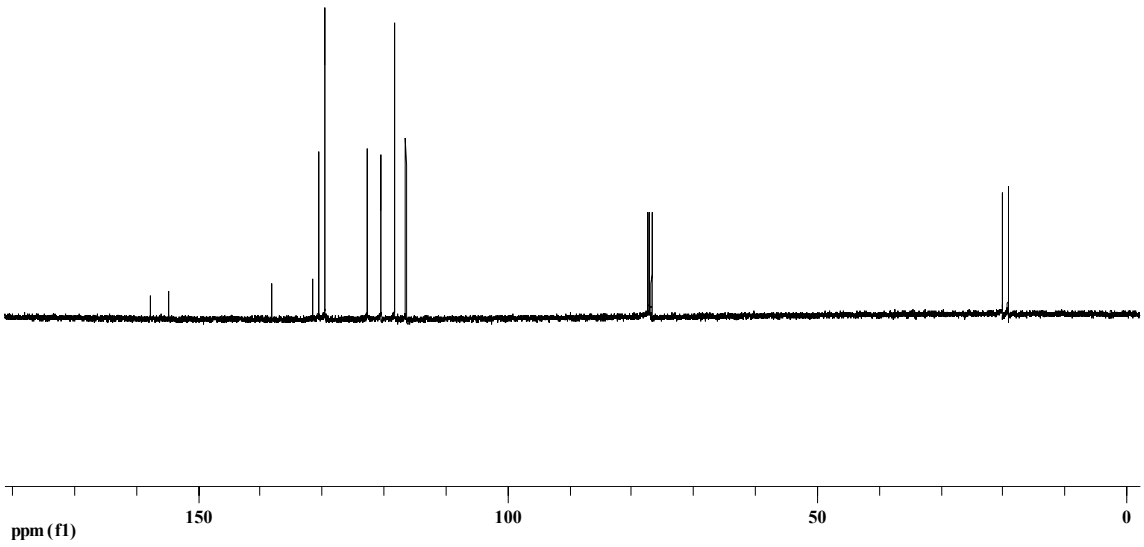
2-Naphthyl phenyl ether (3c)



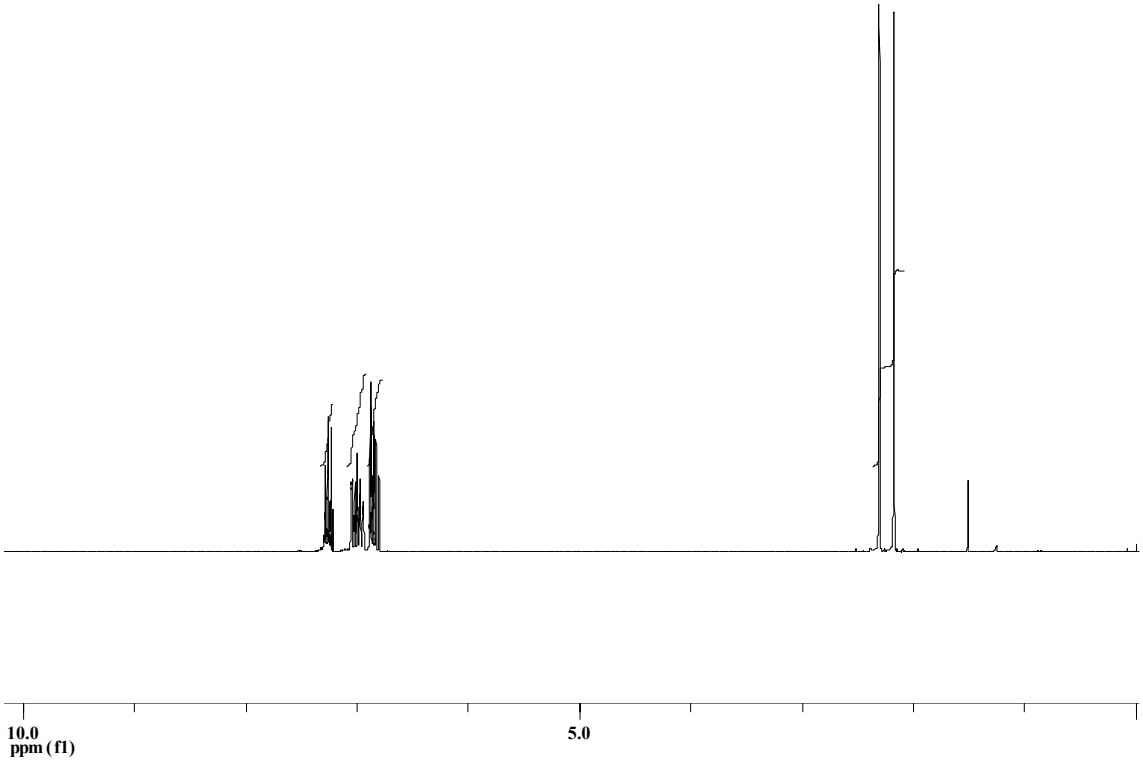


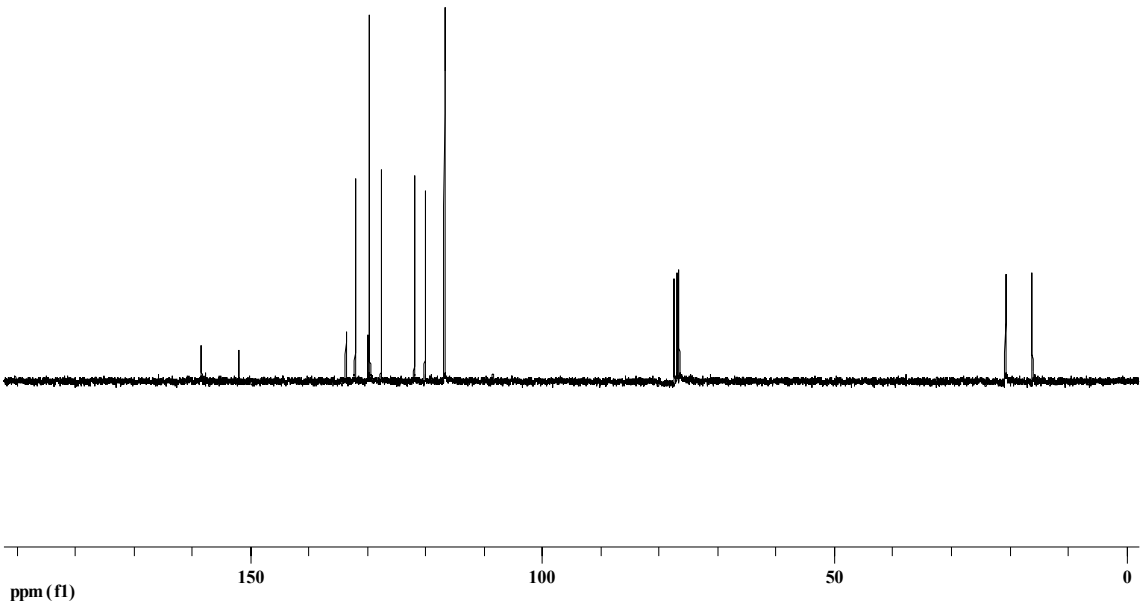
3,4-Dimethylphenyl phenyl ether (3d)



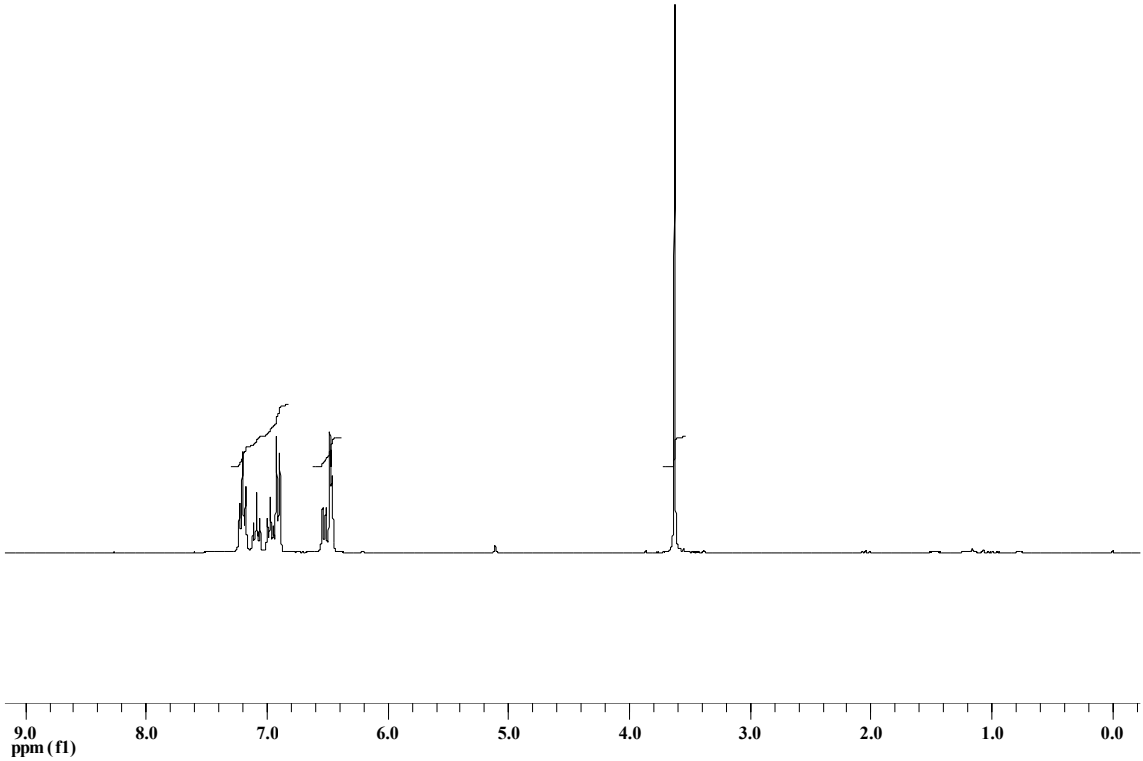


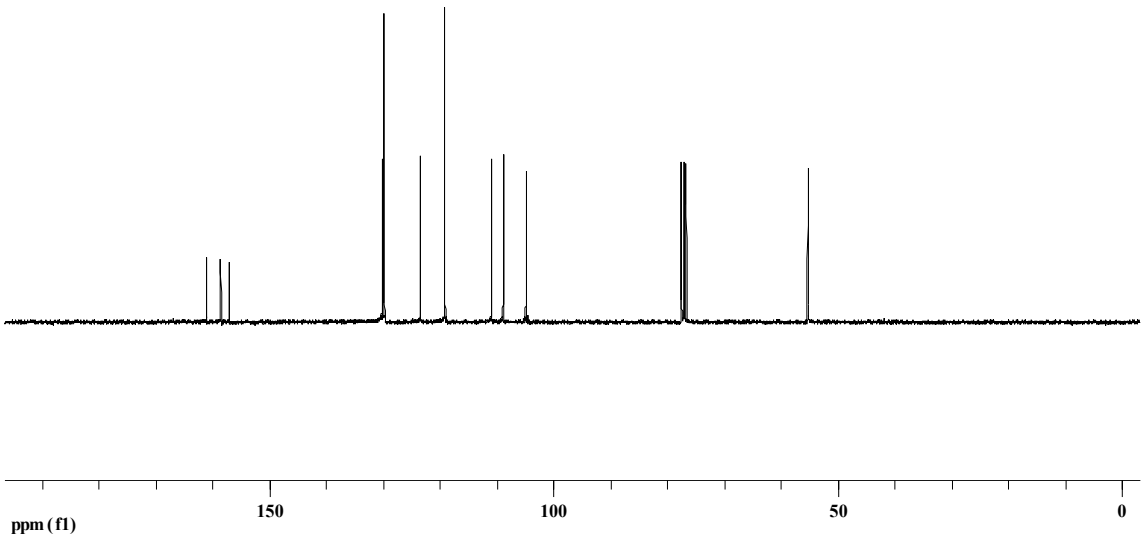
2,4-Dimethylphenyl phenyl ether (3e)



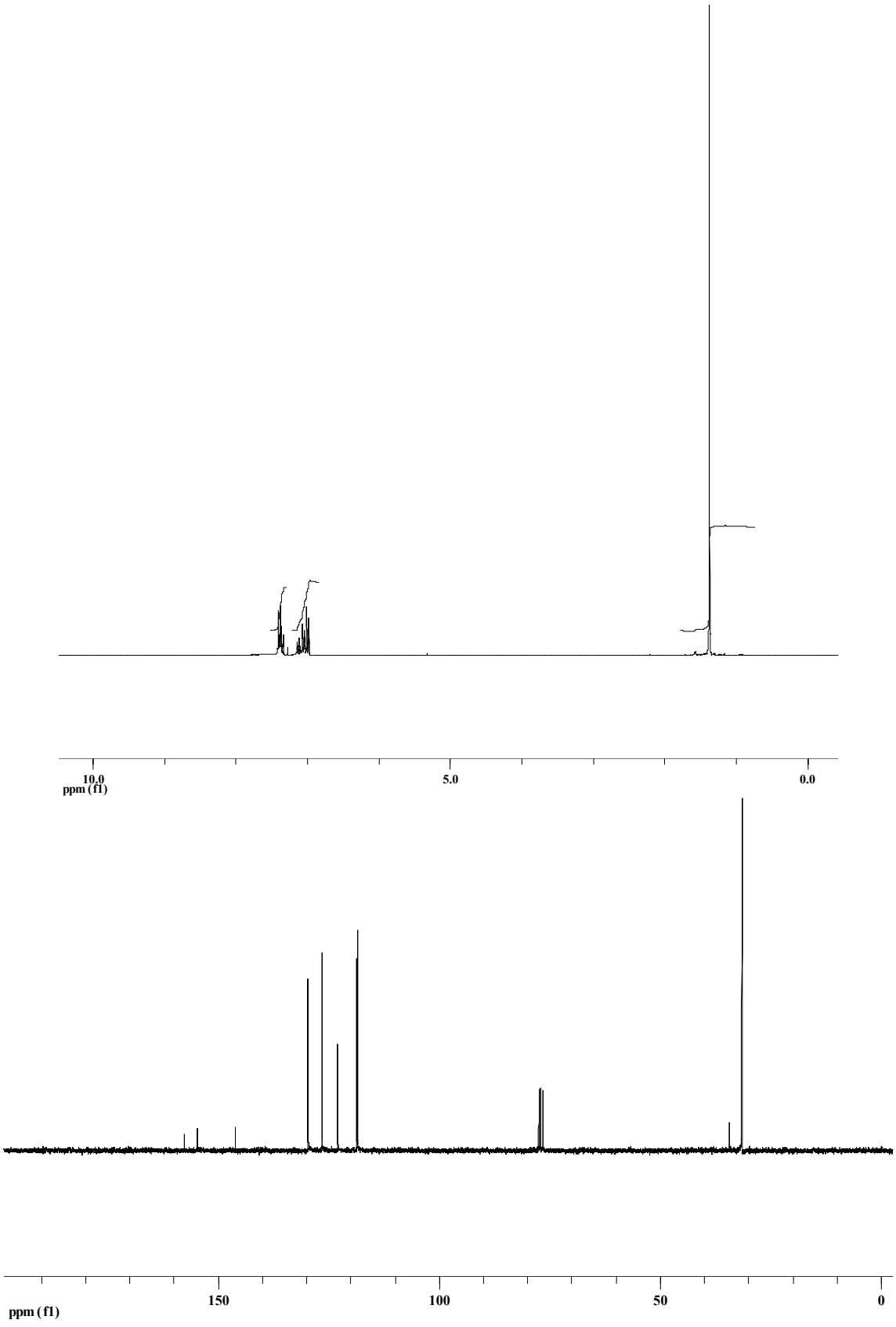


3-Methoxyphenyl phenyl ether (3f)

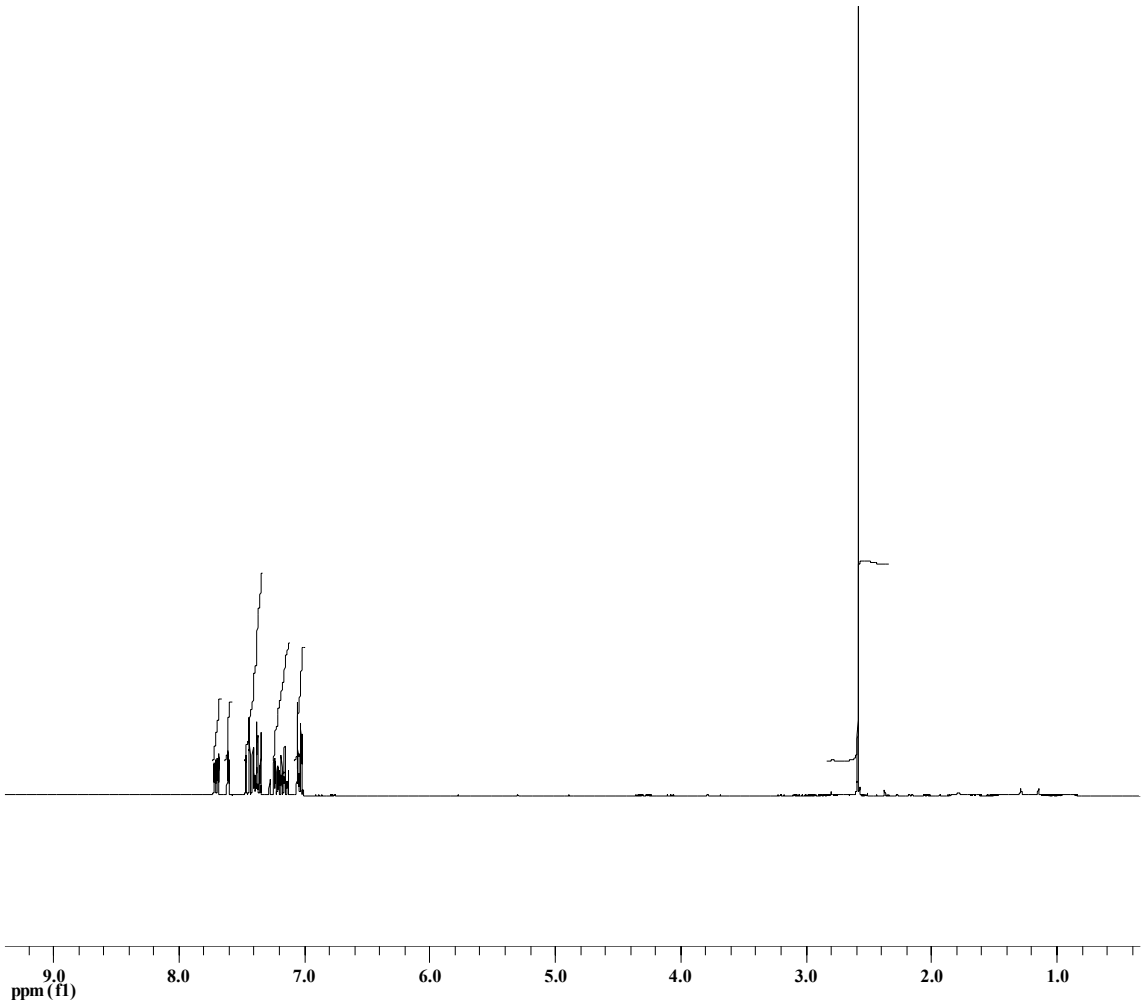


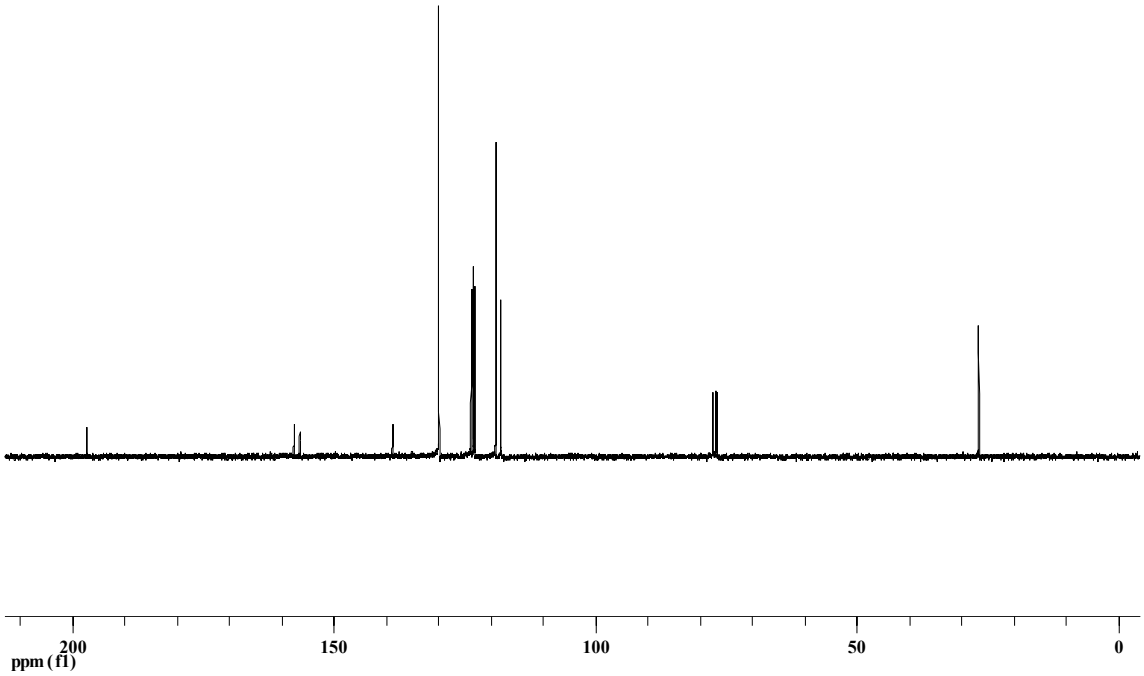


4-^{t}Butylphenyl phenyl ether (3g)

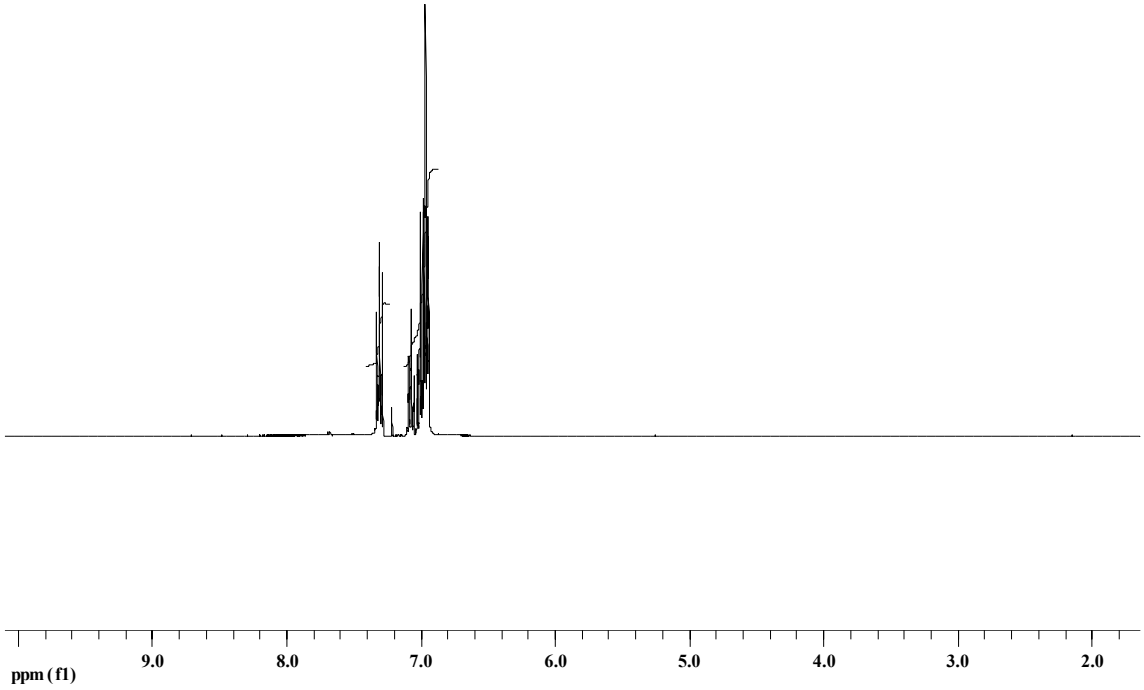


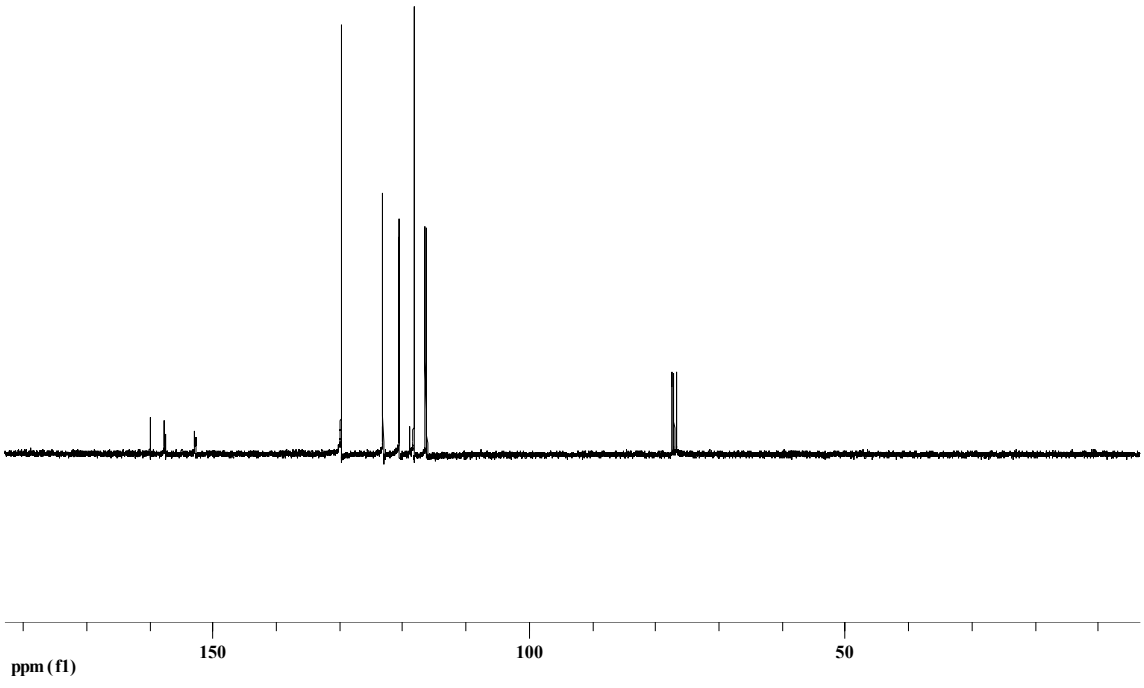
3’-Phenoxyacetophenone (3h)



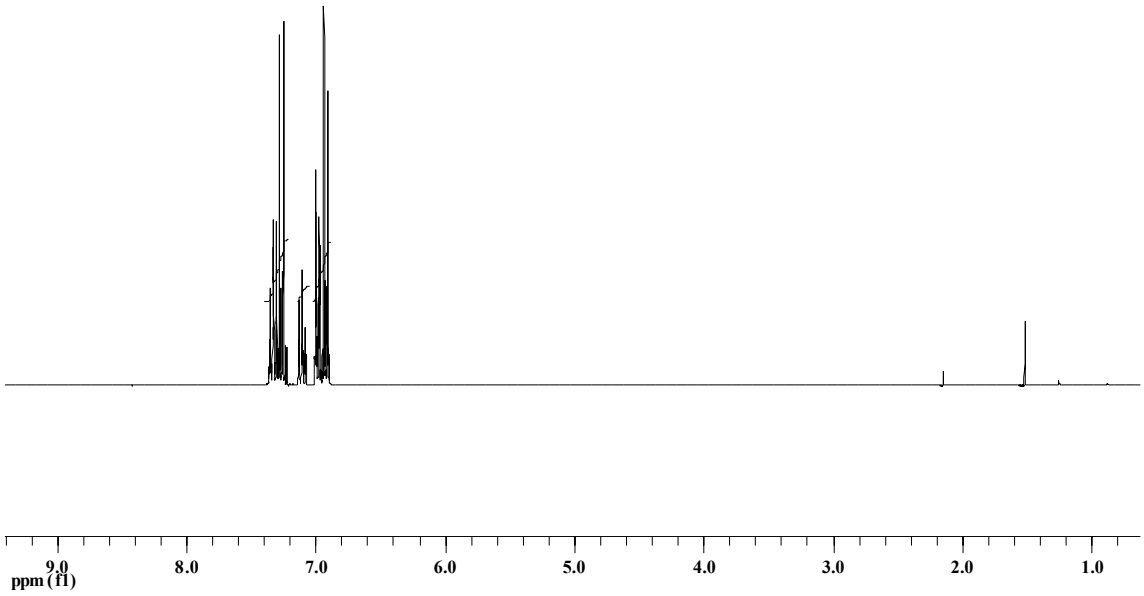


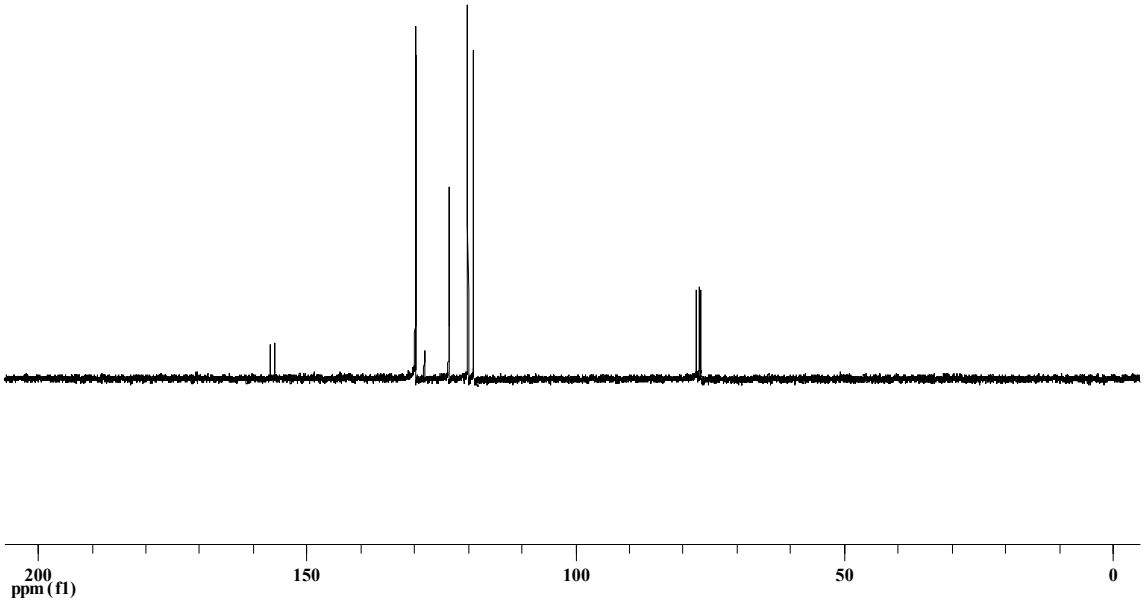
4-Fluorophenyl phenyl ether (3i)



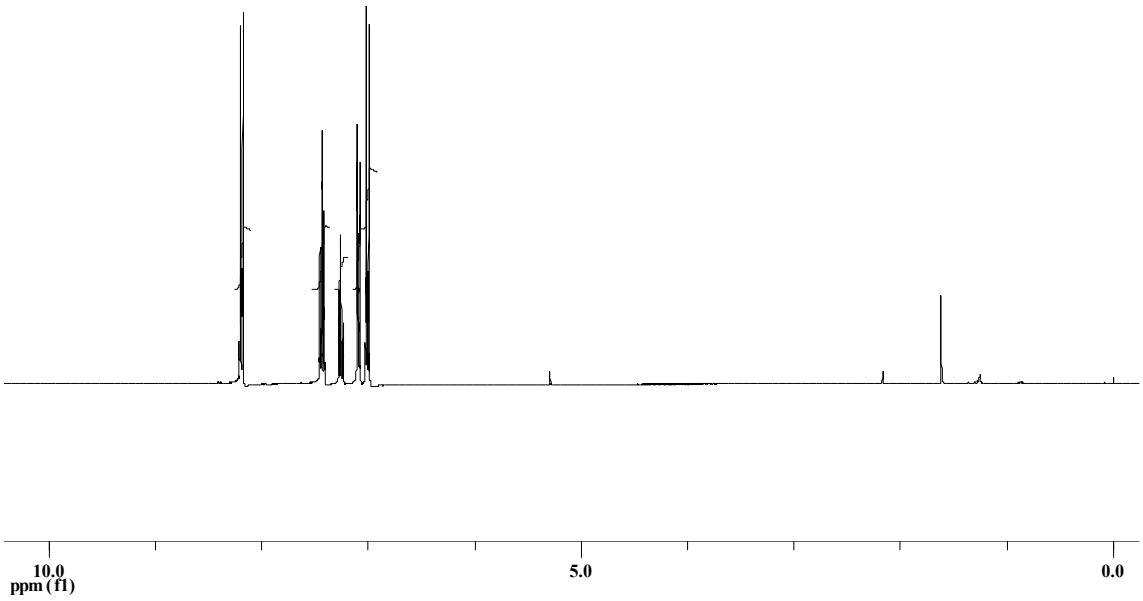


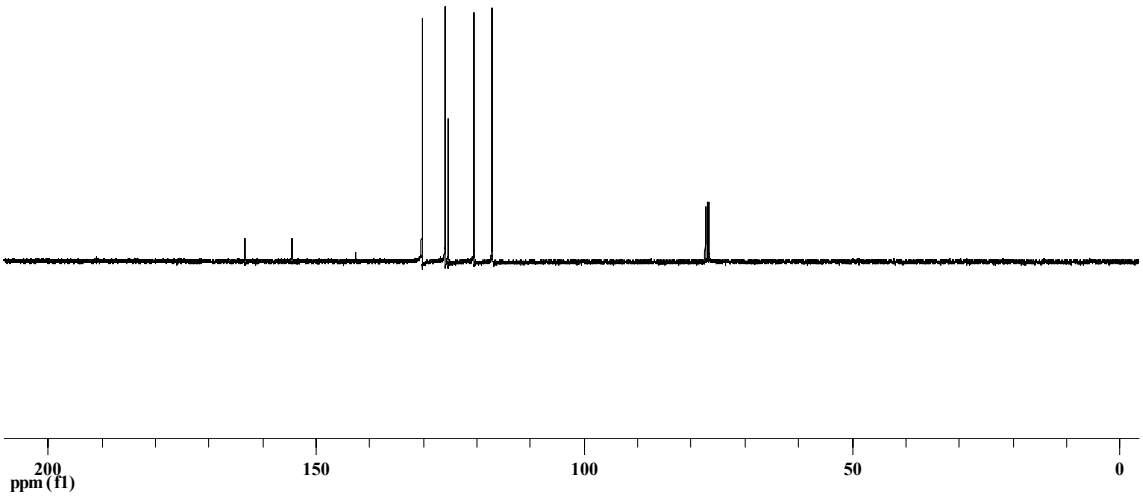
4-Chlorophenyl phenyl ether (3j)



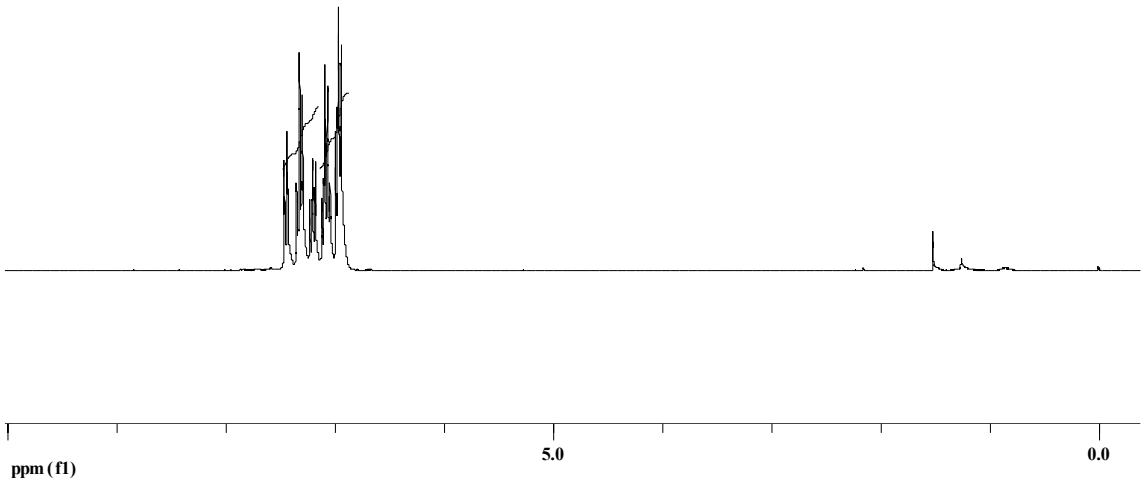


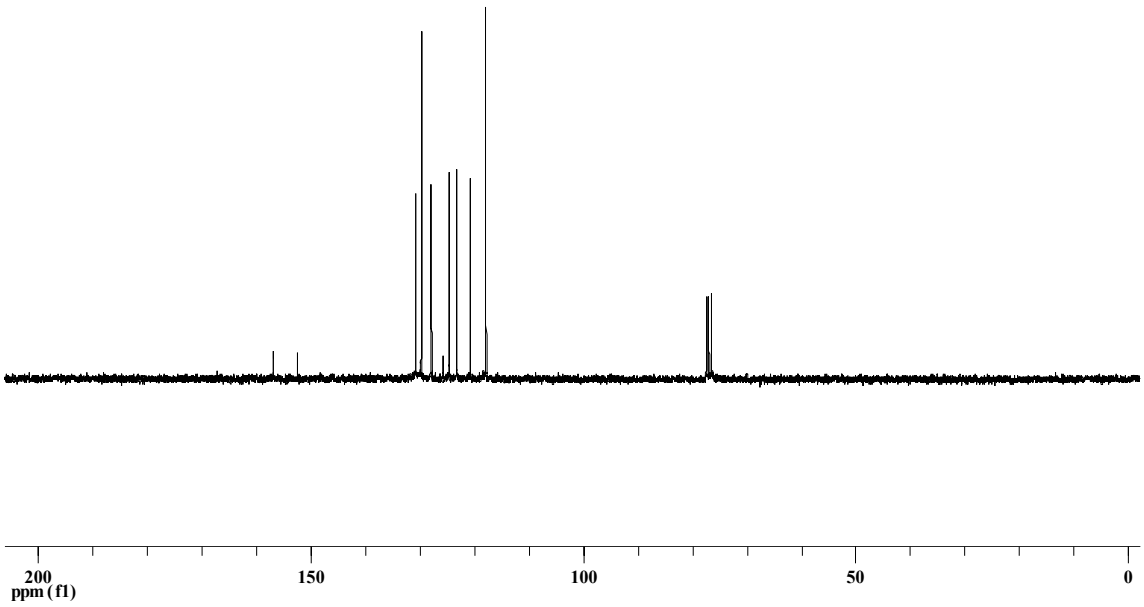
4-Nitrophenyl phenyl ether (3k)



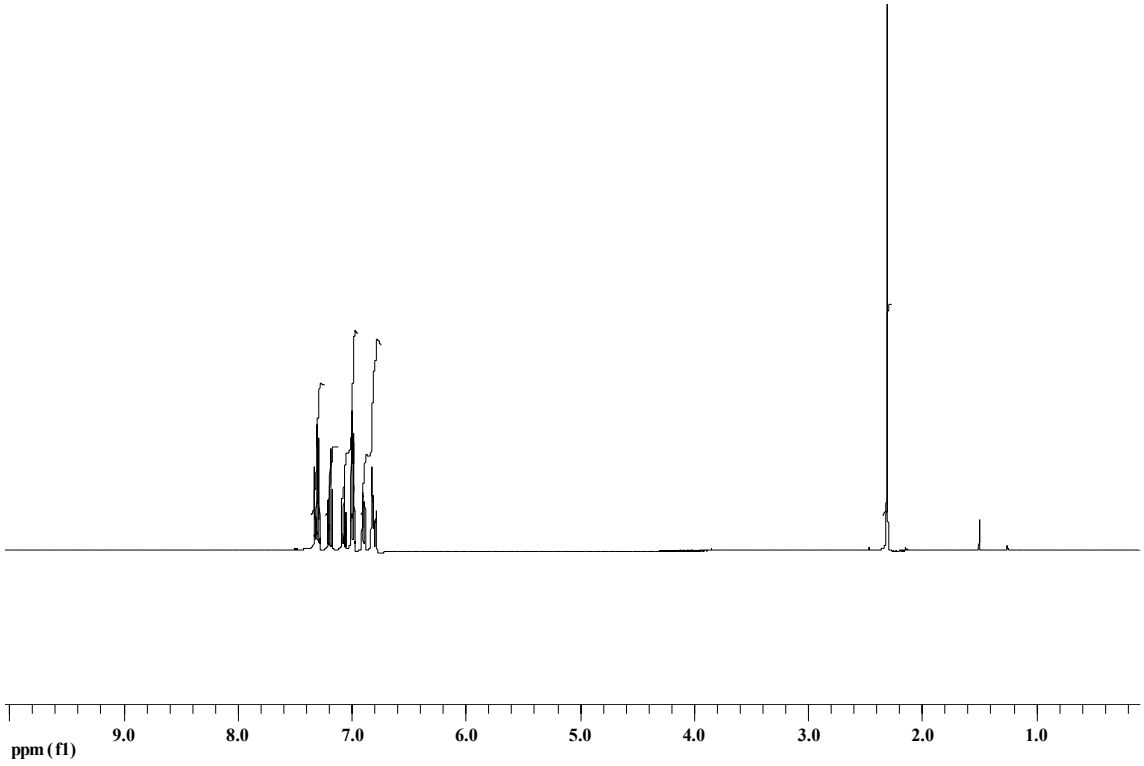


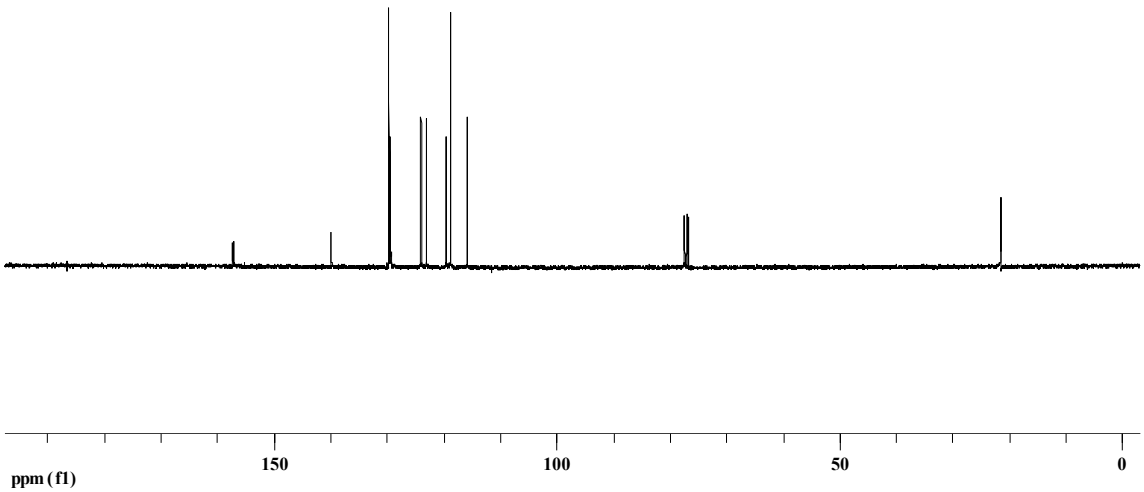
2-Chlorophenyl phenyl ether (3l)



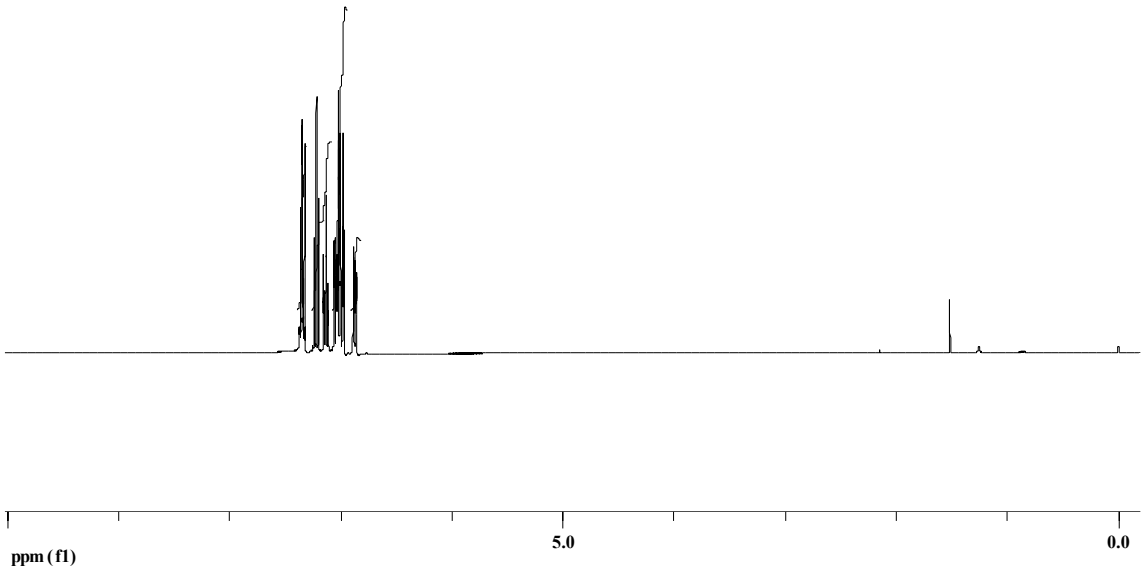


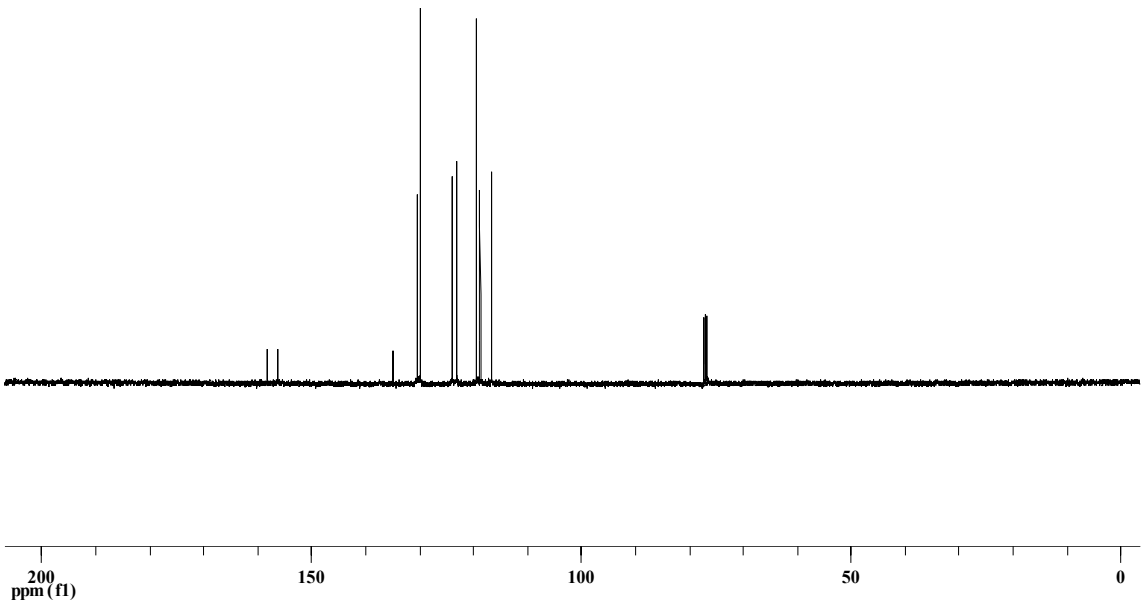
3-Methylphenyl phenyl ether (3n)



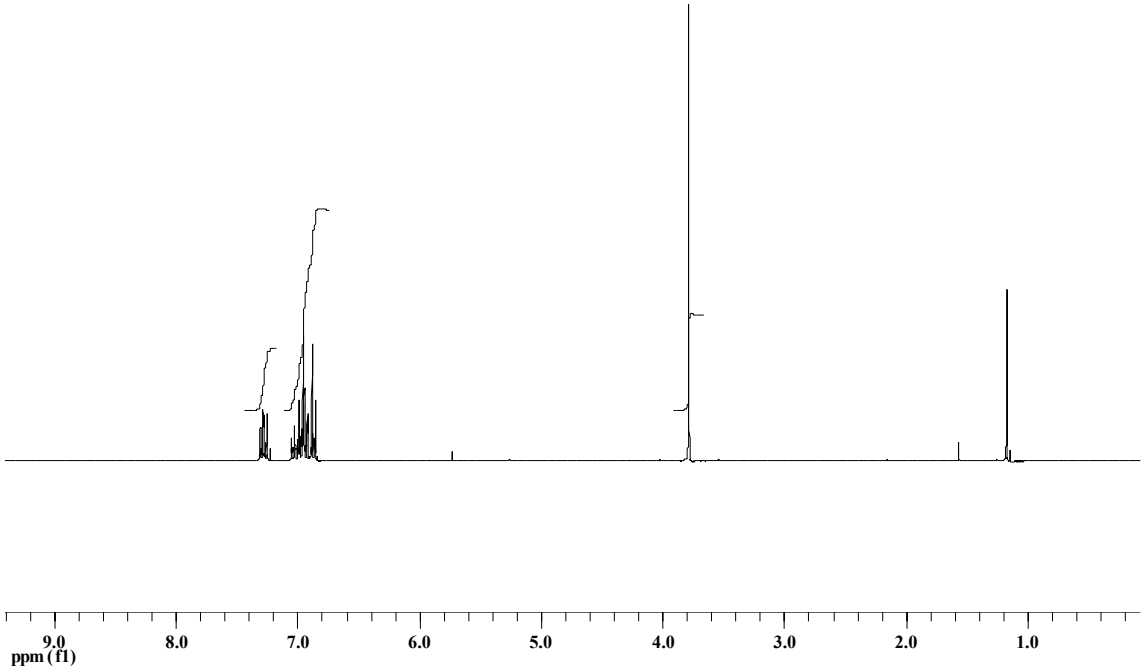


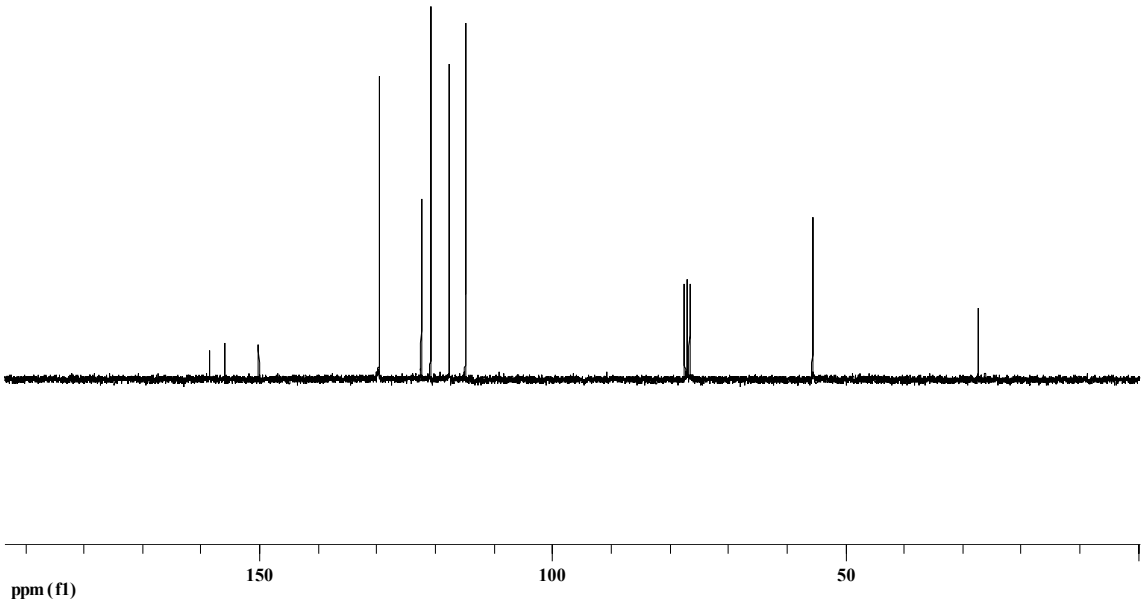
3-Chlorophenyl phenyl ether (3o)



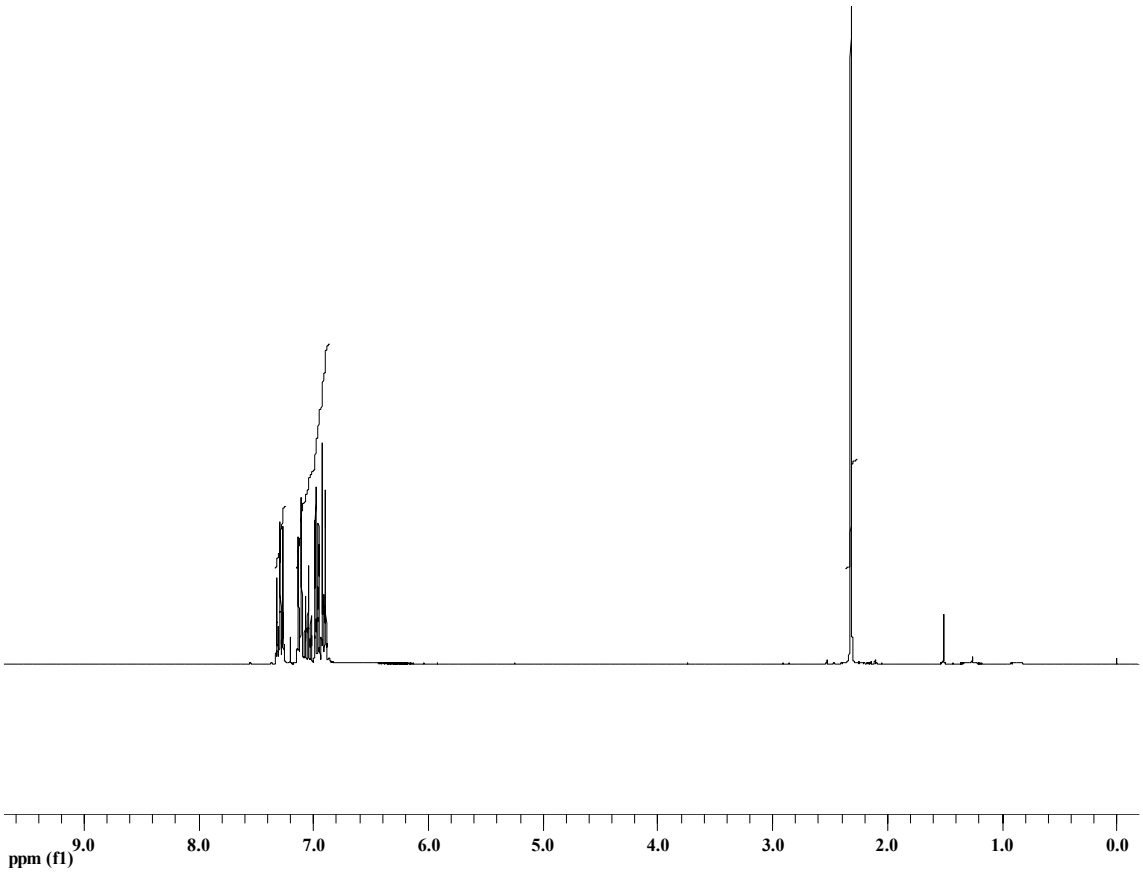


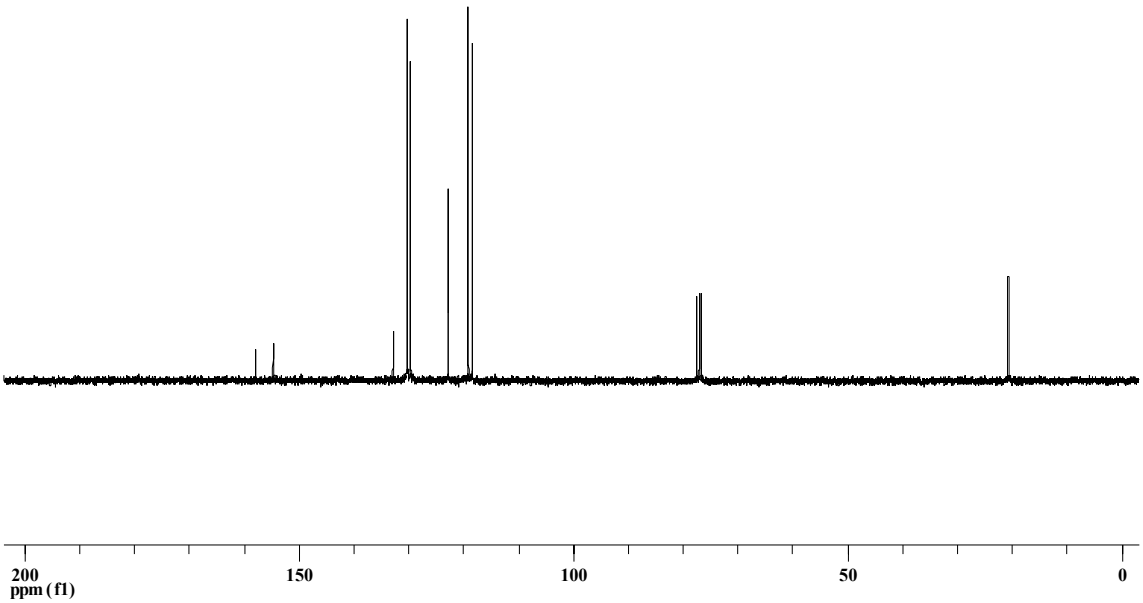
4-Methoxyphenyl phenyl ether (3p)





4-Methylphenyl phenyl ether (3q)





(4-Phenoxy)benzoic acid ethylester (3r)