

Efficient Ullmann-Type C-O Formation Catalyzed by a New

Air-Stable Copper(I)-Bipyridyl Complex

Supporting Information

Jiajia Niu, Hua Zhou, Zhigang Li, Jingwei Xu,^{*} and Shaojing Hu^{*, §}

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China, Changchun 130022, P R China, Graduate School of Chinese Academy of Sciences, and [§]Institute for Diabetes Discovery, Branford, CT 06405, USA

jwxu@ciac.jl.cn and shaojing_hu@betapharma.com

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General Information

All reactions were carried out in sealed test tubes under argon. All the reagents are commercially available and were used without further purification. DMF was distilled under vacuum from CaH_2 . All solid materials were weighed in the air. The copper(I) complexes were characterized by X-ray Single Crystal Diffraction with a CCD diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . Non-hydrogen atoms were refined anisotropically. All products were characterized by ^1H NMR, ^{13}C NMR, GC-MS and elemental analysis. The NMR chemical shifts reported relative to tetramethyl silane (TMS) using residual deuterated solvent signals or TMS as an internal standard. All yields reported in this publication refer to isolated yields (average of two runs) of compounds estimated to be >95% pure as determined by ^1H NMR and GC.

Synthetic details

Preparation of $\text{CuBr}(\text{PPh}_3)_3$

In a flask equipped with a Teflon-coated magnetic stirrer, CuBr (143.5mg, 1 mmol) and triphenylphosphine (768.9mg, 3mmol) was added to dichloromethane (30 ml). The contents of the flask were allowed to stir for 2 hours at room temperature. Afterwards the solvent was removed under dynamic vacuum (rotovap) to afford white solid. Recrystallization was achieved by dissolving the solid in 15 ml of dichloromethane and layered with 15 ml petroleum ether and the solid should be dried in air oven at 100°C (450mg, 77% yield).

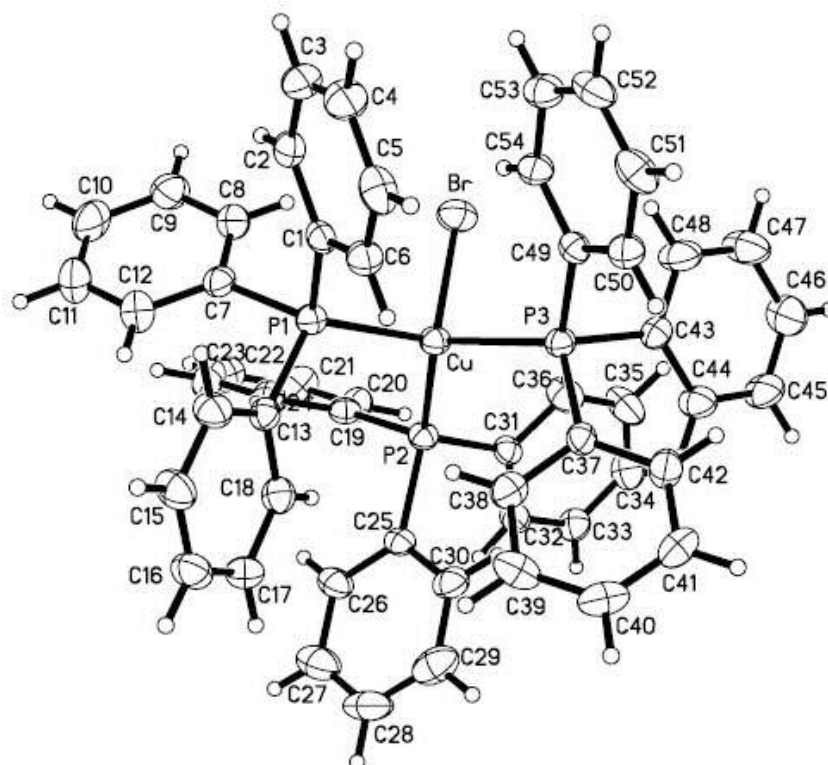


Figure 1: ORTEP figure of $\text{CuBr}(\text{PPh}_3)_3$ (1)

Crystal data

$C_{54}H_{45}BrCuP_3$	$Z = 2$
$M_r = 930.26$	$F_{000} = 956$
Triclinic, $P1$	$D_x = 1.157 \text{ Mg m}^{-3}$
$a = 13.3045 (19) \text{ \AA}$ $\lambda = 0.71073 \text{ \AA}$	Mo $K\alpha$ radiation
$b = 14.323 (2) \text{ \AA}$	Cell parameters from 1578 reflections
$c = 14.830 (2) \text{ \AA}$	$\theta = 2.4\text{--}17.9^\circ$
$\alpha = 71.869 (2)^\circ$	$\mu = 1.28 \text{ mm}^{-1}$
$\beta = 83.843 (3)^\circ$	$T = 298 (2) \text{ K}$
$\gamma = 88.757 (3)^\circ$	Block, red
$V = 2669.9 (7) \text{ \AA}^3$	$0.28 \times 0.21 \times 0.10 \text{ mm}$

Data collection

Bruker APEX CCD area detector diffractometer	10334 independent reflections
Radiation source: fine-focus sealed tube	5349 reflections with $I > 2 \sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.041$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 26.1^\circ$
ϕ and ω scans	$\theta_{\text{min}} = 1.5^\circ$
Absorption correction: Multi-scan SAINT-Plus (Bruker, 2003)	$h = -12 \rightarrow 16$
$T_{\text{min}} = 0.712$, $T_{\text{max}} = 0.879$	$k = -17 \rightarrow 17$
15179 measured reflections	$l = -16 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location:
	difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from
neighbouring sites

$$R[F^2 > 2 \sigma(F^2)] = 0.062$$

H-atom parameters constrained

$$wR(F^2) = 0.143$$
$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2]$$

$$S = 0.85$$

$$(\Delta/\sigma)_{\max} < 0.001$$

10334 reflections

$$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$$

532 parameters

$$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$$

Primary atom site location:

Extinction correction: none

structure-invariant direct methods

Preparation of CuBr(bpy)(PPh₃)

This complex was adapted from the synthesis reported by Barron and coworkers¹.

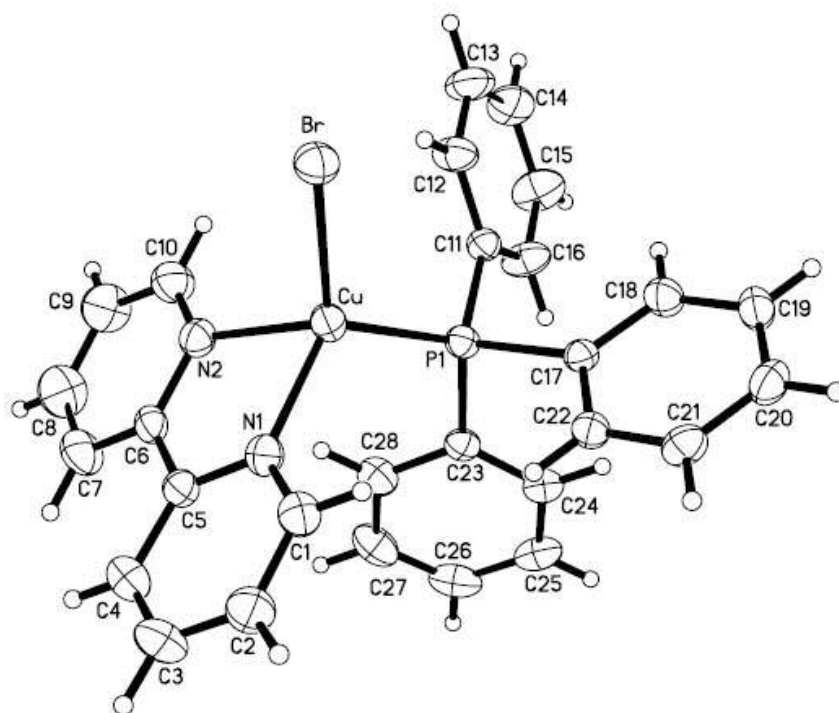


Figure 2: ORTEP figure of CuBr(bpy)(PPh₃) (2)

Crystal data



$$F_{000} = 2272$$

$$M_r = 561.90$$

$$D_x = 1.502 \text{ Mg m}^{-3}$$

Monoclinic, $C2/c$

$$\lambda = 0.71073 \text{ \AA}$$

$$a = 33.585 (6) \text{ \AA}$$

$$b = 9.3792 (16) \text{ \AA}$$

$$c = 18.854 (3) \text{ \AA}$$

$$\beta = 123.208 (2)^\circ$$

$$V = 4969.0 (15) \text{ \AA}^3$$

$$Z = 8$$

Mo $K\alpha$ radiation

Cell parameters from 2784 reflections

$$\theta = 2.3\text{--}21.9^\circ$$

$$\mu = 2.57 \text{ mm}^{-1}$$

$$T = 293 (2) \text{ K}$$

Prism, red

$$0.32 \times 0.26 \times 0.14 \text{ mm}$$

Data collection

Bruker APEX CCD area detector
diffractometer

2599 independent reflections

Radiation source: fine-focus sealed tube

2269 reflections with $I > 2\sigma(I)$

Monochromator: graphite

$$R_{\text{int}} = 0.030$$

$$T = 293(2) \text{ K}$$

$$\theta_{\text{max}} = 20.8^\circ$$

ϕ and ω scans

$$\theta_{\text{min}} = 1.5^\circ$$

Absorption correction: multi-scan
SAINT-Plus (Bruker, 2003)

$$h = -33 \rightarrow 33$$

$$T_{\text{min}} = 0.493, T_{\text{max}} = 0.707$$

$$k = -9 \rightarrow 8$$

8469 measured reflections

$$l = -18 \rightarrow 16$$

Refinement

Refinement on F^2

Secondary atom site location: difference
Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from
neighbouring sites

$$R[F^2 > 2\sigma(F^2)] = 0.028$$

H-atom parameters constrained

$$wR(F^2) = 0.071$$

where $P = (F_o^2 + 2F_c^2)/3$

$$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 1.772P]$$

$$S = 1.03$$

$$(\Delta/\sigma)_{\max} = 0.001$$

2599 reflections

$$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$$

298 parameters

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

Primary atom site location:

Extinction correction: none

structure-invariant direct methods

Preparation of $\text{Cu}(\text{bpy})_2\text{BF}_4$

Acetonitrile was distilled under nitrogen from CaH_2 and stored on 3 Å activated molecular sieves under a nitrogen atmosphere. The starting materials $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4^2$ and 2,2'-bipyridyl was recrystallized in acetonitrile prior to use. In a flask equipped with a Teflon-coated magnetic stirrer, $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ (1mmol) and 2,2'-bipyridyl (2mmol) was added to acetonitrile (10ml). The contents of the flask were allowed to stir for 30 minutes at room temperature. Afterwards the solvent was removed under dynamic vacuum (rotovap) to afford 420mg red solid without further purification. (91% yield)

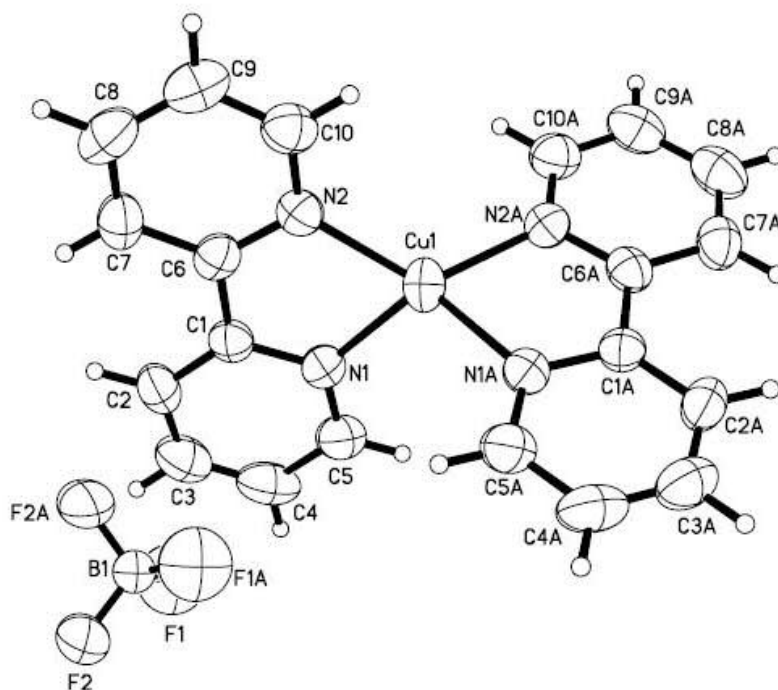
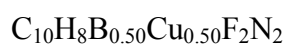


Figure 3: ORTEP figure of $\text{Cu}(\text{bpy})_2\text{BF}_4$ (**3**)

Crystal data



$$D_x = 1.502 \text{ Mg m}^{-3}$$

$$M_r = 231.36$$

Mo $K\alpha$ radiation

$$\lambda = 0.71073 \text{ \AA}$$

Orthorhombic, $C2_22(1)$	Cell parameters from 1922 reflections
$a = 10.937 (3) \text{ \AA}$	$\theta = 2.2\text{--}20.9^\circ$
$b = 20.414 (6) \text{ \AA}$	$\mu = 1.12 \text{ mm}^{-1}$
$c = 9.167 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$V = 2046.7 (10) \text{ \AA}^3$	Block, red
$Z = 8$	$0.32 \times 0.13 \times 0.10 \text{ mm}$
$F_{000} = 936$	

Data collection

Bruker APEX CCD area detector diffractometer	2032 independent reflections
Radiation source: fine-focus sealed tube	1550 reflections with $I > 2 \sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.023$
$T = 293(2) \text{ K}$	$\theta_{\text{max}} = 26.1^\circ$
ϕ and ω scans	$\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan SAINT-Plus (Bruker, 2003)	$h = -11 \rightarrow 13$
$T_{\text{min}} = 0.716, T_{\text{max}} = 0.899$	$k = -14 \rightarrow 24$
5760 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2 \sigma(F^2)] = 0.065$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1443P)^2]$
$wR(F^2) = 0.204$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.04$	$\Delta \rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$

2032 reflections	$\Delta \rho_{\min} = -0.50 \text{ e } \text{\AA}^{-3}$
129 parameters	Extinction correction: none
Primary atom site location:	Absolute structure: Flack H D (1983), Acta
structure-invariant direct methods	Cryst. A39, 876-881
Secondary atom site location:	Flack parameter: $-0.01 (4)$
difference Fourier map	

Experiment details and Characterization data of the product

General procedure for the O-arylation of phenols under catalysis of **3**.

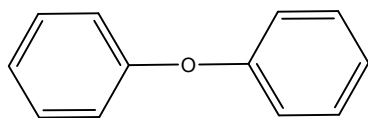
3 (0.5-5 mol %), phenol (1.5 mmol), aryl halide (if solid, 1 mmol), and K_3PO_4 (425mg, 2.0mmol) were added to a screw-capped Schlenk tube under argon. The tube was then evacuated and backfilled with argon (3 cycles). Aryl halide (if liquid, 1.0 mmol) and dry DMF (0.5 ml) were added by syringe at room temperature. The reaction mixture was stirred at needed temperature (90°C or 110°C) for 24h. The reaction mixture was allowed to reach room temperature and then diluted with dichloromethane (10 ml). The slurry was filtered and filter cake was washed with 10 ml dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure for the O-arylation of aliphatic alcohols under catalysis of **3**.

3 (5 mol %), aryl halide (if solid, 1 mmol), and K_3PO_4 (425mg, 2.0mmol) were added to a screw-capped Schlenk tube under argon. The tube was then evacuated and backfilled with argon (3 cycles). Aryl halide (if liquid, 1.0 mmol) and alcohol (1 ml) were added by syringe at room temperature. The reaction mixture was stirred at 110°C for 24h. The reaction mixture was allowed to reach room temperature and then diluted with dichloromethane (10 ml). The slurry was filtered and filter cake was washed with 10 ml dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired product.

Characterization data of the product

(1)



Diphenyl ether (table 1, entry 1)³

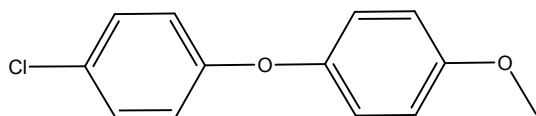
^1H NMR (600 MHz, CDCl_3): δ 7.32-7.35(m, 4H) 7.10(t, $J=7.2\text{Hz}$, 2H), 7.01(dd,

$J=9.0\text{Hz}$, $J=1.2\text{Hz}$, 4H) ppm. ^{13}C NMR (600 MHz, CDCl_3): δ 157.2, 129.7, 123.2,

118.9 ppm. MS m/z 170(M^+), 141, 77, 65, 51, 39. Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}$: C, 84.68;

H, 5.92 Found: C, 84.56; H, 5.90.

(2)



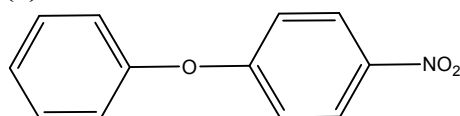
4-Chloro-4'-methoxydiphenylether (table 1, entry 2) ⁴

¹H NMR (600 MHz, CDCl₃): δ 7.23-7.25(m, 2H), 6.95-6.97(m, 2H), 6.86-6.89(m,

4H), 3.80(s, 3H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 157.2, 156.1, 149.8, 129.5,

127.3, 120.8, 118.7, 114.9, 55.6, MS *m/z* 236, 234(M⁺), 221, 219, 140, 111, 95, 75, 63, 50. Anal. Calcd. for C₁₃H₁₁ClO₂: C, 66.53; H, 4.72 Found: C, 66.49; H, 4.85.

(3)

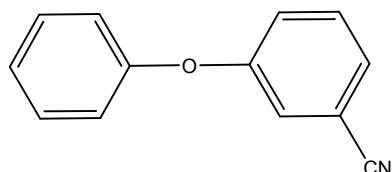


4-Nitrodiphenylether (table 1, entry 3, 5) ³

¹H NMR (600 MHz, CDCl₃): δ 8.20(d, J=9.0Hz, 2H), 7.44(m, 2H), 7.25-7.27(m, 1H), 7.09(d, J=7.2Hz, 2H), 7.01(d, J=9.6Hz, 2H) ppm. ¹³C NMR (600 MHz, CDCl₃):

δ 163.4, 154.7, 142.7, 130.3, 125.9, 125.4, 120.5, 117.1 ppm. MS *m/z* 215 (M⁺), 185, 141, 129, 115, 77, 63, 51. Anal. Calcd. for C₁₂H₉NO₃: C, 66.97; H, 4.22; N, 6.51 Found: C, 66.94; H, 4.11; N, 6.63

(4)



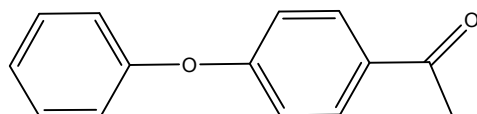
3-Nitrilediphenylether (table 1, entry 4) ⁵

¹H NMR (600 MHz, CDCl₃): δ 7.39-7.43(m, 3H), 7.35(d, J=7.2Hz, 1H), 7.20-7.24(m,

3H), 7.03(d, J=7.8Hz, 2H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 158.1, 155.5, 130.6,

130.2, 126.4, 124.7, 122.7, 121.0, 119.7, 118.2, 113.5 ppm. MS *m/z* 195 (M⁺) 167, 140, 102, 77, 63, 51, 39. Anal. Calcd. for C₁₃H₉NO: C, 79.98; H, 4.65; N, 7.17 Found: C, 79.91; H, 4.61; N, 7.02

(5)

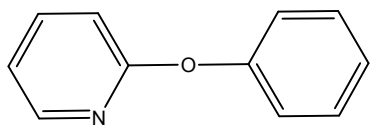


4-Acetyldiphenylether (table 1, entry 6) ⁶

¹H NMR (600 MHz, CDCl₃): δ 7.94(d, J=10.4Hz, 2H), 7.39(m, 2H), 7.20(t, J=7.2Hz,

1H), 7.07(d, J=7.8Hz, 2H), 7.00(d, J=9.0Hz, 2H), 2.57(s, 3H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 196.7, 161.9, 155.5, 131.9, 130.6, 130.0, 124.6, 120.2, 117.3, 26.4 ppm. MS *m/z* 212(M⁺), 197, 141, 115, 99, 77, 63, 51, 43, 39. Anal. Calcd. for C₁₄H₁₂O₂: C, 79.22; H, 5.70 Found: C, 79.19; H, 5.85.

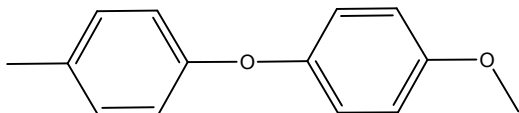
(6)



2-Phenoxypyridine (table 1, entry 7) ⁷

¹H NMR (600 MHz, CDCl₃): δ 8.21(m, 1H), 7.68(m, 1H), 7.14-7.40(m, 5H), 6.99(m, 1H), 6.90(d, J=7.8Hz, 1H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 163.7, 154.1, 147.7, 139.4, 129.6, 124.6, 121.1, 118.4, 111.5 ppm. MS *m/z* 170 (M⁺), 143, 115, 85, 78, 51, 39. Anal. Calcd. for C₁₁H₉NO: C, 77.17; H, 5.30; N, 8.18 Found: C, 77.27; H, 5.16; N, 8.15

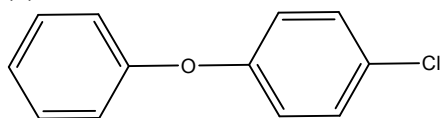
(7)



4-Methoxy-4'-methyl-diphenylether (table 1, entry 8) ⁸

¹H NMR (600 MHz, CDCl₃): δ 7.09(d, J=8.4Hz, 2H), 6.95(d, J=8.4Hz, 2H), 6.84-6.87(m, 4H), 3.79(s, 3H), 2.31(s, 3H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 156.1, 155.6, 150.7, 132.0, 130.1, 120.3, 117.8, 114.8, 55.6, 20.6 ppm. MS *m/z* 214 (M⁺), 199, 171, 143, 128, 91, 77, 65, 39 Anal. Calcd. for C₁₄H₁₄O₂: C, 78.48; H, 6.59 Found: C, 78.44; H, 6.40.

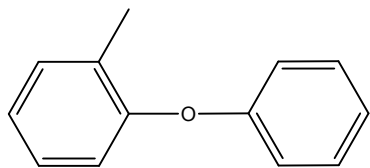
(8)



4-Chloro-diphenylether (table 1, entry 9) ⁶

¹H NMR (600 MHz, CDCl₃): δ 7.33-7.36(m, 2H), 7.27-7.29(m, 2H), 7.12(t, J=7.8Hz, 1H), 6.99(dd, J=8.4Hz, J=1.2Hz, 2H), 6.93-6.95(m, 2H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 156.9, 155.9, 129.9, 129.7, 128.2, 123.6, 120.0, 118.9 ppm. MS *m/z* 206, 204 (M⁺), 169, 141, 115, 77, 51, 39 Anal. Calcd. for C₁₂H₉ClO: C, 70.43; H, 4.43 Found: C, 70.32; H, 4.26.

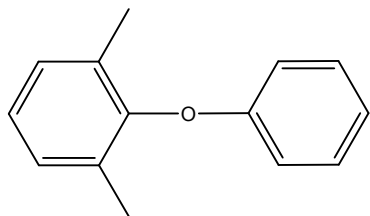
(9)



2-Methyl-diphenylether (table 2, entry 1, 2, 4) ³

¹H NMR (600 MHz, CDCl₃): δ 7.29(m, 2H), 7.24-7.26(m, 1H), 7.16(t, J=7.2Hz, 1H), 7.04-7.07(m, 2H), 6.89-6.90(m, 3H), 2.24(s, 3H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 157.9, 154.4, 131.4, 130.0, 129.6, 127.1, 123.9, 122.3, 119.8, 117.3, 16.2 ppm. MS *m/z* 184(M⁺), 165, 141, 106, 91, 78, 65, 51, 39 Anal. Calcd. for C₁₃H₁₂O: C, 84.75; H, 6.57 Found: C, 84.60; H, 6.66.

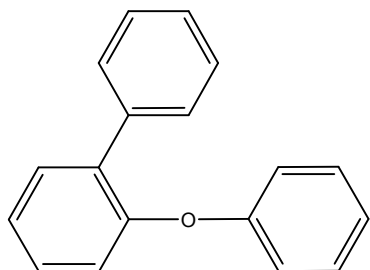
(10)



2,6-Dimethyl-diphenylether (table 2, entry 3, 5) ⁹

¹H NMR (600 MHz, CDCl₃): δ 7.23-7.24(m, 2H), 7.04-7.10(m, 3H), 6.96(t, J=7.2Hz, 1H), 6.75(d, J=7.8Hz, 2H), 2.12(s, 6H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 157.8, 151.1, 131.5, 129.6, 128.9, 125.0, 121.2, 114.6, 16.3 MS *m/z* 198 (M⁺), 183, 165, 155, 120, 105, 91, 77, 65, 51, 39. Anal. Calcd. for C₁₄H₁₄O: C, 84.81; H, 7.12 Found: C, 85.08; H, 6.90.

(11)

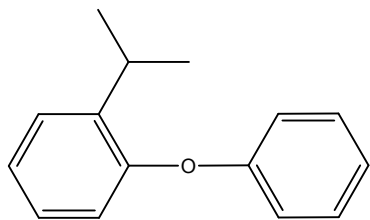


2-Phenyl-diphenylether (table 2, entry 6) ¹⁰

¹H NMR (600 MHz, CDCl₃): δ 7.54(d, J=7.8Hz, 2H), 7.45(dd, J=7.8Hz, J=1.8Hz, 1H), 7.36(m, 2H), 7.27(m, 5H), 7.20(t, J=7.5Hz, 1H), 6.99-7.03(m, 2H), 6.93(d, J=8.4Hz, 2H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 157.8, 153.6, 137.7, 133.7, 131.3, 129.6, 129.2, 128.7, 128.1, 127.2, 124.0, 122.6, 120.1, 118.2 ppm. MS *m/z* 246 (M⁺), 229, 217, 202, 169, 152, 139, 115, 77, 51, 39. Anal. Calcd. for C₁₈H₁₄O: C, 89.57; H, 5.84 Found: C, 89.57; H, 5.84.

87.78; H, 5.73 Found: C, 87.91; H, 5.65.

(12)



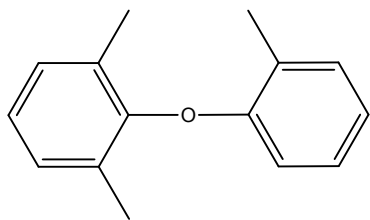
2-Isopropyl-diphenylether (table 2, entry 7) ¹¹

¹H NMR (600 MHz, CDCl₃): δ 7.33(dd, J=9Hz, J=1.8Hz, 1H), 7.28-7.31(m, 2H), 7.12-7.15(m, 2H), 7.03(t, J=7.5Hz, 1H), 6.92(d, J=7.2Hz, 2H), 6.87(dd, J=7.8Hz, J=1.8Hz, 1H), 3.28(m, 1H), 1.23(d, J=7.2Hz, 6H) ppm. ¹³C NMR (600 MHz, CDCl₃):

δ 158.4, 153.6, 140.3, 129.6, 126.9, 126.8, 124.2, 122.3, 119.8, 117.5, 27.1, 22.9 ppm.

MS *m/z* 212 (M⁺), 197, 181, 119, 103, 91, 77, 65, 51, 39. Anal. Calcd. for C₁₅H₁₆O: C, 84.87; H, 7.60 Found: C, 85.05; H, 7.49.

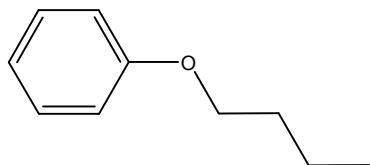
(13)



2,6,2'-Trimethyl-diphenylether (table 2, entry 8) ¹²

¹H NMR (600 MHz, CDCl₃): δ 7.21(d, J=7.2Hz, 1H), 7.10(d, J=7.2Hz, 2H), 7.03-7.06(m, 1H), 6.97(m, 1H), 6.87(t, J=6.9Hz, 1H), 6.25(d, J=7.8Hz, 1H), 2.42(s, 3H), 2.10(s, 6H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 155.7, 151.5, 131.4, 130.9, 128.9, 126.7, 125.9, 124.8, 120.9, 111.8, 16.2, 16.2 ppm. MS *m/z* 212 (M⁺), 197, 120, 104, 91, 77, 65, 51, 39. Anal. Calcd. for C₁₅H₁₆O: C, 84.87; H, 7.60 Found: C, 84.73.; H, 7.84

(14)

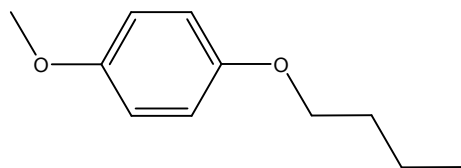


1-Butoxybenzene (table 3, entry 1) ¹³

¹H NMR (600 MHz, CDCl₃): δ 7.25-7.28(m, 2H), 6.92(t, J=7.2Hz, 1H), 6.90(d, J=7.8Hz, 2H), 3.95(t, J=6.6Hz, 2H), 1.75-1.78(m, 2H), 1.47-1.51(m, 2H), 0.97(t, J=7.5Hz, 3H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 159.1, 129.4, 120.4, 114.5, 67.5,

31.4, 19.3, 13.8 ppm. MS m/z 150 (M^+), 94, 77, 66, 57, 51, 41, 29. Anal. Calcd. for $C_{10}H_{14}O$: C, 79.96; H, 9.39 Found: C, 80.12; H, 9.43.

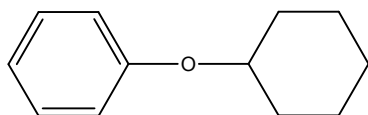
(15)



1-butoxy-4-methoxybenzene (table 3, entry 2) ¹⁴

1H NMR (600 MHz, $CDCl_3$): δ 6.81-6.84(m, 4H), 3.91(t, $J=6.6$ Hz, 2H), 3.76(s, 3H), 1.71-1.75(m, 2H), 1.46-1.50(m, 2H), 0.97(t, $J=7.5$ Hz, 3H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ 153.7, 153.3, 115.5, 114.6, 68.4, 55.7, 31.5, 19.3, 13.9 ppm. MS m/z 180 (M^+), 124, 107, 94, 80, 76, 43. Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95 Found: C, 73.14; H, 9.01.

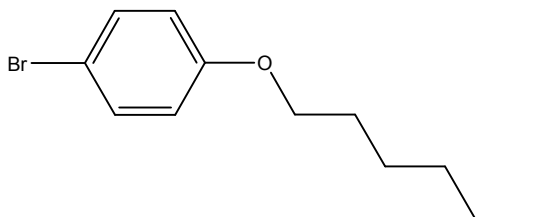
(16)



Cyclohexyloxybenzene (table 3, entry 3) ¹⁵

1H NMR (600 MHz, $CDCl_3$): δ 7.25-7.27(m, 2H), 6.90-6.92(m, 3H), 4.22-4.25(m, 1H), 1.98-2.00(m, 2H), 1.79-1.82(m, 2H), 1.51-1.57(m, 3H), 1.31-1.38(m, 3H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ 157.8, 129.4, 120.5, 116.1, 75.4, 31.9, 25.7, 23.8 ppm. MS m/z 176 (M^+), 94, 77, 67, 55, 41. Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15 Found: C, 81.52; H, 9.08.

(17)

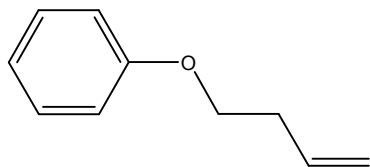


1-Bromo-4-(hexyloxy)benzene (table 3, entry 4) ¹⁶

1H NMR (600 MHz, $CDCl_3$): δ 7.35(d, $J=9.0$ Hz, 2H), 6.76(d, $J=9.0$ Hz, 2H), 3.90(t, $J=6.6$ Hz, 2H), 1.75-1.77(m, 2H), 1.43-1.45(m, 2H), 1.31-1.34(m, 4H), 0.90(t, $J=6.9$ Hz, 3H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$): δ 158.3, 132.2, 116.3, 112.6, 68.3, 31.6, 29.1, 25.7, 22.6, 14.0 ppm. MS m/z 258, 256 (M^+), 174, 172, 155, 143, 93, 76,

65, 43. Anal. Calcd. for C₁₂H₁₇BrO: C, 56.04; H, 6.66 Found: C, 56.25; H, 6.41.

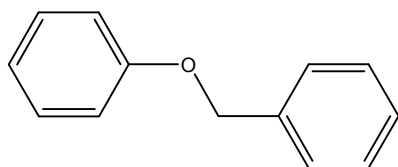
(18)



1-(But-3-enyloxy)benzene (table 3, entry 5)¹⁷

¹H NMR (600 MHz, CDCl₃): δ 7.24-7.28(m, 2H), 6.93(t, J=7.8Hz, 1H), 6.90(d, J=7.8Hz, 2H), 5.89-5.91(m, 1H), 5.17(dd, J=17.4Hz, J=1.8Hz, 1H), 5.10(dd, J=10.2Hz, J=1.2Hz, 1H), 4.01(t, J=6.9Hz, 2H), 2.53-2.56(m, 2H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 158.9, 134.5, 129.4, 120.7, 116.9, 114.6, 67.1, 33.7 MS *m/z* 148 (M⁺), 120, 107, 94, 77, 55, 39. Anal. Calcd. for C₁₀H₁₂O: C, 81.04; H, 8.16 Found: C, 81.22; H, 8.26.

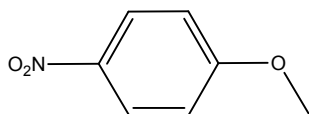
(19)



1-(Phenoxymethyl)benzene (table 3, entry 6)¹⁸

¹H NMR (600 MHz, CDCl₃): δ 7.43(d, J=7.2Hz, 2H), 7.37(m, 2H), 7.32(d, J=7.2Hz, 1H), 7.27-7.30(m, 2H), 6.94-6.98(m, 3H), 5.05(s, 2H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 158.8, 137.1, 129.5, 128.6, 127.9, 127.5, 120.9, 114.8, 65.9 ppm. MS *m/z* 184 (M⁺), 91, 77, 65, 51, 39. Anal. Calcd. for C₁₃H₁₂O: C, 84.75; H, 6.57 Found: C, 84.90; H, 6.51.

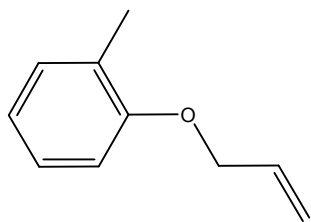
(20)



4-Nitroanisole (table 3, entry 7)¹⁹

¹H NMR (600 MHz, CDCl₃): δ 8.20(d, J=9.0Hz, 2H), 6.96(d, J=9.0Hz, 2H), 3.92(s, 3H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 164.6, 141.5, 125.8, 113.9, 55.9 ppm. MS *m/z* 153 (M⁺), 137, 123, 107, 95, 92, 77, 64, 50, 38. Anal. Calcd. for C₇H₇NO₃: C, 54.90; H, 4.61; N, 9.15 Found: C, 55.12; H, 4.54; N, 9.01.

(21)

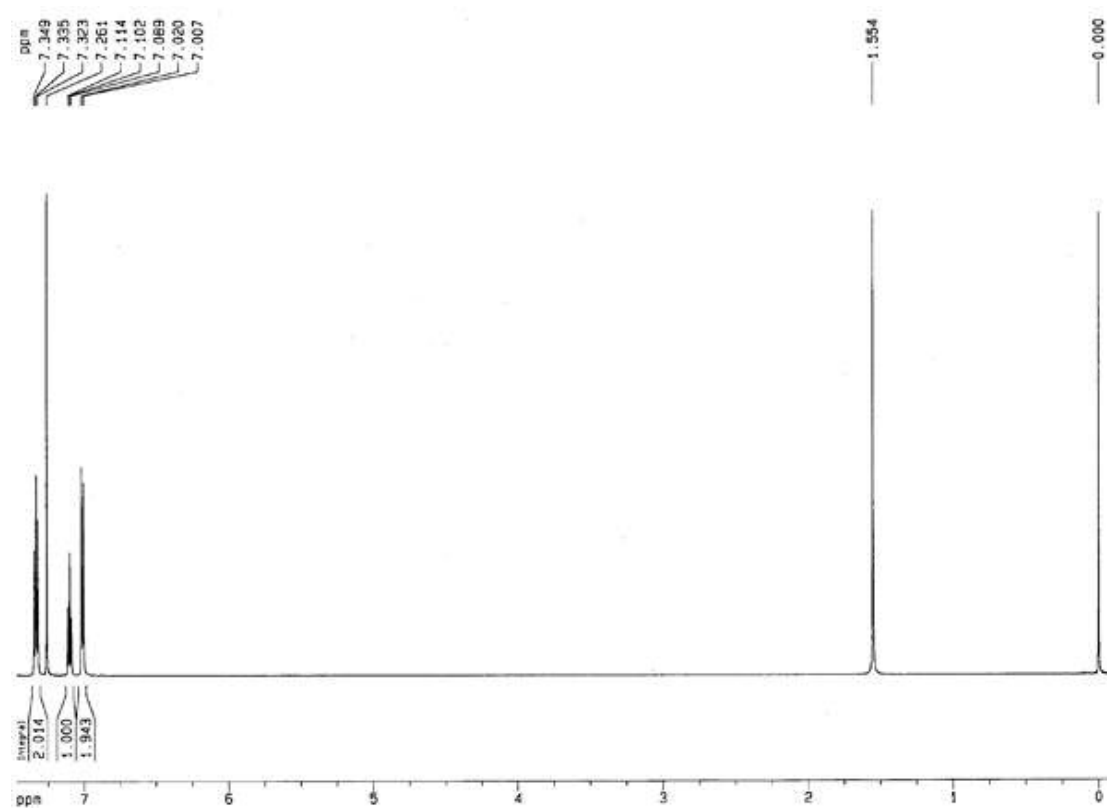


Allyl 2-tolyl ether (table 3, entry 8) ²⁰

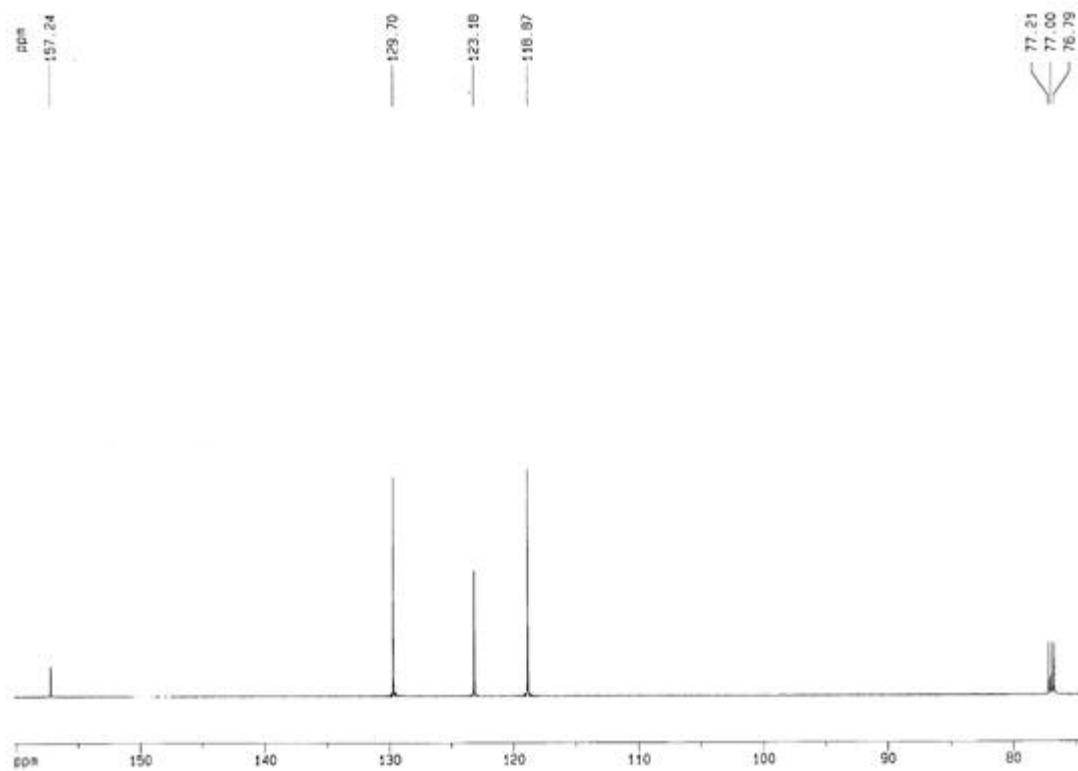
¹H NMR (600 MHz, CDCl₃): δ 7.12-7.15(m, 2H), 6.86(m, 1H), 6.81(d, J=10.2Hz, 1H), 6.05-6.10(m, 1H), 5.43(dd, J=17.1Hz, J=1.5Hz, 1H), 5.27(dd, J=10.4Hz, J=1.2Hz, 1H), 4.54(dd, J=3.6Hz, J=1.8Hz, 2H), 2.26(s, 3H) ppm. ¹³C NMR (600 MHz, CDCl₃): δ 156.71, 133.64, 130.68, 126.96, 126.66, 120.44, 116.84, 111.28, 68.63, 16.25 ppm. MS *m/z* 148 (M⁺), 133, 107, 91, 79, 77, 65, 51, 41, 39. Anal. Calcd. for C₁₀H₁₂O: C, 81.04; H, 8.16 Found: C, 80.89; H, 8.23.

^1H -NMR and ^{13}C -NMR spectra

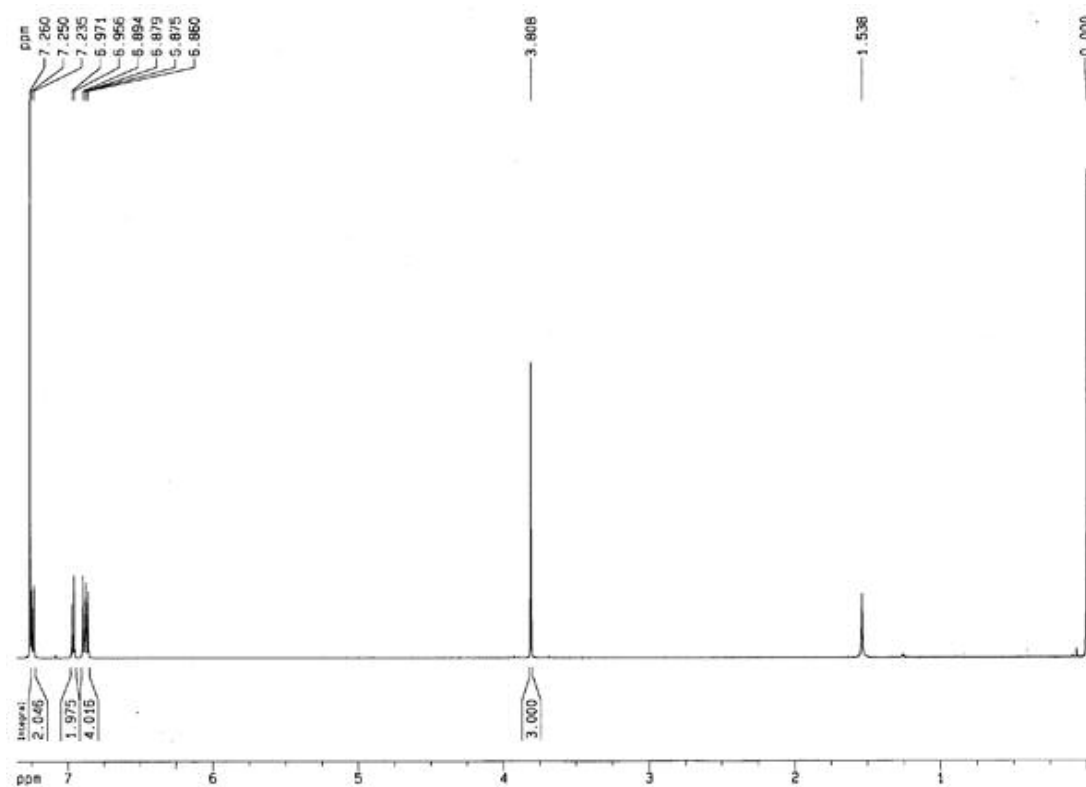
^1H -NMR for diphenyl ether (table 1, entry 1)



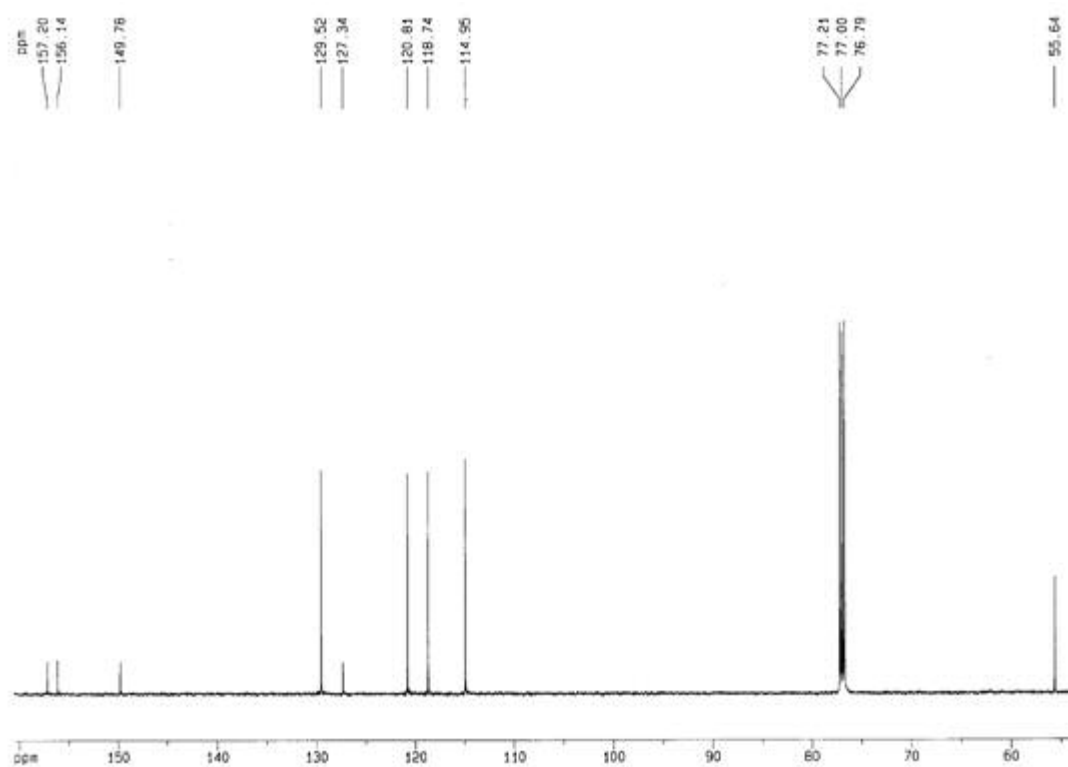
^{13}C -NMR for diphenyl ether (table 1, entry 1)



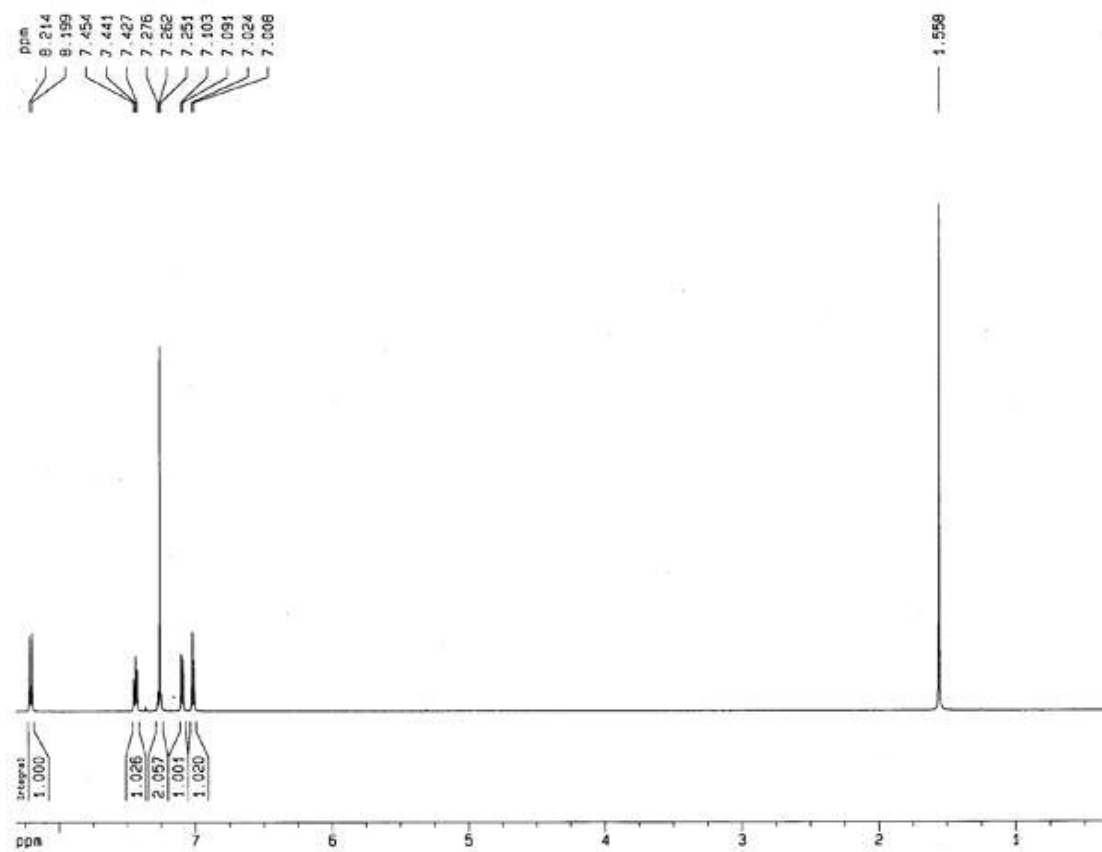
^1H -NMR for 4-Chloro-4'-methoxy-diphenylether (table 1, entry 2)



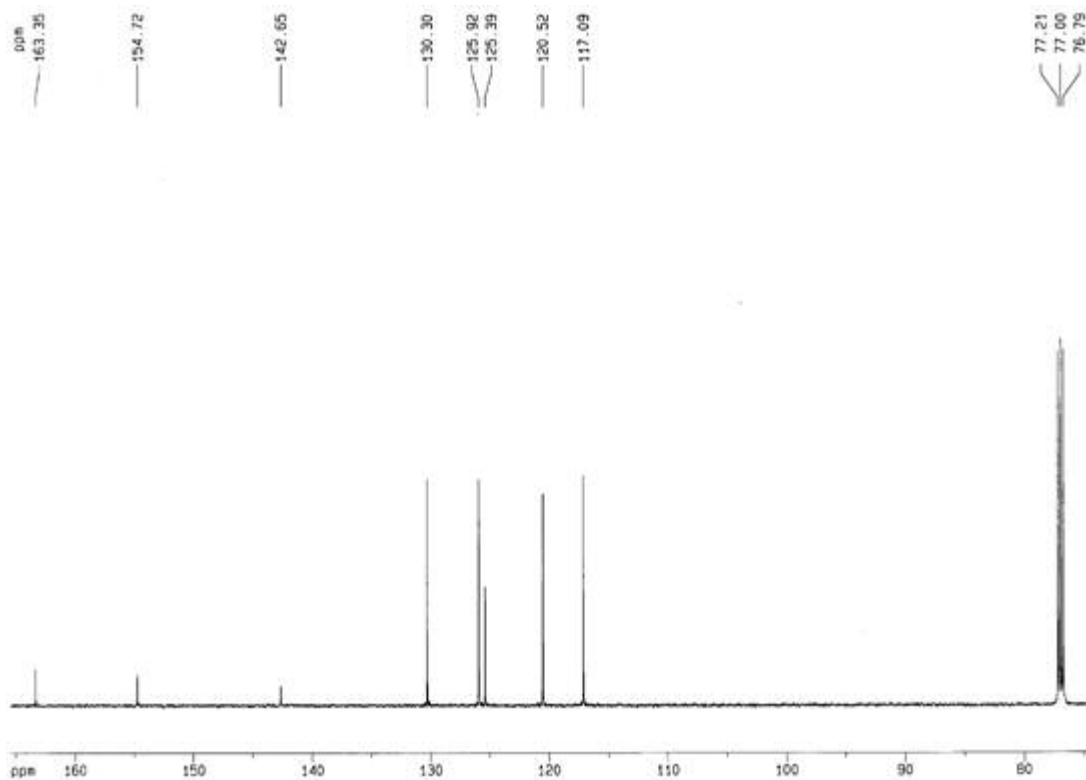
^{13}C -NMR for 4-Chloro-4'-methoxy-diphenylether (table 1, entry 2)



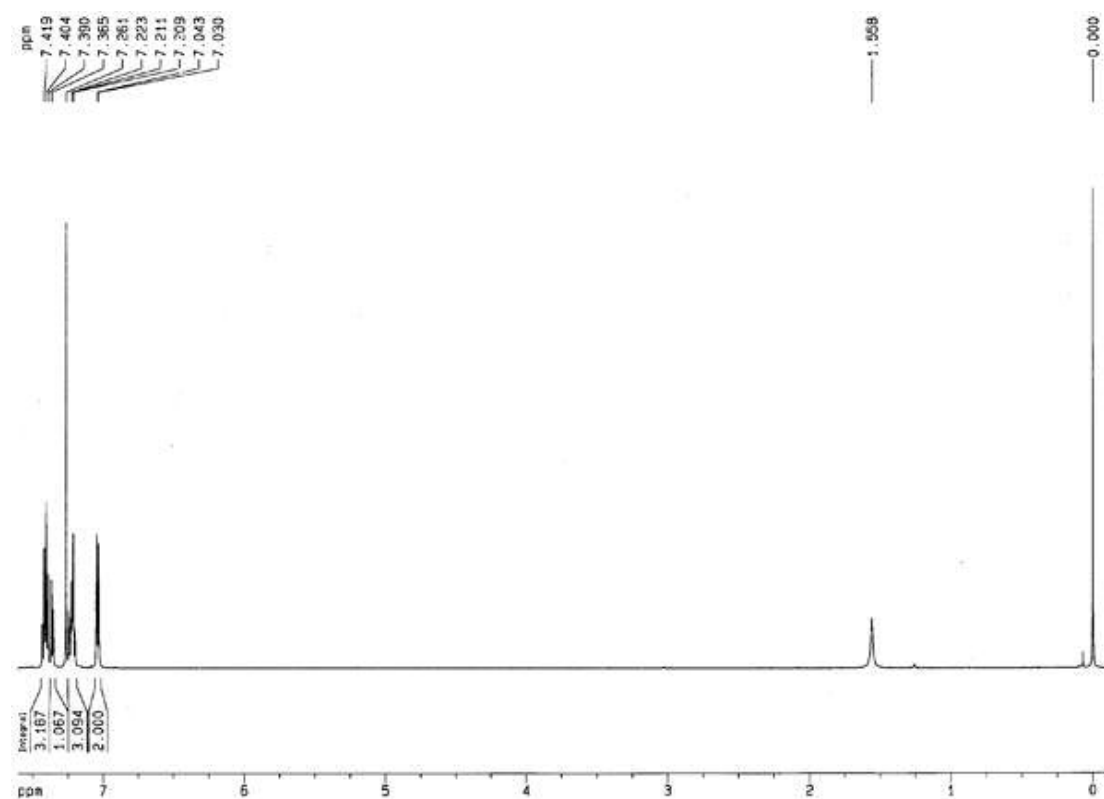
¹H-NMR for 4-nitro-diphenylether (table 1, entry 3, 5)



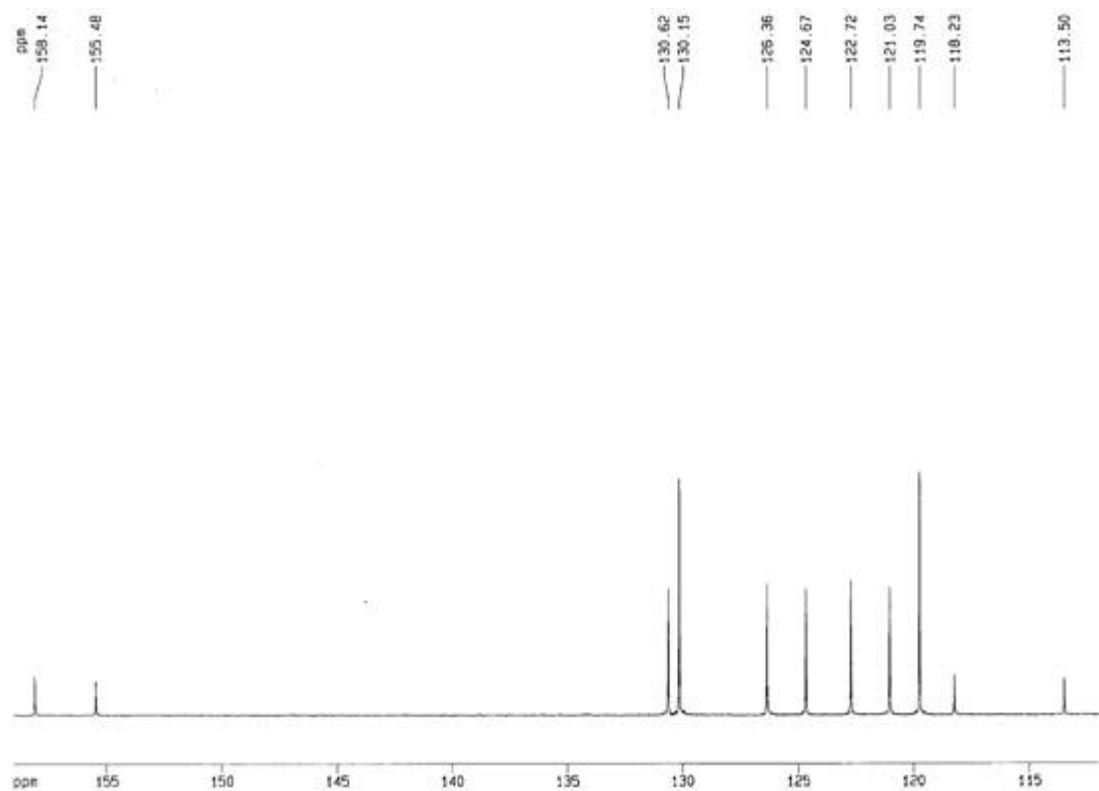
¹³C-NMR for 4-nitro-diphenylether (table 1, entry 3, 5)



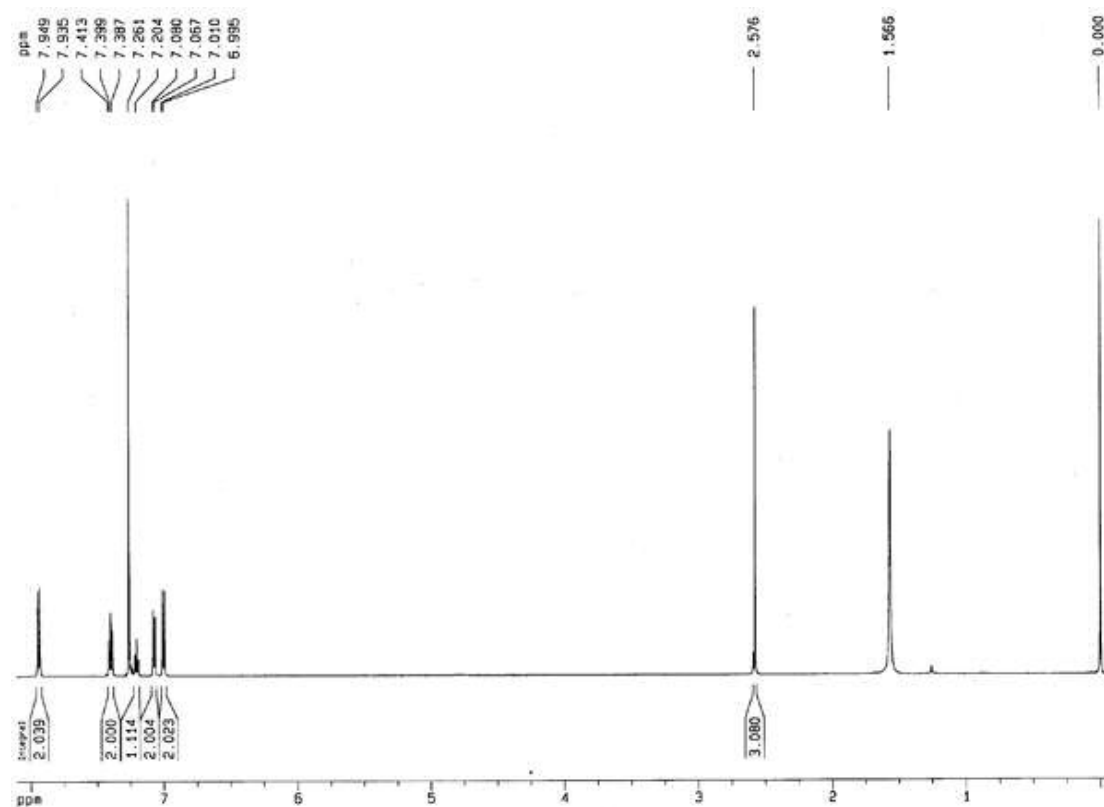
¹H-NMR for 3-nitrile-diphenylether (table 1, entry 4)



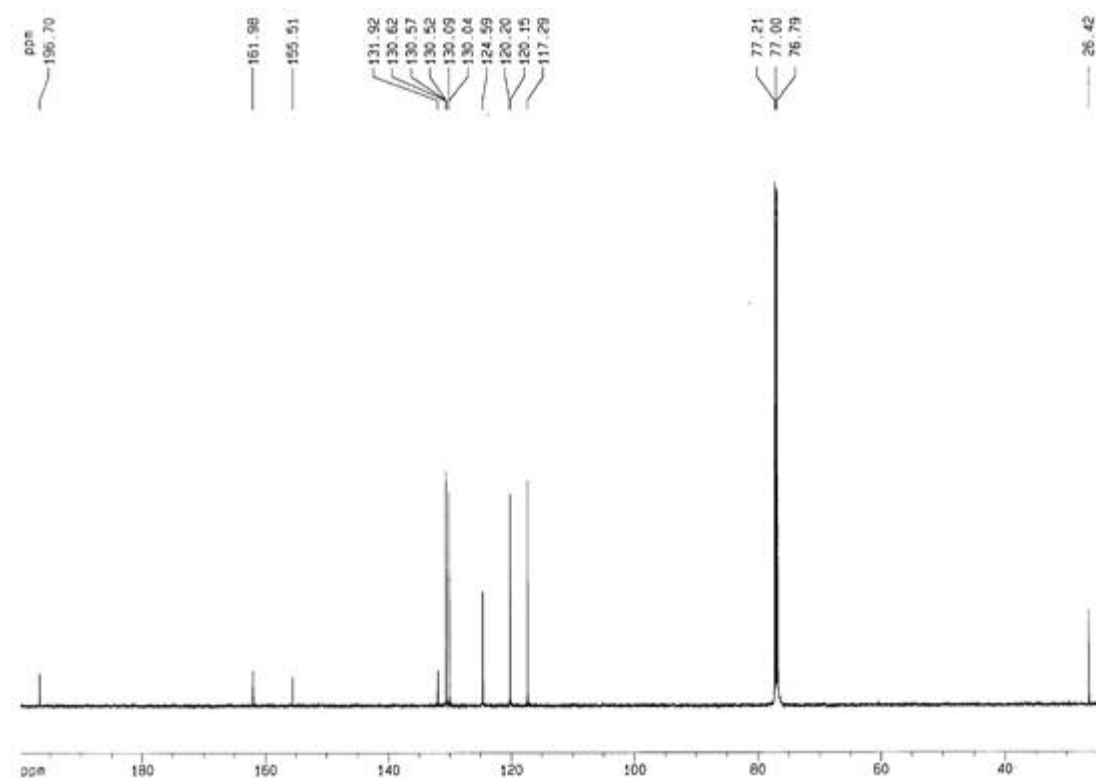
¹³C-NMR for 3-nitrile-diphenylether (table 1, entry 4)



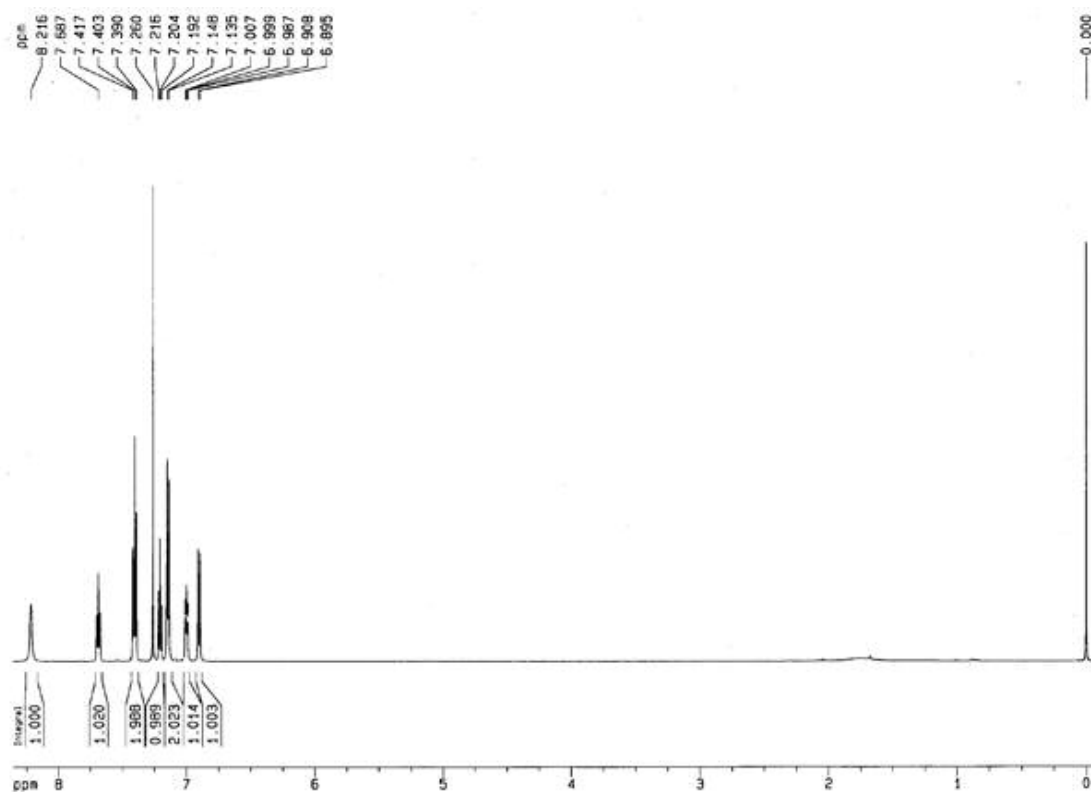
^1H -NMR for 4-acetyl-diphenylether (table 1, entry 6)



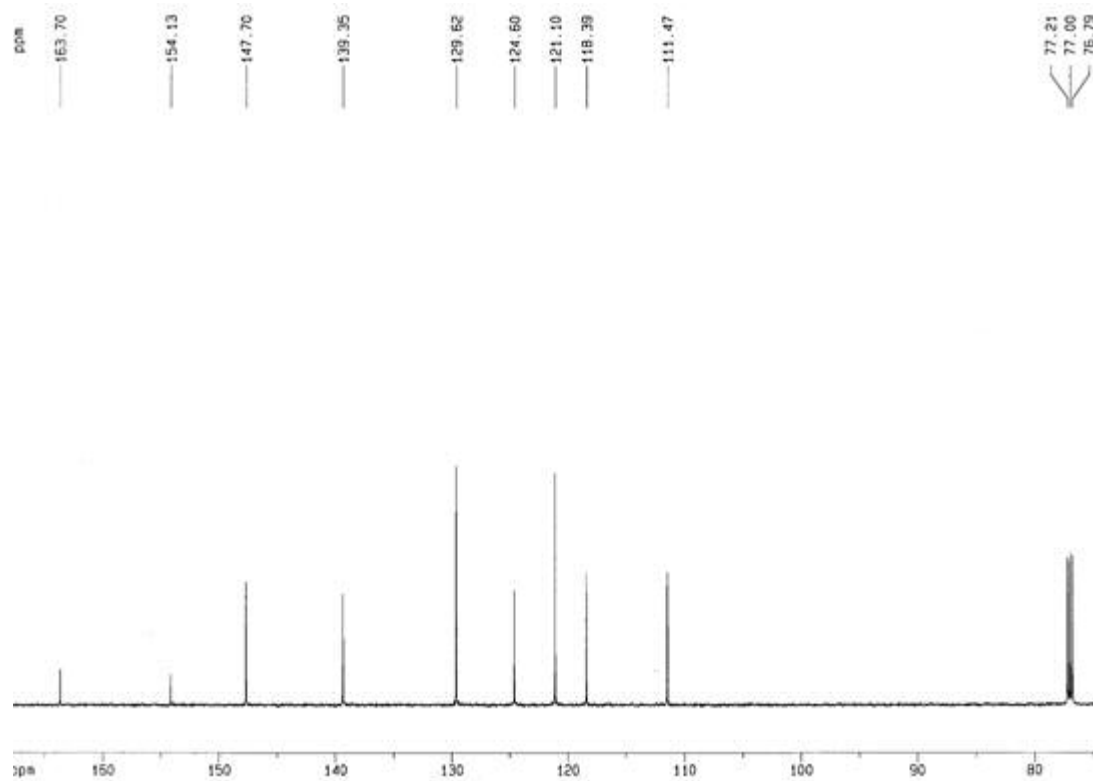
^{13}C -NMR for 4-acetyl-diphenylether (table 1, entry 6)



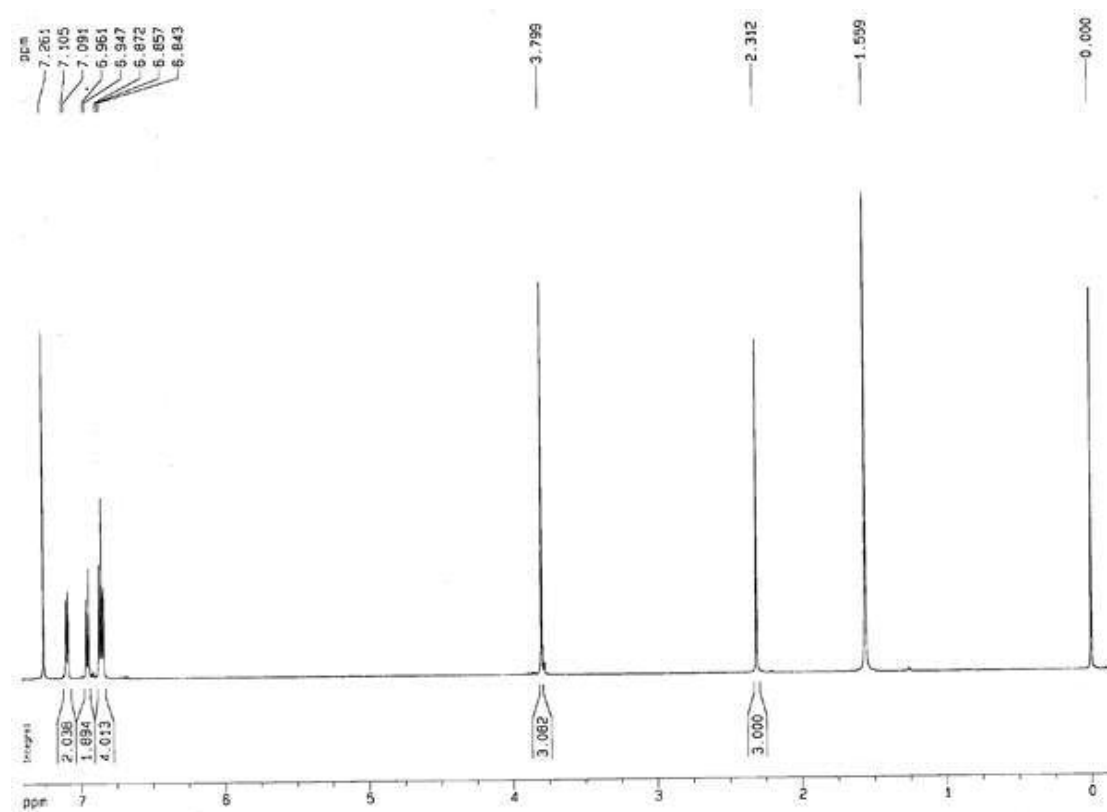
¹H-NMR for 2-phenoxy pyridine (table 1, entry 7)



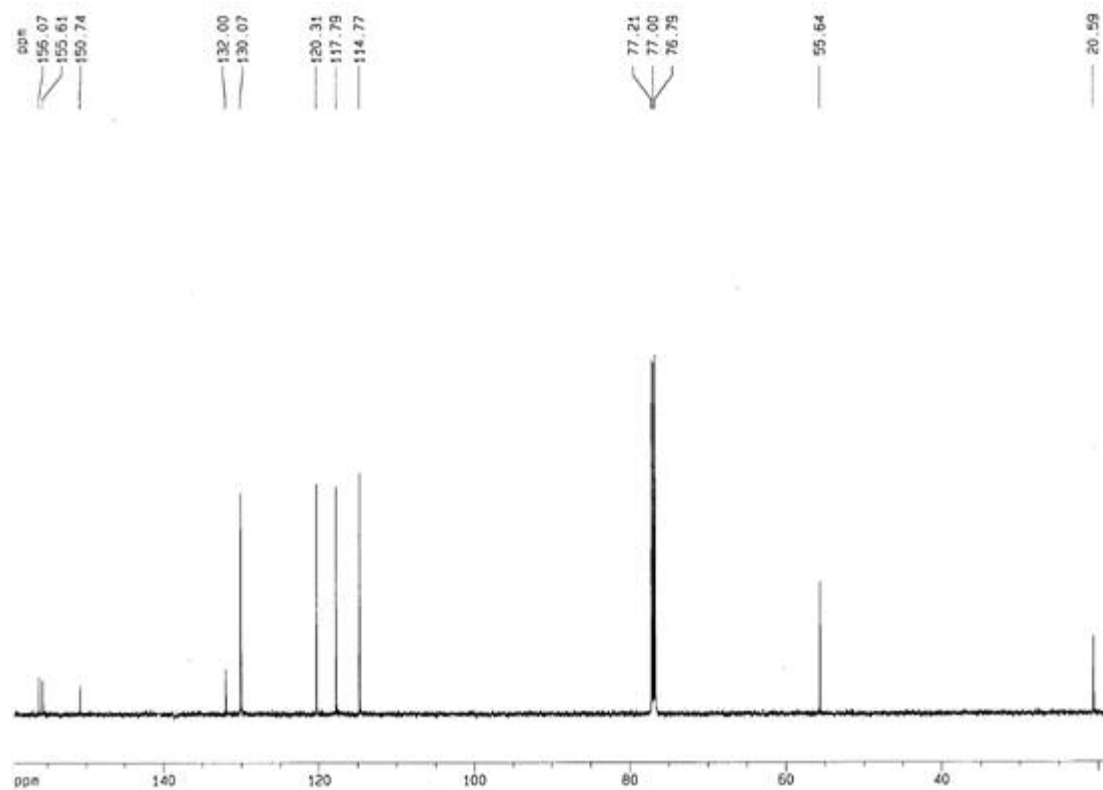
¹³C-NMR for 2-phenoxy pyridine (table 1, entry 7)



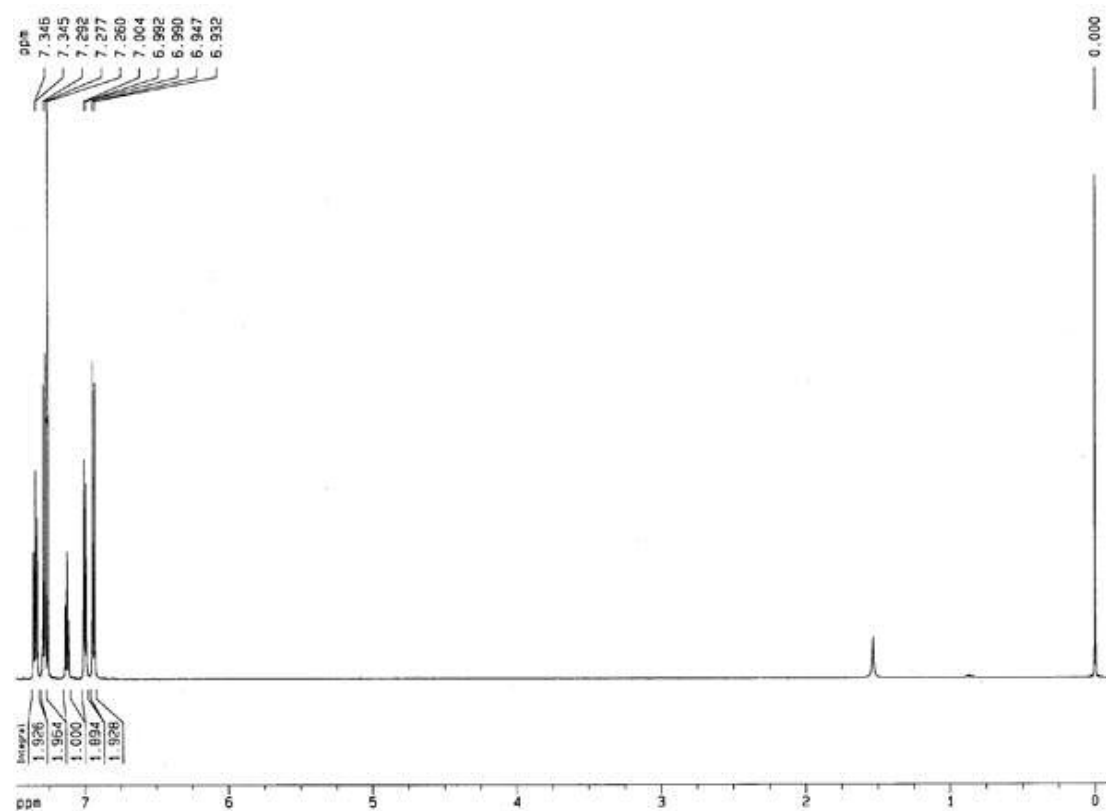
¹H-NMR for 4-methoxy-4'-methyl-diphenylether (table 1, entry 8)



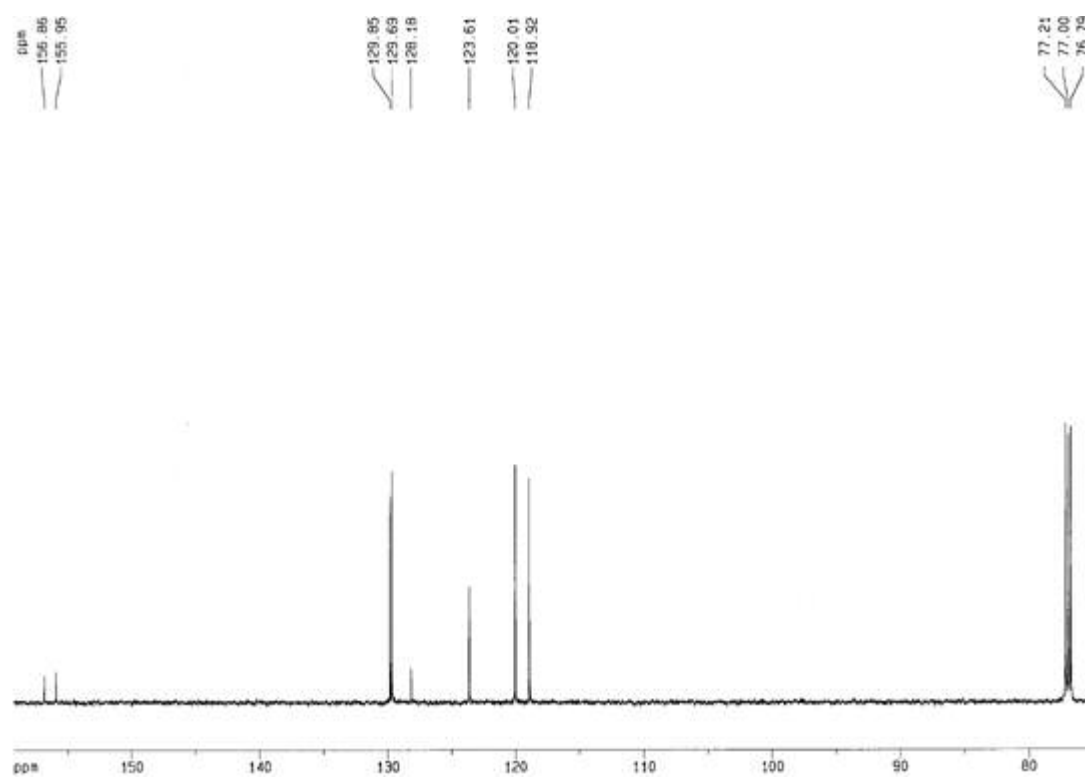
¹³C-NMR for 4-methoxy-4'-methyl-diphenylether (table 1, entry 8)



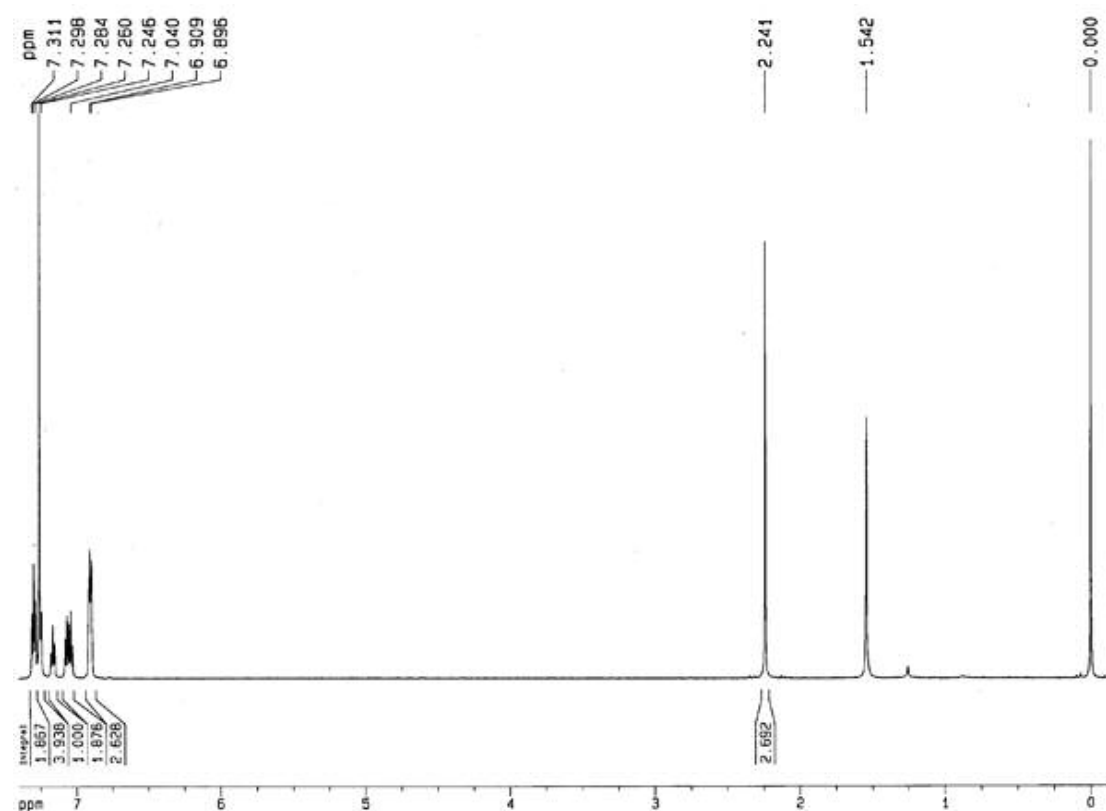
¹H-NMR for 4-chloro-diphenylether (table 1, entry 9)



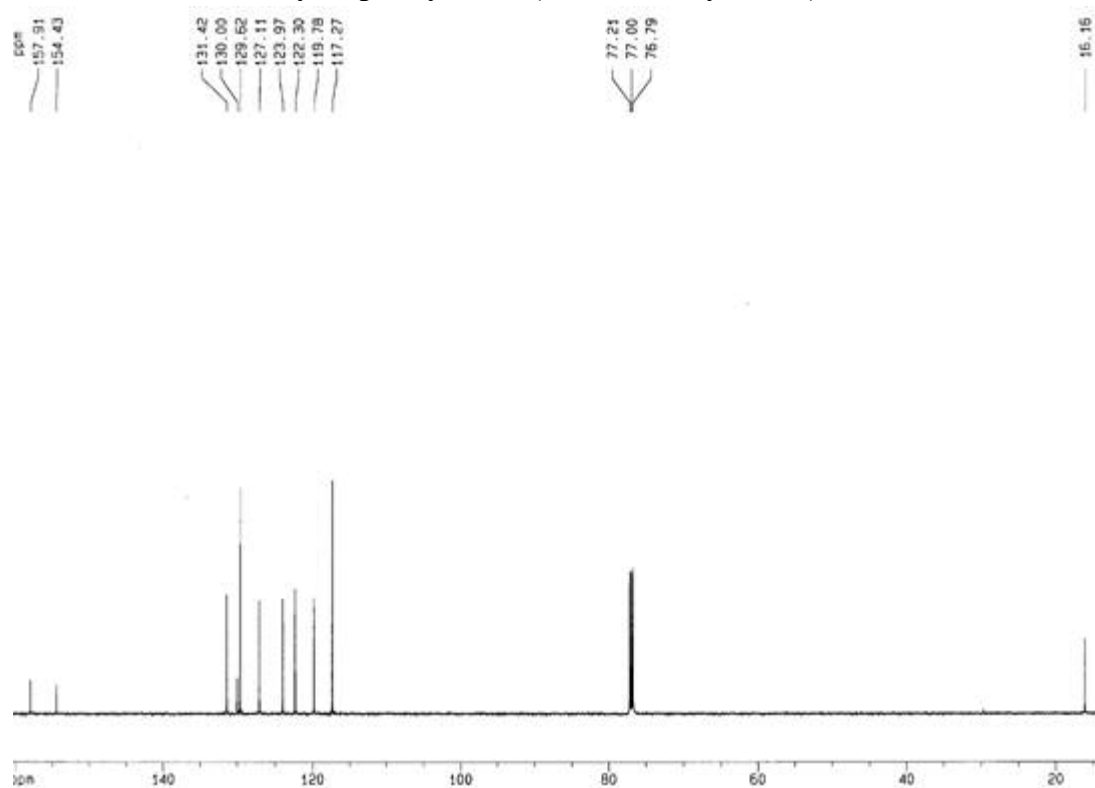
¹³C-NMR for 4-chloro-diphenylether (table 1, entry 9)



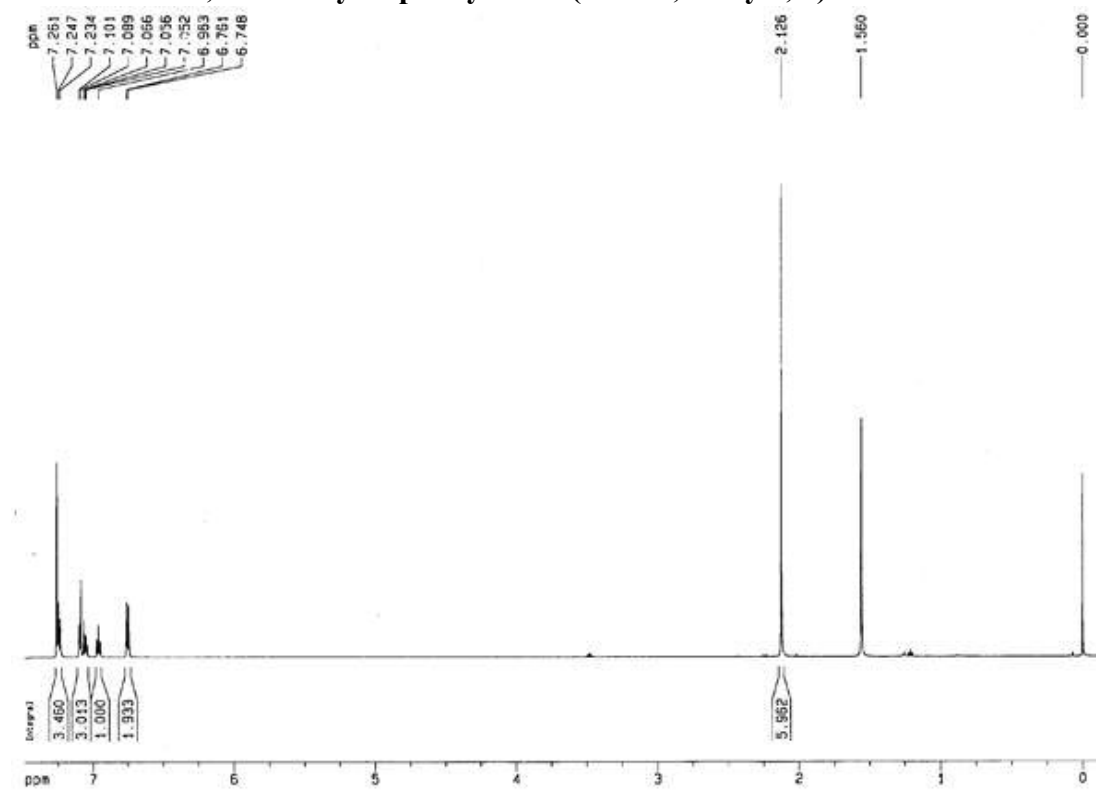
¹H-NMR for 2-methyl-diphenylether (table 2, entry 1, 2, 4)



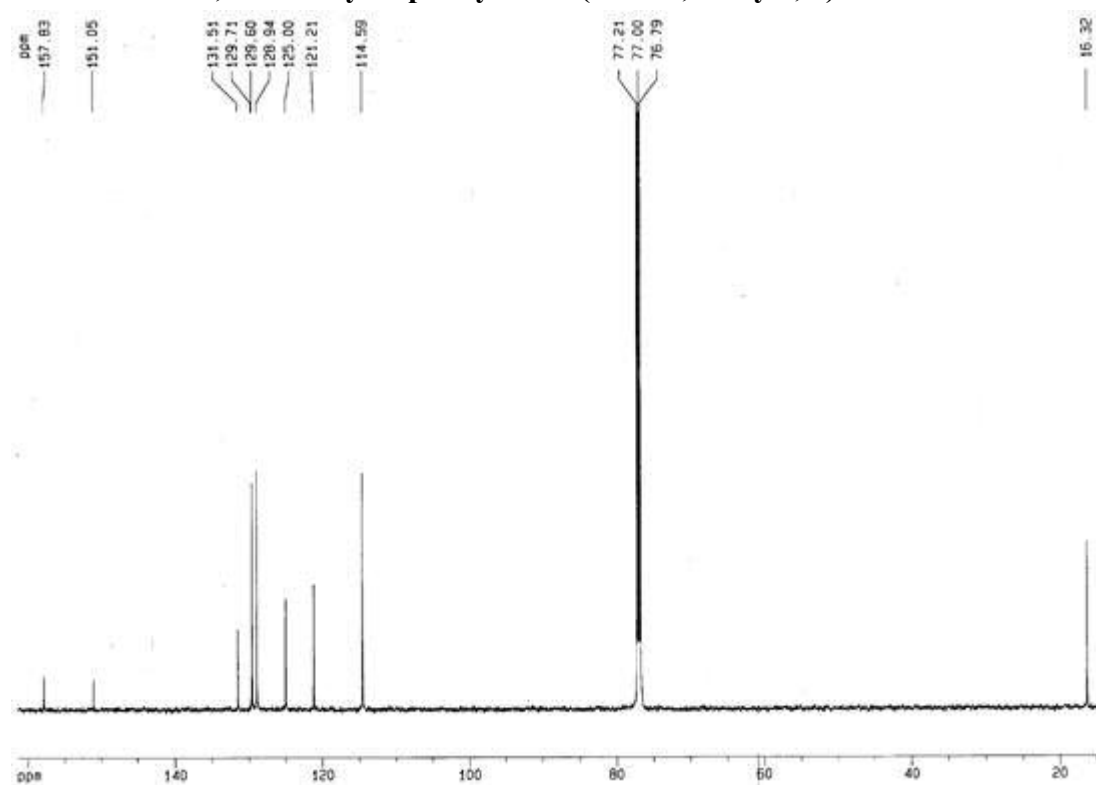
¹³C-NMR for 2-methyl-diphenylether (table 2, entry 1, 2, 4)



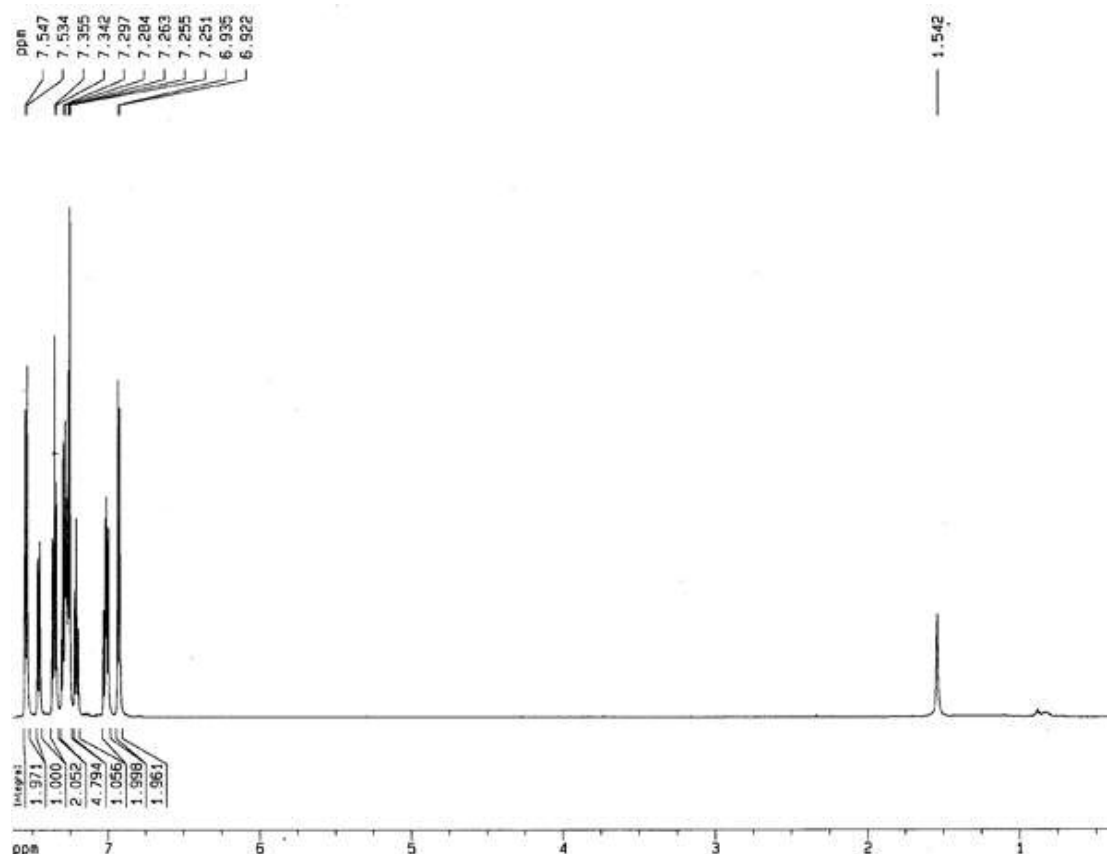
¹H-NMR for 2,6-dimethyl-diphenylether (table 2, entry 3, 5)



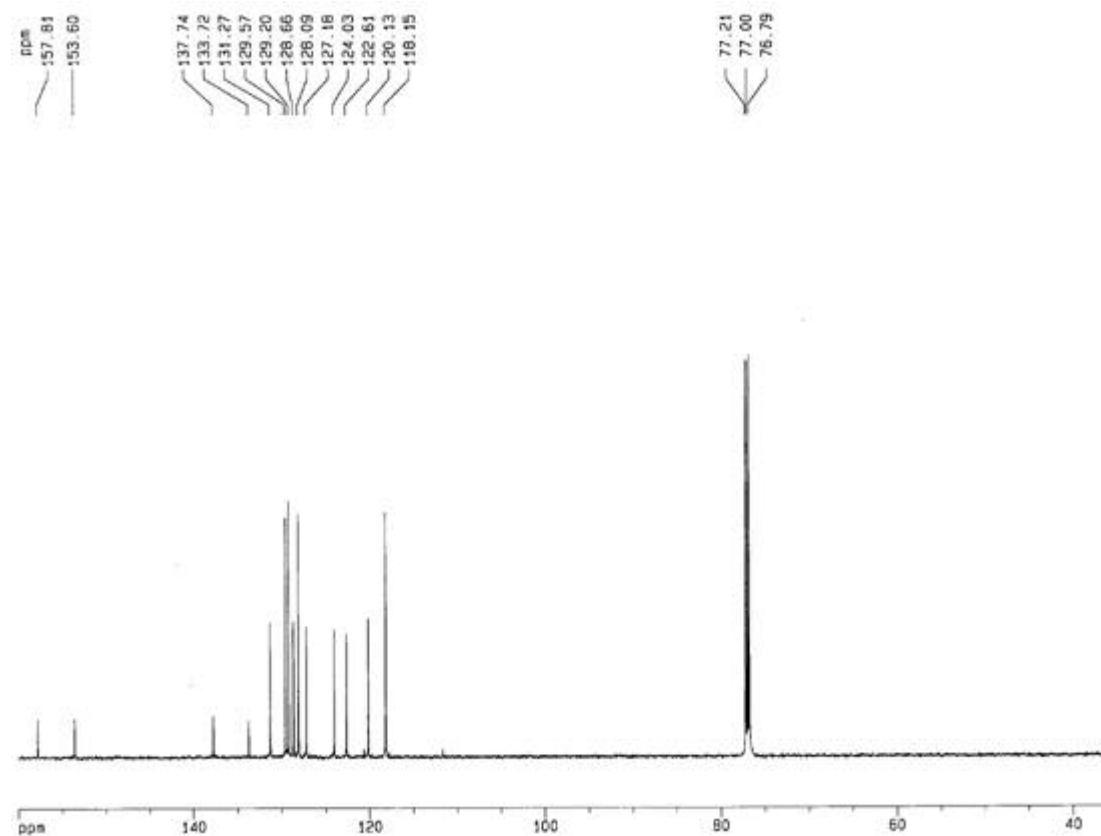
¹³C-NMR for 2,6-dimethyl-diphenylether (table 2, entry 3, 5)



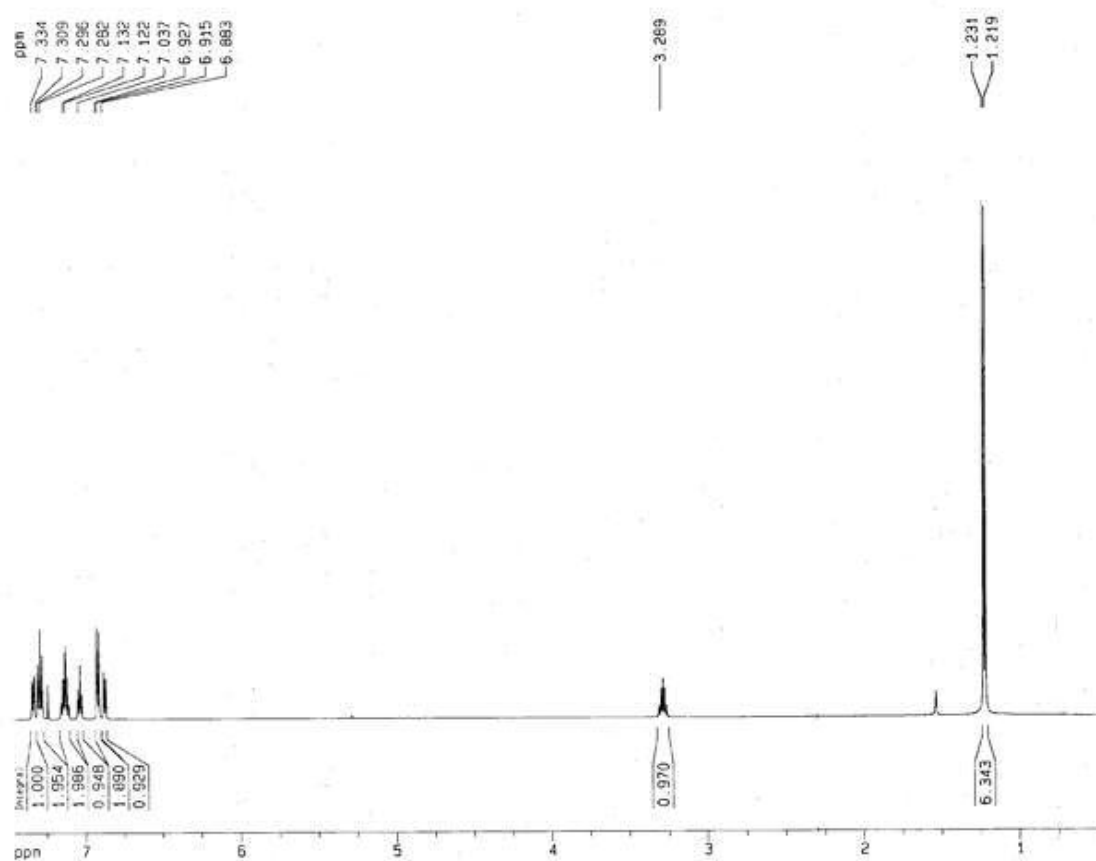
¹H-NMR for 2-phenyl-diphenylether (table 2, entry 6)



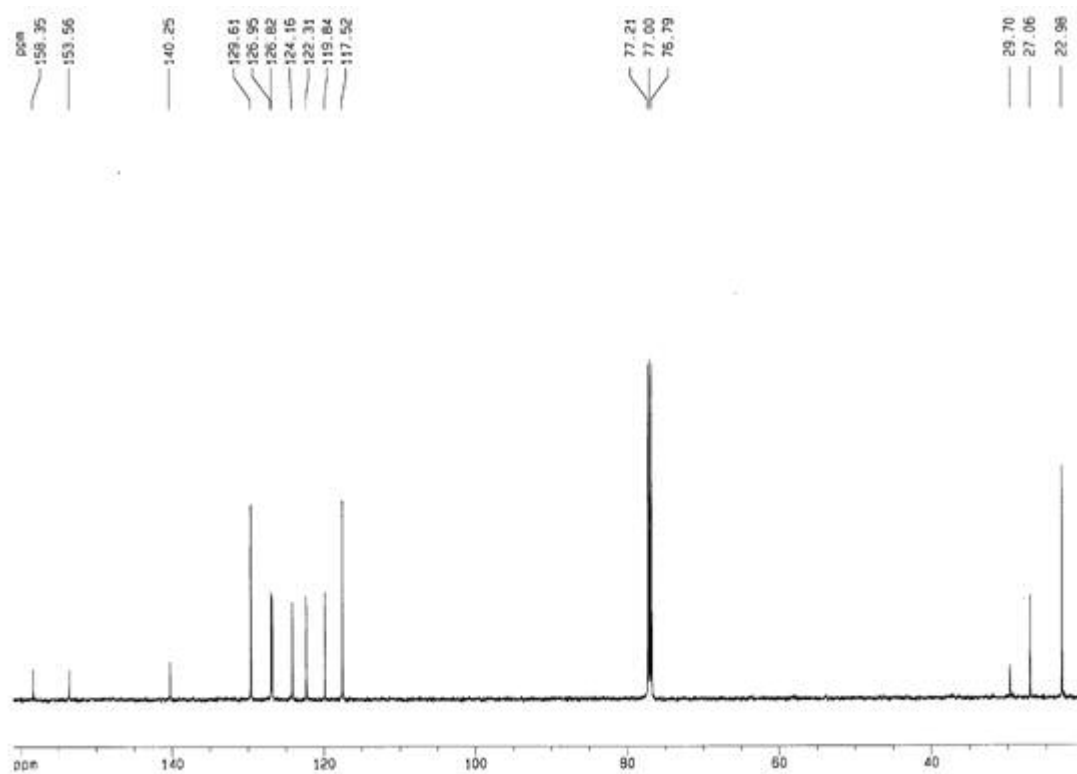
¹³C-NMR for 2-phenyl-diphenylether (table 2, entry 6)



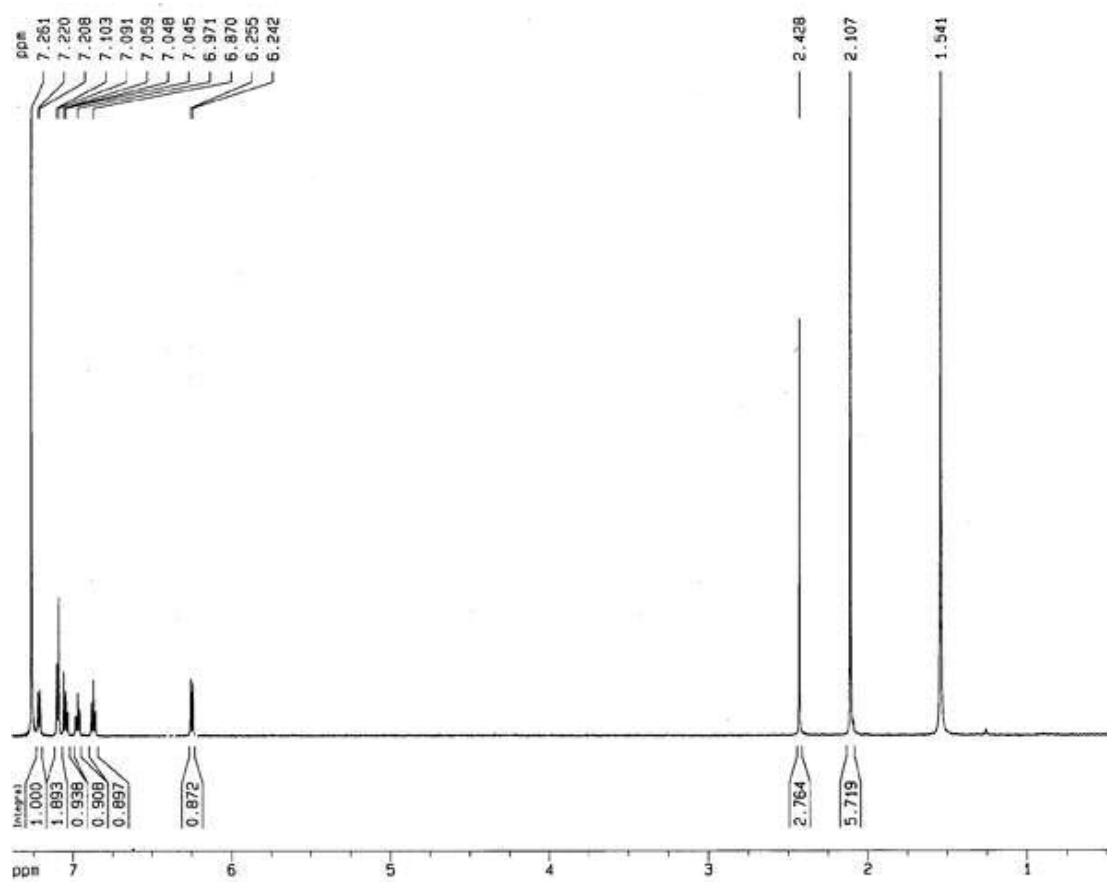
¹H-NMR for 2-isopropyl-diphenylether (table 2, entry 7)



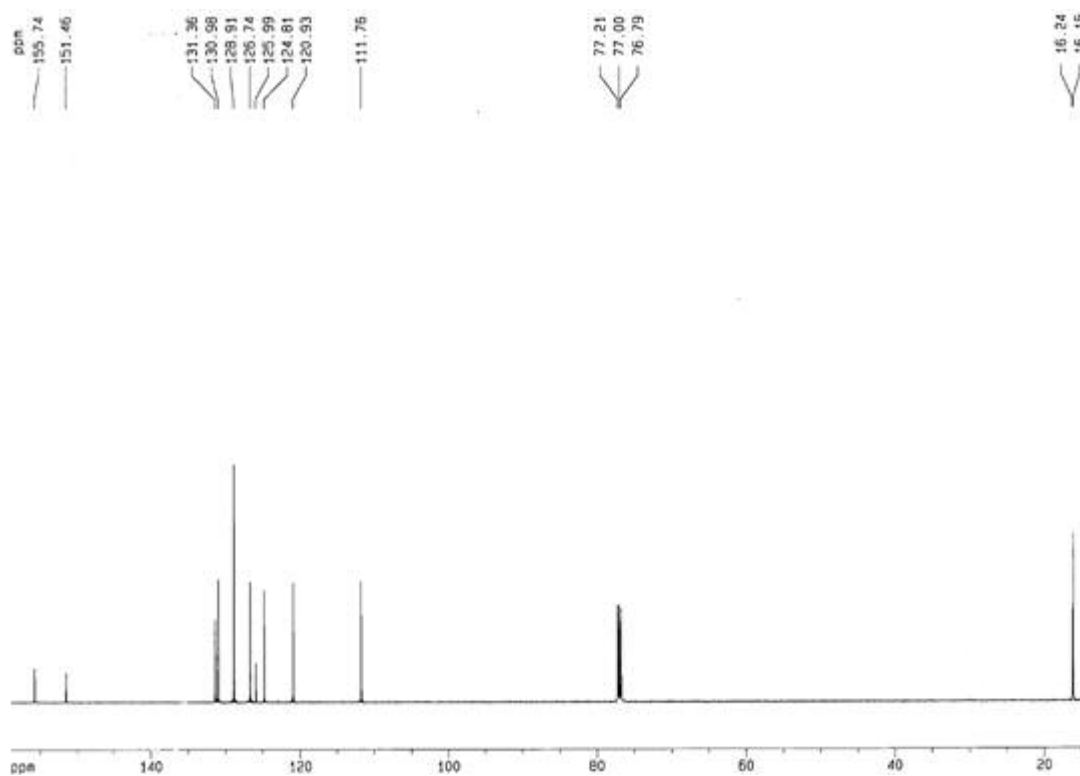
¹³C-NMR for 2-isopropyl-diphenylether (table 2, entry 7)



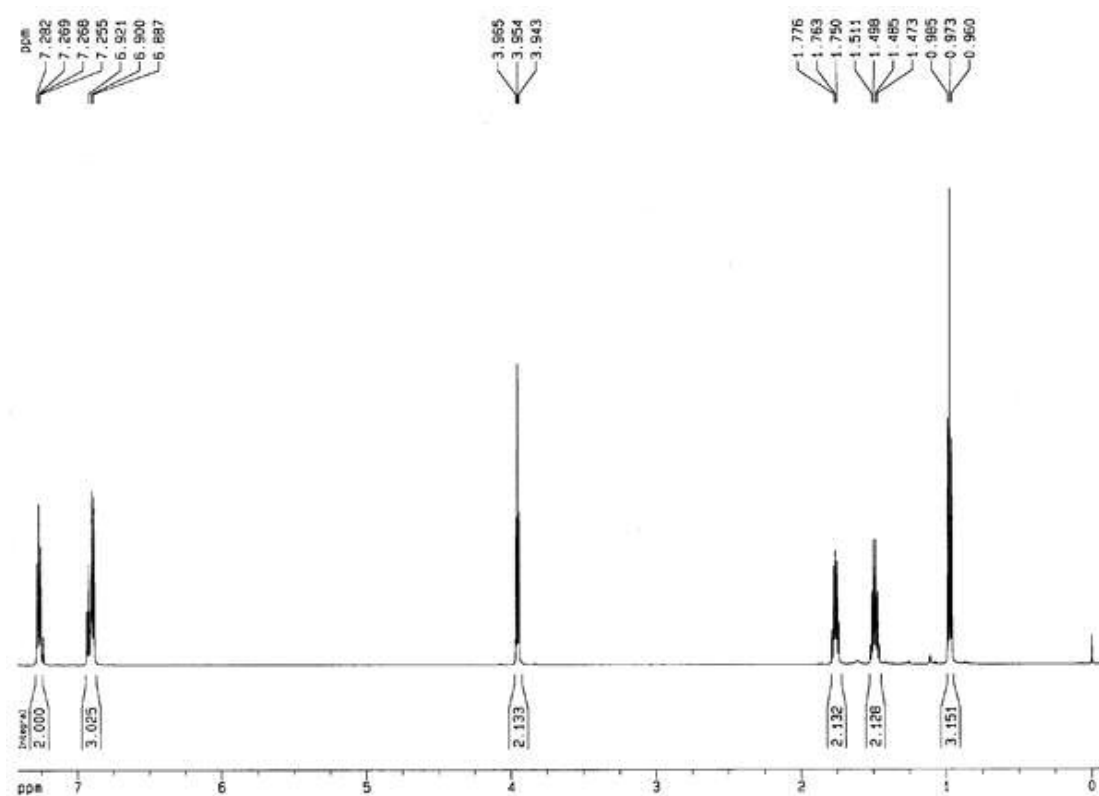
¹H-NMR for 2,6,2'-trimethyl-diphenylether (table 2, entry 8)



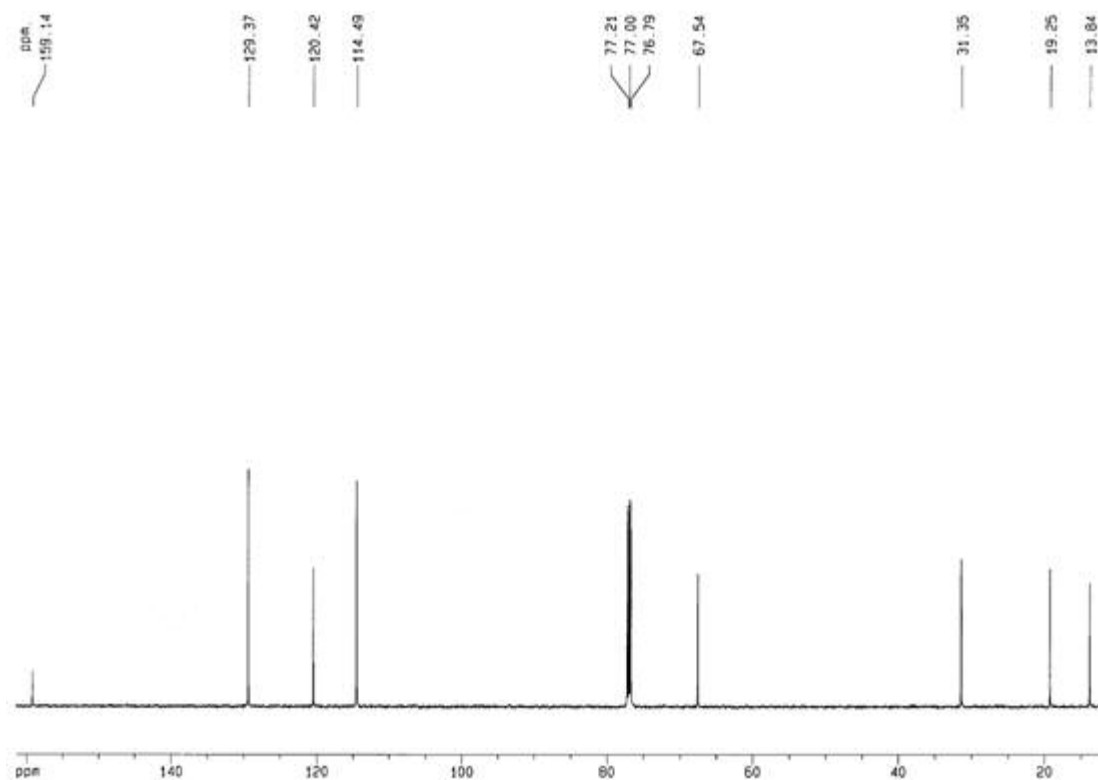
¹³C-NMR for 2,6,2'-trimethyl-diphenylether (table 2, entry 8)



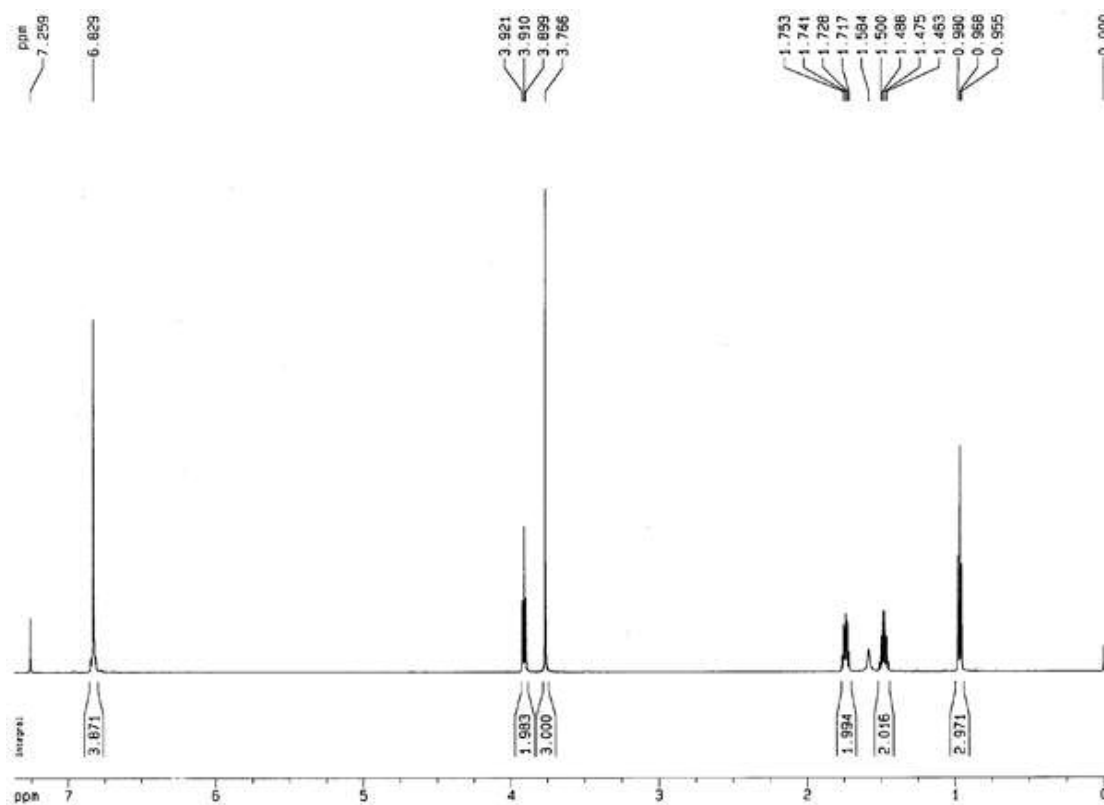
¹H-NMR for 1-butoxybenzene (table 3, entry 1)



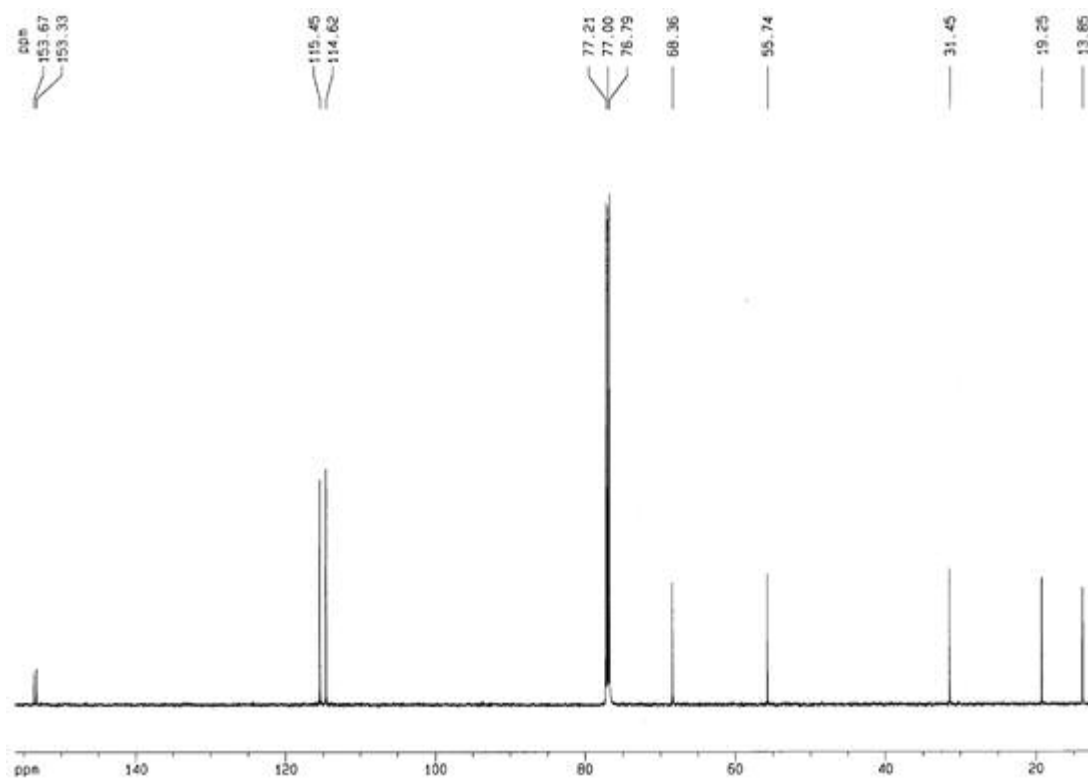
¹³C-NMR for 1-butoxybenzene (table 3, entry 1)



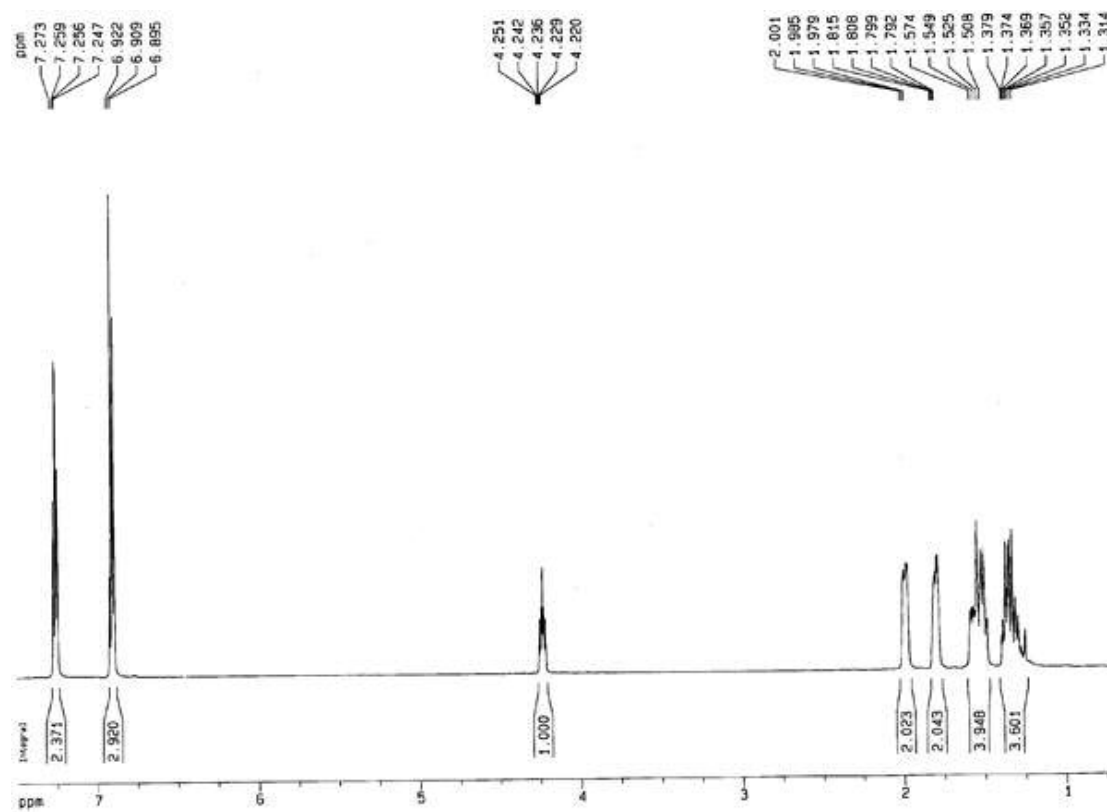
¹H-NMR for 1-butoxy-4-methoxybenzene (table 3, entry 2)



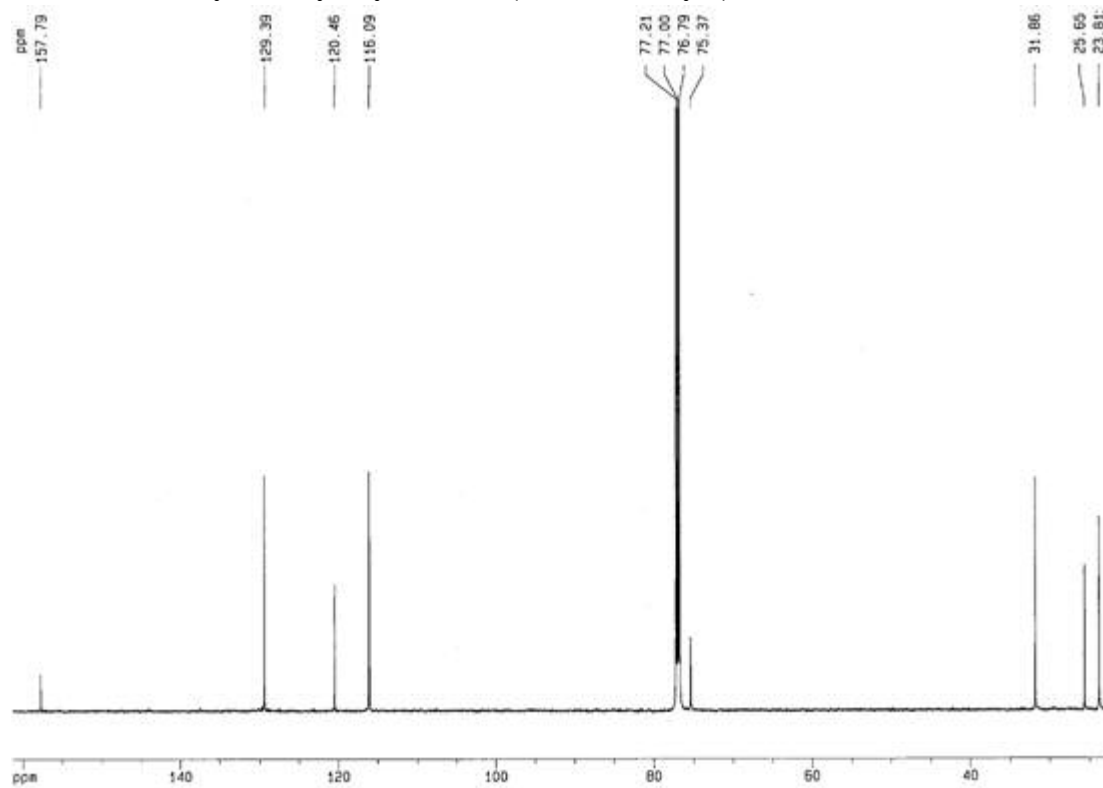
¹³C-NMR for 1-butoxy-4-methoxybenzene (table 3, entry 2)



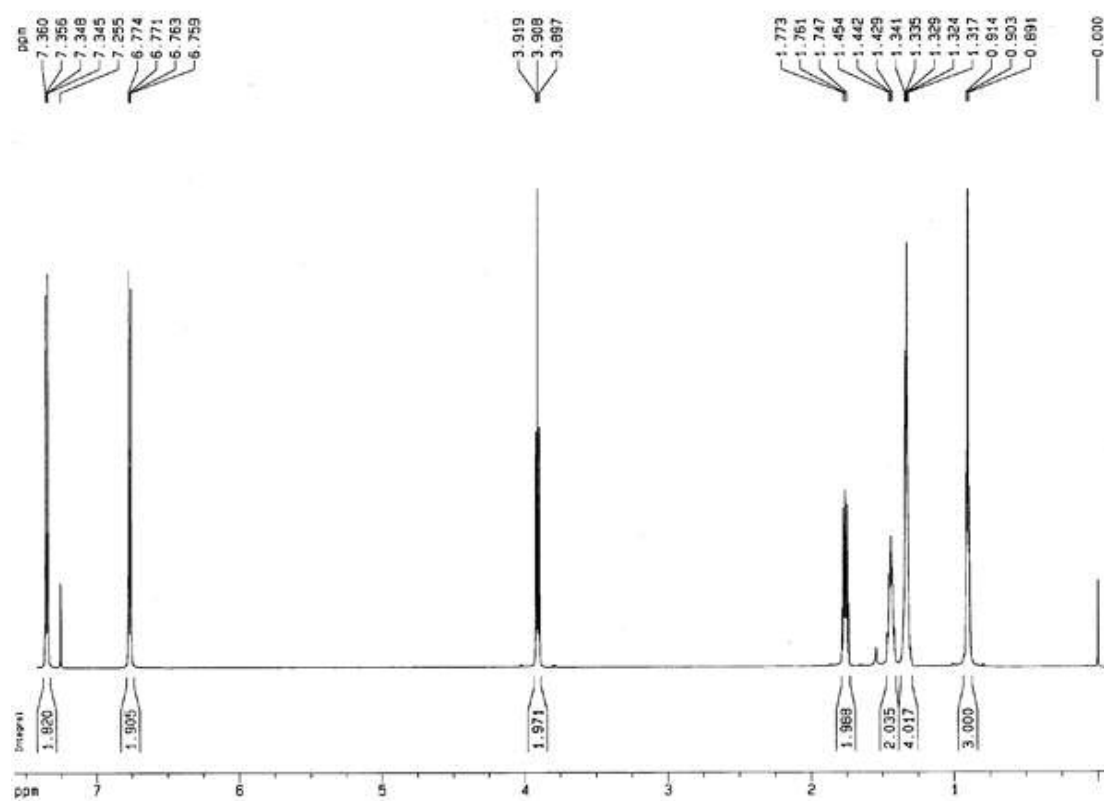
^1H -NMR for cyclohexyloxybenzene (table 3, entry 3)



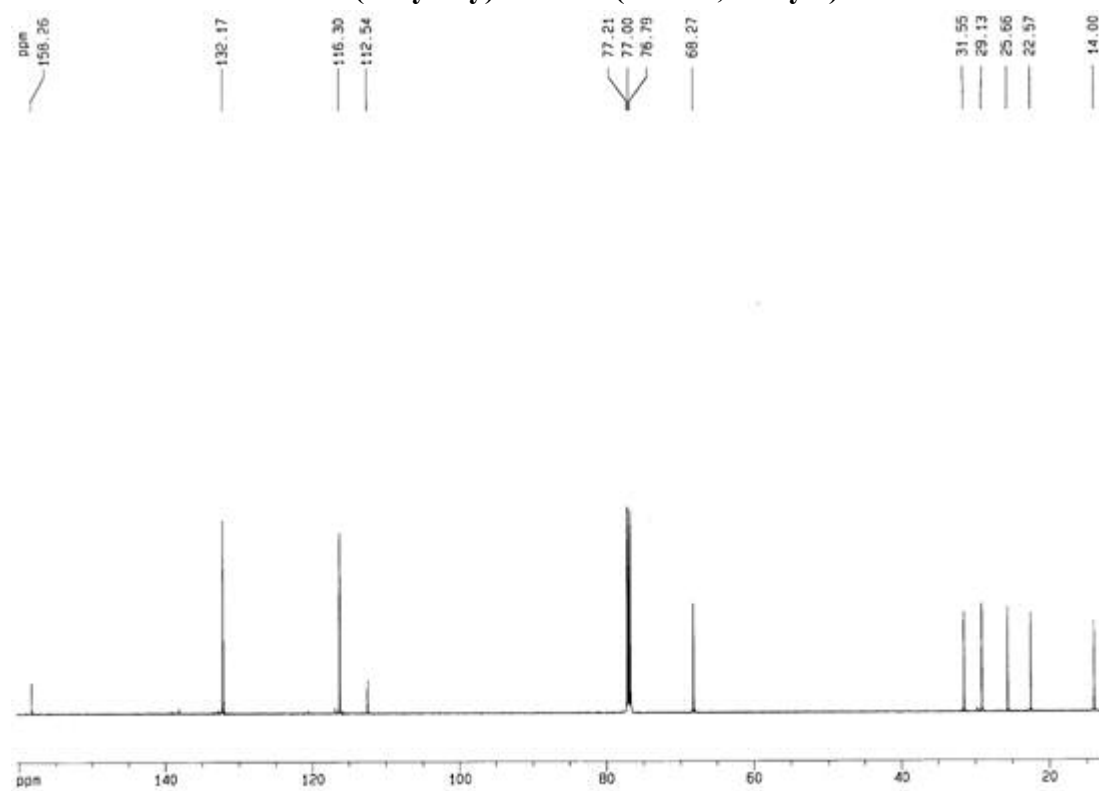
^{13}C -NMR for cyclohexyloxybenzene (table 3, entry 3)



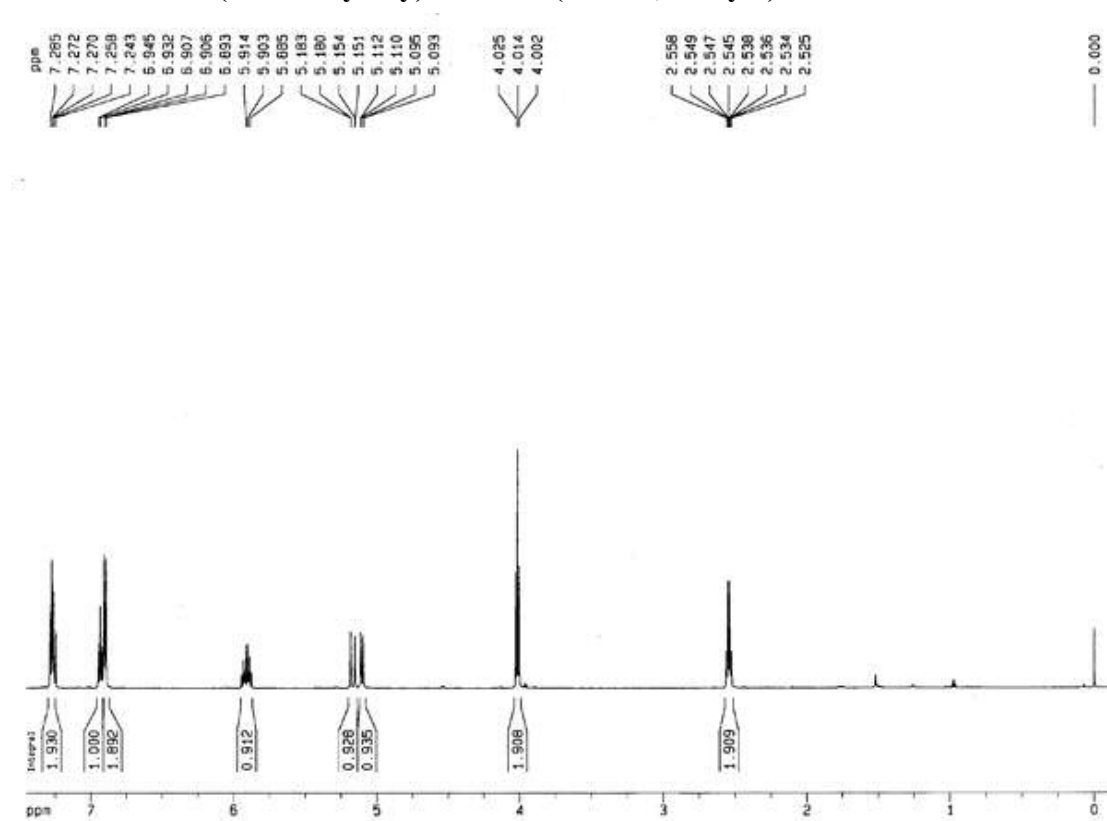
¹H-NMR for 1-bromo-4-(hexyloxy)benzene (table 3, entry 4)



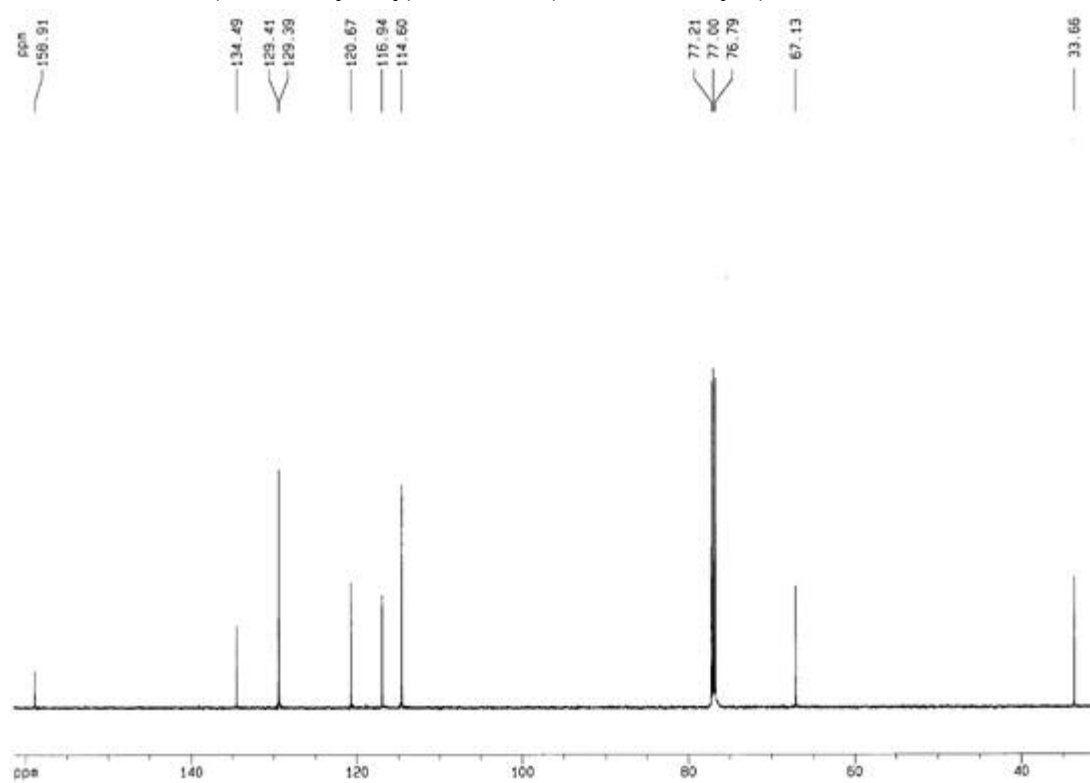
¹³C-NMR for 1-bromo-4-(hexyloxy)benzene (table 3, entry 4)



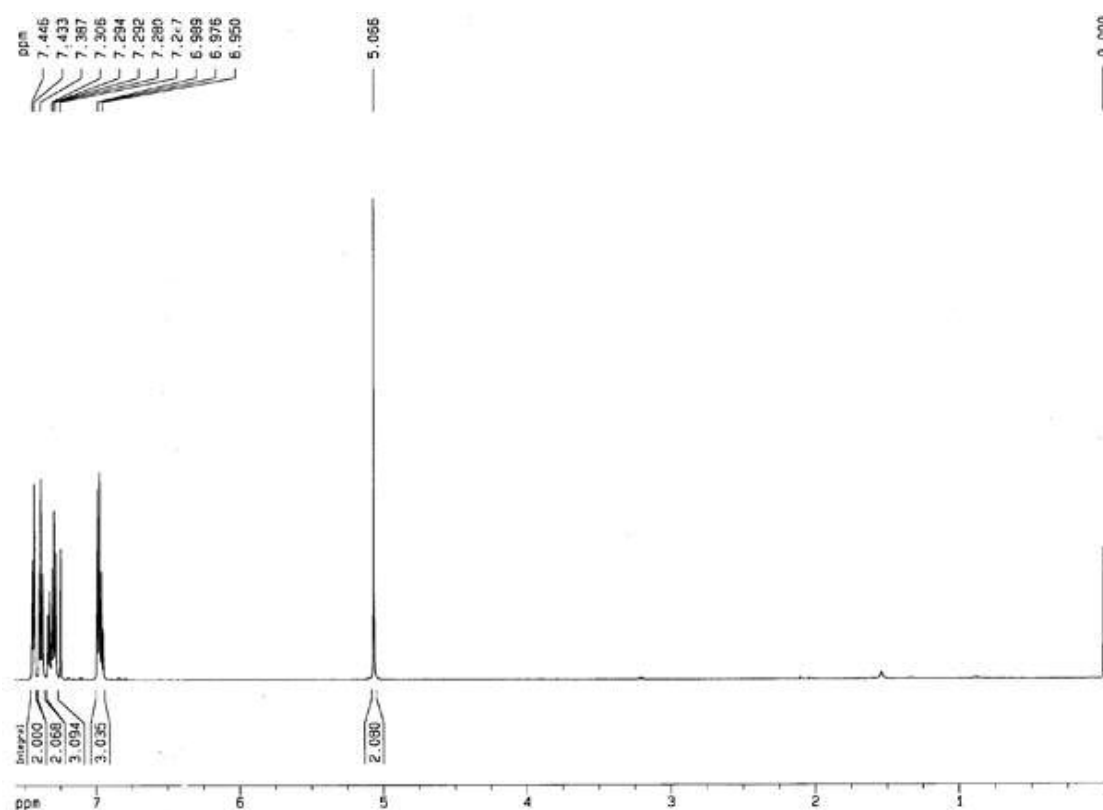
¹H-NMR for 1-(but-3-enyloxy) benzene (table 3, entry 5)



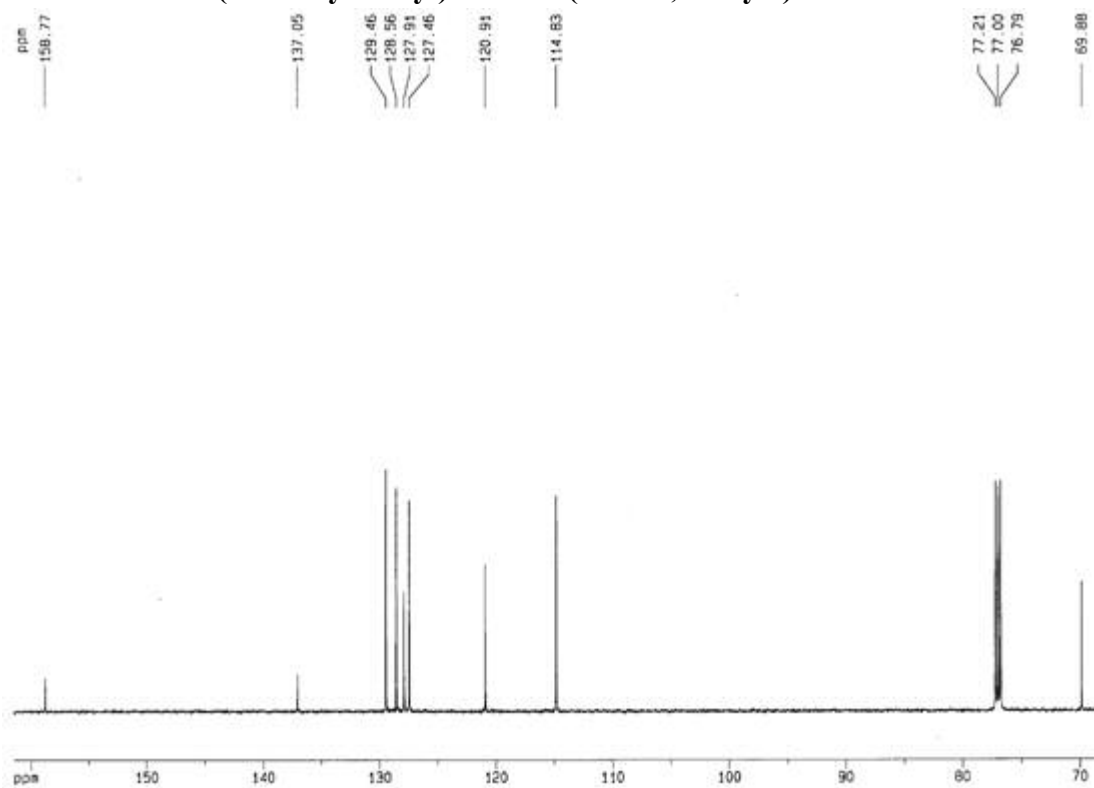
¹³C-NMR for 1-(but-3-enyloxy) benzene (table 3, entry 5)



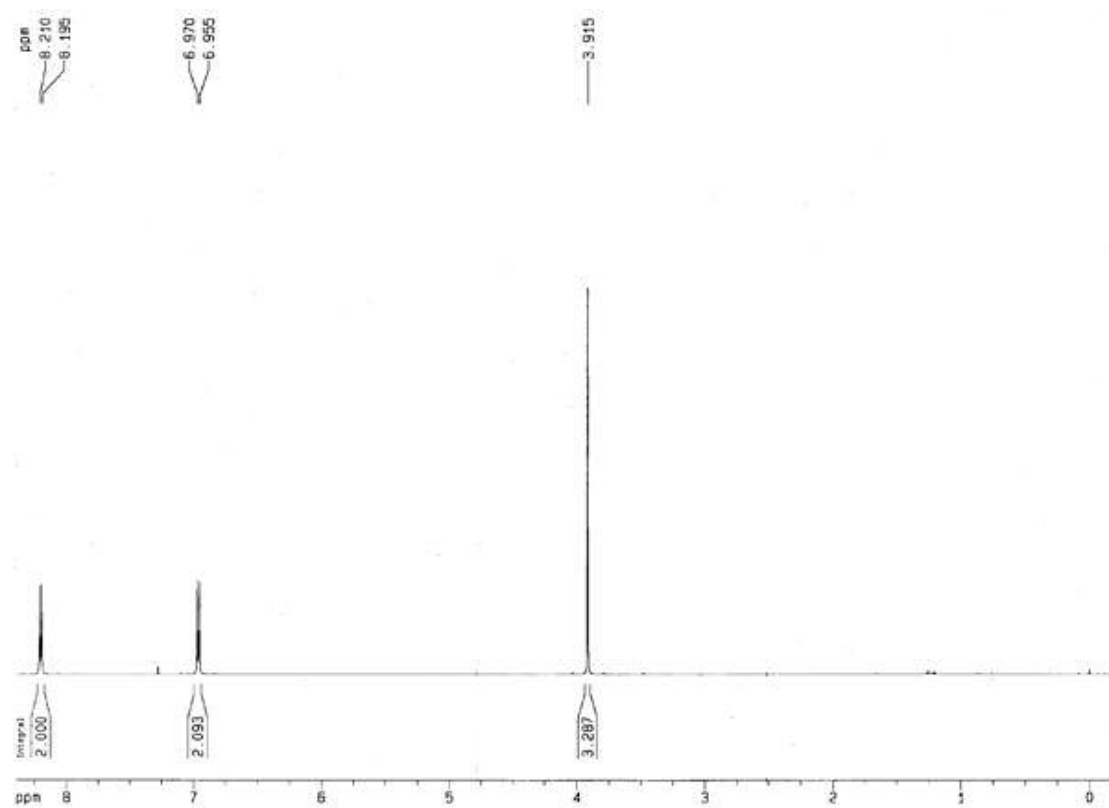
¹H-NMR for 1-(Phenoxymethyl)benzene (table 3, entry 6)



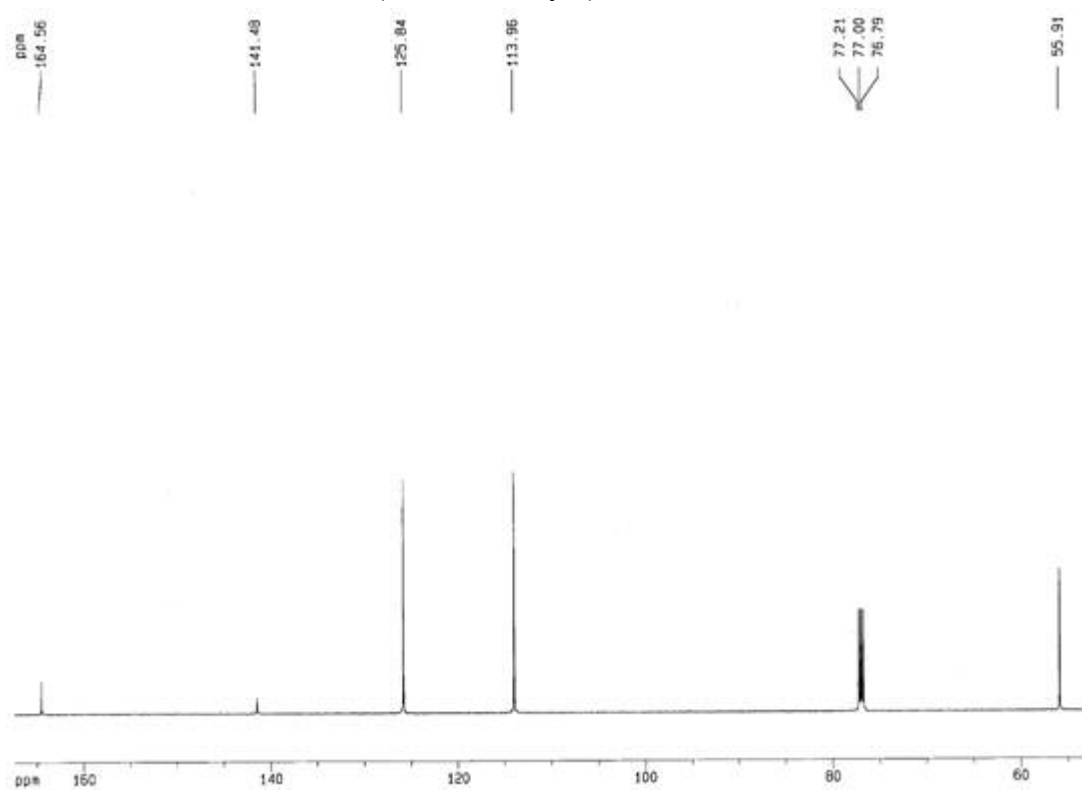
¹³C-NMR for 1-(Phenoxymethyl)benzene (table 3, entry 6)



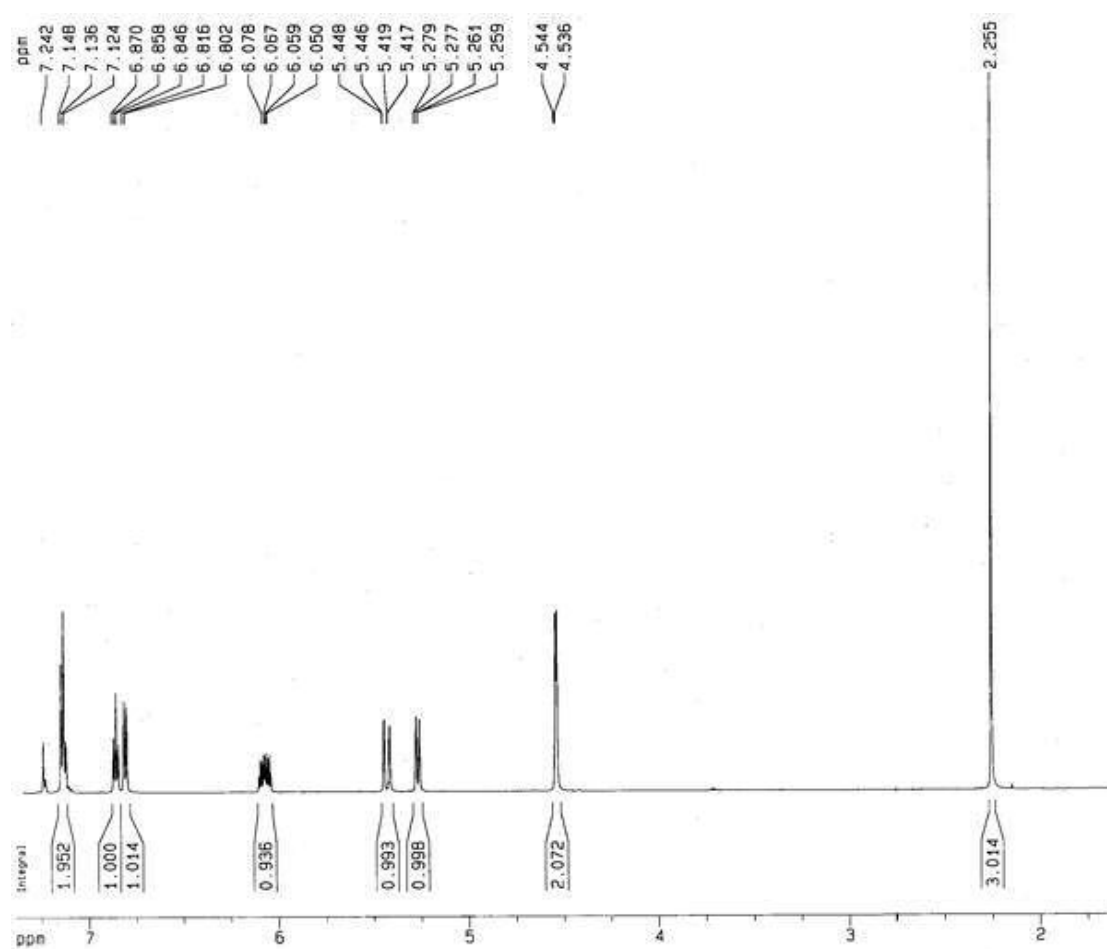
¹H-NMR for 4-nitroanisole (table 3, entry 7)



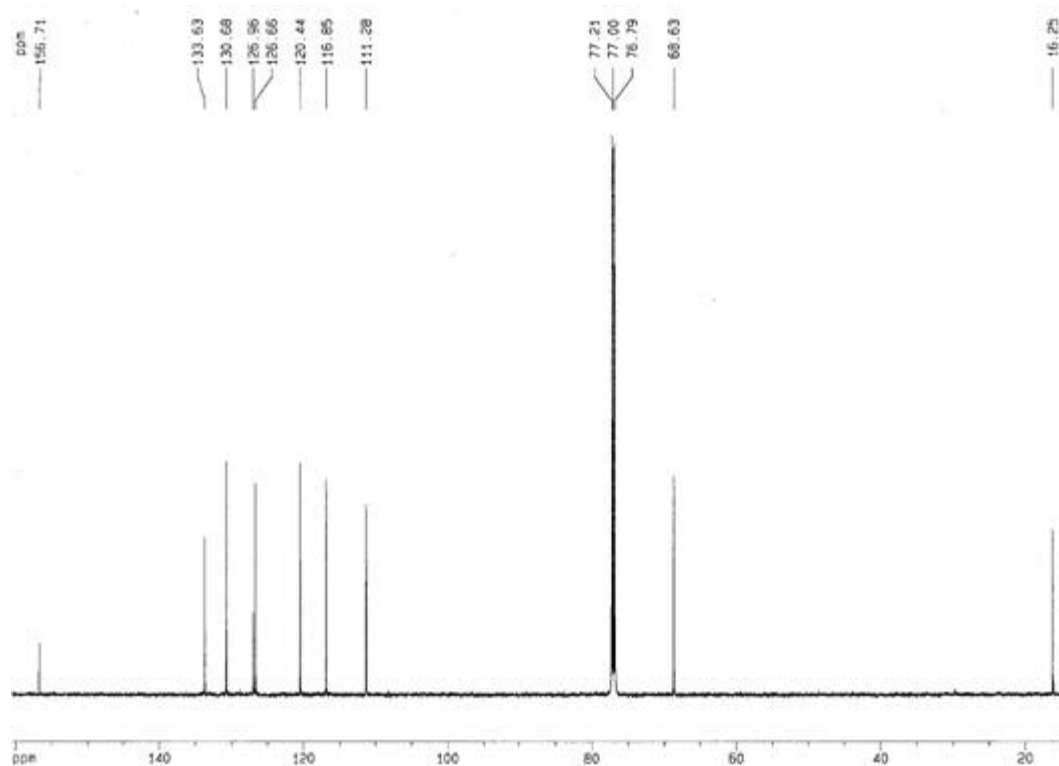
¹³C-NMR for 4-nitroanisole (table 3, entry 7)



¹H-NMR for allyl 2-tolyl ether (table 3, entry 8)



¹³C-NMR for allyl 2-tolyl ether (table 3, entry 8)



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