Supplementary Material (ESI) for Green Chemistry

Supporting Information

Sol-Gel Immobilized and Reusable Copper-Catalyst for Arylation of Phenols from Aryl Bromides.

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General Experimental Procedures

All reactions were carried out in 35 mL Schlenk tubes under a pure and dry nitrogen atmosphere. Methyl isobutyl ketone (MIBK) was distilled and was stored on 4 Å activated molecular sieves under a nitrogen atmosphere. Cesium carbonate (Aldrich) and tri-potassium phosphate (Riedel-de Haën) were ground to a fine powder and stored under vacuum in the presence of P_2O_5. All other solid materials were stored in the presence of P_2O_5 in a bench-top desiccator under vacuum at room temperature and weighed in the air. Copper (I) iodide was purified according to literature procedures[i] and stored protected from light. Aryl bromide was purchased from commercial sources (Aldrich, Acros, Avocado, Fluka, Lancaster). If solids, they were recrystallized in an appropriate solvent [ii]. If liquids, they were distilled under vacum and stored under atmosphere of nitrogen. Special care was taken with bromobenzene which was regularly distilled and stored protected from light. All phenols were also stored protected from light. Column chromatography were performed with SDS 60 A C.C silica gel (35-70 mm). Thin layer chromatography were carried out using Merck silica gel 60 F_{254} plates. All products were characterized by NMR, GC/MS and IR spectra. NMR spectra were recorded at 20 °C on DRX-400 spectrometers working at 400.13 MHz for ^1H and at 62.90 and 100.61 MHz for ^{13}C. Coupling constants are reported in Hz and chemical shifts in ppm/TMS for ^1H and $\{^1H\}^{13}C$ (δ 77.00 for $CDCl_3$ signal). The first-order peak patterns are indicated as s (singulet), d (doublet), t (triplet), q (quadruplet). Complex non-first-order signals are indicated as m (multiplet) and broad signals as br. Gas chromatography - mass spectra (GC/MS) were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973 N mass detector (EI) and a HP5-MS 30 m x 0.25 mm capillary apolar column (Stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 µm). GC/MS method: Initial temperature: 45 °C; Initial time: 2 min; Ramp: 2 °C/min until 50 °C then 10 °C/min; Final temperature: 250 °C; Final time: 10 min. Melting points were determined using a Buchi B-540 appartus and are uncorrected.

<u>Protocol A</u> : General procedure for coupling reaction of phenols with aryl bromide

After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried schlenk tube was charged with CuI (0.1 mmol) , ligand (0.1 mmol), Cs_2CO_3 (3 mmol) phenol (3 mmol) and aryl bromides (2 mmol) if solids. The tube was then evacuated, back-filled with nitrogen and capped with a rubber septum. If liquids, phenols and aryl bromides were added under nitrogen atmosphere by syringe at room temperature. Then 1 mL of anhydrous and degassed MIBK was added under nitrogen atmosphere. The septum was removed and the schlenk sealed under positive nitrogen atmosphere and stirred in an oil bath (110 °C) for 22 hours. After complete consumption of aryl bromides, the reaction mixture was then allowed to cool to r.t. The crude mixture was then filtered on air without any precaution on a frit glass, and washed two times with 5 mL of DCM (the crude could also be washed by 2*5 mL of MIBK). The extracted solution was then filtered on a celite plug, then concentrated under vacuum, and chromatographied on silica gel.

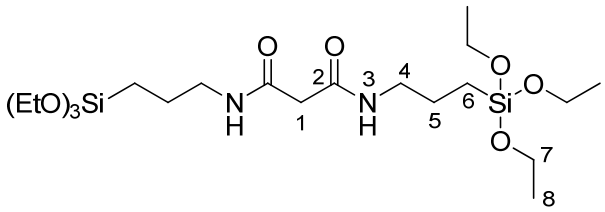
Protocol B : General procedure for recycling experiments and coupling of phenols with aryl bromides: The crude solid mixture obtained previously after filtration and several washing was dried under vacuum. Then Cs_2CO_3 (3 mmol) phenol (3 mmol) and aryl bromides (2 mmol) were charged if solids. The tube was then evacuated, back-filled with nitrogen and capped with a rubber septum. If liquids, phenols and aryl bromides were added under nitrogen atmosphere by syringe at room temperature. Then 1 mL of anhydrous and degassed MIBK was added under nitrogen atmosphere. The septum was removed and the schlenk sealed under positive nitrogen atmosphere and stirred in an oil bath (110 °C) for 22 hours.

General procedure for the synthesis of the precursor P

The preparation of the precursor was considered using a reaction acylation of aminopropyltriéthoxysilane by malonyle dichloride. Two equivalents of diethylamine were added to trap acid chlorydrique formed during the reaction.

Purification of the product, very sensitive to hydrolysis and high molecular weight, could not be achieved. It degrades in effect at its distillation or passing on a column of silica. Nevertheless, very few impurities have been detected in RMN.

Identification



^{1}H NMR ($CDCl_3$): δ=0.58 (4H, H_6, t), 1.15 (18H, H_8, t), 1.58 (4H, H_5, m), 2.85 (2H, H_1, s), 3.09 (4H, H_4, q), 3.75 (12H, H_7, q), 7.21 (1H, H_3, s).

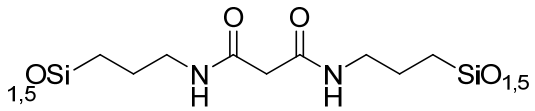
^{13}C NMR: δ=7.77(CH_2Si), 18.28(OCH_2CH_3), 22.73 ($CH_2CH_2CH_2$), 40.83 (CH_2NH), 42.03 ($C(O)CH_2C(O)$), 58.44(OCH_2), 167.35(C(O)).

^{29}Si NMR: δ= -46.6 ($Si(OC_2H_5)_3$).

General procedure for the synthesis hybrid ligand M

The sol-gel hydrolysis-condensation of the alkoxy groups on silicon allowed the formation of bridged silsesquioxane consisting of a siloxane network with diamide crosslinking units. Procedure for the preparation of material : In a schlenk tube, water (3.09 ml, 172 mmol) and TBAF (41.64 µl of 0.1M solution, 1mol%) were added to a stirred mixture of **L** (7.32 g, 14 mmol) in EtOH (14.33 ml) and then the mixture was left under static condition. Immediatly, a precipite was formed. After 2 hours, an orange gel was formed. This was aged for 2 days and then powdered, washed with ethanol, ether, and dried under vacuum for 24h to give a white powder of materel in quantitative yield.

Identification



^{13}C NMR (CP-MAS): δ= 10.5, 24.12(1C, C_{11}), 42.66(1C, C_{10}), 111.54(2C, $C_{5,6}$), 148.99(3C, $C_{2,3,4}$), 156.59(1C, C_8).

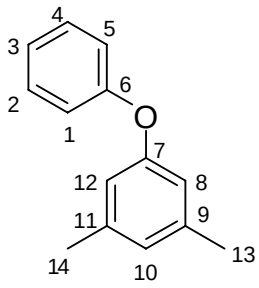
^{29}Si NMR (CP-MAS): δ= -53.5 (T^1), -61.1 (T^2), -67.4 (T^3)

Spectroscopic data for Cross-coupling products (1-12) :

- **1,3-dimethyl-5-phenoxybenzene (1)**

Experimental procedure : Following the general **protocol A** (110 °C, 24h) to provide after flash chromatography on silica gel 392 mg (99 % yield) of the desired product as a colorless oil.

Identification



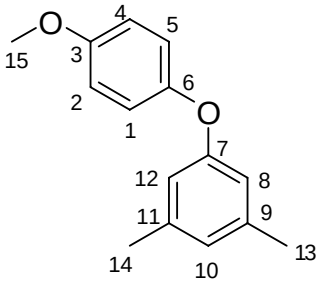
RMN ^{1}H / $CDCl_3$: δ = 7.51-7.47 (m, 2H, $H_{2,4}$), 7.24-7.28 (m, 1H, H_3), 7.20-7.22 (m, 2H, $H_{1,5}$), 6.93 (m, $1H_{10}$), 6.86 (m, 2H, $H_{8,12}$), 2.47 (s, 6H, $H_{13,14}$).

^{13}C NMR / $CDCl_3$: δ = 157.70 (C_6), 157.39 (C7), 139.71 ($C_{9,11}$), 129.84 ($_{2,4}$), 125.21 (C_{10}), 123.14 (C_3), 119.02 ($C_{1,5}$), 116.87 ($C_{8,12}$), 21.47 ($C_{13,14}$).
GC/MS : tr = 16,87 min, M/Z = 198.

- **1-(4-methoxyphenoxy)-3,5-dimethylbenzene (2)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 342 mg (75 % yield) of the desired product as white cristals.

Identification

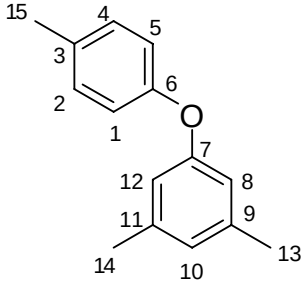


RMN ^{1}H / $CDCl_3$: δ 6.83-6.85 (m, 2H, $H_{2,4}$), 6.73-6.75 (m, 2H, $H_{1,5}$), 6.56 (m, 1H, H_{10}), 6.45 (m, 2H, $H_{8,12}$), 3.65(s, 3H, H_{15}), 2.13 (s, 6H, $H_{13,14}$).
RMN ^{13}C / $CDCl_3$: δ 157.43 (C_3), 154.67 (C_7), 149.21 (C_6), 138.34 ($C_{9,11}$), 123.12 (C_{10}), 129.73 ($C_{1,5}$), 114.24 ($C_{2,4}$), 113.68 ($C_{8,12}$), 54.46 (C_{15}), 20.23 ($C_{13,14}$).

- **1,3-dimethyl-5-(p-tolyloxy)benzene (3)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 326 mg (77 % yield) of the desired product as a colorless oil.

Identification

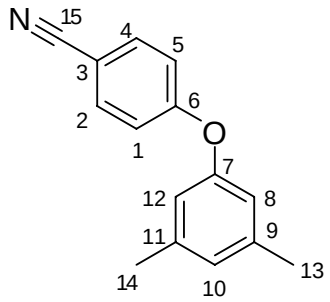


^{1}H NMR / $CDCl_3$: δ = 7.23-7.25 (dd, 2H, $H_{2,4}$), 7.02-7.05 (dd, 2H, $H_{8,12}$), 6.83 (d, 2H, $H_{1,5}$), 6.74 (s, H_{10}), 2.39 (s, 6H, $H_{13,14}$).
^{13}C NMR / $CDCl_3$: δ = 20.79 (C_{15}), 21.40 ($C_{13,14}$), 116.20 ($C_{8,12}$), 119.21 ($C_{6,2}$), 124.68 (C_{10}), 130.26 ($C_{5,3}$),(C_4) 139,55 ($C_{9,14}$), 155,03 (C_1), 157,88 (C_7).

- **4-(3,5-dimethylphenoxy)benzonitrile (4)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 402 mg (90 % yield) of the desired product as white cristals.

Identification



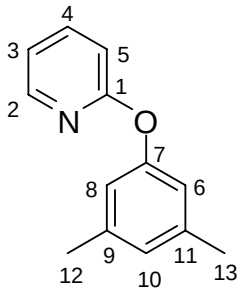
RMN ^{1}H / $CDCl_3$: δ 7.59-7.61 (m, 2H, $H_{2,4}$), 7.00-7.02 (m, 2H, $H_{1,5}$), 6,88 (m, 1H, H_{10}), 6.70 (m, 2H, $H_{8,12}$) 2.34 (s, 6H, $H_{13,14}$)

RMN ^{13}C / $CDCl_3$: δ 161.90 (C_6), 154.72 (C_7), 140.18 ($C_{9,11}$), 134.07 ($C_{2,4}$), 126.84 (C_{10}), 118.95 (C_{15}), 118.01 ($C_{1,5}$), 117.85 ($C_{2,8}$), 105.50 (C_3), 21.28 ($C_{13,14}$)

- **2-(3,5-dimethylphenoxy)pyridine (5)**

Experimental procedure : Following the general **protocol B** (120 °C, 24h) to provide after flash chromatography on silica gel 391 mg (98 % yield) of the desired product as colorless oil.

Identification



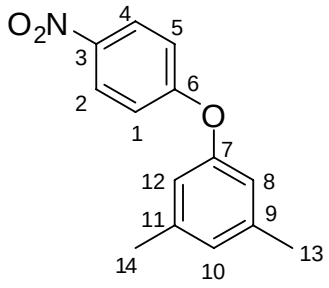
RMN ^{1}H / $CDCl_3$: 8.23-8.24 (1H, H_1), 7.66-7.70 (1H, H_4), 6.98-7.01 (1H, H_3), 6.91 (1H, H_5), 6.86 (1H, H_{10}), 6.78 (2H, $H_{6,8}$), 2.34 (6H, $H_{12,13}$)

RMN ^{13}C / $CDCl_3$:164.03 (C_1), 154.13 (C_7), 147.87 (C_2), 139.48 ($C_{9,11}$), 139.29 (C_4), 126.55 (C_{10}), 118.81 ($C_{6,8}$), 118.23 (C_5), 111.48 (C_3), 21.35 ($C_{12,13}$)

- **1,3-dimethyl-5-(4-nitrophenoxy)benzene (6)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 460 mg (95 % yield) of the desired product as white-pale yellow cristals.

Identification

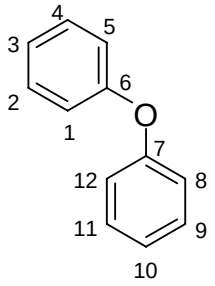


RMN ^{1}H / $CDCl_3$: 8.09-8.11 (m, 2H, $H_{2,4}$), 6.90-6.92 (m, 2H, $H_{1,5}$), 6.80 (m, 1H, H_{10}), 6.62 (m, 2H, $H_{8,12}$), 2.25 (s, 6H, $H_{13,14}$).
RMN ^{13}C / $CDCl_3$:163.64 (C_6), 154.63 (C_7), 140.29(C_3), 140.29 ($C_{9,11}$), 127.09 ($C_{2,4}$), 125.89 (C_{10}), 118.12 ($C_{1,5}$), 117.03 ($C_{8,12}$), 21.29 ($C_{13,14}$).

- **Diphenyl ether (7)**

Experimental procedure : Following the general **protocol A** (110 °C, 24h) to provide after flash chromatography on silica gel 294 mg (87 % yield) of the desired product as a colorless oil.

Identification

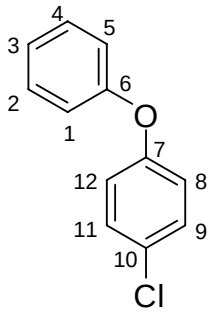


RMN ^{1}H / $CDCl_3$: δ 7.43-7.47 (m, 4H, $H_{2,4,9,11}$), 7.20-7.24 (m, 6H, $H_{1,3,5,8,10,12}$).
RMN ^{13}C / $CDCl_3$: δ 157.40 ($C_{6,7}$), 129.89 ($C_{2,4,9,11}$), 123.35 ($C_{3,10}$), 119.03 ($C_{1,5,8,12}$).

- **1-chloro-4-phenoxybenzene (8)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 265 mg (65 % yield) of the desired product as colorless oil.

Identification



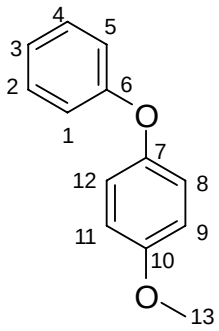
RMN ^{1}H / $CDCl_3$: δ 7.16-7.21 (m, 2H, $H_{8,12}$) 7.11-7.13(m, 2H, $H_{9,11}$) 6.93-6.99(m, 2H, $H_{2,4}$) 6.85-6.89(dd, 1H, H3) 6.77-6.79 (m, 2H, $H_{1,5}$)

RMN ^{13}C / $CDCl_3$: δ 156.98-157.37 (C_1), 156.07 (C_7), 129.82-129.99 ($C_{9,11}$), 123.32-123.75 ($C_{3,5}$), 120.14 (C_4), 118.00-119.05 ($C_{2,6,8,12}$)

- **1-methoxy-4-phenoxybenzene (9)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 369 mg (92 % yield) of the desired product as colorless oil.

Identification



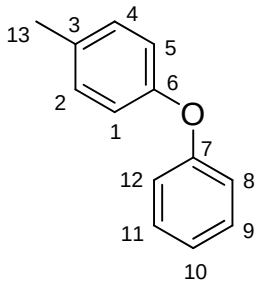
^{1}H NMR / $CDCl_3$: δ = 7.17-7.24 (m, 2H, $H_{2,4}$), 6.94-6.98 (t, 1H, H_3), 6.85-6.92 (m, 2H, $H_{1,5}$), 6.79-6.82 (2H, $H_{8,12}$), 6.80 (2H, $H_{9,11}$), 3.72 (3H, H_{13}).

^{13}C NMR / $CDCl_3$: δ = 158.5 (C_6), 155.9 (C_{10}), 150.2 (C_7), 129.7 ($C_{2,4}$), 122.5 (C_3), 120.9 ($C_{8,12}$), 120.9 ($C_{1,5}$), 117.6 ($C_{9,11}$), 55.6 (C_{13}).

- **1-methyl-3-phenoxybenzene (10)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 349 mg (95 % yield) of the desired product as colorless oil.

Identification



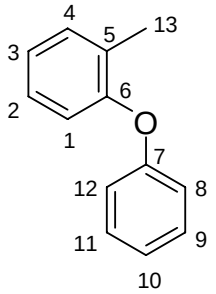
RMN ^{1}H / $CDCl_3$:7.15-7.19 (m, 2H, $H_{3,5}$), 6.99-7.01 (m, 2H, $H_{8,10}$), 6.93-6.95 (m, 1H, H_4), 6.85-6.87 (m, 2H, $H_{2,6}$), 6.79-6.81(m, 2H, $H_{7,11}$), 2.20 (s, 3H, H_{12}).

RMN ^{13}C / $CDCl_3$:157.94 (C_1), 154.83 (C_7), 132.97 (C_{10}), 130.36 ($C_{3,5}$), 129.76 ($C_{9,11}$), 122.90 (C_4), 119.25 ($C_{2,6}$), 118.44 ($C_{8,12}$), 20.82 (C_{13}).

- **1-methyl-2-phenoxybenzene (11)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 339 mg (92 % yield) of the desired product as colorless oil.

Identification



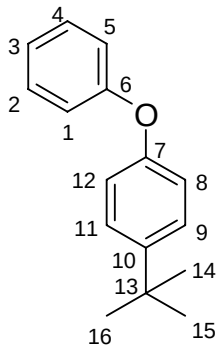
^{1}H NMR / $CDCl_3$: δ = 7.12-7.19 (m, 3H, $H_{4,9,11}$), 7.02-7.07 (m, 1H, H_{10}), 6.90-6.97 (m, 2H, $H_{2,3}$), 6.78-6.81 (m, 3H, $H_{1,8,12}$), 2.13 (s, 3H, H_{13}).

^{13}C NMR / $CDCl_3$: δ =158.01 (C_7), 154.54 (C_6), 131.52 (C_2), 130.1 (C_5), 129.73 ($C_{9,11}$), 127.22 (C_4), 124.07 (C_{10}), 122.40 (C_3), 119.88 (C_1), 117.37 ($C_{8,12}$), 16.26 (C_{13}).

- **1-tert-butyl-4-phenoxybenzene (12)**

Experimental procedure : Following the general **protocol B** (110 °C, 24h) to provide after flash chromatography on silica gel 448 mg (99 % yield) of the desired product as white crystals.

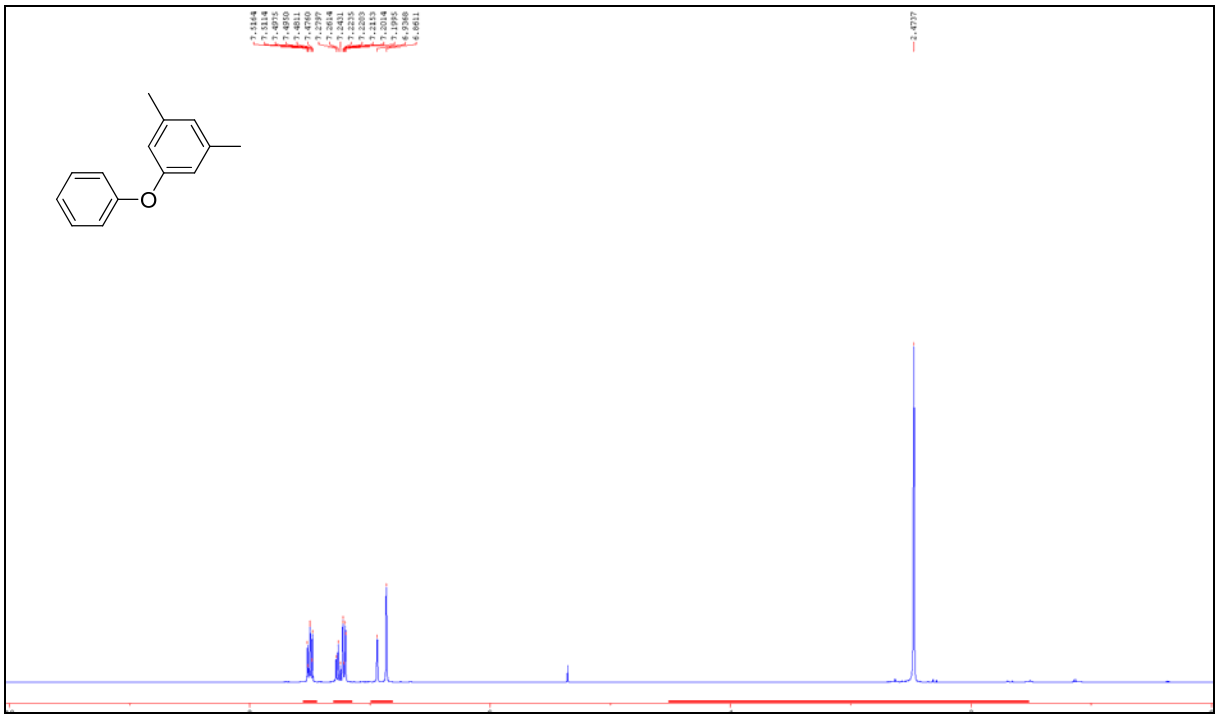
Identification

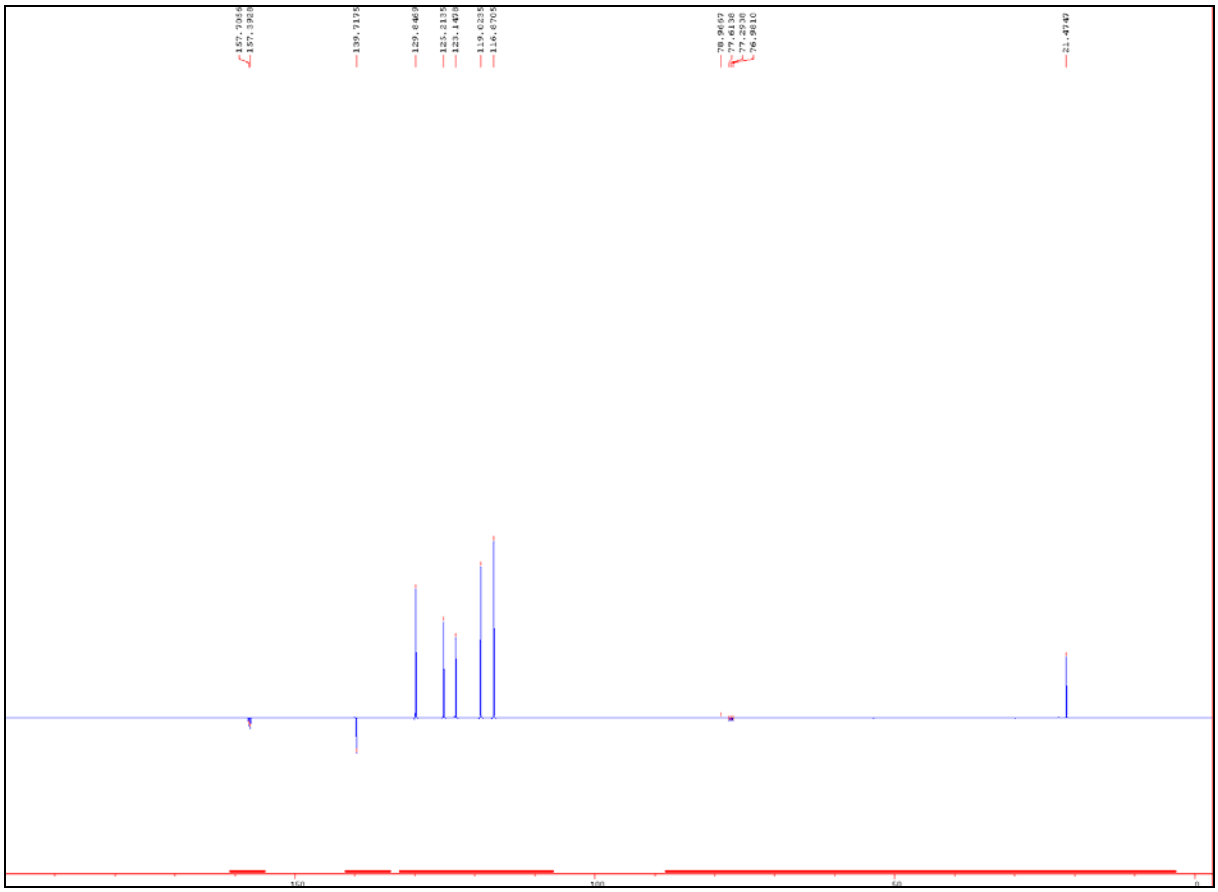


^{1}H NMR / $CDCl_3$: δ = 7.19-7.23 (m, 4H, $H_{2,4,8,12}$), 6.95-6.96 (m, 1H, H_3), 6.88-6.90 (m, 4H, $H_{1,5,9,11}$), 1.21 (s, 9H, $H_{14\text{-}16}$).

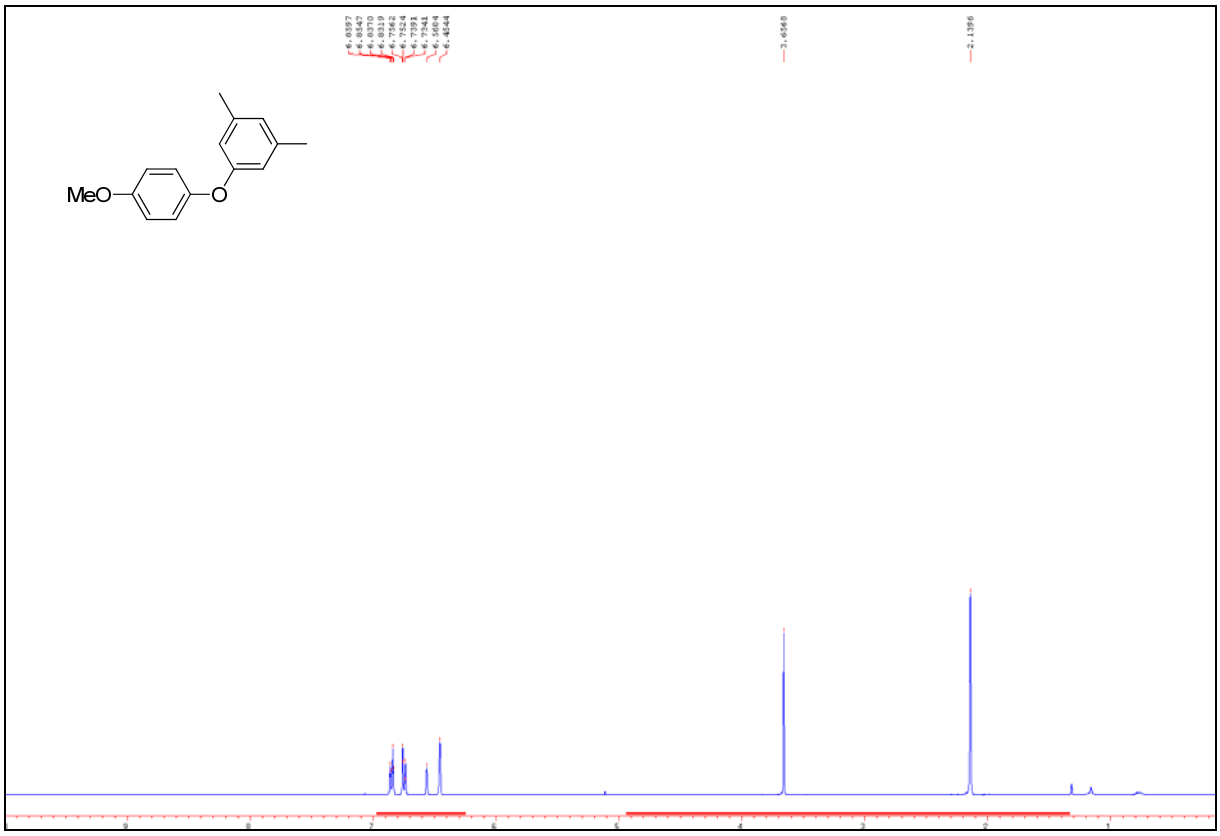
^{13}C NMR / $CDCl_3$: δ = 157.70 (C_6), 154.82 (C_7), 146.17 (C_{10}), 129.73 ($C_{2,4}$), 126.62 ($C_{9,11}$), 122.29 (C_3), 118.57-118.71 ($C_{1,5,8,12}$), 34.38 (C_{13}), 31.61 ($C_{14,15,16}$).

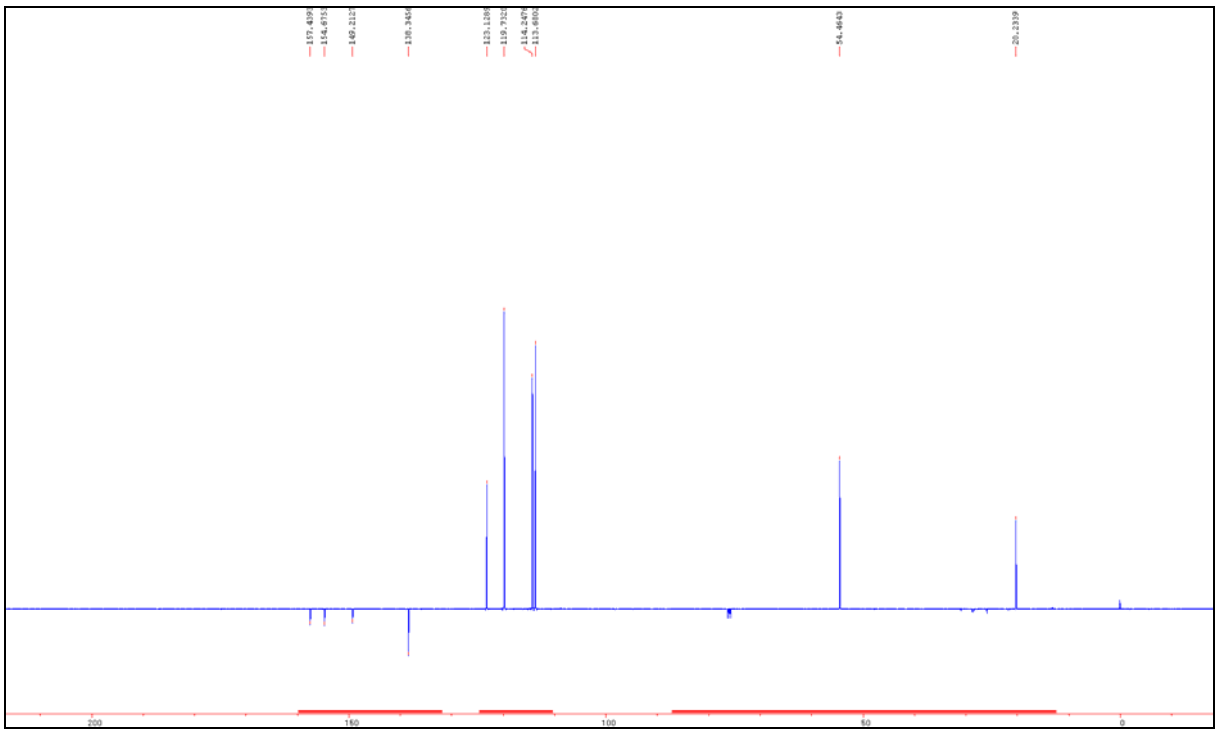
1,3-dimethyl-5-phenoxybenzene **1**



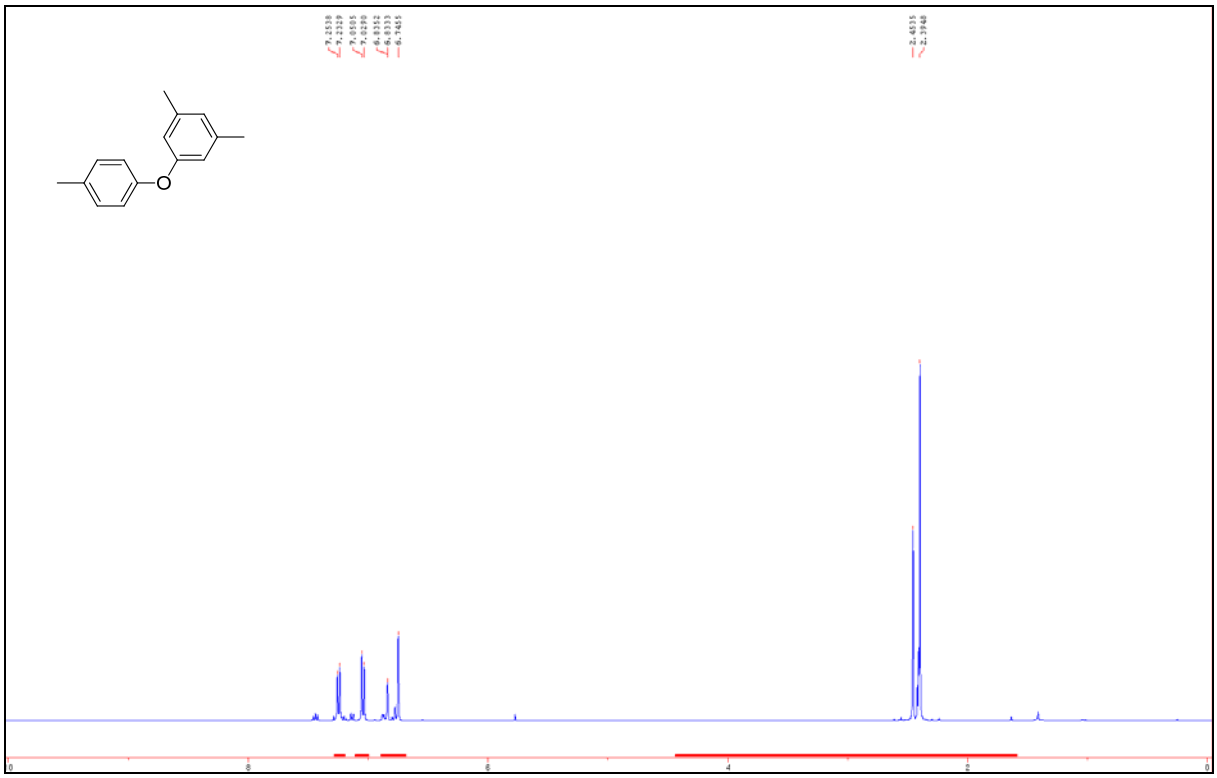


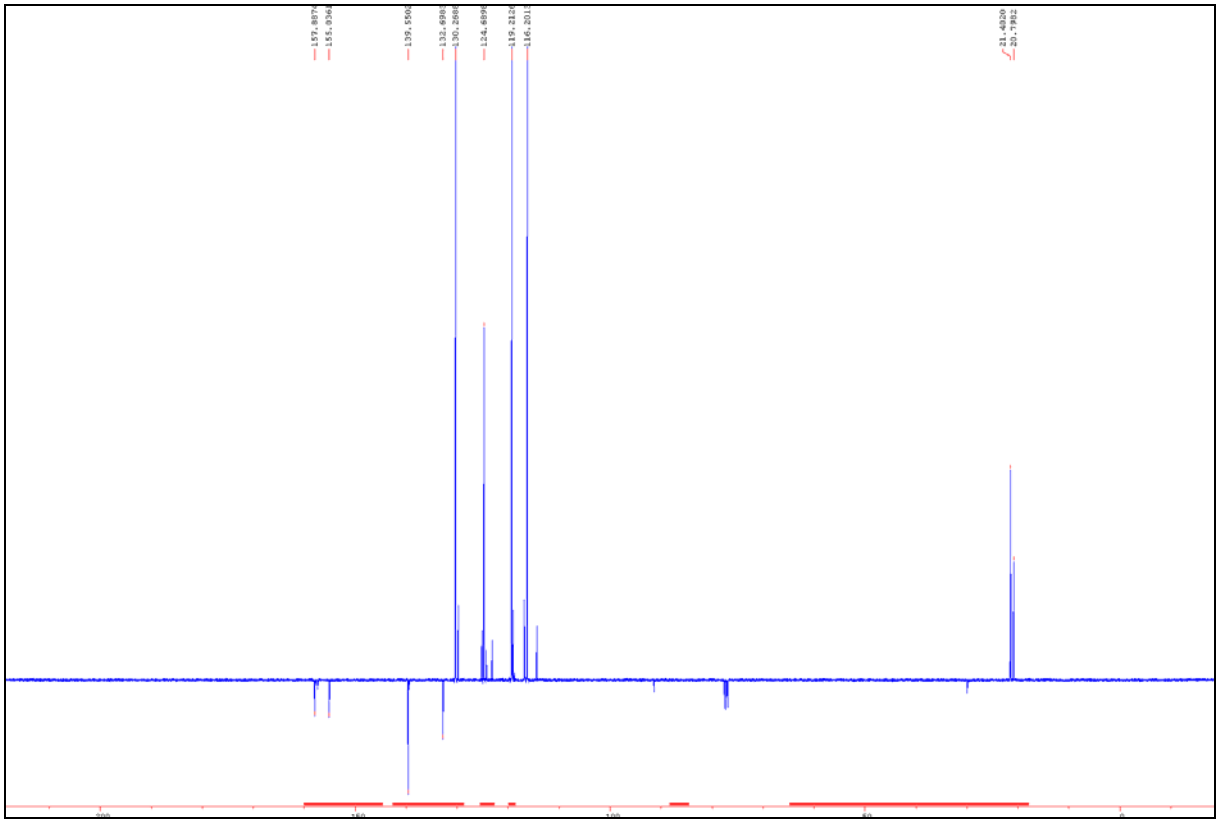
1-(4-methoxyphenoxy)-3,5-dimethylbenzene **2**



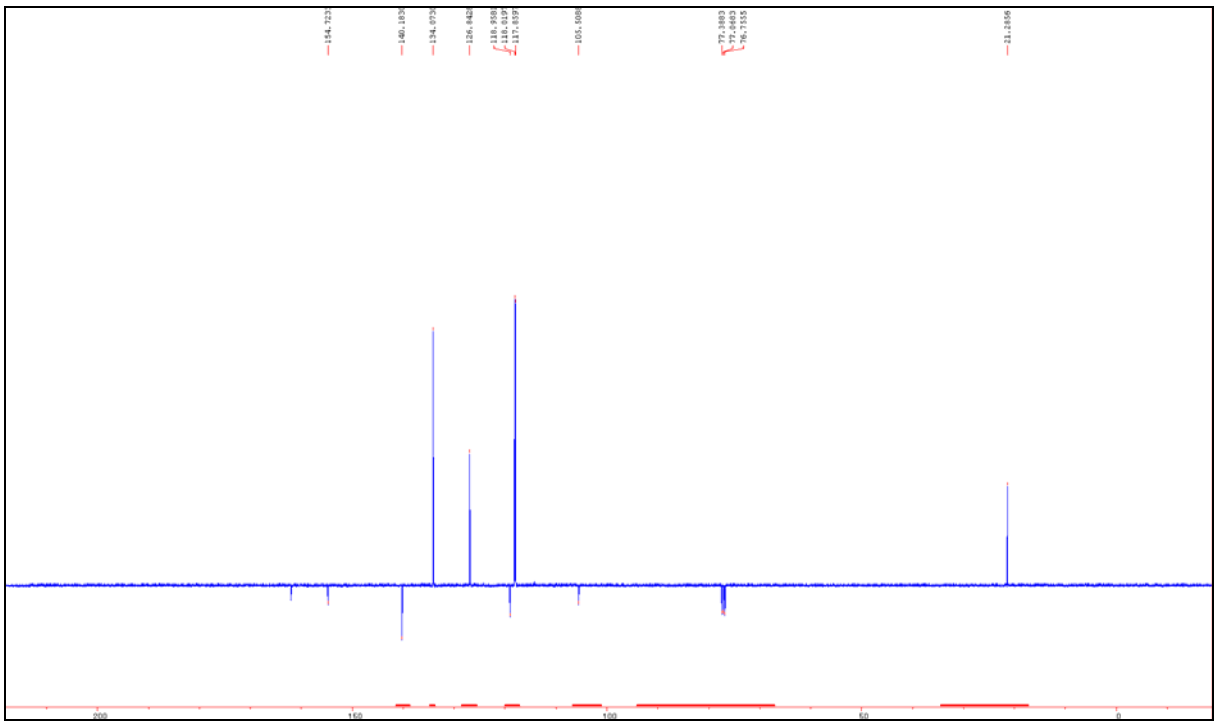


1,3-dimethyl-5-(p-tolyloxy)benzene **3**

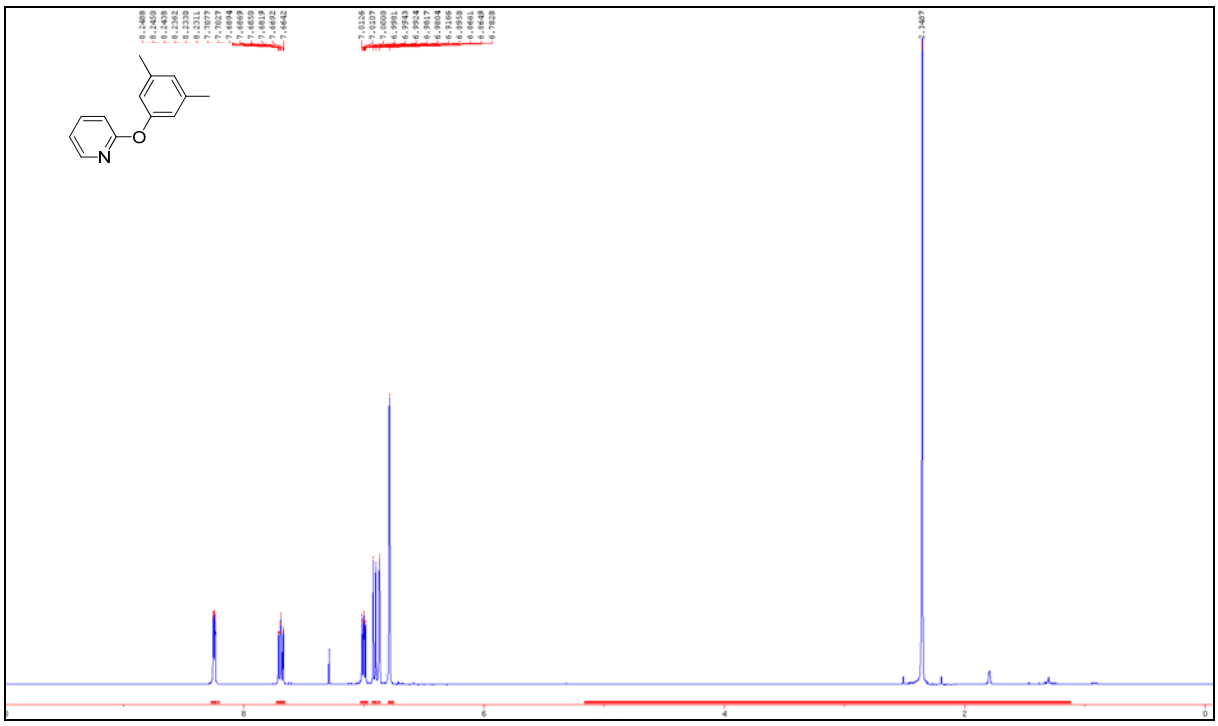


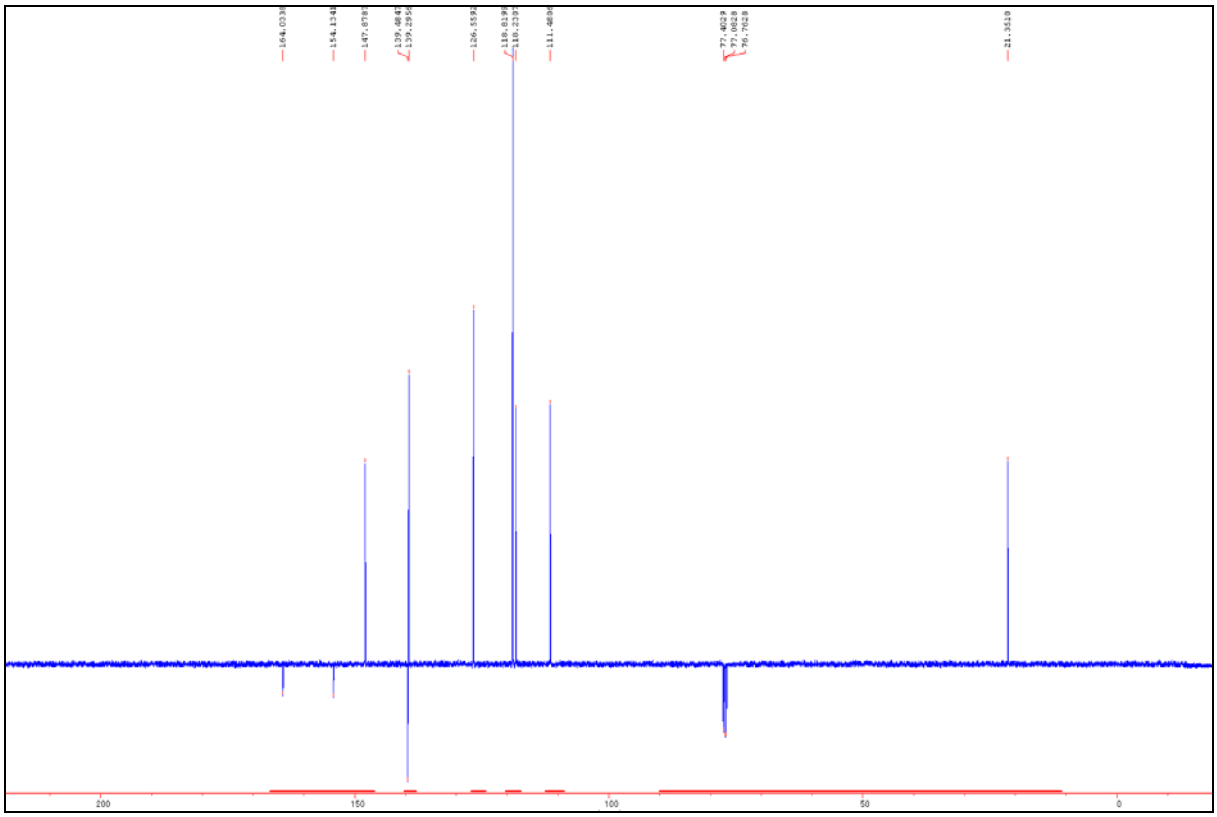


4-(3,5-dimethylphenoxy)benzonitrile **4**

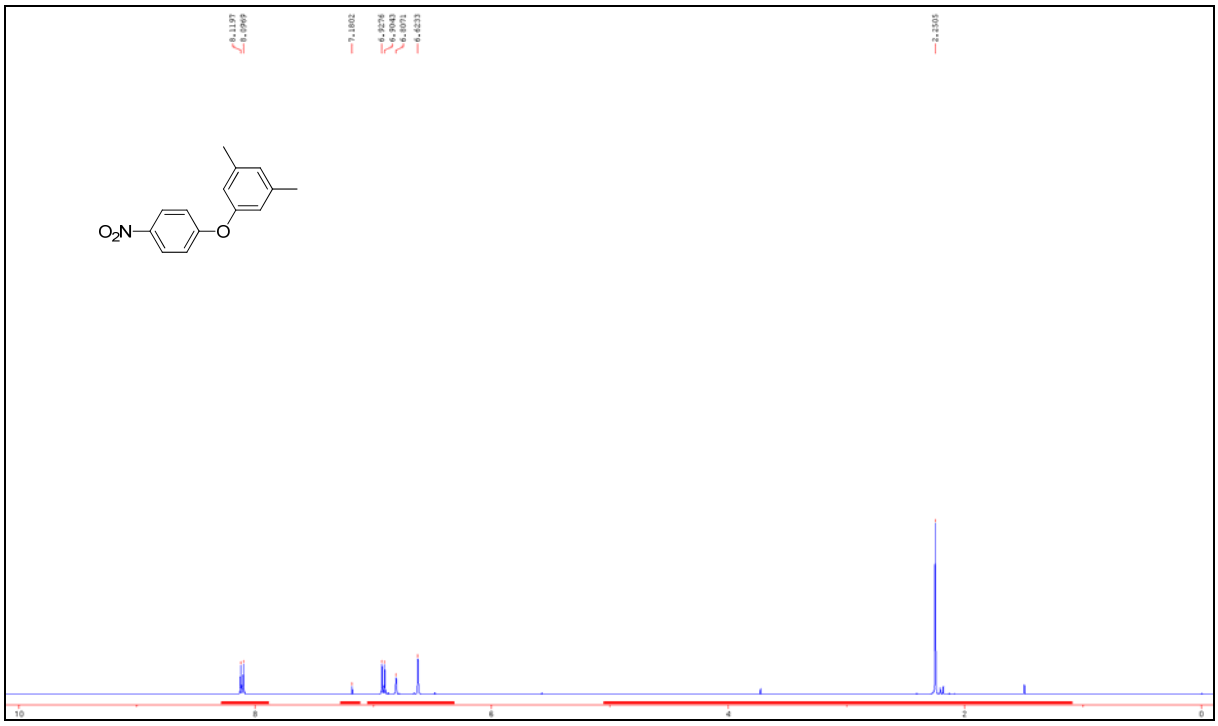


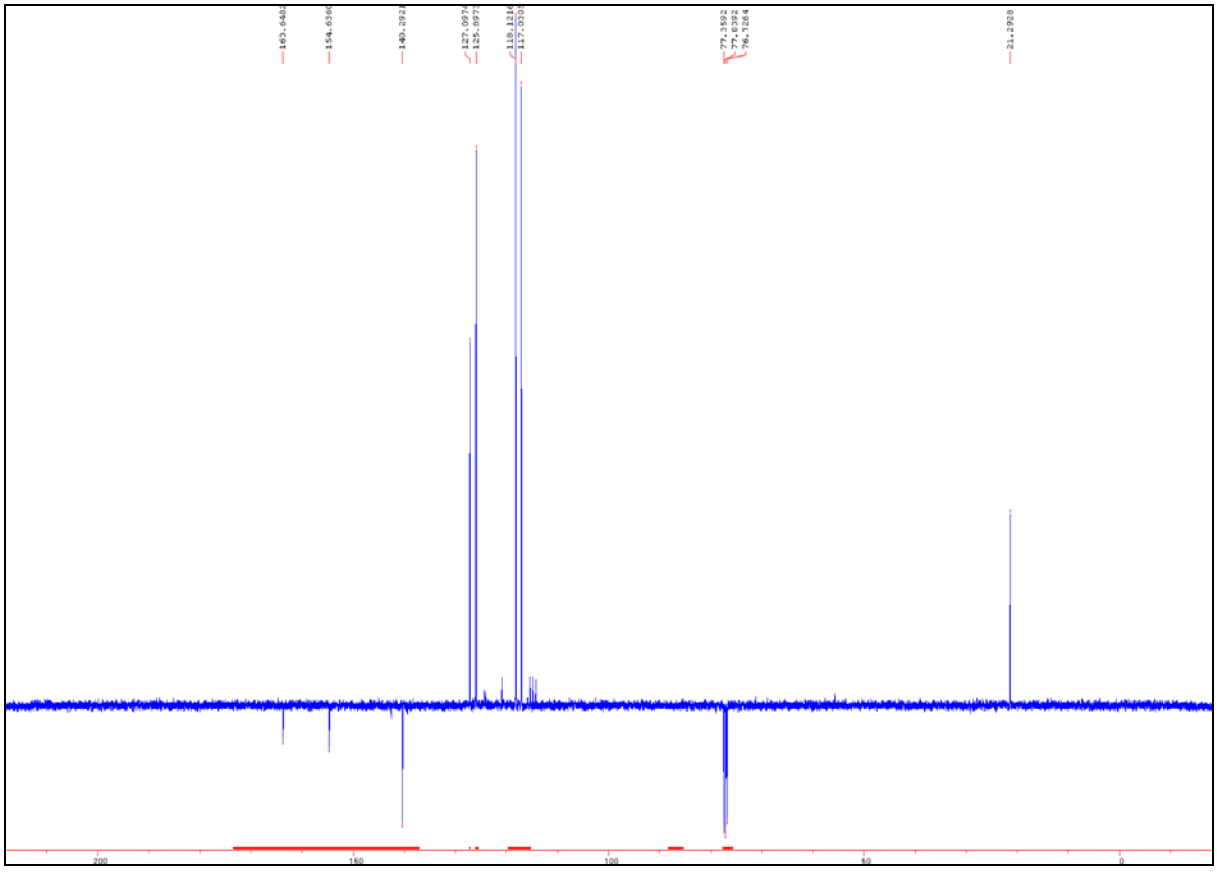
2-(3,5-dimethylphenoxy)pyridine **5**



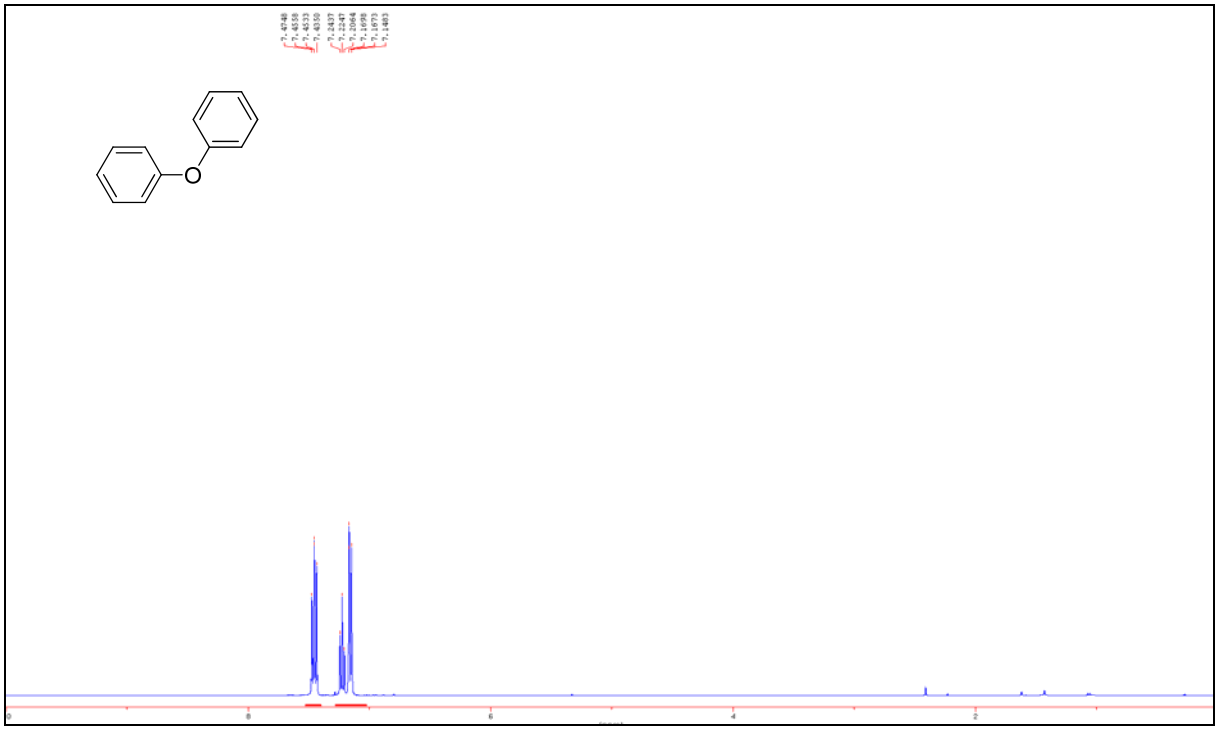


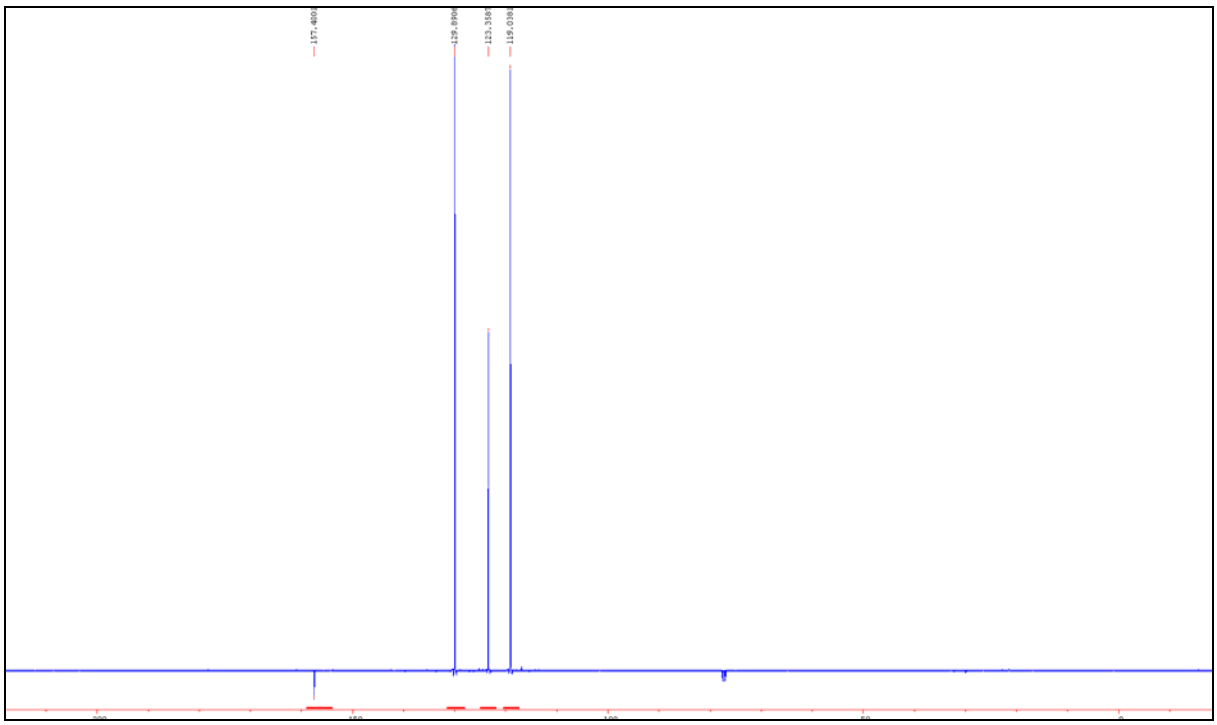
1,3dimethyl-5-(4-nitrophenoxy)benzene **6**



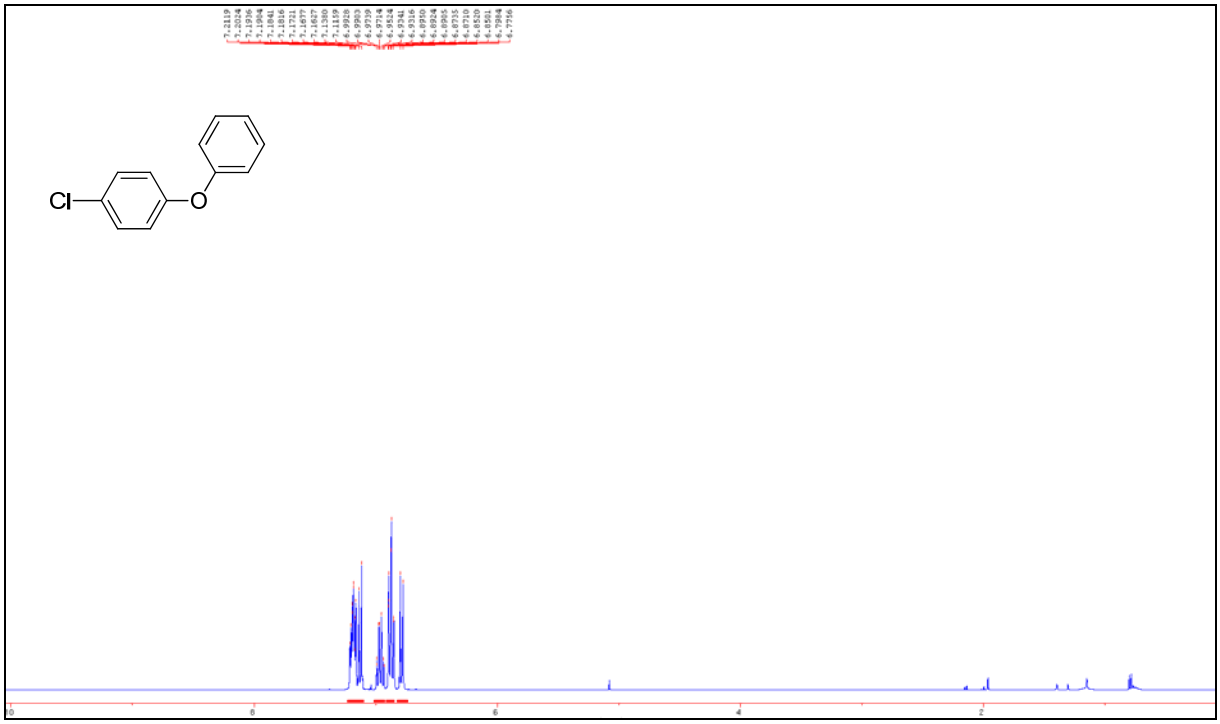


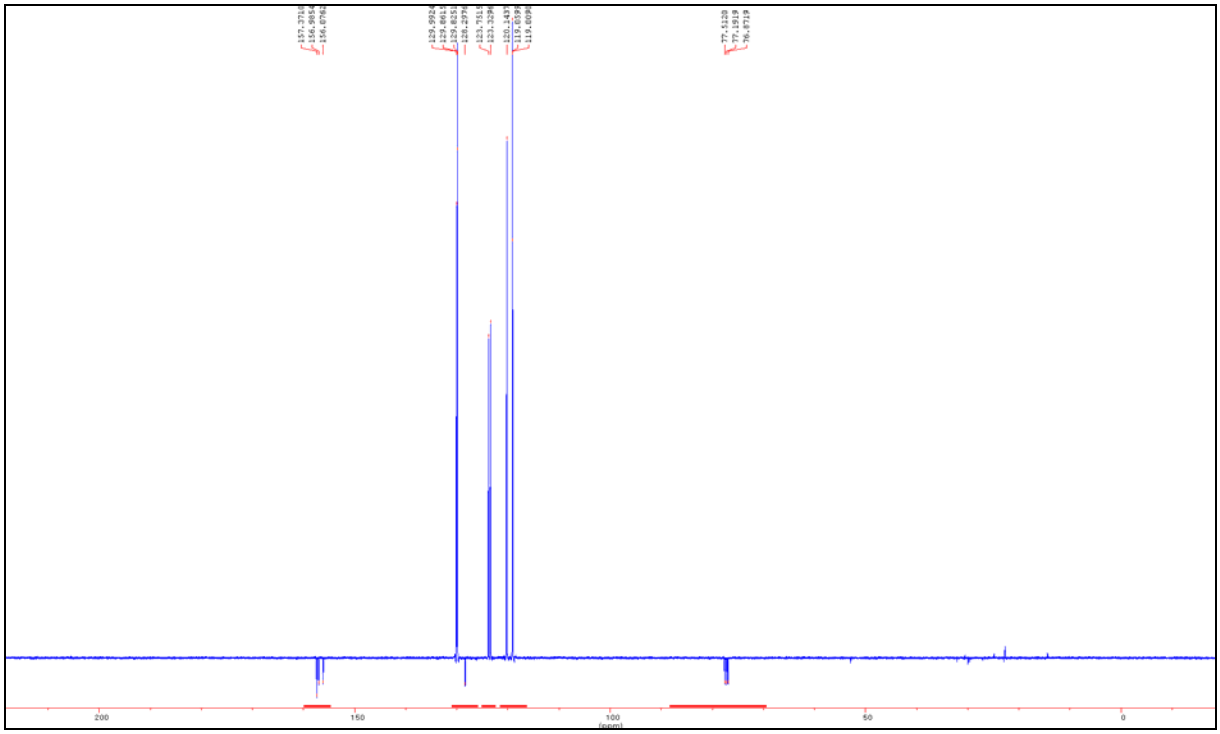
Diphenyl ether **7**



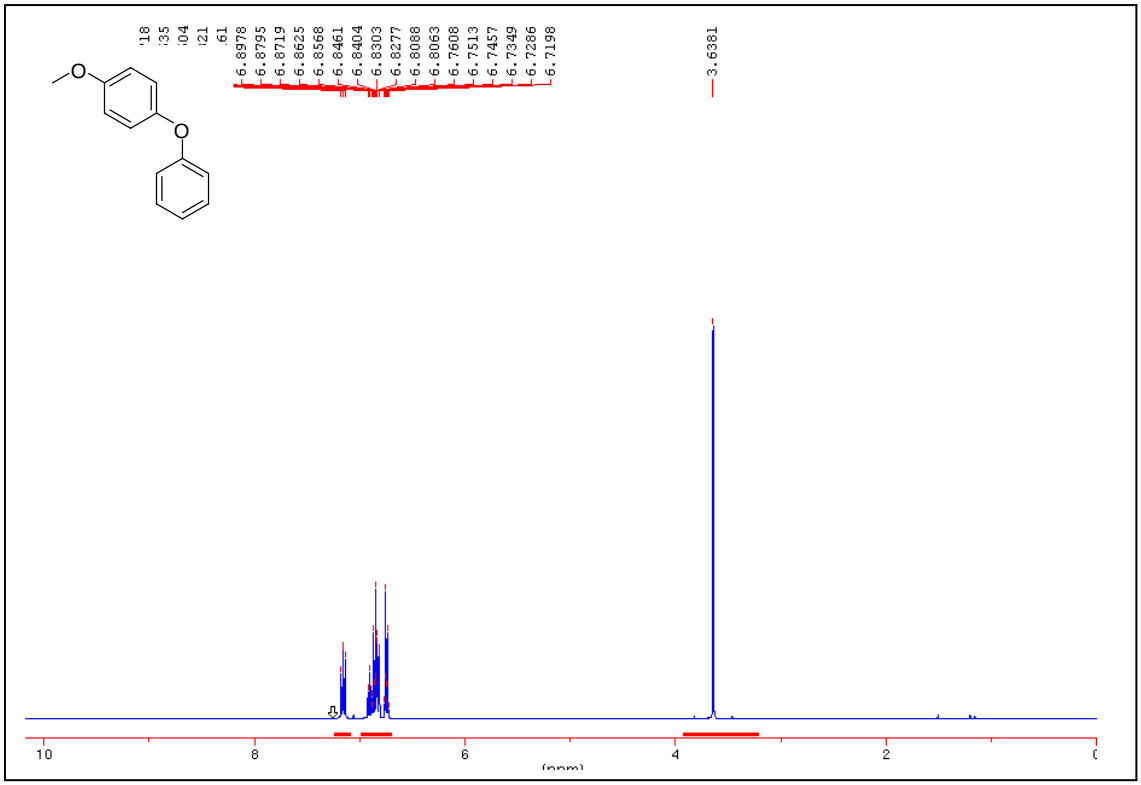


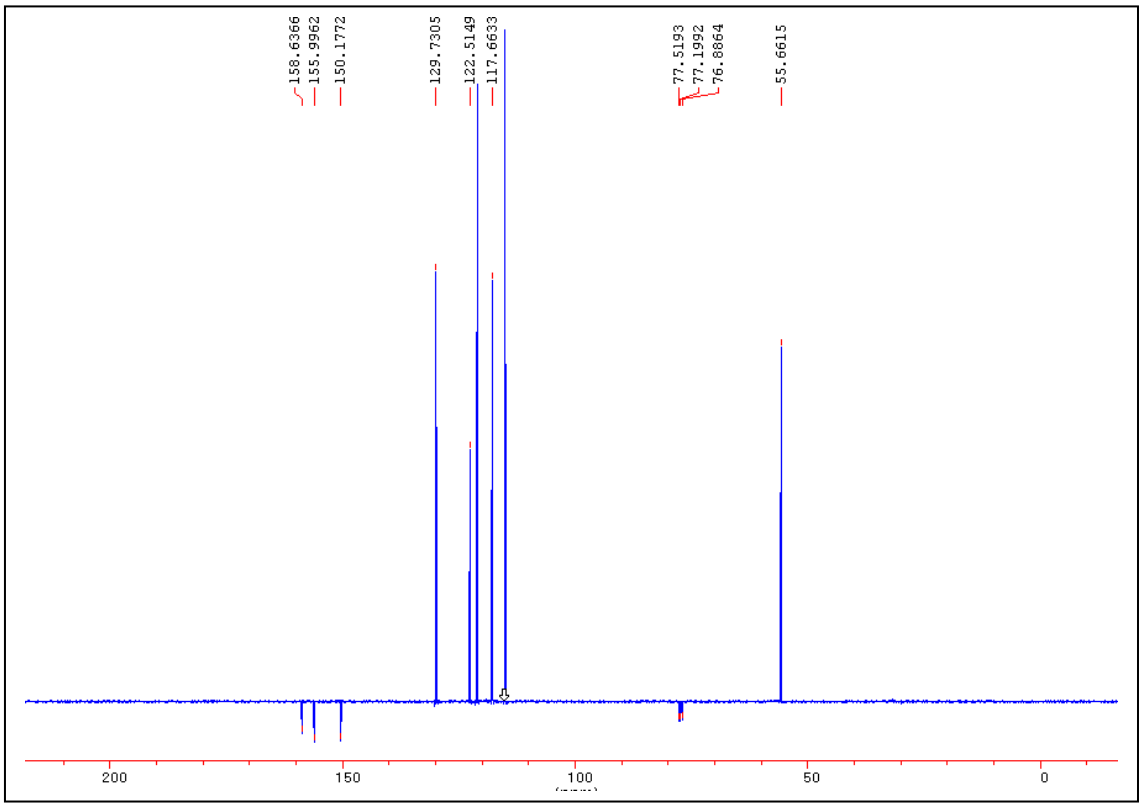
1-Chloro-4-phenoxybenzene **8**



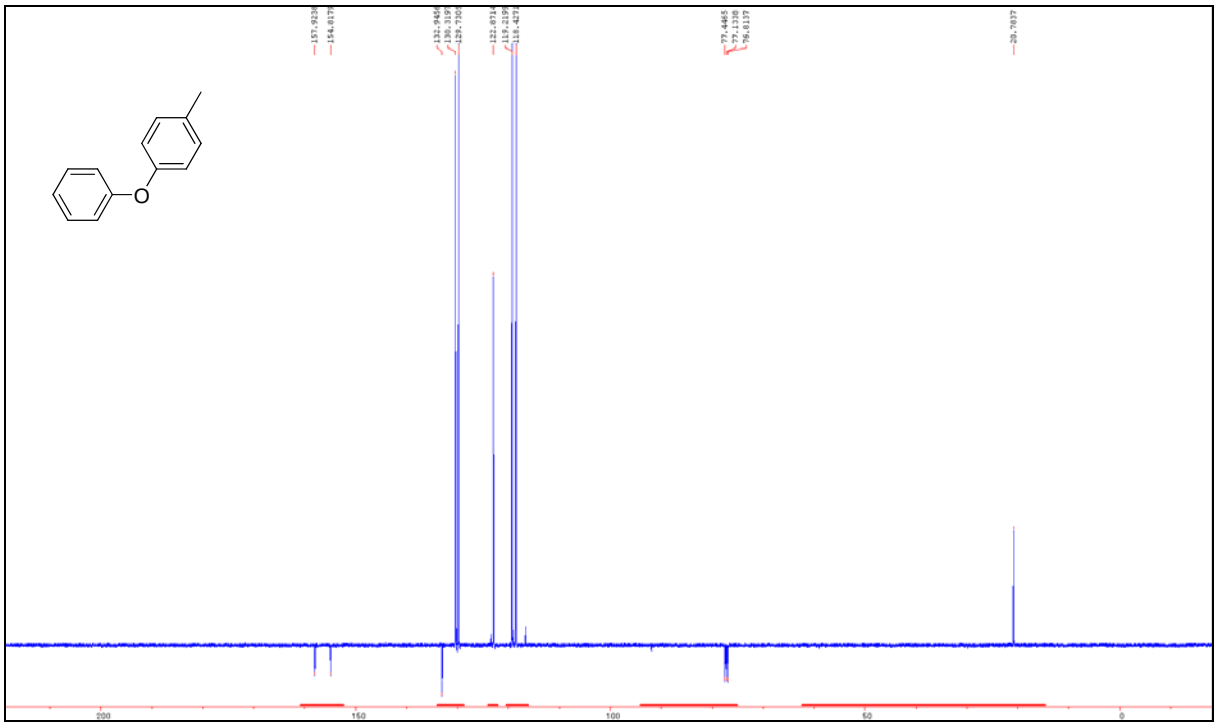


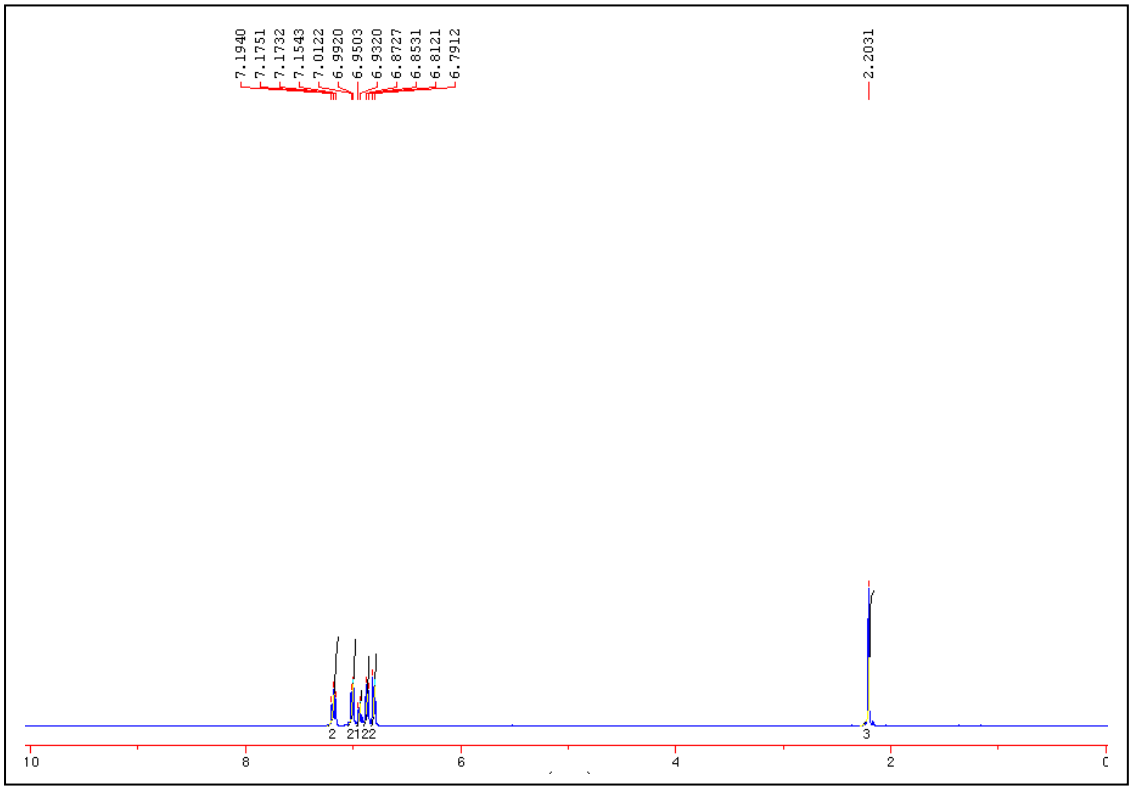
1-methoxy-4-phenoxybenzene **9**



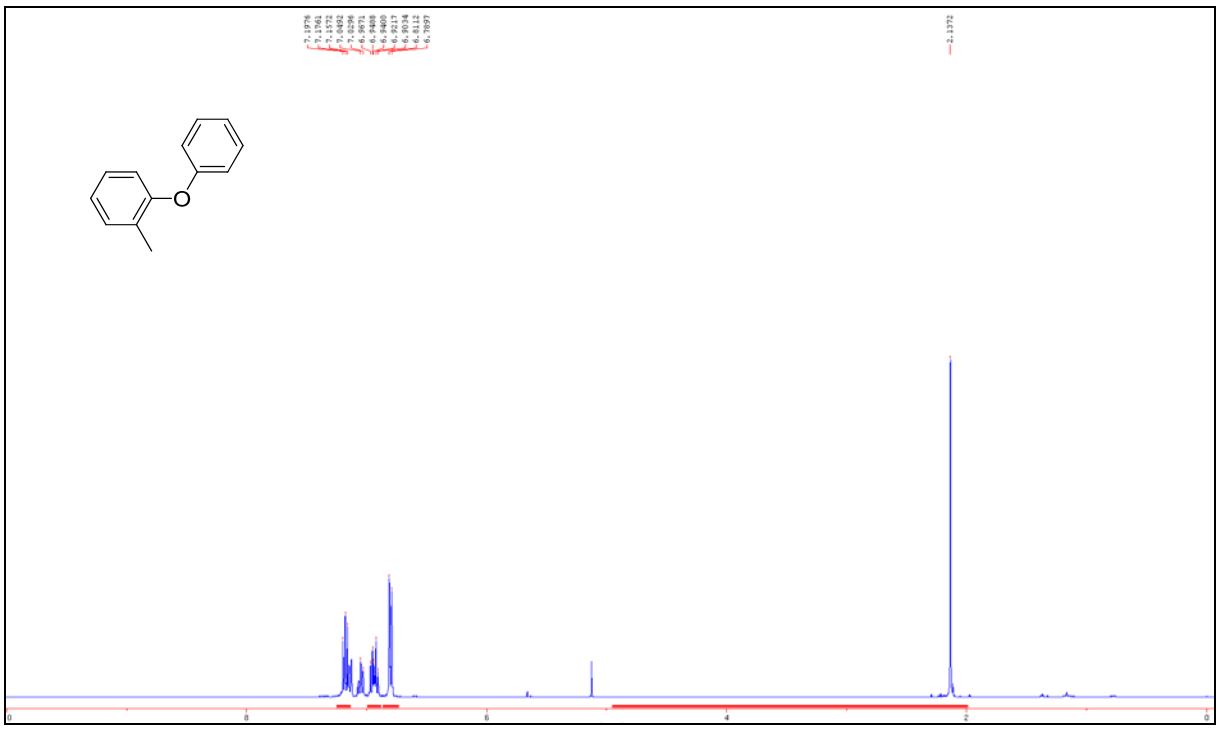


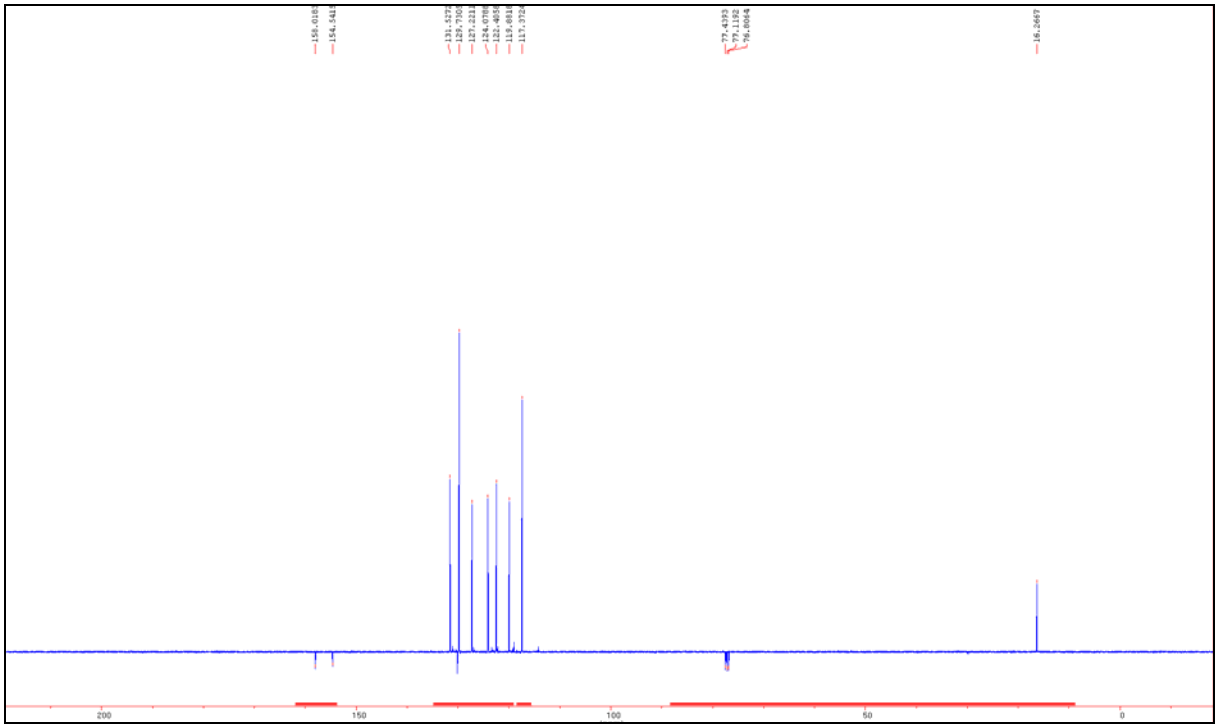
1-methyl-4-phenoxybenzene **10**



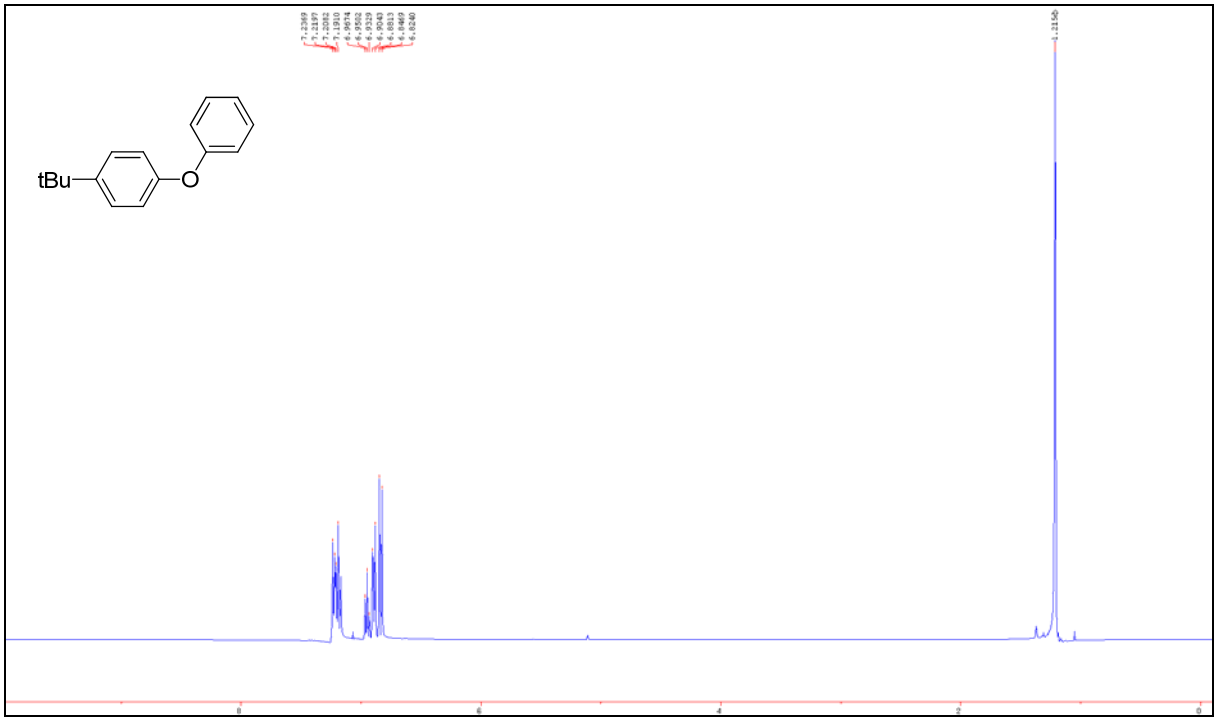


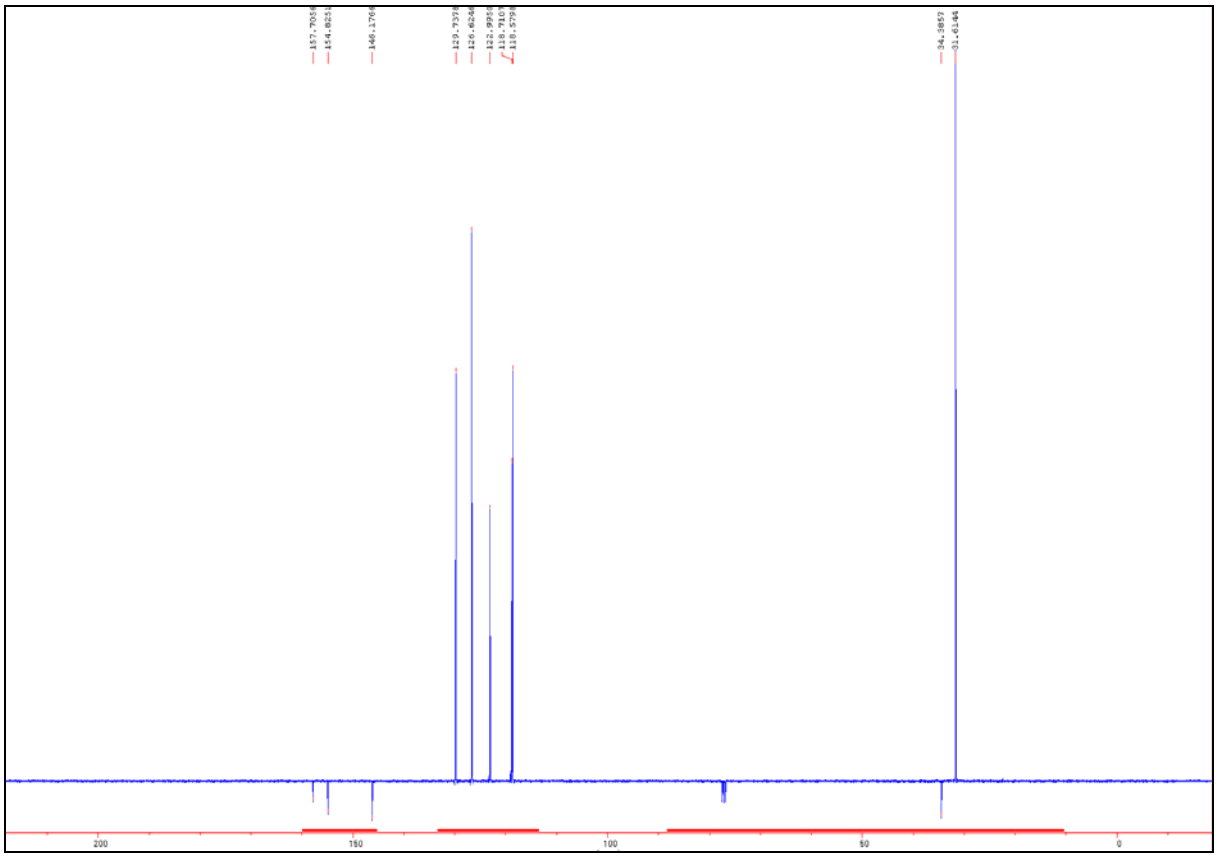
1-methyl-2-phenoxybenzene **11**





1-tert-butyl-4-phenoxybenzene **12**





[i] R. K. Dieter,; L. A.Silks III, J. R. Fiscpaugh, M. E. Kastner, *J. Am. Chem. Soc*., **1985**, *107*, 4679-4692
[ii]D. D.Perrin,, W. L. F.Armarego, D. R. Perrin, *Purification of laboratory chemicals*, 3 rd ed.; Pergamon Press: New-York, **1985**