# Supporting Information

# Formal Cross-Coupling of Diaryl Ethers with Ammonia by Dual C(Ar)-O Bond Cleavages

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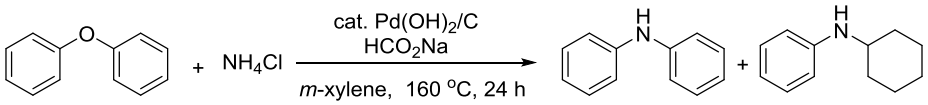
## Ⅰ. General Information

All reagents and solvents were purchased from commercial sources (Adamas-beta, TCI, Acros, Alfa and Ark) and used without further purification unless otherwise stated. $Pd(OH)_2/C$ was purchased from Acros Organic company (Code: 199620100, Lot: A0385402), 20 wt% $Pd(OH)_2$ based on C with 60% moisture. It was dried under reduced pressure for 6 h before using. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out in argon unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents.$^1$H and $^{13}$C NMR spectra were taken on Bruker AV300, Bruker AV400, and Varian Mercury plus 400 with TMS as an internal standard and CDCl3 as solvent. GC-MS analyses were performed with a Thermo TRACE 1300 ISQ LT spectrometer. HRMS analyses were made by Lanzhou University by means of ESI. All solvents were purified and dried by standard techniques.

## Ⅱ. Optimization of Reaction Conditions

**Table S1.** Screening the amount of water

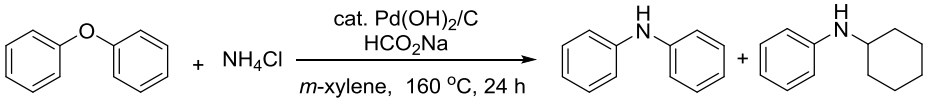



**1a** **2a** **3a** **4a**

| Entry | $H_2O$ | Conv.(%) | Yield[a]/% | |
|---|---|---|---|---|
| | | | **3a** | **4a** |
| 1 | 5 uL | 18 | N.P. | 14 |
| 2 | 10 uL | 26 | N.P. | 22 |
| 3 | 15 uL | 25 | N.P. | 11 |

General conditions: **1a** (0.2 mmol), **2a** (3 equiv), $Pd(OH)_2/C$ (20 mol%), $HCO_2Na$ (3 equiv), and *m*-xylene (1 mL) at 160 ℃ for 24 h under an argon atmosphere. [a]Yields were determined by $^1$H NMR with nitromethane as internal standard.

**Table S2.** Screening the nitrogen source

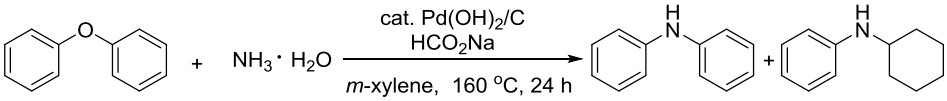



**1a** **2a** **3a** **4a**

| Entry | N source | Conv.(%) | Yield[a]/% | |
|---|---|---|---|---|
| | | | **3a** | **4a** |
| 1 | $NH_4Cl$ | 28 | N.P. | 22 |
| 2 | $NH_4Br$ | 22 | N.P. | 18 |
| 3 | $NH_4F$ | 26 | 8 | 12 |
| 4 | urea | 22 | N.P. | 16 |
| 5 | $NH_4HCO_3$ | 30 | N.P. | 26 |
| 6 | $NH_3{\cdot}H_2O$(no 10 uL $H_2O$) | 36 | N.P. | 30 |
| 7 | $N_2H_4{\cdot}H_2O$(no 10 uL $H_2O$) | 18 | N.P. | 12 |
| 8 | $NH_2OH{\cdot}HCl$ | 6 | N.P. | trace |
| 9 | $NH_3$ | 15 | N.P. | 8 |

General conditions: **1a** (0.2 mmol), **2a** (3 equiv), $Pd(OH)_2/C$ (20 mol%), $HCO_2Na$ (3 equiv), and *m*-xylene (1 mL) at 160 ℃ for 24 h under an argon atmosphere. [a]Yields were determined by $^1H$ NMR with nitromethane as internal standard.

**Table S3.** Screening the amount of **2a**

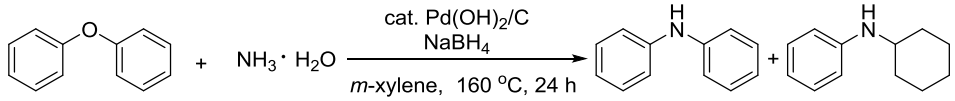



**1a** **2a** **3a** **4a**

| Entry | **2a** (equiv.) | Conv.(%) | Yield[a]/% | |
|---|---|---|---|---|
| | | | **3a** | **4a** |
| 1 | 2 | 15 | N.P. | 9 |
| 2 | 3 | 19 | N.P. | 14 |
| 3 | 4 | 45 | N.P. | 36 |
| 4 | 5 | 50 | N.P. | 43 |
| 5 | 6 | 34 | N.P. | 28 |

General conditions: **1a** (0.2 mmol), **2a** (x equiv), $Pd(OH)_2/C$ (20 mol%), $HCO_2Na$ (3 equiv), and *m*-xylene (1 mL) at 160 ℃ for 24 h under an argon atmosphere. [a]Yields were determined by $^1H$ NMR with nitromethane as internal standard.

**Table S4.** Screening the amount of $NaBH_4$



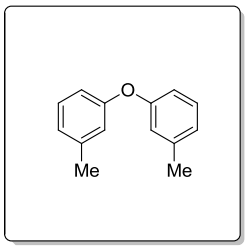

**1a** **2a** **3a** **4a**

| Entry | $NaBH_4$ | Conv.(%) | Yield[a]/% | |
|---|---|---|---|---|
| | | | **3a** | **4a** |
| 1 | 0.5 equiv | 54 | 2 | 48 |
| 2 | 1 equiv | 88 | 3 | 79 |
| 3 | 1.5 equiv | 79 | 2 | 72 |
| 4 | 3 equiv | 64 | trace | 50 |

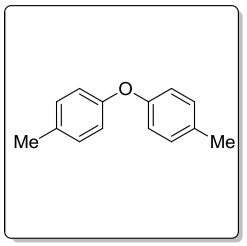
General conditions: **1a** (0.2 mmol), **2a** (5 equiv), $Pd(OH)_2/C$ (20 mol%), $NaBH_4$ (x equiv), and *m*-xylene (1 mL) at 160 ℃ for 24 h under an argon atmosphere. [a]Yields were determined by $^1H$ NMR with nitromethane as internal standard.

## Ⅲ. General Procedure for the Preparation of Starting Materials

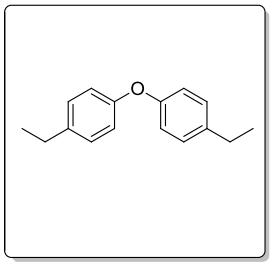
All substituted diphenyl ethers were synthesized by the reaction between the corresponding substituted iodobenzenes and substituted phenols according to the literature procedures.[1,2,3]



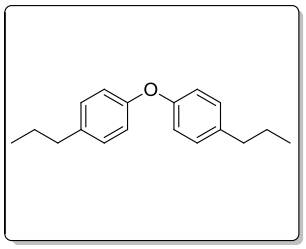

**1b: 3,3'-oxybis(methylbenzene)** $^1H$ NMR ($CDCl_3$, 400 MHz) δ: 7.25 (t, J = 8 Hz, 2H); 6.95 (d, J = 8 Hz, 2H), 6.87-6.84 (m, 4H), 2.37 (s, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ: 157.3, 139.9, 129.4, 123.9, 119.6, 115.9, 21.4.



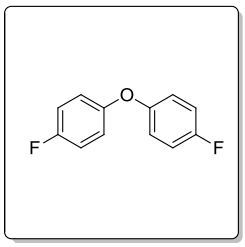

**1c: 4,4'-oxybis(methylbenzene)** $^1H$ NMR ($CDCl_3$, 400 MHz) δ: 7.15 (t, J = 8 Hz, 4H); 6.93 (d, J = 8 Hz, 4H), 2.36 (s, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) δ: 155.3, 132.4, 130.1, 118.6, 20.7



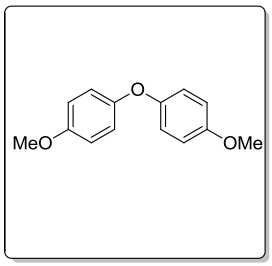
**1d: 4,4'-oxybis(ethylbenzene)** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.18 (d, J = 12 Hz, 4H); 6.96 (d, J = 12 Hz, 4H); 2.67 (q, J = 7.6 Hz, 4H), 1.28 (t, J = 7.6 Hz, 6H).$^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 155.4, 138.8, 128.9, 118.4, 28.1, 15.8.



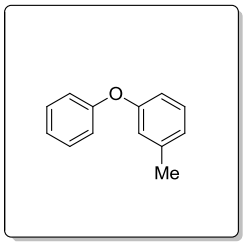
**1e: 4,4'-oxybis(propylbenzene)** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.15 (d, J = 12 Hz, 4H), 6.95 (d, J = 12 Hz, 4H), 2.60 (t, J = 8.4 Hz, 4H), 1.73-1.61 (m, 4H), 0.98 (t, J = 7.3 Hz, 6H). $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 155.5, 137.3, 129.5, 118.6, 37.3, 24.6, 13.8.



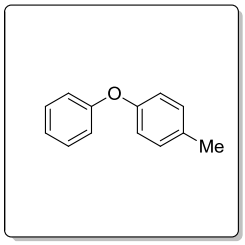
**1f: 4,4'-oxybis(fluorobenzene)** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.07-7.03 (m, 4H), 6.99-6.95 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 158.7 (d, *J* = 241.6 Hz), 153.4 (d, *J* = 2.4 Hz), 119.9 (d, *J* = 8.2 Hz), 116.3 (d, *J* = 23.3 Hz).



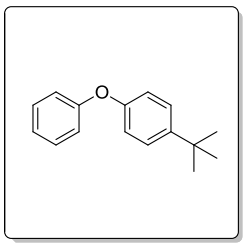
**1g: 4,4'-oxybis(methoxybenzene)** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 6.97-6.93 (m, 4H); 6.89-6.85 (m, 4H), 3.82 (s, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 155.3, 151.6, 119.5, 114.8, 55.7.



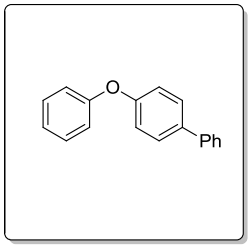

**1h: 1-methyl-3-phenoxybenzene** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.38 (t, J = 8 Hz, 2H); 7.27 (t, J = 8 Hz, 1H), 7.15 (t, J = 8 Hz, 1H), 7.07 (d, J = 12 Hz, 2H), 6.97 (d, J = 8 Hz, 1H), 6.86-6.90 (m, 2H), 2.38 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 157.4, 157.2, 139.9, 129.7, 129.5, 124.1, 123.1, 119.6, 118.9, 115.9, 21.4.



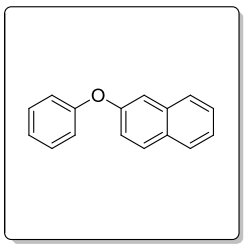

**1i: 1-methyl-4-phenoxybenzene** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.36 (t, J = 8 Hz, 2H); 7.19 (d, J = 8 Hz, 2H), 7.11 (d, J = 6 Hz, 1H), 7.04 (d, J = 12 Hz, 2H), 6.97 (d, J = 8 Hz, 2H), 2.39 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 157.9, 154.8, 132.9, 130.3, 129.7, 122.8, 119.1, 118.4, 20.7.



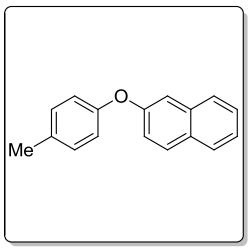

**1j: 1-(*tert*-butyl)-4-phenoxybenzene** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.37-7.28 (m, 4H); 7.10-6.95 (m, 5H), 1.35 (s, 9H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 157.6, 154.7, 146.1, 129.6, 126.5, 122.9, 118.6, 118.4, 34.3, 31.5.



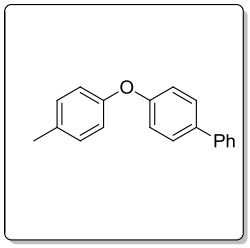

**1k: 4-phenoxy-1,1'-biphenyl** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.60 (dd, J = 8, 4 Hz, 4H); 7.46 (t, J = 4 Hz, 2H), 7.41-7.34 (m, 3H), 7.16 (t, J = 8 Hz, 1H), 7.10 (dd, J = 8, 4 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 157.2, 156.9, 140.6, 136.3, 129.8, 128.8, 128.4, 127.0, 126.9, 123.4, 119.0.



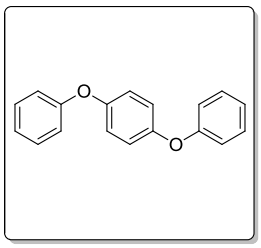

**1l: 2-phenoxynaphthalene** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.88 (dd, J = 8, 4 Hz, 2H); 7.76 (d, J = 8 Hz, 1H), 7.53-7.39 (m, 5H), 7.33 (d, J = 8 Hz, 1H), 7.20 (t, J = 8 Hz, 1H), 7.15 (d, J = 8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 157.2, 155.1, 134.4, 130.2, 129.9, 129.8, 127.8, 127.2, 126.6, 124.7, 123.7, 120.0, 119.2, 114.1.



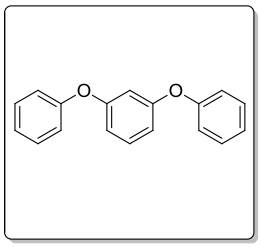

**1m: 2-(*p*-tolyloxy)naphthalene** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.85 (d, J = 8 Hz, 2H); 7.73 (d, J = 8 Hz, 1H), 7.51-7.42 (m, 2H), 7.33-7.31 (m, 2H), 7.23 (d, J = 8 Hz, 2H), 7.05 (d, J = 8 Hz, 2H); 2.42 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 155.7, 154.7, 134.4, 133.2, 130.4, 130.0, 129.8, 127.7, 127.1, 126.5, 124.5, 119.8, 119.4, 113.3, 20.8.




**1n: 4-(*p*-tolyloxy)-1,1'-biphenyl** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.60 (t, J = 12 Hz, 4H); 7.47 (t, J = 8 Hz, 2H), 7.9 (t, J = 8 Hz, 1H), 7.21 (d, J = 12 Hz, 2H), 7.09 (d, J = 8 Hz, 2H), 7.02 (d, J = 8 Hz, 2H), 2.40 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 157.5, 154.6, 140.6, 135.9, 133.2, 130.4, 128.9, 128.4, 127.0,126.9, 119.3, 118.5, 20.9.




**6: 1,4-diphenoxybenzene** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.37 (t, J = 8 Hz, 4H); 7.12 (t, J = 8 Hz, 2H), 7.05-7.03 (m, 8H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 157.8, 152.7, 129.7, 123.0, 120.5, 118.3.

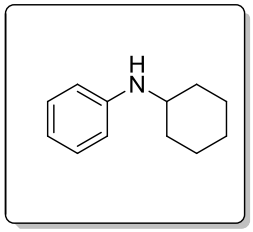



**7: 1,3-diphenoxybenzene** $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.35 (t, J = 8 Hz, 4H); 7.26 (t, J = 12 Hz, 1H), 7.12 (t, J = 9.6 Hz, 2H), 7.04 (d, J = 8 Hz, 4H),6.75-6.69 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 158.6, 156.6, 130.3, 129.8, 123.6, 119.1, 113.1, 109.3.

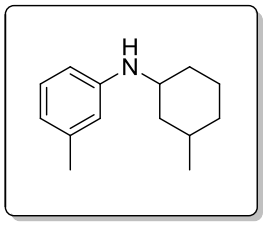
## Ⅳ. General Procedure for the Coupling of Diaryl Ether with Ammonia

In a 20 mL microwave vial was charged with a magnetic stir-bar, $Pd(OH)_2/C$ (28 mg, 20 mol%) and $NaBH_4$ (8 mg, 0.2 mmol). The tube was then evacuated and backfilled with argon. The evacuation/backfill sequence was repeated two additional times. *m*-Xylene (1 mL), diphenyl oxide (0.2 mmol) and $NH_3{\cdot}H_2O$(1 mmol) were added by syringe. The tube was placed in a preheated oil bath at 150 $^{o}$C and the

mixture was stirred under an argon atmosphere for 24 h. The reaction mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated and the resulting residue was purified by preparative TLC on silica gel eluting with hexane: EtOAc (30:1-5:1) to afford the products.



***N*-cyclohexylaniline** Lightly yellow liquid.; $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 7.17 (t, J = 8, 2H), 6.67 (t, J = 8 Hz, 1H), 6.60 (d, J = 8 Hz, 2H), 3.25 (tt, J = 10.0, 3.7 Hz, 1H), 2.09-2.04 (m, 2H), 1.79-1.75 (m, 2H), 1.69-1.65 (m, 1H), 1.43-1.27 (m, 2H), 1.18-1.12 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ: 147.3, 129.2, 116.8, 113.1 , 51.6, 33.4, 25.9, 25.0. $^{1}$H and $^{13}$C NMR data agreed with those reported in the literature.[4]



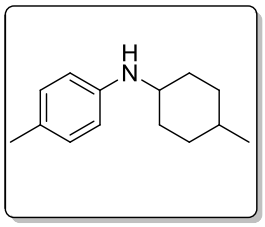
**3-methyl-*N*-(3-methylcyclohexyl)aniline**

*cis*-isomer, lightly yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.08 (dd, J = 8, 7.2 Hz, 1H), 6.51 (d, J = 8 Hz, 1H), 6.43 (d, J = 8 Hz, 2H), 3.74-3.67 (m, 1H), 2.29 (s, 3H), 1.75-1.54 (m, 7H), 1.38-1.27 (m, 1H), 1.09-1.04 (m, 1H), 0.94 (d, J = 6.5 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 147.3, 139.0, 129.1, 117.6, 113.7, 110.0, 47.4, 38.8, 34.0, 30.4, 27.1, 21.8, 21.7, 20.6.

*trans*-isomer, lightly yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.10-7.05 (m, 1H), 6.52 (d, J = 8 Hz, 1H), 6.44 (s, 2H), 3.26 (tt, J = 12, 3.8 Hz, 1H), 2.29 (s, 3H), 2.13-2.10 (m, 2H), 1.84-1.78 (m, 1H), 1.73-1.69 (m, 1H), 1.58-1.46 (m, 1H), 1.42-1.33 (m, 1H), 1.04-0.96 (m, 1H), 0.95 (d, J = 8 Hz, 3H), 0.90-0.70 (m, 2H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 147.4, 139.0, 129.1, 117.8, 113.9, 110.2, 52.0, 42.5, 34.6, 33.4, 32.0, 25.0, 22.5, 21.7. $^{1}$H and $^{13}$C NMR data agreed with those reported in the literature.[5]



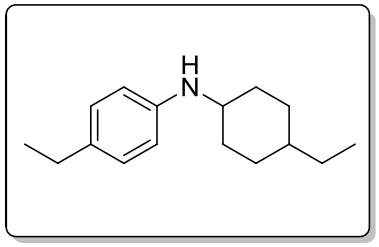
**4-Methyl-*N*-(4-methylcyclohexyl)aniline**

*cis*-isomer, lightly yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 6.98 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.0 Hz, 2H), 3.53 (quint, J = 4.5 Hz, 1H), 2.24 (s, 3H), 1.77-1.73 (m, 2H), 1.67-1.53 (m, 5H), 1.27-1.23 (m, 2H), 0.94 (d, J = 8 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 145.0, 129.7, 125.9, 113.3, 48.3, 30.9, 29.7, 29.2, 21.4, 20.4.

*trans*-isomer, lightly yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.00 (d, J = 8 Hz, 2H), 6.54 (d, J = 8.5 Hz, 2H), 3.19-3.09 (m, 1H), 2.24 (s, 3H), 2.13-2.10 (m, 2H), 1.77-1.75 (m, 2H), 1.44-1.41 (m, 1H), 1.16-1.03 (m, 4H), 0.93 (d, J = 8 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 145.1, 129.7, 126.1, 113.5, 52.4, 34.1, 33.5, 32.3, 22.3, 20.3. $^{1}$H and $^{13}$C NMR data agreed with those reported in the literature.[5]



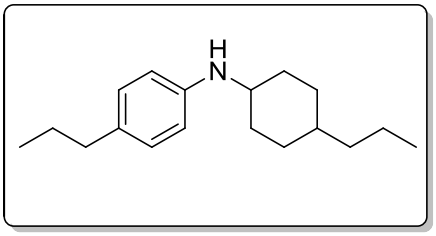
**4-ethyl-*N*-(4-ethylcyclohexyl)aniline**

*cis*-isomer, lightly yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.01 (d, J = 8 Hz, 2H), 6.57 (d, J = 8.6 Hz, 2H), 3.56-3.54 (m, 1H), 2.53 (q, J = 8 Hz, 2H), 1.73-1.59 (m, 6H), 1.38-1.29 (m, 5H), 1.20 (t, J = 8 Hz, 3H), 0.90 (t, J = 8 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 145.3, 132.5, 128.5, 113.2, 48.6, 37.8, 29.4, 28.3, 27.9, 27.4, 16.0, 11.7.

*trans*-isomer, lightly yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.00 (d, J = 8 Hz, 2H), 6.56 (d, J = 8.6 Hz, 2H), 3.20-3.13 (m, 1H), 2.53 (q, J = 8 Hz, 2H), 2.16-2.12 (m, 2H), 1.84-1.81 (m, 2H),1.26-1.15 (m, 8H), 1.08-0.99 (m, 2H), 0.90 (t, J = 8 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 145.4, 132.7, 128.5, 113.3, 52.7, 39.0, 33.6, 31.7, 29.6, 27.9, 16.0, 11.7. $^{1}$H and $^{13}$C NMR data agreed with those reported in the literature.[5]



**4-propyl-*N*-(4-propylcyclohexyl)aniline**

*cis*-isomer, lightly yellow liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 6.98 (d, J = 8 Hz, 2H), 6.55 (d, J = 8 Hz, 2H), 3.55-3.52 (m, 1H), 2.7 (t, J = 8.6 Hz, 2H), 1.77-1.51 (m, 8H), 1.38-1.19 (m, 7H), 0.90 (m, 6H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 145.4, 131.2, 129.2, 113.2, 52.7, 39.4, 37.2, 37.0, 33.7, 32.1, 25.0, 20.2, 14.5, 14.0.

*trans*-isomer, lightly yellow liquid.

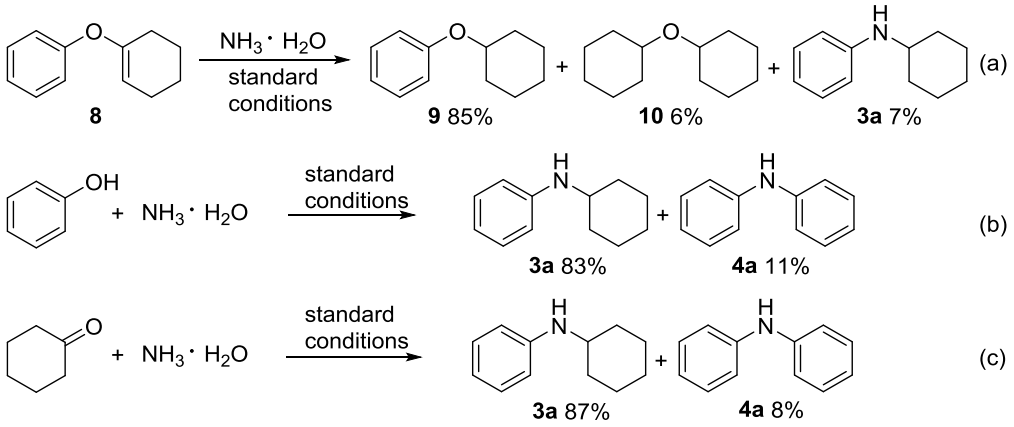
$^{1}$H NMR (400 MHz, $CDCl_3$) δ: 6.98 (d, J = 8 Hz, 2H), 6.54 (d, J = 8.6 Hz, 2H), 3.19-3.12 (m, 1H), 2.47 (t, J = 8 Hz, 2H), 2.14-2.11 (m, 2H), 1.82-1.79 (m, 2H), 1.61-1.58 (m, 2H), 1.36-1.17 (m, 5H), 1.11-1.03 (m, 4H), 0.90-0.88 (m, 6H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 145.3, 131.0, 129.2, 113.1, 48.7, 37.2 (2C), 35.7, 29.4, 27.8, 25.0, 20.2, 14.4, 13.9. $^{1}$H and $^{13}$C NMR data agreed with those reported in the literature.[5]

## Ⅴ. References


1. Sergeev, A. G; Hartwig, J. F. Selective, nickel-catalyzed hydrogenolysis of aryl ethers. *Science* **2011**, *332*, 439–443.
2. Sergeev, A.G; Webb, J. D; Hartwig, J. F. A heterogeneous nickel catalyst for the hydrogenolysis of aryl ethers without arene hydrogenation. *J. Am. Chem. Soc*. **2012**, *134*, 20226–20229.
3. Swapna, K.; Murthy, S. N.; Jyothi, M. T.; Nageswar, Y. V. D. Recyclable heterogeneous copper oxide on alumina catalyzed coupling of phenols and alcohols with aryl halides under ligand-free conditions. *Org. Biomol. Chem*., **2011**, *9*, 5978–5988.
4. Li, J.-S.; Qiu, Z. H.; Li, C.-J. Palladium-catalyzed synthesis of N-cyclohexyl anilines from phenols with hydrazine or hydroxylamine via N-N/O cleavage. *Adv. Synth. Catal*., **2017**, *359*, 3648–3654.
5. Taniguchi, K.; Jin, X. J.; Yamaguchi, K.; Mizuno, N. Supported gold-palladium alloy nanoparticle catalyzed tandem oxidation routes to N-substituted anilines from non-aromatic compounds. *Chem. Commun*., **2015**, *51*, 14969–14972.

## Ⅵ. Control Experiments

In a 20 mL microwave vial was charged with a magnetic stir-bar, $Pd(OH)_2/C$ (28 mg, 20 mol%) and $NaBH_4$ (8 mg, 0.2 mmol). The tube was then evacuated and backfilled with argon. The evacuation/backfill sequence was repeated two additional times. *m*-Xylene (1 mL), cyclohexenylphenyl ether (**8**) (0.2 mmol) (Scheme S1a) (or phenol (Scheme S1b), cyclohexanone (Scheme S1c)) and $NH_3{\cdot}H_2O$(1 mmol) were added sequentially by syringe. The tube was placed in a preheated oil bath at 150 $^oC$ and the mixture was stirred under an argon atmosphere for 24 h. The reaction mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated, and the resulting residue was purified by preparative TLC on silica gel to afford the products.




**Scheme S1**. Control experiments.

In order to understand the entire reaction process, the reaction progress at different times under standard conditions was investigated (Table S5). The experimental operation procedure and detailed data are as follows.

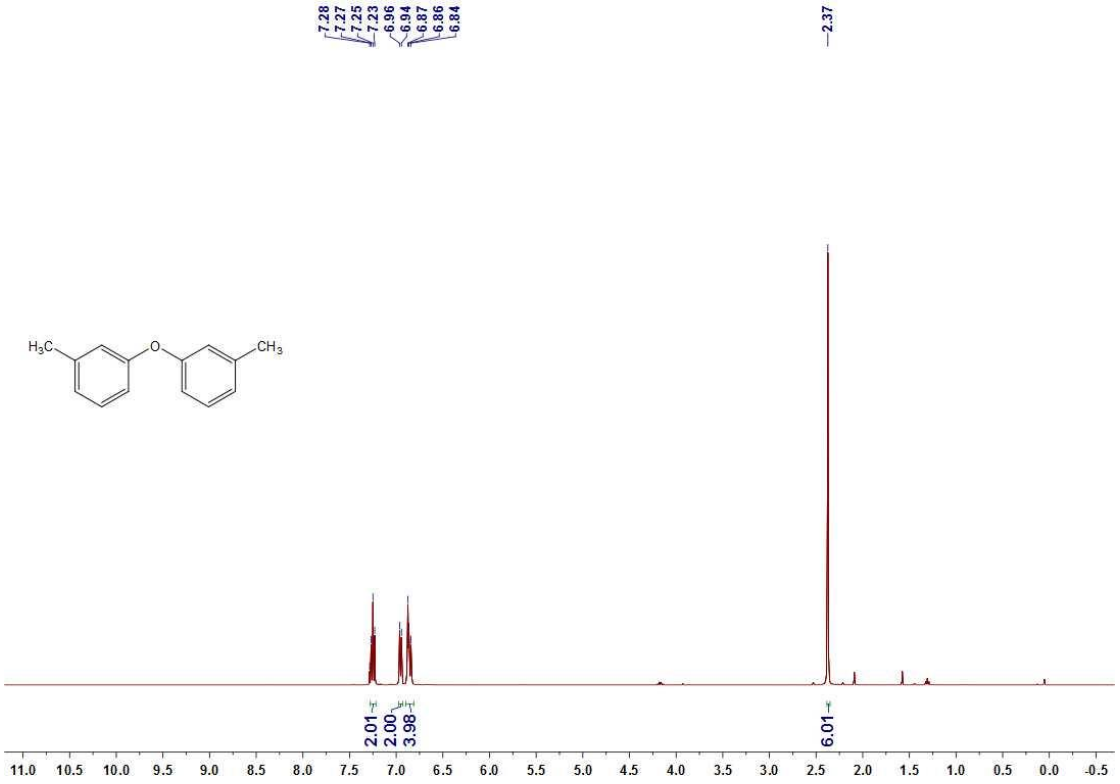
In twelve 20 mL microwave tubes were charged with magnetic stir-bars, $Pd(OH)_2/C$ (28 mg, 20 mol%) and $NaBH_4$ (8 mg, 0.2 mmol), respectively. The tubes were then evacuated and backfilled with argon. The evacuation/backfill sequence was repeated two additional times. *m*-Xylene (1 mL), diphenyl oxide (0.2 mmol) and $NH_3{\cdot}H_2O$ (1 mmol) were added sequentially by syringe. The tubes were placed in a preheated oil bath at 150 $^oC$ and the mixture was stirred under an argon atmosphere. As shown in the following table, the reactions were stopped at regular intervals. Yields of different components were determined by GC-MS.

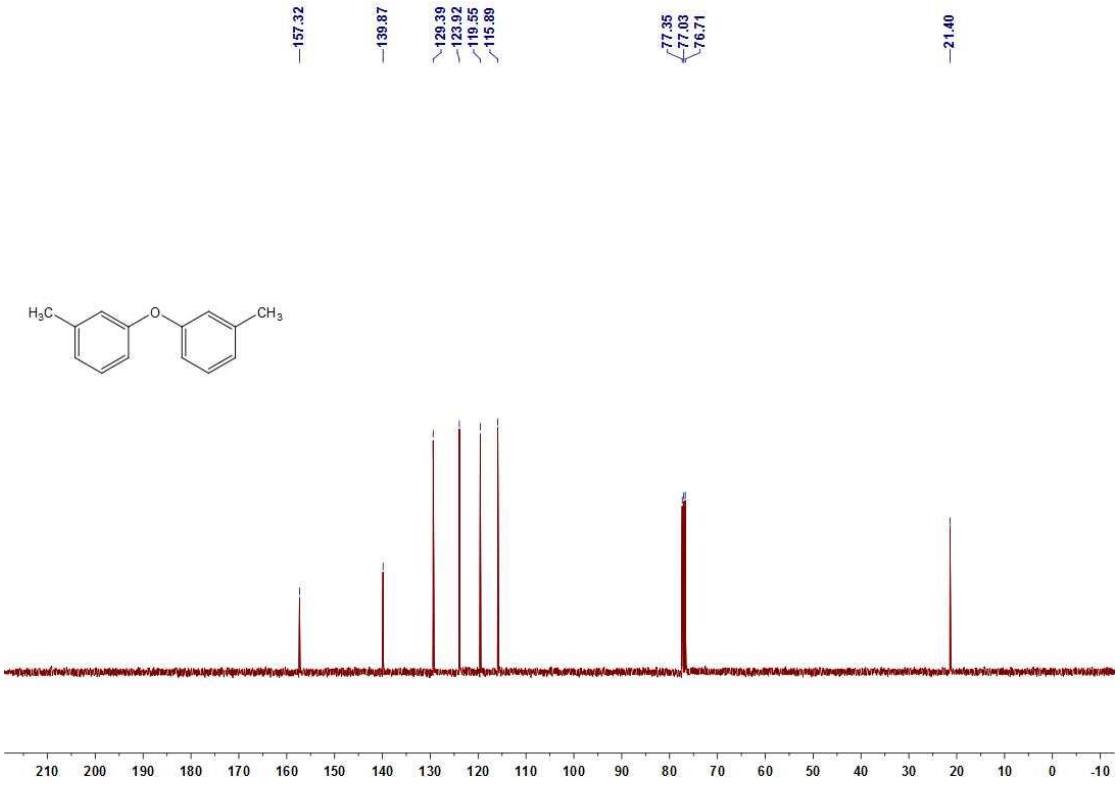
**Table S5.** The concentrations of different components for the cross-coupling of diphenyl ether with ammonia under standard conditions at different reaction time.

| reaction time (*h*) | diphenyl ether (*M*) | benzene /cyclohexane (*M*) | dicyclohexylamine (*M*) | *N*-cyclohexylaniline (*M*) | diphenylamine (*M*) | cyclohexyl phenyl ether (*M*) |
|---|---|---|---|---|---|---|
| 0.5 | 0.200 | 0 | 0 | 0 | 0 | 0 |
| 1 | 0.200 | 0 | 0 | 0 | 0 | 0 |
| 1.5 | 0.200 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0.200 | 0 | 0 | 0 | 0 | 0 |
| 3 | 0.176 | 0.020 | 0.020 | 0 | 0 | 0.002 |
| 4 | 0.160 | 0.036 | 0.028 | 0.008 | 0 | 0.002 |
| 6 | 0.138 | 0.056 | 0.036 | 0.020 | 0 | 0.004 |
| 8 | 0.100 | 0.094 | 0.050 | 0.044 | 0 | 0.004 |
| 12 | 0.056 | 0.136 | 0.046 | 0.088 | 0 | 0.006 |
| 16 | 0.020 | 0.164 | 0.032 | 0.130 | 0.004 | 0.008 |
| 20 | 0.008 | 0.166 | 0.004 | 0.166 | 0.006 | 0.010 |
| 24 | 0 | 0.168 | 0 | 0.174 | 0.010 | 0.010 |

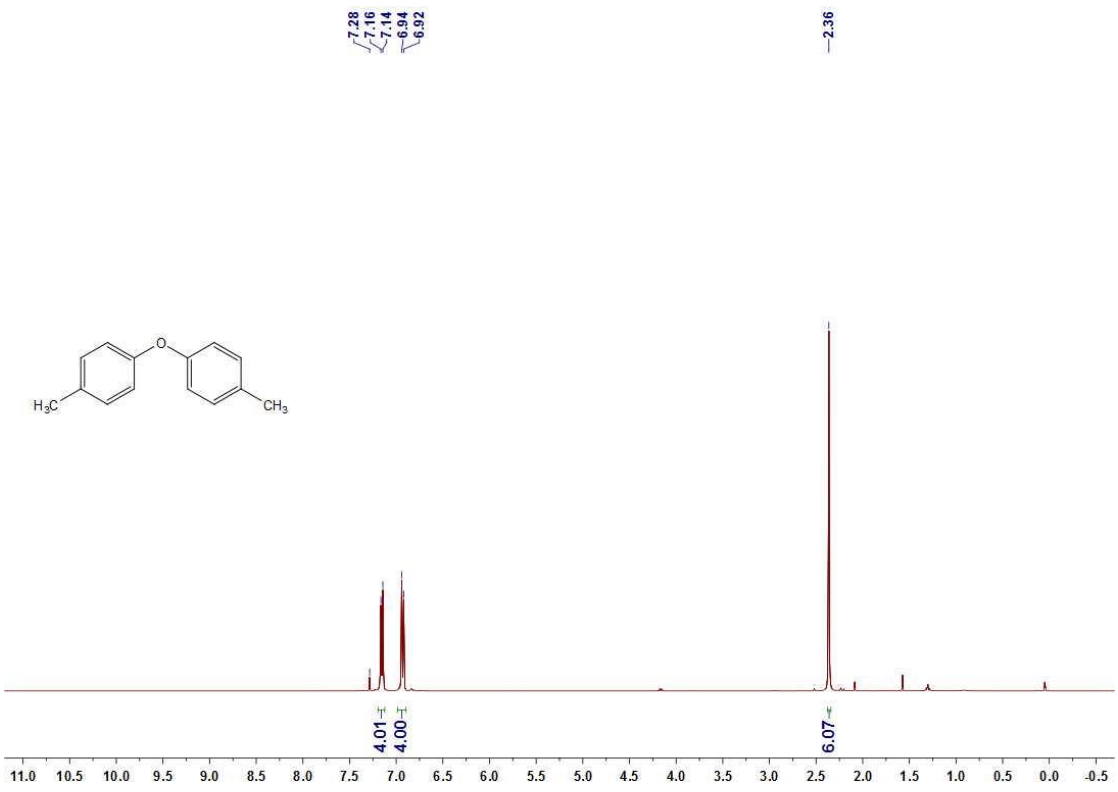
## Ⅶ. Copies of $^{1}$H NMR and $^{13}$C NMR Spectra

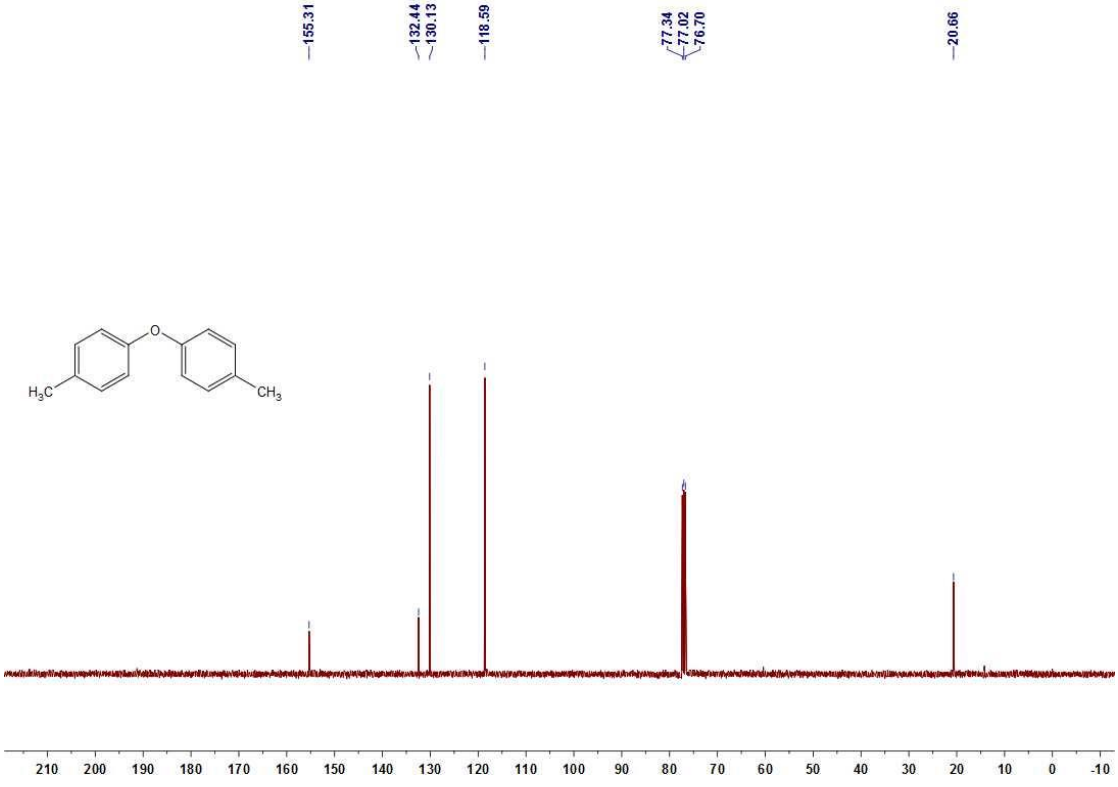
$^{1}$H and $^{13}$C NMR spectra of compound **3,3'-oxybis(methylbenzene)**



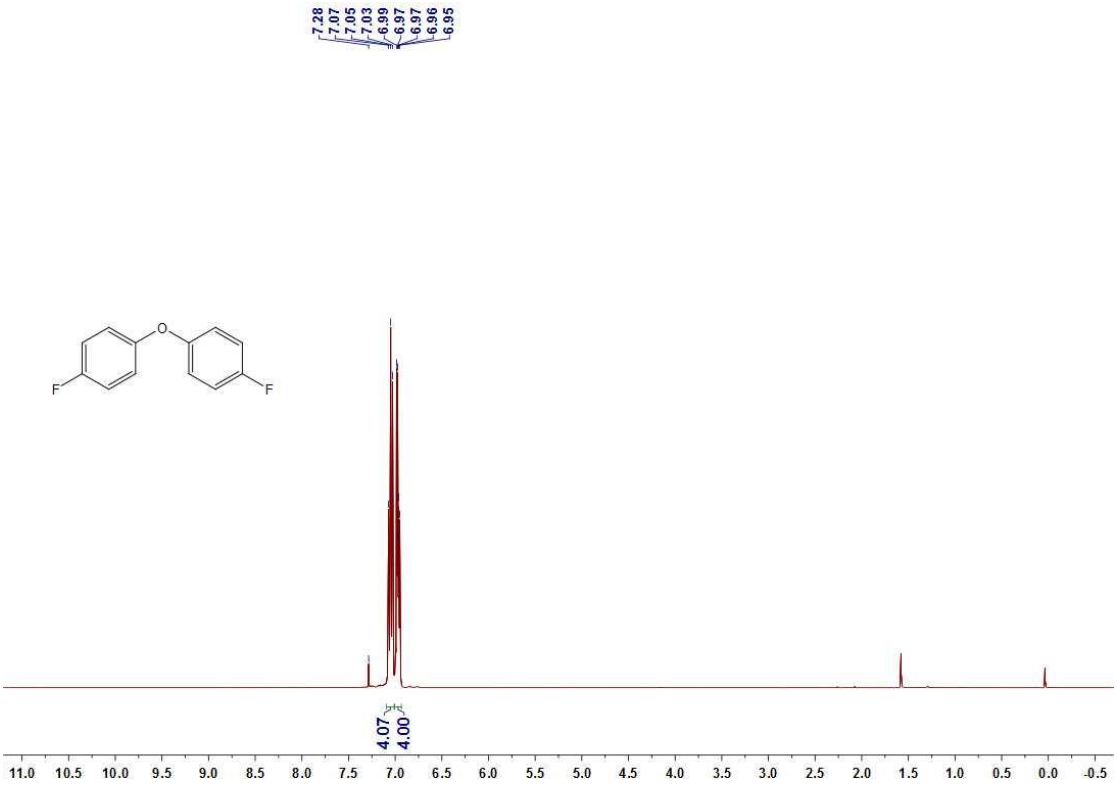



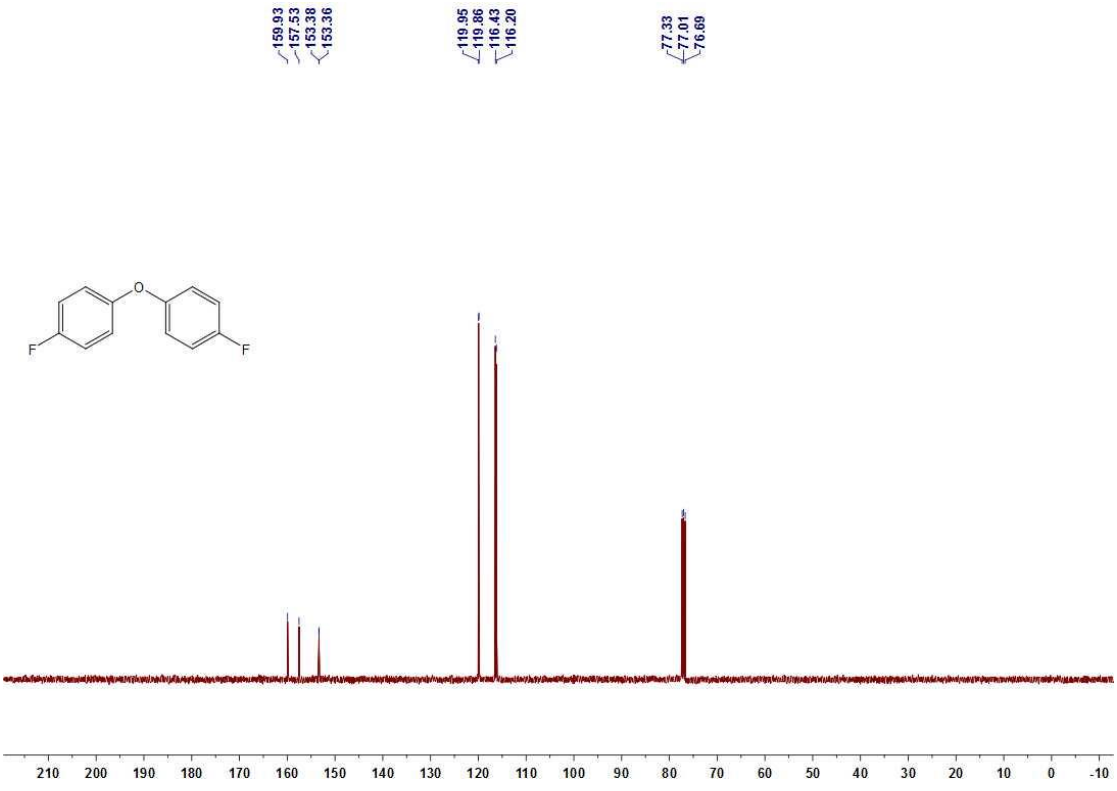
$^{1}H$ and $^{13}C$ NMR spectra of compound **4,4'-oxybis(methylbenzene)**



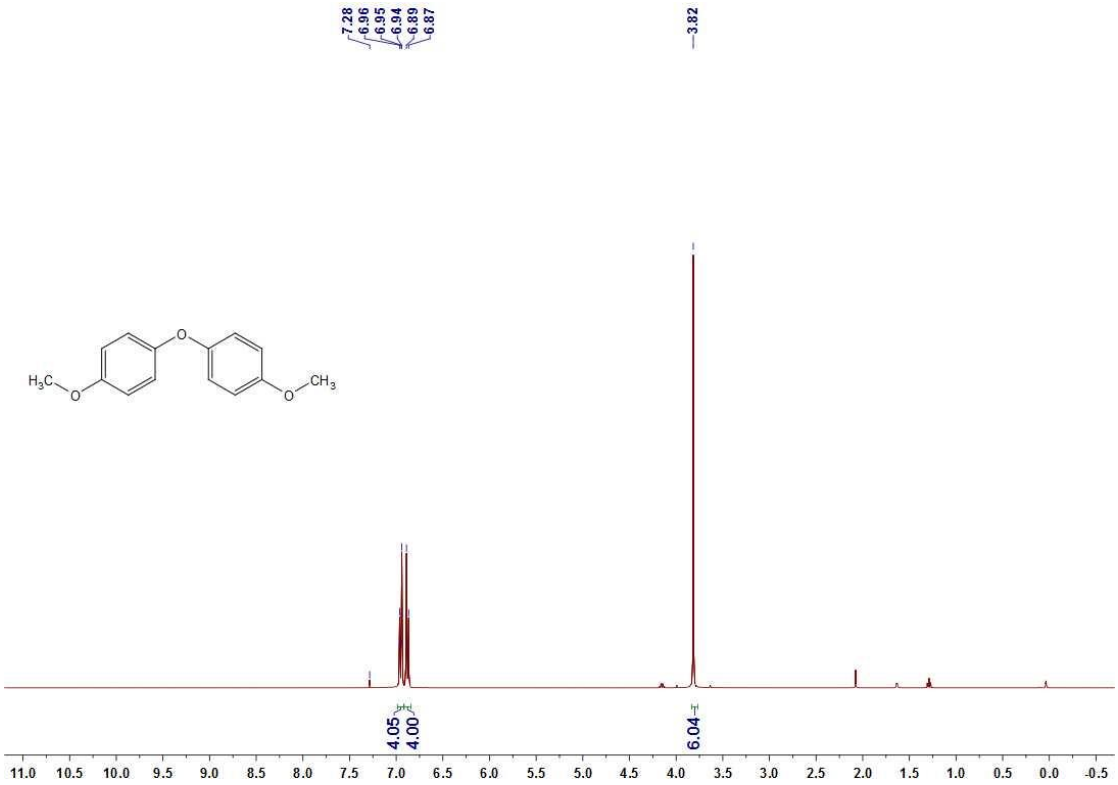



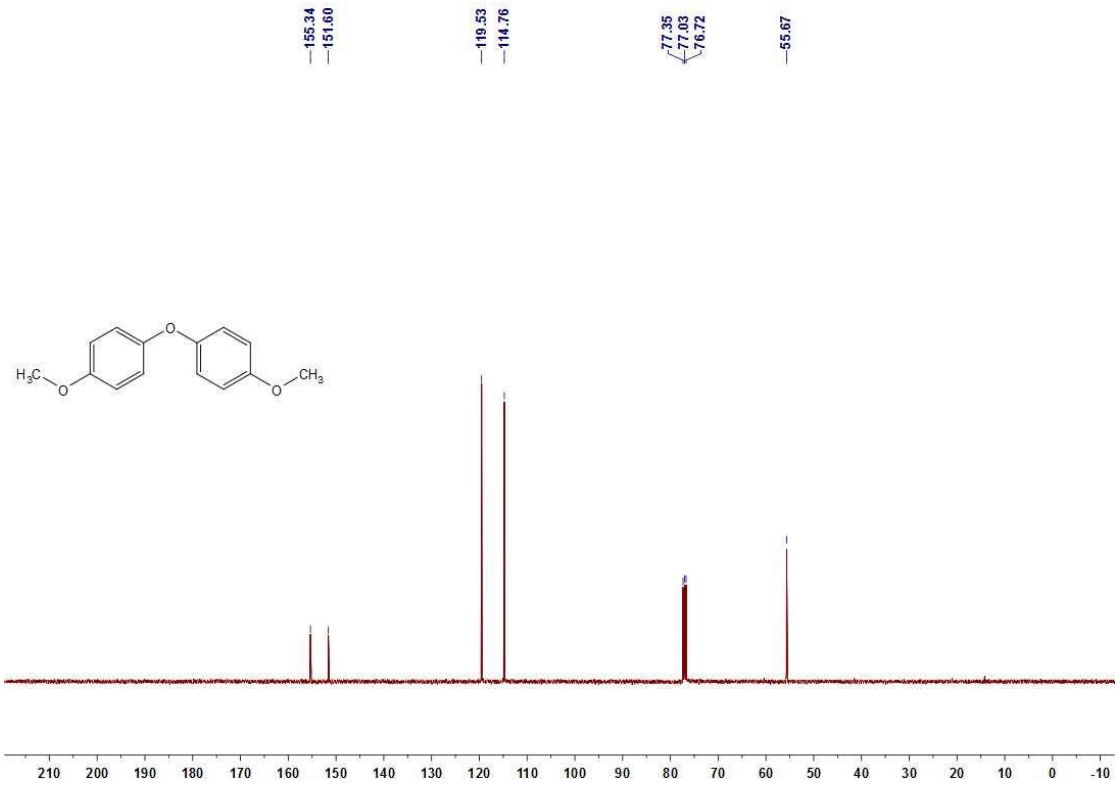
$^{1}H$ and $^{13}C$ NMR spectra of compound **4,4'-oxybis(fluorobenzene)**



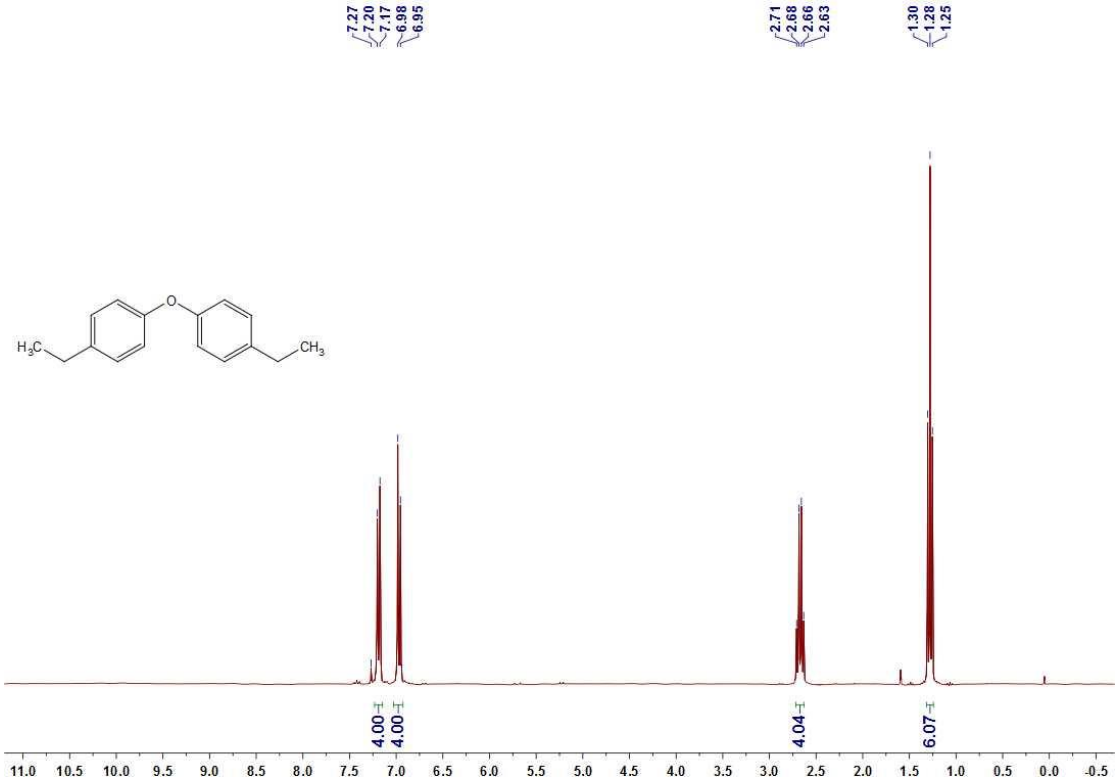



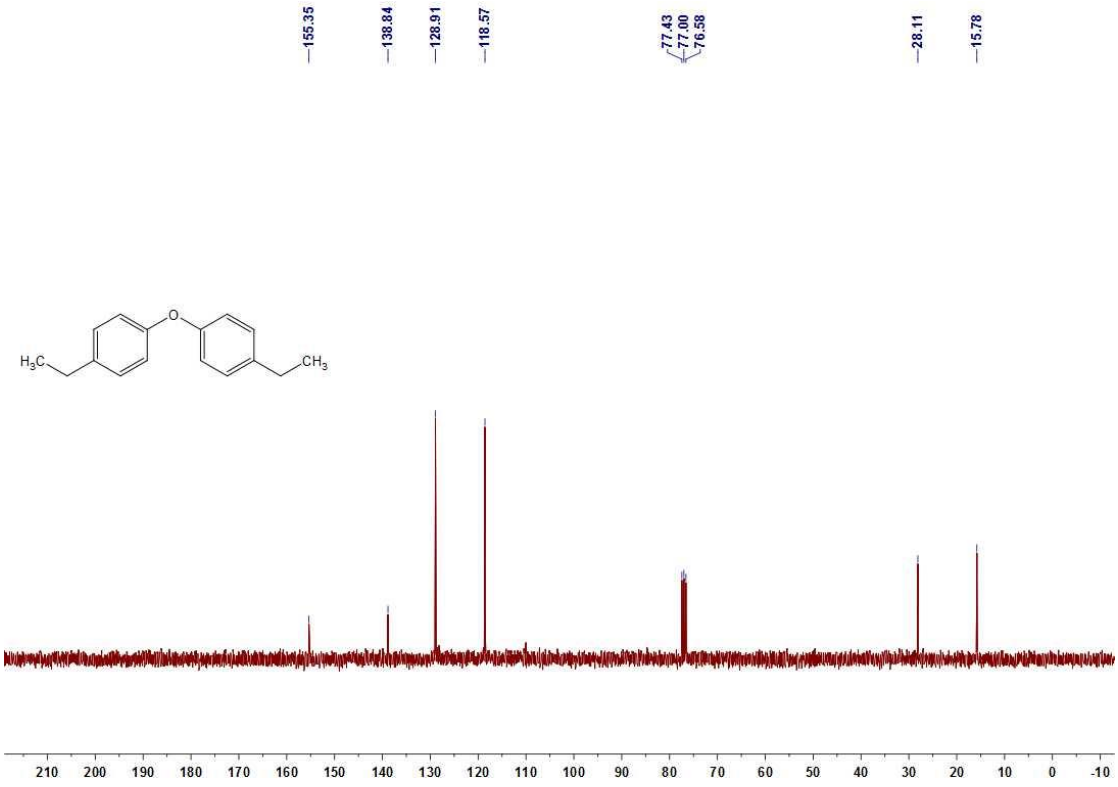
$^{1}$H and $^{13}$C NMR spectra of compound **4,4'-oxybis(methoxybenzene)**



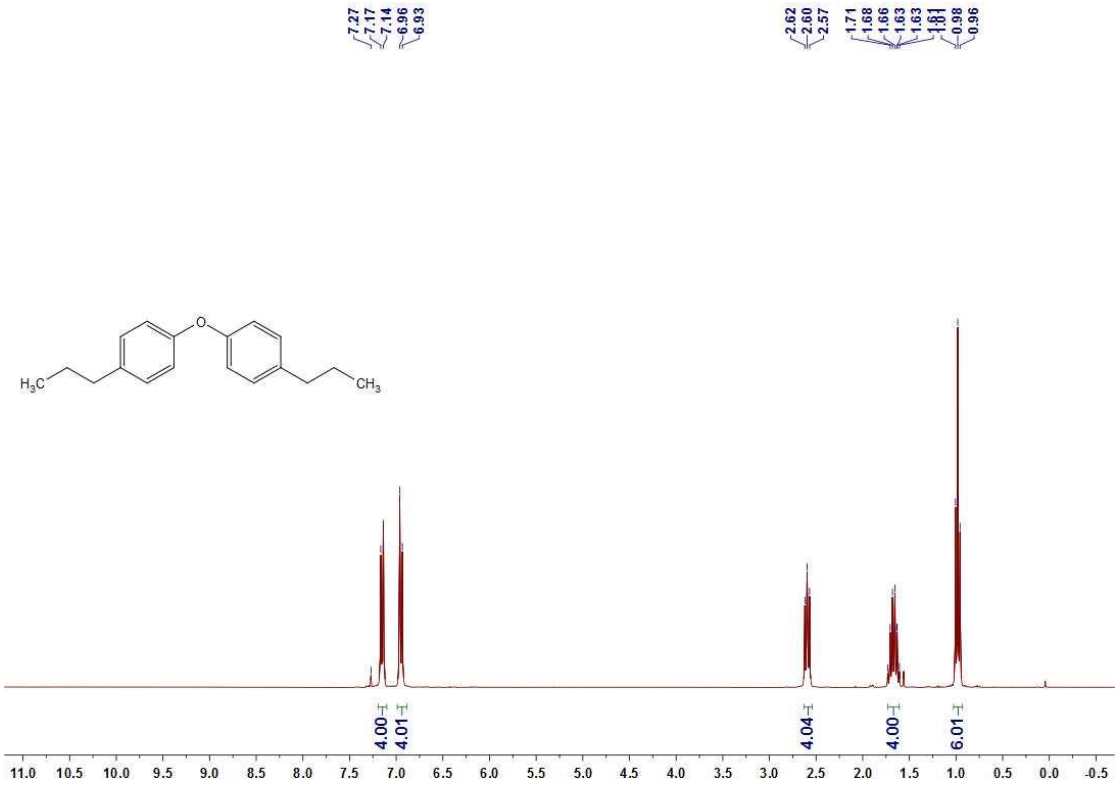



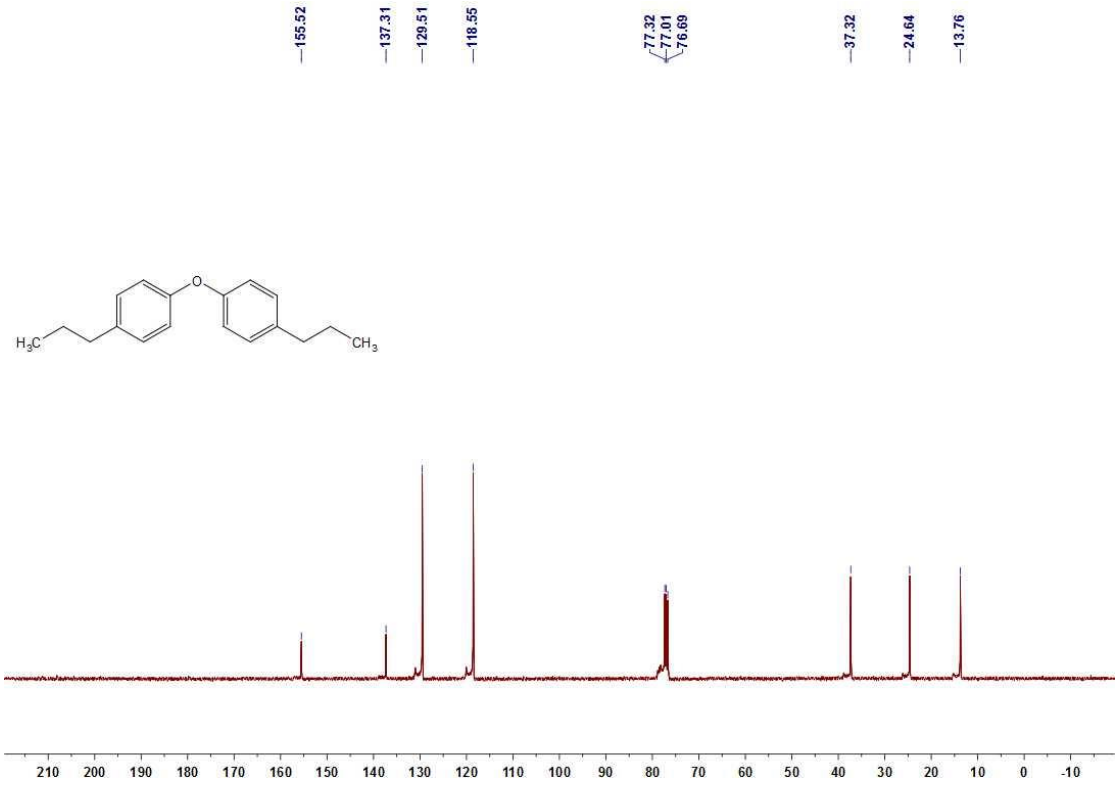
$^{1}H$ and $^{13}C$ NMR spectra of compound **4,4'-oxybis(ethylbenzene)**



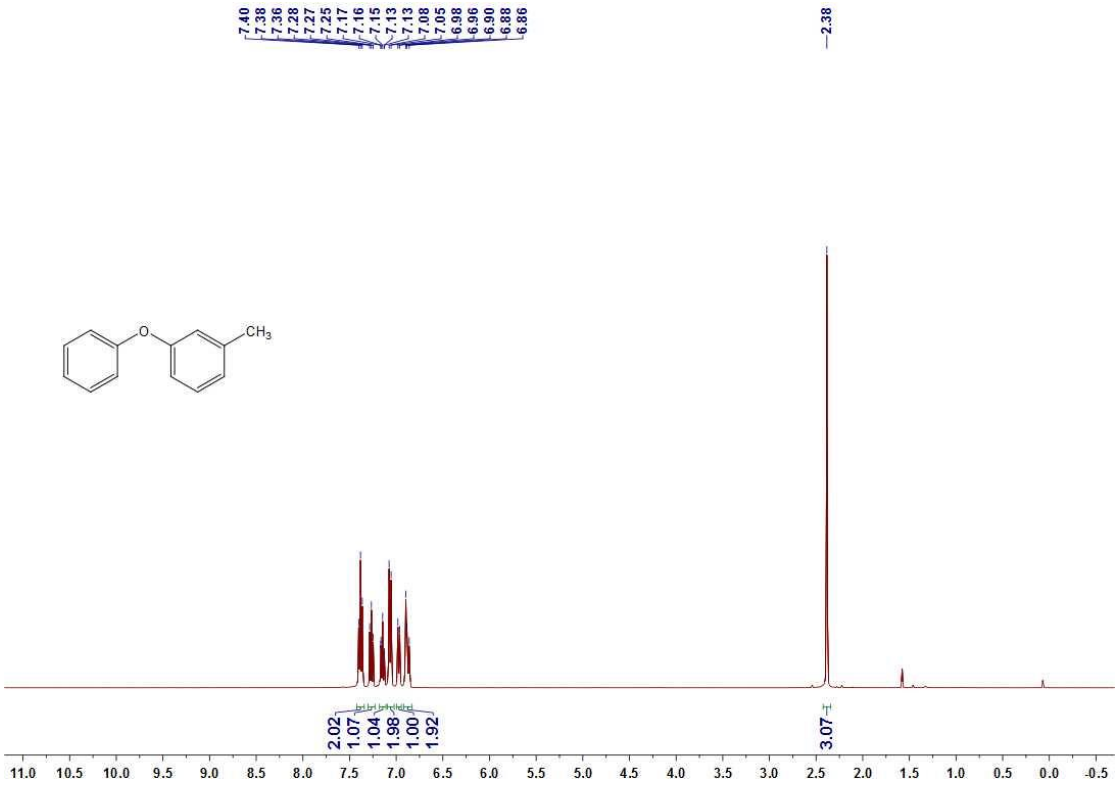



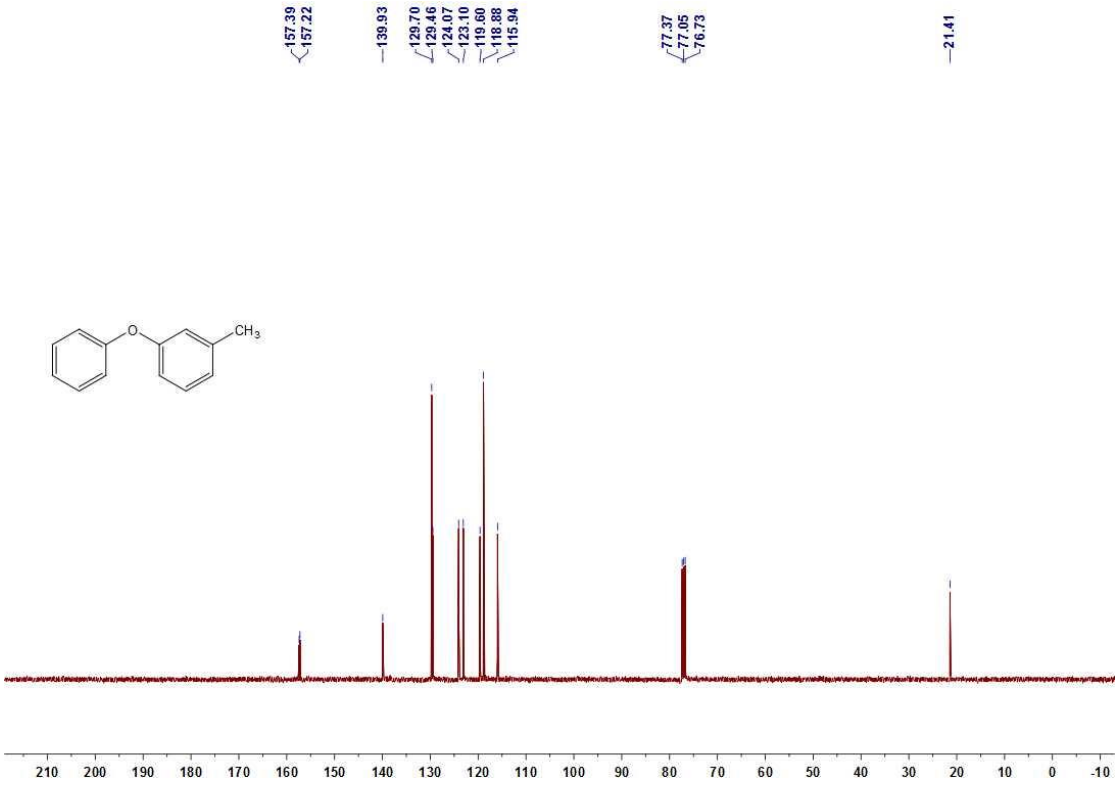
$^{1}H$ and $^{13}C$ NMR spectra of compound **4,4'-oxybis(propylbenzene)**



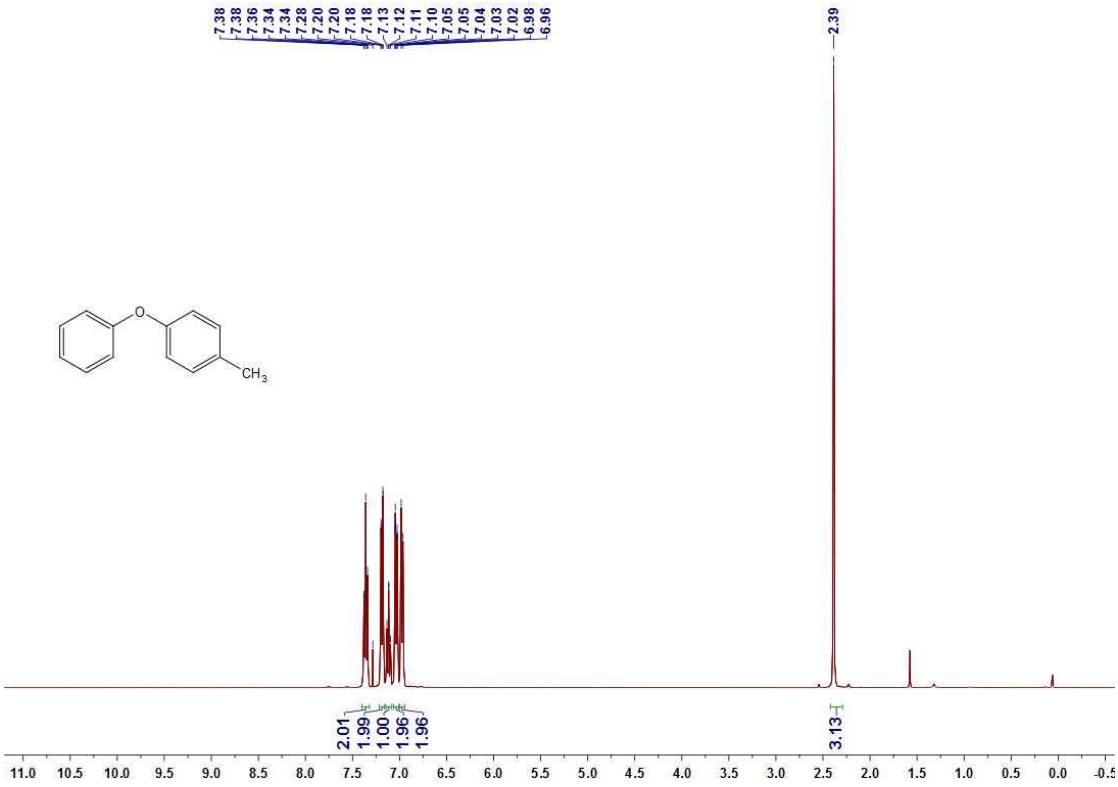



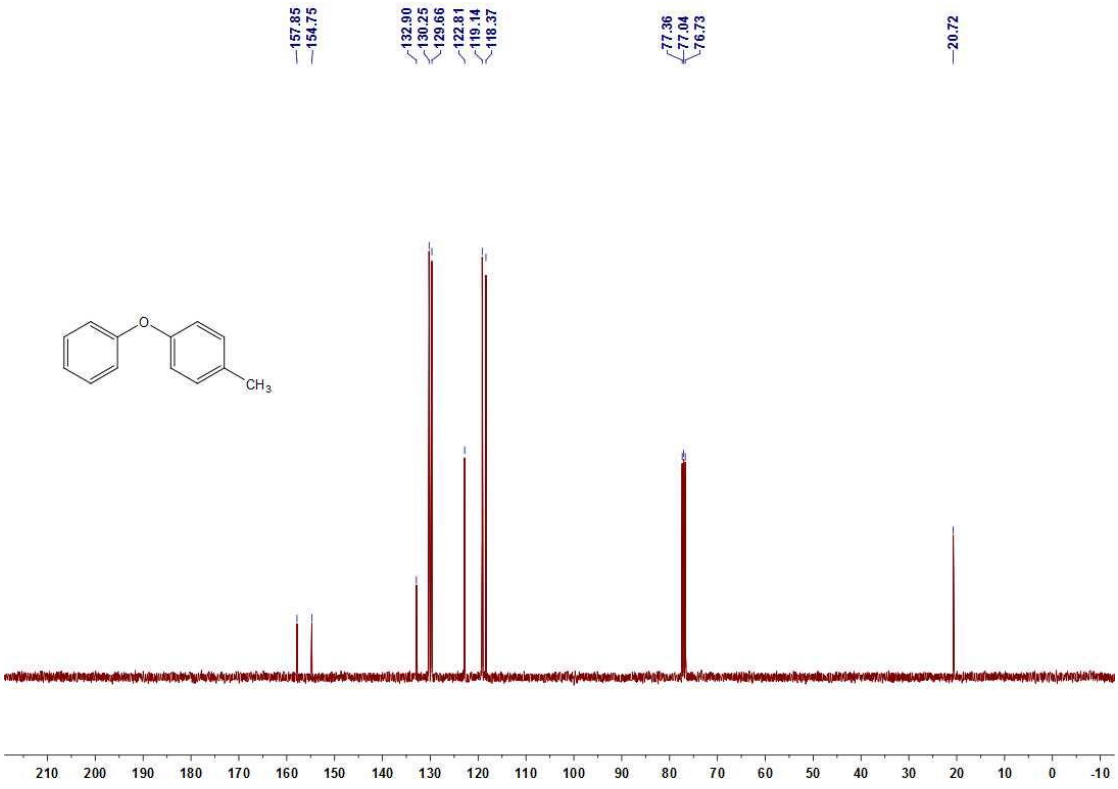
$^{1}H$ and $^{13}C$ NMR spectra of compound **1-methyl-4-phenoxybenzene**



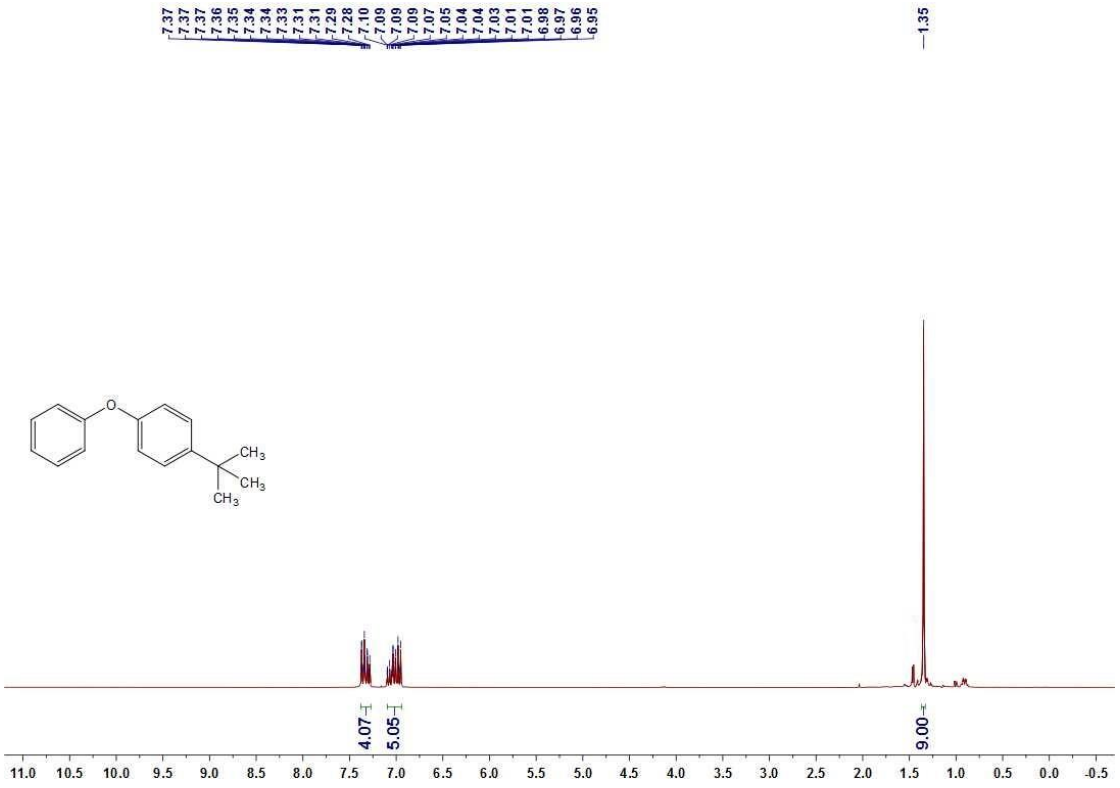



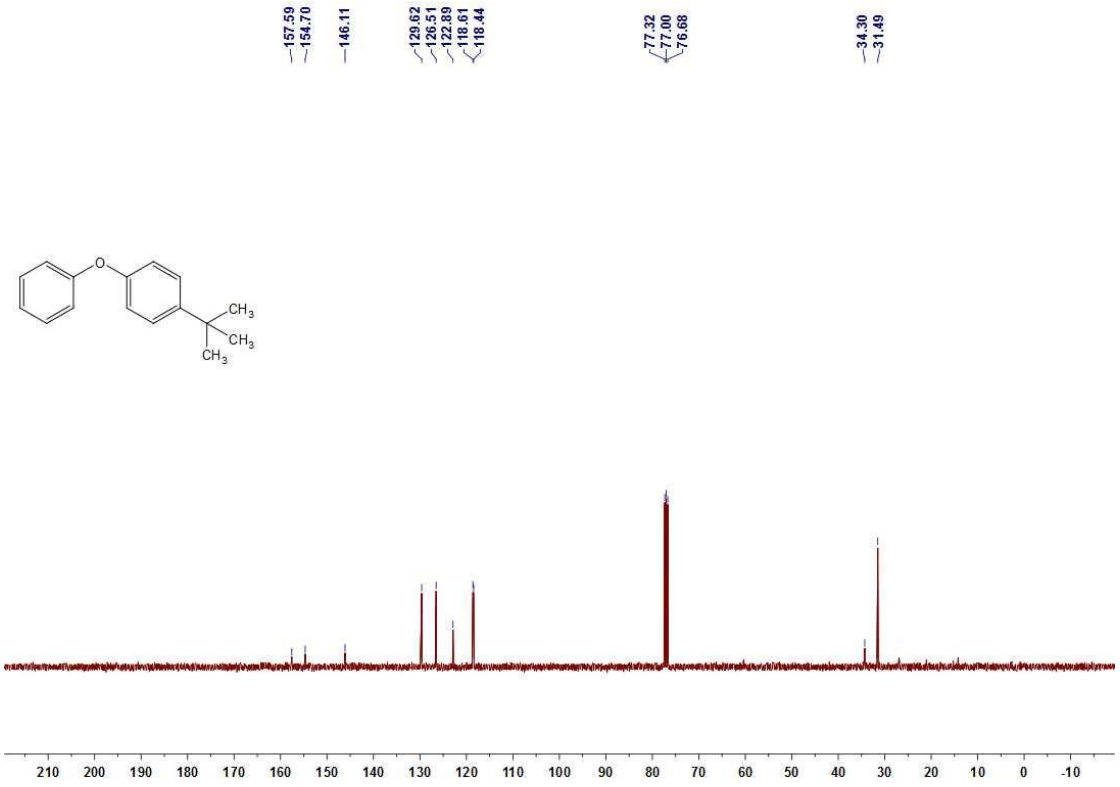
$^{1}H$ and $^{13}C$ NMR spectra of compound **1-methyl-4-phenoxybenzene**



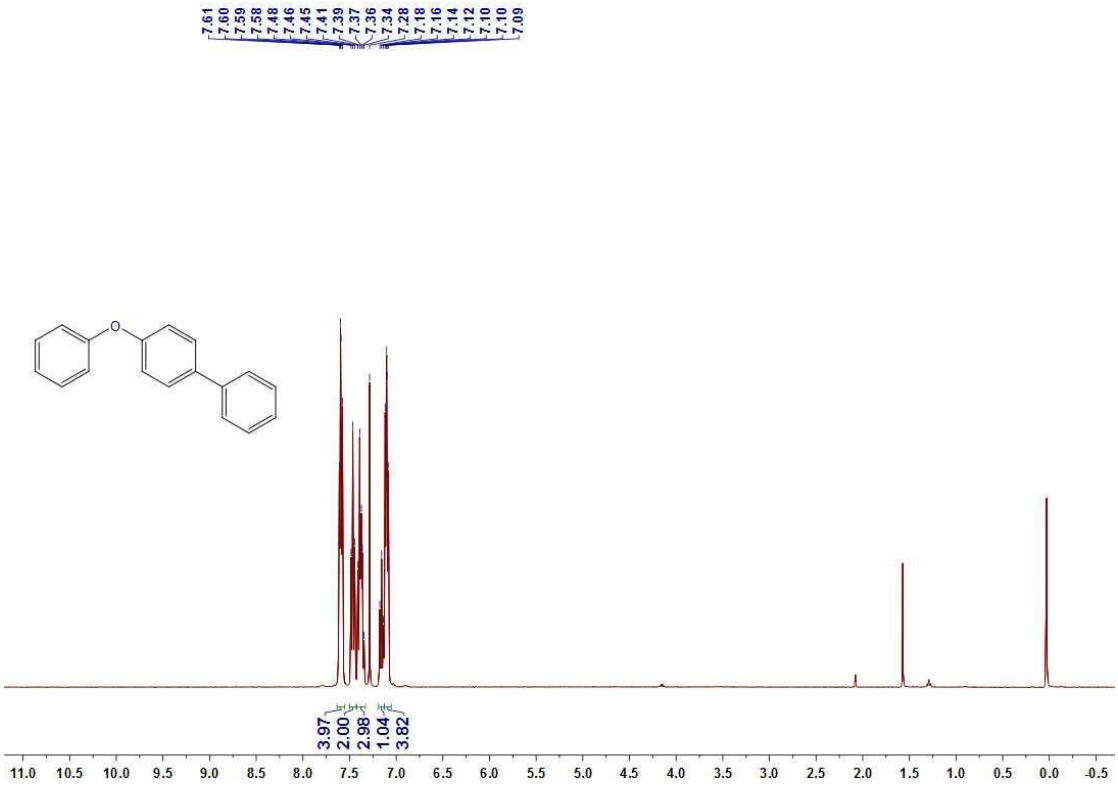



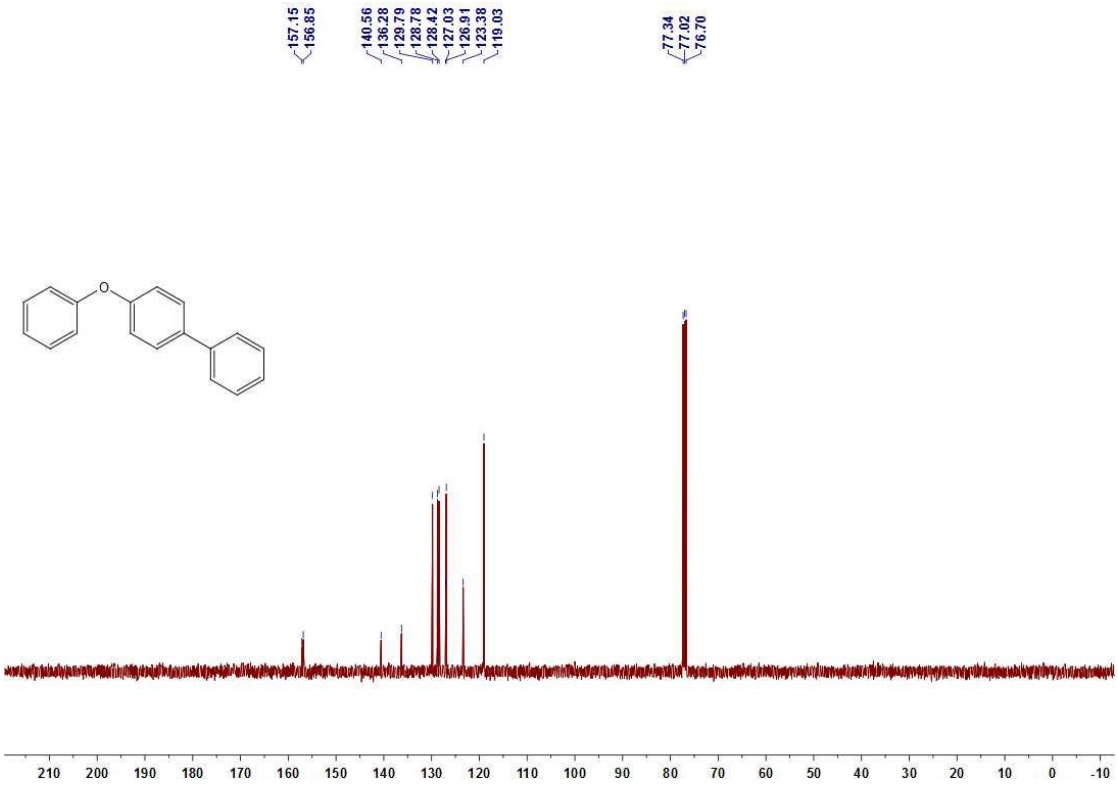
$^{1}H$ and $^{13}C$ NMR spectra of compound **1-(tert-butyl)-4-phenoxybenzene**



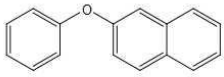



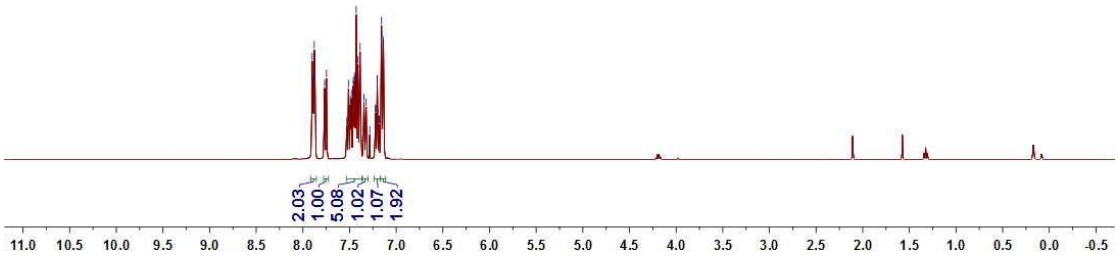
$^{1}H$ and $^{13}C$ NMR spectra of compound **4-phenoxy-1,1'-biphenyl**



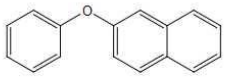



$^{1}H$ and $^{13}C$ NMR spectra of compound **2-phenoxynaphthalene**

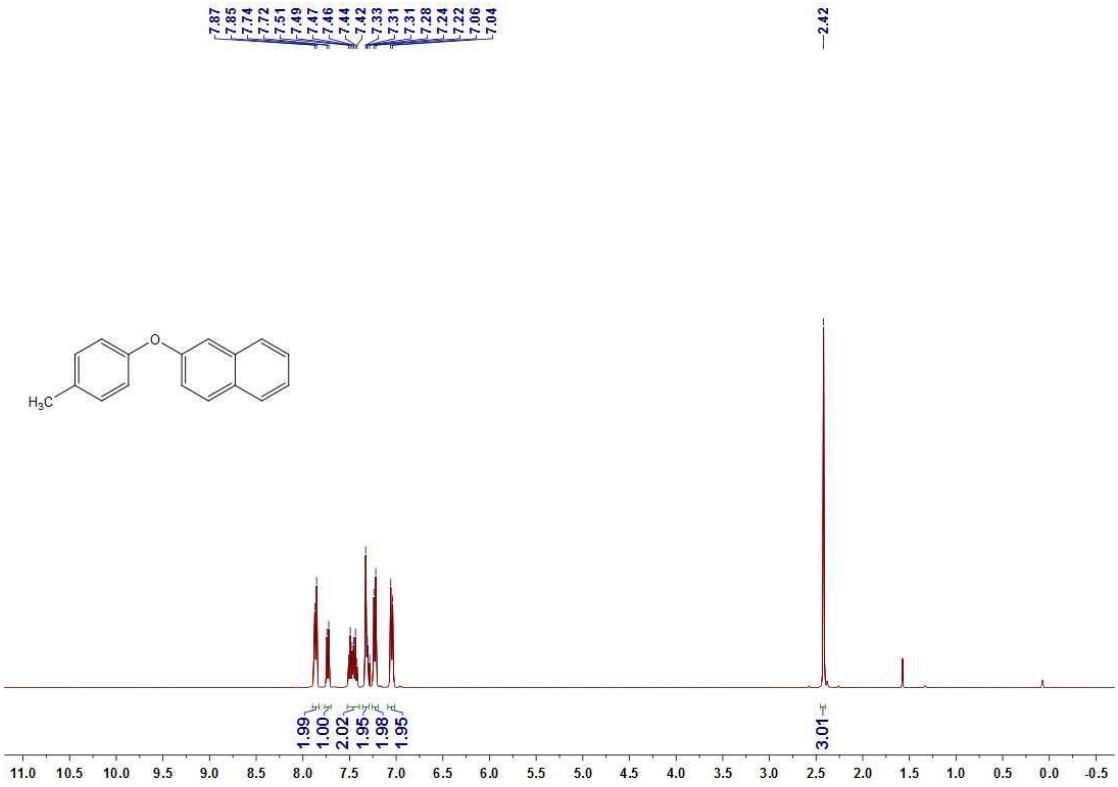



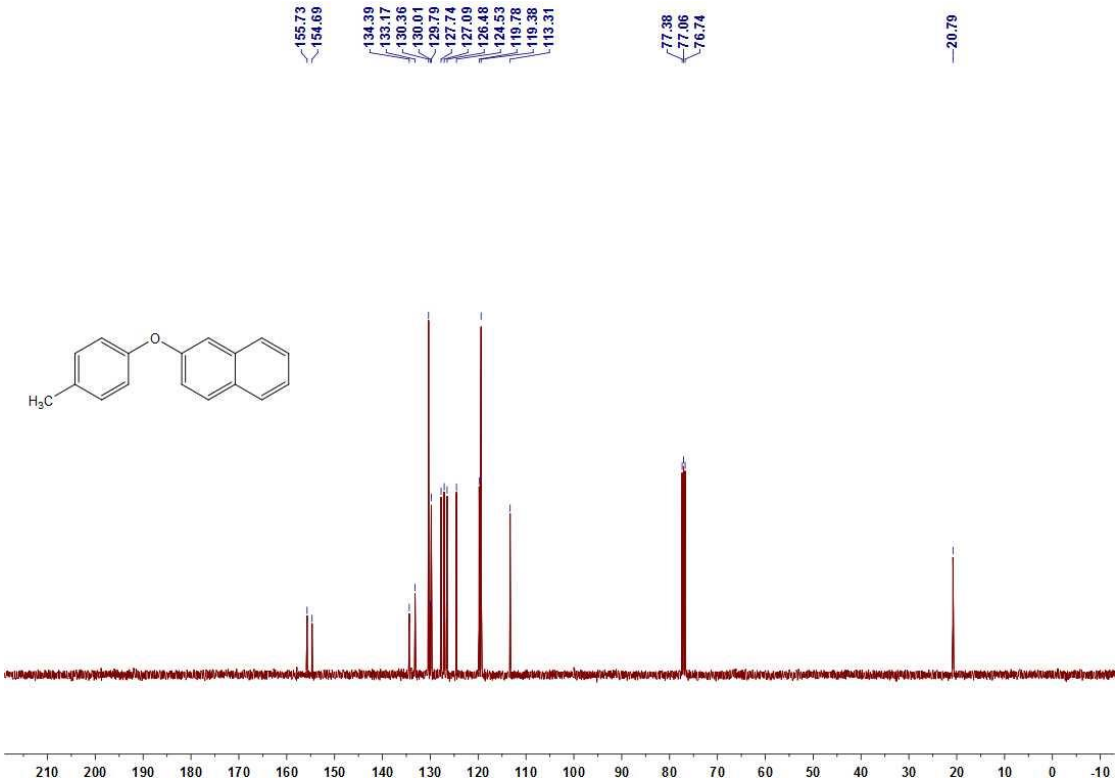




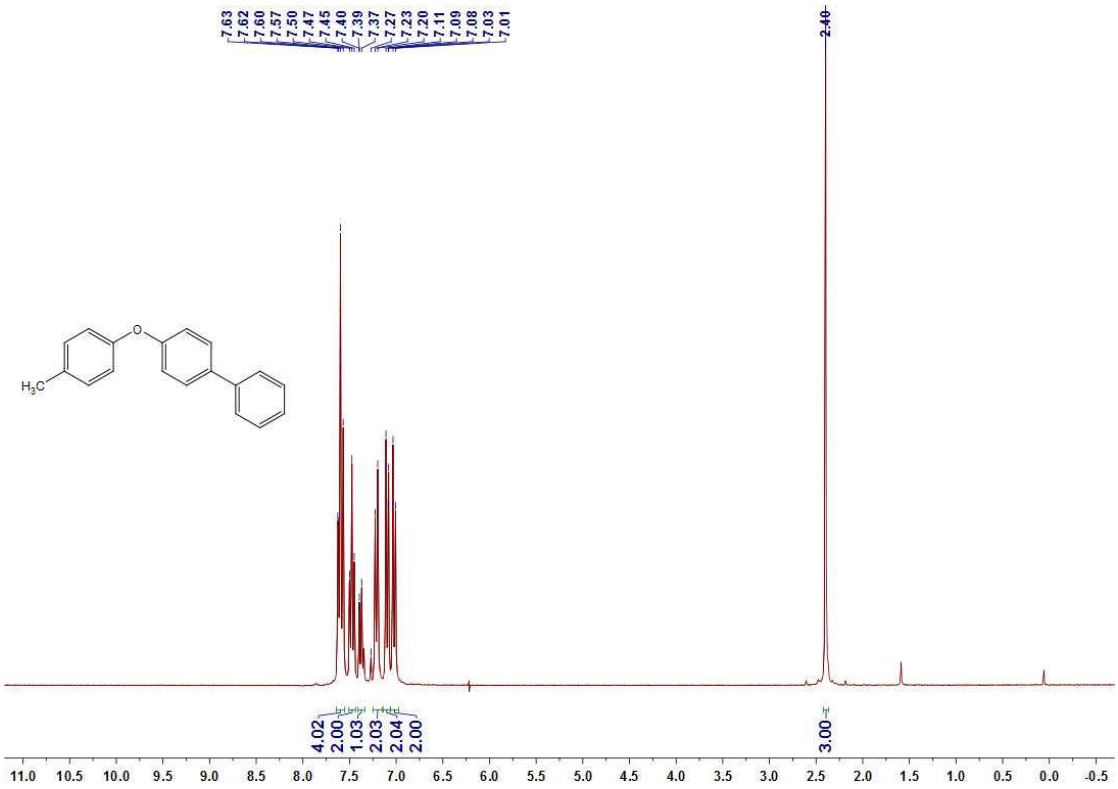


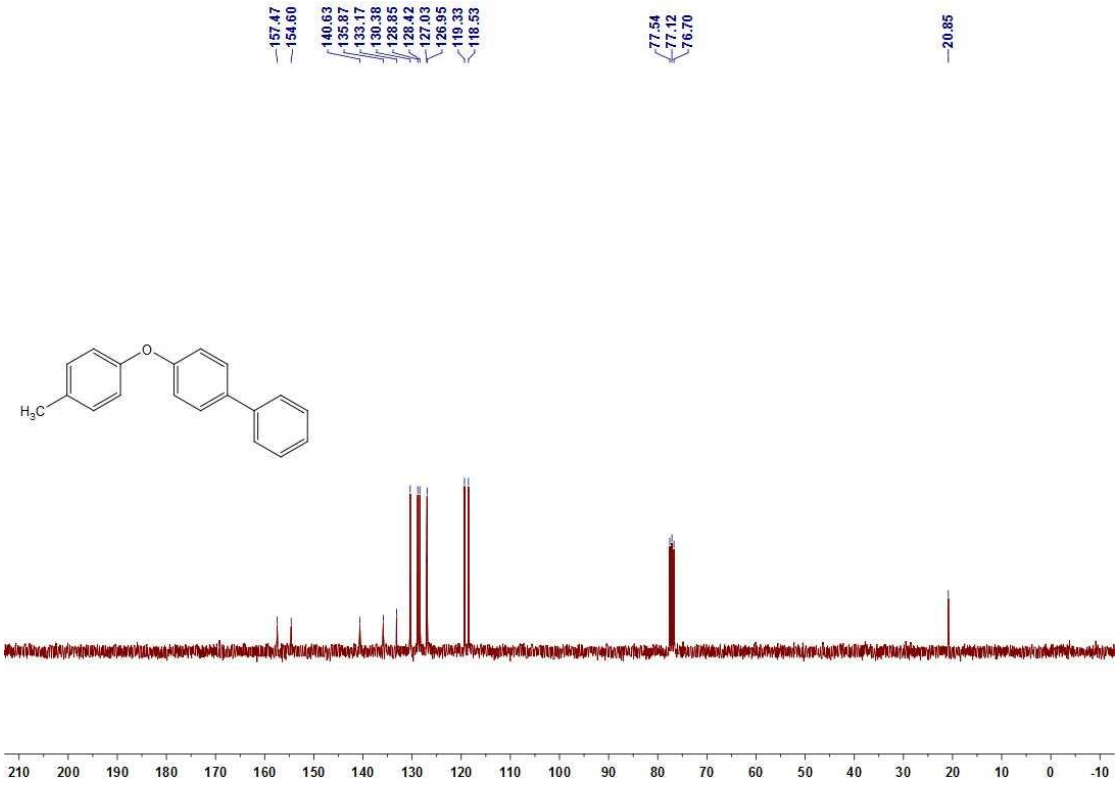
$^{1}H$ and $^{13}C$ NMR spectra of compound **2-(*p*-tolyloxy)naphthalene**



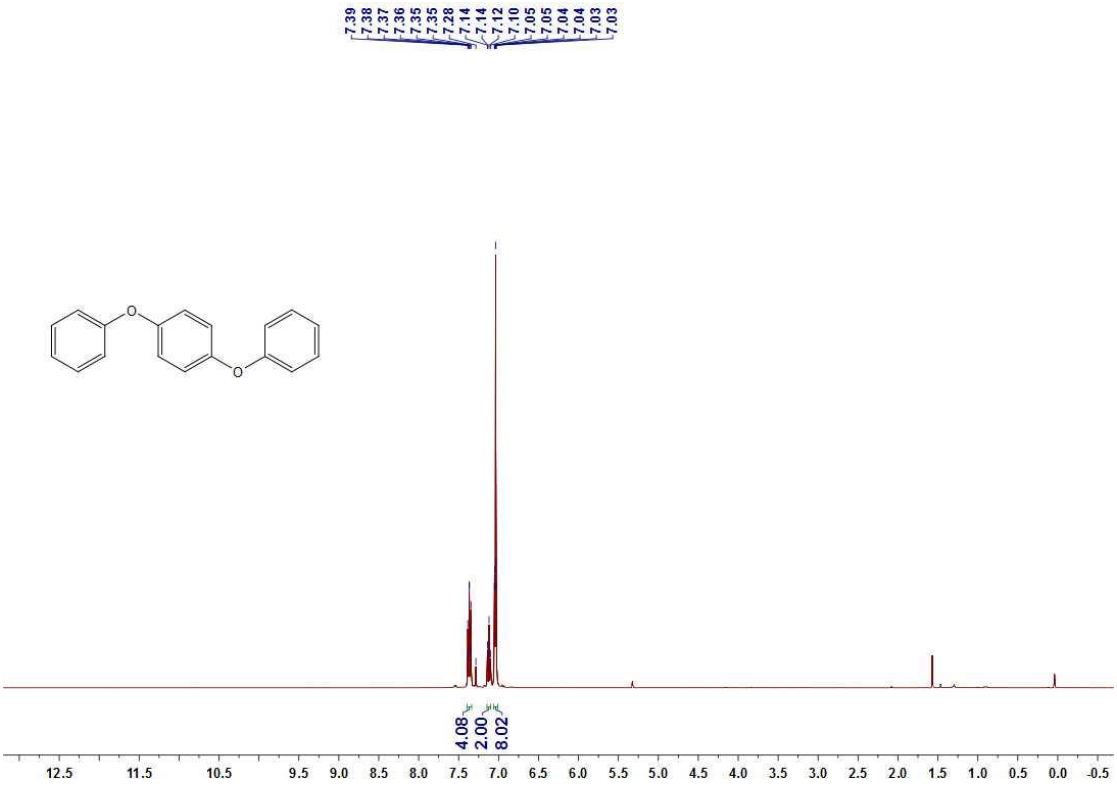



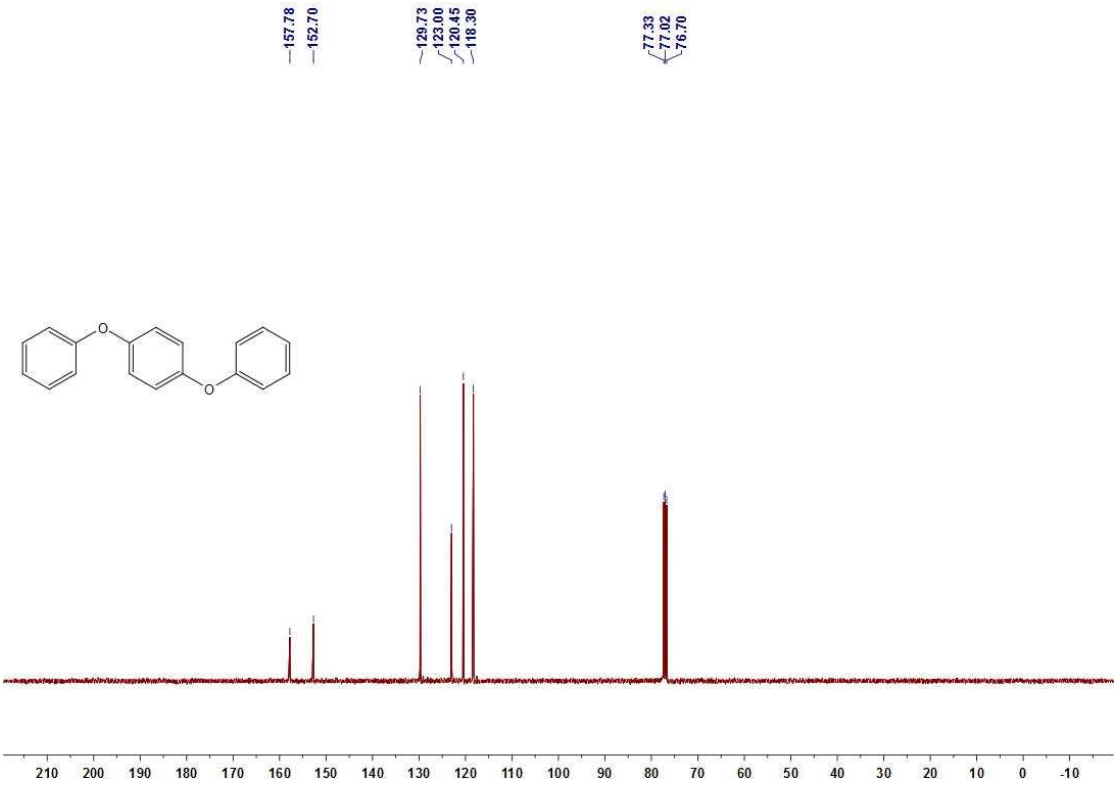
$^{1}$H and $^{13}$C NMR spectra of compound **4-(*p*-tolyloxy)-1,1'-biphenyl**



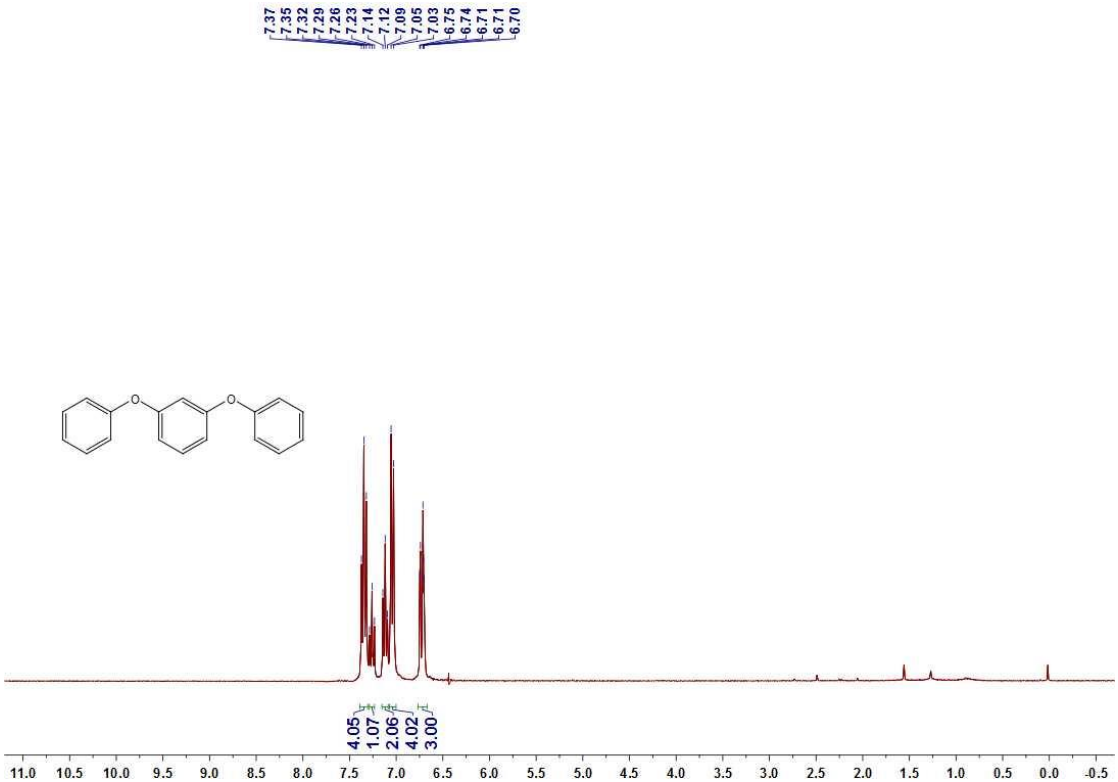



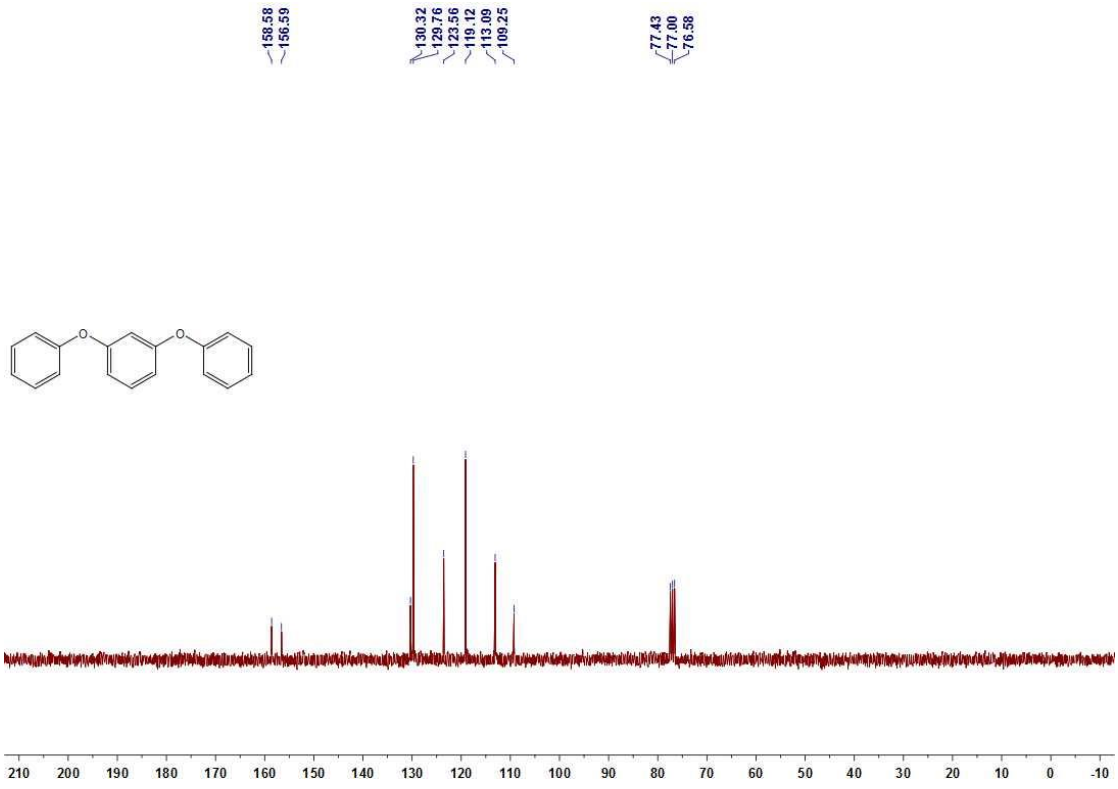
$^{1}H$ and $^{13}C$ NMR spectra of compound **1,4-diphenoxybenzene**



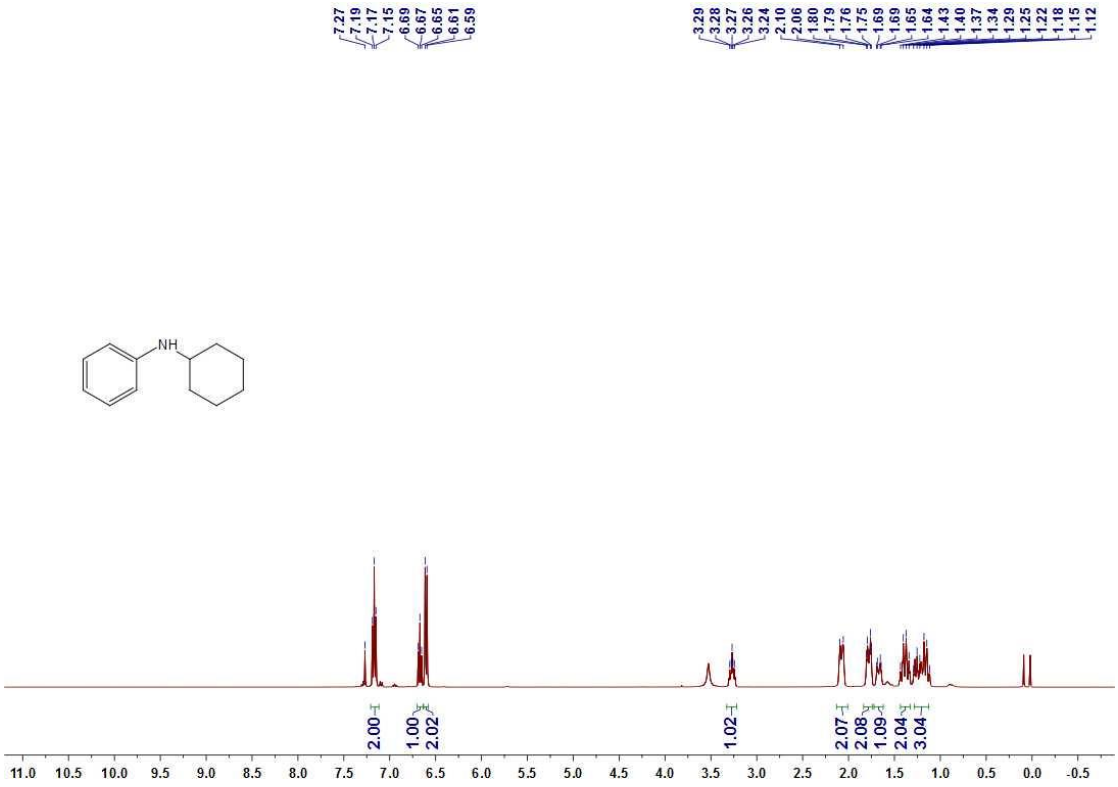



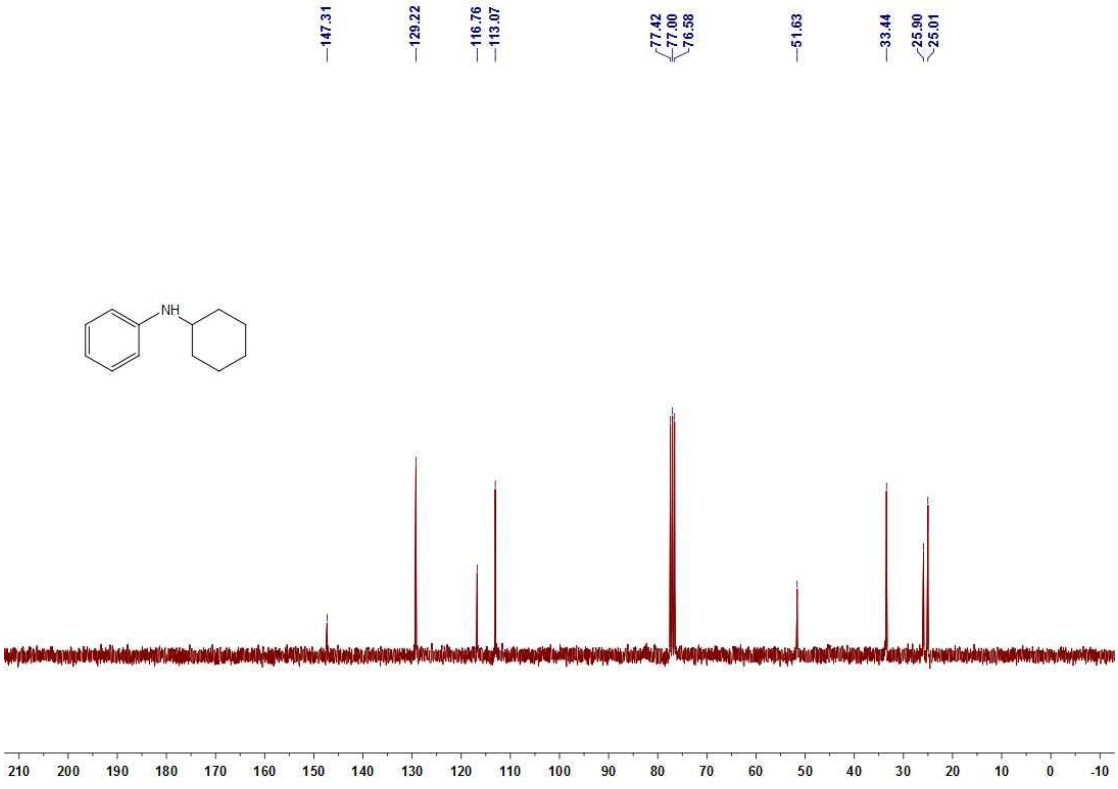
$^{1}H$ and $^{13}C$ NMR spectra of compound **1,4-diphenoxybenzene**



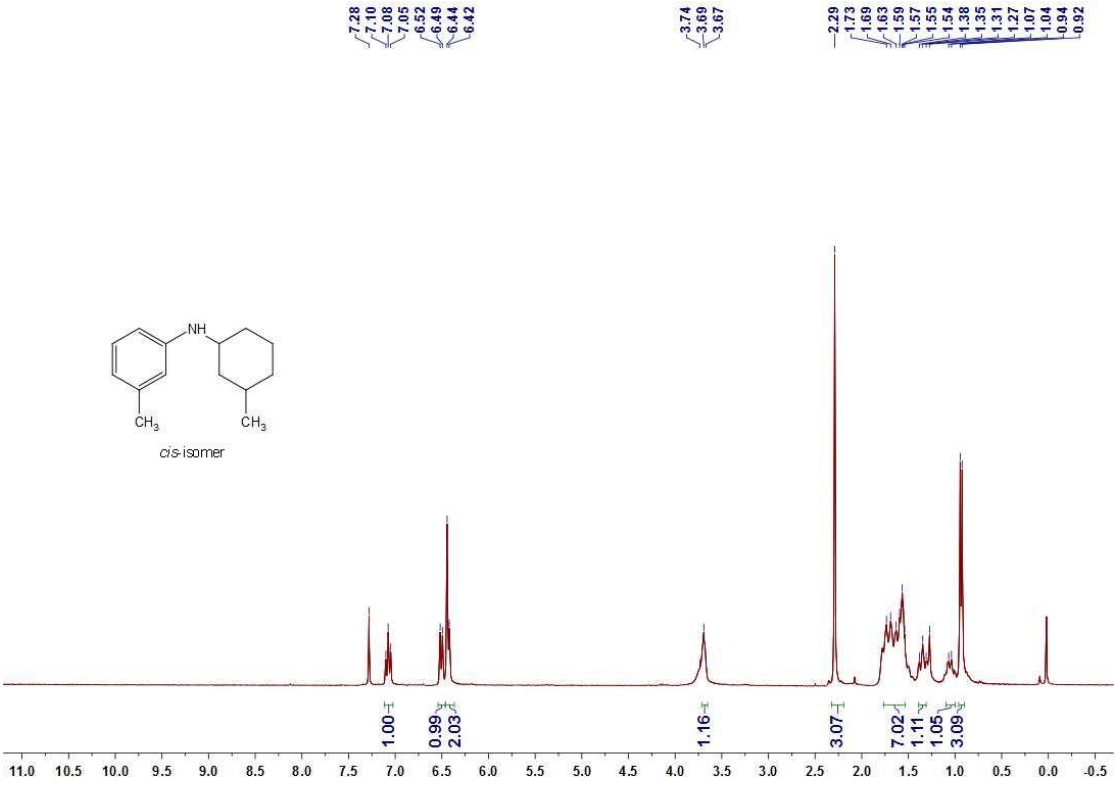



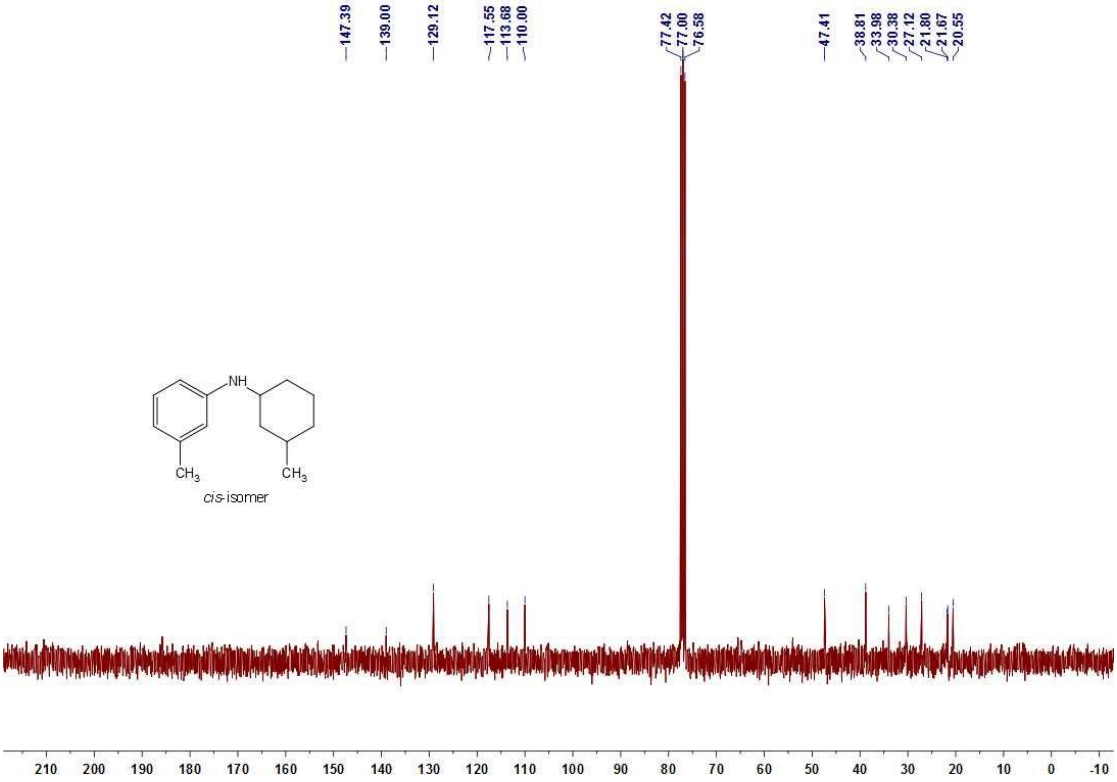
$^{1}$H and $^{13}$C NMR spectra of compound ***N*-cyclohexylaniline**



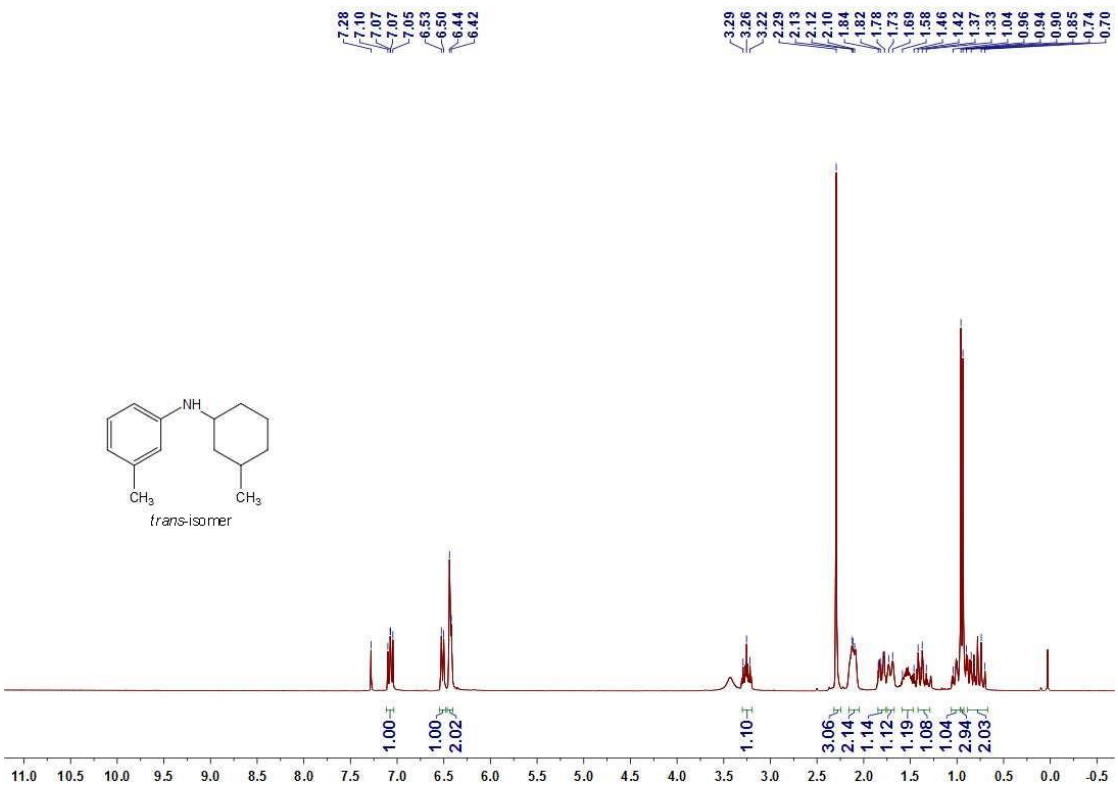



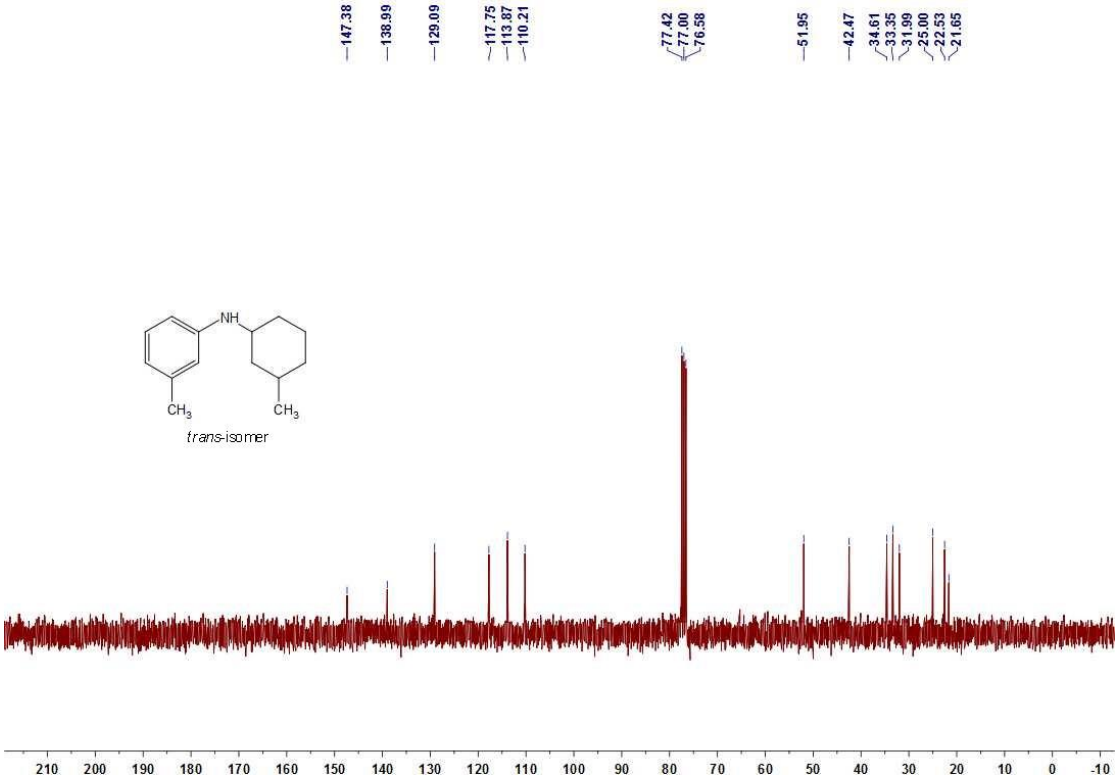
$^{1}$H and $^{13}$C NMR spectra of compound **3-methyl-*N*-(3-methylcyclohexyl)aniline** *cis*-isomer



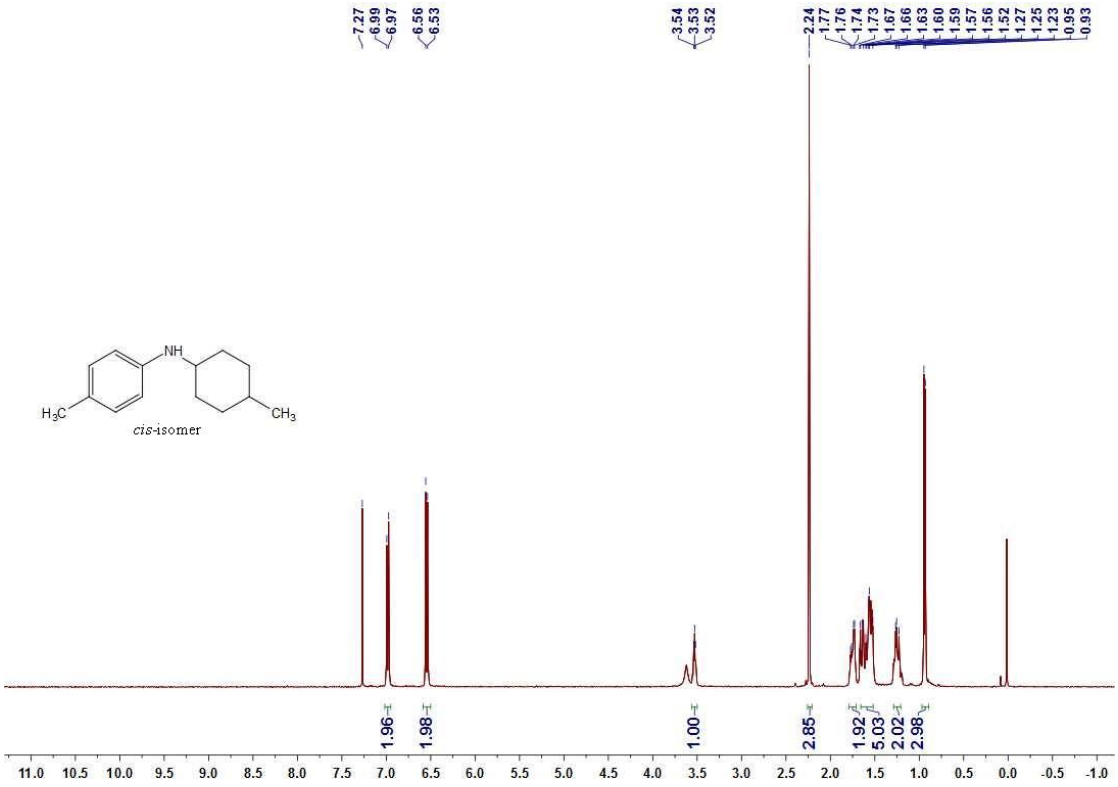



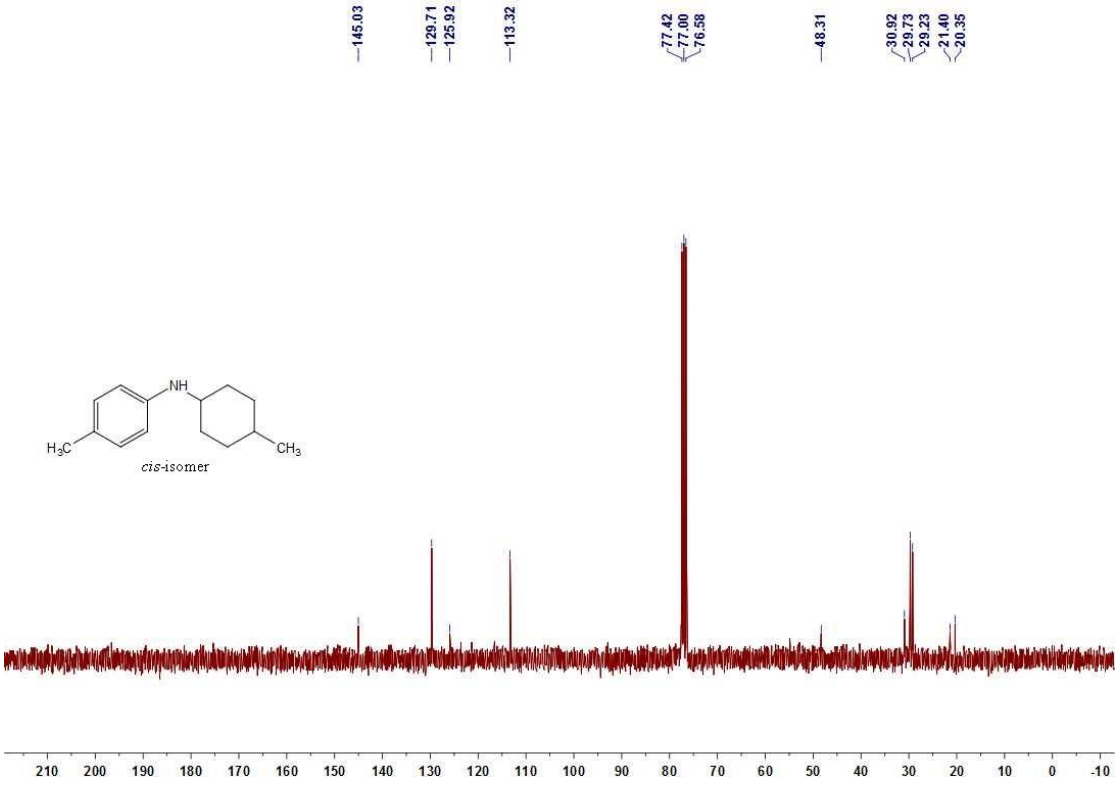
$^{1}$H and $^{13}$C NMR spectra of compound **3-methyl-*N*-(3-methylcyclohexyl)aniline**
*trans*-isomer



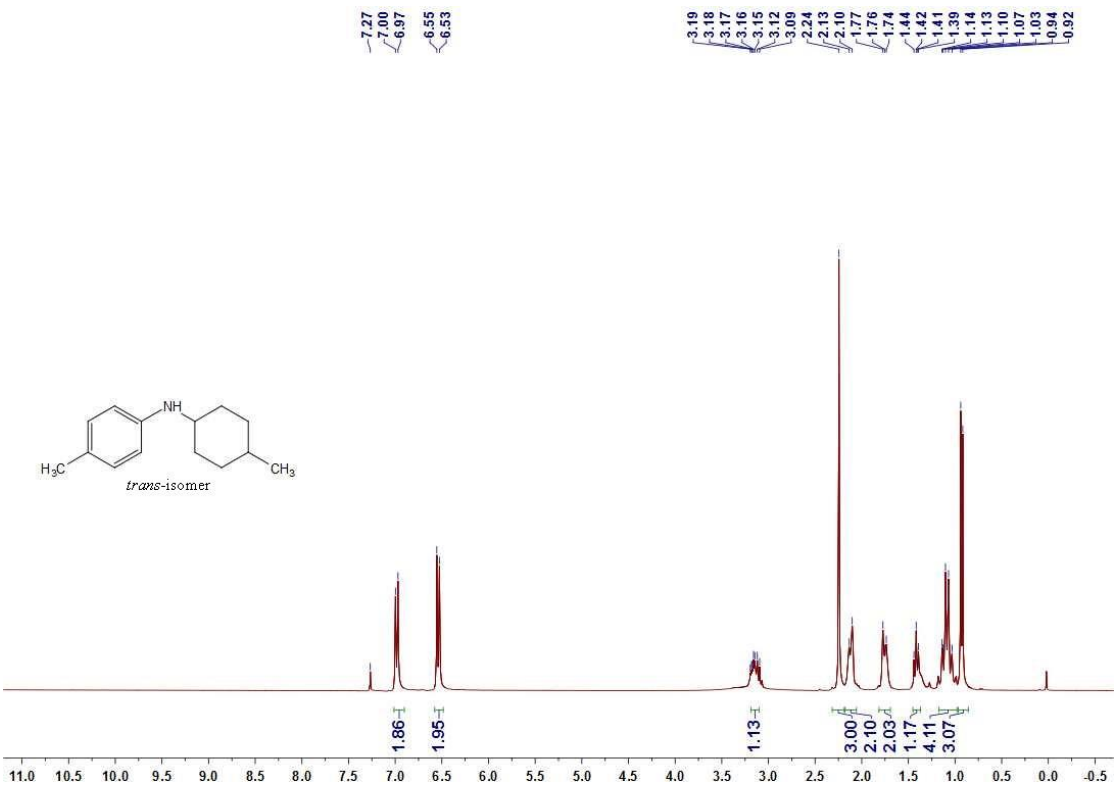



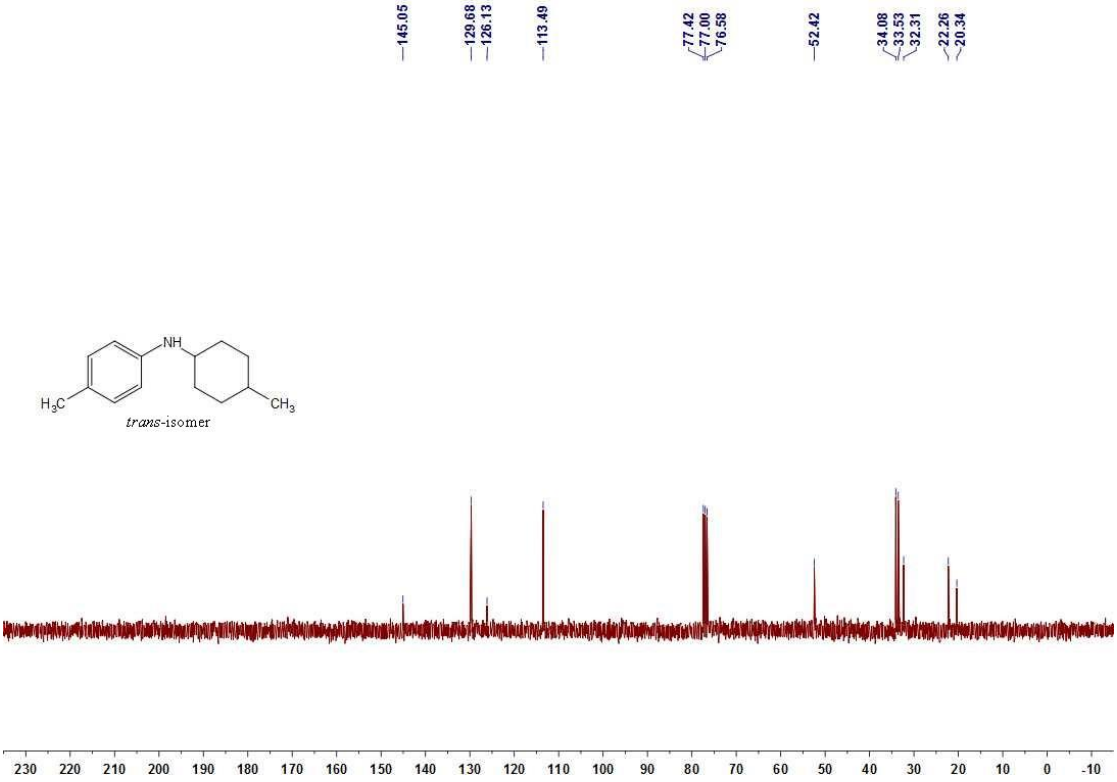
$^{1}$H and $^{13}$C NMR spectra of compound **4-Methyl-*N*-(4-methylcyclohexyl)aniline** *cis*-isomer



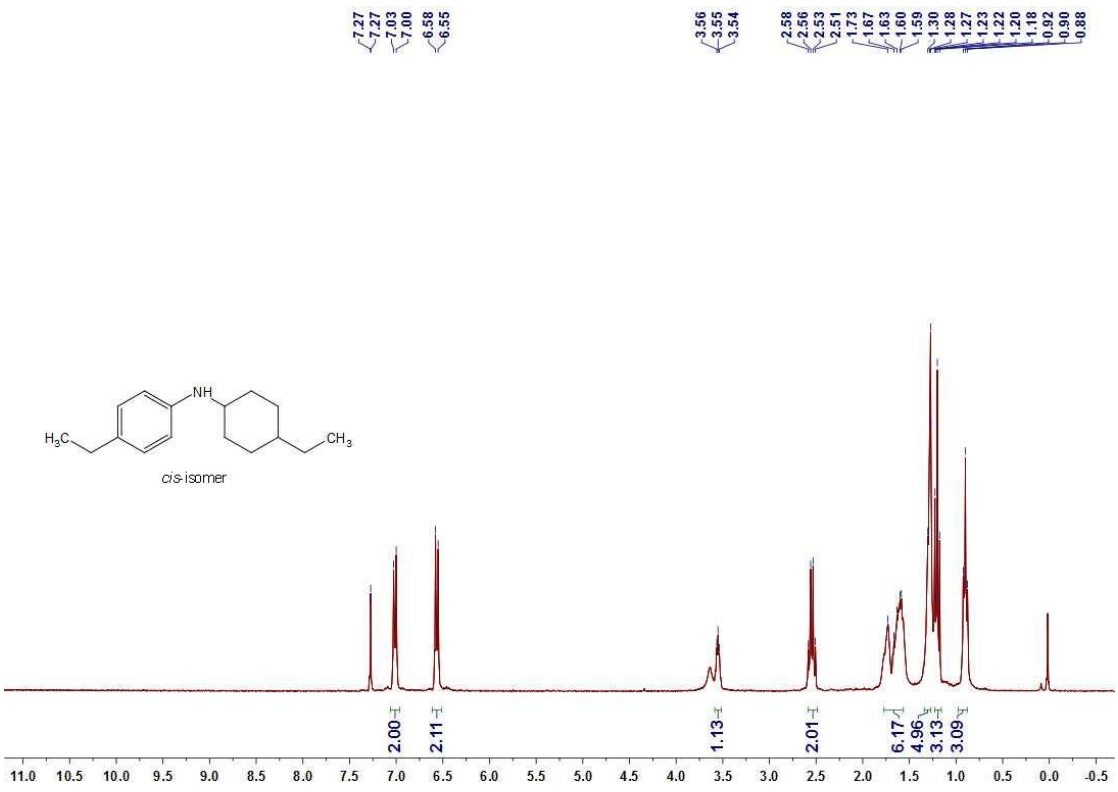



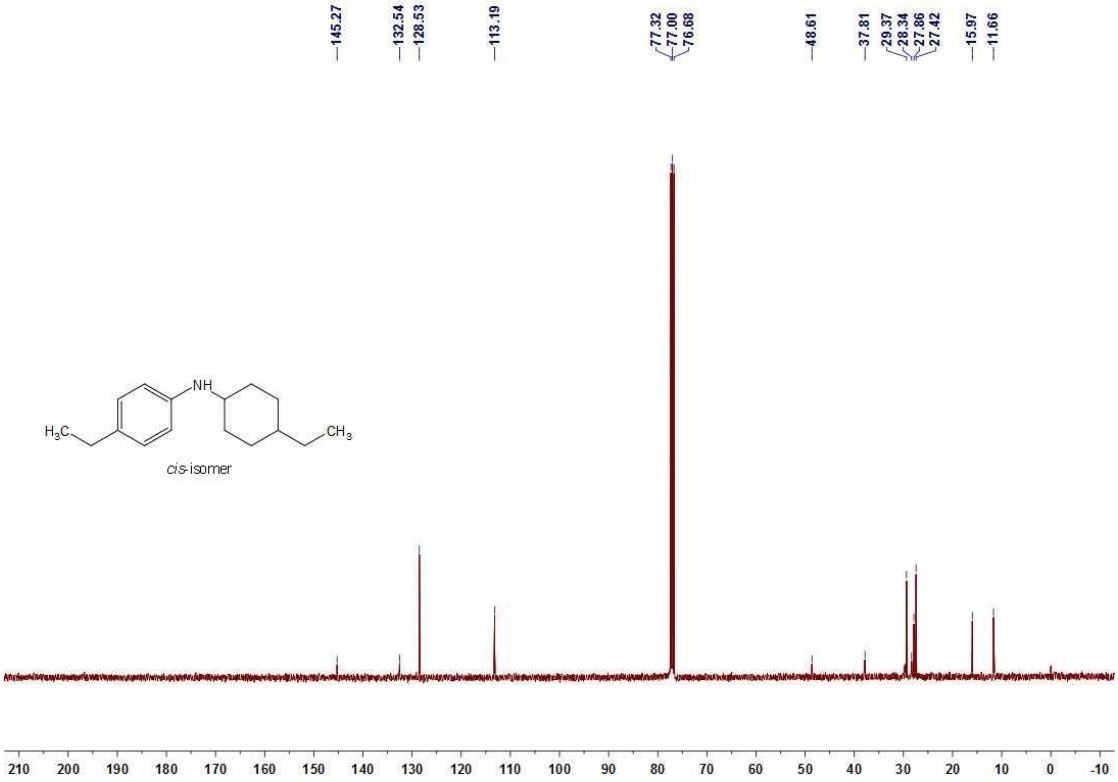
$^{1}$H and $^{13}$C NMR spectra of compound **4-Methyl-*N*-(4-methylcyclohexyl)aniline** *trans*-isomer



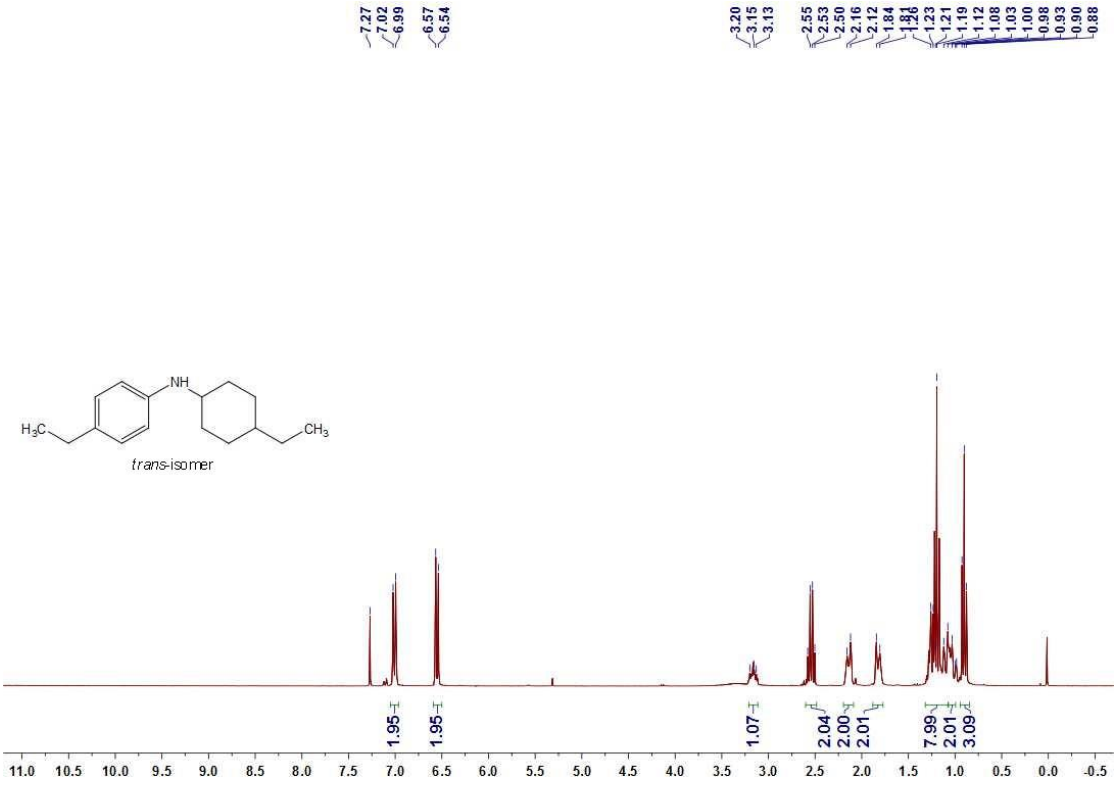



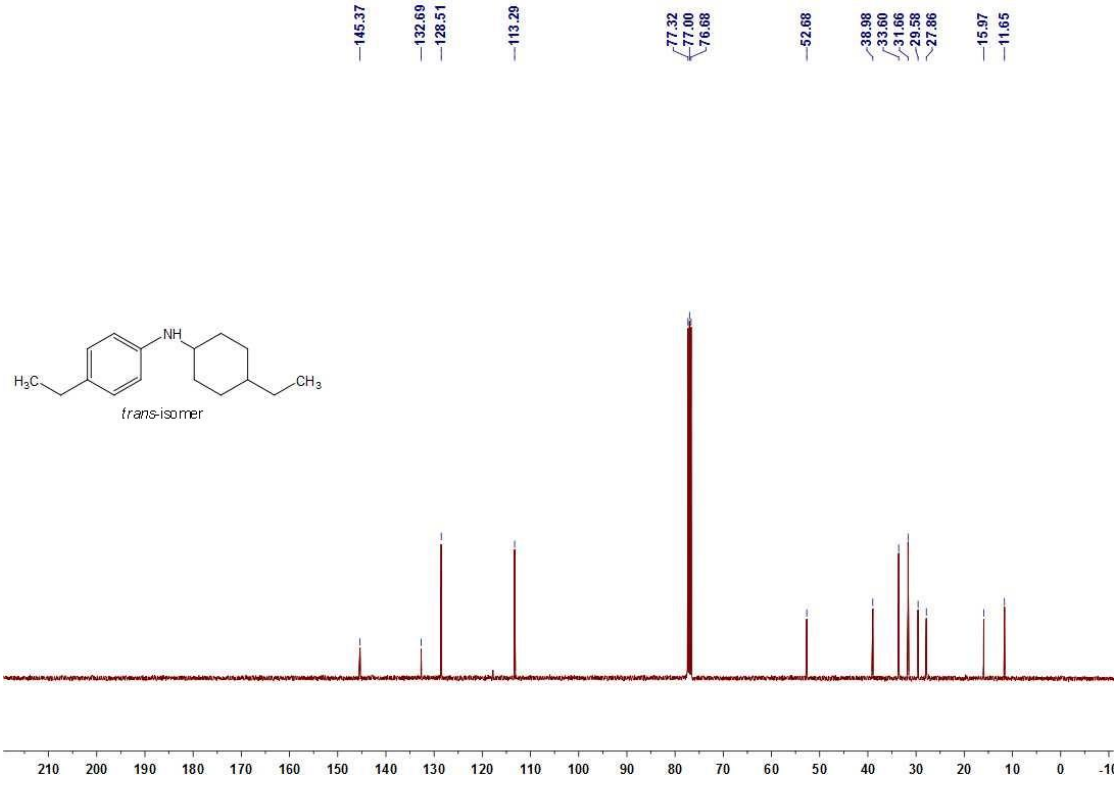
$^{1}$H and $^{13}$C NMR spectra of compound **4-ethyl-*N*-(4-ethylcyclohexyl)aniline**
*cis*-isomer



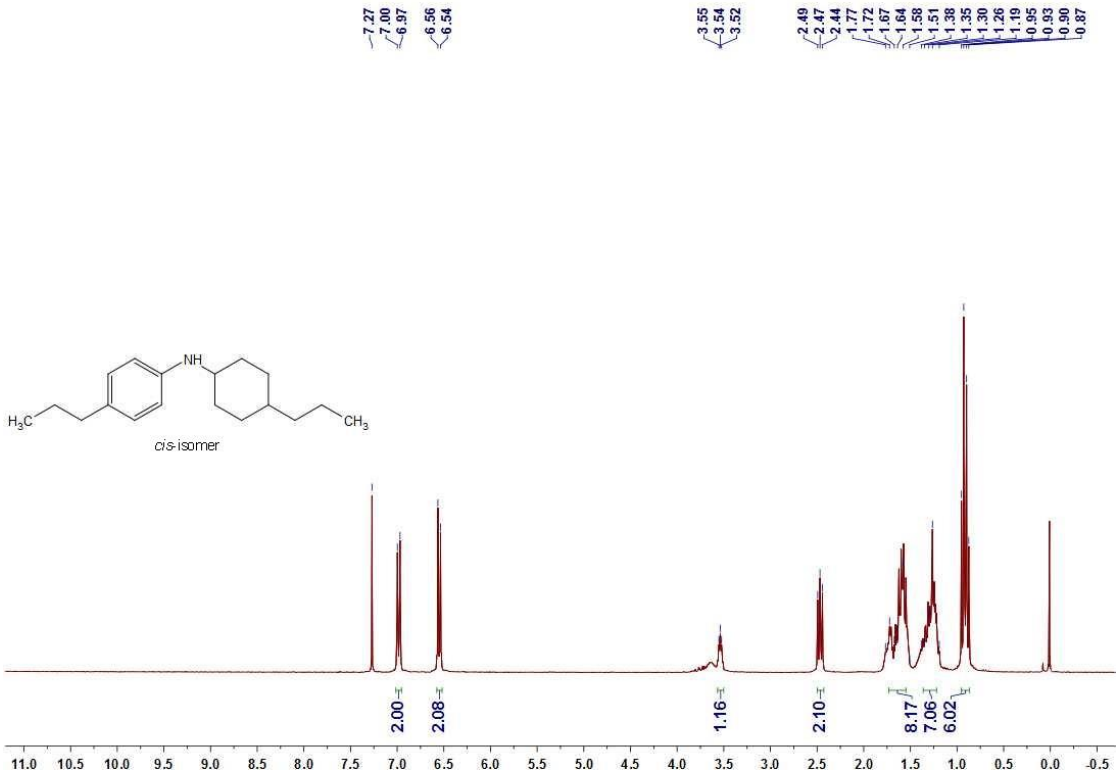



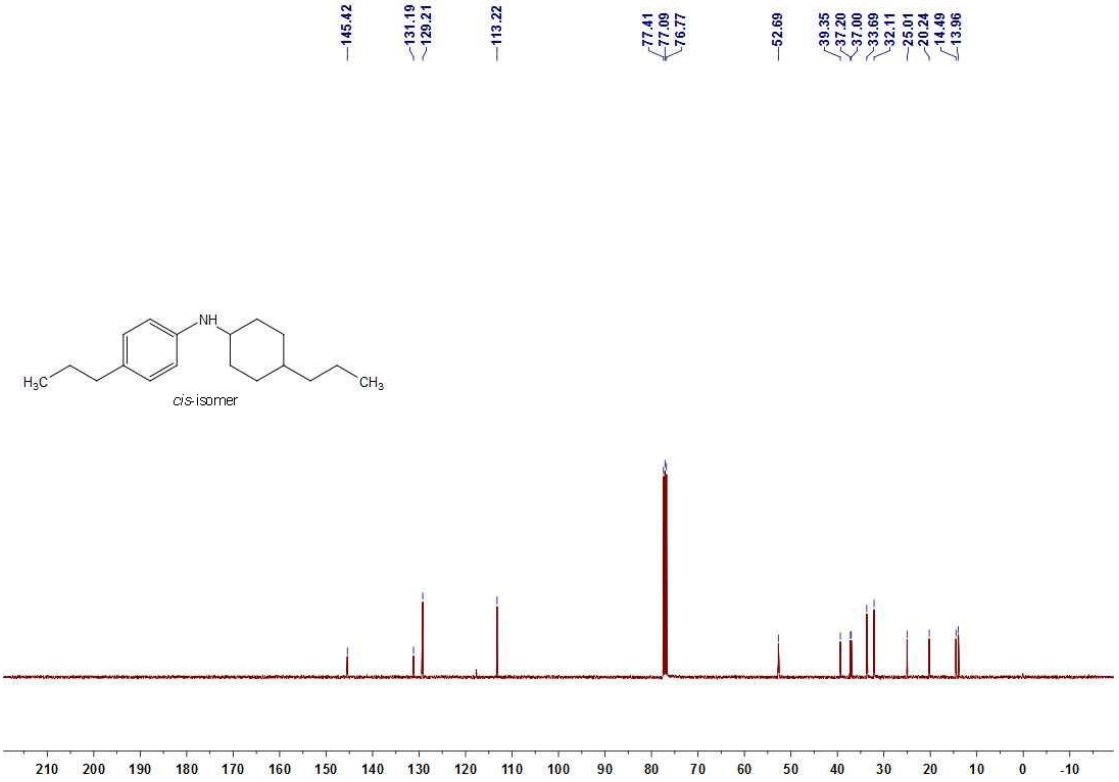
$^{1}$H and $^{13}$C NMR spectra of compound **4-ethyl-*N*-(4-ethylcyclohexyl)aniline**
*trans*-isomer



$^{1}$H and $^{13}$C NMR spectra of compound **4-propyl-*N*-(4-propylcyclohexyl)aniline** *cis*-isomer



$^{1}$H and $^{13}$C NMR spectra of compound **4-propyl-*N*-(4-propylcyclohexyl)aniline**
*trans*-isomer