Supporting Information

Ligand-free coupling of phenols and alcohols with aryl halides by a recyclable heterogeneous copper catalyst

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1. General Information

Chemicals were purchased from commercial sources. All solvents were analytical grade and distilled prior to use.

^{1}H NMR and ^{13}C NMR data were obtained on Bruker Avance III 400 spectrometer using $CDCl_3$ as solvent and tetrmethylsilane (TMS) as an internal standard. Mass spectra were recorded on a GC-MS spectrometer (Shimadzu GCMS-QP5050A equipped with a 0.25 mm × 30 m DB-WAX capillary columnin). Powder X-ray diffraction patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu Kα radiation (40 kV, 30 mA, λ = 0.1543 nm). XPS data were obtained on Axis Ultra DLD using Mono Al Kα (1486.6eV, 10mA×15KV) as x-ray source. Atomic absorption spectroscopy (AAS) was obtained on a HITACHI Z-2300 instrument.

2. Experimental Section

2.1 Synthesis of MOF-253[S1,S2]

MOF-253 was prepared from hydrothermal reaction of $AlCl_3 \cdot 6H_2O$ (151 mg, 0.625 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol), and 10 mL N,N'-dimethylformamide (DMF) at 120 °C for 24 h. The resulting white microcrystalline powder was then filtered and washed with DMF. The solid was washed with methanol via soxhlet extraction for 24 h, and then was collected by filtration and finally dried at 200 °C under vacuum for 12 h.

2.2 Synthesis of MOF-253·0.5CuI

MOF-253·CuI was prepared by addition of MOF-253 (143.5 mg) to a solution of CuI

(57.2 mg, 0.3 mmol) in acetonitrile (5 mL) at 65 °C for 24 h. After cooling to room temperature, the resulting solid was soaked in 15 mL of acetonitrile. After 24 h, the supernatant was decanted and replaced with fresh acetonitrile. The exchanging process was repeated two times, after which the powder was filtered and heated at 150 °C for 12 h under vacuum. The molar ratio of CuI to bpy in MOF-253 was ca. 0.5, as measured by elemental analysis. Calcd for $C_{12}H_7AlCu_{0.5}I_{0.5}N_2O_5$: C, 37.79; H, 1.85; Al, 7.07; Cu, 8.33; N, 7.34. Found: C, 37.57; H, 1.94; Al, 7.11; Cu, 8.26; N, 7.46.

2.3 General procedure for coupling of aryl iodides/bromides with phenols

Aryl halide (0.4 mmol), phenol (0.6 mmol), MOF-253·0.5CuI (0.08 mmol, 20 mol%), and Cs_2CO_3 (0.8 mmol) were added to a Schlenk tube under a nitrogen atmosphere at room temperature. The tube was sealed and the mixture was stirred at the desired temperature. After cooling to room temperature, the solid catalyst was isolated from the solution by filtration and washed with ethyl acetate. The solution was filtered through a short plug of silica gel, and then washed with copious quantities of ethyl acetate. The combined organic phase was concentrated under vacuum. The crude was purified by silica gel chromatography using petroleum ether/ethyl acetate as eluent to afford the desired product.

2.4 General procedure for coupling of alcohols with aryl iodides

Aryl iodide (0.4 mmol), alcohol (2 mmol), MOF-253·0.5CuI (0.08 mmol, 20 mol%), Cs_2CO_3 (0.8 mmol), and DMSO (2 mL) were added to a Schlenk tube under a nitrogen atmosphere at room temperature. The tube was sealed and the mixture was stirred at the desired temperature. After cooling to room temperature, the solid catalyst was isolated from the solution

by filtration and washed with ethyl acetate. The solution was filtered through a short plug of silica gel, and then washed with copious quantities of ethyl acetate. The combined organic phase was concentrated under vacuum. The crude was purified by silica gel chromatography using petroleum ether/ethyl acetate as eluent to afford the desired product.

2.5 Recycling of the MOF-253·0.5CuI catalyst

The recyclability of the MOF-253·0.5CuI catalyst was tested for reaction of iodobenzene with phenol maintaining the same reaction conditions as described above, except using the recovered catalyst. The results of three runs are presented in Table S1. Each time, the reaction mixture was allowed to settle down at the end of reaction and the supernatant liquid was decanted. The solid was thoroughly washed with ethyl acetate, dried, and then reused as catalyst in the next run.

2.6 Metal leaching test of MOF-253·0.5CuI

To study the leaching of Cu during the reaction, after reaction, the mixture was hot filtrated under vacuum. The solid was washed with DMSO, and the liquid phase was analyzed by AAS.

References

(S1) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382.

(S2) H. L. Liu, B. L. Yin, Z. Q. Gao, Y. W. Li and H. F. Jiang, *Chem. Commun.*, 2012, **48**, 2033.

Table S1. Reusability of the MOF-253·0.5CuI catalyst[a]

Use	1st	2nd	3rd
Yield (%)[b]	99	96	97

[a] Reaction conditions: iodobenzene (0.4 mmol), phenol (0.6 mmol), Cs_2CO_3 (0.8 mmol), MOF-253·0.5CuI (20 mol%), DMSO (2 mL), 80 °C, 24 h. [b] Determined by GC-MS.

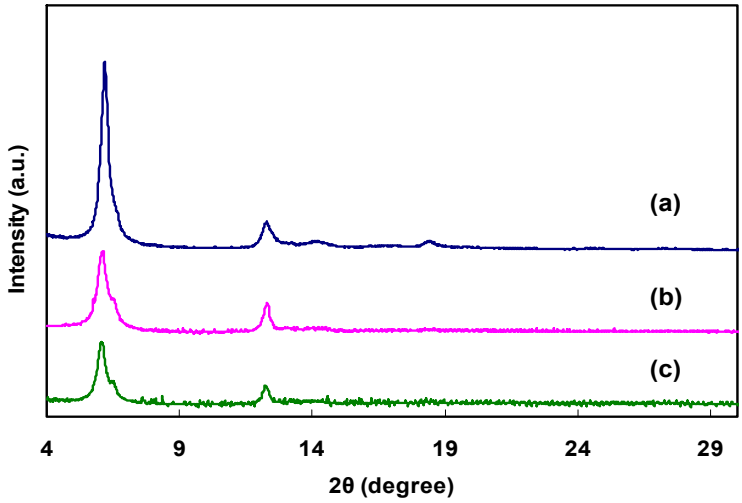
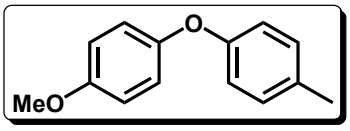


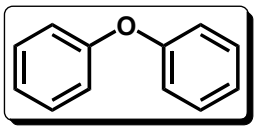
Figure S1. Powder XRD patterns for MOF-253 (a), fresh MOF-253·0.5CuI (b), and reused MOF-253·0.5CuI (c).

3. Spectra Data for the Product



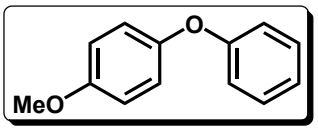
4-methyl-4'-methoxy-diphenylether (3a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 8.4, 2 H), 6.98-7.00 (m, 2 H), 6.89-6.91(m, 4 H), 3.82 (s, 3 H), 2.34 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 155.7, 150.8, 132.0, 130.1, 120.4, 117.8, 114.8, 55.6, 20.7. GC-MS (EI): found: 214(M^+), calcd for $C_{14}H_{14}O_2$(M^+): 214.26.



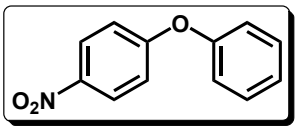
Diphenylether (3b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (t, *J* = 7.8, 4 H), 7.13 (t, *J* = 7.4, 2 H), 7.05 (d, *J* = 8.4, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 129.8, 123.3, 118.9. GC-MS (EI): found: 170 (M^+), calcd for $C_{12}H_{10}O$(M^+): 170.21.



3-methoxy-diphenylether (3c)

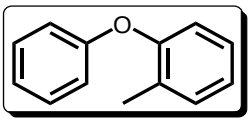
^{1}H NMR (400 MHz, $CDCl_3$): δ =7.31-7.26 (m, 2 H), 7.02 (t, *J* = 7.4, 1 H), 6.98-6.95 (m, 2 H), 6.94 (d, *J* = 8.8, 2 H), 6.87 (d, *J* = 8.6, 2 H), 3.78 (s, 3 H). ^{13}C NMR (100 MHz, CDCl3): δ = 158.6, 155.9, 150.2, 129.7, 122.5, 120.9, 117.6, 114.9, 55.7. GC-MS (EI): found: 200(M^+), calcd for $C_{13}H_{12}O_2$(M^+): 200.23.



4-nitro-diphenylether (3d)

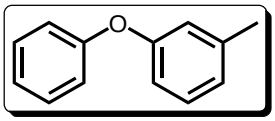
^{1}H NMR (400 MHz, $CDCl_3$): δ =8.19 (d, *J* = 8.0, 2 H), 7.43 (t, *J* = 8.0, 2 H), 7.26 (t, *J* = 7.4, 1 H), 7.09 (d, *J* = 8.0, 2 H), 7.01 (d, *J* = 8.0, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 154.7, 142.7, 130.3, 125.9, 125.4, 120.5, 117.1

GC-MS (EI): found: 215(M^+), calcd for $C_{12}H_9NO_3$ (M^+): 215.2.



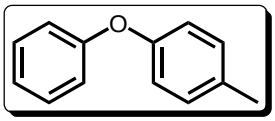
2-Methyl-diphenylether (3e)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (t, *J* =7.4, 2 H), 7.23 (d, *J* =7.6, 1 H), 7.15 (t, *J* = 7.6, 1 H), 7.07-7.00 (m, 2 H), 6.89 (d, *J* = 7.4, 3 H), 2.23 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 154.5, 131.5, 130.1, 129.7, 127.2, 124.1, 122.4, 119.9, 117.3, 16.2. GC-MS (EI): found: 184(M^+), calcd for $C_{13}H_{12}O$ (M^+): 184.23.



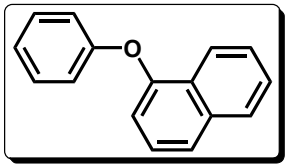
3-Methyl-diphenylether (3f)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.29(m, 2H), 7.19(t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.00-6.98 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.81(t, *J* = 8.0Hz, 2H), 2.31(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 157.3, 140.0, 129.8, 129.5, 124.2, 123.2, 119.7, 118.9, 116.0, 21.5. GC-MS (EI): found: 184(M^+), calcd for $C_{13}H_{12}O$ (M^+): 184.23.



4-Methyl-diphenylether (3g)

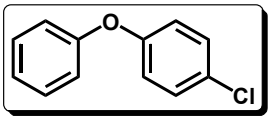
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39(t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 154.8, 132.9, 130.3, 129.7, 122.8, 119.2,118.4, 20.8. GC-MS (EI): found: 184(M+), calcd for $C_{13}H_{12}O$ (M+): 184.23.



1-Naphthyl phenylether (3h)

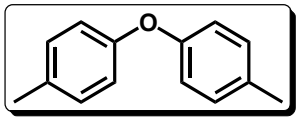
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* =6.8, 1 H), 7.93 (d, *J*=7.8, 1 H), 7.68 (d, *J* = 8.2, 1 H), 7.61-7.51 (m, 2 H), 7.47-7.36 (m, 3 H), 7.18 (d, *J* = 7.4, 1 H), 7.12

(d, *J* = 8.0, 2 H), 7.02 (d, *J* = 7.8, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 153.1, 135.0, 129.9, 127.9, 126.9, 126.6, 126.0, 125.9, 123.4, 123.2, 122.2, 118.6, 113.6. GC-MS (EI): found: 220 (M^+), calcd for $C_{16}H_{12}O$ (M^+): 220.27.



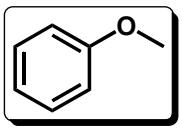
4-Chloro-diphenylether (3i)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (t, *J* = 7.8, 2 H), 7.31 (d, *J* = 8.6, 2 H), 7.15 (t, *J* =7.4, 1 H), 7.03 (d, *J* =8.6, 2 H), 6.97 (d, *J* =8.6, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 156.0, 129.9, 129.8, 128.2, 123.7, 120.1, 119.0. GC-MS (EI): found: 204 (M^+), calcd for $C_{12}H_9OCl$ (M^+): 204.65.



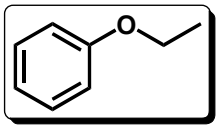
4, 4'-Dimethyl-diphenylether (3j)

^{1}H NMR (400 MHz, CDCl3): δ = 7.20 (d, *J* = 8.2, 4 H), 6.98 (d, *J* = 8.6, 4 H), 2.41 (s, 6 H). ^{13}C NMR (100 MHz, CDCl3): δ = 155.4, 132.5, 130.2, 118.7, 20.7. GC-MS (EI): found: 198(M+), calcd for $C_{14}H_{14}O$ (M+): 198.26.



Methoxybenzene (3k)

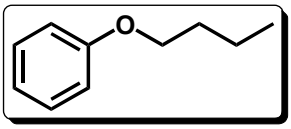
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (t, *J* = 8.6, 2 H), 7.19-7.12 (m, 3 H), 3.95 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 129.7, 120.8, 114.1, 55.1. GC-MS (EI): found: 108(M^+), calcd for C_7H_8O (M^+): 108.14.



anisole (3l)

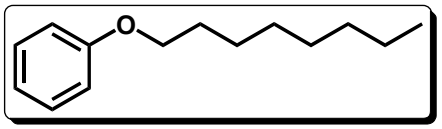
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 8.4, 2H), 6.79 (t, *J* = 8.6, 3H),

3.89-3.87 (m, 2H). 1.29 (t, *J* = 8.0, 3H). δ = 159.1, 129.5, 120.6, 114.6, 63.3, 14.9. GC-MS (EI): found: 122(M^+), calcd for $C_8H_{10}O$ (M^+): 122.16.



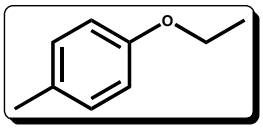
n-butyl phenyl ether (3m)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.23 (m, 2 H), 6.94-6.88 (m, 3 H), 3.95 (t, *J* = 8.6, 2 H), 1.81-1.71 (m, 2 H), 1.54-1.44 (m, 2 H), 0.97 (t, *J* = 7.4, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2 129.4, 120.5 114.5, 67.6, 31.4, 19.3, 13.9. GC-MS (EI): found: 150 (M^+), calcd for $C_{10}H_{14}O$ (M^+): 150.22.



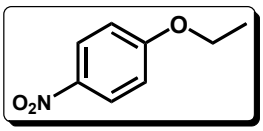
n-octyl phenyl ether (3n)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.25 (m, 2 H), 6.94 -6.88 (m, 3 H), 3.95 (t, *J* = 7.4, 2 H), 1.81-1.74 (m, 2 H), 1.47-1.26 (m, 10 H), 0.89 (t, *J* = 8.0, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =159.2, 129.4, 120.5, 114.5, 67.9, 31.9, 29.4, 29.3, 29.3, 26.1, 22.7, 14.1. GC-MS (EI): found: 206(M+), calcd for $C_{14}H_{22}O$ (M+): 206.32.



4-methyl phenetole (3o)

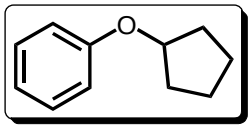
^{1}H NMR (400 MHz, $CDCl_3$): δ =7.08 (d, *J* = 8.4, 2 H), 6.81 (d, *J* = 8.6, 2 H), 4.04-3.99 (m, 2 H), 2.29 (s, 3 H), 1.41 (t, *J* = 8.0, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 130.0, 129.9, 114.3, 63.4, 20.5, 14.9. GC-MS (EI): found: 136 (M^+), calcd for $C_9H_{12}O$ (M^+): 136.19.



4-nitrophenetole (3p)

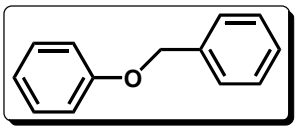
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21-8.18 (m, 2 H), 6.96-6.92 (m, 2 H),

4.13 (m, *J* = 7.0, 2 H), 1.47 (t, *J* = 7.0, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 141.4, 125.9, 114.4, 64.4, 14.6. GC-MS (EI): found: 167 (M+), calcd for $C_8H_9NO_3$ (M^+):167.06.



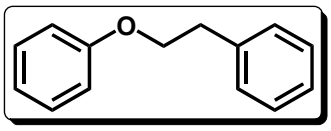
1-(cyclopentyloxy)benzene (3q)

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.31-7.27 (m, 2 H), 6.94 (t, *J* = 8.0, 3 H), 4.29-4.24 (m, 1 H), 2.05-2.00(m, 2 H), 1.85-1.82(m, 2 H), 1.54-1.44 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 129.4, 120.5, 116.1, 75.4, 31.9, 23.8. GC-MS (EI): found: 162(M+), calcd for $C_{11}H_{14}O$ (M^+): 162.23.



1-(Phenoxymethyl)benzene (3r)

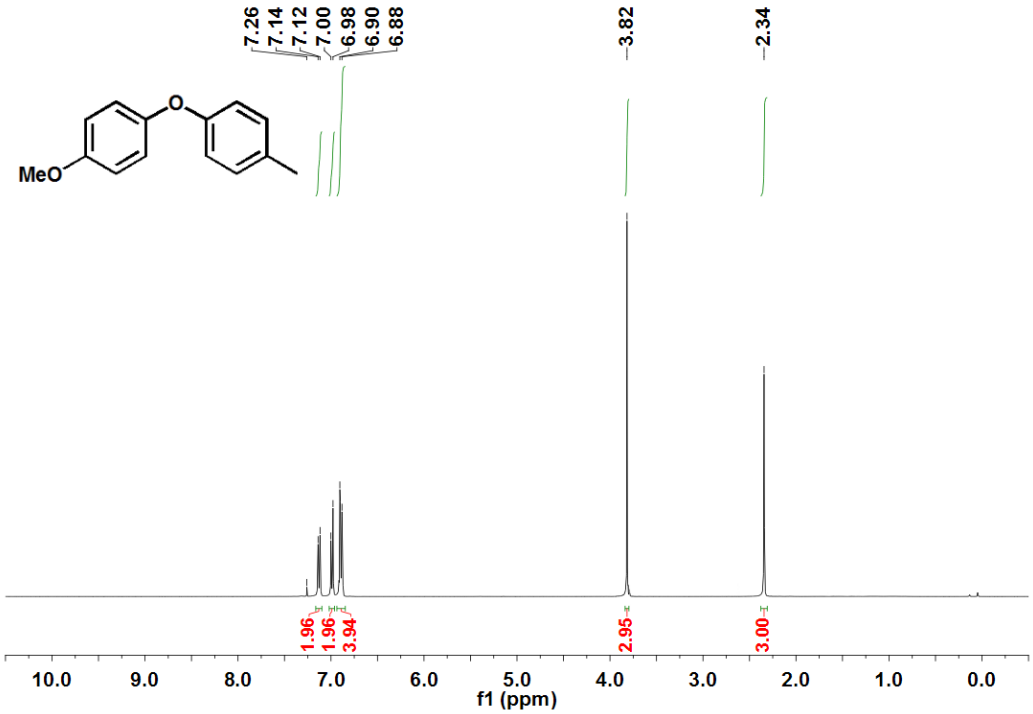
^{1}H NMR (400 MHz, $CDCl_3$) δ =7.47 (d, *J*=7.2, 2 H), 7.41-7.38 (m, 2 H), 7.36 (d, *J*=7.2, 1 H), 7.32-7.29 (m, 2 H), 7.01-6.96 (m, 3 H), 5.08 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 137.1, 129.5, 128.6, 128.0, 127.5, 121.0, 114.9, 69.9. GC-MS (EI): found: 184(M+), calcd for $C_{13}H_{12}O$ (M^+): 184.23.

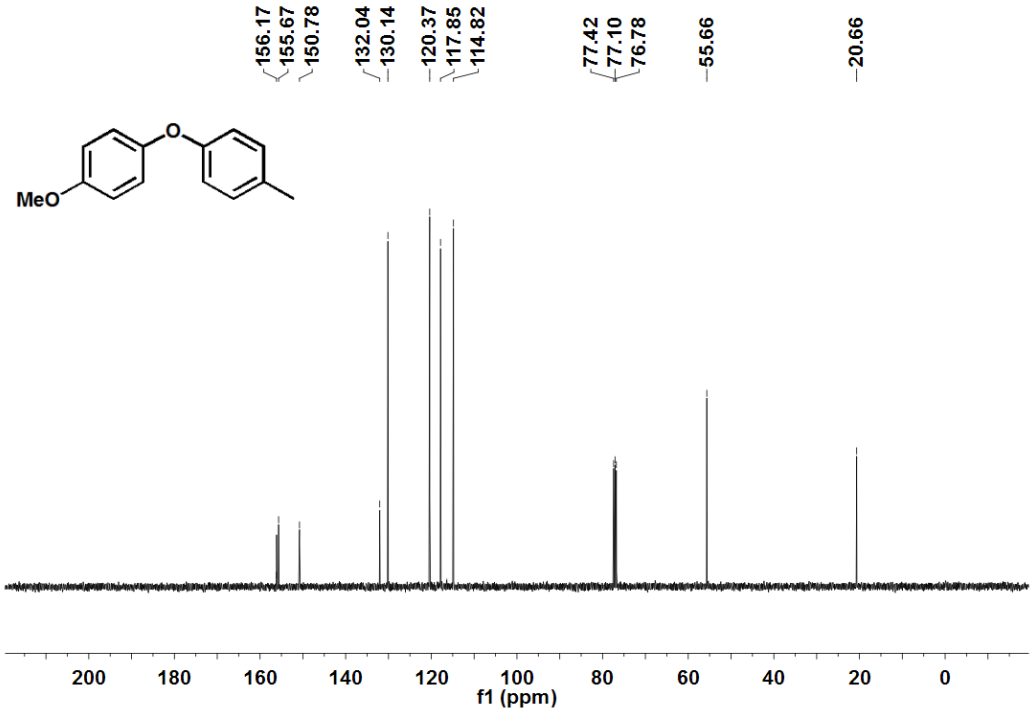


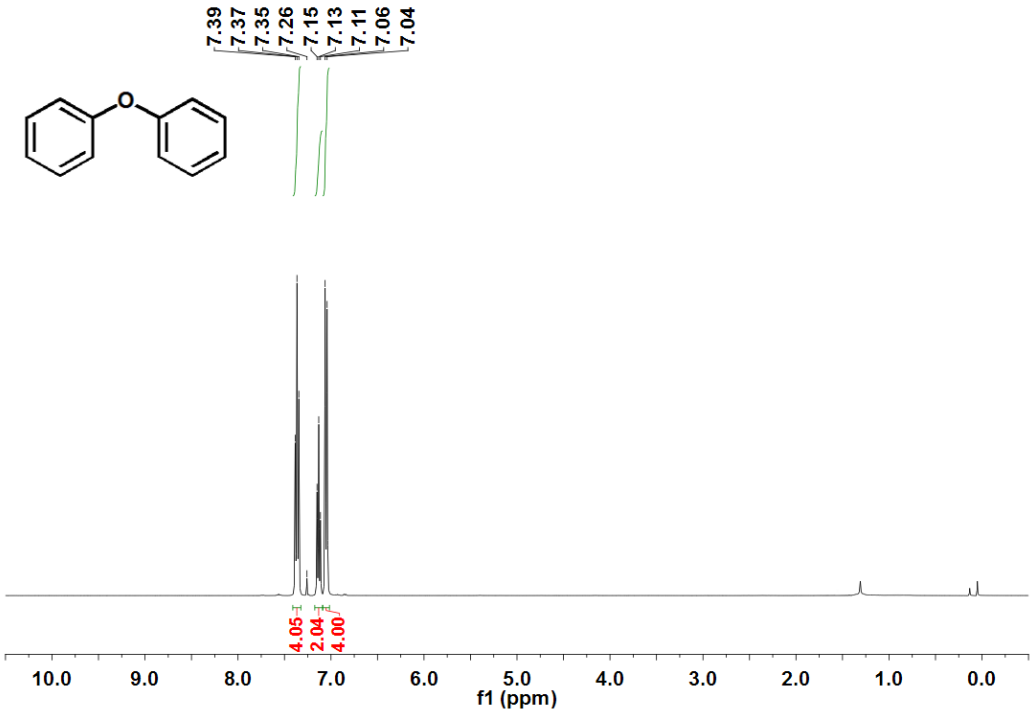
1-(Phenoxyethyl)benzene (3s)

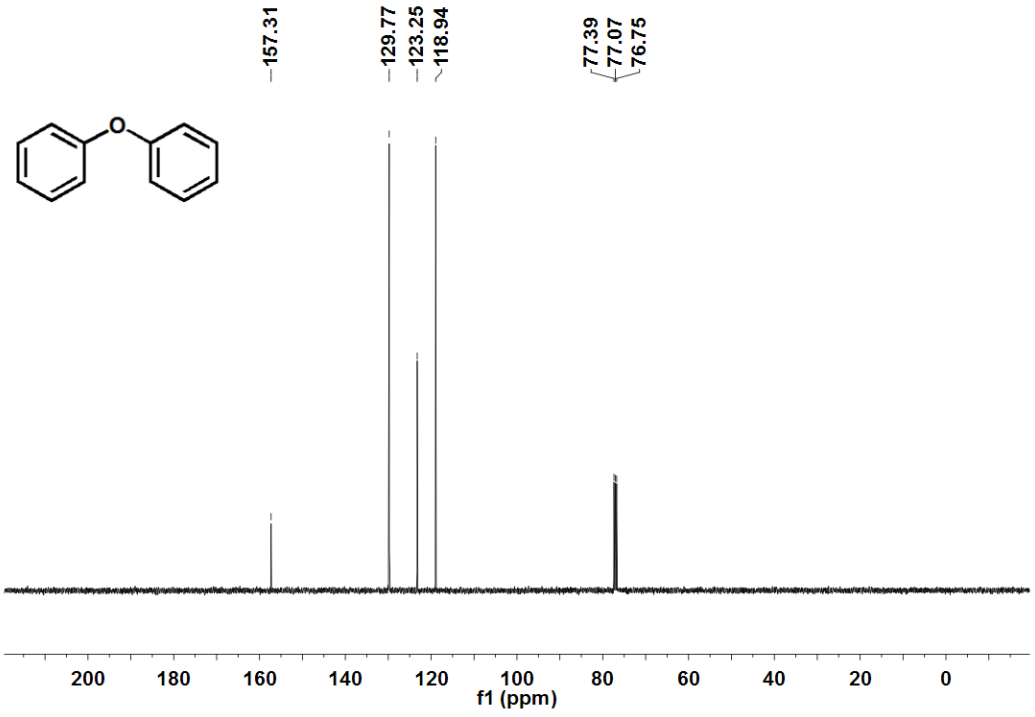
^{1}H NMR (400 MHz, $CDCl_3$): δ =7.26-7.16 (m, 7H), 6.87-6.81 (m, 3H), 4.10 (t, *J* =7.6, 2H), 3.02(t, *J* = 8.0, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 137.2, 128.4, 128.0, 127.5, 125.5, 119.7, 113.5, 67.5, 34.8. GC-MS (EI): found: 198 (M^+), calcd for $C_{14}H_{14}O$ (M^+): 198.26.

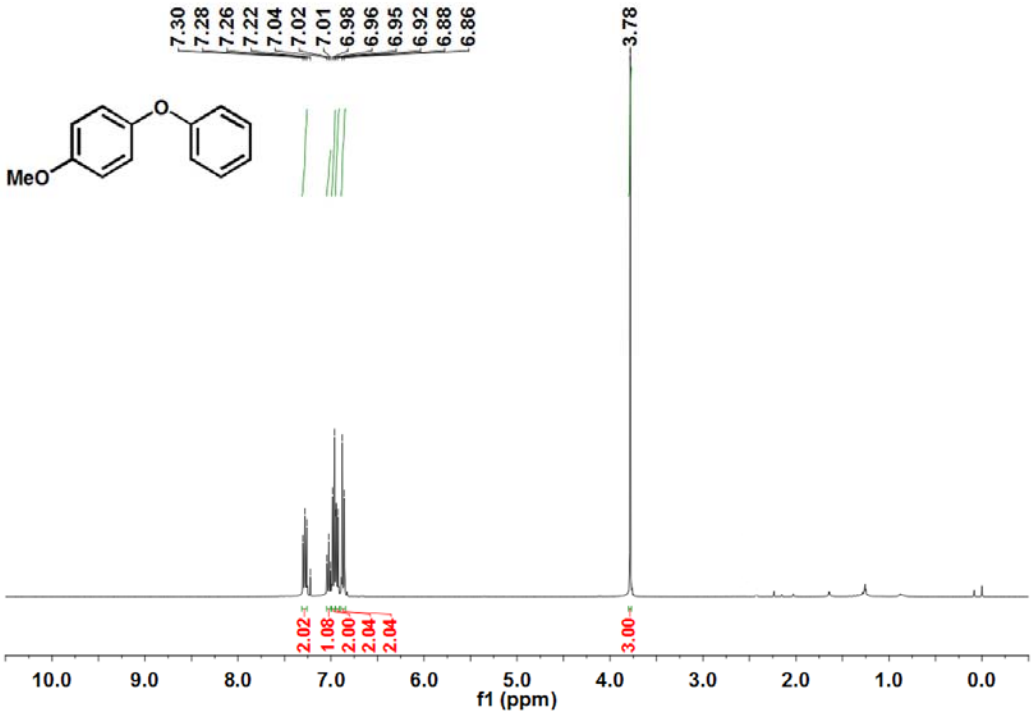
4. ^{1}H NMR and ^{13}C NMR Spectra of products

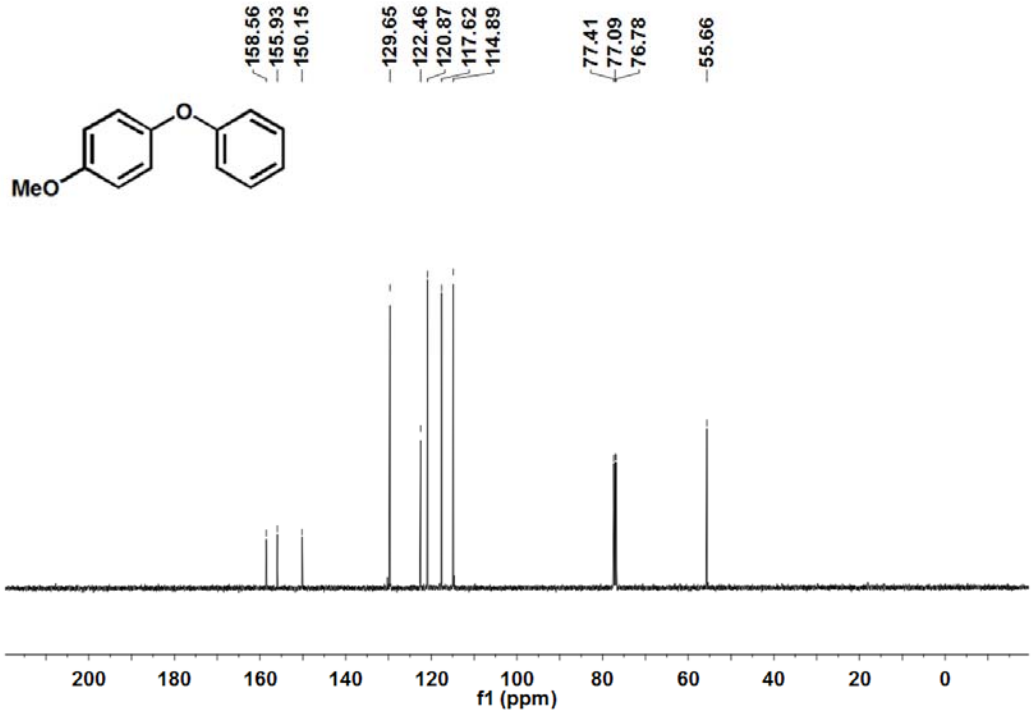


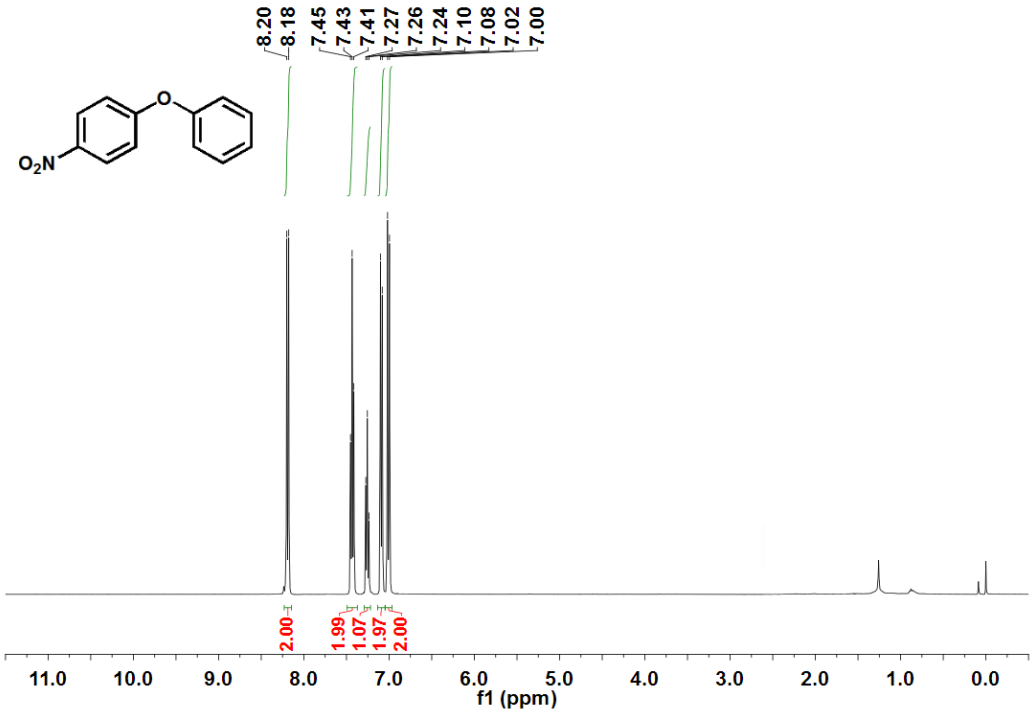


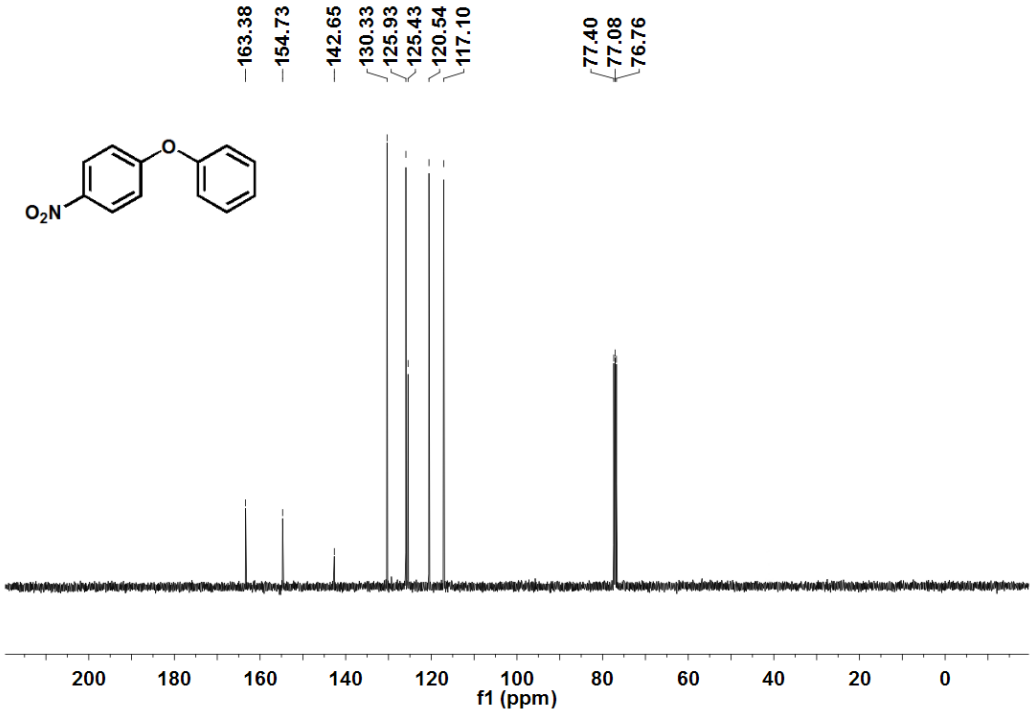


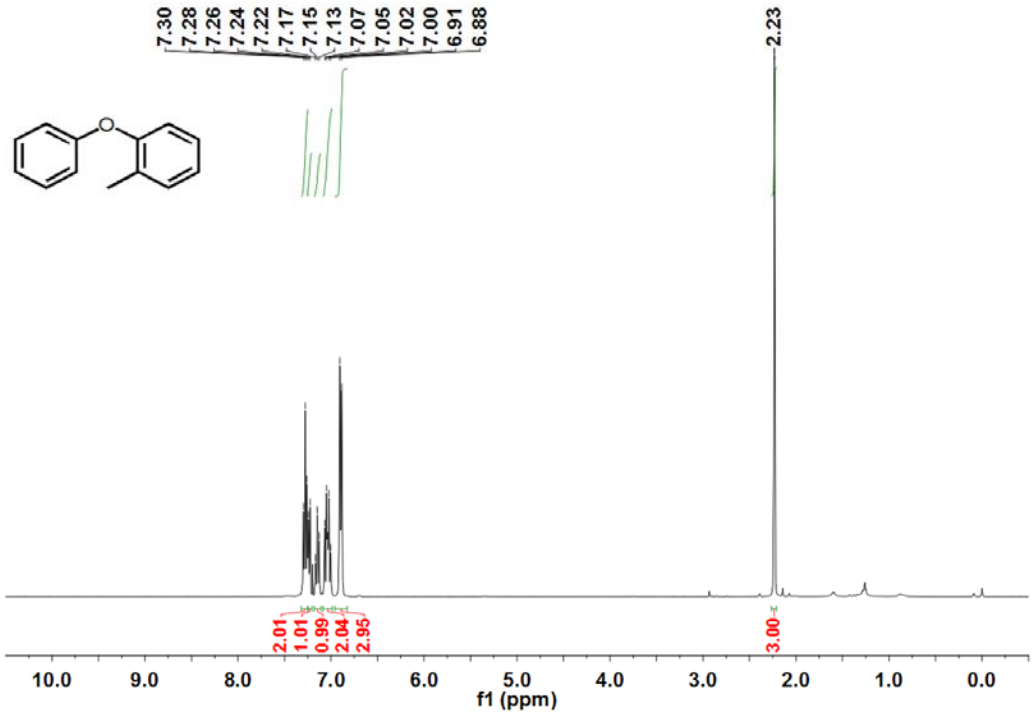


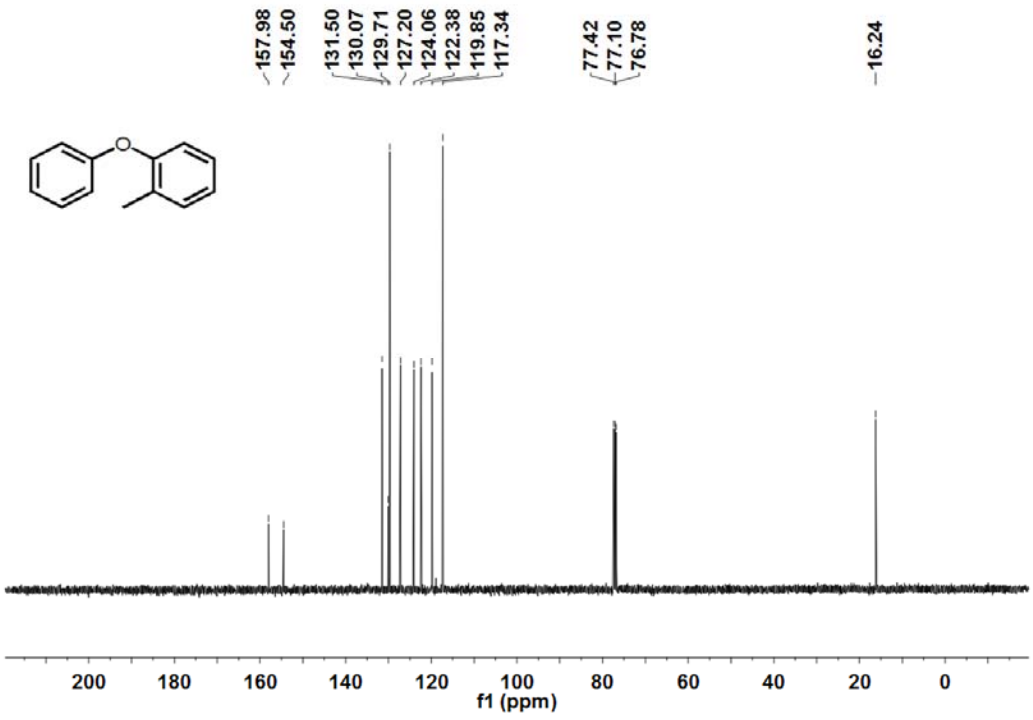


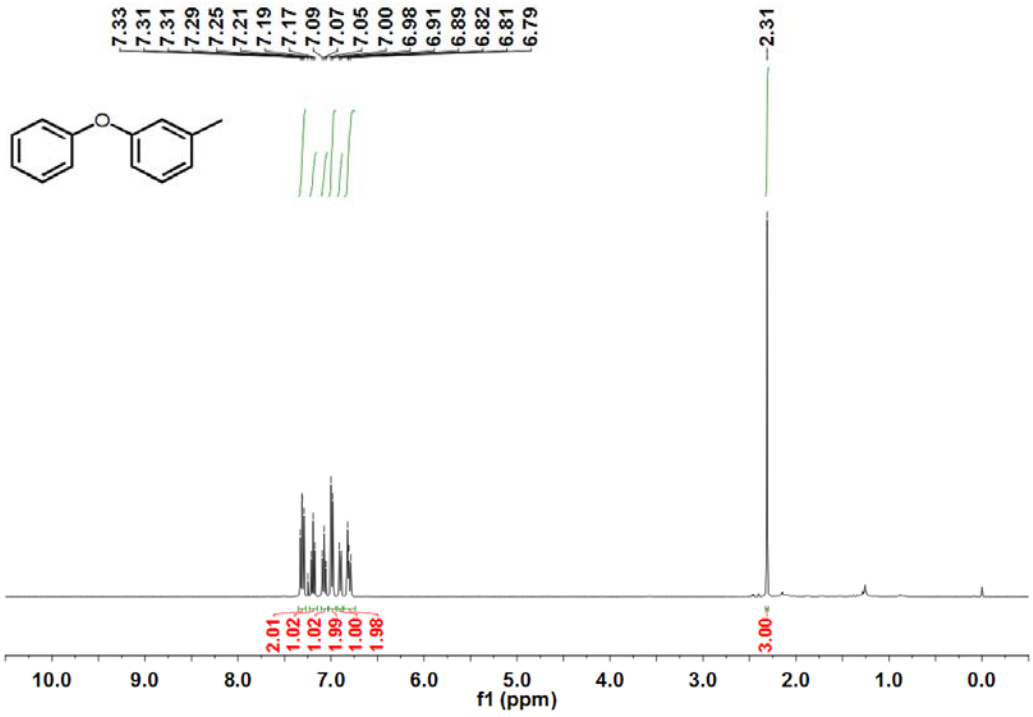


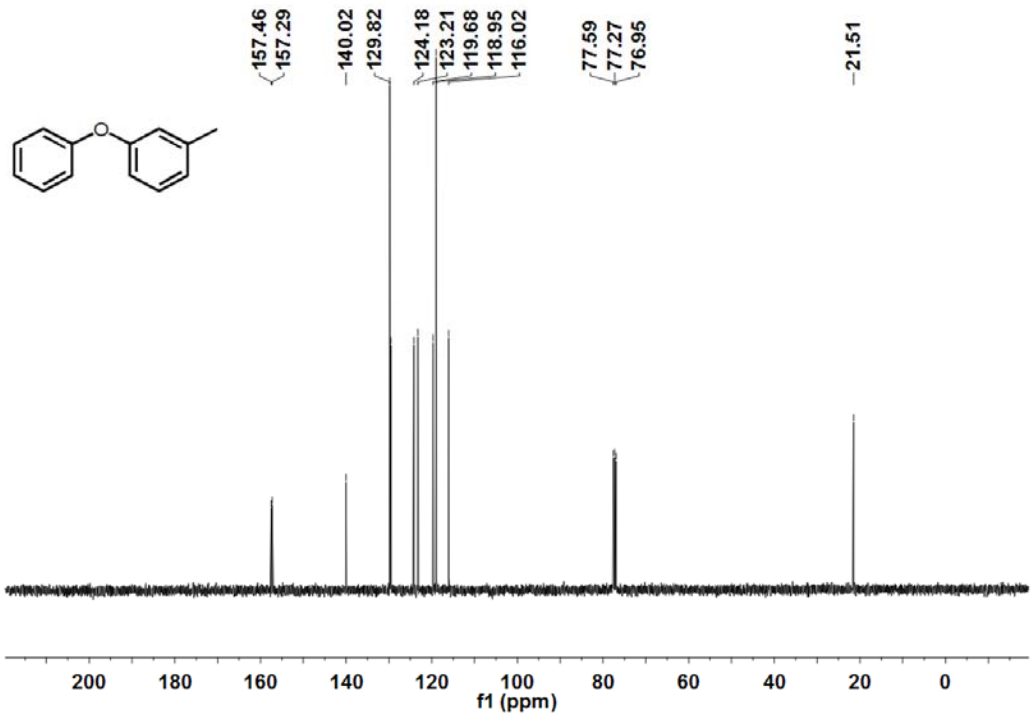


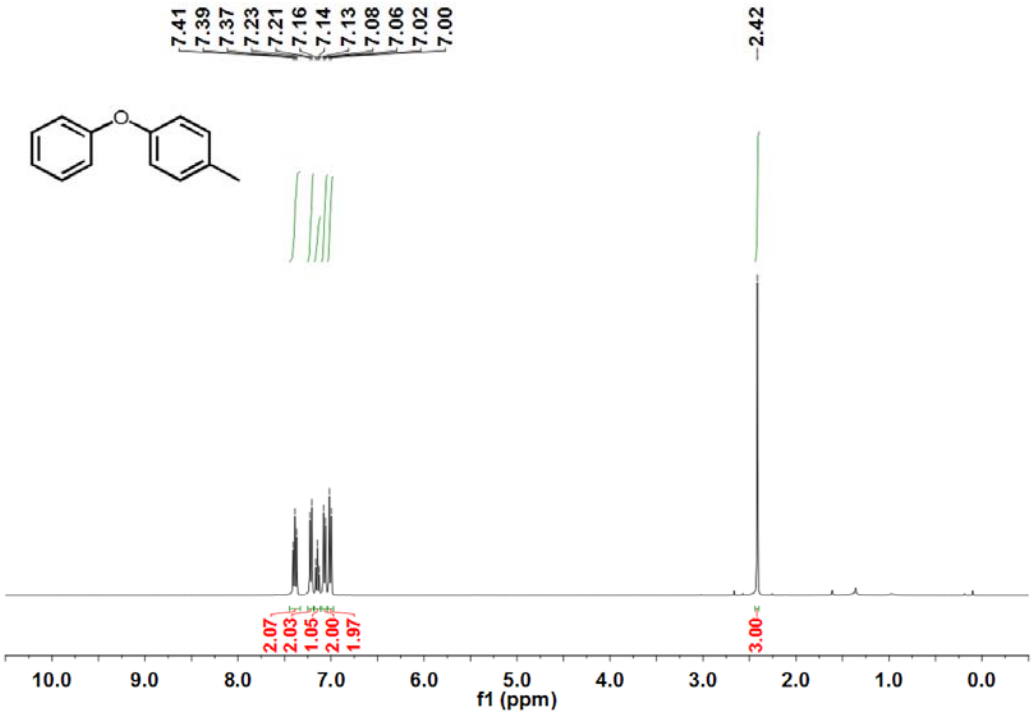


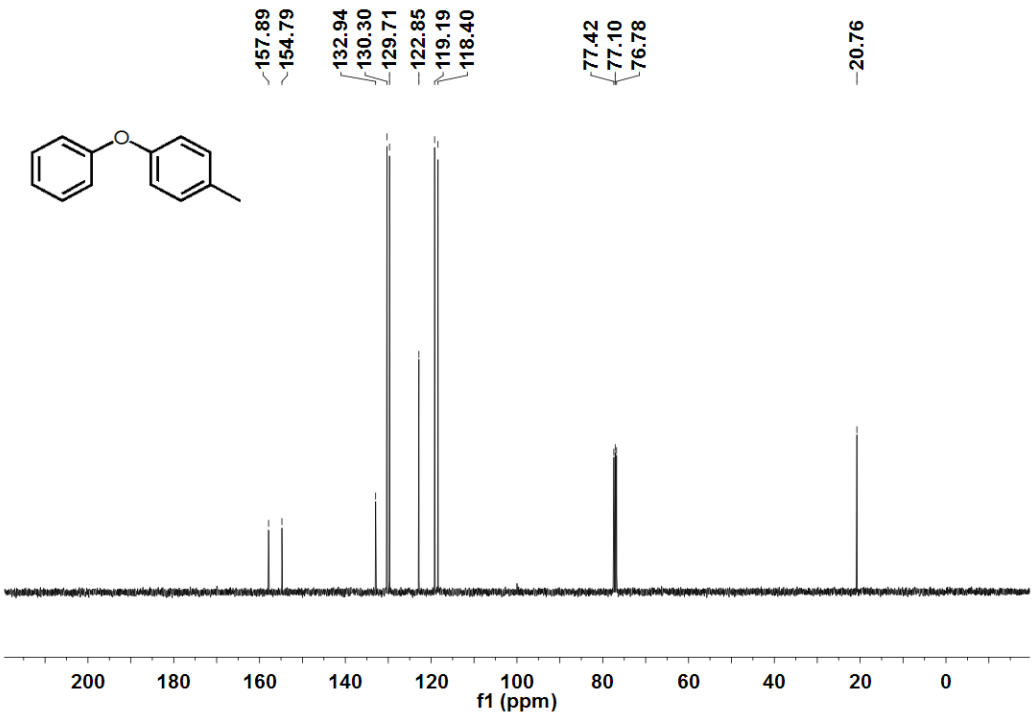


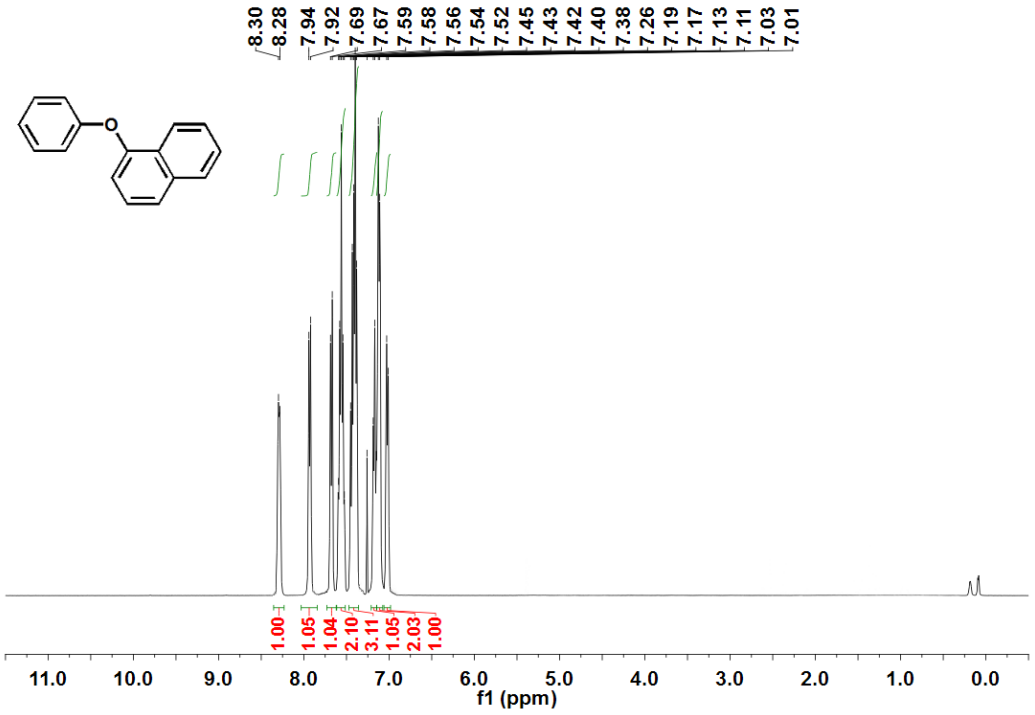


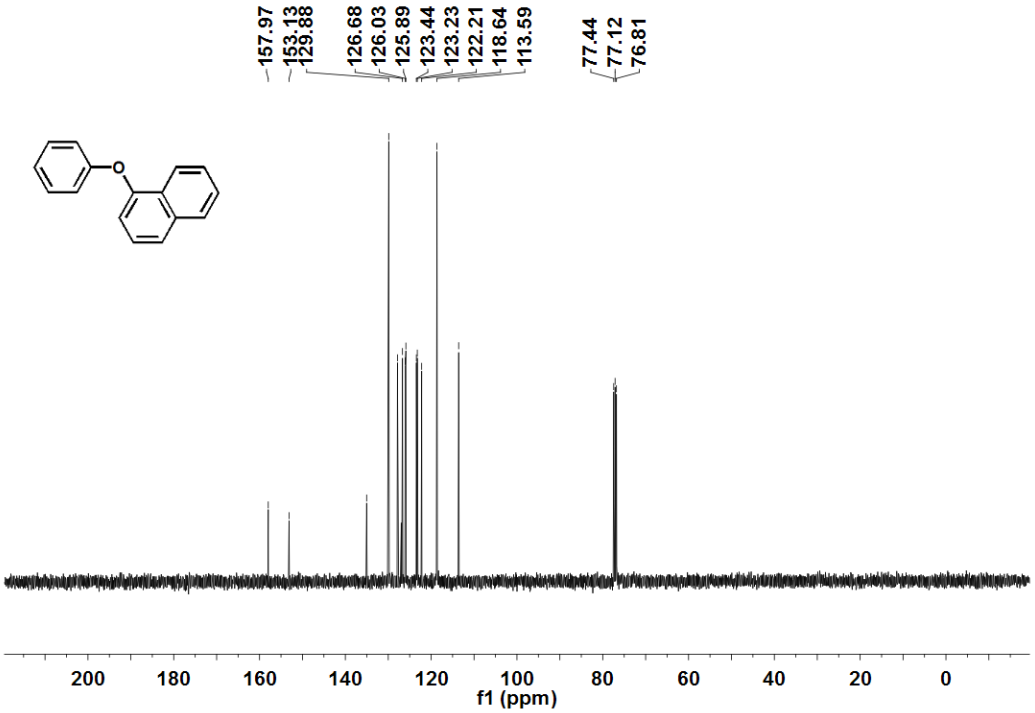


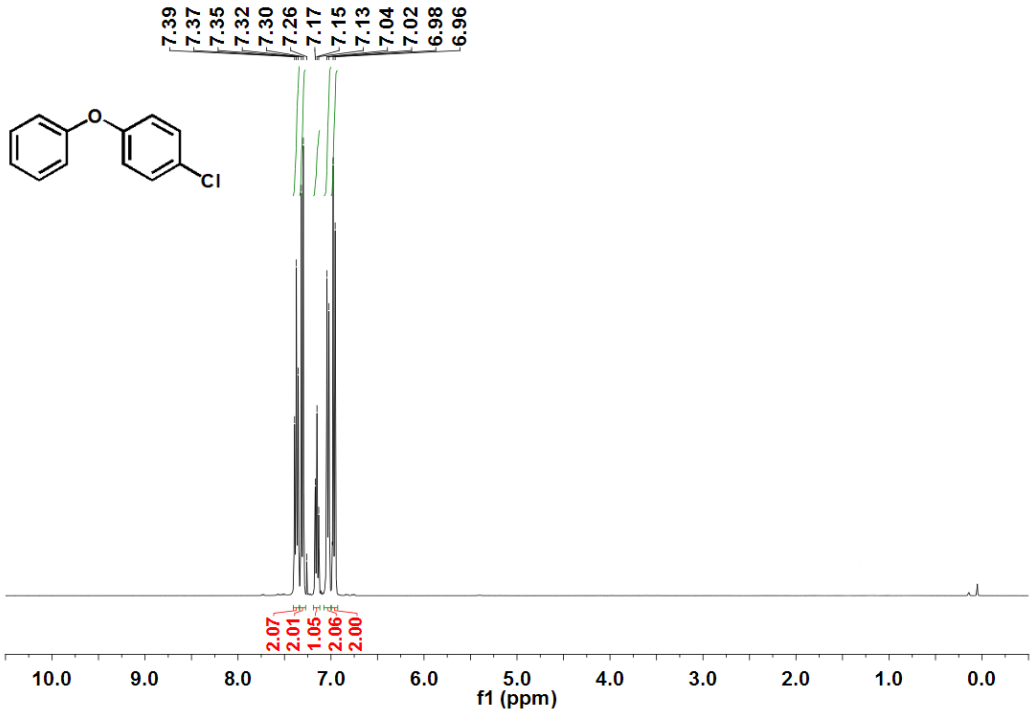


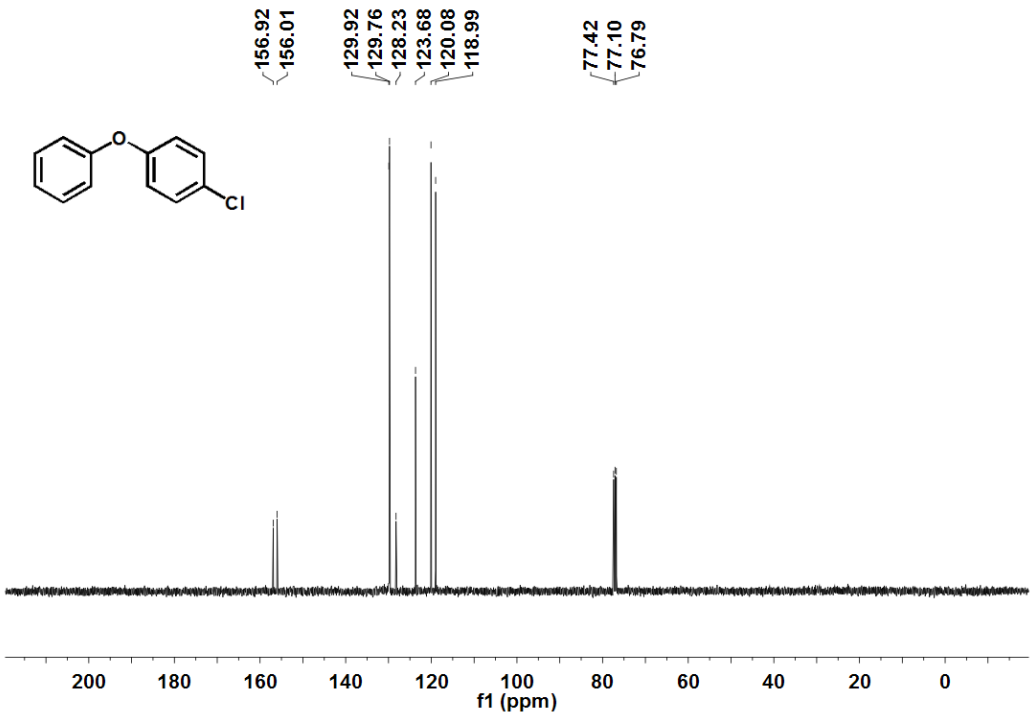

7.41
7.39
7.37
7.23
7.21
7.16
7.14
7.13
7.08
7.06
7.02
7.00
2.42
2.07
2.03
1.05
2.00
1.97
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

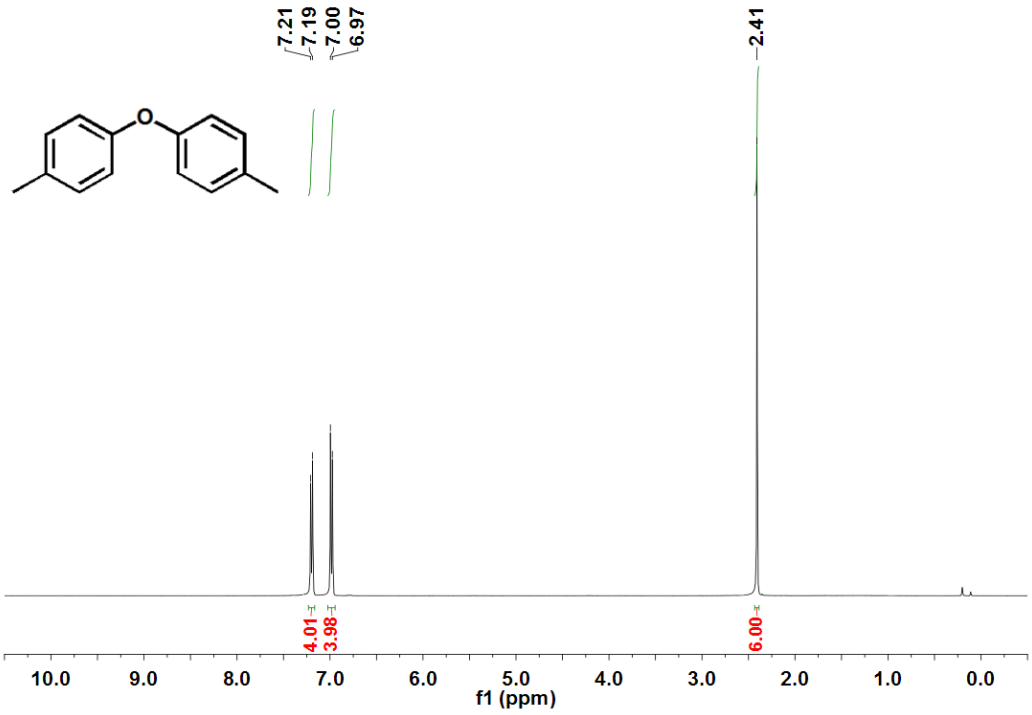

157.89
154.79
132.94
130.30
129.71
122.85
119.19
118.40
77.42
77.10
76.78
20.76
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

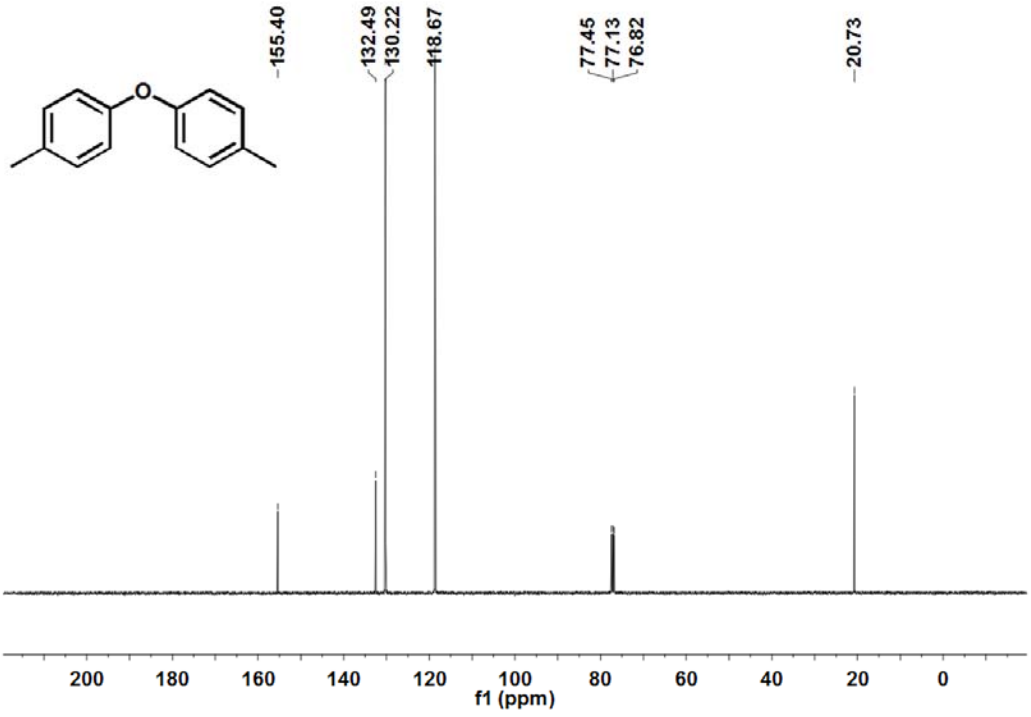


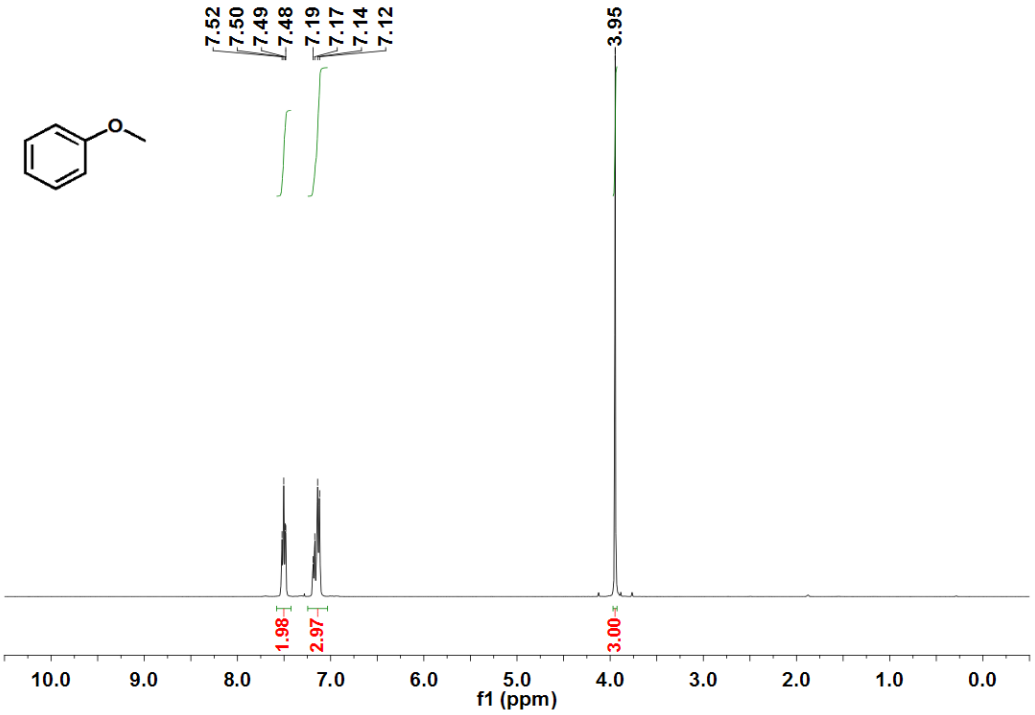


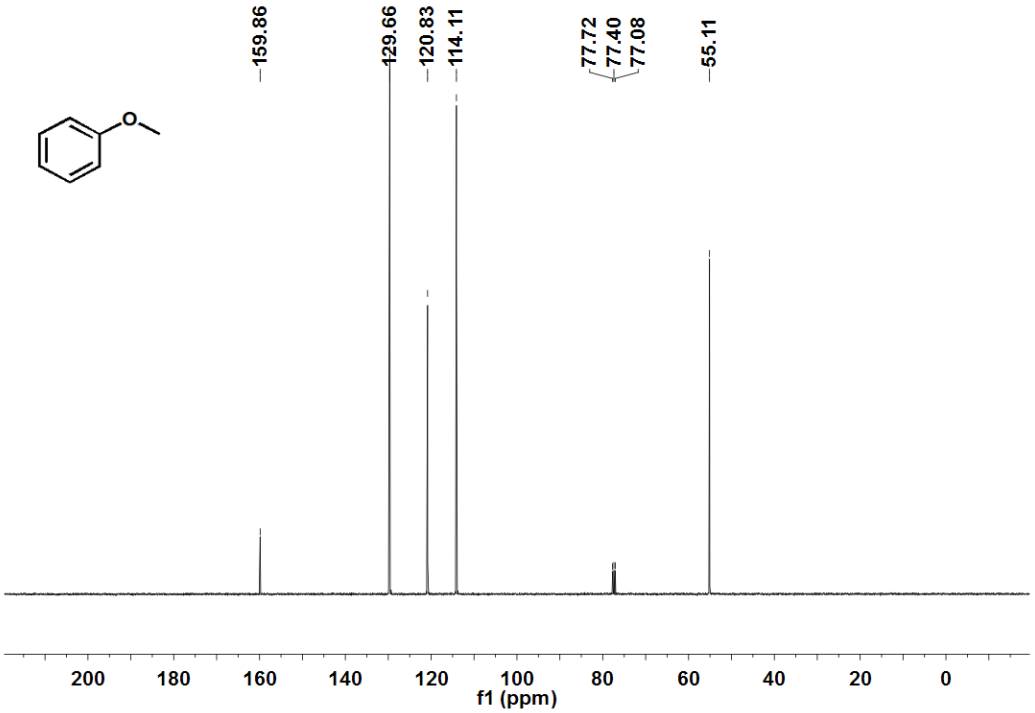


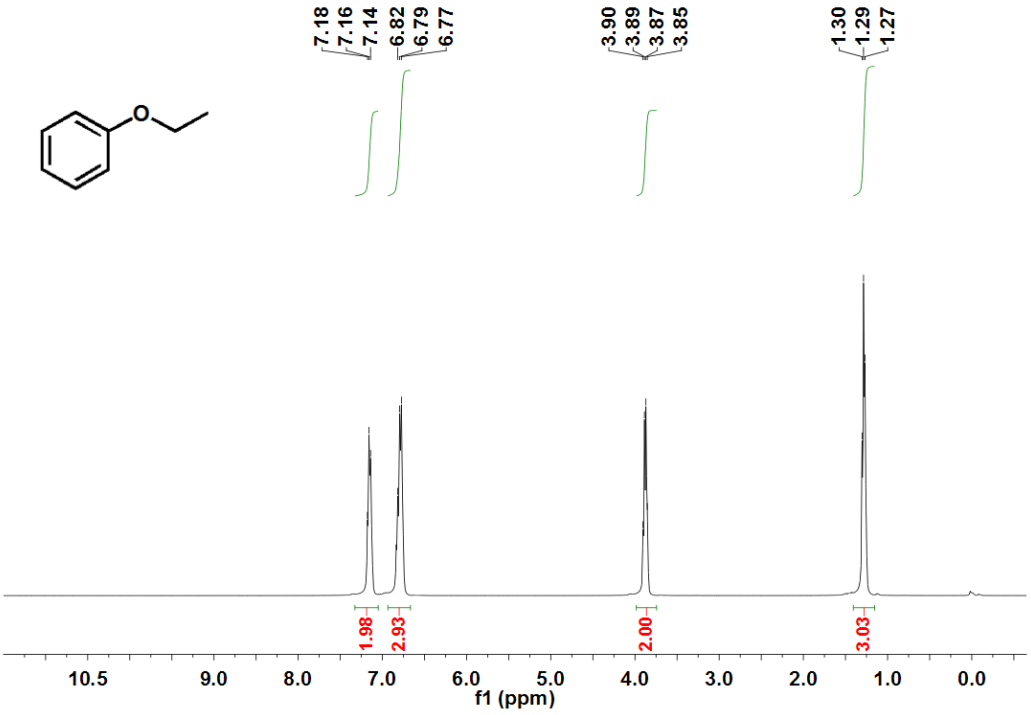


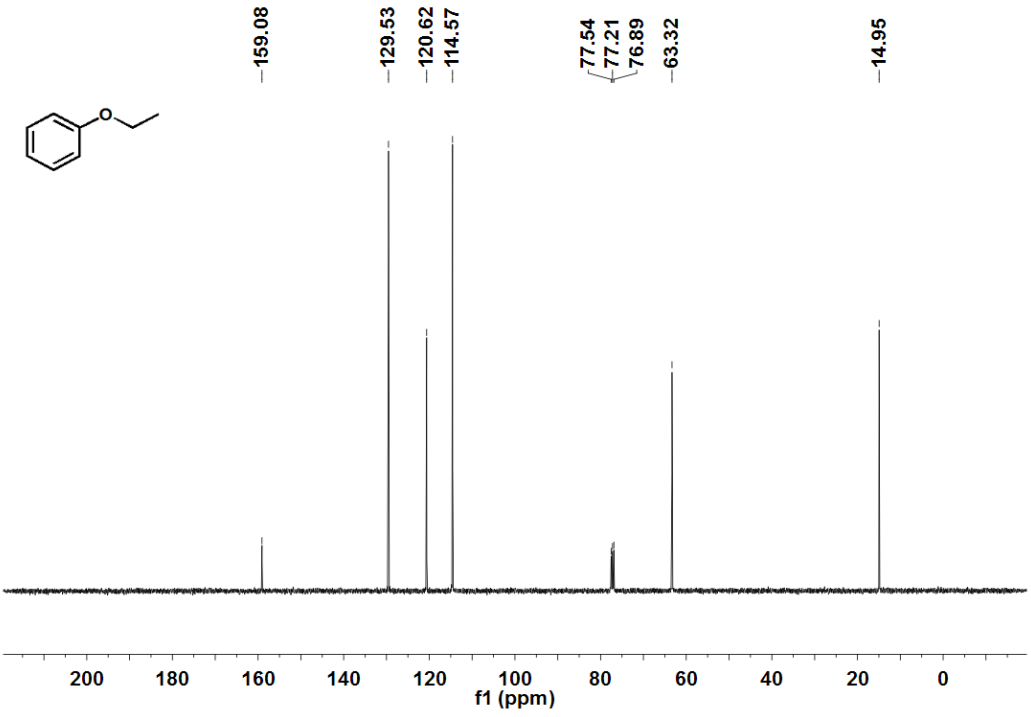


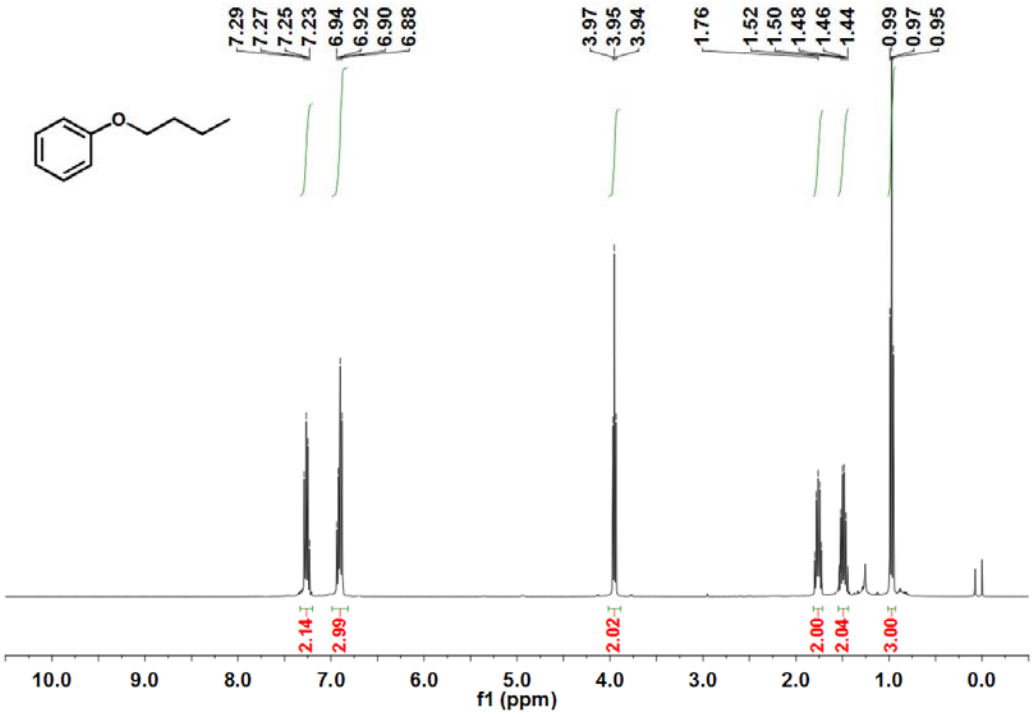


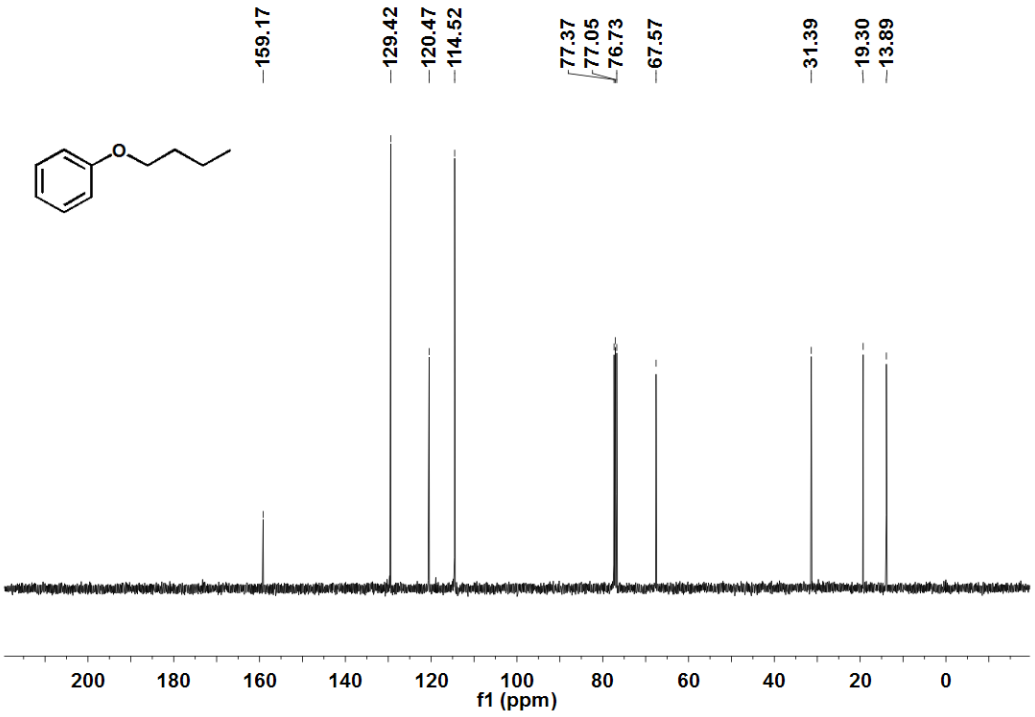


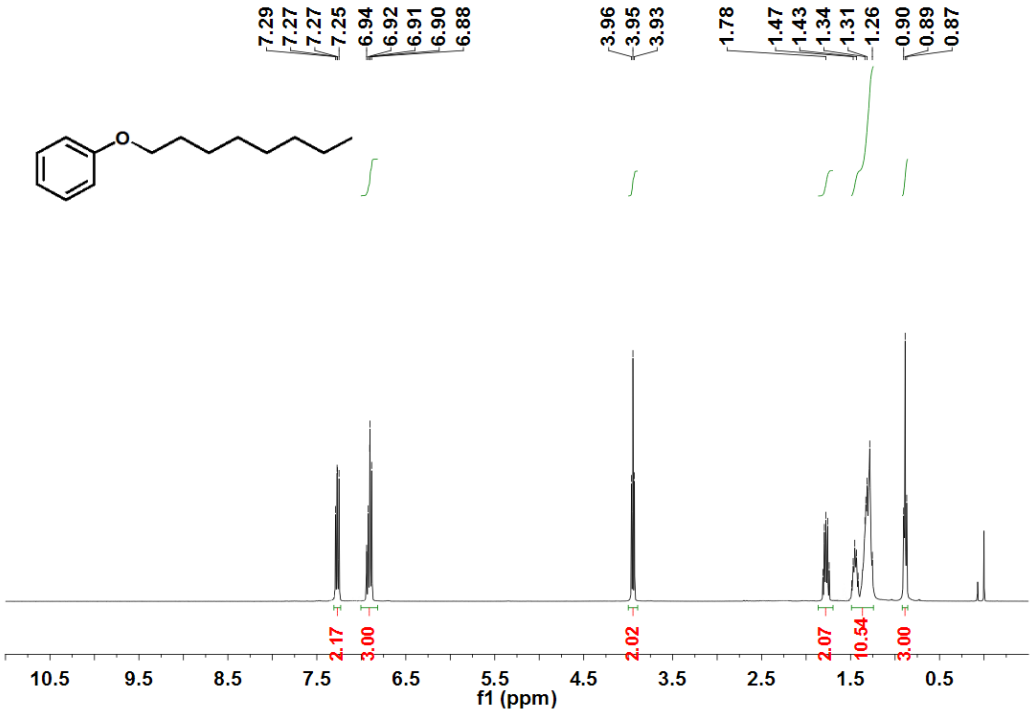


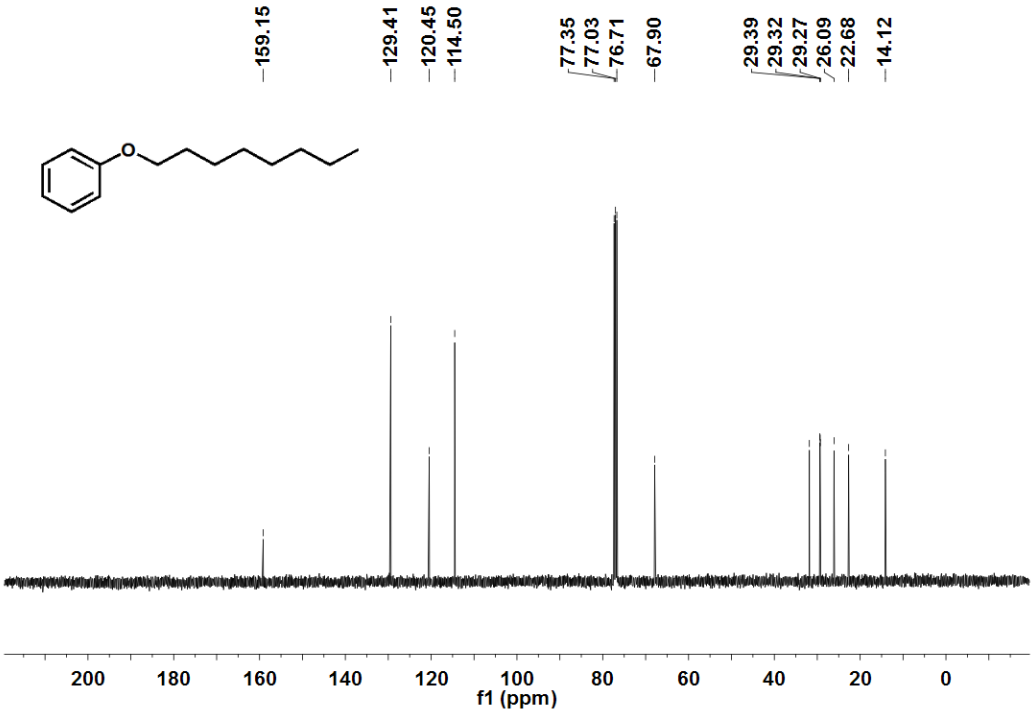









7.29
7.27
7.27
7.25
6.94
6.92
6.91
6.90
6.88
3.96
3.95
3.93
1.78
1.47
1.43
1.34
1.31
1.26
0.90
0.89
0.87
2.17
3.00
2.02
2.07
10.54
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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129.41
120.45
114.50
77.35
77.03
76.71
67.90
29.39
29.32
29.27
26.09
22.68
14.12
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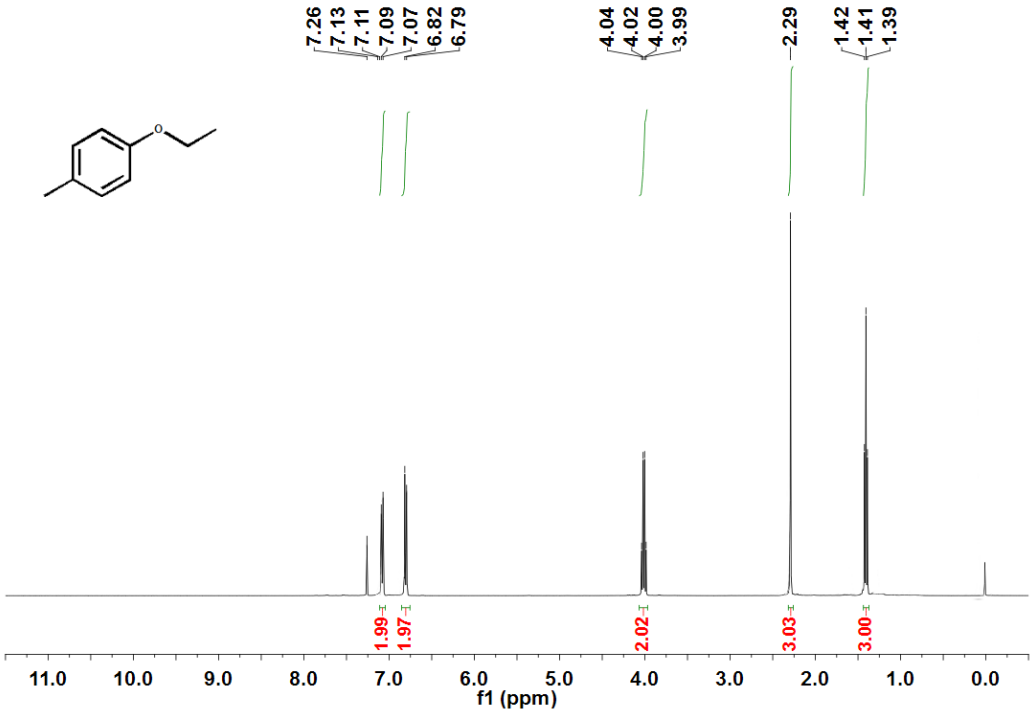
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.26
7.13
7.11
7.09
7.07
6.82
6.79
4.04
4.02
4.00
3.99
2.29
1.42
1.41
1.39
1.99
1.97
2.02
3.03
3.00
11.0
10.0
9.0
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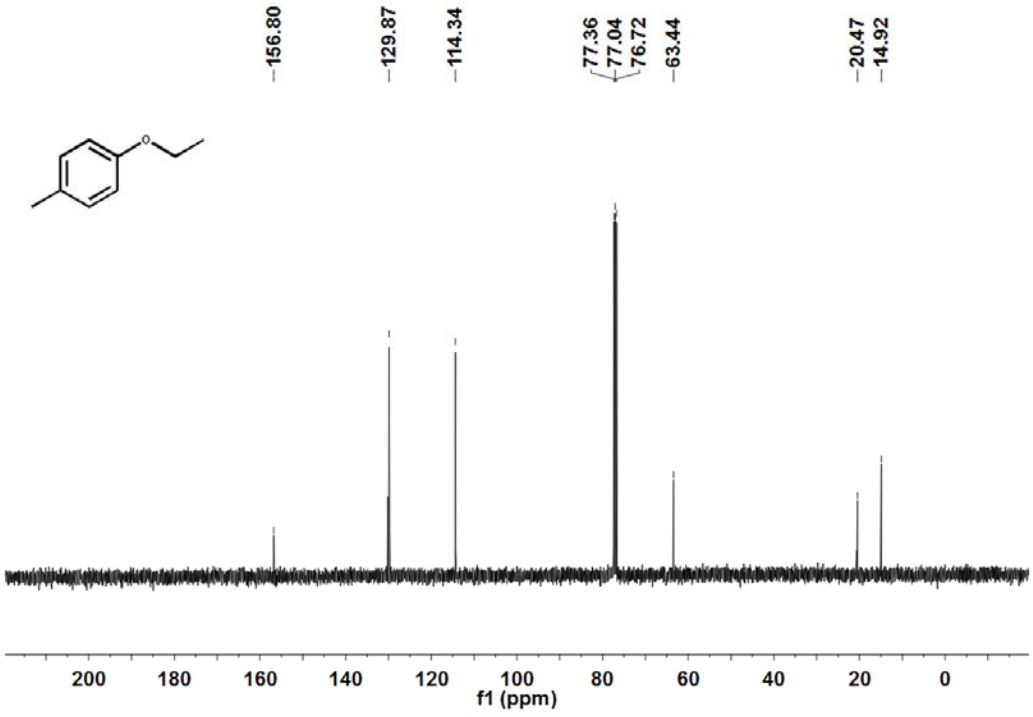
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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114.34
77.36
77.04
76.72
63.44
20.47
14.92
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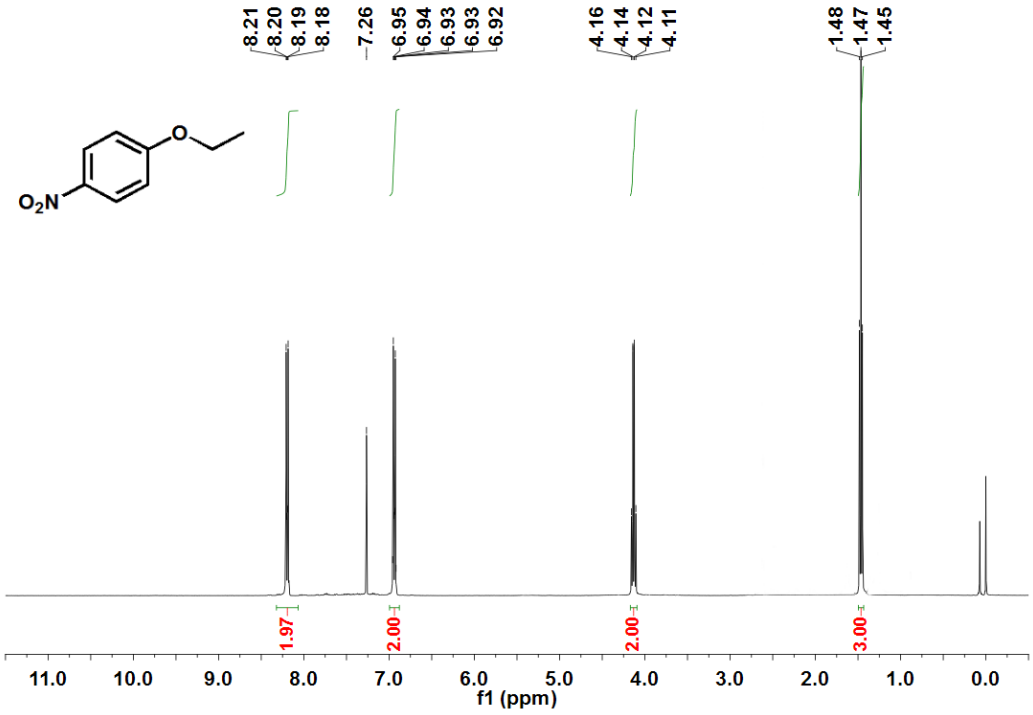
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.21
8.20
8.19
8.18
7.26
6.95
6.94
6.93
6.93
6.92
4.16
4.14
4.12
4.11
1.48
1.47
1.45
O2N
O
1.97
2.00
2.00
3.00
11.0
10.0
9.0
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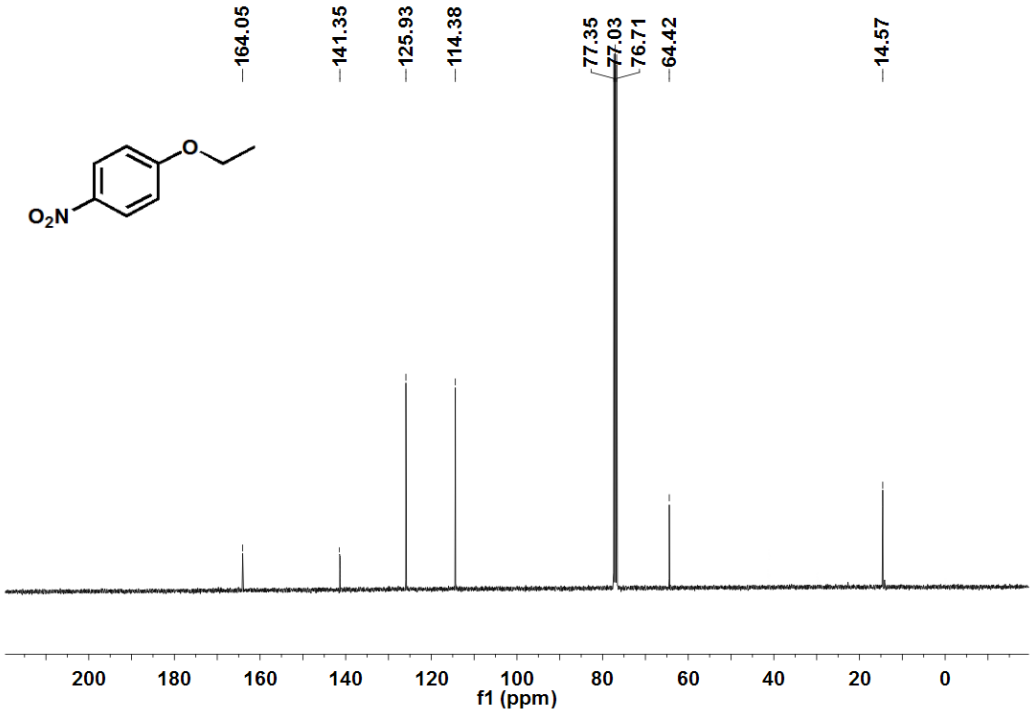
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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114.38
77.35
77.03
76.71
64.42
14.57
O2N
O
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180
160
140
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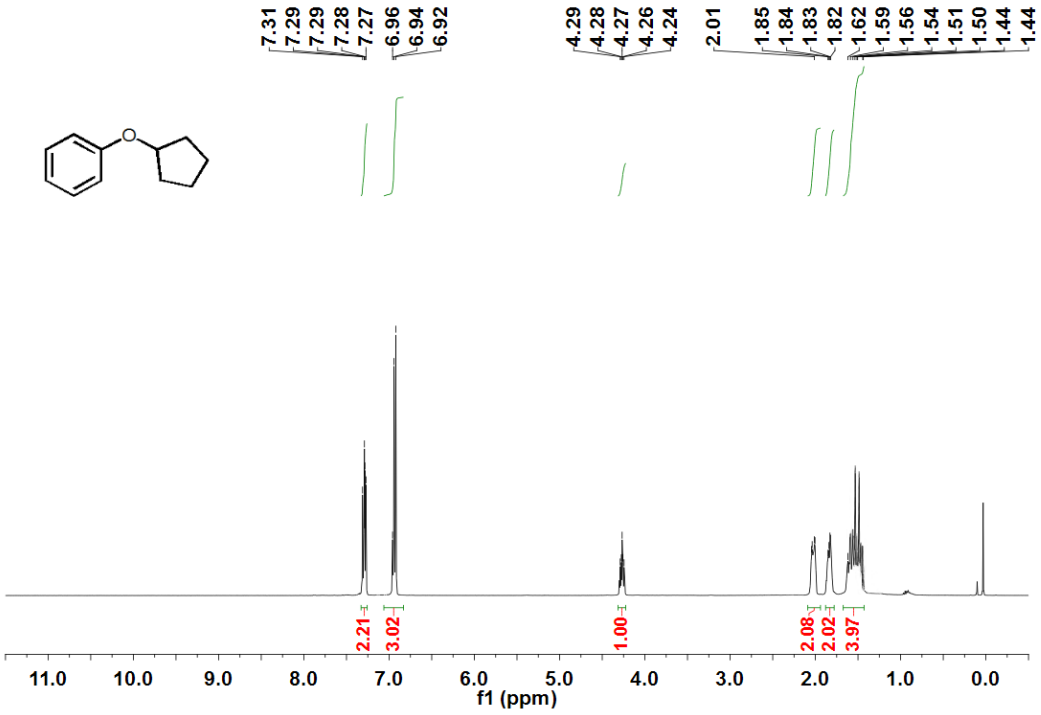
100
80
60
40
20
0
f1 (ppm)


7.31
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7.29
7.28
7.27
6.96
6.94
6.92
4.29
4.28
4.27
4.26
4.24
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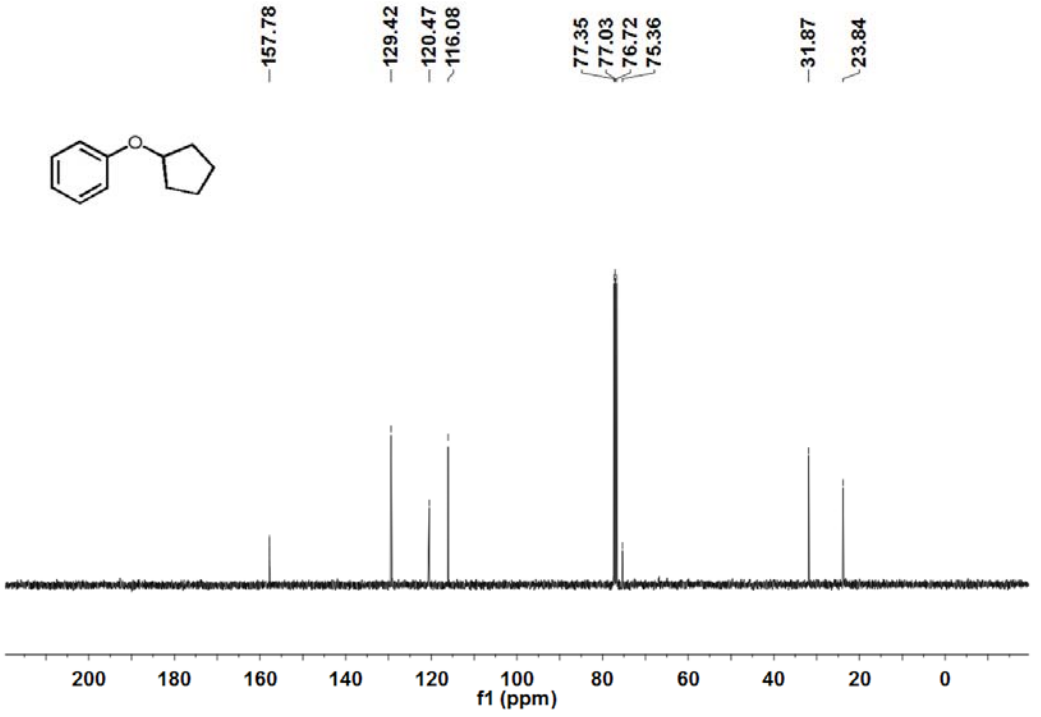
1.84
1.83
1.82
1.62
1.59
1.56
1.54
1.51
1.50
1.44
1.44
2.21
3.02
1.00
2.08
2.02
3.97
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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120.47
116.08
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77.03
76.72
75.36
31.87
23.84
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)