Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Pd-ZnO Nanowire Arrays as Recyclable Catalysts for 4-Nitrophenol Reduction and Suzuki Coupling Reactions

Qiyan Hu,[a,b] Xiaowang Liu,*[a] Lin Tang,[a,b] Dewen Min,[a] Tianchao Shi[a] and Wu Zhang*[a]

[a]College of Chemistry and Materials Science, Anhui Normal University, Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, Wuhu 241000, P.R. China

[b]School of Pharmacy, Wannan Medical College, Wuhu 241002, P.R. China

E-mail: zhangwu@mail.ahnu.edu.cn; xwliu601@mail.ahnu.edu.cn

Content

Characterization of ZnO@Zn and Pd-ZnO@Zn nanowire arrays

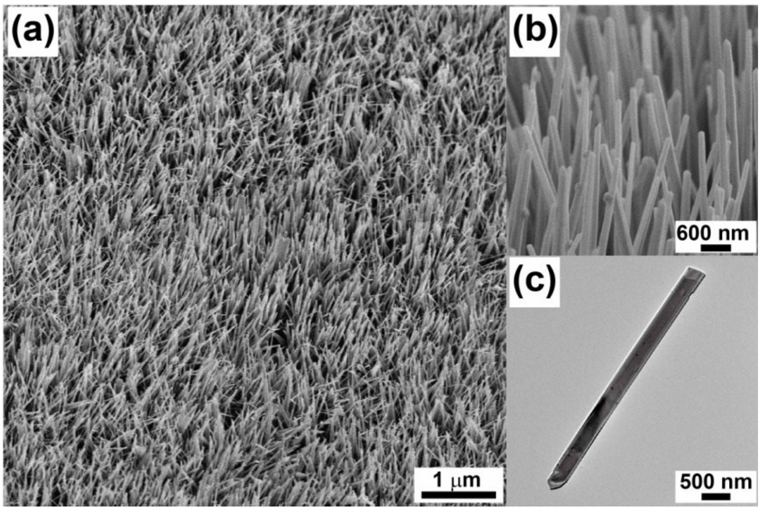


Figure S1. (a and b) Representative SEM images of as-prepared ZnO@Zn nanowire arrays for Pd nanoparticle loading and (c) TEM image of a single ZnO nanowire removed from the nanowire arrays by sonication.

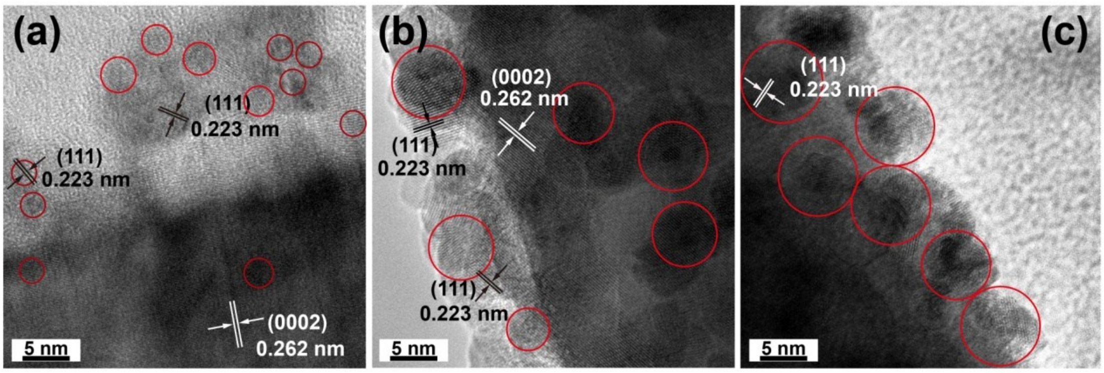


Figure S2. HRTEM images of Pd-ZnO nanowire arrays obtained by immersing ZnO@Zn nanowire arrays into an aqueous solution of Na_2PdCl_4 (5 mM) for different periods of time: (a) 5 s; (b) 15 s; and (c) 25 s.

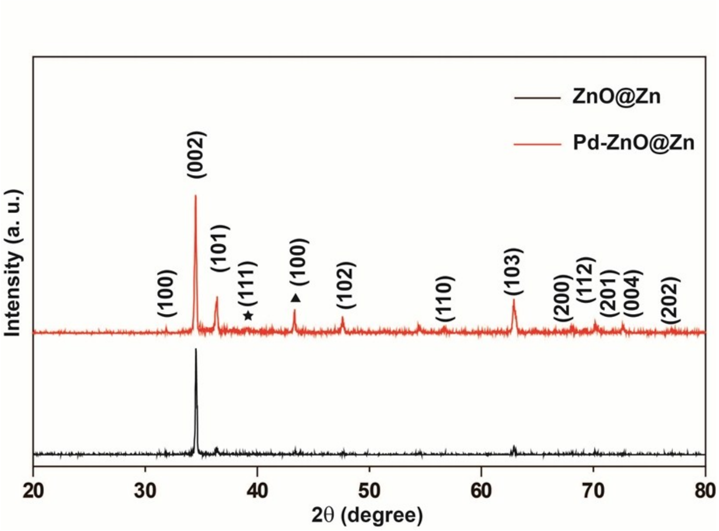


Figure S3. XRD patters of ZnO nanowire arrays before and after the growth of Pd NPs. Note that the diffraction patterns for Pd and Zn (from the substrate) are labeled with "★" and "▲", respectively.

Additional data on Pd-ZnO@Zn nanowire arrays toward 4-nitrophenol reduction

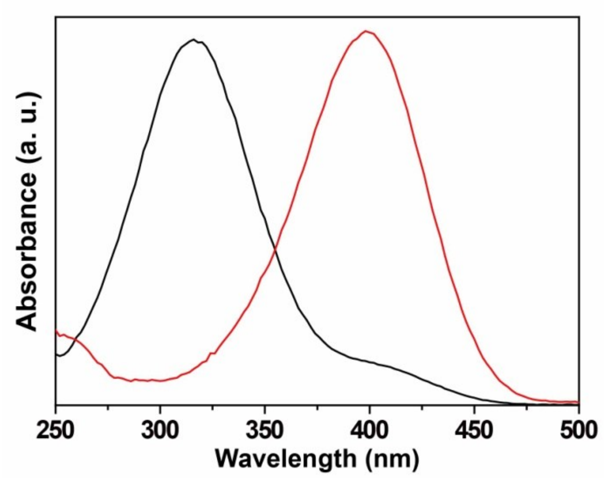


Figure S4. UV-vis spectra of 4-nitrophenol before (black curve) and after (red curve) the addition of $NaBH_4$ solution.

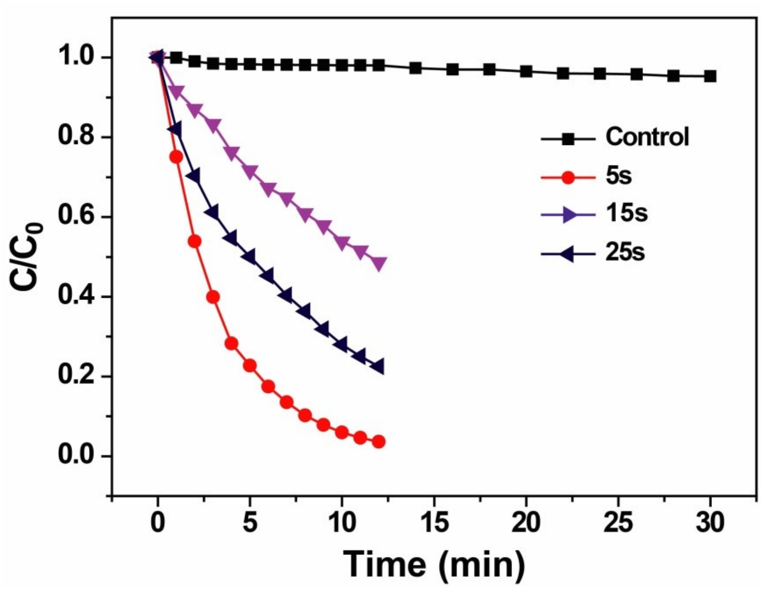


Figure S5. A comparison of the catalytic performance of ZnO@Zn nanowire arrays and Pd-ZnO nanowire arrays prepared by immersing ZnO@Zn nanowire arrays in a Na_2PdCl_4 solution for 5, 15 and 25 s.

Characterization of recycled Pd-ZnO@Zn nanowire arrays

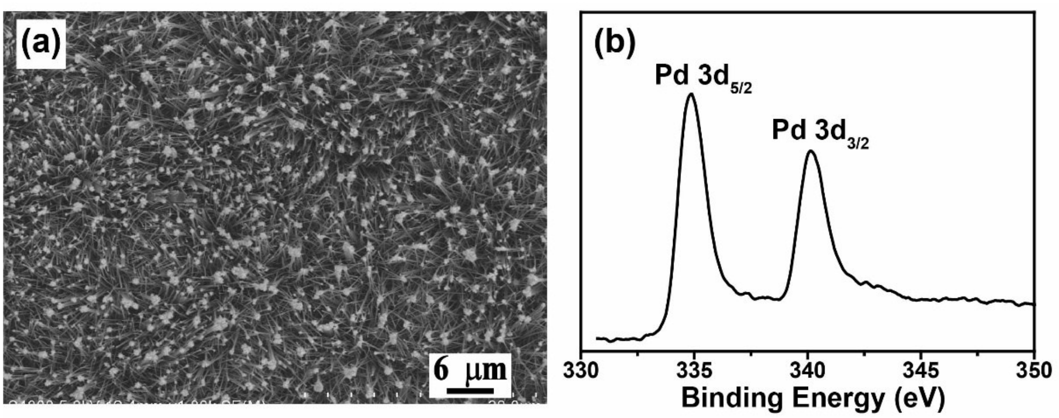


Figure S6. (a) SEM image and (b) XPS profile (Pd 3d) of as-prepared Pd NP-ZnO nanowire arrays after recycled use for 10 times toward 4-nitrophenol reduction.

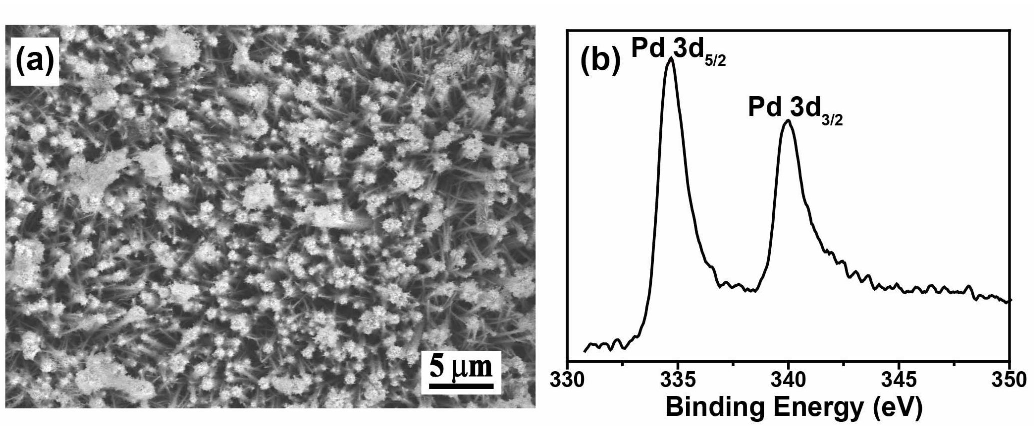
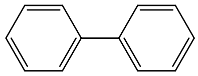


Figure S7. (a) SEM image and (b) XPS profile (Pd 3d) of as-prepared Pd nanoparticle-ZnO nanowire arrays after recycled use for 3 times toward Suzuki reaction.

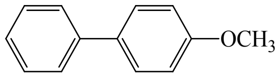
Characterization data for the products

Biphenyl (1a)



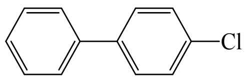
White solid; m.p. 67–68 °C (lit. m.p. 69-70 °C [1]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8Hz, 4H), 7.45-7.40 (m, 4H), 7.36-7.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 128.8, 127.3, 127.2.

4-Methoxybiphenyl (1b)



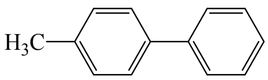
White solid; m.p. 88–89 °C (lit. m.p. 89-90 °C [1]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.51 (m, 4H), 7.41 (t, *J* = 7.2Hz, 2H), 7.32-7.30 (m, 1H), 6.97 (d, *J* = 8.4Hz, 2H), 3.84(s, 3H); ^{13}C NMR (75 MHz,$CDCl_3$) δ 159.5, 141.2, 134.1, 129.1, 128.6, 127.1, 127.1,114.6, 55.7.

4-Chlorobiphenyl (1c)



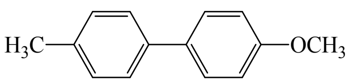
White solid; m.p. 77-78 ºC (lit. m.p. 78-78.5 °C [2]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.49 (m, 4H), 7.46-7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 139.7, 133.4, 128.9, 128.9, 128.4, 127.6, 127.0.

4-Methylbiphenyl (1d)



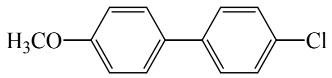
White solid; m.p. 46-47 °C (lit. m.p. 46-47 °C [1]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 7.2Hz, 2H), 7.49 (d, J = 8.1Hz, 2H), 7.44-7.39 (m, 2H), 7.34-7.31 (m, 1H), 7.25-7.21 (m, 2H), 2.39 (s, 3H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 141.2, 138.4, 137.1, 129.5, 128.8, 127.0, 127.0, 21.2.

4-Methoxy-4'-methylbiphenyl (1e)



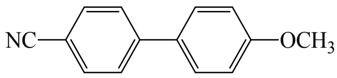
White solid; m.p. 109-111 °C(lit. m.p. 108-109 °C [3]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.43(m, 4H), 7.22 (d, *J* = 7.8Hz, 2H), 6.96 (d, *J* = 8.4Hz, 2H), 3.84 (s, 3H), 2.38(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 138.0, 136.4, 133.7, 129.5, 128.0, 126.6, 114.2, 55.4, 21.1.

4-Chloro-4'-methoxybiphenyl (1f)



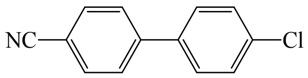
White solid; m.p. 110-112 °C (lit. m.p. 115-115.5 °C [2]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.44 (m, 4H), 7.35 (d, *J* = 8.4Hz, 2H), 6.95 (d, *J* = 8.7Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 139.3, 132.7, 132.5, 128.9, 128.0, 128.0, 114.3, 55.4.

4'-Methoxybiphenyl-4-carbonitrile (1g)



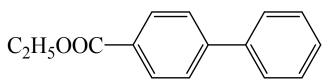
White solid; m.p. 101-103 °C (lit. m.p. 103-105 °C [4]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.62 (m, 4H), 7.54(d, *J* = 8.4Hz, 2H), 7.00(d, *J* = 8.7Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 145.6, 133.0, 131.8, 128.8, 127.5, 119.5, 114.9, 110.4, 55.8.

4'-Chlorobiphenyl-4-carbonitrile (1h)



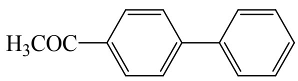
White solid; m.p. 125-126 °C (lit. m.p. 125-126 °C [2]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4Hz, 2H), 7.57(d, *J* = 8.4Hz, 2H), 7.45 (d, *J* = 8.4Hz, 2H), 7.37(d, *J* = 8.7Hz, 2H); ^{13}CNMR (75 MHz, $CDCl_3$): δ 144.4, 137.6, 135.0, 132.7, 129.3, 128.5, 127.6, 118.8, 111.3.

Ethyl biphenyl-4-carboxylate (1i)



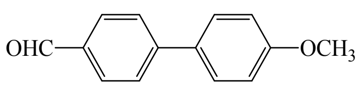
White solid; m.p. 48-49 °C (lit. m.p. 49-50 °C [5]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1Hz, 2H), 7.67-7.61 (m, 4H), 7.49-7.39 (m, 3H), 4.40 (q, *J* = 6.9 Hz, 2H)， 1.41 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 145.9, 140.4, 130.4, 129.6, 129.3, 128.5, 127.7, 127.4, 61.4, 14.8.

1-([1, 1'-biphenyl]-4-yl)ethanone (1j)



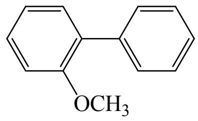
White solid; m.p. 118-120 °C (lit. m.p. 122-123 °C [3]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1Hz, 2H), 7.68-7.60(m, 4H), 7.48-7.39 (m, 3H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 146.2, 140.3, 136.3, 129.4, 129.3, 128.6, 127.7, 127.6, 27.0.

4'-Methoxybiphenyl-4-carbaldehyde (1k)



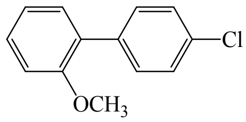
White solid; m.p. 101-102 °C (lit. m.p. 100-101 °C [6]); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 10.03 (s, 1H), 7.93 (d, *J* = 8.1Hz, 2H), 7.71 (d, *J* = 8.1Hz, 2H), 7.59 (d, *J* = 8.7, 2H), 7.01 (d, *J* = 8.7, 2H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 160.1, 146.8, 134.7, 132.0, 130.3, 128.5, 127.1, 114.5, 55.4.

2-Methoxybiphenyl (1l)



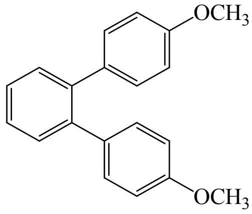
White solid; m.p. 28-30 °C (lit. m.p. 29-30 °C [1]);; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.42-7.28 (m, 5H), 7.04-6.95 (m, 2H), 3.77(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 138.6, 131.0, 130.8, 129.6, 128.7, 128.1, 127.0, 120.9, 111.3, 55.6.

4'-Chloro-2-methoxybiphenyl (1m)



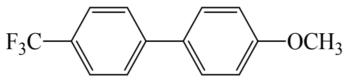
White solid; m.p. 52-54 °C (lit. m.p. 50-52 °C [7]); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.46 (d, *J* = 8.4Hz, 2H), 7.37-7.26 (m, 4H), 7.04-6.95 (m, 2H), 3.79(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 137.0, 132.9, 130.9, 130.7, 129.4, 129.0, 128.2, 120.9, 111.2, 55.6.

4, 4''-dimethoxy-1,1':2',1''-terphenyl (1n)



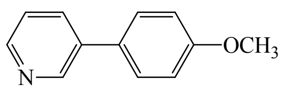
White solid; m.p. 102-104 °C (lit. m.p. 107-108 °C [8]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 4H), 7.06 (d, *J* = 8.4Hz, 4H), 6.76 (d, *J* = 8.4Hz, 4H), 3.77(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 140.1, 134.1, 130.9, 130.6, 127.2, 113.4, 55.2.

4-(4-Trifluoromethylphenyl)anisole (1o)



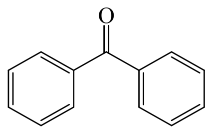
White solid; m.p. 120-122 °C (lit. m.p. 121-122 °C [1]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.54(d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 144.3, 132.1, 128.7 (q, J_{CF} = 32.25Hz),128.4, 126.9, 125.7 (q, J_{CF} = 3.75Hz), 124.4 (q, J_{CF} = 270Hz), 114.4, 55.3.

3-(4-Methoxyphenyl) pyridine (1p)



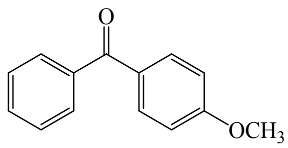
White solid; m.p. 62-63 °C (lit. m.p. 62-64 °C [3]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 1 H), 8.54 (d, *J* = 3.6 Hz, 1 H), 7.82 (d, *J* = 7.8 Hz, 1 H), 7.51 (d, J= 8.7 Hz, 2 H), 7.35-7.31 (m, 1 H), 7.00 (d, J= 8.7 Hz, 2 H), 3.84(s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 147.8, 147.7, 136.3, 133.9, 130.2, 128.2, 123.6, 114.6, 55.4.

Benzophenone (2a)



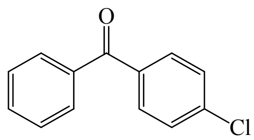
White solid; m.p. 48-49 °C (lit. m.p. 46-47 °C [9]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.79 (m, 4 H), 7.61-7.56 (m, 2 H), 7.51- 7.46 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 137.6, 132.4, 130.1, 128.3.

(4-Methoxyphenyl)(phenyl)methanone (2b)



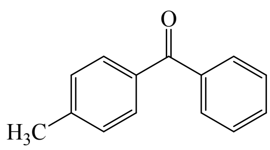
White solid; m.p. 58-60 °C (lit. m.p. 59-60 °C [9]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7Hz, 2H), 7.75 (d, *J* = 7.2Hz, 2H), 7.56 (t, *J* = 7.2Hz, 1H), 7.47 (t, *J* = 7.2Hz, 2H), 6.96 (d, *J* = 9.0Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 163.6, 138.7 132.9, 132.2, 130.6, 130.1, 128.6, 114.0, 55.9.

(4-Chlorophenyl)(phenyl)methanone (2c)



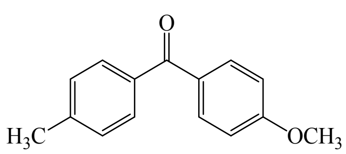
White solid; m.p. 72-73 °C (lit. m.p. 74.3-74.7 °C [10]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.74 (m, 4H), 7.63-7.58 (m, 1H), 7.51-7.45 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 138.9, 137.3, 135.9, 132.6, 131.4, 129.9, 128.6, 128.4.

Phenyl(p-tolyl)methanone (2d)



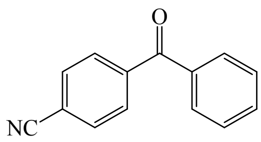
White solid; m.p. 57-58 °C (lit. m.p. 57-58 °C [9]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.2Hz, 1H), 7.48-7.43 (m, 2H), 7.27-7.24 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 143.2, 138.0, 134.9, 132.2, 130.3, 129.9, 129.0, 128.2, 21.7.

(4-Methoxyphenyl)(p-tolyl)methanone (2e)



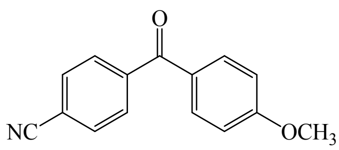
White solid; m.p. 75-77 °C (lit. m.p. 76.3-77 °C [10]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5, 2H), 7.68 (d, *J* = 8.0, 2H), 7.27 (d, *J* = 8.0, 2H), 6.96 (d, *J* = 9.0, 2H), 3.88 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.7, 163.4, 143.0, 136.0, 132.8, 130.9, 130.4, 129.3, 113.9, 55.8, 22.0.

4-Benzoylbenzonitrile (2f)



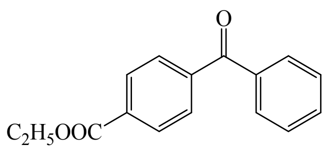
White solid; m.p. 110-112 °C (lit. m.p. 110-111 °C [9]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88(d, *J* = 8.4Hz, 2H), 7.81-7.78(m, 4H), 7.65(t, *J* = 7.5Hz, 1H), 7.52(t, *J* = 7.5Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 141.2, 136.3, 133.3, 132.2, 130.2, 130.1, 128.6, 118.0, 115.6.

4-(4-Methoxybenzoyl)benzonitrile (2g)



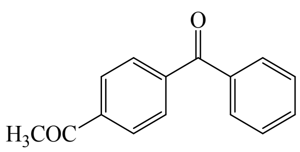
White solid; m.p. 129-131 °C (lit. m.p. 129.3-130.1 °C [10]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84-7.76 (m, 6H), 6.99 (d, *J* = 8.7, 2H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 163.9, 142.1, 132.6, 132.1, 129.9, 129.0, 118.1, 115.1, 113.9, 55.6.

Ethyl 4-benzoylbenzoate (2h)



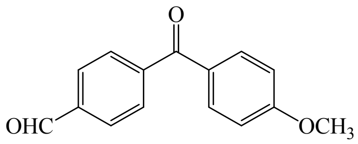
Colorless oil [11]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.83-7.78 (m, 4H), 7.62-7.58 (m, 1H), 7.50-7.45 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 165.8, 141.2, 137.0, 133.6, 132.9, 130.1, 129.7, 129.4, 128.4, 61.4, 14.3.

1-(4-Benzoylphenyl)ethanone (2i)



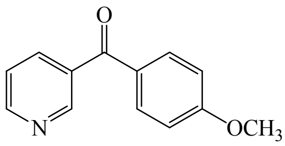
White solid; m.p. 82-84 °C (lit. m.p. 82-83 °C [9]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1Hz, 2H), 7.87(d, *J* = 8.1Hz, 2H), 7.81(d, *J* = 7.2Hz, 2H), 7.63(t, *J* = 7.5Hz, 1H), 7.51(t, *J* = 7.5Hz, 2H), 2.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 195.9, 141.4, 139.6, 137.0, 133.0, 130.1, 130.0, 128.5, 128.2, 26.9.

4-(4-Methoxybenzoyl)benzaldehyde (2j)



White solid; m.p. 100-103 °C (lit. m.p. 104-106 °C [12]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.00 (d, *J* = 7.8, 2H), 7.89-7.82 (m, 4H), 6.99 (d, *J* = 8.7, 2H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 191.6, 163.8, 143.5, 138.2, 132.6, 130.0, 129.7, 129.4, 113.8, 55.6.

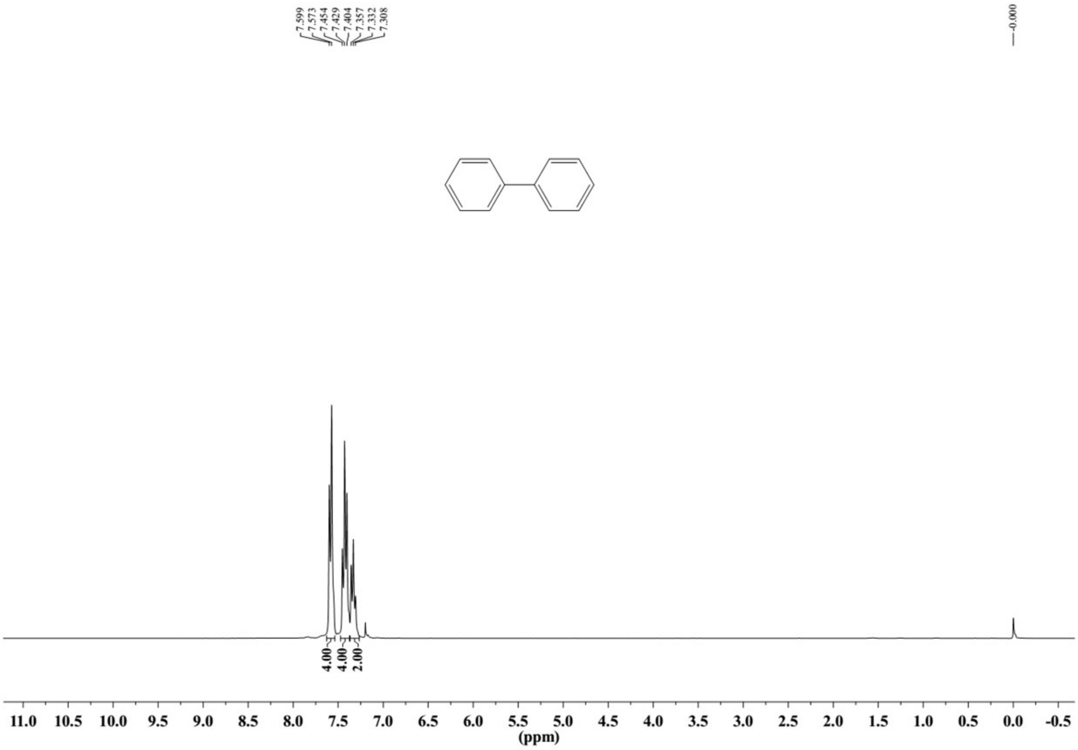
(4-Methoxyphenyl)(pyridin-3-yl)methanone (2k)

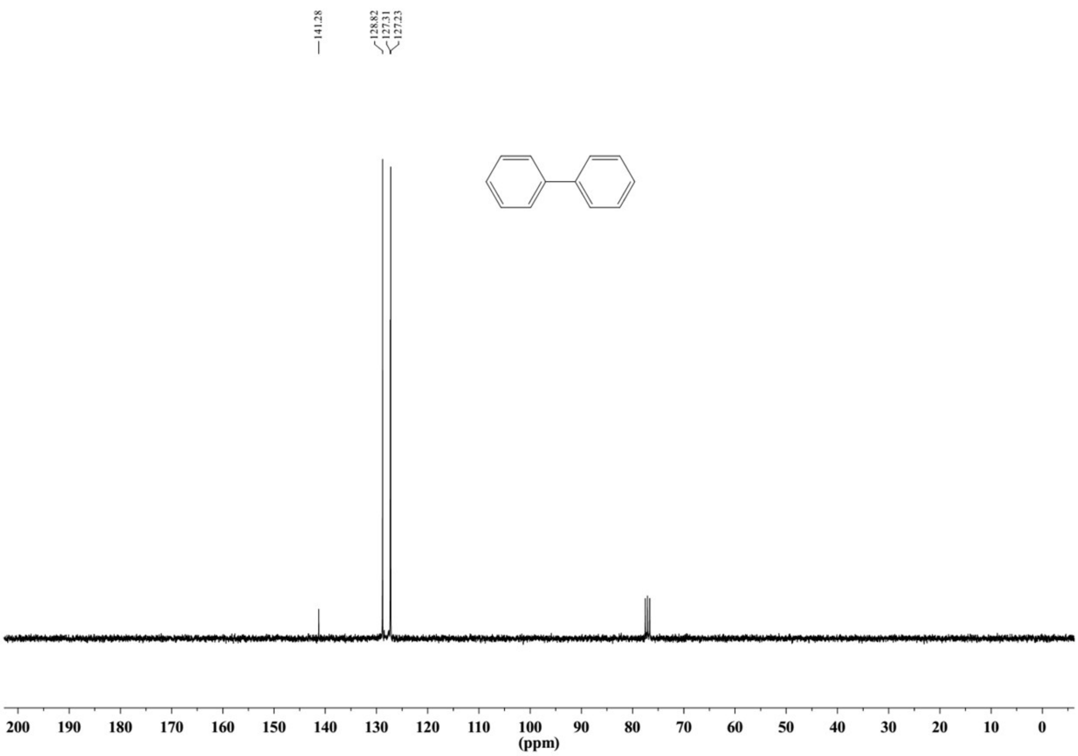


White solid; m.p. 96-98 °C (lit. m.p. 98-99 °C [13]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 1 H), 8.80 (d, *J* = 3.6 Hz, 1 H), 8.09 (d, *J* = 7.8 Hz, 1 H), 7.84 (d, *J* = 9.0 Hz, 2 H), 7.47-7.43 (dd, *J* = 4.8Hz, 7.8 Hz, 1 H), 7.00 (d, *J* = 9.0 Hz, 2 H), 3.91(s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 163.8, 152.3, 150.4, 137.0, 134.0, 132.5, 129.4, 123.4, 113.9, 55.6.

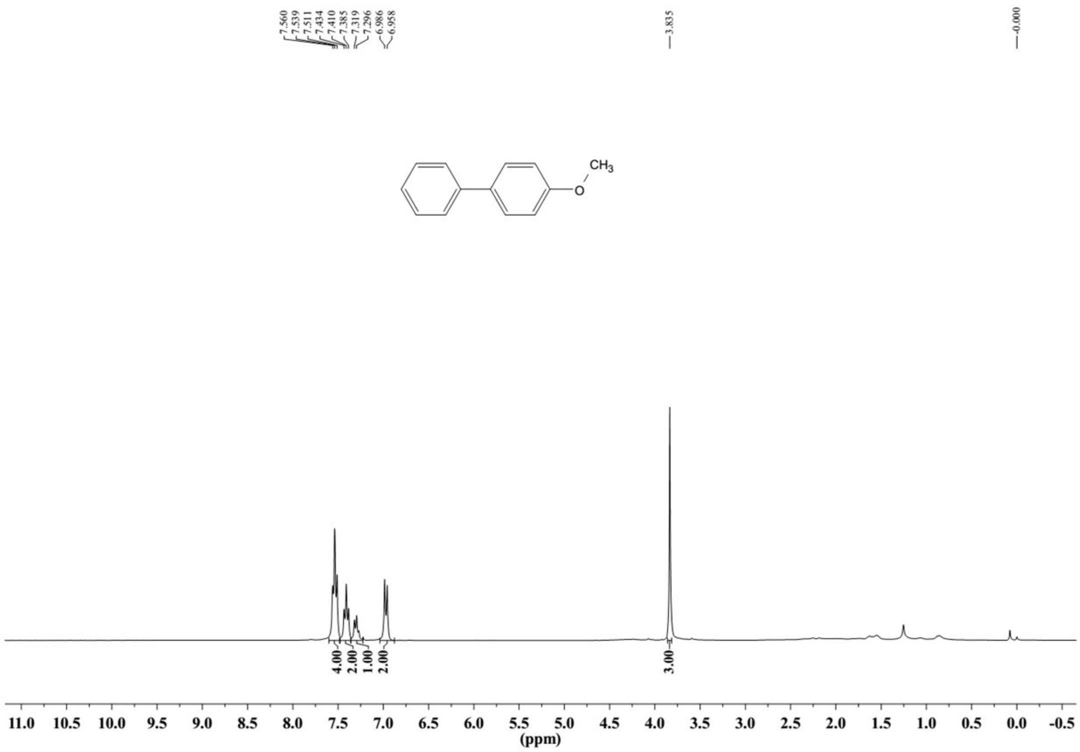
[1]H and [13]C NMR spectra of the products

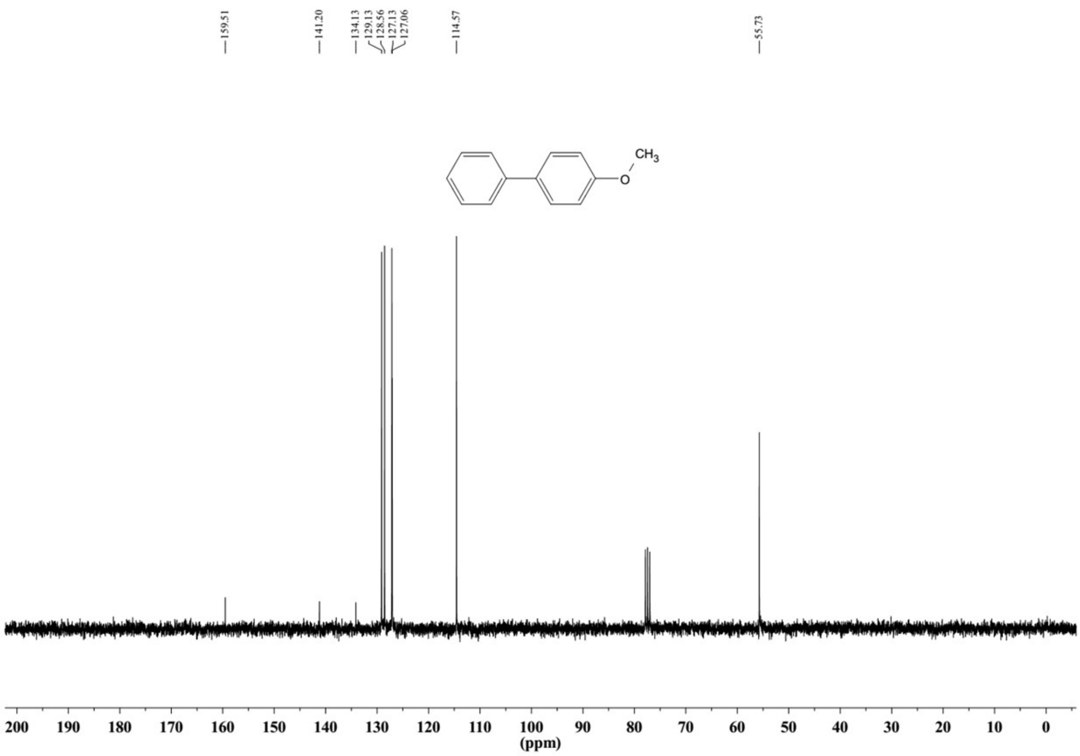
Biphenyl (1a)



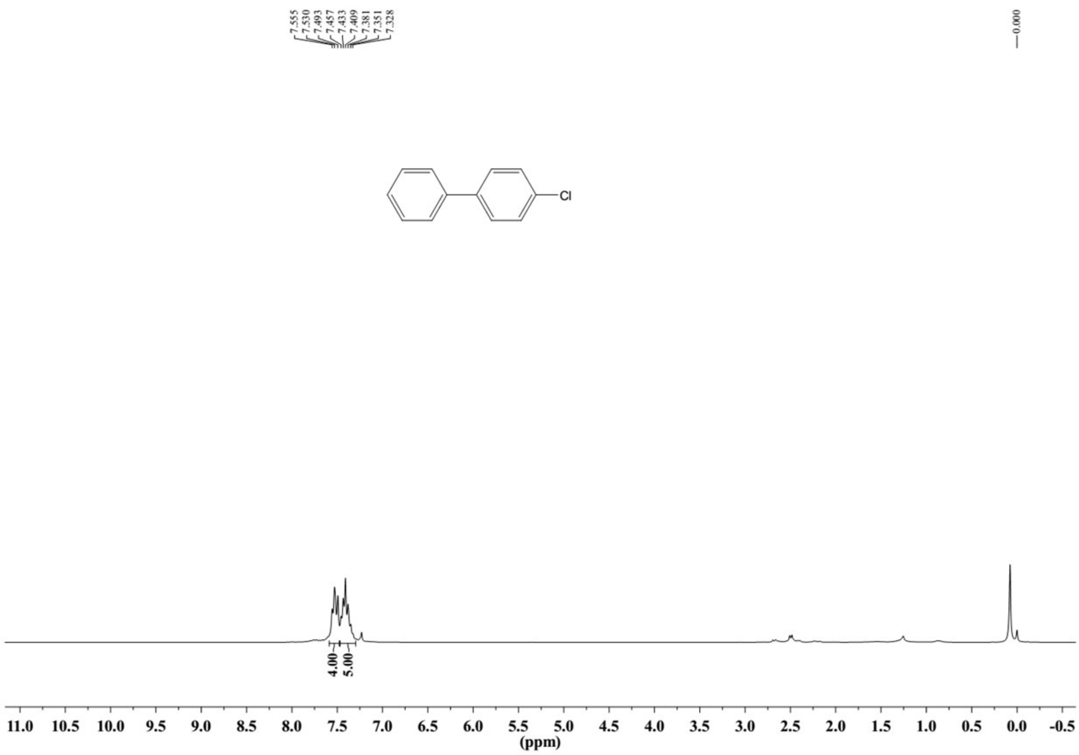


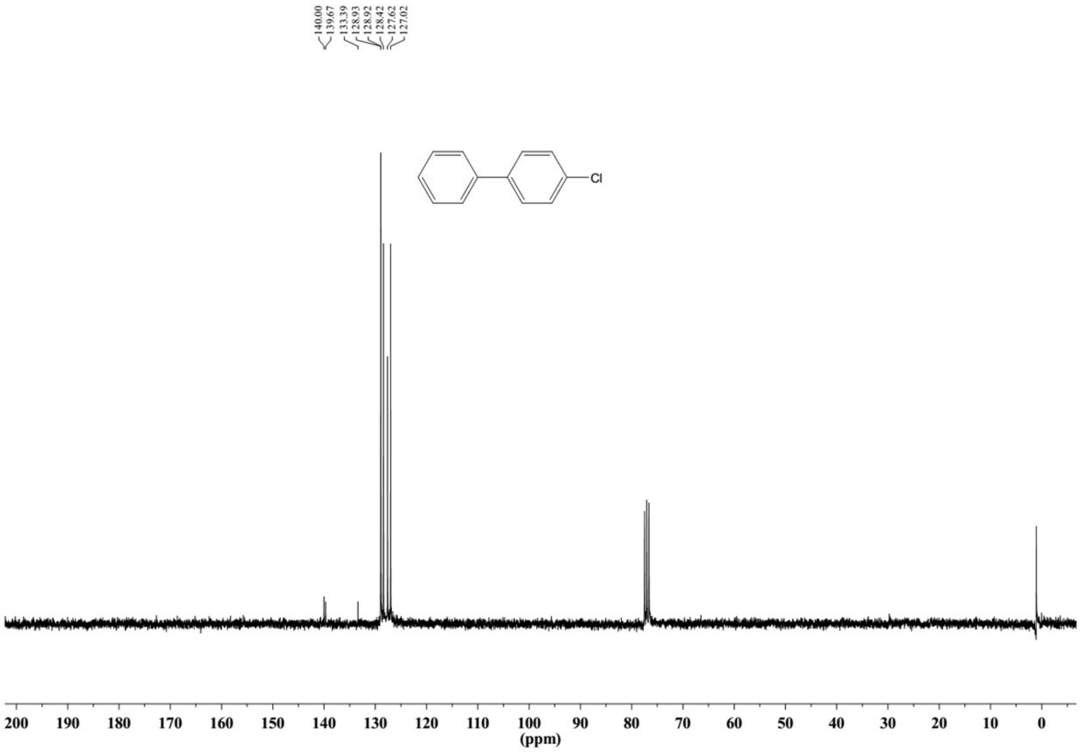
4-Methoxybiphenyl (1b)



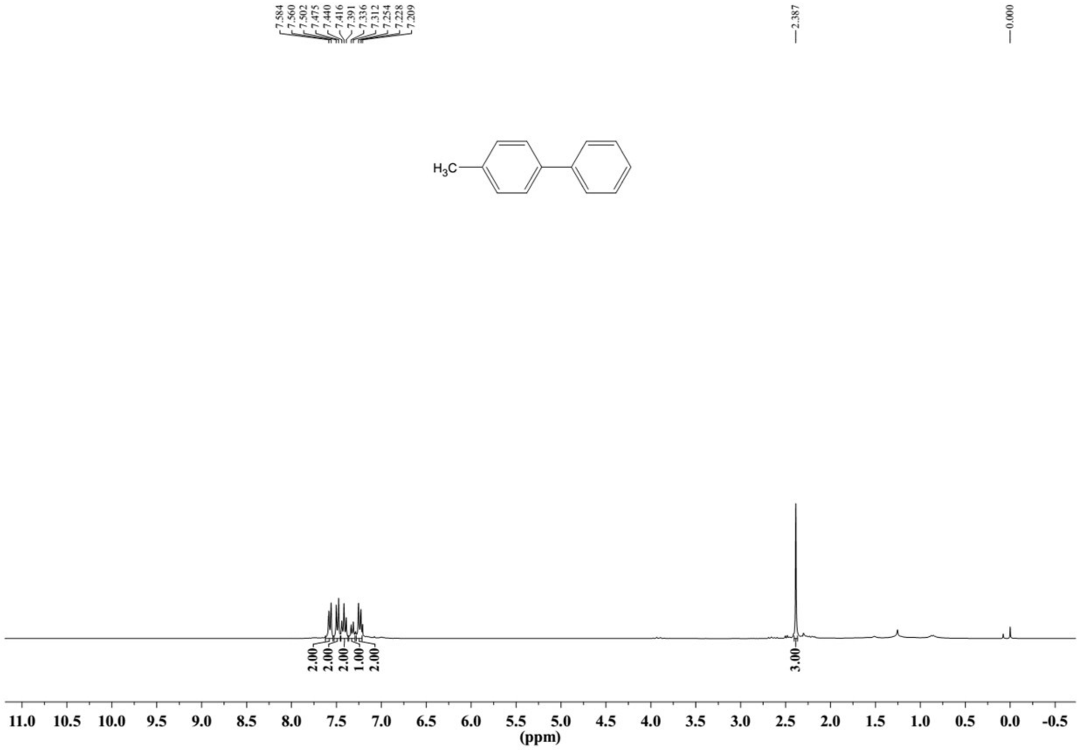


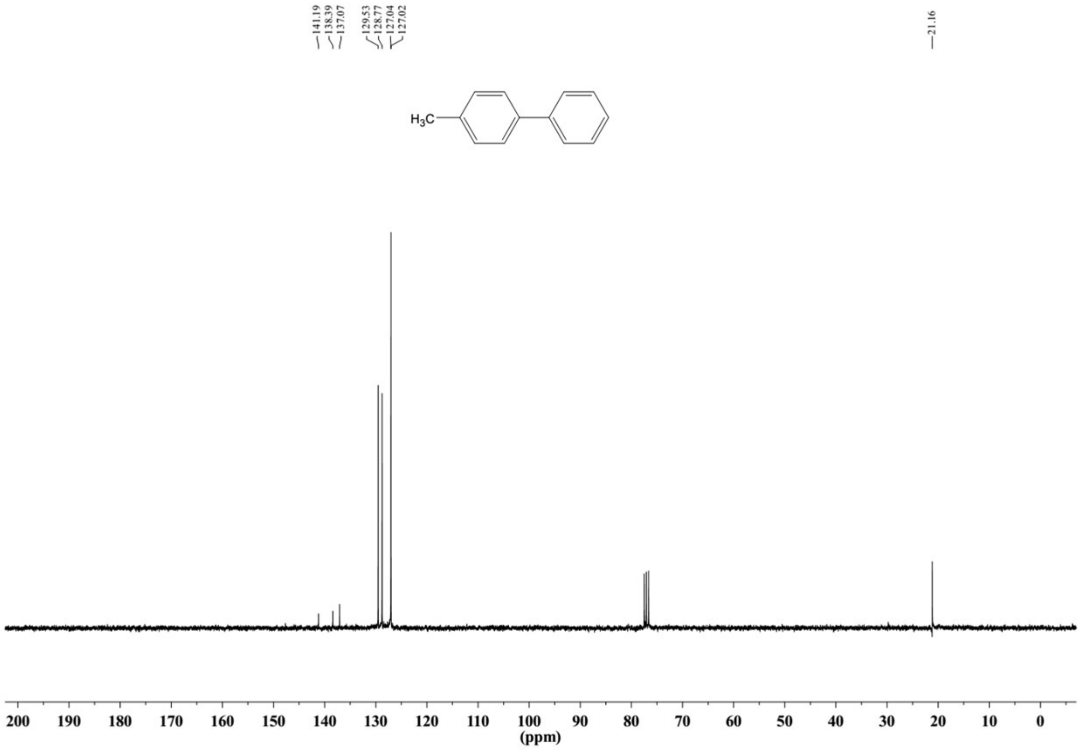
4-Chlorobiphenyl (1c)



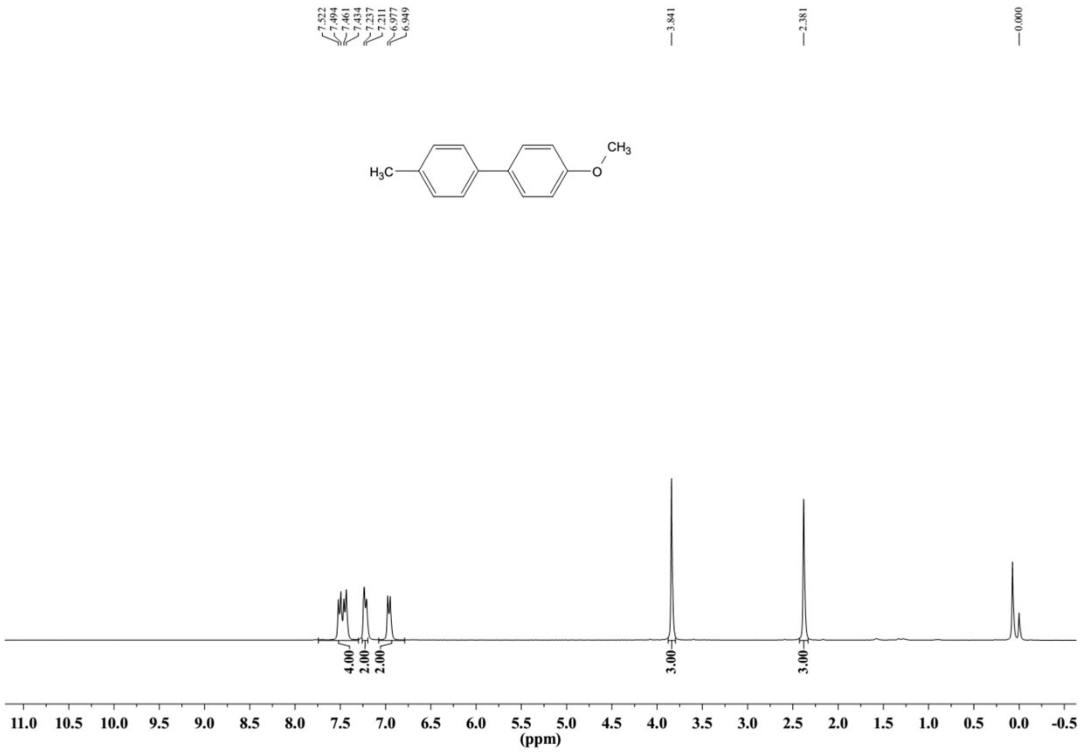


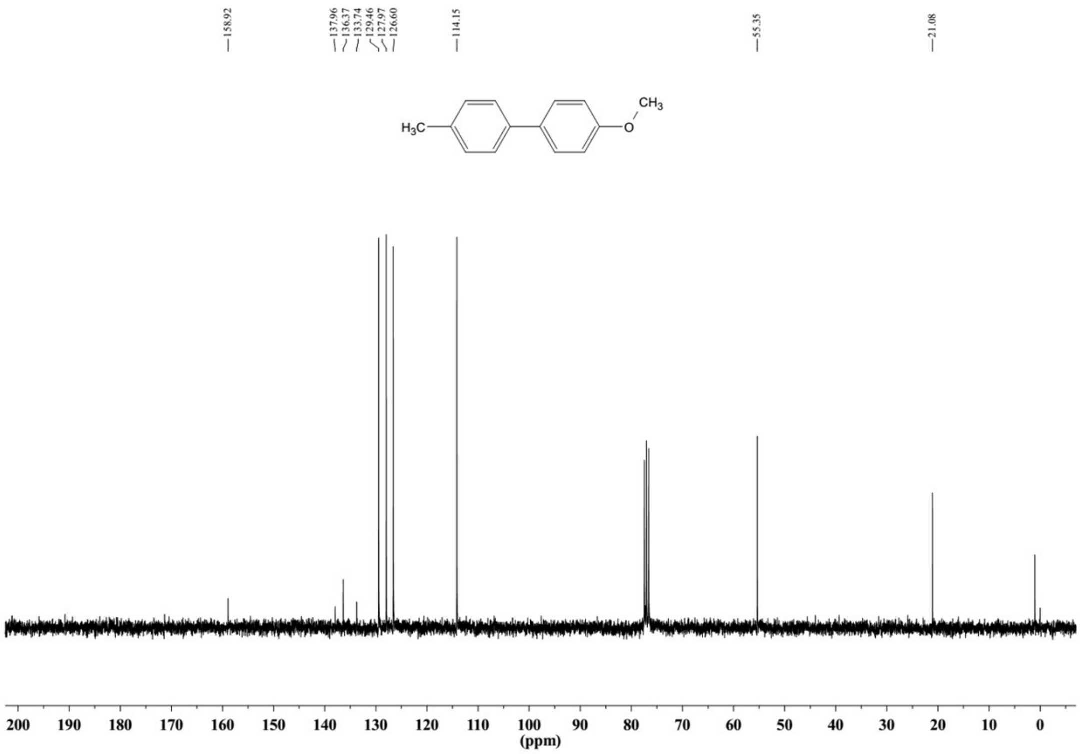
4-Methylbiphenyl (1d)



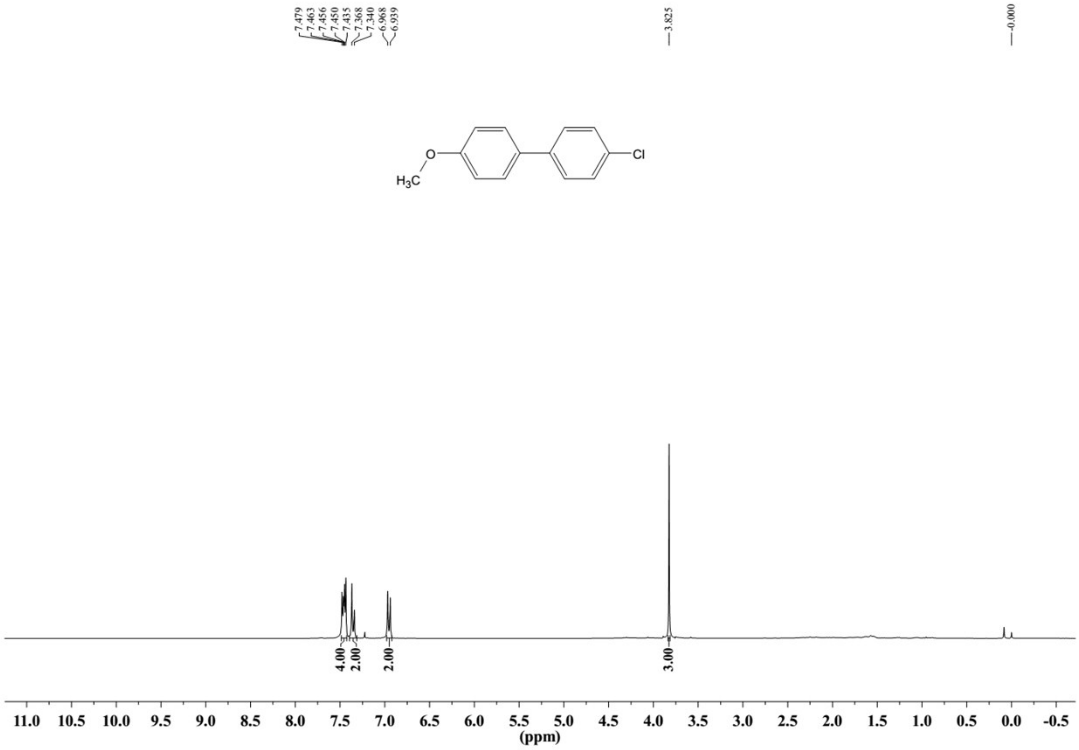


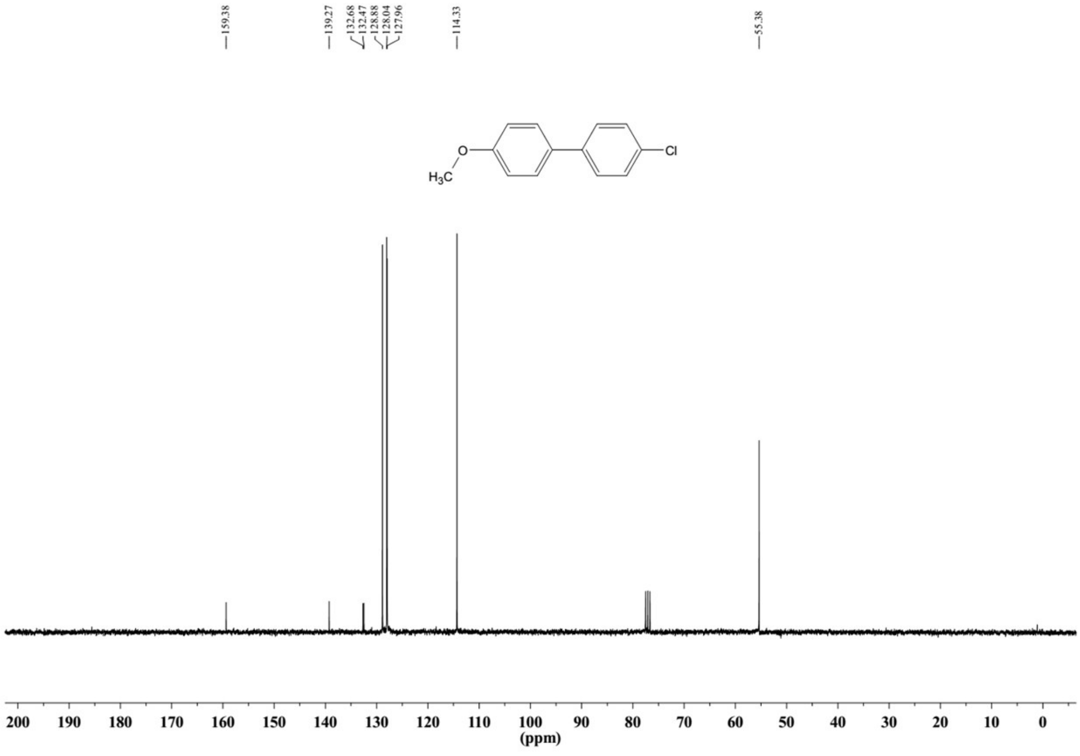
4-Methoxy-4'-methylbiphenyl (1e)



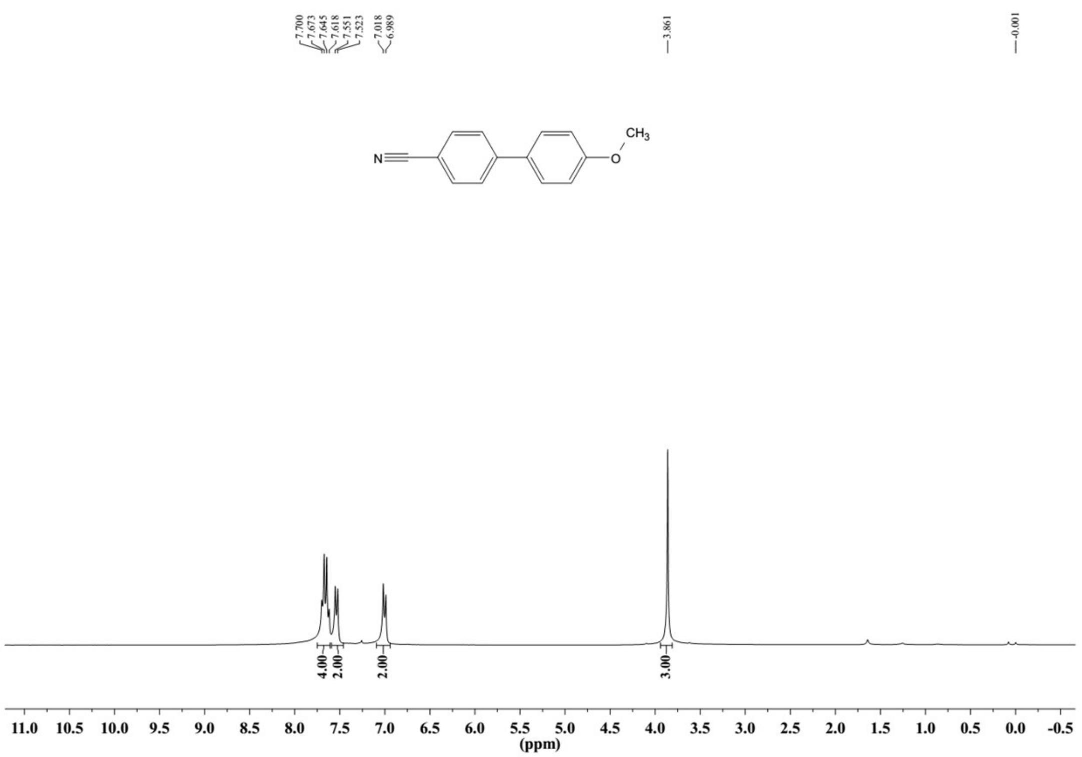


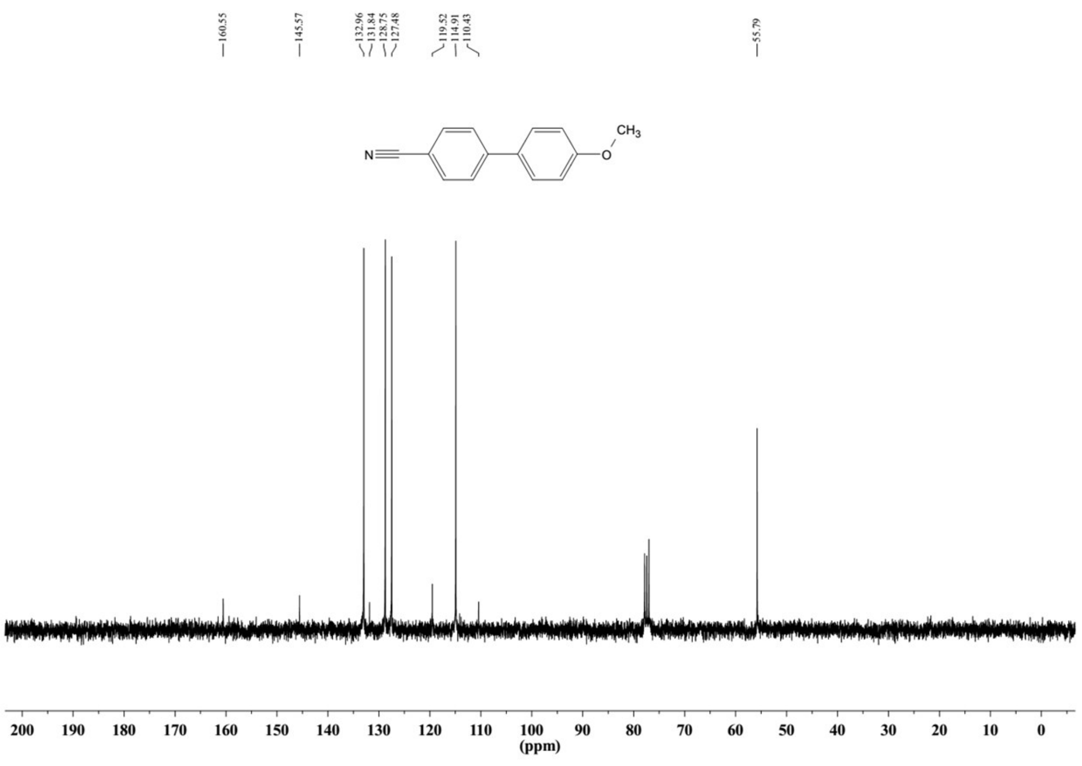
4-Chloro-4'-methoxybiphenyl (1f)



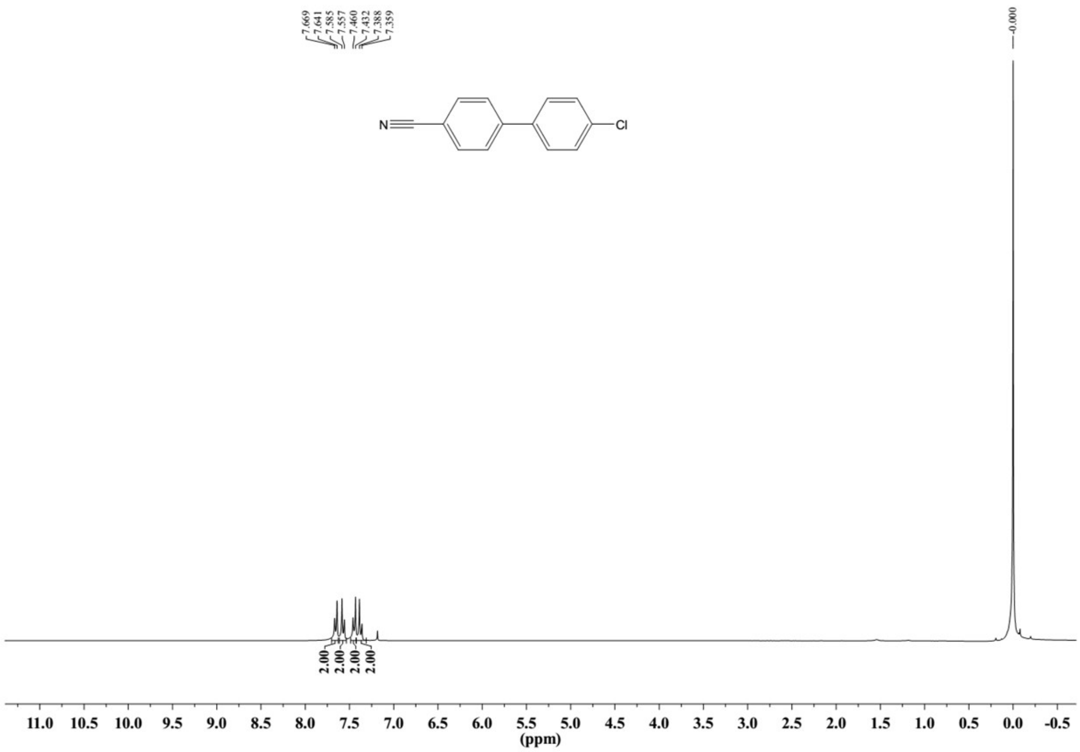


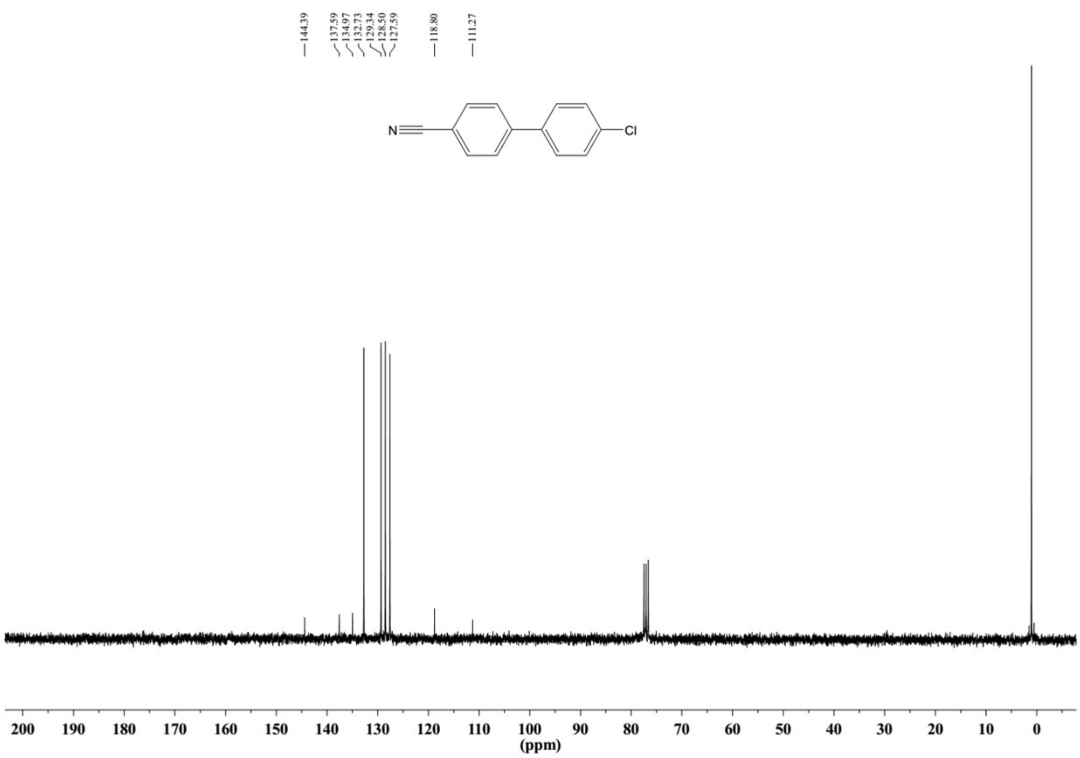
4'-Methoxybiphenyl-4-carbonitrile (1g)



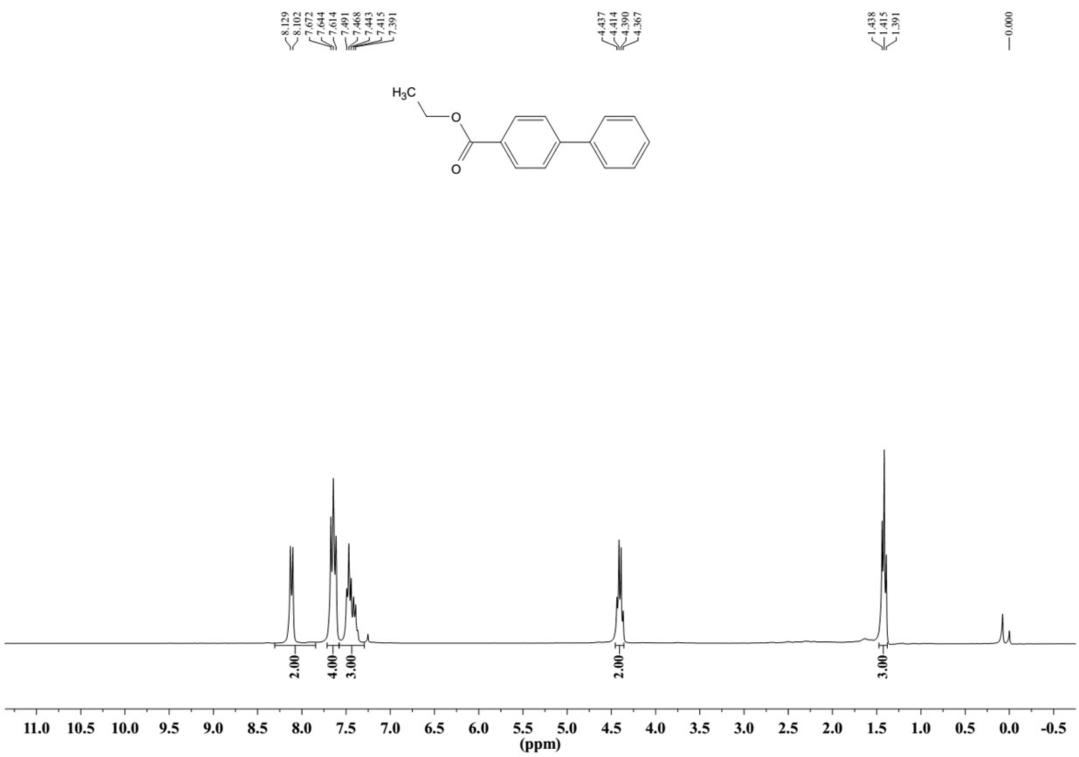


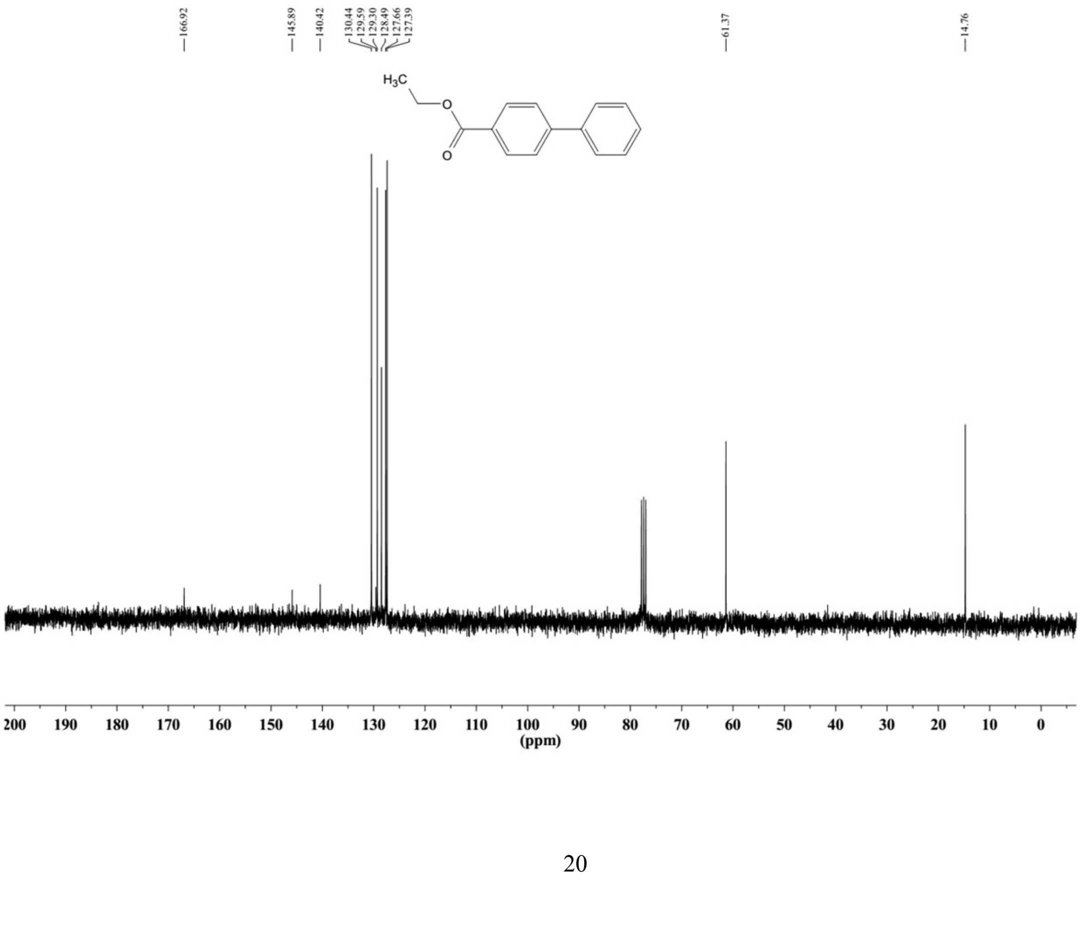
4'-Chlorobiphenyl-4-carbonitrile (1h)



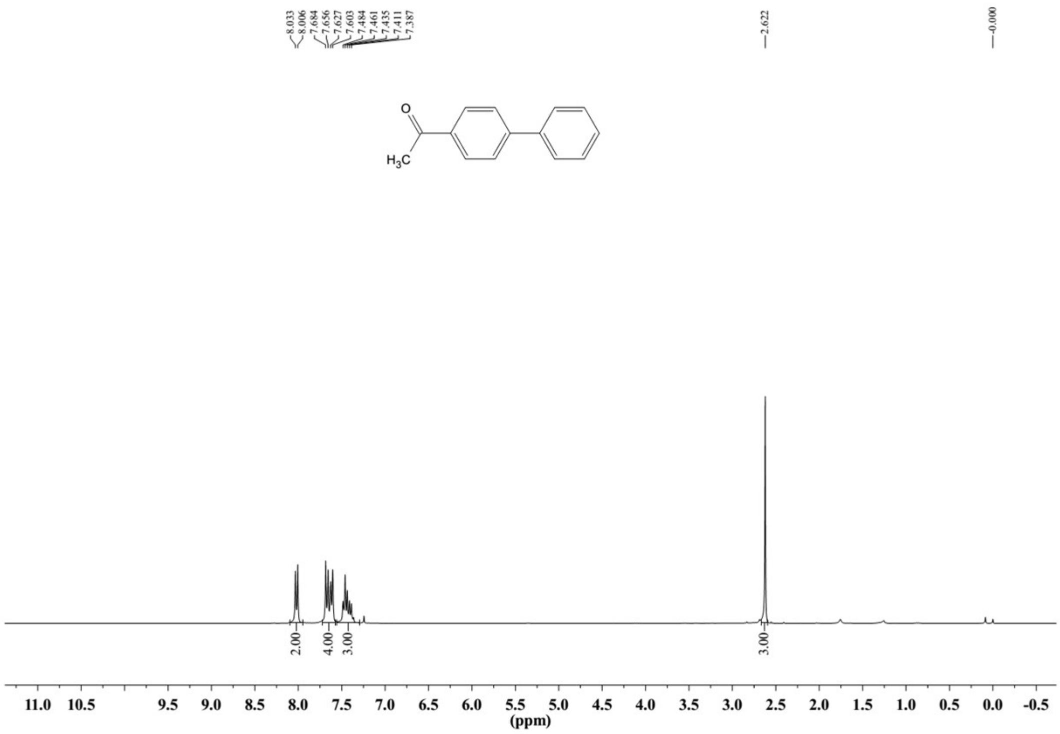


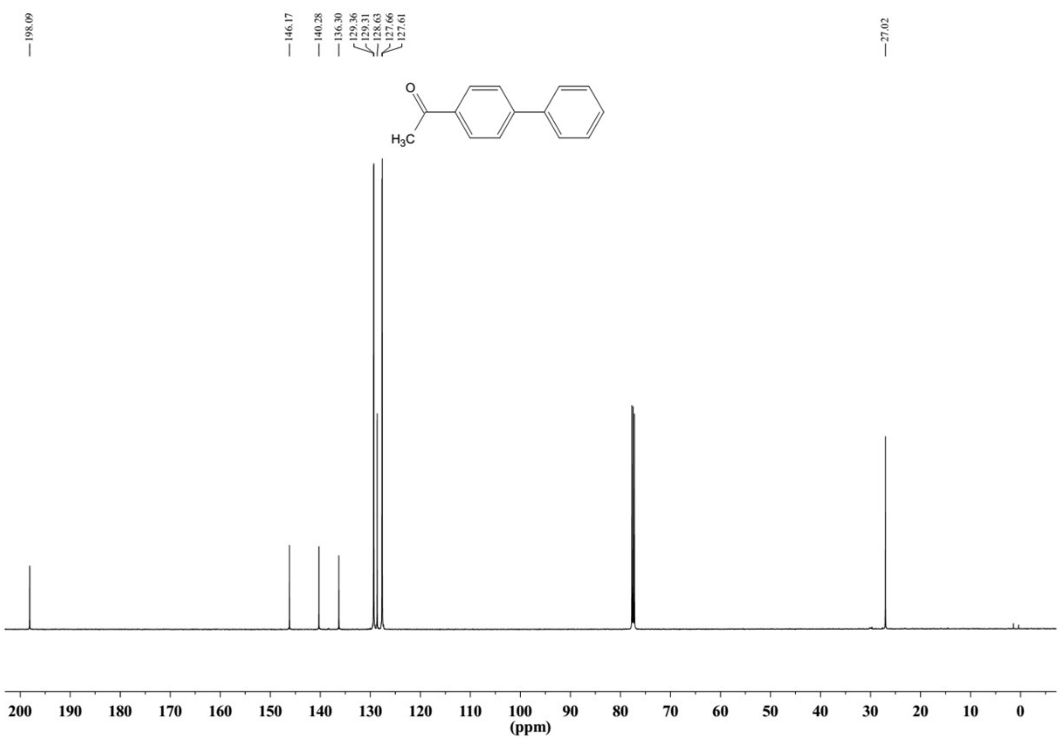
Ethyl biphenyl-4-carboxylate (1i)



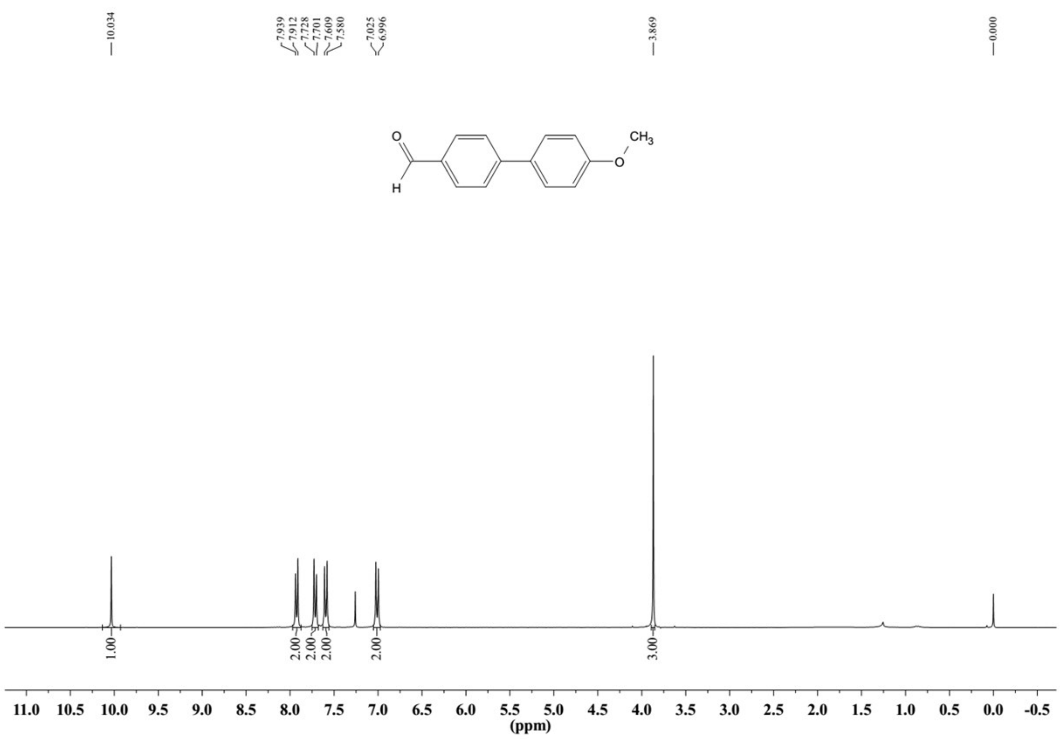


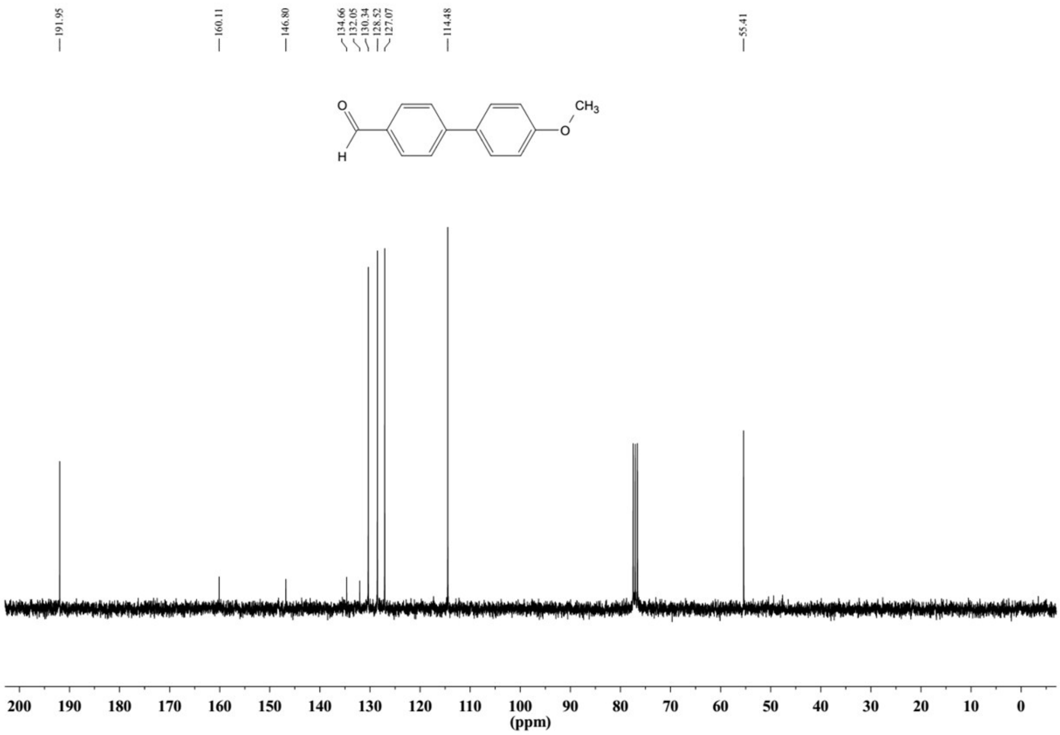
1-([1, 1'-biphenyl]-4-yl)ethanone (1j)



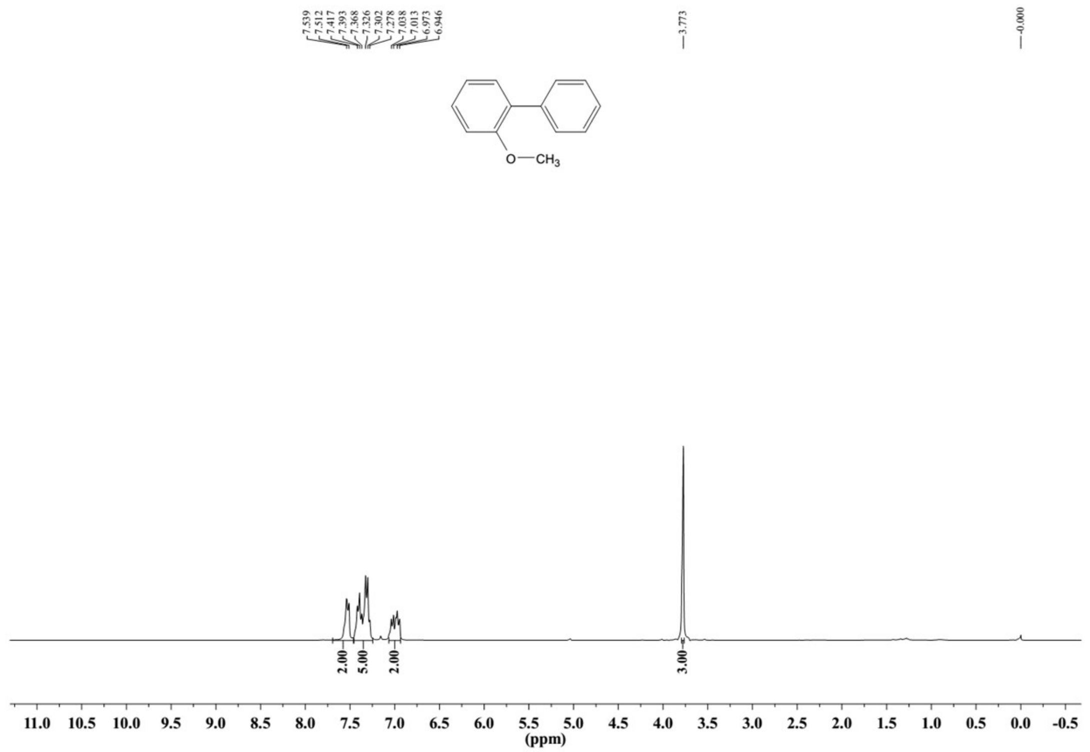


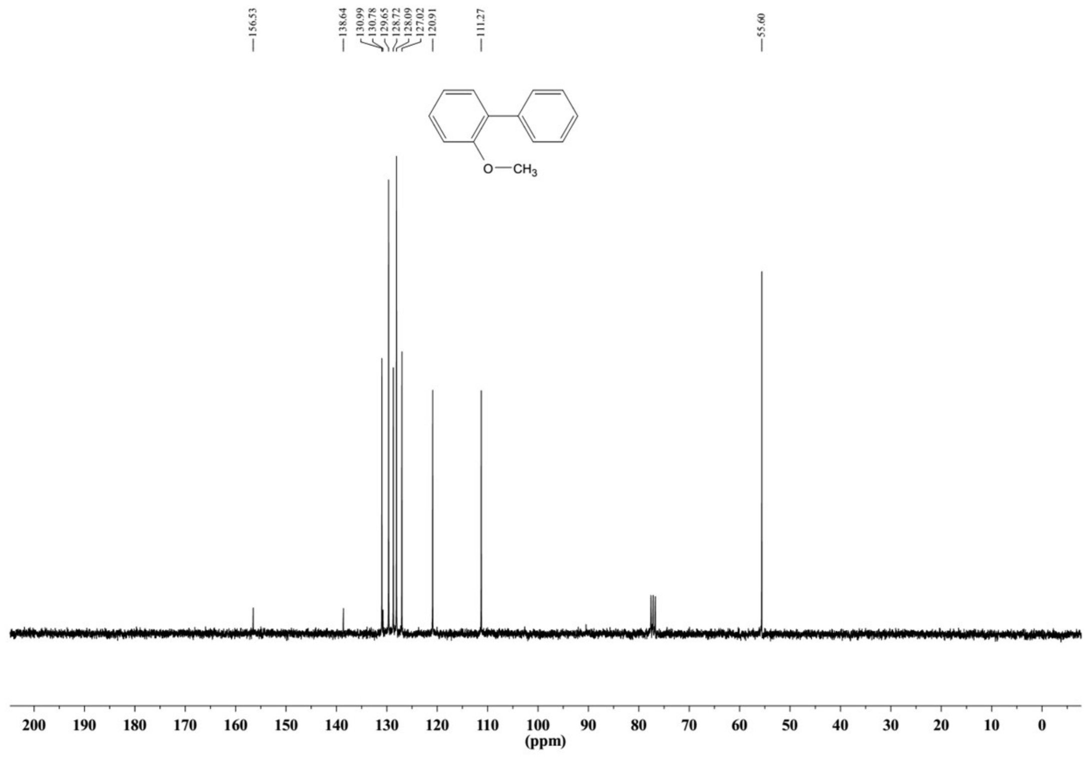
4'-Methoxybiphenyl-4-carbaldehyde (1k)



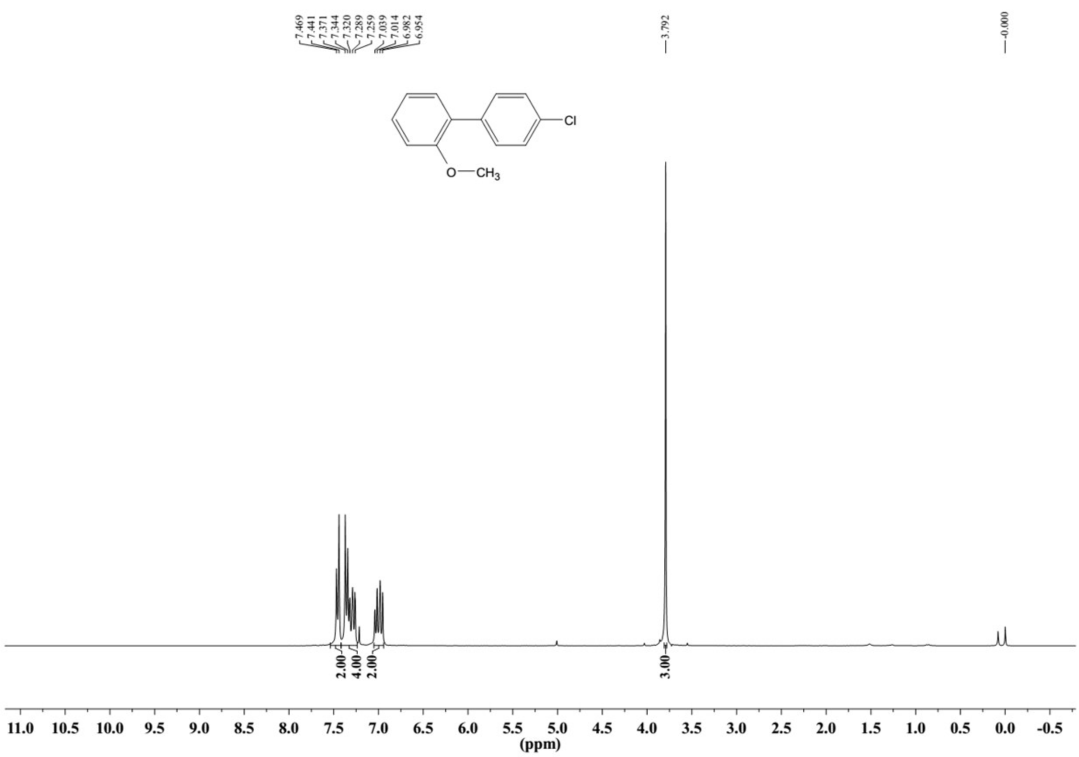


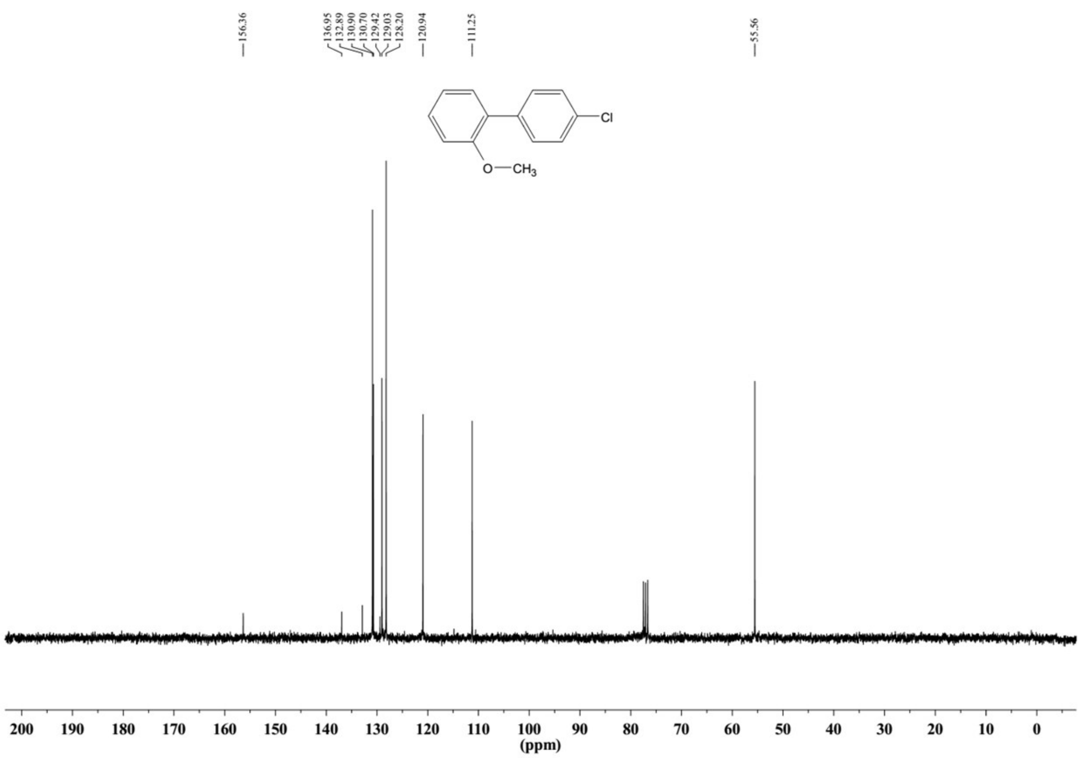
2-Methoxybiphenyl (1l)



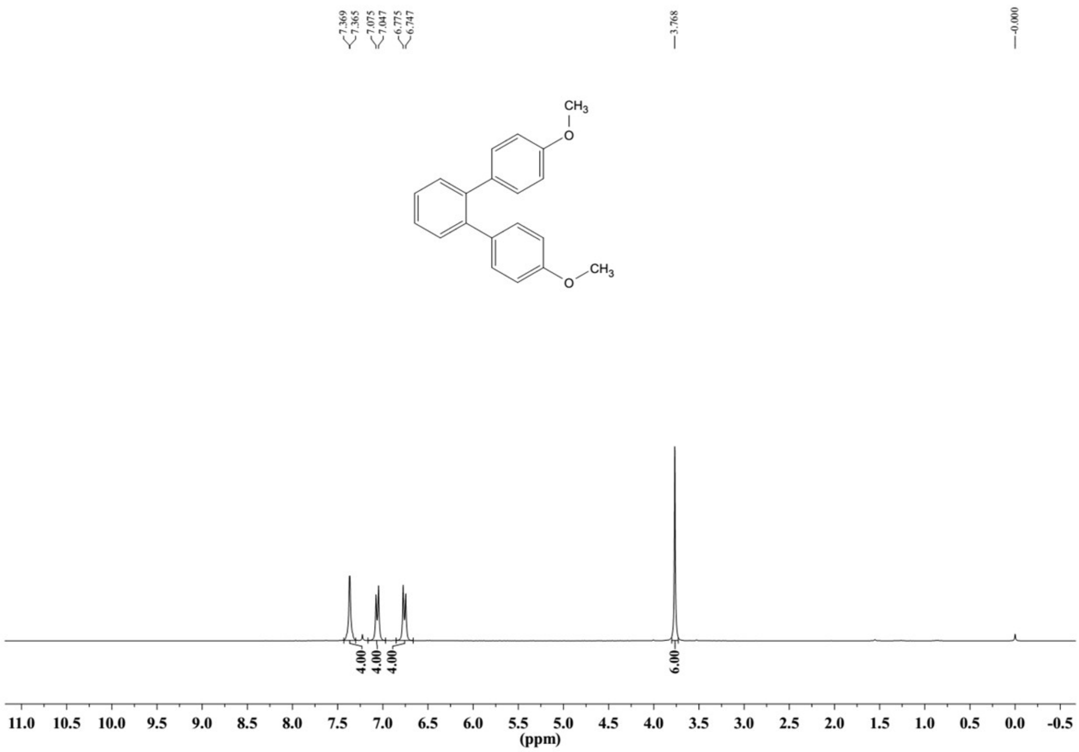


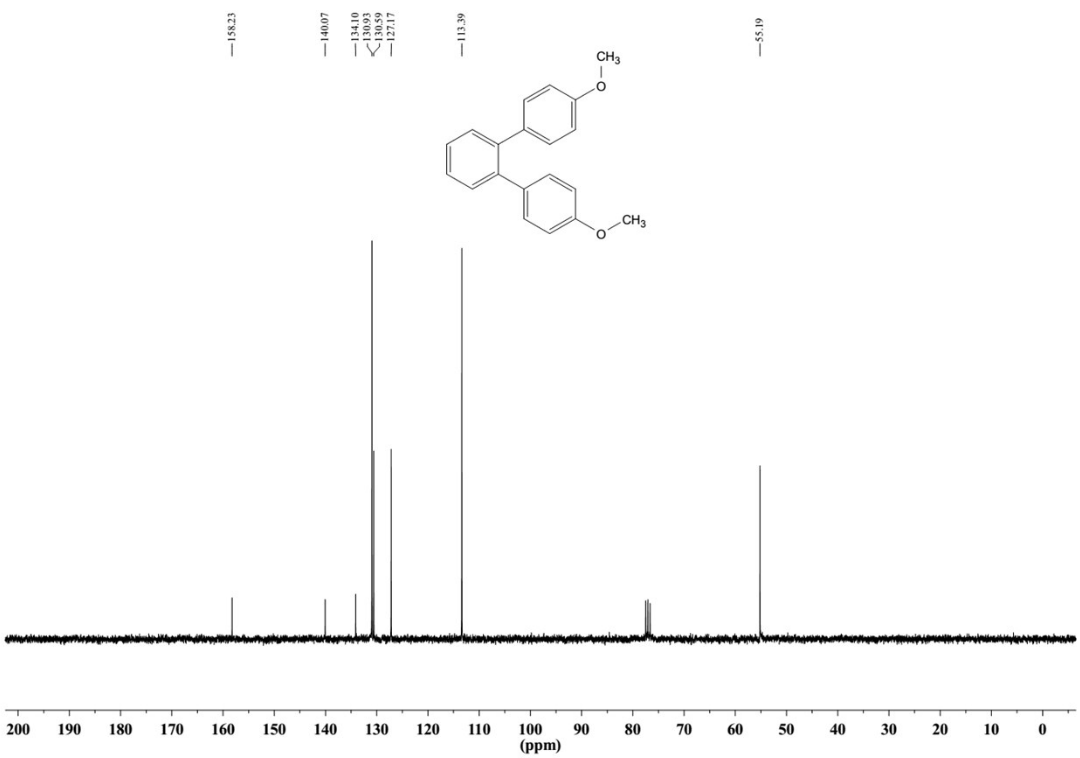
4'-Chloro-2-methoxybiphenyl (1m)



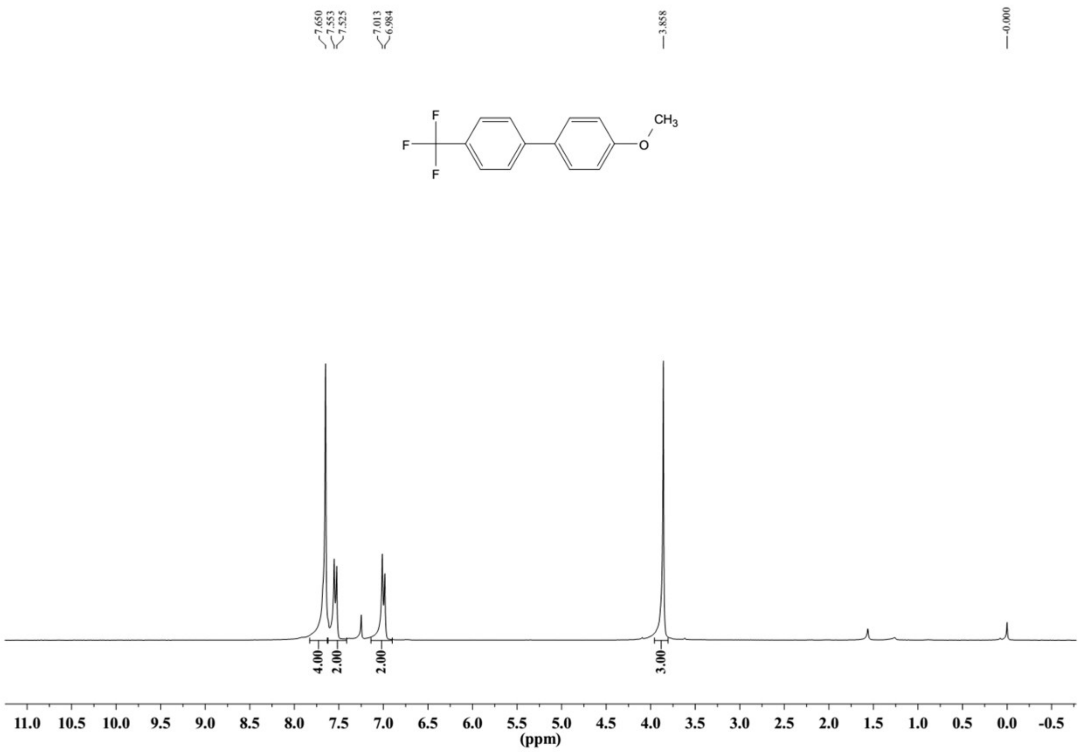


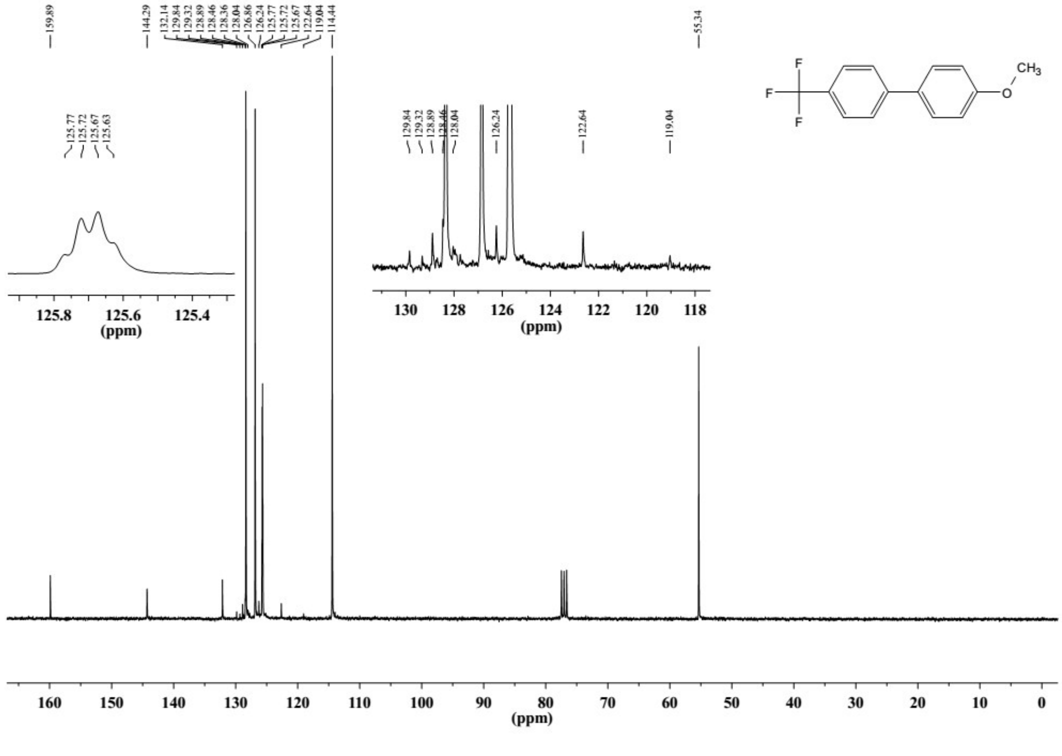
4, 4''-dimethoxy-1,1':2',1''-terphenyl (1n)



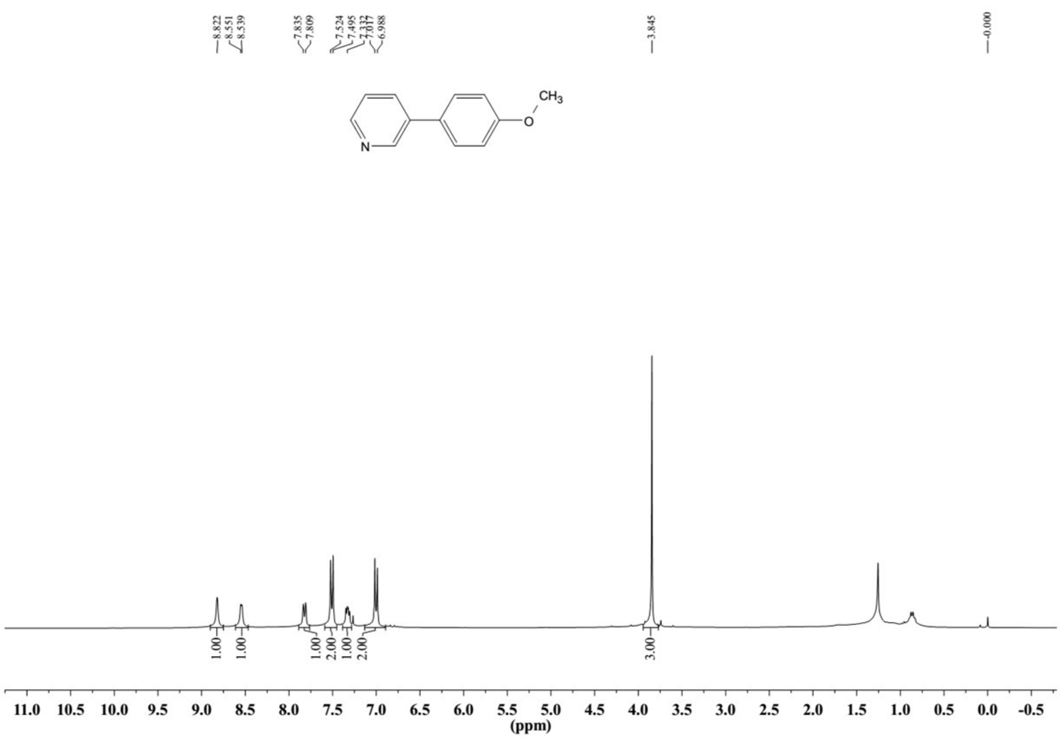


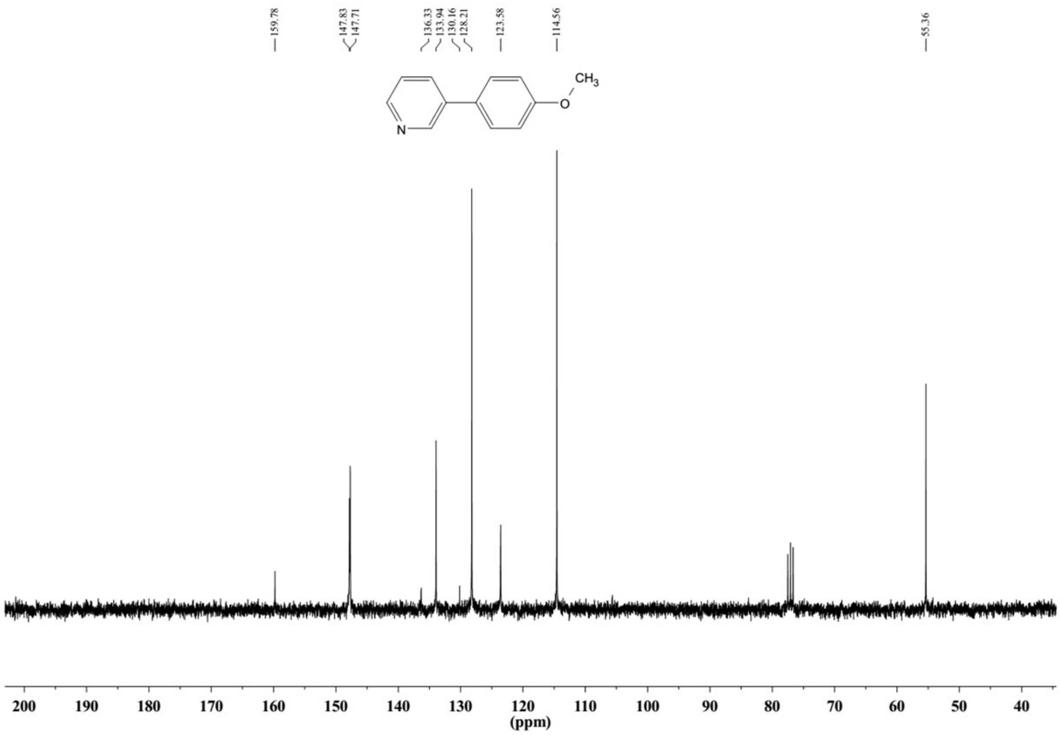
4-(4-Trifluoromethylphenyl)anisole (1o)



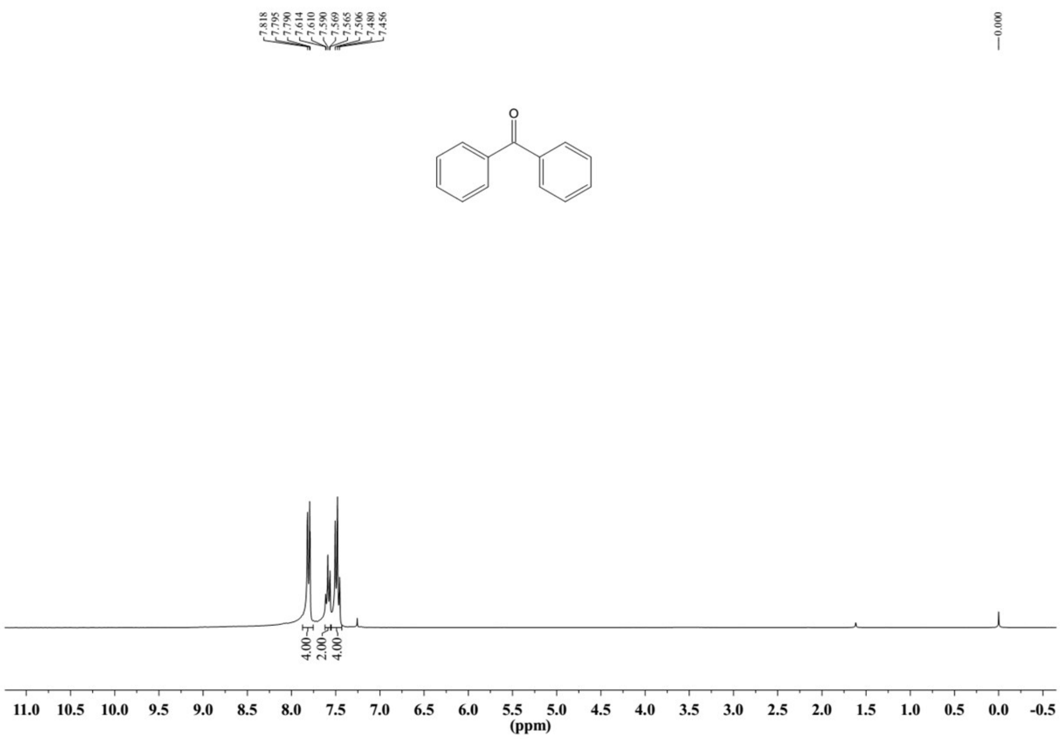


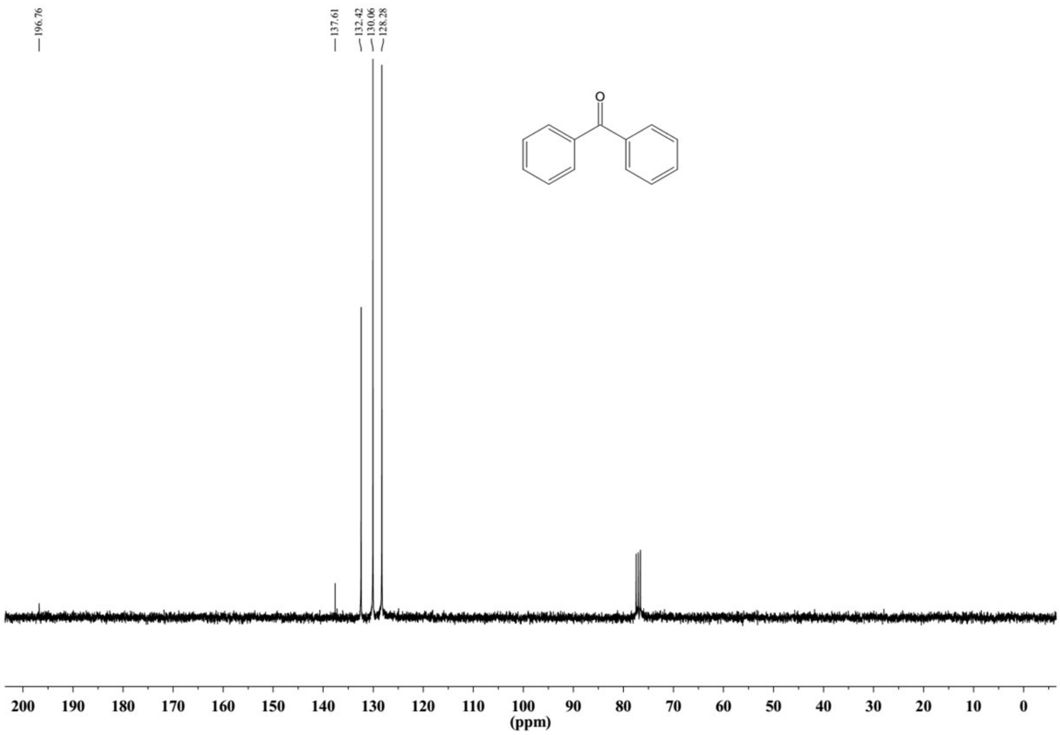
3-(4-Methoxyphenyl) pyridine (1p)



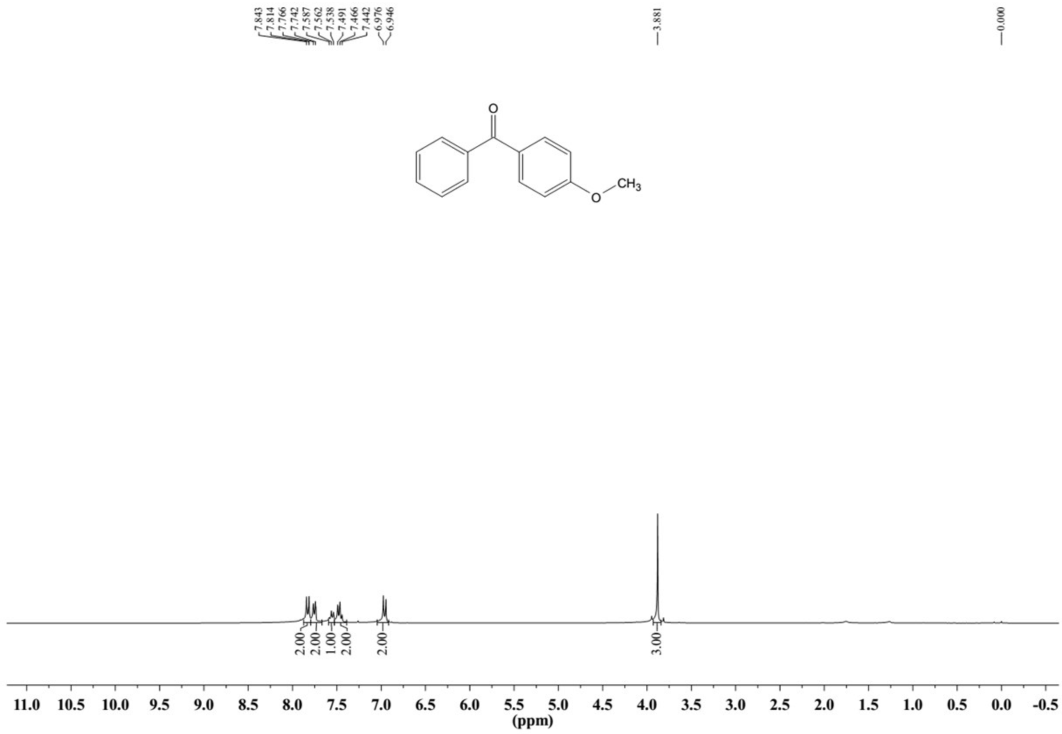


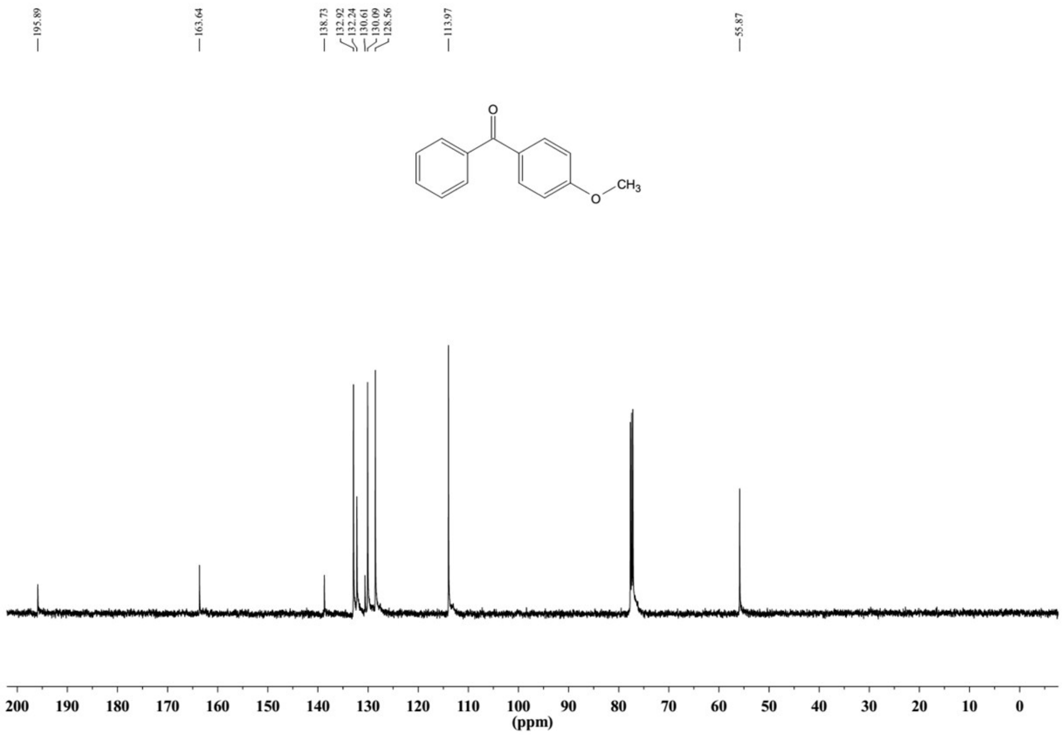
Benzophenone (2a)



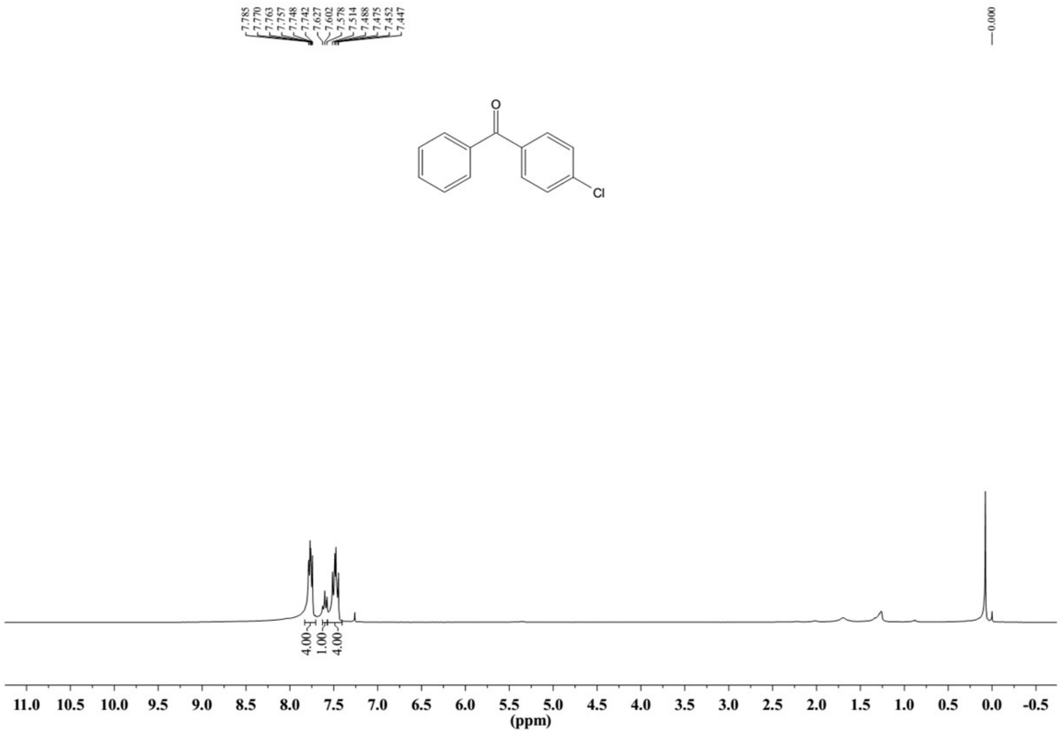


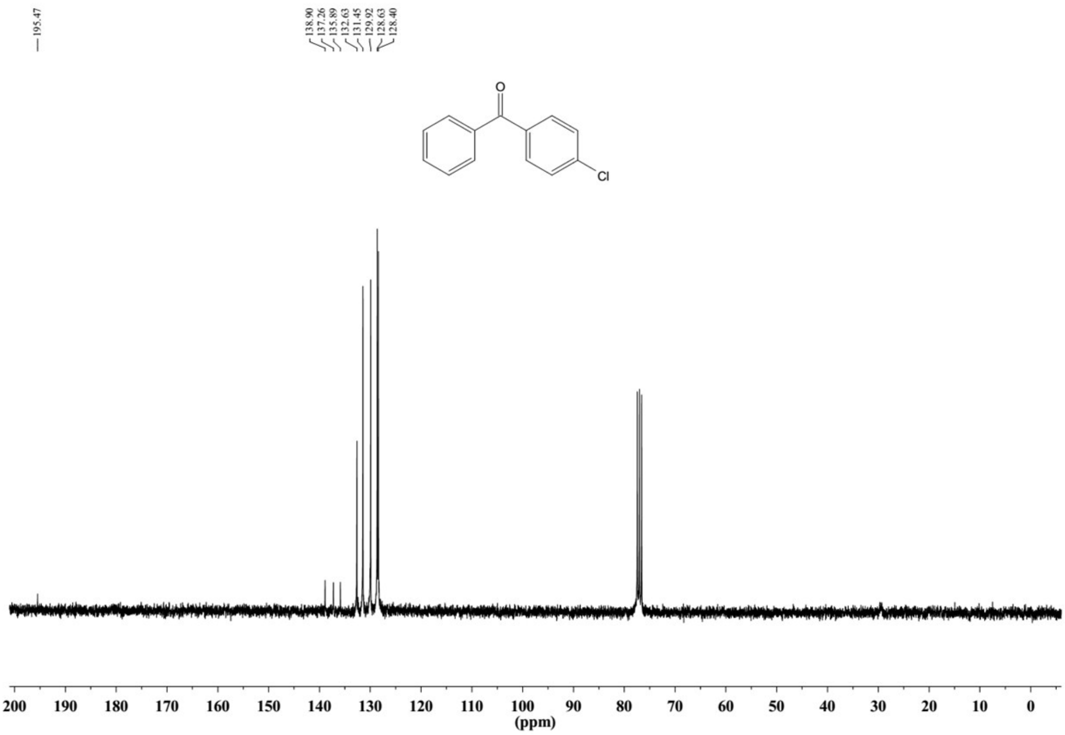
(4-Methoxyphenyl)(phenyl)methanone (2b)



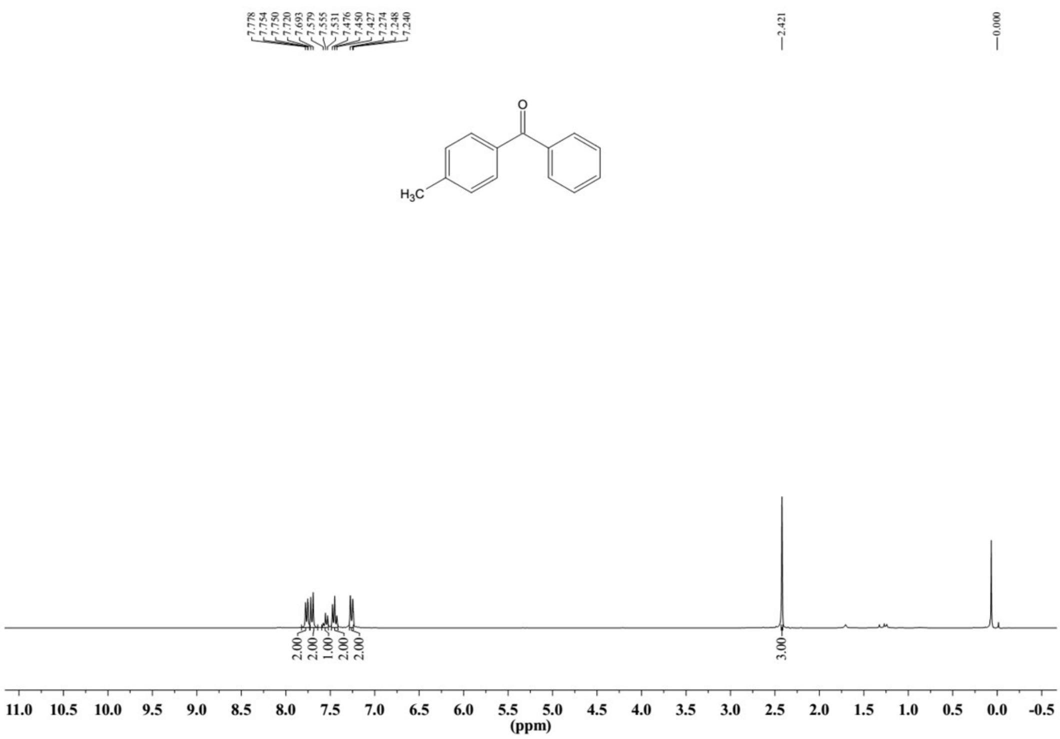


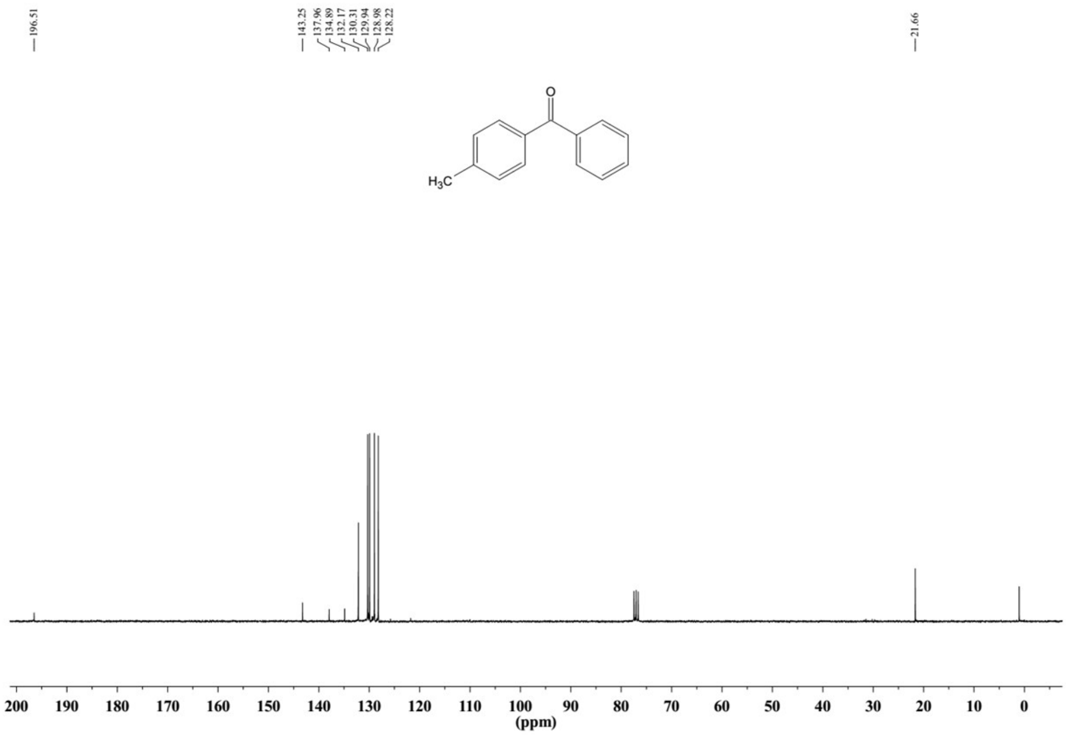
(4-Chlorophenyl)(phenyl)methanone (2c)



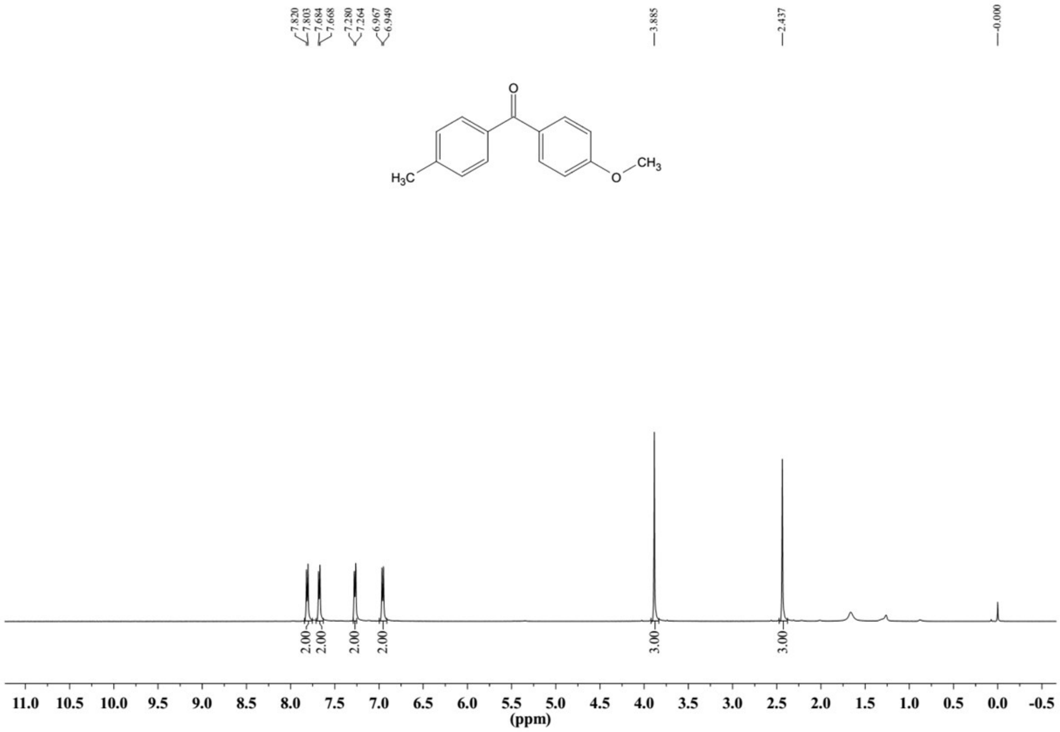


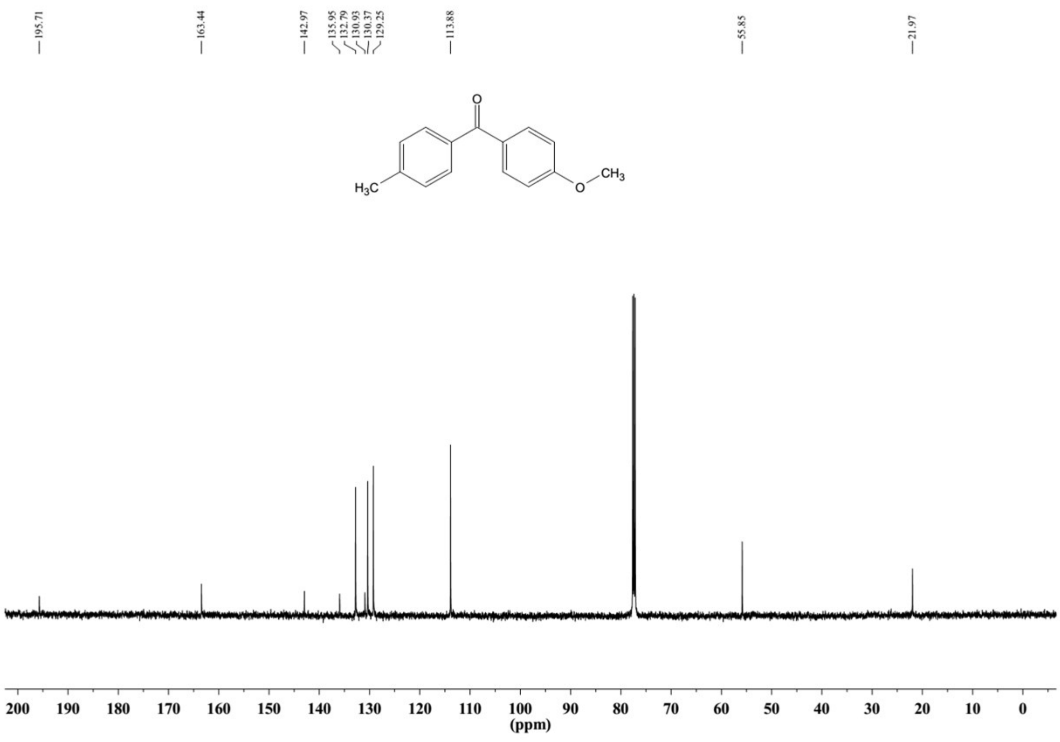
Phenyl(p-tolyl)methanone (2d)



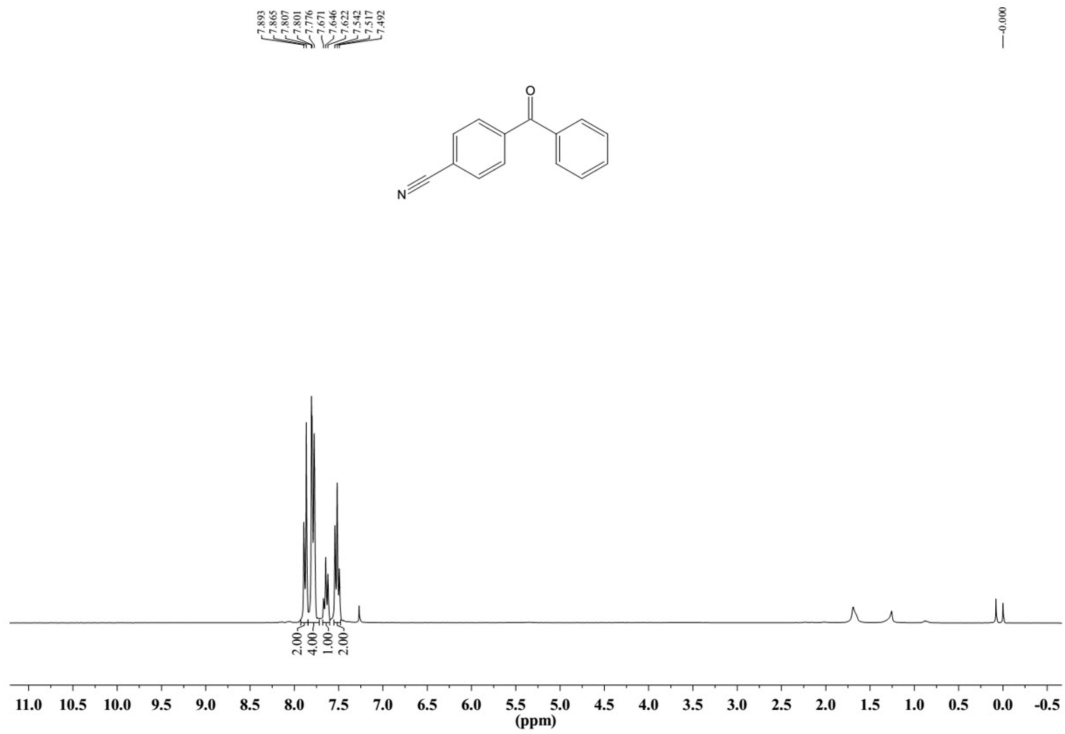


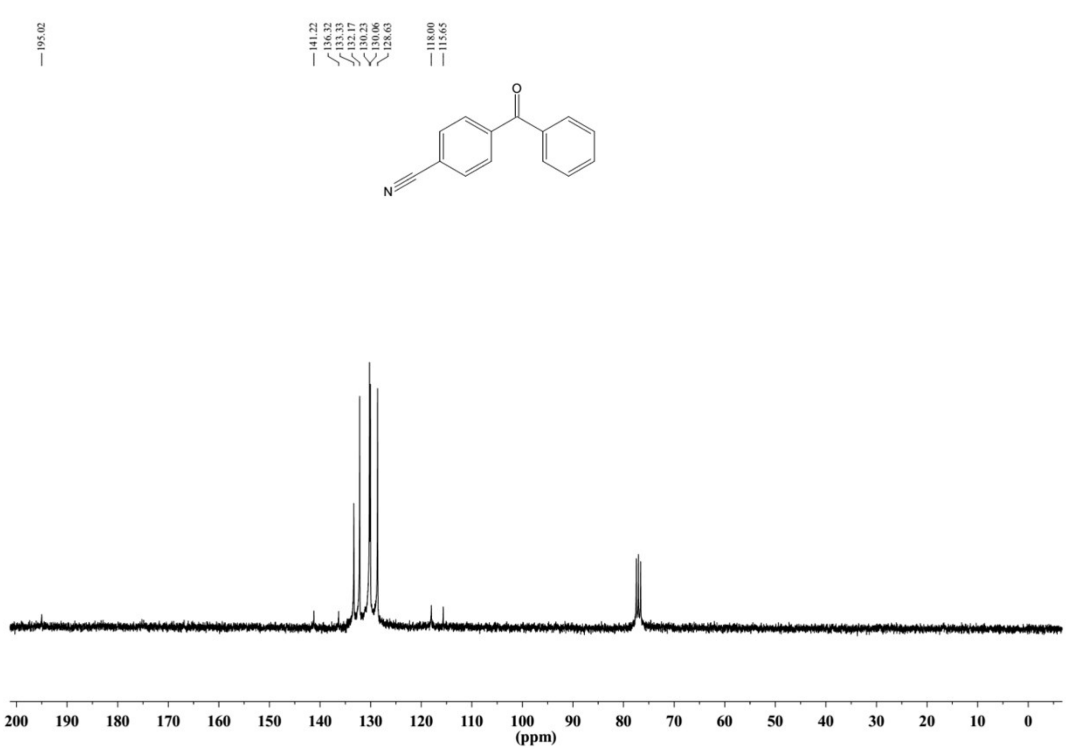
(4-Methoxyphenyl)(p-tolyl)methanone (2e)



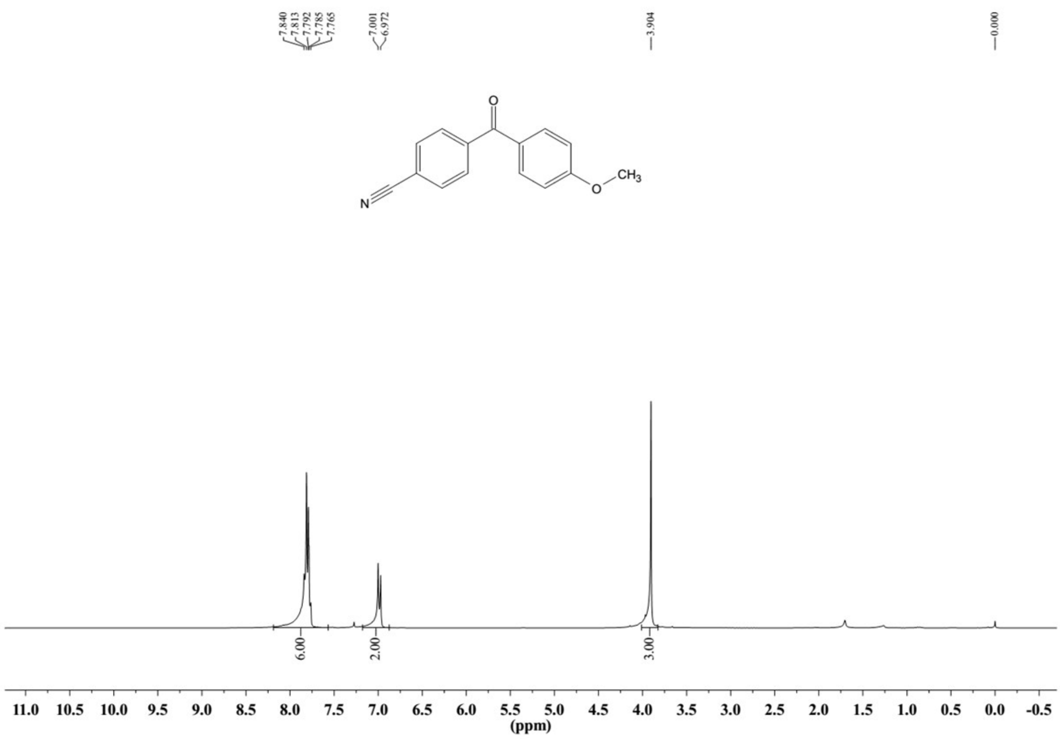


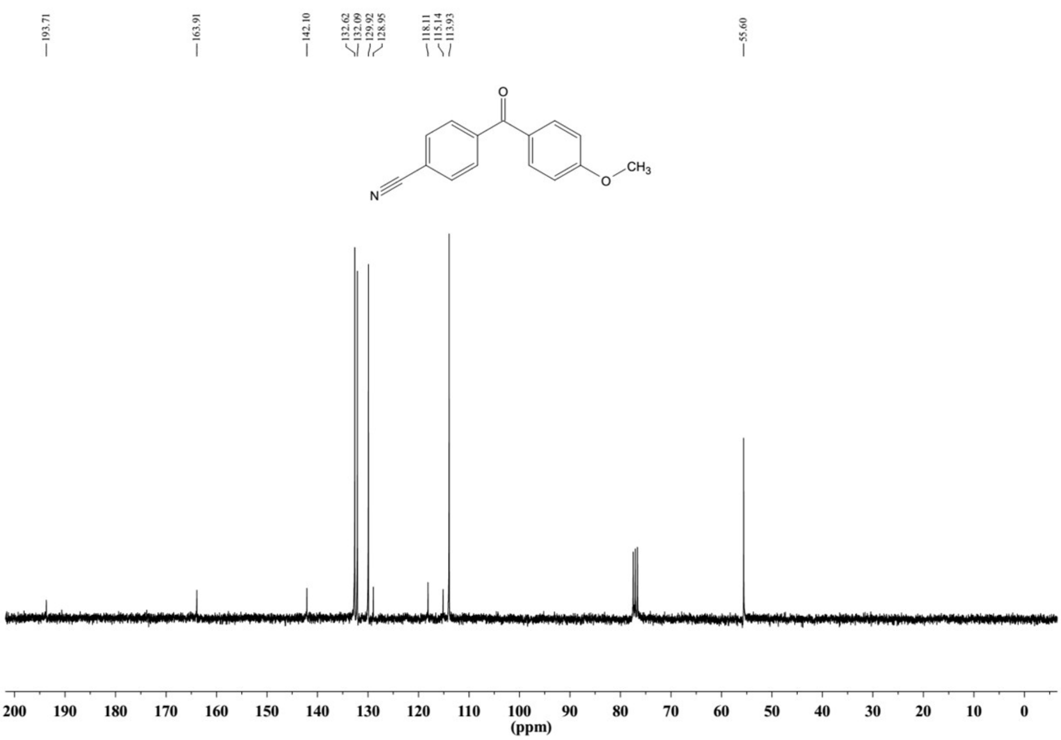
4-Benzoylbenzonitrile (2f)



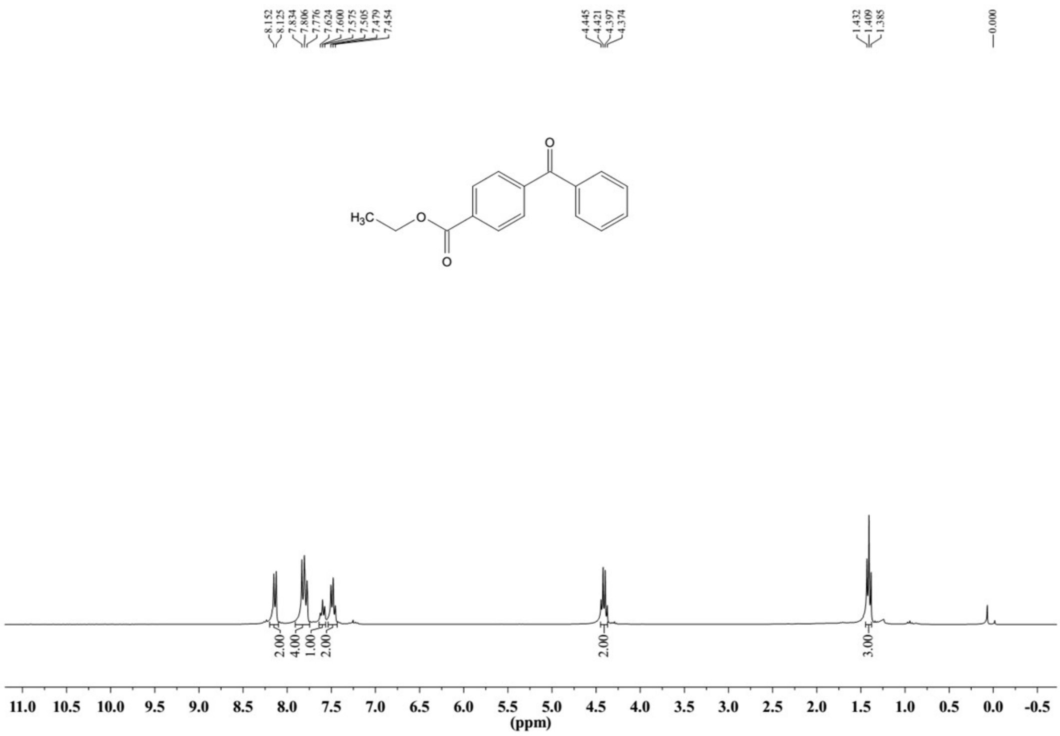


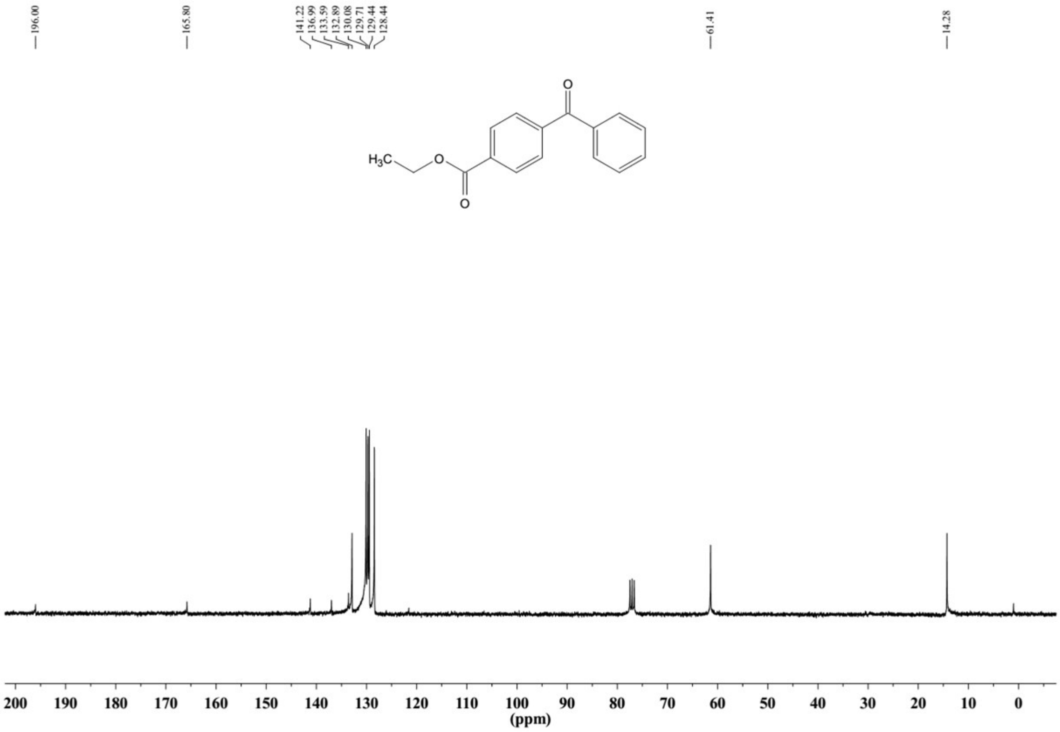
4-(4-Methoxybenzoyl)benzonitrile (2g)



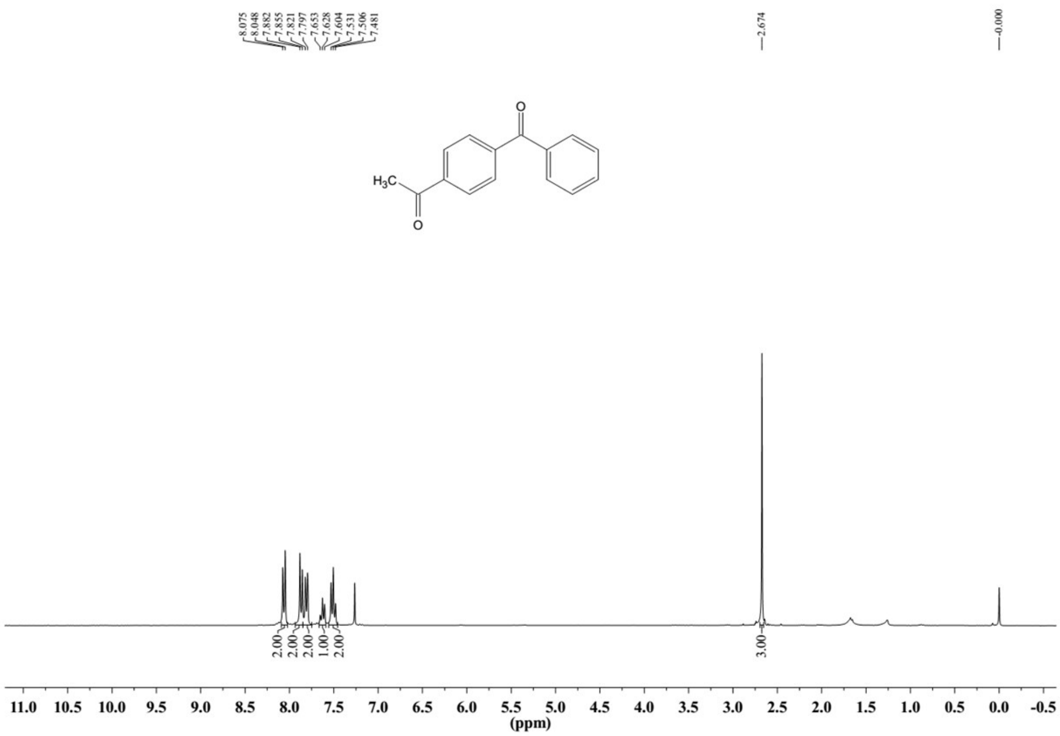


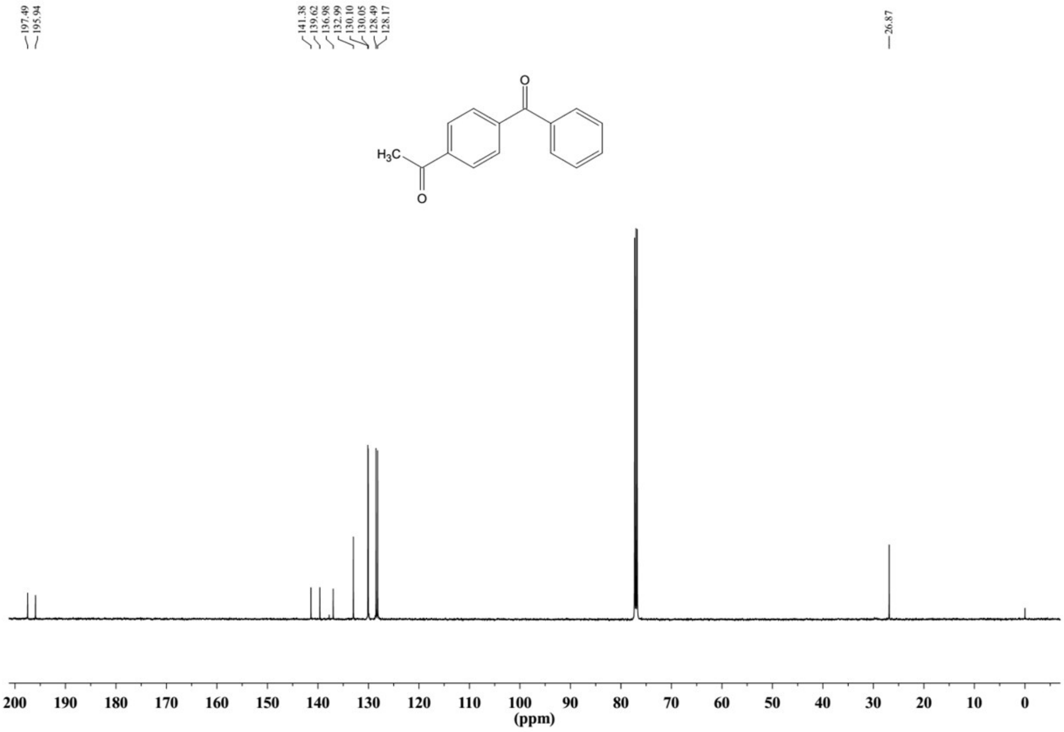
Ethyl 4-benzoylbenzoate (2h)



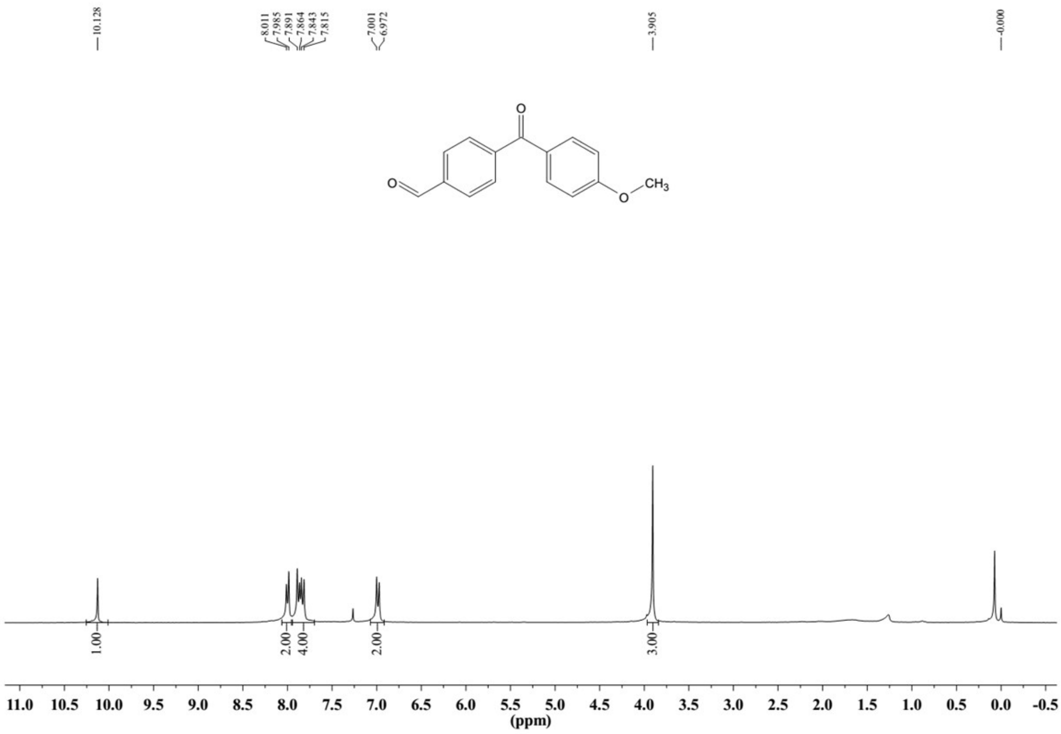


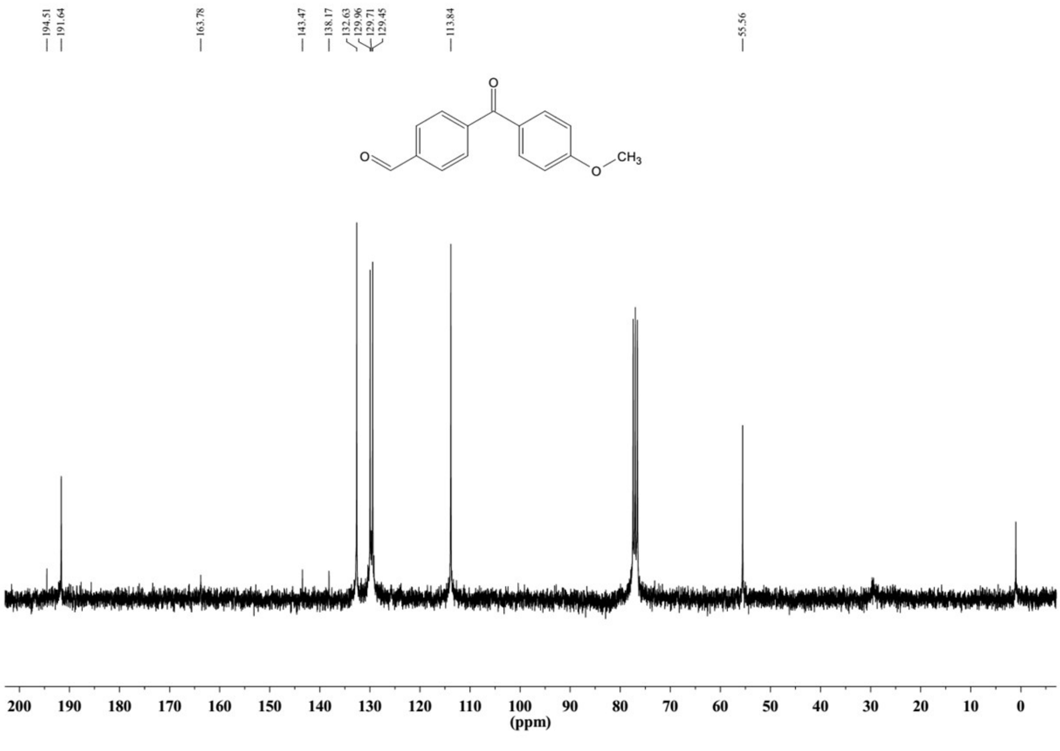
1-(4-Benzoylphenyl)ethanone (2i)



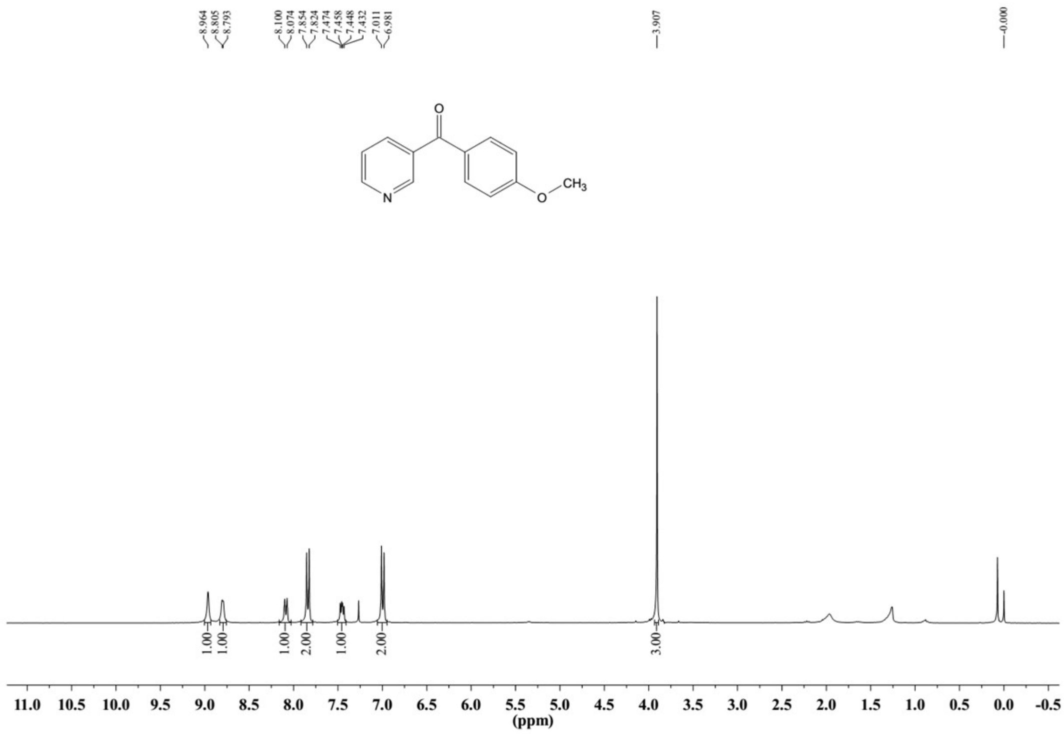


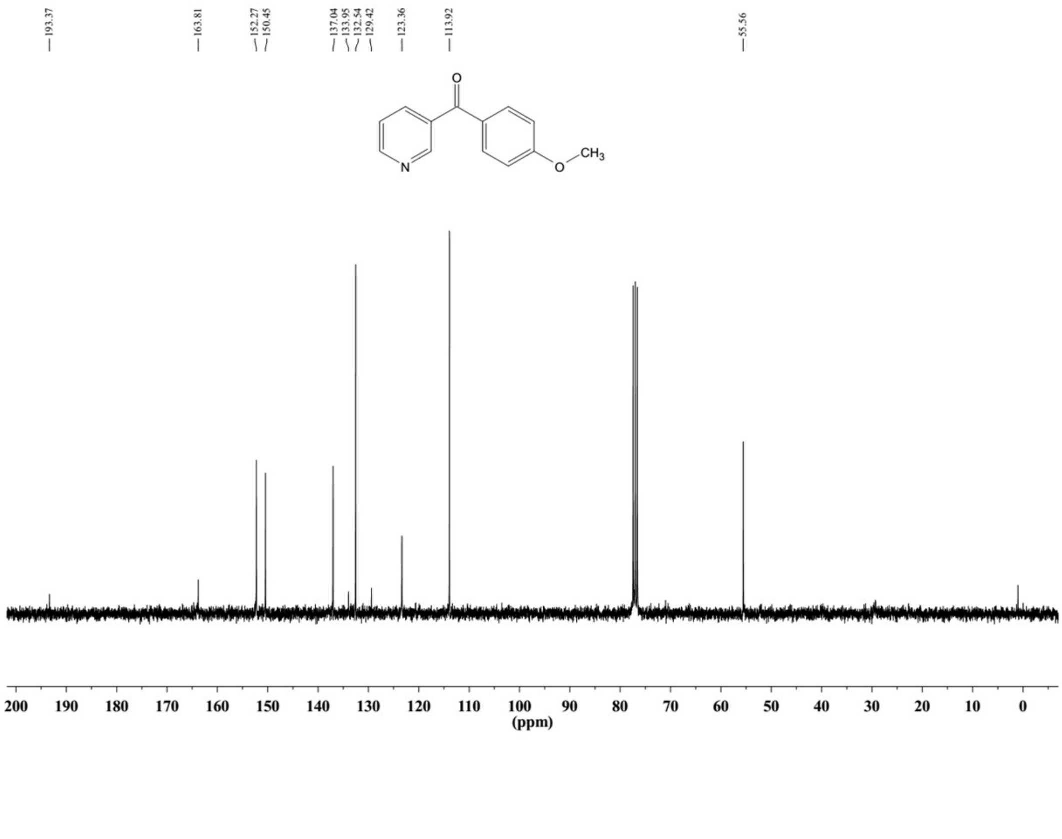
4-(4-Methoxybenzoyl)benzaldehyde (2j)





(4-Methoxyphenyl)(pyridin-3-yl)methanone (2k)





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