

Palladium-catalyzed Suzuki cross-coupling of *N'*-tosyl arylhydrazines

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Supporting Information

- 1. General procedures**
- 2. Typical procedure for Suzuki cross-coupling of *N'*-tosyl arylhydrazines with organoboron reagents**
- 3. Characterization of the products**
- 4. NMR spectra of the compounds**

1. General procedures

The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ¹H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer and referenced internally to the residual proton resonance in CDCl₃ ($\delta = 7.26$ ppm), or with tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), bs (broad singlet). ¹³C NMR spectra were recorded on Bruker spectrometer with complete proton decoupling, and chemical shifts were reported in ppm from TMS with the solvent as the internal reference (CDCl₃, $\delta = 77.0$ ppm). High resolution mass spectra were recorded on an ESI-ion trap mass spectrometer (Shimadzu, LCMS-IT-TOF). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

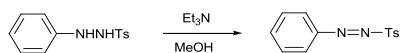
2.1 Typical procedure for Pd-catalyzed Suzuki cross-coupling of *N*'-tosyl arylhydrazines with aryl boronic acids

A mixture of *N*'-tosyl arylhydrazine **1** (0.2 mmol), aryl boronic acid **2** (0.24 mmol), Pd(OAc)₂ (0.004 mmol, 2 mol %), and K₂CO₃ (0.4 mmol, 2 equiv.) was stirred at 60 °C in MeOH (2 mL) for 2-12 h under N₂. After completion of the reaction (indicated by TLC), the mixture was quenched with saturated NaCl solution, extracted by EtOAc, and dried over Na₂SO₄. The crude product was purified by flash column chromatography to provide the corresponding product **3**.

2.2 Typical procedure for Pd-catalyzed Suzuki cross-coupling of *N*'-tosyl arylhydrazines with arylborane and boronic ester

A mixture of *N*'-tosyl arylhydrazine **1** (0.24 mmol), arylborane or boronic ester **2** (0.2 mmol), Pd(OAc)₂ (0.004 mmol, 2 mol %), and K₂CO₃ (0.4 mmol, 2 equiv.) was stirred at 60 °C in DMSO (1 mL) for 2-6 h under N₂. After completion of the reaction (indicated by TLC), the mixture was quenched with saturated NaCl solution, extracted by EtOAc, and dried over Na₂SO₄. The crude product was purified by flash column chromatography to provide the corresponding product **3**.

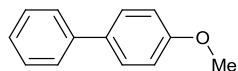
2.3 Procedure for the capture of 1-phenyl-2-tosyldiazene



A mixture of *N*'-tosyl phenylhydrazine **1a** (0.2 mmol) and Et₃N (0.4 mmol, 2 equiv.) in MeOH (1.0 mL) was stirred at room temperature for 2 h. The mixture was quenched with saturated NH₄Cl solution, extracted by EtOAc. The combined organic layer was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to provide 1-phenyl-2-tosyldiazene **1a'** in 26% yield.

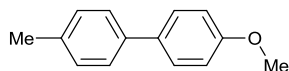
3. Characterization of the products

4-Methoxybiphenyl^[1]



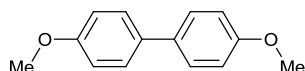
White solid; mp: 90-91 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.51 (m, 4H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.99-6.96 (m, 2H), 3.85 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 159.19, 140.86, 133.83, 128.69, 128.13, 126.73, 126.63, 114.23, 55.33.

4-Methoxy-4'-methylbiphenyl^[1]



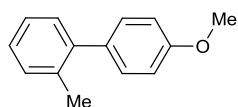
White solid; mp: 107-108 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 158.94, 137.98, 136.35, 133.77, 129.44, 127.95, 126.59, 114.17, 55.34, 21.04.

4, 4'-Dimethoxybiphenyl^[1]



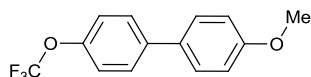
White solid; mp: 169-170 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8.6 Hz, 4H), 6.95 (d, *J* = 8.6 Hz, 4H), 3.84 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 158.71, 133.50, 127.73, 114.18, 55.34.

4'-Methoxy-2-methylbiphenyl^[3]



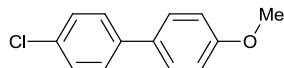
White solid; mp: 52-53 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.22 (m, 6H), 6.96-6.94 (m, 2H), 3.85 (s, 3H), 2.27 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 158.52, 141.56, 135.48, 134.39, 130.27, 130.24, 129.89, 126.95, 125.73, 113.49, 55.28, 20.52.

4-Methoxy-4'-(trifluoromethoxy) biphenyl^[12]



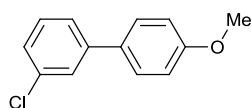
White solid; mp: 95-97 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 3.3 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 159.44, 148.19, 139.63, 132.37, 128.14, 127.95, 121.20, 114.33, 55.35.

4-Chloro-4'-methoxybiphenyl^[3]



White solid; mp: 110-111 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.50 (dd, *J* = 10.6, 3.6 Hz, 4H), 7.40-7.38 (m, 2H), 7.00-6.98 (m, 2H), 3.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 159.38, 139.28, 132.68, 132.51, 128.83, 128.01, 127.93, 114.32, 55.36.

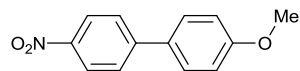
3-Chloro-4'-methoxybiphenyl^[3]



White solid; mp: 52-53 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.53-7.48 (m, 3H), 7.43-7.40 (m, 1H),

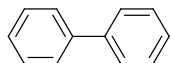
7.33 (t, $J = 7.8$ Hz, 1H), 7.28-7.25 (m, 1H), 6.98-6.96 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 159.59, 142.67, 134.60, 132.30, 129.92, 128.15, 126.82, 126.62, 124.83, 114.33, 55.36.

4-Methoxy-4'-nitrobiphenyl^[1]



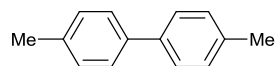
Yellow solid; mp: 104-105 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.27 (d, $J = 8.8$ Hz, 2H), 7.69 (d, $J = 8.8$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 160.46, 147.21, 146.57, 131.09, 128.56, 127.07, 124.13, 114.62, 55.42.

Biphenyl^[1]



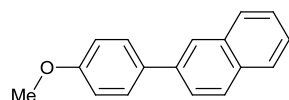
White solid; mp: 68-69 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, $J = 7.4$ Hz, 4H), 7.47 (t, $J = 7.7$ Hz, 4H), 7.37 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ 141.25, 128.74, 127.24, 127.16.

4, 4'-Dimethylbiphenyl^[2]



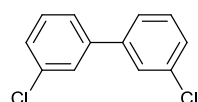
White solid; mp: 119-120 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.51 (d, $J = 8.0$ Hz, 4H), 7.27 (d, $J = 7.8$ Hz, 4H), 2.42 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 138.31, 136.70, 129.44, 126.82, 21.08.

2-(4-Methoxyphenyl) naphthalene^[4]



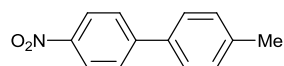
White solid; mp: 130-132 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.89 (dd, $J = 15.8, 9.4$ Hz, 3H), 7.71 (dd, $J = 20.9, 8.6$ Hz, 3H), 7.53-7.45 (m, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 159.25, 138.16, 133.76, 133.65, 132.32, 128.42, 128.33, 128.04, 127.61, 126.22, 125.64, 125.43, 125.03, 114.32, 55.38.

3, 3'-Dichlorobiphenyl^[2]



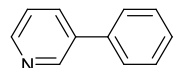
Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, $J = 0.6$ Hz, 2H), 7.45 (dd, $J = 7.0, 0.9$ Hz, 2H), 7.41-7.35 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3): δ 140.62, 133.82, 129.11, 126.87, 126.26, 124.25.

4-Methyl-4'-nitrobiphenyl^[1]



Yellow solid; mp: 140-141 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.28 (d, $J = 8.5$ Hz, 2H), 7.71 (d, $J = 8.6$ Hz, 2H), 7.53 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 147.58, 146.87, 139.08, 135.86, 129.88, 127.47, 127.21, 124.09, 21.19.

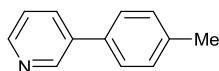
3-Phenylpyridine^[5]



Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.85 (d, $J = 2.1$ Hz, 1H), 8.60-8.58 (m, 1H), 7.88 (dt,

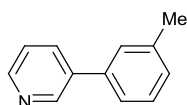
$J = 7.9, 1.6$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.43-7.40 (m, 1H), 7.39-7.35 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 148.31, 148.19, 137.77, 136.73, 134.48, 129.09, 128.14, 127.15, 123.59.

3-*p*-Tolylpyridine^[5]



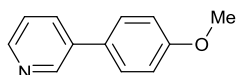
Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.83 (s, 1H), 8.56 (d, $J = 4.7$ Hz, 1H), 7.86-7.84 (m, 1H), 7.48 (d, $J = 7.3$ Hz, 2H), 7.34 (dd, $J = 7.8, 4.9$ Hz, 1H), 7.27 (dd, $J = 11.1, 4.3$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 148.18, 148.16, 138.03, 136.58, 134.93, 134.14, 129.80, 126.97, 123.50, 21.13.

3-*m*-Tolylpyridine^[5]



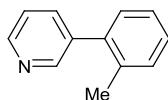
Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.84 (s, 1H), 8.58 (d, $J = 4.4$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.39-7.33 (m, 4H), 7.22 (d, $J = 4.5$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 148.35, 138.76, 137.82, 136.78, 134.36, 128.98, 128.84, 127.91, 124.25, 123.49, 21.50.

3-(4-Methoxyphenyl)pyridine^[3]



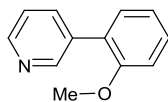
Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.82 (s, 1H), 8.54 (d, $J = 4.0$ Hz, 1H), 7.83 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.52 (d, $J = 8.7$ Hz, 2H), 7.33 (dd, $J = 7.8, 4.9$ Hz, 1H), 7.01 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 159.78, 147.98, 147.85, 133.86, 130.26, 128.22, 123.50, 114.56, 55.38.

3-*o*-Tolylpyridine^[14]



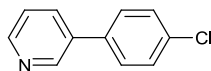
Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.59 (dd, $J = 4.7, 1.5$ Hz, 2H), 7.67-7.64 (m, 1H), 7.36-7.26 (m, 4H), 7.22 (d, $J = 7.0$ Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 149.95, 148.10, 138.09, 137.47, 136.48, 135.59, 130.56, 129.86, 128.11, 126.07, 123.00, 20.38.

3-(2-Methoxyphenyl)pyridine^[15]



Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.78 (s, 1H), 8.56 (d, $J = 4.3$ Hz, 1H), 7.87 (d, $J = 7.1$ Hz, 1H), 7.40-7.32 (m, 3H), 7.09-7.01 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 156.58, 150.26, 147.90, 136.80, 134.22, 130.65, 129.54, 127.06, 122.87, 121.05, 111.30, 55.52.

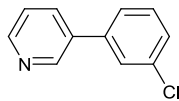
3-(4-Chlorophenyl)pyridine^[5]



Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.82 (d, $J = 2.0$ Hz, 1H), 8.61 (d, $J = 4.8$ Hz, 1H), 7.84 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.37 (dd, $J = 7.9, 4.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 148.77, 148.11, 136.28, 135.52, 134.40, 134.20,

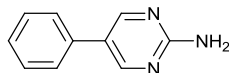
129.29, 128.39, 123.61.

3-(3-Chlorophenyl)pyridine^[6]



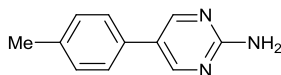
Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, *J* = 2.3 Hz, 1H), 8.50 (dd, *J* = 4.8, 1.3 Hz, 1H), 7.74-7.71 (m, 1H), 7.45 (t, *J* = 1.7 Hz, 1H), 7.35-7.14 (m, 4H); ¹³C NMR (101 MHz, CDCl₃): δ 148.04, 147.21, 138.67, 134.36, 134.03, 133.36, 129.32, 127.15, 126.29, 124.30, 122.62.

5-Phenylpyrimidin-2-amine^[7]



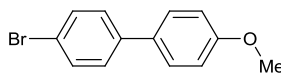
White solid; mp: 161-163 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.54 (s, 2H), 7.48-7.44 (m, 4H), 7.37 (d, *J* = 6.3 Hz, 1H), 5.13 (s, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 162.23, 156.50, 135.25, 129.15, 127.58, 126.06, 125.03.

5-*p*-Tolylpyrimidin-2-amine^[7]



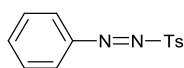
White solid; mp: 192-193 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.51 (s, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 5.33 (s, 2H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 162.13, 156.31, 137.44, 132.34, 129.85, 125.90, 124.95, 21.10.

4-Bromo-4'-methoxybiphenyl^[11]



White solid; mp: 143-144 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.50 (dd, *J* = 17.3, 7.1 Hz, 4H), 7.41 (d, *J* = 6.9 Hz, 2H), 6.97 (d, *J* = 7.0 Hz, 2H), 3.85 (s, 3H).

1-Phenyl-2-tosyldiazene^[10]



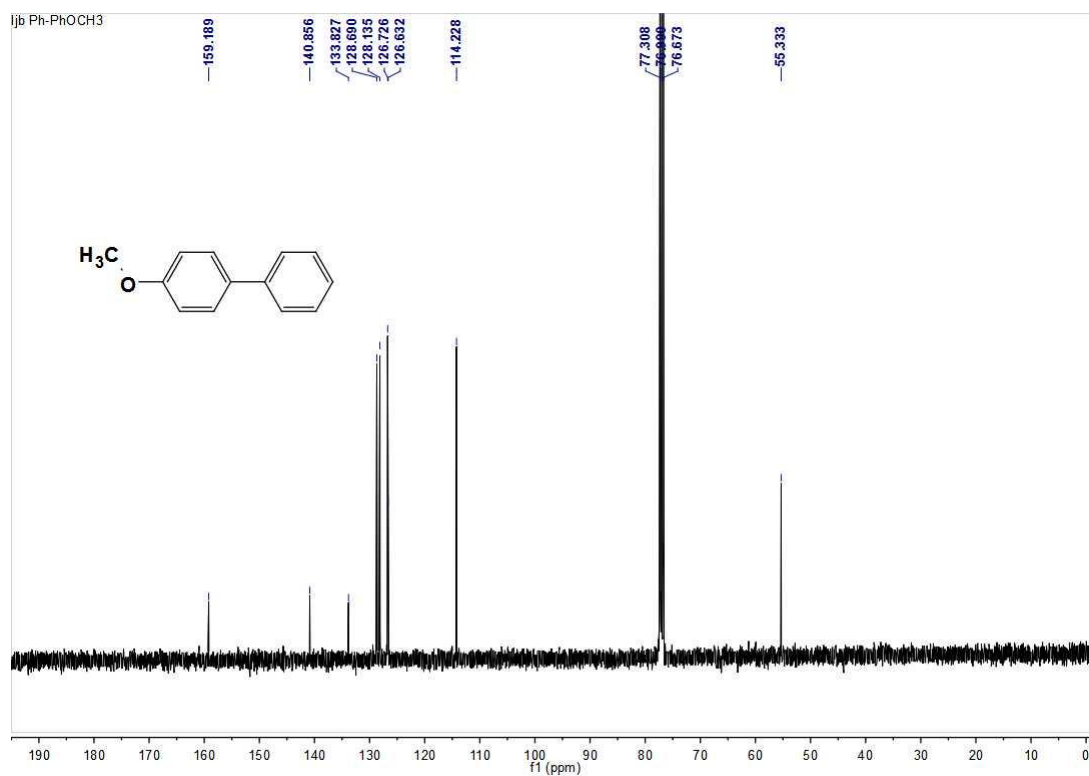
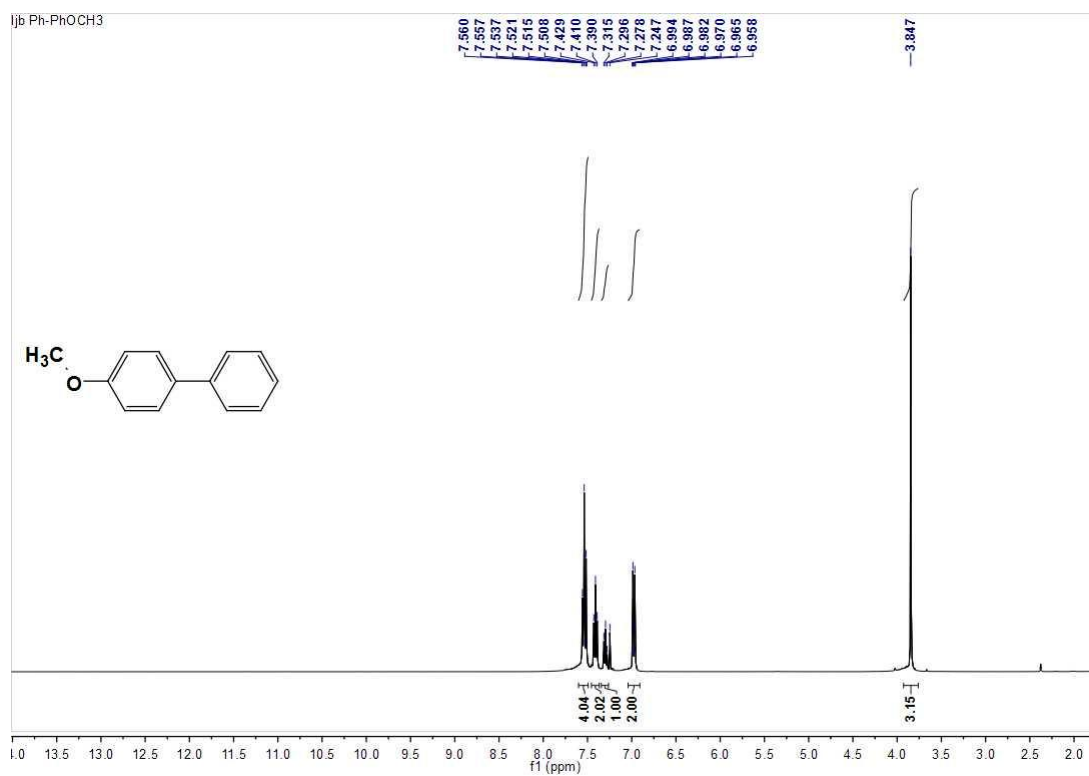
Orange solid; mp: 90-91 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 149.17, 146.01, 134.79, 130.39, 130.00, 129.89, 129.48, 124.50, 21.80.

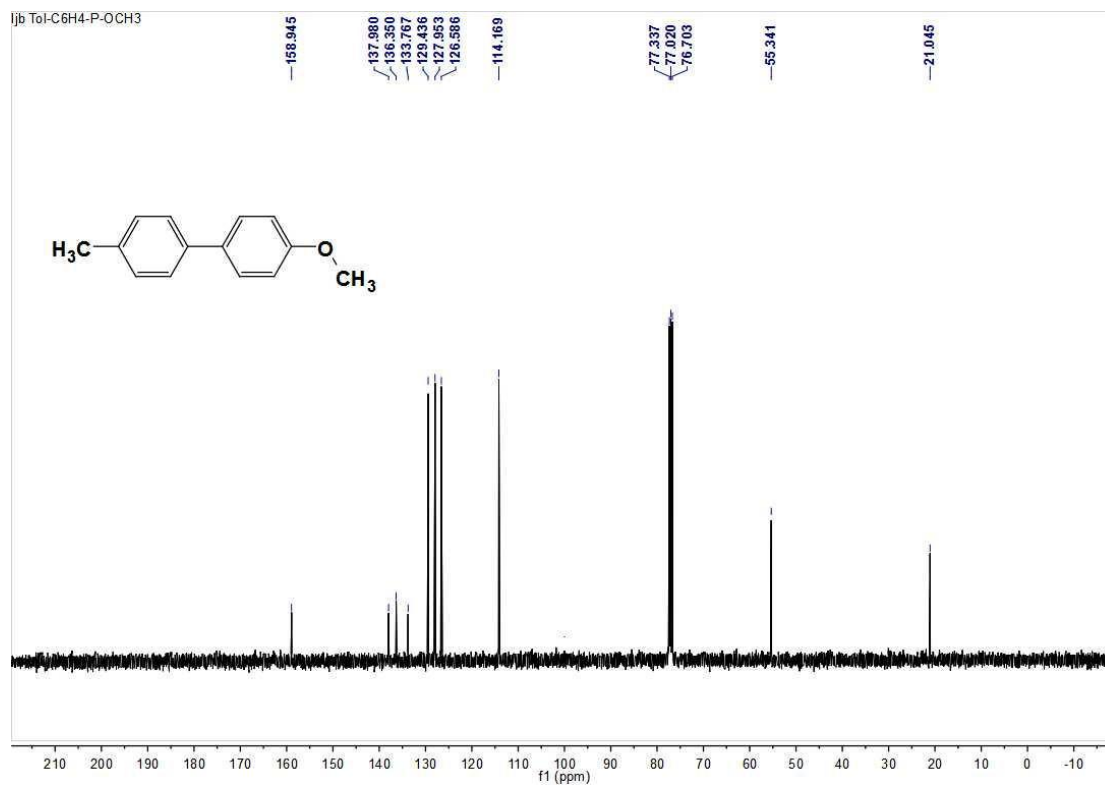
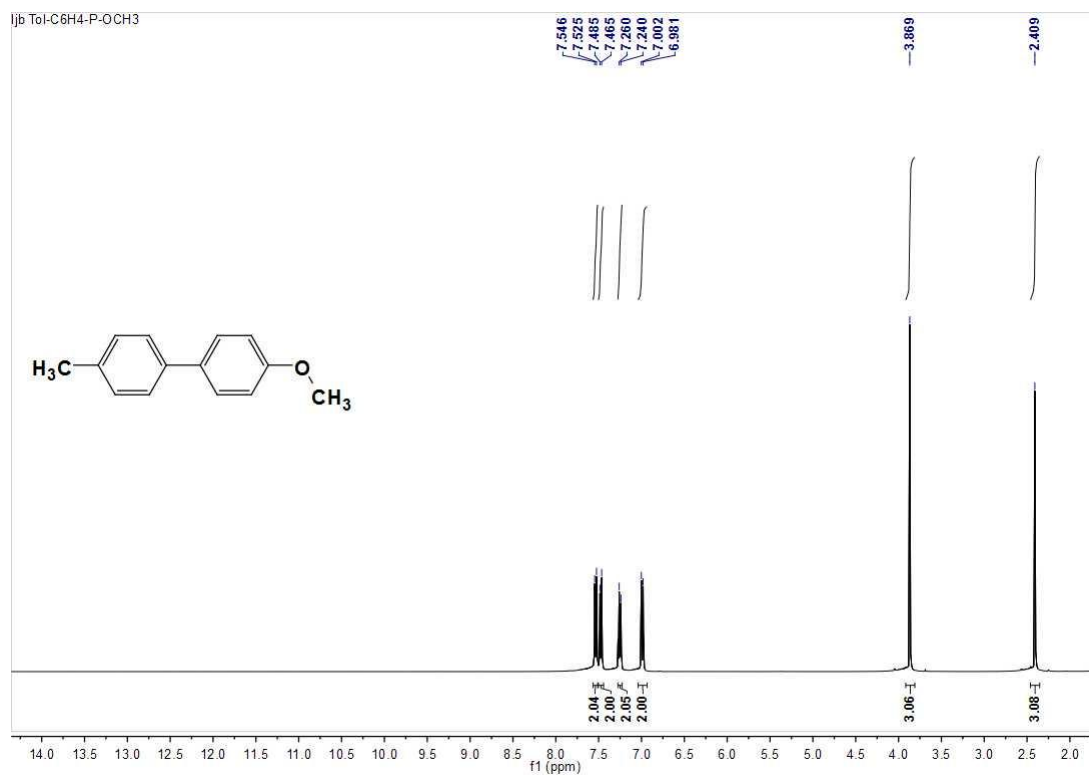
Reference

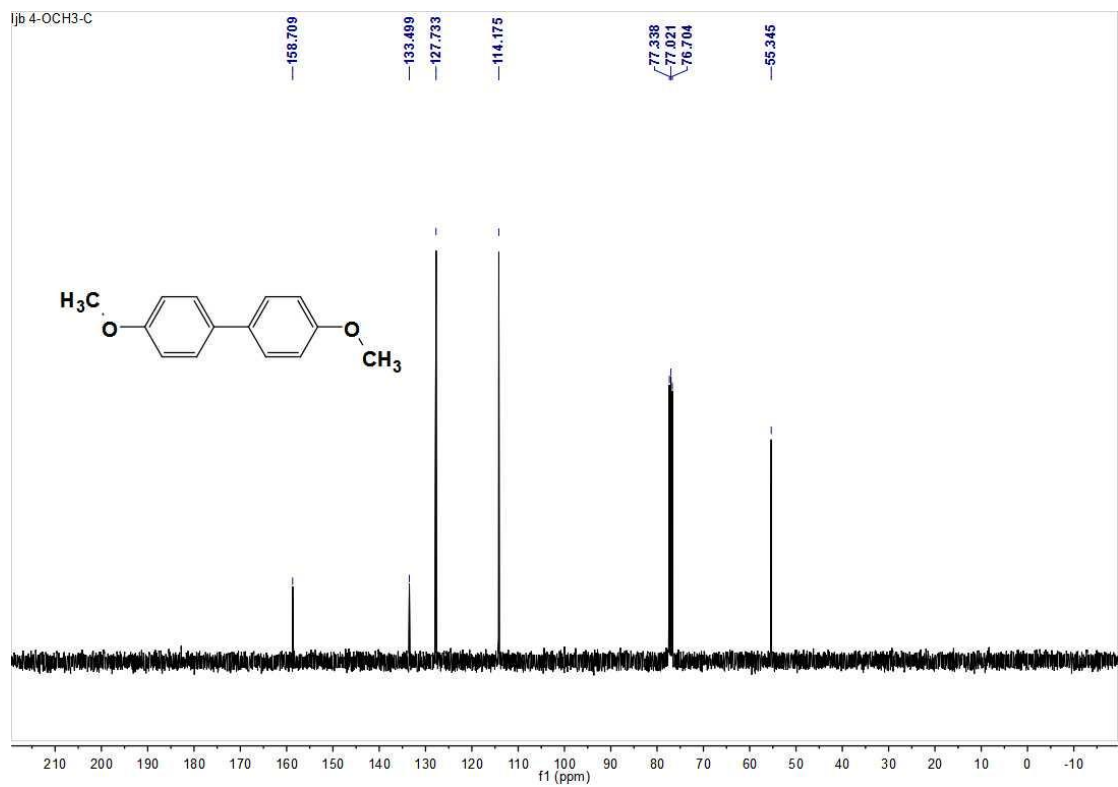
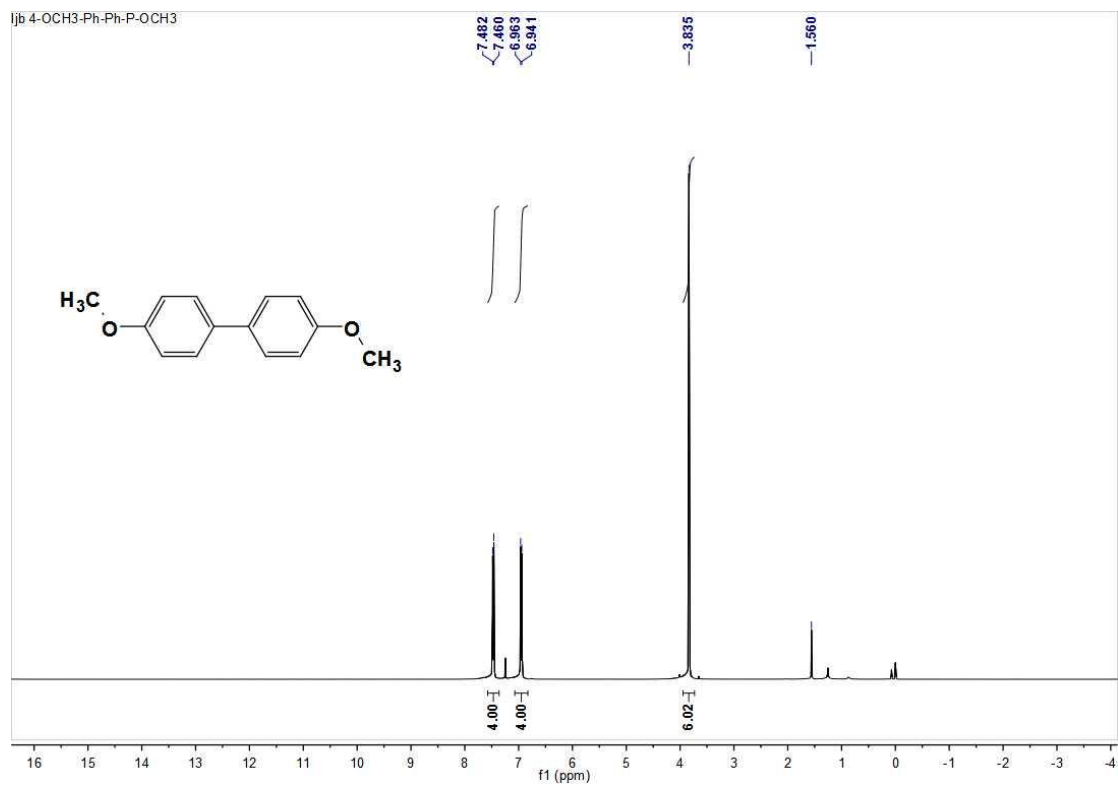
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- [2] M. Zeng, Y. Du, L. Shao, C. Qi, X.-M. Zhang, *J. Org. Chem.* **2010**, *75*, 2556.
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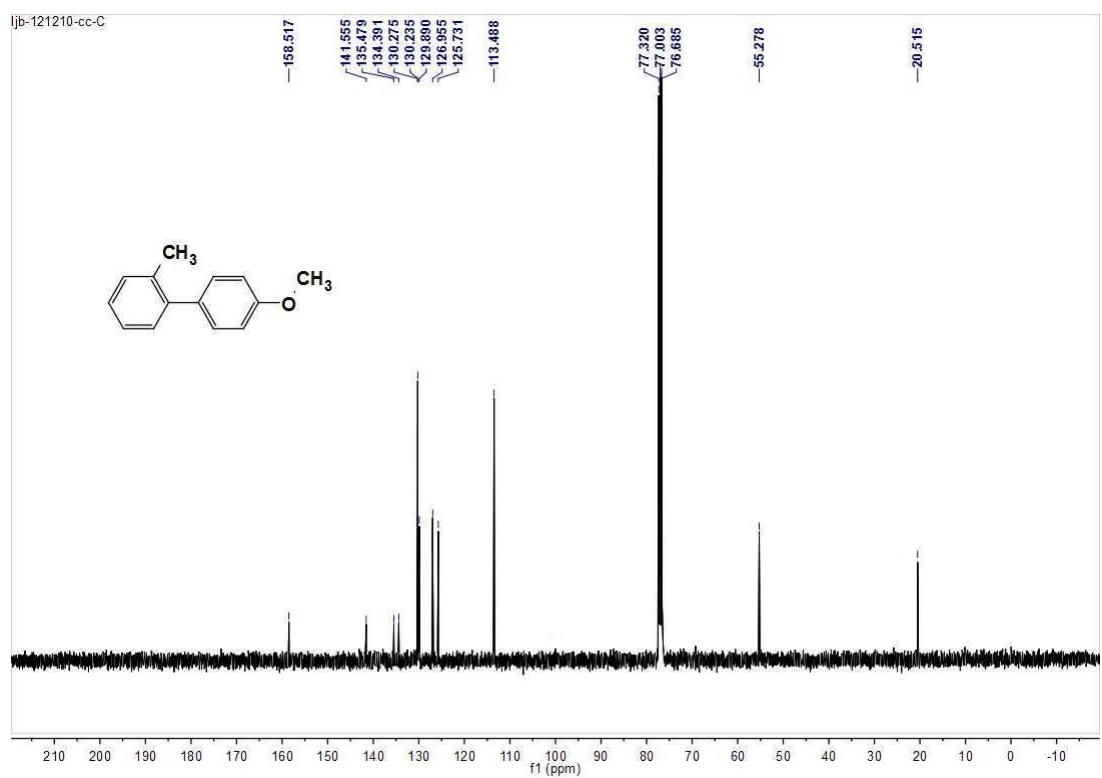
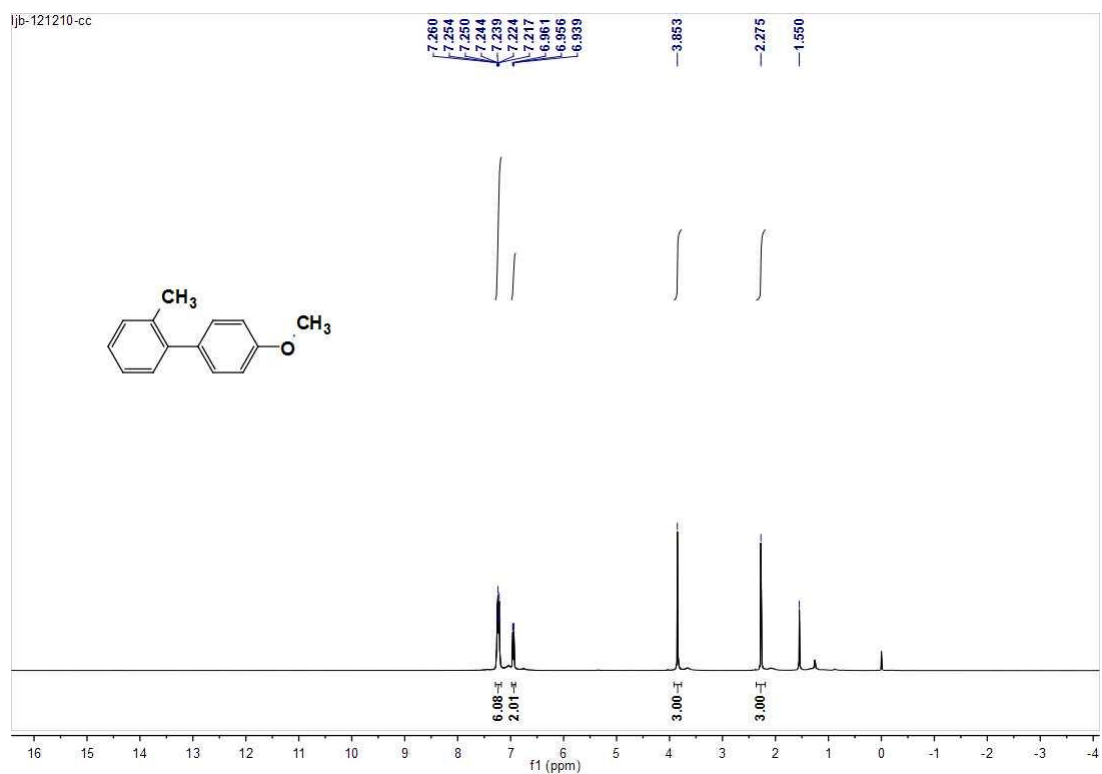
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4. NMR spectra of the compounds

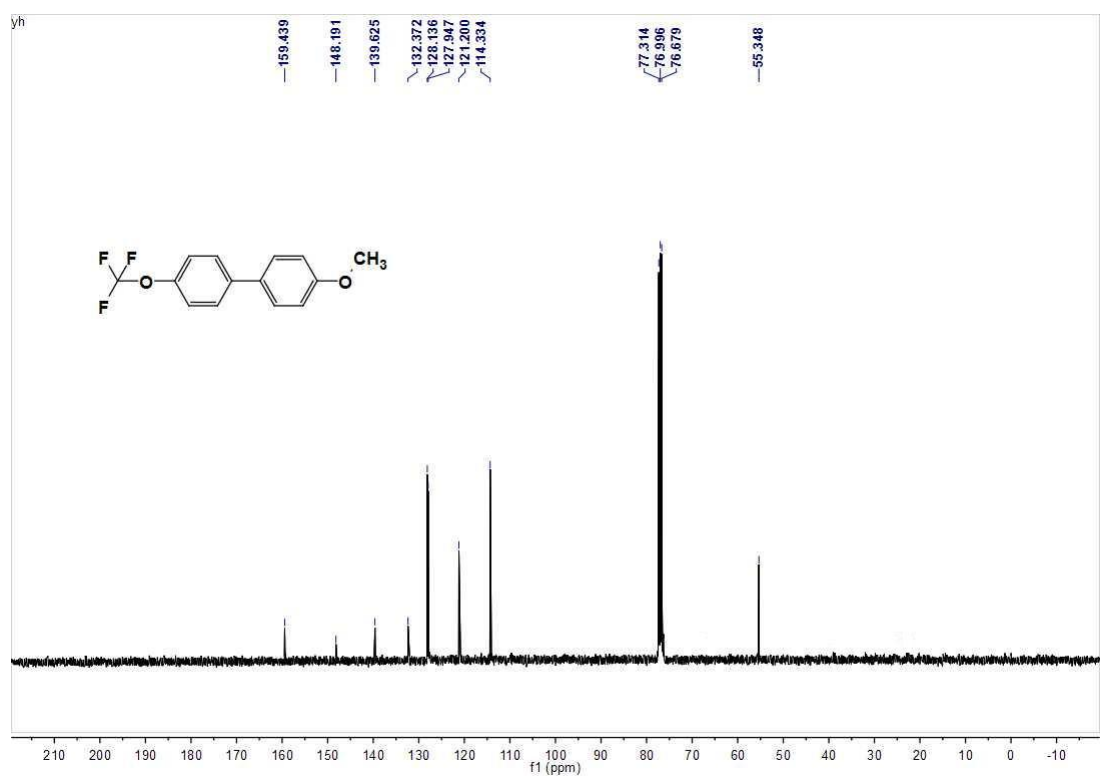
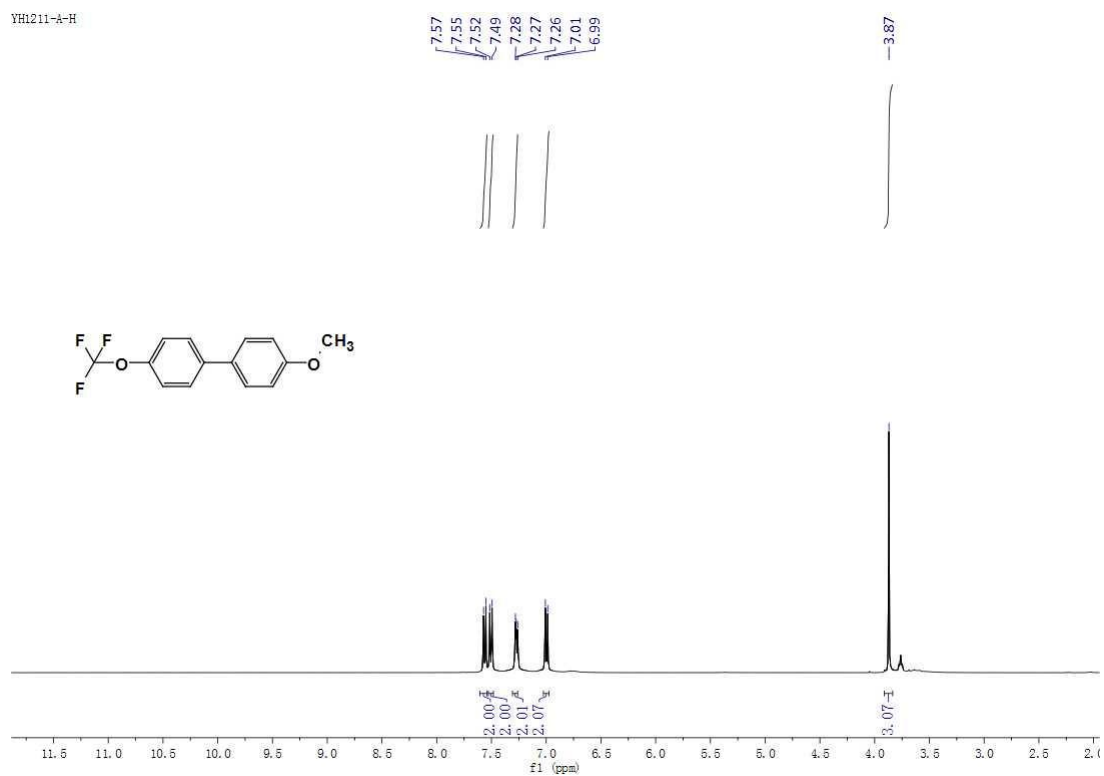


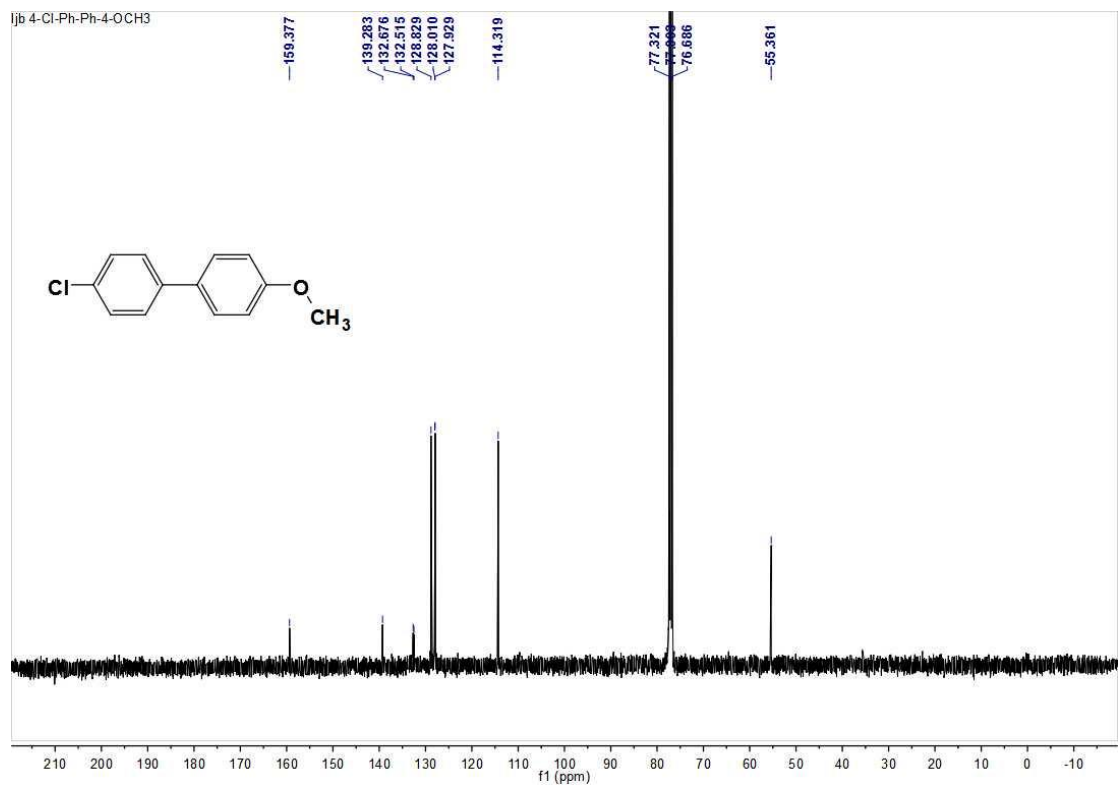
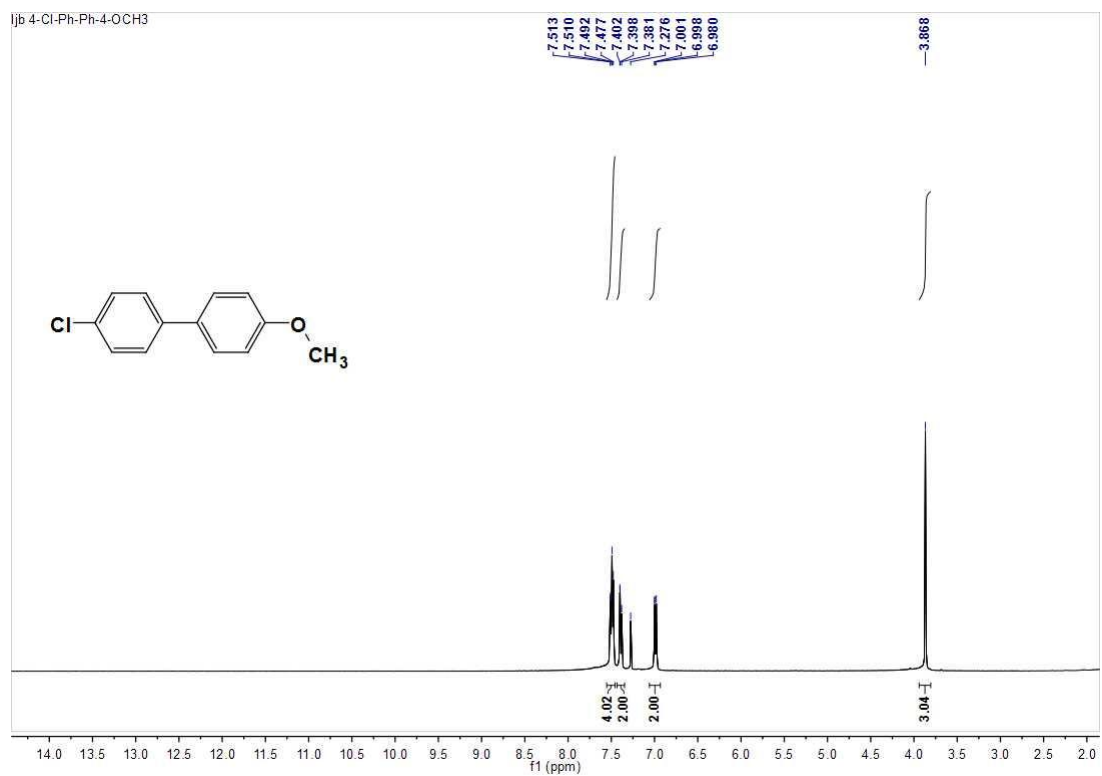


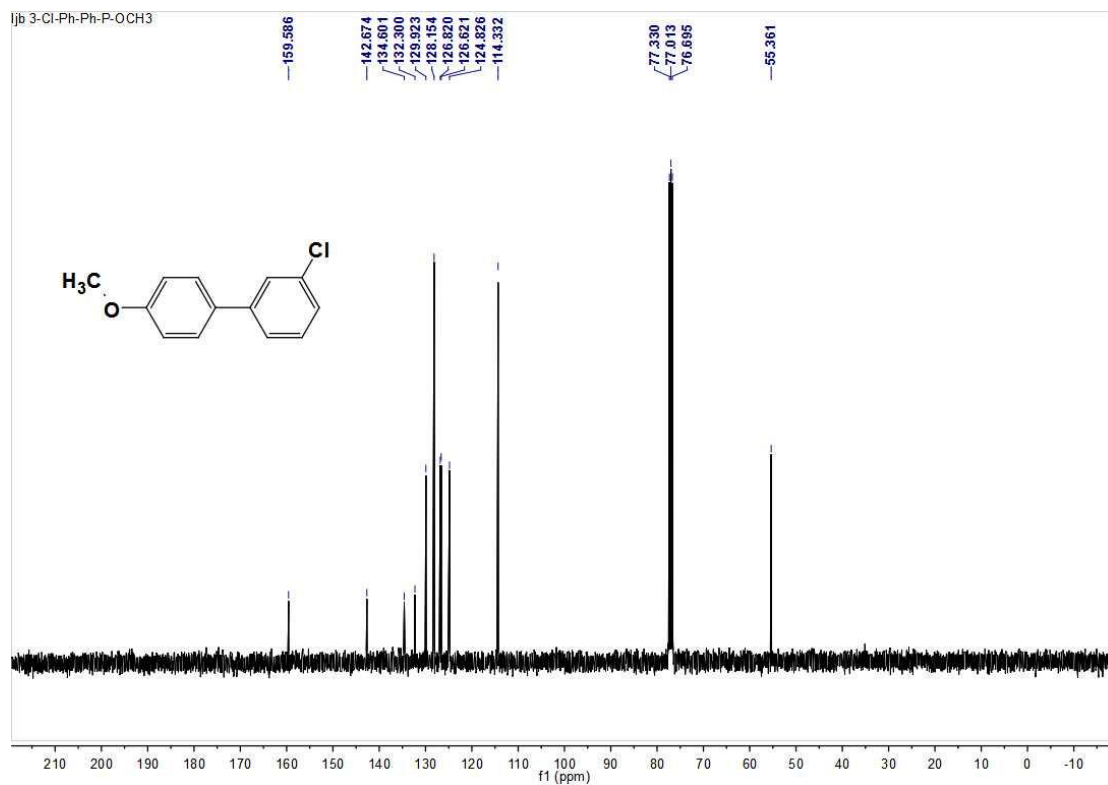
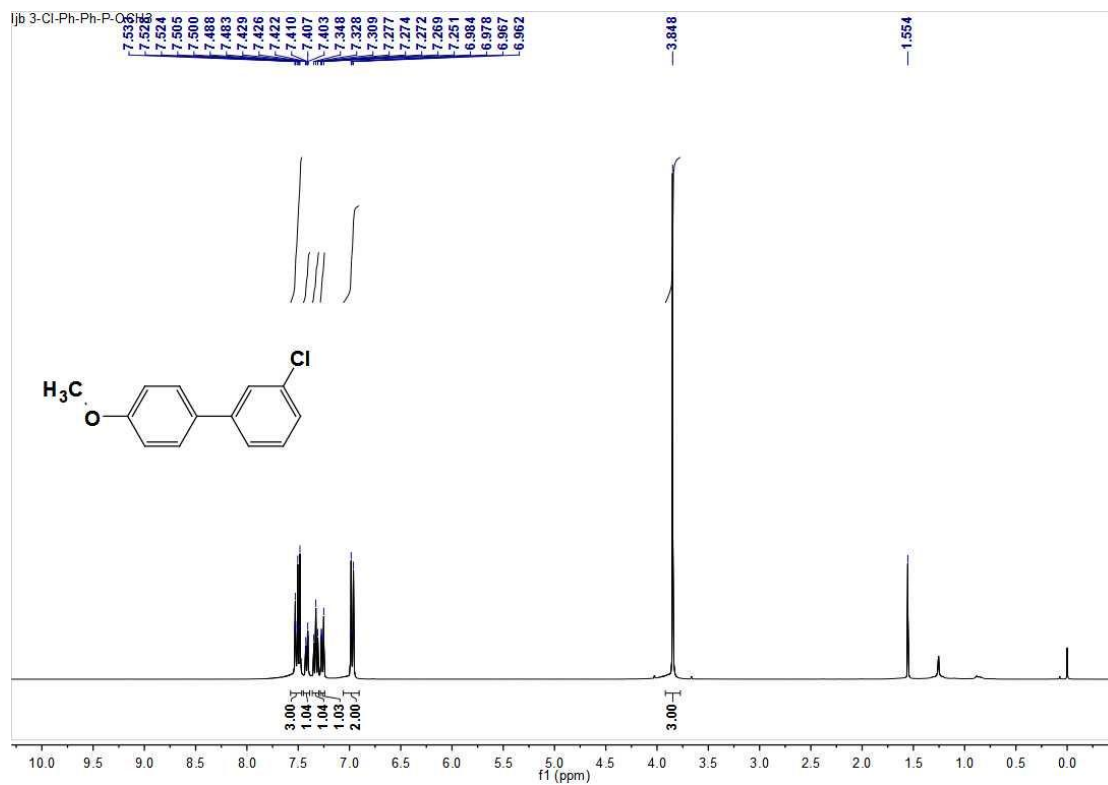


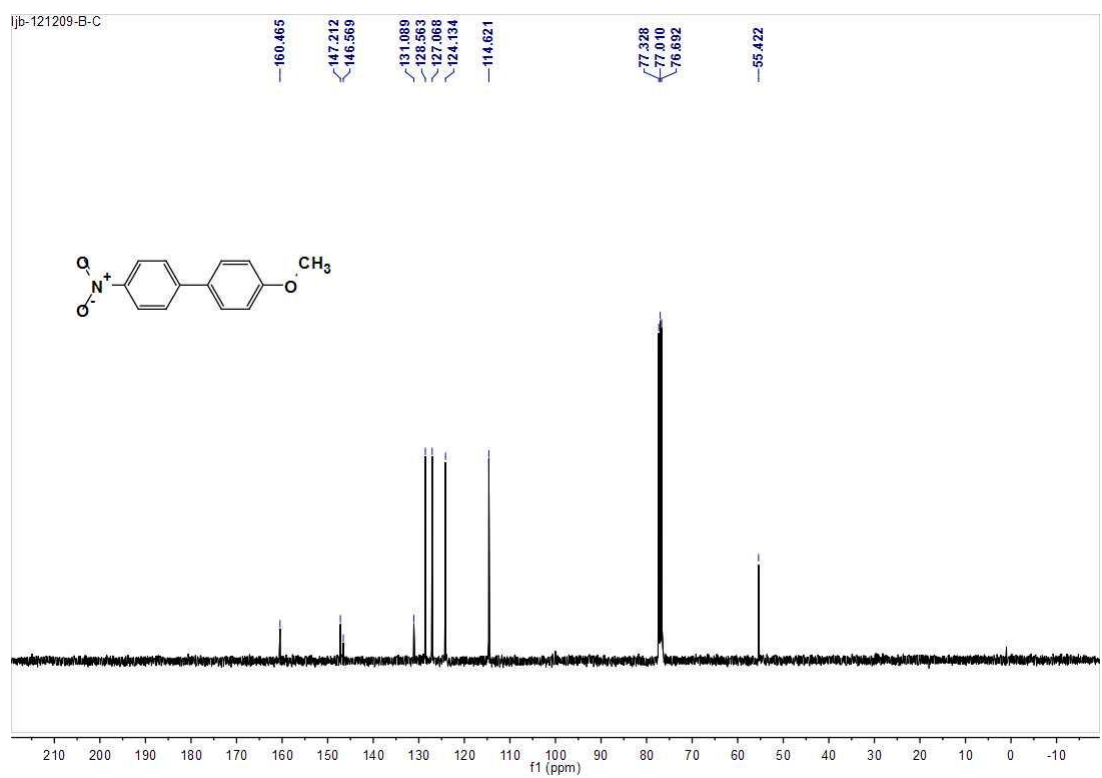
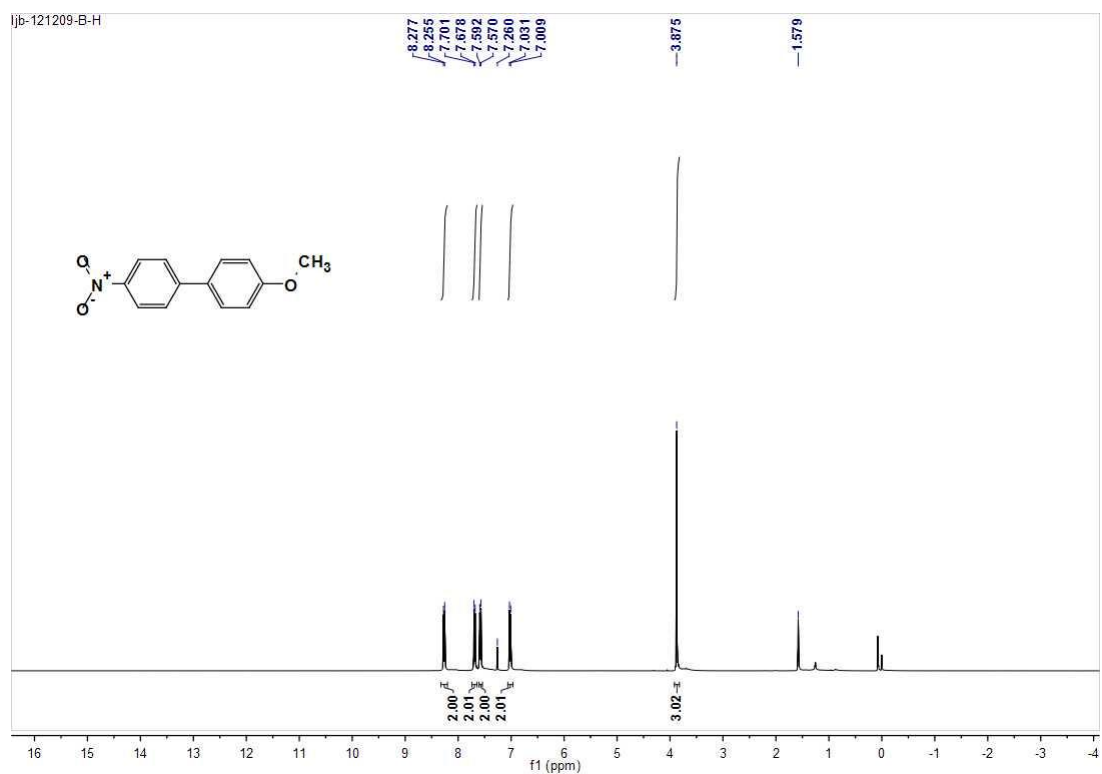


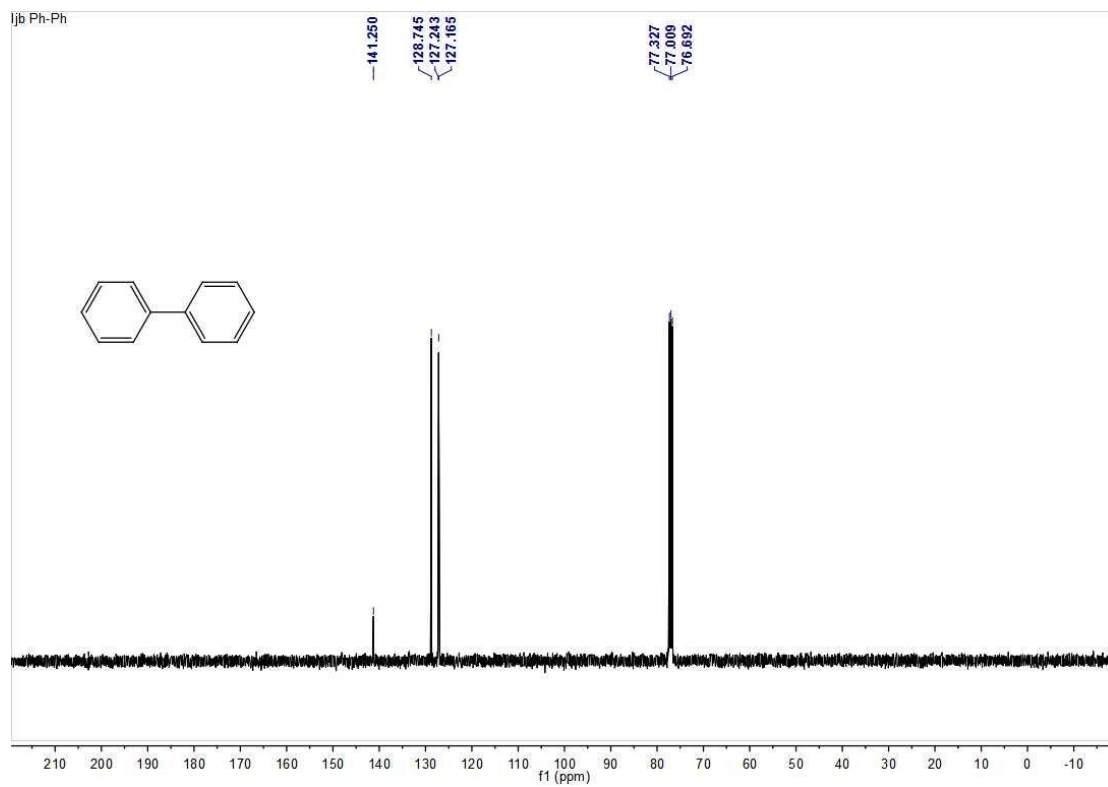
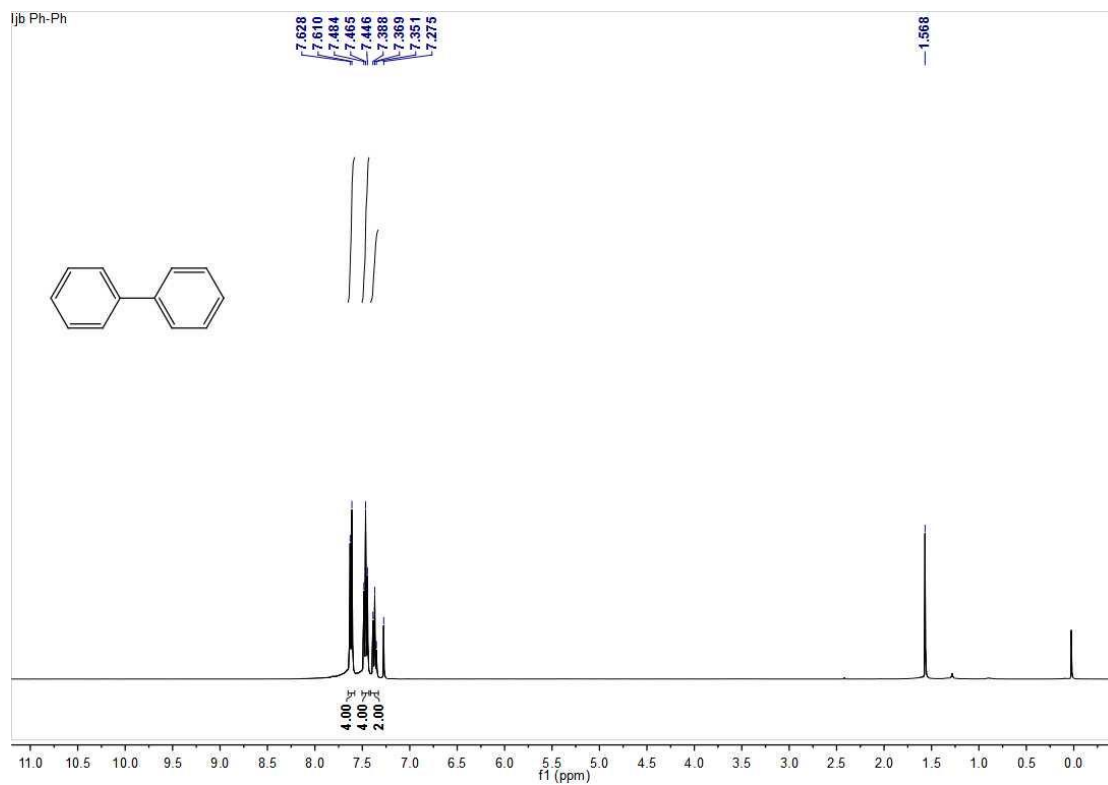
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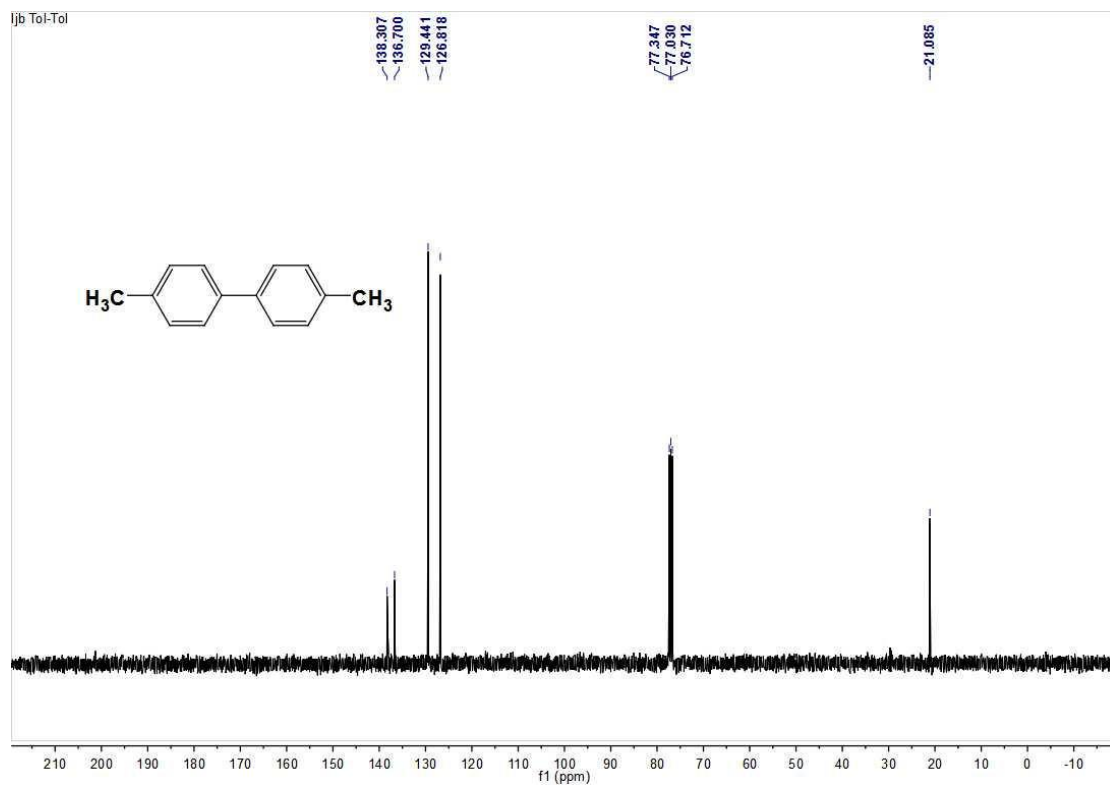
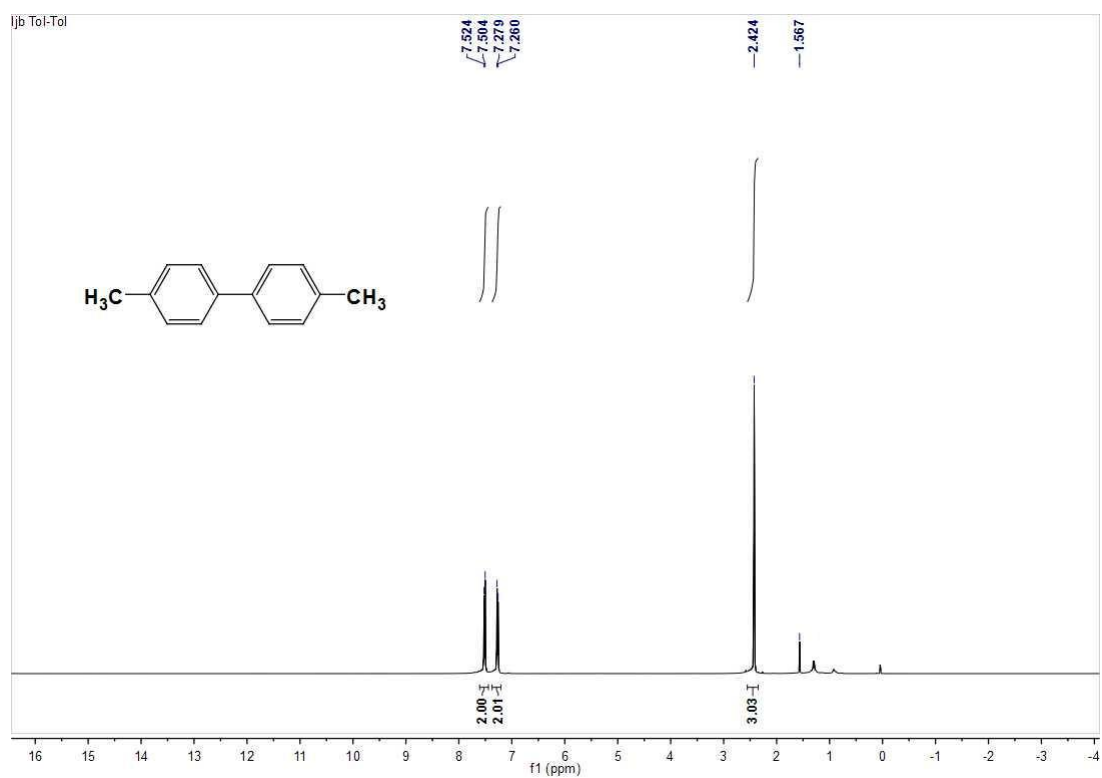


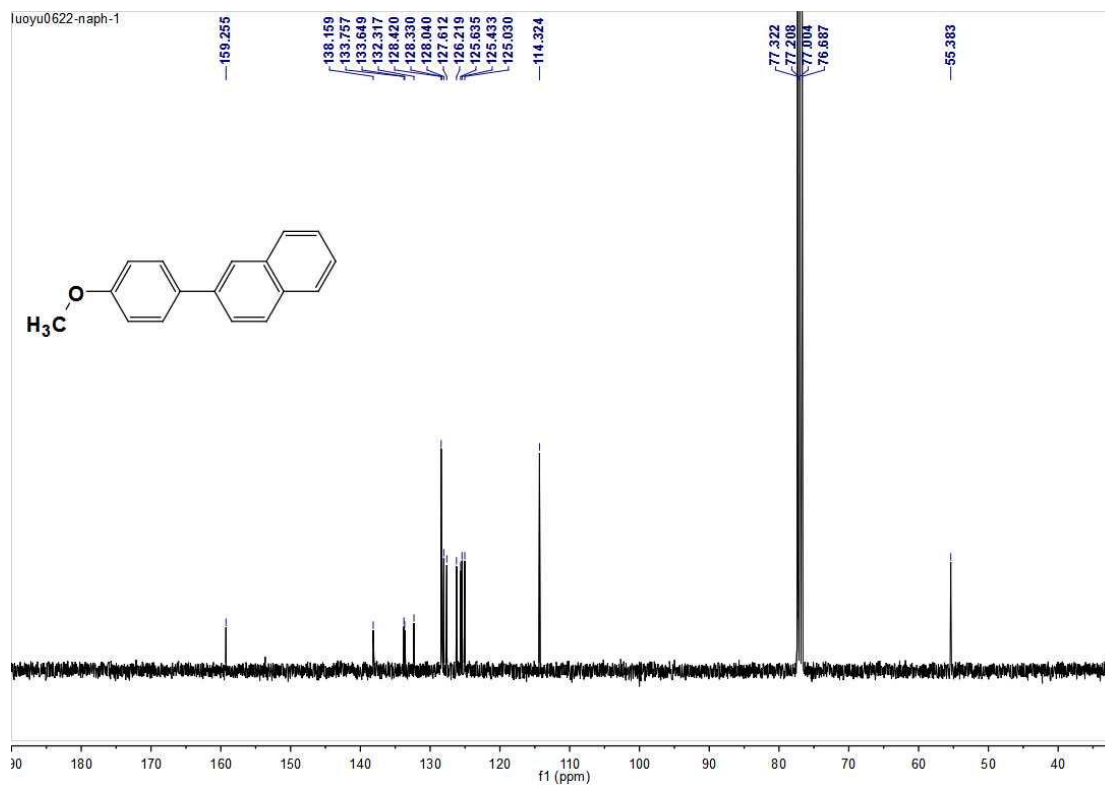
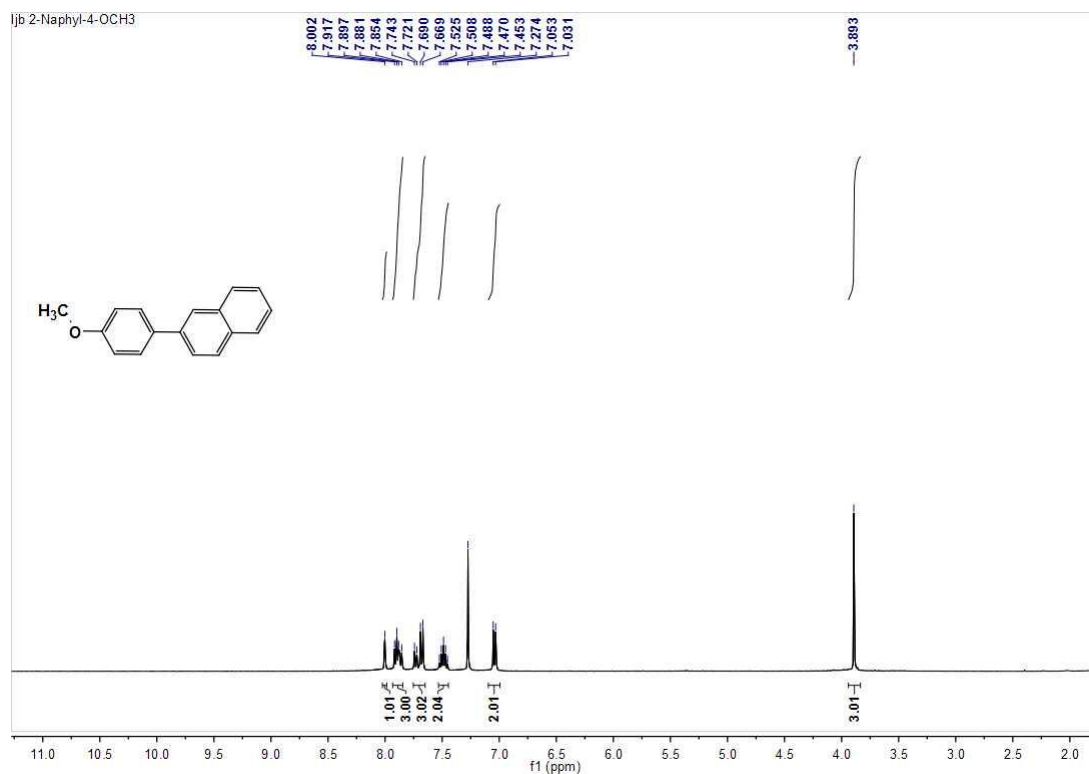


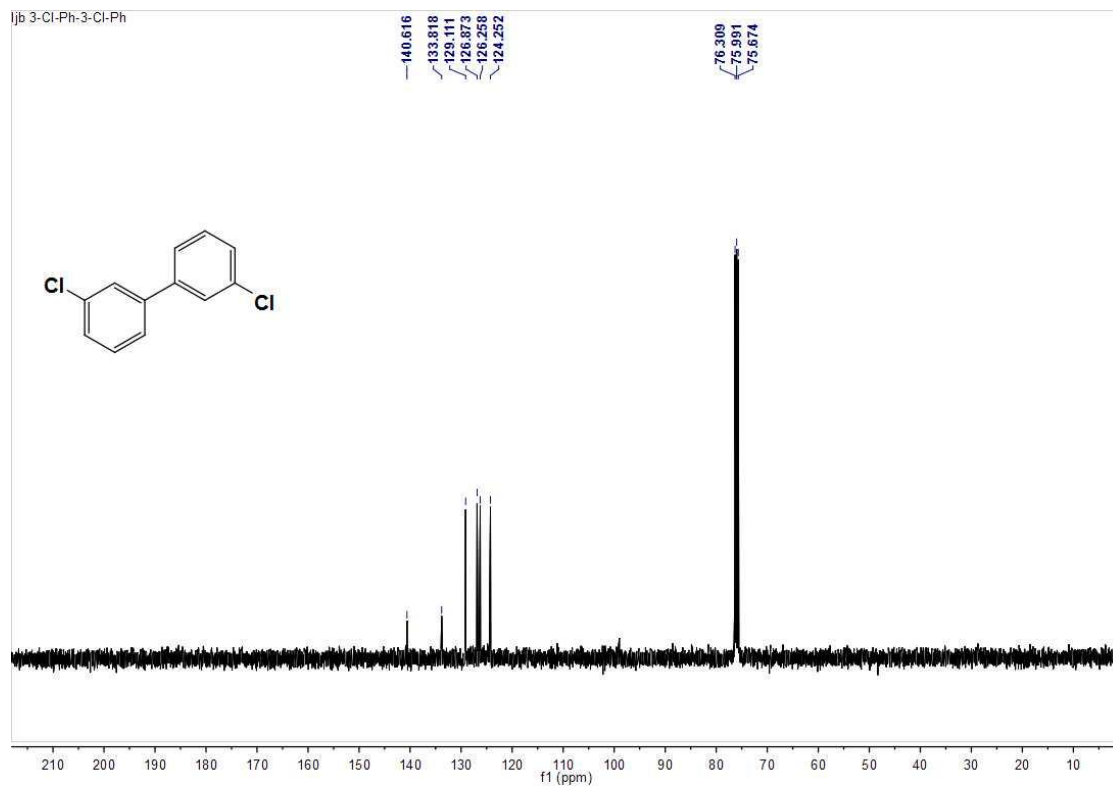
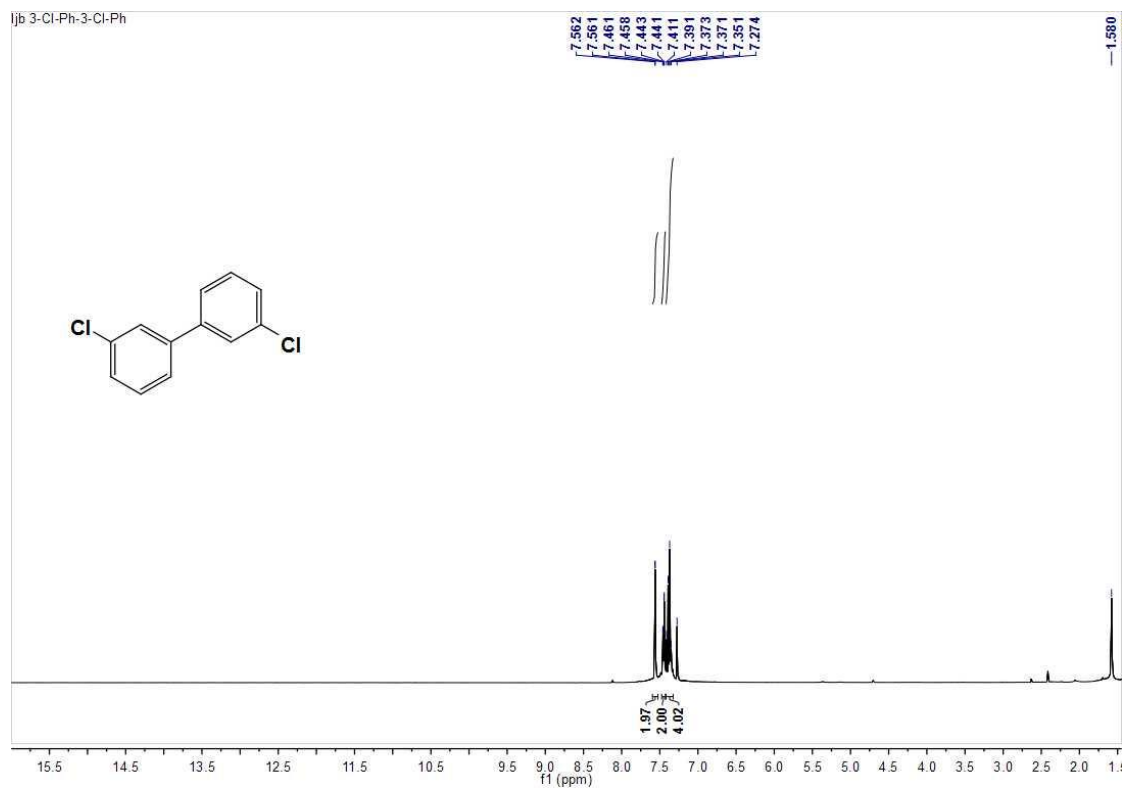


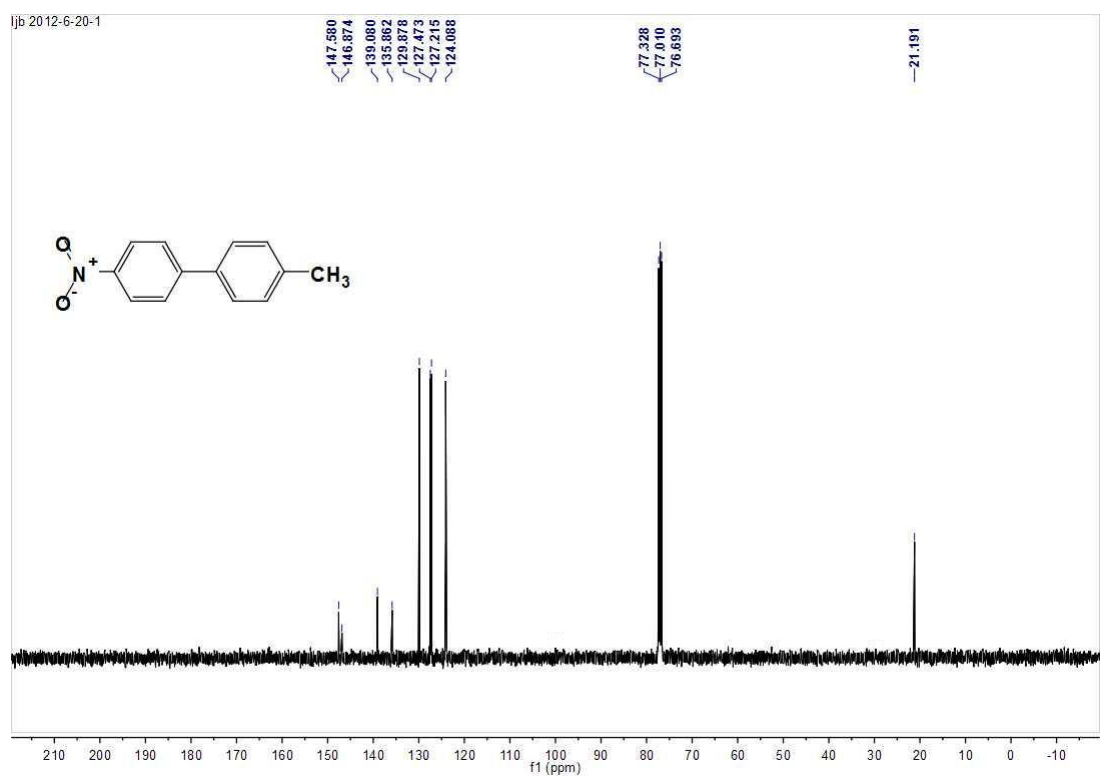
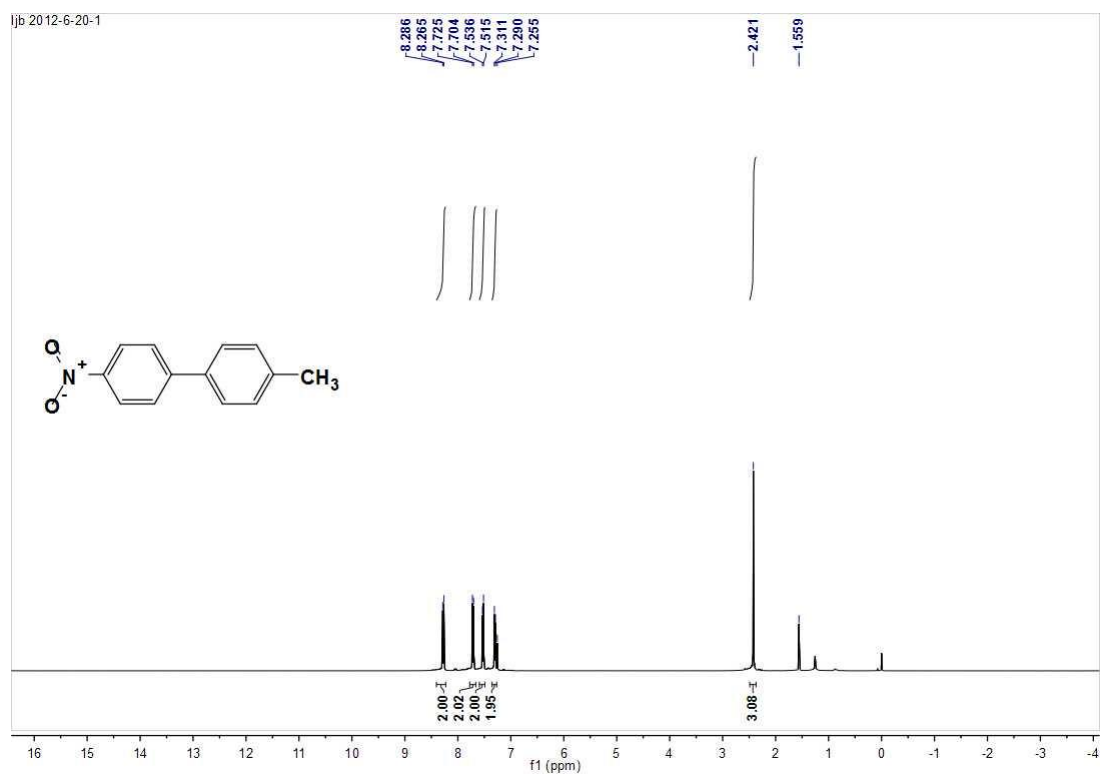


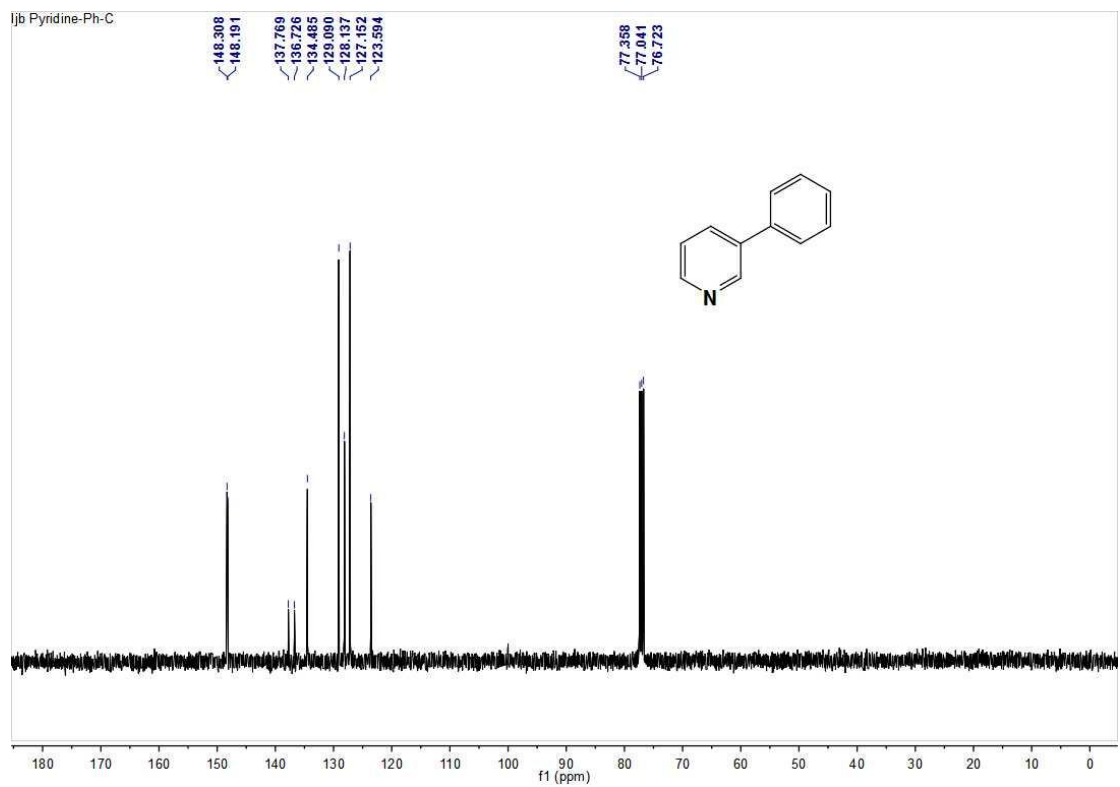
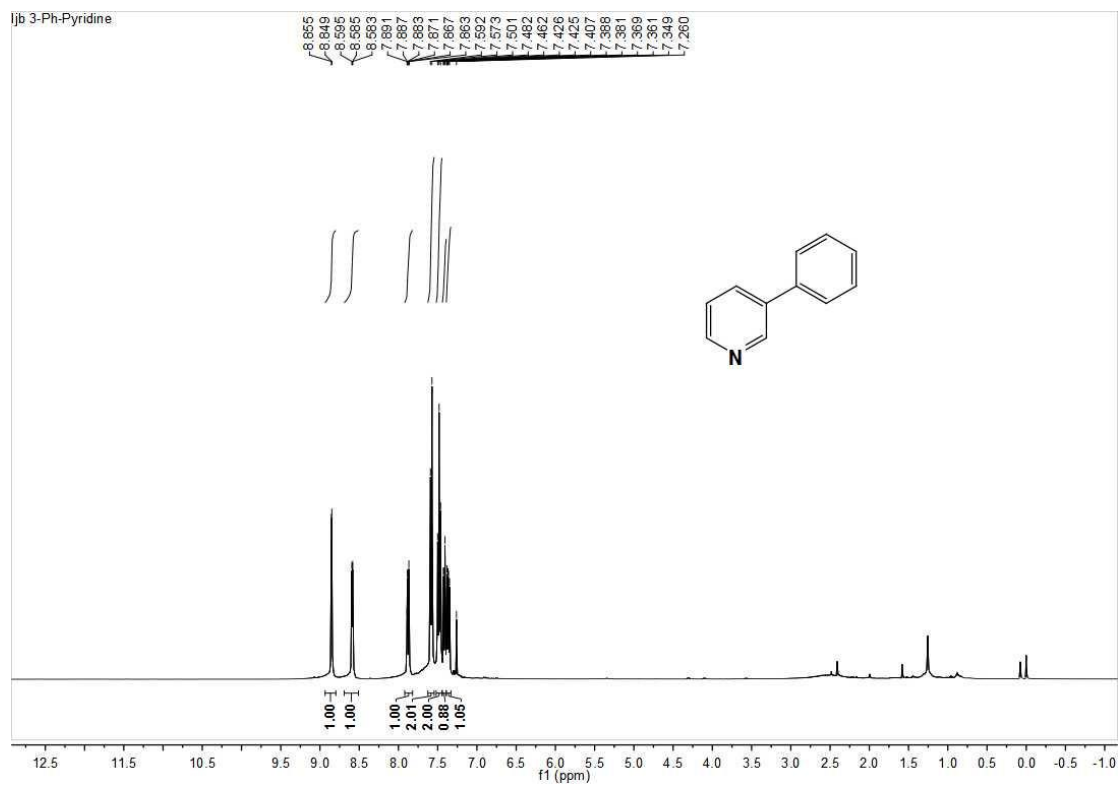


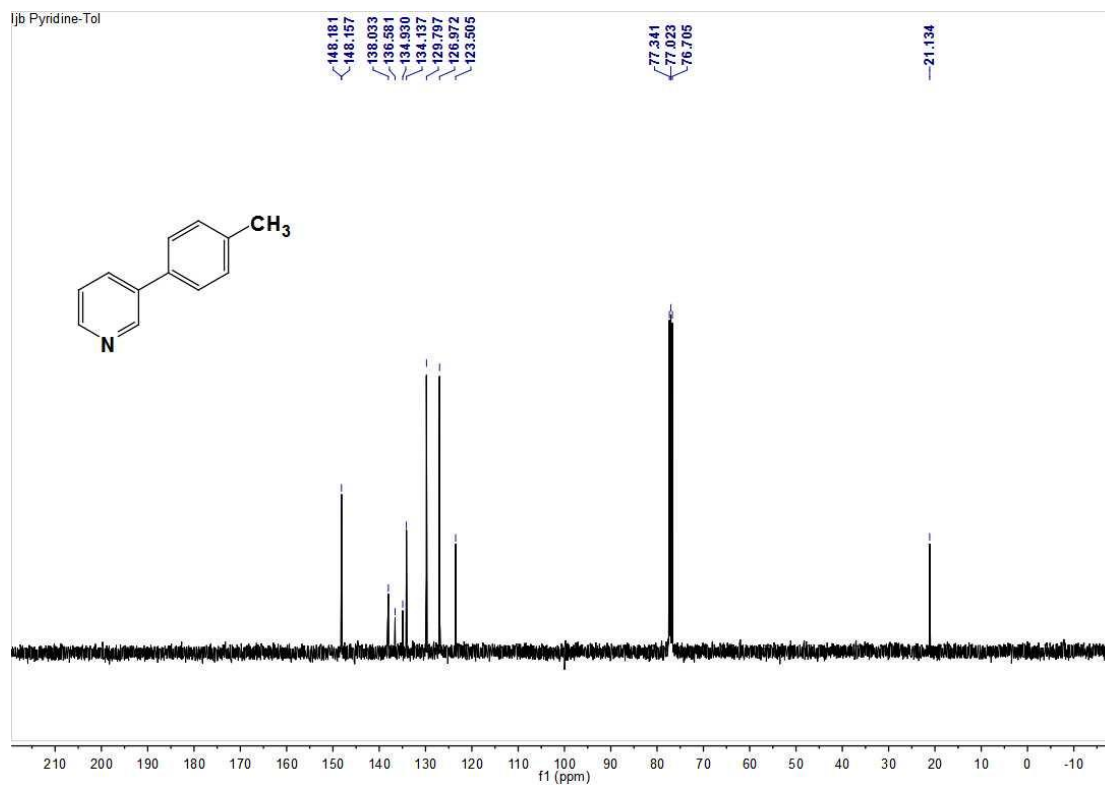
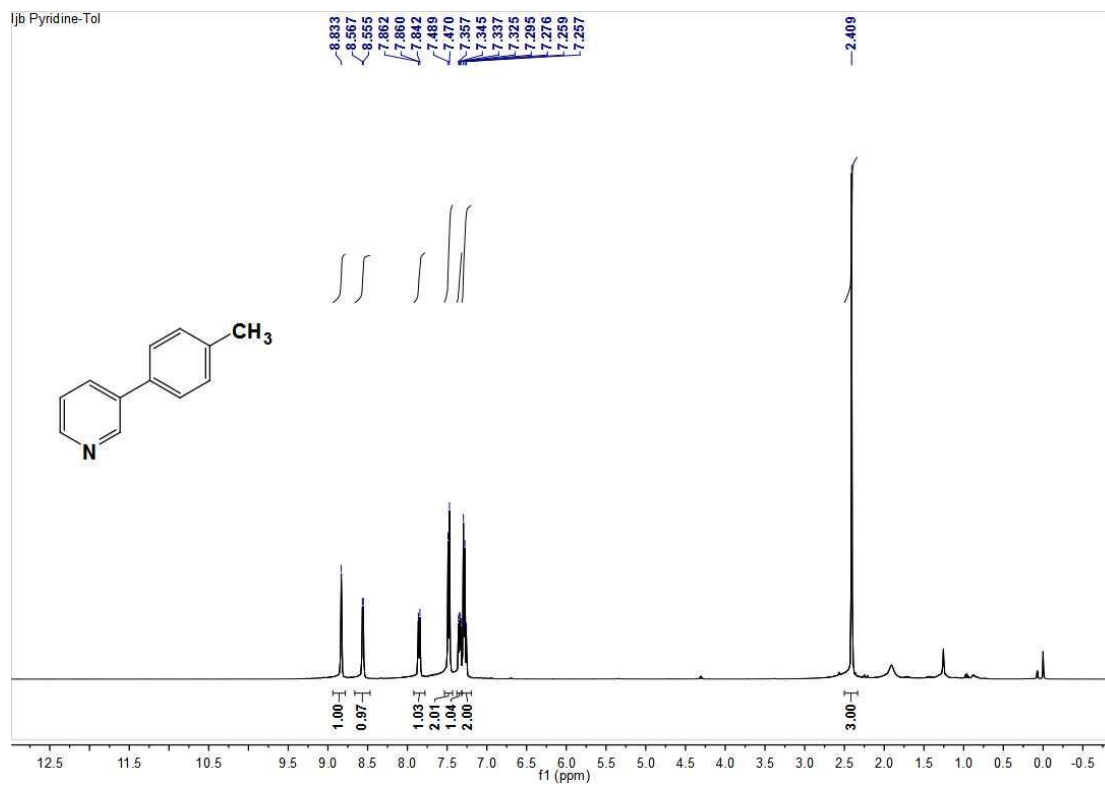


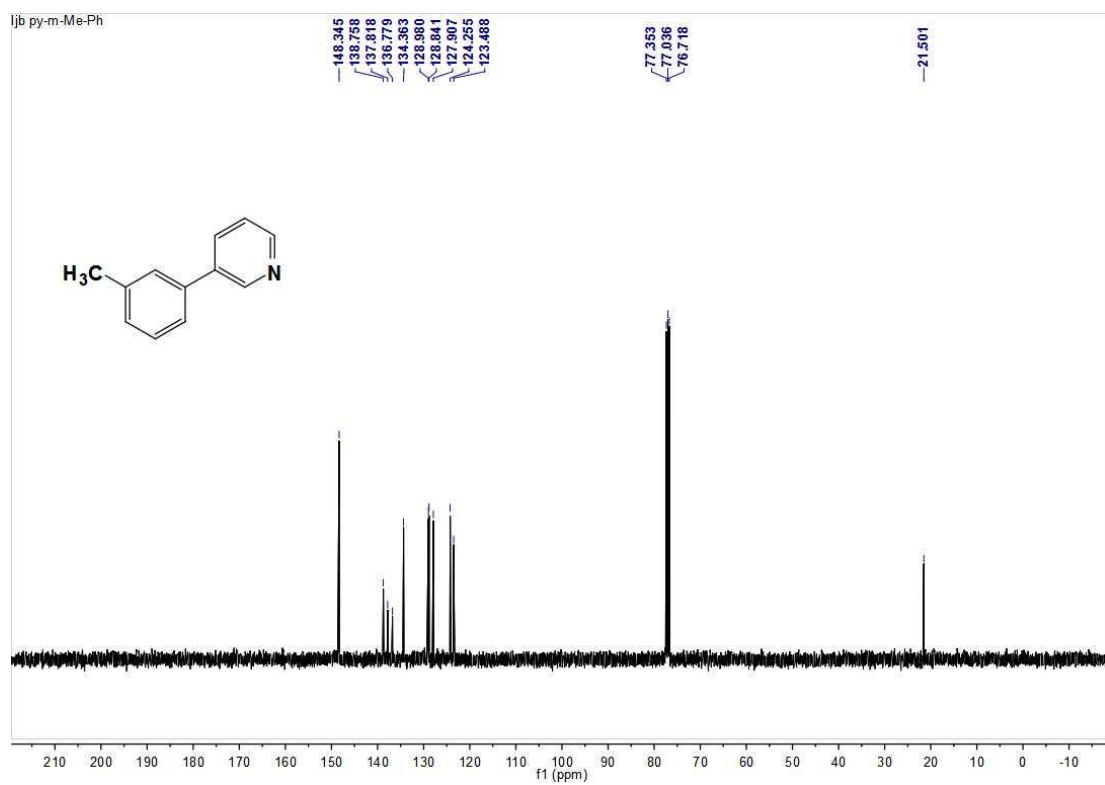
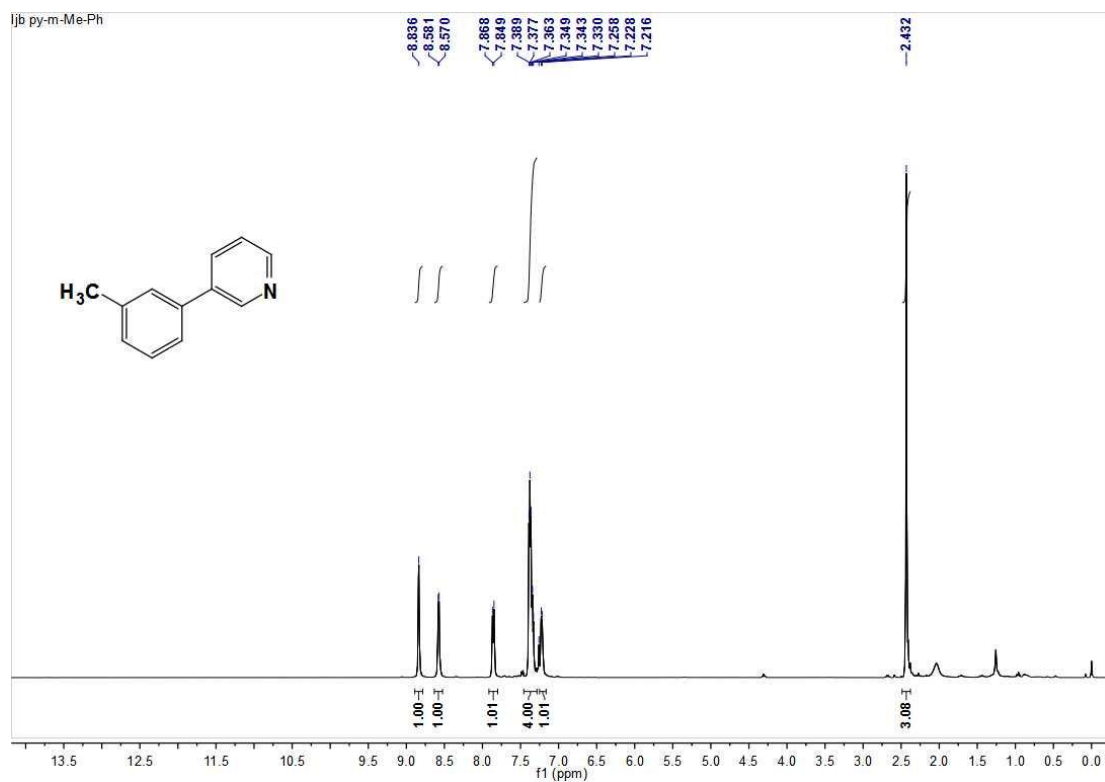


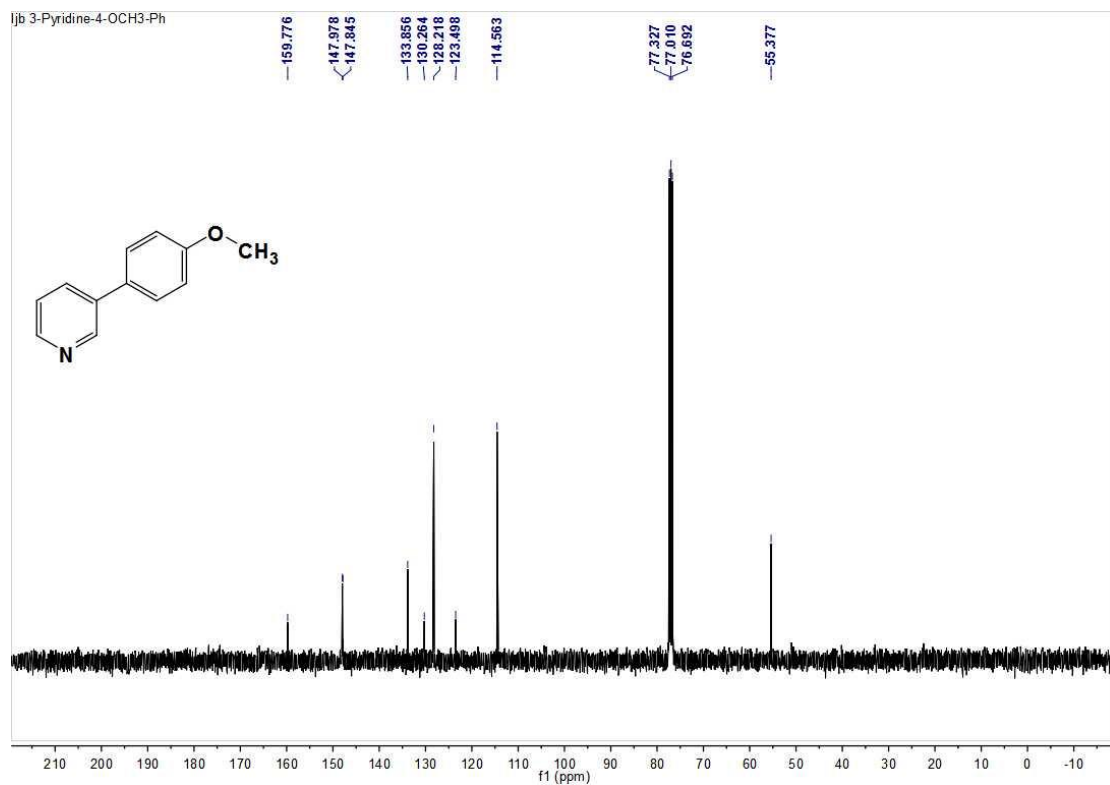
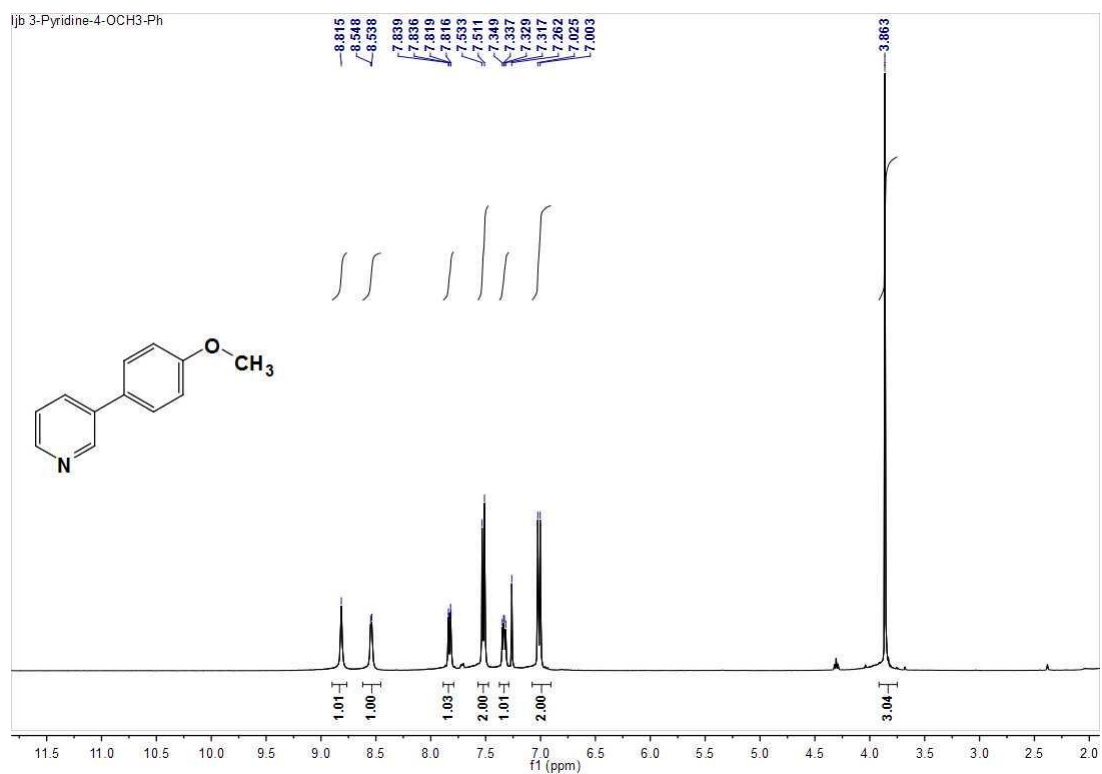


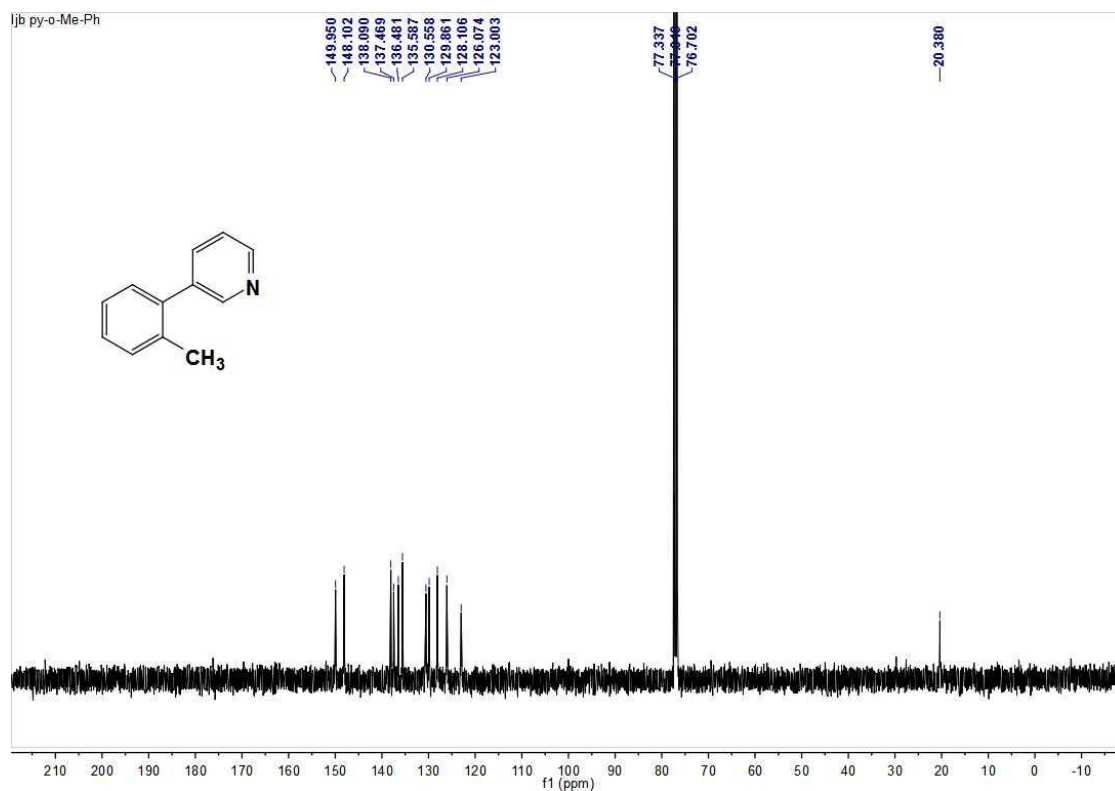
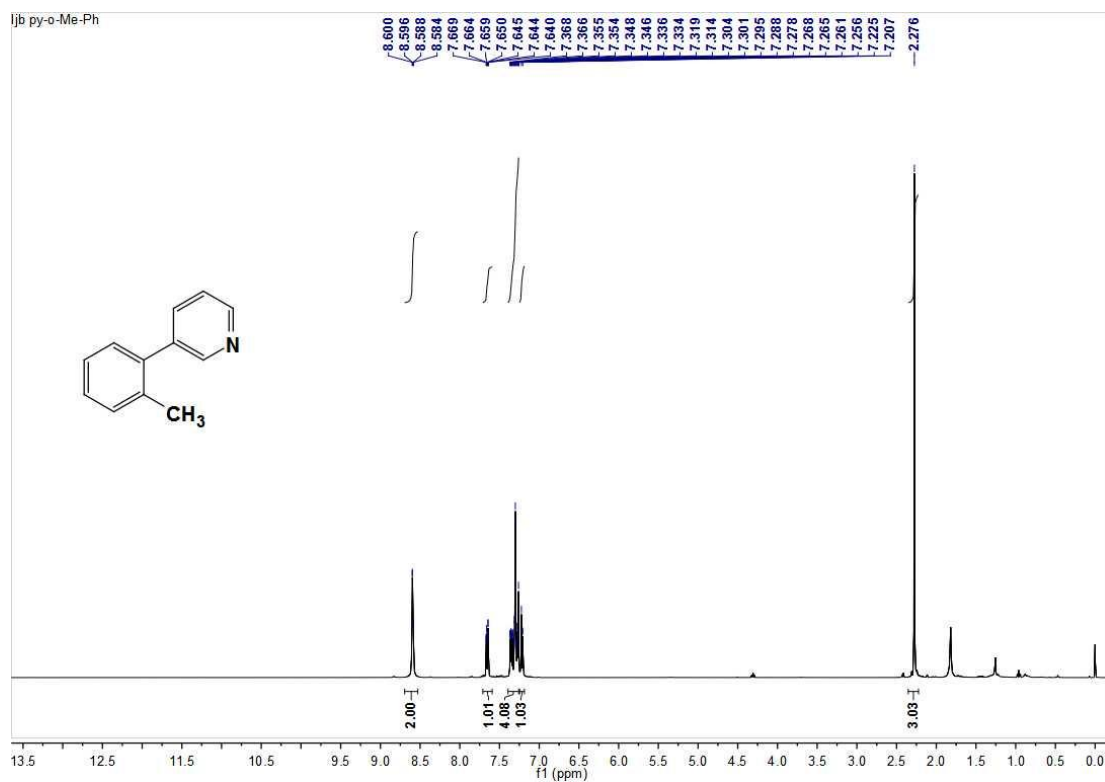


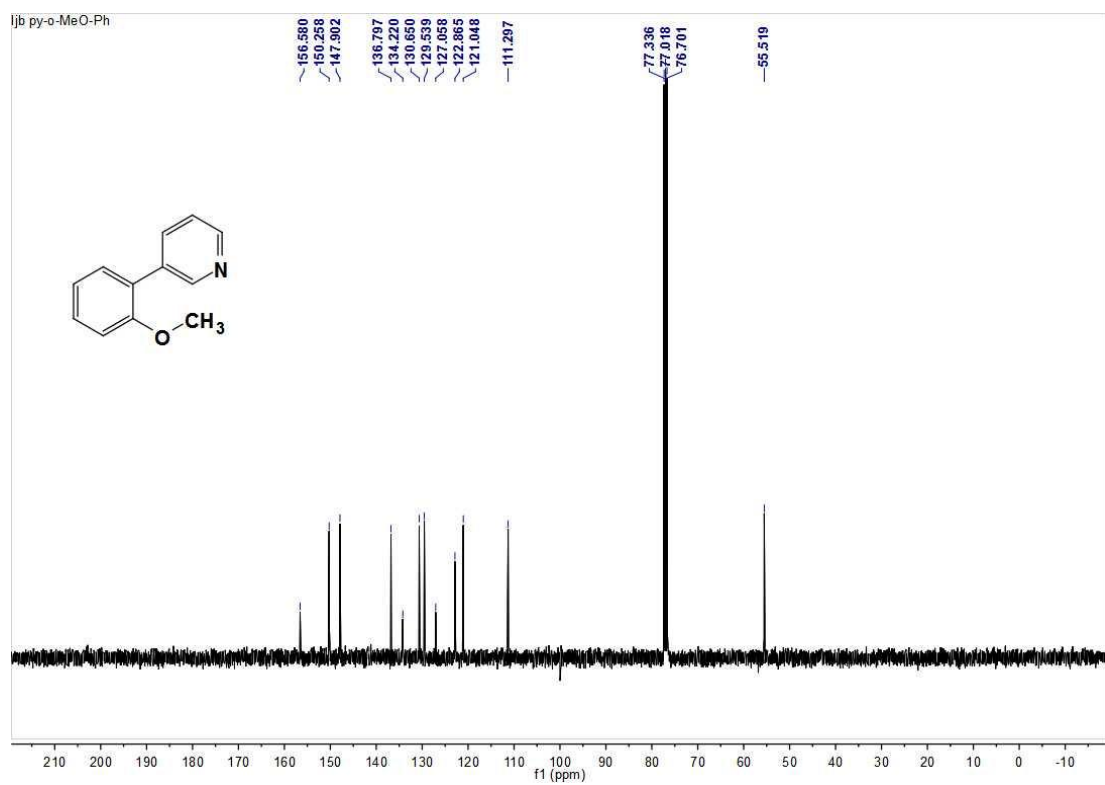
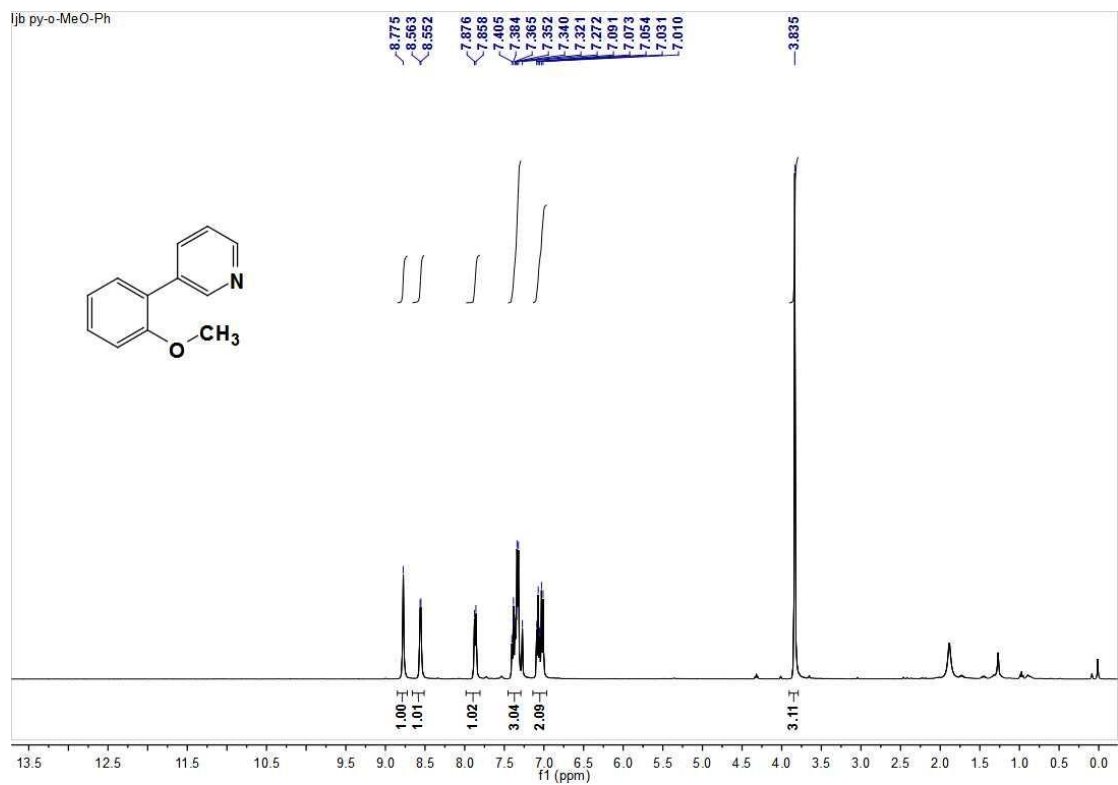




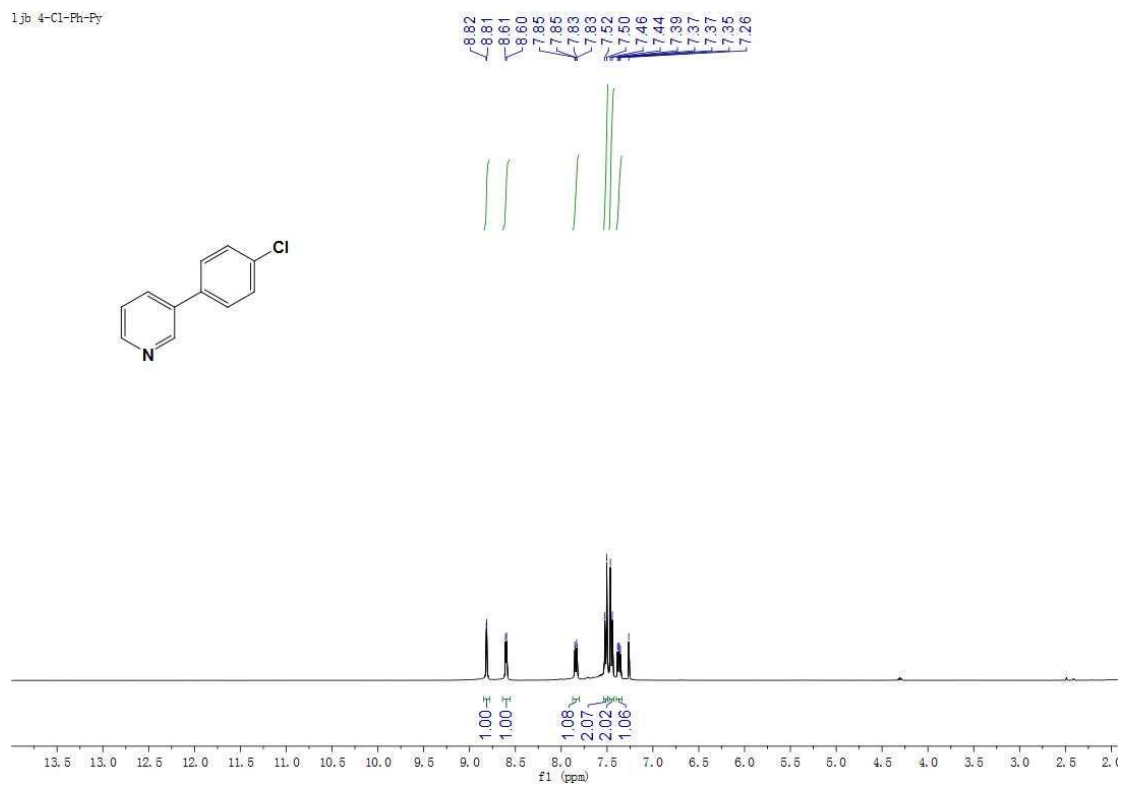
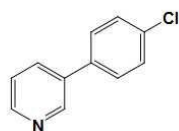








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