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Electronic Supplementary Information

Room temperature Stille cross-coupling reaction of unreactive aryl chlorides and heteroaryl chlorides

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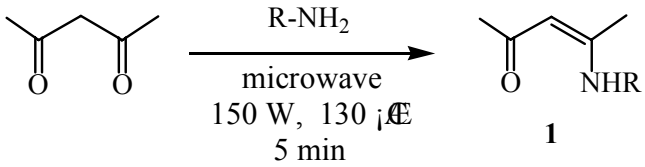
List of Contents for Experimental Section

1. General

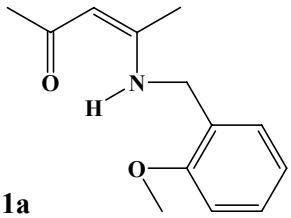
Tributyl(*p*-toly)stannane and tributyl(*o*-toly)stannane were prepared following literature procedures.[1] All other reagents were used as received from commercial source. All manipulations were conducted under an atmosphere of dry nitrogen. ^{1}H, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Varian Unity Inova (400 MHz) NMR spectrometer, Bruker AM 400 (400 MHz) and FT AM 300 (300MHz), respectively. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. ^{31}P NMR spectra were referenced to external PPh_3 (0 ppm relative to free PPh_3). Elemental analyses (EA) were carried out using EA-110 (Thermo Finnigan, Italia). GC/GC-MS analyses were performed on an Agilent 6890N GC coupled to an Agilent 5975 Network Mass Selective Detector. The diffraction data for a single crystal of **2b** were collected with a Bruker CCD diffractometer with Mo-Kα (λ = 0.71073) radiation by employing a 2 kW sealed tube X-ray source operating at 1.6 kW. The reflections were successfully indexed by using an automated indexing routine built into the SMART program. The CCD data were integrated and scaled using the Bruker SAINT program, and the structure was solved and refined by using XPREP and SHELX-97. CCDC-608595 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via *www.ccdc.cam.ac.uk/data_request/cif.*

2. General Procedure for the Synthesis of β-ketoimines 1



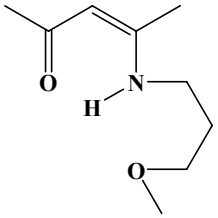
1

2,4-Pentanedione (11.0 mmol) and primary amines (10.0 mmol) were placed in a 10 mL glass tube. The vessel was sealed with a septum and placed into the microwave cavity. The reaction temperature was raised from r.t. to 130 °C under microwave irradiation of 150 W. The power was maintained for 5 min. After allowing the mixture to cool to r.t., the reaction mixture was vacuumed under reduced pressure. The residue was purified by column chromatography (SiO_2; hexane-ethyl acetate, 4:1) to give β-ketoimine **1** as a liquid.



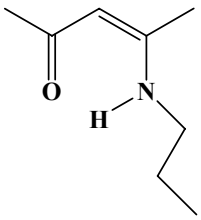
1a

light yellow liquid (2.11 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (br s, 1 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 7.17 (d, *J* = 8.0 Hz, 1 H), 6.91 (t, *J* = 7.6 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 4.99 (s, 1 H), 4.41 (d, *J* = 6.8 Hz, 2 H), 3.84 (s, 3 H), 2.00 (s, 3 H), 1.92 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 162.7, 156.6, 128.4, 127.6, 126.0, 120.3, 110.0, 95.3, 55.1, 42.1, 28.7, 18.6; Anal. Calcd for $C_{13}H_{17}NO_2$ (219.28): C, 71.21; H, 7.81; N, 6.39. Found: C, 71.02; H, 7.54; N, 6.58.



1b

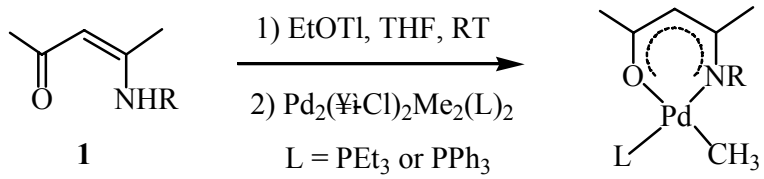
light yellow liquid (1.68 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.833 (br s), 4.96 (s, 1 H), 3.45 (t, *J* = 6.0 Hz, 2 H), 3.35 (s, 3 H), 3.32 (q, *J* = 8.0 Hz, 2 H), 2.00 (s, 3 H), 1.93 (s, 3 H), 1.83 (t, *J* = 6.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 162.4, 94.5, 68.7, 58.0, 39.2, 29.7, 28.1, 18.1; Anal. Calcd for $C_9H_{17}NO_2$ (171.24): C, 63.13; H, 10.01; N, 8.18. Found: C, 63.41; H, 10.18; N, 8.21.



1c

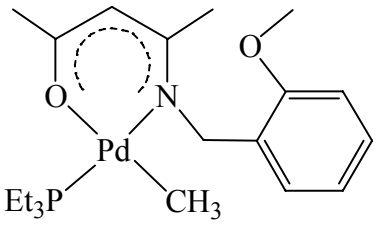
light yellow liquid (1.34 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (br s, 1 H), 4.94 (s, 1 H), 3.20 (q, *J* = 3.6 Hz, 2 H), 1.97 (s, 3 H), 1.91 (s, 3 H), 1.61 (q, *J* = 3.6 Hz, 2 H), 0.98 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 162.2, 94.2, 44.0, 28.0, 22.8, 18.1, 10.7; Anal. Calcd for $C_8H_{15}NO$ (141.21): C, 68.04; H, 10.71; N, 9.02. Found: C, 68.17; H, 10.79; N, 9.32.

3. General Procedure for the Synthesis of phosphanyl-β-ketoiminate Pd 2



1 **2**

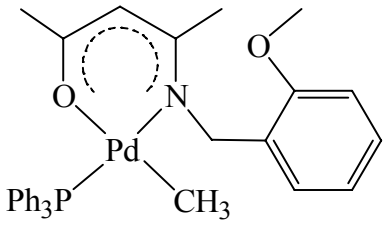
Solution of EtOTl (0.3 g, 1.2 mmol) in THF (10 mL) was added dropwise at r.t. to a solution of β-ketoimine **1** (1.0 mmol) in THF (10 mL). After being stirred at r.t. for 1 h, a solution of $Pd_2(\mu\text{-}Cl)_2Me_2(PPh_3)_2$ or $Pd_2(\mu\text{-}Cl)_2Me_2(PEt_3)_2$[2](0.6 mmol) in THF (5 mL) was added dropwise to the mixture. The reaction mixture was stirred at r.t. for 1 h. The mixture was then filtered through celite on a frit. The solvent was removed under reduced pressure and the residue was washed with hexane (30 mL). Removal of the solvent gave Pd complex **2**.



2a

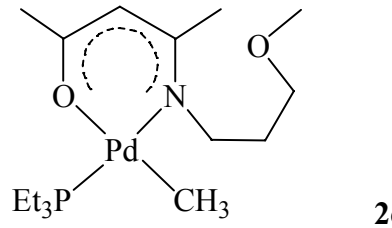
light brown solid (0.38 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (m, 2 H), 6.91 (t, *J* = 4.0 Hz, 1 H), 6.85 (d, *J* = 4.0 Hz, 1 H), 4.90 (s, 1 H), 4.42 (d, *J* = 3.6 Hz, 2 H), 3.85 (s, 3 H), 2.03 (s, 3 H), 1.85 (s, 3 H), 1.70 (m, 6 H), 1.20 (m, 9H), -0.28 (d, *J* = 3.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 166.2, 156.2, 128.7, 127.4, 127.0, 120.6, 109.6, 98.2, 58.0, 55.4, 49.8, 27.4,

21.4, 19.3, 18.9, 18.4, 2.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.11; Anal. Calcd for $C_{20}H_{34}NO_2PPd$ (457.88): C, 52.46; H, 7.48; N, 3.06. Found: C, 52.44; H, 7.31; N, 3.19.



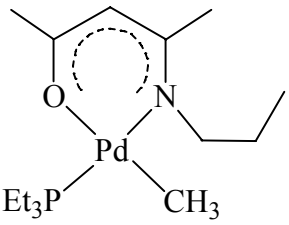
2b

light brown solid (0.45 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.17 (m, 17 H), 6.92 (t, *J* = 4.0 Hz, 1 H), 6.81 (d, *J* = 4.4 Hz, 1 H), 4.83 (s, 1 H), 4.72 (d, *J* = 3.6 Hz, 2 H), 3.81 (s, 3 H), 1.89 (s, 3 H), 1.61 (s, 3 H), -0.08 (d, *J* = 3.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 166.7, 156.0, 134.9, 134.8, 131.4, 131.0, 129.9, 129.9, 127.8, 127.7, 127.1, 126.6, 120.3, 109.2, 97.6, 55.2, 49.0, 26.4, 23.3, 23.2, -0.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.31; Anal. Calcd for $C_{32}H_{34}NO_2PPd$ (602.01): C, 63.84; H, 5.69; N, 2.33. Found: C, 63.74; H, 5.53; N, 2.10.



2c

light brown solid (0.33 g, 80 %). ^{1}H-NMR (400 MHz, $CDCl_3$) *δ* 4.77 (s, 1H), 3.67 (t, *J* = 6.0, 2H), 3.37 (t, *J* = 6.0, 2H), 3.32 (s, 3H), 1.97 (s, 3H), 1.90 (t, *J* = 7.2, 2H), 1.71 (m, 6 H), 1.60 (s, 3H), 1.15 (m, 9H), 0.090 (d, *J* = 3.6, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ* 176,6 164.6, 130.5, 96.3, 70.7, 57.8, 54.9, 53.7, 32.16, 26.8, 23.8, 21.1, 19.8, 8.9, 8.4, 3.2; ^{31}P-NMR (162 MHz, $CDCl_3$) *δ* 33.77; Anal. Calcd. For $C_{16}H_{34}NO_2PPd$ (409.84) C, 46.89; H, 8.36; N, 3.42; Found C, 46.82; H, 8.06; N, 3.22.



2d

brown solid (0.31 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (s, 1 H), 3.38 (m, 2 H), 1.96 (s, 3 H), 1.82 (s, 3 H), 1.73 (m, 6 H), 1.52 (s, 3 H), 1.15 (m, 11H), 0.89 (t, *J* = 3.6 Hz, 3 H), 0.09 (d, *J* = 3.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 165.0, 96.9, 55.4, 50.1, 28.3, 26.7, 22.6, 19.4, 15.4, 13.3, 8.1, 1.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.04. Anal. Calcd for $C_{15}H_{35}NOPPd$ (382.84): C, 47.06; H, 9.21; N, 3.66. Found: C, 47.23; H, 9.71; N, 3.42.

4. General Procedure for the Stille coupling reaction

The reaction was carried out by using a glass vial equipped with a Teflon screw cap. Aryl chloride (1.0 mmol), organostannane (1.1 mmol), CsF (2.0 mmol), and a catalytic amount of Pd complex **2** were mixed in THF (1.0 mL). The reaction mixture was stirred at room temperature and monitored by GC/GC-MS. GC/GC-MS analyses were performed on an Agilent 6890N GC (He carrier gas, HP-5MS column, 30 m × 0.25 m × 0.25 μm) coupled to an Agilent 5975 Network Mass Selective Detector. The GC yield was determined using *n*-dodecane as an internal standard and based on the amount of aryl chloride employed. The reaction mixture was diluted with ether (5 mL) or acetone (5 mL), filtered, and concentrated in vacuo. The residue was purified by short column chromatography on silica gel to afford the desired product. The filtered catalyst was reused without further purification.

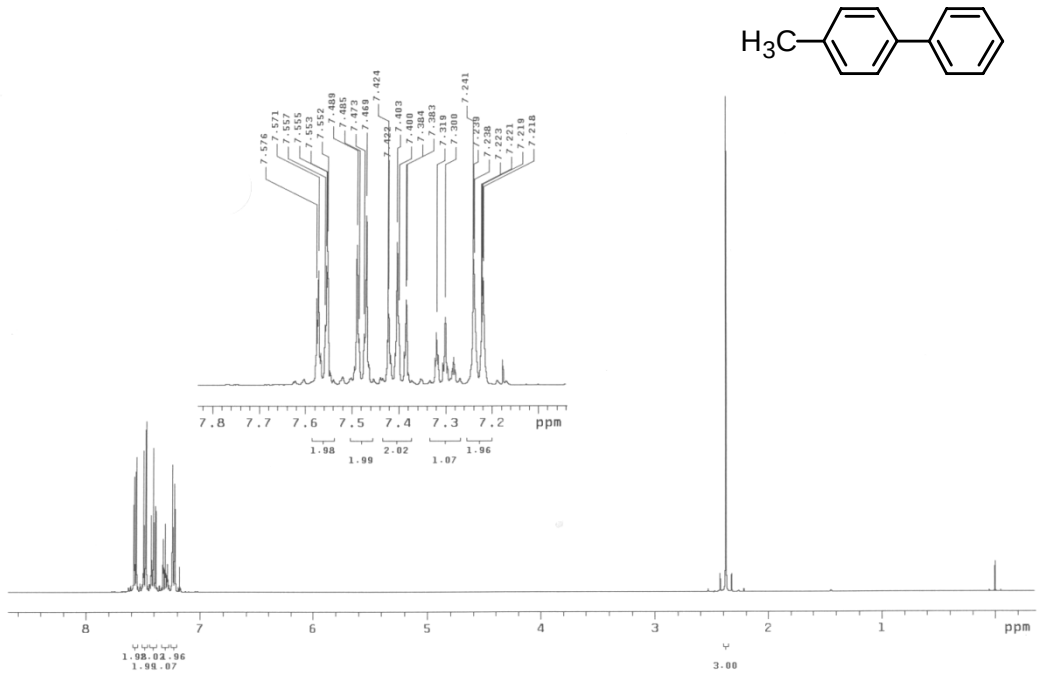
5. References

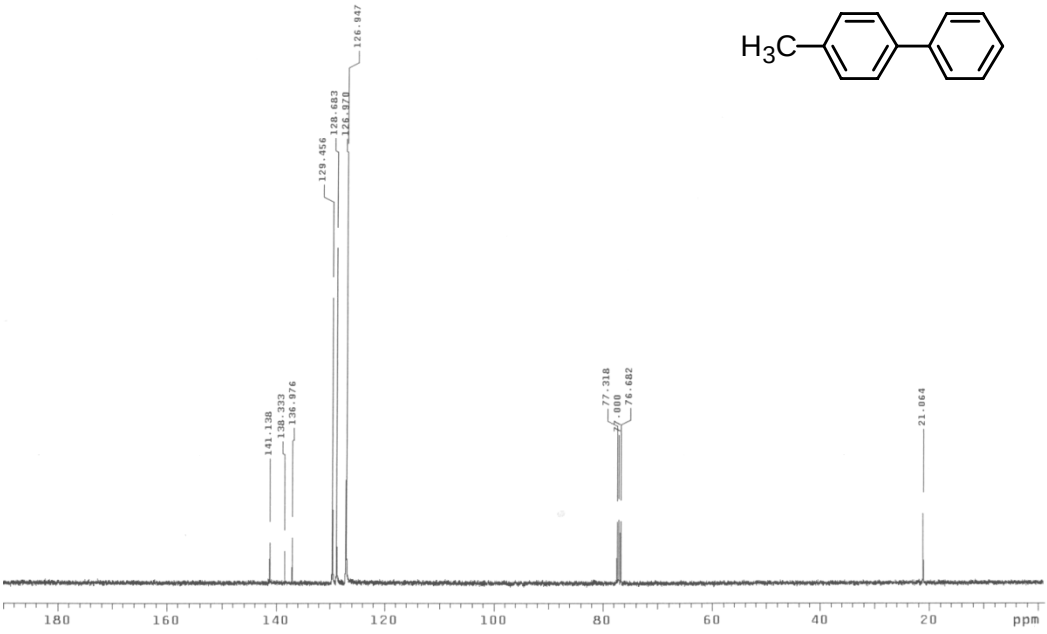
1 A. F. Littke, L. Schwarz and G. C. Fu, *J. Am. Chem. Soc*., 2002, **124**, 6343.

2 F. T. Ladipo and G. K. Anderson, *Organometallics*, 1994, **13**, 303.

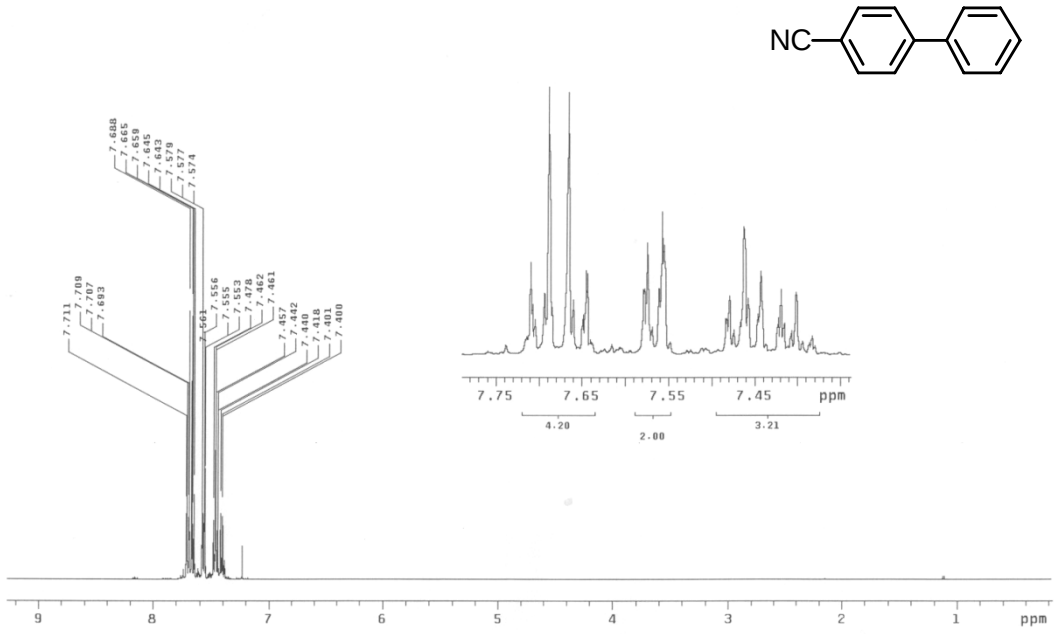
6. ^{1}H and ^{13}C NMR spectra of the coupling products

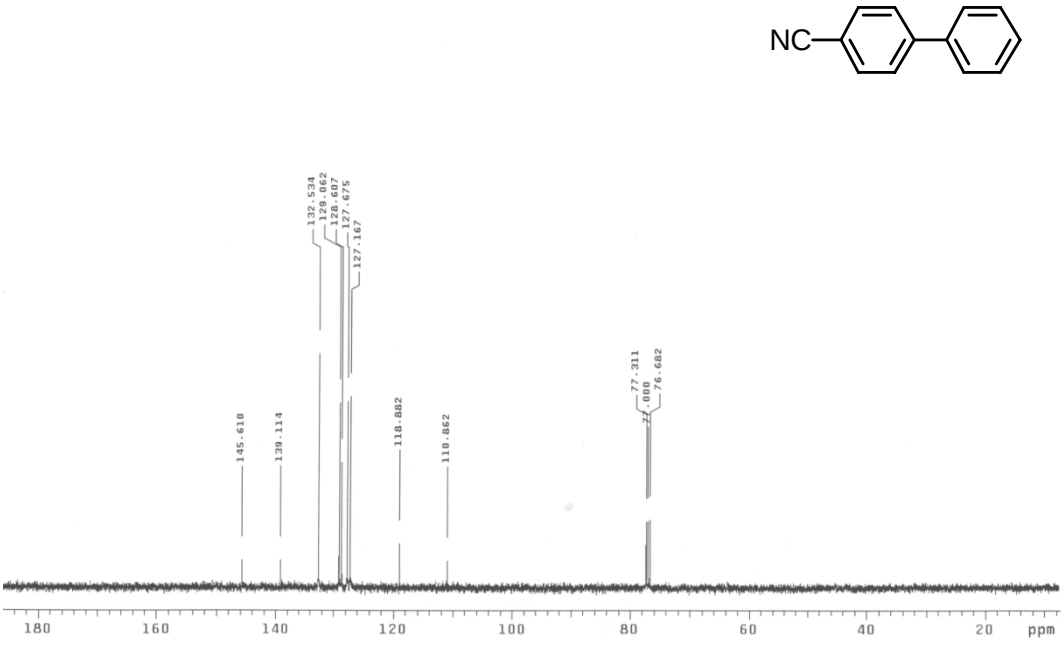
4-Methylbiphenyl



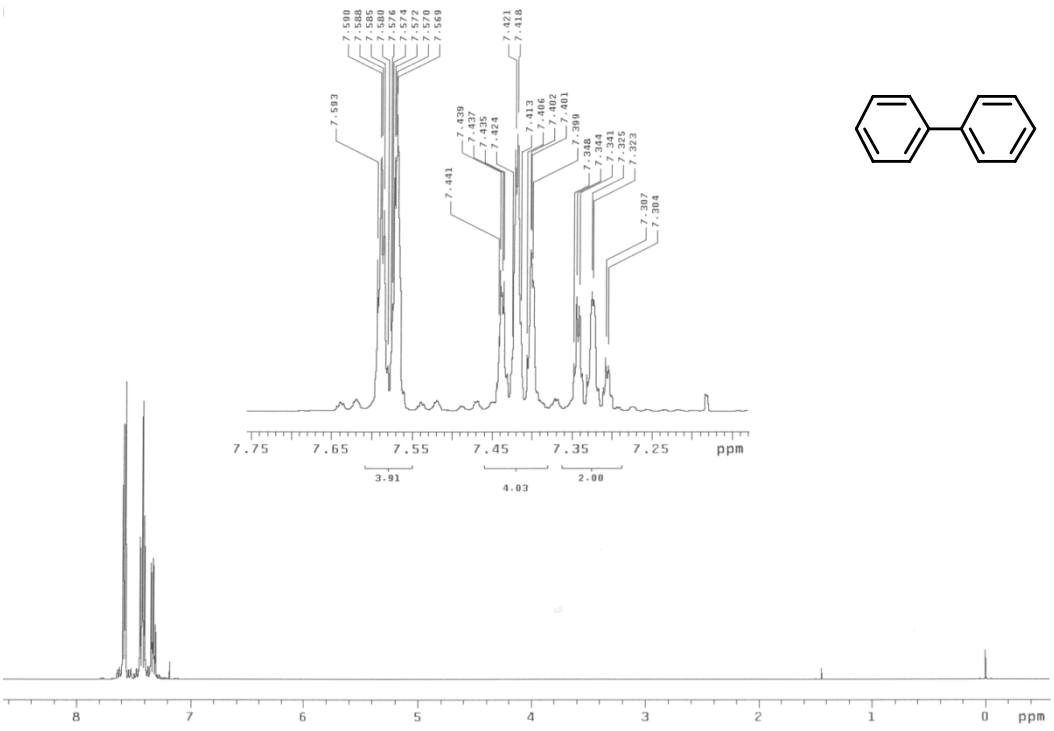


4-Cyanobiphenyl





Biphenyl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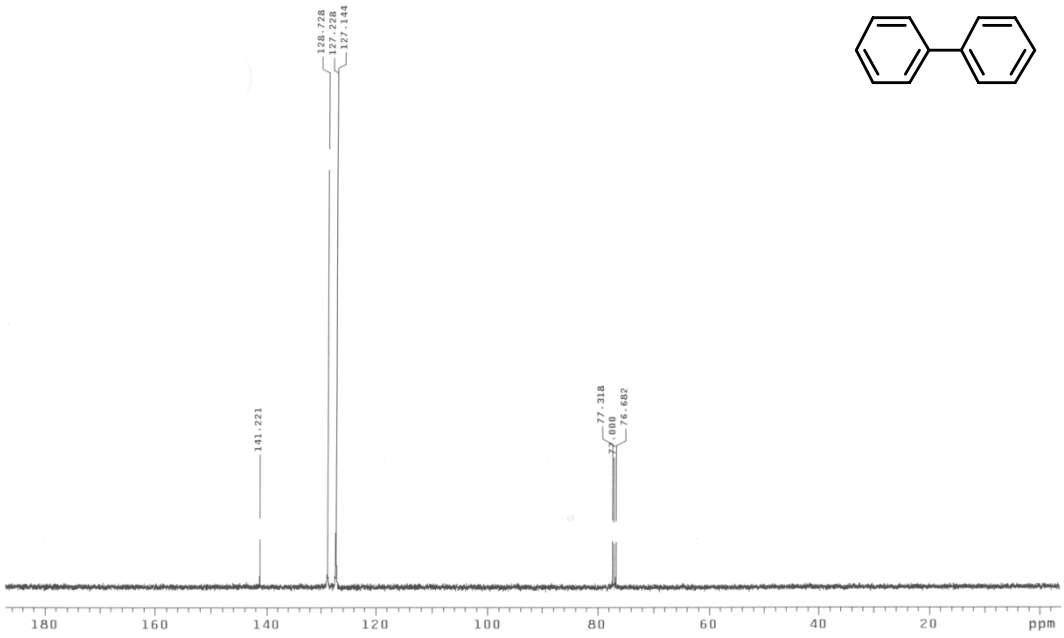
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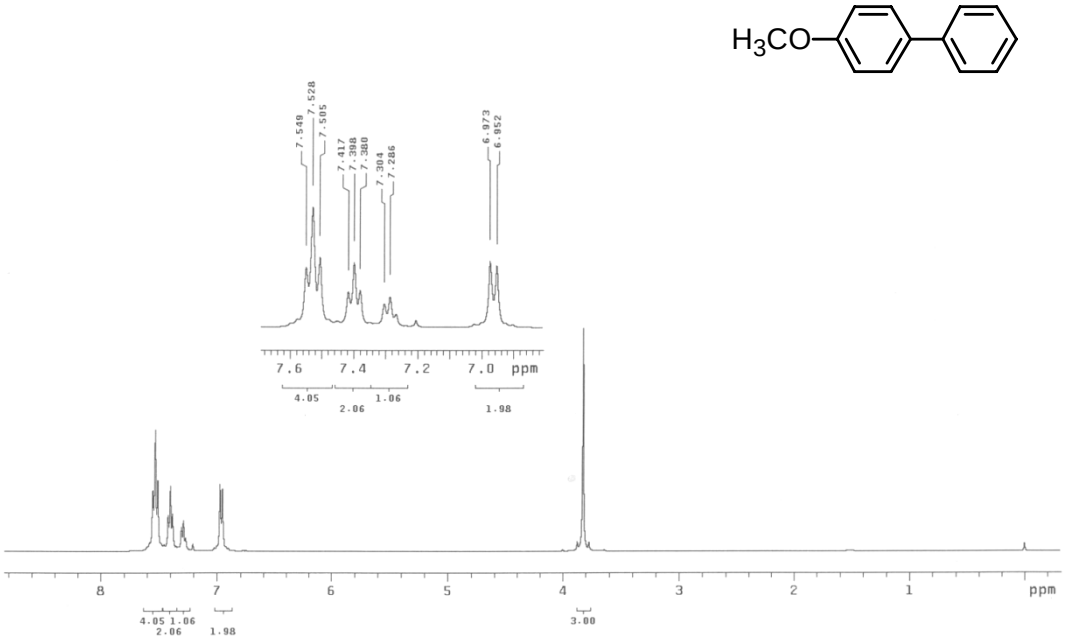
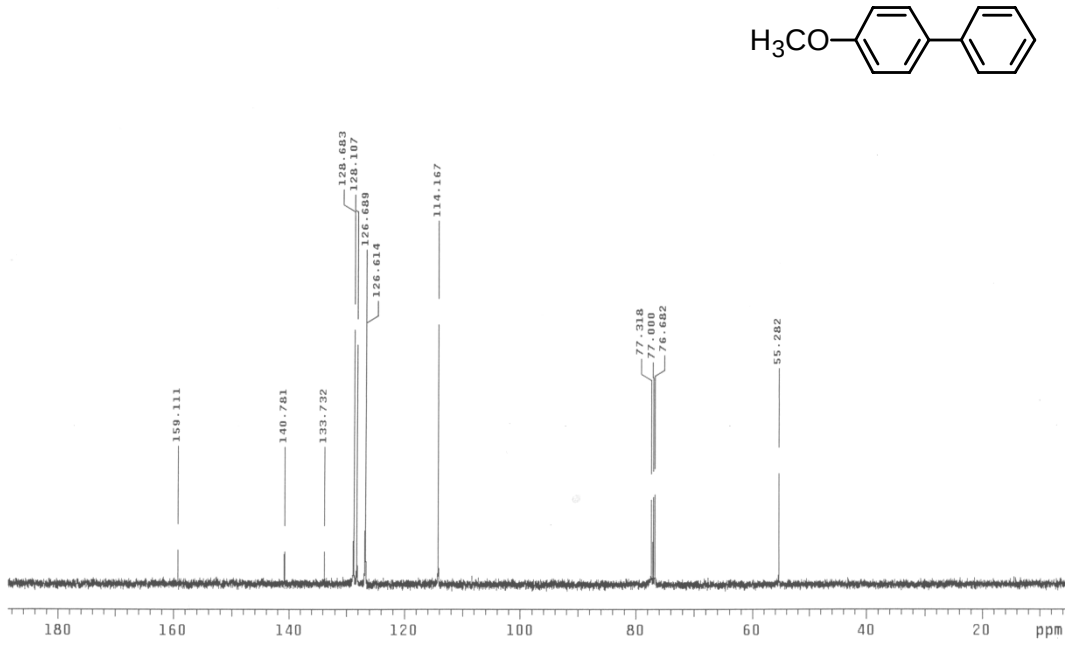
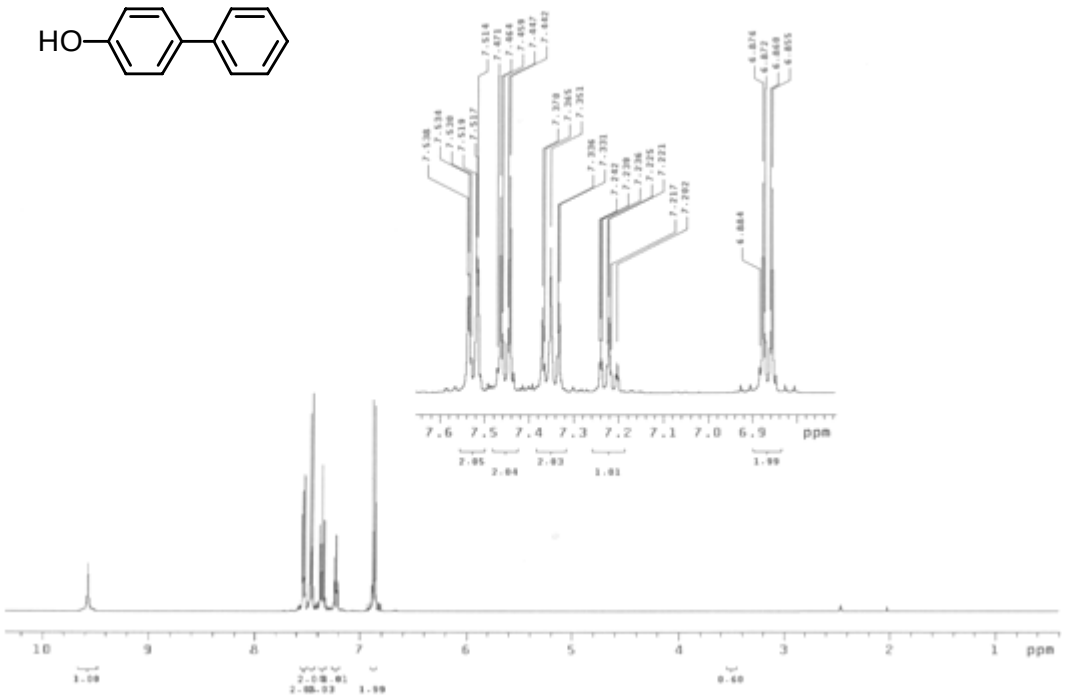
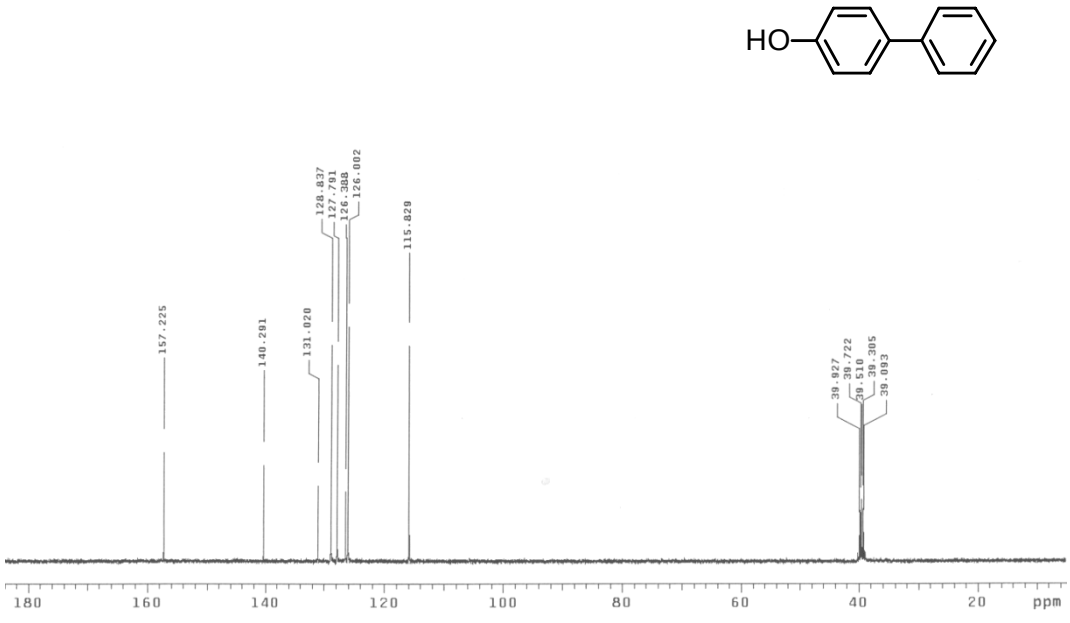
4-Methoxybiphenyl



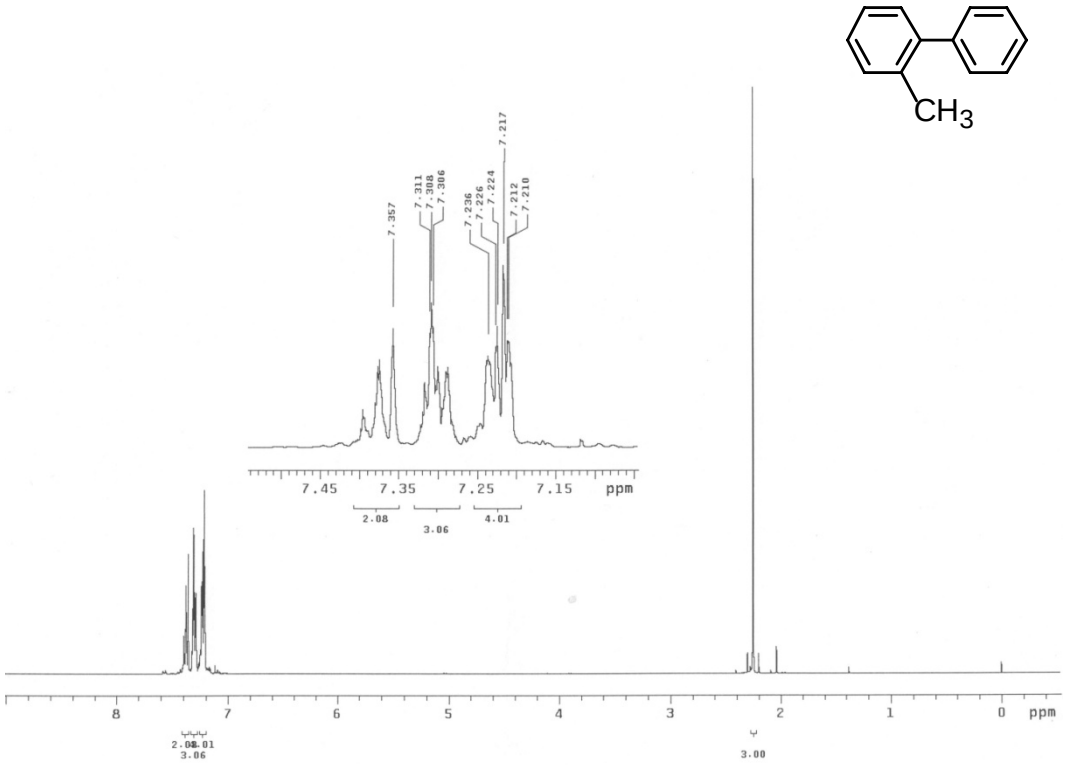


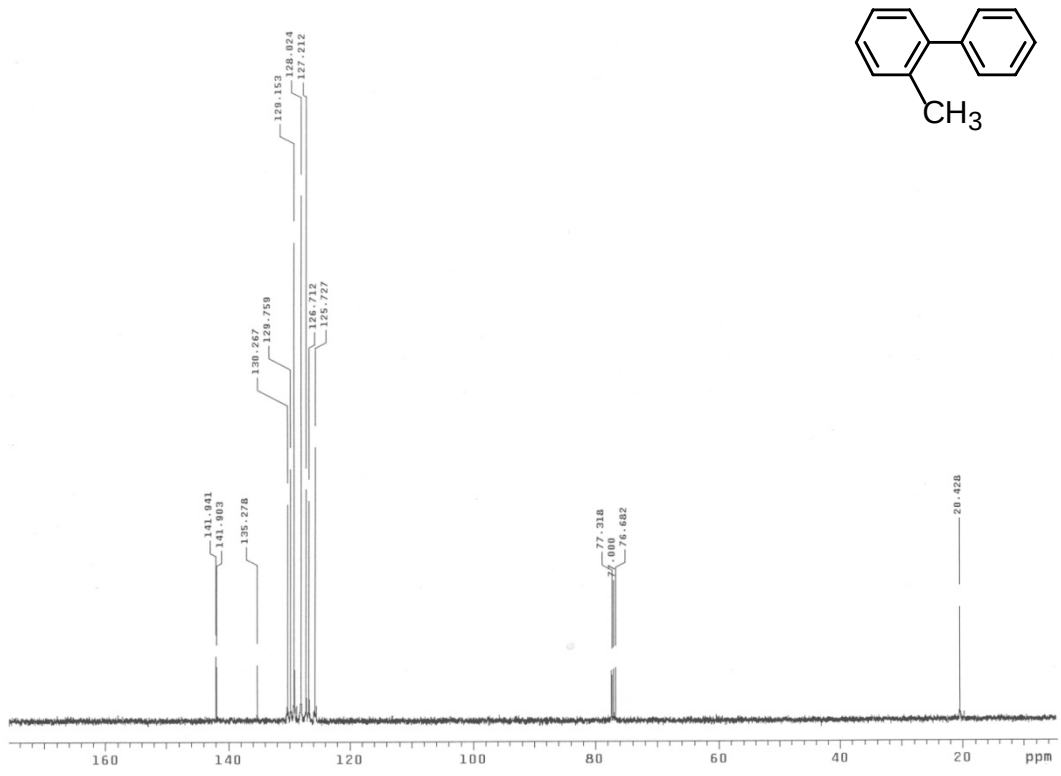
4-Phenylphenol



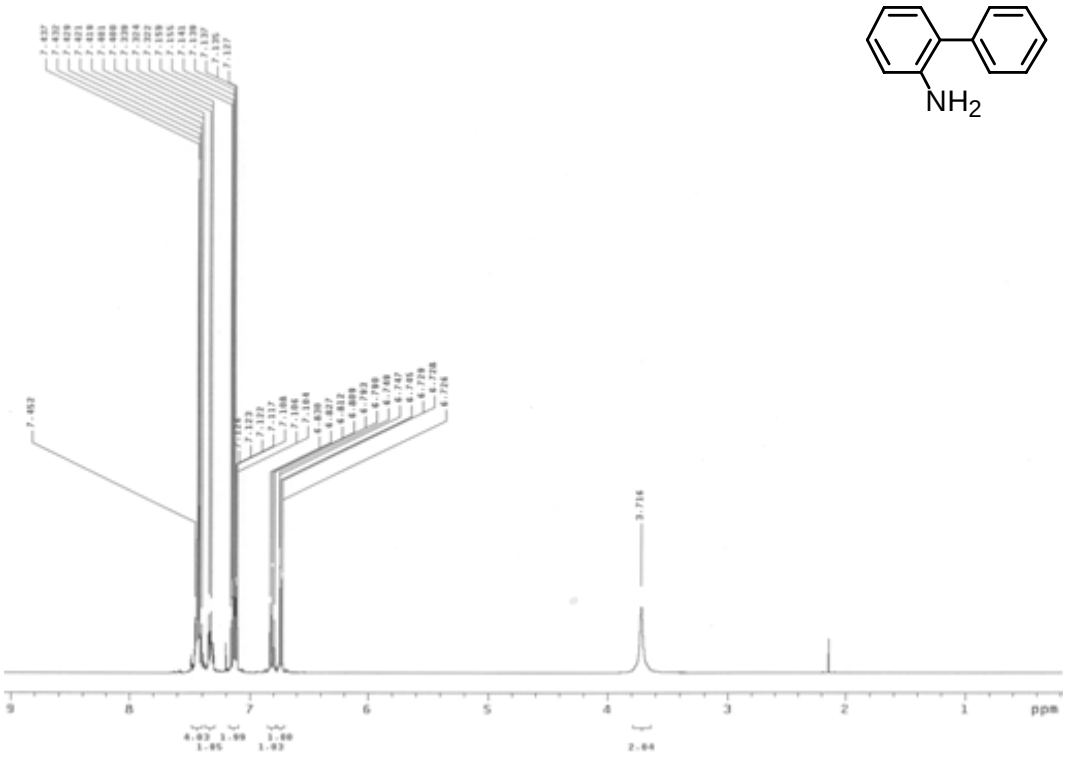


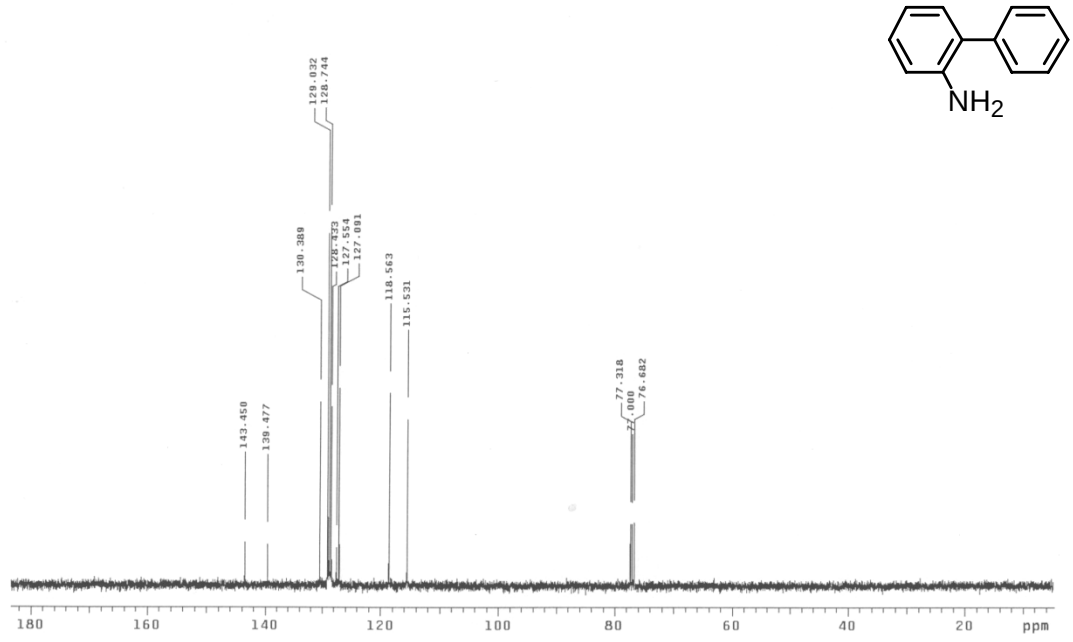
2-Methylbiphenyl



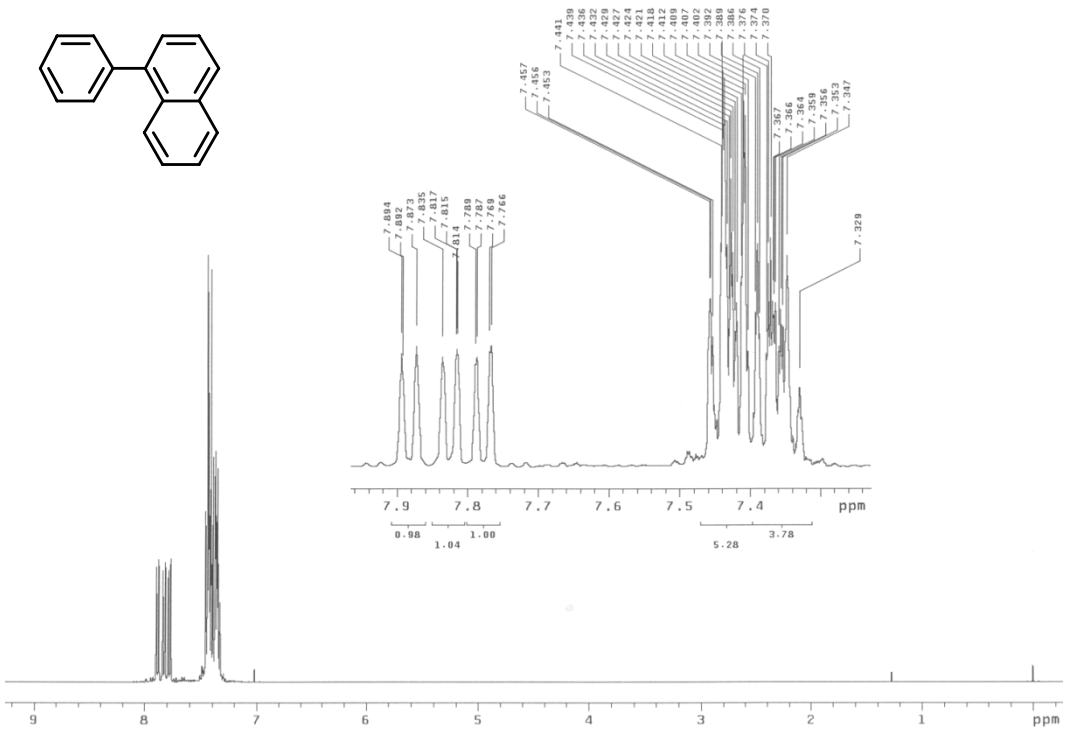


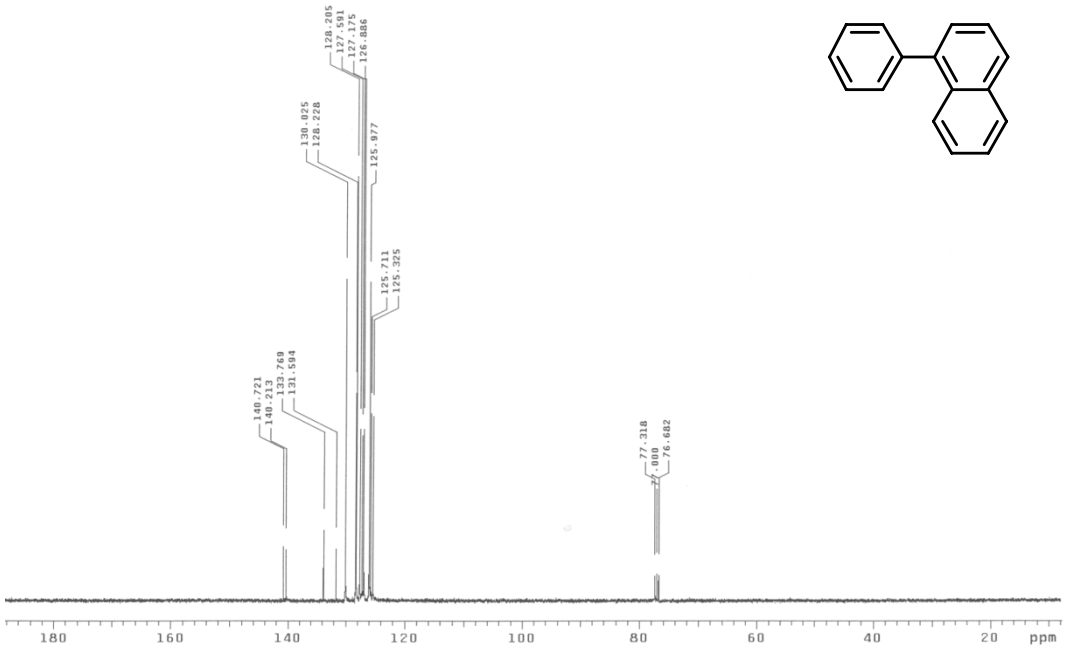
2-Aminobiphenyl



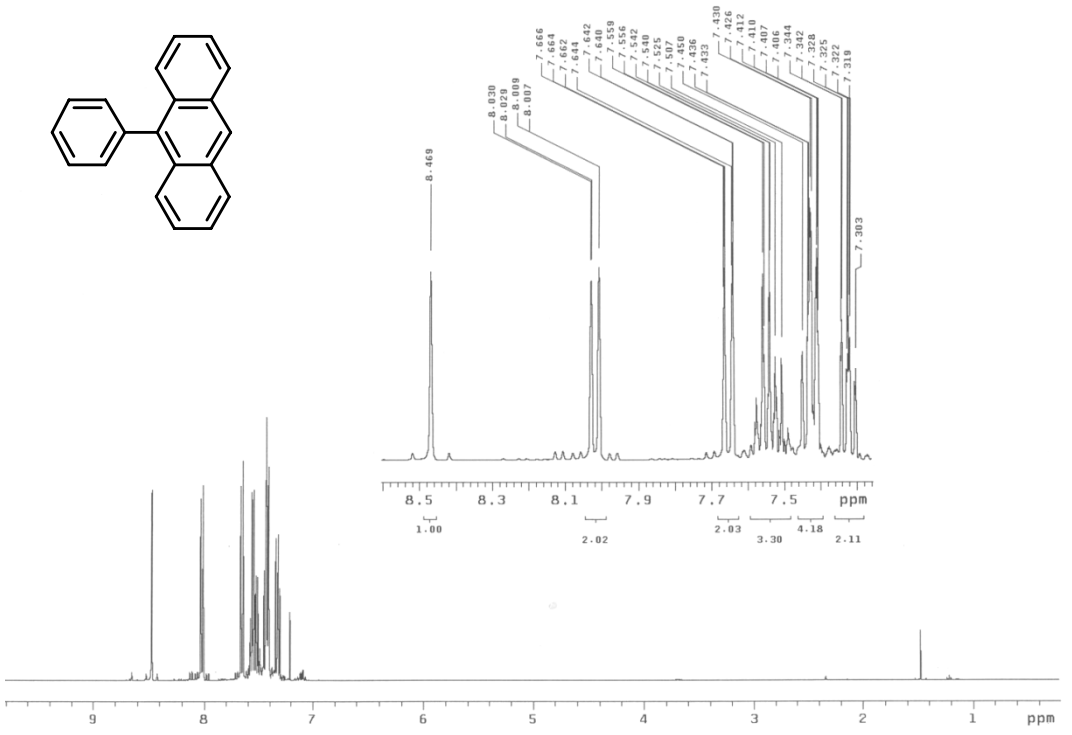


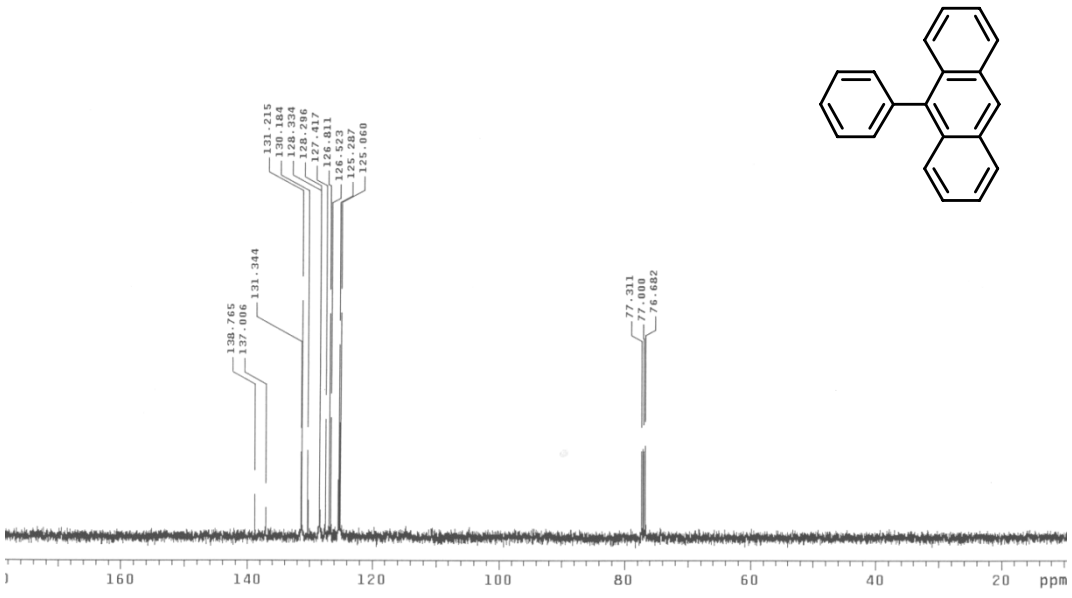
1-Phenylnaphthalene





9-Phenylanthracene





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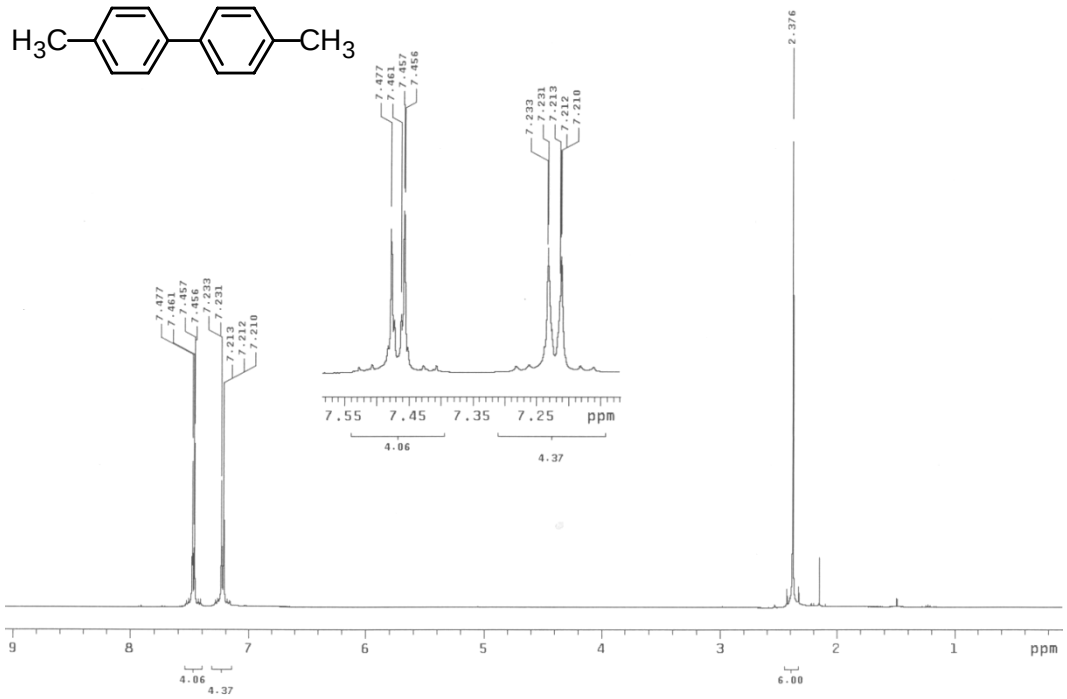

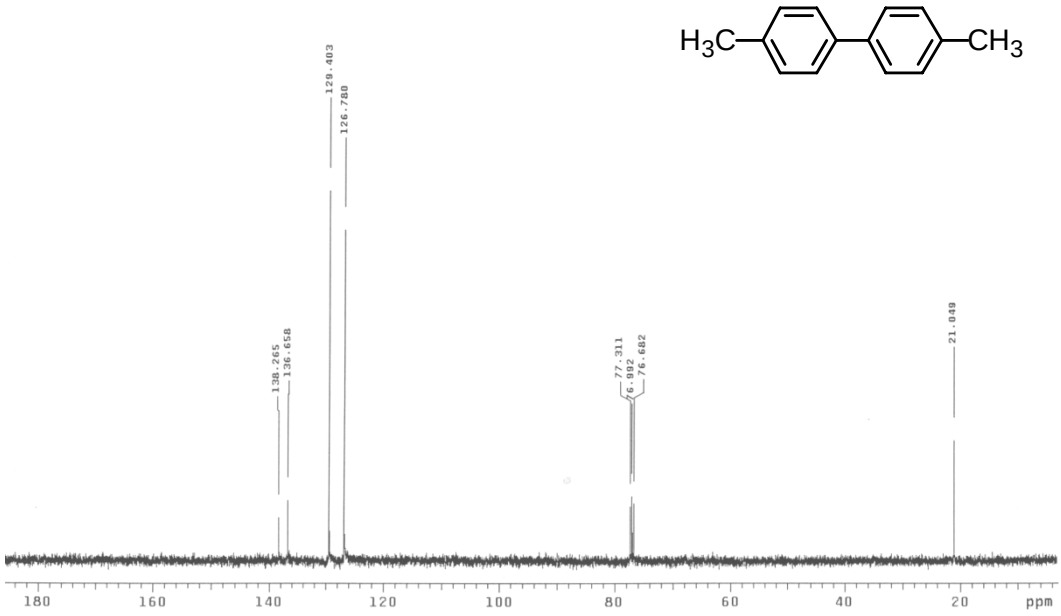

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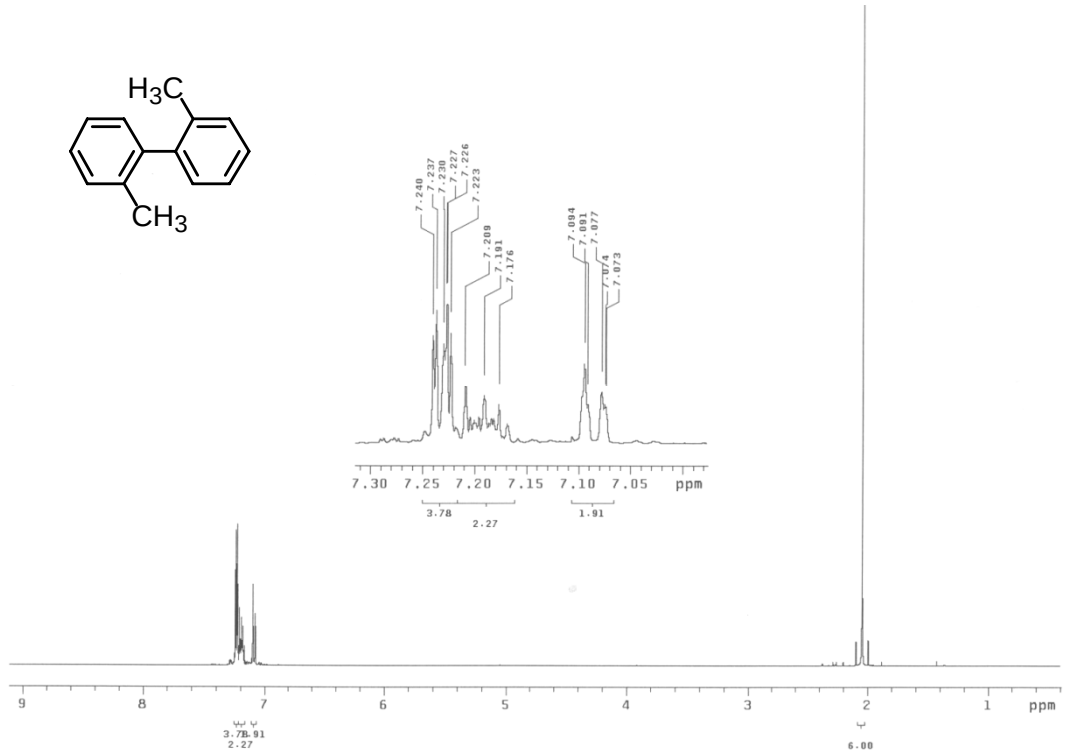
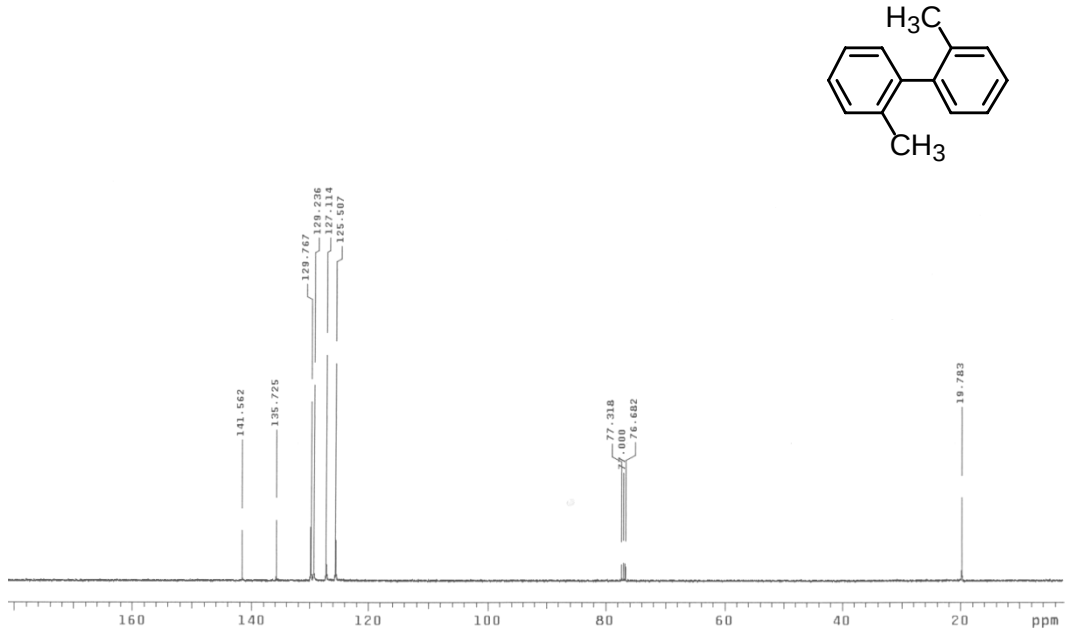
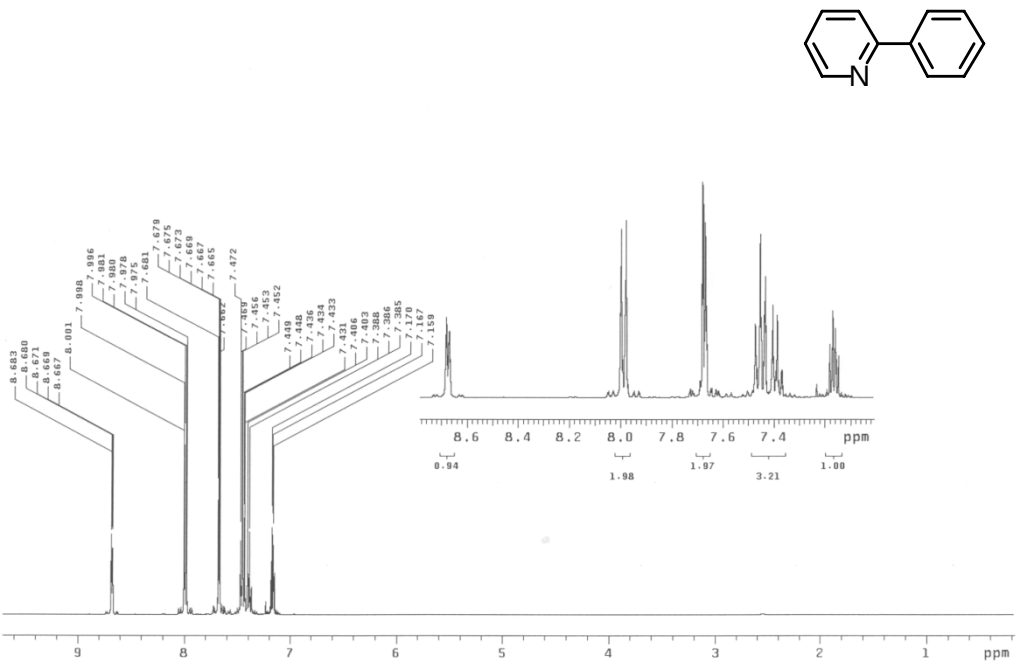
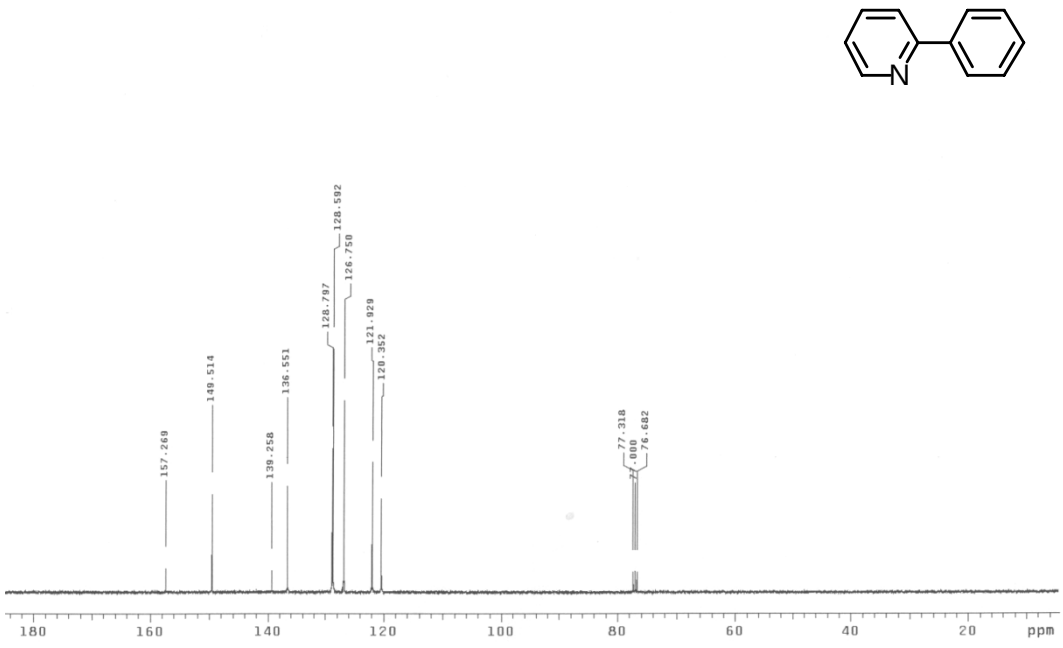


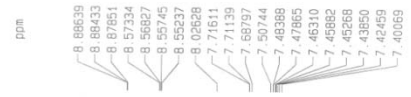


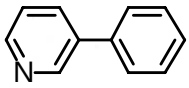
2-Phenylpyridine

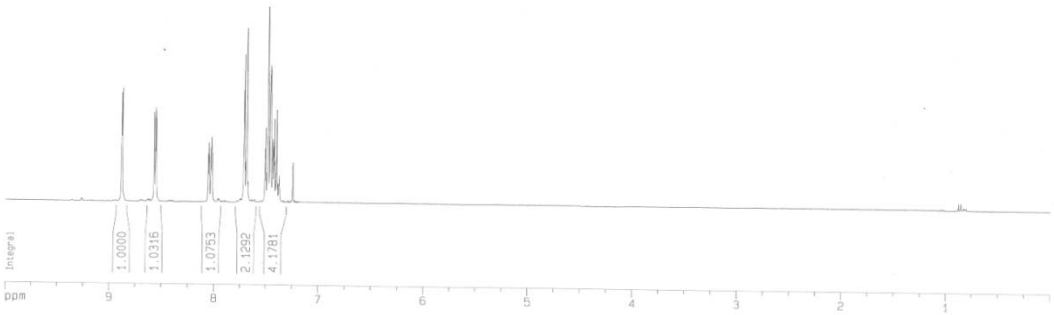


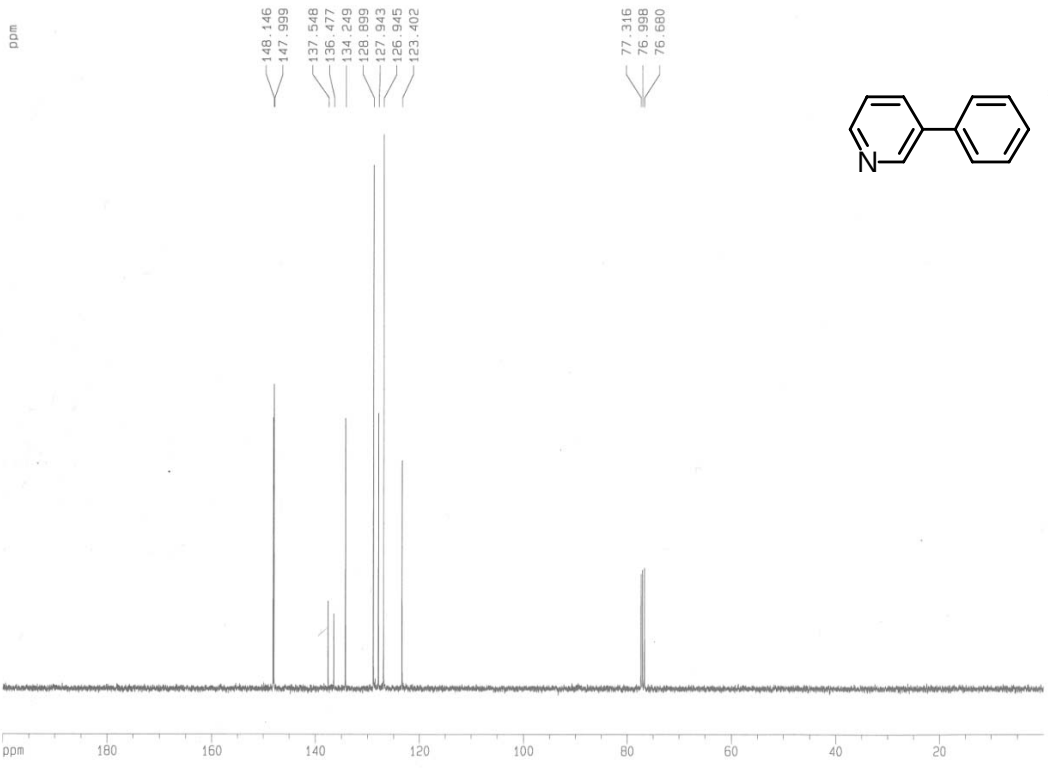


3-Phenylpyridine

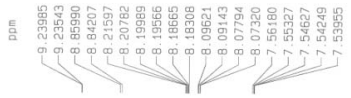


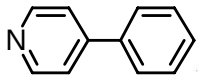


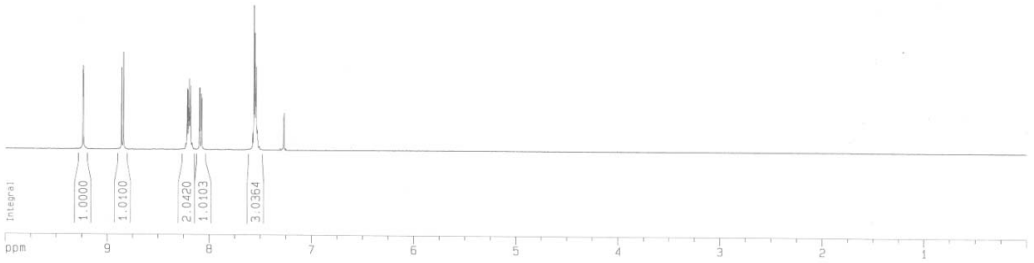


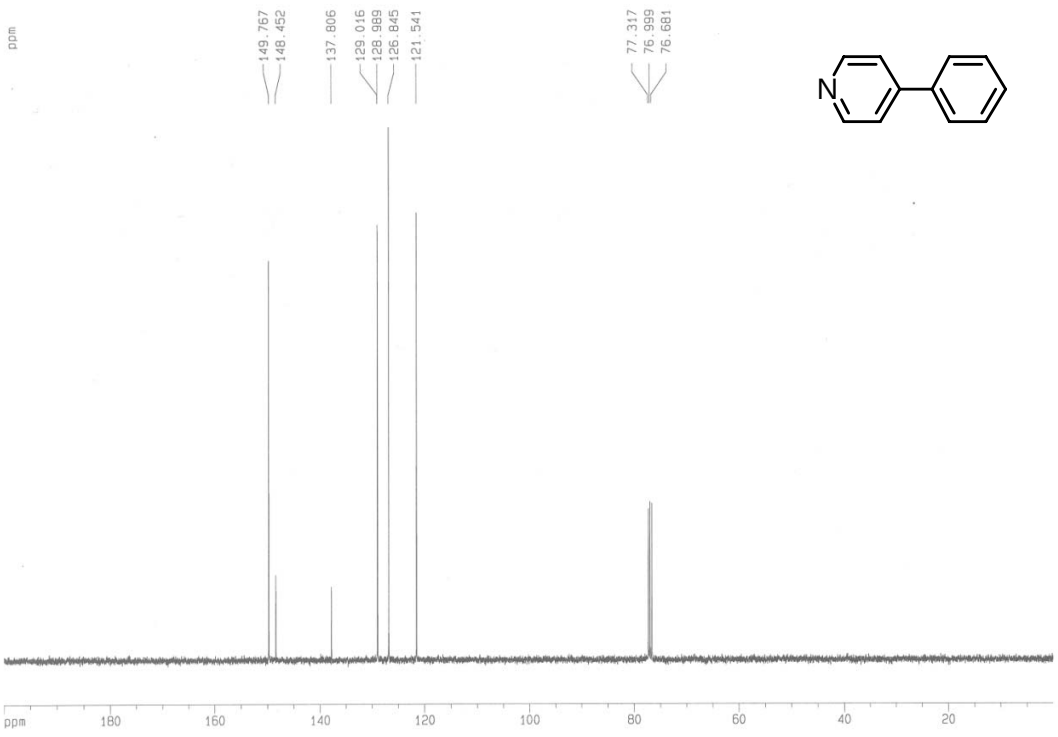


4-Phenylpyridine

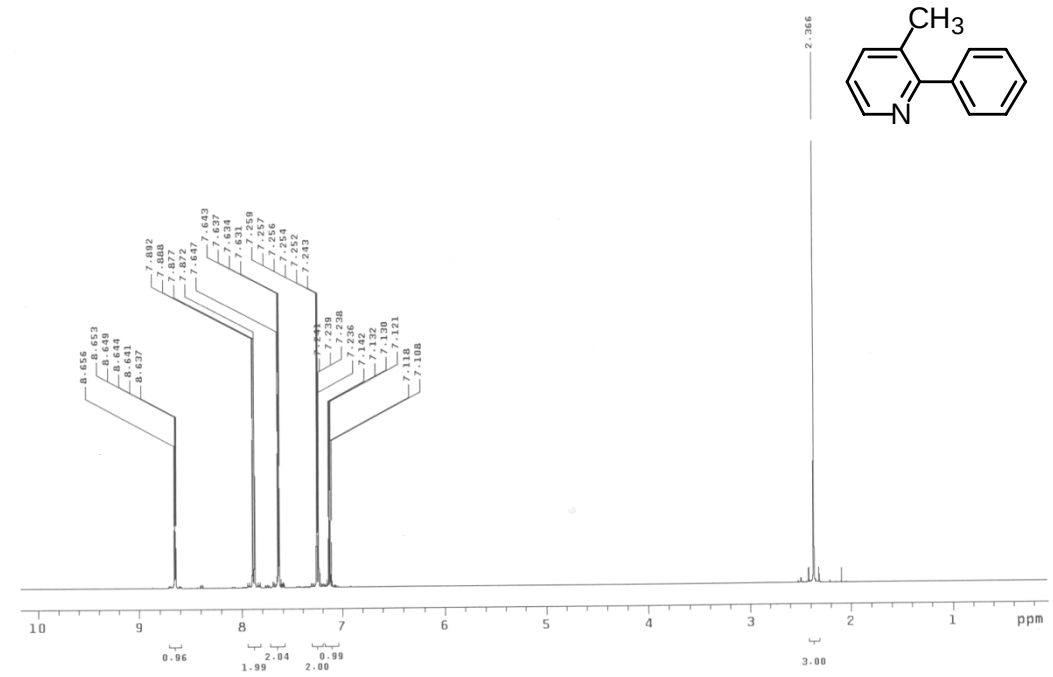


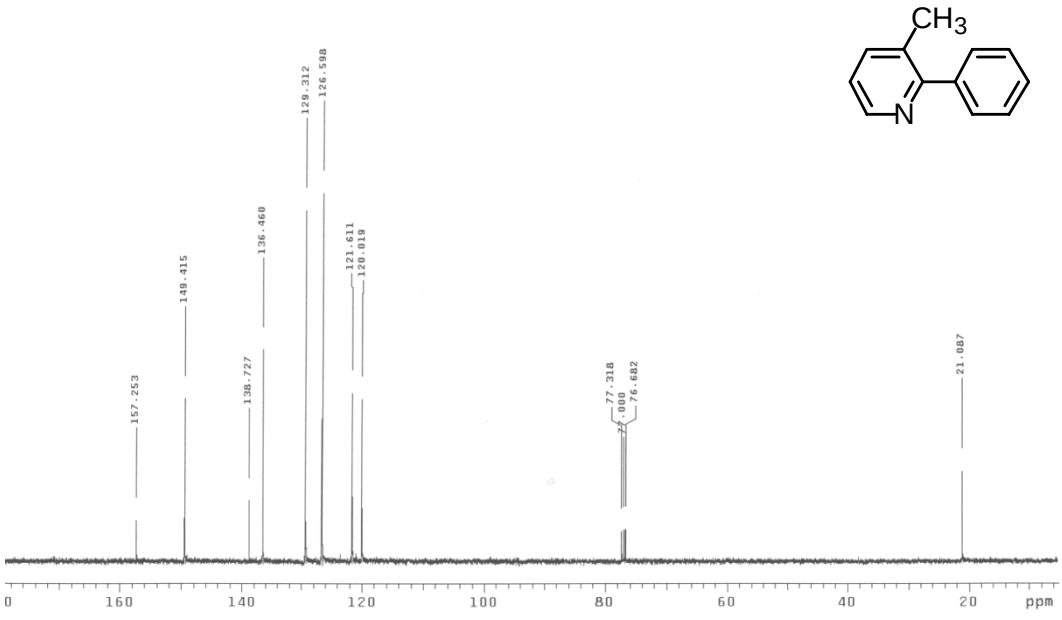




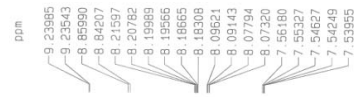


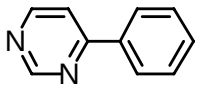
6-Methyl-2-phenylpyridine

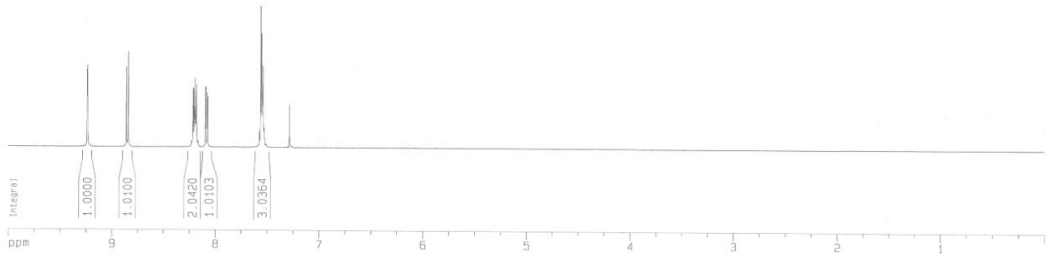


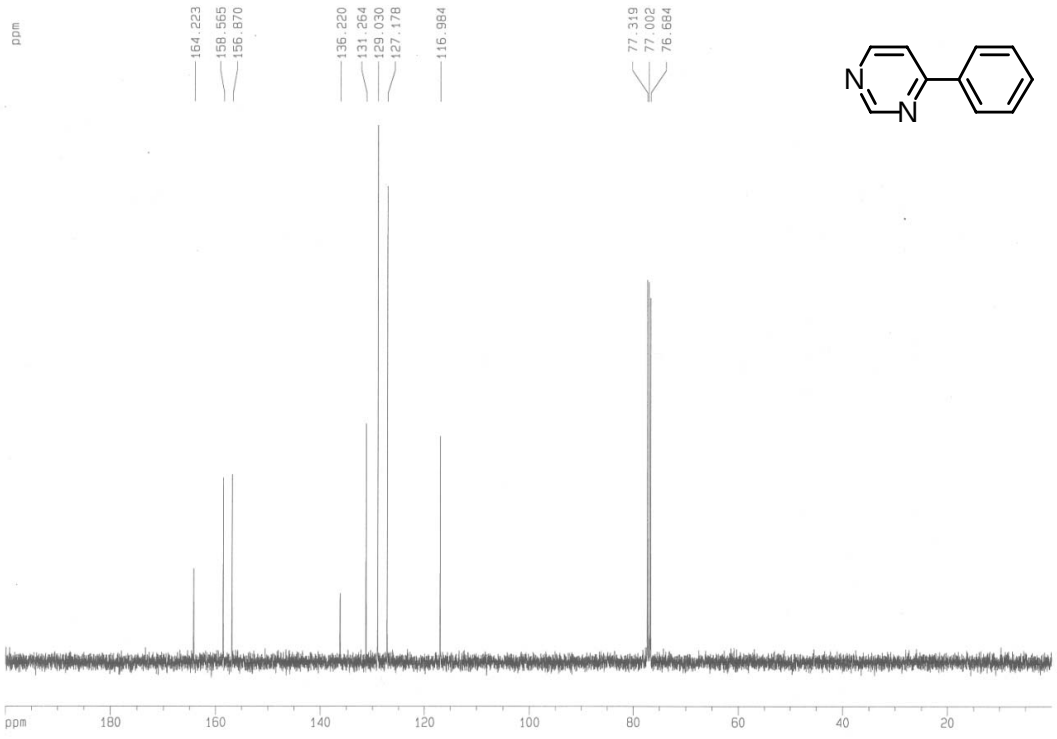


4-Phenylpyrimidine

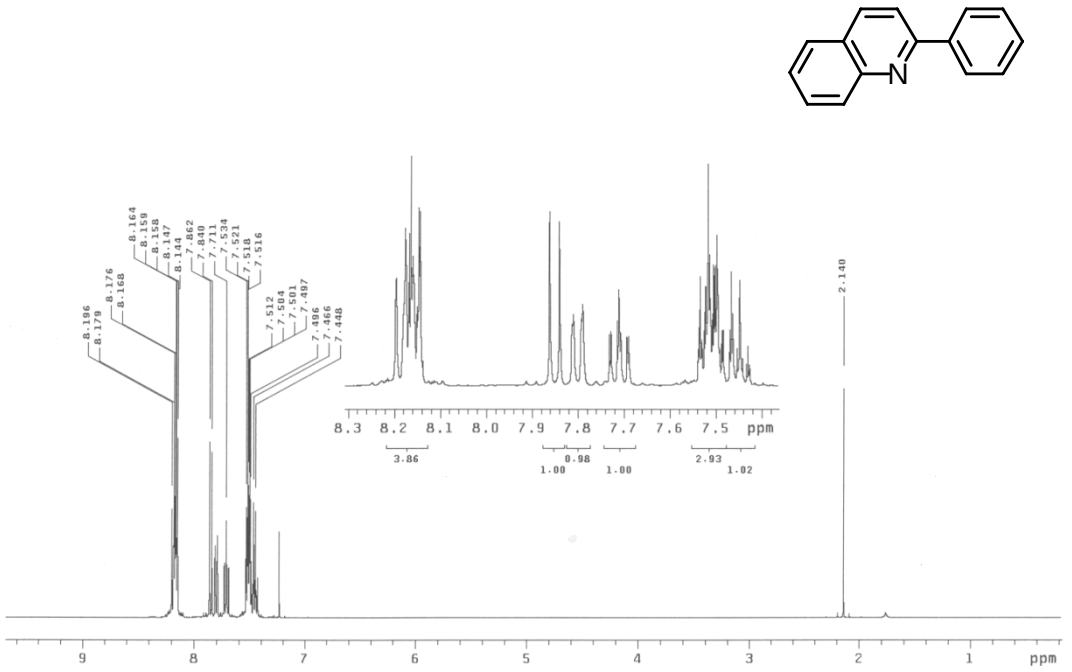


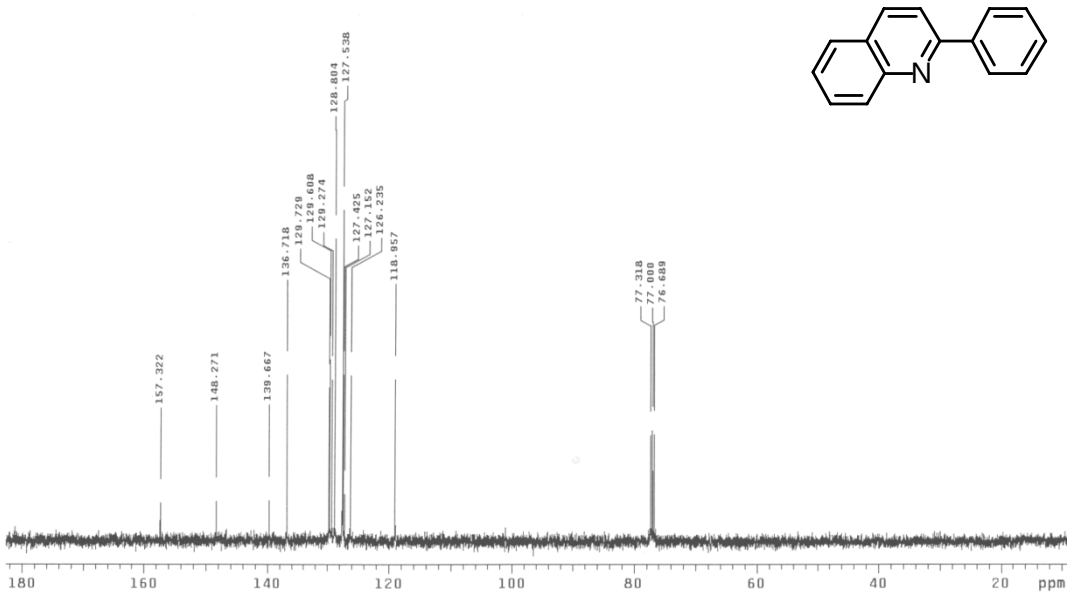




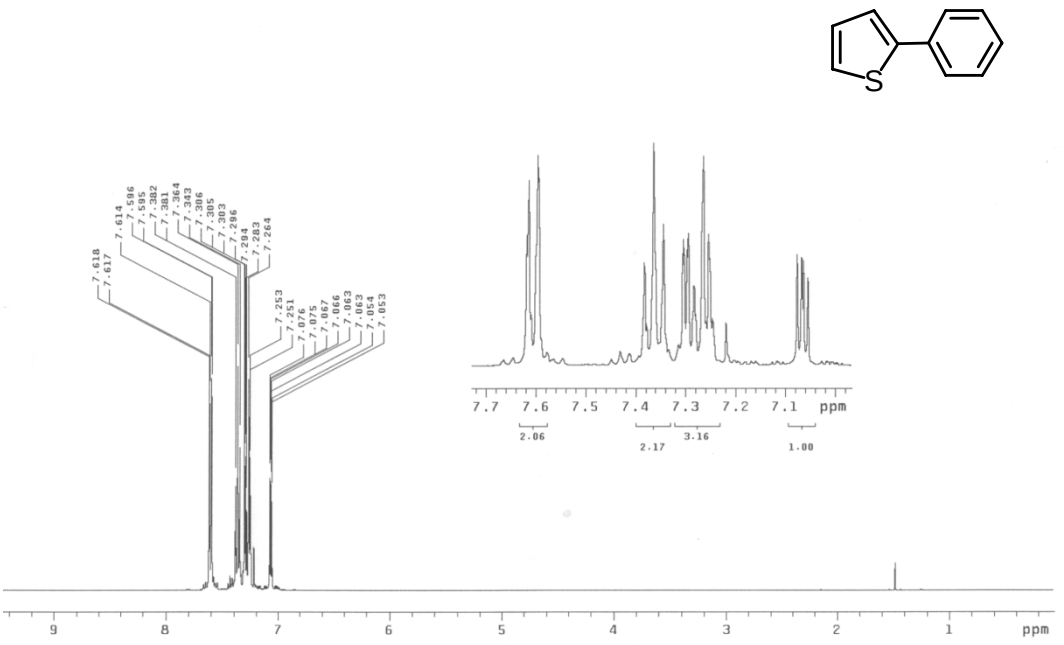


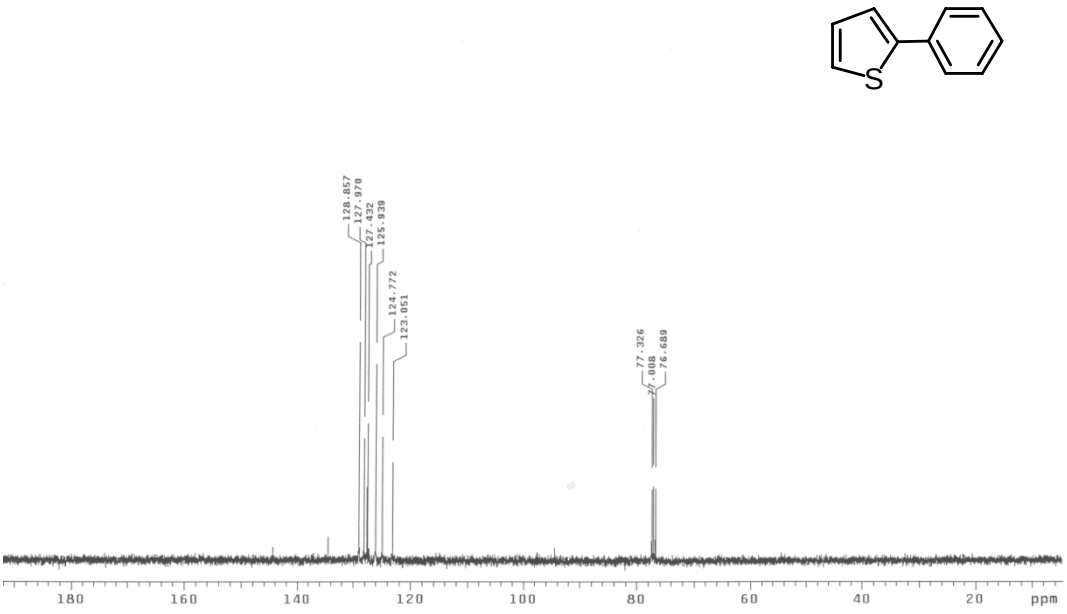
2-Phenylquinoline



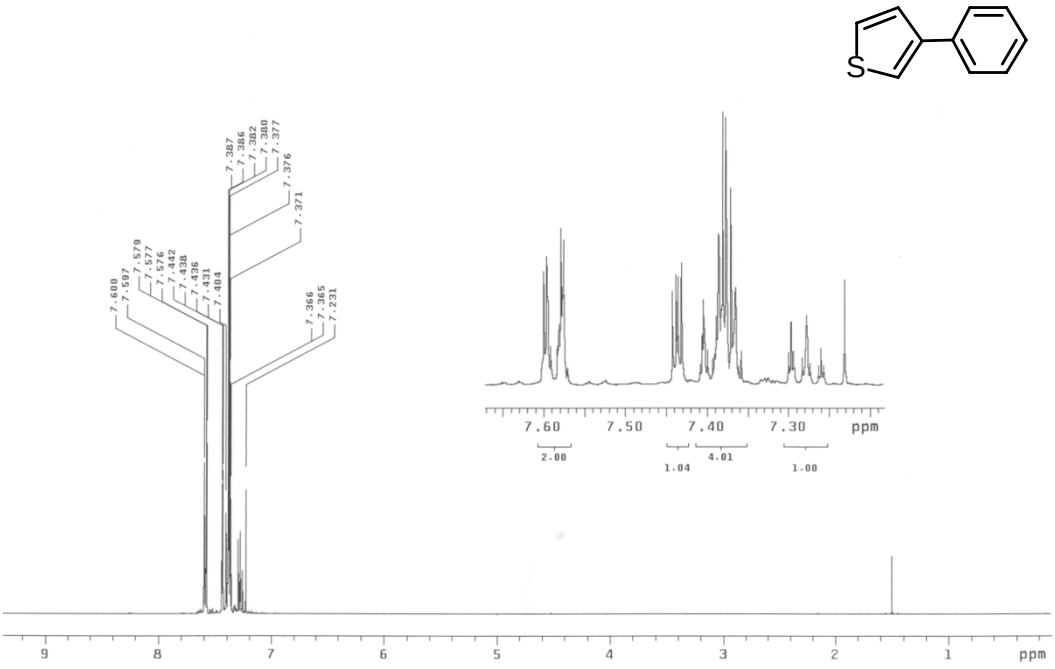


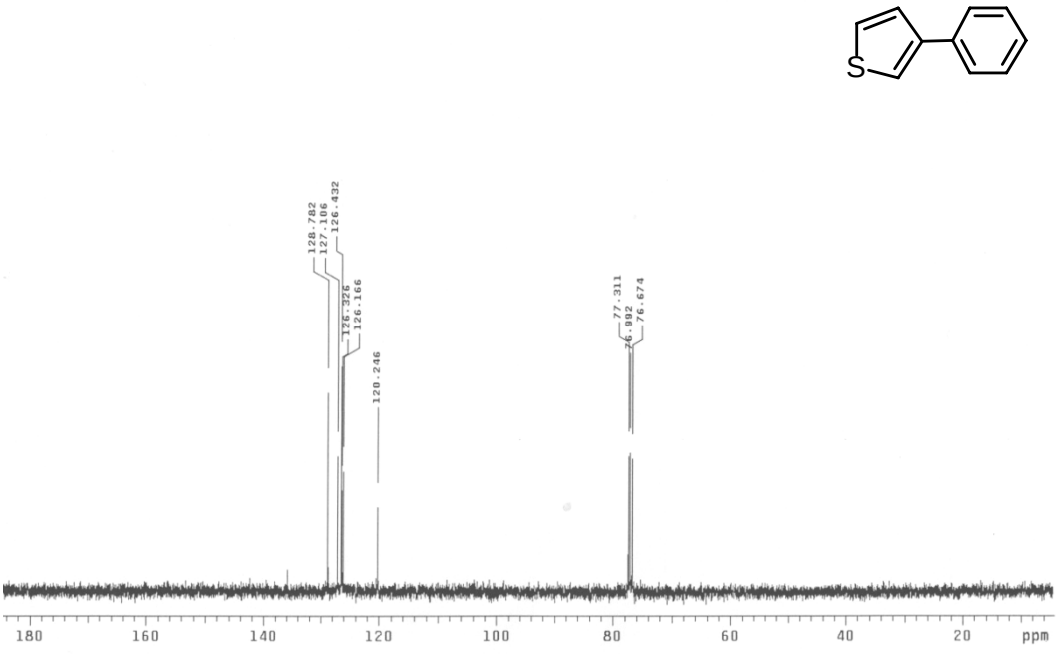
2-Phenylthiophene



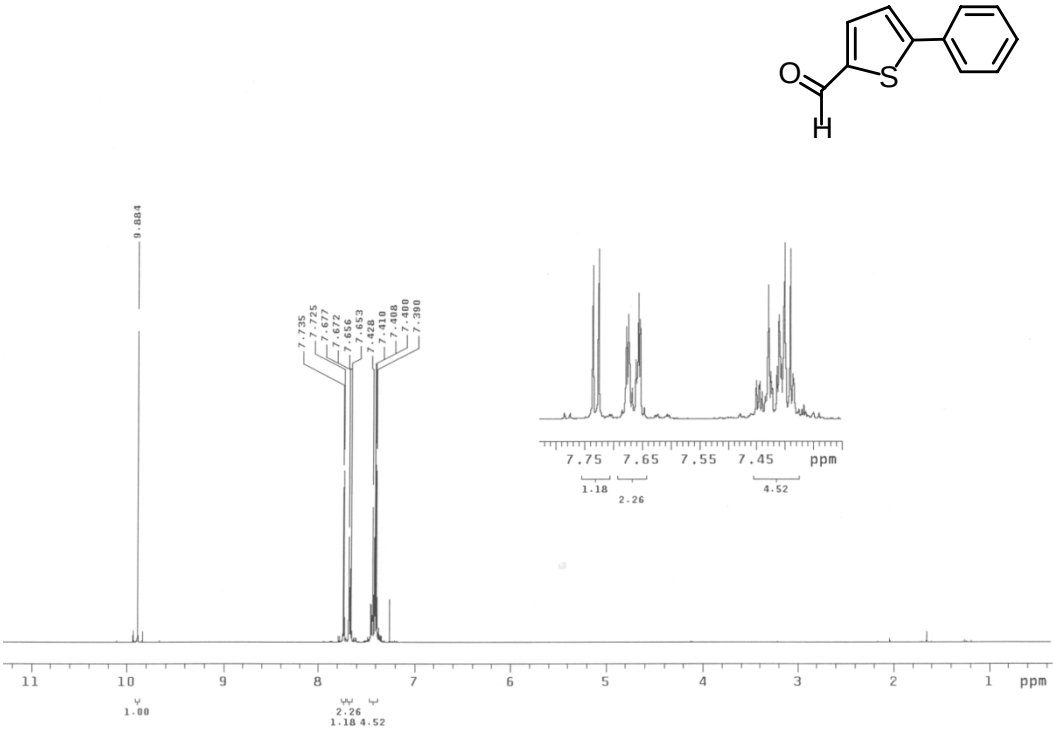


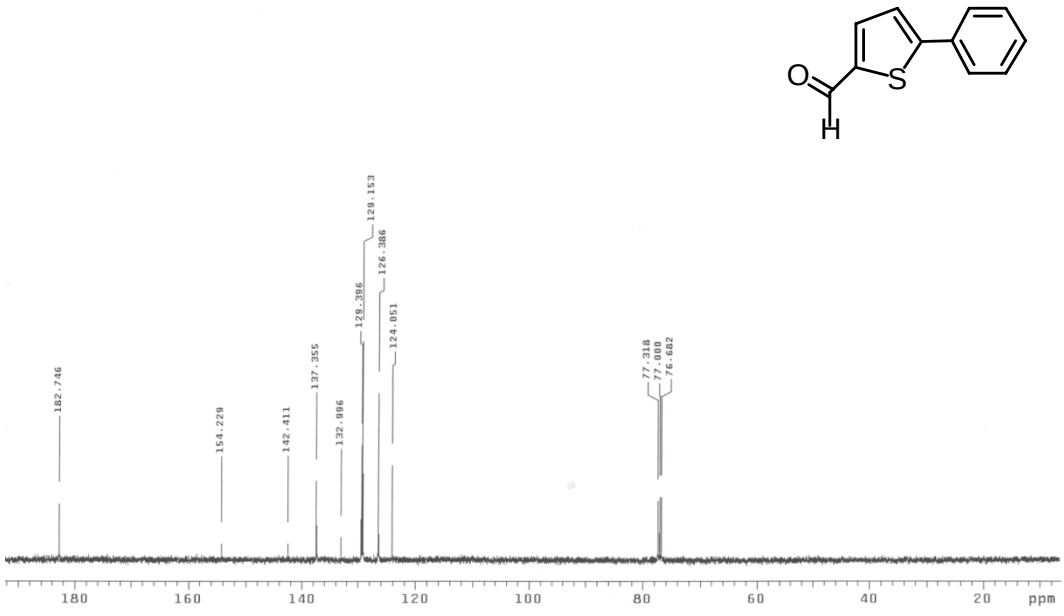
3-Phenylthiophene





5-Phenylthiophene-2-caboxaldehyde





2-(*p*-tolyl)pyridine