Electronic Supplementary Material (ESI) for Chemical Communications

Metal-Free Arylation of Benzene and Pyridine Promoted by Amino-Linked Nitrogen Heterocyclic Carbenes

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SUPPORTING INFORMATION

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General. All air-sensitive manipulations were performed under an atmosphere of nitrogen using Schlenk technique and/or glovebox. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C) and Bruker Avance 300 (300 MHz ^{1}H, 75 MHz ^{13}C) spectrometers in deuterochloroform with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm (δ), coupling constants, *J*, are reported in Hz. GC analyses of organic compounds were performed on an Agilent Technologies 1790 GC (with a SGE-OV1701 25m capillary column) instrument. Mass spectra were recorded on a JEOL JMS-700 spectrometer with an ionization voltage of 70 eV. Data are reported in the form *m*/*e* (intensity relative to base = 100%). High-resolution mass spectra were recorded on a JEOL JMS-700 spectrometer. Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light Column (flash) chromatography was performed using 40-63 μm silicagel. All reagents were purchased from Acros, Aldrich, and Alfa Aesar without further purification in advance before use. Solvents for chromatography were reagent grade. Pyridine was dried over CaH_2 before use. Benzene was dried over Na with benzophenone-ketyl intermediate as indicator.

General Procedure A: Cross-coupling of aryl iodides with benzene.

A solution of aryl iodide **2** (0.5 mmol), **1-*t*Bu** (0.1 mmol, 20 mol%) and KO^{t}Bu (1.5 mmol, 3.0 equiv.) in anhydrous benzene (4 mL) was added to a sealed tube. The resulting reaction mixture was stirred at 80 ^{o}C. After completion of the reaction, the mixture was diluted with dichloromethane, then passed through a filter, and concentrated. The crude product was purified by column hromatography on silica gel using hexanes or hexanes/ethyl acetate as eluent to give desired product **3**.

General Procedure B: Cross-coupling of aryl iodides with pyridine.

A solution of aryl iodide **2** (0.5 mmol), **1-*t*Bu-Im** (0.1 mmol, 20 mol%) and NaO^{t}Bu (1.5 mmol, 3.0 equiv.) in anhydrous pyridine (4 mL) was added to a sealed tube. The resulting reaction mixture was stirred at 110 ^{o}C. After completion of the reaction, the mixture was diluted with dichloromethane, then passed through a filter, and concentrated. The crude product was purified by column chromatography on silica gel using dichloromethane/ethyl ether as eluent to give desired product **4**.

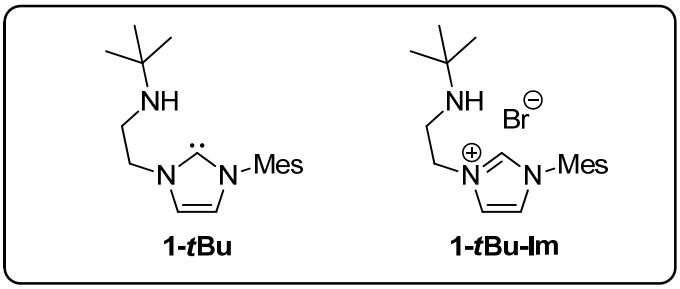
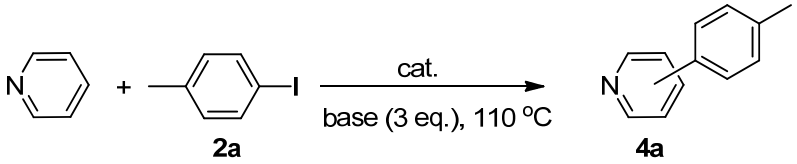


Table S1. Optimization of Direct Arylation of Pyridine[a]



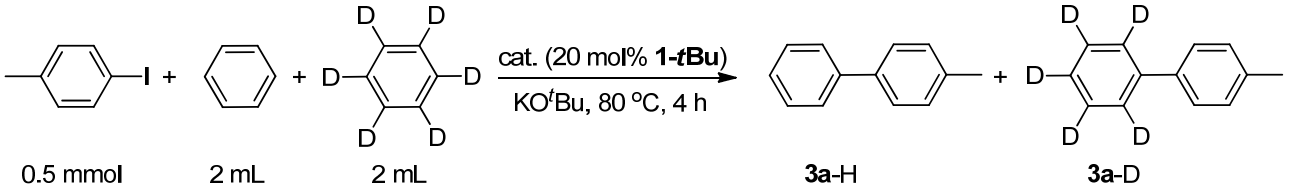
2a **4a**

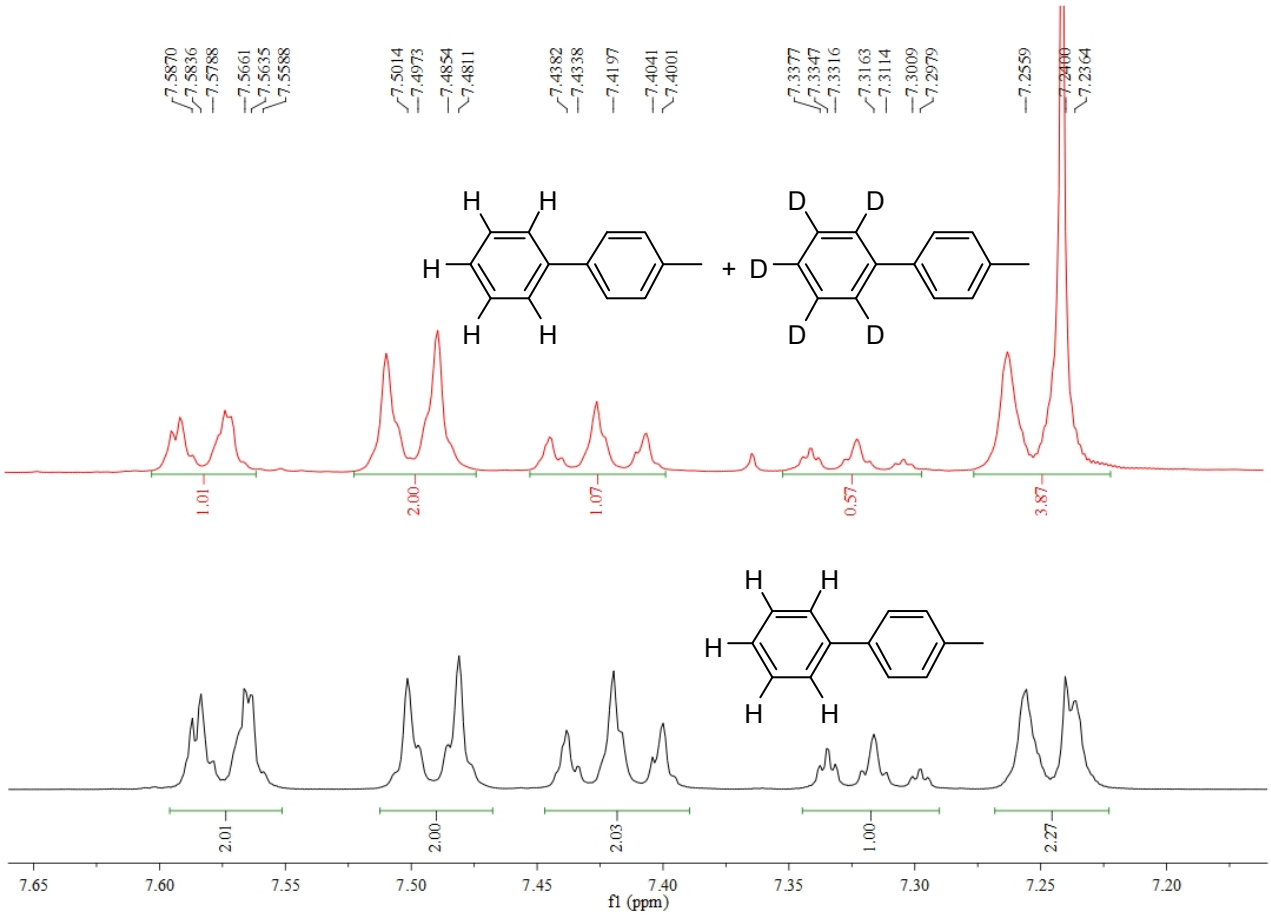
entry	cat. (mol%)	base	time(h)	yield(%)[b]	(*o*/*m*/*p*)[c]
1	**1-*t*Bu** (20)	KO^{t}Bu	4	80	(2.5/1.9/1)
2	**1-*t*Bu-Im**(20)	KO^{t}Bu	4	85	(2.9/2.2/1)
3	**1-*t*Bu-Im**(20)	NaO^{t}Bu	4	84	(2.5/2.1/1)
4	**Py-IMes**(20)	NaO^{t}Bu	4	19	
5	no	NaO^{t}Bu	4	21	

[a] The reactions was carried out under nitrogen atmosphere using **2a** (0.5 mmol), base (1.5 mmol) and pyridine (4 mL) in a sealed tube. [b] Isolated yield based on **2a**. [c] Determined by ^{1}H NMR.

Kinetic Isotope Effect Experiment Using Benzene and Benzene-d_6:

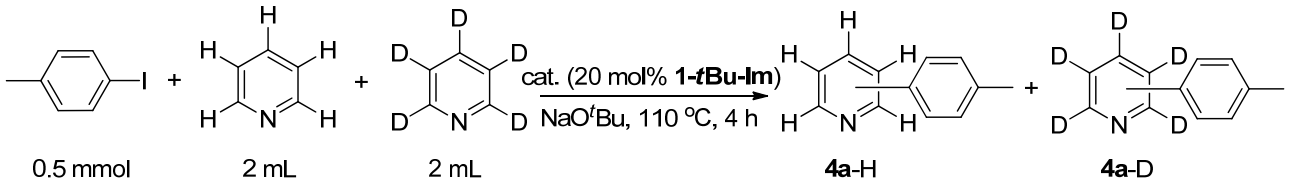
A solution of 4-iodotoluene **2a** (0.5 mmol), **1-*t*Bu** (0.1 mmol, 20 mol%) and KO^{t}Bu (1.5 mmol, 3.0 equiv.) in anhydrous benzene-H_6 (2.0 mL) and benzene-D_6 (2.0 mL) was added to a sealed tube. The resulting reaction mixture was stirred at 80 ^{o}C for 4 h. After completion of the reaction, the mixture was diluted with dichloromethane, then passed through a filter, and concentrated. The crude product distribution (k_H/k_D = 1.05) was analyzed by ^{1}H NMR.

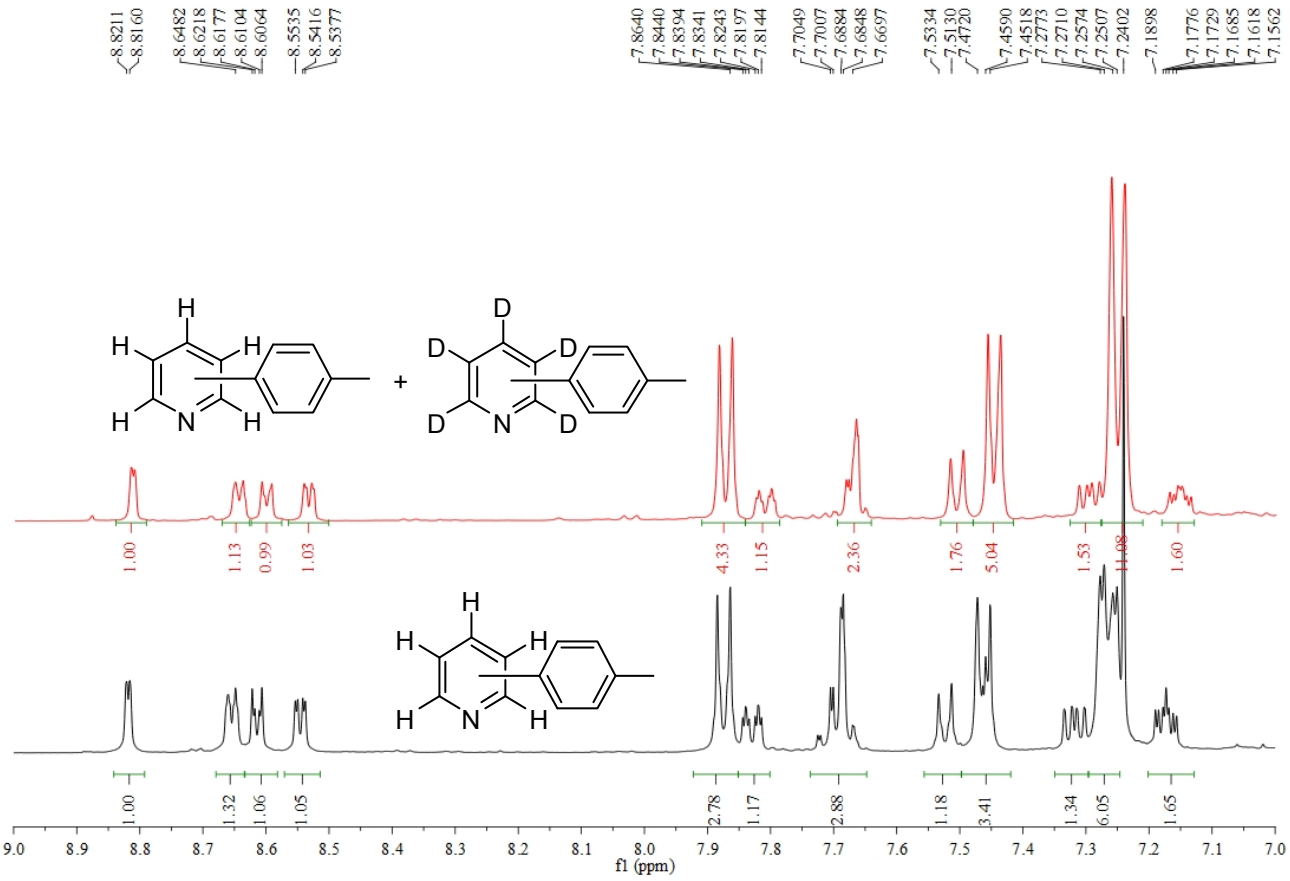




Kinetic Isotope Effect Experiment Using Pyridine and Pyridine-d_5:

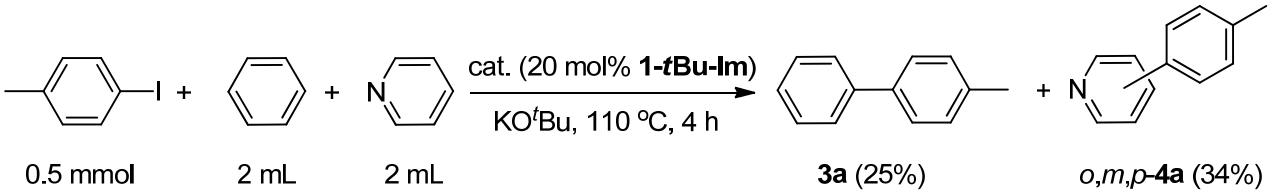
A solution of 4-iodotoluene **2a** (0.5 mmol), **1-*t*Bu-Im** (0.1 mmol, 20 mol%) and NaO^{t}Bu (1.5 mmol, 3.0 equiv.) in anhydrous pyridine-H_5 (2.0 mL) and pyridine-D_5 (2.0 mL) was added to a sealed tube. The resulting reaction mixture was stirred at 110 ^{o}C for 4 h. After completion of the reaction, the mixture was diluted with dichloromethane, then passed through a filter, and concentrated. The crude product distribution (*o*: k_H/k_D = 1.22, *m*: k_H/k_D = 1.38, *p*: k_H/k_D = 1.67) was analyzed by ^{1}H NMR.



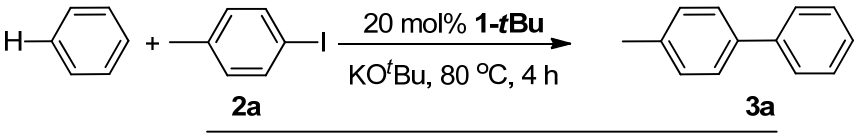


Competition Reaction between Benzene and Pyridine.

A solution of 4-iodotoluene **2a** (0.5 mmol), **1-*t*Bu-Im** (0.1 mmol, 20 mol%) and KO^{t}Bu (1.5 mmol, 3.0 equiv.) in anhydrous benzene (2.0 mL) and pyridine (2.0 mL) was added to a sealed tube. The resulting reaction mixture was stirred at 110 ^{o}C for 4 h. After completion of the reaction, the mixture was diluted with dichloromethane, then passed through a filter, and concentrated. The crude product was purified by column chromatography on silica gel using hexanes and dichloromethane/ethyl ether as eluent to give desired product **3a** and **4a** (**3a**/**4a** = 1/1.36).

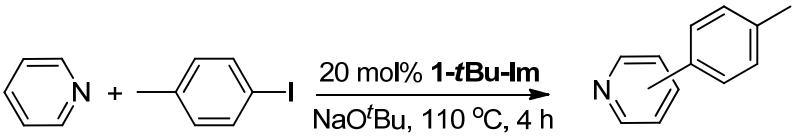


Radical Trapping Experiments



2a **3a**

No Scavenger	78%(GC)
TEMPO 20mol%	0%(GC)



2a **4a**

No Scavenger	84%
TEMPO 20mol%	9%
TEMPO 40mol%	trace
TEMPO 100mol%	0%

EPR spectrum

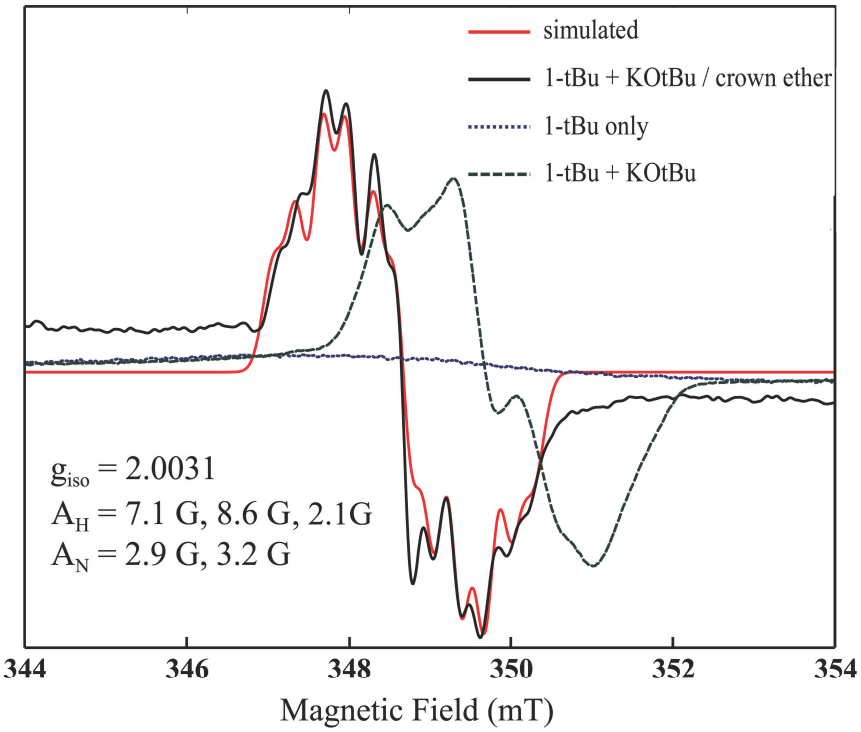
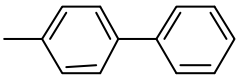
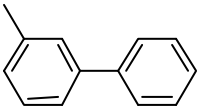


Figure1. Room temperature EPR spectrum of the solution containing equiv. amounts of **1-*t*Bu**, KO^{t}Bu and crown ether (black) dissolved in toluene and the best-fit simulated spectrum (red) of a radical anion with g_{iso} = 2.0031, A_H = 2.1 G, 7.1G, 8.6 G, and A_N = 2.9 G, 3.2 G.

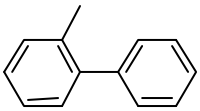
Experimental section and characterization:



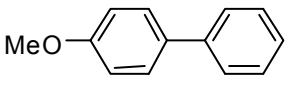
4-methylbiphenyl (3a)[1]: Following Procedure A, 1-iodo-4-methylbenzene (109 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 4 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0, 2H), 7.49 (d, *J* = 8.1, 2H), 7.42 (t, *J* = 7.8, 2H), 7.32 (t, *J* = 7.4, 1H), 7.25 (d, *J* = 7.8, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.3, 137.0 129.5, 128.7, 127.0, 21.1; High Resolution-MS (EI) calcd. For $C_{13}H_{12}$: 168.0939, found: 168.0936.



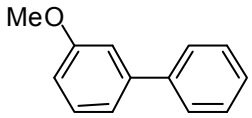
3-methybiphenyl (3b)[2]: Following Procedure A, 1-iodo-3-methylbenzene (109 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 4 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5, 2H), 7.49-7.43 (m, 4H), 7.37 (t, *J* = 8.4, 2H), 7.21 (d, *J* = 7.5, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 141.2, 138.3, 128.7, 128.0, 127.2, 124.3, 21.5; High Resolution-MS (EI) calcd. For $C_{13}H_{12}$: 168.0939, found: 168.0937.



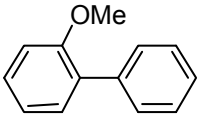
2-methybiphenyl (3c)[2]: Following Procedure A, 1-iodo-2-methylbenzene (109 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.23 (m, 9H), 6.92-6.90 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 135.3, 130.3, 129.8, 129.2, 128.7, 128.0, 127.2, 126.7, 125.7, 20.4; High Resolution-MS (EI) calcd. For $C_{13}H_{12}$: 168.0939, found: 168.0939.



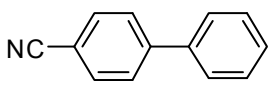
4-methoxybiphenyl (3d)[3]: Following Procedure A, 1-iodo-4-methoxybenzene (117 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 3 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 4H), 7.40 (t, *J* = 7.5, 2H), 7.29 (t, *J* = 7.3, 1H), 6.97 (d, *J* = 8.8, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; High Resolution-MS (EI) calcd. For $C_{13}H_{12}O$: 184.0888, found: 184.0891.



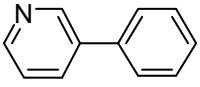
3-methoxybiphenyl (3e)[3]: Following Procedure A, 1-iodo-3-methoxybenzene (117 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 3 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5, 2H), 7.45 (t, *J* = 7.6, 2H), 7.39-7.35 (m, 2H), 7.20 (d, *J* = 7.7, 1H), 7.15 (t, *J* = 2.0, 1H), 6.92 (dd, *J* = 8.2, 2.3, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 142.7, 141.1, 129.7, 128.7, 127.4, 127.2, 119.6, 112.9, 112.7, 55.2; High Resolution-MS (EI) calcd. For $C_{13}H_{12}O$: 184.0888, found: 184.0887.



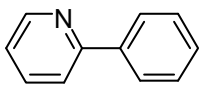
2-methoxybiphenyl (3f)[3]: Following Procedure A, 1-iodo-2-methoxybenzene (117 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3, 2H), 7.41 (t, *J* = 7.6, 2H), 7.34-7.31 (m, 3H), 7.03 (t, *J* = 7.5, 1H), 6.99 (d, *J* = 8.5, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 138.5, 130.9, 130.7, 129.5, 128.6, 127.9, 126.9, 120.8, 111.2, 55.5; High Resolution-MS (EI) calcd. For $C_{13}H_{12}O$: 184.0888, found: 184.0889.



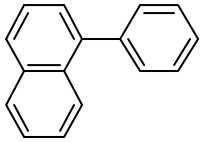
biphenyl-4-carbonitrile (3g)[3]: Following Procedure A, 4-iodobenzonitrile (115 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 4 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5, 2H), 7.67 (d, *J* = 8.6, 2H), 7.58 (d, *J* = 8.6, 2H), 7.47 (t, *J* = 7.3, 2H), 7.41 (t, *J* = 7.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.7, 127.2, 118.9, 110.8; High Resolution-MS (EI) calcd. For $C_{13}H_9N$: 179.0735, found: 179.0733.



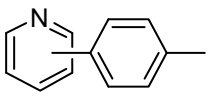
3-phenylpyridine (3h)[4]: Following Procedure A, 3-iodopyridine (103 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 3 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 2.1, 1H), 8.58 (dd, *J* = 4.8, 1.5, 1H), 7.86 (ddd, *J* = 7.9, 2.2, 1.8, 1H), 7.57 (d, *J* = 7.1, 2H), 7.47 (t, *J* = 7.5, 2H), 7.39 (d, *J* = 7.3, 1H), 7.35 (ddd, *J* = 7.8, 4.8, 0.6, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 148.4, 137.9, 136.6, 134.3, 129.1, 128.1, 127.2, 123.5; High Resolution-MS (EI) calcd. For $C_{11}H_9N$: 155.0735, found: 155.0731.



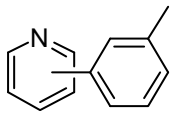
2-phenylpyridine (3i)[5]: Following Procedure A, 2-iodopyridine (103 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 4 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dt, *J* = 4.8, 1.4, 1H), 7.97 (d, *J* = 7.0, 2H), 7.76-7.70 (m, 2H), 7.46 (t, *J* = 7.3, 2H), 7.40 (t, *J* = 7.2, 1H), 7.21 (ddd, *J* = 6.8, 4.9, 2.1, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.6, 139.4, 136.7, 128.7, 126.9, 122.0, 120.5; High Resolution-MS (EI) calcd. For $C_{11}H_9N$: 155.0735, found: 155.0732.



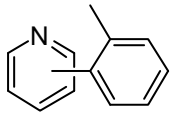
2-phenylnaphthalene (3j)[6]: Following Procedure A, 1-iodonaphthalene (127 mg, 0.5 mmol) was allowed to react with benzene (4 mL) for 4 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.5, 2H), 7.86 (t, *J* = 7.8, 1H), 7.54-7.46 (m, 6H), 7.45-7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.3, 133.8, 131.6, 130.1, 128.2, 127.6, 126.9, 126.02, 125.99, 125.7, 125.4; High Resolution-MS (EI) calcd. For $C_{16}H_{12}$: 204.0939, found: 204.0937.



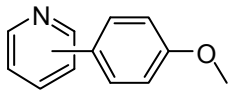
***p*-tolylpyridine (4a)[7]:** Following Procedure B, 1-iodo-4-methylbenzene (109 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.0, 1H), 7.88 (d, *J* = 8.2, 2H), 7.73-7.67 (m, 2H), 7.27 (d, *J* = 8.0, 2H), 7.18 (ddd, *J* = 6.7, 4.9, 2.1, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.6, 138.9, 136.6, 129.4, 126.7, 121.7, 120.2, 21.2; *m*-(**4a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.55 (d, *J* = 4.4, 1H), 7.84 (d, *J* = 7.9, 1H), 7.47 (d, *J* = 8.0, 2H), 7.33 (dd, *J* = 7.8, 4.8, 1H), 7.27 (d, *J* = 7.8, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ148.2, 138.0, 136.6 134.9, 134.1, 129.8, 127.0, 123.5, 21.1; *p*-(**4a**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 6.0, 2H), 7.53 (d, *J* = 8.1, 2H), 7.47 (d, *J* = 6.1, 2H), 7.28 (d, *J* = 8.3, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 148.3, 139.2, 135.2, 129.8, 126.8, 121.4, 21.2; High Resolution-MS (EI) calcd. For $C_{12}H_{11}N$: 169.0891, found: 169.0890.



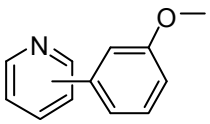
***m*-tolylpyridine (4b)[8]:** Following Procedure B, 1-iodo-3-methylbenzene (109 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dt, *J* = 4.8, 1.3, 1H), 7.82 (s, 1H), 7.75-7.69 (m, 3H), 7.34 (t, *J* = 7.6, 1H), 7.22-7.18 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 149.6, 139.4, 138.5, 136.7, 129.7, 128.6, 127.7, 124.0, 122.0, 120.6, 21.5; *m*-(**4b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.2, 1H), 8.53 (dd, *J* = 4.8, 1.4, 1H), 7.77 (dt, *J* = 7.9, 1.9, 1H), 7.32-7.29 (m, 3H), 7.26 (dd, *J* = 7.9, 4.9, 1H), 7.16 (d, *J* = 4.7, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 148.0, 138.4, 137.5 136.4, 134.0, 128.7, 128.6, 127.6, 124.0, 123.2, 21.2; *p*-(**4b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 6.2, 2H), 7.46 (d, *J* = 6.2, 2H), 7.42 (s, 1H), 7.41 (d, *J* = 7.9, 1H), 7.34 (t, *J* = 7.7, 1H), 7.22 (d, *J* = 7.6, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 138.7, 138.0 129.7, 128.9, 127.6, 124.0, 121.6, 21.4; High Resolution-MS (EI) calcd. For $C_{12}H_{11}N$: 169.0891, found: 169.0887.



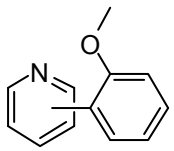
***o*-tolylpyridine (4c)[9]:** Following Procedure B, 1-iodo-2-methylbenzene (109 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 24 h. *o*-(**4c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (ddd, *J* = 4.9, 1.8, 0.9, 1H), 7.72 (td, *J* = 7.7, 1.9, 1H), 7.39-7.37 (m, 2H), 7.29-7.21 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 149.2, 140.5, 136.1, 135.7, 130.7, 129.6, 128.2, 125.8, 124.1, 121.6, 20.2; *m*-(**4c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.3, 1H), 8.56 (dd, *J* = 4.9, 1.6, 1H), 7.61 (dt, *J* = 7.8, 1.9, 1H), 7.31 (dd, *J* = 7.8, 4.8, 1H), 7.28-7.22 (m, 3H), 7.18 (d, *J* = 6.9, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 148.0, 137.9, 137.3, 136.3, 135.4, 130.4, 129.7, 128.0, 125.9, 122.8, 20.2; *p*-(**4c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 6.0, 2H), 7.30-7.24 (m, 5H), 7.19 (d, *J* = 7.2, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.6, 139.1, 135.0, 130.6, 129.2, 128.4, 126.1, 124.2, 20.2; High Resolution-MS (EI) calcd. For $C_{12}H_{10}N$: 168.0813, found: 168.0811 $(M-H)^{+}$.



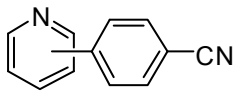
4-methoxyphenylpyridine (4d)[10]: Following Procedure B, 1-iodo-4-methoxybenzene (117 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.6, 1H), 7.93 (d, *J* = 8.9, 2H), 7.68 (td, *J* = 8.1, 1.8, 1H), 7.64 (d, *J* = 7.9, 1H), 7.14 (ddd, *J* = 6.7, 4.8, 1.4, 1H), 6.98 (d, *J* = 8.8, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 157.1, 149.5, 136.6, 132.0, 128.1, 121.4, 119.7, 114.1, 55.3; *m*-(**4d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 1.9, 1H), 8.52 (d, *J* = 4.0, 1H), 7.80 (d, *J* = 7.9, 1H), 7.50 (d, *J* = 8.7, 2H), 7.31 (dd, *J* = 7.8, 4.8, 1H), 6.99 (d, *J* = 8.6, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 148.0, 147.9, 136.2, 133.8, 130.3, 128.2, 123.5, 114.5, 55.4; *p*-(**4d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.1, 2H), 7.58 (d, *J* = 8.7, 2H), 7.45 (d, *J* = 5.6, 2H), 6.99 (d, *J* = 8.7, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 150.2, 147.8, 130.4, 128.1, 121.1, 114.6, 55.4; High Resolution-MS (EI) calcd. For $C_{12}H_{11}ON$: 185.0841, found: 185.0843.



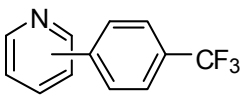
3-methoxyphenylpyridine (4e)[11]: Following Procedure B, 1-iodo-3-methoxybenzene (117 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dt, *J* = 4.9, 1.3, 1H), 7.74-7.69 (m, 2H), 7.58 (t, *J* = 2.1, 1H), 7.53 (dt, *J* = 4.8, 1.2, 1H), 7.36 (t, *J* = 7.9, 1H), 7.21 (ddd, *J* = 6.8, 4.9, 2.0, 1H), 6.95 (ddd, *J* = 8.2, 2.6, 0.7, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 157.3, 149.6, 140.9, 136.7, 129.7, 122.2, 120.7, 119.3, 115.1, 112.0, 55.4; *m*-(**4e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.54 (s, 1H), 7.80 (d, *J* = 7.2, 1H), 7.35-7.29 (m, 2H), 7.11 (d, *J* = 7.1, 1H), 7.06 (s, 1H), 6.90 (d, *J* = 7.7, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 148.4, 148.1, 139.1, 136.3, 134.2, 129.9, 123.3, 119.4, 113.2, 112.8, 55.1; *p*-(**4e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.5, 2H), 7.47 (d, *J* = 4.5, 2H), 7.38 (t, *J* = 7.8, 1H), 7.20 (d, *J* = 7.6, 1H), 7.13 (s, 1H), 6.96 (d, *J* = 8.2, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 150.2, 148.2, 139.6, 130.1 121.7, 119.4, 114.3, 112.8, 55.4; High Resolution-MS (EI) calcd. For $C_{12}H_{11}ON$: 185.0841, found: 185.0839.



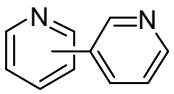
2-methoxyphenylpyridine (4f)[8b,11c,12]**:** Following Procedure B, 1-iodo-2-methoxybenzene (117 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 24 h. *o*-(**4f**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (ddd, *J* = 4.9, 1.8, 0.9, 1H), 7.79 (dt, *J* = 8.0, 1.0, 1H), 7.74 (dd, *J* = 7.6, 1.8, 1H), 7.68 (td, *J* = 7.6, 1.8, 1H), 7.35 (ddd, *J* = 8.3, 7.4, 1.8, 1H), 7.18 (ddd, *J* = 7.4, 4.9, 1.1, 1H), 7.06 (td, *J* = 7.5, 1.0, 1H), 6.99 (d, *J* = 8.3, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.1, 149.4, 135.6, 131.1, 129.9, 129.2, 125.1, 121.6, 121.0, 111.4, 55.6; *m*-(**4f**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 1.8, 1H), 8.52 (dd, *J* = 4.8, 1.2, 1H), 7.82 (dt, *J* = 7.9, 1.9, 1H), 7.34 (td, *J* = 7.8, 1.7, 1H), 7.30-7.27 (m, 2H), 7.03 (t, *J* = 7.5, 1H), 6.97 (d, *J* = 8.3, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 150.1, 147.8, 136.7, 134.1, 130.5, 129.4, 126.9, 122.8, 120.9, 111.2, 55.4; *p*-(**4f**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 2H), 7.45 (s, 2H), 7.37 (t, *J* = 7.8, 1H), 7.32 (d, *J* = 7.5, 1H), 7.04 (t, *J* = 7.2, 1H), 6.99 (d, *J* = 8.2, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 149.4, 146.2, 130.4, 130.1, 129.6, 124.4, 121.1, 111.5, 55.6; High Resolution-MS (EI) calcd. For $C_{12}H_{11}ON$: 185.0841, found: 185.0840.



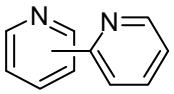
4-pyridinylbenzonitrile (4g)[13]**:** Following Procedure B, 4-iodobenzonitrile (115 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4g**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.7, 1.0, 1H), 8.10 (d, *J* = 8.4, 2H), 7.79 (dd, *J* = 7.9, 1.8, 1H), 7.75-7.73 (m, 3H), 7.30 (ddd, *J* = 7.2, 4.8, 1.4, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 150.1, 143.5, 137.1, 132.5, 127.4, 123.3, 120.9, 118.8, 112.5; *m*-(**4g**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.2, 1H), 8.64 (dd, *J* = 4.8, 1.4, 1H), 7.86 (dt, *J* = 8.0, 2.0, 1H), 7.75 (d, *J* = 8.3, 2H), 7.67 (d, *J* = 8.3, 2H), 7.40 (dd, *J* = 7.9, 4.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 148.2, 142.3, 134.7, 134.4, 132.8, 127.8, 123.7, 118.5, 111.9; *p*-(**4g**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 6.1, 2H), 7.77 (d, *J* = 8.3, 2H), 7.71 (d, *J* = 8.3, H), 7.48 (d, *J* = 6.2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 146.3, 142.6, 132.9, 127.7, 121.6, 118.3, 112.8; High Resolution-MS (EI) calcd. For $C_{12}H_8N_2$: 180.0687, found: 180.0688.



4-(trifluoromethyl)phenylpyridine (4h)[8b,11c,12]**:** Following Procedure B, 1-iodo-4-(trifluoromethyl)benzene (136 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 48 h. *o*-(**4h**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.2, 1H), 8.05 (d, *J* = 8.1, 2H), 7.74-7.66 (m, 4H), 7.22 (d, *J* = 6.9, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 149.9, 142.7, 136.9, 130.9, 130.6, 127.2, 125.7, 125.6, 122.9, 120.8; *m*-(**4h**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.2, 1H), 8.62 (dd, *J* = 4.8, 1.5, 1H), 7.86 (dt, *J* = 7.9, 2.0, 1H), 7.71 (d, *J* = 8.4, 2H), 7.66 (d, *J* = 8.4, 2H), 7.38 (dd, *J* = 7.9, 4.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 148.3, 141.4, 135.3, 134.5, 130.7, 130.4, 130.1, 129.7, 128.1, 127.5, 126.0, 125.4, 123.7, 122.7, 120.0; *p*-(**4h**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 6.1, 2H), 7.72 (s, 4H), 7.49 (d, *J* = 6.1, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 146.9, 141.7, 130.9, 129.8, 127.4, 126.8, 126.1, 122.6, 121.7; High Resolution-MS (EI) calcd. For $C_{12}H_8NF_3$: 223.0609, found: 223.0607.

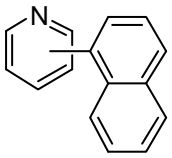


bipyridine (4i)[7a,18b,14]**:** Following Procedure B, 3-iodopyridine (103 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4i**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.0, 1H), 8.62 (d, *J* = 4.8, 1H), 8.55 (dd, *J* = 4.8, 1.3, 1H), 8.22 (dt, *J* = 8.0, 1.9, 1H), 7.68 (td, *J* = 7.9, 1.6, 1H), 7.64 (d, *J* = 7.7, 1H), 7.30 (dd, *J* = 8.0, 4.8, 1H), 7.18 (ddd, *J* = 6.6, 4.9, 1.3, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 149.9, 149.7, 148.0, 136.8, 134.7, 134.1, 123.4, 122.7, 120.4; *m*-(**4i**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.2, 2H), 8.63 (d, *J* = 4.7, 2H), 7.86 (d, *J* = 7.9, 2H), 7.39 (dd, *J* = 7.9, 4.8, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 148.2, 134.4, 133.5, 123.7; *p*-(**4i**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.7, 1H), 8.63-8.61 (m, 2H), 8.59 (dd, *J* = 4.8, 1.6, 1H), 7.84 (dt, *J* = 8.0, 2.0, 1H), 7.43-7.41 (m, 2H), 7.35-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 150.0, 147.9, 145.0, 134.1, 133.6, 121.4; High Resolution-MS (EI) calcd. For $C_{10}H_8N_2$: 156.0687, found: 156.0688.

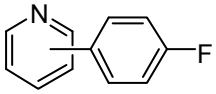


bipyridine (4j)[7a,8b,15]**:** Following Procedure B, 2-iodopyridine (103 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4j**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8, 2H), 8.36 (d, *J* = 8.0, 2H), 7.75 (td, *J* = 7.8, 1.7, 2H), 7.24 (dd, *J* = 7.4,

4.8, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 149.0, 136.8, 123.6, 120.9; *m*-(**4j**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.0, 1H), 8.62 (d, *J* = 4.8, 1H), 8.55 (dd, *J* = 4.8, 1.3, 1H), 8.22 (dt, *J* = 8.0, 1.9, 1H), 7.68 (td, *J* = 7.9, 1.6, 1H), 7.64 (d, *J* = 7.7, 1H), 7.30 (dd, *J* = 7.9, 4.8, 1H), 7.18 (ddd, *J* = 6.6, 4.9, 1.3, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 149.9, 149.7, 148.0, 136.8, 134.7, 134.1, 123.4, 122.7, 120.4; *p*-(**4j**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54-8.52 (m, 3H), 7.71 (d, *J* = 6.0, 2H), 7.58-7.52 (m, 2H), 7.13-7.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 150.0, 149.6, 145.9, 136.6, 123.4, 120.6, 120.4; High Resolution-MS (EI) calcd. For $C_{10}H_8N_2$: 156.0687, found: 156.0691.



(naphthalen-1-yl)pyridine (4k)[10b,16]**:** Following Procedure B, 1-iodonaphthalene (127 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4k**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (ddd, *J* = 4.9, 1.8, 0.9, 1H), 8.08 (d, *J* = 7.3, 1H), 7.90 (d, *J* = 8.2, 2H), 7.80 (td, *J* = 7.7, 1.8, 1H), 7.61-7.45 (m, 5H), 8.79 (ddd, *J* = 7.6, 4.9, 1.1, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 149.5, 138.5, 136.3, 133.9, 131.1, 128.8, 128.3, 127.4, 126.4, 125.8, 125.5, 125.2, 125.0, 121.9; *m*-(**4k**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.67 (d, *J* = 4.3, 1H), 7.90 (t, *J* = 7.7, 2H), 7.80 (d, *J* = 8.5, 2H), 7.55-7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 148.5, 137.2, 136.3, 136.2, 133.7, 131.4, 128.5, 128.4, 127.3, 126.5, 126.0, 125.3, 125.2, 123.1; *p*-(**4k**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 6.0, 2H), 7.92-7.88 (m, 2H), 7.80-7.77 (m, 1H), 7.54-7.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 148.6, 137.2, 133.7, 130.6, 128.8, 128.4, 126.8, 126.5, 126.0, 125.2, 125.1, 124.9; High Resolution-MS (EI) calcd. For $C_{15}H_{11}N$: 205.0891, found: 205.0887.



4-fluorophenylpyridine (4l)[11c,12,17]**:** Following Procedure B, 1-fluoro-4-iodobenzene (111 mg, 0.5 mmol) was allowed to react with pyridine (4 mL) for 4 h. *o*-(**4m**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.8, 0.8, 1H), 7.97-7.94 (m, 2H), 7.71 (td, *J* = 7.8, 1.8, 1H), 7.65 (dd, *J* = 8.0, 0.8, 1H), 7.19 (ddd, *J* = 7.2, 4.8, 1.2, 1H), 7.15-7.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.3, 156.4, 149.6, 136.7, 135.6, 128.7,

128.6, 122.0, 120.1, 115.7, 115.5; *m*-(**4m**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.2, 1H), 8.51 (dd, *J* = 4.8, 1.4, 1H), 7.72 (dt, *J* = 7.9, 2.0, 1H), 7.44 (dd, *J* = 8.7, 5.3, 2H), 7.25 (dd, *J* = 7.8, 4.6, 1H), 7.44 (t, *J* = 8.7, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.5, 148.3, 147.9, 135.4, 133.9, 133.7, 128.6, 128.5, 123.3, 115.9, 115.7; *p*-(**4m**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 6.0, 2H), 7.59 (dd, *J* = 8.7, 5.2, 2H), 7.43 (d, *J* = 6.1, 2H), 7.15 (t, *J* = 8.6, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.2, 150.3, 147.3, 134.2, 128.8, 128.7, 121.4, 116.2, 116.0; High Resolution-MS (EI) calcd. For $C_{11}H_8NF$: 173.0641, found: 173.0638.

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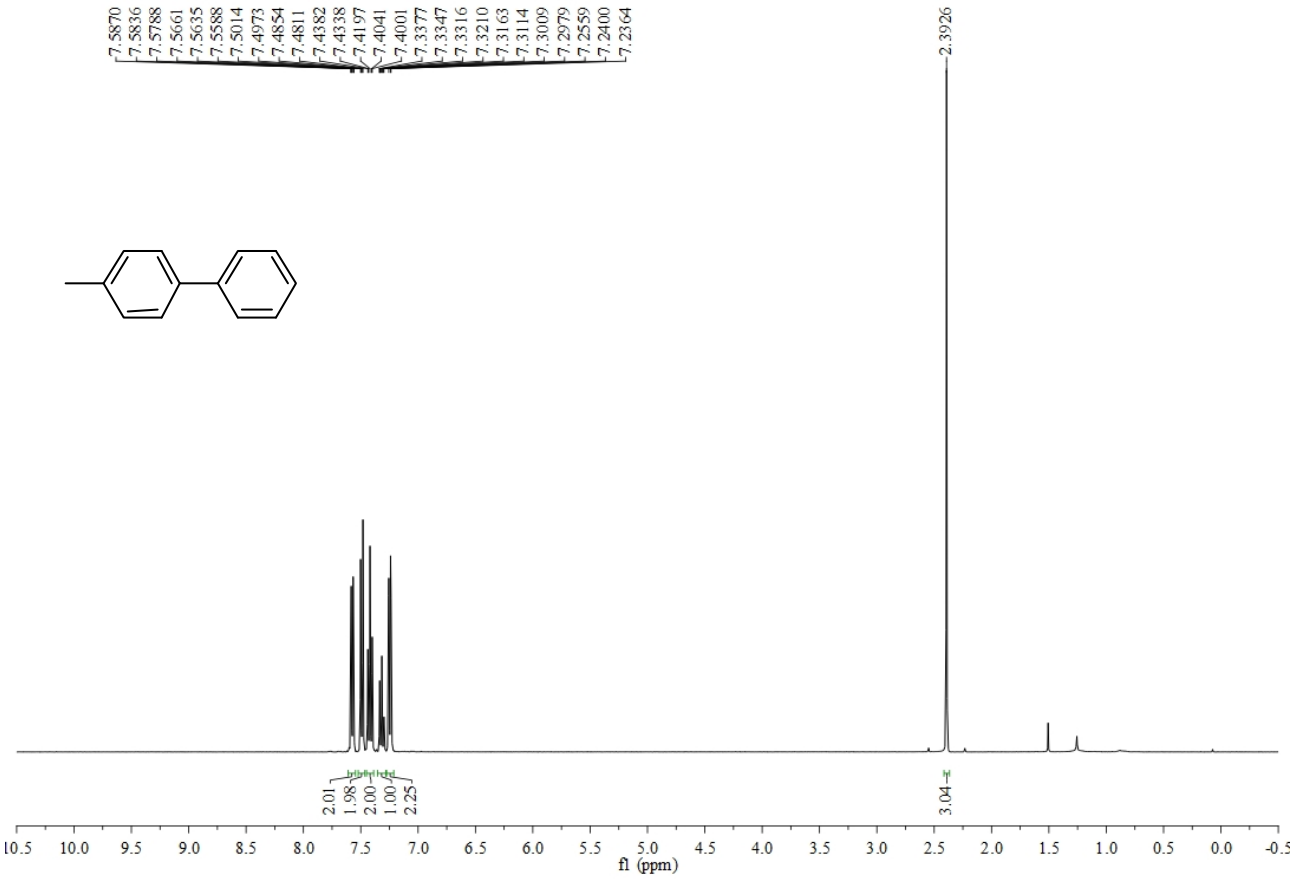
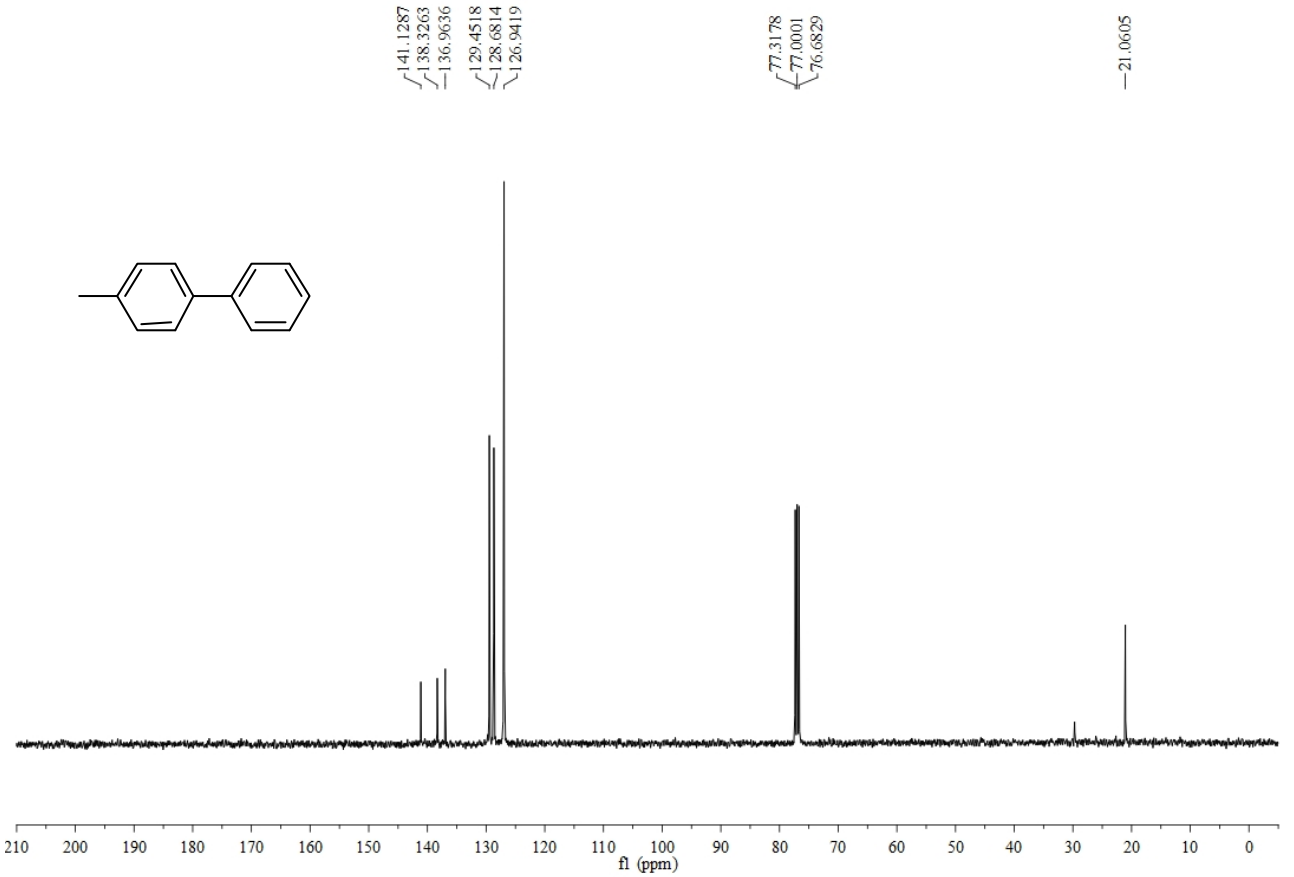
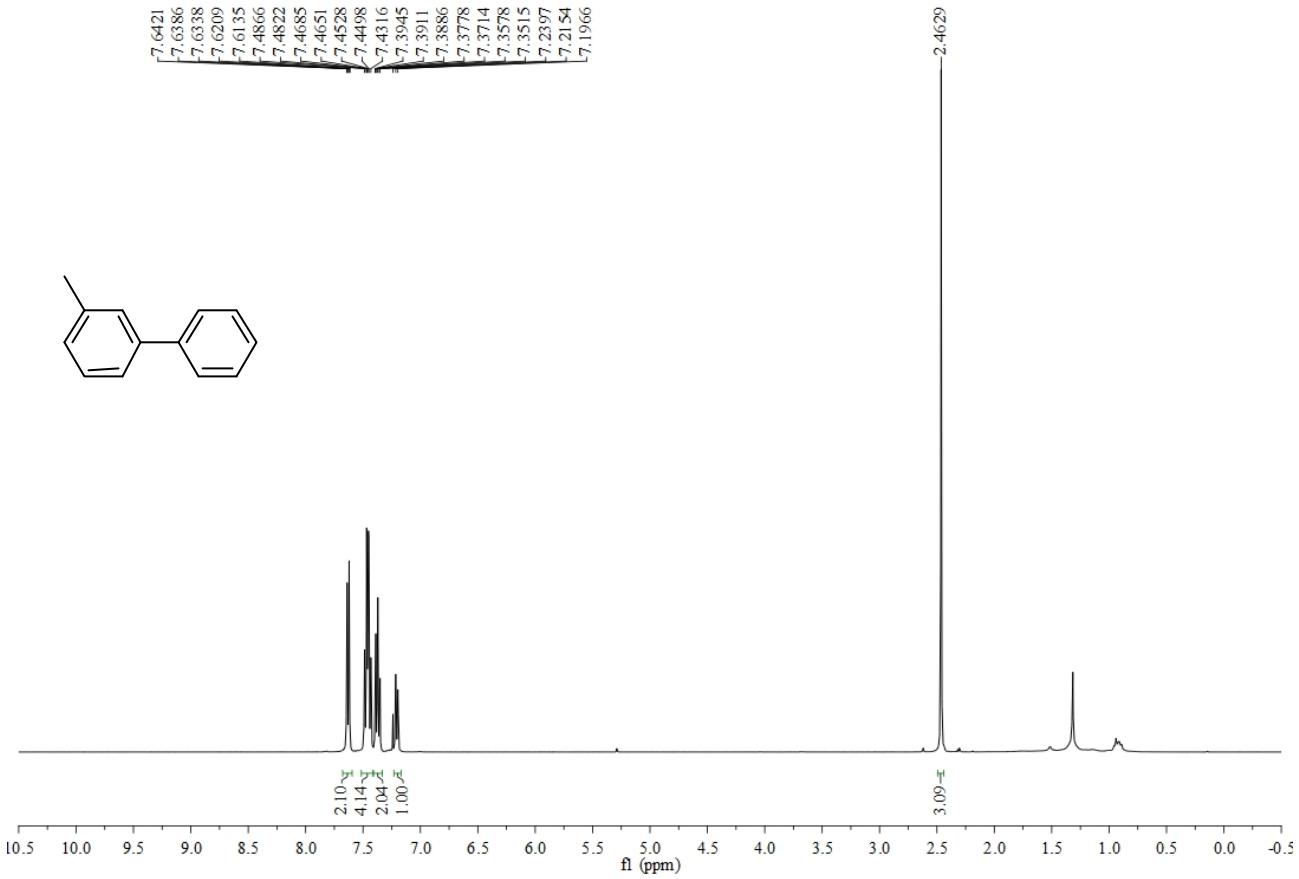
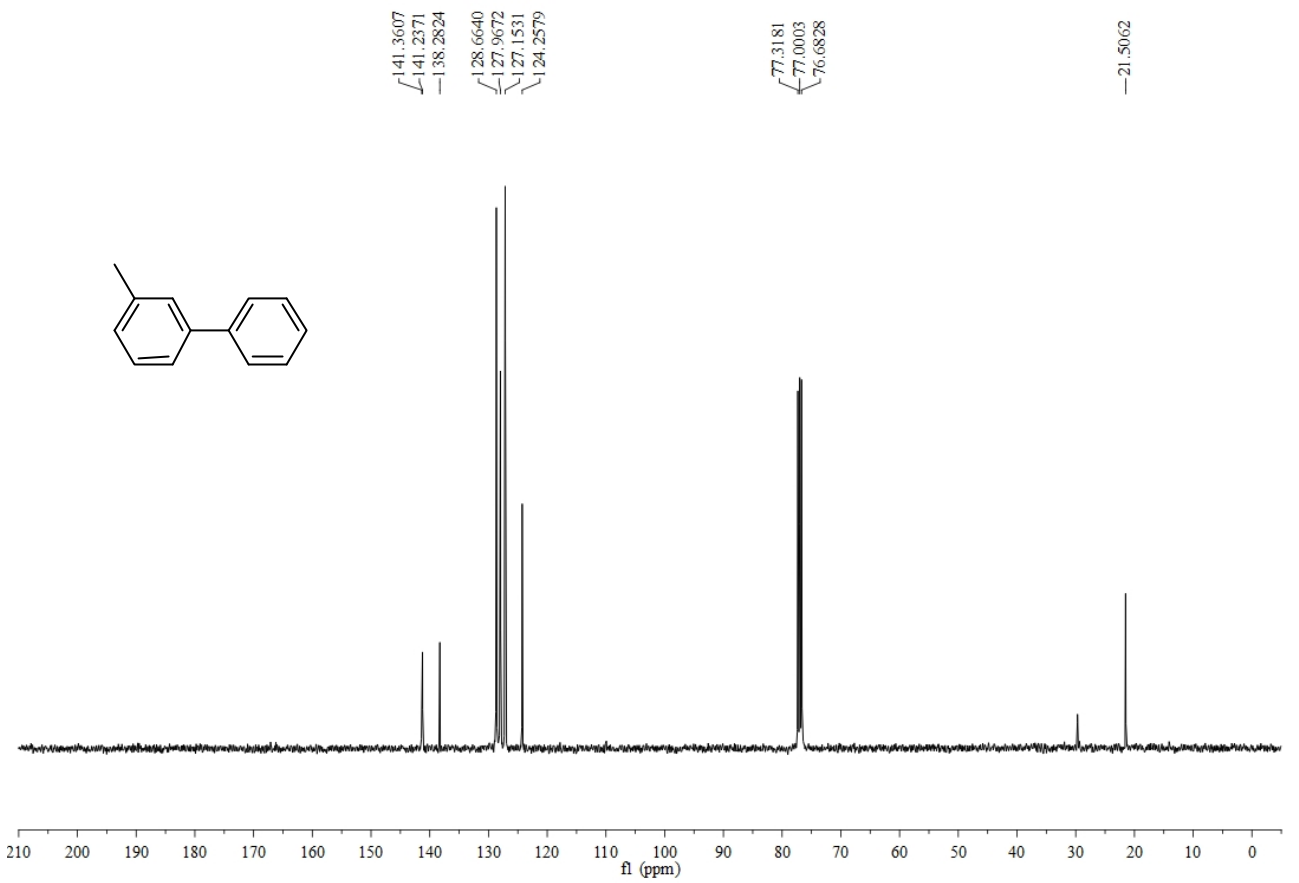




^{1}H and ^{13}C NMR spectra of **3a**





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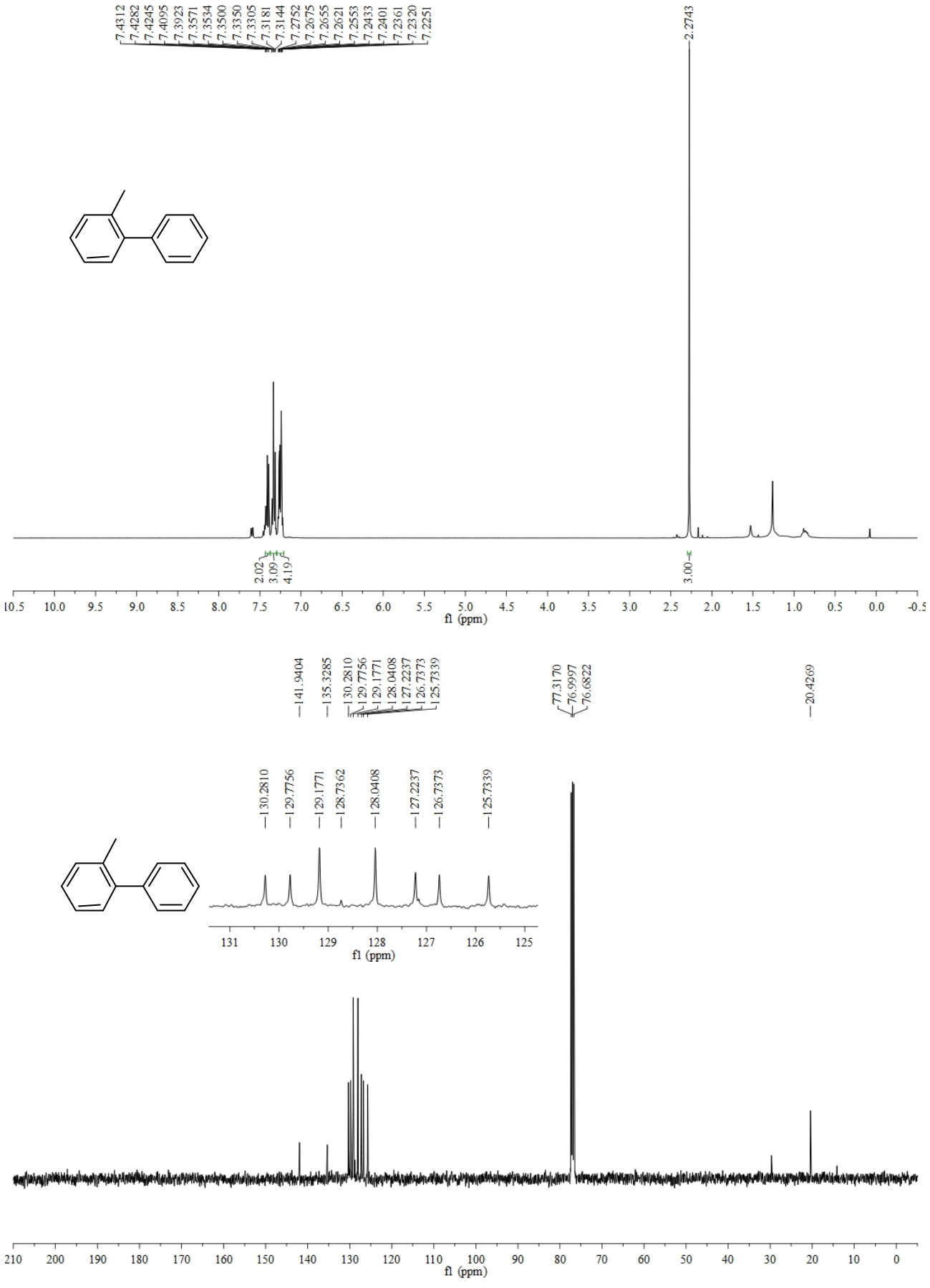

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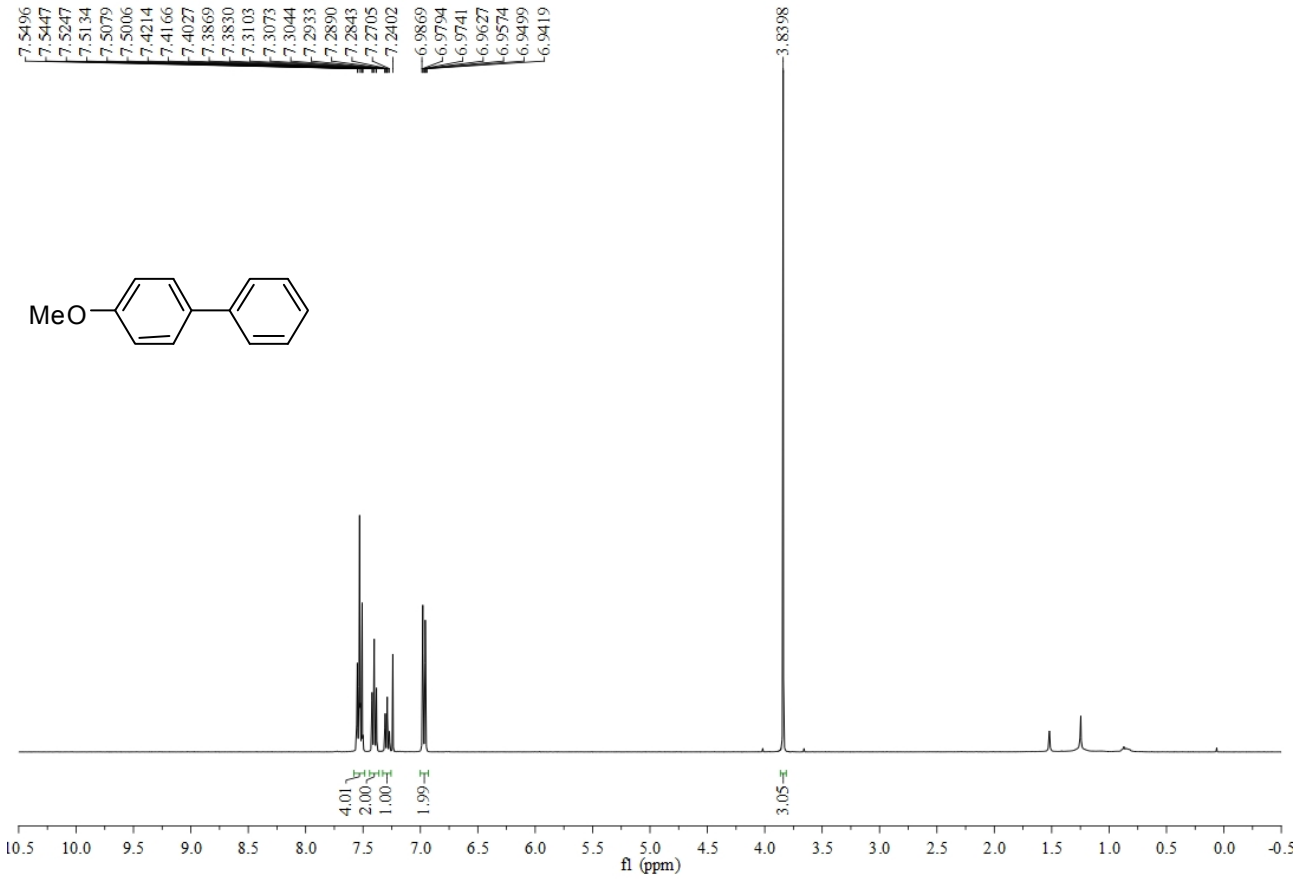

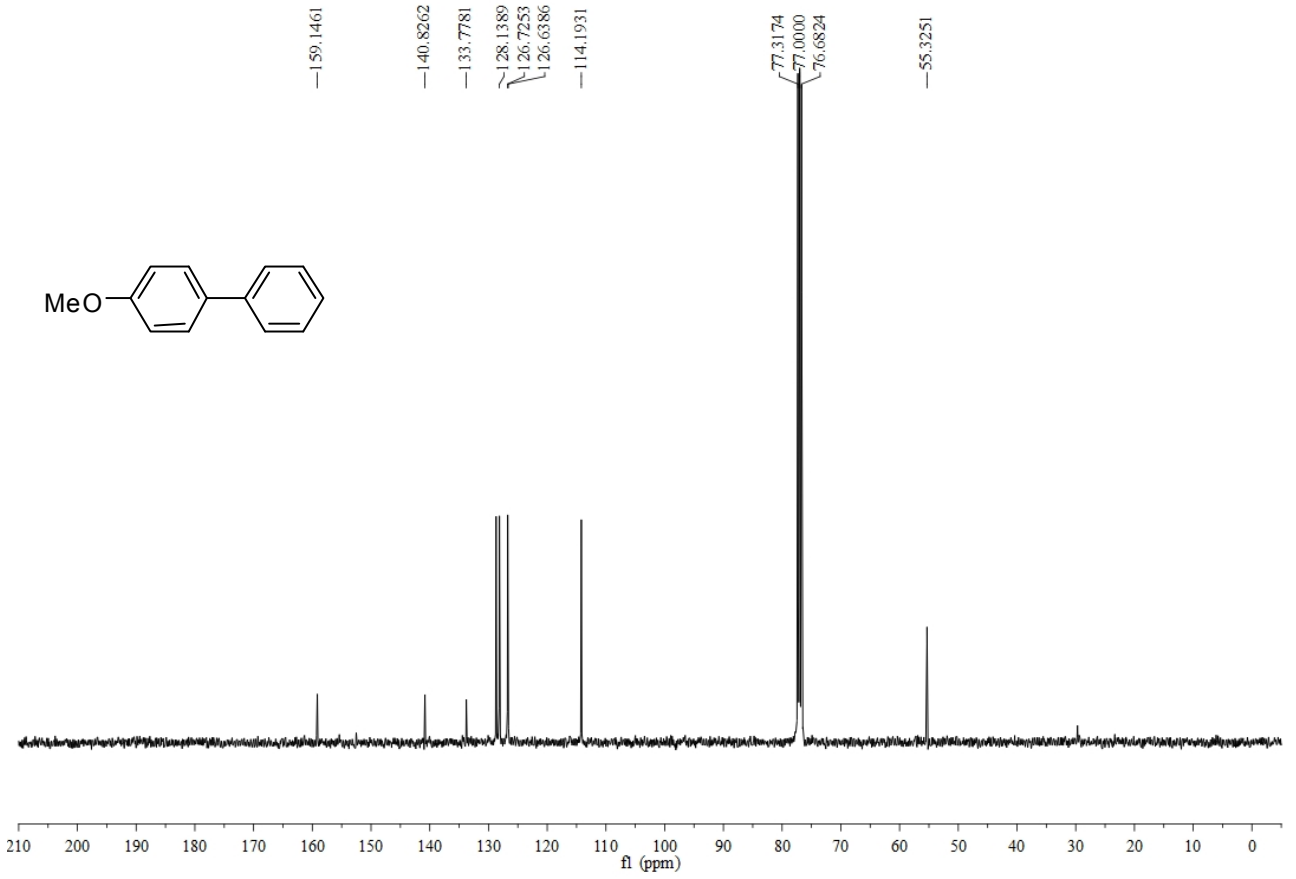

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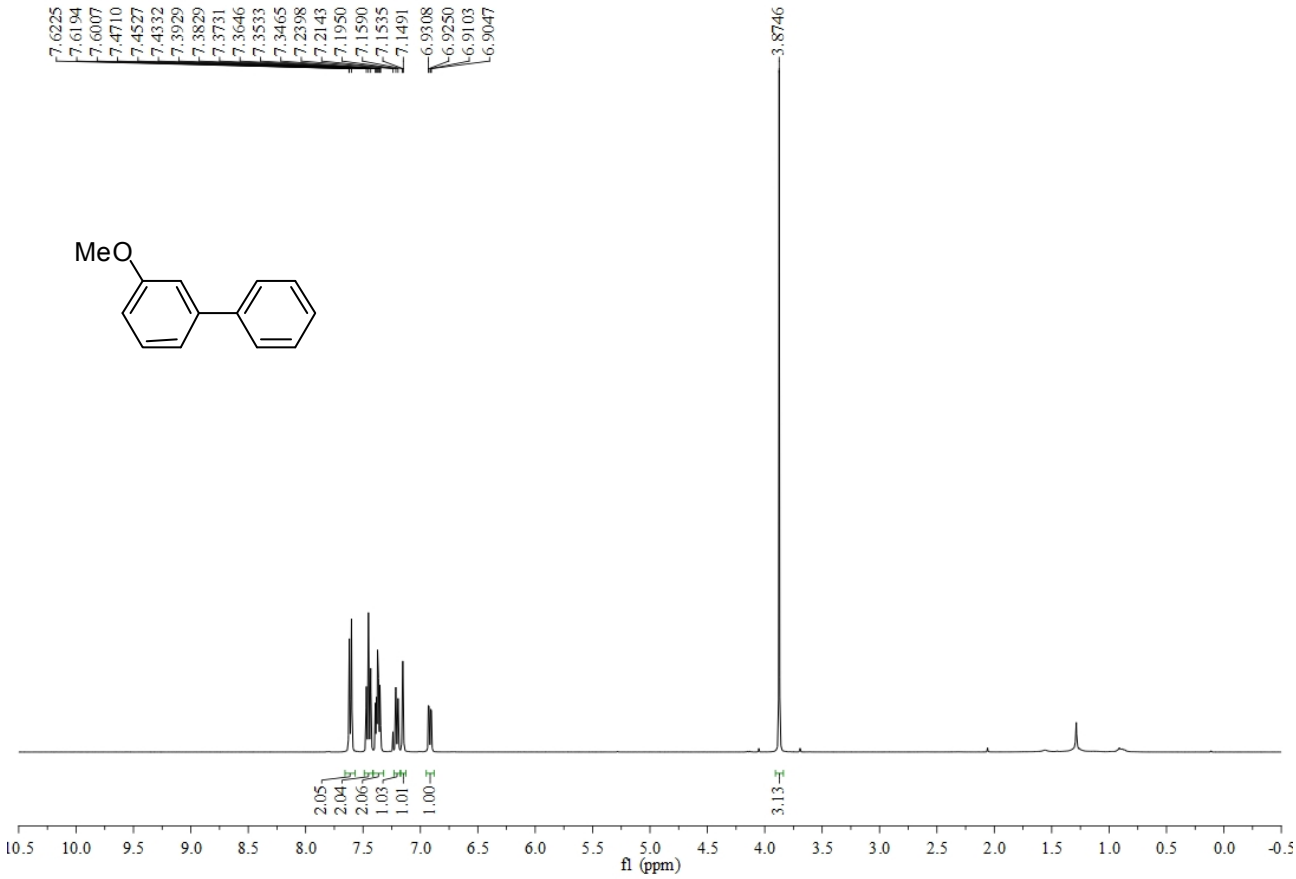

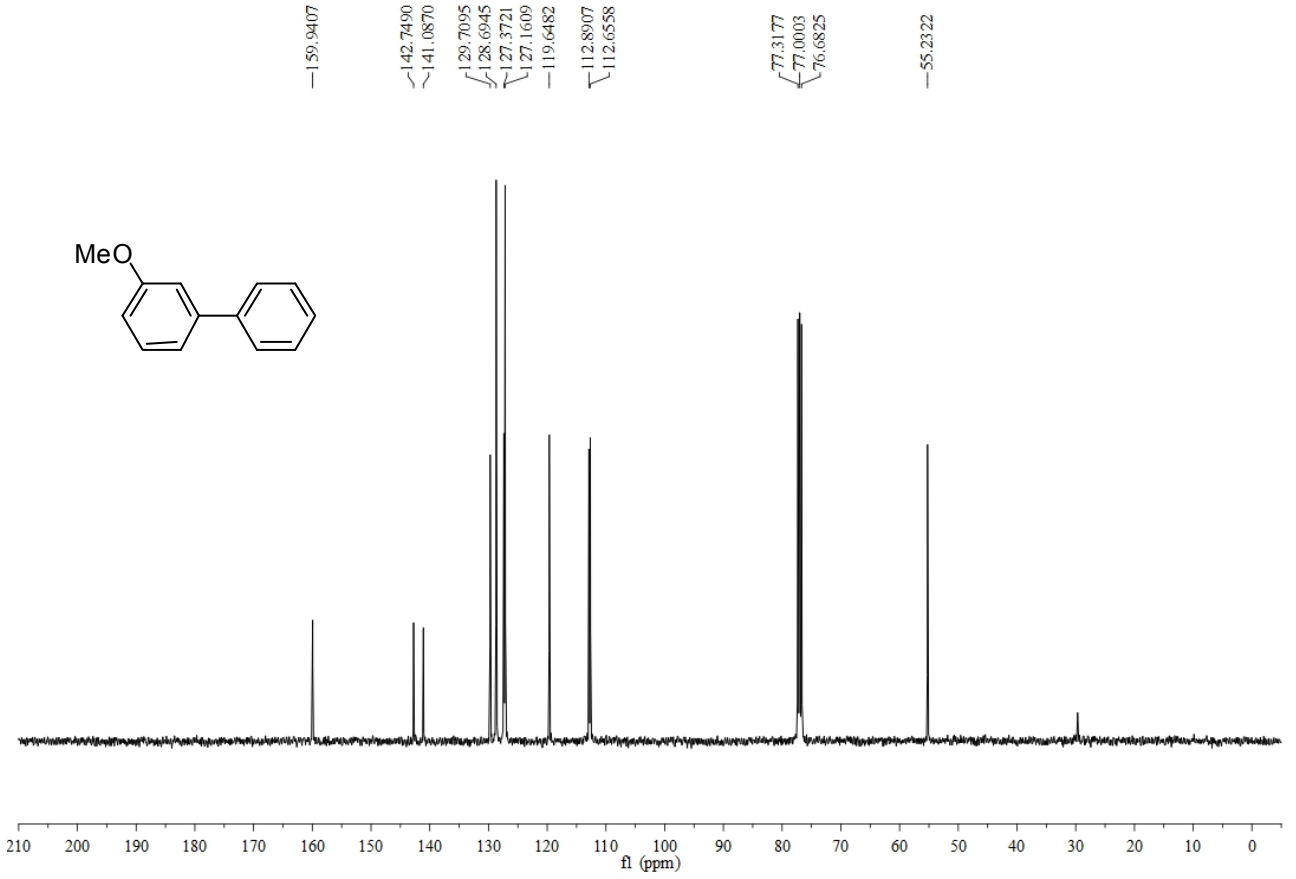

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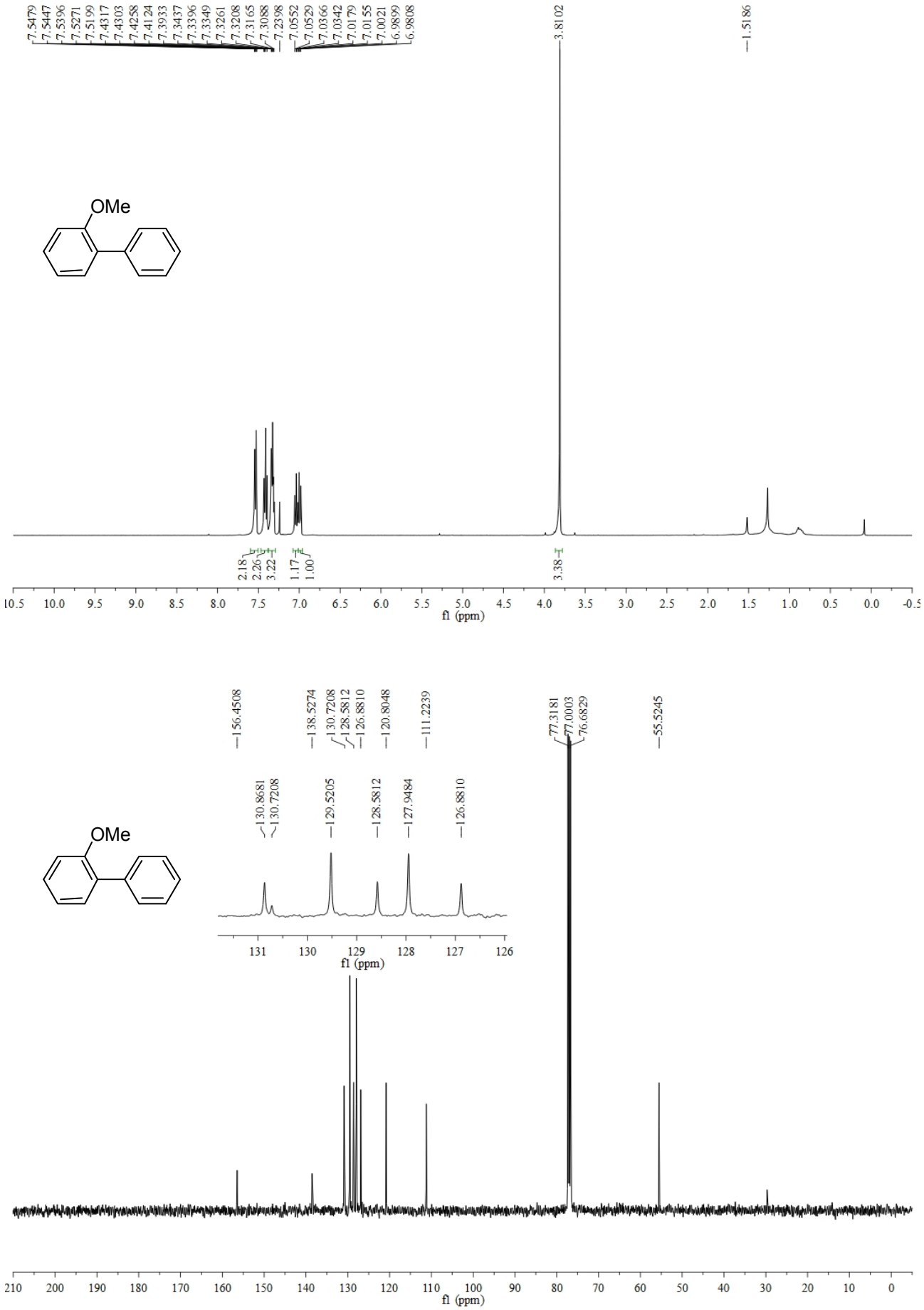

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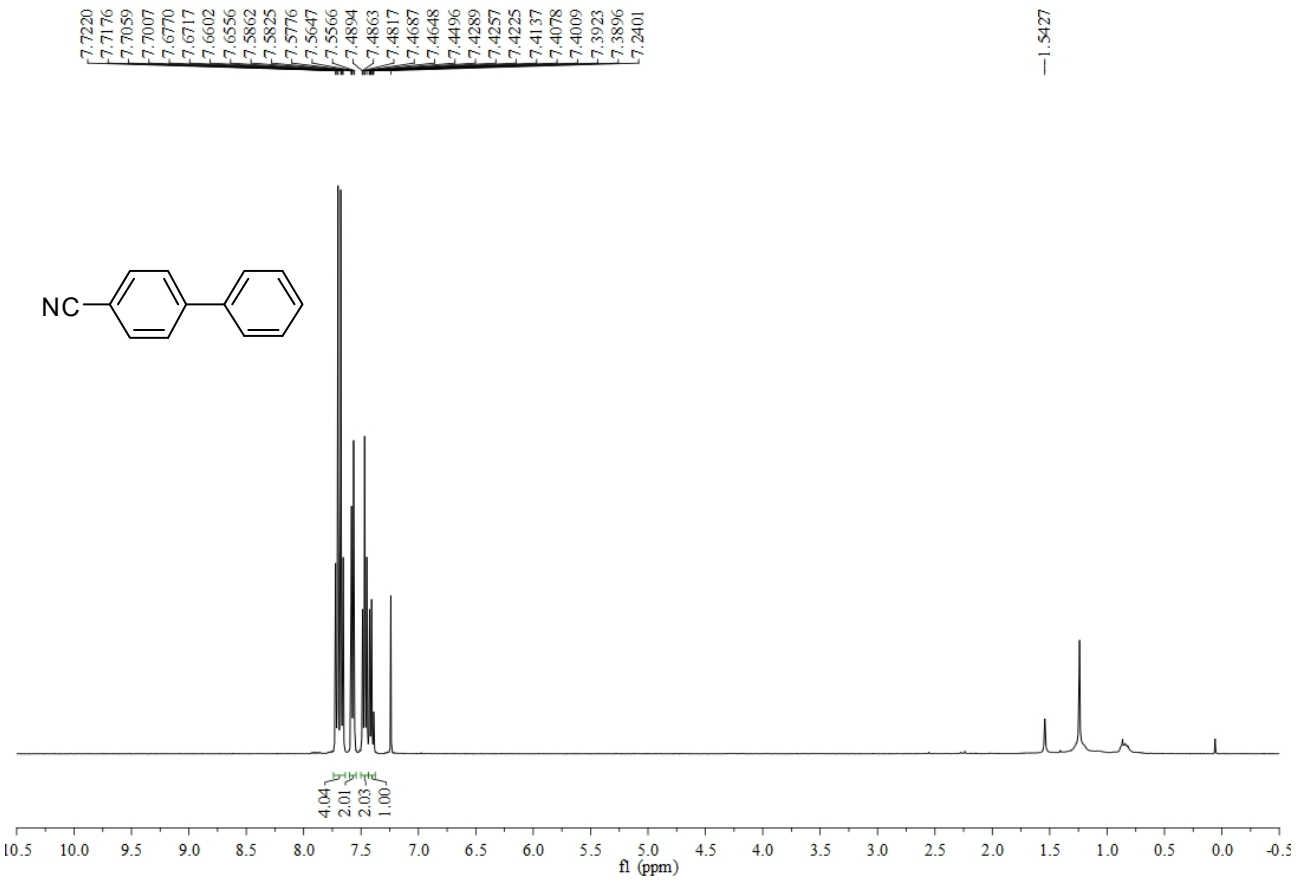
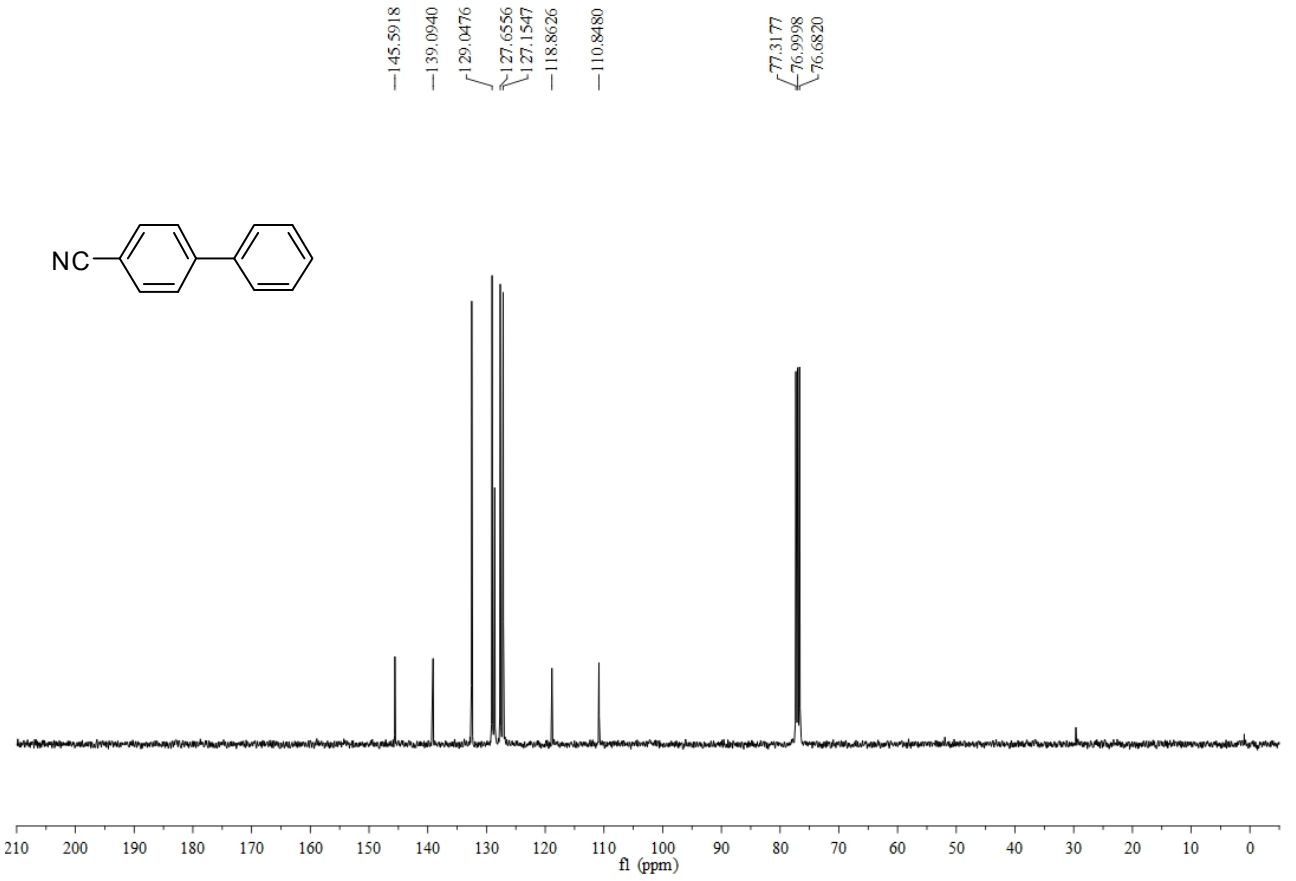
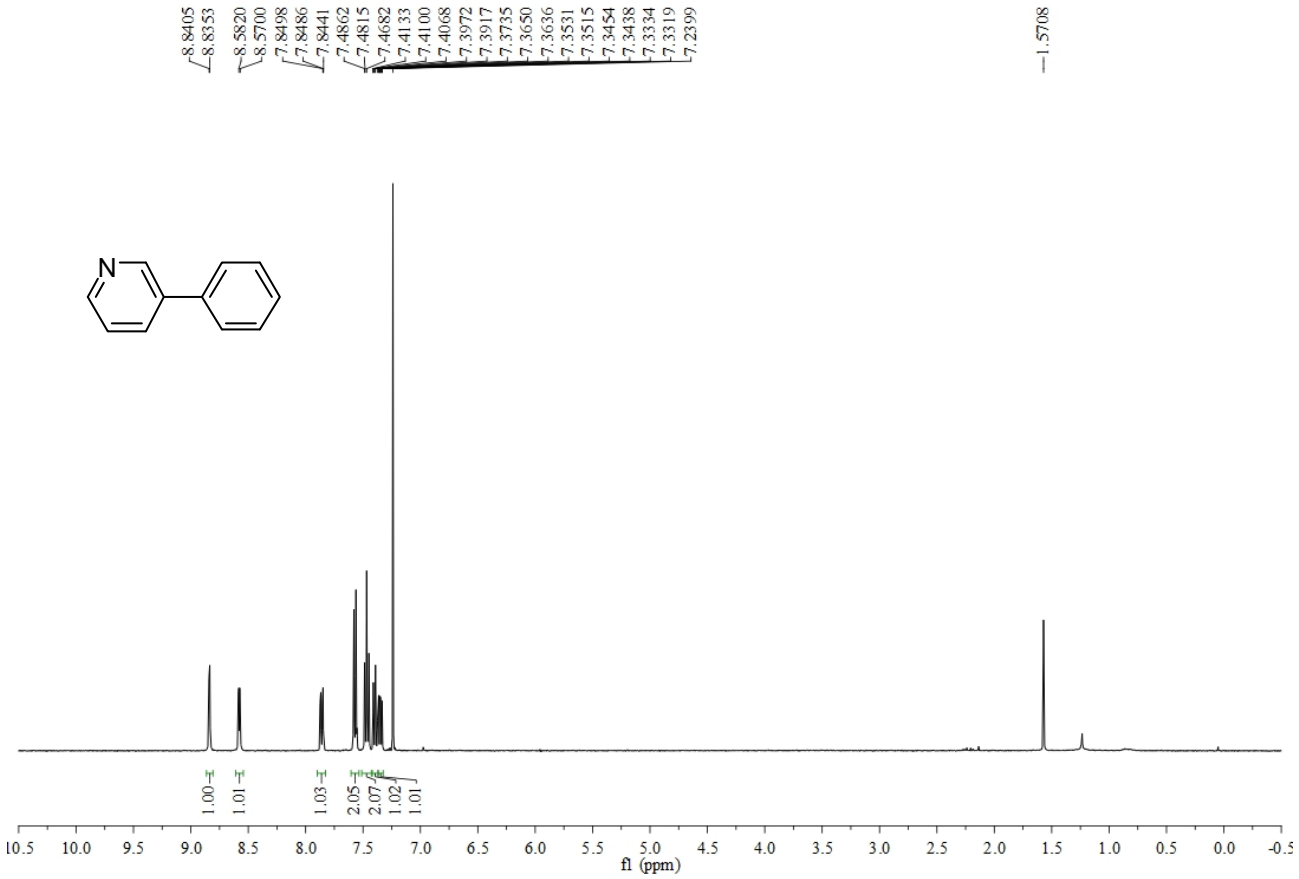
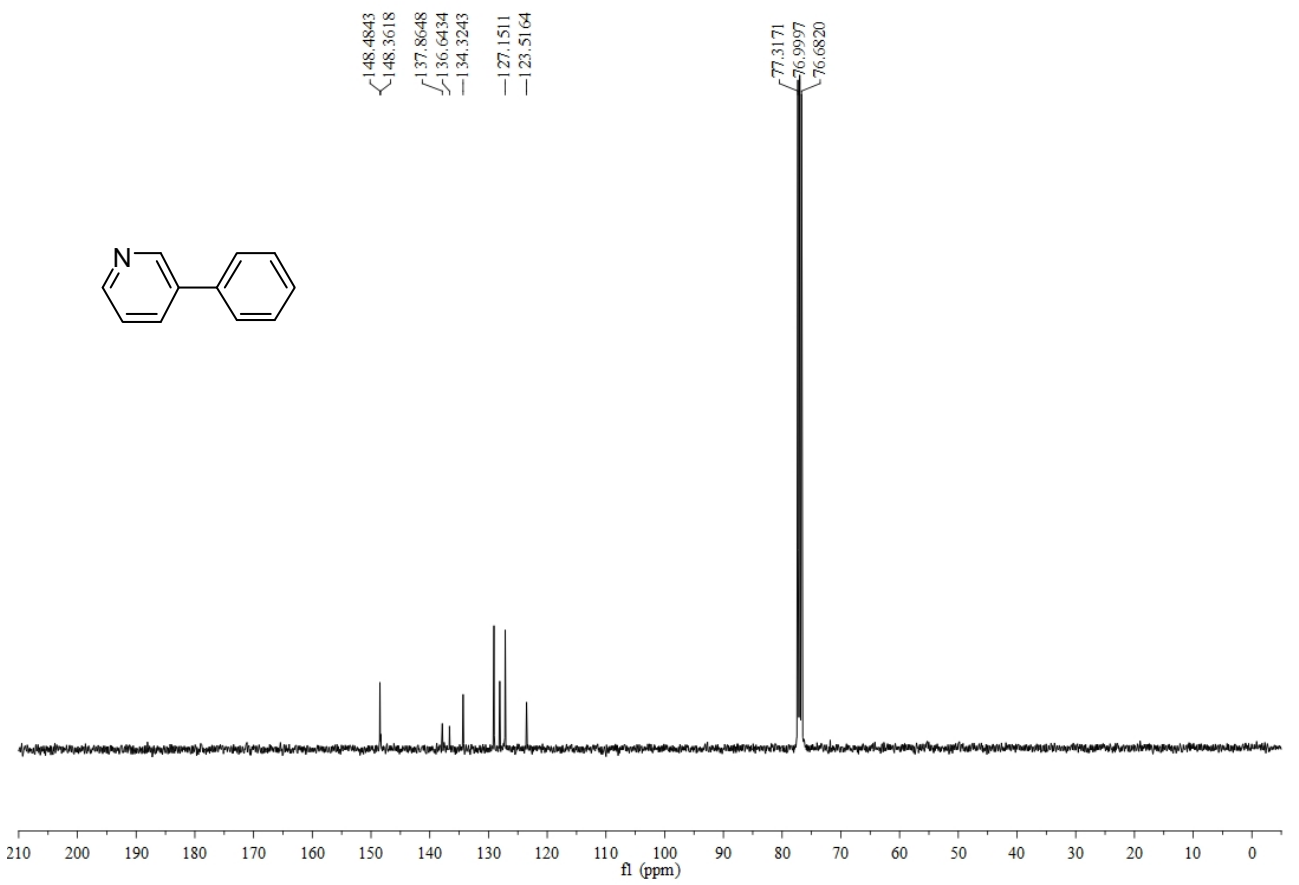




^{1}H and ^{13}C NMR spectra of **3g**





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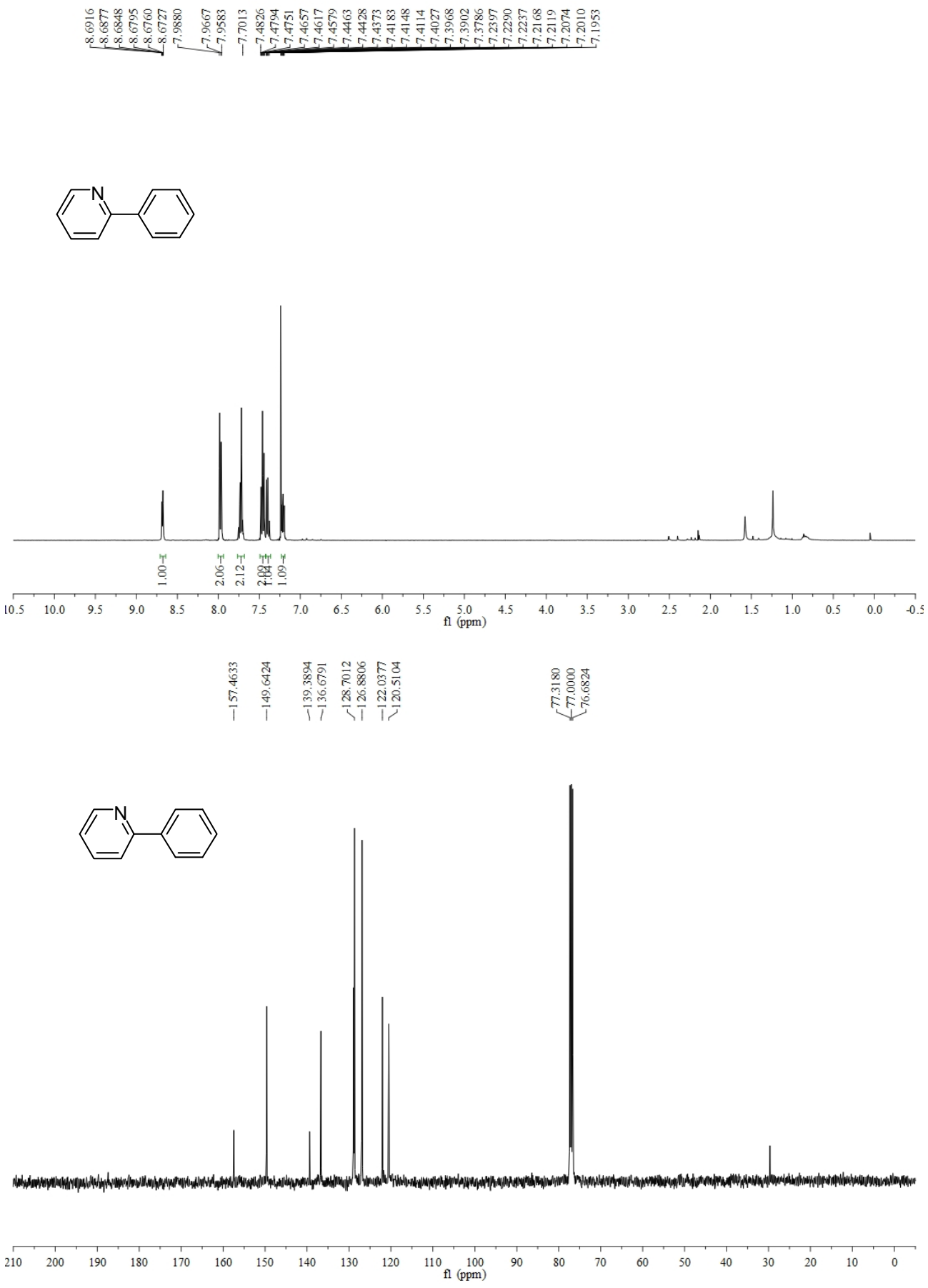
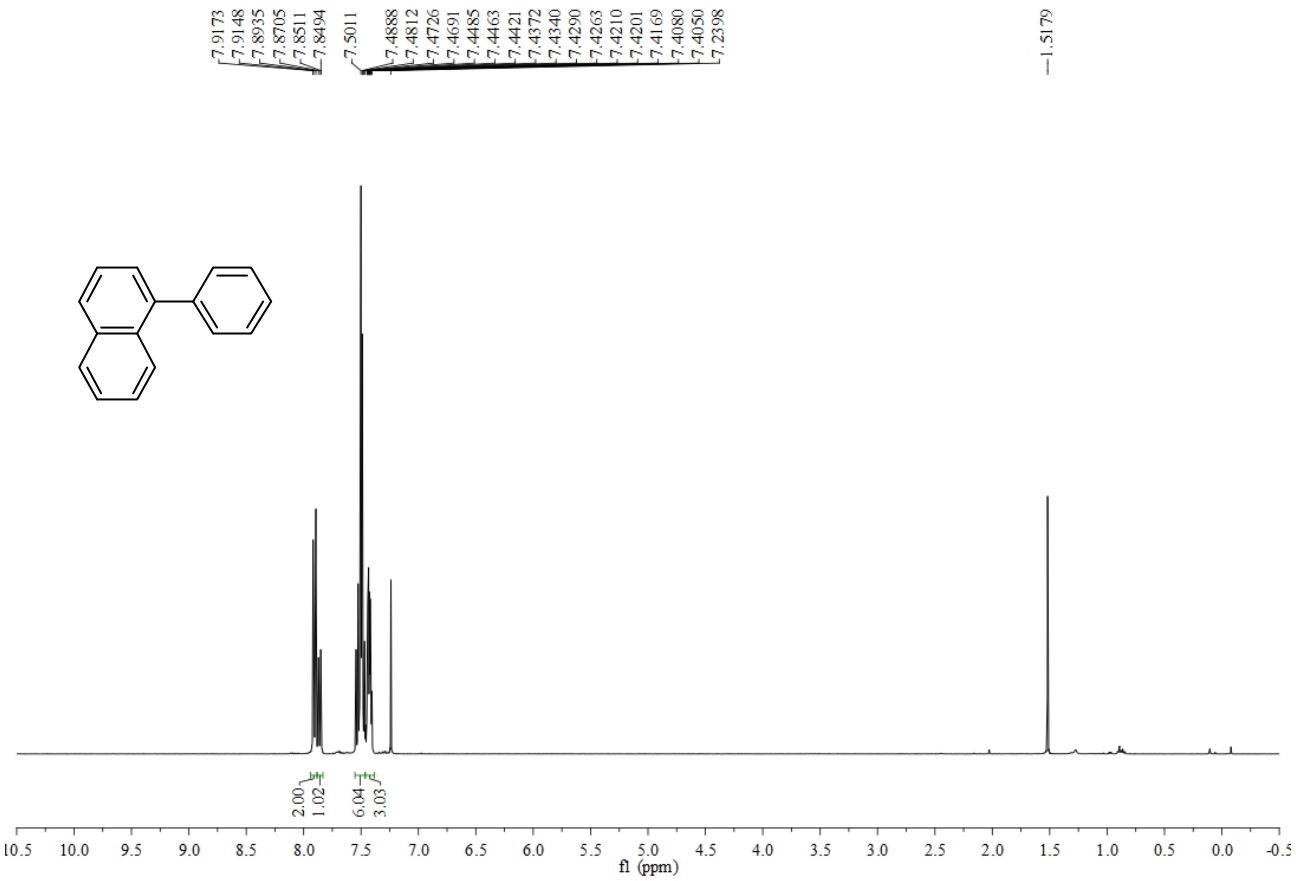
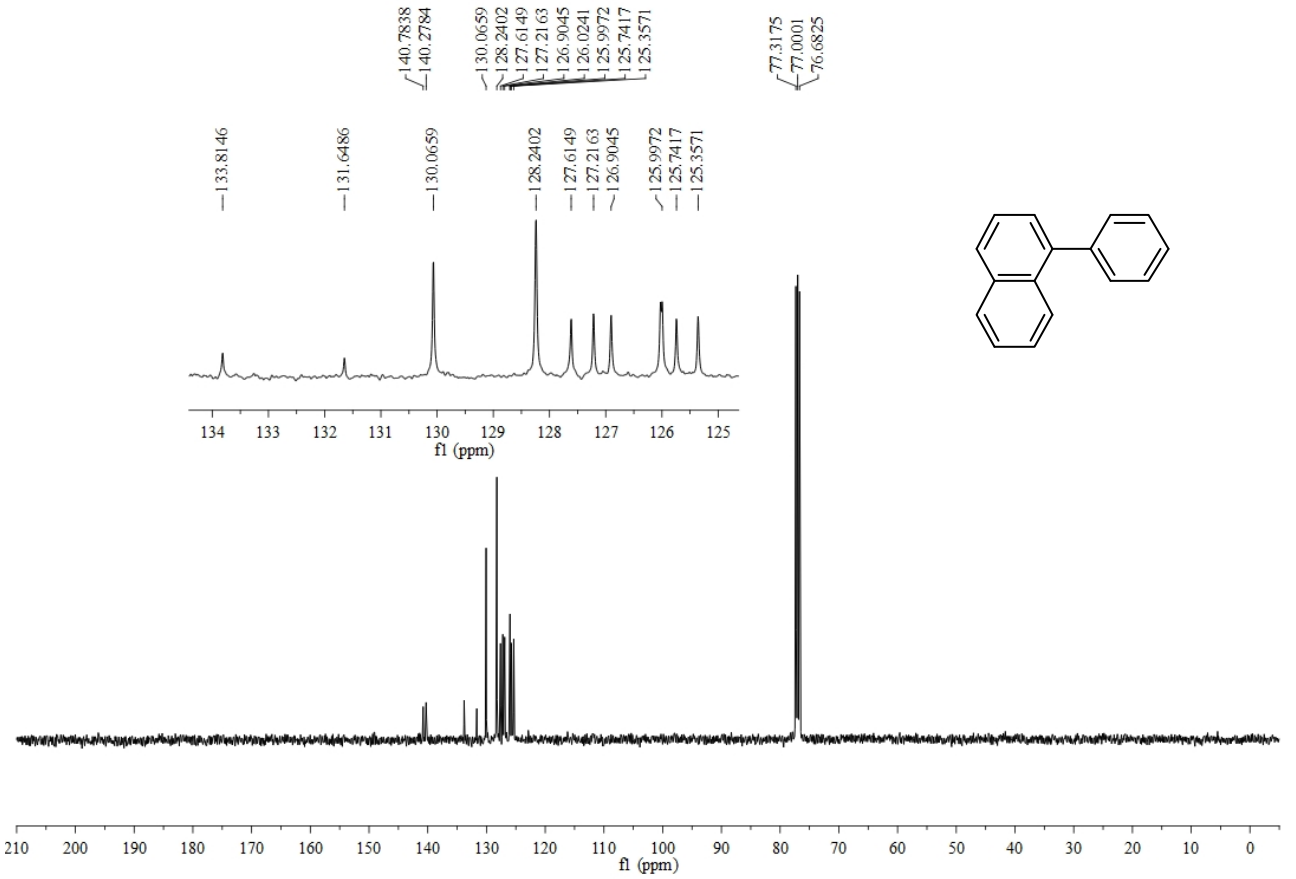


^{1}H and ^{13}C NMR spectra of **3i**





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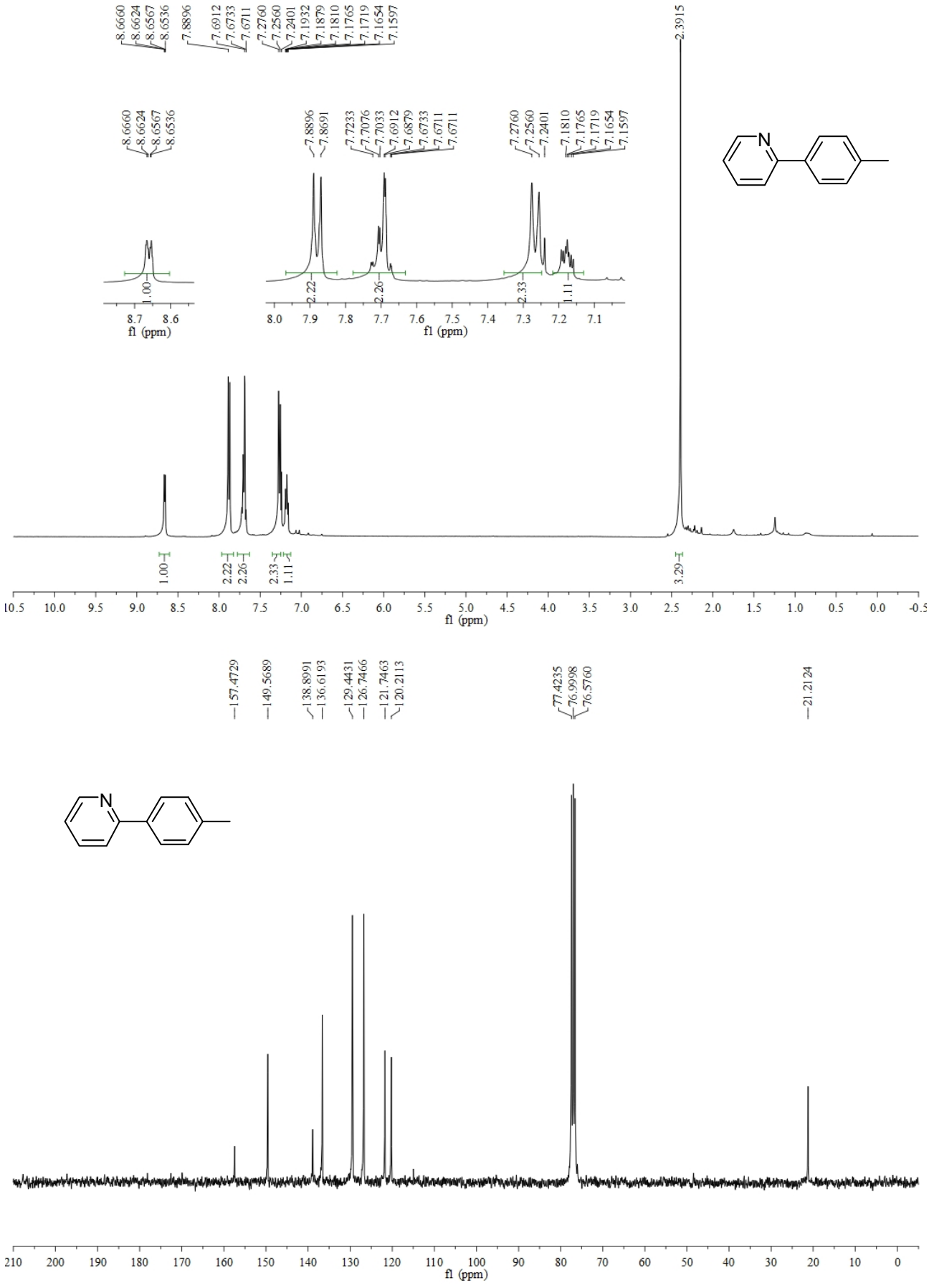
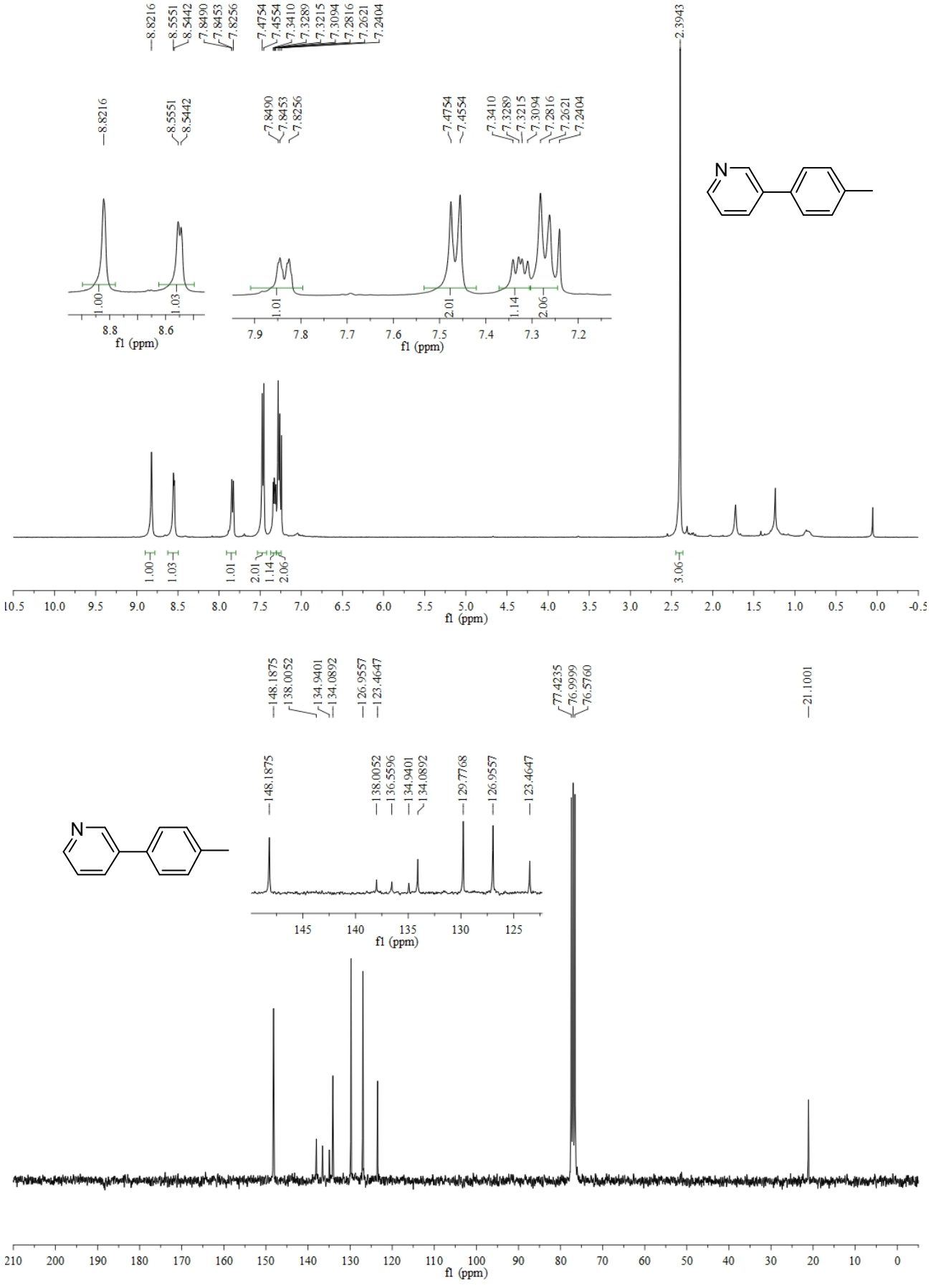


^{1}H and ^{13}C NMR spectra of *o*-**4a**



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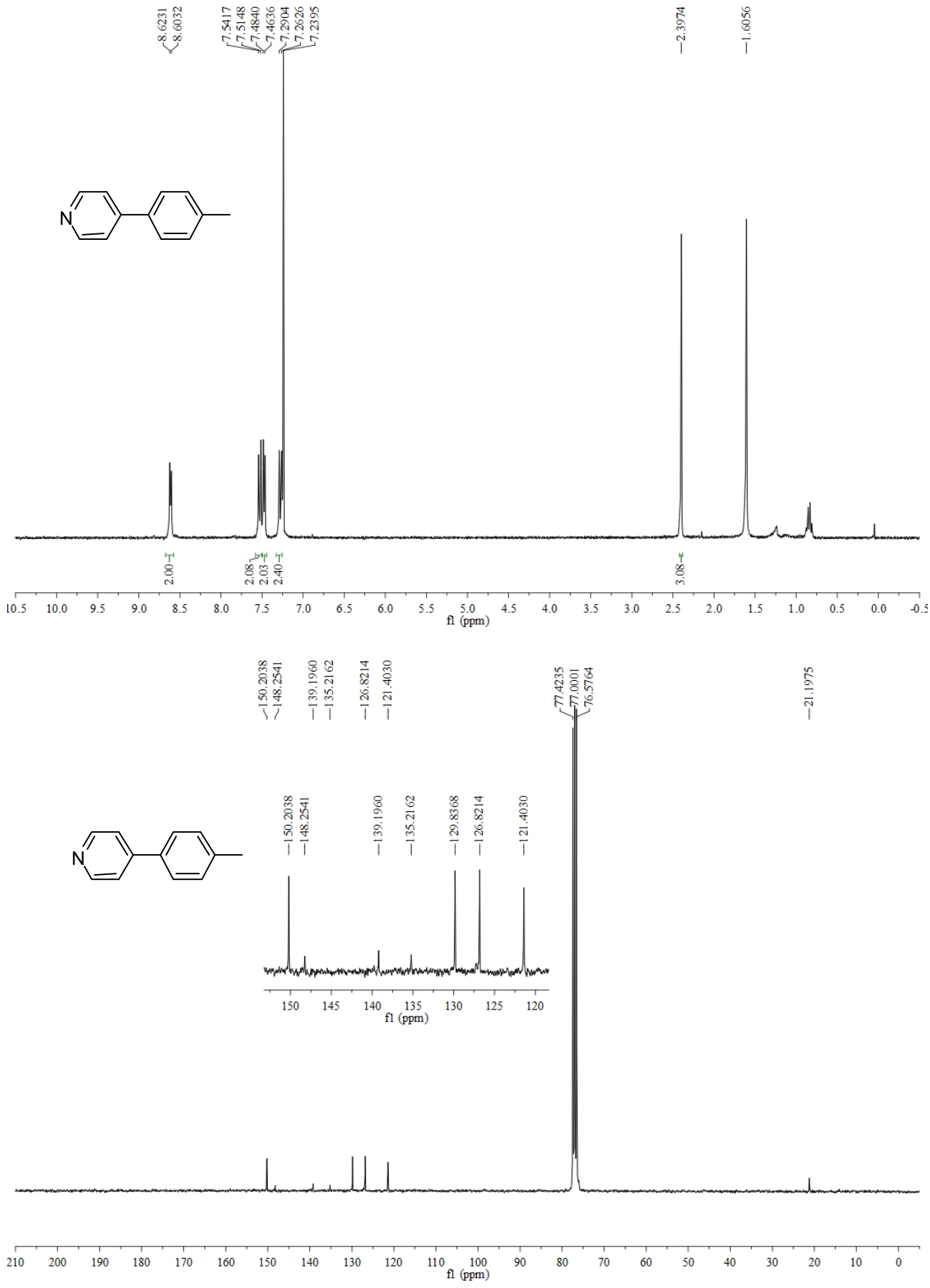

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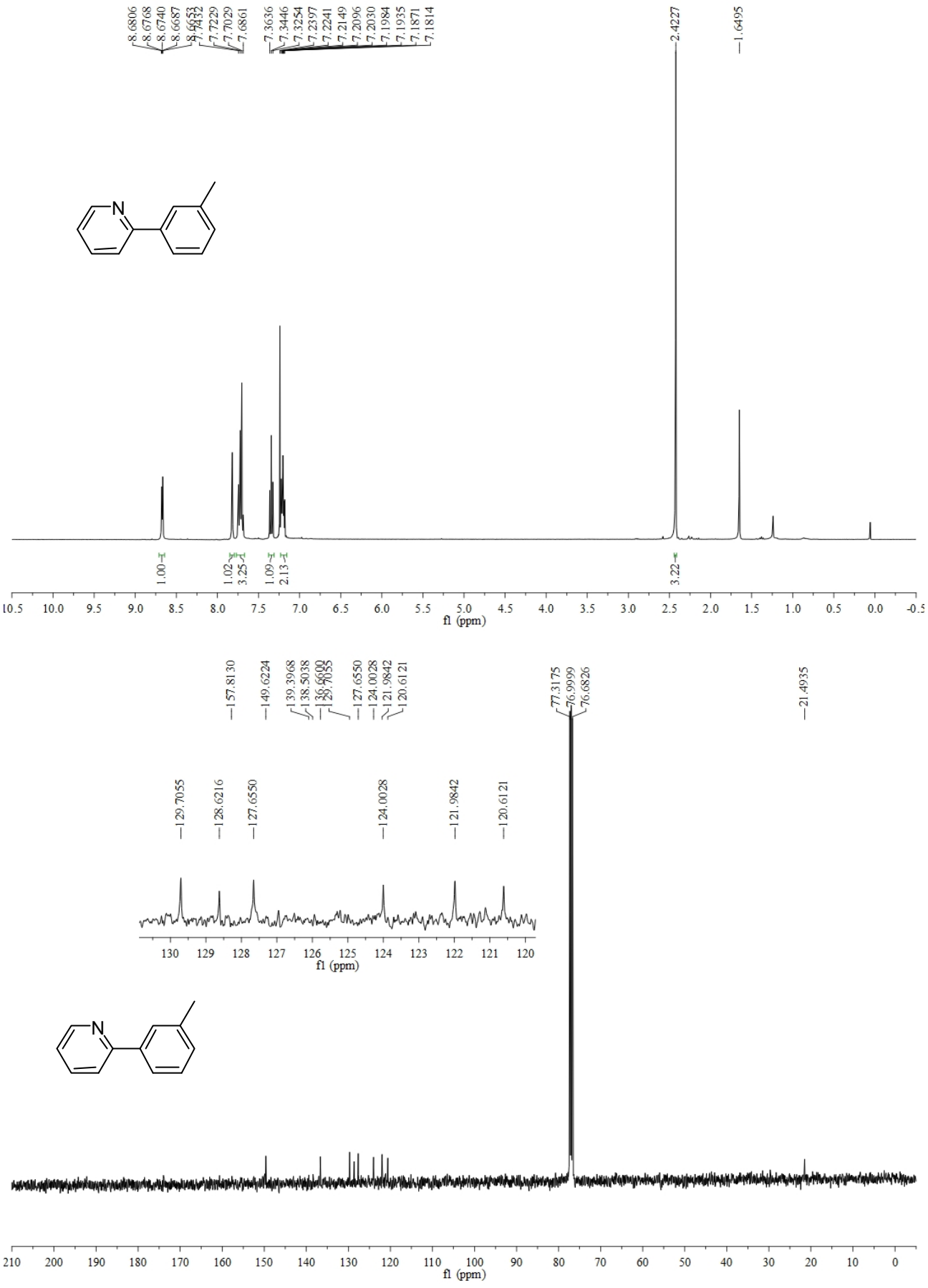

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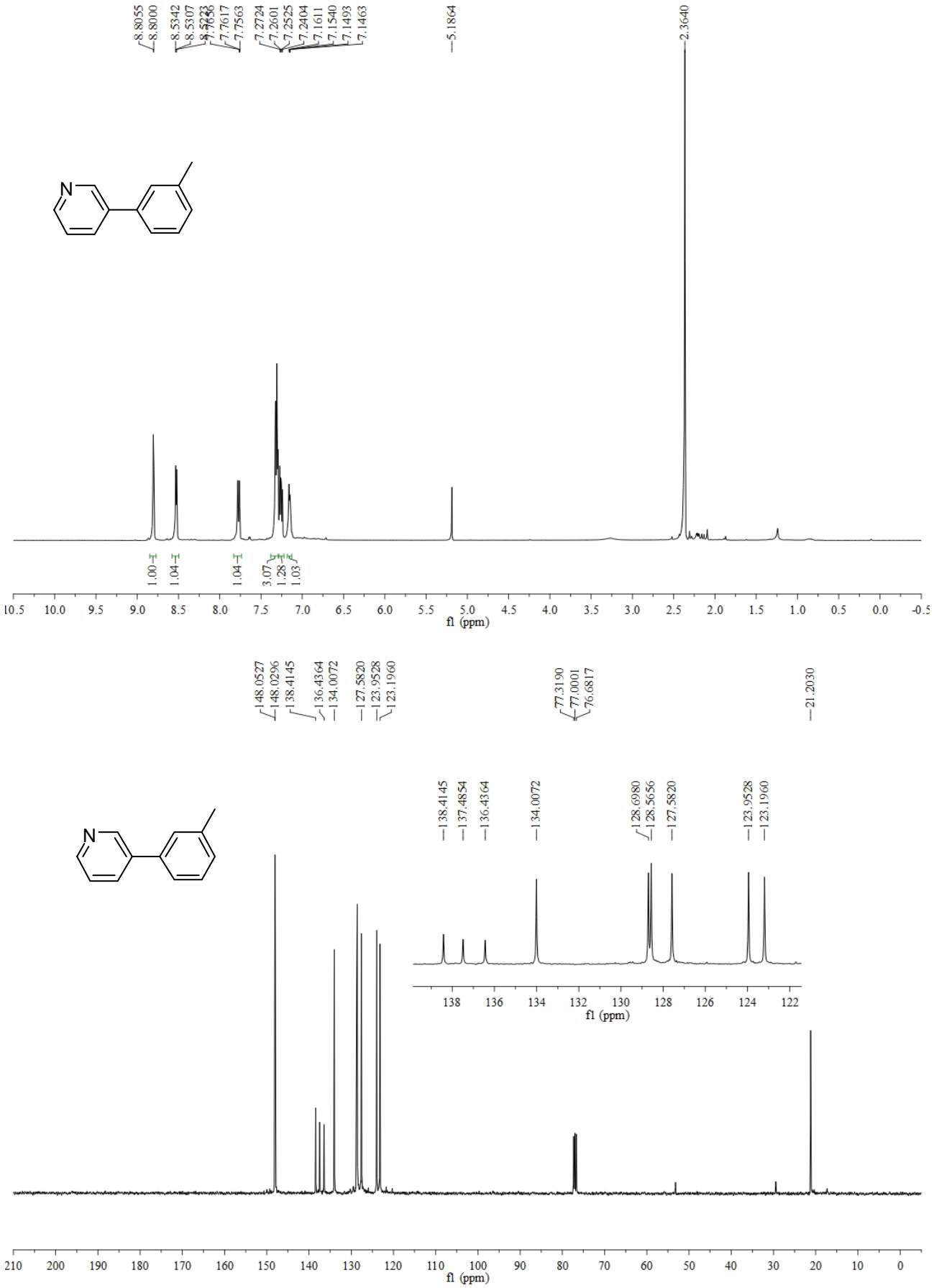

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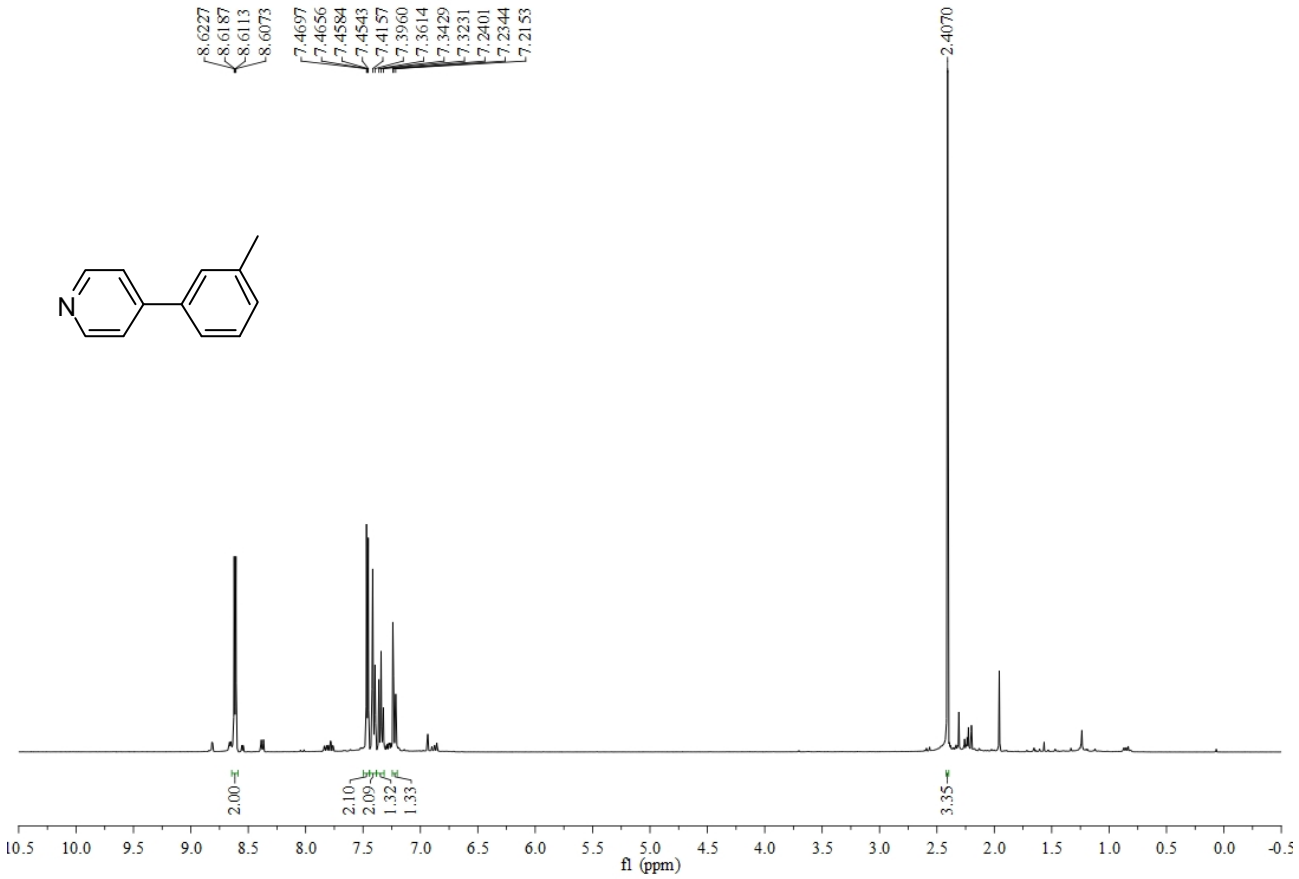

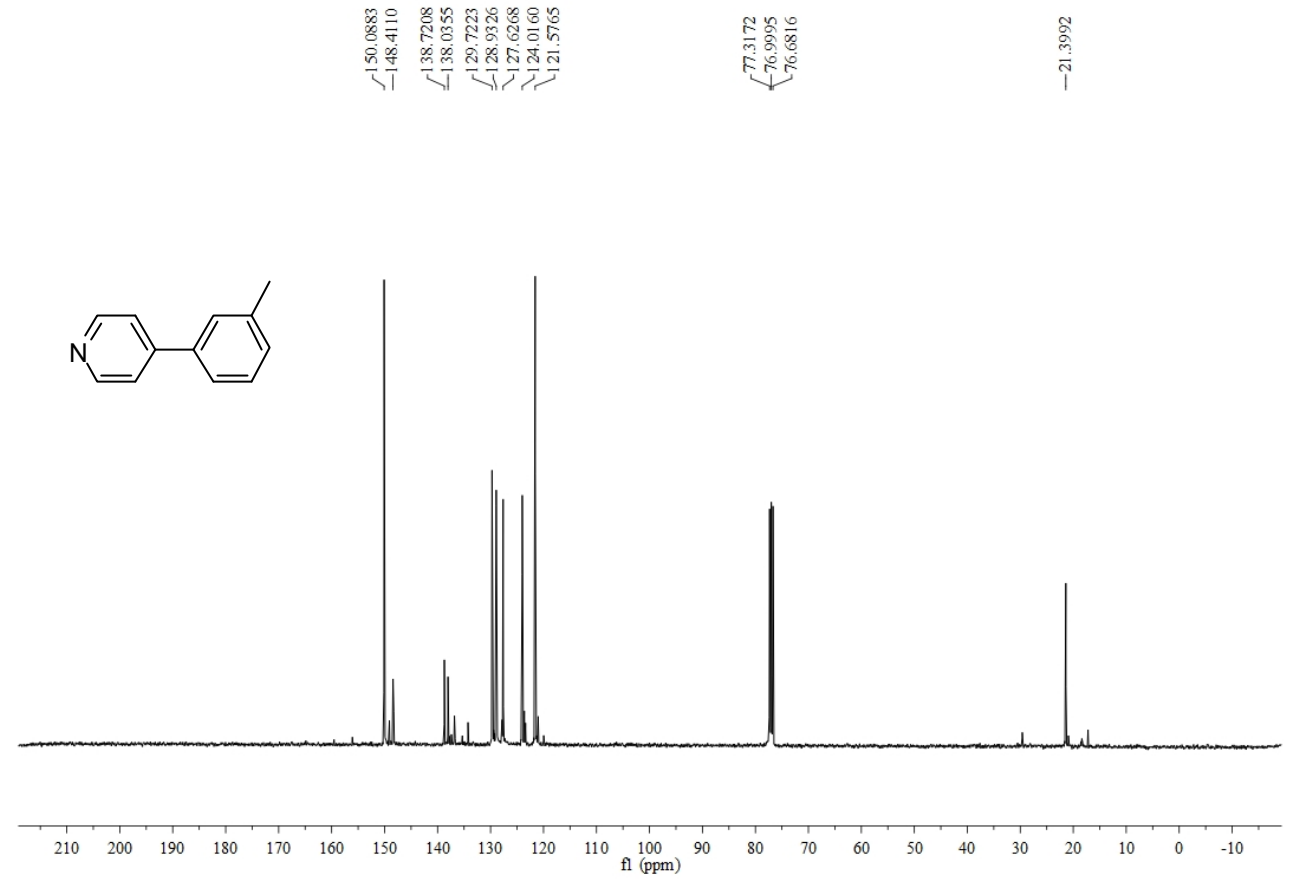

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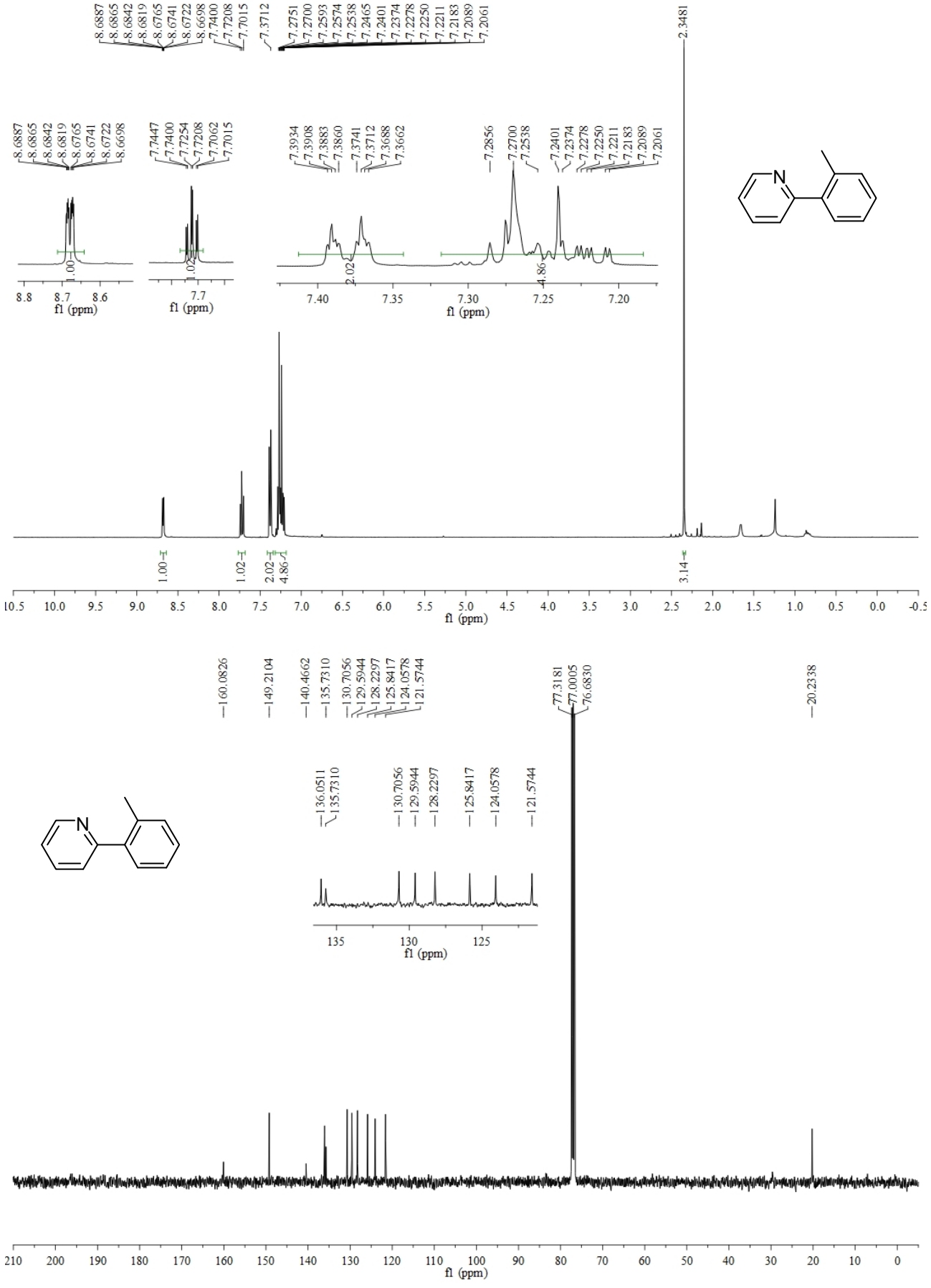

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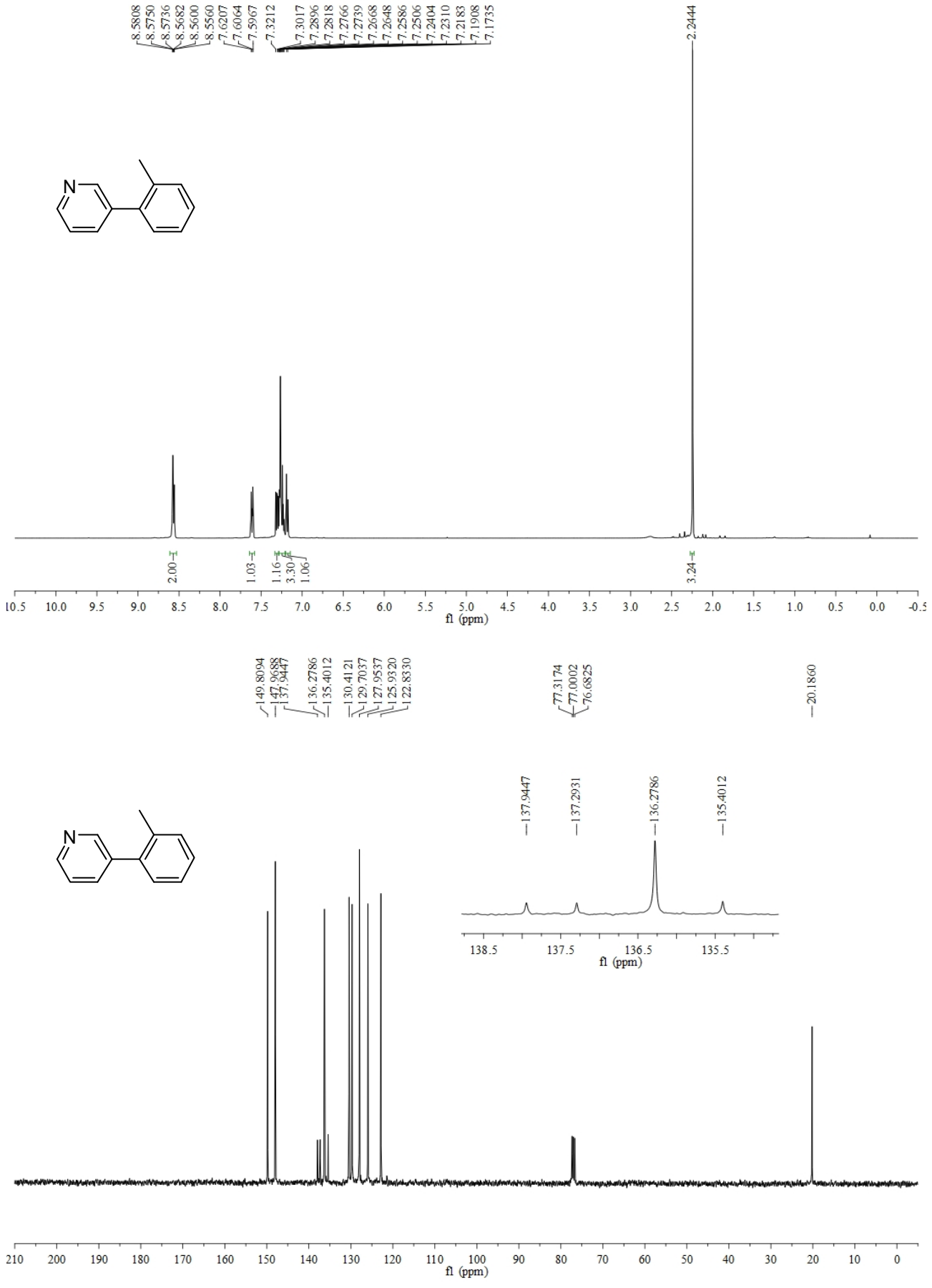

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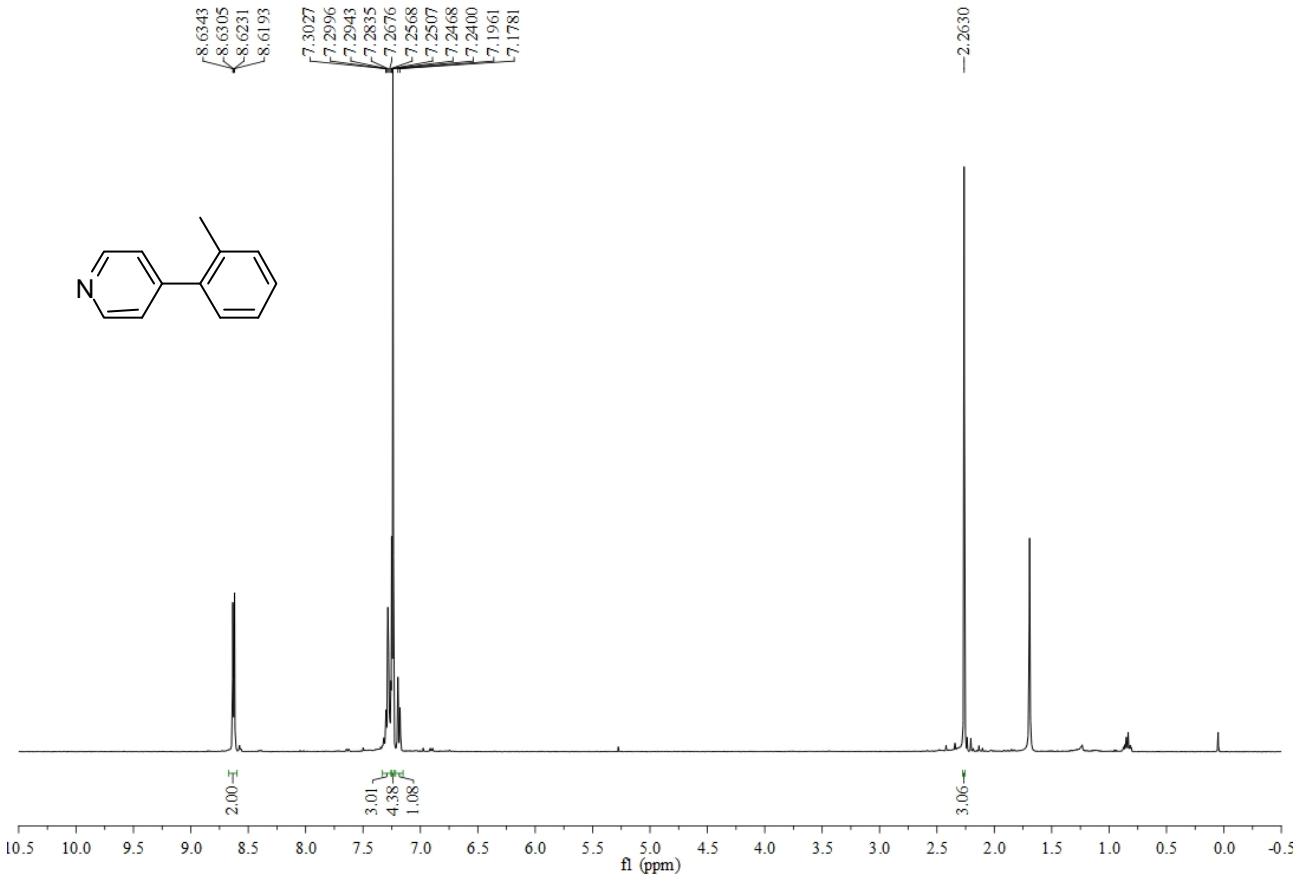

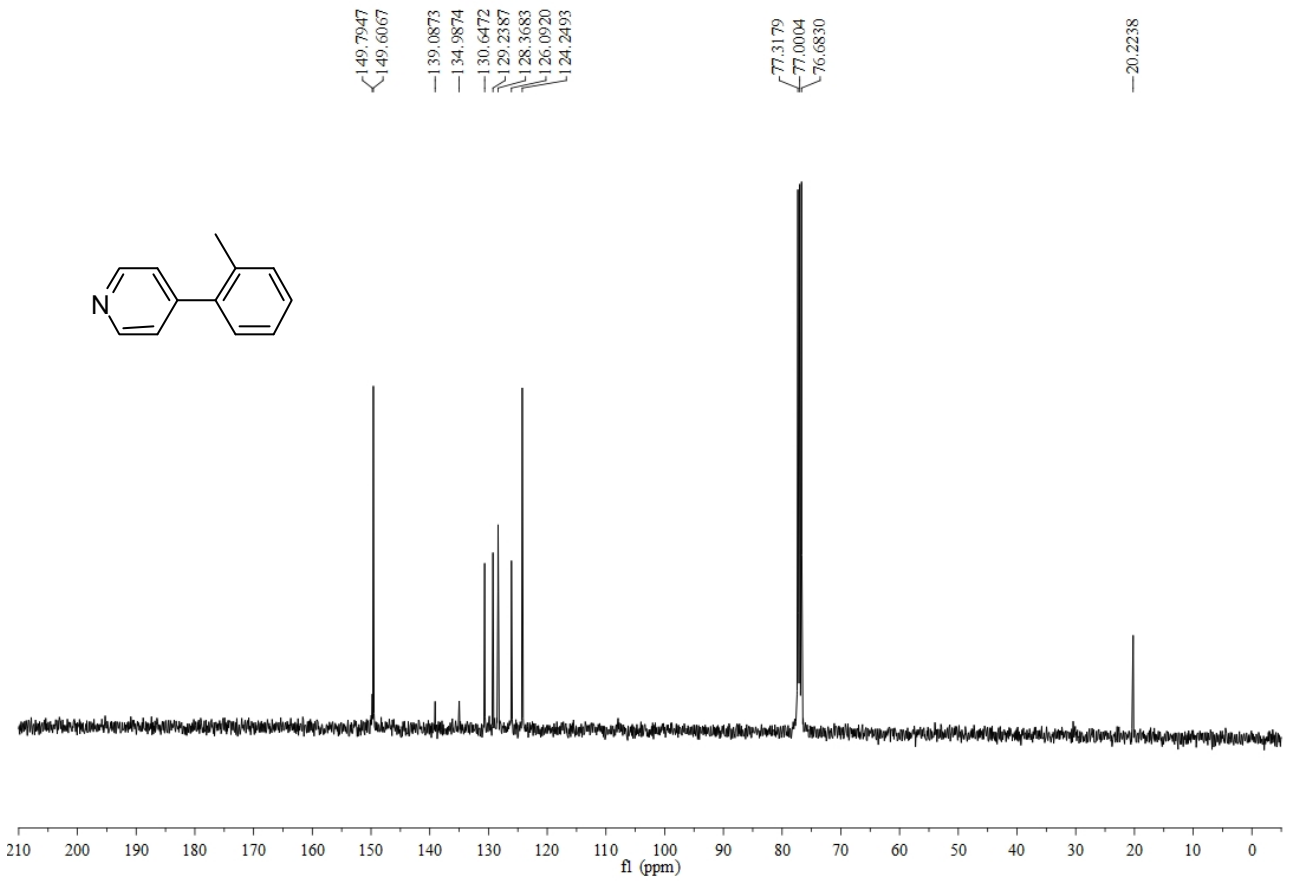

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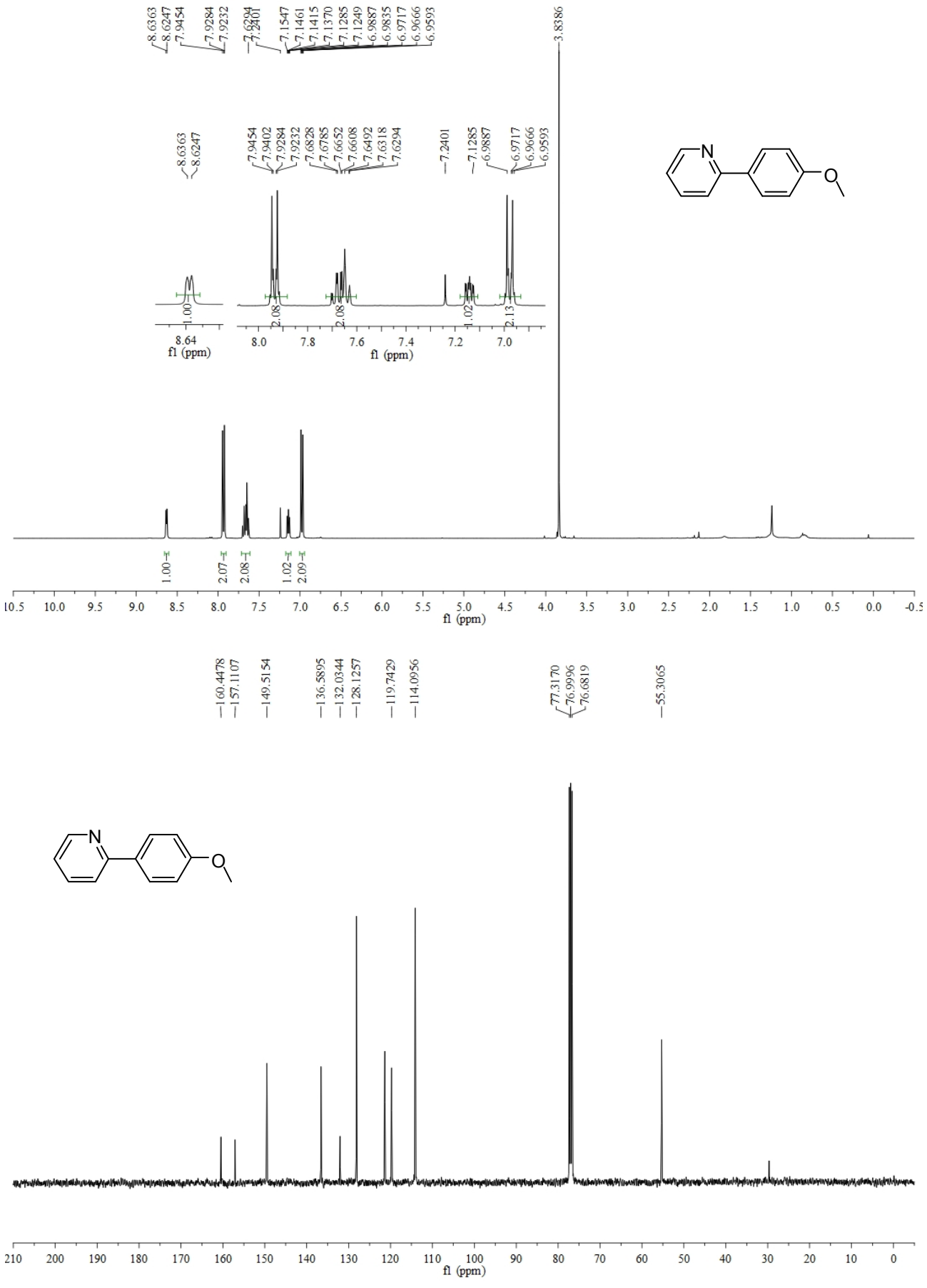

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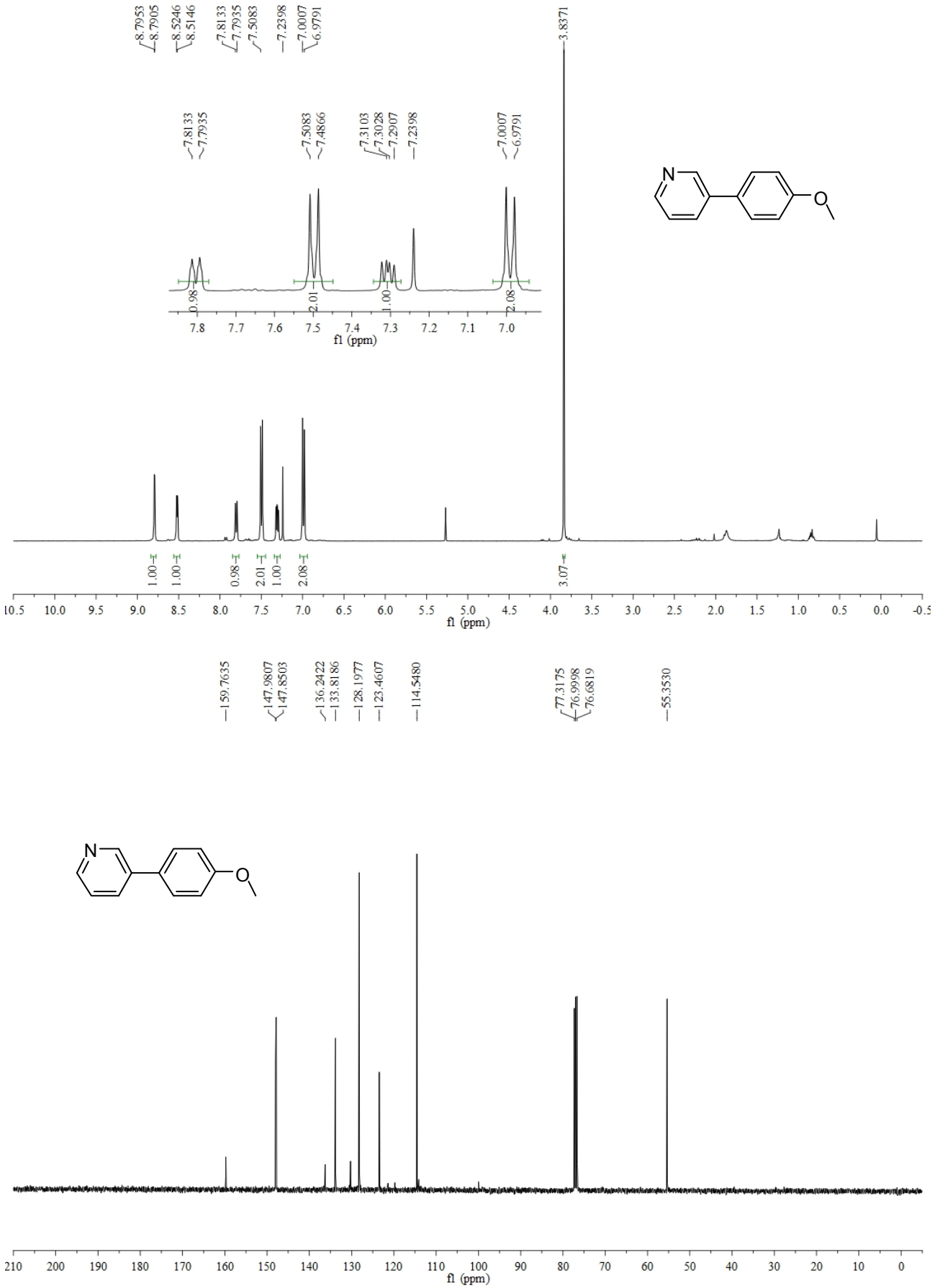

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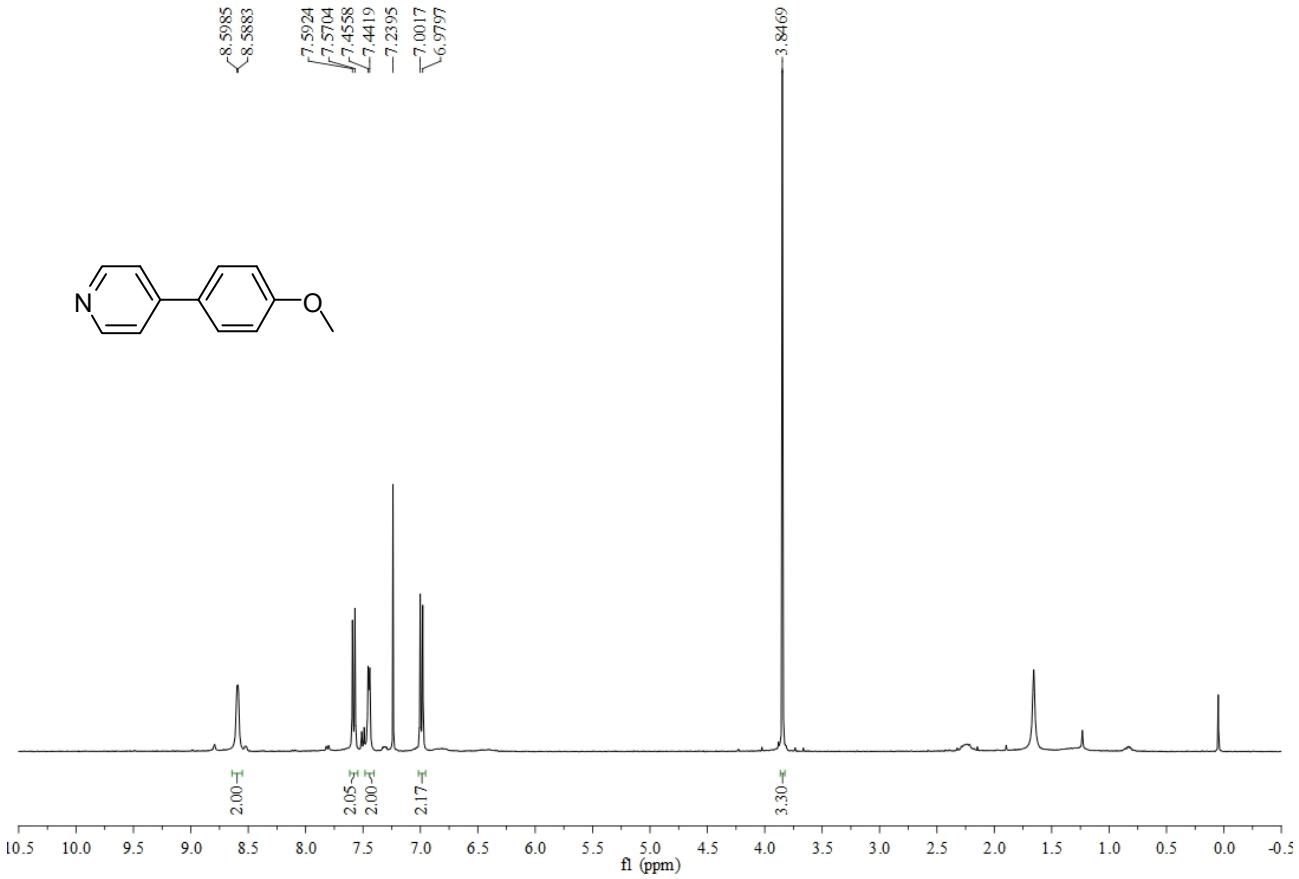

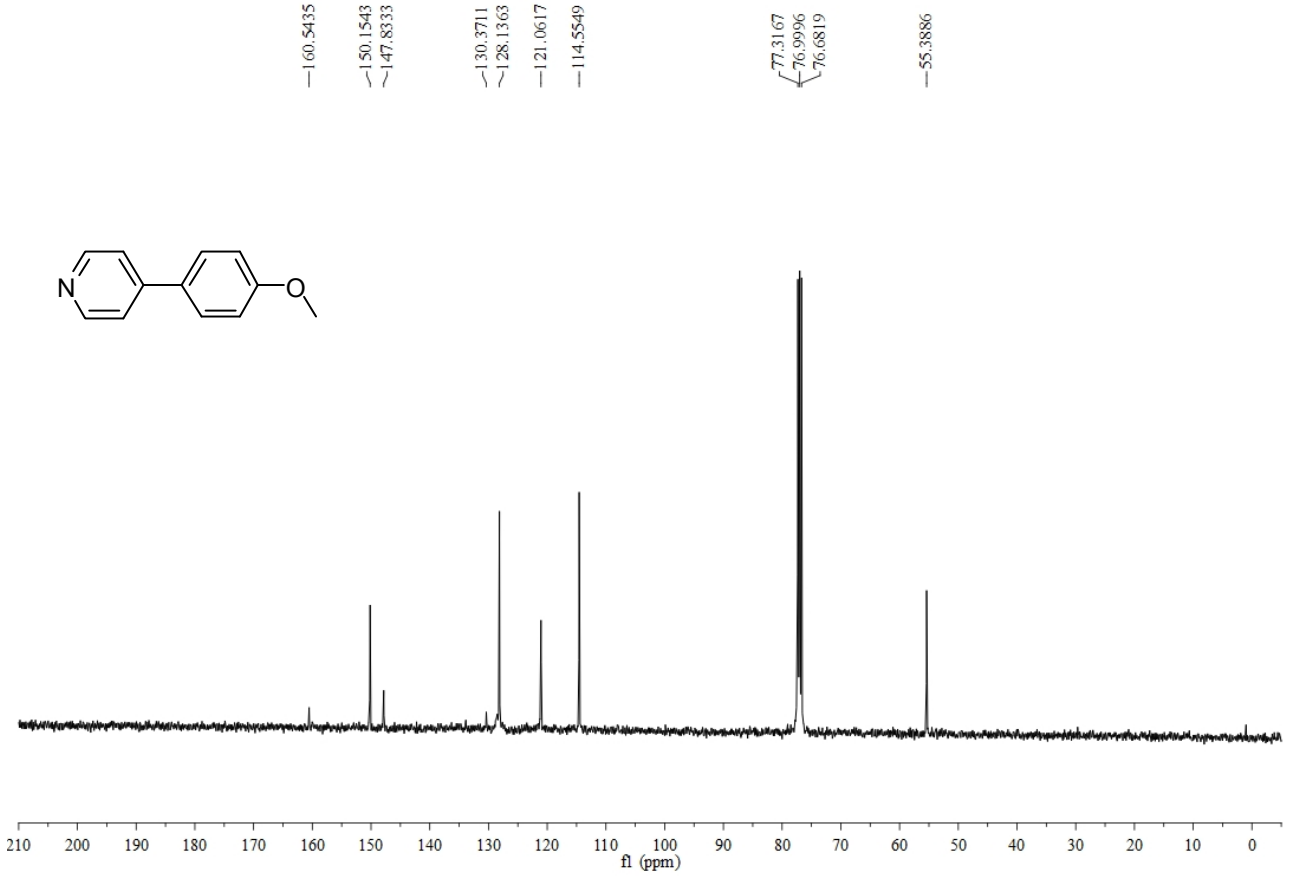

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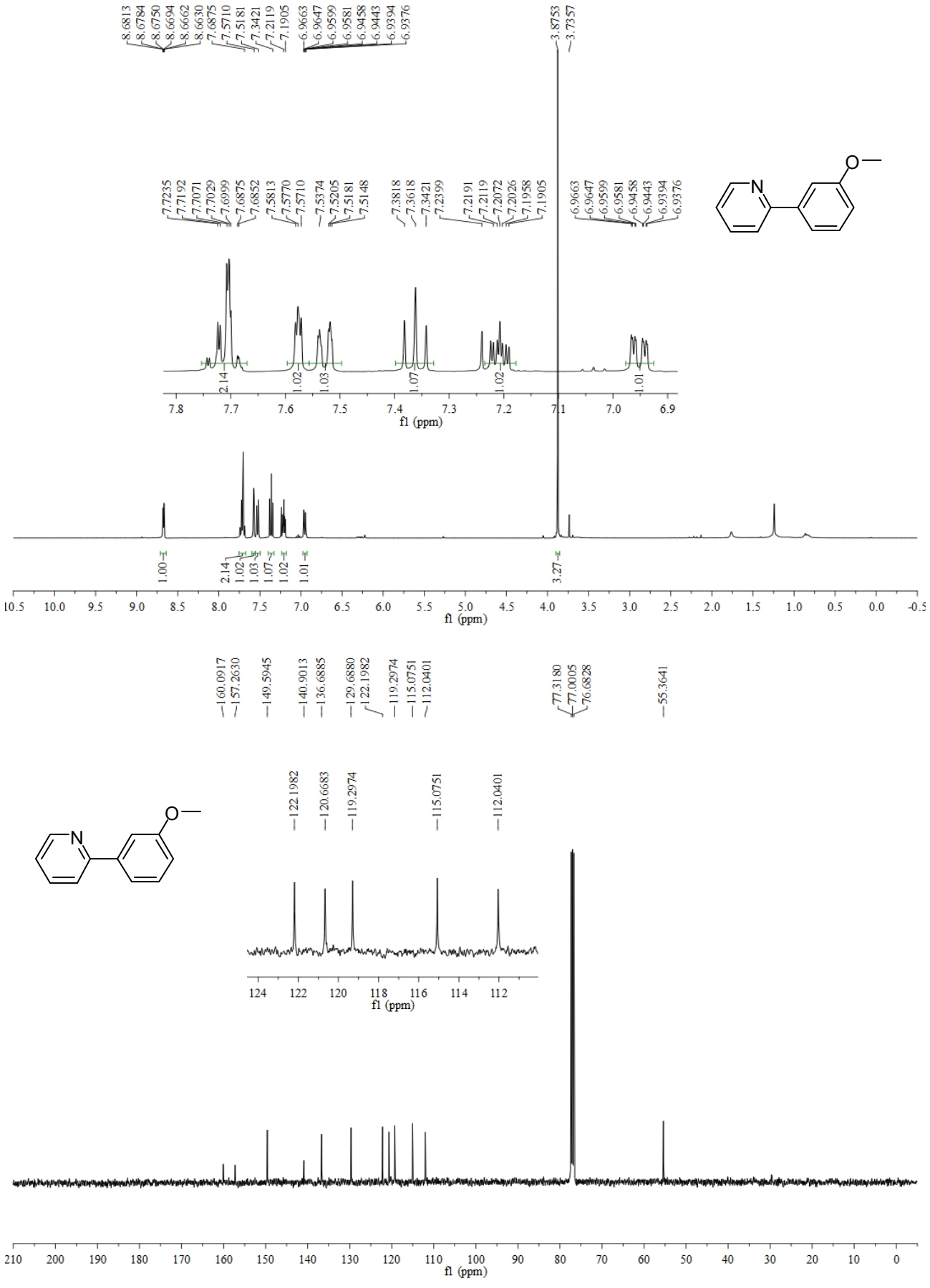
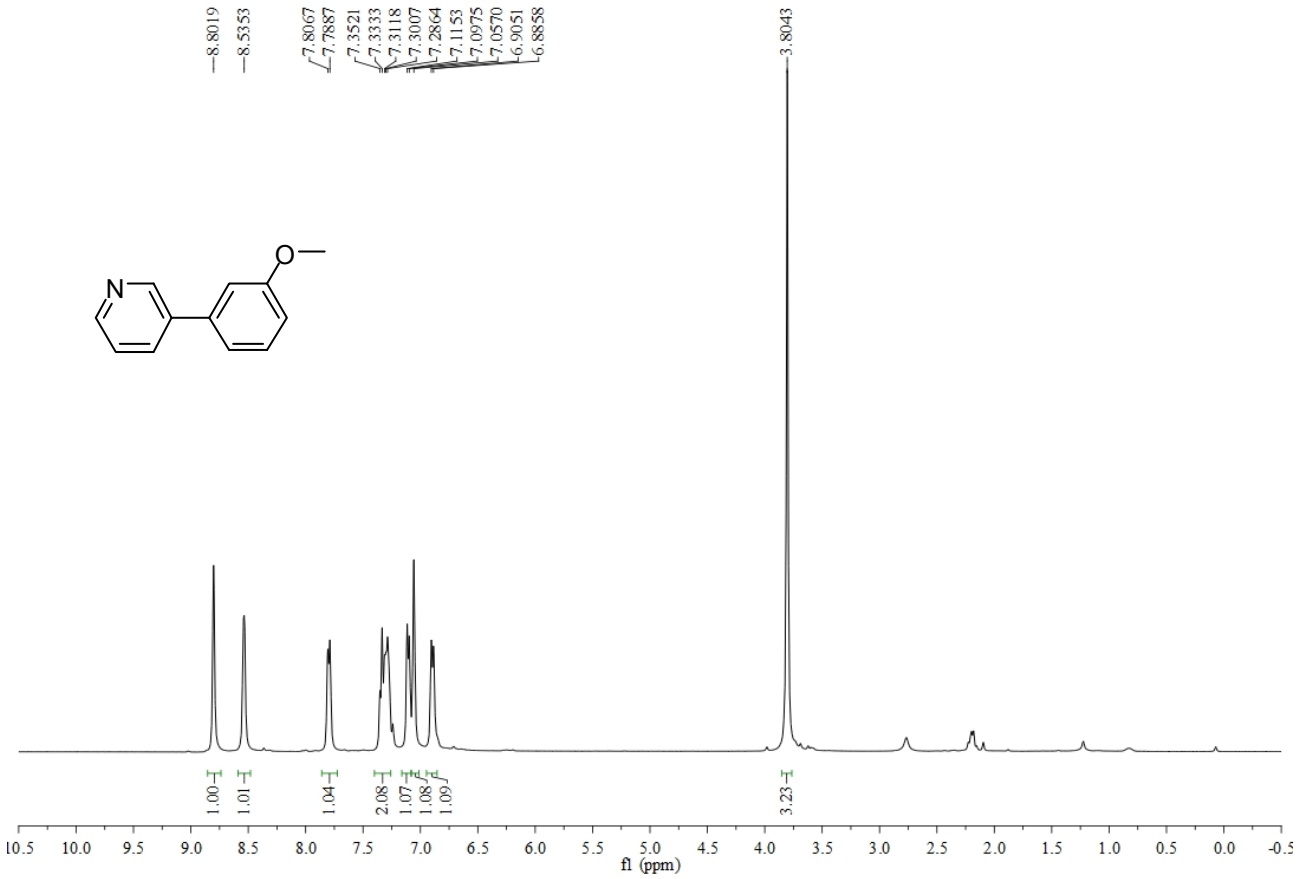
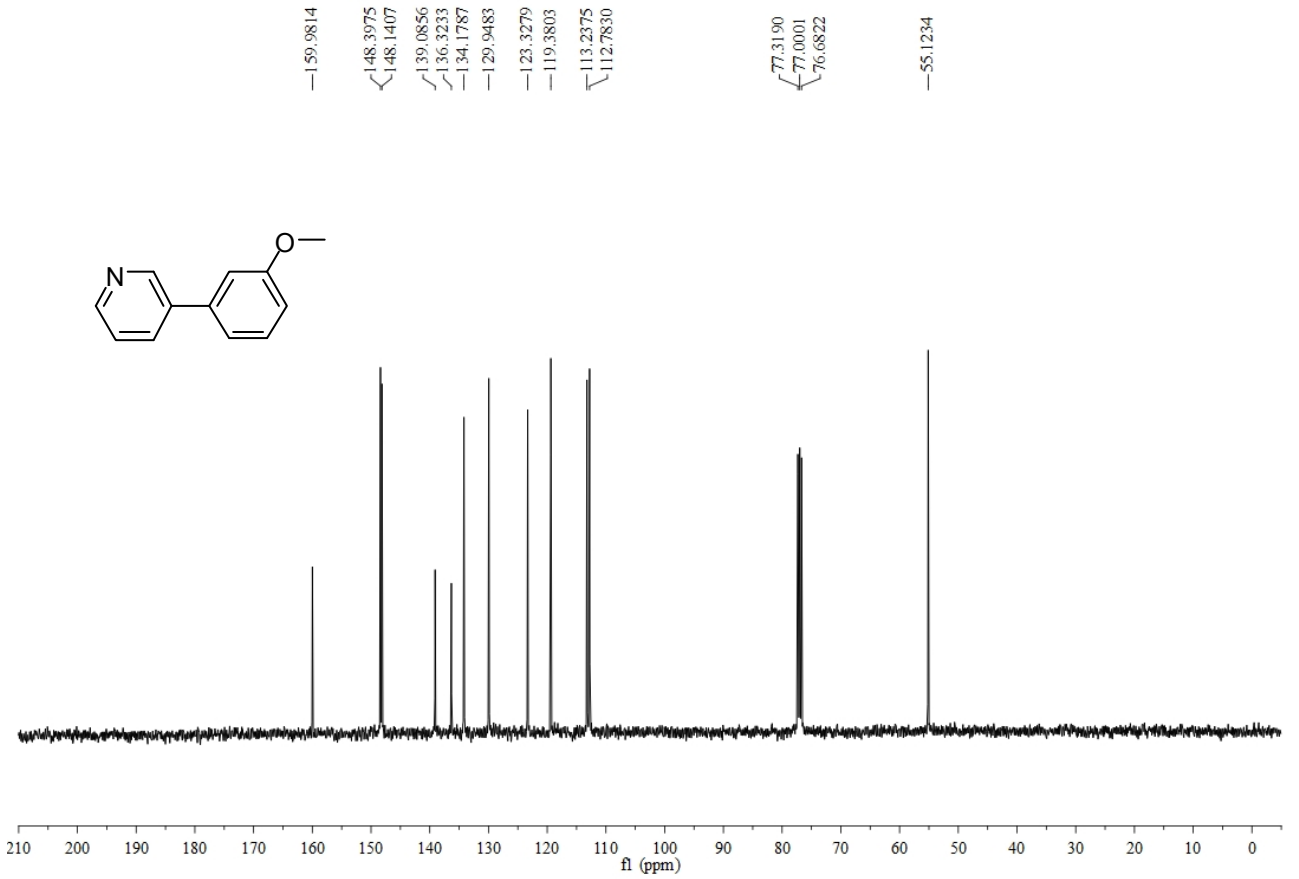
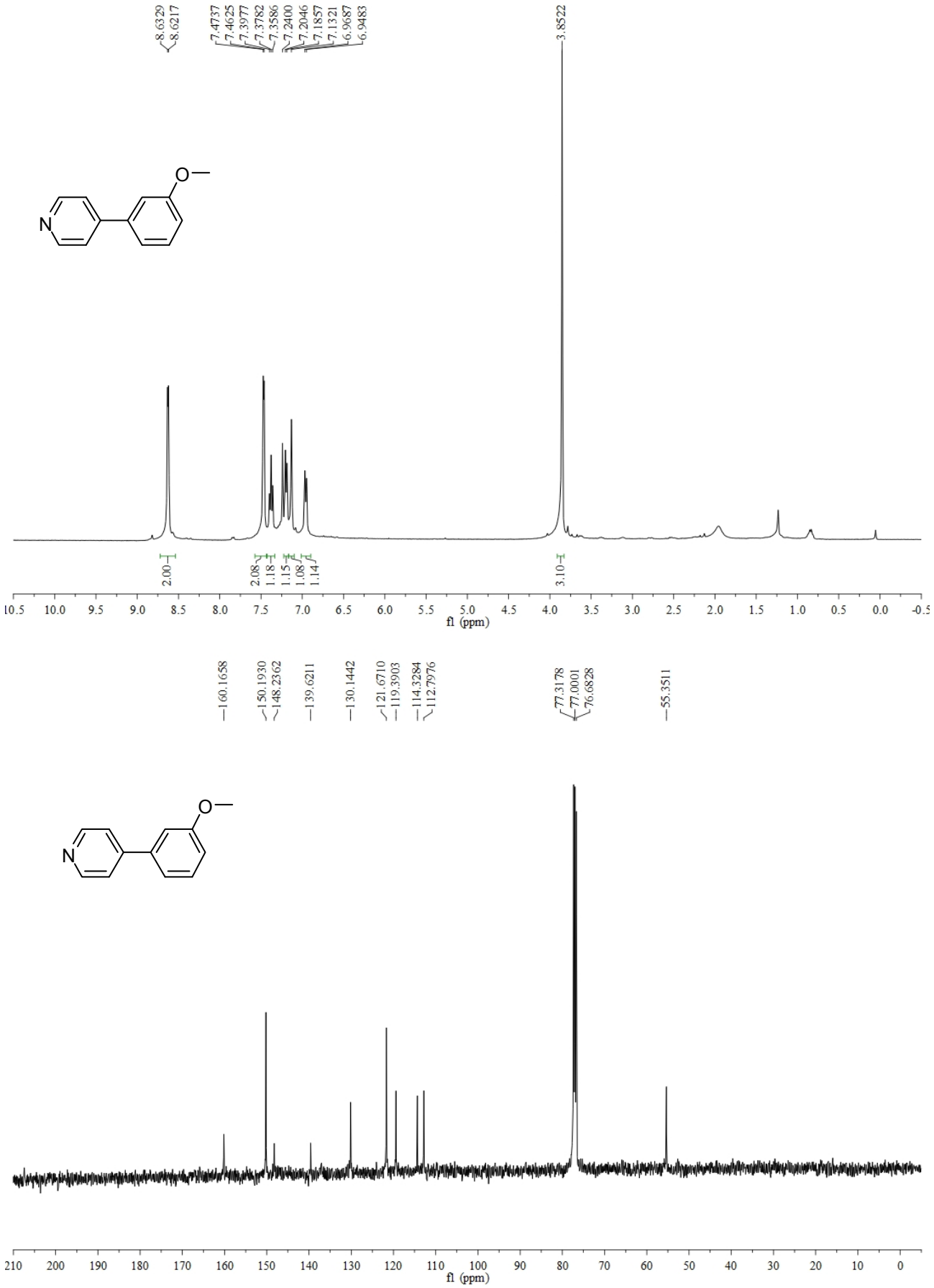


^{1}H and ^{13}C NMR spectra of *o*-**4e**

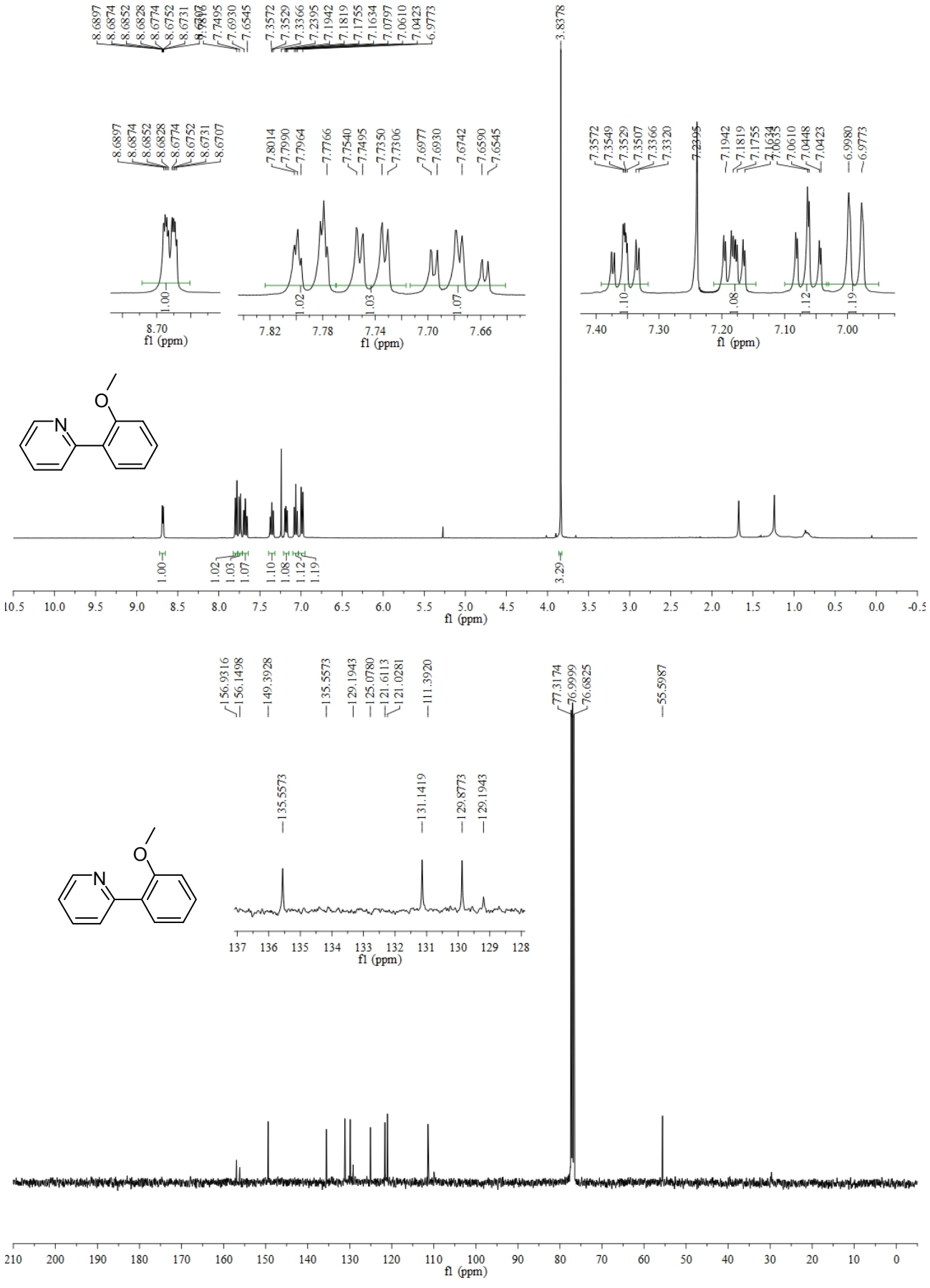




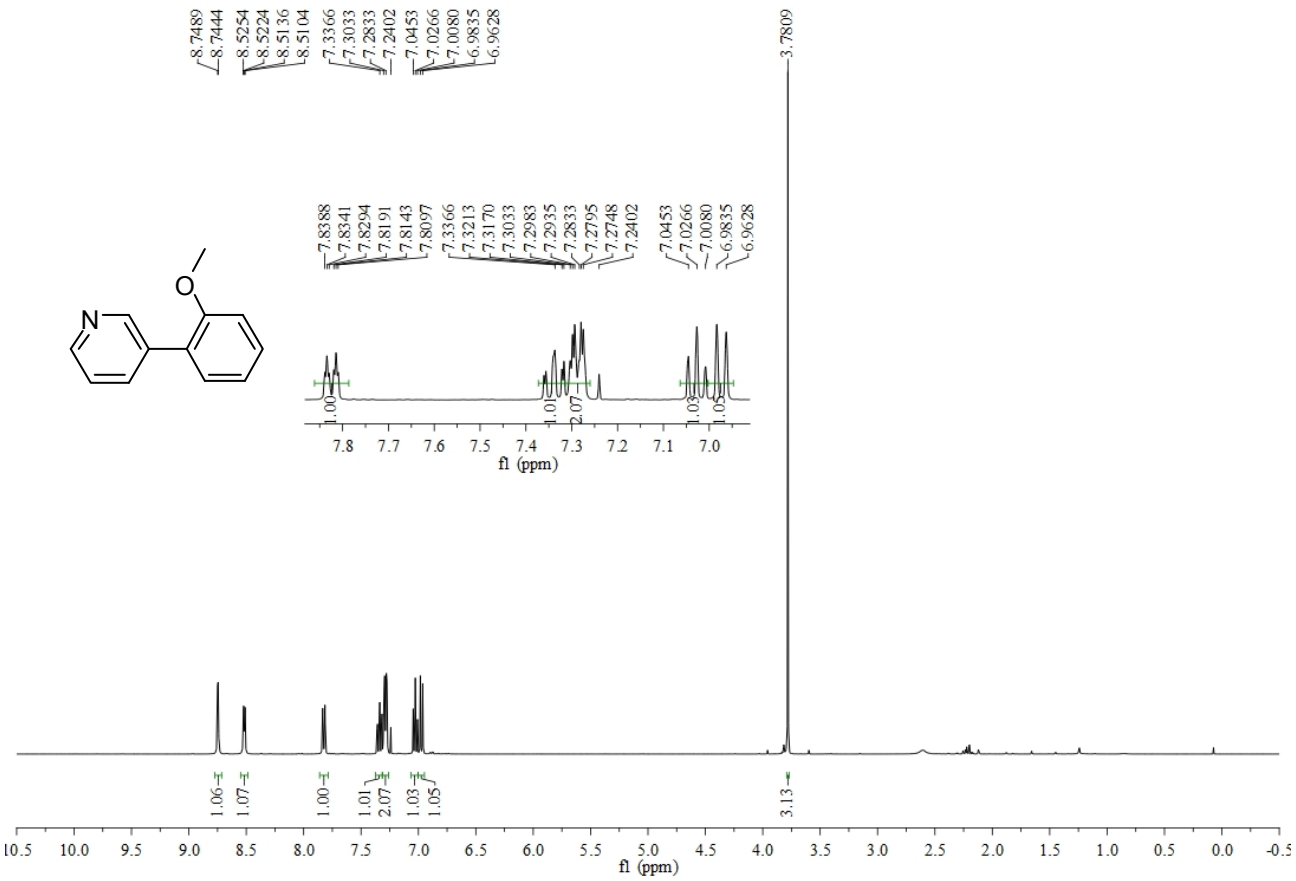
^{1}H and ^{13}C NMR spectra of *m*-**4e**

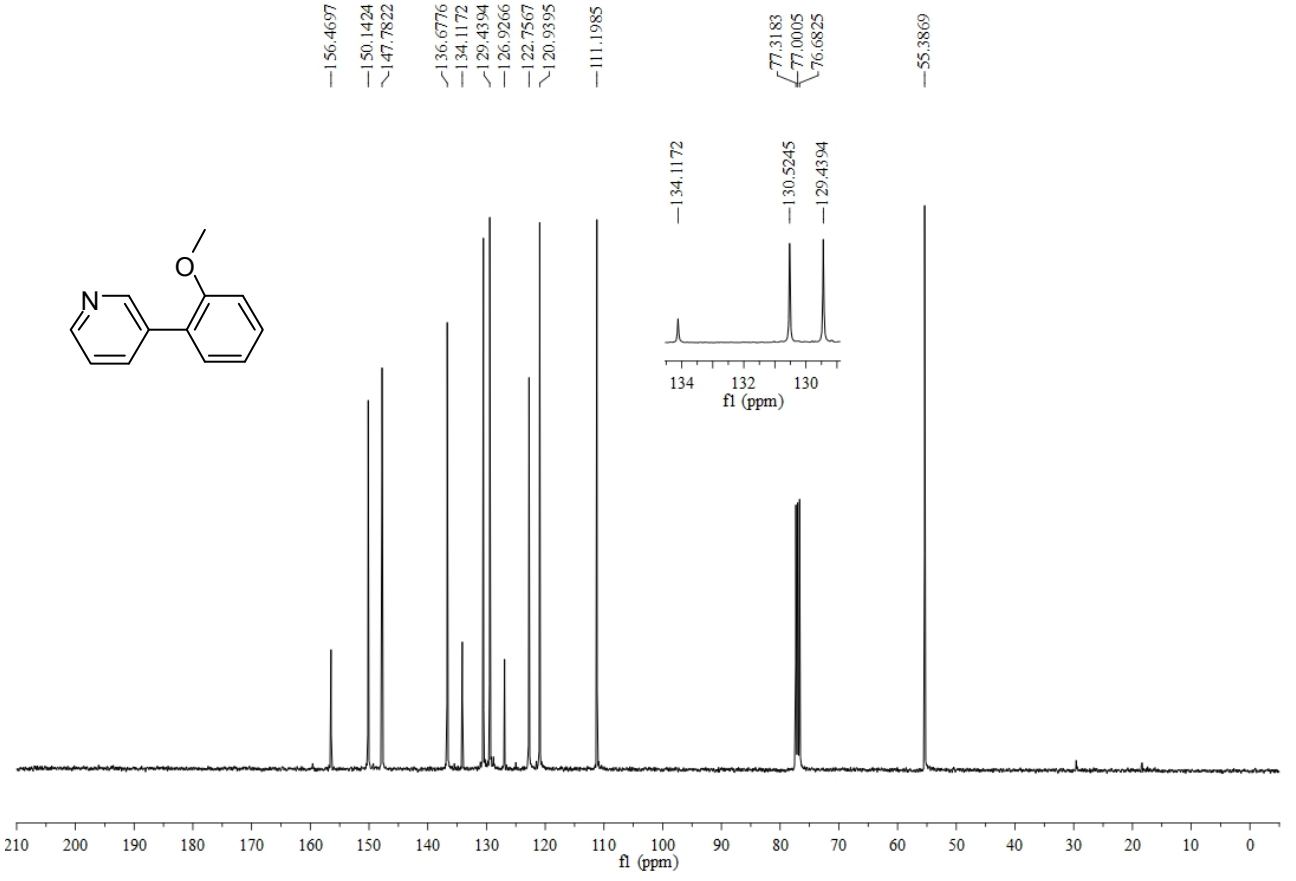


^{1}H and ^{13}C NMR spectra of *p*-**4e**

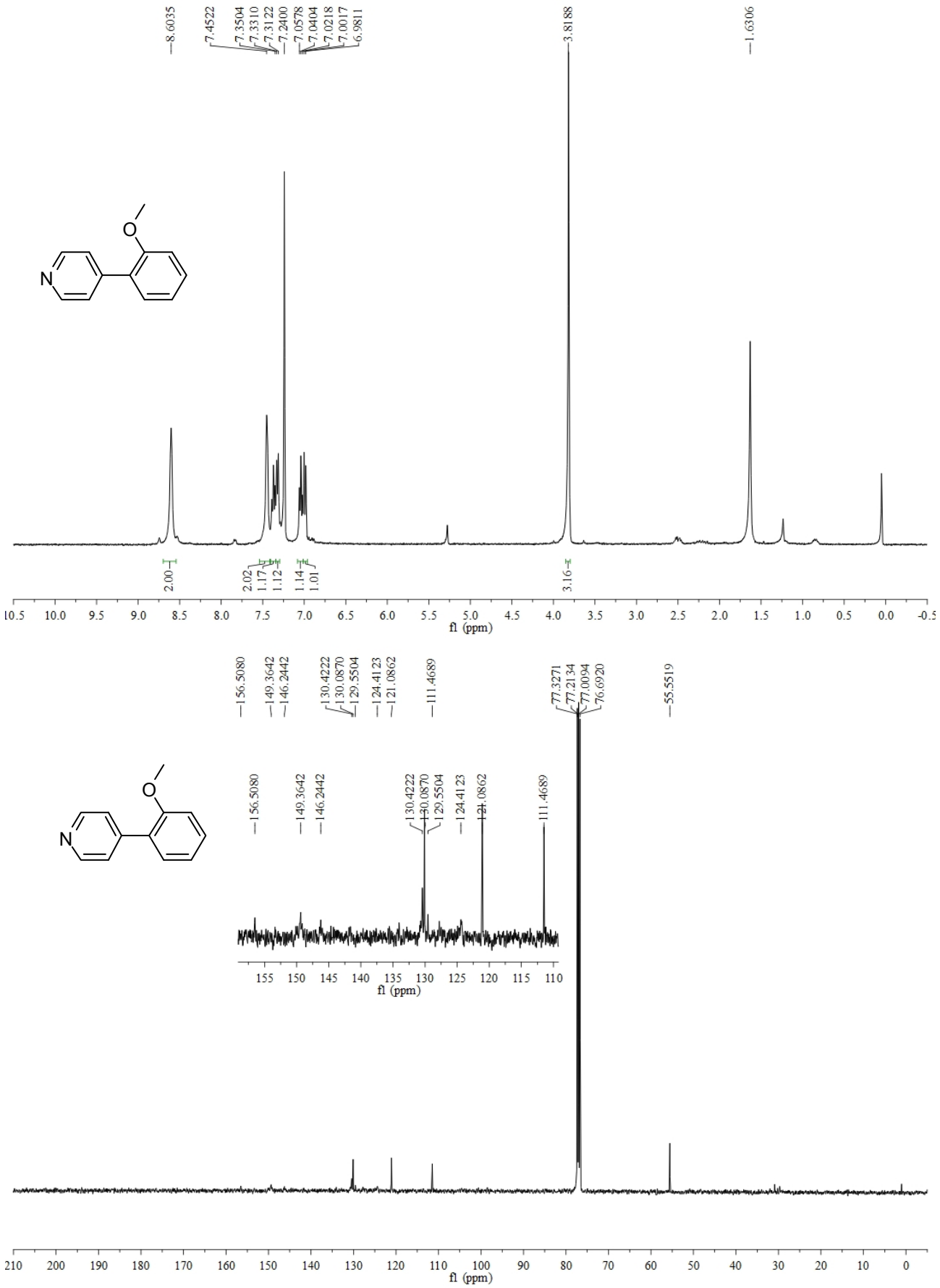


^{1}H and ^{13}C NMR spectra of *o*-**4f**

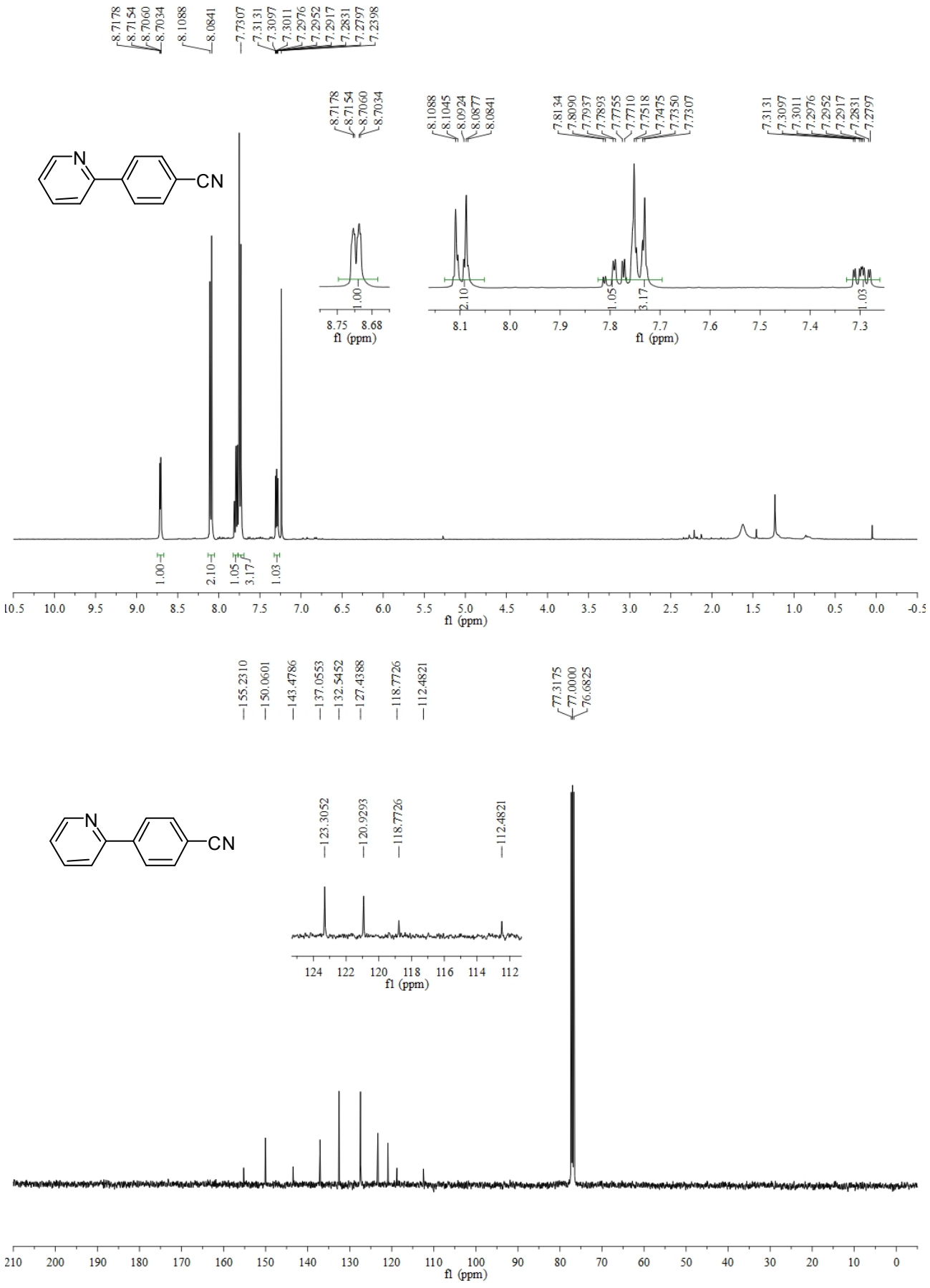




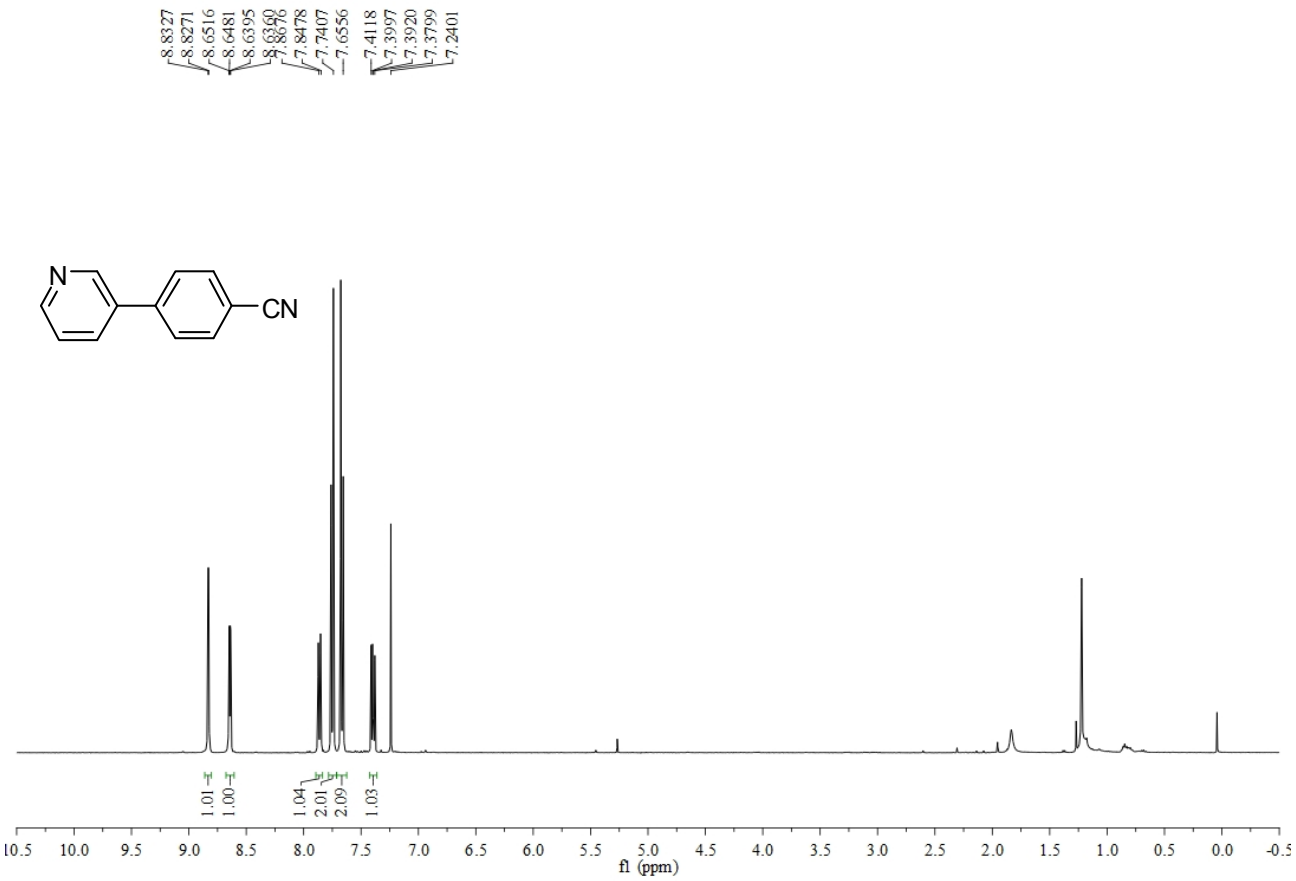
^{1}H and ^{13}C NMR spectra of *m*-**4f**

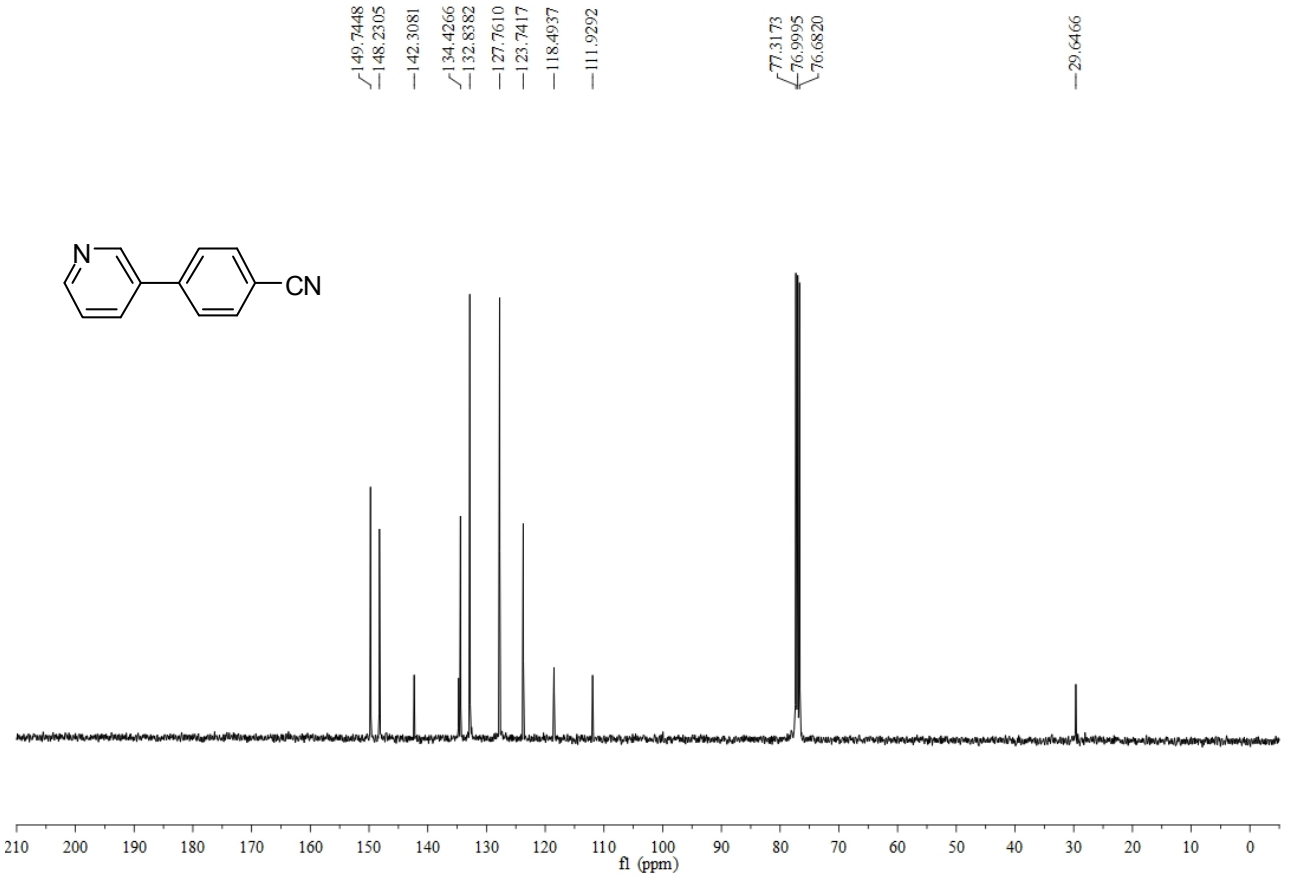


^{1}H and ^{13}C NMR spectra of *p*-**4f**

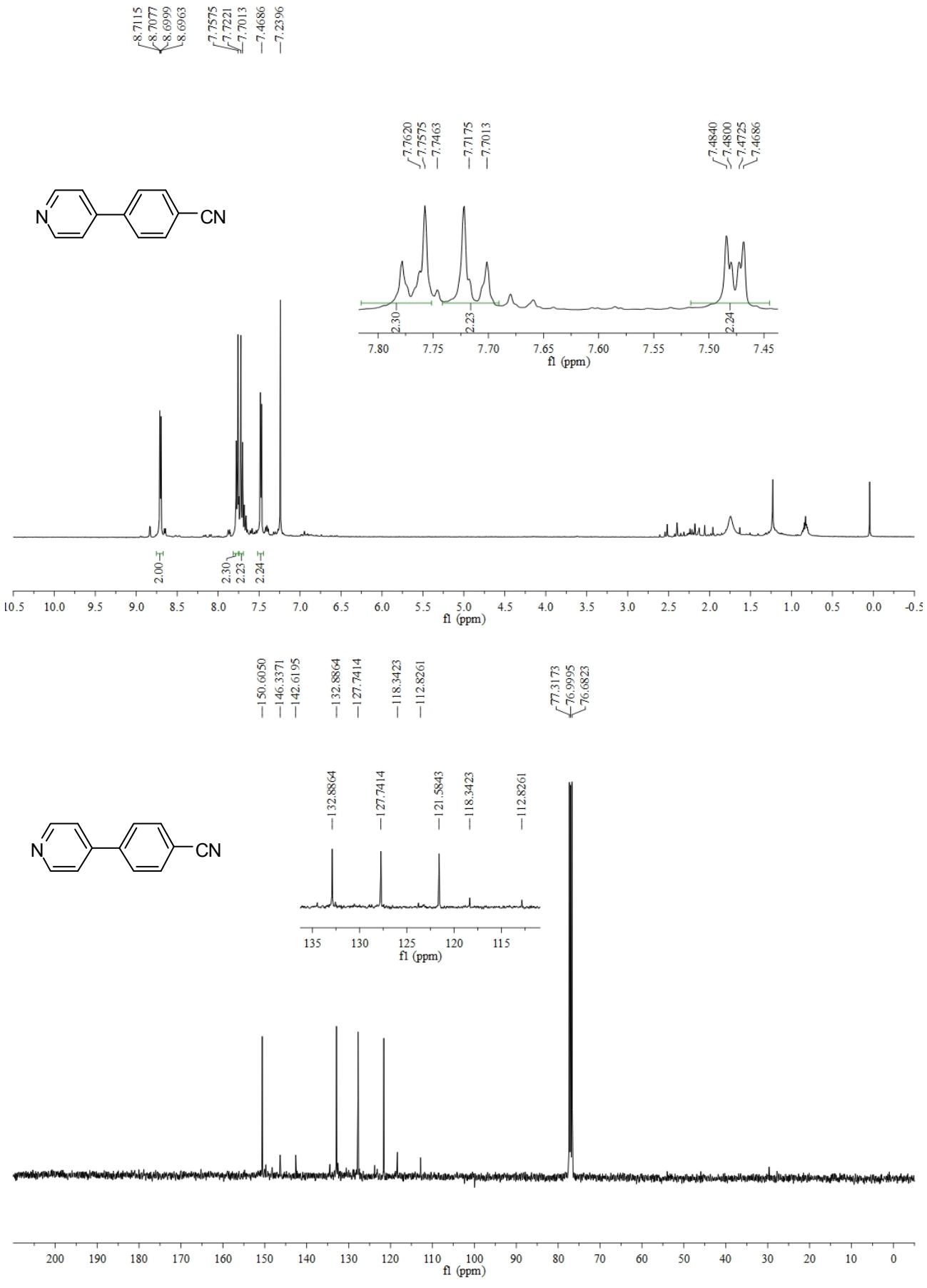


^{1}H and ^{13}C NMR spectra of *o*-**4g**

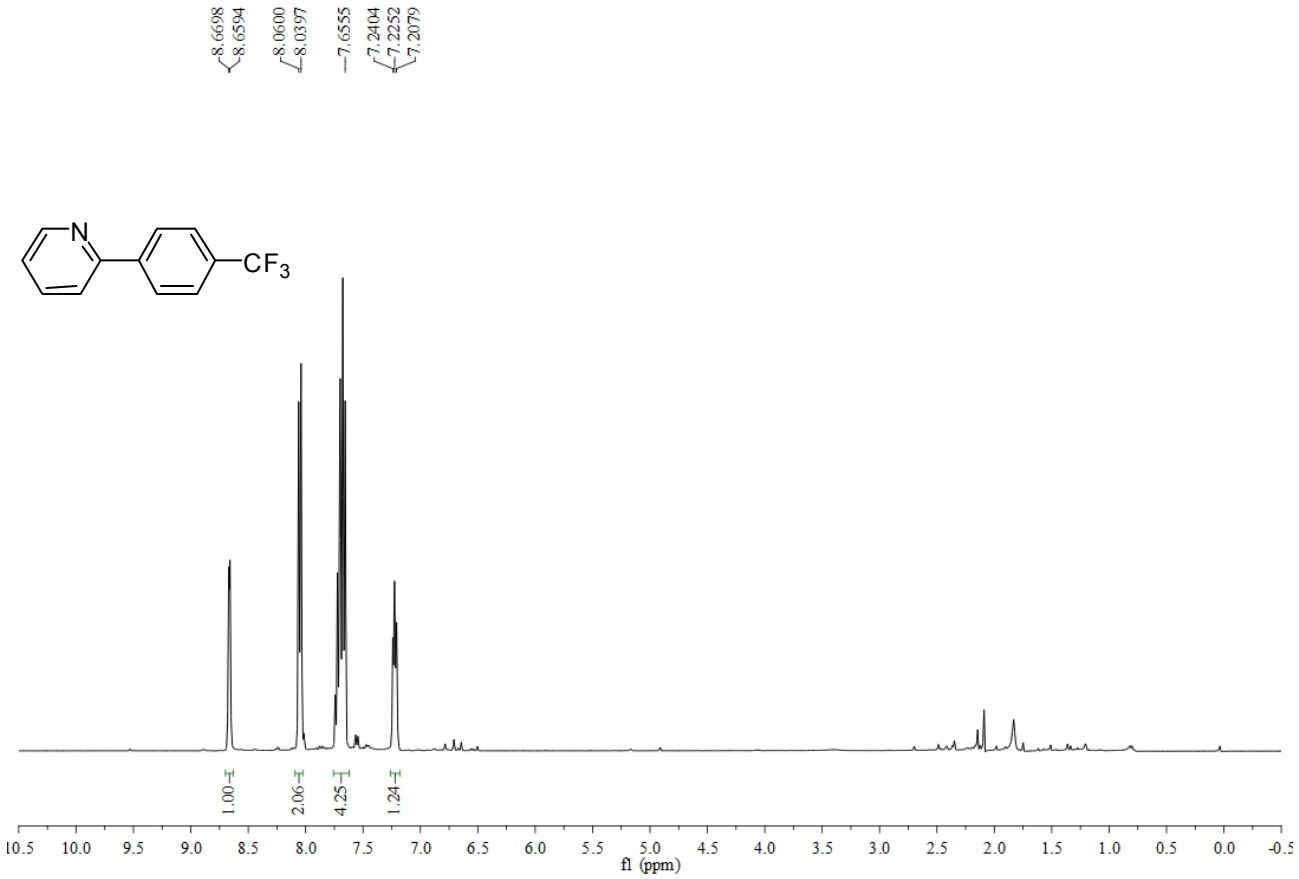


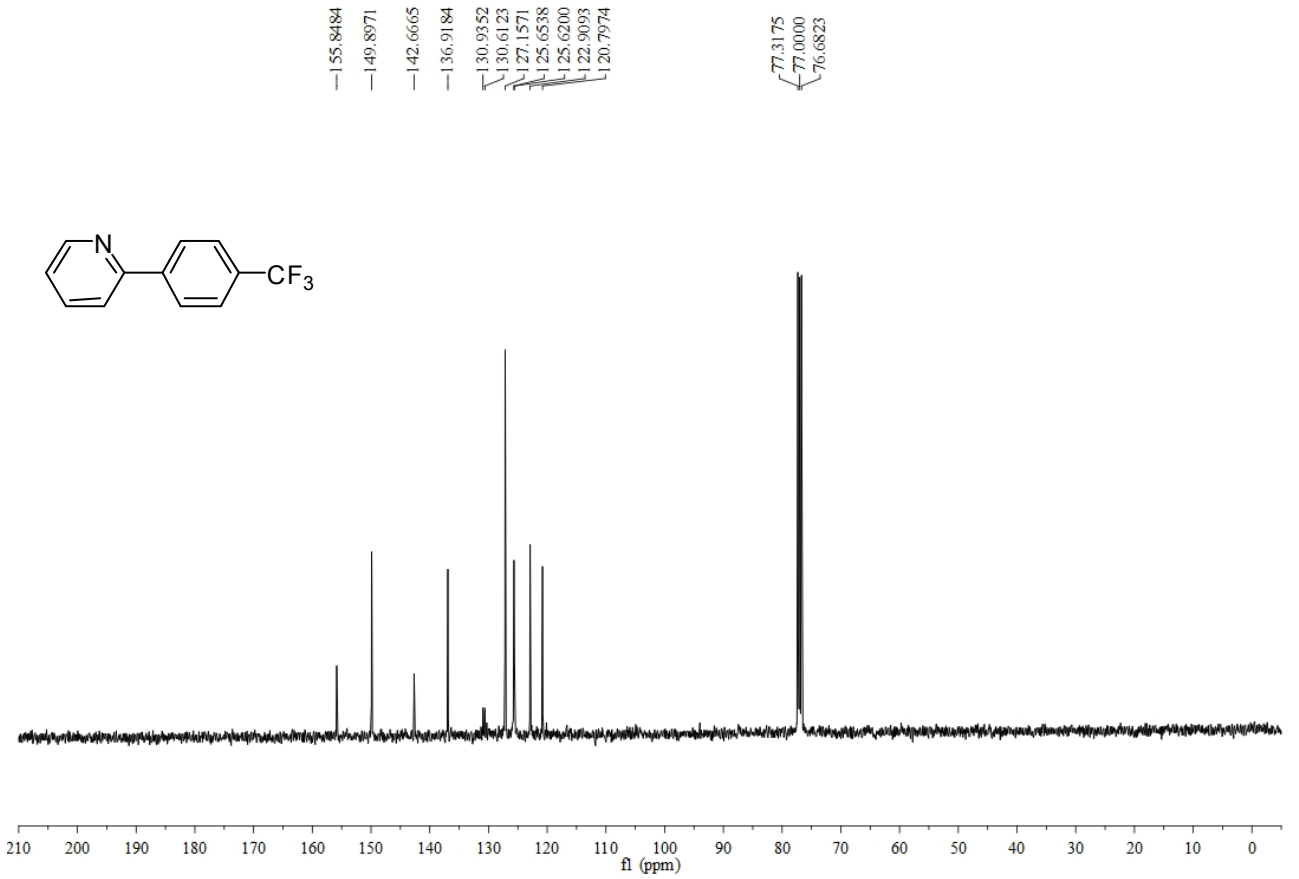


^{1}H and ^{13}C NMR spectra of *m*-**4g**

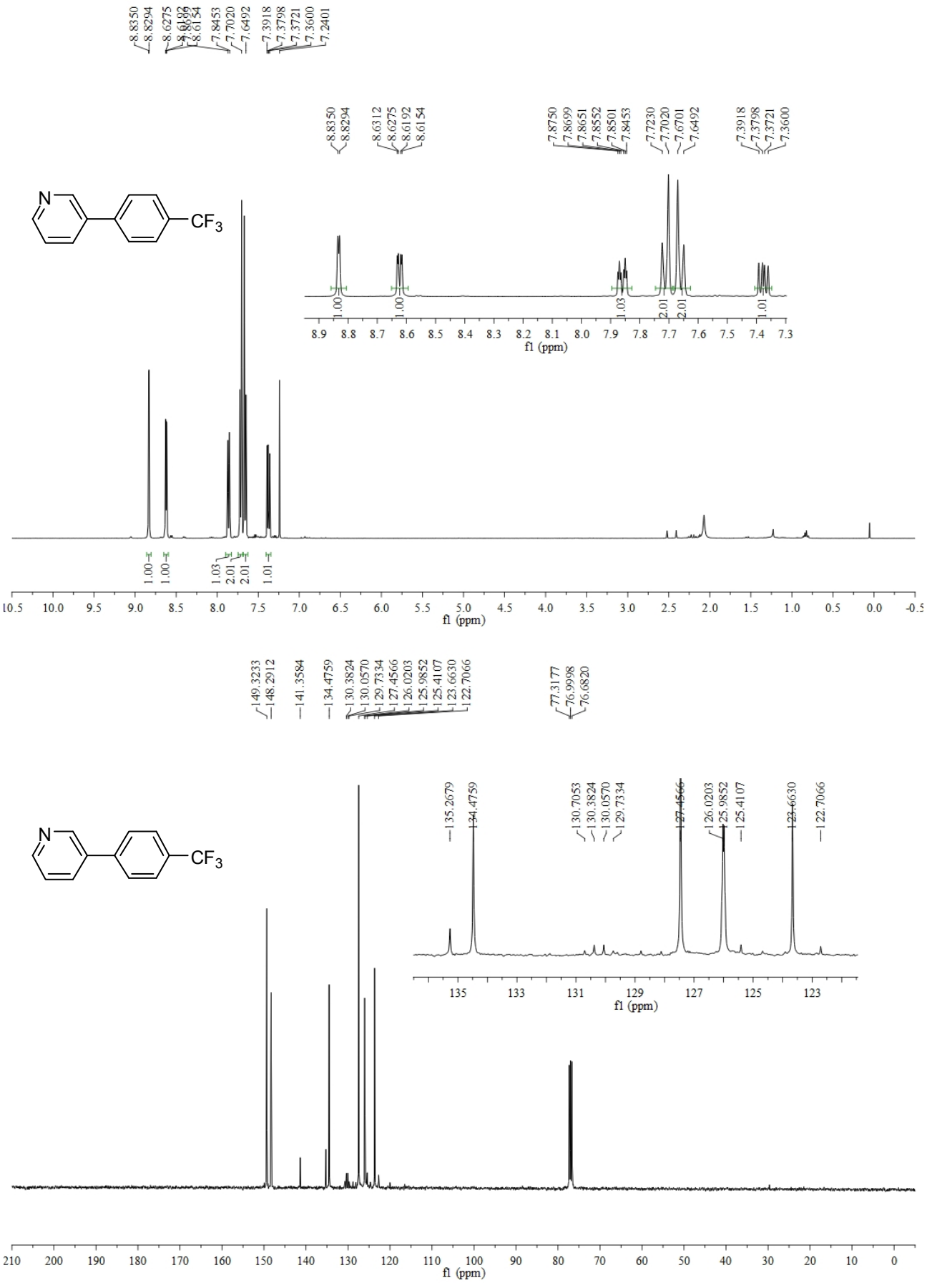


^{1}H and ^{13}C NMR spectra of *p*-**4g**

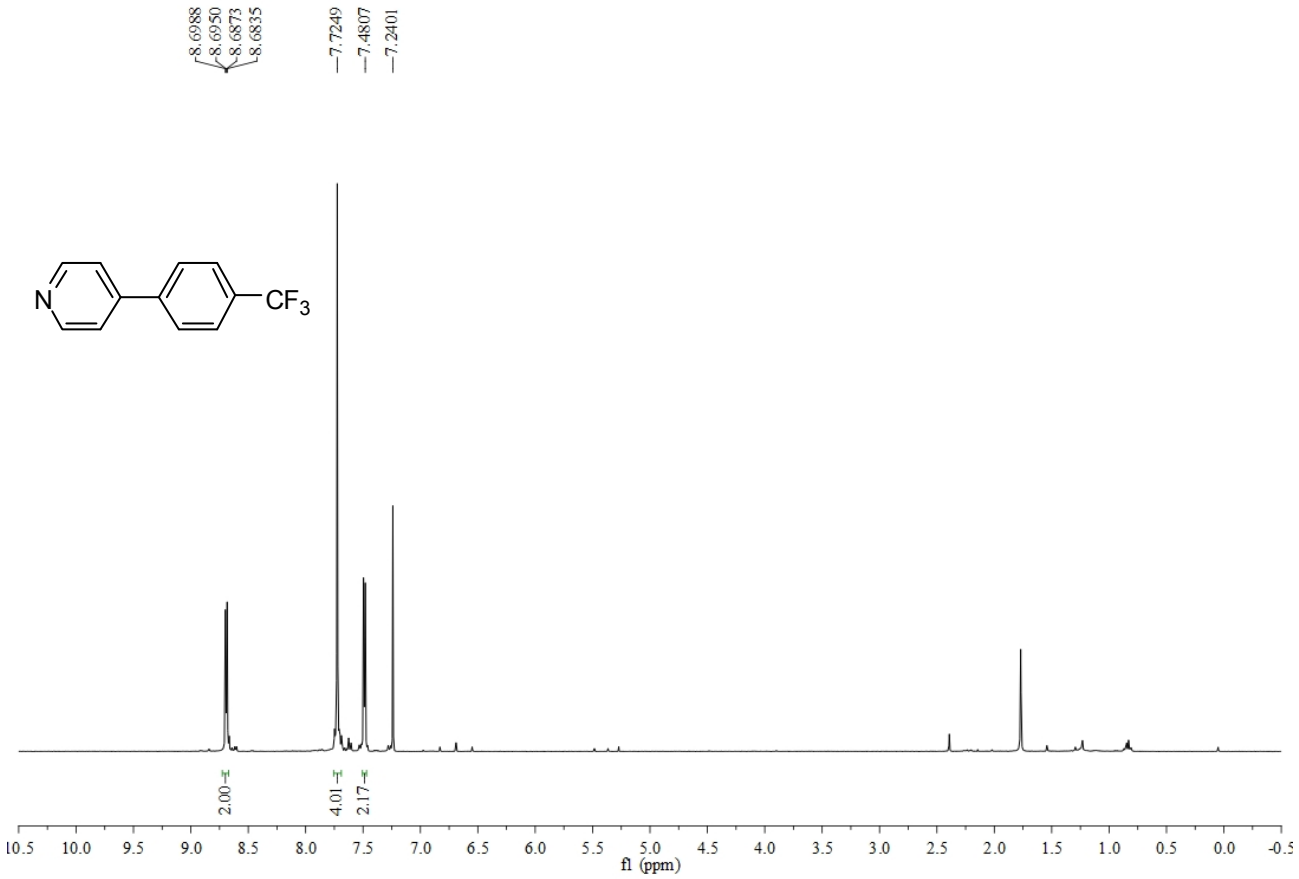


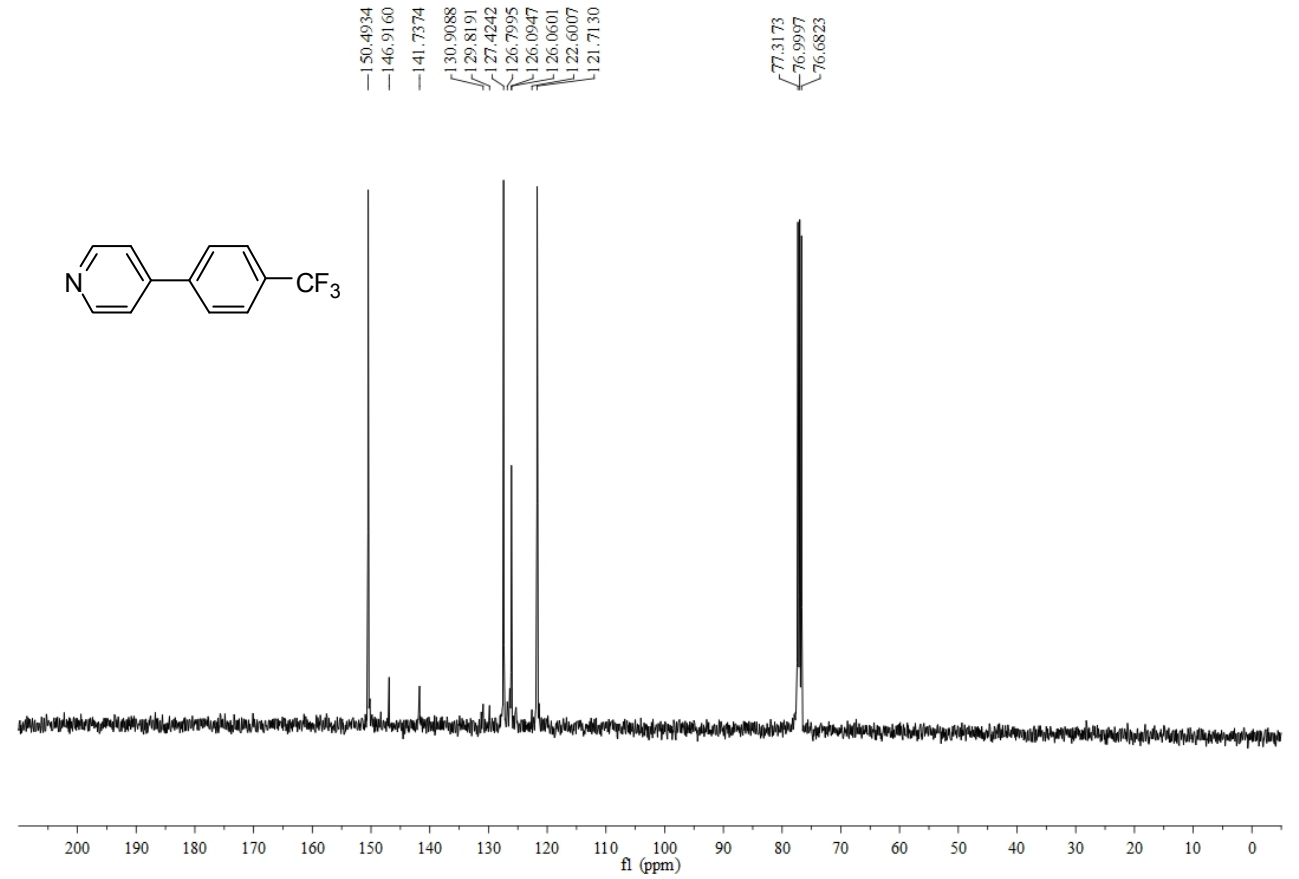


^{1}H and ^{13}C NMR spectra of *o*-**4h**

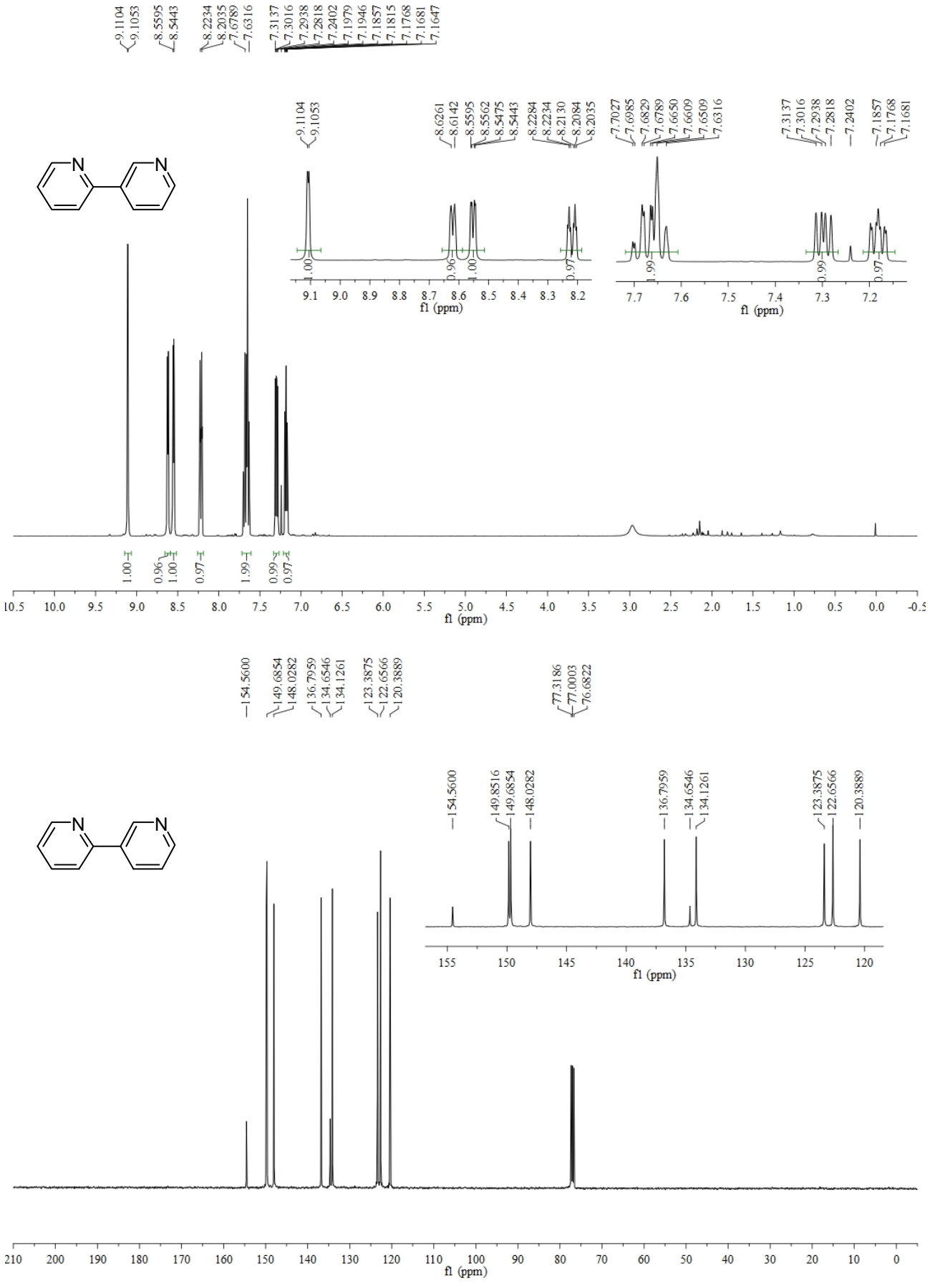


^{1}H and ^{13}C NMR spectra of *m*-**4h**

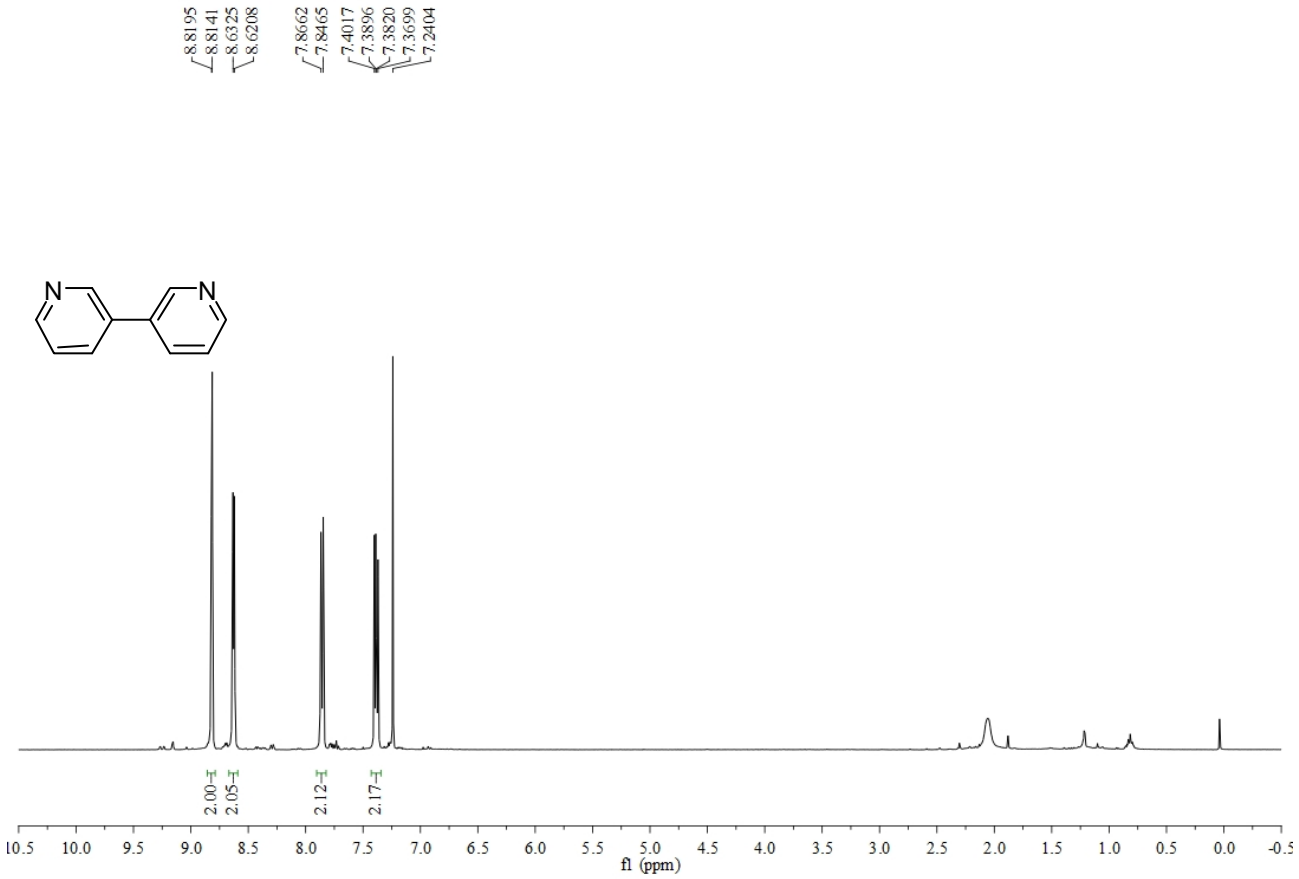


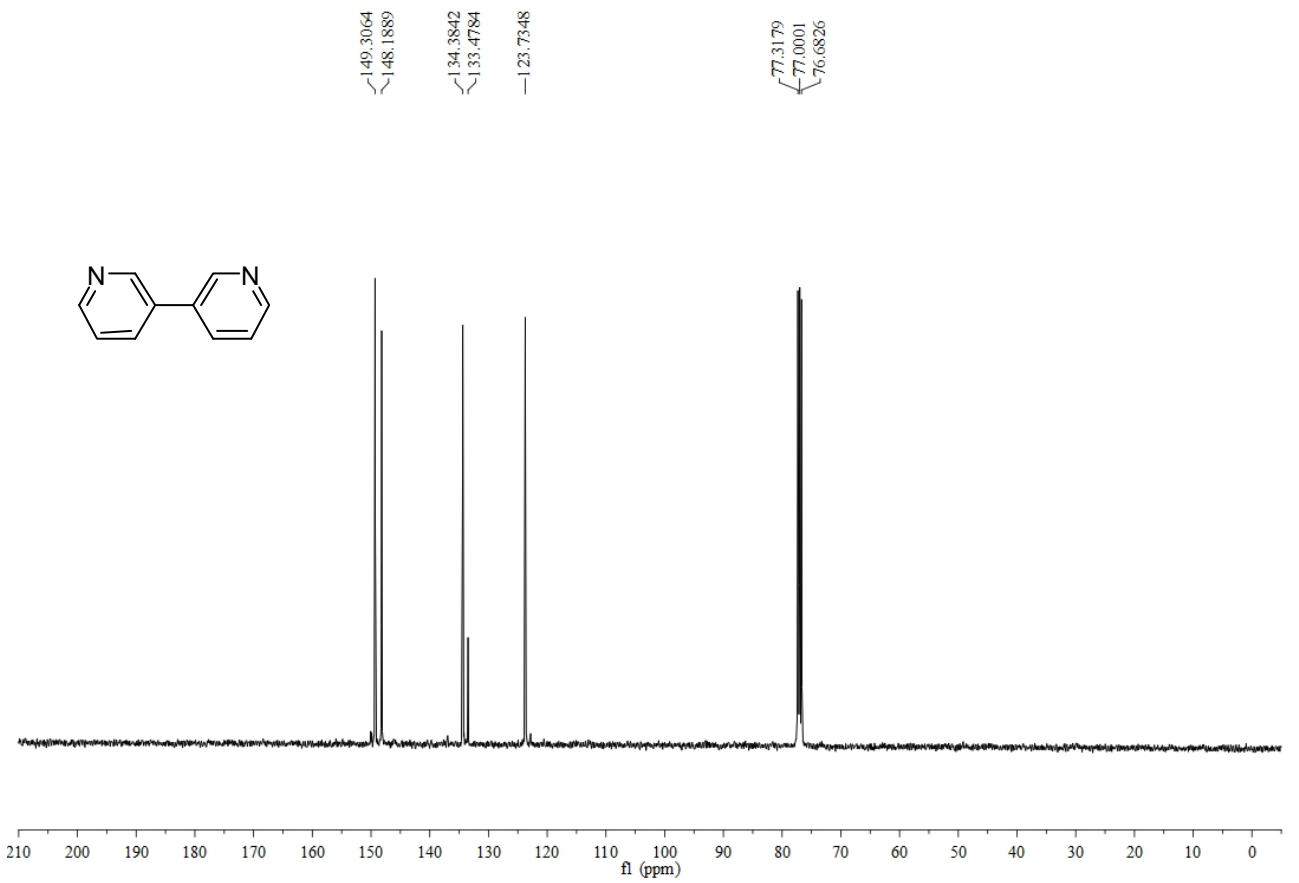


^{1}H and ^{13}C NMR spectra of *p*-**4h**

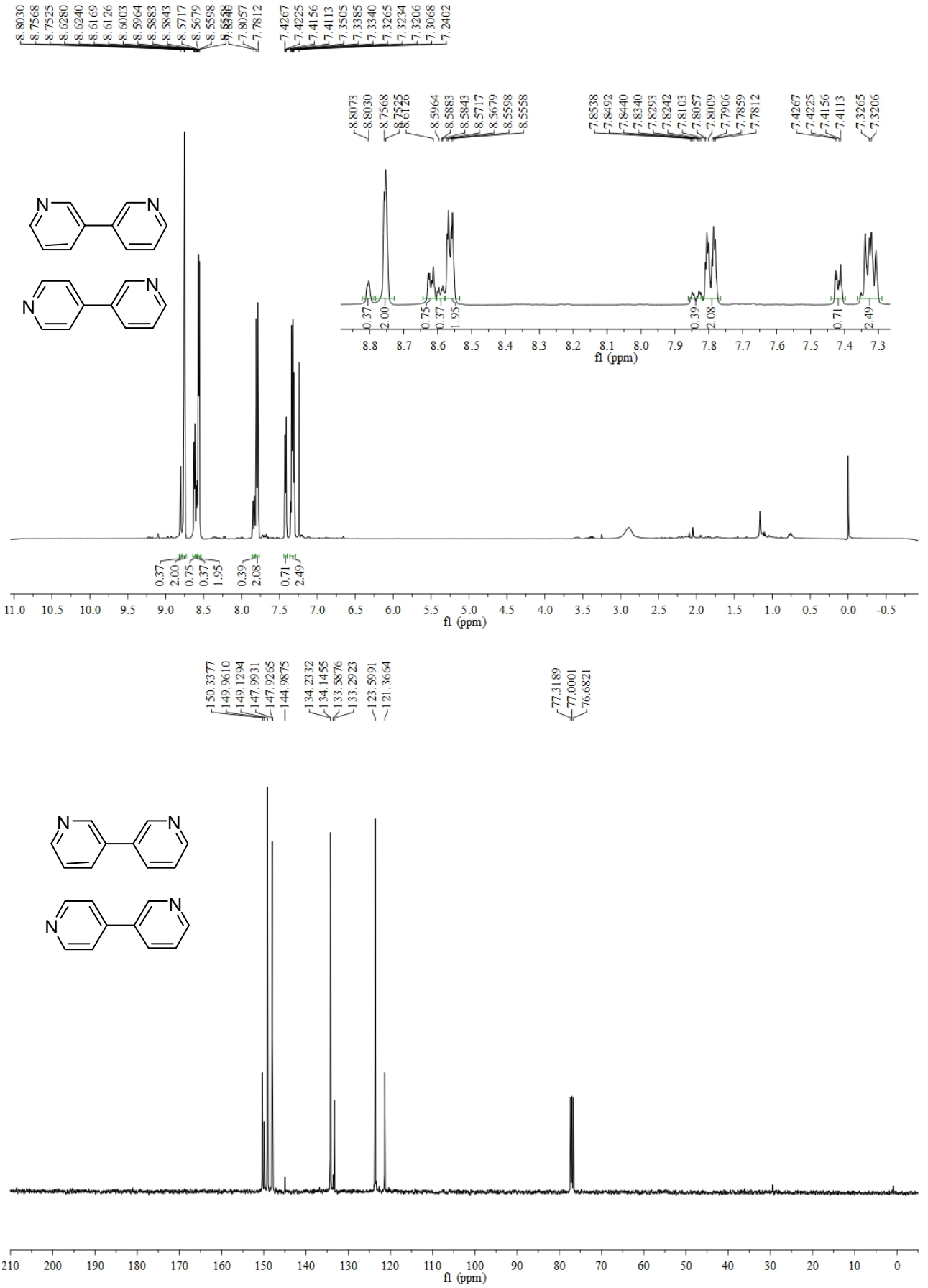


^{1}H and ^{13}C NMR spectra of *o*-**4i**

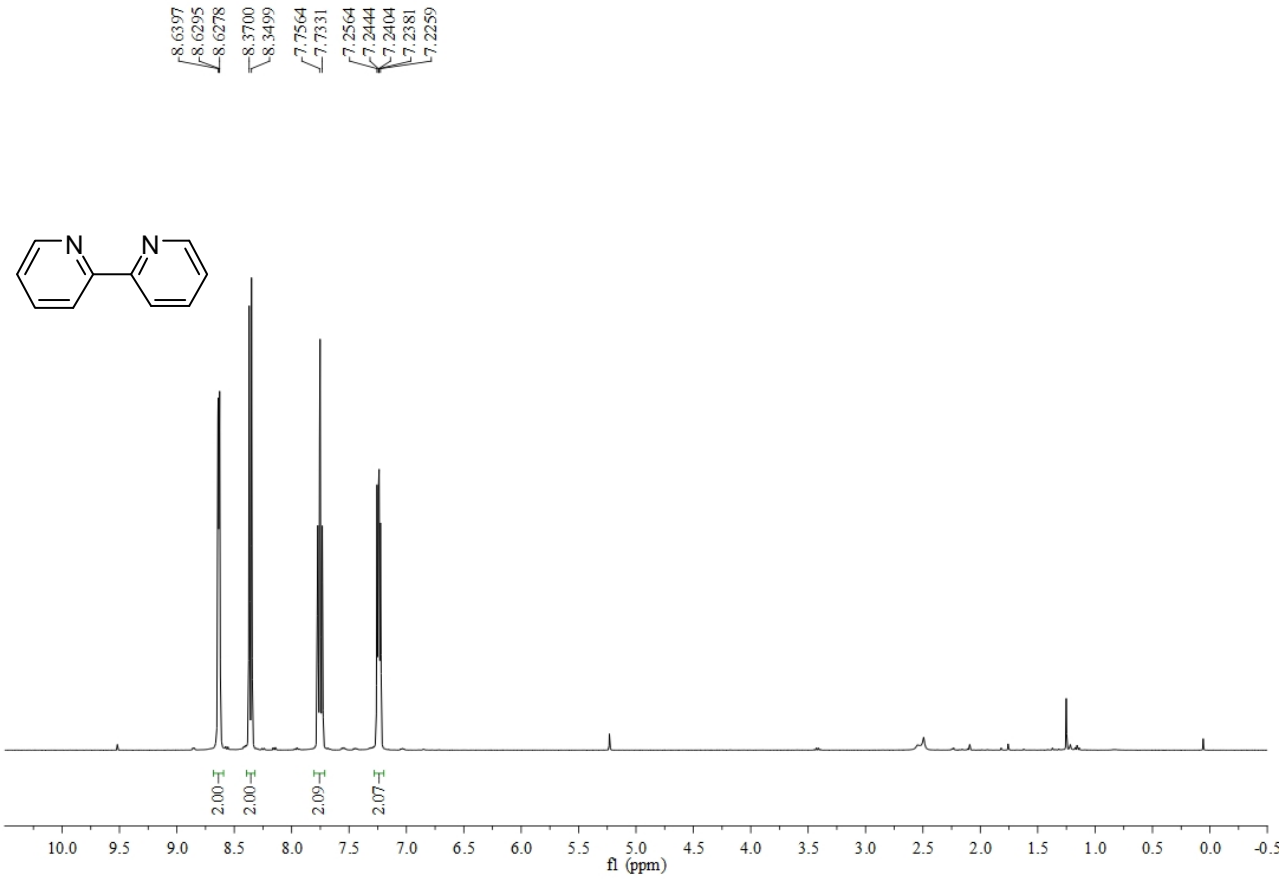


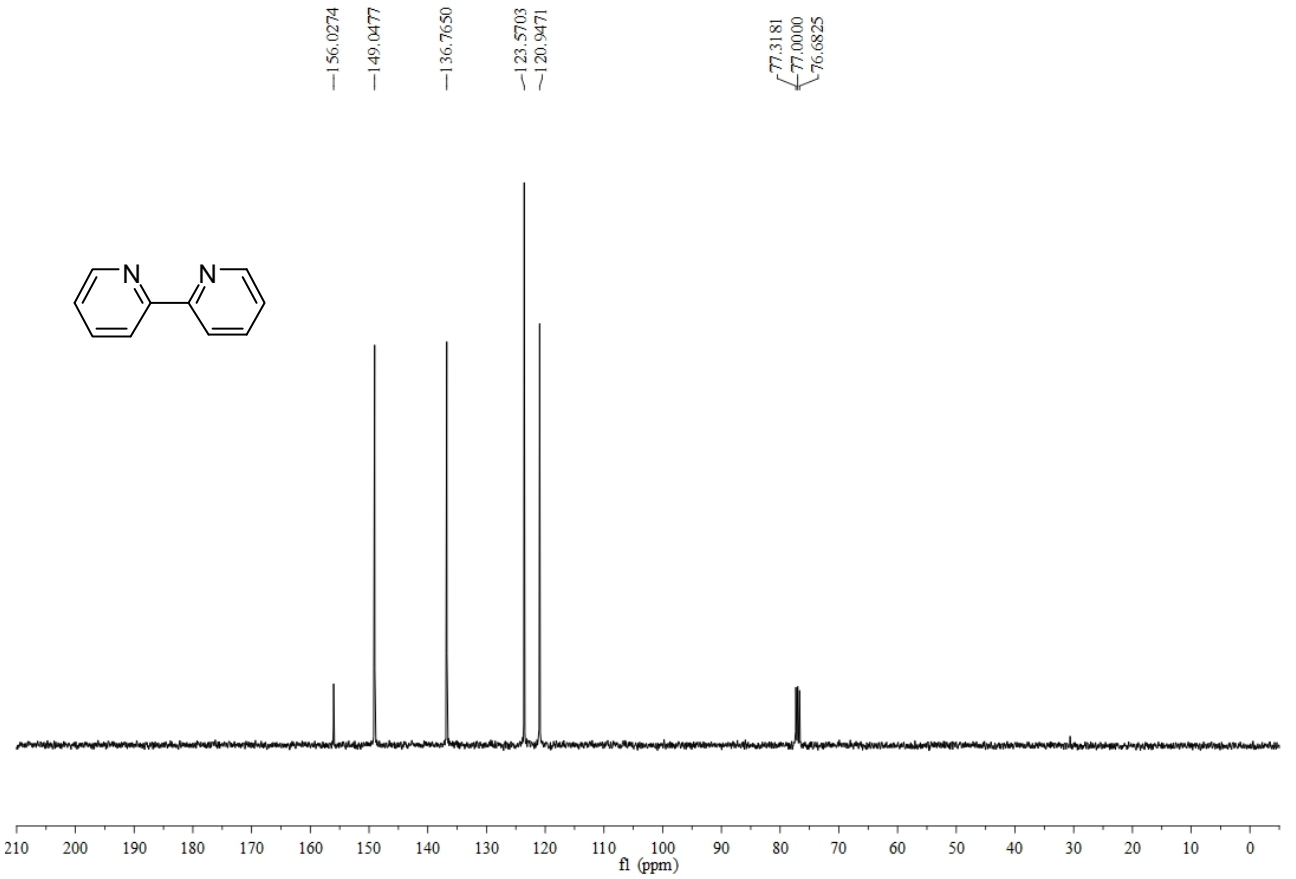


^{1}H and ^{13}C NMR spectra of *m*-**4i**

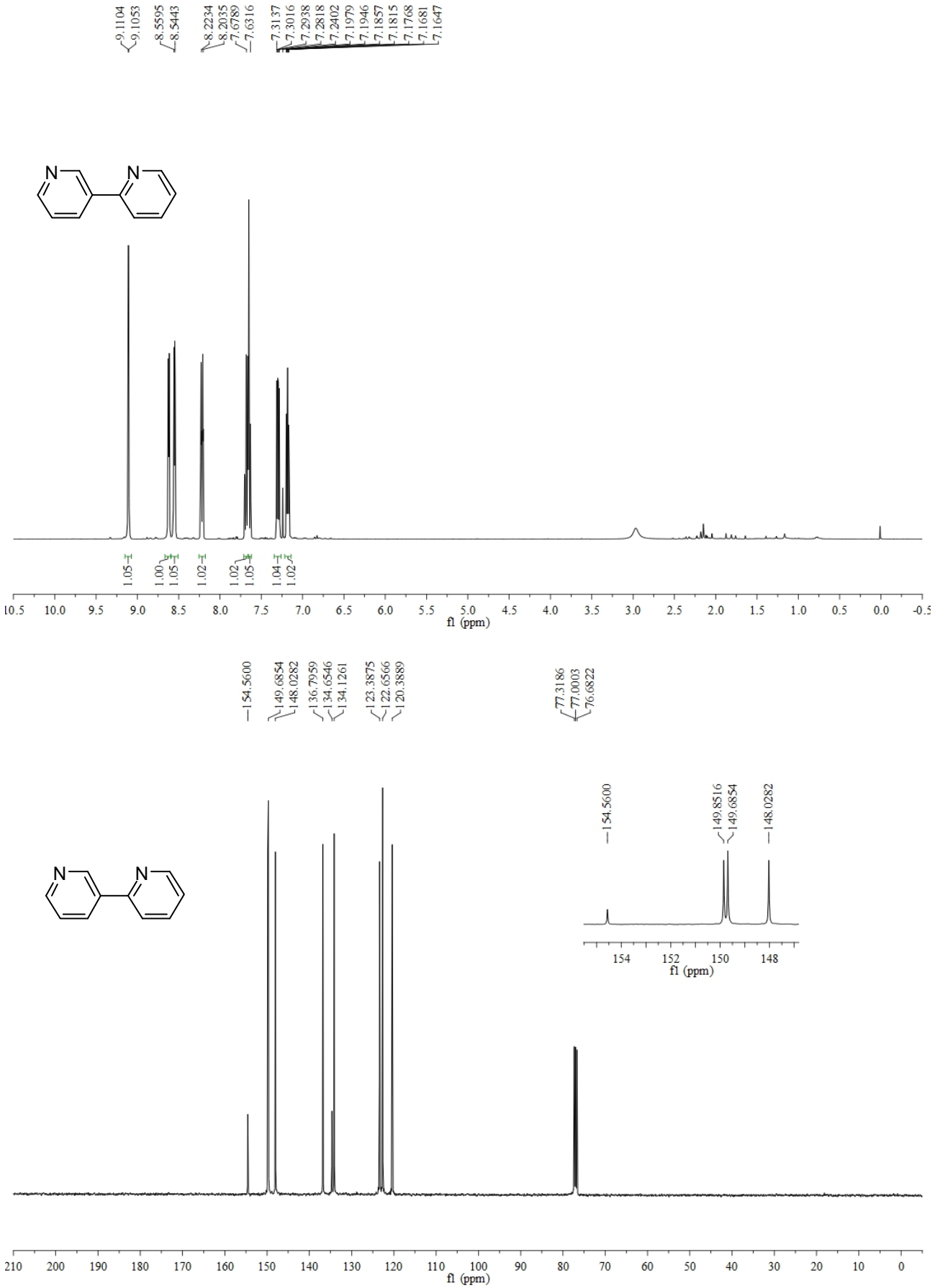


^{1}H and ^{13}C NMR spectra of *m,p*-**4i**

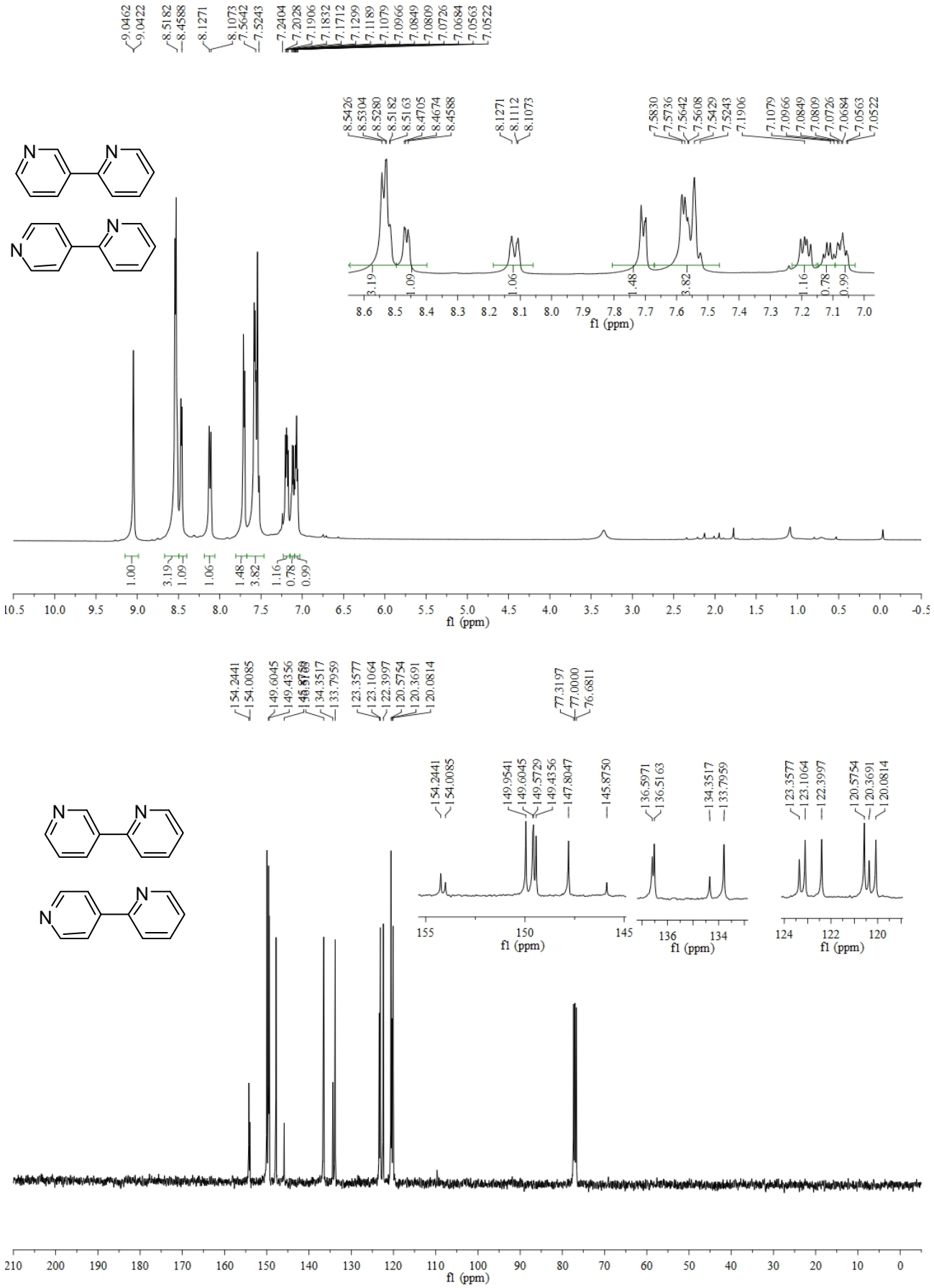




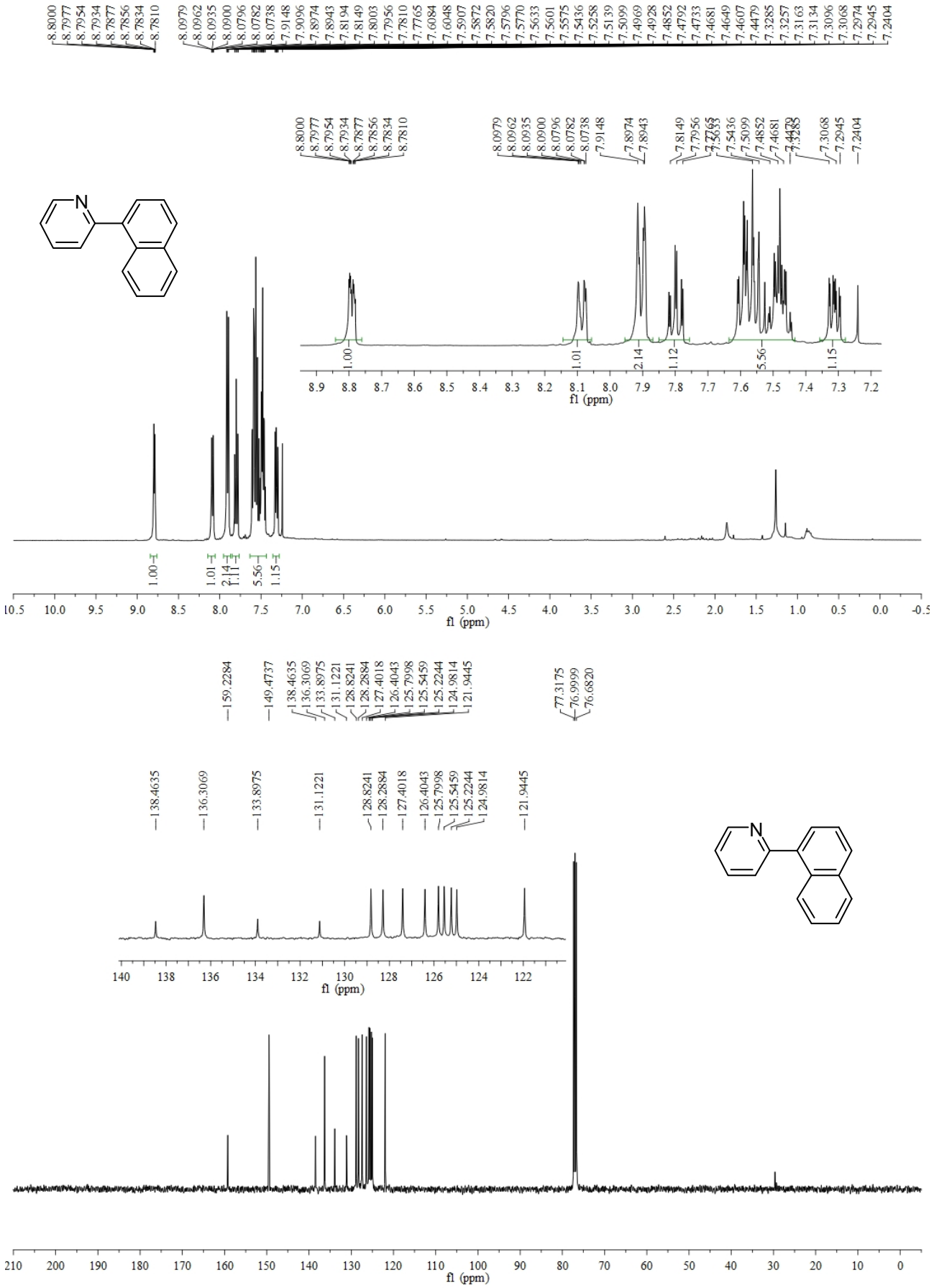
^{1}H and ^{13}C NMR spectra of *o*-**4j**



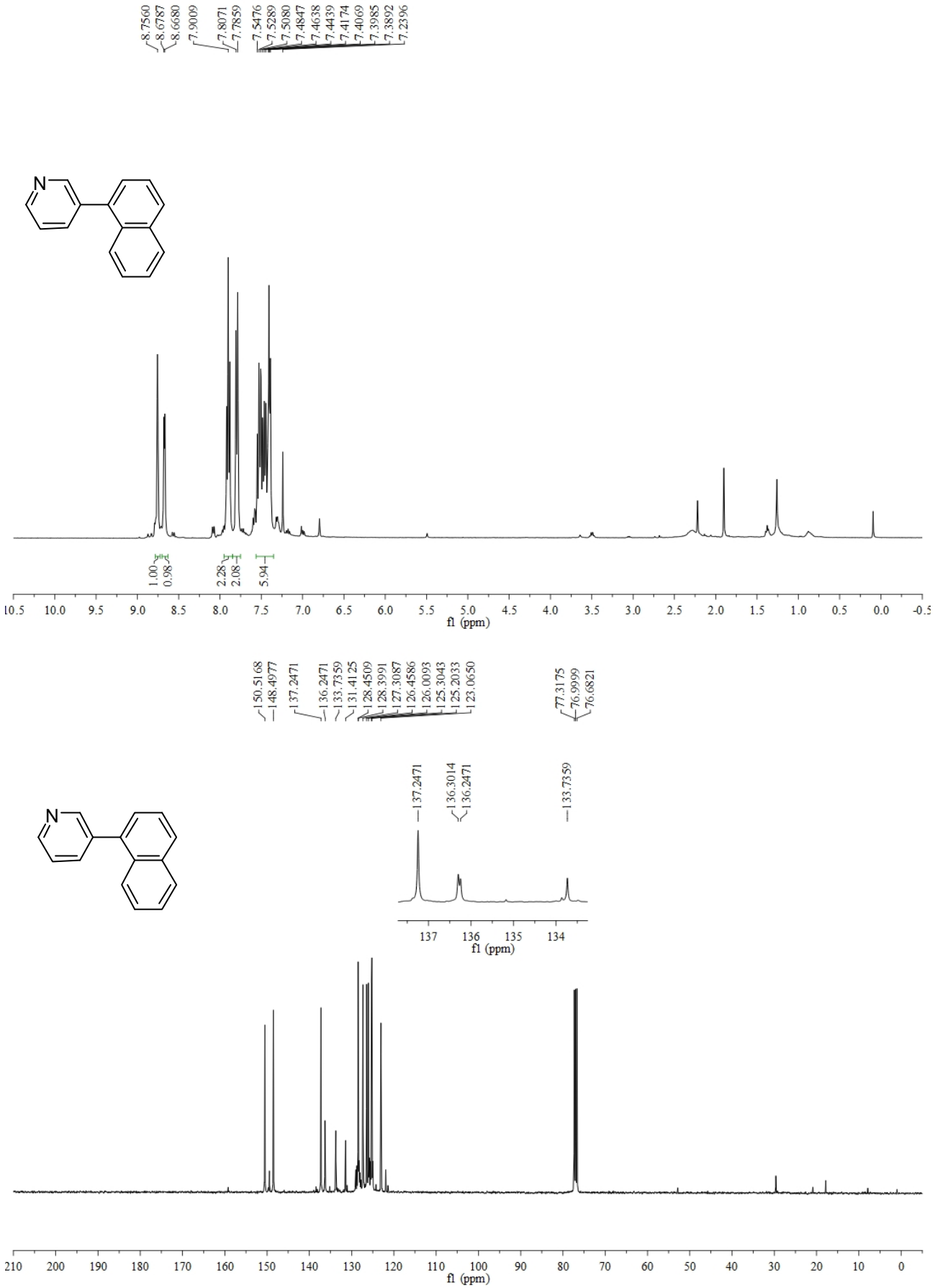
^{1}H and ^{13}C NMR spectra of *m*-**4j**



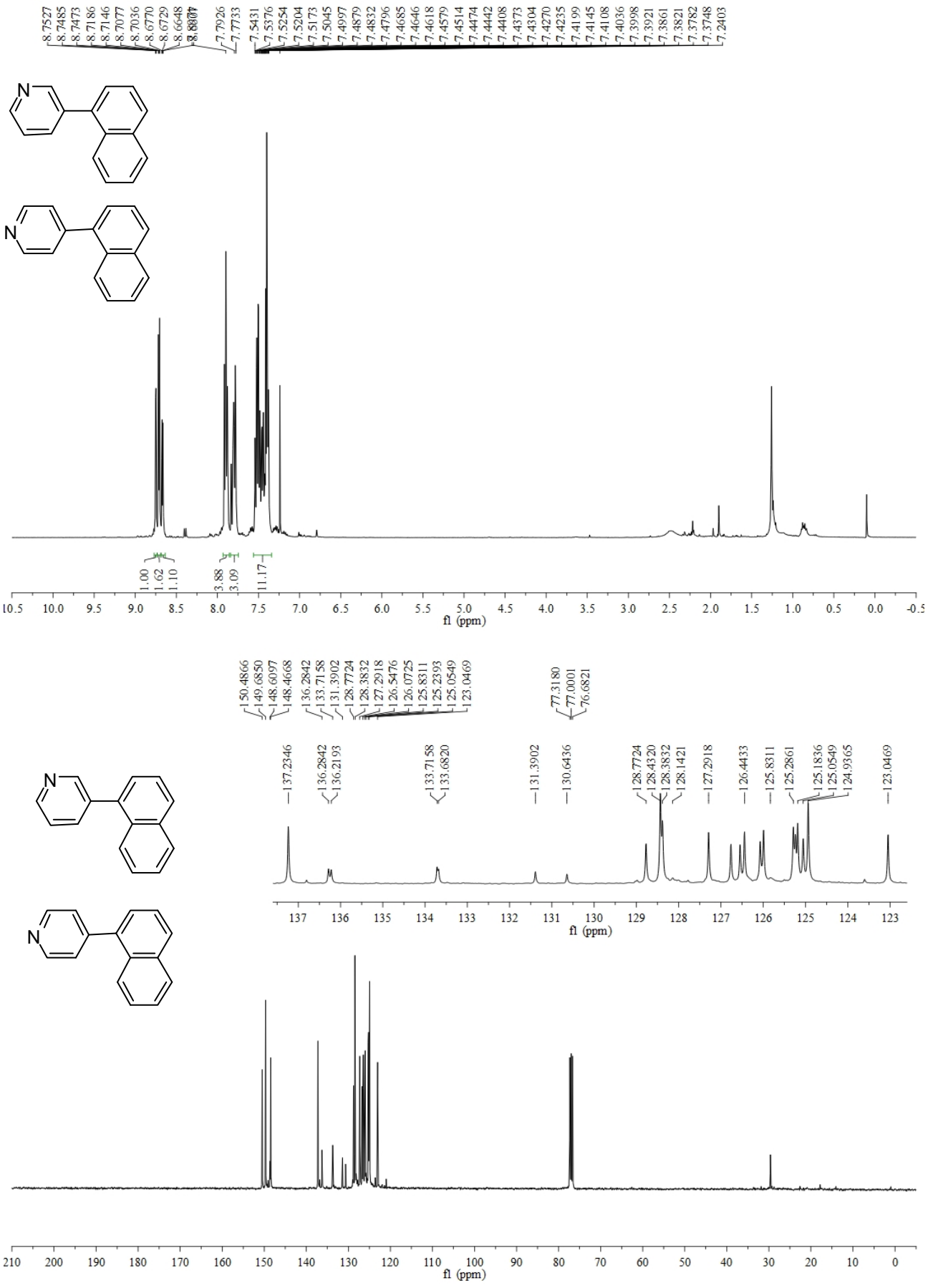
^{1}H and ^{13}C NMR spectra of *m,p*-**4j**



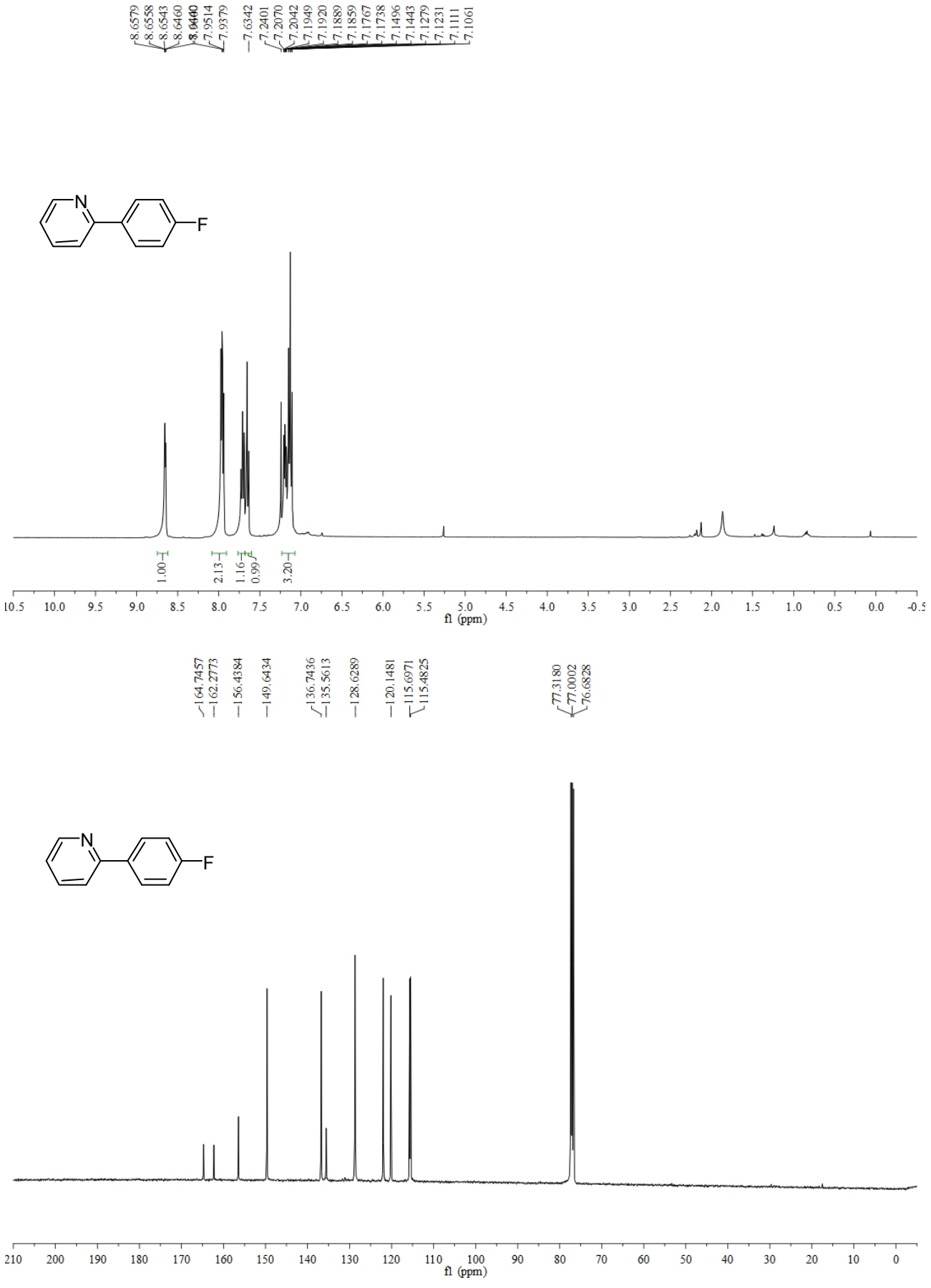
^{1}H and ^{13}C NMR spectra of *o*-**4k**



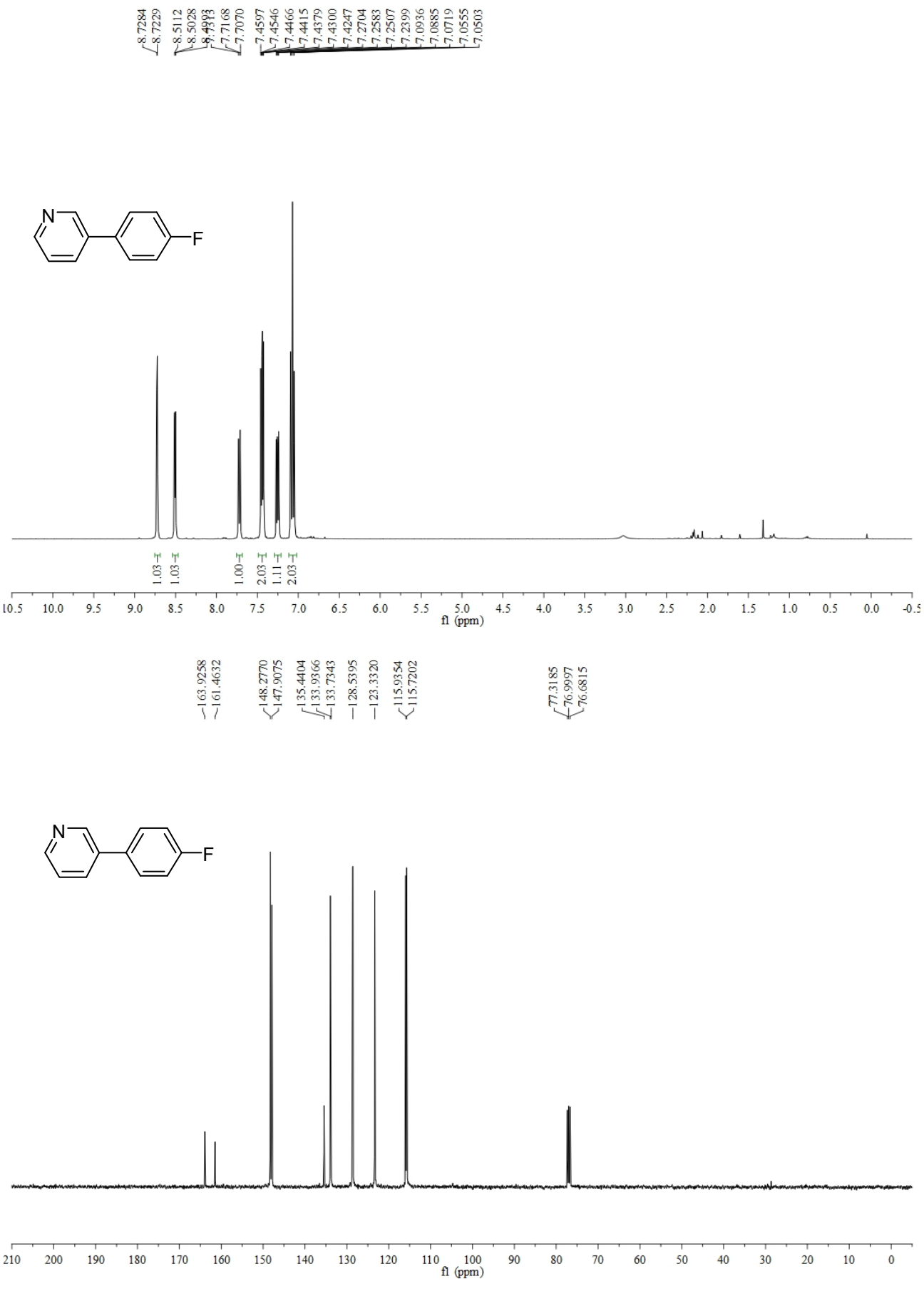
^{1}H and ^{13}C NMR spectra of *m*-**4k**



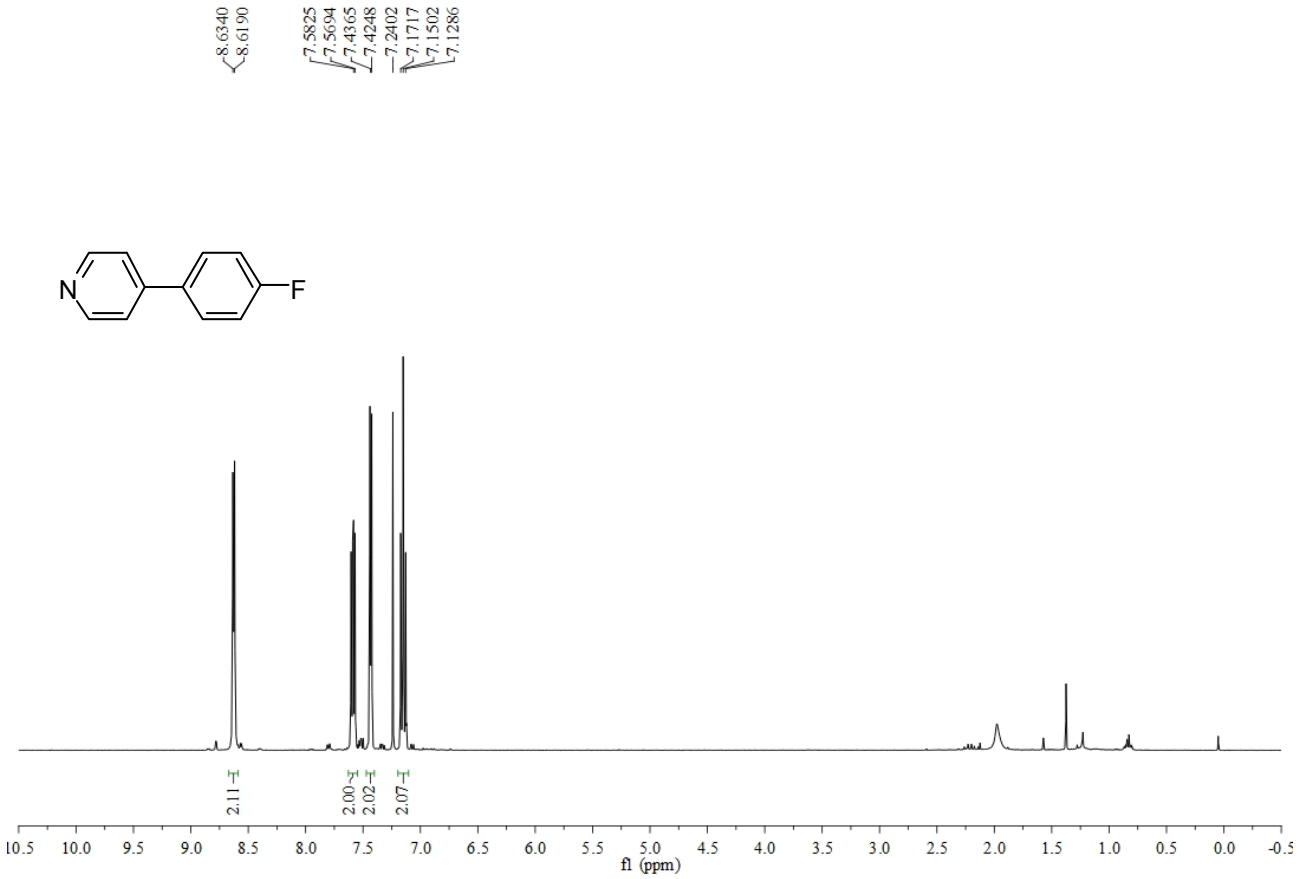
^{1}H and ^{13}C NMR spectra of *m,p*-**4k**

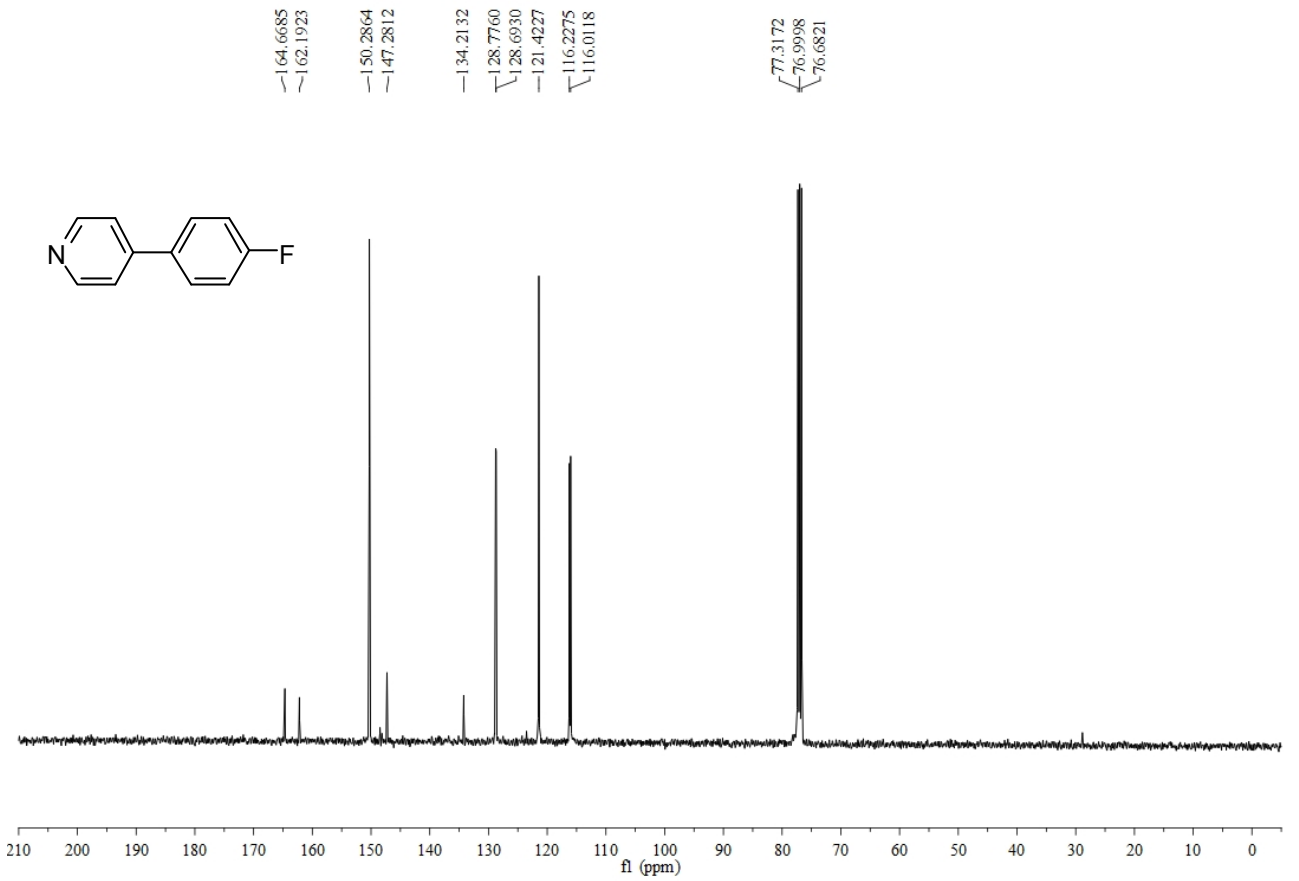


^{1}H and ^{13}C NMR spectra of *o*-**4l**



^{1}H and ^{13}C NMR spectra of *m*-**4l**





^{1}H and ^{13}C NMR spectra of *p*-**4l**