Supporting Information

Transition-Metal-Free Decarboxylative Arylation of 2-Picolinic Acids with Arenes under Air Conditions

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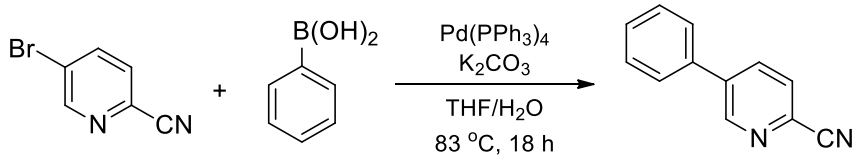
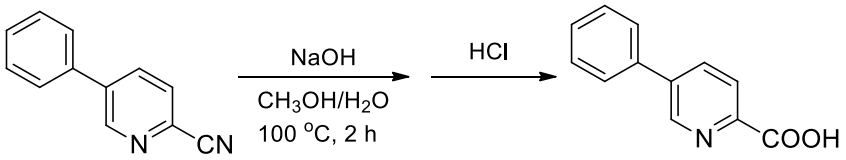
1. General Information

^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ was used as a solvent, while TMS was used as an internal standard. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 meth). GC-MS analysis was performed on an Agilent 7890A GC interfaced to an Agilent 5975C mass-selective detector (30 m × 0.25 mm capillary column, HP-5MS). IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. All reactions were carried out under air atmospheric pressure. The starting materials **1a**–**1h**, **1j**–**1s**, and **2a**–**2n** were purchased from Energy Chemicals Co. Ltd. The 5-phenylpicolinic acid (**1i**) was prepared according to the literature method.

2. Synthesis of 5-Phenylpicolinic Acid (1i)[1]



A reaction flask was charged with a mixture of 5-bromopicolinonitrile (1.83 g, 0.01 mol), phenylboronic acid (1.83 g, 0.015 mol), K_2CO_3 (2.76 g, 0.02 mol), $Pd(PPh_3)_4$ (0.35 g, 0.65 mmol), THF (24 mL), and water (10 mL). The mixture was stirred at 83 °C under nitrogen atmosphere for 18 h. Then the mixture was allowed to cool to room temperature and the product was extracted with dichloromethane (30 mL × 3). The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to give a crude product. The crude product was then purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 7:1) to afford 5-phenylpicolinonitrile as a white solid (1.35 g, 75%).



A reaction flask was charged with a mixture of 5-phenylpicolinonitrile (0.90 g, 5 mmol), methanol (10 mL), and 30% aqueous sodium hydroxide (10 mL). The reaction mixture was stirred at 100 °C for 2 h, and then was cooled to room temperature. After the resultant mixture was concentrated to a volume of about 10 mL, the mixture was neutralized by aqueous HCl (3 M). The formed precipitate was filtered off, washed with water, and dried to give product **1i** as a white solid (0.87 g, 87%).

3. Representative Procedure for the Decarboxylative Arylation

A reaction flask was charged with a mixture of 2-picolinic acid (**1a**, 36.9 mg, 0.3 mmol), K_2CO_3 (20.8 mg, 0.15 mmol), ^{t}BuOCl (102 uL, 0.9 mmol), and benzene (**2a**, 3 mL). The reaction mixture was stirred at 60 °C for 20 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: ethyl acetate : petroleum ether = 1 : 5) to afford 2-phenyl pyridine (**3aa**) as a colorless oil (40.1 mg, 86% yield).

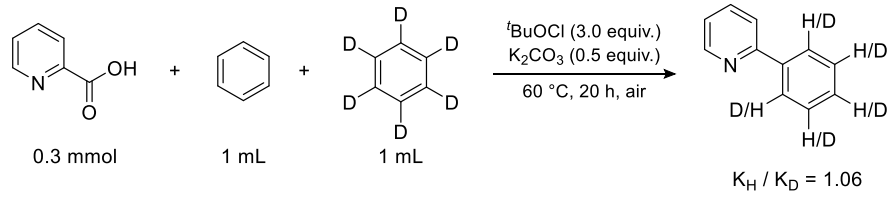
1.0 mmol scale reaction

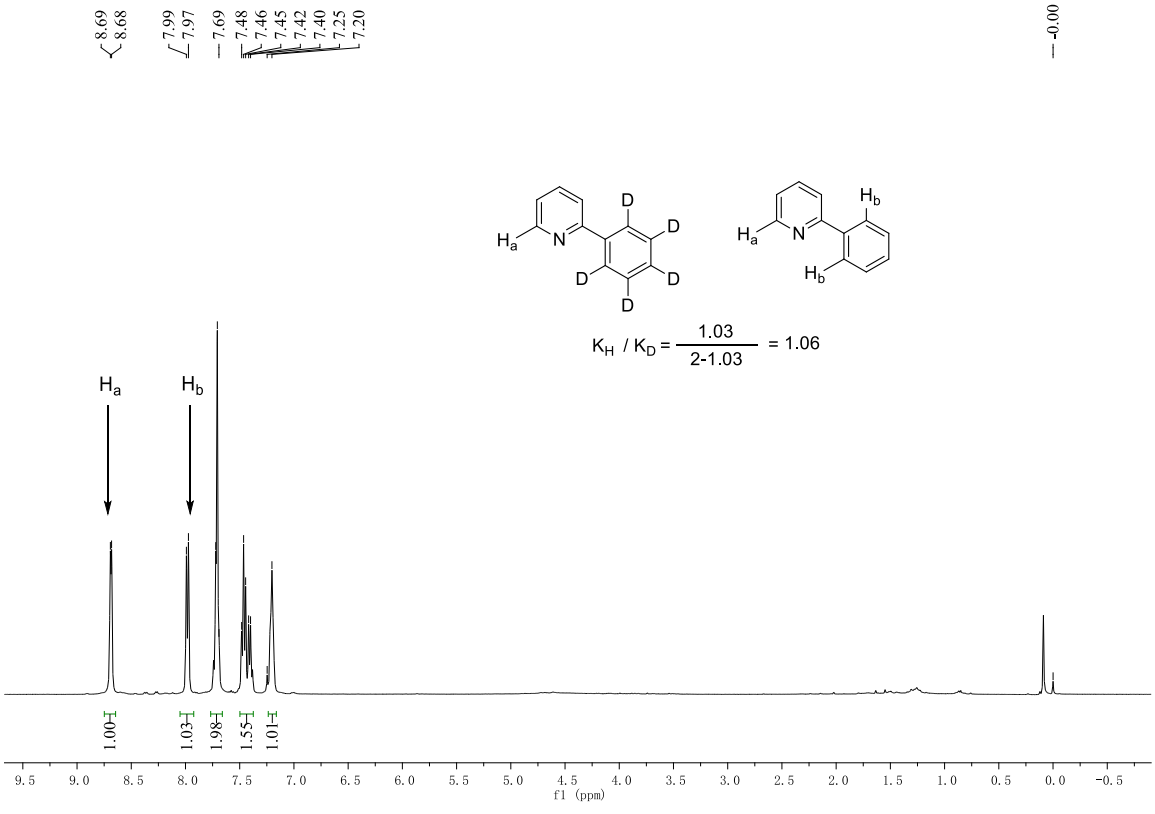
The 1.0 mmol scale reaction was also carried out. A reaction flask was charged with a mixture of 2-picolinic acid (**1a**, 123.1 mg, 1 mmol), K_2CO_3 (69.3 mg, 0.5 mmol), ^{t}BuOCl (340 uL, 3 mmol), and benzene (**2a**, 10 mL). The reaction mixture was stirred at 60 °C for 20 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: ethyl acetate : petroleum ether = 1 : 5) to afford 2-phenyl pyridine (**3aa**) as a colorless oil (132.1 mg, 85% yield).

4. Experiment of Kinetic Isotope Effect

A reaction flask was charged with a mixture of 2-picolinic acid (**1a**, 36.9 mg, 0.3 mmol), K_2CO_3 (20.8 mg, 0.15 mmol), ^{t}BuOCl (102 uL, 0.9 mmol), benzene (1 mL), and benzene-d_6 (1 mL). The reaction mixture was stirred at 60 °C for 20 h, and then was cooled to room temperature. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: ethyl acetate: petroleum ether =

1 : 5) to afford a mixture of products **3aa** and **3aa-*d*$_5$**. A 1.06 ratio of **3aa** to **3aa-*d*$_5$** was observed from ^{1}H NMR spectrum

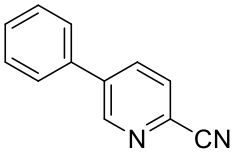




5. Characterization Data of Products

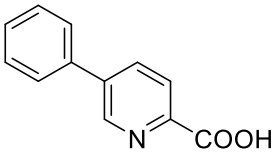
The spectroscopic data of all the products are presented. All the known compounds were in accordance with the data reported in the literatures.

5-phenylpicolinonitrile[1]



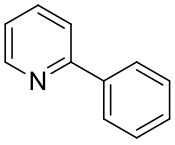
White solid (1.35 g, 75% yield), mp 90–91 °C, (lit.[2] mp 88–90 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.01 (dd, J = 8.0, 2.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.62–7.60 (m, 2H), 7.55–7.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 139.9, 135.9, 134.9, 132.2, 129.5, 128.5, 127.3, 117.4.

5-phenylpicolinic acid (1i)[3]



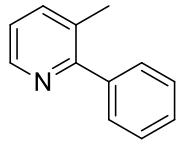
White solid (0.87 g, 87% yield), mp 157–158 °C, (lit.[3] mp 158–159 °C). ^{1}H NMR (400 MHz, DMSO): δ 9.01 (d, J = 2.0 Hz, 1H), 8.22 (dd, J = 8.0, 2.4 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.52–7.49 (m, 2H), 7.46–7.42 (m, 1H). ^{13}C NMR (100 MHz, DMSO): δ 166.5, 148.0, 147.6, 138.8, 136.5, 135.5, 129.7, 129.3, 127.7, 125.3.

2-phenyl pyridine (3aa)[4]



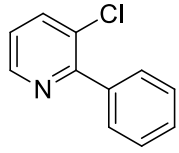
Colorless oil (40.1 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, J = 4.8, 1H), 8.03–7.96 (m, 2H), 7.77–7.69 (m, 2H), 7.51–7.45 (m, 2H), 7.45–7.38 (m, 1H), 7.25–7.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 149.7, 139.4, 136.8, 128.9, 128.7, 126.9, 122.1, 120.6.

3-methyl-2-phenylpyridine (3ba)[5]



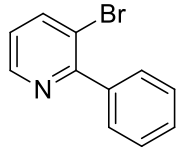
Colorless oil (32.5 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, J = 4.8 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.53–7.50 (m, 2H), 7.46–7.42 (m, 2H), 7.40–7.35 (m, 1H), 7.16 (dd, J = 7.6, 4.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 147.0, 140.6, 138.5, 130.8, 128.9, 128.1, 127.9, 122.1, 20.0.

3-chloro-2-phenylpyridine (3ca)[6]



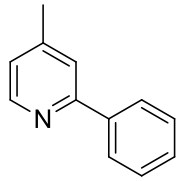
Yellow oil (25.6 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, J = 4.8 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.49–7.42 (m, 3H), 7.23–7.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 156.6, 147.6, 138.2, 138.1, 130.1, 129.3, 128.8, 128.0, 123.0.

3-bromo-2-phenylpyridine (3da)[7]



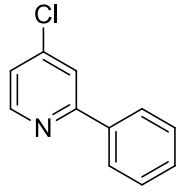
Yellow oil (37.1 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 4.8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.48–7.41 (m, 3H), 7.13 (dd, J = 8.0, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 148.1, 141.3, 139.6, 129.3, 128.8, 128.0, 123.3, 119.8.

4-methyl-2-phenylpyridine (3ea)[8]



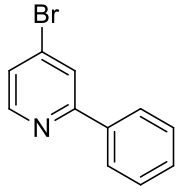
Light yellow solid (38.1 mg, 75% yield), mp 48–49 °C, (lit.[9] mp 47–48 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 4.8 Hz, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.52 (s, 1H), 7.47–7.43 (m, 2H), 7.40–7.37 (m, 1H), 7.04 (d, J = 5.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 149.4, 147.8, 139.5, 128.8, 128.8, 126.9, 123.1, 121.5, 21.2.

4-Chloro-2-phenylpyridine (3fa)[10]



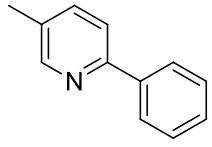
Light yellow oil (42.7 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 5.2 Hz, 1H), 7.98–7.95 (m, 2H), 7.73 (d, J = 1.6 Hz, 1H), 7.48–7.43 (m, 3H), 7.24 (dd, J = 5.2, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 150.5, 144.8, 138.1, 129.6, 128.9, 127.0, 122.3, 120.9.

4-bromo-2-phenylpyridine (3ga)[11]



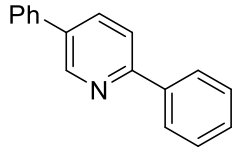
Colorless oil (43.5 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 5.2 Hz, 1H), 7.97–7.94 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 1.6 Hz, 1H), 7.49–7.41 (m, 3H), 7.41 (dd, J = 5.6, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 150.4, 138.1, 133.5, 129.6, 128.9, 127.0, 125.3, 123.9.

5-methyl-2-phenylpyridine (3ha)[12]



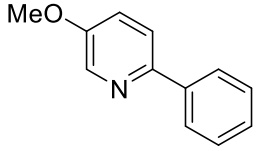
Light yellow solid (35.0 mg, 69% yield), mp 54–55 °C, (lit.[13] mp 52–54 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1 H), 7.96 (d, J = 8.0 Hz, 2 H), 7.60 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.47–7.43 (m, 2H), 7.39–7.35 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 150.1, 139.4, 137.3, 131.6, 128.7, 128.6, 126.7, 120.0, 18.2.

2,5-diphenylpyridine (3ia)[14]



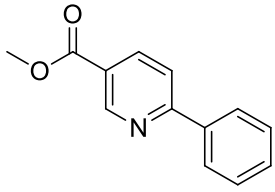
Whitish solid (47.2 mg, 68% yield), mp 167–169 °C, (lit.[14] mp 165–167 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (d, J = 1.6 Hz, 1H), 8.04 (d, J = 7.8 Hz, 2H), 7.93 (dd, J = 8.0, 2.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.62 (d, J =8.0 Hz, 2H), 7.50–7.43 (m, 4H), 7.42–7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 148.1, 139.0, 137.7, 135.1, 134.9, 129.1, 129.0, 128.8, 128.1, 127.0, 126.9, 120.4.

5-methoxy-2-phenylpyridine (3ja)[12]



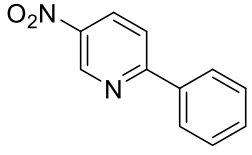
Whitish solid (35.0 mg, 63% yield), mp 53–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 2.8 Hz, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.8 Hz, 1H), 7.46–7.42 (m, 2H), 7.37–7.34 (m, 1H), 7.25 (dd, J = 8.8, 2.8 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 150.1, 139.1, 137.1, 128.7, 128.2, 126.4, 121.3, 120.8, 55.7.

Methyl 6-phenylnicotinate (3ka)[12]



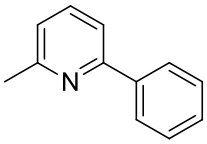
White solid (47.3 mg, 74% yield), mp 112–114 °C, (lit.[15] mp 111–1113 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (d, J = 2.2 Hz, 1H), 8.33 (dd, J = 8.4, 2.0 Hz, 1H), 8.06–8.03 (m, 2H), 7.80 (dd, J = 8.4, 0.8 Hz, 1H), 7.52–7.45 (m, 3H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 160.9, 151.0, 138.3, 137.9, 130.0, 128.9, 127.4, 124.2, 119.9, 53.4.

2-methyl-6-phenylpyridine (3la)[12]



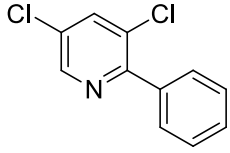
White solid (27.6 mg, 46% yield), mp 119–120 °C, (lit.[16] mp 119–121 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (d, J = 2.0 Hz, 1H), 8.51 (dd, J = 8.8, 2.8 Hz, 1H), 8.10–8.07 (m, 2H), 7.90 (dd, J = 4.8, 0.4 Hz, 1H), 7.54–7.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 145.3, 142.9, 137.1, 130.9, 129.1, 127.7, 120.1.

2-methyl-6-phenylpyridine (3ma)[11]



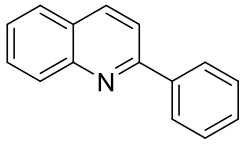
Yellow oil (36.1 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.0 Hz, 2 H), 7.62–7.58 (m, 1H), 7.50–7.43 (m, 3H), 7.38–7.35 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 157.0, 139.8, 136.9, 128.7, 128.7, 127.0, 121.6, 117.6, 24.8.

3,5-dichloro-2-phenylpyridine (3na)[7]



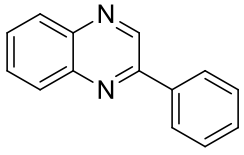
Light yellow solid (30.9 mg, 46%), mp 52–53 °C, (lit.[7] mp 50–51 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56–8.55 (d, J = 2.4 Hz, 1H), 7.83 (d, J = 2.0 Hz, 1H), 7.72–7.69 (m, 2H), 7.50–7.43 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 156.5, 137.5, 137.2, 130.5, 130.2, 129.3, 129.2, 128.2.

2-phenylquinoline (3oa)[12]



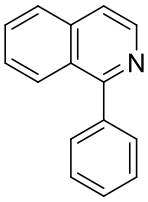
Yellow solid (53.6 mg, 87% yield), mp 82–83 °C, (lit.[17] mp 81–82 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.14 (m, 4H), 7.84 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.71–7.69 (m, 1H), 7.43–7.53 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 148.3, 139.7, 136.8, 129.8, 129.7, 129.4, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0.

2-phenylquinoxaline (3pa)[12]



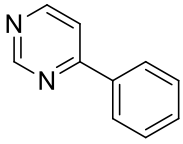
Light yellow solid (40.2 mg, 65% yield), mp 78–80 °C, (lit.[16] mp 78–79 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 8.20–8.10 (m, 4H), 7.79–7.71(m, 2H), 7.58–7.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 143.4, 142.3, 141.6, 136.8, 130.3, 130.2, 129.6, 129.6, 129.2, 129.1, 127.6.

1-Phenylisoquinoline (3qa)[12]



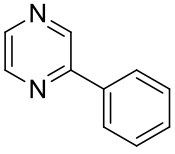
Light yellow solid (53.0 mg, 86% yield), mp 97–98 °C, (lit.[18] mp 95–96 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J = 6.0 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.71–7.64 (m, 4H), 7.55–7.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 142.1, 139.5, 136.9, 130.0, 129.9, 128.6, 128.4, 127.6, 127.2, 127.0, 126.7, 120.0.

4-phenylpyrimidine (3ra)[19]



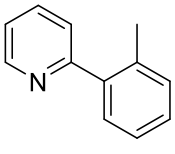
Yellow solid (29.1 mg, 62% yield), mp 61–62 °C, (lit.[20] mp 61–63 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.77 (d, J = 5.2 Hz, 1H), 8.10 (dd, J = 6.4, 3.0 Hz, 2H), 7.72 (dd, J = 5.2, 1.2 Hz, 1H), 7.54–7.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 157.5, 136.5, 131.1, 129.1, 127.2, 117.0.

2-phenylquinoxaline (3sa)[12]



Yellow solid (22.0 mg, 47% yield), mp 71–72 °C, (lit.[16] mp 72–73 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, J = 1.6 Hz, 1H), 8.64 (dd, J = 2.4, 1.6 Hz, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.03−8.01 (m, 2H), 7.54−7.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 144.2, 142.9, 142.3, 136.4, 129.9, 129.1, 127.0.

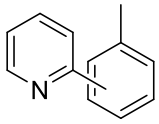
2-(*o*-tolyl)pyridine (*o*-3ab)[4]



Yellow oil (19.3 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 4.4 Hz, 1H), 7.75–7.71 (m, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.30–7.22 (m, 4H), 2.36 (s, 3H). ^{13}C NMR

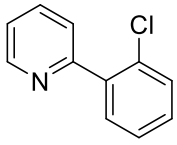
(100 MHz, $CDCl_3$): δ 160.0, 149.2, 140.4, 136.2, 135.8, 130.7, 129.6, 128.3, 125.9, 124.1, 121.6, 20.3.

2-(*m*-tolyl)pyridine(*m*-3ab)[11] and 2-(*p*-tolyl)pyridine (*p*-3ab)[4]



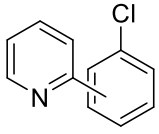
Yellow oil (22.8 mg, 45% yield), ***m*-3ab** : ***p*-3ab** = 1.2 : 1.0 (detected by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69–8.66 (m, 1H), 7.90–7.70 (m, 4H), 7.38–7.19 (m, 3H), 2.44–2.40 (m, 3H).

2-(2-chlorophenyl) pyridine (*o*-3ac)[21]



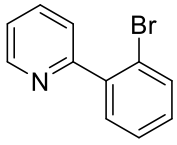
Yellow oil (9.1 mg, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 4.8 Hz, 1H), 7.78–7.74 (m, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.39–7.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 149.5, 139.2, 135.8, 132.2, 131.5, 130.1, 139.6, 127.0, 129, 122.4.

2-(3-chlorophenyl)pyridine (*m*-3ac)[22] and 2-(4-chlorophenyl) pyridine (*p*-3ac)[21]



Yellow oil (35.3 mg, 62% yield), ***m*-3ac** : ***p*-3ac** = 1.2 : 1.0 (detected by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69–8.66 (m, 1H), 8.01–7.84 (m, 2H), 7.76–7.66 (m, 2H), 7.44–7.37 (m, 2H), 7.25–7.20 (m, 1H).

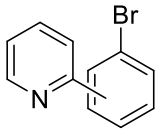
2-(2-bromophenyl)pyridine (*o*-3ad)[23]



Yellow oil (16.2 mg, 23% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 4.4 Hz, 1H), 7.76 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H), 7.67 (dd, J = 8.0, 1.2 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 7.32–7.23 (m, 2H). ^{13}C

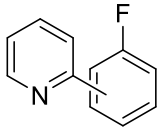
NMR (100 MHz, $CDCl_3$): δ 158.4, 149.4, 141.2, 135.9, 132.3, 131.4, 129.7, 127.6, 124.8, 122.5, 121.8.

2-(3-bromophenyl)pyridine (*m*-3ad)[11] **and 2-(4-bromophenyl) pyridine (*p*-3ad)**[22]



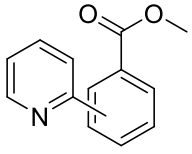
Yellow oil (26.7 mg, 38% yield). ***m*-3ac** : ***p*-3ac** = 1.1 : 1.0 (detected by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71–8.67 (m, 1H), 8.18–7.86 (m, 2H), 7.75–7.68 (m, 2H), 7.61–7.59 (m, 1H), 7.53–7.32 (m, 1H), 7.27–7.23 (m, 1H).

2-(2-fluorophenyl)pyridine (*o*-3ae),[24] **2-(3-fluorophenyl)pyridine (*m*-3ae),**[22] **and 2-(4-fluorophenyl)pyridine (*p*-3ae)**[14]



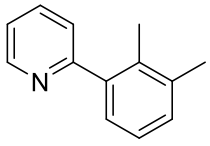
Colorless oil (42.6 mg, 78% yield), ***o*-3ae** : ***m*-3ae** : ***p*-3ae** = 1.4 : 1.0 : 1.5 (detected by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73–8.66 (m, 1H), 7.99–7.95 (m, 1 H), 7.80–7.34 (m, 3H), 7.28–7.07 (m, 3H).

methyl 2-(pyridin-2-yl)benzoate (*o*-3af),[25] **methyl 3-(pyridin-2-yl)benzoate (*m*-3af),**[26] **and methyl 4-(pyridin-2-yl)benzoate (*p*-3af)**[27]



Light yellow oil (20.5 mg, 30% yield), ***o*-3af** : ***m*-3af** : ***p*-3af** = 1.9 : 3.4 : 1.0 (detected by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73–8.72 (m, 1H), 8,64–8.06 (m, 3H), 7.80–7.27 (m, 4H), 3.96–3.95 (m, 3H).

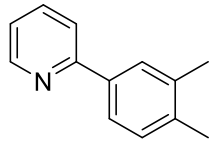
2-(2,3-dimethylphenyl)pyridine (*o*-3ag)



Yellow oil (13.2 mg, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 4.8 Hz, 1H), 7.75–7.71 (m, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.28–7.15 (m, 4H), 2.36 (s, 3H), 2.32 (s, 3H).

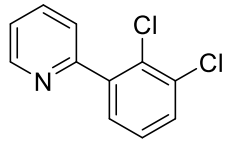
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 149.1, 140.9, 137.5, 136.1, 134.2, 129.8, 127.4, 125.4, 124.4, 121.5, 20.5, 16.7. IR (KBr): ν 3058, 2922, 1583, 1463, 1385, 800, 772, 750, 723 cm^{-1}. HRMS (ESI) calcd for $[C_{13}H_{14}N, M+H]^+$: 184.1121, found: 184.1126.

2-(3,4-dimethylphenyl)pyridine (*m*-3ag)[27]



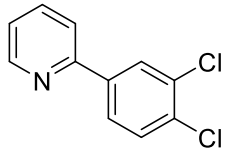
Yellow oil (22.6 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 4.4 Hz, 1H), 7.80 (s, 1H), 7.73–7.68 (m, 3H), 7.24–7.17 (m, 2H), 2.34 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 149.5, 137.6, 137.0, 136.9, 136.6, 130.0, 128.1, 124.3, 121.7, 120.3, 19.9, 19.6.

2-(2,3-dichlorophenyl)pyridine (*o*-3ah)



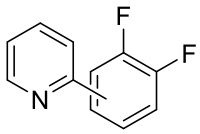
Yellow oil (16.8 mg, 25% yield). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 4.8 Hz, 1H), 7.81–7.77 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.35–7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 141.3, 136.2, 133.7, 130.8, 130.5, 129.7, 127.4, 124.9, 122.8. IR (KBr): ν 3063, 2924, 2853, 1592, 1476, 1049, 799, 773, 748, 739 cm^{-1}. HRMS (ESI) calcd for $[C_{11}H_8NCl_2, M+H]^+$: 224.0034, found: 224.0034.

2-(3,4-dichlorophenyl)pyridine (*m*-3ah)[27]



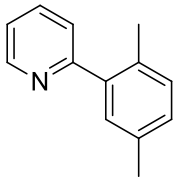
Yellow oil (21.5 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 5.2 Hz, 1H), 8.13 (d, J = 1.6 Hz, 1H), 7.82 (dd, J = 8.4, 1.6 Hz, 1H), 7.80–7.74 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.4, 1H), 7.28–7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 149.9, 139.3, 137.0, 133.1, 133.1, 130.7, 128.8, 125.9, 122.9, 120.4.

2-(2,3-difluorophenyl)pyridine (*o*-3ai) and 2-(3,4-difluorophenyl)pyridine (*m*-3ai)[27]



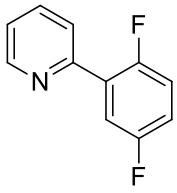
Light yellow oil (35.0 mg, 61% yield), ***o*-3ai**: ***m*-3ai** = 3.1:1 (detected by ^{1}HNMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73–8.66 (m, 1H), 7.88–7.64 (m, 4H), 7.29–7.17 (m, 7.8 Hz, 2H).

2-(2,5-Dimethylphenyl)pyridine (3aj)[28]



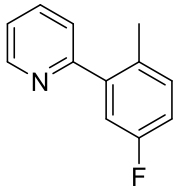
Colorless oil (29.1 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 4.4 Hz, 1H), 7.72 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.23–7.21 (m, 2H), 7.16 (d, J = 7.6 Hz, 1H), 7.12–7.10 (m, 2H), 2.35(s, 3H), 2.32(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 149.2, 140.2, 136.0, 135.3, 132.5, 130.6, 130.3, 129.0, 124.1, 121.5, 20.9, 19.8.

2-(2, 5-Difluorophenyl)pyridine (3ak)[29]



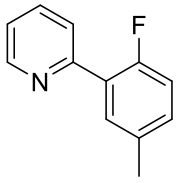
Pale solid (38.4 mg, 67% yield), mp 33–34 °C, (lit.[31] mp 32 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 4.0 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.78–7.73 (m, 2 H), 7.29–7.25 (m, 1H), 7.14–7.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0 (dd, $^{1}J_{C\text{-}F}$ = 240.9 Hz, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 153.7 (dd, $^{1}J_{C\text{-}F}$ = 244.2 Hz, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 152.1 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 149.8, 136.5, 128.6 (dd, $^{2}J_{C\text{-}F}$ = 13.5 Hz, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 124.4 (d, $^{3}J_{C\text{-}F}$ = 10.3 Hz), 122.9, 117.3 (dd, $^{2}J_{C\text{-}F}$ = 26.1 Hz, $^{3}J_{C\text{-}F}$ = 8.5 Hz), 117.1 (dd, $^{2}J_{C\text{-}F}$ = 25.6 Hz, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 116.8 (dd, $^{2}J_{C\text{-}F}$ = 24.2 Hz, $^{3}J_{C\text{-}F}$ = 8.9 Hz).

2-(5-fluoro-2-methylphenyl)pyridine (*o*-3al)



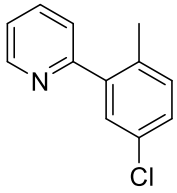
Light yellow oil (13.5 mg, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 4.4 Hz, 1H), 7.77–7.73 (m, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.26–7.20 (m, 2H), 7.12 (d, J = 9.6 Hz, 1H), 7.01–6.97 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3 (d, $^{1}J_{C\text{-}F}$ = 243 Hz), 158.8, 149.3, 141.8 (d, $^{3}J_{C\text{-}F}$ = 7 Hz), 136.4, 132.9 (d, $^{3}J_{C\text{-}F}$ = 7 Hz), 131.4 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 124.0, 122.1, 122.3, 116.3 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 115.0 (d, $^{2}J_{C\text{-}F}$ = 20 Hz), 19.5. IR (KBr): ν 3053, 2924, 1587, 1462, 1060, 886, 814, 792, 760 cm^{-1}. HRMS (ESI) calcd for [$C_{12}H_{11}NF$, M+H]$^{+}$: 188.0879, found: 188.0876.

2-(2-fluoro-5-methylphenyl)pyridine (*m*-3al)



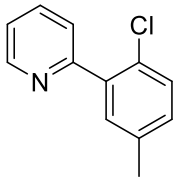
Light yellow oil (10.7 mg, 19% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 4.8 Hz, 1H), 7.76–7.71 (m, 3H), 7.26–7.22 (m, 1H), 7.17–7.14 (m, 1H), 7.06–7.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7 (d, $^{1}J_{C\text{-}F}$ = 246 Hz), 153.7 (d, $^{4}J_{C\text{-}F}$ = 2 Hz), 149.7, 136.3, 134.0 (d, $^{3}J_{C\text{-}F}$ = 6 Hz), 131.1 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 130.9 (d, $^{3}J_{C\text{-}F}$ = 6 Hz), 126.9 (d, $^{2}J_{C\text{-}F}$ = 12 Hz), 124.6 (d, $^{3}J_{C\text{-}F}$ = 9 Hz), 122.3, 115.9 (d, $^{2}J_{C\text{-}F}$ = 23 Hz), 20.7. IR (KBr): ν 3051, 2925, 1586, 1460, 1060, 883, 813, 792, 749. cm^{-1}. HRMS (ESI) calcd for [$C_{12}H_{11}NF$, M+H]$^{+}$: 188.0871; found: 188.0876.

2-(5-chloro-2-methylphenyl)pyridine (*o*-3am)[30]



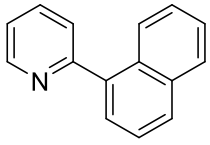
Light yellow oil (20.2 mg, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J = 4.8 Hz, 1H), 7.77–7.73 (m, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.42 (s, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.29–7.26 (m, 1H), 7.14 (d, J = 8.0 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 149.5, 138.8, 136.9, 135.8, 132.1, 130.4, 129.8, 129.0, 124.9, 122.3, 20.8.

2-(2-chloro-5-methylphenyl)pyridine (*m*-3am)



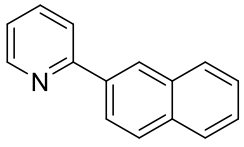
Light yellow oil (15.3 mg, 22% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 4.8 Hz, 1H), 7.77–7.73 (m, 1H), 7.39–7.37 (m, 2H), 7.28–7.25 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 149.4, 141.9, 136.3, 134.3, 132.0, 131.5, 129.5, 128.2, 124.0, 122.1, 19.7. IR (KBr): ν 3053, 2927, 1585, 1472, 1381, 1176, 899, 812, 795, 751 cm^{-1}. HRMS (ESI) calcd for $[C_{12}H_{11}NCl, M+H]^+$: 204.0573, found: 204.0580.

2-(naphthalene-1-yl)pyridine (*α*-3an)[4]



Yellow oil (24.6 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 4.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.83–7.80 (m, 1H), 7.61–7.63 (m, 3H), 7.51–7.46 (m, 2H), 7.34–7.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 149.5, 138.5, 136.5, 134.0, 131.2, 128.9, 128.4, 127.5, 126.5, 125.9, 125.6, 125.3, 125.1, 122.1.

2-(naphthalene-2-yl)pyridine (*β*-3an)[4]



Yellow solid (14.2 mg, 23% yield), mp 78–79 °C, (lit.[3] mp 77–79 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J = 4.4 Hz, 1H), 8.48 (s, 1H), 8.13 (d, J = 8.4, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 7.6 Hz, 2H), 7.78 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.52–7.48 (m, 2H), 7.27–7.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 149.7, 136.9, 136.6, 133.7, 133.5, 128.8, 128.5, 127.7, 126.6, 126.4, 126.3, 124.6, 122.2, 120.9.

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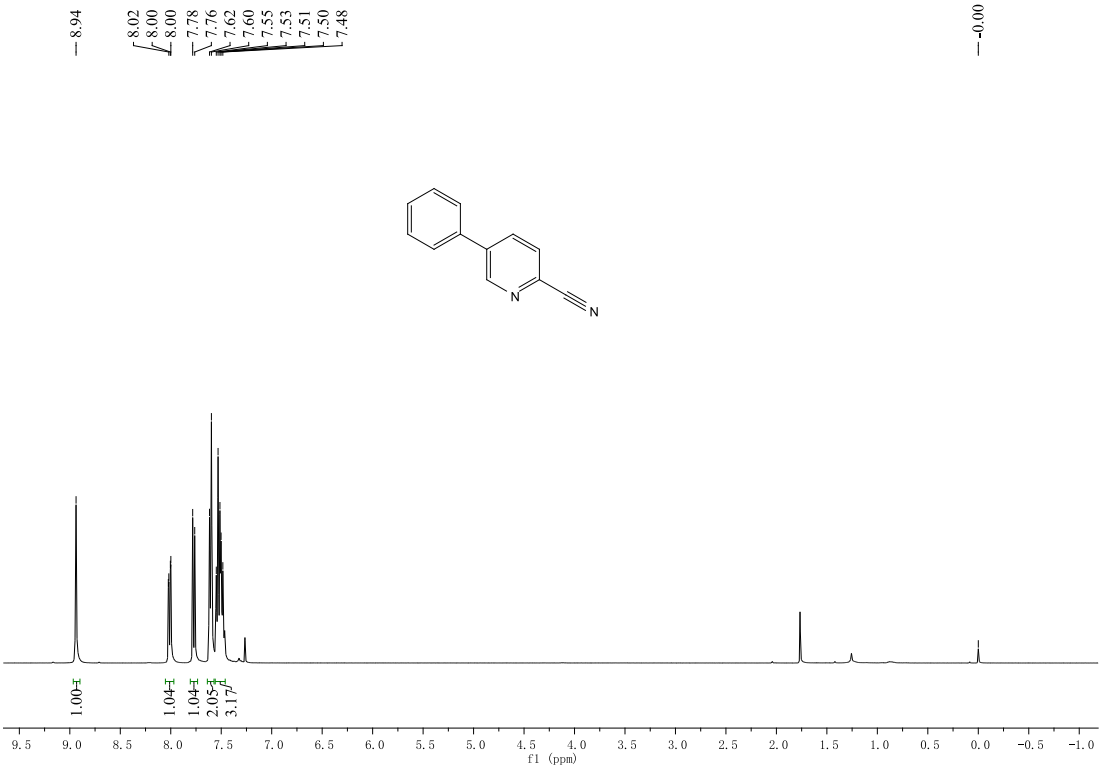
7. Copies of ^{1}H and ^{13}C NMR Spectra of Products

^{1}H NMR, 400 MHz, $CDCl_3$



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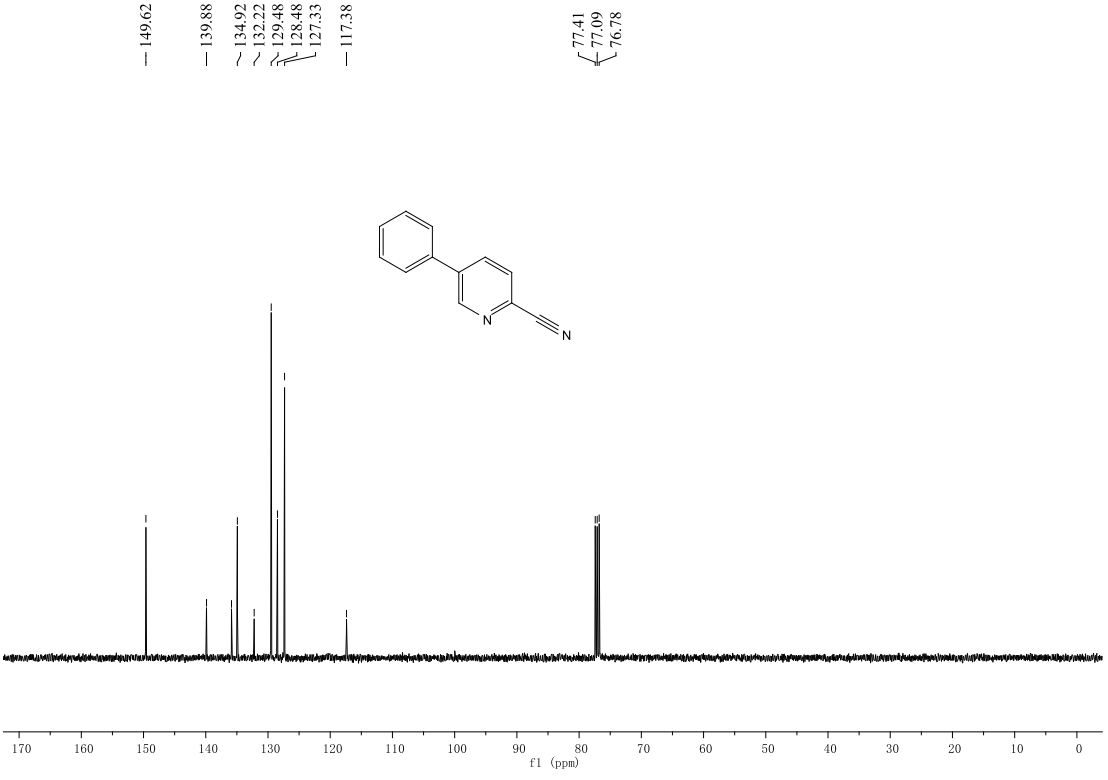

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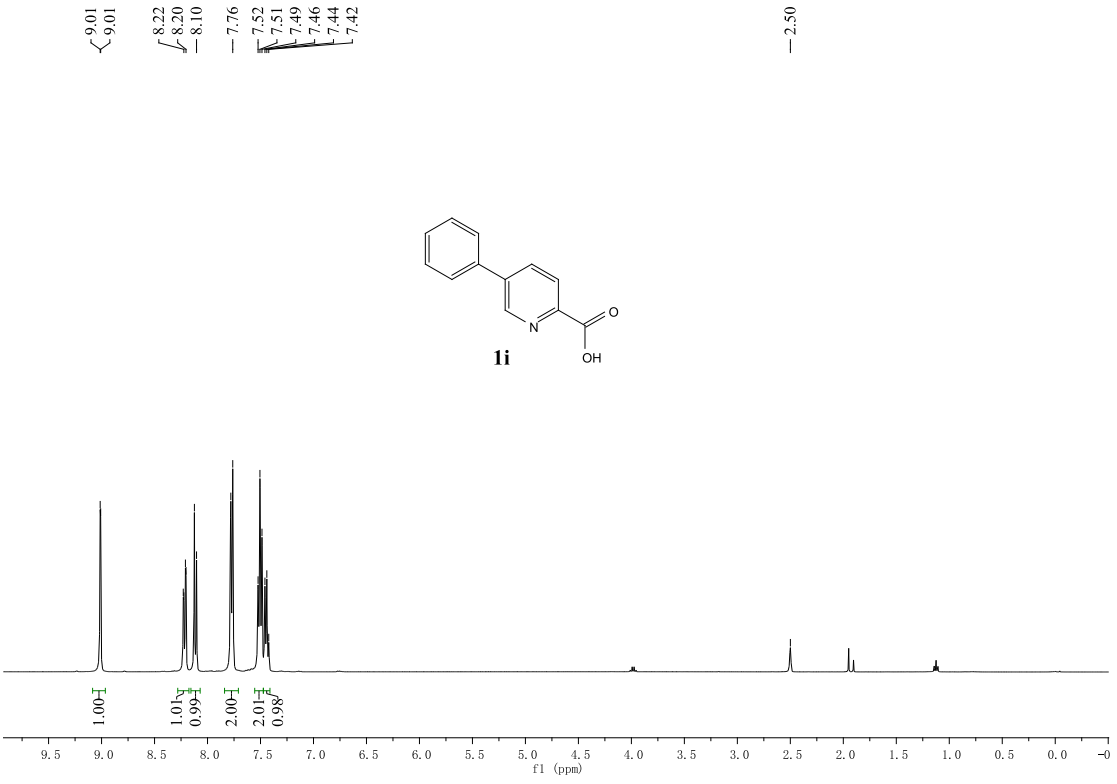

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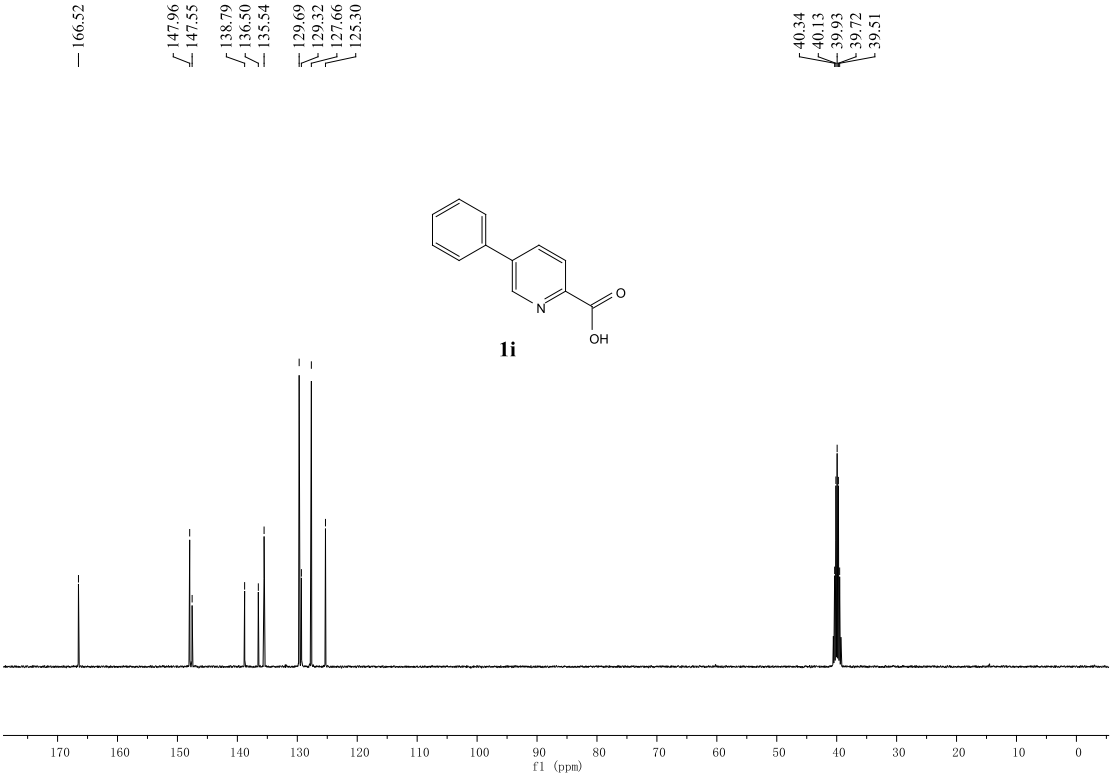

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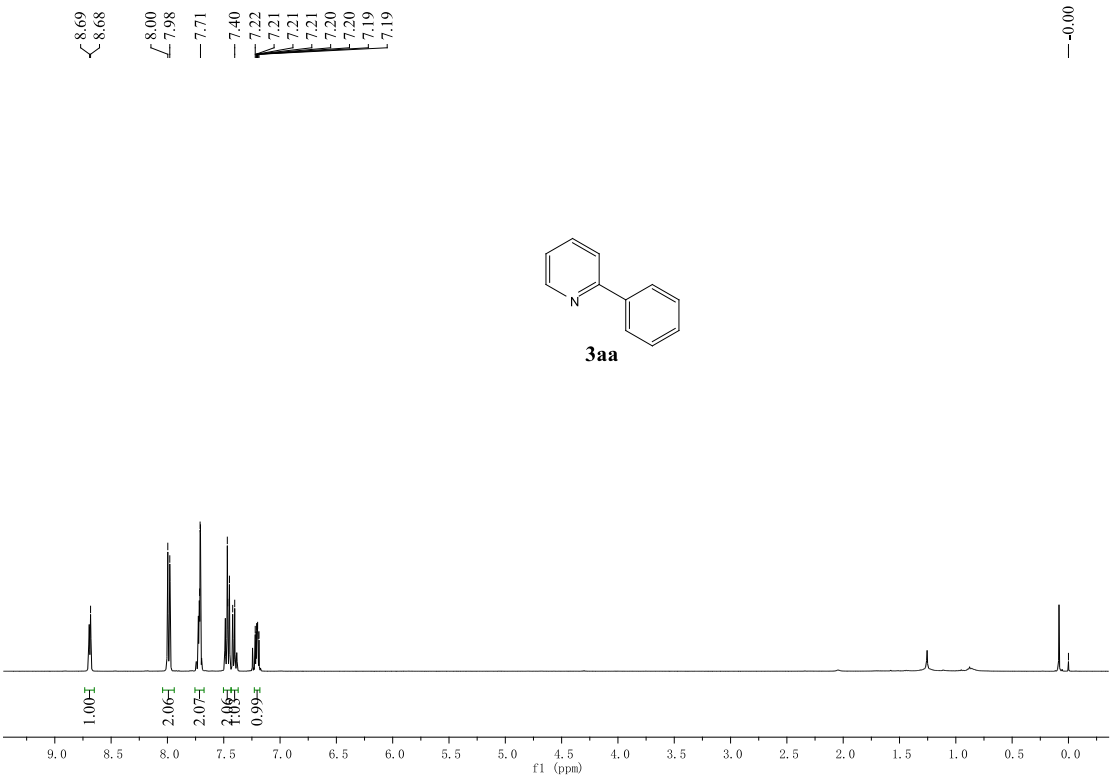

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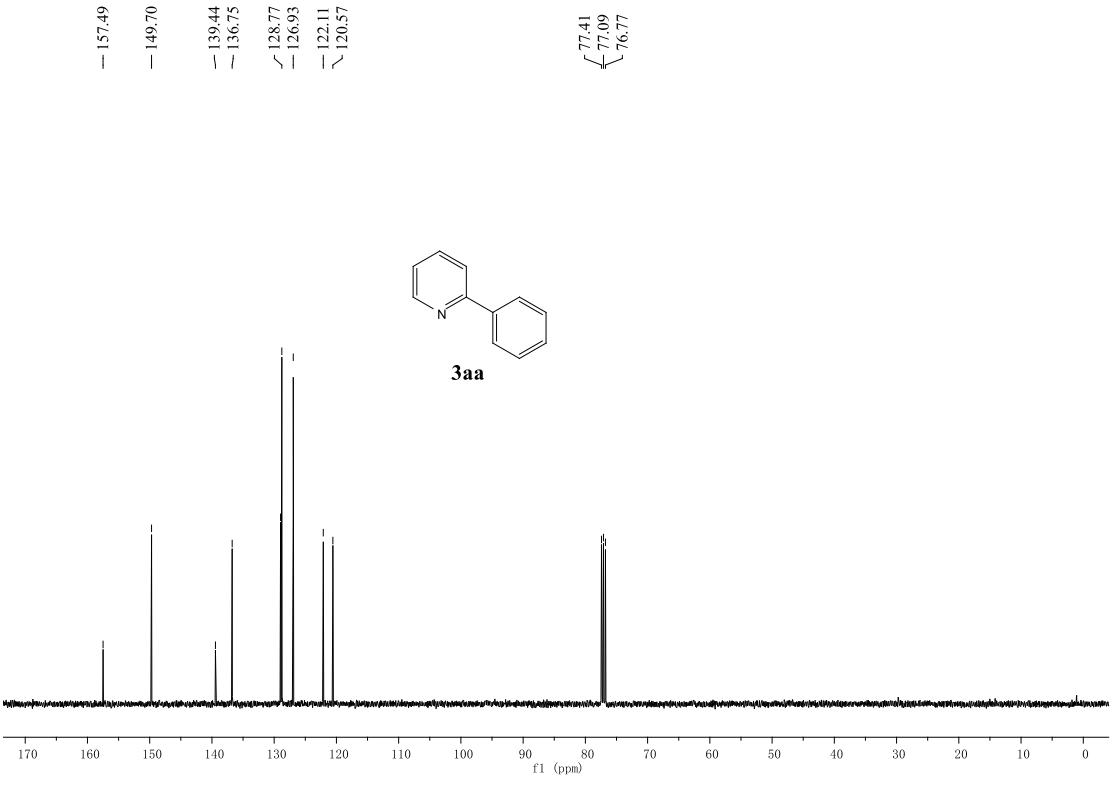

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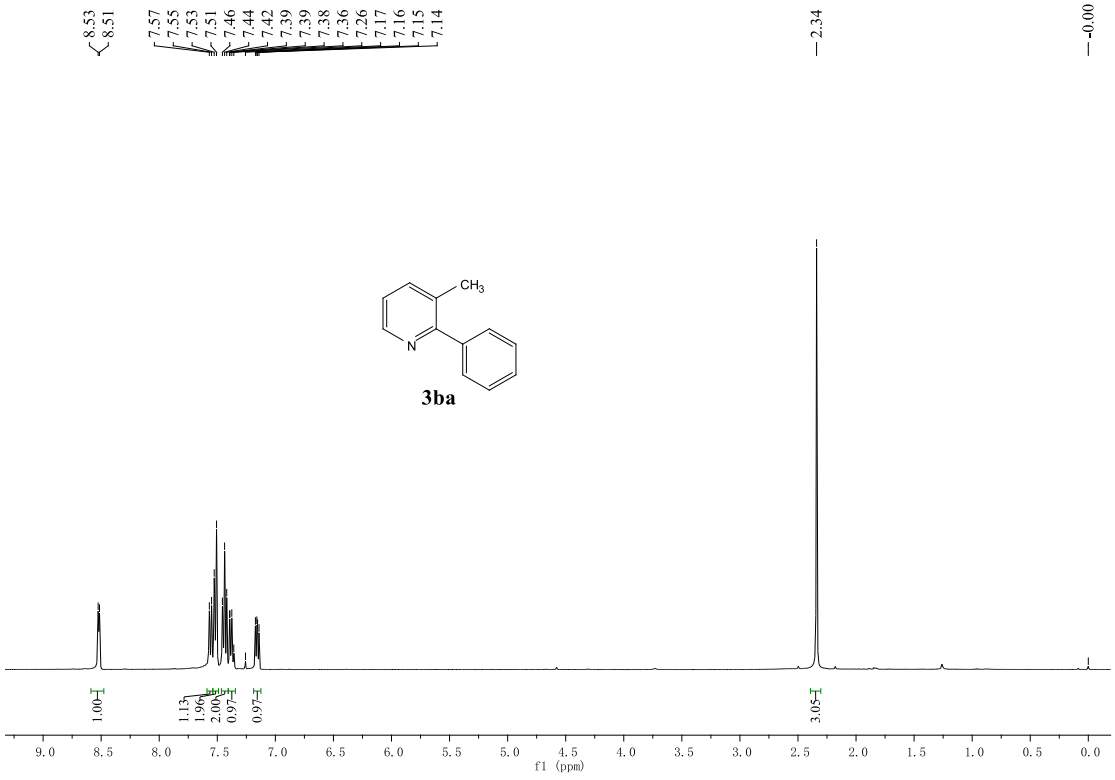

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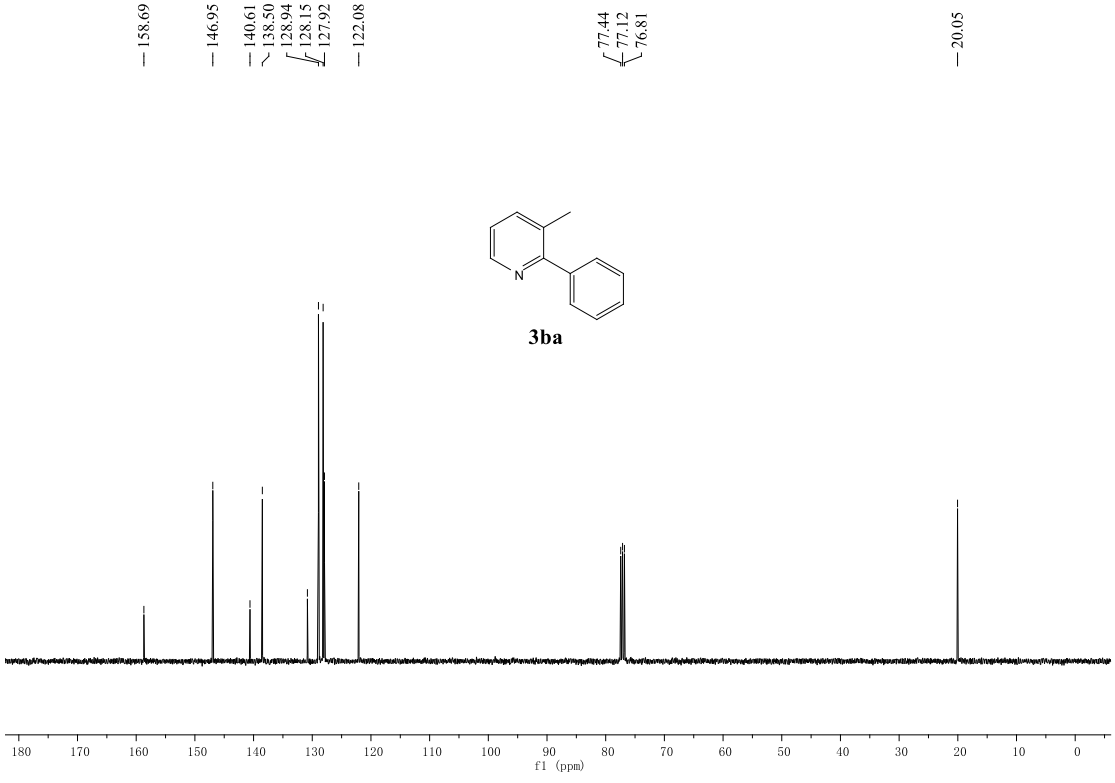

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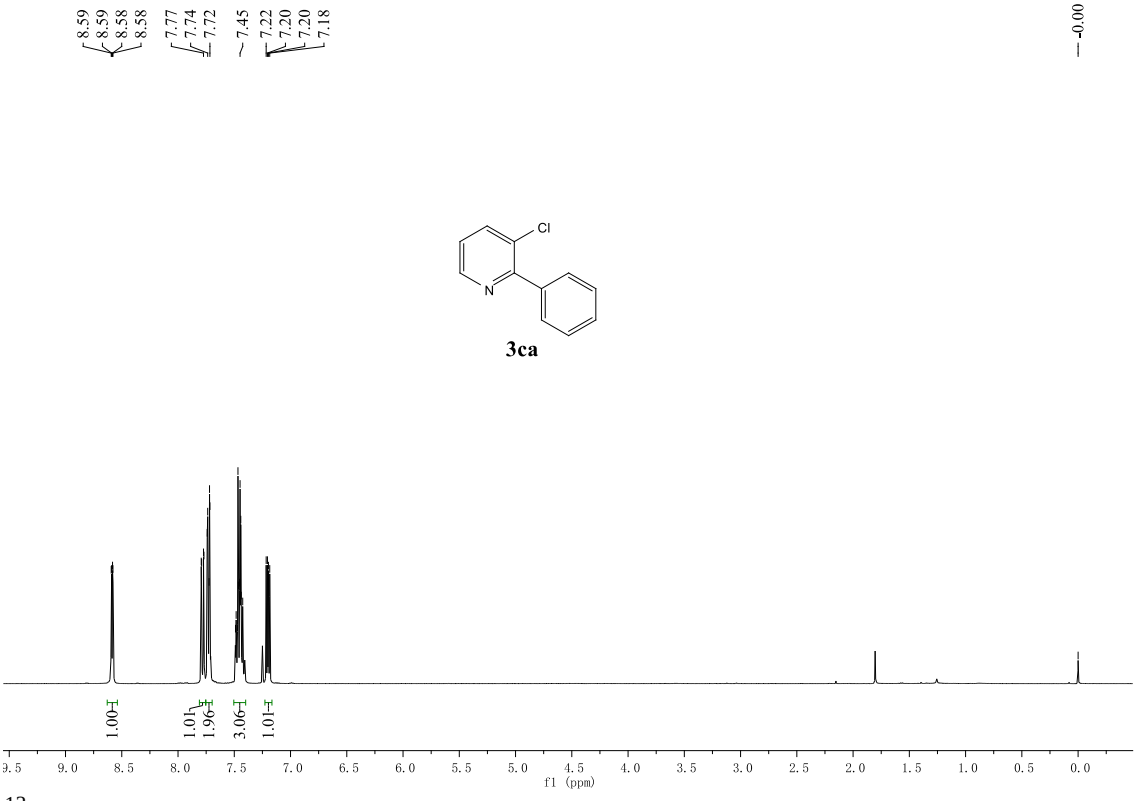

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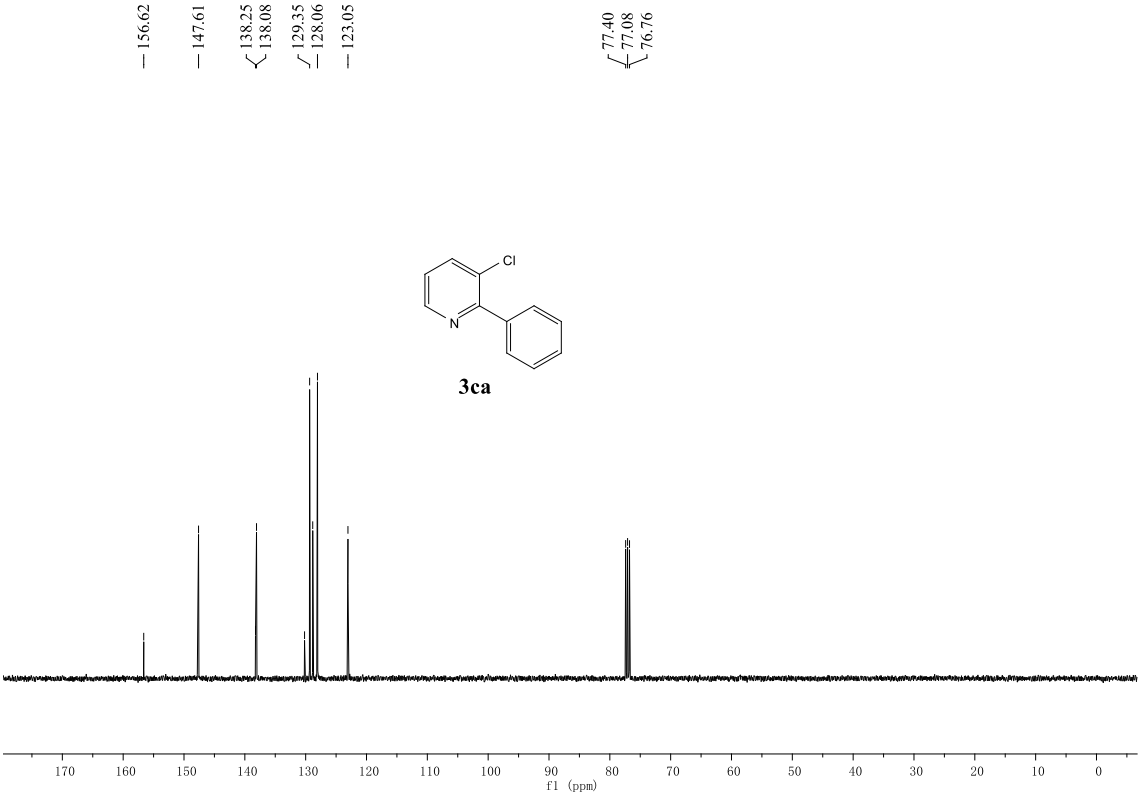

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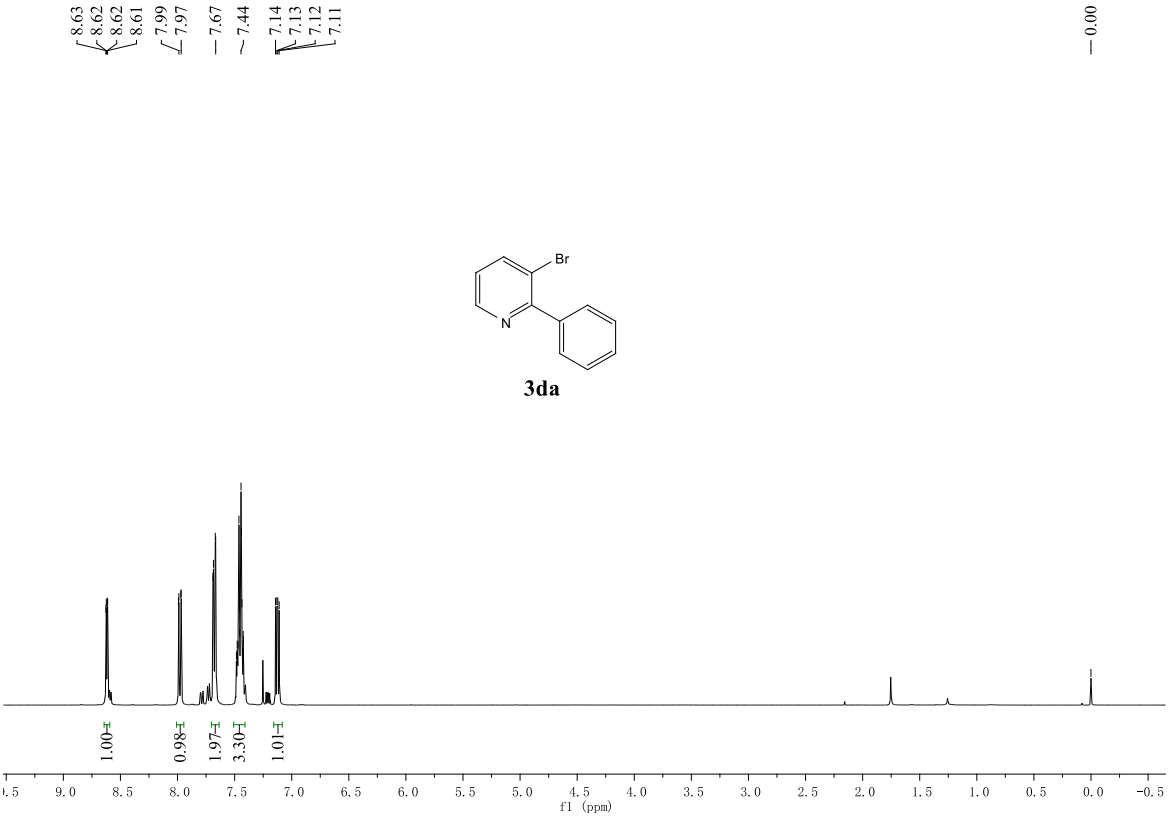

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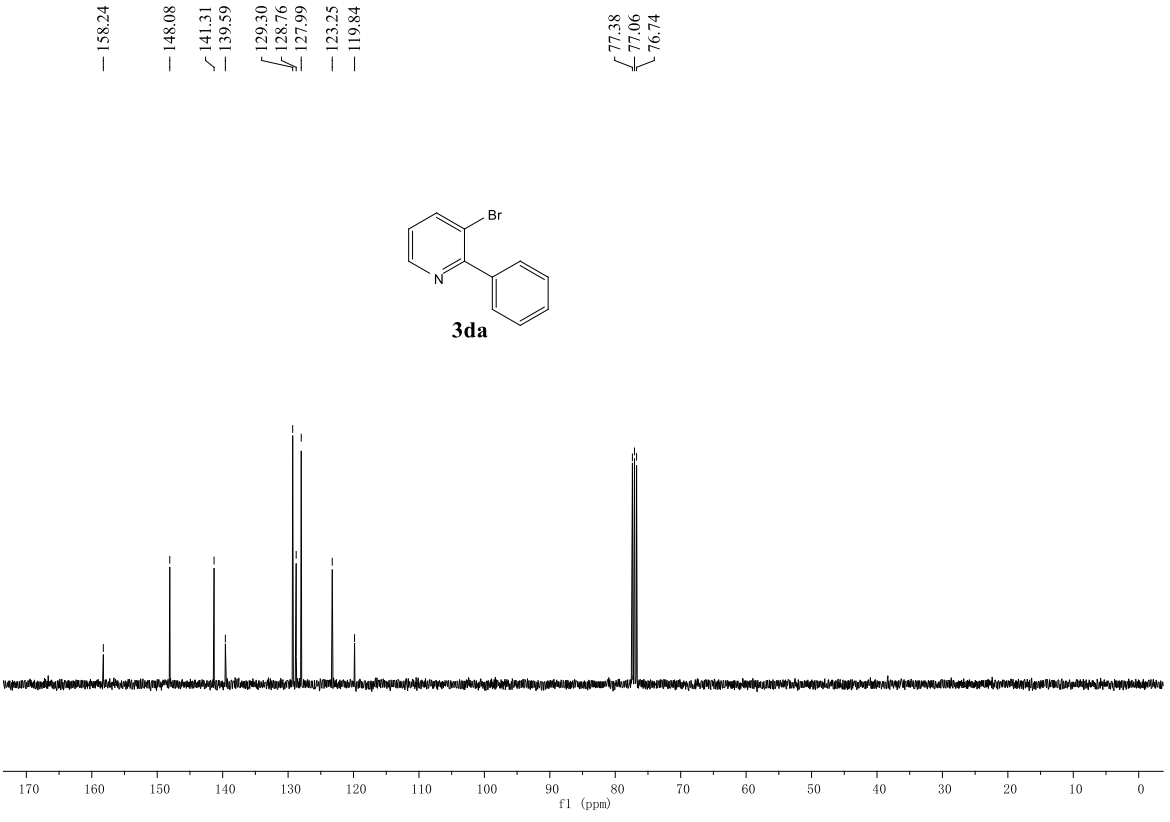

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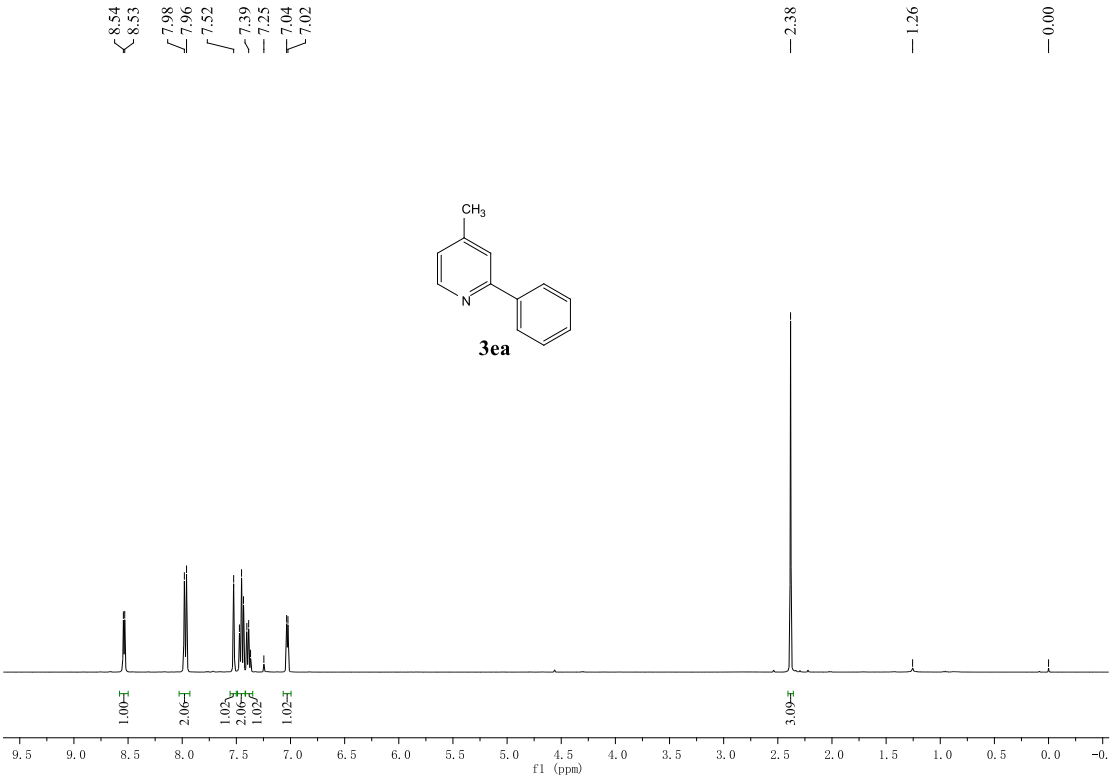

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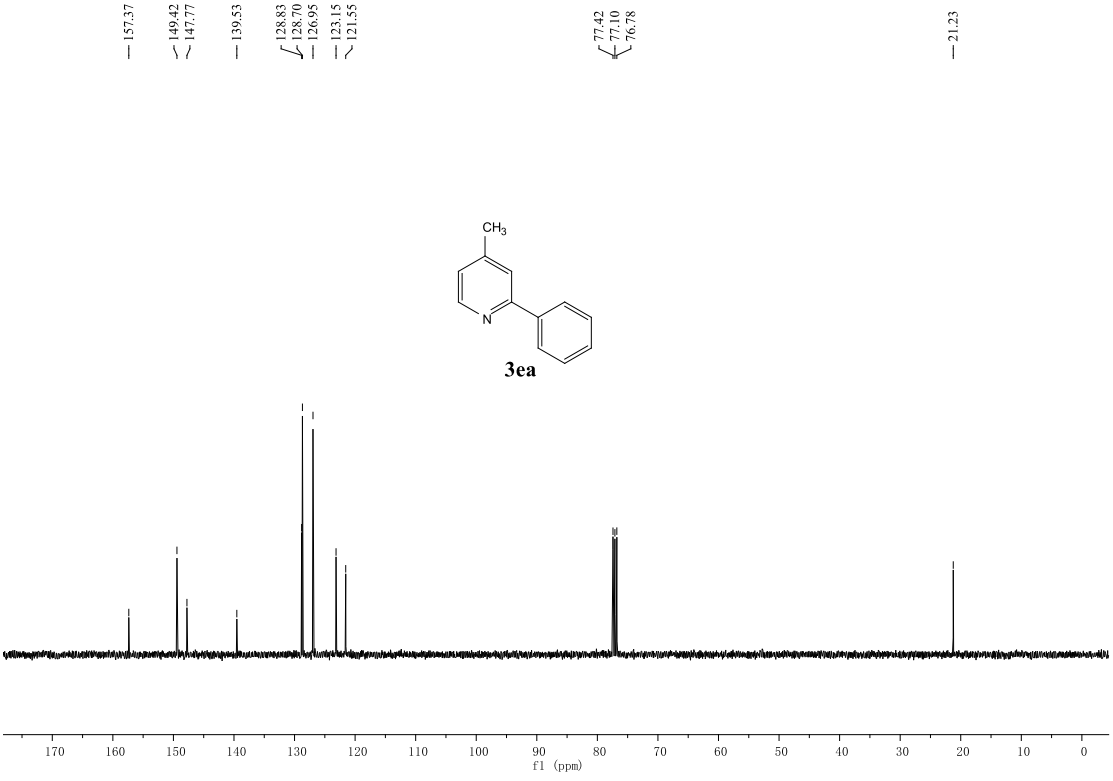

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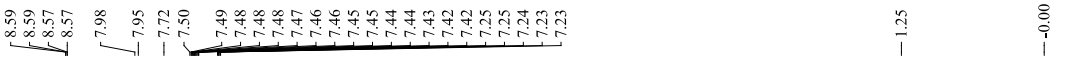

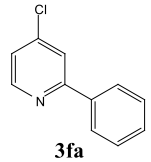

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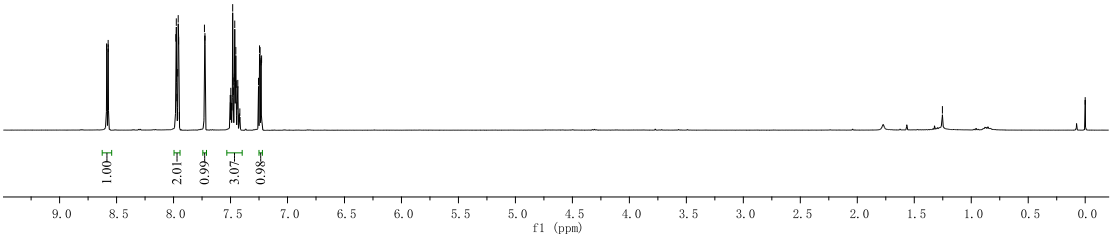

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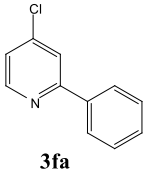

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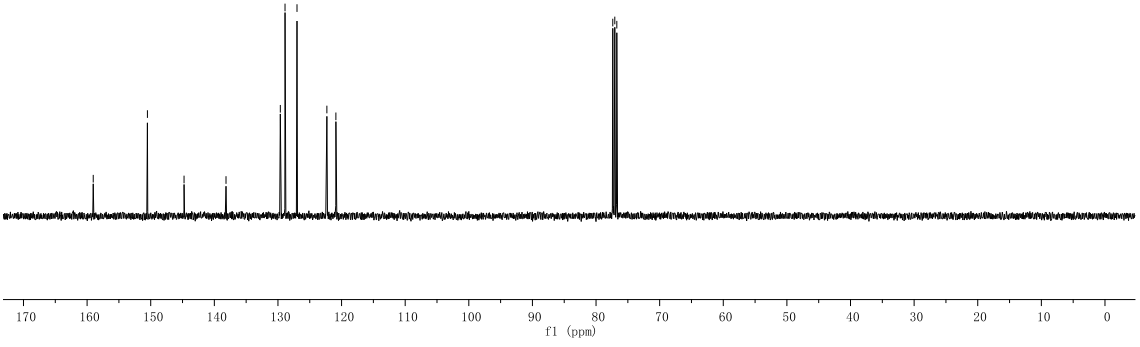

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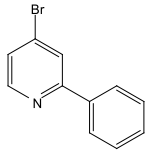

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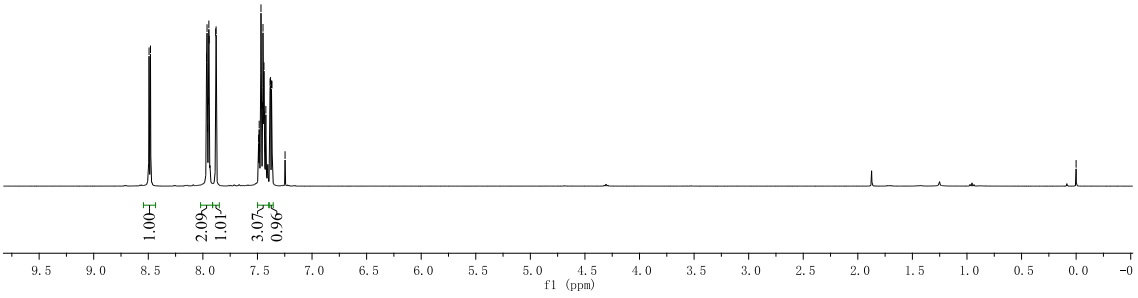

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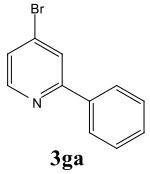

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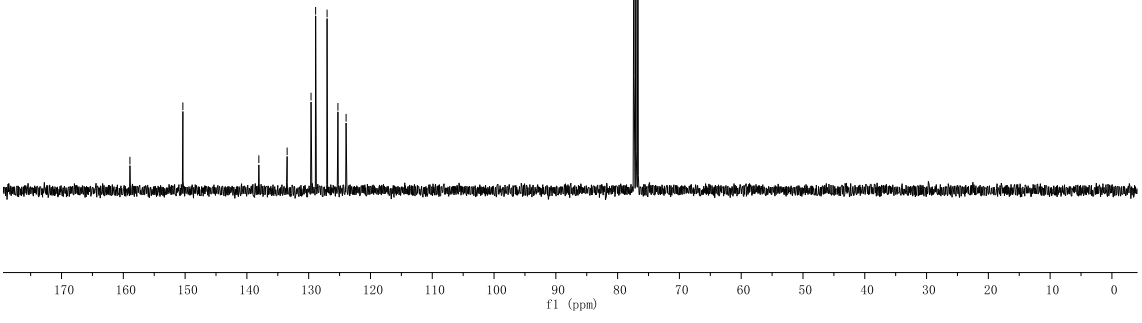

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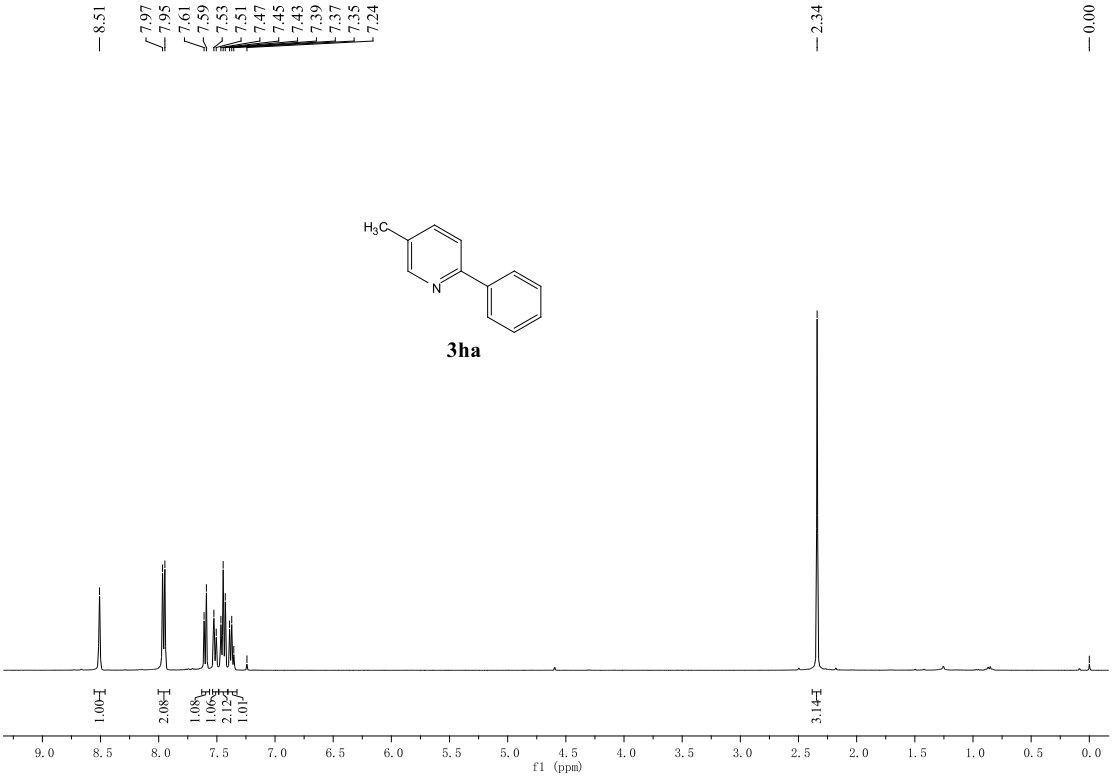

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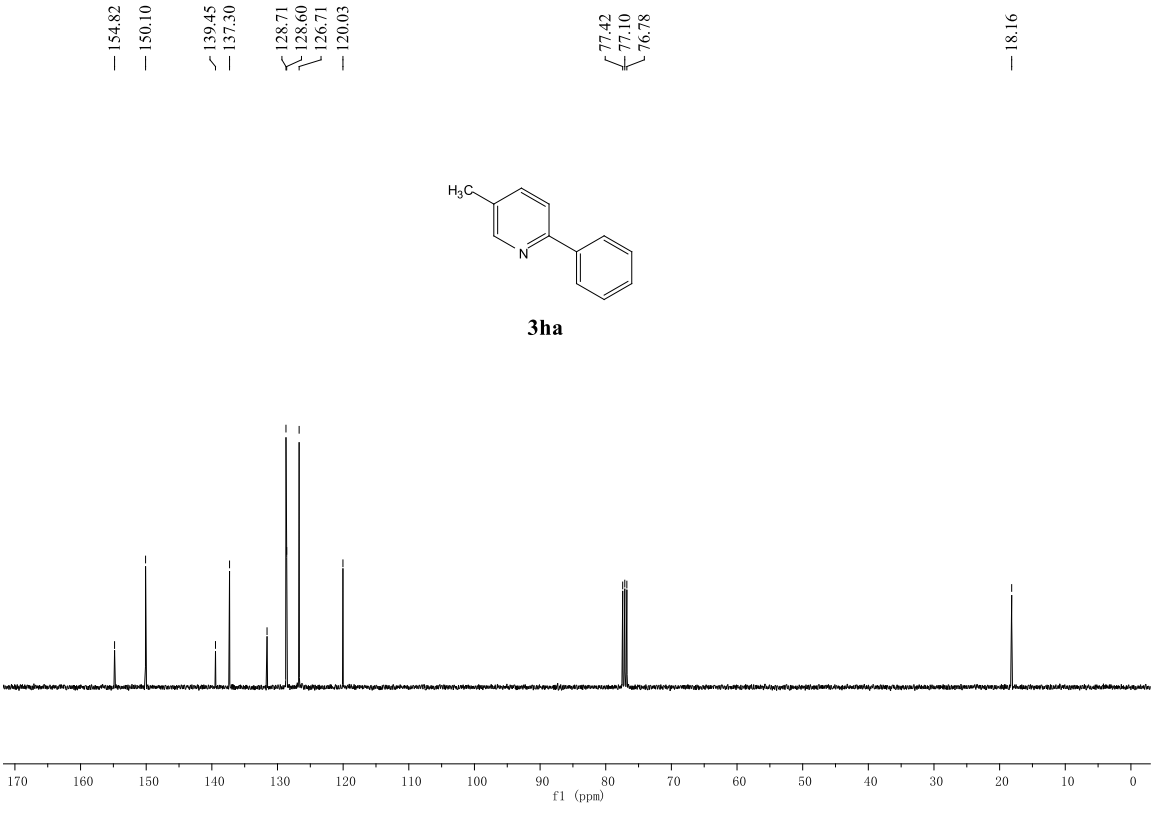

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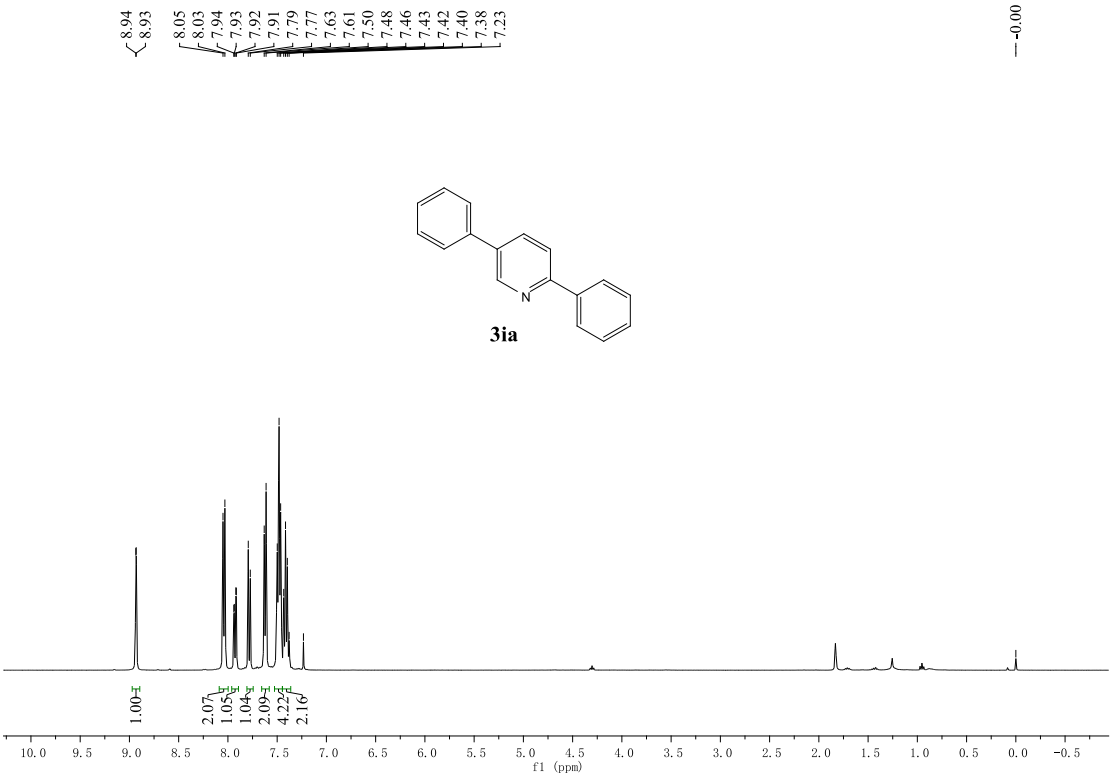

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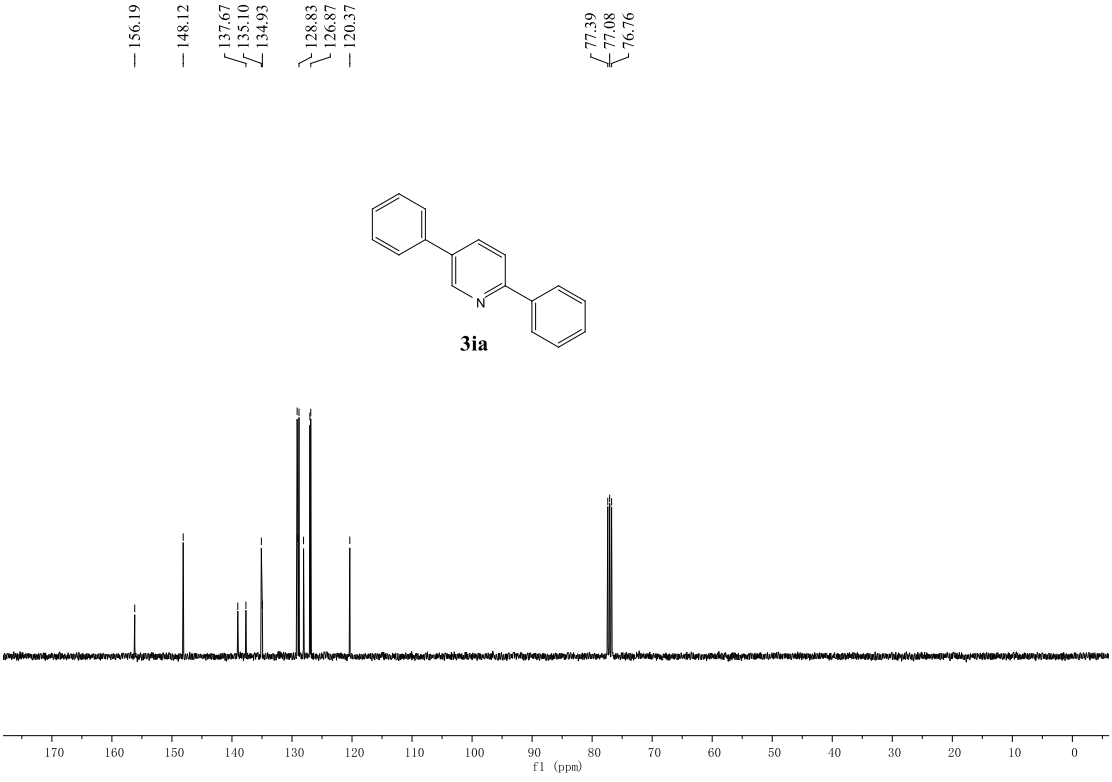

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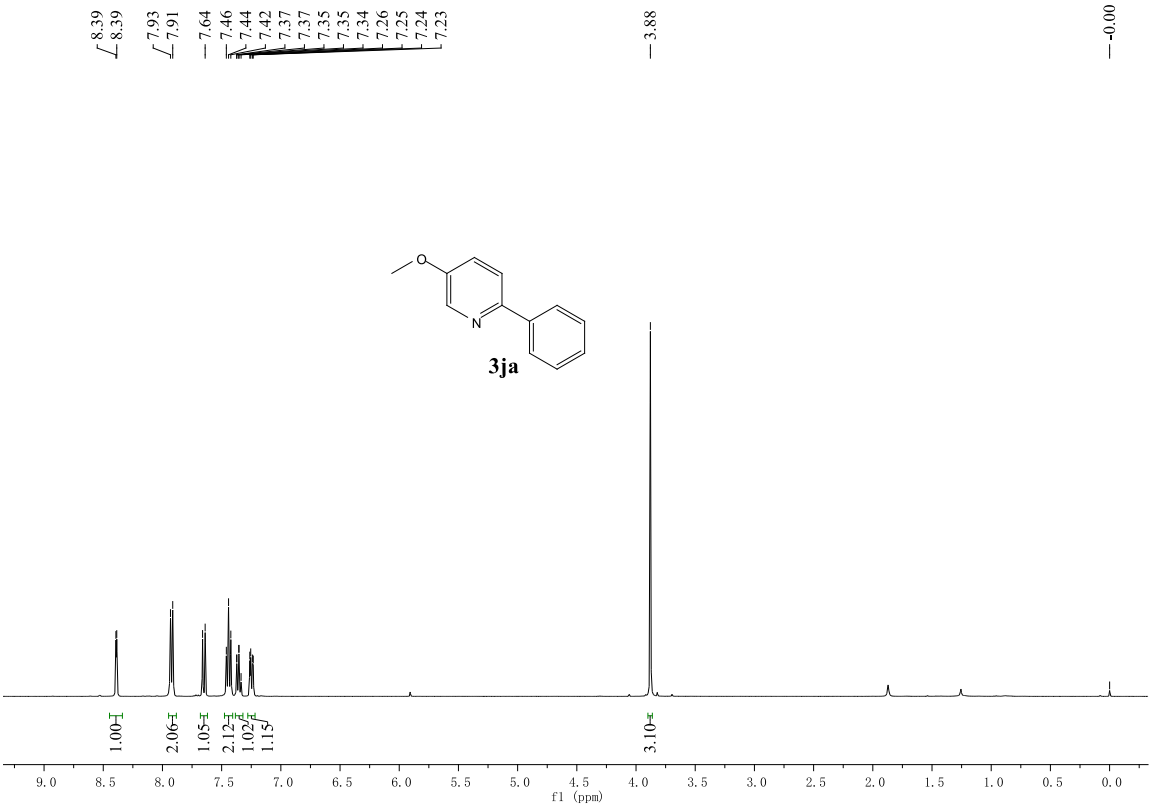

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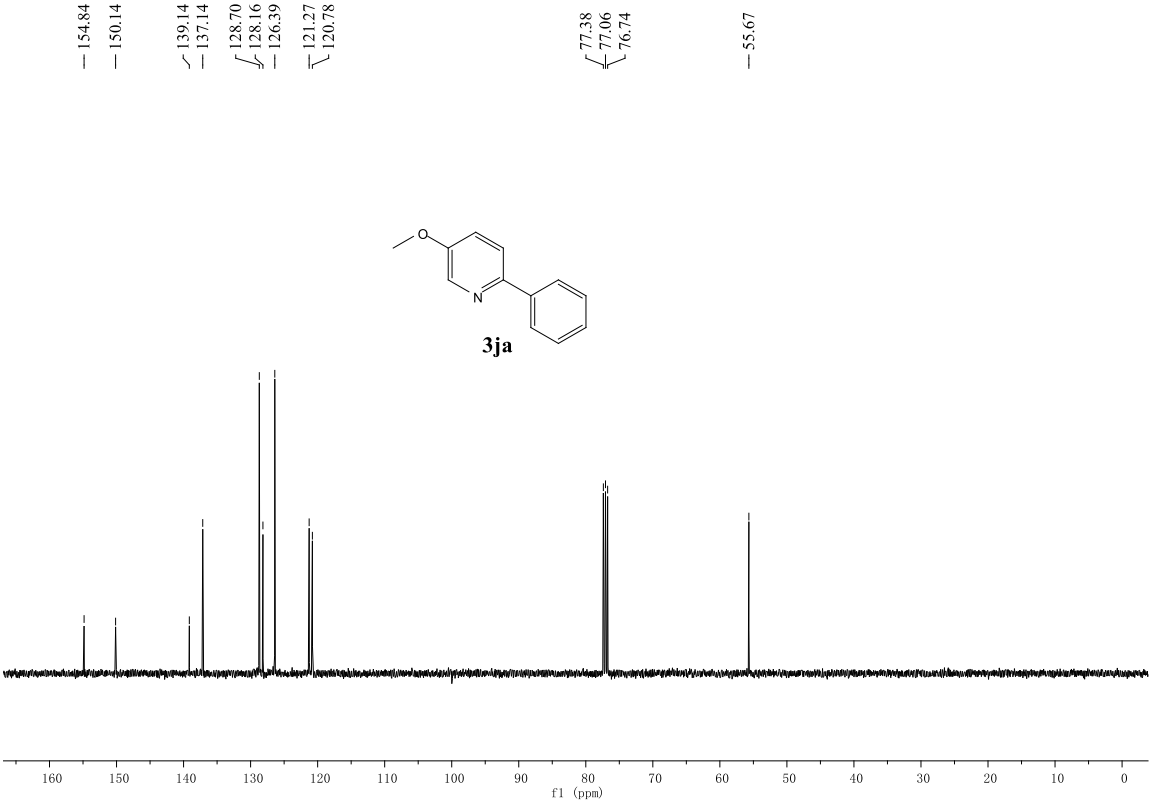

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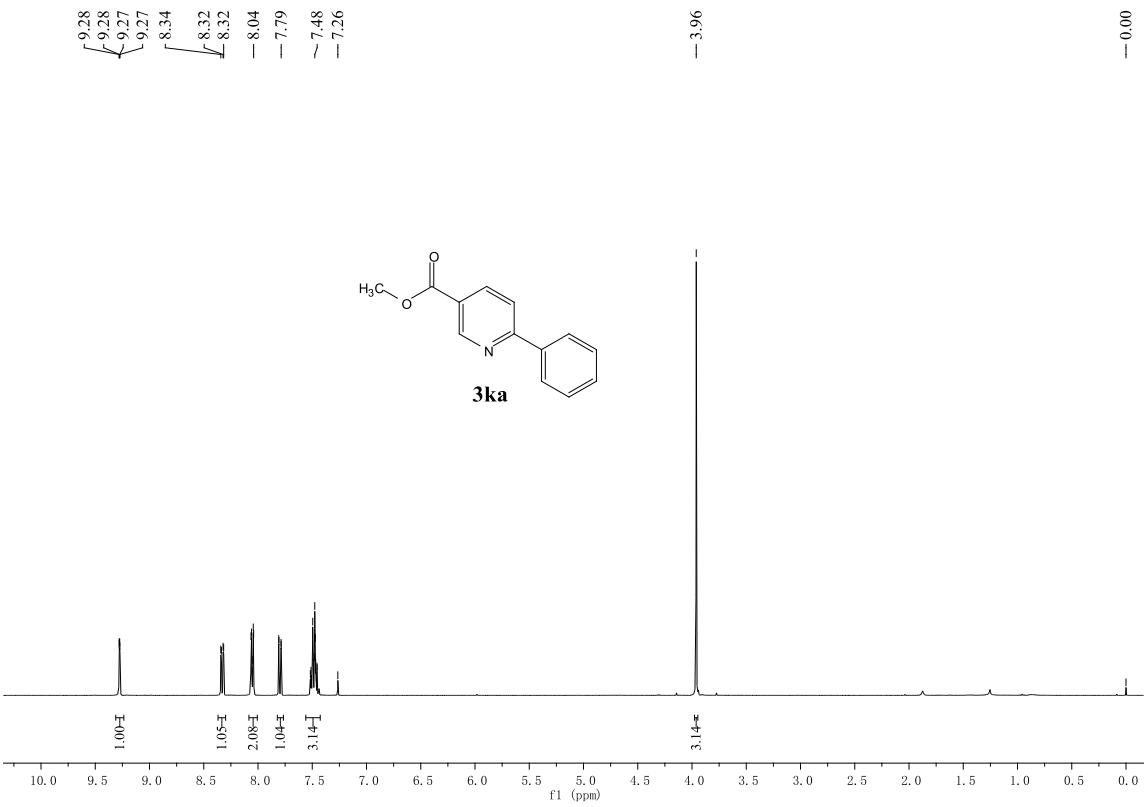

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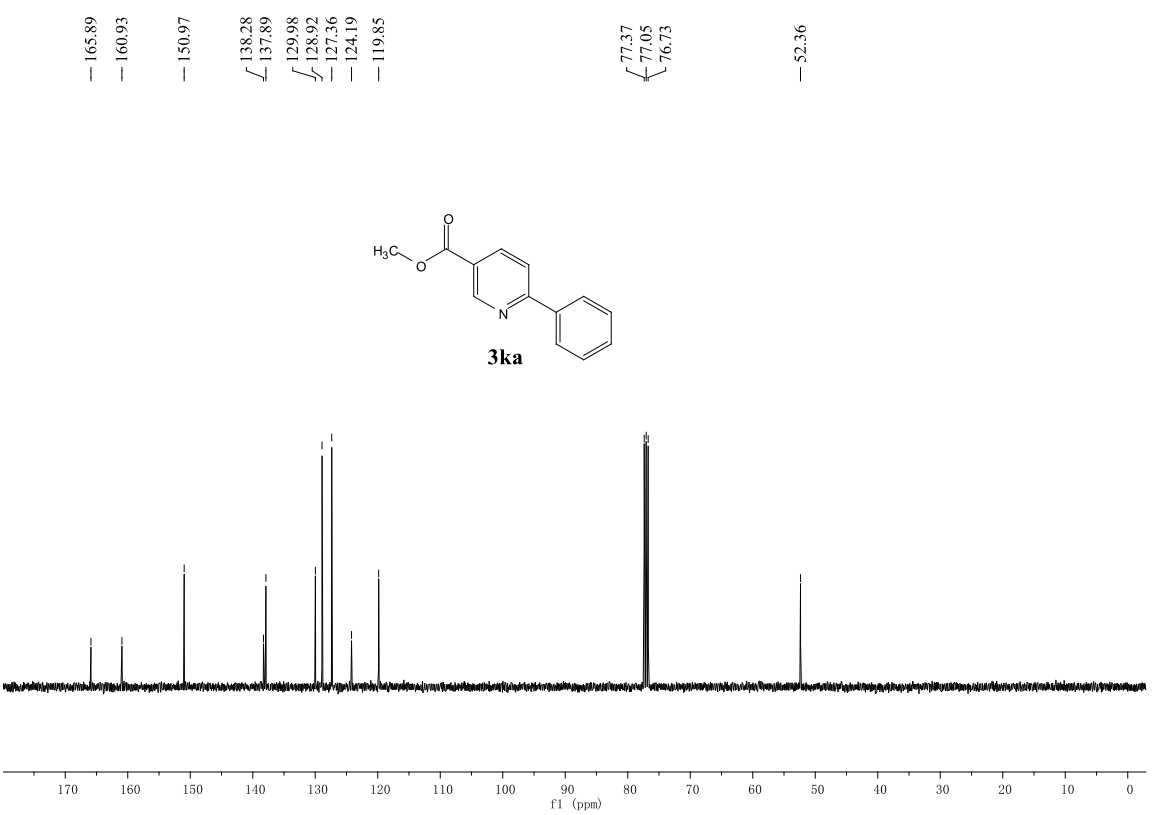

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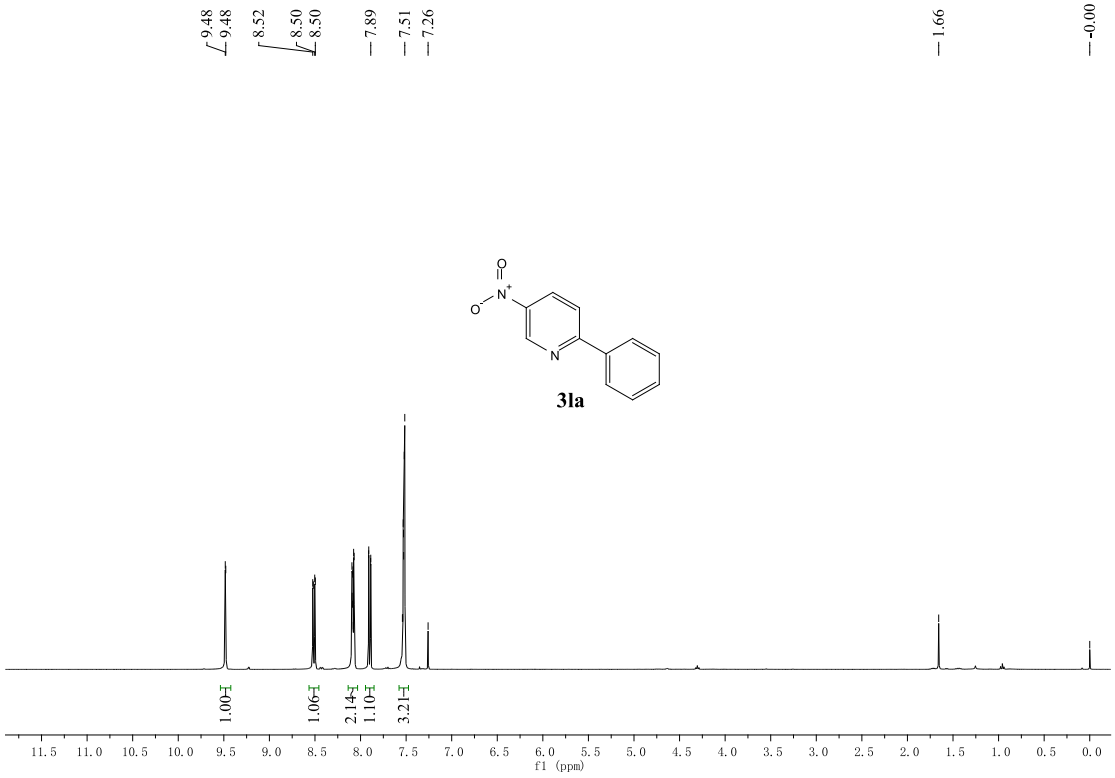

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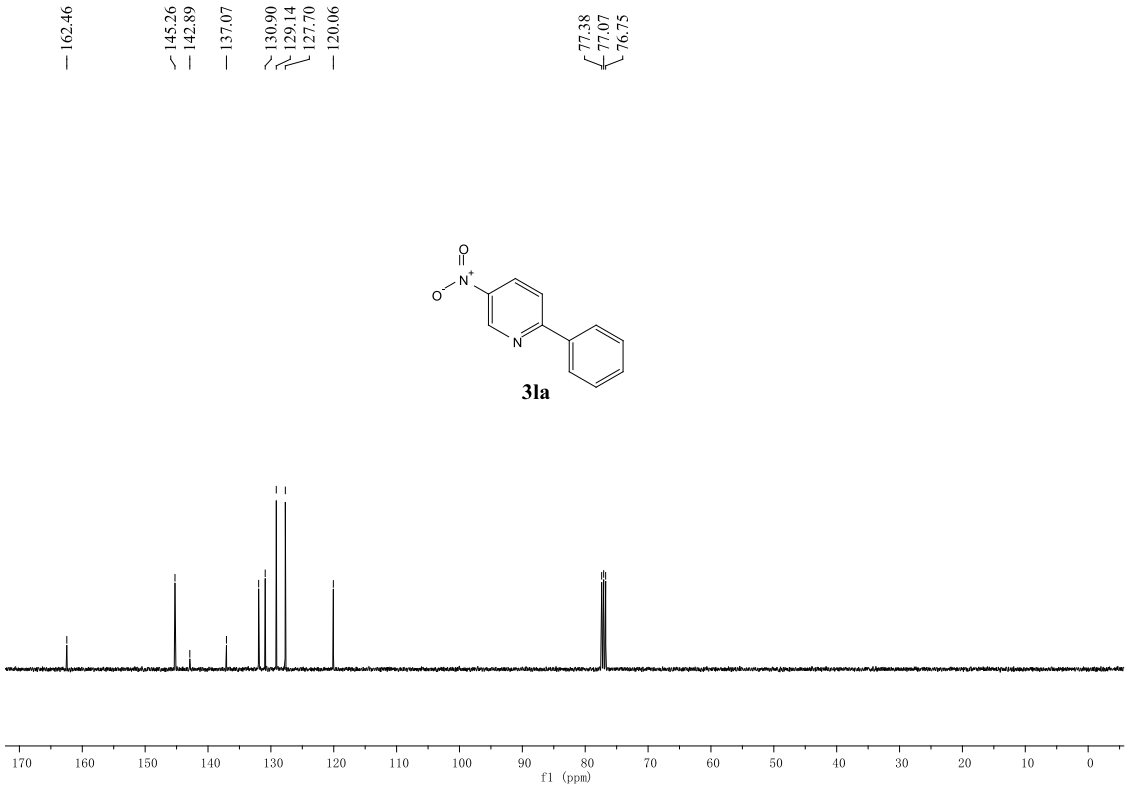

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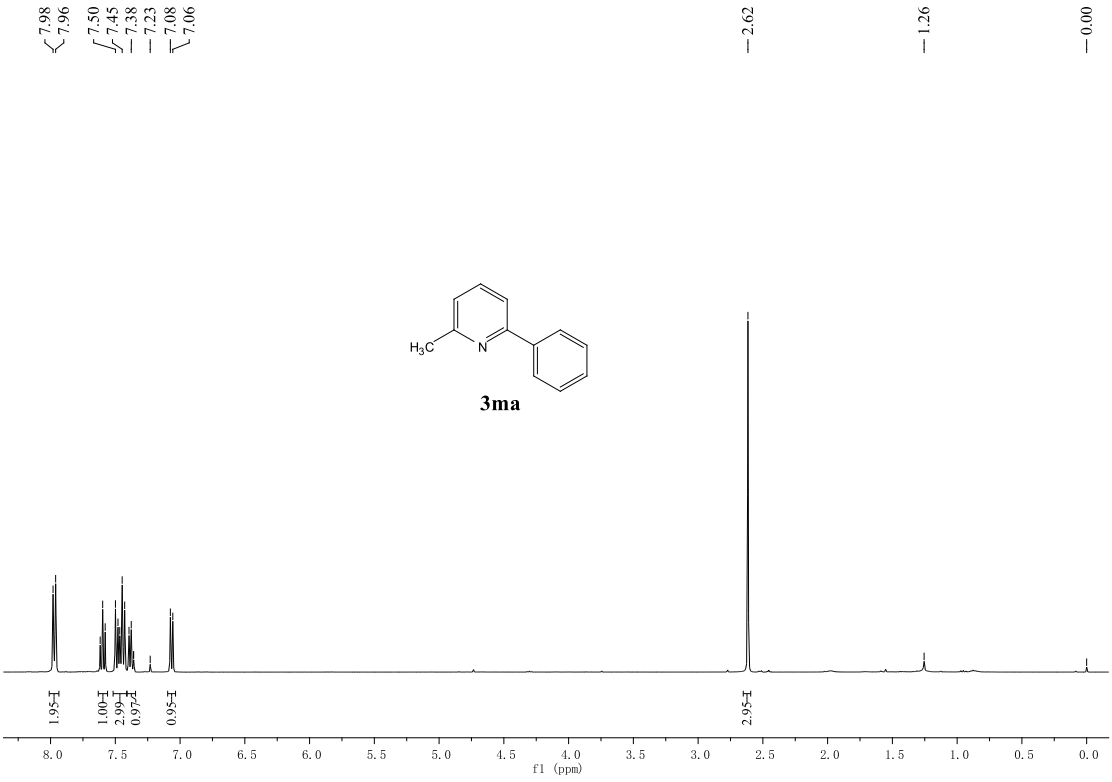

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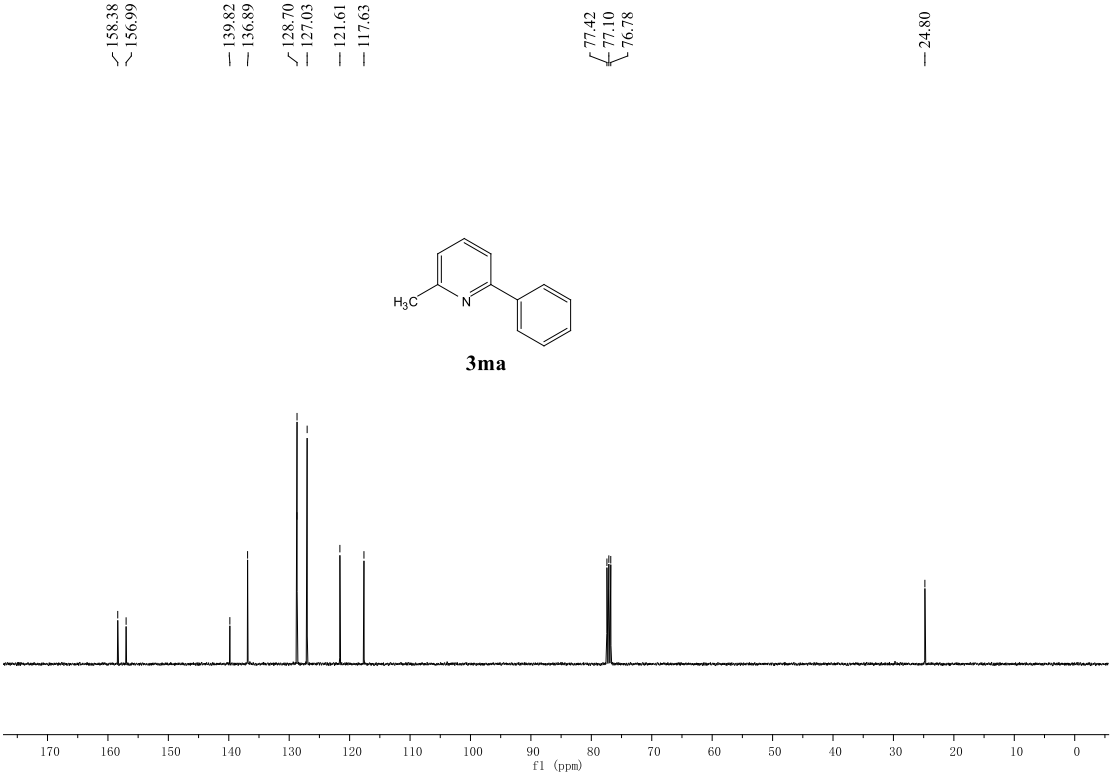

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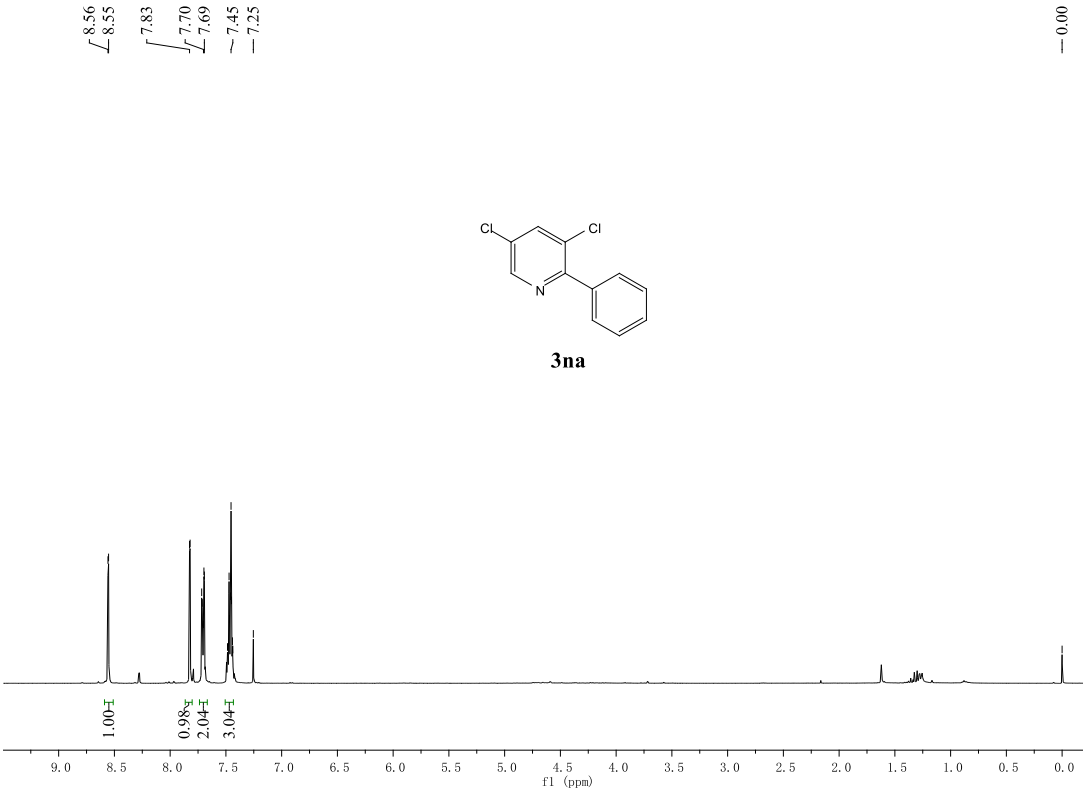

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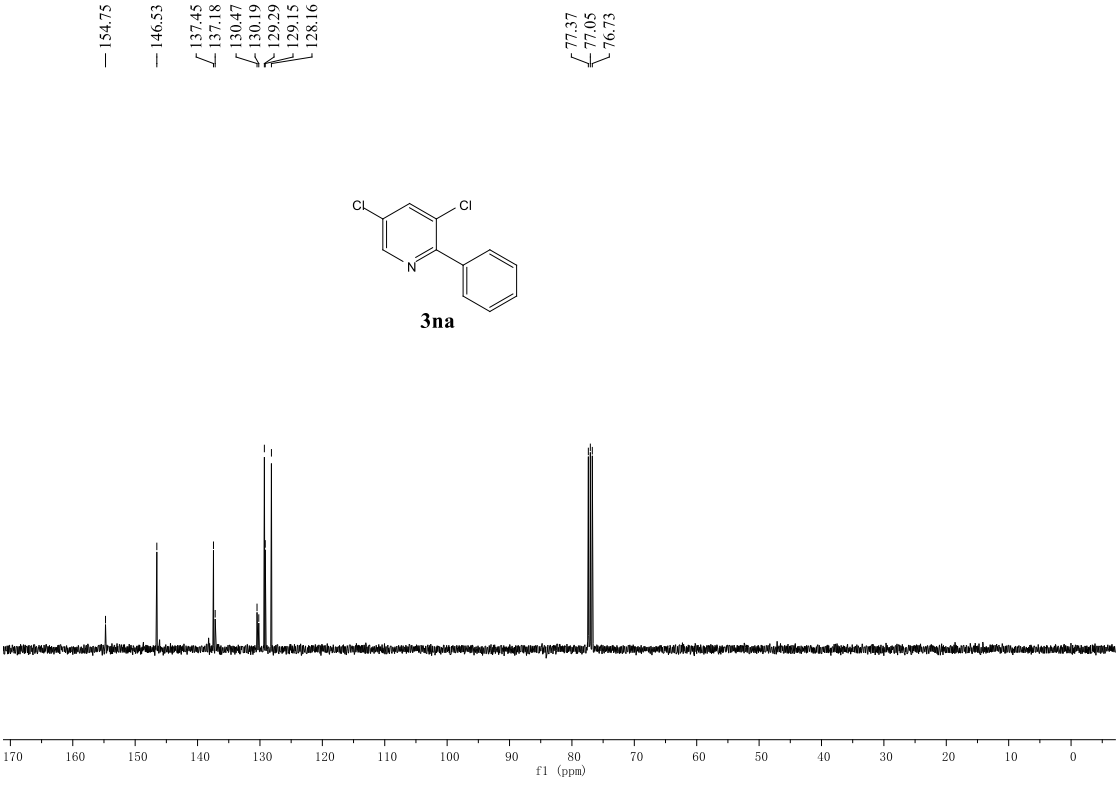
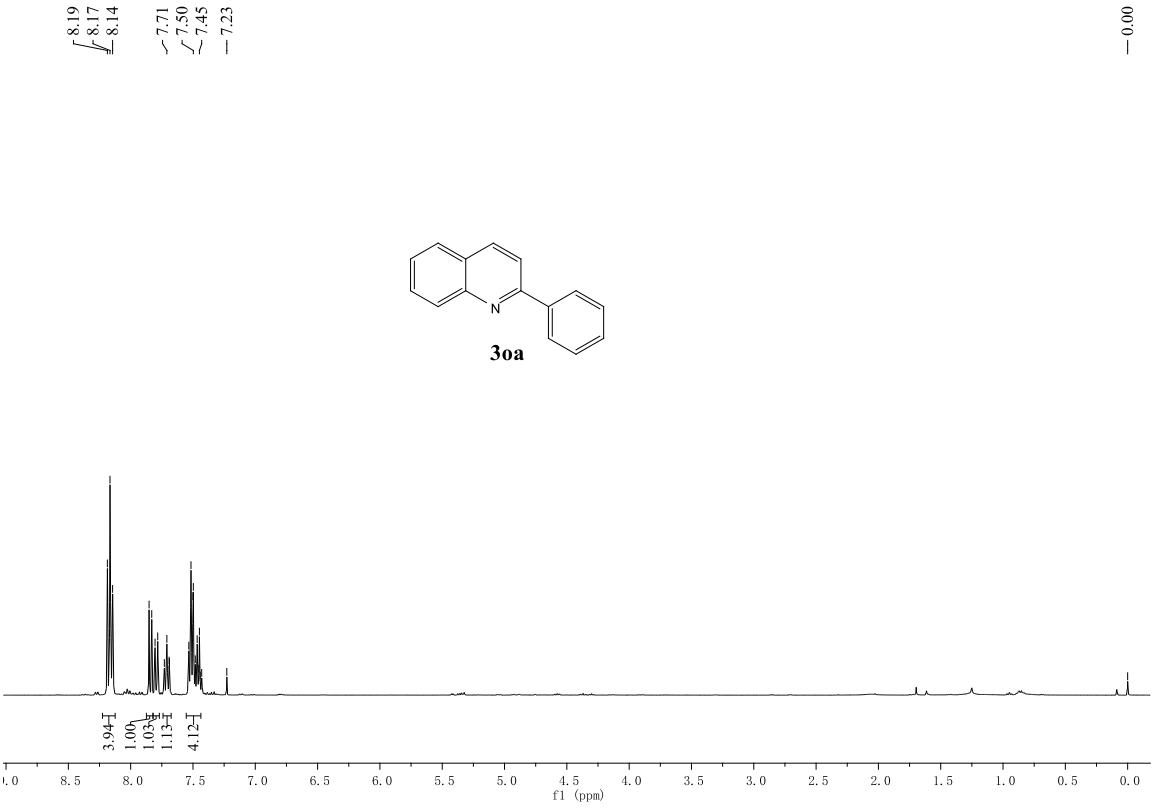
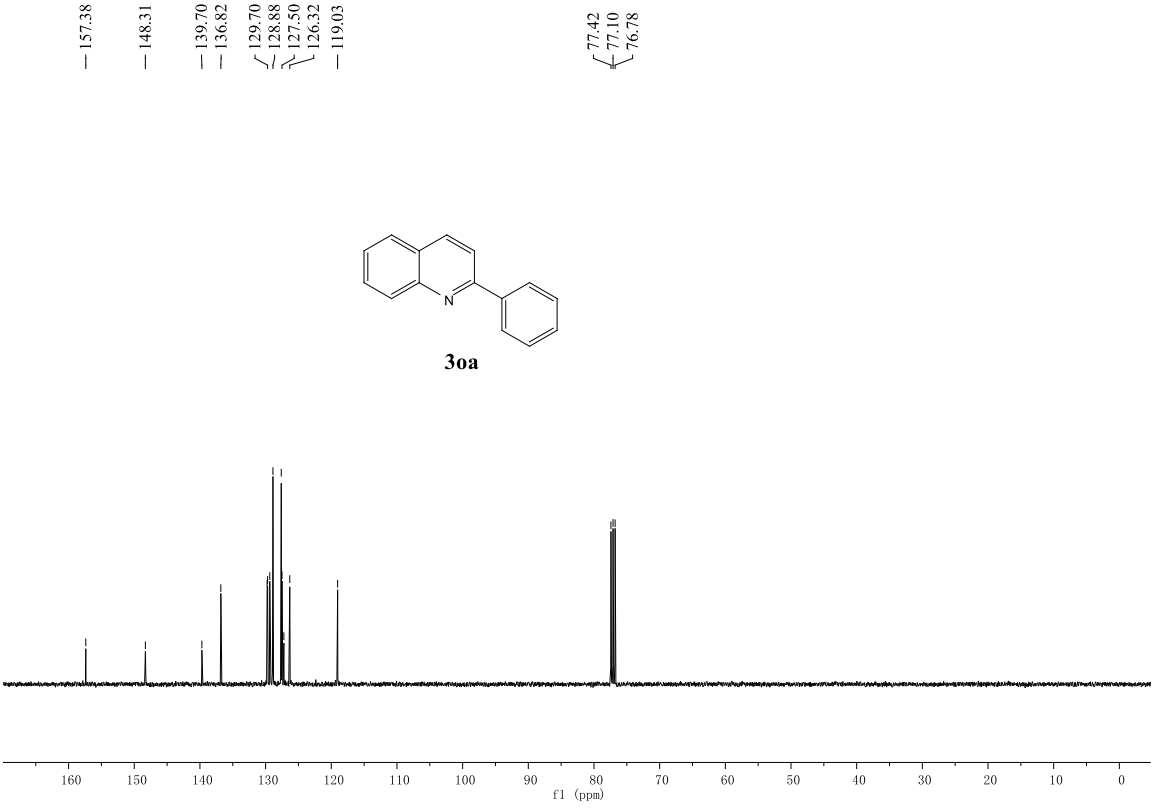


^{1}H NMR, 400 MHz, $CDCl_3$



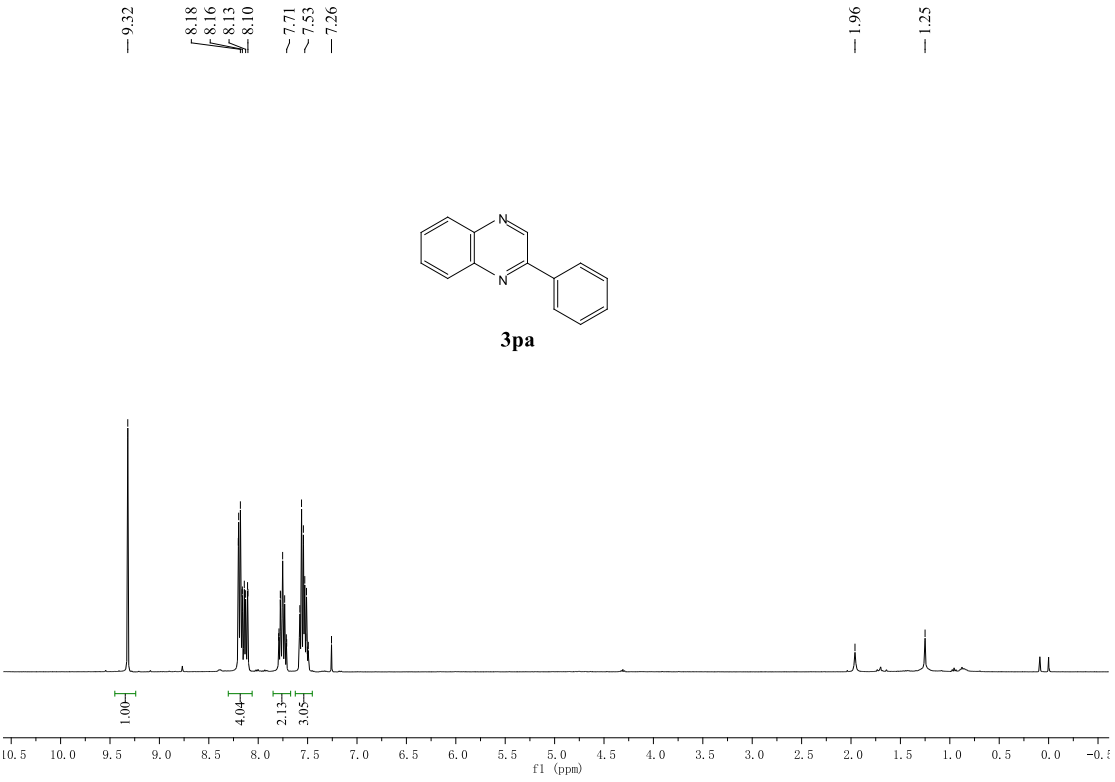
3oa

^{13}C NMR, 100 MHz, $CDCl_3$

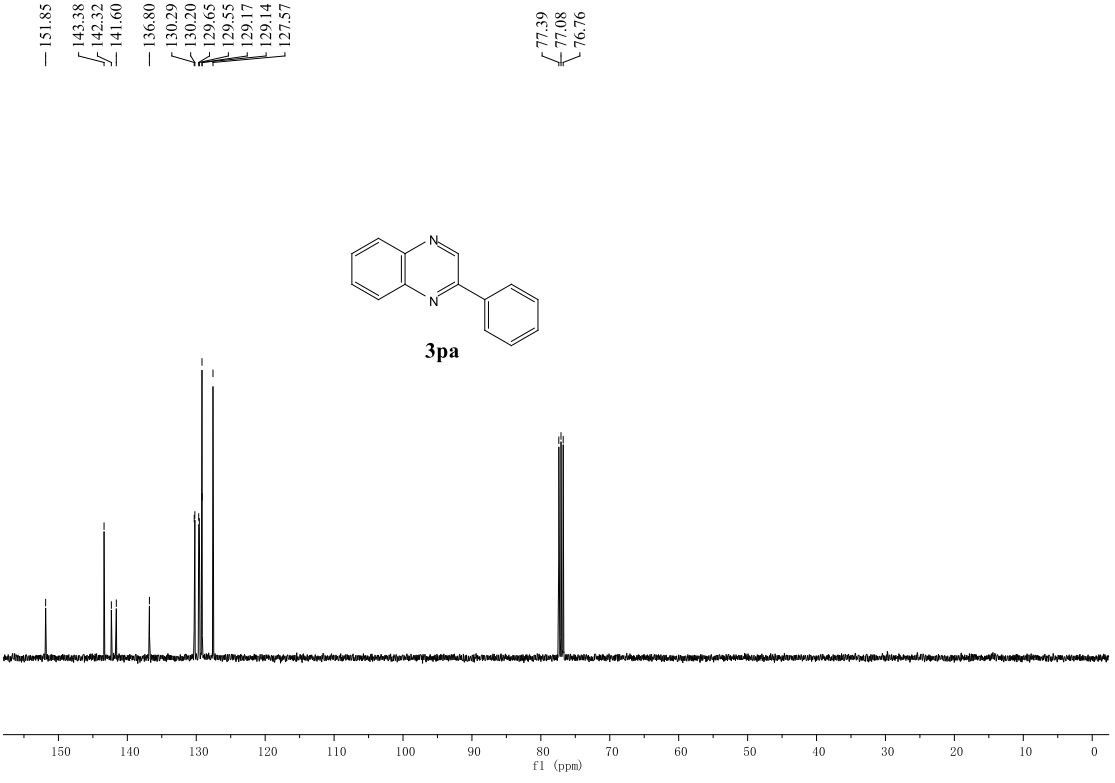


3oa

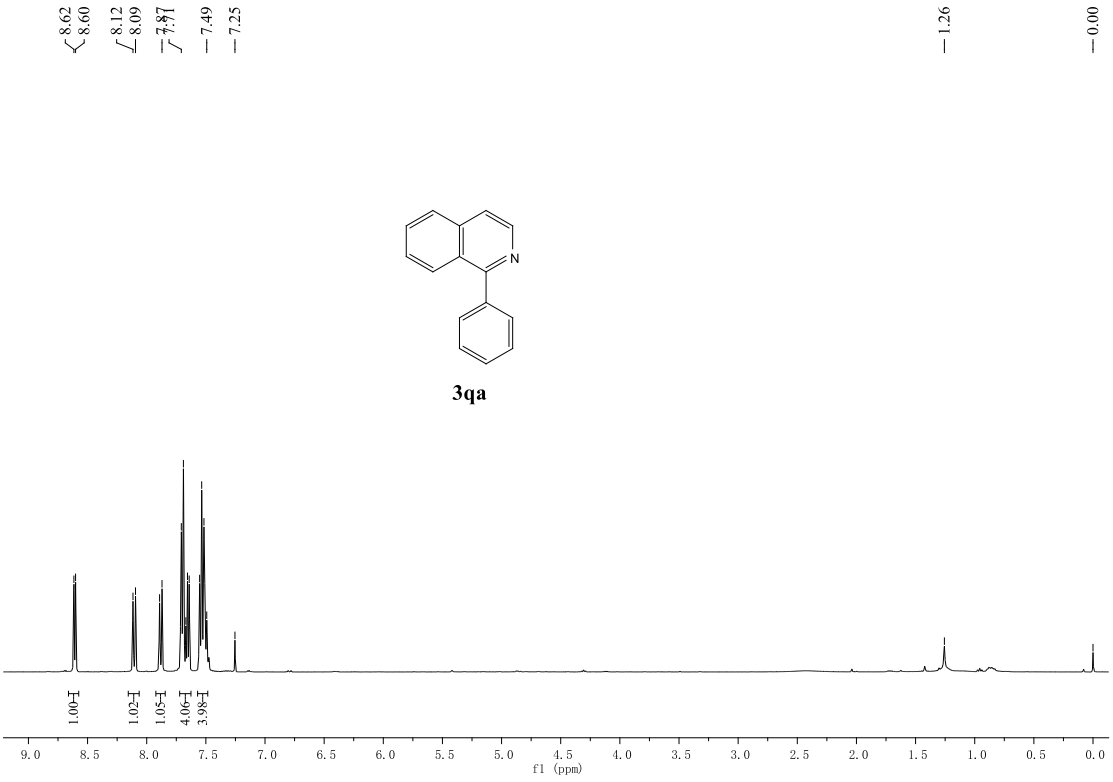
^{1}H NMR, 400 MHz, $CDCl_3$



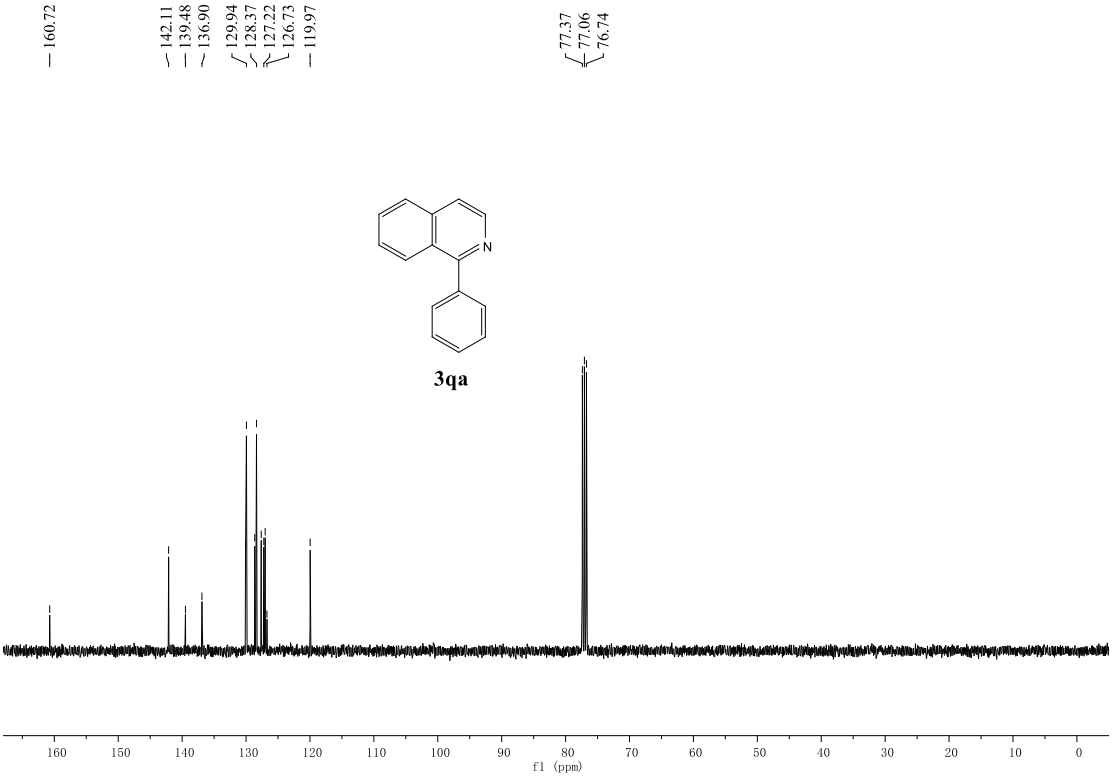
^{13}C NMR, 100 MHz, $CDCl_3$



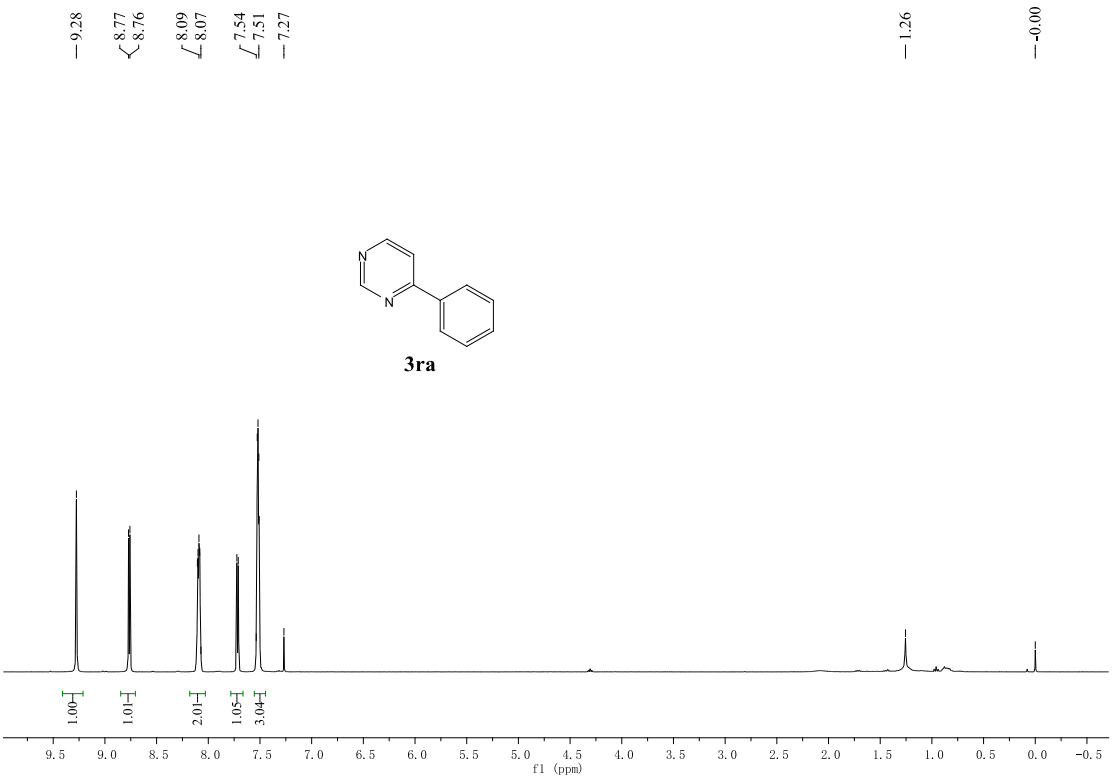
^{1}H NMR, 400 MHz, $CDCl_3$



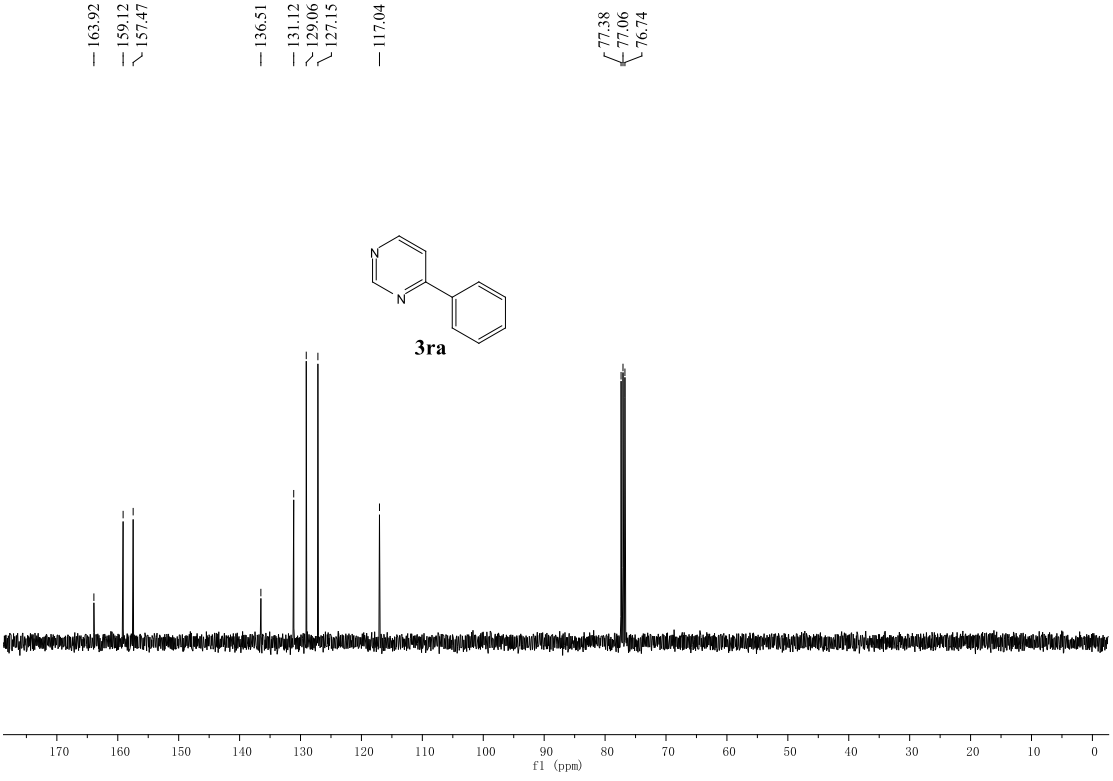
^{13}C NMR, 100 MHz, $CDCl_3$



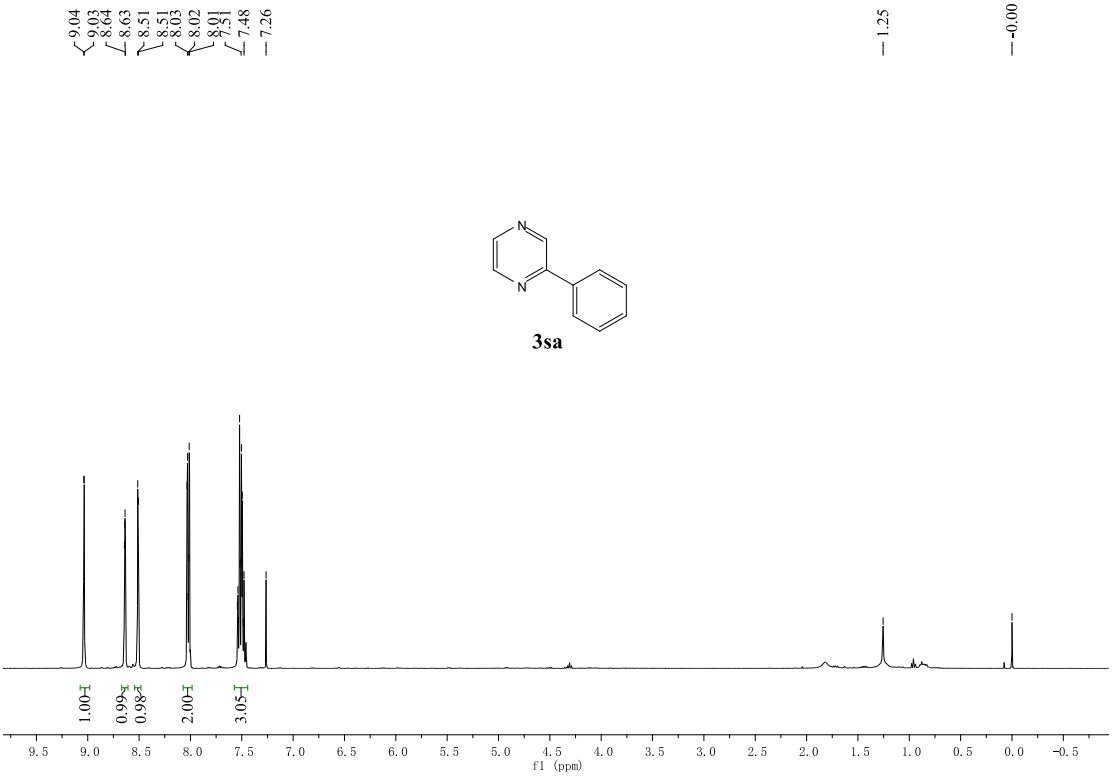
^{1}H NMR, 400 MHz, $CDCl_3$



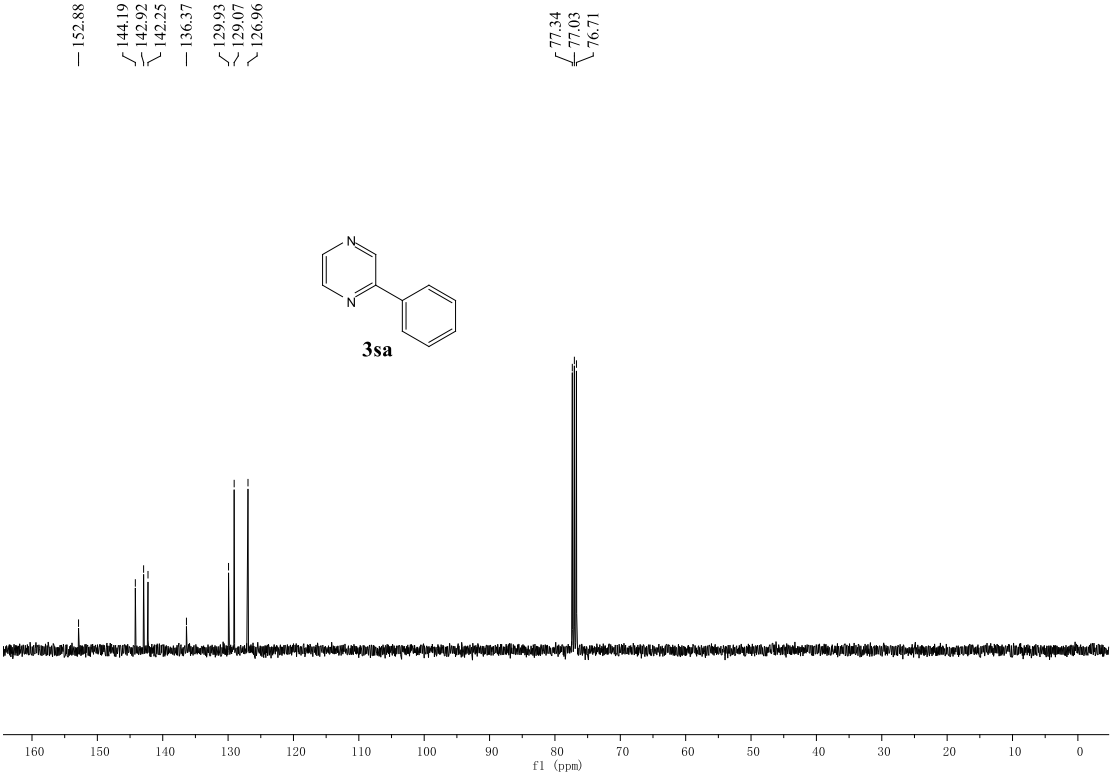
^{13}C NMR, 100 MHz, $CDCl_3$



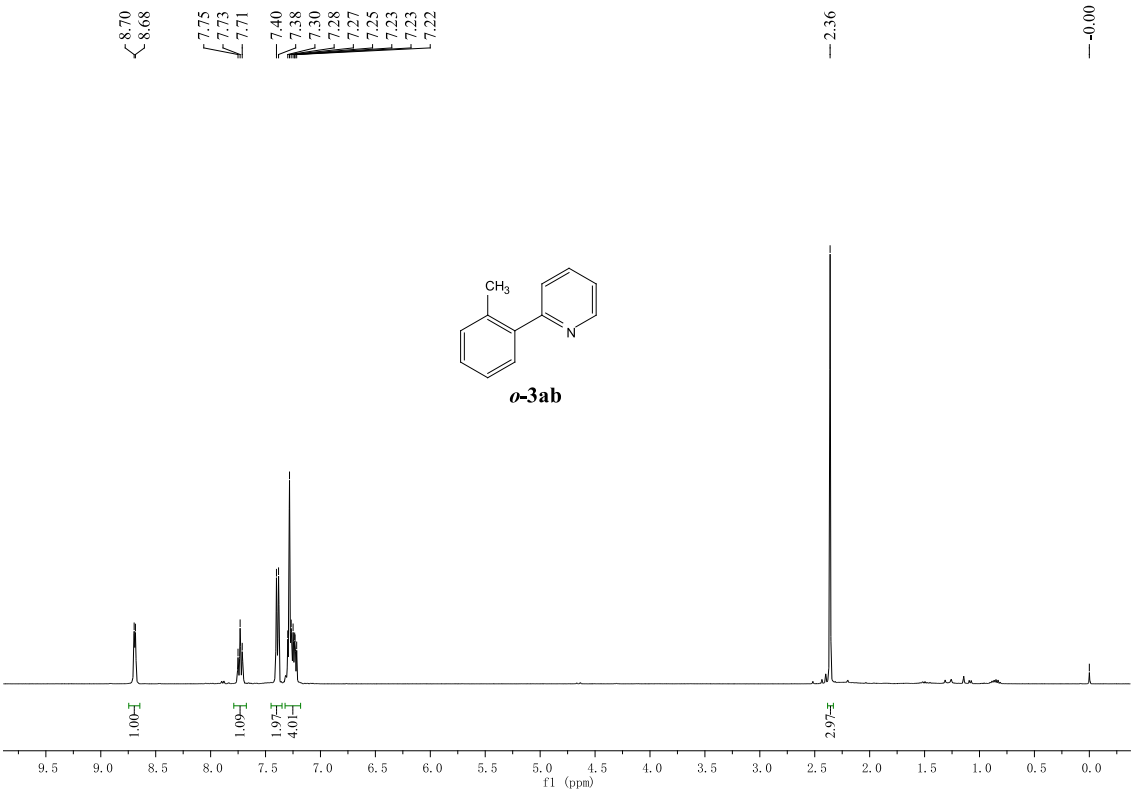
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$

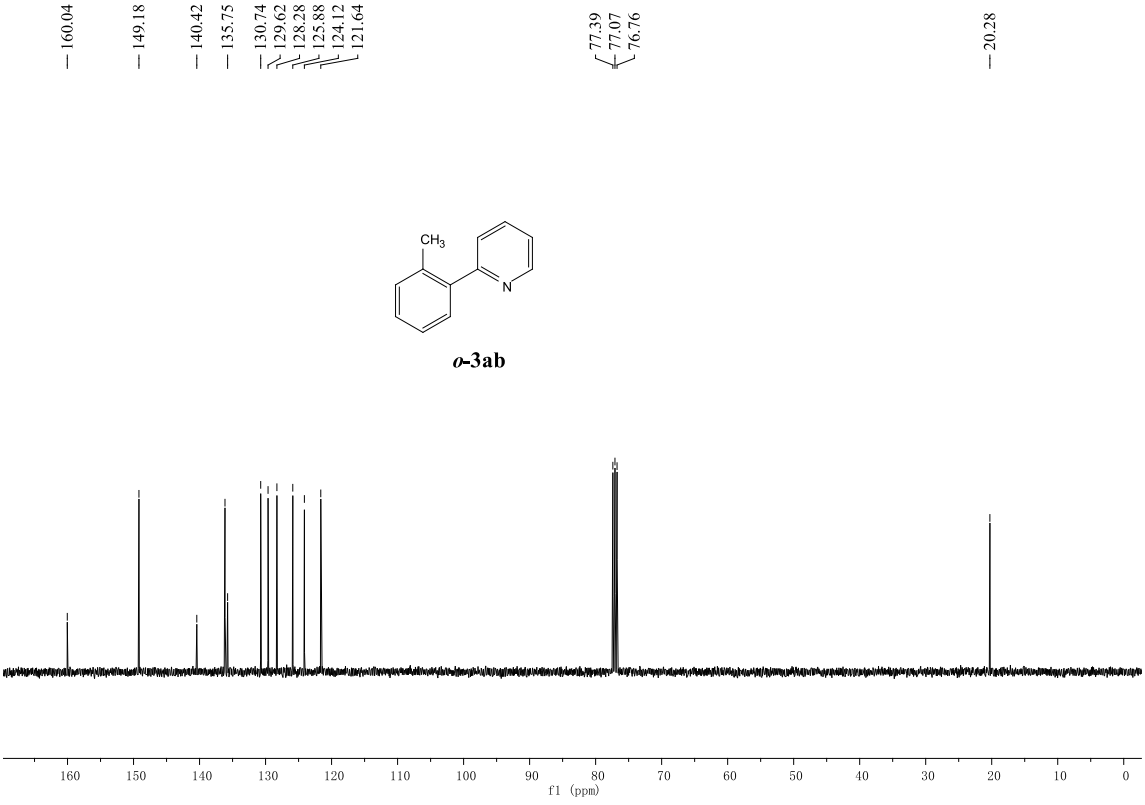


^{1}H NMR, 400 MHz, $CDCl_3$



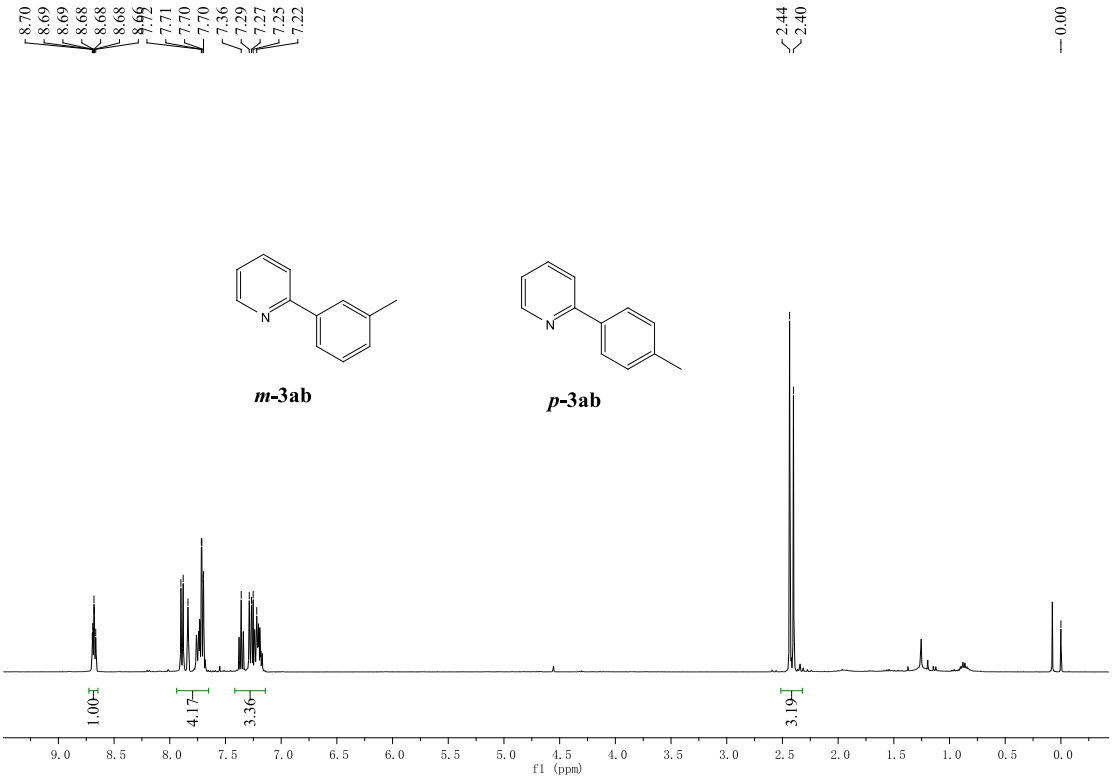
***o*-3ab**

^{13}C NMR, 100 MHz, $CDCl_3$

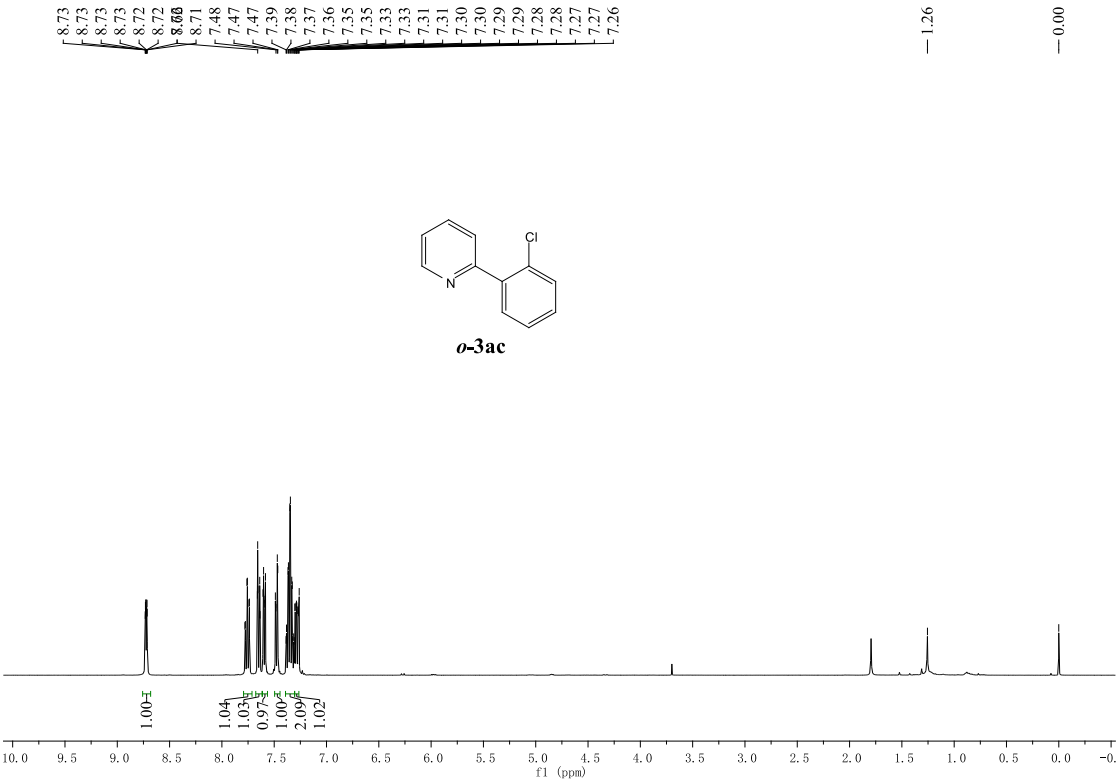


***o*-3ab**

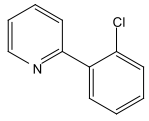
^{1}H NMR, 400 MHz, $CDCl_3$



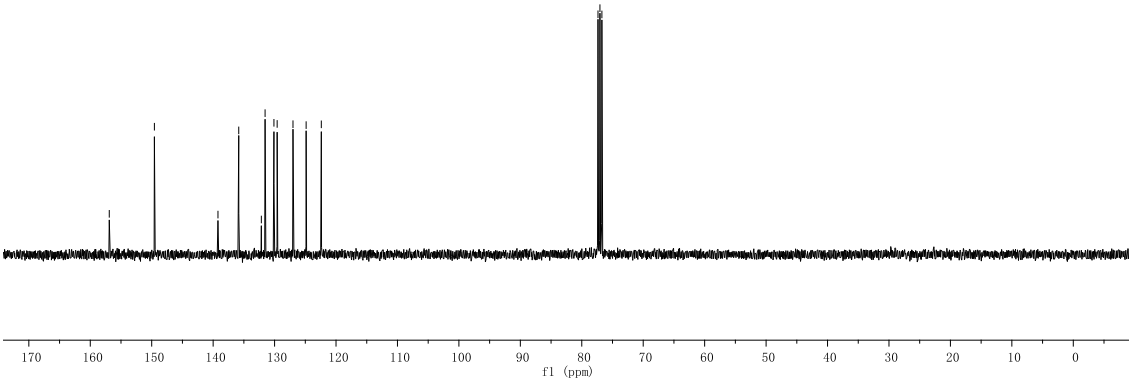
^{1}H NMR, 400 MHz, $CDCl_3$



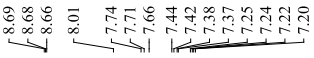
^{13}C NMR, 100 MHz, $CDCl_3$

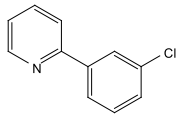


***o*-3ac**

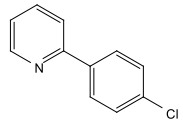


^{1}H NMR, 400 MHz, $CDCl_3$

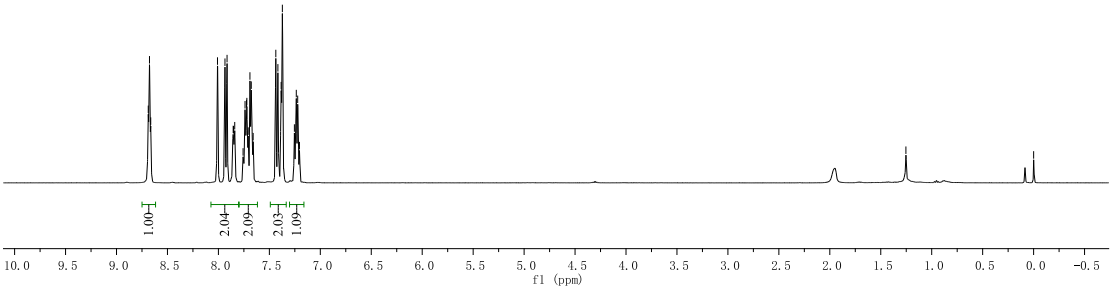




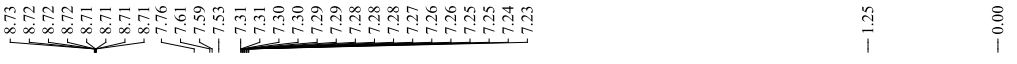
***m*-3ac**

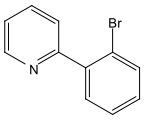


***p*-3ac**

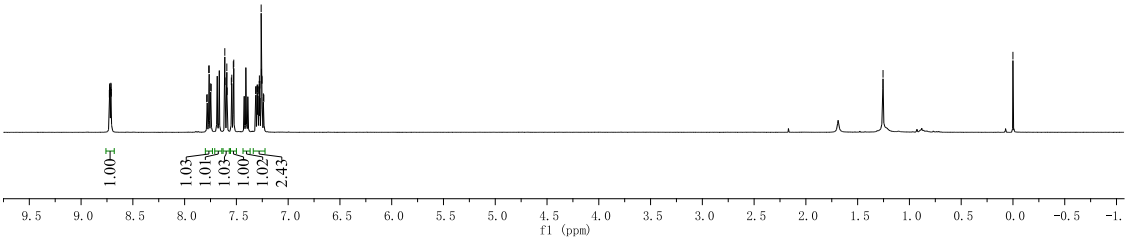


^{1}H NMR, 400 MHz, $CDCl_3$

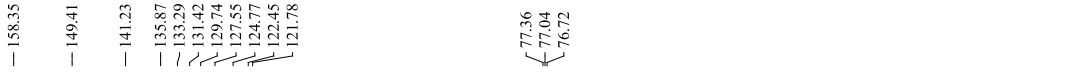


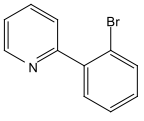


***o*-3ad**



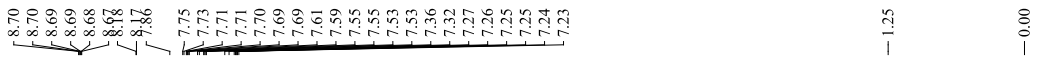
^{13}C NMR, 100 MHz, $CDCl_3$

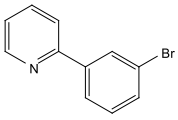




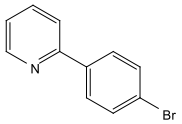
***o*-3ad**

^{1}H NMR, 400 MHz, $CDCl_3$

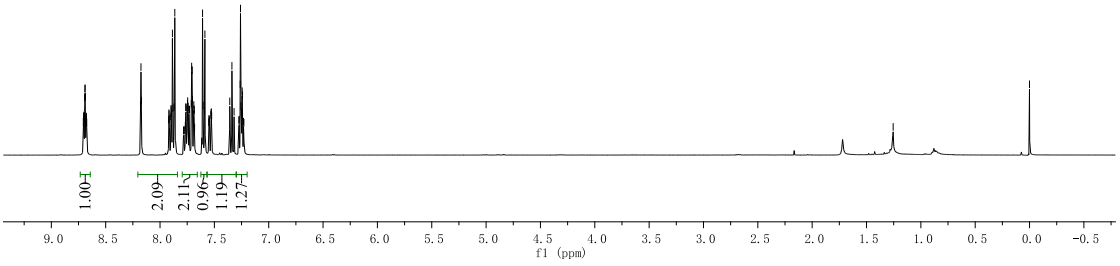




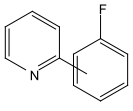
***m*-3ad**



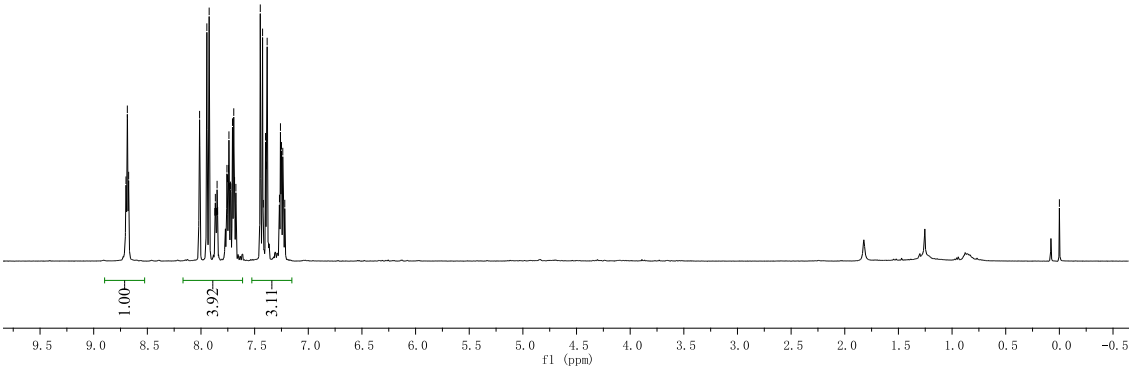
***p*-3ad**



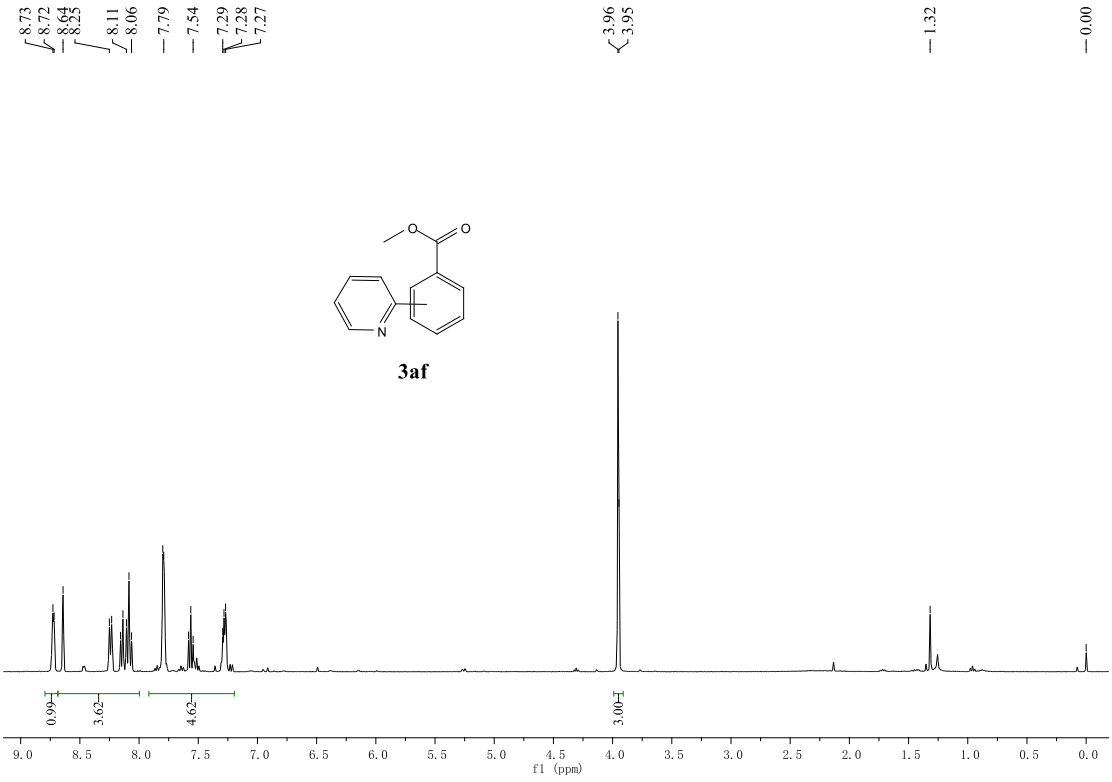
^{1}H NMR, 400 MHz, $CDCl_3$



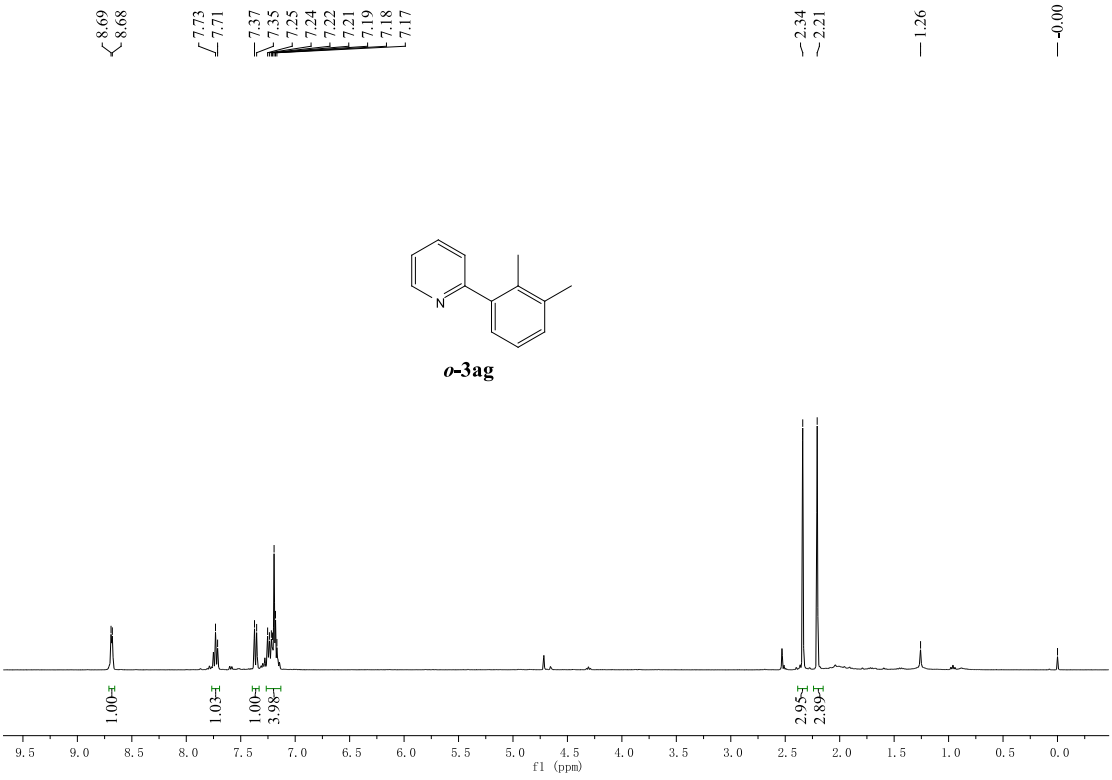
3ae



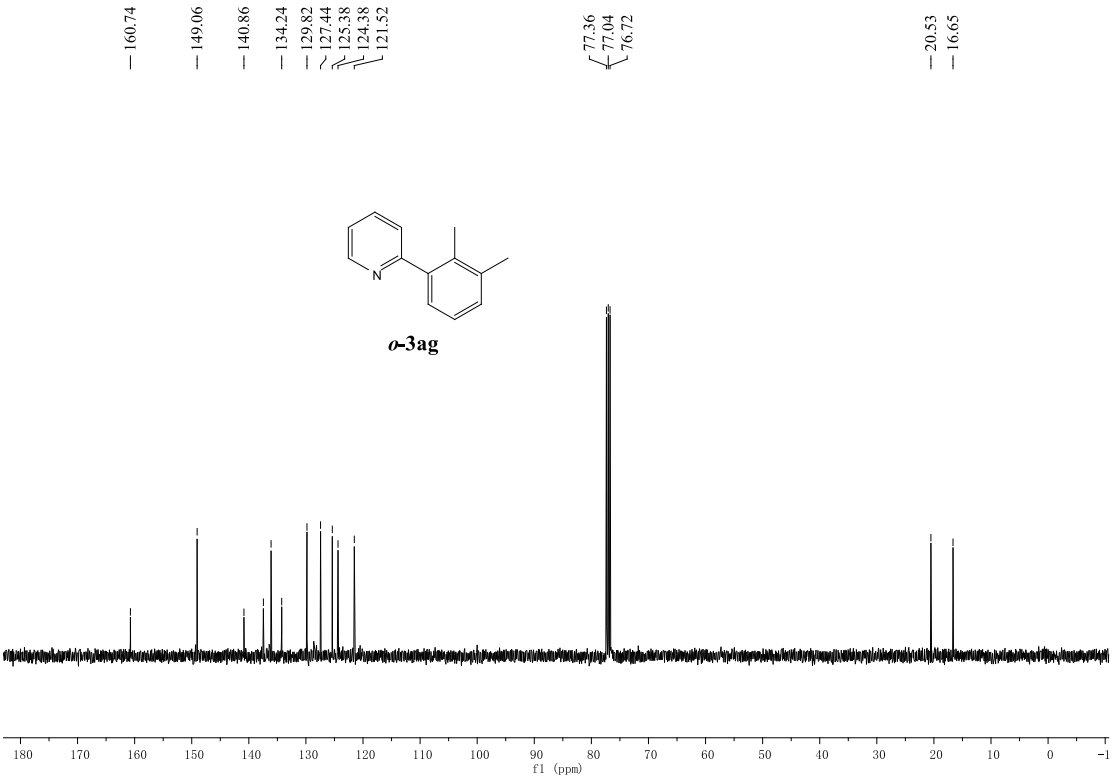
^{1}H NMR, 400 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

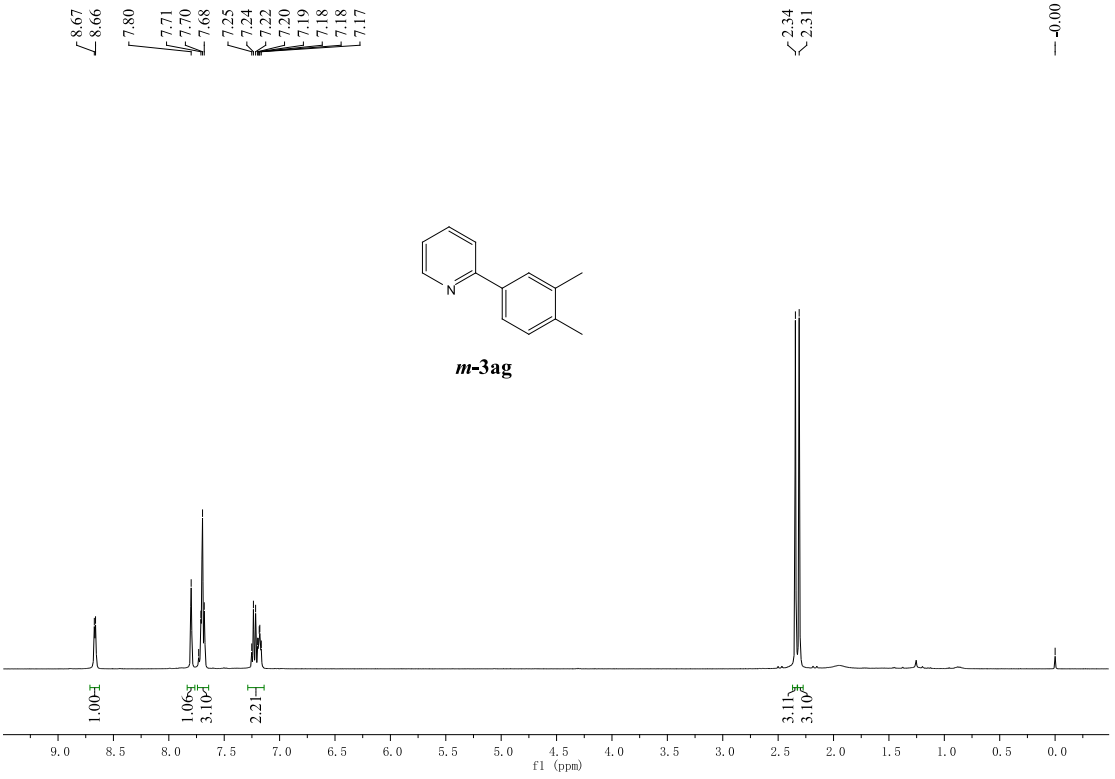


^{13}C NMR, 100 MHz, $CDCl_3$



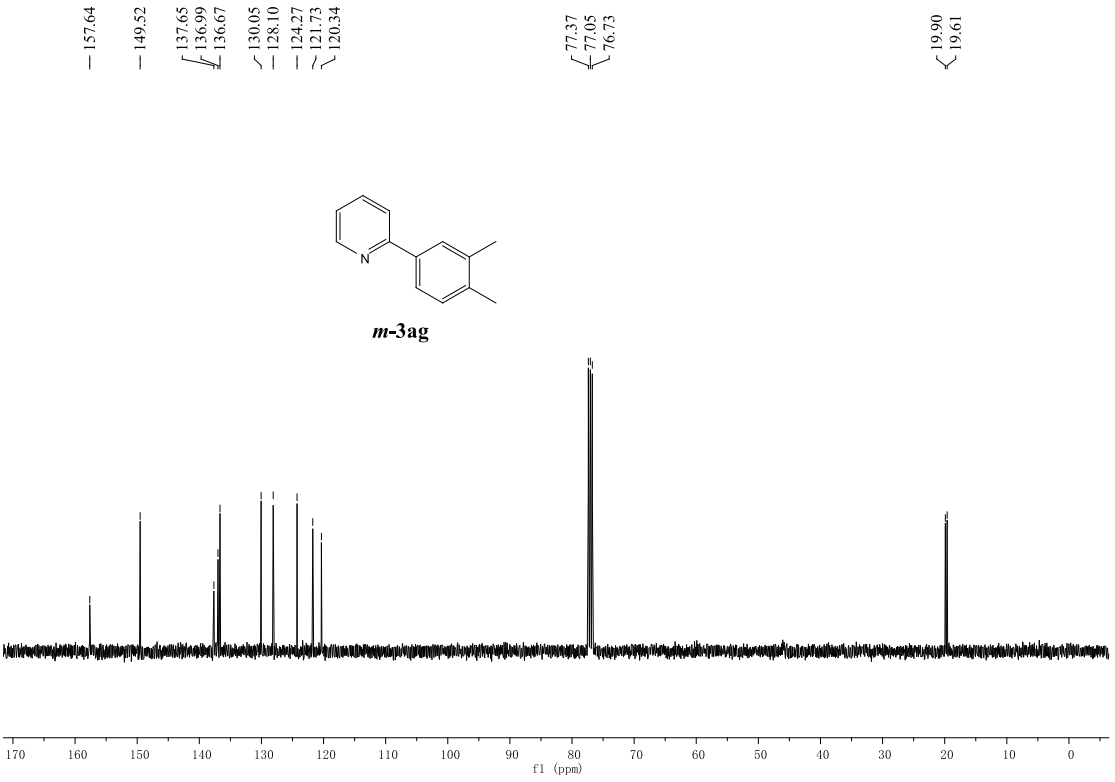
***o*-3ag**

^{1}H NMR, 400 MHz, $CDCl_3$



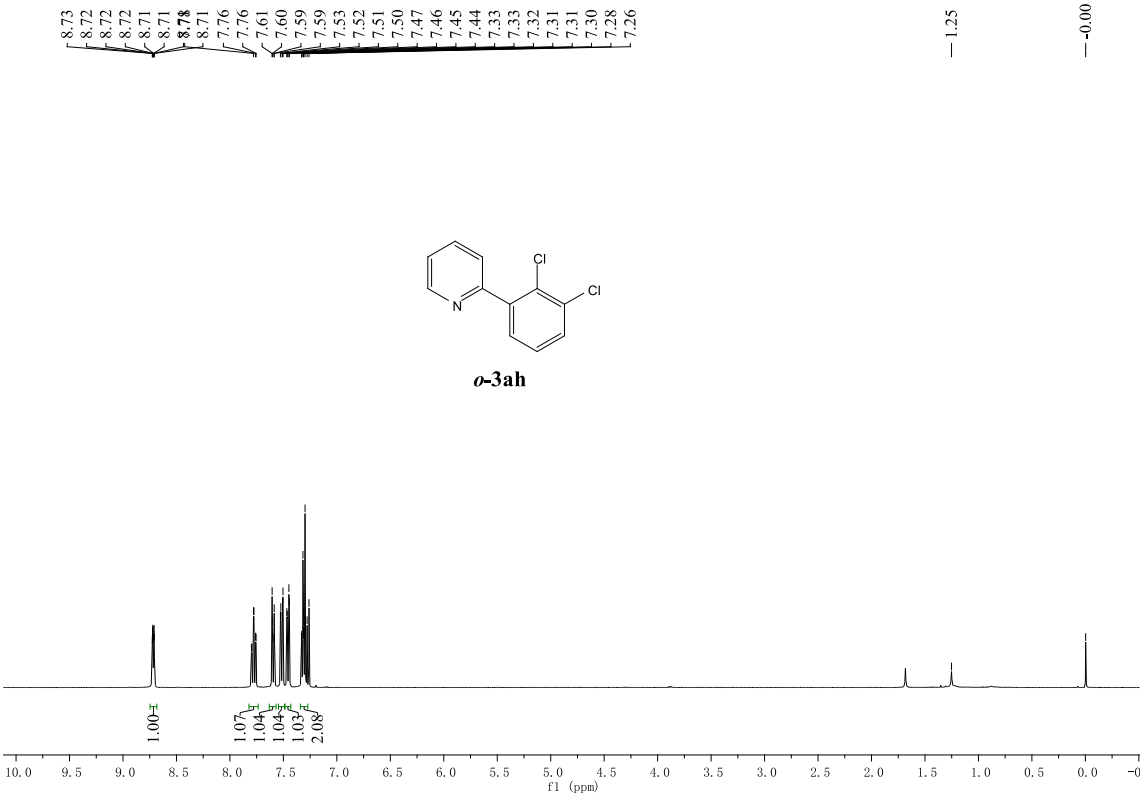
***m*-3ag**

^{13}C NMR, 100 MHz, $CDCl_3$



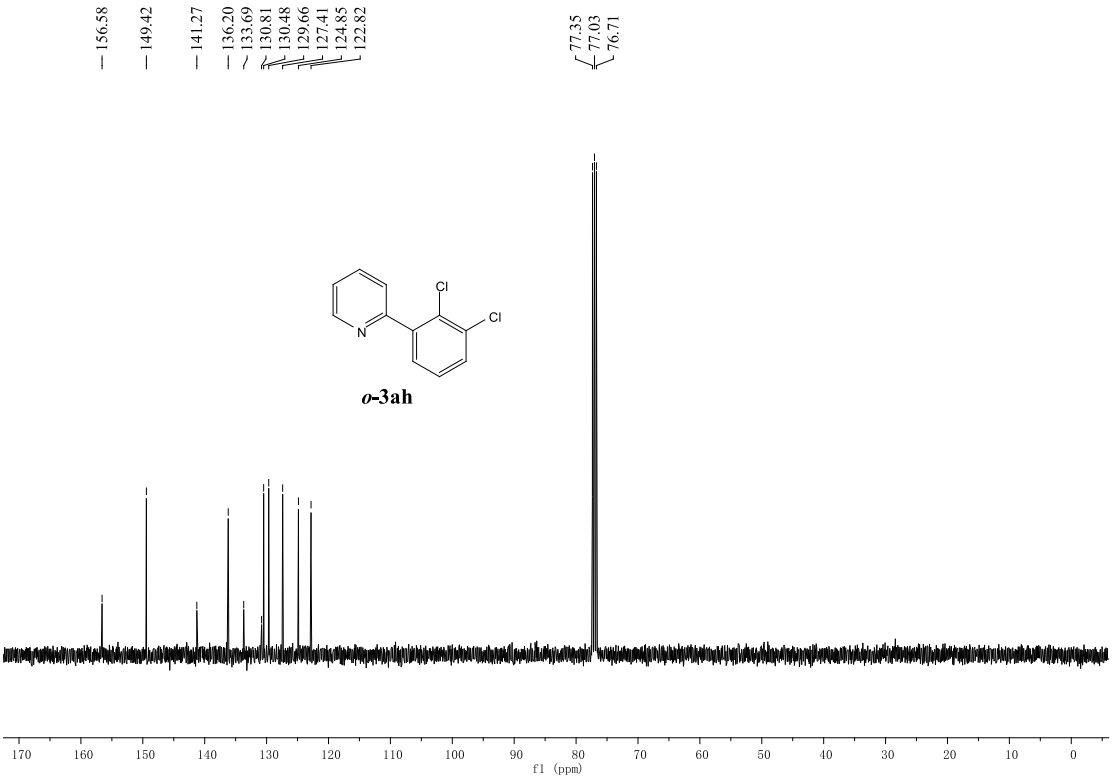
***m*-3ag**

^{1}H NMR, 400 MHz, $CDCl_3$



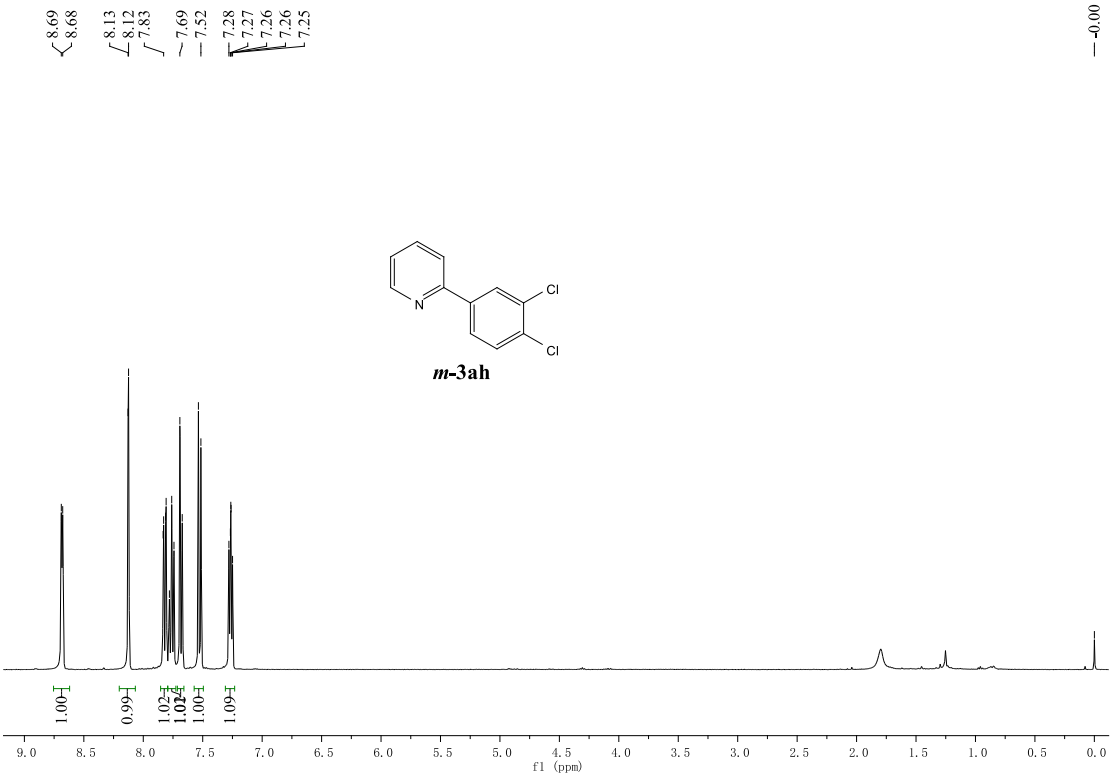
***o*-3ah**

^{13}C NMR, 100 MHz, $CDCl_3$



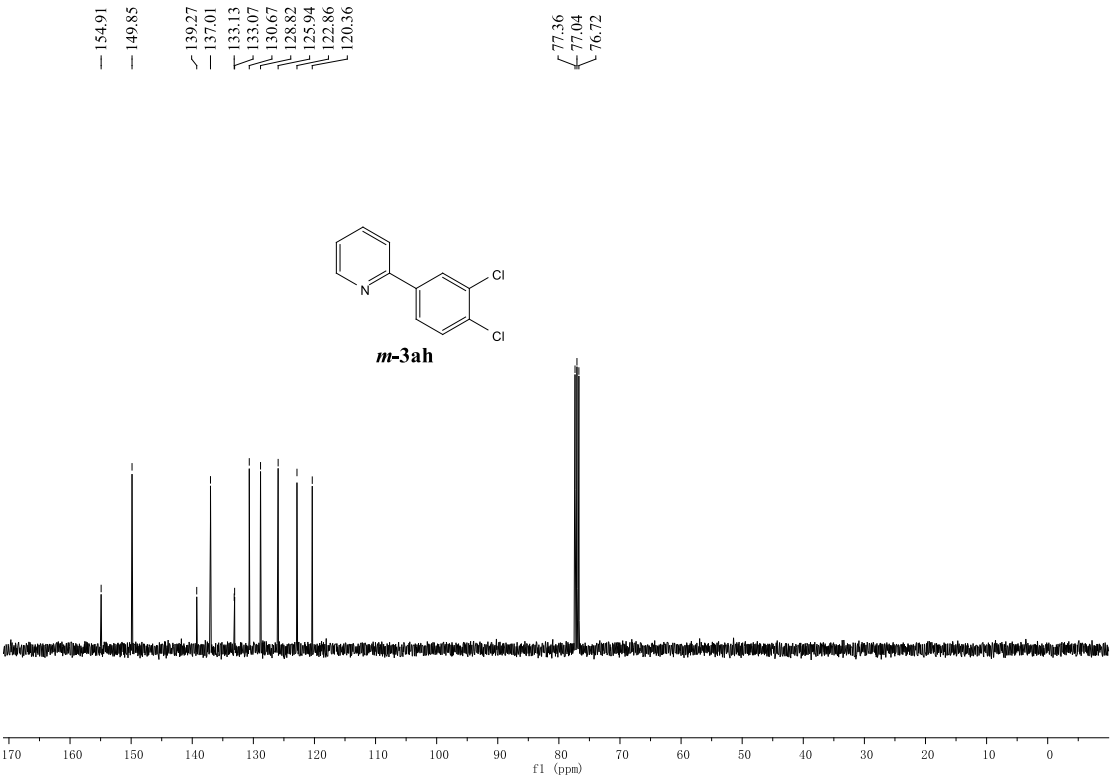
***o*-3ah**

^{1}H NMR, 400 MHz, $CDCl_3$



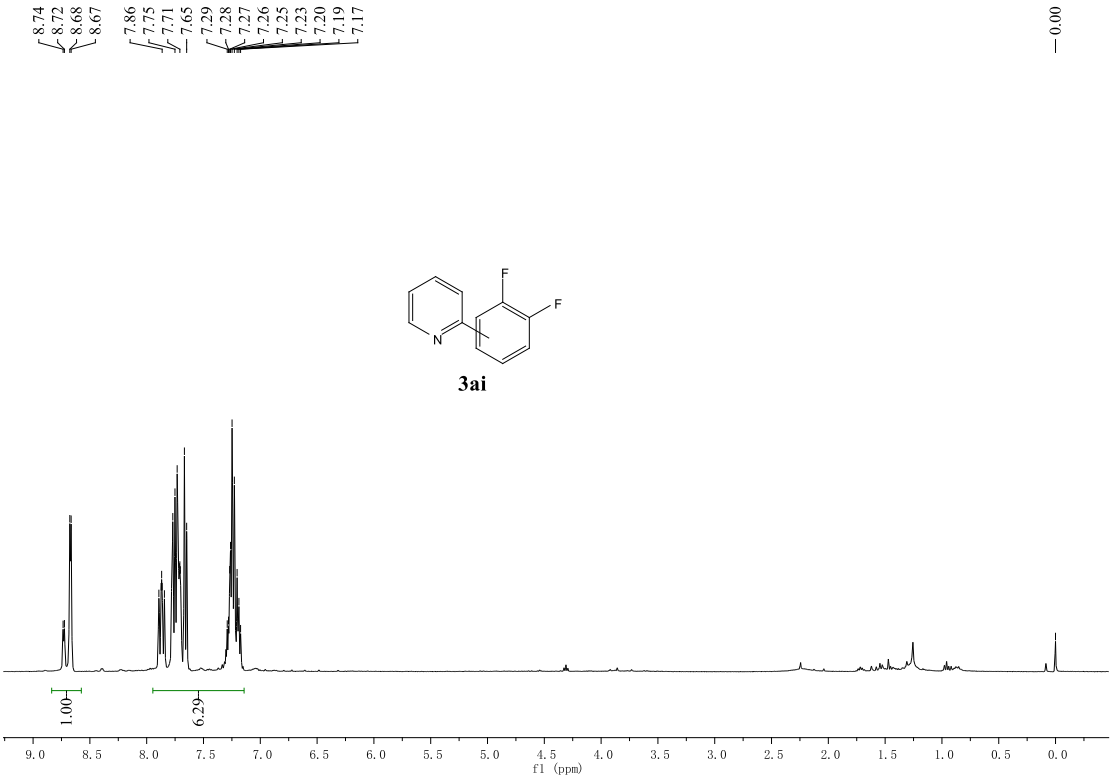
***m*-3ah**

^{13}C NMR, 100 MHz, $CDCl_3$



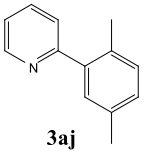
***m*-3ah**

^{1}H NMR, 400 MHz, $CDCl_3$



3ai

^{1}H NMR, 400 MHz, $CDCl_3$



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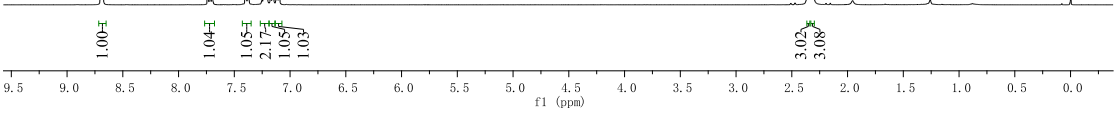
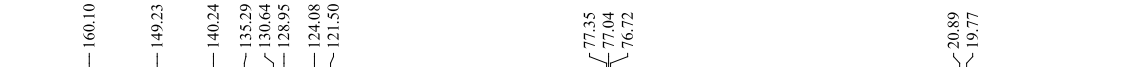
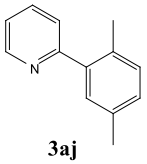


^{13}C NMR, 100 MHz, $CDCl_3$





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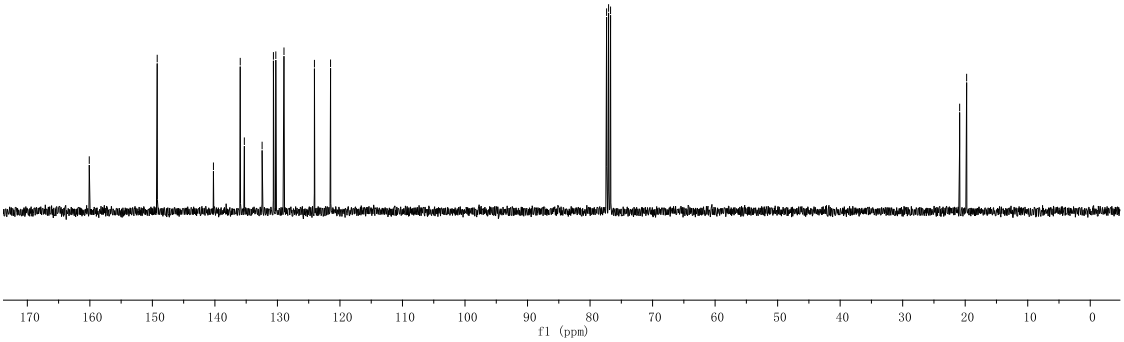
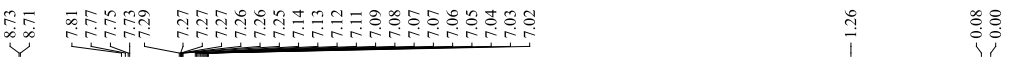
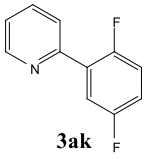


^{1}H NMR, 400 MHz, $CDCl_3$





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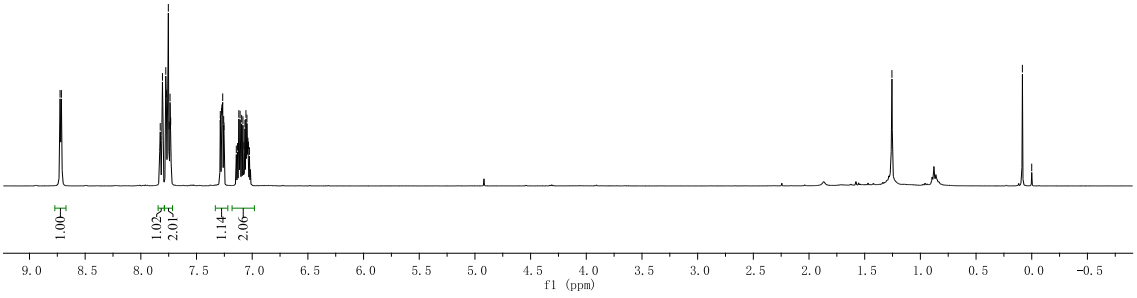
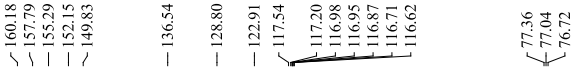
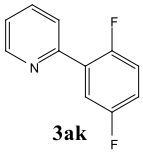


^{13}C NMR, 100 MHz, $CDCl_3$





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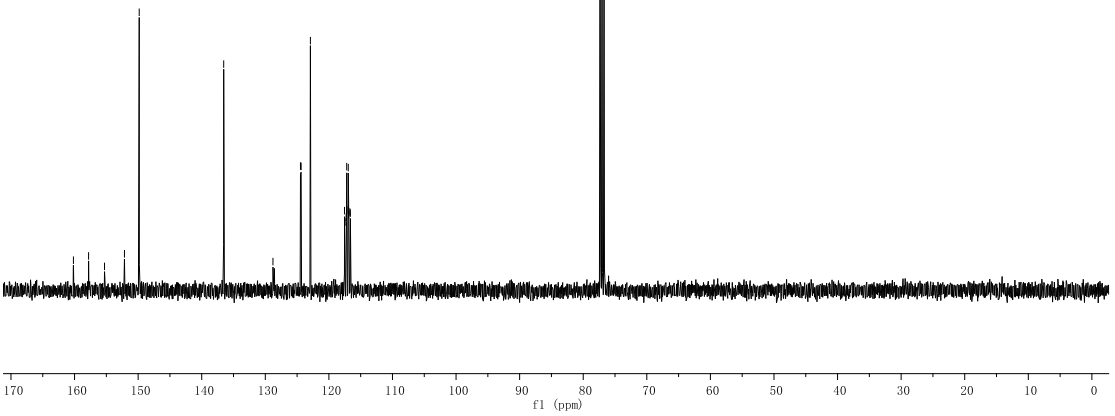
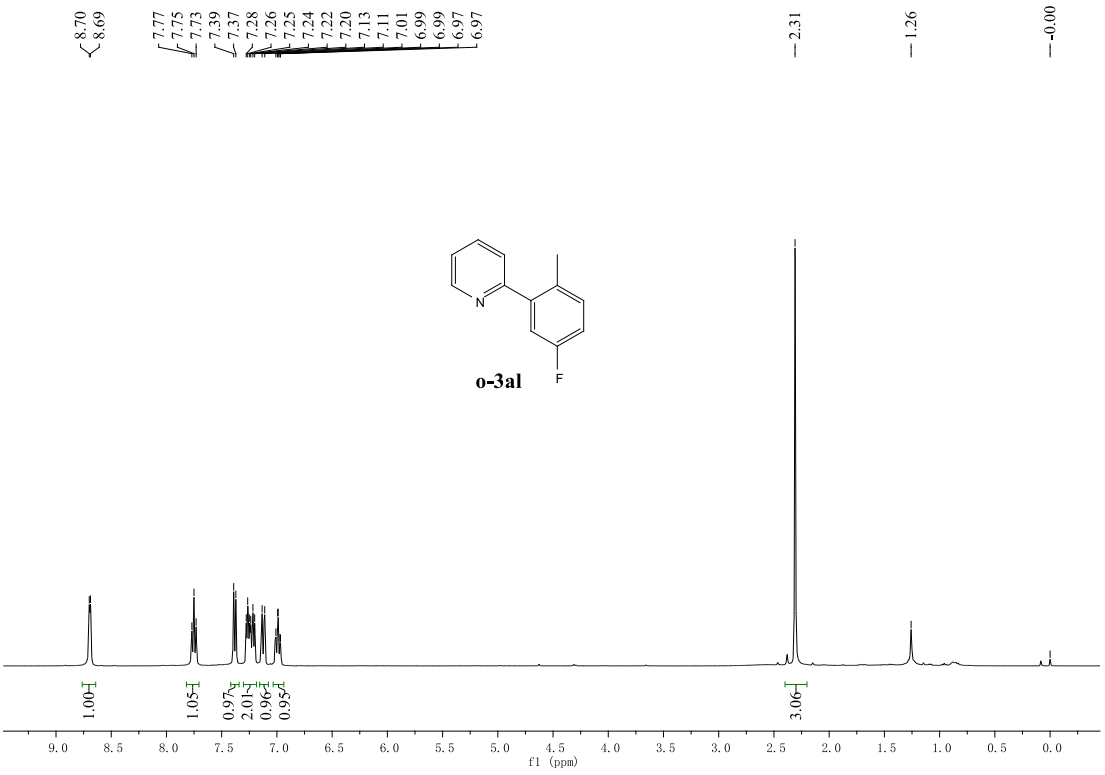
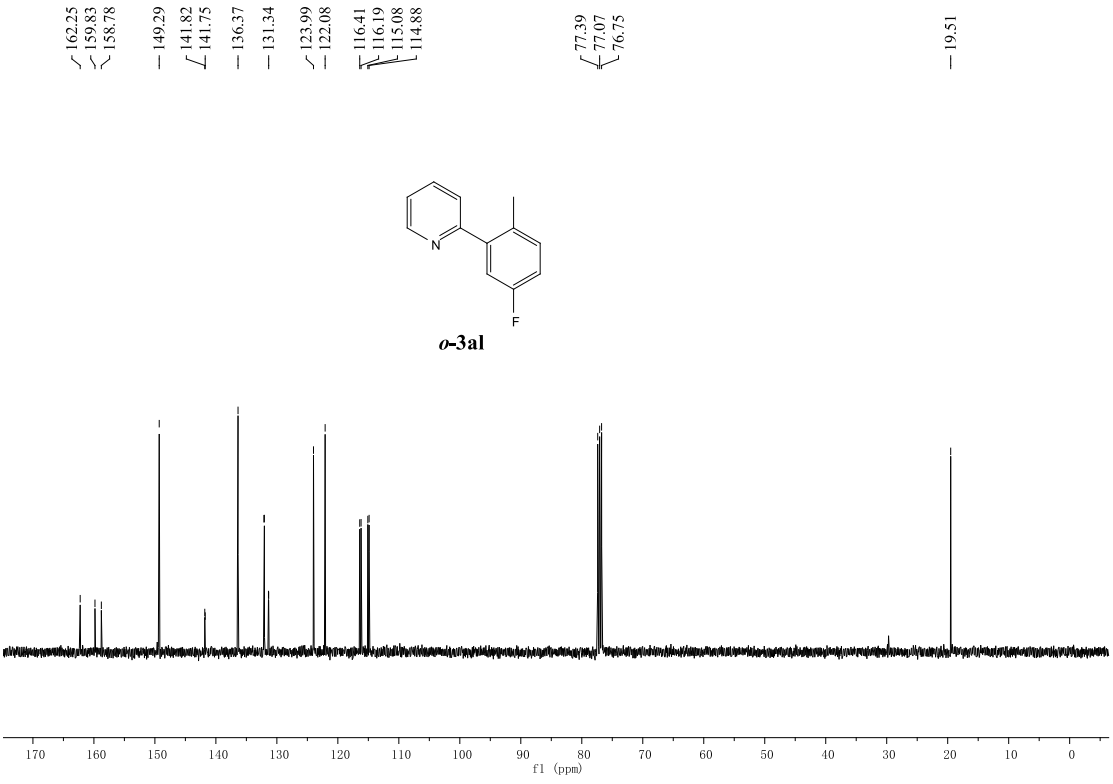


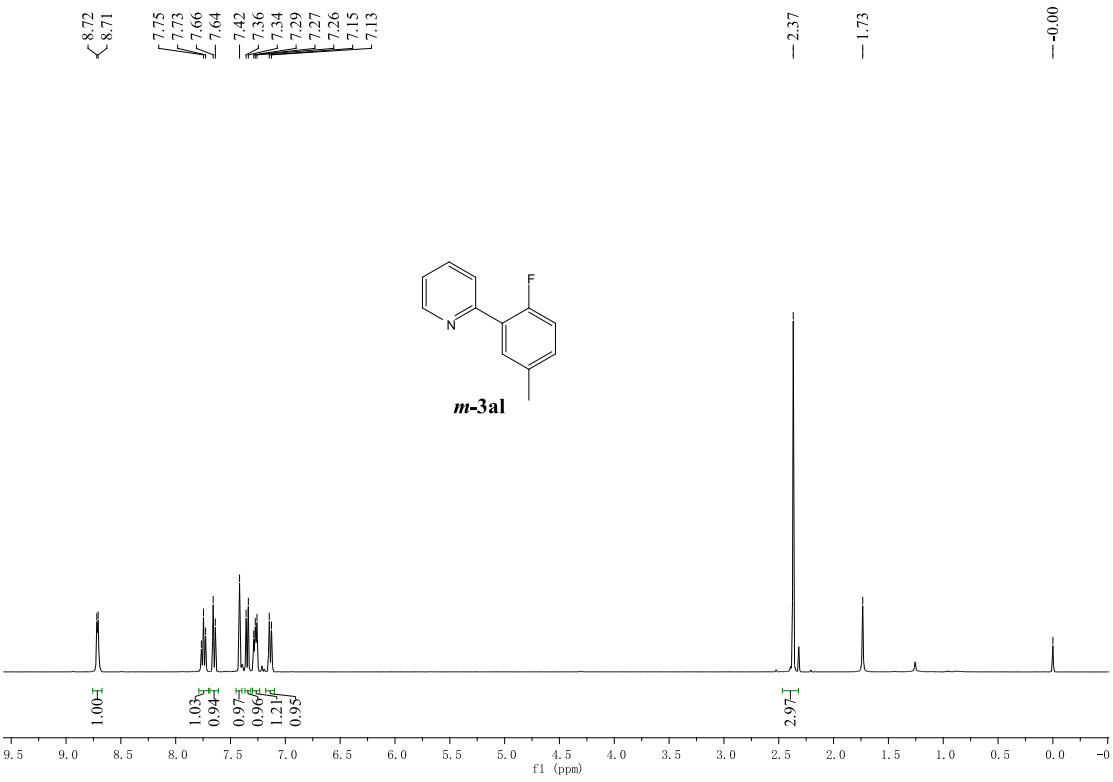
^{1}H NMR, 400 MHz, $CDCl_3$



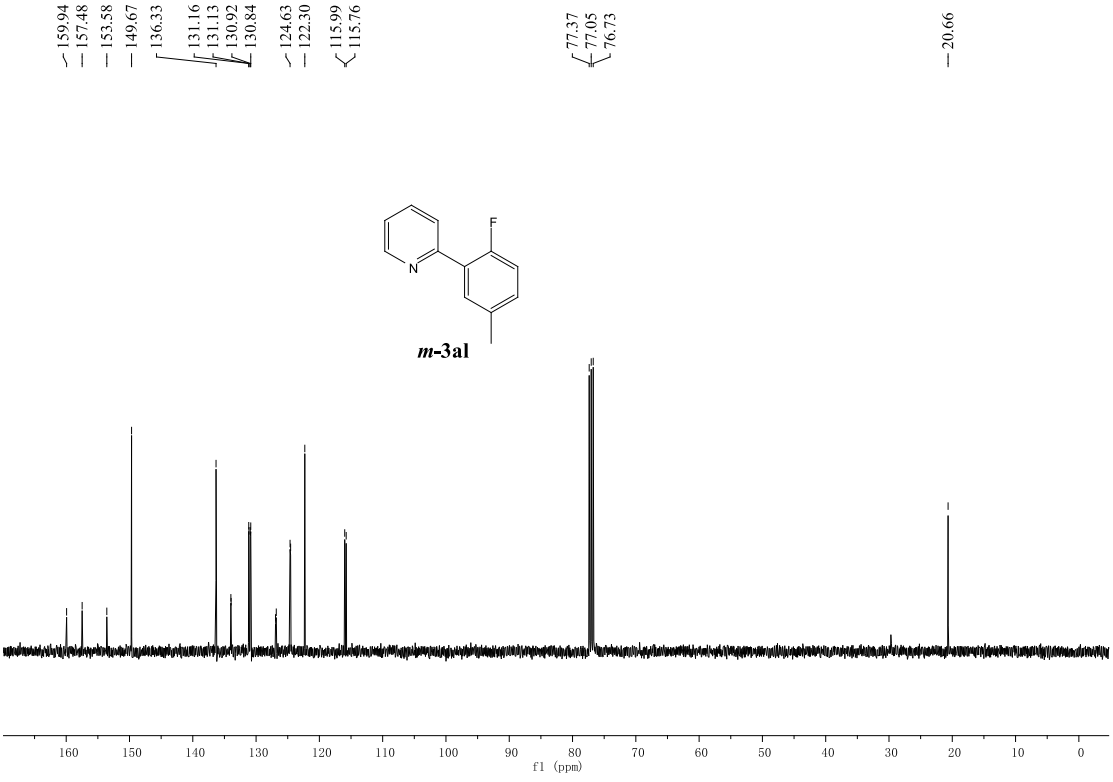
^{13}C NMR, 100 MHz, $CDCl_3$



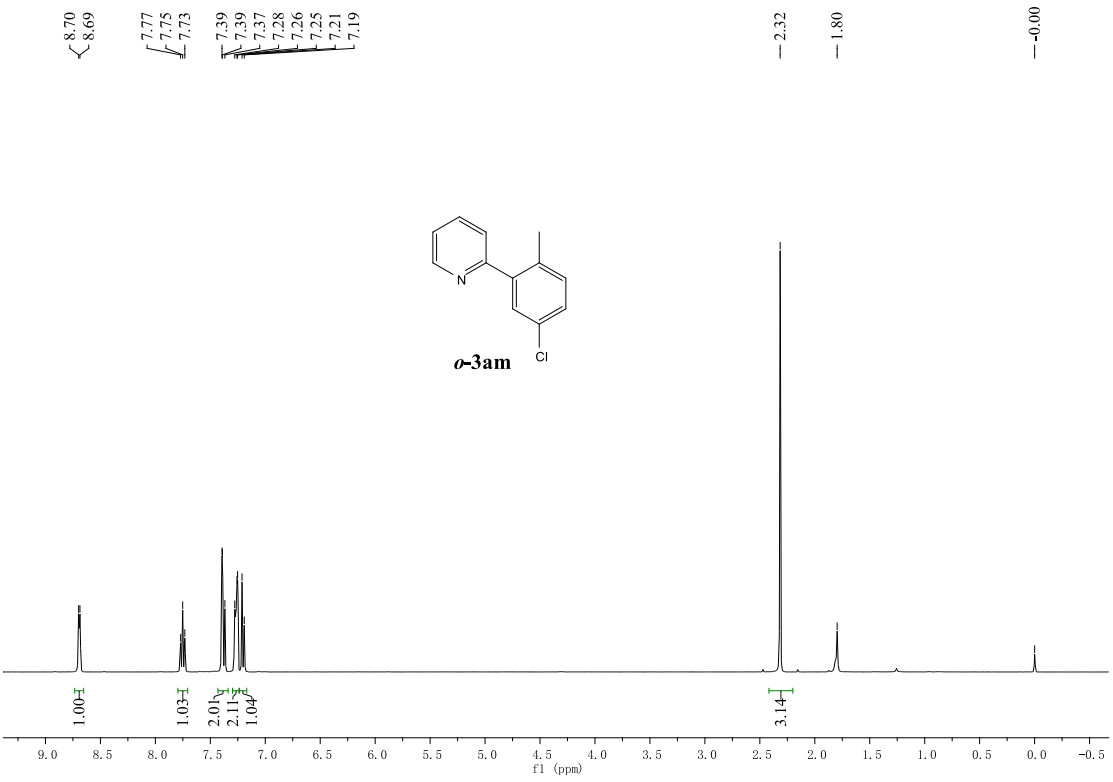
^{1}H NMR, 400 MHz, $CDCl_3$



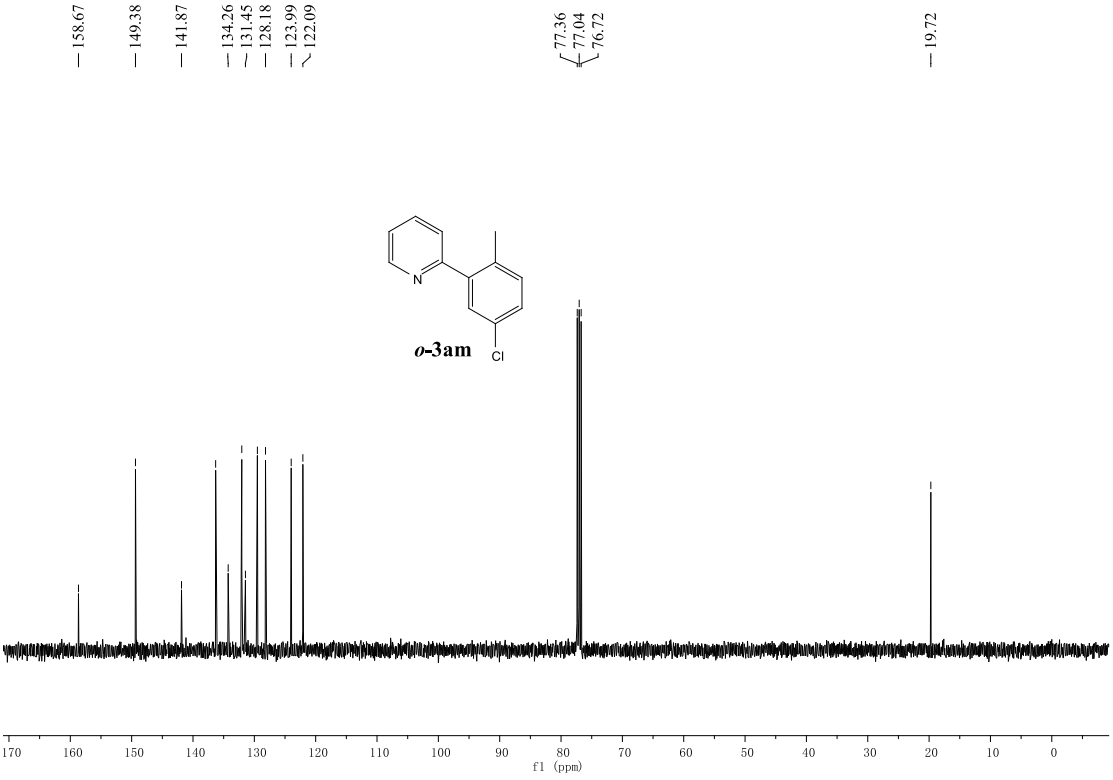
^{13}C NMR, 100 MHz, $CDCl_3$



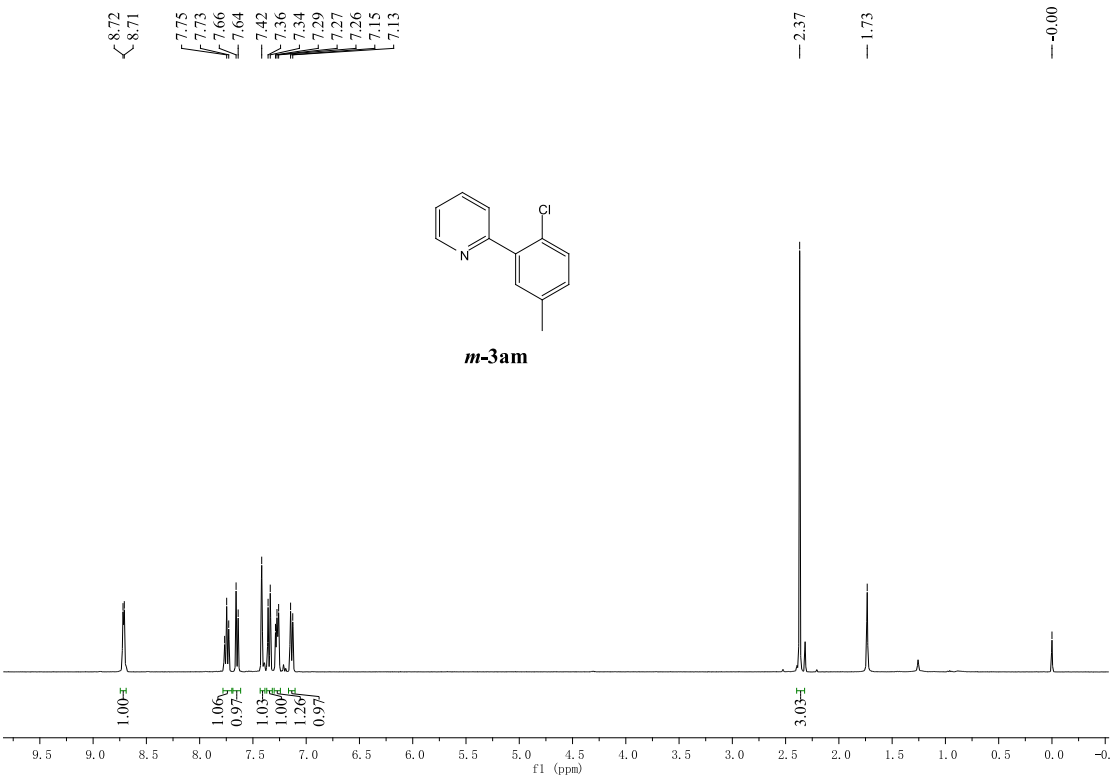
^{1}H NMR, 400 MHz, $CDCl_3$



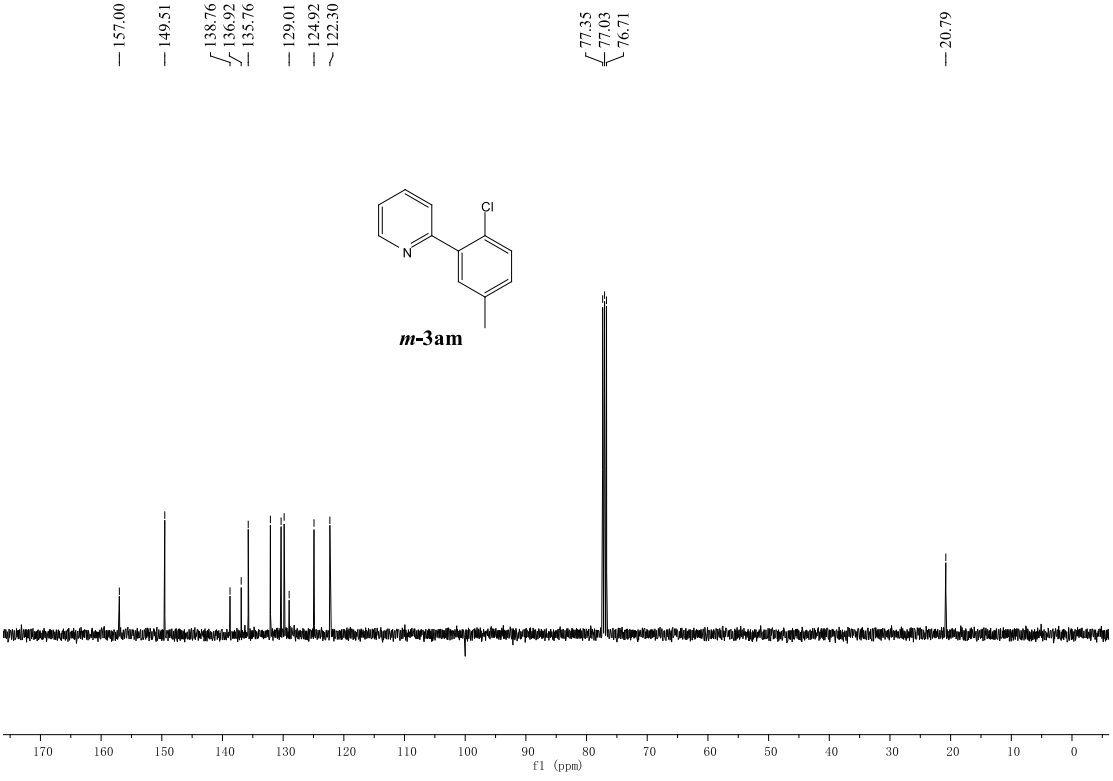
^{13}C NMR, 100 MHz, $CDCl_3$



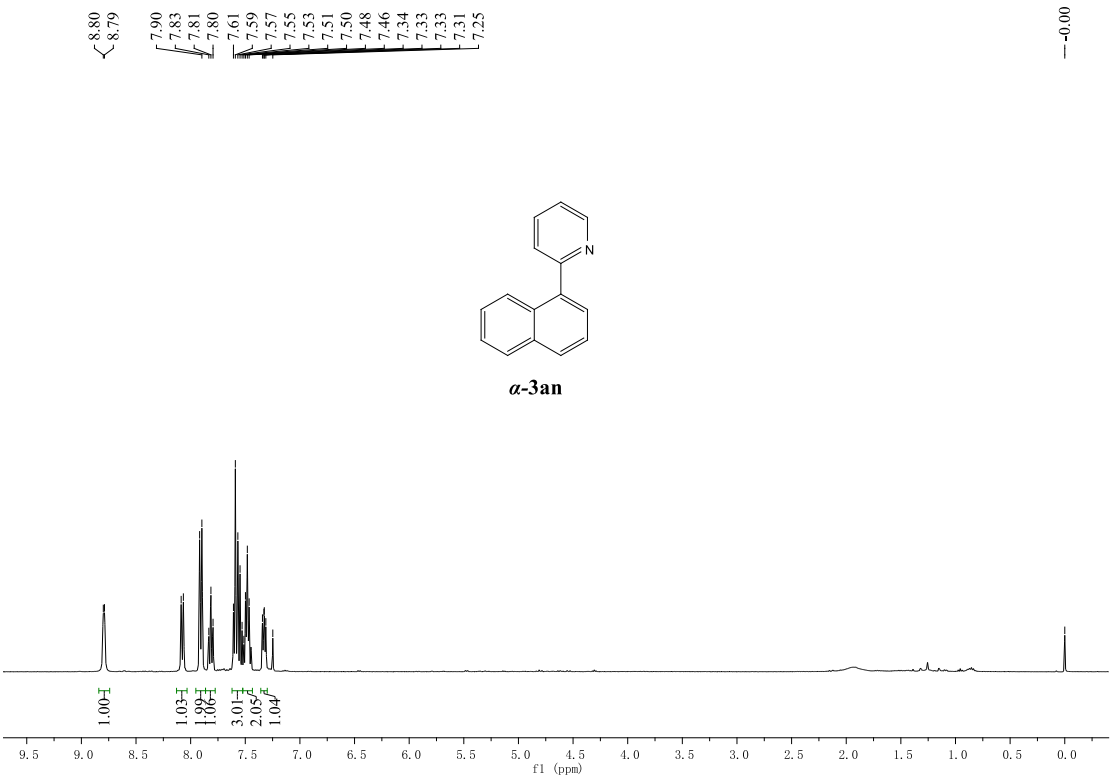
^{1}H NMR, 400 MHz, $CDCl_3$



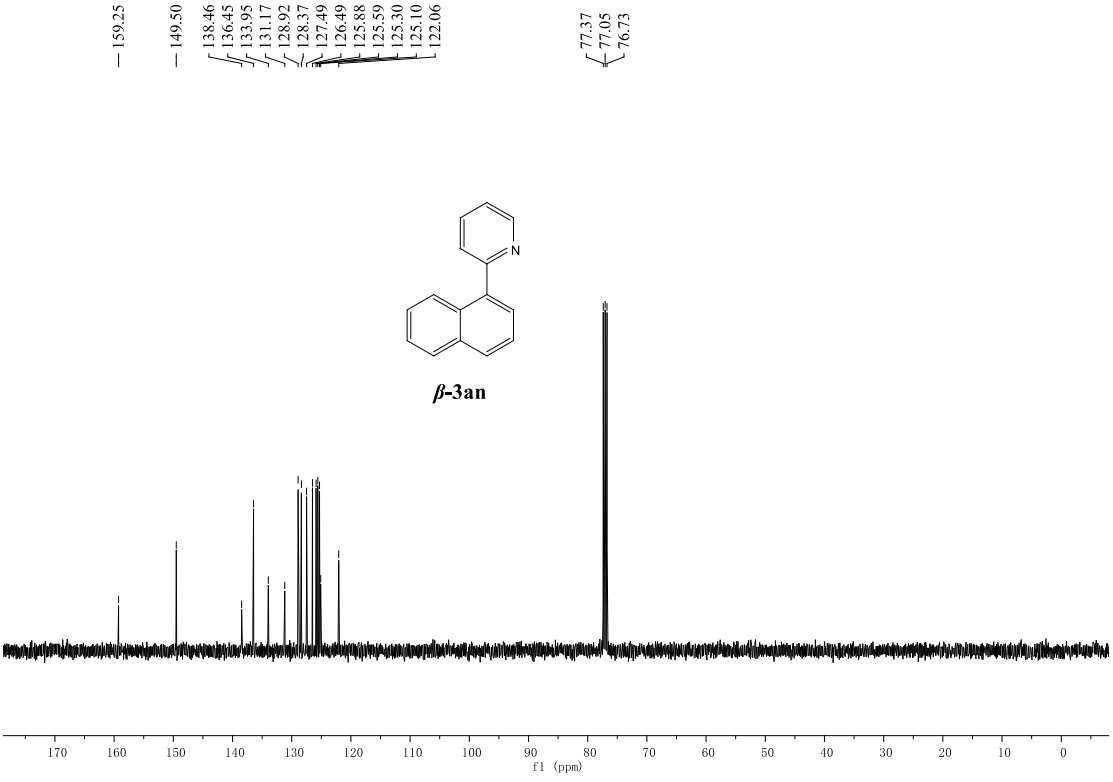
^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



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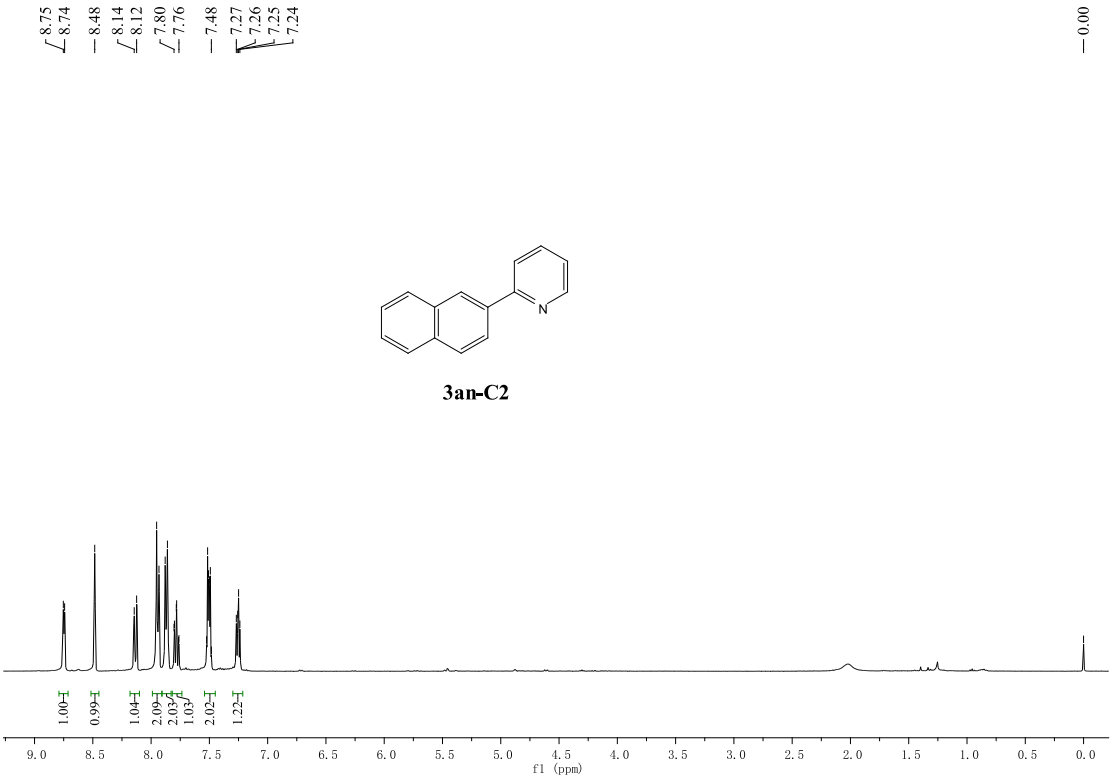

^{13}C NMR, 100 MHz, $CDCl_3$