Supporting Information

Merrifield resin-supported quinone as the Efficient Biomimetic Catalyst for Metal-Free, Base-Free, Chemoselective Synthesis of 2,4,6-Trisubstituted Pyridines†

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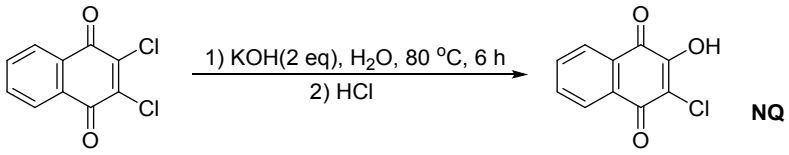
1. General Methods and Materials

All the obtained products were characterized by ^{1}H-NMR, ^{13}C-NMR and melting points (m.p), melting points were measured by an Electrothemal WRS X-4A microscopy digital apparatus and without correction. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker Advance III HD 400 MHz spectrometer and referenced to $CDCl_3$ (7.26 ppm for ^{1}H, and 77.1 ppm for ^{13}C) or DMSO-d_6 (2.50 ppm for ^{1}H, and 39.5 ppm for ^{13}C) with tetramethylsilane as internal standard (0 ppm). TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at shortwave UV light (254 nm). IR spectra were recorded on total reflection Fourier infrared spectrometer (NICOLET 6700). SEM image and EDS spectra was performed on a HITACHI S-4800 field-emission scanning electron microscope. XPS data were recorded with electron energy analyzer (ESCALAB 250Xi, Thermo Fisher Co, USA). Unless otherwise stated, all the reagents were purchased from commercial sources (J&K Chemic, Acros, TCI, SCRC, Energy Chemical), used without further purification.

2. Preparation of NQ-MR catalyst

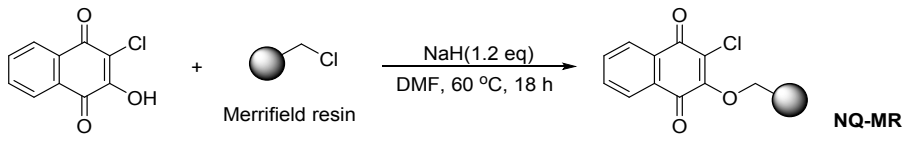
2.1 Synthesis of 2-chloro-3-hydroxy-1,4-naphthoquinone (NQ)



To an oven-dried 50 mL round bottom flask were successively added 2,3-dichloro-1,4-naphthoquinone (1.135 g, 5 mmol) dissolved by deionized water (20 mL) under air. To this suspension, 20 ml aqueous solution of KOH (0.560 g, 10 mmol) was added dropwise at room temperature. Then, the resulting mixture was stirred at 70 °C for 3 hours. Red color solution was obtained. Next, the residual dichloronaphthylquinone was extracted with dichloromethane from the reaction mixture. And then the red mixture in water was acidified with a few drops of concentrated hydrochloric acid till pH ≈ 2. Yellow solid washed with ether and dried over vacuum was our target product **NQ** (0.857 g, 82% yield).

Yellow solid; Mp. 213-215 °C; ^{1}H NMR (400 MHz, DMSO) δ 8.04 – 7.98 (m, 2H), 7.89 – 7.79 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 179.74, 178.64, 156.66, 135.15, 134.08, 131.88, 130.27, 126.80, 126.68, 118.26. HRMS (ESI) m/z Calculated for $C_{10}H_6ClO_3$ $[M+H]^+$ 209.0005, found 209.0002.

2.2 Preparation of NQ-MR



Merrifield resin (MR) was a polystyrene microsphere having a surface rich in chloromethyl groups. The resin used in this experiment was a direct commercial product having a surface chlorine content of 2-3 mmol/g. Pre-washed MR polymer materials (0.420 g, 0.8-1.2 mmol Cl) were allowed to swell in 8 mL DMF for 4 hours. Then the NQ (0.209 g, 1 mmol) was added to the swollen polymer in DMF with NaH (0.048 g, 1.2 mmol) 60% dispersion in mineral oil. The reaction mixture was then stirred at 60 ^{o}C for 18 hours and quenched by a small amount of deionized water. After filtering off the solvent, the crude product was ultrasonic-assisted washed by deionized water, ethanol and diethyl ether sequentially, dried in a vacuum oven, and collected (0.552 g, 32% loading, w/w), leading to brown red solid product NQ-MR.

3. Characterization of NQ-MR catalyst

3.1 FT-IR spectra of Merrifield resin, NQ-MR and NQ

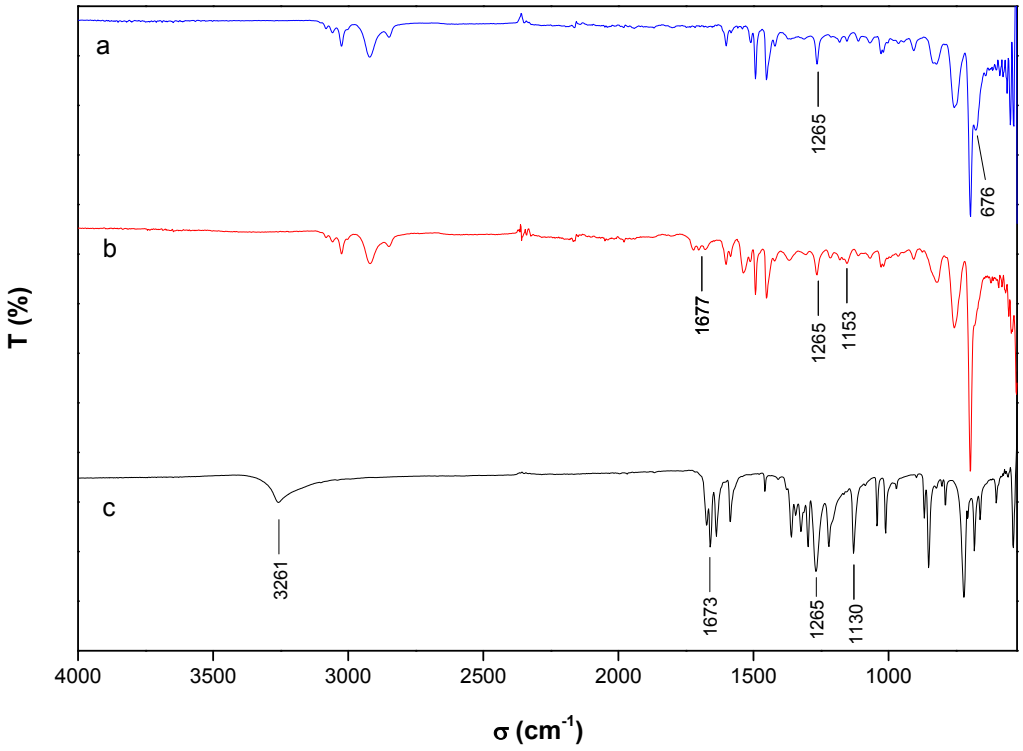


Fig. S1. FT-IR spectra of (a) Merrifield resin, (b) NQ-MR and (c) NQ.

3.2 EDX pattern of Merrifield resin and NQ-MR

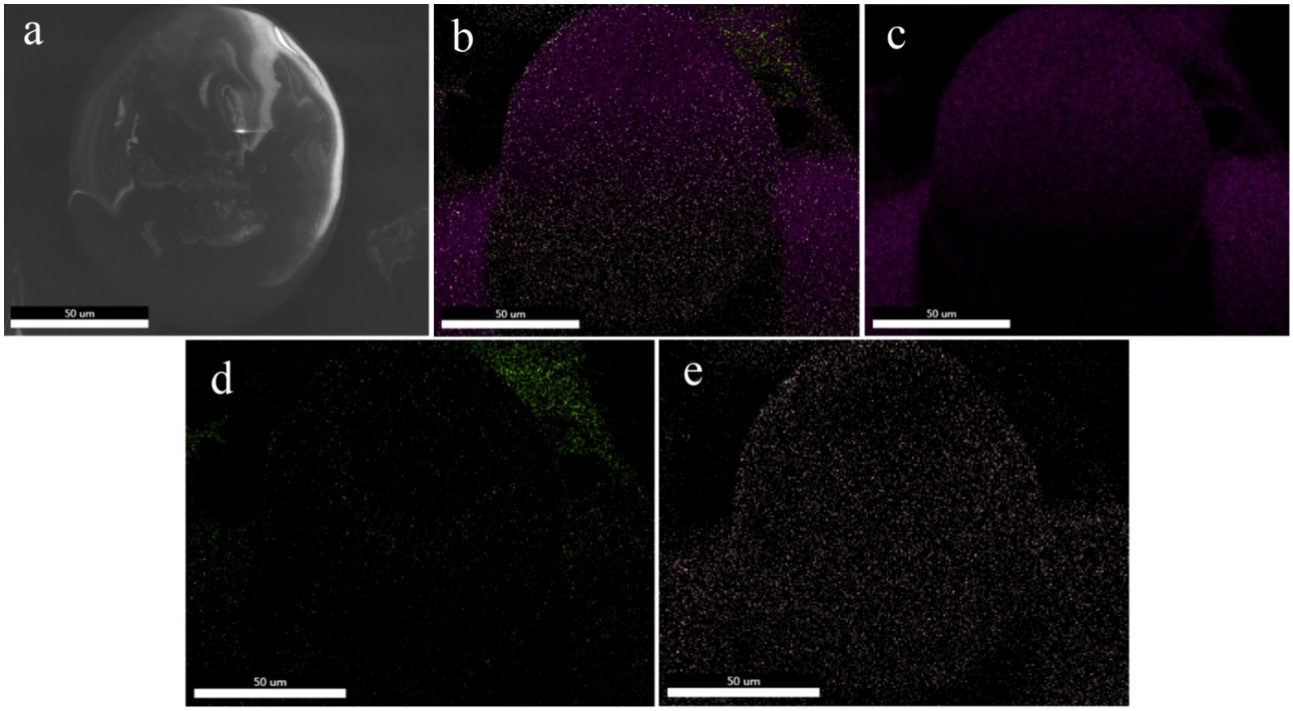


Fig.S2. EDX image of Merrifield resin (a), and corresponding elemental mapping images of (b) Merrifield resin, (c) C, (d) O, (e) Cl.

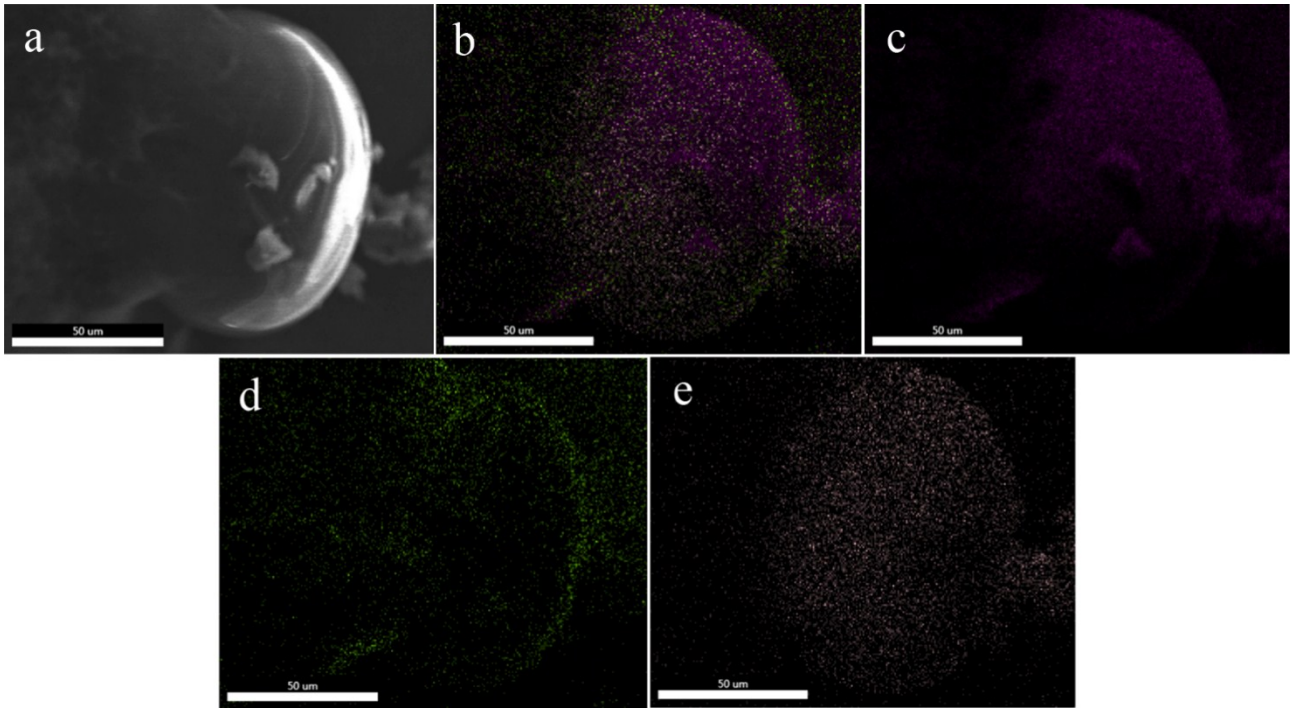


Fig.S3. EDX image of NQ-MR (a), and corresponding elemental mapping images of (b) NQ-MR, (c) C, (d) O, (e) Cl.

3.3 XPS spectra of NQ-MR

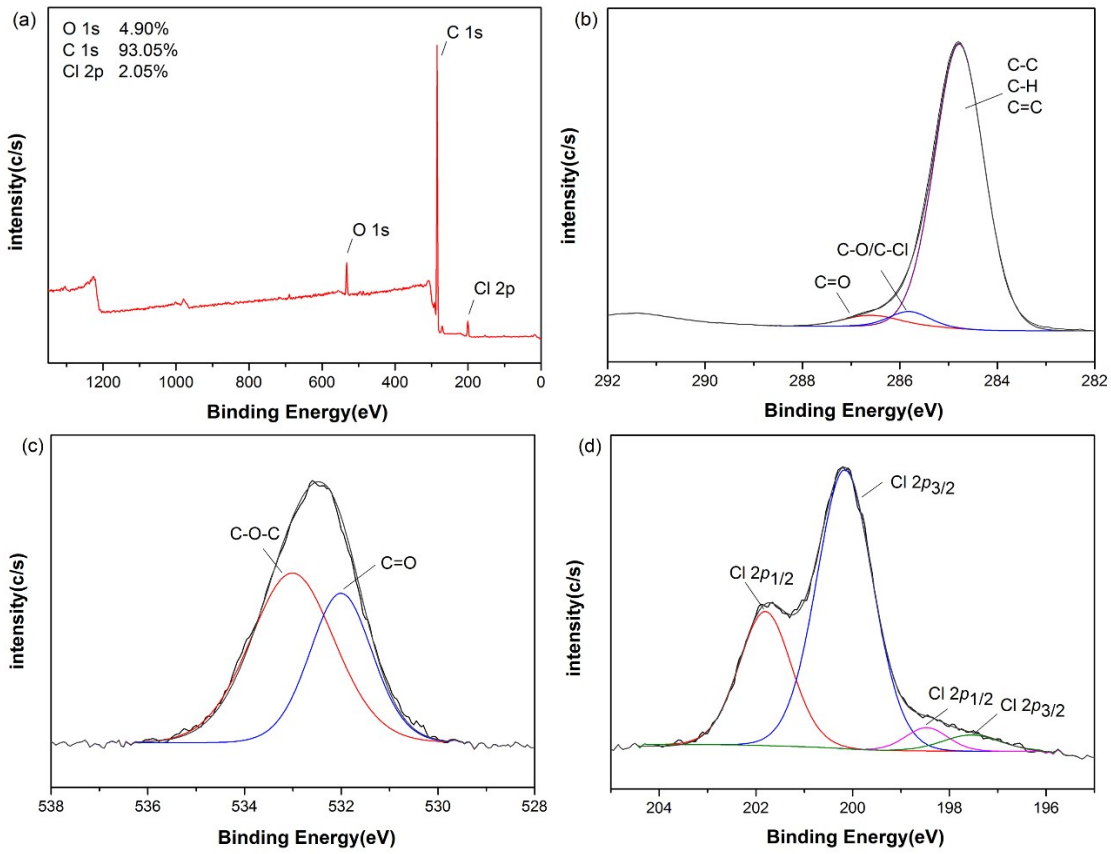
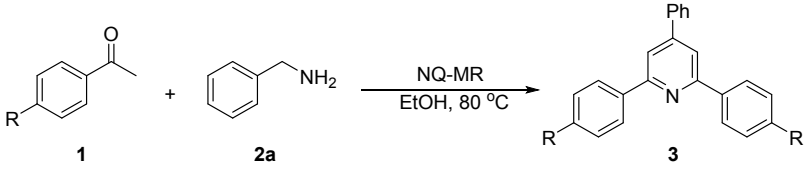


Fig.S4. XPS spectra of NQ-MR (a) surface. C 1s (b), O 1s (b) and Cl 2p (c) core-level spectra of catalyst surface.

4. General procedure for the synthesis of pyridines

Under air atmosphere, acetophenone (2.0 mmol), benzylamine (1.5 mmol), EtOH (3 mL) and catalyst NQ-MR (10 mol%) were introduced in a colorimetric tube (25 mL), successively. Then, the tube was opened and the resulting mixture was stirred at 80 °C for 24 h. After cooling down to room temperature, ethyl alcohol absolute (5 mL) was introduced, the reaction mixture was stirred under air for 2 h. Finally, the reaction mixture was then concentrated by rotary evaporation. In cases where purification was necessary, the residue was purified by column chromatography containing Et_3N-washed Silica gel with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 80:1) as eluent to give the desired product.

5. Hammett plot and mechanism studies

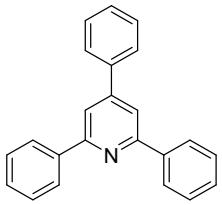


Experimental procedure: Under air, *para*-substituted acetophenone (2.0 mmol), benzylamine (1.5 mmol), NQ-MR (20 mol%), EtOH (3 mL) were introduced in a 25 mL colorimetric tube, successively. Then, the tube was opened and the resulting mixture was stirred at 80 °C for 3 h. After cooling down to room temperature, the alcohol mixture was filtered to recovery the catalyst. Next, the yield of product **3** was determined by GC.

R	**H**	***t*-Bu**	**Me**	**F**	**CF_3**
Yield %	18	16	15	21	25

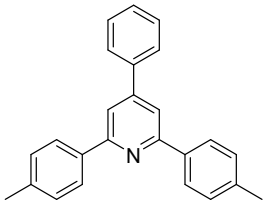
6. Analytical data of the obtained compounds.

(1) 2,4,6-triphenyl-pyridine (3a).



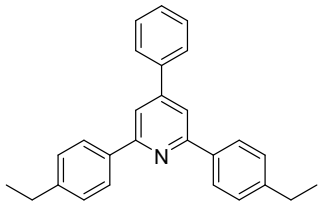
Pale yellow solid; Mp. 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 4H), 7.89 (s, 2H), 7.77 – 7.71 (m, 2H), 7.56 – 7.49 (m, 6H), 7.48 – 7.40 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.54, 150.23, 139.63, 139.11, 129.15, 129.08, 129.01, 128.75, 127.23, 127.17, 117.16.

(2) 2, 6-bis(4-methylphenyl)-4-phenylpyridine (3b).



White solid; Mp. 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.1 Hz, 4H), 7.83 (s, 2H), 7.73 (d, J = 7.1 Hz, 2H), 7.55 – 7.42 (m, 3H), 7.31 (d, J = 8.0 Hz, 4H), 2.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.41, 150.10, 139.29, 139.01, 136.88, 129.43, 129.10, 128.90, 127.22, 127.06, 116.56, 21.35.

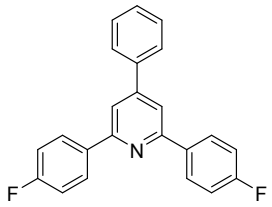
(3) 2,6-bis(4-ethylphenyl)-4-phenylpyridine (3c).



Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.2 Hz, 4H), 7.83 (s, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.55 – 7.42 (m, 3H), 7.34 (d, J = 8.3 Hz, 4H), 2.72 (q, J = 7.6 Hz, 4H), 1.29 (t, J = 7.6 Hz, 6H). ^{13}C NMR (101 MHz,

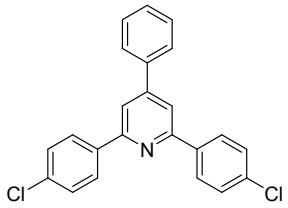
$CDCl_3$) δ 157.48, 150.09, 145.40, 139.27, 137.11, 129.12, 128.92, 128.26, 127.22, 127.18, 116.65, 28.76, 15.63. HRMS (ESI) m/z Calculated for $C_{27}H_{26}N$ $[M+H]^+$ 364.2065, found 364.2068.

(4) 2,6-bis(4-fluorophenyl)-4-phenylpyridine (3d).



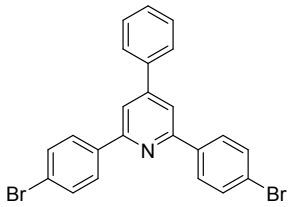
White solid; Mp. 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.7, 5.5 Hz, 4H), 7.82 (s, 2H), 7.73 (d, *J* = 7.0 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.19 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.92, 162.45, 156.50, 150.53, 138.85, 135.56, 135.53, 129.19, 129.16, 128.98, 128.90, 127.19, 116.76, 115.77, 115.56.

(5) 2,6-bis(4-chlorophenyl)-4-phenylpyridine (3e).



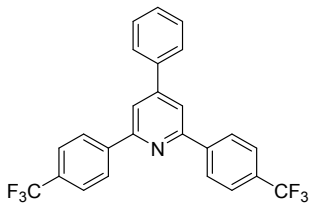
White solid; Mp. 178-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 4H), 7.84 (s, 2H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.56 – 7.45 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.36, 150.60, 138.71, 137.78, 135.32, 129.21, 128.94, 128.38, 127.18, 117.12.

(6) 2,6-bis(4-bromophenyl)-4-phenylpyridine (3f).



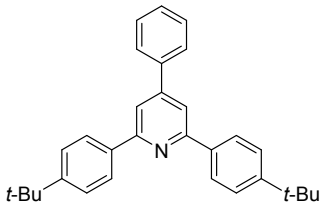
White solid; Mp. 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 4H), 7.86 (s, 2H), 7.72 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 4H), 7.57 – 7.46 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.45, 150.66, 138.67, 138.22, 131.91, 129.24, 129.22, 128.68, 127.19, 123.69, 117.18.

(7) 4-phenyl-2,6-bis(4-(trifluoromethyl)phenyl)pyridine (3g).



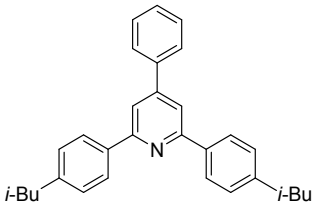
Pale yellow solid; Mp. 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 4H), 7.97 (s, 2H), 7.78 (d, *J* = 8.3 Hz, 4H), 7.76 – 7.74 (m, 2H), 7.59 – 7.51 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.30, 150.96, 142.50, 138.38, 131.28, 130.95, 129.45, 129.32, 127.44, 127.20, 125.77, 125.73, 122.85, 118.27.

(8) 2,6-bis(4-(*tert*-butyl)phenyl)-4-phenylpyridine (3h).



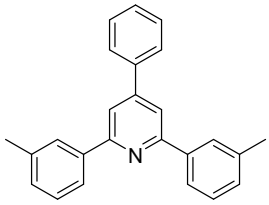
White solid; Mp. 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 4H), 7.89 (s, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.62 – 7.55 (m, 6H), 7.50 (t, *J* = 7.0 Hz, 1H), 1.44 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.45, 152.09, 149.91, 139.28, 136.96, 129.05, 128.82, 127.15, 126.85, 125.60, 116.58, 34.68, 31.33. HRMS (ESI) m/z Calculated for $C_{31}H_{34}N$ $[M+H]^+$ 420.2691, found 420.2693.

(9) 2,6-bis(4-(*iso*-butyl)phenyl)-4-phenylpyridine (3i).



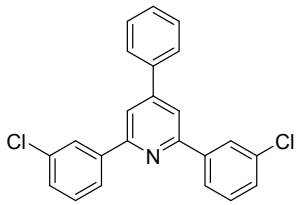
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 4H), 7.83 (s, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.40 (m, 3H), 7.27 (d, *J* = 7.8 Hz, 4H), 2.54 (d, *J* = 7.1 Hz, 4H), 1.97 – 1.86 (m, 2H), 0.93 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.57, 150.03, 142.82, 139.33, 137.27, 129.53, 129.11, 128.90, 127.23, 126.95, 116.62, 45.32, 30.32, 22.47. HRMS (ESI) m/z Calculated for $C_{31}H_{34}N$ $[M+H]^+$ 420.2691, found 420.2695.

(10) 2, 6-bis(3-methylphenyl)-4-phenylpyridine (3j).



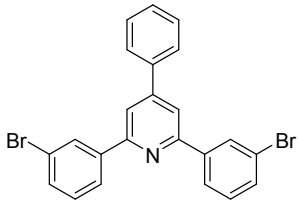
White solid; Mp. 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 4H), 7.86 (s, 2H), 7.77 – 7.72 (m, 2H), 7.55 – 7.45 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 2.48 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.77, 150.11, 139.67, 139.17, 138.33, 129.82, 129.12, 128.95, 128.63, 127.90, 127.23, 124.37, 117.22, 21.65.

(11) 2,6-bis(3-chlorophenyl)-4-phenylpyridine (3k).



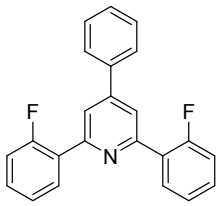
White solid; Mp. 171-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 2H), 8.04 (d, *J* = 6.5 Hz, 2H), 7.84 (s, 2H), 7.71 (d, *J* = 7.0 Hz, 2H), 7.57 – 7.38 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.20, 150.65, 141.12, 138.52, 134.88, 130.00, 129.29, 129.23, 129.19, 127.27, 127.18, 125.23, 117.66.

(12) 2,6-bis(3-bromophenyl)-4-phenylpyridine (3l).



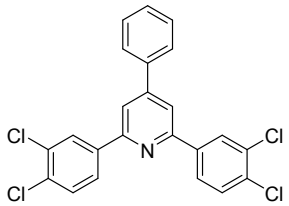
White solid; Mp. 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.86 (s, 2H), 7.73 (d, *J* = 6.9 Hz, 2H), 7.61 – 7.47 (m, 5H), 7.39 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.13, 150.68, 141.37, 138.50, 132.13, 130.31, 130.17, 129.31, 129.24, 127.20, 125.74, 123.07, 117.73.

(13) 2,6-bis(2-fluorophenyl)-4-phenylpyridine (3m).



Pale yellow solid; Mp. 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.13 (m, 2H), 8.00 (d, *J* = 1.6 Hz, 2H), 7.74 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.56 – 7.45 (m, 3H), 7.43 – 7.37 (m, 2H), 7.34 – 7.27 (m, 2H), 7.23 – 7.16 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.99, 159.51, 153.69, 153.67, 149.50, 138.65, 131.38, 131.35, 130.52, 130.43, 129.12, 129.04, 127.66, 127.55, 127.33, 124.54, 124.51, 121.48, 121.39, 116.37, 116.14.

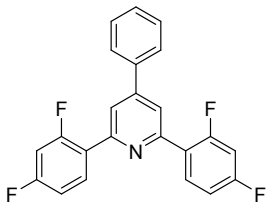
(14) 2,6-bis(3,4-dichlorophenyl)-4-phenylpyridine (3n).



White solid; Mp. 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 2.0 Hz, 2H), 7.99 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.83 (s, 2H), 7.71 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.60 – 7.47 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.25,

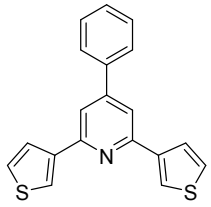
150.96, 139.03, 138.23, 133.49, 133.11, 130.73, 129.46, 129.29, 128.93, 127.16, 126.19, 117.57.

(15) 2,6-bis(2,4-difluorophenyl)-4-phenylpyridine (3o).



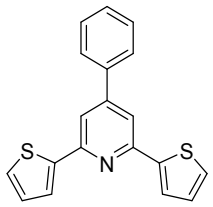
White solid; Mp. 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 15.7, 8.6 Hz, 2H), 7.94 (s, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.50 (dt, *J* = 20.8, 7.0 Hz, 3H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 10.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.64, 164.52, 162.16, 162.04, 159.65, 159.53, 152.83, 149.86, 138.44, 132.46, 132.42, 132.37, 132.32, 129.17, 127.29, 123.88, 123.84, 123.76, 123.73, 121.14, 121.04, 112.04, 112.00, 111.83, 111.79, 104.71, 104.45, 104.44, 104.19. HRMS (ESI) m/z Calculated for $C_{23}H_{14}F_4N$ $[M+H]^+$ 380.1062, found 380.1064.

(16) 4-phenyl-2,6-di(thiophen-3-yl)pyridine (3p).



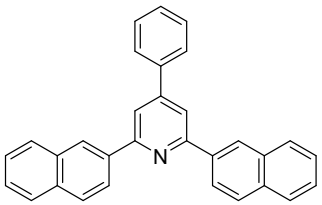
Pale yellow solid; Mp. 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.3 Hz, 2H), 7.77 (d, *J* = 4.9 Hz, 2H), 7.66 (d, *J* = 10.9 Hz, 4H), 7.52 – 7.41 (m, 3H), 7.40 – 7.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.68, 150.15, 142.52, 138.94, 129.14, 129.03, 127.15, 126.53, 126.17, 123.85, 116.62.

(17) 4-phenyl-2,6-di(thiophen-2-yl)pyridine (3q).



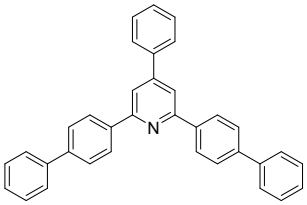
White solid; Mp. 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 6H), 7.55 – 7.46 (m, 3H), 7.42 (d, *J* = 5.0 Hz, 2H), 7.13 (t, *J* = 4.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.66, 150.20, 144.92, 138.60, 129.16, 129.14, 127.97, 127.84, 127.10, 124.87, 115.13.

(18) 2,6-di(naphthalen-2-yl)-4-phenylpyridine (3r).



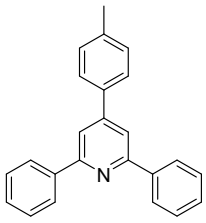
White solid; Mp. 155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 8.41 (dd, *J* = 8.6, 1.5 Hz, 2H), 8.06 – 7.96 (m, 6H), 7.92 – 7.86 (m, 2H), 7.81 (d, *J* = 7.1 Hz, 2H), 7.59 – 7.46 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.53, 150.39, 139.12, 136.96, 133.85, 133.59, 129.20, 129.10, 128.83, 128.46, 127.77, 127.31, 126.57, 126.32, 125.00, 117.54.

(19) 2,6-di([1,1'-biphenyl]-4-yl)-4-phenylpyridine (3s).



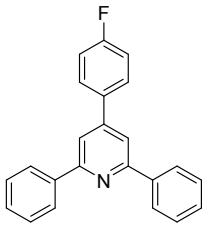
White solid; Mp. 188-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 4H), 7.96 (s, 2H), 7.78 (t, *J* = 7.0 Hz, 6H), 7.70 (d, *J* = 7.3 Hz, 4H), 7.53 – 7.45 (m, 6H), 7.39 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.15, 150.30, 141.86, 140.72, 139.10, 138.48, 129.18, 129.05, 128.87, 127.57, 127.47, 127.25, 127.17, 117.10.

(20) 4-(4-methylphenyl)-2,6-diphenylpyridine (3aa).



White solid; Mp. 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.2 Hz, 4H), 7.92 (s, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 4H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.50, 150.09, 139.73, 139.10, 136.14, 129.86, 129.01, 128.71, 127.17, 127.03, 116.92, 21.28.

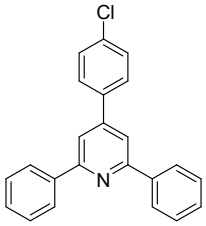
(21) 4-(4-fluorophenyl)-2,6-diphenylpyridine (3ab).



White solid; Mp. 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.2 Hz, 4H), 7.87 (s, 2H), 7.75 (dd, *J* =

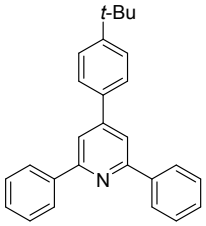
8.7, 5.3 Hz, 2H), 7.61 – 7.46 (m, 6H), 7.26 (dd, *J* = 14.5, 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.67, 162.19, 157.59, 149.15, 139.47, 135.17, 135.14, 129.16, 129.00, 128.91, 128.76, 127.16, 116.91, 116.25, 116.03.

(22) 4-(4-chlorophenyl)-2,6-diphenylpyridine (3ac).



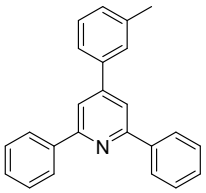
White solid; Mp. 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.5 Hz, 4H), 7.80 (s, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.41 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.68, 148.95, 139.41, 137.48, 135.23, 129.36, 129.21, 128.77, 128.48, 127.17, 116.81.

(23) 4-(4-(tert-butyl)phenyl)-2,6-diphenylpyridine (3ad).



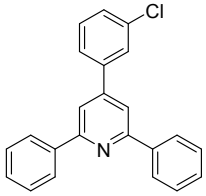
White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, 4H), 7.94 (s, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.54 (m, 6H), 7.49 (t, *J* = 7.3 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48, 152.33, 150.08, 139.73, 136.16, 129.03, 128.73, 127.18, 126.91, 126.12, 117.02, 34.78, 31.36.

(24) 4-(3-methylphenyl)-2,6-diphenylpyridine (3ae).



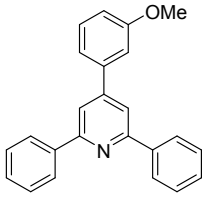
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, 4H), 7.87 (s, 2H), 7.54 – 7.48 (m, 6H), 7.47 – 7.37 (m, 4H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48, 150.38, 139.67, 139.08, 138.87, 129.78, 129.07, 128.75, 127.93, 127.20, 127.04, 124.35, 117.20, 21.60.

(25) 4-(3-chlorophenyl)-2,6-diphenylpyridine (3af).



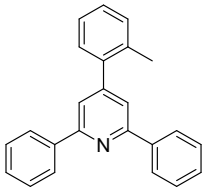
White solid; Mp. 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.4 Hz, 4H), 7.82 (s, 2H), 7.71 (s, 1H), 7.60 (d, *J* = 3.8 Hz, 1H), 7.54 – 7.41 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.72, 148.80, 140.95, 139.36, 135.13, 130.40, 129.23, 129.00, 128.78, 127.37, 127.17, 125.40, 116.93.

(26) 4-(3-methoxyphenyl)-2,6-diphenylpyridine (3ag).



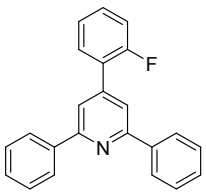
White solid; Mp. 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, 4H), 7.91 (s, 2H), 7.56 (t, *J* = 7.4 Hz, 4H), 7.48 (t, *J* = 8.0 Hz, 3H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.05 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.21, 157.52, 150.17, 140.59, 139.54, 130.21, 129.11, 128.74, 127.19, 119.65, 117.23, 114.26, 113.06, 55.48.

(27) 4-(2-methylphenyl)-2,6-diphenylpyridine (3ah).



White solid; Mp. 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, 4H), 7.66 (s, 2H), 7.49 (t, *J* = 7.4 Hz, 4H), 7.45 – 7.41 (m, 2H), 7.32 (d, *J* = 5.2 Hz, 4H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.86, 151.42, 139.88, 139.54, 135.20, 130.73, 129.30, 129.09, 128.75, 128.41, 127.15, 126.18, 119.41, 20.43.

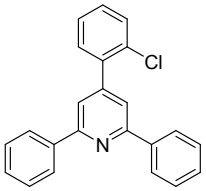
(28) 4-(2-fluorophenyl)-2,6-diphenylpyridine (3ai).



White solid; Mp. 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 4H), 7.86 (s, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 4H), 7.46 – 7.39 (m, 3H), 7.31 – 7.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.20,

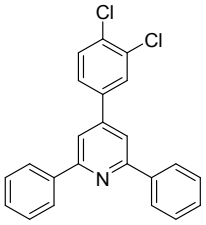
158.72, 157.31, 145.13, 139.49, 130.62, 130.53, 130.47, 130.44, 129.12, 128.74, 127.20, 124.78, 124.75, 118.93, 118.90, 116.61, 116.39.

(29) 4-(2-chlorophenyl)-2,6-diphenylpyridine (3aj).



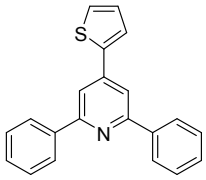
White solid; Mp. 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.3 Hz, 4H), 7.76 (s, 2H), 7.52 – 7.46 (m, 5H), 7.44 – 7.40 (m, 3H), 7.39 – 7.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.94, 148.64, 139.44, 138.57, 132.36, 130.95, 130.34, 129.73, 129.13, 128.75, 127.22, 127.18, 119.50.

(30) 4-(3,4-dichlorophenyl)-2,6-diphenylpyridine (3ak).



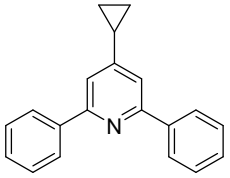
White solid; Mp. 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.5 Hz, 4H), 7.83 – 7.76 (m, 3H), 7.60 – 7.42 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.83, 147.75, 139.17, 139.03, 133.42, 133.33, 131.11, 129.33, 129.06, 128.79, 127.16, 126.41, 116.64.

(31) 2,6-diphenyl-4-(thiophen-2-yl)pyridine (3al).



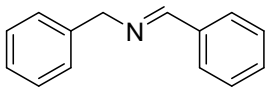
White solid; Mp. 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.5 Hz, 4H), 7.86 (s, 2H), 7.61 (d, *J* = 3.5 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 4H), 7.44 (dd, *J* = 8.2, 6.4 Hz, 3H), 7.17 (t, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.74, 143.07, 141.96, 139.35, 129.20, 128.74, 128.43, 127.16, 126.98, 125.32, 115.39.

(32) 4-cyclopropyl-2,6-diphenylpyridine (3am).



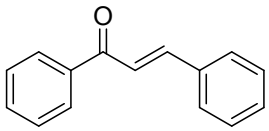
White oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.08 (m, 4H), 7.52 – 7.46 (m, 4H), 7.45 – 7.40 (m, 2H), 7.36 (s, 2H), 2.14 – 1.91 (m, 1H), 1.21 – 1.06 (m, 2H), 0.99 – 0.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.76, 139.50, 137.50, 128.92, 128.63, 127.16, 118.66, 15.54, 10.37. HRMS (ESI) m/z Calculated for $C_{20}H_{18}N$ $[M+H]^+$ 272.1439, found 272.1442.

(33) N-benzylidenebenzylamine (4).



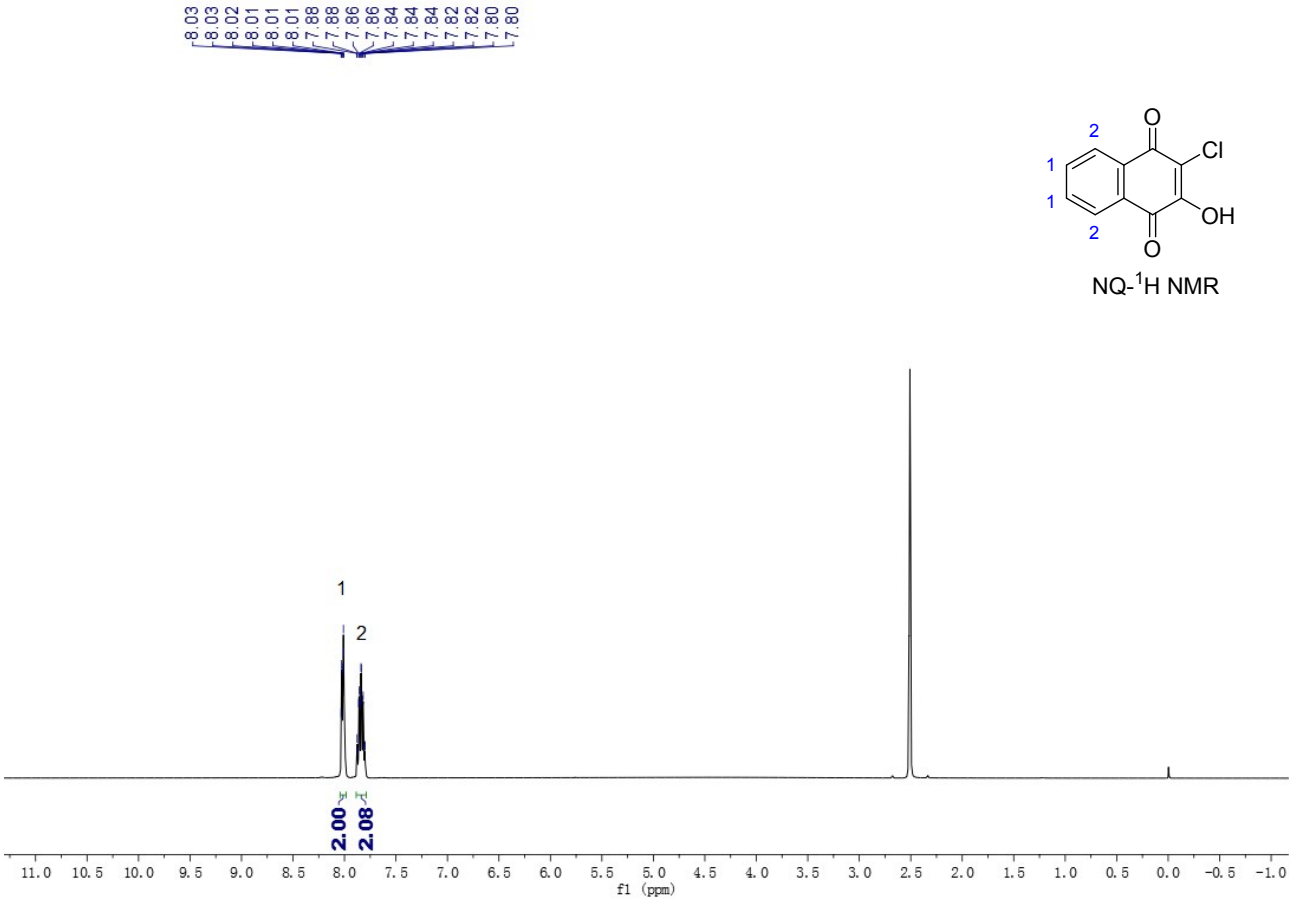
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.94 – 7.79 (m, 2H), 7.56 – 7.45 (m, 3H), 7.41 (d, *J* = 4.4 Hz, 4H), 7.37 – 7.27 (m, 1H), 4.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.03, 139.36, 136.23, 130.80, 128.64, 128.54, 128.33, 128.03, 127.03, 65.07.

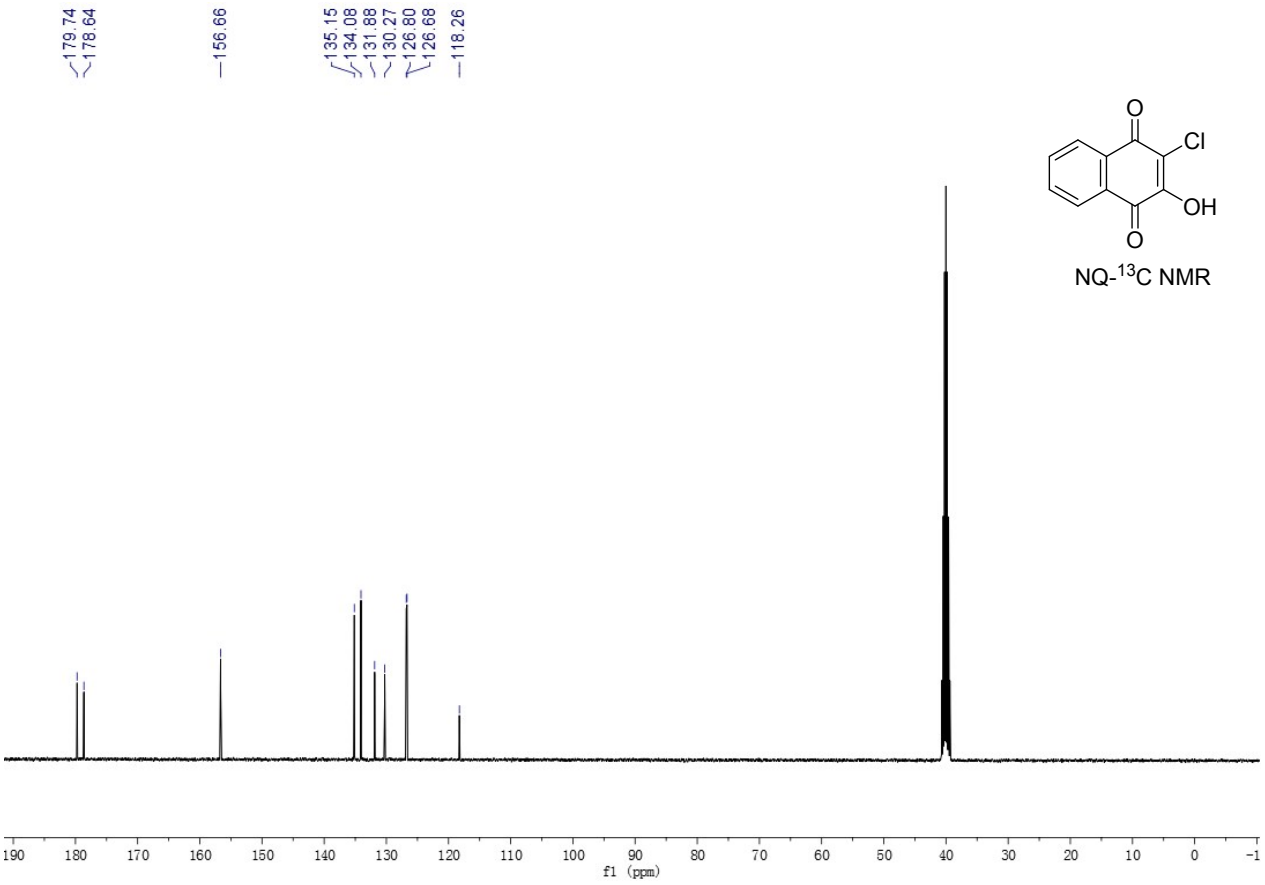
(34) 4-cyclopropyl-2,6-diphenylpyridine (5).



White solid; Mp.55-56 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 2H), 7.84 (d, 1H), 7.67 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.64 – 7.50 (m, 4H), 7.49 – 7.42 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.67, 144.86, 138.30, 134.94, 132.79, 130.56, 128.98, 128.65, 128.53, 128.47, 122.20.

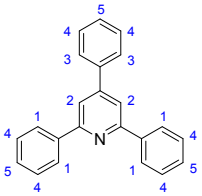
7. NMR spectra of obtained compounds.



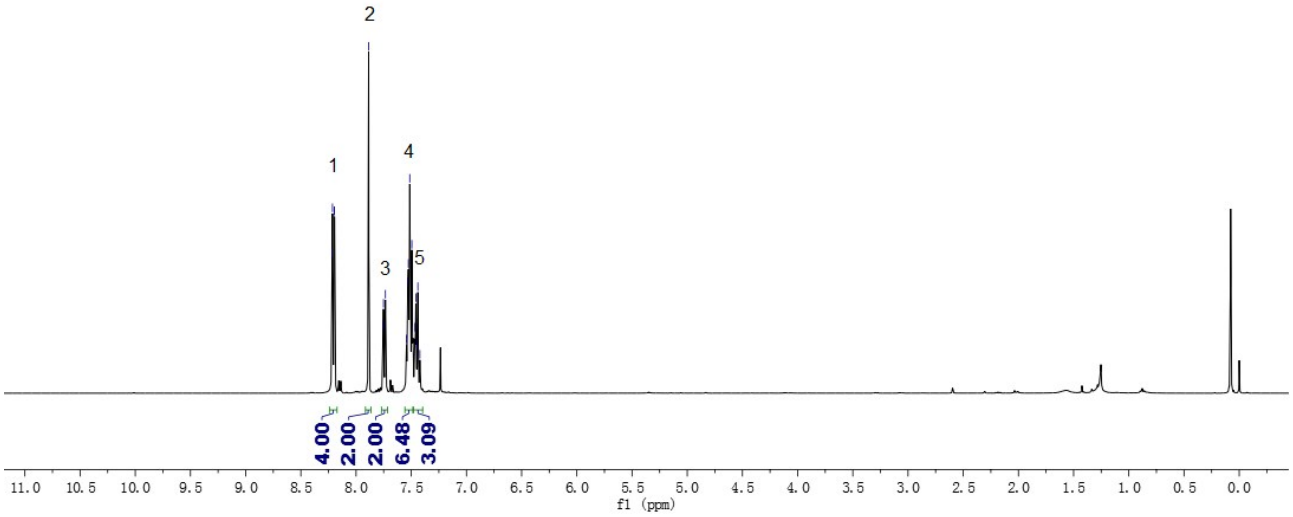

179.74
178.64
156.66
135.15
134.08
131.88
130.27
126.80
126.68
118.26
O
Cl
OH
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

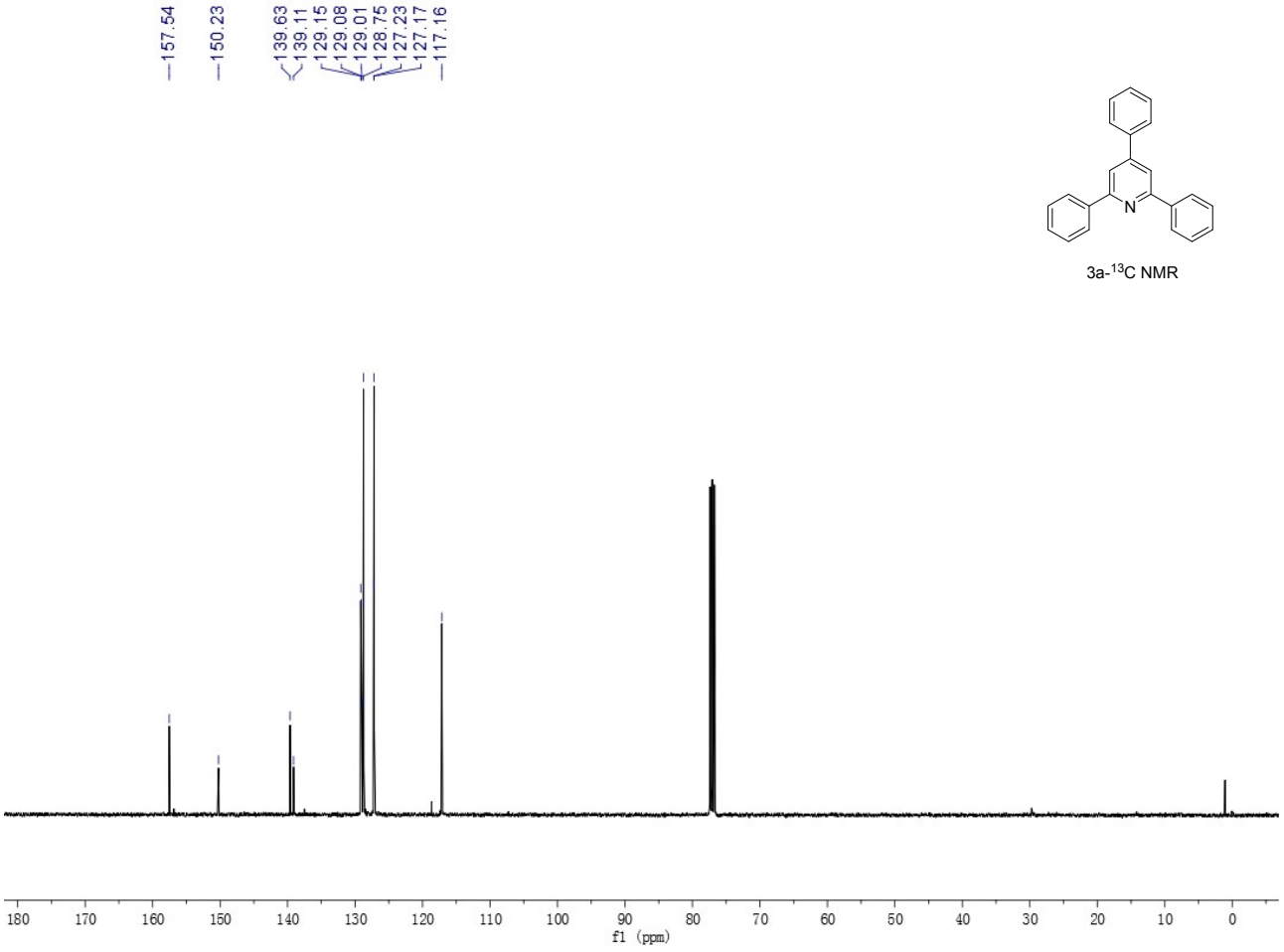
NQ-^{13}C NMR


8.22
8.21
8.20
8.20
7.89
7.76
7.75
7.73
7.54
7.53
7.53
7.51
7.49
7.47
7.46
7.45
7.44
7.42

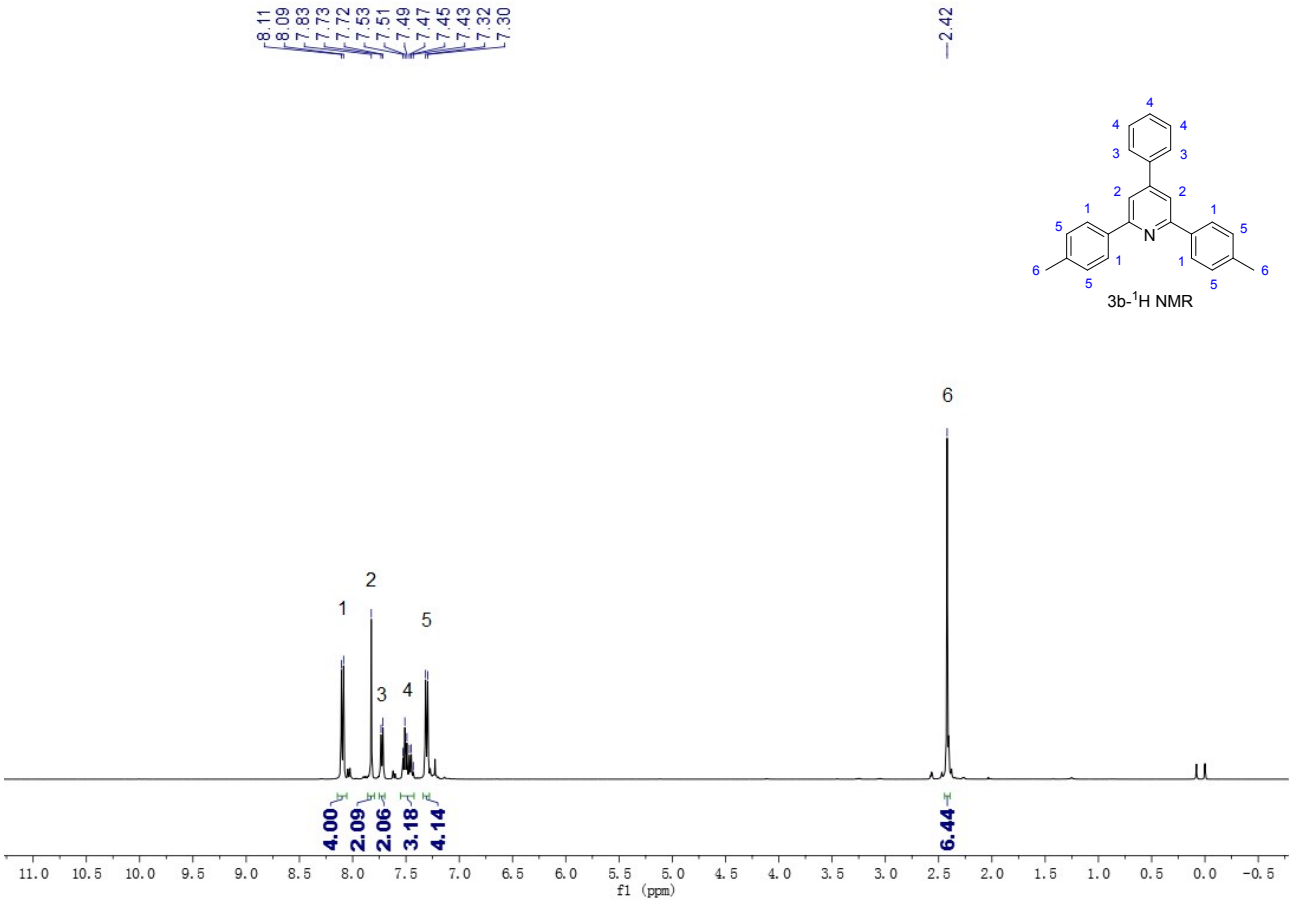

5
4
4
3
3
2
2
1
1
4
N
5
1
1
4
5
4
4

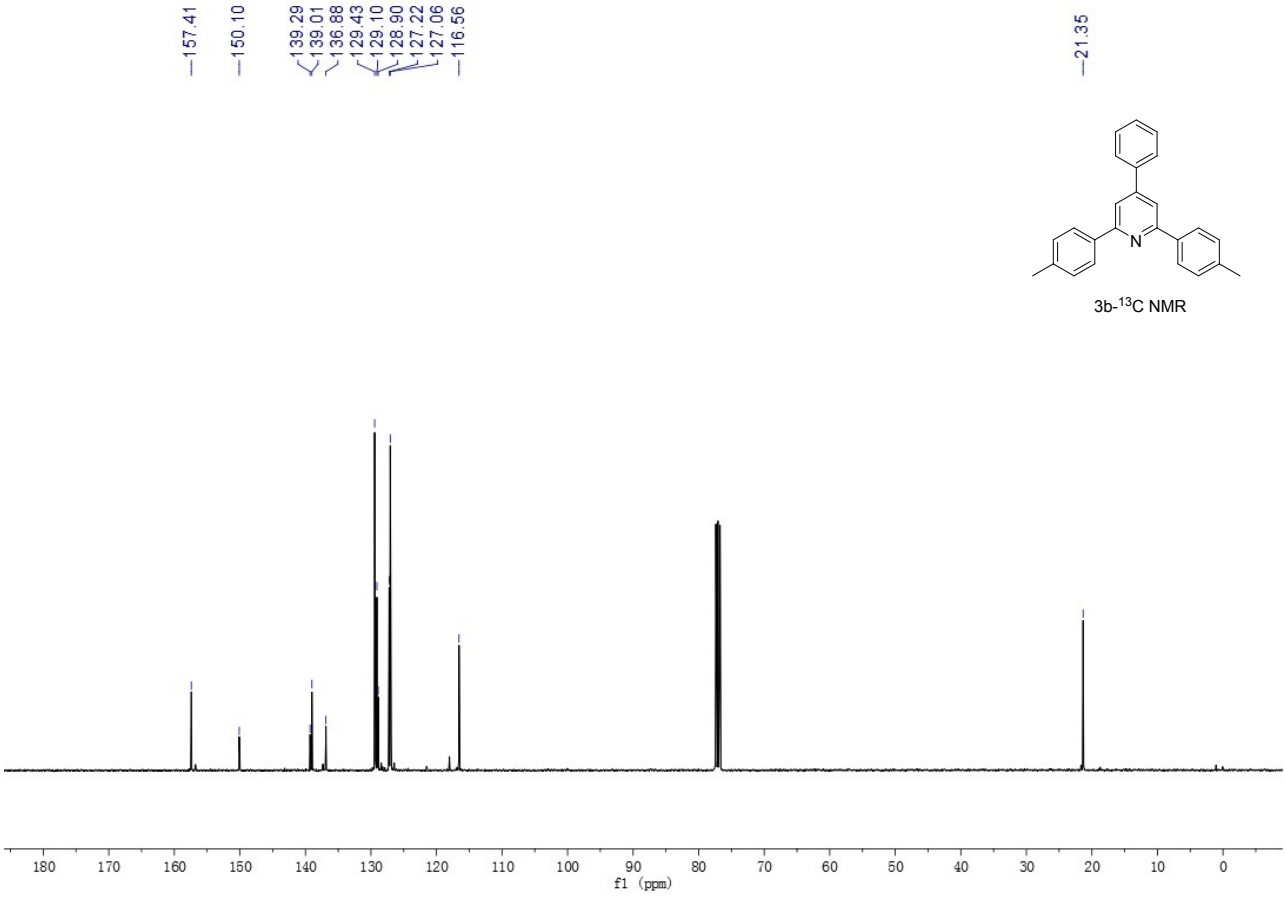
3a-^{1}H NMR


2
1
4
3
5
4.00
2.00
2.00
6.48
3.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

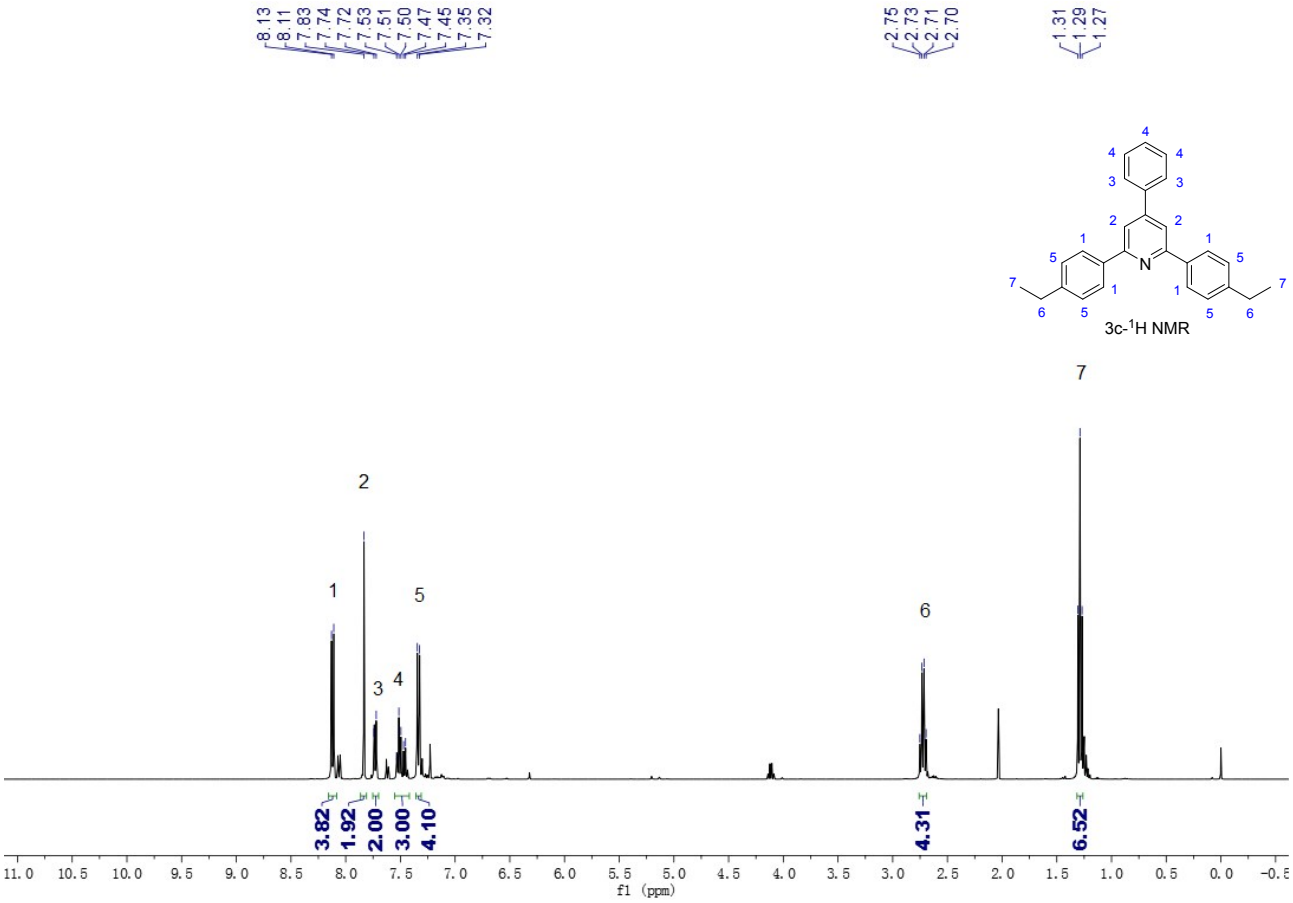

157.54
150.23
139.63
139.11
129.15
129.08
129.01
128.75
127.23
127.17
117.16
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3a-^{13}C NMR


8.11
8.09
7.83
7.73
7.72
7.53
7.51
7.49
7.47
7.45
7.43
7.32
7.30
2.42
3b-1H NMR
1
2
3
4
5
6
4.00
2.09
2.06
3.18
4.14
6.44
f1 (ppm)


157.41
150.10
139.29
139.01
136.88
129.43
129.10
128.90
127.22
127.06
116.56
21.35
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3b-^{13}C NMR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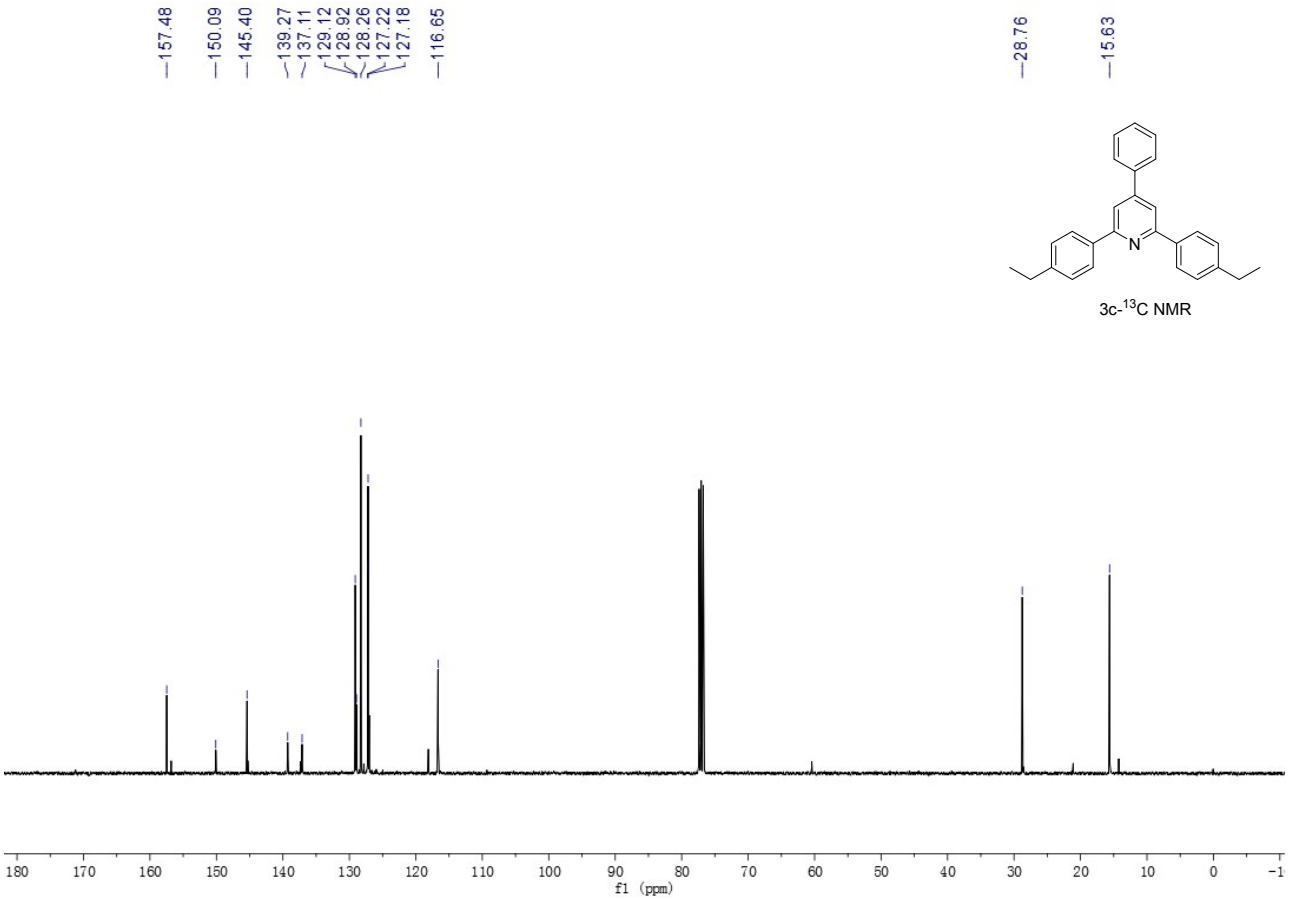
8.11
7.83
7.74
7.72
7.53
7.51
7.50
7.47
7.45
7.35
7.32
2.75
2.73
2.71
2.70
1.31
1.29
1.27
3c-1H NMR
7
2
1
5
3
4
6
3.82
1.92
2.00
3.00
4.10
4.31
6.52
f1 (ppm)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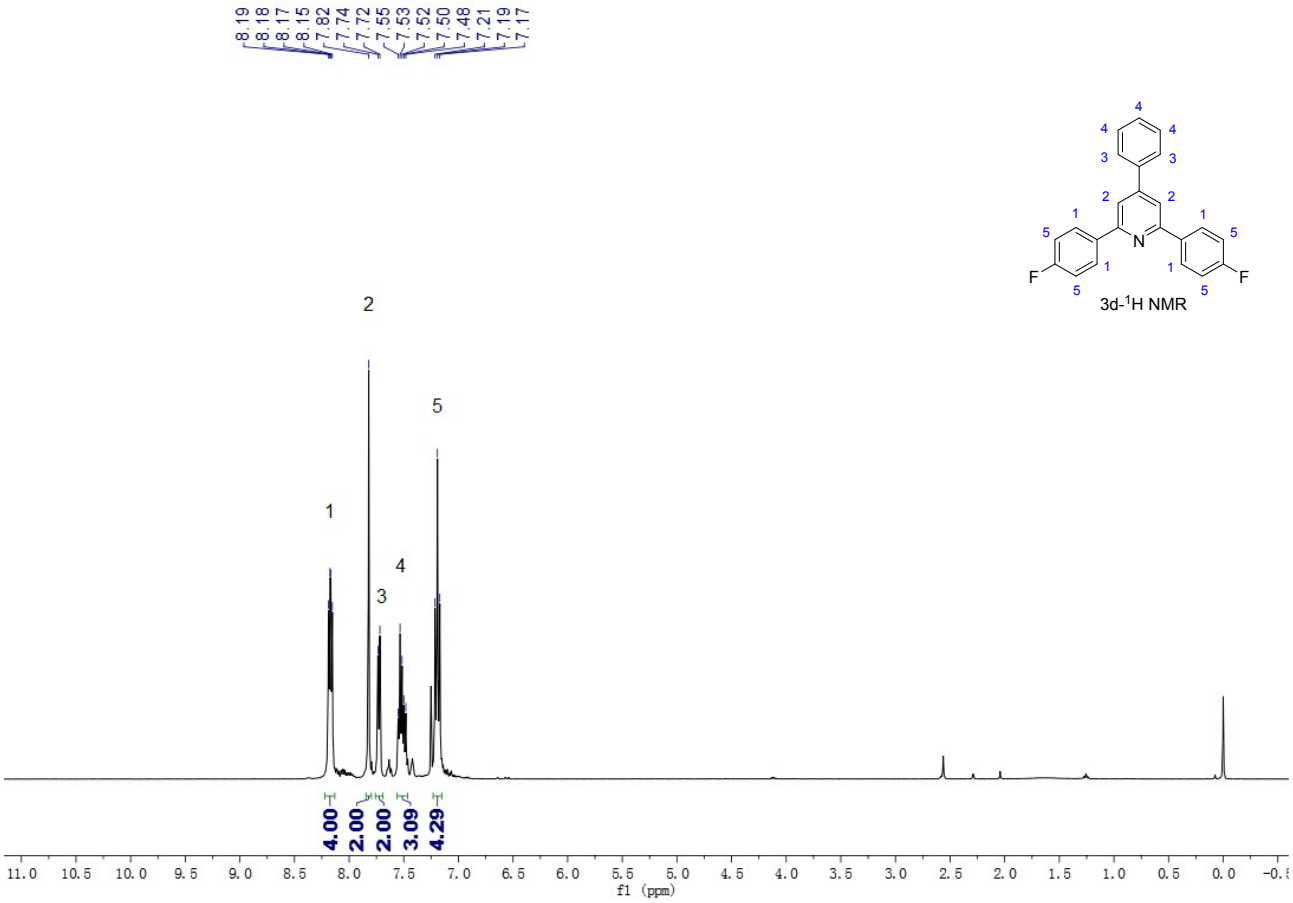
150.09
145.40
139.27
137.11
129.12
128.92
128.26
127.22
127.18
116.65
28.76
15.63
N
3c-13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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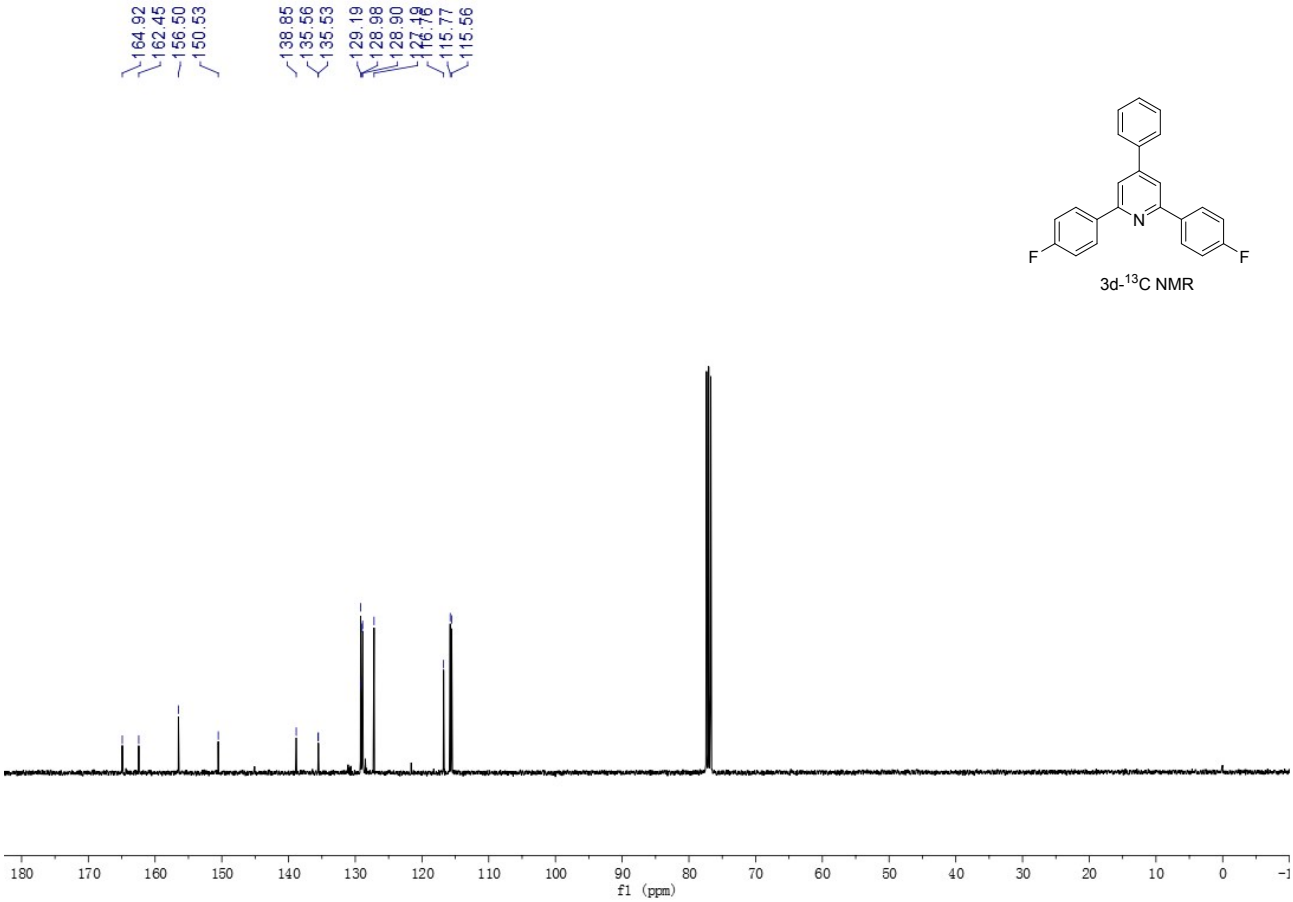
8.18
8.17
8.15
7.82
7.74
7.72
7.55
7.53
7.52
7.50
7.48
7.21
7.19
7.17
1
2
3
4
5
4.00
2.00
2.00
3.09
4.29
f1 (ppm)

3d-^{1}H NMR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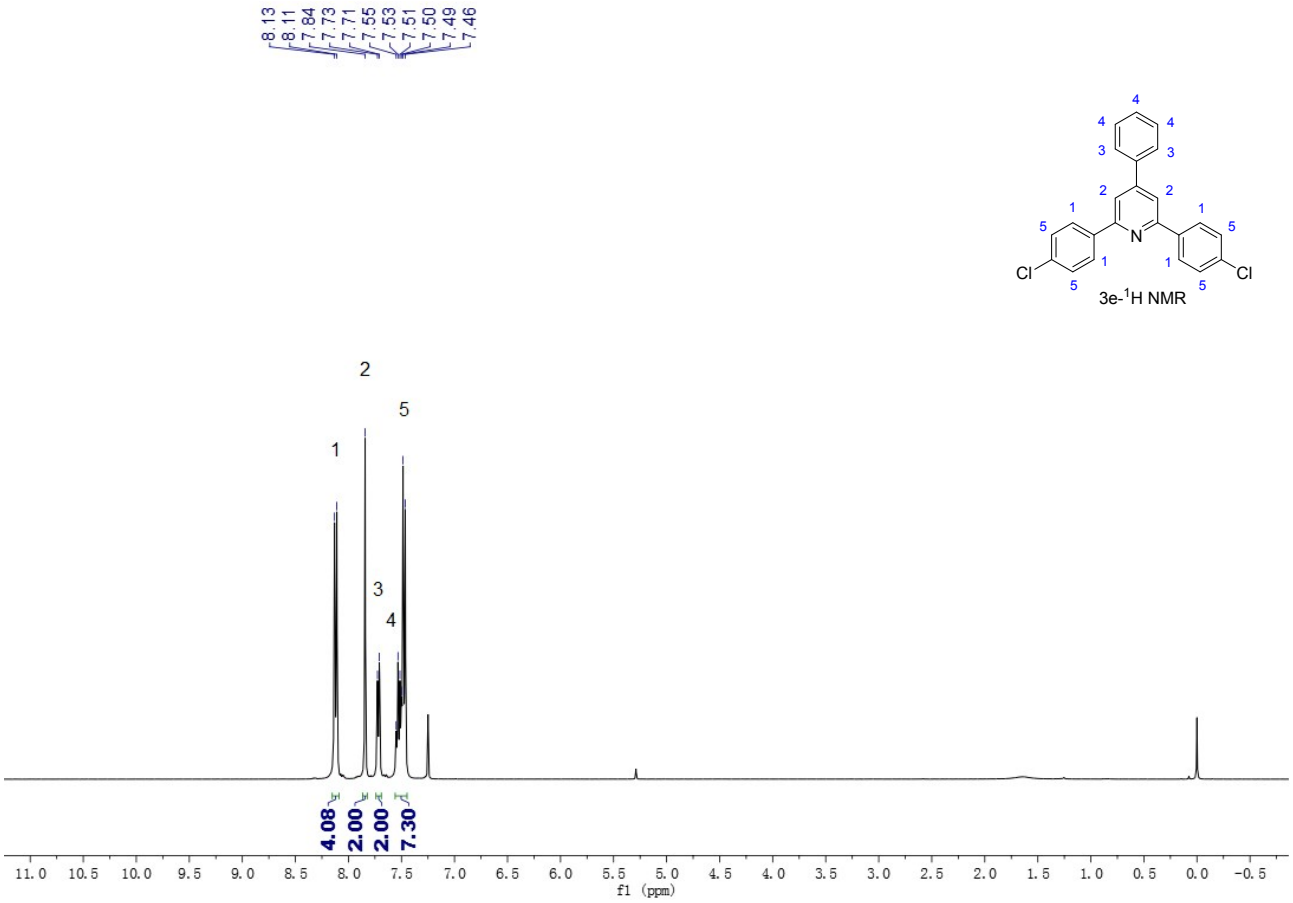
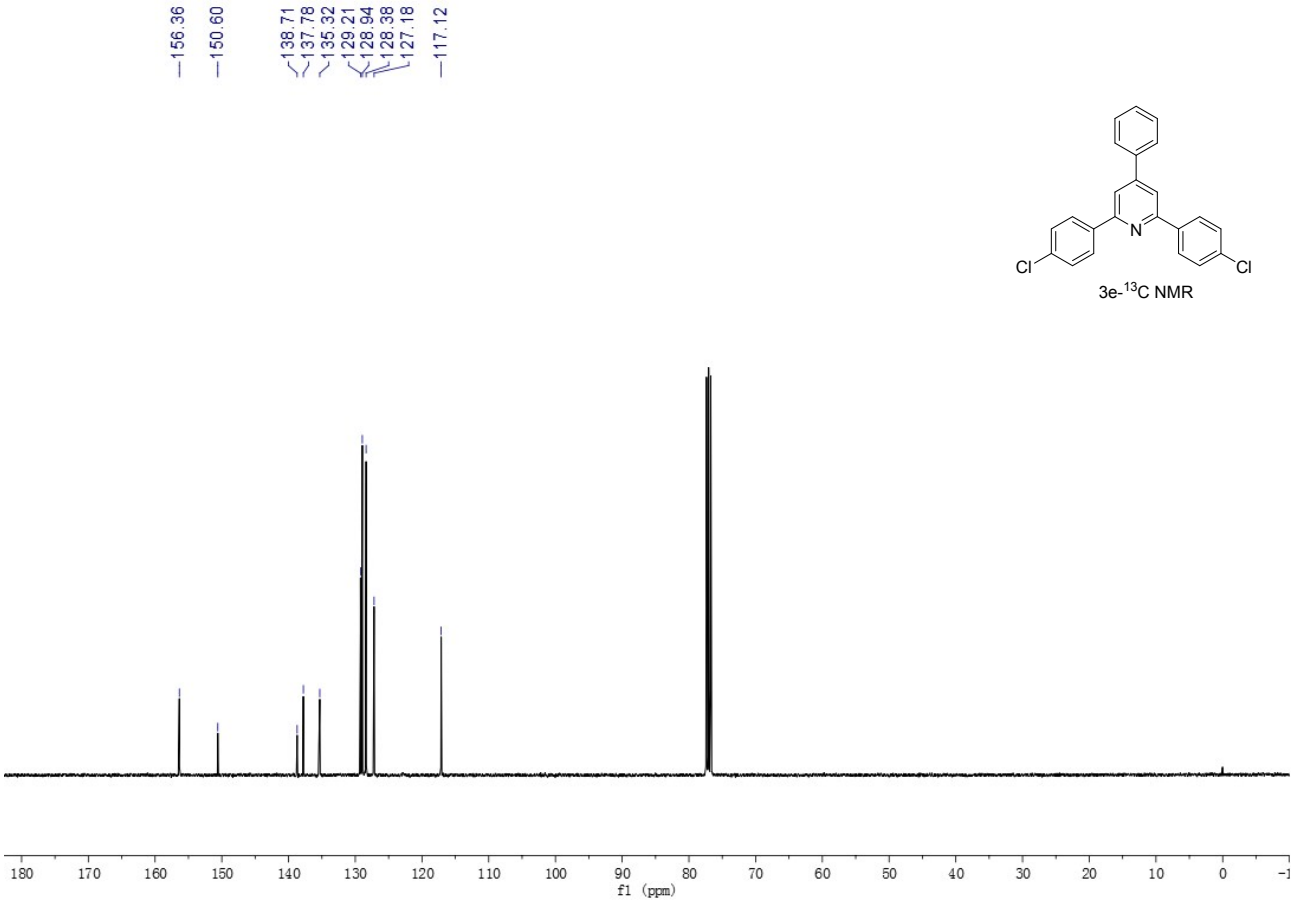
162.45
156.50
150.53
138.85
135.56
135.53
129.19
128.98
128.90
115.77
115.56
N
F
F
3d-13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.13
8.11
7.84
7.73
7.71
7.55
7.53
7.51
7.50
7.49
7.46
Cl
Cl
N
3e-1H NMR
1
2
3
4
5
4.08
2.00
2.00
7.30
f1 (ppm)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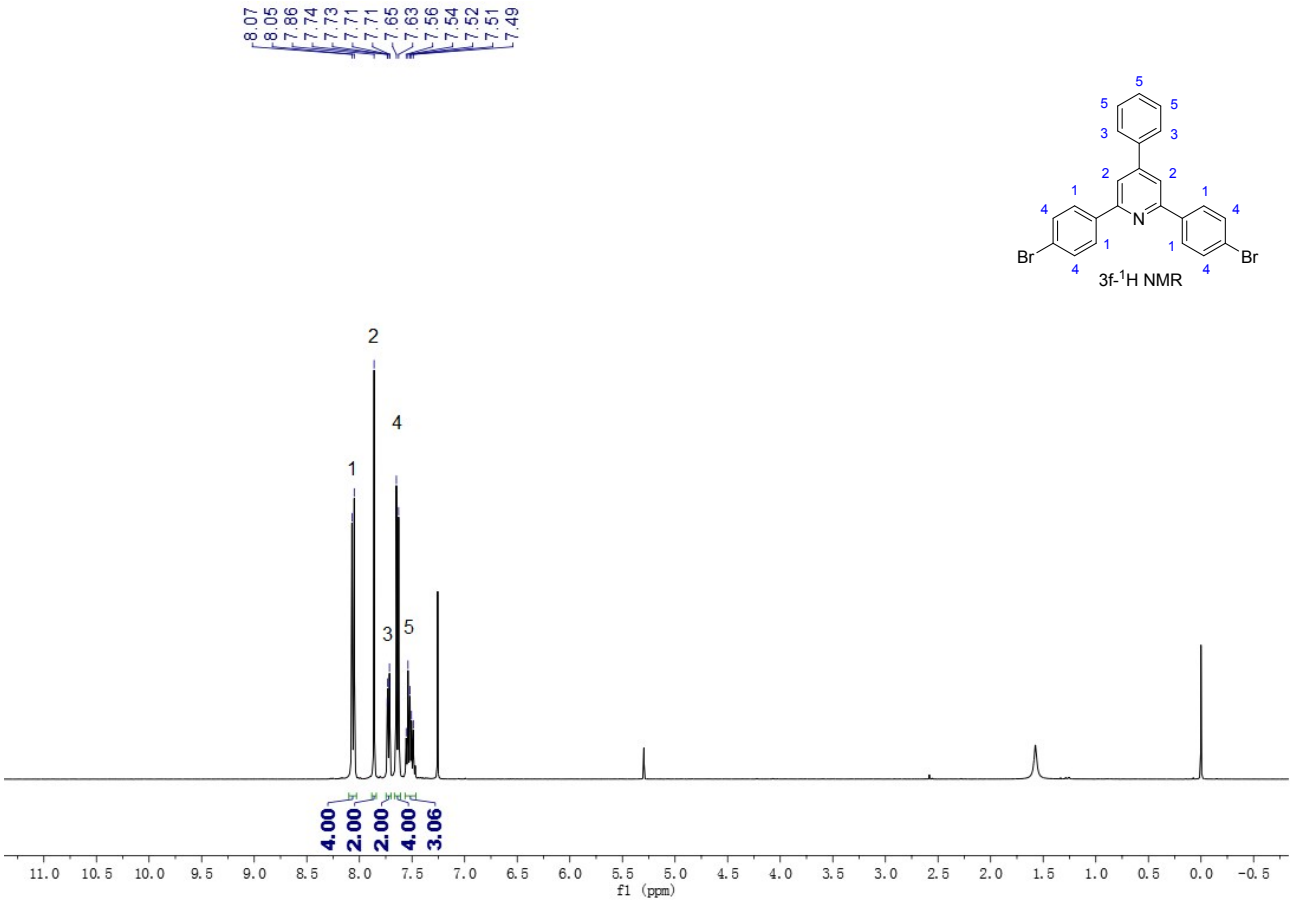
150.60
138.71
137.78
135.32
129.21
128.94
128.38
127.18
117.12
N
Cl
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3e-^{13}C NMR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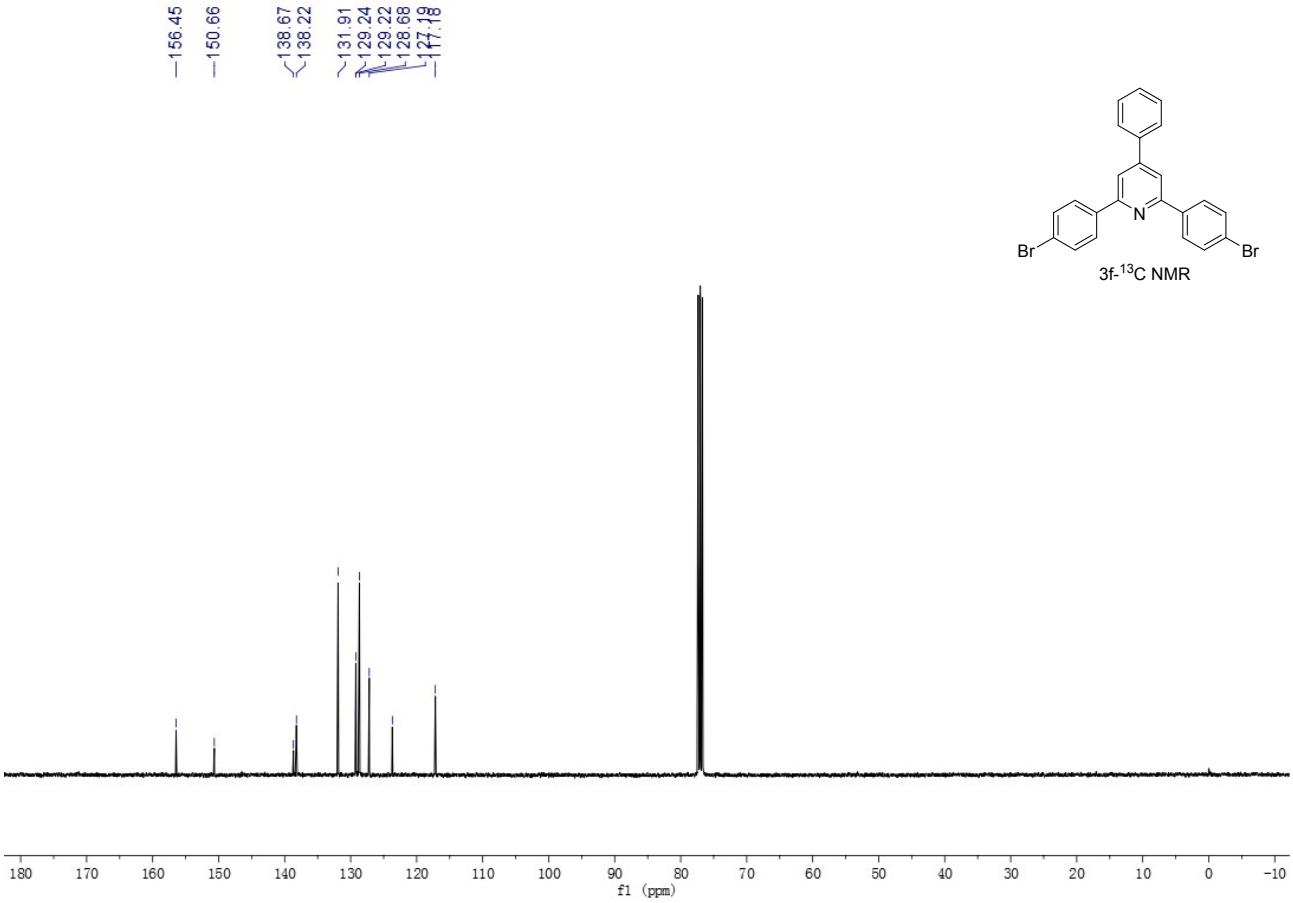
8.05
7.86
7.74
7.73
7.71
7.71
7.65
7.63
7.56
7.54
7.52
7.51
7.49
Br
Br
N
3f-1H NMR
1
2
3
4
5
4.00
2.00
2.00
4.00
3.06
f1 (ppm)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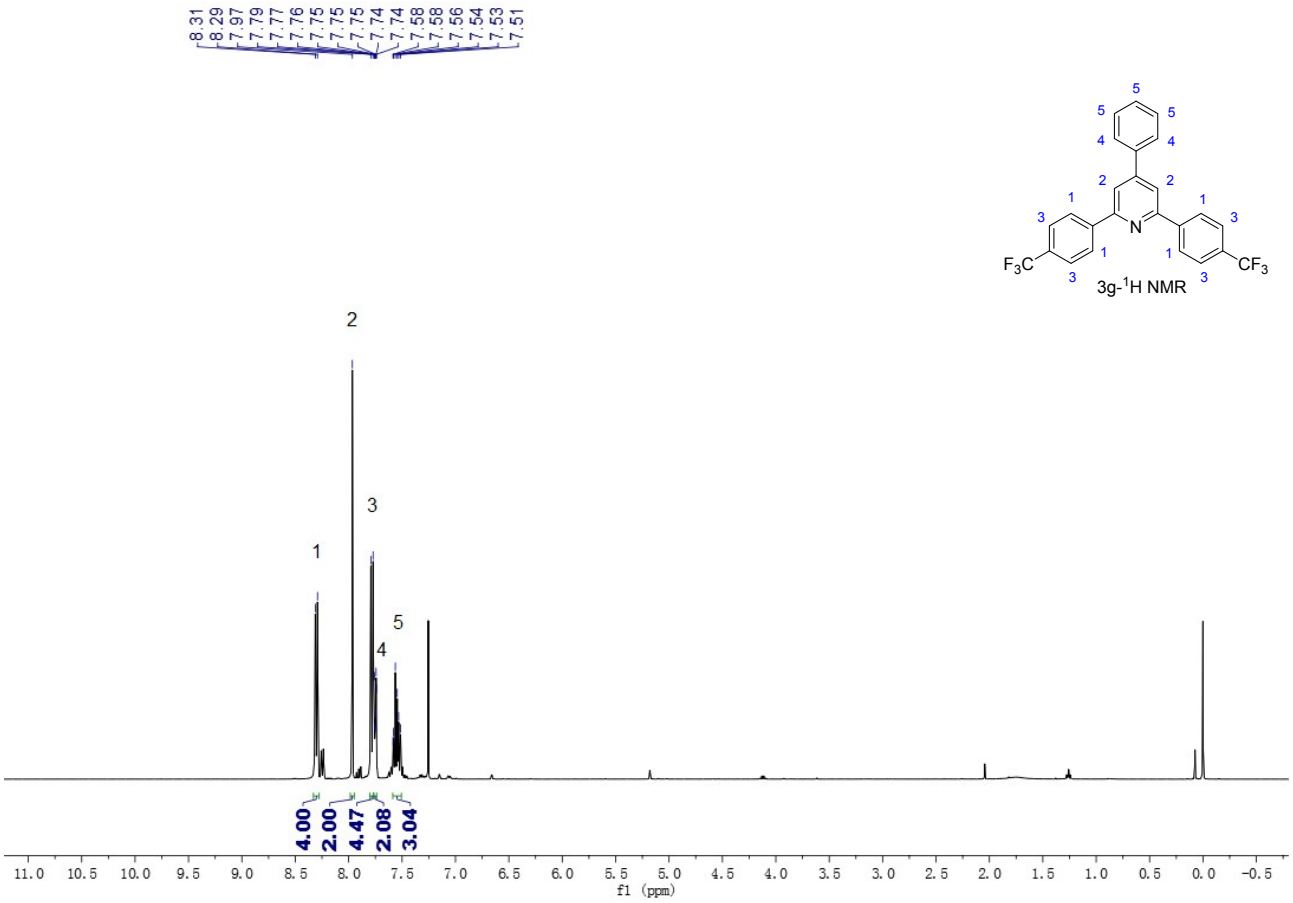
150.66
138.67
138.22
131.91
129.24
129.22
128.68
127.19
117.18
N
Br
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3f-^{13}C NMR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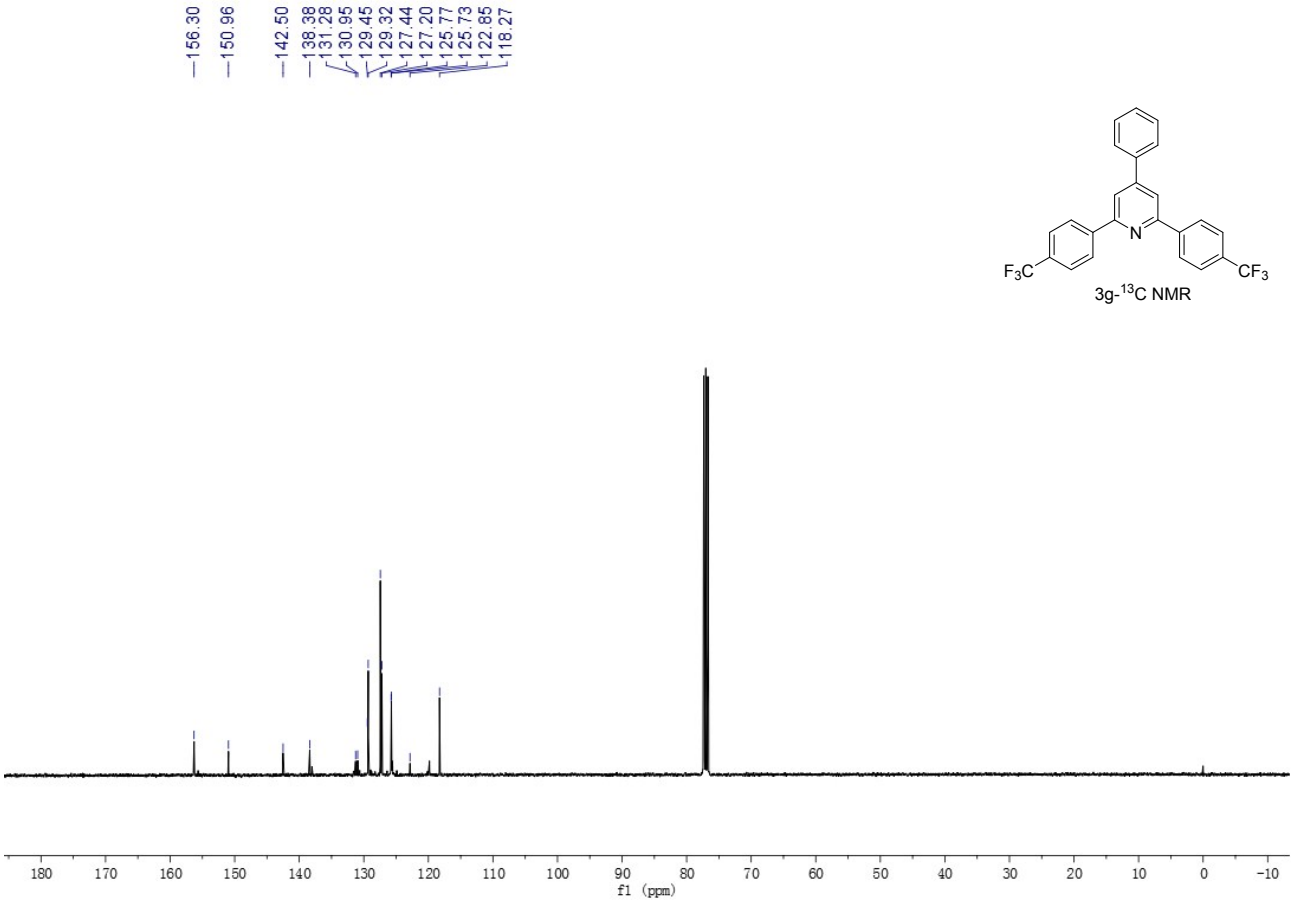
8.29
7.97
7.79
7.77
7.76
7.75
7.75
7.75
7.74
7.74
7.58
7.56
7.54
7.53
7.51
F3C
CF3
3g-1H NMR
1
2
3
4
5
4.00
2.00
4.47
2.08
3.04
f1 (ppm)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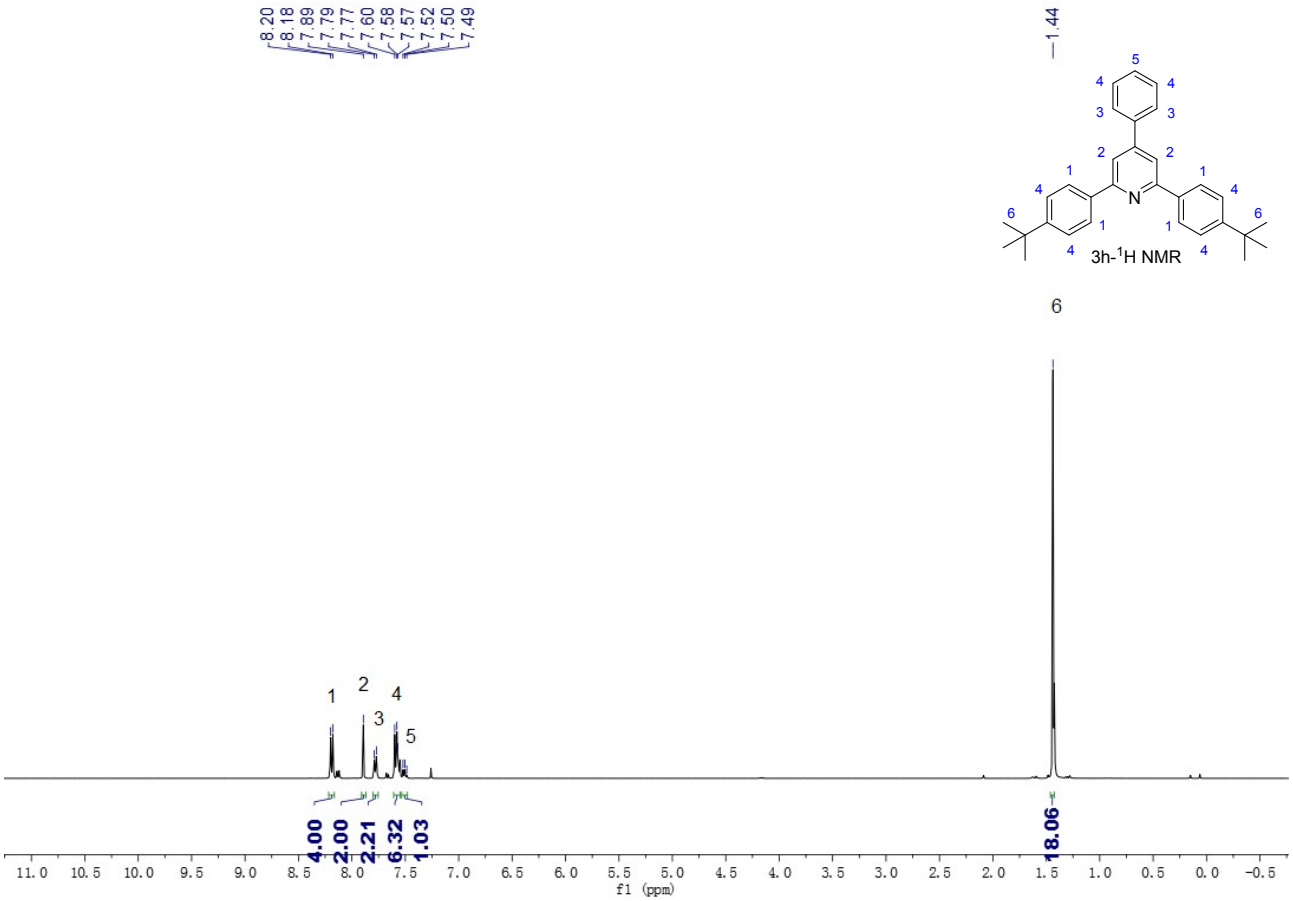
150.96
142.50
138.38
131.28
130.95
129.45
129.32
127.44
127.20
125.77
125.73
122.85
118.27
N
F3C
CF3
3g-13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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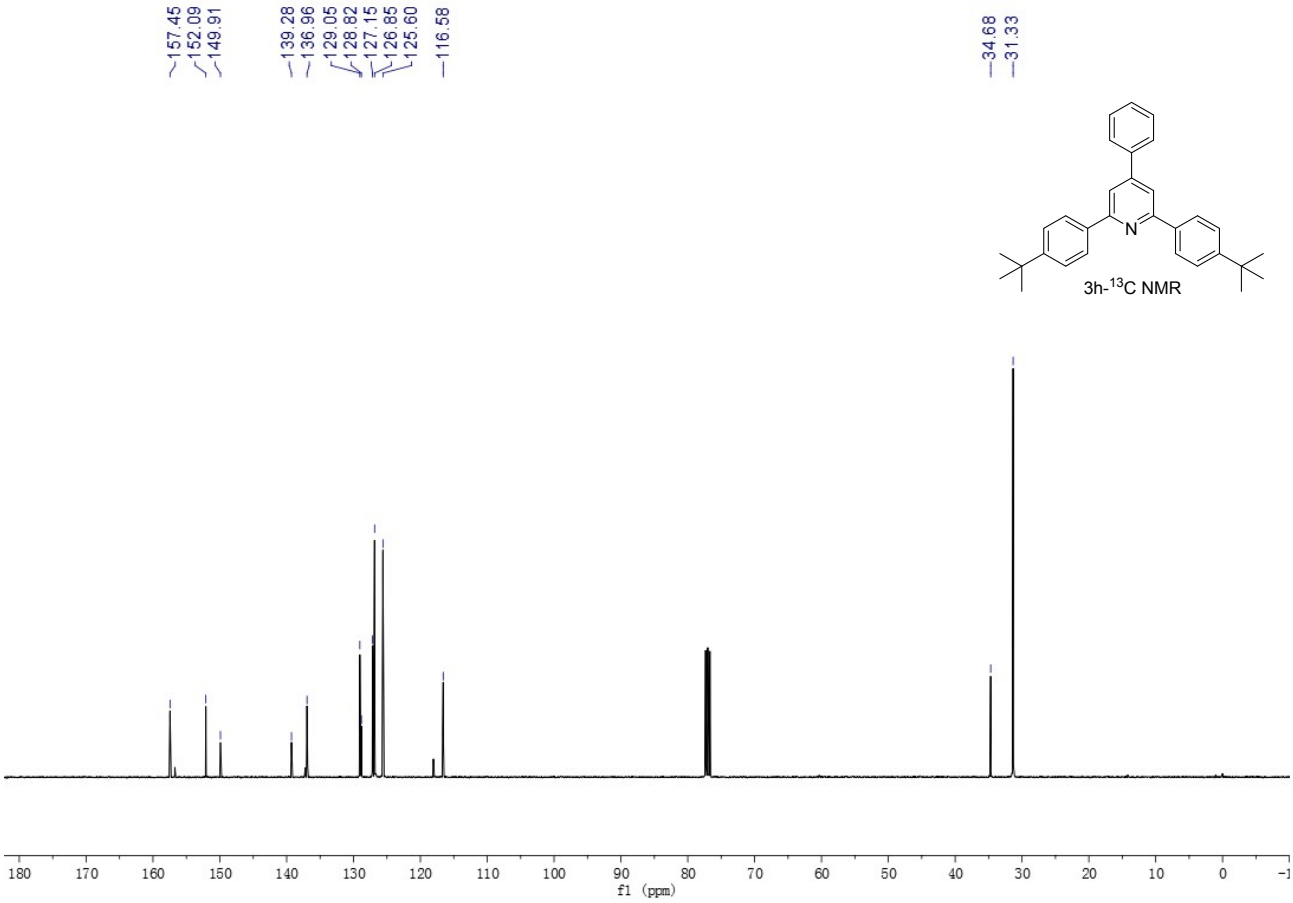
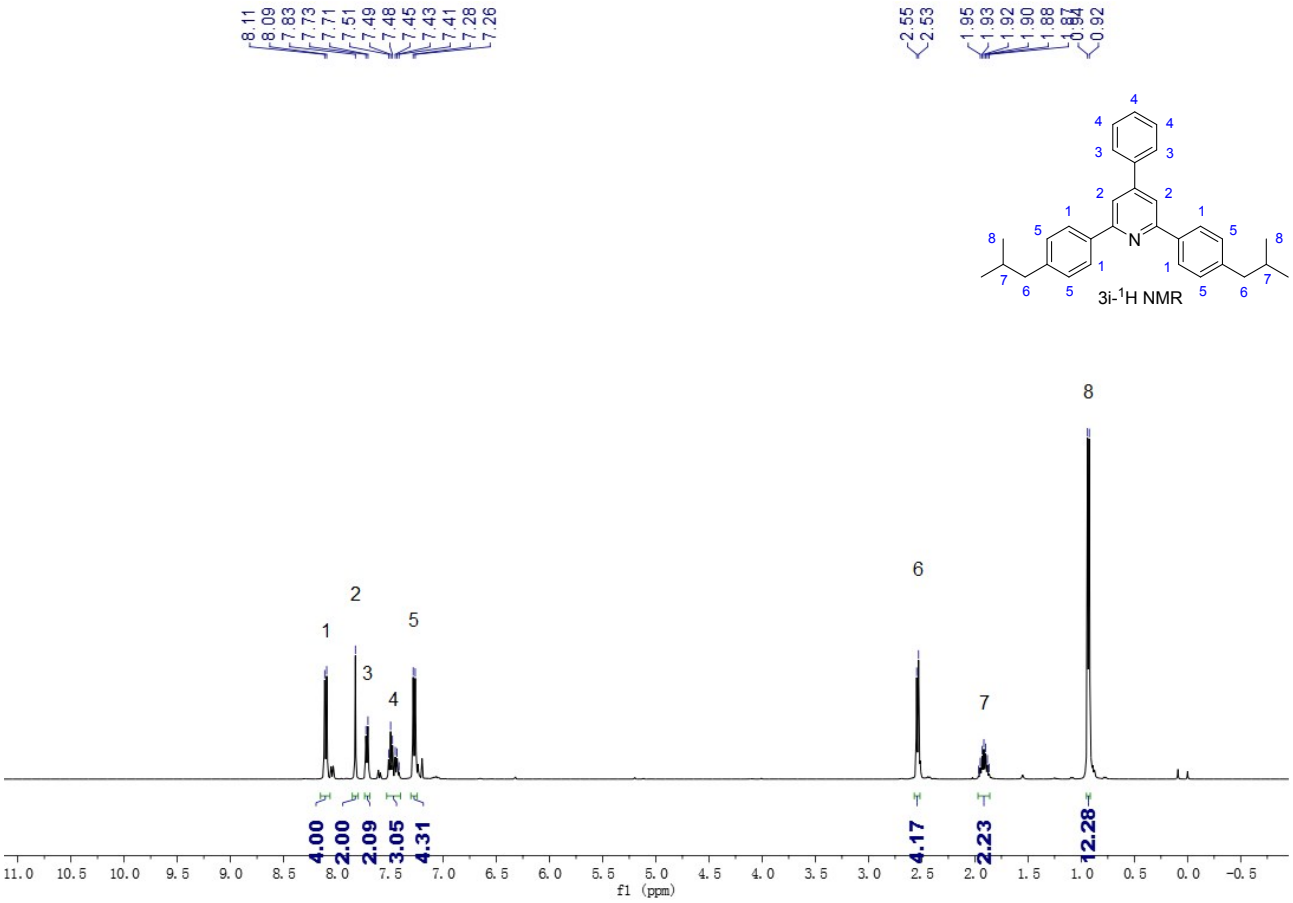
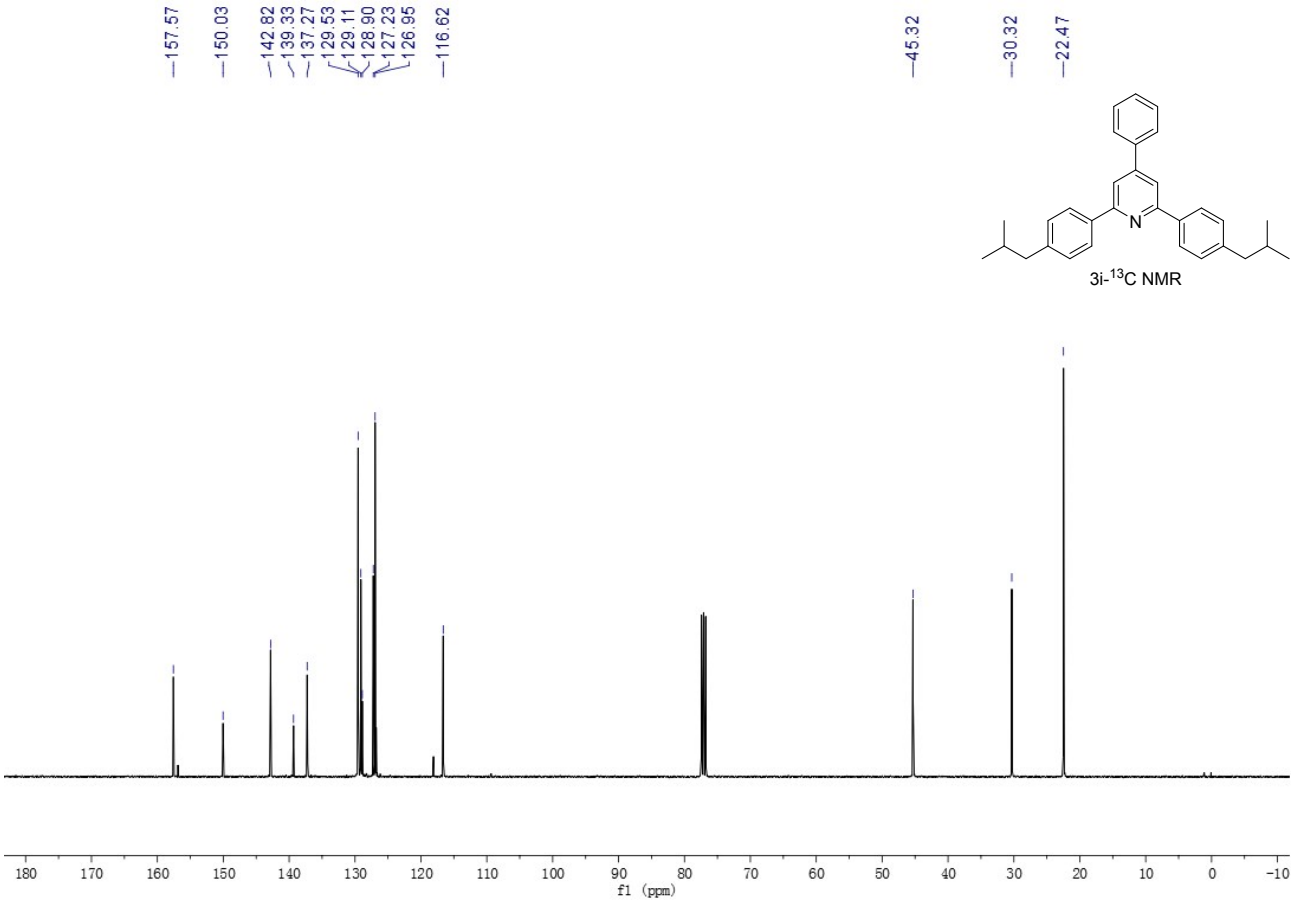
8.18
7.89
7.79
7.77
7.60
7.58
7.57
7.52
7.50
7.49
1.44
3h-1H NMR
6
1
2
3
4
5
4.00
2.00
2.21
6.32
1.03
18.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


157.45
152.09
149.91
139.28
136.96
129.05
128.82
127.15
126.85
125.60
116.58
34.68
31.33
N
3h-13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


8.11
8.09
7.83
7.73
7.71
7.51
7.49
7.48
7.45
7.43
7.41
7.28
7.26
2.55
2.53
1.95
1.93
1.92
1.90
1.88
0.94
0.92
3i-1H NMR
1
2
3
4
5
6
7
8
4.00
2.00
2.09
3.05
4.31
4.17
2.23
12.28
f1 (ppm)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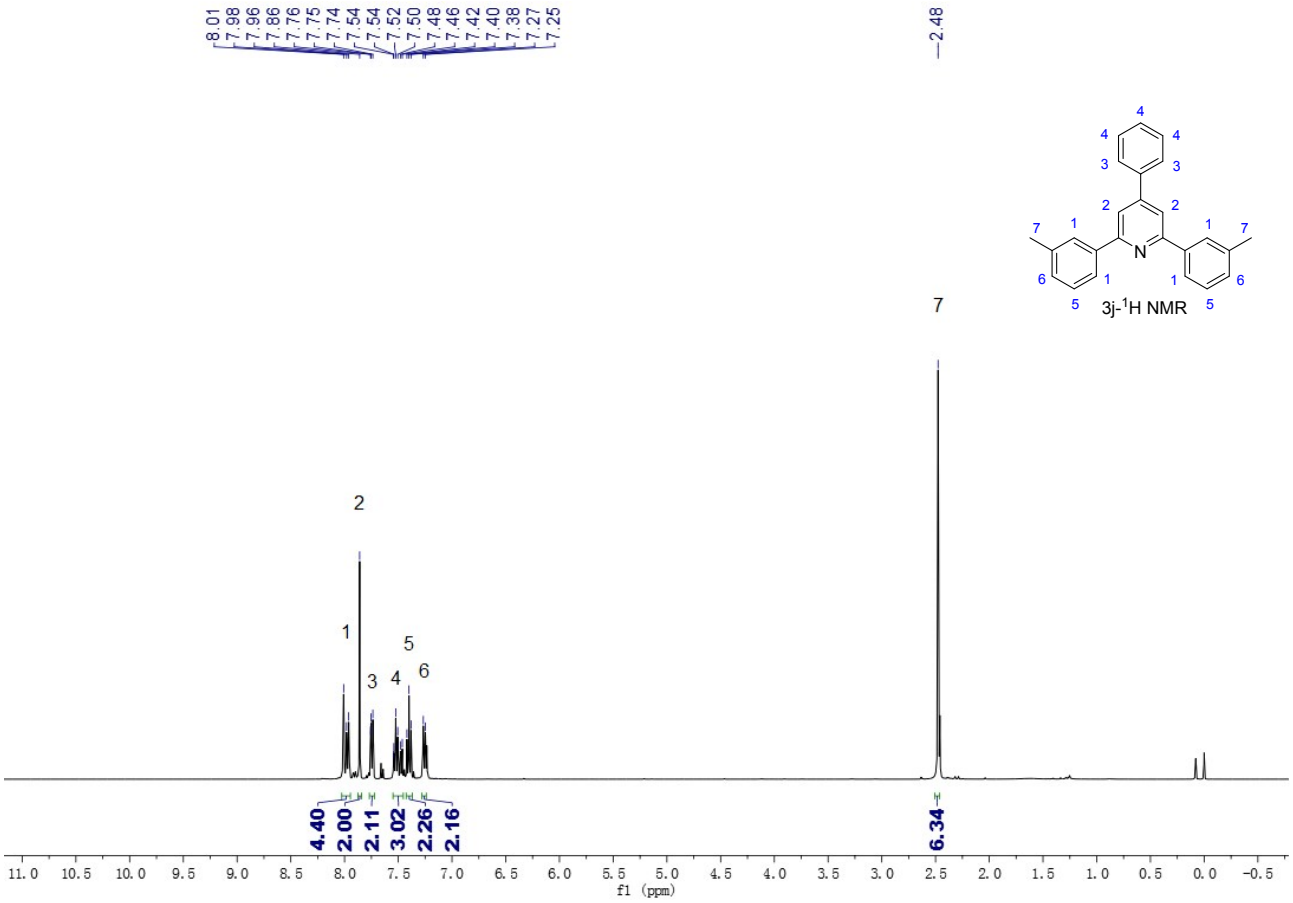
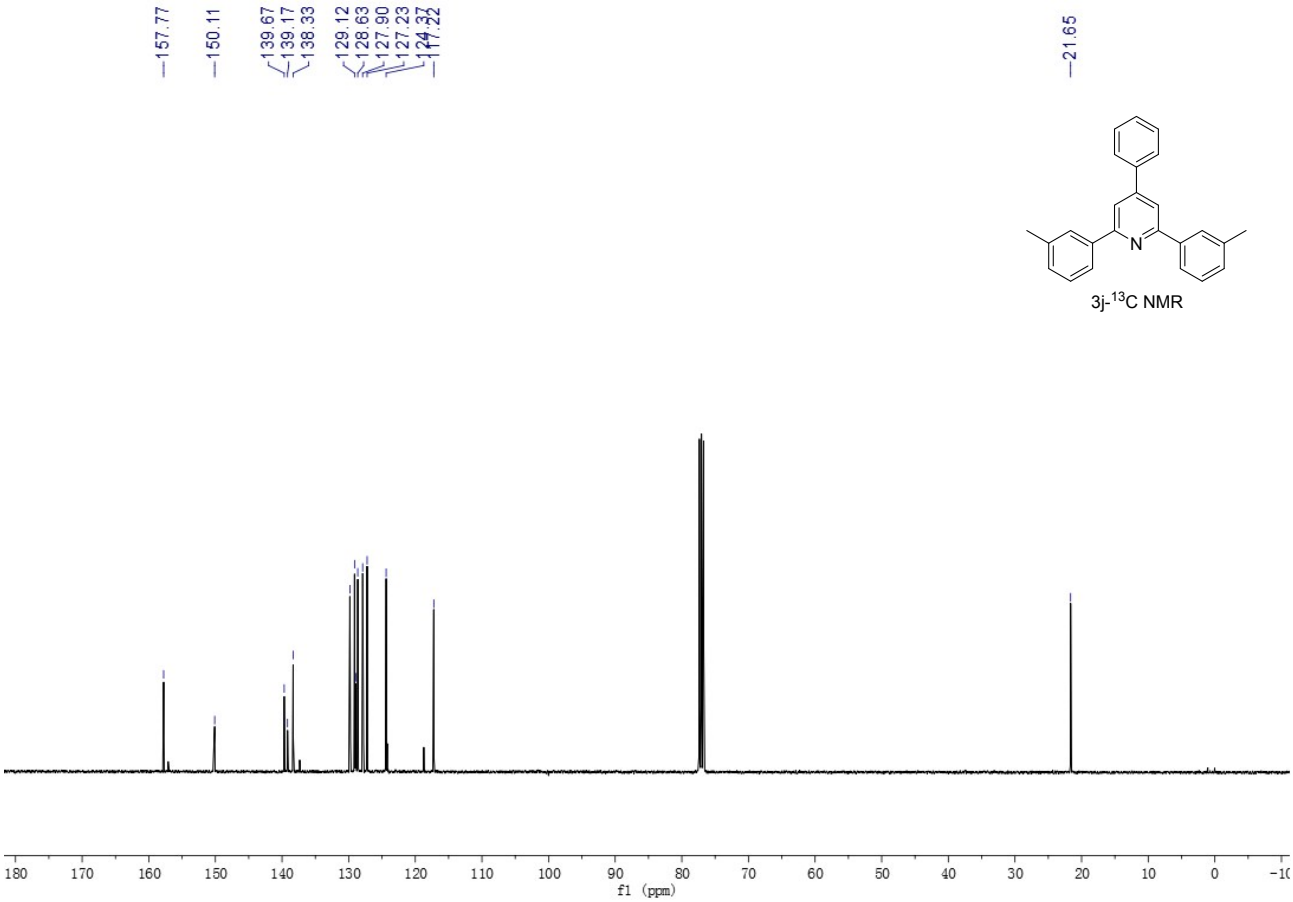
150.03
142.82
139.33
137.27
129.53
129.11
128.90
127.23
126.95
116.62
45.32
30.32
22.47
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3i-^{13}C NMR


8.01
7.98
7.96
7.86
7.76
7.75
7.74
7.54
7.54
7.52
7.50
7.48
7.46
7.42
7.40
7.38
7.27
7.25
2.48
7
2
1
3
4
5
6
4.40
2.00
2.11
3.02
2.26
2.16
6.34
f1 (ppm)

3j-^{1}H NMR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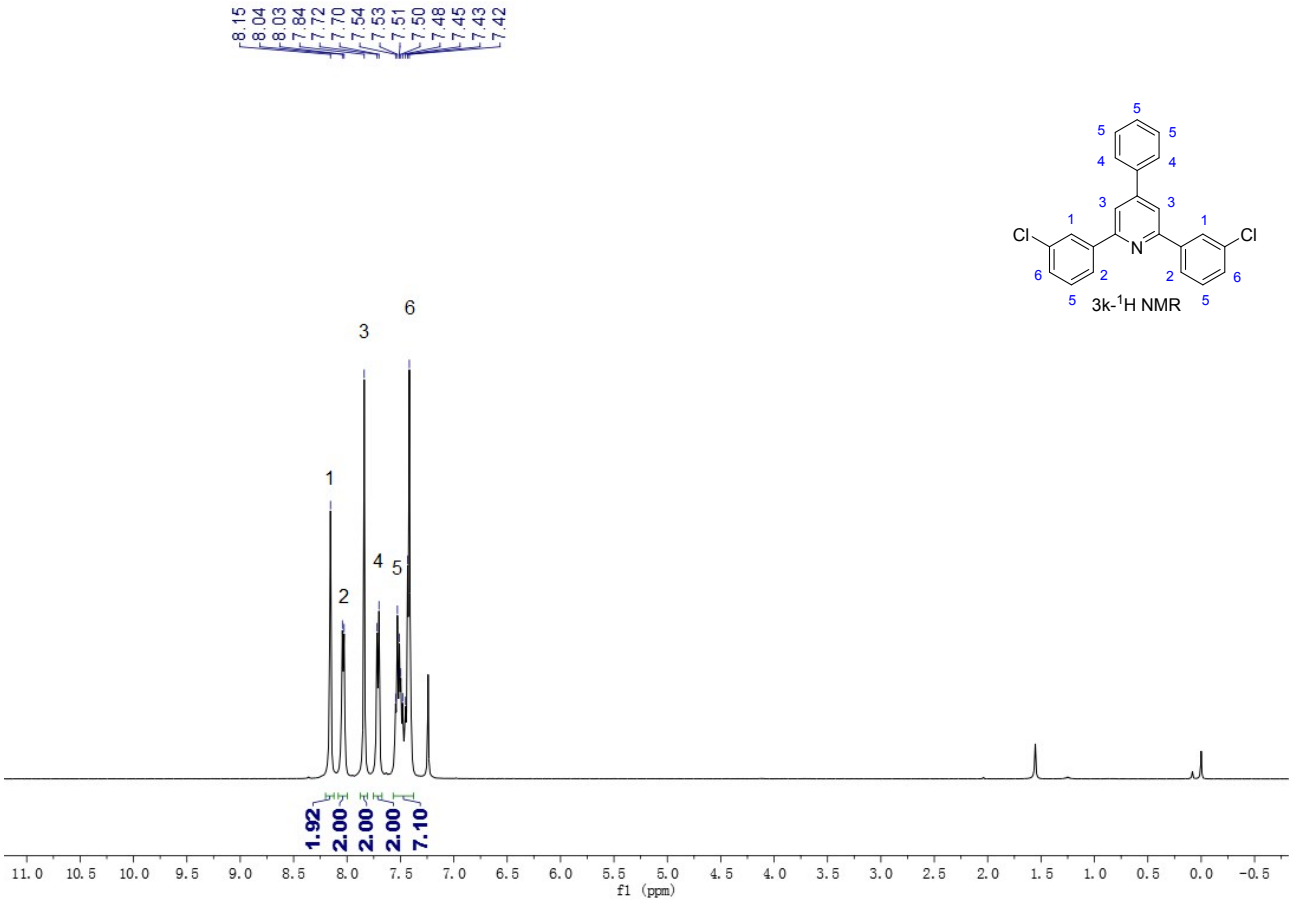
150.11
139.67
139.17
138.33
129.12
128.63
127.90
127.23
124.37
117.22
21.65
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3j-^{13}C NMR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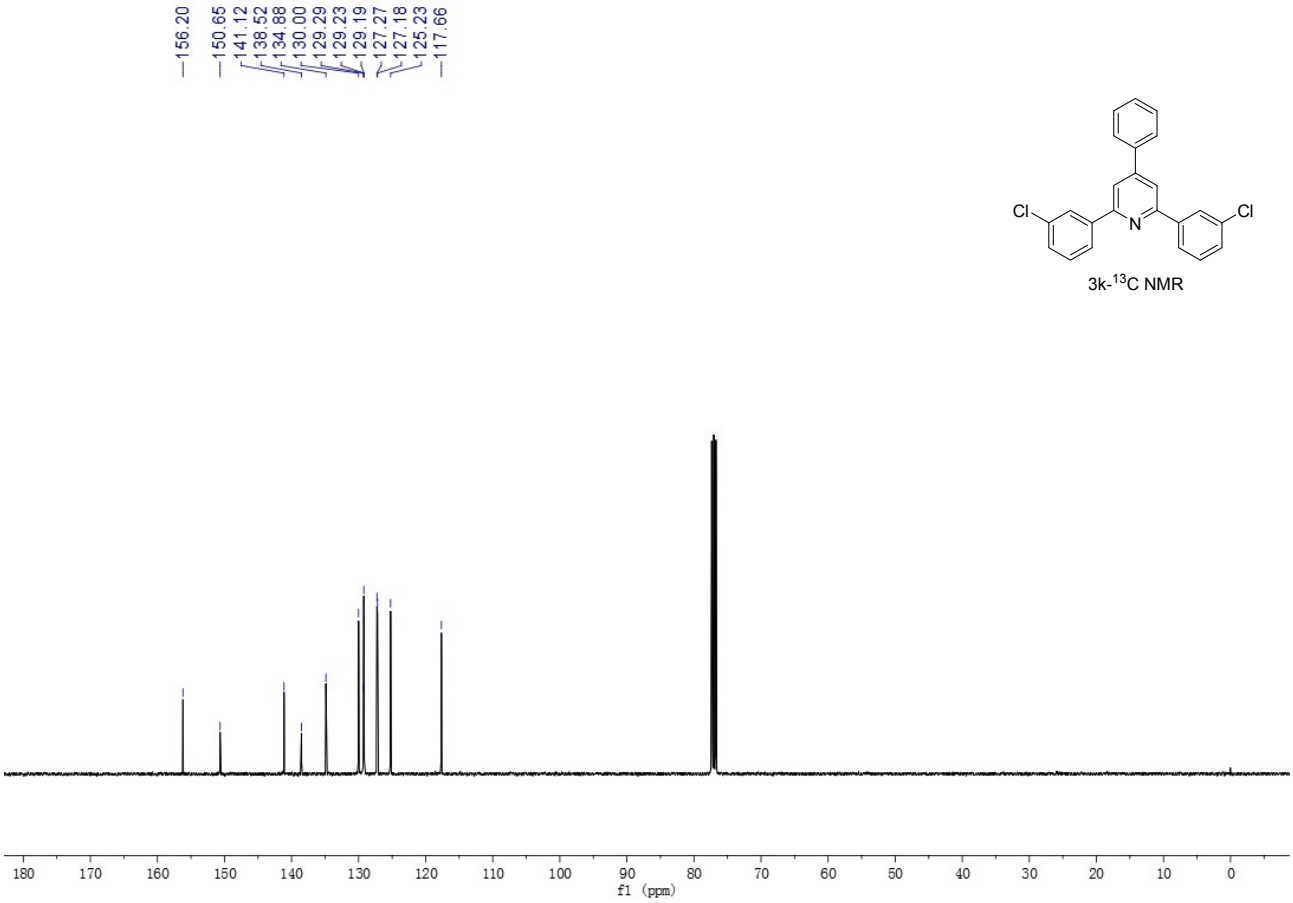
8.04
8.03
7.84
7.72
7.70
7.54
7.53
7.51
7.50
7.48
7.45
7.43
7.42
Cl
Cl
N
3k-1H NMR
1
2
3
4
5
6
1.92
2.00
2.00
2.00
7.10
f1 (ppm)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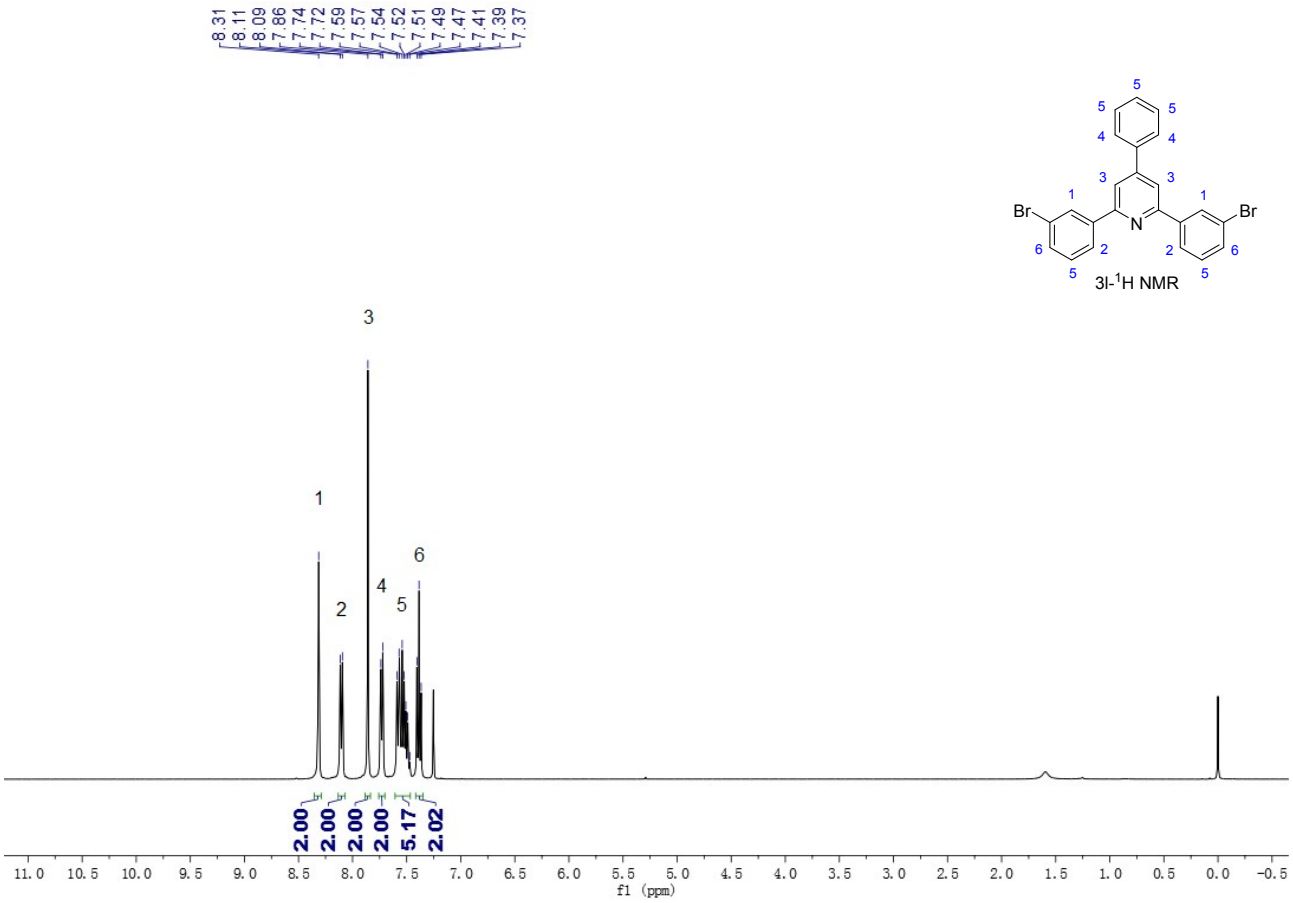
150.65
141.12
138.52
134.88
130.00
129.29
129.23
129.19
127.27
127.18
125.23
117.66
Cl
N
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3k-^{13}C NMR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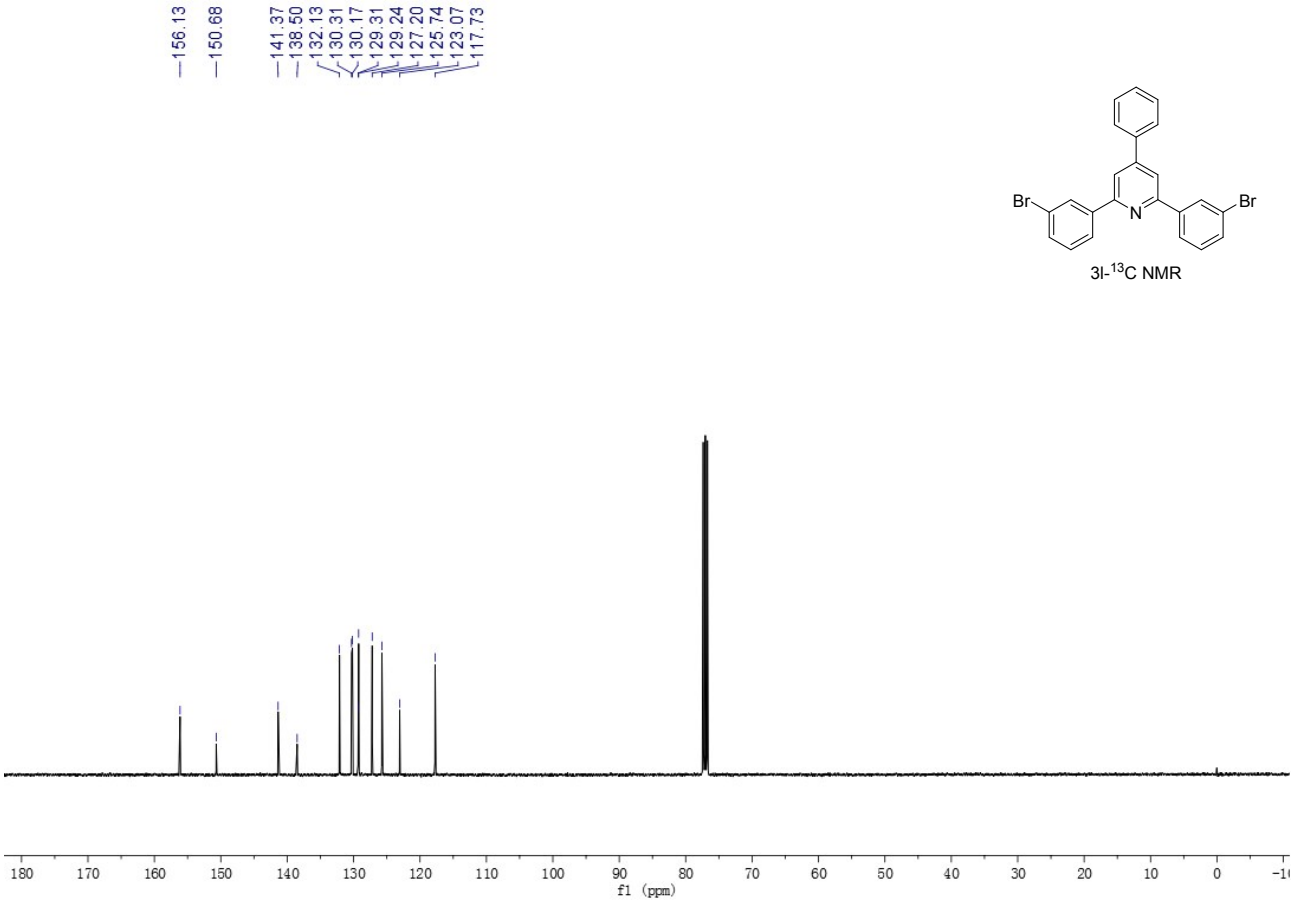
8.11
8.09
7.86
7.74
7.72
7.59
7.57
7.54
7.52
7.51
7.49
7.47
7.41
7.39
7.37
Br
N
Br
3l-1H NMR
1
2
3
4
5
6
2.00
2.00
2.00
2.00
5.17
2.02
f1 (ppm)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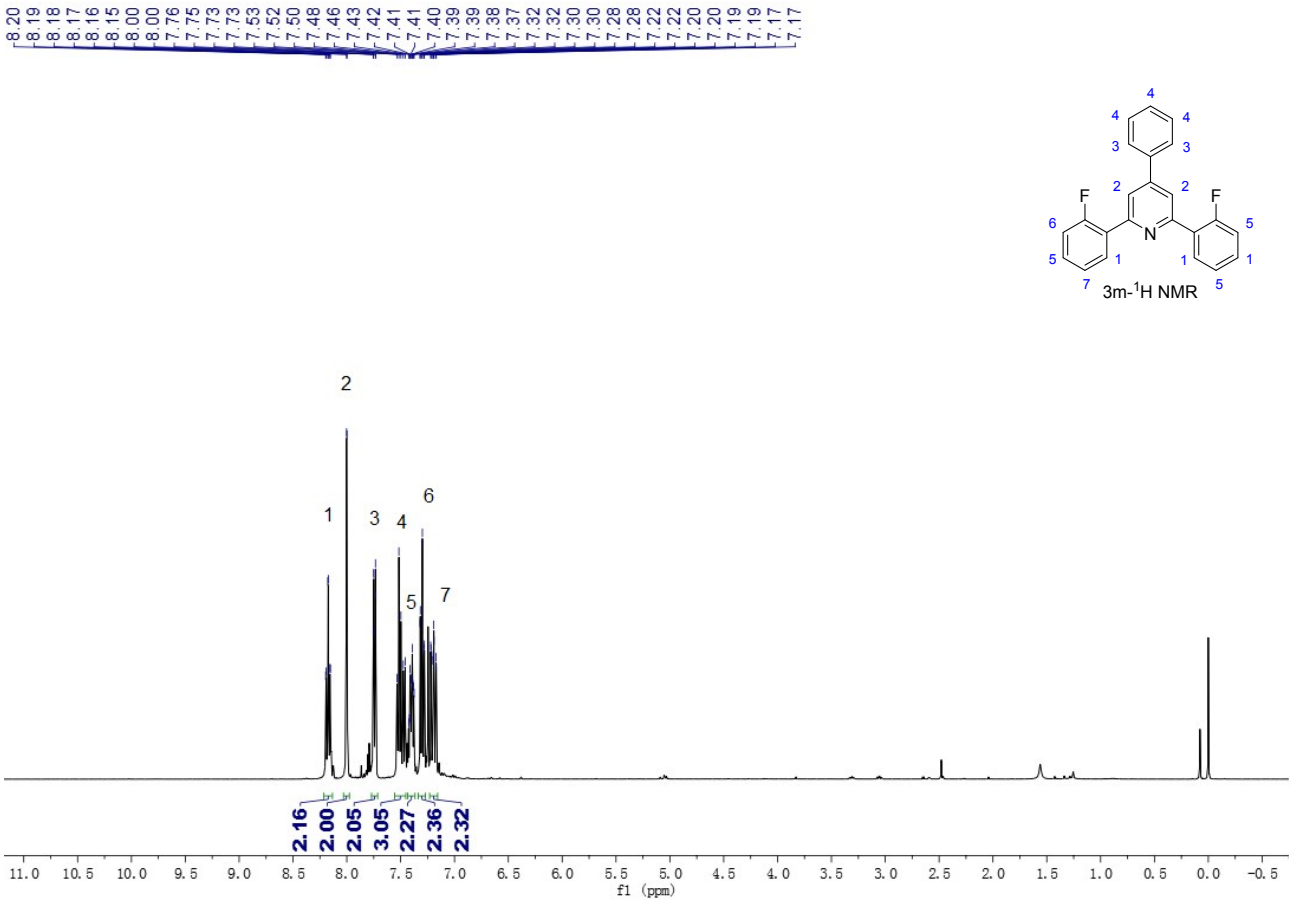
141.37
138.50
132.13
130.31
130.17
129.31
129.24
127.20
125.74
123.07
117.73
Br
N
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3l-^{13}C NMR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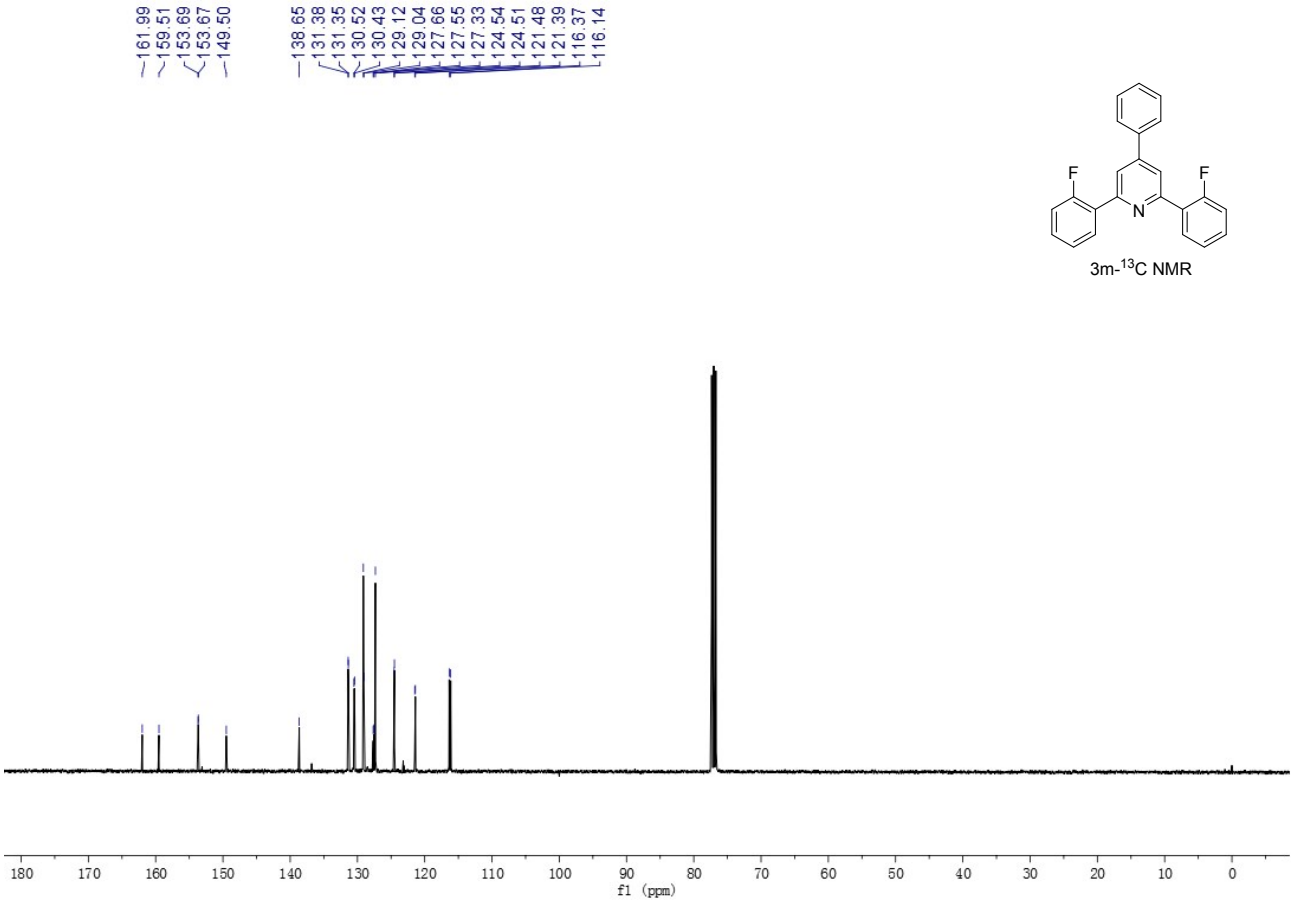
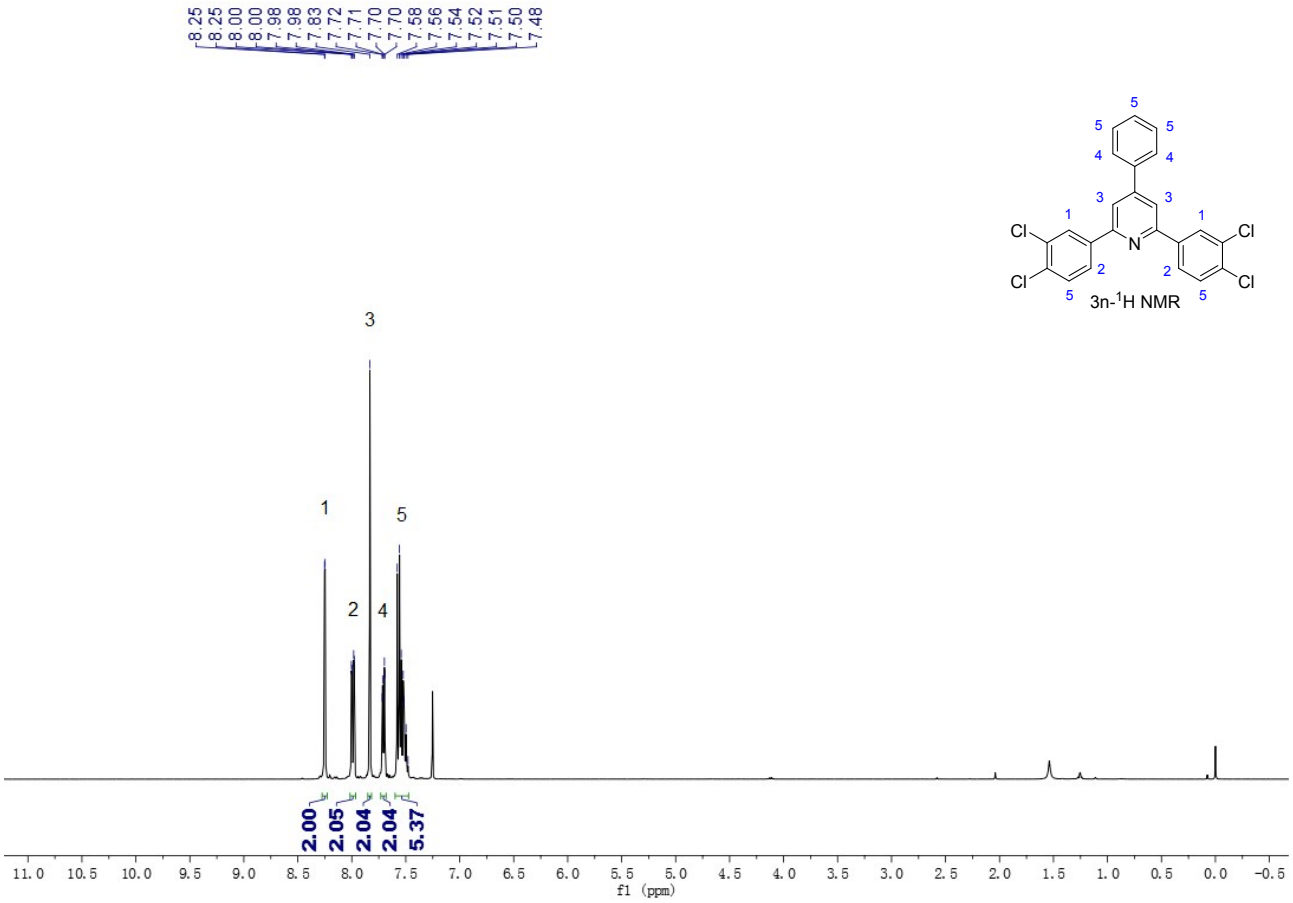
F
F
N
3m-1H NMR
1
2
3
4
5
6
7
2.16
2.00
2.05
3.05
2.27
2.36
2.32
f1 (ppm)


161.99
159.51
153.69
153.67
149.50
138.65
131.38
131.35
130.52
130.43
129.12
129.04
127.66
127.55
127.33
124.54
124.51
121.48
121.39
116.37
116.14
F
F
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3m-^{13}C NMR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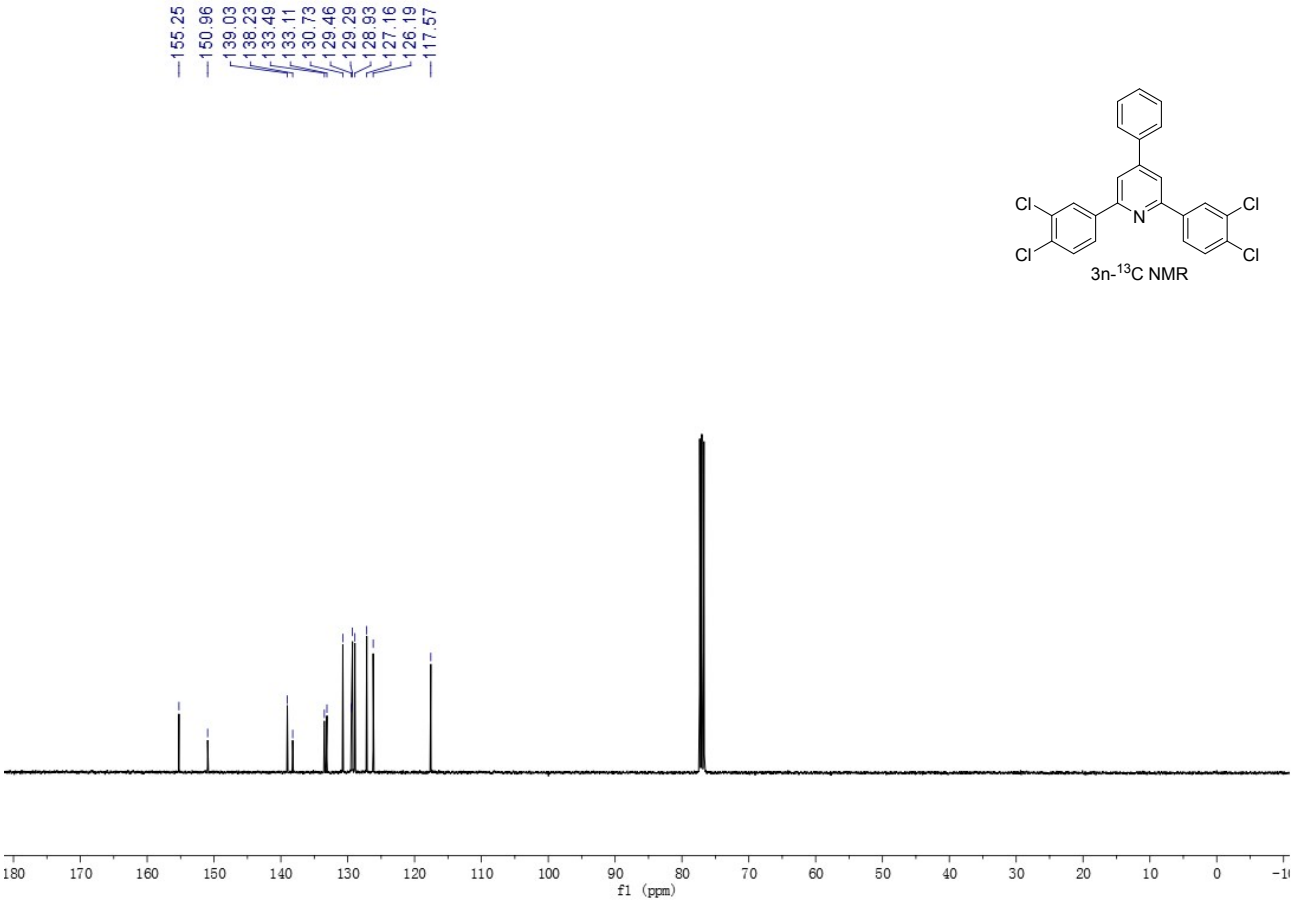
8.25
8.00
8.00
7.98
7.98
7.83
7.72
7.71
7.70
7.70
7.58
7.56
7.54
7.52
7.51
7.50
7.48
Cl
Cl
N
Cl
Cl
3n-1H NMR
1
2
3
4
5
2.00
2.05
2.04
2.04
5.37
f1 (ppm)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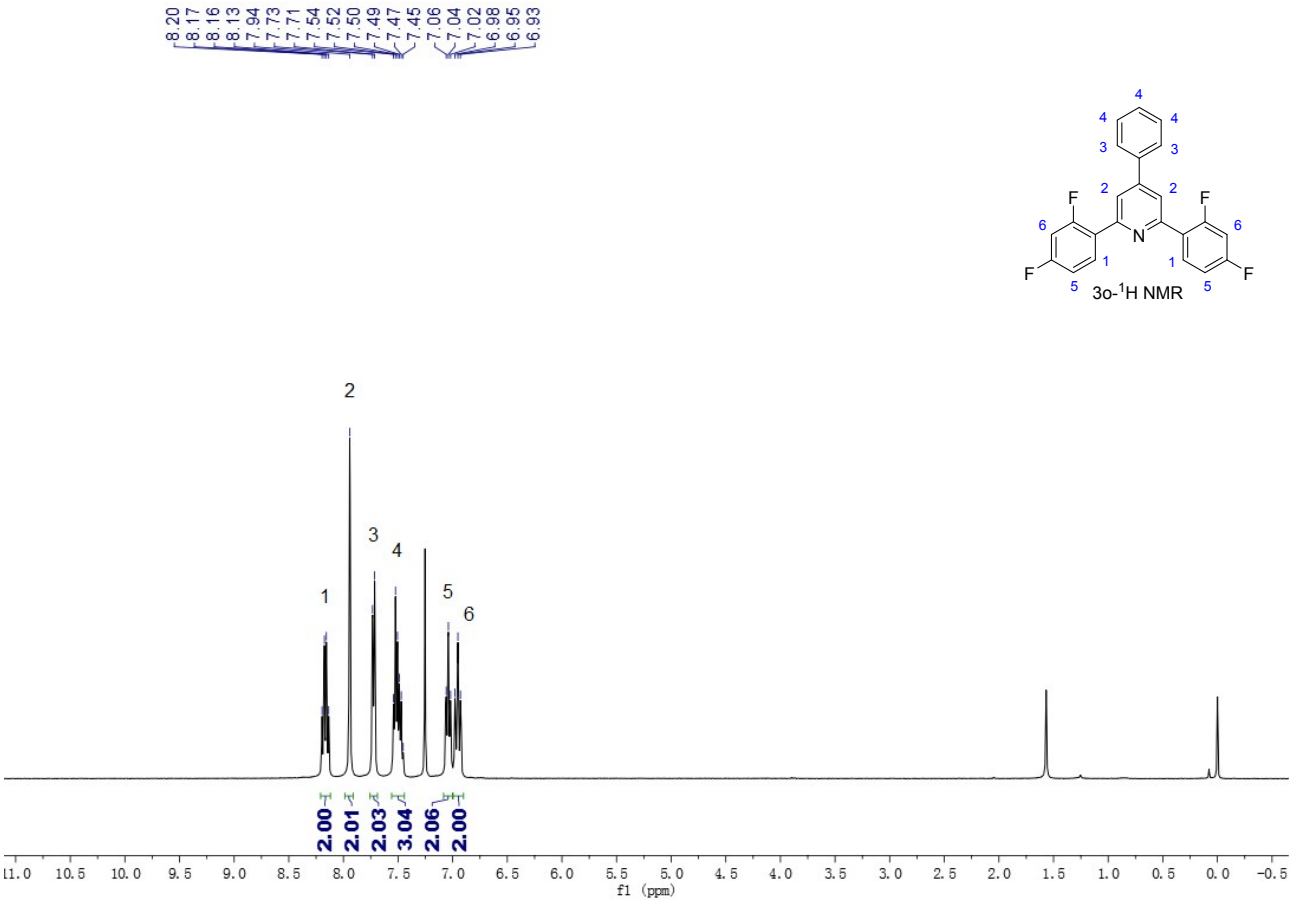
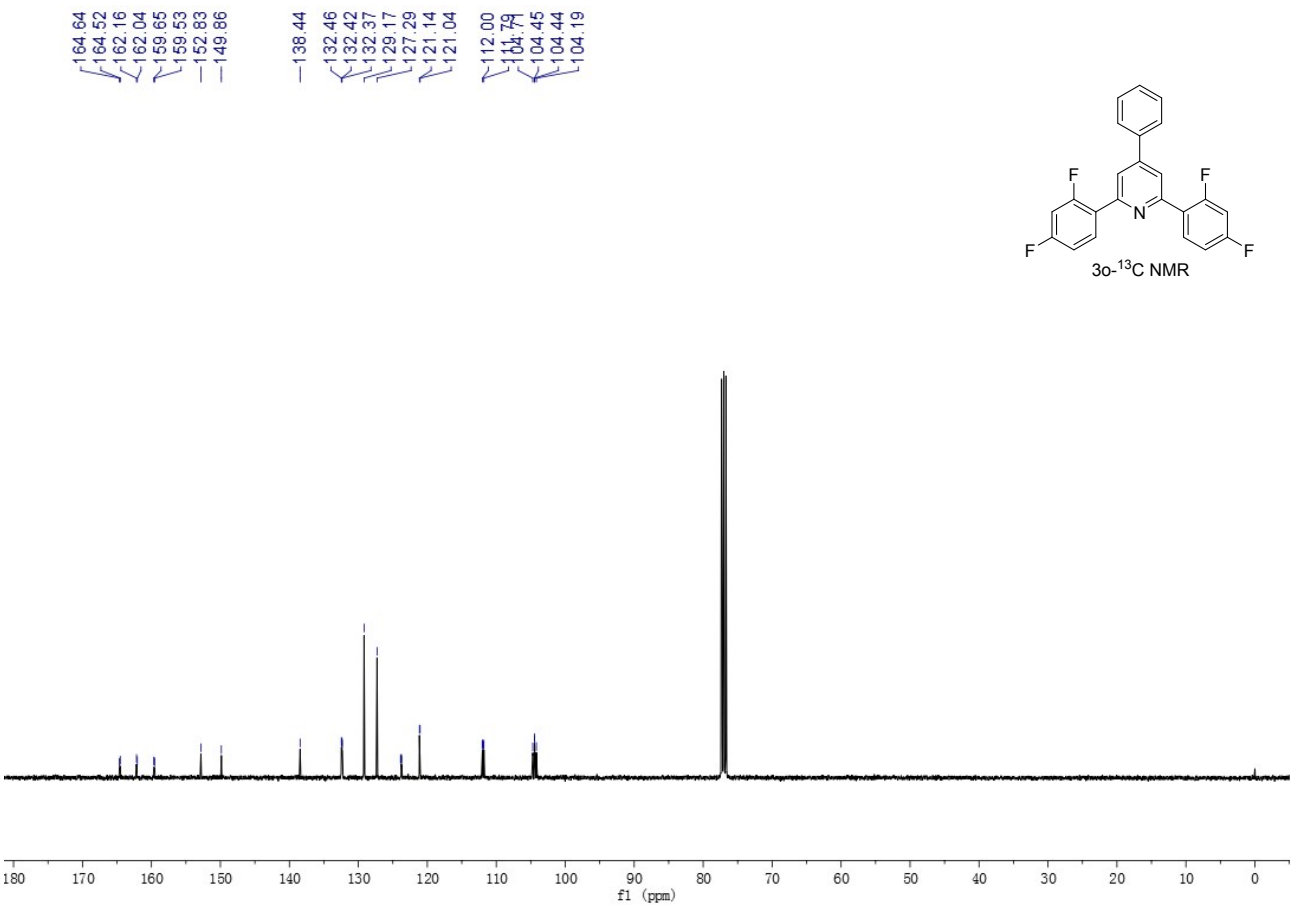
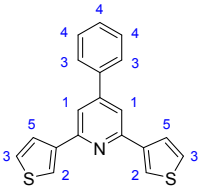
150.96
139.03
138.23
133.49
133.11
130.73
129.46
129.29
128.93
127.16
126.19
117.57
Cl
Cl
N
Cl
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3n-^{13}C NMR

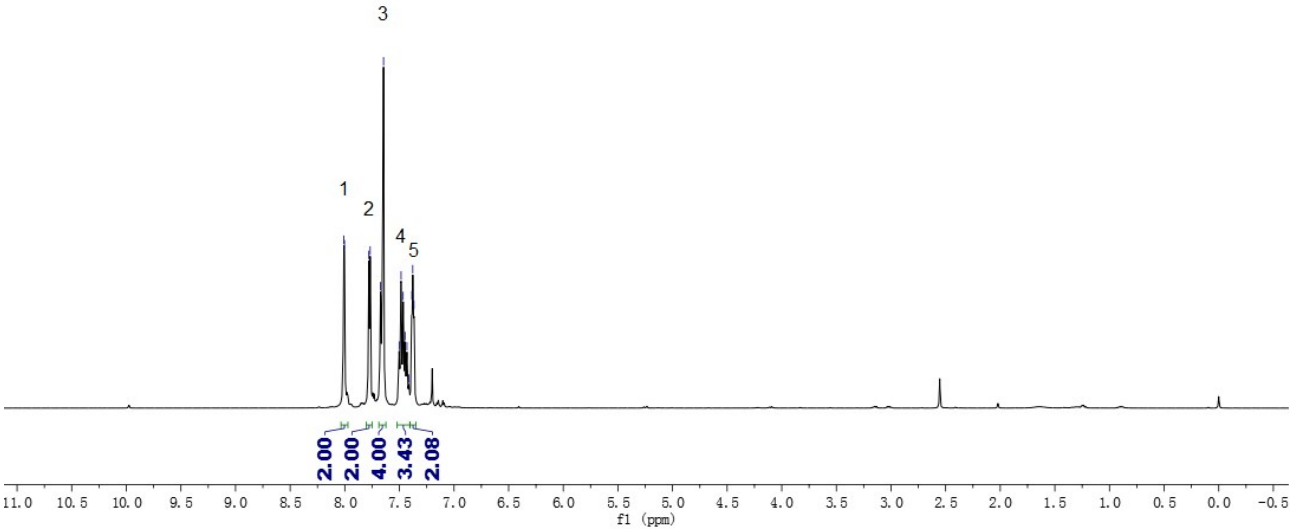

8.20
8.17
8.16
8.13
7.94
7.73
7.71
7.54
7.52
7.50
7.49
7.47
7.45
7.06
7.04
7.02
6.98
6.95
6.93
F
F
F
F
N
3o-1H NMR
1
2
3
4
5
6
2.00
2.01
2.03
3.04
2.06
2.00
f1 (ppm)

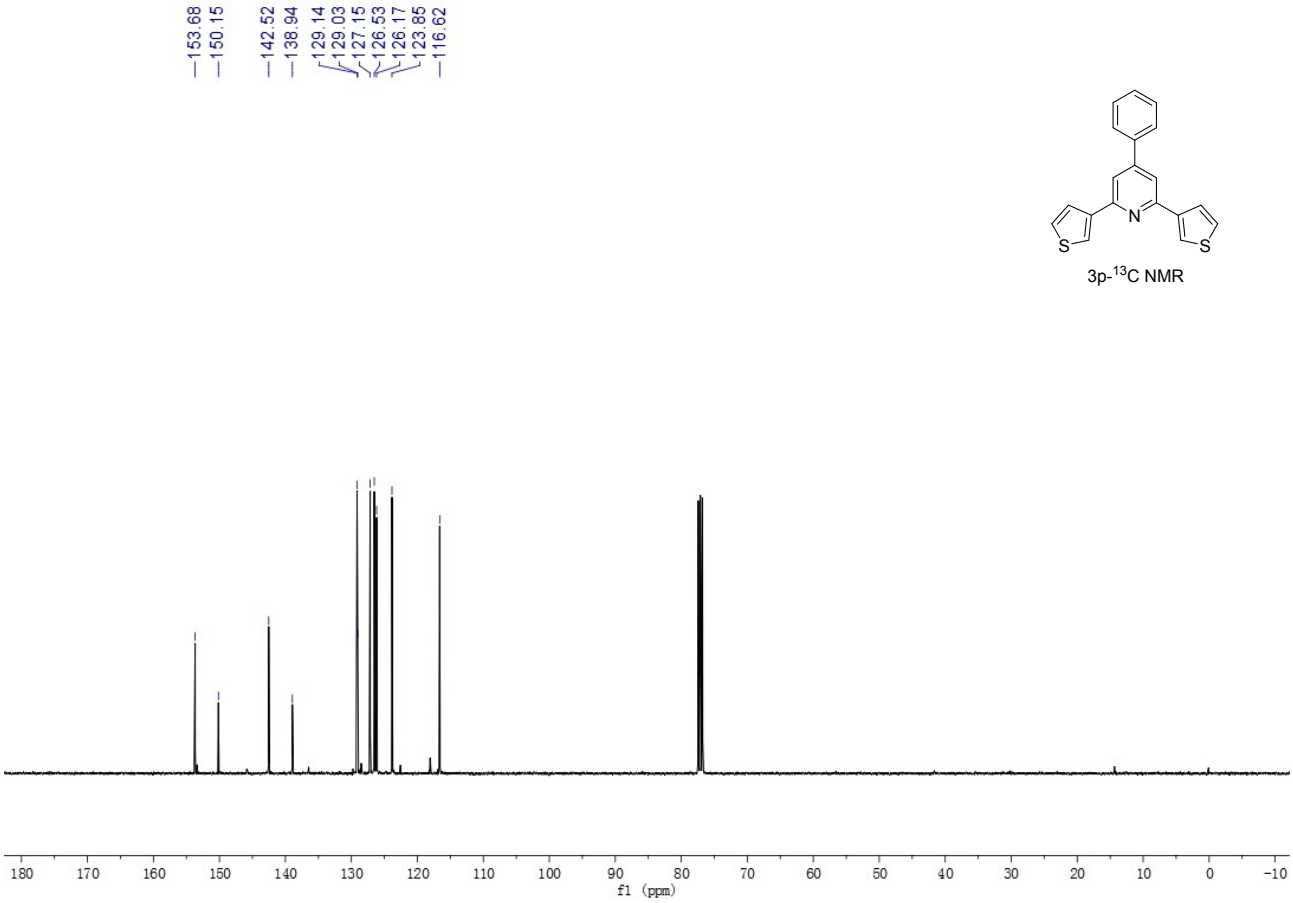

164.64
164.52
162.16
162.04
159.65
159.53
152.83
149.86
138.44
132.46
132.42
132.37
129.17
127.29
121.14
121.04
112.00
111.79
111.71
104.45
104.44
104.19
F
F
F
F
N
3o-13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.01
8.00
7.78
7.77
7.67
7.65
7.50
7.48
7.47
7.45
7.43
7.41
7.39
7.38
7.37

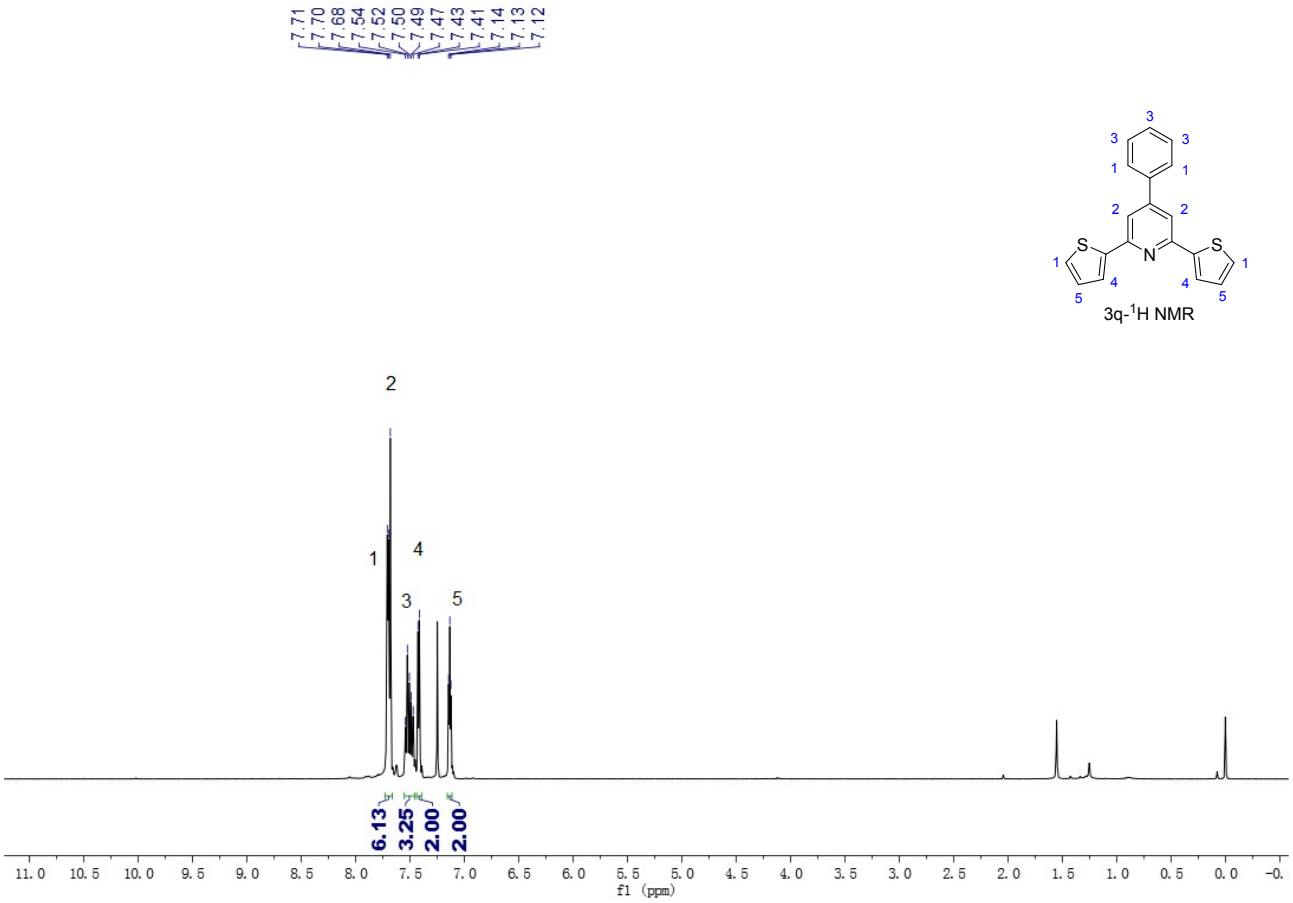

4
4
4
3
3
1
1
5
5
3
3
N
S
2
2
S

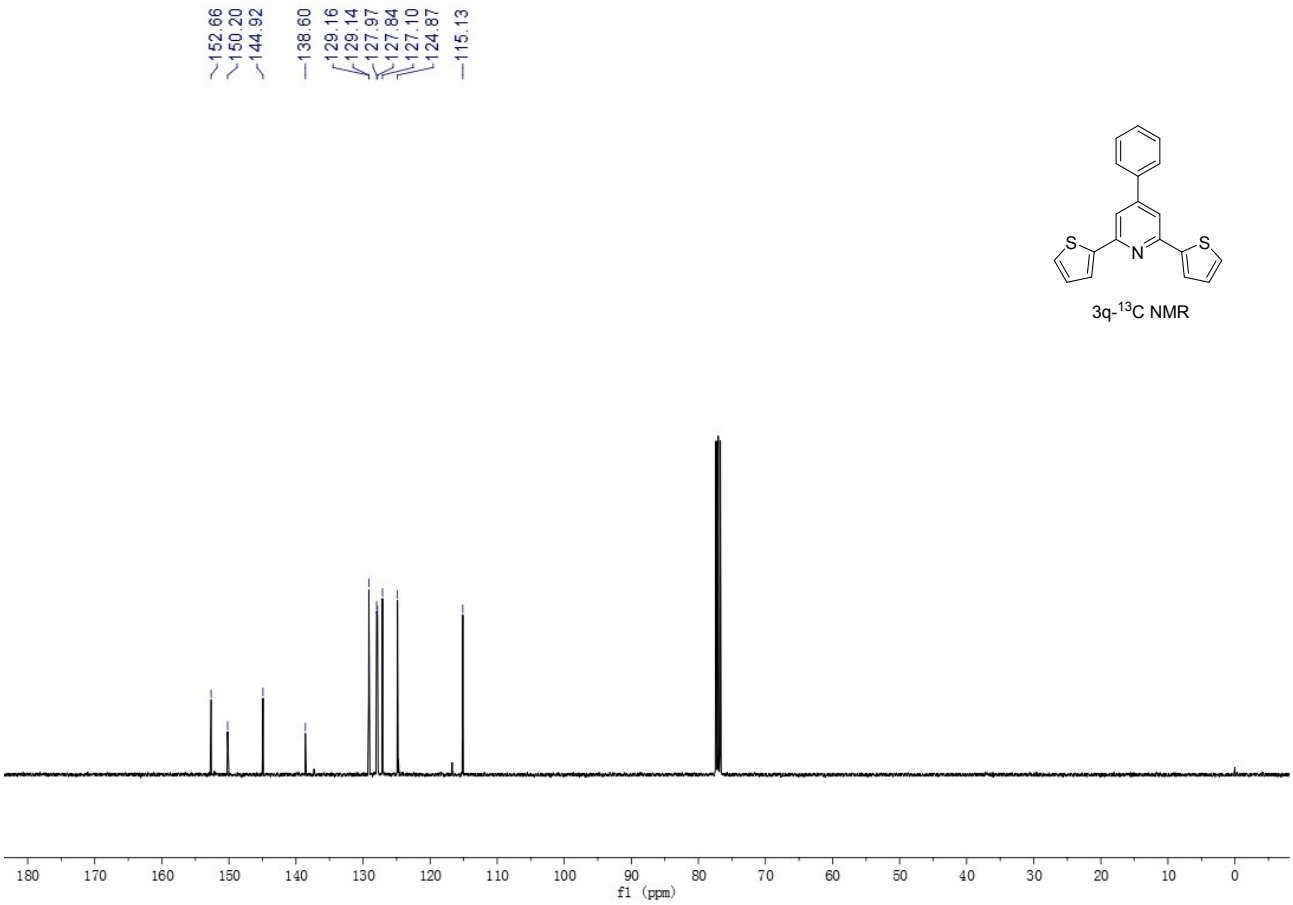
3p-^{1}H NMR


3
1
2
4
5
2.00
2.00
4.00
3.43
2.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

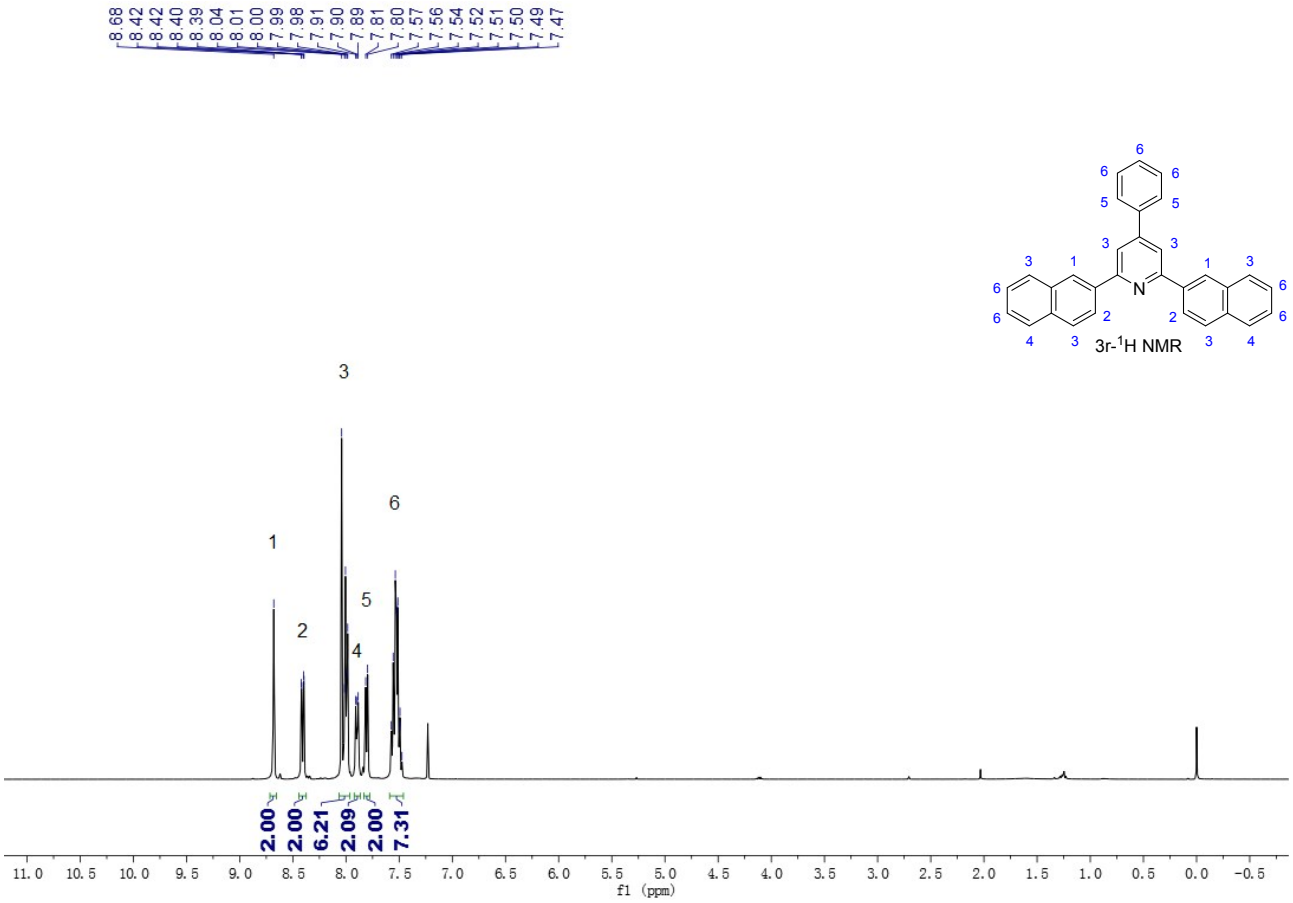

153.68
150.15
142.52
138.94
129.14
129.03
127.15
126.53
126.17
123.85
116.62
N
S
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

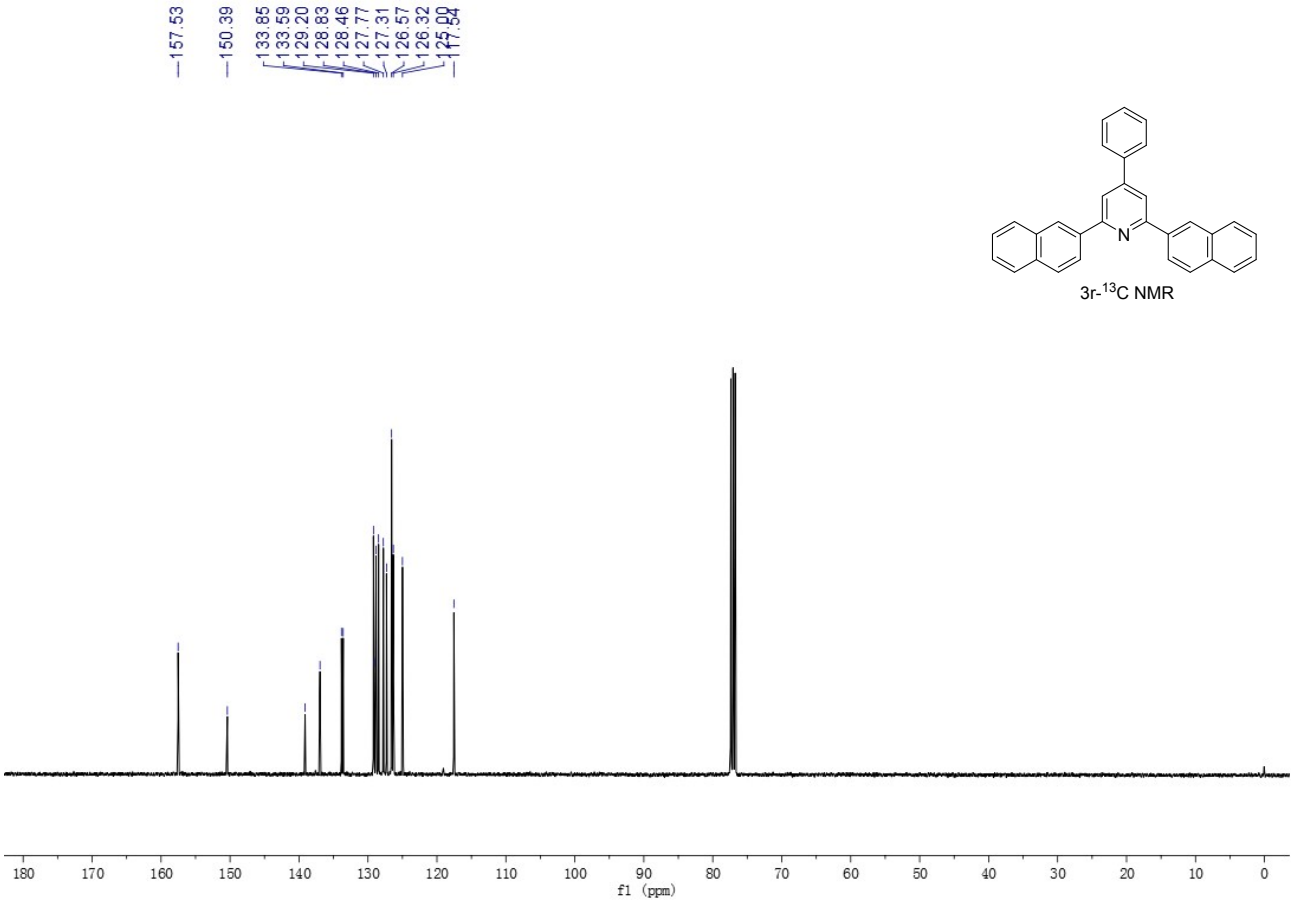
3p-^{13}C NMR


7.71
7.70
7.68
7.54
7.52
7.50
7.49
7.47
7.43
7.41
7.14
7.13
7.12
3
3
3
1
1
2
2
S
N
S
1
1
4
4
5
5
3q-1H NMR
2
1
4
3
5
6.13
3.25
2.00
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.66
150.20
144.92
138.60
129.16
129.14
127.97
127.84
127.10
124.87
115.13
S
N
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

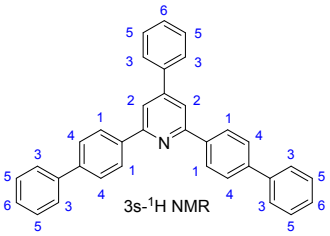
3q-^{13}C NMR

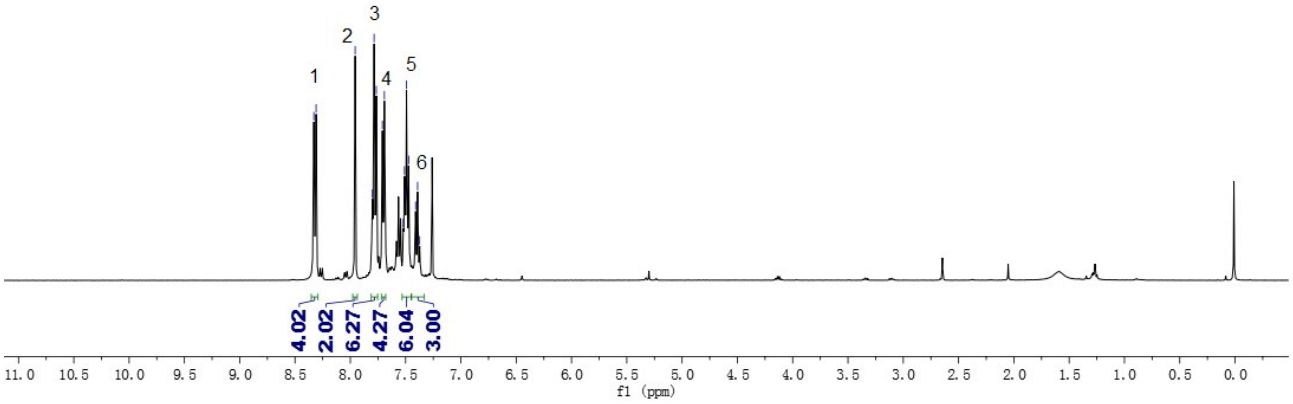

8.68
8.42
8.42
8.40
8.39
8.04
8.01
8.00
7.99
7.98
7.91
7.90
7.89
7.81
7.80
7.57
7.56
7.54
7.52
7.51
7.50
7.49
7.47
N
3r-1H NMR
1
2
3
4
5
6
2.00
2.00
6.21
2.09
2.00
7.31
f1 (ppm)

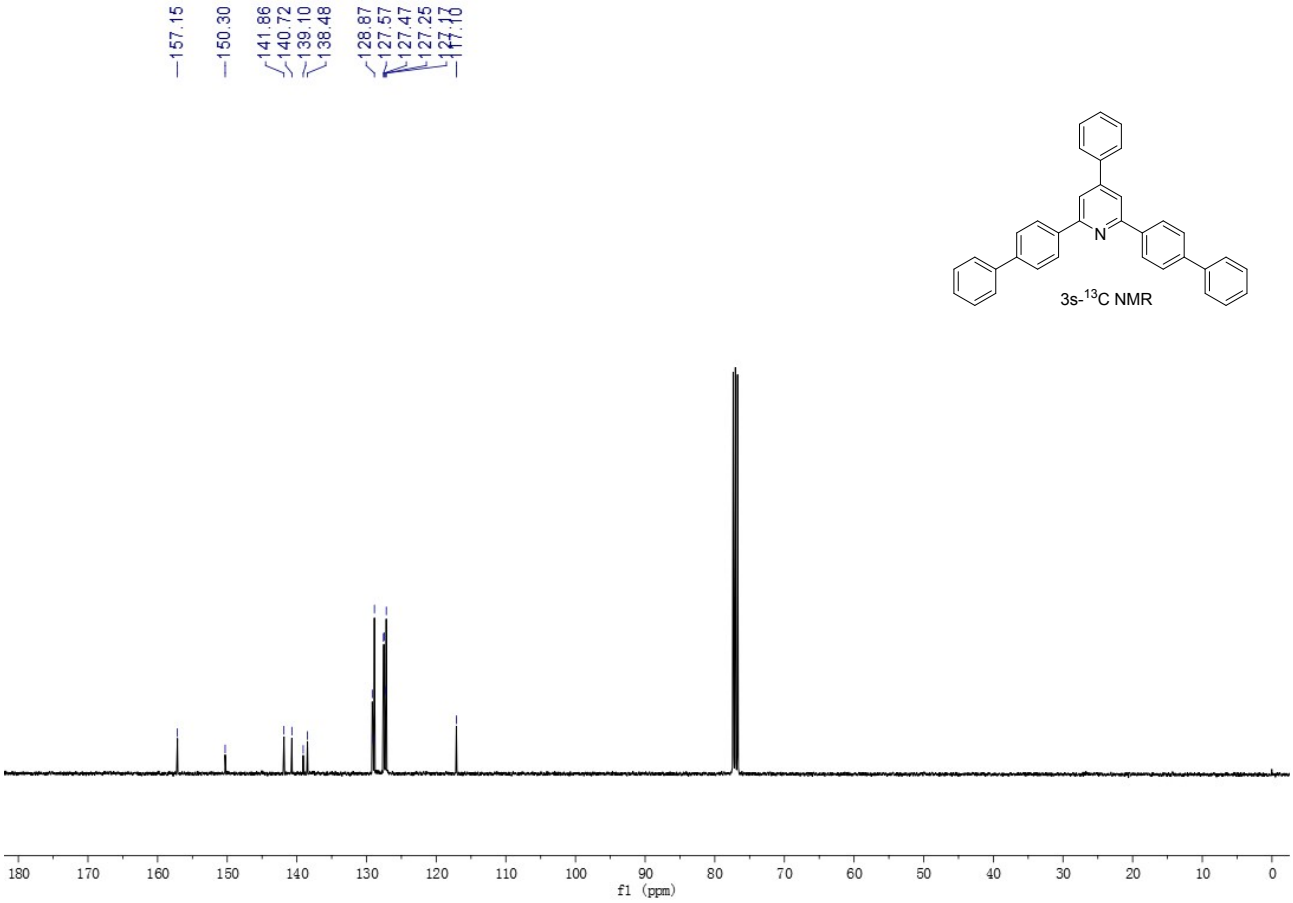

157.53
150.39
133.85
133.59
129.20
128.83
128.46
127.77
127.31
126.57
126.32
125.00
117.54
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

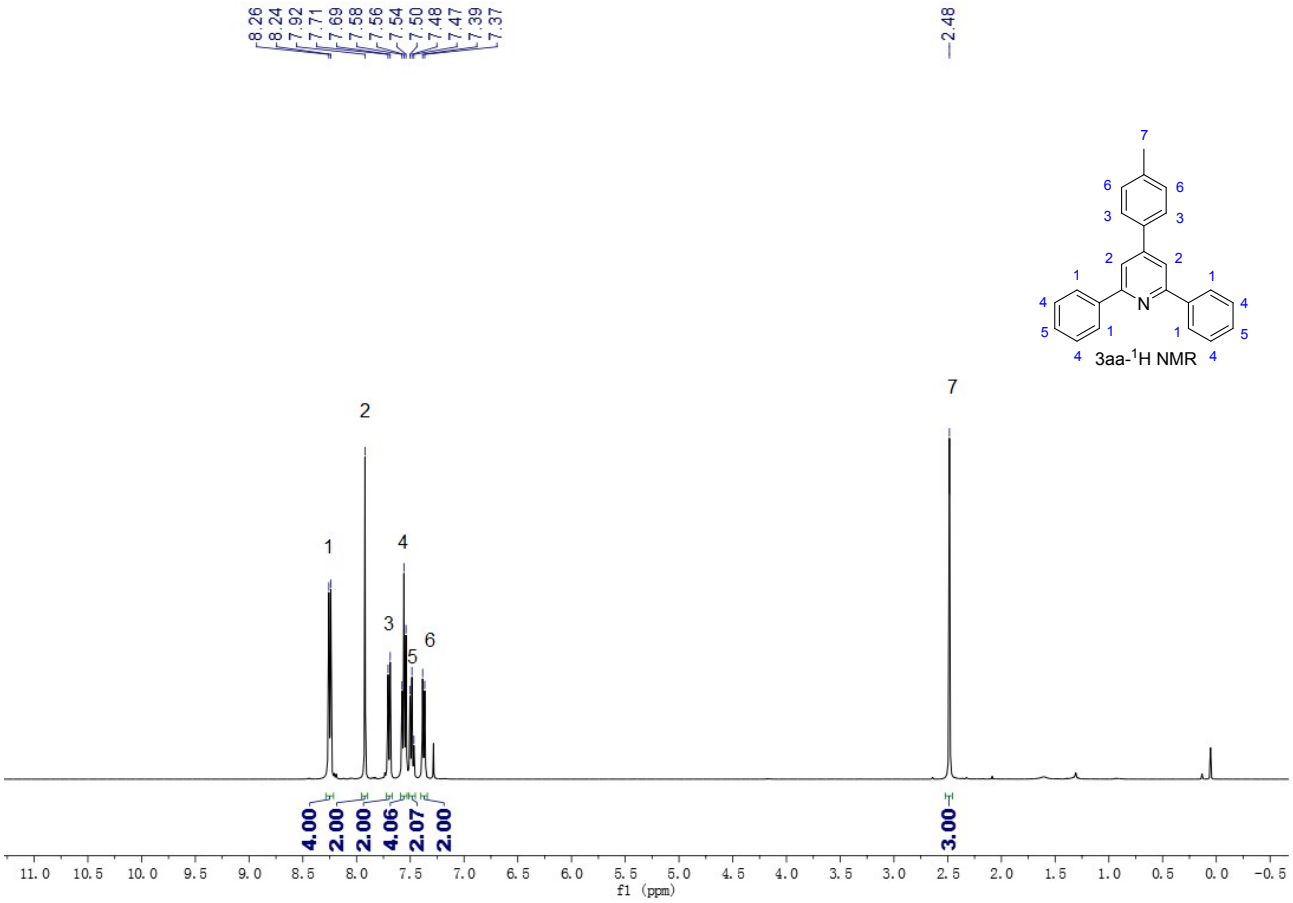
3r-^{13}C NMR

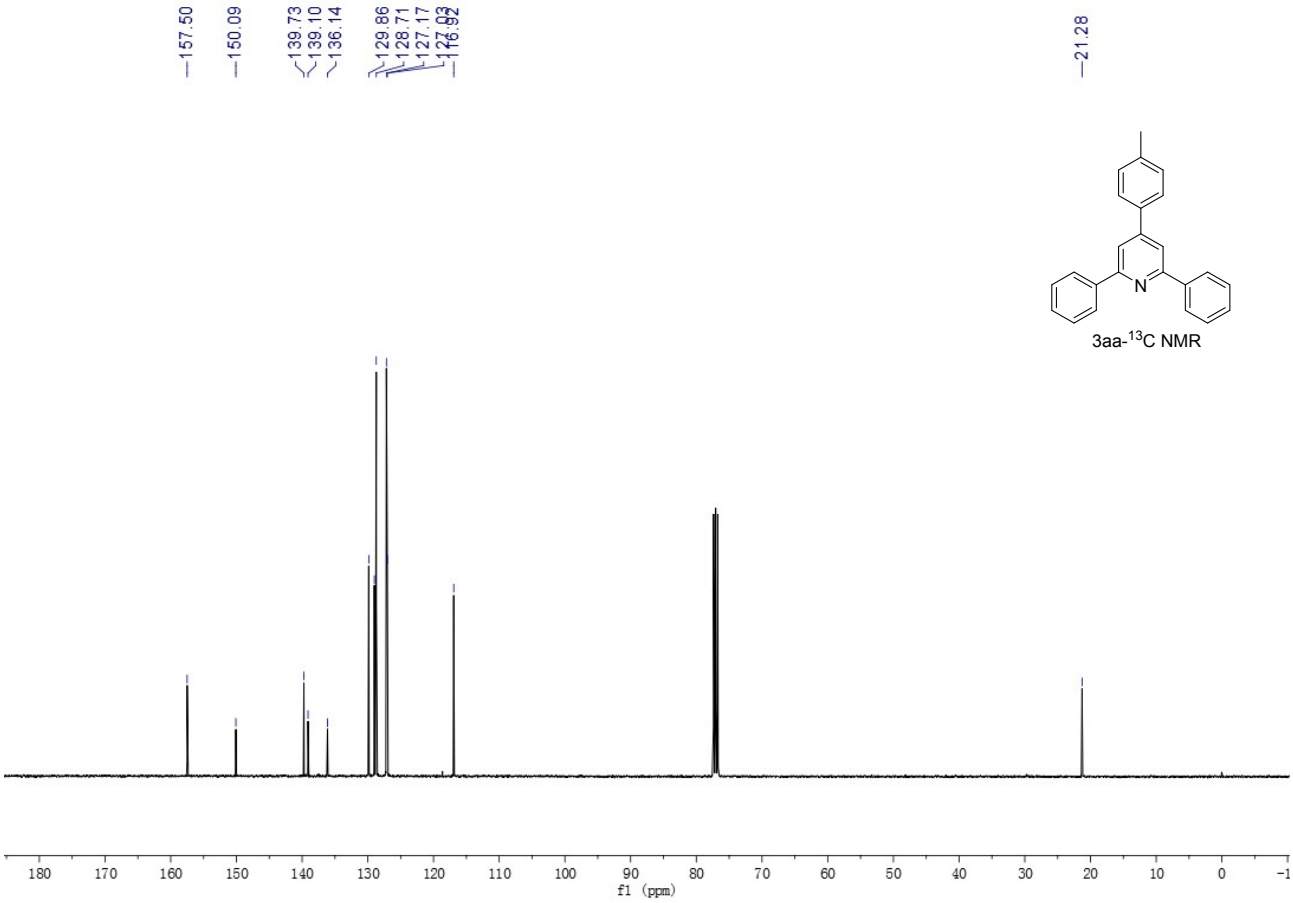

8.33
8.31
7.96
7.80
7.79
7.76
7.71
7.69
7.52
7.51
7.50
7.49
7.47
7.41
7.39
7.37


N
3s-1H NMR


1
2
3
4
5
6
4.02
2.02
6.27
4.27
6.04
3.00
f1 (ppm)


157.15
150.30
141.86
140.72
139.10
138.48
128.87
127.57
127.47
127.25
117.10
N
3s-13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.26
8.24
7.92
7.71
7.69
7.58
7.56
7.54
7.50
7.48
7.47
7.39
7.37
2.48
7
6
6
3
3
2
2
1
1
4
N
5
1
1
4
4
5
4
3aa-1H NMR
7
2
1
4
3
6
5
4.00
2.00
2.00
4.06
2.07
2.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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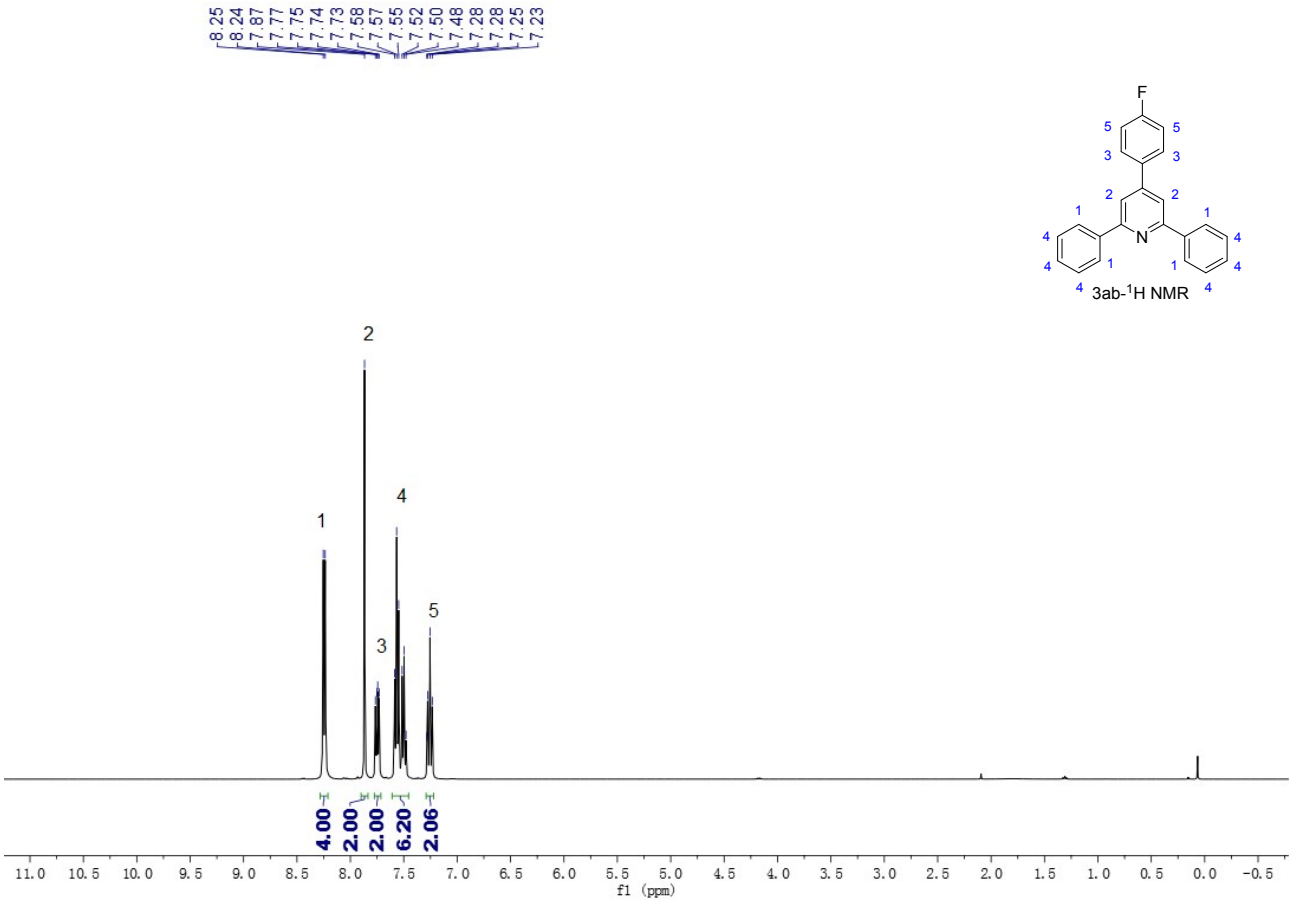
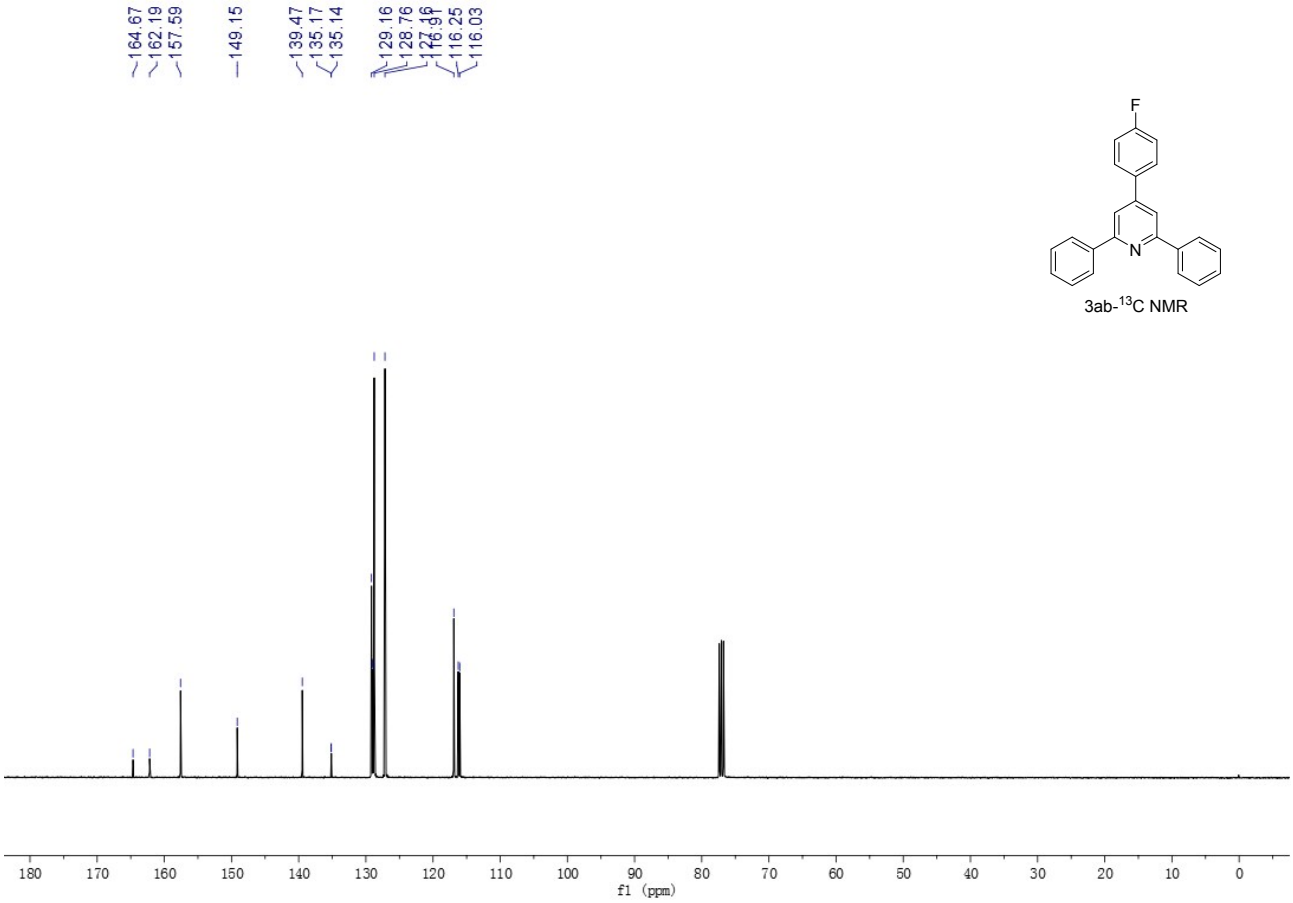
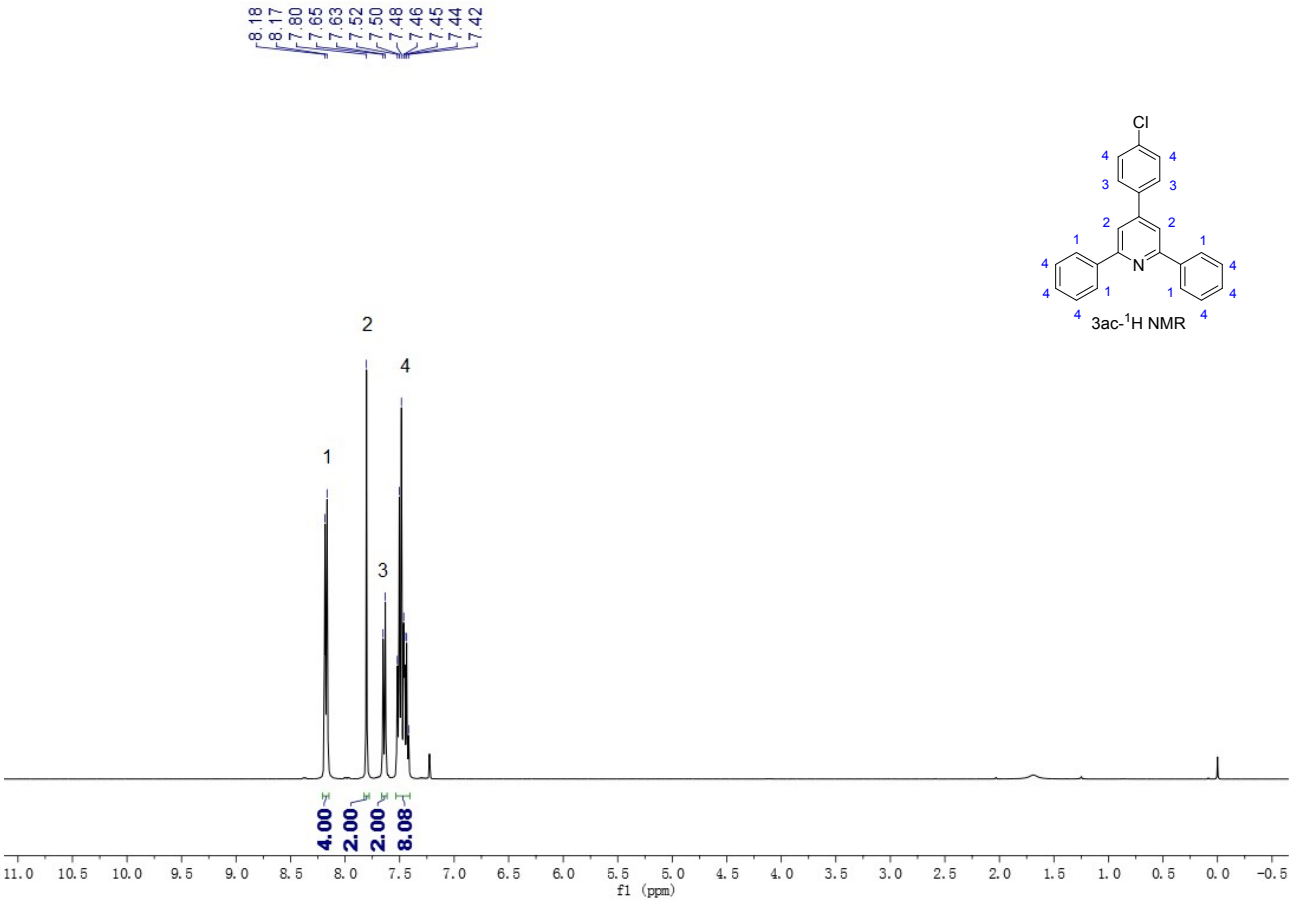
150.09
139.73
139.10
136.14
129.86
128.71
127.17
21.28
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

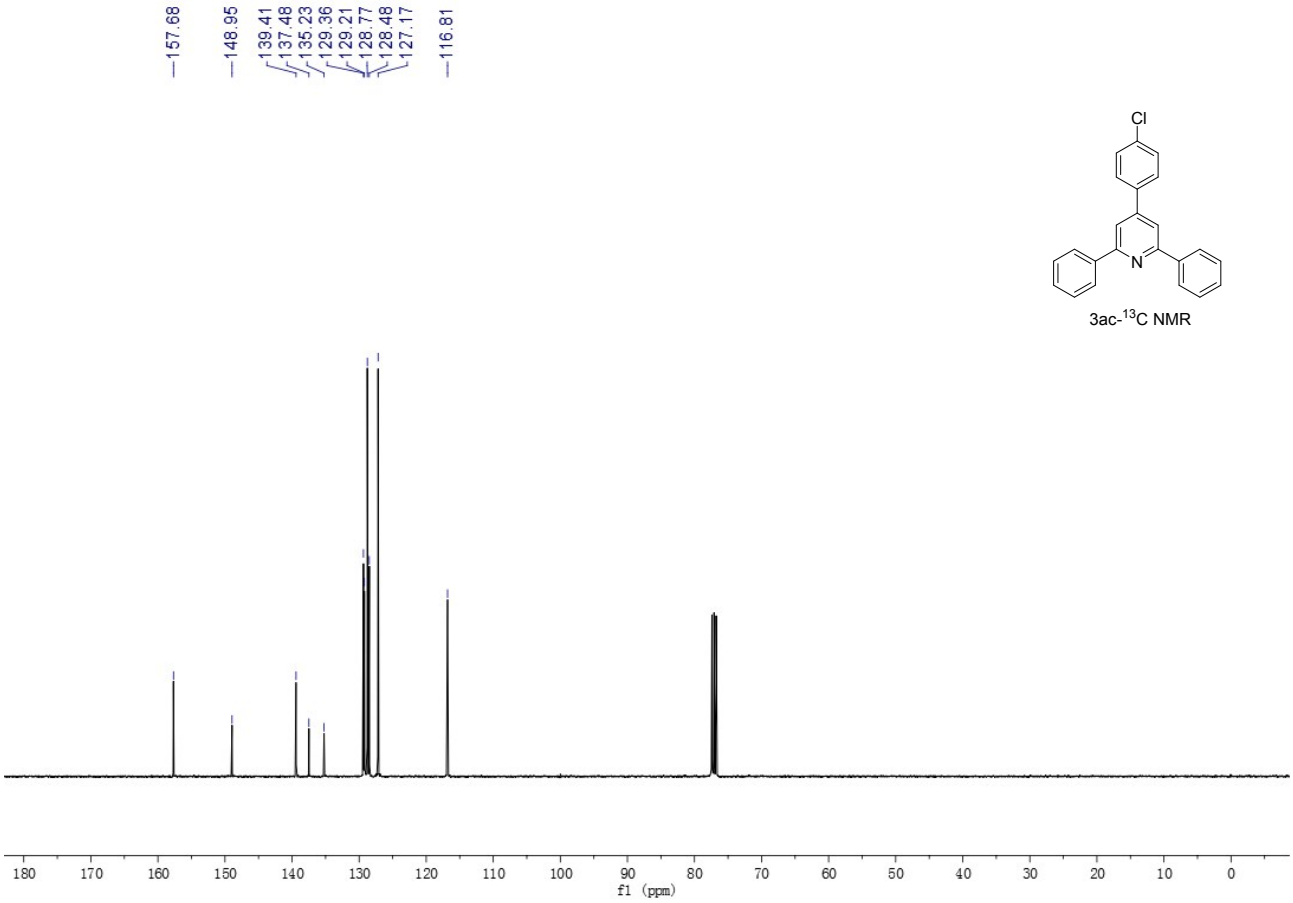
3aa-^{13}C NMR


8.25
8.24
7.87
7.77
7.75
7.74
7.73
7.58
7.57
7.55
7.52
7.50
7.48
7.28
7.25
7.23
F
N
3ab-1H NMR
1
2
3
4
5
4.00
2.00
2.00
6.20
2.06
f1 (ppm)

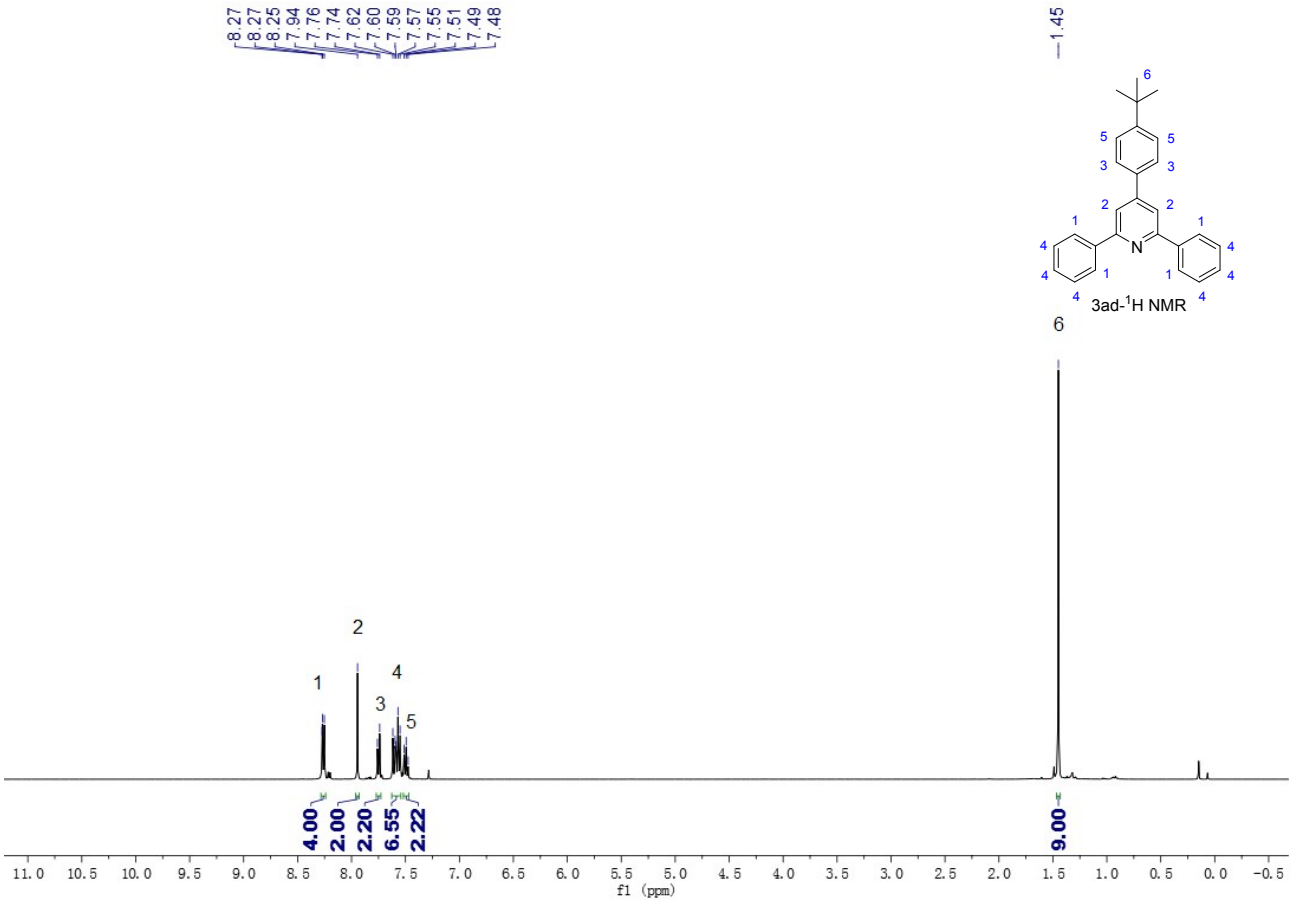

164.67
162.19
157.59
149.15
139.47
135.17
135.14
129.16
128.76
116.25
116.03
F
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

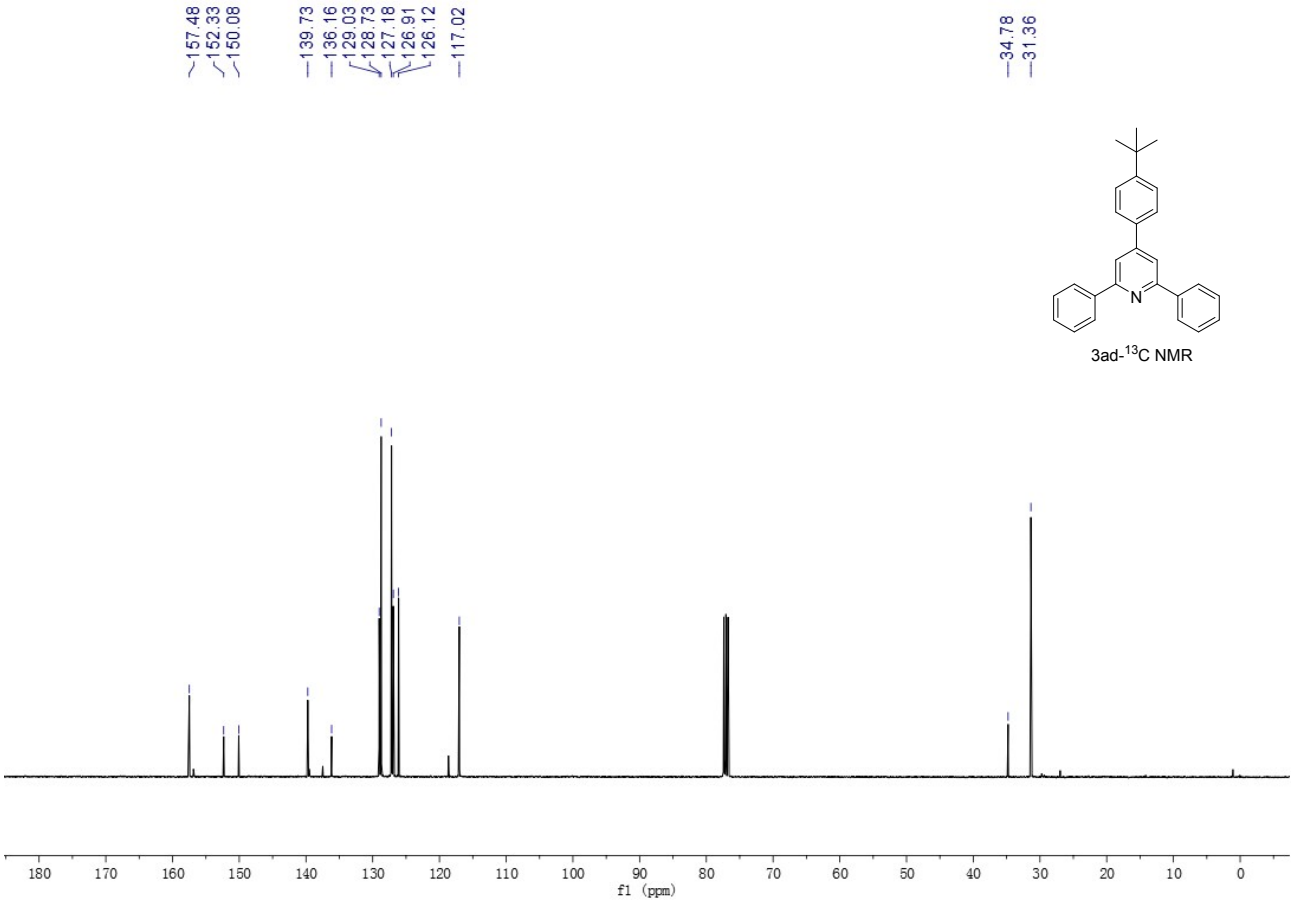
3ab-^{13}C NMR


8.18
8.17
7.80
7.65
7.63
7.52
7.50
7.48
7.46
7.45
7.44
7.42
Cl
N
3ac-1H NMR
1
2
3
4
4.00
2.00
2.00
8.08
f1 (ppm)


157.68
148.95
139.41
137.48
135.23
129.36
129.21
128.77
128.48
127.17
116.81
Cl
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ac-^{13}C NMR


8.27
8.27
8.25
7.94
7.76
7.74
7.62
7.60
7.59
7.57
7.55
7.51
7.49
7.48
1.45
3ad-1H NMR
1
2
3
4
5
6
4.00
2.00
2.20
6.55
2.22
9.00
f1 (ppm)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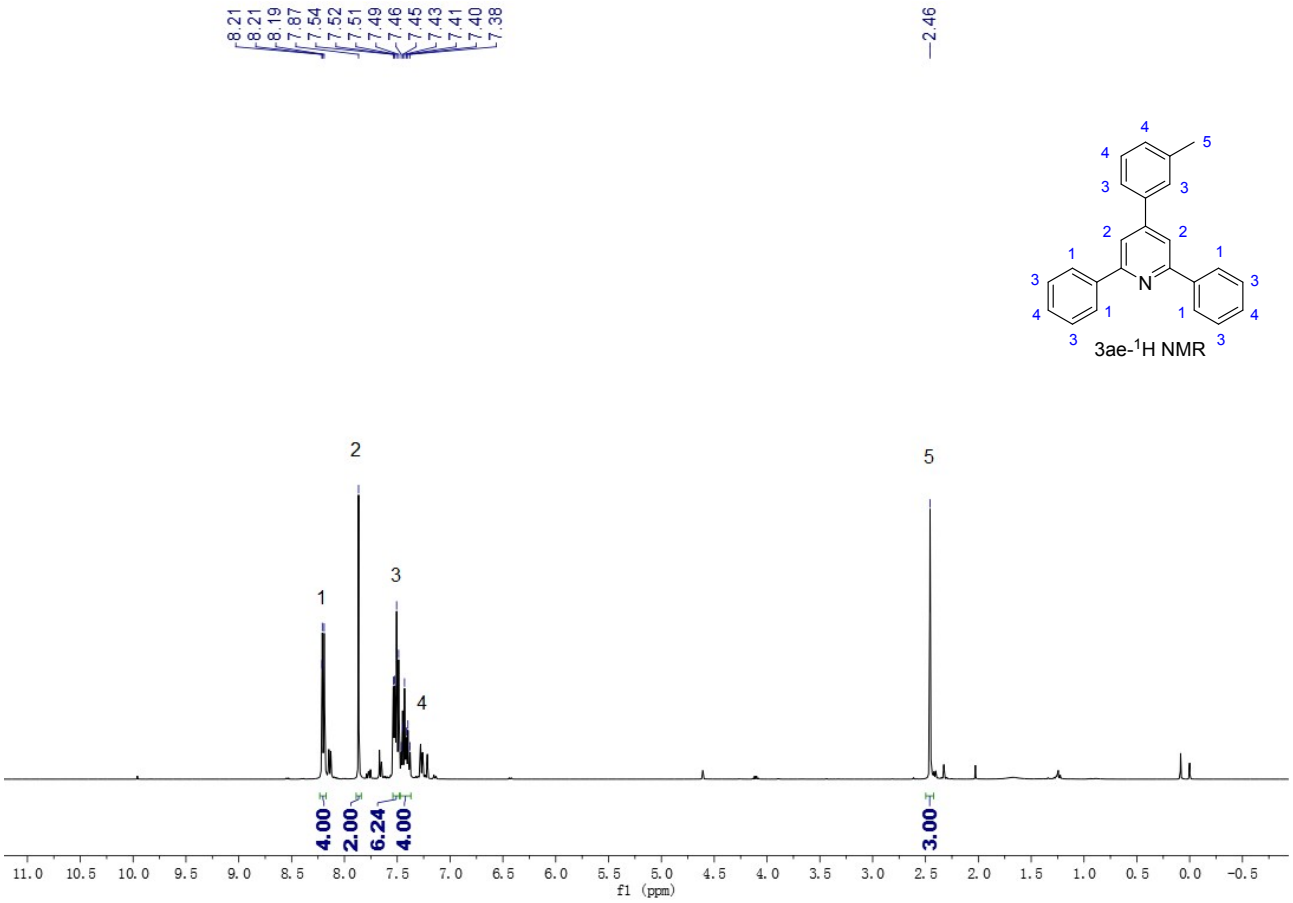
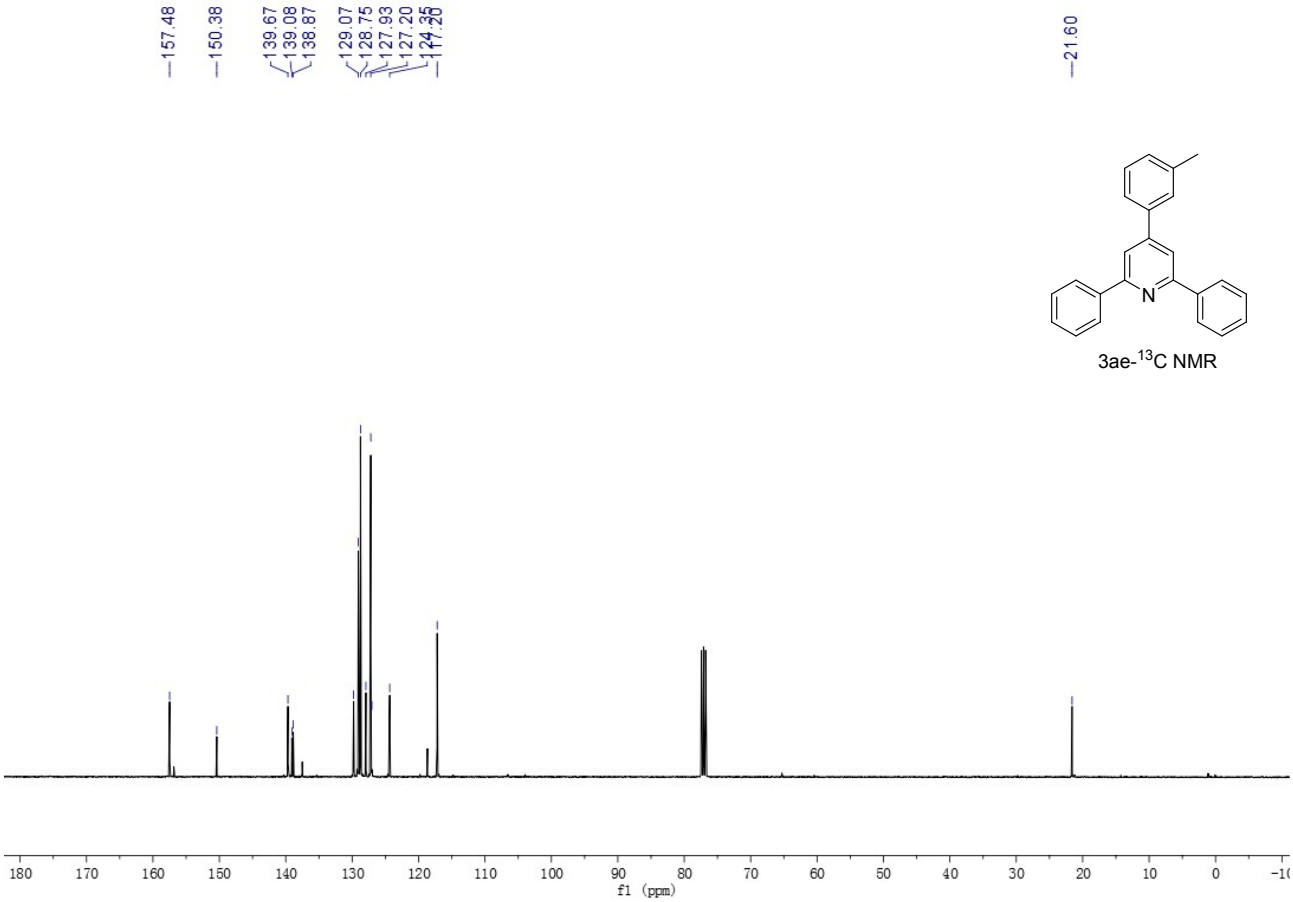
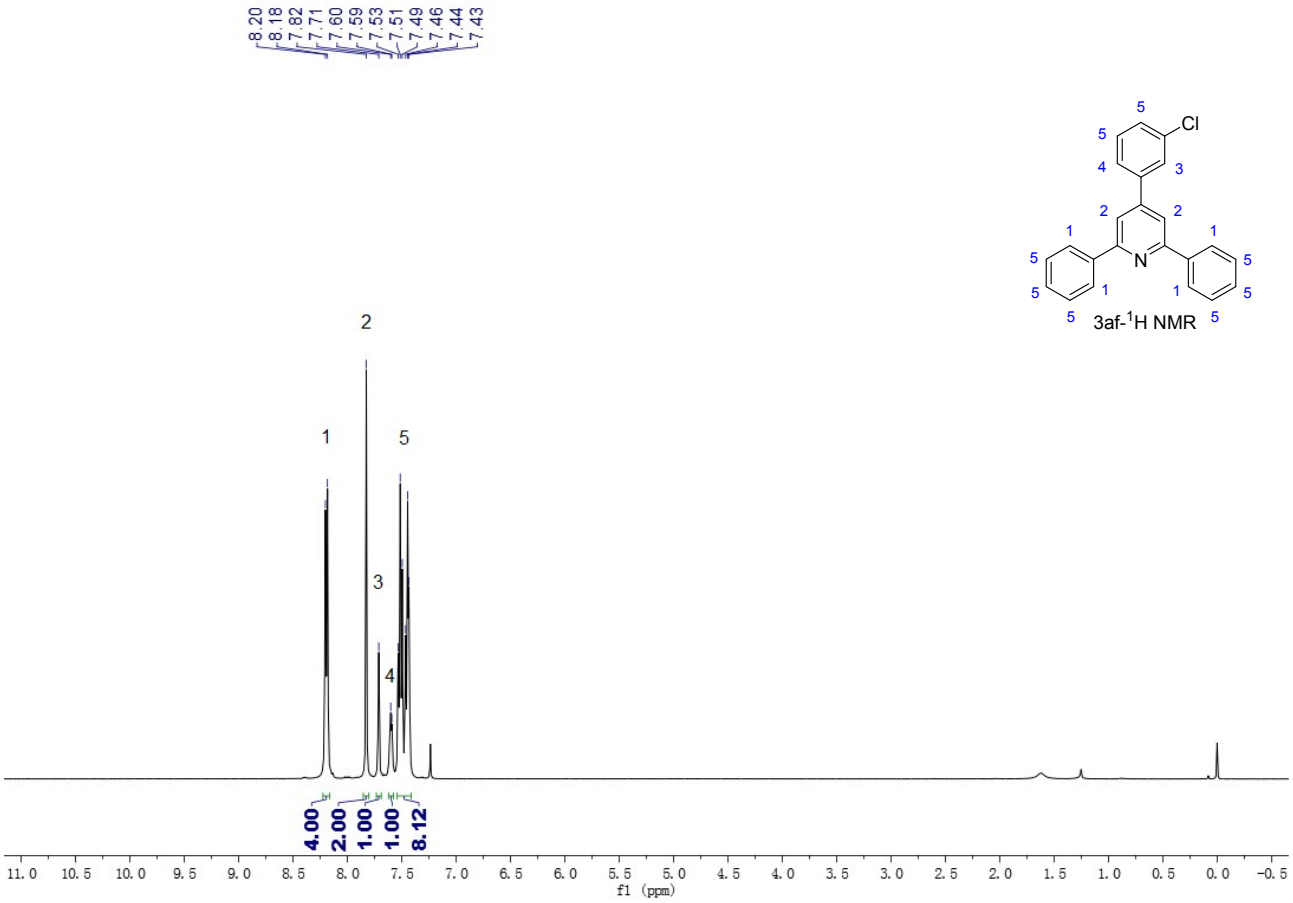
152.33
150.08
139.73
136.16
129.03
128.73
127.18
126.91
126.12
117.02
34.78
31.36
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

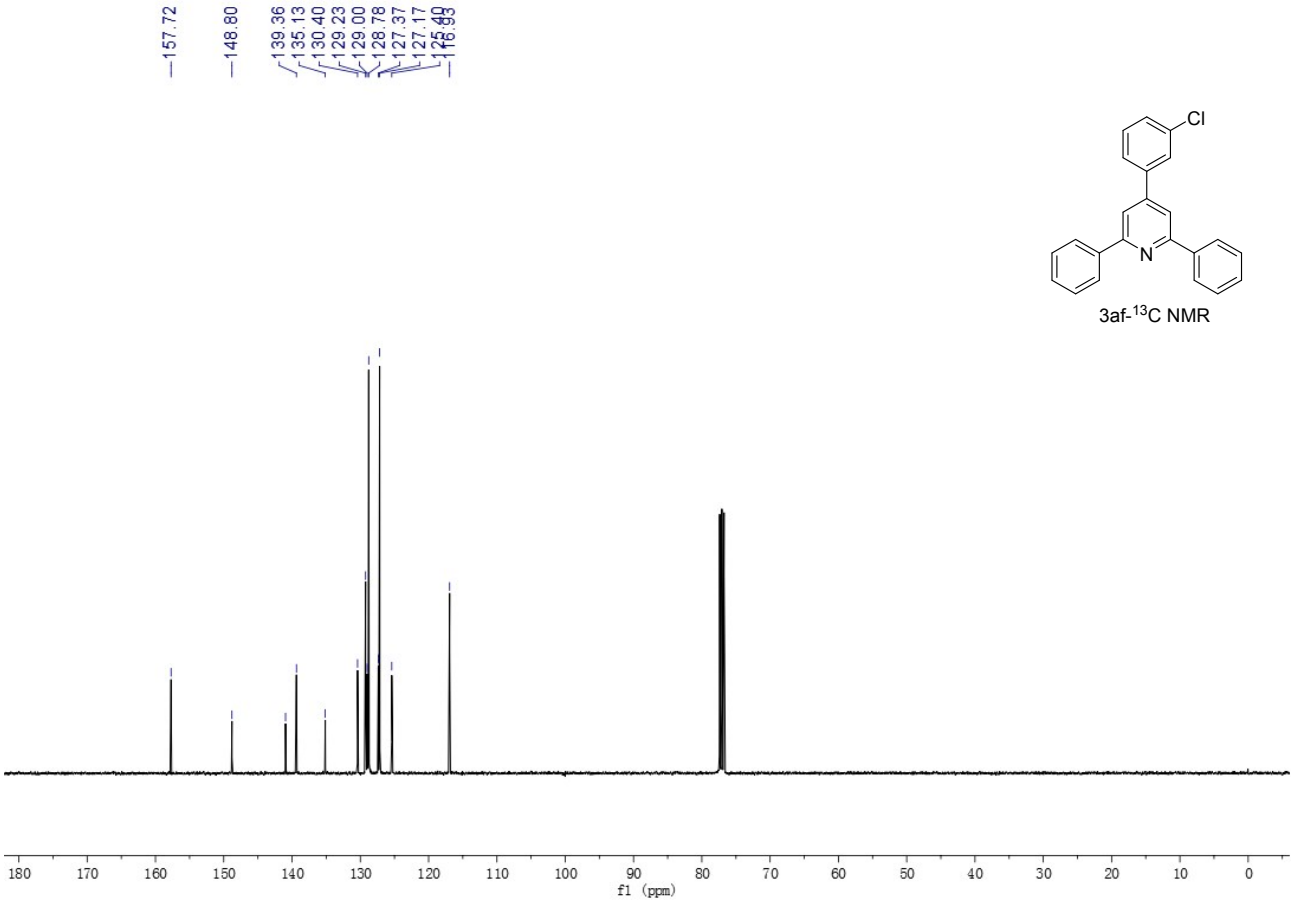
3ad-^{13}C NMR


8.21
8.21
8.19
7.87
7.54
7.52
7.51
7.49
7.46
7.45
7.43
7.41
7.40
7.38
2.46
3ae-1H NMR
1
2
3
4
5
4.00
2.00
6.24
4.00
3.00
f1 (ppm)


157.48
150.38
139.67
139.08
138.87
129.07
128.75
127.93
127.20
124.35
117.20
21.60
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ae-^{13}C NMR


8.20
8.18
7.82
7.71
7.60
7.59
7.53
7.51
7.49
7.46
7.44
7.43
Cl
N
3af-1H NMR
1
2
3
4
5
4.00
2.00
1.00
1.00
8.12
f1 (ppm)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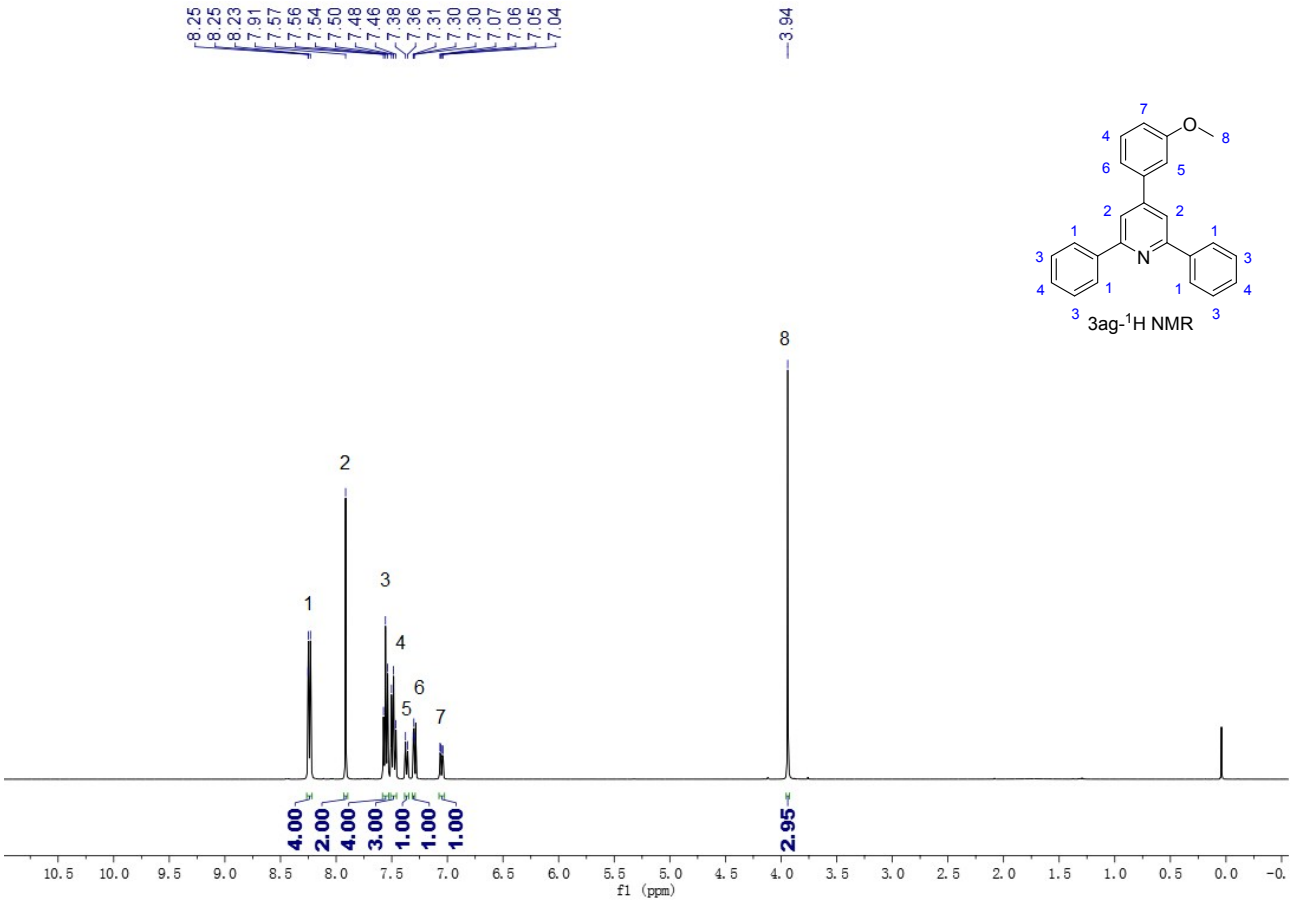
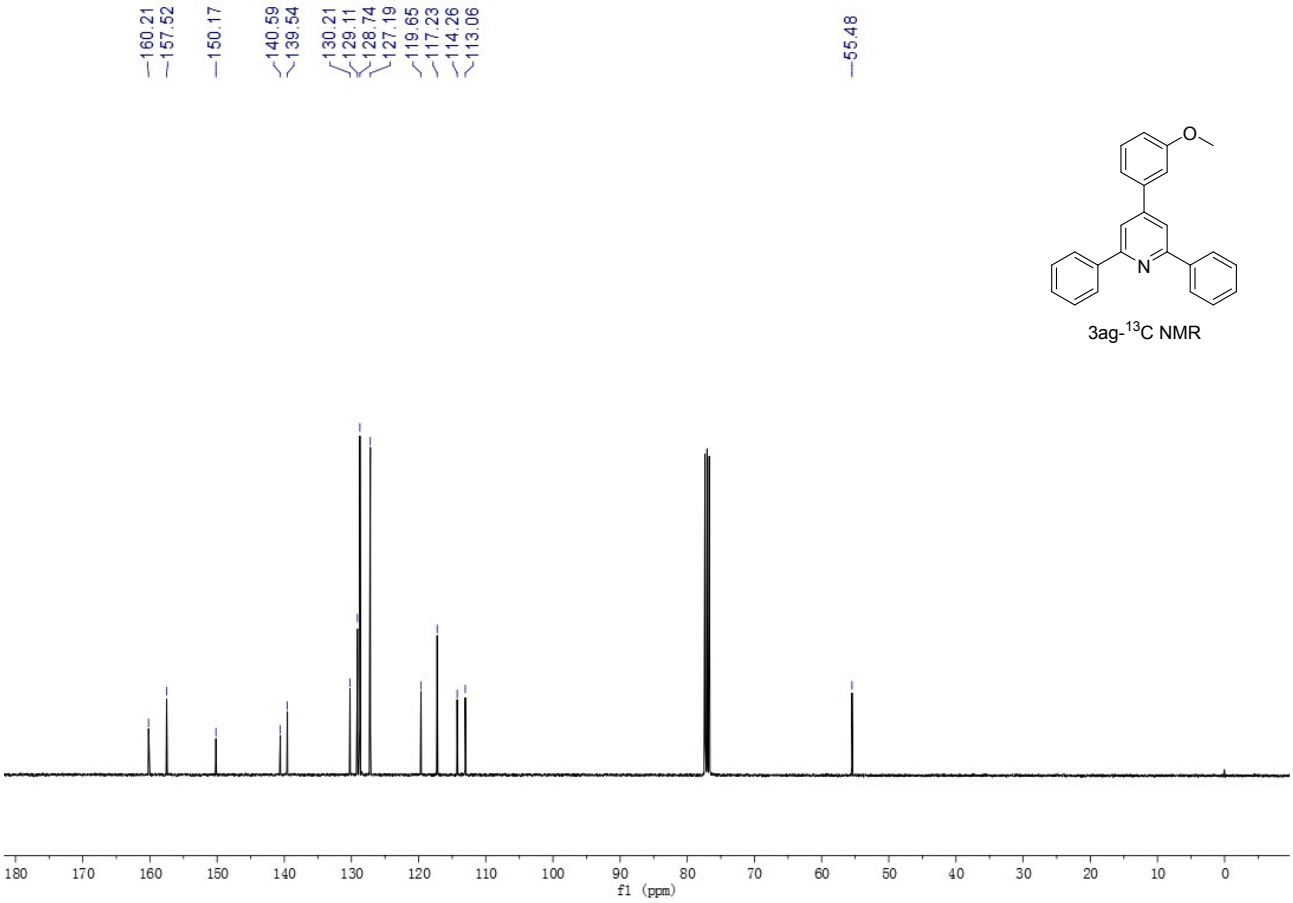
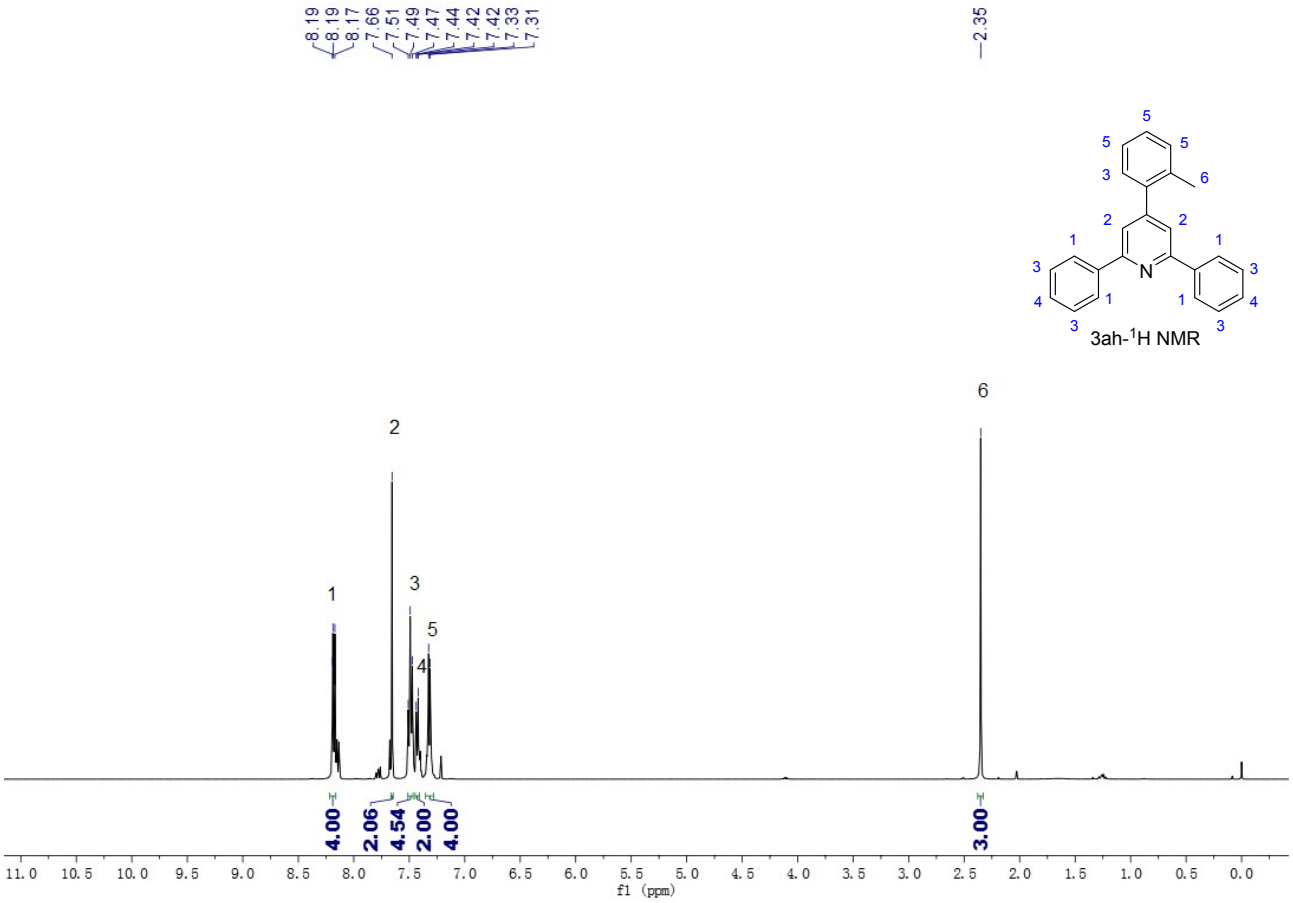
148.80
139.36
135.13
130.40
129.23
129.00
128.78
127.37
127.17
125.40
116.93
Cl
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

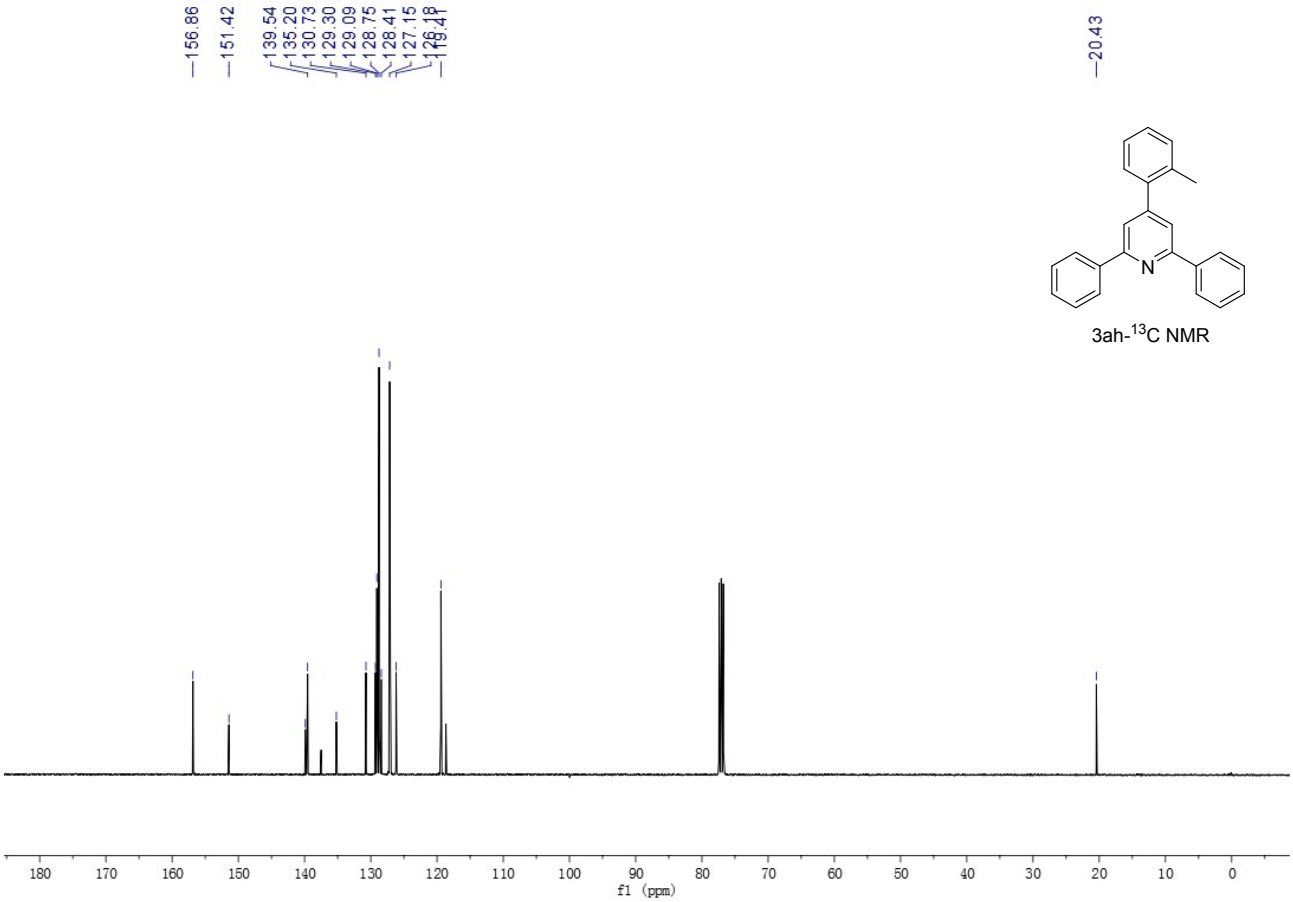
3af-^{13}C NMR


8.25
8.25
8.23
7.91
7.57
7.56
7.54
7.50
7.48
7.46
7.38
7.36
7.31
7.30
7.30
7.07
7.06
7.05
7.04
3.94
7
O
8
4
6
5
2
2
1
1
3
N
3
4
1
1
3
4
3
3
3ag-1H NMR
8
2
1
3
4
6
5
7
4.00
2.00
4.00
3.00
1.00
1.00
1.00
2.95
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


160.21
157.52
150.17
140.59
139.54
130.21
129.11
128.74
127.19
119.65
117.23
114.26
113.06
55.48
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

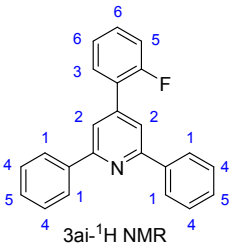
3ag-^{13}C NMR


8.19
8.19
8.17
7.66
7.51
7.49
7.47
7.44
7.42
7.42
7.33
7.31
2.35
5
5
5
3
6
2
2
1
1
3
N
3
4
1
1
4
3
3
3ah-1H NMR
6
2
1
3
5
4
4.00
2.06
4.54
2.00
4.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

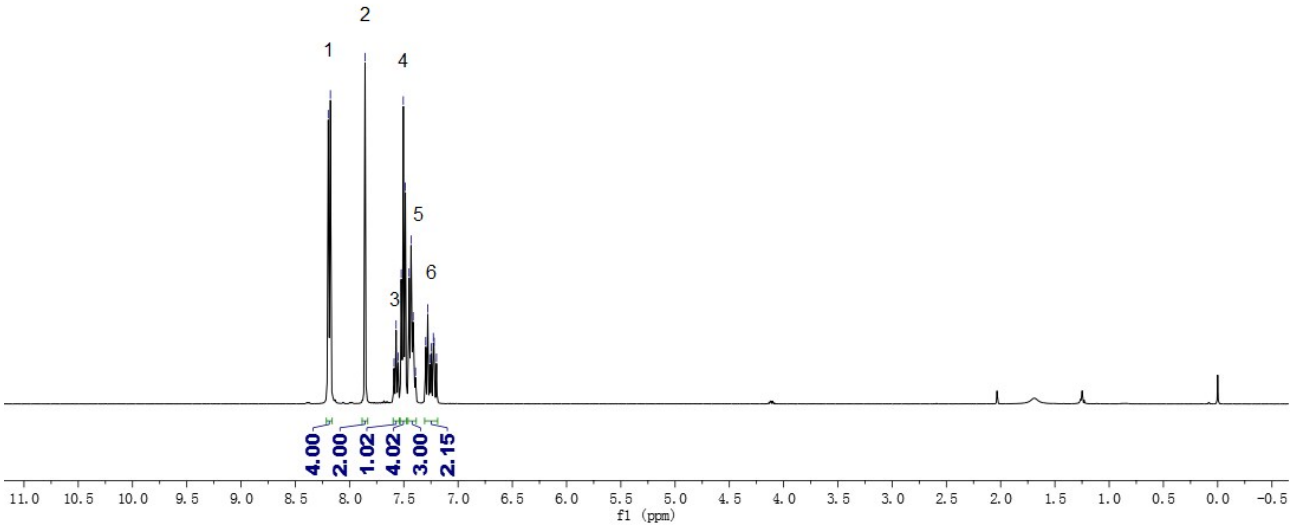

156.86
151.42
139.54
135.20
130.73
129.30
129.09
128.75
128.41
127.15
20.43
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

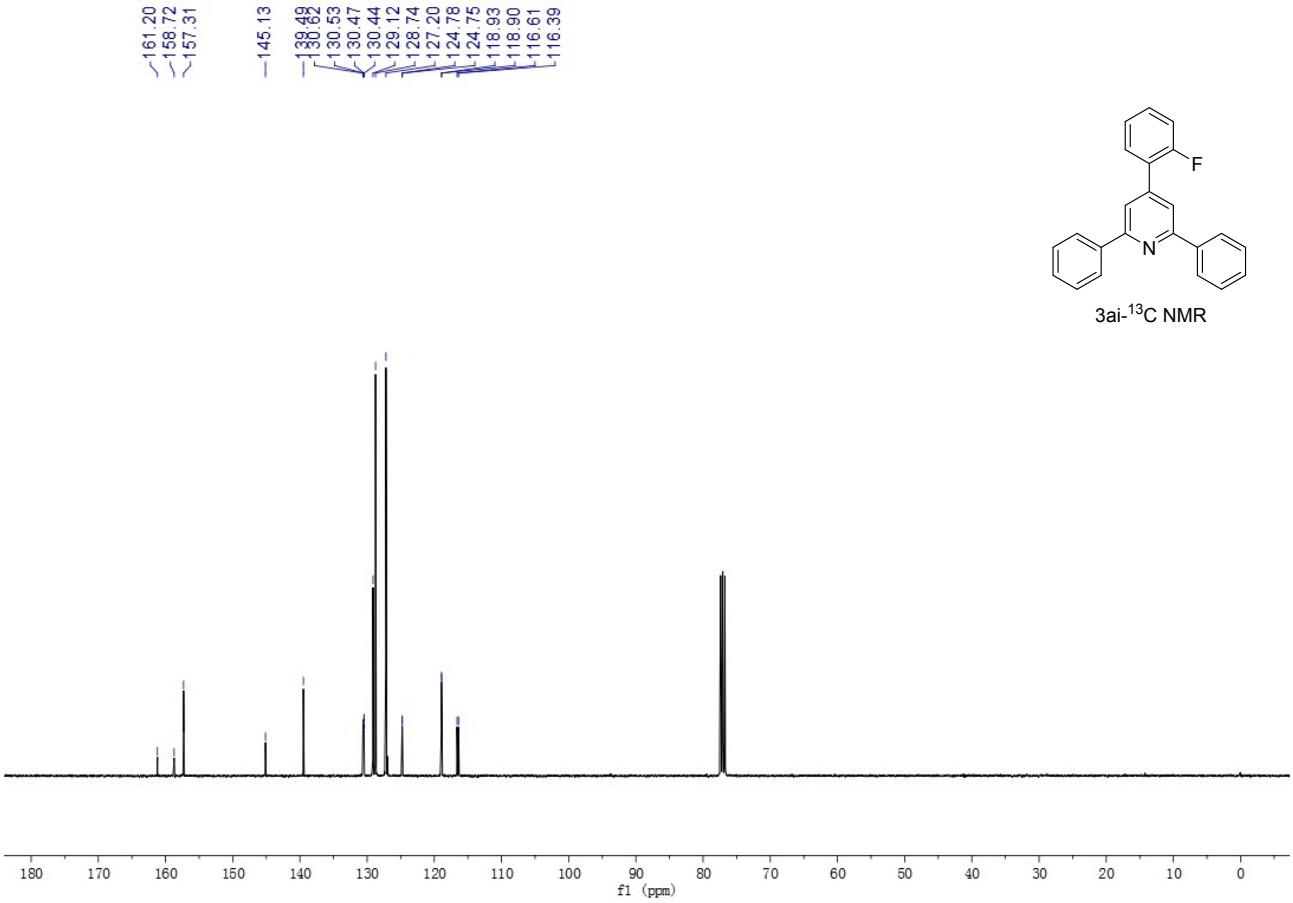
3ah-^{13}C NMR


8.20
8.18
7.86
7.59
7.57
7.55
7.52
7.50
7.49
7.45
7.43
7.41
7.39
7.30
7.28
7.26
7.25
7.23
7.22
7.20

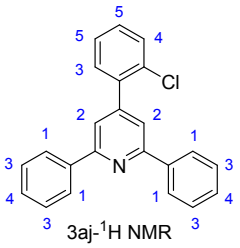

6
6
5
3
F
2
2
1
1
4
N
5
1
1
5
4
4

3ai-^{1}H NMR

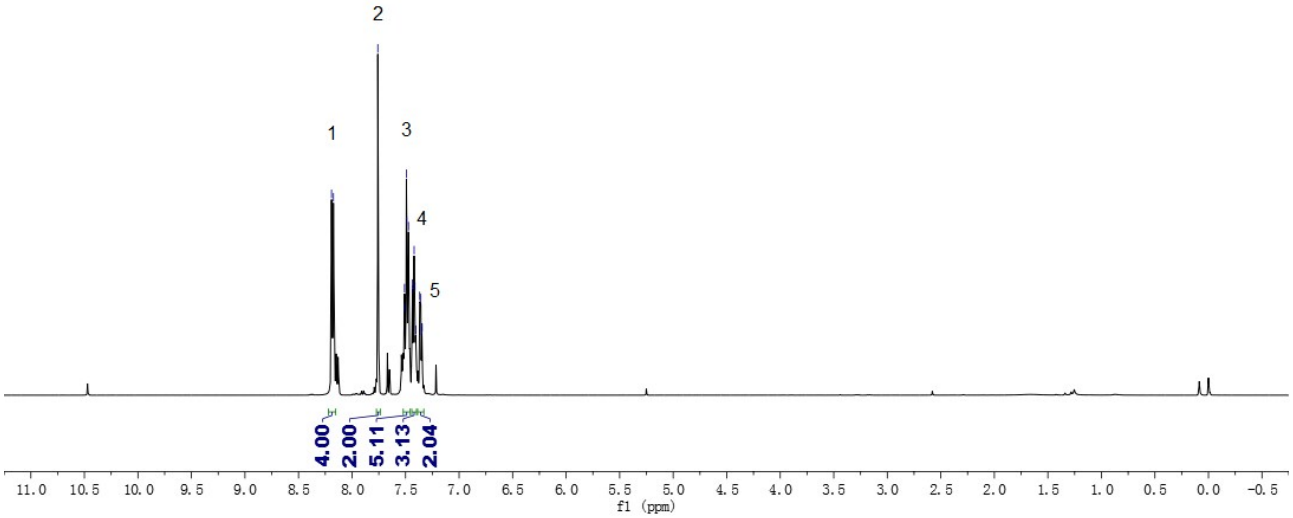

2
1
4
5
6
3
4.00
2.00
1.02
4.02
3.00
2.15
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

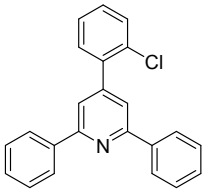

161.20
158.72
157.31
145.13
139.49
130.53
130.47
130.44
129.12
128.74
127.20
124.78
124.75
118.93
118.90
116.61
116.39
F
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ai-^{13}C NMR

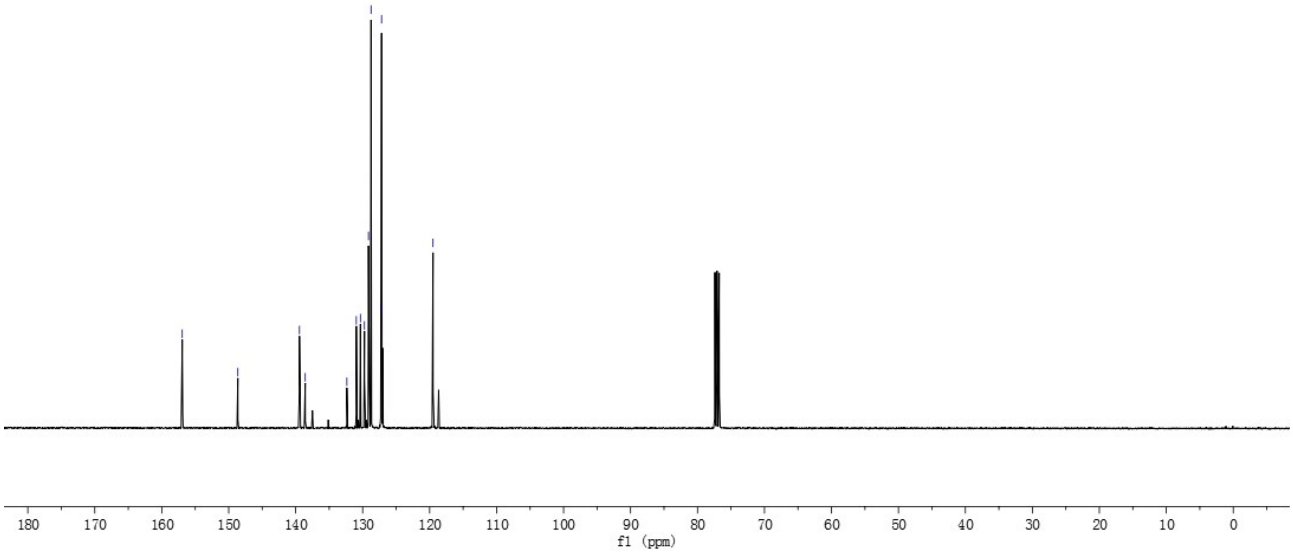


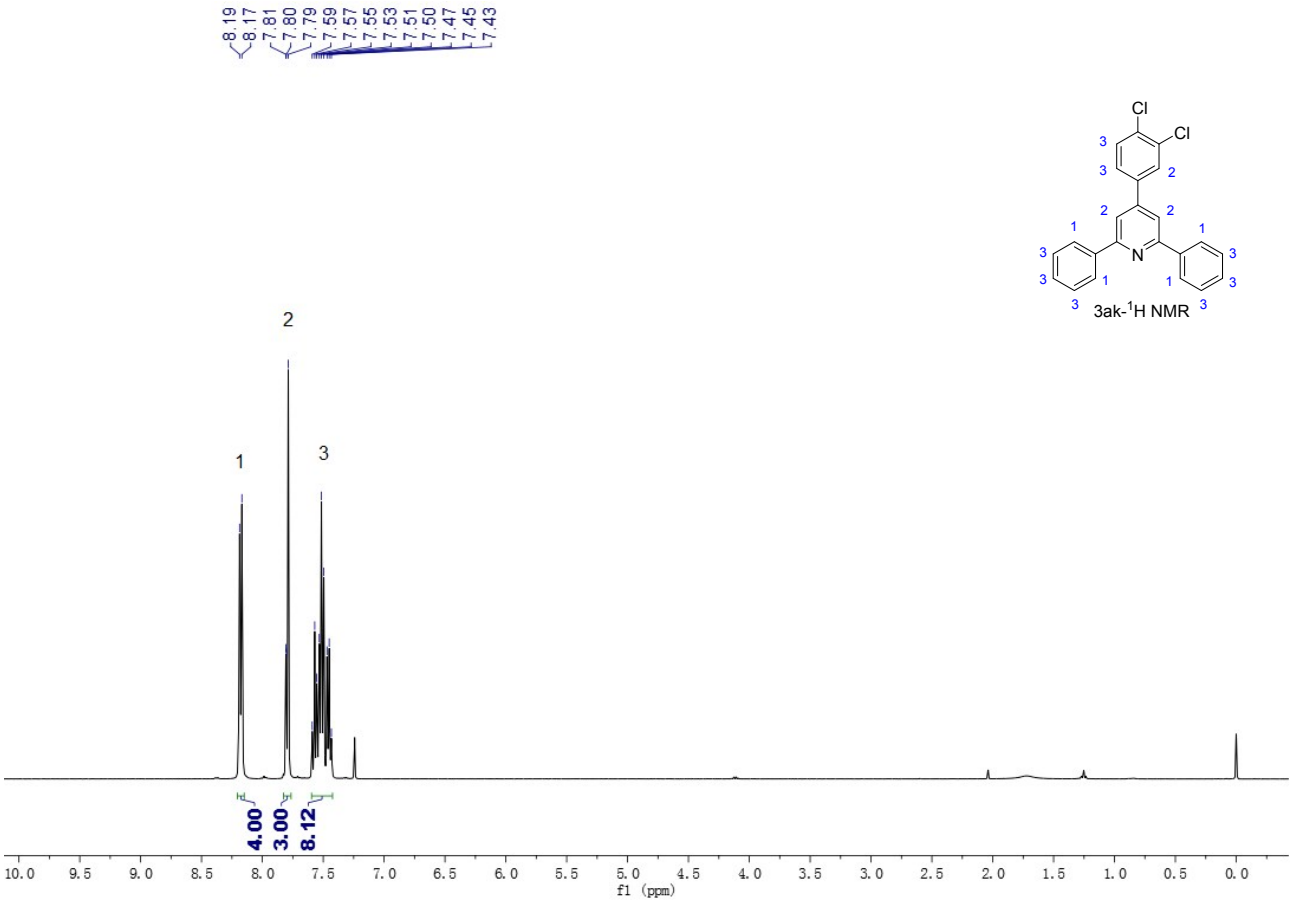
3aj-^{1}H NMR

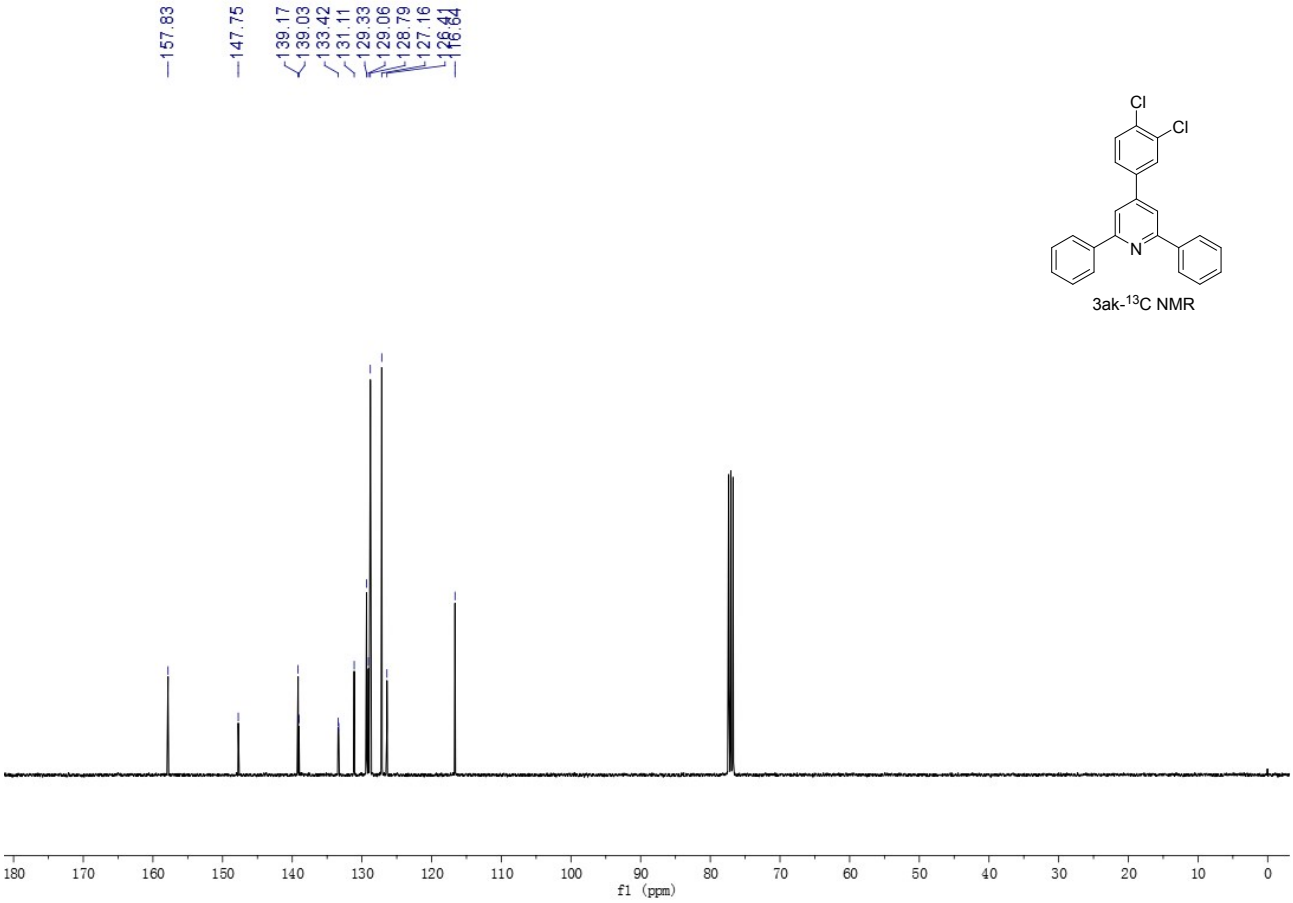




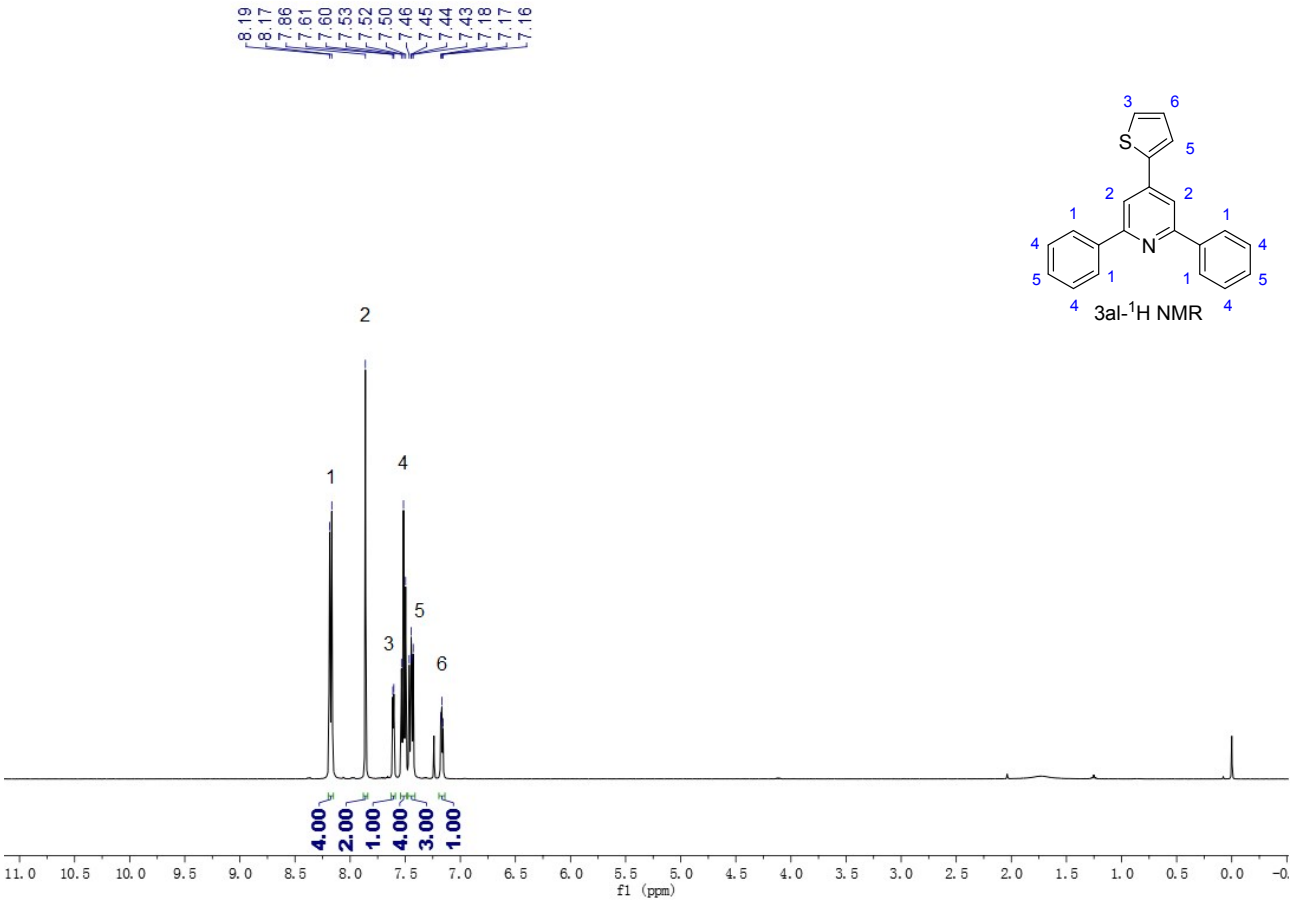
3aj-^{13}C NMR

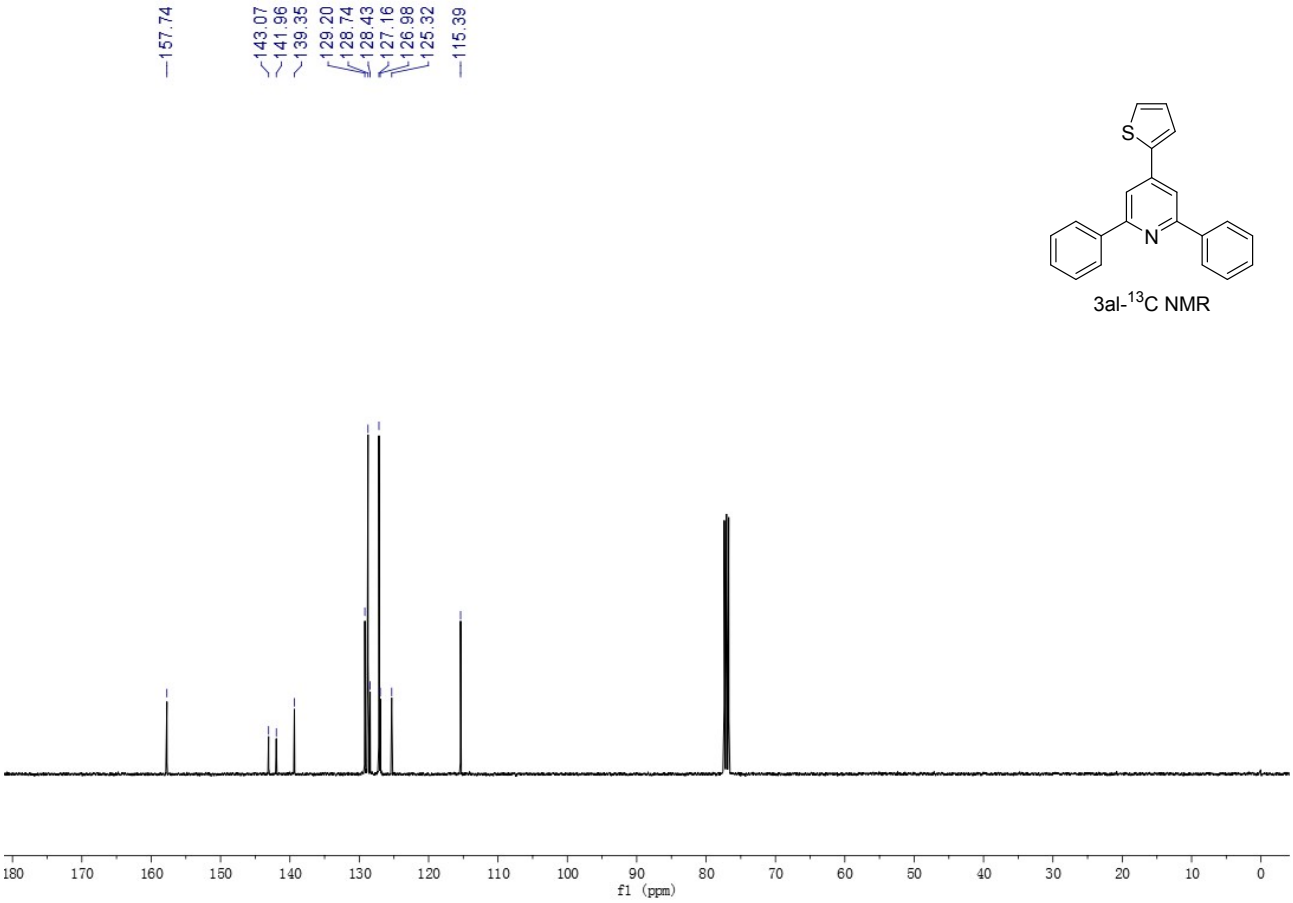



8.19
8.17
7.81
7.80
7.79
7.59
7.57
7.55
7.53
7.51
7.50
7.47
7.45
7.43
Cl
Cl
N
3ak-1H NMR
1
2
3
4.00
3.00
8.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

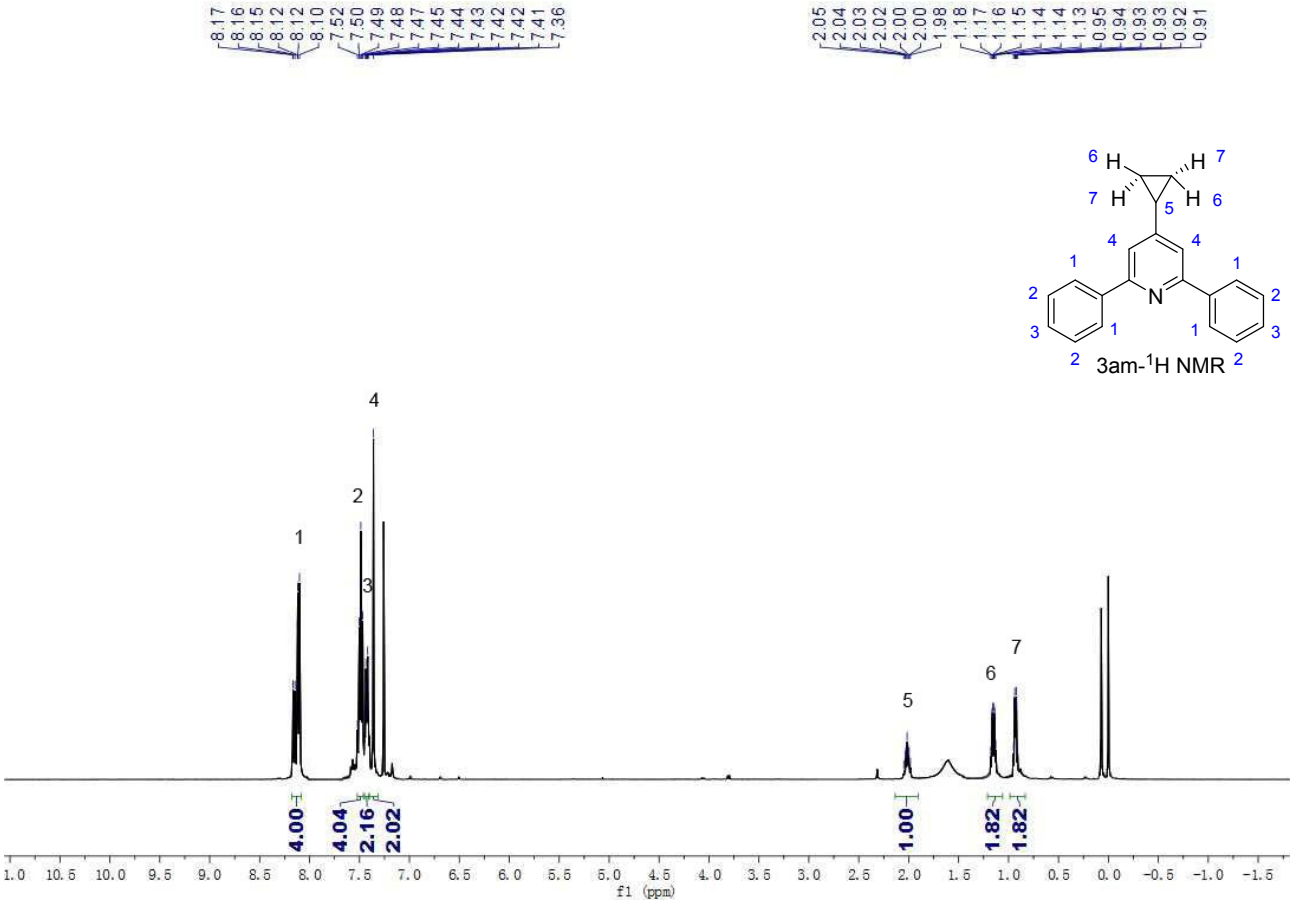

157.83
147.75
139.17
139.03
133.42
131.11
129.33
129.06
128.79
127.16
Cl
Cl
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

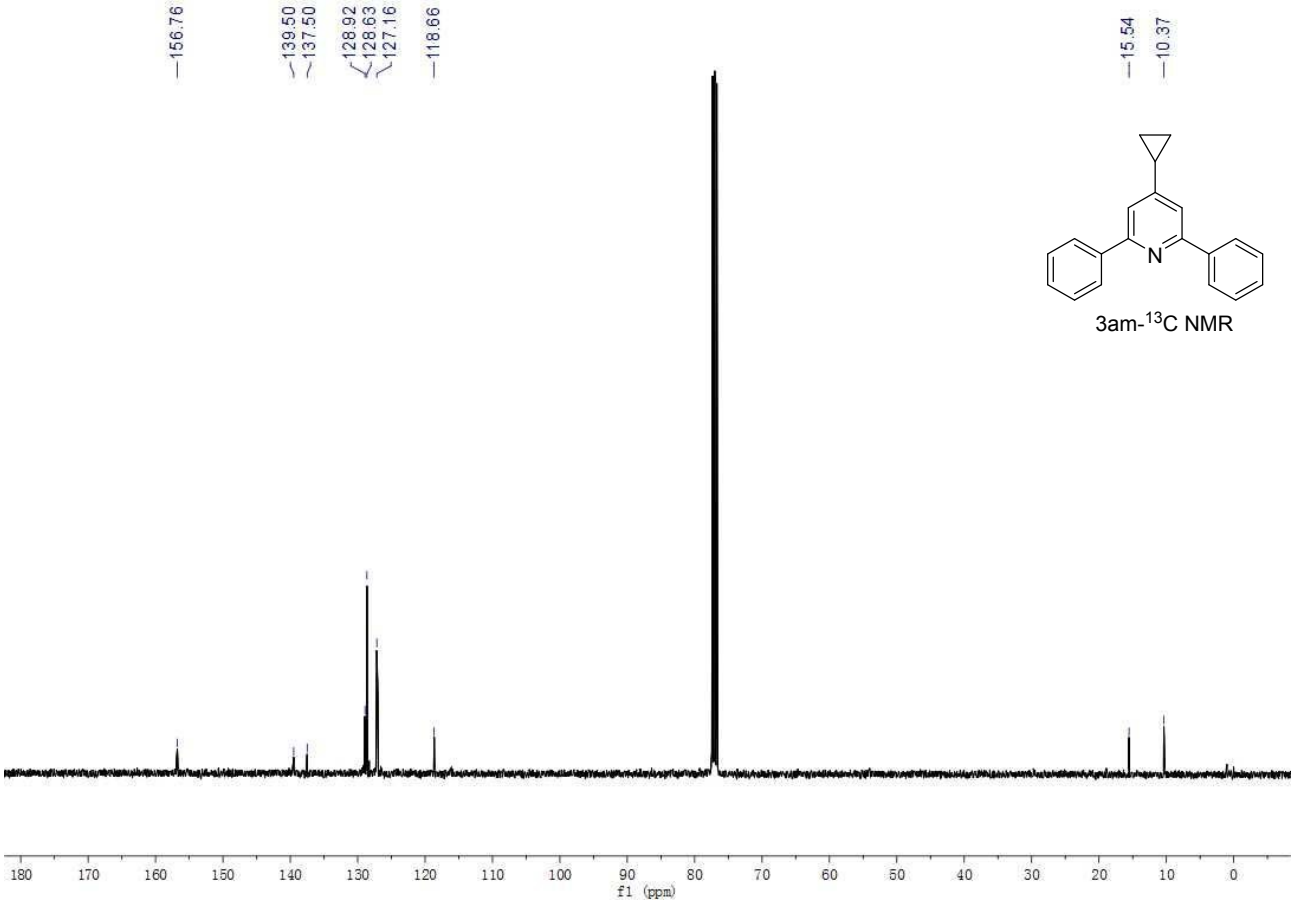
3ak-^{13}C NMR


8.19
8.17
7.86
7.61
7.60
7.53
7.52
7.50
7.46
7.45
7.44
7.43
7.18
7.17
7.16
3
6
S
5
2
2
1
1
4
N
4
5
1
1
5
4
4
3al-1H NMR
2
1
4
5
3
6
4.00
2.00
1.00
4.00
3.00
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

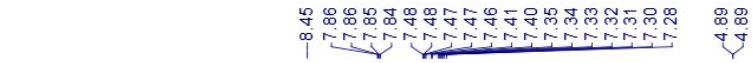

157.74
143.07
141.96
139.35
129.20
128.74
128.43
127.16
126.98
125.32
115.39
S
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

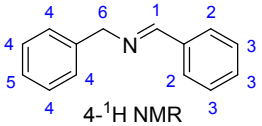
3al-^{13}C NMR


8.17
8.16
8.15
8.12
8.12
8.10
7.52
7.50
7.49
7.48
7.47
7.45
7.44
7.43
7.42
7.42
7.41
7.36
2.05
2.04
2.03
2.02
2.00
2.00
1.98
1.18
1.17
1.16
1.15
1.14
1.14
1.13
0.95
0.94
0.93
0.93
0.92
0.91
H
H
H
H
N
3am-1H NMR
1
2
3
4
5
6
7
4.00
4.04
2.16
2.02
1.00
1.82
1.82
f1 (ppm)

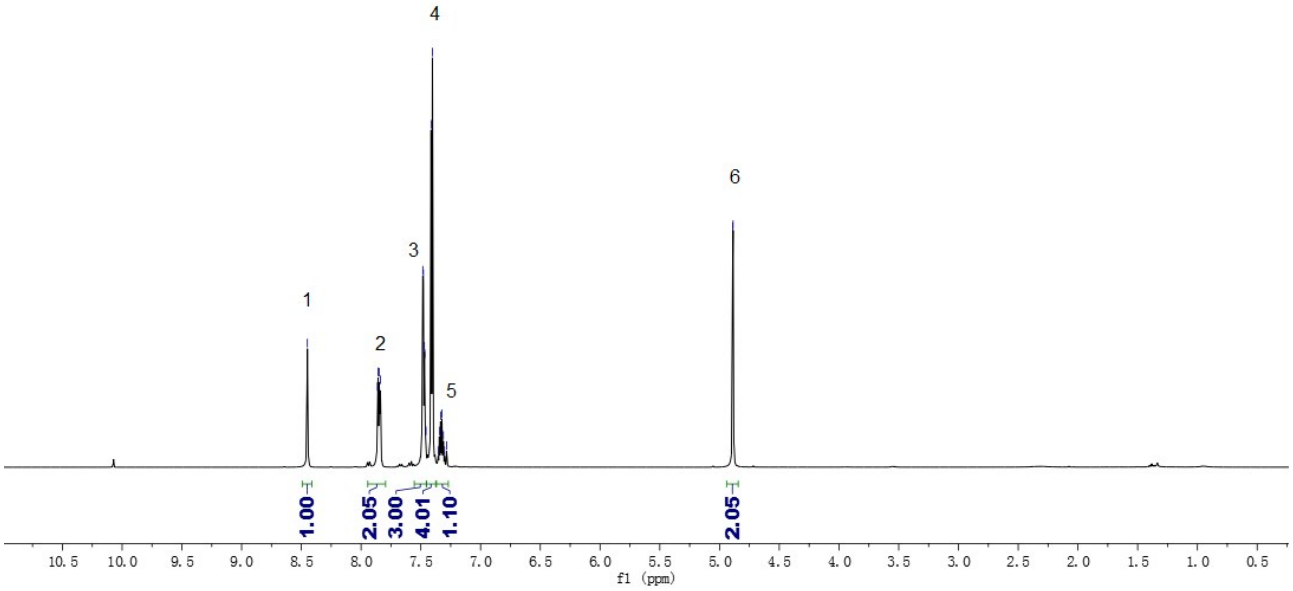

156.76
139.50
137.50
128.92
128.63
127.16
118.66
15.54
10.37
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

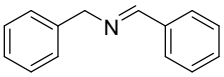
3am-^{13}C NMR



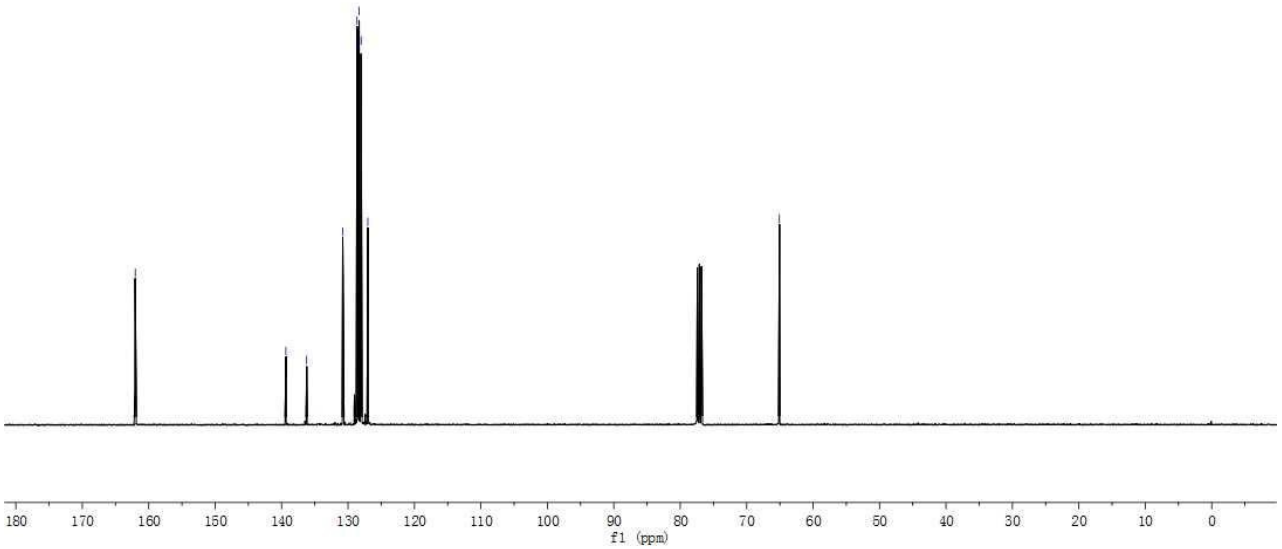


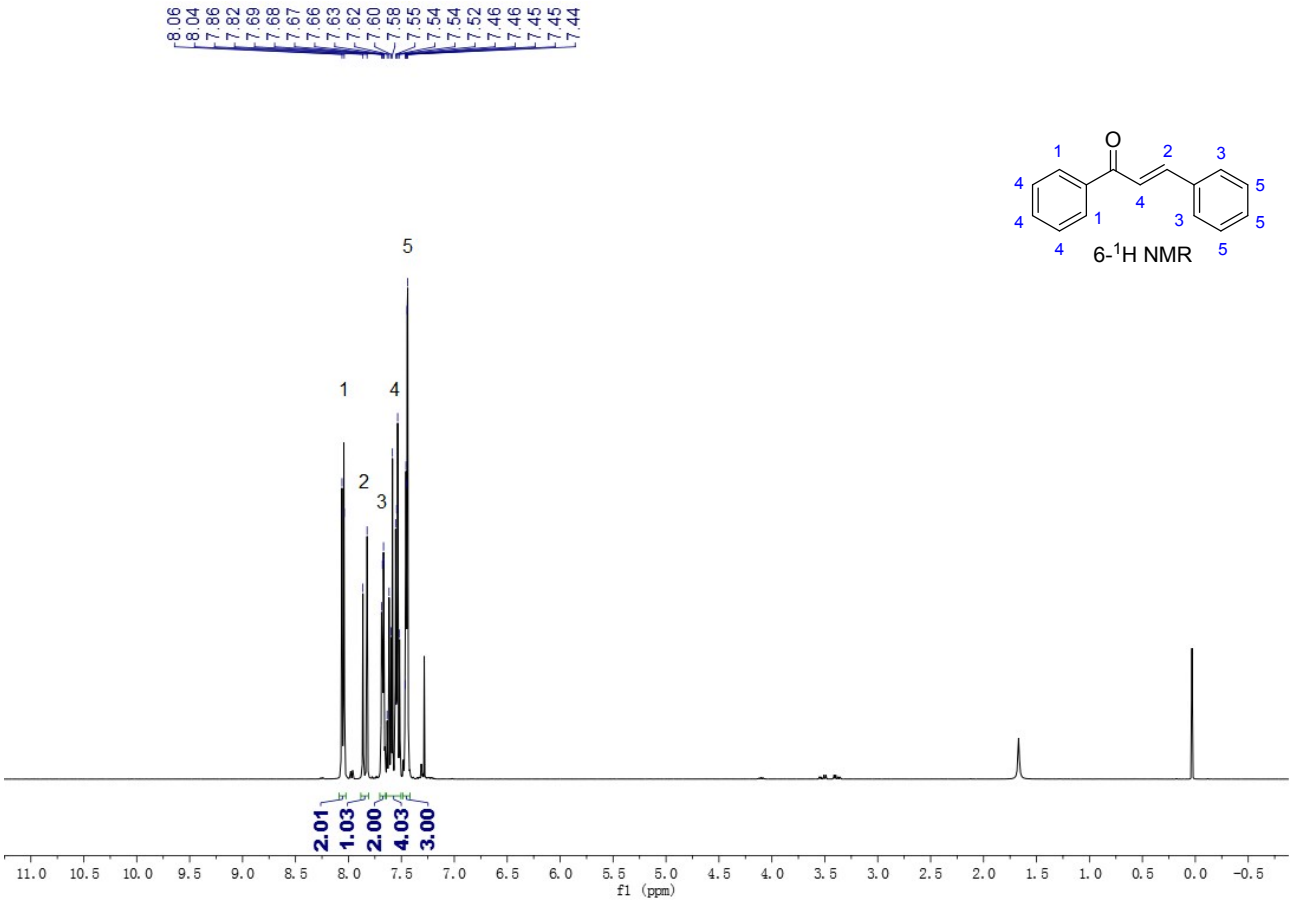
4-^{1}H NMR

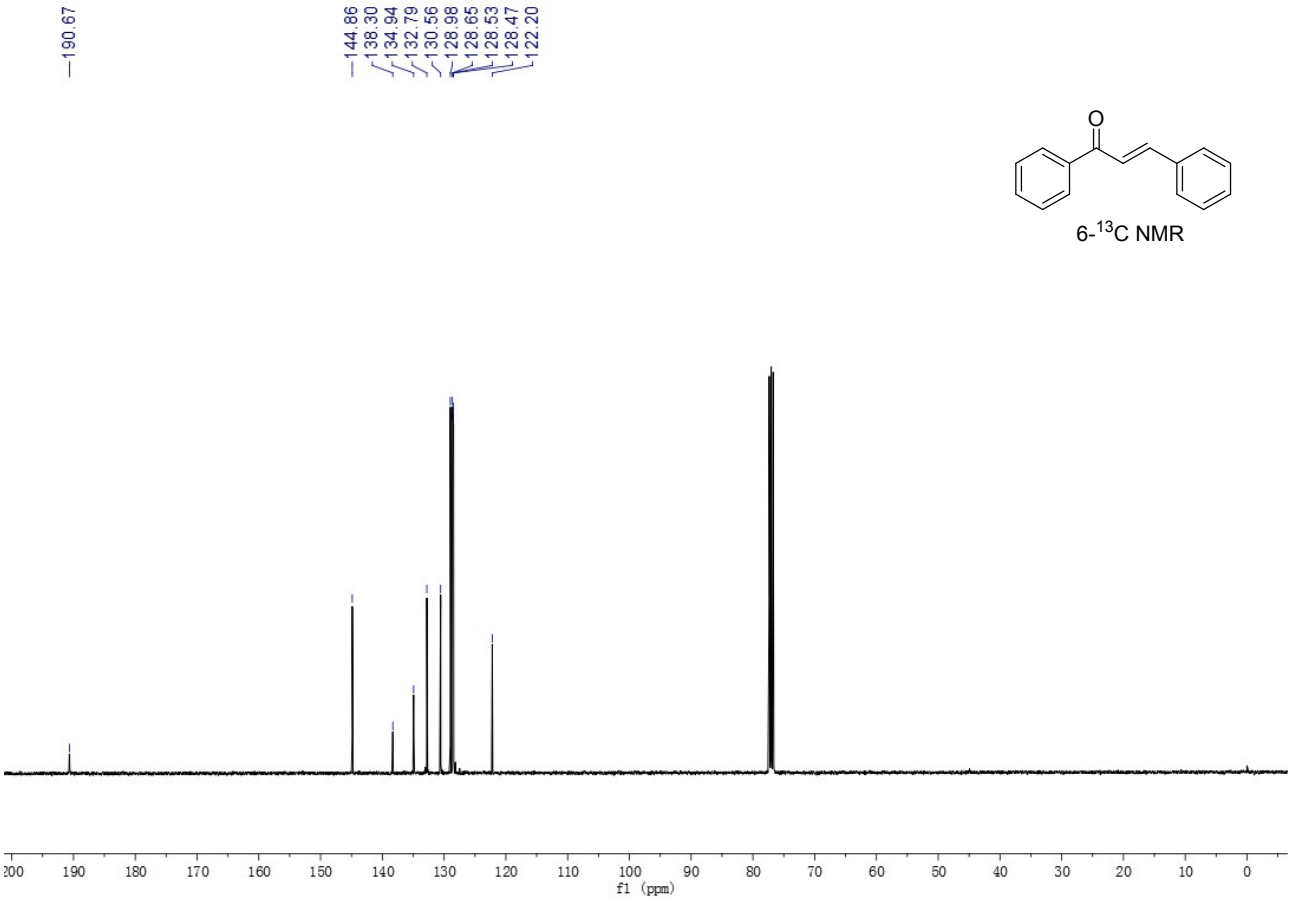




4-^{13}C NMR




8.06
8.04
7.86
7.82
7.69
7.68
7.67
7.66
7.63
7.62
7.60
7.58
7.55
7.54
7.54
7.52
7.46
7.46
7.45
7.45
7.44
O
1
2
3
4
5
6-1H NMR
1
2
3
4
5
2.01
1.03
2.00
4.03
3.00
f1 (ppm)


190.67
144.86
138.30
134.94
132.79
130.56
128.98
128.65
128.53
128.47
122.20
O
f1 (ppm)

6-^{13}C NMR