

Supporting Information

Encapsulation of Pentazole Gold Nanoparticles into Modified Polycyanostyrene and Polynitrostyrene Microspheres as Efficient Catalysts for Cinnoline Synthesis and Hydration

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1. General methods and materials

All the reactions dealing with air were carried out in a high purity argon or nitrogen atmosphere using standard Schlenk techniques or glovebox techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 400 or 101 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm), DMSO (δ 2.50 ppm) for ^1H NMR and CDCl_3 (δ 77.0 ppm), DMSO (δ 40.35 ppm) for ^{13}C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ). IR spectra were recorded on total reflection Fourier infrared spectrometer (NICOLET 6700). The crystal structures were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer. TEM was recorded on a transmission electron microscope (JEM-2100, JEOL, Japan), operating at 200 kV. SEM image and EDS spectra were 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). The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method and the pore volume was calculated by the BJH method from adsorption branches of isotherms.

2. Synthesis of catalyst PA-Au-PCS

PVP (1.400 g) and azoisobutyronitrile (0.100 g) was dissolved in isopropanol (80 mL) , the obtained mixture was heated up to 70 °C in a Schlenk tube, and simultaneously aerated nitrogen to eliminate the effect of oxygen. Subsequently, 4-cyanostyrene (10.0 g) was added into the above-mentioned mixture under vigorous mechanical stirring. The polymerization was proceeded for 24 h untill room temperature under stirring conditions. Finally, the resultant modified polycyanostyrene microspheres (PCS) were collected by centrifugation, washed with water and ethanol for several times, followed by vacuum freeze-drying for 12 h.

p-methoxyaniline (2.460 g) were dissolved in 25 mL methanol in a round-bottom flask and cooled to -5 °C. Then 4 mL concentrated HCl (37 % in water) were added into the above mixture. Next, NaNO₂ (1.730 g) were dissolved in deionized water (10 mL), which was added slowly into the above aniline solution. After 45 min later, the reaction flask was cooled to -40 °C (in EtOH with liquid nitrogen), and NaN₃ (1.730 g) was dissolved in freshly deionized water (10 mL), then added slowly drop-wise into the above solution by using a magnetic stirring bar. After 1 hour reaction at -40 °C, the mixture was filtered through vacuum and the solid was washed with cold MeOH/water (1:1) solution quickly. The purification of the crude product by column chromatography on silica-gel (PE:EA = 10:1) afforded the pure compound as a light-yellow solid.

PPh₃AuCl (1.0 mmol) and AgOTf (1.1 mmol) was dissolved in CH₂Cl₂ (5 mL) at room temperature. The solution was stirred for 15 min, and the ligand was added in above mixture. Then the mixture was stirred for 5 hours at room temperature. The following cloudy solution was filtered through a short pad of celite and washed with CH₂Cl₂ for several times, and the clear solution was concentrated under vacuum. After this, petroleum ether was added slowly drop-wise on the top of the DCM layer. The resultant purple solid was collected and washed with petroleum ether several times, followed dried by vacuum pump.

Modified polycyanostyrene (PCS) microspheres (1.000 g) was dispersed in ethanol (100 mL) under ultrasonication, pentazole gold (50 mg) was dissolved in ethanol (10 mL), was added to above dispersion liquid at 78 °C. After 12 hours later, cooling the reaction to room temperature. The composite (5 % loading, w/w) was collected by centrifugation, washed with ethanol for several times, followed by vacuum freeze-drying for 12 h.

3. Characterization of catalyst PA-Au-PCS

There was a obvious peak at 2220 cm^{-1} in IR spectra of PCS and PA-Au-PCS (Fig.S1.), which revealed cyanogroup were introduced to the PCS successfully compared to PS microspheres. According to a series of characterization, we could find pentazole gold supported by modified polycyanostyrene microspheres (PCS) successfully. The BET surface area are $0.2919\text{ m}^2/\text{g}$ and $4.7429\text{ m}^2/\text{g}$ for the PS microsphere and modified polycyanostyrene microspheres, respectively, and the pore volume are $0.0065\text{ cm}^3/\text{g}$ and $0.0165\text{ cm}^3/\text{g}$ for the PS microsphere and modified polycyanostyrene microspheres, respectively (Fig.S4.).

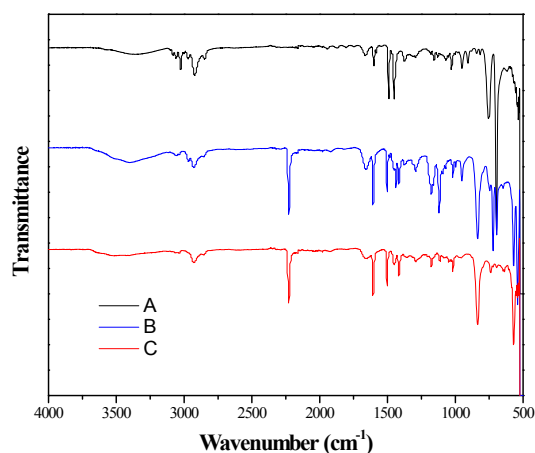


Fig.S1. IR spectra of (A) PS, (B) PCS, (C) PA-Au-PCS

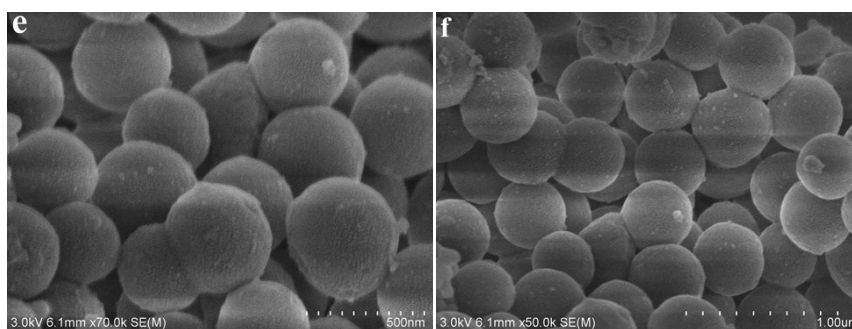


Fig. S2. SEM images of (e), (f) PA-Au-PCS after five runs

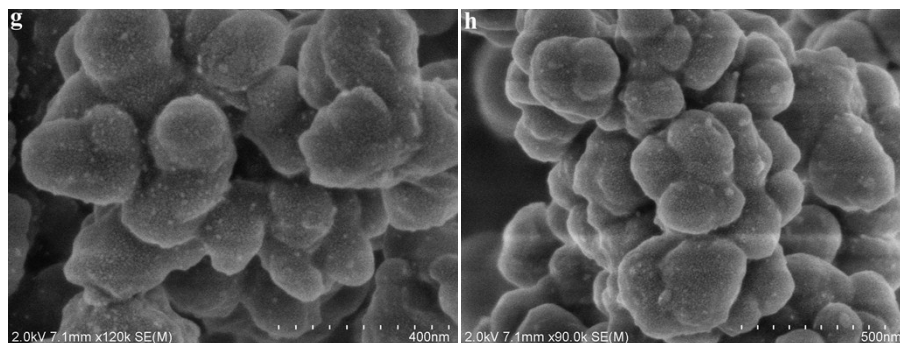


Fig. S3. SEM image of (g) fresh PA-Au-PNS , (h) PA-Au-PNS after five runs

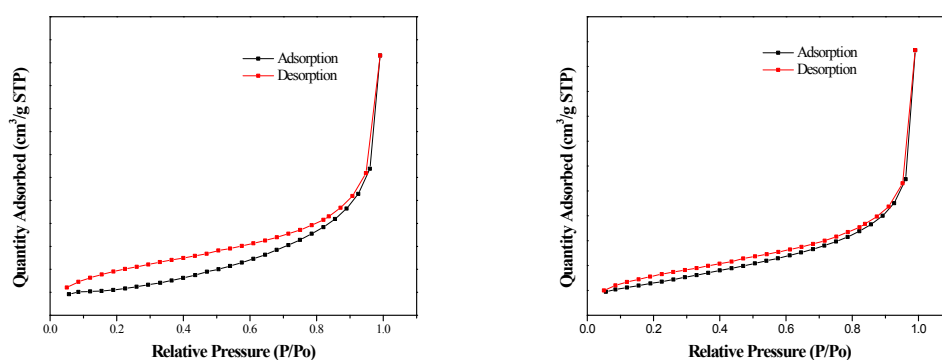


Fig. S4. BET images of PS and PCS

4. General procedure for cinnoline

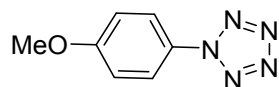
Under N₂ atmosphere, **1a** (1.0 mmol), **2a** (1.0 mmol), PA-Au-PCS (5 wt%, 1%), *t*BuOK (1.0 mmol.), were introduced in a Schlenk tube (20 mL), successively. The tube was evacuated and refilled with high purity nitrogen for three times. Then, the Schlenk tube was closed and the resulting mixture was stirred at 110 °C for 3 h under toluene. After cooling down to room temperature, water was added to quench the reaction and extracted with EtOAc (3x5 mL), the organic phases were concentrated by removing the solvent under vacuum. Finally, the residue was purified by column chromatography with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 40:1) as eluent to give the desired product **3a**. The TON of **3a** was 85.

5. General procedure for hydration of alkynes

To 20 mL Schlenk tube was added PA-Au-PCS (5 wt%, 1%), acetic acid (4.5 mL), water (0.5 mL) and **4a** (1.0 mmol). Then AgOTf (5 mol%) was added and the mixture was stirred at 100 ° C for 12 h. Then the mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous MgSO₄. The solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 50:1) afforded the compound **5a**.

6. Compounds Characterization

2-(4-methoxyphenyl)-2H-pentazole.

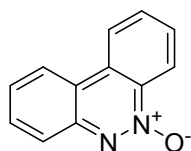


^1H NMR (400 MHz, CDCl_3) δ 7.01 – 6.96 (m, 1H), 6.94 – 6.89 (m, 1H), 3.82 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 157.05 (s), 132.38 (s), 120.01 (s), 115.16 (s), 55.56 (s).

HRMS (ESI) m/z Calculated for $\text{C}_7\text{H}_7\text{N}_5\text{O}$ $[\text{M}+\text{H}]^+$ 178.0729, found 178.0731.

benzo[c]cinnoline 5-oxide (3aa).

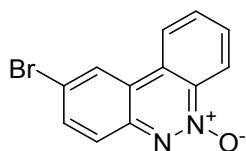


^1H NMR (400 MHz, CDCl_3) δ 8.69 (dd, $J = 8.9, 0.8$ Hz, 2H), 8.28 – 8.13 (m, 2H),

7.86 – 7.80 (m, 2H), 7.79 – 7.69 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.34,

134.84, 131.27, 130.38, 130.07, 119.20.

9-bromobenzo[c]cinnoline 5-oxide (3ab).



^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, $J = 2.1$ Hz, 1H), 8.24 (dd, $J = 6.8, 3.4$ Hz, 2H),

8.12 (d, $J = 9.2$ Hz, 1H), 7.91 (d, $J = 2.1$ Hz, 1H), 7.87 (dd, $J = 5.4, 2.0$ Hz, 2H). ^{13}C

NMR (101 MHz, CDCl_3) δ 143.75, 143.66, 143.51, 142.06, 134.19, 131.65, 131.15,

130.91, 130.82, 129.77, 129.67, 124.91. HRMS (ESI) m/z Calculated for

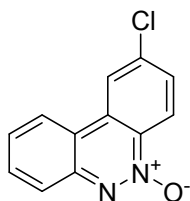
$\text{C}_{12}\text{H}_7\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 274.9820, found 274.9821.

7-chlorobenzo[c]cinnoline 5-oxide (3ac).



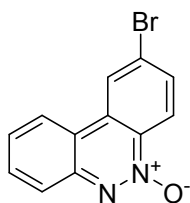
^1H NMR (400 MHz, CDCl_3) δ 8.63 (ddd, $J = 15.6, 8.9, 1.0$ Hz, 2H), 8.33 (dd, $J = 8.7, 0.5$ Hz, 1H), 7.95 (dd, $J = 7.3, 1.2$ Hz, 1H), 7.90 – 7.83 (m, 1H), 7.82 – 7.75 (m, 1H), 7.64 (dd, $J = 9.0, 7.4$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.22, 142.23, 135.91, 134.82, 134.54, 131.71, 130.99, 130.95, 130.78, 129.02, 118.98, 118.27. HRMS (ESI) m/z Calculated for $\text{C}_{12}\text{H}_7\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 231.0325, found 231.0323.

2-chlorobenzo[c]cinnoline 5-oxide (3ad).



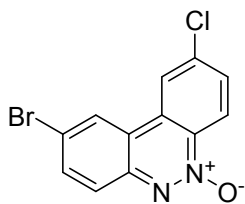
^1H NMR (400 MHz, CDCl_3) δ 8.32 – 8.28 (m, 2H), 8.26 (dd, $J = 10.8, 6.0$ Hz, 2H), 7.93 – 7.87 (m, 2H), 7.81 (dd, $J = 9.3, 2.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.60, 143.30, 143.15, 141.78, 136.80, 132.10, 131.37, 130.95, 130.86, 129.66, 129.47, 127.90. HRMS (ESI) m/z Calculated for $\text{C}_{12}\text{H}_7\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 231.0325, found 231.0323.

2-bromobenzo[c]cinnoline 5-oxide (3ae).



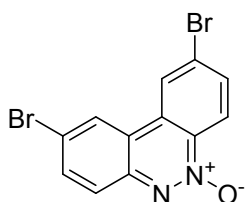
^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, $J = 2.1$ Hz, 1H), 8.26 (dd, $J = 6.8, 3.3$ Hz, 2H), 8.15 (d, $J = 9.2$ Hz, 1H), 7.94 – 7.87 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.78, 143.69, 143.54, 142.09, 134.24, 131.66, 131.21, 130.93, 130.87, 129.77, 129.68, 124.95. HRMS (ESI) m/z Calculated for $\text{C}_{12}\text{H}_7\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 274.9820, found 274.9821.

9-bromo-2-chlorobenzo[c]cinnoline 5-oxide (3af).



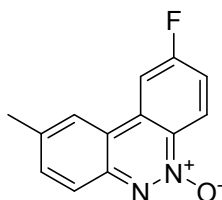
^1H NMR (400 MHz, CDCl_3) δ 8.88 (d, $J = 2.0$ Hz, 1H), 8.65 (d, $J = 9.5$ Hz, 1H), 8.21 (d, $J = 2.0$ Hz, 1H), 8.07 (d, $J = 9.2$ Hz, 1H), 7.92 (dd, $J = 9.2, 2.1$ Hz, 1H), 7.70 (dd, $J = 9.5, 2.1$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.51, 144.73, 138.08, 135.72, 131.79, 131.70, 128.94, 125.19, 121.57, 120.65. HRMS (ESI) m/z Calculated for $\text{C}_{12}\text{H}_6\text{BrClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 308.9430, found 308.9427.

2,9-dibromobenzo[c]cinnoline 5-oxide (3ag).



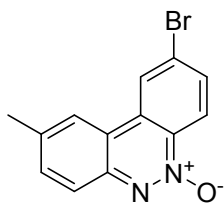
^1H NMR (400 MHz, CDCl_3) δ 8.88 (d, $J = 2.1$ Hz, 1H), 8.56 (d, $J = 9.4$ Hz, 1H), 8.42 (d, $J = 1.8$ Hz, 1H), 8.08 (d, $J = 9.2$ Hz, 1H), 7.92 (dd, $J = 9.2, 2.1$ Hz, 1H), 7.83 (dd, $J = 9.4, 2.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.71, 144.65, 135.75, 134.09, 132.42, 131.83, 126.41, 125.26, 121.58, 120.57. HRMS (ESI) m/z Calculated for $\text{C}_{12}\text{H}_6\text{Br}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 352.8925, found 352.8924.

2-fluoro-9-methylbenzo[c]cinnoline 5-oxide(3ah).



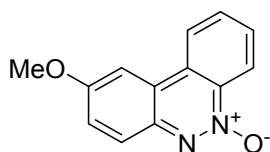
^1H NMR (400 MHz, CDCl_3) δ 8.26 (dd, $J = 9.5, 5.9$ Hz, 1H), 8.13 (d, $J = 8.9$ Hz, 1H), 8.01 (s, 1H), 7.85 (dd, $J = 9.4, 2.7$ Hz, 1H), 7.75 – 7.61 (m, 2H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.04 (s), 161.51 (s), 143.30 (d, $J = 13.5$ Hz), 142.52 (s), 141.24 (s), 140.83 (s), 134.29 (s), 131.77 (d, $J = 10.1$ Hz), 128.68 (s), 127.69 (s), 122.38 (d, $J = 28.3$ Hz), 111.65 (d, $J = 21.1$ Hz), 22.21 (s). HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_9\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 229.0777, found 229.0776.

2-bromo-9-methylbenzo[c]cinnoline 5-oxide(3ai).



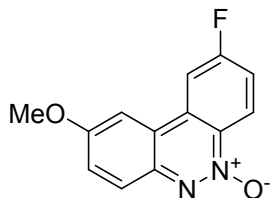
^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, $J = 2.0$ Hz, 1H), 8.12 (dd, $J = 10.3, 9.4$ Hz, 2H), 7.99 (s, 1H), 7.89 (dd, $J = 9.2, 2.1$ Hz, 1H), 7.72 (dd, $J = 8.9, 1.7$ Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.69, 143.23, 142.62, 142.07, 141.72, 134.27, 134.00, 131.62, 130.80, 129.12, 127.77, 124.19, 22.29. HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_9\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 288.9977, found 288.9975.

9-methoxybenzo[c]cinnoline 5-oxide(3aj).



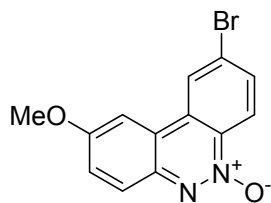
^1H NMR (400 MHz, CDCl_3) δ 8.26 – 8.17 (m, 2H), 8.12 (d, $J = 9.5$ Hz, 1H), 7.82 (dddd, $J = 20.3, 8.2, 6.7, 1.5$ Hz, 2H), 7.54 (dd, $J = 9.5, 2.7$ Hz, 1H), 7.44 (d, $J = 2.7$ Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.38, 145.03, 143.25, 141.93, 140.81, 130.71, 130.55, 129.66, 129.11, 128.82, 126.49, 104.44, 55.96. HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 227.0821, found 227.0822.

2-fluoro-9-methoxybenzo[c]cinnoline 5-oxide(3ak).



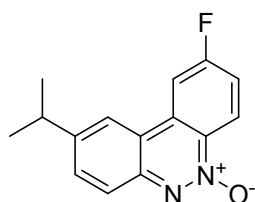
^1H NMR (400 MHz, CDCl_3) δ 8.20 (dd, $J = 9.5, 5.9$ Hz, 1H), 8.09 (d, $J = 9.5$ Hz, 1H), 7.83 (dd, $J = 9.4, 2.7$ Hz, 1H), 7.65 (ddd, $J = 9.6, 8.0, 2.8$ Hz, 1H), 7.56 (dd, $J = 9.5, 2.7$ Hz, 1H), 7.42 (d, $J = 2.7$ Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.43 (s), 161.26 (s), 144.44 (s), 142.22 (d, $J = 13.3$ Hz), 141.11 (s), 140.60 (s), 130.99 (d, $J = 10.1$ Hz), 130.32 (s), 127.10 (s), 122.25 (d, $J = 28.0$ Hz), 111.87 (d, $J = 21.2$ Hz), 104.46 (s), 55.97 (s). HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_9\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 245.0726, found 245.0725.

2-bromo-9-methoxybenzo[c]cinnoline 5-oxide(3al).



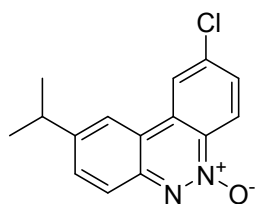
^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, $J = 2.1$ Hz, 1H), 8.07 (dd, $J = 17.4, 9.3$ Hz, 2H), 7.88 (dd, $J = 9.2, 2.1$ Hz, 1H), 7.55 (dd, $J = 9.5, 2.7$ Hz, 1H), 7.40 (d, $J = 2.7$ Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.72, 145.00, 142.17, 141.72, 141.13, 134.17, 131.65, 130.71, 130.02, 127.23, 123.09, 104.40, 56.03. HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_9\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 304.9926, found 304.9923.

2-fluoro-9-isopropylbenzo[c]cinnoline 5-oxide(3am).



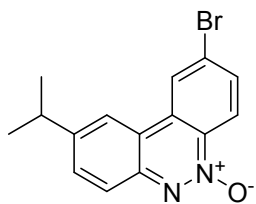
^1H NMR (400 MHz, CDCl_3) δ 8.26 (dd, $J = 9.5, 5.9$ Hz, 1H), 8.17 (d, $J = 9.0$ Hz, 1H), 8.04 (d, $J = 1.8$ Hz, 1H), 7.83 (ddd, $J = 11.0, 9.2, 2.3$ Hz, 2H), 7.66 (ddd, $J = 9.5, 7.9, 2.8$ Hz, 1H), 3.22 (dt, $J = 13.7, 6.9$ Hz, 1H), 1.44 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.02 (s), 161.49 (s), 151.61 (s), 143.41 (d, $J = 13.4$ Hz), 142.88 (s), 140.89 (s), 132.30 (s), 131.77 (d, $J = 10.2$ Hz), 128.87 (s), 124.86 (s), 122.28 (d, $J = 28.3$ Hz), 111.68 (d, $J = 21.1$ Hz), 34.40 (s), 23.32 (s). HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{13}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 257.1090, found 257.1091.

2-chloro-9-isopropylbenzo[c]cinnoline 5-oxide(3an).



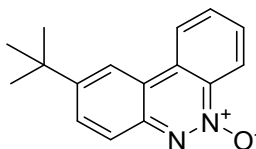
^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, $J = 9.5$ Hz, 1H), 8.48 (d, $J = 1.8$ Hz, 1H), 8.19 (d, $J = 2.0$ Hz, 1H), 8.12 (d, $J = 9.0$ Hz, 1H), 7.78 (dd, $J = 9.0, 1.9$ Hz, 1H), 7.66 (dd, $J = 9.5, 2.1$ Hz, 1H), 3.21 (dt, $J = 13.7, 6.9$ Hz, 1H), 1.42 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.40, 145.30, 144.89, 137.14, 134.81, 133.41, 132.55, 130.91, 130.18, 128.73, 120.66, 114.70, 34.71, 23.33. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{13}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 273.0795, found 273.0796.

2-bromo-9-isopropylbenzo[c]cinnoline 5-oxide(3ao).



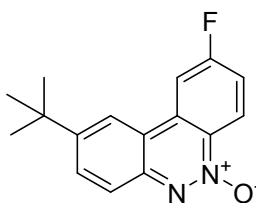
^1H NMR (400 MHz, CDCl_3) δ 8.60 (d, $J = 9.4$ Hz, 1H), 8.49 (d, $J = 1.8$ Hz, 1H), 8.42 (d, $J = 1.9$ Hz, 1H), 8.14 (d, $J = 9.0$ Hz, 1H), 7.80 (ddd, $J = 9.0, 4.5, 2.0$ Hz, 2H), 3.22 (dt, $J = 13.7, 6.9$ Hz, 1H), 1.43 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.49, 145.25, 145.16, 134.86, 133.68, 133.32, 132.59, 132.23, 130.25, 125.45, 120.62, 114.72, 34.74, 23.32. HRMS (ESI) m/z Calculated for $\text{C}_{15}\text{H}_{13}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 317.0290, found 317.0292.

9-(*tert*-butyl)benzo[c]cinnoline 5-oxide(3ap).



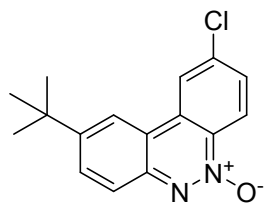
^1H NMR (400 MHz, CDCl_3) δ 8.26 – 8.20 (m, 2H), 8.16 (dd, $J = 11.2, 5.6$ Hz, 2H), 7.94 (dd, $J = 9.2, 2.1$ Hz, 1H), 7.85 – 7.75 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.85, 143.61, 143.49, 143.20, 142.34, 130.32, 130.19, 129.89, 129.61, 129.45, 128.93, 123.95, 35.49, 30.73. HRMS (ESI) m/z Calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 253.1341, found 253.1341.

9-(*tert*-butyl)-2-fluorobenzo[c]cinnoline 5-oxide(3aq).



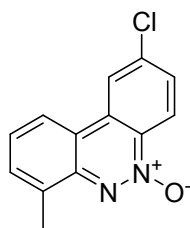
^1H NMR (400 MHz, CDCl_3) δ 8.27 (dd, $J = 9.5, 5.9$ Hz, 1H), 8.21 – 8.14 (m, 2H), 8.01 (dd, $J = 9.2, 2.1$ Hz, 1H), 7.86 (dd, $J = 9.5, 2.7$ Hz, 1H), 7.67 (ddd, $J = 10.5, 8.0, 2.8$ Hz, 1H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.08 (s), 161.55 (s), 153.96 (s), 143.41 (s), 142.50 (s), 140.89 (s), 131.74 (d, $J = 10.2$ Hz), 131.16 (s), 128.50 (s), 123.99 (s), 122.32 (d, $J = 28.3$ Hz), 111.67 (d, $J = 21.2$ Hz), 35.54 (s), 30.73 (s). HRMS (ESI) m/z Calculated for $\text{C}_{16}\text{H}_{15}\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 271.1247, found 271.1245.

9-(*tert*-butyl)-2-chlorobenzo[*c*]cinnoline 5-oxide(3ar).



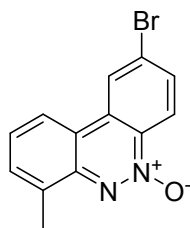
^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, $J = 9.5$ Hz, 1H), 8.60 (d, $J = 2.0$ Hz, 1H), 8.20 (d, $J = 2.0$ Hz, 1H), 8.13 (d, $J = 9.2$ Hz, 1H), 7.97 (dd, $J = 9.2, 2.1$ Hz, 1H), 7.66 (dd, $J = 9.5, 2.1$ Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.72, 144.97, 137.18, 134.61, 133.47, 131.48, 130.87, 129.83, 128.71, 120.68, 113.68, 35.89, 30.73. HRMS (ESI) m/z Calculated for $\text{C}_{16}\text{H}_{15}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 287.0951, found 287.0949.

2-chloro-7-methylbenzo[*c*]cinnoline 5-oxide(3as).



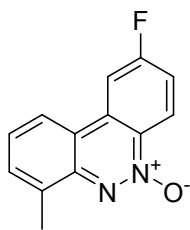
^1H NMR (400 MHz, CDCl_3) δ 8.64 (d, $J = 9.5$ Hz, 1H), 8.52 (dd, $J = 8.3, 1.5$ Hz, 1H), 8.27 (d, $J = 2.0$ Hz, 1H), 7.73 – 7.60 (m, 3H), 2.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.75, 144.51, 139.09, 137.19, 135.04, 132.97, 131.14, 130.95, 130.21, 129.20, 120.59, 116.88, 17.95. HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 245.0482, found 245.0482.

2-bromo-7-methylbenzo[*c*]cinnoline 5-oxide(3at).



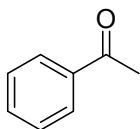
^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, $J = 9.4$ Hz, 1H), 8.51 – 8.46 (m, 1H), 8.43 (d, $J = 1.9$ Hz, 1H), 7.77 (dd, $J = 9.4, 2.0$ Hz, 1H), 7.69 – 7.60 (m, 2H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.62, 144.68, 139.10, 135.06, 133.30, 133.21, 132.64, 131.15, 130.25, 125.51, 120.51, 116.88, 17.95. HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_9\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 288.9977, found 288.9976.

2-fluoro-7-methylbenzo[*c*]cinnoline 5-oxide (3au).



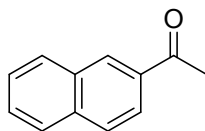
^1H NMR (400 MHz, CDCl_3) δ 8.28 (dd, $J = 9.5, 6.0$ Hz, 1H), 8.10 (d, $J = 9.2$ Hz, 1H), 7.91 (dd, $J = 9.6, 2.7$ Hz, 1H), 7.79 – 7.60 (m, 3H), 2.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.10 (s), 161.57 (s), 143.48 (s), 143.17 (d, $J = 13.6$ Hz), 140.41 (s), 137.68 (s), 131.63 (d, $J = 10.2$ Hz), 130.38 (s), 130.20 (s), 127.50 (s), 122.36 (d, $J = 28.4$ Hz), 112.09 (d, $J = 20.9$ Hz), 17.64 (s). HRMS (ESI) m/z Calculated for $\text{C}_{13}\text{H}_9\text{FN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 229.0777, found 229.0776.

acetophenone (5aa).



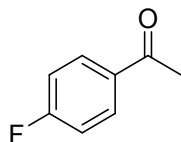
^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.7$ Hz, 2H), 7.58 (t, $J = 7.3$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.08, 137.16, 133.07, 128.55, 128.29, 26.57.

1-(naphthalen-2-yl)ethan-1-one (5ab).



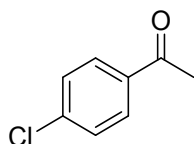
^1H NMR (400 MHz, CDCl_3) δ 8.48 (s, 1H), 8.05 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.90 (dd, $J = 8.3, 5.3$ Hz, 2H), 7.59 (dddd, $J = 19.4, 8.1, 6.9, 1.3$ Hz, 2H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.05, 135.59, 134.51, 132.53, 130.18, 129.55, 128.47, 128.42, 127.79, 126.78, 123.90, 26.68.

1-(4-fluorophenyl)ethan-1-one (5ac).



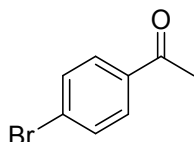
^1H NMR (400 MHz, CDCl_3) δ 8.03 – 7.95 (m, 2H), 7.17 – 7.09 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.45 (s), 167.00 (s), 164.47 (s), 133.58 (d, $J = 3.0$ Hz), 130.92 (d, $J = 9.4$ Hz), 115.62 (d, $J = 21.9$ Hz), 26.50 (s).

1-(4-chlorophenyl)ethan-1-one (5ad).



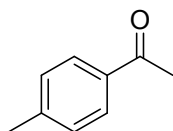
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 – 7.86 (m, 2H), 7.50 – 7.35 (m, 2H), 2.60 (s, 3H).
 $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 196.76, 139.54, 135.45, 129.71, 128.87, 26.52.

1-(4-bromophenyl)ethan-1-one (5ae).



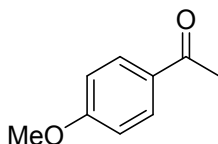
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 – 7.68 (m, 2H), 7.68 – 7.52 (m, 2H), 2.60 (s, 3H).
 $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.02, 135.84, 131.90, 129.85, 128.31, 26.55.

1-(p-tolyl)ethan-1-one (5af).



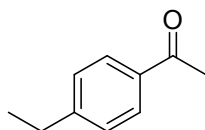
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.8$ Hz, 2H), 7.27 (d, $J = 7.8$ Hz, 2H), 2.59 (s, 3H), 2.42 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.75, 143.82, 134.75, 129.22, 128.42, 26.47, 21.59.

1-(4-methoxyphenyl)ethan-1-one (5ag).



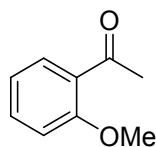
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.6$ Hz, 2H), 6.95 (d, $J = 8.6$ Hz, 2H), 3.88 (s, 3H), 2.57 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 196.80, 163.48, 130.59, 130.33, 113.68, 55.47, 26.36.

1-(4-ethylphenyl)ethan-1-one (5ah)



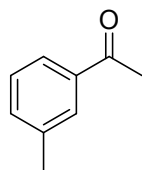
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 2.72 (q, $J = 7.6$ Hz, 2H), 2.59 (s, 3H), 1.27 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.81, 150.04, 134.97, 128.55, 128.06, 28.93, 26.51, 15.19.

1-(2-methoxyphenyl)ethan-1-one (5ai).



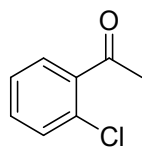
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.52 – 7.44 (m, 1H), 7.06 – 6.93 (m, 2H), 3.92 (s, 3H), 2.63 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 199.88, 158.91, 133.64, 130.34, 128.29, 120.54, 111.58, 55.48, 31.81.

1-(m-tolyl)ethan-1-one (5aj).



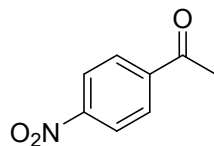
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 10.6$ Hz, 2H), 7.37 (m, 2H), 2.61 (s, 3H), 2.43 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.32, 138.33, 137.21, 133.82, 128.77, 128.43, 125.57, 26.62, 21.31.

1-(2-chlorophenyl)ethan-1-one (5ak).



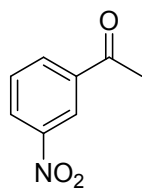
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 (d, $J = 7.4$ Hz, 1H), 7.41 (q, $J = 8.0$ Hz, 2H), 7.33 (t, $J = 7.1$ Hz, 1H), 2.66 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 200.38, 139.17, 131.95, 131.29, 130.63, 129.37, 126.91, 30.68.

1-(4-nitrophenyl)ethan-1-one (5al).



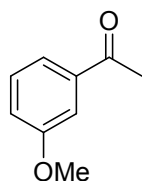
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.37 – 8.27 (m, 2H), 8.21 – 8.06 (m, 2H), 2.70 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 196.29, 150.39, 141.41, 129.31, 123.86, 26.96.

1-(3-nitrophenyl)ethan-1-one (5am).



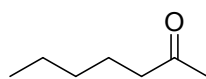
^1H NMR (400 MHz, CDCl_3) δ 8.76 (s, 1H), 8.42 (d, $J = 9.3$ Hz, 1H), 8.29 (d, $J = 7.7$ Hz, 1H), 7.70 (t, $J = 8.0$ Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.66, 148.46, 138.27, 133.78, 129.93, 127.38, 123.19, 26.70.

1-(3-methoxyphenyl)ethan-1-one (5an).



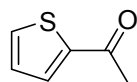
^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 7.6$ Hz, 1H), 7.50 (s, 1H), 7.38 (t, $J = 7.9$ Hz, 1H), 7.12 (d, $J = 8.1$ Hz, 1H), 3.87 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.94, 159.81, 138.49, 129.56, 121.12, 119.61, 112.35, 55.43, 26.72.

heptan-2-one (5ao).



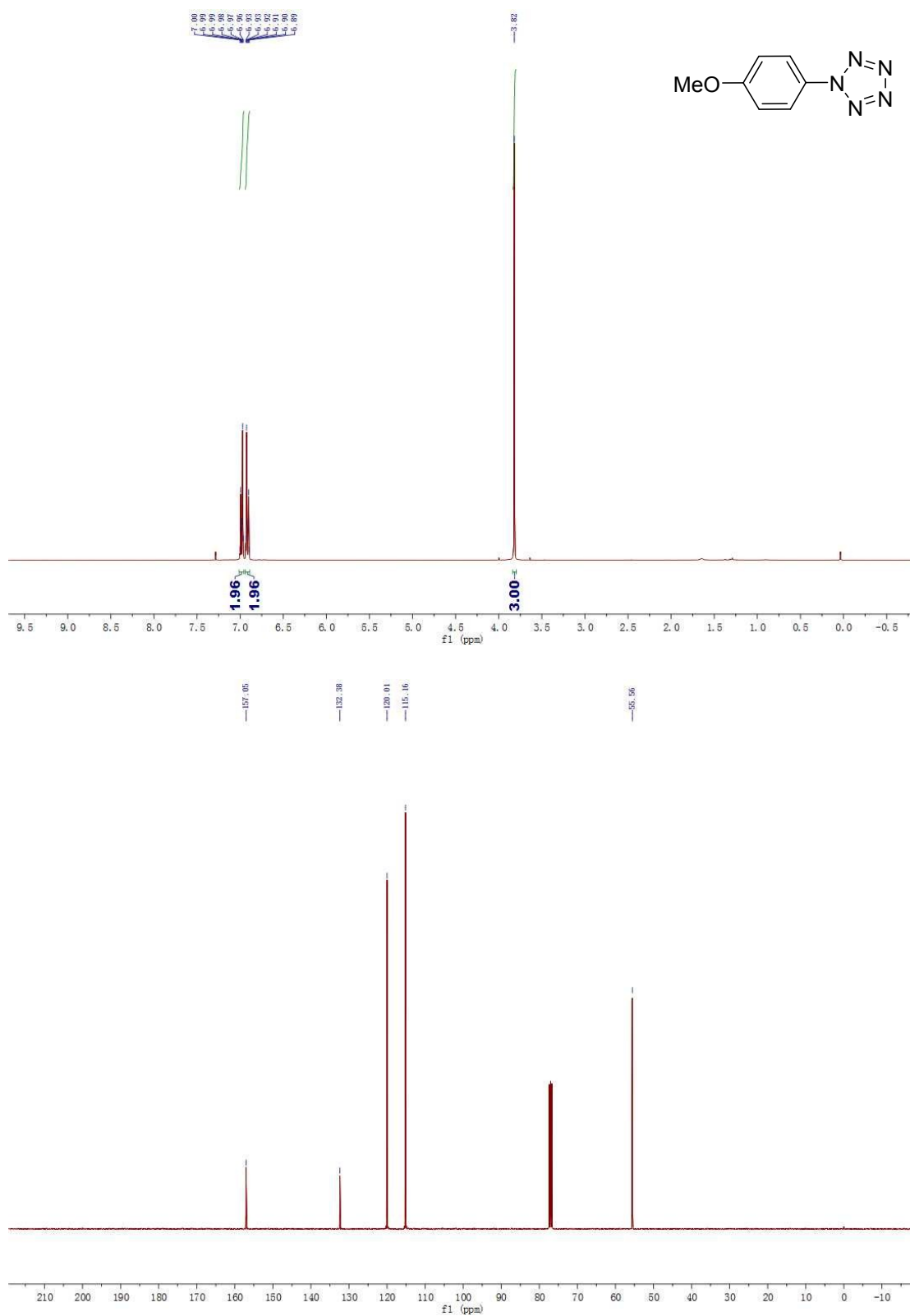
^1H NMR (400 MHz, CDCl_3) δ 2.41 (t, $J = 7.5$ Hz, 2H), 2.12 (s, 3H), 1.56 (dt, $J = 14.8, 7.5$ Hz, 2H), 1.37 – 1.17 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 209.30, 43.73, 29.78, 29.78, 23.52, 22.41, 13.86.

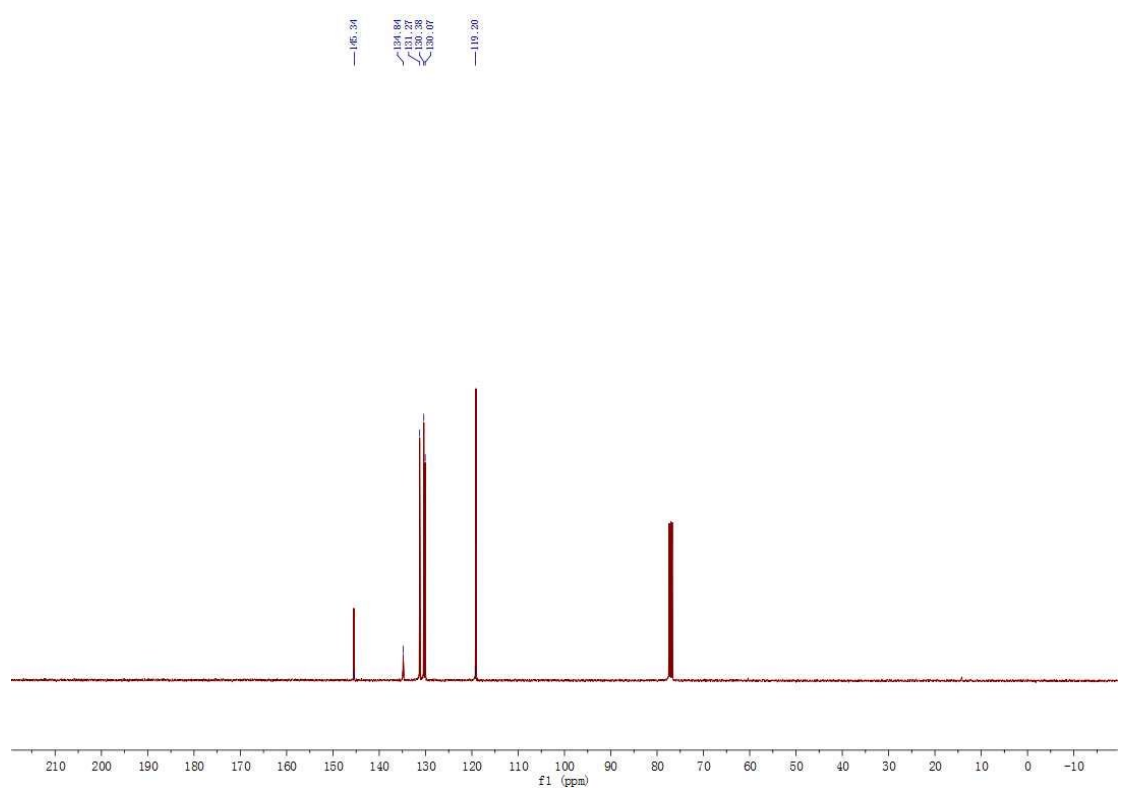
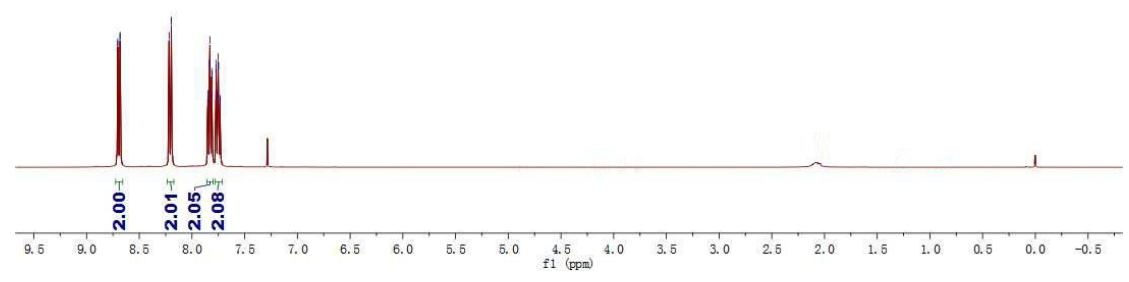
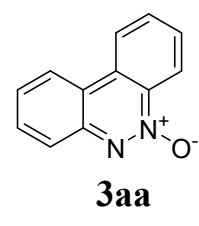
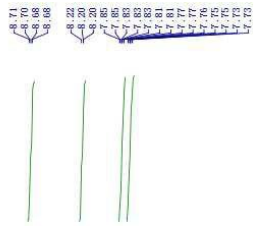
1-(thiophen-2-yl)ethan-1-one (5ap)

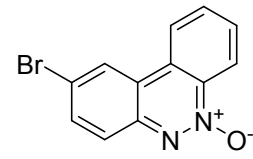
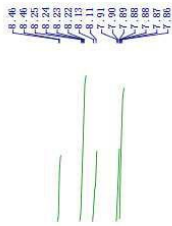


^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, $J = 3.8, 1.1$ Hz, 1H), 7.63 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.13 (dd, $J = 4.9, 3.8$ Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.71, 144.57, 133.77, 132.48, 128.13, 26.90.

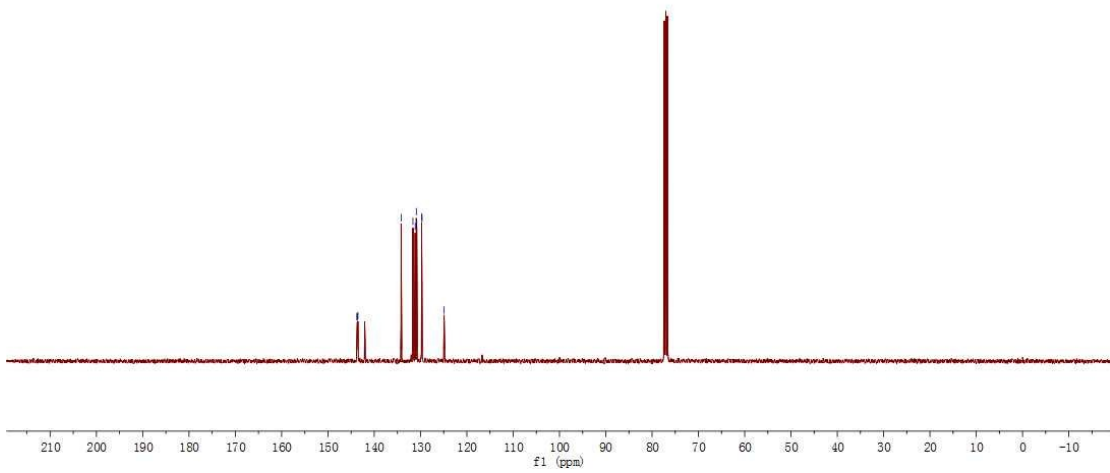
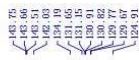
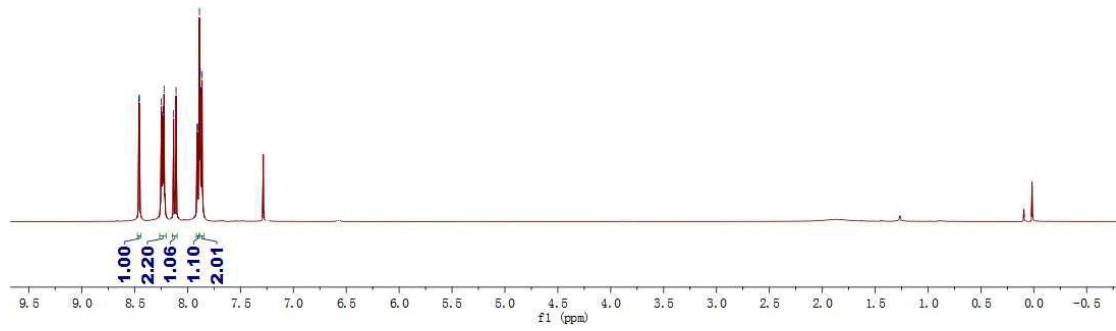
7. ^1H NMR and ^{13}C NMR Spectra



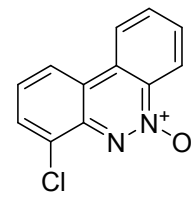
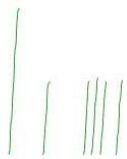




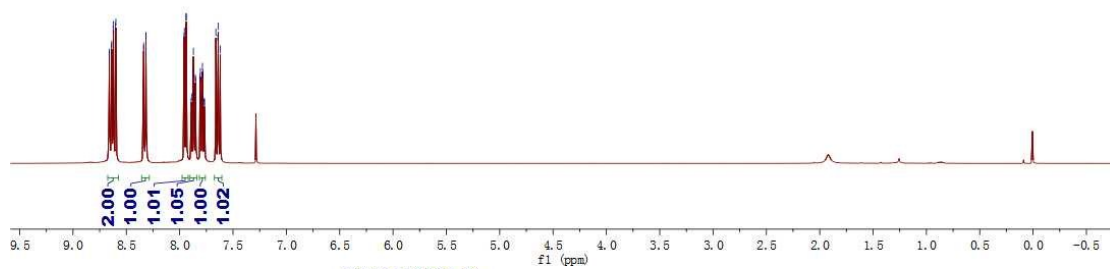
3ab



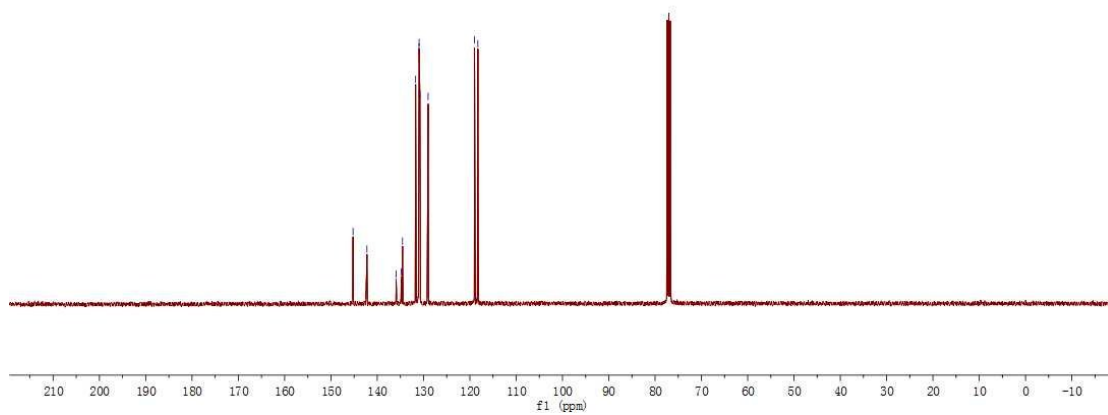
8.06
8.04
8.04
8.02
8.00
8.00
7.94
7.94
7.94
7.94
7.94
7.88
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7.79
7.79
7.77
7.77
7.64
7.64
7.62

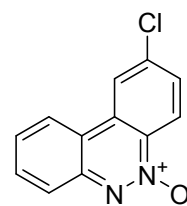
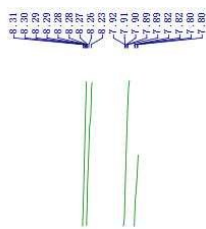


3ac

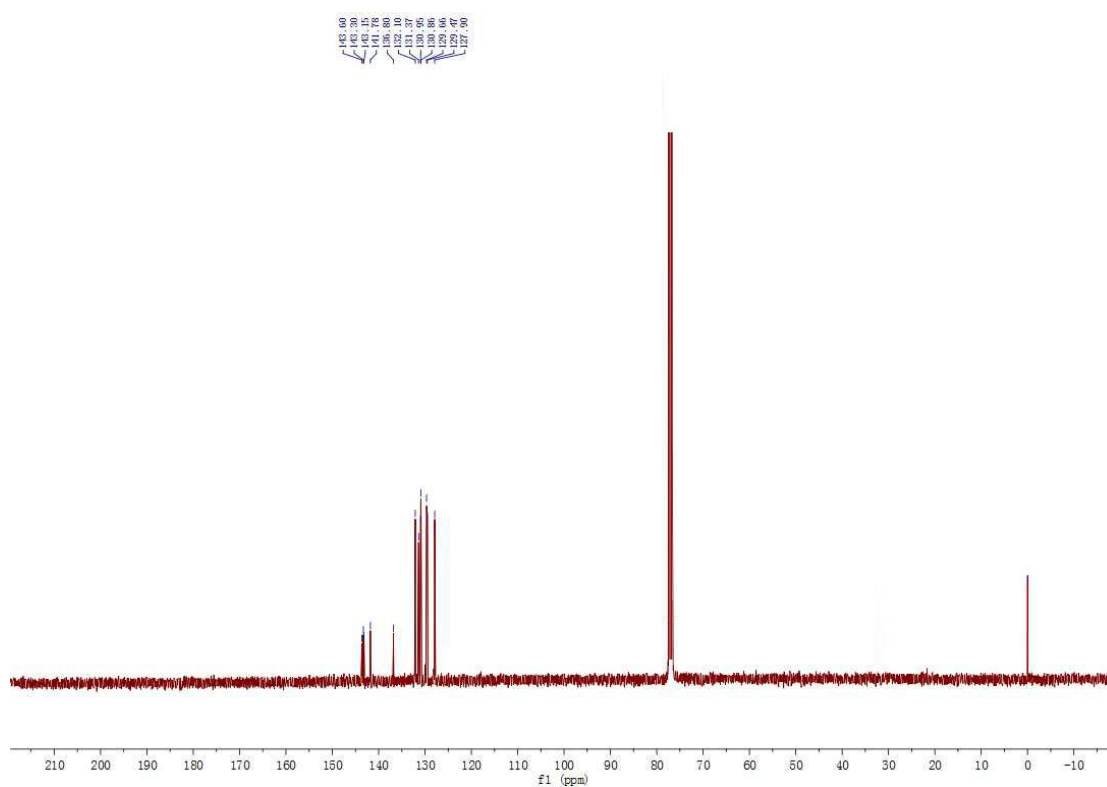
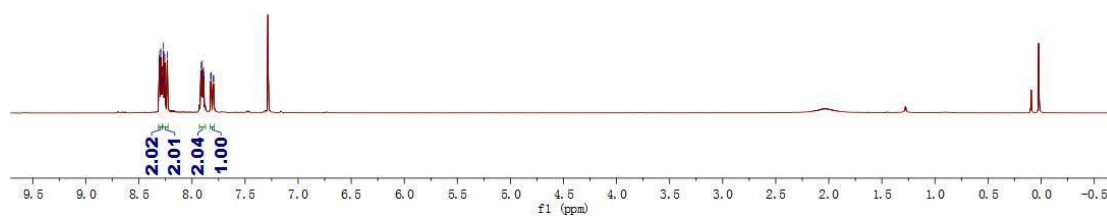


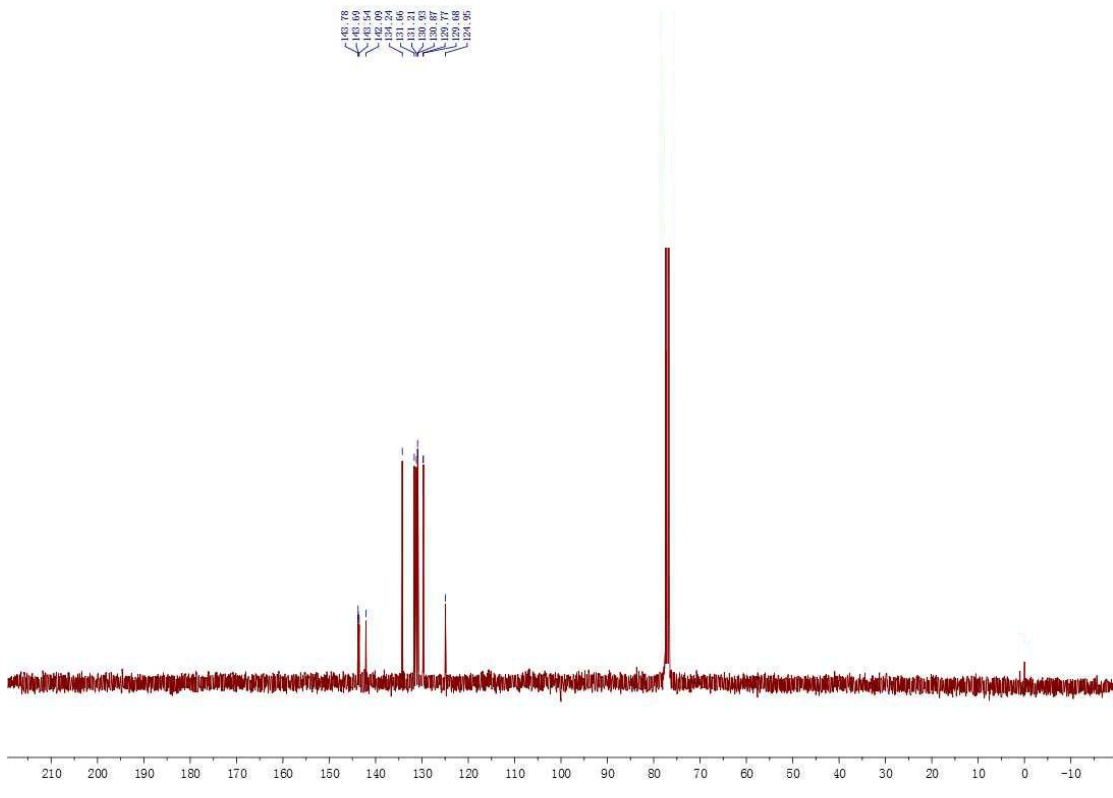
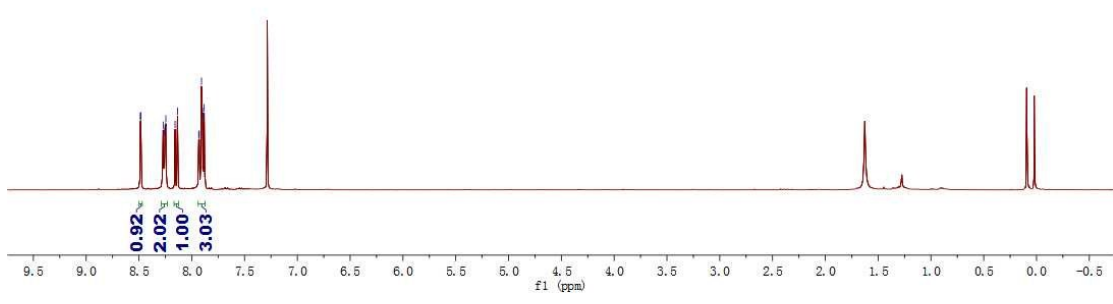
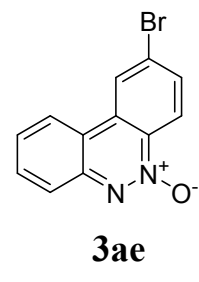
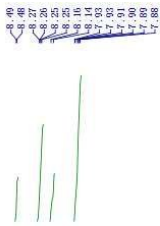
146.22
142.23
135.81
134.94
133.71
130.78
129.02
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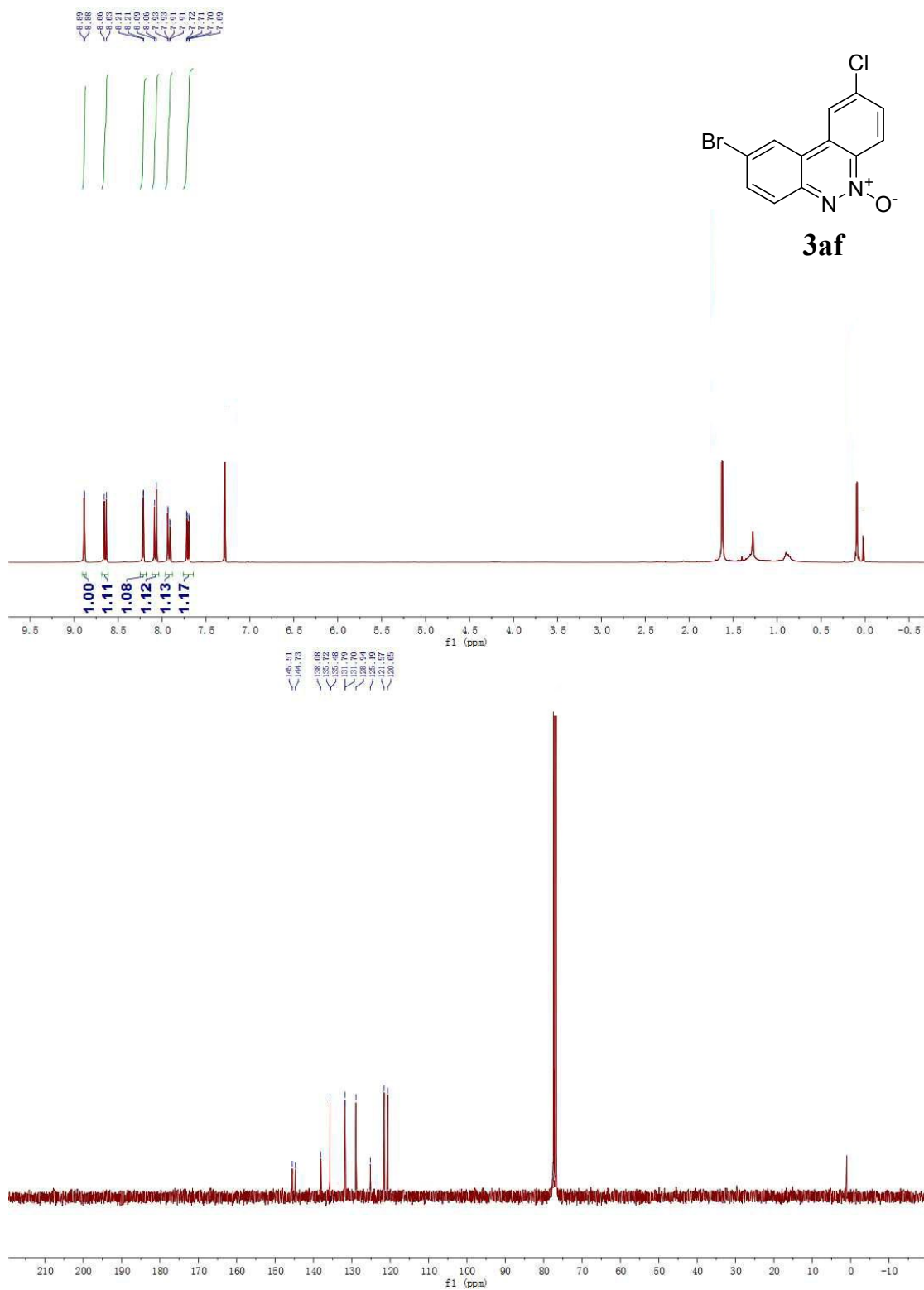


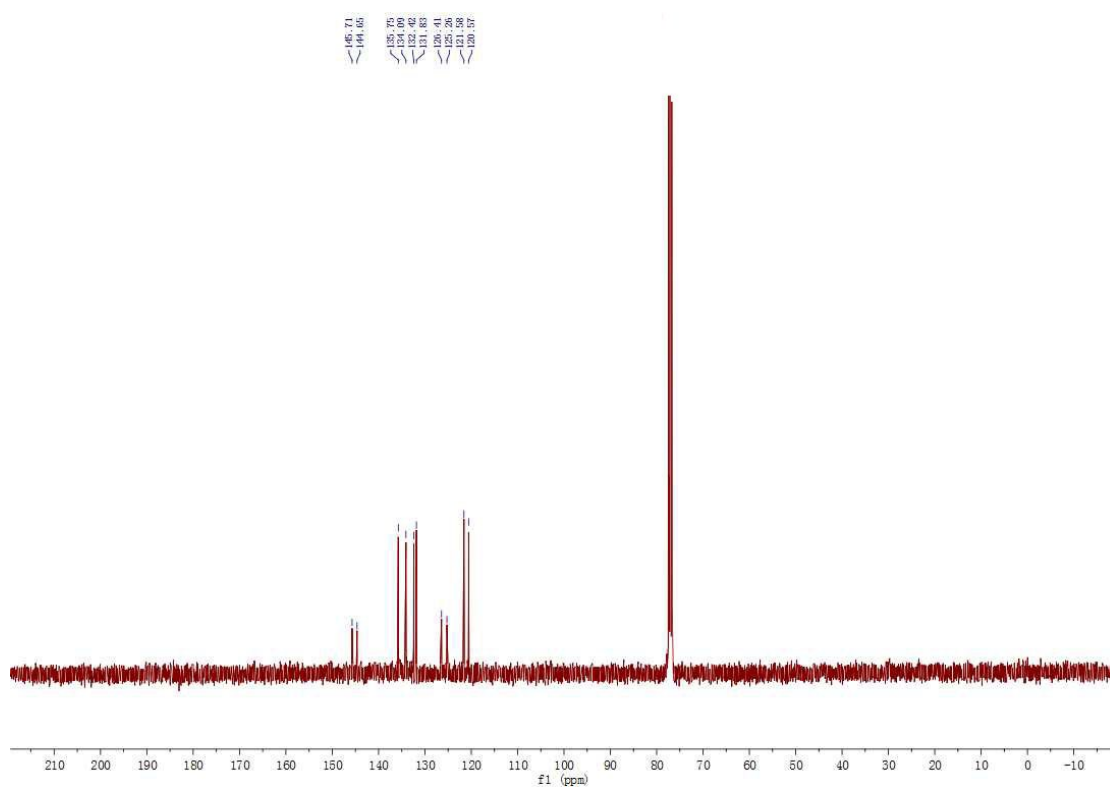
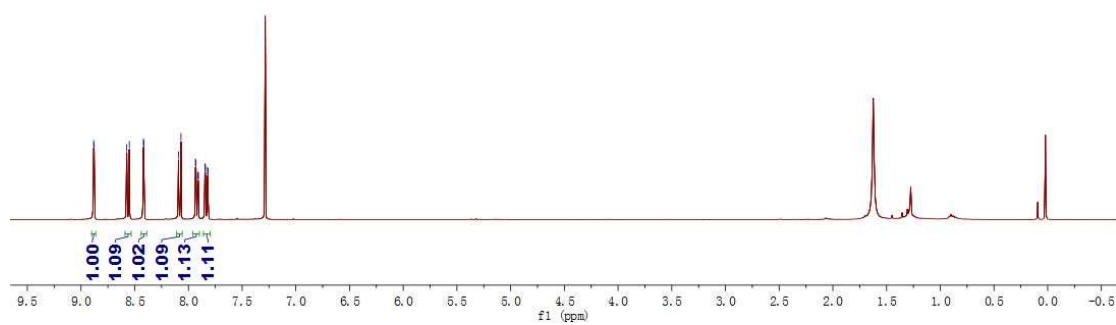
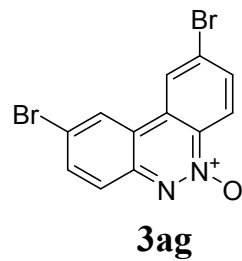
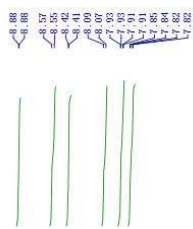


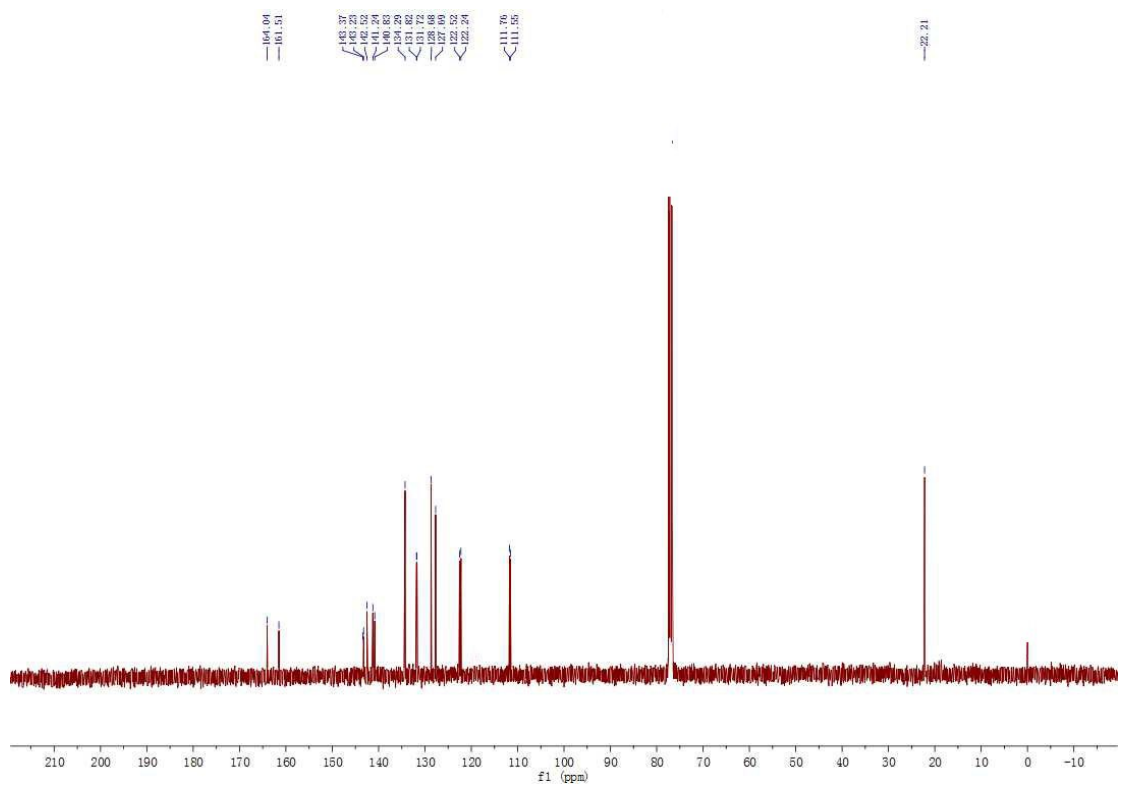
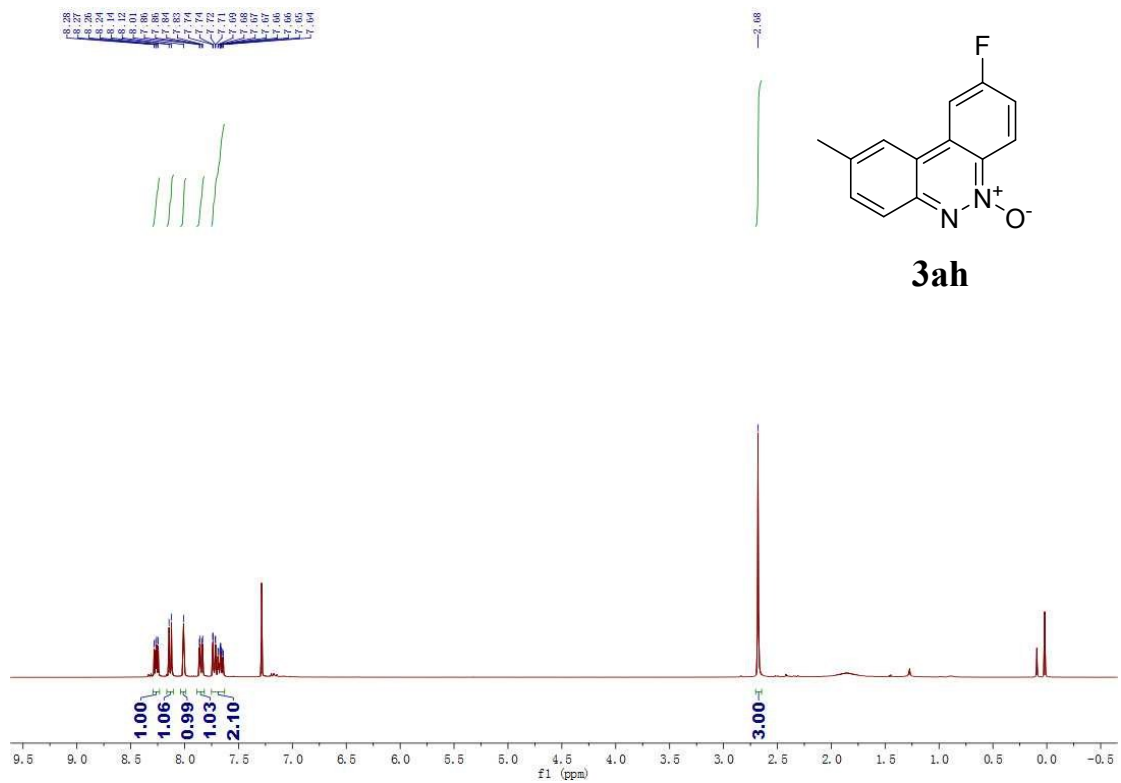
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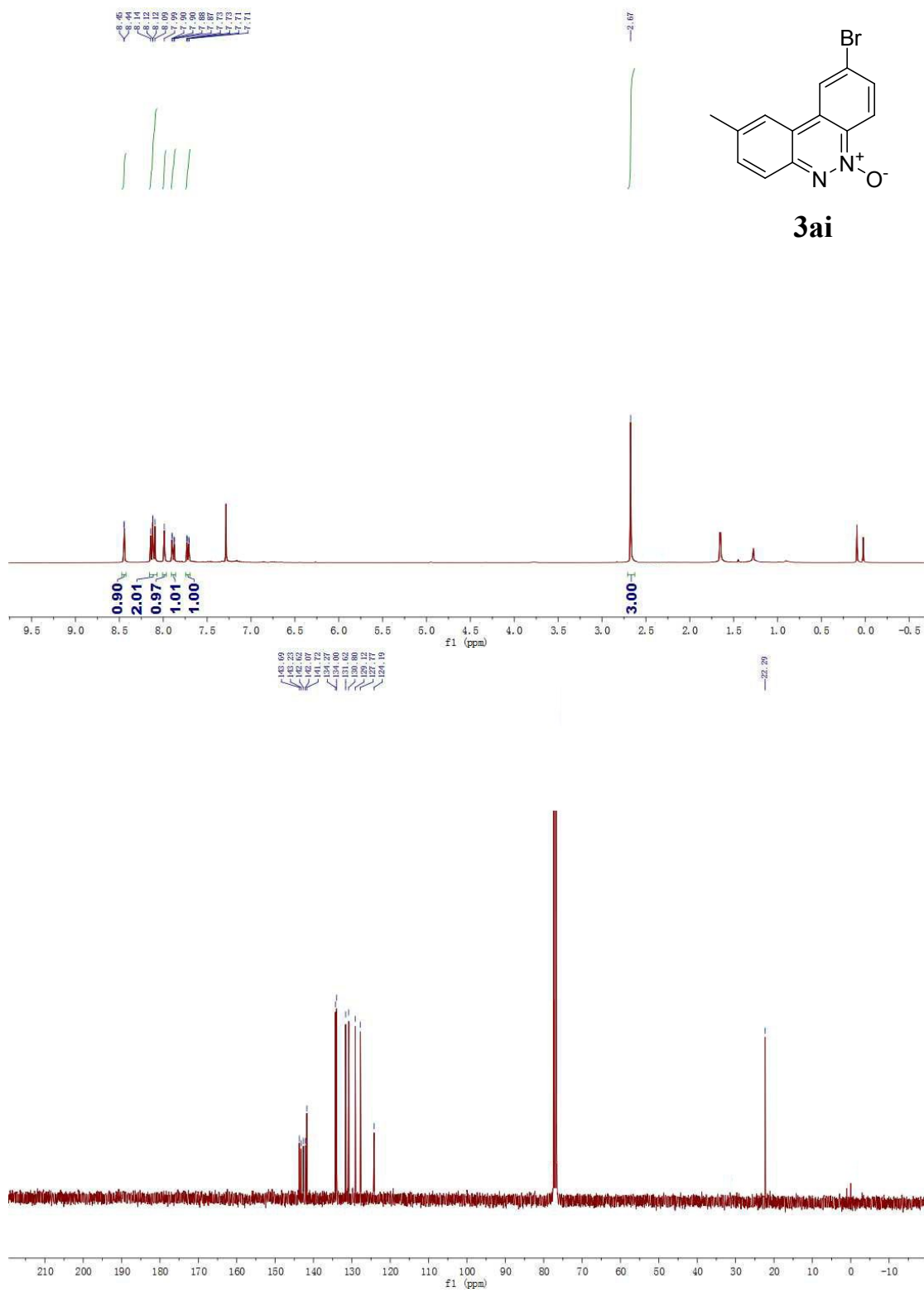


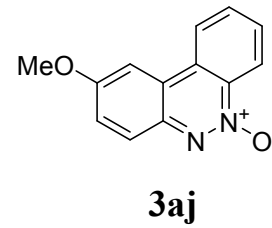
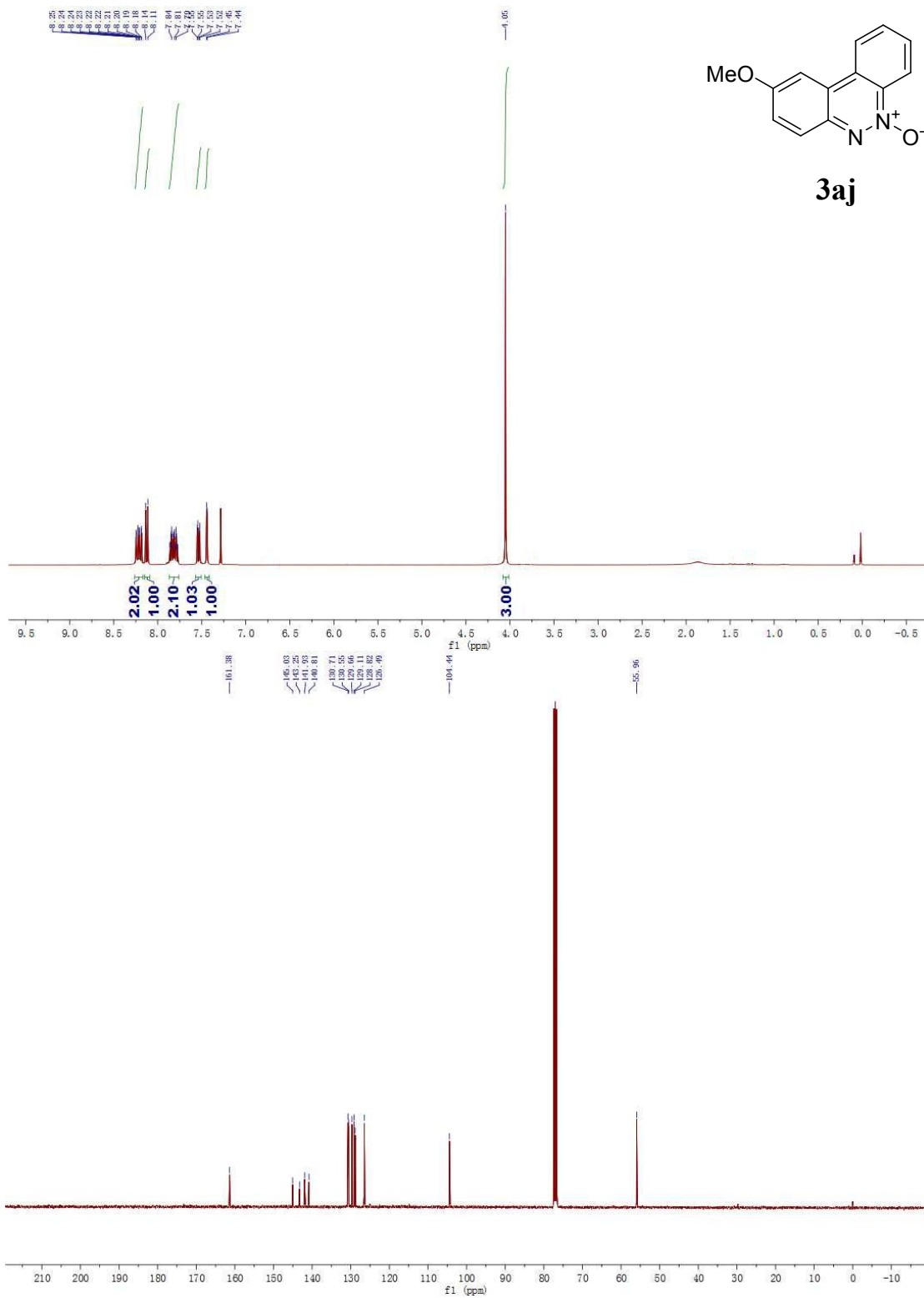


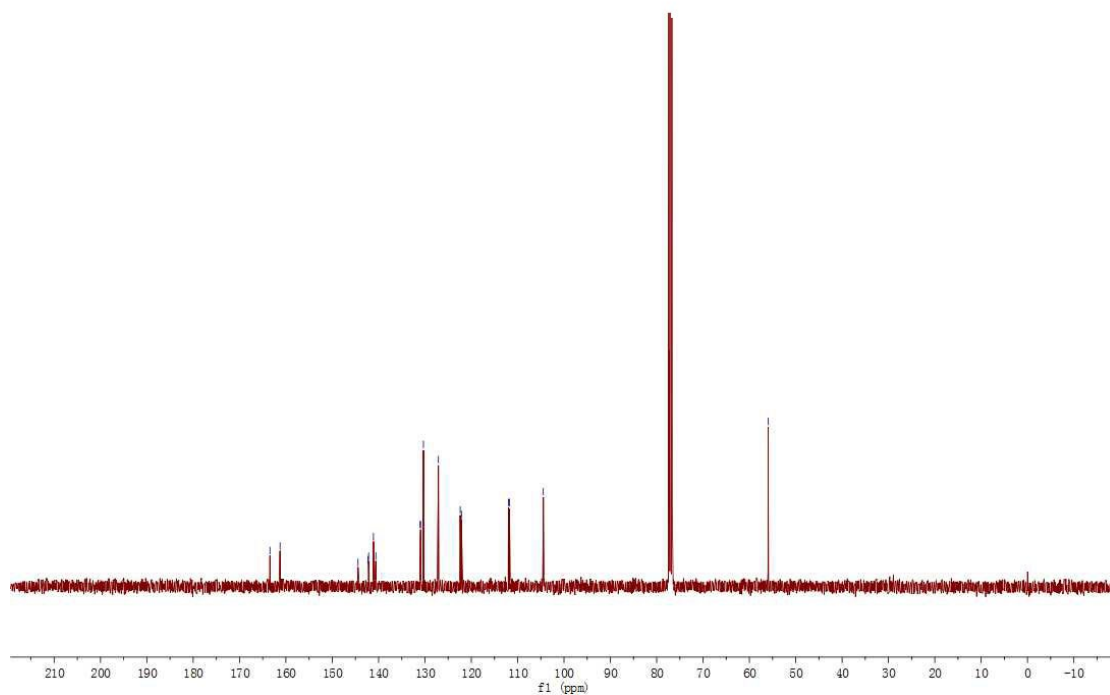
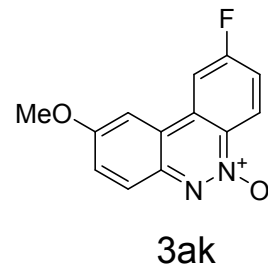
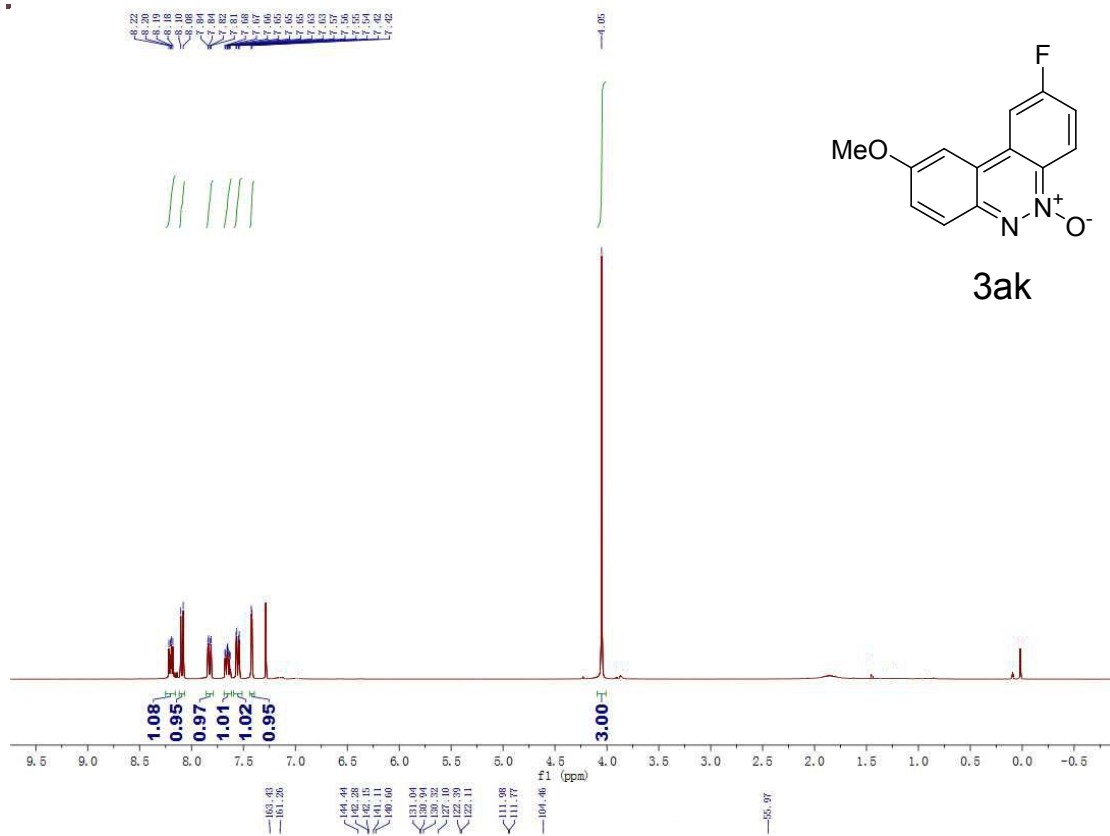


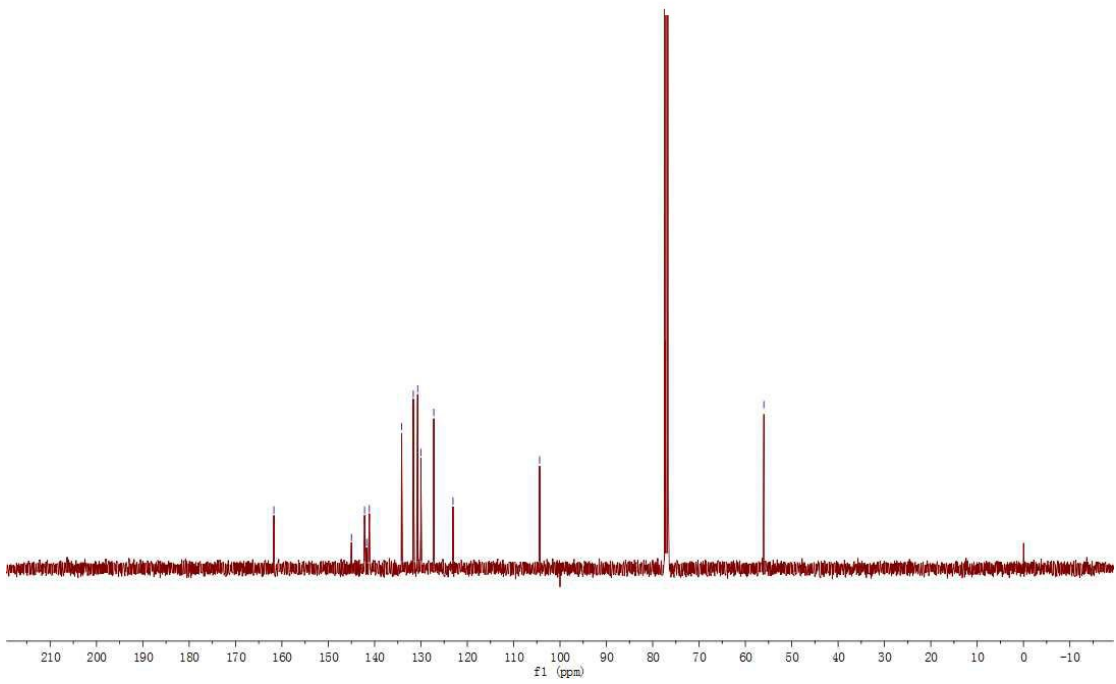
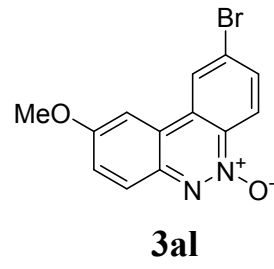
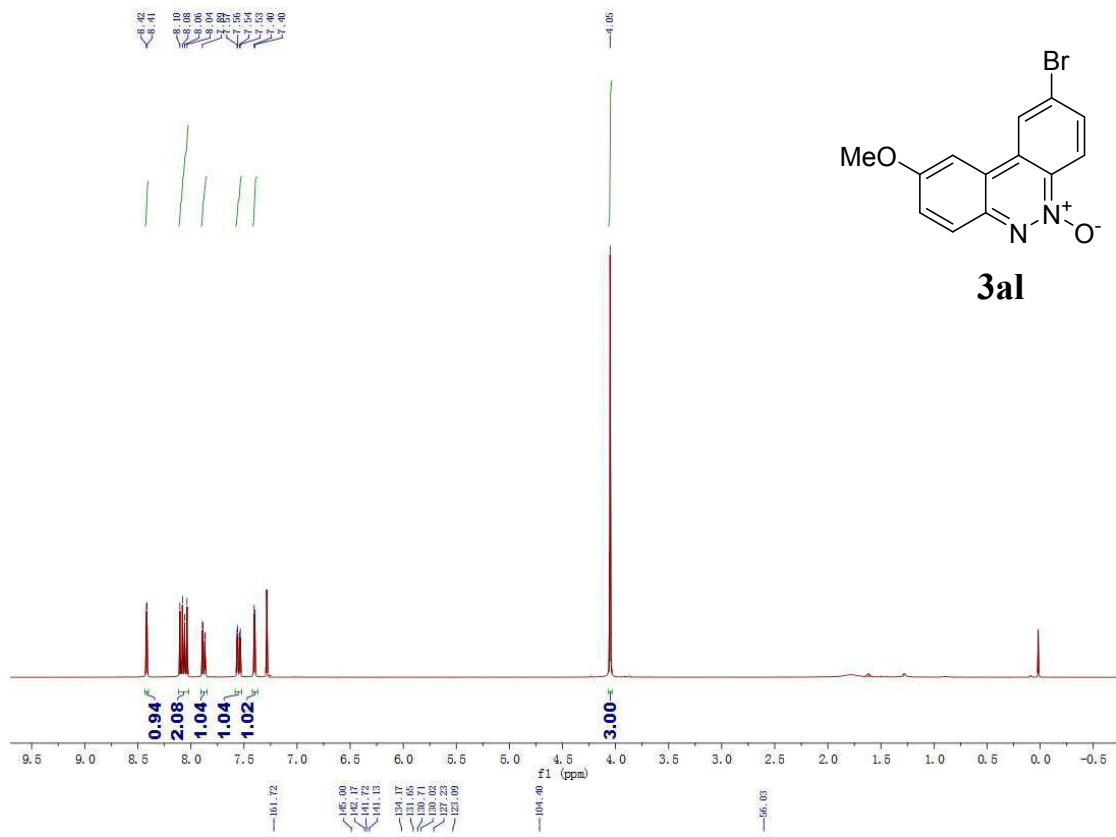


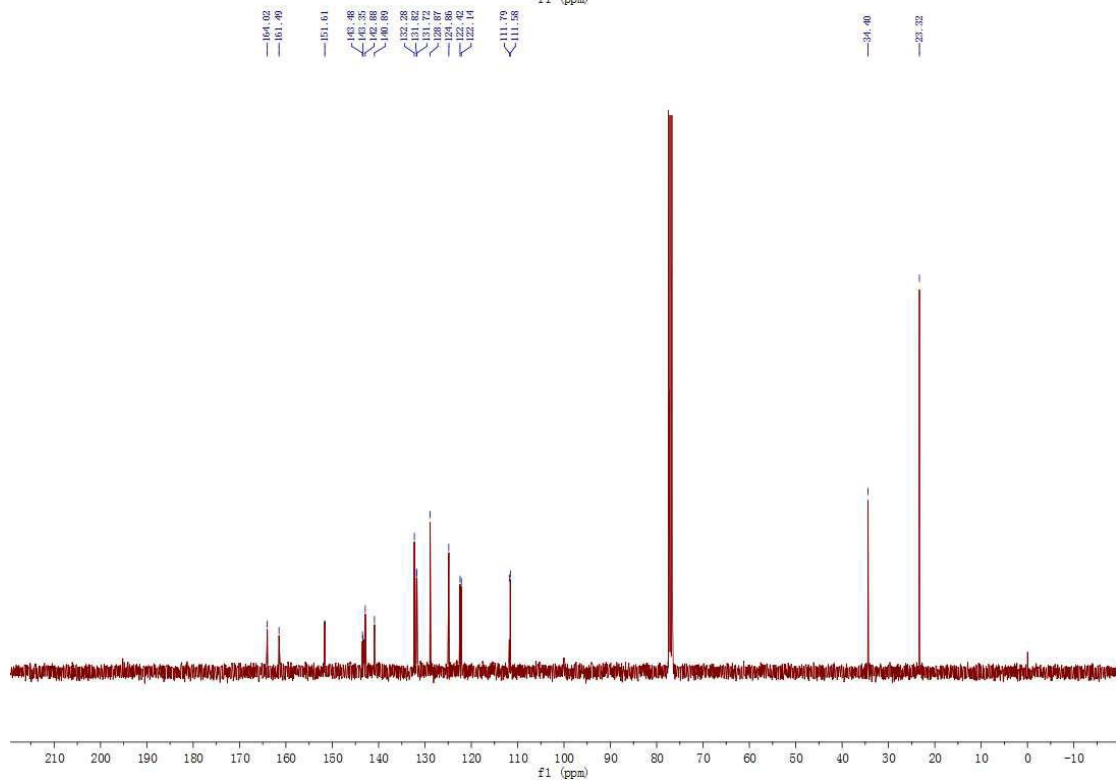
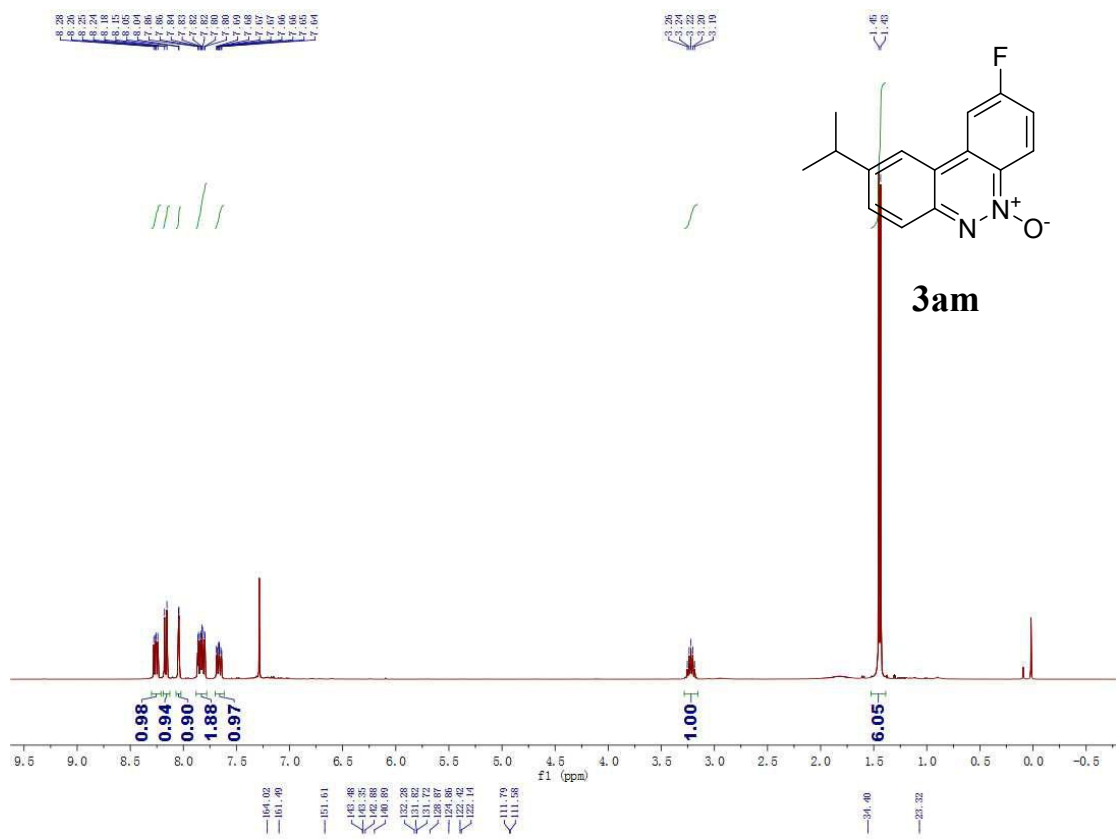


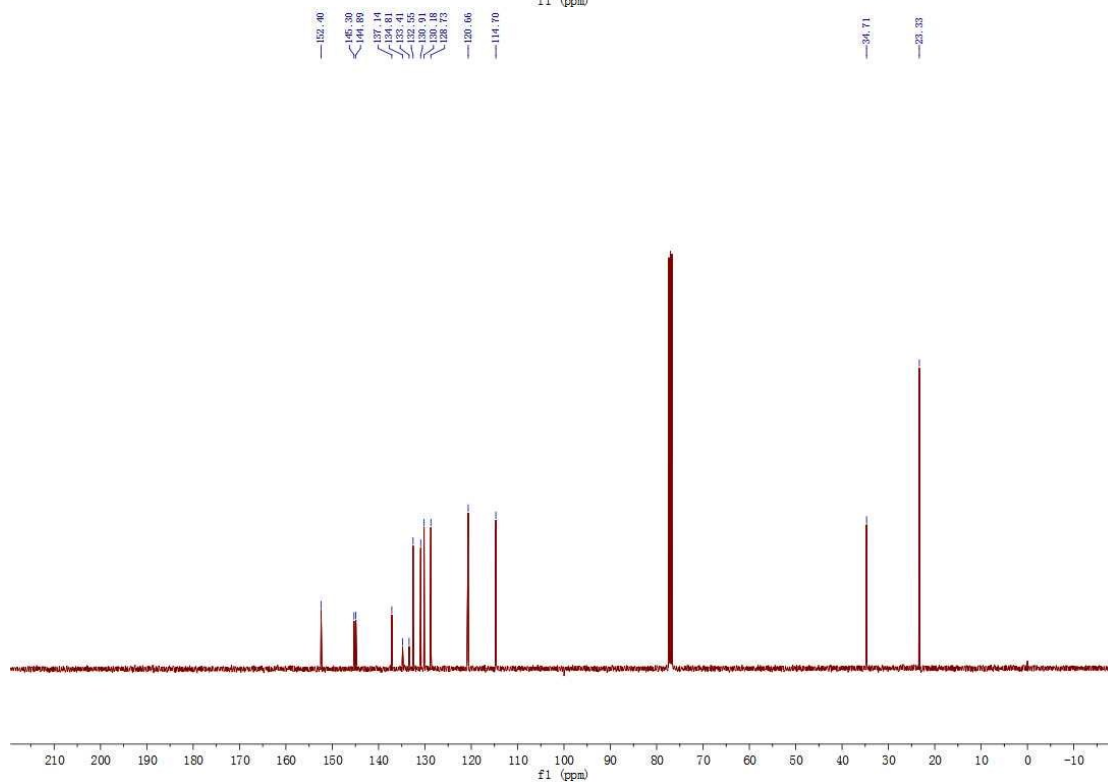
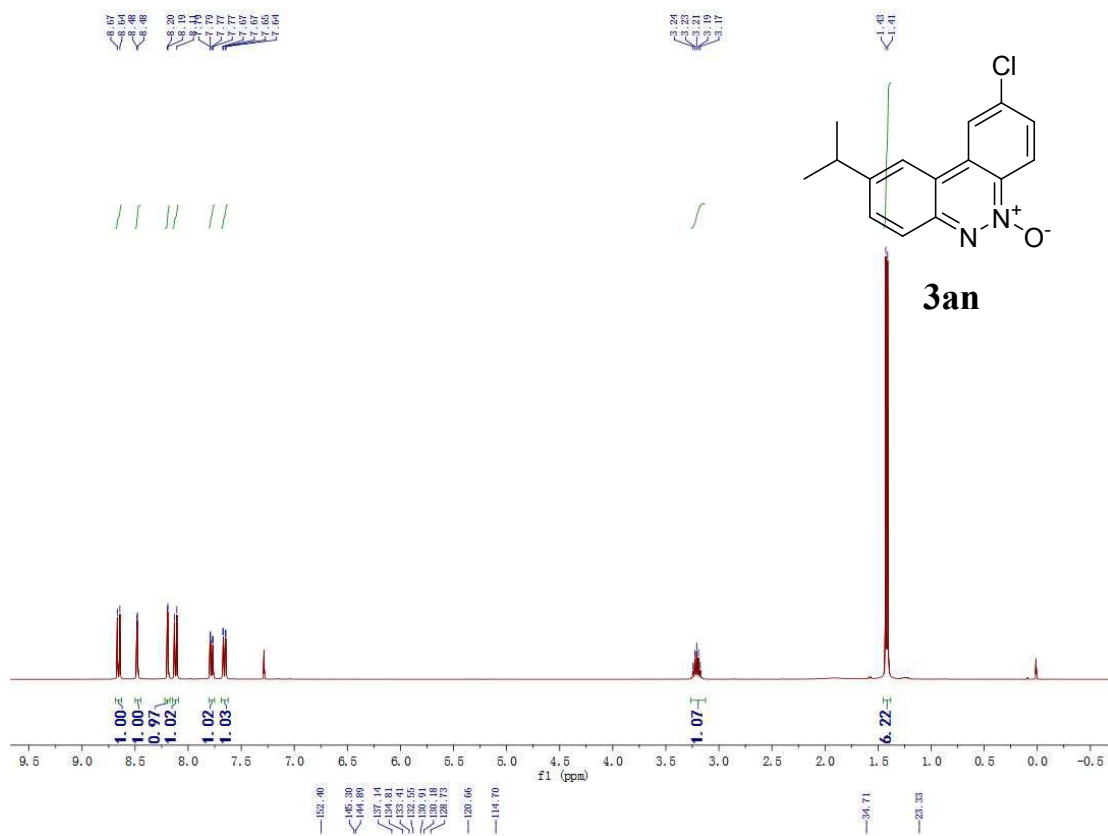


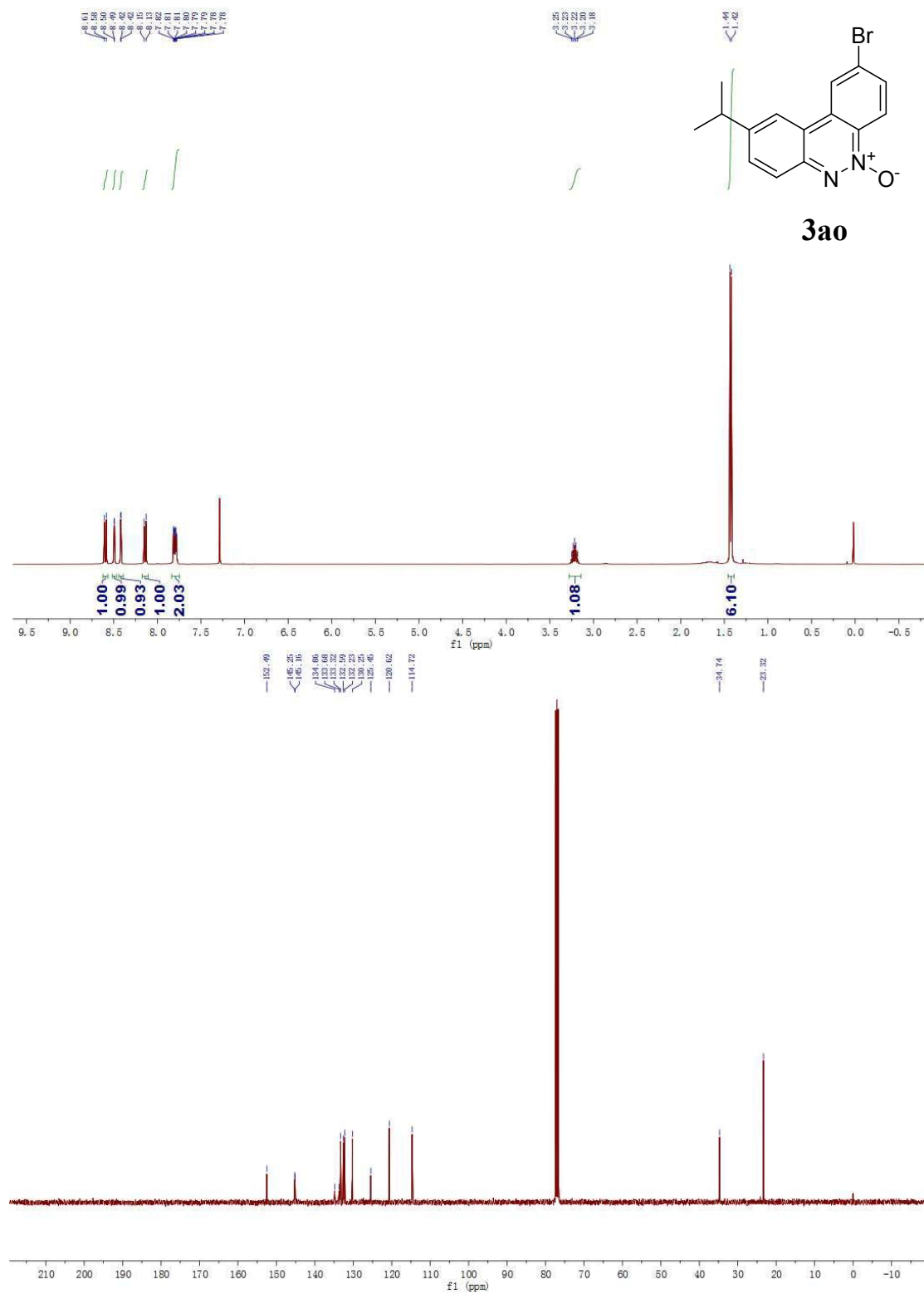


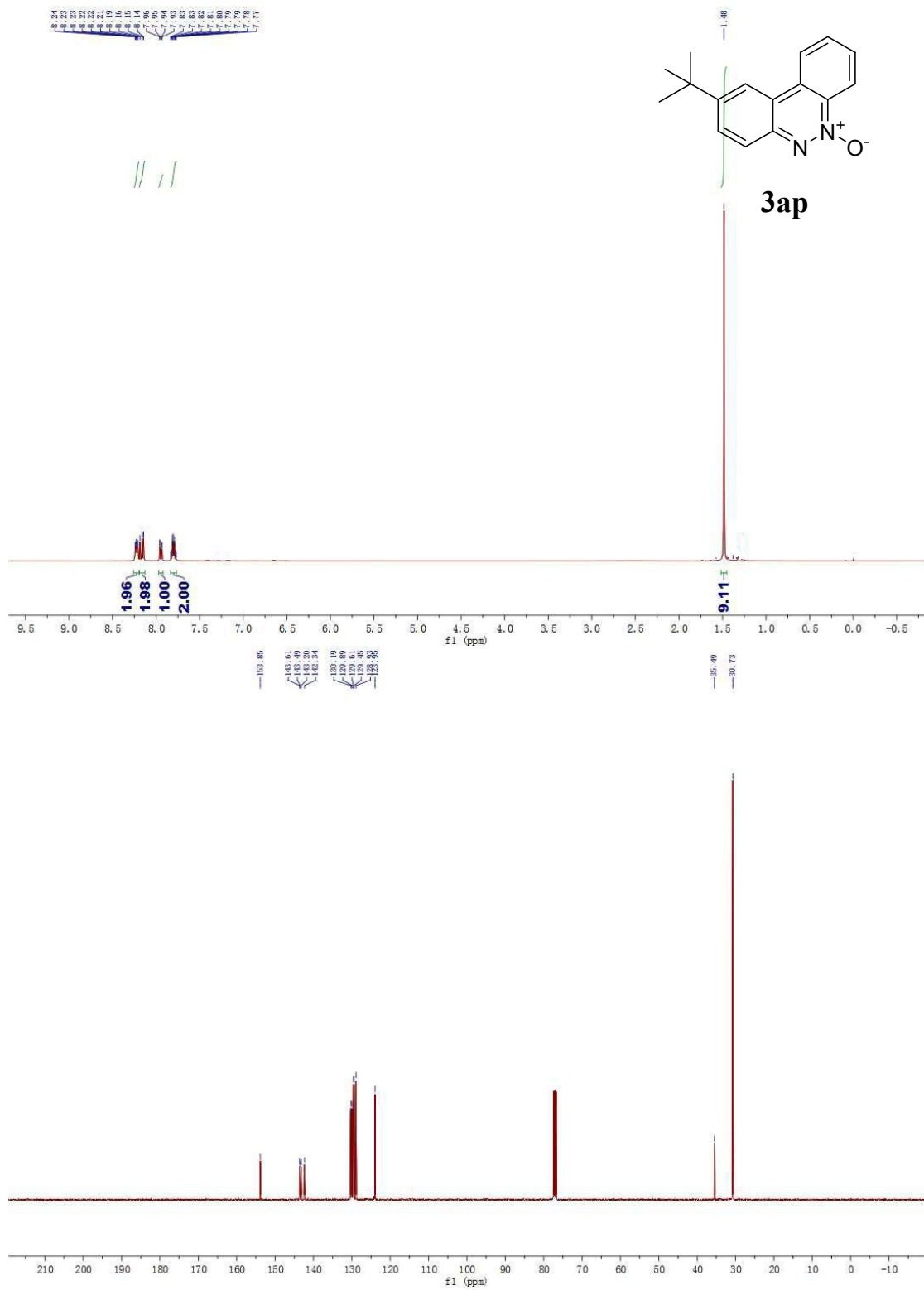


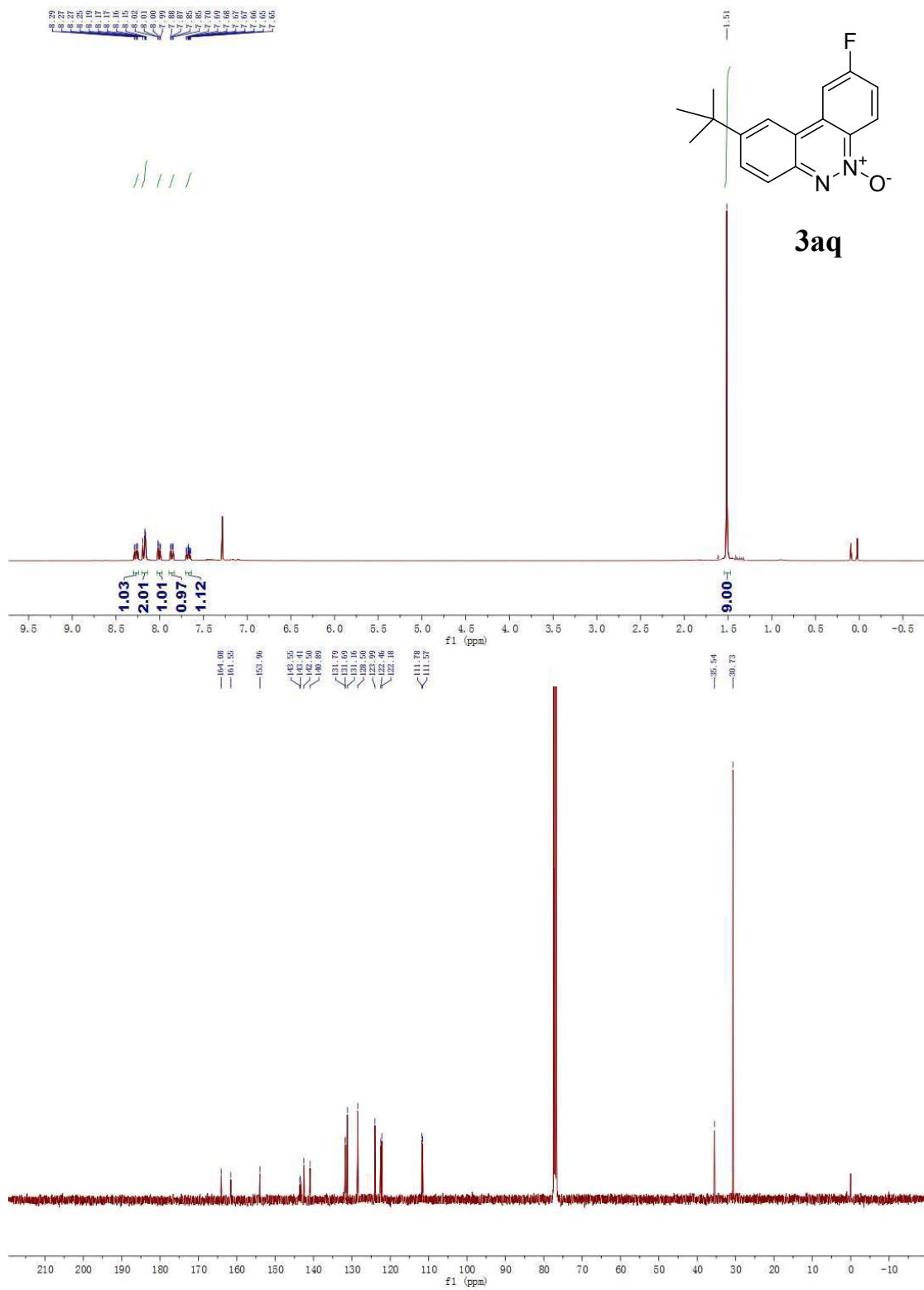


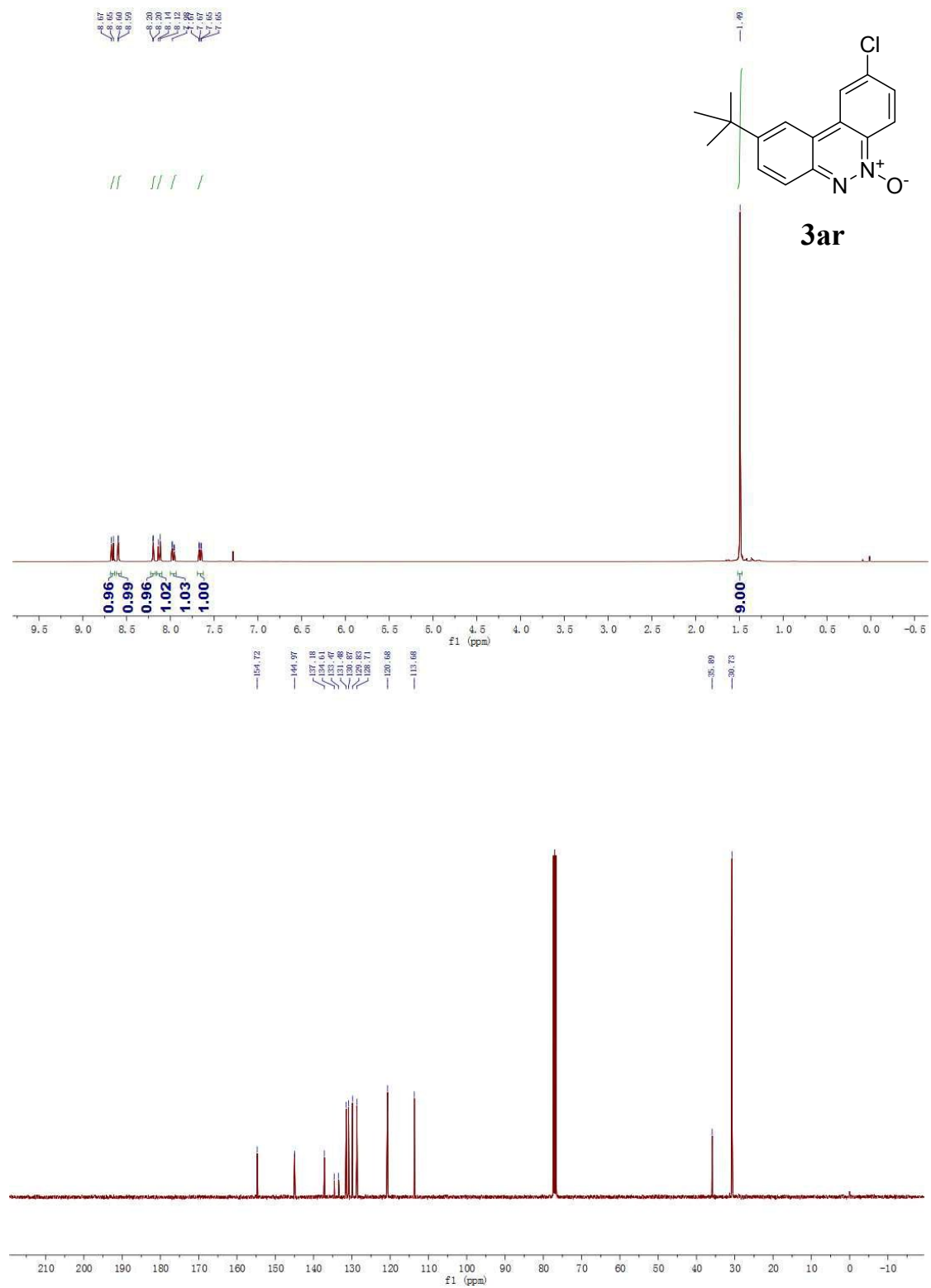


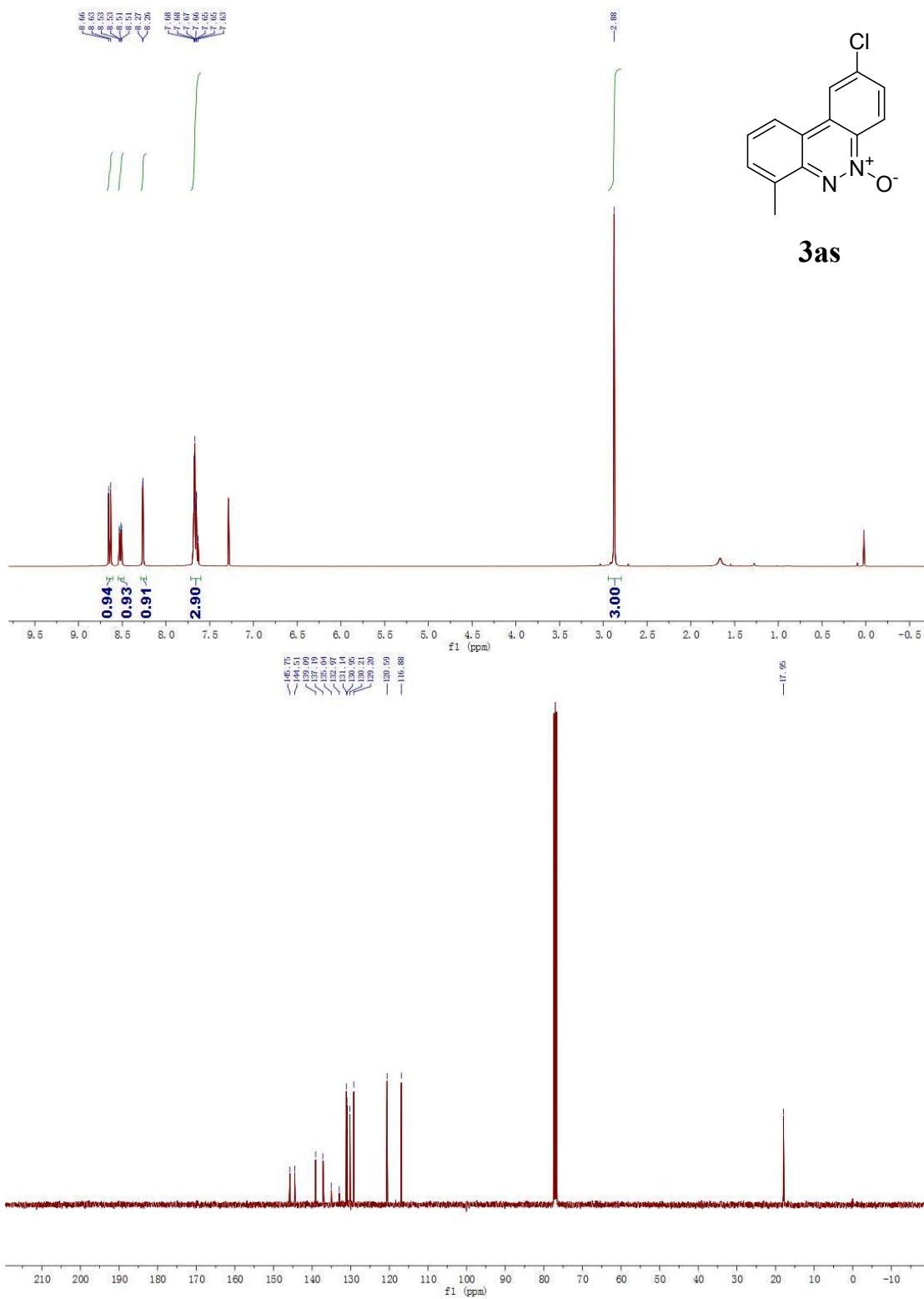


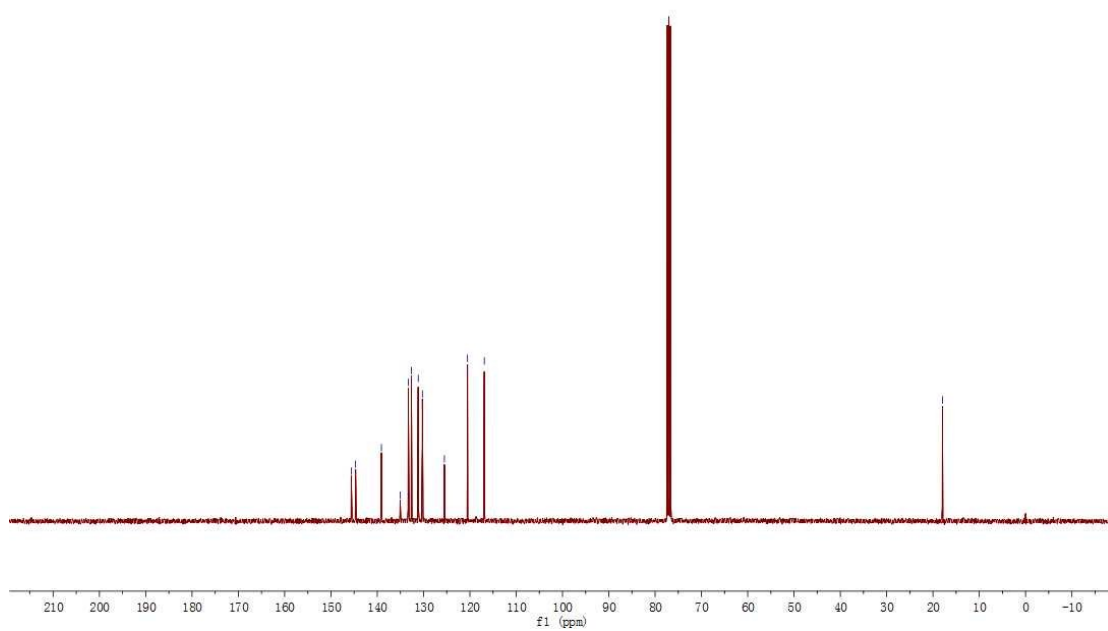
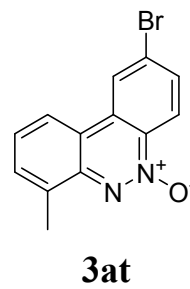
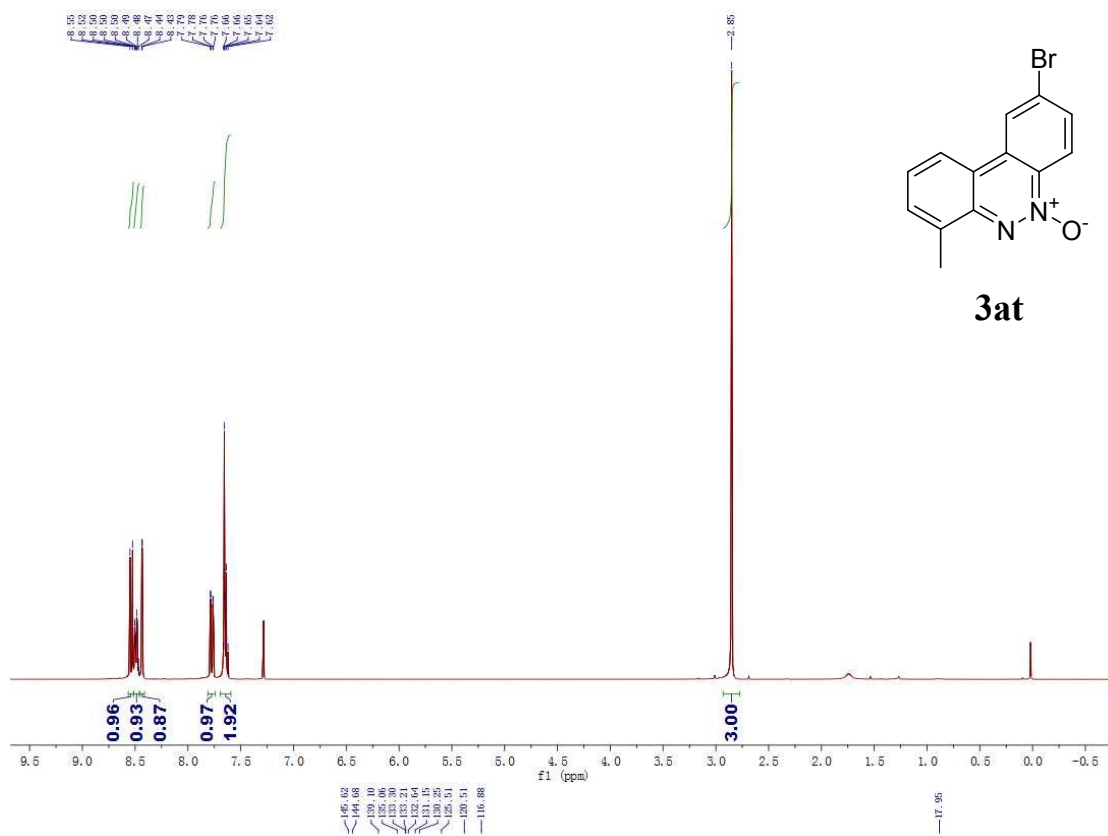


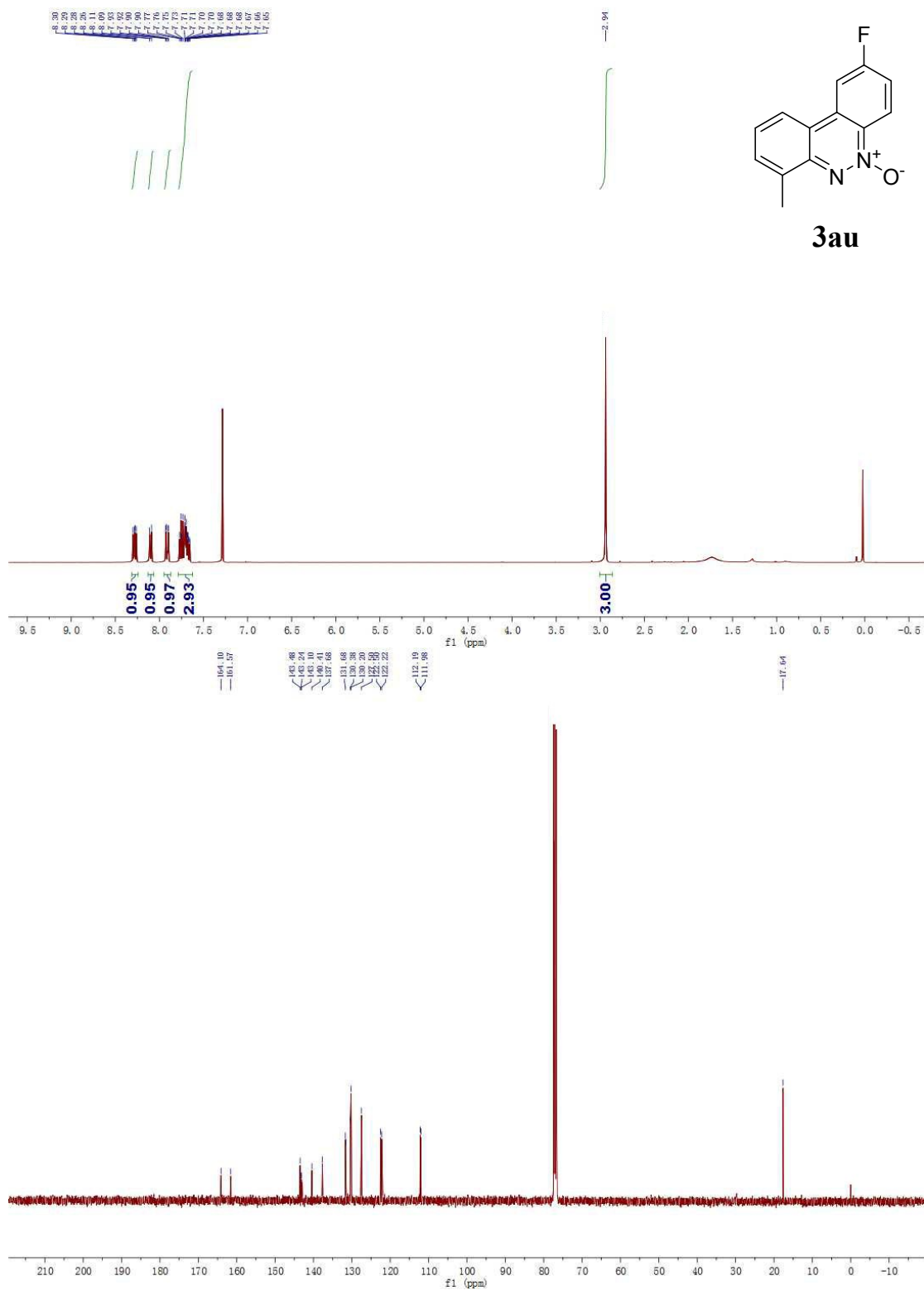


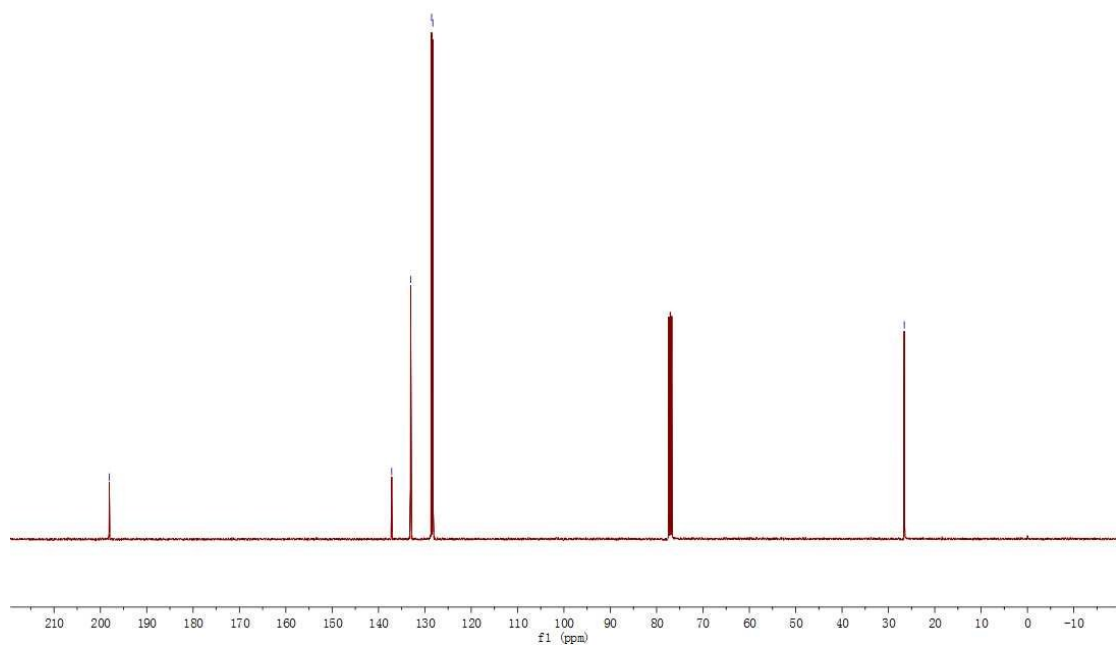
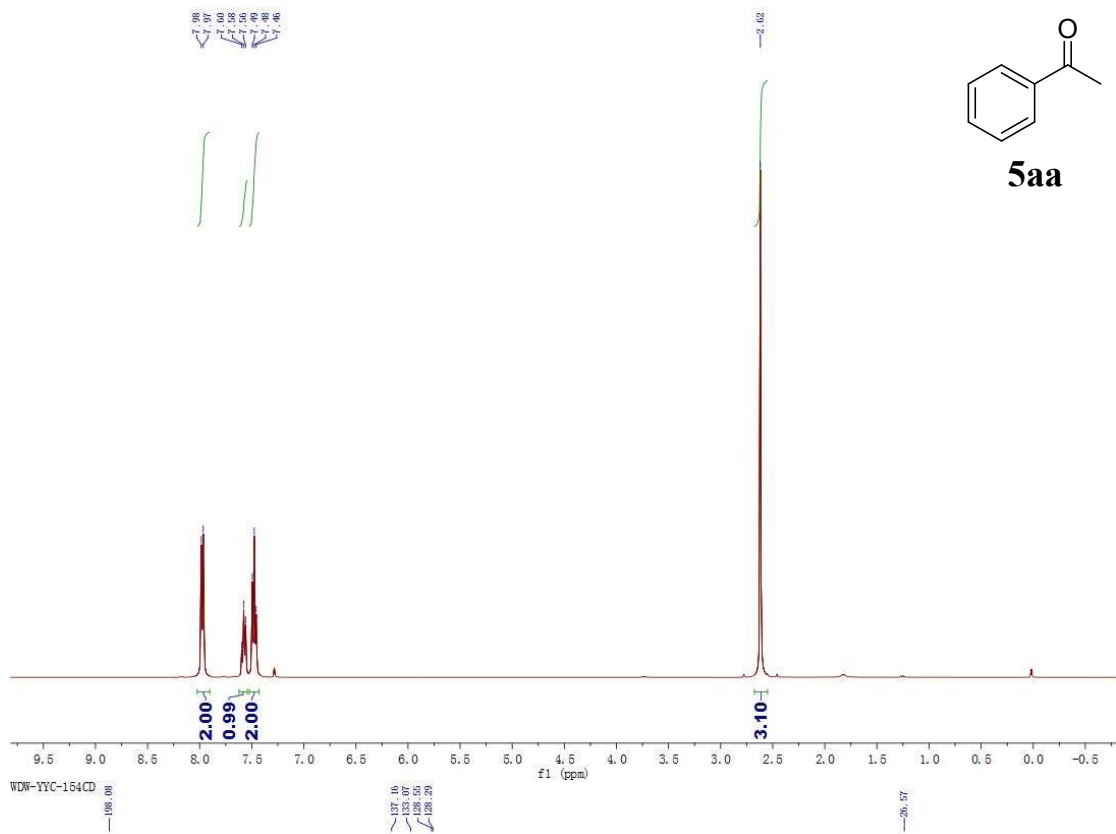


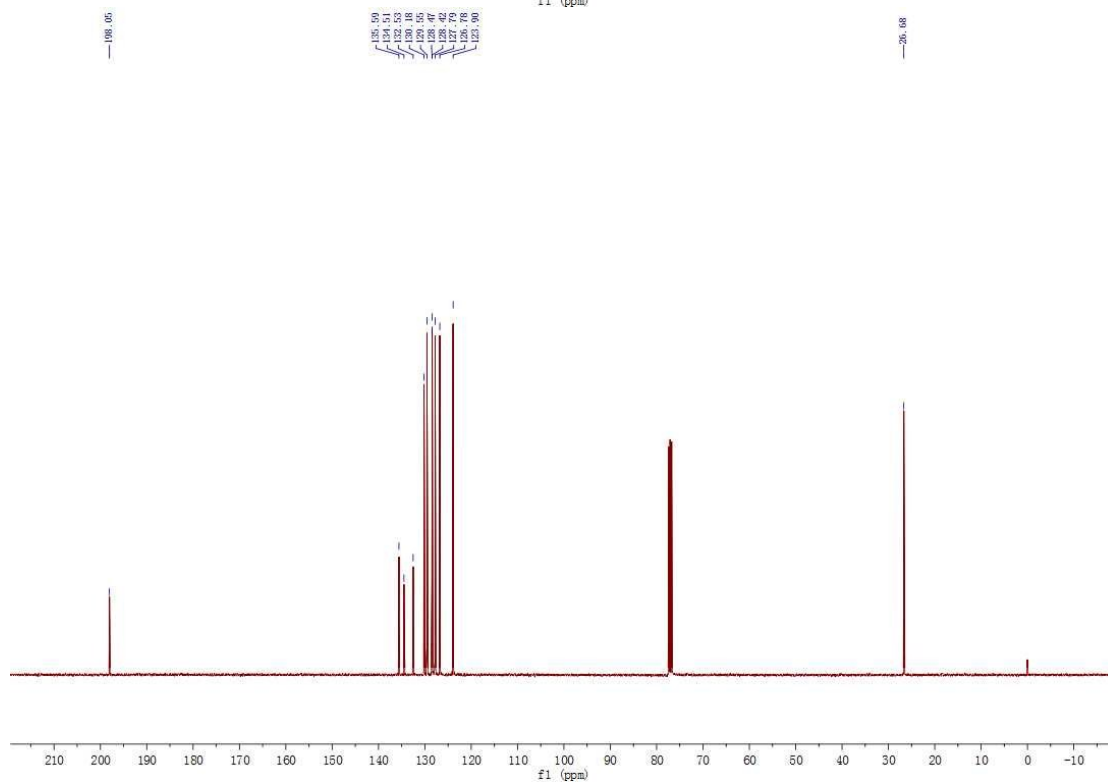
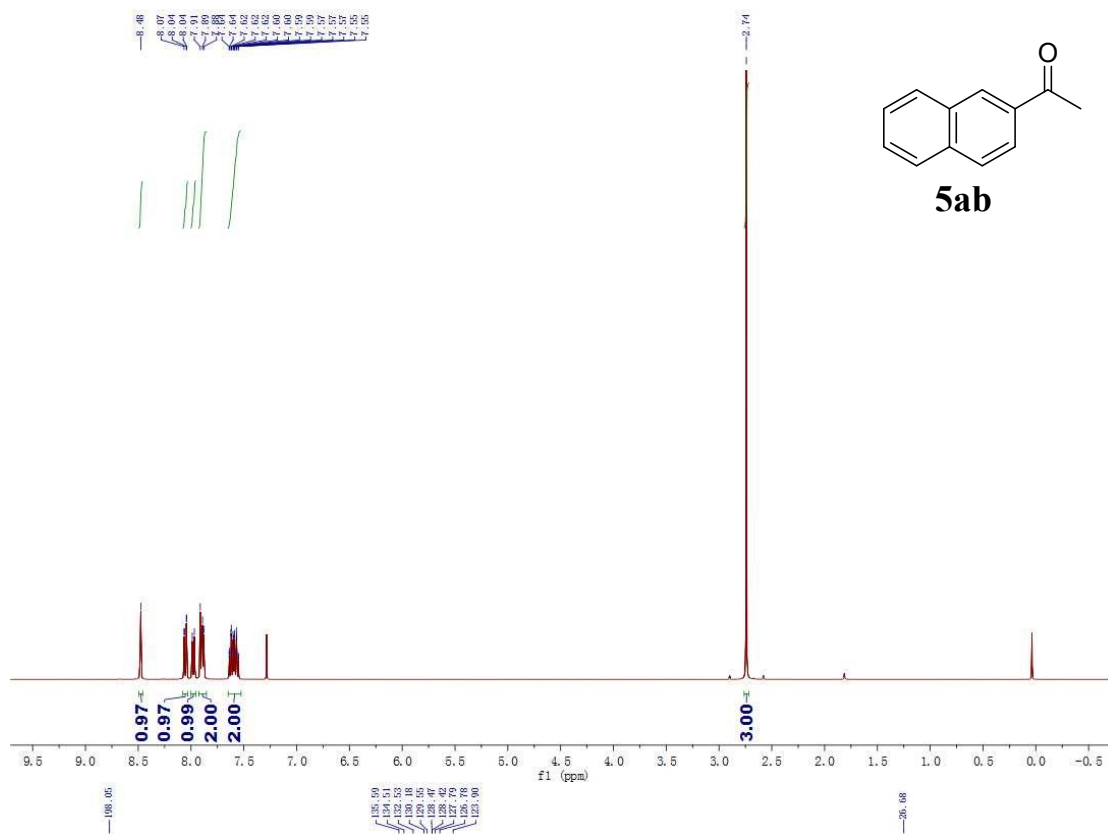


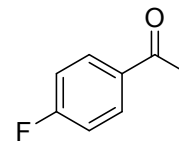
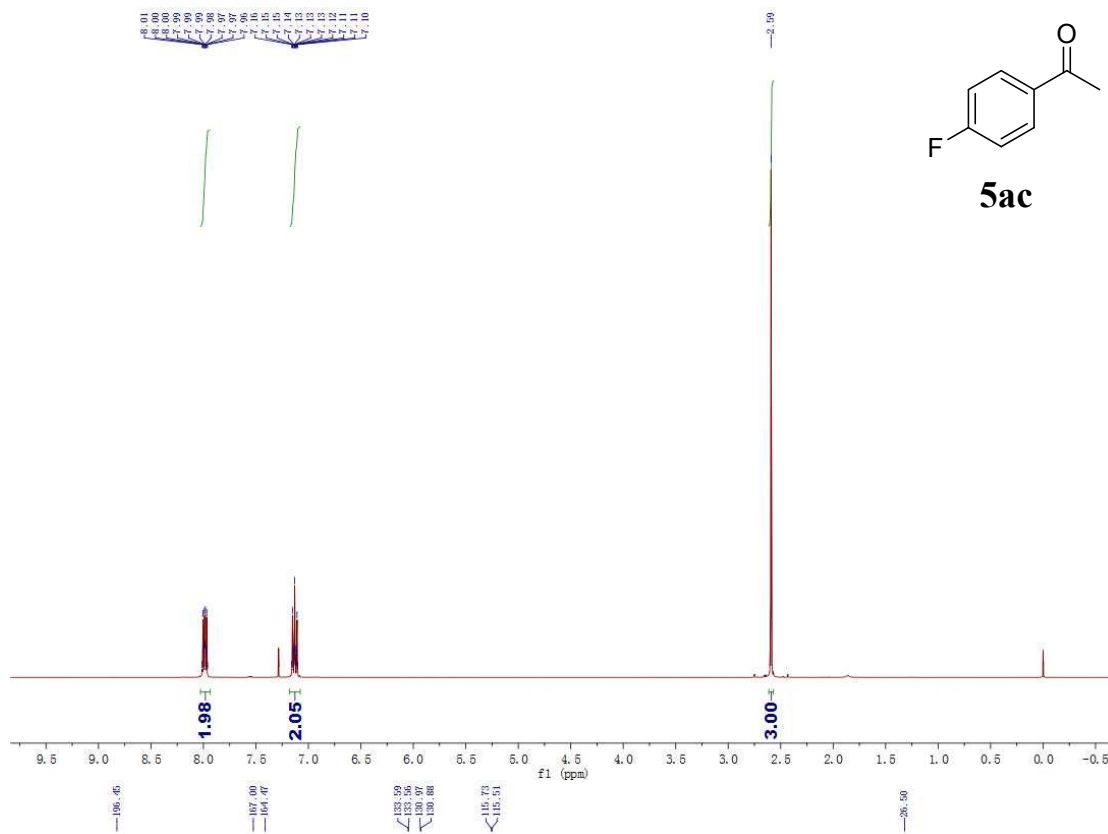












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