Supporting Information

Synthesis of benzo[*a*]carbazoles and indolo[2,3-a]carbazoles via photoinduced carbene-mediated C-H insertion reaction

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General methods

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 MHz spectrometer in $CDCl_3$ and D_6-DMSO. The chemical shifts in ^{1}H NMR spectra were determined with $(CH_3)_4Si$ as the internal standard (δ = 0.00 ppm). The chemical shifts in ^{13}C NMR spectra were determined based on the chemical shift of $CDCl_3$ (δ = 77.00 ppm) and D_6-DMSO (δ = 39.00 ppm). The spin-spin coupling constants (*J*) in ^{1}H NMR spectra are given in Hertz. The EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI or a Bruker micrOTOF QII by ESI. The X-ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. Melting points were measured on an XT-4 melting point apparatus and were uncorrected. Flash column chromatography was carried out with silica gel (200-300 mesh). All reagents were purchased from commercial suppliers and used without further purification. All solvents were dried and redistilled before use. Compounds **1** and **2** were prepared according to the reported procedure.[1]

General Procedure for the photoreaction of 1 and 2

To a 25 mL flame dried Pyrex flask was added compound **1** or **2** (0.1 mmol) dissolved in 20 mL anhydrous acetone. The mixture was bubbled with argon for half an hour and then sealed and irradiated at $\lambda \geq 300$ nm (through pyrex with a medium-pressure Hg lamp (500 W) at ambient temperature). After the reaction complete as monitored by TLC, the solvent was removed under reduced pressure and the product (s) was separated by silica gel column chromatography (eluted with hexane/acetone) to afford products **3** or **4** and **7**.

Synthesis of 9, 10 and 12

2-2'-Bi-1*H*-indole (C)[2] KOt-Bu (56 g, 500 mmol) was added at room temperature to a slurry of oxalyl-otoluidide (B) (13.8 g, 100 mmol) in t-BuOH (100 ml) in a 250 ml 3-neck round bottom flask equipped with a distillation neck, thermometer and a stopcock. The mixture was slowly heated to 225 ^{0}C under a slow stream of nitrogen until all the solvent was distilled off. The temperature was then carefully increased with concomitant gas evolution until the solid cake completely melted at 270 ^{0}C to give a brown viscous liquid. The temperature was kept at 270 ^{0}C for 15 min and then carefully raised to 300 ^{0}C with vigorous gas evolution. Then the mixture was cooled to rt. Water (100 ml) was added and stirred to a homogenous slurry. The mixture was filtered and washed with water. The solid was recrystallized to give a gray solid (6.96 g, 60 %). mp 296–298 ^{o}C: ^{1}H NMR (400 MHz, DMSO): δ 6.96 (s, 2H), 7.01 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 11.81 (s, 2H); ^{13}C NMR (100 MHz, DMSO): δ 97.89, 110.62, 118.84, 119.45, 121.07, 127.96, 130.99, 136.43.

β-oxo-[2,2'-Bi-1*H*-indole]-3-propanenitrile (D).[3] A solution of the cyanoacetic acid (183 mg, 2.16 mmol) in acetic anhydride (10 mL) was heated at 85 °C for 10 min. then **C** (500 mg, 2.16 mmol) was added to the reaction mixture and heating was continued under reflux for further 60 min. The reaction mixture was left to cool and then poured onto cooled water. The solid product so formed was collected by filtration without further purify to give **D** (523 mg, 81 %). yellow solid, mp 261–263 ^{o}C; ^{1}H NMR (300 MHz, DMSO): δ 4.53 (s, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.22–7.35 (m, 3H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 7.2 Hz, 1H), 12.12 (s, 1H), 12.62 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 32.17, 104.17, 110.98, 111.58, 111.71, 115.59, 119.62, 120.23, 120.67, 121.96, 122.72, 123.17, 125.75, 127.05, 127.55, 135.45, 136.00, 137.18, 184.32; ESI-HRMS: m/z Calcd for $C_{19}H_{13}N3O$+H: 300.1137, found 300.1131.

α-diazo-β-oxo-[2,2'-Bi-1*H*-indole]-3-propanenitrile (E).[1] In a flame dried flask containing a solution of **D** (300.11 mg, 1.00 mmol) in 10 mL acetonitrile was added NEt_3 (111.31 mg, 1.1 mmol). After vigorous stirring for 5 minutes, tosyl azide (216.70 mg, 1.1 mmol) was added, and the reaction was allowed to stir for 3 hours. After complete disappearance of starting material, mixture was concentrated in vacuo, followed by flash column chromatography (eluted with hexane/acetone) to furnish **E** as a yellow solid (130.44 mg, 40 %).

1-methyl-2-2'-Bi-1*H*-indole (F) and 1-1'-dimethyl-2-2'-Bi-1*H*-indole (H). To a solution of **C** (1.00 g, 4.31 mmol) in 50 ml acetone was added KOH (242 mg, 4.31 mmol) at 0 ^{0}C. After 15 min, CH_3I (0.612 g, 4.31 mmol) was slowly added to the mixture at 0 ^{0}C. After completion of the reaction as monitored by TLC, the mixture was poured into 100 ml ice-water to give a solid. The solid was collected by filtration and purified by flash column chromatography (eluted with hexane/acetone) to afford products **F** and **H**. **F** (0.318 g, 30 %): white solid, mp 175–177 ^{o}C; ^{1}H NMR (400 MHz, DMSO): δ 3.97 (s,3H), 6.86 (s, 1H), 6.86 (s, 1H), 6.91–7.15 (m, 2H),

7.17–7.23 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 11.55 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 30.99, 100.33, 100.68, 109.45, 110.66, 118.91, 119.19, 119.60, 119.68, 121.19, 121.42, 126.68,127.95, 129.16, 132.61, 136.16, 137.70. **H** (0.392 g, 35 %) white solid, mp 130–132 ^{o}C; ^{1}H NMR (400 MHz, DMSO): δ 3.72 (s, 6H), 6.73 (s, 2H), 7.11 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ 31.27, 104.23, 110.72, 120.21, 120.83, 122.43, 127.61, 131.60, 138.12.

1-methyl-β-oxo-[2,2'-Bi-1*H*-indole]-3-propanenitrile(J). A solution of the cyanoacetic acid (104 mg, 1.22 mmol) in acetic anhydride (10 mL) was heated at 85 °C for 10 min. Then **F** (300 mg, 1.22 mmol) was added to the reaction mixture and the heating was continued under reflux for further 60 min. The reaction mixture was left to cool and poured onto cooled water. The solid product so formed was collected by filtration without further purify to give product **J** (286 mg, 75 %). yellow solid, mp 235–237 ^{o}C; ^{1}H NMR (400 MHz, DMSO): δ 3.681 (s, 3H), 3.76 (s, 2H), 6.94 (s, 1H), 7.14 (t, *J* = 7.6 Hz, 1H),7.25 (t, *J* = 7.6 Hz, 1H), 7.35–7.43 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 11.76 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 29.84, 30.77, 105.99, 111.43, 113.43, 115.24, 119.48, 120.38, 120.93, 122.39, 122.68, 123.51, 124.66, 125.29, 127.02, 136.39, 138.63, 182.76; ESI-HRMS: m/z Calcd for $C_{20}H_{15}N3O$+H: 314.1293, found 314.1288.

α-diazo-1-methyl-β-oxo-[2,2'-Bi-1*H*-indole]-3-propanenitrile(G).[1] In a flame dried flask containing a solution of **J** (200.00 mg, 0.64 mmol) in 10 mL acetonitrile was added NEt_3 (77.95 mg, 0.70 mmol). After vigorous stirring for 5 minutes, tosyl azide (151.69 mg, 0.70 mmol) was added, and the reaction was allowed to stir for 3 hours. After complete disappearance of starting material, mixture was concentrated in vacuo, followed by flash column chromatography (eluted with hexane/acetone) to furnish **G** as a yellow solid (102.31 mg, 47%).

1-1'-dimethyl-β-oxo-[2,2'-Bi-1*H*-indole]-3-propanenitrile(K). A solution of the cyanoacetic acid (98 mg, 1.15 mmol) in acetic anhydride (10 mL) was heated at 85 °C for 10 min. then **H** (300 mg,1.15 mmol) was added to the reaction mixture and the heating was continued under reflux for further 60 min. The reaction mixture was left to cool and poured onto cooled water. The solid product so formed was collected by filtration without further purify to give product **K** (315.88 mg,84 %). yellow solid, mp 210–212 ^{o}C; ^{1}H NMR (400 MHz, DMSO): δ 3.58 (s, 6H), 3.64 (d, *J* = 19.2 Hz, 1H), 3.84 (d, *J* = 19.2 Hz, 1H), 6.91 (s, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.37–7.45 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 6.4 Hz, 2H), 8.32 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 30.00, 30.28, 30.48, 105.21, 110.19, 110.75, 114.35, 115.18, 119.61, 120.49, 121.12, 122.26, 122.73, 123.58, 125.14, 126.38, 127.18, 136.37, 136.94, 137.20; ESI-HRMS: m/z Calcd for $C_{21}H_{17}N3Or$+H: 328.1450, found 328.1444.

α-diazo-1-1'-dimethyl-β-oxo-[2,2'-Bi-1*H*-indole]-3-propanenitrile (I).[1] In a flame dried flask containing a solution of **K** (200.00 mg, 0.61 mmol) in 10 mL acetonitrile was added NEt_3 (67.84 mg, 0.67 mmol). After vigorous stirring for 5 minutes, tosyl

azide (132.19 mg, 0.67 mmol) was added, and the reaction was allowed to stir for 3 hours. After complete disappearance of starting material, mixture was concentrated in vacuo, followed by flash column chromatography (eluted with hexane/acetone) to furnish **I** as a yellow solid (97.7 mg, 45%).

Compounds **9**, **10** and **12** were prepared from E, F and H following the same procedure as that for **4**.

Spectroscopic data for the products

Ethyl 6-hydroxy-11-methyl-11-*H*-benzo[*a*]carbazole-carboxylate (3a). White solid, mp 114–116 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (t, *J* = 7.2 Hz, 3H), 4.31 (s, 3H), 4.57 (q, *J* = 7.2 Hz, 2H), 7.35–7.43 (m, 2H), 7.46–7.51 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 2H), 9.01 (d, *J* = 9.0 Hz, 1H),13.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.43, 34.17, 61.37, 97.53, 108.85, 109.86, 118.85, 121.06, 122.0, 122.58, 122.63, 123.06, 124.66, 126.51, 132.27 (2C), 140.22, 140.57, 163.06, 172.71; FT-IR (KBr, cm^{-1}): 3441, 2925, 1631, 1266, 740; ESI-HRMS: m/z Calcd for $C_{20}H_{17}NO_3$+H: 320.1278, found 320.1276.

Ethyl 8-chloro-6-hydroxy-11-methyl-11-*H*-benzo[*a*]carbazole-carboxylate (3b). White solid, mp 180–182 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (t, *J* = 7.2 Hz, 3H), 4.27 (s, 1H), 4.56 (q, *J* = 7.2 Hz, 2H), 7.36–7.45 (m, 3H), 7.53 (t, *J* = 7.5 Hz, 1H), 8.47 (s, 1H), 8.50 (d, *J* = 8.1 Hz, 1H), 8.98 (d, 9.0 Hz, 1H), 13.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14,41, 34.28, 61.48, 97.60, 108.96, 109.76, 118.59, 122.31, 122.47, 122.63, 123.34, 124.67, 126.43, 126.48, 126.81, 132.33, 138.71, 140.50, 162.61, 172.53; FT-IR (KBr, cm^{-1}): 3441, 2980, 1631, 1266, 741; ESI-HRMS: m/z Calcd for $C_{20}H_{16}NO_3Cl$+H: 341.0821, found 341.0824.

Ethyl 6-hydroxy-8,11-dimethyl-11-*H*-benzo[*a*]carbazole-carboxylate (3c). Colorless solid; mp 128–130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (t, *J* = 7.2 Hz, 3H), 2.58 (s, 1H), 4.26 (s, 3H), 4.58 (q, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.36-7.43 (m, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 8.33 (s, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 9.00 (d, *J* = 8.8 Hz, 1H), 13.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.47, 21.49, 34.37, 61.39, 97.42, 108.59, 109.69, 119.06, 122.54, 122.64, 122.83, 122.92, 126.18, 126.52, 126.60, 130.67, 132.31, 138.08, 140.50, 163.24, 172.82; FT-IR (KBr, cm^{-1}): 3303, 2925, 1631, 1266, 735; ESI-HRMS: m/z Calcd for $C_{21}H_{19}NO_3$+H: 334.1443, found 334.1445.

Ethyl 3-bromo-6-hydroxy-11-methyl-11-*H*-benzo[*a*]carbazole-carboxylate (3d). Yellow solid, mp 210–212 ^{o}C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 1.46 (t, *J* = 6.8 Hz, 3H), 4.39 (s, 1H), 4.53 (q, *J* = 6.8 Hz, 2H), 7.36 (t, *J* =7.0 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.70 (d, *J* = 8.8 Hz, 1H), 9.10 (s, 1H), 12.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.10, 34.09, 61.59, 96.66, 108.91, 117.16, 121.22, 122.27, 122.90, 123.42, 123.79, 124.93, 125.41, 128.94, 129.45, 133.38, 134.10, 140.48, 163.40, 172.09; FT-IR (KBr, cm^{-1}): 3442, 2920, 1631, 1266, 741; ESI-HRMS: m/z Calcd for $C_{20}H_{16}NO_3Br$+H: 398.0392, found 398.0394.

Ethyl 6-hydroxy-3,11-dimethyl-11-*H*-benzo[*a*]carbazole-carboxylate (3e)

White solid, mp 118–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56 (t, *J* = 7.2 Hz, 3H), 2.54 (s, 3H), 4.20 (s, 3H), 4.56 (q, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* =7.2 Hz, 1H), 7.42–7.49 (m, 2H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.50 (d, *J* = 7.6 Hz, 1H), 8.79 (s, 1H), 13.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.36, 22.28, 34.11, 61.30, 97.19, 108.78, 109.32, 116.82, 121.02, 122.43, 122.79, 123.95, 124.19, 124.46, 126.37, 132.60, 136.27, 140.50, 140.54, 163.12, 172.71; FT-IR (KBr, cm^{-1}): 3441, 2925, 1631, 1266, 735; ESI-HRMS: m/z Calcd for $C_{21}H_{19}NO_3$+H: 334.1443, found 334.1445.

Ethyl 6-hydroxy-3-methoxy-11-methyl-11-*H*-benzo[*a*]carbazole-carboxylate (3f).
Colorless solid; mp 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56 (t, *J* = 7.2 Hz, 3H), 3.96 (s, 3H), 4.30 (s, 3H), 4.57 (q, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 1H), 7.35 (td, *J* = 6.0Hz, 3.2Hz 1H), 7.45–7.51 (m, 2H), 8.47 (d, *J* = 9.2 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 2.4 Hz 1H), 13.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.43, 34.17, 55.03, 61.30, 97.03, 107.82, 108.55, 108.76, 112.98, 113.48, 121.11, 122.83, 122.91, 124.05, 124.35, 134.43, 140.54, 140.92, 158.27, 163.88, 172.83; FT-IR (KBr, cm^{-1}): 3440, 2980, 1631, 1266, 735; ESI-HRMS: m/z Calcd for $C_{21}H_{19}NO_4$+H: 350.1392, found 350.1394.

6-hydroxy-11-methyl-11*H*-benzo[*a*]carbazole-3-carbonitrile (4a).
White solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 4.40 (s, 3H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.50 (td, *J* =8.0Hz, 1.2 Hz, 1H), 7.56 (td, *J* = 8.0Hz, 1.2 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 33.54, 84.28, 109.57, 109.64, 117.01, 117.47, 120.36, 120.62, 121.60, 123.04, 123.44, 123.52, 124.53, 126.91, 131.98, 138.32, 139.68, 157.63; FT-IR (KBr, cm^{-1}): 3220, 2213, 1434, 754; ESI-HRMS: m/z Calcd for $C_{18}H_{12}N_2O$+H: 273.1028, found 273.1026.

8-chloro-6-hydroxy-11-methyl-11*H*-benzo[*a*]carbazole-3-carbonitrile (4b).
White solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 4.39 (s, 3H), 7.50 (dd, *J* = 8.8Hz, 2.2 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 11.90 (s, 1H); ^{13}C NMR (125 MHz, DMSO): δ 33.81, 84.42, 109.06, 111.37, 117.04, 117.23, 120.47, 121,71, 123.12, 123.46, 124.21, 124.59, 127.29, 129.69, 132.42, 138.14, 139.00, 158.12; FT-IR (KBr, cm^{-1}): 3220, 2213, 1434, 760; ESI-HRMS: m/z Calcd for $C_{18}H_{11}N_2OCl$+H: 307.0638, found 307.0637.

6-hydroxy-8,11-dimethyl-11*H*-benzo[*a*]carbazole-3-carbonitrile (4c).
White solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 2.50 (s, 3H), 4.35 (s, 3H), 7.31 (t, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.67 – 7.77 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 8,17 (s, 1H), 8.74 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 20.68, 33.57, 84.01, 109.30, 109.40, 117.27, 117.53, 120.81, 121.38, 123.02, 123.38, 123.50, 125.97, 126.85, 129.23, 131.98, 138.10, 138.38, 157.86; FT-IR (KBr, cm^{-1}): 3221, 2213 ,1434, 762; ESI-HRMS: m/z Calcd for $C_{19}H_{14}N_2O$+H: 287.1184, found 287.1187.

3-bromo-6-hydroxy-11-methyl-11*H*-benzo[*a*]carbazole-3-carbonitrile (4d).
White solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 4.39 (s, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz,

1H), 8.13 (s, 1H), 8.37 (d, *J* = 8.8 Hz, 1H), 8.73 (d, *J* = 8.8 Hz, 1H). 12.04 (s, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 33.44, 83.33, 109.71, 109.84, 116.09, 116.59, 120.43, 120.45, 120.63, 121.64, 124.86, 125.14, 125.29, 126.07, 133,53, 138.00, 139.72, 158.31; FT-IR (KBr, cm^{-1}): 3221, 2213, 1434, 754; ESI-HRMS: m/z Calcd for $C_{18}H_{11}N_2OBr$: 351.0133, found 351.0135.

6-hydroxy-3,11-dimethyl-11*H*-benzo[*a*]carbazole-3-carbonitrile (4e).

White solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 2.54 (s, 3H), 4.37 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.38 (dd, *J* = 8.8Hz, 1.6 Hz, 1H), 7.49 (dd, *J* = 8.0Hz, 1.2 Hz, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 7.6 Hz, 1H), 8.66 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 20.82, 33.45, 83.91, 109.10, 109.49, 115.46, 117.13, 120.28, 120.72, 121.47, 122.09, 122.93, 124.34, 125.21, 132.35, 136.57, 138.50, 139.60, 157.69; FT-IR (KBr, cm^{-1}): 3221, 2213, 1434, 754; ESI-HRMS: m/z Calcd for $C_{19}H_{14}N_2O$: 287.1184, found 287.1186.

6-hydroxy-3-methoxy-11-methyl-11*H*-benzo[*a*]carbazole-3-carbonitrile (4f).

White solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 3.95 (s, 3H), 4.36 (s, 3H), 7.19 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.70 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 33.32, 55.61, 84.79, 104.95, 109.13, 110.34, 112.89, 114.76, 118.19, 121.21, 121.79, 122.25, 125.05, 125.83, 135.29, 139.83, 140.49, 158.92, 159.13; FT-IR (KBr, cm^{-1}): 3220, 2213, 1434, 760; ESI-HRMS: m/z Calcd for $C_{19}H_{14}N_2O_2$+H: 303.1133, found 303.1131.

(5bE, 7*Z*, 9*Z*)-10a,11-dihydro-5-methyl-11-oxo-5*H*-azuleno[1,2-*b*] indole-10a-carbonitrile (7a)

Yellow solid, mp 296–298 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (s, 3H), 6.01 (d, *J* = 9.6 Hz, 1H), 6.47 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 6.77–6.83 (m, 3H), 7.31–7.37 (m, 2H), 7.41–7.45 (m, 1H), 7.94 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.68, 55.14, 110.43, 115.62, 119.73, 119.96, 121.22, 121.94, 122.33, 123.80, 124.97, 126.18, 130.30, 130.63, 133.13, 144.77, 156.16, 182.91; FT-IR (KBr, cm^{-1}): 2920, 2230, 1694, 734; ESI-HRMS: m/z Calcd for $C_{18}H_{12}N_2O$+H: 273.1028, found 273.1027.

(5bE, 7*Z*, 9*Z*)-2-chloro-10a,11-dihydro-5-methyl-11-oxo-5*H*-azuleno[1,2-*b*]indole- 10a-carbonitrile (7b)

White solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 4.02 (s, 1H), 5.95 (d, *J* = 9.6 Hz, 1H), 6.58 (dd, *J* = 9.6, 6.4 Hz, 1H), 6.83 (dd, *J* = 11.2Hz, 6.4 Hz, 1H), 6.91 (dd, *J* = 11.2Hz, 6.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.48 (dd, *J* = 8.8Hz, 6.0 Hz, 1H), 7.77 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 28.52, 54.17, 113.45, 115.40, 119.14, 119.55, 120.76, 121.86, 123.41, 125.42, 127.87, 129.14, 130.49, 130.59, 132.85, 142.82, 156.76, 181.67; FT-IR (KBr, cm^{-1}): 2925, 2231, 1693, 749; ESI-HRMS: m/z Calcd for $C_{18}H_{11}N_2OCl$+H: 307.0638, found 307.0636.

(5bE, 7*Z*, 9*Z*)-10a,11-dihydro-2,5-dimethyl-11-oxo-5*H*-azuleno[1,2-*b*] indole-10a-carbonitrile (7c)

Yellow solid, mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 3.93 (s, 3H), 6.01 (d, *J* = 9.6 Hz, 1H), 6.46 (dd, *J* = 9.6Hz, 5.6 Hz, 1H), 6.73–6.83 (m, 3H), 7.24 (d,

J = 6.8 Hz, 2H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.34, 29.69, 55.17, 110.02, 115.68, 119.64, 121.44, 121.83, 122.52, 125.04, 127.70, 130.30, 130.59, 133.00, 133.75, 137.72, 143.14, 155.96, 182.89; FT-IR (KBr, cm^{-1}): 2954, 2230, 1694, 748; ESI-HRMS: m/z Calcd for $C_{19}H_{14}N_2O$+H: 287.1184, found 287,1187.

(5bE, 7Z, 9Z)-8-bromo-10a,11-dihydro-5-methyl-11-oxo-5*H*-azuleno [1,2-*b*]indole-10a-carbonitrile (7d)

Yellow solid, mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97 (s, 3H), 5.94 (d, *J* = 10.0 Hz, 1H), 6.61 (m, 2H), 7,23 (d, *J* = 7.6 Hz, 1H), 7.34–7.39 (m, 2H), 7.43–7.48 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.38, 54.86, 110.51, 114.98, 118.59, 121.19, 122.09, 122.82, 124.05, 125.53, 126.56, 126.75, 129.72, 132.52, 134.63, 137.02, 163.17, 181.88; FT-IR (KBr, cm^{-1}): 2954, 2230, 1694, 734; ESI-HRMS: m/z Calcd for $C_{18}H_{11}N_2OBr$+H: 351.1133, found 351.1135.

(5bE, 7Z, 9Z)-10a,11-dihydro-5,8-dimethyl-11-oxo-5*H*-azuleno[1,2-*b*]indole- 10a-carbonitrile (7e)

Yellow solid, mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 3.94 (s, 3H), 5.96 (d, *J* = 10.4 Hz, 1H), 6.32 (d, *J* = 10.4 Hz, 1H), 6.59 (d, *J* = 6.8 Hz, 1H), 6.71 (d, *J* = 6.8 Hz, 1H), 7.30–7.35 (m, 2H), 7.39–7.43 (m, 1H), 7.93 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.10, 31.81, 54.73, 110.31, 115.94, 119.26, 120.04, 120.54, 121.29, 121.84, 123.68, 123.92, 125.90, 127.22, 133.95, 143.41, 144.67, 156.57, 183.03; FT-IR (KBr, cm^{-1}): 2925, 2230, 1693, 743; ESI-HRMS: m/z Calcd for $C_{19}H_{14}N_2O+H^+$: 287.1184, found 287.1186.

(5bE, 7Z, 9Z)-10a,11-dihydro-8-methoxy-5-methyl-11-oxo-5*H*-azuleno[1,2-*b*]indole-10a-carbonitrile (7f)

Yellow solid, mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H), 3.94 (s, 1H), 5.98 (d, *J* = 6.8 Hz, 1H), 6.11 (d, *J* = 10.4 Hz, 1H), 6.36 (dd, *J* = 10.4Hz, 6.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 7.29–7.34 (m, 2H), 7.38–7.41 (m, 1H), 7.92 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.65, 54.49, 55.31, 103.03, 110.19, 115.95, 116.89, 118.31, 119.72, 121.36, 121.68, 123.58, 125.62, 125.68, 129.32, 144.58, 157.31, 161.78, 182.51; FT-IR (KBr, cm^{-1}): 2925, 2230, 1693, 743; ESI-HRMS: m/z Calcd for $C_{19}H_{14}N_2O_2+H^+$: 303.1133, found 303.1134.

6-cyano-5-hydroxy-12-methylindolo[2,3-a]carbazole (9)

Yellow solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 4.34 (s, 1H), 7.26 (t, *J* = 6.8 Hz, 2H), 7.32- 7.53 (m, 2H), 7.70 (t, *J* = 8.0 Hz, 2H), 8.36 (d, *J* = 7.6 Hz, 1H), 8.45 (d, *J* = 7.6 Hz, 1H), 10.71 (s, 1H), 12.00 (s, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 32.22, 82.17, 110.39, 112.10, 112.55, 118.00, 118.95, 119.55, 120.04, 120.68, 121.47, 122.44, 122.55, 122.61, 125.49, 125.94, 139.84, 144.03, 152.94; FT-IR (KBr, cm^{-1}): 3346, 2206; ESI-HRMS: m/z Calcd for C20H13N3O+H^+: 312.1059, found 312.1050.

6-cyano-5-hydroxy-11,12-dihydroindolo[2,3-a]carbazole (10)

Yellow solid, mp > 300 °C; ^{1}H NMR (400 MHz, D_6-DMSO): δ 7.24–7.30 (m, 2H), 7.42–7.47 (m, 2H), 7.72 (dd, *J* = 8.0Hz, 4.8 Hz, 2H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 10.63 (s, 1H), 11.21 (s, 1H), 11.60 (s, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 80.92, 110.58, 111.15, 111.72, 117.32, 118.04, 118.64, 118.98, 119.63, 119.83, 121.16, 121.44, 122.14, 124.37, 124.81, 129.10, 138.16, 138.98, 151.92; FT-

IR (KBr, cm^{-1}): 3345, 2206; ESI-HRMS: m/z Calcd for C19H11N3O+H^+: 298.0902, found 298.0906.

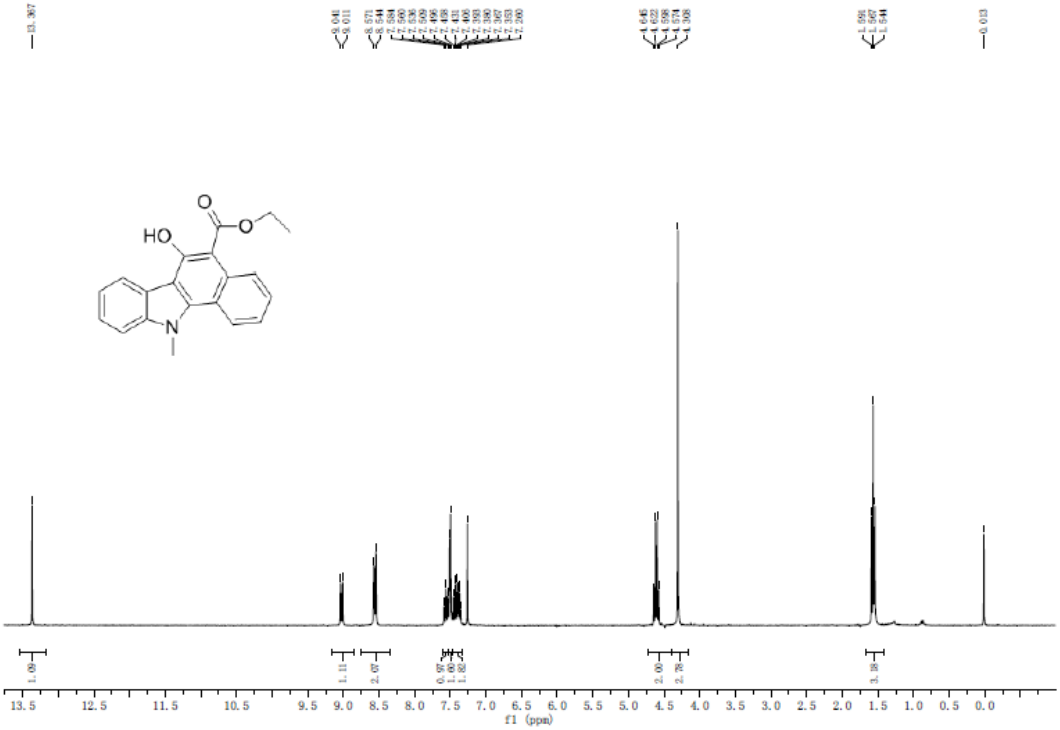
6-cyano-5-hydroxy-11,12-dimethylindolo[2,3-a]carbazole (12)

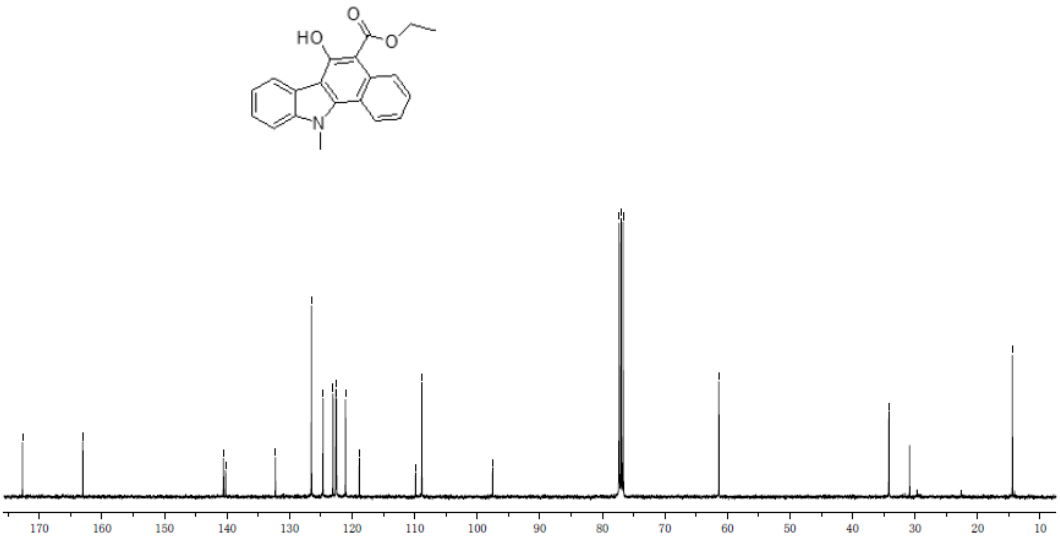
Yellow solid, mp > 300 ^oC; ^1H NMR (400 MHz, D_6-DMSO): δ 4.18 (s, 3H), 4.26 (s, 3H), 7.30–7.36 (m, 2H), 7.53 (d, *J* = 6.8 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 8.41 (d, *J* = 7.6 Hz, 1H), 8.49 (d, *J* = 7.6 Hz, 1H), 10.85 (s, 1H); ^{13}C NMR (100 MHz, D_6-DMSO): δ 36.54, 37.13, 82.83, 110.79, 111.63, 113.28, 118.70, 120.07, 120.29, 120.72, 121.18, 122.20, 122.57, 122.94, 124.01, 125.85, 126.59, 132.85, 142.22, 143.89, 153.07; FT-IR (KBr, cm^{-1}): 3350, 2211; ESI-HRMS: m/z Calcd for C21H15N3O+H^+: 326.1215, found 326.1218.

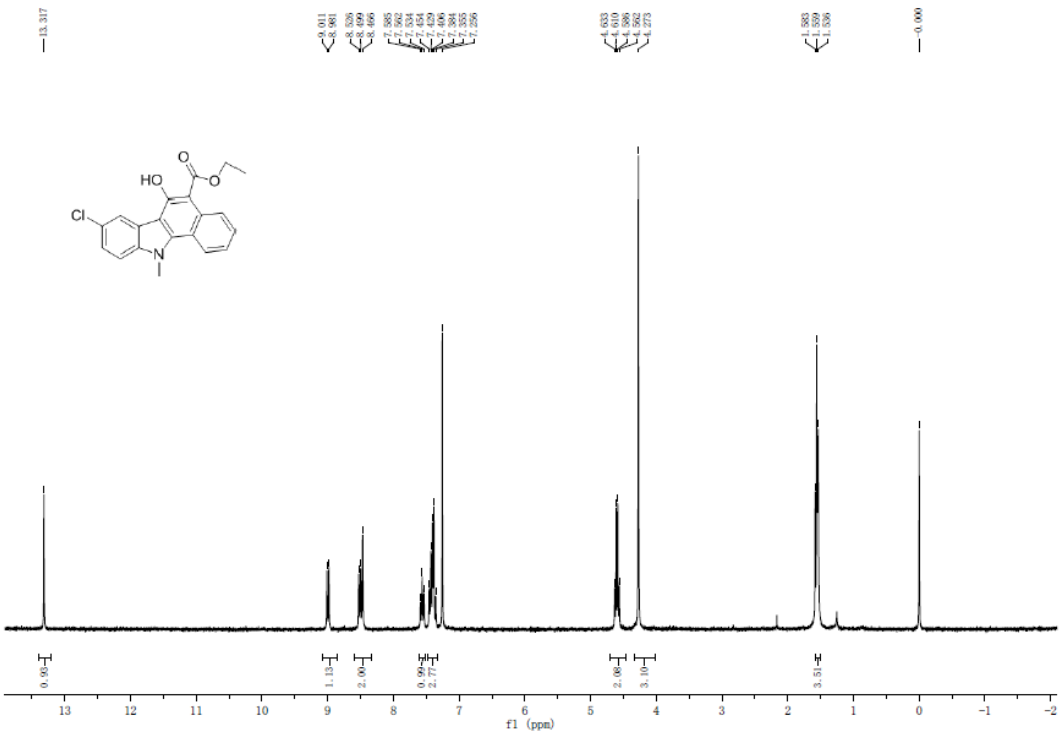
References

1. D. V. Patil, L. H. Phun and S. France, *Org. Lett.*, 2010, **12**, 5684.
2. J. Bergman,; E. Koch and B. Pelcman, *Tetrahedron*, 1995, **51**, 5631.
3. R. M. Abdel-Motaleb, A. A. Makhloof, H. M. Ibrahim and M. H. Elnagdi; *J. Heterocyclic Chem.*, 2007, **44**, 109.

Copys of ^{1}H NMR and ^{13}C NMR of the products



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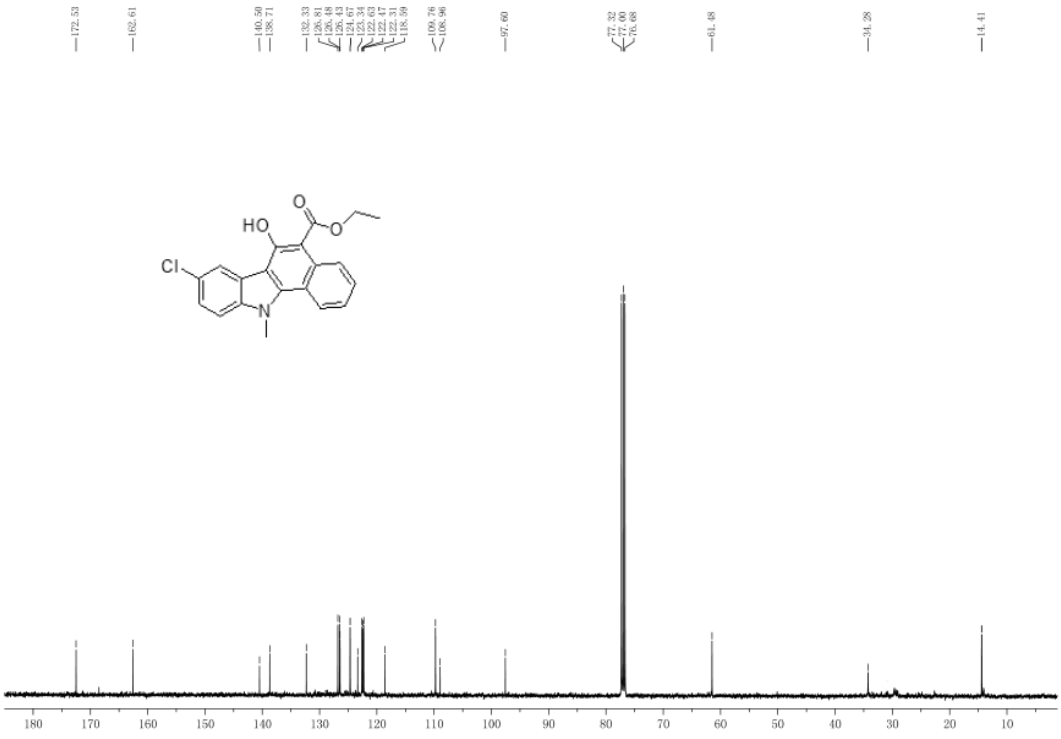
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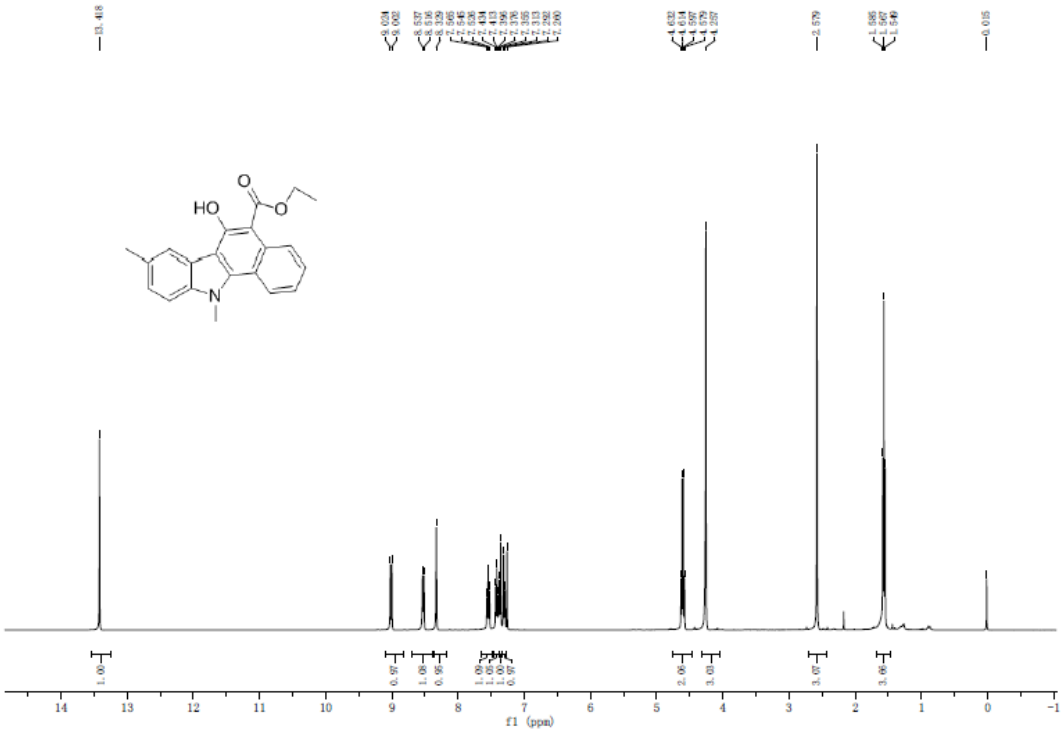
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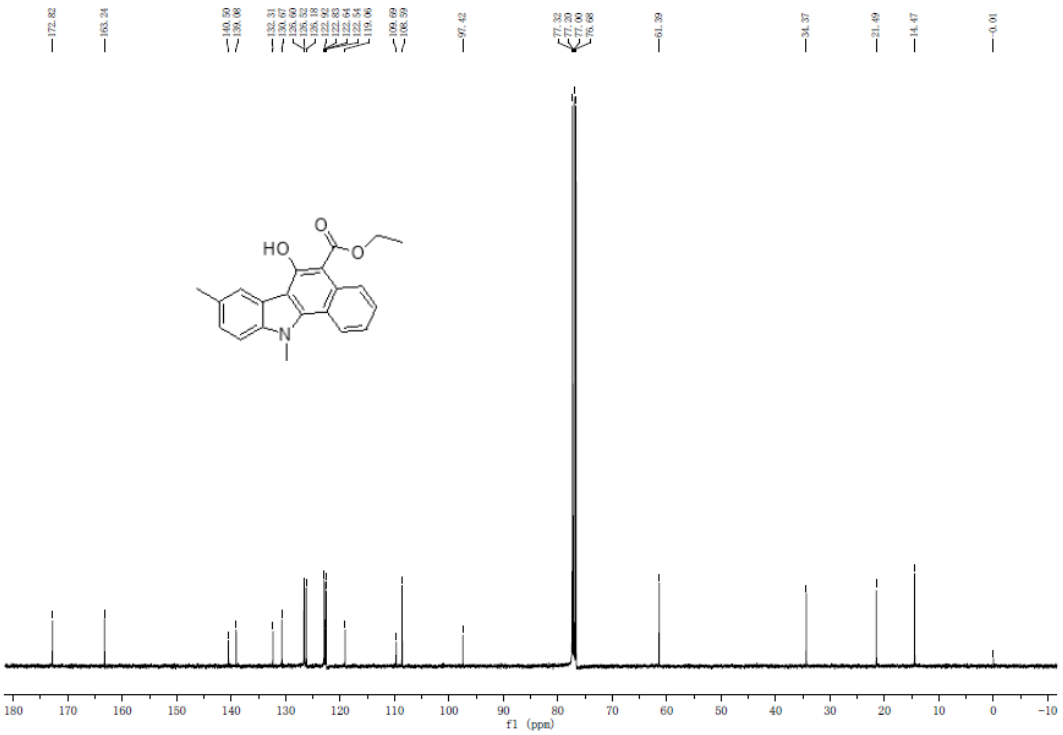
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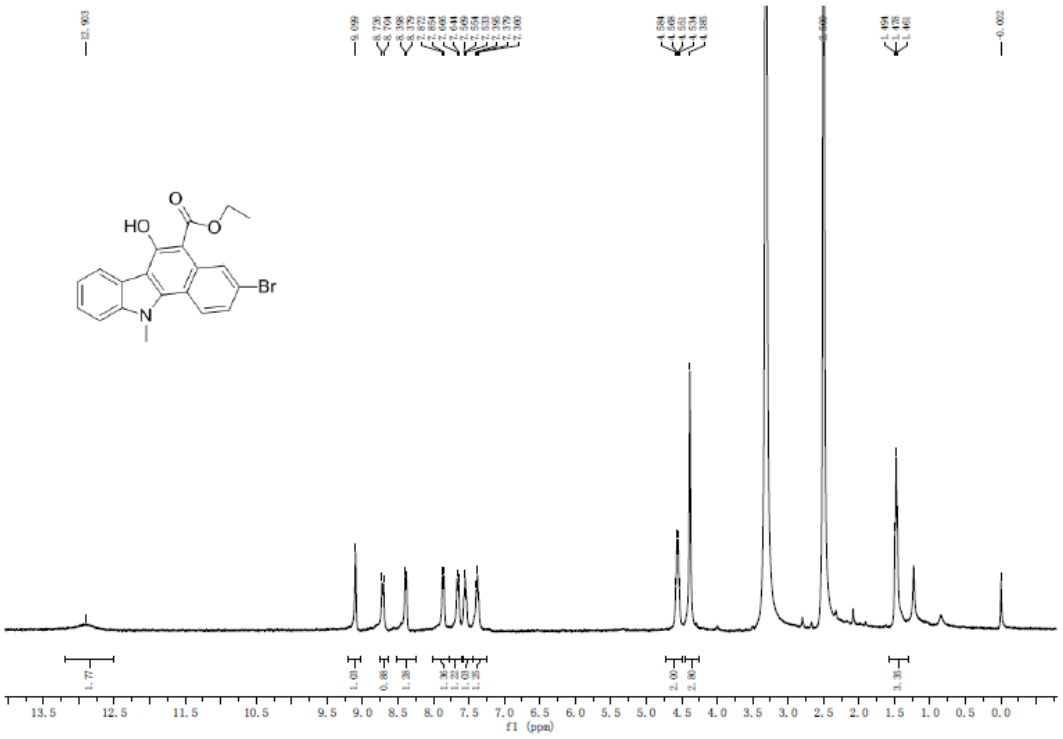
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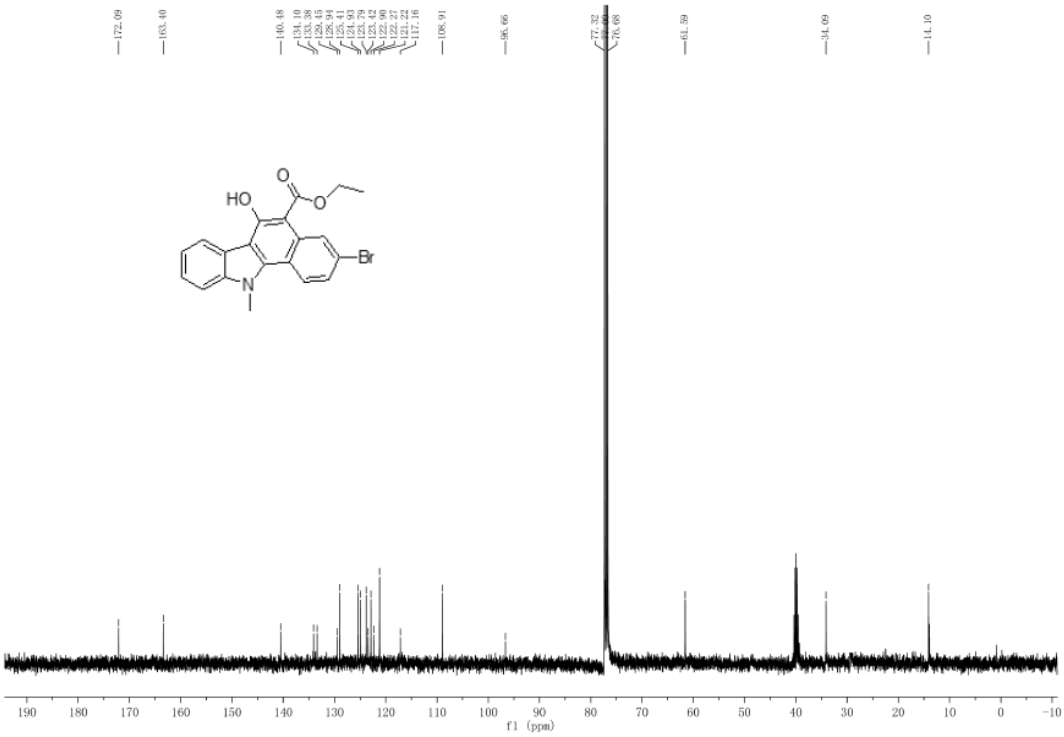
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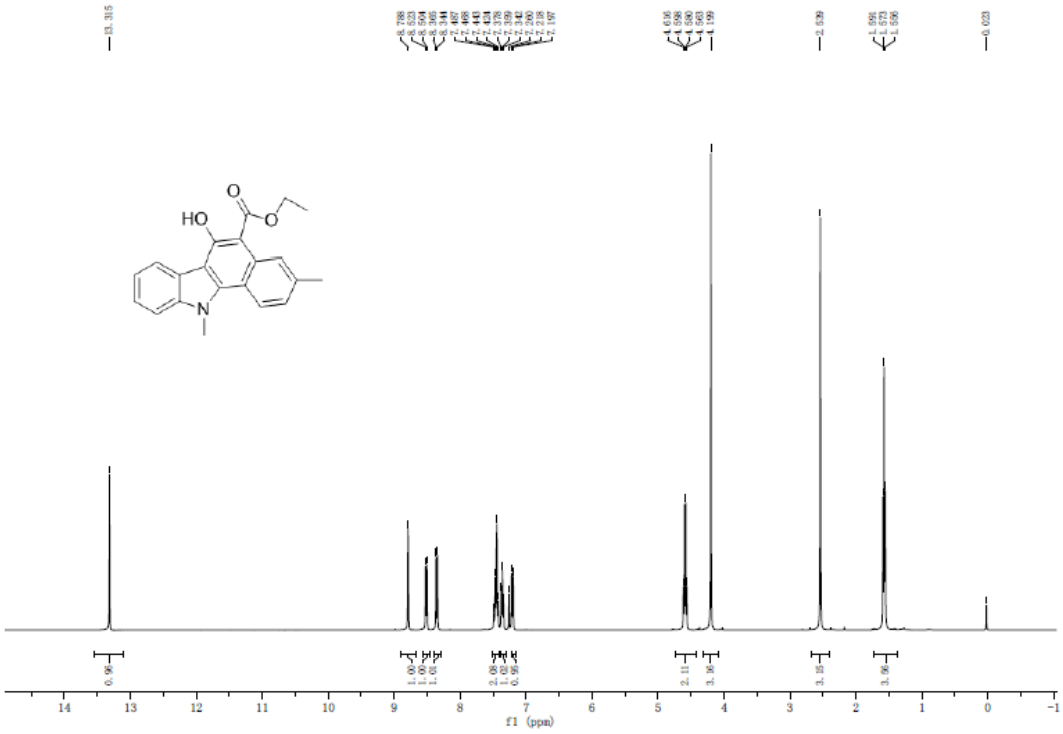
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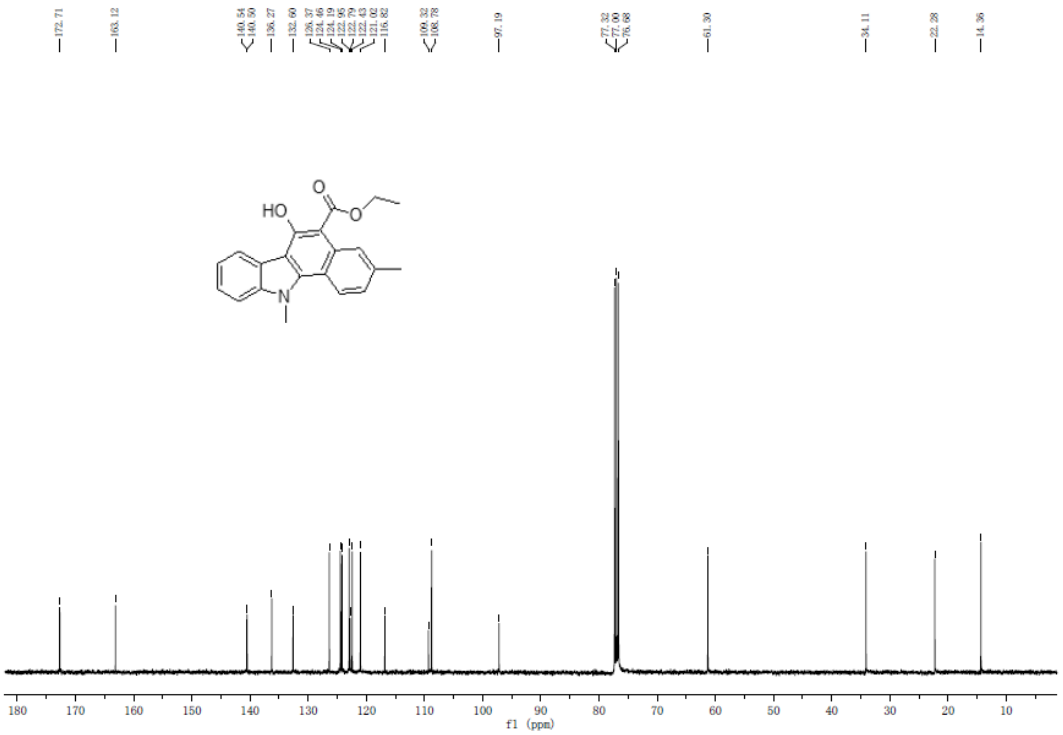
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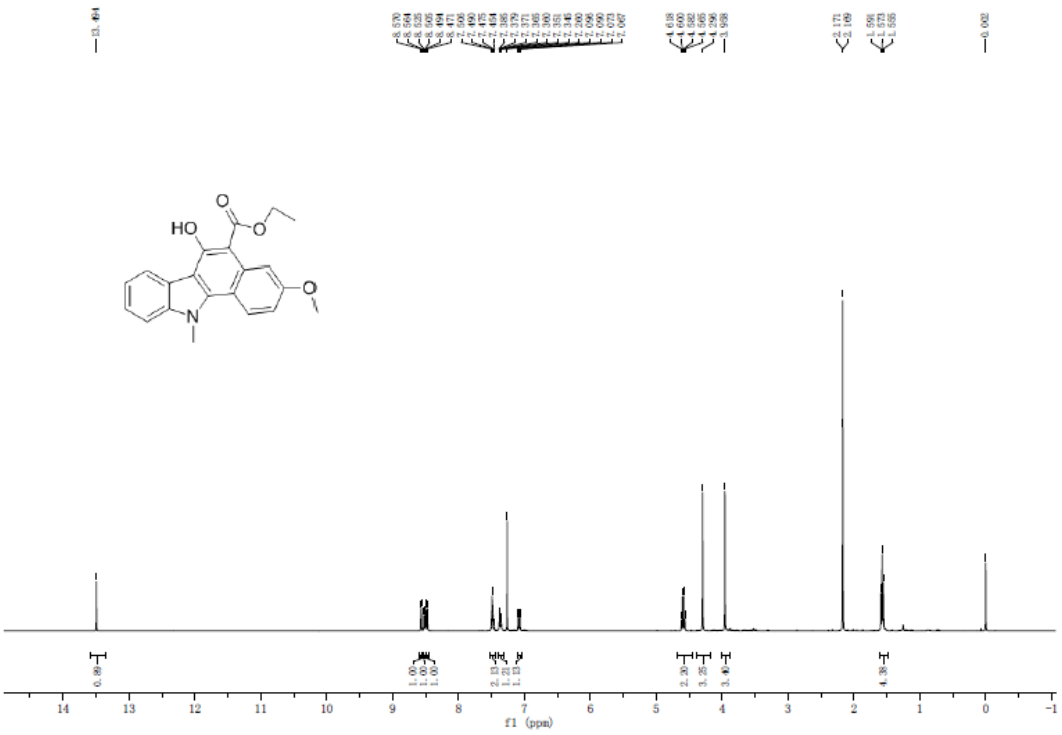
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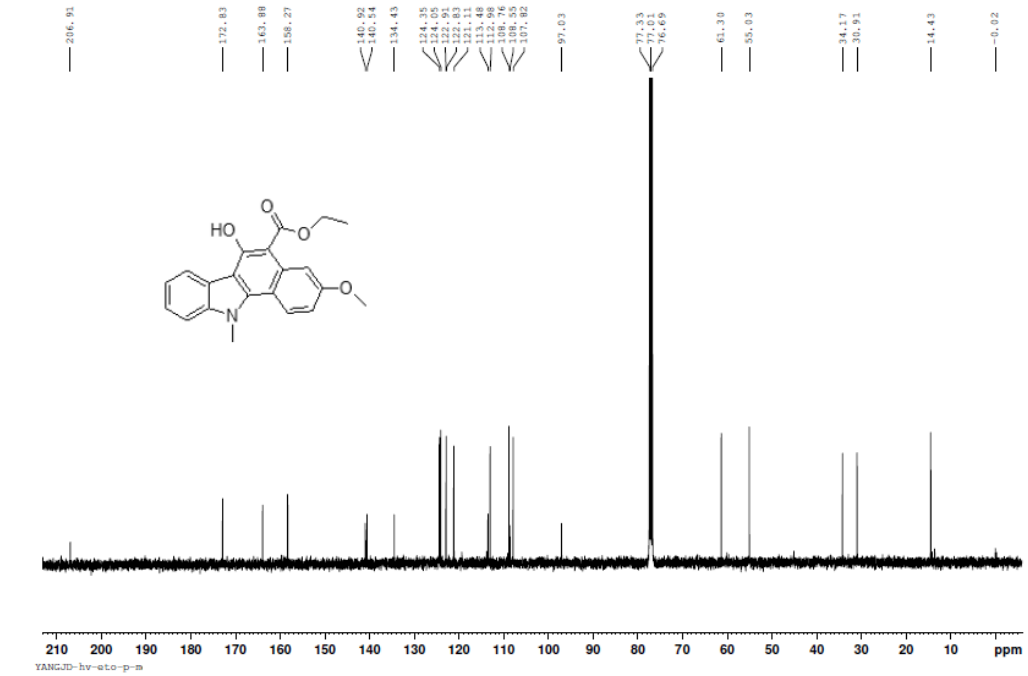
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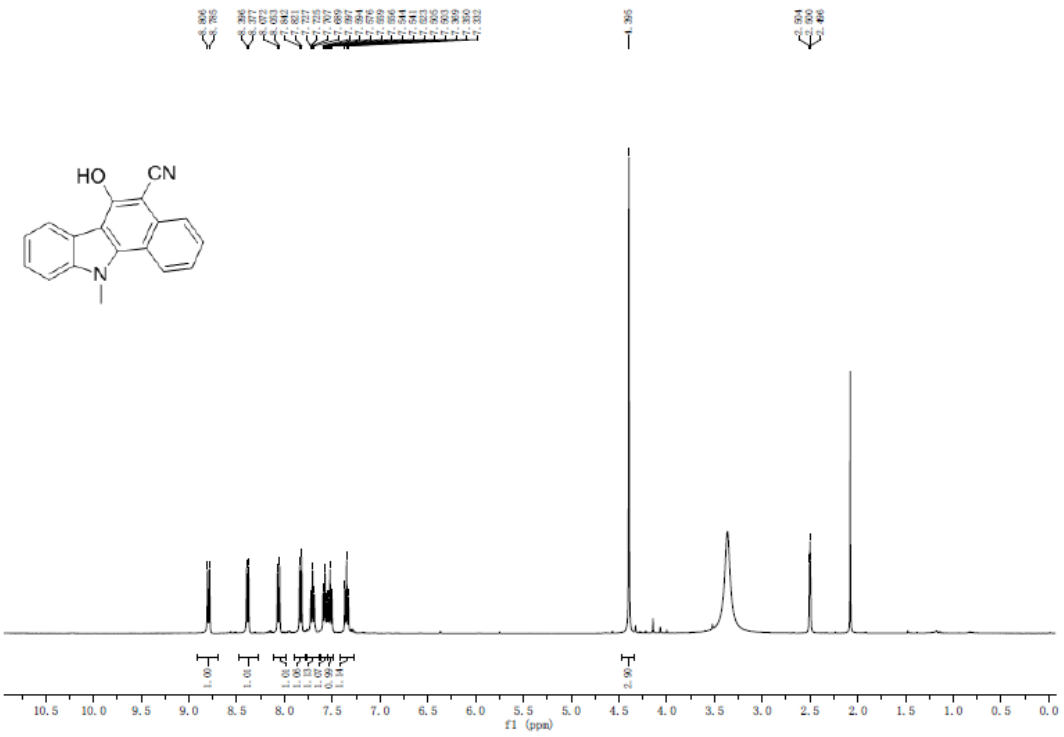
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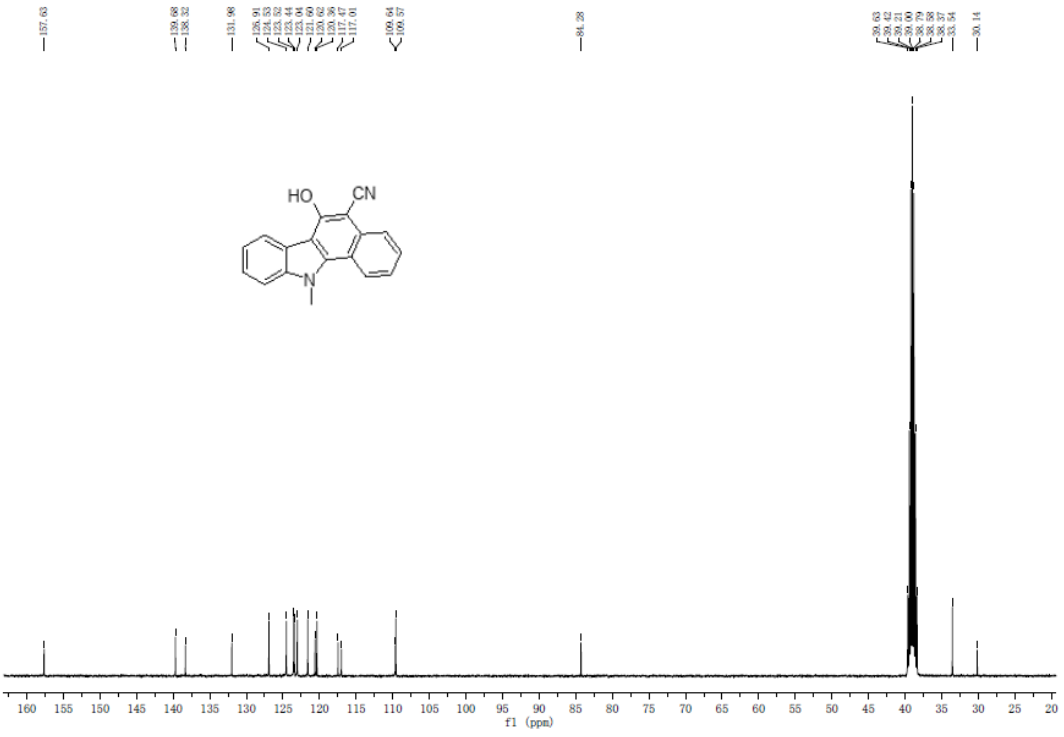
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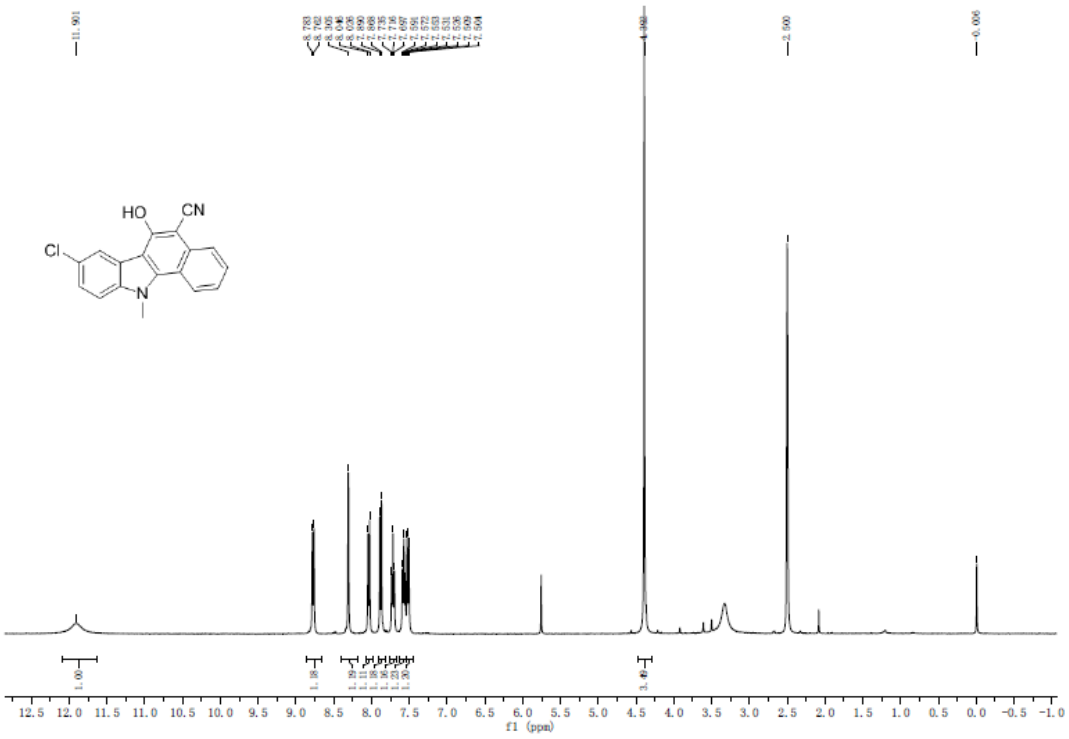
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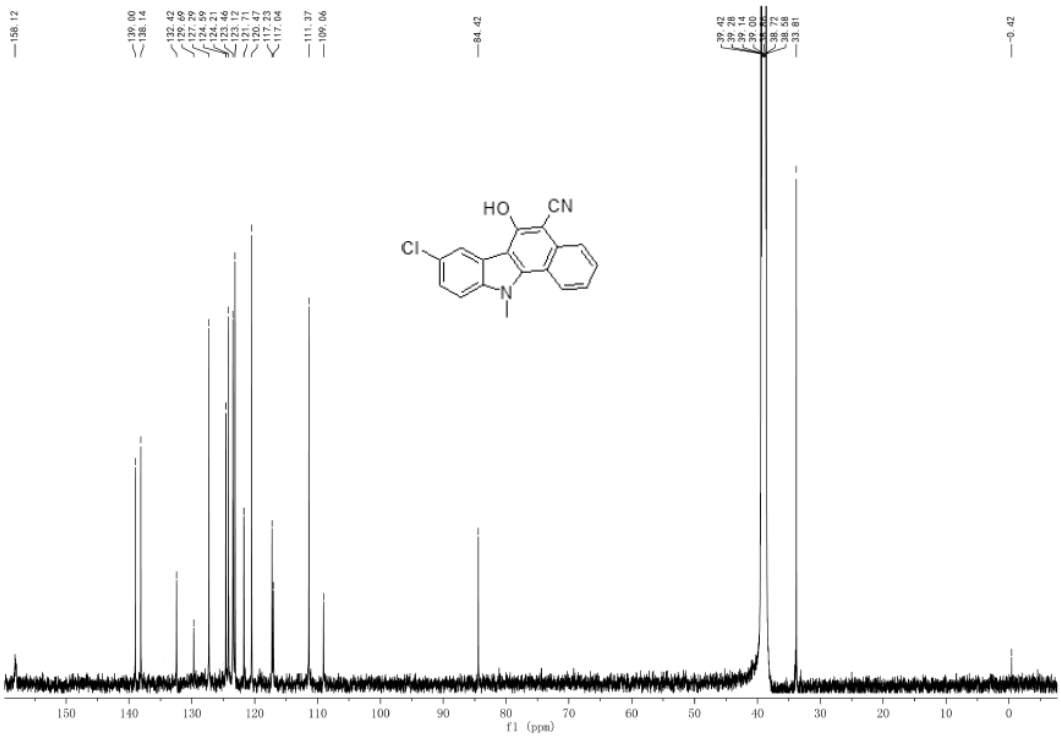
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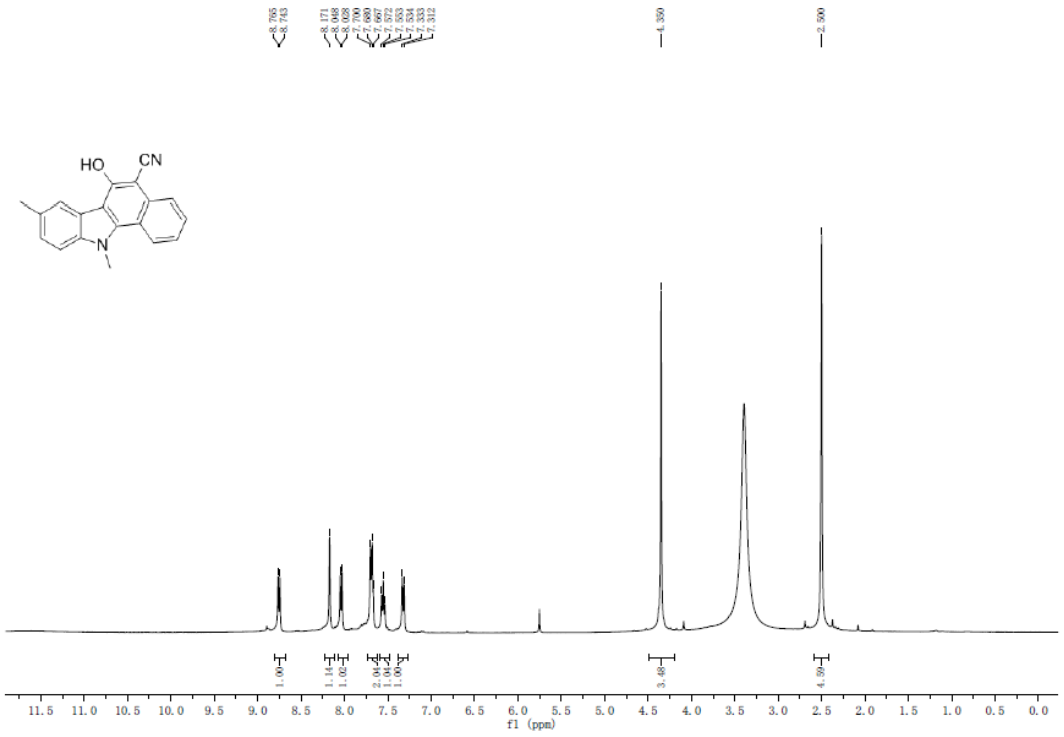
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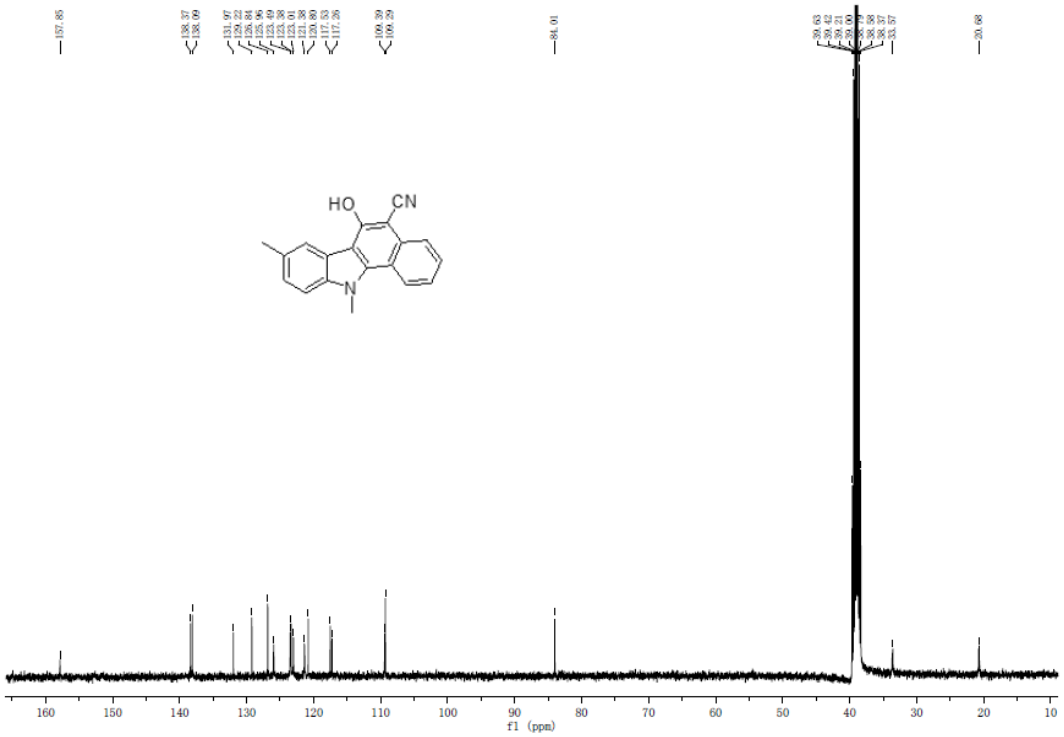
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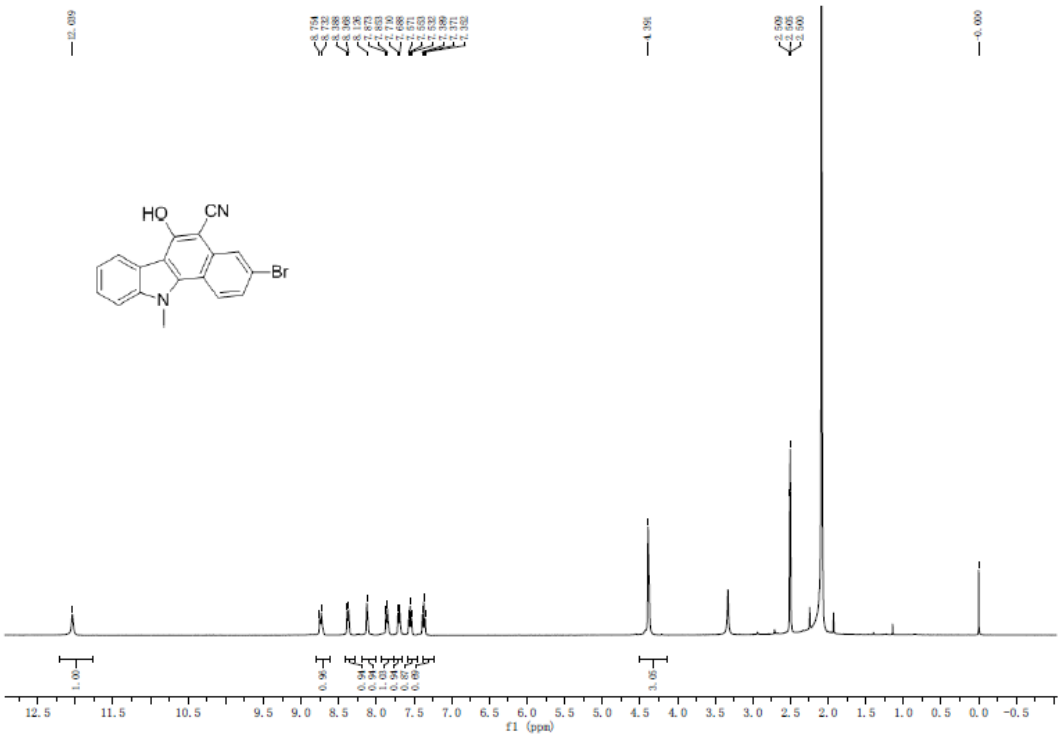
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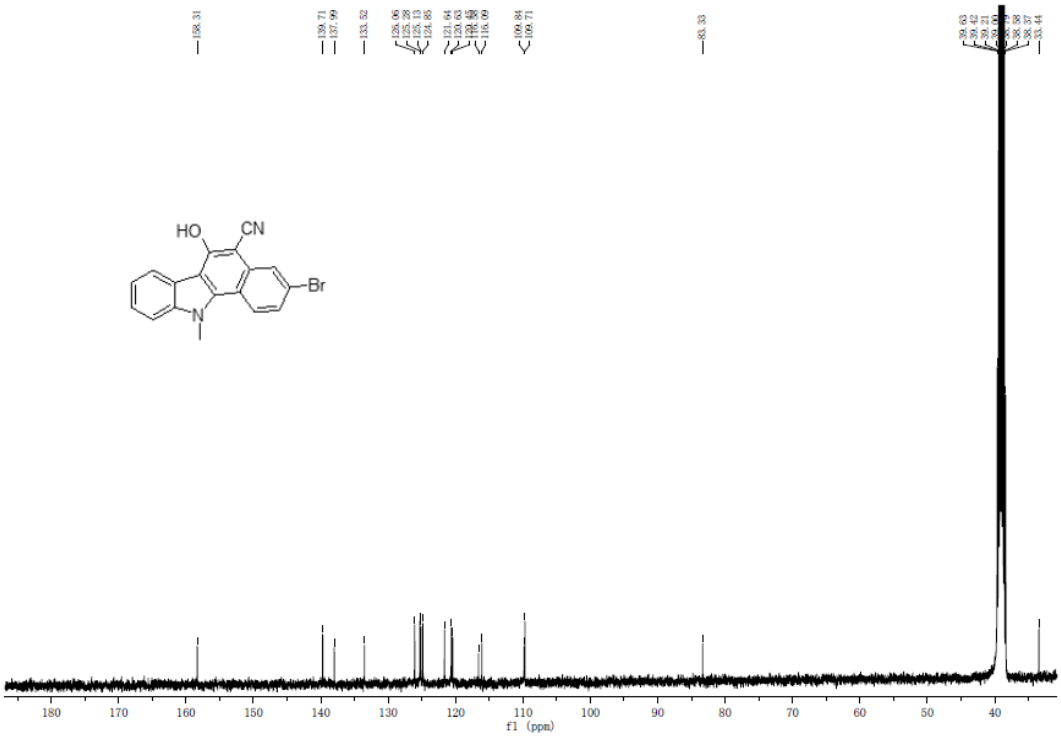
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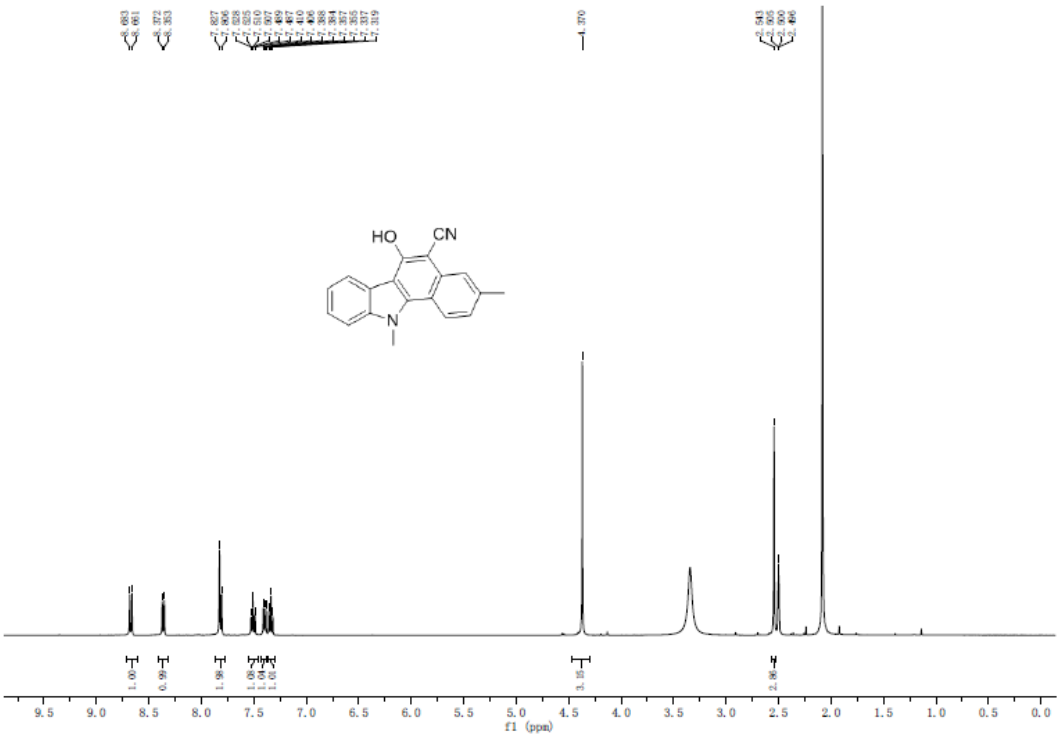
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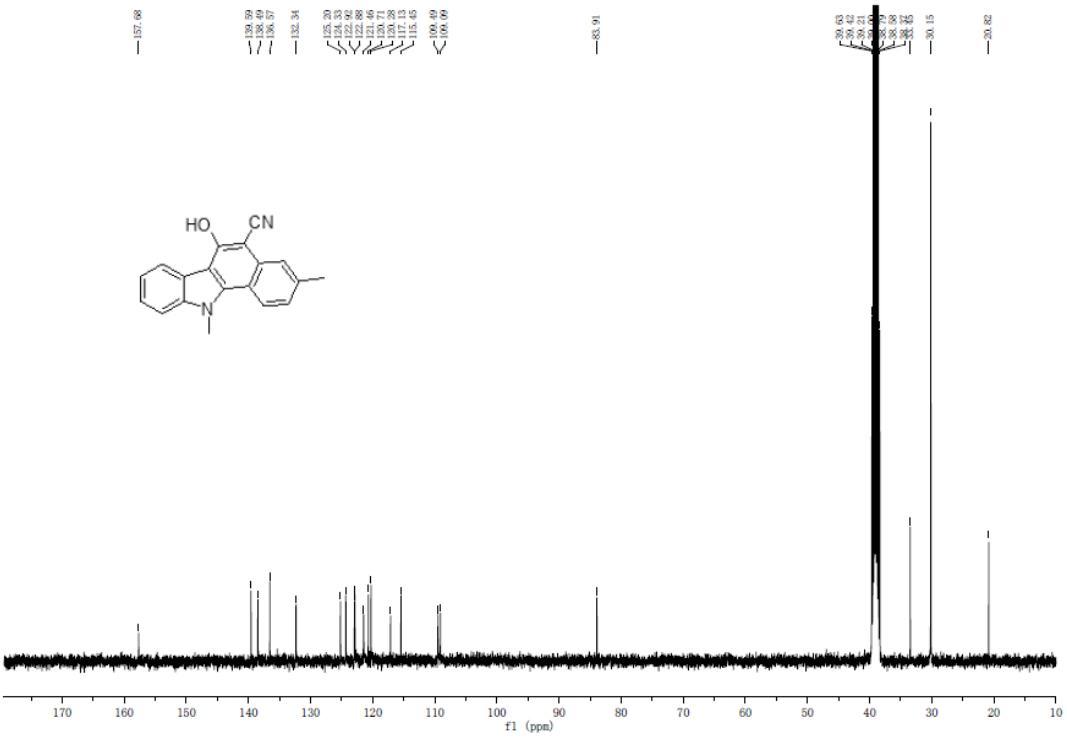
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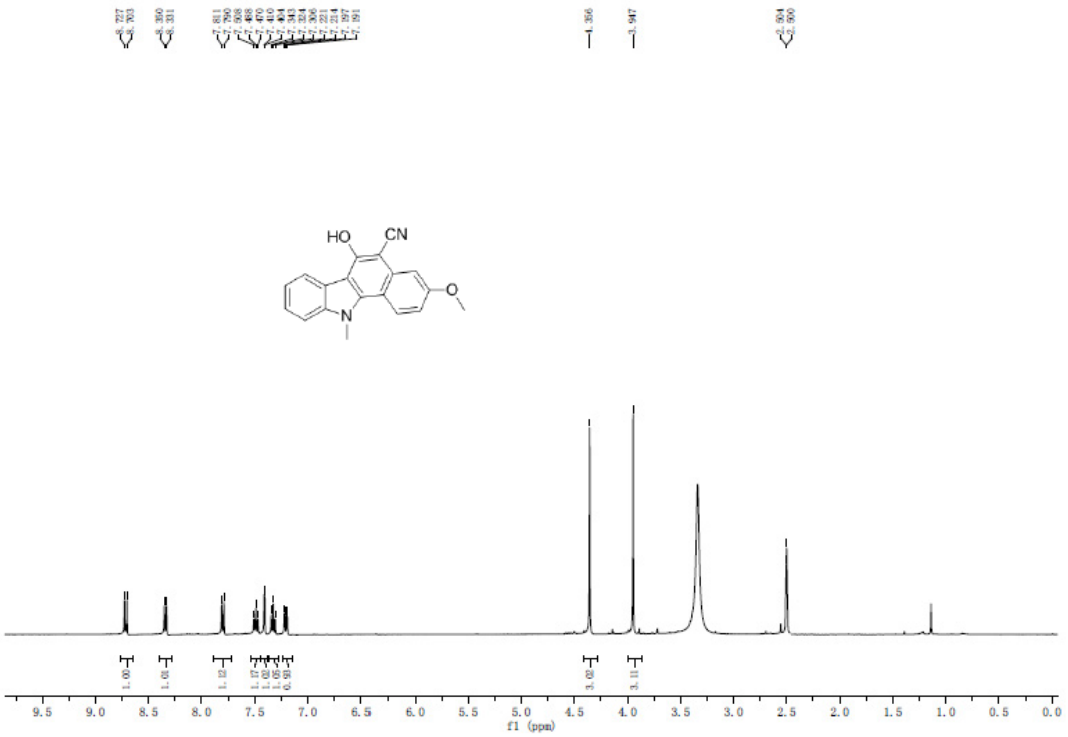
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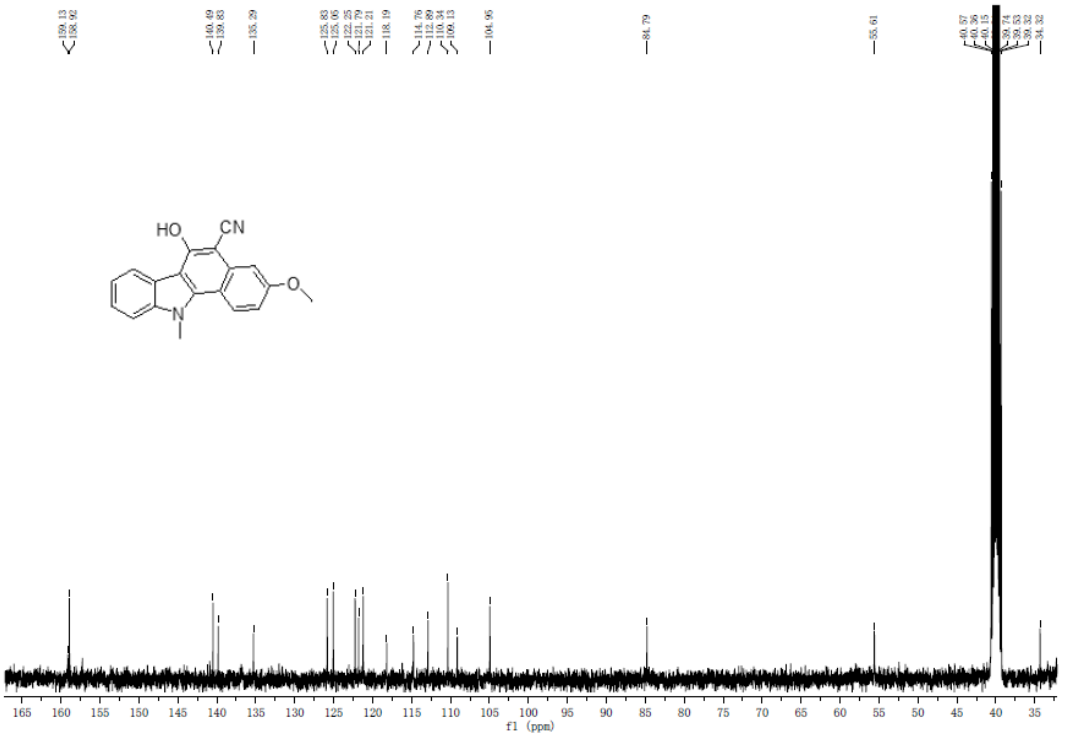
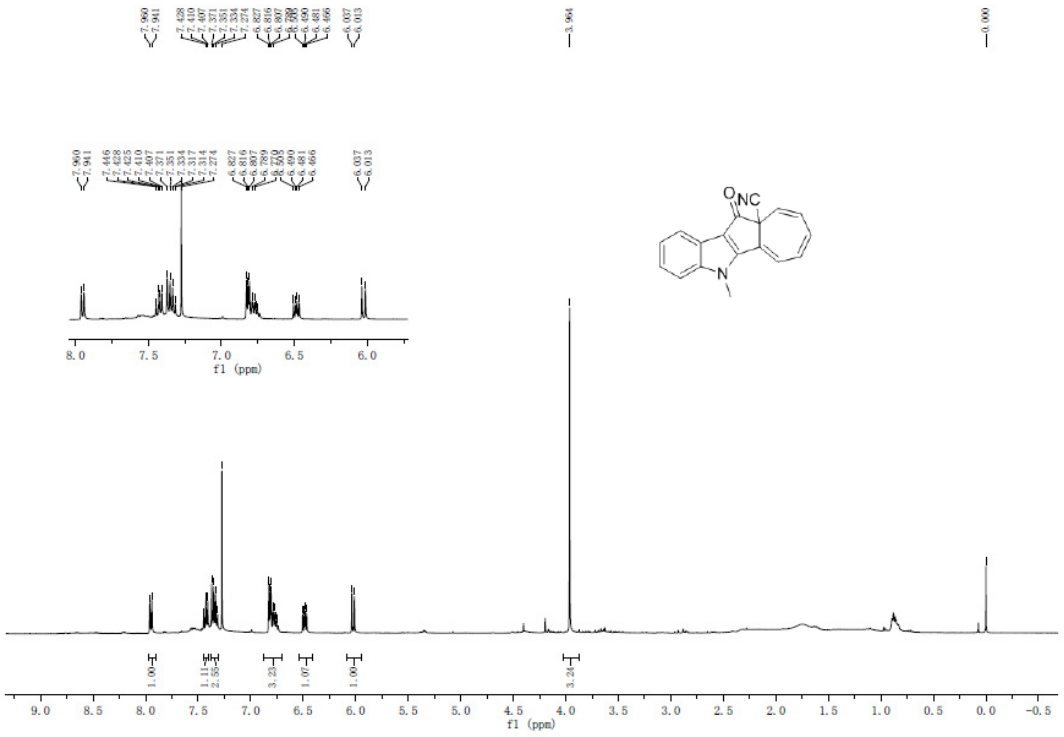
f1 (ppm)


HO
CN
O
N
f1 (ppm)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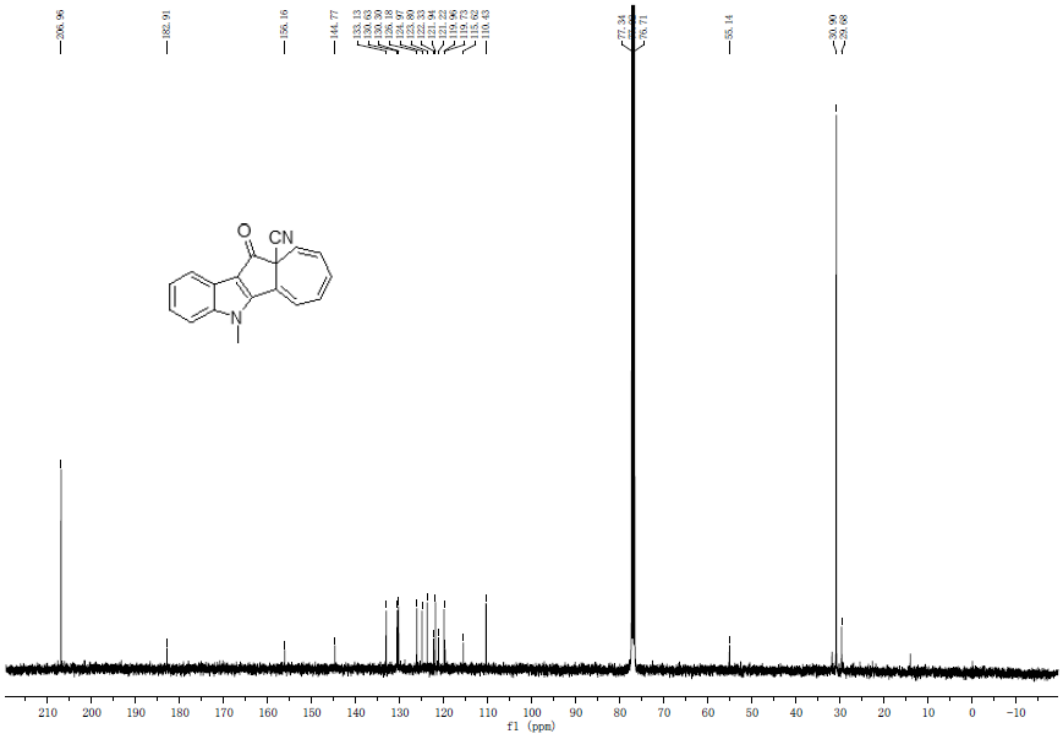
7.941
7.428
7.410
7.407
7.351
7.334
7.317
7.314
7.274
6.827
6.816
6.807
6.789
6.503
6.490
6.481
6.466
6.037
6.013
3.964
0.000
O
NC
N
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
1.00
1.11
2.35
3.23
1.07
1.00
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)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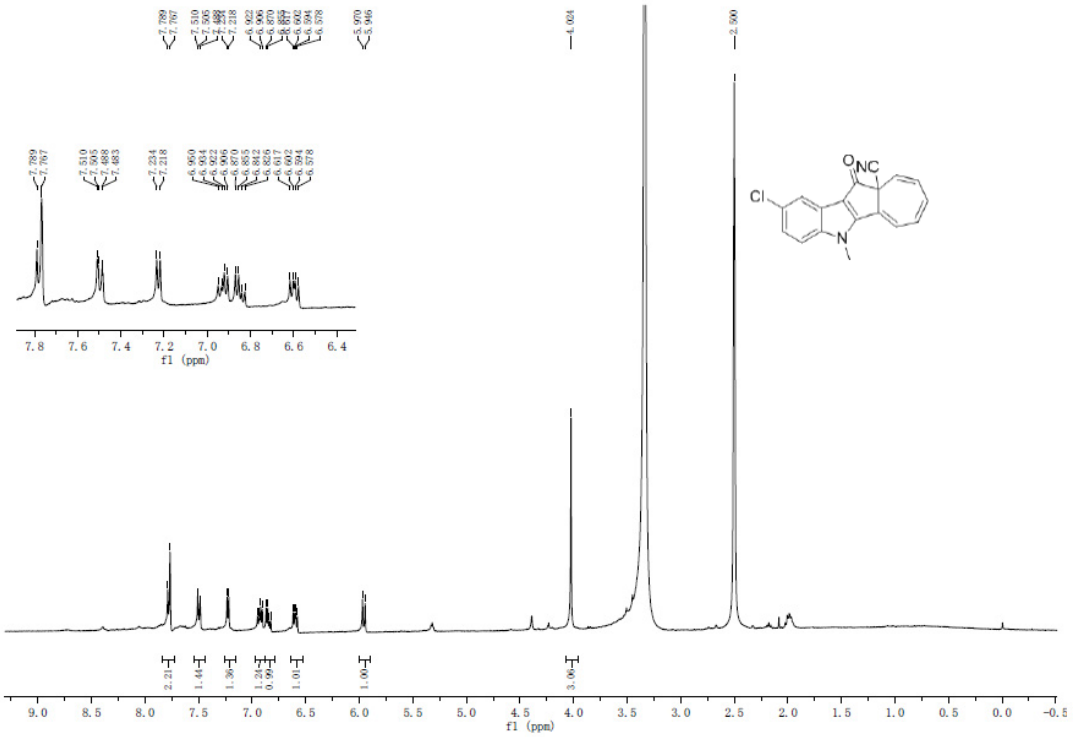
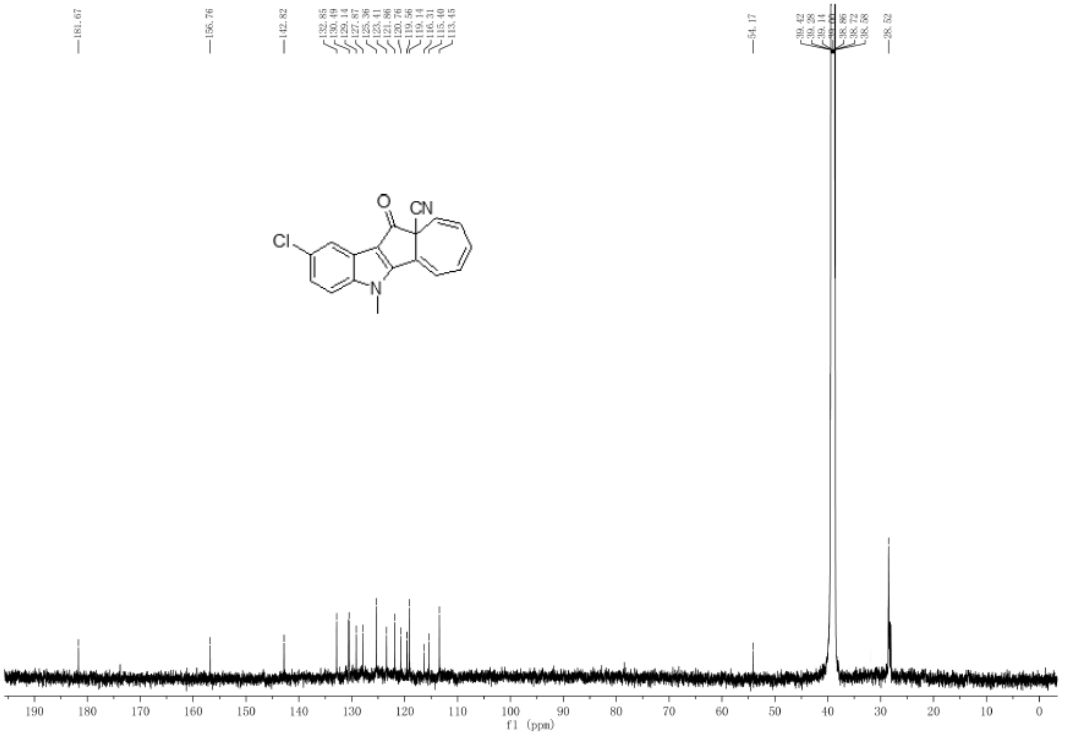
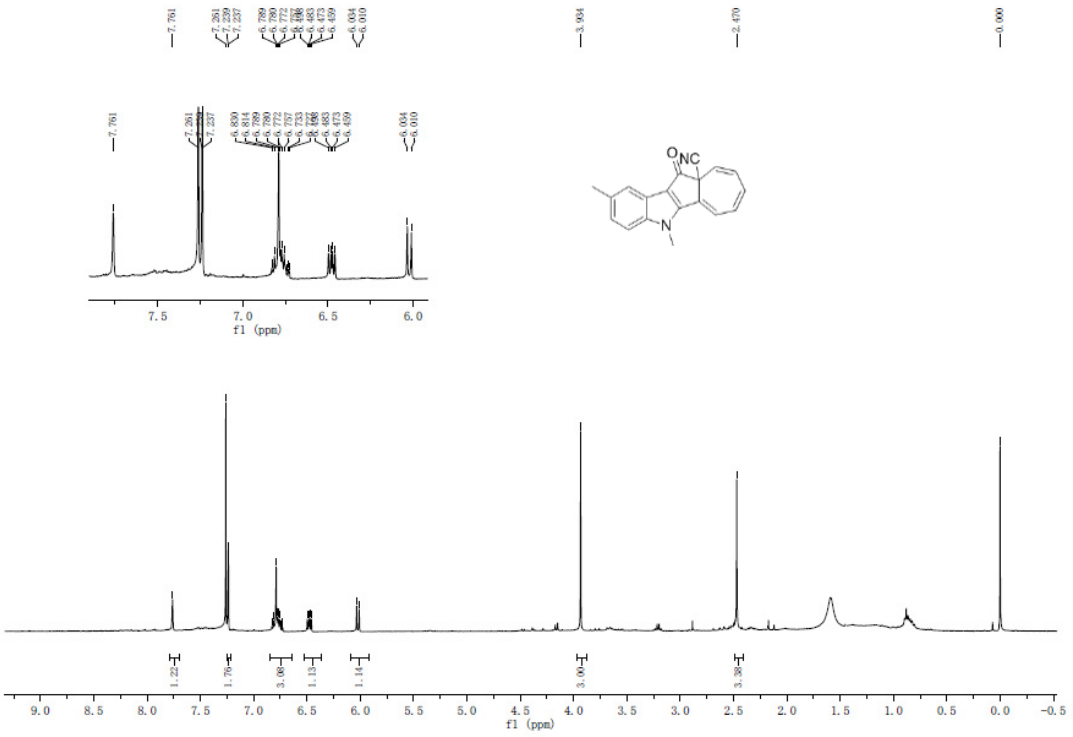
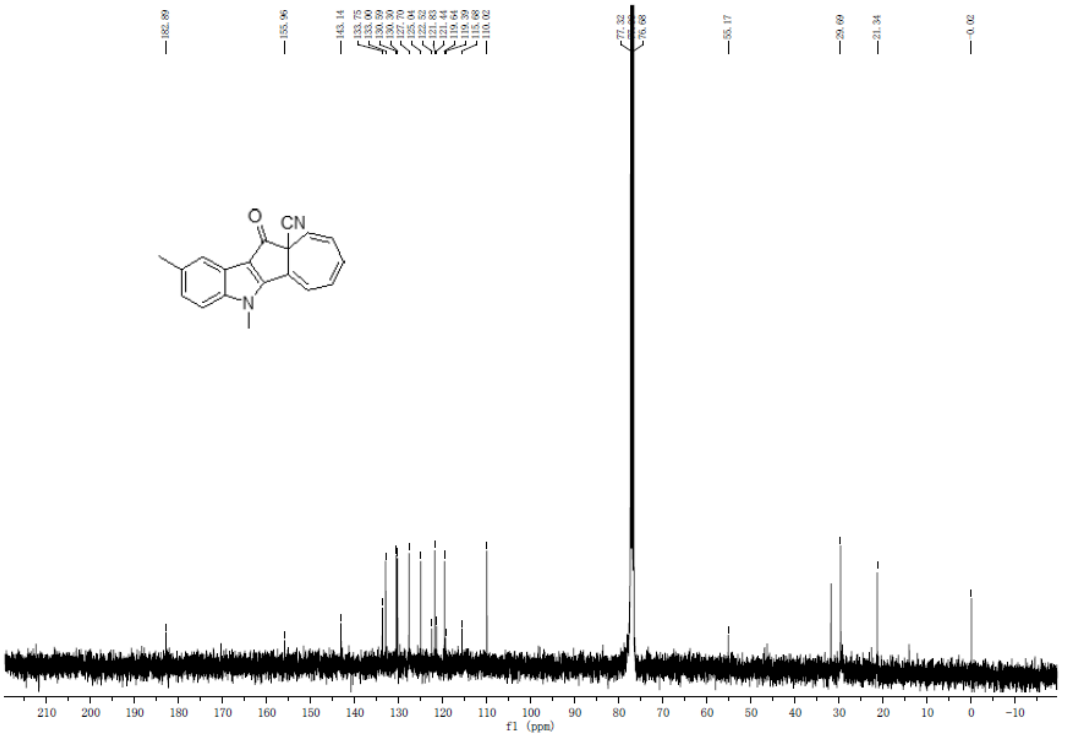
182.91
156.16
144.77
135.13
130.39
126.18
124.97
123.89
122.33
121.94
121.22
119.96
119.25
115.62
110.43
77.34
77.03
76.71
55.14
30.99
28.68
O
CN
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.789
7.767
7.510
7.505
7.488
7.483
7.234
7.218
6.960
6.934
6.922
6.906
6.870
6.855
6.842
6.826
6.617
6.602
6.594
6.578
5.979
5.946
4.024
2.500
O
NC
Cl
N
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)
2.21
1.44
1.36
1.24
0.99
1.01
1.00
3.06
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)


181.67
156.76
142.82
132.85
130.49
129.14
127.87
125.98
123.41
121.86
120.76
119.56
119.14
116.31
115.40
113.45
64.17
39.42
39.28
39.14
38.86
38.72
38.58
28.52
O
CN
Cl
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.761
7.261
7.239
7.237
6.839
6.814
6.789
6.772
6.757
6.733
6.465
6.459
6.453
6.439
6.034
6.010
3.934
2.479
0.000
f1 (ppm)
O
NC
N
1.22
1.76
3.08
1.13
1.14
3.00
3.38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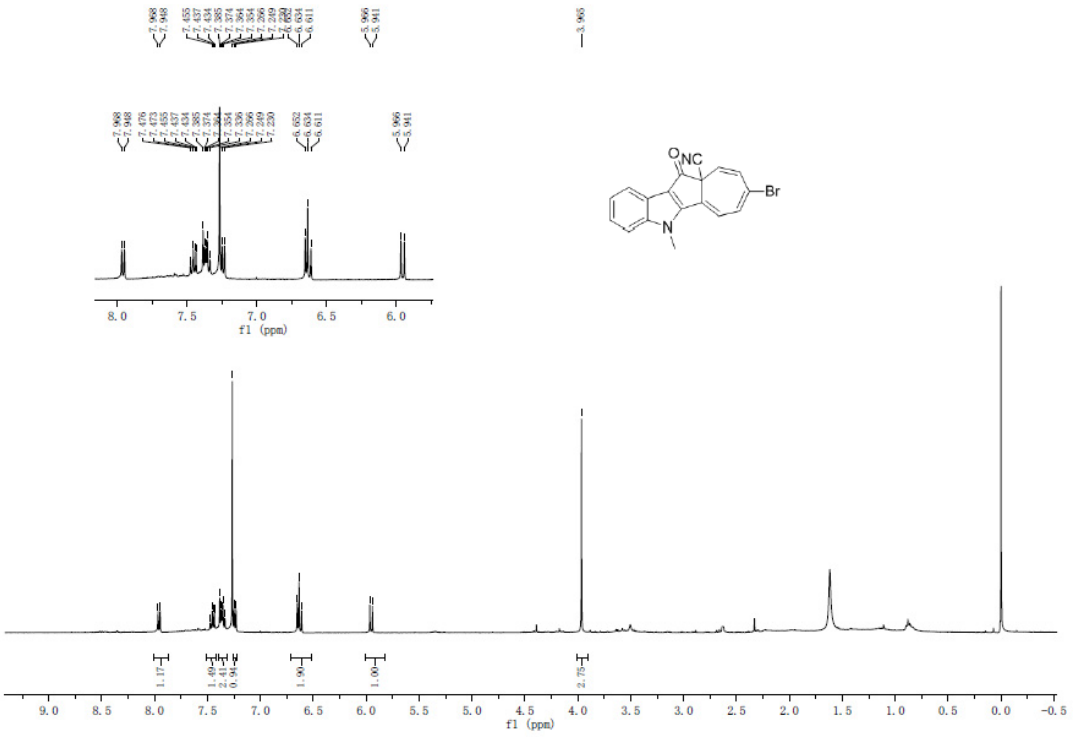
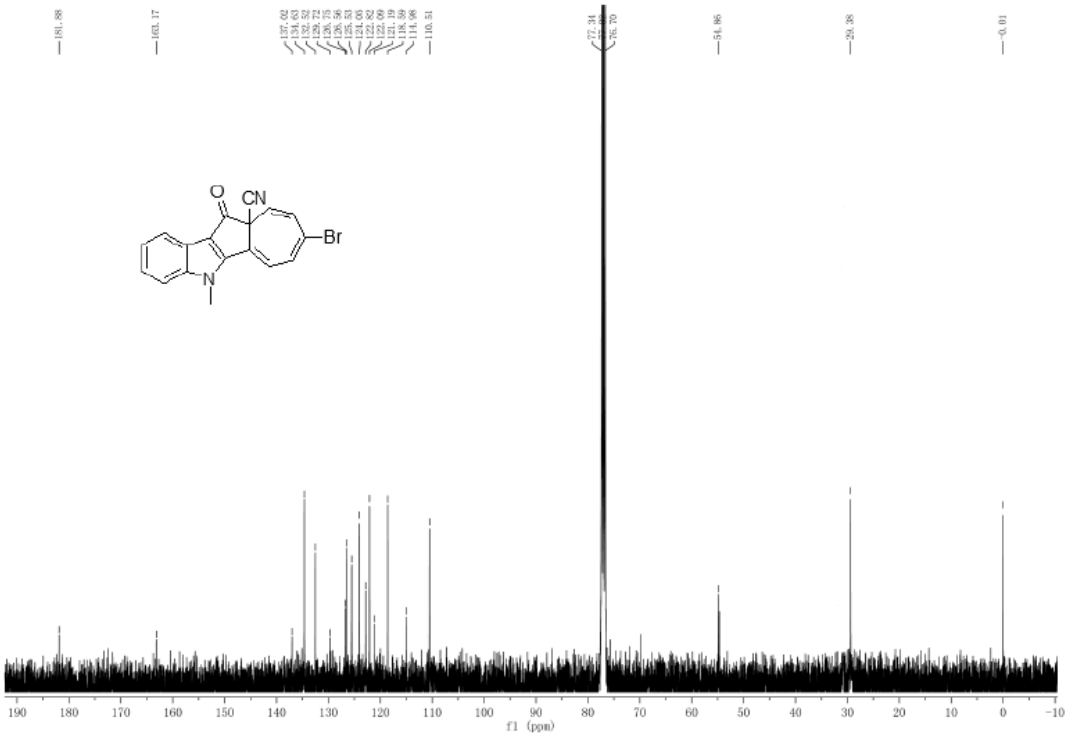
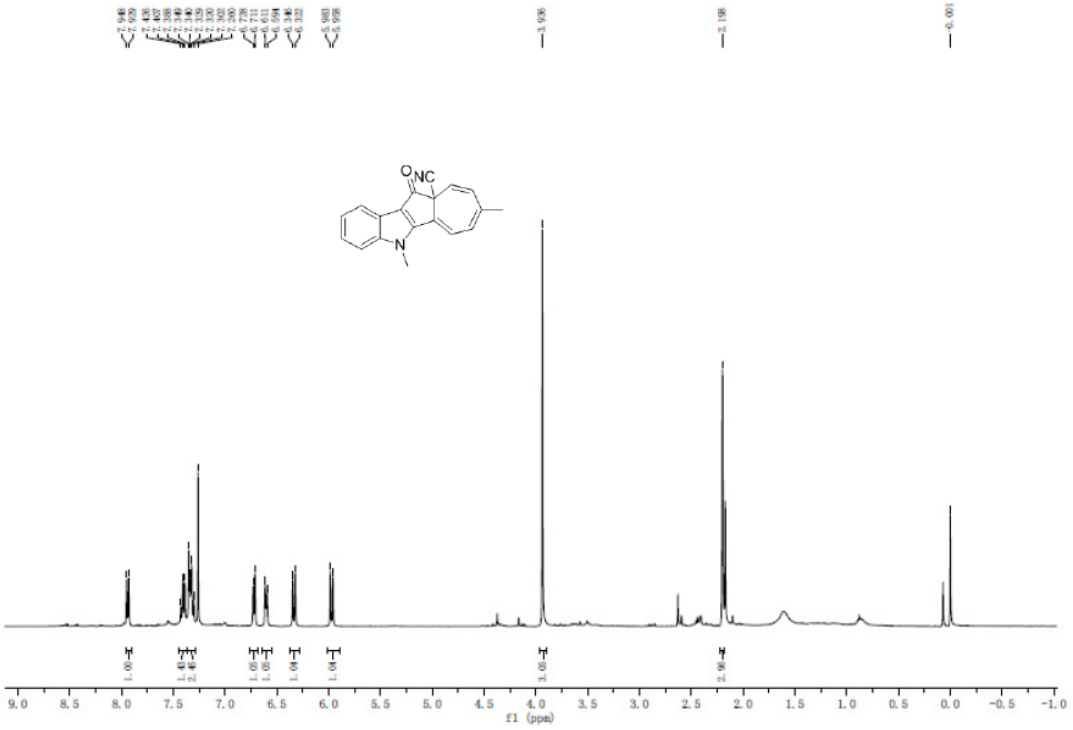
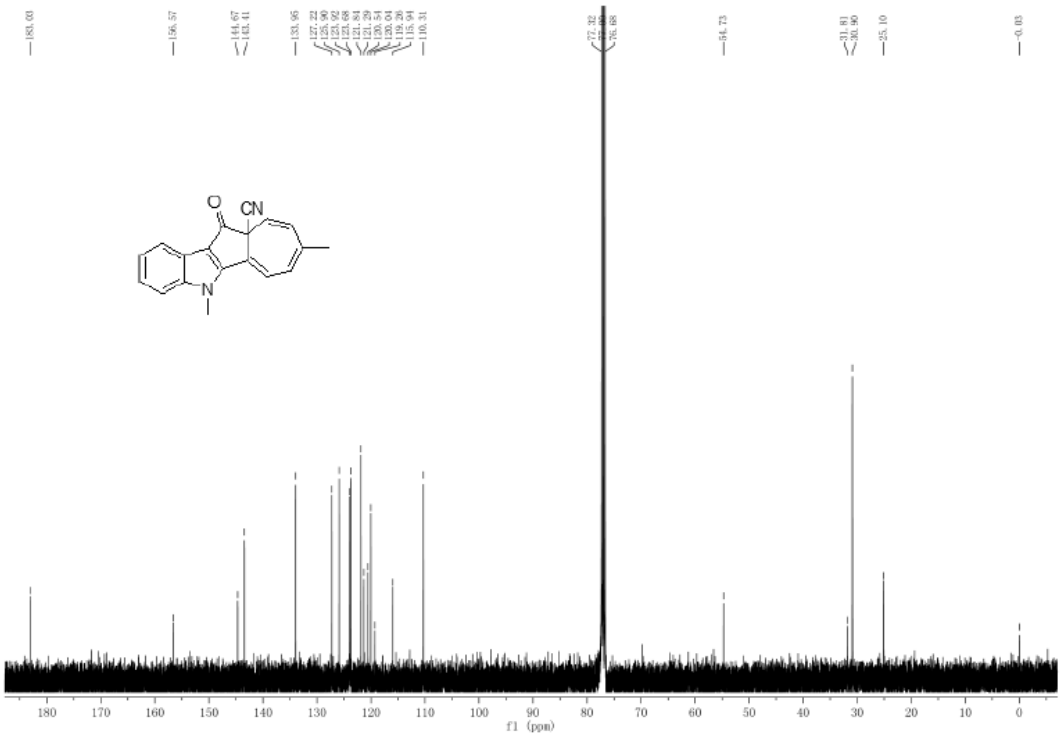
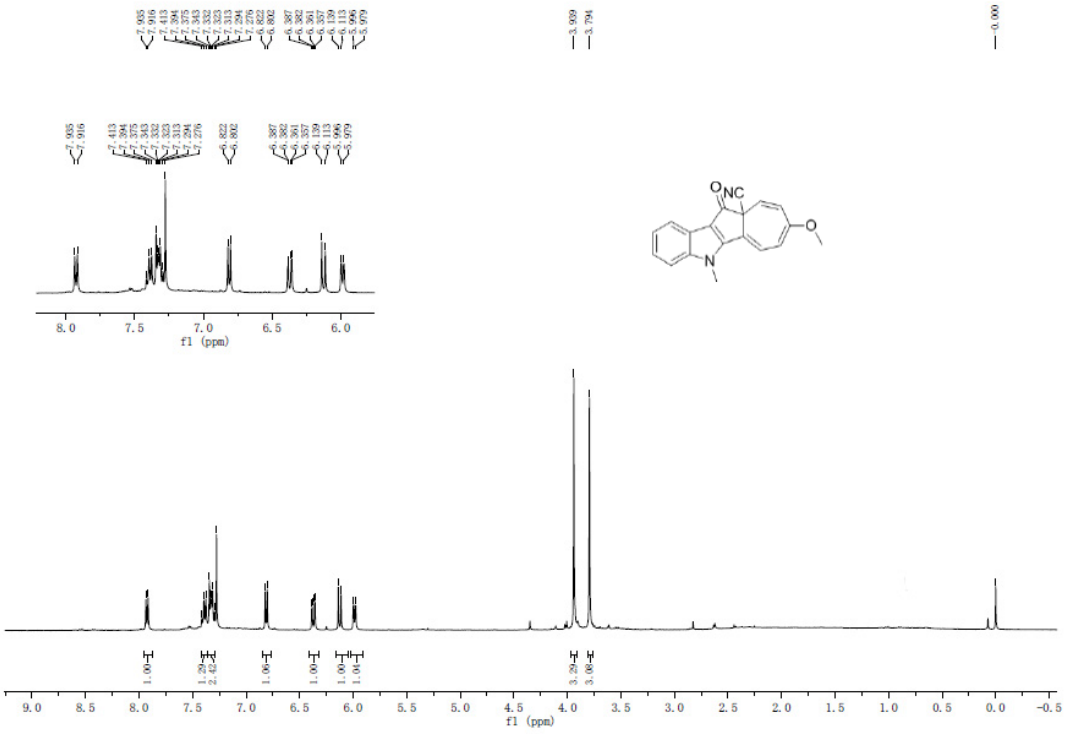
155.96
143.14
133.75
133.09
131.39
130.39
127.70
125.04
122.53
121.83
121.44
119.64
118.38
115.68
110.02
77.32
77.00
76.68
55.17
29.69
21.34
0.02
O
CN
N
f1 (ppm)

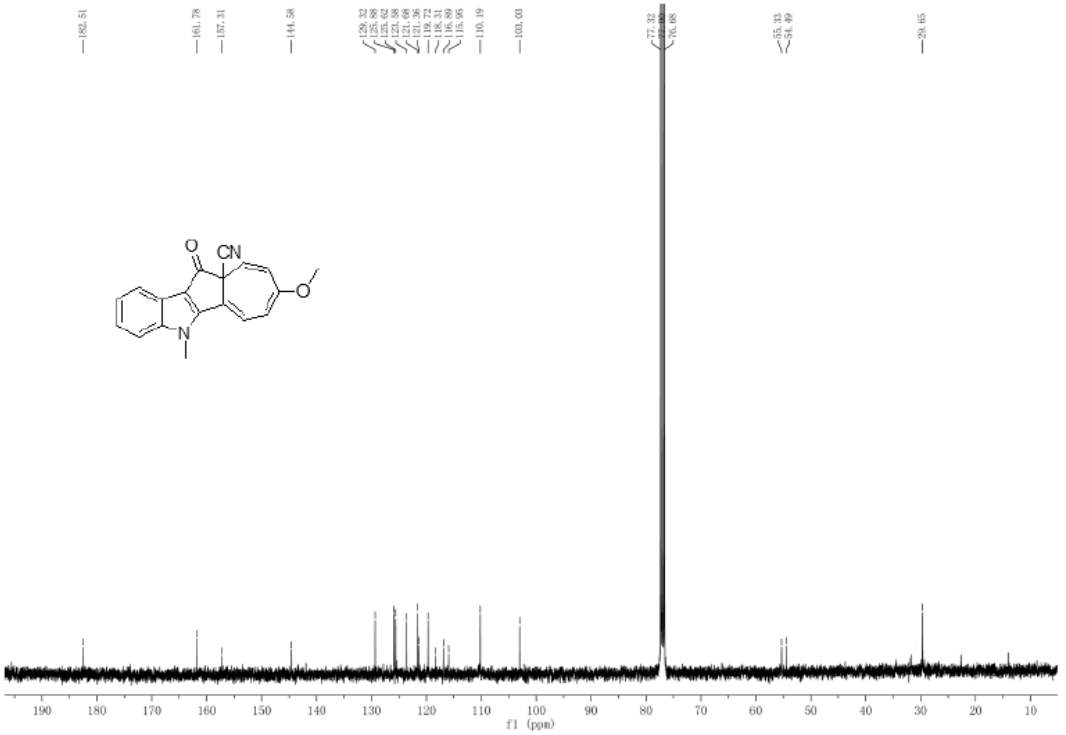

O
NC
Br
N
f1 (ppm)


O
CN
Br
N
f1 (ppm)


O
NC
N
f1 (ppm)


O
CN
N
f1 (ppm)


7.935
7.916
7.413
7.394
7.375
7.343
7.332
7.323
7.313
7.294
7.276
6.822
6.802
6.387
6.382
6.363
6.357
6.139
6.113
5.986
5.979
3.999
3.794
0.000
O
NC
O
N
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
1.00
1.29
2.62
1.00
1.00
1.00
1.04
3.29
3.08
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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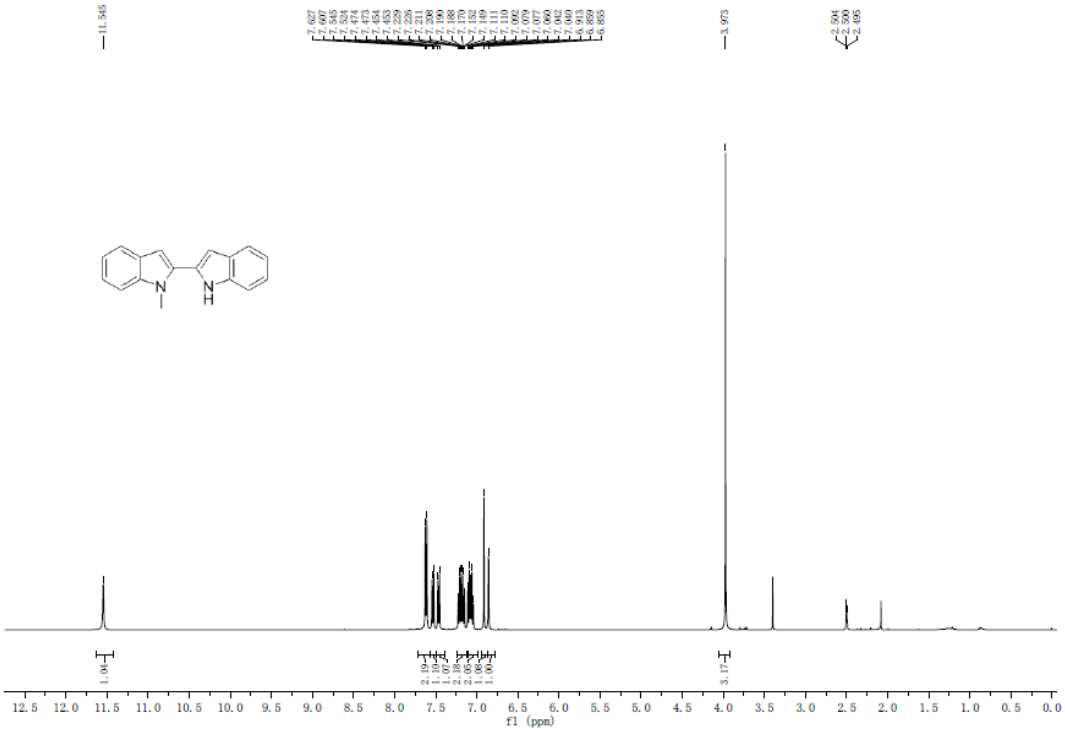
129.32
125.88
125.62
123.38
121.68
121.36
119.72
118.31
116.89
115.95
110.19
103.03
77.32
77.00
76.68
55.33
54.49
29.65
O
CN
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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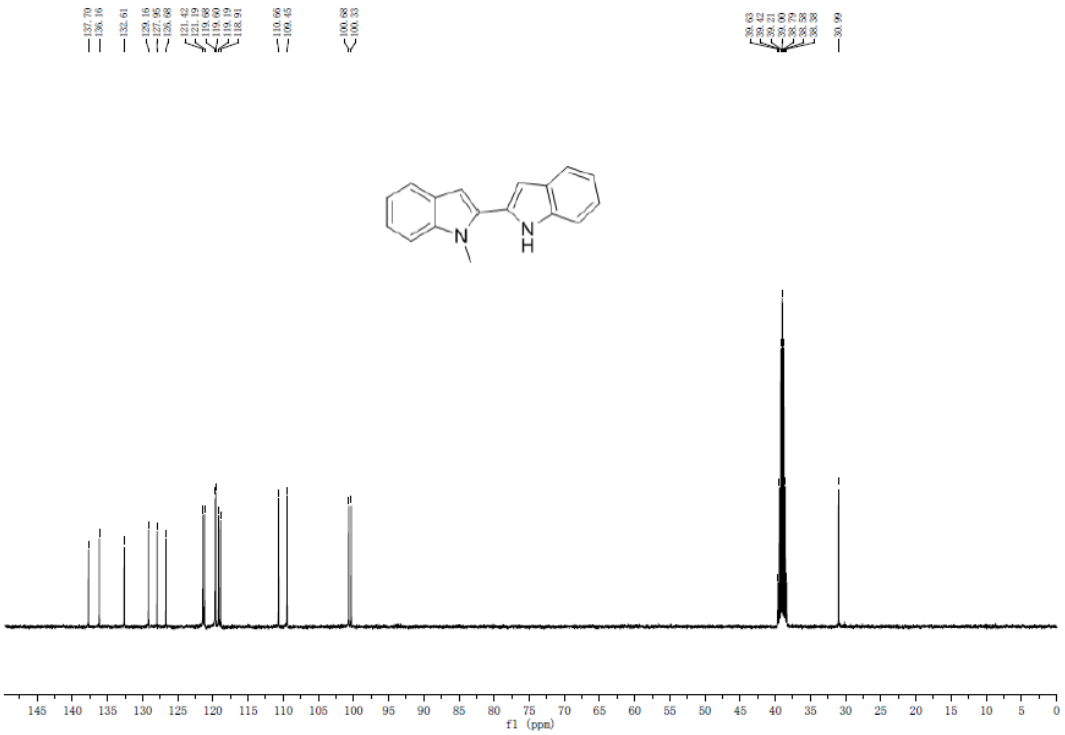
7.607
7.545
7.524
7.474
7.455
7.454
7.453
7.229
7.223
7.211
7.208
7.190
7.188
7.170
7.152
7.149
7.111
7.110
7.092
7.079
7.077
7.059
7.042
7.040
6.913
6.909
6.895
3.973
2.504
2.500
2.495
1.00
2.19
1.04
1.07
2.18
2.05
1.08
1.00
3.17
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


137.79
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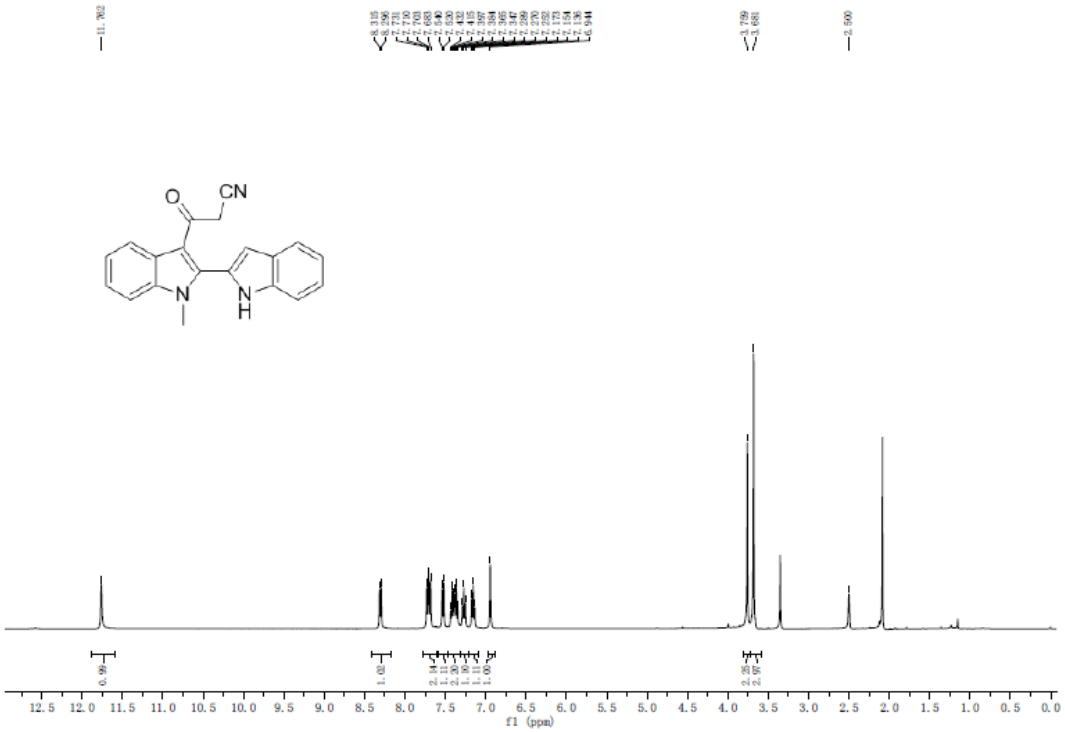
132.61
129.15
127.95
126.68
121.42
121.19
119.68
119.60
119.19
118.91
110.66
109.45
100.68
100.33
39.63
39.42
39.21
39.00
38.79
38.58
38.38
30.99
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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8.296
7.731
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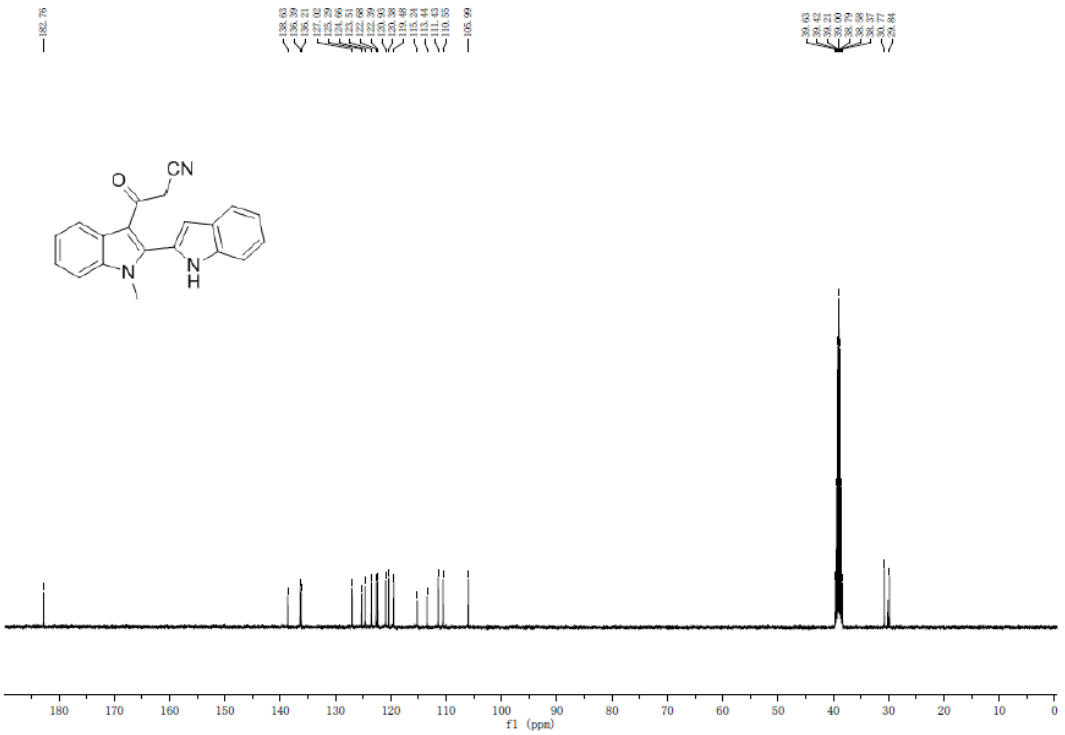
7.540
7.520
7.432
7.415
7.397
7.384
7.365
7.347
7.299
7.283
7.253
7.173
7.154
7.136
6.944
3.739
3.688
2.500
O
CN
N
H
6.99
1.00
2.11
2.26
1.22
1.00
2.95
2.95
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.63
136.39
136.21
127.02
125.29
124.96
123.51
122.68
122.39
120.93
120.38
119.68
115.24
111.45
110.55
105.99
39.63
39.42
39.21
39.00
38.79
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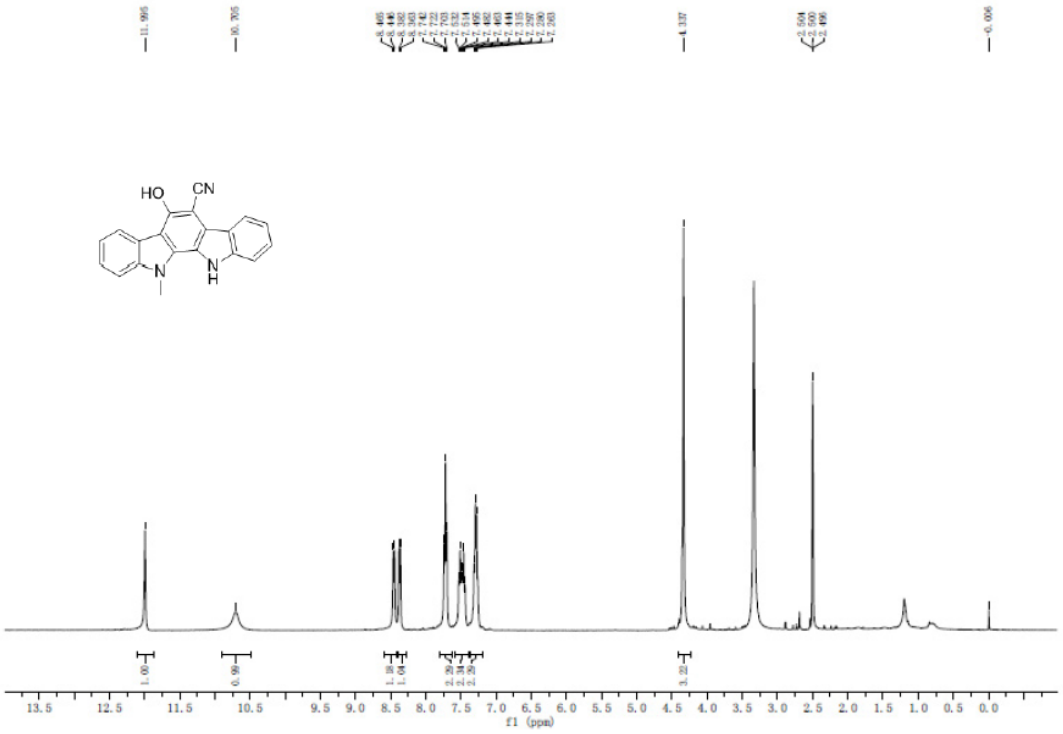
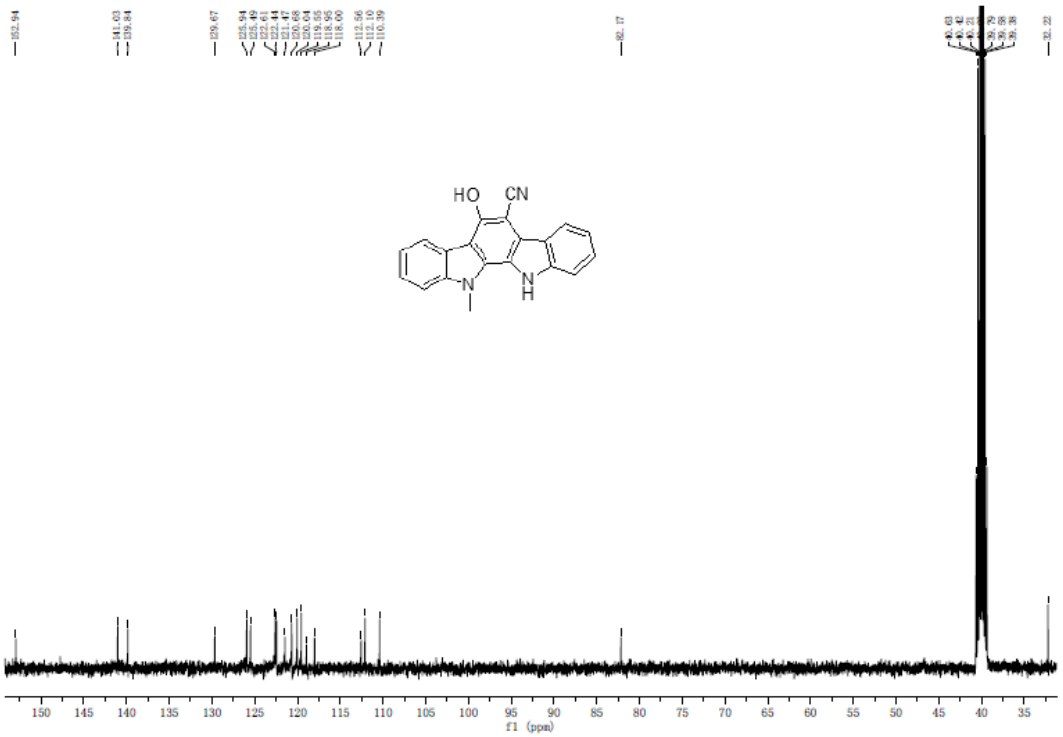
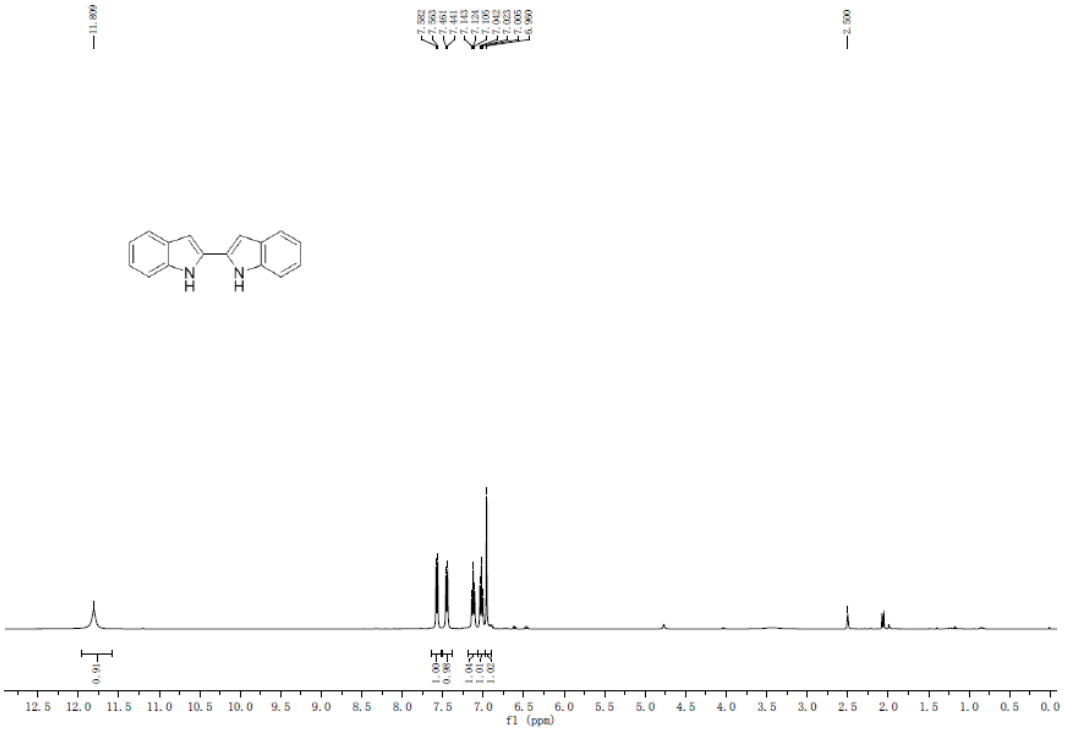
29.84
O
CN
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


HO
CN
N
H
f1 (ppm)


HO
CN
N
H
f1 (ppm)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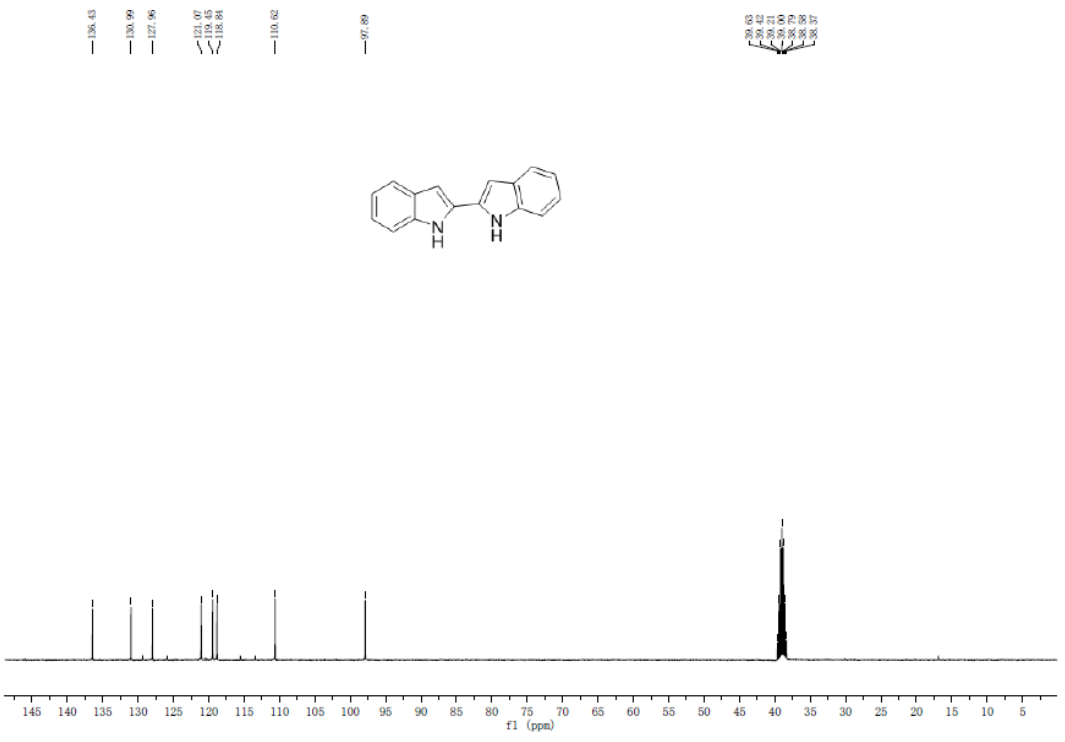
7.461
7.441
7.145
7.124
7.105
7.062
7.043
7.005
6.960
2.500
0.91
1.00
0.98
1.04
1.01
1.02
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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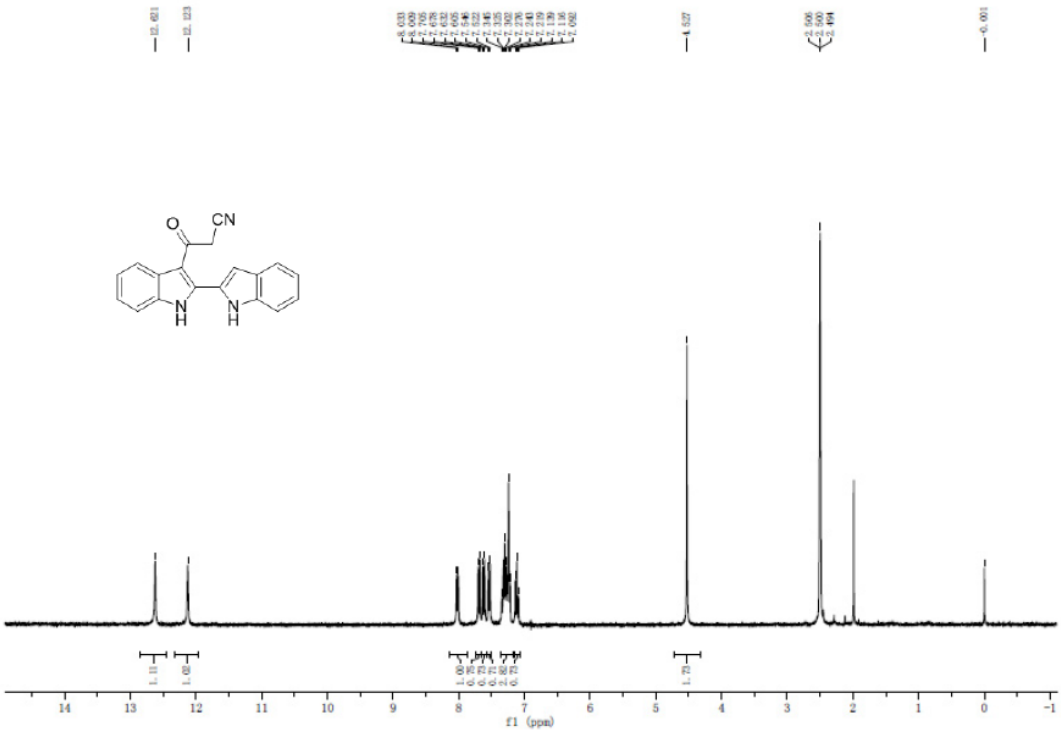
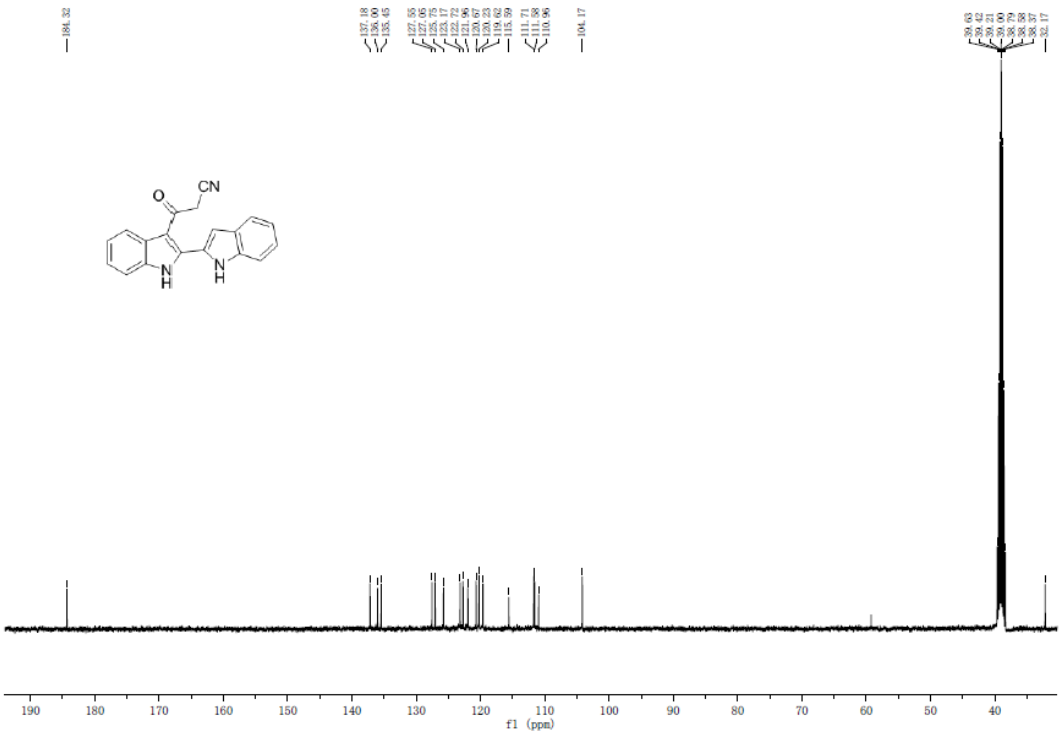
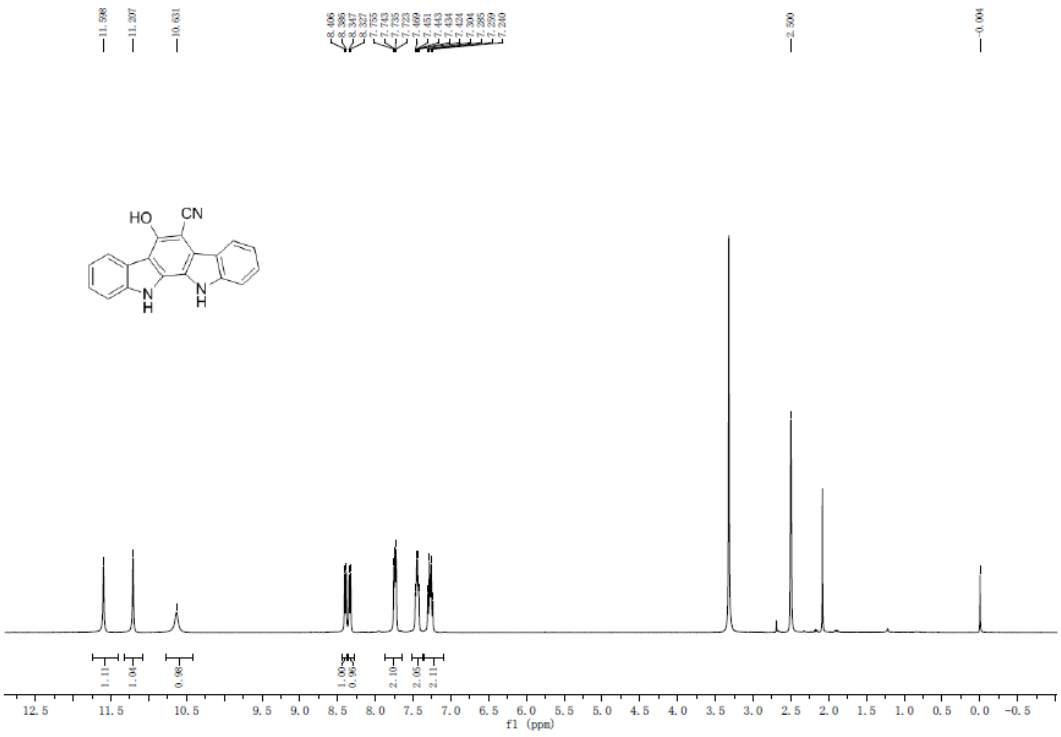
121.07
119.45
118.84
110.62
97.89
39.63
39.42
39.21
39.00
38.79
38.58
38.37
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


O
CN
N
H
N
H
f1 (ppm)


O
CN
N
H
N
H
f1 (ppm)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8.406
8.395
8.347
8.327
7.755
7.743
7.735
7.723
7.469
7.451
7.443
7.434
7.424
7.304
7.295
7.289
7.249
2.500
-0.004
HO
CN
N
H
N
H
1.11
1.04
0.98
1.00
0.96
2.10
2.05
2.11
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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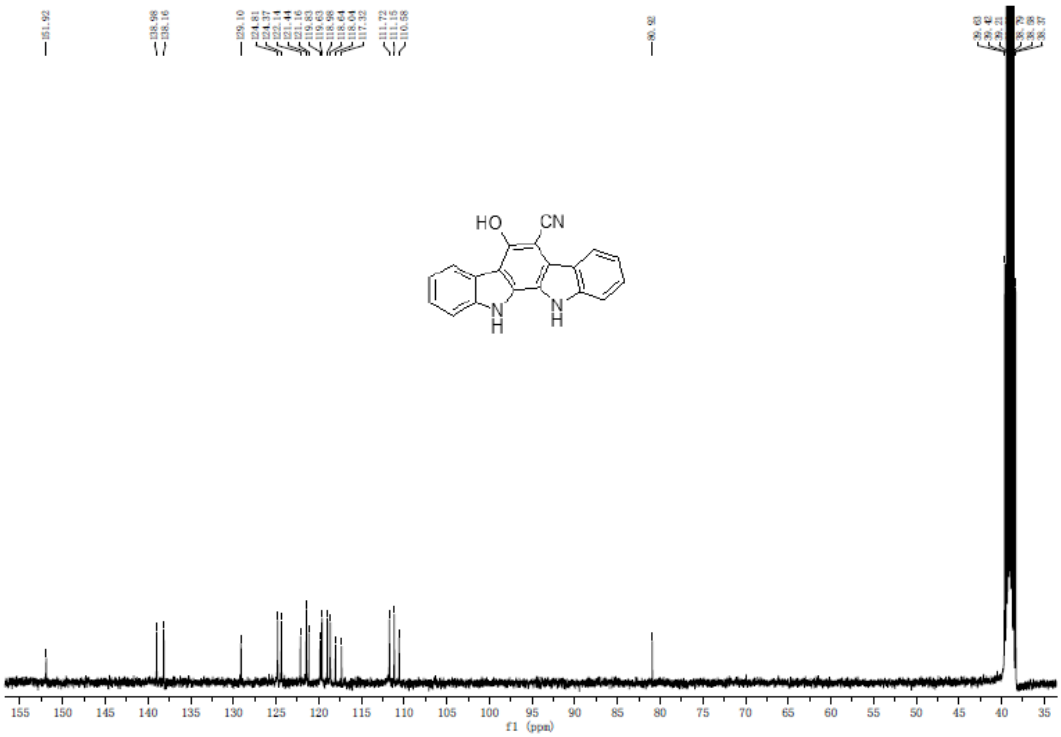
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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121.44
121.16
120.80
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118.98
118.64
118.04
117.32
111.72
111.15
110.58
80.92
39.63
39.42
39.21
38.79
38.09
38.37
HO
CN
N
H
N
H
155
150
145
140
135
130
125
120
115
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100
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90
85
80
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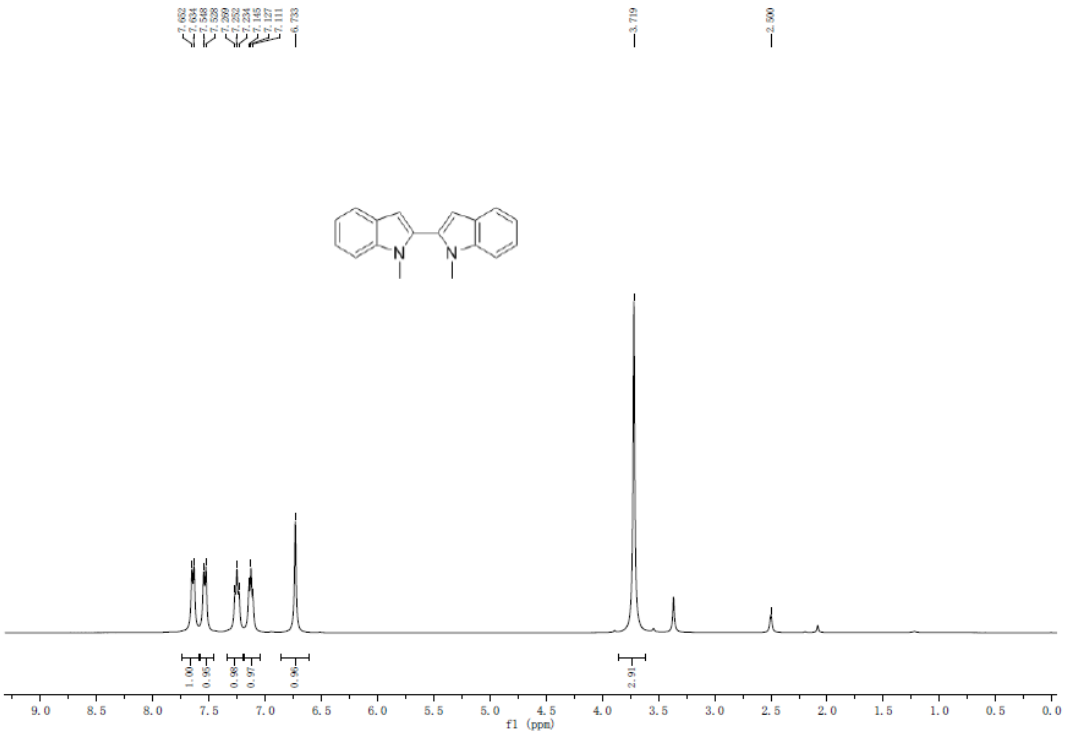
60
55
50
45
40
35
f1 (ppm)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7.536
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7.252
7.234
7.145
7.137
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3.719
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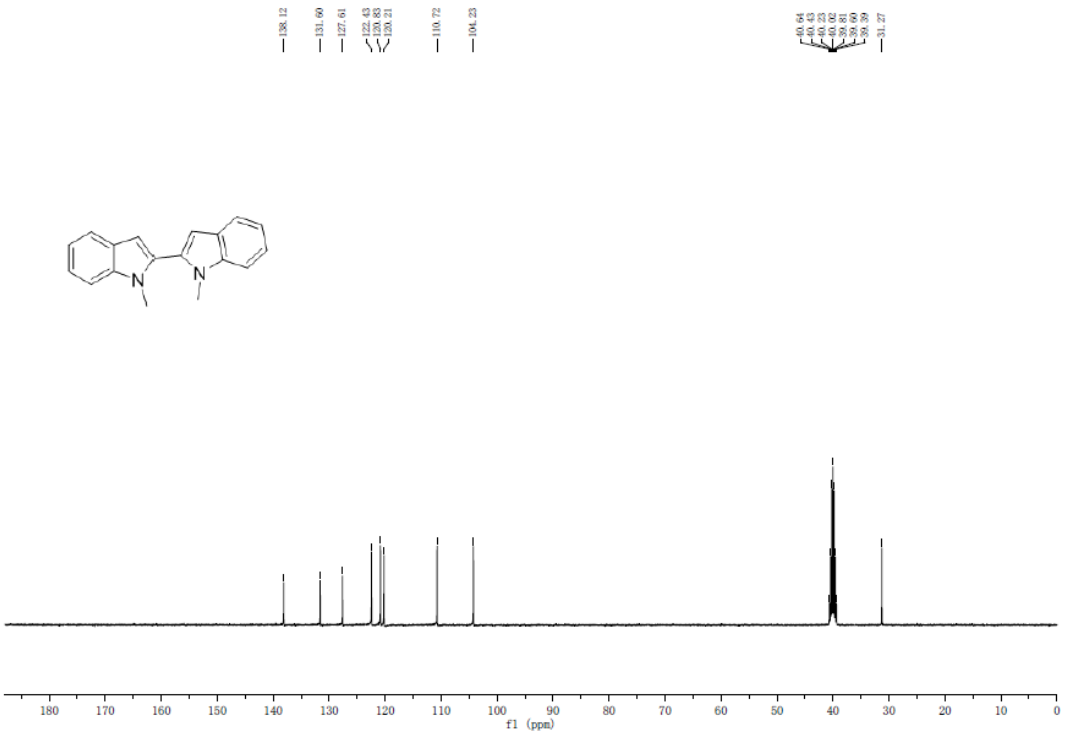
1.00
0.95
0.86
0.97
0.96
2.91
f1 (ppm)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40.23
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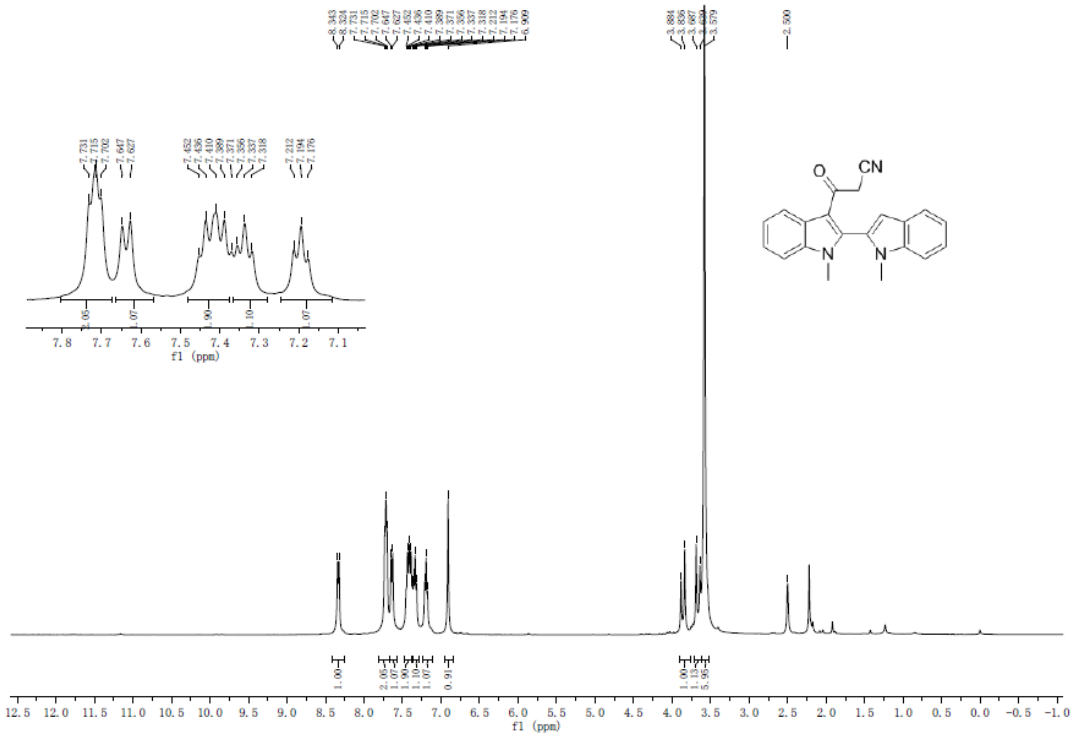
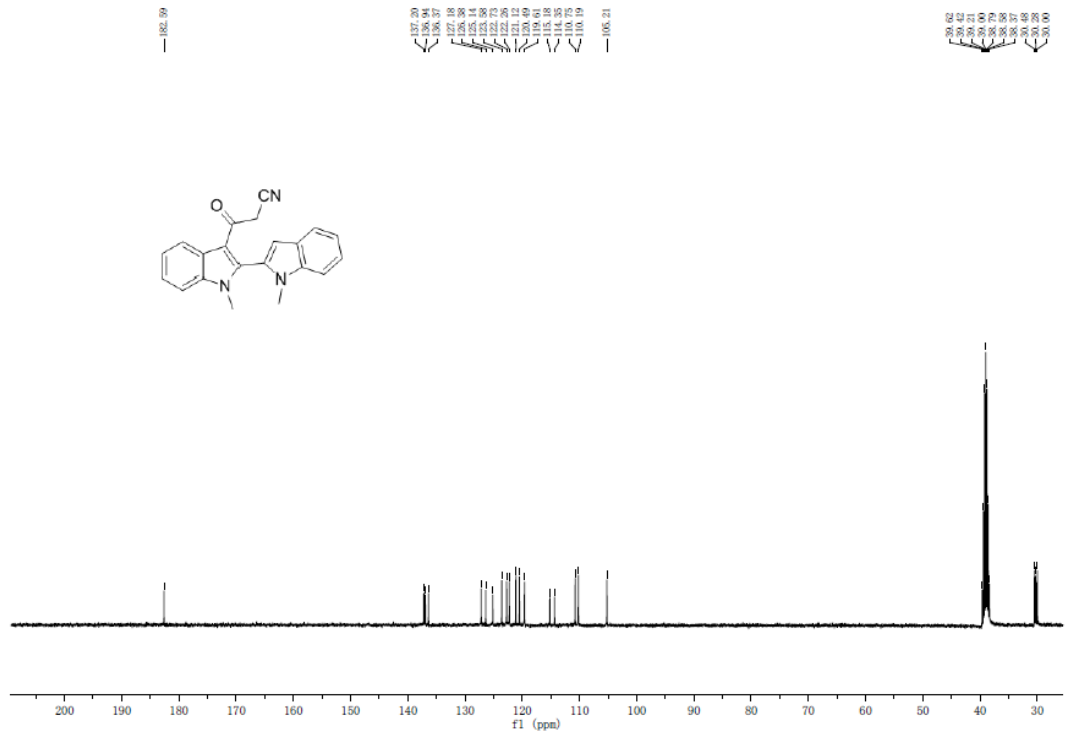
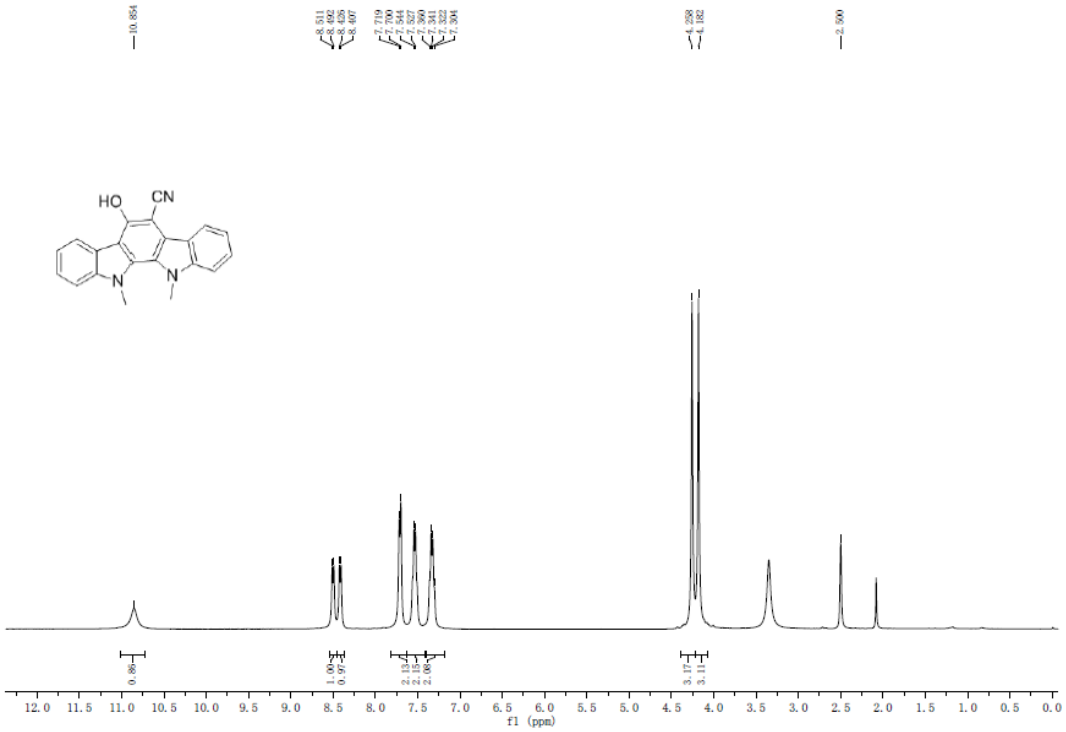
39.39
31.27
f1 (ppm)


f1 (ppm)


f1 (ppm)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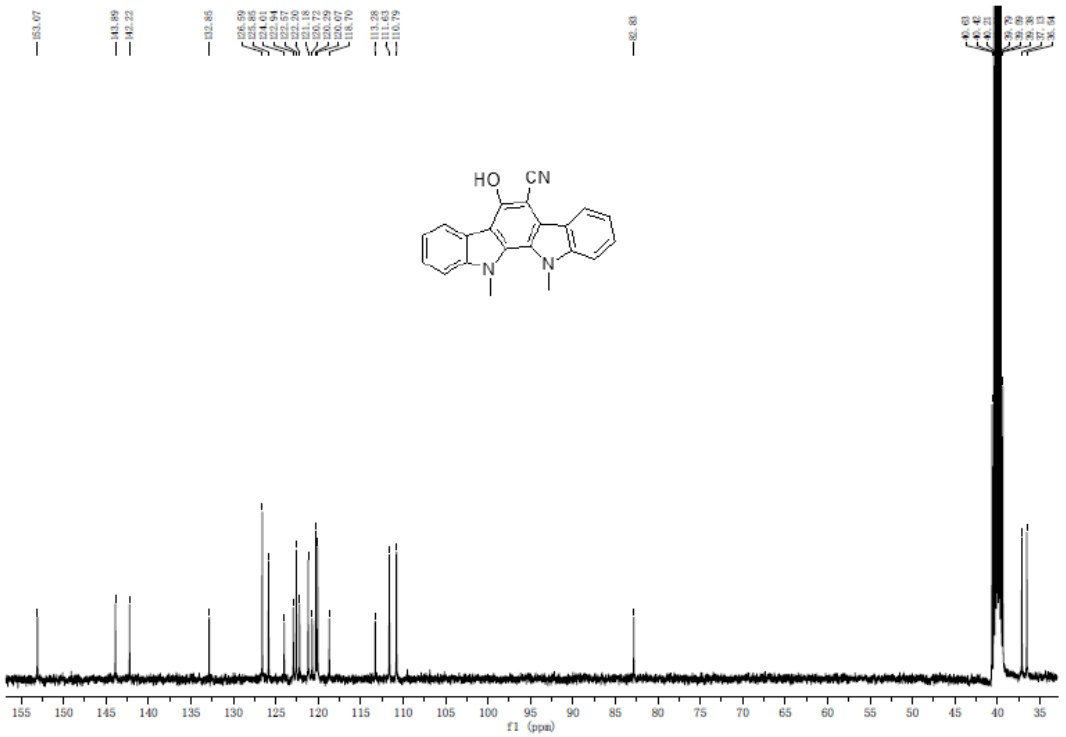
7.544
7.527
7.368
7.341
7.322
7.304
4.258
4.182
2.500
HO
CN
N
N
0.86
1.00
0.97
2.13
2.15
2.08
3.17
3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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143.89
142.22
132.85
126.59
125.85
124.61
122.94
122.57
122.30
121.18
120.72
120.09
120.07
118.70
113.28
111.63
110.79
82.83
40.63
40.42
40.21
39.79
39.59
39.38
39.17
37.13
36.54
HO
CN
N
N
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)