Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Reaction Conditions-Dependent Divergent Synthesis of Spirooxindoles and Bisoxindoles

Guo-Shu Chen,[a] Yu-Bo Fang,[a] Zhi Ren,[*b] Xu Tian,[c] and Yun-Lin Liu[*a]

Email: ylliu@gzhu.edu.cn

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1. General Information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 or DPX-500 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

Anhydrous solvents such as CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, THF, toluene and EtOAc were purchased from Energy Chemical. Unless otherwise stated, all purchased reagents were used without further purification. All reactions involving air- or moisture-sensitive compounds were carried out under nitrogen atmosphere in dried Schlenk tube. The MBH carbonates **1**,[1] 3-formylchromones **4**,[2] *β*-isocupreidine (*β*-ICD) and its derivatives[3] were prepared using the literature procedures.

All computational studies were performed with GAUSSIAN 16 suite.[4] The gas-phase calculations were conducted on M06-2x functional,[5] with the basis set 6-31G(d). All optimized structures in gas-phase were confirmed by frequency calculations, and intermediates have no negative frequency and transition states have only one negative frequency. In addition, transition states were verified by intrinsic reaction coordinate analysis (IRC) calcutions. The effect of solvent was considered by the SMD solvent model.[6] The solution-phase calculations were performed using the single point calculation on the gas-phase geometries with the same functional using a larger basis set 6-311+G(2d,p).[7] Solution-state Gibbs free energies of all structures were corrected by using the gas-phase Gibbs free energy correction, and all these energies correspond to the reference state of 1 atmosphere at 298 K. The unit of Gibbs free energies is kcal/mol, and the unit of bond length is angstrom (Å). The images are generated by CYLview.

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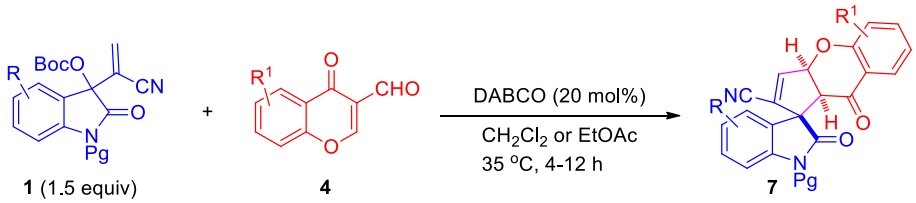
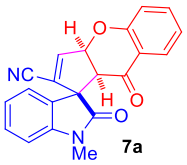
2. General procedure and spectral data of products 7

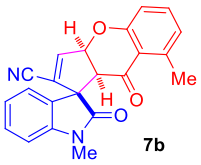


General Procedure: To a 10.0 mL Schlenk tube were successively added MBH carbonates **1** (0.15 mmol), 3-formylchromones **4** (0.1 mmol) and anhydrous CH_2Cl_2 or EtOAc (1.0 mL). The reaction mixture was stirred vigorously at room temperature to ensure full dissolution of 3-formylchromones **4**. Then, 1,4-diaza bicyclo[2.2.2]octane (DABCO, 0.02 mmol) was added in one portion. The reaction mixture was stirred at 35 °C under N_2 atmosphere for 4-12 h, and monitored by TLC. After completion, the reaction mixture was directly subjected to flash chromatography on silica gel using petroleum ether/EtOAc (from 10:1-1:1) as the eluent to afford the benzopyrone fused spirocyclopentene oxindoles **7**.



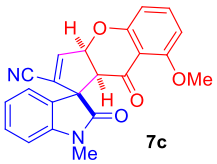
7a

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7a** in 95% yield as a white solid (m.p. 150-152 °C). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.72 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.53 (td, *J* = 9.0, 2.0 Hz, 1H), 7.41 (td, *J* = 8.0, 1.5 Hz, 1H), 7.20-7.15 (m, 3H), 7.06-7.02 (m, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.77 (dd, *J* = 7.5, 2.5 Hz, 1H), 3.59 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.83, 172.04, 159.64, 146.30, 144.26, 136.91, 130.36, 127.07, 126.85, 124.43, 123.65, 122.92, 122.31, 121.53, 118.43, 112.48, 109.23, 80.91, 65.78, 54.88, 26.88. HRMS (ESI): Exact mass calcd for $C_{21}H_{14}N_2NaO_3$ $[M+Na]^+$: 365.0895, Found: 365.0897.



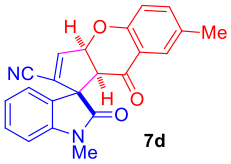
7b

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7b** in 86% yield as a white solid (m.p. 180-182 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 1H), 7.35 (t, *J* = 8.0 Hz 1H), 7.19-7.15 (m, 2H), 7.14 (d, *J* = 2.8 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.68 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.65 (d, *J* = 8.0 Hz, 1H), 3.23 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.72, 172.62, 160.82, 146.13, 144.23, 141.52, 135.42, 130.26, 127.50, 125.90, 124.56, 123.55, 122.83, 121.66, 116.50, 112.54, 109.27, 80.56, 65.43, 57.28, 26.93, 21.67; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_3$ $[M+Na]^+$: 379.1053, Found: 379.1053.



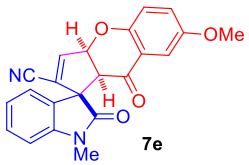
7c

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent**,** affording product **7c** in 84% yield as a white solid (m.p. 190-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.16-7.10 (m, 3H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 5.64 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.80 (s, 3H), 3.66 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.72, 172.63, 161.45, 160.02, 145.78, 144.40, 136.67, 130.07, 127.44, 124.79, 123.33, 122.79, 113.30, 110.64, 109.11, 105.38, 80.77, 65.15, 57.61, 56.05, 26.94; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_4$ $[M+Na]^+$: 395.1002, Found: 395.1001.



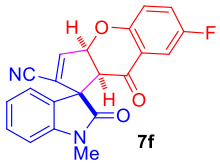
7d

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7d** in 90% yield as a white solid (m.p. 203-205 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.6 Hz, 1H), 7.43-7.38 (m, 1H), 7.33 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.19-7.14 (m, 3H), 6.95-6.91 (m, 2H), 5.73 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.56 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.99, 172.09, 157.65, 146.50, 144.20, 138.03, 131.81, 130.31, 127.13, 126.42. 124.22, 123.63, 122.90, 121.11, 118.17, 112.52, 109.20, 80.77, 65.70, 54.86, 26.87, 20.41; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_3$ $[M+Na]^+$: 379.1053, Found: 379.1049.



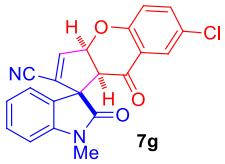
7e

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent**,** affording product **7e** in 82% yield as a white solid (m.p. 165-166 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.39 (m, 1H), 7.20-7.11 (m, 5H), 6.99-6.96 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.73 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.76 (s, 3H), 3.56 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.84, 172.08, 154.62, 154.20, 146.49, 144.21, 130.34, 127.12, 125.94, 124.23, 123.67, 122.92, 121.43, 119.71, 112.50, 109.20, 107.41, 80.81, 65.66, 55.67, 54.78, 26.90; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_4$ $[M+Na]^+$: 395.1002, Found: 395.1001.



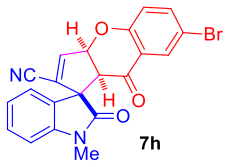
7f

The reaction was run at 35 °C for 4 h by using EtOAc as the solvent, affording product **7f** in 62% yield as a white solid (m.p. 178-180 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 1H), 7.37 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.28-7.22 (m, 1H), 7.20-7.15 (m, 3H), 7.03 (dd, *J* = 8.8, 4.0 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.77 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.57 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.27, 171.96, 157.62 (d, *J* = 241.9 Hz), 155.8 (d, *J* = 1.8 Hz), 146.07, 144.20, 130.50, 126.81, 124.52, 124.47 (d, *J* = 24.4 Hz), 123.77, 122.93, 121.81 (d, *J* = 6.8 Hz) , 120.18 (d, *J* = 7.5 Hz), 112.22 (d, *J* = 27.9 Hz), 111.85, 109.34, 81.07, 65.80, 54.42 (d, *J* = 1.3 Hz), 26.92; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}FN_2NaO_3$ $[M+Na]^+$: 383.0802, Found: 383.0801.



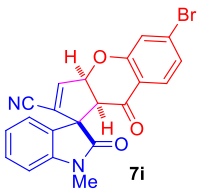
7g

The reaction was run at 35 °C for 4 h by using EtOAc as the solvent, affording product **7g** in 55% yield as a white solid (m.p. 207-208 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.8 Hz, 1H), 7.46 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.44-7.40 (m, 1H), 7.20-7.17 (m, 2H), 7.15 (d, *J* = 2.8 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.77 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.85, 171.90, 158.03, 145.96, 144.18, 136.76, 130.52, 127.78, 126.72, 126.15, 124.56, 123.79, 122.94, 121.94, 120.14, 112.31, 109.35, 81.11, 65.89, 54.29, 26.91; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ $[M+Na]^+$: 399.0507, Found: 399.0512.



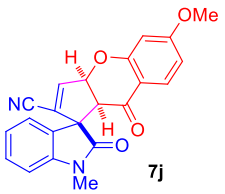
7h

The reaction was run at 35 °C for 4 h by using EtOAc as the solvent, affording product **7h** in 65% yield as a white solid (m.p. 185-187 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.4 Hz, 1H), 7.59 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.46-7.39 (m, 1H), 7.19-7.17 (m, 2H), 7.15 (d, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.76 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.58 (d, *J* = 7.6 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.70, 171.88, 158.48, 145.94, 145.90, 144.16, 139.53, 130.52, 129.22, 126.68, 124.55, 123.79, 122.93, 122.38, 120.45, 114.95, 112.30, 109.35, 81.09, 65.89, 54.24, 26.92; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ $[M+Na]^+$: 443.0002, Found: 442.9993.



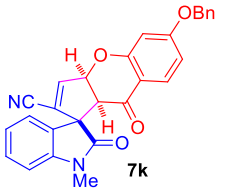
7i

The reaction was run at 35 °C for 4 h by using EtOAc as the solvent, affording product **7i** in 67% yield as a white solid (m.p. 215-217 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.24-7.23 (m, 1H), 7.20-7.15 (m, 4H), 6.93 (d, *J* = 7.6 Hz, 1H), 5.78 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.58 (d, *J* = 7.6 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.99, 171.88, 159.77, 144.19, 131.64, 130.50, 128.02, 126.74, 125.92, 124.68, 123.78, 122.94, 121.60, 120.08, 112.32, 109.33, 81.33, 65.87, 54.42, 26.91; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ $[M+Na]^+$: 443.0002, Found: 443.0010.



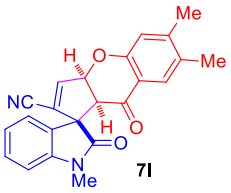
7j

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7j** in 71% yield as a white solid (m.p. 165-167 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (d, *J* = 2.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.19 (dt, *J* = 7.6 Hz,1.0 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.64 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 5.90 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.93 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.89, 172.72, 166.62, 162.11, 149.40, 144.32, 130.38, 128.52, 128.22, 124.06, 123.78, 122.28, 115.48, 113.72, 110.71, 109.73, 101.69, 82.19, 65.63, 56.41, 54.02, 27.00; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_4$ $[M+Na]^+$: 395.1002, Found: 395.0994.



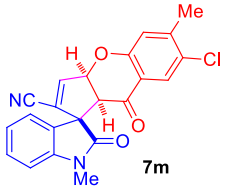
7k

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7k** in 83% yield as a white solid (m.p. 232-234 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 1H), 7.42-7.36 (m, 6H), 7.20-7.14 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.66 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 5.75 (dd, *J* = 7.6, 2.8 Hz, 1H), 5.09 (s, 2H), 3.53 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.77, 171.98, 165.95, 161.70, 146.31, 144.24, 135.68, 130.31, 128.74, 128.37, 127.52, 127.08, 124.55, 123.65, 122.92, 115.30, 112.53, 111.47, 109.20, 102.07, 81.20, 70.43, 65.61, 54.50, 26.90; HRMS (ESI): Exact mass calcd for $C_{28}H_{20}N_2NaO_4$ $[M+Na]^+$: 471.1315, Found: 471.1316.



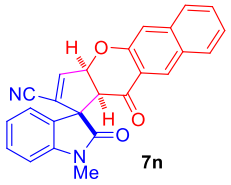
7l

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7l** in 65% yield as a white solid (m.p. 160-162 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.43-7.38 (m, 1H), 7.20-7.14 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 5.72 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.53 (d, *J* = 7.6 Hz, 1H), 3.17 (s, 3H), 2.26 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.34, 172.06, 157.94, 147.84, 146.64, 144.24, 130.99, 130.28, 127.18, 126.80, 124.25, 123.63, 122.92, 119.14, 118.79, 112.58, 109.18, 80.73, 65.66, 54.76, 26.88, 20.60, 18.80; HRMS (ESI): Exact mass calcd for $C_{23}H_{18}N_2NaO_3$ $[M+Na]^+$: 393.1210, Found: 393.1212.



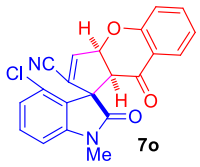
7m

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7m** in 72% yield as a white solid (m.p. 150-152 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.44-7.39 (m, 1H), 7.19-7.15 (m, 3H), 6.94-6.92 (m, 2H), 5.75 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.54 (d, *J* = 7.6 Hz, 1H), 3.17 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.40, 171.88, 157.87, 146.34, 146.13, 144.20, 130.47, 128.46, 126.79, 126.51, 124.55, 123.77, 122.94, 120.39, 120.07, 112.39, 109.31, 81.03, 65.80, 54.25, 26.91, 20.95; HRMS (ESI): Exact mass calcd for $C_{22}H_{15}ClN_2NaO_3$ $[M+Na]^+$: 413.0663, Found: 413.0659.



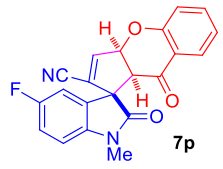
7n

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7n** in 66% yield as a white solid (m.p. 192-194 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.66-7.61 (m, 1H), 7.57-7.53 (m, 1H), 7.45-7.40 (m, 2H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.24-7.16 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.95 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.70 (d, *J* = 8.4 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.92, 171.93, 158.03, 146.15, 144.26, 137.93, 130.38, 130.10, 127.86, 127.01, 126.42, 124.79, 124.73, 123.88, 123.68, 122.98, 121.87, 121.21, 115.86, 112.52, 109.25, 81.59, 65.85, 54.48, 26.88; HRMS (ESI): Exact mass calcd for $C_{25}H_{16}N_2NaO_3$ $[M+Na]^+$: 415.1053, Found: 415.1055.



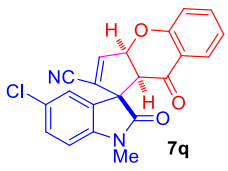
7o

The reaction was run at 35 °C for 4 h by using EtOAc as the solvent, affording product **7o** in 64% yield as a white solid (m.p. 170-172 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.06-7.02 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.83 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.42, 171.66, 159.66, 147.32, 146.00, 136.97, 131.61, 130.63, 126.80, 124.27, 122.73, 122.31, 121.61, 118.46, 112.33, 107.76, 80.87, 66.10, 51.06, 27.15; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ $[M+Na]^+$: 399.0507, Found: 399.0508.



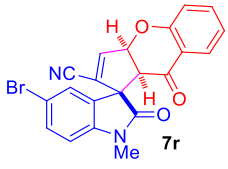
7p

The reaction was run at 35 °C for 12 h by using EtOAc as the solvent, affording product **7p** in 86% yield as a white solid (m.p. 150-151 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56-7.51 (m, 1H), 7.20 (d, *J* = 2.8 Hz, 1H), 7.13 (td, *J* = 8.8, 2.8 Hz, 1H), 7.07-7.03 (m, 2H), 6.96 (dd, *J* = 7.2, 2.4 Hz, 1H), 6.87 (dd, *J* = 8.8, 4.0 Hz, 1H), 5.77 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.68, 171.78, 159.67 (d, *J* = 241.6 Hz), 159.64, 146.75, 140.22, 137.10, 128.44 (d, *J* = 7.8 Hz), 126.88, 123.83, 122.43, 121.43, 118.47, 116.79 (d, *J* = 23.2 Hz), 112.26, 111.30 (d, *J* = 25.2 Hz), 109.96 (d, *J* = 8.1 Hz), 80.74, 65.91, 54.81, 27.06; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}FN_2NaO_3$ $[M+Na]^+$: 383.0802, Found: 383.0810.



7q

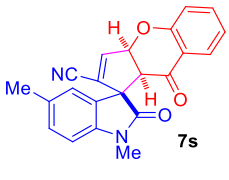
The reaction was run at 35 °C for 8 h by using EtOAc as the solvent, affording product **7q** in 64% yield as a white solid (m.p. 185-187 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.56-7.51 (m, 1H), 7.39 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.19 (s, 2H), 7.07-7.03 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.76 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.57 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.66, 171.68, 159.62, 146.81, 142.83, 137.09, 130.37, 128.99, 128.64, 126.87, 123.70, 123.63, 122.45, 121.45, 118.46, 112.25, 110.22, 80.72, 65.65, 54.86, 27.03; Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ $[M+Na]^+$: 399.0507, Found: 399.0502.



7r

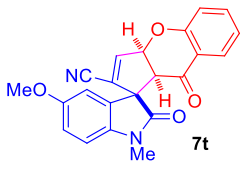
The reaction was run at 35 °C for 8 h by using EtOAc as the solvent, affording product **7r** in 63% yield as a white solid (m.p. 195-196 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.56-7.52 (m, 2H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.20 (d, *J* = 2.8 Hz, 1H), 7.07-7.03 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.77 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.57 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.68, 171.60, 159.63,

146.83, 143.33, 137.12, 133.27, 128.99, 126.90, 126.36, 123.72, 122.47, 121.46, 118.48, 116.16, 112.26, 110.70, 80.72, 65.58, 54.89, 27.03; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ $[M+Na]^+$: 443.0002, Found: 442.9995.



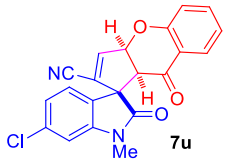
7s

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7s** in 88% yield as a white solid (m.p. 180-181 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55-7.50 (m, 1H), 7.20 (d, *J* = 9.2 Hz, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.05-7.02 (m, 2H), 7.01 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.76 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.57 (d, *J* = 7.6 Hz, 1H), 3.16 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.92, 171.95, 159.64, 146.19, 141.84, 136.91, 133.29, 130.70, 126.95, 126.85, 124.62, 123.74, 122.28, 121.49, 118.42, 112.58, 108.97, 80.91, 65.87, 54.82, 26.91, 21.16; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_3$ $[M+Na]^+$: 379.1053, Found: 379.1055.



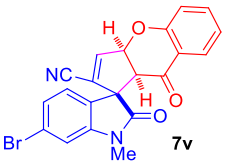
7t

The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7t** in 91% yield as a white solid (m.p. 105-107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.05-7.02 (m, 2H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 5.76 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.80 (s, 3H), 3.56 (d, *J* = 8.0 Hz, 1H), 3.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.82, 171.65, 159.62, 156.70, 146.35, 137.58, 136.93, 128.18, 126.85, 124.40, 122.30, 121.45, 118.42, 114.31, 112.49, 110.58, 109.66, 80.87, 66.12, 55.77, 54.86, 26.97; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_4$ $[M+Na]^+$: 395.1002, Found: 395.1005.



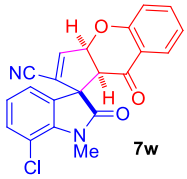
7u

The reaction was run at 35 °C for 8 h by using EtOAc as the solvent, affording product **7u** in 72% yield as a white solid (m.p. 160-162 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56-7.51 (m, 1H), 7.19 (d, *J* = 2.8 Hz, 1H), 7.17-7.11 (m, 2H), 7.07-7.03 (m, 2H), 6.94 (d, *J* = 1.6 Hz, 1H), 5.77 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.72, 172.07, 159.63, 146.68, 145.40, 137.11, 136.33, 126.89, 125.36, 123.94, 123.90, 123.59, 122.44, 121.44, 118.46, 112.30, 110.11, 80.72, 65.32, 54.86, 27.04; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ $[M+Na]^+$: 399.0507, Found: 399.0513.



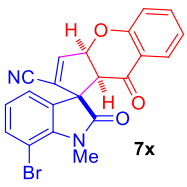
7v

The reaction was run at 35 °C for 8 h by using EtOAc as the solvent, affording product **7v** in 65% yield as a white solid (m.p. 205-206 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 7.09 (s, 1H), 7.04 (t, *J* = 8.0 Hz, 3H), 5.75 (d, *J* = 7.6 Hz, 1H), 3.54 (d, *J* = 8.0 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.69, 171.94, 159.62, 146.72, 145.47, 137.10, 126.88, 126.52, 125.93, 124.24, 124.16, 123.77, 122.43, 121.44, 118.45, 112.86, 112.29, 80.72, 65.37, 54.82, 27.02; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ $[M+Na]^+$: 443.0002, Found: 443.0007.



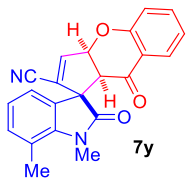
7w

The reaction was run at 35 °C for 8 h by using EtOAc as the solvent, affording product **7w** in 73% yield as a white solid (m.p. 185-186 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.56-7.52 (m, 1H), 7.36-7.32 (m, 1H), 7.19 (d, *J* = 2.8 Hz, 1H), 7.08-7.03 (m, 4H), 5.77 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.68, 172.38, 159.63, 146.69, 140.24, 137.11, 132.73, 129.75, 126.90, 124.33, 123.97, 122.46, 121.57, 121.47, 118.46, 116.63, 112.27, 80.74, 65.38, 55.31, 30.35; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ $[M+Na]^+$: 399.0507, Found: 399.0516.

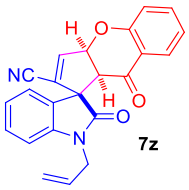


7x

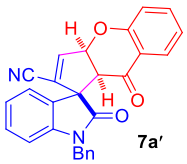
The reaction was run at 35 °C for 12 h by using EtOAc as the solvent, affording product **7x** in 62% yield as a white solid (m.p. 190-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55-7.50 (m, 2H), 7.18 (d, *J* = 2.8 Hz, 1H), 7.11-6.99 (m, 4H), 5.76 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.56 (d, *J* = 4.8 Hz, 1H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.65, 172.58, 159.61, 146.71, 141.65, 137.08, 136.04, 130.04, 126.88, 124.67, 123.94, 122.45, 122.13, 121.46, 118.45, 112.26, 103.45, 80.72, 65.33, 55.34, 30.56; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ $[M+Na]^+$: 443.0002, Found: 443.0007.



The reaction was run at 35 °C for 12 h by using EtOAc as the solvent, affording product **7y** in 89% yield as a white solid (m.p. 198-200 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55-7.49 (m, 1H), 7.16 -7.10 (m, 2H), 7.06-6.99 (m, 4H), 5.76 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H), 3.44 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.96, 172.76, 159.63, 146.11, 141.95, 136.88, 134.10, 127.65, 126.83, 124.69, 123.54, 122.28, 121.54, 120.86, 120.84, 118.41, 112.55, 80.93, 65.38, 55.25, 30.24, 18.93; HRMS (ESI): Exact mass calcd for $C_{22}H_{16}N_2NaO_3$ $[M+Na]^+$: 379.1053, Found: 379.1056.

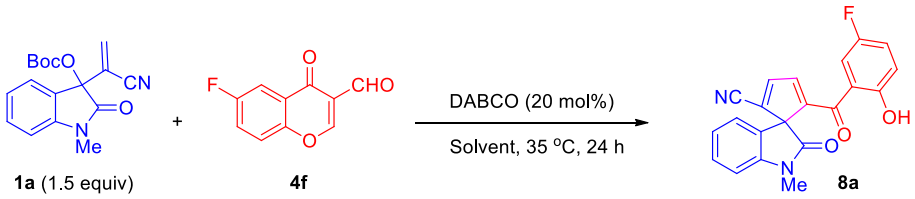


The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7z** in 85% yield as a white solid (m.p. 176-178 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.37 (td, *J* = 7.6, 1.6 Hz, 1H), 7.21-7.14 (m, 3H), 7.05-7.01 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.81-5.72 (m, 2H), 5.29-5.20 (m, 2H), 4.35-4.22 (m, 2H), 3.61 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.70, 171.87, 159.62, 146.28, 143.37, 136.93, 130.24, 130.24, 127.01, 126.84, 124.46, 123.64, 123.00, 122.29, 121.51, 118.38, 117.67, 112.49, 110.20, 80.92, 65.78, 54.81, 42.77; HRMS (ESI): Exact mass calcd for $C_{23}H_{16}N_2NaO_3$ $[M+Na]^+$: 391.1053, Found: 391.1054.



The reaction was run at 35 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **7a′** in 86% yield as a white solid (m.p. 184-186 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.33-7.28 (m, 2H), 7.26-7.22 (m, 4H), 7.19-7.15 (m, 2H), 7.12-7.08 (m, 1H), 7.05-7.01 (m, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.76 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.90-4.82 (m, 2H), 3.63 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.68, 172.28, 159.62, 146.36, 143.24, 136.97, 134.64, 130.24, 128.75, 127.63, 127.01, 126.99, 126.83, 124.46, 123.01, 122.28, 121.47, 118.38, 110.38, 112.52, 80.93, 65.85, 54.77, 44.38; HRMS (ESI): Exact mass calcd for $C_{27}H_{18}N_2NaO_3$ $[M+Na]^+$: 441.1210, Found: 441.1207.

3. Optimization of the reaction conditions for the preparation of product 8a[a-b]

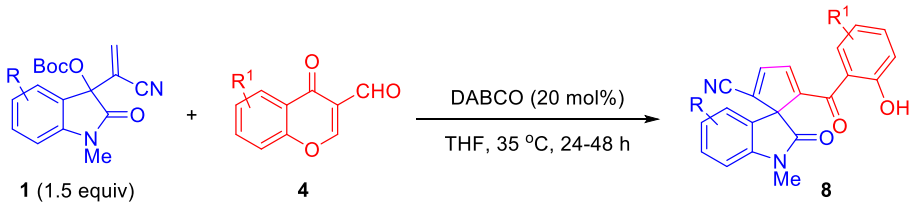


1a (1.5 equiv) **4f** **8a**

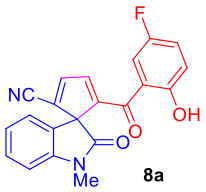
Entry[a]	Solvent	Yield[b] (%)
1	CH_2Cl_2	40
2	$ClCH_2CH_2Cl$	28
3	Toluene	21
4	EtOAc	35
5	CH_3CN	28
6	THF	72
7	Dioxane	47

[a]Reaction conditions: **1a** (0.15 mmol), **4f** (0.10 mmol) and DABCO (20 mol%) in solvent (1.0 mL) were stirred at 35 °C under N_2 atmosphere. [b] Isolated yields after purification by column chromatography.

4. General procedure and spectral data of products 8.

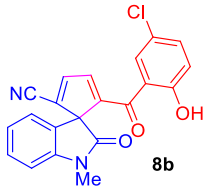


General Procedure: To a 10.0 mL Schlenk tube were successively added MBH carbonates **1** (0.15 mmol), 3-formylchromones **4** (0.1 mmol) and anhydrous THF (1.0 mL). The reaction mixture was stirred vigorously at room temperature to ensure full dissolution of 3-formylchromones **4**. Then, 1,4-diaza bicyclo[2.2.2]octane (DABCO, 0.02 mmol) was added in one portion. The reaction mixture was stirred at 35 °C under N_2 atmosphere for 24-48 h, and monitored by TLC. After completion, the reaction mixture was directly subjected to flash chromatography on silica gel using petroleum ether/EtOAc (from 10:1-1:1) as the eluent to afford the spirocyclopentadiene 2-oxindoles **8** incorporating a 2-hydroxybenzoyl moiety.



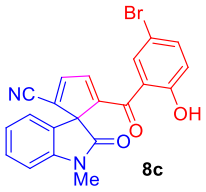
8a

The reaction was run at 35 °C for 24 h by using THF as the solvent, affording product **8a** in 72% yield as a yellow solid (m.p. 190-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.42-7.38 (m, 3H), 7.25-7.21 (m, 1H), 7.04-7.00 (m, 2H), 6.95 (dd, *J* = 9.2, 4.8 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.26 (d, *J* =2.5 Hz), 168.28, 158.61 (d, *J* =1.5 Hz), 155.99, 153.60, 149.36, 146.46, 145.29, 143.11, 130.55, 125.35, 124.24 (d, *J* =23.4 Hz), 123.25 (d, *J* = 26.0 Hz), 120.29, 120.15 (d, *J* = 26.0 Hz), 118.74 (d, *J* = 6.3 Hz), 115.66 (d, *J* = 23.8 Hz), 112.82, 109.78, 71.11, 27.81; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}FN_2NaO_3$ $[M+Na]^+$: 383.0802, Found: 383.0795.



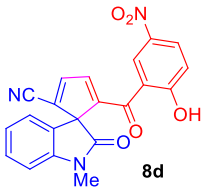
8b

The reaction was run at 35 °C for 48 h by using THF as the solvent, affording product **8b** in 67% yield as a yellow solid (m.p. 192-193 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 7.66 (d, *J* = 2.8 Hz, 1H), 7.51 (d, *J* = 3.2 Hz, 1H), 7.45-7.38 (m, 3H), 7.05-7.01 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.0 Hz, 1H), 3.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.17, 168.25, 160.88, 149.24, 146.47, 145.28, 143.44, 136.49, 130.55, 129.66, 125.47, 123.84, 123.39, 123.18, 120.40, 120.27, 119.92, 112.81, 109.77, 71.11, 27.82; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ $[M+Na]^+$: 399.0507, Found: 399.0509.



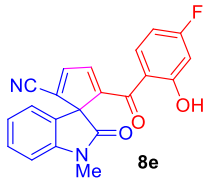
8c

The reaction was run at 35 °C for 24 h by using THF as the solvent, affording product **8c** in 66% yield as a yellow solid (m.p. 195-196 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.01 (s, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.52 (d, *J* = 2.8 Hz, 1H), 7.42-7.38 (m, 2H), 7.05-7.01 (m, 2H), 6.92-6.87 (m, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.06, 168.25, 161.31, 149.23, 146.48, 145.27, 143.52, 139.26, 132.64, 130.56, 125.50, 123.40, 123.20, 120.78, 120.58, 120.27, 112.80, 110.70, 109.77, 71.11, 27.83; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ $[M+Na]^+$: 443.0002, Found: 443.0003.



8d

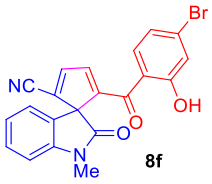
The reaction was run at 35 °C for 24 h by using THF as the solvent, affording product **8d** in 88% yield as a yellow solid (m.p. 215-217 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 8.71 (d, *J* = 2.8 Hz, 1H), 8.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.55-7.54 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 9.2 Hz, 1H), 7.06-7.02 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.99, 168.07, 167.07, 148.52, 146.39, 145.23, 144.73, 139.66, 131.13, 130.71, 126.86, 126.33, 123.53, 123.30, 120.05, 119.84, 118.07, 112.60, 109.87, 71.22, 27.87; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}N_3NaO_5$ $[M+Na]^+$: 410.0747, Found: 410.0745.



8e

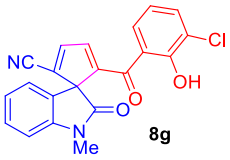
The reaction was run at 35 °C for 24 h by using THF as the solvent, affording product **8e** in 75% yield as a yellow solid (m.p. 172-174 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 1H), 7.77-7.73 (m, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.39 (td, *J* = 7.6, 0.8 Hz, 1H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.03-6.99 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.66-6.61 (m, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.20, 167.66 (d, *J* = 64.2 Hz), 168.31, 165.14 (d, *J* = 14.4 Hz), 149.65, 146.47, 145.29, 142.44, 133.15 (d, *J* = 11.8 Hz), 130.51, 124.97, 123.21 (d, *J* = 23.8 Hz), 120.31, 116.46, 112.88, 109.75, 107.45 (d, *J* = 22.8 Hz), 105.43 (d, *J* = 23.7 Hz), 71.12, 27.80; HRMS

(ESI): Exact mass calcd for $C_{21}H_{13}FN_2NaO_3$ [M+Na]$^+$: 383.0802, Found: 383.0804.



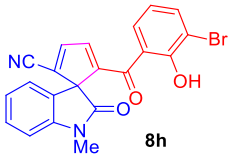
8f

The reaction was run at 35 °C for 48 h by using THF as the solvent, affording product **8f** in 70% yield as a yellow solid (m.p. 188-189 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.36 (d, *J* = 2.8 Hz, 1H), 7.17 (d, *J* = 1.6 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.04-6.99 (m, 2H), 6.87 (dd, *J* = 8.0, 1.2 Hz 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.68, 168.26, 162.87, 149.55, 146.43, 145.31, 142.79, 131.59, 131.45, 130.55, 125.24, 123.37, 123.10, 122.66, 121.97, 120.30, 118.28, 112.85, 109.79, 71.12, 27.82; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ [M+Na]$^+$: 443.0002, Found: 442.9991.



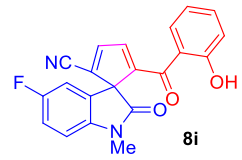
8g

The reaction was run at 35 °C for 48 h by using THF as the solvent, affording product **8g** in 72% yield as a yellow solid (m.p. 180-182 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (s, 1H), 7.66 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.42-7.37 (m, 2H), 7.04-6.99 (m, 2H), 6.91-6.86 (m, 2H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.01, 168.17, 157.98, 149.37, 146.38, 145.29, 143.33, 136.61, 130.56, 129.23, 125.36, 123.35, 123.30, 123.06, 120.39, 120.22, 119.17, 112.82, 109.81, 71.14, 27.84; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ [M+Na]$^+$: 399.0507, Found: 399.0503.



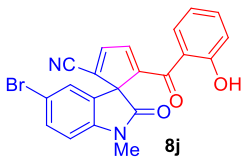
8h

The reaction was run at 35 °C for 48 h by using THF as the solvent, affording product **8h** in 75% yield as a yellow solid (m.p. 187-188 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 7.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.42-7.37 (m, 2H), 7.03-6.99 (m, 2H), 6.87-6.82 (m, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.95, 168.17, 158.83, 149.31, 146.38, 145.30, 143.27, 139.81, 130.57, 130.00, 125.36, 123.36, 123.07, 120.30, 120.22, 119.78, 112.83, 112.47, 109.82, 71.17, 27.84. HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ [M+Na]$^+$: 443.0002, Found: 443.0002.



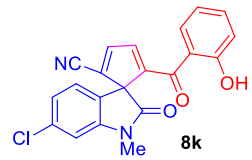
8i

The reaction was run at 35 °C for 24 h by using THF as the solvent, affording product **8i** in 70% yield as a yellow solid (m.p. 175-176 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.53-7.49 (m, 2H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.10 (td, *J* = 8.8, 2.4 Hz, 1H), 7.00-6.91 (m, 3H), 6.65 (dd, *J* = 7.2, 2.4 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.03, 168.12, 162.51, 159.14 (d, *J* = 241.7 Hz), 149.52, 146.87, 142.95, 141.39 (d, *J* = 2.2 Hz), 136.88, 130.69, 124.45, 122.08 (d, *J* = 8.6 Hz), 119.33, 119.17, 118.81, 116.86 (d, *J* = 23.3 Hz), 112.74, 111.35 (d, *J* = 241.7 Hz), 110.27 (d, *J* = 8.1 Hz), 70.96, 27.98; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}FN_2NaO_3$ [M+Na]$^+$: 383.0802, Found: 383.0804.



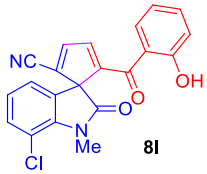
8j

The reaction was run at 35 °C for 48 h by using THF as the solvent, affording product **8j** in 65% yield as a yellow solid (m.p. 192-194 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55-7.48 (m, 3H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.02-6.87 (m, 4H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.88, 167.98, 162.52, 149.56, 146.92, 144.41, 143.09, 136.89, 133.32, 130.69, 126.22, 124.43, 122.66, 119.31, 119.19, 118.82, 115.66, 112.73, 111.07, 70.57, 27.92; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ [M+Na]$^+$: 443.0002, Found: 442.9996.



8k

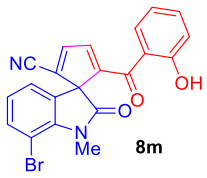
The reaction was run at 35 °C for 48 h by using THF as the solvent, affording product **8k** in 67% yield as a yellow solid (m.p. 174-175 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 7.00-6.97 (m, 2H), 6.94-6.90 (m, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.08, 168.43, 162.52, 149.64, 146.84, 146.48, 142.82, 136.88, 136.36, 130.65, 124.46, 124.00, 123.23, 119.30, 119.13, 118.83, 118.82, 112.77, 110.54, 70.43, 27.91; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ [M+Na]$^+$: 399.0507, Found: 399.0506.



8l

The reaction was run at 35 °C for 48h by using THF as the solvent, affording product **8l** in 74% yield as a yellow solid (m.p. 195-196 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.52-

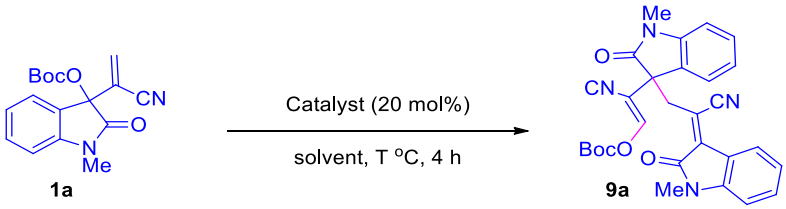
7.48 (m, 2H), 7.38-7.36 (m, 1H), 7.31 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.98 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.94-6.89 (m, 2H), 6.74 (dd, *J* = 7.6, 1.0 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.98, 168.73, 162.53, 149.85, 146.86, 141.34, 136.86, 132.89, 130.63, 124.70, 123.91, 123.01, 121.50, 119.33, 119.12, 118.84, 116.86, 112.74, 70.49, 31.28; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}ClN_2NaO_3$ $[M+Na]^+$: 399.0507, Found: 399.0504.



8m

The reaction was run at 35 °C for 48 h by using THF as the solvent, affording product **8m** in 67% yield as a yellow solid (m.p. 170-171 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.53-7.48 (m, 3H), 7.37 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.96, 168.95, 162.53, 149.89, 146.87, 142.71, 136.86, 136.22, 130.63, 124.74, 124.27, 123.22, 122.02, 119.33, 119.12, 118.84, 112.73, 103.62, 70.47, 31.55; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}BrN_2NaO_3$ $[M+Na]^+$: 443.0002, Found: 442.9995.

5. Optimization of the reaction conditions for the preparation of product 9a[a-b]

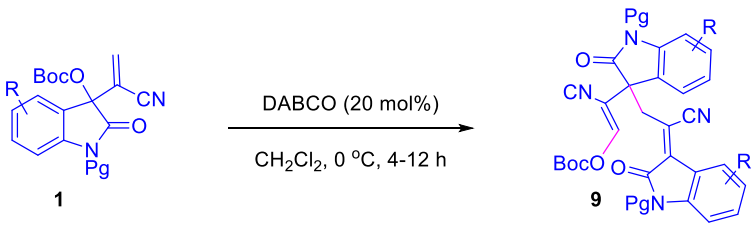


1a **9a**

Entry[a]	Catalyst	Solvent	T/°C	Yield[b] (%)
1	DABCO	CH_2Cl_2	35	55
2	DABCO	$ClCH_2CH_2Cl$	35	45
3	DABCO	Toluene	35	33
4	DABCO	EtOAc	35	40
5	DABCO	THF	35	40
6	DABCO	Dioxane	35	35
7	DABCO	CH_3CN	35	37
8	DABCO	CH_2Cl_2	0	66
9	DABCO	CH_2Cl_2	-10	48
10	DBU	CH_2Cl_2	0	mess
11	TBD	CH_2Cl_2	0	16
12	DMAP	CH_2Cl_2	0	25
13	Et_3N	CH_2Cl_2	0	34

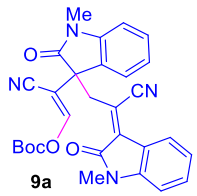
[a]Reaction conditions: **1a** (0.15 mmol) and catalyst (20 mol%) in solvent (1.0 mL) were stirred at the indicated temperature under N_2 atmosphere. [b] Isolated yields after purification by column chromatography.

6. General procedure and spectral data of products 9



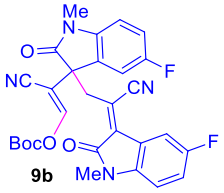
1 **9**

General Procedure: To a solution of MBH carbonates **1** (0.15 mmol) in anhydrous CH_2Cl_2 (1.0 mL) at 0 °C was added DABCO (20 mol%) under N_2 atmosphere. Then, the reaction mixture was kept at this temperature for 4-12 h under stirring, and monitored by TLC. After completion, the reaction mixture was directly subjected to flash chromatography on silica gel using petroleum ether/EtOAc (from 4:1-1:1) as the eluent to afford the bisoxindoles **9**.



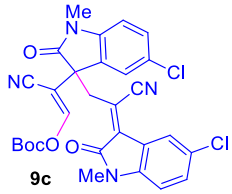
9a

The reaction was run at 0 °C for 4 h by using CH_2Cl_2 as the solvent, affording product **9a** in 66% yield as a yellow solid (m.p. 125-126 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.35 (td, *J* = 7.5, 1.0 Hz, 1H), 7.31 (td, *J* = 7.5, 1.0 Hz, 1H), 7.06-6.99 (m, 2H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 4.82 (d, *J* = 13.5 Hz, 1H), 3.48 (d, *J* = 13.5 Hz, 1H), 3.27 (s, 3H), 3.17 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.50, 165.52, 150.76, 148.82, 144.03, 143.09, 138.87, 132.73, 129.93, 126.82, 124.83, 124.37, 123.18, 122.90, 119.51, 116.62, 113.28, 112.11, 109.01, 108.33, 98.00, 85.86, 50.78, 33.82, 27.47, 26.79, 25.97; HRMS (ESI): Exact mass calcd for $C_{29}H_{26}N_4NaO_5$ [M+Na]$^+$: 533.1795, Found: 533.1800.



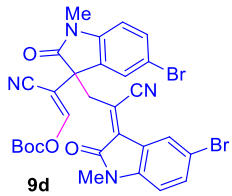
9b

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9b** in 53% yield as a yellow solid (m.p. 112-113 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.79 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.09 (td, *J* = 8.5, 2.5 Hz, 1H), 7.03 (td, *J* = 9.0, 2.5 Hz, 1H), 6.84 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.71 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.86 (d, *J* = 14.0 Hz, 1H), 3.41 (d, *J* = 14.0 Hz, 1H), 3.26 (s, 3H), 3.18 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.05, 165.28, 160.02 (d, *J* = 35 Hz), 158.10 (d, *J* = 33 Hz), 151.04, 148.72, 140.24, 139.04, 138.61 (d, *J* = 2.9 Hz), 128.37 (d, *J* = 8.4 Hz), 120.20 (d, *J* =8.9 Hz), 119.30 (d, *J* = 23.8 Hz), 116.50 (d, *J* = 23.4 Hz), 116.09, 113.15 (d, *J* = 9.5 Hz), 113.04, 112.91, 112.16 (d, *J* = 26.6 Hz), 109.71 (d, *J* = 7.9 Hz), 109.05 (d, *J* = 7.9 Hz), 97.25, 86.11, 51.07, 33.78, 27.46, 26.97, 26.13; HRMS (ESI): Exact mass calcd for $C_{29}H_{24}F_2N_4NaO_5$ [M+Na]$^+$: 569.1607, Found: 569.1614.



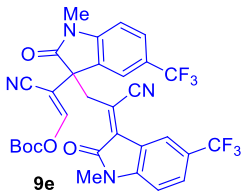
9c

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9c** in 61% yield as a brown solid (m.p. 142-143 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.79 (d, *J* = 1.0 Hz, 1H), 7.48 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 9.2 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.81 (d, *J* = 13.6 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 3.25 (s, 3H), 3.17 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.85, 165.12, 151.06, 148.68, 142.50, 141.53, 138.28, 132.64, 130.01, 129.46, 128.65, 128.56, 128.46, 125.25, 124.44, 120.47, 116.16, 113.00, 110.02, 109.45, 96.99, 86.16, 51.03, 33.91, 27.45, 26.95, 26.10; HRMS (ESI): Exact mass calcd for $C_{29}H_{24}Cl_2N_4NaO_5$ [M+Na]$^+$: 601.1016, Found: 601.1023.



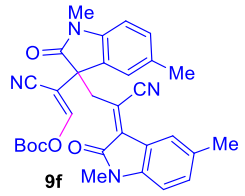
9d

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9d** in 63% yield as a yellow solid (m.p. 148-150 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.0 Hz, 1H), 7.79 (s, 1H), 7.60 (d, *J* = 1.5 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 4.81 (d, *J* = 13.5 Hz, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 3.25 (s, 3H), 3.18 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.79, 165.02, 151.07, 148.71, 142.98, 142.07, 138.16, 135.55, 132.91, 128.81, 128.07, 127.15, 120.91, 116.16, 115.68, 113.03, 110.48, 109.89, 97.06, 86.17, 51.12, 34.00, 27.48, 26.93, 26.11; HRMS (ESI): Exact mass calcd for $C_{29}H_{24}Br_2N_4NaO_5$ [M+Na]$^+$: 689.0006, Found: 689.0010.



9e

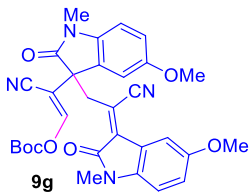
The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9e** in 52% yield as a yellow solid (m.p. 160-161 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.82 (s, 1H), 7.74 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 9.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.92 (d, *J* = 13.6 Hz, 1H), 3.42 (d, *J* = 13.6 Hz, 1H), 3.31 (s, 3H), 3.20 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.34, 165.34, 151.16, 148.63, 146.41 (q, *J* = 1.3 Hz), 145.92 (q, *J* = 1.5 Hz), 137.90, 130.26 (q, *J* = 4.0 Hz), 129.46, 127.71 (q, *J* = 4.0 Hz), 127.39, 125.67, 125.34 (q, *J* = 12 Hz), 125.13, 122.19 (q, *J* = 3.8 Hz), 121.26 (q, *J* = 3.8 Hz), 119.27, 116.03, 113.46, 112.88, 108.97, 108.50, 96.73, 86.31, 51.01, 33.99, 27.44, 27.09, 26.11; HRMS (ESI): Exact mass calcd for $C_{31}H_{24}F_6N_4NaO_5$ [M+Na]$^+$: 669.1543, Found: 669.1547.



9f

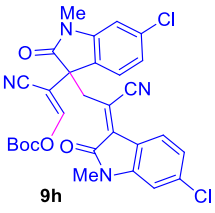
The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9f** in 75% yield as a yellow solid (m.p. 145-146 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.77 (s, 1H), 7.29 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H)), 6.77 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 14.0 Hz, 1H), 3.47 (d, *J* = 14.0 Hz, 1H), 3.24 (s, 3H), 3.14 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.38, 165.58, 150.69, 148.85, 141.86, 140.70, 139.13, 133.11, 132.75,

132.51, 130.16, 127.00, 125.56, 124.95, 119.57, 116.72, 113.34, 111.74, 108.67, 108.03, 98.13, 85.80, 50.95, 33.84, 29.67, 27.48, 26.78, 25.89, 21.06; HRMS (ESI): Exact mass calcd for $C_{31}H_{30}N_4NaO_5$ [M+Na]$^+$: 561.2108, Found: 561.2108.



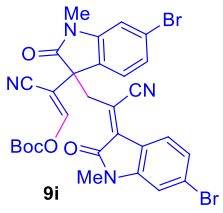
9g

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9g** in 60% yield as a brown solid (m.p. 128-129 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.90 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.79 (d, *J* = 3.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 4.89 (d, *J* = 13.5 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.40 (d, *J* = 14.0 Hz, 1H), 3.24 (s, 3H), 3.13 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.21, 165.46, 156.15, 155.93, 150.77, 148.81, 139.23, 137.87, 136.42, 127.81, 120.10, 118.53, 116.50, 115.53, 113.22, 112.34, 111.19, 110.29, 109.58, 108.88, 98.05, 85.85, 55.86, 55.78, 51.30, 33.67, 27.46, 26.86, 25.94; HRMS (ESI): Exact mass calcd for $C_{31}H_{30}N_4NaO_7$ [M+Na]$^+$: 593.2007, Found: 593.1997.



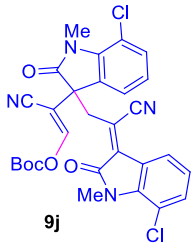
9h

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9h** in 63% yield as a brown solid (m.p. 142-143 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.04-6.99 (m, 2H), 6.90 (d, *J* = 1.6 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H), 4.78 (d, *J* = 14.4 Hz, 1H), 3.41 (d, *J* = 12.0 Hz, 1H), 3.25 (s, 3H), 3.16 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.35, 165.44, 150.96, 148.71, 145.08, 144.20, 139.01, 138.01, 135.99, 125.71, 125.36, 125.14, 123.15, 122.96, 117.74, 116.51, 113.12, 112.01, 109.87, 109.27, 97.27, 86.12, 50.41, 33.86, 27.44, 26.92, 26.14; HRMS (ESI): Exact mass calcd for $C_{29}H_{24}Cl_2N_4NaO_5$ [M+Na]$^+$: 601.1016, Found: 601.1031.



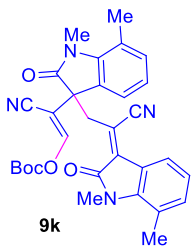
9i

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9i** in 64% yield as a yellow solid (m.p. 115-116 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.19-7.16 (m, 2H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 4.77 (d, *J* = 14.0 Hz, 1H), 3.39 (d, *J* = 14.0 Hz, 1H), 3.24 (s, 3H), 3.16 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.26, 165.34, 151.00, 148.74, 145.05, 144.33, 138.15, 127.30, 126.09, 126.05, 125.97, 125.76, 125.49, 123.90, 118.23, 116.54, 113.09, 112.65, 112.24, 112.11, 97.26, 86.14, 50.45, 33.92, 27.47, 26.93, 26.14; HRMS (ESI): Exact mass calcd for $C_{29}H_{24}Br_2N_4NaO_5$ [M+Na]$^+$: 689.0006, Found: 689.0018.



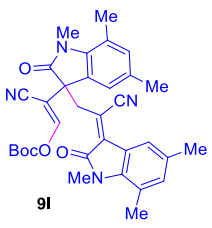
9j

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9j** in 50% yield as a yellow solid (m.p. 138-140 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.74 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.01-6.93 (m, 2H), 4.76 (d, *J* = 16.8 Hz, 1H), 3.63 (s, 3H), 3.55 (s, 3H), 3.45 (d, *J* = 13.6 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.51, 165.83, 151.21, 148.70, 139.80, 138.96, 137.76, 134.93, 132.29, 129.77, 123.99, 123.67, 123.13, 122.93, 122.01, 116.54, 116.49, 116.01, 113.17, 112.72, 97.33, 86.11, 50.31, 34.36, 30.27, 29.43, 27.45; HRMS (ESI): Exact mass calcd for $C_{29}H_{24}Cl_2N_4NaO_5$ [M+Na]$^+$: 601.1016, Found: 601.1027.



9k

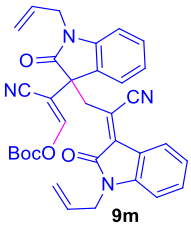
The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9k** in 52% yield as a brown solid (m.p. 145-146 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 8.0 Hz, 1H), 4.87 (d, *J* = 14.0 Hz, 1H), 3.53 (s, 3H), 3.45 (s, 3H), 3.44 (d, *J* = 14.0 Hz, 1H), 2.56 (s, 3H), 2.51 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.33, 166.36, 150.66, 148.85, 141.85, 140.92, 138.43, 136.58, 133.59, 127.41, 123.06, 122.72, 122.65, 122.31, 120.63, 120.22, 119.91, 116.82, 113.31, 111.66, 98.52, 85.78, 50.23, 33.96, 30.19, 29.36, 27.45, 19.09, 19.06; HRMS (ESI): Exact mass calcd for $C_{31}H_{30}N_4NaO_5$ [M+Na]$^+$: 561.2108, Found: 561.2120.



9l

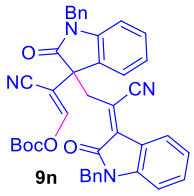
The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9l** in 61% yield as a pale yellow solid (m.p. 137-138 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.71 (s, 1H), 7.11 (s, 1H), 6.89 (s,

1H), 6.82 (s, 1H), 4.79 (d, *J* = 14.0 Hz, 1H), 3.50 (s, 3H), 3.43 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.18, 166.41, 150.58, 148.87, 139.61, 138.72, 138.44, 137.14, 134.04, 132.50, 132.21, 127.68, 123.27, 122.78, 120.38, 120.20, 119.54, 116.91, 113.38, 111.28, 98.64, 85.71, 50.42, 33.98, 30.11, 29.22, 27.47, 20.75, 18.89; HRMS (ESI): Exact mass calcd for $C_{33}H_{34}N_4NaO_5$ $[M+Na]^+$: 589.2421, Found: 589.2433.



9m

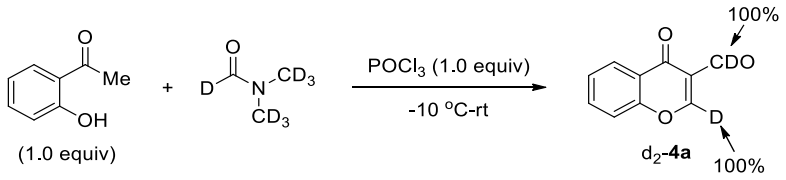
The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9m** in 64% yield as a brown solid (m.p. 115-116 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.78 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.32 (td, *J* = 8.0, 1.2 Hz, 1H), 7.27 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (td, *J* = 7.6, 1.0 Hz, 1H), 7.03 (td, *J* = 7.6, 1.0 Hz, 1H), 7.02 (td, *J* = 7.6, 1.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.93-5.73 (m, 2H), 5.30-5.13 (m, 4H), 4.43-4.21 (m, 4H), 3.57 (d, *J* = 13.6 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.98, 165.26, 150.76, 148.77, 143.26, 142.24, 138.92, 132.70, 130.99, 130.50, 129.80, 126.93, 124.87, 124.50, 123.10, 122.88, 119.56, 118.25, 117.63, 116.83, 113.30, 111.95, 109.94, 109.12, 97.94, 85.87, 50.87, 43.08, 41.92, 33.80, 27.45; HRMS (ESI): Exact mass calcd for $C_{33}H_{30}N_4NaO_5$ $[M+Na]^+$: 585.2108, Found: 585.2112.



9n

The reaction was run at 0 °C for 12 h by using CH_2Cl_2 as the solvent, affording product **9n** in 47% yield as a brown solid (m.p. 123-124 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.34-7.18 (m, 12H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.11 (d, *J* = 16.4 Hz, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.81-4.67 (m, 3H), 3.75 (d, *J* = 14.4 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.45, 165.66, 150.87, 148.76, 143.25, 142.22, 139.04, 135.04, 135.00, 132.75, 129.84, 128.86, 128.83. 127.84, 127.70, 127.25, 127.09, 127.03, 124.91, 124.61, 123.22, 122.98, 119.65, 112.06, 110.10, 109.29, 97.92, 85.90, 50.94, 44.47. 43.42, 33.84, 27.47; HRMS (ESI): Exact mass calcd for $C_{41}H_{34}N_4NaO_5$ $[M+Na]^+$: 685.2421, Found: 685.2424.

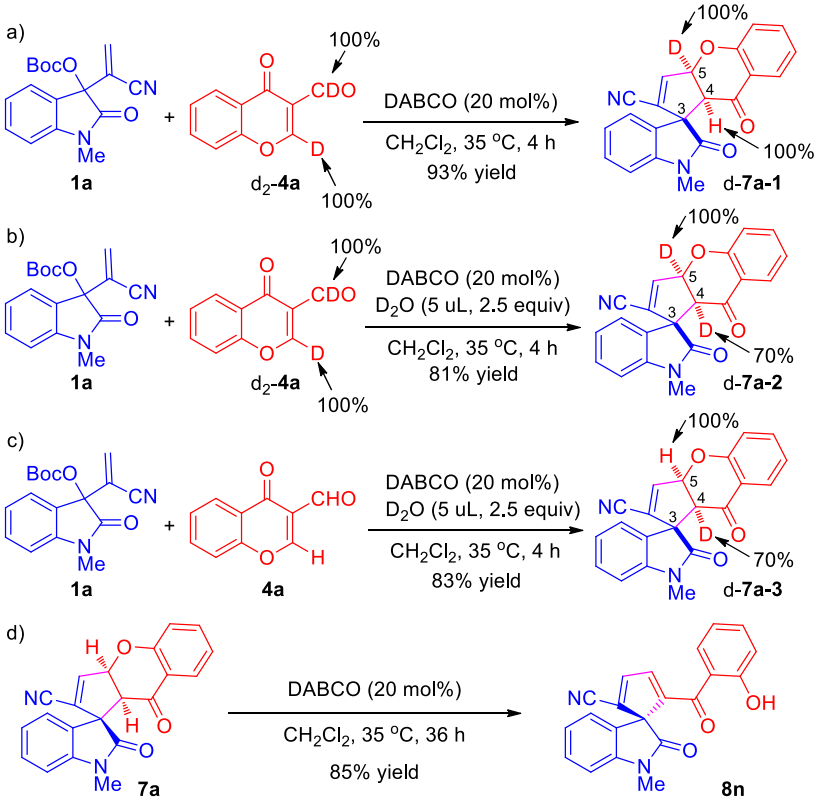
7. Control experiments



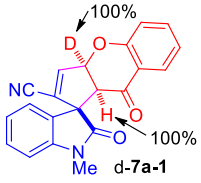
The preparation of d_2-**4a**: To a solution of 2-hydroxyacetophenone (136 mg, 1 mmol) in deuterated dimethylformamide (0.6 mL) was added phosphorus oxychloride (0.5 mL, 5 mmol) dropwise at -10°C. The reaction mixture was then stirred at rt for 24 h before the reaction was quenchedby addition of H_2O (5 mL). The resulting solid was collected and dried in vacuo to afford deuterated 3-formylchromone d_2-**4a** in 85% yield (150 mg, 0.85 mmol). The deuterated ratio of d_2-**4a** was determined by ^{1}H NMR analysis using $CDCl_3$ as the NMR solvent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.78-7.73 (m, 1H), 7.55-7.49 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.99, 156.15, 156.14, 134.80, 126.63, 126.16, 125.30, 118.60.



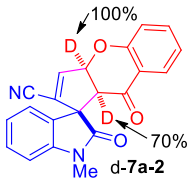
The preparation of d-**7a-1**: To a solution of MBH carbonate **1a** (0.15 mmol) and deuterated 3-formylchromone d_2-**4a** (0.10 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was added DABCO (0.02 mmol) at rt. The reaction mixture was then stirred vigorously at 35 °C under N_2 atmosphere for 4 h. After completion of the reaction as indicated by TLC, the mixture was directly subjected to flash chromatography on silica gel using petroleum ether/EtOAc (4:1) as the eluent to afford the deuterated product d-**7a-1** in 93% yield. The deuterated ratio of d-**7a-1** was determined by ^{1}H NMR analysis using $CDCl_3$ as the NMR solvent.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55-7.50 (m, 1H), 7.43-7.39 (m, 1H), 7.21-7.15 (m, 3H), 7.06-7.02 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 3.59 (s, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.86, 172.05, 159.65, 146.27, 144.25, 136.93, 130.37, 127.05, 126.86, 124.48, 123.67, 122.92, 122.31, 121.51, 118.43, 112.48, 109.24, 65.77, 54.76, 26.89; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}DN_2NaO_3$ $[M+Na]^+$: 366.0959, Found: 366.0960.

The preparation of d-**7a-2**: To a solution of MBH carbonate **1a** (0.15 mmol), deuterated 3-formylchromone d_2-**4a** (0.10 mmol) and D_2O (5 μL, 0.25 mol) in anhydrous CH_2Cl_2 (1.0 mL) was added DABCO (0.02 mmol) at rt. The reaction mixture was then stirred

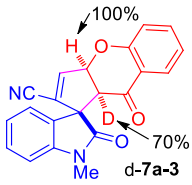
vigorously at 35 °C under N_2 atmosphere for 4 h. After completion of the reaction as indicated by TLC, the mixture was directly subjected to flash chromatography on silica gel using petroleum ether/EtOAc (4:1) as the eluent to afford the deuterated product d-**7a-2** in 81% yield. The deuterated ratio of d-**7a-2** was determined by ^{1}H NMR analysis using $CDCl_3$ as the NMR solvent.



d-**7a-2**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.44-7.39 (m,1H), 7.20-7.15 (m, 3H), 7.06-7.02 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 3.59 (s, 0.3H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.83, 172.05, 159.68, 146.25, 144.28, 136.93, 130.38, 127.05, 126.86, 124.52, 123.67, 122.92, 122.30, 121.51, 118.44, 112.48, 109.24, 65.75, 54.80, 26.90; HRMS (ESI): Exact mass calcd for $C_{21}H_{12}D_2N_2NaO_3$ $[M+Na]^+$: 367.1022, Found: 367.1013.

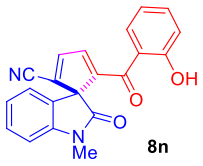
The preparation of d-**7a-3**: To a solution of MBH carbonate **1a** (0.15 mmol), 3-formylchromone **4a** (0.1 mmol) and D_2O (5 μL, 0.25 mol) in anhydrous CH_2Cl_2 (1.0 mL) was added DABCO (0.02 mmol) at rt. The reaction mixture was then stirred vigorously at 35 °C under N_2 atmosphere for 4 h. After completion of the reaction as indicated by TLC, the mixture was directly subjected to flash chromatography on silica gel using petroleum ether/EtOAc (4:1) as the eluent to afford the deuterated product d-**7a-3** in 83% yield. The deuterated ratio of d-**7a-3** was determined by ^{1}H NMR analysis using $CDCl_3$ as the NMR solvent.



d-**7a-3**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.44-7.40 (m, 1H), 7.20-7.17 (m, 3H), 7.06-7.02 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.79-5.77 (m, 1H), 3.59 (d, *J* = 7.6 Hz, 0.3H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.83, 172.04, 159.67, 146.31, 144.28, 136.93, 130.38, 127.05, 126.86, 124.48, 123.67, 122.92, 122.32, 121.52, 118.44, 112.48, 109.24, 80.75, 65.74, 54.90, 26.90; HRMS (ESI): Exact mass calcd for $C_{21}H_{13}DN_2NaO_3$ $[M+Na]^+$: 366.0959, Found: 366.0952.

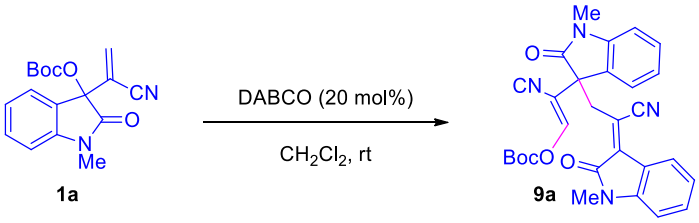
The preparation of 8n: To a solution of compound **7a** (0.10 mmol, 34.2 mg, 88% ee) in anhydrous CH_2Cl_2 (1.0 mL) was added DABCO (0.02 mmol) at rt. The reaction mixture was then stirred vigorously at 35 °C under N_2 atmosphere for 36 h. After the full consumption of **7a** as indicated by TLC, the mixture was directly subjected to flash chromatography on silica gel using petroleum ether/EtOAc (4:1) as the eluent to afford the title compound **8n** in 85% yield.



8n

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51-7.46 (m, 2H), 7.41-7.34 (m, 2H), 7.03-6.95 (m, 3H), 6.93-6.88 (m, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.26, 168.40, 162.39, 149.78, 146.57, 145.29, 142.66, 136.65, 130.74, 130.39, 124.82, 123.23, 123.04, 120.45, 119.39, 119.02, 118.64, 112.94, 109.66, 71.02, 27.73; HRMS (ESI): Exact mass calcd for $C_{21}H_{14}N_2NaO_3$ $[M+Na]^+$: 365.0897, Found: 365.0891.

8. ESI-MS studies:



General Procedure: To a solution of MBH carbonate **1a** (0.10 mmol) in anhydrous CH_2Cl_2 (1.0 mL) at room temperature was added DABCO (20 mol%) under N_2 atmosphere. Then, the reaction mixture was stirred at rt for 15 min and the solution was studied by ESI-MS immediately.

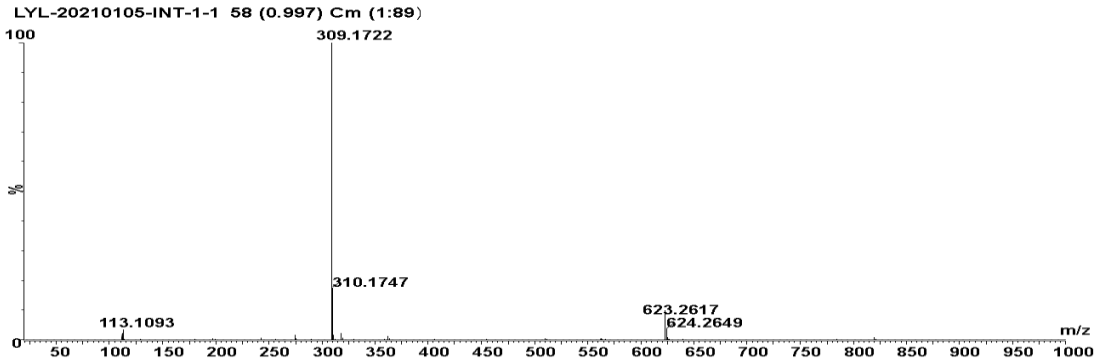
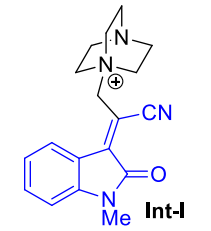


Figure S1: A full positive ESI-MS spectrum for the solution of DABCO and **1a** after reacting for 15 minutes.



Chemical Formula

$[C_{18}H_{21}N_4O]^+$

m/z calcd: 309.1715

found: 309.1722

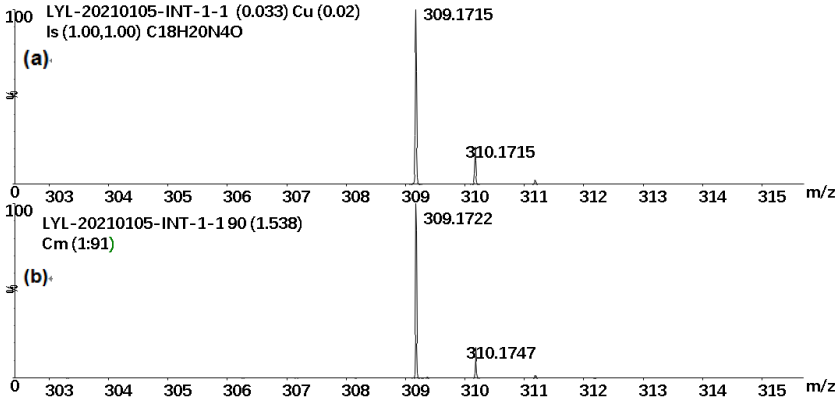
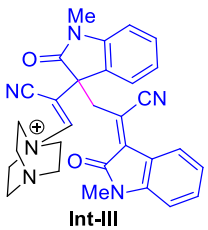


Figure S2: The simulated (a) and experimental (b) ESI-MS spectra of intermediate **Int-I**.



Chemical Formula

$[C_{30}H_{29}N_6O_2]^+$

m/z: calcd 505.2352

found 505.2356

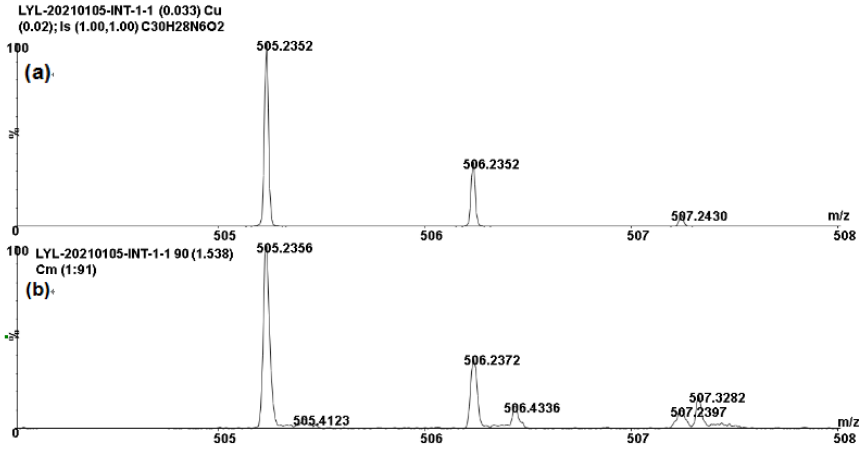
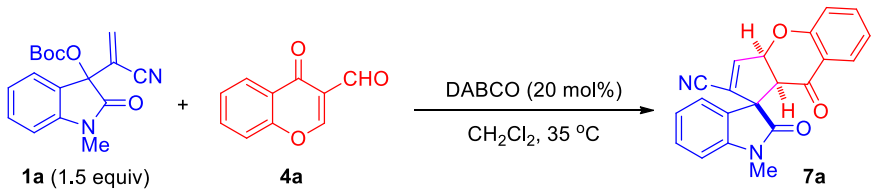


Figure S3: The simulated (a) and experimental (b) ESI-MS spectra of intermediate **Int-III**.



General Procedure: To a 10 mL Schlenk tube equipped with a magnetic stirrer bar were added MBH carbonate **1a** (0.15 mmol), 3-formylchromone **4a** (0.1 mmol) and anhydrous CH_2Cl_2 (1 mL). The reaction mixture was stirred vigorously at room temperature to ensure full dissolution of 3-formylchromone **4a.** Then, DABCO (0.02 mmol) was added. The resulting mixture was stirred at 35 °C under N_2 atmosphere for 15 min and the solution was studied by ESI-MS immediately.

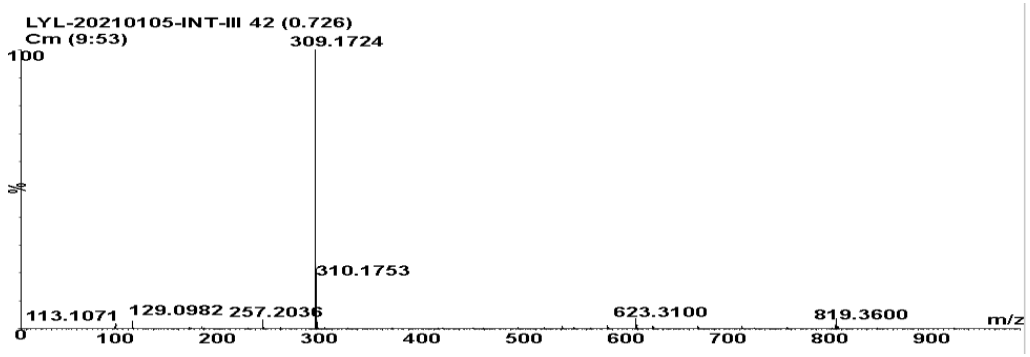
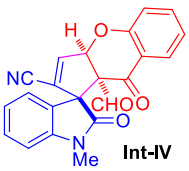


Figure S4: A full positive ESI-MS spectrum for the solution of **1a**, **4a** and DABCO after reacting for 15 minutes.



Int-IV

Chemical Formula

$C_{22}H_{14}N_2O_4$

$[M+Na]^+$

m/z: calcd 393.0851

found 393.0864

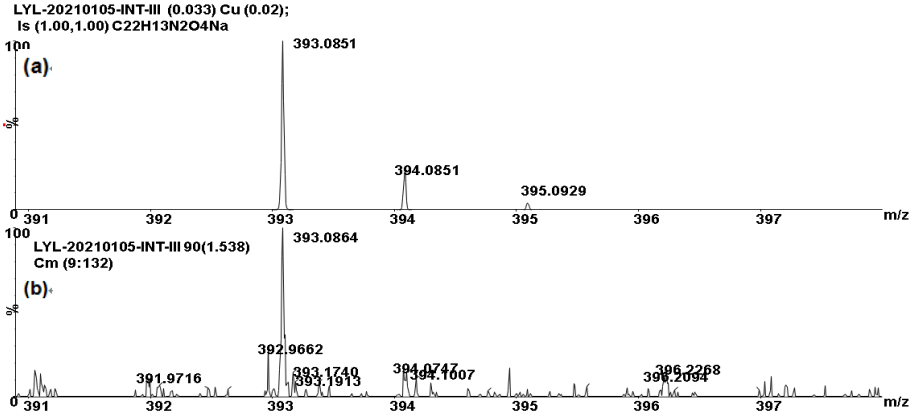
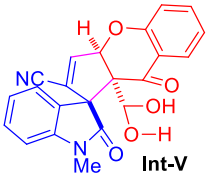


Figure S5: The simulated (a) and experimental (b) ESI-MS spectra of intermediate **Int-IV**.



Int-V

Chemical Formula

$C_{22}H_{16}N_2O_5$

$[M + Na]^+$

m/z: calcd 411.0957

found 411.0973

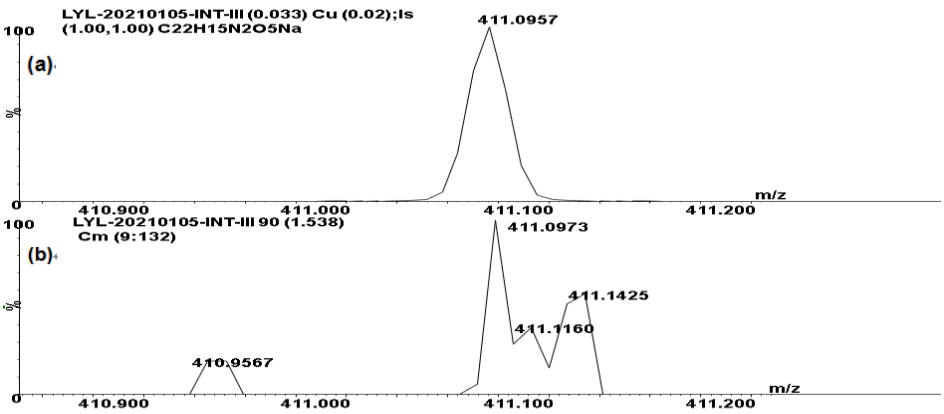


Figure S6: The simulated (a) and experimental (b) ESI-MS spectra of intermediate **Int-V**.

9. Theoretical calculations

To get more information about the origin of regioselectivity of this switchable catalytic approach, DFT calculations were then performed using Gaussian 16 suite. In the DABCO-catalyzed allylic alkylation reaction, the C-C bond formation involved in nucleophilic addition between *γ*- or *α*-carbon of *N*-allylic ylide intermediate **Int-II** and *α*-carbon of MBH carbonate **1a** via transition states TS1 and TS2 respectively, was studied. As shown in Figure **S7**, the calculated energy barrier of TS1 was 2.8 kcal/mol lower than that of TS2 as the *γ*-position of **Int-II** was sterically less hindered. In addition, the positively charged nitrogen on DABCO could stabilize the build up negative charge on nitrogen of the nitrile group in the transition state **TS1** (3.52 Å between the two nitrogen atoms), but there was no such stabilization effect available in **TS2**. As such, both steric and electronic effect render the *γ*-regioselective allylic alkylation more favorable, which was consistent with the experiment data.

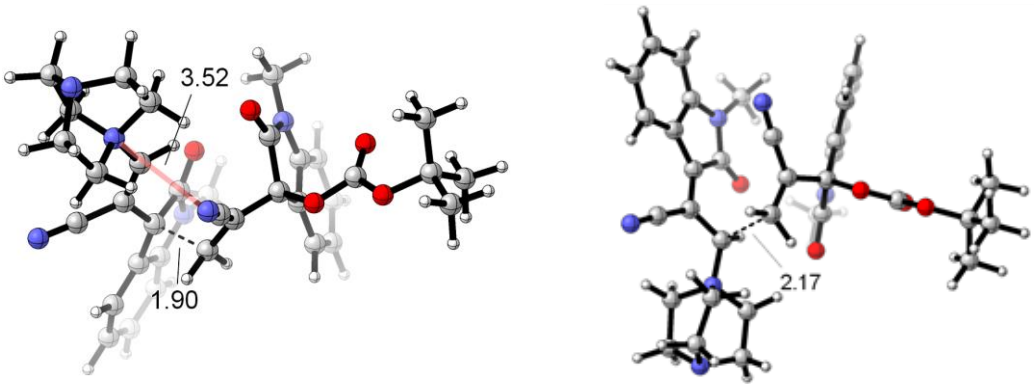


Figure S7. Optimized structures and energies of **TS1** and **TS2**.

In the DABCO-catalyzed [3+2] annulation reaction between **1a** and **4a**, DFT calculations supported the stepwise mechanism as no concerted transition state was identified. In the stepwise pathway, the reaction underwent through two C-C addition steps to form the five-membered ring, and the second C-C addition step would be crucial for controlling the actual selectivity. Both *γ*- and *α*-regioselective annulation were considered. As shown in Figure **S8**, the *γ*-regioselective annulation transition state **TS4** having the formyl group and the bulky ammonium moiety located at the same side was higher in energy barrier than *α*-regioselective annulation transition state **TS3** (**TS4**, 13.6 kcal/mol vs **TS3**, 11.2 kcal/mol) due to the unfavorable steric repulsion. Therefore, the regioselectivity trends observed in this case might be mainly dominated by steric effect in the second C-C addition step.

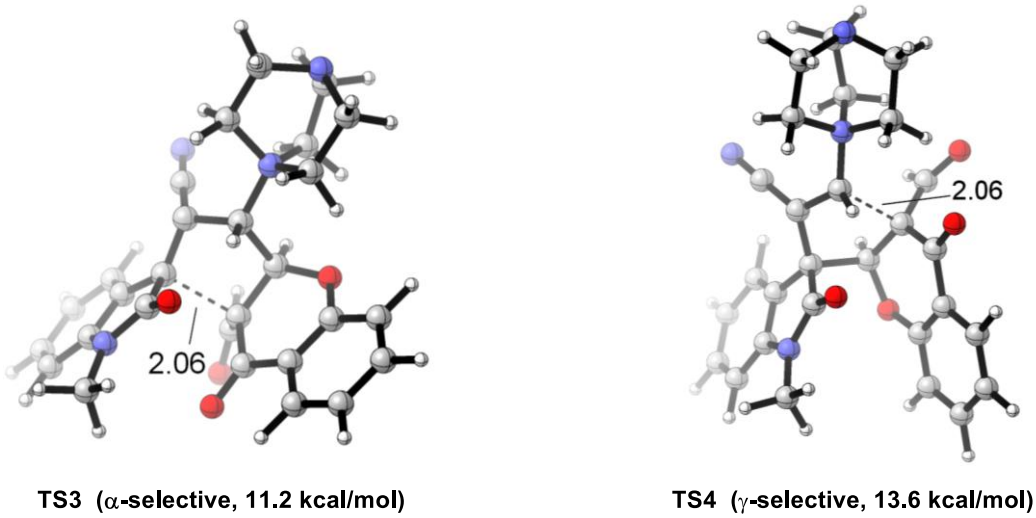
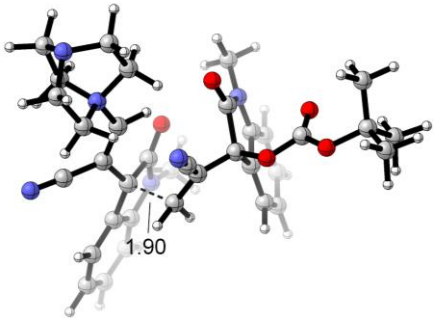


Figure S8. Optimized structures and energies of **TS3** and **TS4**.

Computaional data:

TS1

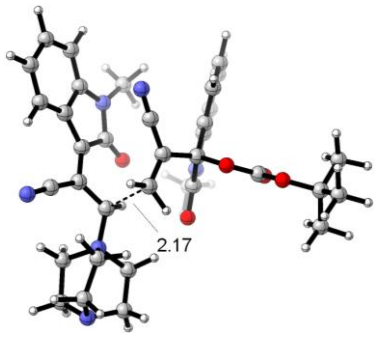


Zero-point correction= 0.697643 (Hartree/Particle)
Thermal correction to Energy= 0.738939
Thermal correction to Enthalpy= 0.739883
Thermal correction to Gibbs Free Energy= 0.624676
SCF Done: E(SOV) = -2061.01564050 A.U.

C	-5.29887900	0.81154100	-2.34817700
C	-3.76613800	1.02783200	-2.41057400
N	-3.18793000	0.73218300	-1.04493200
C	3.53769600	-0.78848800	-2.91210400
C	4.37833300	0.30685300	-3.09048700
C	3.96909100	1.59430000	-2.73197000
C	2.69421000	1.73776400	-2.20897800
C	1.82279500	0.64619600	-2.03403500
C	2.25893500	-0.62887200	-2.36720900
N	2.06271500	2.90580800	-1.78263700
C	0.78117100	2.63811000	-1.34725600
C	0.62016400	1.15506100	-1.33901300
O	-0.03525400	3.48196500	-1.00068300
C	2.63154800	4.22912500	-1.84645000
C	-1.79189200	1.20154200	-0.96233200
C	-0.73052000	0.64782300	-1.59286400
C	-0.87113000	-0.47334800	-2.48220400
H	-5.62796600	0.23890900	-3.21966200
H	-5.82405200	1.77111600	-2.35943800
H	-3.48502800	2.05447200	-2.65386800
H	-3.26811600	0.35036800	-3.10830400
H	3.87797100	-1.77966400	-3.19269700
H	5.36893600	0.16274900	-3.51007600
H	4.62551500	2.44948000	-2.85832500
H	1.61835000	-1.49333100	-2.22158000
H	2.91649100	4.47535600	-2.87518700
H	3.50834900	4.30232800	-1.19470500
H	1.87035500	4.92782000	-1.49674800
H	-1.68309300	2.10752400	-0.38331100
C	-3.97868100	1.50789600	-0.00469400
H	-3.92173100	2.55733600	-0.30412700
H	-3.44524000	1.39664000	0.94140700
C	-5.41844300	0.95285700	0.02496800
H	-6.13820400	1.77603500	0.03250100
H	-5.57792700	0.35938900	0.92944300
N	-5.67798300	0.09718100	-1.13367600
C	-3.37582100	-0.74412300	-0.72957000

H	-3.09224300	-0.85464400	0.31979300
H	-2.69349100	-1.31582800	-1.35372500
C	-4.85343900	-1.10399500	-1.01556000
H	-5.24081600	-1.72610500	-0.20434700
H	-4.94291300	-1.67201000	-1.94659700
N	-1.00820800	-1.34980700	-3.22818900
C	3.63830900	3.97915800	2.07436500
C	3.27596700	5.23777400	1.60219700
C	1.93931600	5.56585700	1.35004000
C	0.98347300	4.58955200	1.58574300
C	1.33685800	3.31659900	2.04757200
C	2.65694600	3.00647000	2.30777600
N	-0.39612000	4.68618500	1.43499500
C	-1.01495900	3.51566900	1.77776900
O	-2.20568600	3.28510400	1.67226300
C	-1.06812100	5.77217500	0.77198100
C	0.96102400	0.76815200	0.48869900
C	0.00449100	1.21450800	1.43384100
C	-1.07439500	0.37047000	1.78514600
H	4.68123600	3.75341000	2.26974800
H	4.04371000	5.98667800	1.43076700
H	1.66094500	6.55259300	0.99383200
H	2.92143800	2.02265000	2.68636300
H	-0.70780700	5.85591500	-0.25921700
H	-0.90327500	6.71201500	1.30812200
H	-2.13371200	5.54013300	0.76954600
H	1.01914300	-0.31197700	0.35789400
N	-1.96057200	-0.33077600	2.08387100
H	1.95109800	1.21999000	0.54219100
C	0.08266100	2.49767600	2.22397300
O	-0.11287000	2.08920400	3.59961500
C	-0.33870400	3.03272300	4.51977300
O	-0.43970300	2.42269300	5.69620900
C	-0.70436700	3.20629400	6.89466100
C	-2.05169000	3.91215600	6.77396700
H	-2.30060700	4.38063600	7.73143000
H	-2.02537300	4.68004200	5.99978200
H	-2.83308800	3.18507500	6.53214400
C	0.43999400	4.18361300	7.14750600
H	0.47781100	4.95629200	6.37858200
H	0.29856500	4.65964700	8.12291500
H	1.39329800	3.64606200	7.16318000
C	-0.75094200	2.14117700	7.98369800
H	-0.94602700	2.60732100	8.95380000
H	-1.54233300	1.41657900	7.77325100
H	0.20267000	1.60810700	8.03428100
O	-0.42820400	4.21793200	4.30153500

TS2

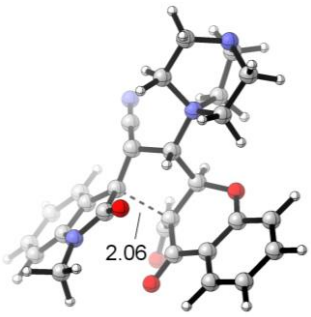


Zero-point correction= 0.698578 (Hartree/Particle)
Thermal correction to Energy= 0.739564
Thermal correction to Enthalpy= 0.740508
Thermal correction to Gibbs Free Energy= 0.625908
SCF Done: E(SOV) = -2061.01252792 A.U.

C	-5.43835800	-0.61279400	3.23664500
C	-4.04533300	-0.00970300	2.93550900
N	-3.91916300	0.21106300	1.44085700
C	3.22184100	0.55576500	1.83172100
C	3.78021600	1.82112400	1.65302700
C	2.97147600	2.94601300	1.49378900
C	1.59938700	2.75947600	1.52945300
C	1.01050300	1.49145200	1.71672200
C	1.83898900	0.37945900	1.85650700
N	0.60228400	3.72154100	1.39891300
C	-0.65171700	3.14900200	1.46132900
C	-0.42736300	1.68960000	1.63115900
O	-1.70656800	3.78456600	1.44569100
C	0.83189500	5.12121300	1.15075000
C	-2.72945200	1.05207400	1.08805700
C	-1.45694700	0.76710900	1.65506300
C	-1.12885000	-0.58939900	2.00777900
H	-5.34328700	-1.42765600	3.95948000
H	-6.10661500	0.13892000	3.66671400
H	-3.88233100	0.96404500	3.40104400
H	-3.23330500	-0.67819600	3.22356300
H	3.87032500	-0.30697900	1.94352100
H	4.85948300	1.93459400	1.62750800
H	3.40050900	3.92989400	1.33471100
H	1.42666400	-0.61503400	1.98295800
H	1.51994000	5.53189700	1.89715500
H	1.24445200	5.27338000	0.14676800
H	-0.13040100	5.62877900	1.22268900
H	-3.01185500	2.09758700	1.07275100
C	-5.16056900	0.95018200	0.99432900
H	-5.22457200	1.83706400	1.62981300
H	-4.98727900	1.29725000	-0.02427100
C	-6.37578300	0.00896500	1.14637300
H	-7.22182600	0.55761500	1.56938000
H	-6.68938900	-0.38328500	0.17446400
N	-6.05401000	-1.12402000	2.01349600
C	-3.92978000	-1.12981700	0.73991200
H	-4.07220100	-0.90841100	-0.31948700

H	-2.95781700	-1.60062900	0.87602800
C	-5.08457600	-1.97564200	1.32501500
H	-5.58752500	-2.52156100	0.52205100
H	-4.70272700	-2.71043700	2.03988300
N	-0.93386500	-1.68909000	2.32211300
C	0.62755400	5.99363700	-2.60120100
C	0.03137100	6.98588200	-1.82797600
C	-1.16644800	6.75348700	-1.14398200
C	-1.73716100	5.49732900	-1.26750600
C	-1.14867000	4.49156800	-2.04081000
C	0.03547500	4.72852900	-2.71269600
N	-2.93755600	5.04602700	-0.71858900
C	-3.22198700	3.77968100	-1.11982900
O	-4.22383600	3.14541400	-0.83232900
C	-3.71506800	5.76714500	0.25503200
C	-2.21070500	0.96212200	-1.01983400
C	-1.40636500	2.03089300	-1.36984200
C	0.01037800	1.91249300	-1.41994900
H	1.55748400	6.19849100	-3.12070000
H	0.50187400	7.96152800	-1.75072300
H	-1.63246600	7.52922500	-0.54493400
H	0.50002300	3.94593700	-3.30378300
H	-3.11508700	5.92357000	1.15714800
H	-4.05046700	6.72557200	-0.15346400
H	-4.58335200	5.15366400	0.49687800
H	-3.24140500	0.98609700	-1.36194800
N	1.16869700	1.84343400	-1.50866100
H	-1.75203300	-0.01781500	-0.93096900
C	-2.03179300	3.26738000	-1.98305400
O	-2.49724100	2.83839300	-3.28737100
C	-3.27083800	3.68660800	-3.97792500
O	-3.53047000	3.12153300	-5.15284900
C	-4.36800000	3.82054100	-6.11936500
C	-4.40237400	2.84922700	-7.29330800
H	-3.39172200	2.67625200	-7.67355600
H	-5.01679400	3.26020500	-8.09943800
H	-4.82515900	1.89003600	-6.98133200
C	-3.71295100	5.13584500	-6.52938600
H	-3.69240000	5.84282200	-5.69938500
H	-4.27655800	5.57712700	-7.35743500
H	-2.68922200	4.95263800	-6.87017900
C	-5.76809700	4.02384700	-5.54784100
H	-5.75401400	4.71923400	-4.70788100
H	-6.17764300	3.06541200	-5.21356400
H	-6.42274300	4.42364900	-6.32848100
O	-3.65538900	4.76081800	-3.58150400

TS-3

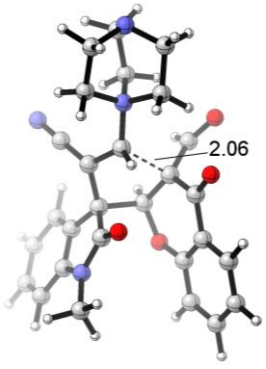


Zero-point correction= 0.508128 (Hartree/Particle)
Thermal correction to Energy= 0.536359
Thermal correction to Enthalpy= 0.537303
Thermal correction to Gibbs Free Energy= 0.450931
SCF Done: E(SOV) = -1602.32555299 A.U.

C	-4.70990700	-2.22456500	1.05881500
C	-5.63236800	-1.52878900	0.28290300
C	-5.22031900	-0.61463900	-0.69101300
C	-3.85892600	-0.42726900	-0.85087300
C	-2.91407100	-1.10974500	-0.06970600
C	-3.33806300	-2.01322900	0.89332000
N	-3.20946200	0.39067900	-1.78047900
C	-1.85111800	0.32232700	-1.63421400
C	-1.57604700	-0.60191100	-0.44844400
O	-1.03816900	0.91331300	-2.32671900
C	-3.86354700	1.37831800	-2.60509000
C	0.75247400	-0.35489400	-0.37163400
C	-0.36388300	-1.34893500	-0.41752000
C	-1.02585300	0.90846100	0.84224900
C	0.43703300	0.51731800	0.90793900
H	-5.05704900	-2.92882800	1.80692500
H	-6.69426200	-1.69611400	0.43416200
H	-5.93980700	-0.07297900	-1.29586200
H	-2.62228400	-2.54674200	1.51060900
H	-4.55583900	0.90128200	-3.30554100
H	-4.40172300	2.08847200	-1.96943500
H	-3.08477000	1.90311700	-3.15915100
H	0.68947100	0.30728700	-1.24121400
H	0.59867300	-0.11571300	1.78679800
C	-1.82702500	0.51529600	2.02130100
O	-2.84840600	1.02458600	2.41242100
C	2.68905800	-1.36914300	0.92401600
H	1.92233400	-1.98142400	1.40006600
H	2.84180300	-0.45422400	1.50205300
C	3.11782600	0.11954600	-0.96089800
H	2.94595100	1.03559600	-0.39987600
H	2.82602700	0.28261300	-2.00164300
C	2.21682800	-2.10459300	-1.37527600
H	1.66578600	-1.80831900	-2.26966000
H	1.67980800	-2.92112000	-0.89308300
N	4.56464700	-1.85776600	-0.62534500
C	4.56374600	-0.41048500	-0.82203100
H	5.13729900	-0.16494700	-1.71999700

H	5.06733300	0.05337600	0.03130800
C	4.00503300	-2.14913300	0.69512400
H	4.73305200	-1.87846200	1.46483600
H	3.83009500	-3.22662500	0.76406900
C	3.69880600	-2.45709200	-1.64106000
H	3.82477200	-3.54294000	-1.62674700
H	4.02348200	-2.09746700	-2.62199900
N	2.16793200	-0.92689400	-0.42228100
C	-0.25961800	-2.49995400	0.39038900
N	-0.05911600	-3.47155200	1.00906900
C	-1.32956100	2.22143700	0.24003700
H	-1.39774900	-0.37127500	2.54985200
O	-2.46458300	2.60928300	0.01380600
C	-0.15150200	3.06729600	-0.09791400
C	-0.32620700	4.25869000	-0.80651100
C	1.12612000	2.72915200	0.35166000
C	0.74727100	5.09741400	-1.06219800
H	-1.33324500	4.49812700	-1.13309800
C	2.21248400	3.57404100	0.11649000
C	2.01701000	4.75348700	-0.58935400
H	0.60368900	6.01969200	-1.61484500
H	3.18736300	3.30293200	0.51120400
H	2.86102500	5.41194600	-0.77096500
O	1.36797300	1.58625700	1.06098700

TS4



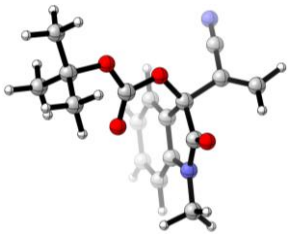
Zero-point correction= 0.507861 (Hartree/Particle)
Thermal correction to Energy= 0.536180
Thermal correction to Enthalpy= 0.537124
Thermal correction to Gibbs Free Energy= 0.450456
SCF Done: E(SOV) = -1602.32128226 A.U.

C	-4.54008000	-1.35382600	1.07802000
C	-5.33408700	-0.64776200	0.18048100
C	-4.76636800	0.15308200	-0.81609800
C	-3.38420000	0.21216600	-0.87259200
C	-2.56979600	-0.49111400	0.02328000
C	-3.14354400	-1.27315200	1.00842900
N	-2.58826700	0.92083400	-1.78050700
C	-1.25499200	0.71175000	-1.53940100
C	-1.13502600	-0.14112300	-0.26105900
O	-0.34156500	1.14624100	-2.21759100
C	-3.08246100	1.75907600	-2.84580200
C	1.16257400	-0.65558100	-0.50388000

C	-0.11713500	-1.22879000	-0.38560600
C	-0.54881600	0.79790000	0.90740300
C	0.93749500	0.96377500	0.75537800
H	-5.00421500	-1.97286400	1.83824300
H	-6.41514300	-0.71814700	0.24981700
H	-5.38541900	0.70450000	-1.51643500
H	-2.52524500	-1.83015200	1.70656600
H	-2.21469000	2.14792800	-3.38030200
H	-3.71203300	1.18280900	-3.53158100
H	-3.66099400	2.59283700	-2.43439500
H	1.33344800	0.05780700	-1.30720800
C	2.58233700	-2.20640900	0.93881900
H	1.63463300	-2.65084900	1.23706700
H	2.87736500	-1.43669100	1.65016600
C	3.62048500	-0.62906100	-0.61232300
H	3.54225000	0.24168000	0.04134500
H	3.55661300	-0.28440900	-1.64768600
C	2.35626800	-2.53503200	-1.49736300
H	2.04362700	-2.01370600	-2.40439100
H	1.58363300	-3.25422400	-1.21941200
N	4.53667300	-2.92643400	-0.40034100
C	4.86649300	-1.49960600	-0.34327400
H	5.64016300	-1.27826400	-1.08365900
H	5.27933100	-1.28083200	0.64578800
C	3.70066700	-3.25703200	0.75459500
H	4.31971300	-3.28744900	1.65520500
H	3.27926800	-4.25515500	0.60192800
C	3.75906800	-3.17421800	-1.61221700
H	3.65830100	-4.25238100	-1.76516200
H	4.30871600	-2.76433800	-2.46471700
N	2.39452500	-1.49699500	-0.38909000
C	-0.37006700	-2.52184500	0.10289100
N	-0.53700400	-3.61825800	0.46853000
C	-0.89346800	3.08801900	0.31422900
C	-1.82281800	4.12006200	0.16358000
C	0.39861100	3.21627900	-0.20611000
C	-1.45463900	5.27656100	-0.50765300
H	-2.81573700	3.98698500	0.58007900
C	0.74619900	4.38723300	-0.88715500
C	-0.16747300	5.41678300	-1.03902300
H	-2.17902200	6.07730800	-0.62241000
H	1.75280100	4.45214800	-1.28791600
H	0.10906900	6.32262200	-1.56770100
C	1.74206000	0.62970500	1.92487700
H	1.16945600	0.08117600	2.70860000
O	2.93300900	0.84281200	2.09237700
H	-0.77434800	0.25278100	1.83089200
C	1.38899000	2.12705600	-0.04620400

O	2.51168200	2.19714300	-0.52508100
O	-1.31643500	1.98696600	0.98828100

1a

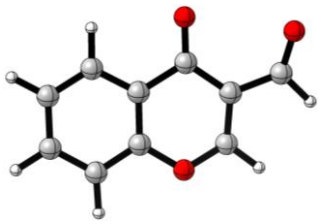


Zero-point correction= 0.330527 (Hartree/Particle)
Thermal correction to Energy= 0.352545
Thermal correction to Enthalpy= 0.353489
Thermal correction to Gibbs Free Energy= 0.279166
SCF Done: E(SOV) = -1068.97734754 A.U.

C	0.85855700	5.41389000	2.63860900
C	0.37572500	6.40262300	1.78662300
C	-0.84800300	6.26130300	1.12401400
C	-1.56109400	5.09579400	1.34686900
C	-1.08205900	4.09224100	2.19532800
C	0.12661800	4.23942700	2.84967300
N	-2.80564000	4.73503300	0.81727000
C	-3.24609600	3.54842600	1.34318900
O	-4.31960100	3.02428800	1.15455900
C	-3.65418100	5.61448800	0.04830700
C	-2.01920000	1.12566300	0.42965400
C	-1.51302700	1.71430600	1.51508900
C	-0.33749900	1.17024000	2.15038800
H	1.80940300	5.55190200	3.14155100
H	0.95638400	7.30664000	1.63150800
H	-1.22431200	7.03892300	0.46761800
H	0.49715500	3.46285200	3.51187500
H	-3.15826600	5.90444300	-0.88269100
H	-3.89757900	6.51231400	0.62618300
H	-4.57050400	5.06823100	-0.17823900
H	-2.92304400	1.49625500	-0.03969200
N	0.60793800	0.75384700	2.67114700
H	-1.54353800	0.24686100	0.00839300
C	-2.07845500	2.95642200	2.18465100
O	-2.50908200	2.51411900	3.46795300
C	-3.20825900	3.41412300	4.18981500
O	-3.51700000	2.84575900	5.34081500
C	-4.29849500	3.58732400	6.32989900
C	-4.45496400	2.57177700	7.45463400
H	-3.47508300	2.25759100	7.82419600
H	-5.01729000	3.01673700	8.28027900
H	-4.99212000	1.68859600	7.09792600
C	-3.50811900	4.80339100	6.80077300
H	-3.38339800	5.53024500	5.99679600
H	-4.04148700	5.28193200	7.62783300
H	-2.52284500	4.49298600	7.16200700
C	-5.65756000	3.96355500	5.74964200

H	-5.56207400	4.71351700	4.96399400
H	-6.14872800	3.07580500	5.33975300
H	-6.28736700	4.36677200	6.54864300
O	-3.47780200	4.52648300	3.80624800

4a

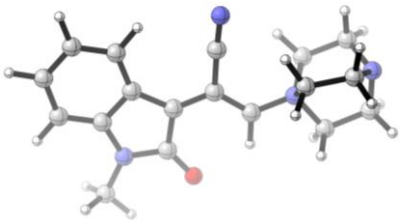


Zero-point correction= 0.365043 (Hartree/Particle)
Thermal correction to Energy= 0.384176
Thermal correction to Enthalpy= 0.385121
Thermal correction to Gibbs Free Energy= 0.317273
SCF Done: E(SOV) = -992.038859845 A.U.

C	-4.97652100	-1.81842700	-1.57824200
C	-3.88795000	-0.73731100	-1.78106500
N	-3.59370800	-0.08279600	-0.44595700
C	3.46970600	0.51578700	-1.74226200
C	4.01940300	1.79044000	-1.61690600
C	3.21546700	2.87644500	-1.26258800
C	1.86731400	2.64243700	-1.04292400
C	1.28291500	1.35463100	-1.16442600
C	2.10997300	0.28805800	-1.51973200
N	0.88561700	3.55314600	-0.68325800
C	-0.35093300	2.92068200	-0.55593700
C	-0.12559800	1.51696800	-0.85780500
O	-1.39140000	3.50948700	-0.24334800
C	1.08181800	4.96091200	-0.46951100
C	-2.48914400	0.89415900	-0.51191600
C	-1.17976500	0.58708700	-0.82131800
C	-0.83700200	-0.78162600	-1.14385000
H	-4.53769000	-2.81953400	-1.61682300
H	-5.72511900	-1.75137100	-2.37268800
H	-4.20265600	0.07711100	-2.43718200
H	-2.95548900	-1.15090400	-2.16038800
H	4.10638400	-0.31909100	-2.01837600
H	5.07908200	1.94454300	-1.79487000
H	3.63099200	3.87462600	-1.16043600
H	1.71429600	-0.71592000	-1.62618900
H	1.44224900	5.45130900	-1.38131700
H	1.80458600	5.13940100	0.33493400
H	0.11344600	5.37928800	-0.18961900
H	-2.75774700	1.90677700	-0.25509100
C	-4.83545600	0.67379200	-0.04412600
H	-4.90297600	1.53215100	-0.71507000
H	-4.64825800	1.04179500	0.96744100
C	-6.05888200	-0.26851300	-0.13761600
H	-6.68215500	-0.00819400	-0.99793800
H	-6.67549900	-0.17410100	0.76041300

N	-5.63580900	-1.65821600	-0.28319100
C	-3.37167200	-1.16145400	0.59874100
H	-3.05525200	-0.63699100	1.50165000
H	-2.54478800	-1.77665900	0.24438400
C	-4.68018900	-1.97196200	0.77699600
H	-5.15103600	-1.74671400	1.73852200
H	-4.46464800	-3.04344100	0.75502500
N	-0.61803600	-1.89103500	-1.39704800

Int-II



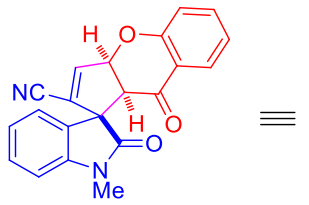
Zero-point correction= 0.365043 (Hartree/Particle)
Thermal correction to Energy= 0.384176
Thermal correction to Enthalpy= 0.385121
Thermal correction to Gibbs Free Energy= 0.317273
SCF Done: E(SOV) = -992.038859845 A.U.

C	-4.97652100	-1.81842700	-1.57824200
C	-3.88795000	-0.73731100	-1.78106500
N	-3.59370800	-0.08279600	-0.44595700
C	3.46970600	0.51578700	-1.74226200
C	4.01940300	1.79044000	-1.61690600
C	3.21546700	2.87644500	-1.26258800
C	1.86731400	2.64243700	-1.04292400
C	1.28291500	1.35463100	-1.16442600
C	2.10997300	0.28805800	-1.51973200
N	0.88561700	3.55314600	-0.68325800
C	-0.35093300	2.92068200	-0.55593700
C	-0.12559800	1.51696800	-0.85780500
O	-1.39140000	3.50948700	-0.24334800
C	1.08181800	4.96091200	-0.46951100
C	-2.48914400	0.89415900	-0.51191600
C	-1.17976500	0.58708700	-0.82131800
C	-0.83700200	-0.78162600	-1.14385000
H	-4.53769000	-2.81953400	-1.61682300
H	-5.72511900	-1.75137100	-2.37268800
H	-4.20265600	0.07711100	-2.43718200
H	-2.95548900	-1.15090400	-2.16038800
H	4.10638400	-0.31909100	-2.01837600
H	5.07908200	1.94454300	-1.79487000
H	3.63099200	3.87462600	-1.16043600
H	1.71429600	-0.71592000	-1.62618900
H	1.44224900	5.45130900	-1.38131700
H	1.80458600	5.13940100	0.33493400
H	0.11344600	5.37928800	-0.18961900
H	-2.75774700	1.90677700	-0.25509100
C	-4.83545600	0.67379200	-0.04412600
H	-4.90297600	1.53215100	-0.71507000

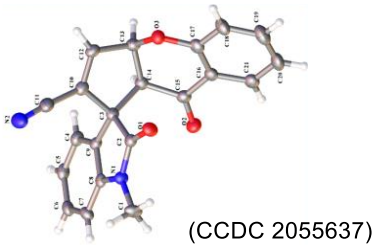
H	-4.64825800	1.04179500	0.96744100
C	-6.05888200	-0.26851300	-0.13761600
H	-6.68215500	-0.00819400	-0.99793800
H	-6.67549900	-0.17410100	0.76041300
N	-5.63580900	-1.65821600	-0.28319100
C	-3.37167200	-1.16145400	0.59874100
H	-3.05525200	-0.63699100	1.50165000
H	-2.54478800	-1.77665900	0.24438400
C	-4.68018900	-1.97196200	0.77699600
H	-5.15103600	-1.74671400	1.73852200
H	-4.46464800	-3.04344100	0.75502500
N	-0.61803600	-1.89103500	-1.39704800

10. X-Ray crystallographic data for compounds 7a, 8d, and 9a.

Data intensity of racemic compound **7a** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 100 (10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC 2055637 (racemic **7a**).



7a

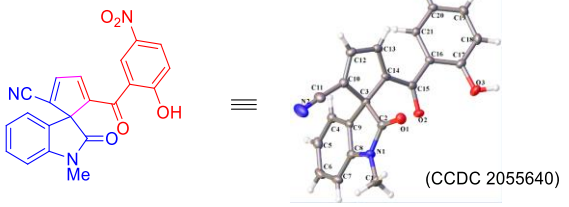


(CCDC 2055637)

X-ray structure of racemic compound **7a**

Crystal data	
Identification code	20191130-1
Empirical formula	$C_{21}H_{14}N_2O_3$
Formula weight	342.34
Temperature/K	100.00(10)
Crystal system	hexagonal
Space group	$P6_1$
a/Å	19.9112(5)
b/Å	19.9112(5)
c/Å	9.2146(3)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3163.73(15)
Z	6
ρ_{calc}g/cm^3	1.3455
μ/mm^{-1}	2.983
F(000)	1328.2
Crystal size/mm^3	0.11 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.12 to 147.26
Index ranges	-23 ≤ h ≤ 9, -16 ≤ k ≤ 24, -11 ≤ l ≤ 11
Reflections collected	8009
Independent reflections	3821 [R_{int} = 0.0420, R_{sigma} = 0.0540]
Data/restraints/parameters	3821/1/263
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, Wr_2 = 0.0981
Final R indexes [all data]	R_1 = 0.0485, Wr_2 = 0.1027
Largest diff. Peak/hole / e Å^{-3}	0.22/-0.30

Data intensity of racemic compound **8d** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 149.99(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC 2055640 (**8d**).

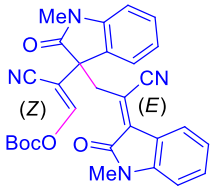


8d

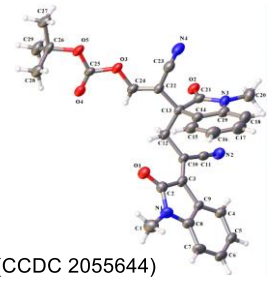
X-ray structure of racemic product **8d**

Crystal data	
Identification code	lyl-10-19-01
Empirical formula	$C_{21}H_{13}N_3O_5$
Formula weight	387.34
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.6966(5)
b/Å	8.9106(5)
c/Å	13.8343(9)
α/°	74.371(5)
β/°	81.939(5)
γ/°	71.066(5)
Volume/Å^3	862.80(10)
Z	2
ρ_{calc}g/cm^3	1.491
μ/mm^{-1}	0.109
F(000)	400.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.978 to 58.806
Index ranges	-9 ≤ h ≤ 10, -8 ≤ k ≤ 11, -12 ≤ l ≤ 18
Reflections collected	6640
Independent reflections	3985 [R_{int} = 0.0248, R_{sigma} = 0.0482]
Data/restraints/parameters	3985/0/268
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, Wr_2 = 0.1142
Final R indexes [all data]	R_1 = 0.0631, Wr_2 = 0.1255
Largest diff. Peak/hole / e Å^{-3}	0.33/-0.25

Data intensity of racemic compound **9a** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 100.00(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC 2055644 (**9a**).



9a

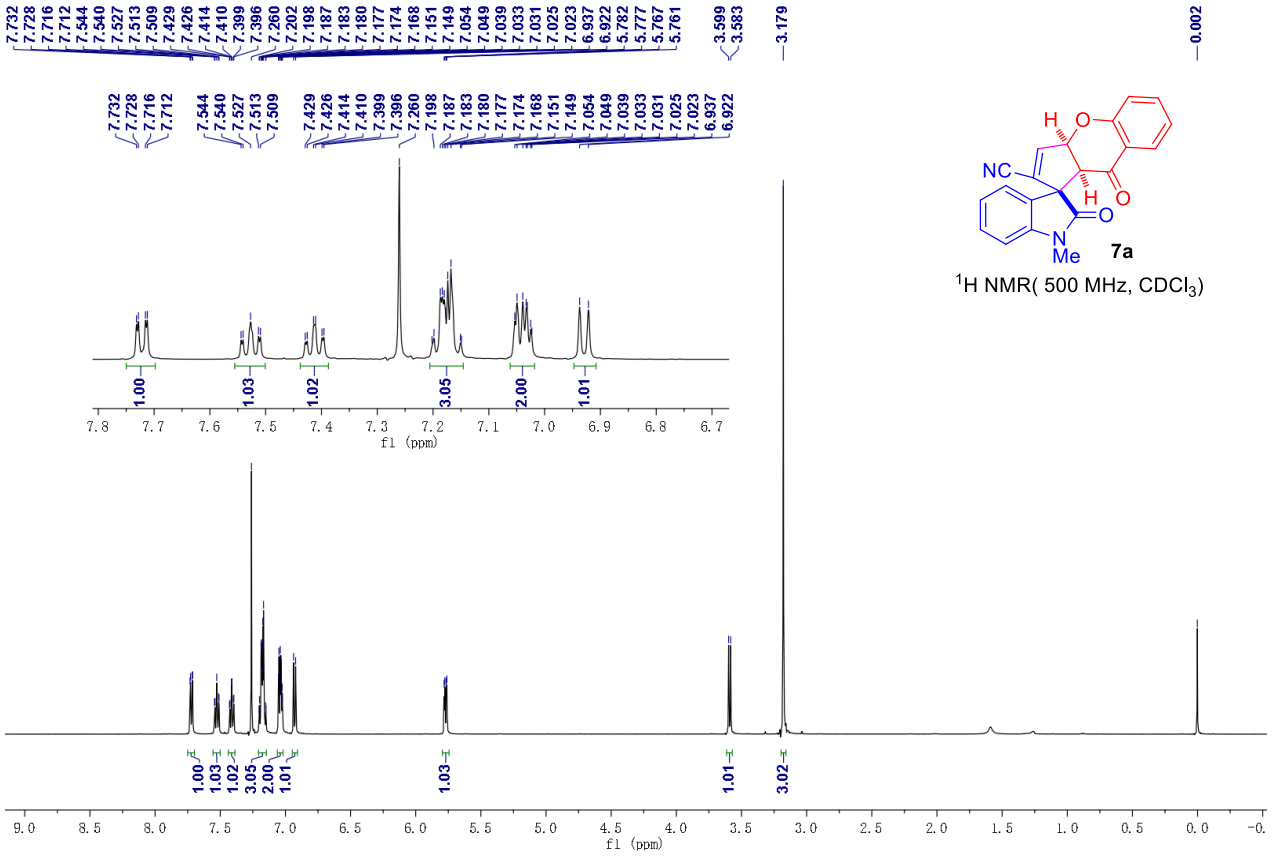


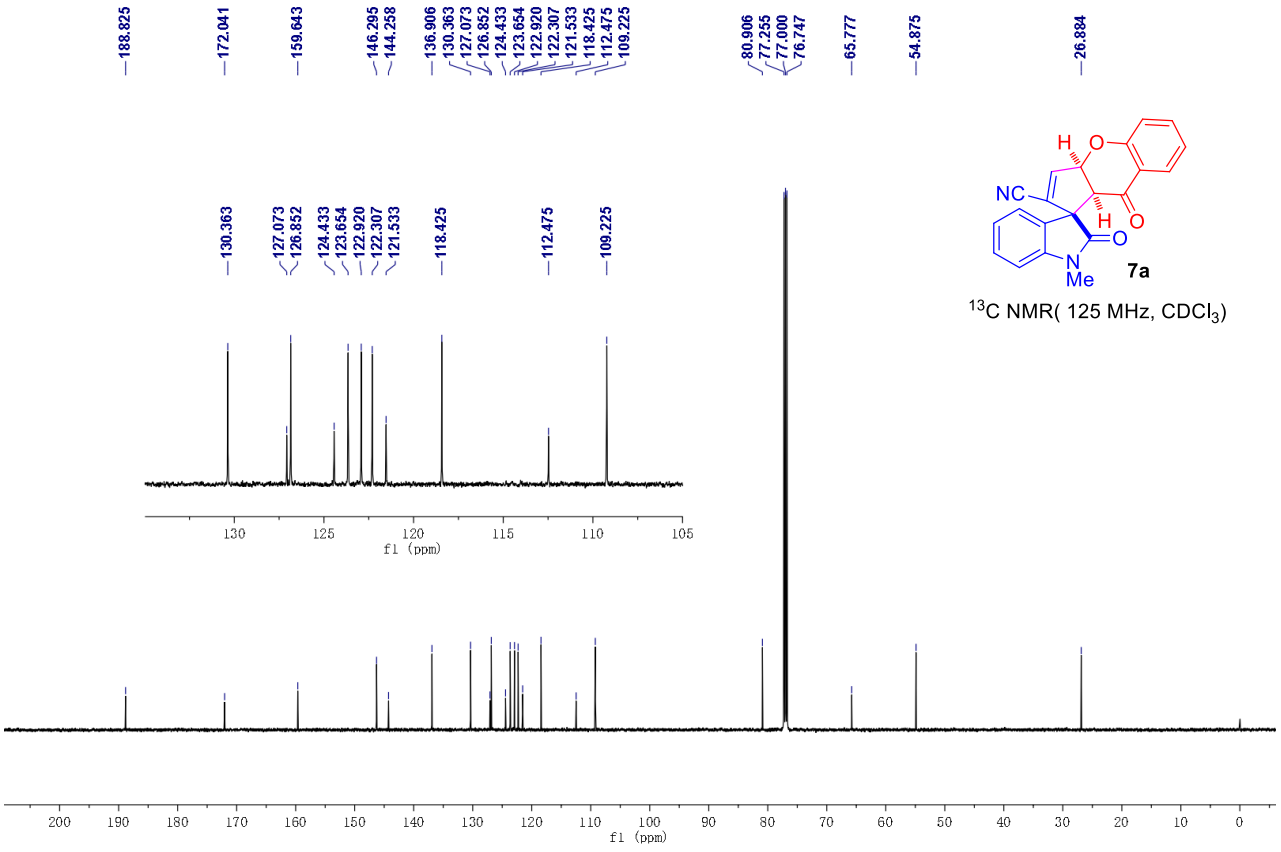
(CCDC 2055644)

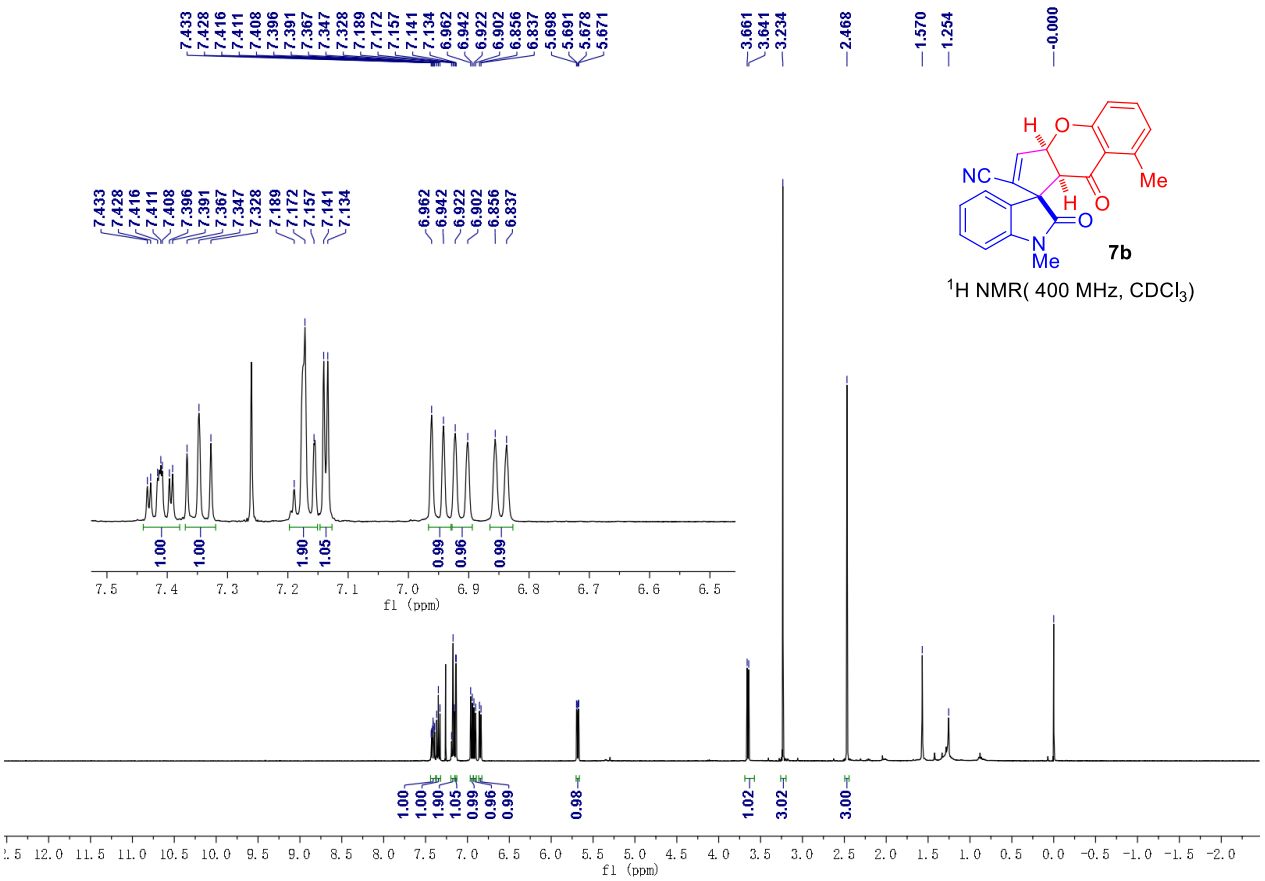
X-ray structure of racemic product **9a**

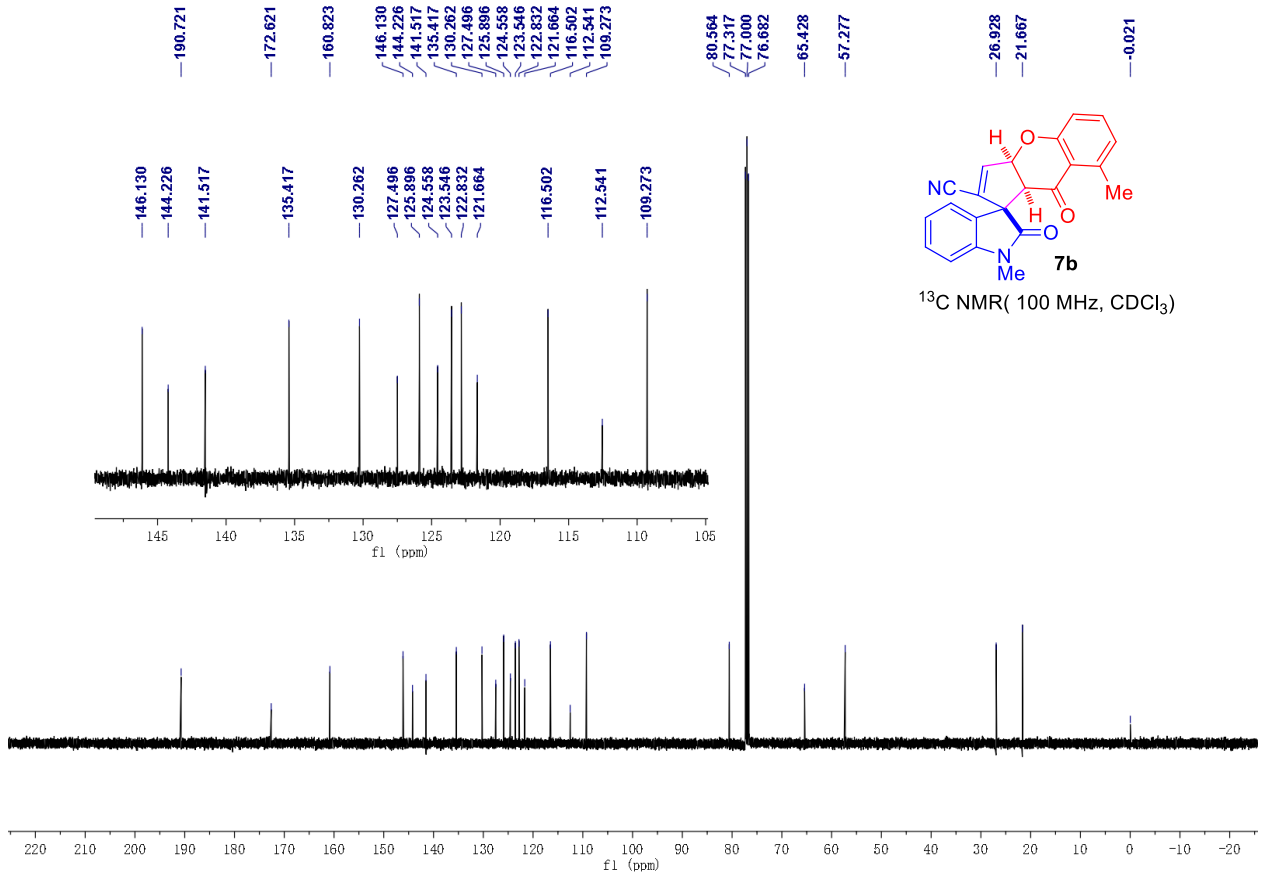
Crystal data	
Identification code	20191113
Empirical formula	$C_{29}H_{26}N_4O_5$
Formula weight	510.54
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.538(3)
b/Å	12.0654(11)
c/Å	12.568(2)
α/°	94.880(10)
β/°	104.196(17)
γ/°	91.692(12)
Volume/Å^3	1687.7(5)
Z	2
ρ_{calc}g/cm^3	1.005
μ/mm^{-1}	0.573
F(000)	536.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.288 to 147.738
Index ranges	-14 ≤ h ≤ 13, -14 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	11284
Independent reflections	6558 [R_{int} = 0.0808, R_{sigma} = 0.1102]
Data/restraints/parameters	6558/0/348
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.1011, Wr_2 = 0.2790
Final R indexes [all data]	R_1 = 0.1462, Wr_2 = 0.3325
Largest diff. Peak/hole / e Å^{-3}	0.41/-0.43

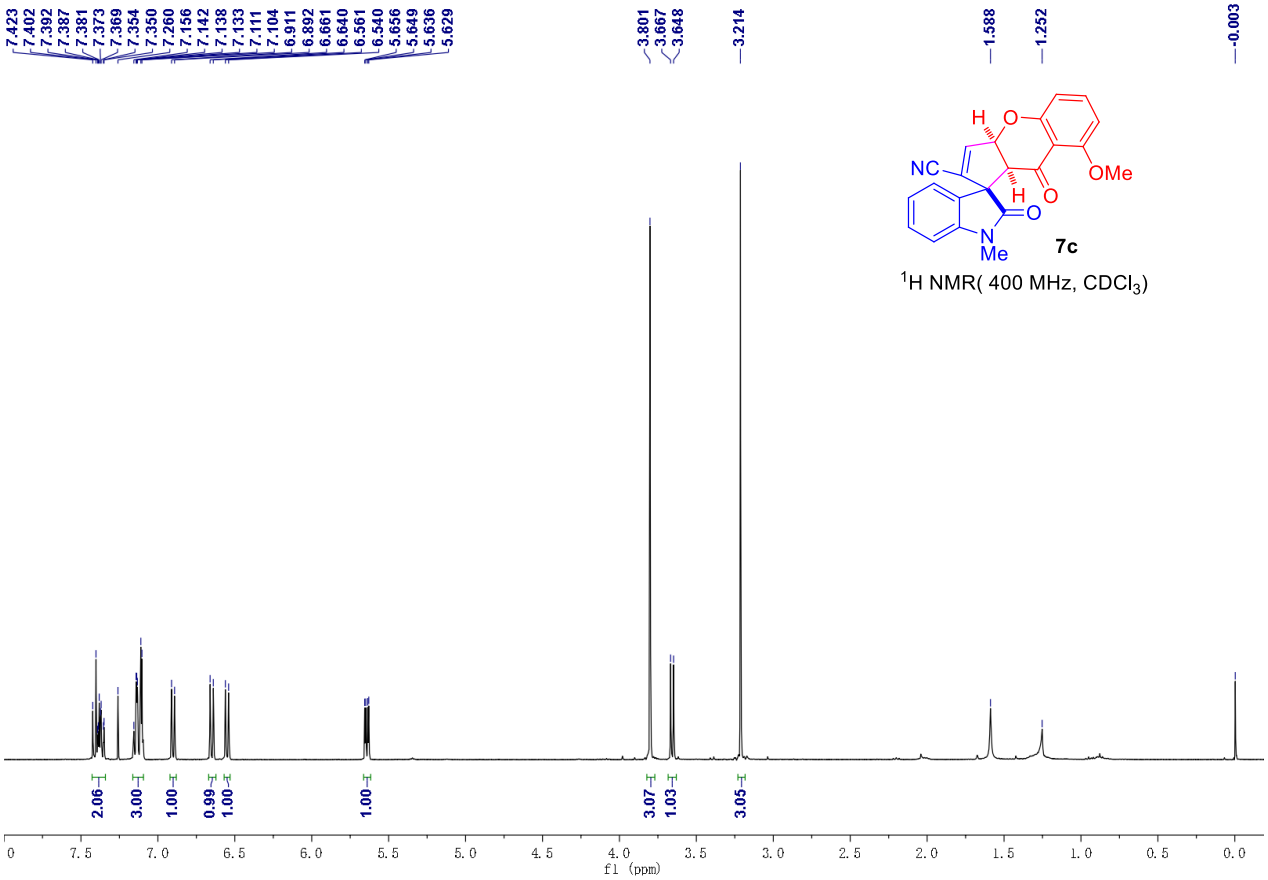
11. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Compounds 7, 8, and 9

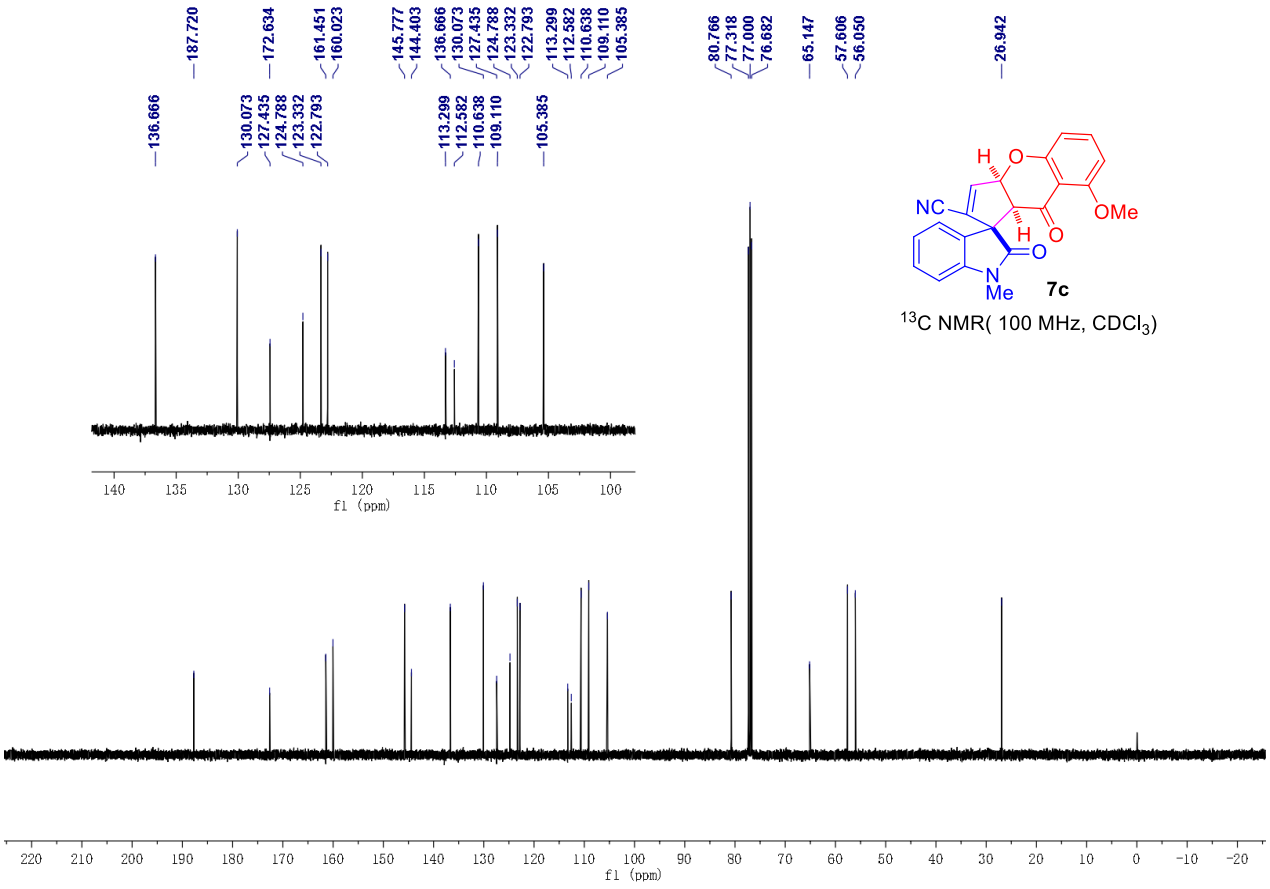


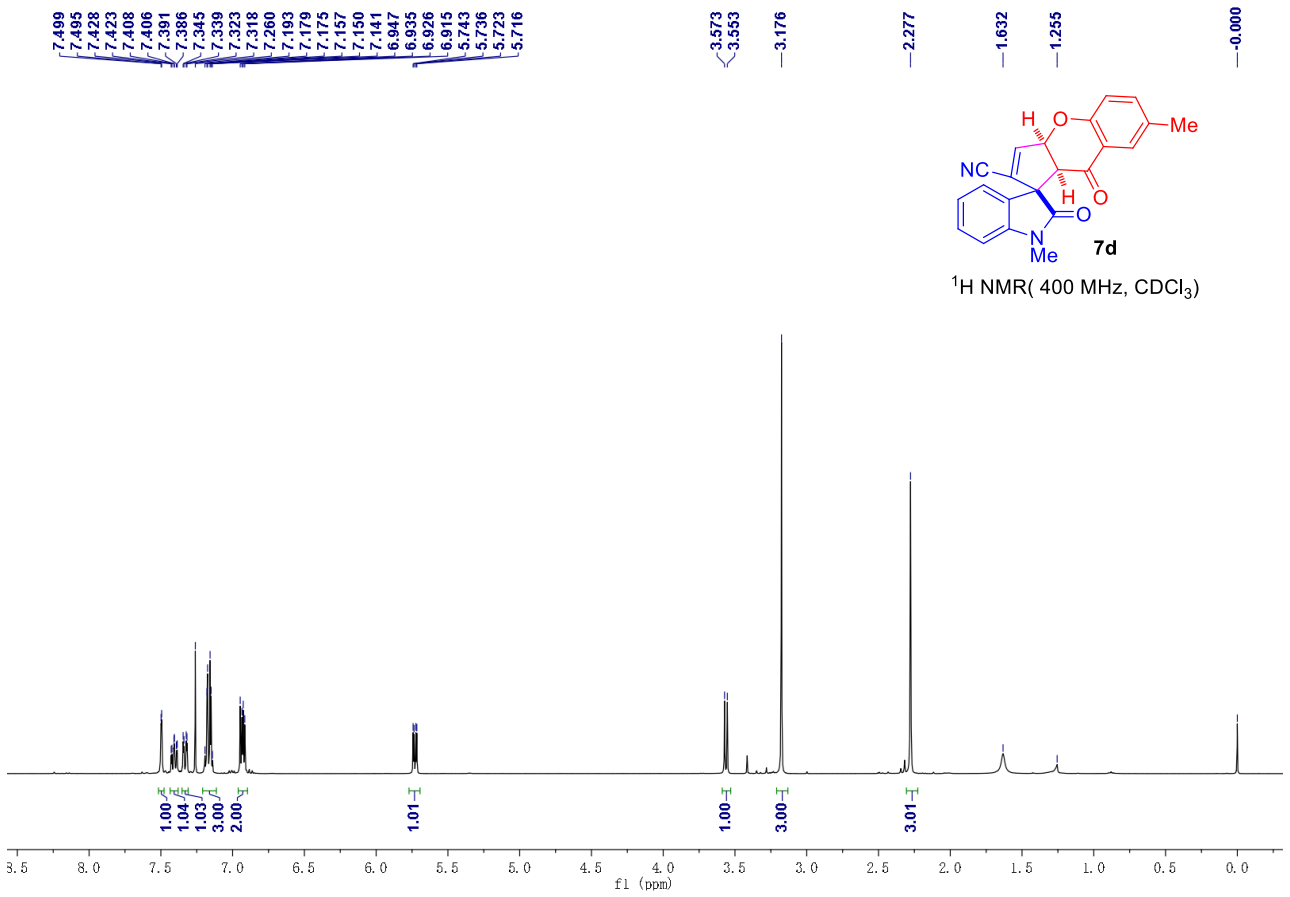



7.433
7.428
7.416
7.411
7.408
7.396
7.391
7.367
7.347
7.328
7.189
7.172
7.157
7.141
7.134
6.962
6.942
6.922
6.902
6.856
6.837
5.698
5.691
5.678
5.671
3.661
3.641
3.234
2.468
1.570
1.254
-0.000
NC
H
O
Me
H
O
O
N
Me
7b
1H NMR(400 MHz, CDCl3)
1.00
1.00
1.90
1.05
0.99
0.96
0.99
0.98
1.02
3.02
3.00
f1 (ppm)

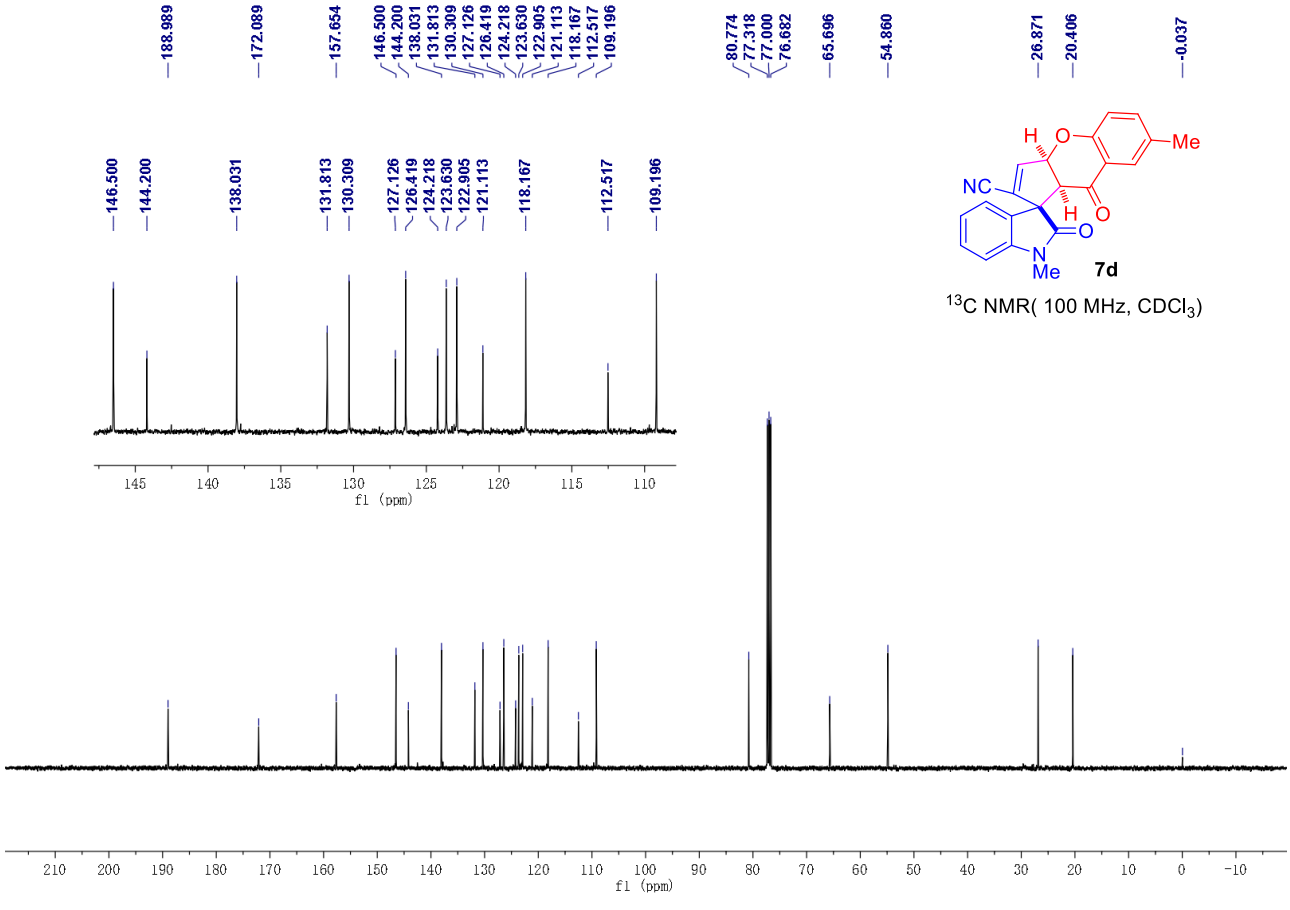

190.721
172.621
160.823
146.130
144.226
141.517
135.417
130.262
127.496
125.896
124.558
123.546
122.832
121.664
116.502
112.541
109.273
80.564
77.317
77.000
76.682
65.428
57.277
26.928
21.667
-0.021
NC
H
O
Me
H
O
O
N
Me
7b
13C NMR(100 MHz, CDCl3)
f1 (ppm)


7.423
7.402
7.392
7.387
7.381
7.373
7.369
7.354
7.350
7.260
7.156
7.142
7.138
7.133
7.111
7.104
6.911
6.892
6.661
6.640
6.561
6.540
5.656
5.649
5.636
5.629
3.801
3.667
3.648
3.214
1.588
1.252
-0.003
2.06
3.00
1.00
0.99
1.00
1.00
3.07
1.03
3.05
f1 (ppm)
H
O
NC
OMe
H
O
N
Me
7c
1H NMR(400 MHz, CDCl3)

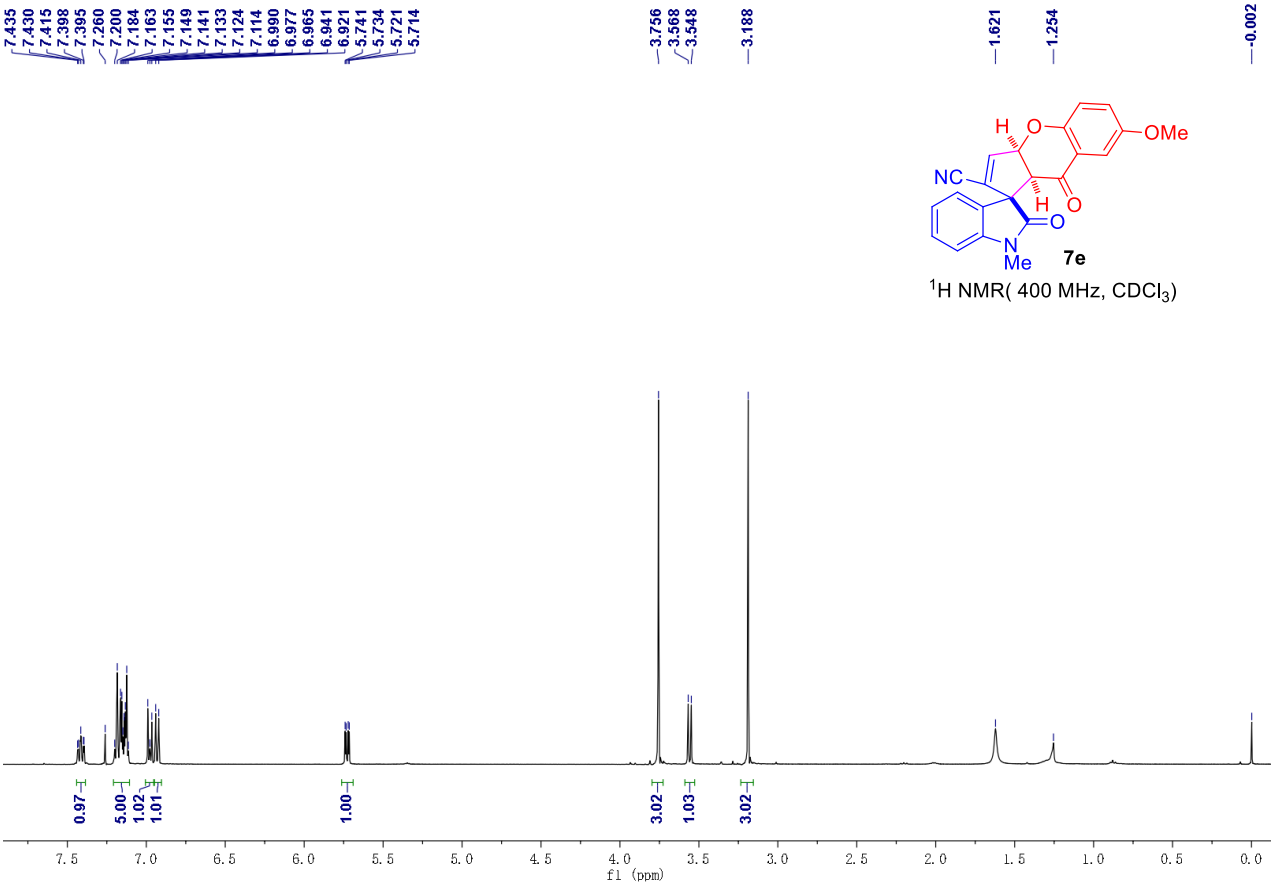

187.720
172.634
161.451
160.023
145.777
144.403
136.666
130.073
127.435
124.788
123.332
122.793
113.299
112.582
110.638
109.110
105.385
80.766
77.318
77.000
76.682
65.147
57.606
56.050
26.942
f1 (ppm)
H
O
NC
OMe
H
O
N
Me
7c
13C NMR(100 MHz, CDCl3)



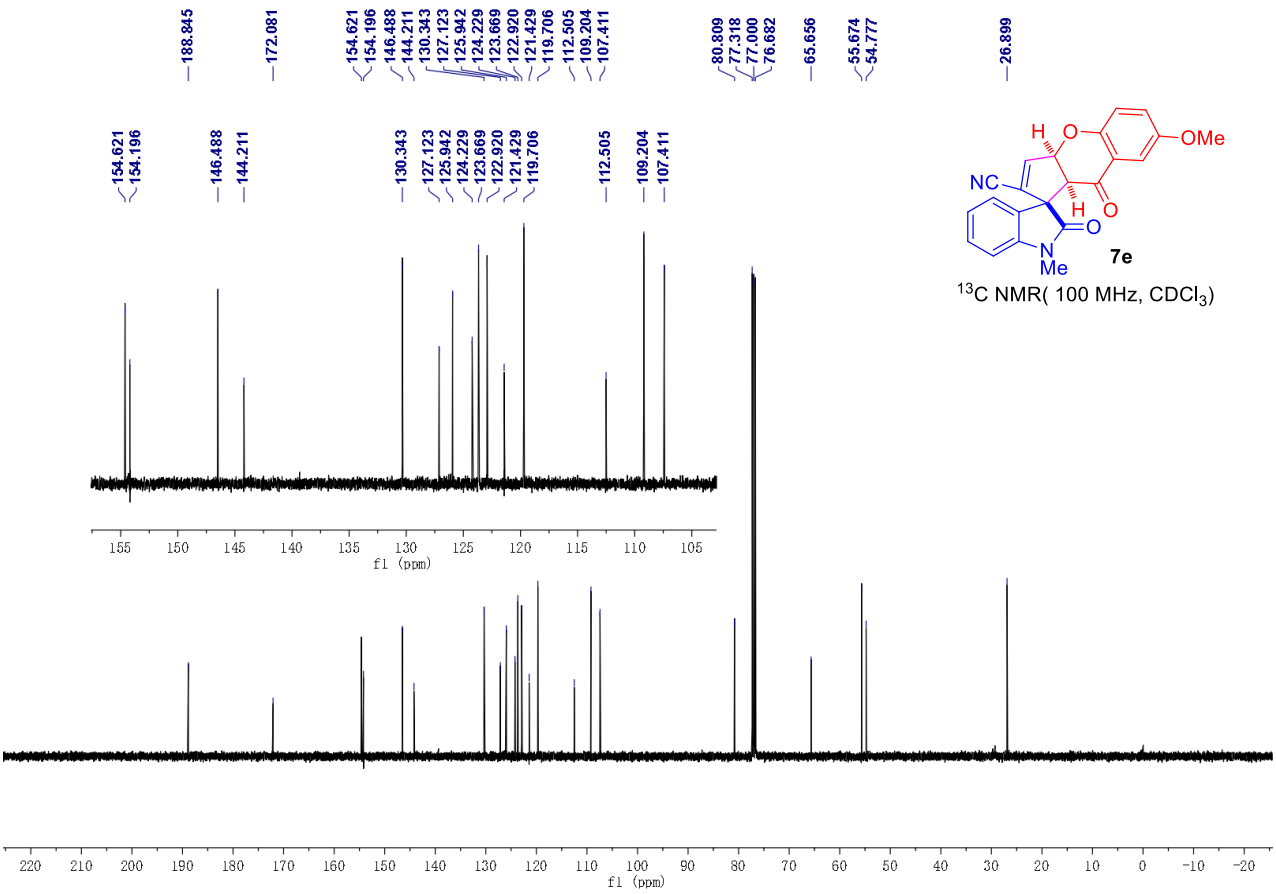
^{1}H NMR(400 MHz, $CDCl_3$)



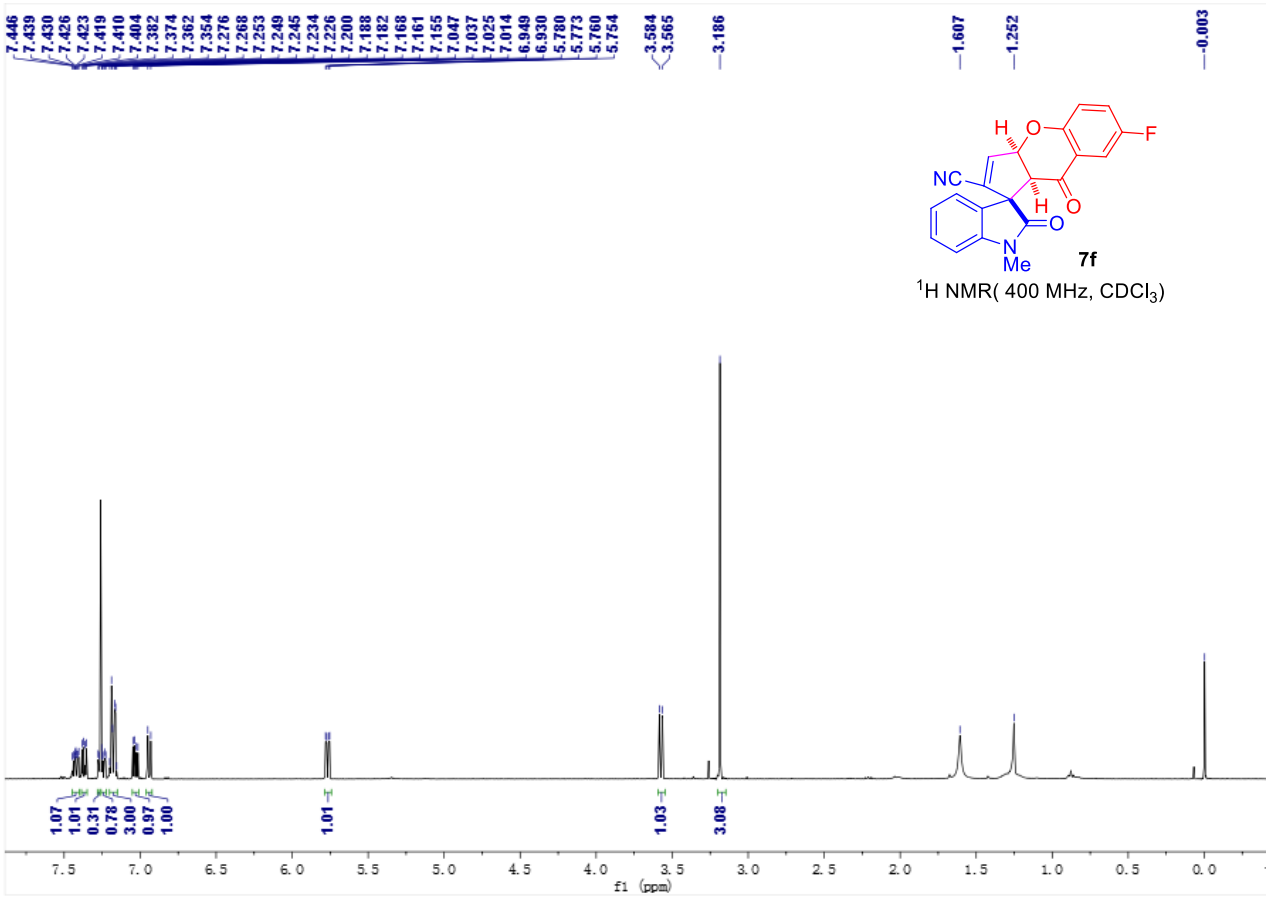
^{13}C NMR(100 MHz, $CDCl_3$)

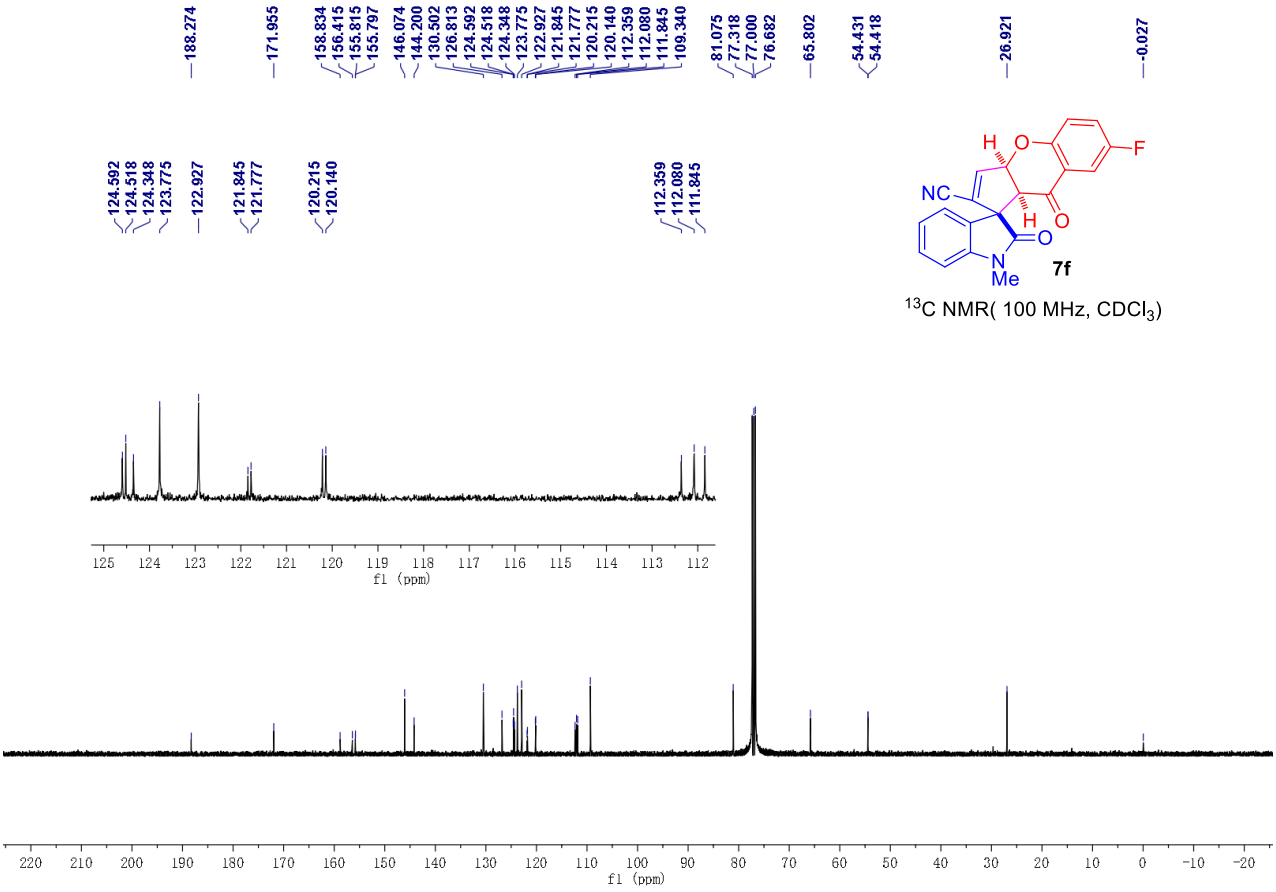


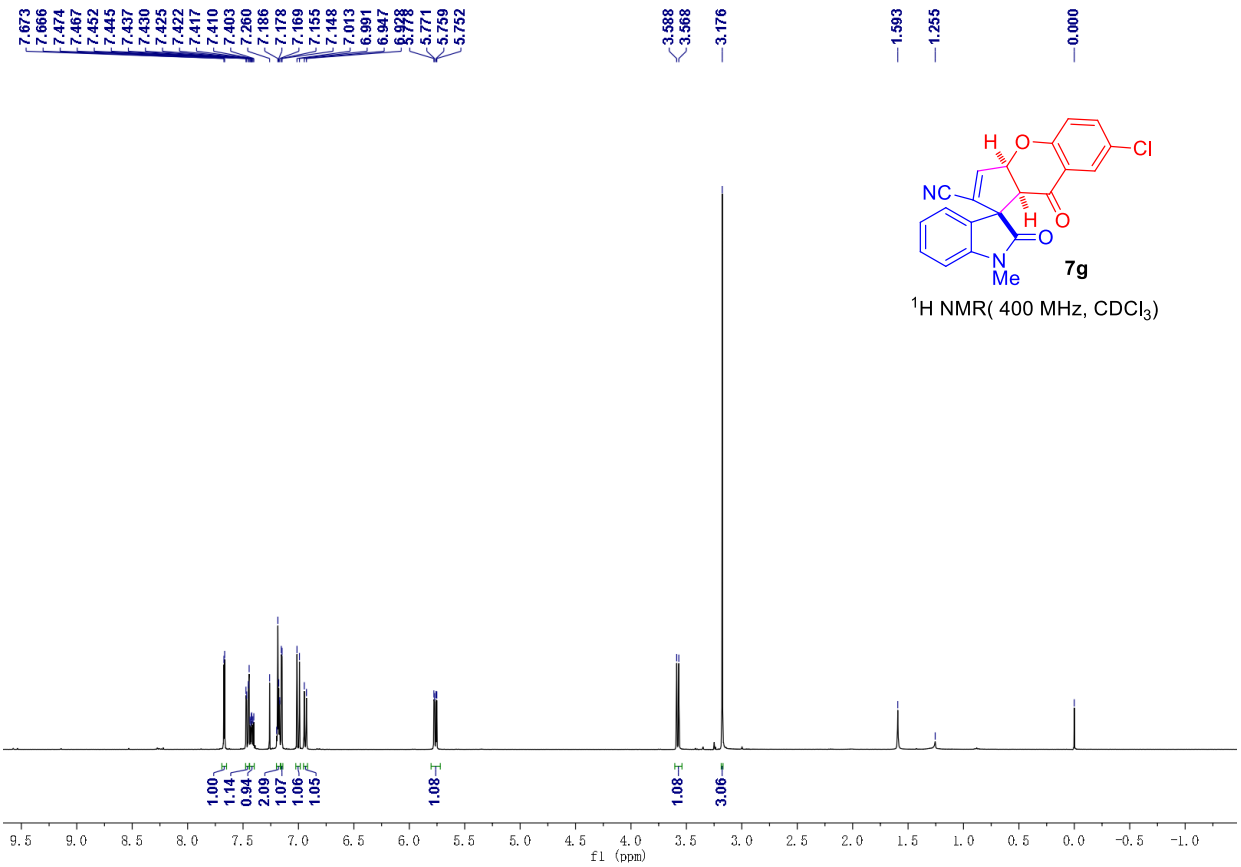
^{1}H NMR(400 MHz, $CDCl_3$)



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

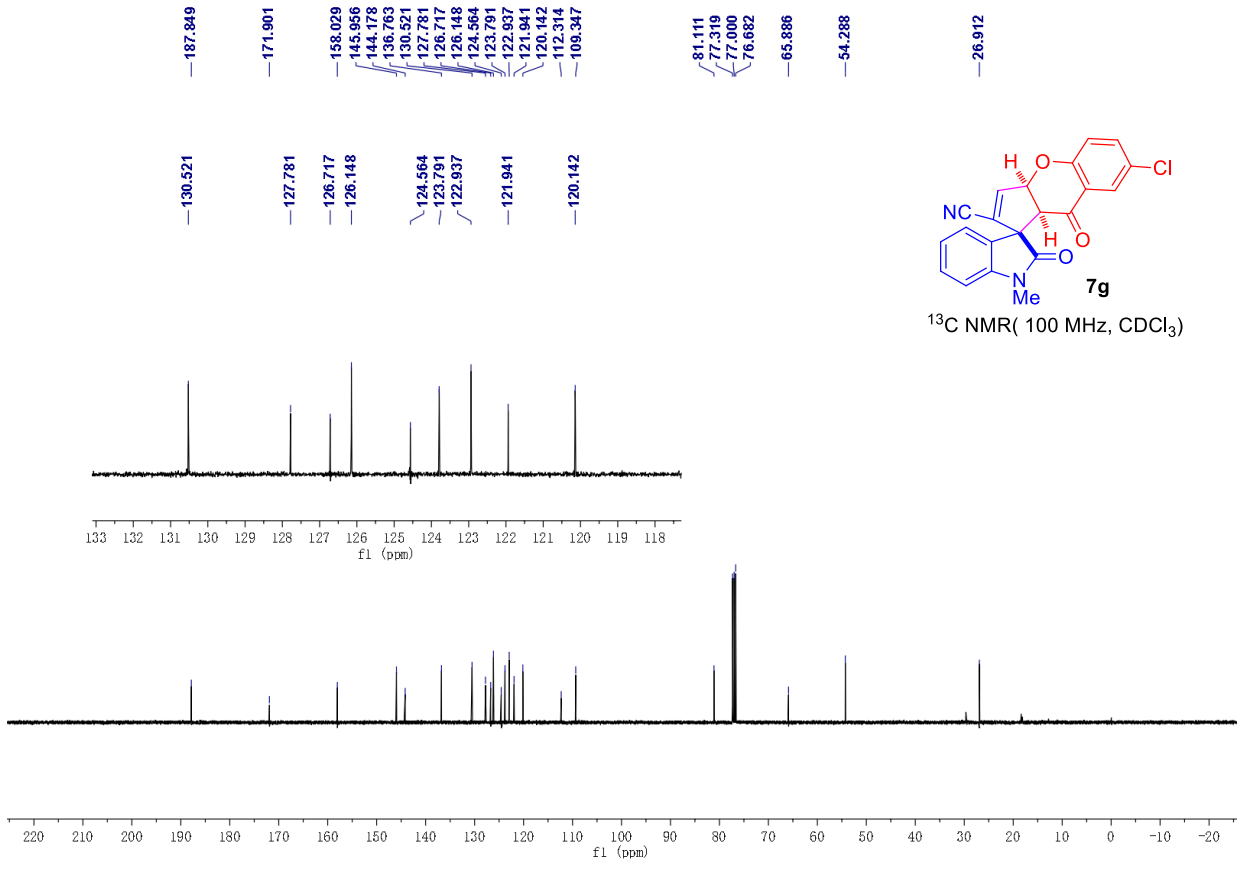

7.446
7.439
7.430
7.426
7.423
7.419
7.410
7.404
7.382
7.374
7.362
7.354
7.276
7.268
7.253
7.249
7.245
7.234
7.226
7.200
7.188
7.182
7.168
7.161
7.155
7.047
7.037
7.025
7.014
6.949
6.930
5.780
5.773
5.760
5.754
3.584
3.565
3.186
1.607
1.252
-0.003
1.07
1.01
0.31
0.78
3.00
0.97
1.00
1.01
1.03
3.08
f1 (ppm)
7f
1H NMR(400 MHz, CDCl3)


188.274
171.955
158.834
156.415
155.815
155.797
146.074
144.200
130.502
126.813
124.592
124.518
124.348
123.775
122.927
121.845
121.777
120.215
120.140
112.359
112.080
111.845
109.340
81.075
77.318
77.000
76.682
65.802
54.431
54.418
26.921
-0.027
f1 (ppm)
7f
13C NMR(100 MHz, CDCl3)



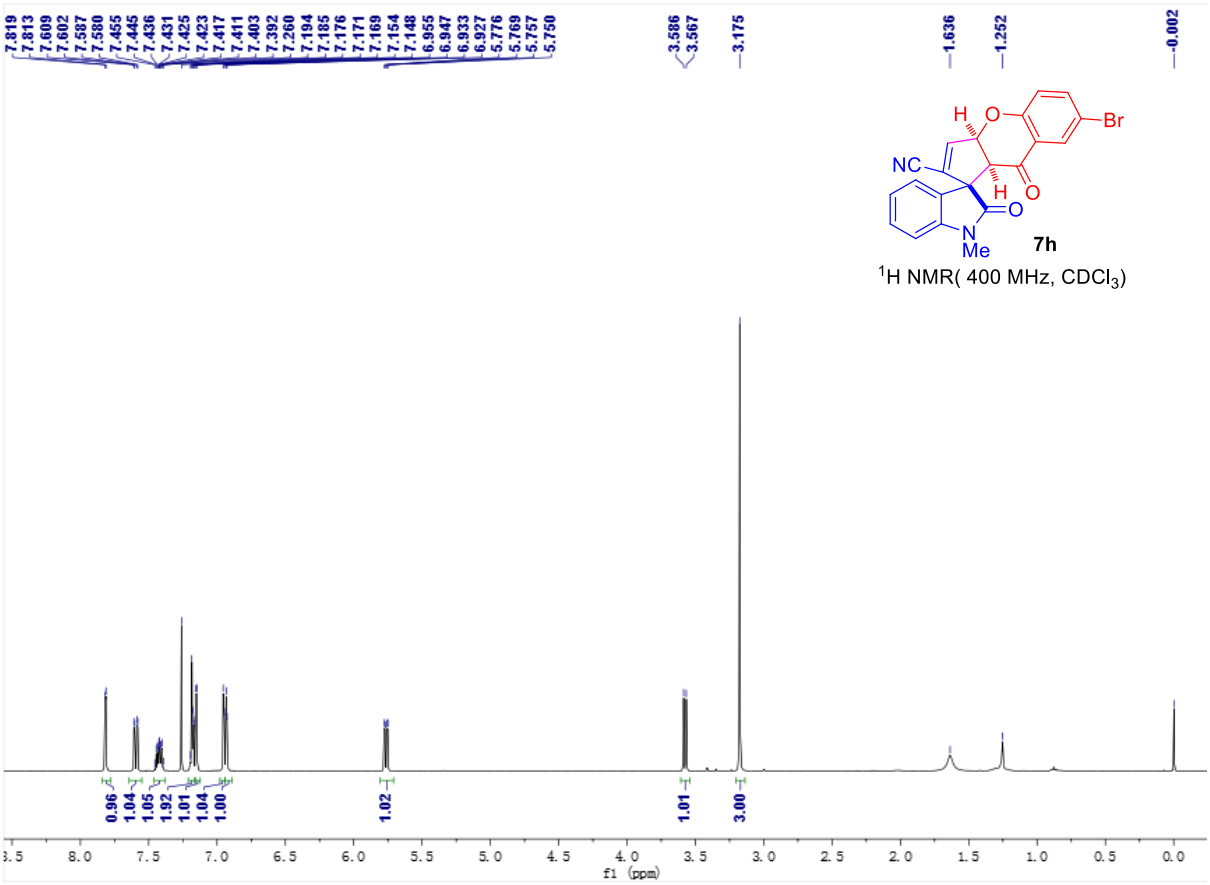
7g

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



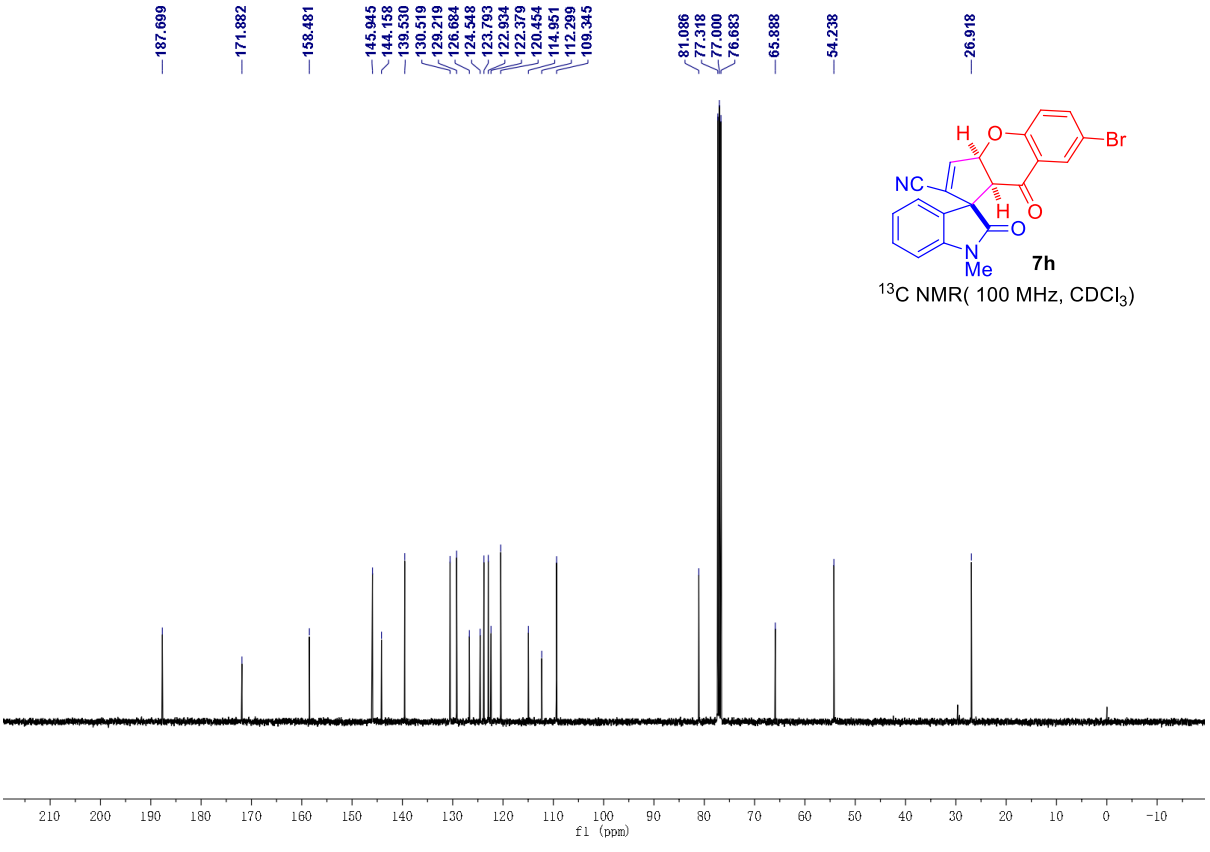
7g

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



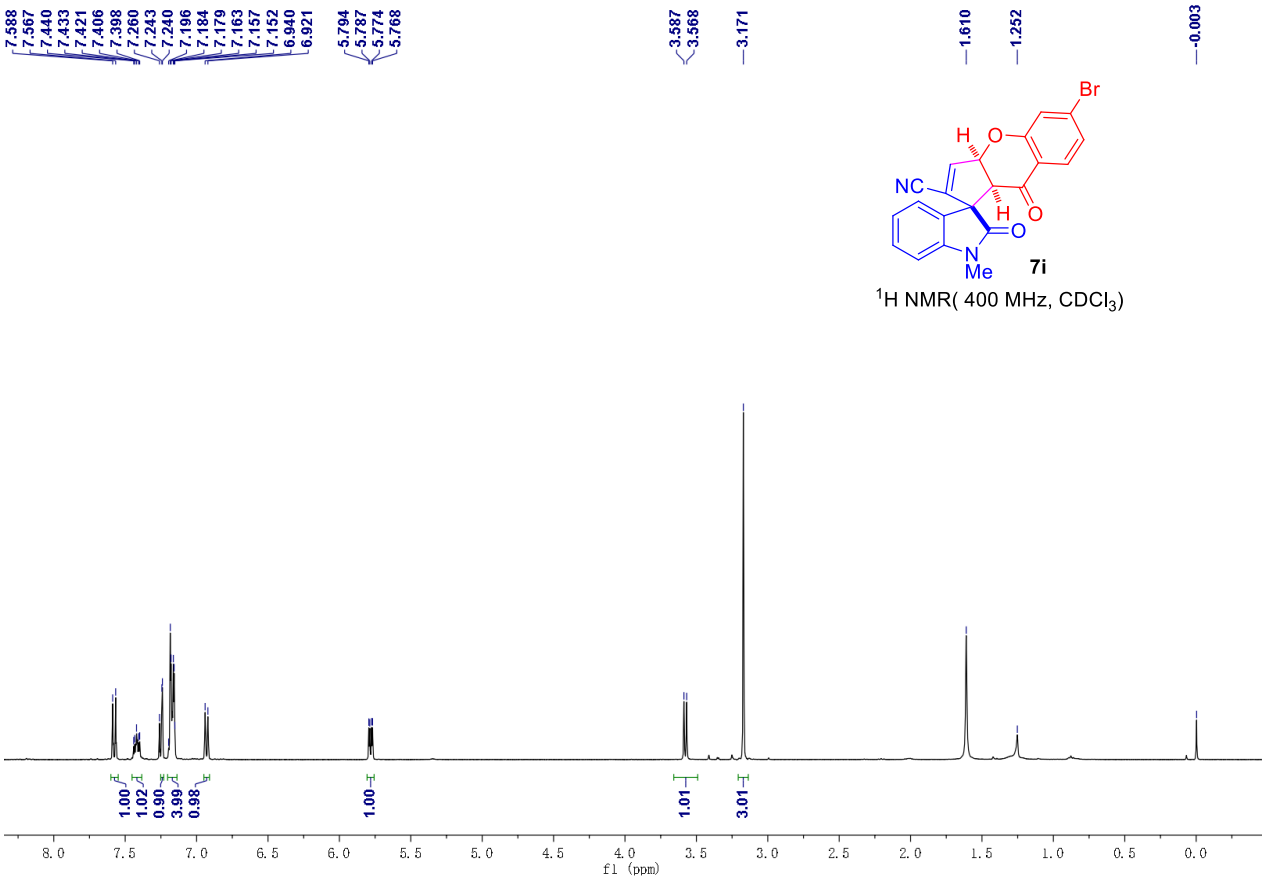
7h

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

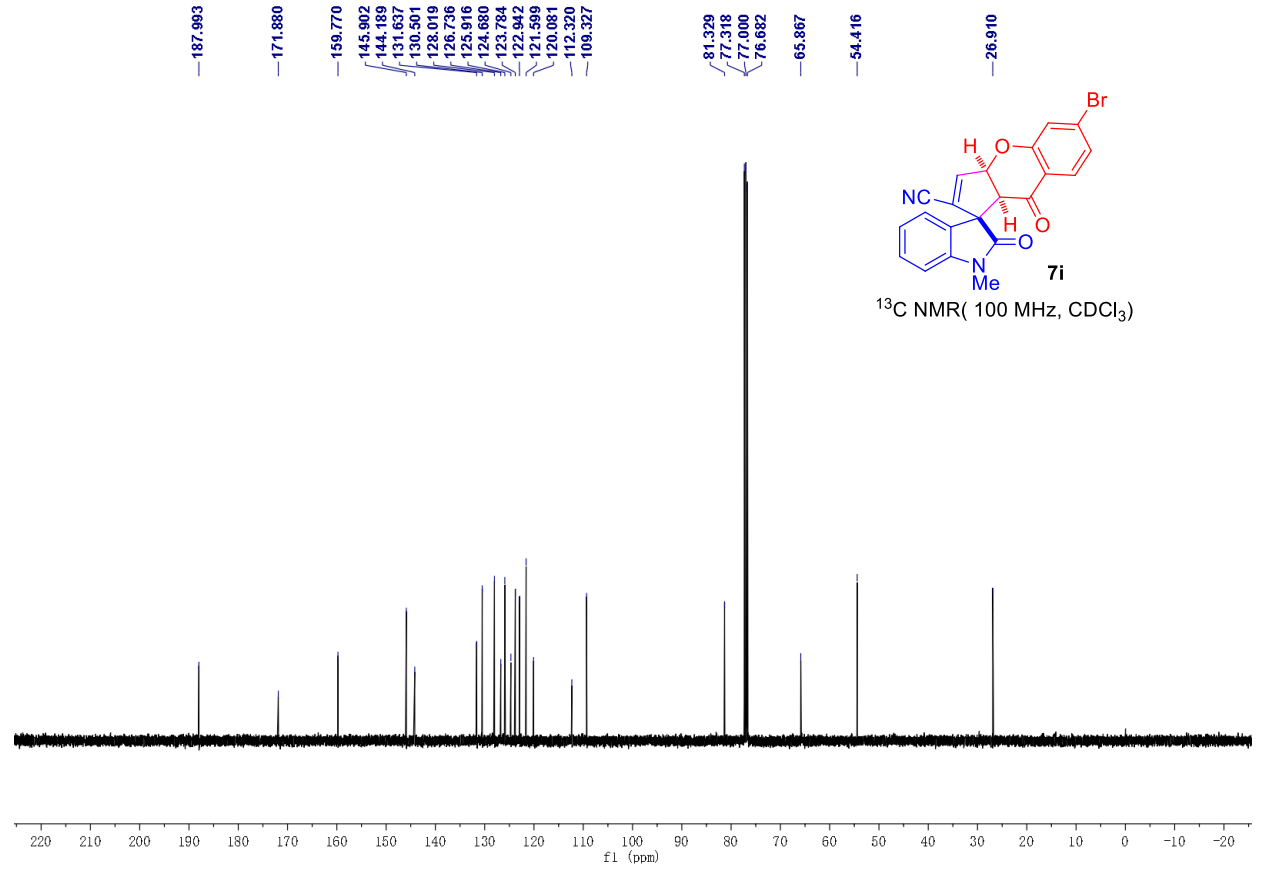


7h

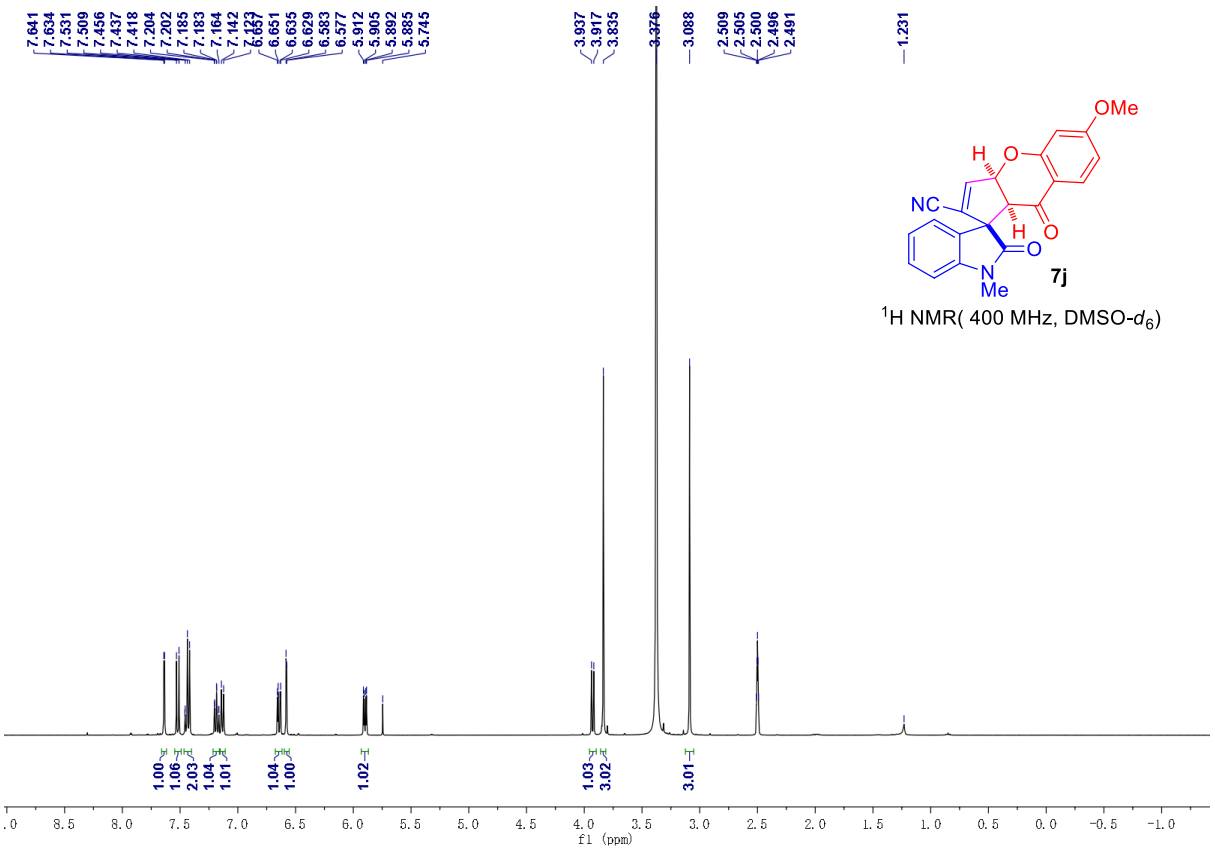
^{13}C NMR(100 MHz, $CDCl_3$)



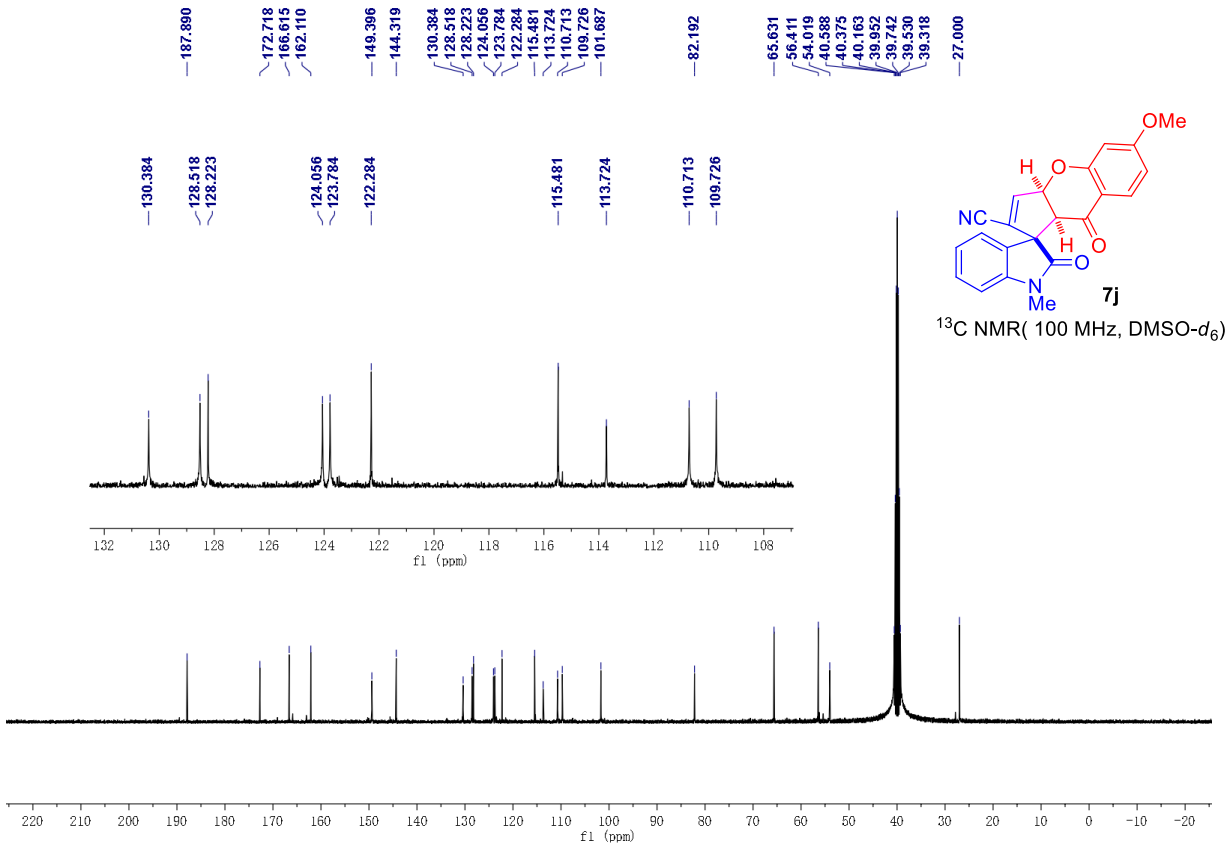
^{1}H NMR(400 MHz, $CDCl_3$)



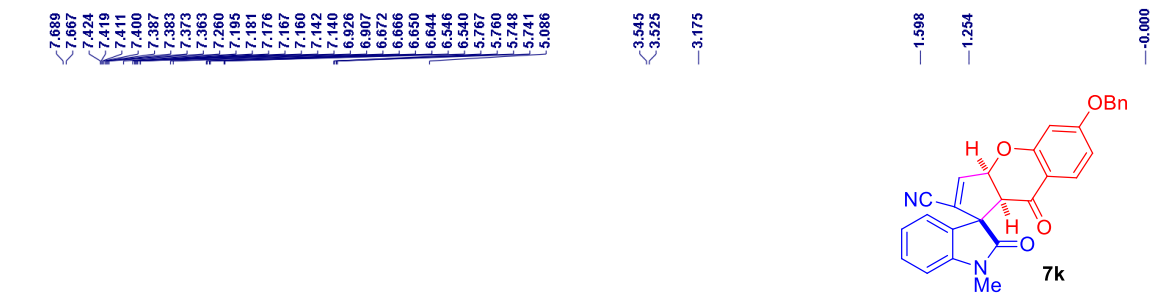
^{13}C NMR(100 MHz, $CDCl_3$)



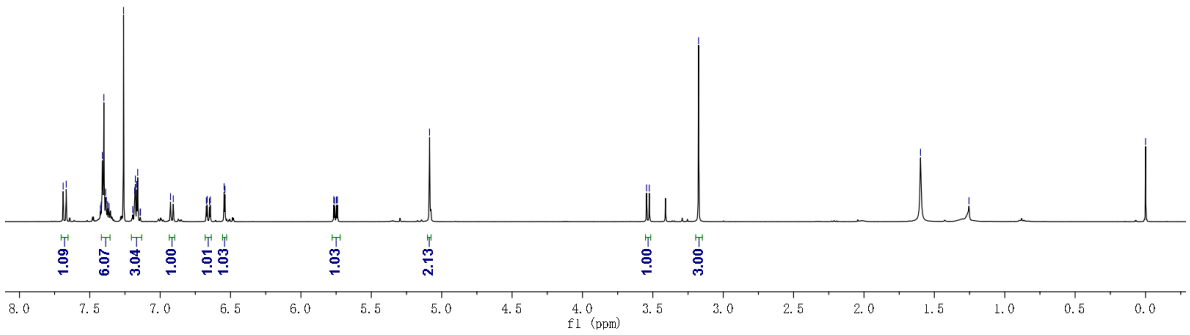
^{1}H NMR(400 MHz, DMSO-d_6)

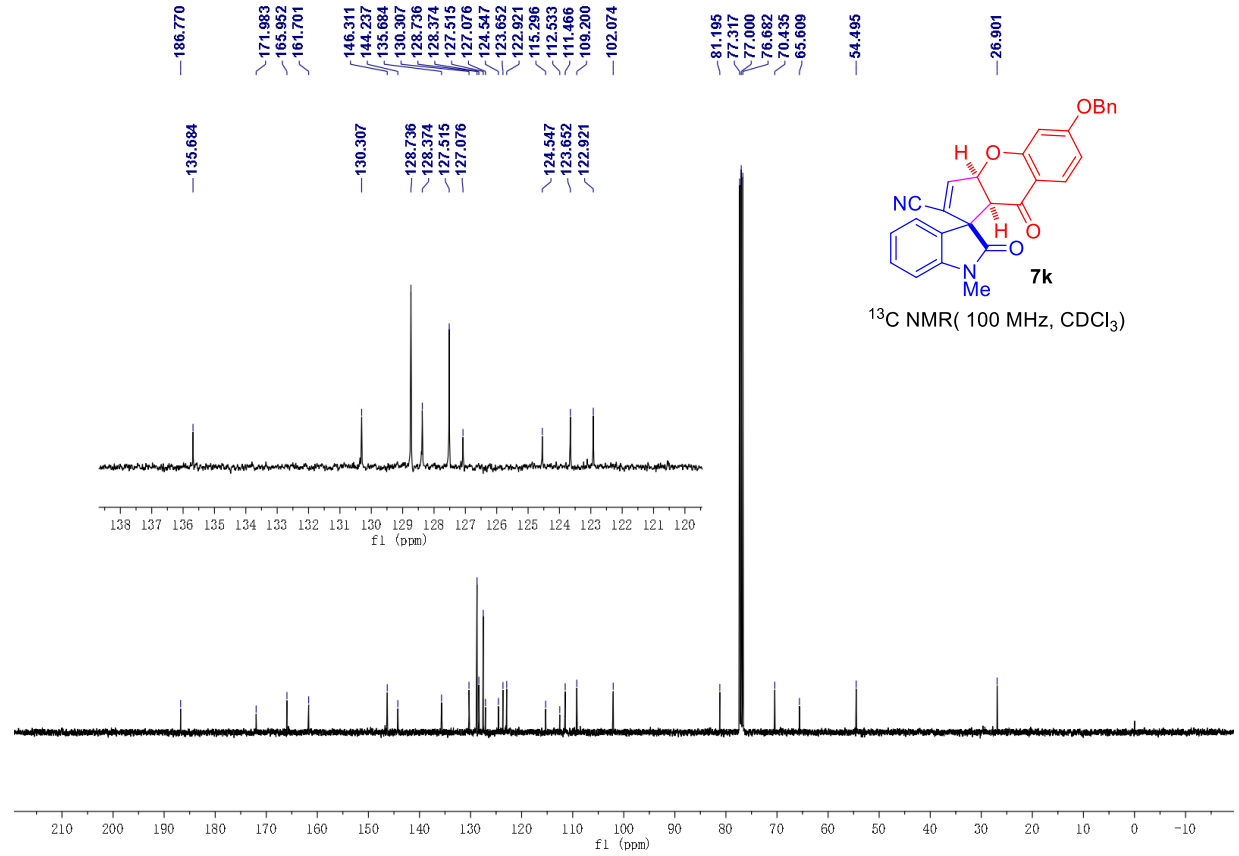


^{13}C NMR(100 MHz, DMSO-d_6)

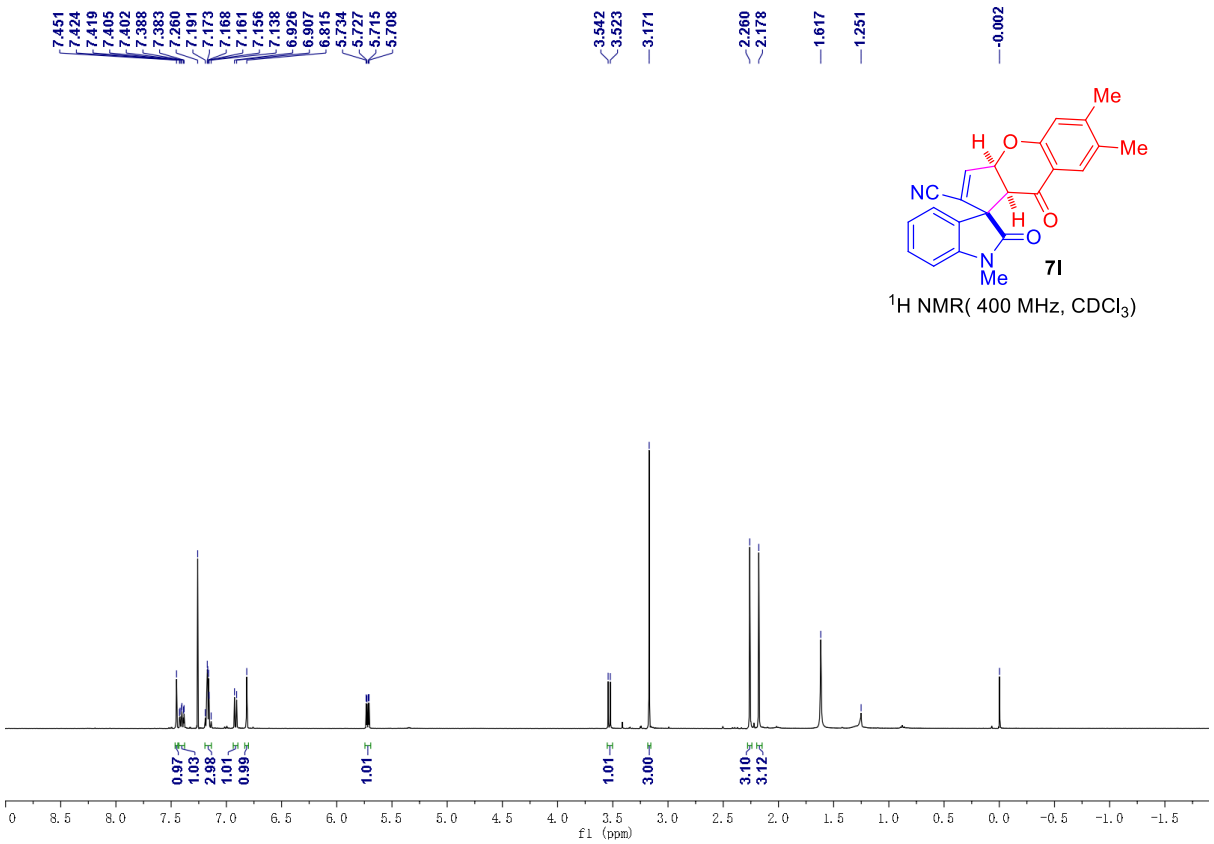


^{1}H NMR(400 MHz, $CDCl_3$)

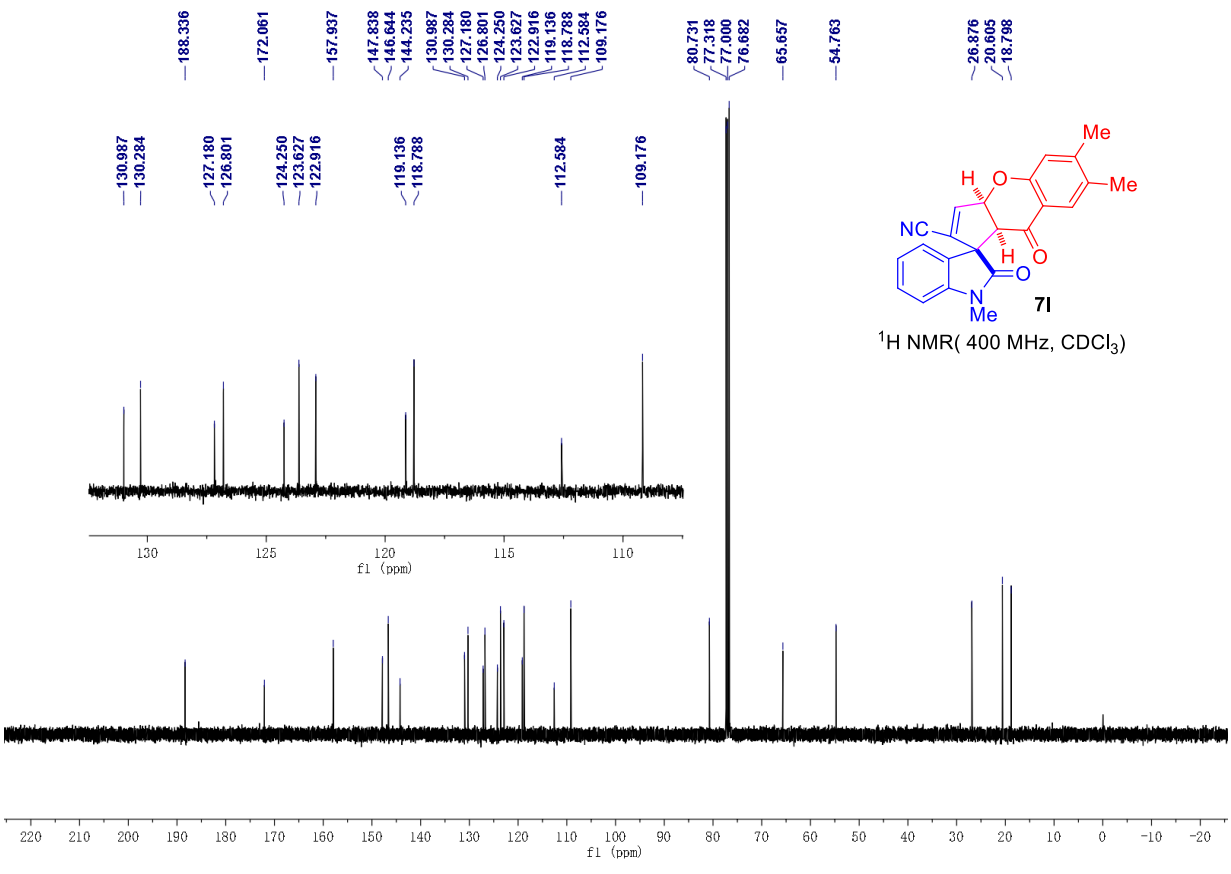




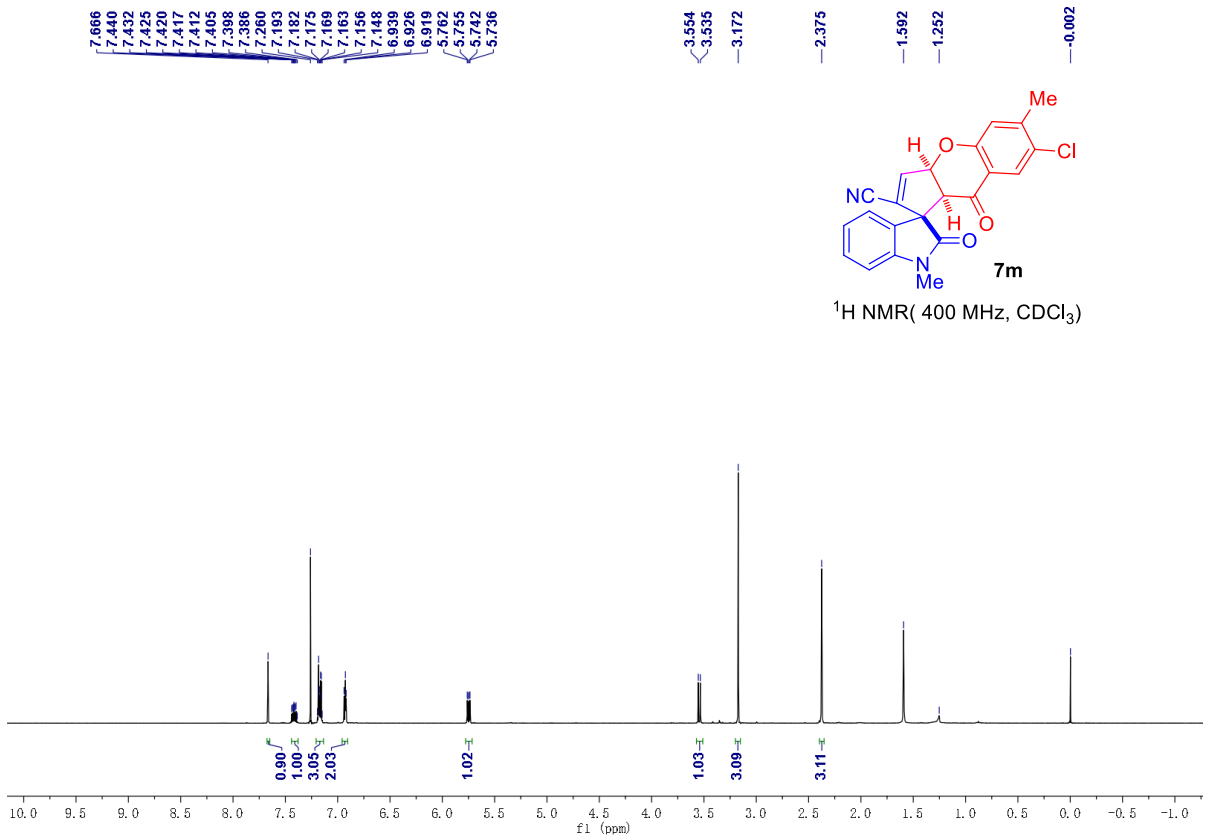
^{13}C NMR(100 MHz, $CDCl_3$)



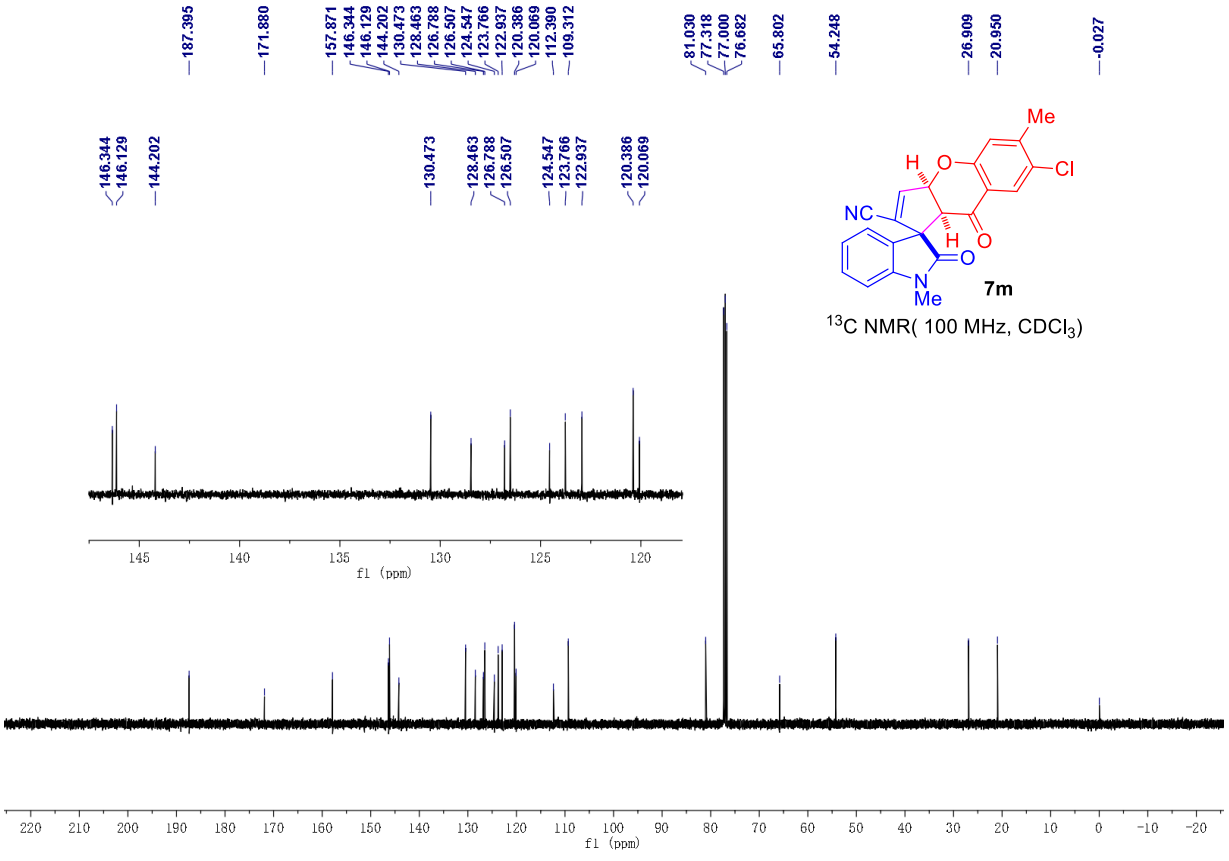
^{1}H NMR(400 MHz, $CDCl_3$)



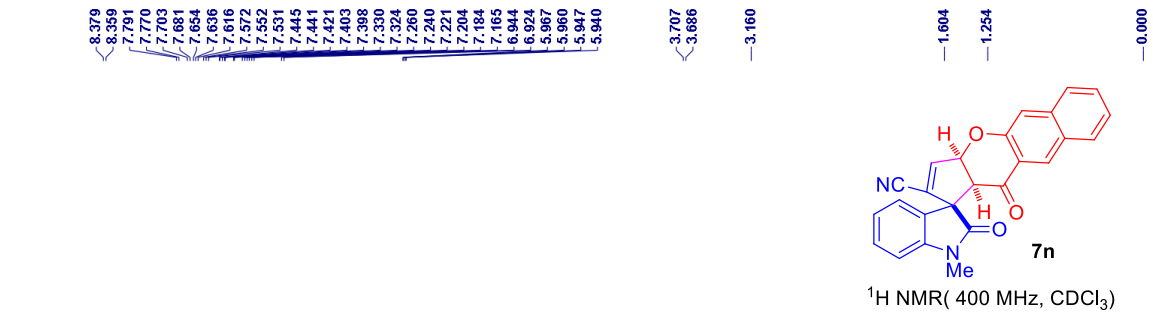
^{1}H NMR(400 MHz, $CDCl_3$)



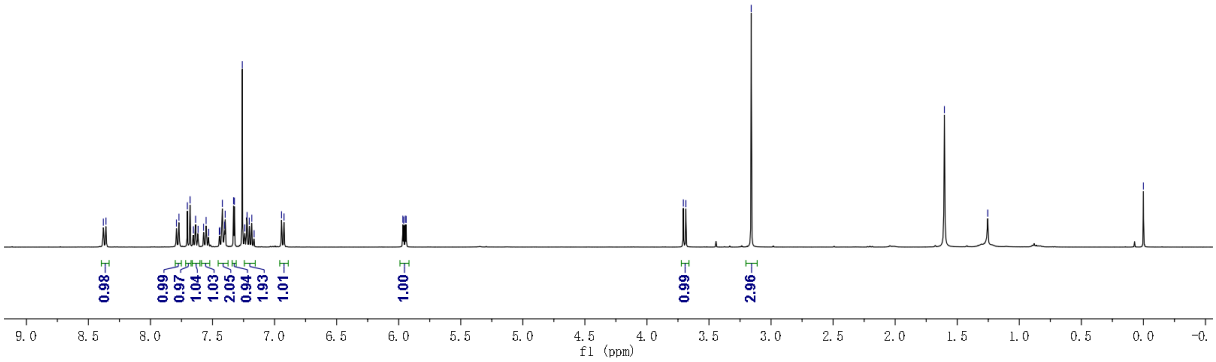
^{1}H NMR(400 MHz, $CDCl_3$)

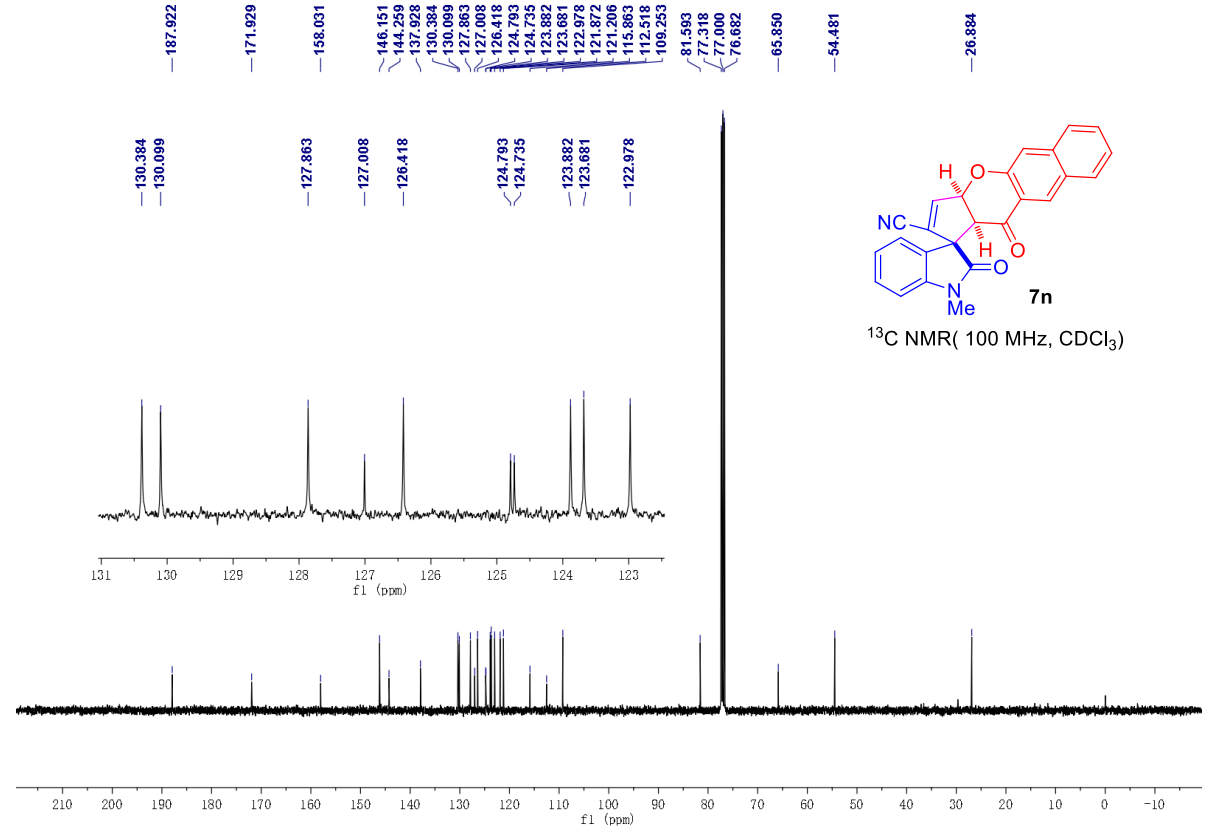


^{13}C NMR(100 MHz, $CDCl_3$)

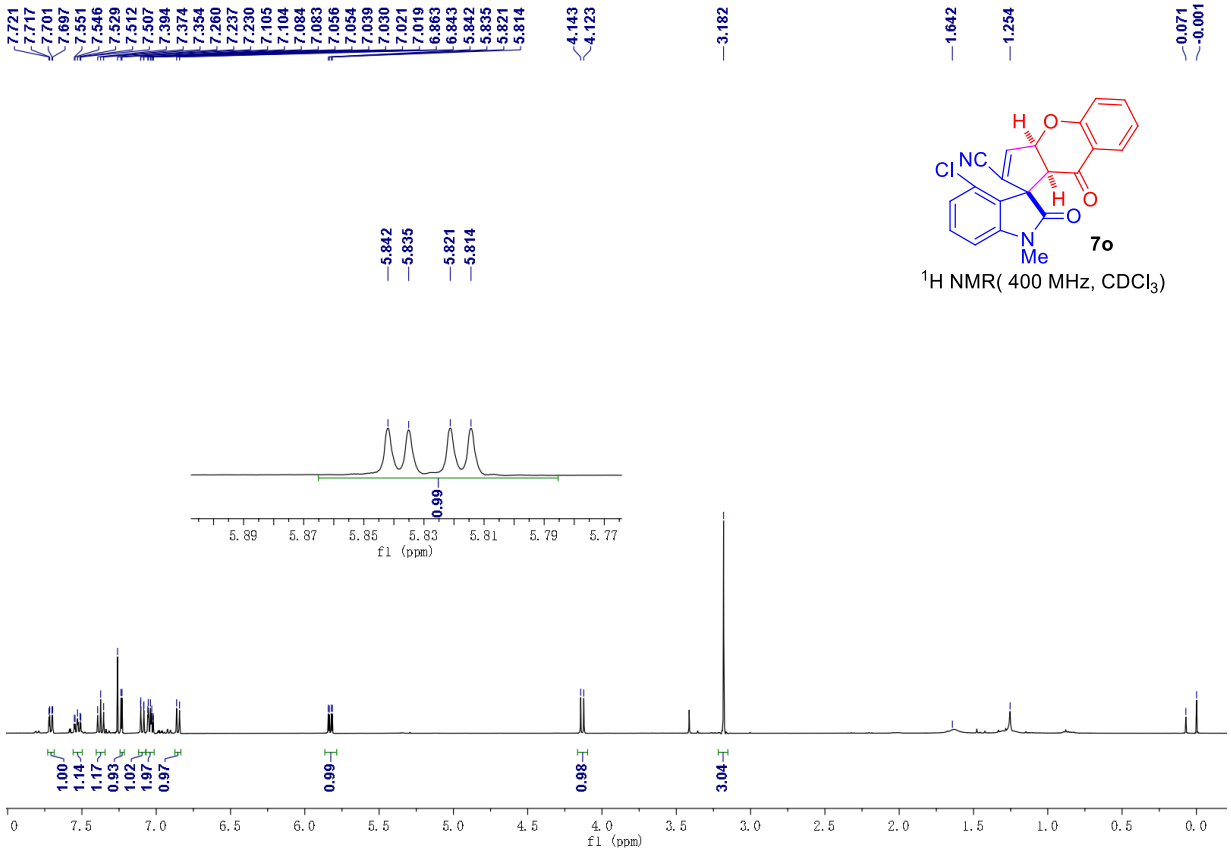


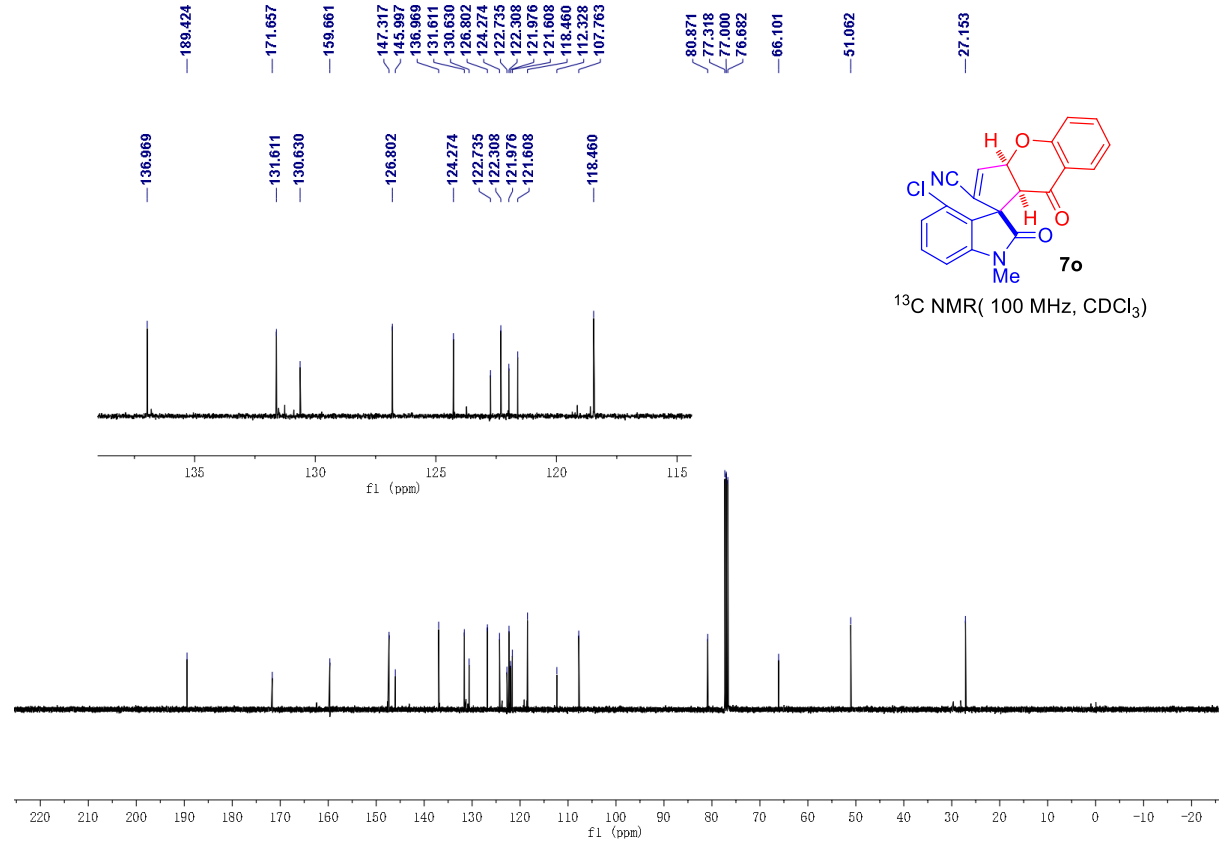
^{1}H NMR(400 MHz, $CDCl_3$)

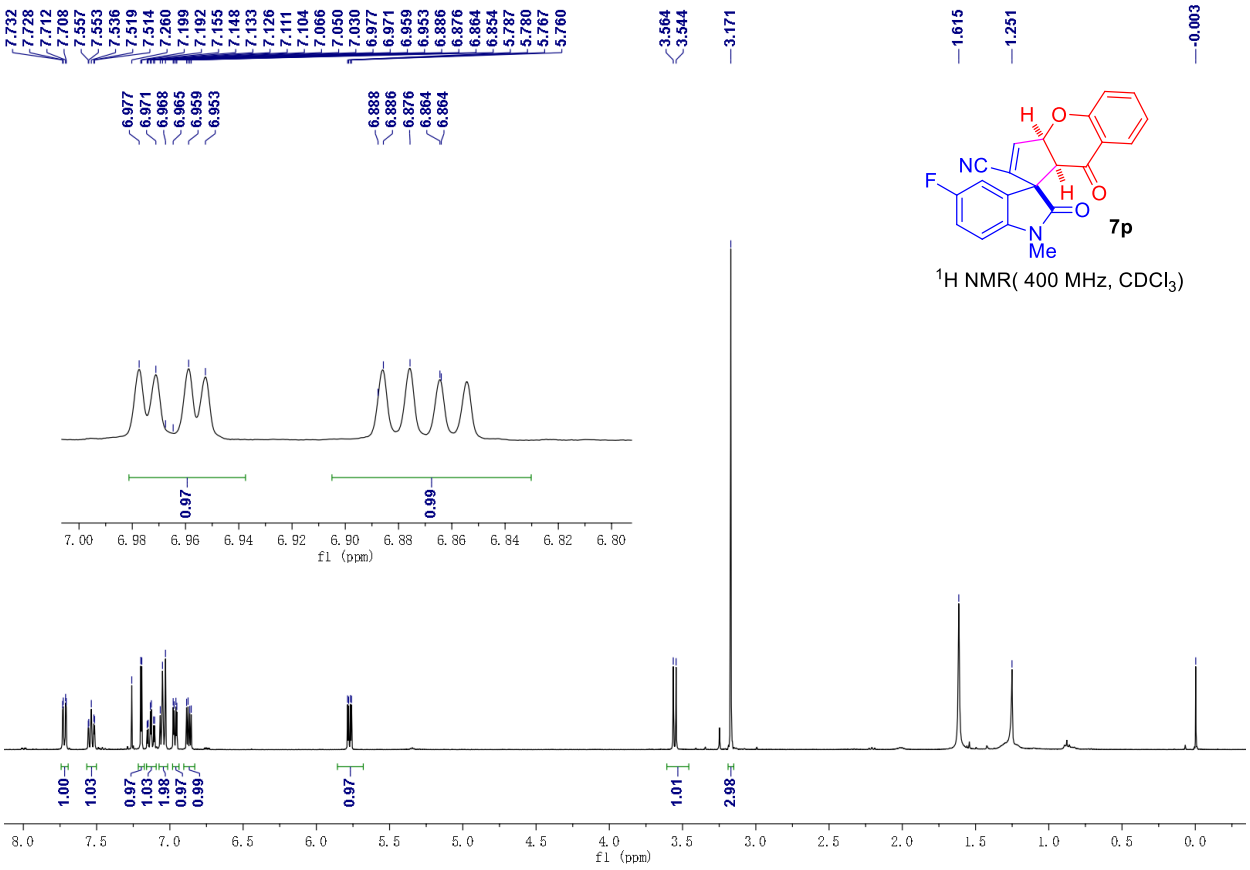


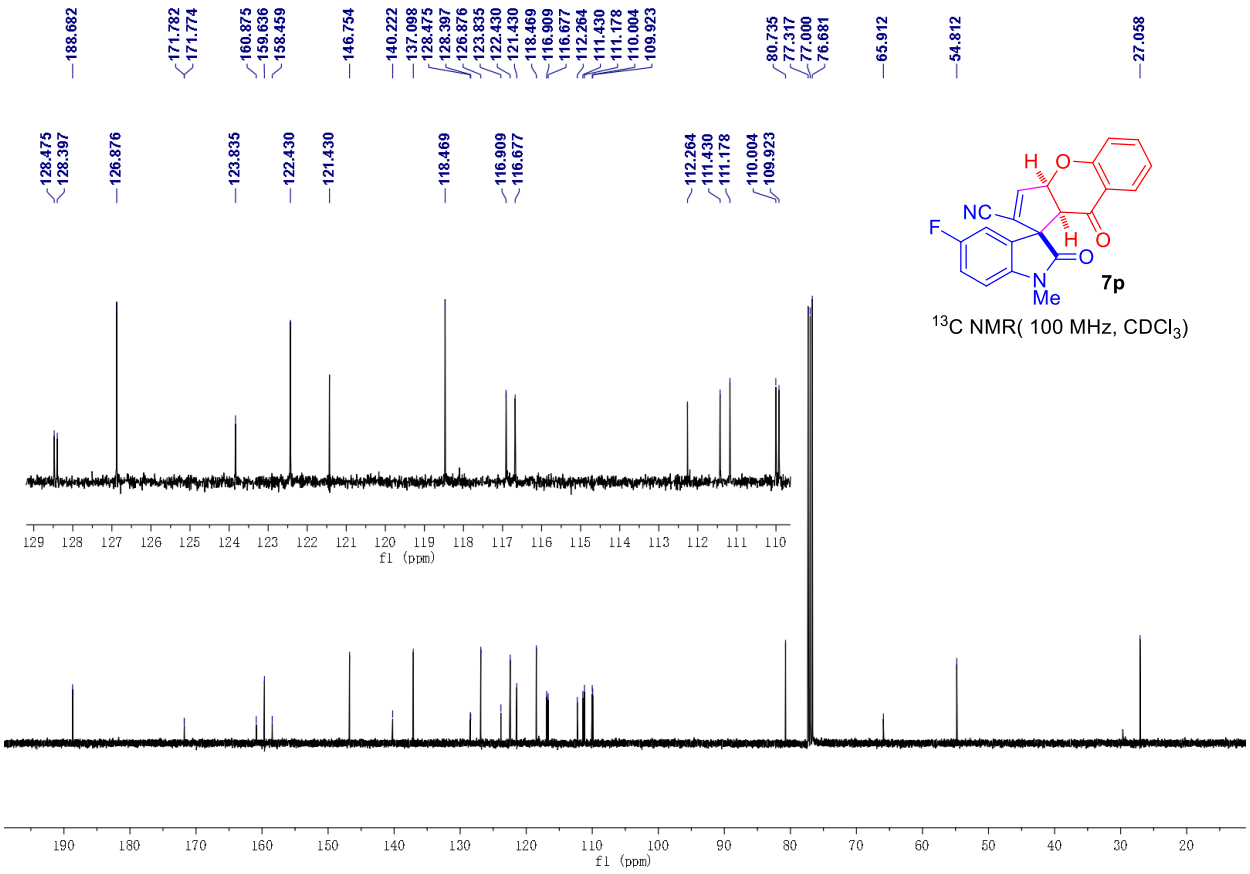


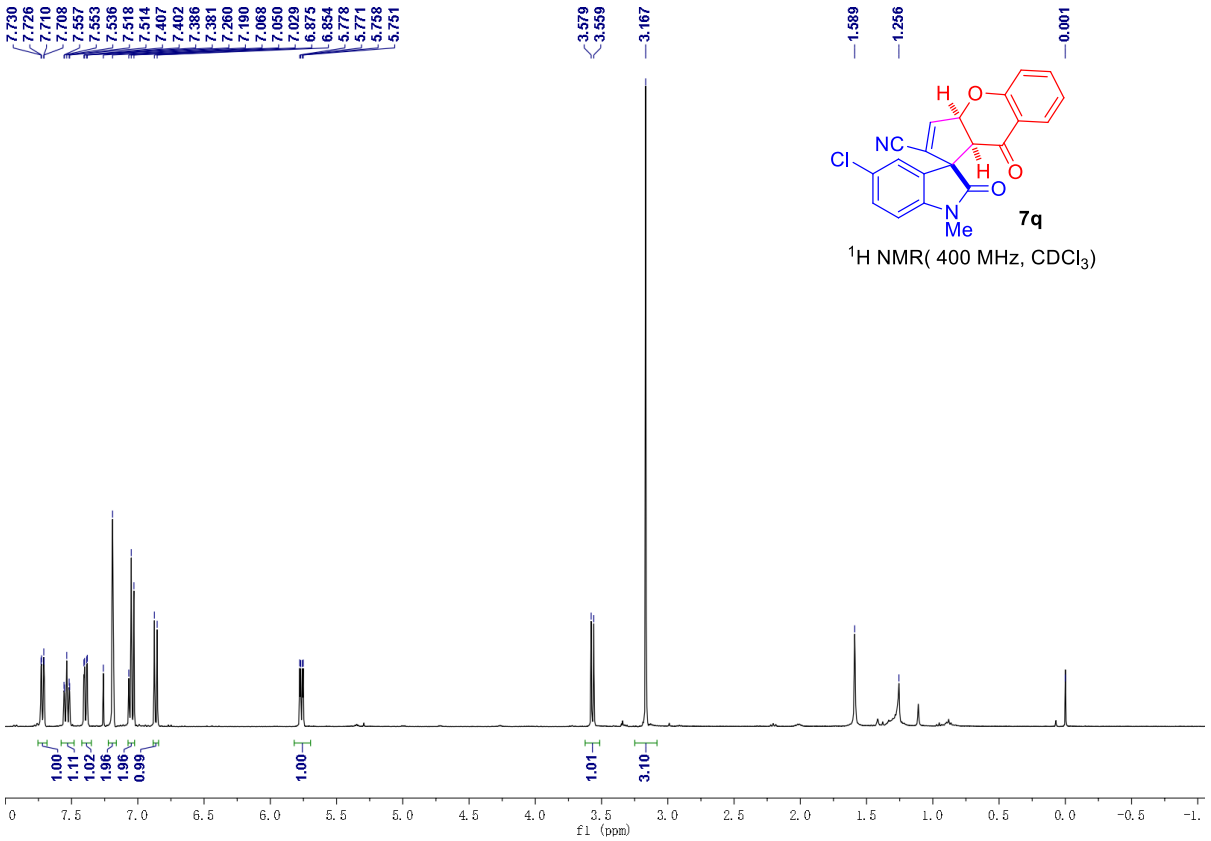
^{13}C NMR(100 MHz, $CDCl_3$)

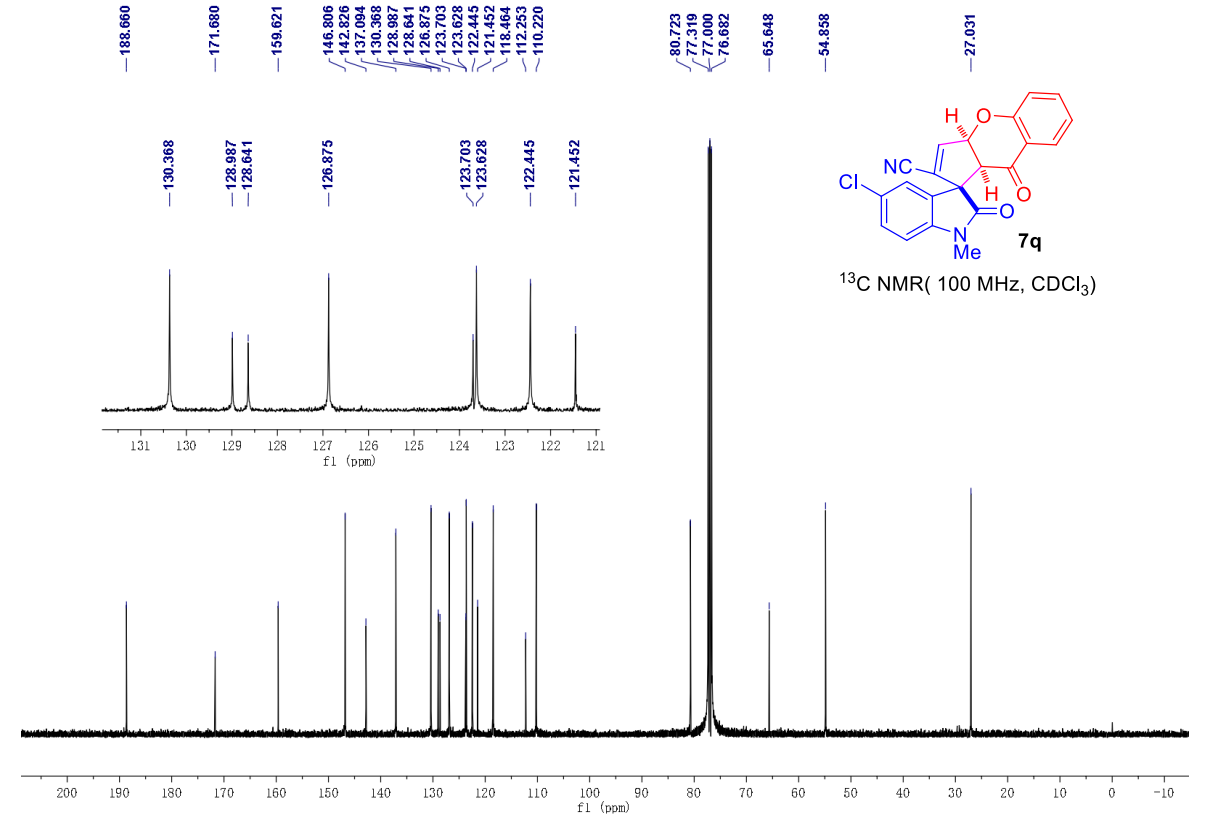

7.721
7.717
7.701
7.697
7.551
7.546
7.529
7.512
7.507
7.394
7.374
7.354
7.260
7.237
7.230
7.105
7.104
7.084
7.083
7.056
7.054
7.039
7.030
7.021
7.019
6.863
6.843
5.842
5.835
5.821
5.814
4.143
4.123
3.182
1.642
1.254
0.071
-0.001
5.842
5.835
5.821
5.814
0.99
5.89
5.87
5.85
5.83
5.81
5.79
5.77
f1 (ppm)
1.00
1.14
1.17
0.93
1.02
1.97
0.97
0.99
0.98
3.04
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)
H
O
Cl
NC
H
O
O
N
Me
7o
1H NMR(400 MHz, CDCl3)

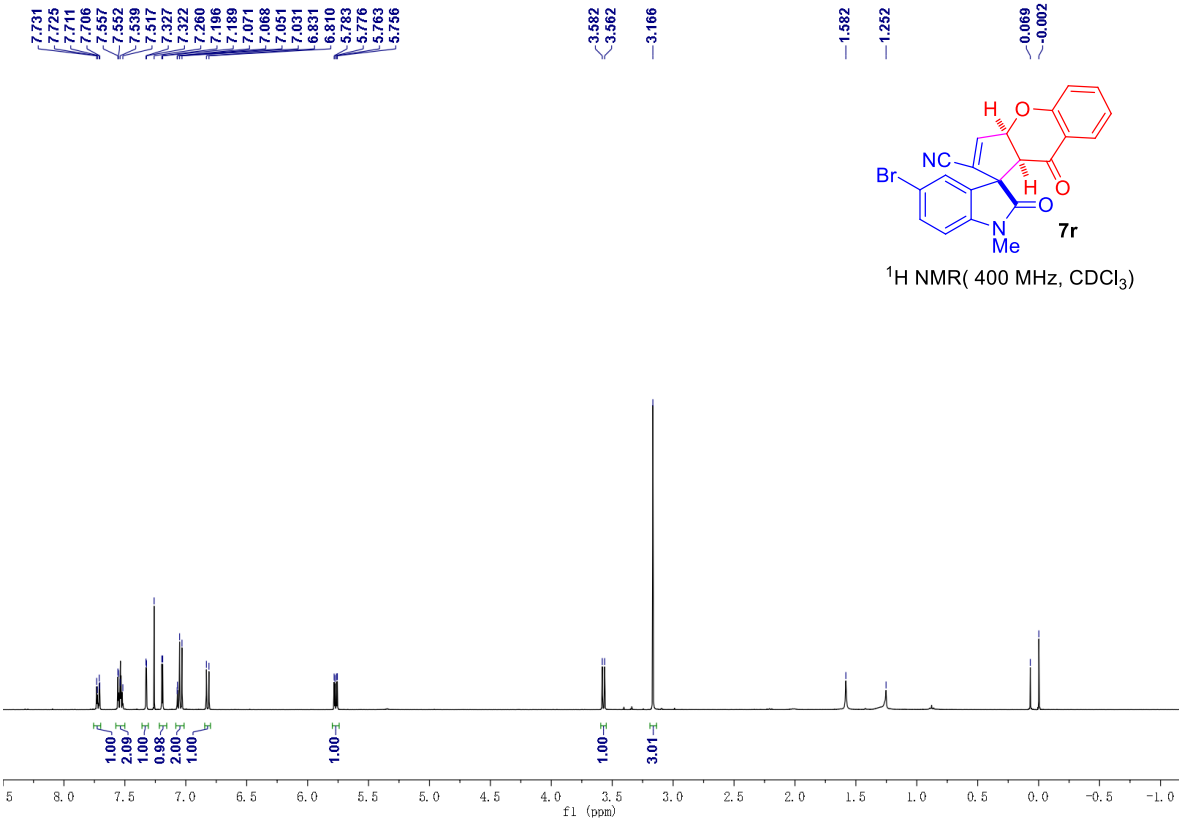

189.424
171.657
159.661
147.317
145.997
136.969
131.611
130.630
126.802
124.274
122.735
122.308
121.976
121.608
118.460
112.328
107.763
80.871
77.318
77.000
76.682
66.101
51.062
27.153
136.969
131.611
130.630
126.802
124.274
122.735
122.308
121.976
121.608
118.460
135
130
125
120
115
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
H
O
Cl
NC
H
O
O
N
Me
7o
13C NMR(100 MHz, CDCl3)


7p
^{1}H NMR(400 MHz, $CDCl_3$)

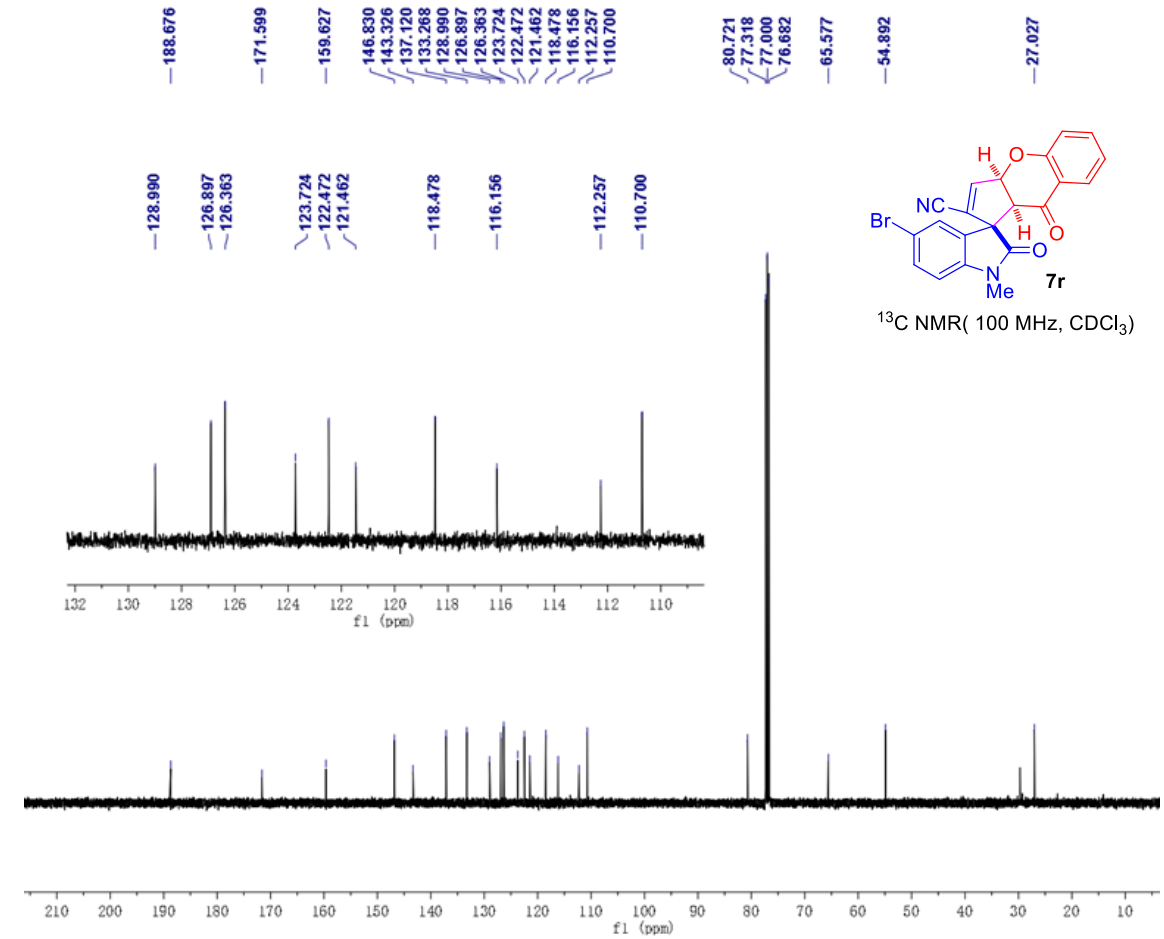

7p
^{13}C NMR(100 MHz, $CDCl_3$)


7.730
7.726
7.710
7.708
7.557
7.553
7.536
7.518
7.514
7.407
7.402
7.386
7.381
7.260
7.190
7.068
7.050
7.029
6.875
6.854
5.778
5.771
5.758
5.751
3.579
3.559
3.167
1.589
1.256
0.001
1.00
1.11
1.02
1.96
1.96
0.99
1.00
1.01
3.10
f1 (ppm)
7q
^{1}H NMR(400 MHz, CDCl$_3$)

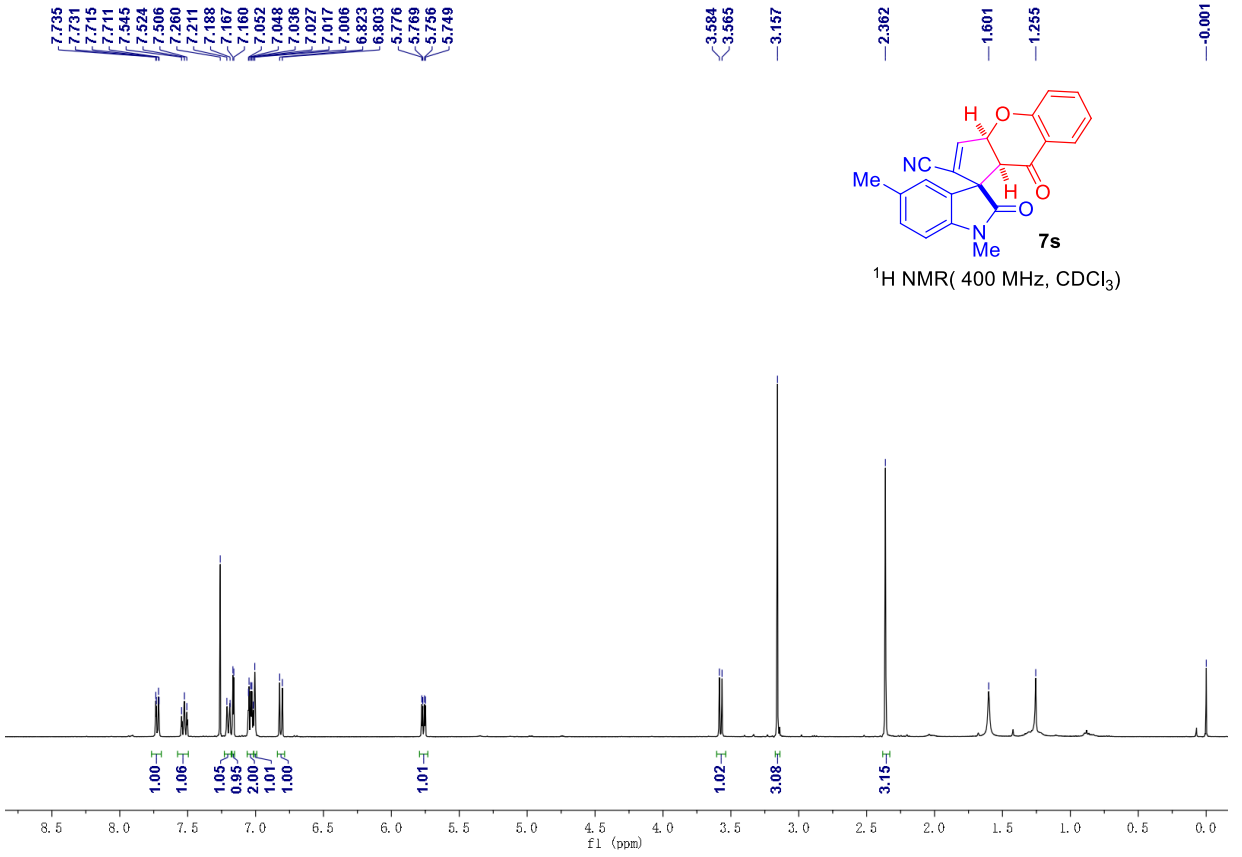

188.660
171.680
159.621
146.806
142.826
137.094
130.368
128.987
128.641
126.875
123.703
123.628
122.445
121.452
118.464
112.253
110.220
80.723
77.319
77.000
76.682
65.648
54.858
27.031
130.368
128.987
128.641
126.875
123.703
123.628
122.445
121.452
f1 (ppm)
7q
^{13}C NMR(100 MHz, CDCl$_3$)



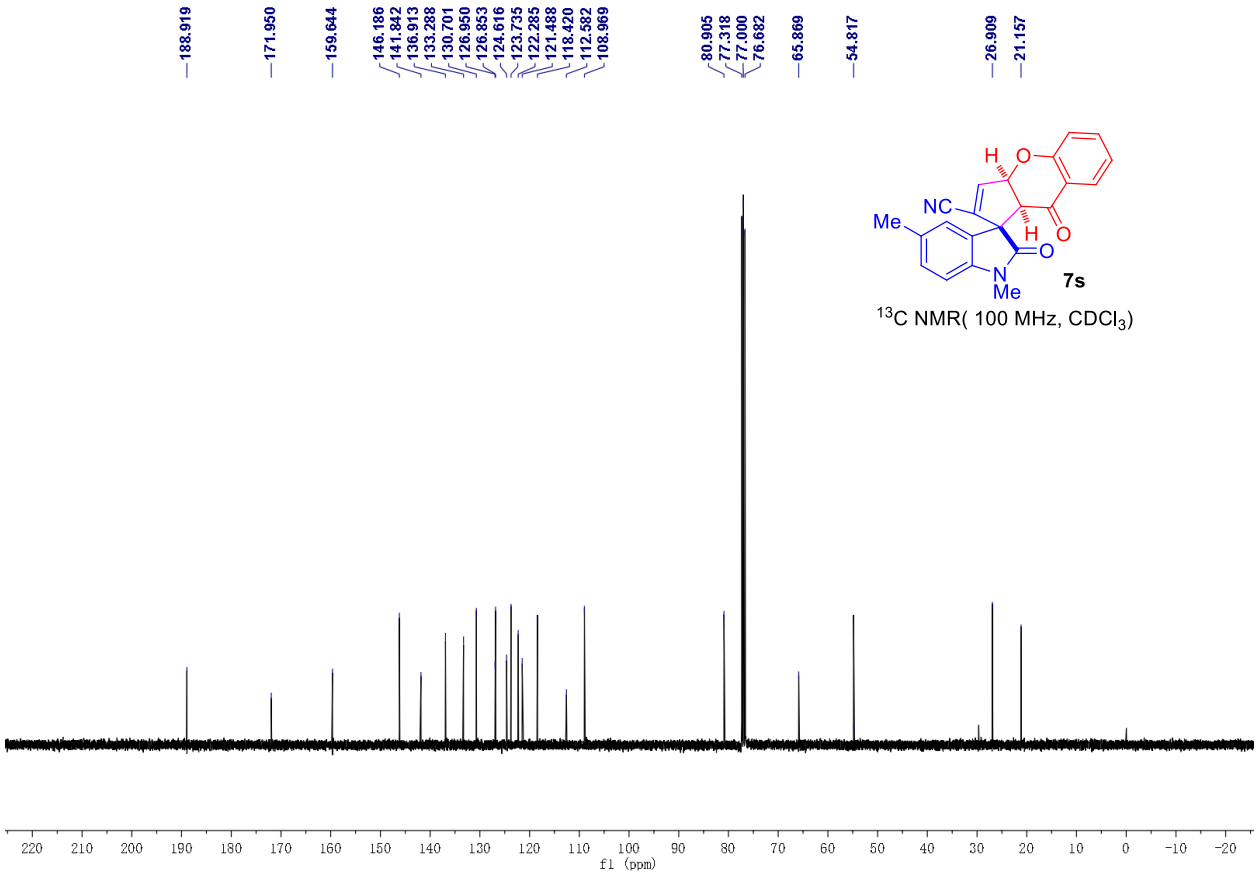
^{1}H NMR(400 MHz, $CDCl_3$)



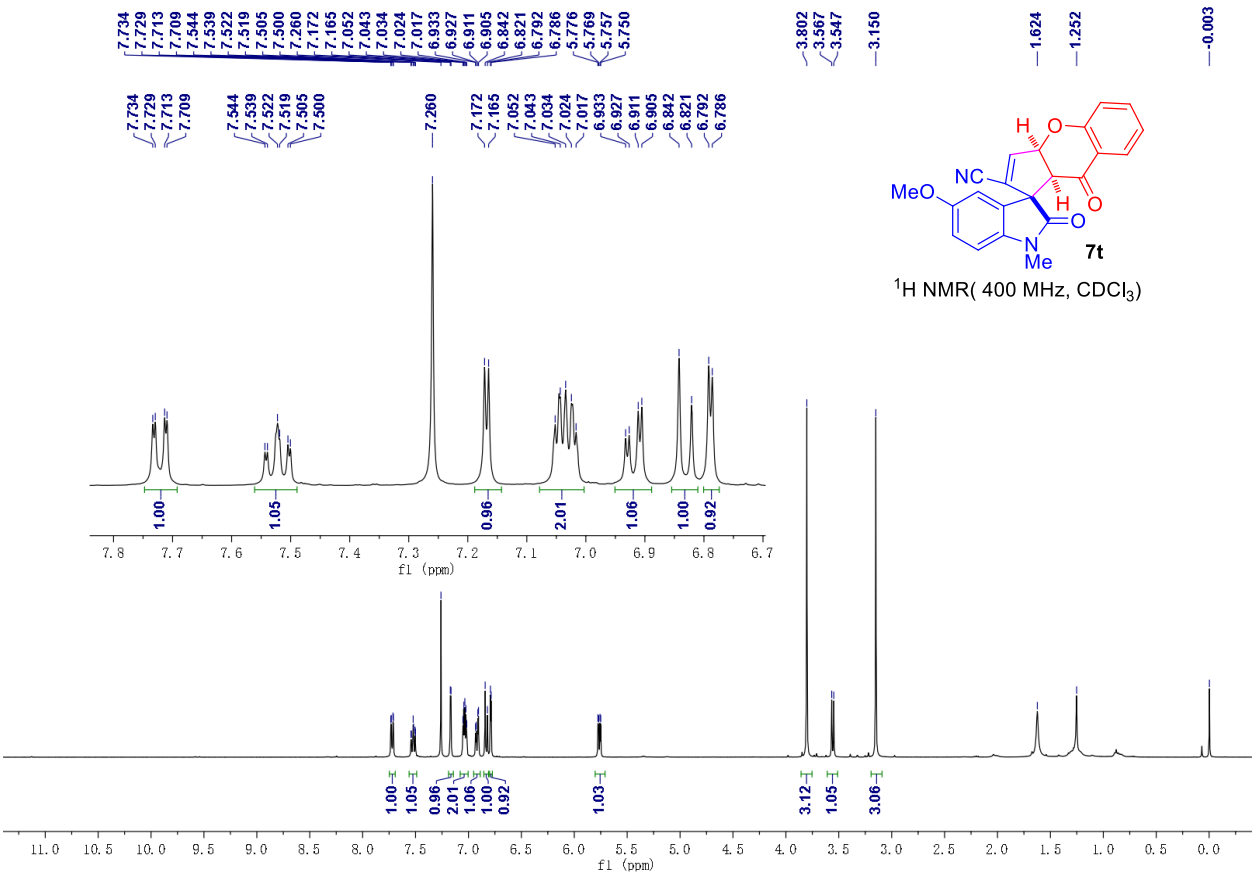
^{13}C NMR(100 MHz, $CDCl_3$)



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

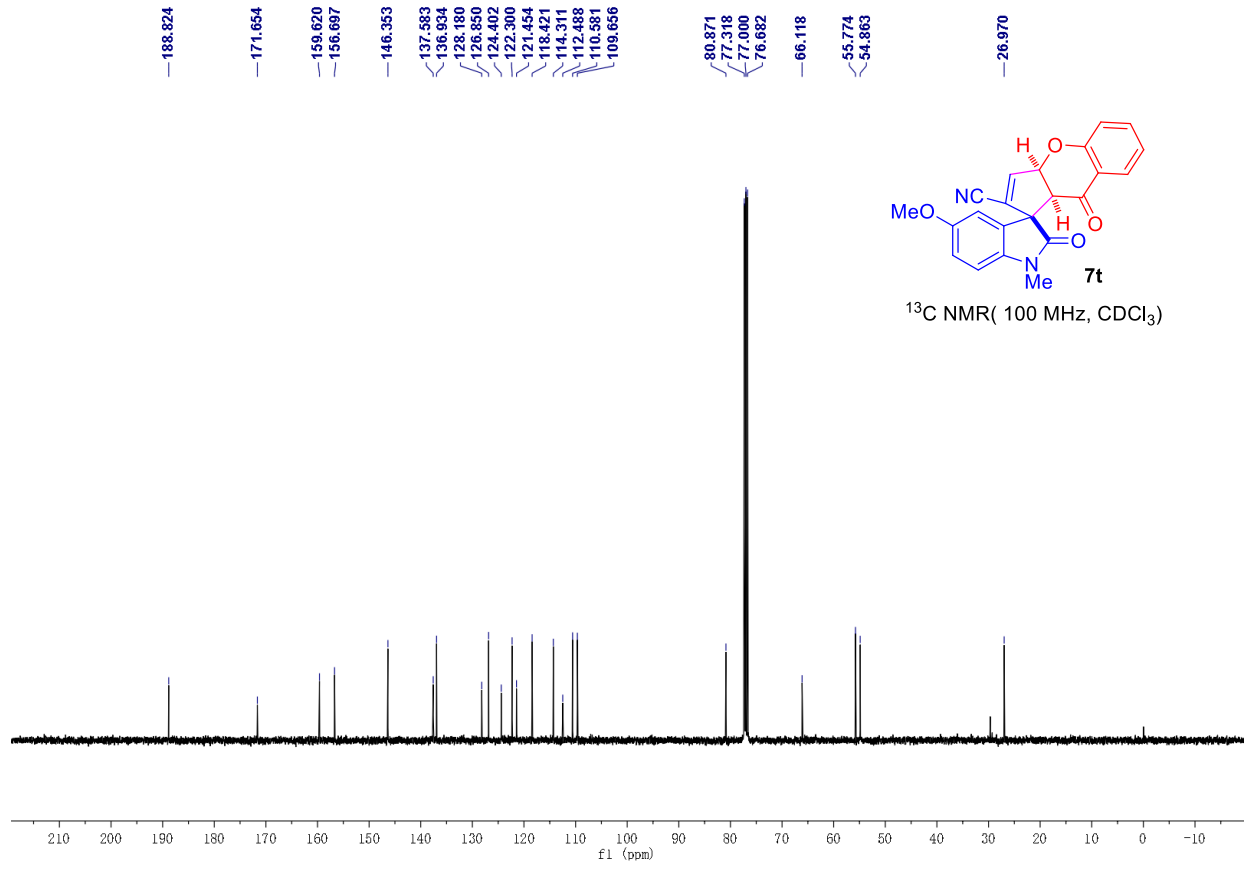


^{13}C NMR(100 MHz, $CDCl_3$)



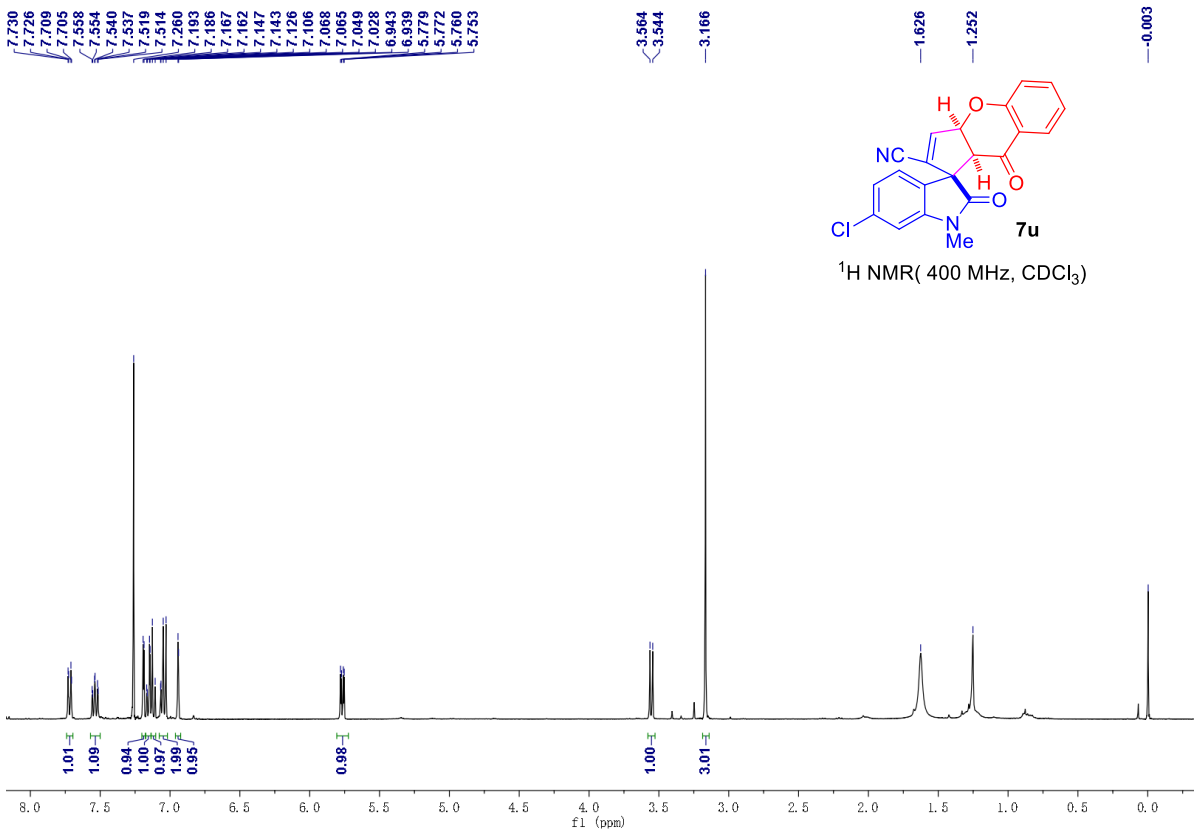
7t

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

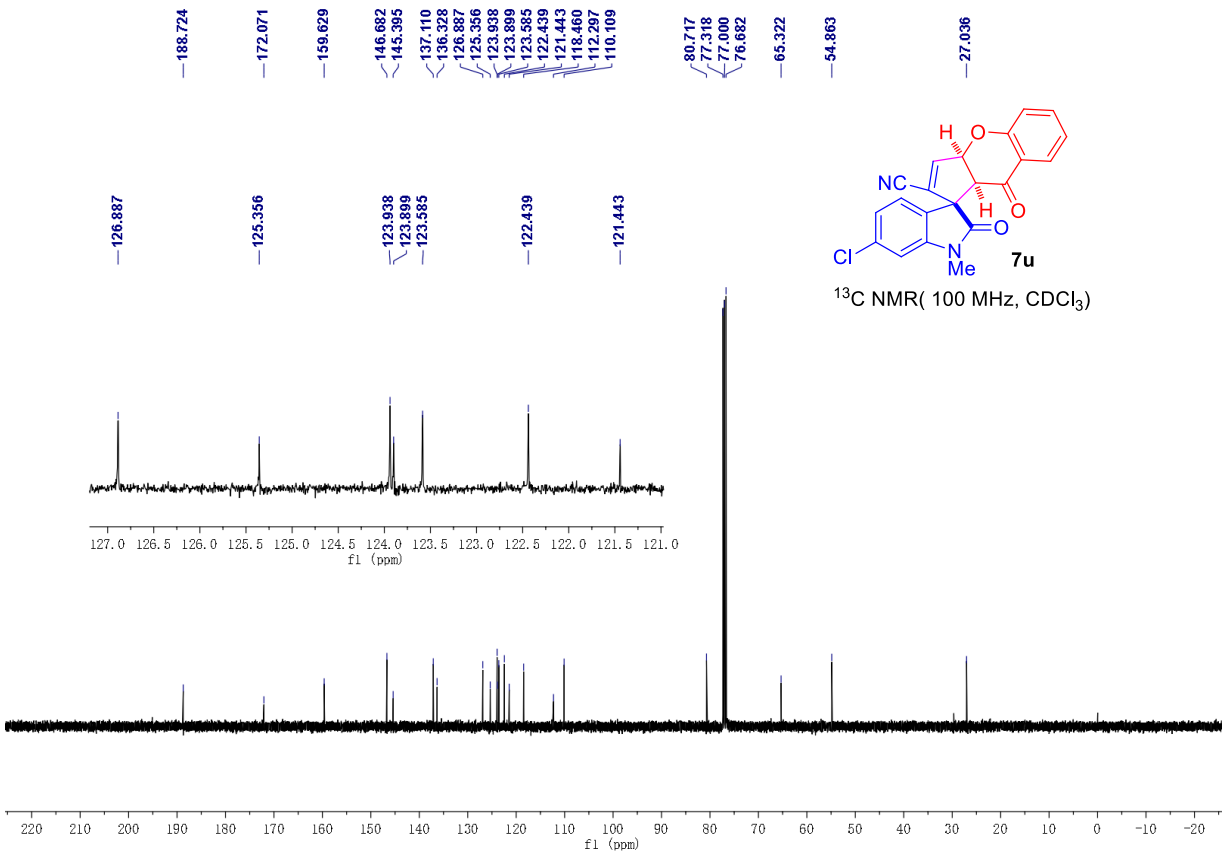


7t

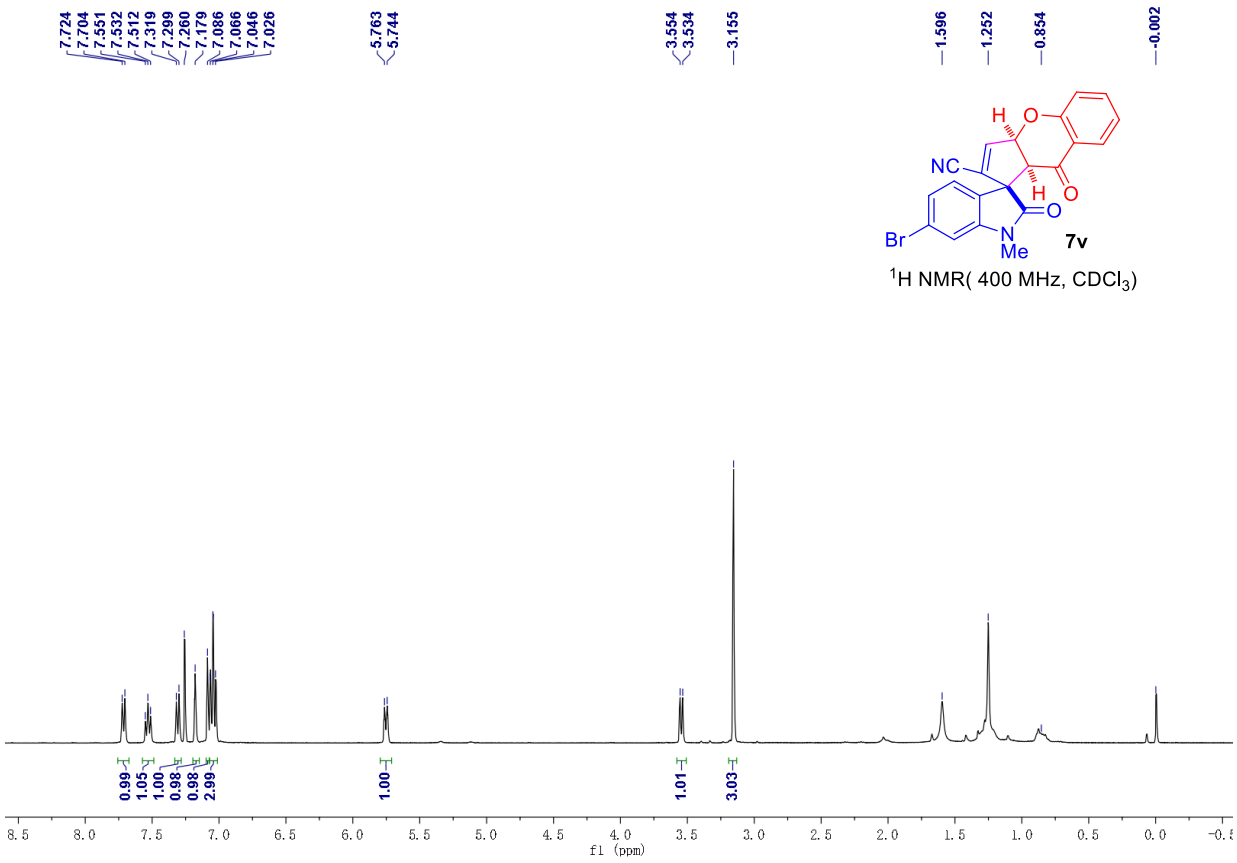
^{13}C NMR(100 MHz, $CDCl_3$)



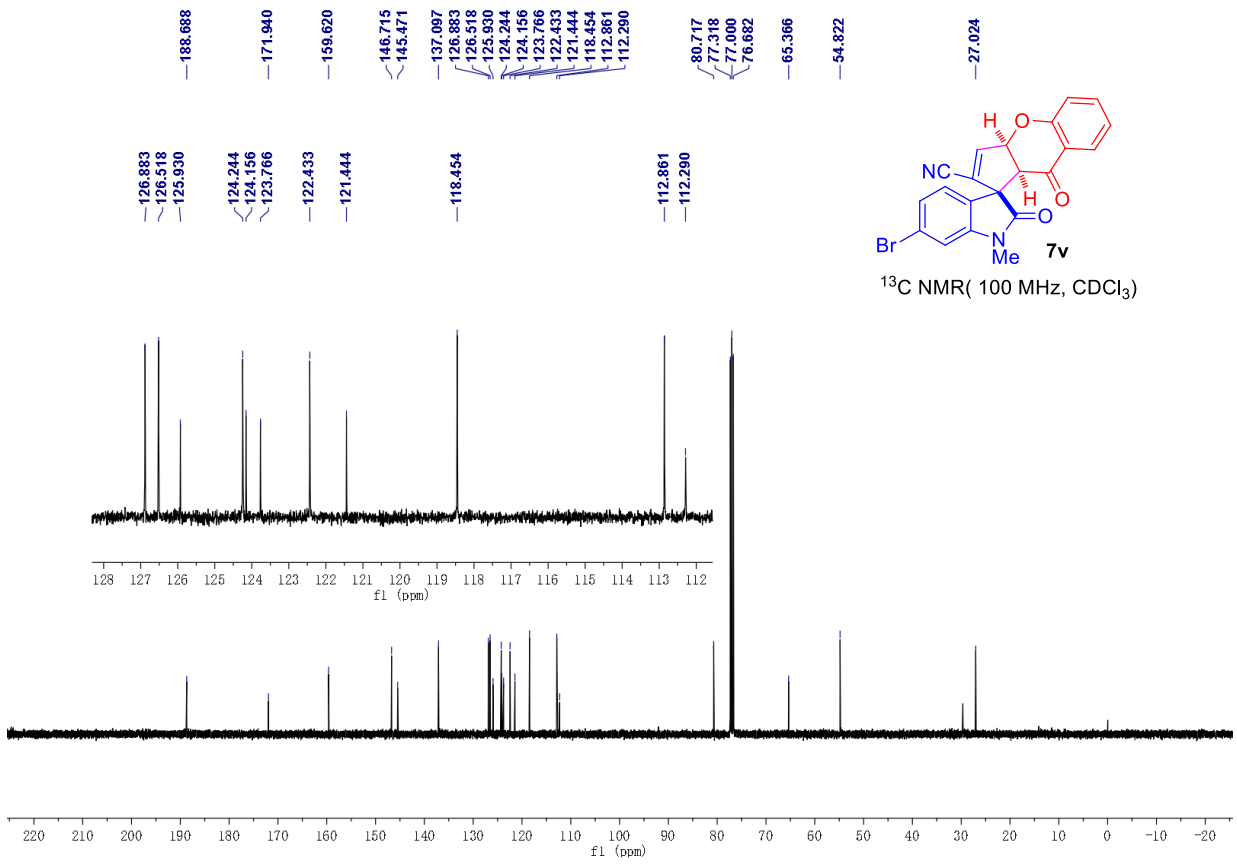
^{1}H NMR(400 MHz, $CDCl_3$)



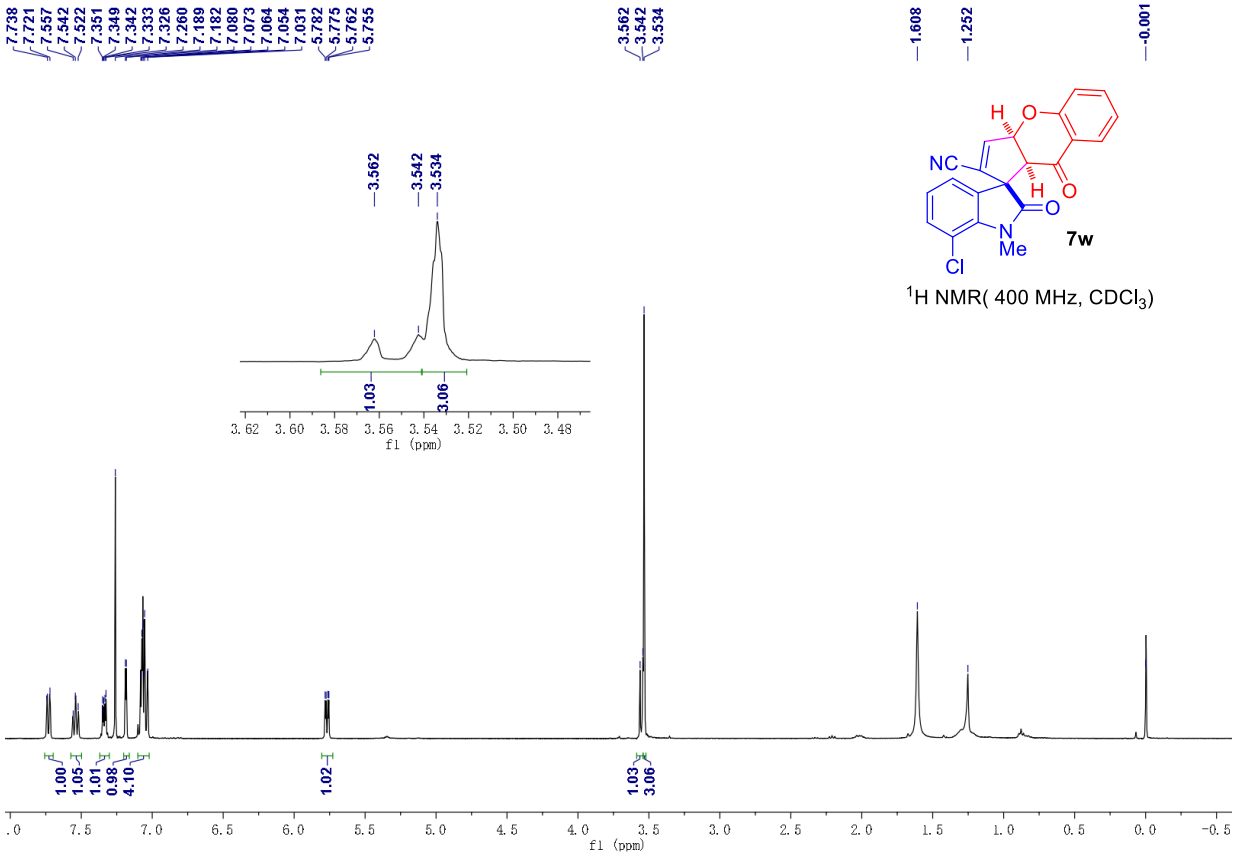
^{13}C NMR(100 MHz, $CDCl_3$)

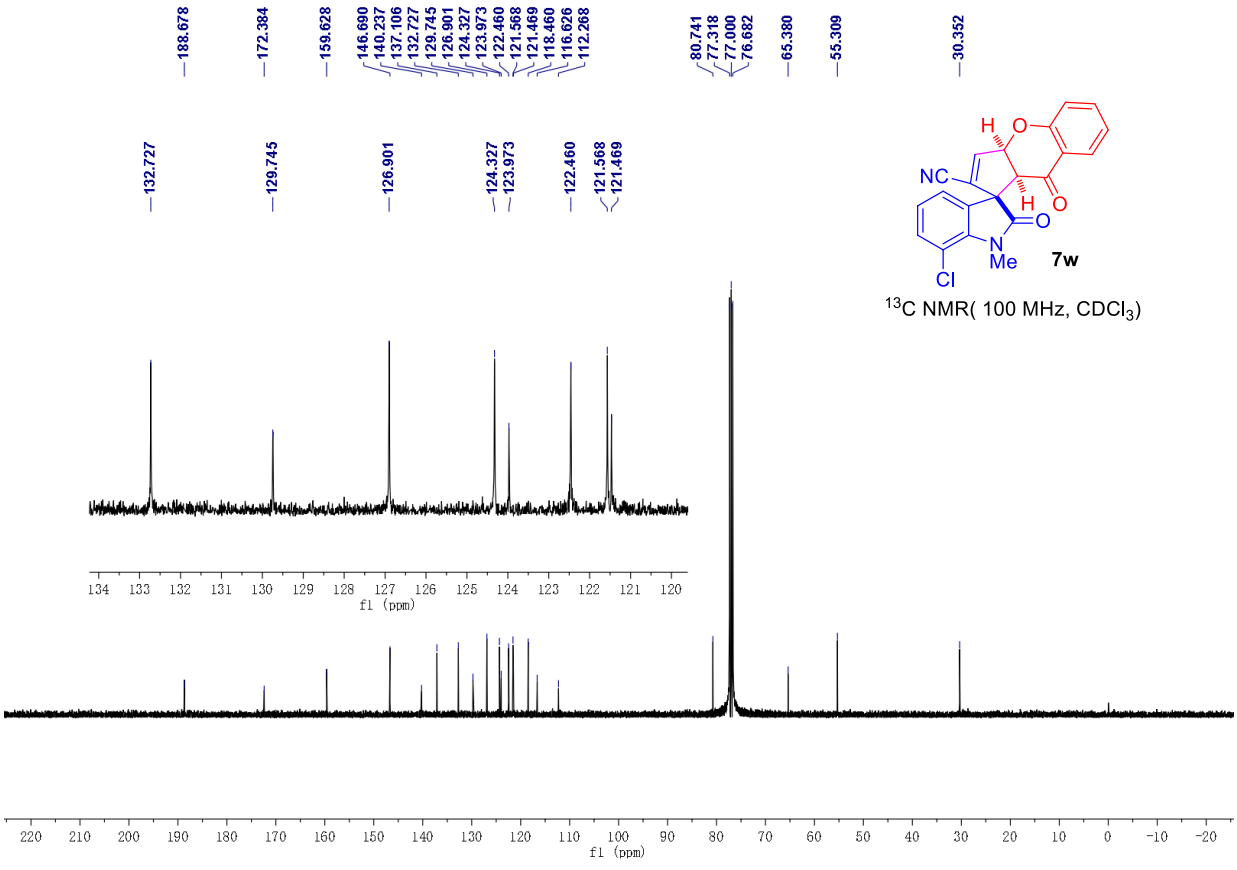


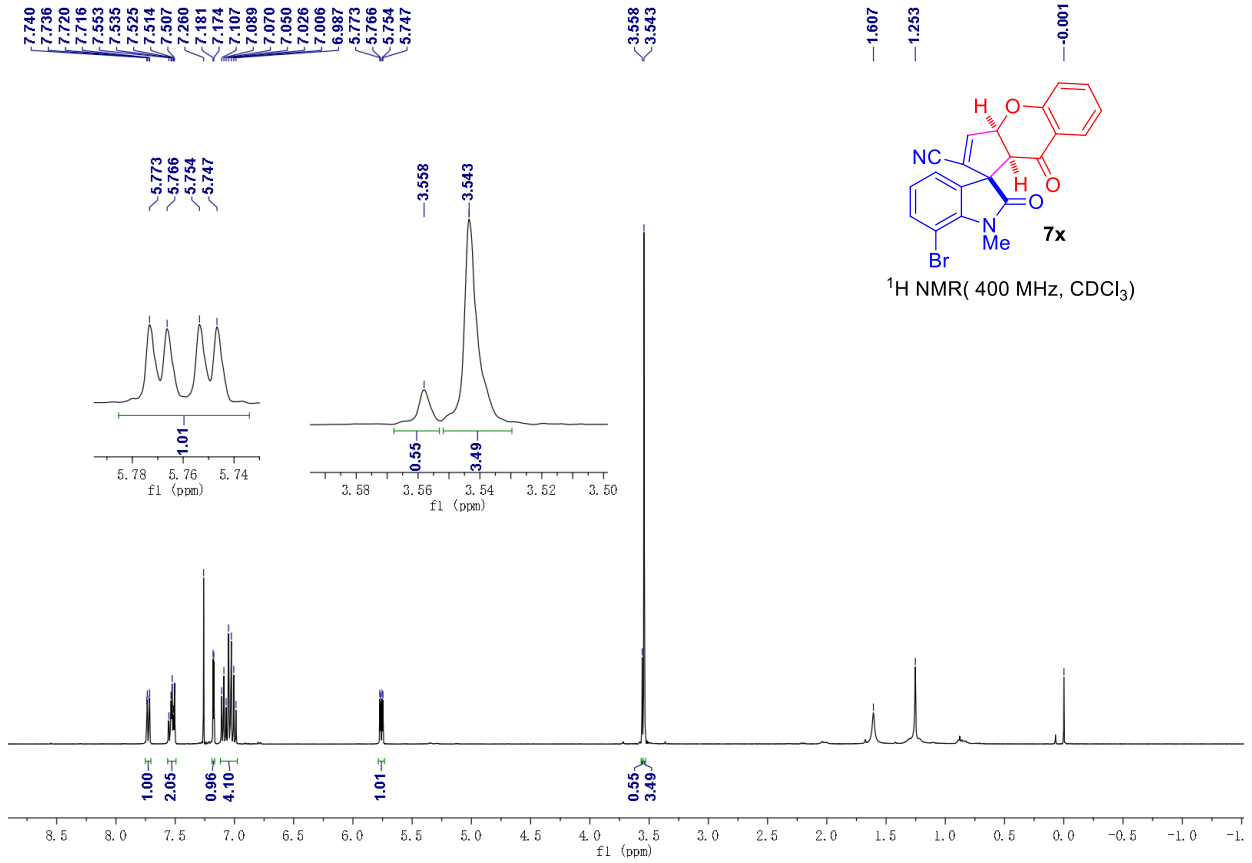
^{1}H NMR(400 MHz, $CDCl_3$)

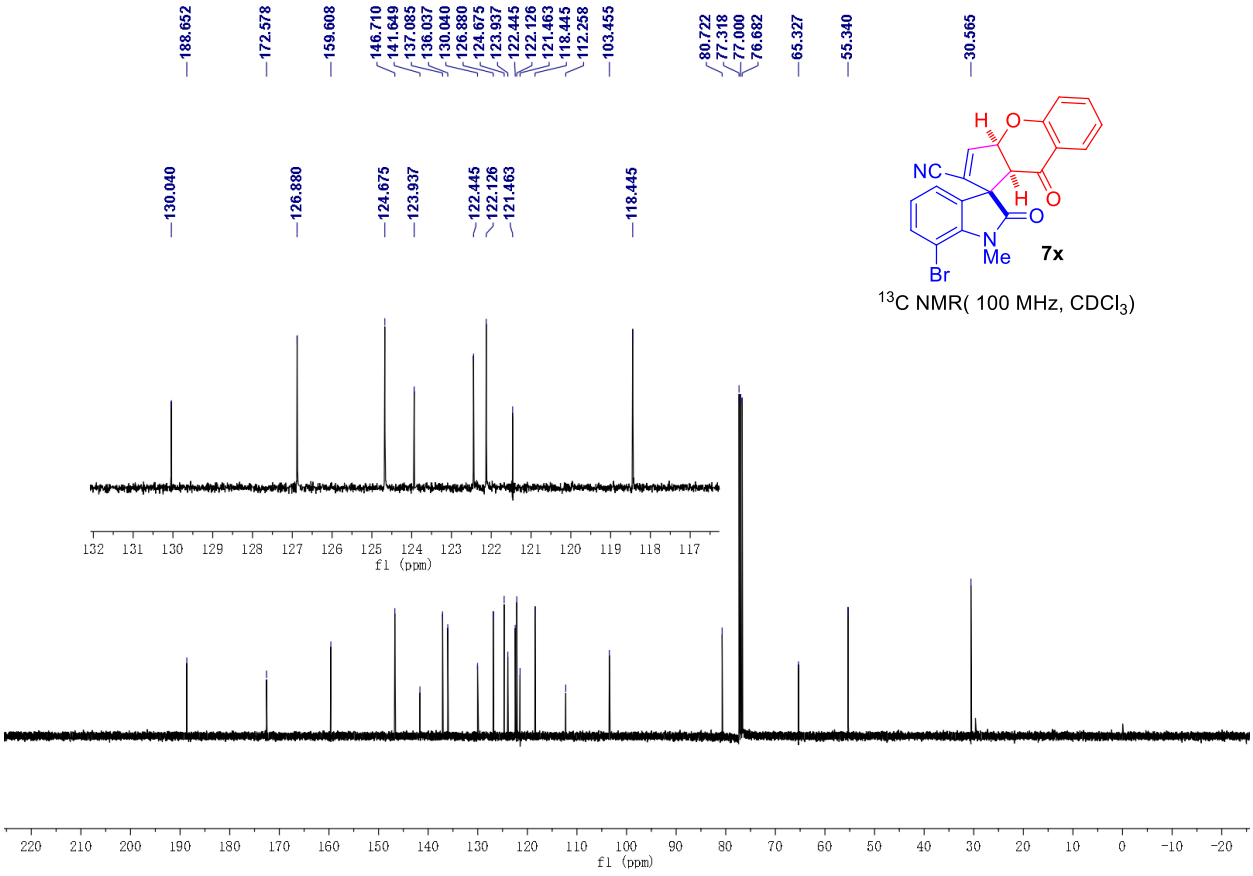


^{13}C NMR(100 MHz, $CDCl_3$)

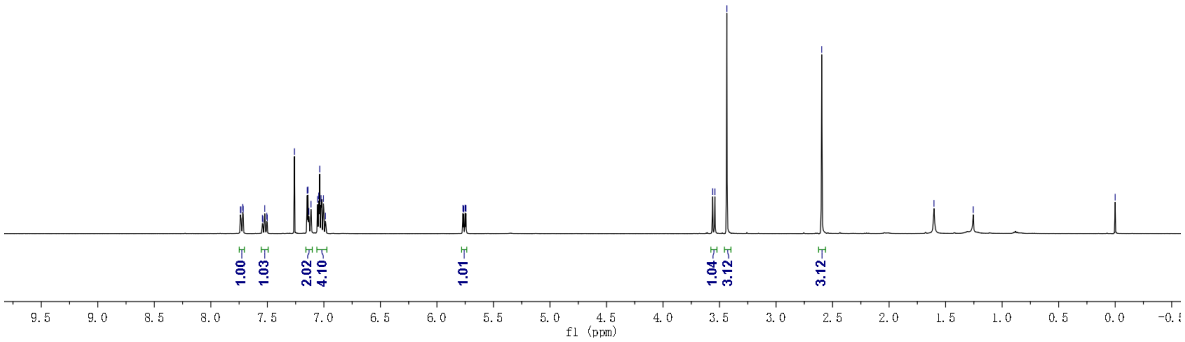

7.738
7.721
7.557
7.542
7.522
7.351
7.349
7.342
7.333
7.326
7.260
7.189
7.182
7.080
7.073
7.064
7.054
7.031
5.782
5.775
5.762
5.755
3.562
3.542
3.534
1.608
1.252
0.001
1.03
3.06
1.00
1.05
1.01
0.98
4.10
1.02
1.03
3.06
f1 (ppm)
7w
^{1}H NMR(400 MHz, CDCl$_3$)

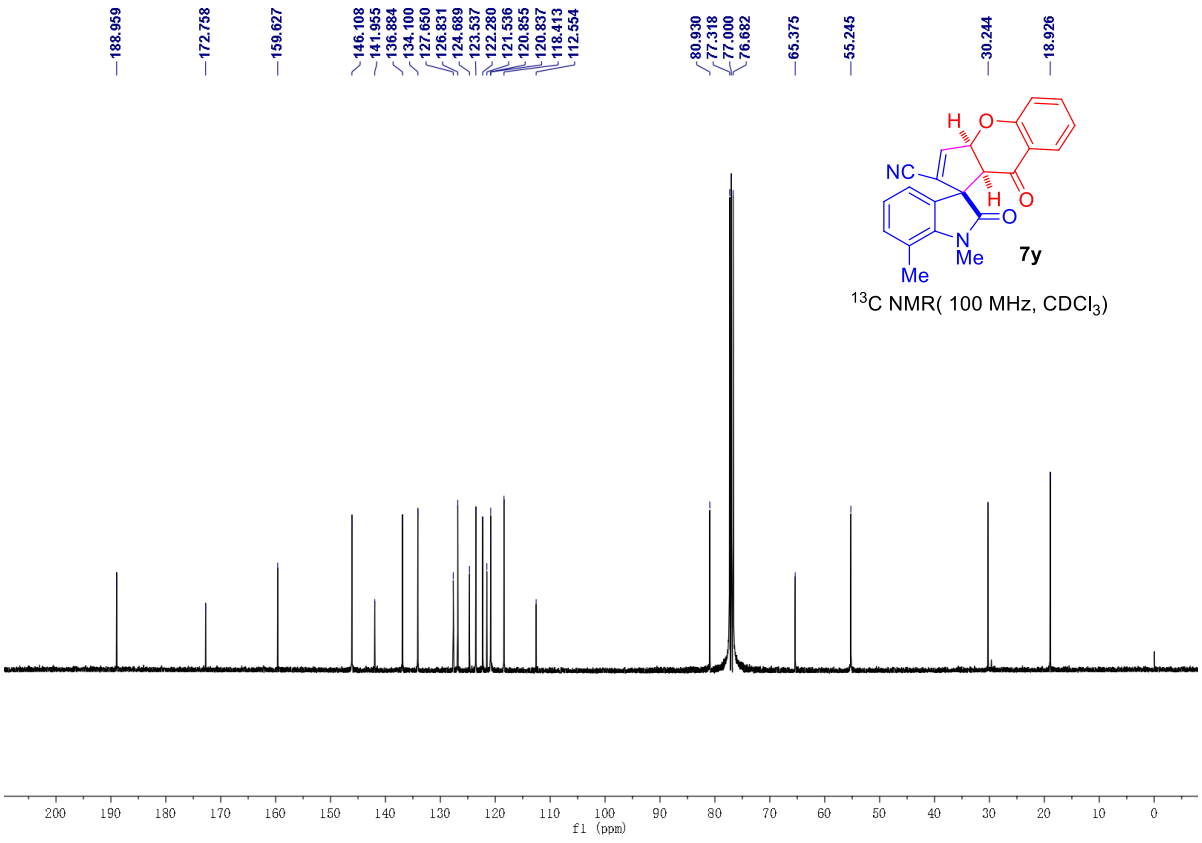

188.678
172.384
159.628
146.690
140.237
137.106
132.727
129.745
126.901
124.327
123.973
122.460
121.568
121.469
118.460
116.626
112.268
80.741
77.318
77.000
76.682
65.380
55.309
30.352
f1 (ppm)
7w
^{13}C NMR(100 MHz, CDCl$_3$)


7.740
7.736
7.720
7.716
7.553
7.535
7.525
7.514
7.507
7.260
7.181
7.174
7.107
7.089
7.070
7.050
7.026
7.006
6.987
5.773
5.766
5.754
5.747
3.558
3.543
1.607
1.253
0.001
1.01
0.55
3.49
1.00
2.05
0.96
4.10
1.01
0.55
3.49
f1 (ppm)
NC
H
O
H
O
N
Me
Br
7x
1H NMR(400 MHz, CDCl3)

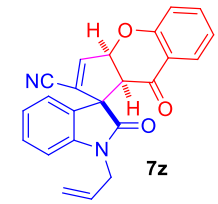

188.652
172.578
159.608
146.710
141.649
137.085
136.037
130.040
126.880
124.675
123.937
122.445
122.126
121.463
118.445
112.258
103.455
80.722
77.318
77.000
76.682
65.327
55.340
30.565
130.040
126.880
124.675
123.937
122.445
122.126
121.463
118.445
f1 (ppm)
NC
H
O
H
O
N
Me
Br
7x
13C NMR(100 MHz, CDCl3)

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



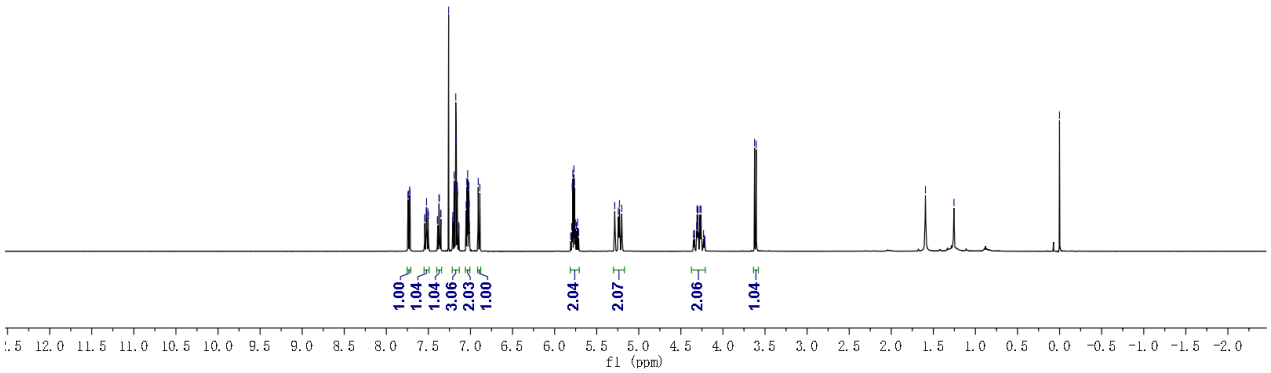


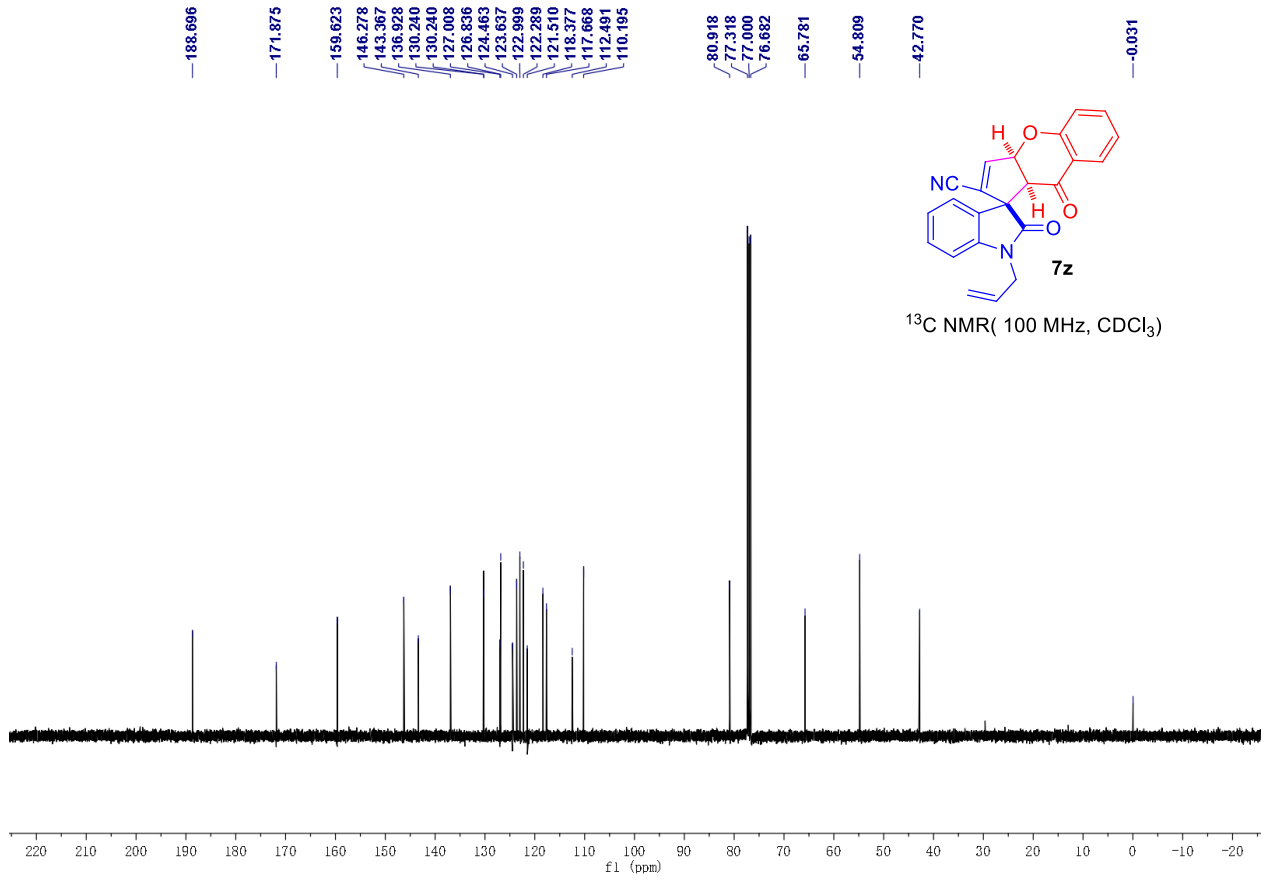
^{13}C NMR(100 MHz, $CDCl_3$)



7z

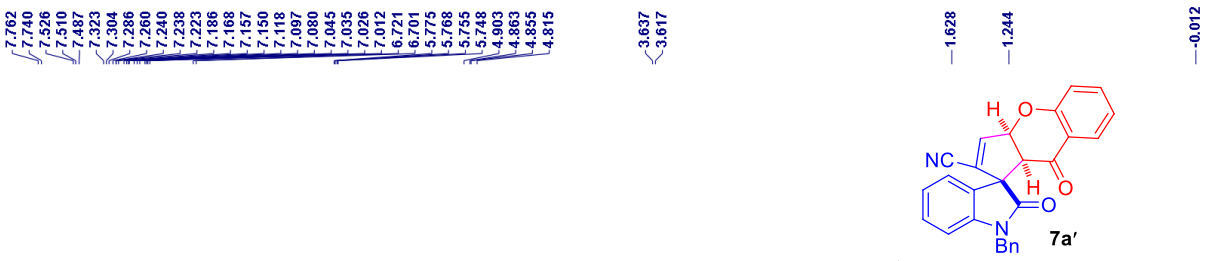
^{1}H NMR(400 MHz, $CDCl_3$)



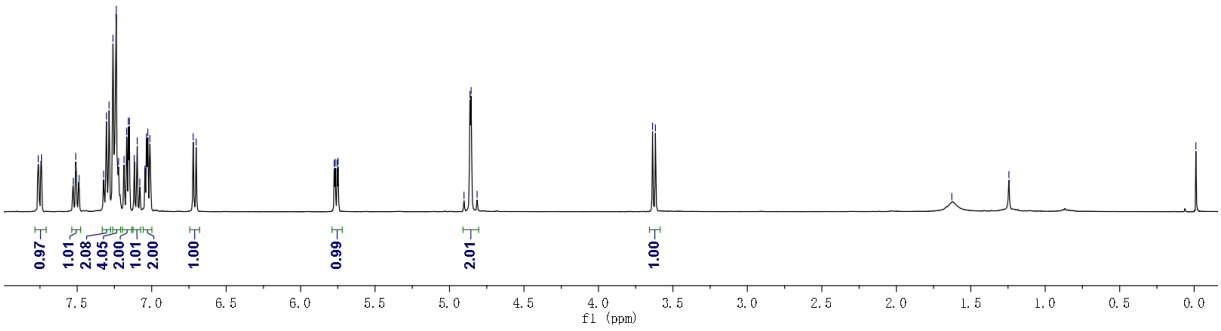


7z

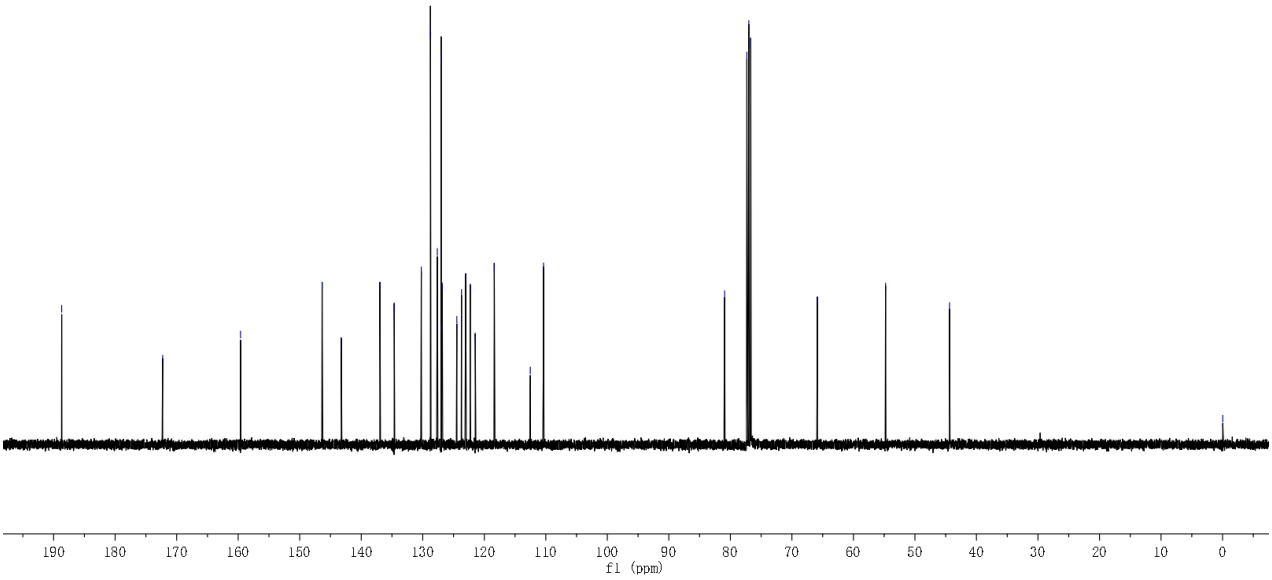
^{13}C NMR(100 MHz, $CDCl_3$)

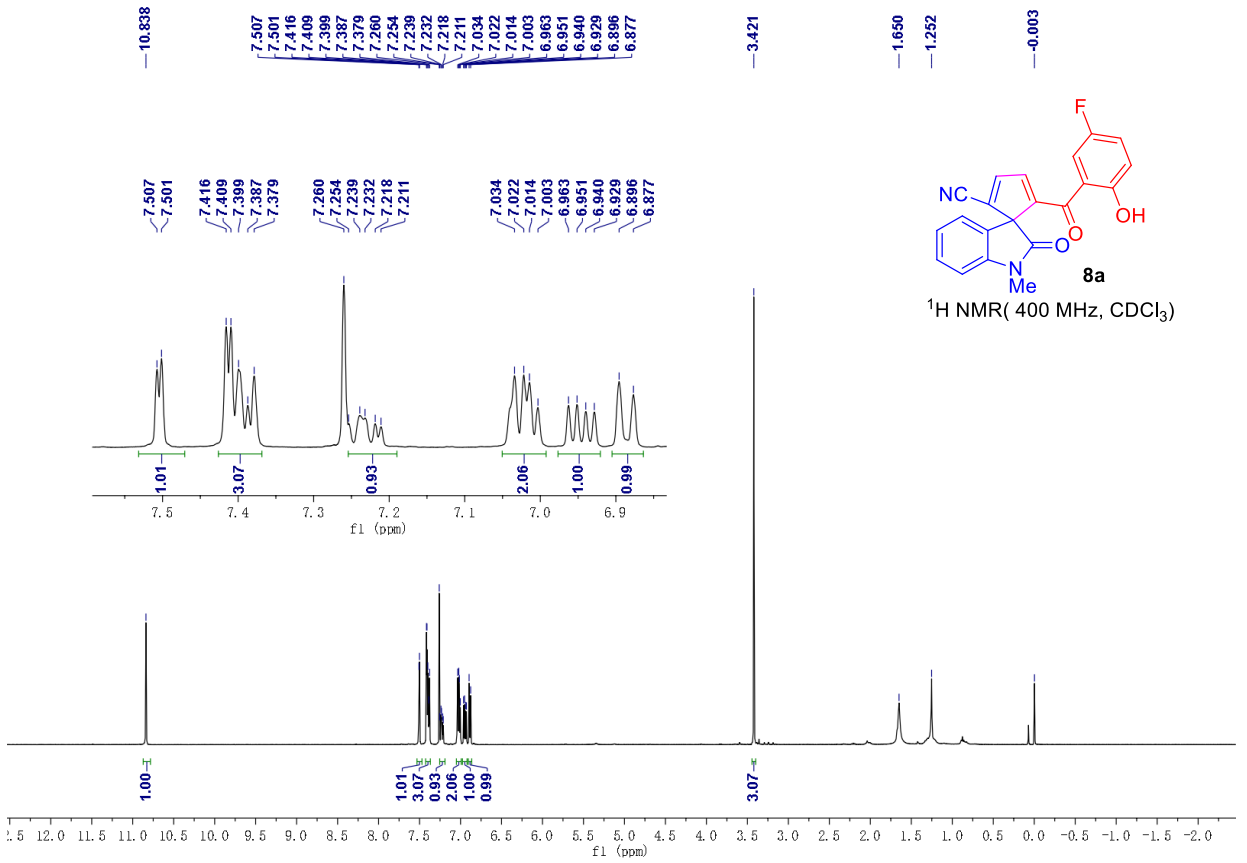


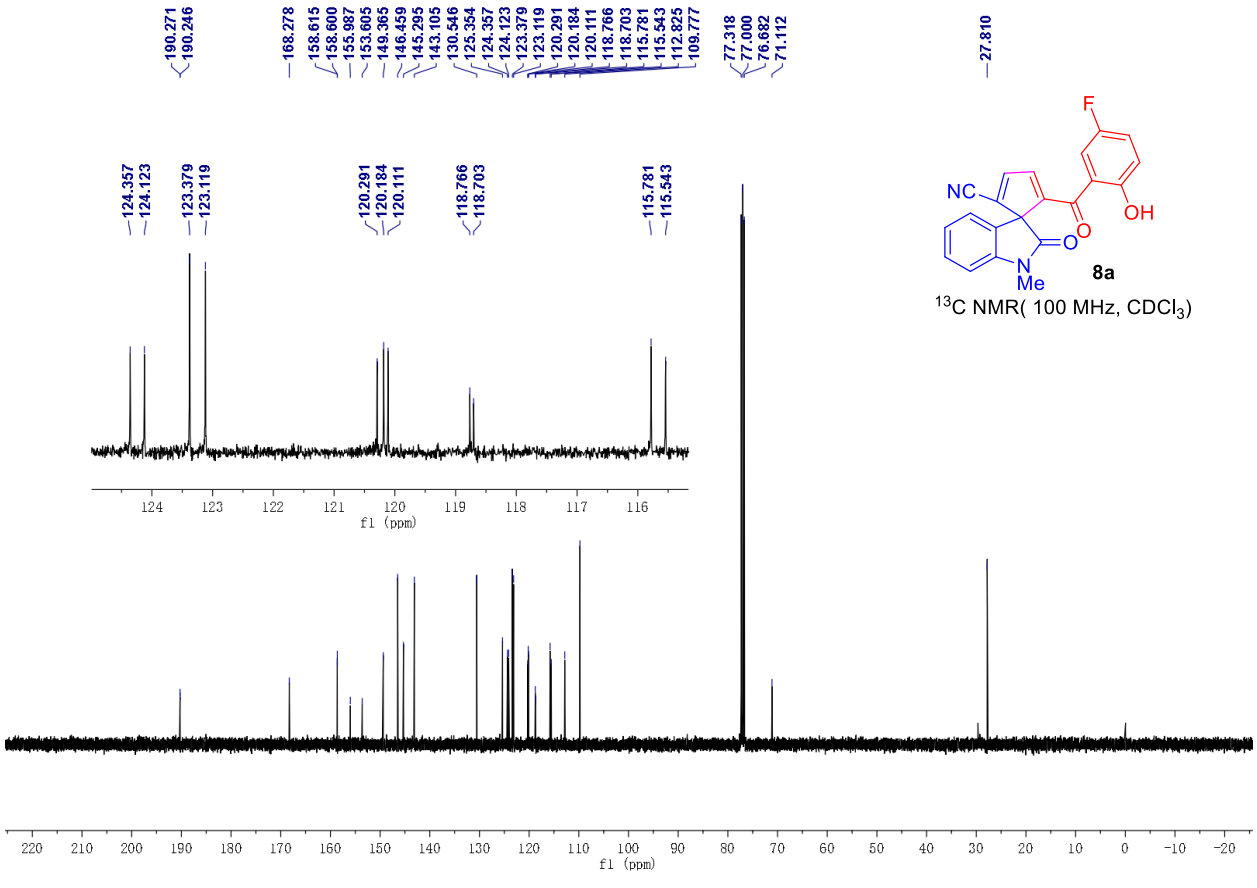
^{1}H NMR(400 MHz, $CDCl_3$)

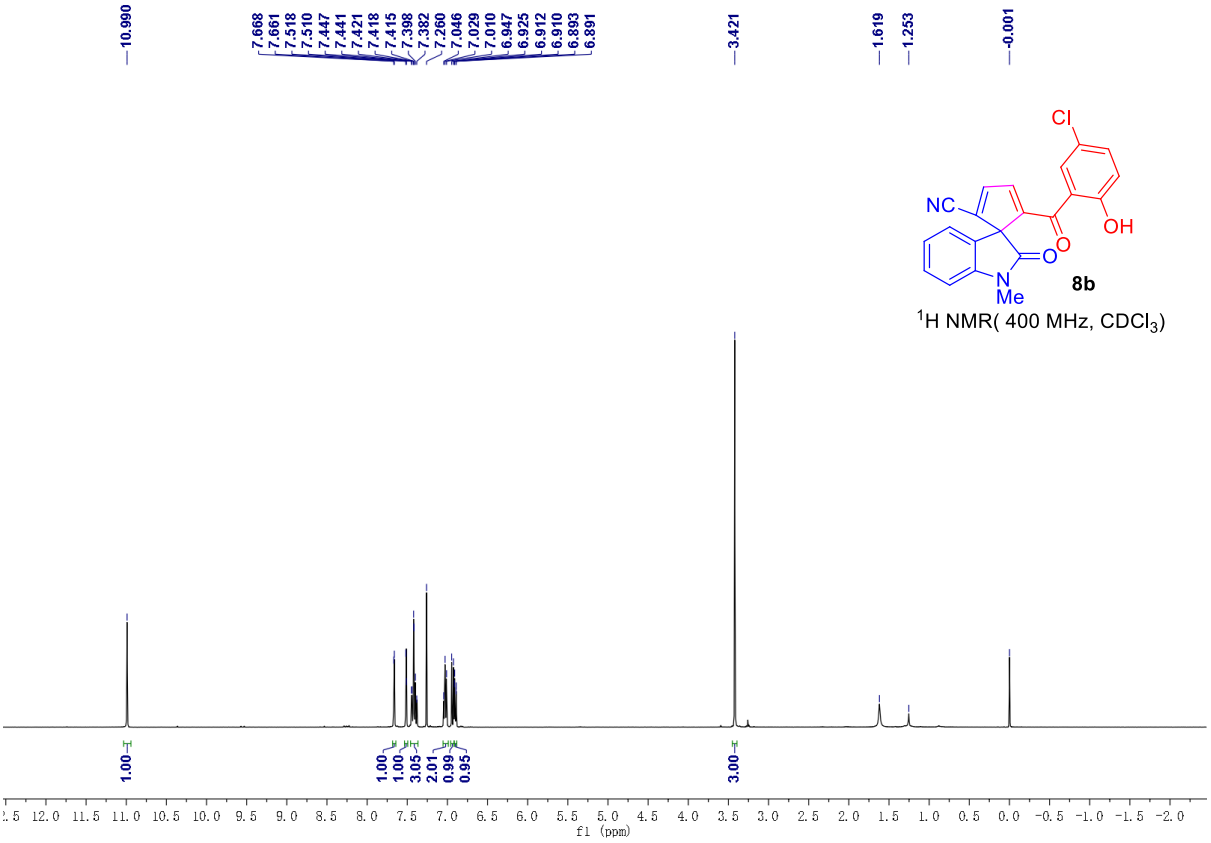


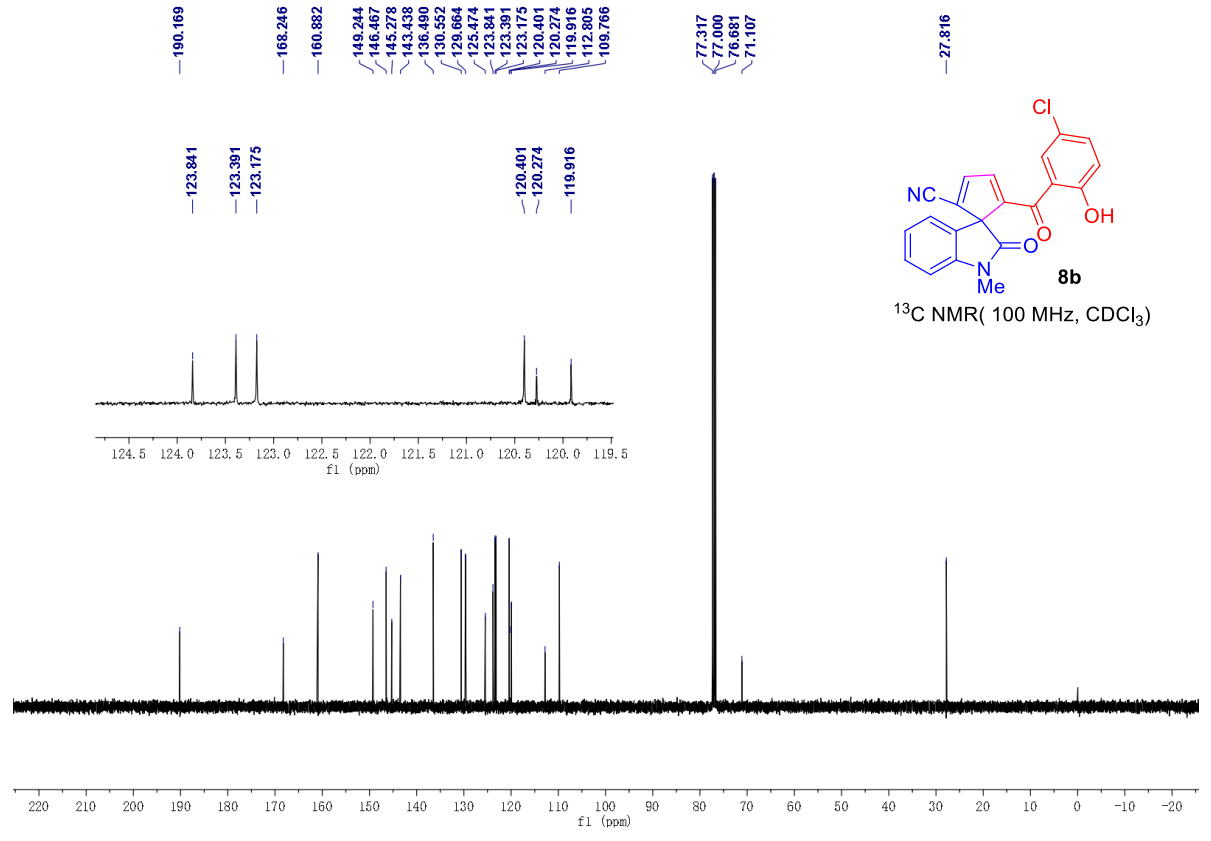
^{13}C NMR(100 MHz, $CDCl_3$)

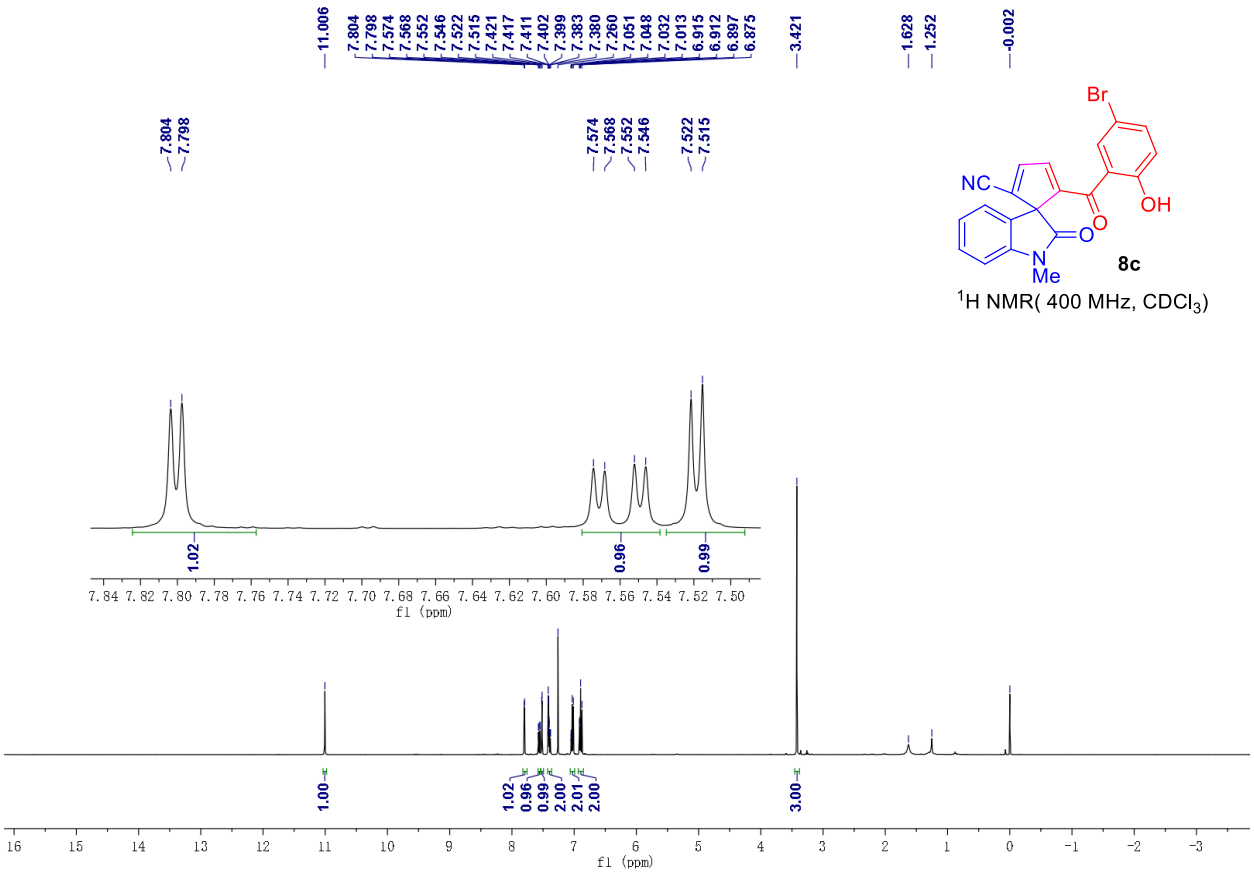


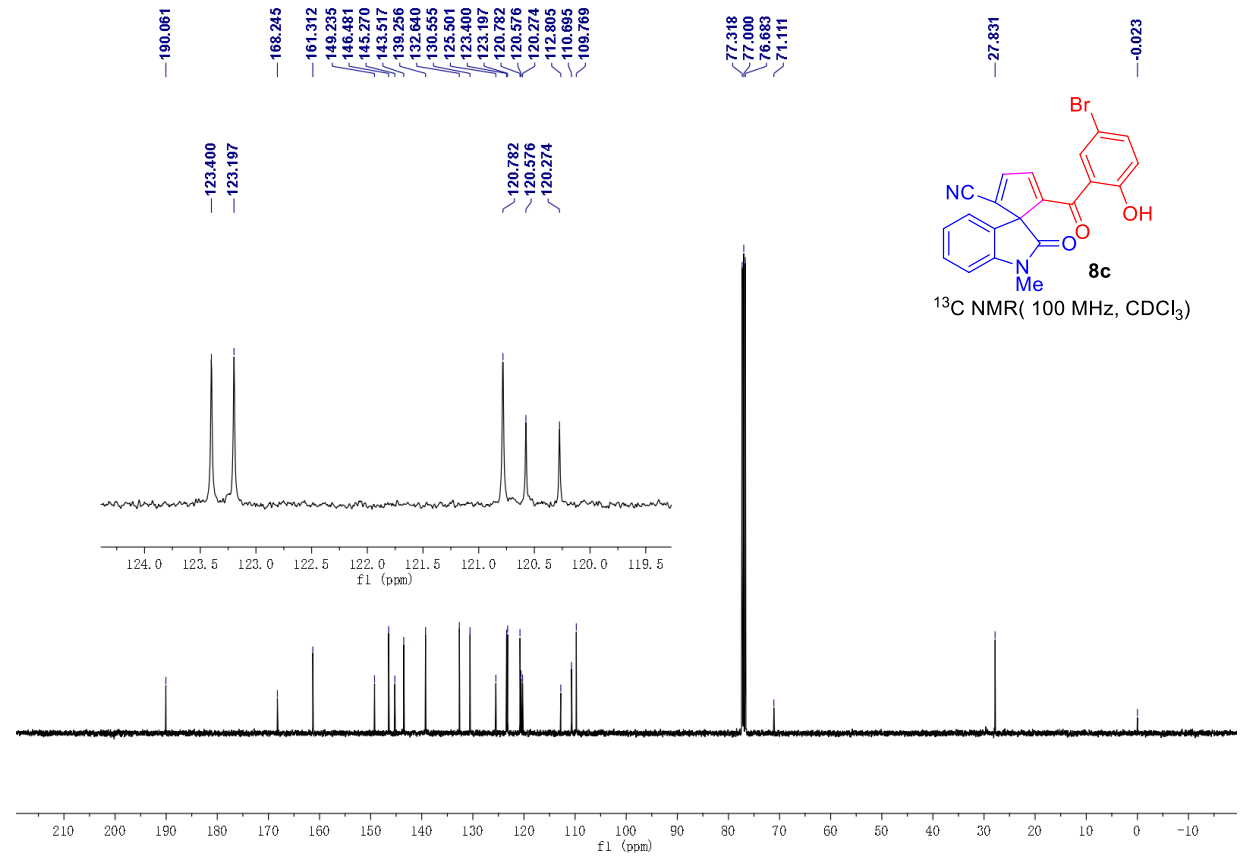

10.838
7.507
7.501
7.416
7.409
7.399
7.387
7.379
7.260
7.254
7.239
7.232
7.218
7.211
7.034
7.022
7.014
7.003
6.963
6.951
6.940
6.929
6.896
6.877
3.421
1.650
1.252
-0.003
F
NC
OH
O
O
N
Me
8a
1H NMR(400 MHz, CDCl3)
1.01
3.07
0.93
2.06
1.00
0.99
f1 (ppm)

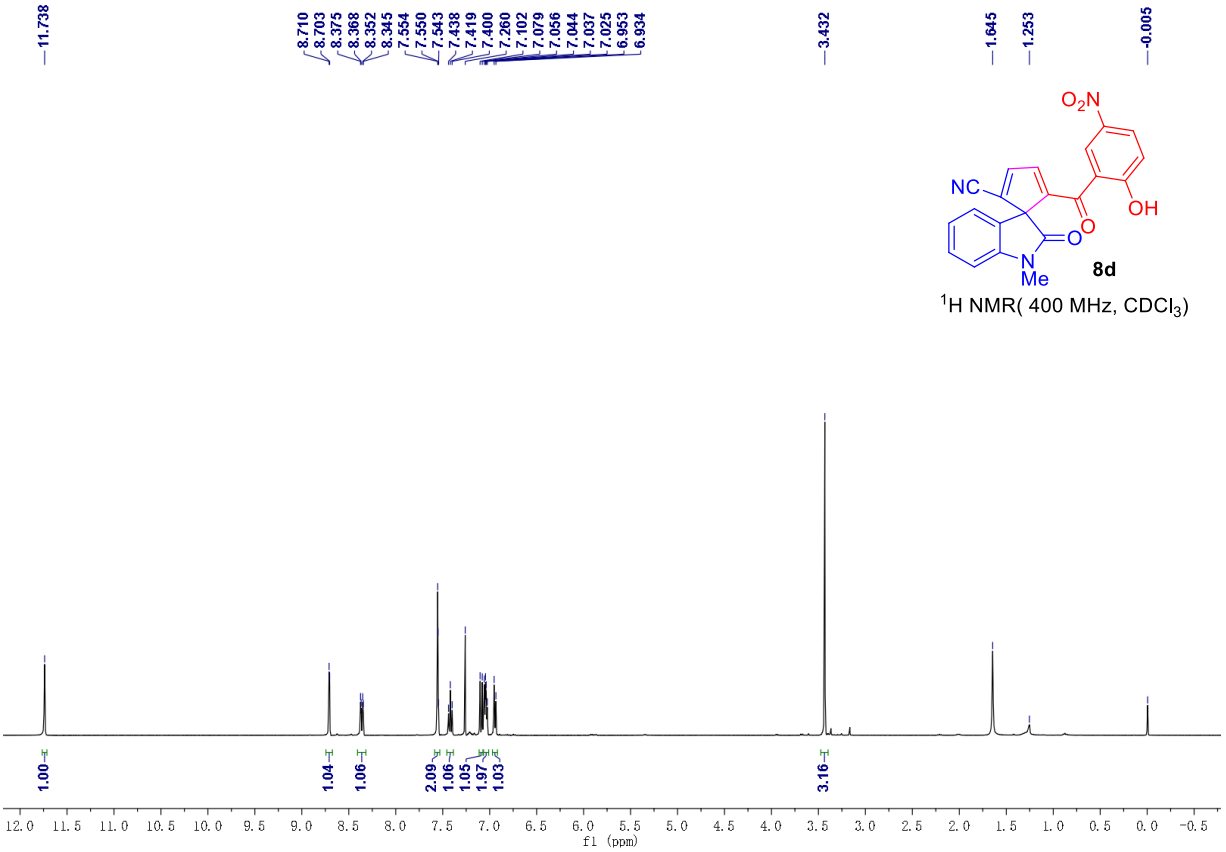

190.271
190.246
168.278
158.615
158.600
155.987
153.605
149.365
146.459
145.295
143.105
130.346
125.354
124.357
124.123
123.379
123.119
120.291
120.184
120.111
118.766
118.703
115.781
115.543
112.825
109.777
77.318
77.000
76.682
71.112
27.810
F
NC
OH
O
O
N
Me
8a
13C NMR(100 MHz, CDCl3)
f1 (ppm)

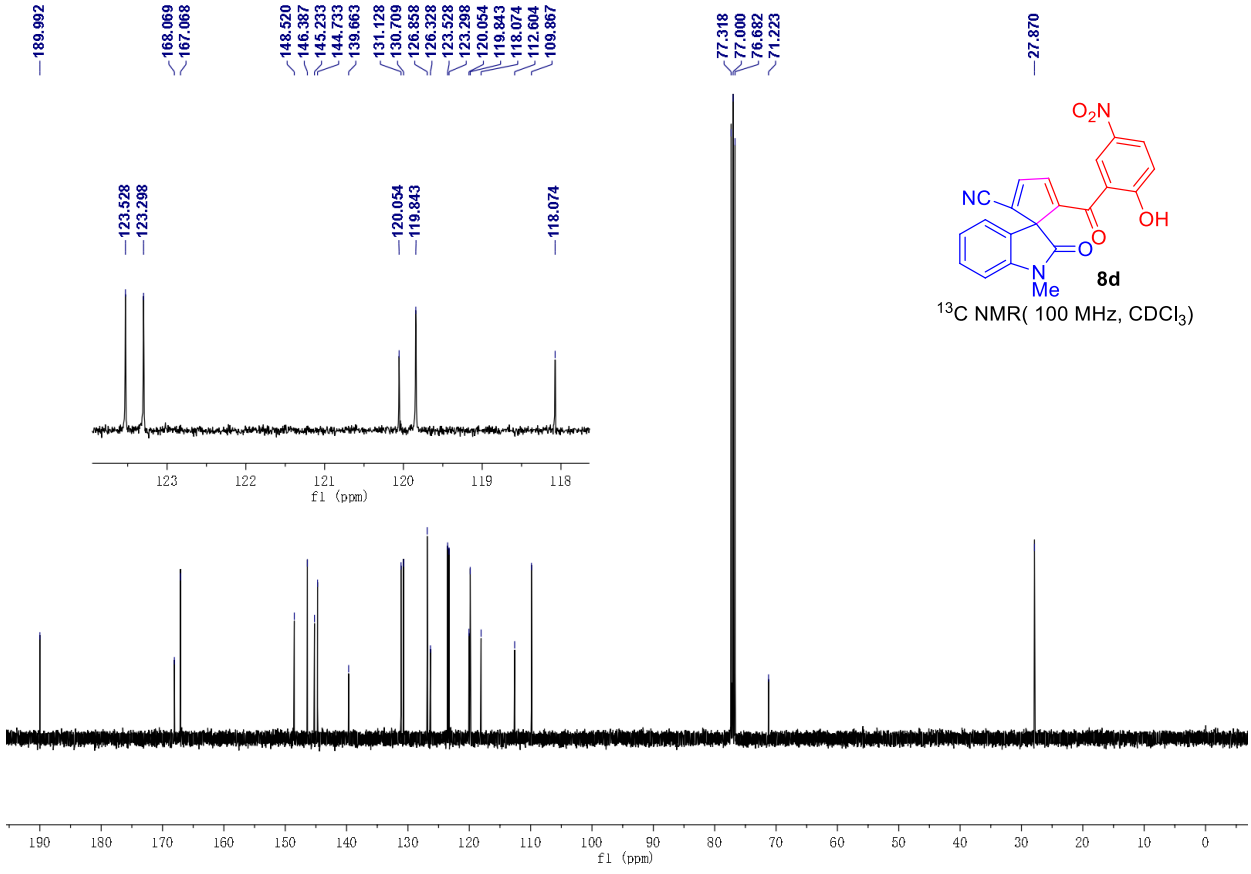

10.990
7.668
7.661
7.518
7.510
7.447
7.441
7.421
7.418
7.415
7.398
7.382
7.260
7.046
7.029
7.010
6.947
6.925
6.912
6.910
6.893
6.891
3.421
1.619
1.253
-0.001
Cl
NC
OH
O
O
N
Me
8b
1H NMR(400 MHz, CDCl3)
1.00
1.00
1.00
3.05
2.01
0.99
0.95
3.00
f1 (ppm)

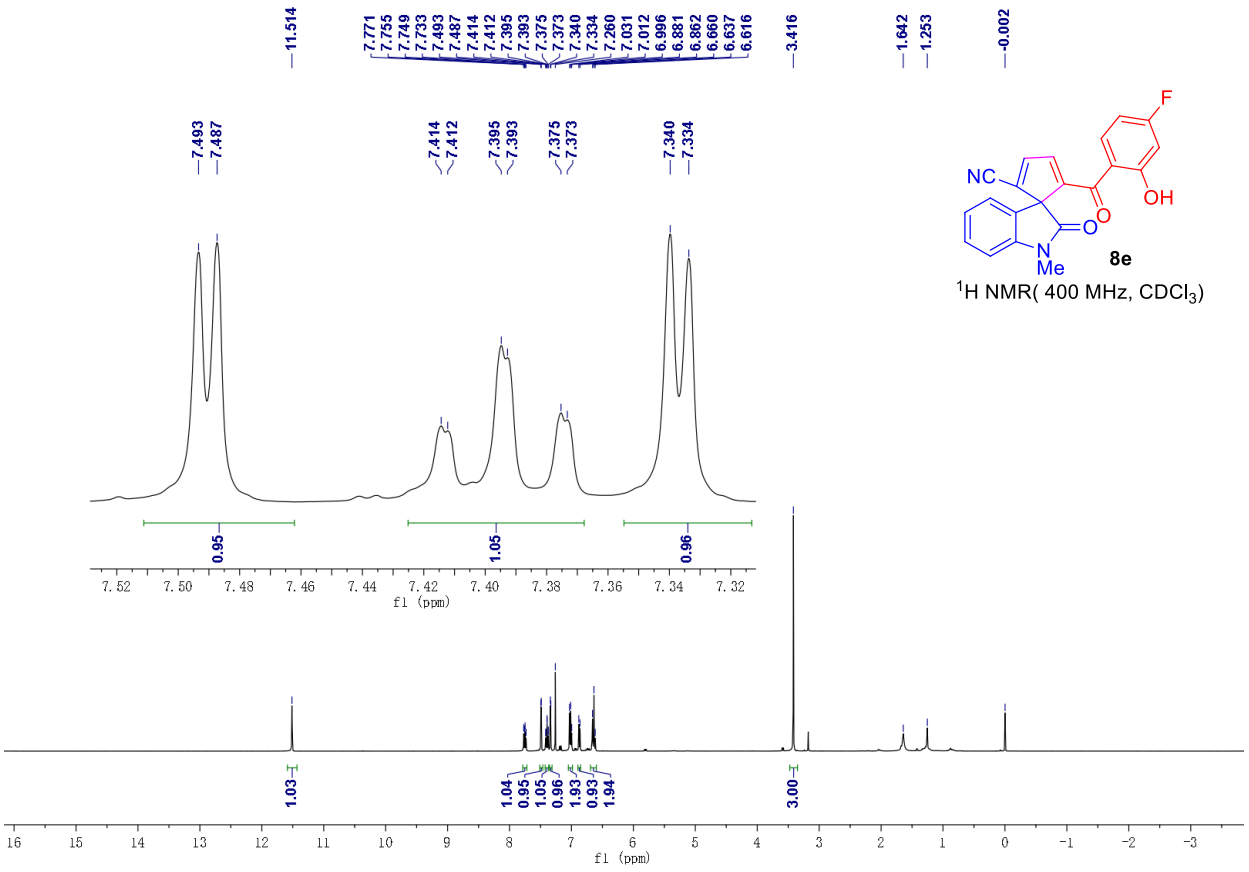

190.169
168.246
160.882
149.244
146.467
145.278
143.438
136.490
130.552
129.664
125.474
123.841
123.391
123.175
120.401
120.274
119.916
112.805
109.766
77.317
77.000
76.681
71.107
27.816
123.841
123.391
123.175
120.401
120.274
119.916
Cl
NC
OH
O
O
N
Me
8b
13C NMR(100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)


11.006
7.804
7.798
7.574
7.568
7.552
7.546
7.522
7.515
7.421
7.417
7.411
7.402
7.399
7.383
7.380
7.260
7.051
7.048
7.032
7.013
6.915
6.912
6.897
6.875
3.421
1.628
1.252
-0.002
Br
NC
OH
O
O
N
Me
8c
1H NMR(400 MHz, CDCl3)
1.02
0.96
0.99
1.00
1.02
0.96
0.99
2.00
2.01
2.00
3.00
f1 (ppm)

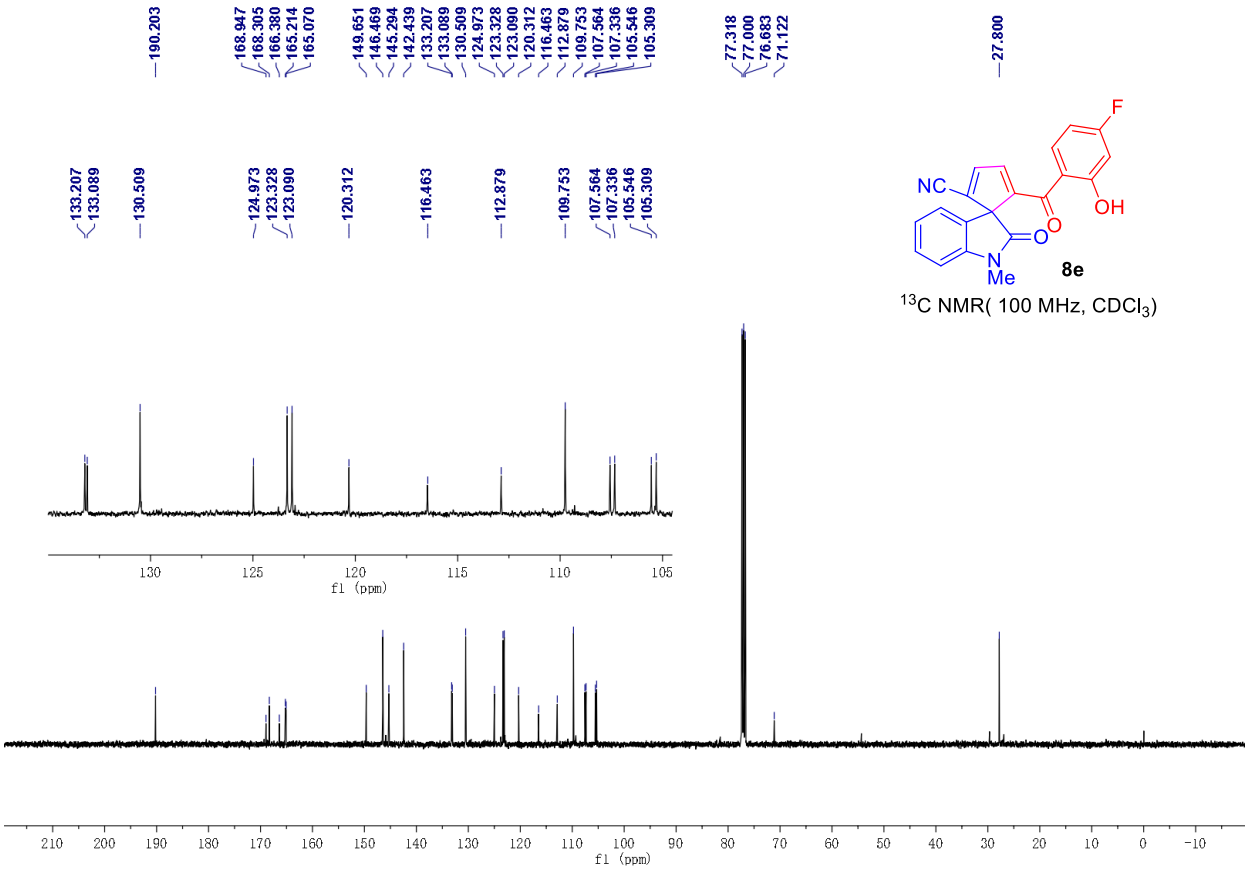

190.061
168.245
161.312
149.235
146.481
145.270
143.517
139.256
132.640
130.555
129.501
123.400
123.197
120.782
120.576
120.274
112.805
110.695
109.769
77.318
77.000
76.683
71.111
27.831
-0.023
Br
NC
OH
O
O
N
Me
8c
13C NMR(100 MHz, CDCl3)
f1 (ppm)


11.738
8.710
8.703
8.375
8.368
8.352
8.345
7.554
7.550
7.543
7.438
7.419
7.400
7.260
7.102
7.079
7.056
7.044
7.037
7.025
6.953
6.934
3.432
1.645
1.253
-0.005
O2N
NC
OH
O
O
N
Me
8d
1H NMR(400 MHz, CDCl3)
1.00
1.04
1.06
2.09
1.06
1.05
1.97
1.03
3.16
f1 (ppm)

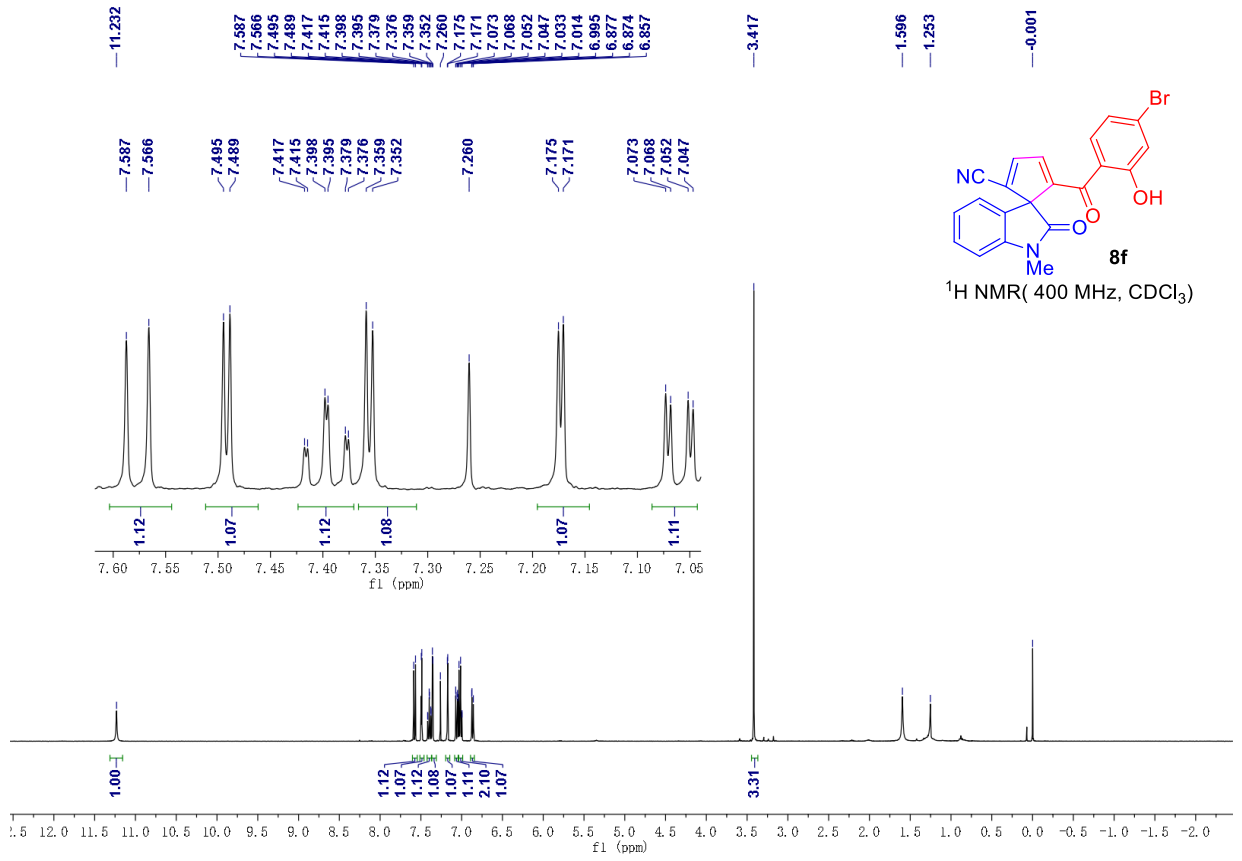

189.992
168.069
167.068
148.520
146.387
145.233
144.733
139.663
131.128
130.709
126.858
126.328
123.528
123.298
120.054
119.843
118.074
112.604
109.867
77.318
77.000
76.682
71.223
27.870
123.528
123.298
120.054
119.843
118.074
O2N
NC
OH
O
O
N
Me
8d
13C NMR(100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

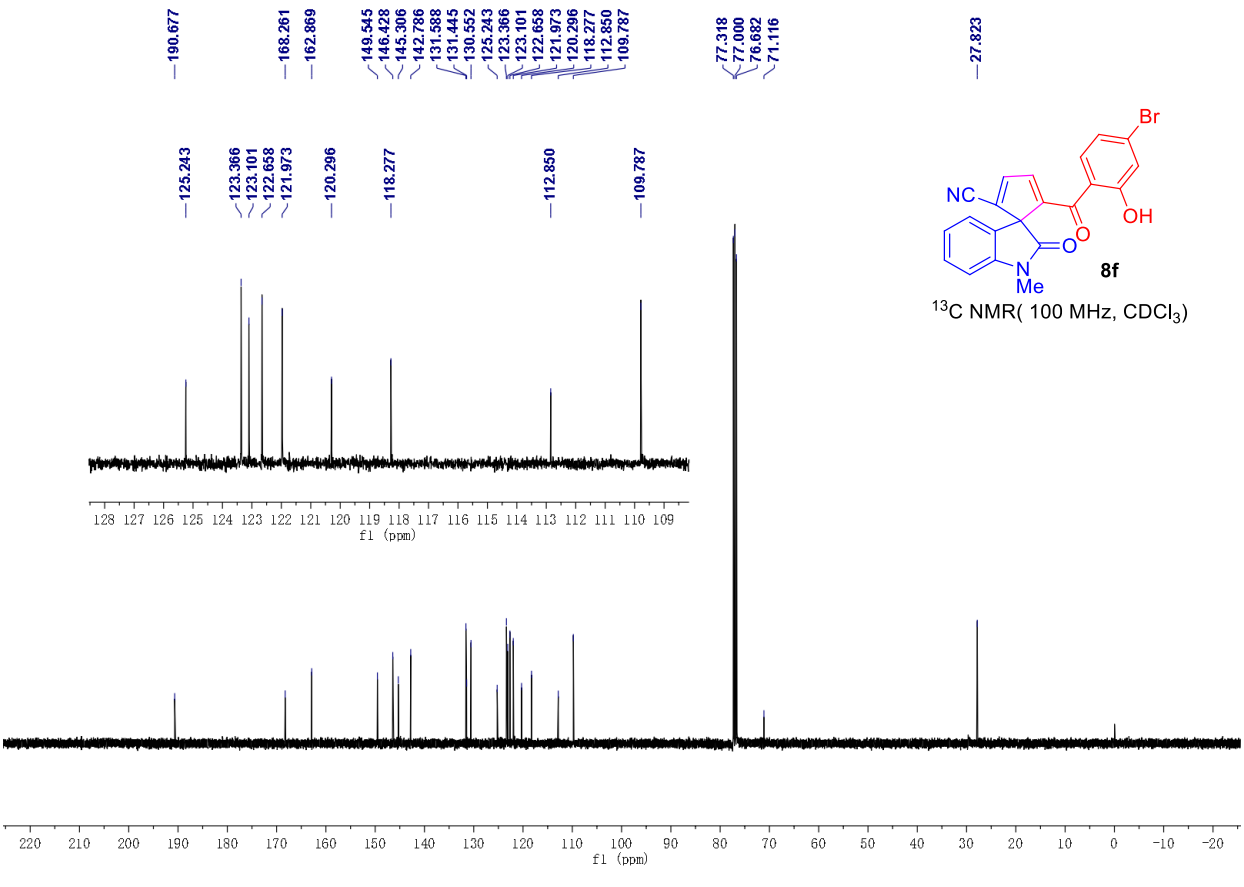


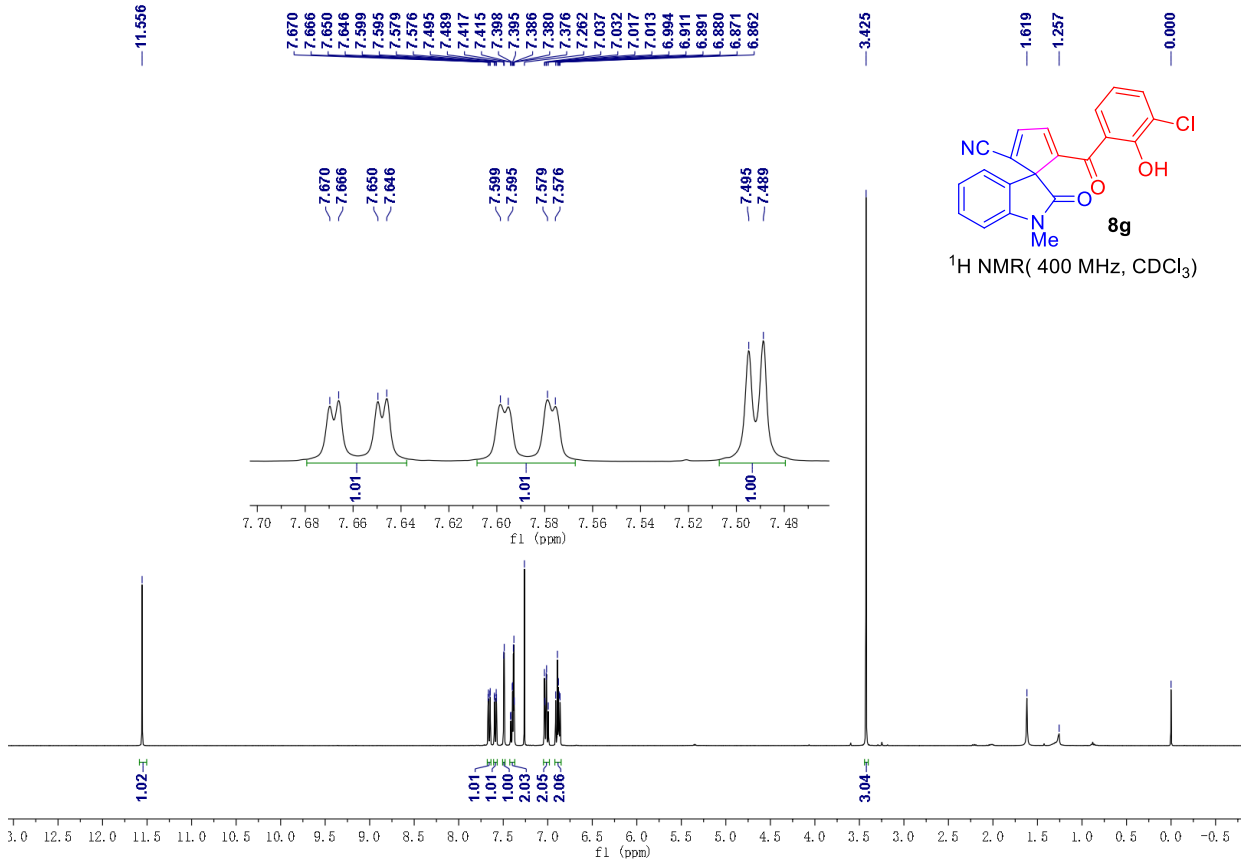
^{1}H NMR(400 MHz, $CDCl_3$)

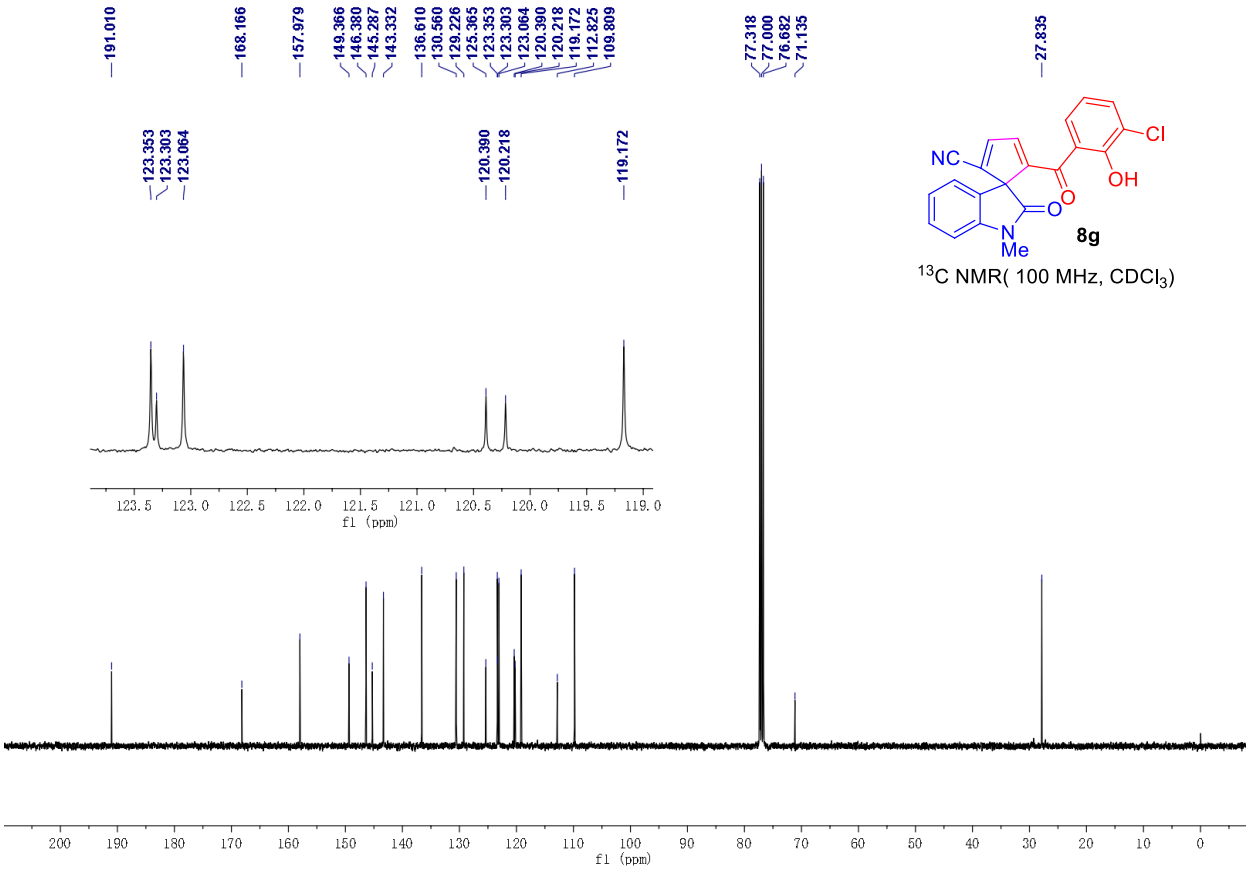


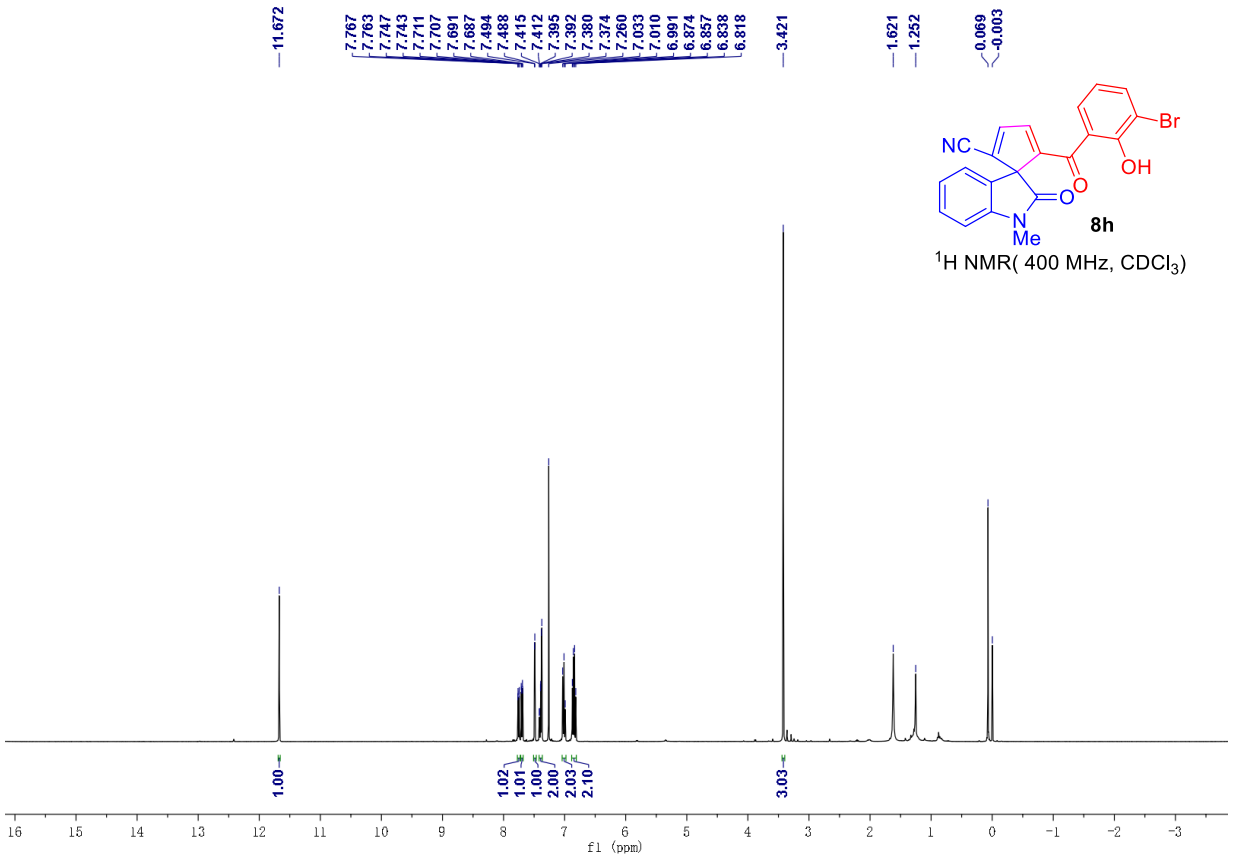
^{13}C NMR(100 MHz, $CDCl_3$)

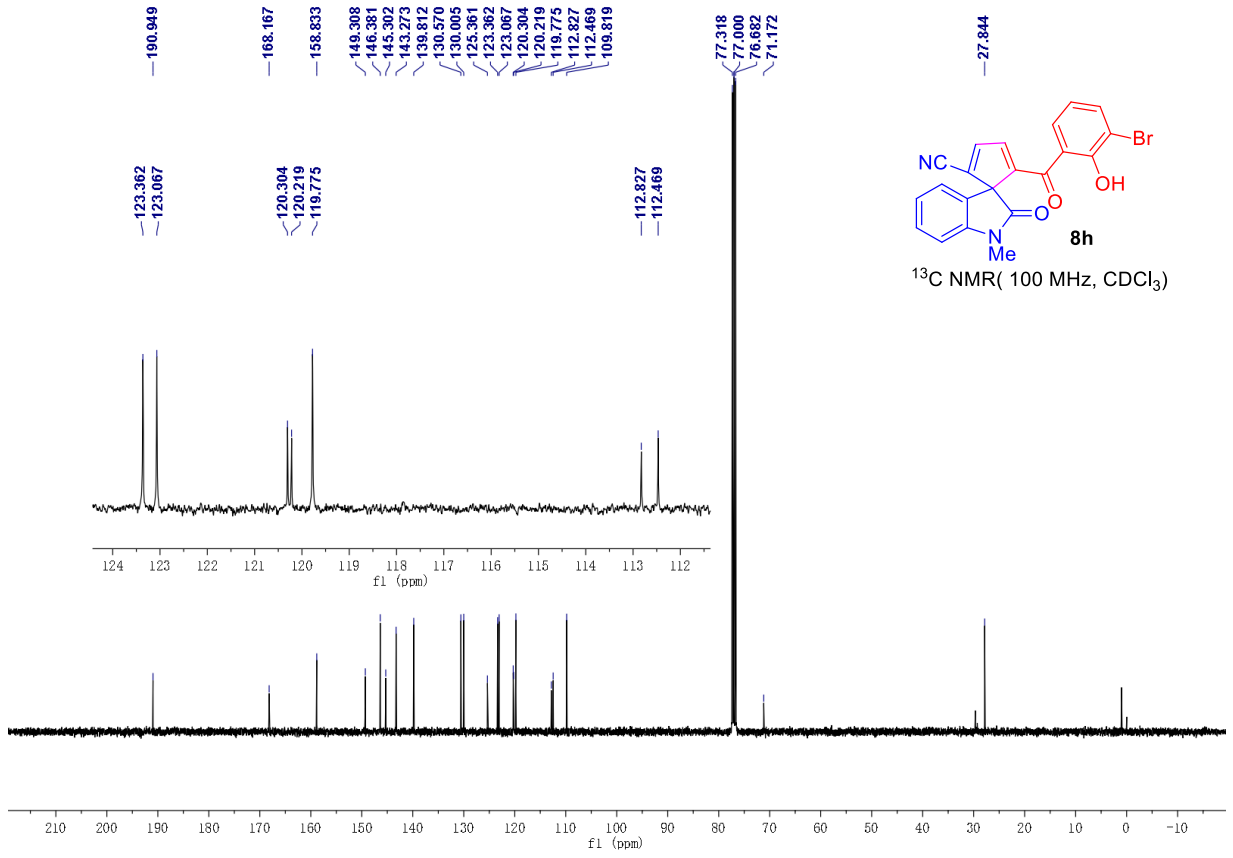

11.232
7.587
7.566
7.495
7.489
7.417
7.415
7.398
7.395
7.379
7.376
7.359
7.352
7.260
7.175
7.171
7.073
7.068
7.052
7.047
7.033
7.014
6.995
6.877
6.874
6.857
3.417
1.596
1.253
-0.001
Br
NC
OH
O
O
N
Me
8f
1H NMR(400 MHz, CDCl3)
1.12
1.07
1.12
1.08
1.07
1.11
1.00
1.12
1.07
1.12
1.08
1.07
1.11
2.10
1.07
3.31
f1 (ppm)

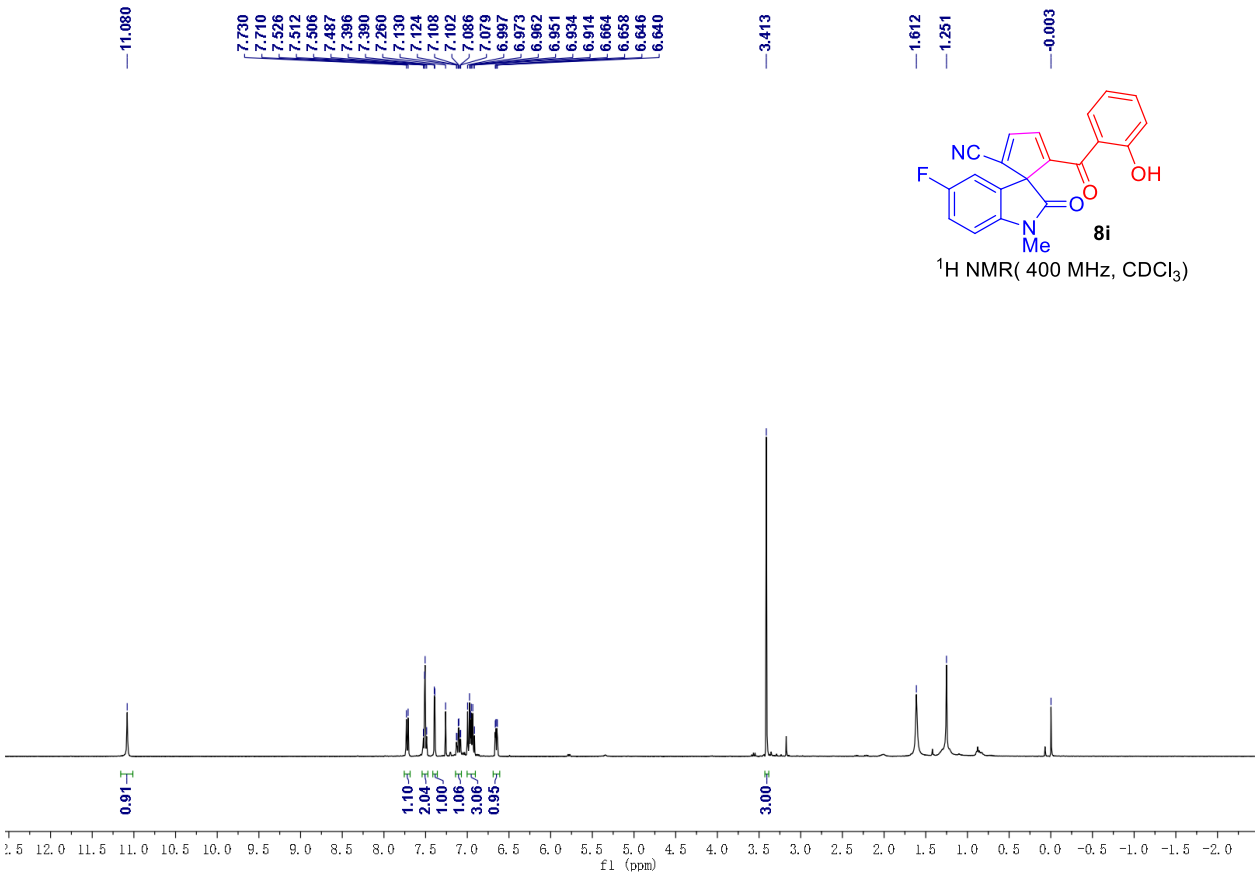

190.677
168.261
162.869
149.545
146.428
145.306
142.786
131.588
131.445
130.552
125.243
123.366
123.101
122.658
121.973
120.296
118.277
112.850
109.787
77.318
77.000
76.682
71.116
27.823
Br
NC
OH
O
O
N
Me
8f
13C NMR(100 MHz, CDCl3)
f1 (ppm)


11.556
7.670
7.666
7.650
7.646
7.599
7.595
7.579
7.576
7.495
7.489
7.417
7.415
7.398
7.395
7.386
7.380
7.376
7.262
7.037
7.032
7.017
7.013
6.994
6.911
6.891
6.880
6.871
6.862
3.425
1.619
1.257
0.000
NC
Cl
OH
O
O
N
Me
8g
1H NMR(400 MHz, CDCl3)
1.02
1.01
1.01
1.00
2.03
2.05
2.06
3.04
f1 (ppm)

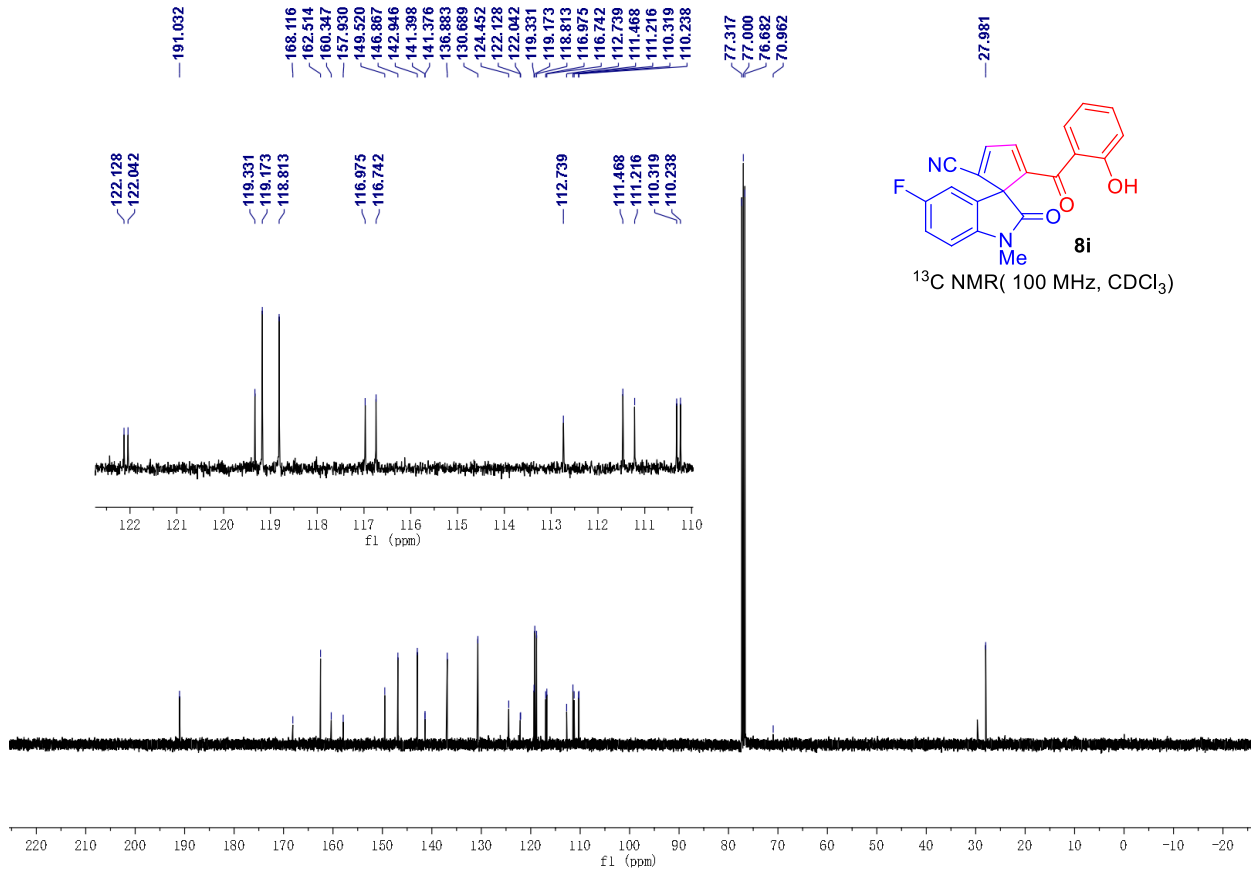

191.010
168.166
157.979
149.366
146.380
145.287
143.332
136.610
130.560
129.226
125.365
123.353
123.303
123.064
120.390
120.218
119.172
112.825
109.809
77.318
77.000
76.682
71.135
27.835
NC
Cl
OH
O
O
N
Me
8g
13C NMR(100 MHz, CDCl3)
f1 (ppm)


11.672
7.767
7.763
7.747
7.743
7.711
7.707
7.691
7.687
7.494
7.488
7.415
7.412
7.395
7.392
7.380
7.374
7.260
7.033
7.010
6.991
6.874
6.857
6.838
6.818
3.421
1.621
1.252
0.069
-0.003
Br
NC
OH
O
O
N
Me
8h
1H NMR(400 MHz, CDCl3)
1.00
1.02
1.01
1.00
2.00
2.03
2.10
3.03
f1 (ppm)

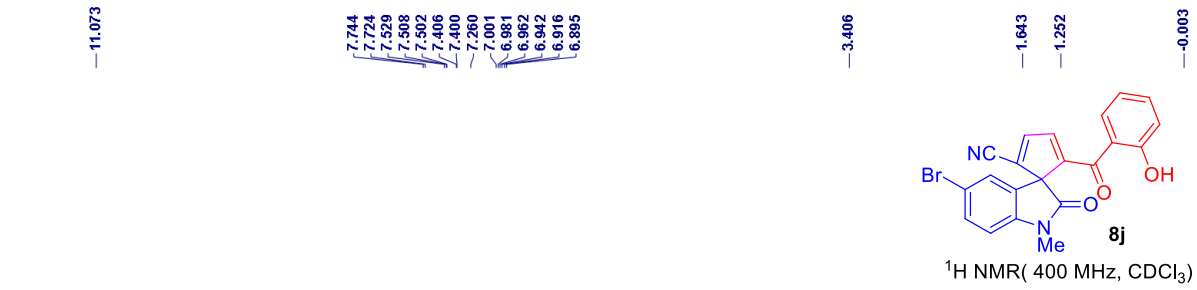

190.949
168.167
158.833
149.308
146.381
145.302
143.273
139.812
130.570
130.005
125.361
123.362
123.067
120.304
120.219
119.775
112.827
112.469
109.819
77.318
77.000
76.682
71.172
27.844
Br
NC
OH
O
O
N
Me
8h
13C NMR(100 MHz, CDCl3)
f1 (ppm)



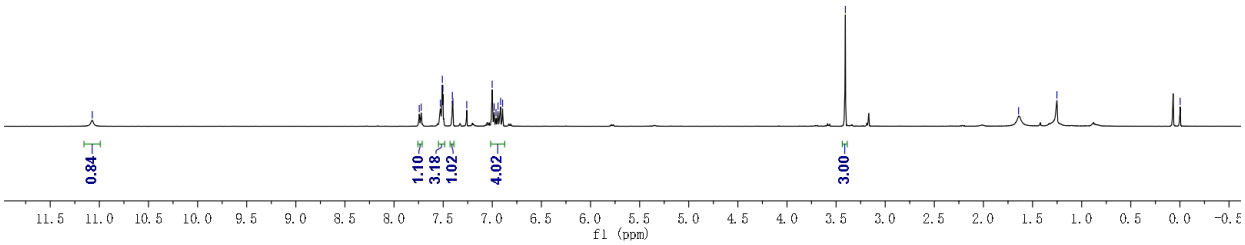
^{1}H NMR(400 MHz, $CDCl_3$)

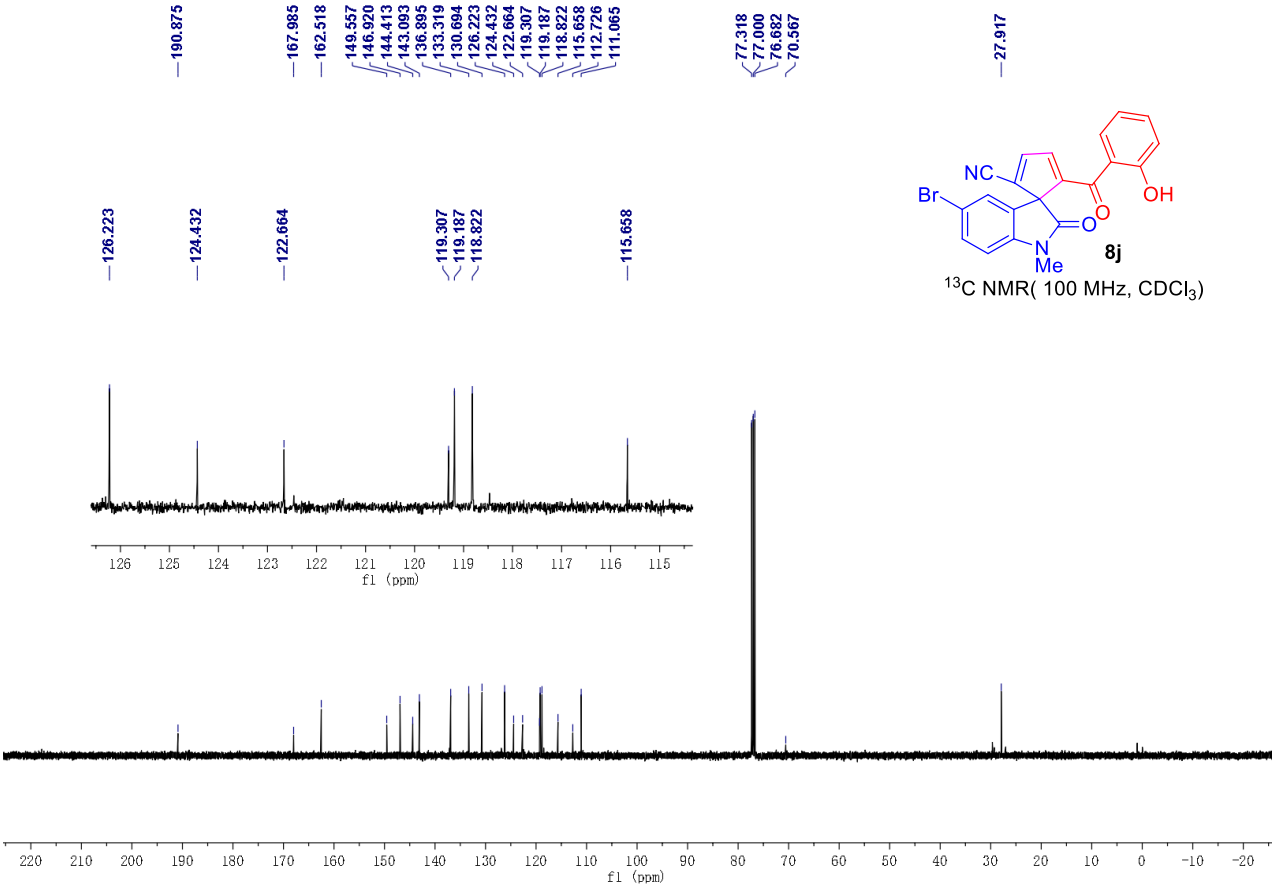


^{13}C NMR(100 MHz, $CDCl_3$)

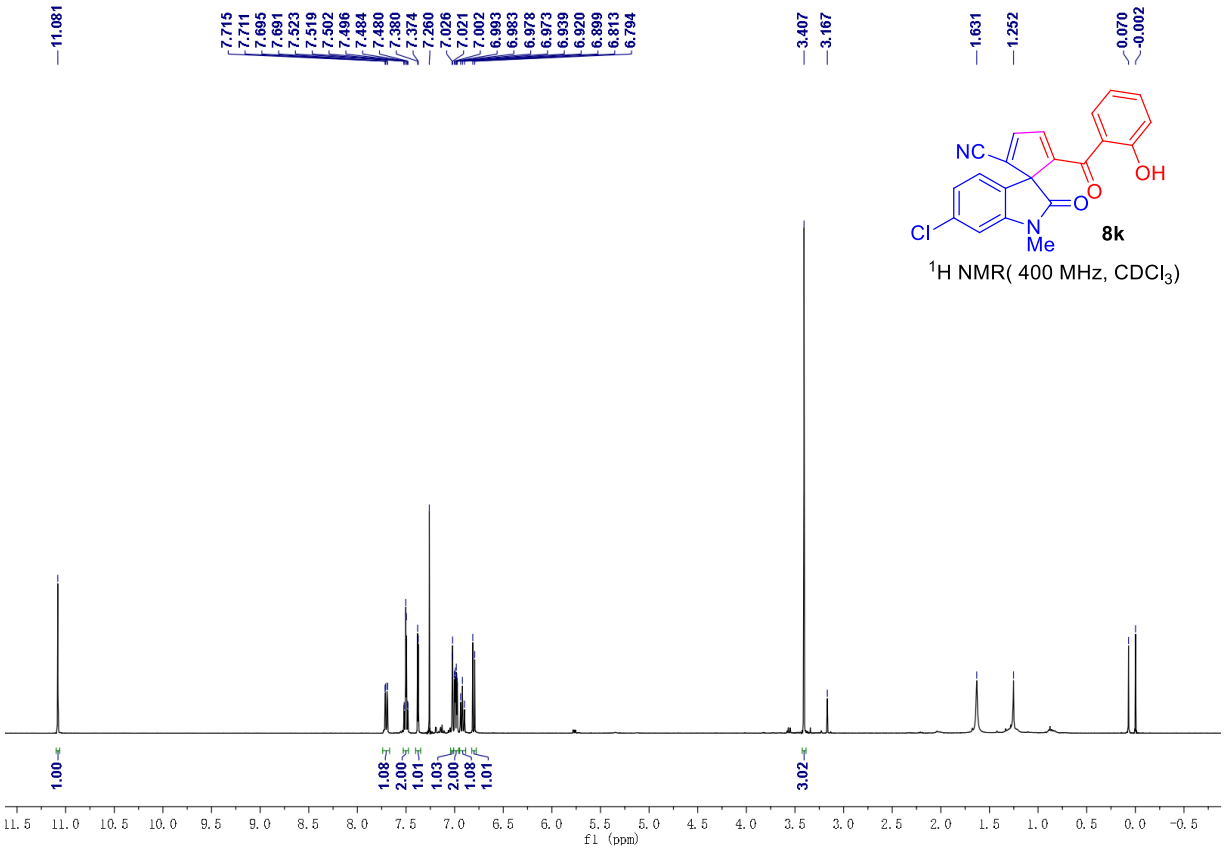


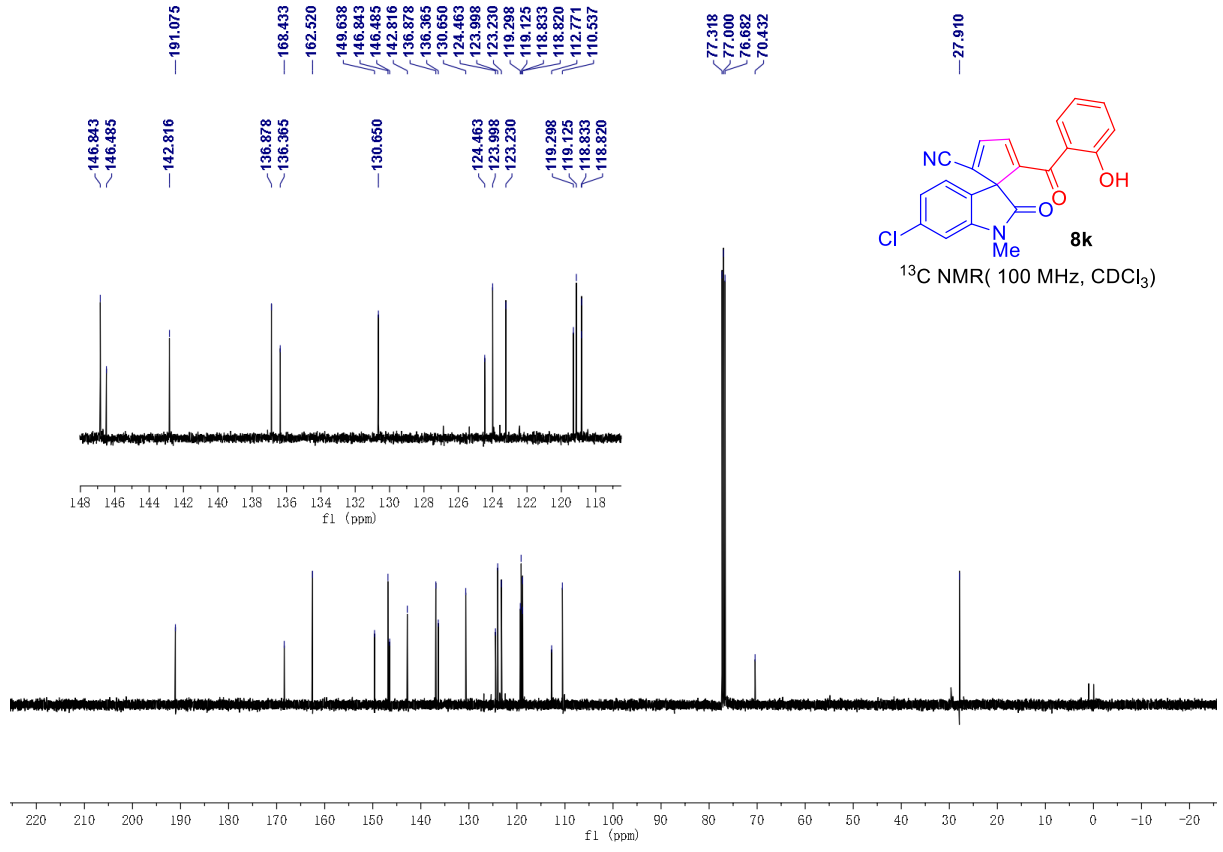
^{1}H NMR(400 MHz, $CDCl_3$)

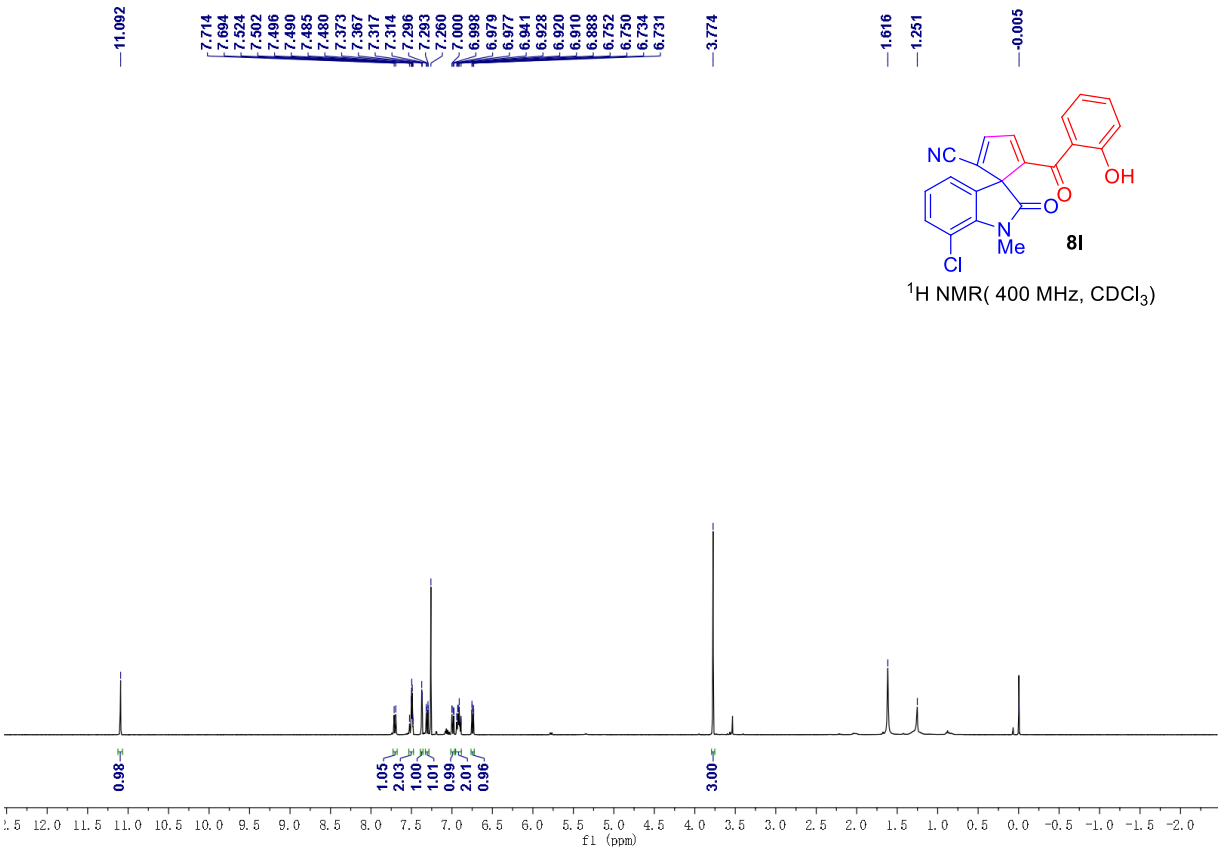




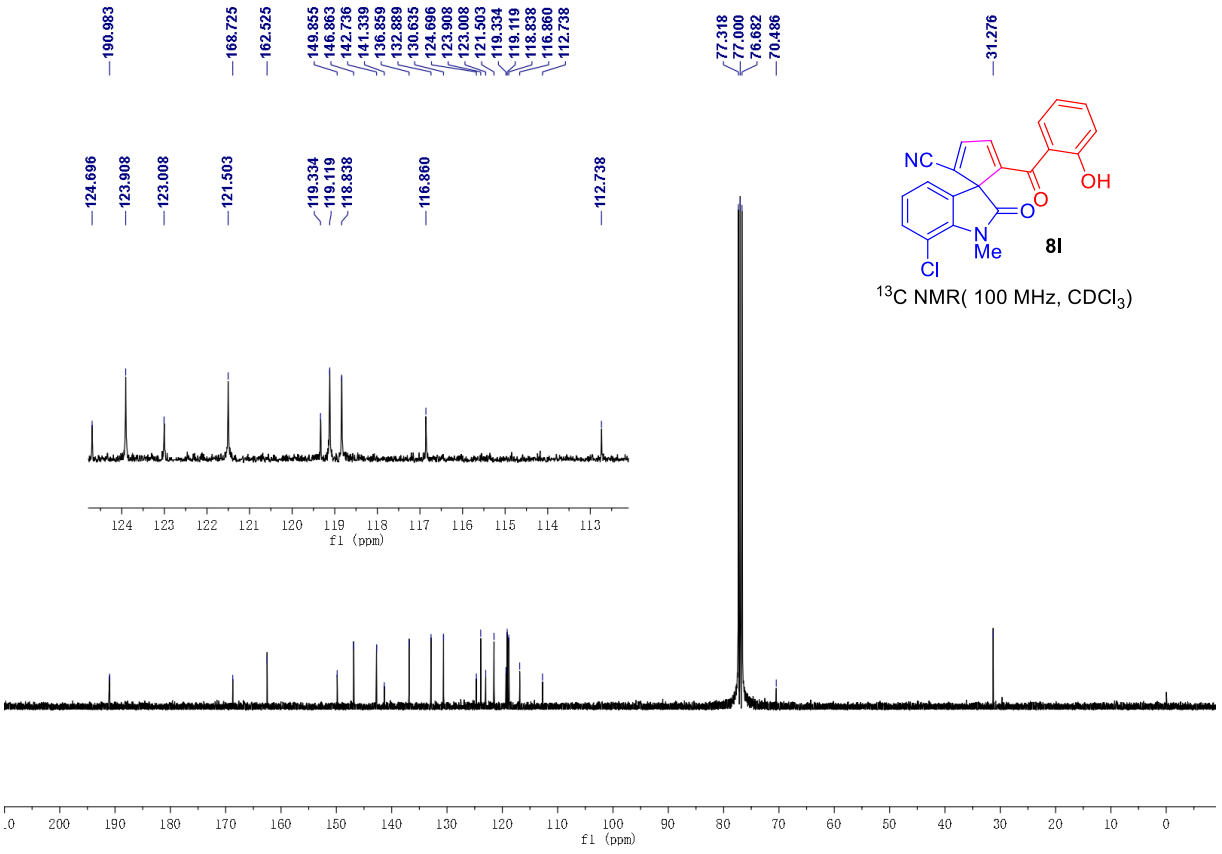
^{13}C NMR(100 MHz, $CDCl_3$)


11.081
7.715
7.711
7.695
7.691
7.523
7.519
7.502
7.496
7.484
7.480
7.380
7.374
7.260
7.026
7.021
7.002
6.993
6.983
6.978
6.973
6.939
6.920
6.899
6.813
6.794
3.407
3.167
1.631
1.252
0.070
-0.002
NC
OH
O
O
N
Me
Cl
8k
1H NMR(400 MHz, CDCl3)
1.00
1.08
2.00
1.01
1.03
2.00
1.08
1.01
3.02
f1 (ppm)

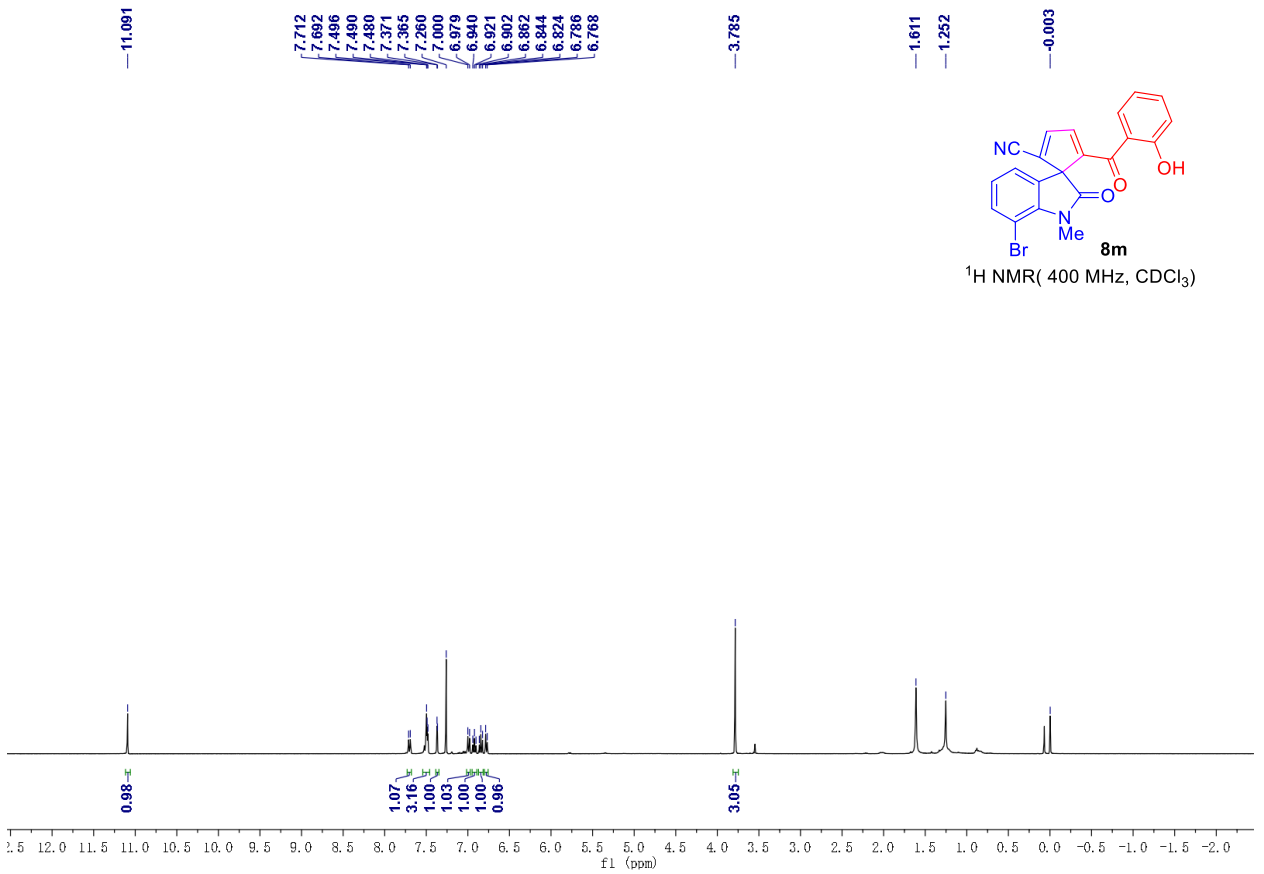

191.075
168.433
162.520
149.638
146.843
146.485
142.816
136.878
136.365
130.650
124.463
123.998
123.230
119.298
119.125
118.833
118.820
112.771
110.537
77.318
77.000
76.682
70.432
27.910
NC
OH
O
O
N
Me
Cl
8k
13C NMR(100 MHz, CDCl3)
f1 (ppm)



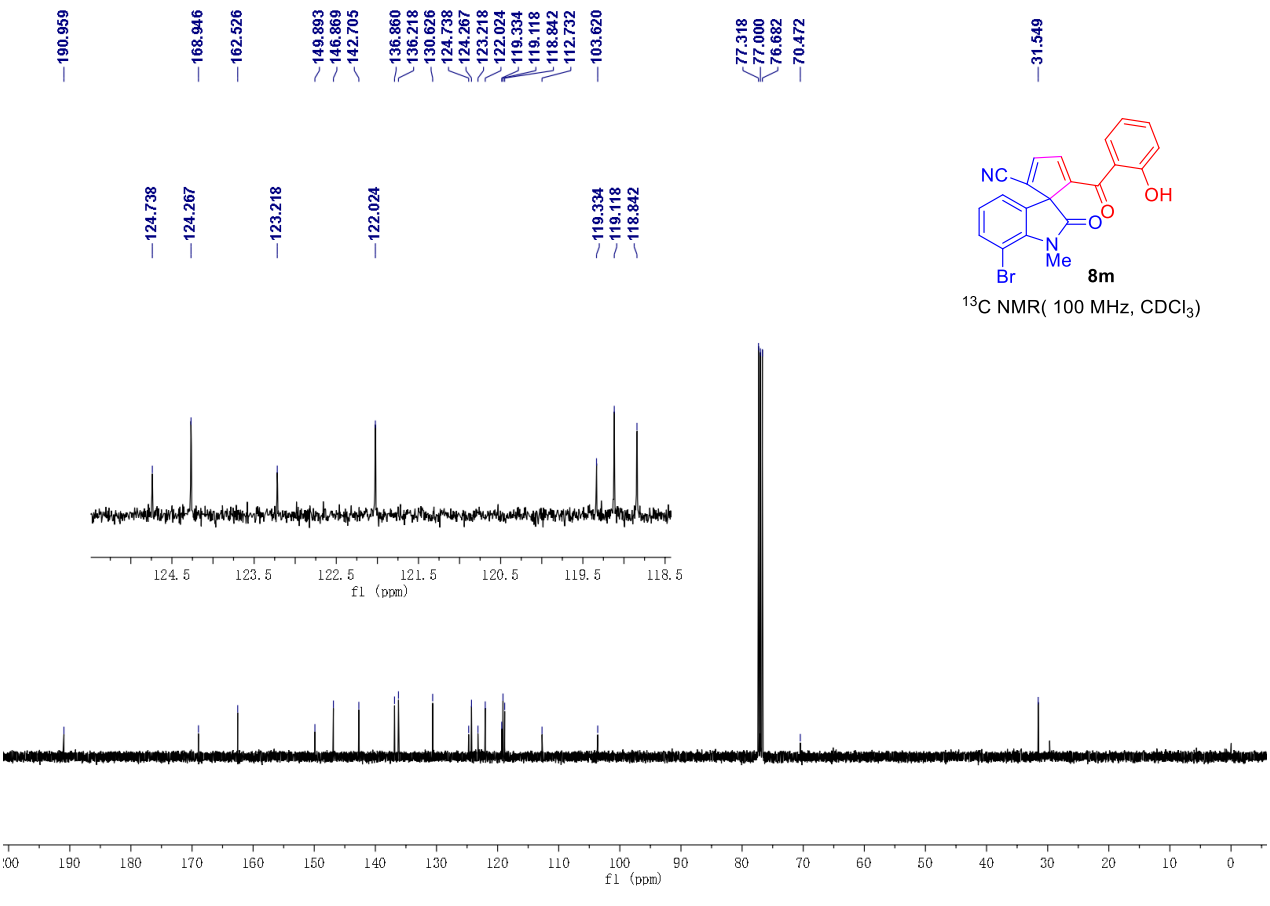
^{1}H NMR(400 MHz, $CDCl_3$)



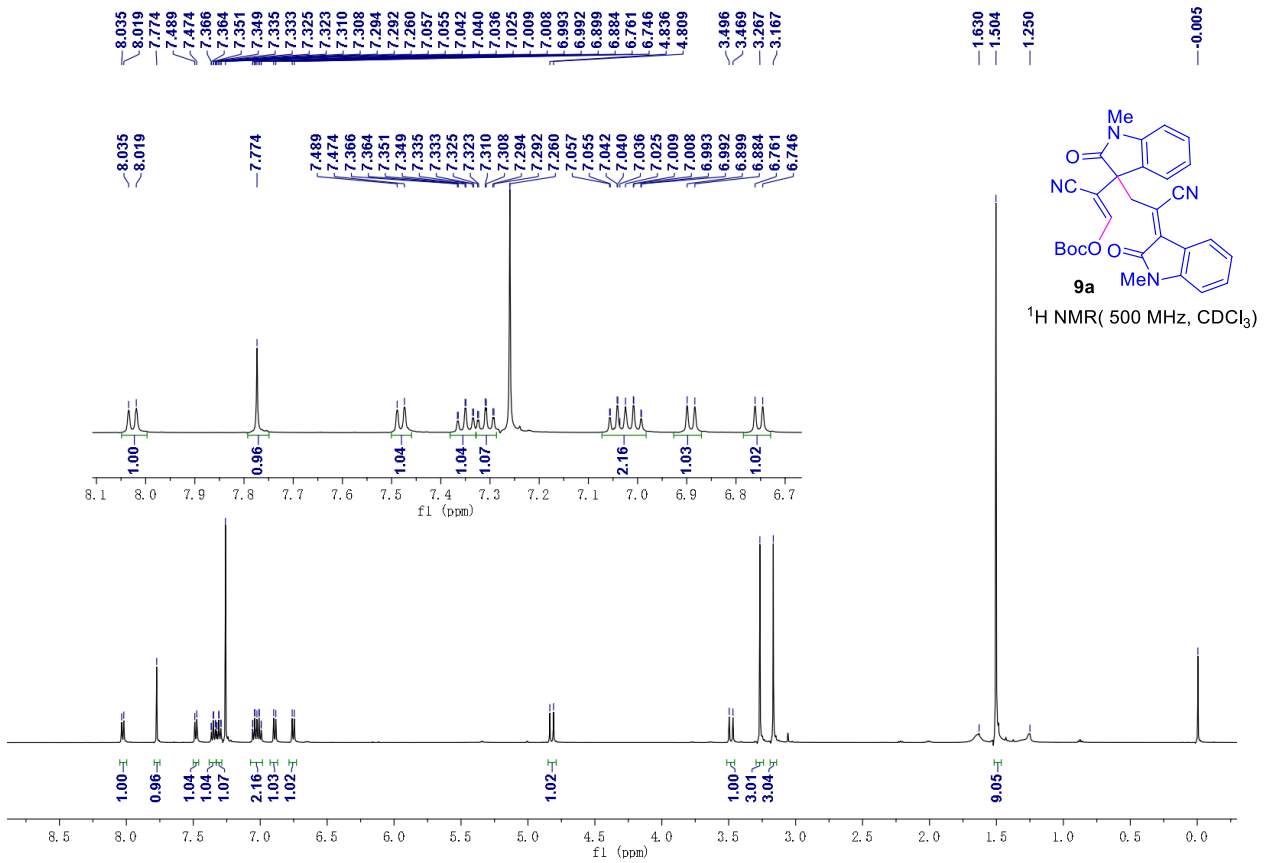
^{13}C NMR(100 MHz, $CDCl_3$)

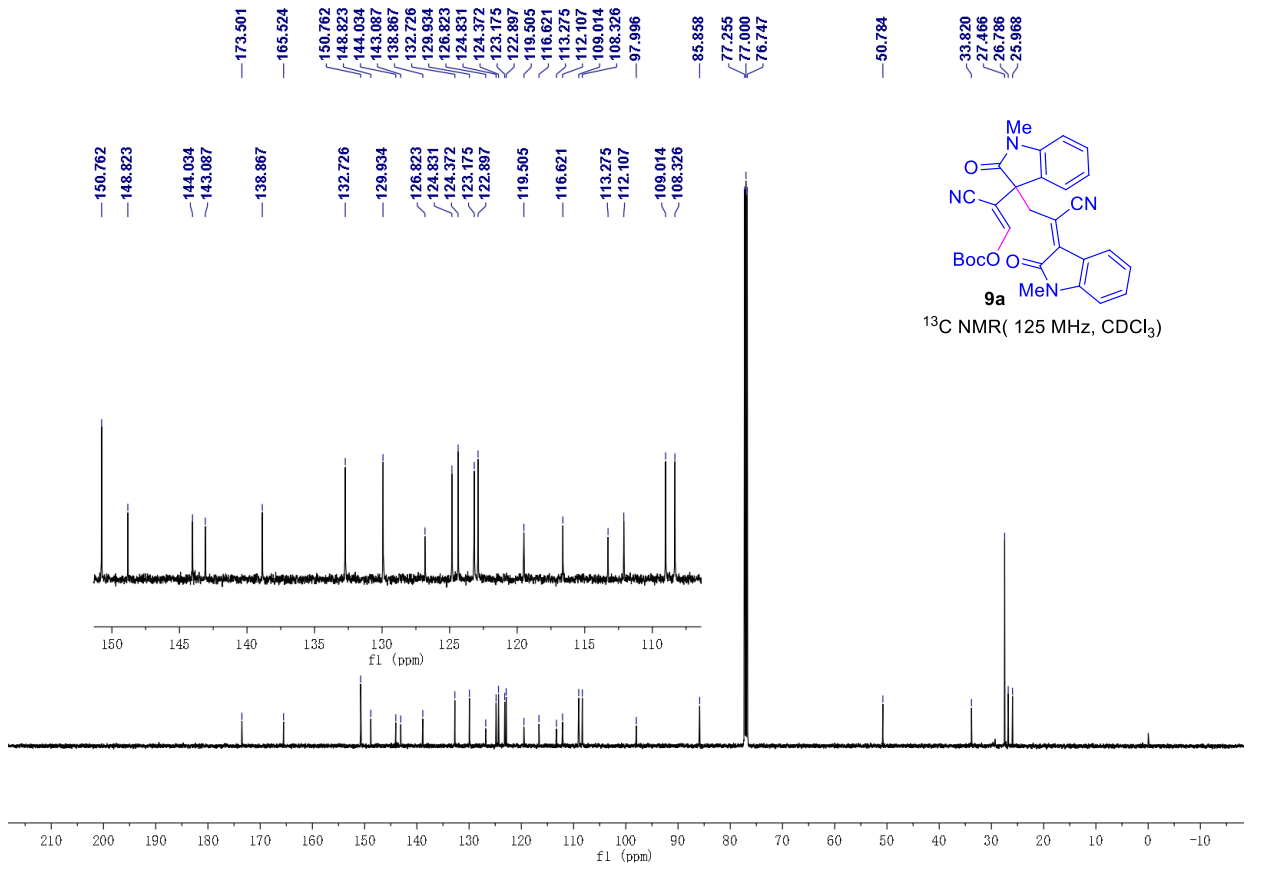


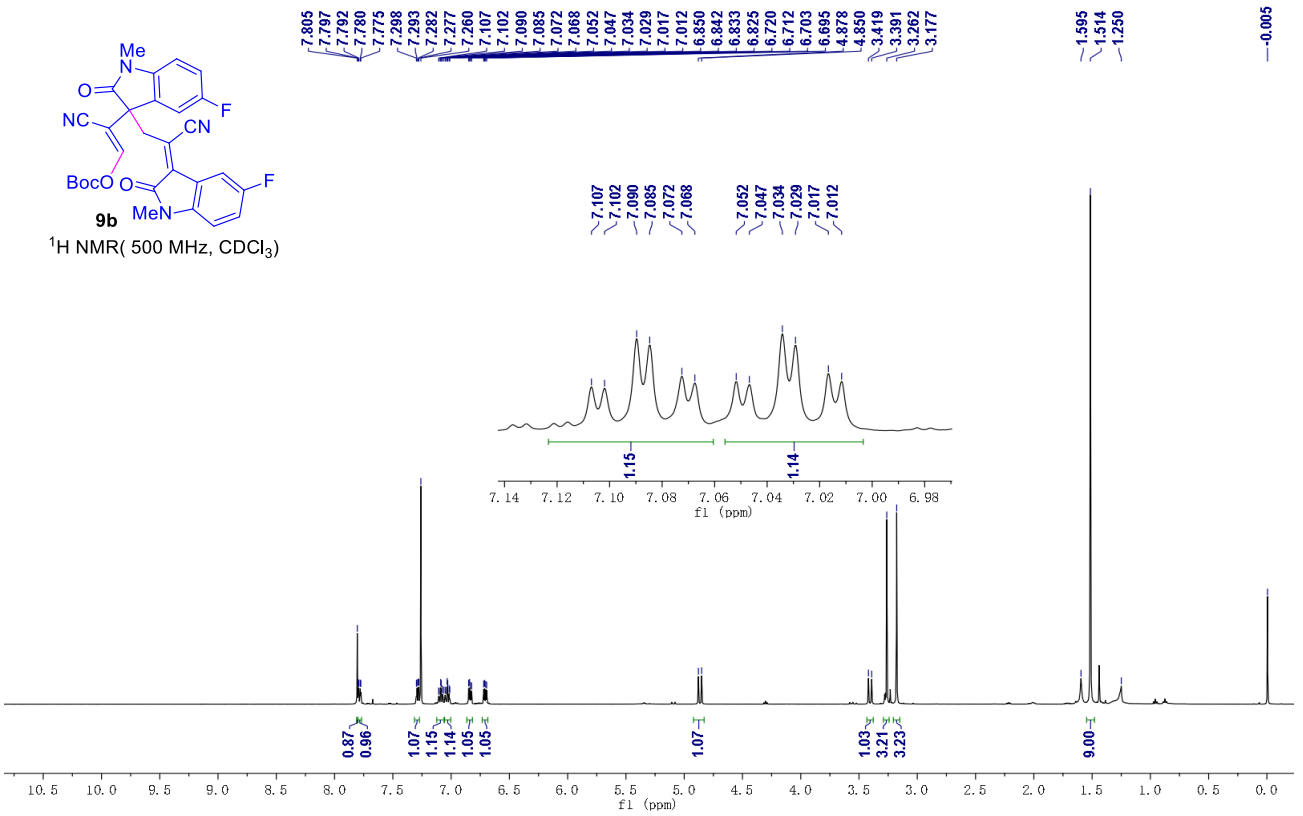
^{1}H NMR(400 MHz, $CDCl_3$)

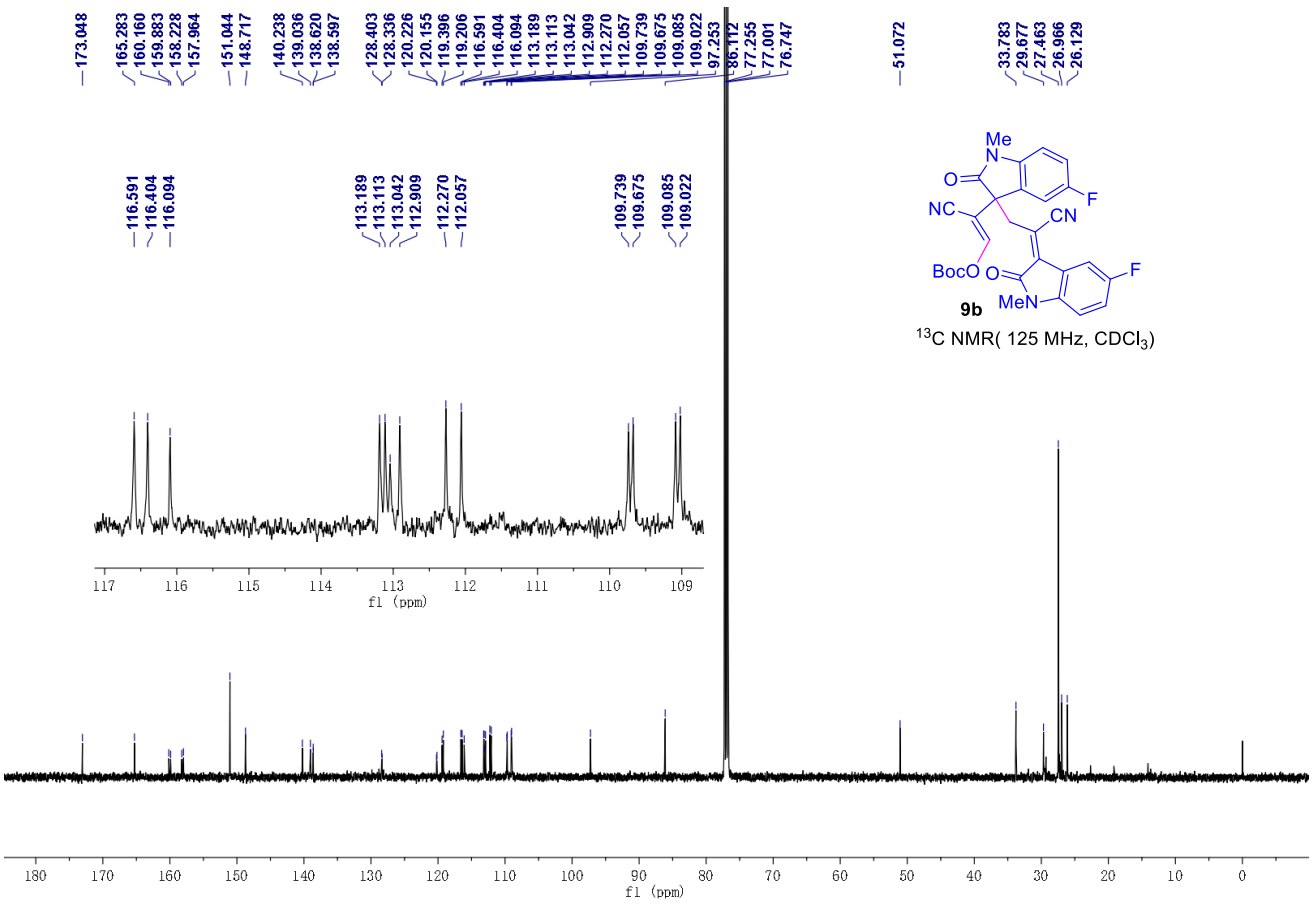


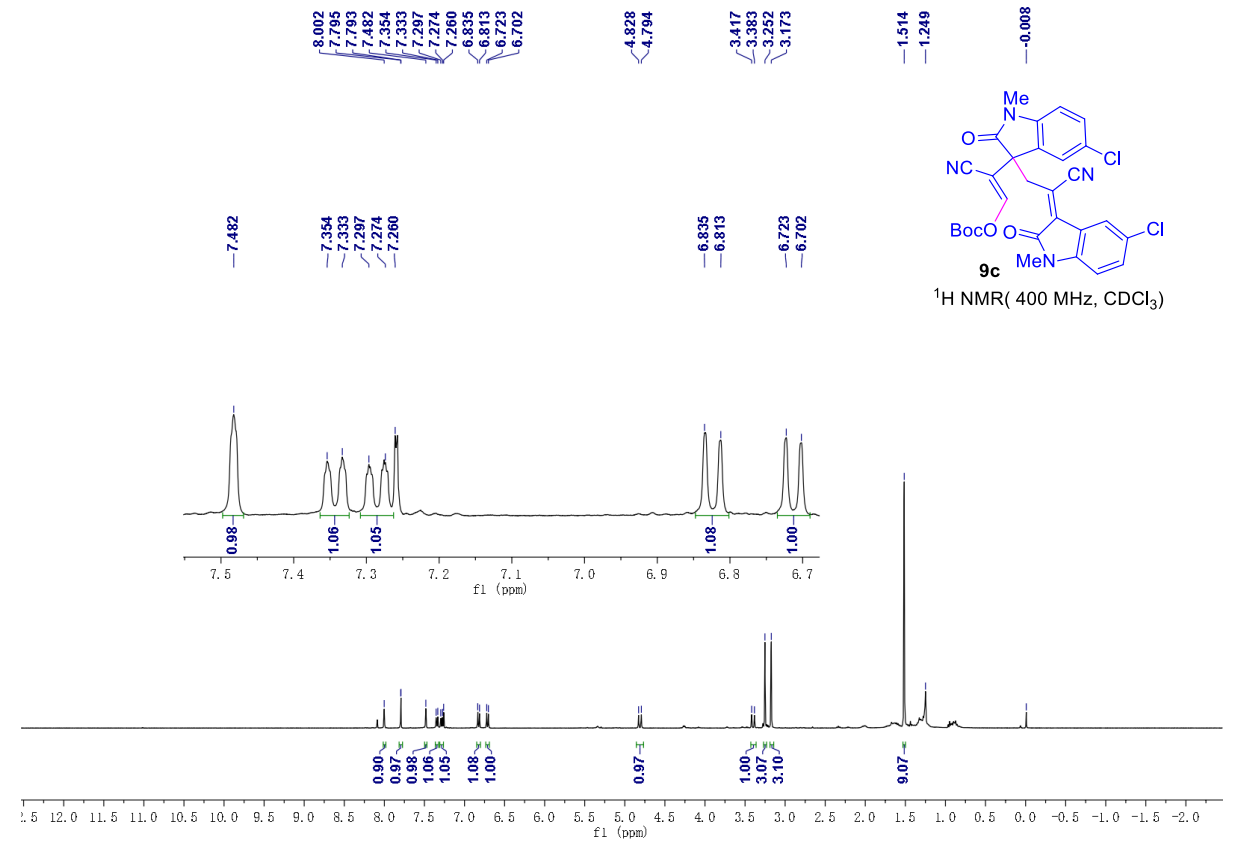
^{13}C NMR(100 MHz, $CDCl_3$)


9a
^{1}H NMR(500 MHz, $CDCl_3$)

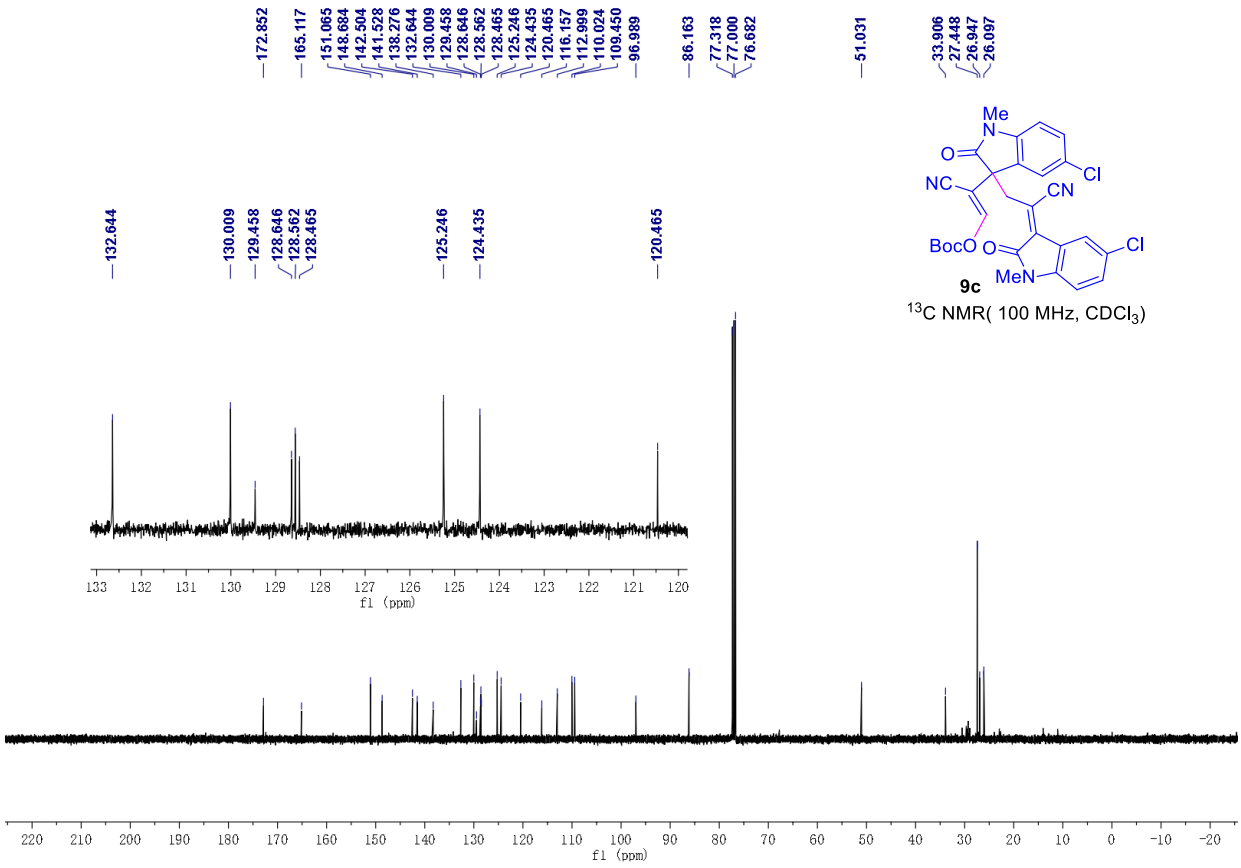

9a
^{13}C NMR(125 MHz, $CDCl_3$)


9b
^{1}H NMR(500 MHz, CDCl$_3$)
fl (ppm)

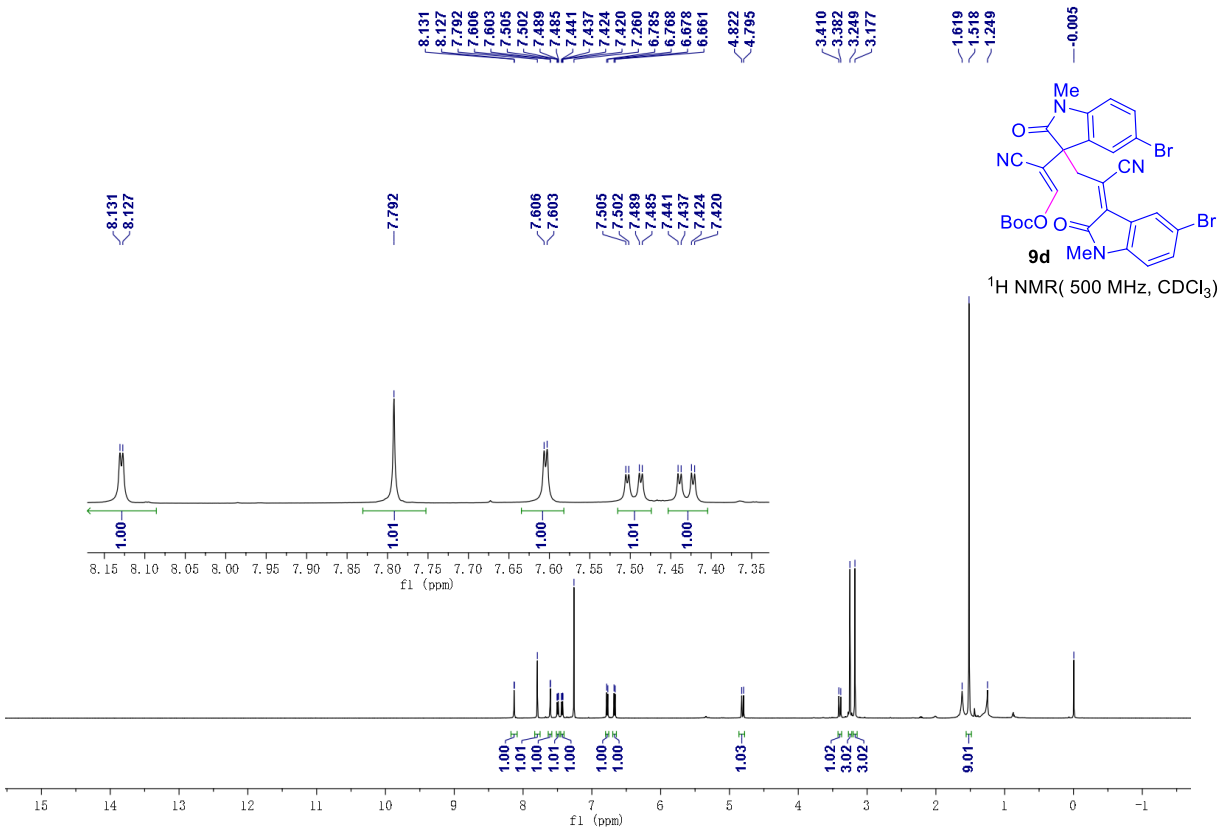

9b
^{13}C NMR(125 MHz, CDCl$_3$)
fl (ppm)



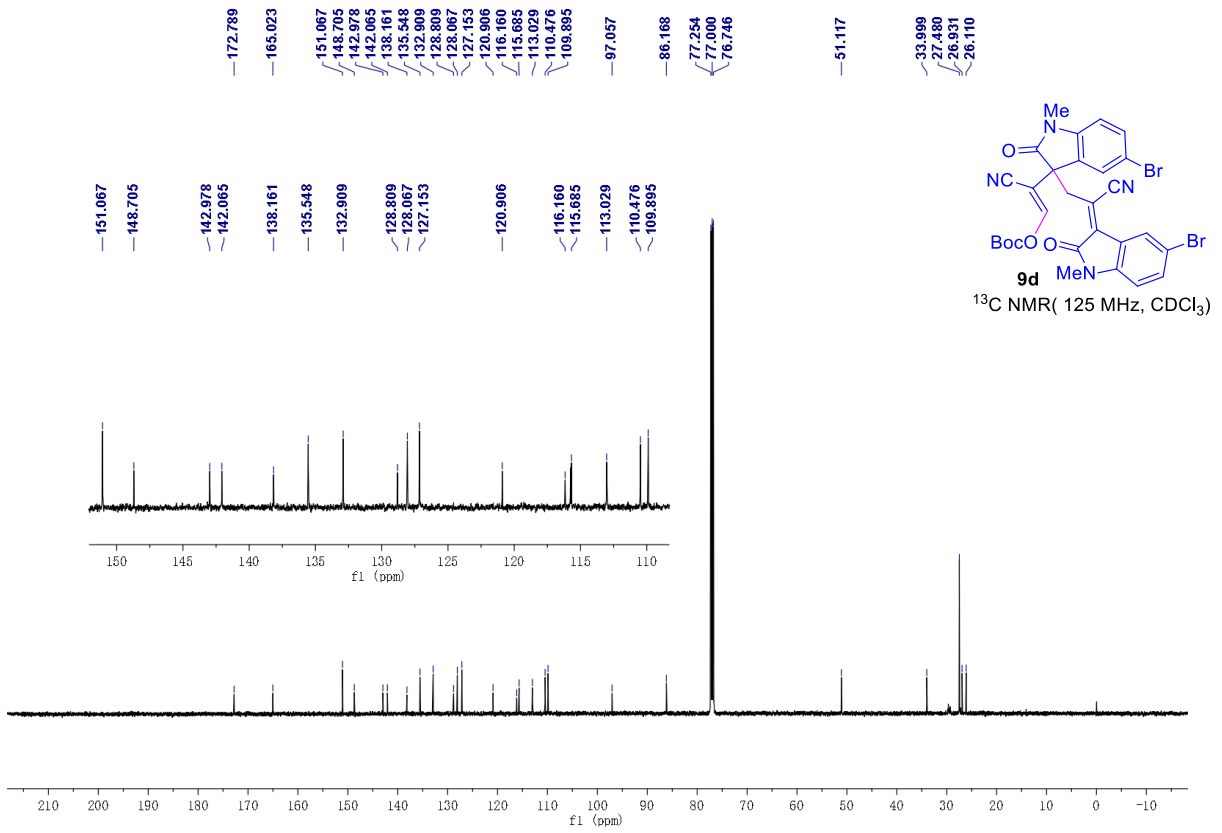
^{1}H NMR(400 MHz, $CDCl_3$)



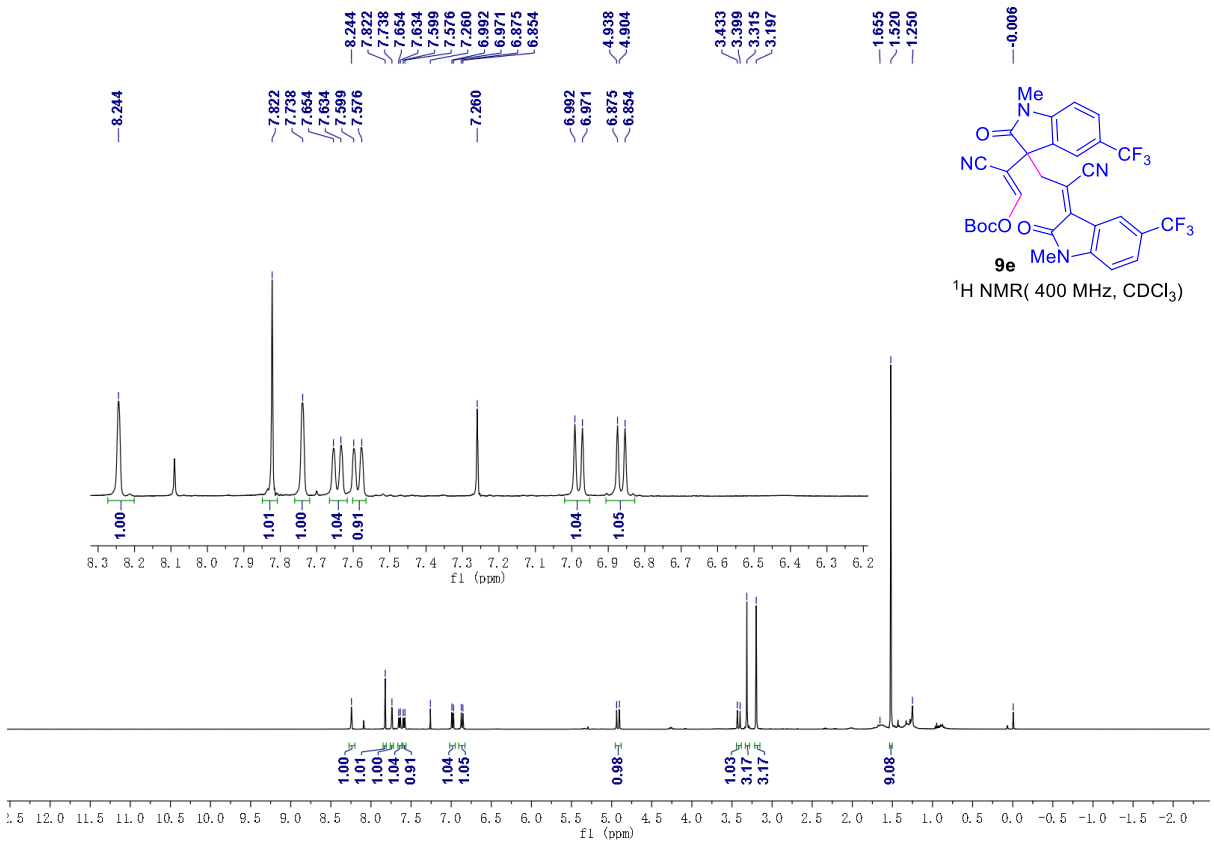
^{13}C NMR(100 MHz, $CDCl_3$)

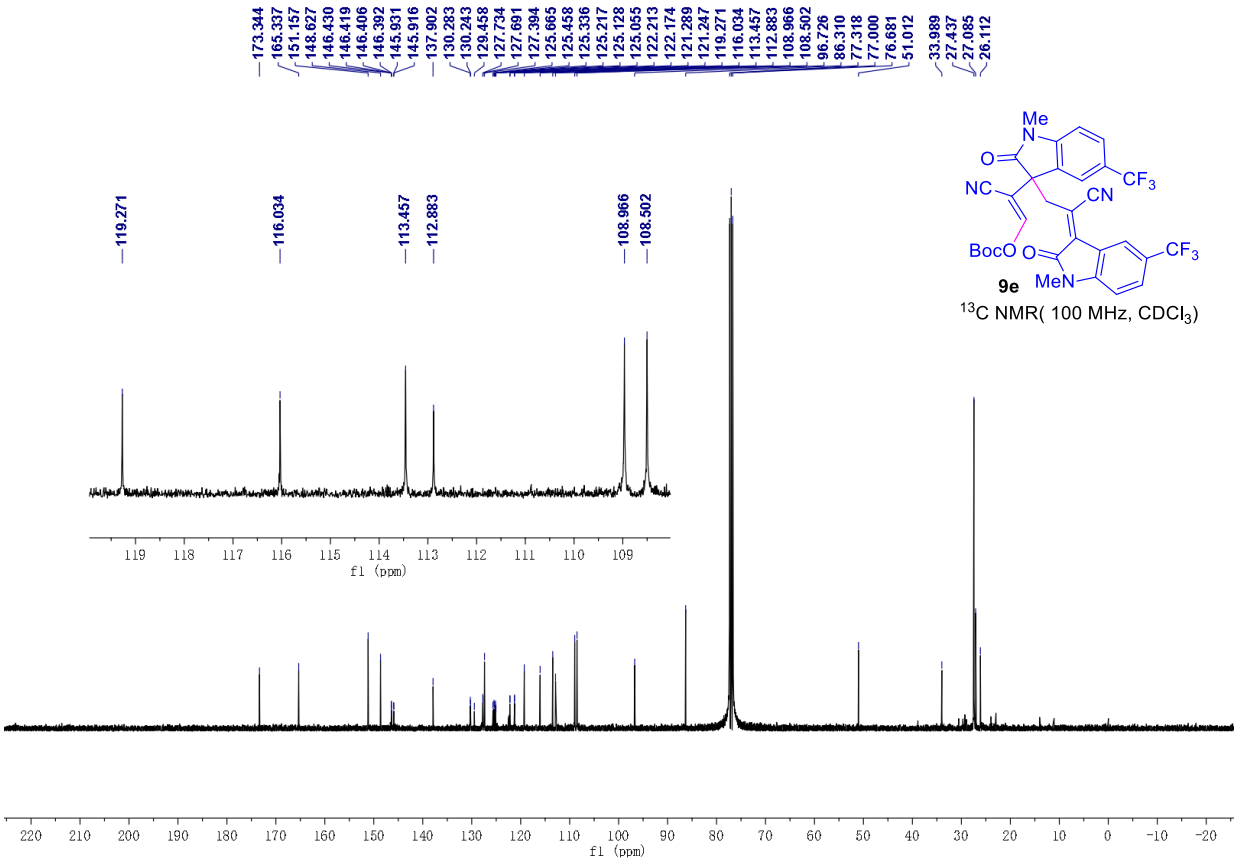


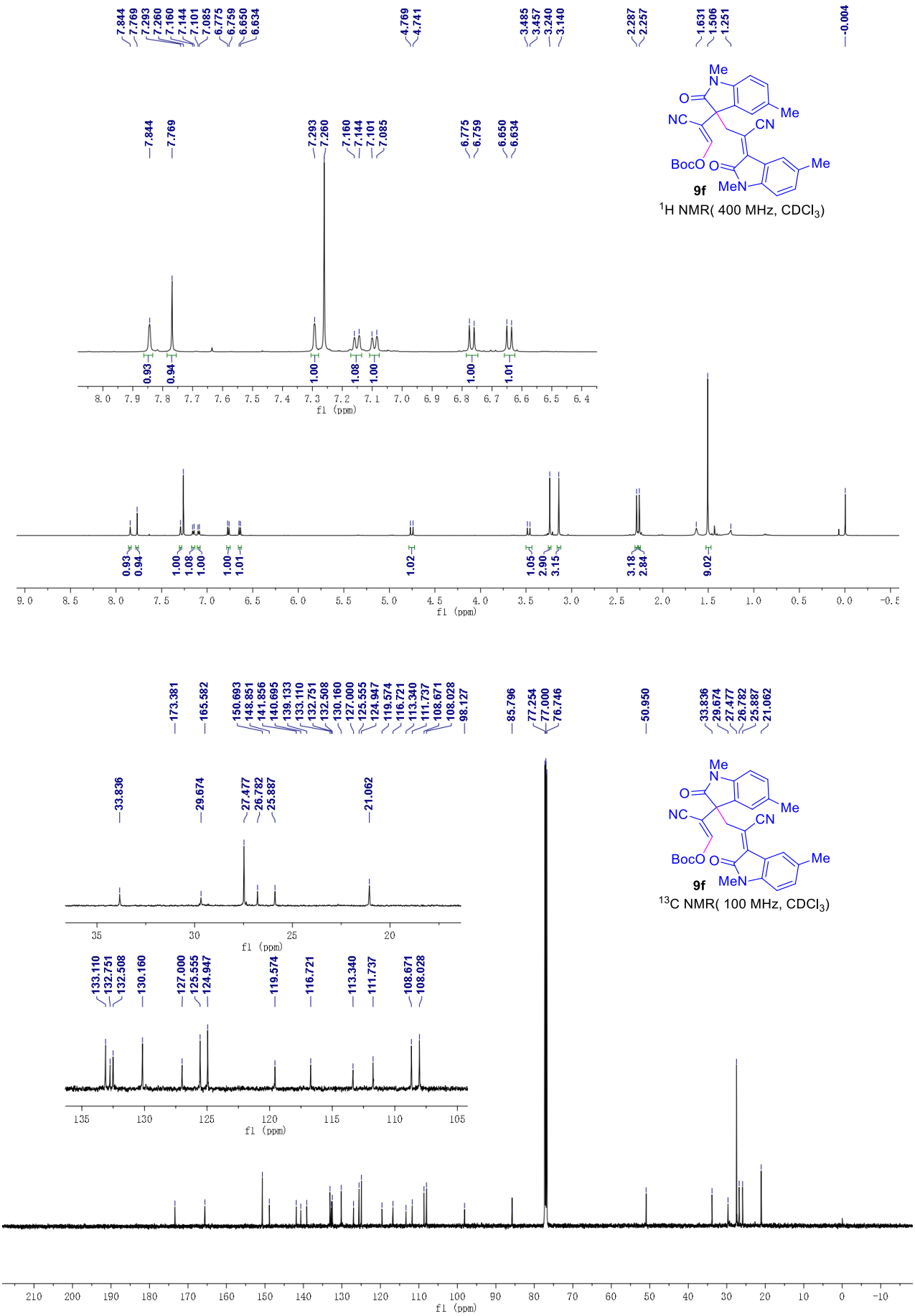
^{1}H NMR(500 MHz, $CDCl_3$)

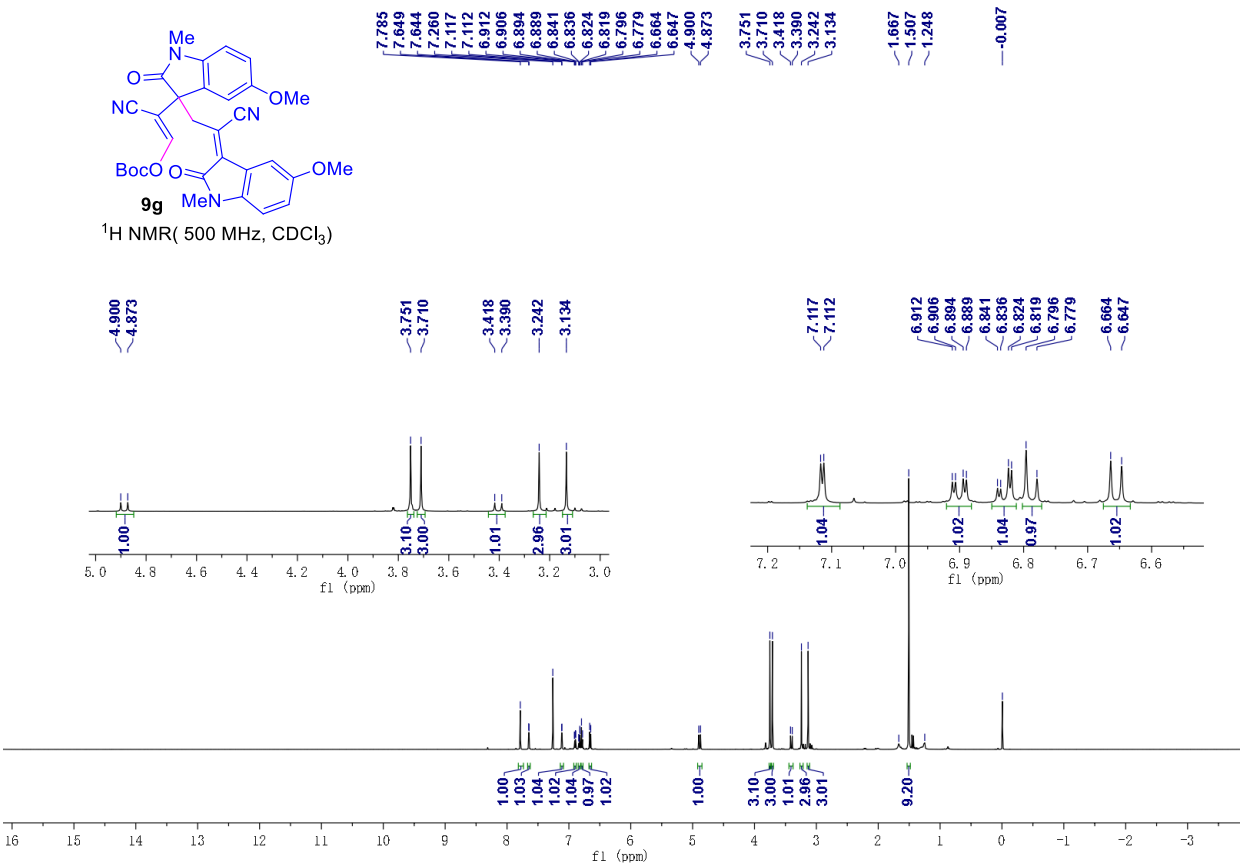


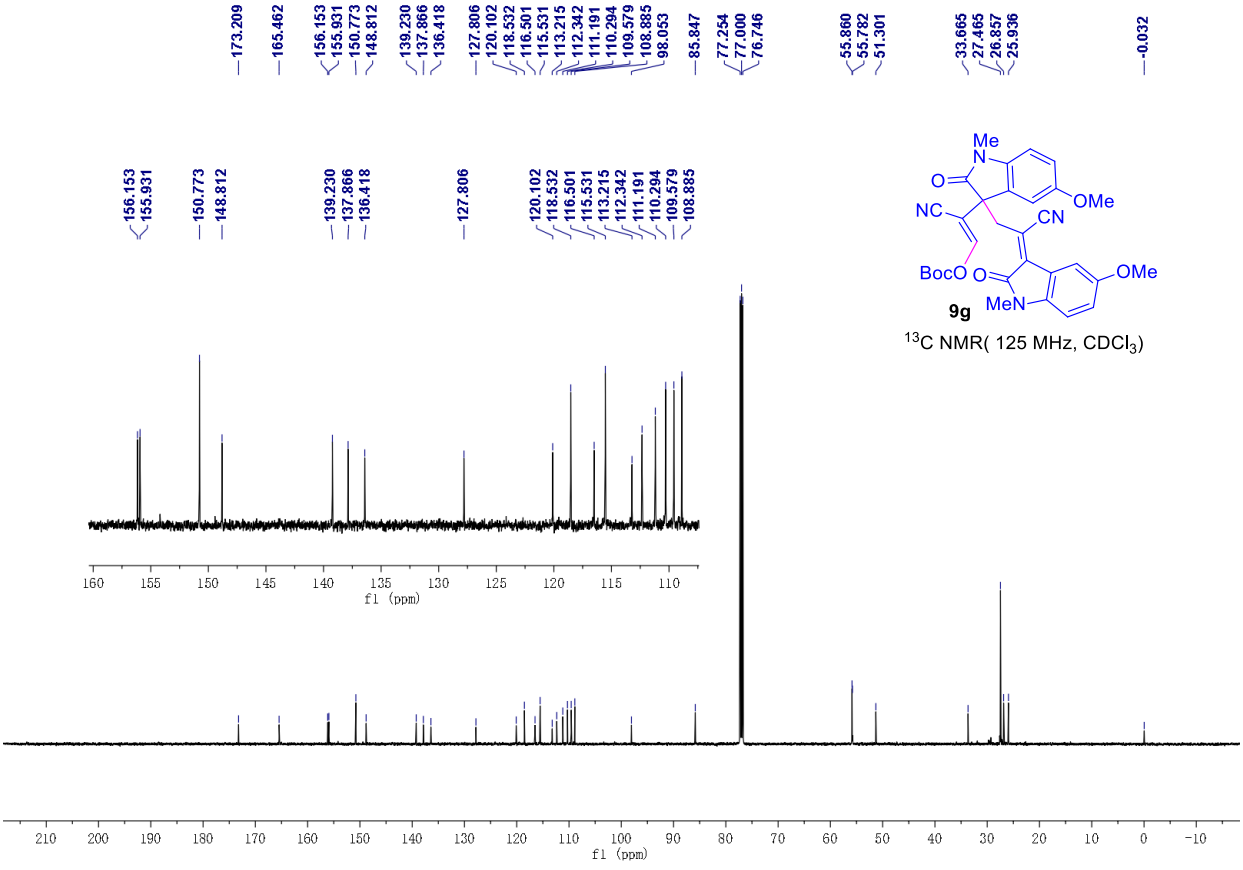
^{13}C NMR(125 MHz, $CDCl_3$)

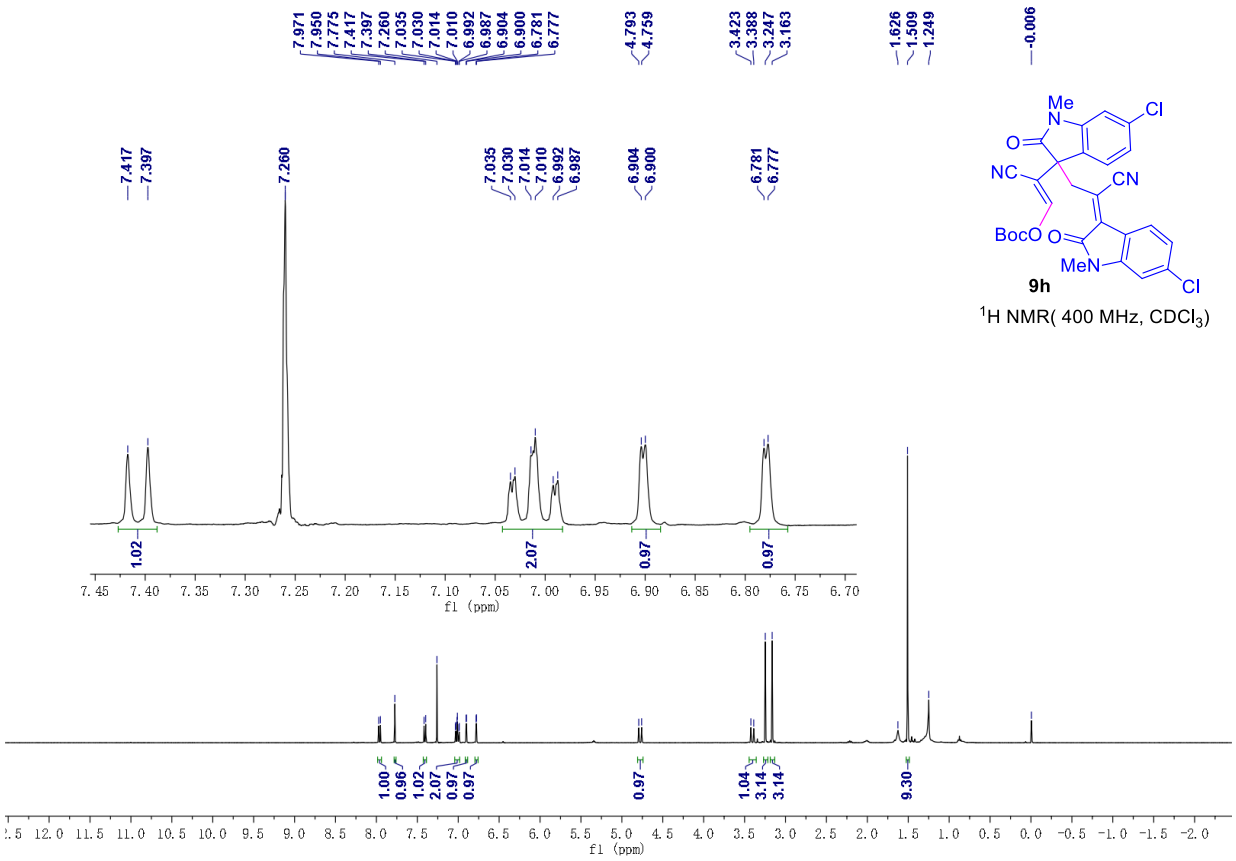

8.244
7.822
7.738
7.654
7.634
7.599
7.576
7.260
6.992
6.971
6.875
6.854
4.938
4.904
3.433
3.399
3.315
3.197
1.655
1.520
1.250
-0.006
Me
N
O
NC
CF3
CN
BocO
O
CF3
MeN
9e
1H NMR(400 MHz, CDCl3)
1.00
1.01
1.00
1.04
0.91
1.04
1.05
0.98
1.03
3.17
3.17
9.08
f1 (ppm)

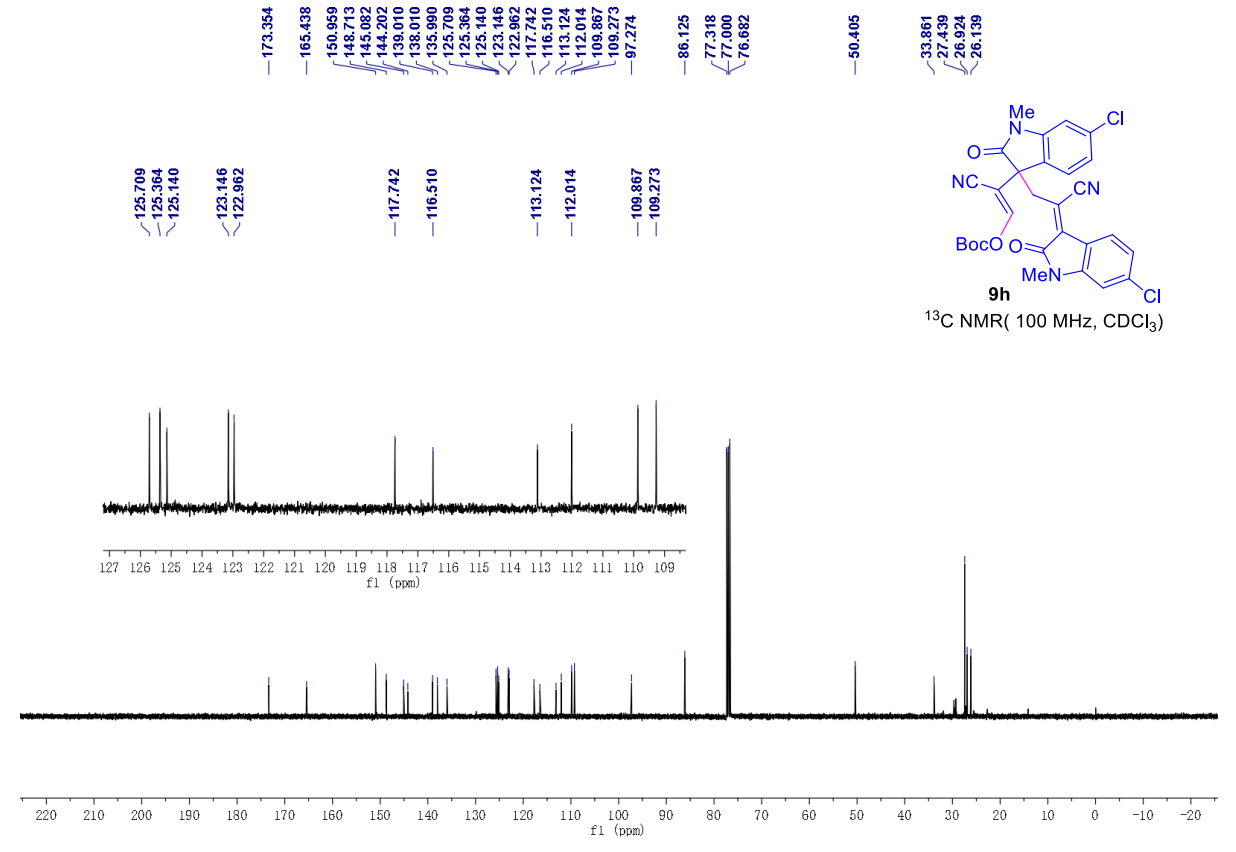

173.344
165.337
151.157
148.627
146.430
146.419
146.406
146.392
145.931
145.916
137.902
130.283
130.243
129.458
127.734
127.691
127.394
125.665
125.458
125.336
125.217
125.128
125.055
122.213
122.174
121.289
121.247
119.271
116.034
113.457
112.883
108.966
108.502
96.726
86.310
77.318
77.000
76.681
51.012
33.989
27.437
27.085
26.112
119.271
116.034
113.457
112.883
108.966
108.502
Me
N
O
NC
CF3
CN
BocO
O
CF3
MeN
9e
13C NMR(100 MHz, CDCl3)
f1 (ppm)

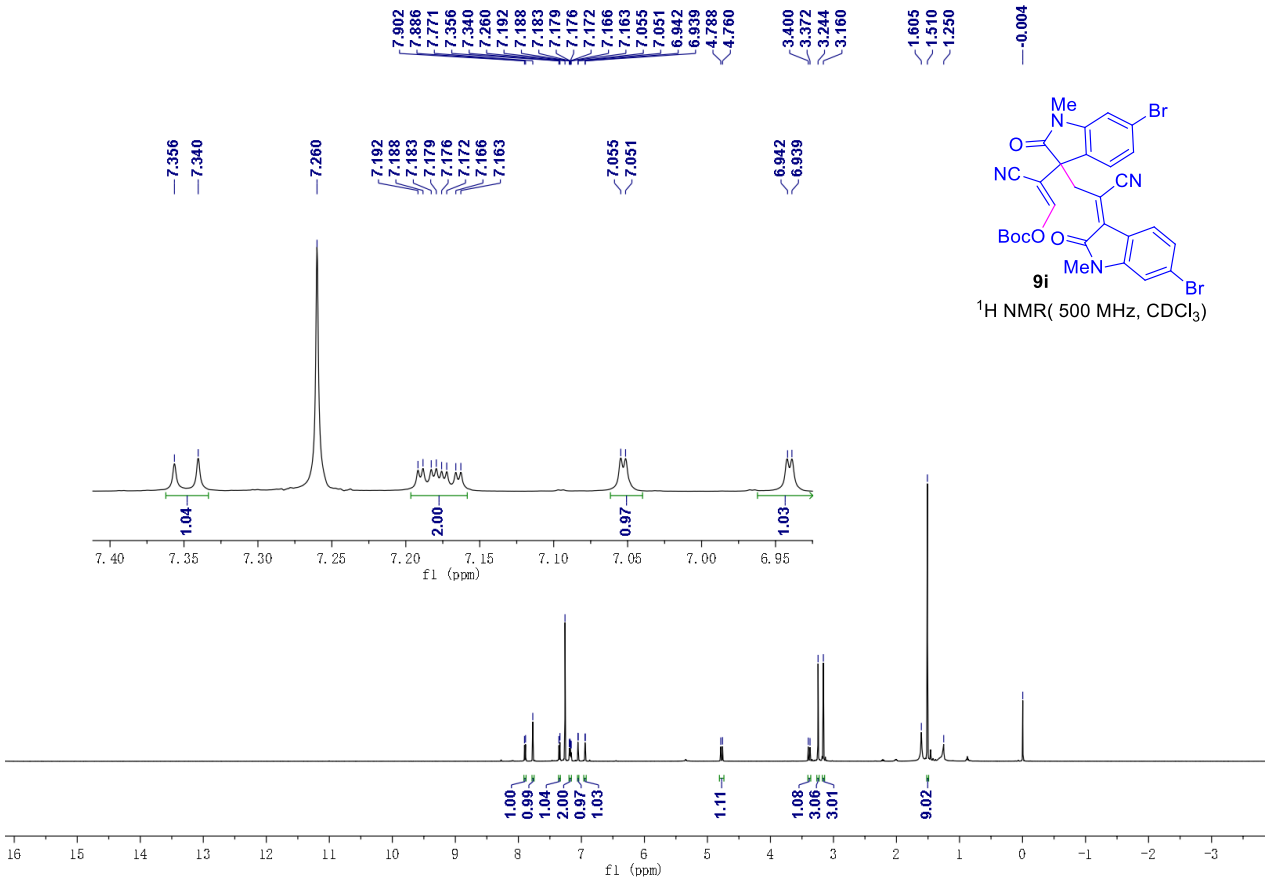

9f
^{1}H NMR(400 MHz, CDCl$_3$)
9f
^{13}C NMR(100 MHz, CDCl$_3$)

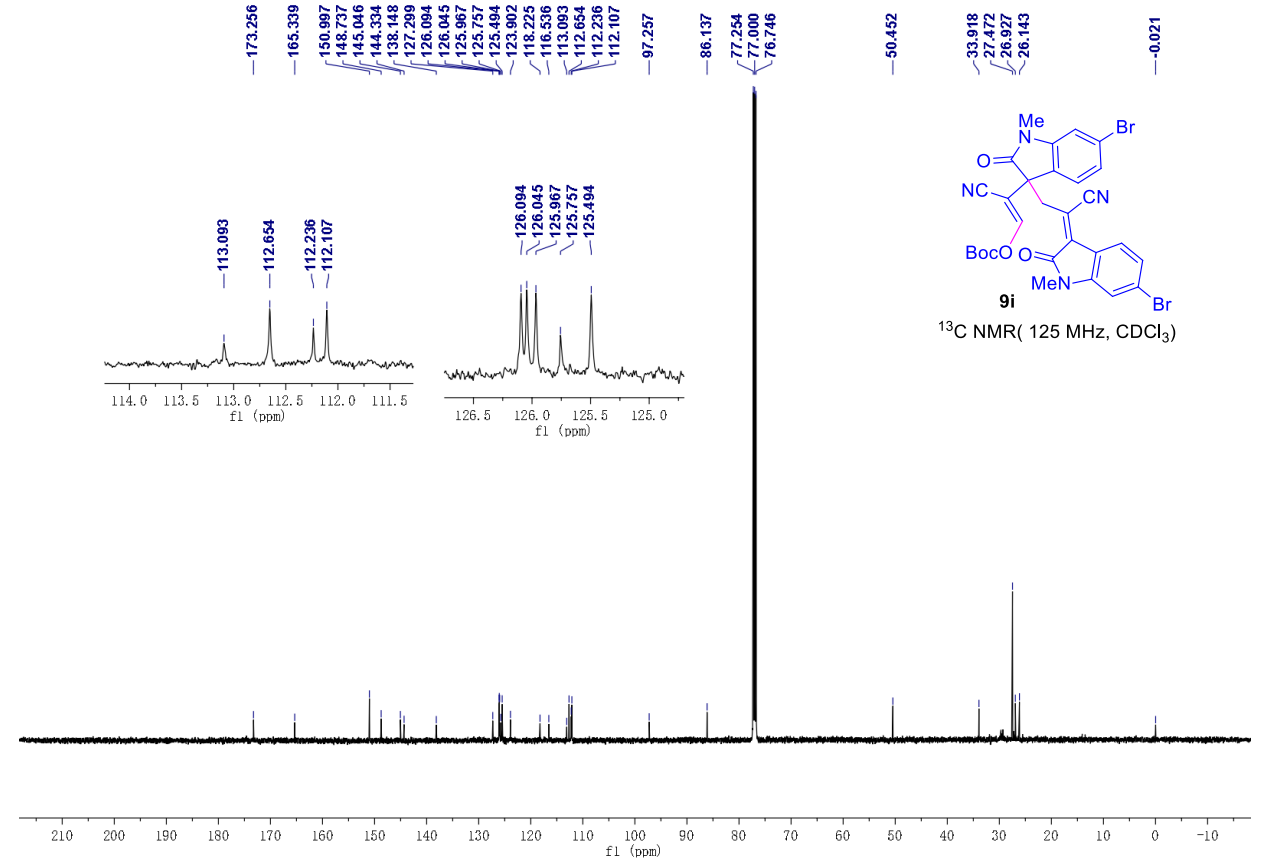

9g
1H NMR(500 MHz, CDCl3)
fl (ppm)

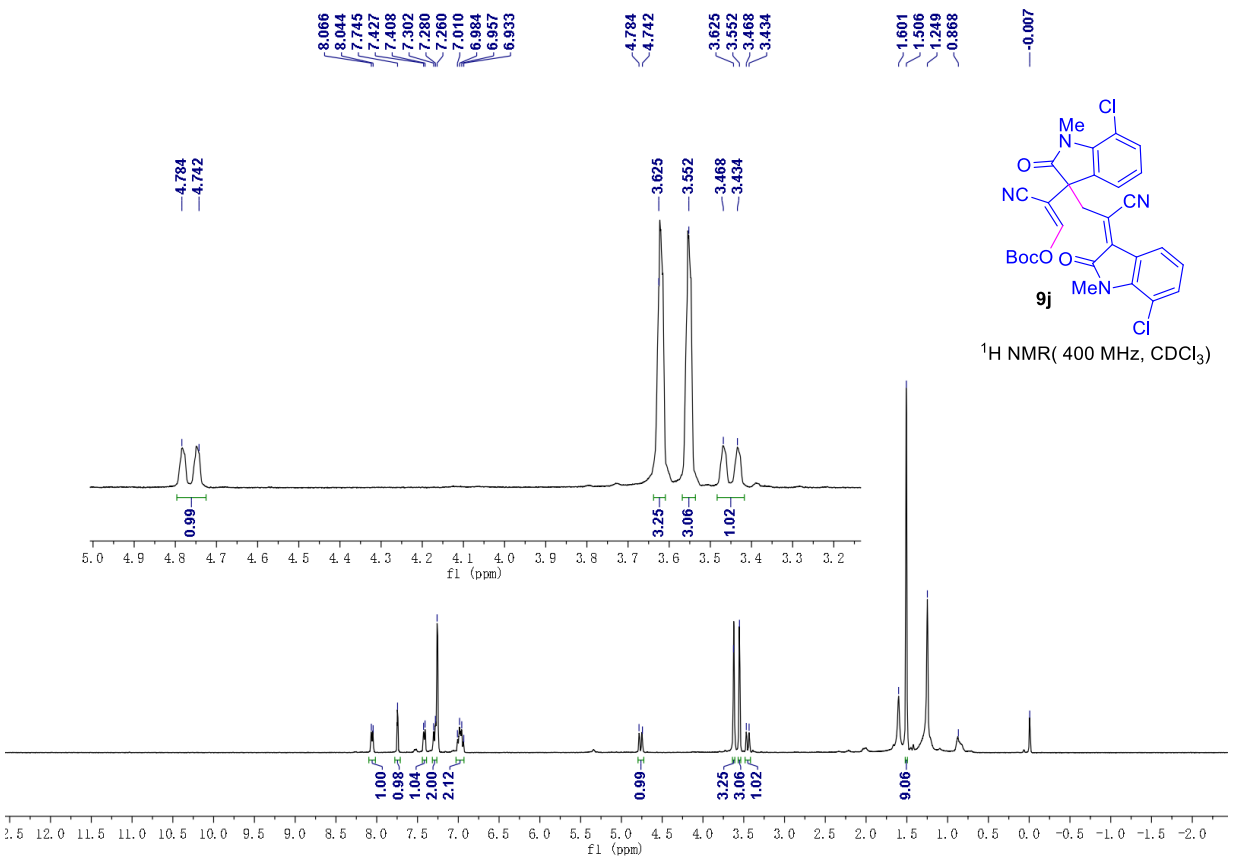

9g
13C NMR(125 MHz, CDCl3)
fl (ppm)

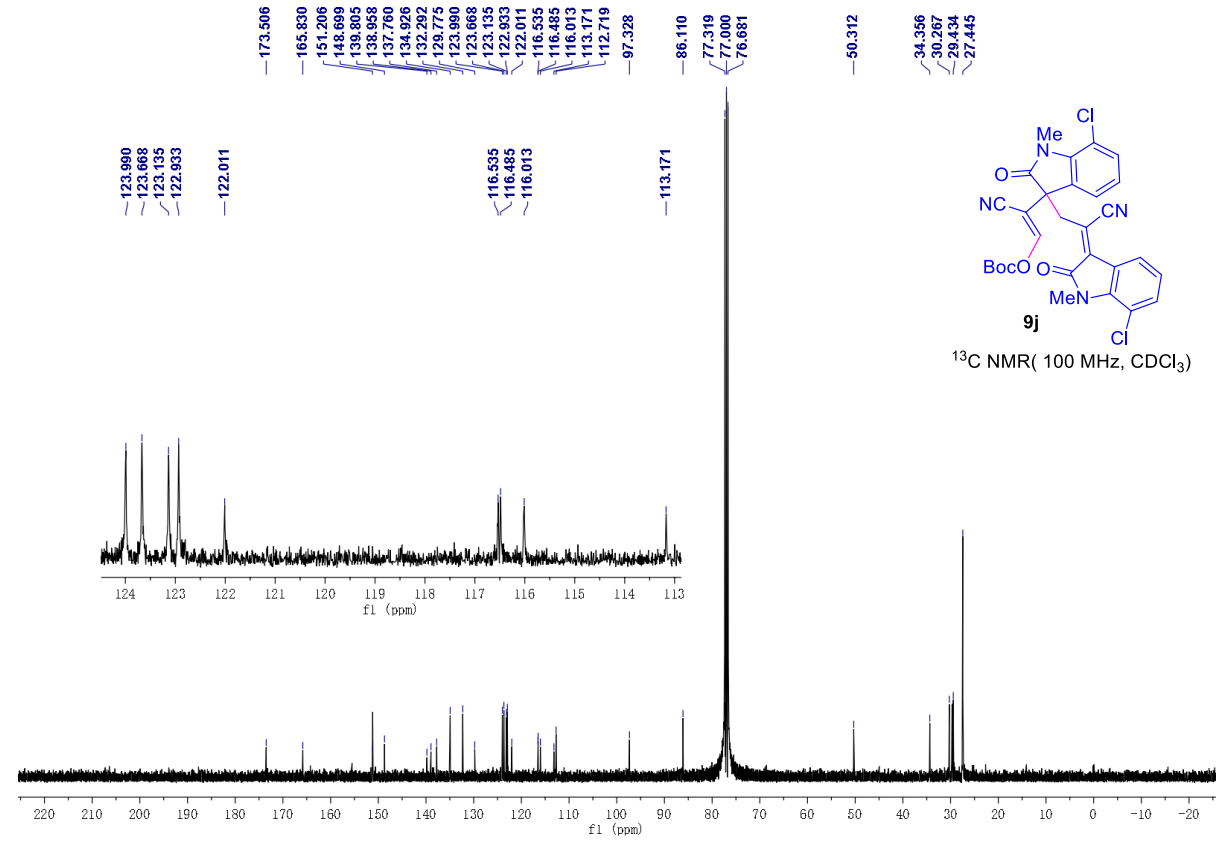

9h
^{1}H NMR(400 MHz, CDCl$_3$)

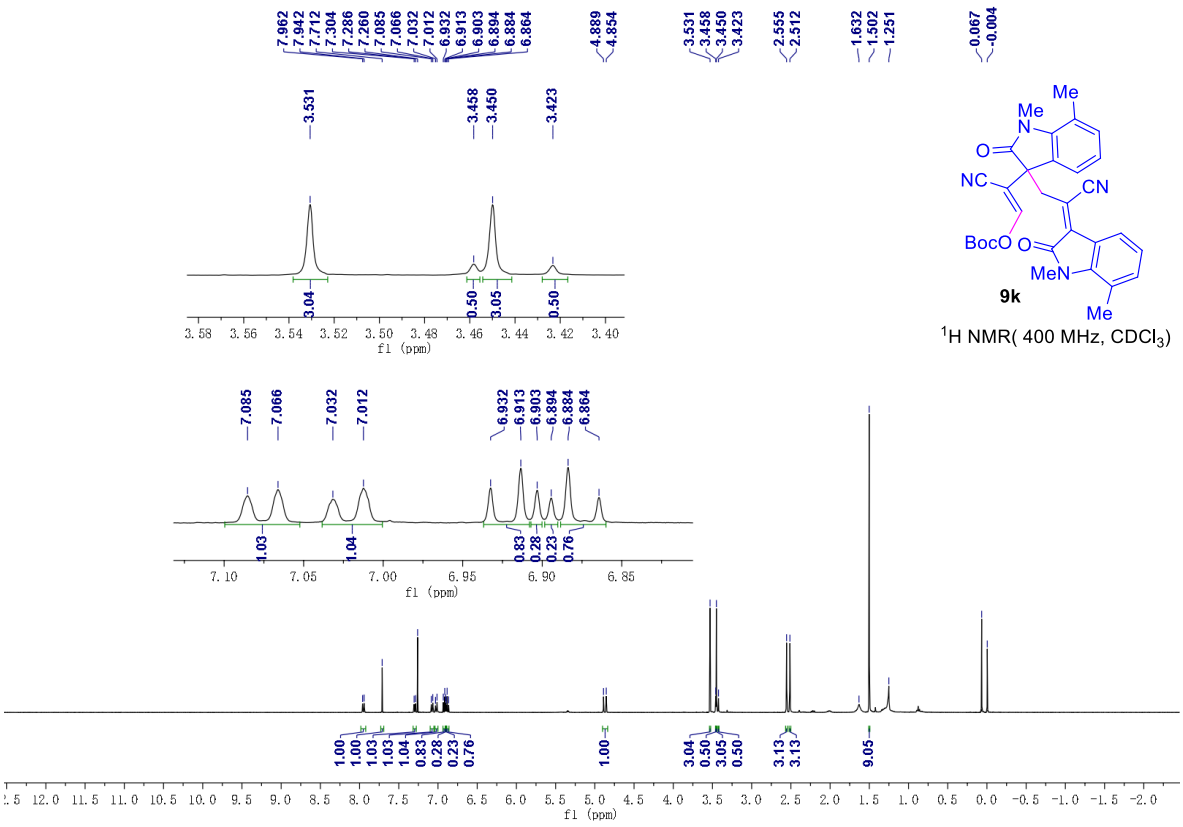

9h
^{13}C NMR(100 MHz, CDCl$_3$)

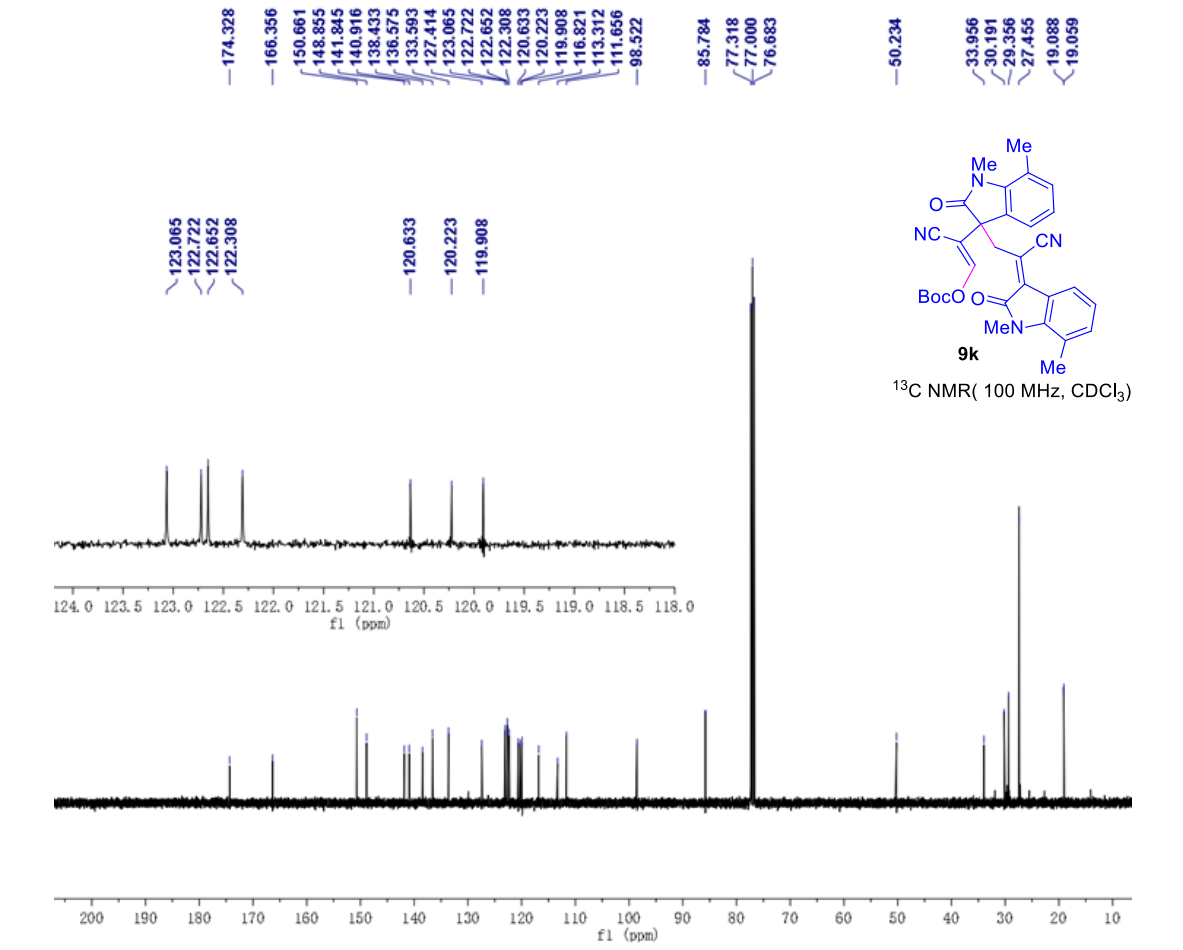

9i
^{1}H NMR(500 MHz, CDCl$_3$)
fl (ppm)

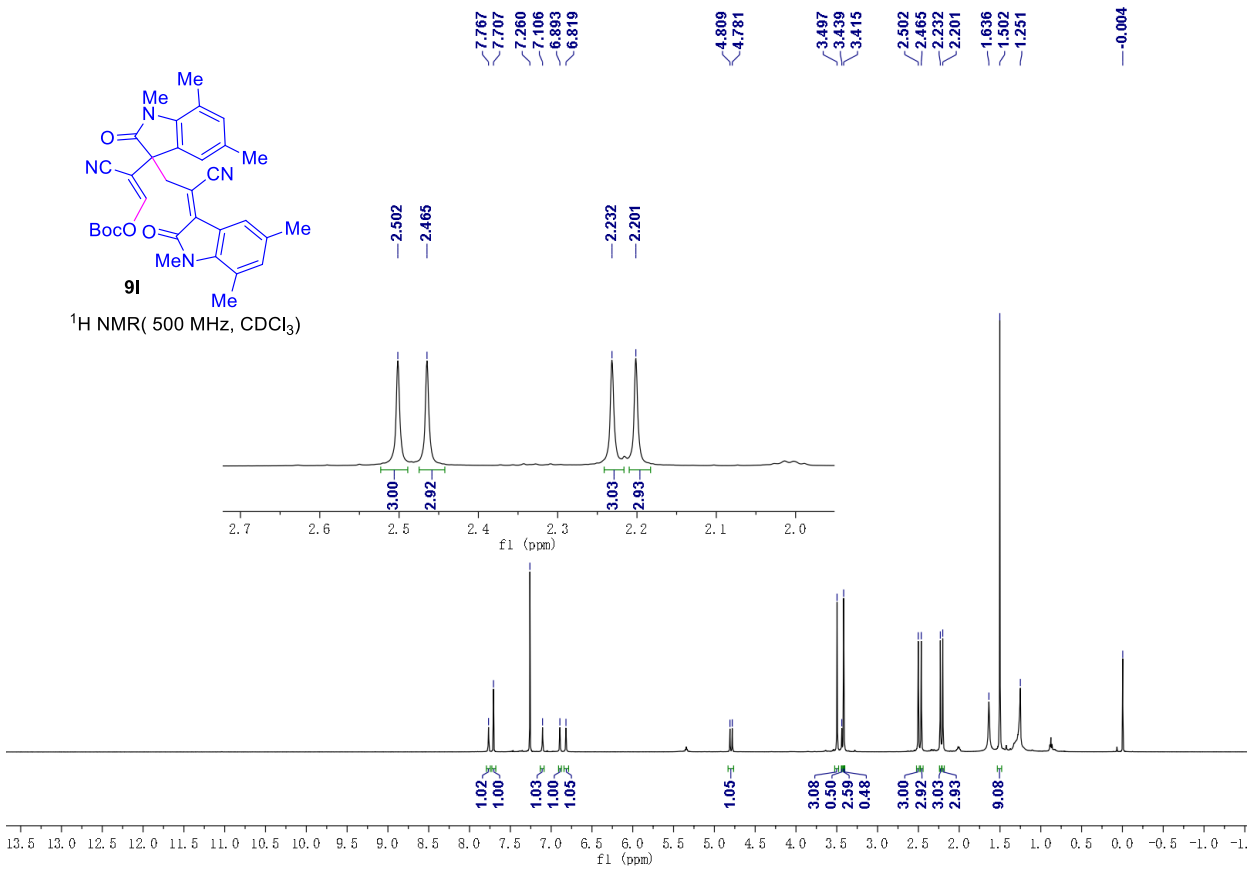

9i
^{13}C NMR(125 MHz, CDCl$_3$)
fl (ppm)

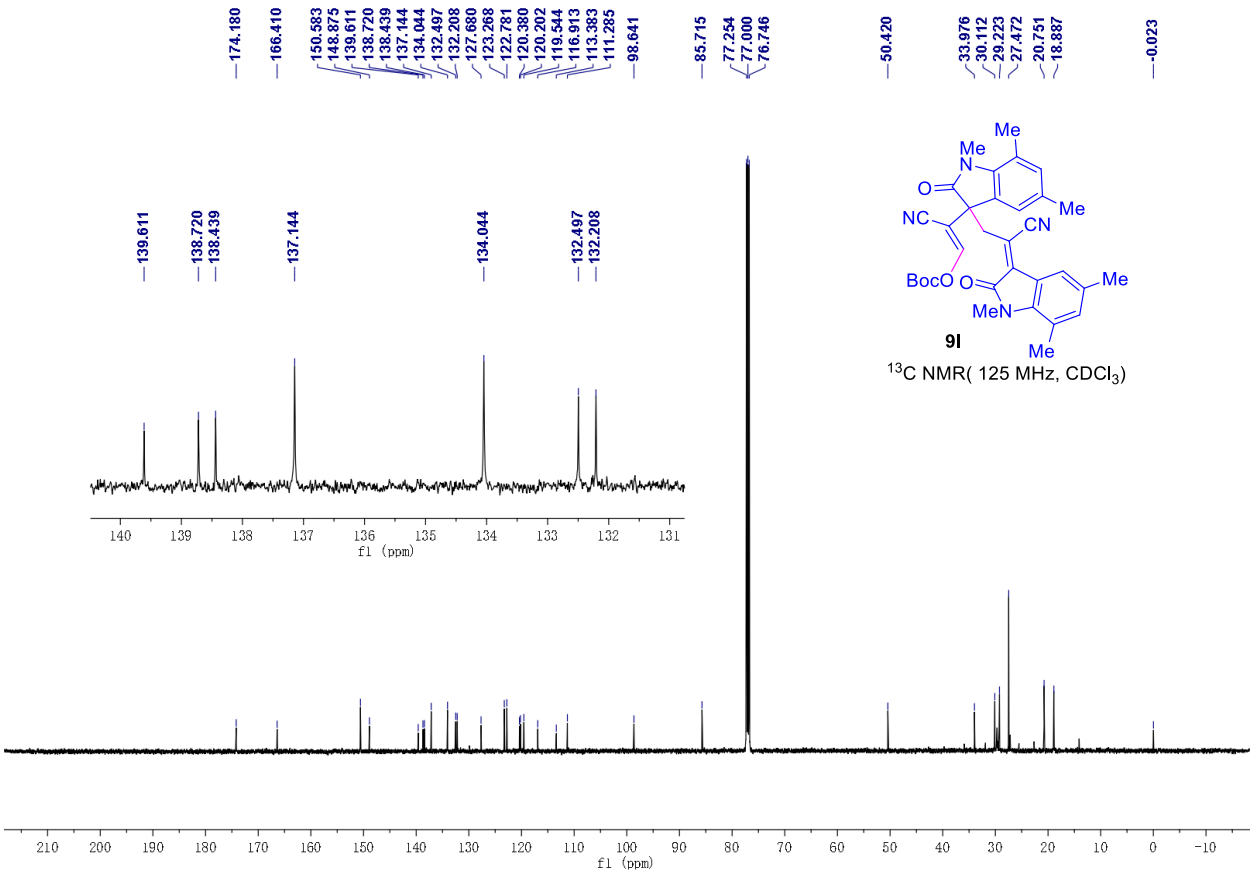

8.066
8.044
7.745
7.427
7.408
7.302
7.280
7.260
7.010
6.984
6.957
6.933
4.784
4.742
3.625
3.552
3.468
3.434
1.601
1.506
1.249
0.868
-0.007
Cl
Me
N
O
NC
CN
BocO
O
MeN
Cl
9j
1H NMR(400 MHz, CDCl3)
0.99
3.25
3.06
1.02
fl (ppm)
1.00
0.98
1.04
2.00
2.12
0.99
3.25
3.06
1.02
9.06

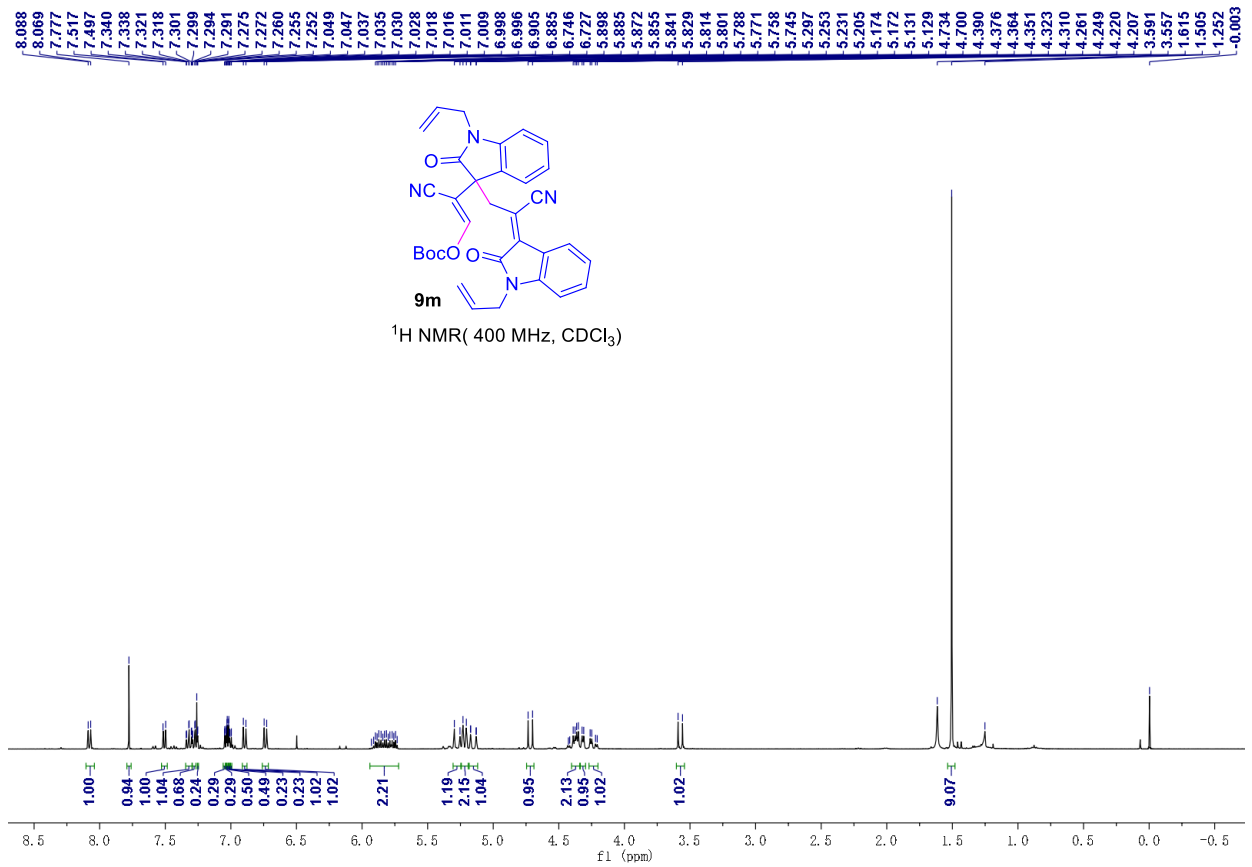

173.506
165.830
151.206
148.699
139.805
138.958
137.760
134.926
132.292
129.775
123.990
123.668
123.135
122.933
122.011
116.535
116.485
116.013
113.171
112.719
97.328
86.110
77.319
77.000
76.681
50.312
34.356
30.267
29.434
27.445
Cl
Me
N
O
NC
CN
BocO
O
MeN
Cl
9j
13C NMR(100 MHz, CDCl3)
fl (ppm)

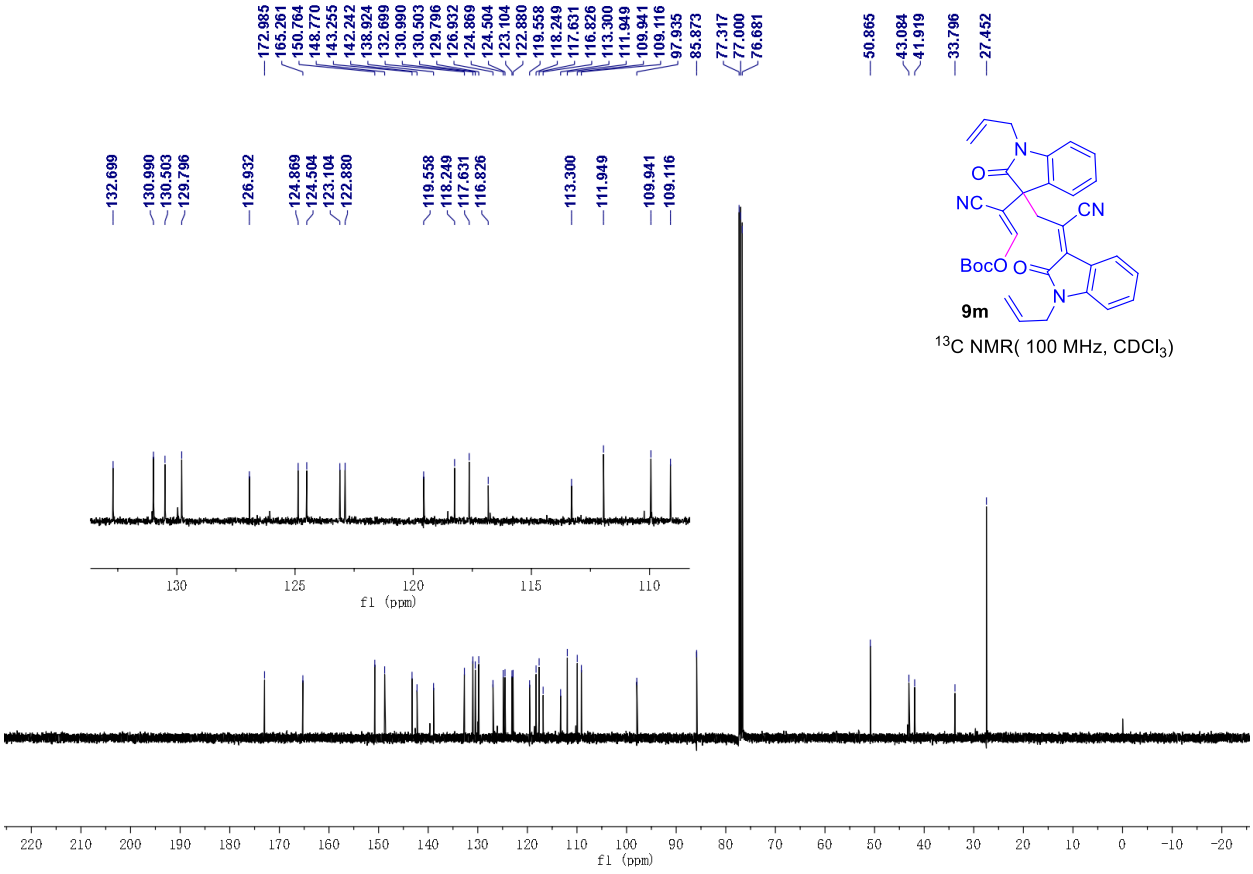

9k
^{1}H NMR(400 MHz, CDCl$_3$)

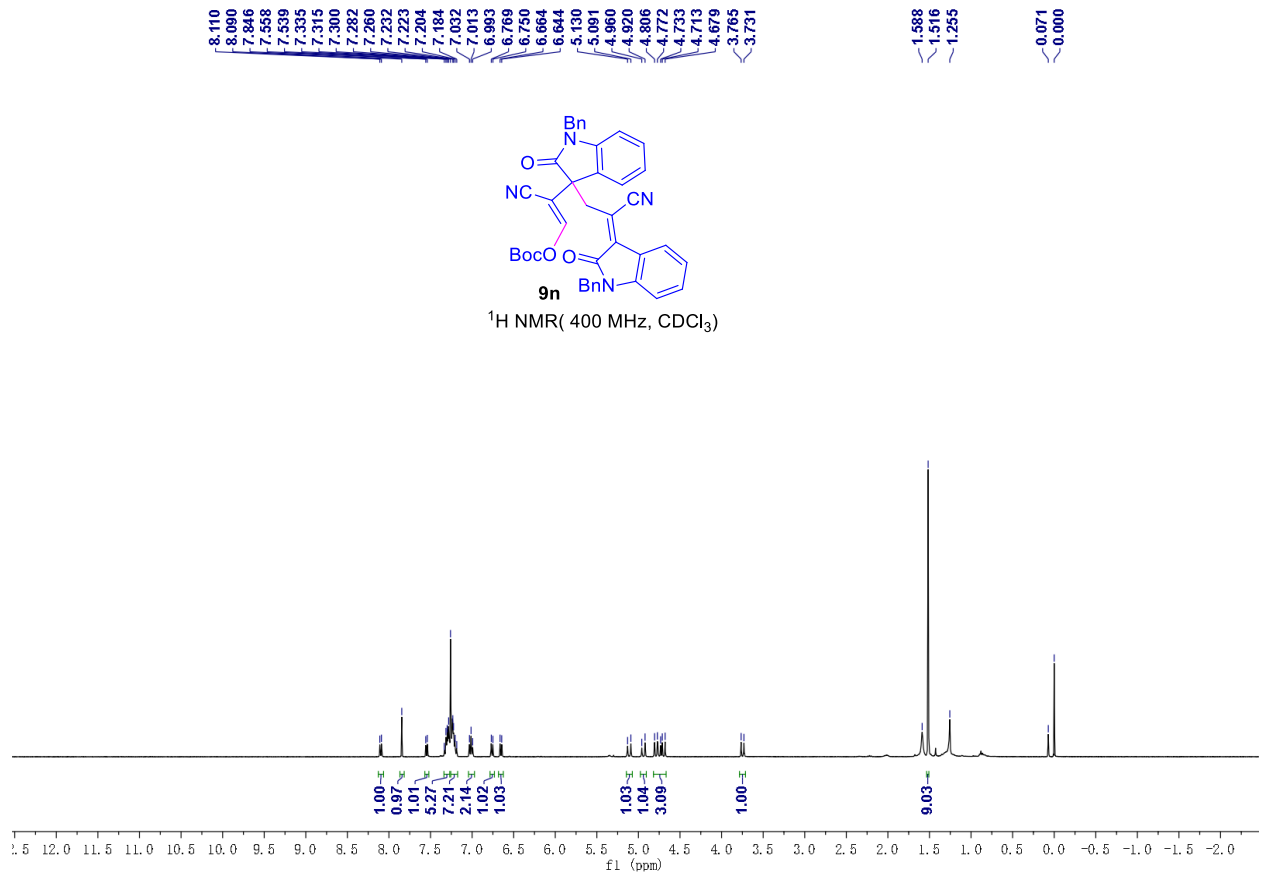

9k
^{13}C NMR(100 MHz, CDCl$_3$)

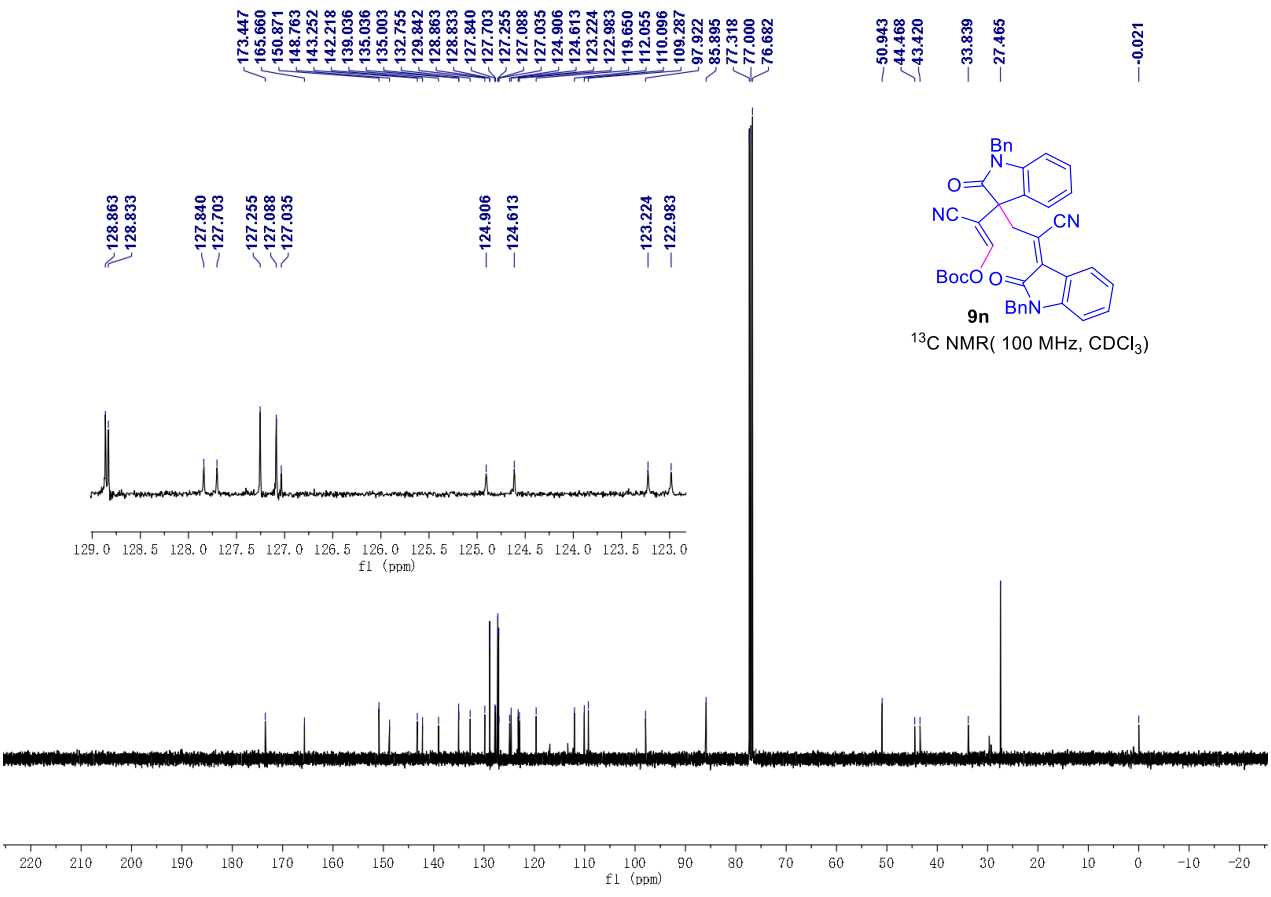

9l
^{1}H NMR(500 MHz, $CDCl_3$)
fl (ppm)

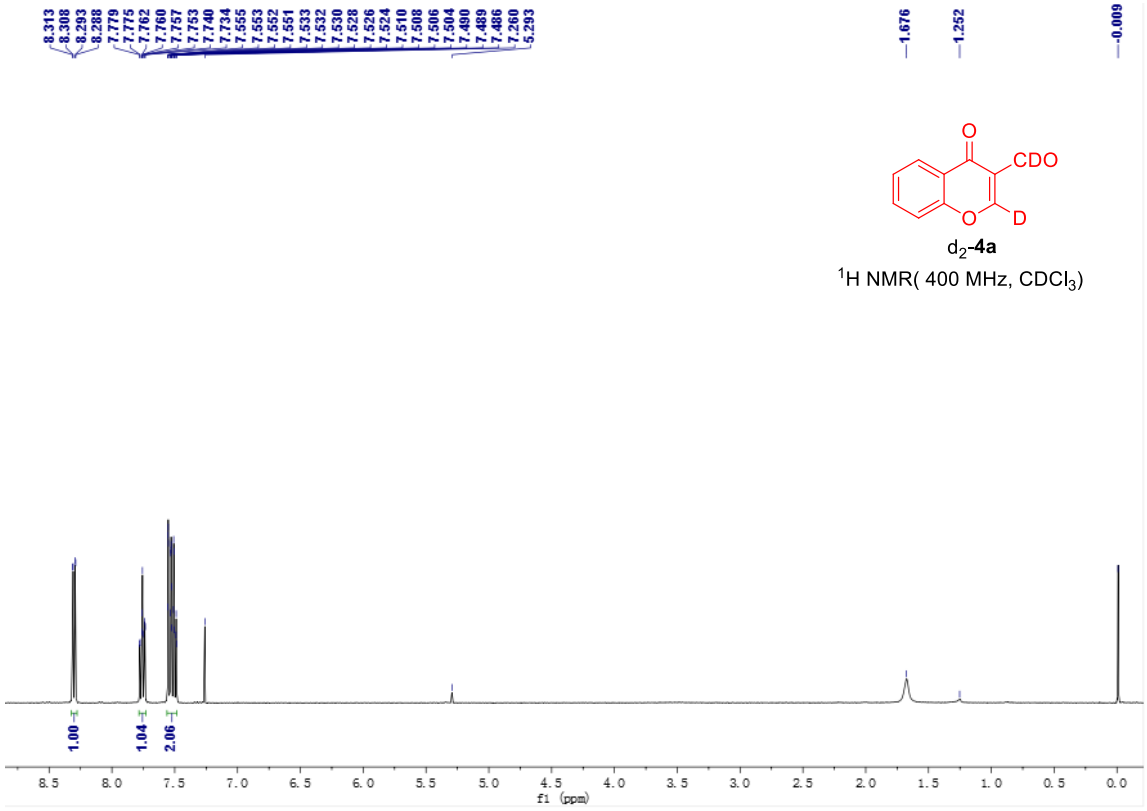

9l
^{13}C NMR(125 MHz, $CDCl_3$)
fl (ppm)


9m
^{1}H NMR(400 MHz, CDCl$_3$)
fl (ppm)


9m
^{13}C NMR(100 MHz, CDCl$_3$)
fl (ppm)

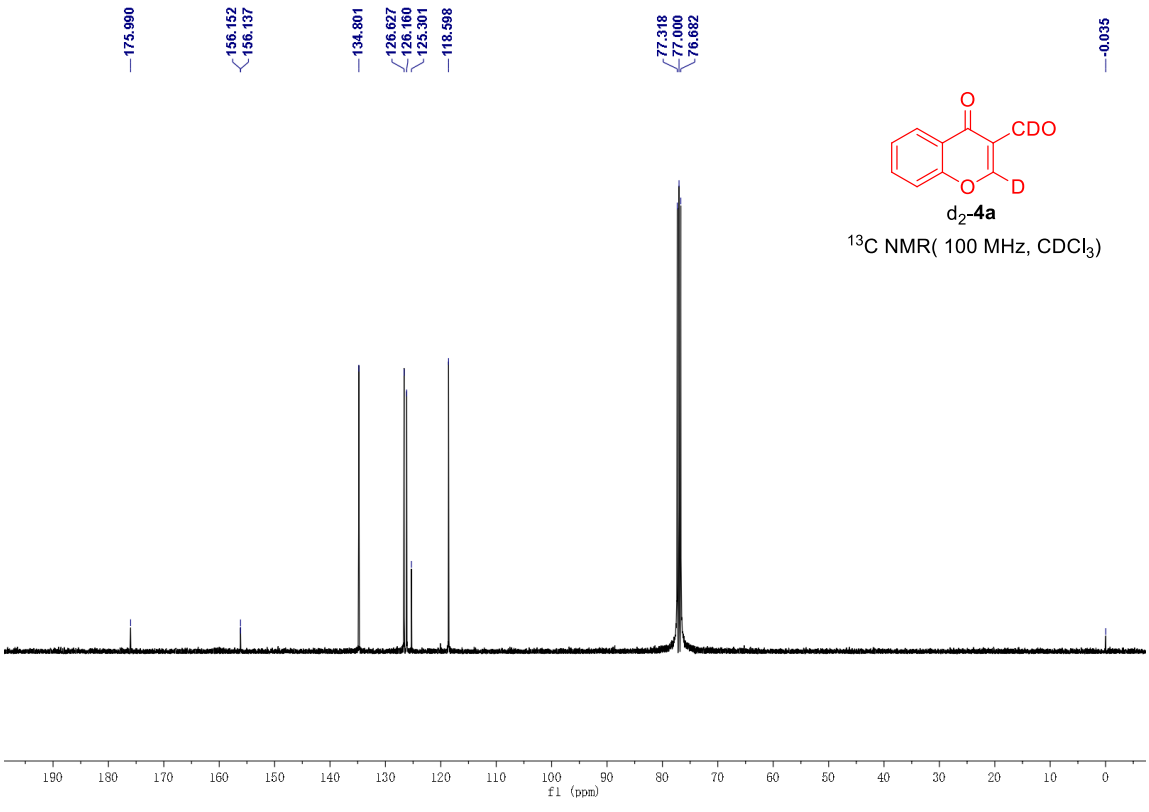

8.110
8.090
7.846
7.558
7.539
7.335
7.315
7.300
7.282
7.260
7.232
7.223
7.204
7.184
7.032
7.013
6.993
6.769
6.750
6.664
6.644
5.130
5.091
4.960
4.920
4.806
4.772
4.733
4.713
4.679
3.765
3.731
1.588
1.516
1.255
0.071
0.000
Bn
N
O
NC
CN
BocO
O
BnN
9n
1H NMR(400 MHz, CDCl3)
1.00
0.97
1.01
5.27
7.21
2.14
1.02
1.03
1.03
1.04
3.09
1.00
9.03
f1 (ppm)


173.447
165.660
150.871
148.763
143.252
142.218
139.036
135.036
135.003
132.755
129.842
128.863
128.833
127.840
127.703
127.255
127.088
127.035
124.906
124.613
123.224
122.983
119.650
112.055
110.096
109.287
97.922
85.895
77.318
77.000
76.682
50.943
44.468
43.420
33.839
27.465
-0.021
128.863
128.833
127.840
127.703
127.255
127.088
127.035
124.906
124.613
123.224
122.983
Bn
N
O
NC
CN
BocO
O
BnN
9n
13C NMR(100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)



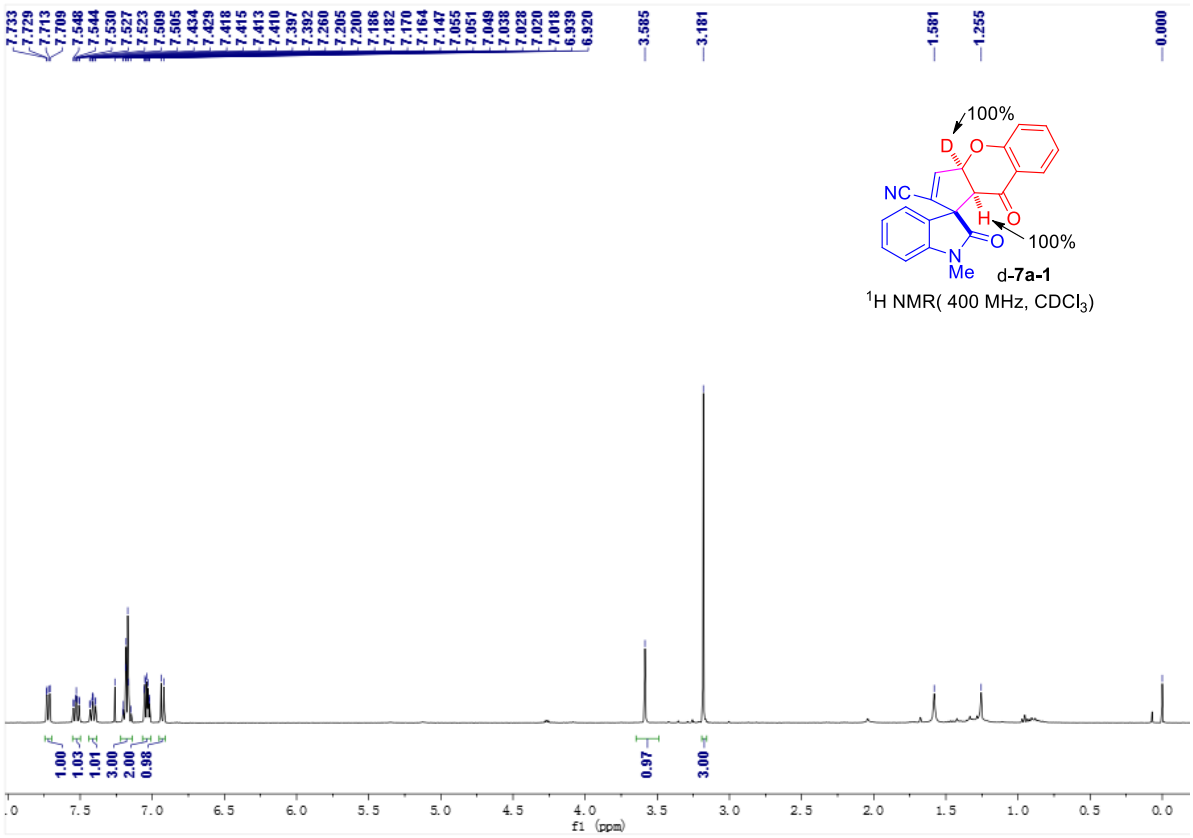
d_2-**4a**

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

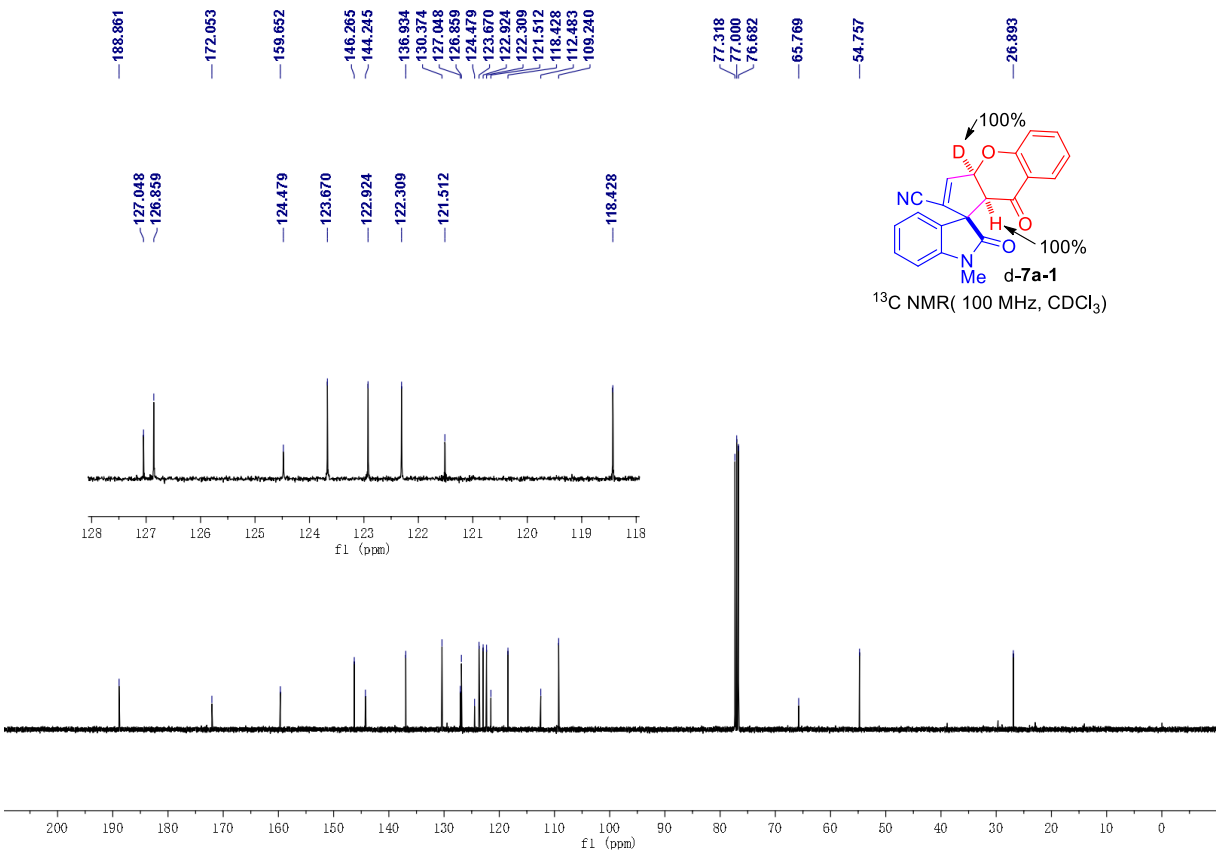


d_2-**4a**

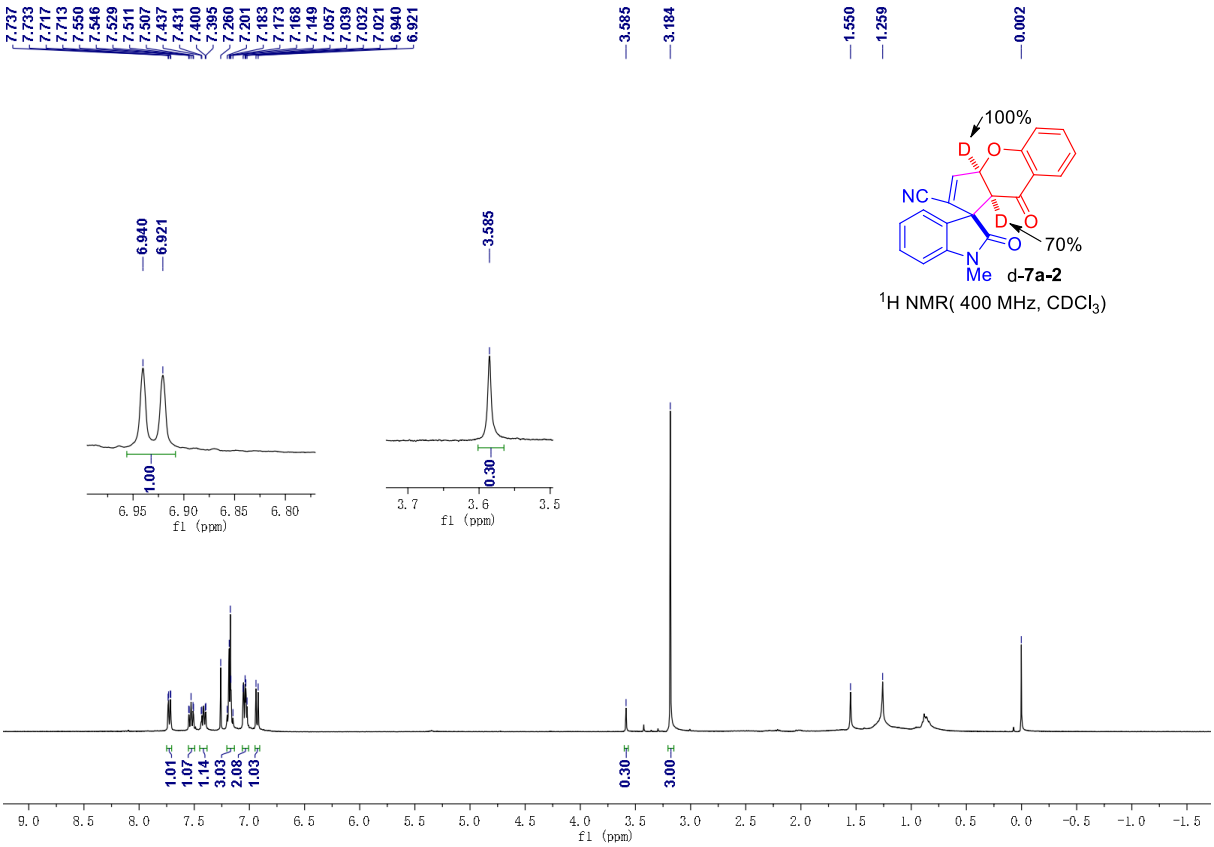
^{13}C NMR(100 MHz, $CDCl_3$)

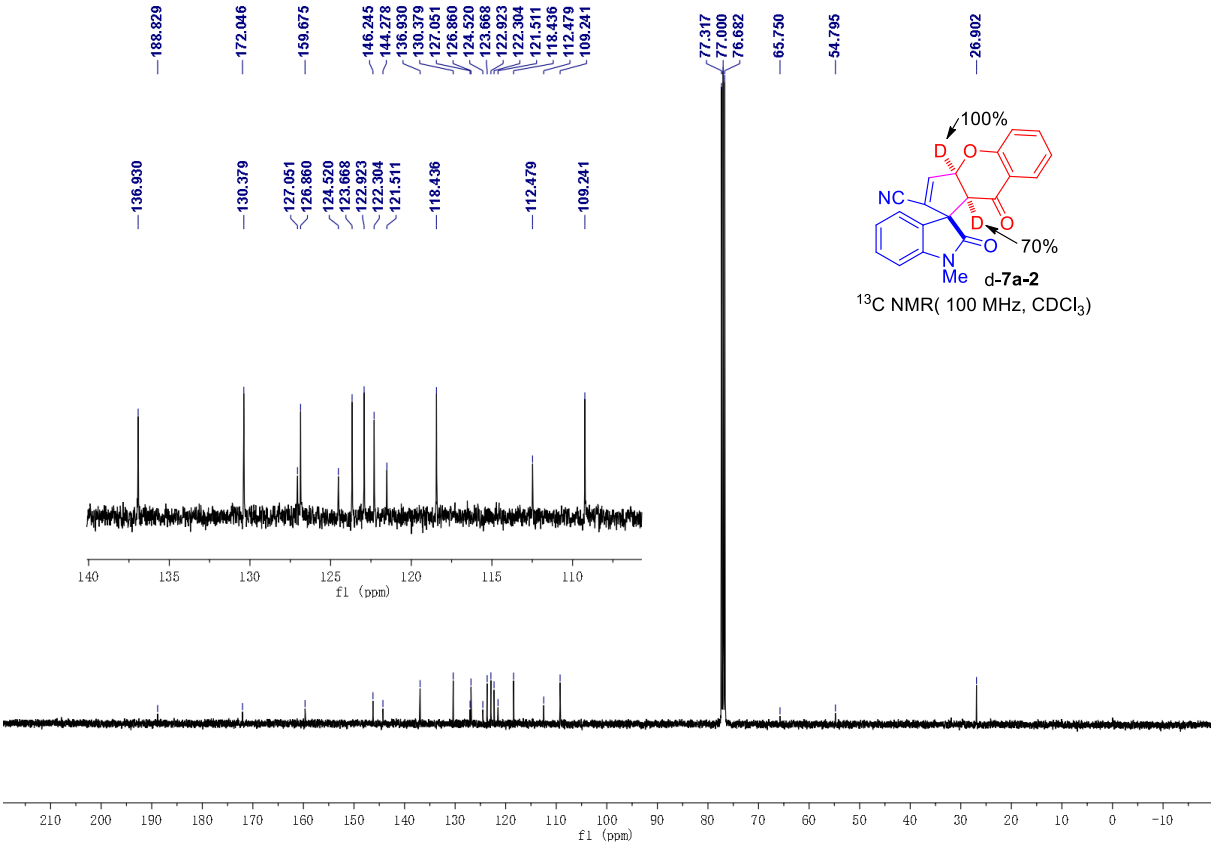


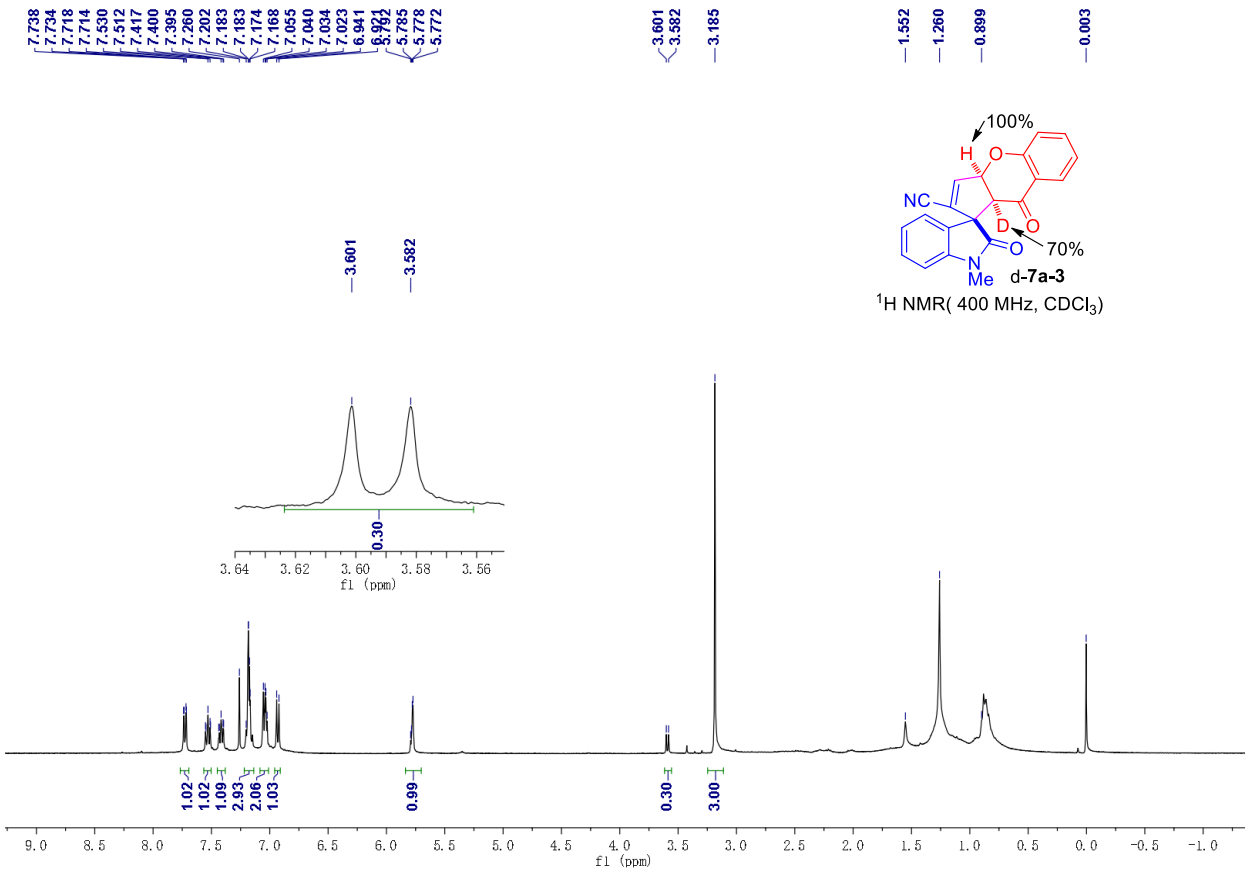
^{1}H NMR(400 MHz, $CDCl_3$)

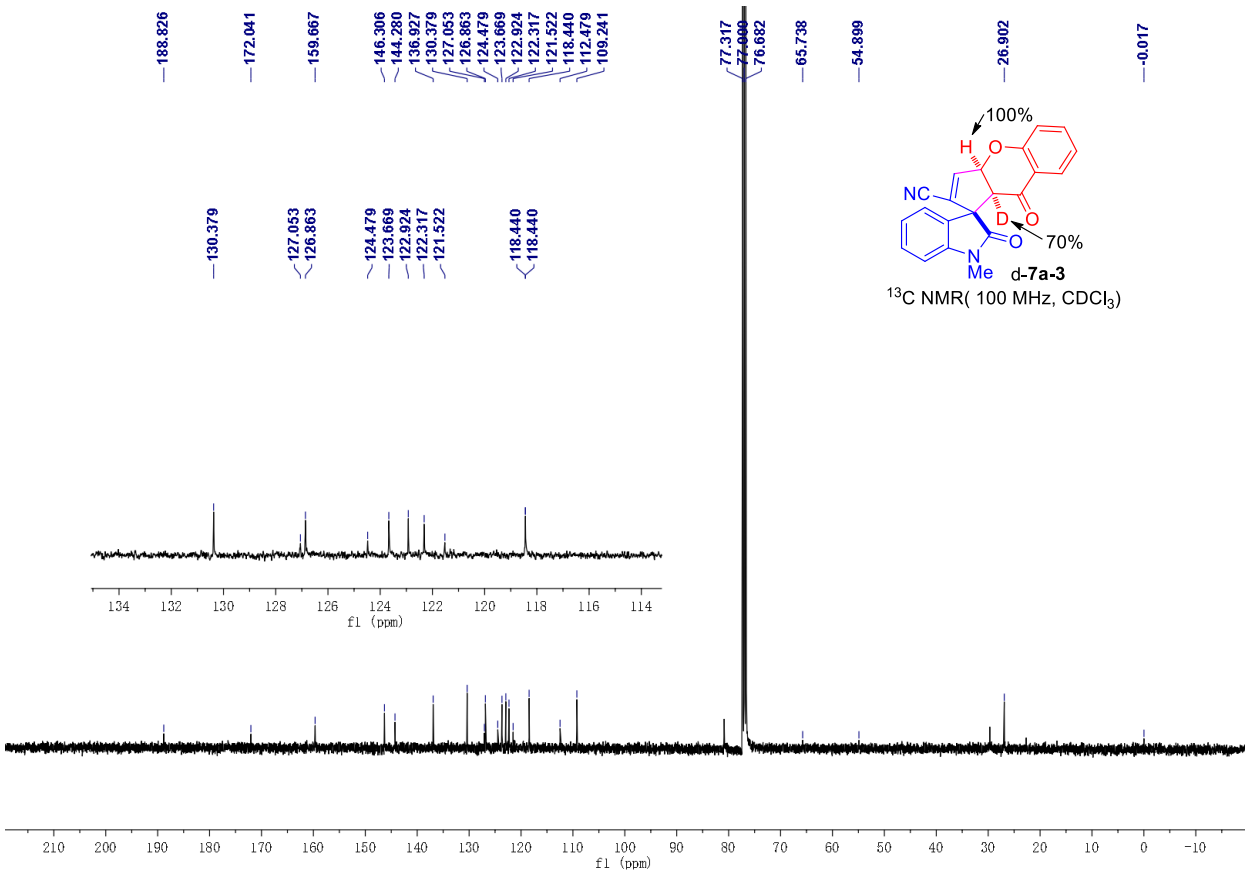


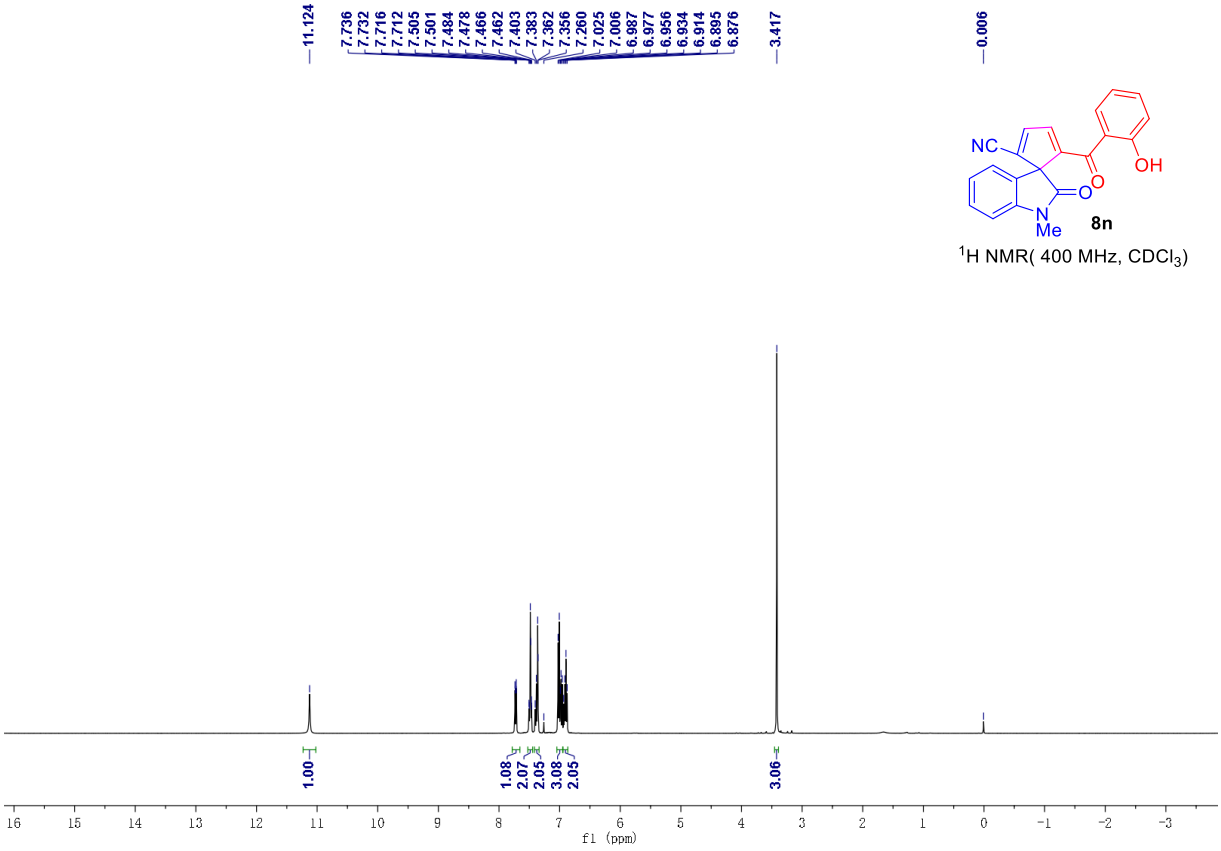
^{13}C NMR(100 MHz, $CDCl_3$)


7.737
7.733
7.717
7.713
7.550
7.546
7.529
7.511
7.507
7.437
7.431
7.400
7.395
7.260
7.201
7.183
7.173
7.168
7.149
7.057
7.039
7.032
7.021
6.940
6.921
3.585
3.184
1.550
1.259
0.002
100%
D
O
NC
D
O
O
70%
N
Me
d-7a-2
1H NMR(400 MHz, CDCl3)
6.940
6.921
3.585
1.00
0.30
6.95
6.90
6.85
6.80
3.7
3.6
3.5
f1 (ppm)
1.01
1.07
1.14
3.03
2.08
1.03
0.30
3.00
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
-1.0
-1.5
f1 (ppm)

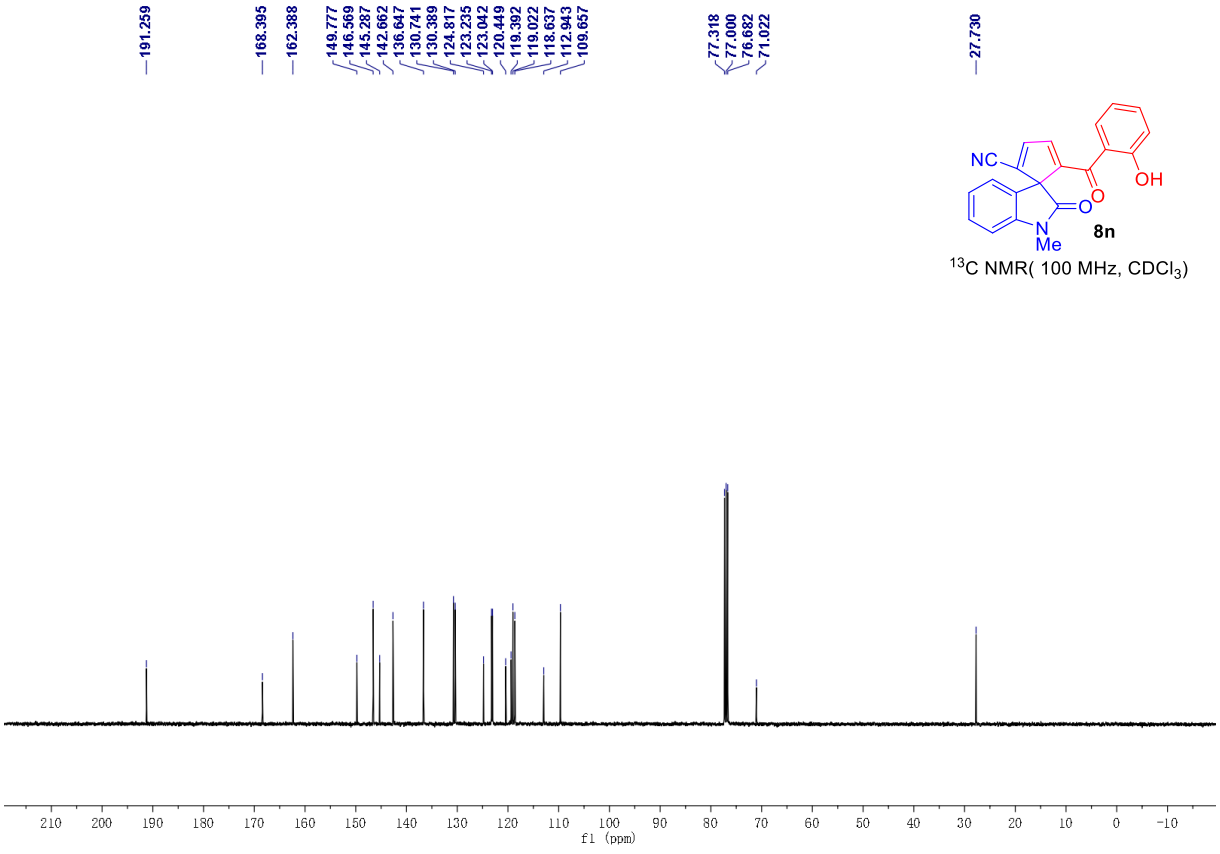

188.829
172.046
159.675
146.245
144.278
136.930
130.379
127.051
126.860
124.520
123.668
122.923
122.304
121.511
118.436
112.479
109.241
77.317
77.000
76.682
65.750
54.795
26.902
136.930
130.379
127.051
126.860
124.520
123.668
122.923
122.304
121.511
118.436
112.479
109.241
100%
D
O
NC
D
O
O
70%
N
Me
d-7a-2
13C NMR(100 MHz, CDCl3)
140
135
130
125
120
115
110
f1 (ppm)
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)


7.738
7.734
7.718
7.714
7.530
7.512
7.417
7.400
7.395
7.260
7.202
7.183
7.174
7.168
7.055
7.040
7.034
7.023
6.941
6.921
5.785
5.778
5.772
3.601
3.582
3.185
1.552
1.260
0.899
0.003
100%
70%
d-7a-3
1H NMR(400 MHz, CDCl3)
1.02
1.02
1.09
2.93
2.06
1.03
0.99
0.30
3.00
f1 (ppm)


188.826
172.041
159.667
146.306
144.280
136.927
130.379
127.053
126.863
124.479
123.669
122.924
122.317
121.522
118.440
112.479
109.241
77.317
77.000
76.682
65.738
54.899
26.902
-0.017
100%
70%
d-7a-3
13C NMR(100 MHz, CDCl3)
f1 (ppm)



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



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