

Palladium-Catalyzed Intramolecular Diastereoselective Dearomatization Reaction of Indoles with *N*-Tosylhydrazones

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Supporting Information

Table of Contents

1. General methods and materials	2
2. General Procedures	2
2.1 Synthesis of substrates 1	2
2.2 Synthesis of substrates 4	2
3. Efficient Construction of Fused Indolines 3a-9 via an Intramolecular Heck Cyclization.	3
3.1 Procedure for the dearomative arylvinylation of indoles with <i>N</i> -arylsulfonylhydrazones	3
3.2 Characterization data of 3a-9	3
4. NMR Charts	18
5. X-ray Single Crystal Diffraction Data of 3j and 9	59

1. General methods and materials

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-P 400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) in CDCl_3 (with TMS as internal standard). Chemical shifts (δ) were measured in ppm. Coupling constants, J , are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer and Bruker O-TOF Compact Mass Spectrometry. Melting points (uncorrected) were obtained on Shanghai Inesa WRS-3 melting point apparatus. The starting materials were purchased from Innochem or Energy Chemicals and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". The crude products were purified by flash column chromatography on silica gel and the reported yields are the actual isolated yields of pure products. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm).

2. General Procedures

2.1 Synthesis of substrates 1

To a solution of indole derivative (1.0 equiv, 0.5 M) in THF was added 60% dispersion of NaH (1.2 equiv) in portions at 0 °C. After stirring at 0 °C for 30 min, a solution of acid chloride in THF was added dropwise to the reaction system. The mixture was then allowed to stir at room temperature. When the reaction was completed, the reaction mixture was quenched by aqueous NH_4Cl and extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography using the indicated fluent to give the substrates.

2.2 Synthesis of substrates 4

A 60% dispersion of NaH in mineral oil (1.2 equiv) was added to a stirred solution of the appropriate indole derivative (1 equiv, ~0.5 M) in THF at 0 °C and the corresponding solution was stirred for 5 minutes before warming to room temperature where it was stirred for 30 minutes. The solution of the sodium indolate was re-cooled to 0 °C at which time a solution of appropriate 2-bromobenzoyl chloride derivative (2 equiv or 2.2 equiv, ~1 M) in THF was added dropwise. Once the addition was complete, the reaction was allowed to warm to room temperature and then was stirred at 65 °C for 30 minutes. At this time the extent of completion of the reaction was determined by conversion of the indole derivative by TLC analysis. The reaction was cooled to room temperature and quenched with a saturated solution of NH_4Cl . The reaction mixture was then diluted with water and EtOAc, and after separating the layers, the aqueous layer was extracted with EtOAc (3x). The combined organic layers were washed sequentially with water and brine, dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude *N*-(2-bromobenzoyl) indole derivative was purified by flash column gel chromatography using the indicated solvent system.

3. Efficient Construction of Fused Indolines 3a-9 via an Intramolecular Heck Cyclization.

3.1 Procedure for the dearomative arylvinylation of indoles with *N*-arylsulfonylhydrazones

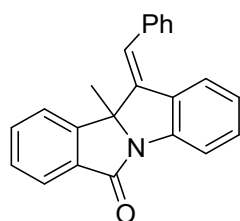
3.1.1 Synthesis of products 3

An oven-dried Schlenk tube charged with *N*-(2-Iodobenzoyl)indole derivative **1** (0.2 mmol), *N*-tosylhydrazone **2a** (2.0 equiv), Pd(CF₃COO)₂ (10 mol%), PPh₃ (3.0 equiv), KHCO₃ (2.0 equiv), H₂O (8.0 equiv) in PhCH₃ (4.0 mL) was conducted at 100 °C under Ar atmosphere for 12.0 h. The reaction was monitored by TLC. After reaction, the reaction mixture was cooled down to room temperature and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel to afford the corresponding products.

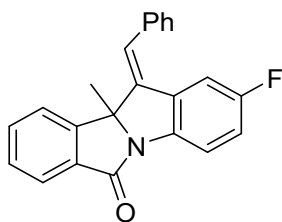
3.1.2 Synthesis of products 5 and 6

An oven-dried Schlenk tube charged with *N*-(2-bromobenzoyl)indole derivative **4** (0.2 mmol), *N*-tosylhydrazone **2** (2.0 equiv), Pd(CF₃COO)₂ (10 mol%), PPh₃ (3.0 equiv), KHCO₃ (2.0 equiv), H₂O (16.0 equiv) in 1,4-dioxane (4.0 mL) was conducted at 100 °C under Ar atmosphere for 12.0 h. The reaction was monitored by TLC. After reaction, the reaction mixture was cooled down to room temperature and evaporated under reduced pressure. The residue was further purified by chromatography on silica gel to afford the corresponding products.

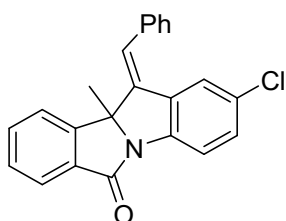
3.2 Characterization data of 3a-9



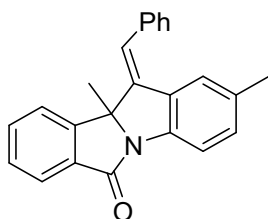
(3a)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow liquid; 47.2 mg, 73% yield. ¹H NMR (400 MHz, CDCl₃) δ: 7.83 (d, *J* = 8.0 Hz, 1H), 7.68-7.58 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.30-7.11 (m, 7H), 6.83-6.79 (t, *J* = 8.0 Hz, 2H), 1.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 169.04, 150.28, 142.10, 141.10, 136.23, 133.37, 132.41, 131.46, 130.07, 128.85, 128.57, 128.39, 127.67, 125.28, 124.89, 124.18, 123.16, 122.09, 117.78, 74.39, 30.40; HRMS (ESI): *m/z* calcd for C₂₃H₁₇NNaO⁺ [*M*+Na]⁺ 346.1202. Found 346.1200.



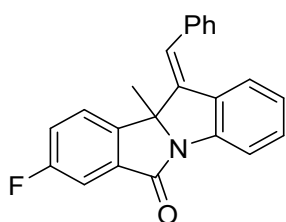
(3b)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); white solid, m.p. = 222-224 °C; 34.1 mg, 50% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.72-7.66 (m, 3H), 7.55-7.51 (m, 1H), 7.41-7.32 (m, 5H), 7.01 (td, *J* = 8.7, 2.6 Hz, 1H), 6.93 (s, 1H), 6.85 (dd, *J* = 9.4, 2.5 Hz, 1H), 1.86 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.18, 159.53 (d, *J* = 240 Hz), 150.12, 140.65, 138.30, 135.58, 133.50, 132.93 (d, *J* = 9 Hz), 132.19, 128.98, 128.76, 128.22, 128.06, 125.36, 124.59, 122.04, 118.51 (d, *J* = 8 Hz), 116.73 (d, *J* = 24 Hz), 111.79 (d, *J* = 26 Hz), 74.89, 30.31. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆FNNaO⁺ [M+Na]⁺ 364.1108. Found 364.1108.



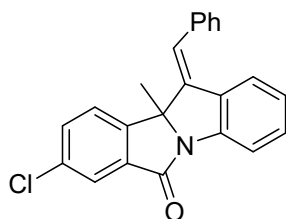
(3c)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 188-190 °C; 40.8 mg, 57% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.91 (d, *J* = 8.0 Hz, 1H), 7.72-7.66 (m, 3H), 7.56-7.52 (m, 1H), 7.38 (dt, *J* = 22.5, 7.5 Hz, 5H), 7.29-7.27 (m, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 6.94 (s, 1H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.99, 150.09, 140.67, 140.18, 135.53, 133.61, 132.99, 132.09, 129.91, 129.56, 129.01, 128.76, 128.21, 128.14, 125.41, 124.79, 124.65, 122.07, 118.59, 74.68, 30.40. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆ClNNaO⁺ [M+Na]⁺ 380.0813. Found 380.0813.



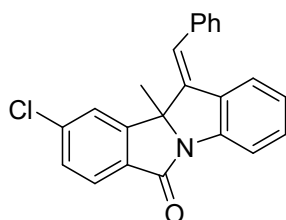
(3d)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 168-170 °C; 50.6 mg, 75% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.72-7.62 (m, 3H), 7.54-7.50 (m, 1H), 7.38-7.30 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.86 (s, 1H), 2.15 (s, 3H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.00, 150.29, 141.24, 139.93, 136.30, 133.71, 133.24, 132.54, 131.51, 130.79, 128.79, 128.48, 128.43, 127.66, 125.37, 125.23, 122.93, 122.07, 117.46, 74.63, 30.32, 21.21. **HRMS** (ESI): *m/z* calcd for C₂₄H₁₉NNaO⁺ [M+Na]⁺ 360.1359. Found 360.1355.



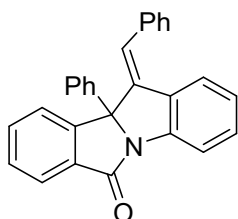
(3e)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); white solid, m.p. = 238-240 °C; 50.5 mg, 74% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.73 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.56 (dd, *J* = 7.5, 2.4 Hz, 1H), 7.40-7.30 (m, 7H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 167.77, 163.23 (d, *J* = 268 Hz), 145.80, 141.76, 140.89, 136.05, 134.66 (d, *J* = 8 Hz), 131.43, 130.16, 128.63, 128.37, 127.80, 124.98, 124.45, 123.59 (d, *J* = 8 Hz), 123.34, 120.84 (d, *J* = 23 Hz), 117.82, 111.81 (d, *J* = 23 Hz), 74.18, 30.38. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆FNNaO⁺ [M+Na]⁺ 364.1108. Found 364.1108.



(3f)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v); white solid, m.p. = 236-238 °C; 53.7 mg, 75% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.86 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66-7.62 (m, 2H), 7.40-7.29 (m, 6H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.92-6.88 (m, 1H), 6.83 (s, 1H), 1.84 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 167.55, 148.35, 141.72, 140.69, 135.97, 135.24, 134.27, 133.46, 131.36, 130.19, 128.63, 128.35, 127.82, 125.26, 124.98, 124.48, 123.38, 123.33, 117.83, 74.24, 30.27. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆ClNNaO⁺ [M+Na]⁺ 380.0813. Found 380.0814.

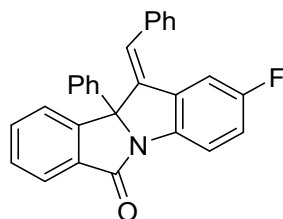


(3g)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 206-208 °C; 64.4 mg, 90% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.86 (d, *J* = 8.0 Hz, 1H), 7.77-7.73 (m, 2H), 7.55-7.52 (m, 1H), 7.42-7.39 (m, 3H), 7.38-7.30 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 1.89 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 167.94, 151.77, 141.91, 140.57, 139.79, 135.97, 130.19, 129.50, 129.10, 128.75, 128.64, 128.39, 127.84, 126.49, 124.97, 124.41, 123.45, 122.67, 117.79, 74.07, 30.32. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆ClNNaO⁺ [M+Na]⁺ 380.0813. Found 380.0813.

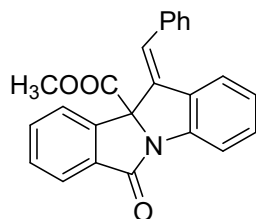


(3h)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); white solid, m.p. = 160-162 °C; 53.9 mg, 70% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 8.00 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.70-7.66 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.60-7.53 (m, 2H), 7.49-7.42 (m, 4H), 7.40 – 7.22 (m, 6H), 7.14 (s, 1H), 6.90 (t, *J* = 8.0 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃)

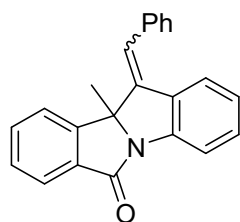
δ : 169.11, 149.59, 141.88, 141.48, 138.89, 135.87, 133.50, 132.50, 130.09, 129.20, 128.91, 128.60, 128.43, 128.04, 127.90, 126.70, 126.53, 125.97, 125.27, 124.76, 124.42, 123.58, 118.05, 79.41. **HRMS** (ESI): m/z calcd for $C_{28}H_{19}NNaO^+$ $[M+Na]^+$ 408.1359. Found 408.1359.



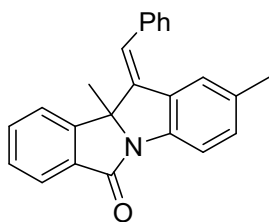
(3i)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); white solid, m.p. = 190-192 °C; 43.5 mg, 54% yield. **1H NMR** (400 MHz, $CDCl_3$) δ : 8.00 (d, J = 8.0 Hz, 1H), 7.71-7.63 (m, 4H), 7.58-7.54 (m, 2H), 7.46-7.30 (m, 8H), 7.17 (s, 1H), 7.02 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ : 169.23, 159.68 (d, J = 241 Hz), 149.43, 141.17, 138.19 (d, J = 31 Hz), 135.23, 134.01 (d, J = 9 Hz), 133.62, 132.25, 129.05, 128.79, 128.68, 128.27, 128.20, 128.08, 125.93, 125.35, 123.54, 118.81 (d, J = 8 Hz), 116.72 (d, J = 24 Hz), 111.83 (d, J = 26 Hz), 79.91. **HRMS** (ESI): m/z calcd for $C_{28}H_{18}FNNaO^+$ $[M+Na]^+$ 426.1265. Found 426.1261.



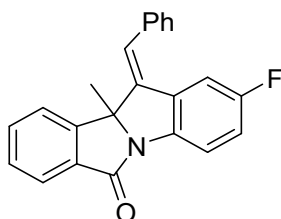
(3j)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); white solid, m.p. = 90-92 °C; 53.6 mg, 73% yield. **1H NMR** (400 MHz, $CDCl_3$) δ : 8.02 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.39-7.30 (m, 7H), 7.18 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 8.0 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ : 170.21, 168.79, 143.92, 143.17, 135.71, 135.42, 133.60, 132.80, 130.96, 130.23, 129.92, 128.61, 128.34, 128.04, 126.89, 125.12, 124.48, 124.39, 124.11, 117.34, 78.70, 53.67. **HRMS** (ESI): m/z calcd for $C_{24}H_{17}NNaO_3^+$ $[M+Na]^+$ 390.1101. Found 390.1101.



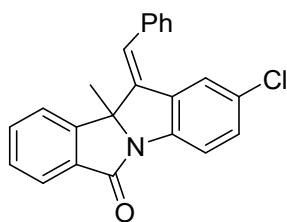
(5a)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow liquid; 58.1 mg, 90% yield (E/Z : 2:1). **1H NMR** (400 MHz, $CDCl_3$) δ : 7.90 (d, J = 8.0 Hz, 1H), 7.88-7.64 (m, 4H), 7.56-7.50 (m, 1.5H), 7.44-7.40 (m, 1.5H), 7.37-7.36 (m, 4.5H), 7.32-7.29 (m, 2H), 7.27-7.23 (m, 3H), 7.18 (d, J = 8.0 Hz, 1.5H), 6.90-6.86 (m, 2H), 1.85 (s, 3H), 1.84 (s, 1.5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ : 169.05, 150.30, 142.12, 141.12, 136.24, 133.38, 132.41, 131.46, 130.06, 128.84, 128.57, 128.39, 127.67, 125.28, 124.90, 124.17, 123.17, 122.08, 117.79, 74.38, 30.41. **HRMS** (ESI): m/z calcd for $C_{23}H_{17}NNaO^+$ $[M+Na]^+$ 346.1202. Found 346.1205.



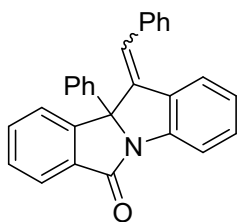
(5b)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 168-170 °C; 38.4 mg, 57% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.89 (d, *J* = 8 Hz, 1H), 7.66 (dt, *J* = 23.1, 7.8 Hz, 3H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.37-7.30 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.85 (s, 1H), 2.14 (s, 3H), 1.83 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.99, 150.30, 141.25, 139.94, 136.31, 133.70, 133.23, 132.54, 131.51, 130.79, 128.78, 128.47, 128.42, 127.66, 125.37, 125.22, 122.93, 122.06, 117.46, 74.62, 30.32, 21.19. **HRMS** (ESI): *m/z* calcd for C₂₄H₁₉NNaO⁺ [M+Na]⁺ 360.1359. Found 360.1358.



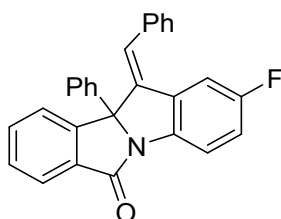
(5c)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 222-224 °C; 32.7 mg, 48% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.71-7.65 (m, 3H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.41-7.37 (m, 2H), 7.35-7.32 (m, 3H), 7.01 (td, *J* = 8.7, 2.5 Hz, 1H), 6.93 (s, 1H), 6.84 (dd, *J* = 9.4, 2.4 Hz, 1H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.21, 159.54 (d, *J* = 240 Hz), 150.13, 140.64, 138.30, 135.58, 133.51, 132.94 (d, *J* = 9 Hz), 132.18, 128.99, 128.76, 128.22, 128.07, 125.38, 124.60, 122.04, 118.52 (d, *J* = 9 Hz), 116.73 (d, *J* = 24 Hz), 111.80 (d, *J* = 25 Hz), 74.90, 30.31. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆FNNaO⁺ [M+Na]⁺ 364.1108. Found 364.1108.



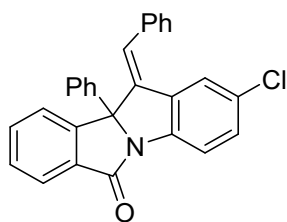
(5d)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 193-195 °C; 47.3 mg, 66% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.91 (d, *J* = 8.0 Hz, 1H), 7.73-7.66 (m, 3H), 7.56 – 7.52 (m, 1H), 7.43-7.34 (m, 5H), 7.30-7.27 (m, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 6.94 (s, 1H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.98, 150.07, 140.65, 140.16, 135.51, 133.60, 132.98, 132.07, 129.89, 129.54, 129.00, 128.74, 128.19, 128.12, 125.39, 124.78, 124.65, 122.06, 118.58, 74.66, 30.38. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆ClNNaO⁺ [M+Na]⁺ 380.0813. Found 380.0811.



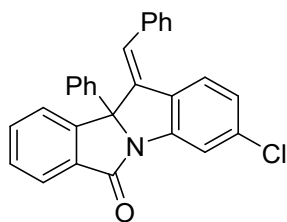
(5e)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); white liquid; 53.9 mg, 70% yield (*E/Z*: 3:1). **¹H NMR** (400 MHz, CDCl₃) δ: 7.95 (d, *J* = 8.0 Hz, 0.3H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73-7.68 (m, 1.4H), 7.66-7.58 (m, 2H), 7.55-7.49 (m, 0.7H), 7.44-7.36 (m, 4.5H), 7.34-7.28 (m, 4.5H), 7.24-7.17 (m, 5.8H), 7.14-7.08 (m, 1.7H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.07 (d, *J* = 8.0 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.11, 149.59, 141.88, 141.48, 138.89, 135.87, 133.50, 132.50, 130.09, 129.20, 128.91, 128.60, 128.43, 128.04, 127.90, 126.70, 126.53, 125.97, 125.27, 124.76, 124.42, 123.58, 118.05, 79.41. **HRMS** (ESI): *m/z* calcd for C₂₈H₁₉NNaO⁺ [M+Na]⁺ 408.1359. Found 408.1360.



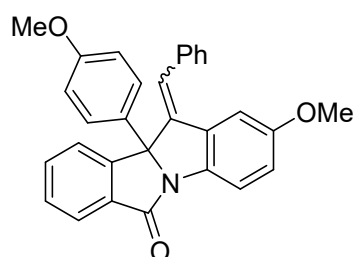
(5f)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 182-184 °C; 55.6 mg, 69% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.61-7.54 (m, 4H), 7.48-7.45 (m, 2H), 7.35-7.20 (m, 8H), 7.07 (s, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.27, 159.71 (d, *J* = 241 Hz), 149.45, 141.18, 138.36, 138.02, 135.25, 134.03 (d, *J* = 9 Hz), 133.64, 132.27, 129.07, 128.81, 128.70, 128.29, 128.22, 128.09, 125.95, 125.38, 123.55, 118.84 (d, *J* = 9 Hz), 116.74 (d, *J* = 24 Hz), 111.98, 111.72, 79.94. **HRMS** (ESI): *m/z* calcd for C₂₈H₁₈FNNaO⁺ [M+Na]⁺ 426.1265. Found 426.1265.



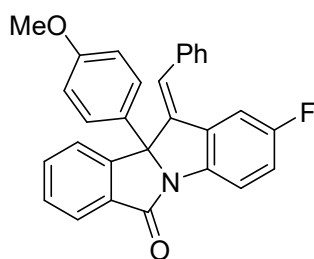
(5g)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); white solid, m.p. = 153-155 °C; 39.5 mg, 47% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.92 (d, *J* = 8.0 Hz, 1H), 7.61-7.55 (m, 4H), 7.51-7.47 (m, 2H), 7.38 (s, 4H), 7.31-7.24 (m, 3H), 7.22-7.20 (m, 2H), 7.09 (d, *J* = 4.0 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.06, 149.40, 141.12, 140.40, 137.93, 135.20, 134.05, 133.74, 132.21, 129.95, 129.89, 129.11, 128.81, 128.71, 128.38, 128.28, 128.25, 128.14, 125.94, 125.43, 124.76, 123.59, 118.90, 79.70. **HRMS** (ESI): *m/z* calcd for C₂₈H₁₈ClNNaO⁺ [M+Na]⁺ 442.0969. Found 442.0970.



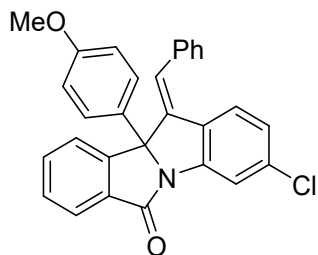
(5h)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); white solid, m.p. = 176-178 °C; 24.4 mg, 29% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.96 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.63-7.58 (m, 3H), 7.54-7.50 (m, 2H), 7.40-7.27 (m, 8H), 7.08-7.05 (m, 2H), 6.82 (dd, *J* = 8.3, 1.5 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.99, 149.50, 142.79, 141.16, 137.96, 135.66, 135.60, 133.80, 132.10, 131.06, 129.09, 128.73, 128.70, 128.35, 128.24, 128.12, 127.12, 125.92, 125.46, 125.37, 124.68, 123.60, 118.44, 79.74. **HRMS** (ESI): *m/z* calcd for C₂₈H₁₈ClNNaO⁺ [M+Na]⁺ 442.0968mn. Found 442.0965.



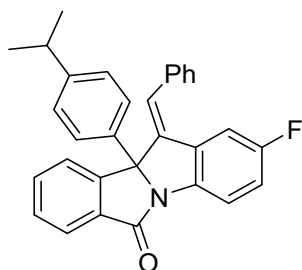
(5i)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow liquid; 79.2 mg, 89% yield (*E/Z*: 3:1). **¹H NMR** (400 MHz, CDCl₃) δ: 7.94 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 0.36H), 7.60-7.57 (m, 2.6H), 7.51-7.48 (m, 4H), 7.44-7.29 (m, 6.66H), 7.16-7.09 (m, 1.31H), 7.04 (d, *J* = 8.0 Hz, 1.31H), 6.84-6.77 (m, 4H), 6.69 (d, *J* = 4 Hz, 1H), 3.86 (s, 1H), 3.77 (s, 1H), 3.75 (s, 3H), 3.51 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.23, 159.36, 156.63, 149.80, 139.28, 135.84, 135.63, 133.68, 133.33, 132.58, 129.24, 128.85, 128.57, 127.98, 127.40, 126.69, 125.17, 123.49, 118.65, 116.16, 113.91, 110.02, 105.66, 79.69, 55.33, 55.24. **HRMS** (ESI): *m/z* calcd for C₃₀H₂₃NNaO₃⁺ [M+Na]⁺ 468.1570. Found 468.1570.



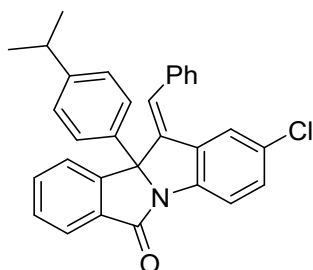
(5j)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v); yellow liquid; 44.2 mg, 51% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.94 (d, *J* = 8.0 Hz, 1H), 7.64-7.59 (m, 2H), 7.53-7.47 (m, 4H), 7.43-7.35 (m, 5H), 7.07 (s, 1H), 6.96 (td, *J* = 8.7, 2.6 Hz, 1H), 6.86-6.83 (m, 3H), 3.75 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.26, 159.69 (d, *J* = 241 Hz), 159.47, 149.78, 138.47, 137.98, 135.30, 134.09 (d, *J* = 10 Hz), 133.63, 133.18, 132.24, 129.00, 128.80, 128.28, 127.91, 127.39, 125.32, 123.53, 118.89 (d, *J* = 8 Hz), 116.72 (d, *J* = 24 Hz), 113.99, 111.93, 111.67, 79.71, 55.25. **HRMS** (ESI): *m/z* calcd for C₂₉H₂₀FNNaO₂⁺ [M+Na]⁺ 456.1370. Found 456.1370.



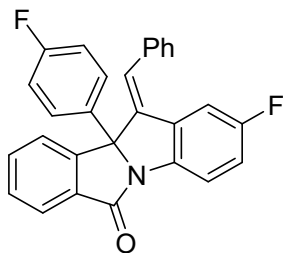
(5k)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); yellow liquid; 64.8 mg, 72% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.82 (d, *J* = 8.0 Hz, 1H), 7.61-7.59 (m, 2H), 7.41-7.24 (m, 6H), 7.16-7.09 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.07 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.87, 159.60, 147.64, 139.15, 138.63, 137.37, 136.23, 135.15, 133.05, 132.70, 130.54, 129.87, 129.17, 128.91, 128.48, 128.03, 127.87, 126.18, 124.55, 124.45, 120.47, 118.69, 113.94, 80.05, 55.25. **HRMS** (ESI): *m/z* calcd for C₂₉H₂₀ClNNaO₂⁺ [M+Na]⁺ 472.1075. Found 472.1076.



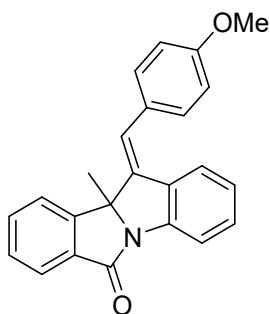
(5l)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v); yellow liquid; 49.8 mg, 56% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.94 (d, *J* = 8.0 Hz, 1H), 7.65-7.58 (m, 2H), 7.54-7.48 (m, 4H), 7.40-7.32 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 6.98-6.94 (m, 1H), 6.84-6.82 (m, 1H), 2.91-2.82 (m, 1H), 1.20-1.18 (d, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.29, 159.68 (d, *J* = 241 Hz), 149.66, 148.86, 138.52, 135.35, 133.58, 129.19 (d, *J* = 5 Hz), 128.97, 128.79, 128.54, 128.43, 128.29, 128.25, 127.87, 126.74, 126.46, 125.93, 125.30, 123.59, 118.81 (d, *J* = 9 Hz), 116.67 (d, *J* = 24 Hz), 111.82 (d, *J* = 25 Hz), 79.85, 33.61, 23.79. **HRMS** (ESI): *m/z* calcd for C₃₁H₂₄FNNaO⁺ [M+Na]⁺ 468.1734. Found 468.1731.



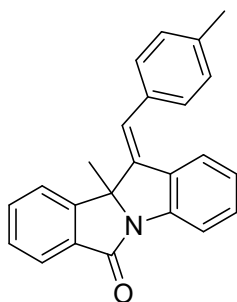
(5m)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow liquid; 45.3 mg, 49% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.94 (d, *J* = 8.0 Hz, 1H), 7.67-7.59 (m, 3H), 7.55-7.47 (m, 4H), 7.40 (s, 3H), 7.24-7.16 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.91-2.80 (m, 1H), 1.20 (s, 3H), 1.18 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.08, 149.60, 148.90, 140.45, 138.45, 138.10, 135.30, 134.14, 133.68, 132.22, 129.89, 129.80, 129.01, 128.79, 128.32, 128.28, 127.91, 126.76, 125.92, 125.35, 124.73, 123.63, 118.88, 79.61, 33.62, 23.79. **HRMS** (ESI): *m/z* calcd for C₃₁H₂₄ClNNaO⁺ [M+Na]⁺ 484.1439. Found 484.1440.



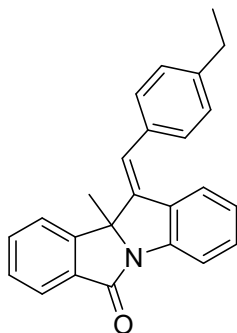
(5n)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow liquid; 27.8 mg, 33% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.95 (d, $J = 8.0$ Hz, 1H), 7.65-7.60 (m, 2H), 7.57-7.54 (m, 2H), 7.51-7.48 (m, 1H), 7.42-7.36 (m, 5H), 7.09 (s, 1H), 7.03-6.96 (m, 4H), 6.87-6.84 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 169.21, 162.51 (d, $J = 246$ Hz), 159.75 (d, $J = 241$ Hz), 149.31, 138.26, 137.87, 136.99, 135.07, 133.77, 132.16, 129.23, 128.85, 128.54, 128.41, 128.25, 127.97, 127.88, 125.49, 123.48, 118.94 (d, $J = 8$ Hz), 116.90 (d, $J = 24$ Hz), 115.57 (d, $J = 22$ Hz), 111.85 (d, $J = 26$ Hz), 79.49. **HRMS** (ESI): m/z calcd for $\text{C}_{28}\text{H}_{17}\text{F}_2\text{NNaO}^+$ $[\text{M}+\text{Na}]^+$ 444.1170. Found 444.1170.



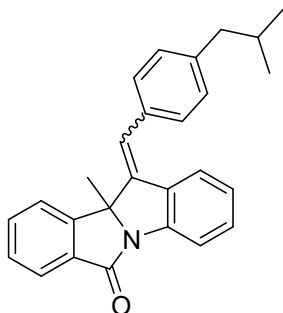
(6a)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v); yellow liquid; 45.9 mg, 65% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.89 (d, $J = 8.0$ Hz, 1H), 7.74-7.64 (m, 3H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.32-7.26 (m, 4H), 6.92-6.88 (m, 3H), 6.82 (s, 1H), 3.84 (s, 3H), 1.83 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 169.06, 159.11, 150.43, 142.02, 140.24, 133.32, 132.45, 131.71, 129.84, 129.70, 128.79, 128.48, 125.25, 124.74, 124.15, 123.00, 122.11, 117.80, 113.94, 74.44, 55.26, 30.34. **HRMS** (ESI): m/z calcd for $\text{C}_{24}\text{H}_{19}\text{NNaO}_2^+$ $[\text{M}+\text{Na}]^+$ 376.1308. Found 376.1308.



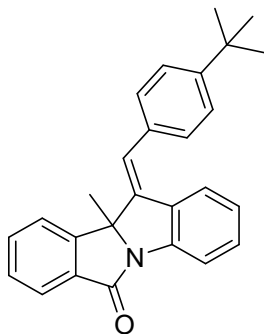
(6b)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 192-194 °C; 43.8 mg, 65% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.90 (d, $J = 8.0$ Hz, 1H), 7.75-7.65 (m, 3H), 7.52 (t, $J = 8.0$ Hz, 1H), 7.33-7.27 (m, 4H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.90 (t, $J = 8.0$ Hz, 1H), 6.86 (s, 1H), 2.39 (s, 3H), 1.85 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 169.07, 150.40, 142.06, 140.62, 137.49, 133.34, 133.22, 132.44, 131.64, 129.91, 129.24, 128.80, 128.29, 125.26, 124.89, 124.14, 123.30, 122.10, 117.76, 74.42, 30.41, 21.30. **HRMS** (ESI): m/z calcd for $\text{C}_{24}\text{H}_{19}\text{NNaO}^+$ $[\text{M}+\text{Na}]^+$ 360.1359. Found 360.1352.



(6c)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); white solid, m.p. = 167-169 °C; 35.8 mg, 51% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.89 (d, J = 8.0 Hz, 1H), 7.74-7.64 (m, 3H), 7.52-7.49 (m, 1H), 7.32-7.27 (m, 4H), 7.20 (d, J = 8.0 Hz, 2H), 6.89 (t, J = 8.0 Hz, 1H), 6.85 (s, 1H), 2.68 (q, J = 8.0 Hz, 2H), 1.84 (s, 3H), 1.27 (t, J = 8.0 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 169.08, 150.42, 143.89, 142.08, 140.58, 133.45, 133.34, 132.45, 131.64, 129.92, 128.80, 128.36, 128.02, 125.27, 124.88, 124.15, 123.33, 122.10, 117.77, 74.44, 30.41, 28.65, 15.44. **HRMS** (ESI): m/z calcd for $\text{C}_{25}\text{H}_{21}\text{NNaO}^+$ $[\text{M}+\text{Na}]^+$ 374.1515. Found 374.1515.

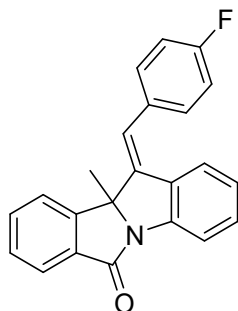


(6d)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v); yellow liquid; 33.4 mg, 44% yield (E/Z : 1.4:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.89 (d, J = 8.0 Hz, 0.6H), 7.78-7.64 (m, 2.7H), 7.56-7.49 (m, 1H), 7.41-7.37 (m, 0.4H), 7.32-7.28 (m, 2.3H), 7.24-7.19 (m, 1.8H), 7.18-7.13 (m, 2.5H), 7.06-7.02 (m, 0.4H), 6.91-6.86 (m, 1.3H), 2.59 (d, J = 8.0 Hz, 0.8H), 2.50 (d, J = 8.0 Hz, 1.2H), 2.01-1.87 (m, 1H), 1.84 (d, J = 4.0 Hz, 3H), 1.02 (d, J = 8.0 Hz, 2.5H), 0.92 (d, J = 8.0 Hz, 3.5H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 169.08, 168.46, 150.41, 148.35, 142.07, 141.41, 141.38, 141.00, 140.59, 140.33, 134.33, 134.26, 133.50, 133.33, 132.44, 132.41, 132.10, 131.66, 129.91, 129.77, 129.28, 129.12, 128.80, 128.27, 128.15, 125.26, 124.87, 124.71, 124.61, 124.18, 124.14, 123.38, 122.10, 121.49, 120.90, 117.77, 117.46, 75.05, 74.44, 45.21, 45.18, 31.08, 30.38, 30.18, 22.33, 22.27. **HRMS** (ESI): m/z calcd for $\text{C}_{27}\text{H}_{25}\text{NNaO}^+$ $[\text{M}+\text{Na}]^+$ 402.1828. Found 402.1828.

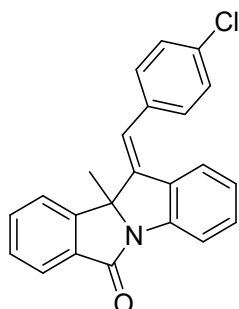


(6e)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v);

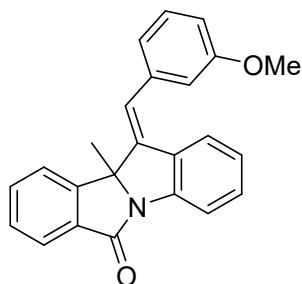
white solid, m.p. = 188-190 °C; 43.9 mg, 58% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.89 (d, *J* = 8.0 Hz, 1H), 7.75-7.63 (m, 3H), 7.52-7.48 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.34-7.29 (m, 4H), 6.91 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 6.84 (s, 1H), 1.84 (s, 3H), 1.34 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.08, 150.86, 150.42, 142.08, 140.51, 133.32, 133.16, 132.44, 131.63, 129.93, 128.79, 128.10, 125.41, 125.25, 124.87, 124.15, 123.25, 122.08, 117.76, 74.47, 34.65, 31.30, 30.39. **HRMS** (ESI): *m/z* calcd for C₂₇H₂₅NNaO⁺ [M+Na]⁺ 402.1828. Found 402.1831.



(6f)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 258-260 °C; 43.6 mg, 64% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.34-7.31 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 1.84 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.00, 162.21 (d, *J* = 246 Hz), 150.22, 142.22, 141.61, 133.43, 132.45, 132.21, 131.29, 130.24, 130.16, 128.92, 125.37, 124.78, 124.24, 122.07, 121.98, 117.95, 115.63 (d, *J* = 22 Hz), 74.38, 30.35. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆FNNaO⁺ [M+Na]⁺ 364.1108. Found 364.1108.

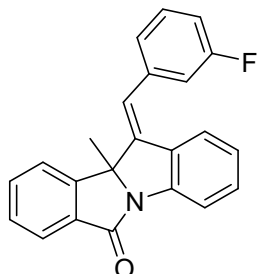


(6g)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 224-226 °C; 45.8 mg, 64% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.91 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.74-7.66 (m, 2H), 7.55-7.51 (m, 1H), 7.36-7.29 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.95, 150.10, 142.26, 141.94, 134.70, 133.45, 132.41, 131.14, 130.88, 130.37, 129.86, 128.95, 128.83, 125.37, 124.84, 124.27, 122.06, 121.71, 117.96, 74.41, 30.32. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆ClNNaO⁺ [M+Na]⁺ 380.0813. Found 380.0811.

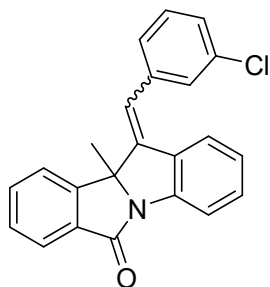


(6h)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v);

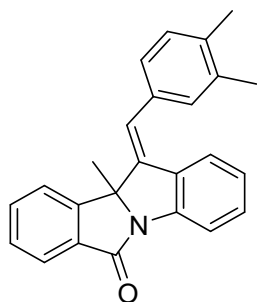
white solid, m.p. = 120-122 °C; 49.4 mg, 70% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.75-7.65 (m, 3H), 7.56-7.50 (m, 1H), 7.35-7.28 (m, 2H), 7.23-7.18 (m, 1H), 6.95-6.85 (m, 5H), 3.77 (s, 3H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.05, 159.73, 150.29, 142.15, 141.26, 137.57, 133.39, 131.42, 130.11, 129.66, 128.86, 125.29, 125.13, 124.73, 124.19, 123.01, 122.10, 120.77, 117.80, 113.79, 113.30, 74.40, 55.25, 30.37. **HRMS** (ESI): *m/z* calcd for C₂₄H₁₉NNaO₂⁺ [M+Na]⁺ 376.1308. Found 376.1308.



(6i)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 227-229 °C; 30.7 mg, 45% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.54-7.50 (m, 1H), 7.36-7.31 (m, 2H), 7.18-7.13 (m, 2H), 7.08-6.99 (m, 2H), 6.91 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 6.81 (s, 1H), 1.85 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.96, 162.90 (d, *J* = 246 Hz), 150.07, 142.29, 142.19, 138.47 (d, *J* = 8 Hz), 133.46, 132.40, 131.00, 130.43, 130.16 (d, *J* = 8 Hz), 128.96, 125.37, 124.94, 124.30, 124.21 (d, *J* = 3 Hz), 122.04, 121.63 (d, *J* = 2 Hz), 117.93, 115.36 (d, *J* = 22 Hz), 114.55 (d, *J* = 21 Hz), 74.37, 30.36. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆FNNaO⁺ [M+Na]⁺ 364.1108. Found 364.1111.

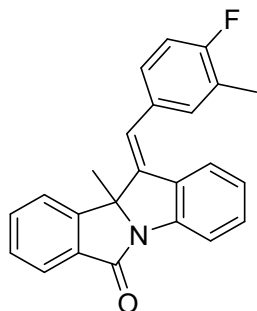


(6j)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow liquid; 40.1 mg, 56% yield (*E/Z*: 1.2:1). **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.79-7.74 (m, 2H), 7.70-7.65 (m, 1.8H), 7.55-7.50 (m, 1.8H), 7.44-7.29 (m, 5.5H), 7.21-7.14 (m, 5.5H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 1.84 (s, 3H), 1.61 (s, 2.5H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.96, 150.02, 147.85, 142.33, 140.52, 138.08, 134.48, 133.47, 132.31, 130.47, 129.87, 129.65, 128.52, 127.75, 126.60, 125.37, 124.37, 122.03, 121.42, 119.60, 117.94, 74.35, 30.35. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₆ClNNaO⁺ [M+Na]⁺ 380.0813. Found 380.0812.

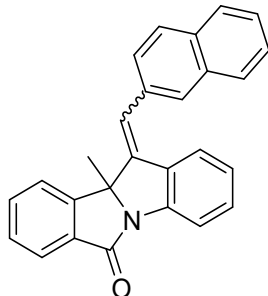


(6l)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v);

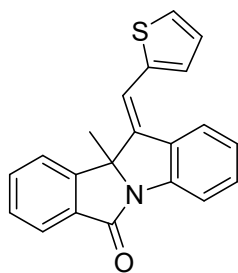
white solid, m.p. = 202-204 °C; 40.7 mg, 58% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.89 (d, *J* = 8.0 Hz, 1H), 7.74-7.64 (m, 3H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.32-7.27 (m, 2H), 7.13-7.09 (m, 3H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.83 (s, 1H), 2.29 (s, 3H), 2.25 (s, 3H), 1.84 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.12, 150.46, 142.04, 140.40, 136.74, 136.12, 133.64, 133.33, 132.44, 131.73, 129.84, 129.77, 129.54, 128.78, 125.74, 125.26, 124.91, 124.13, 123.47, 122.10, 117.74, 74.42, 30.42, 19.65, 19.59. **HRMS** (ESI): *m/z* calcd for C₂₅H₂₁NNaO⁺ [M+Na]⁺ 374.1515. Found 374.1517.



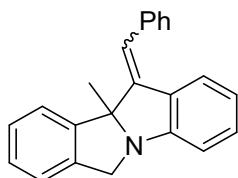
(6m)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 181-183°C; 36.2 mg, 51% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.70-7.65 (m, 2H), 7.53-7.50 (m, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.18-7.13 (m, 3H), 7.02-6.97 (m, 1H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 2.26 (s, 3H), 1.84 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.03, 160.71 (d, *J* = 245 Hz), 150.23, 142.11, 141.19, 133.39, 132.39, 131.85, 131.81, 131.55, 131.50, 131.41, 130.09, 128.87, 127.36 (d, *J* = 8 Hz), 125.31, 124.79, 124.20, 122.17 (d, *J* = 24 Hz), 117.87, 115.18 (d, *J* = 23 Hz), 74.34, 30.34, 14.46. **HRMS** (ESI): *m/z* calcd for C₂₄H₁₈FNNaO⁺ [M+Na]⁺ 378.1265. Found 378.1263.



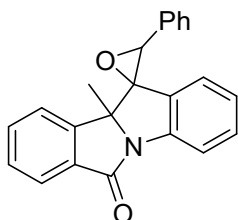
(6n)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); yellow liquid; 60.4 mg, 81% yield (*E/Z*: 2:1). **¹H NMR** (400 MHz, CDCl₃) δ: 7.94-7.88 (m, 1.2H), 7.84-7.65 (m, 6.2H), 7.60-7.39 (m, 4H), 7.35-7.28 (m, 1.3H), 7.24-7.18 (m, 1.5H), 7.02 (s, 0.7H), 6.85-6.78 (m, 1H), 1.89(s, 2H), 1.87(s, 1.87). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.04, 168.54, 150.30, 148.20, 142.22, 141.45, 140.46, 134.29, 134.22, 133.69, 133.41, 133.35, 133.06, 132.73, 132.57, 132.43, 132.26, 132.14, 131.47, 130.15, 129.92, 128.87, 128.28, 128.22, 128.14, 128.10, 127.93, 127.90, 127.82, 127.72, 127.34, 127.32, 126.57, 126.52, 126.35, 126.30, 126.17, 125.30, 124.91, 124.77, 124.71, 124.22, 124.15, 123.09, 122.11, 121.32, 120.95, 117.83, 117.57, 75.04, 74.51, 30.81, 30.39. **HRMS** (ESI): *m/z* calcd for C₂₇H₁₉NNaO⁺ [M+Na]⁺ 396.1359. Found 396.1359.



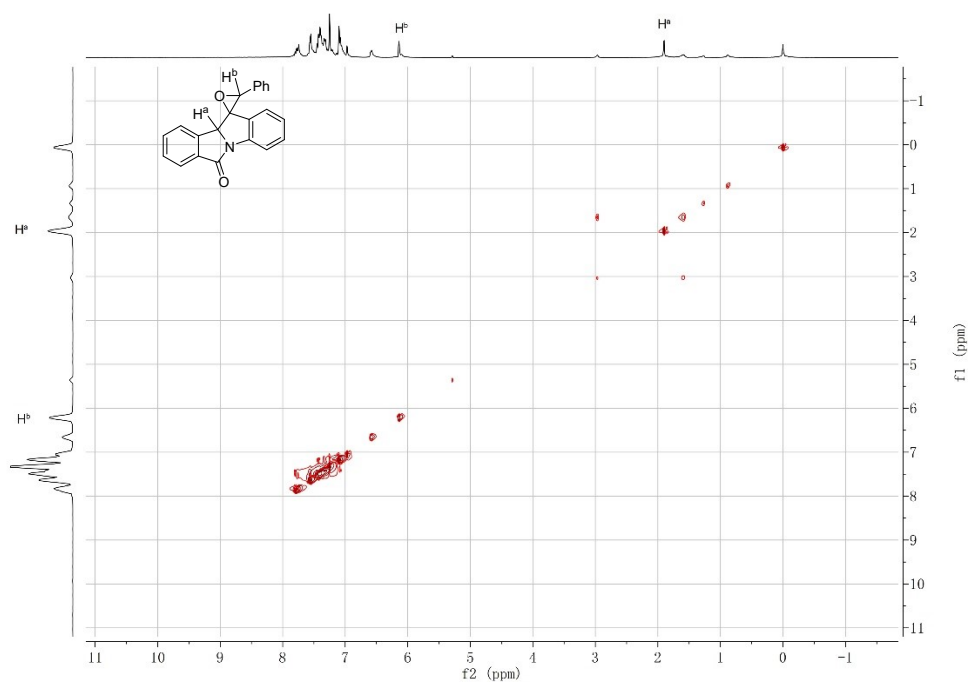
(6)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, m.p. = 172-174 °C; 32.9 mg, 50% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.37-7.33 (m, 2H), 7.12 (d, *J* = 4.0 Hz, 1H), 7.06-7.03 (m, 1H), 7.01-6.97 (m, 1H), 6.80 (s, 1H), 1.84 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 168.93, 149.97, 142.61, 142.26, 138.01, 133.46, 132.41, 131.14, 130.46, 128.94, 127.34, 127.08, 126.01, 125.36, 125.00, 124.35, 122.11, 117.84, 115.23, 74.61, 30.18. **HRMS** (ESI): *m/z* calcd for C₂₁H₁₅NNaOS⁺ [M+Na]⁺ 352.0767. Found 352.0762.



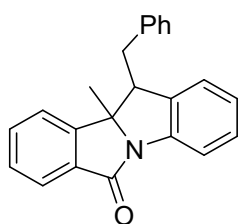
(7)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4 (v/v); yellow liquid; 47.0 mg, 76% yield (*E/Z*: 2:1). **¹H NMR** (400 MHz, CDCl₃) δ: 7.62-7.59 (m, 0.7H), 7.54 (d, *J* = 8.0 Hz, 0.3H), 7.45-7.43 (m, 0.8H), 7.34-7.29 (m, 5.6H), 7.24-7.14 (m, 1.8H), 7.09 (d, *J* = 4.0 Hz, 0.3H), 7.00-6.88 (m, 1.6H), 6.81-6.75 (m, 1H), 6.70-6.67 (m, 0.7H), 6.62 (d, *J* = 8.0 Hz, 0.5H), 5.82 (s, 0.7H), 4.71-4.63 (m, 1H), 4.24-4.19 (m, 1H), 1.83 (s, 2H), 1.81 (s, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ: 150.29, 148.25, 143.27, 141.38, 137.26, 132.06, 131.65, 130.45, 128.35, 128.16, 127.20, 127.09, 127.00, 125.14, 124.66, 120.66, 120.23, 112.65, 70.13, 63.94, 29.91. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₉NNa⁺ [M+Na]⁺ 332.1410. Found 332.1410.



(8)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether; white solid; 49.5 mg, 73% yield. **¹H NMR** (400 MHz, CDCl₃) δ: 7.81-7.76 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.46-7.39 (m, 4H), 7.37-7.32 (m, 2H), 7.13-7.09 (m, 2H), 6.97 (s, 1H), 6.15 (s, 1H), 1.90 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ: 169.61, 134.70, 133.78, 133.72, 132.52, 131.01, 130.24, 129.83, 129.52, 129.31, 128.75, 128.63, 128.29, 124.91, 124.55, 123.92, 118.12, 99.34, 74.91, 56.80, 23.91. **HRMS** (ESI): *m/z* calcd for C₂₃H₁₇NNaO₂⁺ [M+Na]⁺ 362.1151. Found 362.1151.



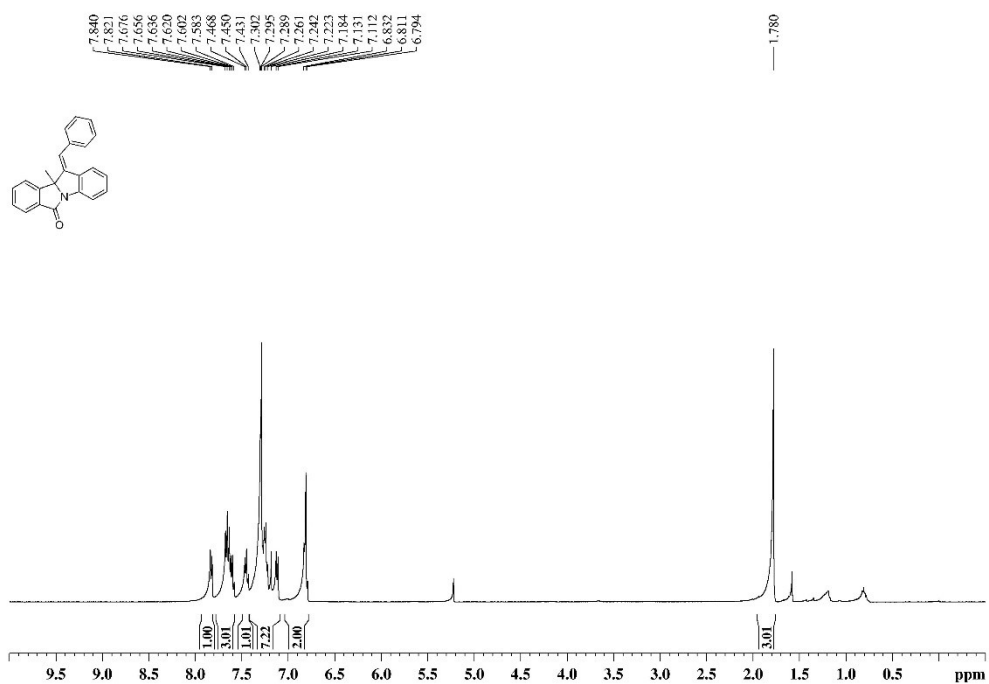
NOE spectrum of **8**



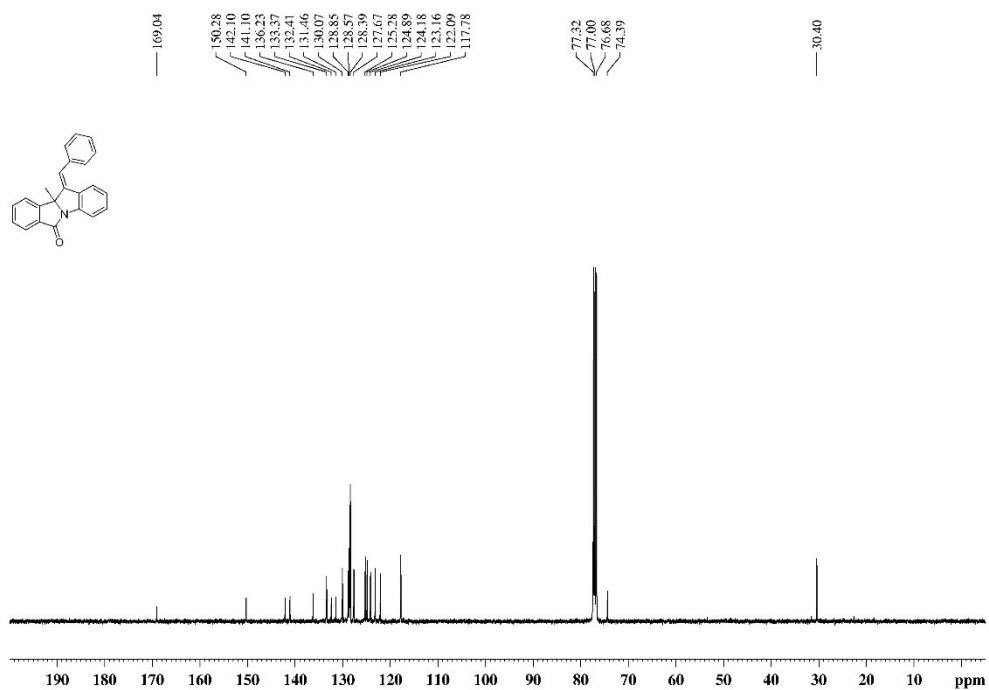
(9)-Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether; white solid, m.p. = 175-177 °C; 63.1 mg, 97% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.79 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.40-7.29 (m, 7H), 7.24-7.15 (m, 2H), 7.09 (td, $J = 8.0, 1.0$ Hz, 1H), 5.95 (d, $J = 8.0$ Hz, 1H), 3.74 (dd, $J = 10.0, 6.0$ Hz, 1H), 3.53 (dd, $J = 14.0, 6.0$ Hz, 1H), 3.09 (dd, $J = 14.0, 10.0$ Hz, 1H), 1.58 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 166.96, 150.38, 139.56, 139.16, 138.69, 132.72, 132.19, 129.22, 128.89, 128.29, 128.18, 126.85, 124.53, 124.42, 123.90, 122.59, 117.20, 75.60, 50.59, 33.55, 21.45. **HRMS** (ESI): m/z calcd for $\text{C}_{23}\text{H}_{19}\text{NNaO}^+$ [$\text{M}+\text{Na}$] $^+$ 348.1359. Found 348.1360.

4. NMR Charts

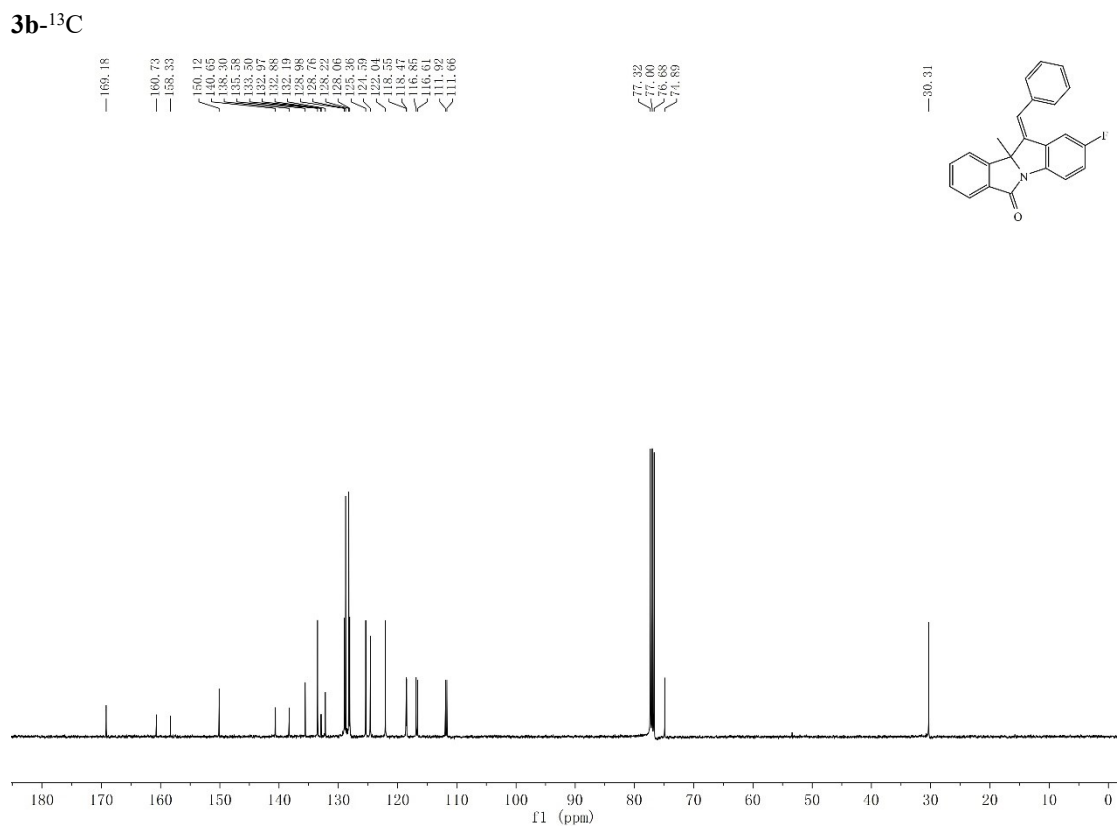
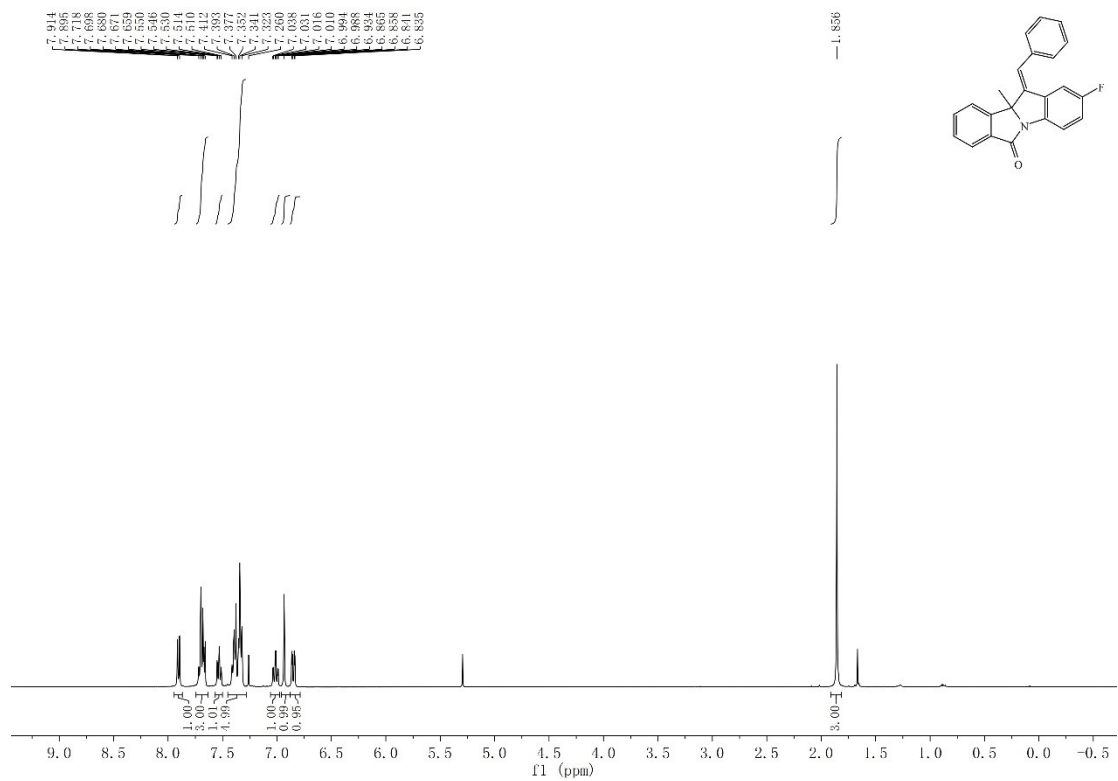
3a- ^1H



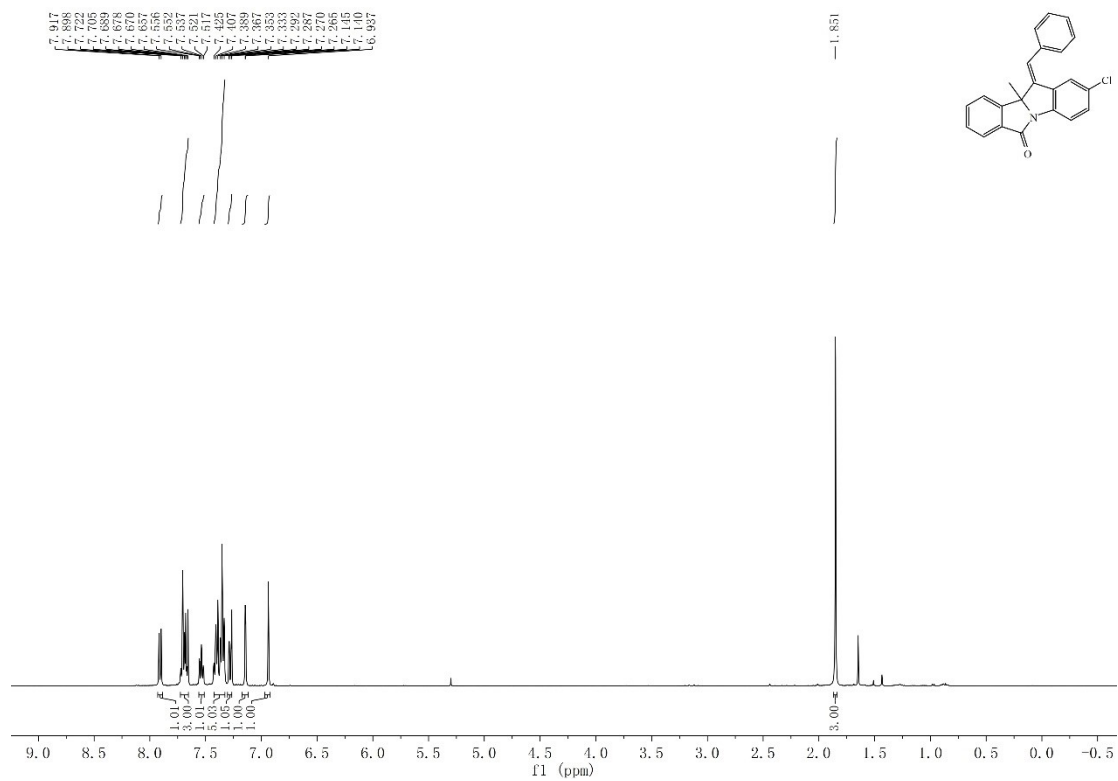
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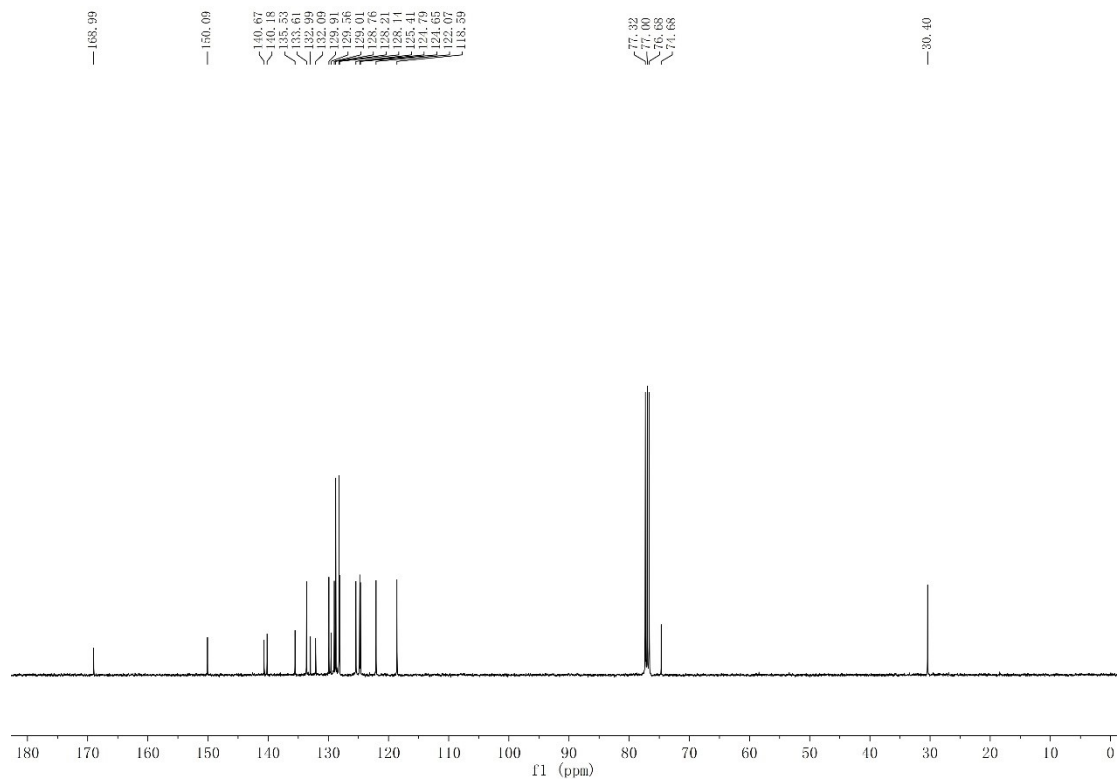
3b-¹H



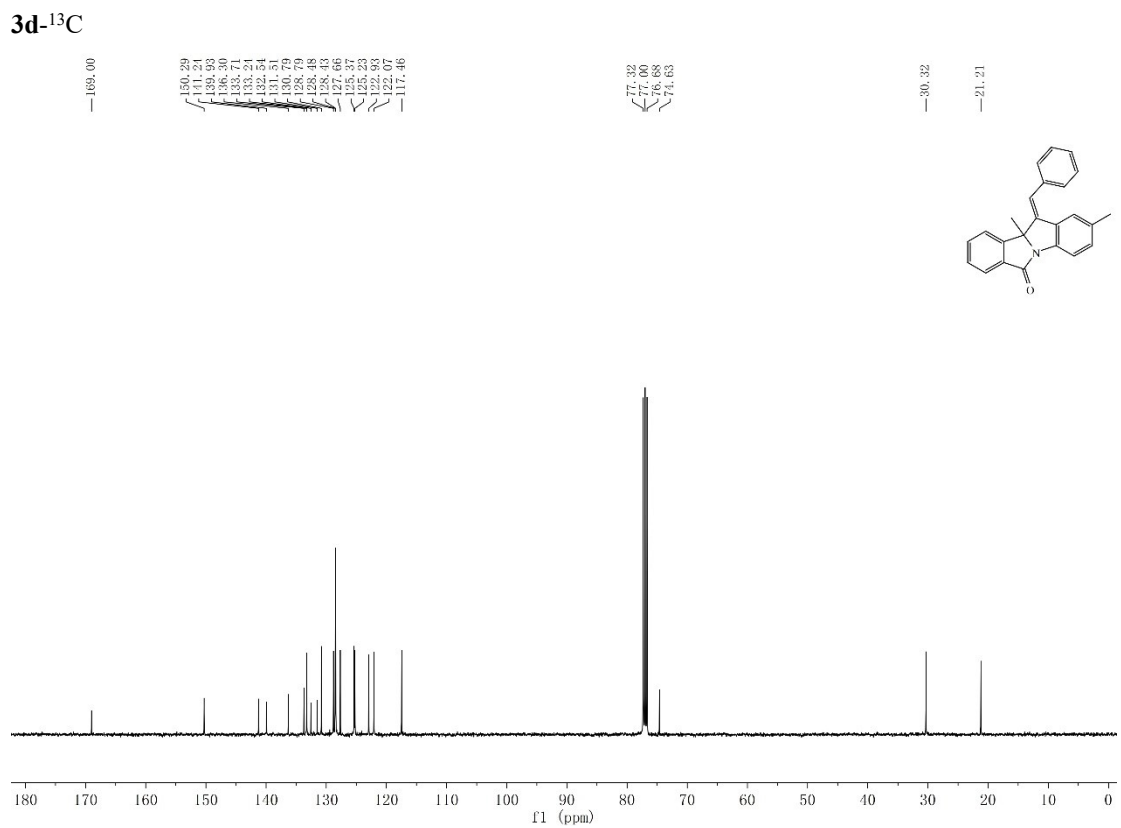
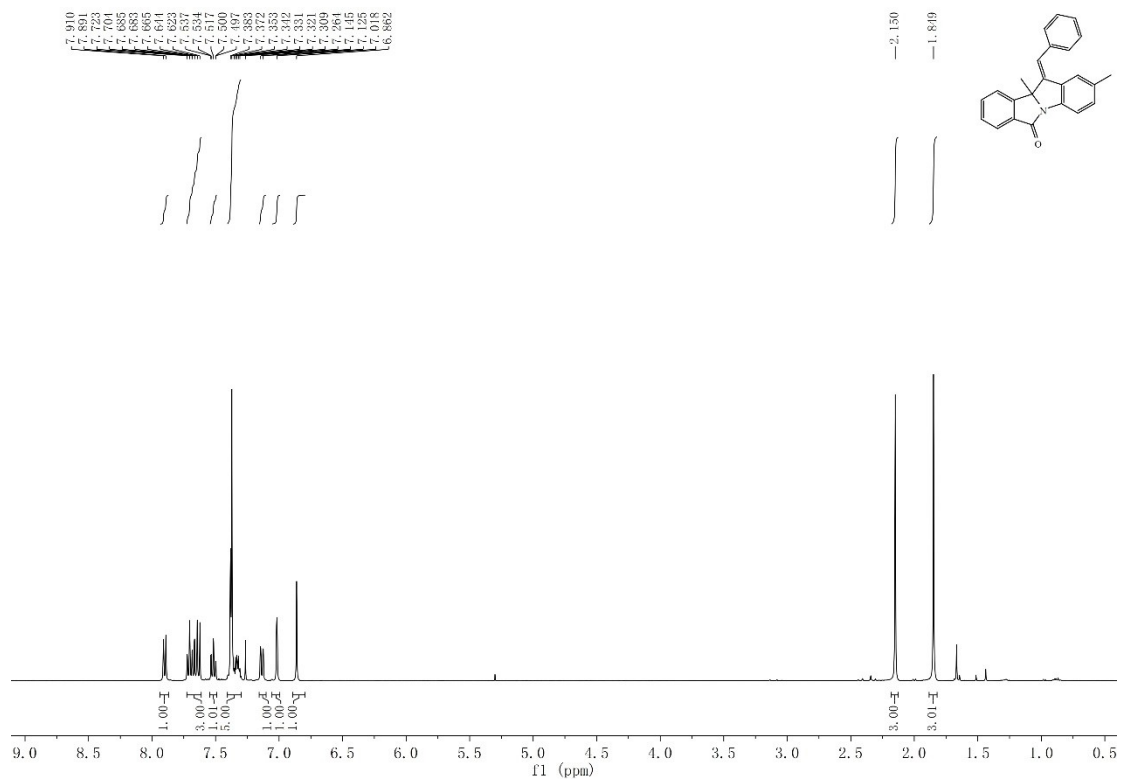
3c-¹H



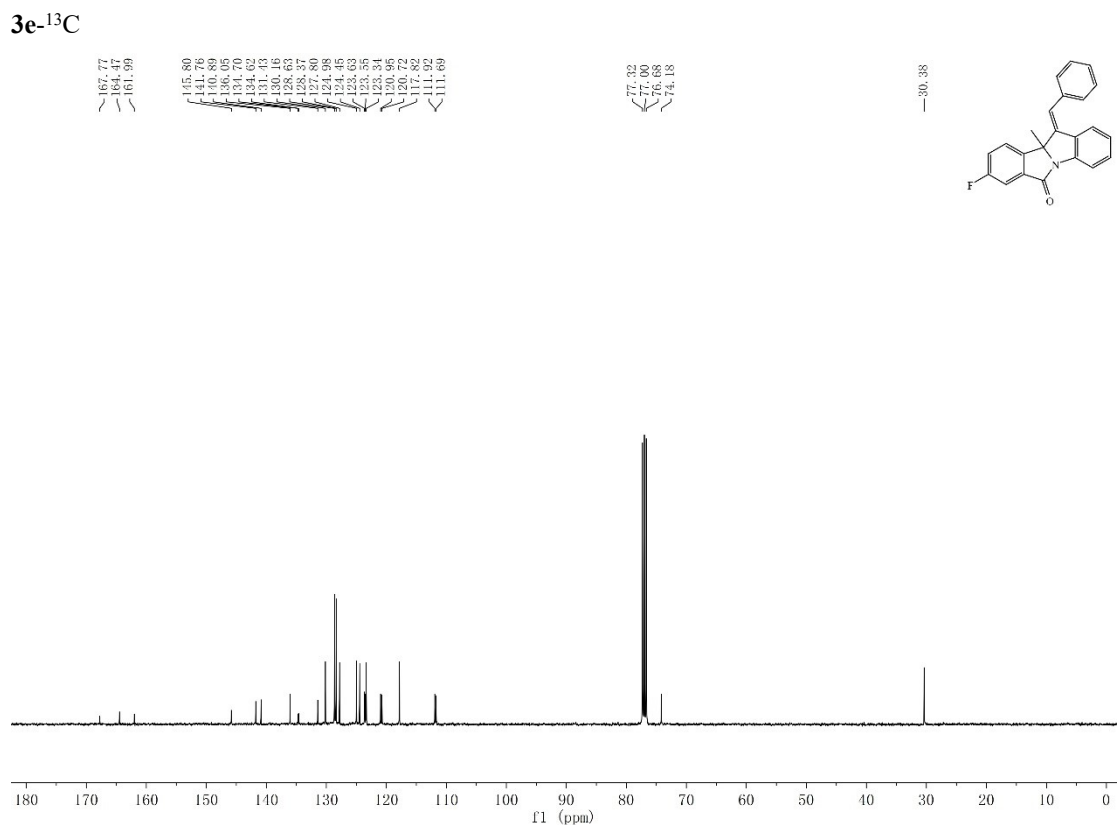
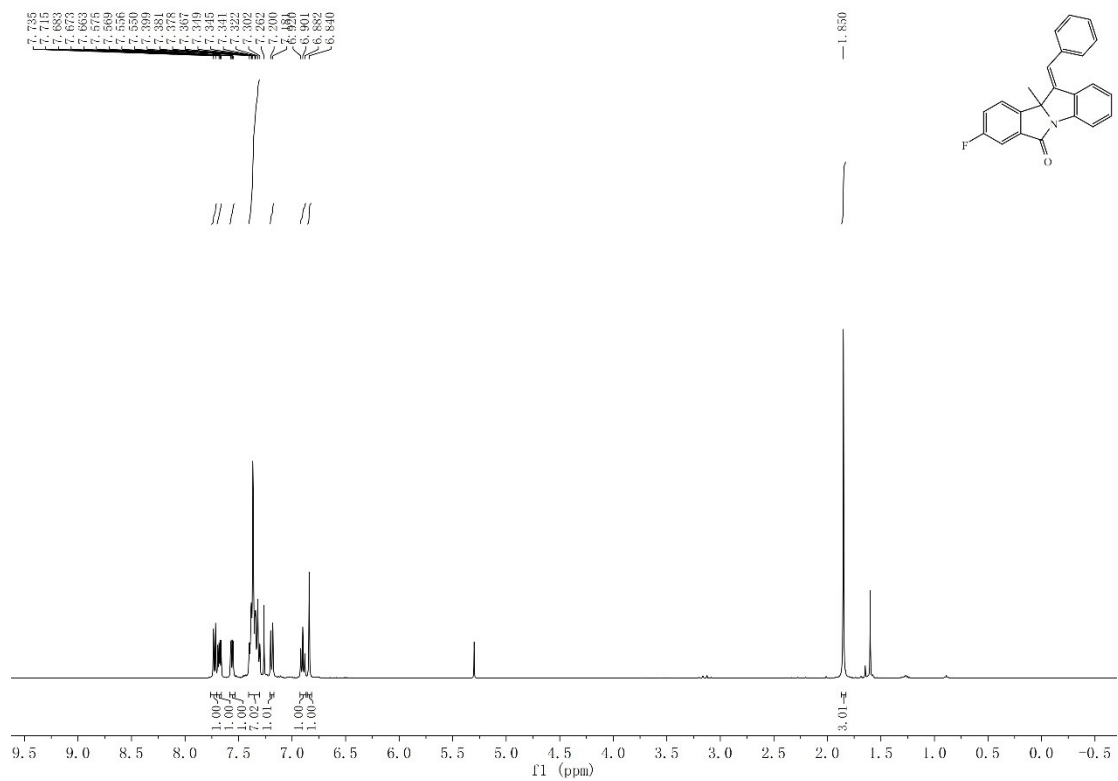
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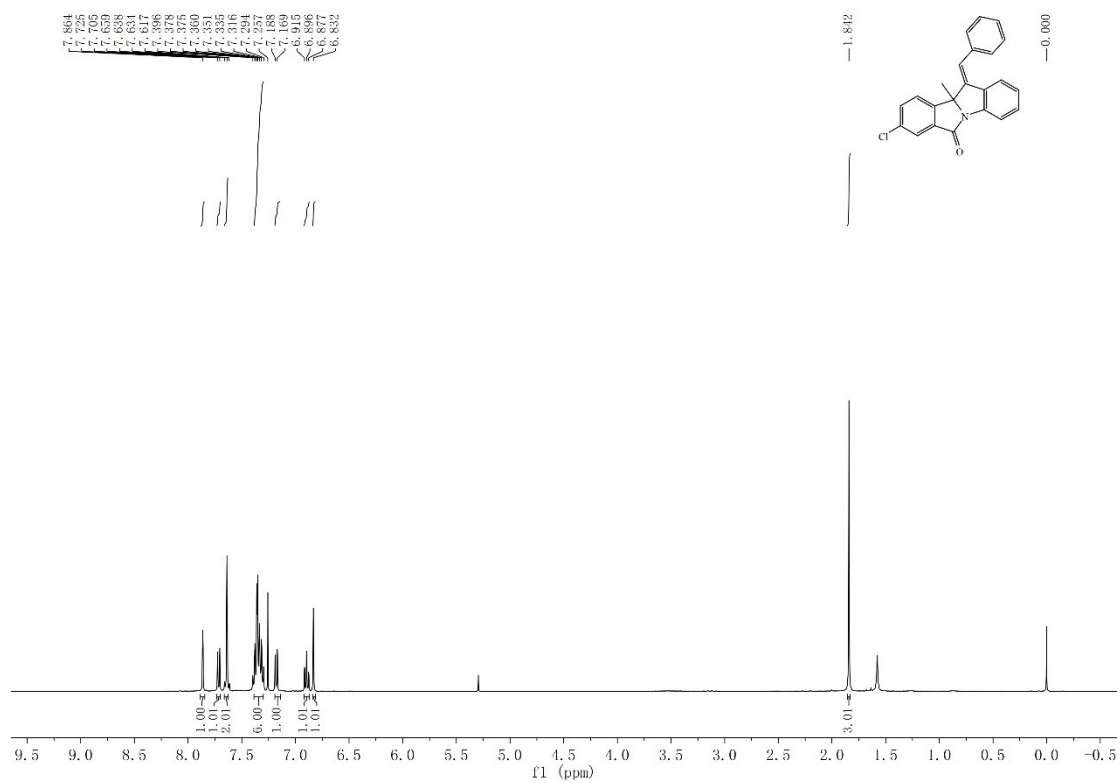
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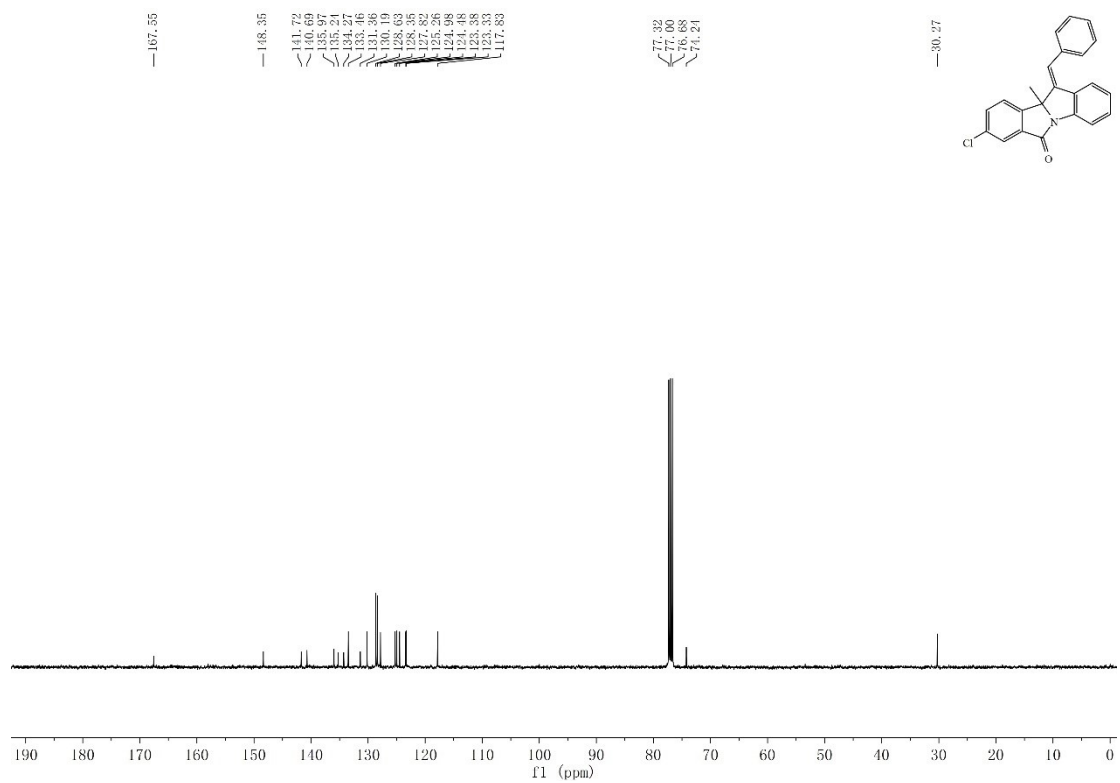
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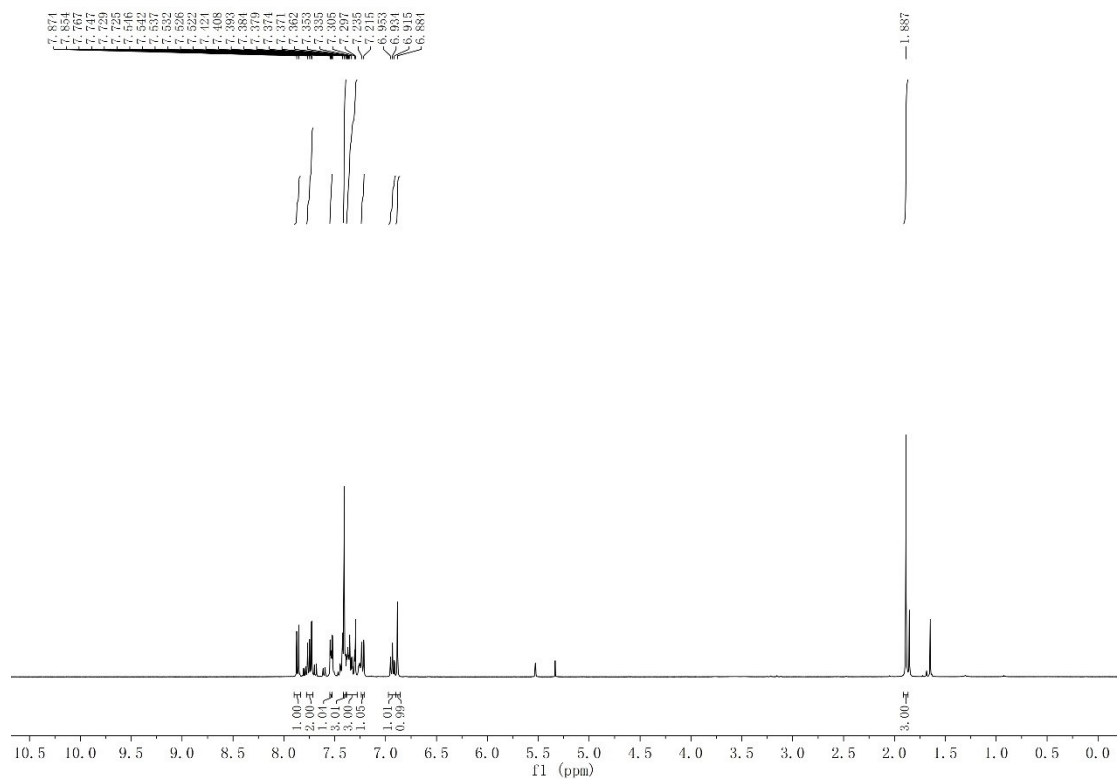
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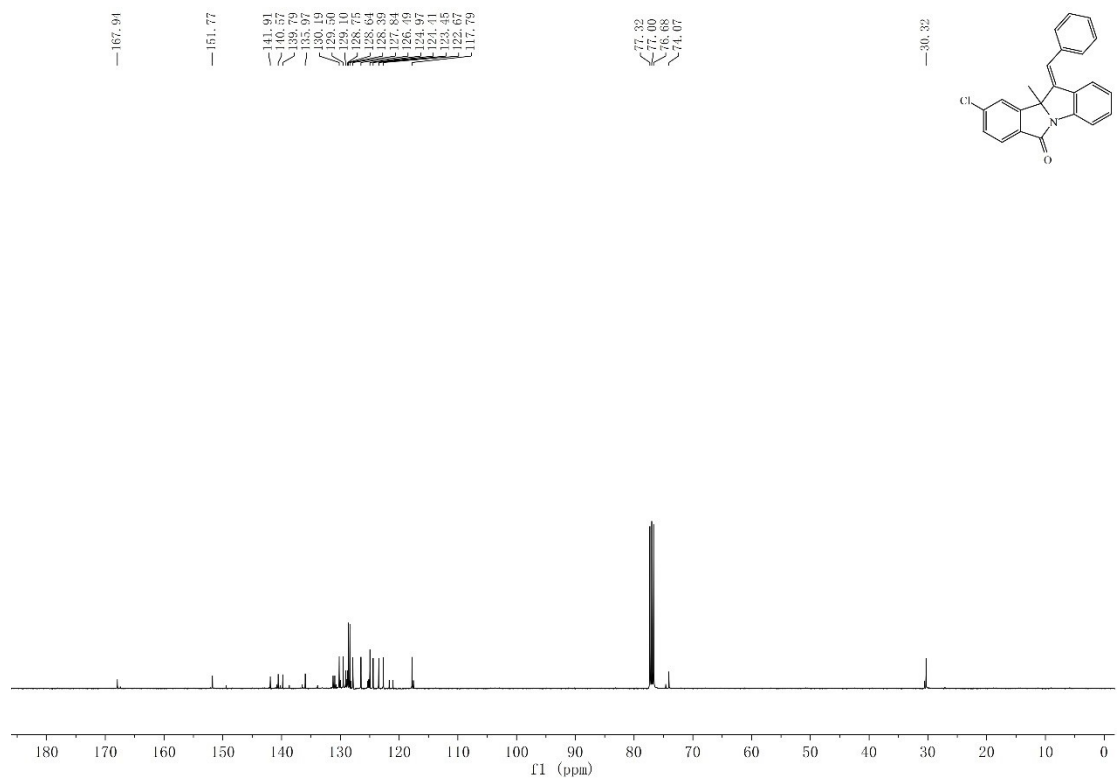
3f-¹³C



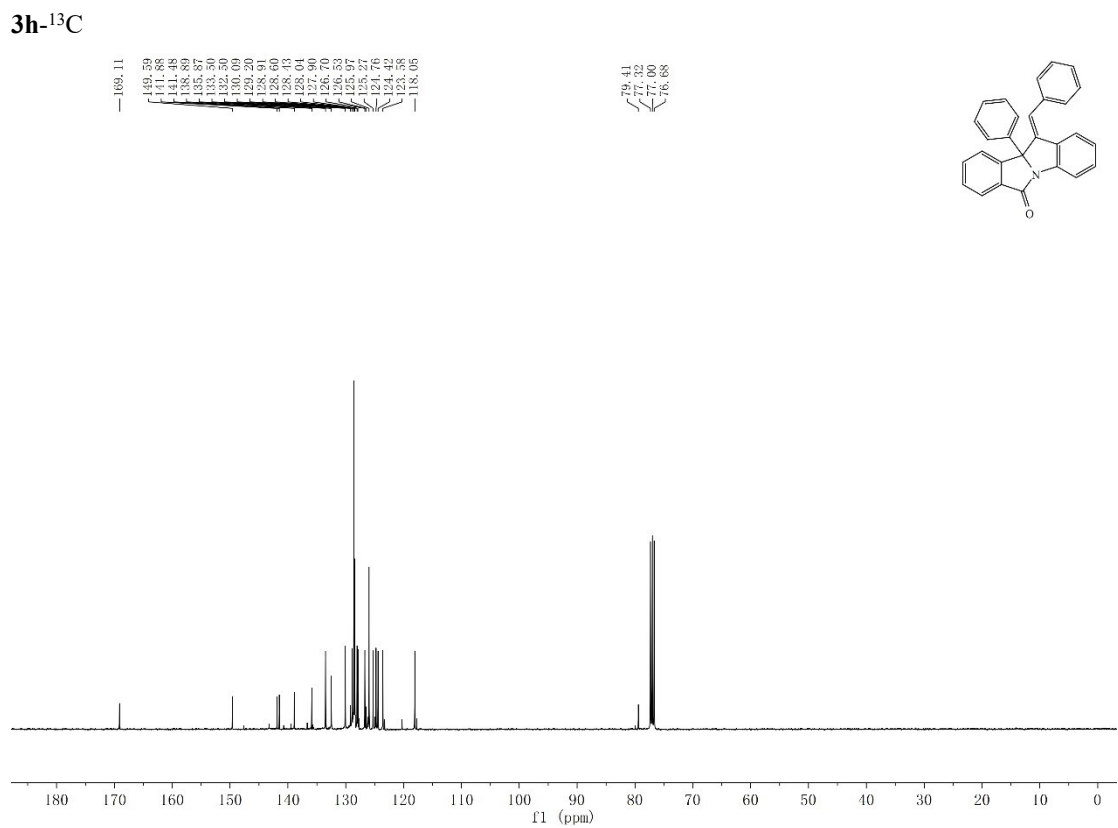
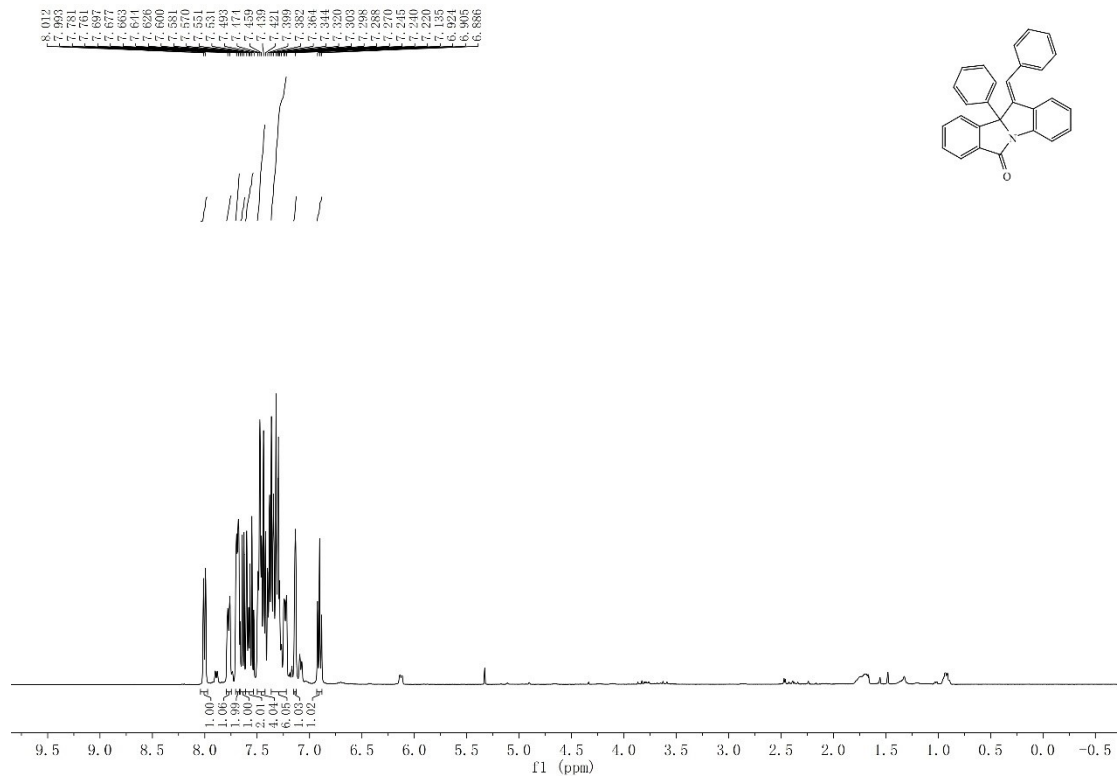
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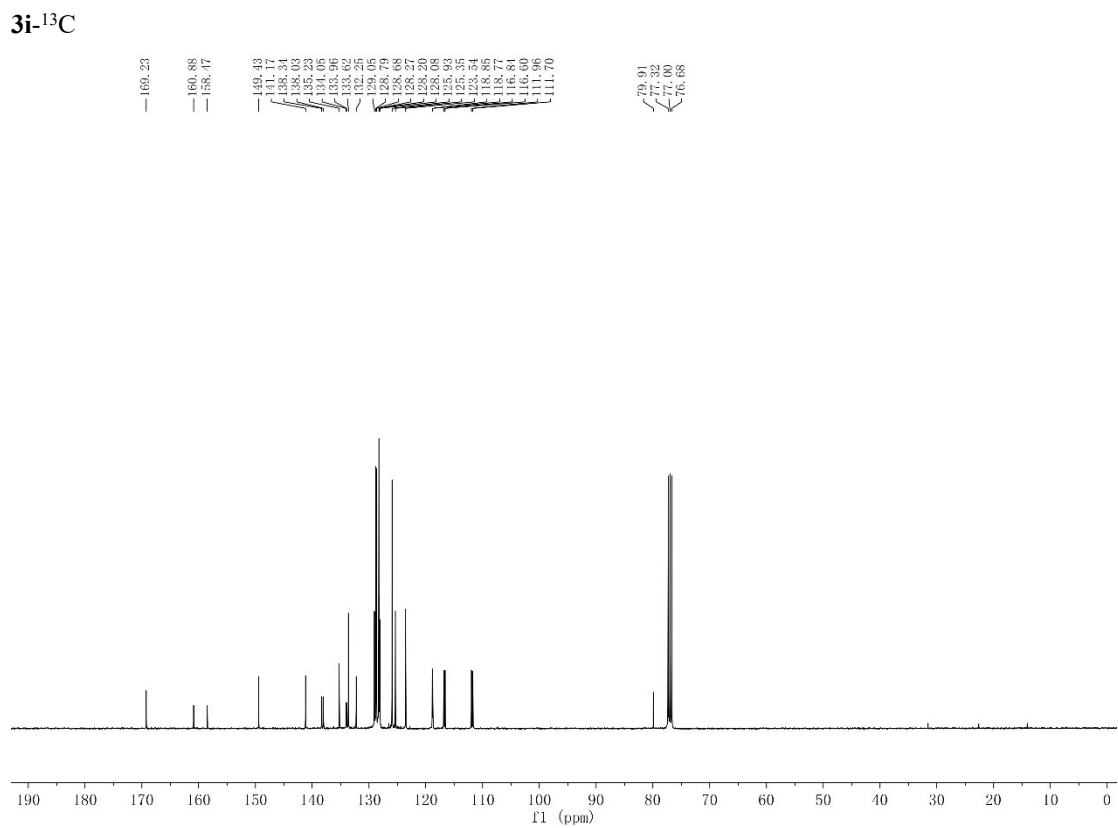
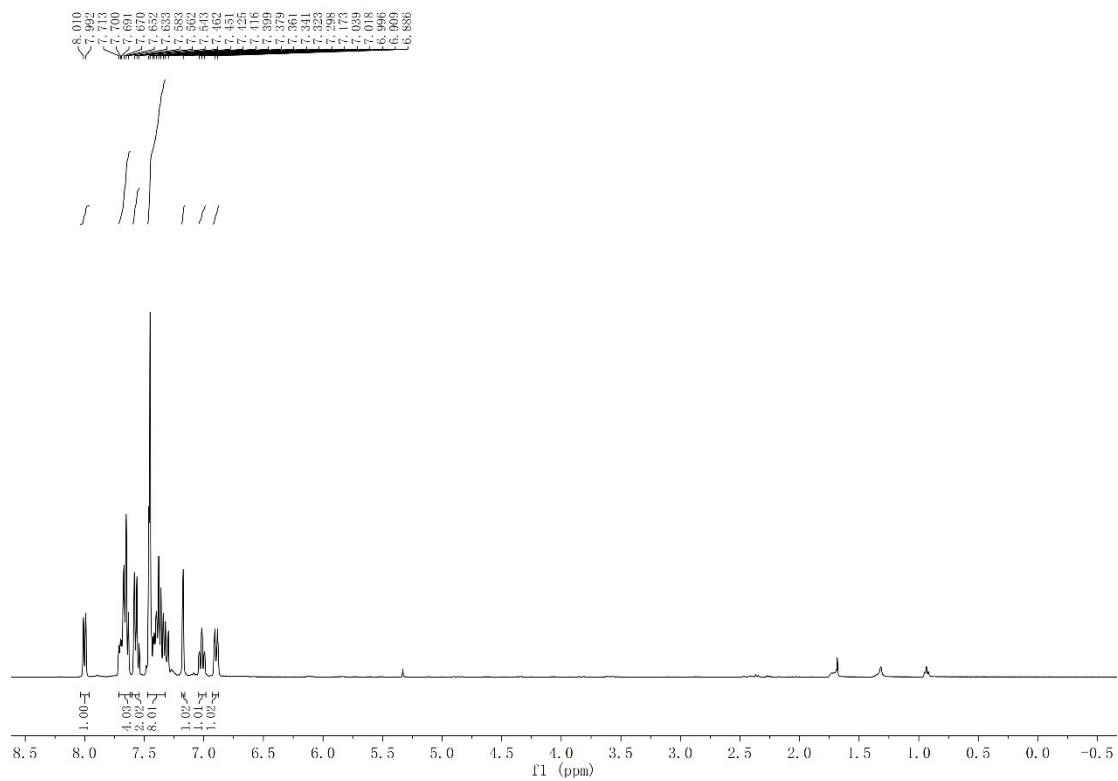
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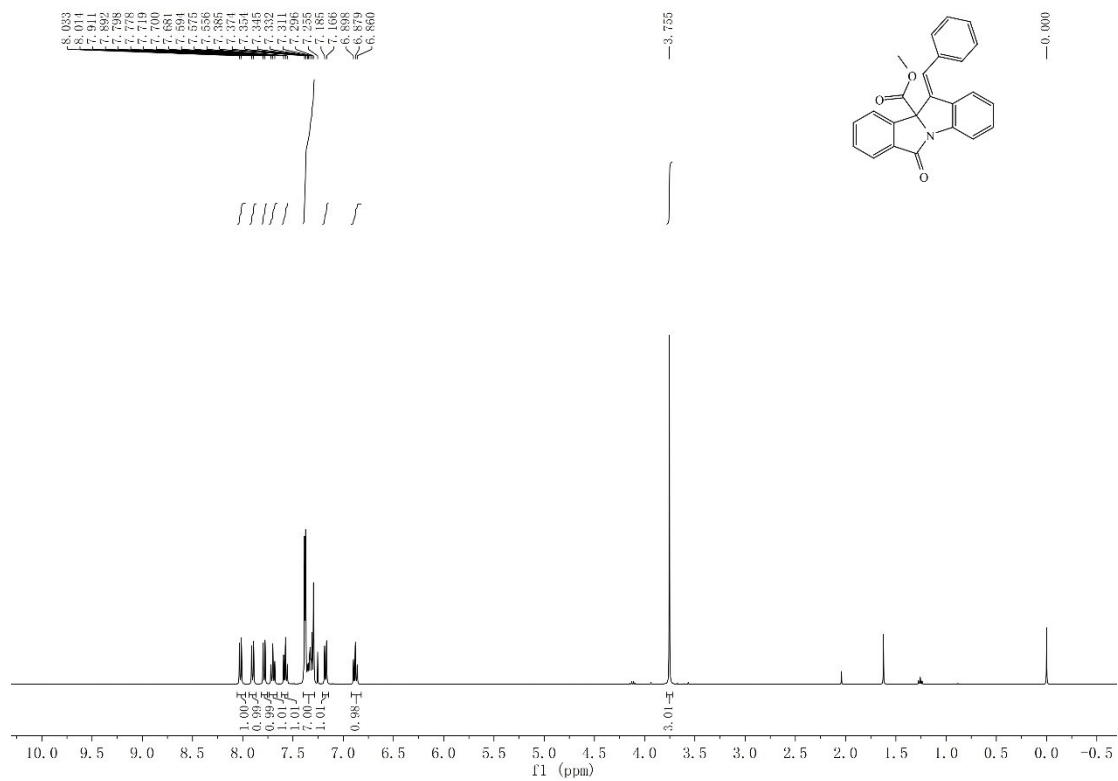
3h-¹H



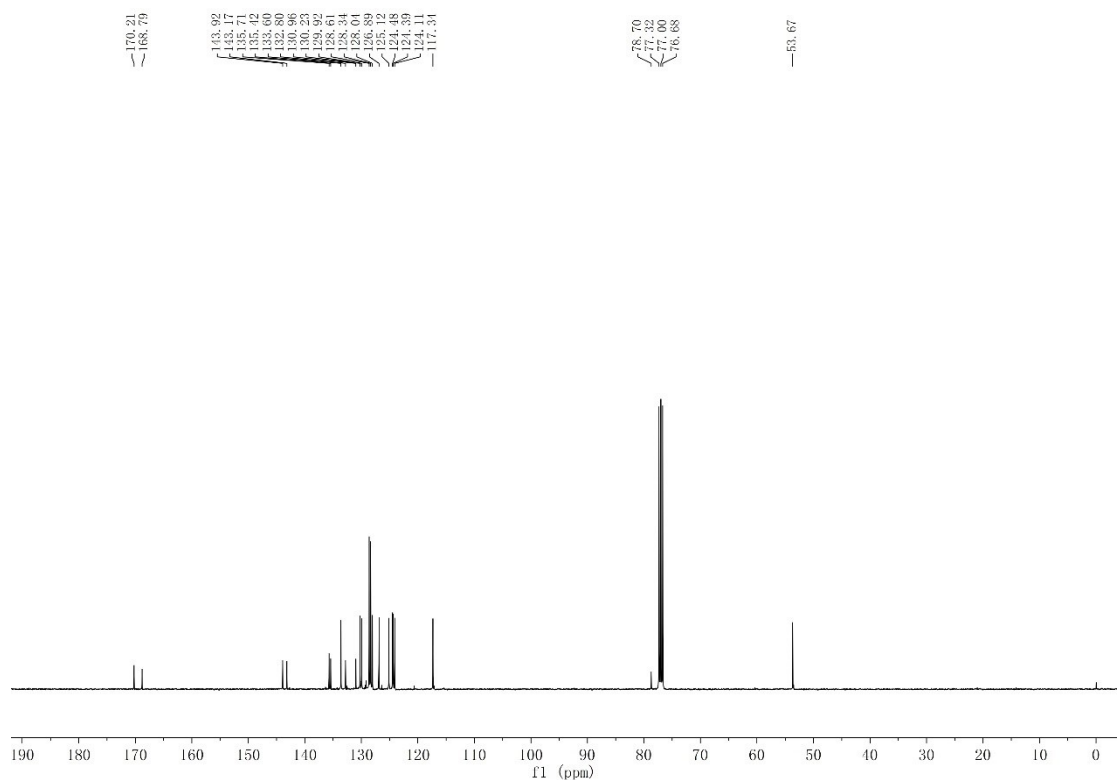
3i-¹H



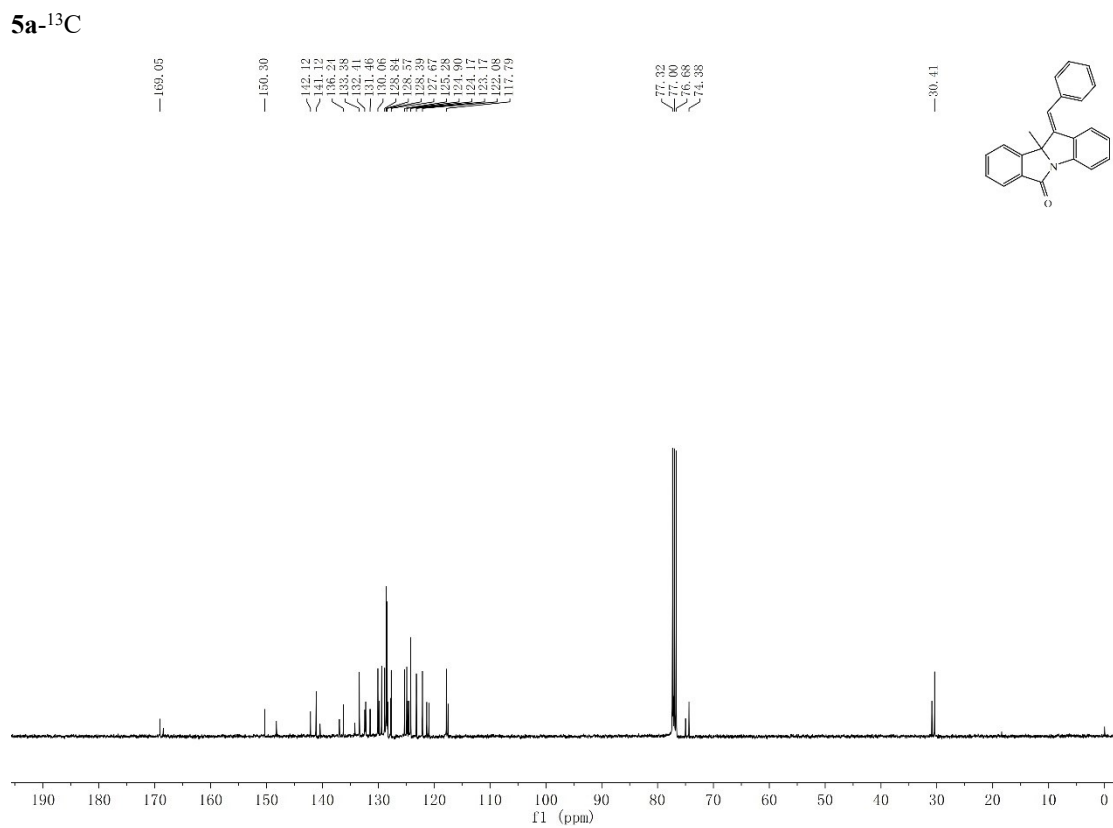
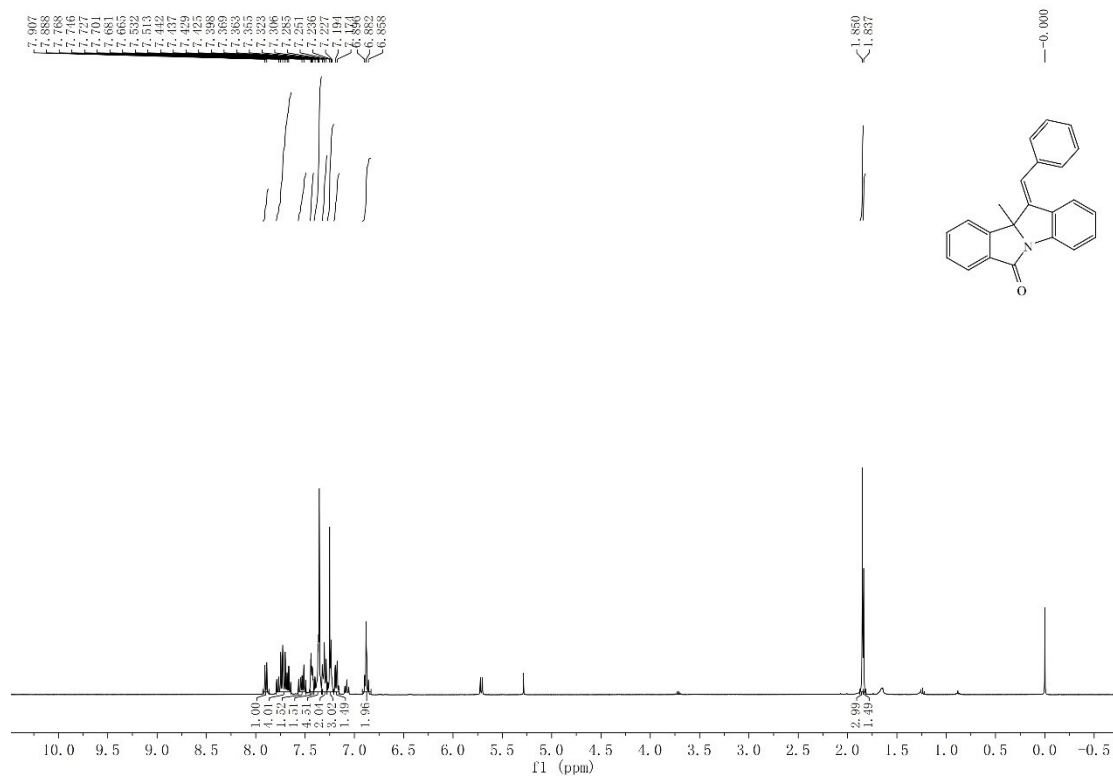
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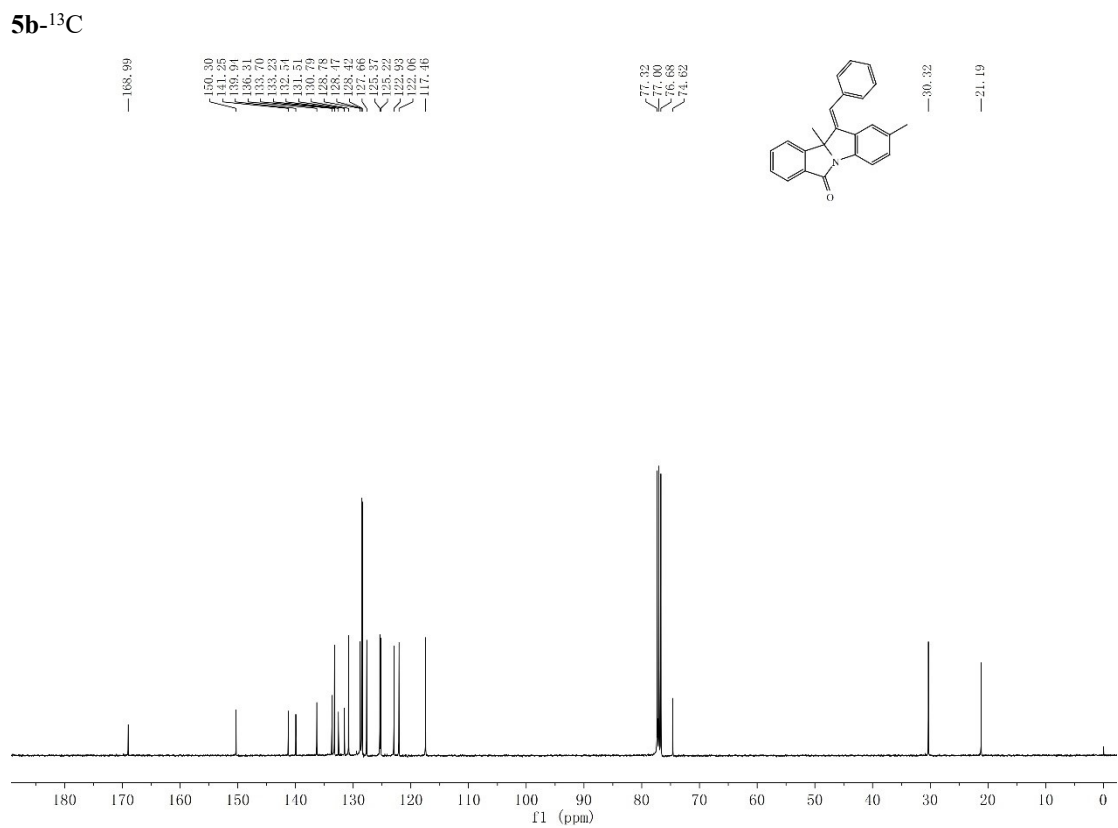
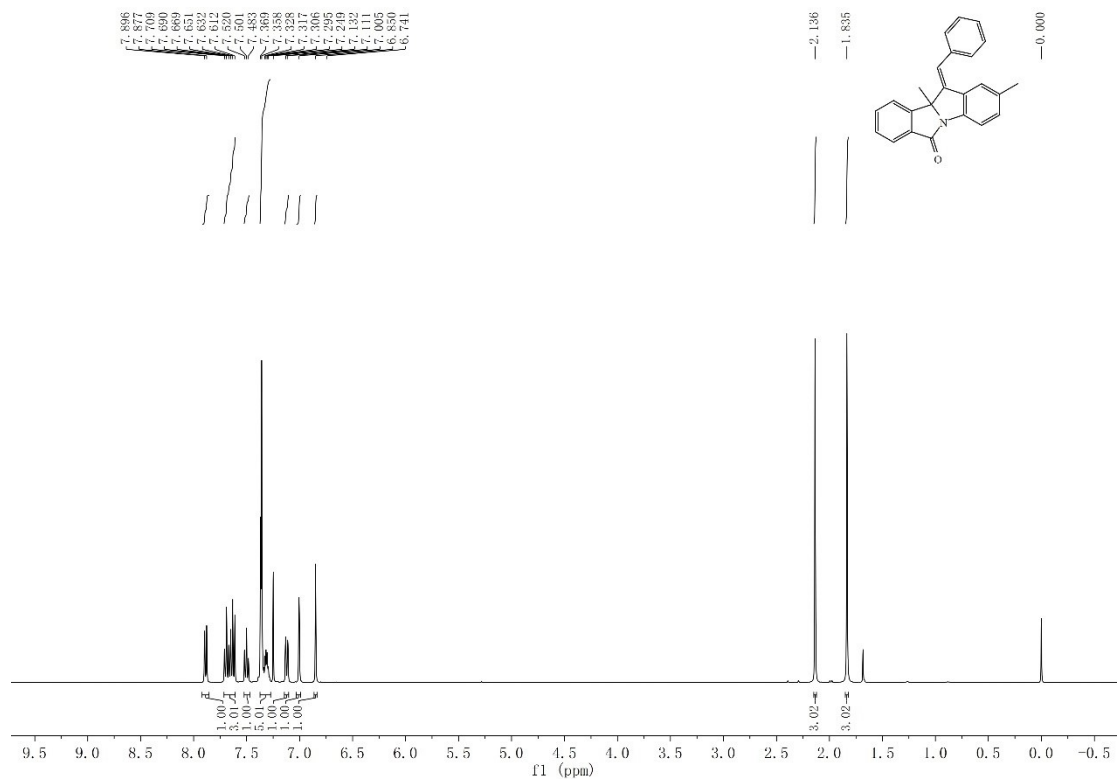
3j-¹³C



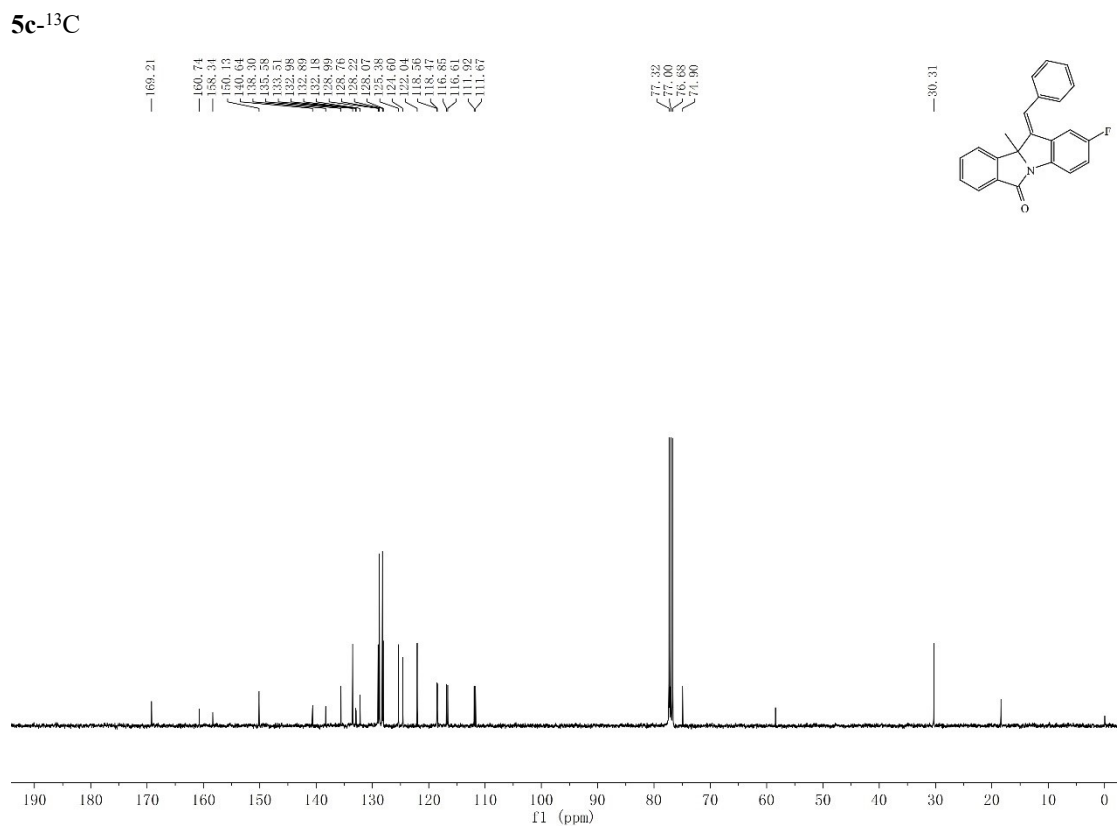
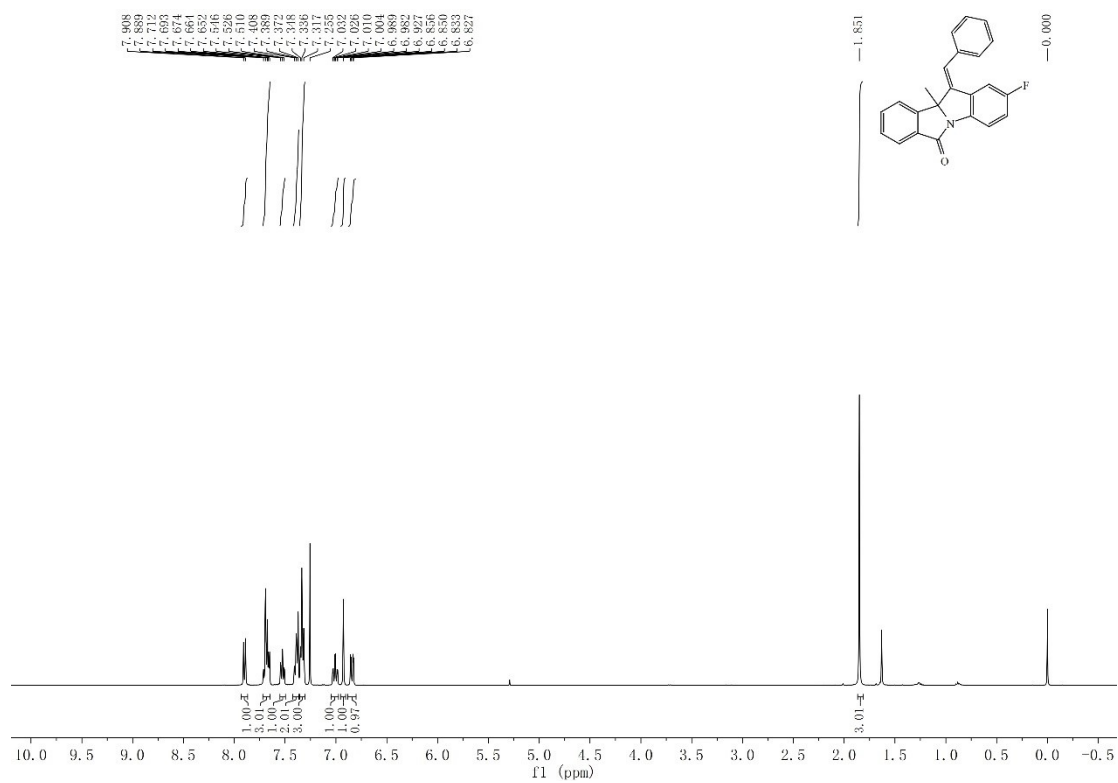
5a-¹H



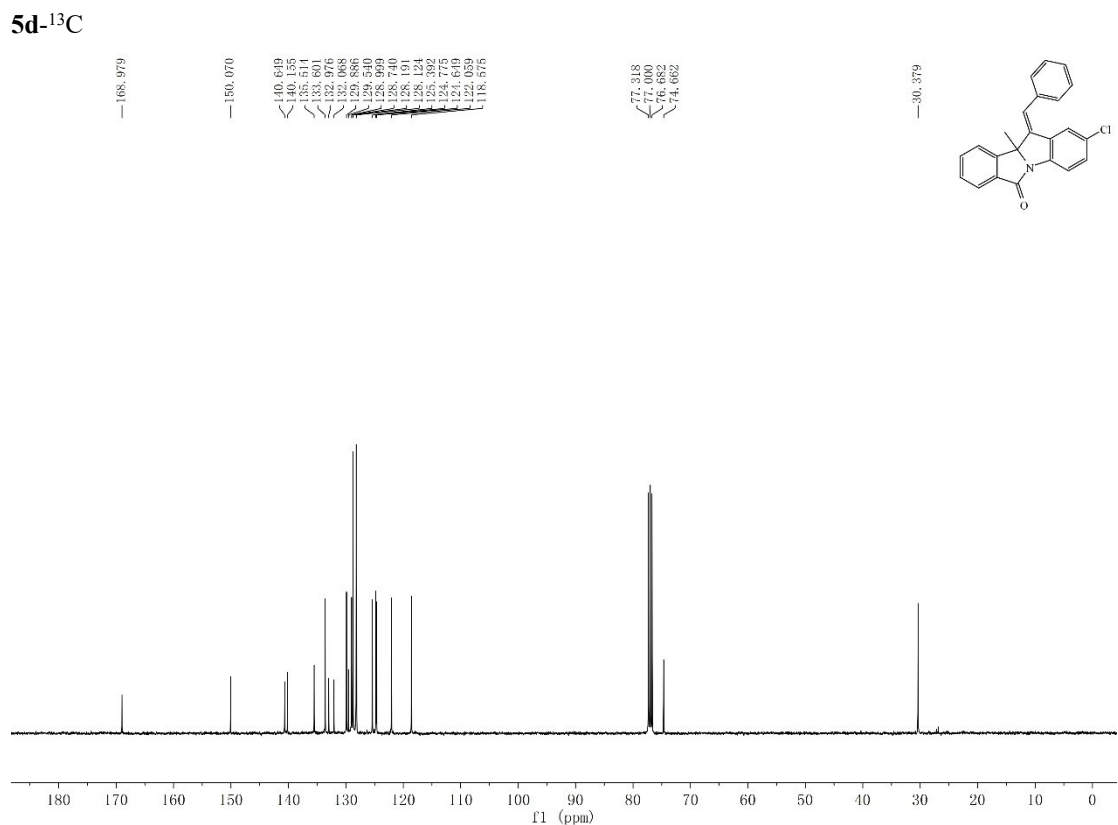
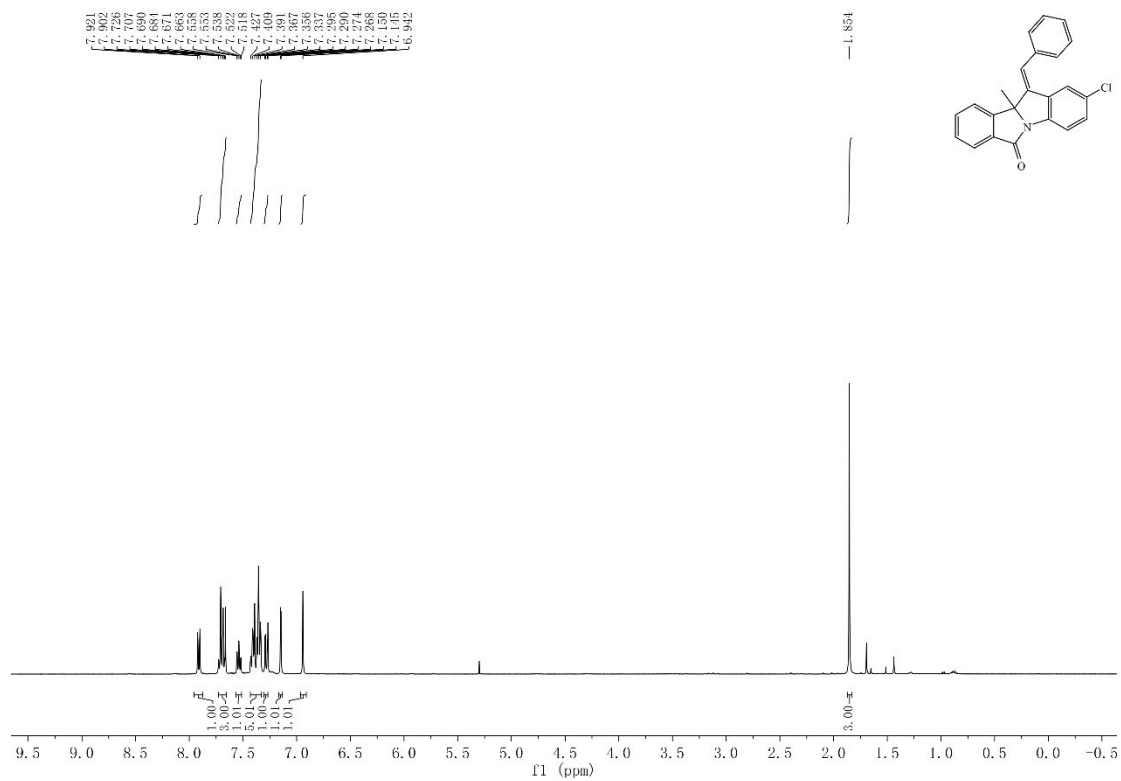
5b-¹H



5c-¹H

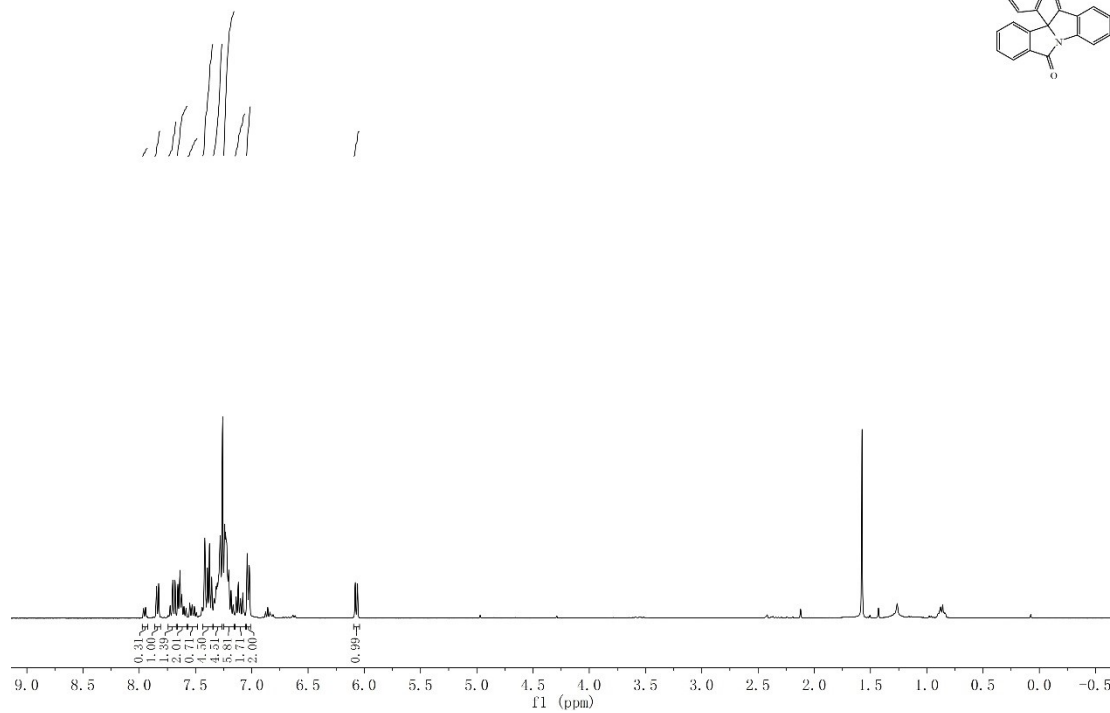
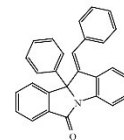


5d-¹H



5e-¹H

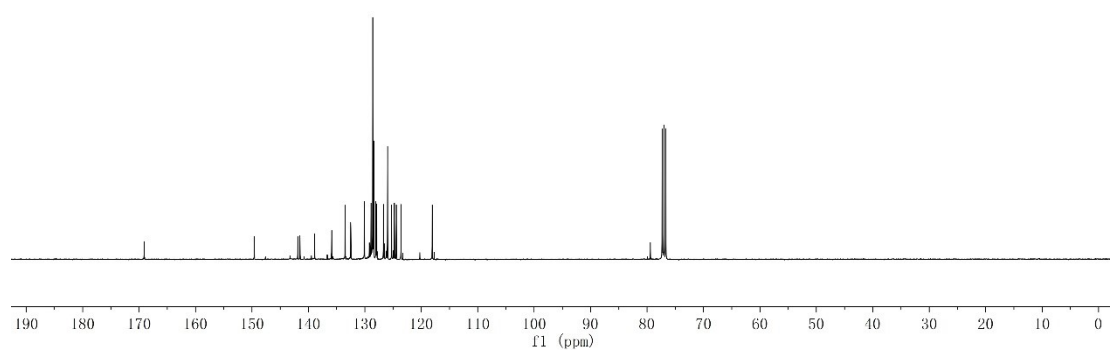
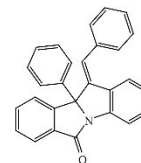
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7.022
6.980



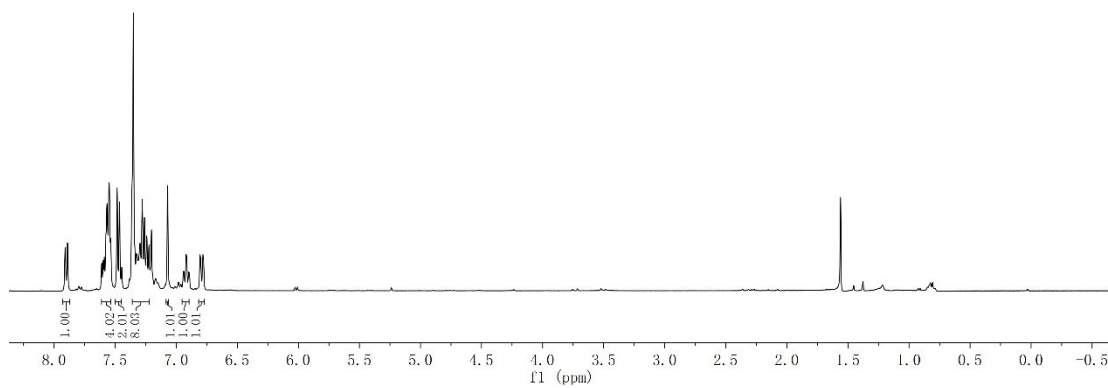
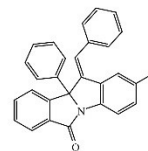
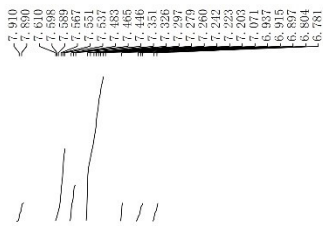
5e-¹³C

169.11
149.59
141.88
141.48
135.89
135.50
132.50
130.09
128.20
128.60
128.43
128.04
127.70
126.53
125.97
125.27
124.46
123.58
118.05

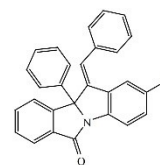
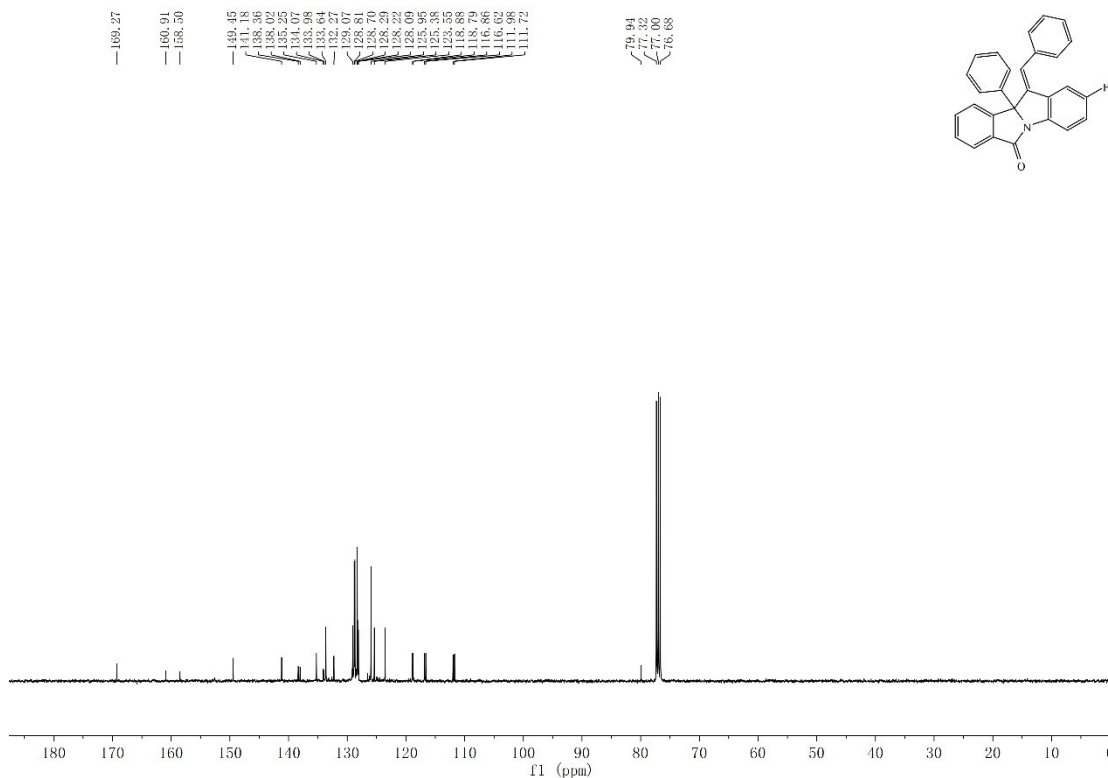
79.41
77.32
77.00
76.08



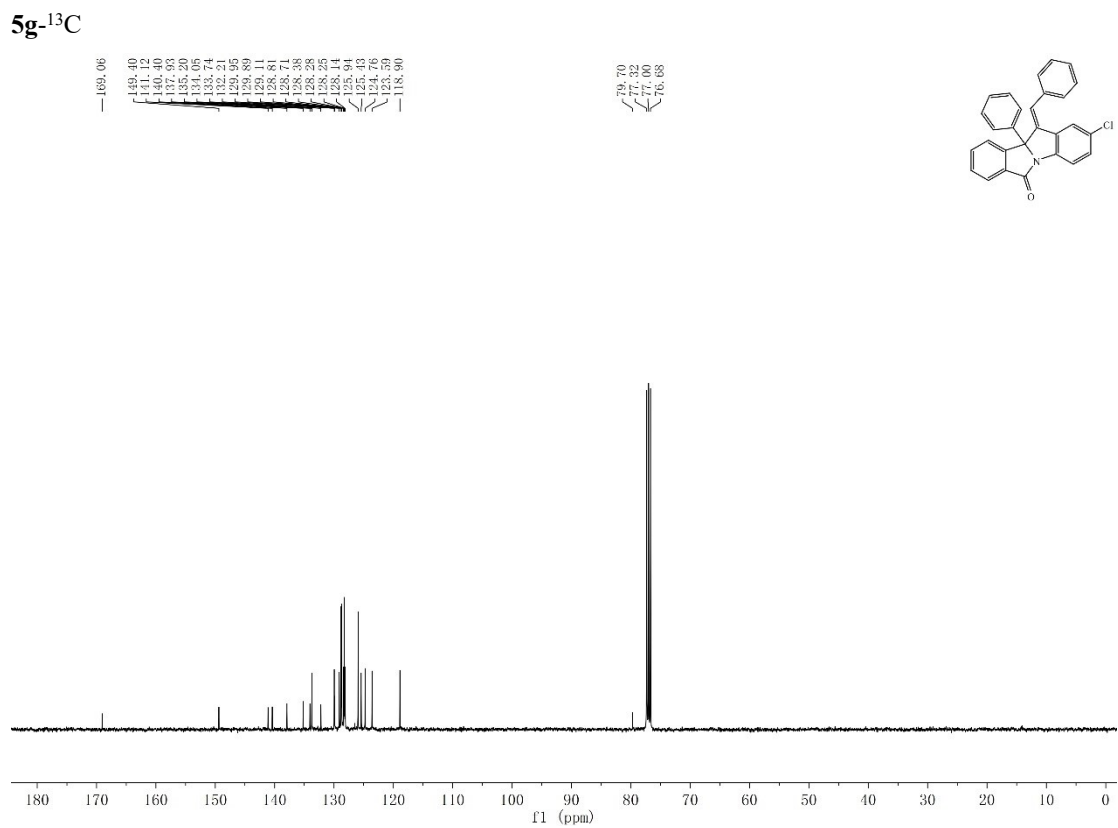
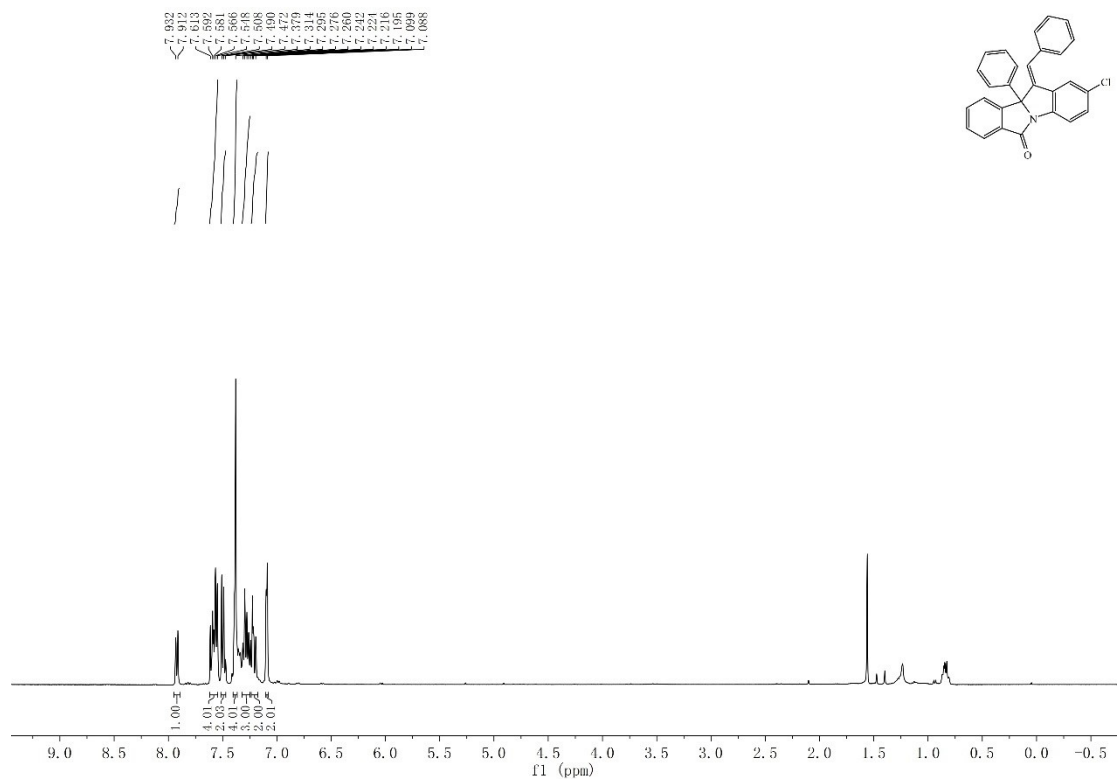
5f-¹H



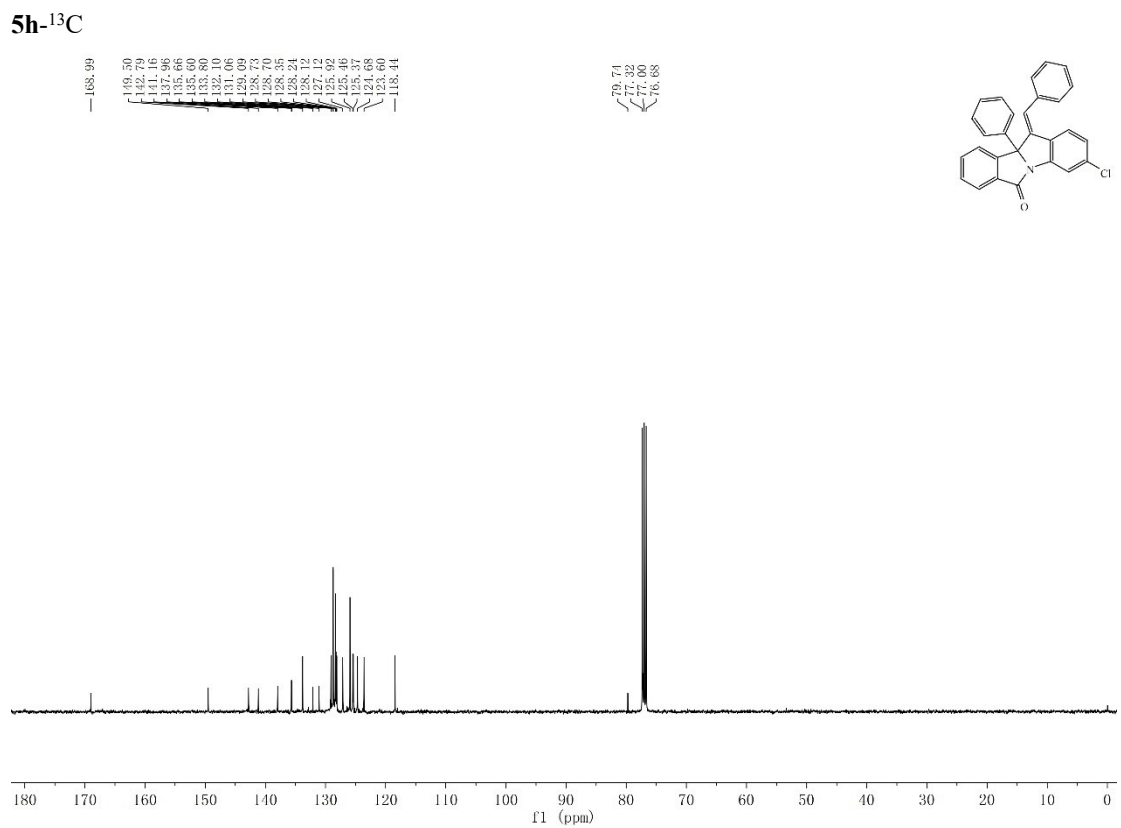
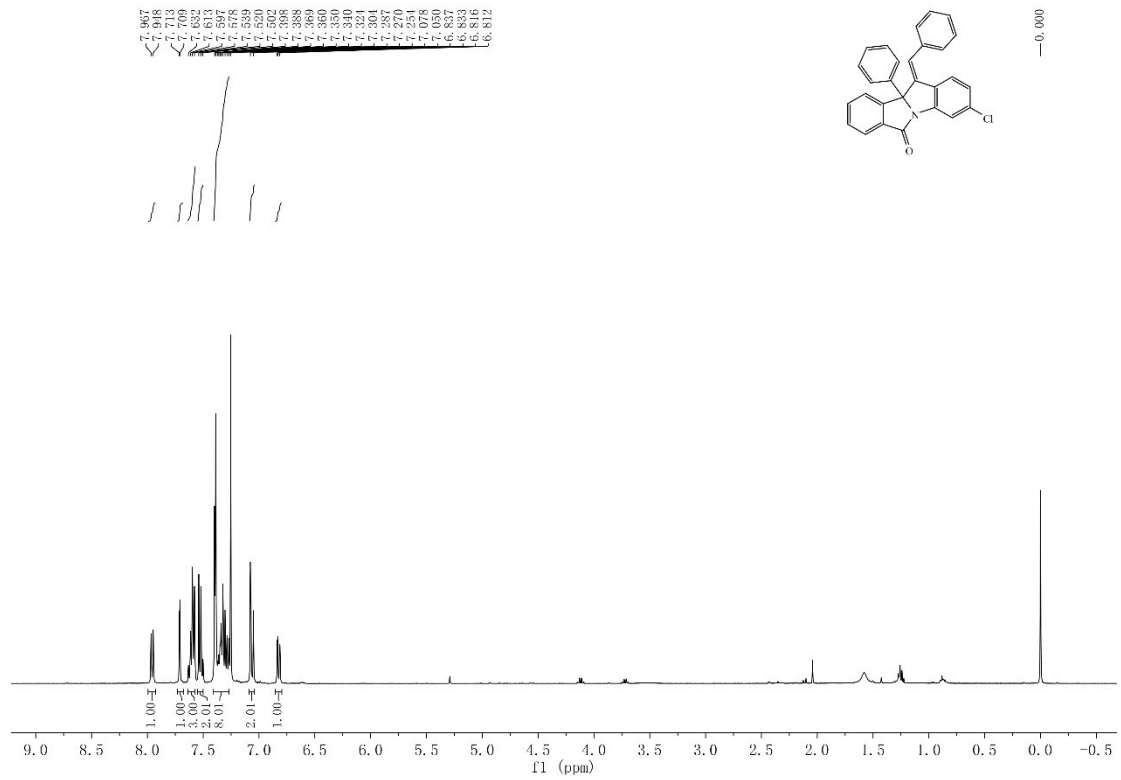
5f-¹³C



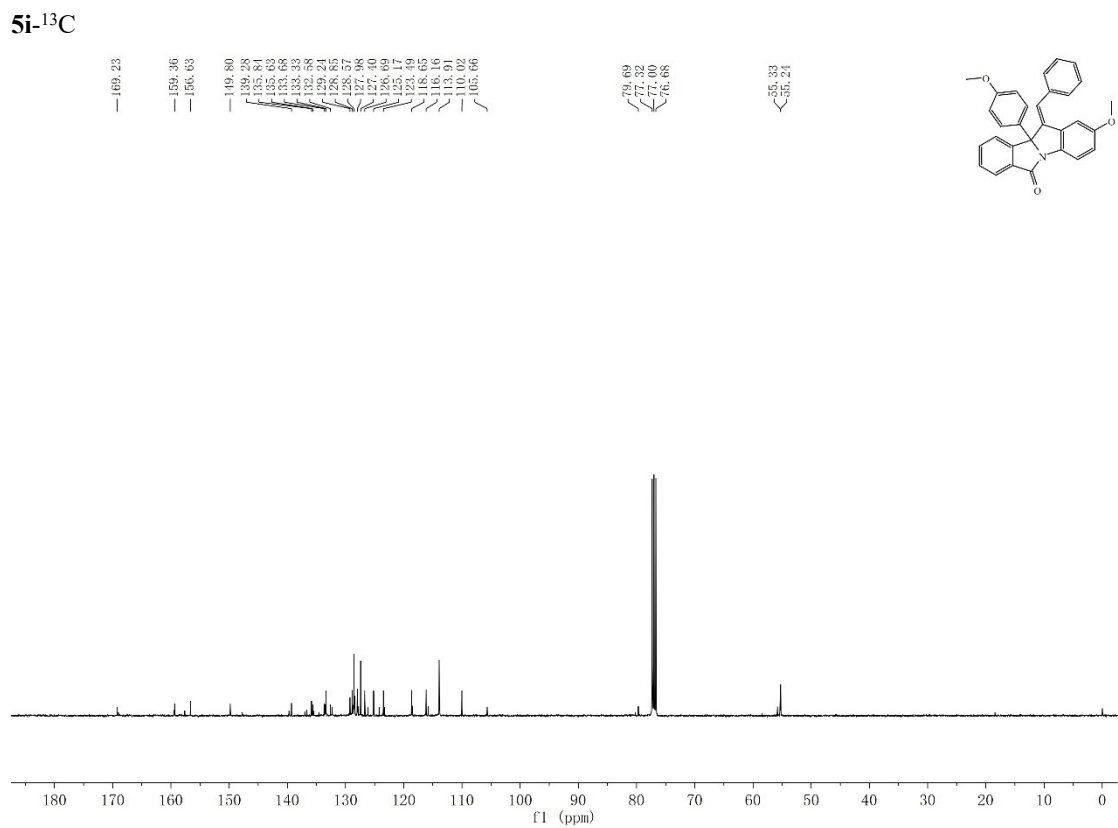
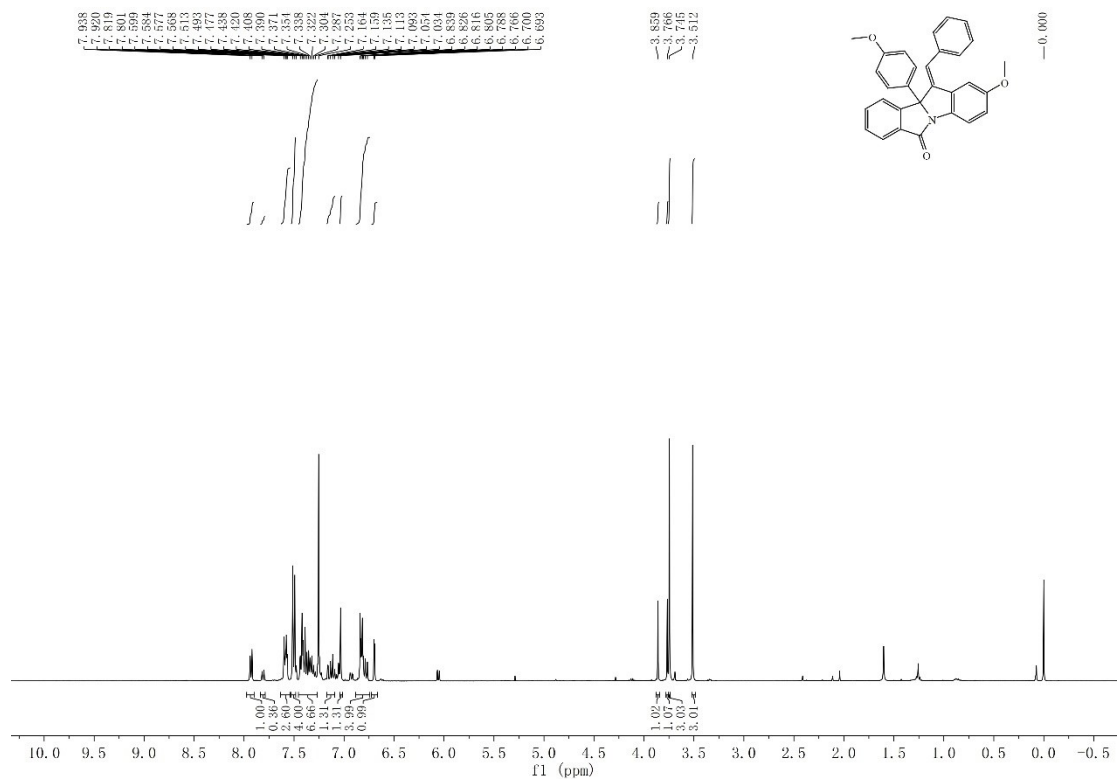
5g-¹H



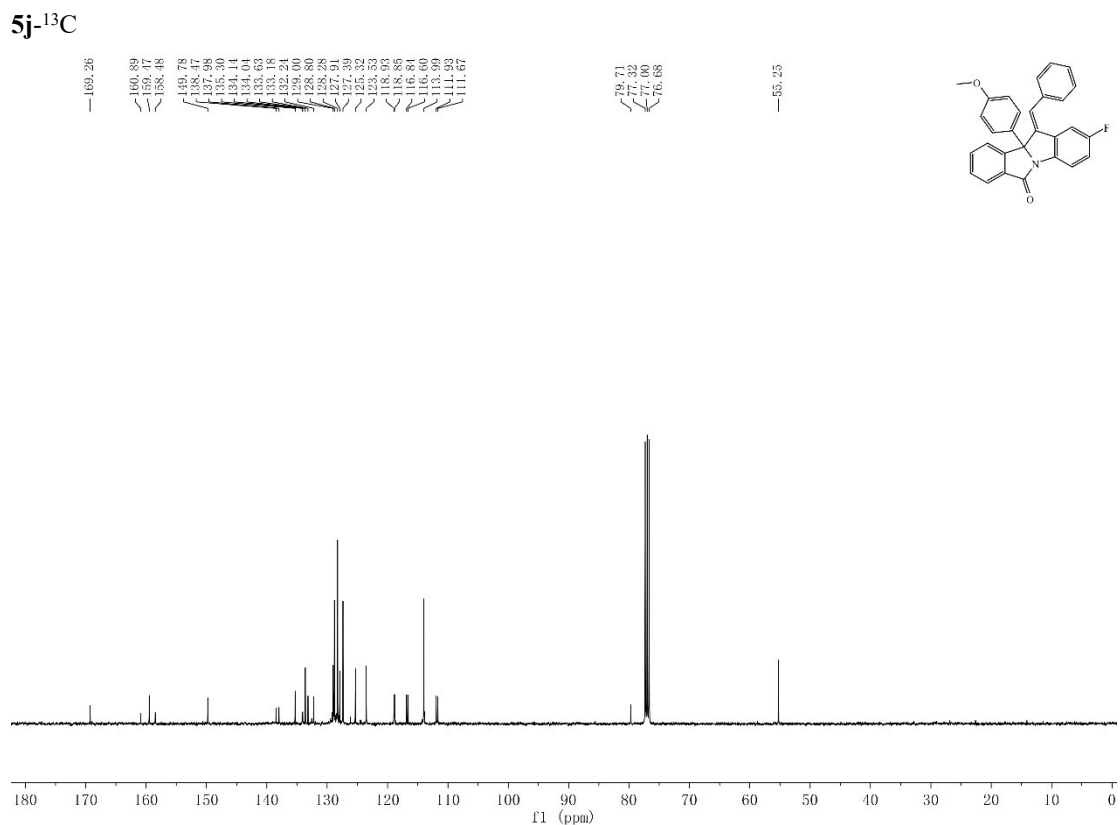
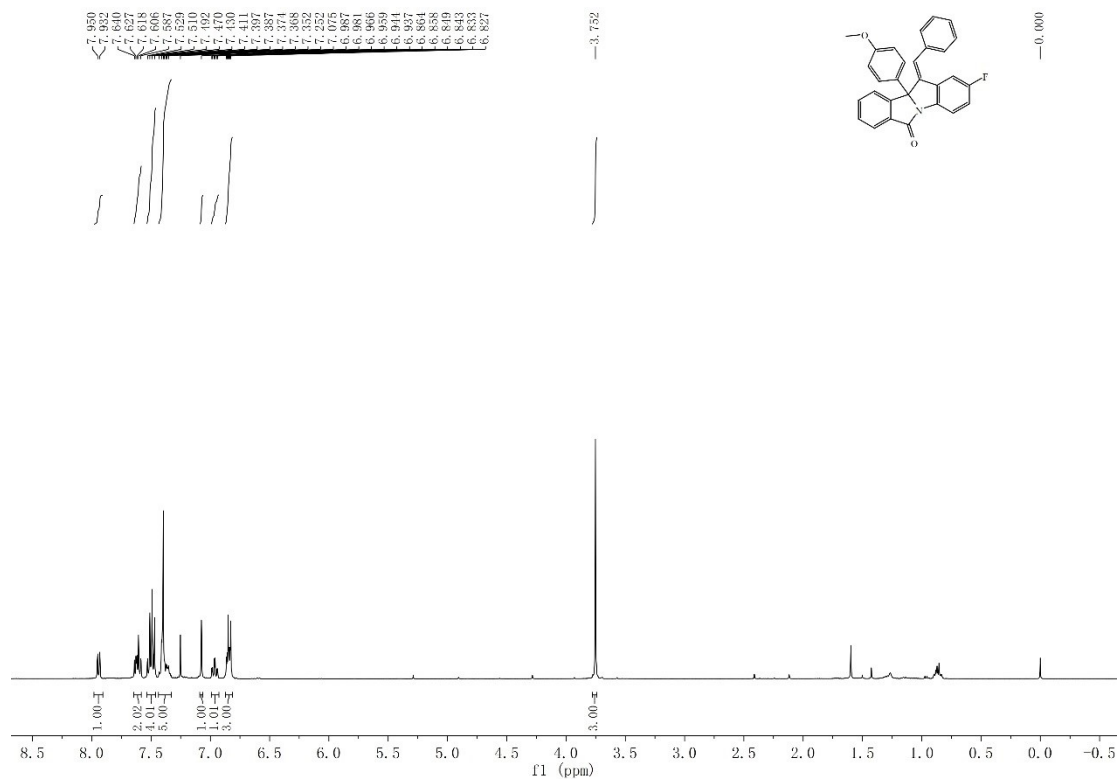
5h-¹H



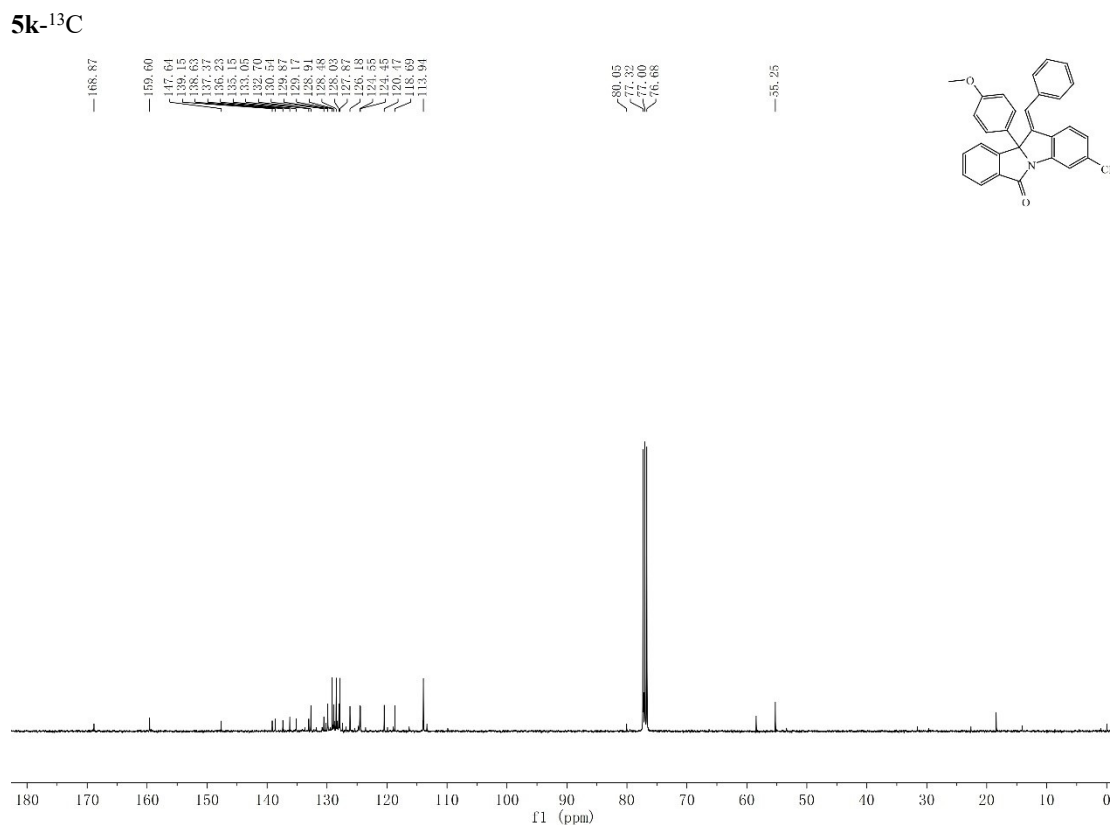
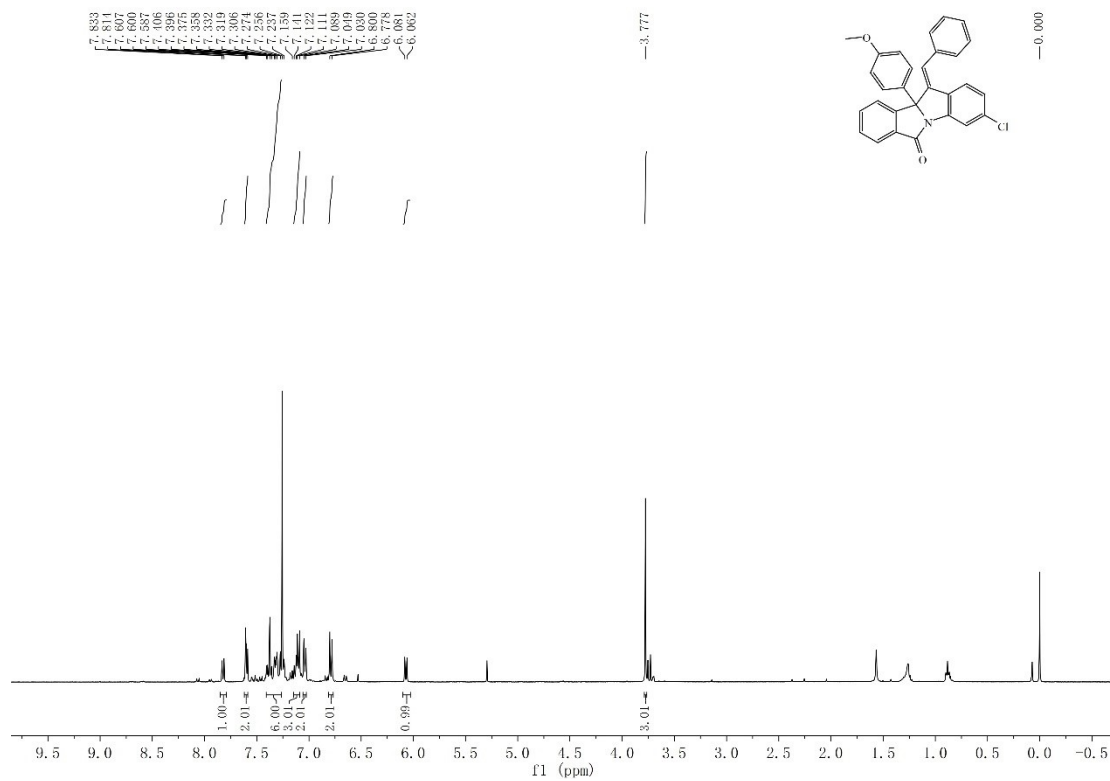
5i-¹H



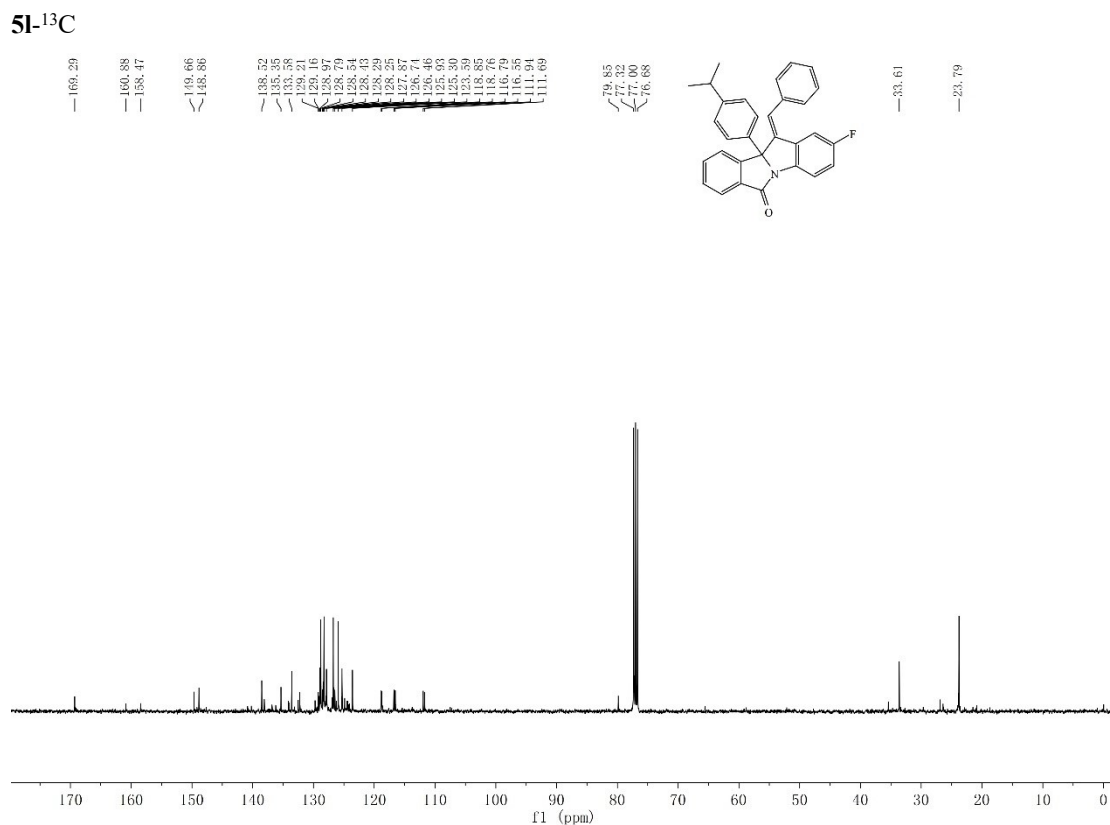
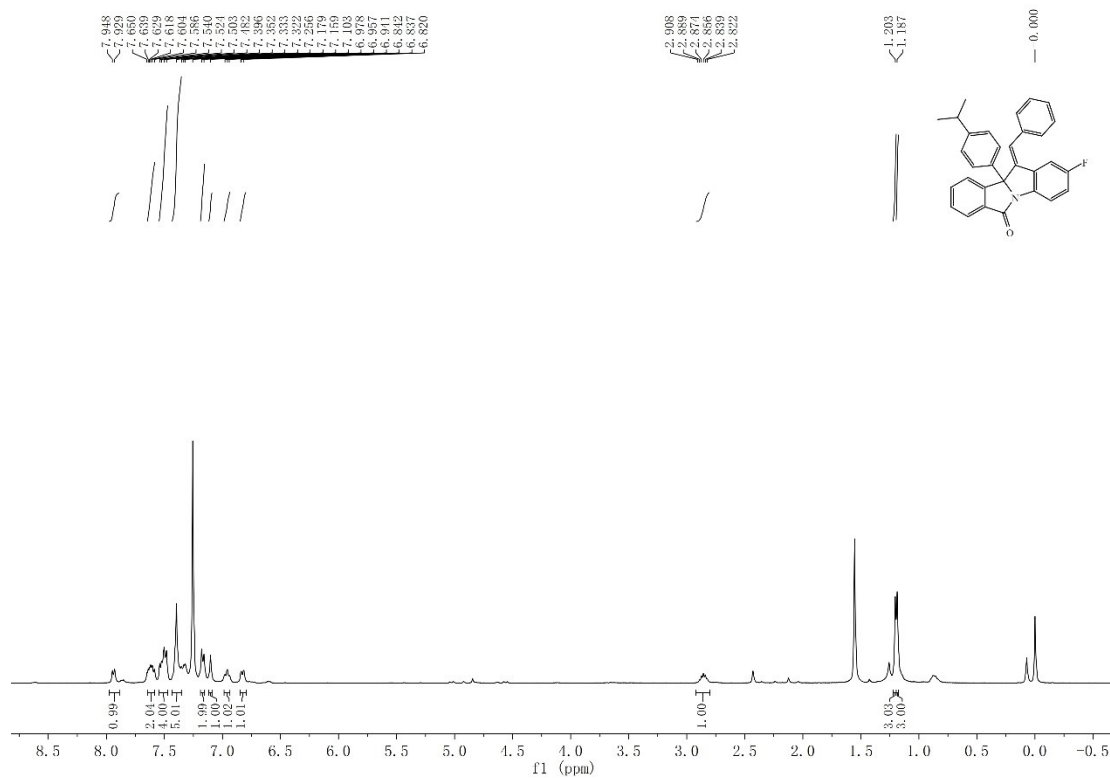
5j-¹H



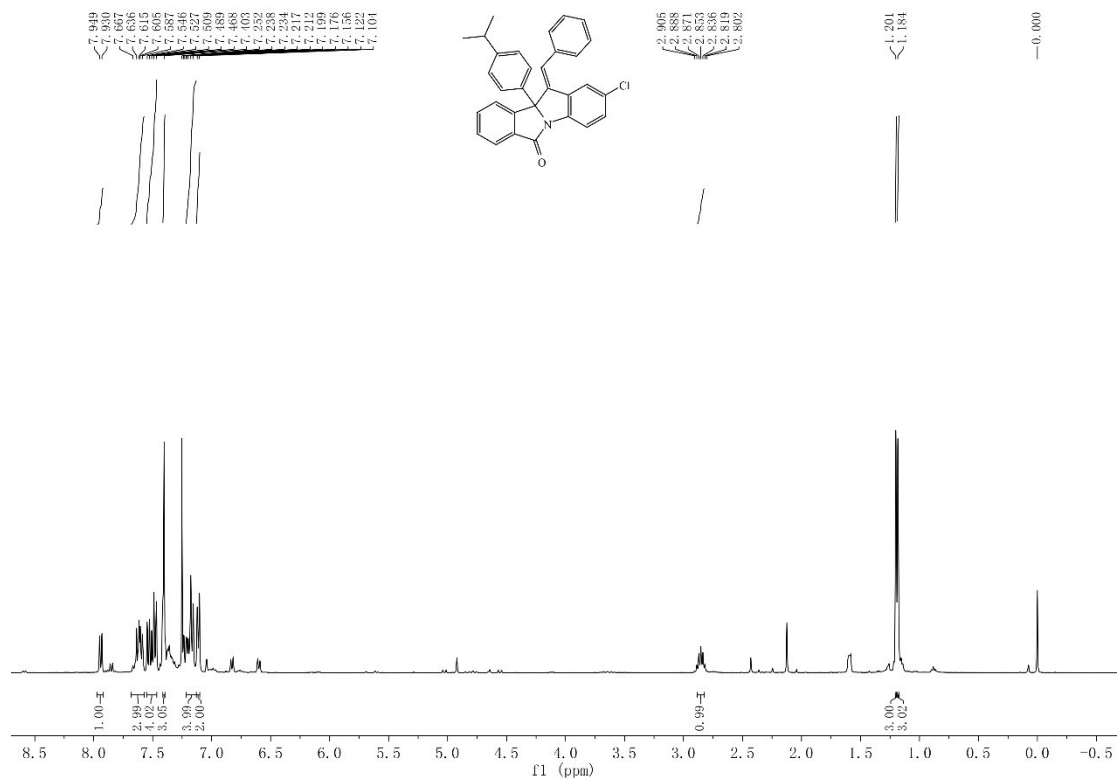
5k-¹H



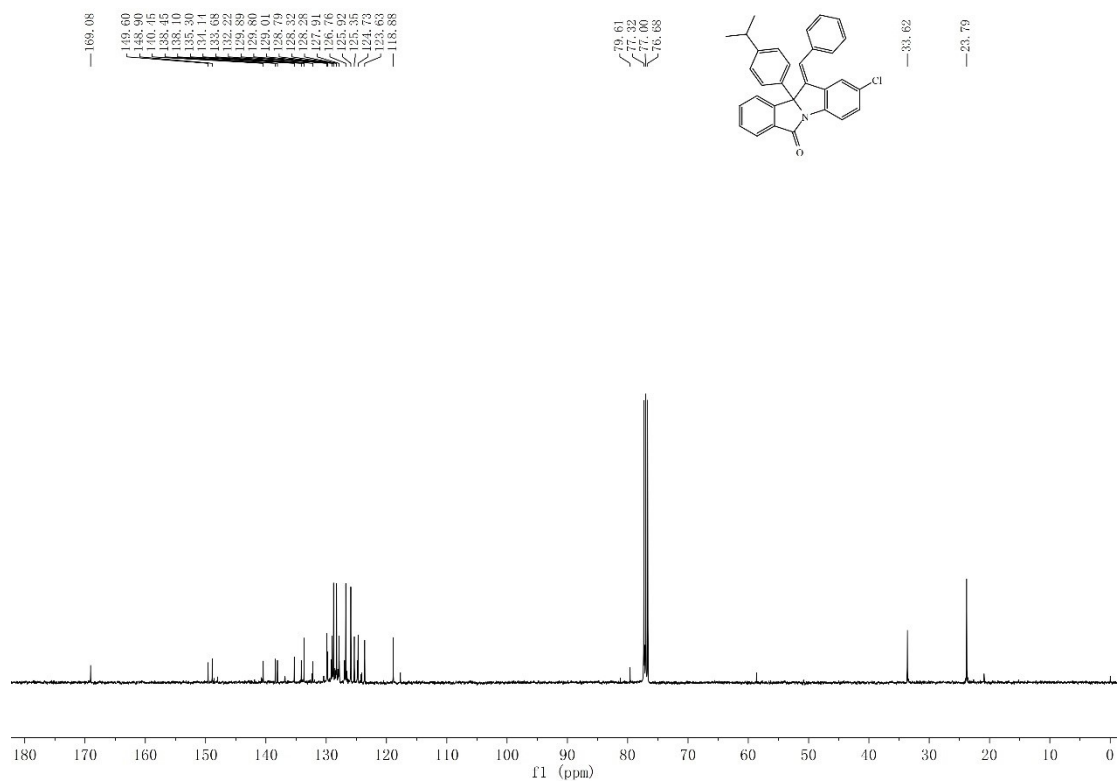
5l-¹H



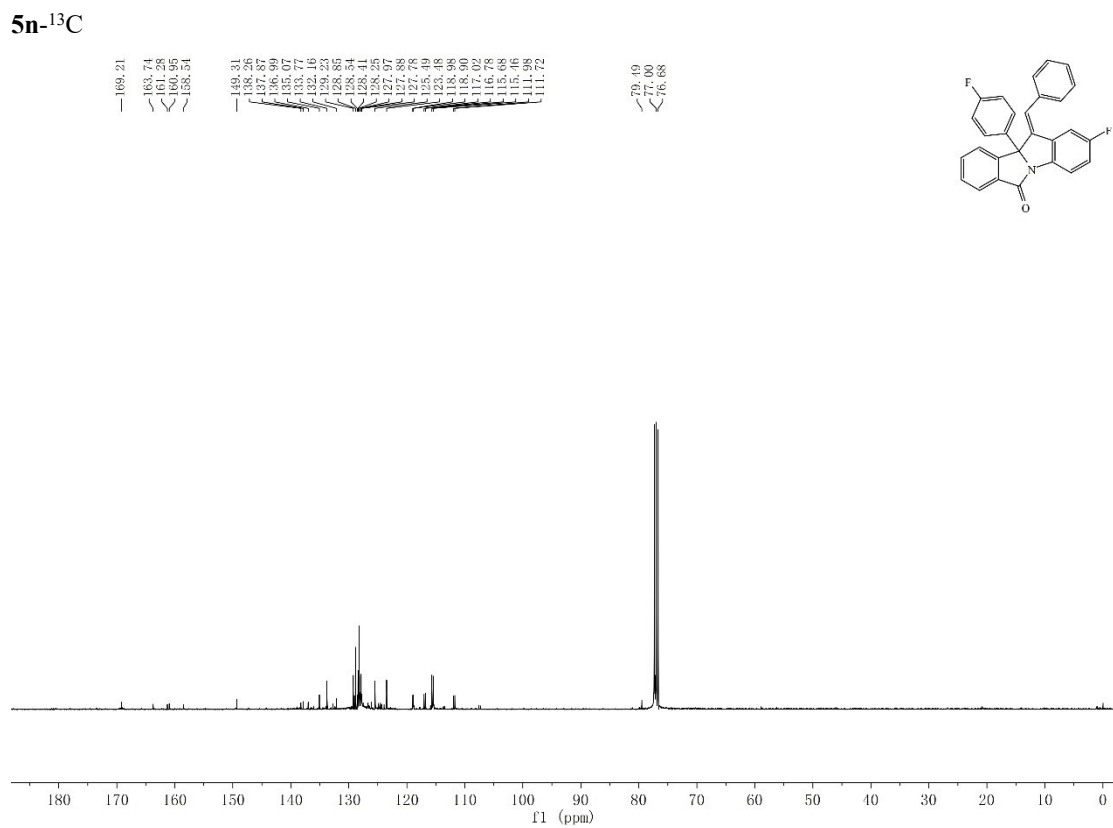
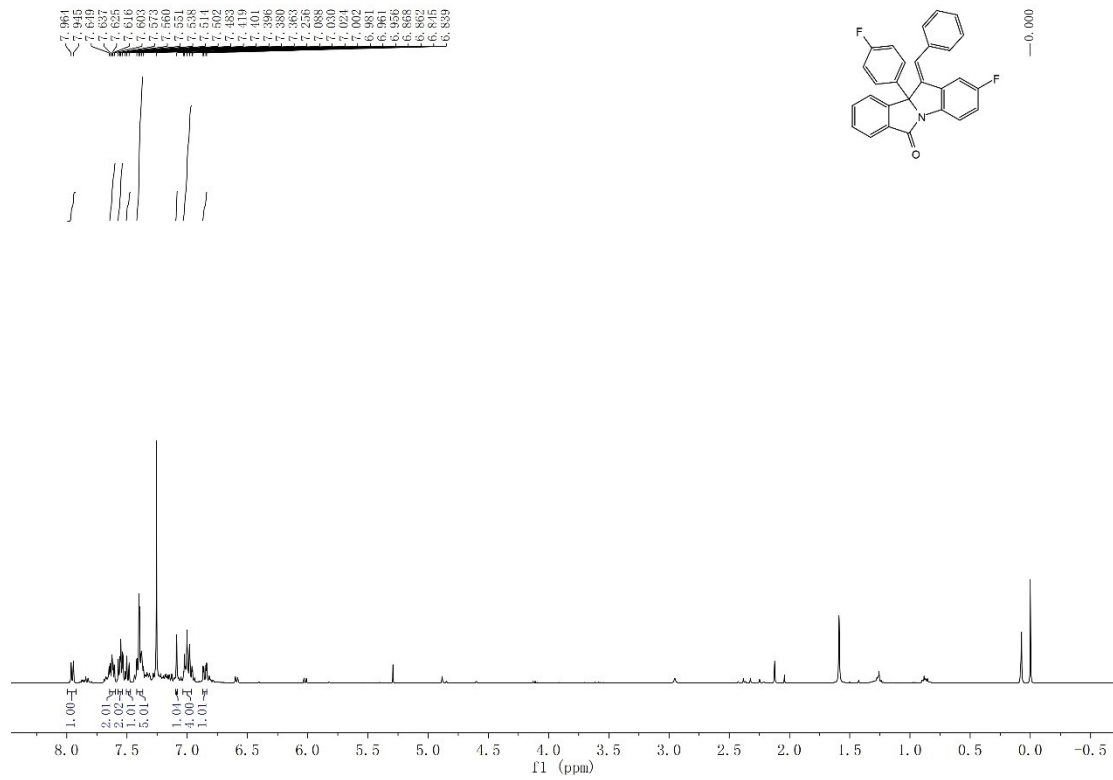
5m-¹H



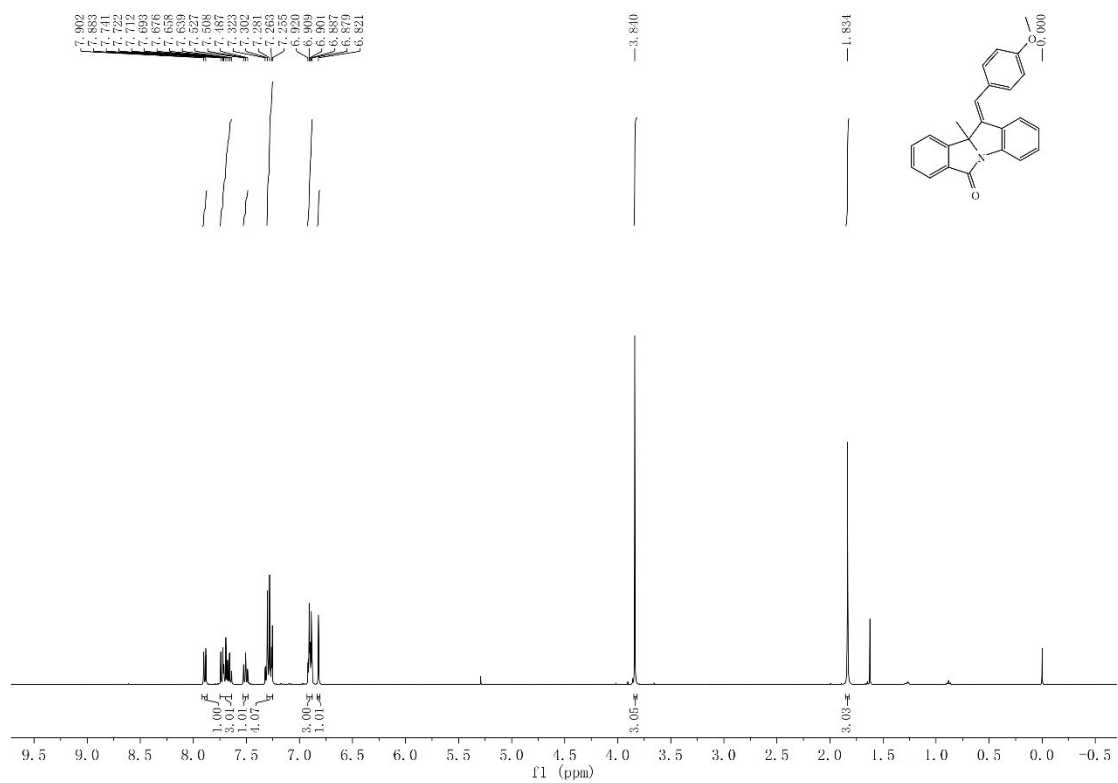
5m-¹³C



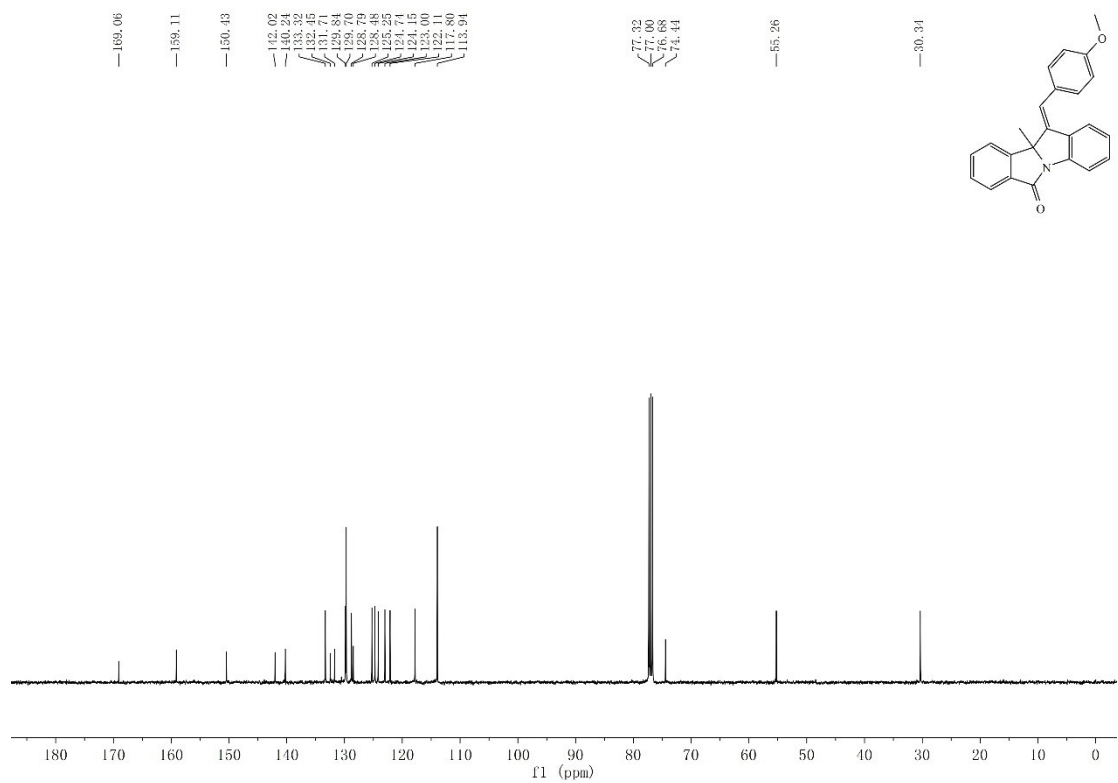
5n-¹H



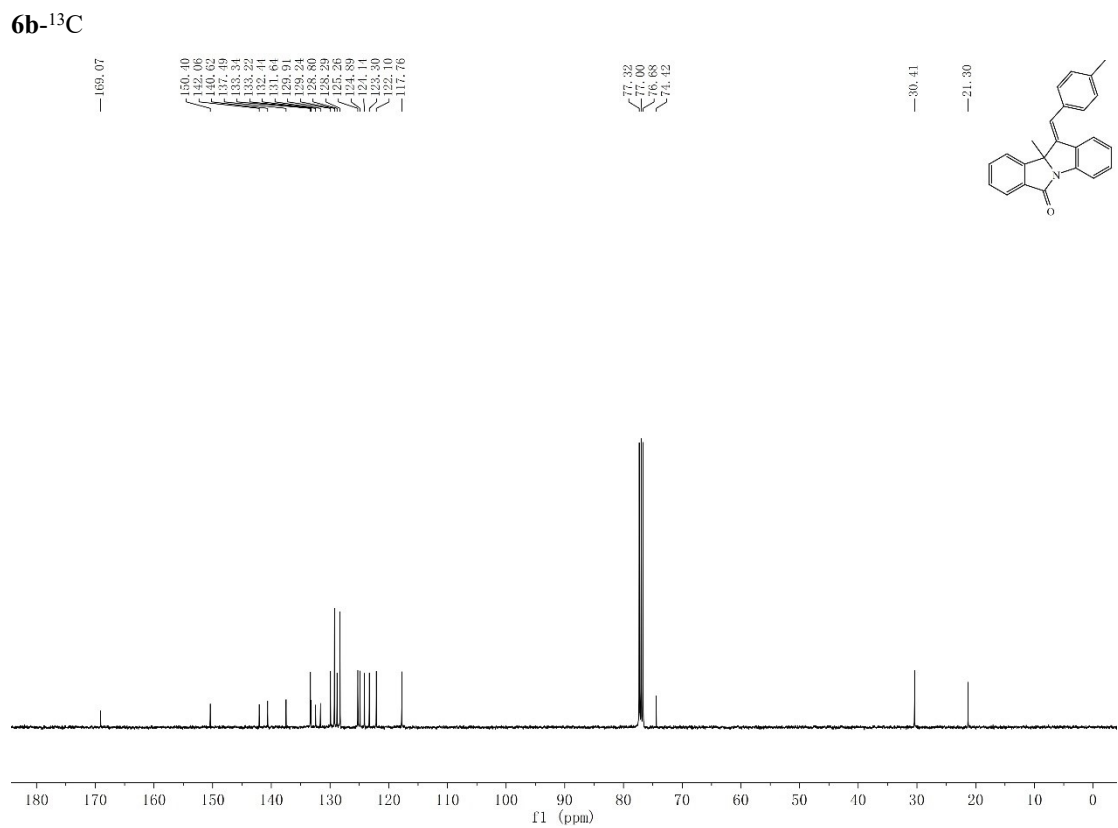
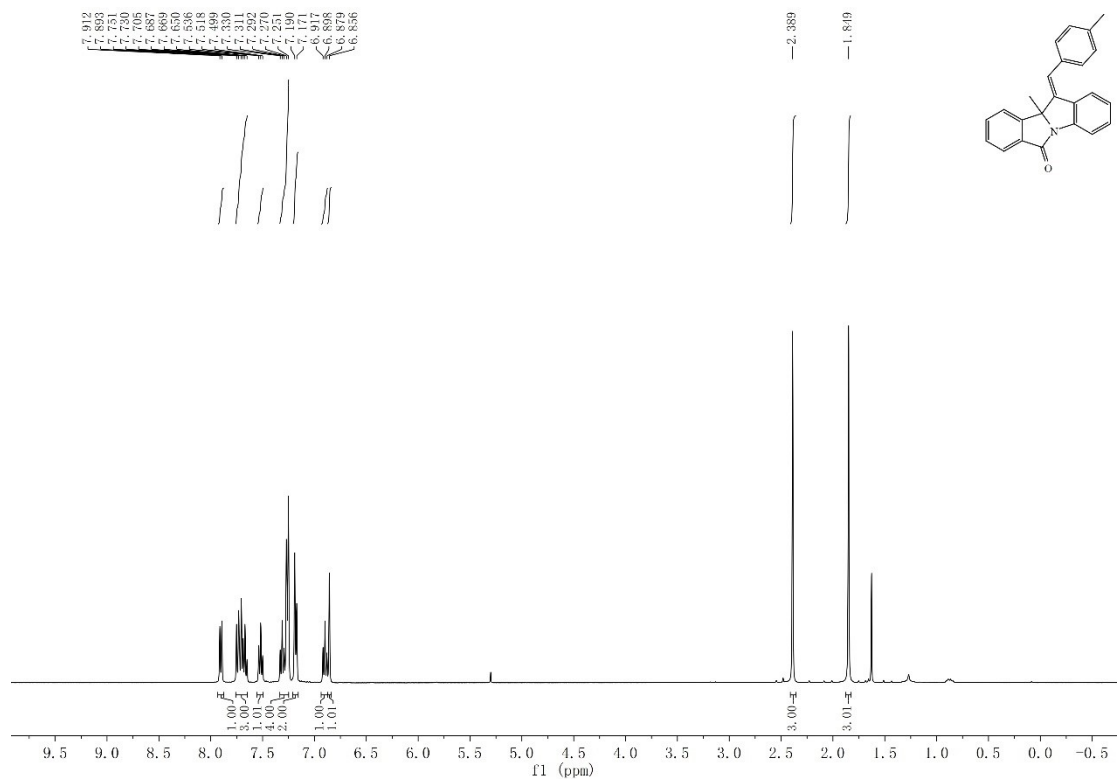
6a-¹H



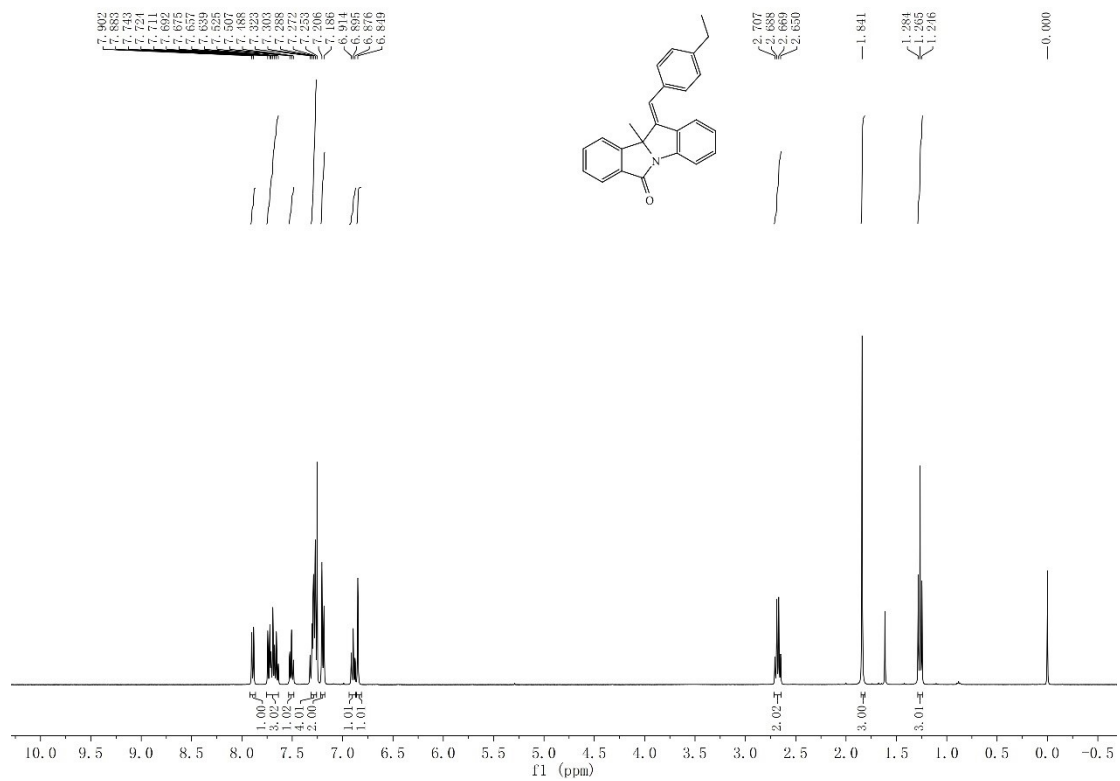
6a-¹³C



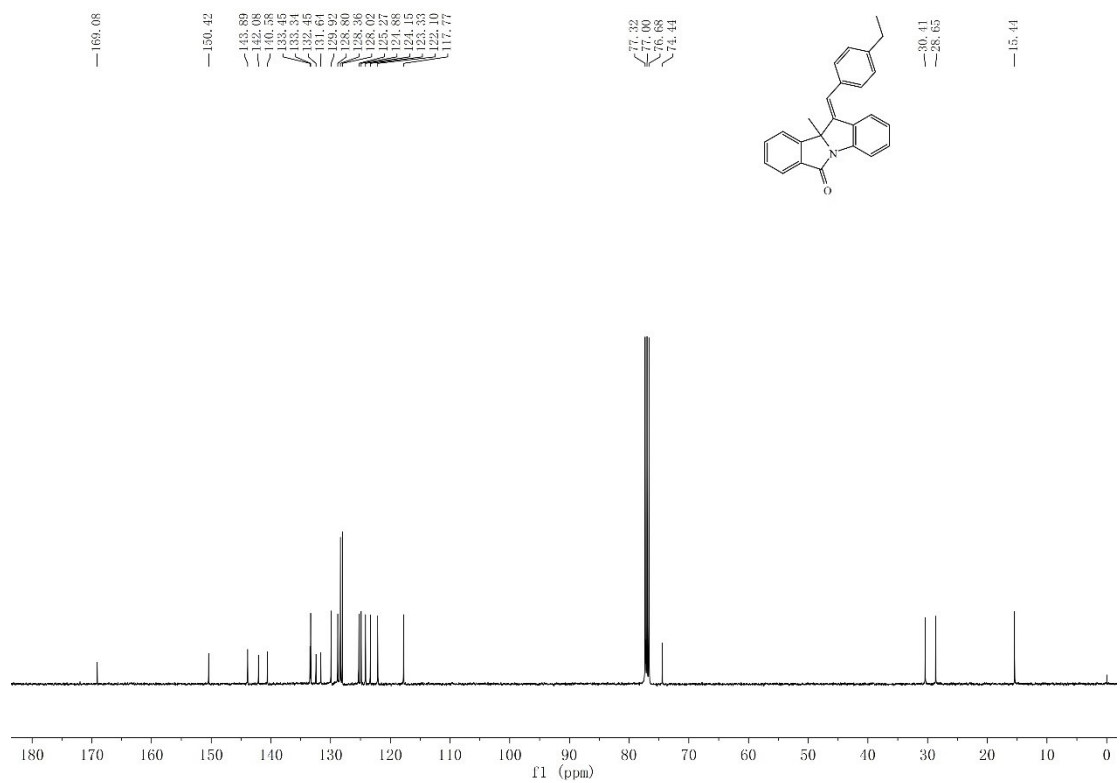
6b-¹H



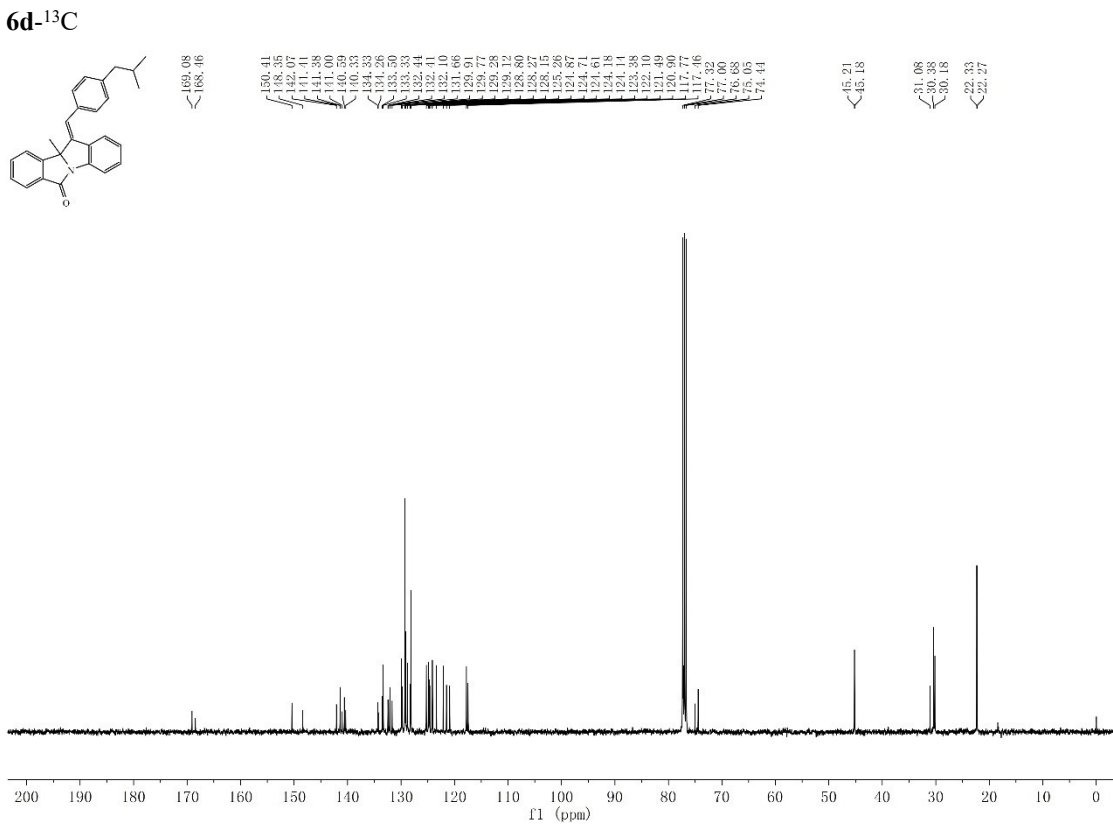
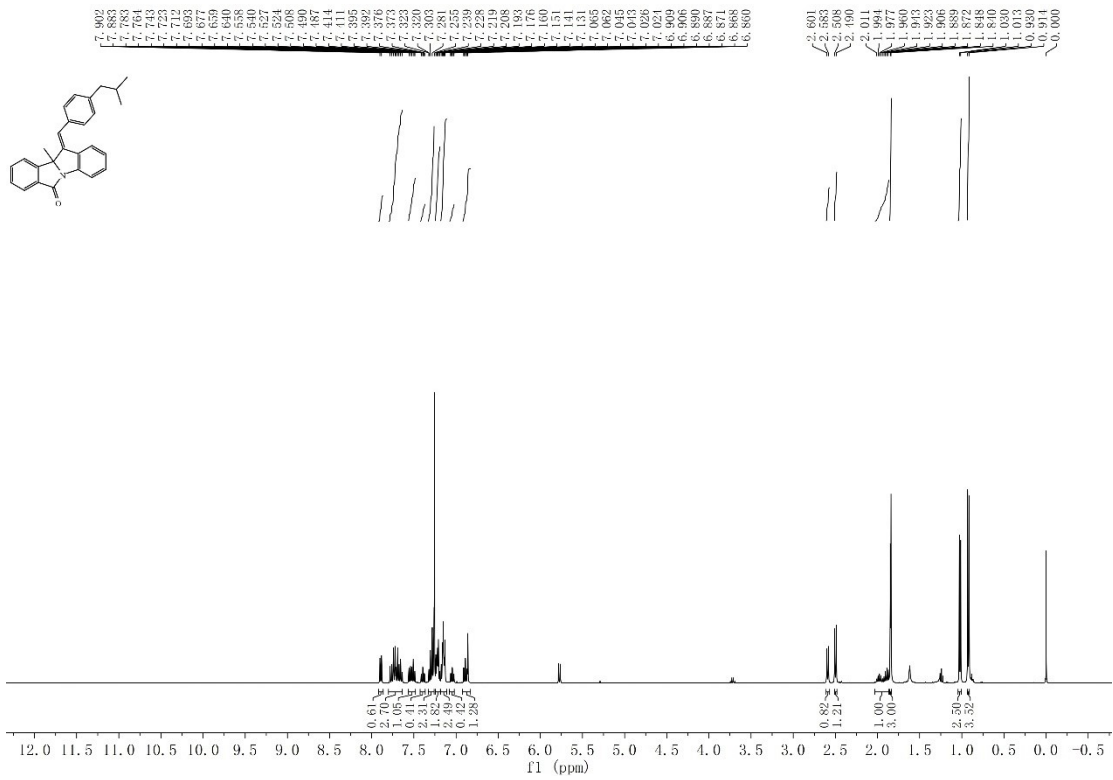
6c-¹H



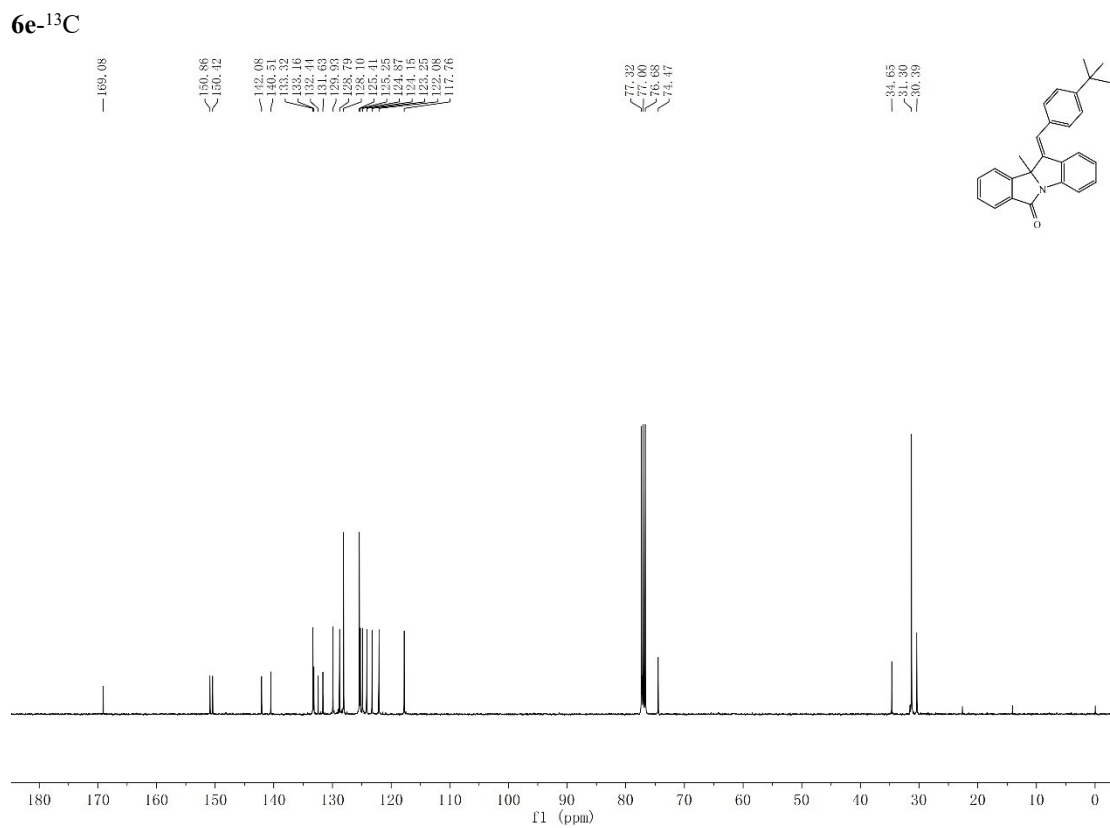
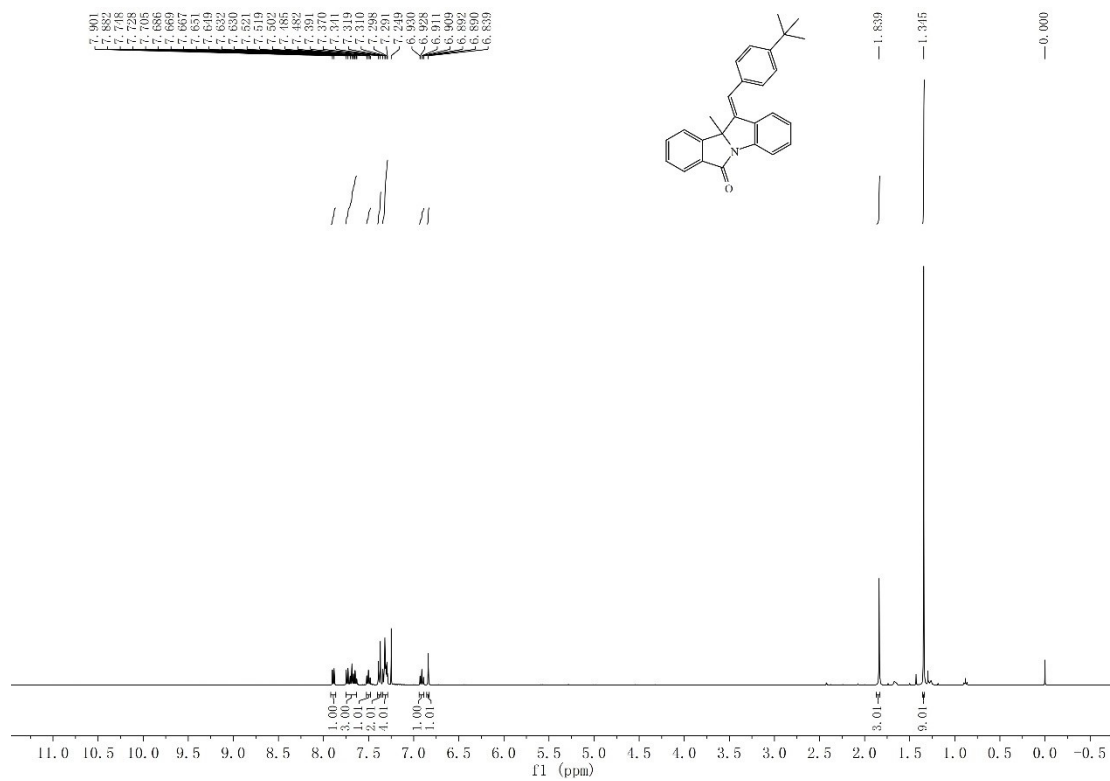
6c-¹³C



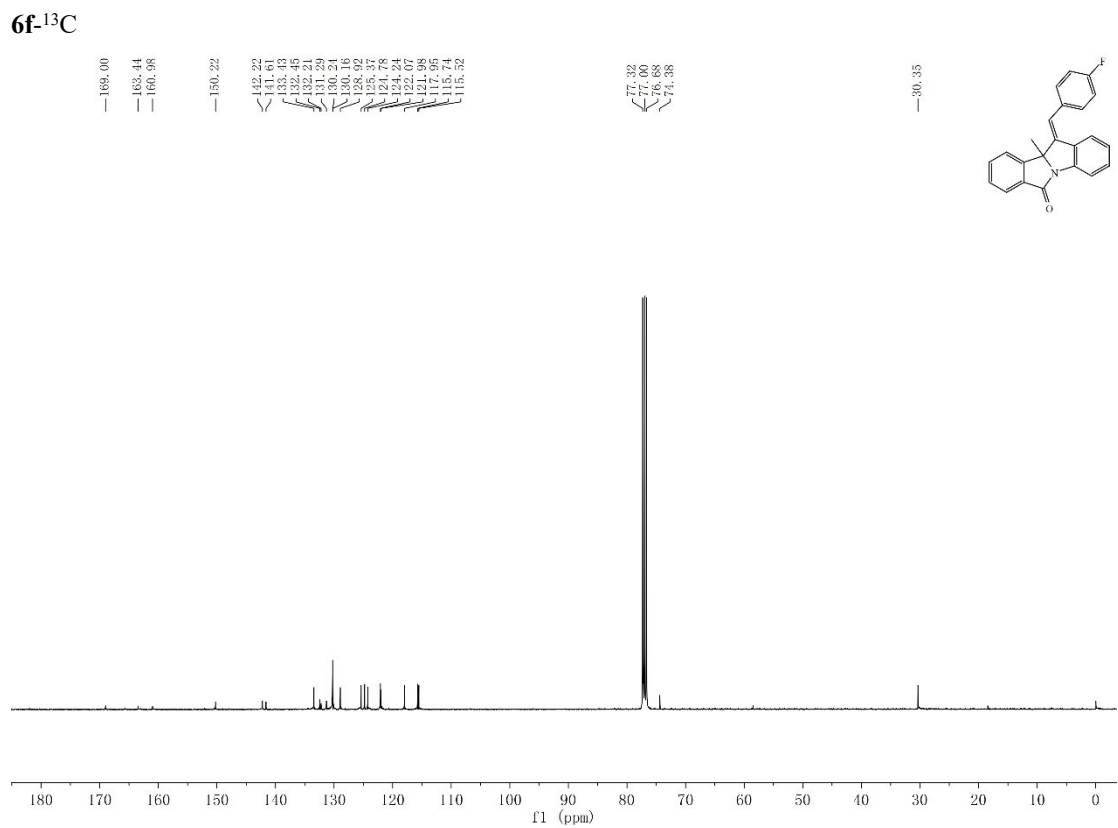
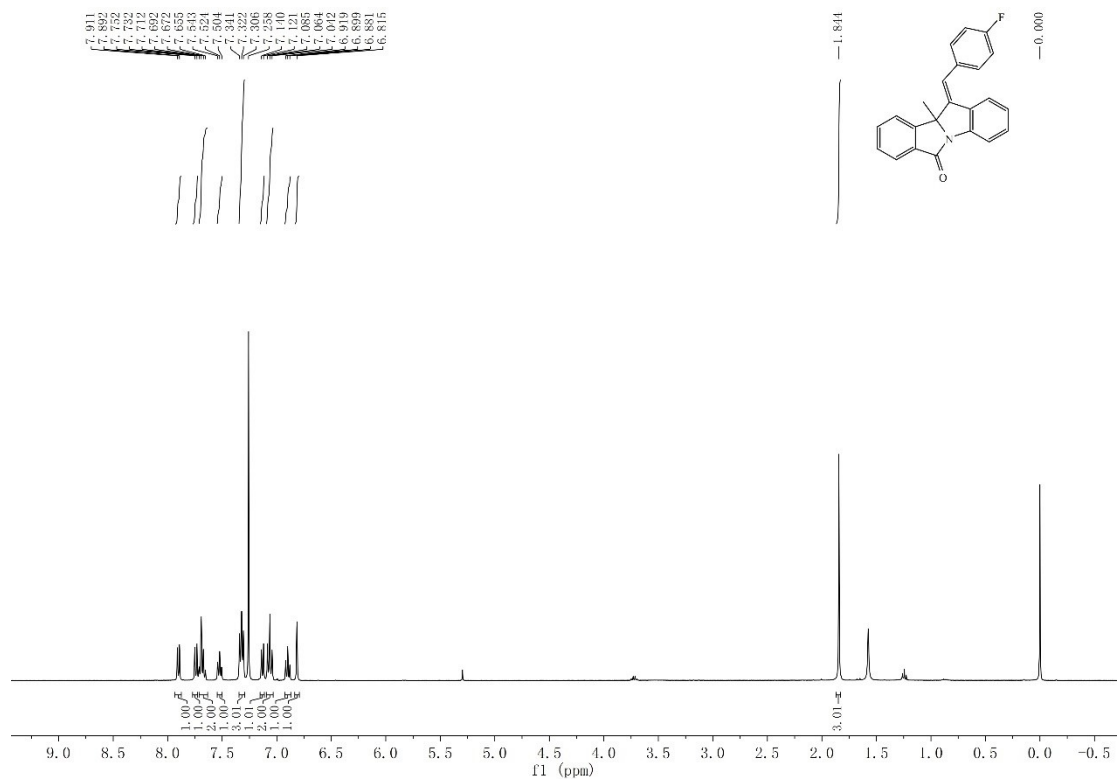
6d-¹H



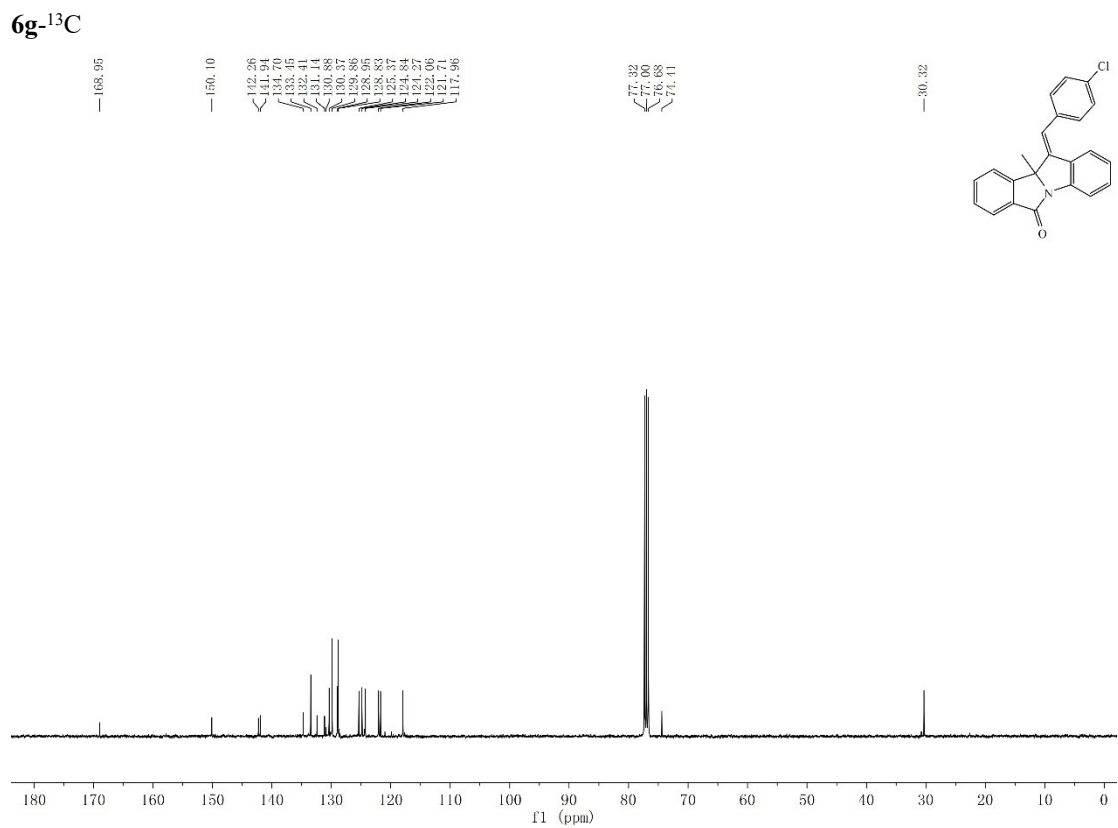
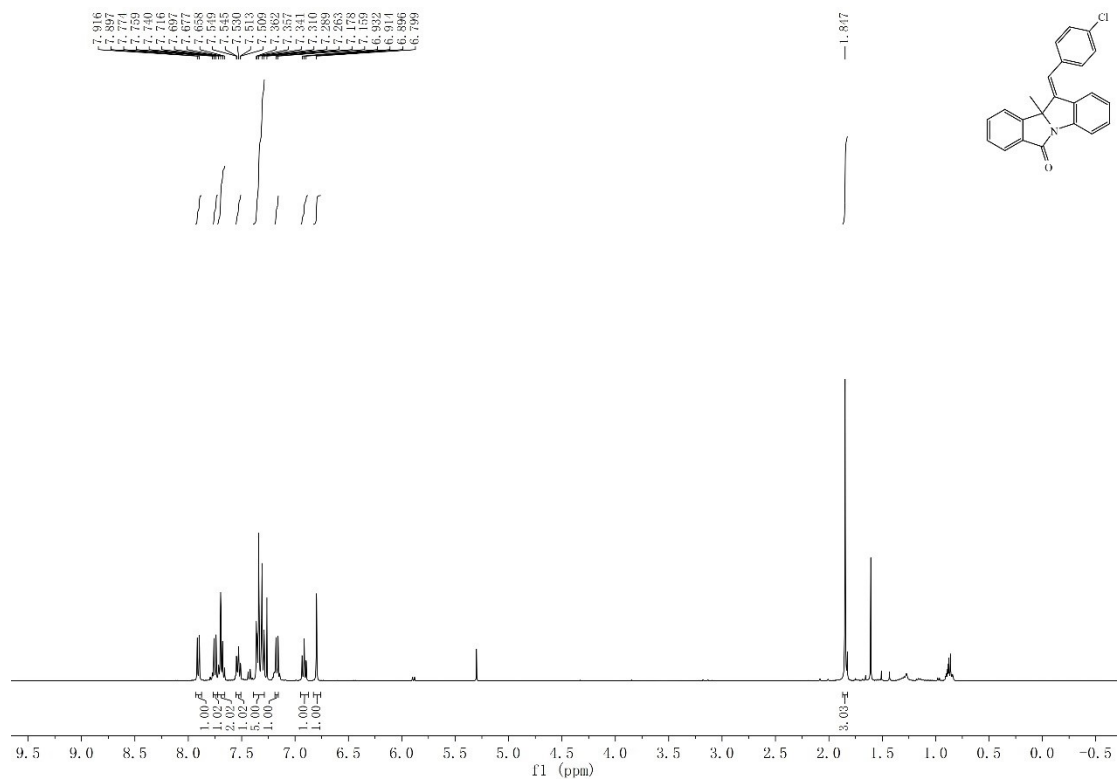
6e-¹H



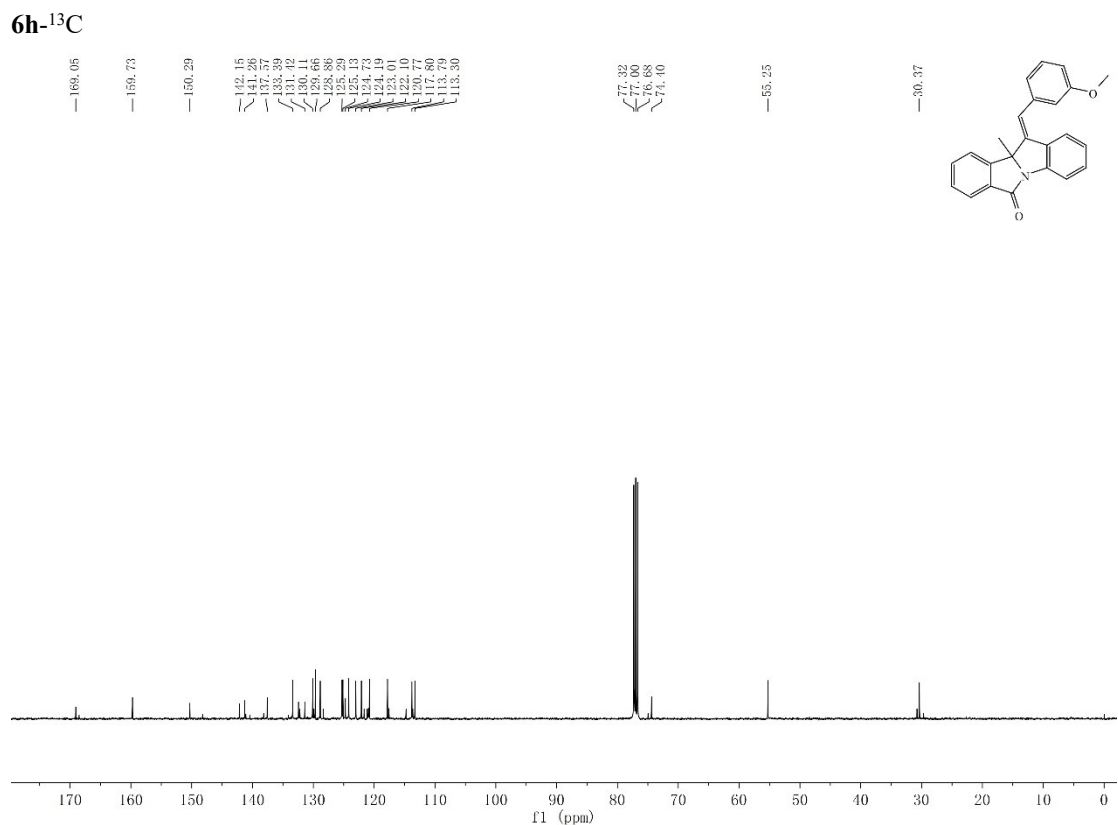
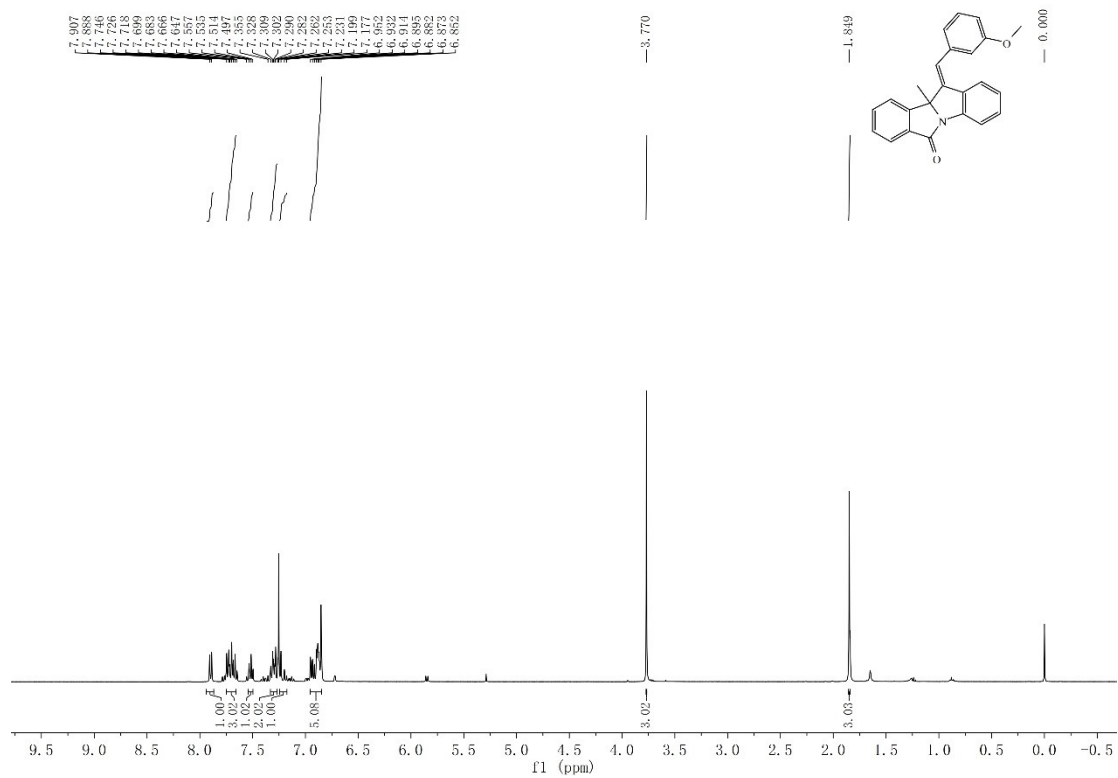
6f-¹H



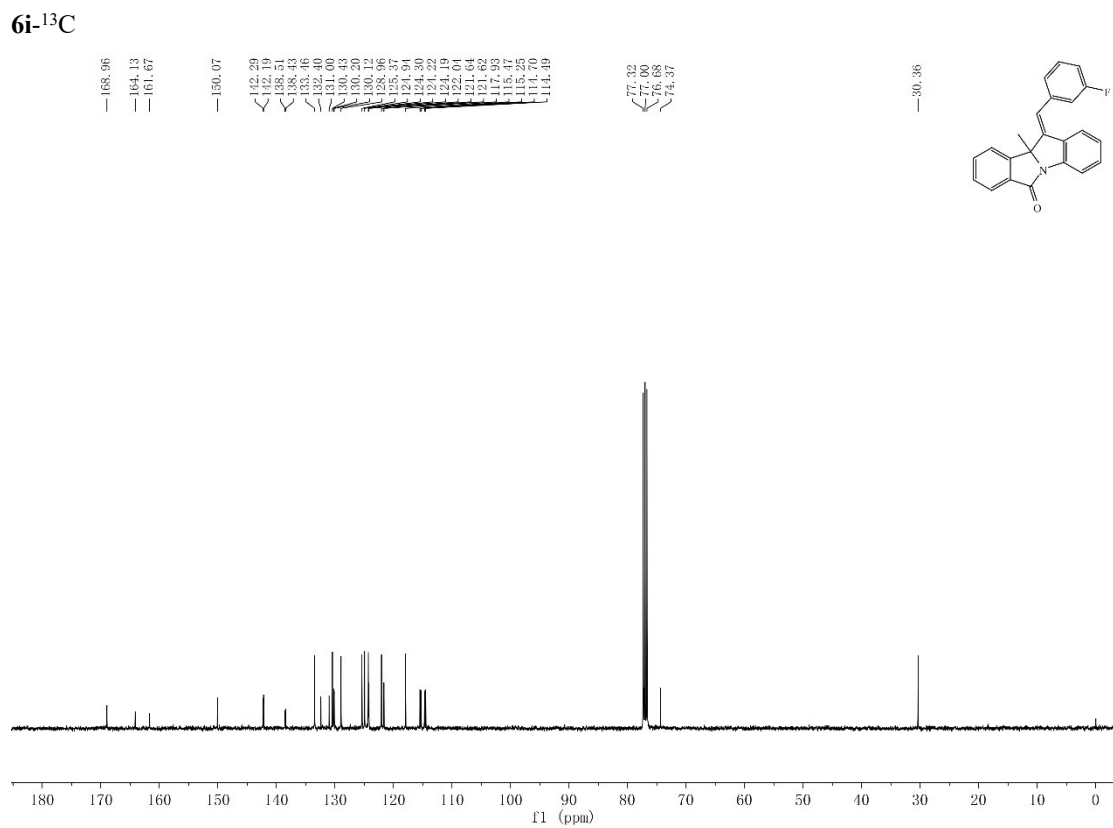
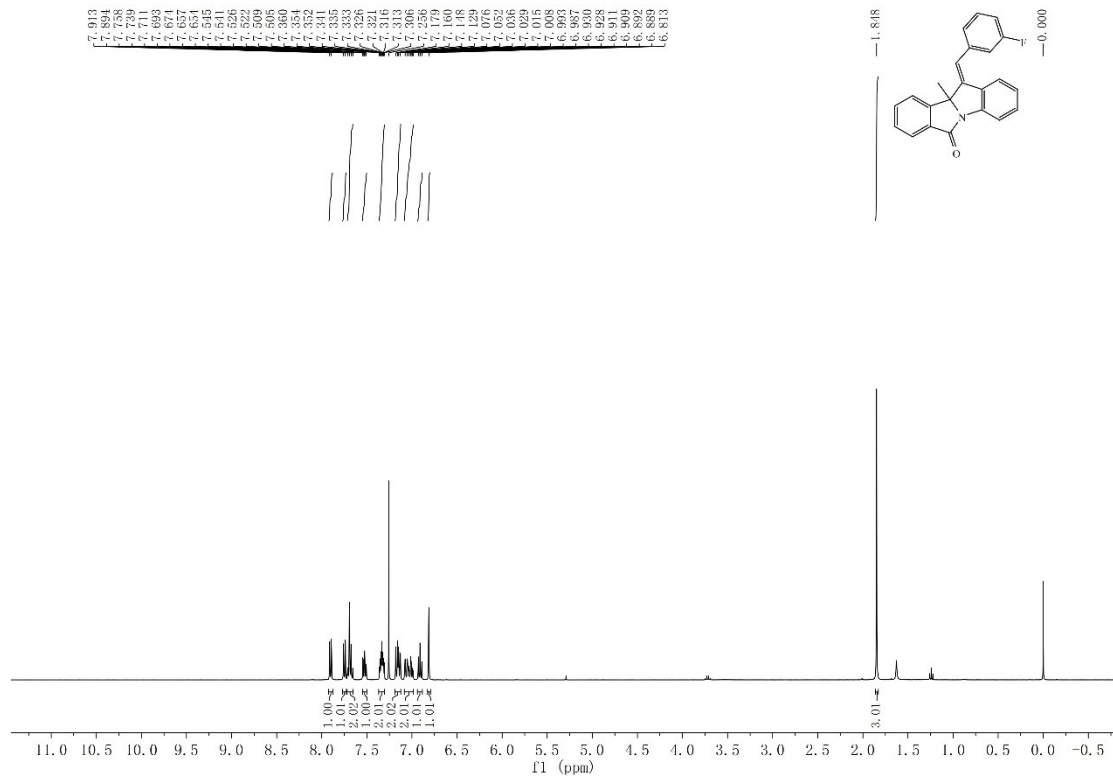
6g-¹H



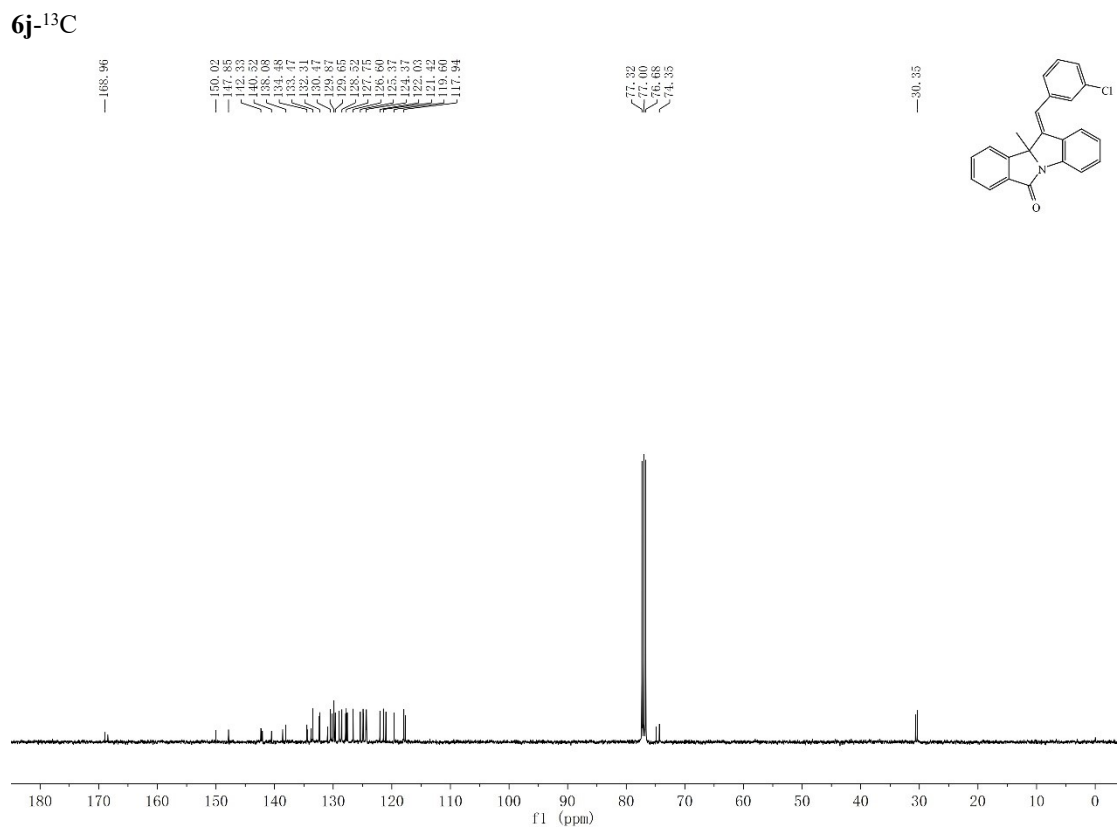
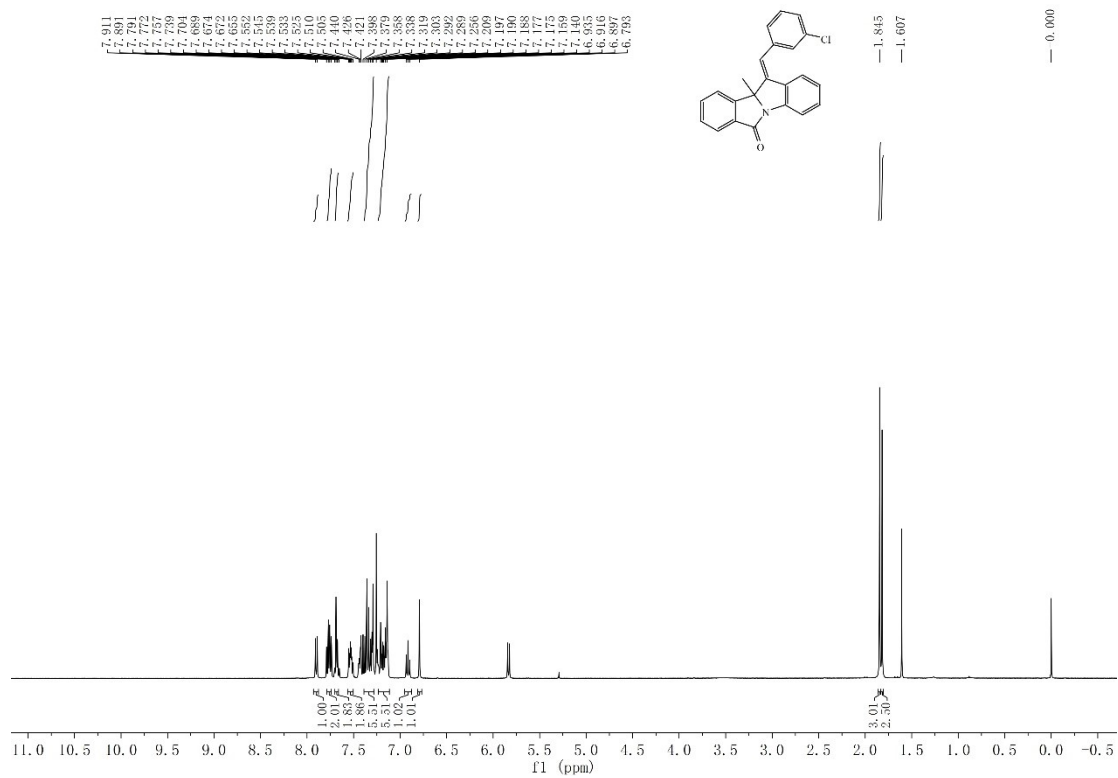
6h-¹H



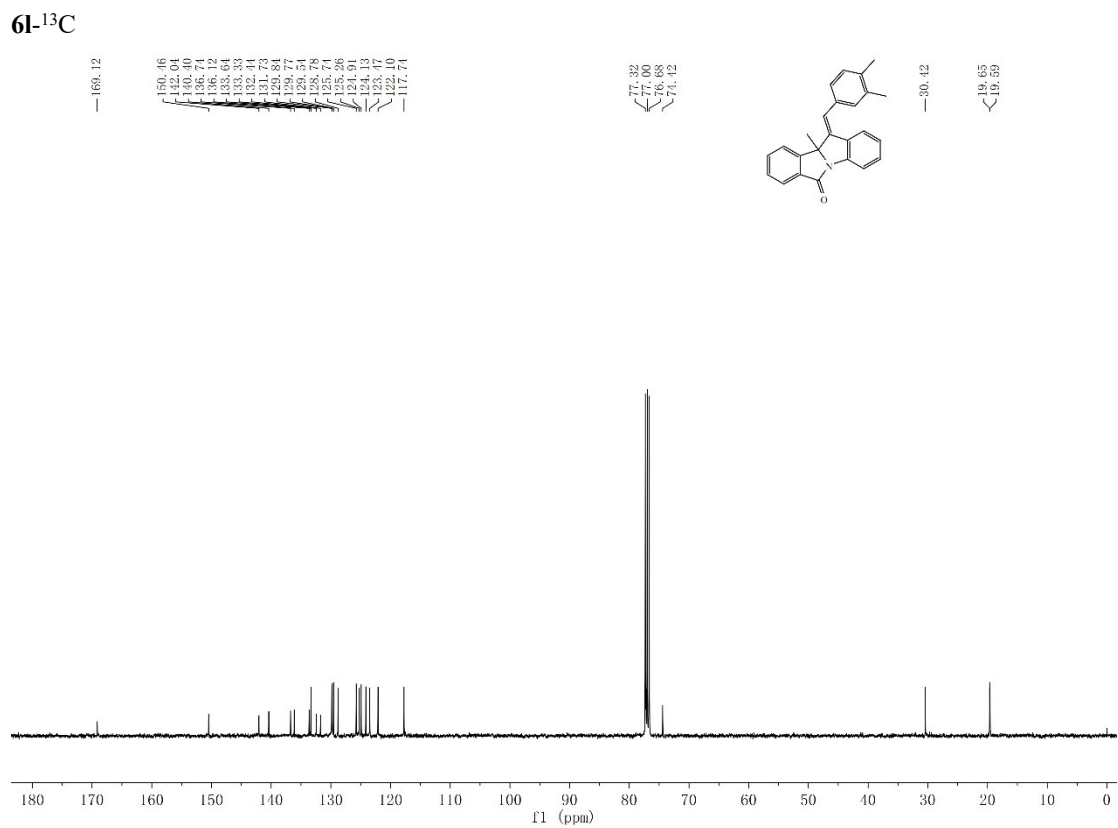
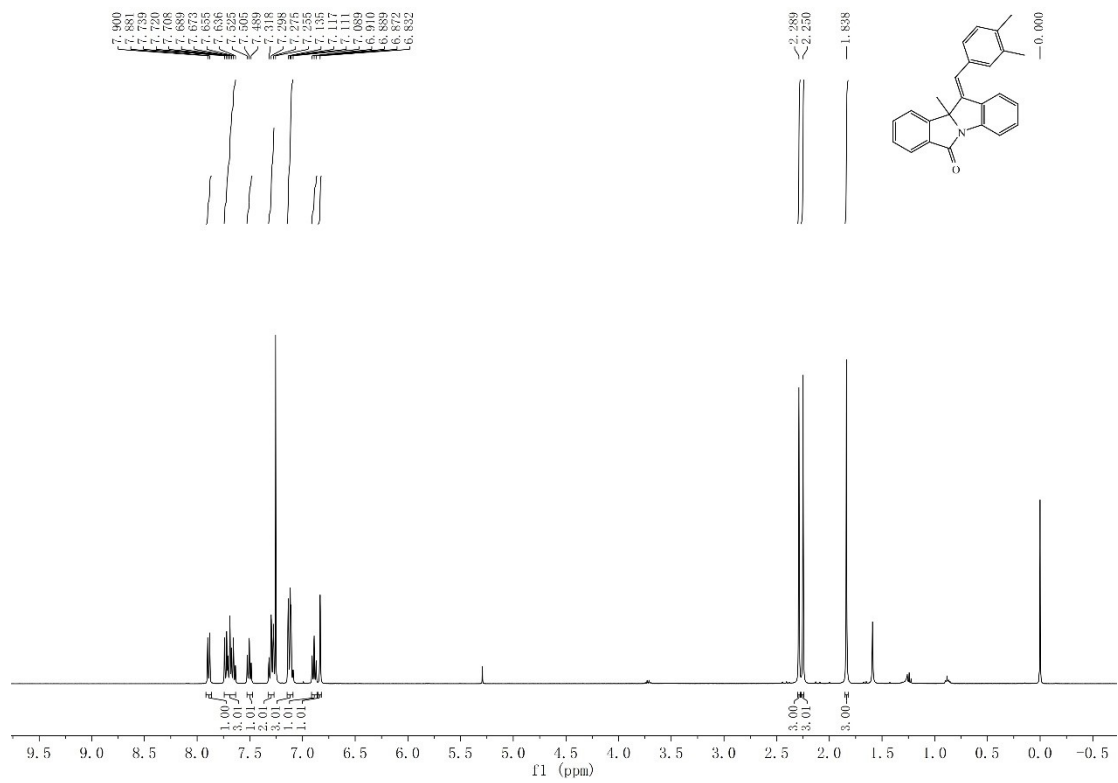
6i-¹H



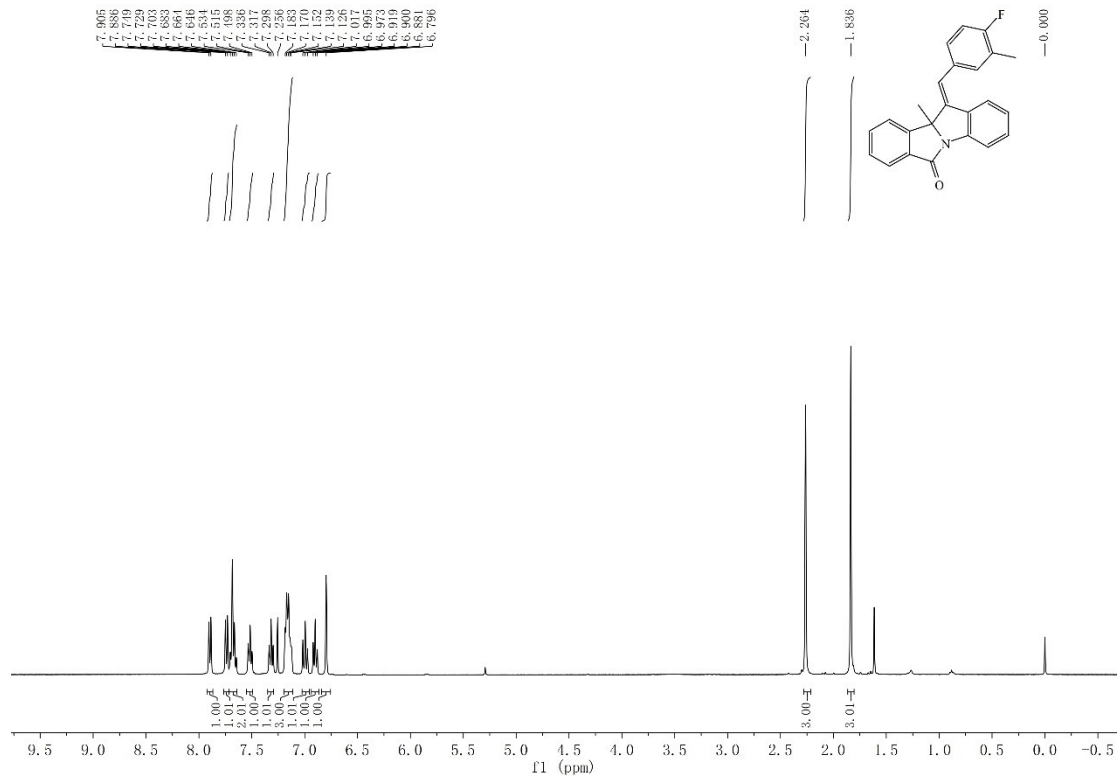
6j-¹H



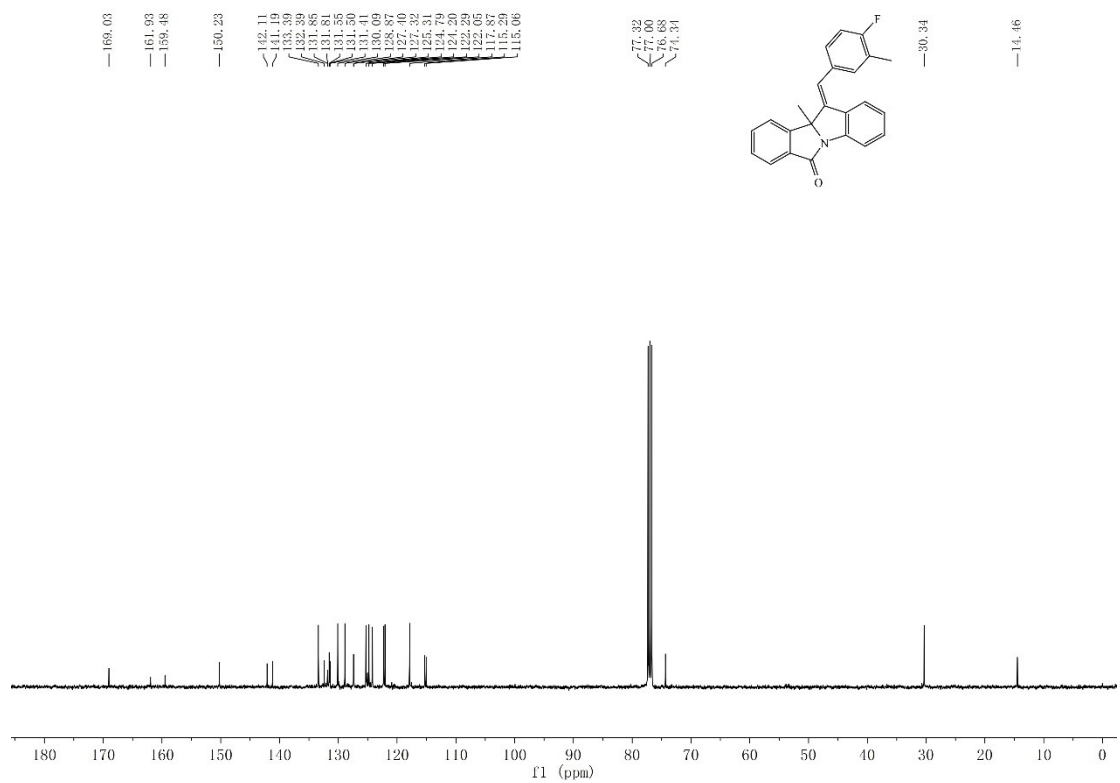
6l-¹H



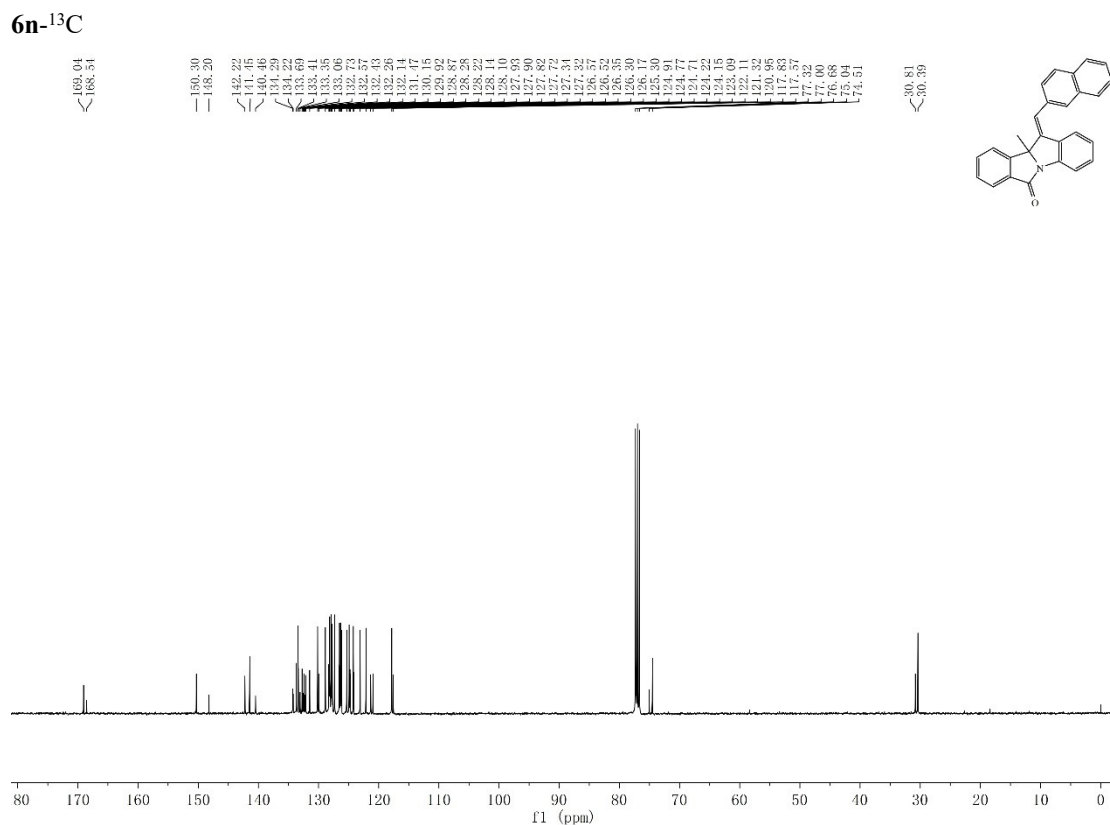
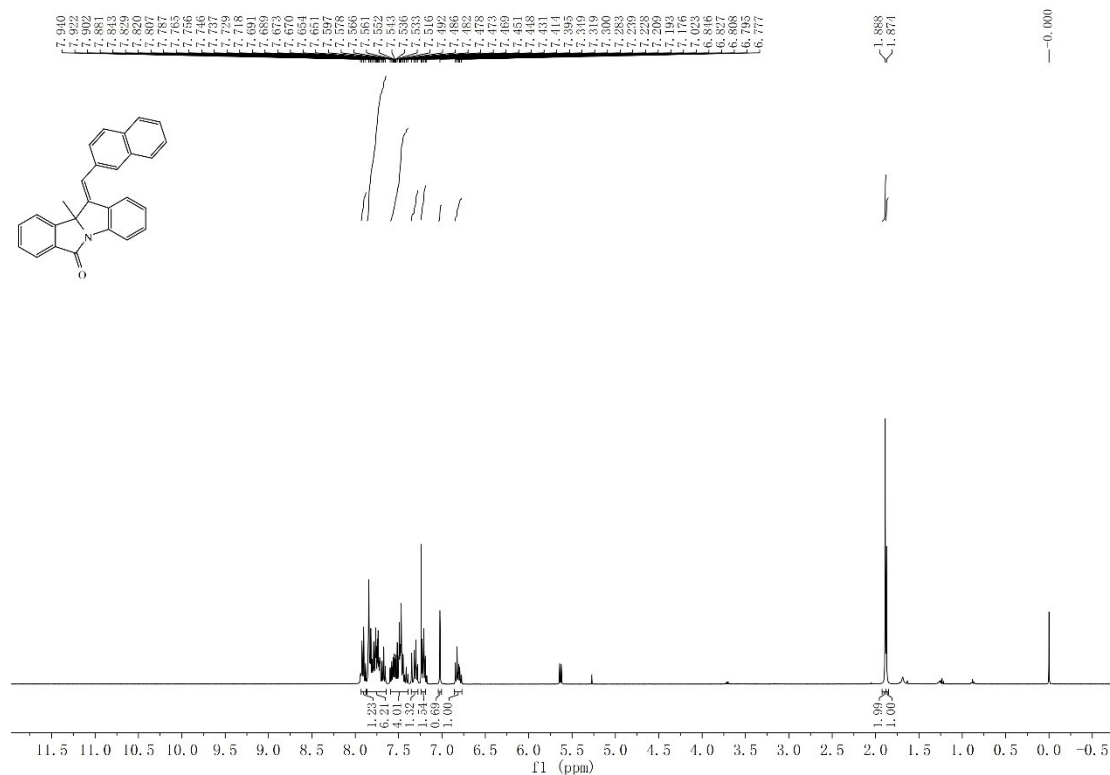
6m-¹H



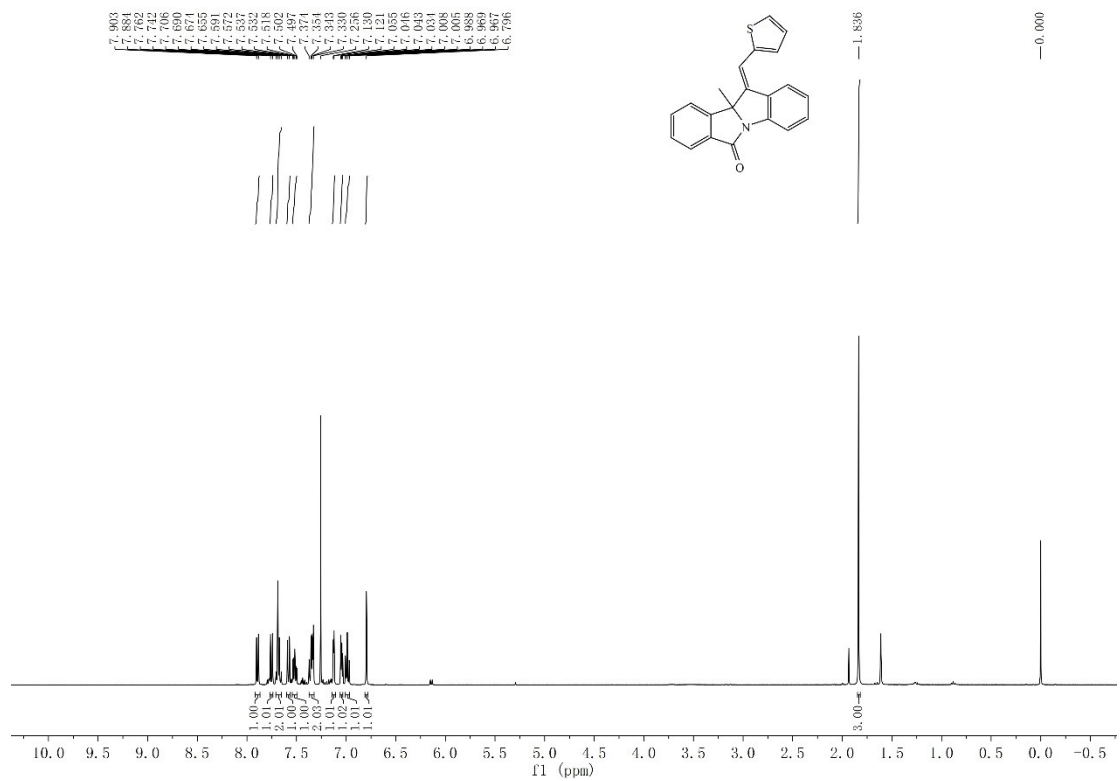
6m-¹³C



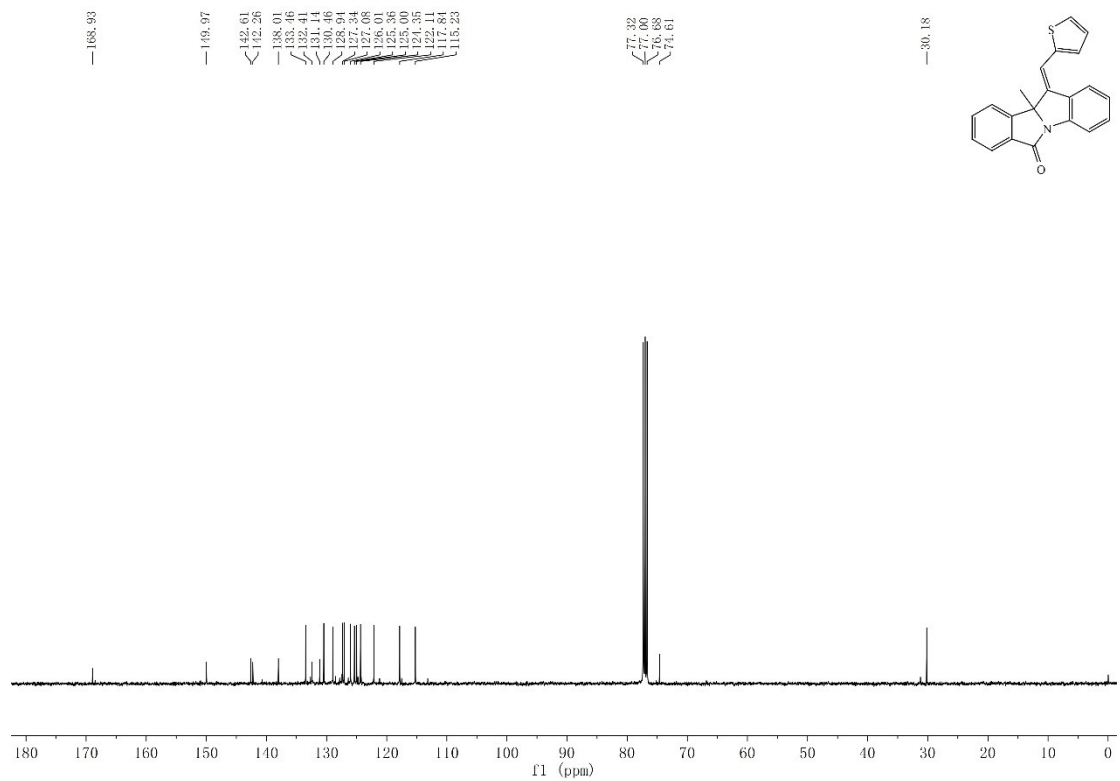
6n-¹H



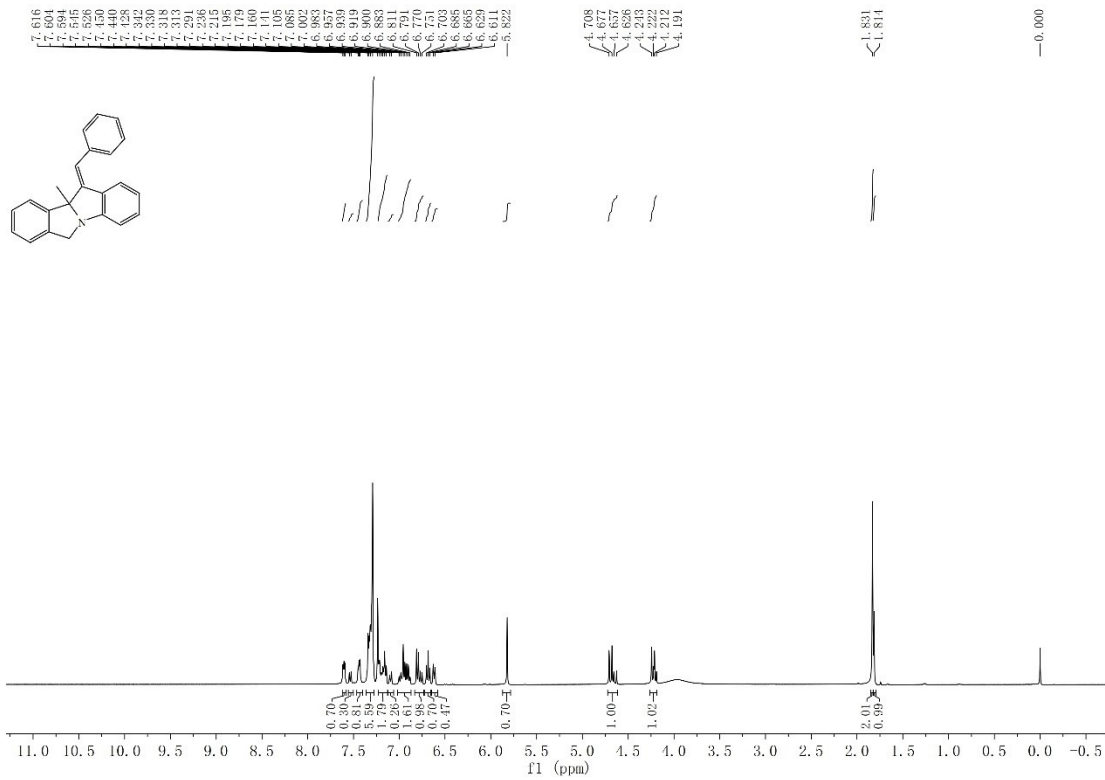
6n-¹H



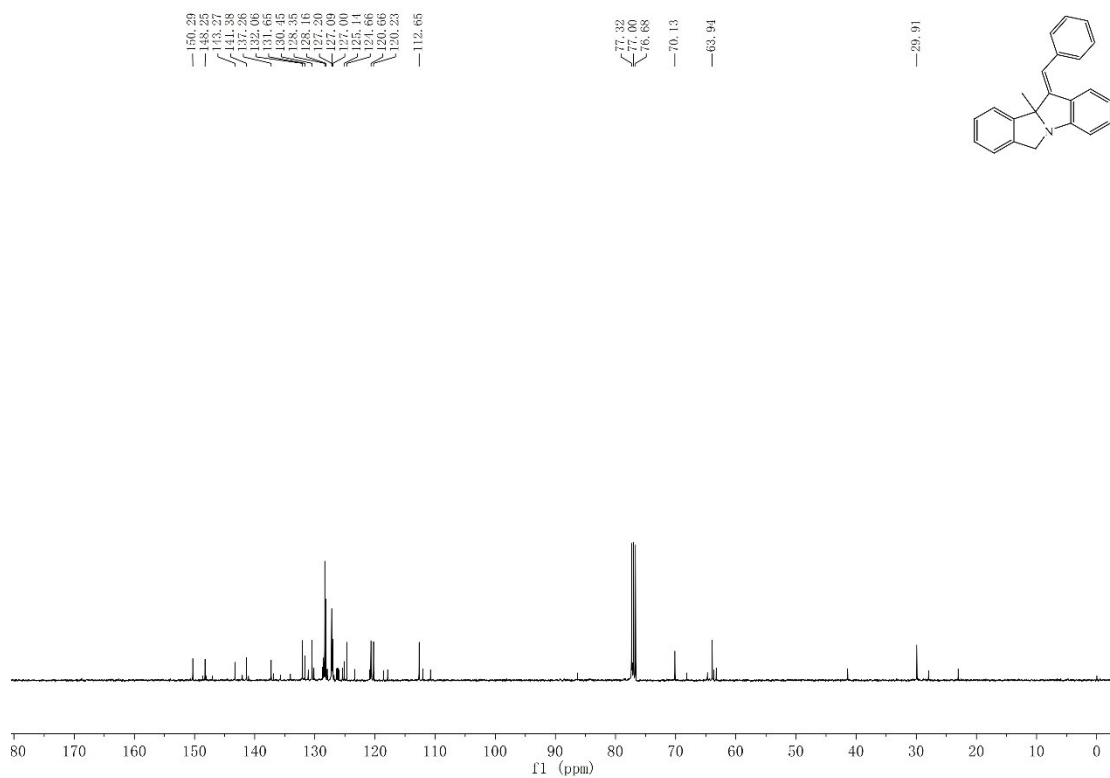
60-¹³C



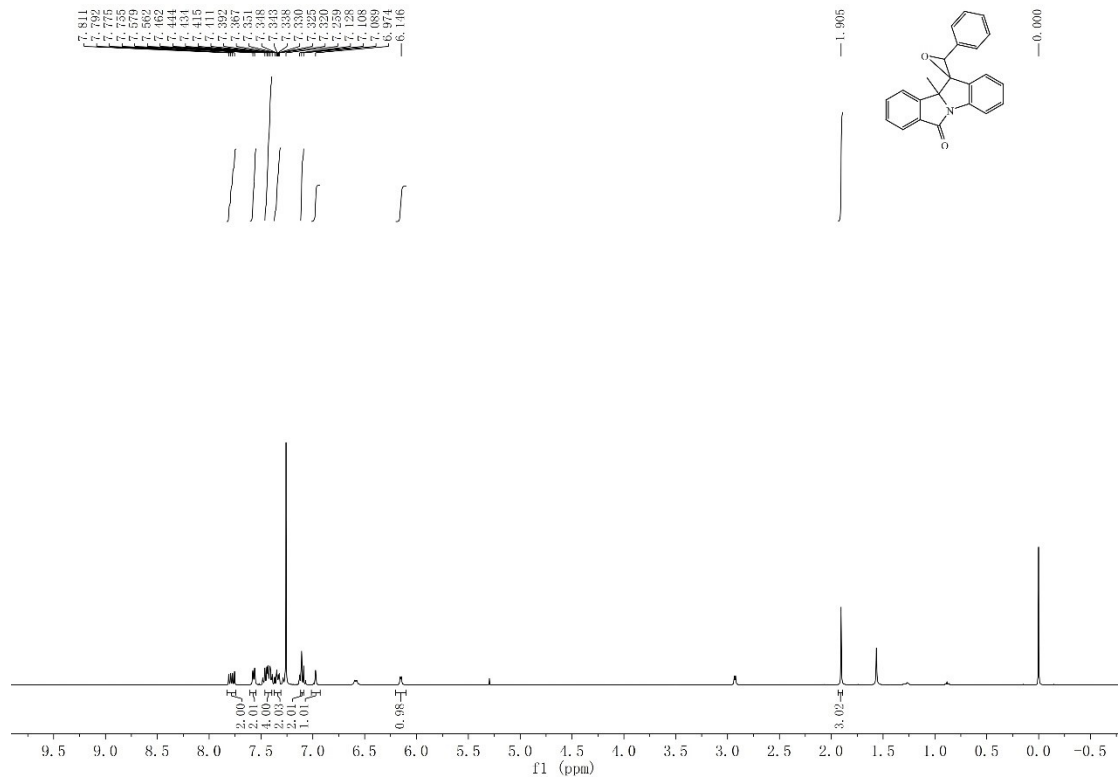
7-¹H



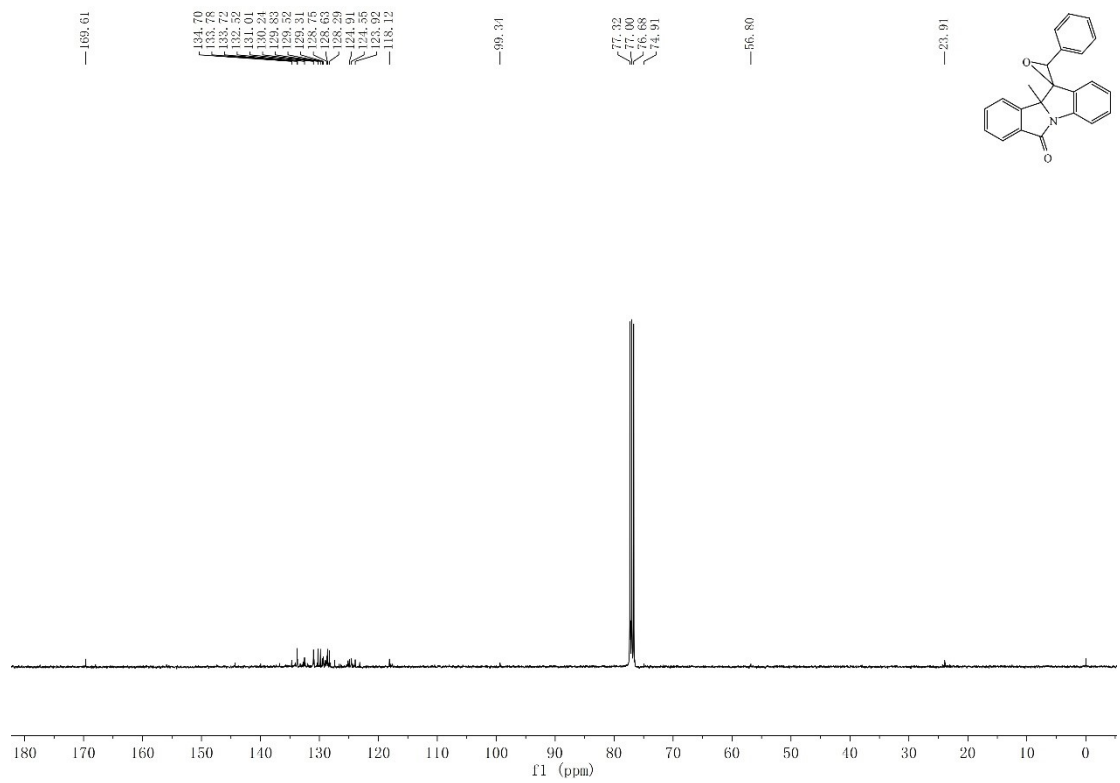
7-¹³C



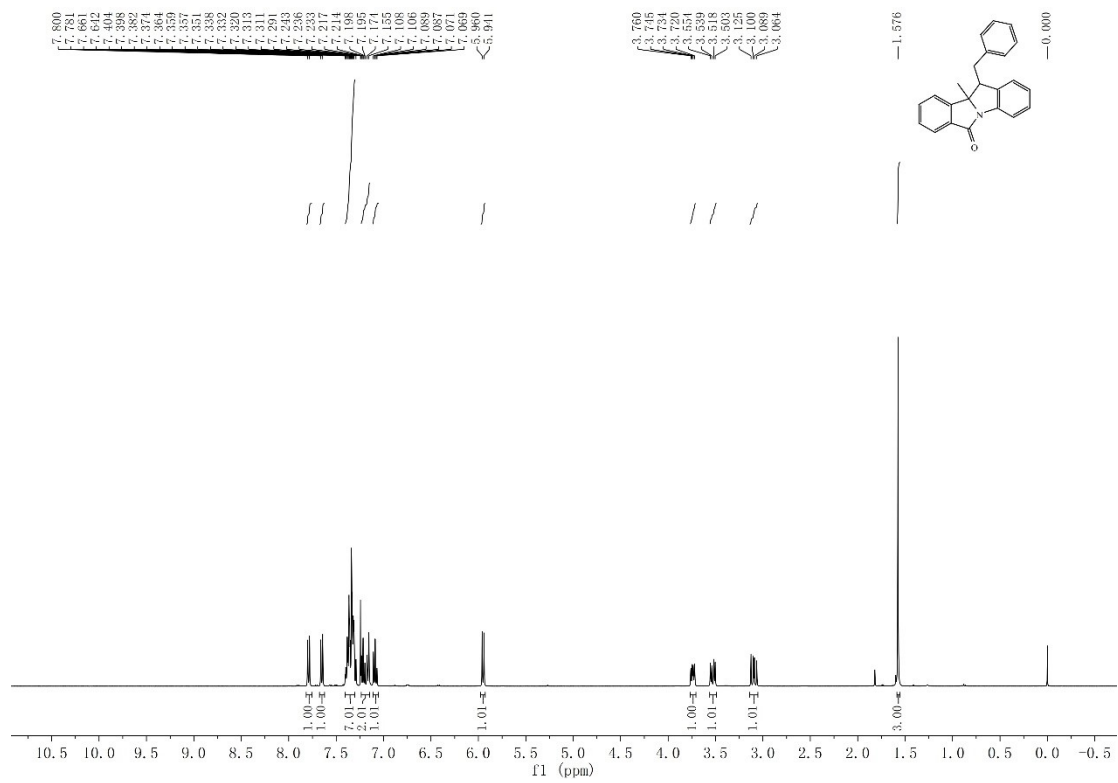
8-¹H



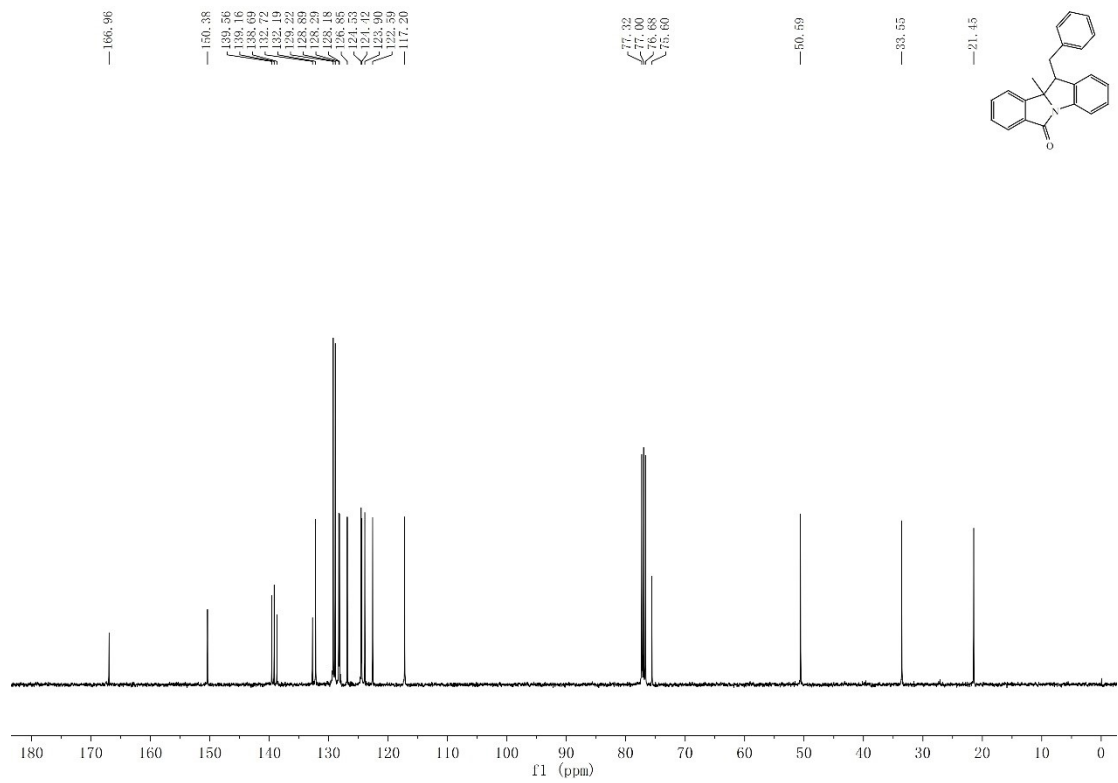
8- ^{13}C

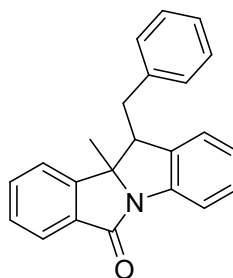
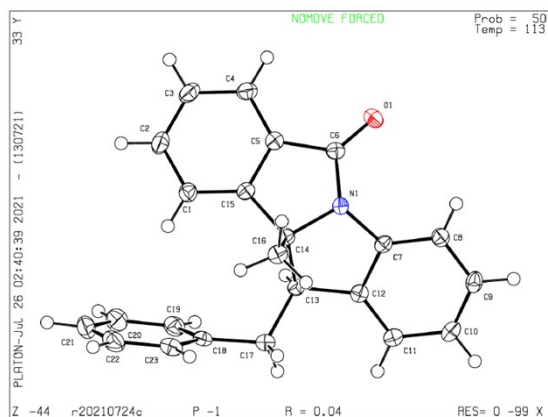


9- ^1H



9-¹³C





9

Bond precision: C-C = 0.0017 Å

Wavelength=0.71073

Cell: a=8.6337(5) b=9.0522(5) c=11.8733(4)
 alpha=76.152(4) beta=79.612(4) gamma=71.252(5)
 Temperature: 113 K

	Calculated	Reported
Volume	847.76(8)	847.76(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₂₃ H ₁₉ N O	C ₂₃ H ₁₉ N O
Sum formula	C ₂₃ H ₁₉ N O	C ₂₃ H ₁₉ N O
Mr	325.39	325.39
Dx, g cm ⁻³	1.275	1.275
Z	2	2
Mu (mm ⁻¹)	0.077	0.077
F000	344.0	344.0
F000'	344.13	
h, k, lmax	10, 11, 14	10, 11, 14
Nref	3455	3367
Tmin, Tmax	0.981, 0.986	0.790, 1.000
Tmin'	0.981	

Correction method= # Reported T Limits: Tmin=0.790 Tmax=1.000
 AbsCorr = MULTI-SCAN

Data completeness= 0.975

Theta(max)= 26.364

R(reflections)= 0.0388(2993)

wR2(reflections)= 0.0980(3367)

S = 1.055

Npar= 227

CCDC 2099487