Supporting Information

Copper-Catalyzed [3+2]/[3+2] Carboannulation of Dienynes and Arylsulfonyl Chlorides Enabled by Smiles Rearrangement: Access to Cyclopenta[a]indene-Fused Quinolinones

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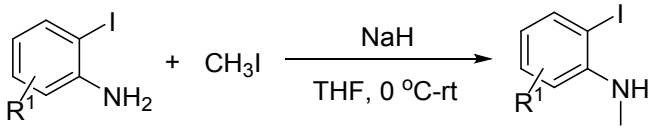
Table of Contenes

1. General Information

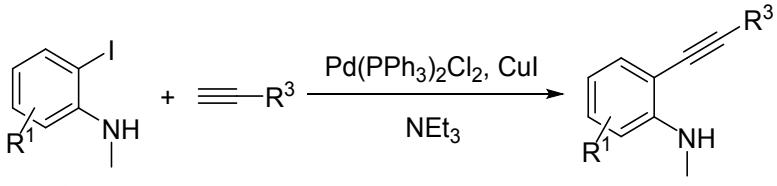
^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CD(H)Cl_3$ (7.26 ppm), ^{13}C NMR: $CD(H)Cl_3$ (77.00 ppm). Signal patterns are indicated as s, singlet; d, doublet; t, triplet, and m, multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC system coupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

2. General Procedures for the Synthesis of dienynes (1a-1u)[1-5]



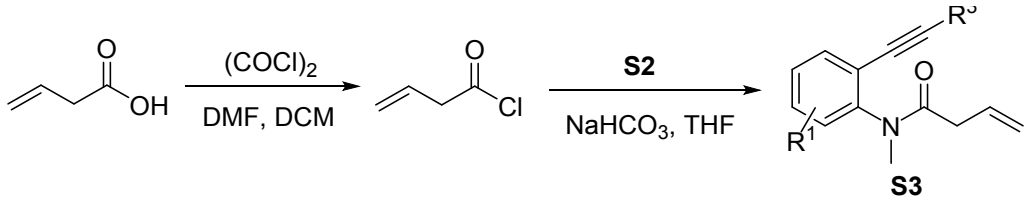
S1

An oven-dried flask was charged with the corresponding *o*-iodoanilines (5.0 mmol, 1.0 equiv), iodomethane (6.0 mmol, 1.2 equiv), and anhydrous THF (10 mL). NaH (7.5 mmol, 1.5 equiv, 300 mg, 60% in mineral oil) was added to the above solution at 0 °C in portions and then returned to room temperature and stirred overnight until complete consumption of starting material was indicated by TLC. The mixture was quenched with water and the organic layer extracted with ethyl acetate. The combined extracts were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography to afford the corresponding 2-iodo-*N*-methylanilines **S1**. This procedure was carried out according to refs. 1 and 2.



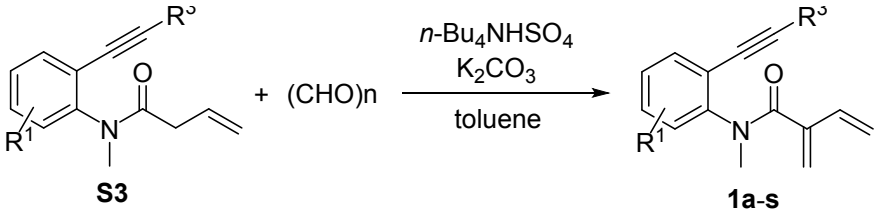
S1 **S2**

To a 50 mL Schlenk tube were added 2-iodo-*N*-methylanilines **S1** (4.5 mmol, 1.0 equiv), alkyne (5.0 mmol, 1.1 equiv), $PdCl_2(PPh_3)_2$ (0.0675 mmol, 1.5 mol%, 47.3 mg), CuI (0.045 mmol, 1.0 mol%, 8.6 mg) and NEt_3 (10 mL). Then the tube was evacuated briefly under high vacuum and charged with nitrogen through using standard Schlenk techniques; this process was repeated three times. The reaction mixture was stirred at room temperature for 2 h until complete consumption of 2-iodo-*N*-methylanilines. The reaction mixture was diluted with 25.0 mL water and extracted with EtOAc (2 × 25 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. Removal of the solvent under reduced pressure and purification by column chromatography on silica gel furnished products **S2**. This procedure was carried out according to refs. 1 and 3.



S3

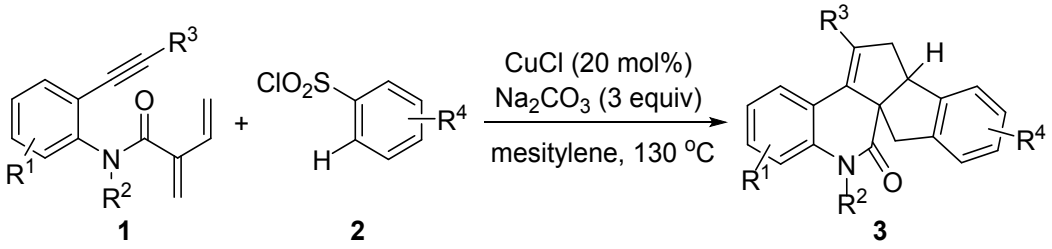
A round-bottom flask was charged with but-3-enoic acid (4.8 mmol, 1.2 equiv), dried DCM (10 mL) and a drop of DMF. The mixture was cooled to 0°C, whereupon oxalyl chloride (5.8 mmol, 1.44 equiv, 0.49 mL) was added slowly. The reaction mixture was stirred for 3 h at room temperature and then removed the solvent DCM under reduced pressure to afford but-3-enoyl chloride. To a solution of N-benzyl-2-iodoaniline (4.0 mmol, 1.0 equiv, 830 mg) and $NaHCO_3$ (12.0 mmol, 3 equiv, 1.01g) in anhydrous THF (10 mL) was then added but-3-enoyl chloride at 0°C. The reaction mixture was returned to room temperature and stirred for 30 min. The reaction mixture was quenched with H_2O, extracted with EA, then dried over $MgSO_4$. The organic layers were finally evaporated to yield the crude product **S3**, which was purified by column chromatography. This procedure was carried out according to ref. 4.



S3 **1a-s**

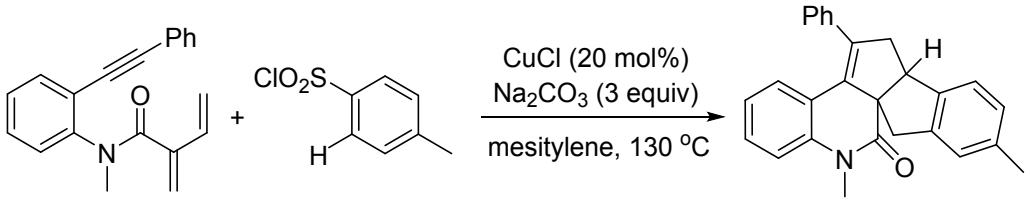
To a solution of enynes **S3** (3.0 mmol, 1.0 equiv) in anhydrous toluene (10 mL), K_2CO_3 (4.5 mmol, 1.5 equiv, 621 mg), tetrabutylammonium bisulfate (0.3 mmol, 10 mol%, 102 mg), and formaldehyde (9.0 mmol, 3.0 equiv, 270 mg) were added. The reaction mixture was heated at 80 °C for 12 h, quenched with H_2O (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 10:1) to provide dienynes **1a-1u**. This procedure was carried out according to ref. 5.

3. General Procedures for the Synthesis of Cyclopenta[*a*]indene-fused quinolinones



To a Schlenk tube were added dienynes **1a** (0.2 mmol, 1.0 equiv, 57.4 mg), arylsulfonyl chlorides **2a** (0.4 mmol, 2.0 equiv, 76 mg), CuCl (0.04mmol, 20 mol%, 4 mg), Na_2CO_3 (0.6 mmol, 3.0 equiv, 63.6 mg), and mesitylene (2 mL) under air. Then the tube was evacuated briefly under high vacuum and charged with nitrogen through using standard Schlenk techniques; this process was repeated three times. Then the reaction mixture was stirred at 130 °C (oil bath temperature) for the indicated time (about 12 h) until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered through Celite to give a yellow solution, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate= 10:1) to afford the desired products **3aa** (58%, 43.7 mg).

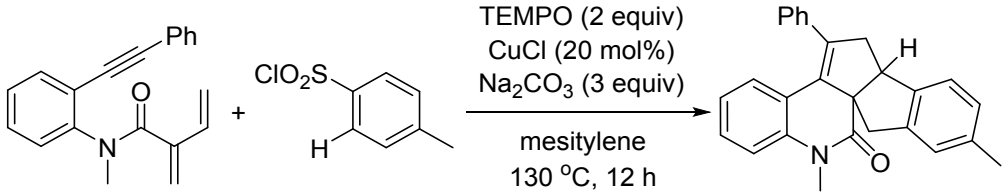
3.1 General Procedure for the Synthesis of 3aa from 1 mmol Scale of 1a



1a **2a** **3aa**

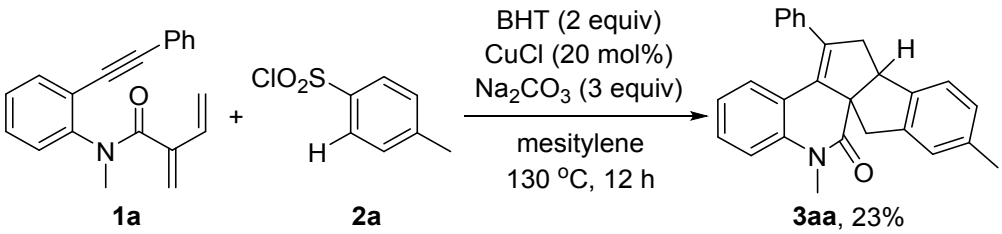
To Schlenk tube were added *N*-methyl-2-methylene-*N*-(2-(phenylethynyl)phenyl) -but-3-enamide **1a** (1.0 mmol, 1.0 equiv, 287 mg), 4-methylbenzenesulfonyl chloride **2a** (2.0 mmol, 2.0 equiv, 380 mg), CuCl (0.2 mmol, 20 mol%, 19.8 mg), Na_2CO_3 (3.0 mmol, 3.0 equiv, 318 mg), and mesitylene (8 mL). Then the tube was charged with nitrogen, and was stirred at 130 °C (oil bath temperature) for the indicated time (about 12 h) until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (petroleum ether/EtOAc = 10:1) to give product **3aa** (46%, 173.4 mg).

4. Mechanistic Studies



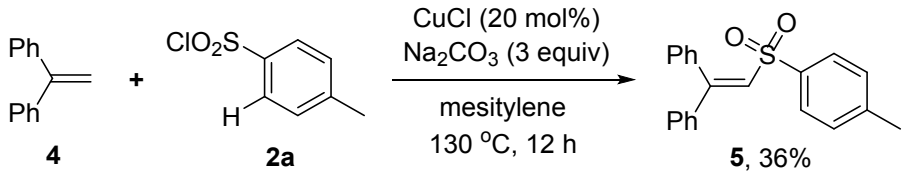
1a **2a** **3aa**, 0%

To a Schlenk tube were added dienynes **1a** (0.2 mmol, 1.0 equiv, 57.4 mg), 4-methylbenzenesulfonyl chloride **2a** (0.4 mmol, 2.0 equiv, 76 mg), CuCl (0.04 mmol, 20 mol%, 4 mg), Na_2CO_3 (0.6 mmol, 3.0 equiv, 63.6 mg), TEMPO (2.0 equiv), and mesitylene (2 mL) under air. Then the tube was evacuated briefly under high vacuum and charged with nitrogen through using standard Schlenk techniques; this process was repeated three times. Then the reaction mixture was stirred at 130 °C (oil bath temperature) for the indicated time (about 12 h). No target product **3aa** was detected by TLC and/or GC-MS analysis.



1a **2a** **3aa**, 23%

To a Schlenk tube were added dienynes **1a** (0.2 mmol, 1.0 equiv, 57.4 mg), 4-methylbenzenesulfonyl chloride **2a** (0.4 mmol, 2.0 equiv, 76 mg), CuCl (0.04 mmol, 20 mol%, 4 mg), Na_2CO_3 (0.6 mmol, 3.0 equiv, 63.6 mg), BHT (2.0 equiv), and mesitylene (2 mL) under air. Then the tube was evacuated briefly under high vacuum and charged with nitrogen through using standard Schlenk techniques; this process was repeated three times. Then the reaction mixture was stirred at 130 °C (oil bath temperature) for the indicated time (about 12 h). After the reaction was finished, the reaction mixture was filtered through Celite to give a yellow solution, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired products **3aa** in 23% yield.

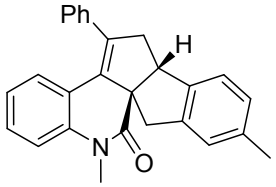


4 **2a** **5**, 36%

To a Schlenk tube were added 1,1-diphenyl ethylene **4** (0.2 mmol, 1.0 equiv, 36 mg), 4-methylbenzenesulfonyl chloride **2a** (0.4 mmol, 2.0 equiv, 76 mg), CuCl (0.04mmol, 20 mol%, 4 mg), Na_2CO_3 (0.6 mmol, 3.0 equiv, 63.6mg), and mesitylene (2 mL) under air. Then the tube was evacuated briefly under high vacuum and charged with nitrogen through using standard Schlenk techniques; this process was repeated three times. Then the reaction mixture was stirred at 130 °C (oil bath temperature) for the indicated time (about 12 h) until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered through Celite to give a yellow solution, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired products **5** in 36% yield.

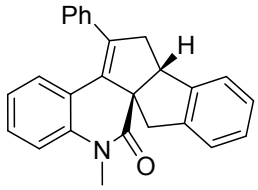
5. Characterization of the Products

(6a*R*,11a*R*)-9,13-dimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*- benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (3aa)



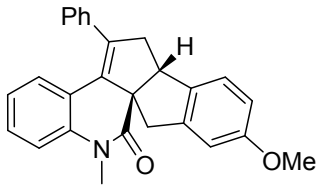
White solid, Mp = 203.8-204.9 °C. Yield = 58%, m = 43.7 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.30-7.22 (m, 7H), 7.12-7.07 (m, 3H), 6.88-6.85 (m, 2H), 4.57 (d, *J* = 7.5 Hz, 1H), 3.47 (s, 3H), 3.32-3.27 (m, 1H), 3.13-3.00 (m, 3H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.8, 144.4, 140.1, 139.6, 137.8, 136.7, 136.3, 131.3, 128.3, 128.2 (2C), 128.1, 127.6, 127.5, 125.2, 124.3, 123.1, 122.3, 115.3, 65.8, 48.2, 46.3, 42.5, 30.1, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}NO^+$ 378.1852; found 378.1850.

(6a*R*,11a*R*)-13-methyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5]pentaleno [6a,1-*c*]quinolin-12-one (3ab)



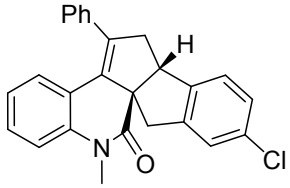
White solid, Mp = 186.0-187.5 °C. Yield = 56%, m = 40.7 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.0 Hz, 1H), 7.28-7.22 (m, 7H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14-7.11 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 4.62 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.47 (s, 3H), 3.35-3.30 (m, 1H), 3.16 -3.05 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.8, 147.3, 140.1, 139.5, 137.8, 136.3, 131.3, 128.3, 128.2 (2C), 127.6 (2C), 127.2, 127.0, 124.7 (2C), 123.10, 122.4, 115.4, 65.6, 48.6, 46.3, 42.7, 30.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}NO^+$ 364.1696; found 364.1694.

(6a*R*,11a*R*)-9-methoxy-13-methyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*- benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (**3ac**)



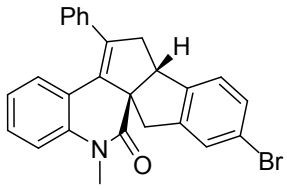
White solid, **Mp** = 193.0-195.2 °C. Yield = 53%, m = 41.8 mg (eluent: petroleum ether/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.30-7.22 (m, 7H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.57 (s, 1H), 4.54 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.75 (s, 3H), 3.47 (s, 3H), 3.31-3.26 (m, 1H), 3.11-3.01 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.7, 159.2, 141.0, 140.1, 139.5, 137.9, 136.4, 131.3, 128.3, 128.2 (2C), 127.6, 127.5, 125.2, 123.1, 122.3, 115.3, 113.6, 109.5, 66.2, 55.3, 47.8, 46.4, 42.8, 30.1. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}NO_2^+$ 394.1802; found 394.1799.

(6a*R*,11a*R*)-9-chloro-13-methyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (**3ad**)



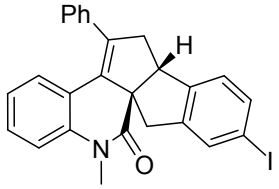
White solid, **Mp** = 233.5-234.1 °C. Yield = 43%, m = 34.2 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 7.25-7.23 (m, 6H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.01 (s, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 4.56 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.47 (s, 3H), 3.33-3.28 (m, 1H), 3.10-3.01 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.3, 145.8, 141.6, 140.0, 137.8, 136.1, 132.6, 131.1, 128.5, 128.2 (2C), 127.7, 127.6, 127.5, 125.7, 124.8, 122.8, 122.5, 115.4, 65.9, 48.1, 46.2, 42.5, 30.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}ClNO^+$ 398.1306; found 398.1304.

(6a*R*,11a*R*)-9-bromo-13-methyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (3ae)



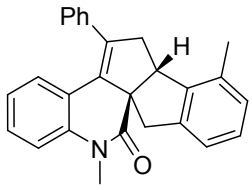
White solid, **Mp** = 222.5-223.9 °C. Yield = 50%, m = 44.1 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 6.5 Hz, 1H), 7.29-7.23 (m, 7H), 7.17-7.12 (m, 3H), 6.89 (t, *J* = 6.5 Hz, 1H), 4.54 (d, J = 7.5 Hz, 1H), 3.47 (s, 3H), 3.33-3.28 (m, 1H), 3.09-3.02 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.3, 146.3, 142.0, 140.0, 137.8, 136.1, 131.1, 130.3, 128.5, 128.2 (2C), 127.7 (2C), 127.6, 126.1, 122.8, 122.5, 120.6, 115.4, 65.8, 48.2, 46.1, 42.4, 30.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}BrNO^+$ 442.0801; found 442.0801.

(6a*R*,11a*R*)-9-iodo-13-methyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (3af)



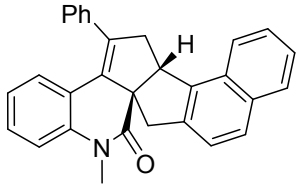
White solid, **Mp** = 214.8-215.9 °C. Yield = 51%, m = 50.0 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.0 Hz, 1H), 7.38 (s, 1H), 7.31-7.23 (m, 6H), 7.12 (d, *J* = 6.5 Hz, 3H), 6.89 (t, *J* = 7.0 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 3.47 (s, 3H), 3.33-3.28 (m, 1H), 3.09-3.01 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.3, 147.1, 142.4, 140.0, 137.9, 136.2, 136.1, 133.8, 131.1, 128.5, 128.3, 128.2, 127.7, 127.6, 126.5, 122.8, 122.5, 115.4, 92.0, 65.6, 48.3, 46.1, 42.3, 30.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}INO^+$ 490.0662; found 490.0659.

(6a*R*,11a*R*)-7,13-dimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] Pentaleno[6a,1-*c*]quinolin-12-one (3ag)



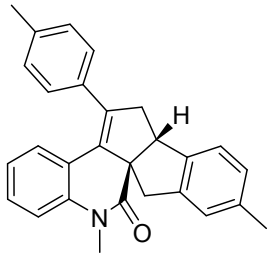
White solid, **Mp** = 208.1-209.7 °C. Yield =58%, m = 43.8 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.29-7.24 (m, 6H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.11-7.04 (m, 3H), 6.89-6.85 (m, 2H), 4.63-4.60 (m, 1H), 3.46 (s, 3H), 3.34-3.29 (m, 1H), 3.17 (d, *J* = 17.0 Hz, 1H), 3.06 (d, *J* = 17.0 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 174.2, 145.7, 140.3, 139.6, 137.6, 136.5, 133.9, 131.5, 128.4, 128.2 (2C), 128.1, 127.6 (2C), 127.3, 122.8, 122.3, 122.1, 115.3, 65.0, 48.6, 45.2, 43.6, 30.1, 19.1. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}NO^+$ 378.1852; found 378.1852.

(6a*R*,13a*R*)-15-methyl-5-phenyl-6,6a,13,15-tetrahydro-14*H*-naphtho[1',2':4,5] pentaleno[6a,1-*c*]quinolin-14-one (3ah)



White solid, **Mp** > 250 °C. Yield = 47%, m = 38.9 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91-7.87 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.22-7.13 (m, 8H), 6.89 (t, *J* = 7.5 Hz, 1H), 5.06 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.54-3.50 (m, 4H), 3.33-3.20 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 174.1, 142.0, 140.4, 137.9, 136.4, 136.1, 133.3, 131.4, 129.9, 128.6, 128.5, 128.2 (2C), 128.0, 127.7, 127.6, 126.2, 125.1, 124.5, 123.1, 122.9, 122.4, 115.4, 65.6, 48.3, 45.7, 44.2, 30.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}NO^+$ 414.1852; found 414.1850.

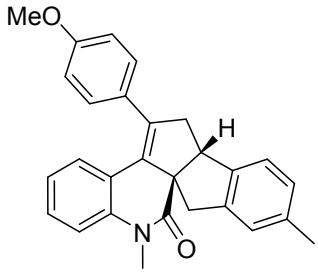
(6a*R*,11a*R*)-9,13-dimethyl-5-(p-tolyl)-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (3ba)



White solid, **Mp** = 188.7-189.8 °C. Yield = 56%, m = 43.8 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.29-7.24 (m, 2H), 7.19-7.07 (m, 5H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.90-6.85 (m, 2H), 4.55 (d, *J* = 7.0 Hz, 1H), 3.46 (s, 3H), 3.30-3.24 (m, 1H), 3.12-3.00 (m, 3H), 2.30 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.9, 144.5, 140.1, 139.7, 137.8, 137.4, 136.7, 133.4, 130.7, 129.6, 128.9, 128.4, 128.2, 128.1, 127.6, 125.2, 124.4, 123.4, 122.3, 115.3, 65.8, 48.2, 46.3, 42.5, 30.1, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO^+$ 392.2009; found 392.2006.

(6a*R*,11a*R*)-5-(4-methoxyphenyl)-9,13-dimethyl-6,6a,11,13-tetrahydro-12*H*-benzo

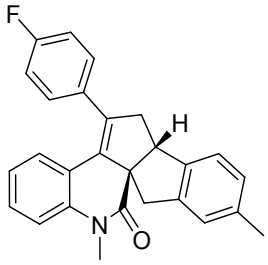
[4,5]pentaleno[6a,1-*c*]quinolin-12-one (3ca)



White solid, **Mp** = 187.9-189.8 °C. Yield = 46%, m = 37.5 mg (eluent: petroleum ether/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.29-7.24 (m, 2H), 7.20-7.18 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 4.55 (d, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 3.46 (s, 3H), 3.29-3.23 (m, 1H), 3.11-2.98 (m, 3H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.9, 158.9, 144.5, 140.2, 139.7, 137.3, 136.7, 130.0, 129.5, 128.6, 128.1 (2C), 127.6, 125.2, 124.3, 123.5, 122.3, 115.3, 113.5, 65.7, 55.1, 48.1, 46.2, 42.4, 30.1, 21.2. **HRMS** (ESI-

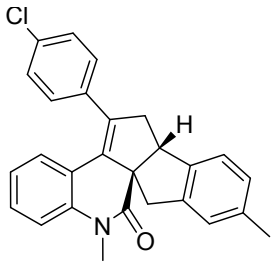
TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_2^+$ 408.1958; found 408.1957.

(6a*R*,11a*R*)-5-(4-fluorophenyl)-9,13-dimethyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3da)



White solid, **Mp** = 197.7-198.8 °C. Yield = 51%, m = 40.4 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.29 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.22-7.19 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.09 (t, *J* = 6.5 Hz, 2H) 6.93-6.88 (m, 3H), 6.85 (s, 1H), 4.56 (d, *J* = 7.0 Hz, 1H), 3.46 (s, 3H), 3.30-3.25 (m, 1H), 3.10-2.99 (m, 3H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.7, 162.0 (d, *J* = 245.8 Hz), 144.3, 140.2, 139.6, 136.8, 136.6, 132.3 (d, *J* = 3.6 Hz), 131.6, 130.0 (d, *J* = 7.8 Hz), 128.4, 128.2, 127.5, 125.2, 124.3, 123.0, 122.4, 115.4, 115.2 (d, *J* = 21.3 Hz), 65.8, 48.2, 46.4, 42.4, 30.1, 21.2; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -113.8. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}FNO^+$ 396.1758; found: 396.1758.

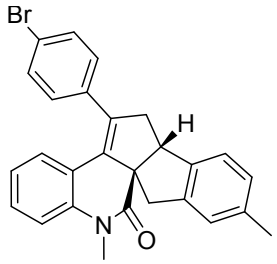
(6a*R*,11a*R*)-5-(4-chlorophenyl)-9,13-dimethyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3ea)



White solid, **Mp** = 189.8-190.5 °C. Yield =45%, m = 37.1 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.30 (t, *J* = 7.5 Hz, 1H), 7.24 (s, 1H), 7.18 (dd, *J* = 11.5, 3.5 Hz, 4H), 7.13-7.08 (m, 3H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.85 (s, 1H), 4.56 (d, *J* = 8.5 Hz, 1H), 3.46 (s, 3H), 3.27 (dd, *J* = 17.5, 10.0 Hz, 1H), 3.09-3.00 (m, 3H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.6, 144.2, 140.2, 139.6, 136.8, 136.4, 134.8, 133.3, 132.2, 129.6, 128.6, 128.4, 128.2, 127.5, 125.2,

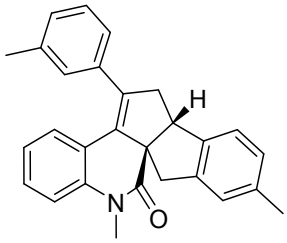
124.4, 122.9, 122.4, 115.5, 65.9, 48.1, 46.2, 42.5, 30.2, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO^+$ 412.1463; found 412.1460.

(6a*R*,11a*R*)-5-(4-bromophenyl)-9,13-dimethyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3fa)



White solid, **Mp** = 188.7-189.1 °C. Yield = 53%, m = 48.3 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.30 (t, *J* = 7.8 Hz, 1H), 7.25-7.22 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.16-7.08 (m, 5H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 4.56 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.46 (s, 3H), 3.31-3.26 m, 1H), 3.09-3.00 (m, 3H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.6, 144.2, 140.2, 139.5, 138.3, 136.8, 136.1, 134.1, 132.8, 129.5, 128.7, 128.2 (2C), 127.6, 127.4, 126.4, 125.2, 124.3, 122.6, 122.4, 115.5, 65.9, 48.1, 46.3, 42.5, 30.1, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}BrNO^+$ 456.0958; found 456.0954.

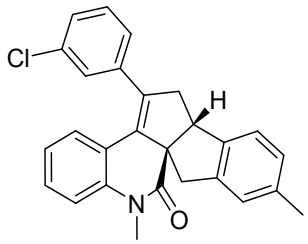
(6a*R*,11a*R*)-9,13-dimethyl-5-(m-tolyl)-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (3ga)



White solid, **Mp** = 185.2-186.0 °C. Yield = 57%, m = 44.6 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.29-7.24 (m, 2H), 7.13-7.01 (m, 7H), 6.88-6.85 (m, 2H), 4.55 (d, *J* = 8.5 Hz, 1H), 3.47 (s, 3H), 3.31-3.26 (m, 1H), 3.11-3.00 (m, 3H), 2.30 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.8, 144.5, 140.1, 139.7, 138.0, 137.7, 136.6, 136.3, 131.2, 128.8, 128.3, 128.2, 128.1, 128.0, 127.6, 125.3, 125.2, 124.4, 123.2, 122.2, 115.3, 65.8, 48.2, 46.5, 42.6, 30.1, 21.3, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO^+$ 392.2009; found

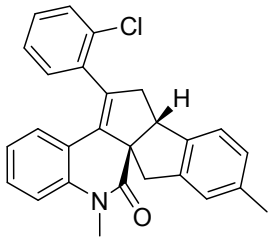
392.2008.

(6a*R*,11a*R*)-5-(3-chlorophenyl)-9,13-dimethyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3ha)



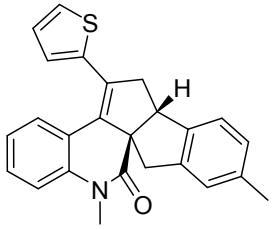
White solid, **Mp** = 203.5-205.7 °C. Yield = 54%, m = 44.4 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18-7.15 (m, 1H), 7.12-7.07 (m, 4H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 4.56 (d, *J* = 7.0 Hz, 1H), 3.46 (s, 3H), 3.29-3.24 (m, 1H), 3.08-2.99 (m, 3H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.6, 144.2, 140.2, 139.5, 136.8, 136.3, 135.3, 132.3, 131.4, 129.9, 129.0, 128.6, 128.2, 127.4, 125.2, 124.3, 122.8, 122.4, 121.5, 115.4, 65.9, 48.1, 46.1, 42.5, 30.1, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO^+$ 412.1463; found 412.1463.

(6a*R*,11a*R*)-5-(2-chlorophenyl)-9,13-dimethyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3ia)



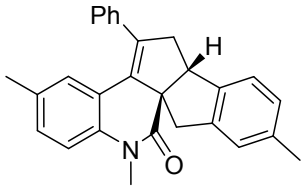
White solid, **Mp** = 194.8-195.5 °C. Yield = 52%, m = 42.7 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.5 Hz, 1H), 7.25-7.14 (m, 4H), 7.07-7.05 (m, 3H), 6.87 (s, 1H), 6.80-6.74 (m, 2H), 4.59 (d, *J* = 7.0 Hz, 1H), 3.45 (s, 3H), 3.30-3.25 (m, 1H), 3.17-3.02 (m, 3H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.6, 144.1, 139.8, 139.5, 136.7, 136.5, 136.0, 134.3, 133.0, 130.4, 129.6, 128.7, 128.3, 128.0, 126.8, 126.7, 125.2, 124.3, 122.5, 122.4, 115.0, 65.1, 49.0, 46.3, 43.3, 30.1, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO^+$ 412.1463; found 412.1463.

(6a*R*,11a*R*)-9,13-dimethyl-5-(thiophen-2-yl)-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3ja)



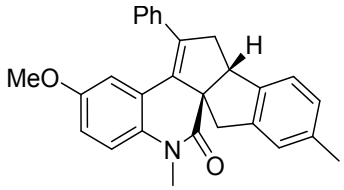
White solid, **Mp** = 198.6-199.3 °C. Yield = 43%, m = 33.0 mg (eluent: petroleum ether/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.16-7.12 (m, 3H), 7.09-7.05 (m, 2H), 6.91 (t, *J* = 4.3 Hz, 1H), 6.84 (s, 1H), 4.55 (d, *J* = 9.0 Hz, 1H), 3.47-3.42 (m, 4H), 3.13 (dd, *J* = 17.0, 2.0 Hz, 1H), 3.04-2.96 (m, 2H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.5, 144.1, 140.0, 139.5, 138.1, 136.9, 130.9, 130.2, 128.8, 128.1 (2C), 126.8, 126.7, 125.2, 125.1, 124.3, 123.4, 122.3, 115.4, 66.4, 47.7, 45.9, 41.7, 30.2, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}NOS^+$ 384.1417; found: 384.1417.

(6a*R*,11a*R*)-3,9,13-trimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] Pentaleno[6a,1-*c*]quinolin-12-one (3la)



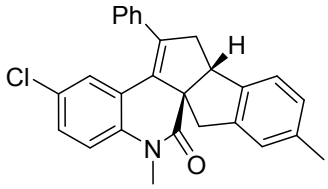
White solid, **Mp** = 226.7-227.9 °C. Yield = 59 %, m = 46.1 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.26-7.21 (m, 6H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.85 (s, 1H), 4.55 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.44 (s, 3H), 3.32-3.26 (m, 1H), 3.13-2.99 (m, 3H), 2.30 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.7, 144.5, 139.7, 137.8, 137.4, 136.6, 136.4, 131.8, 131.6, 128.8, 128.2, 128.1, 128.0, 127.5, 125.2, 124.3, 123.1, 115.2, 66.0, 48.1, 46.3, 42.6, 30.1, 21.2, 20.5. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO^+$ 392.2009; found 392.2006.

(6a*R*,11a*R*)-3-methoxy-9,13-dimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3ma)



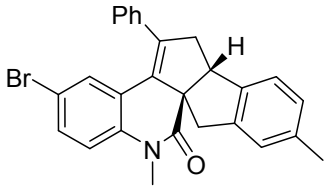
White solid, **Mp** = 185.7-187.8 °C. Yield = 50%, m = 40.8mg (eluent: petroleum ether/EtOAc = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.26-7.21 (m, 6H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.86 (s, 1H), 6.82 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 4.55 (dd, *J* = 9.5, 2.5 Hz, 1H), 3.54 (s, 3H), 3.44 (s, 3H), 3.33-3.28 (m, 1H), 3.12-3.01 (m, 3H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.4, 154.7, 144.4, 139.7, 138.2, 136.7, 136.3, 133.9, 131.7, 128.3, 128.2, 128.1, 127.7, 125.2, 124.4, 124.2, 116.3, 114.2, 112.4, 65.8, 55.3, 48.2, 46.4, 42.7, 30.2, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_2^+$ 408.1958; found 408.1958.

(6a*R*,11a*R*)-3-chloro-9,13-dimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3na)



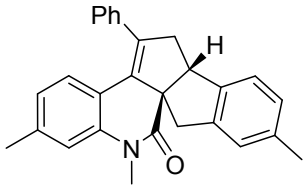
White solid, **Mp** = 198.6-199.4 °C. Yield = 45%, m = 37.1 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.26-7.21 (m, 7H), 7.09-7.06 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.86 (s, 1H), 4.55 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.44 (s, 3H), 3.32-3.27 (m, 1H), 3.13-2.99 (m, 3H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.5, 144.1, 139.6, 139.4, 138.7, 136.8, 135.7, 130.0, 128.3, 128.2, 128.1, 128.0, 127.7, 127.2, 125.2, 124.7, 124.3, 116.6, 65.6, 48.3, 46.4, 42.5, 30.3, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO^+$ 412.1463; found 412.1462.

(6a*R*,11a*R*)-3-bromo-9,13-dimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3oa)



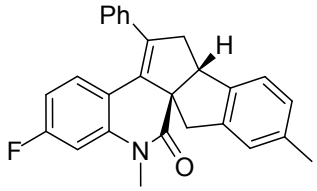
White solid, **Mp** = 187.3-189.2 °C. Yield = 50%, m = 45.5 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.38 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.25-7.21 (m, 7H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.87 (s, 1H), 4.55 (d, *J* = 7.0 Hz, 1H), 3.44 (s, 3H), 3.32-3.27 (m, 1H), 3.14-2.99 (m, 3H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.5, 144.1, 139.6, 139.4, 139.3, 136.8, 135.7, 131.0, 130.0, 129.9, 128.3, 128.2, 128.1, 128.0, 125.2, 125.1, 124.3, 116.9, 115.2, 65.6, 48.3, 46.3, 42.5, 30.2, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}BrNO^+$ 456.0958; found: 456.0958.

(6a*R*,11a*R*)-2,9,13-trimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (3pa)



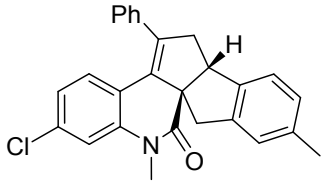
White solid, **Mp** = 234.5-236.8 °C. Yield = 57%, m = 44.6 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.24-7.21 (m, 6H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.93 (s, 1H), 6.85 (s, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 3.45 (s, 3H), 3.31-3.26 (m, 1H), 3.10-2.99 (m, 3H), 2.38 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.9, 144.5, 140.1, 139.7, 138.3, 136.9, 136.6 (2C), 131.4, 128.2, 128.1 (2C), 127.4 (2C), 125.2, 124.3, 123.1, 120.3, 116.1, 65.9, 48.2, 46.3, 42.7, 30.1, 21.8, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO^+$ 392.2009; found 392.2006.

(6a*R*,11a*R*)-2-fluoro-9,13-dimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3qa)



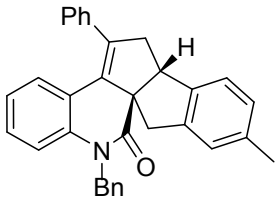
White solid, **Mp** = 189.9-190.6 °C. Yield = 48%, m = 37.9 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.26-7.20 (m, 6H), 7.09-7.04 (m, 2H), 6.87 (s, 1H), 6.83 (dd, *J* = 10.5, 2.0 Hz, 1H), 6.58 (td, *J* = 8.0, 2.0 Hz, 1H), 4.55 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.44 (s, 3H), 3.28 (dd, *J* = 17.0, 9.5 Hz, 1H), 3.11-3.00 (m, 3H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.7, 162.6 (d, *J* = 244.4 Hz), 144.3, 141.8 (d, *J* = 9.9 Hz), 139.5, 137.8, 136.8, 136.2, 130.3, 128.8 (d, *J* = 9.4 Hz), 128.3, 128.2 (2C), 127.6, 125.2, 124.4, 119.0, 108.9 (d, *J* = 21.4 Hz), 103.3 (d, J = 26.6 Hz), 65.7, 48.3, 46.3, 42.6, 30.2, 21.2. **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -111.4. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}FNO^+$ 396.1758; found 396.1756.

(6a*R*,11a*R*)-2-chloro-9,13-dimethyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo [4,5]pentaleno[6a,1-*c*]quinolin-12-one (3ra)

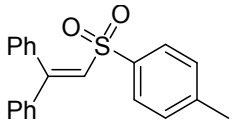


White solid, **Mp** = 201.4-202.6 °C. Yield = 42%, m = 34.5 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.25-7.19 (m, 6H), 7.11-7.08 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.86-6.84 (m, 2H), 4.55 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.44 (s, 3H), 3.31-3.26 (m, 1H), 3.11-2.99 (m, 3H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.6, 144.2, 141.3, 139.4, 138.8, 136.8, 136.1, 133.9, 130.3, 128.5, 128.3 (2C), 128.2, 127.8, 125.3, 124.4, 122.3, 121.5, 115.7, 65.7, 48.3, 46.4, 42.6, 30.2, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}ClNO^+$ 412.1463; found 412.1460.

(6a*R*,11a*R*)-13-benzyl-9-methyl-5-phenyl-6,6a,11,13-tetrahydro-12*H*-benzo[4,5] pentaleno[6a,1-*c*]quinolin-12-one (3sa)



White solid, **Mp** = 231.4-232.1 °C. Yield = 63%, m = 57.1 mg (eluent: petroleum ether/EtOAc = 20:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33 (t, *J* = 7.5 Hz, 2H), 7.29-7.21 (m, 9H), 7.14-7.09 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.60 (d, *J* = 16.5 Hz, 1H), 4.90 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 7.0 Hz, 1H), 3.38-3.33 (m, 1H), 3.19 (s, 2H), 3.15 (dd, J = 17.0, 3.0 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 173.8, 144.4, 139.6, 139.5, 138.0, 137.4, 136.8, 136.4, 131.3, 128.8, 128.3, 128.2, 127.7, 127.60, 127.1, 126.3, 125.3, 124.4, 123.4, 122.5, 116.2, 66.0, 48.1, 46.8, 46.4, 42.5, 21.2. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{28}NO^+$ 454.2165; found: 454.2166.



(2-tosylethene-1,1-diyl)dibenzene (5)

White solid, Yield = 36%, m = 24.0 mg. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.0 Hz, 2H), 7.39-7.35 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 154.7, 143.7, 139.2, 138.6, 135.6, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 127.7, 21.5.

6. Crystal Structure of 3aa (CCDC: 2059099)

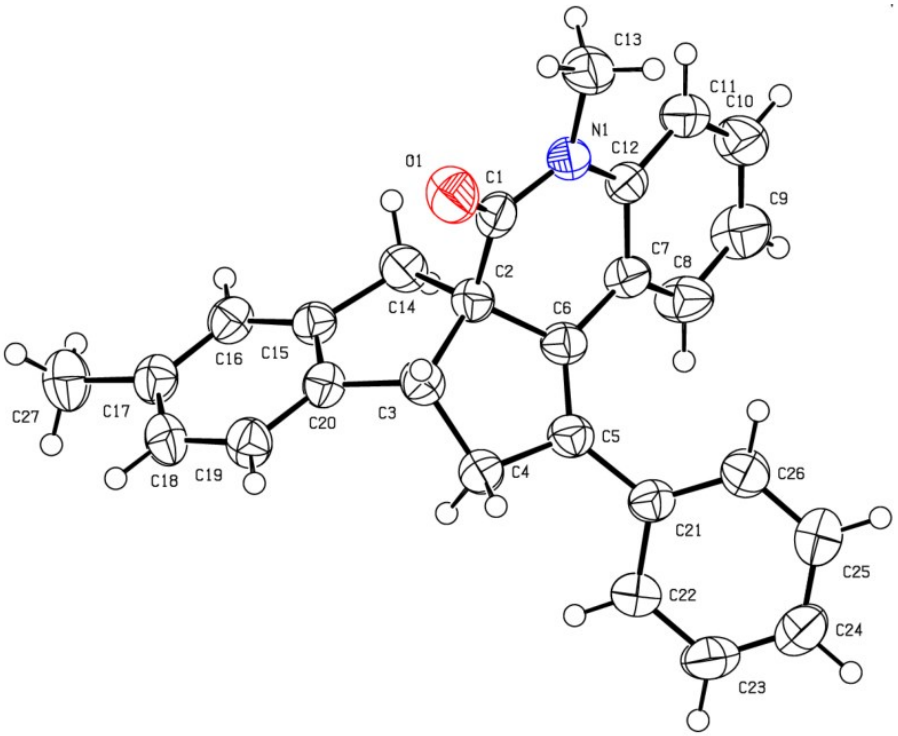


Figure S1 X-ray crystal structure of **3aa.** The thermal ellipsoids are 50% probability level

Table 1. Crystal data and structure refinement for ZXM249.

Identification code	zxm249
Empirical formula	$C_{27}H_{23}NO$
Formula weight	377.46
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.809(2) A alpha = 90 deg. b = 18.238(3) A beta = 94.369(3) deg. c = 10.0836(18) A gamma = 90 deg.
Volume	1982.1(6) A^3
Z, Calculated density	4, 1.265 Mg/m^3
Absorption coefficient	0.076 mm^-1
F(000)	800
Crystal size	0.230 x 0.220 x 0.190 mm
Theta range for data collection	1.889 to 26.457 deg.
Limiting indices	-13<=h<=12, -11<=k<=22, -11<=l<=12
Reflections collected / unique	11271 / 4085 [R(int) = 0.0338]
Completeness to theta = 25.242	99.9 %

Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4085 / 0 / 264
Goodness-of-fit on F^2	1.250
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1537
R indices (all data)	R1 = 0.0550, wR2 = 0.1651
Extinction coefficient	n/a
Largest diff. peak and hole	0.218 and -0.197 e.A^-3

7. References

[1] C. M. Le, T. Sperger, R. Fu, X. Hou, Y. H. Lim, F. Schoenebeck, M. Lautens, *J. Am. Chem. Soc.* **2016***, 138,* 14441.

[2] C. M. Le, X. Hou, T. Sperger, F. Schoenebeck, M. Lautens, *Angew. Chem. Int. Ed.* **2015***, 54,* 15897; *Angew. Chem.* **2015***, 127,* 16127.

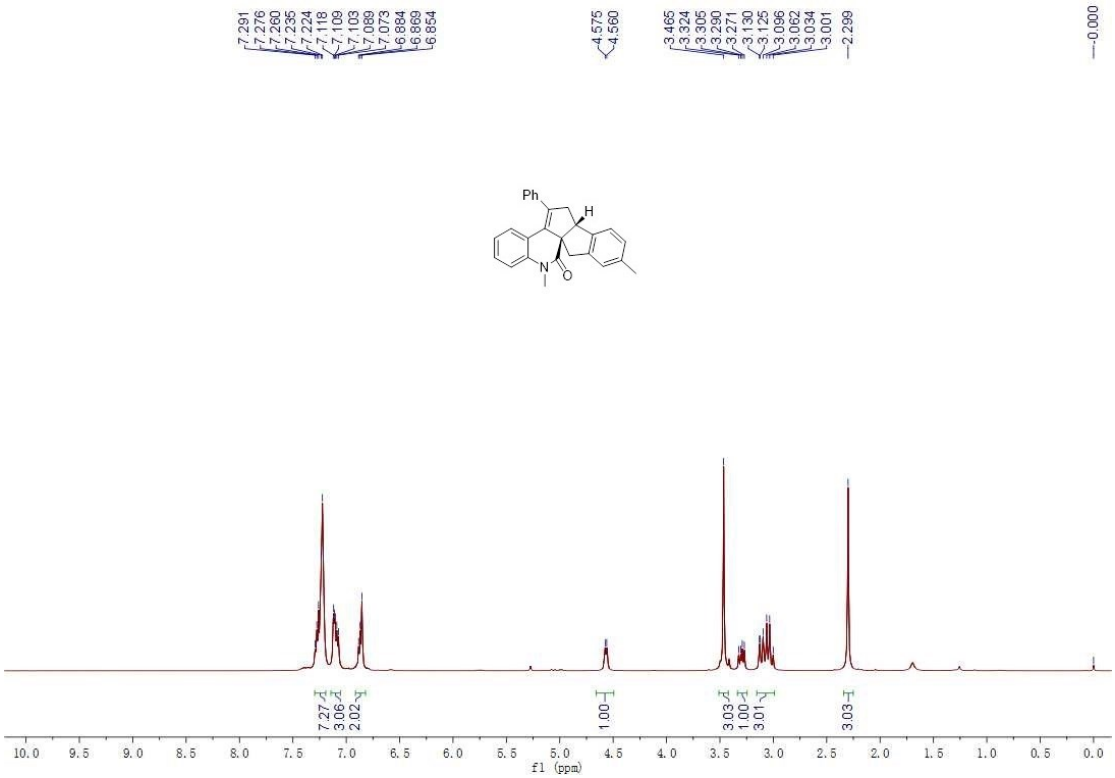
[3] B. Liu, J.-X. Yu, Y. Li, J.-H. Li, D.-L. He, *Org. Lett.* **2018**, *20,* 2129.

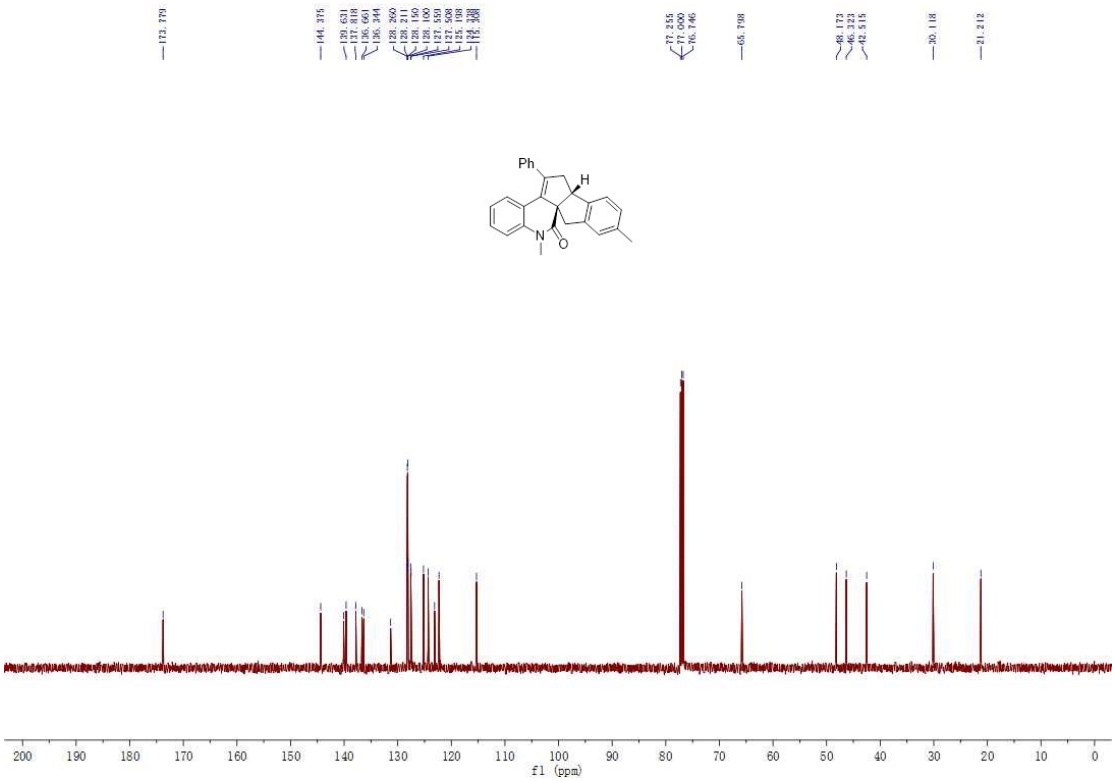
[4] Y.-M. Li, M. Sun, H.-Li. Wang, Q.-P. Tian, S.-D Yang, *Angew. Chem. Int. Ed.* **2013***, 52,* 3972; *Angew. Chem.* **2013***, 125,* 4064.

[5] X. Luo, L. Zhou, H. Lu, G Deng, Y. Liang, C. Yang, Y. Yang, *Org. Lett.* **2019**, *21*, 9960.

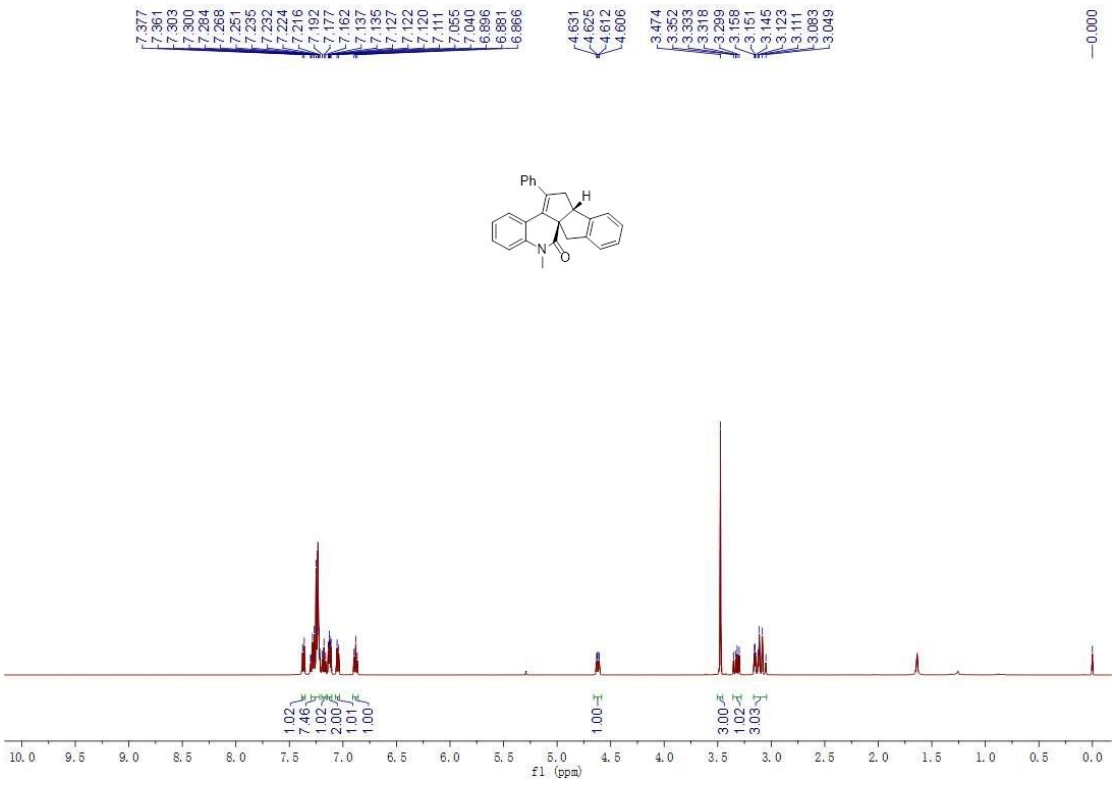
8. Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

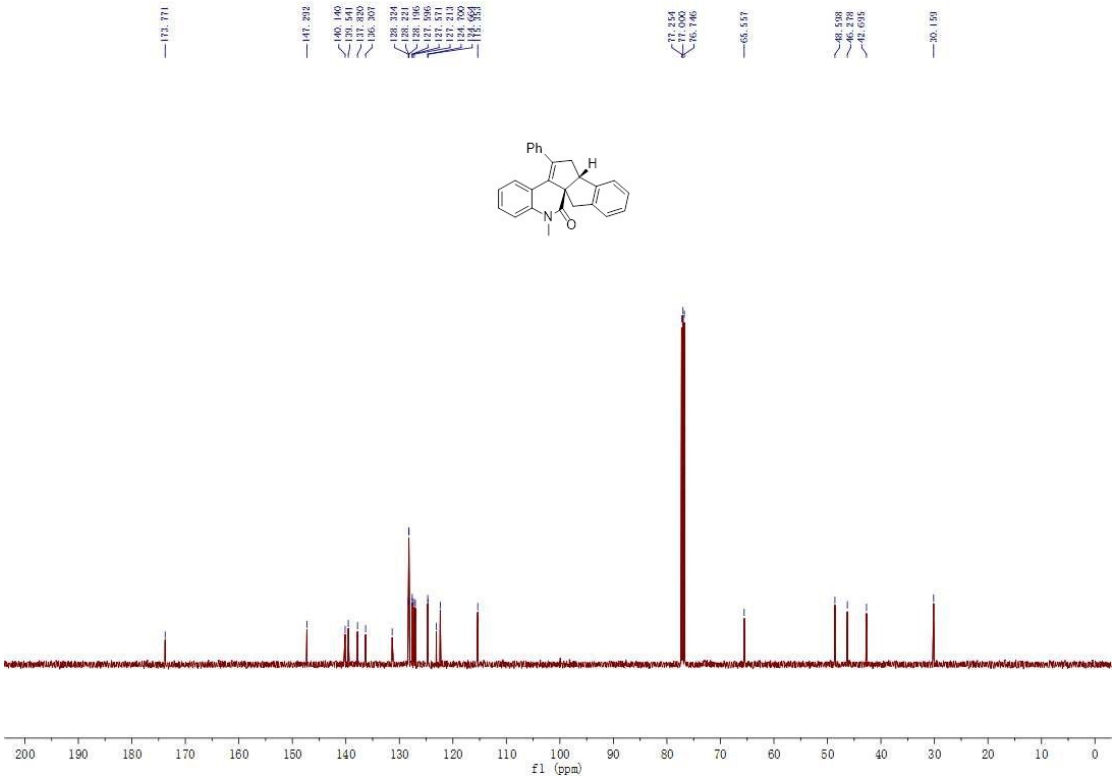
^{1}H NMR of **3aa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aa** (125 MHz, $CDCl_3$)



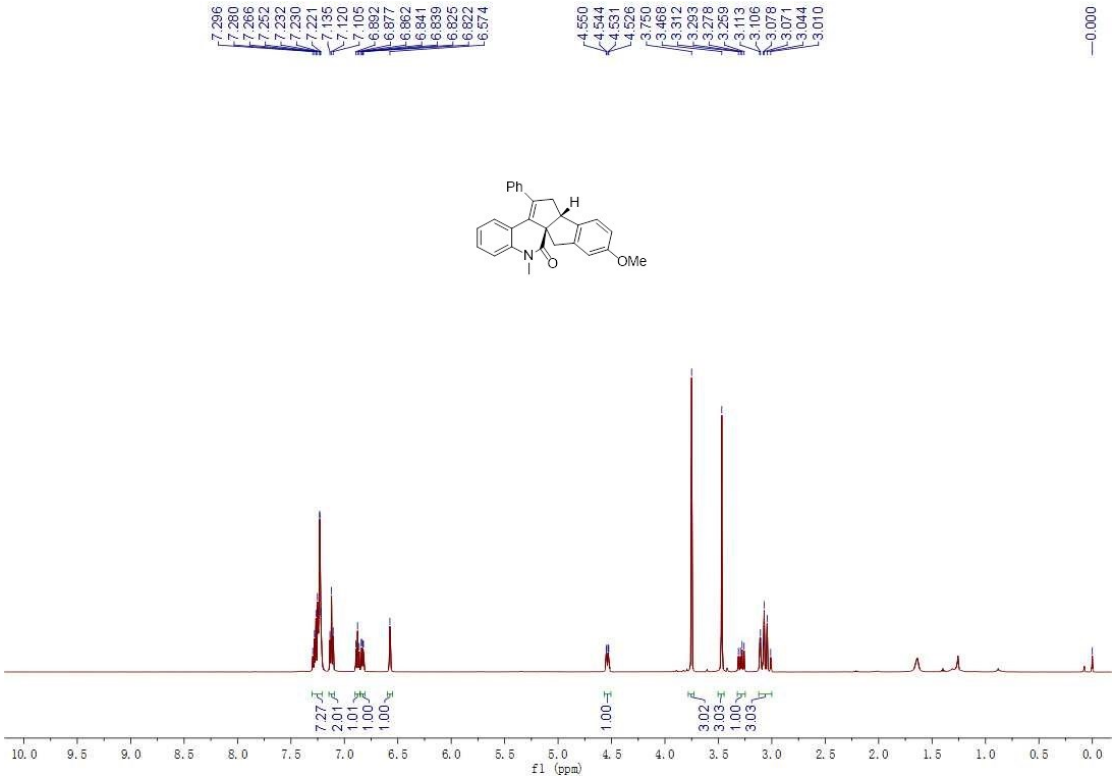


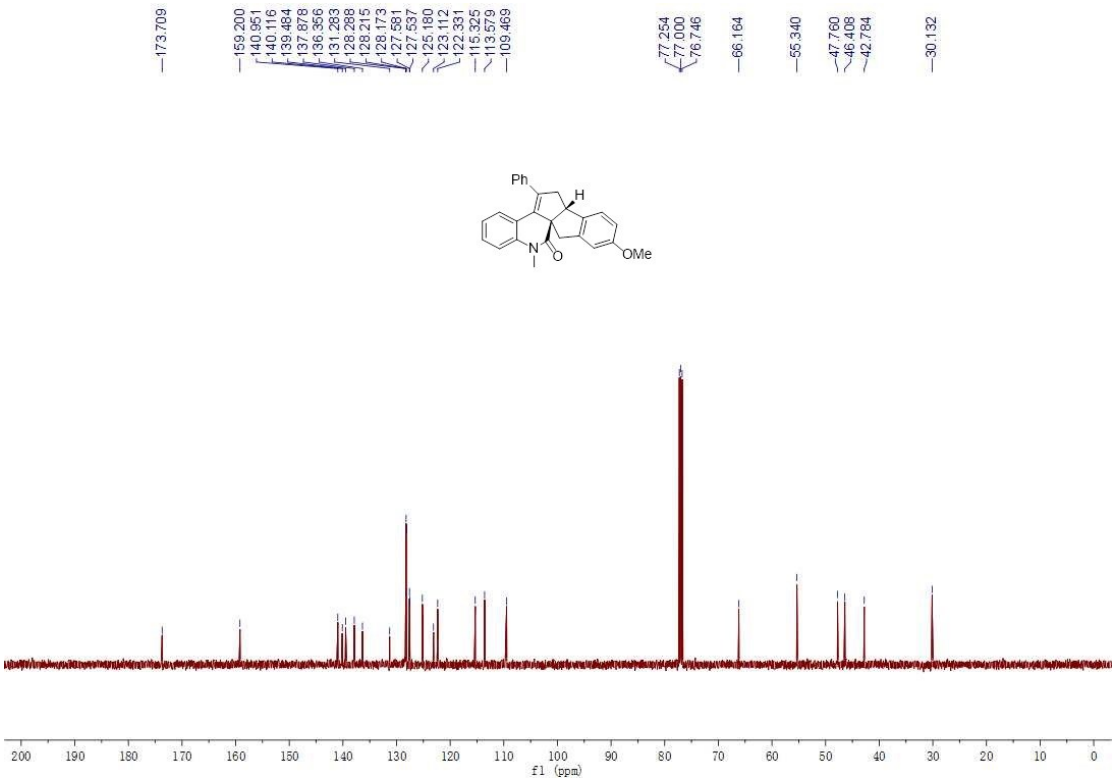
^{1}H NMR of **3ab** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ab** (125 MHz, $CDCl_3$)



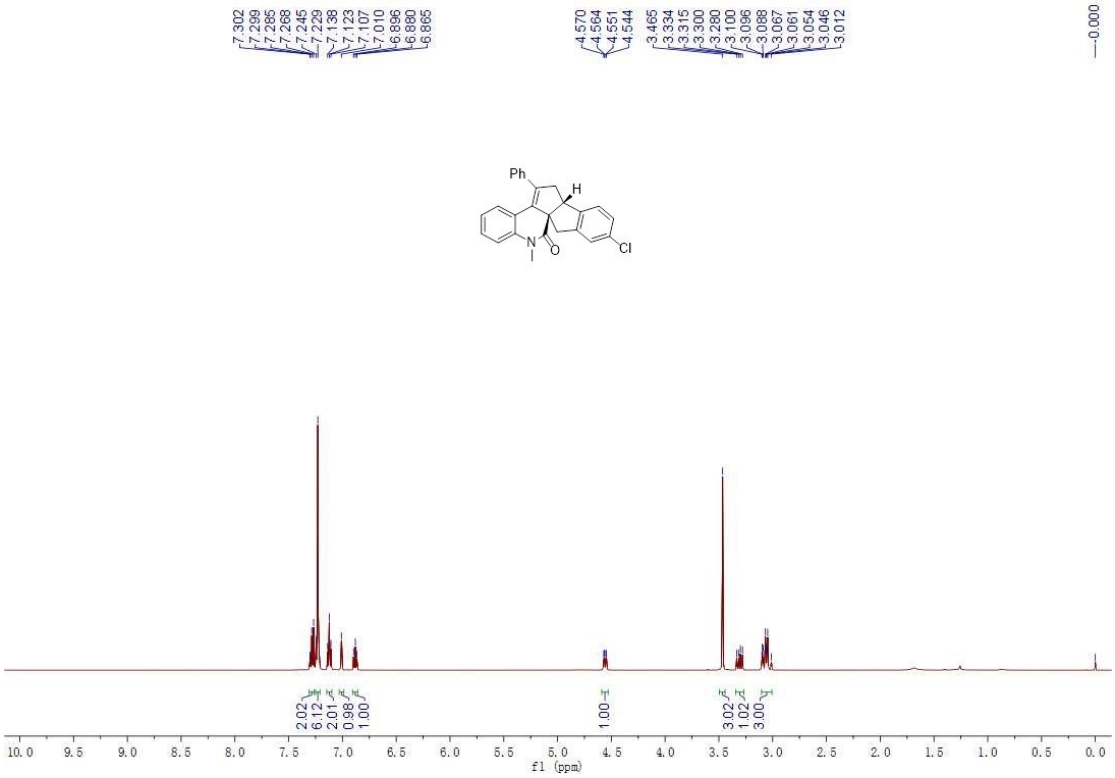


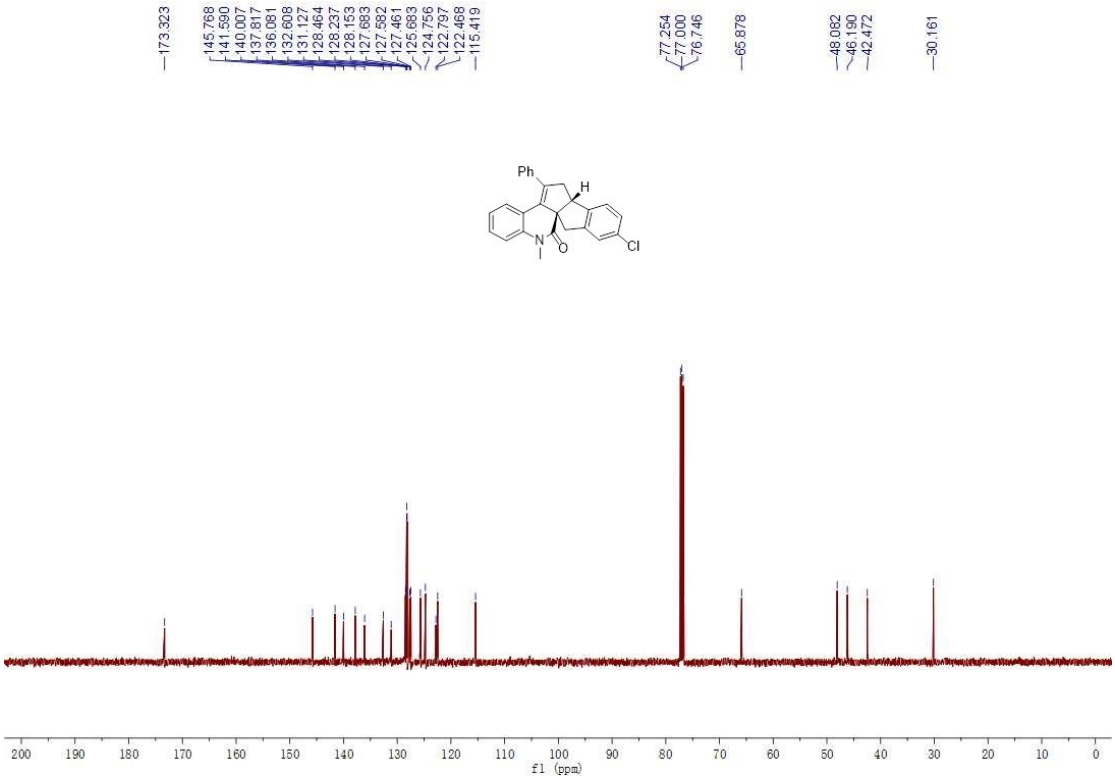
^{1}H NMR of **3ac** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ac** (125 MHz, $CDCl_3$)



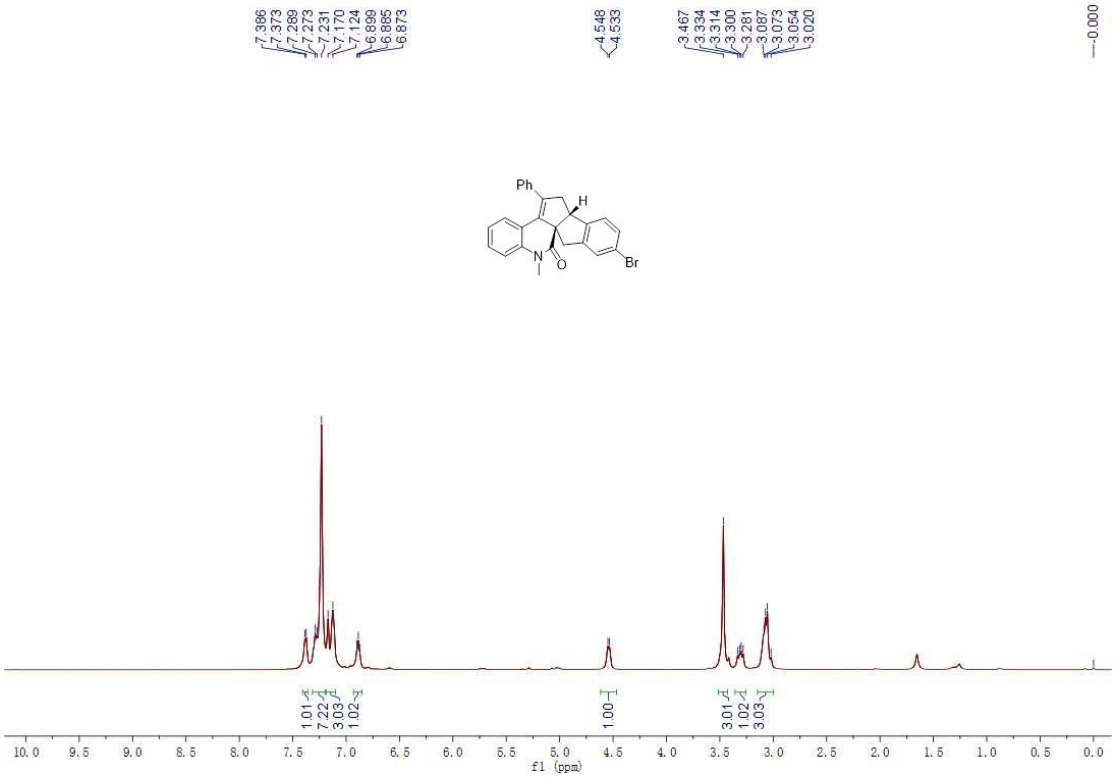


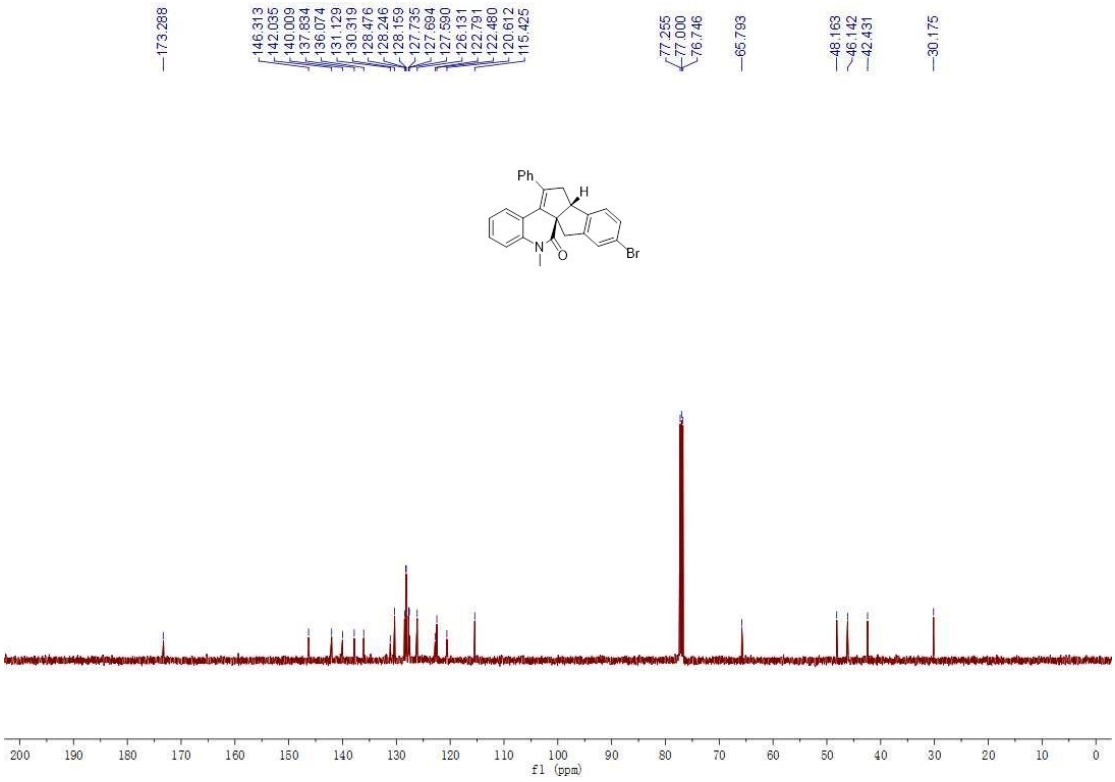
^{1}H NMR of **3ad** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ad** (125 MHz, $CDCl_3$)



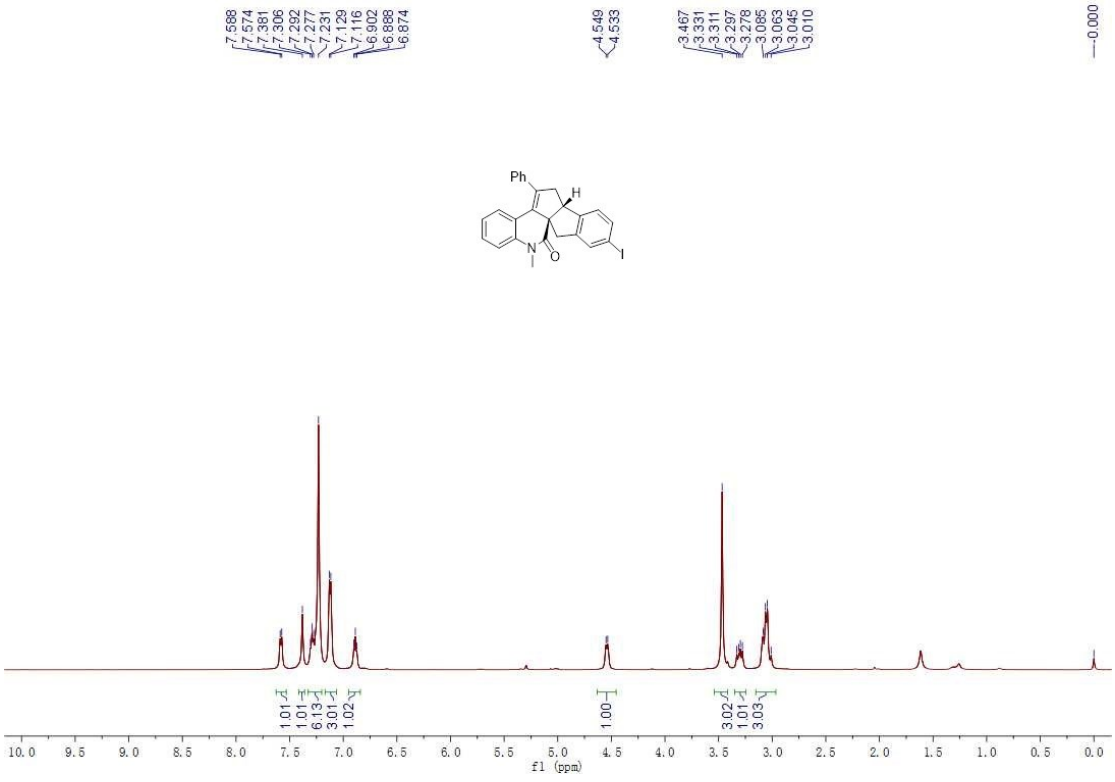


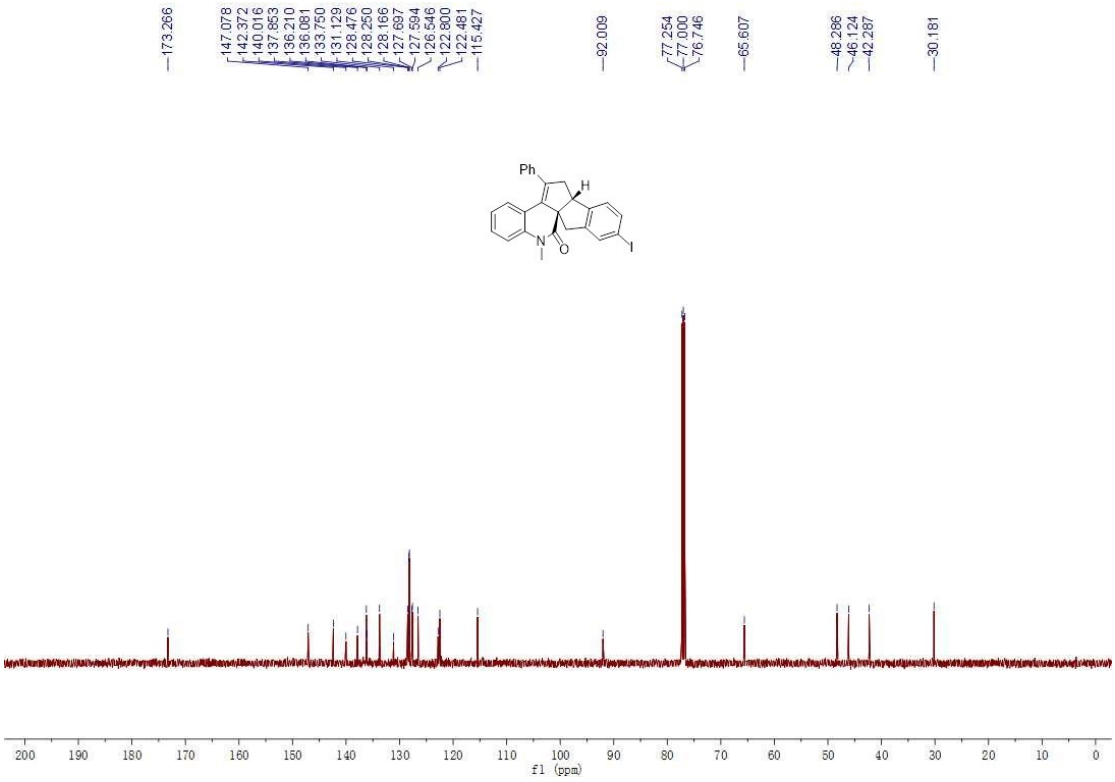
^{1}H NMR of **3ae** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ae** (125 MHz, $CDCl_3$)



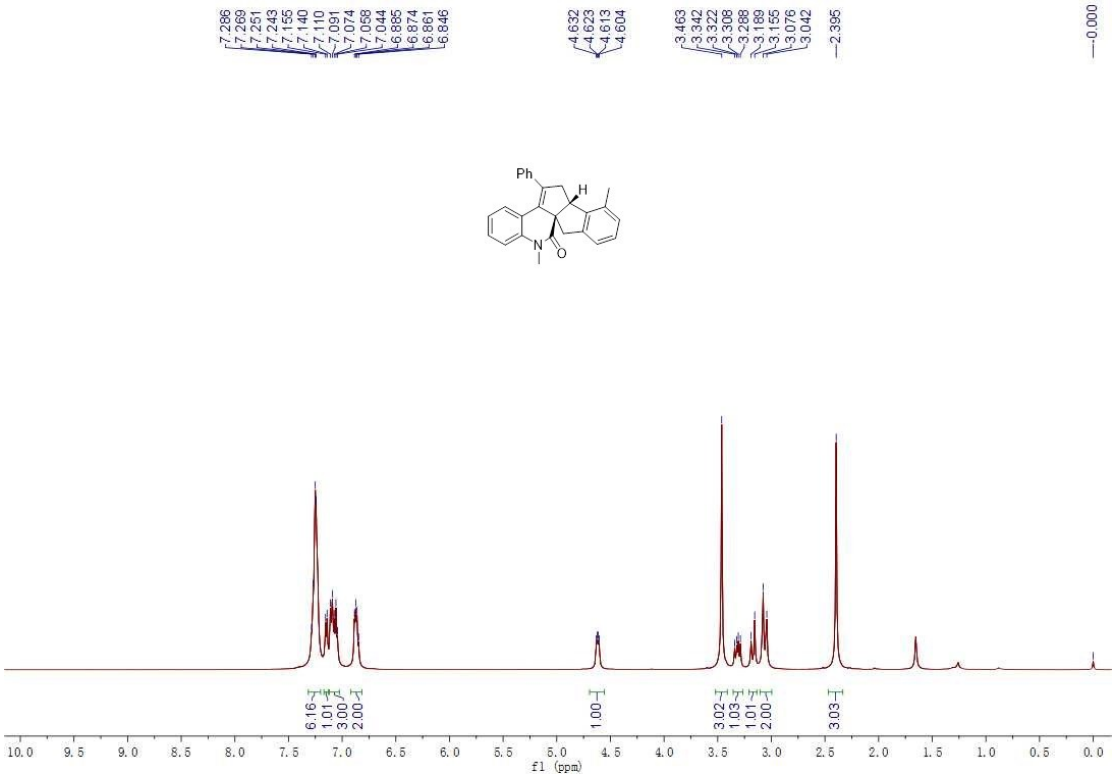


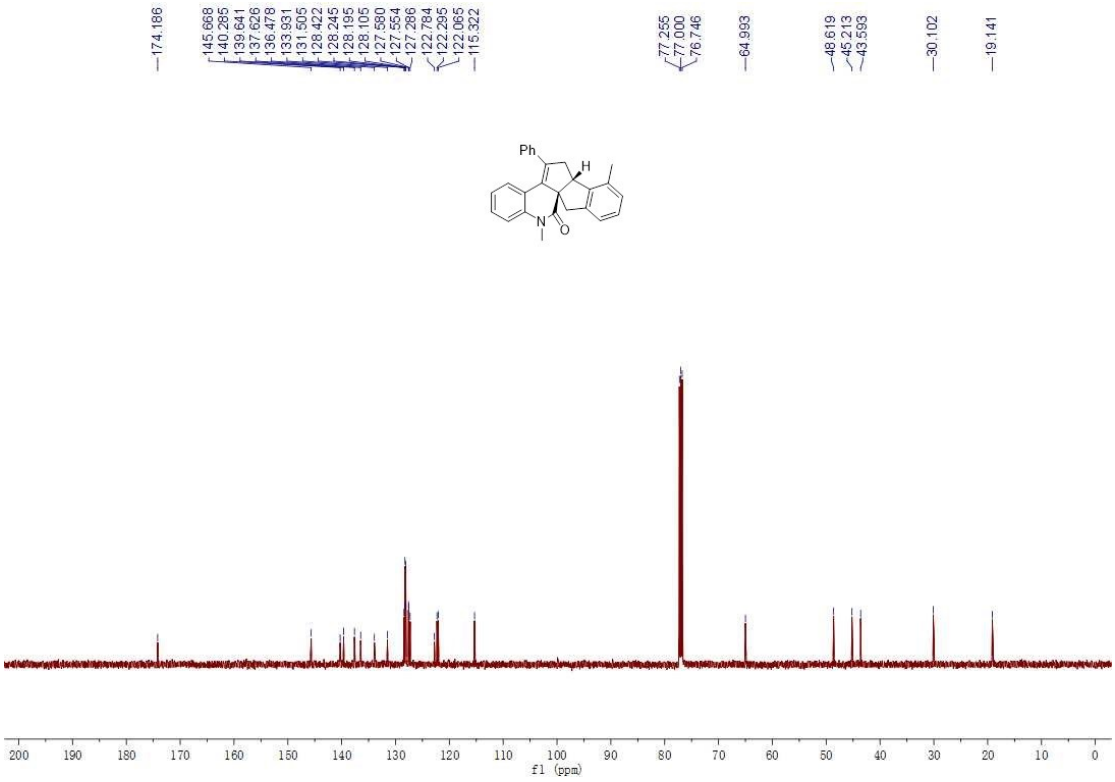
^{1}H NMR of **3af** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3af** (125 MHz, $CDCl_3$)



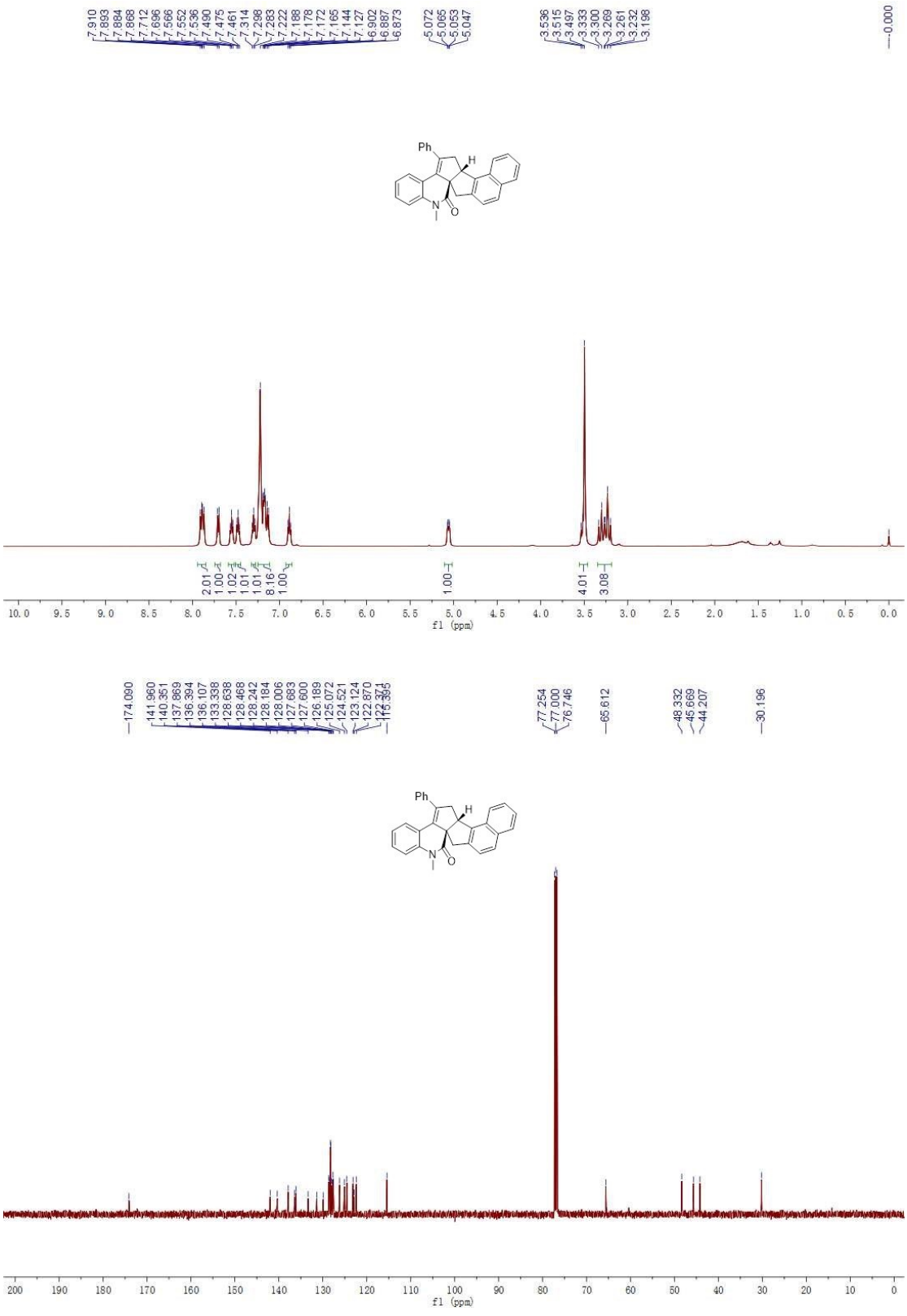


^{1}H NMR of **3ag** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ag** (125 MHz, $CDCl_3$)

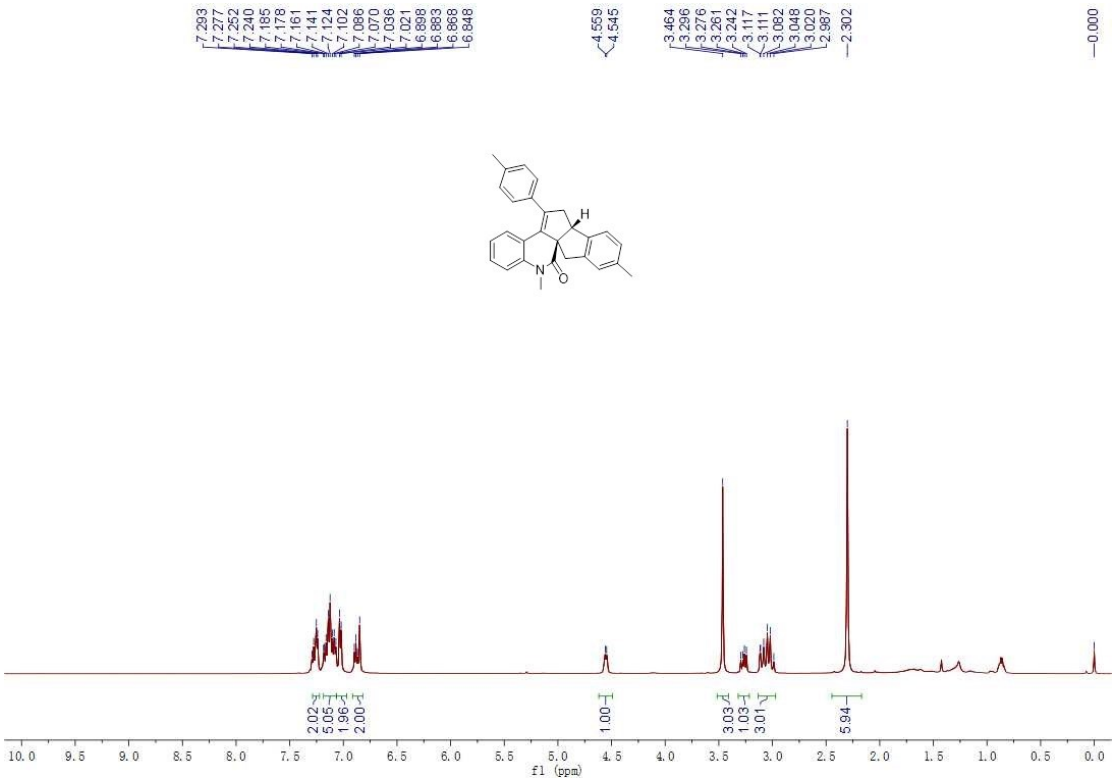




^{1}H NMR of **3ah** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ah** (125 MHz, $CDCl_3$)



^{1}H NMR of **3ba** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ba** (125 MHz, $CDCl_3$)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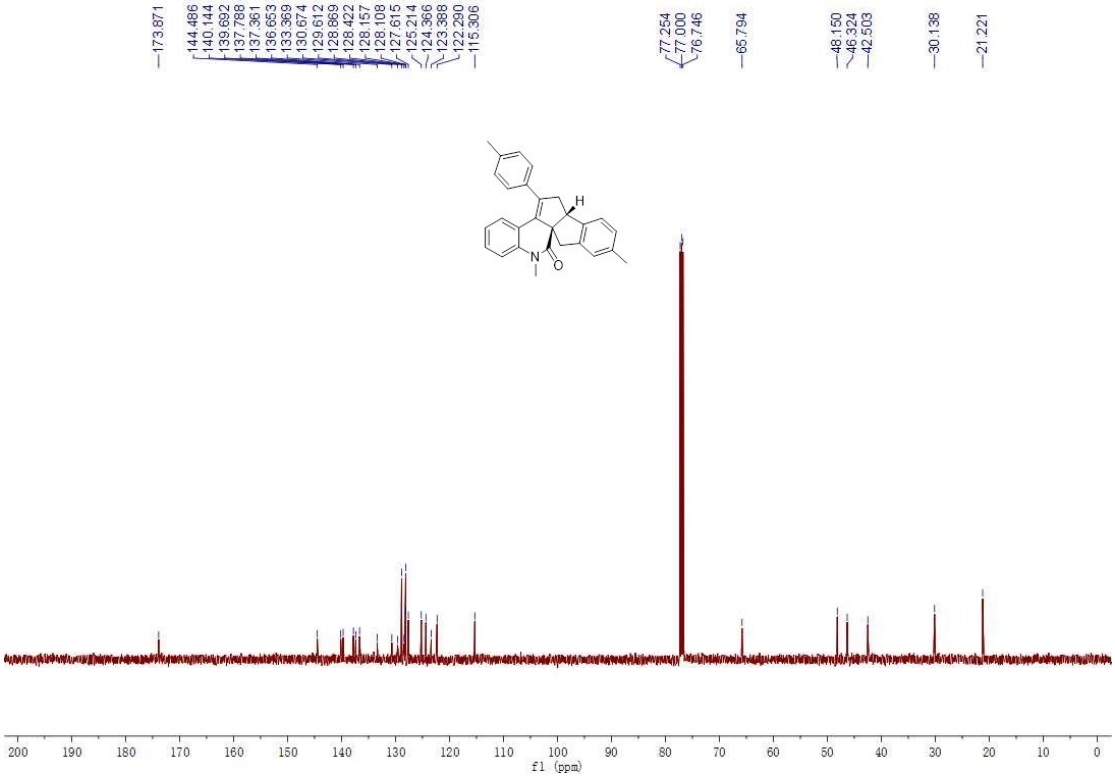
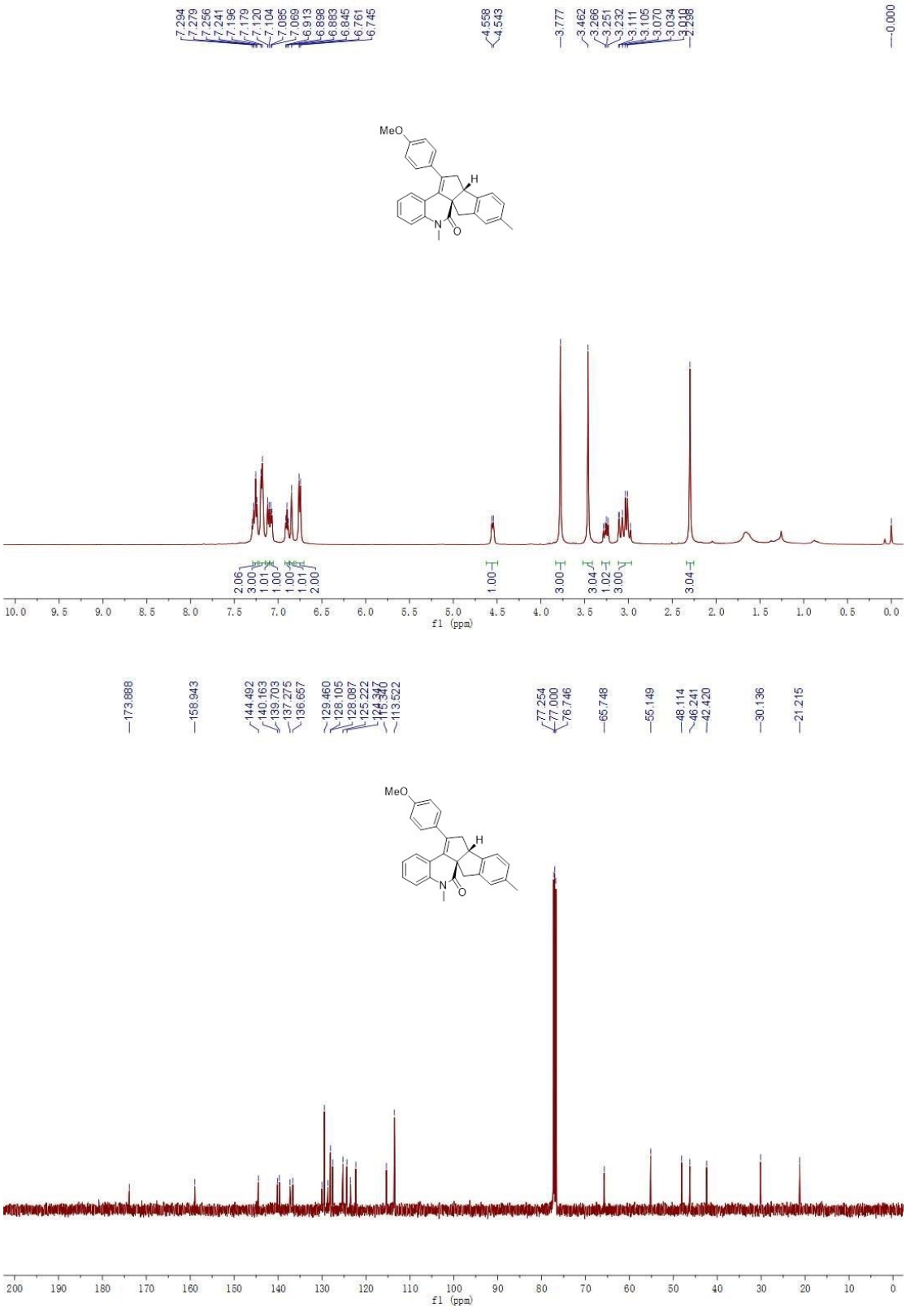
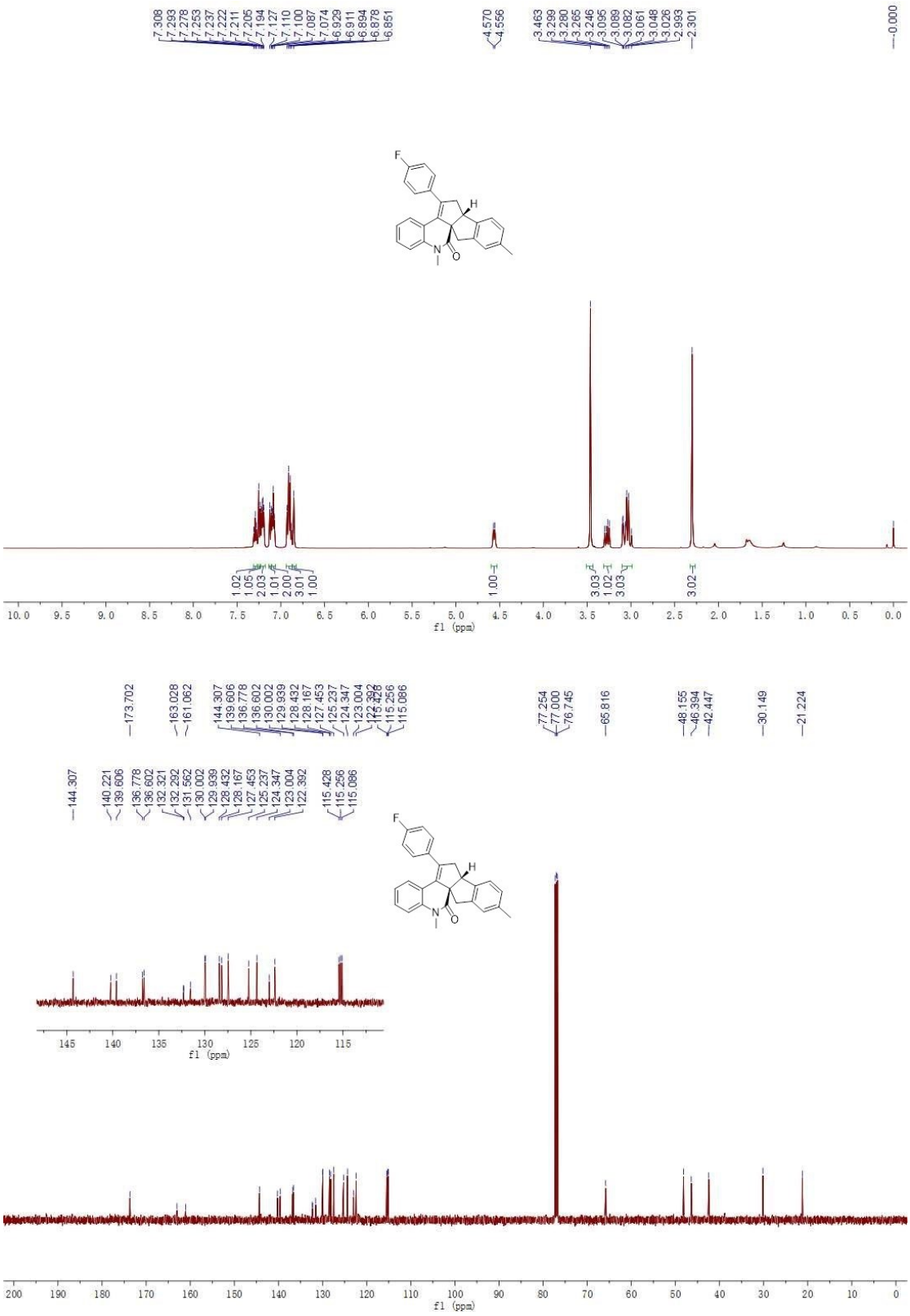
7.277
7.252
7.240
7.185
7.178
7.161
7.141
7.124
7.102
7.086
7.070
7.036
7.021
6.898
6.883
6.868
6.848
4.559
4.545
3.464
3.296
3.276
3.261
3.242
3.117
3.111
3.082
3.048
3.020
2.987
2.302
0.000
H
N
O
2.02
5.05
1.96
2.00
1.00
3.03
1.03
3.01
5.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.871
144.486
140.144
139.692
137.788
137.361
136.653
133.369
130.674
129.612
128.869
128.422
128.157
128.108
127.615
125.214
124.366
123.388
122.290
115.306
77.254
77.000
76.746
65.794
48.150
46.324
42.503
30.138
21.221
H
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

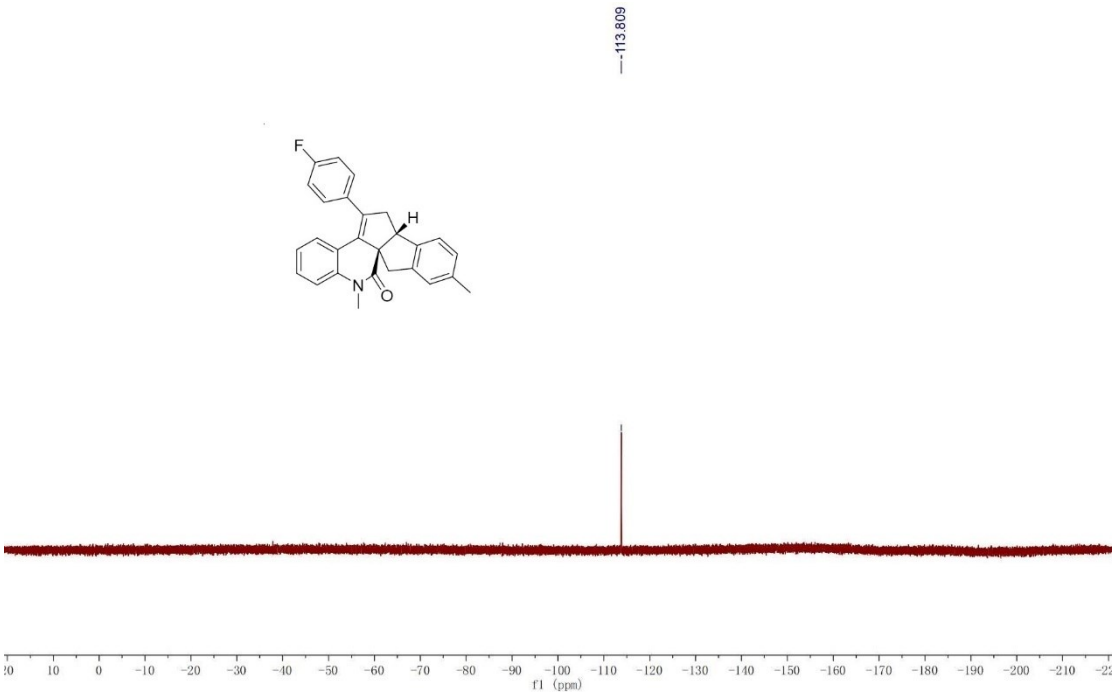
^{1}H NMR of **3ca** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ca** (125 MHz, $CDCl_3$)



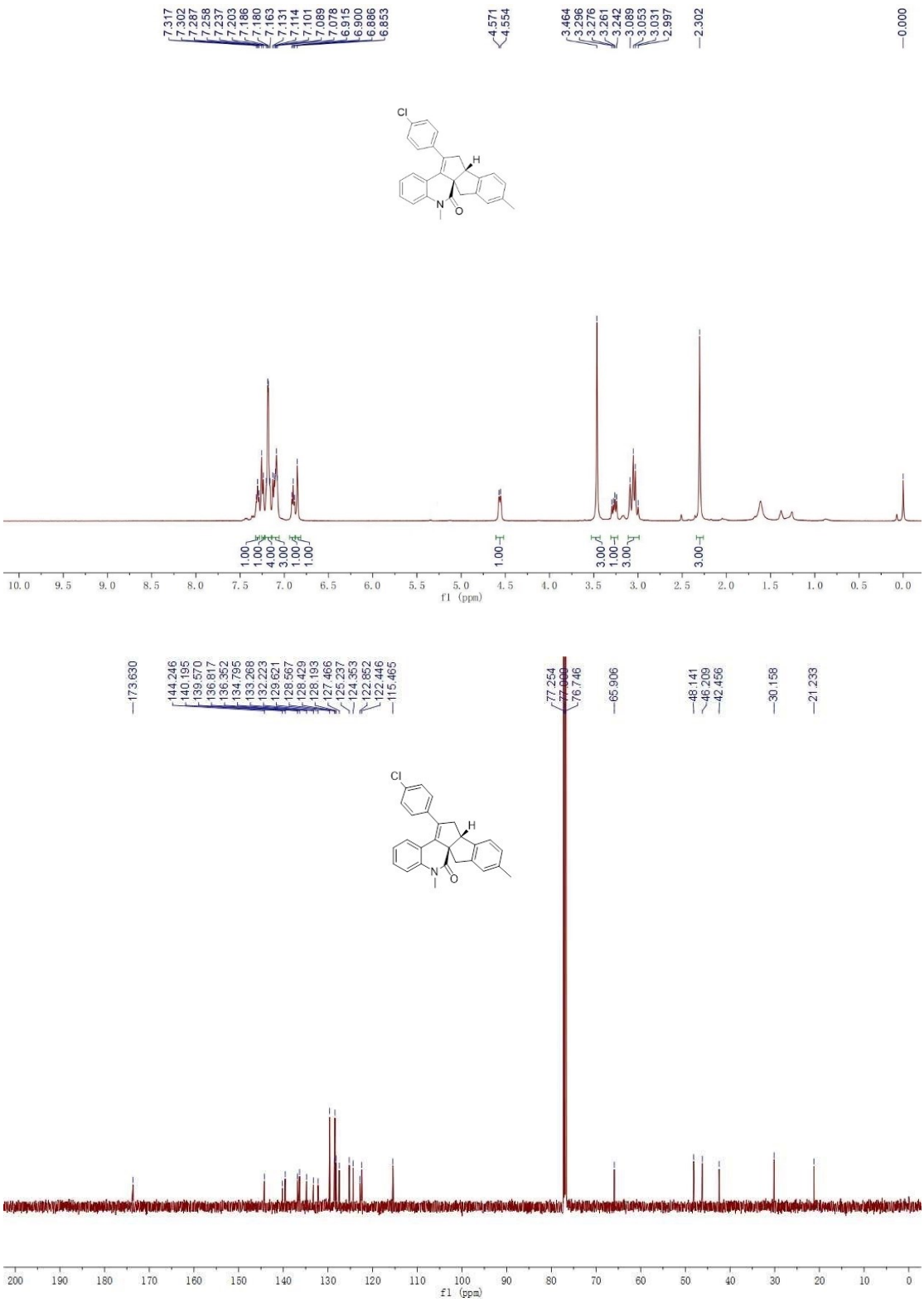
^{1}H NMR of **3da** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3da** (125 MHz, $CDCl_3$)



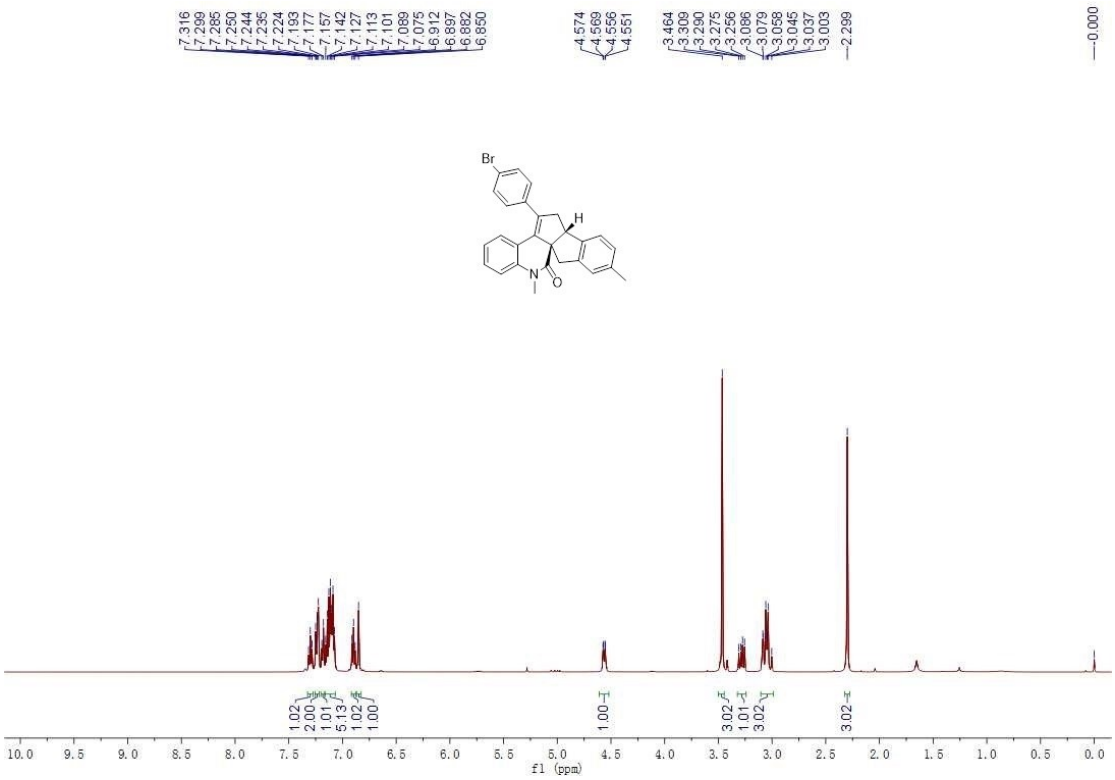
^{19}F NMR of **3da** (470 MHz, $CDCl_3$)

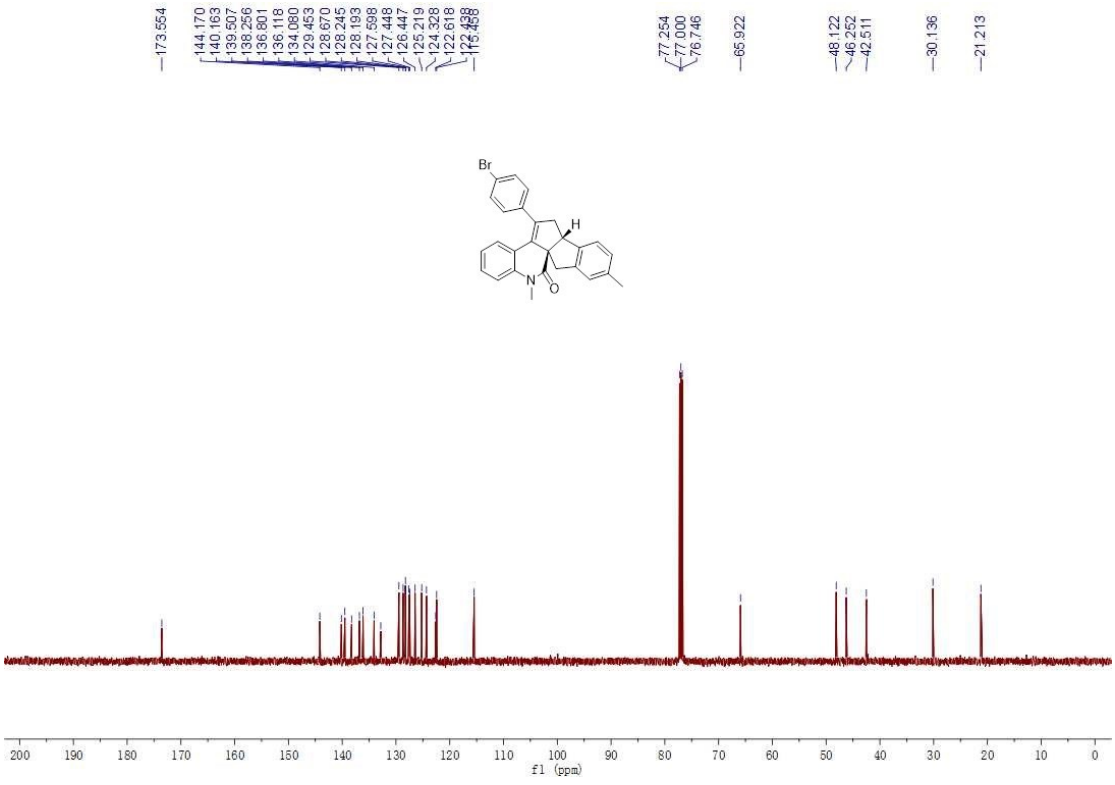


^{1}H NMR of **3ea** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ea** (125 MHz, $CDCl_3$)

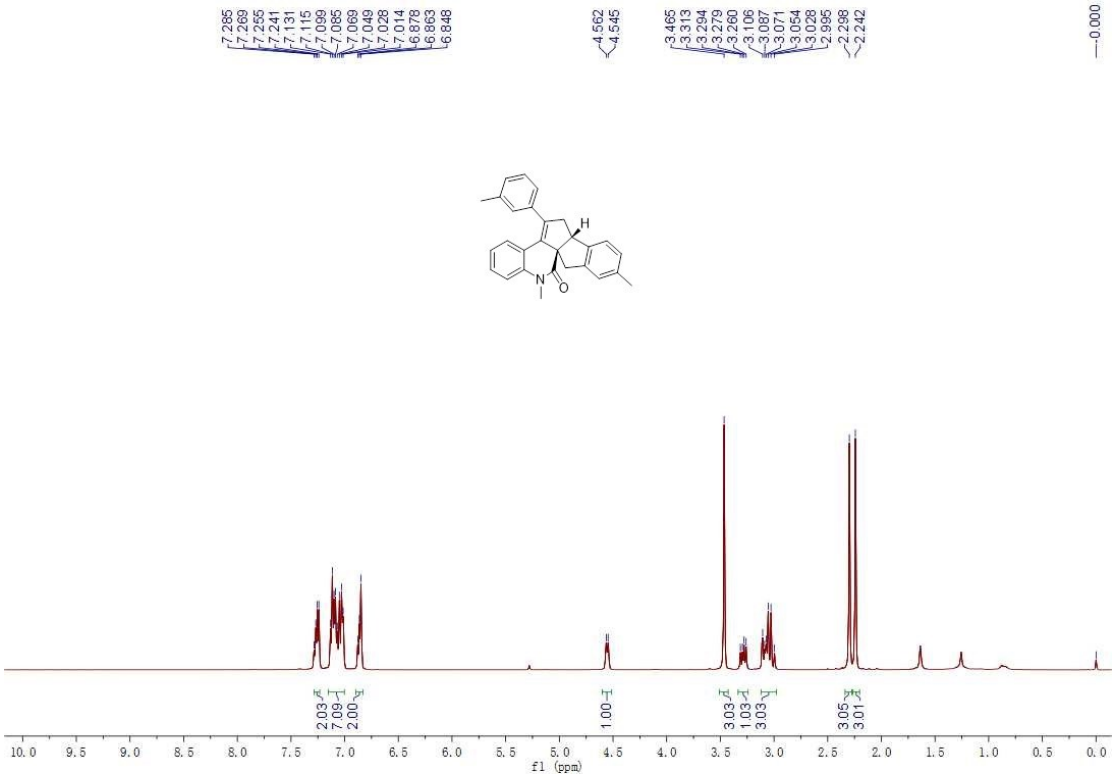


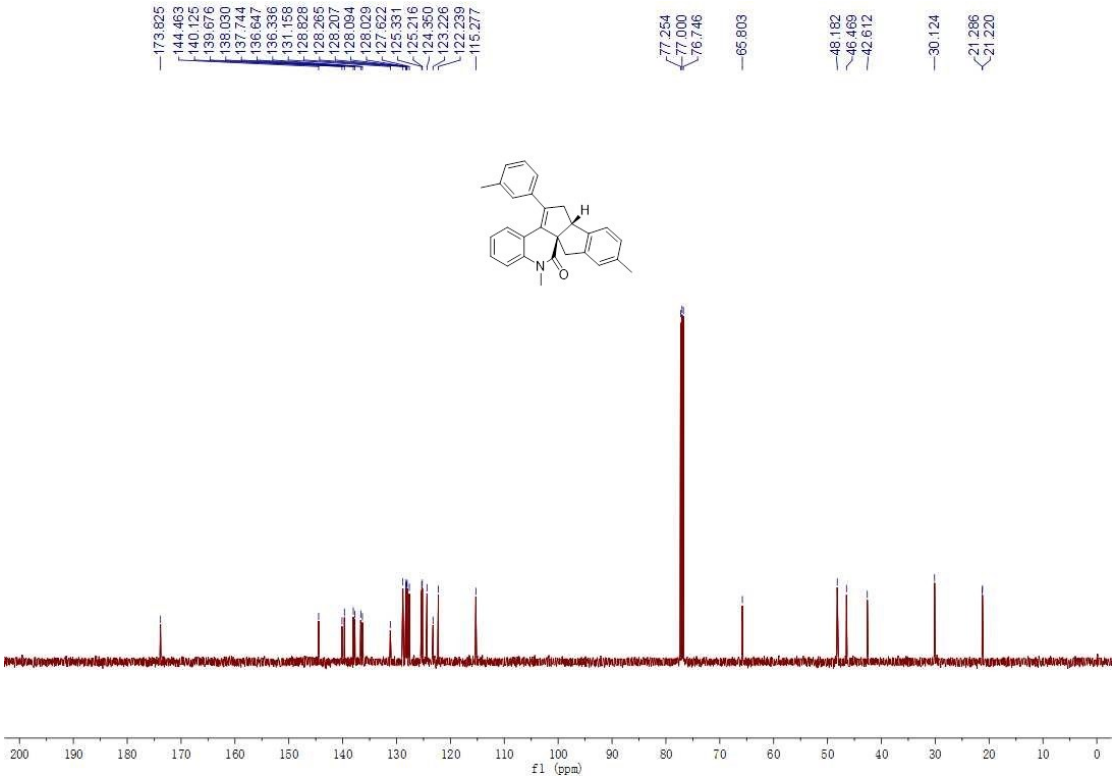
^{1}H NMR of **3fa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3fa** (125 MHz, $CDCl_3$)



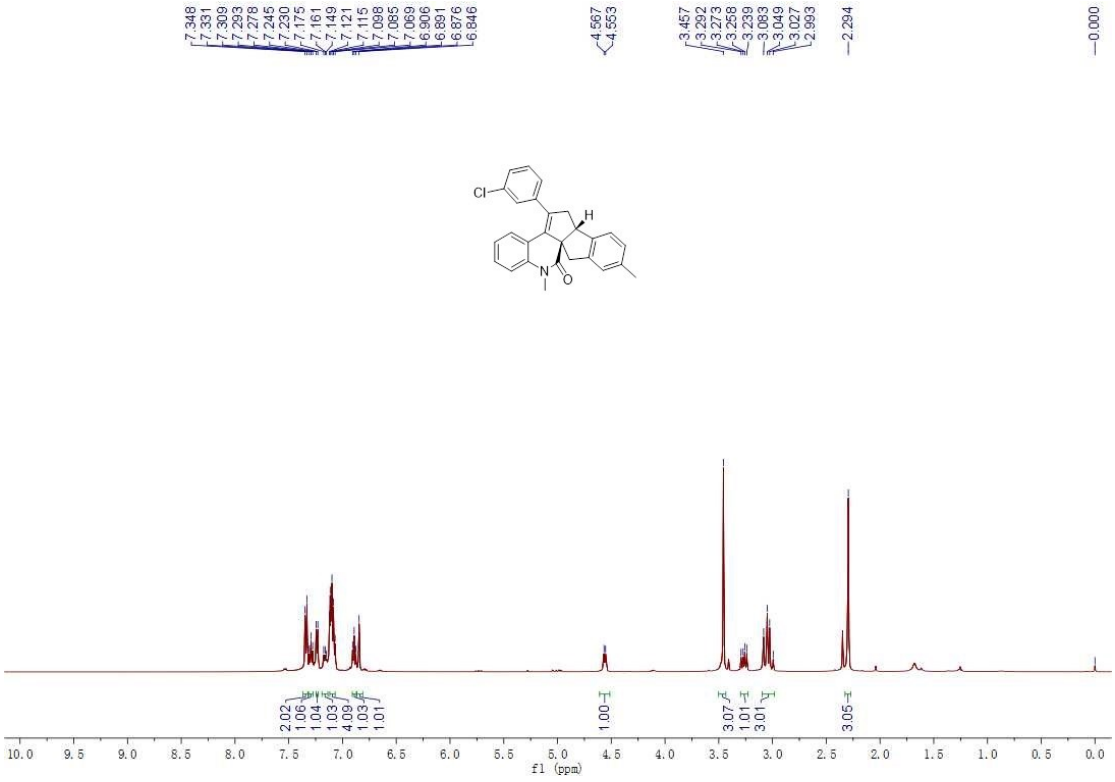


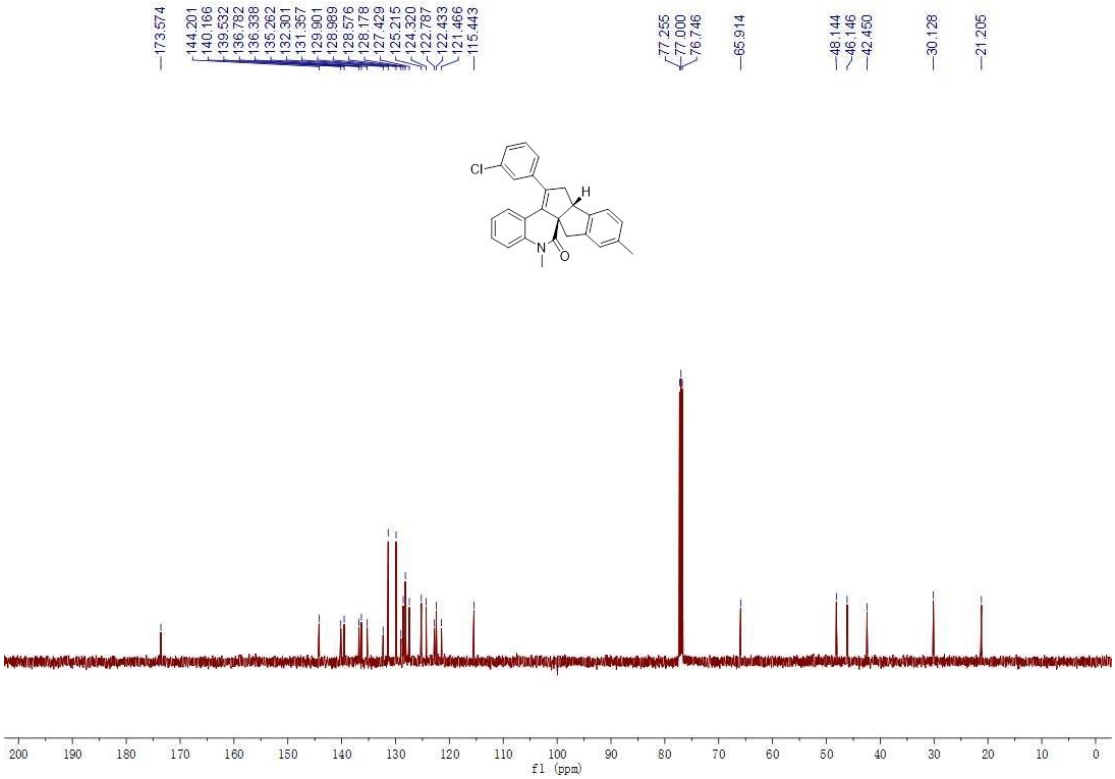
^{1}H NMR of **3ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ga** (125 MHz, $CDCl_3$)



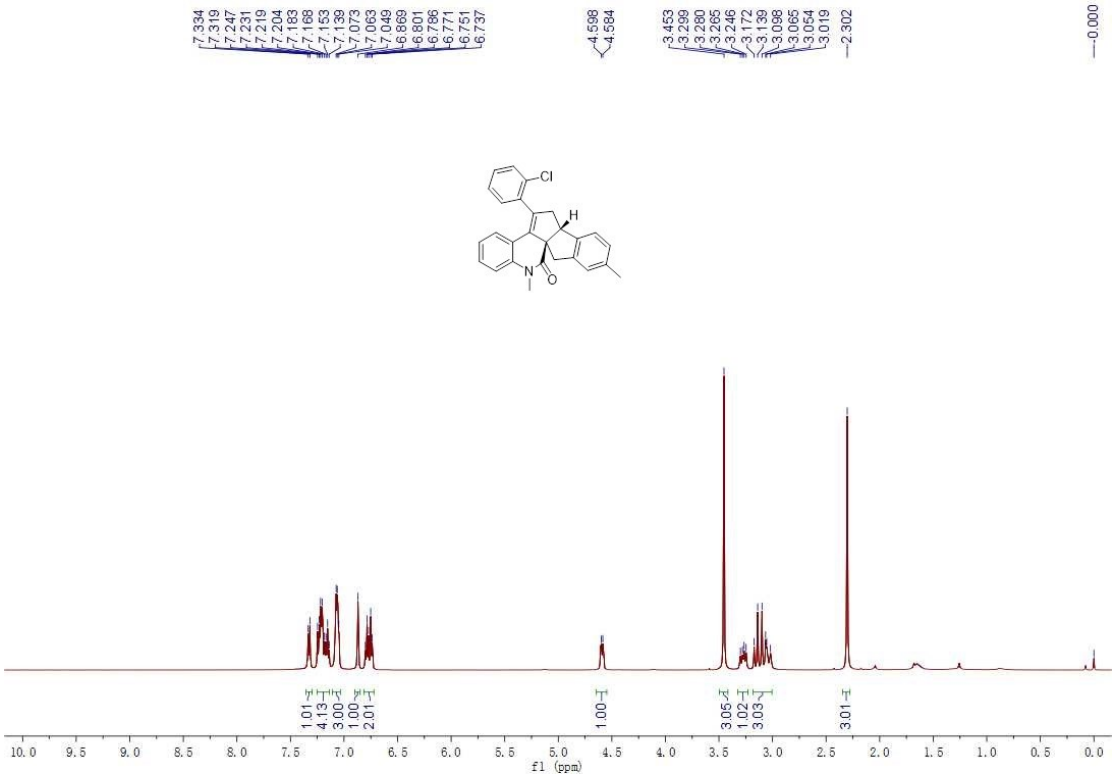


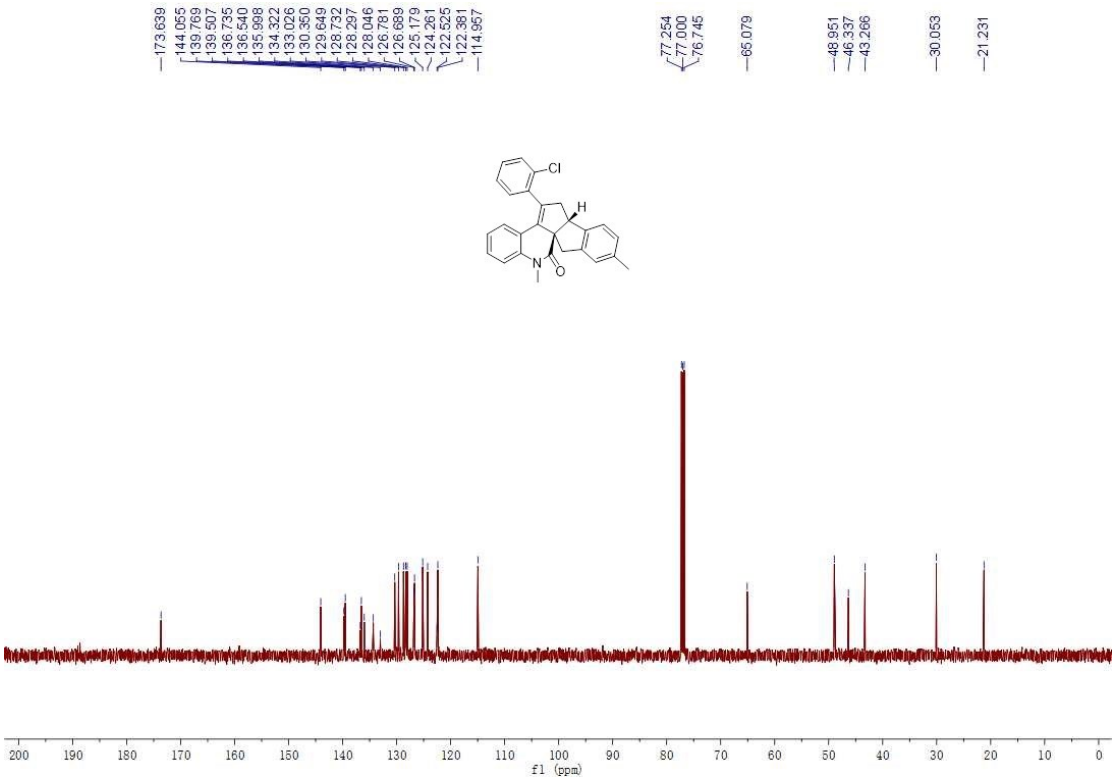
^{1}H NMR of **3ha** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ha** (125 MHz, $CDCl_3$)



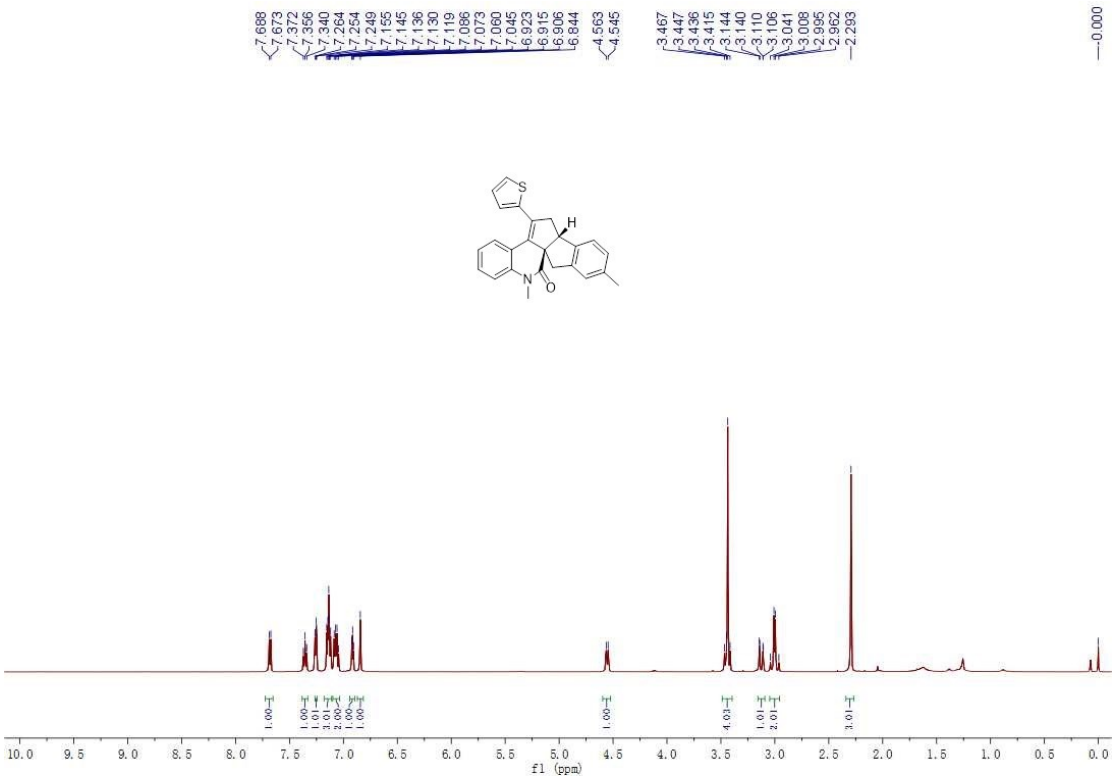


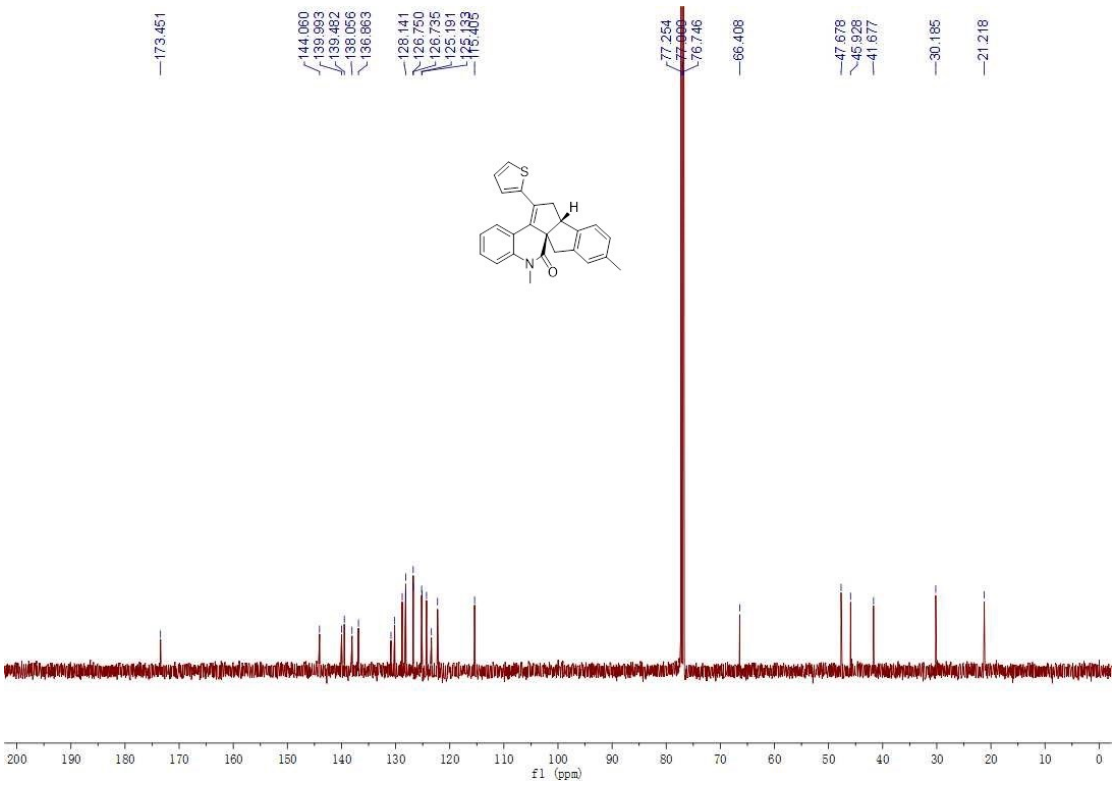
^{1}H NMR of **3ia** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ia** (125 MHz, $CDCl_3$)



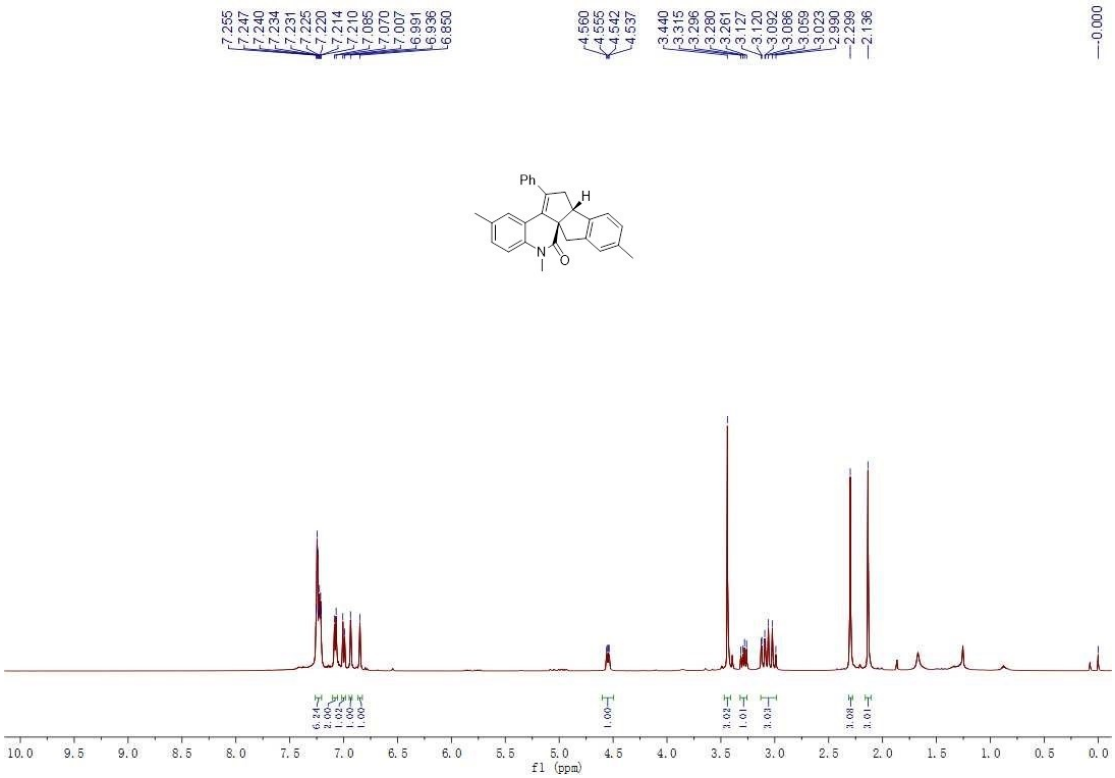


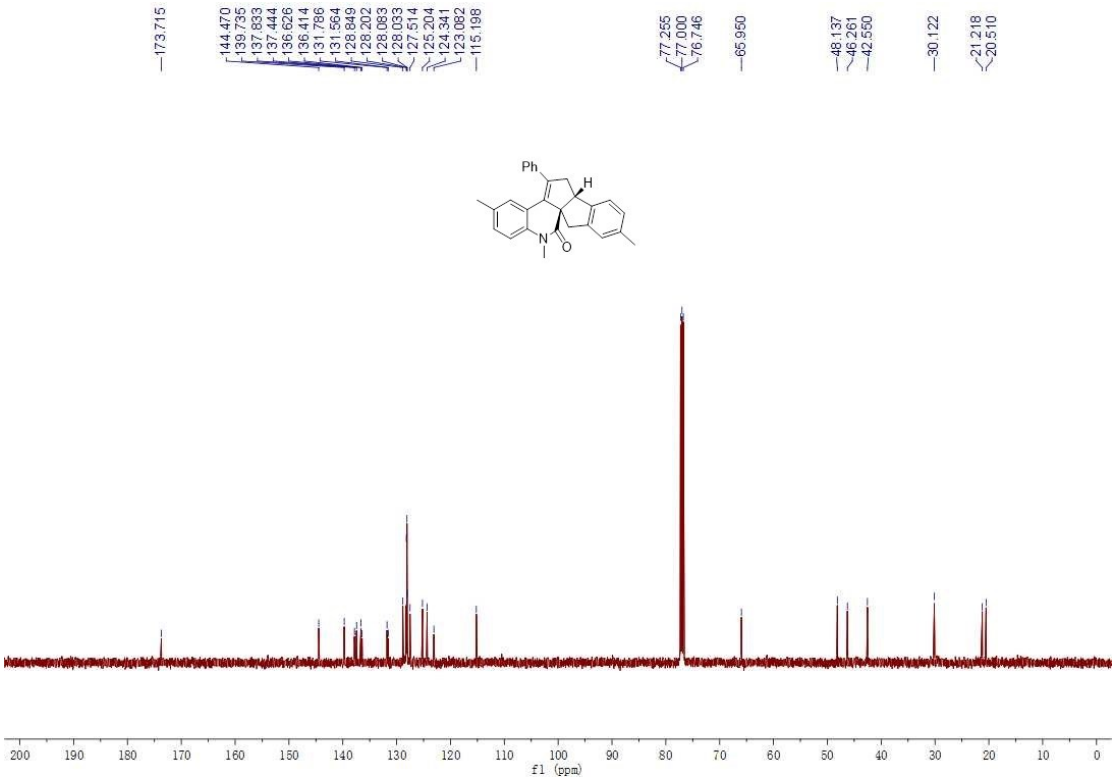
^{1}H NMR of **3ja** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ja** (125 MHz, $CDCl_3$)


7.688
7.673
7.372
7.356
7.340
7.264
7.254
7.249
7.155
7.145
7.136
7.130
7.119
7.086
7.073
7.060
7.045
6.923
6.915
6.906
6.844
4.563
4.545
3.467
3.447
3.436
3.415
3.144
3.140
3.110
3.106
3.041
3.008
2.995
2.962
2.293
0.000
S
H
N
O
1.00
1.01
3.01
2.00
1.00
1.00
4.03
1.01
2.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

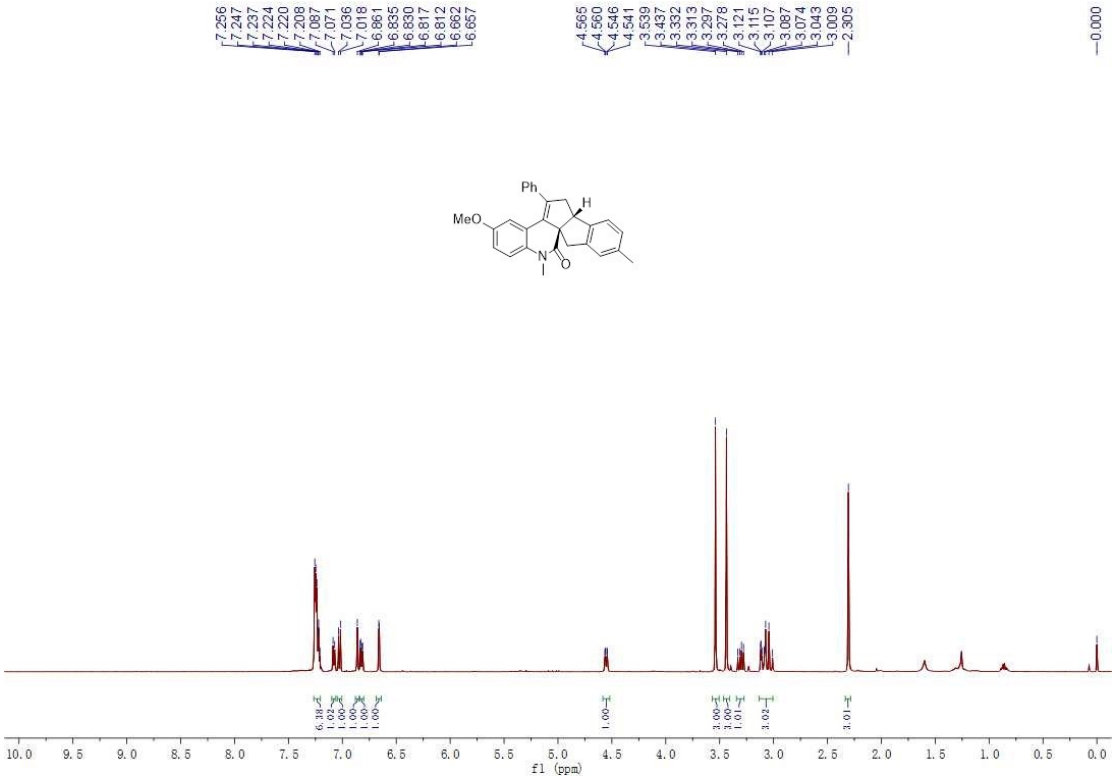

173.451
144.060
139.993
139.482
138.056
136.863
128.141
126.750
126.735
125.191
115.403
77.254
77.000
76.746
66.408
47.678
45.928
41.677
30.185
21.218
S
H
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

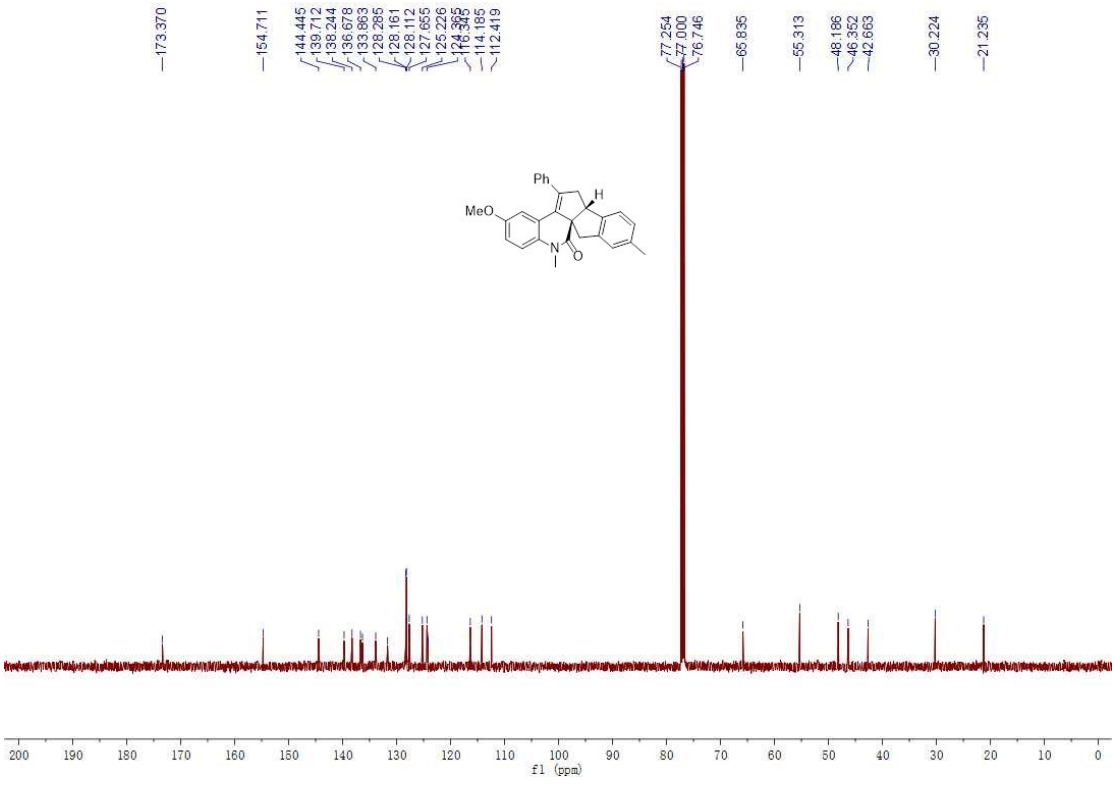
^{1}H NMR of **3la** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3la** (125 MHz, $CDCl_3$)



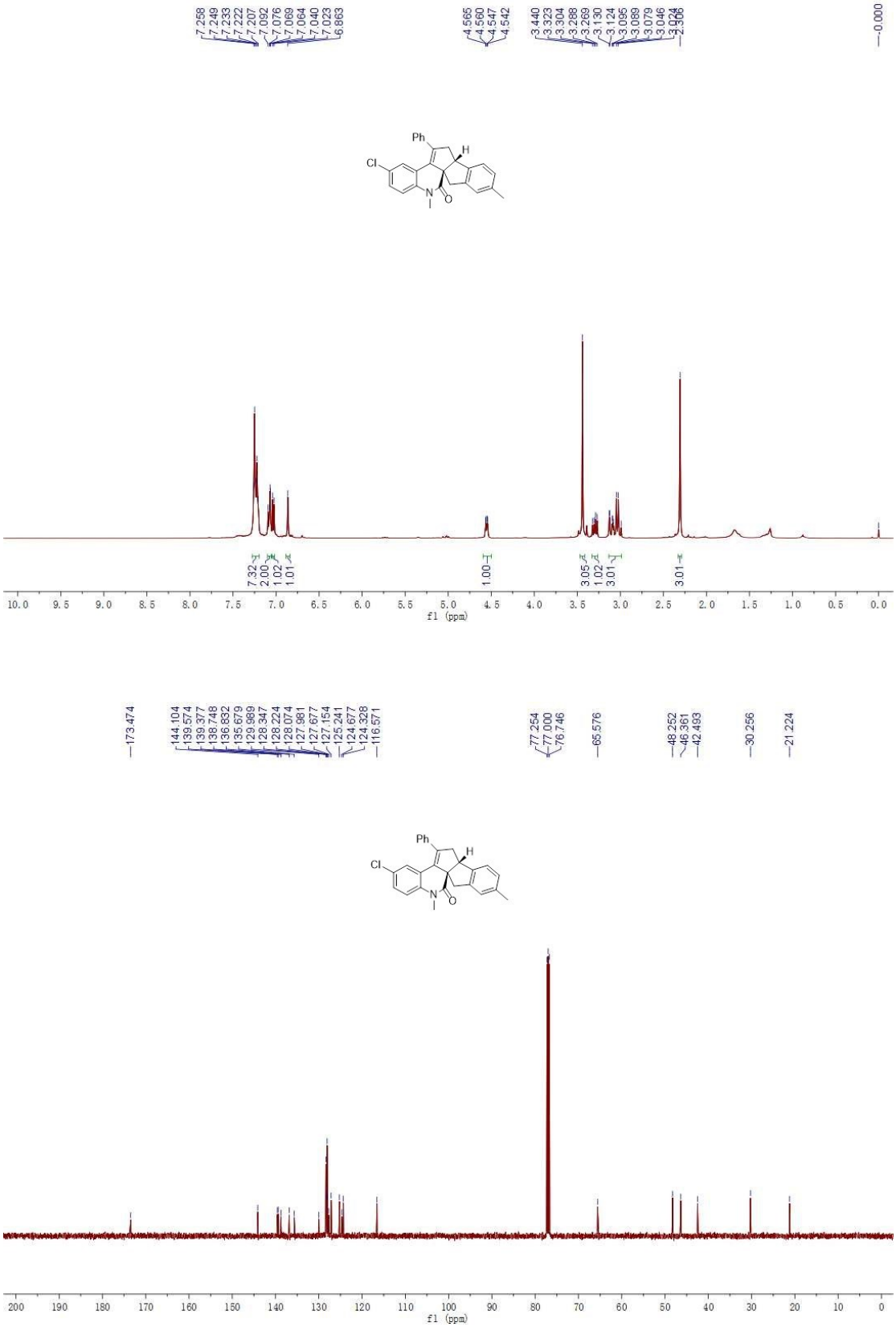


^{1}H NMR of **3ma** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ma** (125 MHz, $CDCl_3$)

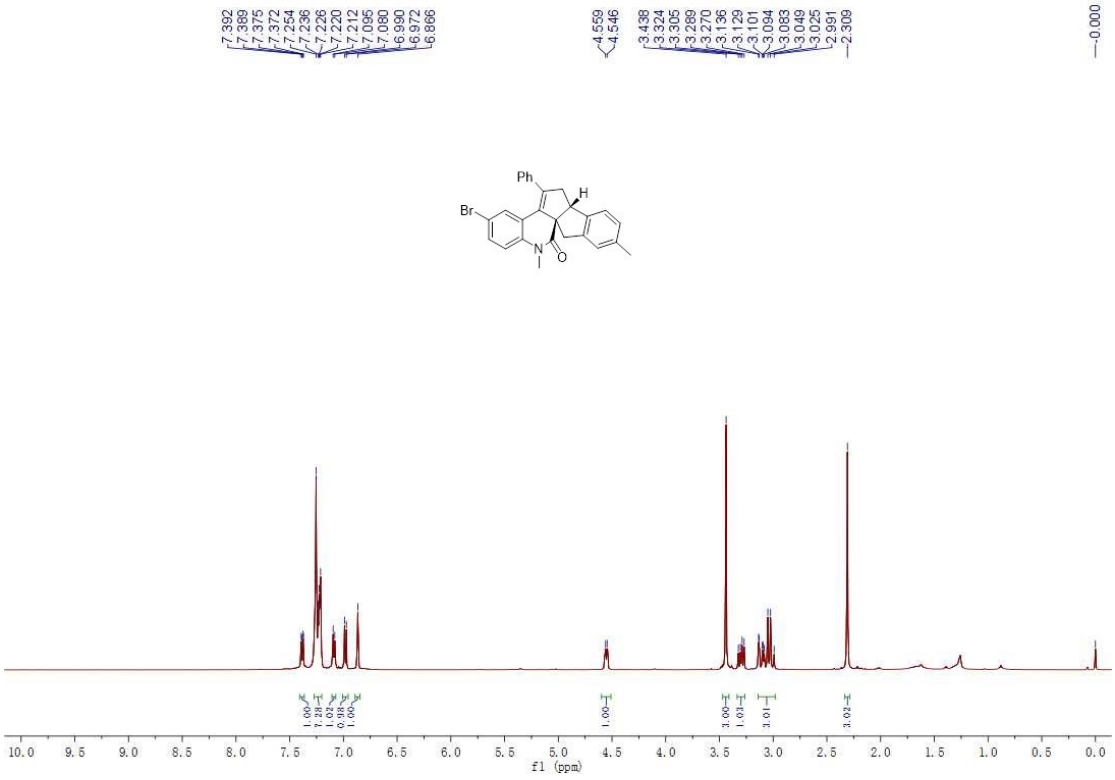


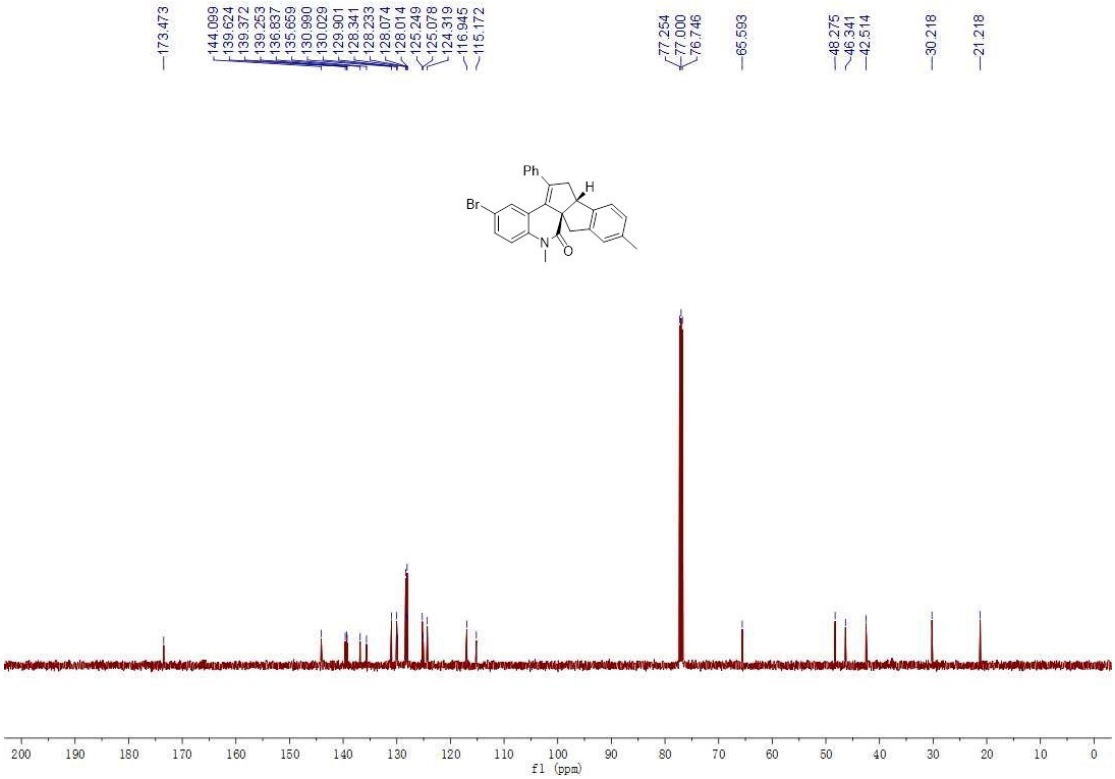


^{1}H NMR of **3na** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3na** (125 MHz, $CDCl_3$)

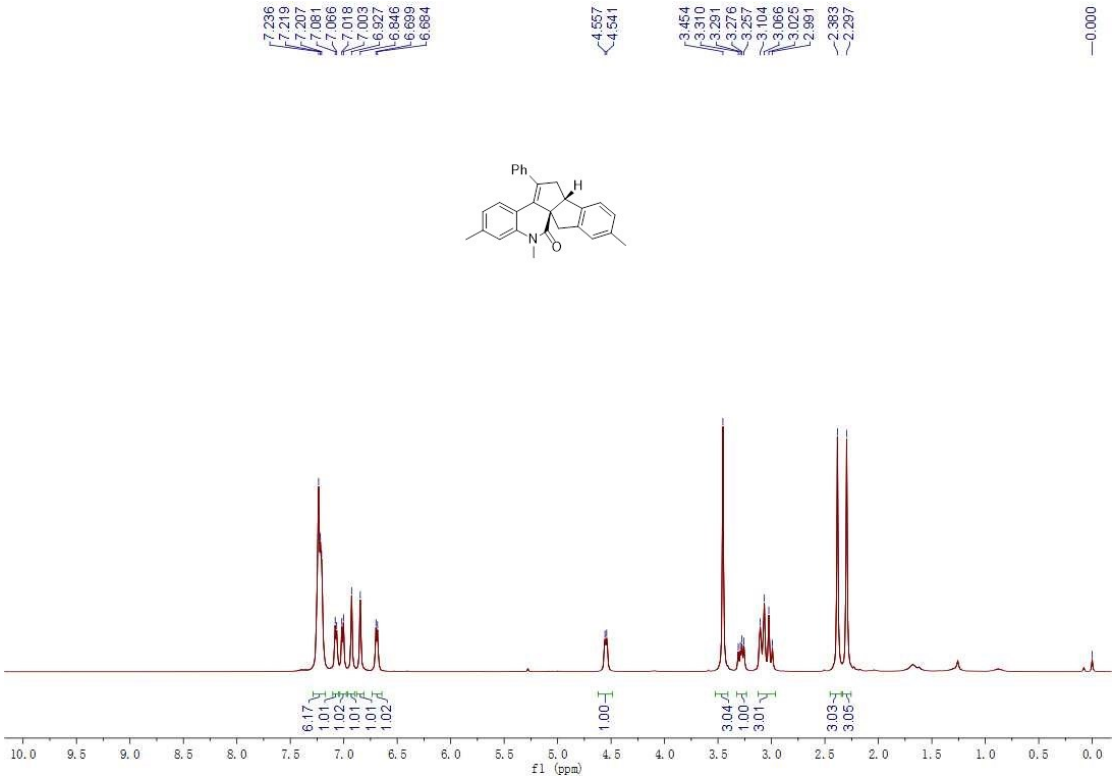


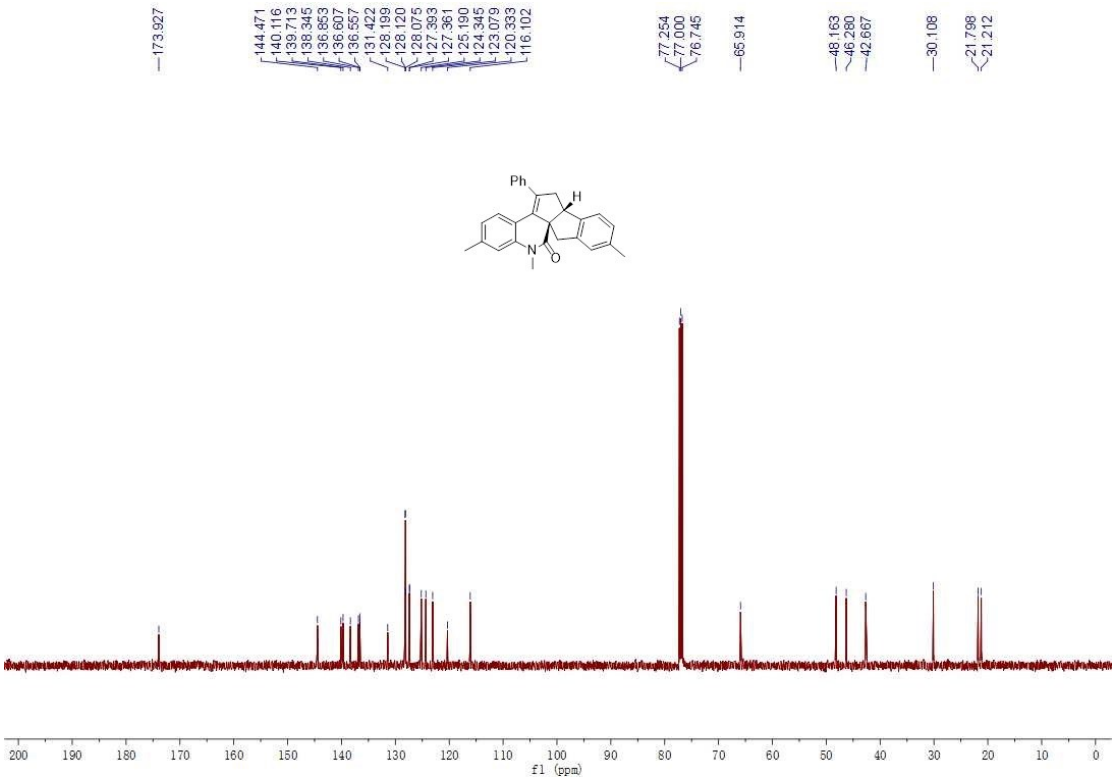
^{1}H NMR of **3oa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3oa** (125 MHz, $CDCl_3$)



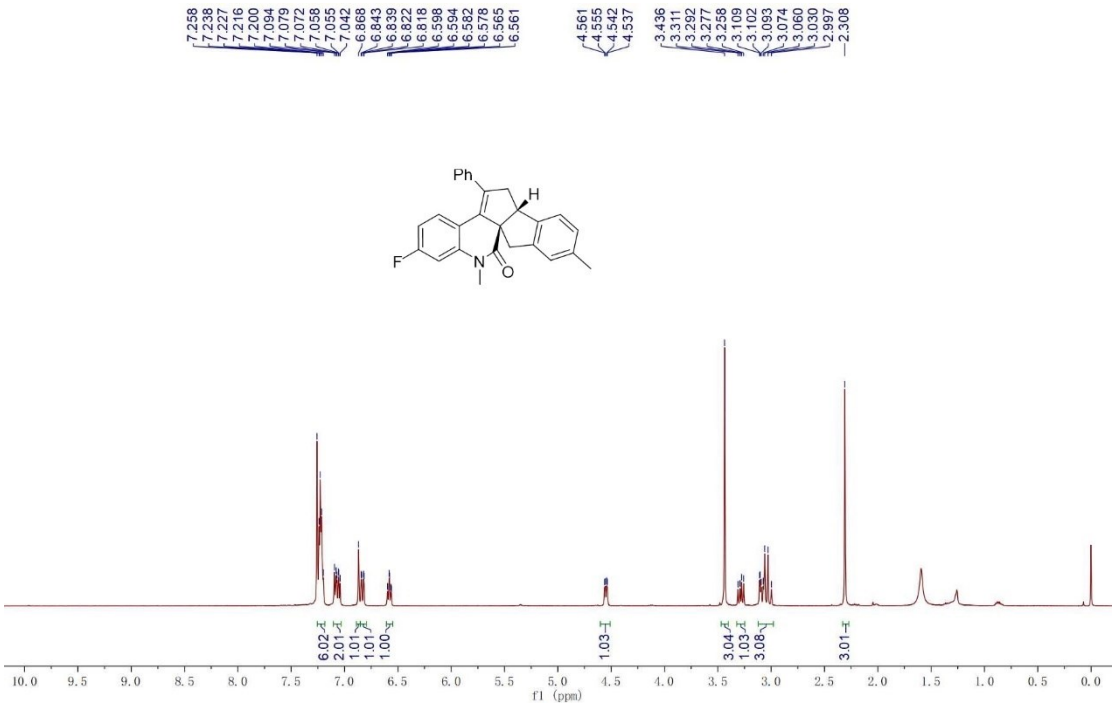


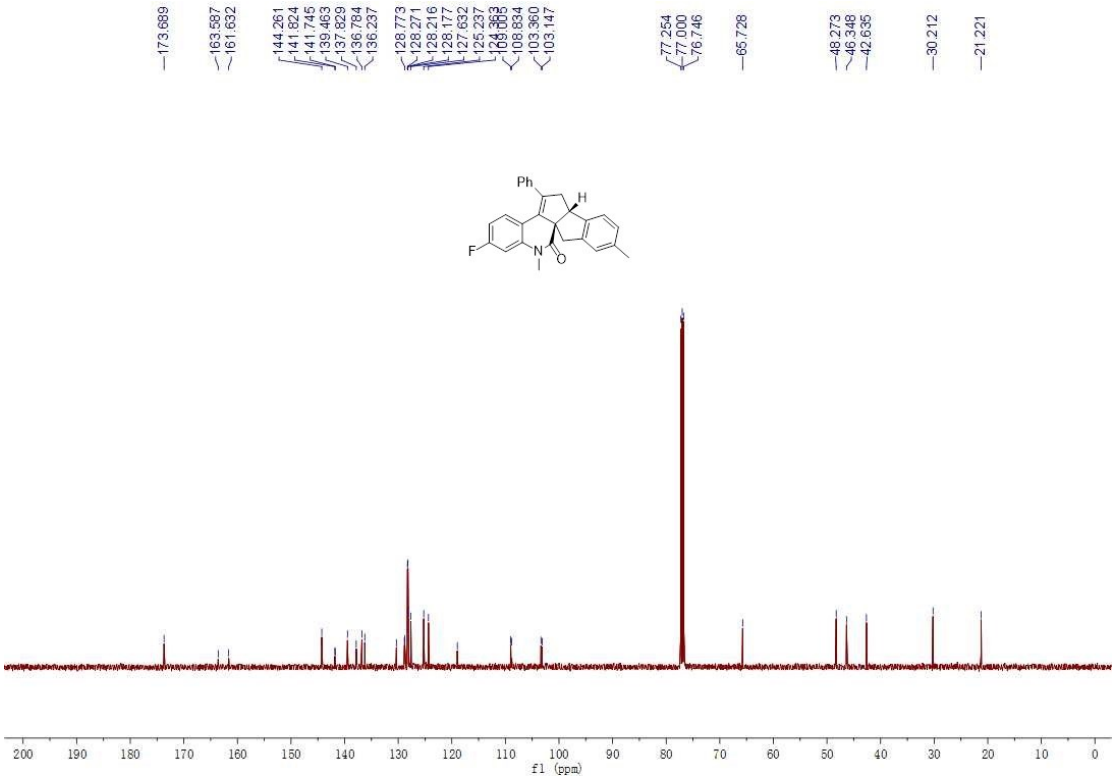
^{1}H NMR of **3pa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3pa** (125 MHz, $CDCl_3$)



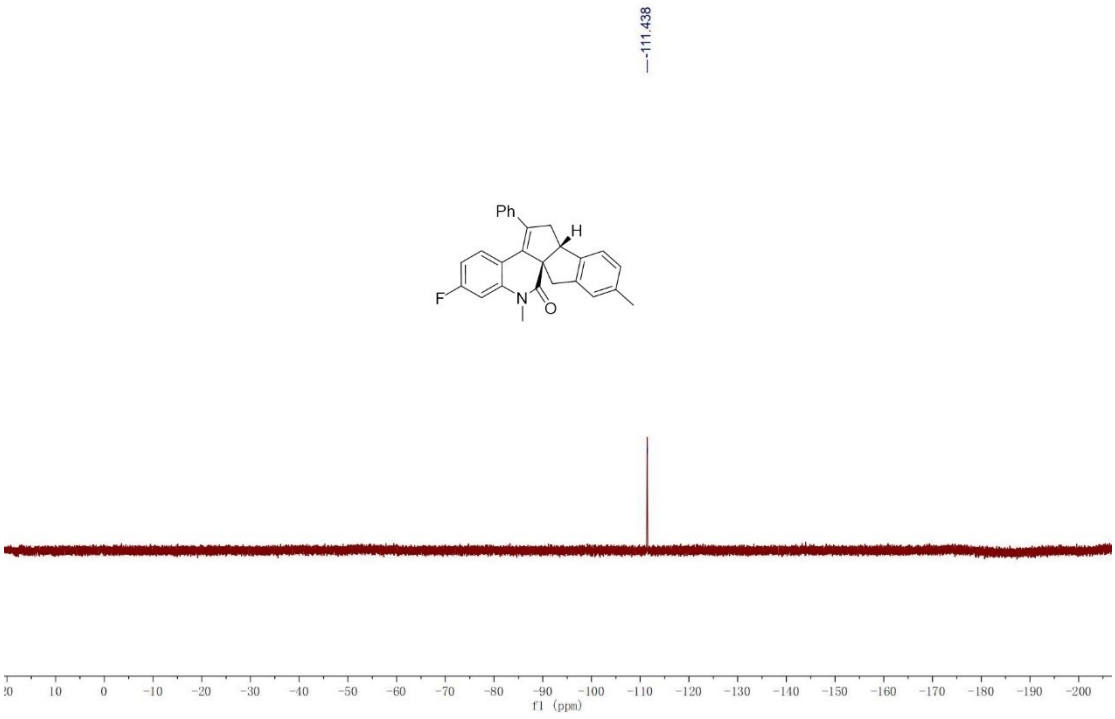


^{1}H NMR of **3qa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3qa** (125 MHz, $CDCl_3$)

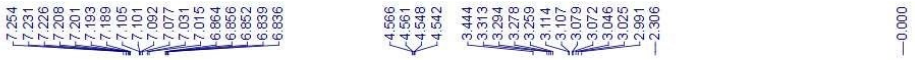


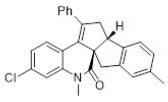


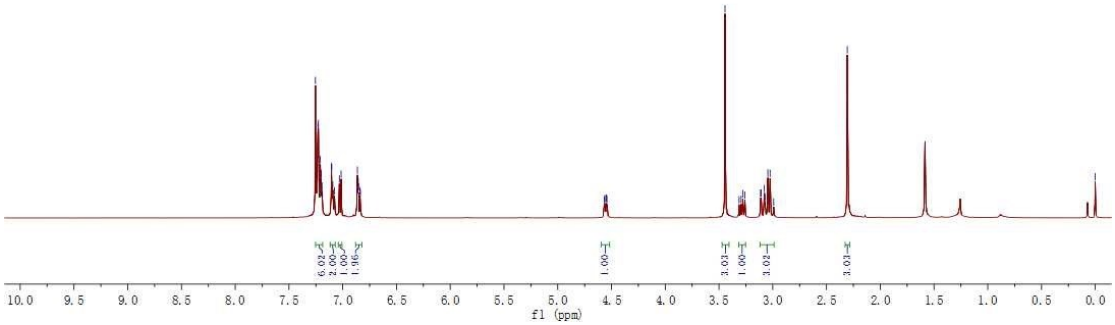
^{19}F NMR of **3qa** (470 MHz, $CDCl_3$)

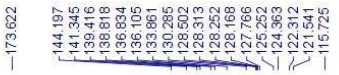


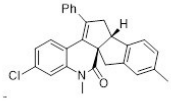
^{1}H NMR of **3ra** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ra** (125 MHz, $CDCl_3$)


7.254
7.231
7.226
7.208
7.201
7.193
7.189
7.105
7.101
7.092
7.077
7.031
7.015
6.864
6.856
6.852
6.839
6.836
4.566
4.561
4.548
4.542
3.444
3.313
3.294
3.278
3.259
3.114
3.107
3.079
3.072
3.046
3.025
2.991
2.306
0.000


Ph
H
Cl
N
O

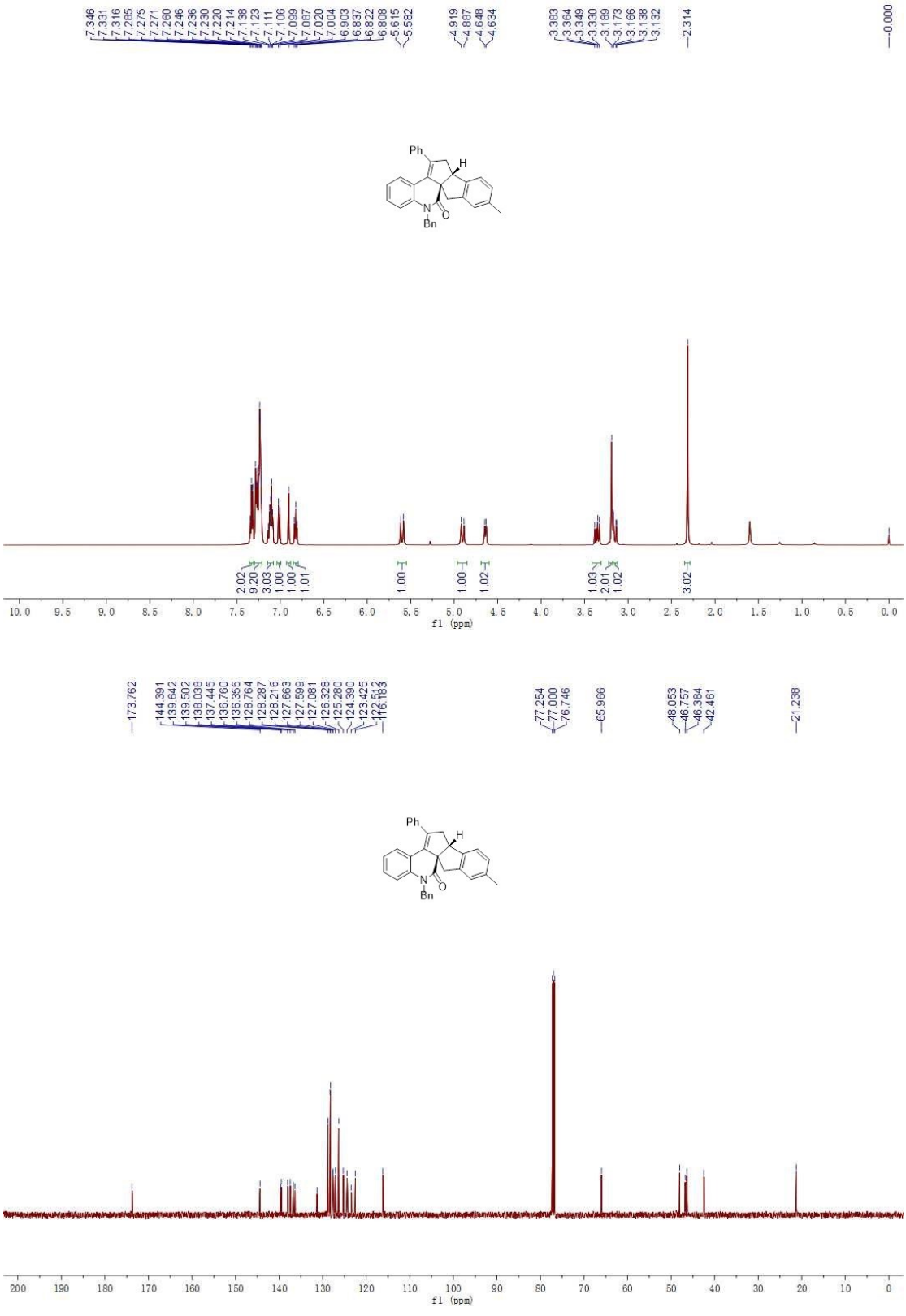

6.02
2.06
2.04
1.00
1.06
1.00
3.01
1.00
3.03
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.622
144.197
141.345
139.416
138.818
136.834
136.105
133.861
130.285
128.502
128.313
128.252
128.168
127.766
125.252
124.363
122.312
121.541
115.725
77.254
77.000
76.746
65.650
48.325
46.427
42.646
30.196
21.218


Ph
H
Cl
N
O

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR of **3sa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3sa** (125 MHz, $CDCl_3$)



^{1}H NMR of **5** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5** (125 MHz, $CDCl_3$)