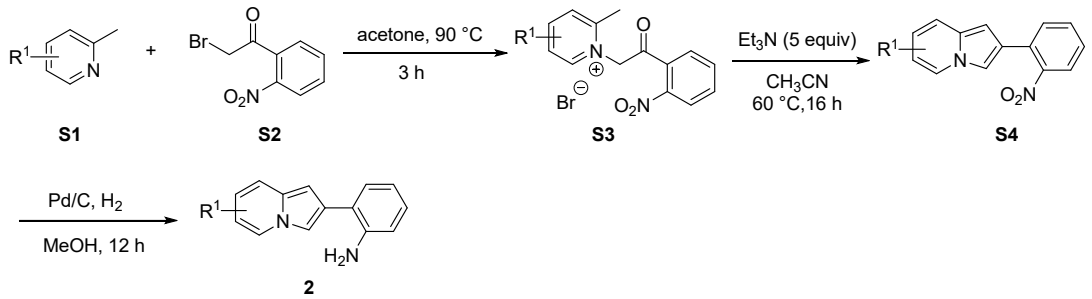
Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Content

1. General information

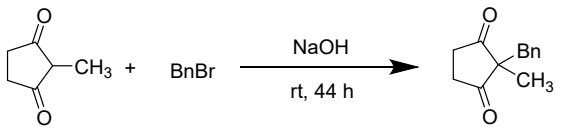
The products were purified by column chromatography on silica gel (200-300 mesh). For thin-layer chromatography (TLC) analysis, silica gel plates (HSGF254) were used. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or staining potassium permanganate solution followed by heating using a heat gun. High resolution mass spectra on a Bruker Apex IV RTMS spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE-400 (400 MHz) spectrometer and Bruker AVANCE-500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Melting points were determined on a SGW X-4 melting apparatus. UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2450 and Edinburgh FS5 spectrometers, 190-900 nm scan range). Fluorescence emission spectra were recorded on a Hitachi F-4600 FL Spectrophotometer. Quantum yields were determined on an absolute PL quantum yield Specrometer (Hamamatsu Quantaurus-QY C11347).

2. General procedure for the preparation of 2-(2-aminophenyl)indolizines.

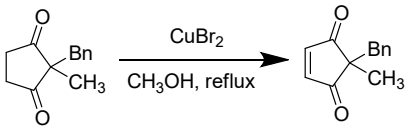


To a mixture of 2-bromo-2'-nitroacetophenone **S2** (2.00 mmol) in acetone (10 mL), 2-methyl pyridine **S1** (2.40 mmol) was added. Then, the reaction mixture stirred at 90 ºC for 3 h. After cooled to room temperature, the reaction mixture was suction-filtered and washed with CH_2Cl_2 (10 mL). The solid was used directly for the next step without further purification. To a mixture of indolizinium salt **S3** (1.50 mmol) and Et_3N (5.0 equiv) in CH_3CN (15 mL) was stirred at 60 ºC for 16 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford 2-(2-nitrophenyl)indolizines **S4**. To the solution of **S4** in MeOH (10 mL) was added Pd/C (10 mol%) under hydrogen atmosphere. The reaction mixture was stirred at room temperature. The reaction was monitored by TLC until **S4** was consumed completely. After that, filtration to remove solids, then the solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (silica flash, 10~40% ethyl acetate in petroleum ether) to give the corresponding **2**.

3. General procedure for the preparation of cyclopentene-1,3-diones.

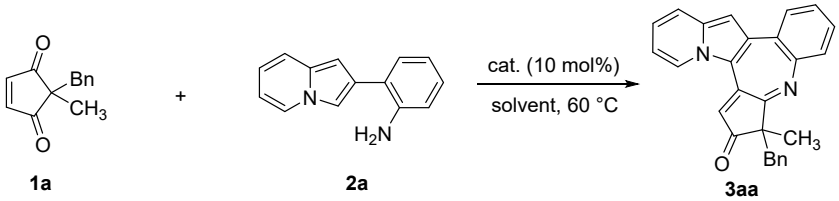


2-Methylcyclopentane-1,3-dione (1.0 equiv) was stirred with 1 M NaOH solution (aq., 1.0 equiv) at room temperature for 10 min. To this suspension was added benzyl bromide (2.0 equiv) at once and the resulting bi-phasic solution was stirred vigorously. After being stirred for 48 hours, the reaction mixture was diluted with EtOAc (10 mL). The aqueous phase was back-extracted with EtOAc twice (10 mL×2). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 15% EtOAc in petroleum ether) to obtain a white solid.(Note: Reactions were performed at room temperature for all liquid alkyl bromides and the reactions with solid alkyl bromides were carried out at the temperature slightly above melting point).



To a solution of 2,2-disubstituted cyclopentane-1,3-dione (8.00 mmol, 1.0 equiv) in MeOH (50 mL, 0.16 M) under argon atmosphere was added copper(II) bromide (3.93 g, 17.60 mmol, 2.2 equiv) and the resulting brown solution was stirred under reflux for 1 hour. The reaction mixture was cooled to room temperature and then added the following solution in sequence: 10 mL of H_2O, 10 mL of HCl (aq., 1 M), and 20 mL of DCM. The aqueous phase was separated and extracted for 2 times with DCM. The collected organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure.

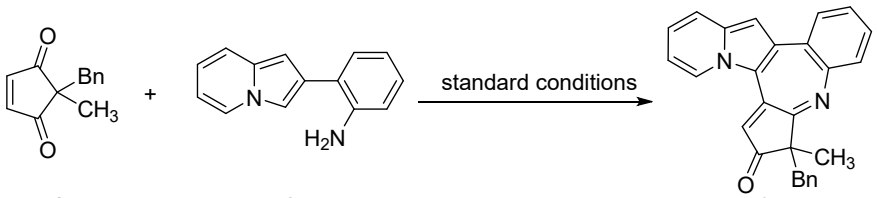
4. General procedure for the formal [5+2] cycloaddition



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

To a 4 mL vial was added cyclopentene-1,3-diones **1a** (0.10 mmol, 1.0 equiv.), indolizine **2a** (0.12 mmol, 1.2 equiv.) and *p*-NO_2BzOH (0.01mmol, 10 mol%) in 1.0 mL *o*-xylene. The mixture was stirred at 60 °C and monitored by TLC until completion of the reaction. The solvent was removed by a rotary evaporator and the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to afford the product **3aa**.

5. Large-scale synthesis of the product 3aa.

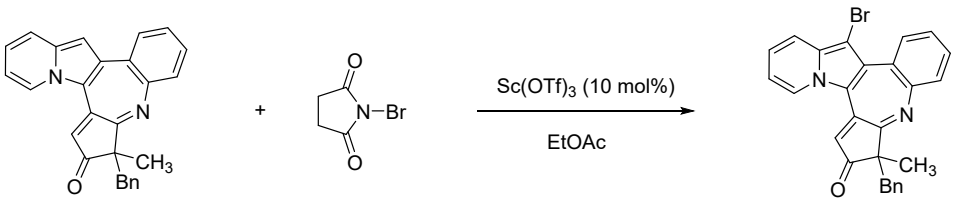


1a 1.00 mmol **2a** 1.20 mmol **3aa**

To a flask was added cyclopentene1,3-diones **1a** (200.2 mg, 1.00 mmol, 1.0 equiv.), indolizine **2a** (249.9 mg, 1.20 mmol, 1.2 equiv.) and *p*-NO_2BzOH (16.7 mg, 0.10 mmol, 10 mol%) in 10 mL *o*-xylene. The mixture was stirred at 60 ºC and monitored by TLC until completion of the reaction. The solvent was removed by a rotary evaporator and the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to afford the product **3aa** in 236.0 mg (61% yield).

6. Procedure for the late-stage functionalizations of 3aa.

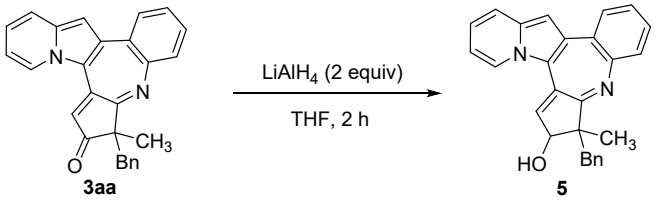
a. Procedure for the bromination of 3aa.



3aa **4**

To a 4 mL vial was added **3aa** (19.4 mg, 0.05 mmol, 1.0 equiv.), NBS (10.7 mg, 0.06 mmol, 1.2 equiv.) and $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 10 mol%) in 2 mL EtOAc. The mixture was stirred at room temperature (20 ºC) and monitored by TLC until completion of the reaction. The solvent was removed by a rotary evaporator and the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 2:1) to afford the product **4** (20.0 mg, 86%yield).

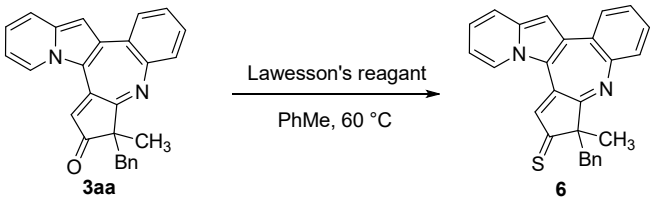
b. Procedure for the reduction of 3aa.



3aa **5**

Compound **3aa** (38.8 mg, 0.10 mmol) was dissolved in THF (2.0 mL), $LiAlH_4$ (1 M in THF, 0.2 mL, 0.20 mmol, 2.0 equiv) was added slowly at 0 ºC. The reaction mixture was then allowed to stir at room temperature (20 ºC). The reaction system was monitored by TLC until **3aa** was consumed completely. Then, the reaction mixture was quenched by a drop of water and directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate 8:1) to provide compound **5** as a yellow solid (14.3 mg, 37% yield).

c. Procedure for the sulfuration of 3aa.



Compound **3aa** (38.8 mg, 0.10 mmol) was dissolved in dry toluene (2.0 mL), and Lawesson's reagent (48.5 mg, 1.2 equiv) was added into the solution. The reaction mixture was then allowed to stir at 60 ºC. The reaction system was monitored by TLC until **3aa** was consumed completely. Then, the solvent was removed by a rotary evaporator and the residue was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to provide compound **6** (12.7 mg, 63% yield).

7. ESI-MS spectrum

The model reaction was performed under the optimal condition. Retrieve the sample at different time intervals for the ESI-MS test. Figure S1a shown the result on the reaction after 1 hour, indicating the formation of the intermediate of *m/z* 409. After the reaction for 12 h, the intermediate of m/z 409 disappeared from Figure S1b and another intermediate of m/z 407 was formed.

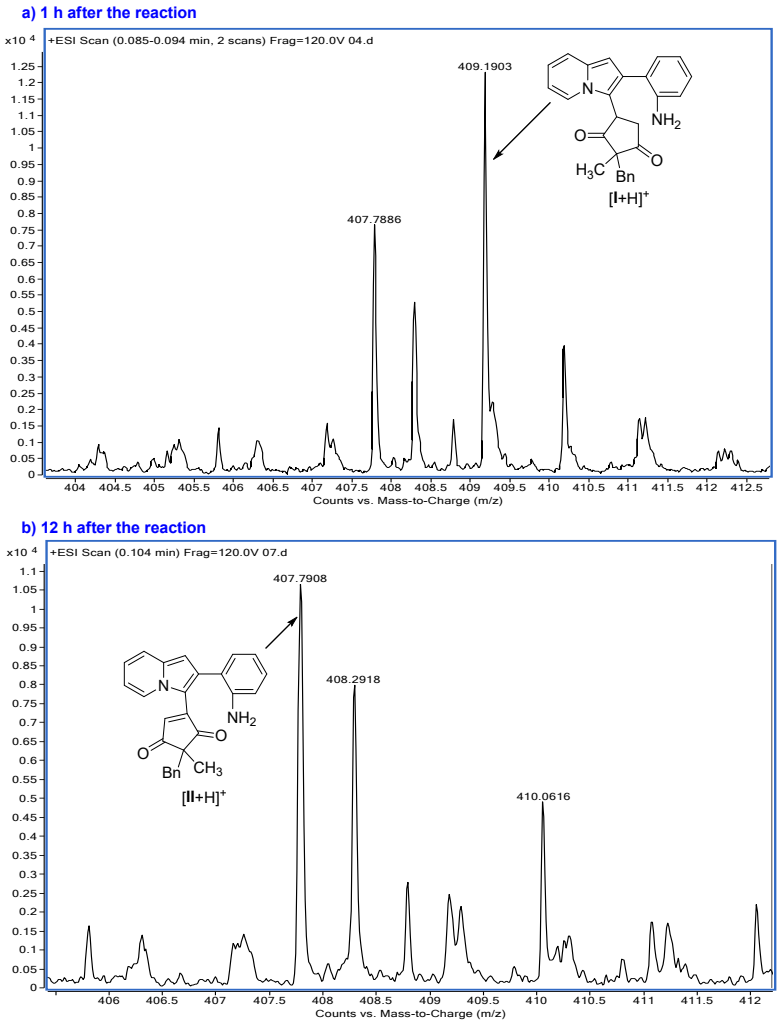
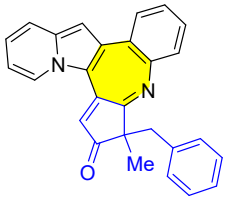


Figure S1. ESI-(+)-MS spectrum after 1 h (a) and 12 h (b).

8. Analytical data



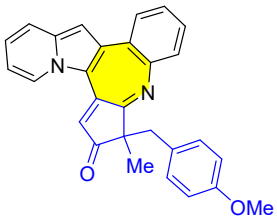
The compound **3aa** was obtained as a yellow solid (30.3 mg, 78% yield).

Melting point 221-223 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.3, 1.0 Hz, 1H), 8.06 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.54 (td, *J* = 7.6, 1.5 Hz, 1H), 7.49 (dt, *J* = 8.9, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.14 (s, 1H), 7.04 (ddd, *J* = 8.9, 6.6, 0.9 Hz, 1H), 6.99 (dd, *J* = 7.4, 2.3 Hz, 2H), 6.92 – 6.85 (m, 3H), 6.70 (td, *J* = 6.9, 1.4 Hz, 1H), 6.41 (s, 1H), 3.27 – 3.12 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.7, 170.5, 147.4, 142.5, 139.5, 137.5, 135.2, 133.3, 129.9, 129.5, 128.6, 128.0, 127.5, 126.3, 126.2, 125.7, 123.3, 120.2, 119.1, 117.4, 113.0, 101.1, 55.0, 43.4, 21.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{21}N_2O^+$389.1649; Found:389.1652.



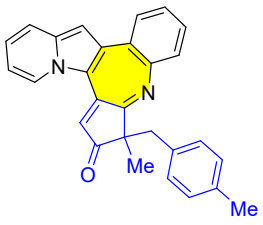
The compound **3ba** was obtained as a yellow solid (28.1 mg, 67% yield).

Melting point 248-255 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 15.6, 7.6 Hz, 2H), 7.89 (d, *J* = 9.1 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.14 (s, 1H), 7.08 – 7.01 (m, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.70 (t, *J* = 6.9 Hz, 1H), 6.44 – 6.36 (m, 3H), 3.47 (s, 3H), 3.20 – 3.05 (m, 2H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.8, 170.8, 157.9, 147.5, 142.6, 139.5, 135.1, 133.2, 130.8, 129.6, 129.4, 128.5, 128.1, 126.3, 125.5, 123.3, 120.5, 119.1, 117.5, 112.9, 112.9, 101.1, 55.4, 54.9, 42.8, 21.3.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O_2^+$419.1754; Found:419.1752.



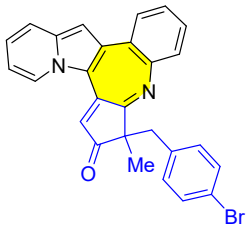
The compound **3ca** was obtained as a yellow solid (32.4 mg, 80% yield).

Melting point 220-235 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.97 (m, 2H), 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.43 (s, 1H), 7.13 (s, 1H), 7.09 – 7.01 (m, 1H), 6.88 – 6.81 (m, 2H), 6.74 – 6.62 (m, 3H), 6.37 (s, 1H), 3.22 – 3.07 (m, 2H), 1.97 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.7, 170.7, 147.6, 142.6, 139.4, 135.7, 135.0, 134.3, 133.2, 129.7, 129.4, 128.5, 128.2, 128.1, 126.7, 125.5, 123.2, 120.6, 119.1, 117.5, 112.8, 101.1, 55.5, 43.3, 21.3, 20.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O^+$403.1802; Found:403.1812.



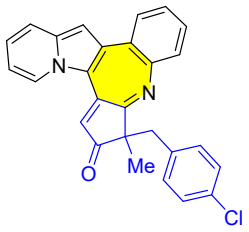
The compound **3da** was obtained as a yellow solid (29.8 mg, 64% yield).

Melting point 311-319 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 7.3 Hz, 1H), 8.09 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.48 – 7.43 (m, 1H), 7.19 (s, 1H), 7.11 (dd, *J* = 8.8, 6.6 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.79 (t, *J* = 6.8 Hz, 1H), 6.43 (s, 1H), 3.20 – 3.07 (m, 2H), 1.47 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 206.7, 170.5, 155.3, 142.8, 140.1, 136.9, 135.5, 133.8, 132.0, 131.0, 129.9, 129.1, 128.5, 126.8, 125.9, 124.1, 120.7, 120.3, 119.6, 117.8, 113.8, 101.7, 55.2, 42.9, 22.2.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{19}BrN_2O^+$467.0754; Found:467.0763.



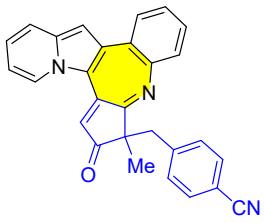
The compound **3ea** was obtained as a yellow solid (27.4 mg, 65% yield).

Melting point 301-303 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 3.6 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.46 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.19 (s, 1H), 7.12 – 7.08 (m, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.83 – 6.76 (m, 1H), 6.44 (s, 1H), 3.22 – 3.09 (m, 2H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.7, 170.5, 147.8, 140.1, 136.4, 135.5, 133.8, 132.5, 131.6, 129.9, 129.1, 128.5, 128.0, 126.7, 125.9, 124.0, 120.4, 119.6, 118.1, 113.7, 108.1, 101.7, 53.8, 42.8, 22.2.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}ClN_2O^+$423.1259; Found:423.1249.



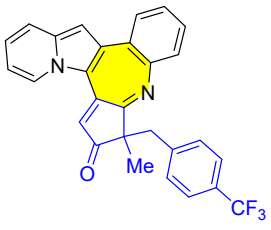
The compound **3fa** was obtained as a yellow solid (36.0 mg, 87% yield).

Melting point 275-280 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 9.5 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.47 (t, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 3H), 7.12 (d, *J* = 8.2 Hz, 3H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.45 (s, 1H), 3.34 – 3.14 (m, 2H), 1.49 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 205.8, 169.4, 147.2, 143.3, 142.2, 139.9, 135.2, 133.7, 131.3, 130.8, 129.7, 129.0, 128.2, 126.3, 125.6, 124.0, 119.4, 119.4, 118.9, 117.3, 113.6, 110.1, 101.6, 54.6, 42.7, 22.3.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{20}N_3O^+$414.1601; Found:414.1600.



The compound **3ga** was obtained as a yellow solid (28.2 mg, 62% yield).

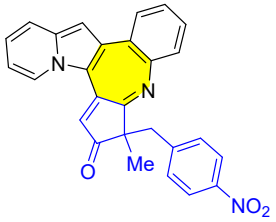
Melting point 246-250 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.3 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.90 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 (td, *J* = 7.6, 1.5 Hz, 1H), 7.51 (dd, *J* = 8.8, 1.3 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.16 (d, *J* = 7.4 Hz, 3H), 7.14 – 7.08 (m, 2H), 7.08 – 7.04 (m, 1H), 6.41 (s, 1H), 3.34 – 3.14 (m, 2H), 1.49 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.1, 169.8, 147.3, 142.3, 141.7, 139.8, 135.2, 133.4, 130.2, 129.6, 128.8, 128.1, 126.3, 125.5, 124.5, 124.5, 124.4, 124.4, 123.8, 119.7, 119.2, 117.3, 113.4, 101.4, 54.8, 42.7, 22.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{20}F_3N_2O^+$457.1522; Found:457.1531.



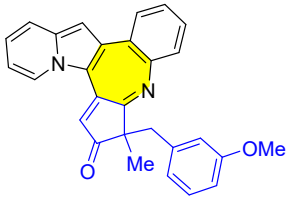
The compound **3ha** was obtained as a yellow solid (26.4 mg, 61% yield).

Melting point 273-278 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 7.3 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.21 (s, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.07 (m, 1H), 6.78 (t, *J* = 6.9 Hz, 1H), 6.47 (s, 1H), 3.37 – 3.20 (m, 2H), 1.51 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 206.2, 169.6, 147.6, 146.9, 145.9, 142.5, 140.4, 135.5, 134.1, 131.2, 130.1, 129.4, 128.6, 126.7, 126.0, 124.4, 123.2, 119.8, 119.6, 117.7, 113.9, 102.0, 55.0, 42.6, 22.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}N_3O_3^+$434.1499; Found:434.1511.

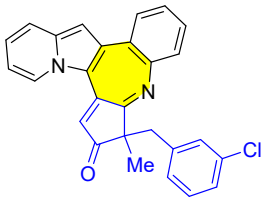


The compound **3ia** was obtained as a yellow solid (26.2 mg, 63% yield). Melting point 175-181 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.3 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.48 (d, *J* = 10.1 Hz, 1H), 7.42 (t, *J* = 6.8 Hz, 1H), 7.11 (s, 1H), 7.08 – 7.00 (m, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.70 (t, *J* = 6.9 Hz, 1H), 6.66 – 6.59 (m, 1H), 6.48 (s, 1H), 6.45 – 6.40 (m, 1H), 6.39 (s, 1H), 3.28 (s, 3H), 3.25 – 3.11 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 170.7, 158.7, 147.4, 142.5, 139.5, 139.0, 135.1, 133.2, 129.4, 128.6, 128.1, 126.4, 125.7, 123.4, 122.4, 120.4, 119.1, 117.4, 114.5, 113.0, 112.7, 101.1, 55.2, 54.6, 43.6, 29.7, 21.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O_2^+$419.1754; Found:419.1747.

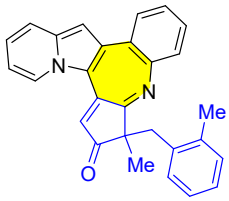


The compound **3ja** was obtained as a yellow solid (36.1 mg, 85% yield). Melting point 207-216 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 8.05 (d, *J* = 9.6 Hz, 1H), 7.89 (d, *J* = 6.5 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.14 (s, 1H), 7.10 – 7.03 (m, 1H), 7.00 (s, 1H), 6.88 (d, *J* = 4.7 Hz, 1H), 6.84 (d, *J* = 5.4 Hz, 2H), 6.74 (t, *J* = 6.9 Hz, 1H), 6.42 (s, 1H), 3.15 (q, *J* = 12.7 Hz, 2H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.2, 170.0, 147.4, 142.4, 139.7, 139.6, 135.1, 133.5, 133.3, 129.9, 129.5, 128.8, 128.7, 128.2, 128.1, 126.4, 126.3, 125.6, 123.6, 119.9, 119.2, 117.3, 113.2, 101.3, 54.9, 42.8, 21.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}ClN_2O^+$423.1259; Found:423.1257.

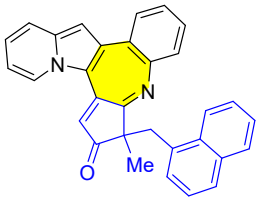


The compound **3ka** was obtained as a yellow solid (27.8 mg, 69% yield). Melting point 192-195 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 6.8 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.07 (s, 1H), 3.23 – 3.07 (m, 2H), 1.79 (s, 3H), 1.49 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.5, 170.8, 147.5, 142.6, 139.4, 137.4, 137.0, 135.0, 133.1, 130.5, 129.4, 128.5, 128.1, 127.5, 127.1, 126.8, 126.4, 125.5, 123.2, 120.5, 119.0, 117.4, 112.8, 101.0, 55.5, 43.9, 21.2, 20.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O^+$403.1805; Found:403.1801.

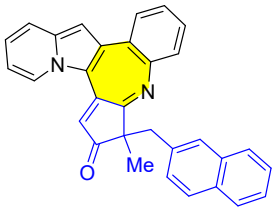


The compound **3la** was obtained as a yellow solid (24.7 mg, 56% yield). Melting point 241-252 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 9.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 9.4 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.07 – 7.02 (m, 2H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.92 (s, 1H), 3.75 – 3.59 (m, 2H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 170.7, 147.4, 142.4, 139.1, 134.9, 134.1, 133.3, 132.9, 132.0, 129.2, 128.3, 128.2, 128.1, 127.6, 127.1, 126.5, 125.2, 125.1, 125.0, 124.7, 123.0, 120.6, 118.8, 117.0, 112.5, 100.7, 56.4, 40.9, 20.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{31}H_{23}N_2O^+$439.1805; Found:439.1795.

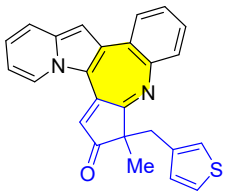


The compound **3ma** was obtained as a yellow solid (22.3 mg, 51% yield). Melting point 248-255 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 9.5 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.39 (s, 1H), 7.37 – 7.32 (m, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.15 – 7.09 (m, 2H), 7.02 (s, 1H), 6.91 – 6.84 (m, 1H), 6.31 (t, *J* = 6.9 Hz, 1H), 6.22 (s, 1H), 3.43 – 3.27 (m, 2H), 1.55 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 205.3, 169.6, 146.5, 141.5, 138.3, 134.0, 133.9, 132.1, 131.8, 131.0, 128.3, 127.4, 127.1, 126.1, 126.1, 125.9, 125.4, 124.4, 124.0, 123.7, 122.2, 119.2, 117.8, 116.2, 111.7, 100.0, 54.7, 42.9, 20.3.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{31}H_{23}N_2O^+$439.1805; Found:439.1805.

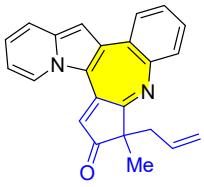


The compound **3na** was obtained as a yellow solid (14.2 mg, 36% yield). Melting point 224-228 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 7.3 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.18 (s, 1H), 7.07 (dd, *J* = 8.9, 6.6 Hz, 1H), 6.85 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.82 – 6.73 (m, 2H), 6.69 (d, *J* = 4.9 Hz, 1H), 6.49 (s, 1H), 3.34 – 3.14 (m, 2H), 1.45 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 205.9, 169.6, 146.2, 141.5, 138.6, 136.7, 134.2, 132.3, 128.5, 128.4, 127.6, 127.0, 125.3, 124.8, 123.2, 122.4, 121.7, 119.0, 118.2, 116.4, 112.1, 100.2, 53.4, 36.3, 20.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{25}H_{19}N_2OS^+$395.1213; Found:395.1213.

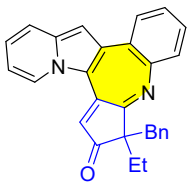


The compound **3oa** was obtained as a yellow solid (24.8 mg, 73% yield). Melting point 200-207 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 7.2 Hz, 1H), 8.12 (d, *J* = 9.6 Hz, 1H), 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.60 (dt, *J* = 8.9, 1.3 Hz, 1H), 7.52 (td, *J* = 7.6, 1.6 Hz, 1H), 7.45 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.26 (s, 1H), 7.14 (ddd, *J* = 8.9, 6.6, 0.9 Hz, 1H), 6.89 (td, *J* = 6.9, 1.4 Hz, 1H), 6.75 (s, 1H), 5.66 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.03 (ddt, *J* = 17.0, 2.5, 1.3 Hz, 1H), 4.93 – 4.83 (m, 1H), 2.75 – 2.56 (m, 2H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.2, 170.5, 146.8, 142.5, 139.7, 135.4, 133.7, 133.5, 129.5, 128.6, 127.9, 126.2, 126.0, 123.5, 119.4, 119.4, 118.0, 117.6, 113.4, 101.3, 52.5, 41.1, 21.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{23}H_{19}N_2O^+$339.1492; Found:339.1482.

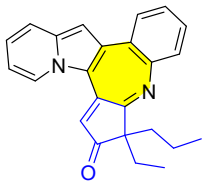


The compound **3pa** was obtained as a yellow solid (23.5 mg, 58% yield). Melting point 189-192 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 9.5 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.11 (s, 1H), 7.05 – 6.95 (m, 3H), 6.88 (d, *J* = 7.0 Hz, 3H), 6.68 (d, *J* = 6.9 Hz, 1H), 6.48 (s, 1H), 3.26 – 3.09 (m, 2H), 2.16 – 1.98 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.4, 169.7, 148.8, 142.5, 139.5, 137.3, 135.3, 133.3, 130.0, 129.5, 128.6, 128.0, 127.5, 126.2, 126.2, 125.7, 123.3, 121.9, 119.1, 117.3, 112.9, 101.1, 59.8, 43.1, 29.3, 9.0.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O^+$403.1805; Found:403.1805.

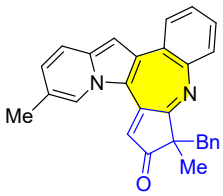


The compound **3qa** was obtained as a yellow solid (6.2 mg, 18% yield). Melting point 201-210 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 7.2 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 9.5 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.17 – 7.08 (m, 1H), 6.88 (t, *J* = 7.7 Hz, 1H), 6.85 (s, 1H), 2.01 – 1.75 (m, 4H), 1.12 (dddd, *J* = 26.4, 19.3, 9.9, 4.6 Hz, 2H), 0.79 (t, *J* = 7.3 Hz, 3H), 0.70 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.1, 170.6, 148.4, 142.6, 139.7, 135.6, 133.7, 129.5, 128.5, 127.9, 126.1, 123.5, 121.5, 119.4, 117.4, 113.4, 101.3, 57.3, 39.1, 29.7, 17.8, 14.6, 8.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{24}H_{23}N_2O^+$355.1805; Found:355.1804.

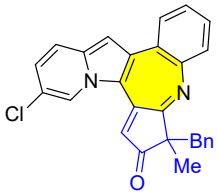


The compound **3ab** was obtained as a yellow solid (27.6 mg, 68% yield). Melting point 214-219 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.82 (s, 1H), 7.54 – 7.47 (m, 1H), 7.39 (td, *J* = 7.7, 7.2, 1.5 Hz, 1H), 7.32 (dd, *J* = 9.0, 0.9 Hz, 1H), 7.01 (d, *J* = 5.1 Hz, 3H), 6.89 (dd, *J* = 6.9, 1.2 Hz, 3H), 6.85 (dd, *J* = 8.9, 1.3 Hz, 1H), 6.40 (s, 1H), 3.29 – 3.12 (m, 2H), 2.22 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.8, 170.3, 147.4, 142.3, 138.4, 137.6, 135.2, 132.8, 129.9, 129.2, 128.5, 127.9, 127.5, 126.6, 126.4, 126.2, 123.6, 122.7, 119.9, 118.4, 117.2, 100.9, 55.1, 43.4, 21.7, 18.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O^+$403.1805; Found:403.1807.

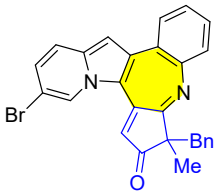


The compound **3ac** was obtained as a yellow solid (25.6 mg, 62% yield). Melting point 212-218 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.3 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 9.5 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.43 (t, *J* = 6.8 Hz, 1H), 7.12 (s, 1H), 7.04 (d, *J* = 6.6 Hz, 1H), 7.00 (dd, *J* = 7.4, 2.5 Hz, 2H), 6.92 – 6.85 (m, 3H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.41 (s, 1H), 3.28 – 3.12 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.8, 170.5, 147.4, 142.5, 139.5, 137.5, 135.2, 133.3, 129.9, 129.5, 128.6, 128.0, 127.6, 126.3, 126.2, 125.7, 123.4, 120.2, 119.1, 117.4, 113.0, 101.1, 55.0, 43.4, 21.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}ClN_2O^+$423.1259; Found:423.1284.



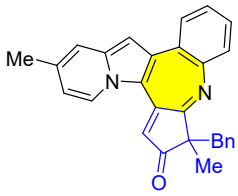
The compound **3ad** was obtained as a yellow solid (33.6 mg, 72% yield).

Melting point 216-221 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 6.5 Hz, 1H), 7.90 (d, *J* = 6.4 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.11 (s, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.93 – 6.86 (m, 3H), 6.68 (t, *J* = 7.0 Hz, 1H), 6.40 (s, 1H), 3.27 – 3.12 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.8, 170.5, 147.4, 142.5, 139.5, 137.5, 135.2, 133.3, 129.9, 129.5, 128.6, 128.0, 127.6, 126.3, 126.2, 125.7, 123.4, 120.2, 119.1, 117.4, 113.0, 101.1, 55.0, 43.4, 21.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}BrN_2O^+$467.0754; Found:467.0755.



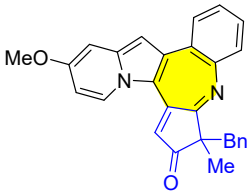
The compound **3ae** was obtained as a yellow solid (26.0 mg, 65% yield).

Melting point 214-219 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.95 (m, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.46 – 7.38 (m, 1H), 7.20 (s, 1H), 7.01 (d, *J* = 5.7 Hz, 2H), 6.97 (s, 1H), 6.95 – 6.86 (m, 3H), 6.51 (d, *J* = 7.4 Hz, 1H), 6.34 (s, 1H), 3.27 – 3.11 (m, 2H), 2.33 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 170.5, 147.1, 142.5, 140.1, 137.6, 135.2, 134.6, 133.6, 129.9, 129.4, 128.5, 128.0, 127.5, 126.4, 126.2, 125.3, 119.1, 117.5, 117.0, 115.7, 99.9, 54.9, 43.3, 21.8, 21.1.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O^+$403.1805; Found:403.1801.



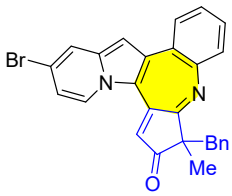
The compound **3af** was obtained as a yellow solid (32.6 mg, 78% yield).

Melting point 195-200 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.41 (t, *J* = 6.8 Hz, 1H), 7.01 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.94 – 6.87 (m, 4H), 6.68 (d, *J* = 2.6 Hz, 1H), 6.40 (dd, *J* = 7.8, 2.7 Hz, 1H), 6.25 (s, 1H), 3.86 (s, 3H), 3.28 – 3.09 (m, 2H), 1.47 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 170.8, 156.5, 146.8, 142.6, 141.6, 137.6, 135.2, 134.4, 130.0, 129.5, 128.5, 127.9, 127.5, 127.2, 126.2, 126.2, 117.8, 116.7, 107.7, 99.5, 95.9, 55.6, 54.9, 43.3, 21.9.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O_2^+$419.1754; Found:419.1751.



The compound **3ag** was obtained as a yellow solid (24.2 mg, 52% yield).

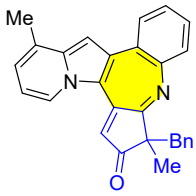
Melting point 210-223 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H), 7.05 (dd, *J* = 8.8, 6.6 Hz, 1H), 6.99 (dd, *J* = 7.2,

2.3 Hz, 2H), 6.89 (d, *J* = 6.3 Hz, 3H), 6.70 (t, *J* = 6.9 Hz, 1H), 6.41 (s, 1H), 3.27 – 3.12 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.1, 170.9, 147.8, 142.9, 139.9, 137.9, 135.6, 133.6, 130.3, 129.8, 129.0, 128.4, 127.9, 126.7, 126.6, 126.1, 123.7, 120.6, 119.5, 117.8, 113.3, 101.5, 55.4, 43.8, 22.0.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}BrN_2O^+$467.0754; Found:467.0764.

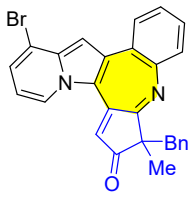


The compound **3ah** was obtained as a yellow solid (18.6 mg, 46% yield). Melting point 214-221 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 6.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 8.3 Hz, 1H), 7.10 (s, 1H), 7.00 (d, *J* = 6.7 Hz, 2H), 6.89 (d, *J* = 5.4 Hz, 3H), 6.83 (d, *J* = 6.7 Hz, 1H), 6.62 (t, *J* = 7.0 Hz, 1H), 6.39 (s, 1H), 3.28 – 3.12 (m, 2H), 2.48 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.7, 170.6, 147.6, 142.5, 140.3, 137.5, 135.2, 132.8, 129.9, 129.4, 128.5, 128.2, 128.0, 127.6, 126.4, 126.2, 123.7, 122.7, 120.2, 117.9, 113.0, 99.5, 55.0, 43.4, 21.7, 18.1.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{23}N_2O^+$403.1805; Found:403.1800.

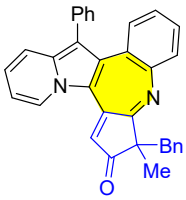


The compound **3aj** was obtained as a yellow solid (35.0 mg, 75% yield). Melting point 204-212 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.44 (s, 1H), 7.12 (s, 1H), 7.04 (d, *J* = 6.6 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 5.4 Hz, 3H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.41 (s, 1H), 3.28 – 3.11 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.8, 170.5, 147.4, 142.5, 139.5, 137.5, 135.2, 133.3, 129.9, 129.5, 128.6, 128.0, 127.6, 126.3, 126.2, 125.7, 123.4, 120.2, 119.1, 117.4, 113.0, 101.1, 55.0, 43.4, 21.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}BrN_2O^+$467.0754; Found:467.0763.

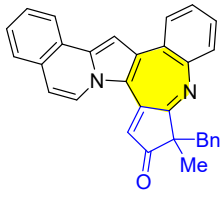


The compound **3ak** was obtained as a yellow solid (38.6mg, 83% yield). Melting point 193-194 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 6.4 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 3H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.04 (dd, *J* = 9.0, 6.6 Hz, 1H), 6.95 (d, *J* = 7.1 Hz, 3H), 6.72 (t, *J* = 8.3 Hz, 3H), 6.67 (d, *J* = 5.8 Hz, 1H), 6.30 (s, 1H), 3.26 – 3.12 (m, 2H), 1.53 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.1, 172.0, 147.7, 144.0, 139.3, 137.3, 134.8, 132.8, 132.3, 130.7, 129.7, 129.6, 129.2, 128.7, 127.3, 127.2, 126.7, 126.3, 125.9, 124.4, 123.5, 121.4, 118.7, 118.1, 117.3, 113.7, 56.2, 44.3, 21.0.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{33}H_{25}N_2O^+$465.1962; Found:469.1952.



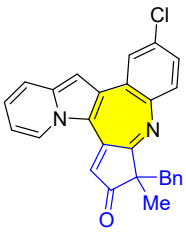
The compound **3al** was obtained as a yellow solid (21.9mg, 50% yield). Melting point 124-136 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.91 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.47 (m, 6H), 7.44 (td, *J* =

7.6, 1.7 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.91 (dd, *J* = 8.9, 6.9 Hz, 3H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.36 (s, 1H), 3.29 – 3.14 (m, 2H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 170.5, 147.7, 142.6, 137.5, 137.5, 135.3, 132.1, 129.9, 129.3, 128.6, 128.3, 128.0, 127.8, 127.6, 127.0, 126.8, 126.4, 126.4, 124.5, 123.4, 122.7, 121.1, 119.3, 112.6, 100.6, 55.3, 43.6, 21.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{31}H_{23}N_2O^+$439.1805; Found:439.1808.

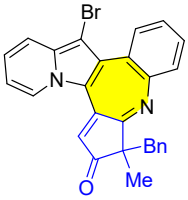


The compound **3am** was obtained as a yellow solid (20.0 mg, 47% yield). Melting point 233-237 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 6.1 Hz, 1H), 7.96 (d, *J* = 2.4 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.07 – 7.03 (m, 2H), 6.98 (d, *J* = 5.8 Hz, 2H), 6.90 (d, *J* = 6.8 Hz, 3H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.41 (s, 1H), 3.24 – 3.12 (m, 2H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.6, 170.8, 147.1, 141.0, 139.5, 137.4, 136.6, 134.1, 131.7, 129.9, 129.9, 129.3, 127.8, 127.6, 127.6, 126.3, 125.7, 123.5, 120.7, 119.3, 117.4, 113.3, 101.3, 55.0, 43.4, 21.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}ClN_2O^+$423.1259; Found:423.1261.

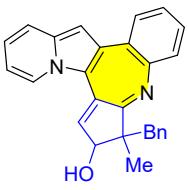


The compound **4** was obtained as a yellow solid (40.1 mg, 86% yield). Melting point 205-211 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.68 (dt, *J* = 8.9, 1.2 Hz, 1H), 7.55 (td, *J* = 7.5, 1.6 Hz, 1H), 7.47 (td, *J* = 7.6, 1.6 Hz, 1H), 7.21 (ddd, *J* = 8.9, 6.7, 1.0 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.77 (ddd, *J* = 14.1, 7.7, 6.0 Hz, 3H), 6.66 (td, *J* = 6.9, 1.4 Hz, 1H), 6.34 (d, *J* = 6.9 Hz, 1H), 3.19 (s, 2H), 1.58 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.1, 171.2, 147.3, 144.4, 137.3, 136.9, 132.9, 130.5, 129.7, 129.3, 129.2, 129.1, 127.7, 127.4, 127.3, 125.2, 123.8, 118.9, 117.4, 116.4, 112.1, 90.2, 58.2, 44.9, 20.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{20}BrN_2O^+$467.0754; Found:467.0767.

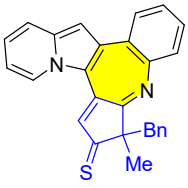


The compound **5** was obtained as a yellow solid (14.3 mg, 36% yield). Melting point 233-237 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.2 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 7.30 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.25 (s, 2H), 7.03 – 6.95 (m, 3H), 6.89 (s, 1H), 6.79 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.55 – 6.49 (m, 1H), 6.44 (d, *J* = 2.9 Hz, 1H), 4.80 – 4.58 (m, 1H), 3.33 – 2.96 (m, 2H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 143.0, 139.3, 136.2, 133.8, 133.6, 131.4, 130.5, 129.9, 128.3, 128.2, 128.1, 128.0, 127.6, 127.6, 127.2, 126.0, 123.4, 119.4, 118.9, 116.5, 111.4, 98.8, 56.2, 40.7, 23.2.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{23}N_2O^+$391.1805; Found:391.1797.



The compound **6** was obtained as a yellow solid (24.6 mg, 61% yield). Melting point 206-212 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 7.2 Hz, 1H), 8.09 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.59 (td, *J* = 7.5, 1.5 Hz, 1H), 7.54 –

7.45 (m, 2H), 7.20 (d, *J* = 3.8 Hz, 2H), 7.14 (dd, *J* = 8.9, 6.6 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.84 – 6.79 (m, 3H), 6.73 (td, *J* = 6.9, 1.4 Hz, 1H), 3.44 – 3.20 (m, 2H), 1.60 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 234.2, 172.5, 141.3, 141.3, 139.3, 136.4, 134.6, 134.0, 133.4, 128.9, 128.8, 127.7, 126.9, 126.2, 125.6, 125.2, 125.2, 123.5, 118.2, 116.8, 112.4, 101.2, 62.8, 45.4, 23.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{27}H_{21}N_2S^+$405.1420; Found:405.1429.

9. X-ray crystallographic analysis

Single crystals of **3ah** suitable for X-ray analysis were obtained by diffusion method of *n*-hexane/DCM.

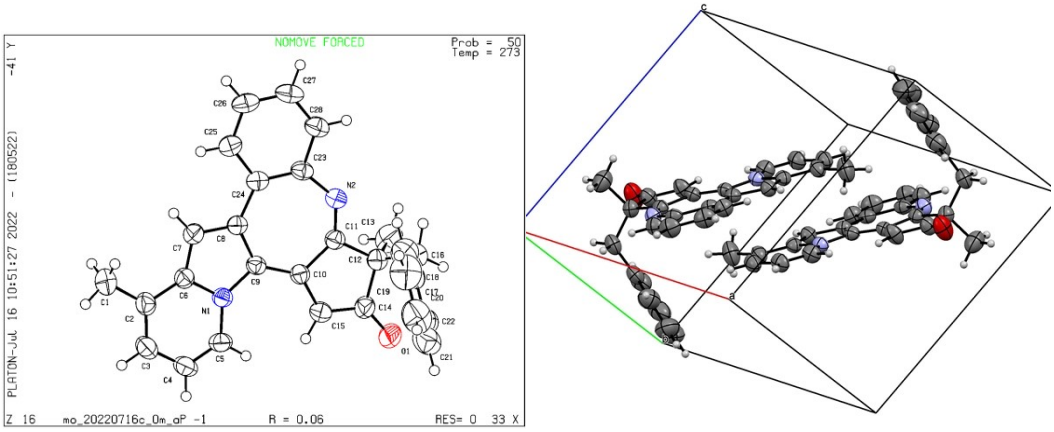


Figure S2. X-ray structure (at 50% probability level) and packing structure of **3ah**.

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=9.820(4) b=10.002(5) c=11.566(5)

α=74.516(14) β=81.314(13) γ=76.320(13)

Temperature: 273 K

Calculated	Reported	
Volume	1059.0(8)	1059.1(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C28 H22 N2 O [+ solvent]	C28 H22 N2 O
Sum formula	C28 H22 N2 O [+ solvent]	C28 H21 N2 O
Mr	402.48	401.47
Dx,g/cm^3	1.262	1.259
Z	2	2
Mu (mm^{-1})	0.077	0.077
F000	424.0	422.0
F000’	424.16	
h,k,lmax	12,13,15	12,12,15
Nref	4885	4849
Tmin,Tmax	0.984,0.985	0.691,0.746
Tmin’	0.984	

Correction method= # Reported T Limits: T =0.691 T_{max}=0.746

AbsCorr = NONE

Data completeness= 0.993 Theta(max)= 27.562

R(reflections)= 0.0638(2928) wR_2(reflections)=0.1888(4849)

S = 1.031 Npar= 282

10. Photophysical properties

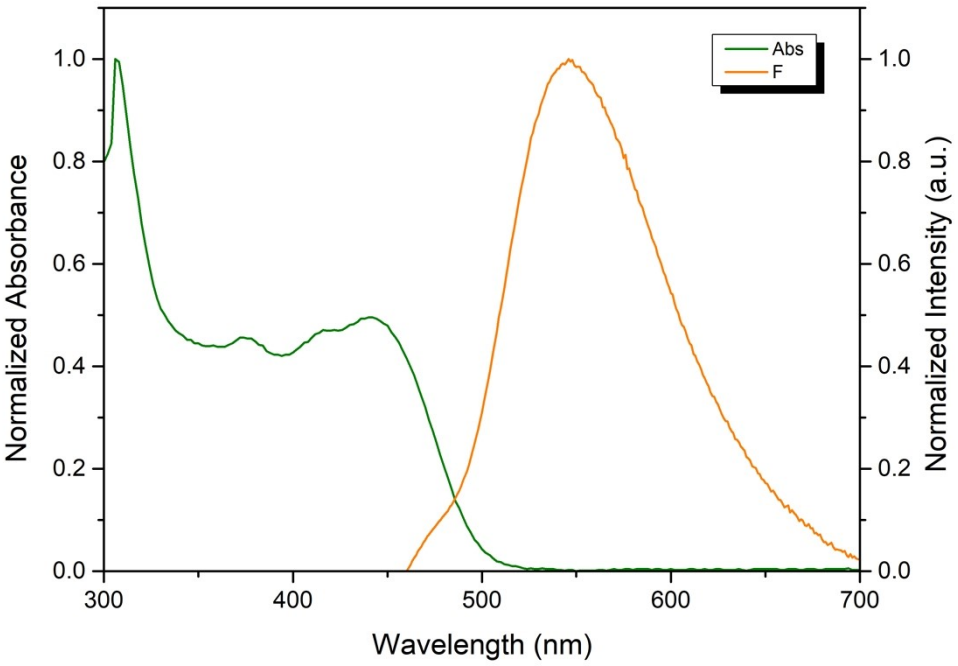


Figure S3. Normalized absorption (left) and emission (right) spectra of **3ma** recorded in DCM, excited at 450 nm, QY=19.0%.

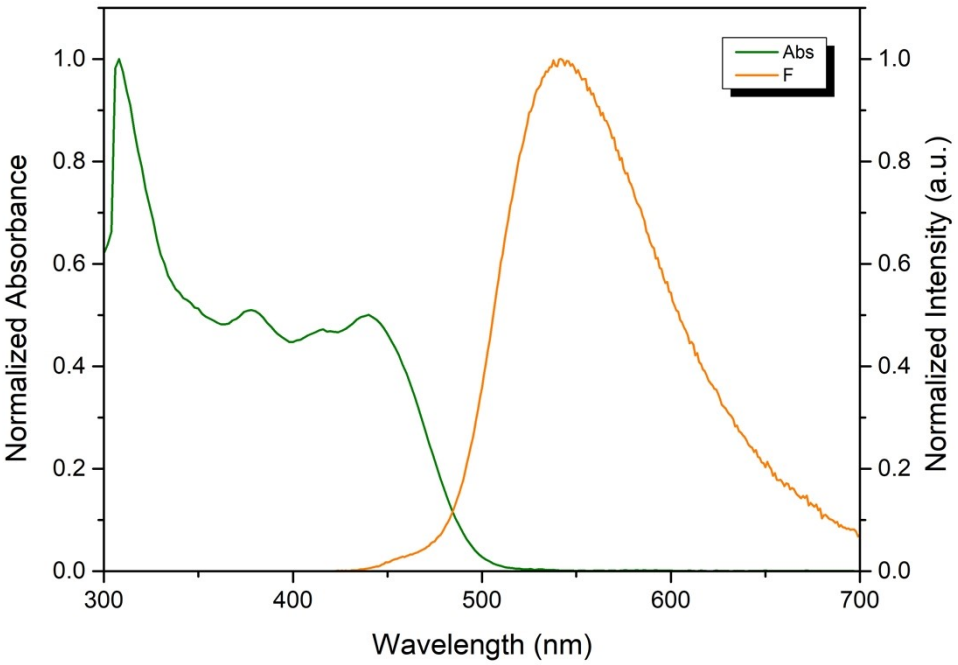


Figure S4. Normalized absorption (left) and emission (right) spectra of **3am** recorded in DCM, excited at 450 nm, QY=10.6%.

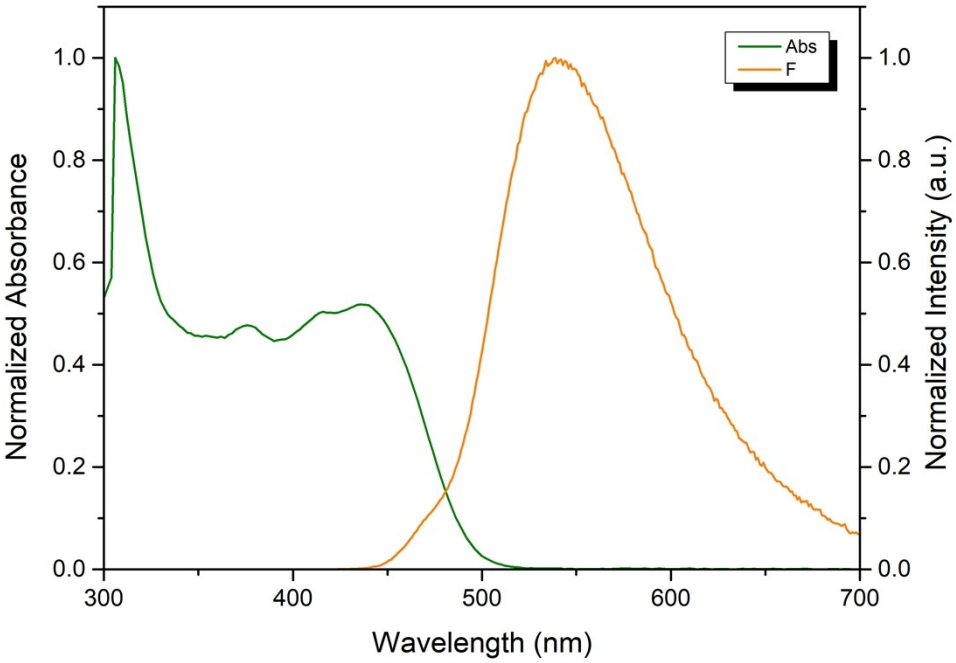


Figure S5. Normalized absorption (left) and emission (right) spectra of **3ac** recorded in DCM, excited at 450 nm, QY=15.1%.

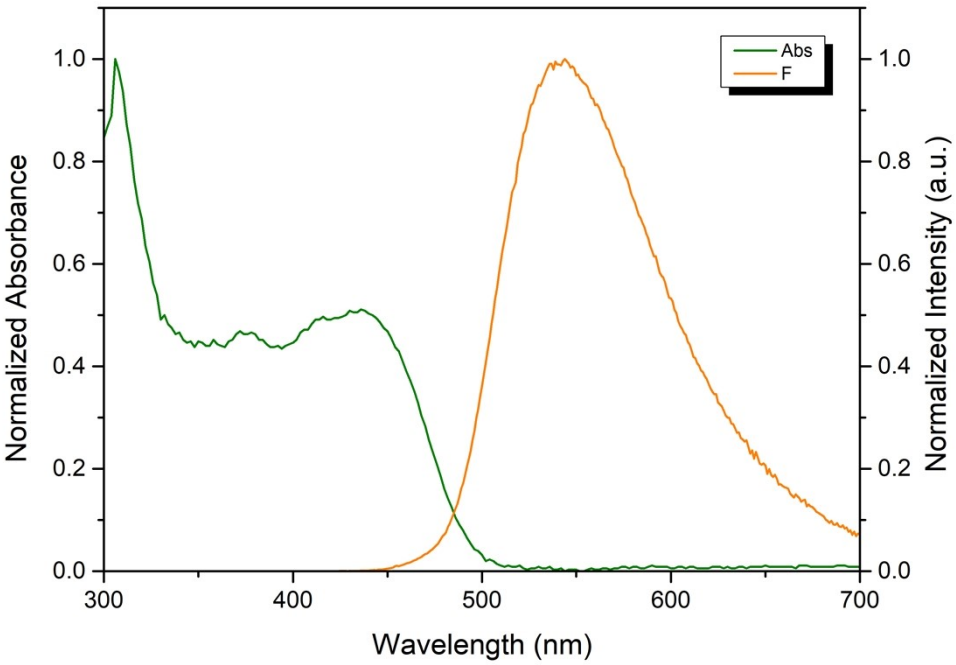


Figure S6. Normalized absorption (left) and emission (right) spectra of **3ag** recorded in DCM, excited at 450 nm, QY=13.3%.

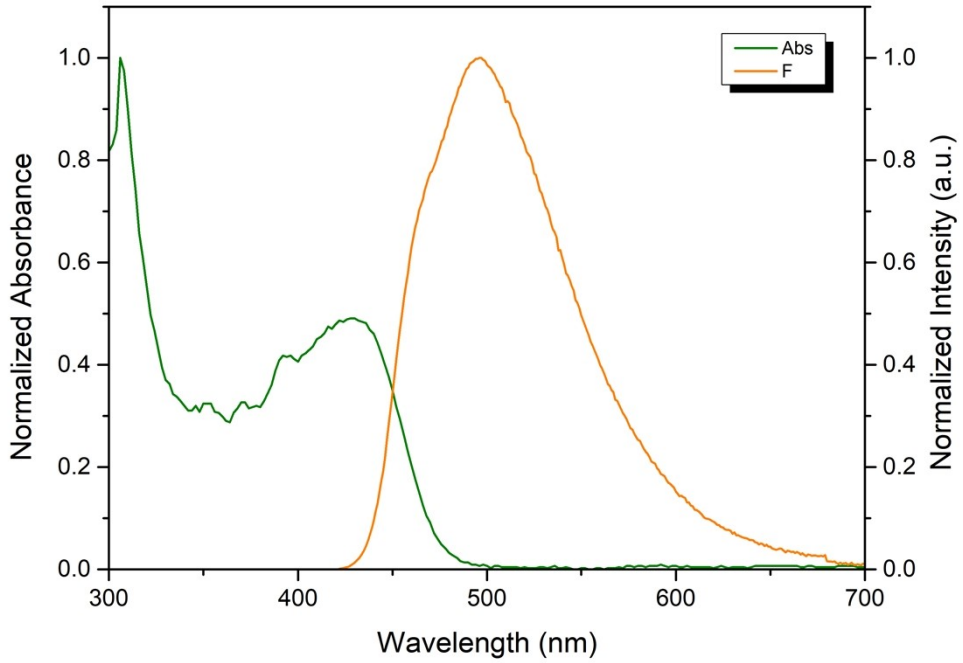


Figure S7. Normalized absorption (left) and emission (right) spectra of **3al** recorded in DCM, excited at 450 nm, QY=25.8%.

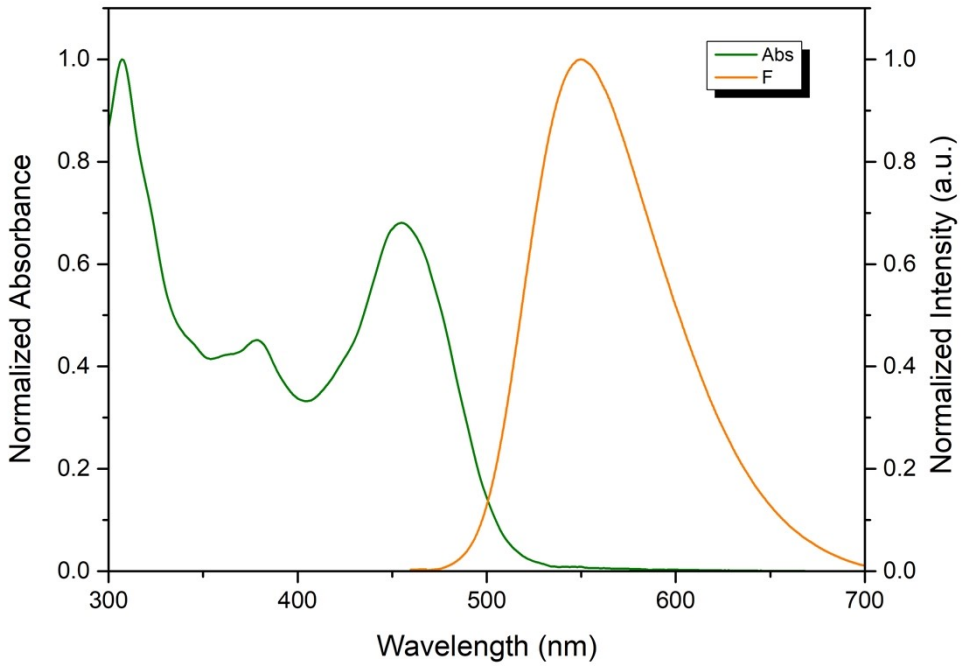
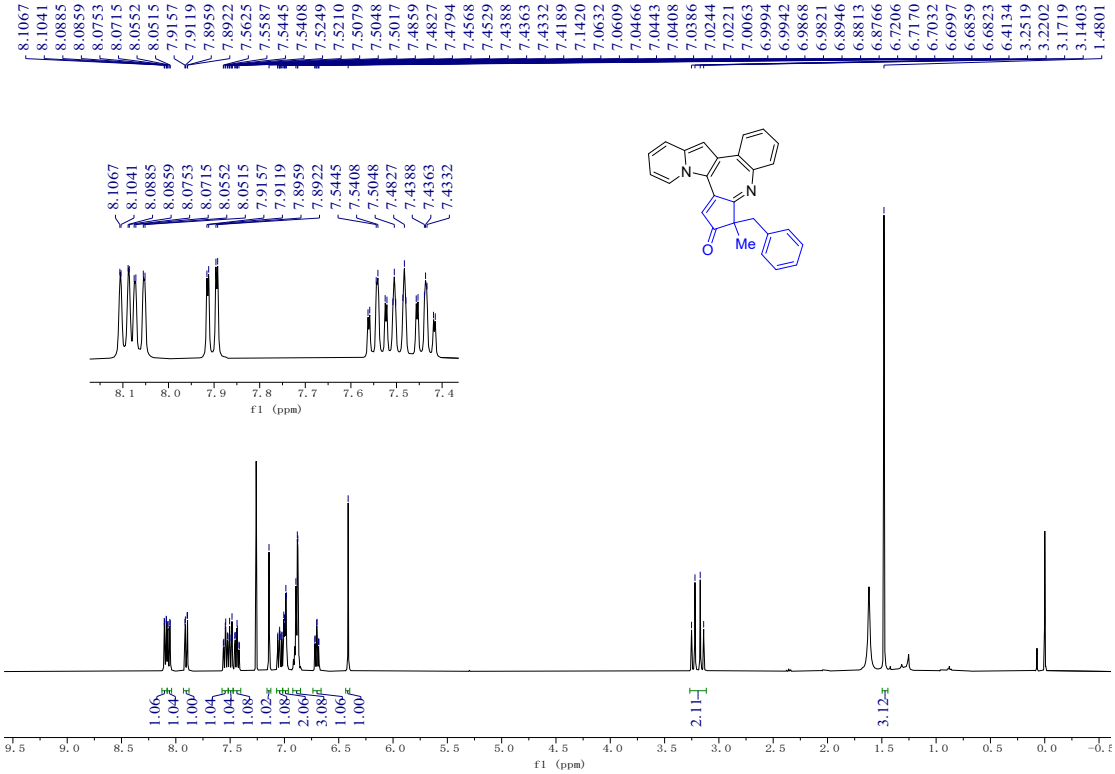


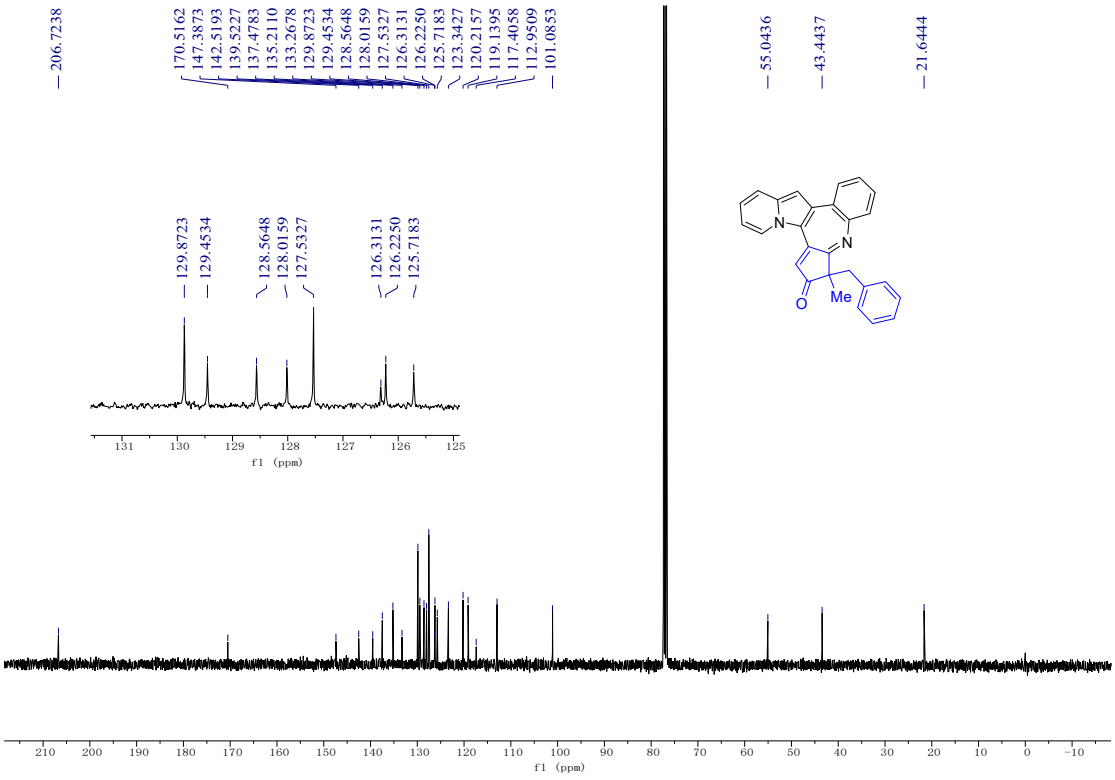
Figure S8. Normalized absorption (left) and emission (right) spectra of **3af** recorded in DCM, excited at 450 nm, QY=7.4%.

11. Copies of NMR spectroscopy

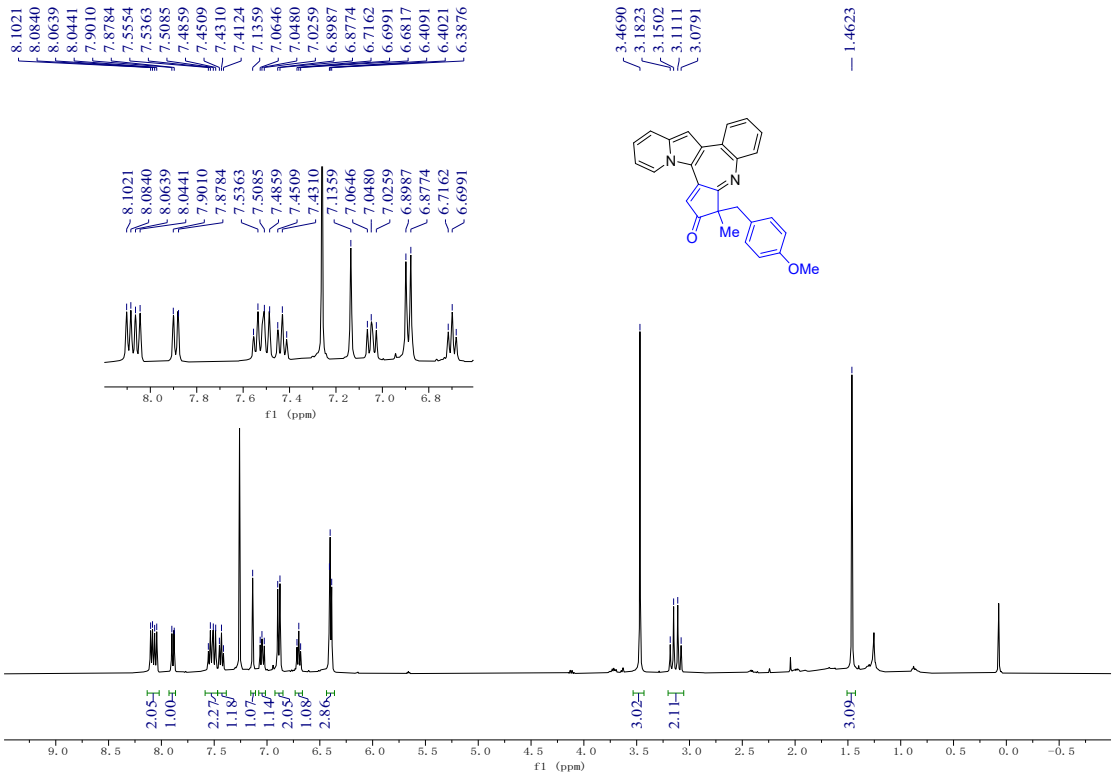
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$)



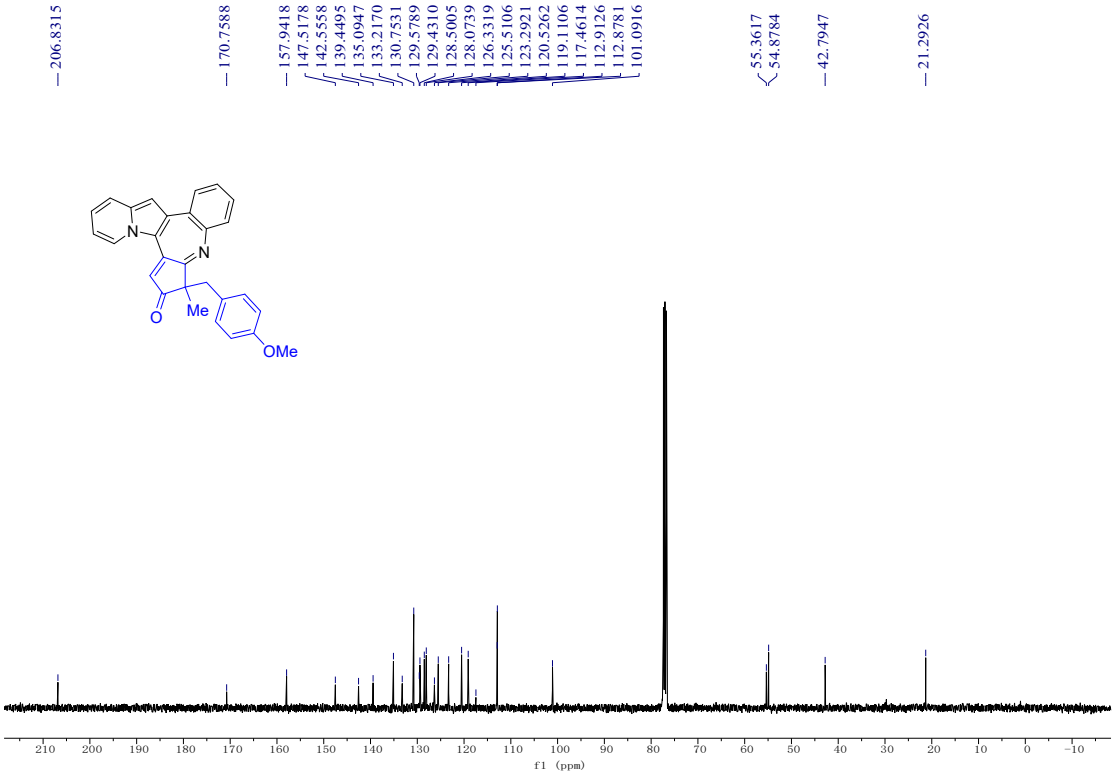
^{13}C NMR of **3aa** (101 MHz, $CDCl_3$)



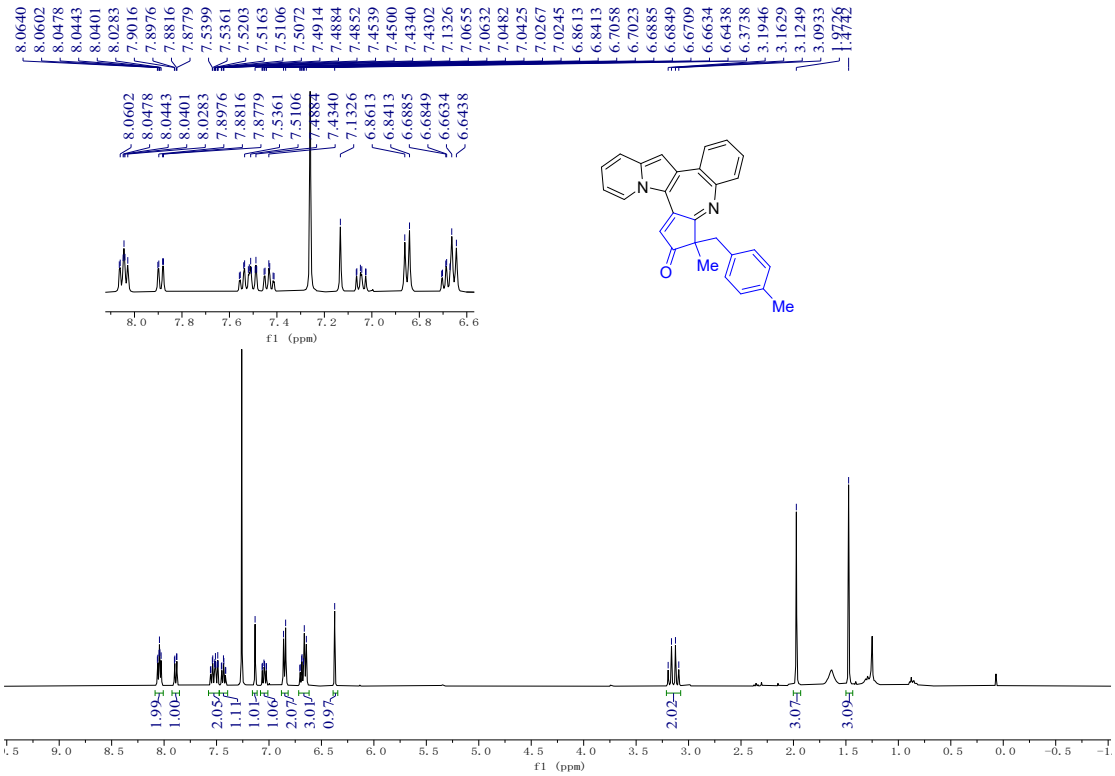
^{1}H NMR of **3ba** (400 MHz, $CDCl_3$)



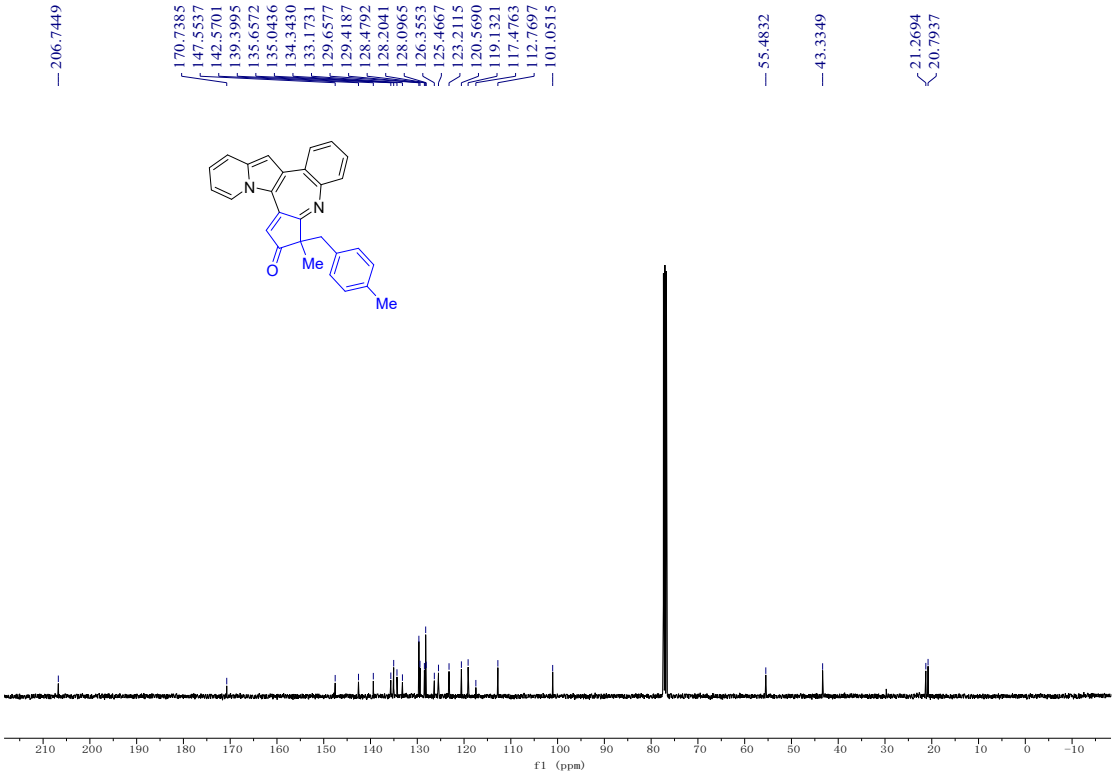
^{13}C NMR of **3ba** (101 MHz, $CDCl_3$)



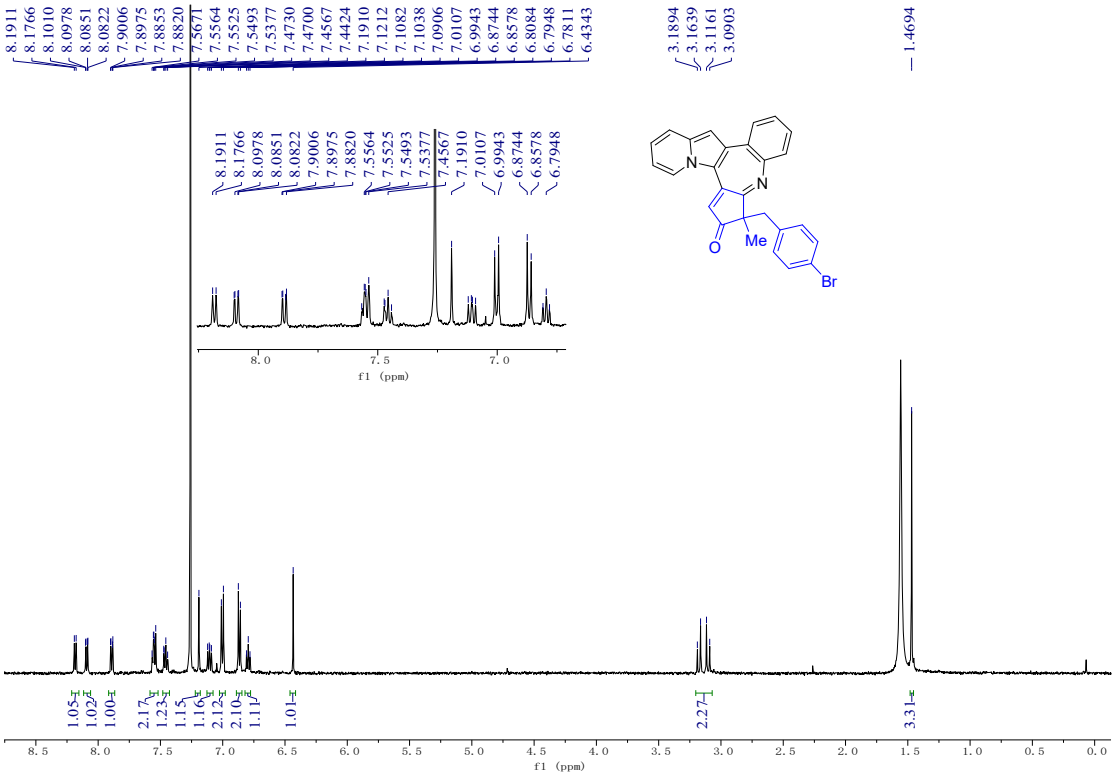
^{1}H NMR of **3ca** (400 MHz, $CDCl_3$)



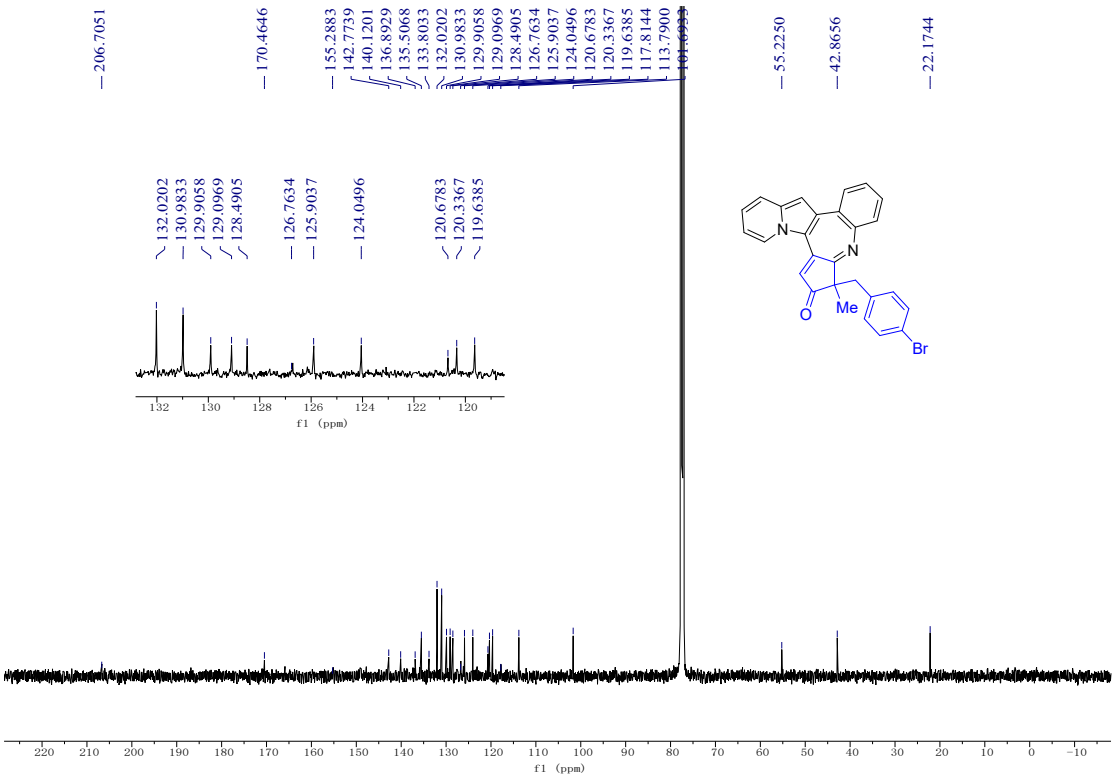
^{13}C NMR of **3ca** (101 MHz, $CDCl_3$)



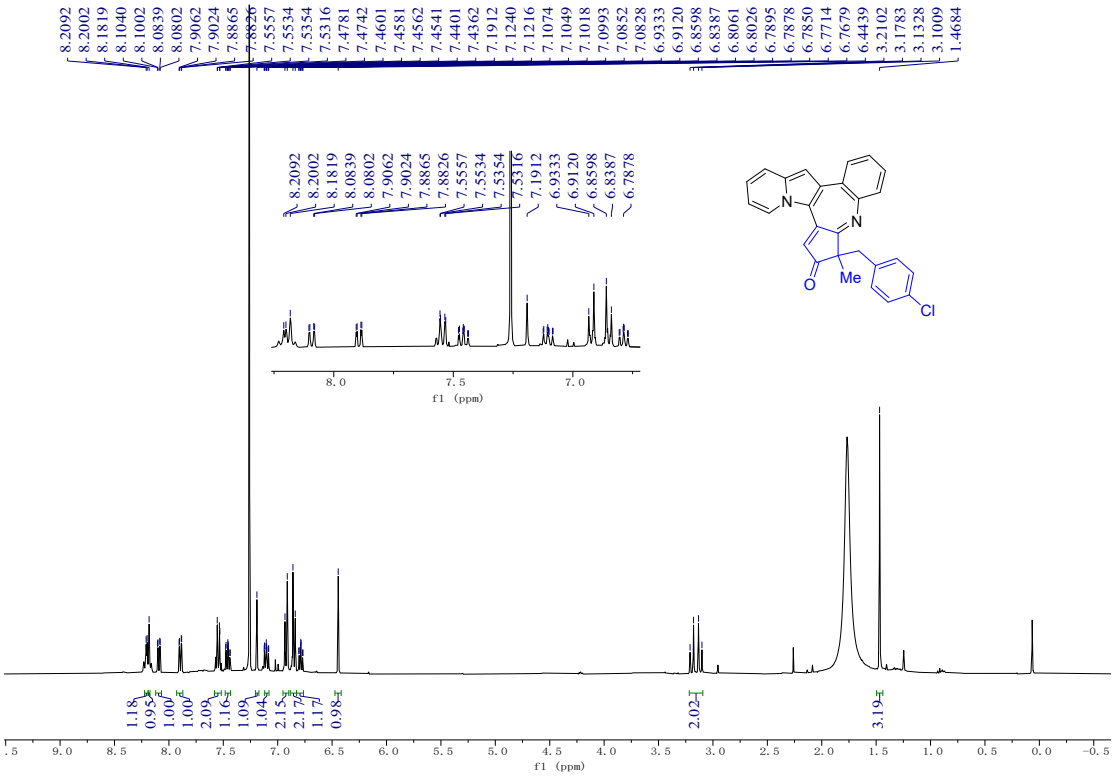
^{1}H NMR of **3da** (500 MHz, $CDCl_3$)



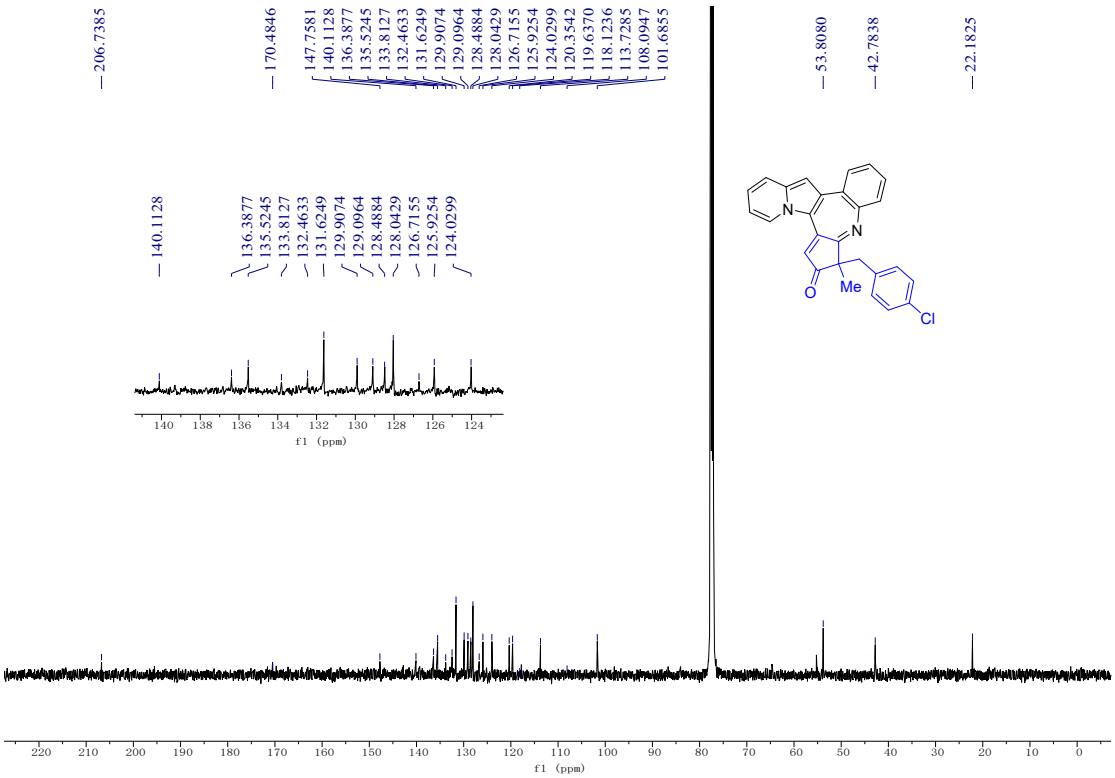
^{13}C NMR of **3da** (125 MHz, $CDCl_3$)



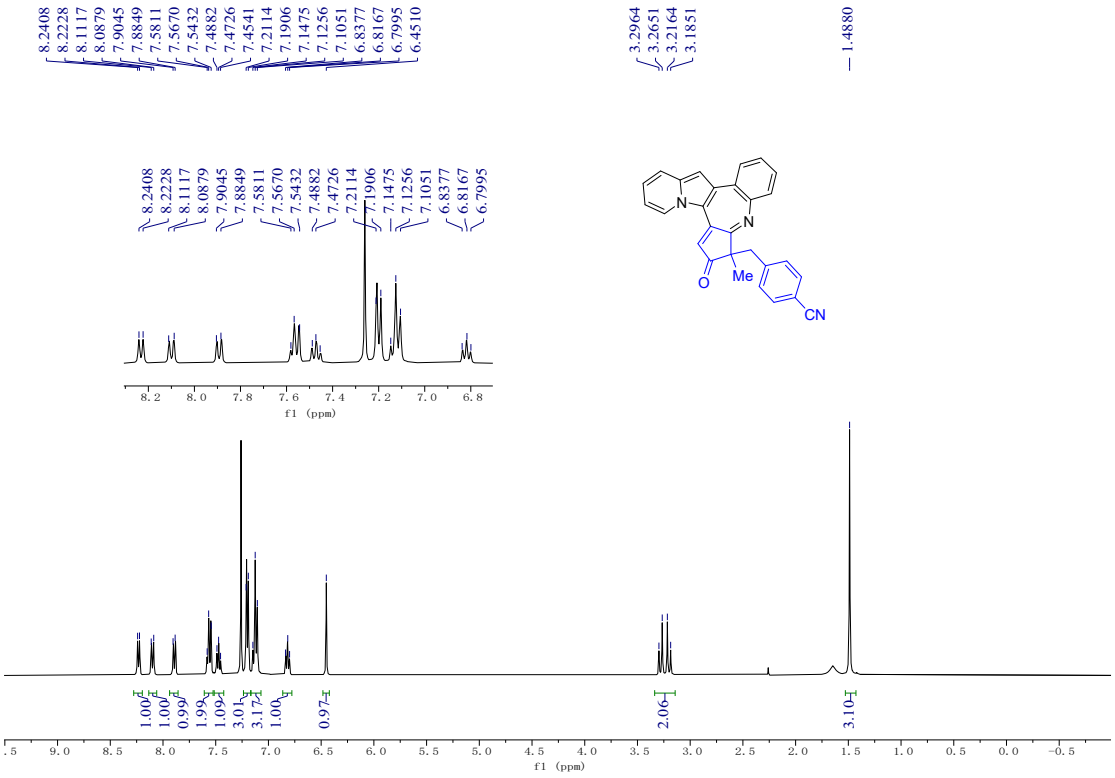
^{1}H NMR of **3ea** (400 MHz, $CDCl_3$)



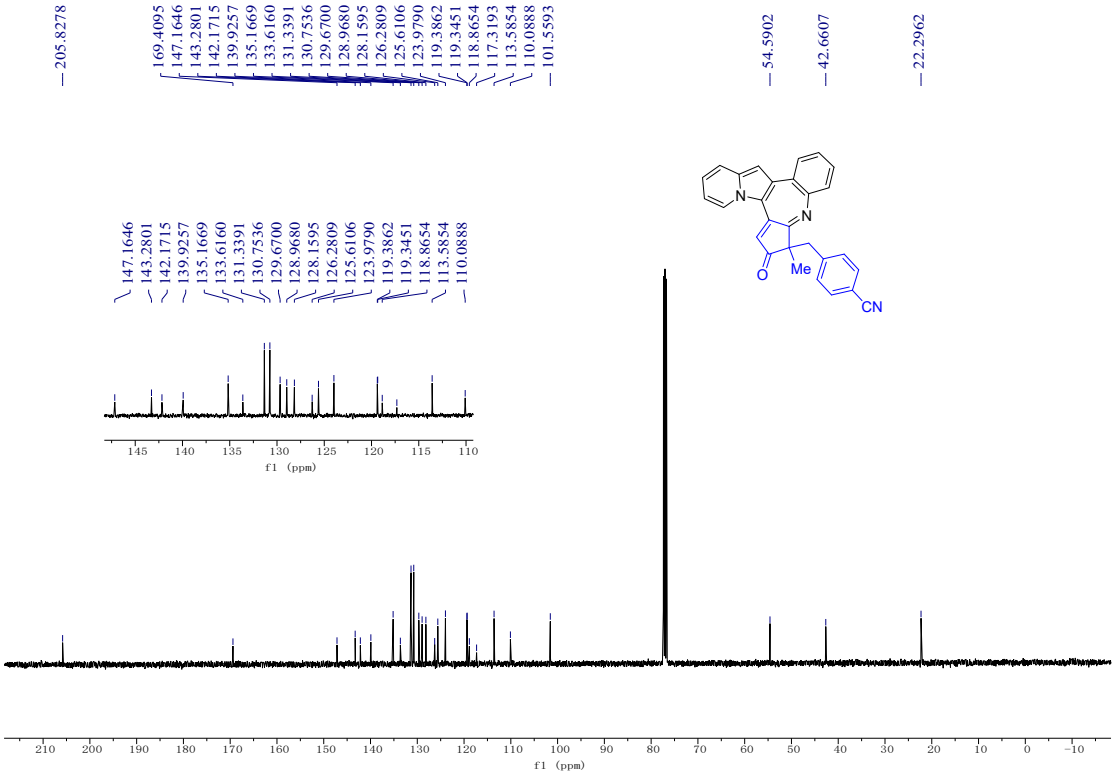
^{13}C NMR of **3ea** (101 MHz, $CDCl_3$)



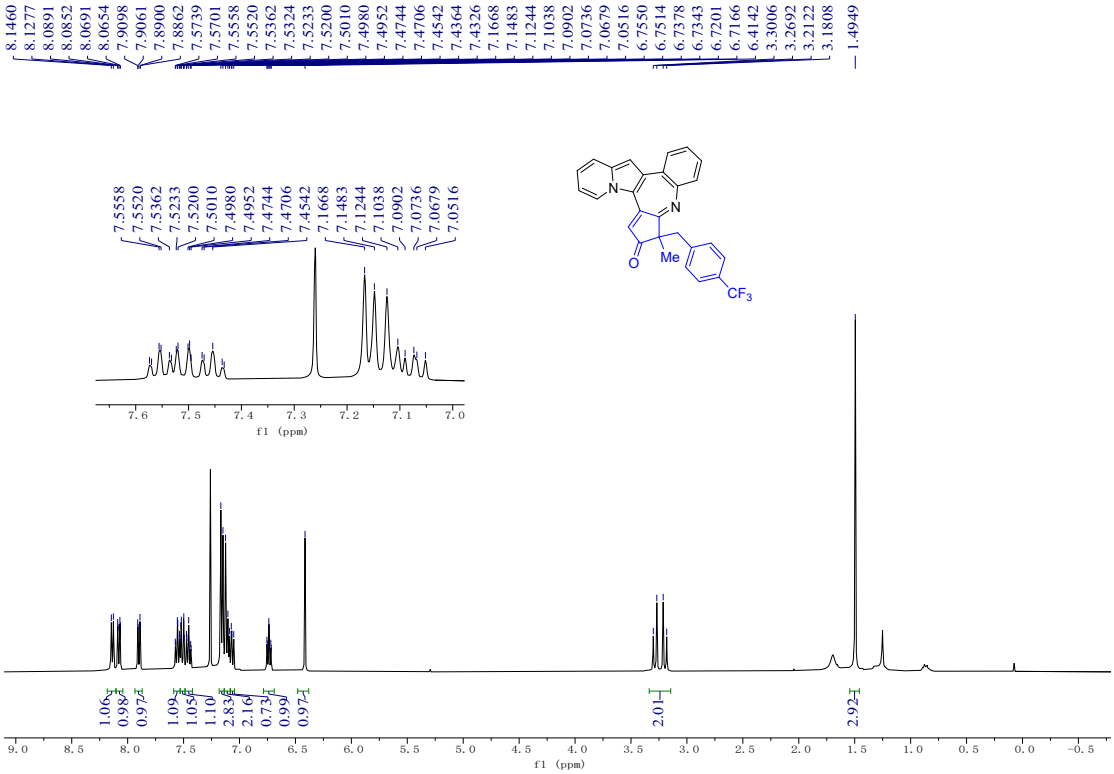
^{1}H NMR of **3fa** (400 MHz, $CDCl_3$)



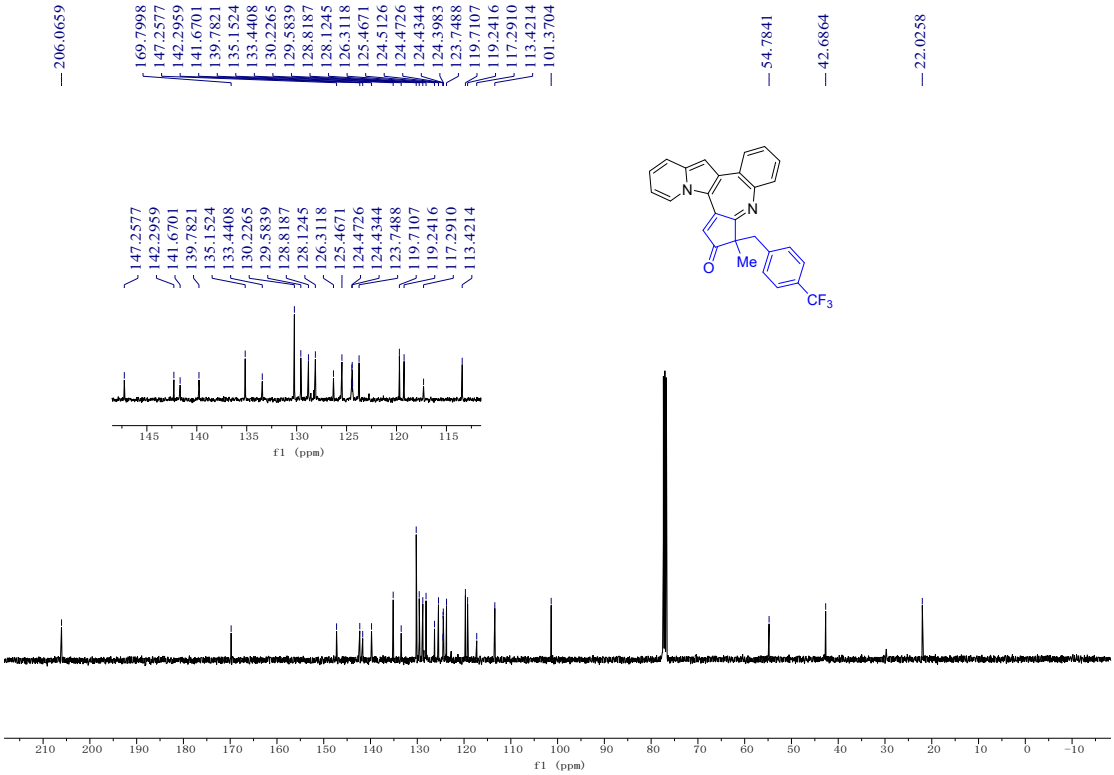
^{13}C NMR of **3fa** (101 MHz, $CDCl_3$)



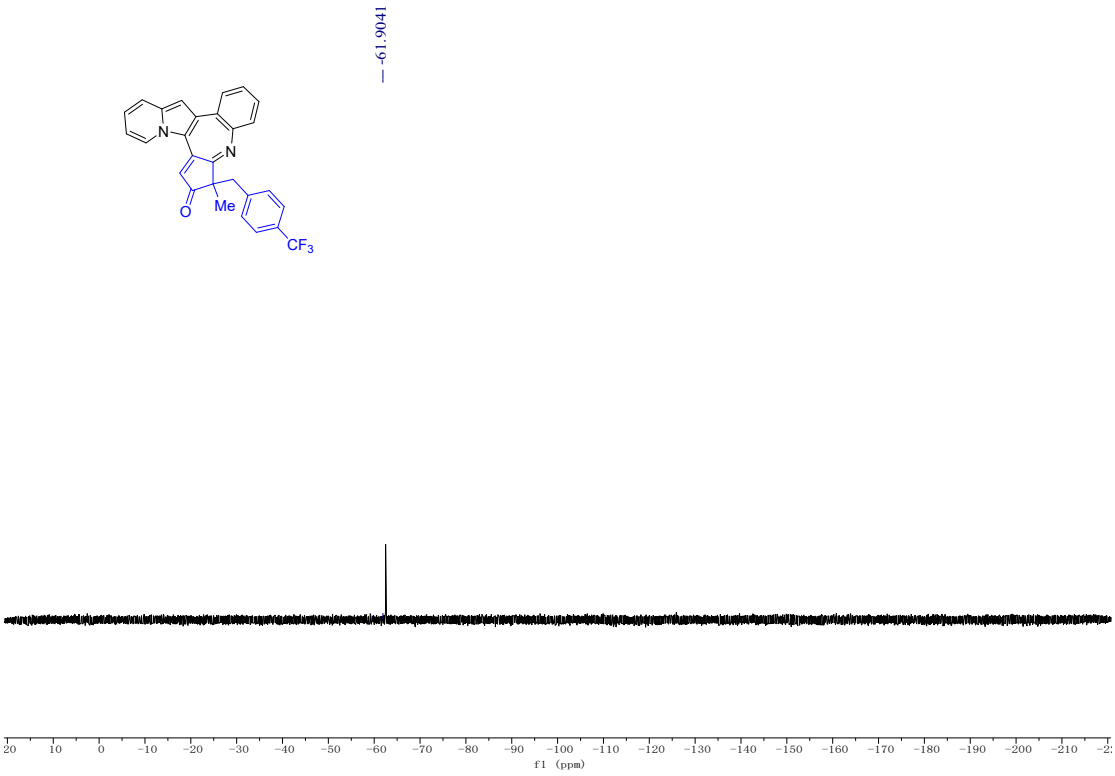
^{1}H NMR of **3ga** (400 MHz, $CDCl_3$)



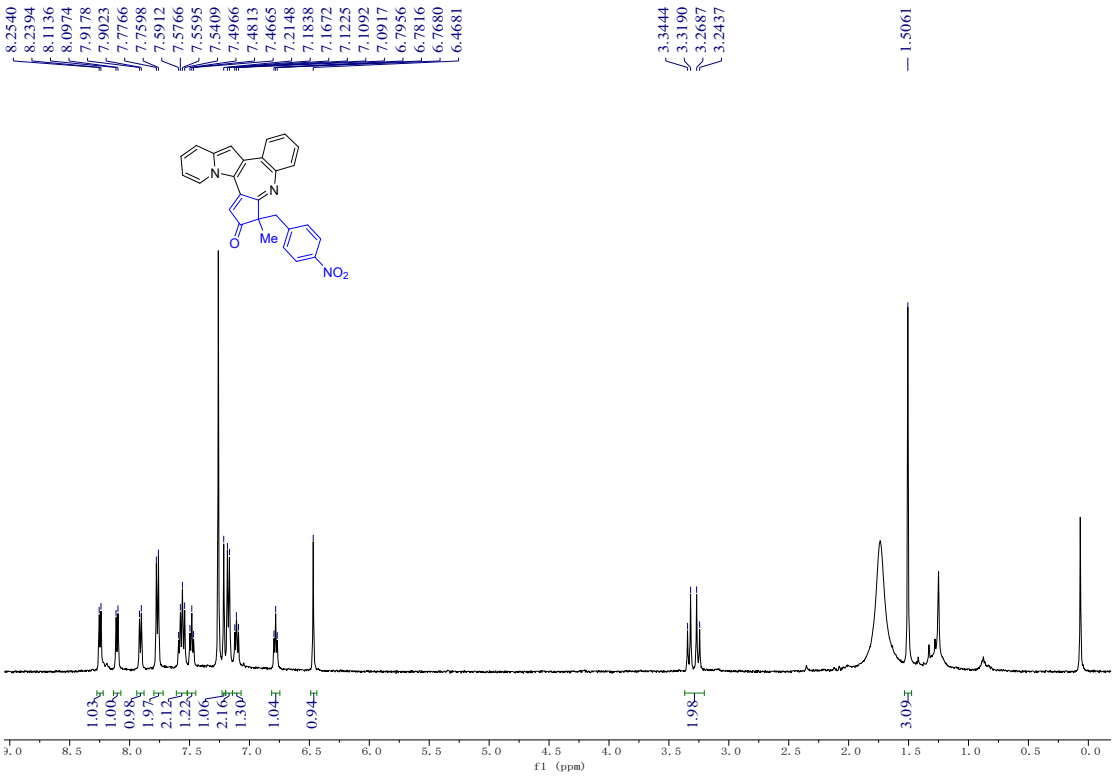
^{13}C NMR of **3ga** (101 MHz, $CDCl_3$)



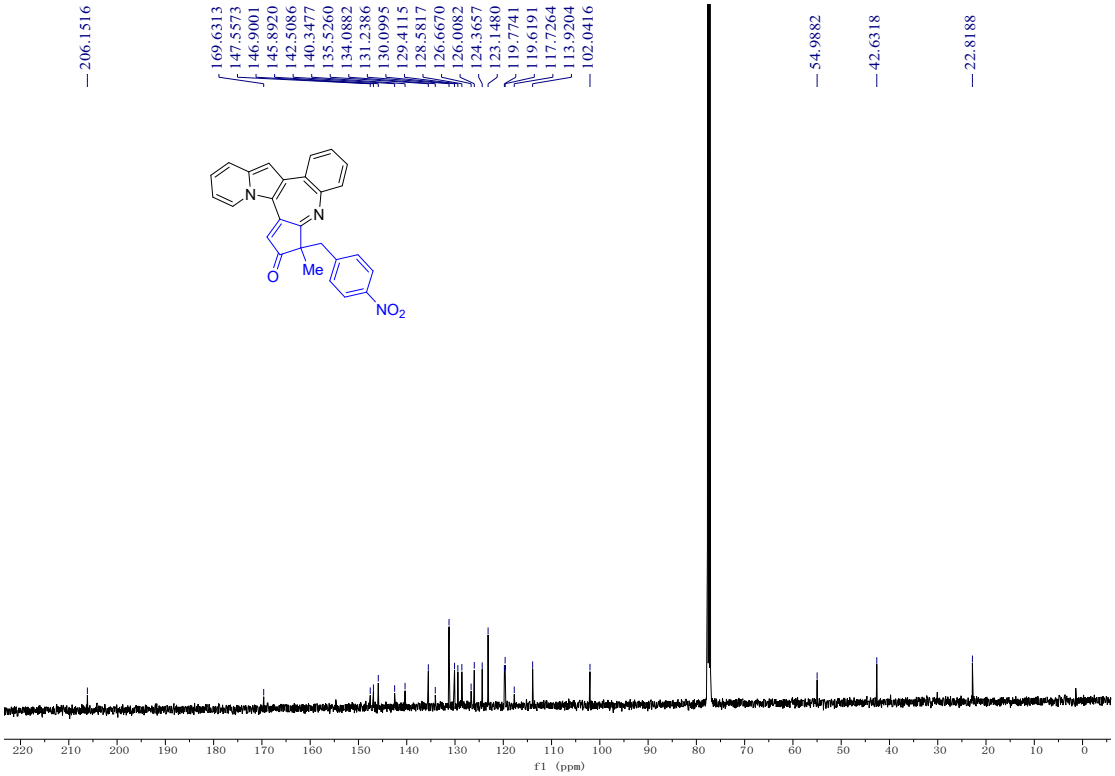
^{19}F NMR of **3ga** (376 MHz, $CDCl_3$)



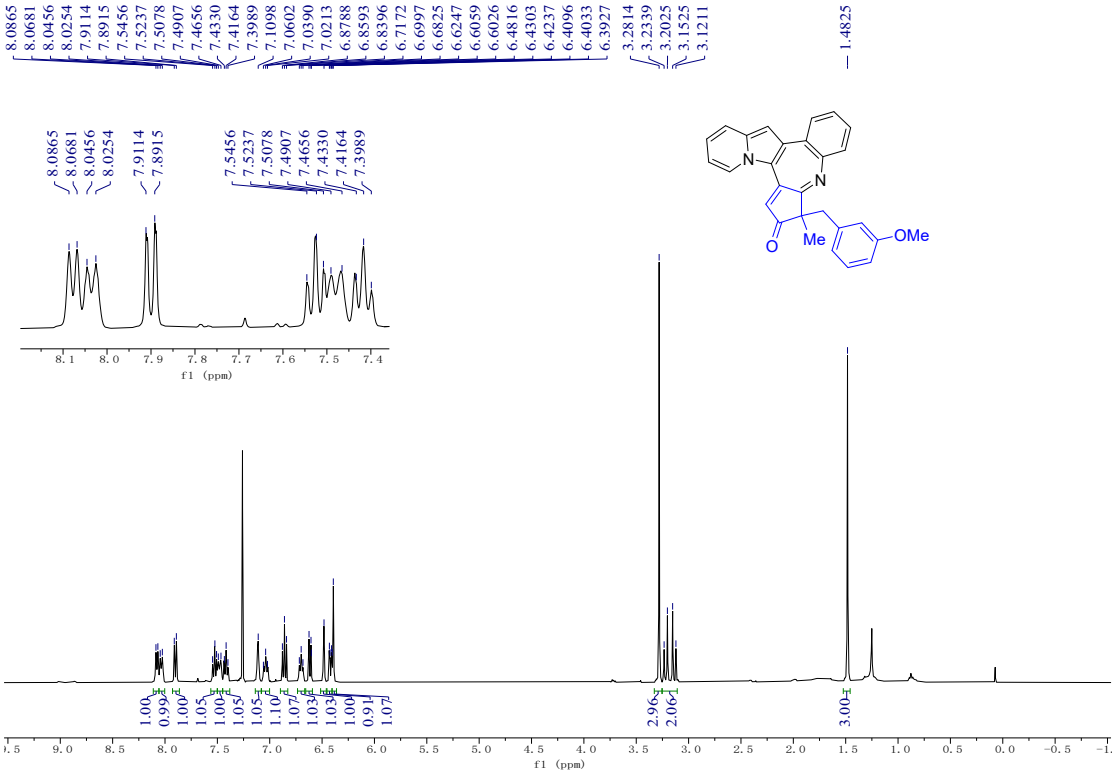
^{1}H NMR of **3ha** (500 MHz, $CDCl_3$)



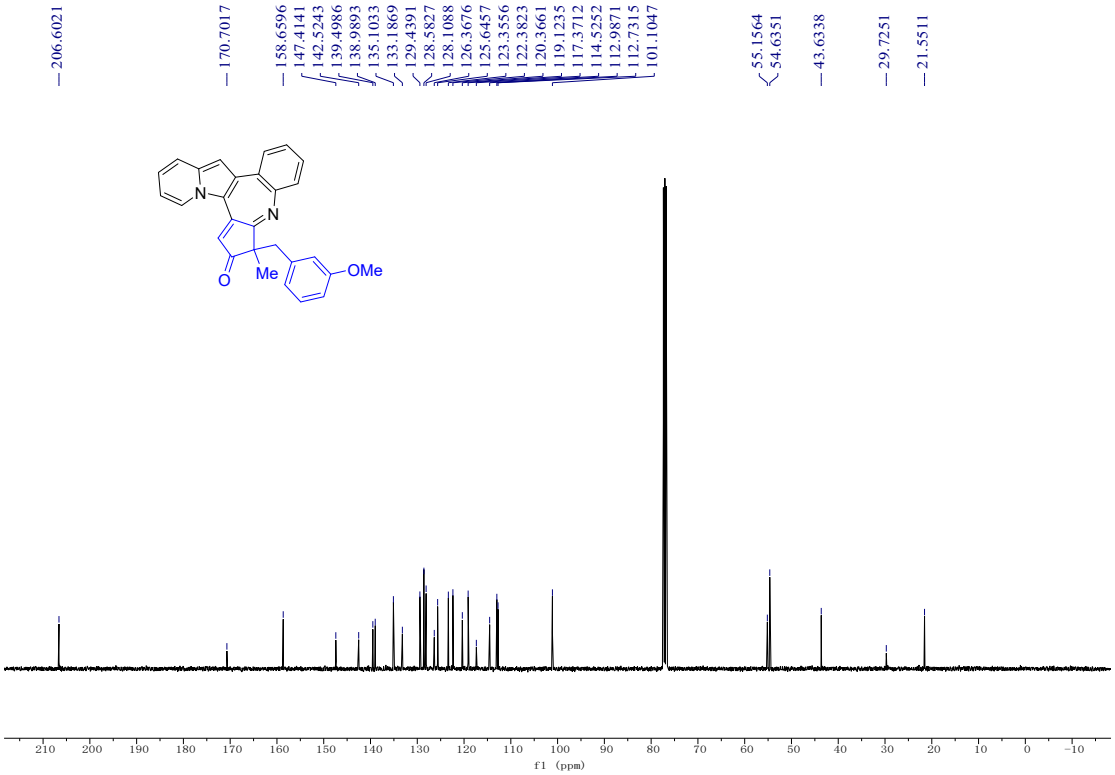
^{13}C NMR of **3ha** (125 MHz, $CDCl_3$)



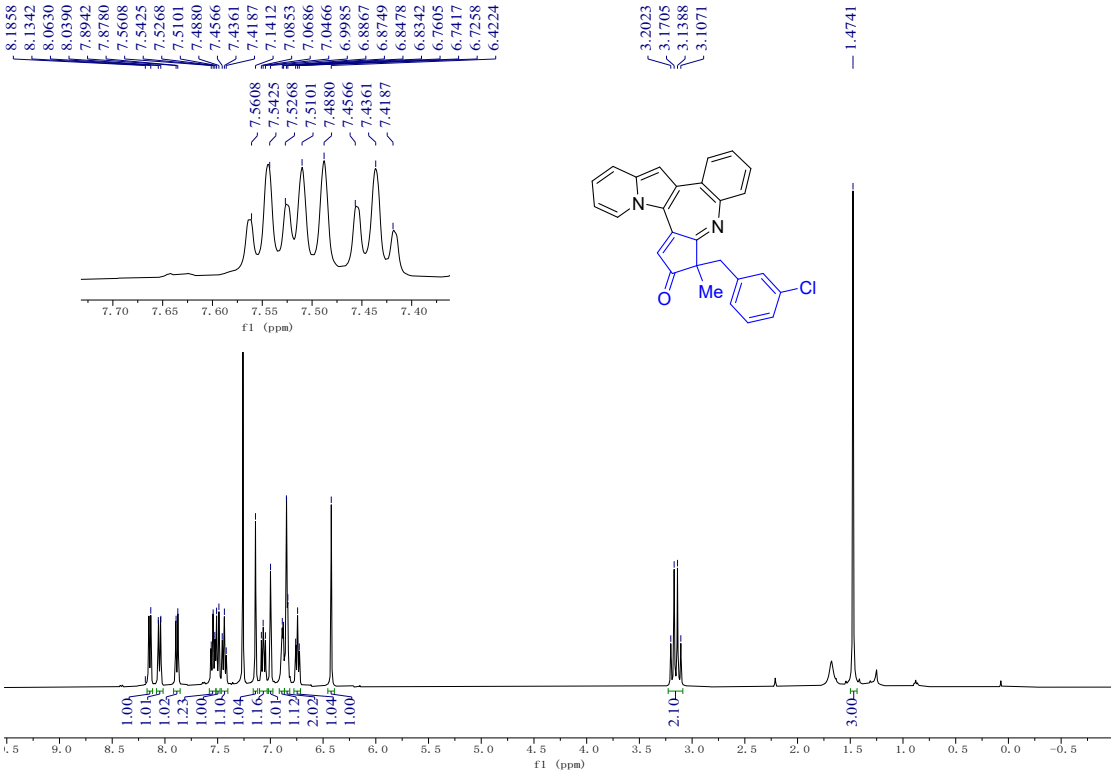
^{1}H NMR of **3ia** (400 MHz, $CDCl_3$)



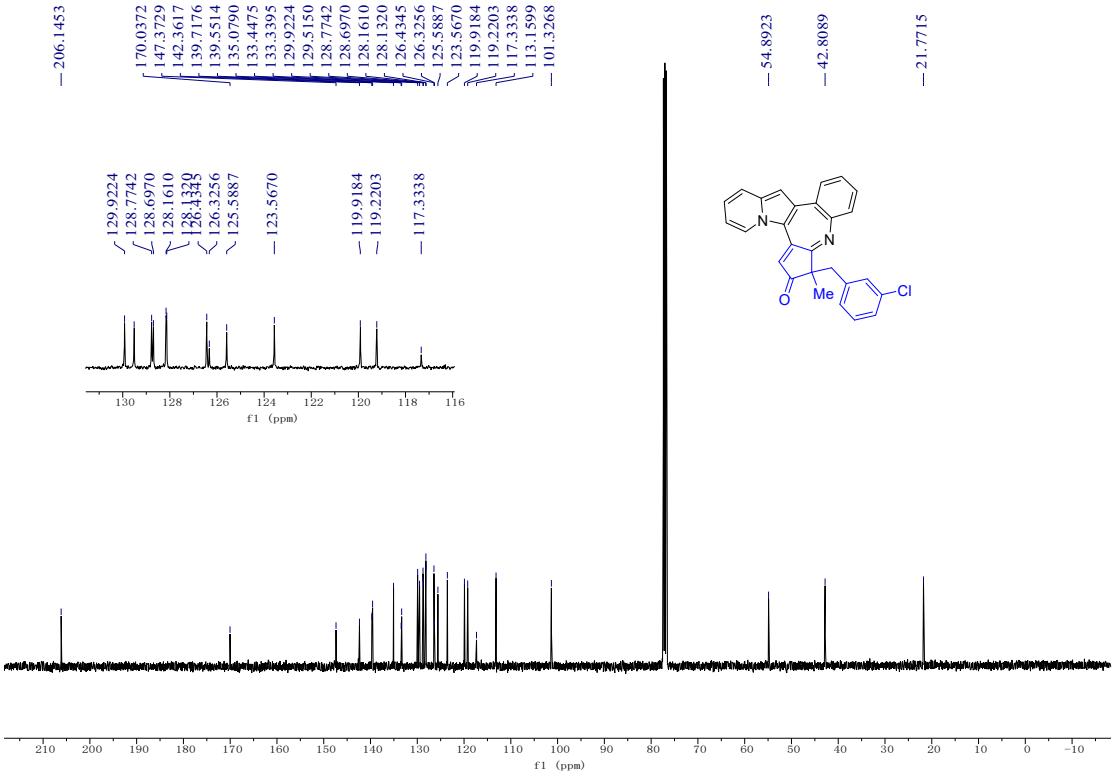
^{13}C NMR of **3ia** (101 MHz, $CDCl_3$)



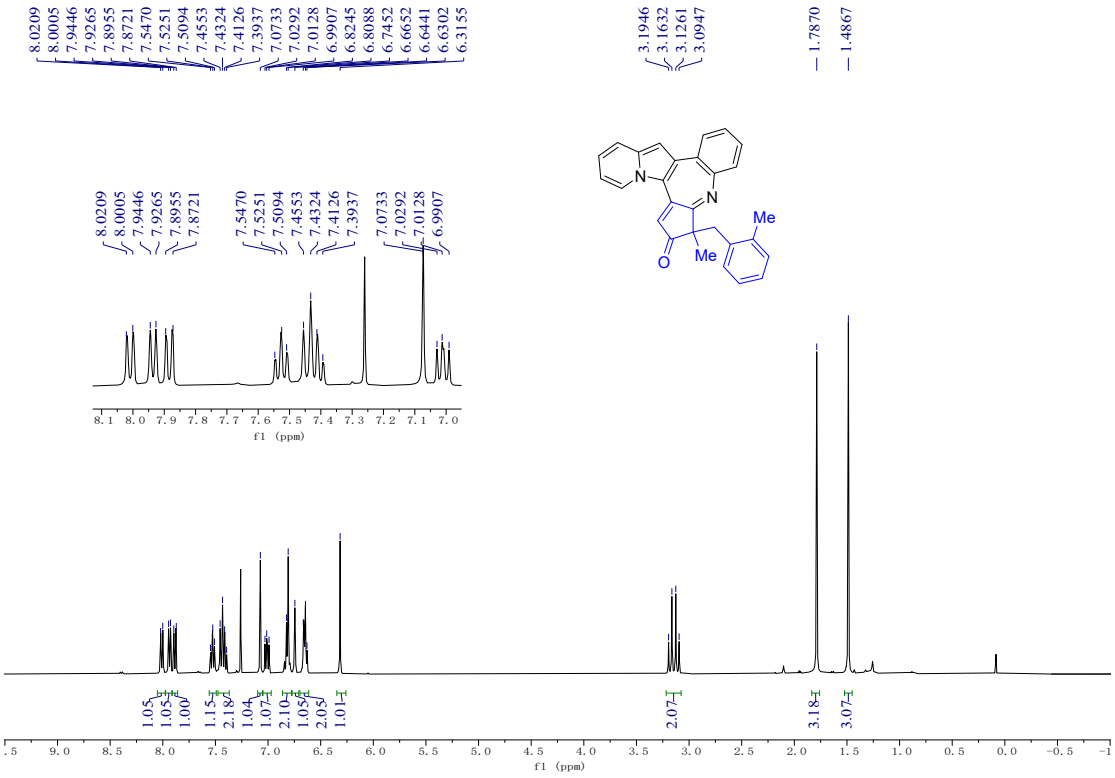
^{1}H NMR of **3ja** (400 MHz, $CDCl_3$)



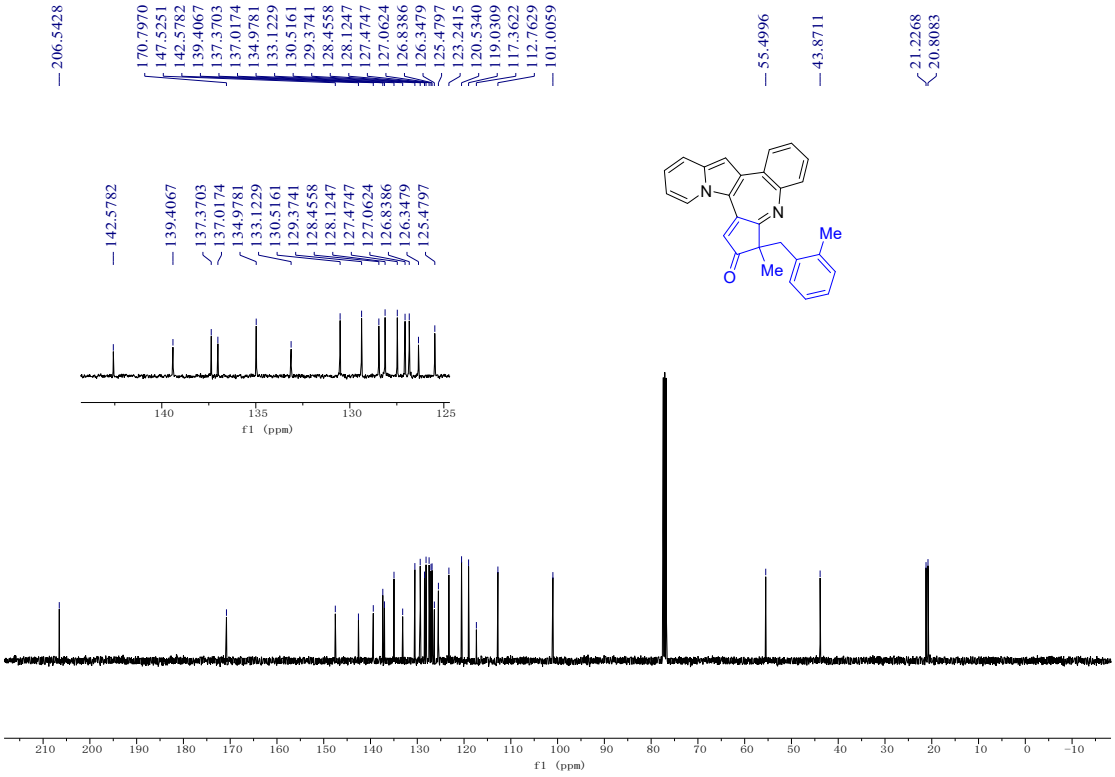
^{13}C NMR of **3ja** (101 MHz, $CDCl_3$)



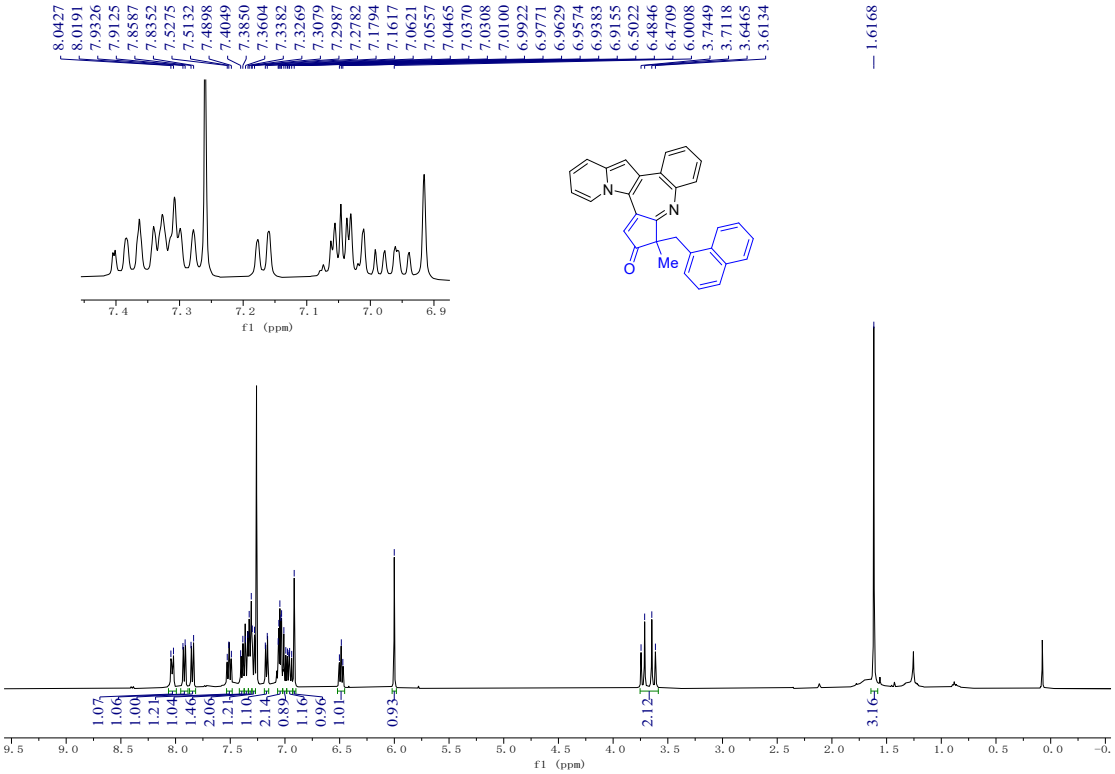
^{1}H NMR of **3ka** (400 MHz, $CDCl_3$)



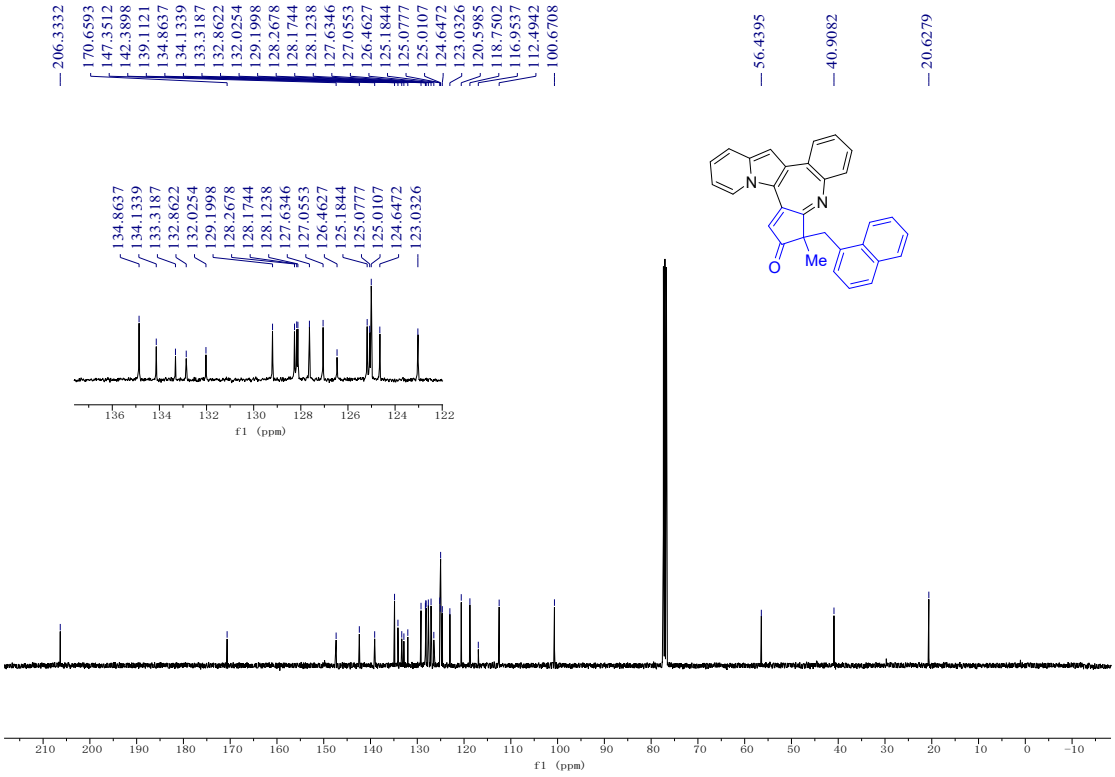
^{13}C NMR of **3ka** (101 MHz, $CDCl_3$)



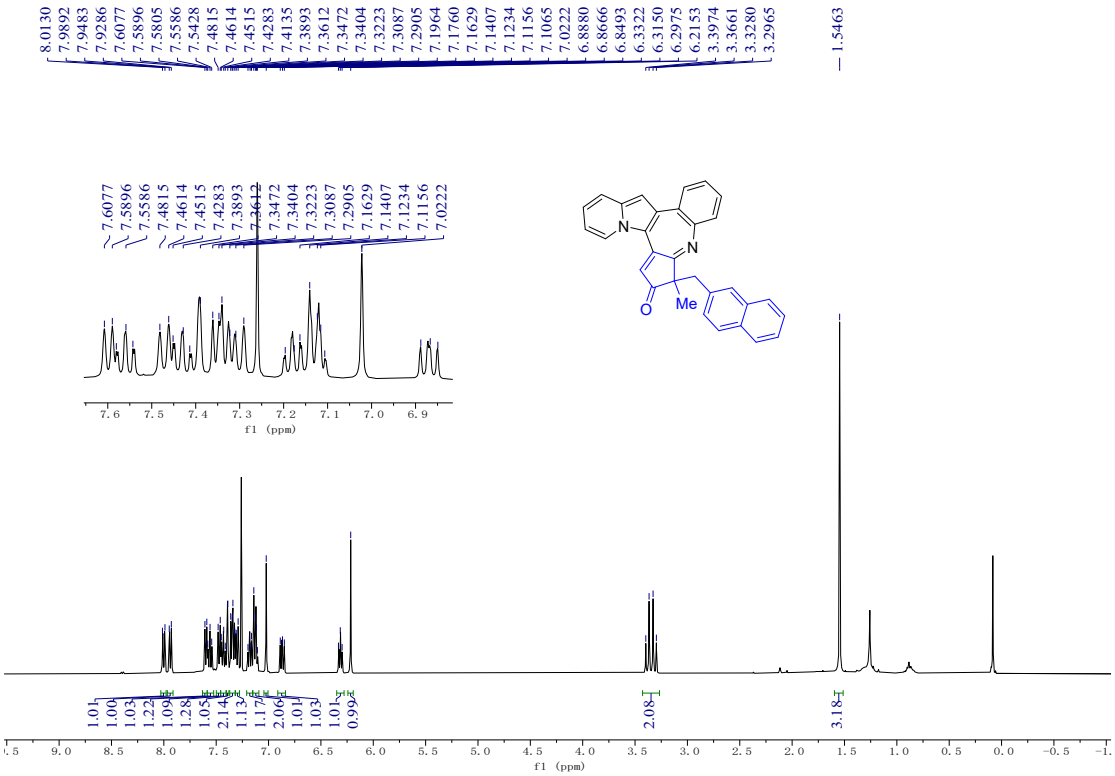
^{1}H NMR of **3la** (400 MHz, $CDCl_3$)



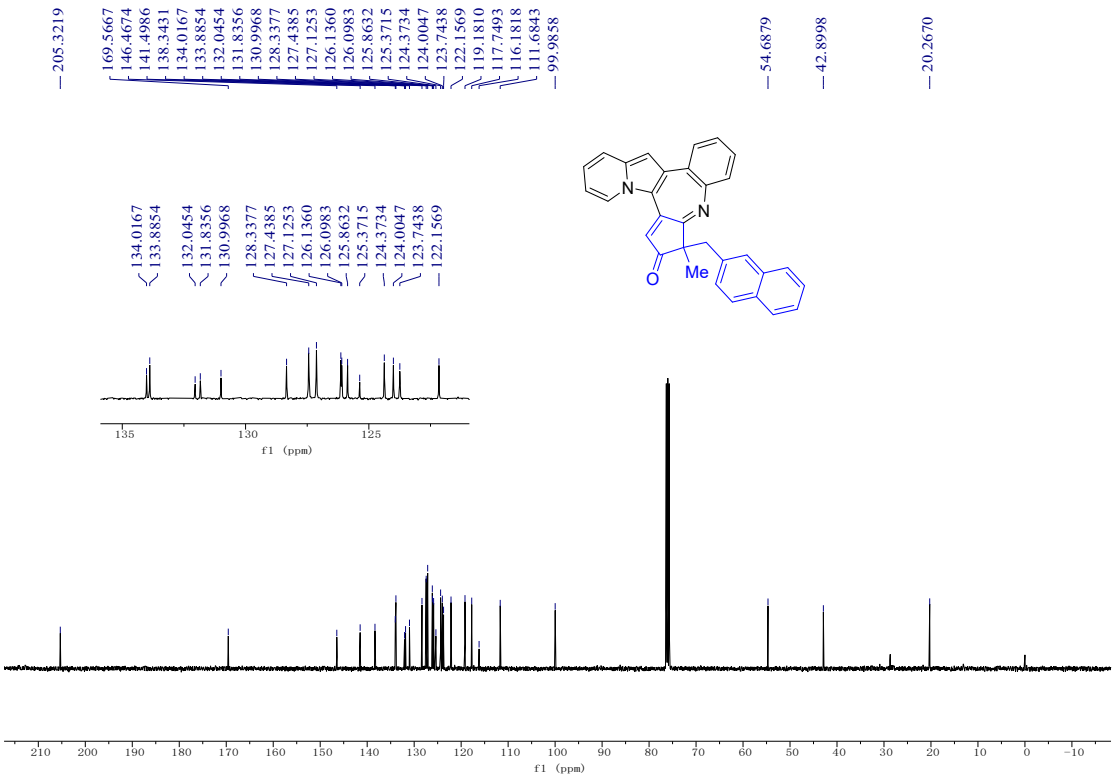
^{13}C NMR of **3la** (101 MHz, $CDCl_3$)



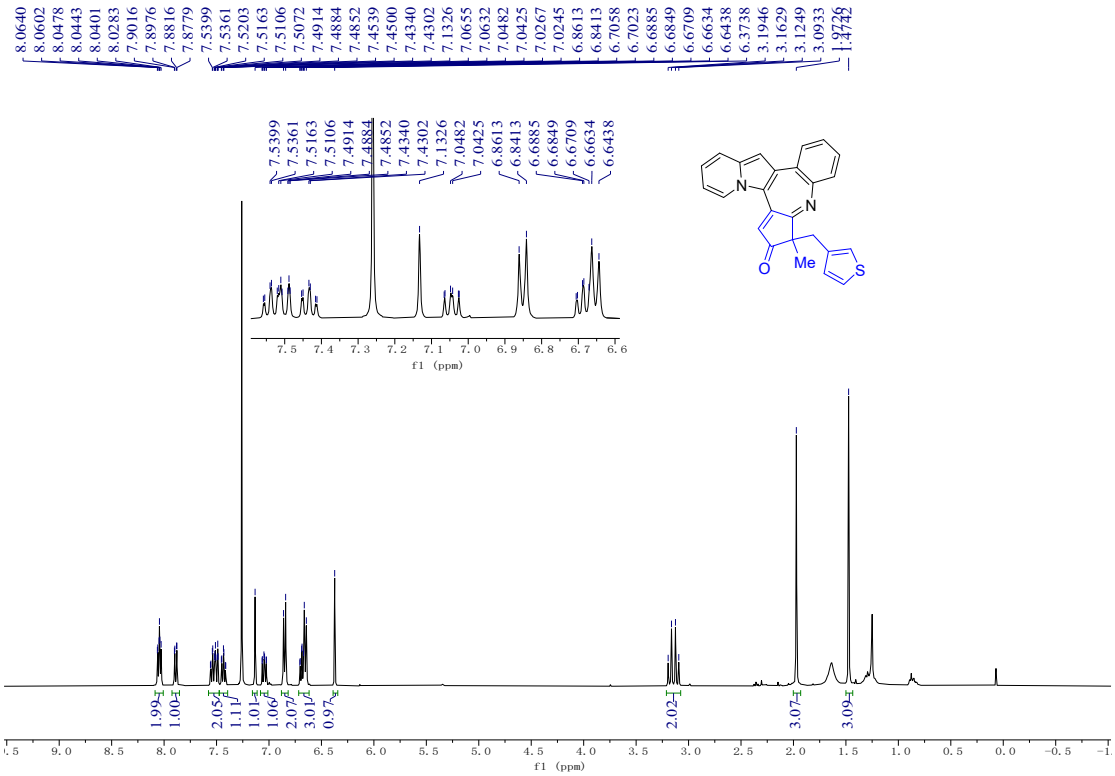
^{1}H NMR of **3ma** (400 MHz, $CDCl_3$)



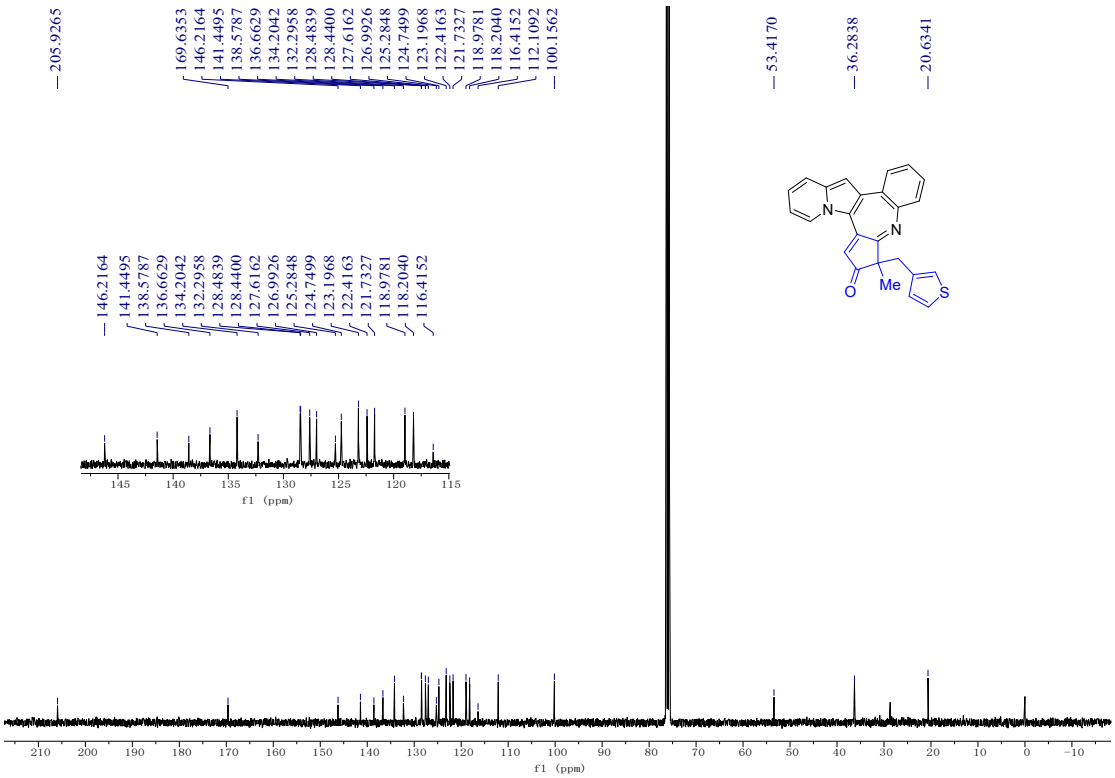
^{13}C NMR of **3ma** (101 MHz, $CDCl_3$)



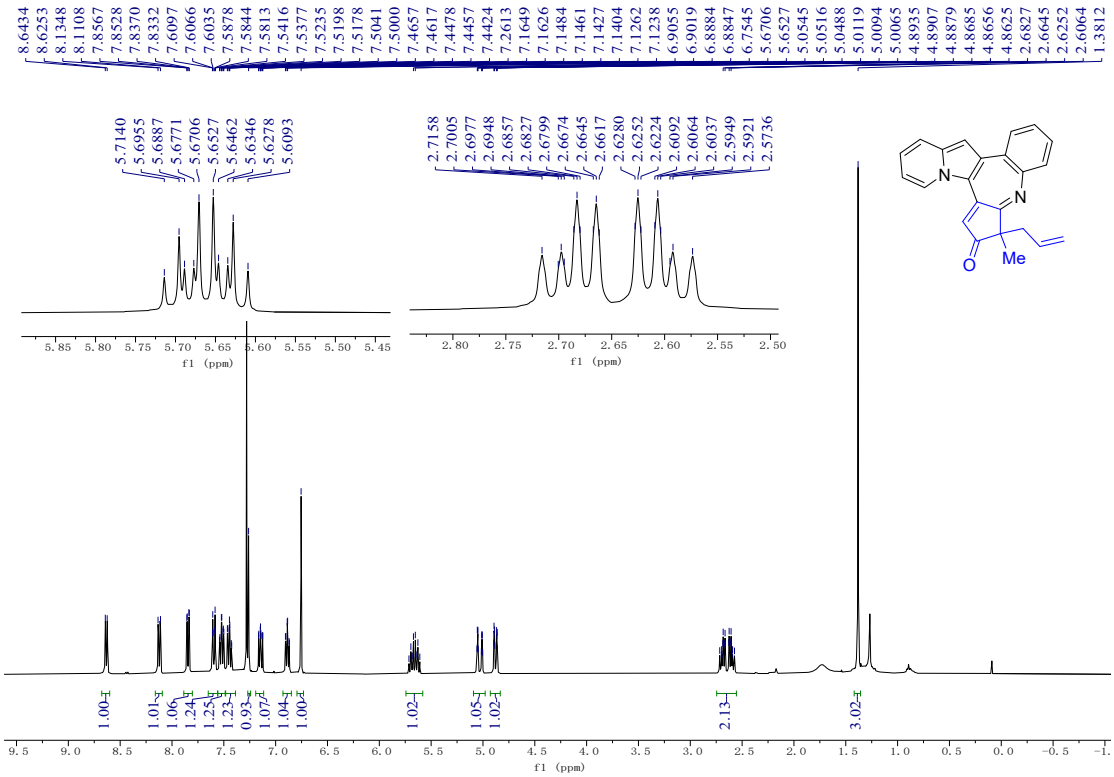
^{1}H NMR of **3na** (400 MHz, $CDCl_3$)



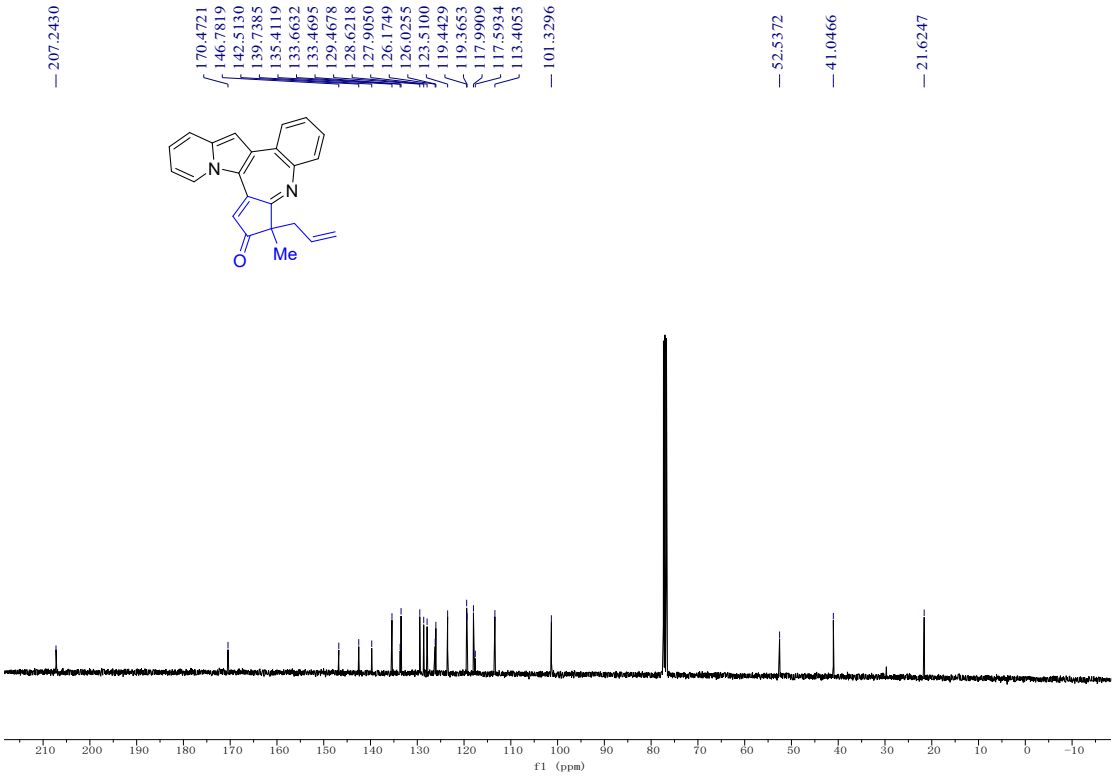
^{13}C NMR of **3na** (101 MHz, $CDCl_3$)



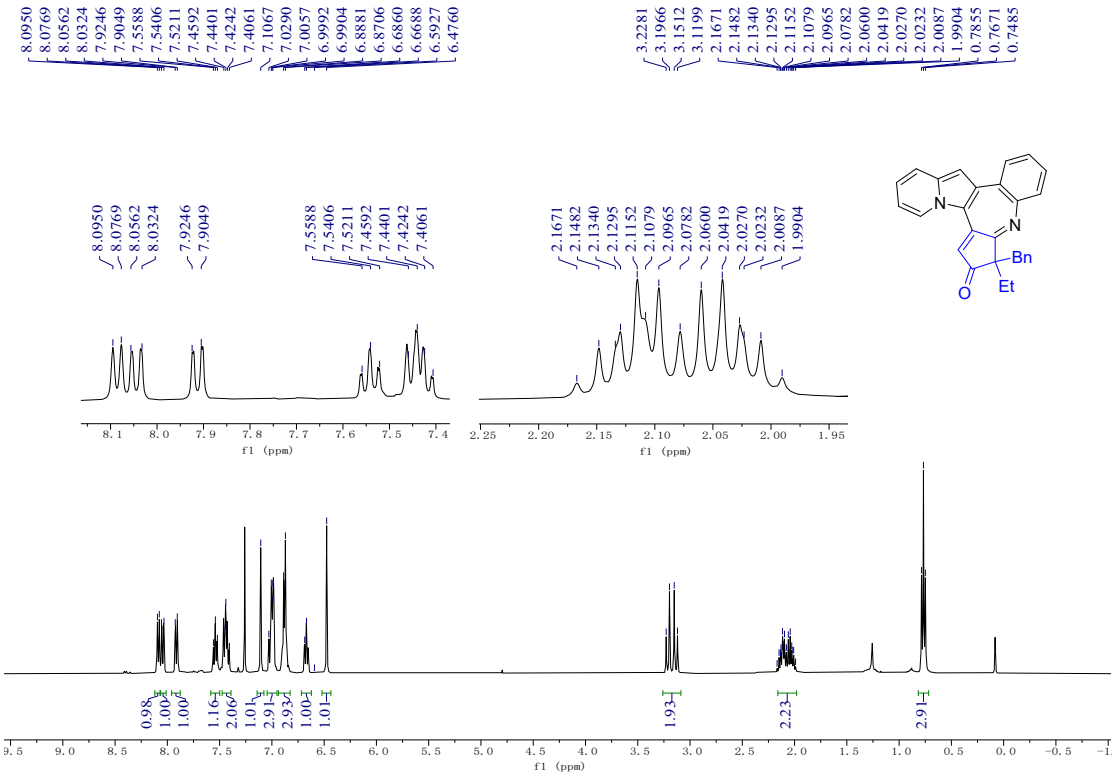
^{1}H NMR of **3oa** (400 MHz, $CDCl_3$)



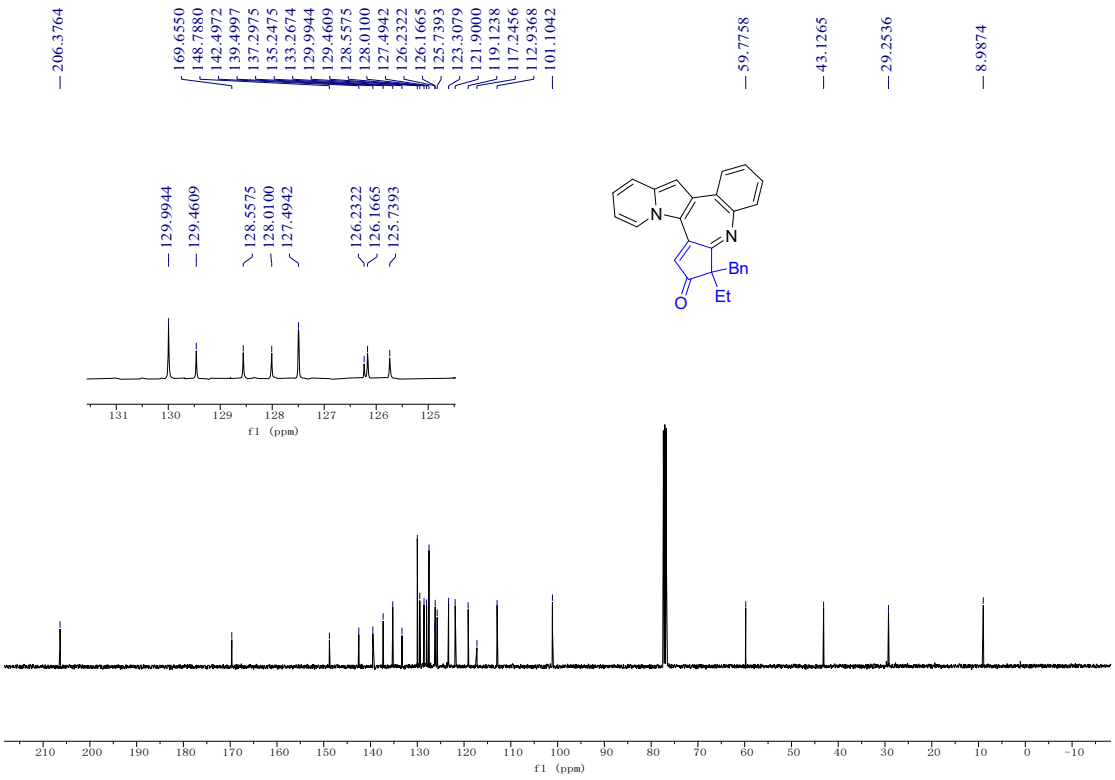
^{13}C NMR of **3oa** (101 MHz, $CDCl_3$)



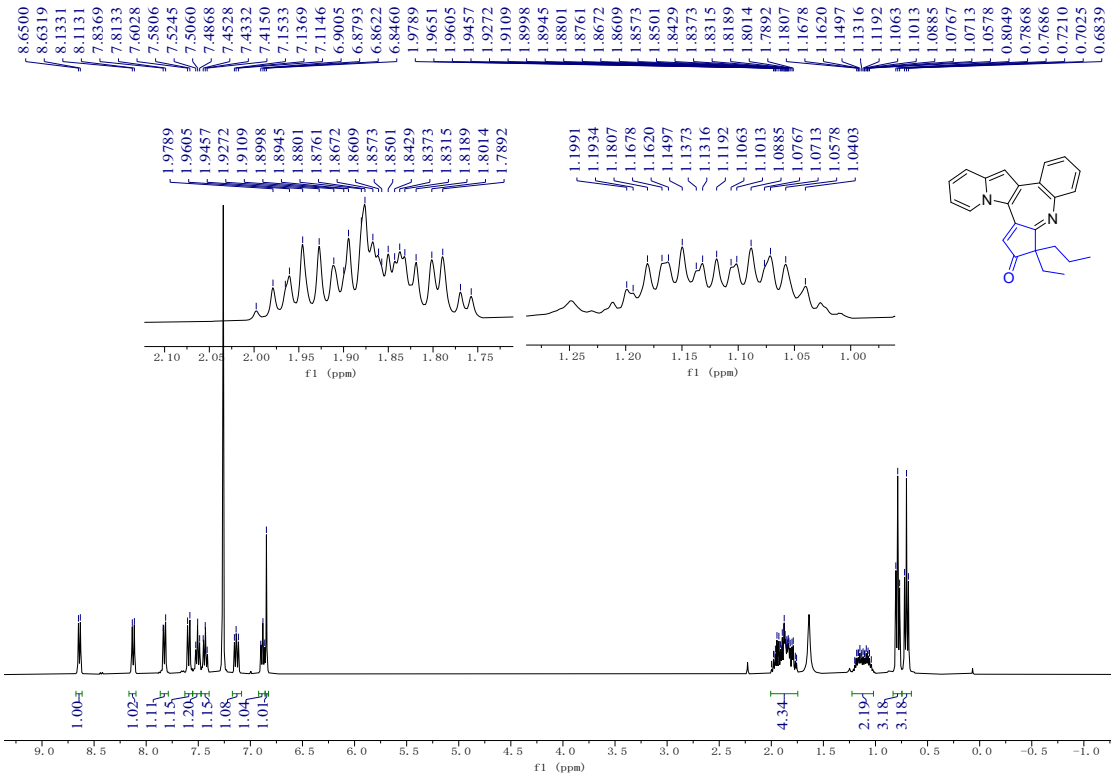
^{1}H NMR of **3pa** (400 MHz, $CDCl_3$)



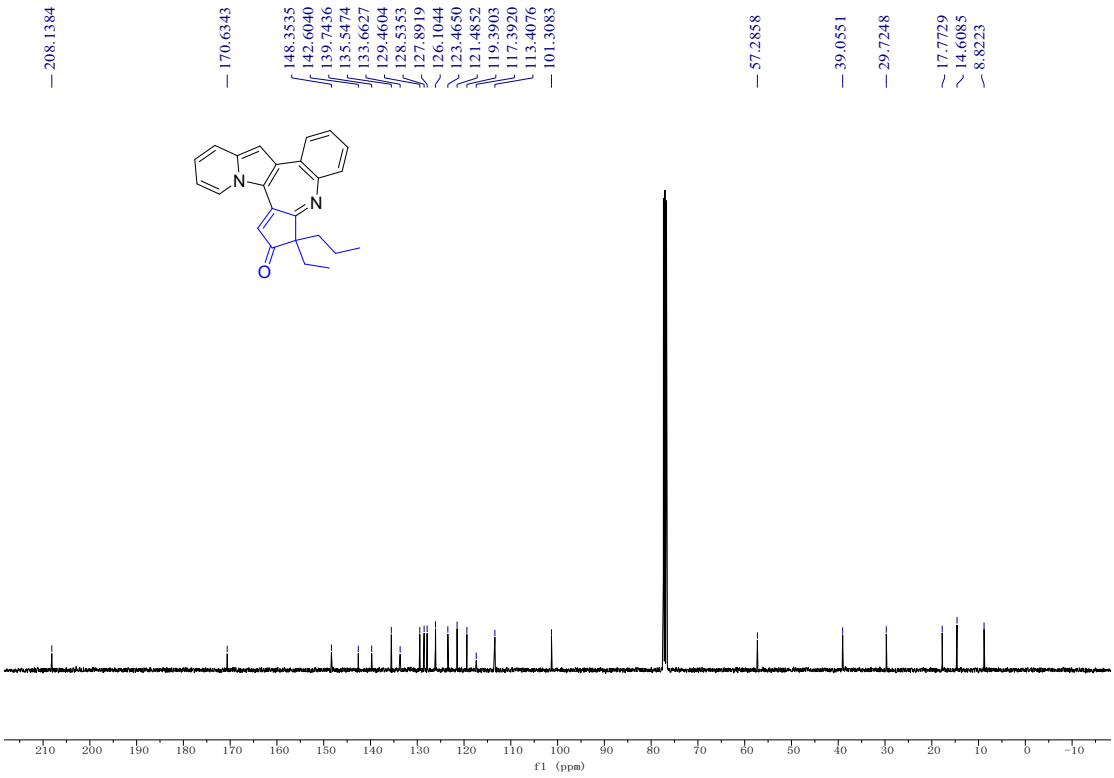
^{13}C NMR of **3pa** (101 MHz, $CDCl_3$)



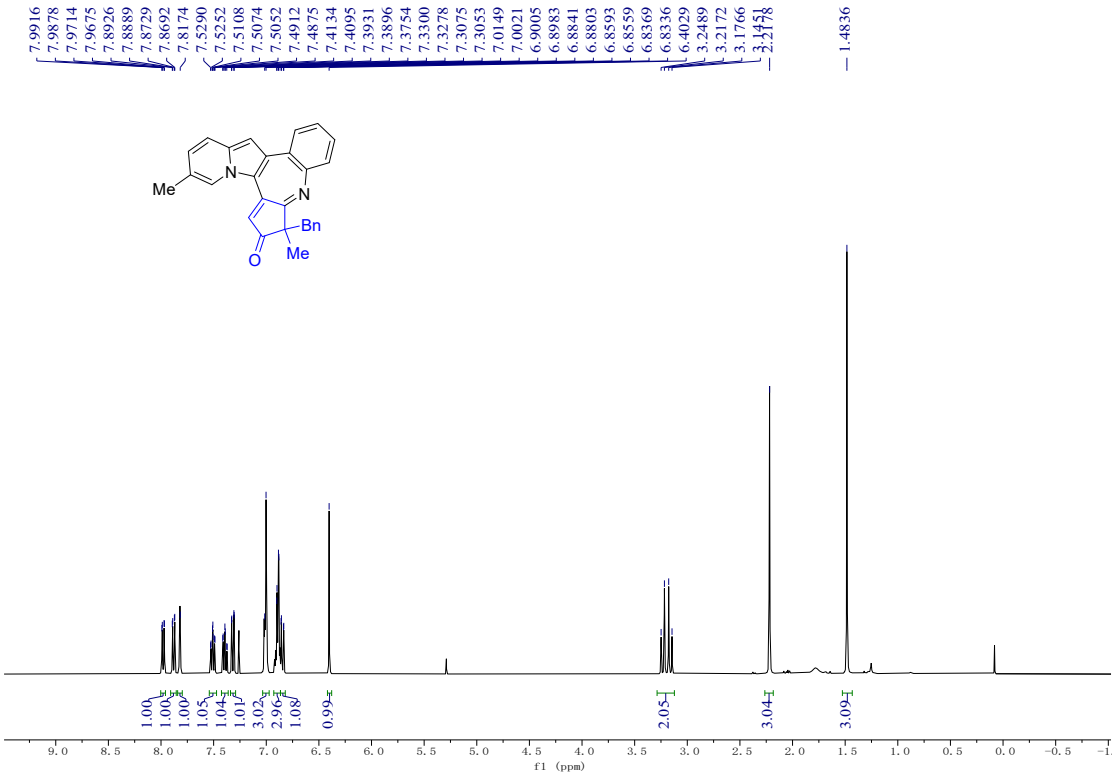
^{1}H NMR of **3qa** (400 MHz, $CDCl_3$)



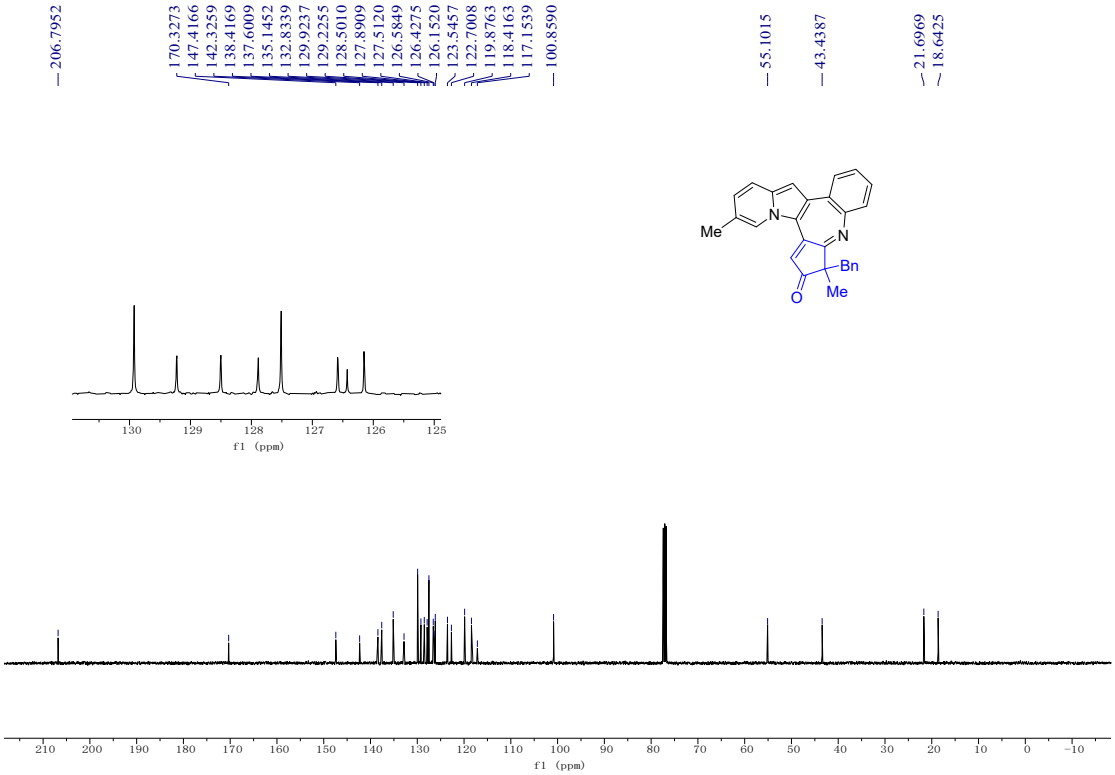
^{13}C NMR of **3qa** (101 MHz, $CDCl_3$)



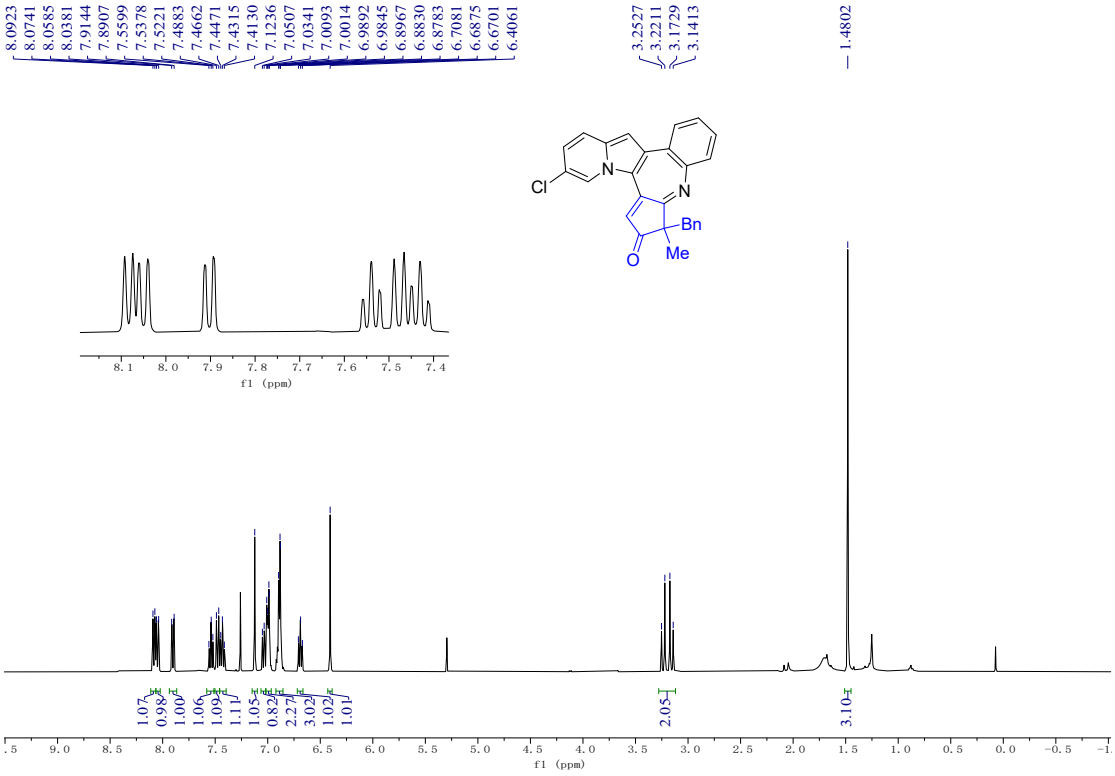
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$)



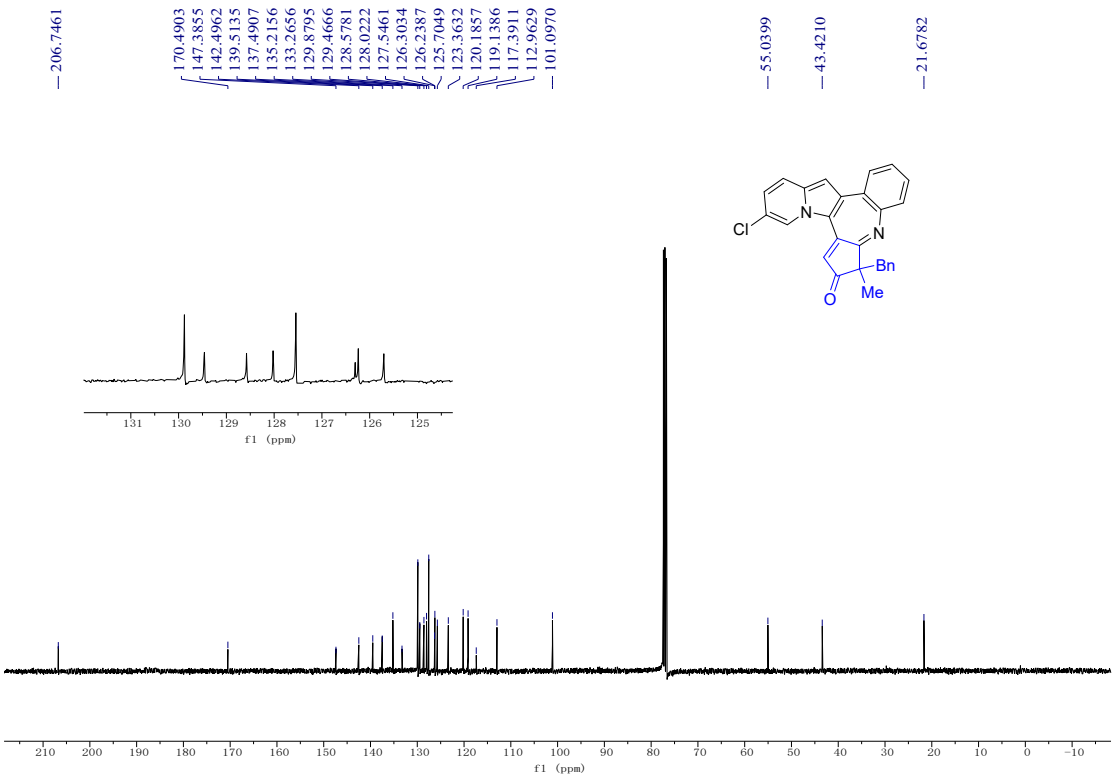
^{13}C NMR of **3ab** (101 MHz, $CDCl_3$)



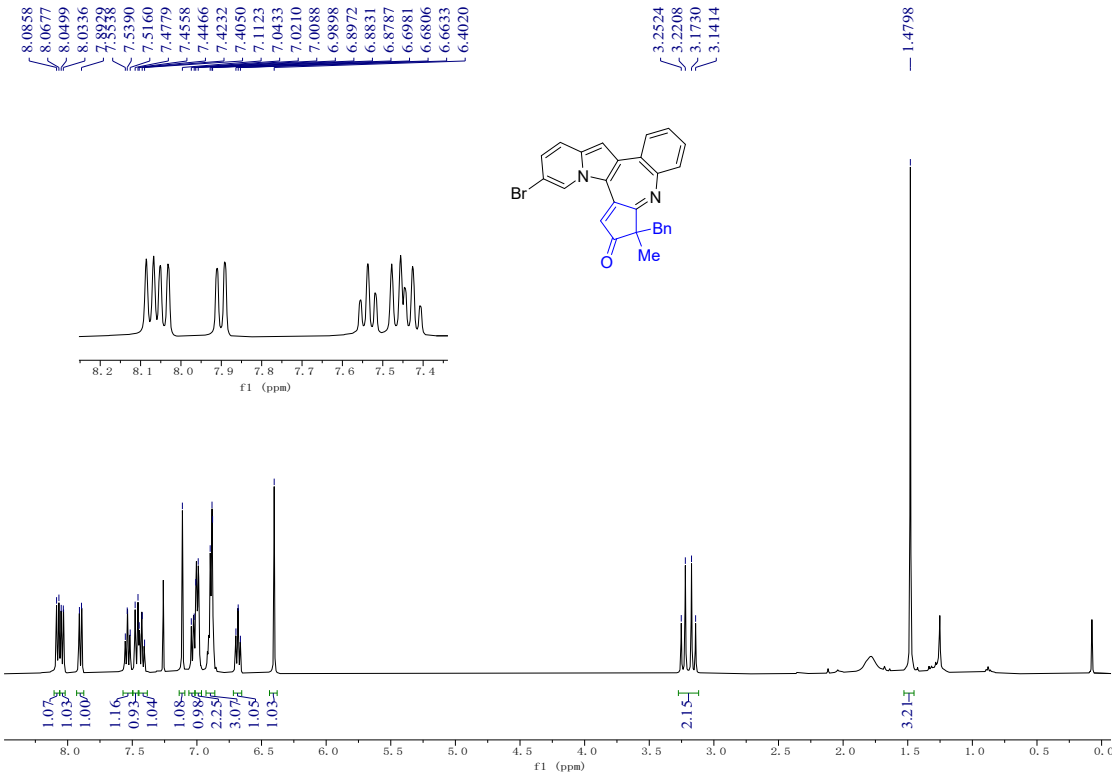
^{1}H NMR of **3ac** (400 MHz, $CDCl_3$)



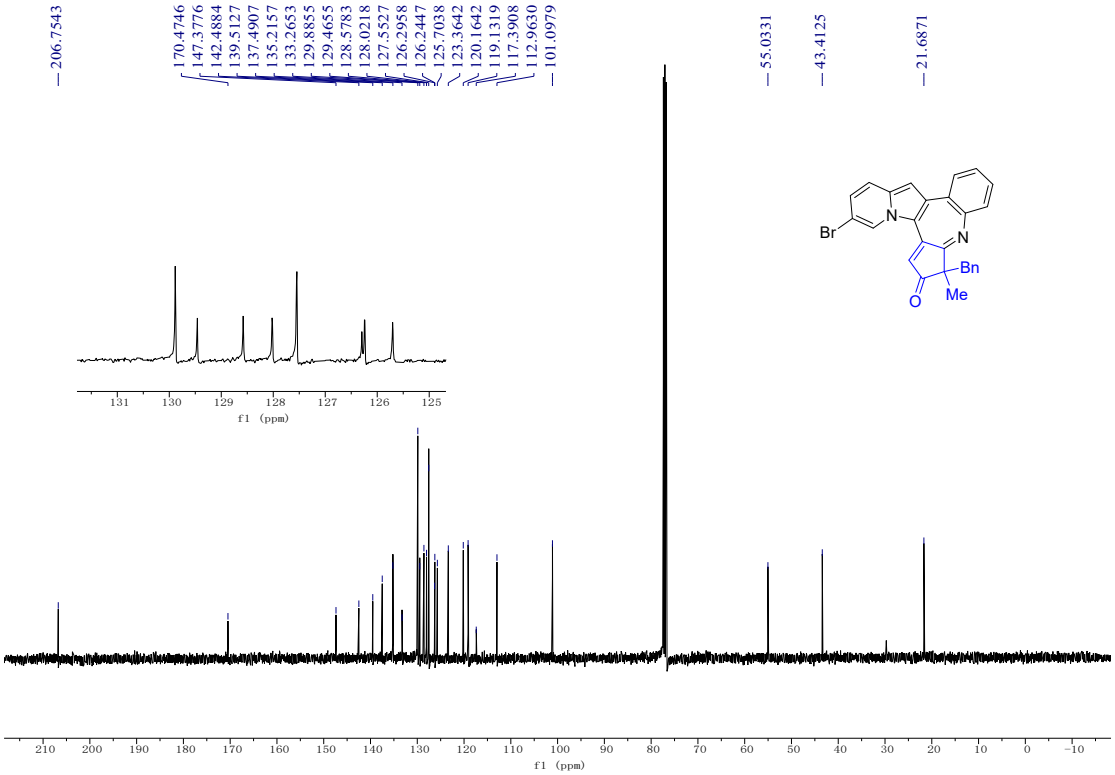
^{13}C NMR of **3ac** (101 MHz, $CDCl_3$)



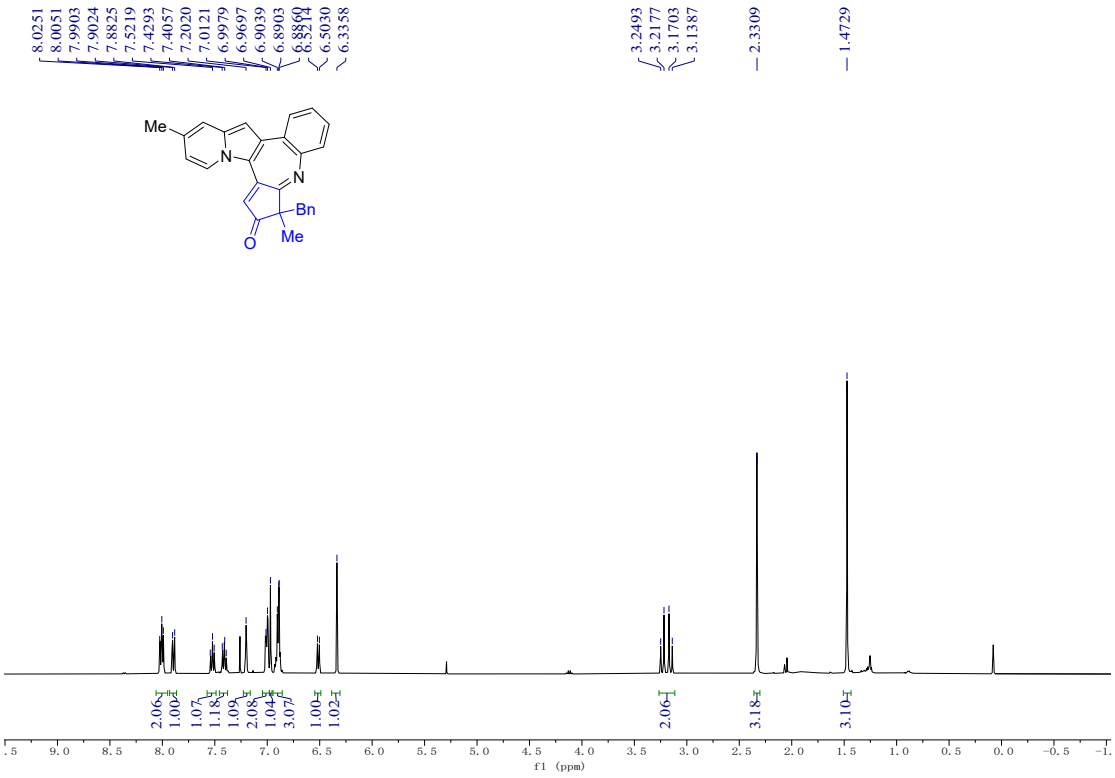
^{1}H NMR of **3ad** (400 MHz, $CDCl_3$)



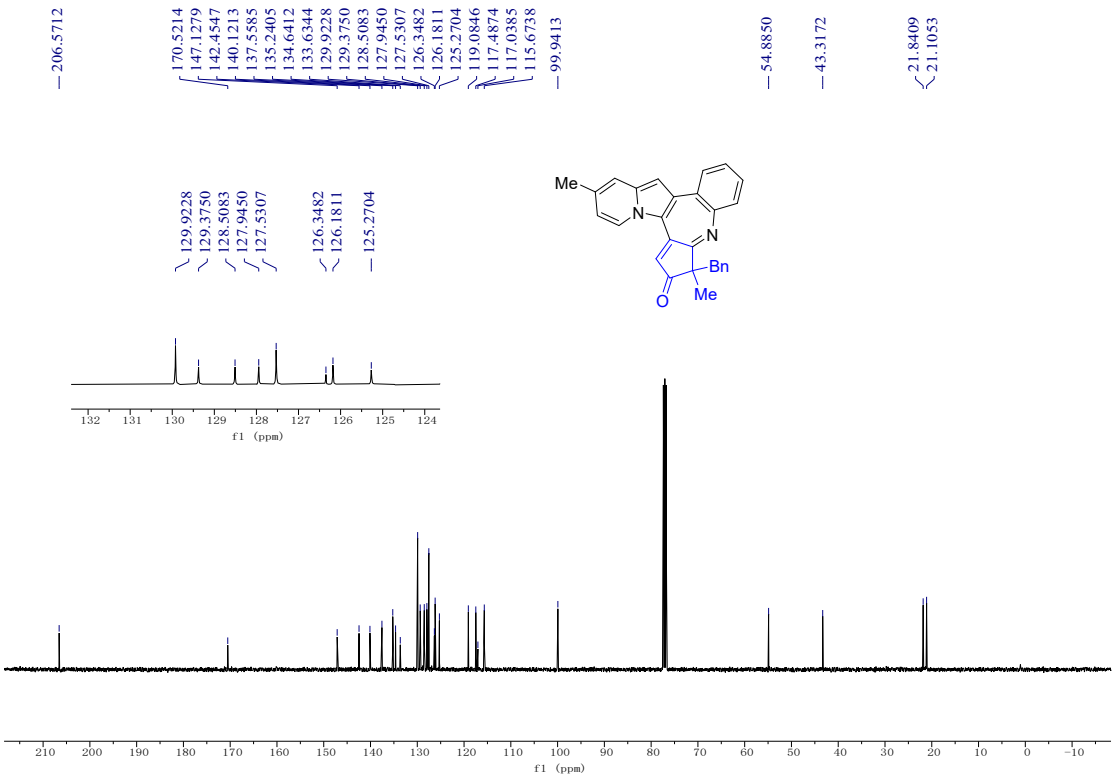
^{13}C NMR of **3ad** (101 MHz, $CDCl_3$)



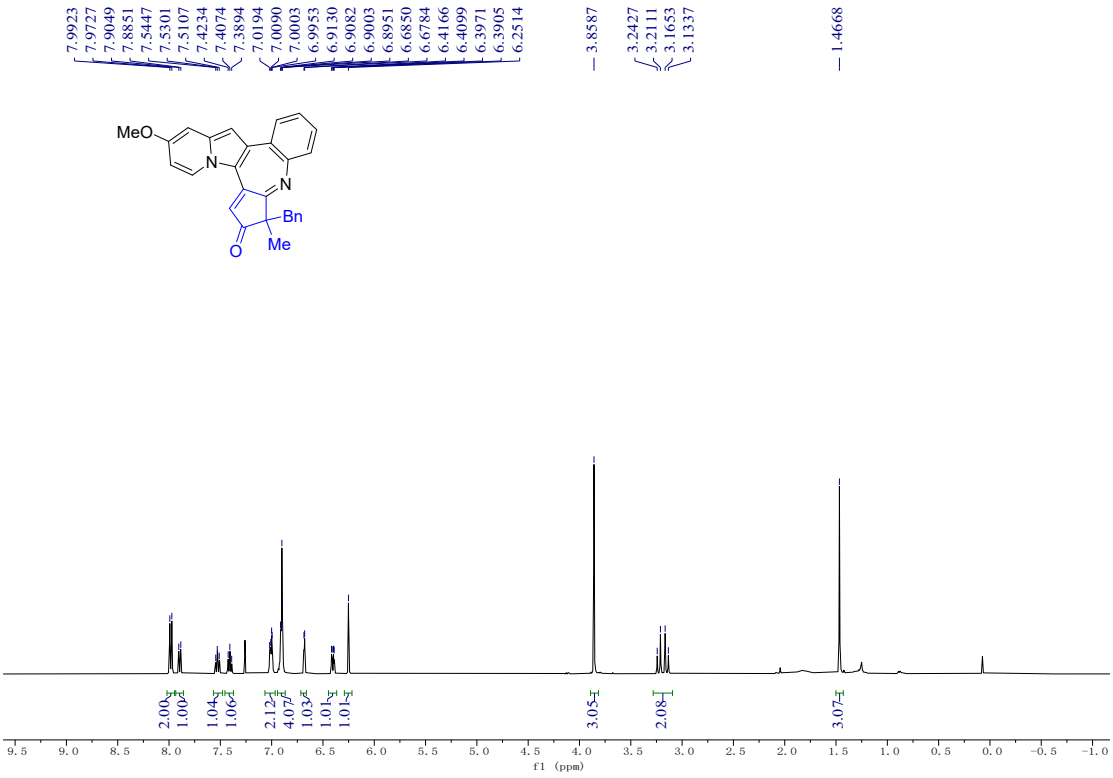
^{1}H NMR of **3ae** (400 MHz, $CDCl_3$)



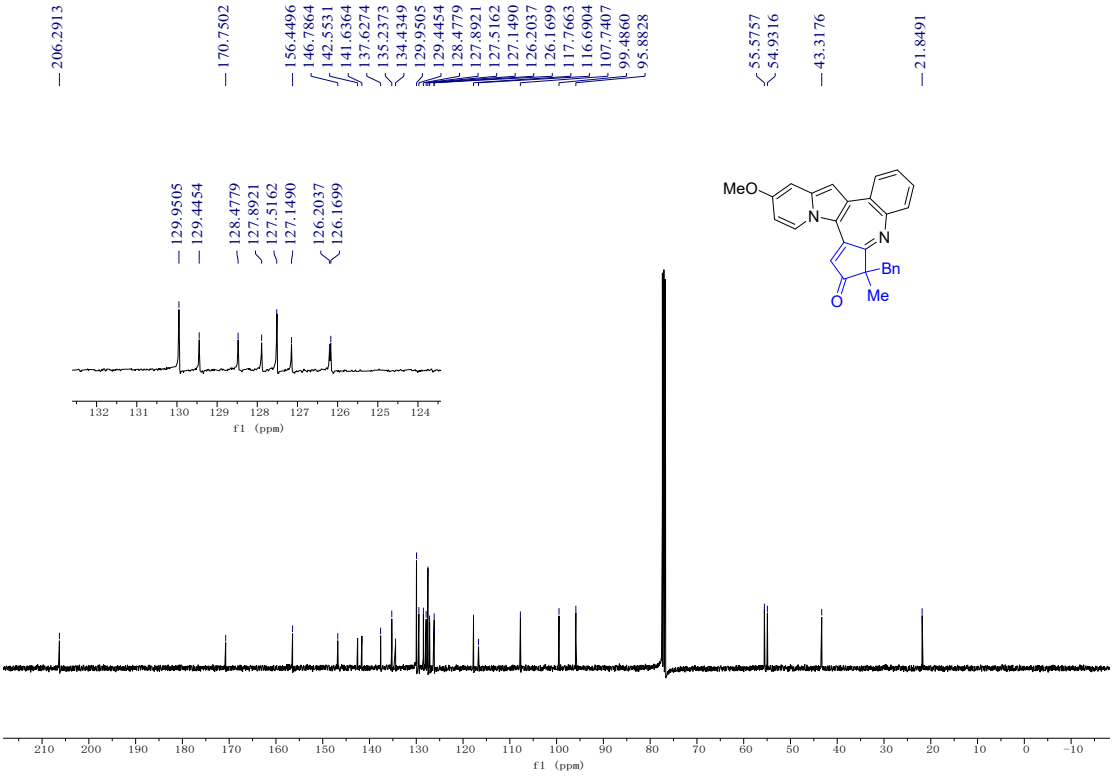
^{13}C NMR of **3ae** (101 MHz, $CDCl_3$)



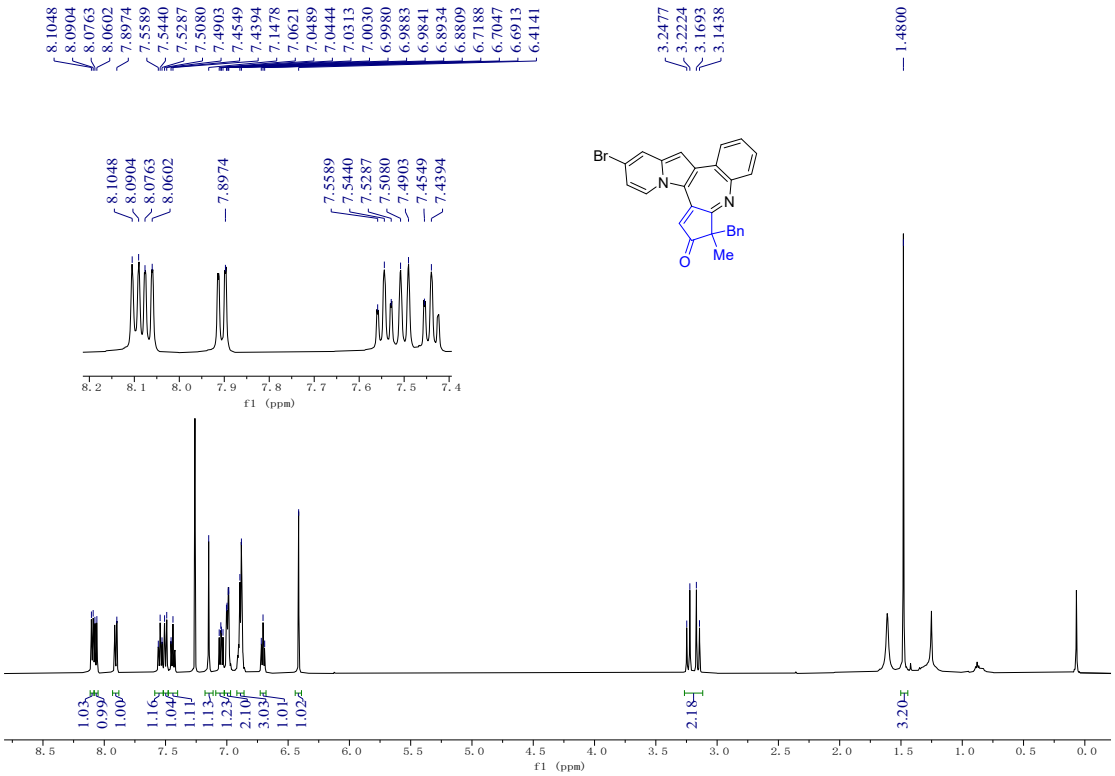
^{1}H NMR of **3af** (400 MHz, $CDCl_3$)



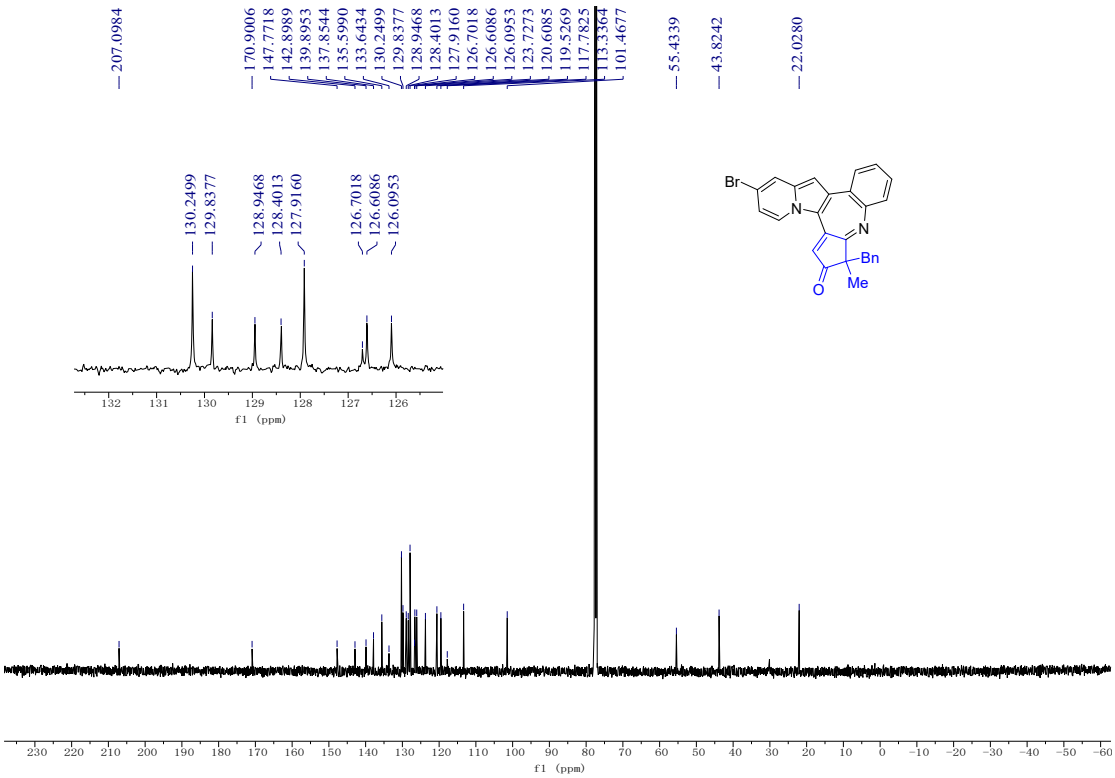
^{13}C NMR of **3af** (101 MHz, $CDCl_3$)



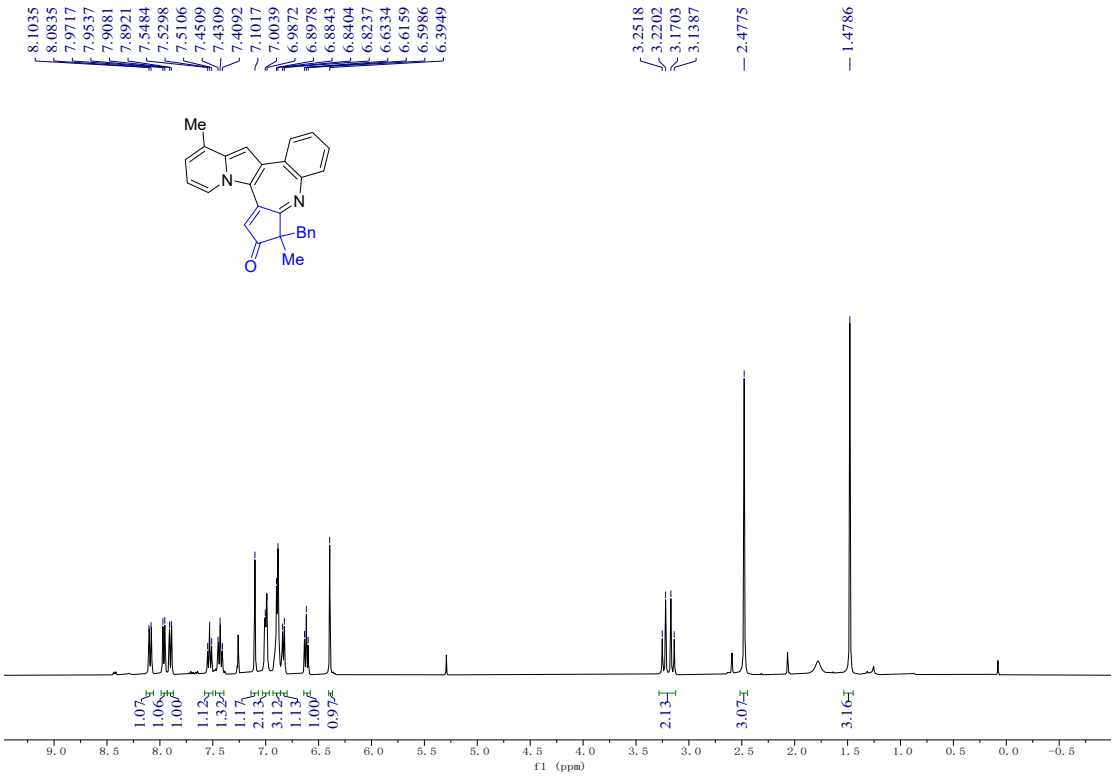
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$)



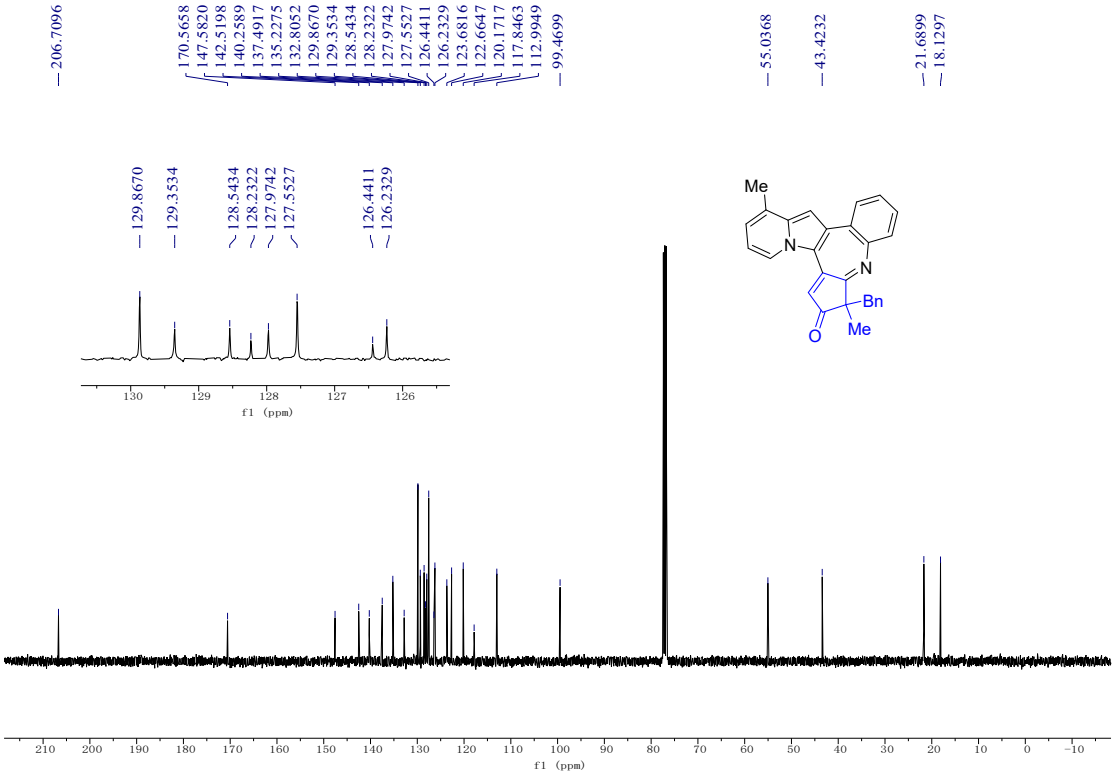
^{13}C NMR of **3ag** (101 MHz, $CDCl_3$)



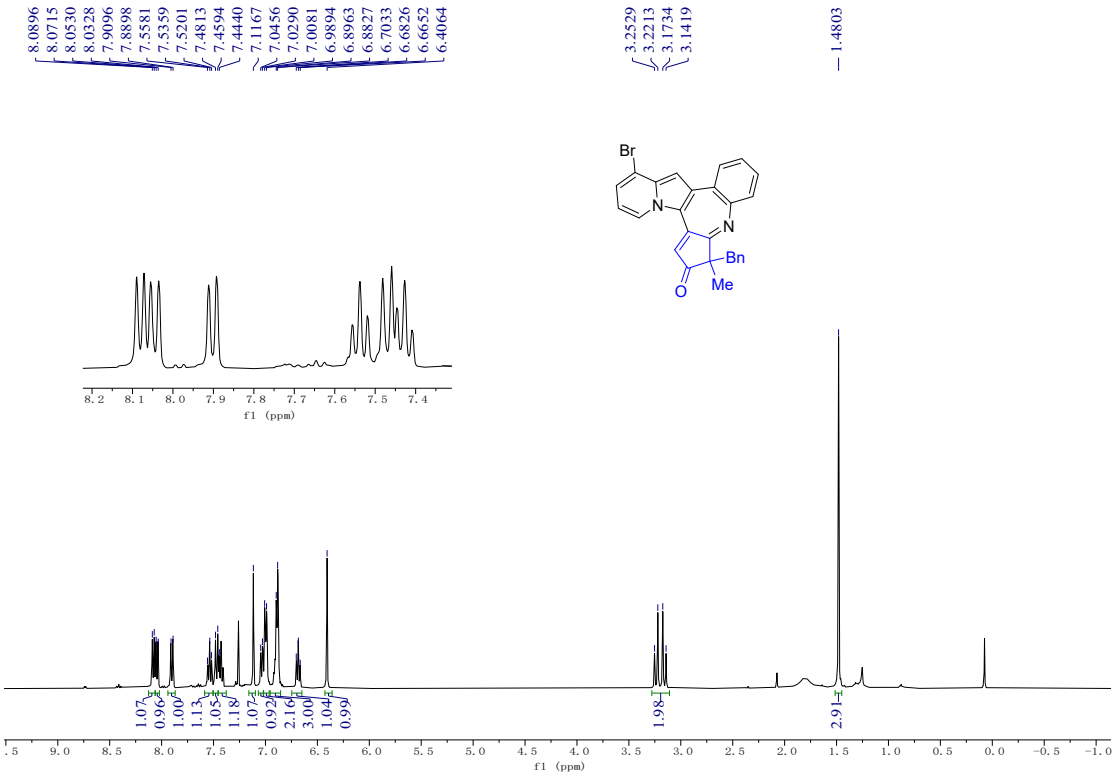
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$)



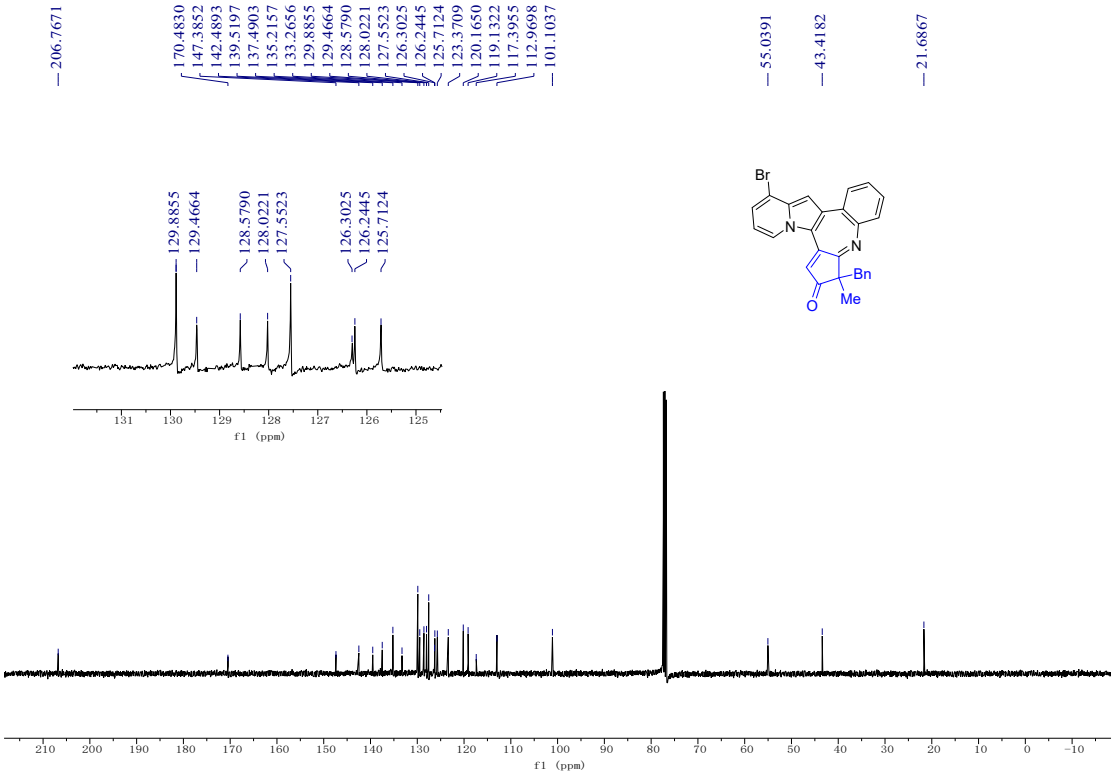
^{13}C NMR of **3ah** (101 MHz, $CDCl_3$)



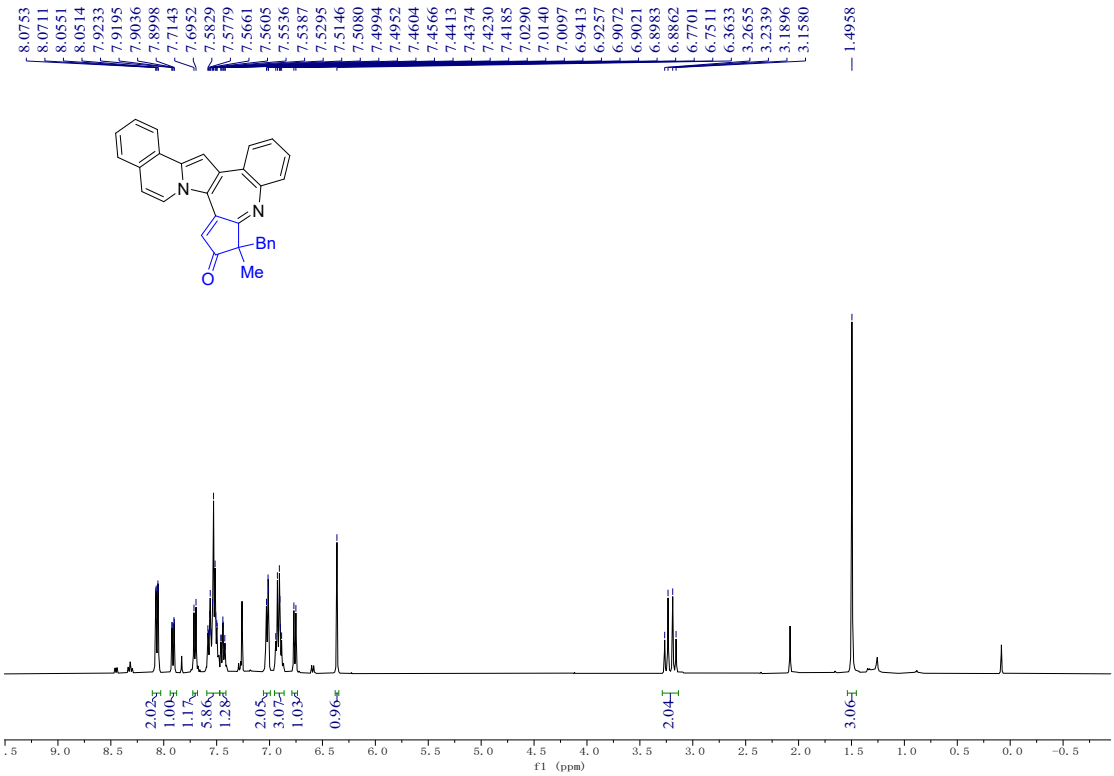
^{1}H NMR of **3aj** (400 MHz, $CDCl_3$)



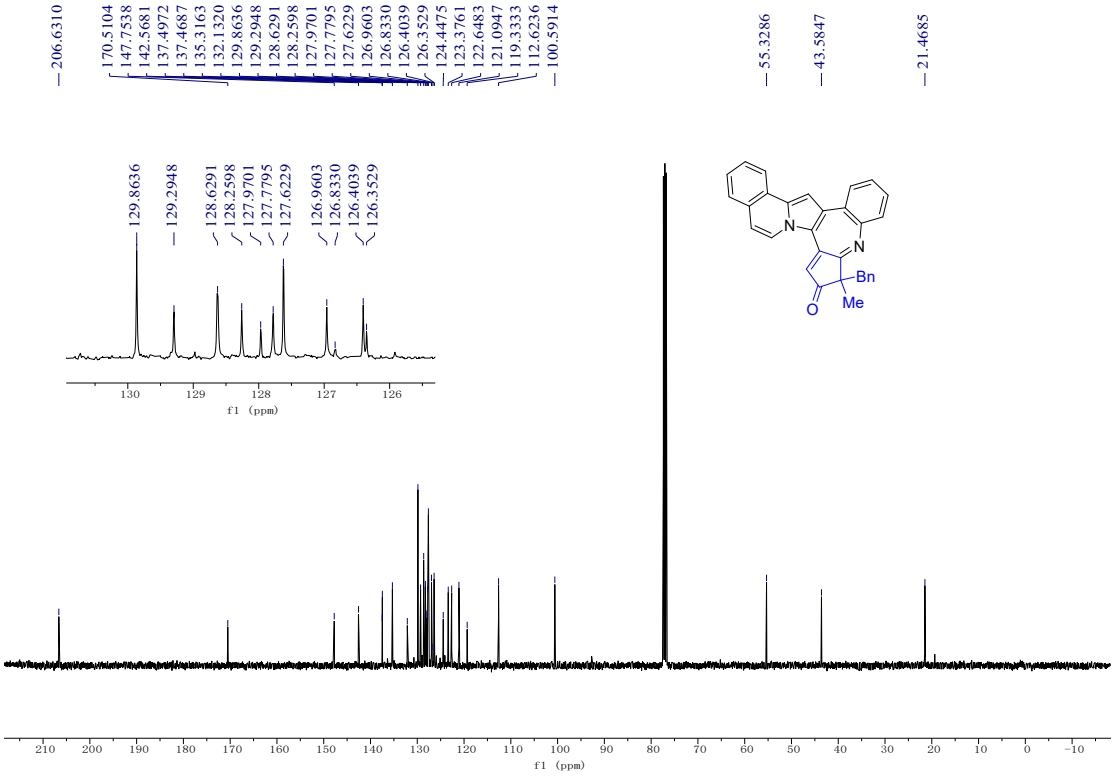
^{13}C NMR of **3aj** (101 MHz, $CDCl_3$)



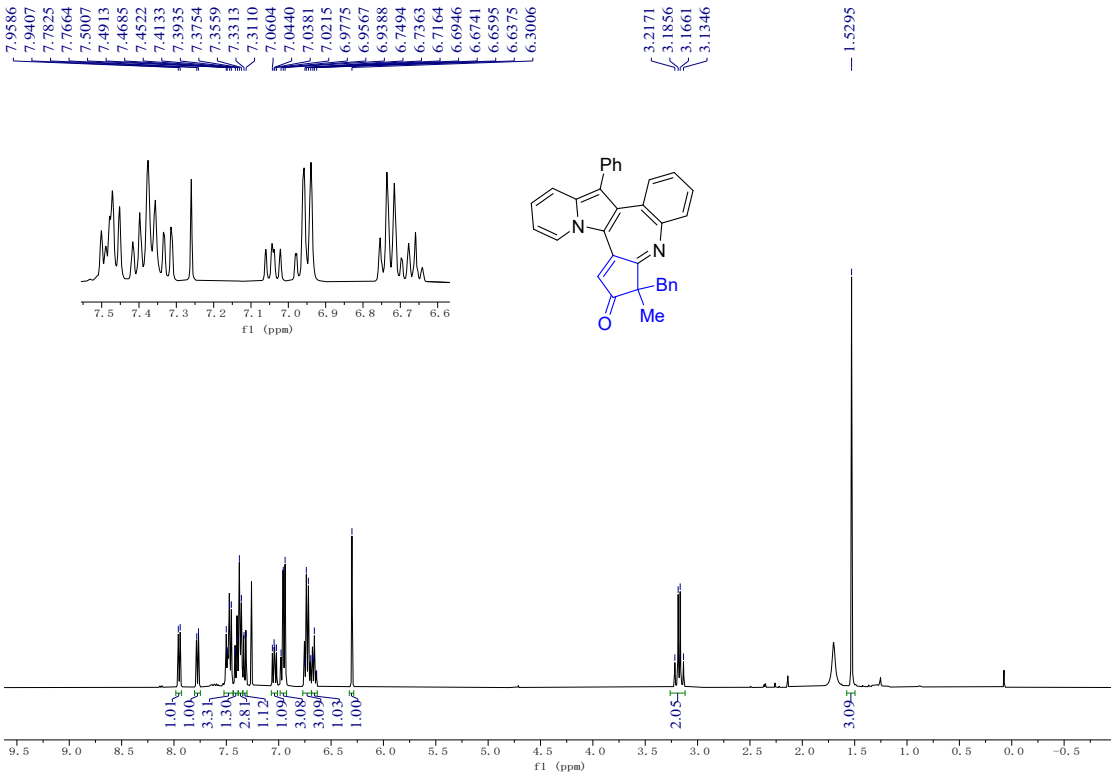
^{1}H NMR of **3ak** (400 MHz, $CDCl_3$)



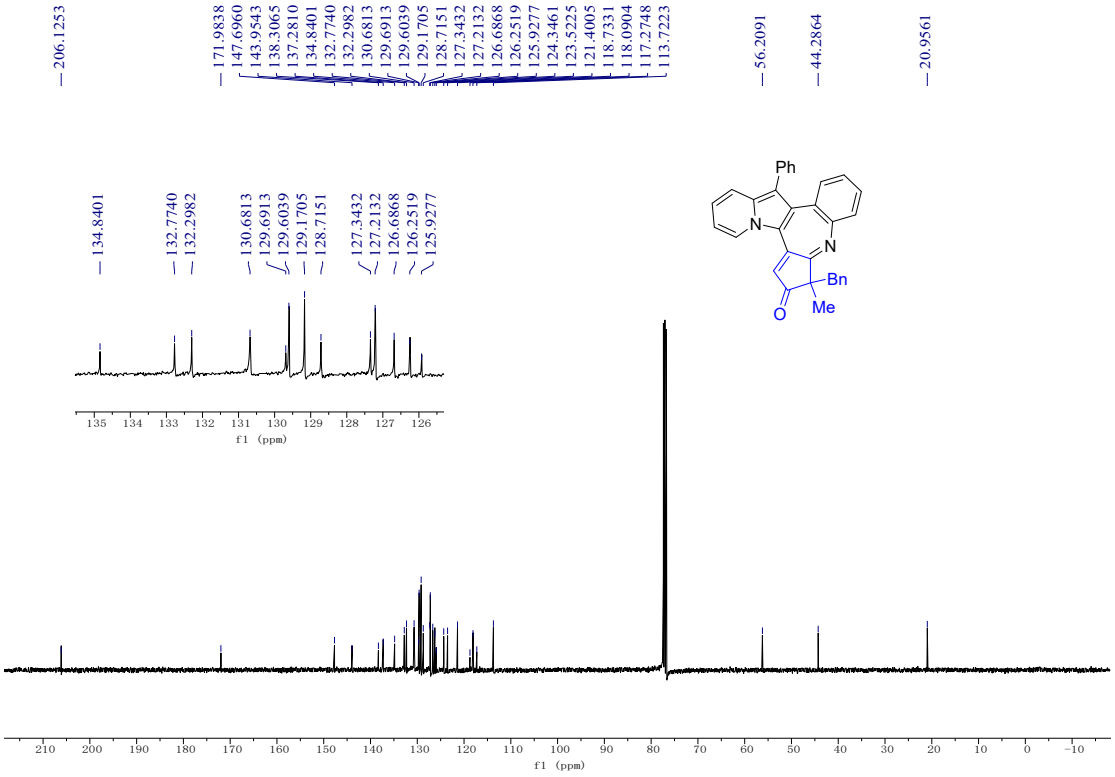
^{13}C NMR of **3ak** (101 MHz, $CDCl_3$)



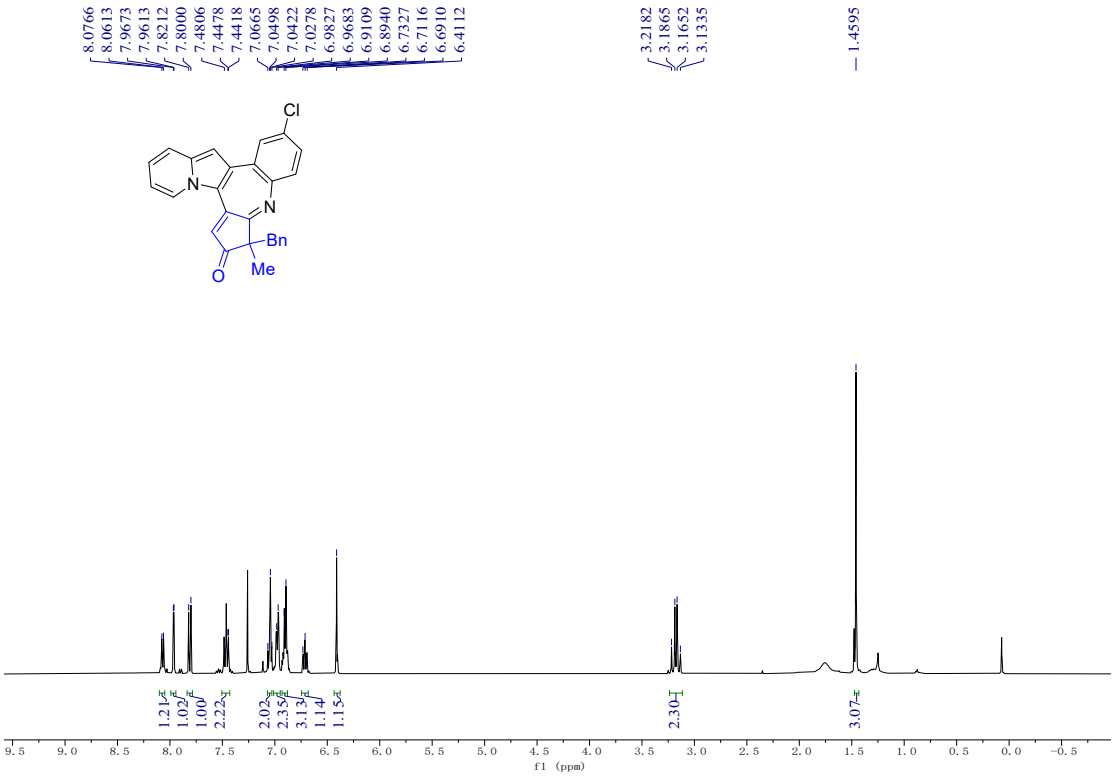
^{1}H NMR of **3al** (400 MHz, $CDCl_3$)



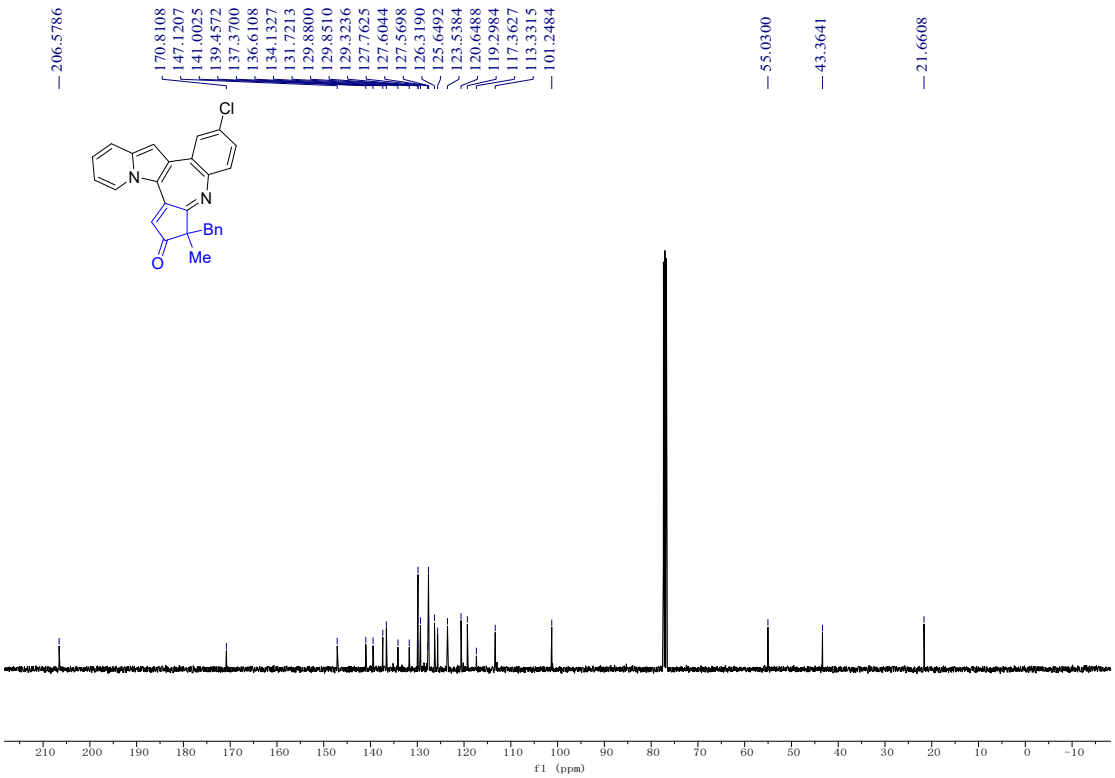
^{13}C NMR of **3al** (101 MHz, $CDCl_3$)



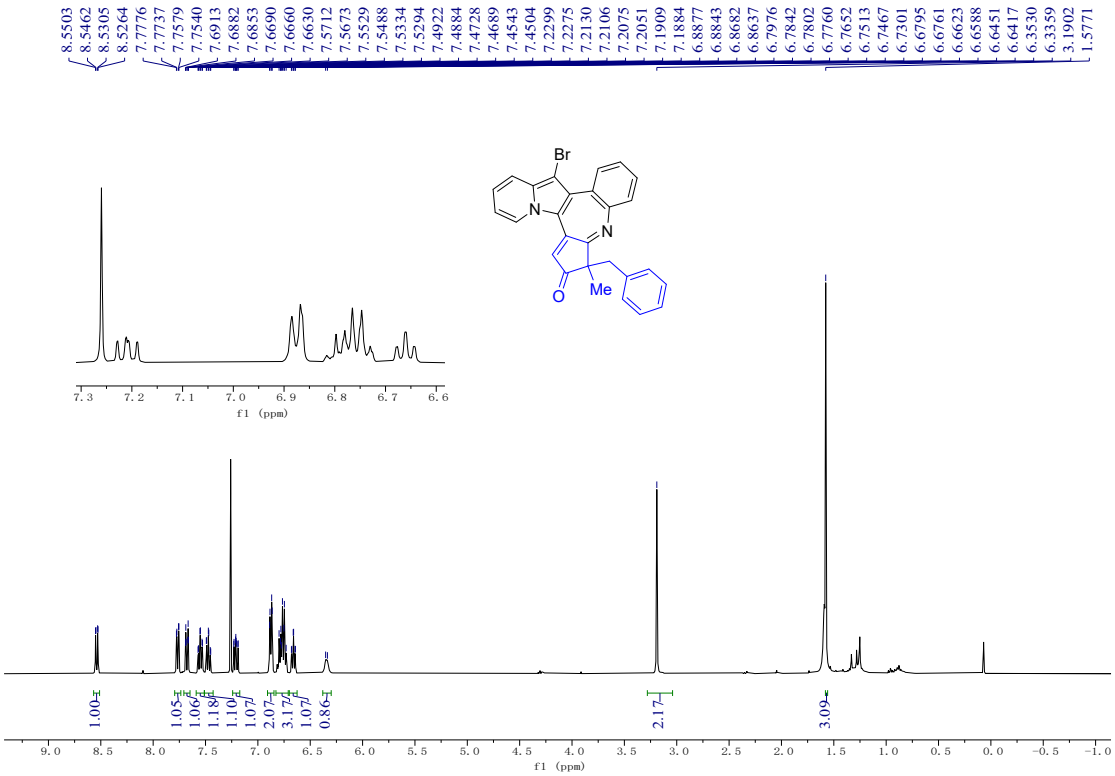
^{1}H NMR of **3am** (400 MHz, $CDCl_3$)



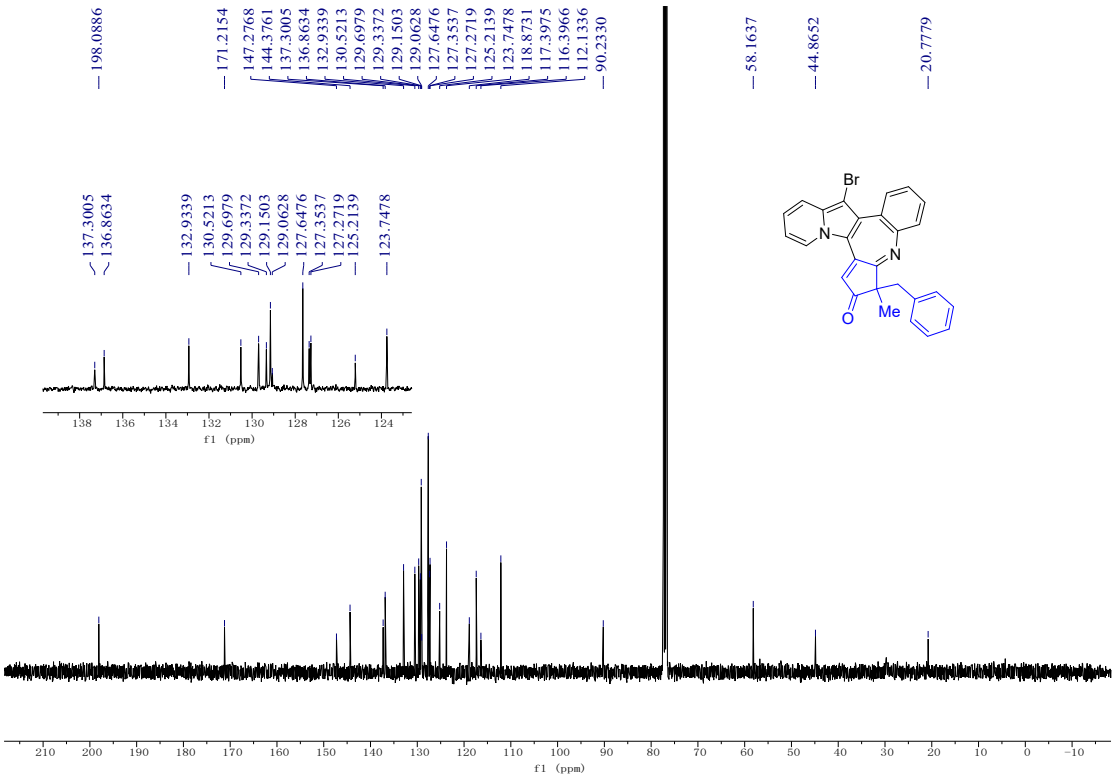
^{13}C NMR of **3am** (101 MHz, $CDCl_3$)



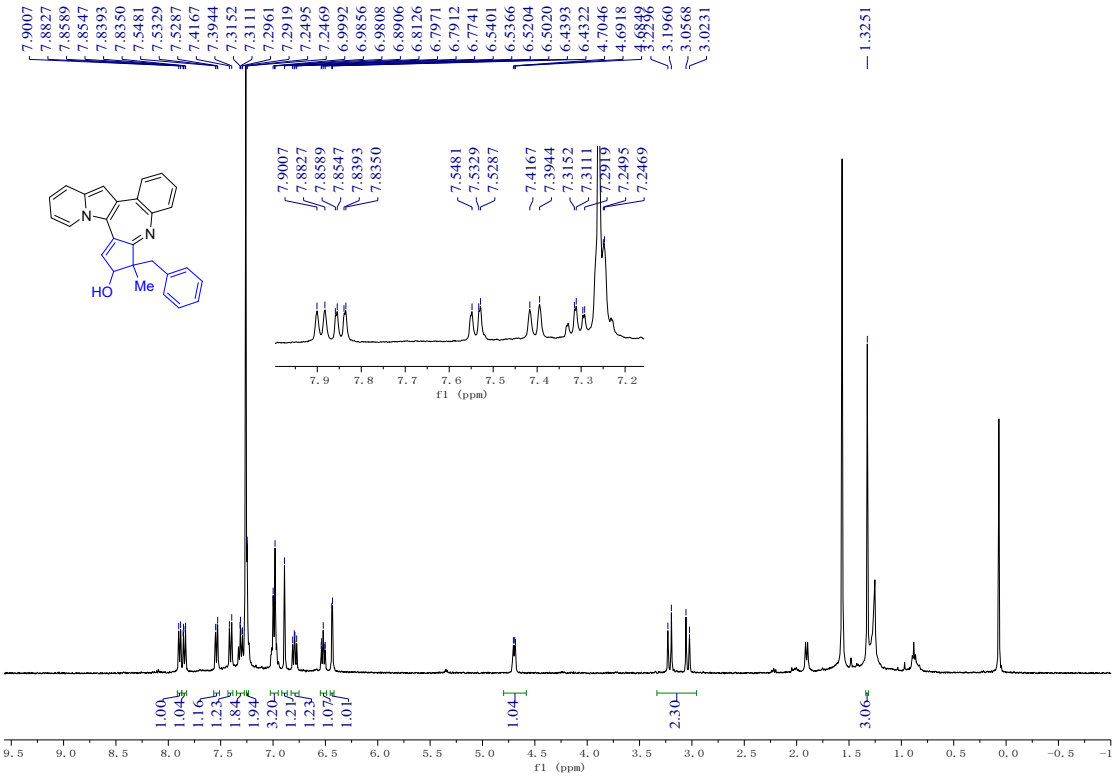
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



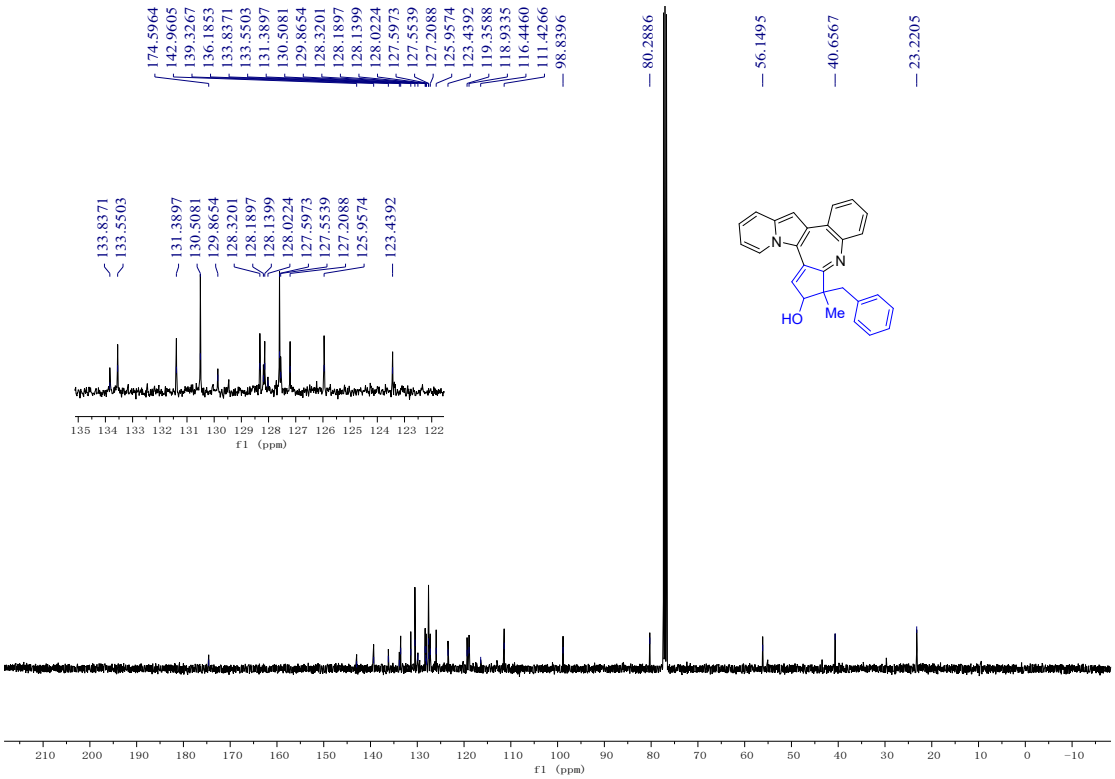
^{13}C NMR of **4** (101 MHz, $CDCl_3$)



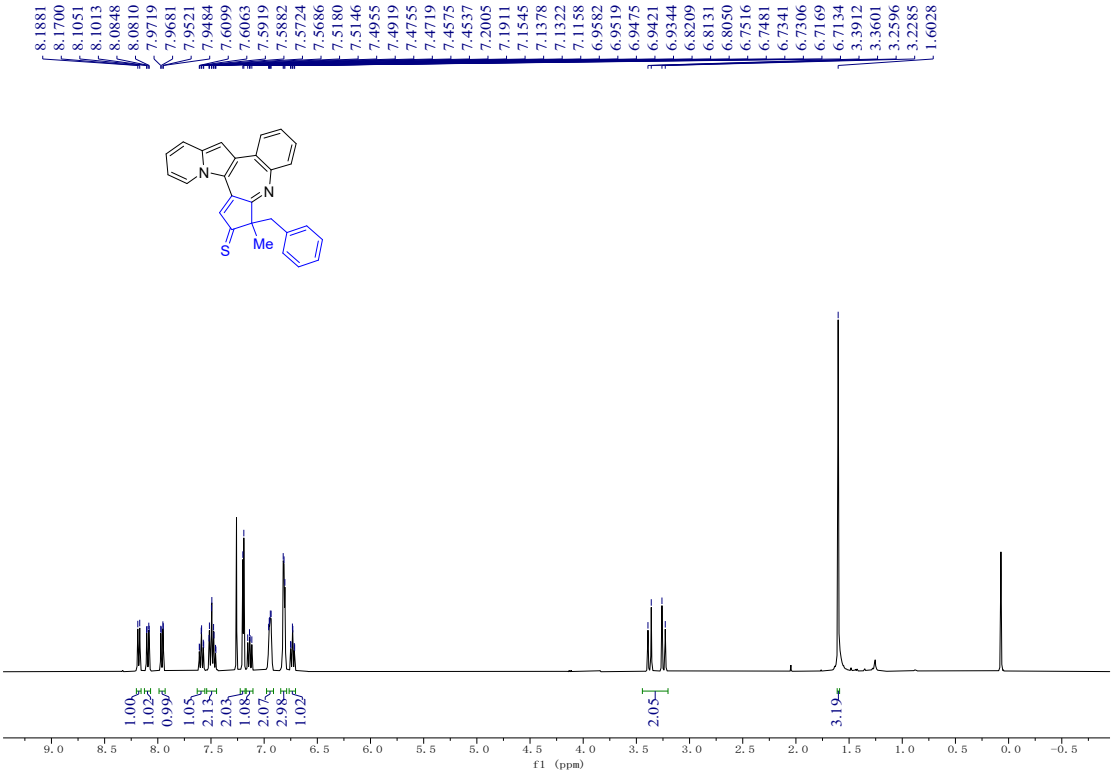
^{1}H NMR of **5** (400 MHz, $CDCl_3$)



^{13}C NMR of **5** (101 MHz, $CDCl_3$)



^{1}H NMR of **6** (400 MHz, $CDCl_3$)



^{13}C NMR of **6** (101 MHz, $CDCl_3$)