Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed Heck/[4+1] Decarboxylative Cyclization Cascade to Access Diverse Heteropolycycles by α-Bromoacrylic Acids as C1 Insertion Unit

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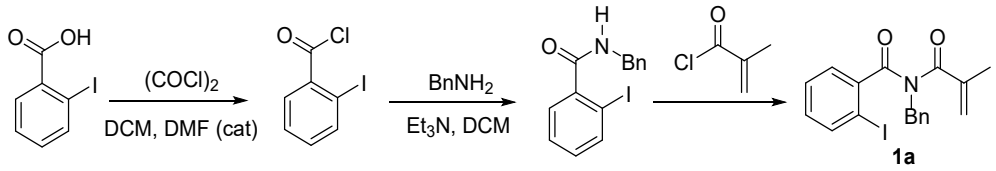
1 General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments or Avance-400 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; dd, doublets of 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 Preparation of Substrates

2.1 General Procedure for the Synthesis of Substrates 1a-1k [1,2]

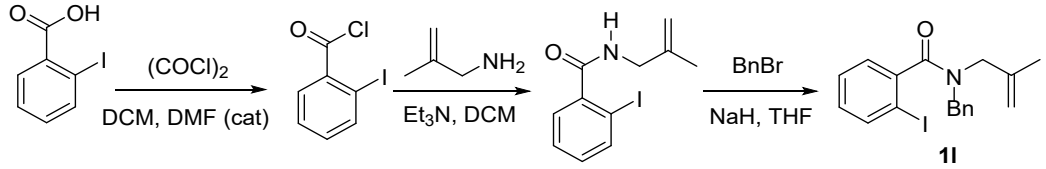


An oven dried reaction tube containing a PTFE-coated stir bar was charged with 2-iodobenzoic acid (5.0 mmol, 1.0 equiv, 1.24 g), oxalyl chloride (6.0 mmol, 1.2 equiv, 0.5 mL) in dichloromethane (10 mL) and DMF (3 drops). The mixture was stirred by 2 hours at 0 °C and was warmed at room temperature. The solvent was evaporated and the crude was used directly in the next step. The 2-iodobenzoyl chloride (5.0 mmol, 1.0 equiv, 1.33 g) was dissolved in dichloromethane (10 mL). Phenylmethanamine (10.0 mmol, 2.0 equiv, 1.1 mL) (in some cases is necessary to add 2.0 equiv more) and Et_3N (10.0 mmol, 2.0 equiv, 1.4 mL) were added and the mixture was stirred at 0 °C until consumption of acylchloride. The corresponding amide was isolated after addition of 5 mL of saturated Na_2CO_3 solution and extraction with dichoromethane. It was used

without any purification in the next step. Methacryloyl chloride (5.0 mmol, 1.0 equiv, 0.59 mL) in dichoromethane (5 mL) was added on a mixture of 2-iodo-*N*-methylbenzamide (5.0 mmol, 1.0 equiv, 1.31 g), triethylamine (10.0 mmol, 2.0 equiv, 1.4 mL) and DMAP (0.25 mmol, 0.05 equiv, 30.54 mg) in toluene (5 mL). The mixture was stirred overnight at reflux in oil bath. The reaction was quenched with saturated aqueous Na_2CO_3 (5 mL), then the mixture was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1) affording the corresponding product **1a**.

The procedures of **1b** to **1k** were similar to **1a**.

2.2 General Procedure for the Synthesis of Substrates 1l [3,4]

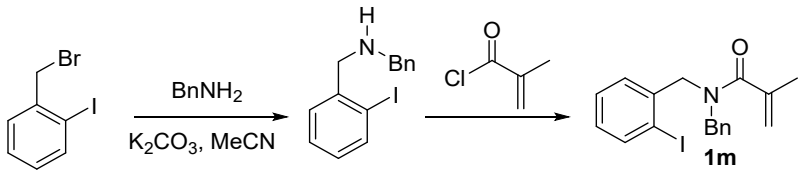


An oven dried reaction tube containing a PTFE-coated stir bar was charged with 2-iodobenzoic acid (5.0 mmol, 1.0 equiv, 1.24 g), oxalyl chloride (6.0 mmol, 1.2 equiv, 0.5 mL) in dichloromethane (10 mL) and DMF (3 drops). The mixture was stirred by 2 hours at 0 °C and was warmed at room temperature. The solvent was evaporated and the crude was used directly in the next step. The 2-iodobenzoyl chloride (5.0 mmol, 1.0 equiv, 1.33 g) was dissolved in dichloromethane (10 mL). 2-Methylprop-2-en-1-amine (10.0 mmol, 2.0 equiv, 0.91 mL) (in some cases is necessary to add 2.0 equiv more) and Et_3N (10.0 mmol, 2.0 equiv, 1.4 mL) were added and the mixture was stirred at 0 °C until consumption of acyl chloride. The corresponding amide was isolated after addition of 5 mL of saturated Na_2CO_3 solution and extraction with dichoromethane. It was used without any purification in the next step.

NaH (2.0 mmol, 2.0 equiv, 0.08 g, 60% in mineral oil) was added to a solution of the above product in THF (5 mL) at 0 °C in portions. After stirring for 20 min at 0 °C, (bromomethyl)benzene (3.0 mmol, 3.0 equiv, 0.4 mL) was added dropwise and the reaction mixture was allowed to room temperature and stirred for another 1 h. After

completion of the reaction (monitored by TLC), the residue was quenched with water and extracted into ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and the solution was evaporated to dryness. The crude product was purified by column chromatography (eluent: petroleum ether/EtOAc=10:1) to provide the desired product **1l.**

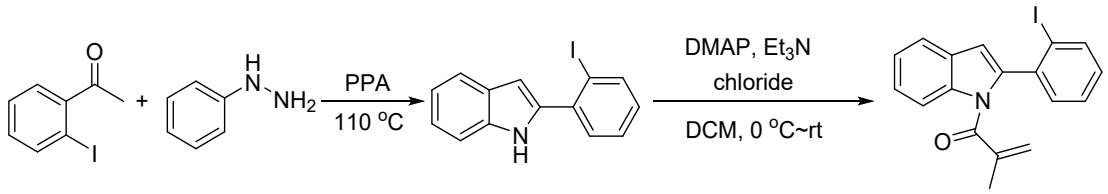
2.3 General Procedure for the Synthesis of Substrates 1m [5]



The 1-(bromomethyl)-2-iodobenzene (5.0 mmol, 1.0 equiv, 1.48 g) was dissolved in dichloromethane (10 mL). Phenylmethanamine (10.0 mmol, 2.0 equiv, 1.1 mL) (in some cases is necessary to add 2.0 equiv more) and K_2CO_3 (10.0 mmol, 2.0 equiv, 1.38 g) were added and the mixture was stirred at 0 °C overnight. The reaction was quenched with saturated aqueous Na_2CO_3 (5 mL), then the mixture was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 30:1).

Methacryloyl chloride (5.0 mmol, 2.0 equiv, 0.6 mL) in dichoromethane (5 mL) was added on a mixture of amide (2.5 mmol, 1.0 equiv, 0.81 g), triethylamine (10.0 mmol, 2.0 equiv, 1.4 mL) and DMAP (0.25 mmol, 0.05 equiv, 30.54 mg) in dichoromethane (10 mL). The mixture was stirred overnight at reflux in oil bath. The reaction was quenched with saturated aqueous Na_2CO_3 (5 mL), then the mixture was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1) affording the corresponding product **1m**.

2.4 General Procedure for the Synthesis of Substrates 4a-4f [6,7,8]

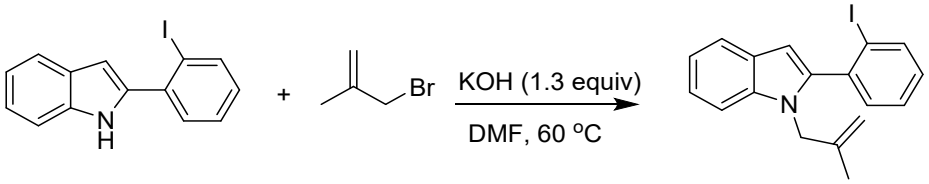


S1 **4a**

A mixture of 2-iodoacetophenone (5.0 mmol, 1.0 equiv, 1.23 g), phenylhydrazine (6.0 mmol, 1.2 equiv, 0.65 mg) and polyphosphoric acid (PPA, 15.00 g) was added to a round bottom flask and stirred at 110 °C for 6 h. After the completion of the reaction, the residue was quenched with ice water and extracted into ethyl acetate. The organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the corresponding substituted indole **S1.**

According to a literature procedure, to the solution of indole **S1** (3.5 mmol, 1.0 equiv, 1.12 g) and DMAP (0.7 mmol, 0.2 equiv, 85.52 mg) in dichoromethane (7 mL) was added Et_3N (7 mmol, 2.0 equiv, 0.71 g) and chloride (4.2 mmol, 1.2 equiv, 0.44 mg) at 0 °C. The solution was warmed up to room temperature and stirred for overnight. The mixture was diluted with dichoromethane (20 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with dichoromethane (20 mL × 2). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give a residue, which was purified by flash chromatography and then recrystallized from n-hexane/EtOAc to afford the product **4a**. The synthesis process of substrates **4b-4f** is similar to **4a**.

2.5 General Procedure for the Synthesis of Substrates 4g [6,7,9]

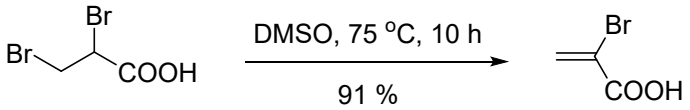


S1 **4g**

According to a literature procedure, a solution of **S1** (3.0 mmol, 1.0 equiv, 0.96 g) in DMF (5 mL) and powdered KOH (3.9 mmol, 1.3 equiv, 0.22 g) was stirred at 60 °C for 10 min, cooled to room temperature, and treated with 3-bromo-2-methylprop-1-ene (4.5 mmol, 1.5 equiv, 0.60 g). The reaction mixture was stirred at 60 °C for 12-18 h,

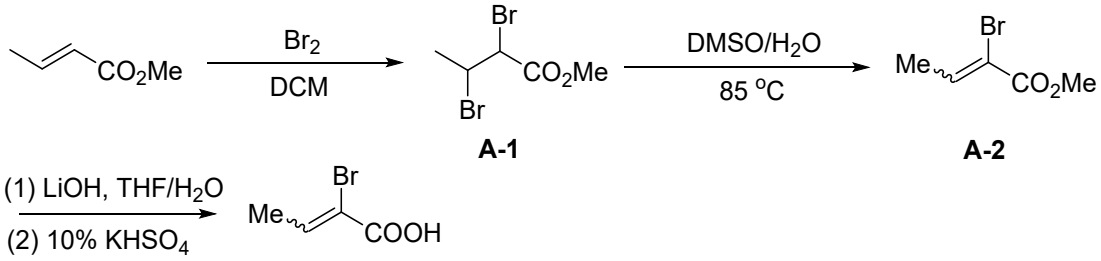
poured onto ice and diluted with 15 mL of EtOAc. The combined organic layers were washed with H_2O, brine, dried Na_2SO_4, concentrated in vacuo and purified by chromatography on SiO_2 (hexane) to afford the desired product **4g**.

2.6 General Procedure for the Synthesis of Substrates 2a-2t [10]



2h

General DMSO dehydrohalogenation procedures: A solution of 2,3-dibromopropanoic acid (3.0 mmol, 0.70 g) in 9 mL of DMSO with 1.0 mL of water was heated at 75 °C for 10 hours. The reaction mixture was loaded onto prep HPLC and purified (Gilson gradient of water and acetonitrile, see general experimental). The pH of the combined fractions was adjusted to pH = 8 using aqueous NaOH (2 N). Lyophilization of the fractions gave 0.47 g (91%) of the α-bromoacrylic acid sodium salt as a white solid.



A-1 **A-2**

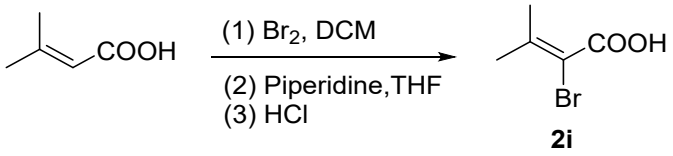
2t

In a dried flask under Ar charged with methyl crotonate (10.0 mmol, 1.0 equiv, 1.1 mL) in DCM (25 mL) was added dropwise at 0 °C over a period of 1 h Br_2 (22.0 mmol, 1.1 equiv, 1.1 mL). The resulting mixture was stirred 15 min at 0 °C and then at RT for 1 h. The mixture was concentrated under reduced pressure (P = 10 mm bar; T = 35 °C) to afford crude dibrominated product **A-1** which was used directly as such in the next step.

A solution under Ar of crude dibrominated product **A-1** in DMSO/H_2O (95/5; 30 mL) was stirred at 85 °C for 16 h. The mixture was cooled to RT and poured into a cold half-saturated aqueous solution of $NaHCO_3$ (60 mL) and the biphasic mixture was then extracted with Et_2O (x2). The combined organic layers were washed with brine (x1), dried over Na_2SO_4, filtered and concentrated under reduced pressure (P = 10 mm bar;

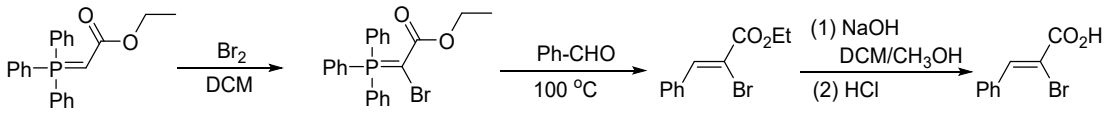
T = 35 °C) to afford crude conjugated ester **A-2** as a *Z/E* mixture (8/1). The crude mixture was used directly as such in the next step.

In a flask under Ar charged with crude conjugated ester **A-2** in THF (10 mL) was added dropwise at RT a solution of LiOH (30.0 mmol, 3.0 equiv, 0.72 g) in H_2O (10 mL) and the resulting mixture was stirred at RT for 12 h. The mixture was quenched with an aqueous solution of 10% $KHSO_4$ (70 mL) and was then extracted with EtOAc (x2). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude acid **2t** as a *Z/E* mixture (8/1). The crude solids were washed with PE (1x10 mL and then 1x5 mL) and dried under reduced pressure to afford 1.07 g (65% over 3 steps) of pure (*Z*)-acid **2t**.



2i

To a stirred solution of 3-methylbut-2-enoic acid (2.00 mmol, 1.0 equiv, 0.20 g) in DCM (2 mL), was added Br_2 (2.20 mmol, 1.1 equiv, 0.35 g) dropwise at 0 °C. The mixture was stirred 12 hours. Then quenched with saturated solution of $Na_2S_2O_3$ to remove excess of bromine and extracted three times with DCM. The organic layer was dried over $MgSO_4$ and concentrated to give the dibrominated acid. The product was dissolved in THF and Piperidine (9.80 mmol, 4.9 equiv, 967 µL) was added in one portion at 0 °C. The solution was stirred for 24 h at room temperature and then quenched with aq. HCl (5 M). The product was extracted with ethyl acetate. The collected organic layers were dried over $MgSO_4$ and concentrated to give the 2-bromo-3-methylbut-2-enoic acid **2i** as a yellow powder (1.78 mmol, 0.30 g, 85% yield).



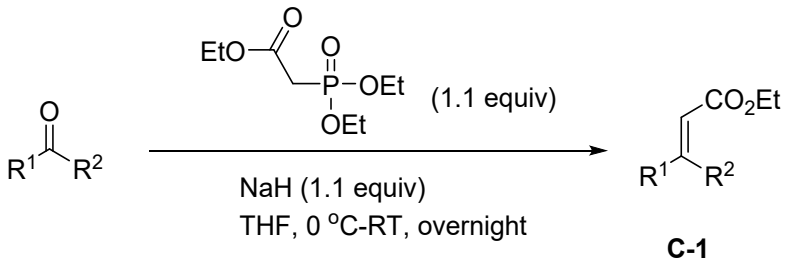
B-1 **B-2** **2**

Carboethoxymethylidenetriphenyl-phosphorane (10 mmol, 3.50 g) was dissolved in DCM (20 mL) and the solution was cooled to 5 °C in ice-water bath. A solution of bromine (10 mmol, 1.60 g) in DCM (10 mL) was slowly added dropwise, and the batch was stirred overnight. The organic phase was washed with water (20 mL), and then

twice with $NaHCO_3$ solution (20 mL) until HBr was neutralized. The DCM phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was recrystallized from acetone/n-hexane (2:1) (27 mL). The crystals were dried in vacuo to afford **B-1** as a yellow solid, yield 69% (3.02 g).

A mixture of aldehyde (5 mmol) and **B-1** (5 mmol) was added to a two-neck round bottom flask with a magnetic stirrer under nitrogen atmosphere. The mixture was heated to 100 °C. A homogeneous melt formed, and the ensuing mixture was kept at 100 °C for 8 h. After cooling to room temperature, the mixture was subjected to column chromatography on silica gel to get **B-2**.

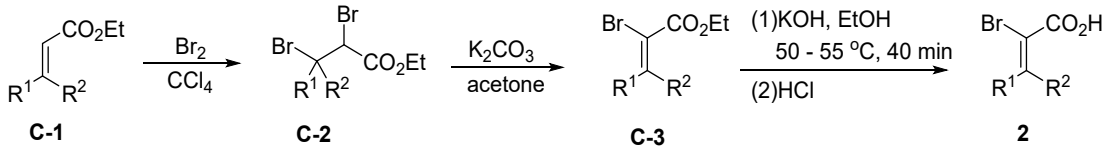
B-2 (5 mmol) was dissolved in DCM/CH_3OH (9:1) (30 mL), and the solution was cooled to 5 °C in ice-water bath. NaOH (15 mmol, 0.60 g) was added, and the mixture was stirred for 12 h at room temperature. The solvents were then removed under vacuum, the residue was diluted with water, and the aqueous solution was extracted with diethyl ether in order to remove the remaining ester. The aqueous phase was then cooled, acidified to pH 2-3 with dilute HCl, and extracted with Et_2O. The combined organic layer was dried over Na_2SO_4, and the solvent was removed to afford **2**.



C-1

NaH (1.1 equiv, 60% dispersion in mineral oil) and THF were added to a dried Schlenk tube equipped with a magnetic stir bar under a positive stream of argon. The reaction mixture was cooled to 0 °C and the phosphorus species (1.1 equiv) was added slowly (Warning: strong hydrogen evolution occurs). The reaction mixture was stirred at room temperature for 30 minutes and the corresponding ketone (1.0 equiv) was added. The reaction mixture was stirred at room temperature overnight and then carefully quenched with a saturated $NaHCO_3$ solution. The reaction mixture was transferred to a separation funnel using EtOAc/water. The aqueous phase was extracted with EtOAc (x3). The combined organic phases were washed with brine (x1), dried

over $MgSO_4$, filtered and concentrated under reduced pressure. Final purification was accomplished by silica gel column chromatography to get the product **C-1**.

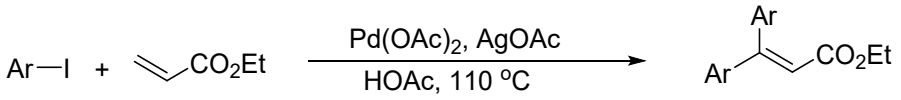


C-1 **C-2** **C-3** **2**

To a solution of **C-1** (10 mmol) in CCl_4 (10 mL) at 0 °C was added a solution of Br_2 (10 mmol, 1.60 g) in CCl_4 (25 mL) over a period of 2.5 h. When the addition was complete, the solution was allowed to warm slowly to room temperature, and stirred overnight. After evaporation of the solvent, **C-2** was obtained (quant) as an oil which was used without further purification.

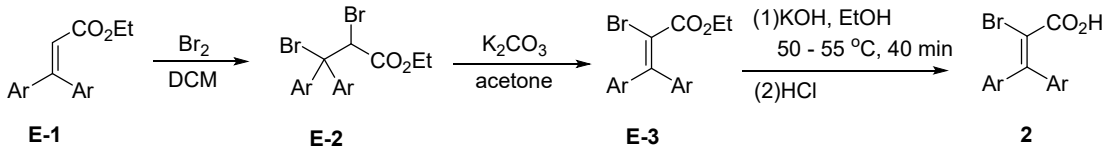
A solution of **C-2** (10 mmol) in acetone (55 mL) in the presence of K_2CO_3 (2.10 g) was refluxed for 48 h. After filtration and evaporation of the solvent, the product **C-3** was isolated by flash chromatography.

A mixture of **C-3** (5 mmol), 10 mL of ethanol and 10 mL of 20% potassium hydroxide solution was heated at 50-55 °C for 40 minutes. After the solution had been cooled, 5 mL of con-centrated hydrochloric acid was added dropwise, and the mixture was allowed to stand 1.3 hour. The aqueous phase extracted with Et_2O. The combined organic layer was dried over Na_2SO_4, and the solvent was removed to afford **2**.



E-1

To a suspension of AgOAc (15.5 mmol, 2.59 g) and $Pd(OAc)_2$ (0.05 mmol, 11.20 mg) in AcOH (15 mL) was added iodo-benzene (15.5 mmol, 1.73 mL) and ethyl acrylate (5.0 mmol, 0.54 mL). The mixture was stirred under an atmosphere of argon, at 110 °C for 6 h then allowed cool at RT and diluted with EtOAc (20 mL). The mixture was filtered through a pad of Celite, washed with EtOAc (200 mL) and the filtrate concen-trated in vacuo. Purification by column chromatography (hexane : EtOAc = 15 : 1) afforded ethyl 3,3-diphenylacrylate as a yellow oil.

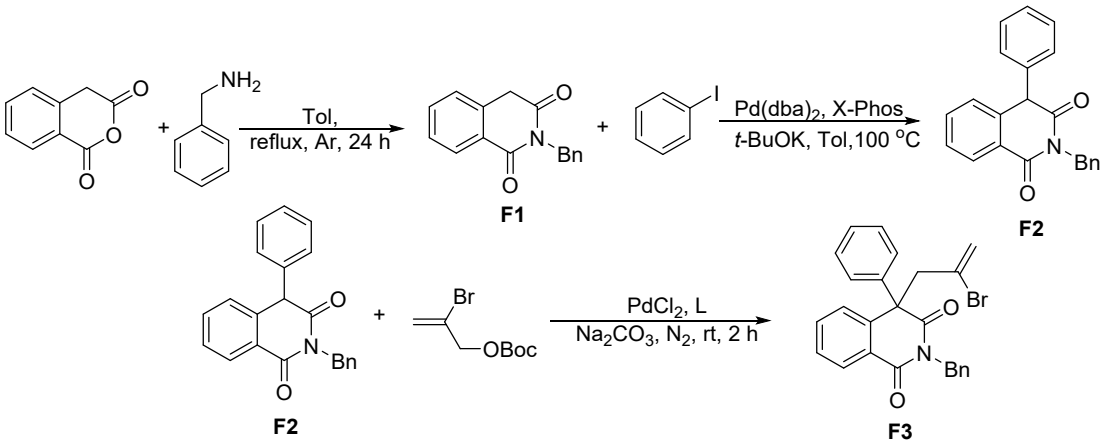


To a solution of **E-1** (10 mmol) in DCM (10 mL) at 0 °C was added a solution of Br_2 (10 mmol, 1.60 g) in DCM (25 mL) carefully. When the addition was complete, the solution was allowed to warm slowly to room temperature, and stirred overnight. After evaporation of the solvent, **E-2** was obtained which was used without further purification. The same procedure was applied to **E-1** to produce **E-2** in quantitative yield.

A solution of **E-2** (10 mmol) in acetone (55 mL) in the presence of K_2CO_3 (30 mmol) was refluxed for 24 h. After filtration and evaporation of the solvent, the product **E-3** was isolated by flash chromatography.

A mixture of **E-3** (5 mmol), 10 mL of ethanol and 10 mL of 20% potassium hydroxide solution was heated at 50-55 °C for 40 minutes. After the solution had been cooled, 5 mL of con-centrated hydrochloric acid was added dropwise, and the mixture was allowed to stand 1.3 hour. The aqueous phase extracted with Et_2O. The combined organic layer was dried over Na_2SO_4, and the solvent was removed to afford **2**.

2.7 General Procedure for the Synthesis of Substrates F3 [11]



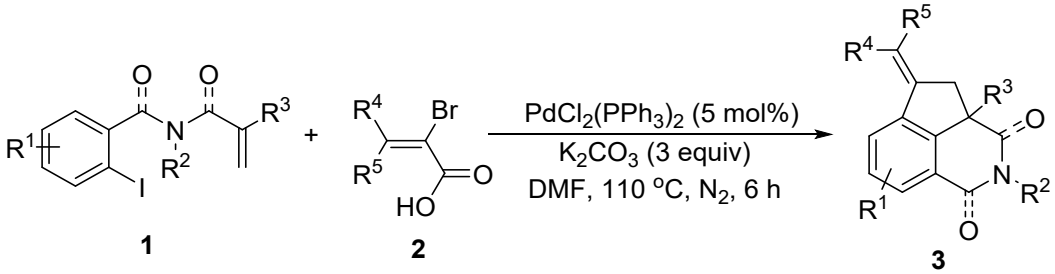
A mixture of isochroman-1,3-dione (4.0 mmol, 0.64 g), benzylamine (4.8 mmol, 0.51 g), and toluene (2.5 mL) was refluxed for 24 h under argon. Afterwards the resulting mixture was cooled to room temperature, transferred to silica gel column directly and purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 6:1) affording the corresponding product **F1**.

To a Schlenk tube were added 2-benzyl-isoquinoline-1,3(2*H*,4*H*)-dione **F1** (0.5 mmol, 125.64 mg), iodobenzene (0.6 mmol, 122.42 mg), $Pd(dba)_2$ (0.01 mmol, 5.75 mg), 3% mol X-Phos (0.015 mmol, 7.15 mg), and *t*-BuOK (0.6 mmol, 67.33 mg). The mixture was subjected to a vacuum and was back filled with nitrogen 5 times to remove air; then fresh distilled degassed toluene (0.5 mL) was added. The tube was sealed and heated to 100 °C for 12 h, and then 1 mL of NH_4Cl (saturated) was added to quench the reaction. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1) affording the corresponding product **F2**

To a solution of 2-benzyl-4-phenylisoquinoline-1,3(2*H*,4*H*)-dione **F2** (0.2 mmol, 65.48 mg), $PdCl_2$ (0.005mmol, 0.89 mg), N,N'-((1*R*,2*R*)-1,2-diphenylethane-1,2-diyl)bis(2-(diphenylphosphaneyl)benzamide) (0.01 mmol, 7.89 mg), Na_2CO_3 (0.4 mmol, 42.40 mg) in anhydrous THF (2 mL) was reacted at 25 °C under N_2 atmosphere. After 10 minutes, 2-bromoallyl *tert*-butyl carbonate (0.4 mmol, 94.84 mg) was added, and the mixture was stirred at the same temperature for 2 h until **F2** was completely consumed (monitored by TLC). To the mixture, saturated aqueous NH_4Cl solution was added, and the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1) affording the corresponding product **F3** (87%, 77.66 mg)

3 Typical Procedures

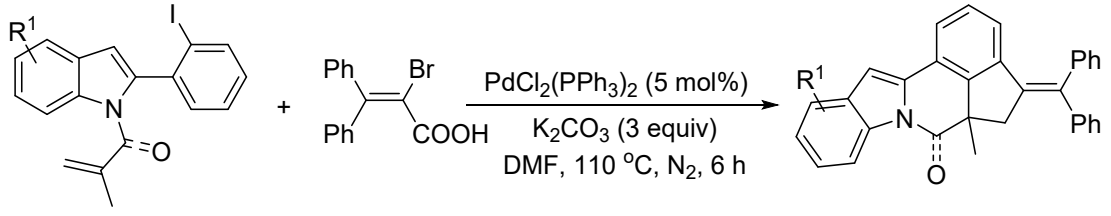
3.1 Typical Procedures for the Synthesis of Isoquinolinedione-Fused Benzocycloheptanones 3



The mixture of *N*-benzyl-2-iodo-*N*-methacryloylbenzamide **1a** (0.2 mmol, 1.0 equiv, 81.05 mg), 2-bromo-3,3-diphenylacrylic acid **2a** (0.26 mmol, 1.3 equiv, 78.82

mg), $PdCl_2(PPh_3)_2$ (0.01 mmol, 5 mol%, 7.01 mg), and K_2CO_3 (0.6 mmol, 3.0 equiv, 82.93 mg) in DMF (2 mL) was stirred under nitrogen atmosphere at 110 °C for 6 h (oil bath temperature). After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **3aa** (88%, 80.18 mg).

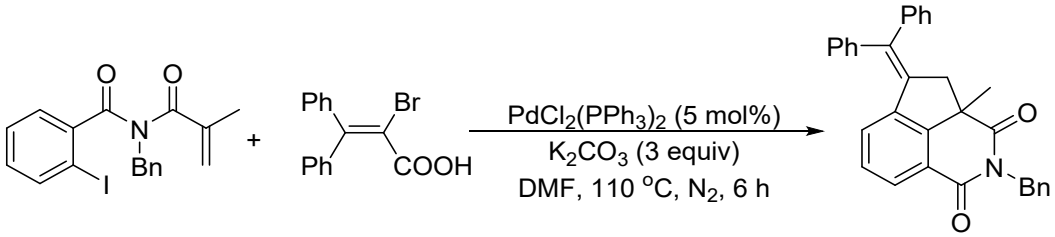
3.2 General Procedure for the Synthesis of Indolo[2,1-*a*]isoquinolinone-Fused Benzocycloheptanones 5



4 **2** **5**

To a Schlenk tube were added alkene-tethered aryl iodides **4a** (0.2 mmol, 1.0 equiv, 77.44 mg), 2-bromo-3,3-diphenylacrylic acid **2a** (0.26 mmol, 1.3 equiv, 78.82 mg), $PdCl_2(PPh_3)_2$ (0.01 mmol, 5 mol%, 7.01 mg), and K_2CO_3 (0.6 mmol, 3.0 equiv, 82.93 mg) in DMF (2 mL) was stirred under nitrogen atmosphere at 110 °C for 6 h (oil bath temperature). After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **5aa** (62%, 54.26 mg).

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

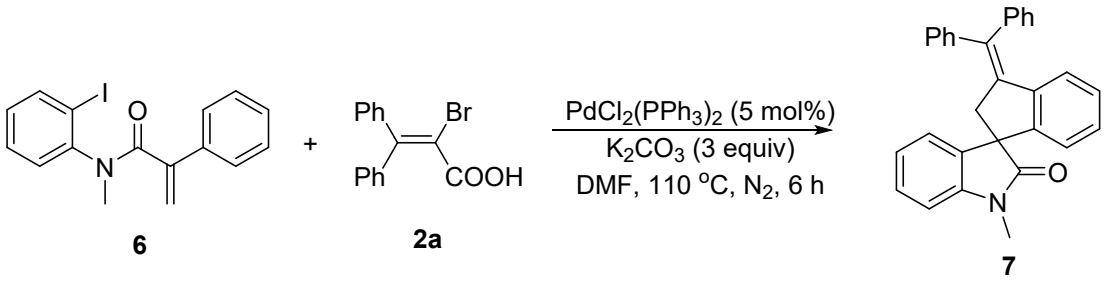


The mixture of *N*-benzyl-2-iodo-*N*-methacryloylbenzamide **1a** (1 mmol, 1.0 equiv, 405.24 mg), 2-bromo-3,3-diphenylacrylic acid **2a** (1.3 mmol, 1.3 equiv, 394.10

mg), $PdCl_2(PPh_3)_2$ (0.05 mmol, 5 mol%, 35.10 mg), and K_2CO_3 (3 mmol, 3.0 equiv, 414.63 mg) in DMF (8 mL) was stirred under nitrogen atmosphere at 110 °C for 6 h (oil bath temperature). After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **3aa** (76%, 346.22 mg).

4 Mechanistic Studies

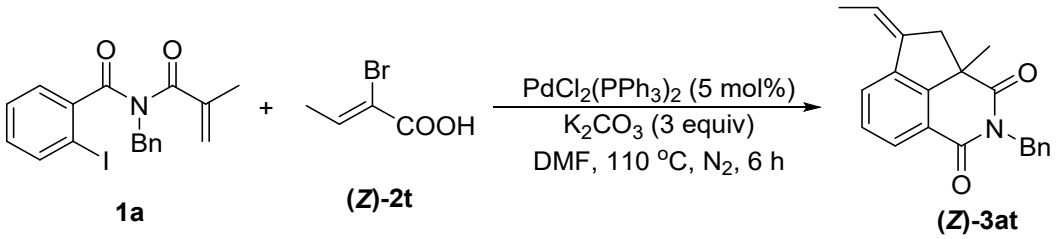
4.1 Synthesis of 7 from (*Z*)-2t



6 **2a** **7**

The mixture of N-(2-iodophenyl)-N-methyl-2-phenylacrylamide **6** (0.2 mmol, 1.0 equiv, 72.44 mg), 2-bromo-3,3-diphenylacrylic acid **2a** (0.26 mmol, 1.3 equiv, 78.82 mg), $PdCl_2(PPh_3)_2$ (0.01 mmol, 5 mol%, 7.01 mg), and K_2CO_3 (0.6 mmol, 3.0 equiv, 82.93 mg) in DMF (2 mL) was stirred under nitrogen atmosphere at 110 °C for 6 h (oil bath temperature). After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **7** (58%, 47.97 mg).

4.2 Synthesis of (*Z*)-3at from (*Z*)-2t

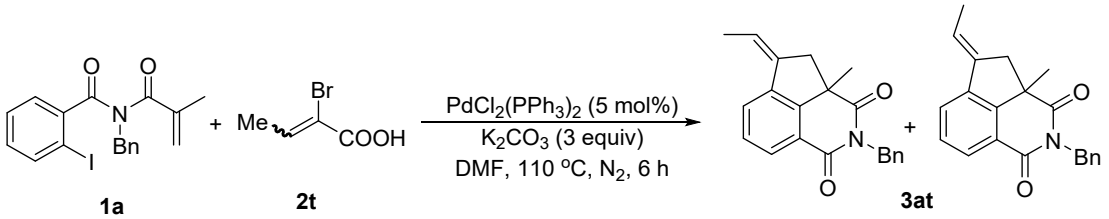


1a **(*Z*)-2t** **(*Z*)-3at**

To a Schlenk tube were added *N*-benzyl-2-iodo-*N*-methacryloylbenzamide **1a** (0.2 mmol, 1.0 equiv, 81.05 mg), (*Z*)-2-bromobut-2-enoic acid **(*Z*)-2t** (0.26 mmol, 1.3 equiv, 42.90 mg), $PdCl_2(PPh_3)_2$ (0.01 mmol, 5 mol%, 7.01 mg), and K_2CO_3 (0.6 mmol, 3.0

equiv, 82.93 mg) in DMF (2 mL) was stirred under nitrogen atmosphere at 110 °C for 6 h (oil bath temperature). After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **(*Z*)-3at** (52%, 33.01 mg).

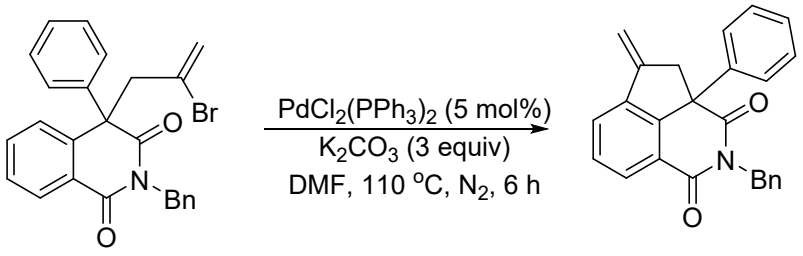
4.3 Synthesis of 3at from 2t



1a **2t** **3at**

To a Schlenk tube were added *N*-benzyl-2-iodo-*N*-methacryloylbenzamide **1a** (0.2 mmol, 1.0 equiv, 81.05 mg), 2-bromobut-2-enoic acid **2t** (0.26 mmol, 1.3 equiv, 42.90 mg，*Z:E* = 10:1), $PdCl_2(PPh_3)_2$ (0.01 mmol, 5 mol%, 7.01 mg), and K_2CO_3 (0.6 mmol, 3.0 equiv, 82.93 mg) in DMF (2 mL) was stirred under nitrogen atmosphere at 110 °C for 6 h (oil bath temperature). After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure, the crude product was purified by column chromatography (eluent: petroleum ether/EtOAc = 10:1) to provide the desired product **3at** (53%, 36.18 mg, *Z:E* = 4:1).

4.4 Synthesis of 3ih from 8



8 **3ih**

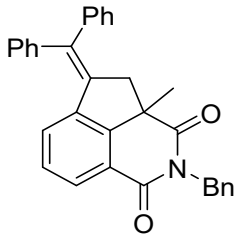
The mixture of 2-benzyl-4-(2-bromoallyl)-4-phenylisoquinoline-1,3(2*H*,4*H*)-dione **8** (0.1 mmol, 1.0 equiv, 44.63 mg), $PdCl_2(PPh_3)_2$ (0.005 mmol, 5 mol%, 3.51 mg), and K_2CO_3 (0.3 mmol, 3.0 equiv, 41.46 mg) in DMF (2 mL) was stirred under nitrogen atmosphere at 110 °C for 6 h (oil bath temperature). However, the target

product was not monitored by TLC.

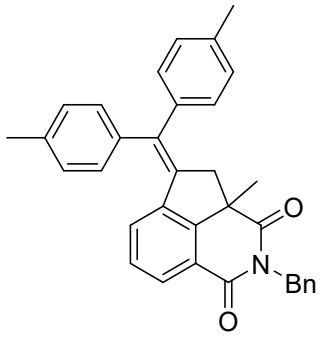
5 Crystal Culture Procedure of Product 3ia

To a round-bottom flask (25 mL) was added 2-benzyl-5-(diphenylmethylene)-3a-phenyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione **3ia** (10 mg). Dichloromethane (1.0 mL) were added slowly to make it dissolve completely. Then petroleum ether (5.0 mL) was added. Finally, the round-bottom flask was sealed with a rubber stopper, and connected the air with a syringe needle. Putting the flask in a dry and ventilated place to make the organic solvent volatilize slowly. After a few days, the crystal of **3ia** were separated out.

6 Characterization Data

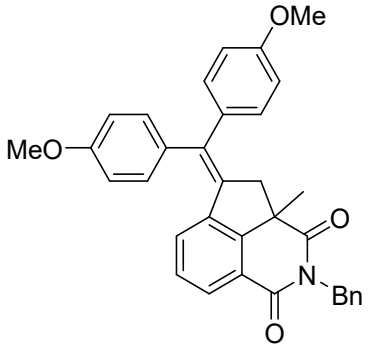


2-benzyl-5-(diphenylmethylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3aa): white solid, isolated yield 88% (80.18 mg), 91% (82.91 mg); (*N*-benzyl-2-bromo-*N*-methacryloylbenzamide was used); (eluent: petroleum ether/EtOAc = 10:1); mp: 187.6-191.9 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 5H), 7.33-7.22 (m, 10H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 5.17 (d, *J* = 8.0 Hz, 2H), 5.04 (d, *J* = 8.0 Hz, 2H), 3.52 (d, *J* = 15.0 Hz, 1H), 3.01 (d, *J* = 15.0 Hz, 1H), 1.49 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.4, 164.8, 150.5, 141.7, 141.6, 140.4, 139.0, 137.3, 134.7, 129.6, 129.4, 129.1, 128.9, 128.7, 128.5, 128.3, 128.1, 127.9, 127.5, 127.4, 126.2, 122.9, 49.3, 45.2, 43.6, 30.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_2^+$ 456.1958; found 456.1965.

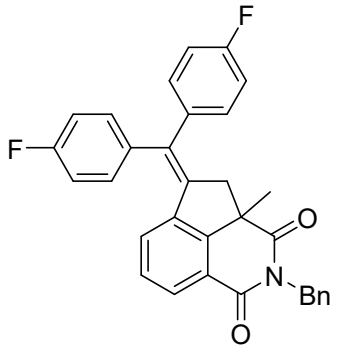


2-benzyl-5-(di-*p*-tolylmethylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ab): pale yellow solid, isolated yield 95% (91.89 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 203.3-208.6 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.29-7.13 (m, 10H), 7.06-7.02 (m, 2H), 6.51 (d, *J* = 7.5 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 5.04 (d, *J* = 14.0 Hz, 1H), 3.50 (d, *J* = 15.0 Hz, 1H), 3.00 (d, *J* = 15.0 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 1.48 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.5, 164.9, 150.5, 140.4, 139.4, 139.1, 138.8, 137.6, 137.4, 137.3, 133.9, 129.6,

129.5, 129.3, 129.0, 128.8, 128.7, 128.4, 128.2, 127.3, 125.9, 122.9, 49.3, 45.4, 43.6, 30.0, 21.3, 21.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{30}NO_2^+$ 484.2271; found 484.2264.

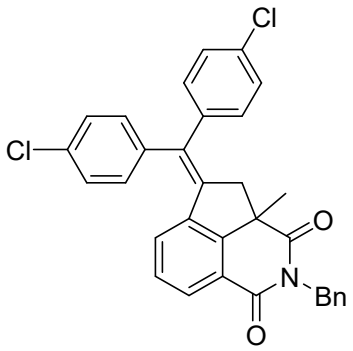


2-benzyl-5-(bis(4-methoxyphenyl)methylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ac): yellow solid, isolated yield 71% (73.22 mg); (eluent: petroleum ether/EtOAc = 7:1); mp: >250 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 7.5 Hz, 1H), 7.43-7.40 (m, 3H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.30- 7.09 (m, 8H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 7.5 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 5.04 (d, *J* = 14.0 Hz, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.49 (d, *J* = 15.0 Hz, 1H), 2.96 (d, *J* = 15.0 Hz, 1H), 1.49 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.2, 164.6, 155.6, 155.2, 150.5, 138.6, 137.2, 136.7, 135.2, 135.1, 134.7, 134.3, 133.8, 129.9, 129.3, 129.0, 128.6, 128.4, 128.3, 127.3, 126.3, 123.0, 112.1, 111.9, 111.5, 111.3, 56.2, 56.2, 49.3, 45.4, 43.6, 30.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{30}NO_4^+$ 516.2169; found 516.2175.

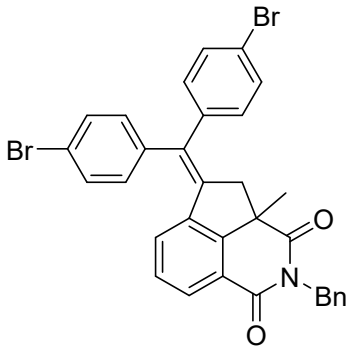


2-benzyl-5-(bis(4-fluorophenyl)methylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ad): pale yellow solid, isolated yield 86% (84.54 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 202.2-207.6 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 7.5 Hz, 1H), 7.69

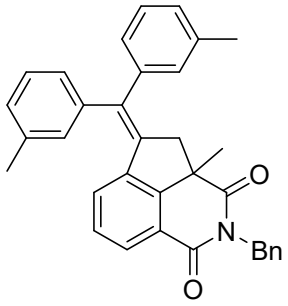
(d, J = 7.5 Hz, 1H), 7.46- 7.44 (m, 5H), 7.30 (t, J = 7.0 Hz, 3H), 7.25-7.22 (m, 2H), 7.10 (t, J = 8.5 Hz, 4H), 5.18 (d, J = 14.0 Hz, 1H), 5.08 (d, J = 14.0 Hz, 1H), 3.46 (dd, J = 15.5, 2.5 Hz, 1H), 3.20 (dd, J = 15.5, 1.0 Hz, 1H), 1.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.3, 164.7, 161.9 (d, C-F, $^1J_{C\text{-}F}$ = 247.0 Hz), 148.9, 139.7, 137.4, 137.3 (d, C-F, $^3J_{C\text{-}F}$ = 7.6 Hz), 132.9 (d, C-F, $^4J_{C\text{-}F}$ = 3.3 Hz),132.9, 130.2 (d, C-F, $^3J_{C\text{-}F}$ = 7.9 Hz), 129.2, 128.8, 128.4, 127.4, 126.7, 125.1, 123.3 (d, C-F, $^3J_{C\text{-}F}$ = 8.8 Hz), 115.6 (d, C-F, $^3J_{C\text{-}F}$ = 21.3 Hz), 50.3, 43.7, 42.2, 31.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{24}F_2NO_2^+$ 492.1770; found 492.1765.



2-benzyl-5-(bis(4-chlorophenyl)methylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ae): pale yellow solid, isolated yield 84% (88.11 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 210.6-215.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.0 Hz, 1H), 7.38 (dd, J = 15.0, 8.0 Hz, 4H), 7.29 (d, J = 8.5 Hz, 2H), 7.25-7.16 (m, 7H), 7.08 (t, J = 7.5 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 5.14 (d, J = 14.0 Hz, 1H), 5.02 (d, J = 14.0 Hz, 1H), 3.51 (d, J = 15.0 Hz, 1H), 2.98 (d, J = 15.0 Hz, 1H), 1.49 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 176.8, 164.4, 150.6, 139.6, 139.4, 138.3, 137.5, 137.1, 135.8, 133.9, 133.4, 131.0, 130.3, 129.2, 129.1, 128.5, 128.3, 128.3, 128.2, 127.2, 126.5, 123.0, 49.2, 45.3, 43.4, 29.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{24}Cl_2NO_2^+$ 524.1179; found 524.1107.

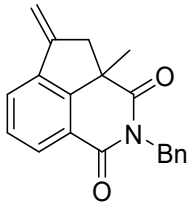


2-benzyl-5-(bis(4-bromophenyl)methylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3af): pale yellow solid, isolated yield 56% (68.70 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 214.0-220.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 6.5 Hz, 1H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.54-7.43 (m, 5H), 7.36-7.30 (m, 8H), 7.04 (s, 1H), 5.18 (d, *J* = 14.0 Hz, 1H), 5.08 (d, *J* = 14.0 Hz, 1H), 3.46 (d, *J* = 15.5 Hz, 1H), 3.20 (d, *J* = 16.0 Hz, 1H), 1.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.2, 164.7, 149.0, 139.6, 138.5, 137.3, 135.6, 131.8, 130.0, 129.3, 128.8, 128.4, 127.5, 126.9, 125.2, 123.3, 123.2, 121.4, 50.3, 43.8, 42.3, 31.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{24}Br_2NO_2^+$ 612.0168; found 612.0173.

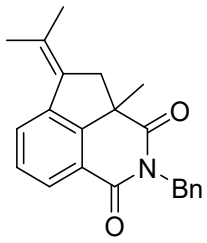


2-benzyl-5-(di-*m*-tolylmethylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ag): pale yellow soild, isolated yield 91% (88.02 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 205.9-210.7 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.30-7.20 (m, 8H), 7.09-7.03 (m, 4H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.17 (d, *J* = 14.0 Hz, 1H), 5.04 (d, *J* = 14.0 Hz, 1H), 3.49 (d, *J* = 15.0 Hz, 1H), 2.99 (d, *J* = 15.0 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 1.49 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =177.5, 164.9, 150.5, 141.6, 140.7, 139.2, 137.7, 137.4, 134.3, 130.0, 129.5, 129.4,

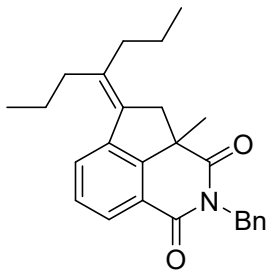
128.7, 128.7, 128.5, 128.4, 128.0, 127.4, 126.6, 126.2, 126.0, 122.8, 49.3, 45.1, 43.6, 30.1, 21.5, 21.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{30}NO_2^+$ 484.2271; found 484.2221.



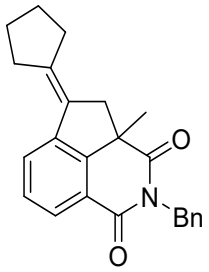
2-benzyl-3a-methyl-5-methylene-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ah): white solid, isolated yield 46% (27.91 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 89.5-94.8 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.43-7.40 (m, 3H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 5.64 (d, *J* = 2.5 Hz, 1H), 5.33 (d, *J* = 2.5 Hz, 1H), 5.15 (d, *J* = 14.0 Hz, 1H), 5.07 (d, *J* = 14.0 Hz, 1H), 3.20 (d, *J* = 15.5 Hz, 1H), 2.88 (d, *J* = 15.5 Hz, 1H), 1.44 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.3, 164. 8, 149.8, 144.7, 138.3, 137.3, 129.0, 128.7, 128.4, 127.4, 127.0, 125.6, 123.3, 108.4, 49.4, 43.7, 43.3, 30.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}NO_2^+$ 304.1332; found 304.1367.



2-benzyl-3a-methyl-5-(propan-2-ylidene)-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ai): white solid, isolated yield 85% (56.34 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 89.3-92.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.30-7.21 (t, *J* = 8.0 Hz, 1H), 7.25 (m, 3H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.02 (d, *J* = 14.0 Hz, 1H), 2.9 (d, *J* = 14.0 Hz, 1H), 2.11 (s, 3H), 1.94 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.0, 150.1, 139.0, 137.4, 131.8, 130.2, 128.7, 128.6, 128.3, 127.3, 124.8, 123.0, 48.7, 43.5, 42.0, 30.6, 23.6, 21.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{22}NO_2^+$ 332.1645; found 332.1651.

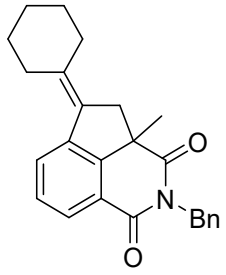


2-benzyl-5-(heptan-4-ylidene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3aj): white solid, isolated yield 72% (55.80 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 108.8-133.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.43-7.36 (m, 3H), 7.29-7.20 (m, 3H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 14.5 Hz, 1H), 2.95 (d, *J* = 14.5 Hz, 1H), 2.55-2.49 (m, 1 H), 2.35-2.29 (m, 1H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.62-1.48 (m, 4H) 1.41 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.0, 150.1, 141.5, 138.6, 137.3, 130.6, 128.7, 128.6, 128.6, 128.3, 127.3, 124.9, 123.0, 48.6, 43.5, 41.7, 37.3, 34.9, 30.2, 21.4, 21.3, 14.3, 14.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_2^+$ 388.2271; found 388.2271.

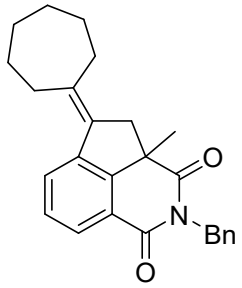


2-benzyl-5-cyclopentylidene-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ak): white solid, isolated yield 78% (55.76 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 169.7-172.8 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.43-7.37 (m, 3H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.07 (d, *J* = 14.0 Hz, 1H), 3.08 (d, *J* = 15.0 Hz, 1H), 2.76 (d, *J* = 15.0 Hz, 1H), 2.67 (d, *J* = 18.0 Hz, 1H), 2.50-2.47 (m, 2H), 2.38 (d, *J* = 18.0 Hz, 1H), 1.94-1.1 (m, 1H), 1.85-1.68 (m, 3H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.1, 149.7, 143.0, 139.1, 137.5, 128.8, 128.7, 128.3, 127.6, 127.3, 126.7, 124.7, 123.0, 49.3, 43.6, 41.9, 33.5, 32.0, 31.2,

27.6, 26.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NO_2^+$ 358.1802; found 358.1805.

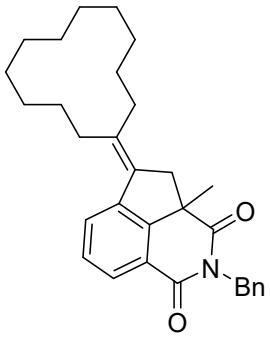


2-benzyl-5-cyclohexylidene-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3al): white liquid, isolated yield 88% (65.38 mg); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 2.99-2.98 (m, 2H), 2.69-2.63 (m, 2H), 2.39-2.27 (m, 2H), 1.68-1.62 (m, 6H), 1.44 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.1, 150.4, 140.7, 139.1, 137.4, 129.0, 128.7, 128.5, 128.3, 127.3, 126.9, 124.9, 123.0, 48.6, 43.5, 42.1, 33.4, 31.1, 29.8, 28.0, 27.9, 26.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}NO_2^+$ 372.1958; found 372.1965.

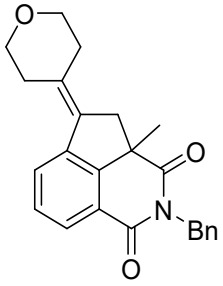


2-benzyl-5-cycloheptylidene-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3am): white liquid, isolated yield 85% (65.54 mg); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.42-7.35 (m, 4H), 7.29-7.21 (m, 2H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 14.5 Hz, 1H), 2.93 (d, *J* = 14.5 Hz, 1H), 2.81-2.77 (m, 1H), 2.64-2.56 (m, 1H), 2.48-2.39 (m, 2H), 1.90-1.61 (m, 8H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.8, 165.1, 150.2, 142.4, 138.8, 137.4, 130.2, 129.0, 128.7, 128.6, 128.4, 127.3, 124.9, 123.0, 48.8, 43.6, 41.6, 34.2, 32.8, 30.6, 29.7,

29.3, 29.3, 27.6, 27.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_2^+$ 386.2115; found 386.2115.

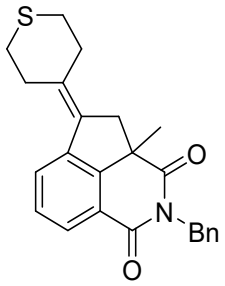


2-benzyl-5-cyclododecylidene-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3an): white solid, isolated yield 72% (65.61 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 168.7-172.9 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.04 (d, *J* = 14.5 Hz, 1H), 2.95 (d, *J* = 14.0 Hz, 1H), 2.60-2.54 (m, 1H), 2.44-2.39 (m, 1H), 2.31-2.26 (m, 1H), 2.19-2.13 (m, 1H), 1.69-1.59 (m, 4H), 1.50-1.34 (m, 17H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.1, 150.2, 141.3, 138.9, 137.4, 131.0, 128.7, 128.6, 128.5, 128.3, 127.3, 125.0, 123.0, 48.6, 43.5, 42.4, 31.0, 29.9, 28.6, 25.7, 25.7, 23.7, 23.5, 23.2, 23.1, 22.2, 22.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{38}NO_2^+$ 456.2897; found 456.2903.

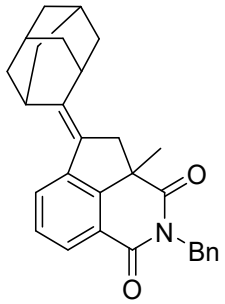


2-benzyl-3a-methyl-5-(tetrahydro-4*H*-pyran-4-ylidene)-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ao): white liquid, isolated yield 80% (59.75 mg); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 6.5 Hz, 1H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.42-7.35 (m, 3H), 7.28-7.22 (m, 3H), 5.15 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.89-3.87 (m, 2H), 3.73-3.67 (m, 2H), 2.99 (q, *J* = 14.5 Hz, 2H), 2.82-2.79 (m, 2H), 2.52-2.46 (m, 2H),

1.45 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.4, 164.9, 150.5, 138.4, 137.3, 134.1, 129.2, 128.8, 128.7, 128.3, 127.3, 125.5, 123.3, 68.5, 68.3, 48.7, 43.6, 41.8, 33.2, 31.5, 29.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NO_3^+$ 374.1751; found 374.1758.

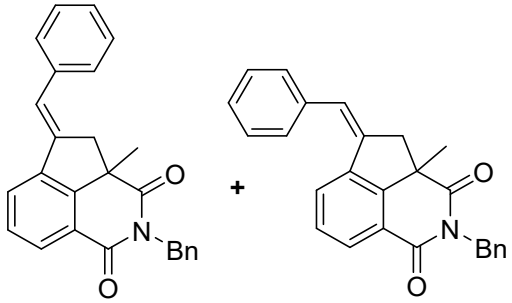


2-benzyl-3a-methyl-5-(tetrahydro-4*H*-thiopyran-4-ylidene)-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ap): white liquid, isolated yield 78% (60.76 mg); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 6.5 Hz, 1H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 10.0 Hz, 3H), 7.29-7.24 (m, 3H), 5.15 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.12-2.95 (m, 4H), 2.81-2.71 (m, 6H), 1.44 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.4, 164.9, 150.6, 138.3, 137.3, 136.9, 129.8, 129.2, 128.7, 128.7, 128.4, 127.4, 125.6, 123.3, 48.7, 43.6, 42.2, 35.0, 32.9, 30.3, 30.1, 29.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NO_2S^+$ 390.1522; found 390.1522.

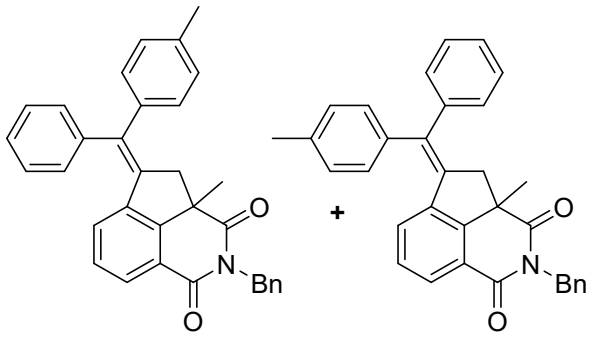


5-(adamantan-2-ylidene)-2-benzyl-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3aq): pale yellow solid, isolated yield 93% (78.78 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 169.5-173.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.55 (s, 1H), 2.98 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 14.0 Hz, 1H), 2.81 (s, 1H), 2.03-

1.89 (m, 10H), 1.80 (d, J = 12.5 Hz, 2H), 1.45 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.1, 150.3, 148.9, 139.2, 137.4, 128.8, 128.6, 128.5, 128.3, 127.3, 124.7, 123.0, 122.9, 48.6, 43.5, 41.6, 39.6, 39.6, 38.6, 38.4, 36.8, 36.2, 33. 8, 29.6, 27.8, 27.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}NO_2^+$ 424.2271; found 424.2271.

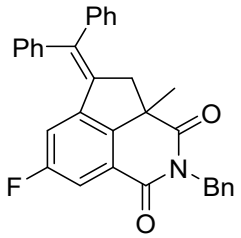


2-benzyl-5-benzylidene-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ar): yellow liquid, isolated yield 89% (67.54 mg, *Z:E* = 1:2); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.83-7.77 (m, 2H), 7.70 (d, J = 7.5 Hz, 1H), 7.44-7.39 (m, 11H), 7.30-7.25 (m, 6H), 7.12 (s, 1H), 6.83 (s, 1H), 5.17 (t, J = 12.0 Hz, 2H), 5.08 (d, J = 14.0 Hz, 1H), 3.49 (d, J = 15.5 Hz, 1H), 3.33-3.24 (m, 1H), 1.55 (s, 2H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =177.3, 177.2, 164.8, 164.7, 151.4, 148.9, 139.9, 137.7, 137.4, 137.3, 137.0, 136.9, 136.7, 129.2, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 127.5, 127.4, 127.0, 126.6, 126.5, 125.1, 124.4, 123.2, 50.3, 48.9, 45.4, 43.7, 43.6, 42.3, 31.2, 30.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}NO_2^+$ 380.1645; found 380.1653.

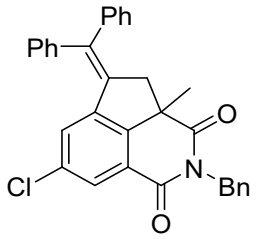


2-benzyl-3a-methyl-5-(phenyl(*p*-tolyl)methylene)-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3as): yellow solid, isolated yield 82% (77.01 mg, *Z:E* = 1:1); (eluent: petroleum ether/EtOAc = 10:1); mp: 209.4-

216.8 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (s, 2H), 7.41-7.38 (m, 8H), 7.32-7.25 (m, 13H), 7.18-7.14 (m, 8H), 7.07-7.02 (m, 2H), 6.54 (d, *J* = 7.0 Hz, 1H), 6.42 (d, *J* = 7.0 Hz, 1H), 5.17 (d, *J* = 13.5 Hz, 2H), 5.04 (d, *J* = 14.0 Hz, 2H), 3.54-3.49 (m, 2H), 3.04-2.97 (m, 2H), 2.41 (s, 3H), 2.36 (s, 3H), 1.49 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.5, 164.9, 150.5, 150.5, 141.9, 141.8, 140.4, 140.3, 139.2, 138.8, 138.6, 137.6, 137.5, 137.3, 134.4, 134.2, 129.7, 129.6, 129.5, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 127.8, 127.5, 127.4, 126.0, 126.0, 122.9, 49.3, 49.3, 45.3, 45.3, 43.6, 30.1, 21.3, 21.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{28}NO_2^+$ 470.2115; found 470.2127.

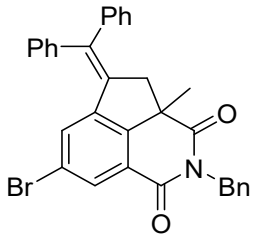


2-benzyl-5-(diphenylmethylene)-7-fluoro-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ba): pale yellow liquid, isolated yield 92% (87.13 mg); (*N*-benzyl-2-bromo-5-fluoro-*N*-methacryloylbenzamide was used); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.41-7.40 (m, 5H), 7.38-7.32 (m, 3H), 7.30-7.21 (m, 8H), 6.08 (dd, *J* = 10.0, 2.5 Hz, 1H), 5.16 (d, *J* =14.0 Hz, 1H), 5.03 (d, *J* =14.0 Hz, 1H) 3.55 (d, *J* = 15.0 Hz, 1H), 3.03 (d, *J* = 15.0 Hz, 1H), 1.48 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.0, 163.8, 162.8 (d, C-F, $^1J_{C\text{-}F}$ = 244.4 Hz), 146.0, 146.0, 141.8, 141.2 (d, C-F, $^3J_{C\text{-}F}$ = 8.5 Hz), 141.0, 137.1, 133.8 (d, C-F, $^4J_{C\text{-}F}$ = 3.0 Hz), 129.4, 129.1, 129.0, 128.7, 128.4, 128.2, 128.2, 127.8, 127.5, 123.8 (d, C-F, $^3J_{C\text{-}F}$ = 9.3 Hz), 116.8 (d, C-F, $^2J_{C\text{-}F}$ = 25.6 Hz), 112.7 (d, C-F, $^2J_{C\text{-}F}$ = 25.9 Hz), 48.8, 45.4, 43.8, 30.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{25}FNO_2^+$ 474.1864; found 474.1872.

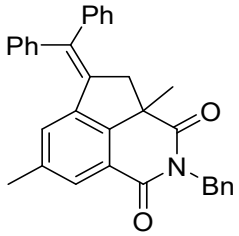


2-benzyl-7-chloro-5-(diphenylmethylene)-3a-methyl-4,5-

dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ca): pale yellow liquid, isolated yield 82% (80.36 mg); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 2.0 Hz, 1H), 7.43-7.39 (m, 5H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.31-7.23 (m, 8H), 6.31 (s, 1H), 5.15 (d, *J* = 14.0 Hz, 1H), 5.03 (d, *J* = 14.0 Hz, 1H), 3.53 (d, *J* = 15.0 Hz, 1H), 3.02 (d, *J* = 15.0 Hz, 1H), 1.48 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 176.8, 163.7, 148.6, 141.9, 141.2, 141.0, 140.9, 137.0, 134.5, 133.6, 129.4, 129.1, 129.1, 128.7, 128.4, 128.3, 128.2, 127.9, 127.5, 125.8, 123.8, 48.9, 45.3, 43.8, 30.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{25}ClNO_2^+$ 490.1568; found 490.1571.

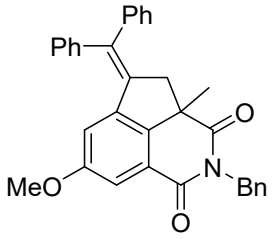


2-benzyl-7-bromo-5-(diphenylmethylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3da): pale yellow liquid, isolated yield 48% (51.31 mg); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.43-7.28 (m, 10H), 7.24 (m, 5H), 6.45 (s, 1H), 5.15 (d, *J* = 14.0 Hz, 1H), 5.03 (d, *J* = 14.0 Hz, 1H), 3.52 (d, *J* = 15.0 Hz, 1H), 3.00 (d, *J* = 15.0 Hz, 1H), 1.48 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 176.8, 163.6, 149.1, 142.0, 141.2, 141.0, 137.1, 133.5, 132.3, 129.4, 129.1, 129.1, 128.8, 128.7, 128.4, 128.3, 128.2, 127.9, 127.5, 124.2, 122.2, 49.0, 45.2, 43.8, 29.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{25}BrNO_2^+$ 534.1063; found 534.1075.

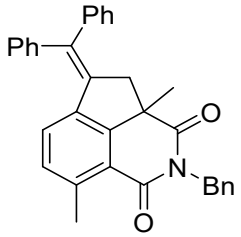


2-benzyl-5-(diphenylmethylene)-3a,7-dimethyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ea): pale yellow solid, isolated yield 88% (82.65 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 178.4-182.2°C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.52 (s, 1H), 7.44-7.36 (m,

5H), 7.33 (t, *J* = 7.0 Hz, 2H), 7.28-7.22 (m, 8H), 6.21 (s, 1H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.03 (d, *J* = 14.0 Hz, 1H), 3.50 (d, *J* = 15.0 Hz, 1H), 3.00 (d, *J* = 15.0 Hz, 1H), 2.11 (s, 3H), 1.48 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.0, 148.1, 141.7, 140.1, 139.2, 138.3, 137.4, 134.9, 130.2, 129.7, 129.1, 128.9, 128.7, 128.4, 128.2, 127.8, 127.5, 127.3, 126.6, 122.5, 49.0, 45.5, 43.6, 30.2, 21.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{28}NO_2^+$ 470.2115; found 470.2135.

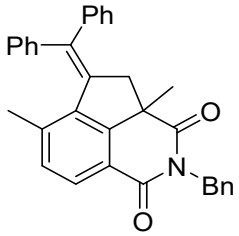


2-benzyl-5-(diphenylmethylene)-7-methoxy-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3fa): pale yellow solid, isolated yield 98% (95.17 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 156.3-159.9 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.42-7.37 (m, 5H), 7.34-7.21 (m, 11H), 5.97 (s, 1H), 5.16 (d, *J* = 14.0 Hz, 1H), 5.03 (d, *J* = 14.0 Hz, 1H), 3.54 (m, 4H), 3.01 (d, *J* = 15.0 Hz, 1H), 1.47 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.6, 164.7, 160.0 143.1, 141.5, 141.5, 140.5, 140.3, 137.3, 134.7, 129.6, 129.0, 128.9, 128.7, 128.3, 128.1, 127.9, 127.5, 127.3, 123.1, 116.1, 110.7, 55.5, 48.6, 45.5, 43.7, 30.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}NO_3^+$ 480.2064; found 480.2075.

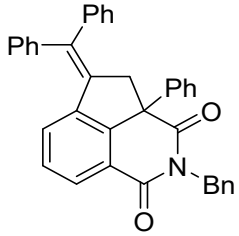


2-benzyl-5-(diphenylmethylene)-3a,8-dimethyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ga): pale yellow solid, isolated yield 92% (86.40 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 160.1-162.4 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.42-7.21 (m, 15H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 5.18 (d, *J* = 14.0 Hz, 1H), 5.00 (d, *J* = 14.0 Hz, 1H), 3.53 (d, *J* = 15.0 Hz, 1H), 2.98 (d, *J* = 15.0 Hz, 1H), 2.61 (s, 3H), 1.47 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.2, 165.2, 151.2, 141.8, 140.3, 139.1, 137.5, 136.8,

134.6, 131.3, 129.7, 129.1, 128.9, 128.8, 128.6, 128.3, 128.1, 127.7, 127.3, 127. 3, 120.8, 49.5, 45.1, 43.5, 30.2, 20.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{28}NO_2^+$ 470.2115; found 470.2118.

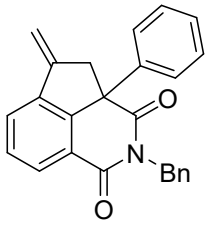


2-benzyl-5-(diphenylmethylene)-3a,6-dimethyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ha): pale yellow solid, isolated yield 77% (72.32mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 200.6-205.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.0 Hz, 1H), 7.47-7.26 (m, 14H), 7.09-7.04 (m, 2H), 5.20 (d, *J* = 14.0 Hz, 1H), 5.08 (d, *J* = 14.0 Hz, 1H), 3.46 (d, *J* = 13.0 Hz, 1H), 2.98 (d, *J* = 13.5 Hz, 1H), 1.59 (s, 3H), 1.45 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.5, 165.0, 150.8, 143.1, 143.0, 142.0, 140.5, 138.5, 137.4, 135.9, 131.5, 130.8, 123.0, 129.7, 129.0, 128.7, 128.3, 128.1, 127.7, 127.5, 127.3, 126.4, 120.4, 49.6, 49.5, 43.5, 27.9, 20.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{28}NO_2^+$ 470.2115; found 470.2125.

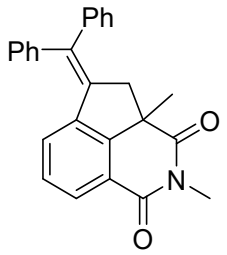


2-benzyl-5-(diphenylmethylene)-3a-phenyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ia): white solid, isolated yield 84% (86.96 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 214.4-220.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 7.5 Hz, 1H), 7.36-7.38 (m, 3H), 7.28-7.09 (m, 14H), 7.05 (d, *J* = 6.5 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.54 (d, *J* = 7.5 Hz, 1H), 5.04 (d, *J* = 14.5 Hz, 1H), 4.93 (d, *J* = 14.5 Hz, 1H), 3.94 (d, *J* = 15.0 Hz, 1H), 3.34 (d, *J* = 15.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 175.3, 164.8, 146.5, 141.7, 141.6, 141.5, 141.0, 140.1, 136.8, 134.3, 129.6, 129.3, 129.1, 128.9, 128.9, 128.7, 128.2, 128.0, 128.0, 127.9, 127.8, 127.5, 127.0, 126.3, 126.1, 124.9, 57.5,

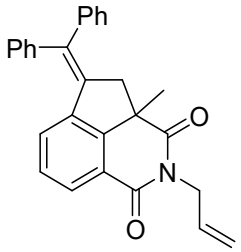
47.5, 43.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{37}H_{28}NO_2^+$ 518.2115; found 518.2123.



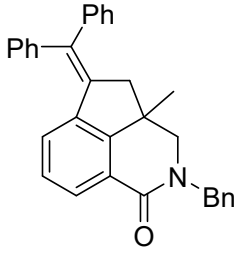
2-benzyl-5-methylene-3a-phenyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ih): white liquid, isolated yield 31% (22.66 mg); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.21-7.09 (m, 6H), 7.04 (d, J = 7.5 Hz, 2H), 6.86 (d, *J* = 7.5 Hz, 2H), 5.57 (d, *J* = 2.5 Hz, 1H), 5.19 (d, *J* = 2.5 Hz, 1H), 4.99 (q, *J* = 14.0 Hz, 2H), 3.61 (dt, *J* = 15.5, 2.5 Hz, 1H), 3.21 (d, *J* = 15.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 175.0, 164.7, 145.7, 144.3, 141.8, 140.0, 136.7, 129.6, 128.7, 128.1, 128.0, 127.8, 127.0, 126.9, 126.1, 125.6, 125.3, 108.3, 57.6, 45.8, 44.0. HRMS (ESI-TOF) m/z: [M+H]+ Calcd for $C_{25}H_{20}NO_2^+$ 366.1489; found 366.1495.



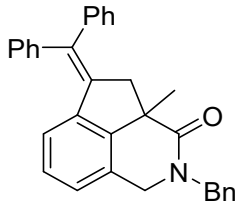
5-(diphenylmethylene)-2,3a-dimethyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ja): white solid, isolated yield 85% (64.51 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 164.2-167.6 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 7.5 Hz, 1H), 7.40-7.38 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 5H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 3.50 (d, *J* = 15.0 Hz, 1H), 3.32 (s, 3H), 3.03 (d, *J* = 15.0 Hz, 1H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.7, 165.1, 150.6, 141.7, 141.6, 140.3, 139.0, 134.7, 129.6, 129.3, 129.1, 128.9, 128.2, 128.1, 127.8, 127.5, 126.0, 122.8, 49.2, 45.3, 30.2, 27.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}NO_2^+$ 380.1645; found 380.1649.



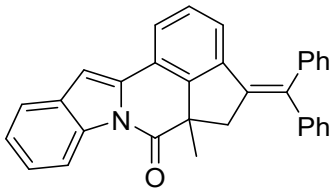
2-allyl-5-(diphenylmethylene)-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3ka): white solid, isolated yield 42% (34.06 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 162.3-167.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.0 Hz, 1H), 7.39-7.25 (m, 11H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 5.83-5.89 (m, 1H), 5.25-5.15 (m, 2H), 4.61 (dd, *J* = 14.5, 6.0 Hz, 1H), 4.46 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.52 (d, *J* = 15.0 Hz, 1H), 3.02 (d, *J* = 15.0 Hz, 1H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.1, 164.6, 150.6, 141.7, 141.6, 140.4, 139.1, 134.8, 132.3, 129.6, 129.4, 129.1, 129.0, 128.3, 128.2, 127.9, 127.5, 126.1, 122.9, 117.6, 49.3, 45.3, 42.4, 30.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{24}NO_2^+$ 406.1802; found 406.1809.



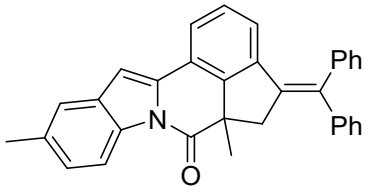
2-benzyl-5-(diphenylmethylene)-3a-methyl-3,3a,4,5-tetrahydrocyclopenta[*de*]isoquinolin-1(2*H*)-one (3la): white solid, isolated yield 72% (63.59 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 165.9-169.7 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.5 Hz, 1H), 7.36-7.20 (m, 15H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 4.84 (d, *J* = 14.5 Hz, 1H), 4.70 (d, *J* = 14.5 Hz, 1H), 3.57 (d, *J* = 12.0 Hz, 1H), 3.30 (d, *J* = 12.0 Hz, 1H), 2.96 (d, *J* = 14.5 Hz, 1H), 2.69 (d, *J* = 14.5 Hz, 1H), 1.16 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 163.8, 153.2, 142.4, 141.9, 138.4, 138.2, 137.3, 137.1, 129.7, 129.0, 128.8, 128.5, 127.9, 127.5, 127.5, 127.4, 127.0, 125.6, 125.4, 58.1, 50.9, 48.3, 39.5, 24.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{28}NO^+$ 442.2165; found 442.2168.



2-benzyl-5-(diphenylmethylene)-3a-methyl-1,3a,4,5-tetrahydrocyclopenta[*de*]isoquinolin-3(2*H*)-one (3ma): pale yellow liquid, isolated yield 59% (52.10 mg); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.36-7.23 (m, 15H), 6.85 (s, 2H), 6.20 (d, *J* = 5.6 Hz, 1H), 4.83 (d, *J* = 15.0 Hz, 1H), 4.68-4.58 (m, 2H), 4.16 (d, *J* = 15.5 Hz, 1H), 3.61 (d, *J* = 15.5 Hz, 1H), 2.97 (d, *J* = 15.5 Hz, 1H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.9, 147.1, 142.1, 142.0, 138.7, 138.2, 136.9, 136.6, 129.7, 129.0, 128.5, 128.5, 127.8, 127.5, 127.2, 127.1, 126.8, 126.7, 123.7, 122.9, 50.1, 49.7, 47.6, 45.9, 23.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{28}NO^+$ 442.2165; found 442.2170.

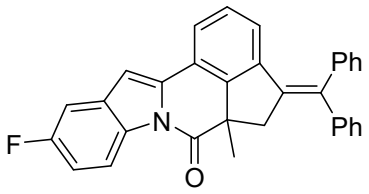


4-(diphenylmethylene)-5a-methyl-5,5a-dihydrocyclopenta[*de*]indolo[2,1-*a*]isoquinolin-6(4*H*)-one (5aa): white solid, isolated yield 62% (54.21 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 231.3-235.5 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.44 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.43-7.28 (m, 13H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.23 (d, *J* = 7.5 Hz, 1H), 3.60 (d, *J* = 14.5 Hz, 1H), 3.07 (d, *J* = 15.0 Hz, 1H), 1.56 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.3, 146.2, 142.1, 142.0, 139.7, 139.2, 136.3, 135.8, 135.5, 130.6, 129.8, 129.2, 128.8, 128.2, 128.1, 127.7, 127.3, 125.5, 124.6, 124.0, 123.0, 121.9, 120.6, 115.8, 103.4, 50.7, 44.8, 29.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{24}NO^+$ 438.1852; found 438.1854.

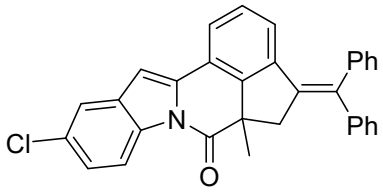


4-(diphenylmethylene)-5a,10-dimethyl-5,5a-dihydrocyclopenta[*de*]indolo[2,1-

***a*]isoquinolin-6(4*H*)-one (5ba):** pale yellow solid, isolated yield 66% (38.17 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 231.7-234 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 8.5 Hz, 1H), 7.37-7.28 (m, 12H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.81 (s, 1H), 6.20 (d, *J* = 8.5 Hz, 1H), 3.55 (d, *J* = 15.0 Hz, 1H), 3.04 (d, *J* = 15.0 Hz, 1H), 2.43 (s, 3H), 1.52 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.9, 146.2, 142.1, 142.0, 139.6, 139.1, 136.3, 135.9, 133.6, 133.5, 130.7, 129.8, 129.1, 128.8, 128.1, 127.6, 127.3, 126.7, 124.4, 123.0, 121.8, 120.6, 115.4, 103.2, 50.5, 44.8, 29.0, 21.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{26}NO^+$ 452.2009; found 452.2016.

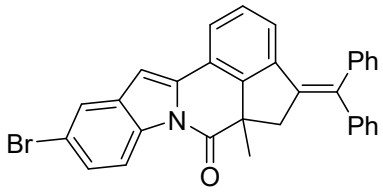


4-(diphenylmethylene)-10-fluoro-5a-methyl-5,5a-dihydrocyclopenta[de]indolo[2,1-*a*]isoquinolin-6(4*H*)-one (3ca): pale yellow solid, isolated yield 42% (38.26 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: > 250 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 7.39-7.19 (m, 11H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.05-7.00 (m, 2H), 6.86 (s, 1H), 6.23 (d, *J* = 7.0 Hz, 1H), 3.57 (d, *J* = 15.0 Hz, 1H), 3.05 (d, *J* = 15.0 Hz, 1H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.0, 159.9 (d, C-F, $^1J_{C\text{-}F}$ = 238.8 Hz), 146.4, 142.0 (d, C-F, $^3J_{C\text{-}F}$ = 12.8 Hz), 139.9, 139.2, 137.8, 135.6, 131.8,131.6 (d, C-F, $^3J_{C\text{-}F}$ = 10.0 Hz), 129.8, 129.1, 128.9, 128.3, 128.2, 127.7, 127.4, 124.9, 122.6, 122.0, 116.7 (d, C-F, $^3J_{C\text{-}F}$ = 8.9 Hz), 113.0 (d, C-F, $^2J_{C\text{-}F}$ = 24.5 Hz), 106.1, 102.9 (d, C-F, $^4J_{C\text{-}F}$ = 4 Hz), 50.5, 44.8, 29.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{33}H_{23}FNO^+$ 456.1758; found 456.1768.

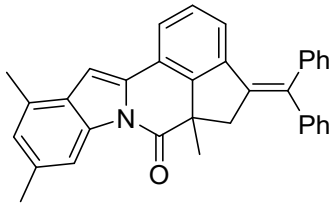


10-chloro-4-(diphenylmethylene)-5a-methyl-5,5a-dihydrocyclopenta[*de*]indolo[2,1-*a*]isoquinolin-6(4*H*)-one (5da): pale yellow solid, isolated yield 50% (47.20 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: > 250 °C

(uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.34 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.41-7.39 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.31-7.26 (m, 7H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.25 (d, *J* = 7.5 Hz, 1H), 3.58 (d, *J* = 14.5 Hz, 1H), 3.06 (d, *J* = 14.5 Hz, 1H), 1.56 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =174.1, 146.3, 142.0, 141.9, 140.0, 139.3, 137.6, 135.6, 133.8, 131.8, 129.8, 129.1, 128.9, 128.3, 128.2, 127.7, 127.4, 125.5, 125.0, 122.5, 122.1, 120.2, 116.7, 102.4, 50.6, 44.8, 29.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{23}ClNO^+$ 472.1468; found 472.1496.

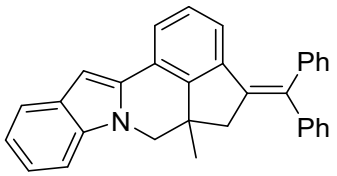


10-bromo-4-(diphenylmethylene)-5a-methyl-5,5a-dihydrocyclopenta[*de*]indolo[2,1-*a*]isoquinolin-6(4*H*)-one (5ea): yellow solid, isolated yield 36% (37.18 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 236.7-240.1 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.28 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.39-7.29 (m, 12H), 7.00 (s, 1H), 6.84 (s, 1H), 6.24 (d, *J* = 7.5 Hz, 1H), 3.57 (d, *J* = 14.5 Hz, 1H), 3.05 (d, *J* = 14.5 Hz, 1H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.1, 146.3, 142.0, 141.9, 140.0, 139.3, 137.5, 135.6, 134.2, 132.3, 129.8, 129.1, 128.9, 128.3, 128.2, 127.7, 127.4, 125.0, 123.2, 122.4, 122.1, 117.3, 117.1, 102.2, 50.6, 44.8, 29.1. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{32}H_{22}BrNO^+$ 515.0885; found 515.0880.

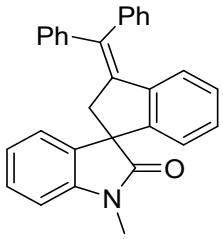


4-(diphenylmethylene)-5a,9,11-trimethyl-5,5a-dihydrocyclopenta[*de*]indolo[2,1-*a*]isoquinolin-6(4*H*)-one (5fa): pale yellow solid, isolated yield 55% (51.22 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: > 250 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.11 (s, 1H), 7.39-7.25 (m, 11H), 7.00-6.93 (m, 3H), 6.20 (d, *J* = 7.5 Hz, 1H), 3.59 (d, *J* = 15.0 Hz, 1H), 3.05 (d, *J* = 15.0 Hz, 1H), 2.52 (s, 3H), 2.46 (s, 3H), 1.54 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.3, 146.0, 142.2, 142.1, 139.6, 139.1,

136.0, 135.9, 135.7, 135.2, 129.8, 129.7, 129.2, 128.8, 128.2, 127.8, 127.6, 127.3, 126.0, 124.2, 123.3, 121.7, 113.5, 102.0, 50.7, 44.8, 29.0, 21.9, 18.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{28}NO^+$ 466.2165; found 466.2176.

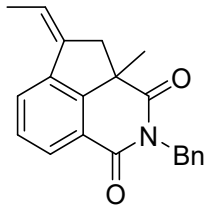


4-(diphenylmethylene)-5a-methyl-4,5,5a,6-tetrahydrocyclopenta[*de*]indolo[2,1-*a*]isoquinoline (5ga): yellow solid, isolated yield 65% (55.06 mg); (eluent: petroleum ether/EtOAc = 10:1); mp: 224.6-228.2 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 7.5 Hz, 1H), 7.40-7.30 (m, 11H), 7.24 (s, 1H), 7.21 (s, 1H), 7.10 (s, 1H), 6.96 (s, 1H), 6.87 (s, 1H), 6.24 (d, *J* = 7.5 Hz, 1H), 4.43 (d, *J* = 11.0 Hz, 1H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.21 (d, *J* = 14.5 Hz, 1H), 2.89 (d, *J* = 14.5 Hz, 1H), 1.21 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 147.5, 142.8, 142.2, 138.8, 138.1, 137.8, 137.3, 134.2, 129.9, 129.2, 129.0, 128.8, 128.0, 127.8, 127.5, 127.0, 125.6, 123.9, 122.0, 121.8, 120.8, 119.8, 108.9, 96.9, 52.4, 48.1, 41.8, 24.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO^+$ 424.2060; found 424.2067.

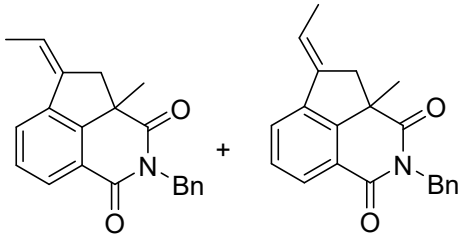


3-(diphenylmethylene)-1'-methyl-2,3-dihydrospiro[indene-1,3'-indolin]-2'-one: white solid, isolated yield 58% (47.97 mg); (eluent: petroleum ether/EtOAc = 15:1); mp: 210.2-212.3 °C (uncorrected); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.39-7.34 (m, 5H), 7.27-7.23 (m, 5H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.02-7.00 (m, 2H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 3.57 (d, *J* = 15.0 Hz, 1H), 3.25 (s, 3H), 3.17 (d, *J* = 15.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 178.9, 147.3, 143.1, 142.9, 142.1, 141.7, 137.2, 136.5, 134.1, 129.9, 129.2, 128.8, 128.2, 128.2, 128.0, 127.4, 127.3, 126.9, 125.4, 123.3, 123.1, 123.0, 108.0, 58.0, 46.5, 26.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for

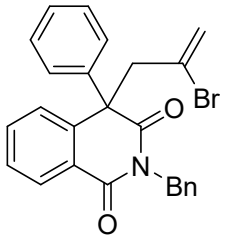
$C_{30}H_{24}NO^+$ 414.1852; found 414.1855.



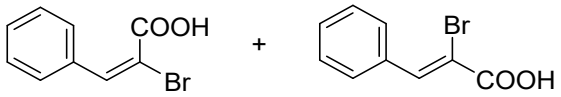
(*Z*)-2-benzyl-5-ethylidene-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione ((*Z*)-3at): white liquid, isolated yield 52% (33.01 mg); (eluent: petroleum ether/EtOAc = 15:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 3H), 7.30-7.21 (m, 4H), 5.91 (qd, *J* = 7.0, 2.5 Hz, 1H), 5.15 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.16 (d, *J* = 14.5 Hz, 1H), 2.77 (d, *J* = 14.5 Hz, 1H), 2.04 (dd, *J* = 7.5, 2.5 Hz, 3H), 1.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.4, 164.9, 150.8, 137.9, 137.4, 136.3, 129.1, 128.7, 128.4, 127.4, 125.9, 123.2, 122.3, 48.9, 44.6, 43.6, 29.7, 14.8.



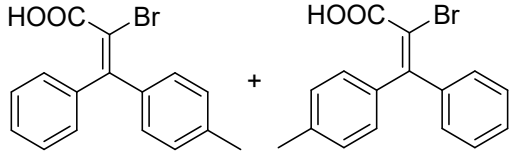
2-benzyl-5-ethylidene-3a-methyl-4,5-dihydrocyclopenta[*de*]isoquinoline-1,3(2*H*,3a*H*)-dione (3at): white liquid, isolated yield 53% (33.64 mg, *Z:E* = 4:1); (eluent: petroleum ether/EtOAc = 15:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.5Hz, 0.25H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 0.25H), 7.43-7.34 (m, 4H), 7.30-7.21 (m, 3H), 6.19 (qd, *J* = 7.0, 2.5 Hz, 0.25H), 5.91 (qd, *J* = 7.0, 2.5 Hz, 1H), 5.15 (d, *J* = 14.0 Hz, 1.25H), 5.06 (d, *J* = 14.0 Hz, 1.25H), 3.15 (d, *J* = 14.5 Hz, 1H), 3.02 (d, *J* = 15.0 Hz, 0.25H), 2.94 (d, *J* = 15.0 Hz, 0.25H), 2.77 (d, *J* = 14.5 Hz, 1H), 2.04 (dd, *J* = 7.0, 2.5 Hz, 3H), 1.87 (dd, *J* = 7.0, 1.5 Hz, 0.75H), 1.43 (s, 3.75H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.5, 177.4, 164.9, 150.8, 148.9, 139.0, 137.9, 137.4, 136.3, 129.0, 128.8, 128.7, 128.3, 127.3, 125.9, 125.8, 124.7, 123.2, 123.1, 122.3, 120.0, 49.4, 48.9, 44.6, 43.6, 43.6, 39.4, 31.0, 29.6, 15.2, 14.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}NO_2^+$ 318.1489; found 318.1499.



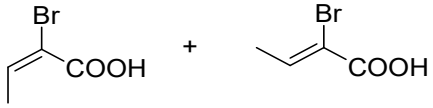
2-benzyl-4-(2-bromoallyl)-4-phenylisoquinoline-1,3(2*H*,4*H*)-dione (8) [11c]: white solid, isolated yield 87% (77.66 mg); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.34 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.34-7.33 (m, 2H), 7.24-7.17 (m, 6H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.06-7.04 (m, 2H), 5.27 (d, *J* = 14.0 Hz, 1H), 5.20-5.18 (m, 2H), 5.05 (d, *J* = 14.0 Hz, 1H), 4.28 (d, *J* = 14.5 Hz, 1H), 3.42 (d, *J* = 14.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.4, 164.0, 142.8, 140.7, 136.5, 133.7, 129.0, 128.9, 128.8, 128.4, 128.1, 127.9, 127.8, 127.3, 127.0, 126.8, 126.2, 121.8, 55.3, 49.5, 44.1.



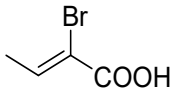
2-bromo-3-phenylacrylic acid (2r): white solid (*Z:E* = 1:1.3), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 10.95 (s, 2.3H), 8.33 (s, 1H), 7.89-7.89 (m, 2H), 7.52 (s, 1.3H), 7.44-7.42 (m, 3H), 7.33 (s, 7H).



2-bromo-3-phenyl-3-(*p*-tolyl)acrylic acid (2s): white solid (*Z:E* = 1:1), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.88-7.53 (m, 2H), 7.36-7.32 (m, 4H), 7.30-7.26 (m, 4H), 7.18-7.16 (m, 6H), 7.10-7.05 (m, 4H), 2.36 (s, 3H), 2.33 (s, 3H).



2-bromobut-2-enoic acid (2t): white solid (*Z:E* = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 10.72 (s, 1.1H), 7.56 (q, *J* = 7.0 Hz, 1H), 6.98 (q, *J* = 7.0 Hz, 1H), 2.11 (d, *J* = 7.5 Hz, 0.3H), 2.00 (d, *J* = 7.0 Hz, 3H).



(*Z*)-2-bromobut-2-enoic acid ((*Z*)-2t): white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.43 (s, 1H), 7.56 (q, *J* = 7.0 Hz, 1H), 2.01 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.7, 144.6, 116.6, 18.2.

7 References

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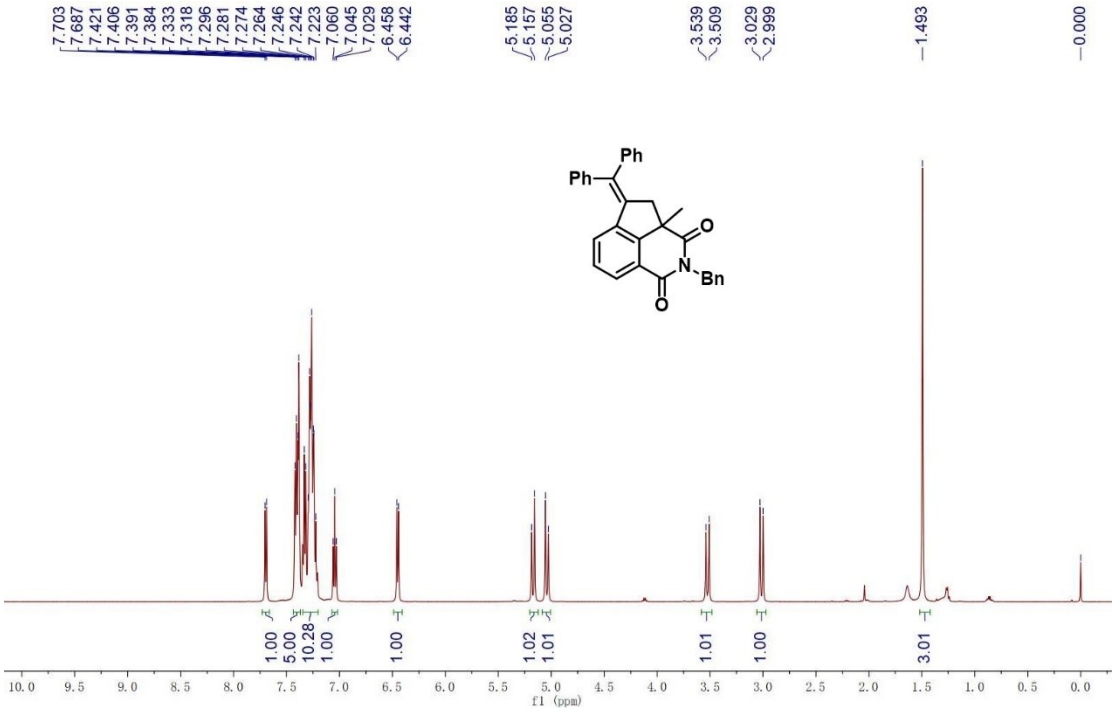
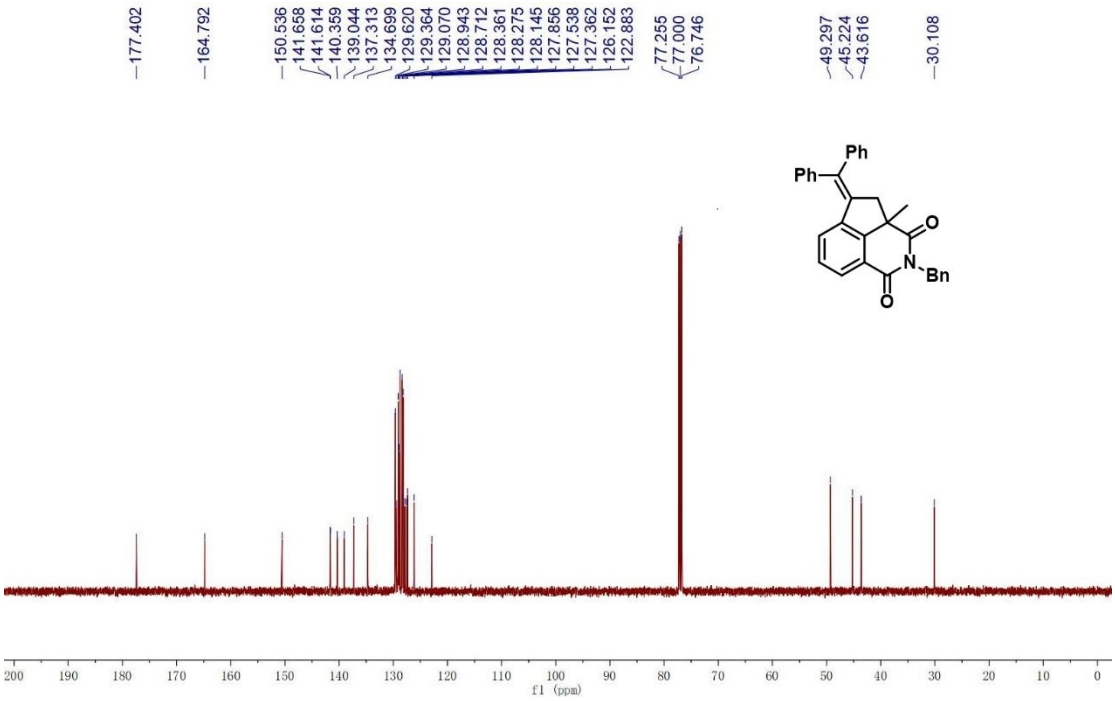
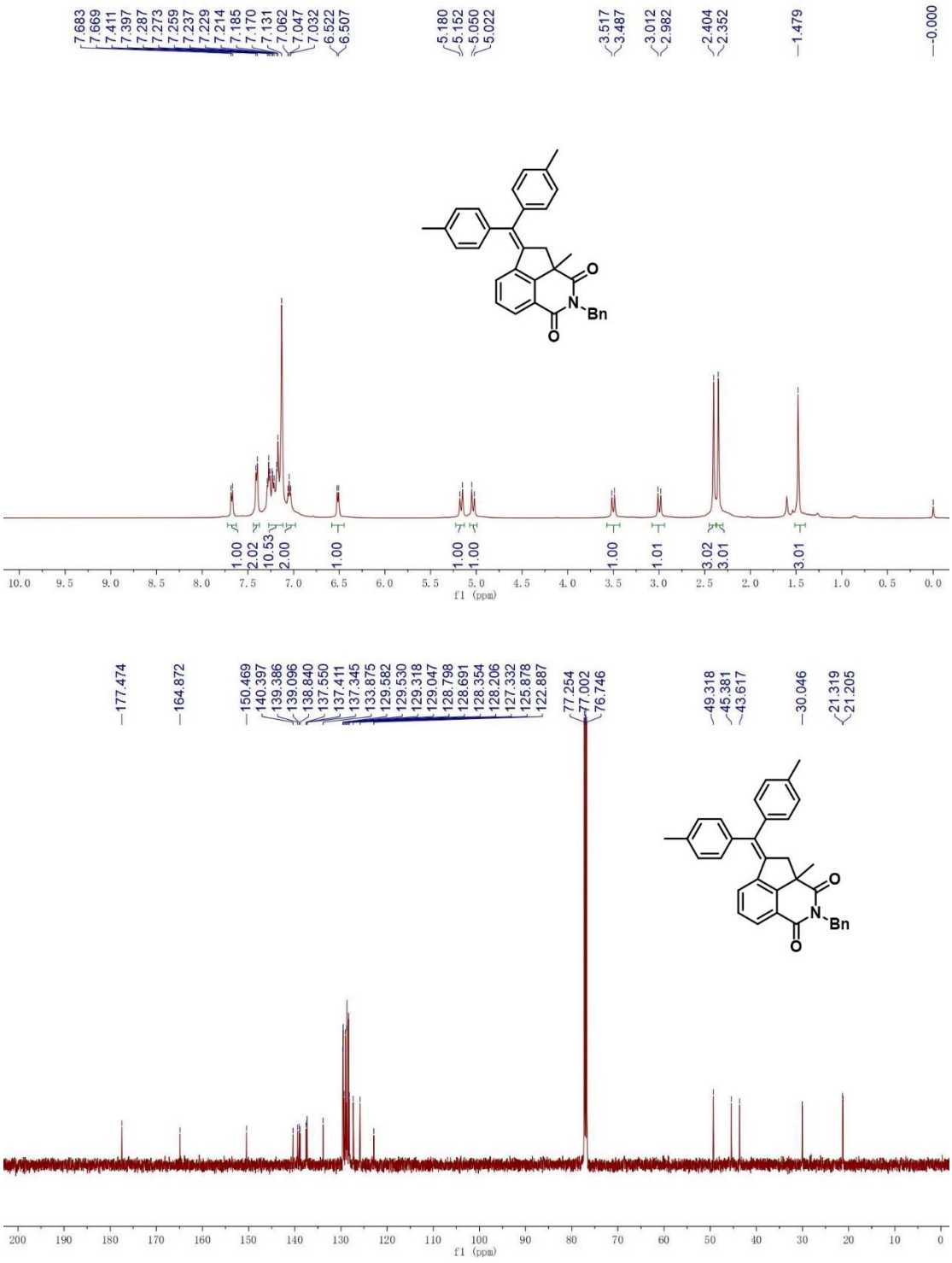
8 Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

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

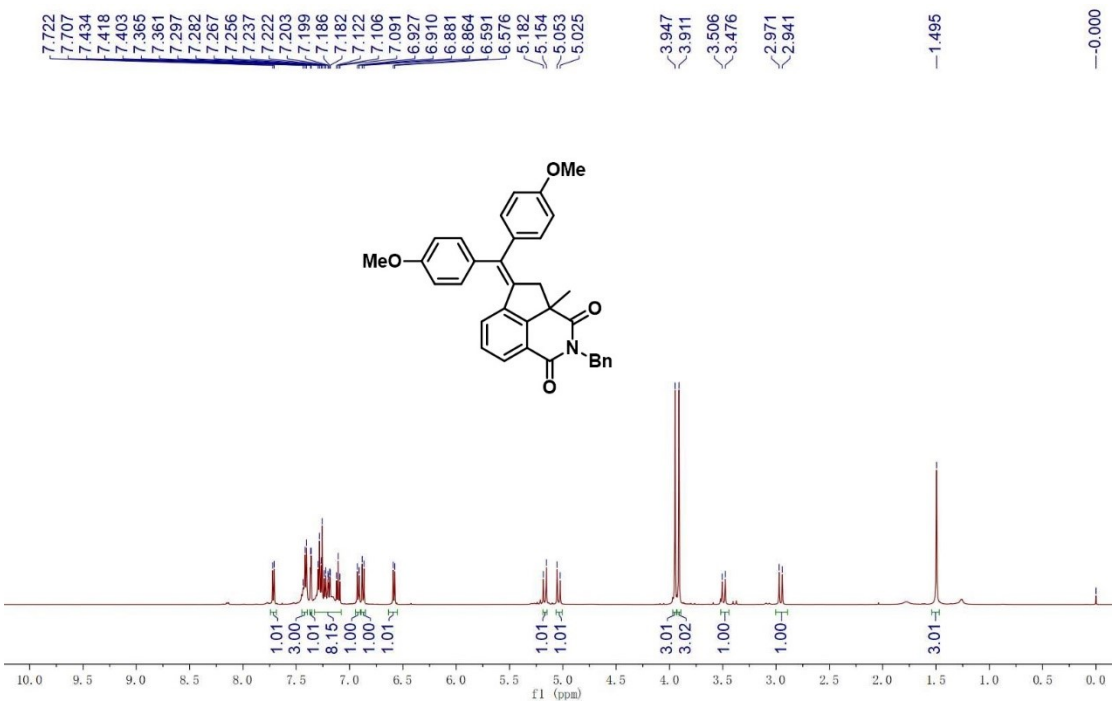


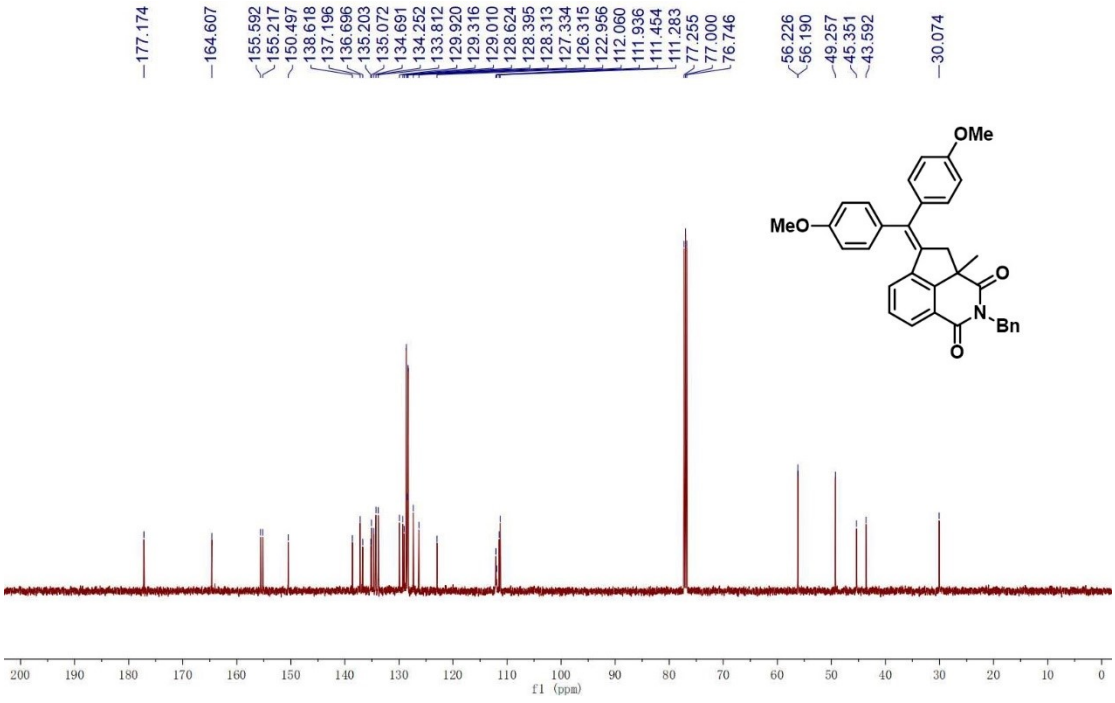


^{1}H NMR of **3ab** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ab** (125 MHz, $CDCl_3$)

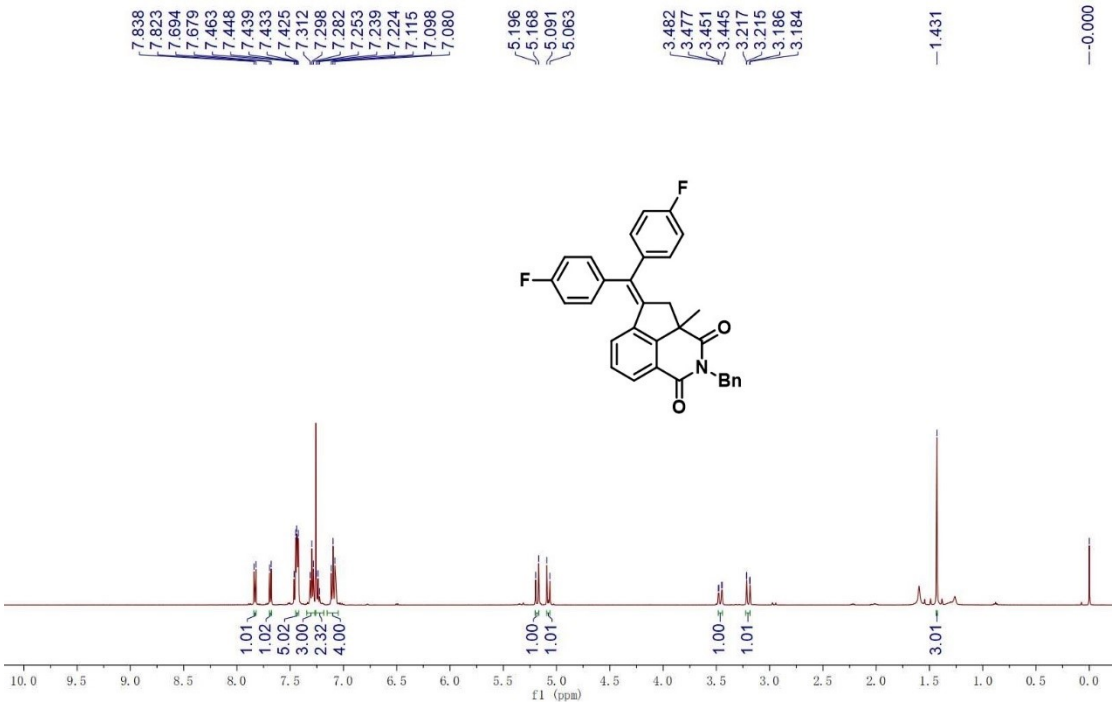


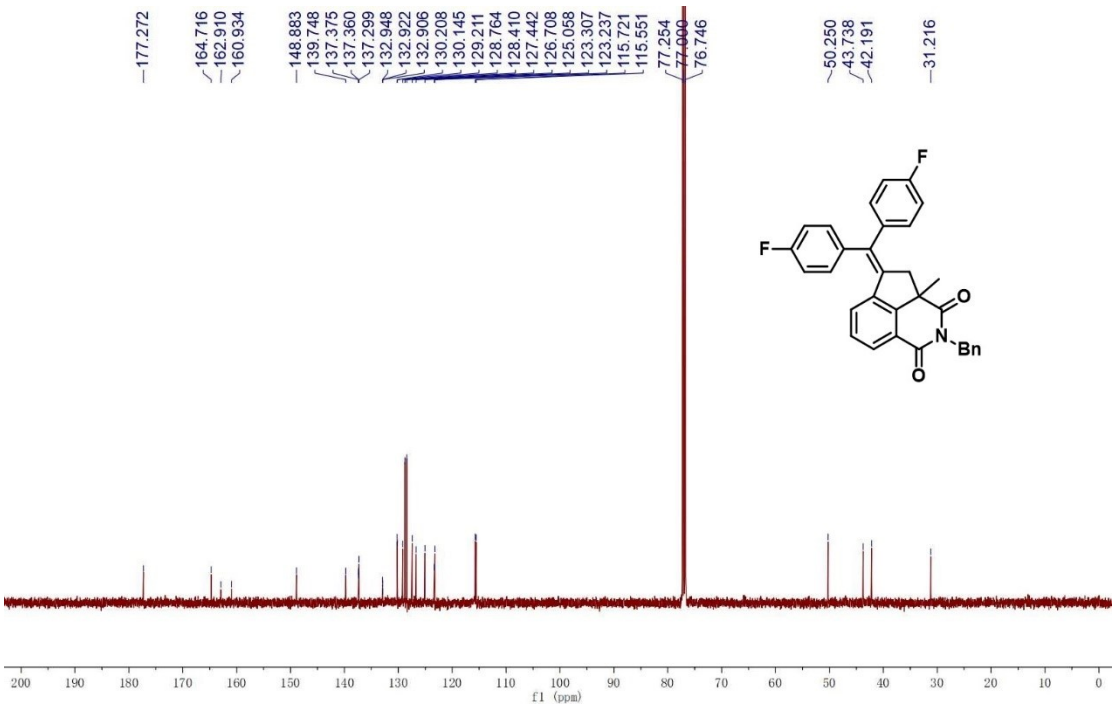
^{1}H NMR of **3ac** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ac** (125 MHz, $CDCl_3$)



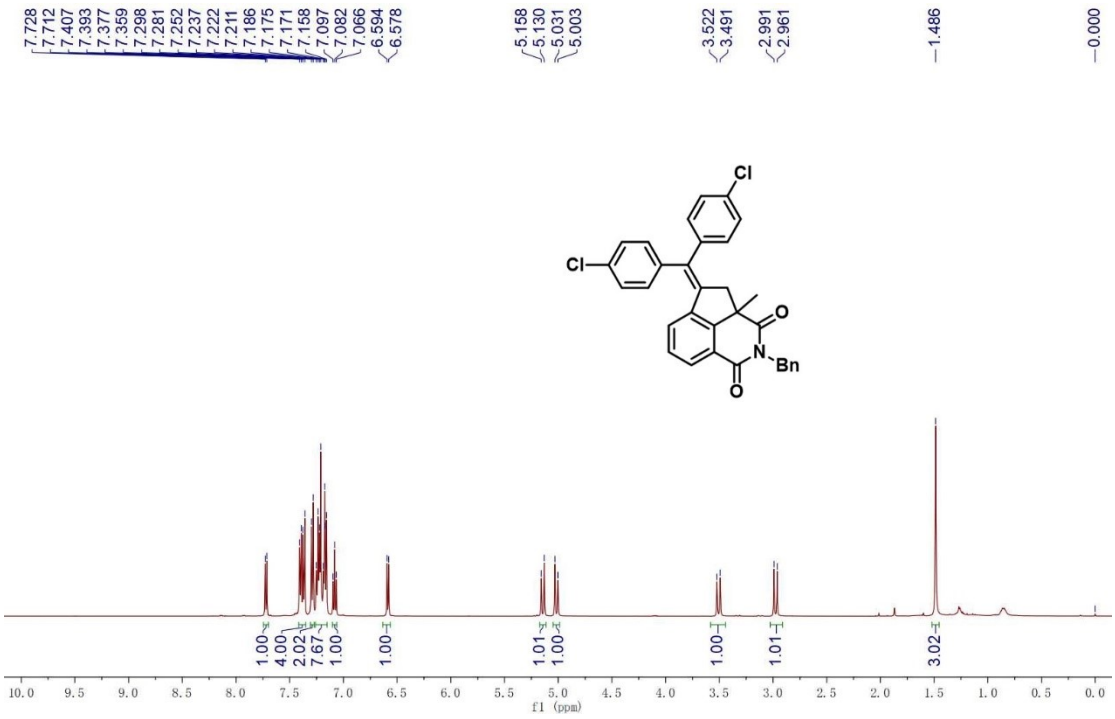


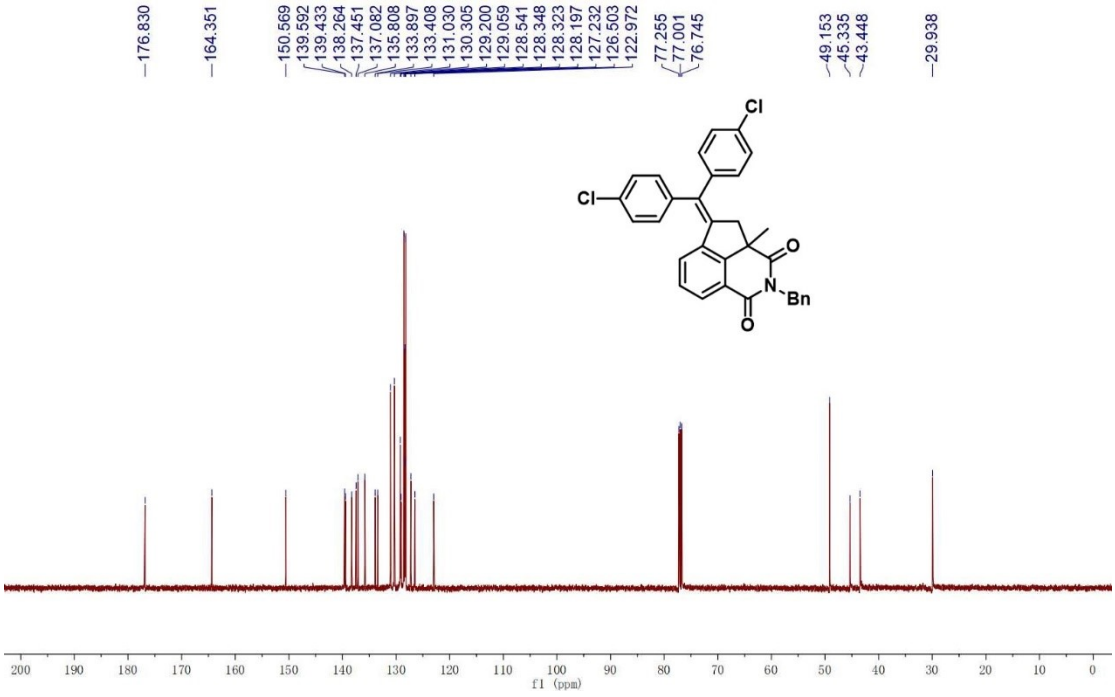
^{1}H NMR of **3ad** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ad** (125 MHz, $CDCl_3$)



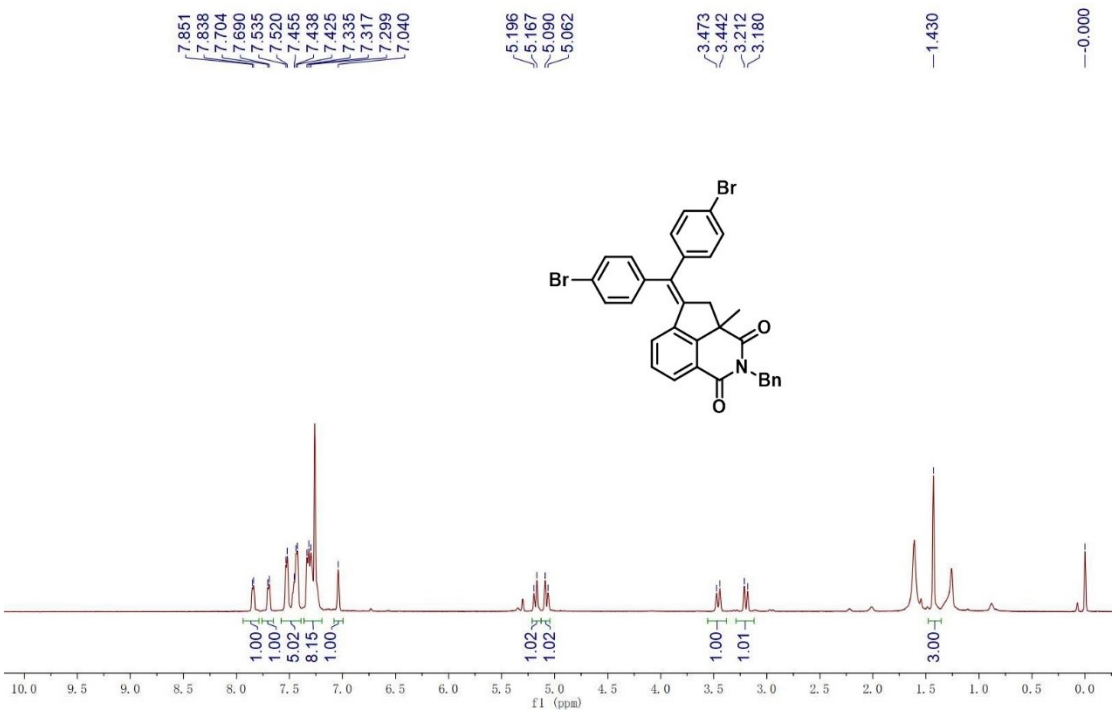


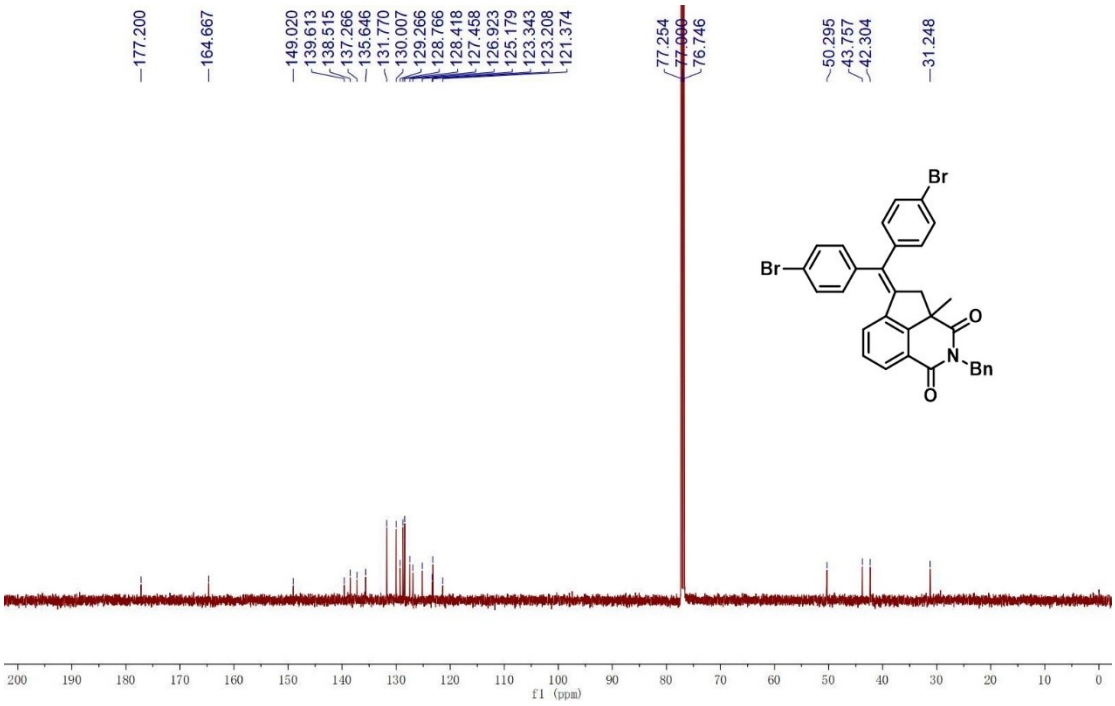
^{1}H NMR of **3ae** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ae** (125 MHz, $CDCl_3$)



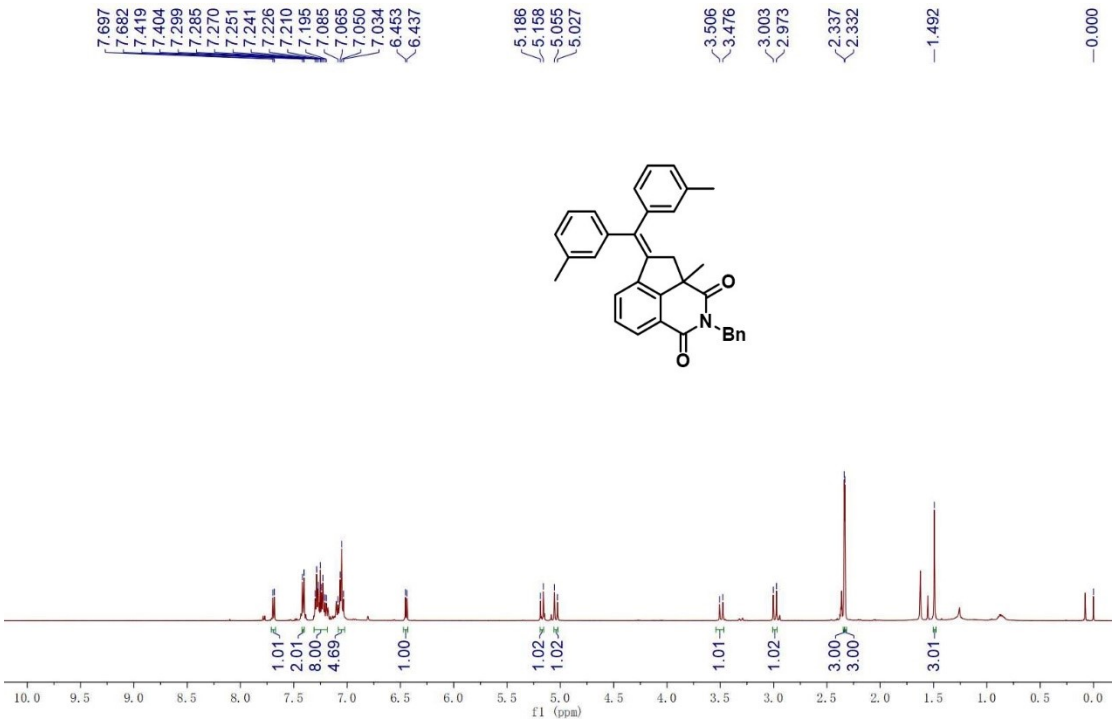


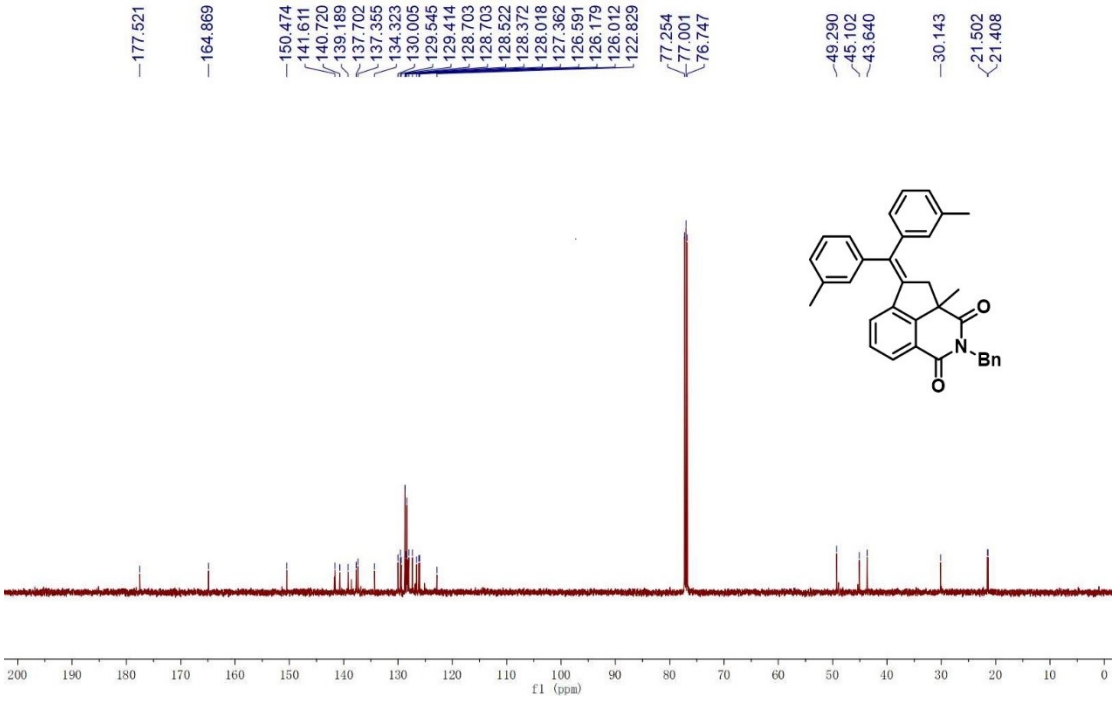
^{1}H NMR of **3af** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3af** (125 MHz, $CDCl_3$)



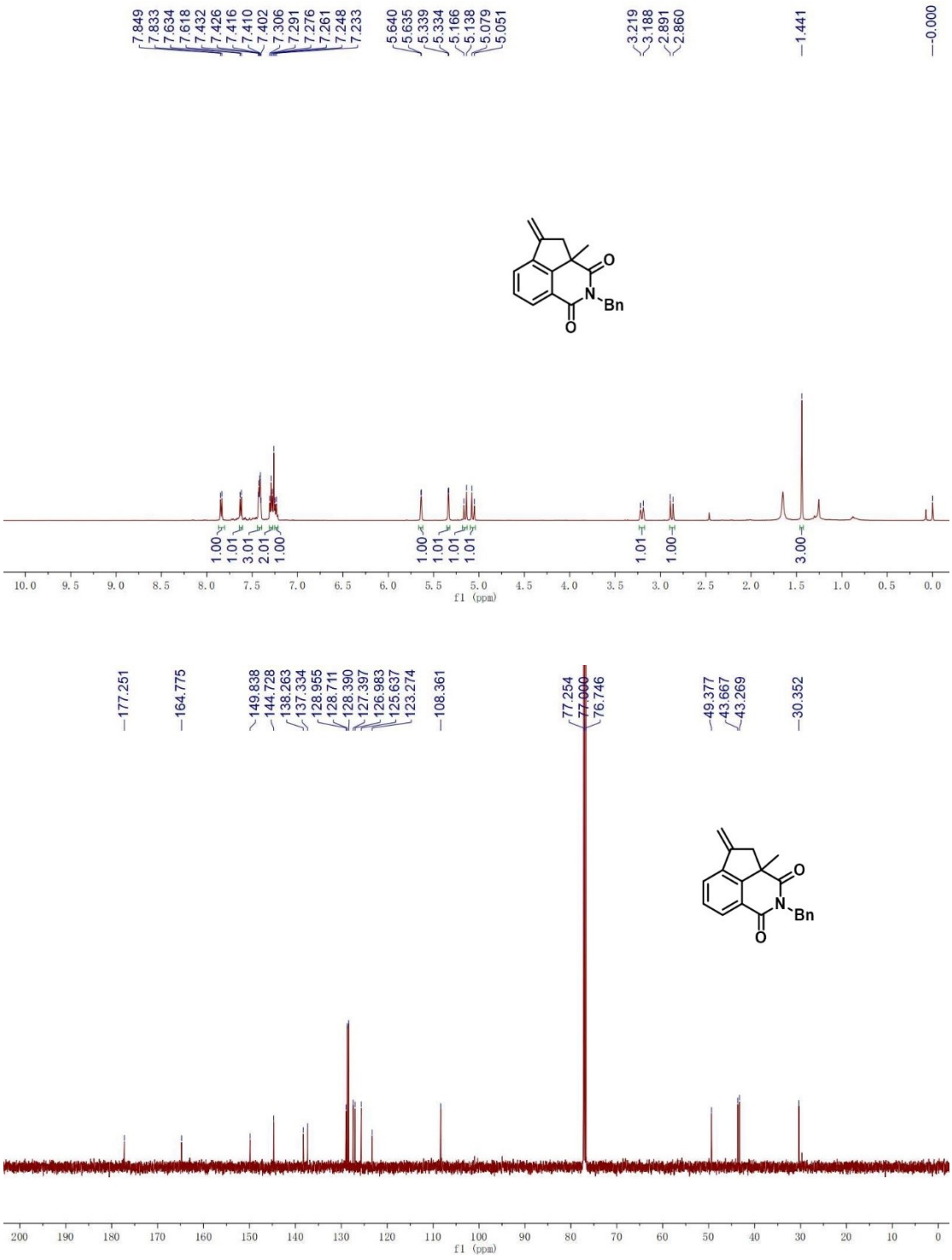


^{1}H NMR of **3ag** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ag** (125 MHz, $CDCl_3$)

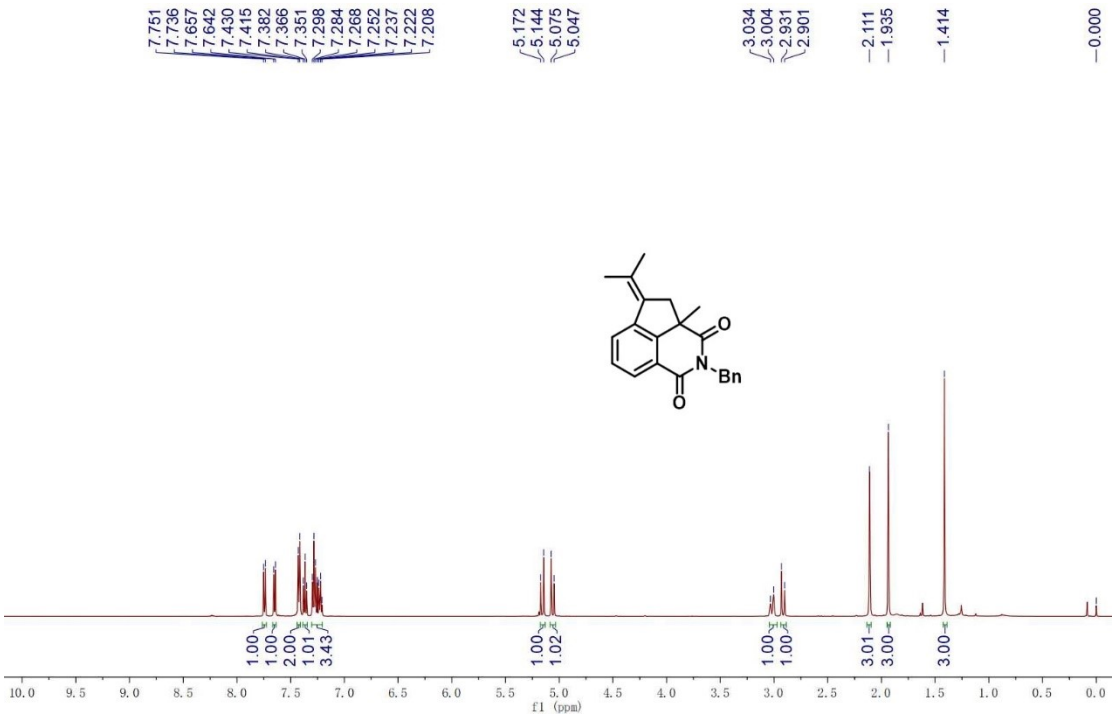


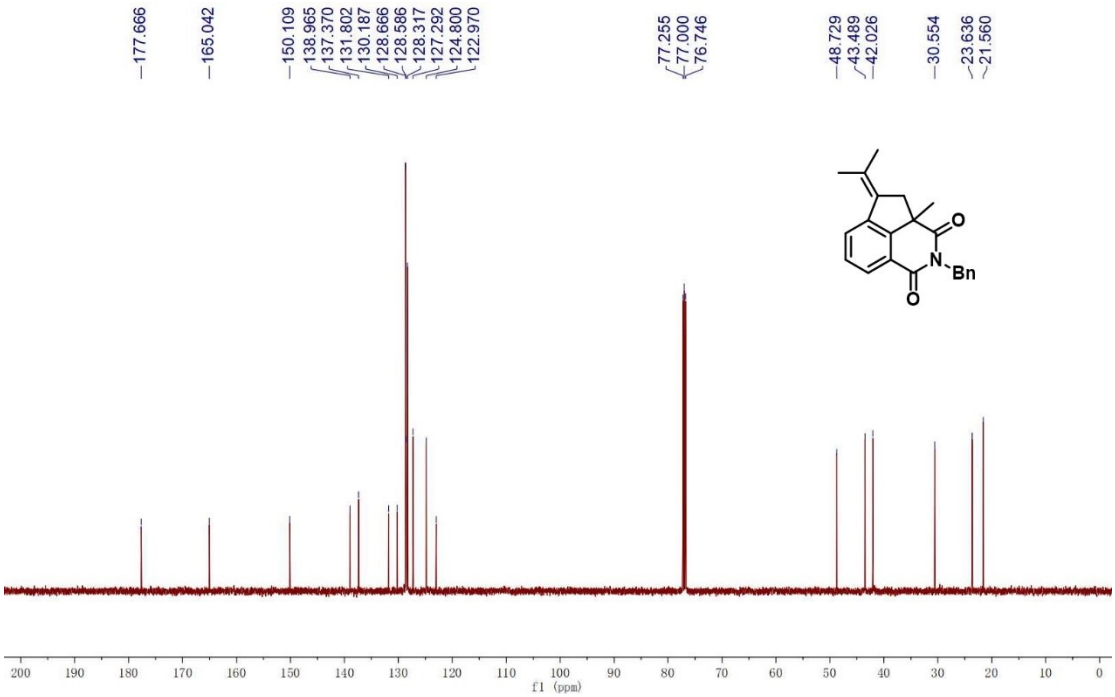


^{1}H NMR of **3ah**(500 MHz, $CDCl_3$) and ^{13}C NMR of **3ah** (125 MHz, $CDCl_3$)

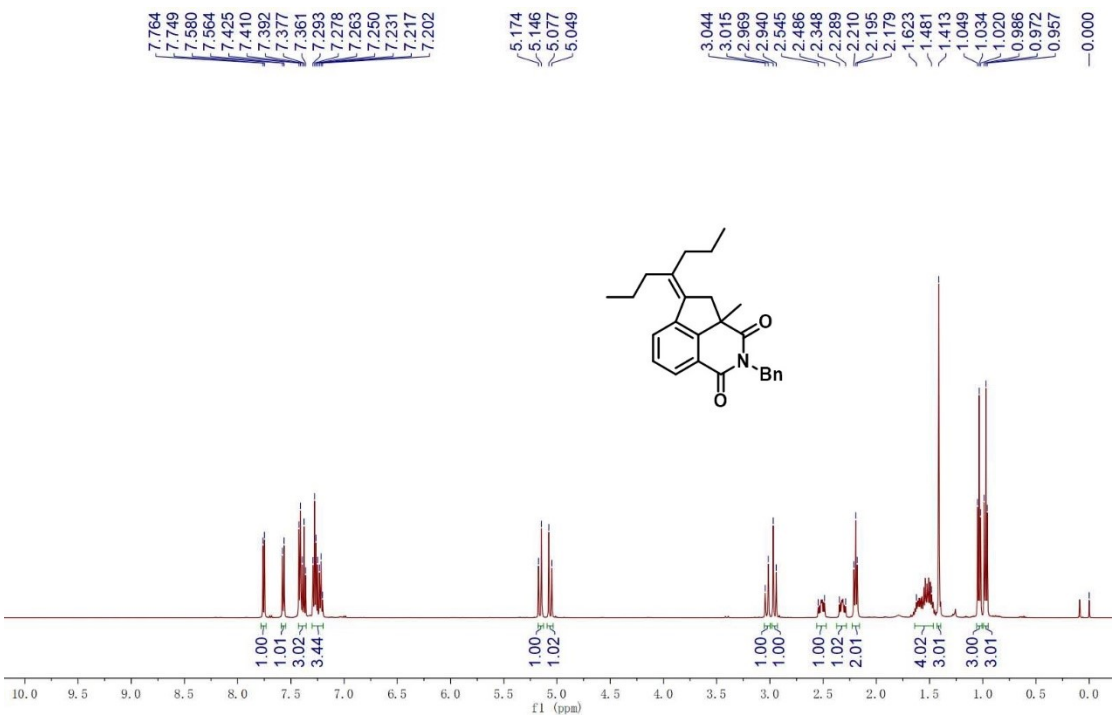


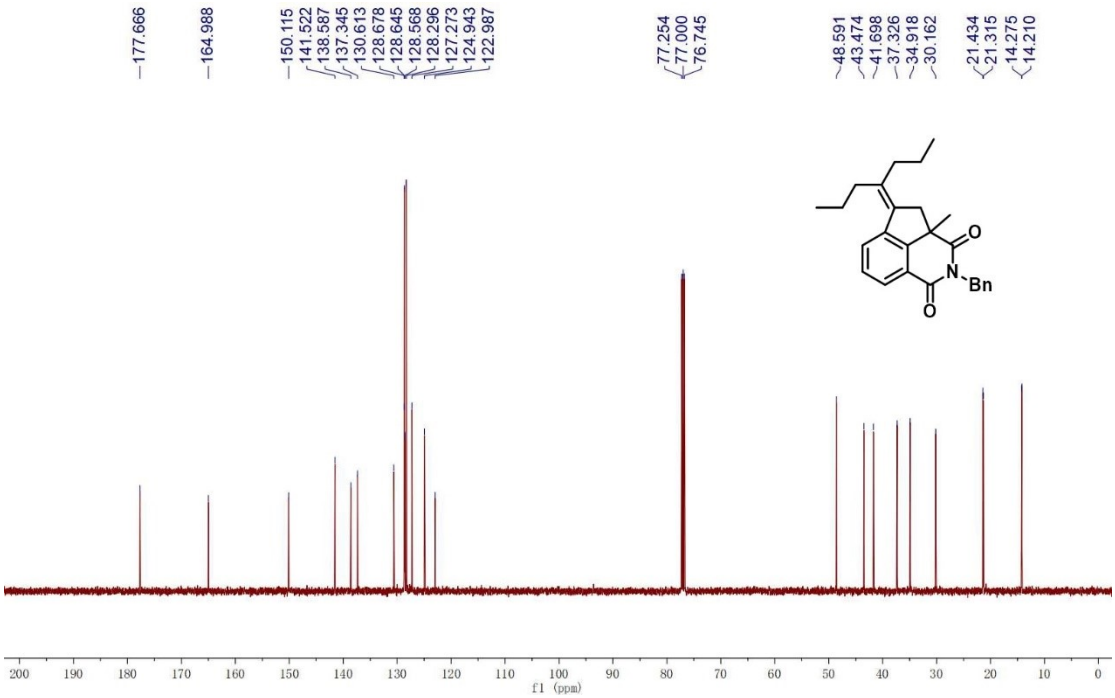
^{1}H NMR of **3ai** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ai** (125 MHz, $CDCl_3$)



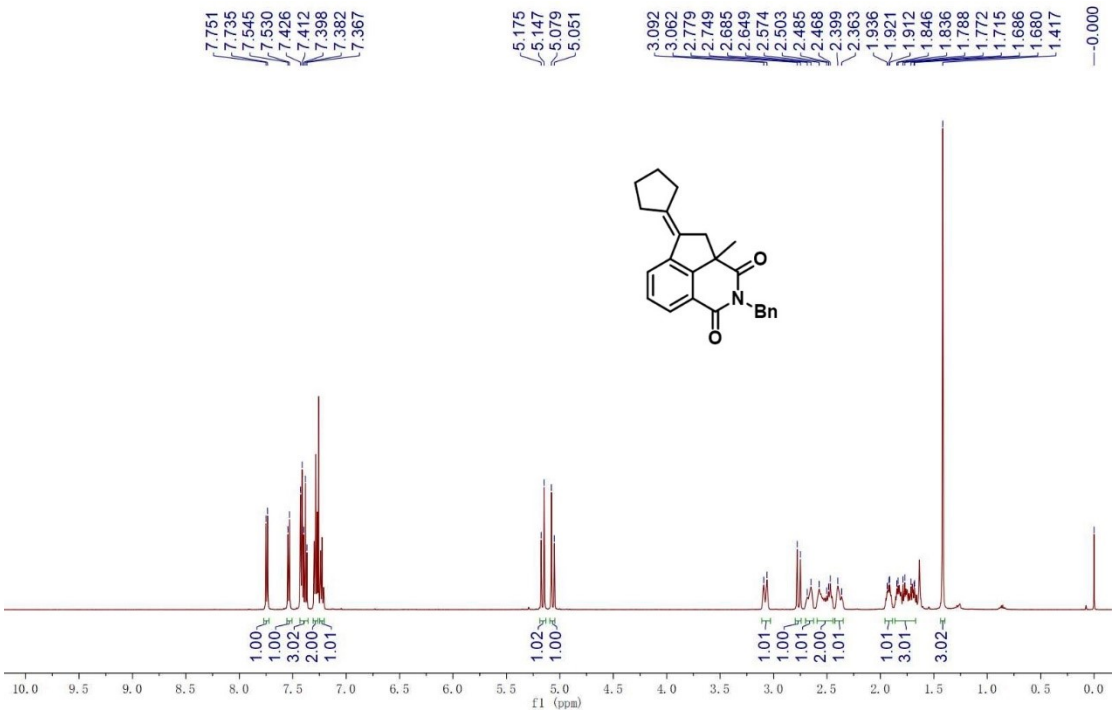


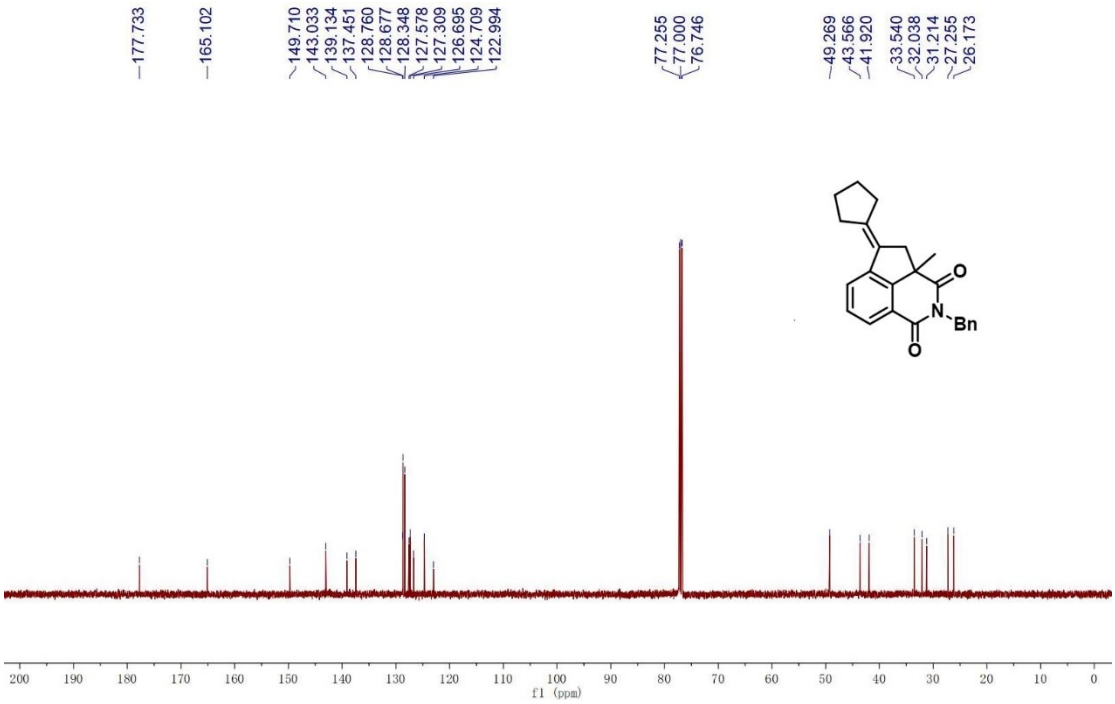
^{1}H NMR of **3aj** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aj** (125 MHz, $CDCl_3$)



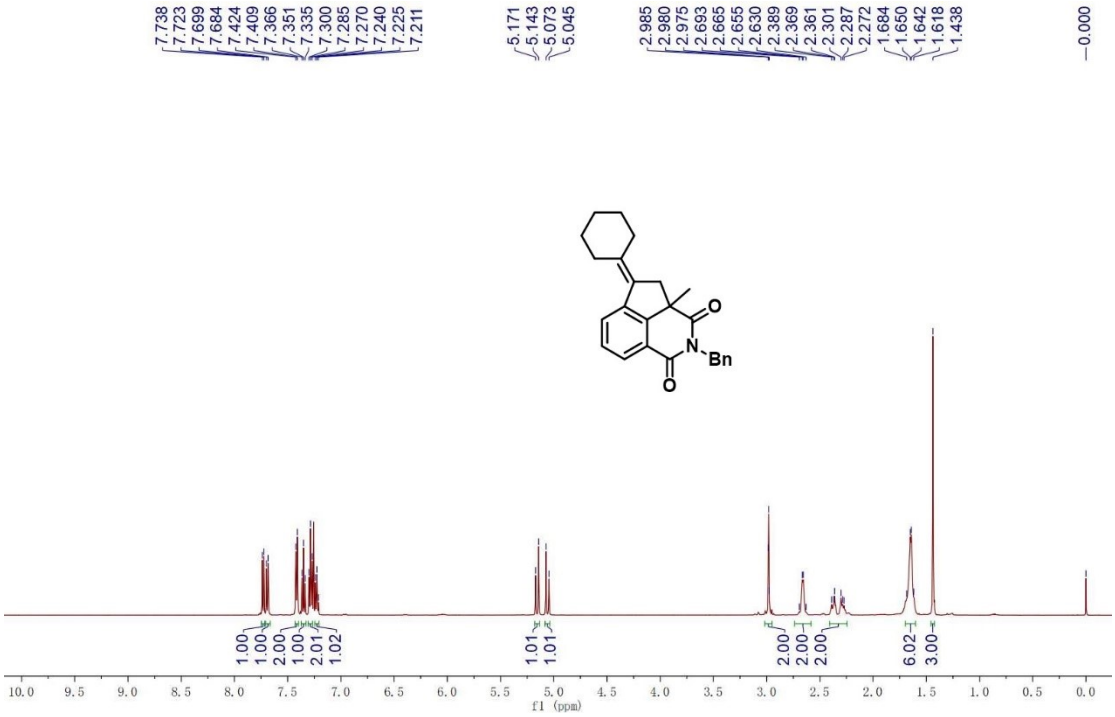


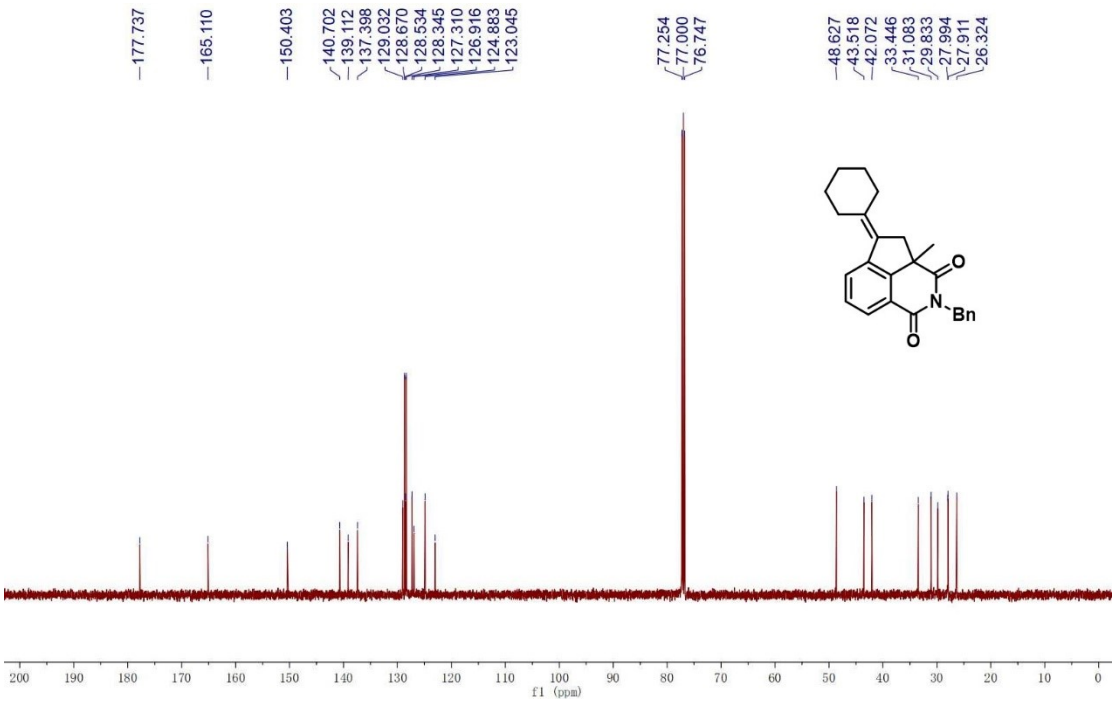
^{1}H NMR of **3ak** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ak** (125 MHz, $CDCl_3$)



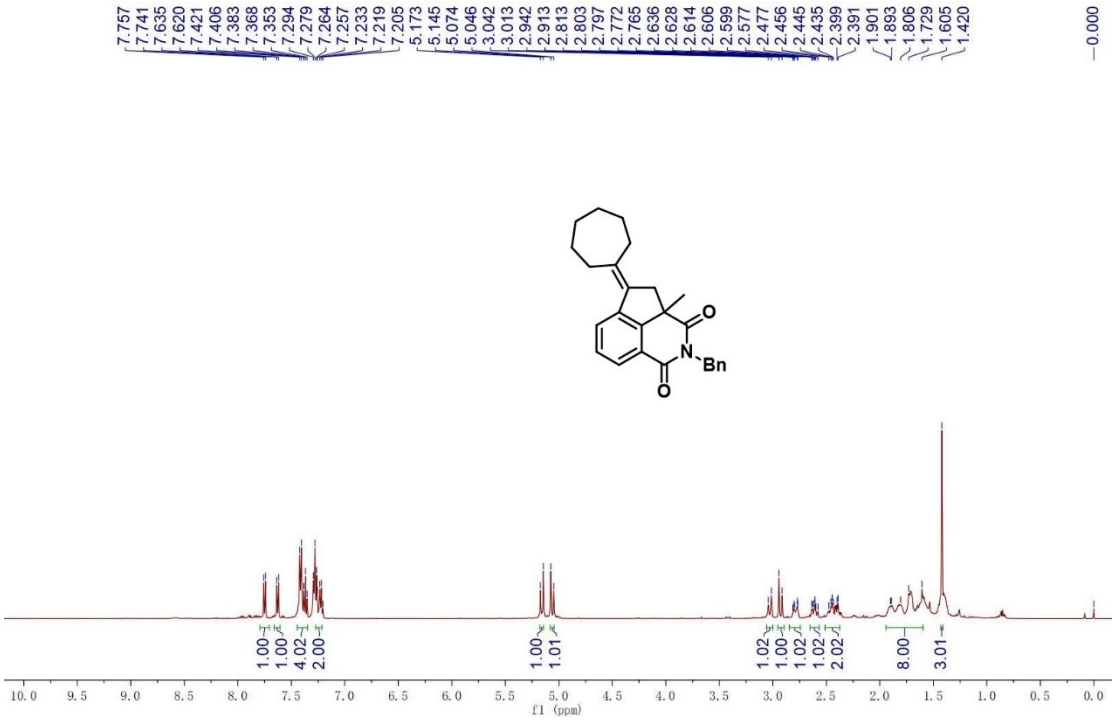


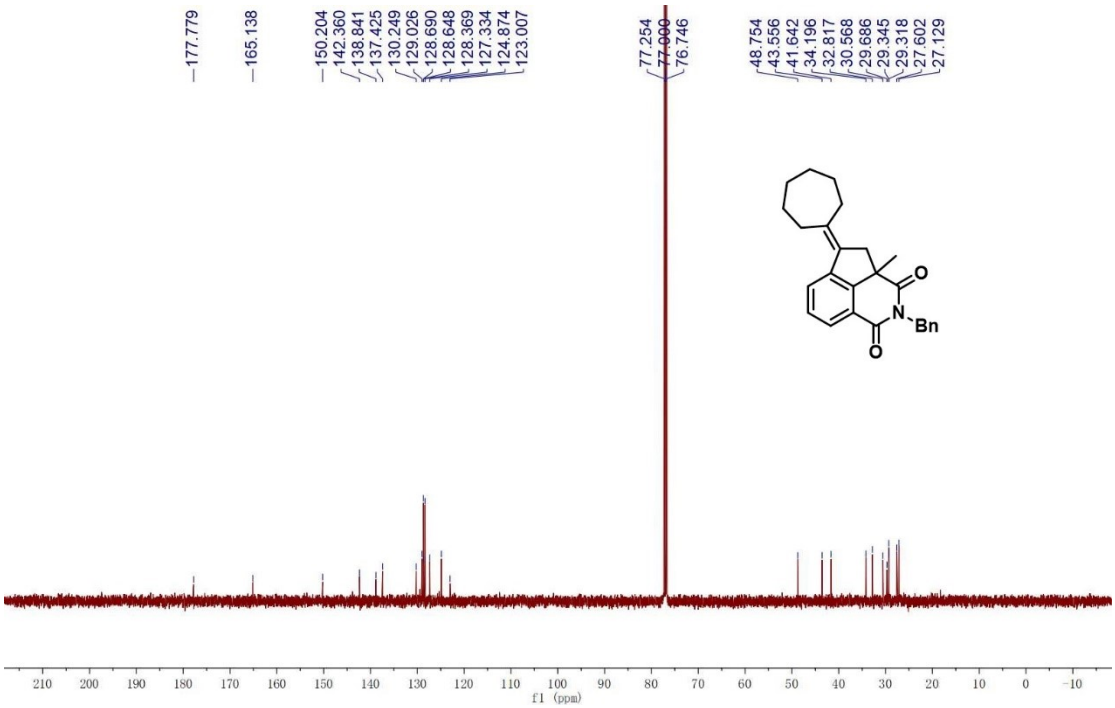
^{1}H NMR of **3al** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3al** (125 MHz, $CDCl_3$)



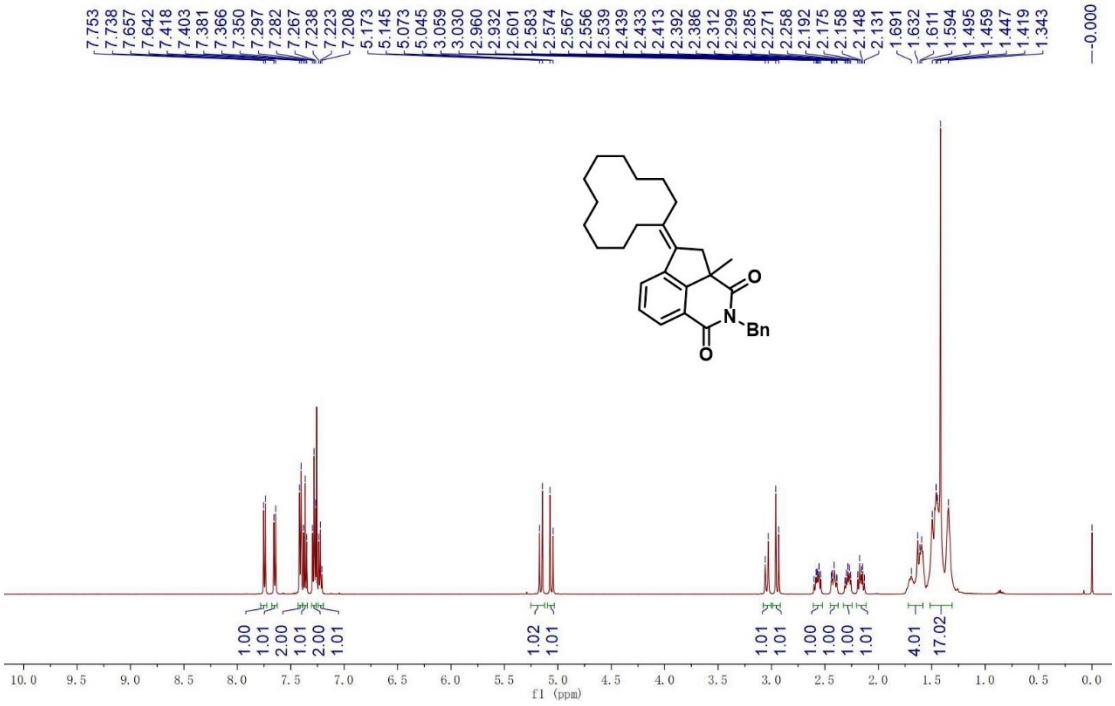


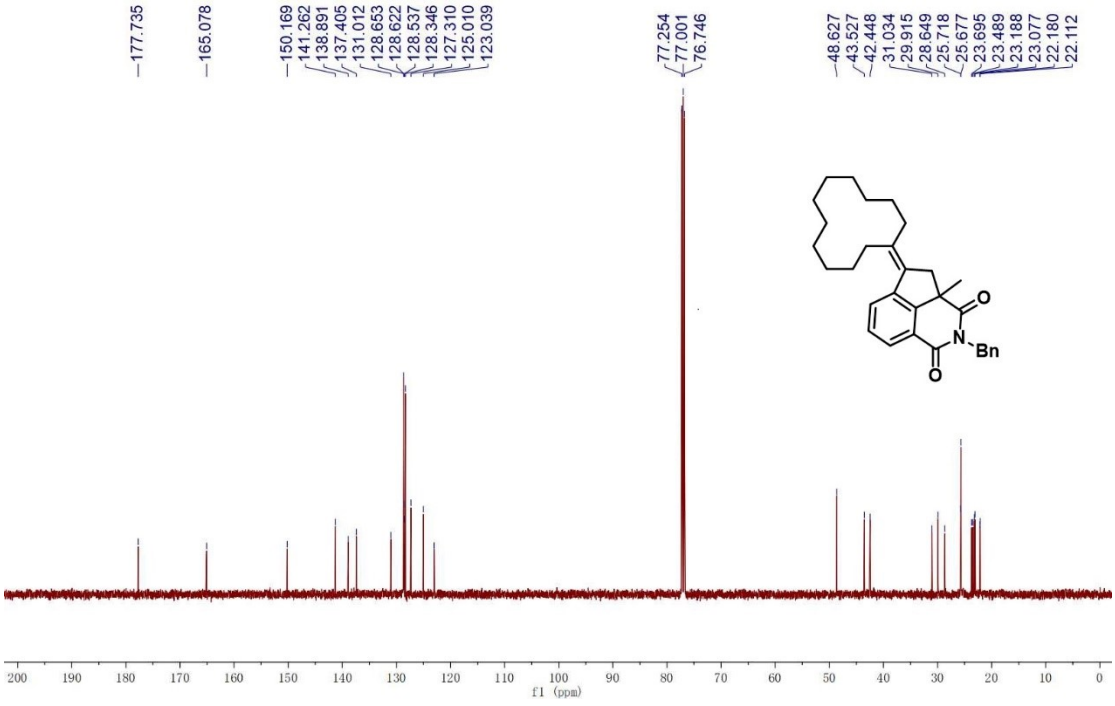
^{1}H NMR of **3am** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3am** (125 MHz, $CDCl_3$)



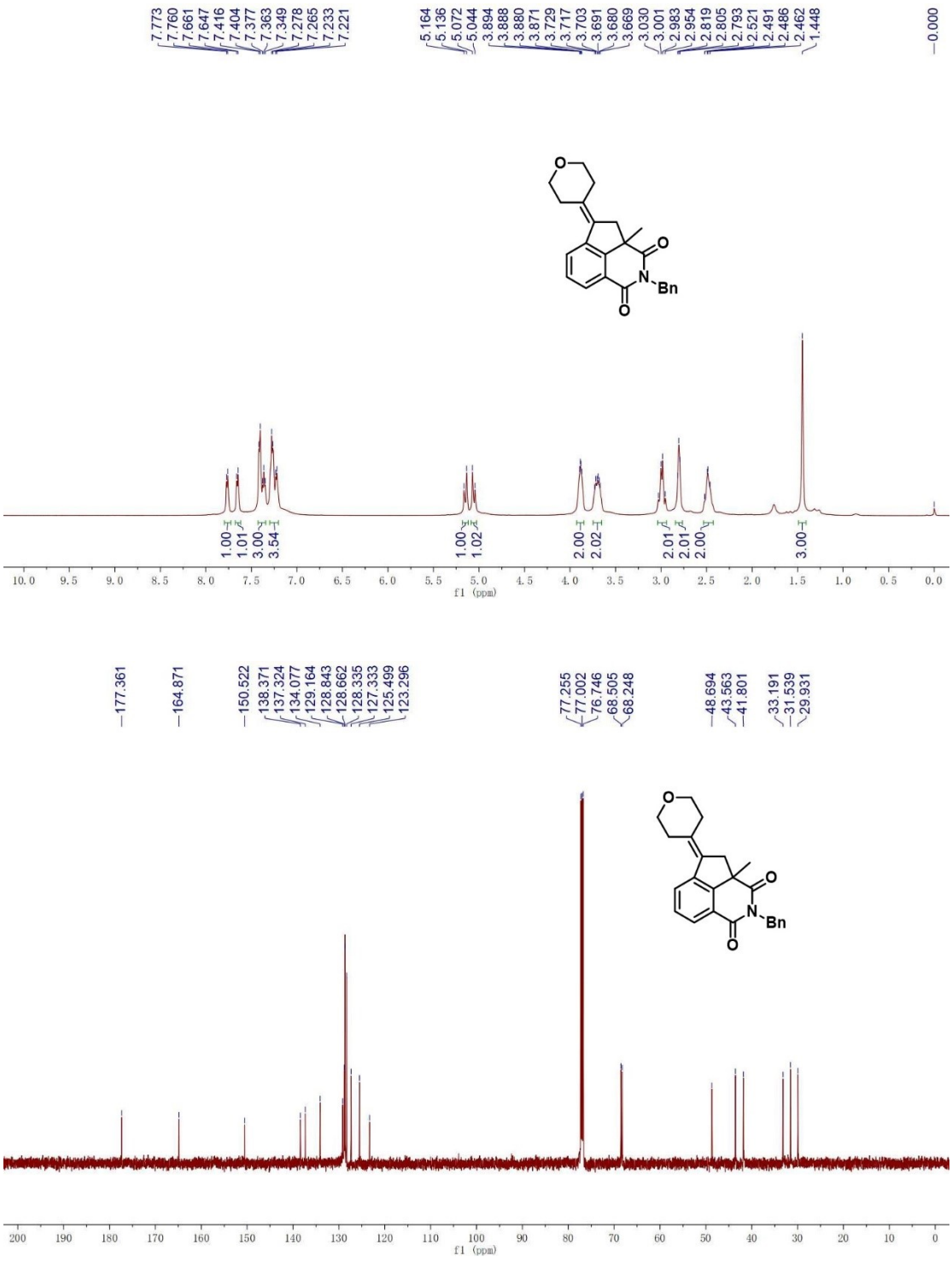


^{1}H NMR of **3an** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3an** (125 MHz, $CDCl_3$)

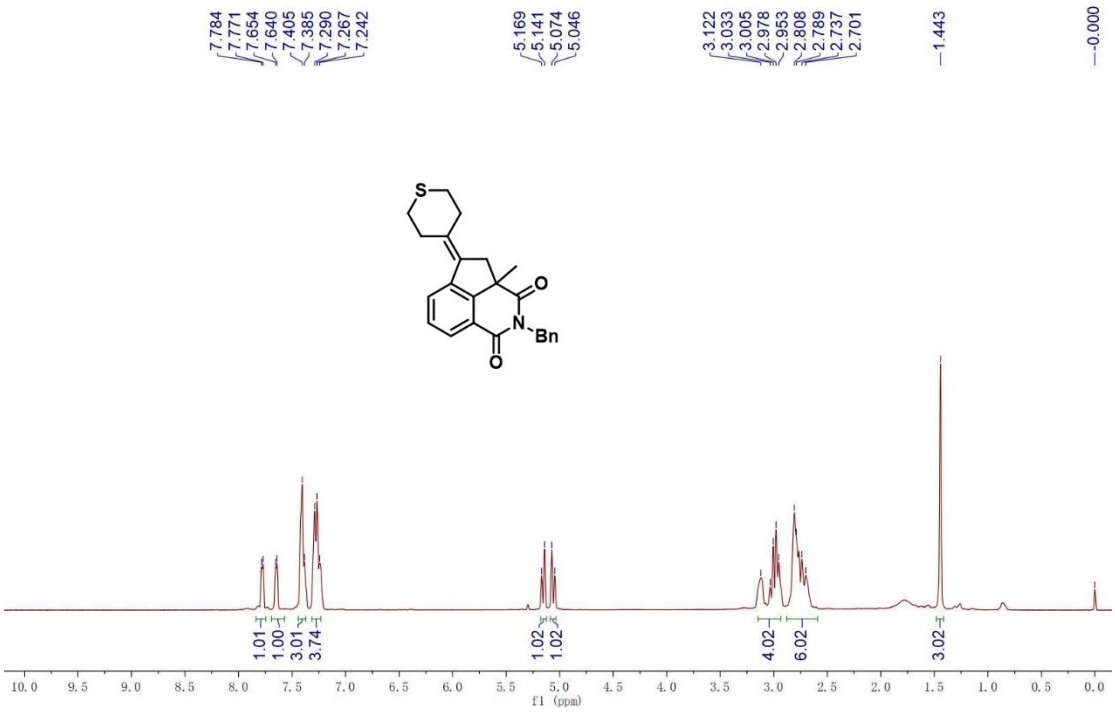


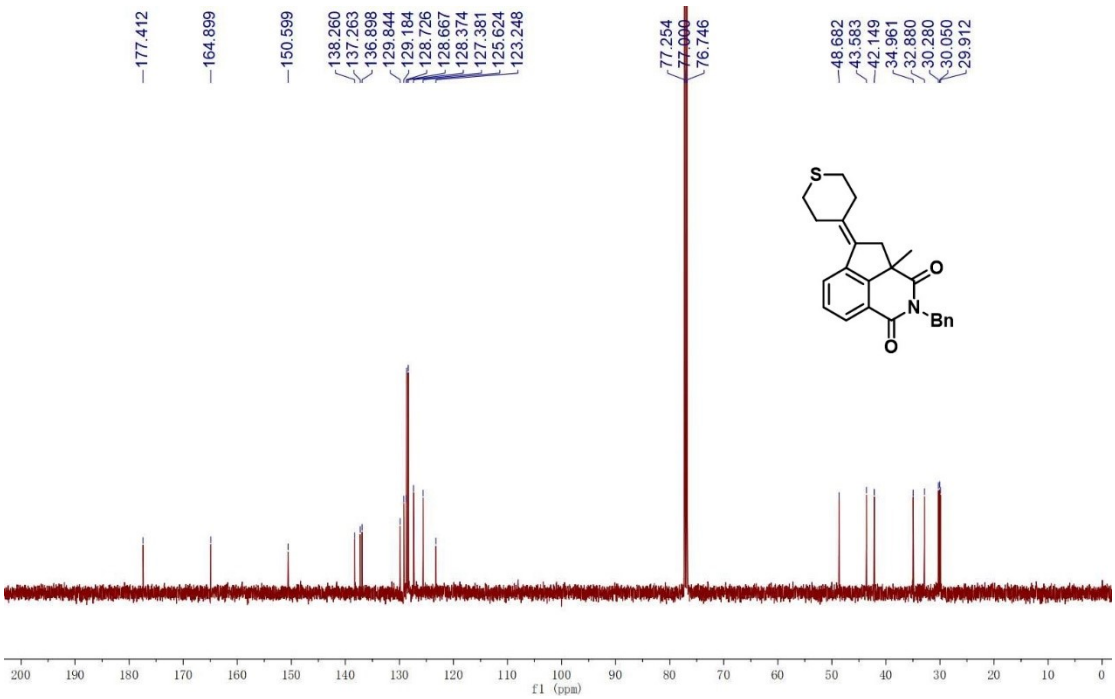


^{1}H NMR of **3ao** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ao** (125 MHz, $CDCl_3$)

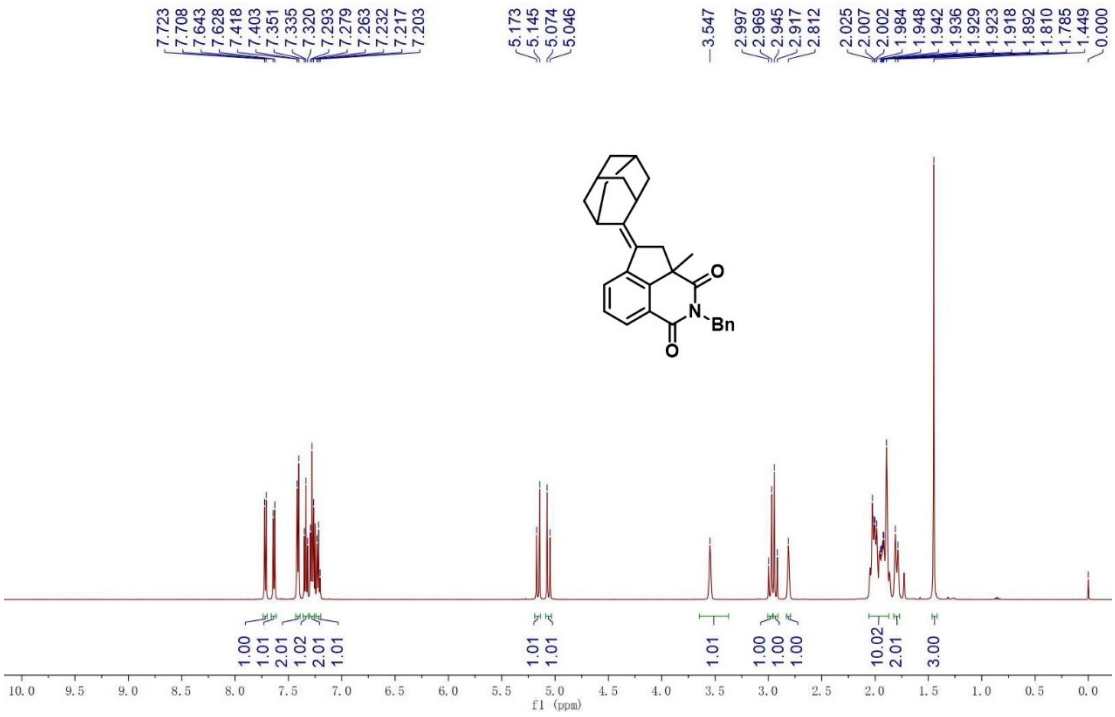


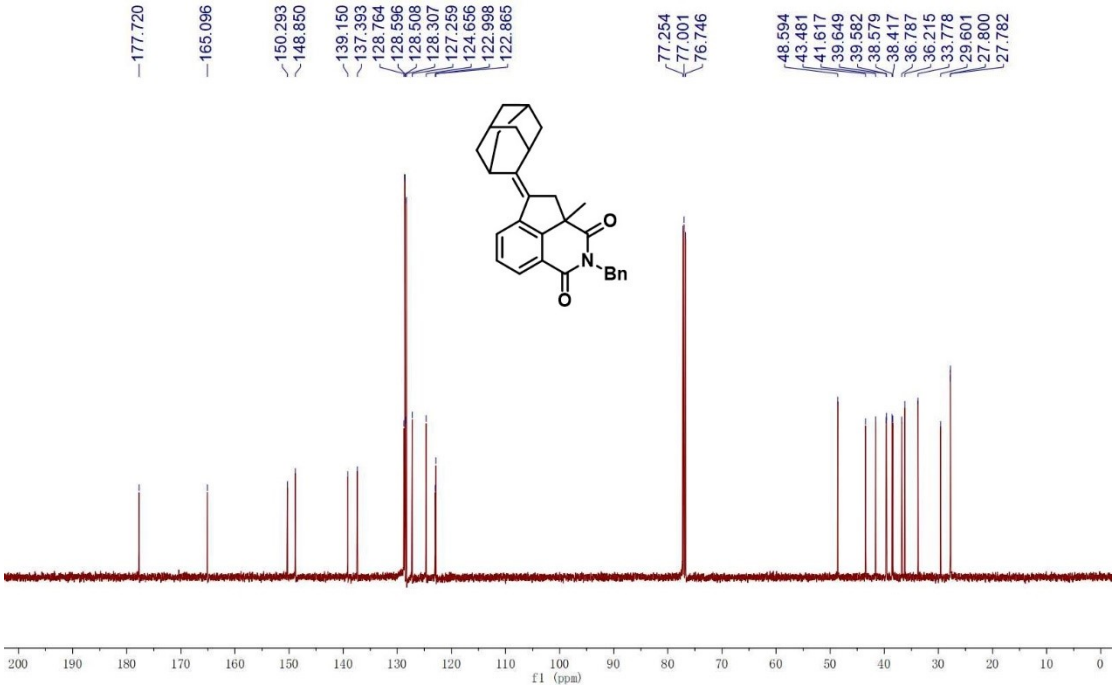
^{1}H NMR of **3ap** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ap** (125 MHz, $CDCl_3$)



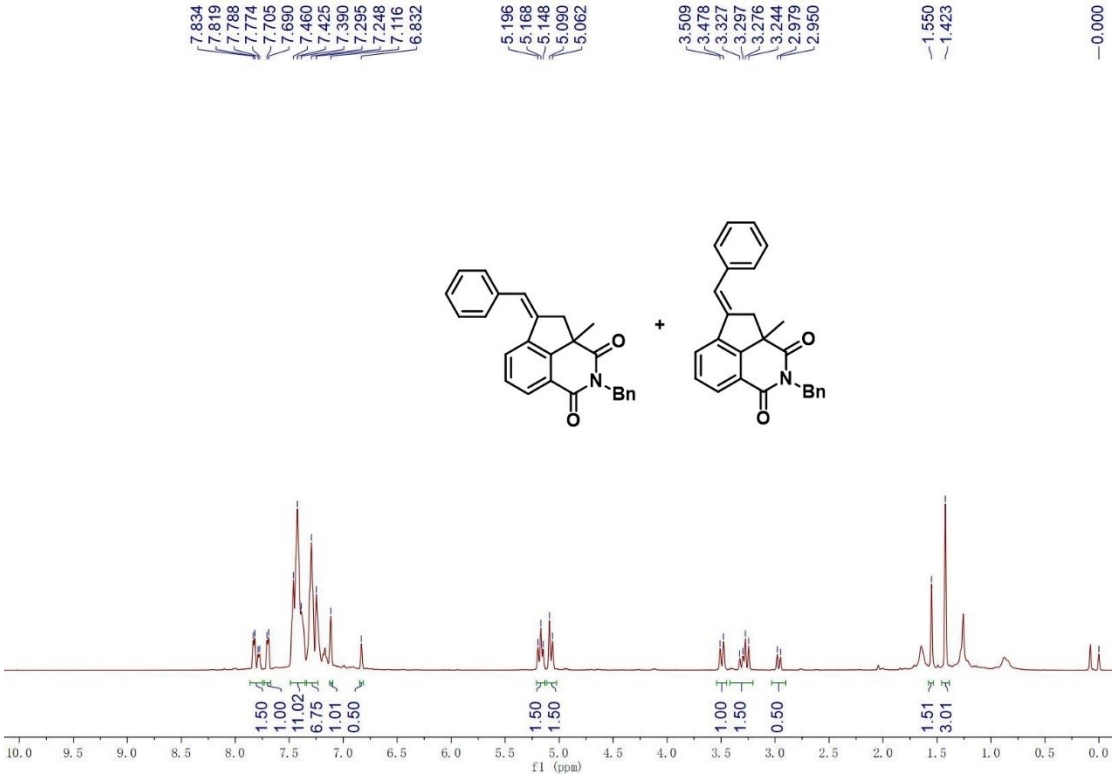


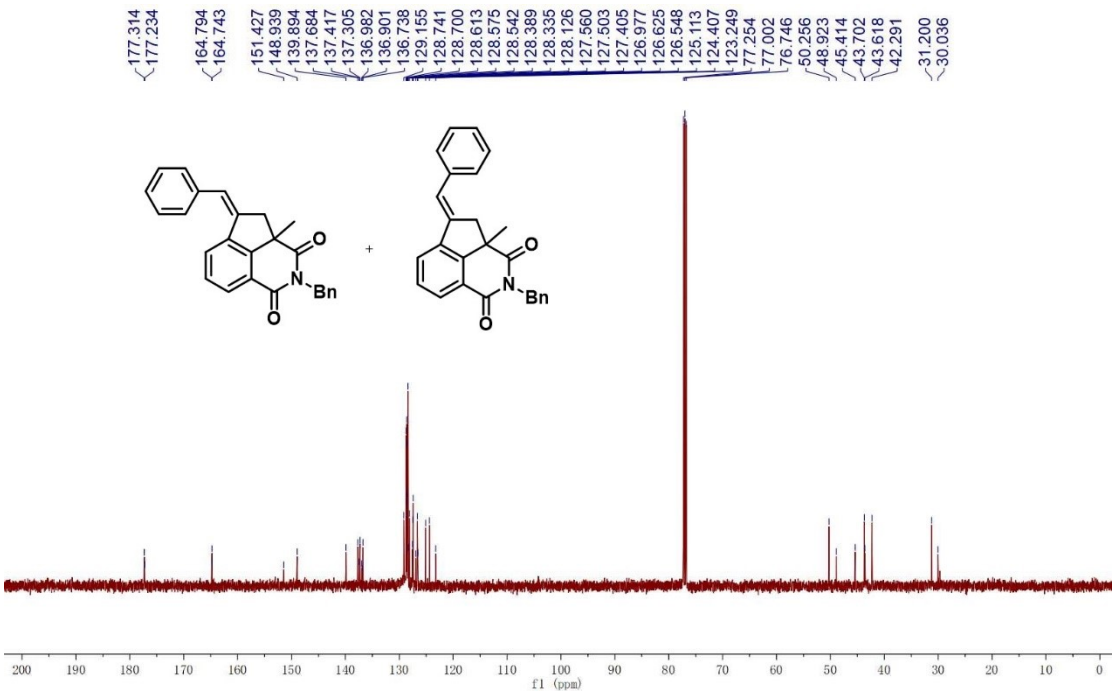
^{1}H NMR of **3aq** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aq** (125 MHz, $CDCl_3$)



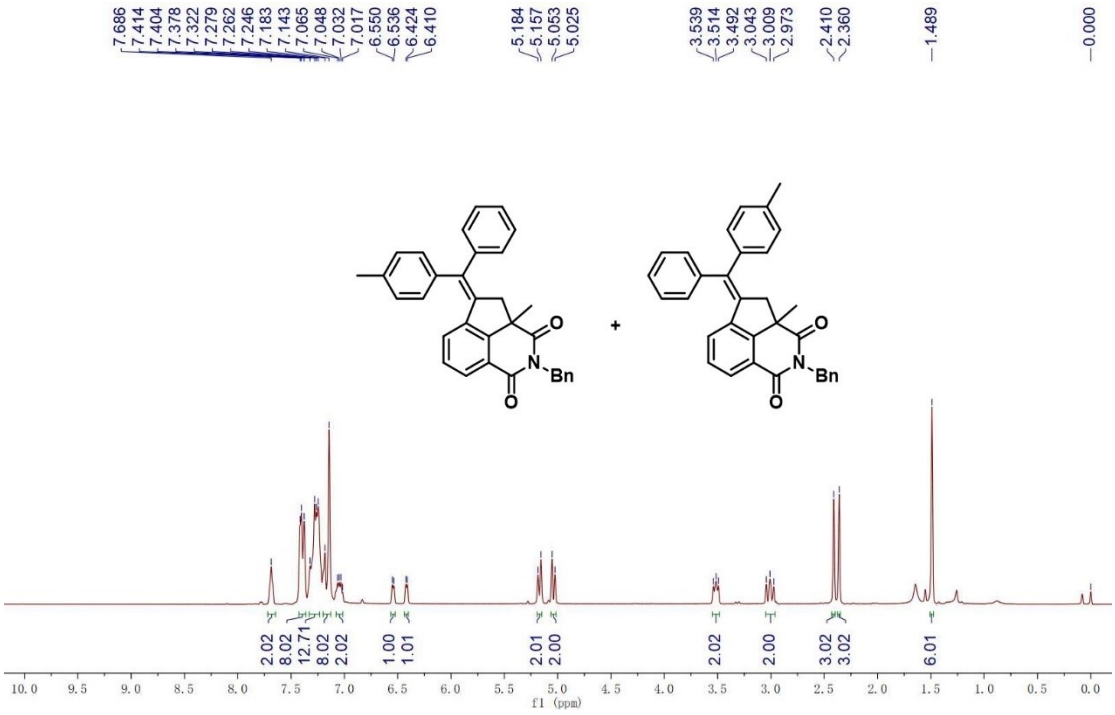


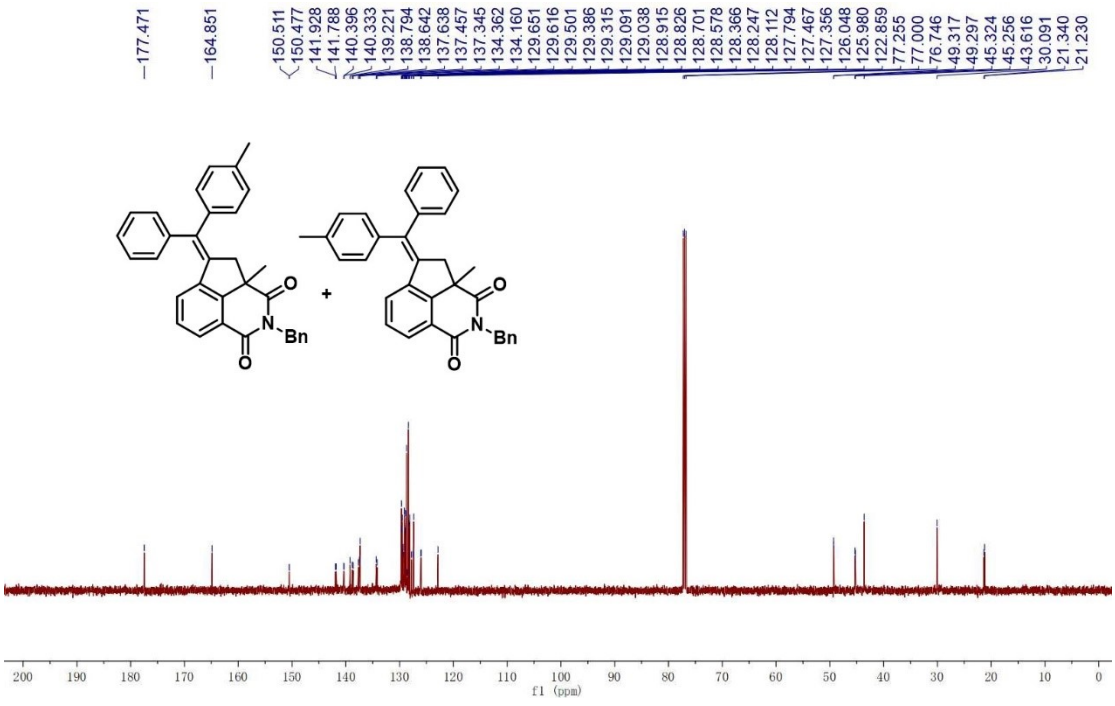
^{1}H NMR of **3ar** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ar** (125 MHz, $CDCl_3$)



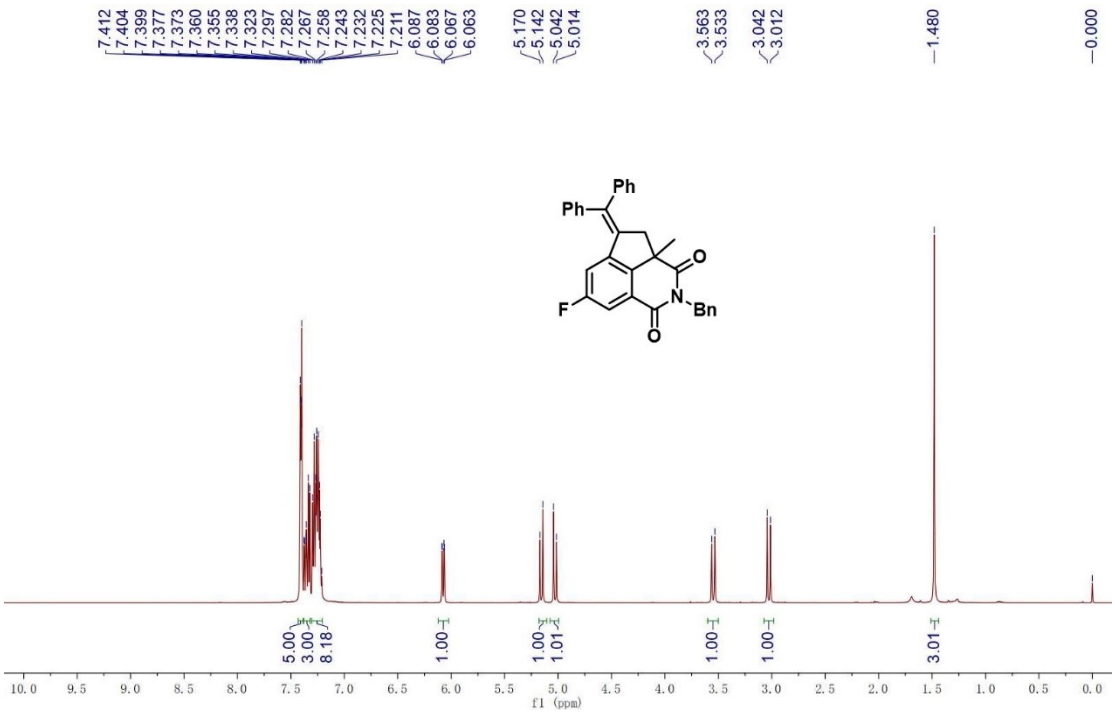


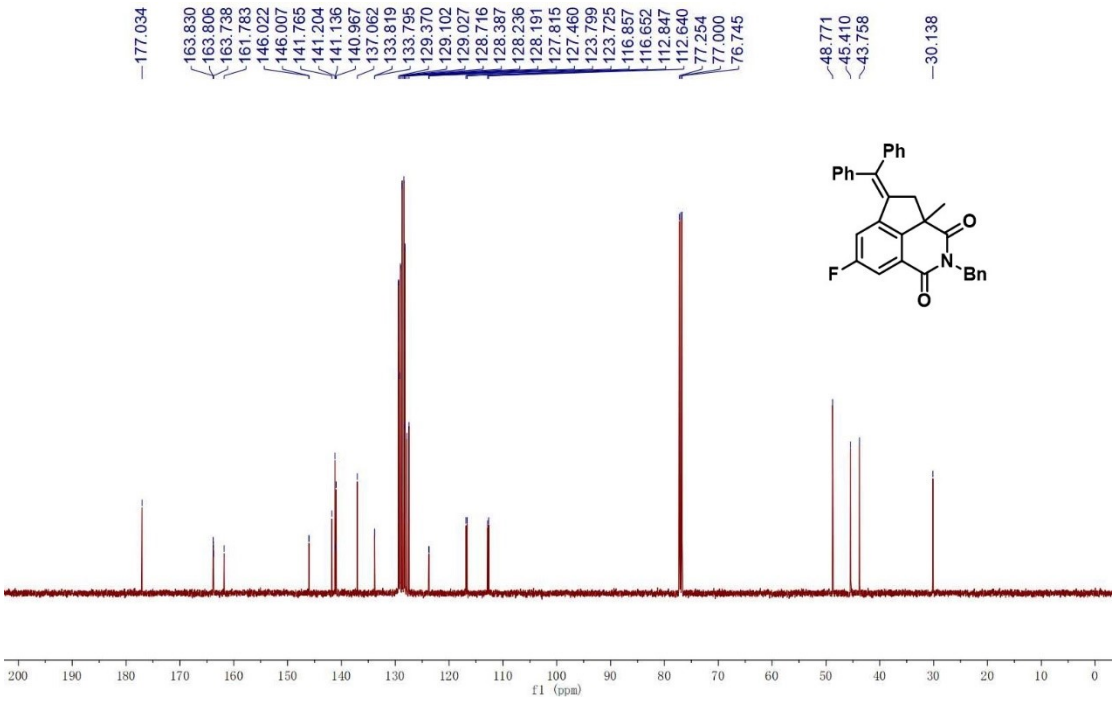
^{1}H NMR of **3as** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3as** (125 MHz, $CDCl_3$)



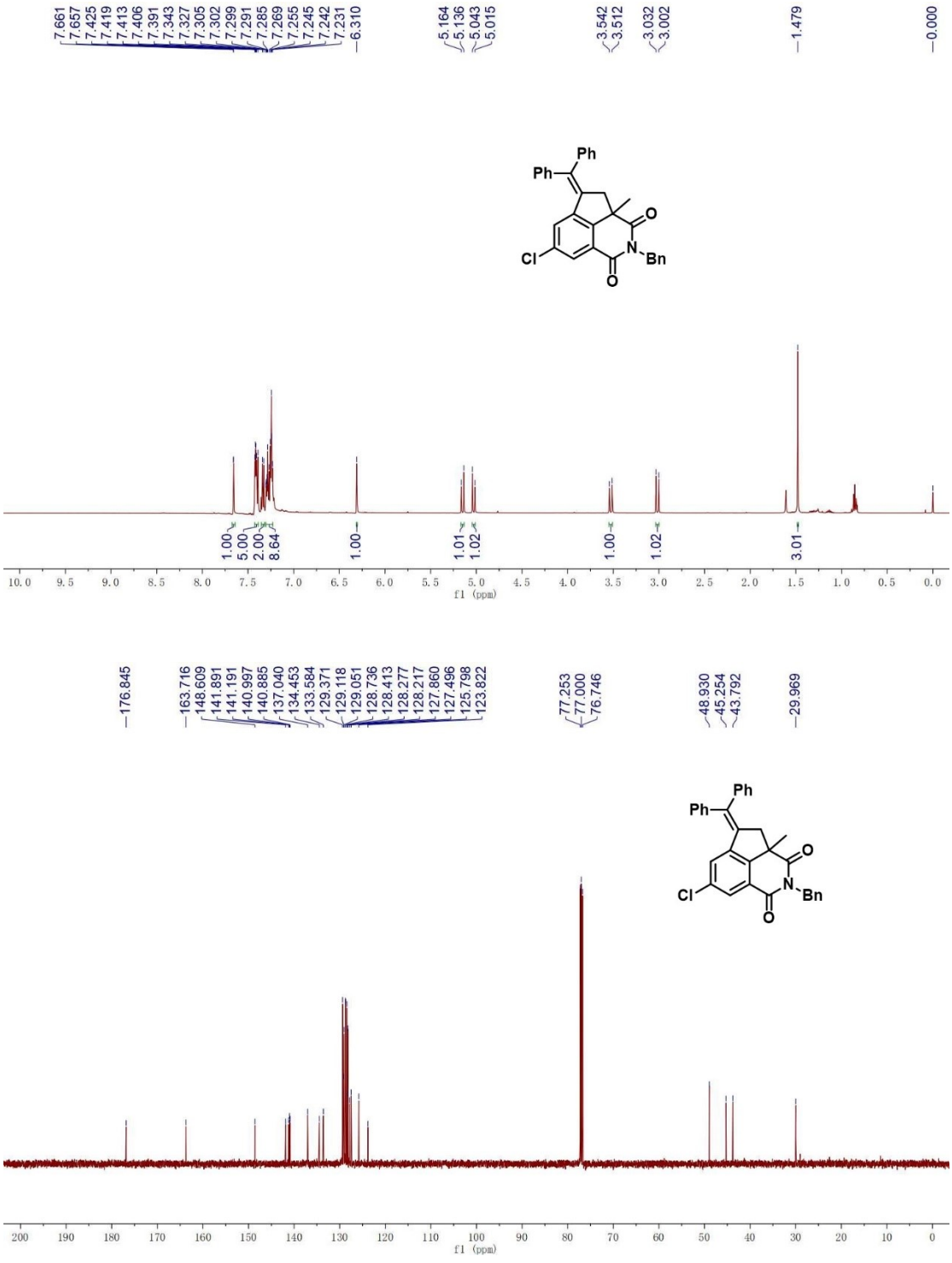


^{1}H NMR of **3ba** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ba** (125 MHz, $CDCl_3$)

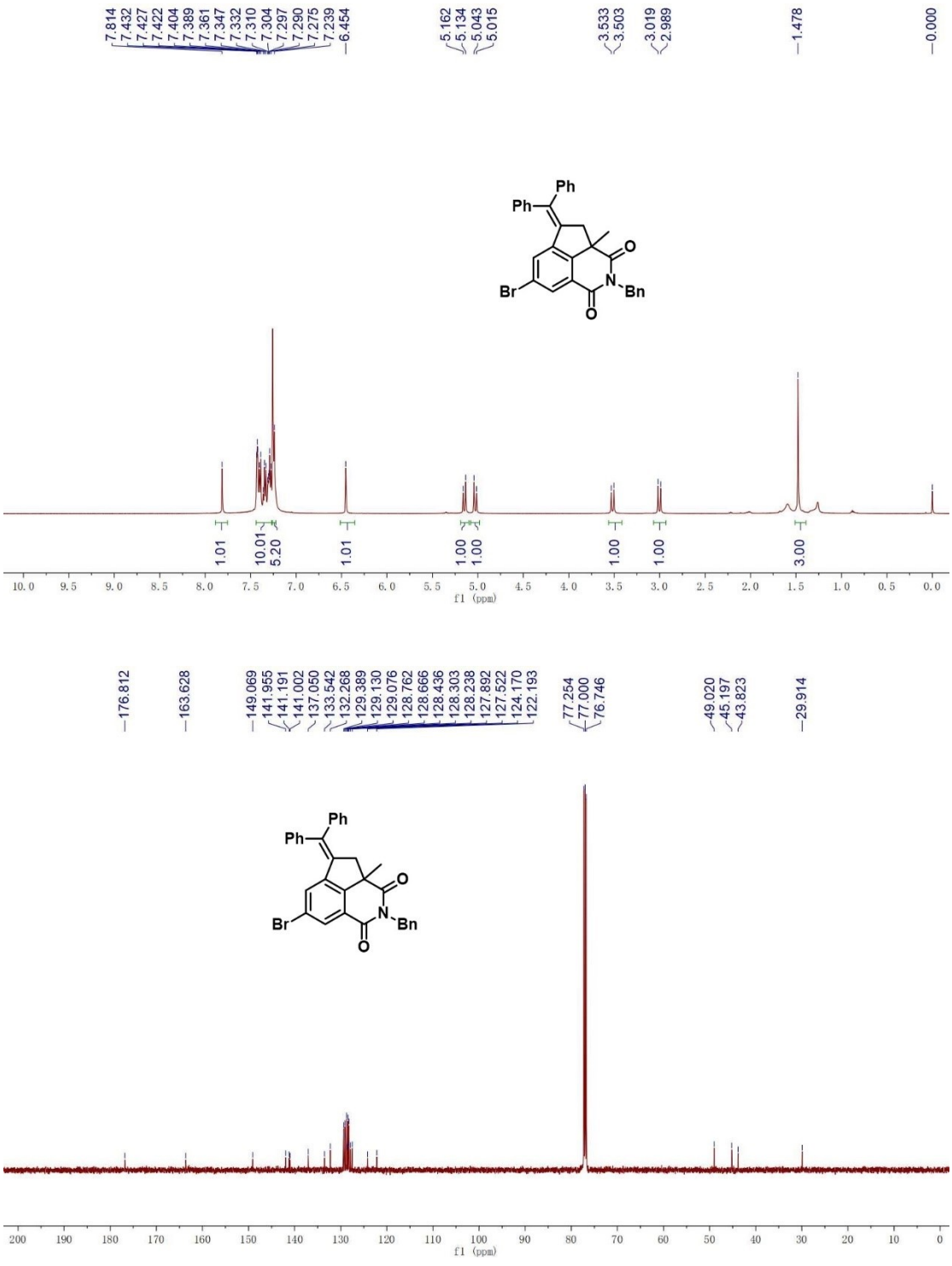




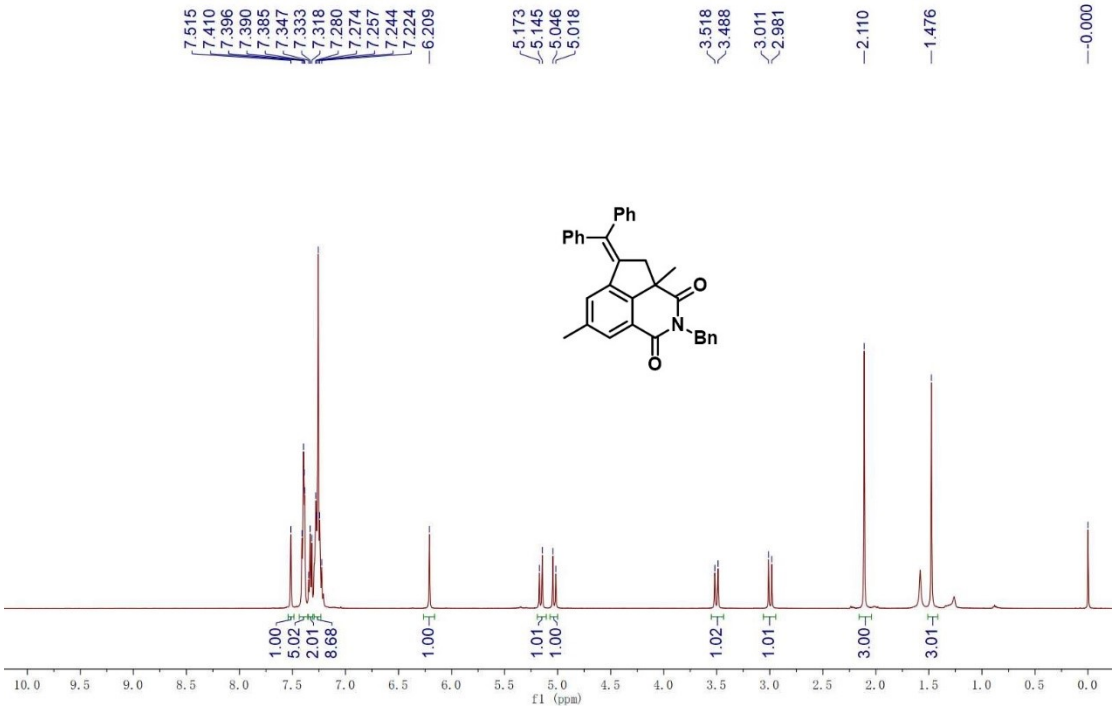
^{1}H NMR of **3ca** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ca** (125 MHz, $CDCl_3$)

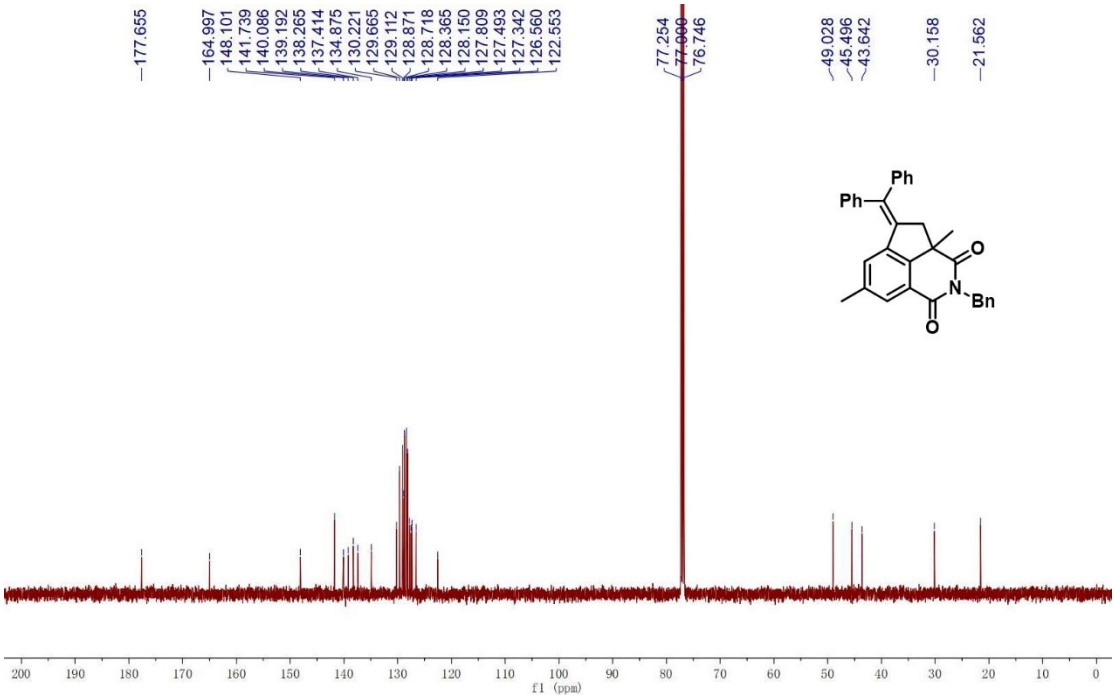


^{1}H NMR of **3da** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3da** (125 MHz, $CDCl_3$)

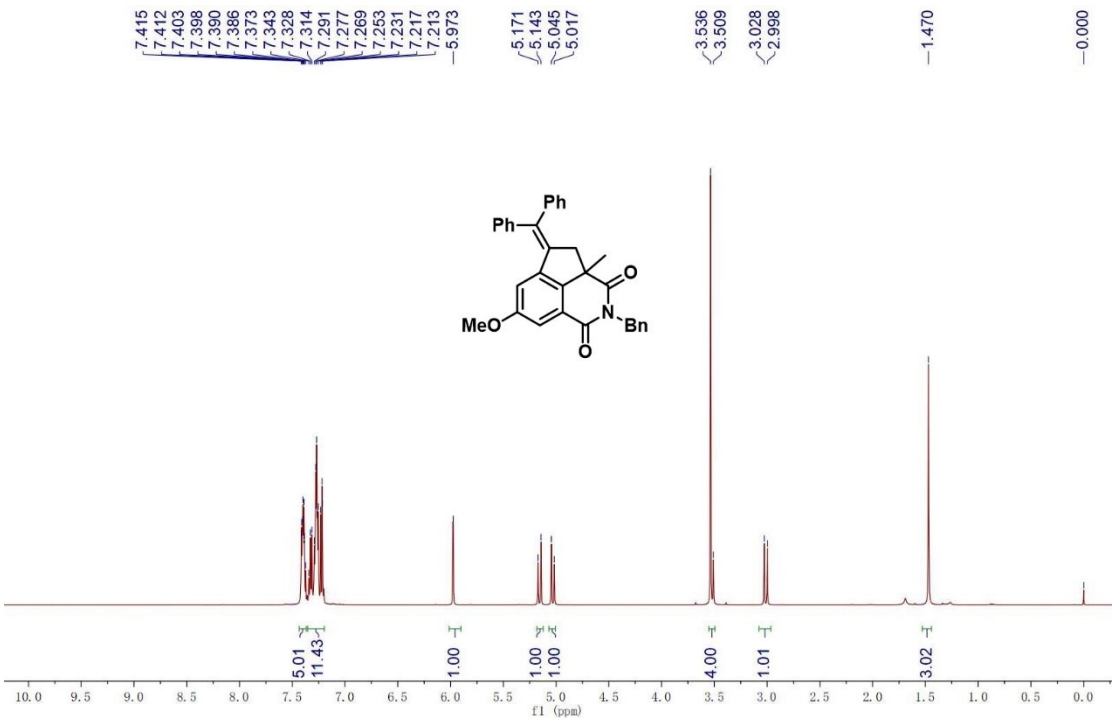


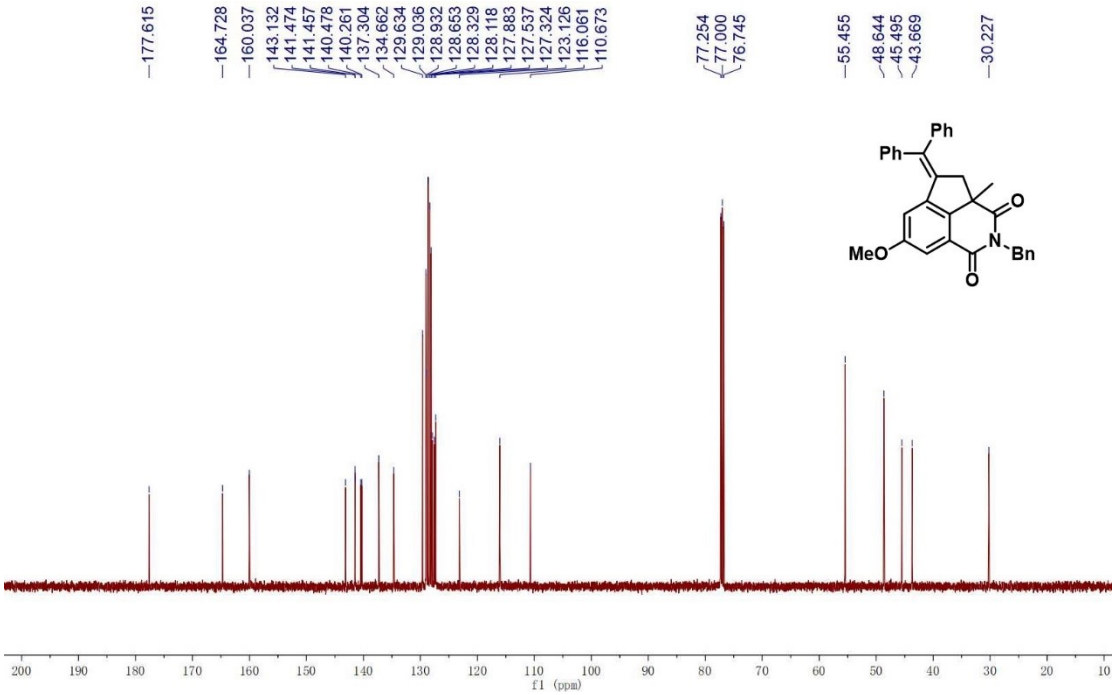
^{1}H NMR of **3ea** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ea** (125 MHz, $CDCl_3$)



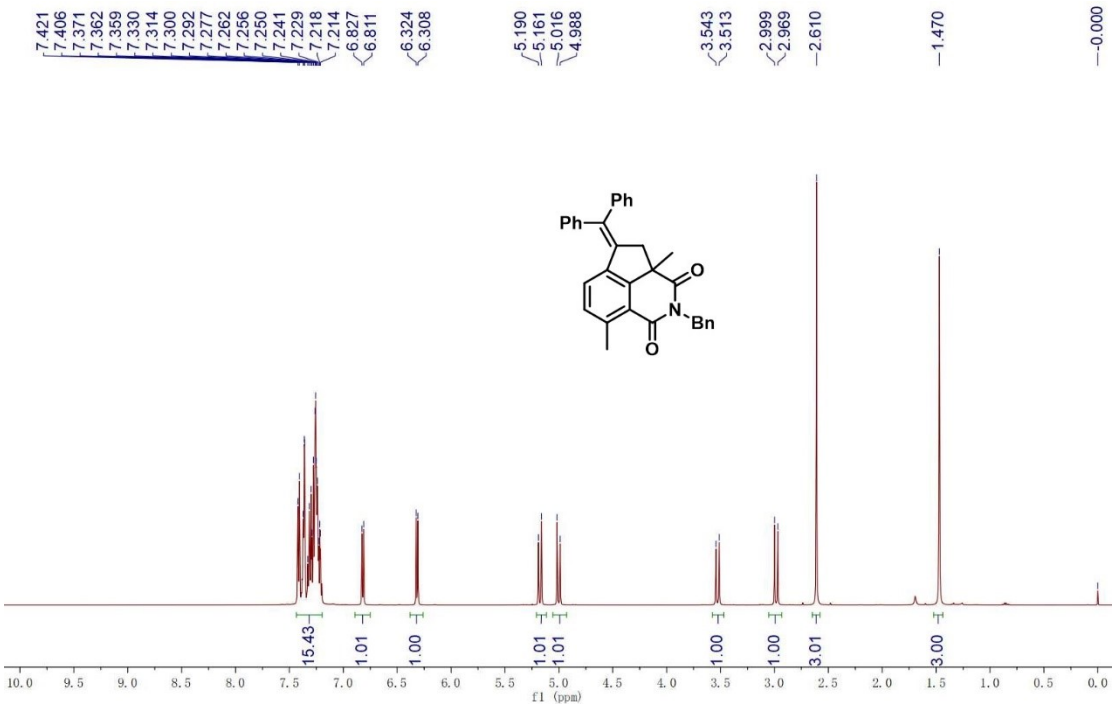


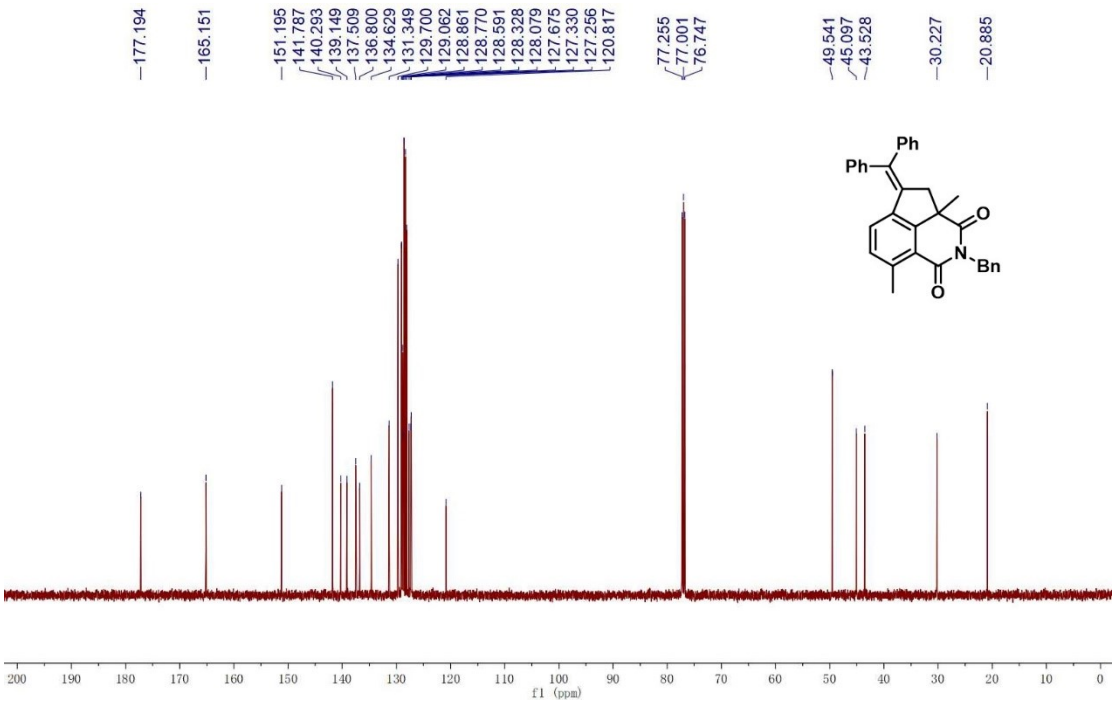
^{1}H NMR of **3fa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3fa** (125 MHz, CDCl



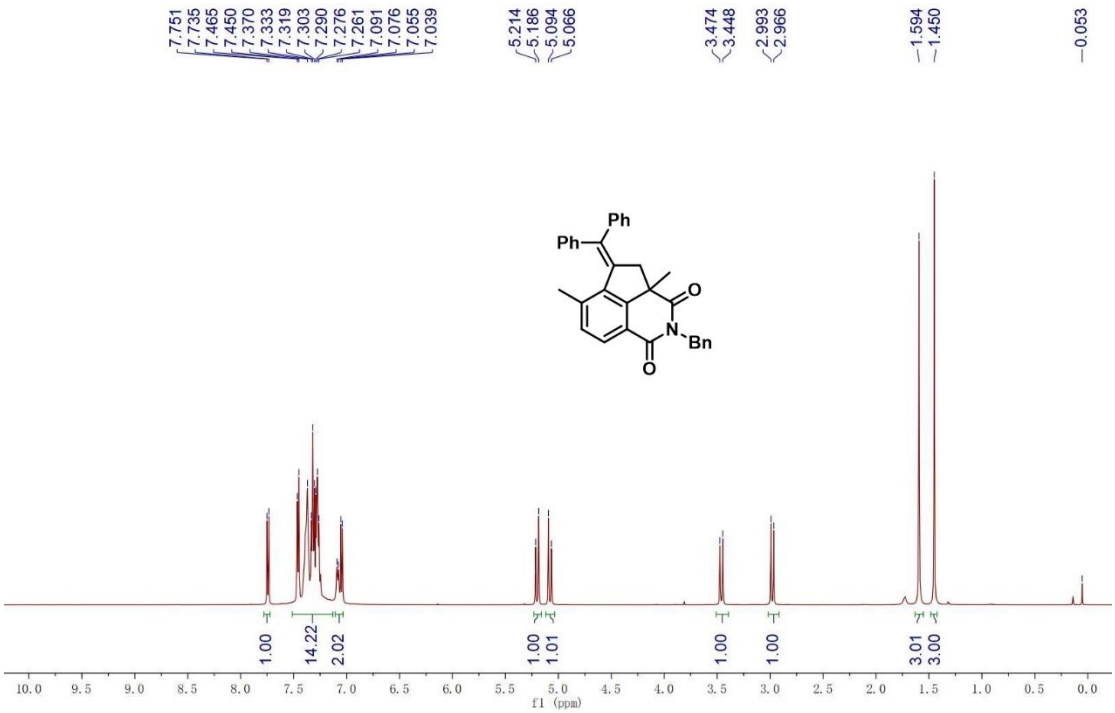


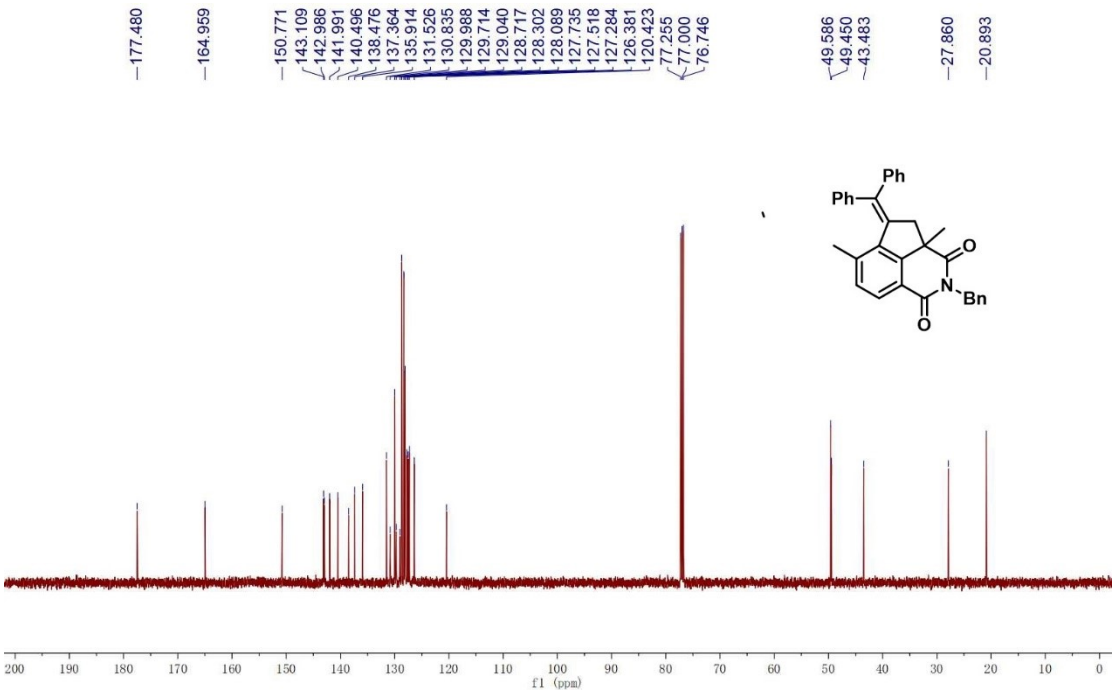
^{1}H NMR of **3ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ga** (125 MHz, $CDCl_3$)



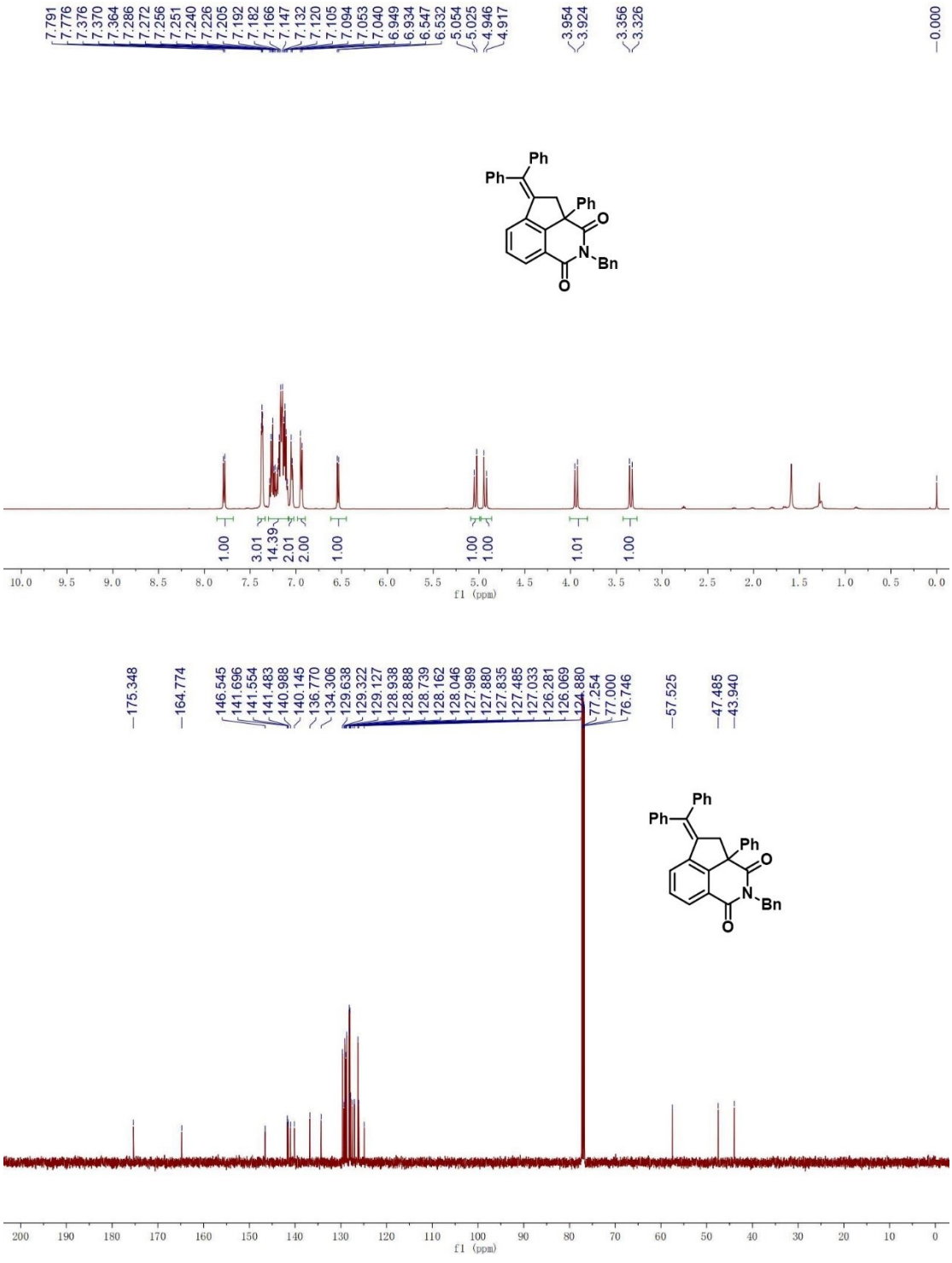


^{1}H NMR of **3ha** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ha** (125 MHz, $CDCl_3$)

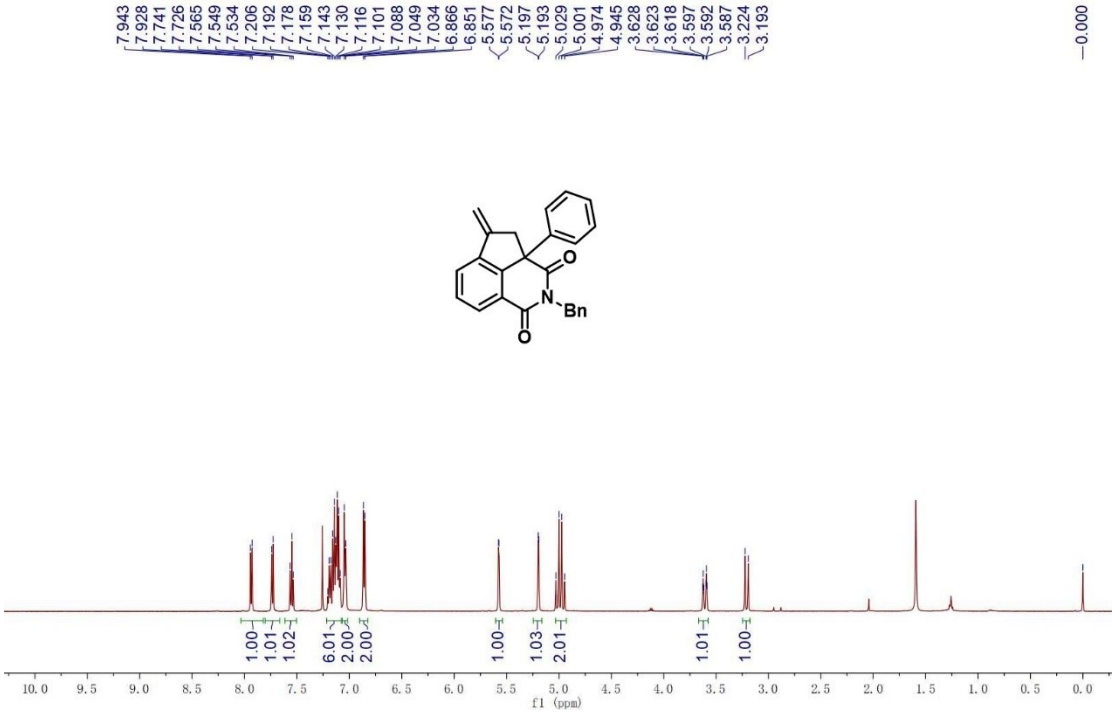


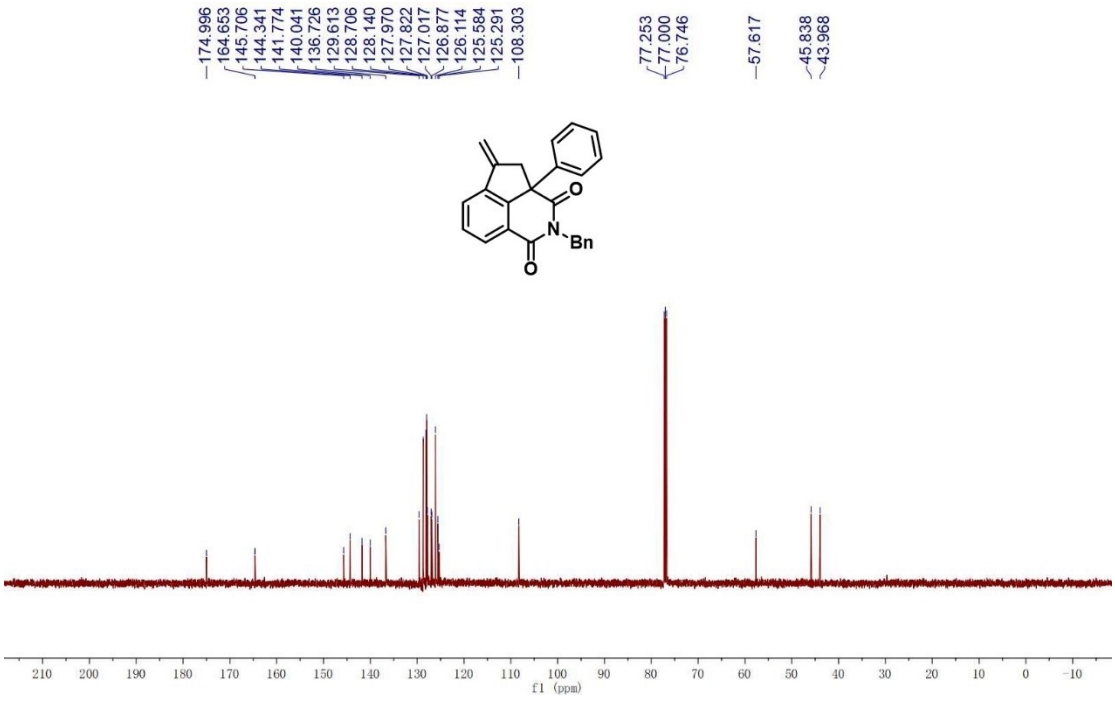


^{1}H NMR of **3ia** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ia** (125 MHz, $CDCl_3$)

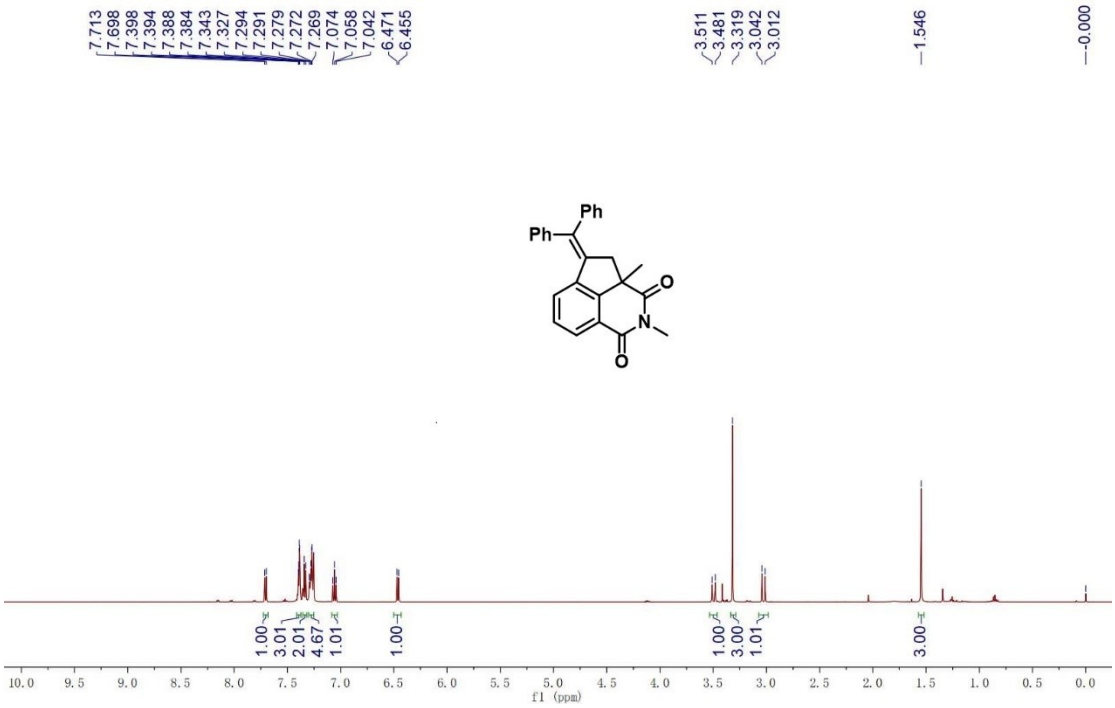


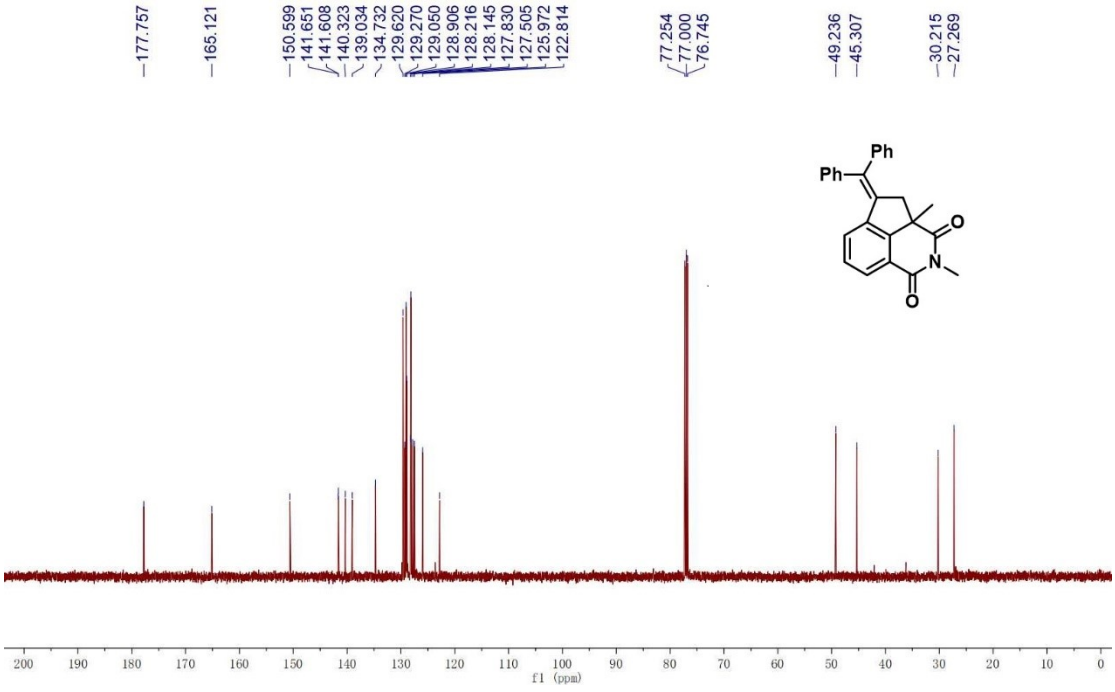
^{1}H NMR of **3ih** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ih** (125 MHz, $CDCl_3$)



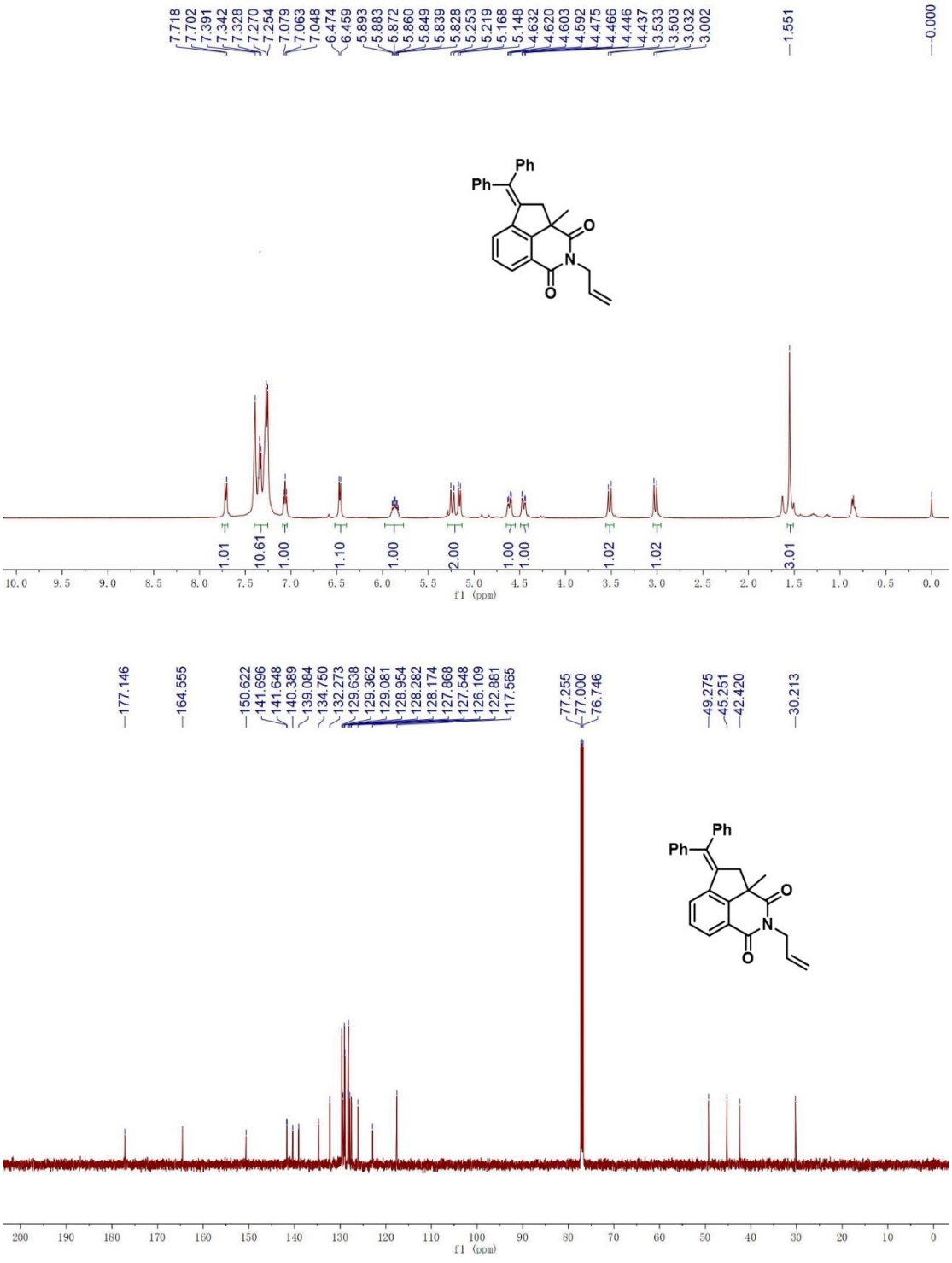


^{1}H NMR of **3ja** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ja** (125 MHz, $CDCl_3$)

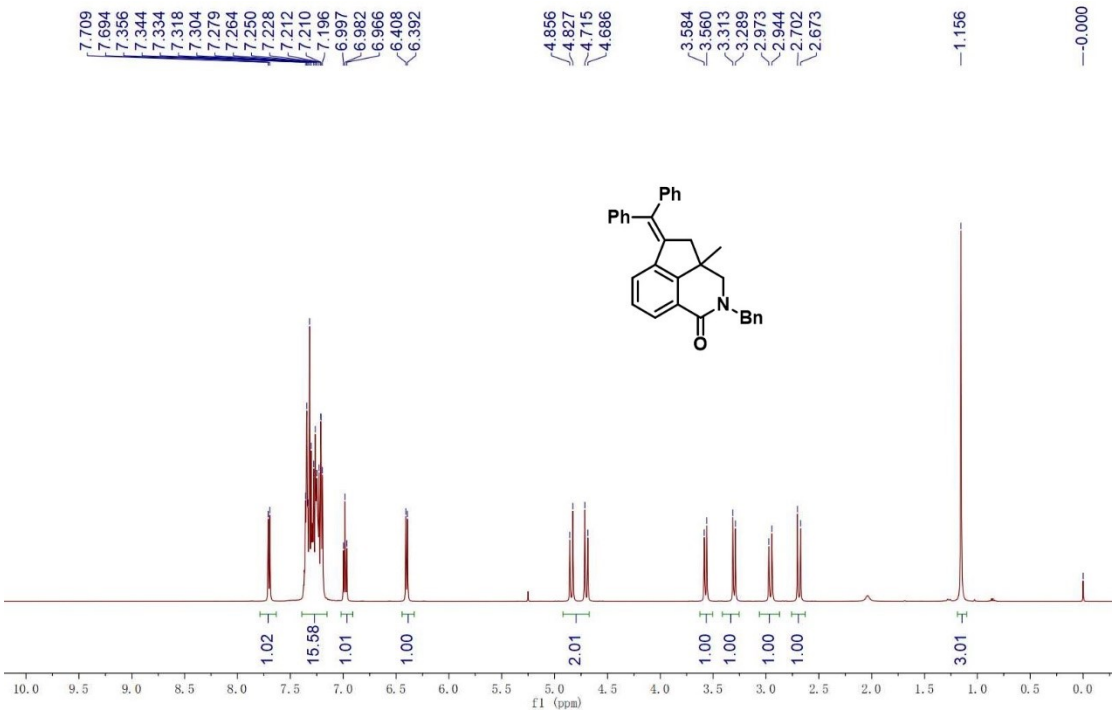


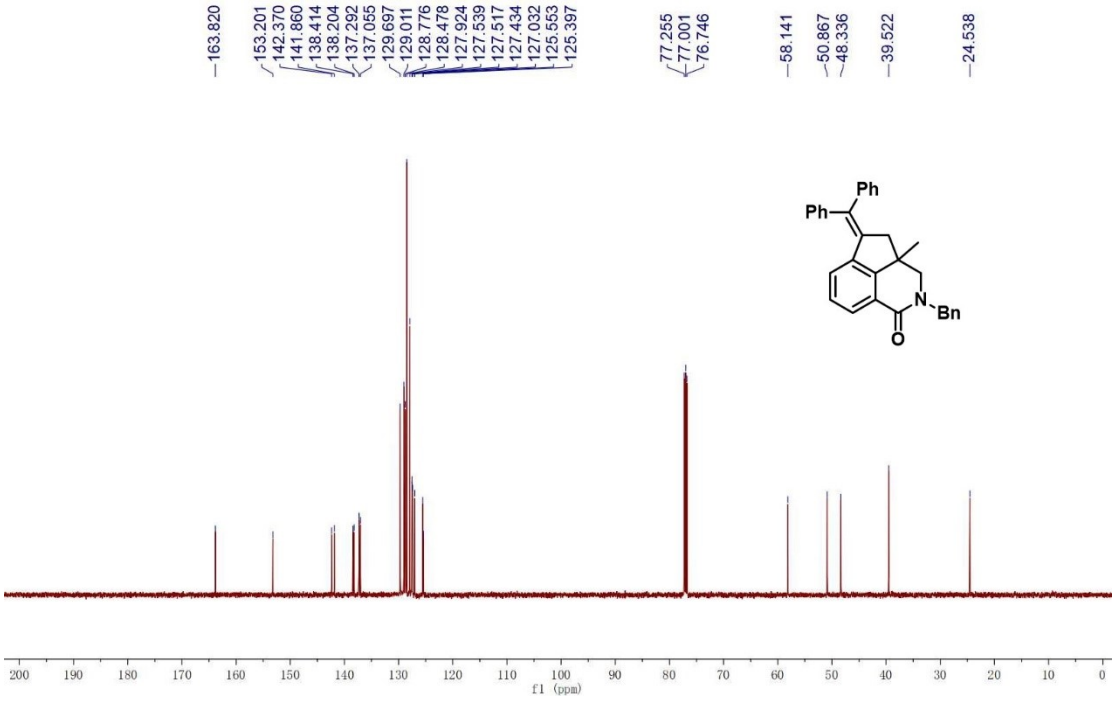


^{1}H NMR of **3ka** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ka** (125 MHz, $CDCl_3$)

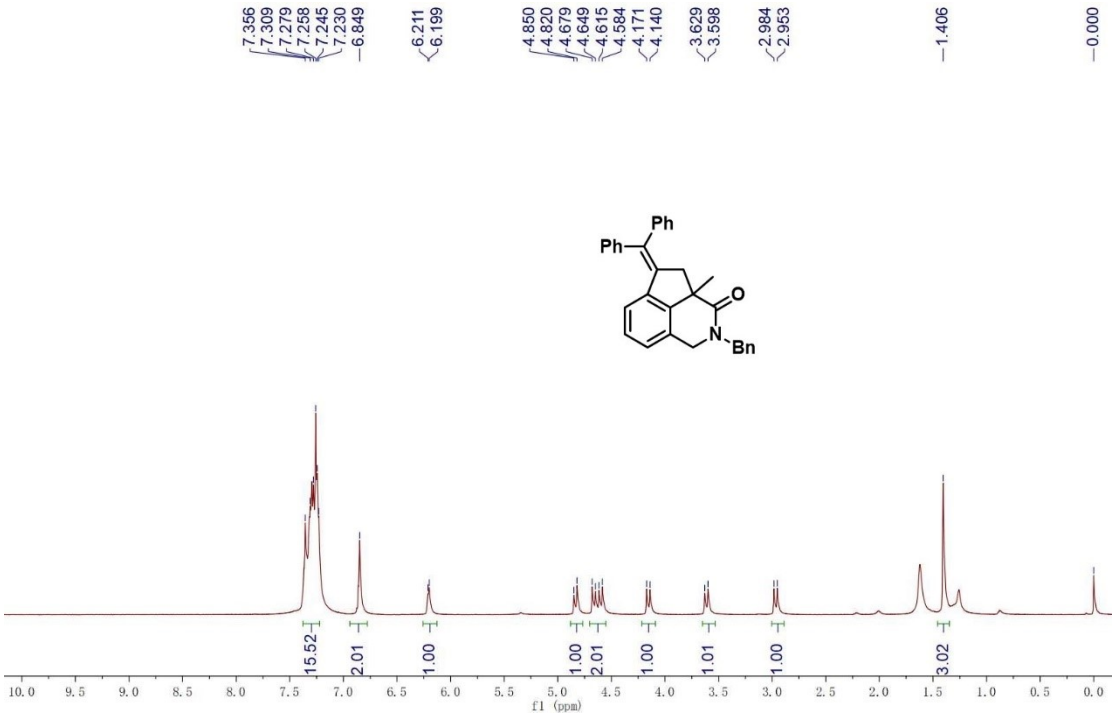


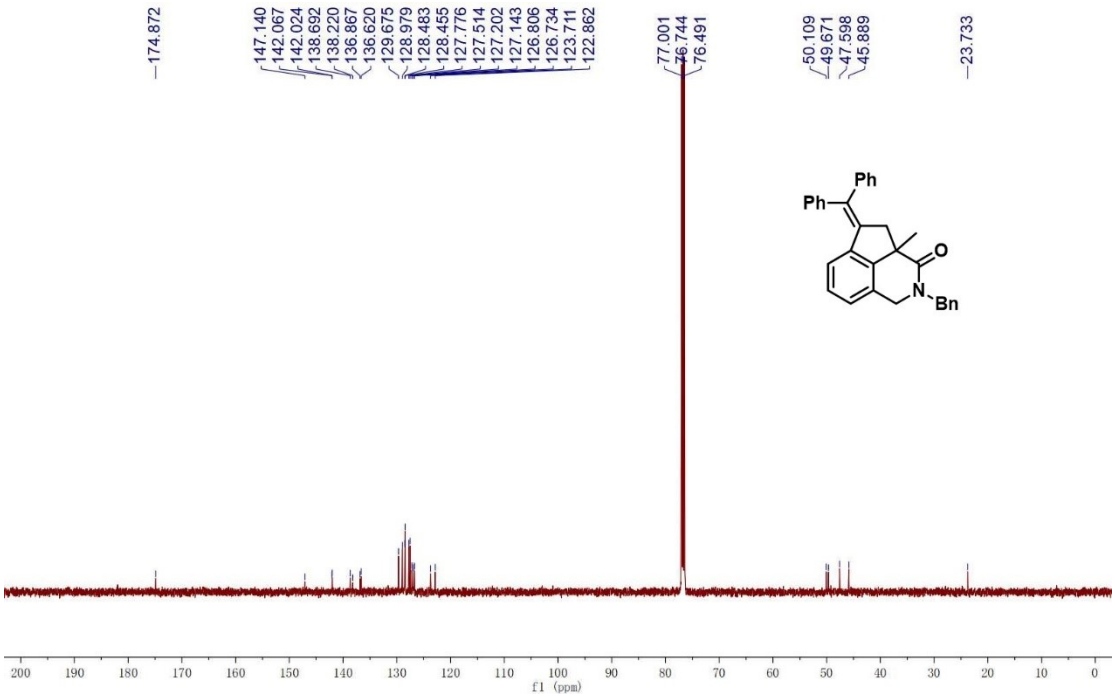
^{1}H NMR of **3la** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3la** (125 MHz, $CDCl_3$)



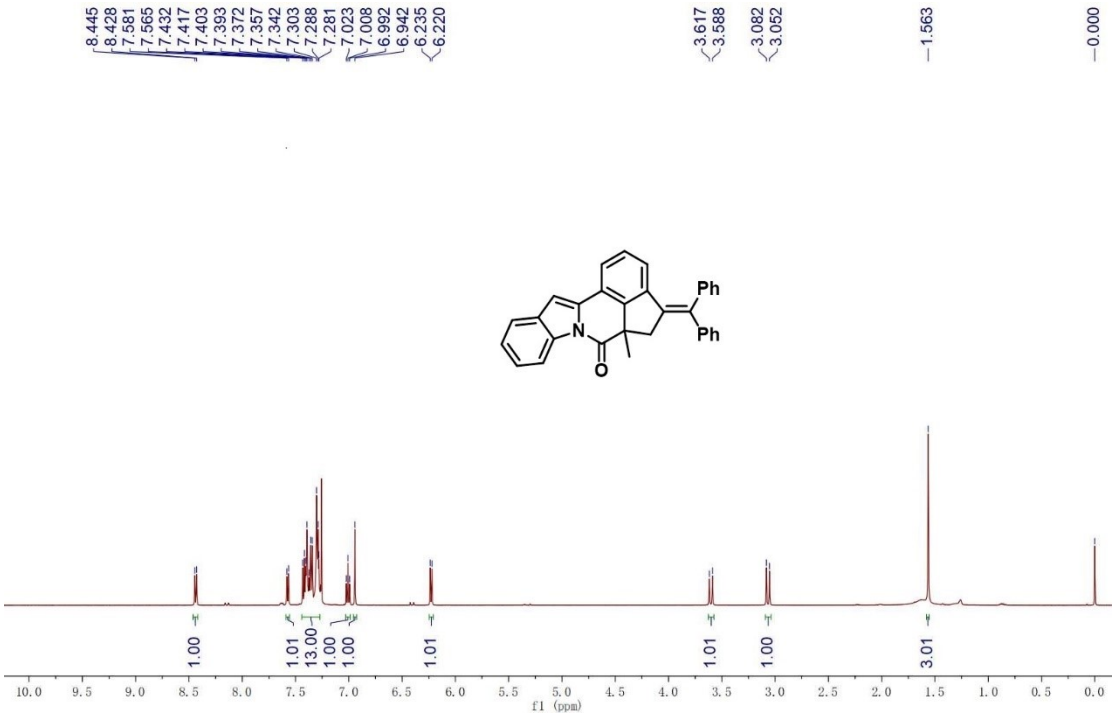


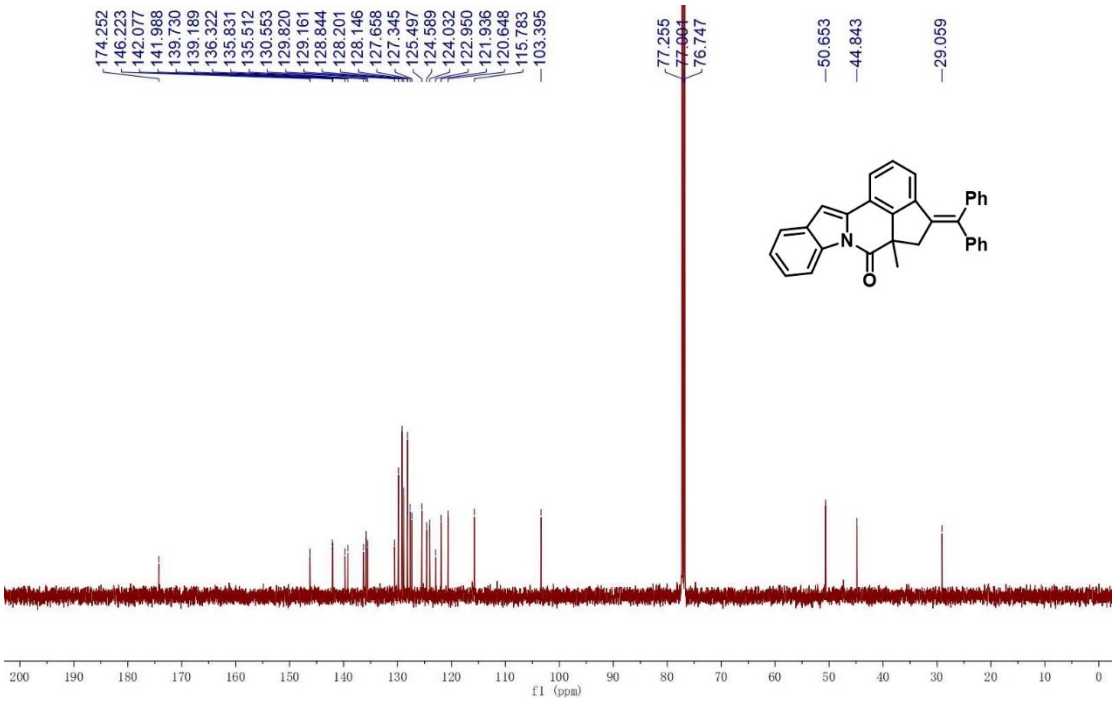
^{1}H NMR of **3ma** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ma** (125 MHz, $CDCl_3$)



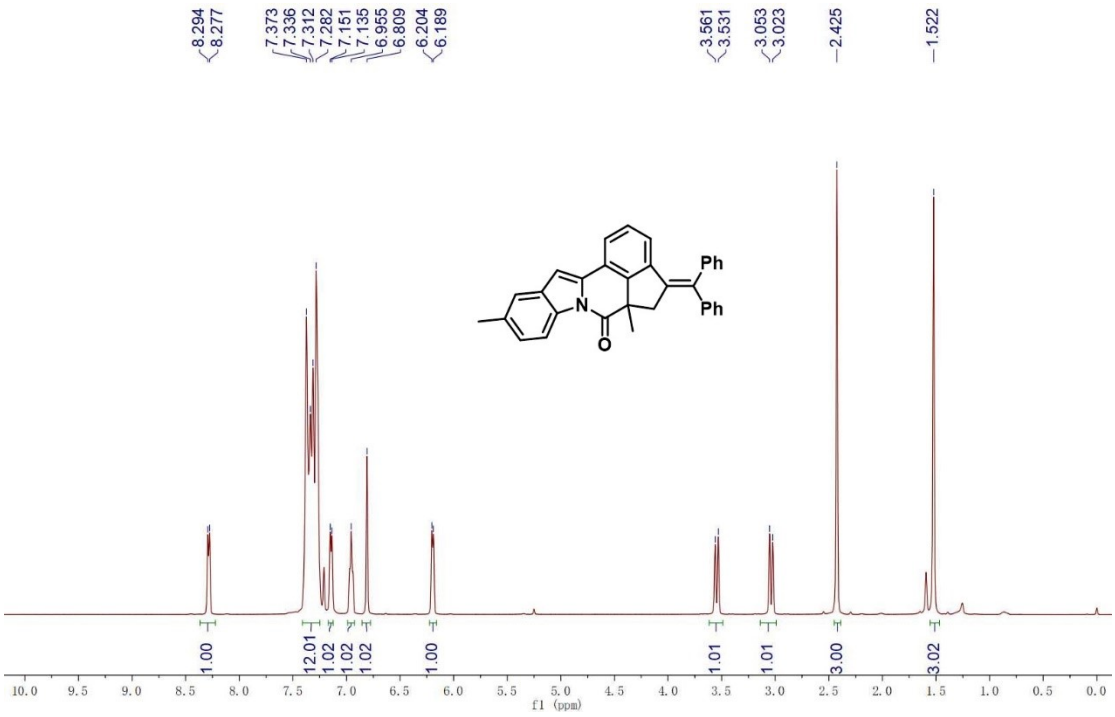


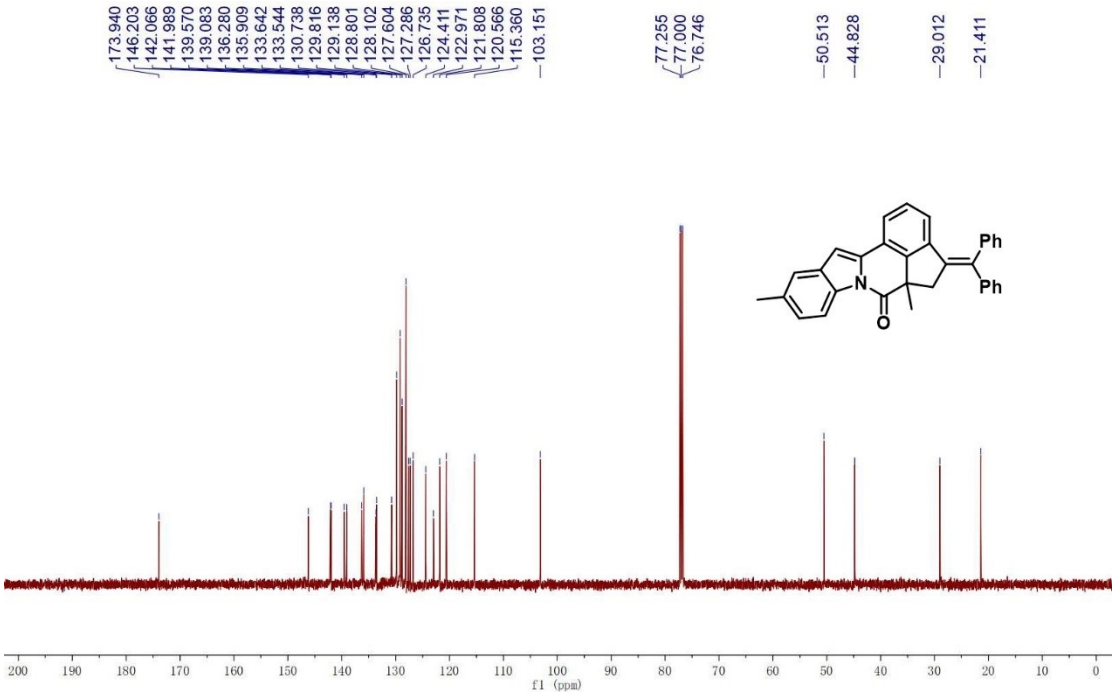
^{1}H NMR of **5aa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5aa** (125 MHz, $CDCl_3$)



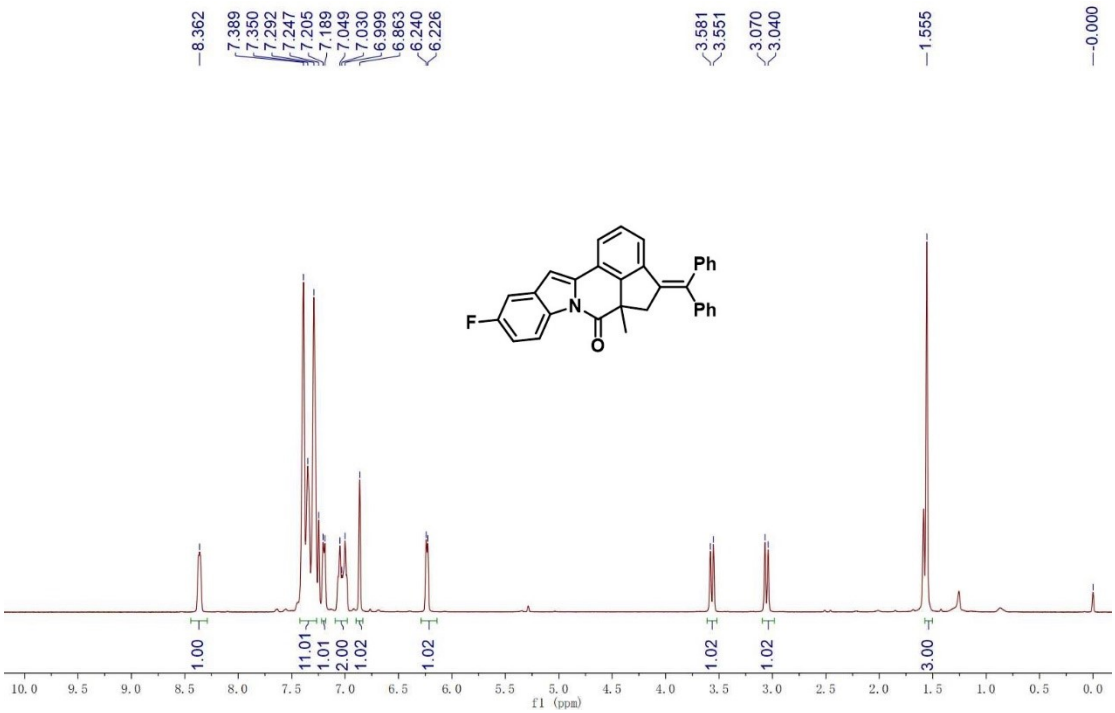


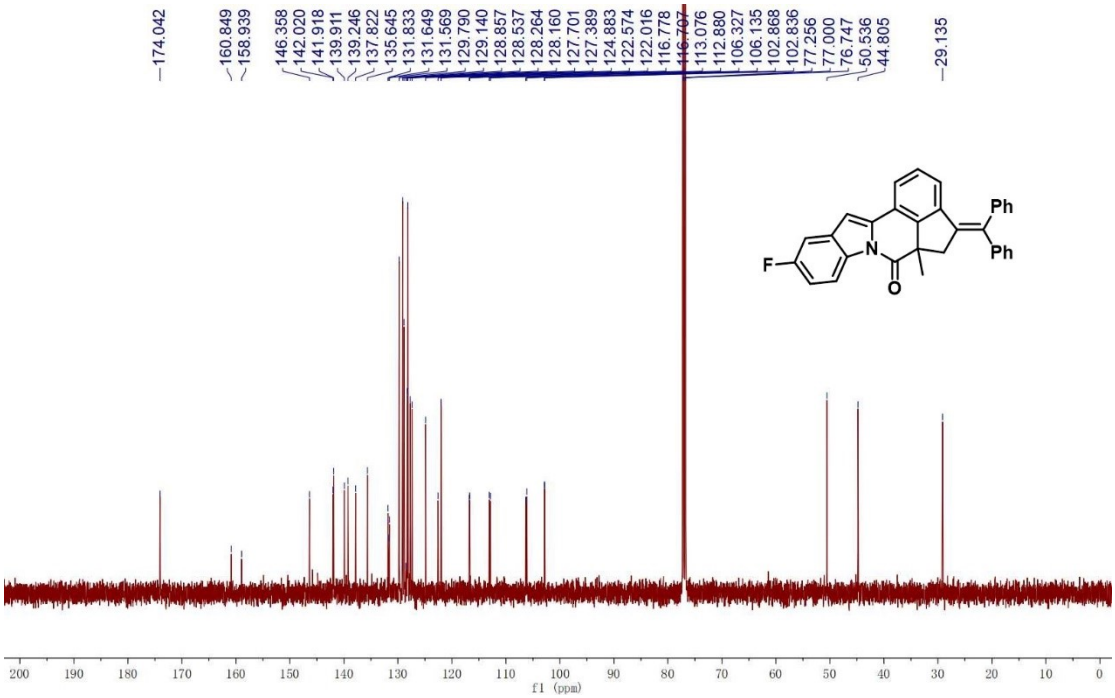
^{1}H NMR of **5ba** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ba** (125 MHz, $CDCl_3$)



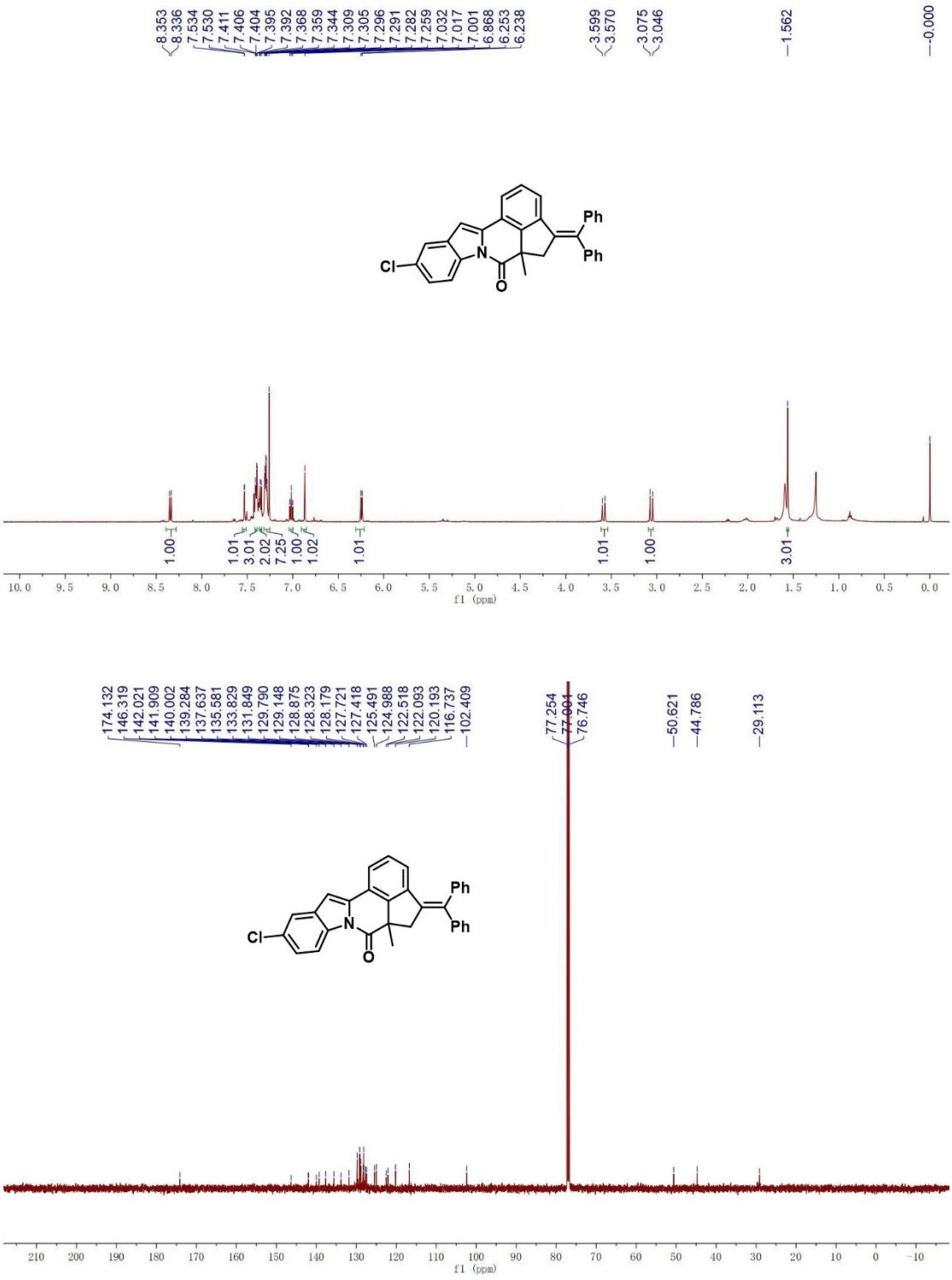


^{1}H NMR of **5ca** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ca** (125 MHz, $CDCl_3$)

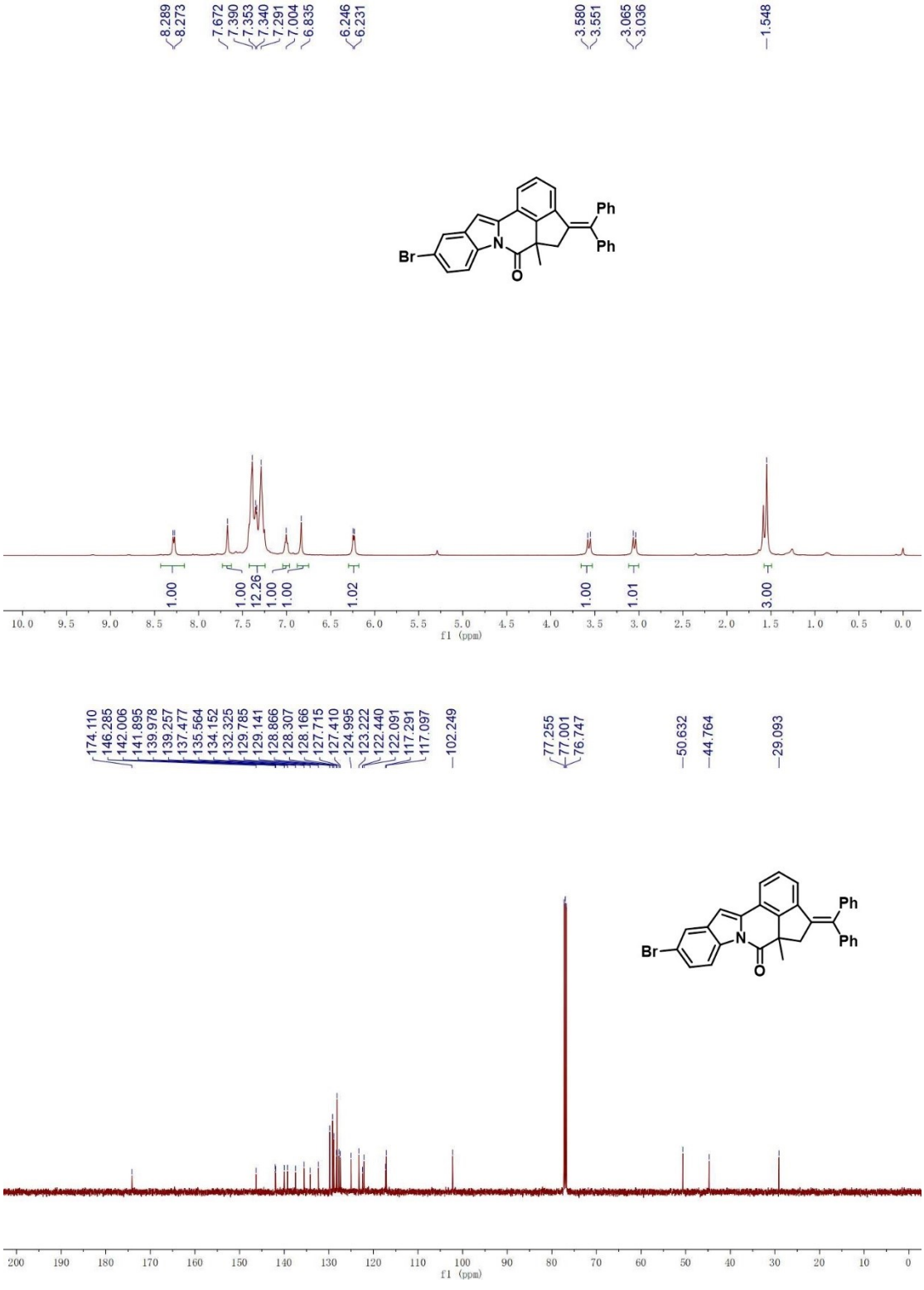




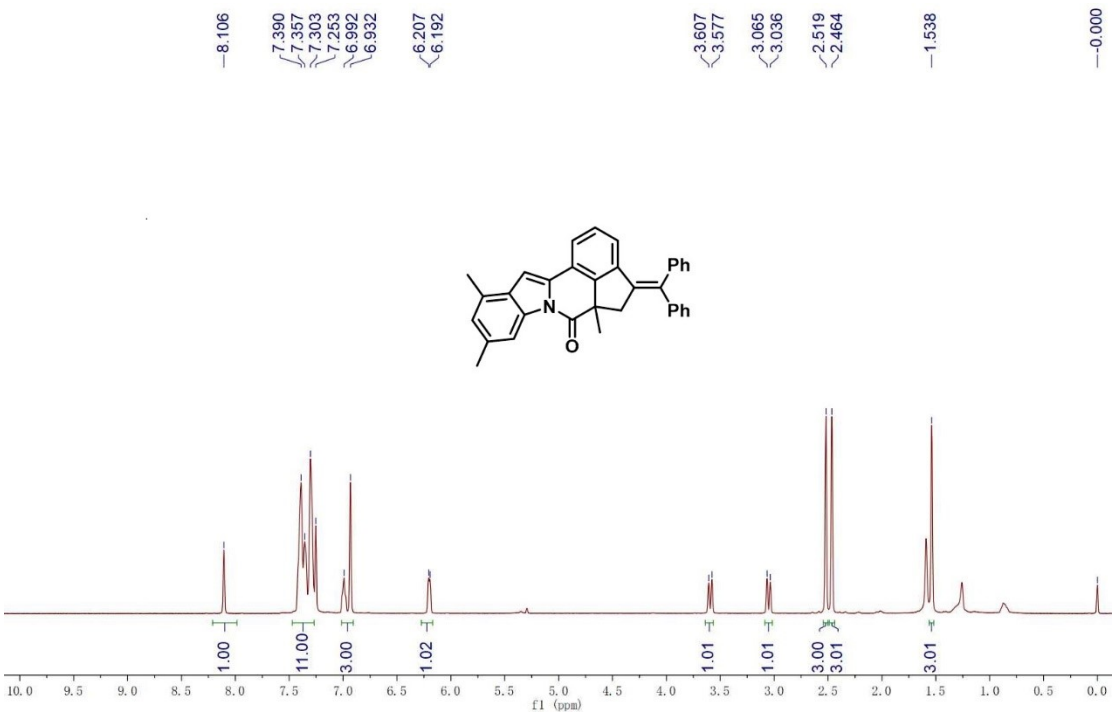
^{1}H NMR of **5da** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5da** (125 MHz, $CDCl_3$)

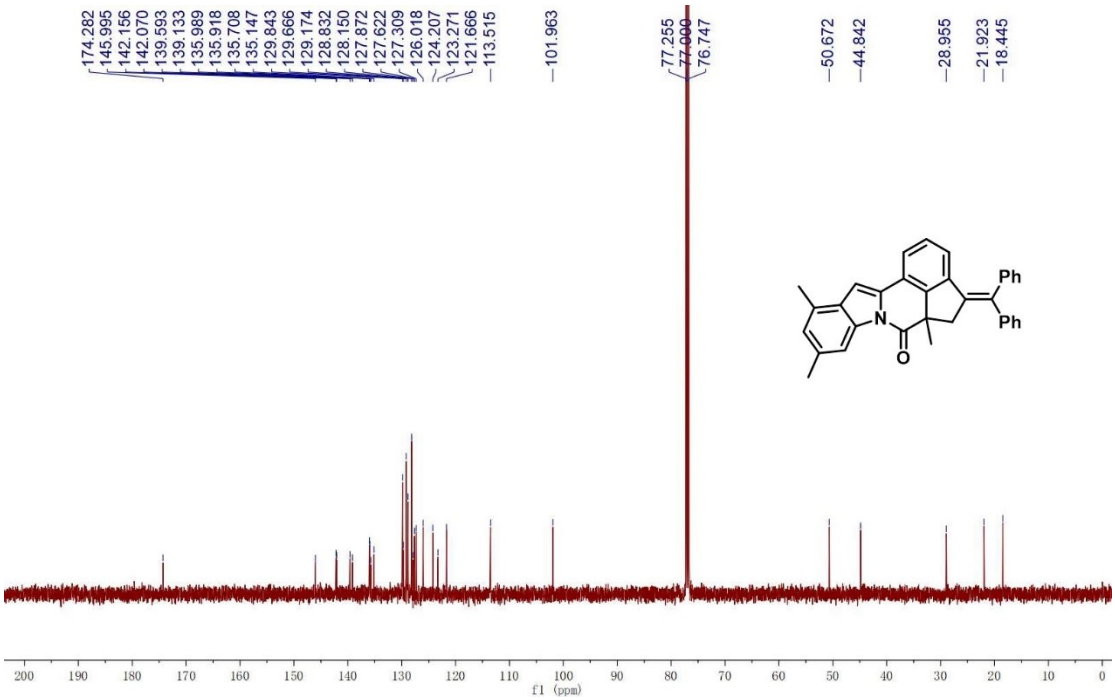


^{1}H NMR of **5ea** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ea** (125 MHz, $CDCl_3$)

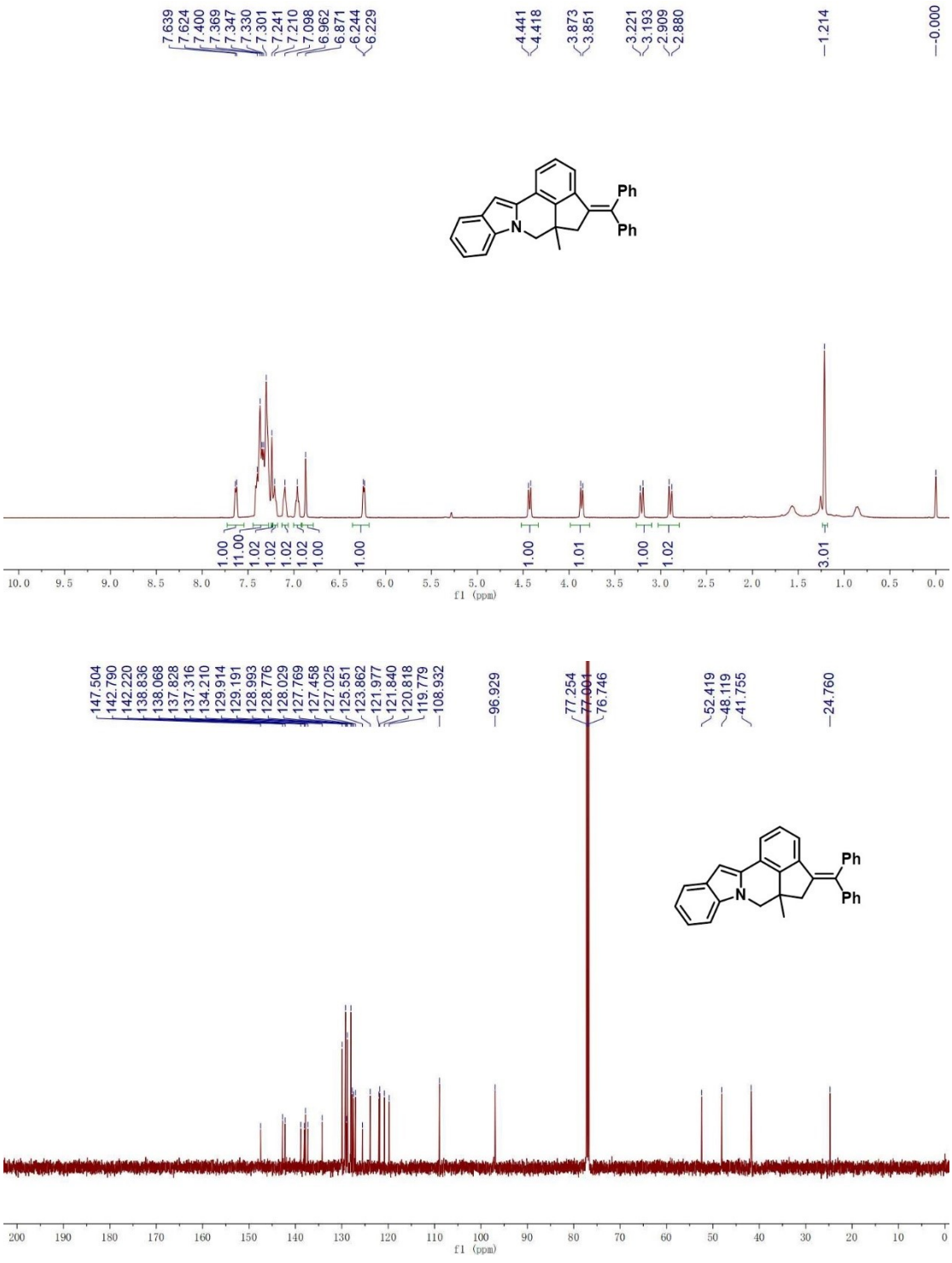


^{1}H NMR of **5fa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5fa** (125 MHz, $CDCl_3$)

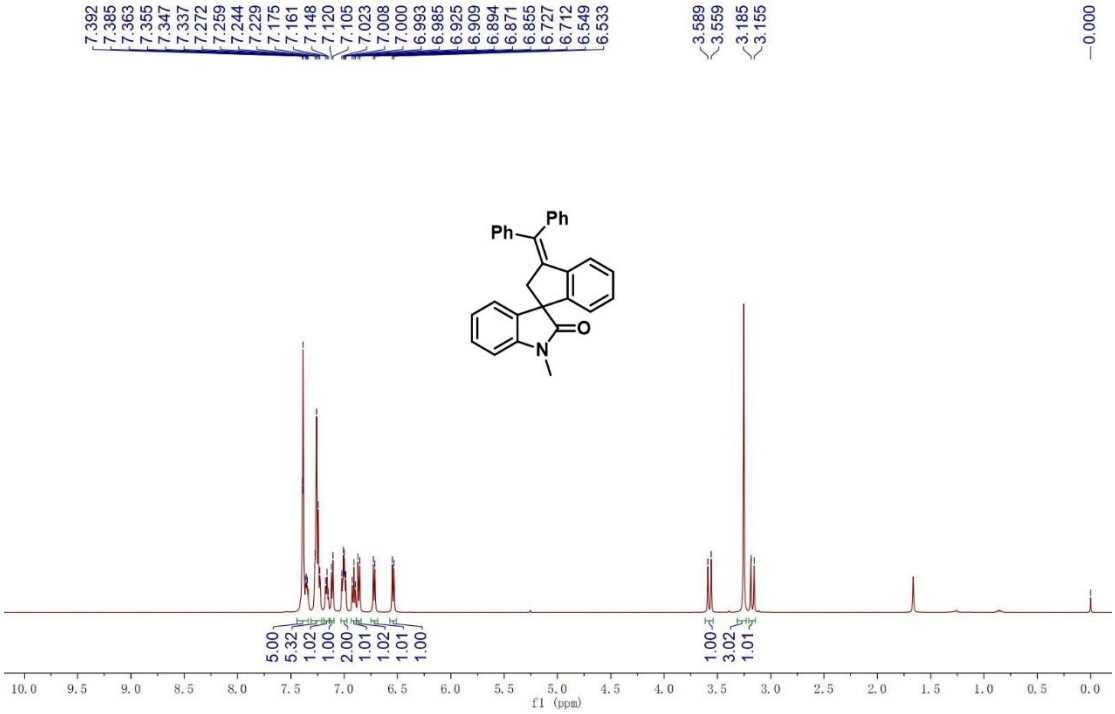


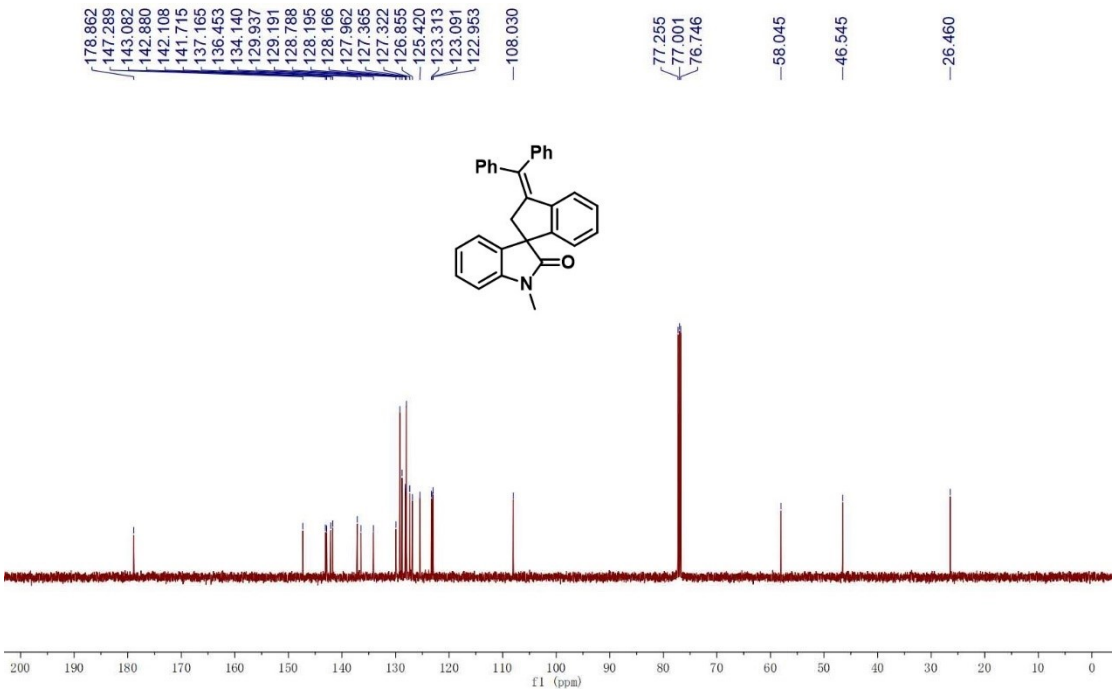


^{1}H NMR of **5ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ga** (125 MHz, $CDCl_3$)

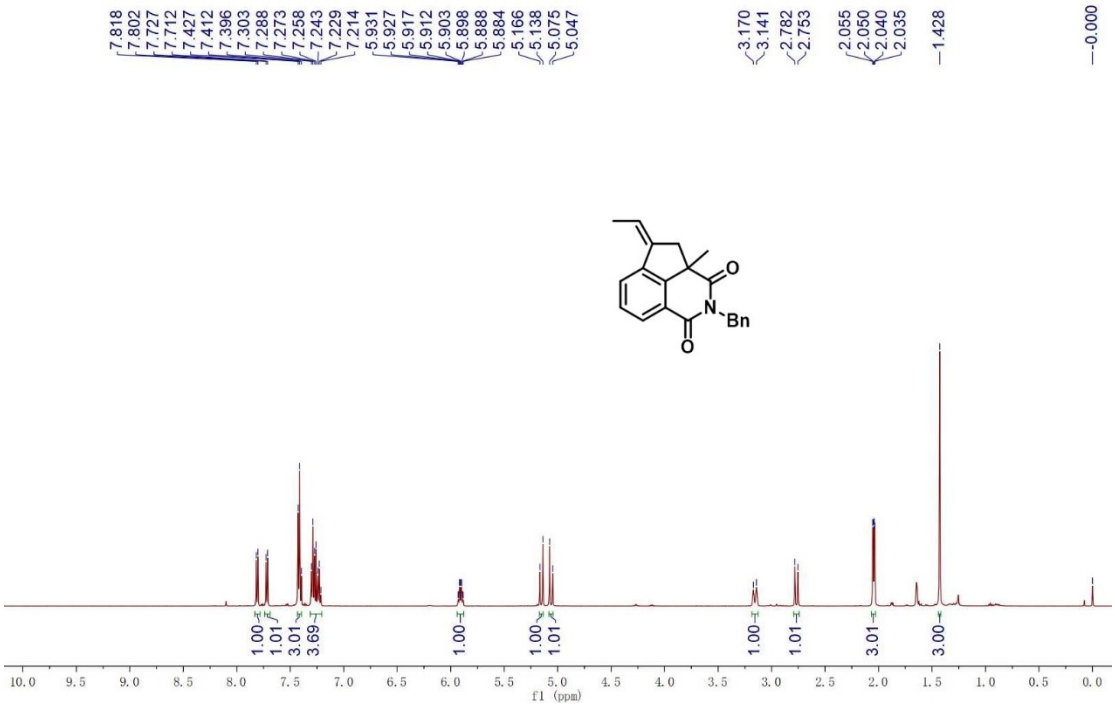


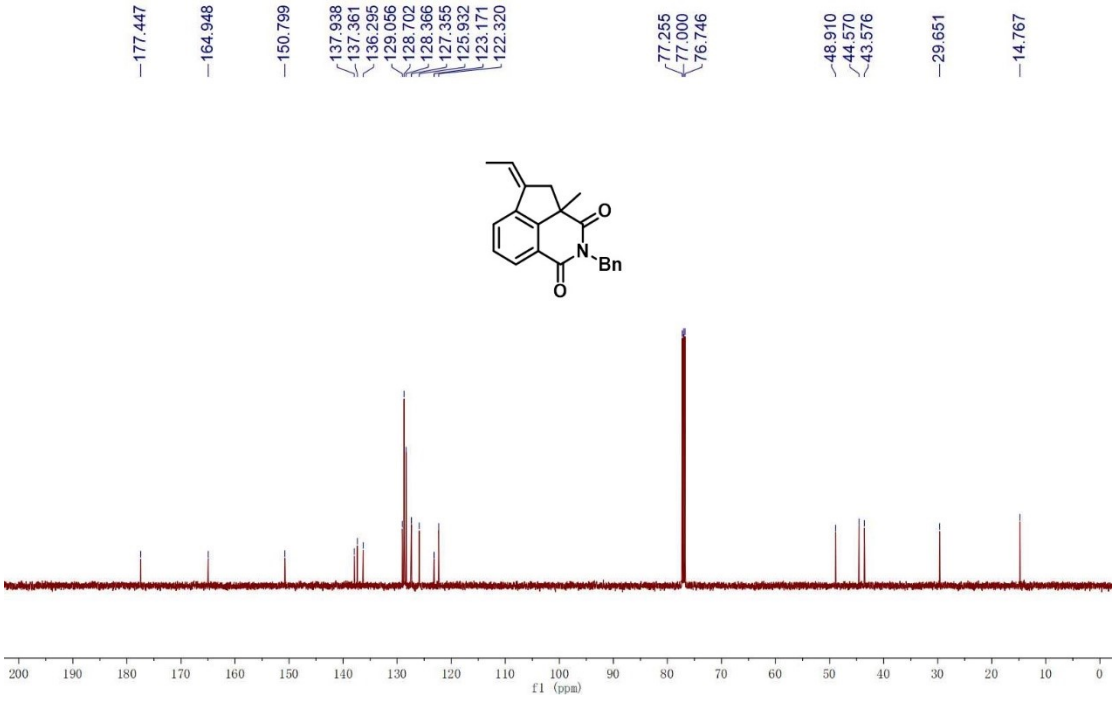
^{1}H NMR of **7** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7** (125 MHz, $CDCl_3$)



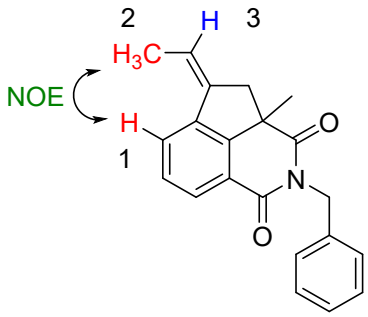


^{1}H NMR of **(*Z*)-3at** (500 MHz, $CDCl_3$) and ^{13}C NMR of **(*Z*)-3at** (125 MHz, $CDCl_3$)





NOESY of product *Z*-3at



NOE of product *Z*-3at: By analyzing the **NOESY**, we found that only 1-H and 2-H have **NOE**-related signals, while 3-H has no **NOE**-related signals with 2-H. This phenomenon illustrates：the methyl group is cis to the phenyl group. Therefore, the structure of the product is identified as *Z* configuration.

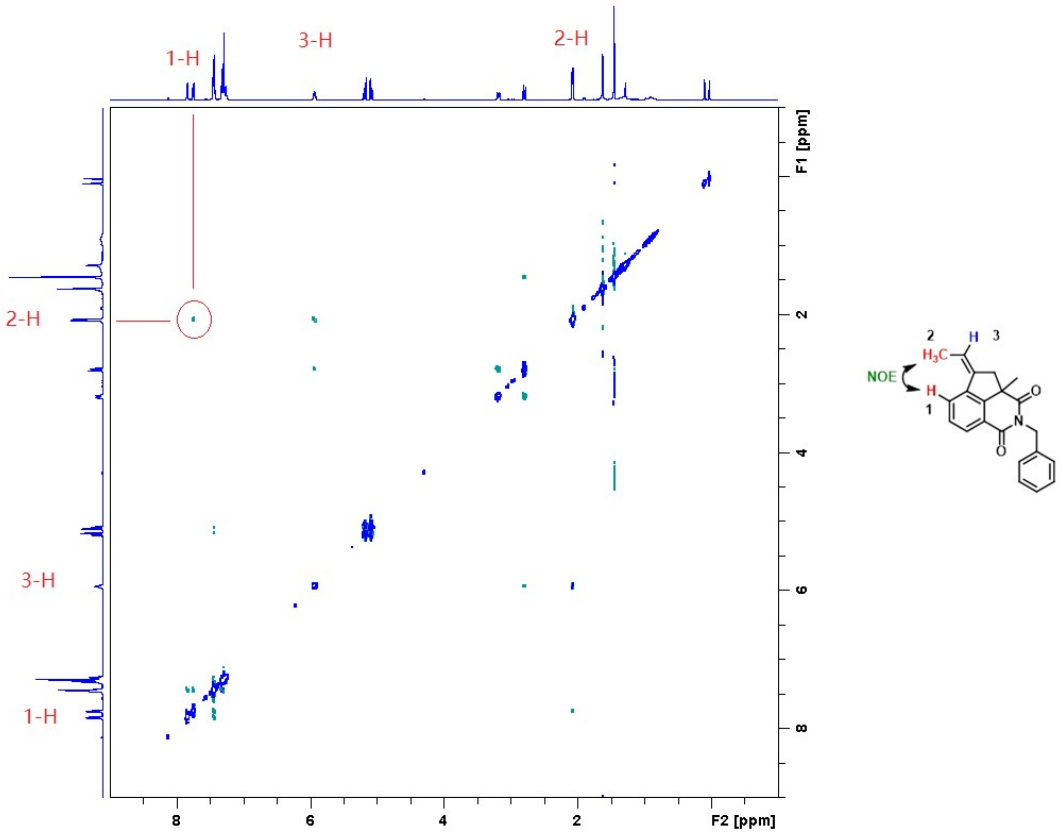
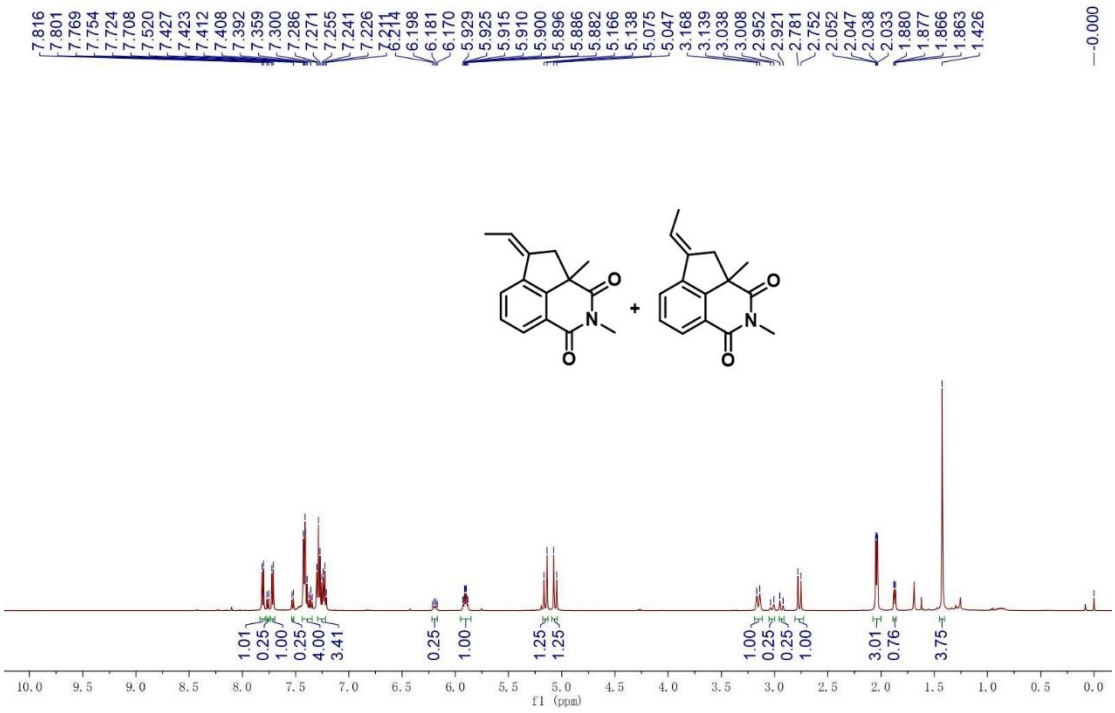
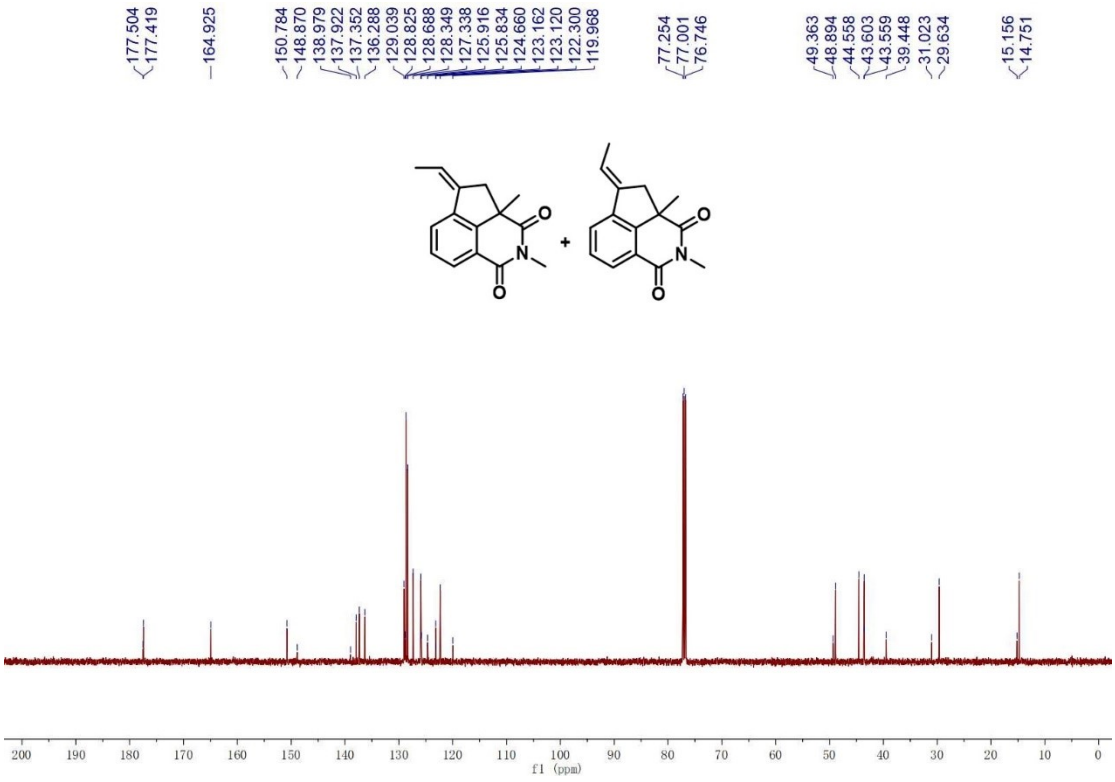


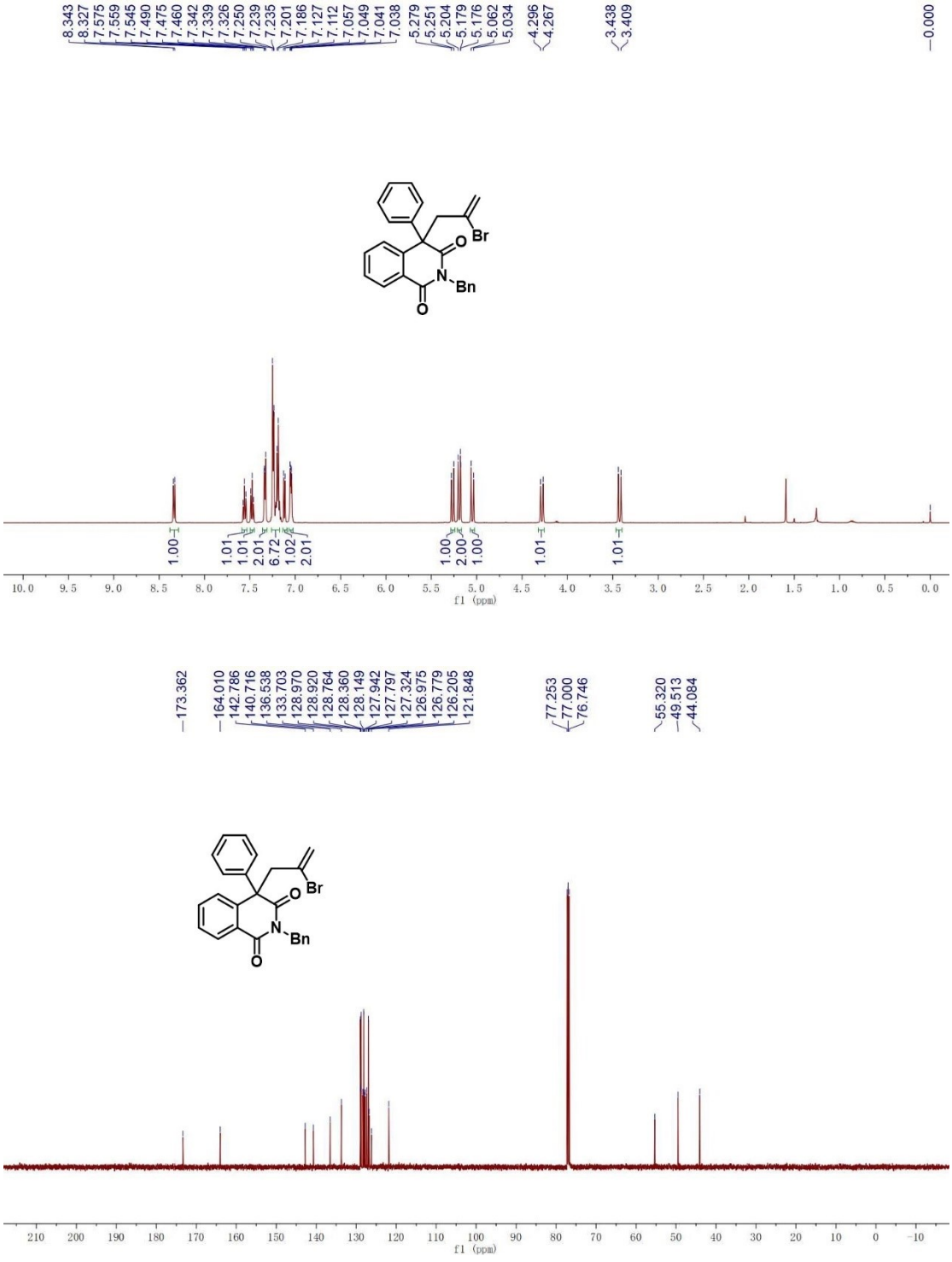
Figure S1 NOE of product ***Z*-3at**.

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

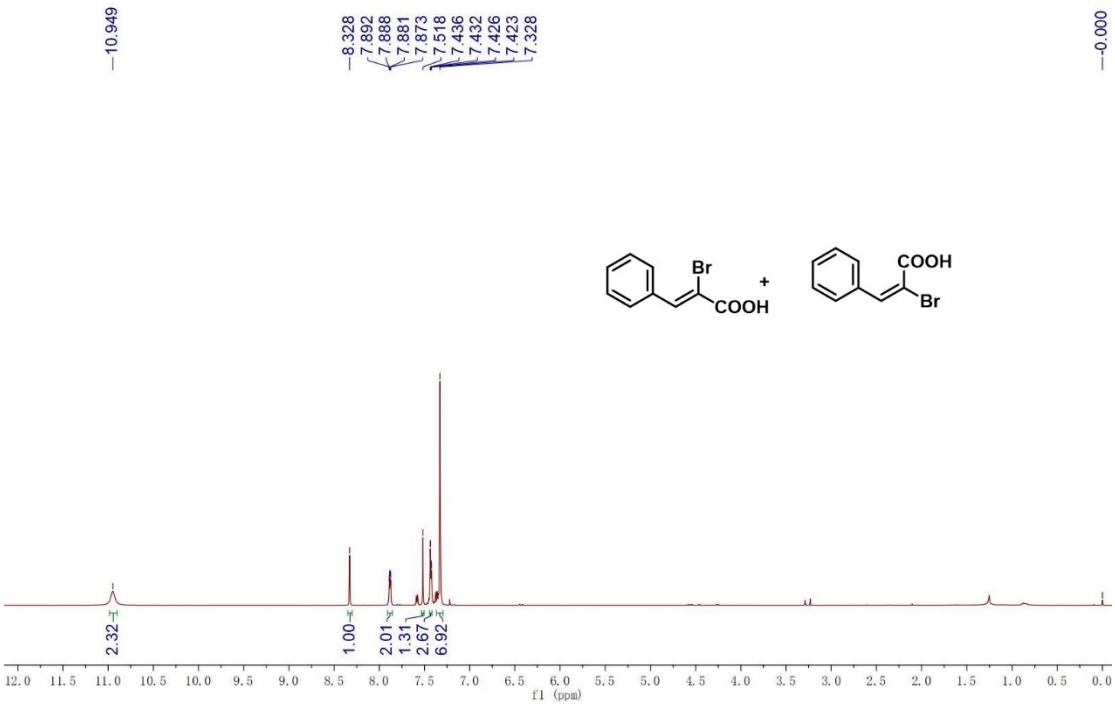




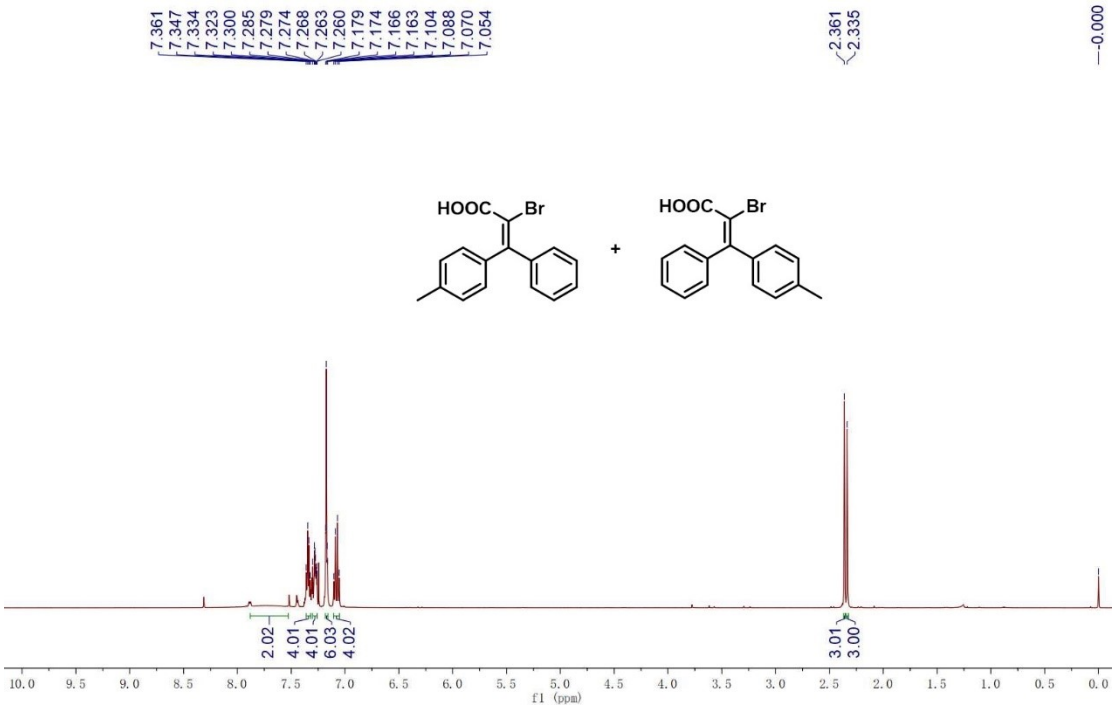
^{1}H NMR of **8** (500 MHz, $CDCl_3$) and ^{13}C NMR of **8** (125 MHz, $CDCl_3$)



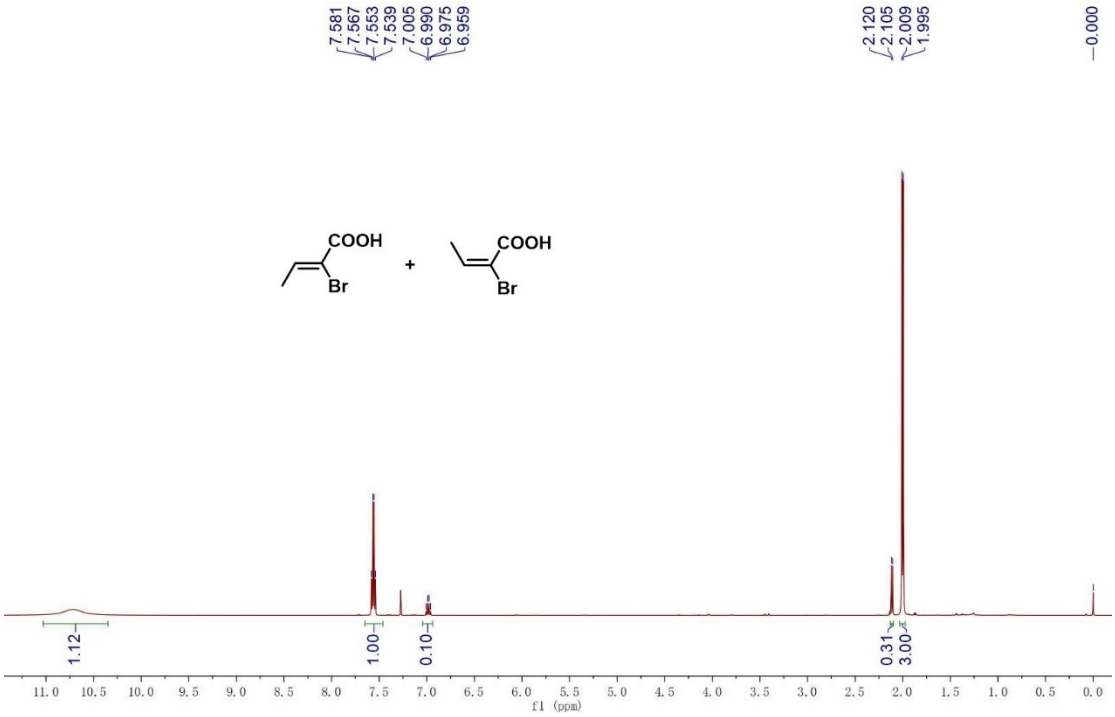
^{1}H NMR of **2r** (500 MHz, $CDCl_3$)



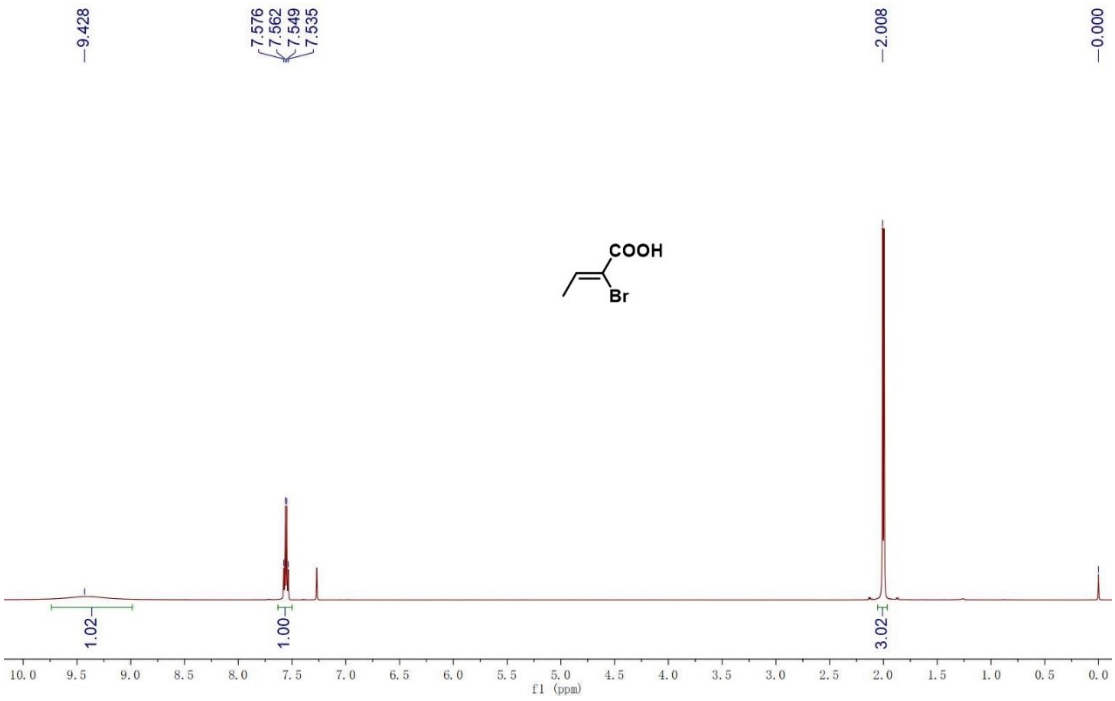
^{1}H NMR of **2s** (500 MHz, $CDCl_3$)

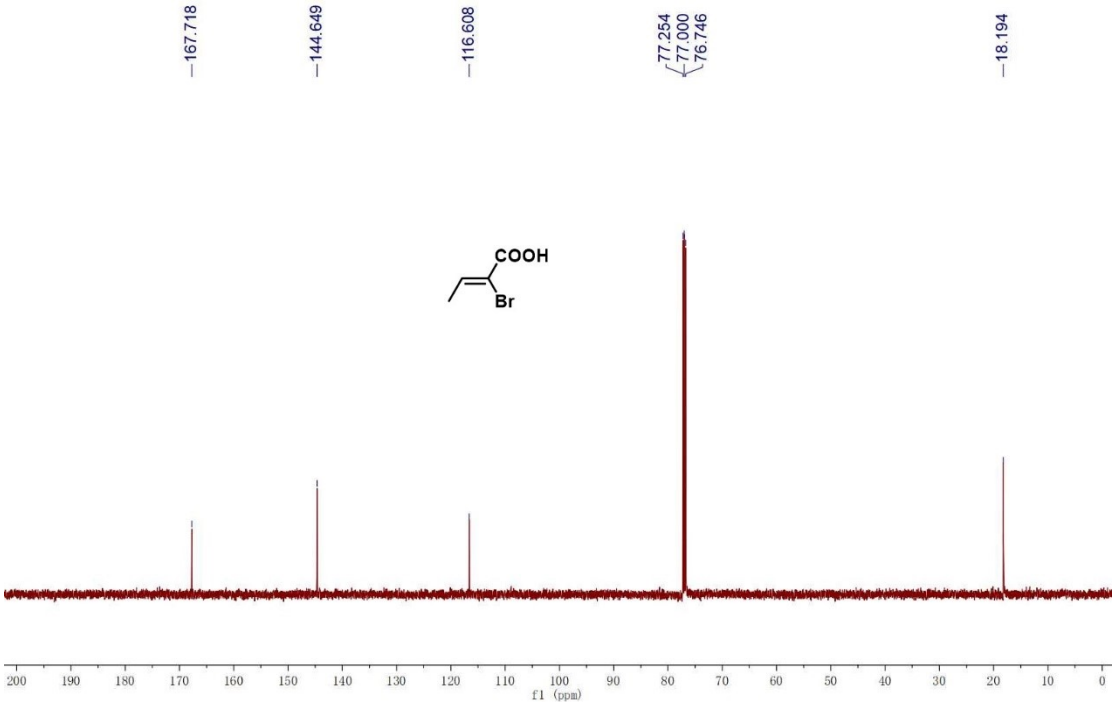


^{1}H NMR of **2t** (500 MHz, $CDCl_3$)



^{1}H NMR of ***Z*-2t** (500 MHz, $CDCl_3$) and ^{13}C NMR of ***Z*-2t** (125 MHz, $CDCl_3$)





9 Crystal Structure of 3ia (CCDC: 2084415)

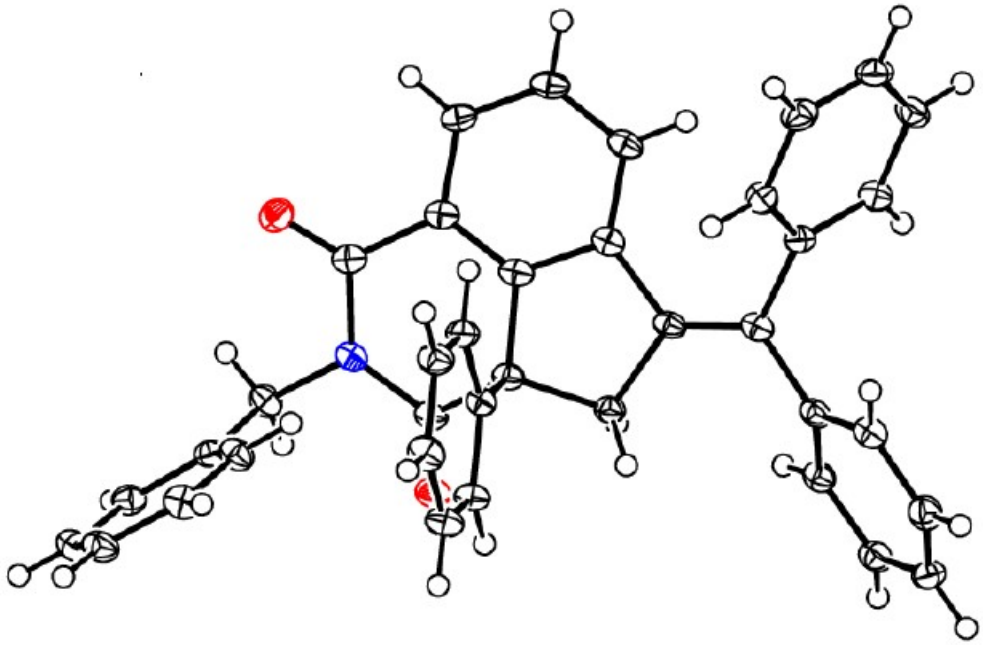


Figure S2 X-ray crystal structure of **3ia**. The thermal ellipsoids are 50% probability level.

Table S1 Crystal data and structure refinement for exp_1537.

Identification code	exp_1537
Empirical formula	$C_{30}H_{23}NO$
Formula weight	413.49
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$Pn2_1a$
a/Å	14.3078(2)
b/Å	9.09519(16)
c/Å	33.7020(6)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	4385.72(13)
Z	8
ρ_{calc}g/cm^3	1.252
μ/mm^{-1}	0.582
F(000)	1744.0
Crystal size/mm^3	0.3 × 0.3 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.244 to 143.85
Index ranges	-17 ≤ h ≤ 10, -7 ≤ k ≤ 10, -24 ≤ l ≤ 41
Reflections collected	10487
Independent reflections	6016 [R_{int} = 0.0189, R_{sigma} = 0.0291]
Data/restraints/parameters	6016/1/579
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.1163
Final R indexes [all data]	R_1 = 0.0451, wR_2 = 0.1182
Largest diff. peak/hole / e Å^{-3}	0.39/-0.23
Flack parameter	0.0(2)