Supporting Information

Palladium-catalyzed dearomative Heck/[4 + 3] decarboxylative cyclization of indoles with *α*-oxocarboxylic acids via C−H activation

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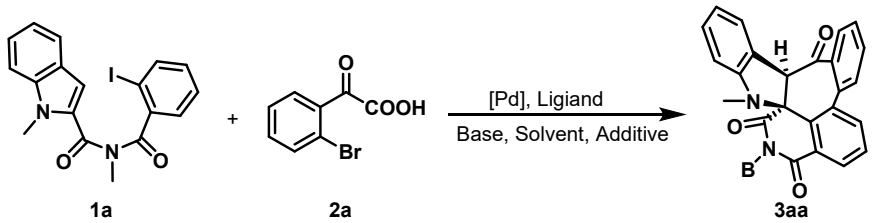
1 General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instrument (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz and ^{19}F NMR at 471MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26 ppm), ^{13}C NMR: $CDCl_3$ (77.00 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; dd, doublets of doublet; t, triplet, and m, multiplet. X-ray data were taken on an agilent Super Nova, X-ray diffractometer equipped with a large area CCD detector. 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). High-resolution mass spectra (HRMS) were equipped with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) sources. Reactions were monitored by thin-layer chromatography (TLC). 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 Optimization of the Reaction Conditions

Table S1. Optimization of reaction conditions for the synthesis of 3aa[a]



Entry	Pd source	Ligand	Base	Solvent	Additive	Yield[b] /%
1	$PdCl_2(MeCN)_2$	dippf	Na_2CO_3	DMF	--	55%
2	$Pd(OAc)_2$	dippf	Na_2CO_3	DMF	--	61%
3	$PdCl_2$	dippf	Na_2CO_3	DMF	--	57%
4	$Pd(dba)_2$	dippf	Na_2CO_3	DMF	--	trace
5	$PdCl_2(PhCN)_2$	dippf	Na_2CO_3	DMF	--	38%

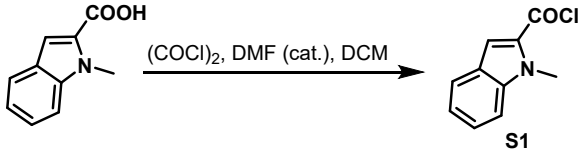
6	$PdCl_2(dppf)_2$	dippf	Na_2CO_3	DMF	--	trace
7	$Pd(OAc)_2$	PPh_3	Na_2CO_3	DMF	--	40%
8	$Pd(OAc)_2$	PCy_3	Na_2CO_3	DMF	--	56%
9	$Pd(OAc)_2$	dppf	Na_2CO_3	DMF	--	57%
10	$Pd(OAc)_2$	Xant-phos	Na_2CO_3	DMF	--	49%
11	$Pd(OAc)_2$	$PCy_3{\cdot}HBF_4$	Na_2CO_3	DMF	--	45%
12	$Pd(OAc)_2$	DcHPF	Na_2CO_3	DMF	--	61%
13	$Pd(OAc)_2$	DtBPF	Na_2CO_3	DMF	--	60%
14	$Pd(OAc)_2$	dippf	K_2CO_3	DMF	--	23%
15	$Pd(OAc)_2$	dippf	Cs_2CO_3	DMF	--	trace
16	$Pd(OAc)_2$	dippf	K_3PO_4	DMF	--	54%
17	$Pd(OAc)_2$	dippf	$NaHCO_3$	DMF	--	59%
18	$Pd(OAc)_2$	dippf	CH_3COONa	DMF	--	54%
19	Pd(OAc)2	dippf	NaOPiv	DMF	--	62%
20	$Pd(OAc)_2$	dippf	Li_2CO_3	DMF	--	trace
21	$Pd(OAc)_2$	dippf	NaH_2PO_4	DMF	--	NR
22	$Pd(OAc)_2$	dippf	Na_2HPO_4	DMF	--	NR
23	$Pd(OAc)_2$	dippf	NaOPiv	DMA	--	78%
24	$Pd(OAc)_2$	dippf	NaOPiv	DMSO	--	47%
25	$Pd(OAc)_2$	dippf	NaOPiv	NMP	--	trace
26	$Pd(OAc)_2$	dippf	NaOPiv	Dioxant	--	NR
27[c]	$Pd(OAc)_2$	dippf	NaOPiv	DMA	--	70%
28[d]	$Pd(OAc)_2$	dippf	NaOPiv	DMA	--	65%
29	$Pd(OAc)_2$	dippf	NaOPiv	DMA	TBAI	70%
30	$Pd(OAc)_2$	dippf	NaOPiv	DMA	TBAB	84%
31	$Pd(OAc)_2$	dippf	NaOPiv	DMA	TBAC	74%
32	$Pd(OAc)_2$	dippf	NaOPiv	DMA	PivOH	79%
33[e]	$Pd(OAc)_2$	dippf	NaOPiv	DMA	TBAB	76%
34[f]	$Pd(OAc)_2$	dippf	NaOPiv	DMA	TBAB	75%

35[g]	$Pd(OAc)_2$	dippf	NaOPiv	DMA	TBAB	42%
36[h]	$Pd(OAc)_2$	dippf	NaOPiv	DMA	TBAB	74%

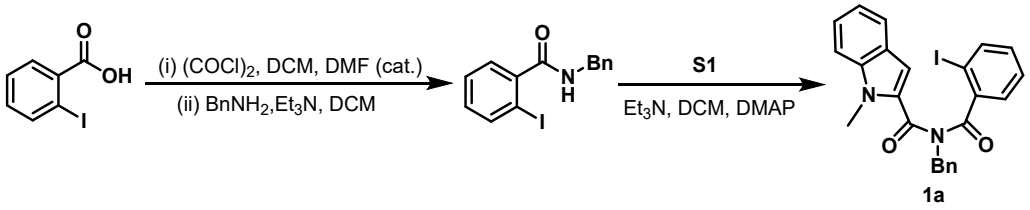
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (3.0 equiv), palladium catalyst (10 mol%), monodentate ligand (20 mol%) or bidentate ligand (10 mol%), base (5.0 equiv), additive (1.0 equiv), and solvent (2.0 mL) at 130 °C under nitrogen atmosphere for 12 h. [b]Isolated yields. [c]120 °C. [d]140 °C. [e]**2a** (2.0 equiv). [f]$Pd(OAc)_2$ (5.0 mol%), dippf (5.0 mol%). [g]NaOPiv (3.0 equiv). [h]DMA (1.0 mL). dippf =1,1'-Bis(diisopropylphosphino)ferrocene. dr > 20:1. The diastereomeric ratio (dr) was determined by 1H NMR spectra of the corresponding product.

3 General Procedure for the Synthesis of Starting Materials

3.1 General procedure for the synthesis of substrates 1a-l[1]



An oven dried reaction tube containing a PTFE-coated stir bar was charged with 1-methyl-1*H*-indole-2-carboxylic acid (5.0 mmol, 1.0 equiv, 0.87 g), oxalyl chloride (7.5 mmol, 1.5 equiv, 0.6 mL) in dichloromethane (10.0 mL), and DMF (7 drops). The mixture was stirred by 1 h at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for another 3 h. The solvent was evaporated and the crude **S1** was used directly in the next step.



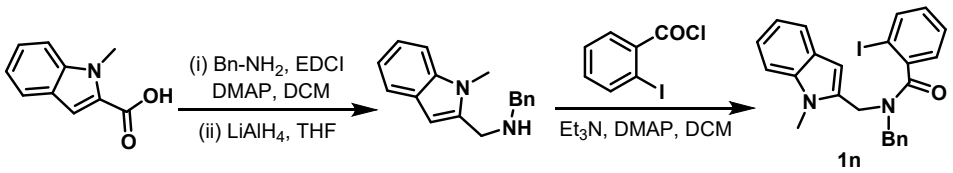
An oven dried reaction tube containing a PTFE-coated stir bar was charged with 2-iodobenzoic acid (5.0 mmol, 1.0 equiv, 1.24 g), oxalyl chloride (6.0 mmol, 1.2 equiv, 0.5 mL) in dichloromethane (10.0 mL) and DMF (3 drops). The mixture was stirred for 2 hours at 0 °C and then warmed at room temperature. 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 (10.0 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 5.0 mL of saturated Na_2CO_3 solution and extraction with dichoromethane. It was used without any purification in the next step.

S1 (5.0 mmol, 1.2 equiv, 1.16 g) in dichoromethane (5.0 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, 39.0 mg) in toluene (5.0 mL). The mixture was stirred overnight at reflux in oil bath. The reaction was quenched with saturated aqueous Na_2CO_3 (5.0 mL), then the mixture was extracted with dichloromethane (3 × 5.0 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 for **1b-m** were similar to that for **1a**.

3.2 General procedure for the synthesis of substrate 1n[1]

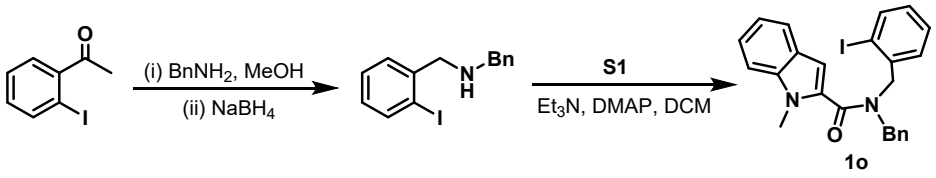


An oven dried reaction tube containing a PTFE-coated stir bar was charged with 1-methyl-1H-indole-2-carboxylic acid (4.0 mmol, 1.0 equiv, 0.7 g) and phenylmethanamine (5.0 mmol, 1.25 equiv, 0.5 g) was added in CH_2Cl_2 (20.0 mL). DMAP (0.5 mmol, 0.125 equiv, 61.1 mg) and EDCI (6.0 mmol, 1.5 equiv, 1.2 g) were added and the mixture was stirred at 0 °C. After 5 minutes, the reaction was allowed to warm to room temperature and was stirred for 16 h and afterwards diluted by excess amount of CH_2Cl_2. The organic solution was washed by water and dried over Na_2SO_4. The solvent was evaporated and the crude was used directly in the next step. *N*-benzyl-1-methyl-1*H*-indole-2-carboxamide (5.0 mmol, 1.0 equiv, 1.3 g) were dissolved in THF (15.0 mL) and $LiAlH_4$ (10.0 mmol, 2.0 equiv, 379.5 mg) was added at 0 °C. The mixture

was stirred for 4 h at 70 °C. The reaction mixture was washed with water and extracted with EtOAc. The organic layers were combined and dried with Na_2SO_4. Subsequently, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5:1) to afford the corresponding product *N*-benzyl-1-(1-methyl-1*H*-indol-2-yl)methanamine.

An oven dried reaction tube containing a PTFE-coated stir bar was charged with 2-iodobenzoic acid (5.0 mmol, 1.0 equiv, 1.2 g), oxalyl chloride (6.0 mmol, 1.2 equiv, 0.5 mL) in dichloromethane (10.0 mL) and DMF (3 drops). The mixture was stirred by 2 h 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, 1.5 equiv, 1.3 g) was dissolved in dichloromethane (10.0 mL). *N*-benzyl-1-(1-methyl-1*H*-indol-2-yl)methanamine (3.3 mmol, 1.0 equiv, 0.8 g) 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 reaction mixture was washed with water and extracted with DCM. The organic layers were combined and dried with Na_2SO_4. Subsequently, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5:1) to afford the corresponding product **1n**.

3.3 General procedure for the synthesis of substrate 1o[1]

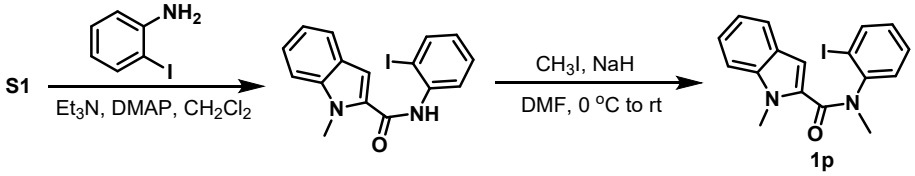


To a solution of *o*-iodoacetophenone (5.0 mmol, 1.0 equiv, 1.2 g) in MeOH (30.0 mL) at 0 °C was added benzylamine (10.0 mmol, 2.0 equiv, 1.1 g) slowly, and the reaction mixture was stirred at 0 °C for 30 minutes, then at rt for 3 h. The reaction mixture was again cooled to 0 °C, and $NaBH_4$ (7.5 mmol, 1.5 equiv, 0.3 g) was added every 10 min in three portions. Then it was stirred at rt for 1 h, and the solvent was evaporated to 1/3 of its original volume under reduced pressure. H_2O (10.0 mL) and

$NaHCO_3$ (0.4 g) were added, and the reaction mixture was stirred at rt for 10 minutes. Aqueous phase was separated and extracted with CH_2Cl_2 three times. Combined organic layers were dried over K_2CO_3, filtered, and concentrated. The obtained residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 2:1) to afford *N*-benzyl-1-(2-iodophenyl)methanamine as a colorless oil.

S1 (5.0 mmol, 1.2 equiv, 1.2 g) in CH_2Cl_2 (5.0 mL) was added to a mixture of *N*-benzyl-1-(2-iodophenyl)methanamine (5.0 mmol, 1.0 equiv, 1.6 g), triethylamine (10.0 mmol, 2.0 equiv, 1.4 mL) and DMAP (0.25 mmol, 0.05 equiv, 39.0 mg) in CH_2Cl_2 (5.0 mL). The mixture was stirred overnight at reflux in oil bath. The reaction was quenched with saturated aqueous Na_2CO_3 (5.0 mL), then the mixture was extracted with dichloromethane (3 × 5.0 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) to afford the corresponding product **1o**.

3.4 General procedure for the synthesis of substrate 1p[1]

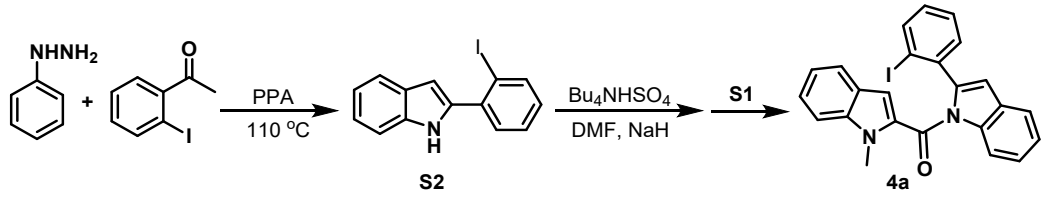


To a solution of *o*-iodoaniline (5.0 mmol, 1.0 equiv, 1.1 g) in CH_2Cl_2 (20.0 mL) at 0 °C was added **S1** (7.5 mmol, 1.5 equiv, 1.4 g) in CH_2Cl_2 (5.0 mL) slowly, and the reaction mixture was stirred at 0 °C for 30 minutes, then allowed to warm to room temperature and stirred for 2 h. The reaction mixture was washed with water and extracted with CH_2Cl_2. The organic layers were combined and dried with Na_2SO_4. Subsequently, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5:1) to afford the corresponding product *N*-(2-iodophenyl)-1-methyl-1*H*-indole-2-carboxamide.

To a solution of *N*-(2-iodophenyl)-1-methyl-1*H*-indole-2-carboxamide (4.0 mmol, 1.0 equiv, 1.5 g) in DMF (20.0 mL) was added sodium hydride (60% dispersion in

mineral oil, 6.0 mmol, 1.5 equiv, 240.0 mg) in small portions at 0 °C. After stirring at room temperature for 1 h, the reaction mixture was cooled to 0 °C. Methyl iodide (8.0 mmol, 2.0 equiv, 0.5 mL) was added dropwise and the mixture was allowed to warm to room temperature and stirred for 3 h. The solution was poured into an ice-water mixture and extracted with EtOAc (3 x 25.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by silica gel chromatography (eluent: petroleum ether/EtOAc= 10:1) to afford **1p**.

3.5 General procedure for the synthesis of substrates 4a-h[1]

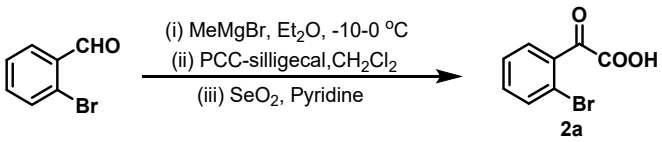


(1) A mixture of 2-iodoacetophenone (5.0 mmol, 1.0 equiv, 1.23 g), phenylhydrazine (6.0 mmol, 1.2 equiv, 0.65 g) and polyphosphoric acid (PPA, 15.0 g) was added to a round bottom flask and stirred at 110 ℃ for 6 h. Upon completion of the reaction, the residue was quenched with ice water and extracted 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 afford the corresponding substituted indole **S2**.

(2) **S2** (1.0 equiv) and tetrabutylammonium hydrogensulfate (5 mol%) were dissolved in DMF and sodium hydride (2.5 equiv) was added at 0 °C. The mixture was stirred for 20 minutes, after which **S1** (2.0 equiv) was added dropwise under air followed by stirring for 8 h at 40 ℃. The reaction mixture was washed with water and extracted with DCM. The organic layers were combined and dried with Na_2SO_4. Subsequently, the solvent was evaporated under vacuum. The residue was purified by flash chromatography over silica gel with *n*-pentane/ethyl acetate to yield the pure products **4a**.

The procedures for **4b-h** were similar to that for **4a**.

3.6 General procedure for the preparation of *α*-oxocarboxylic acids[2]



2a

According to a literature procedure, to a cold (-10 °C) magnetically stirred solution of a 2-bromobenzaldehyde (5.0 mmol, 1.0 equiv, 0.92 g) in dry ether (20.0 mL) was added methylmagnesium bromide (5.0 mmol, 1.0 equiv) [prepared from magnesium (5.0 mmol, 1.0 equiv, 0.12 g) and methyl bromomethane (5.0 mmol, 1.0 equiv, 0.48 g) and a catalytic amount of iodine in 10.0 mL of dry ether]. The reaction mixture was stirred at -10 °C for 3 h. It was then poured into a saturated aqueous NH_4Cl solution and extracted with EtOAc (3 × 15.0 mL). The ethyl acetate extract was dried with Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel column chromatography using petroleum ether/EtOAc as eluent furnished the 1-(2-bromophenyl)ethan-1-ol. To a magnetically stirred solution of the 1-(2-bromophenyl)ethan-1-ol (5.0 mmol, 1.0 equiv, 1.0 g) in dry CH_2Cl_2 (20.0 mL) was added a homogeneous mixture of PCC (15.0 mmol, 3.0 equiv, 3.23 g) and silica gel. The resulted reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then filtered through a short silica gel column and eluted with excess CH_2Cl_2. Evaporation of the solvent furnished the 1-(2-bromophenyl)ethan-1-one.

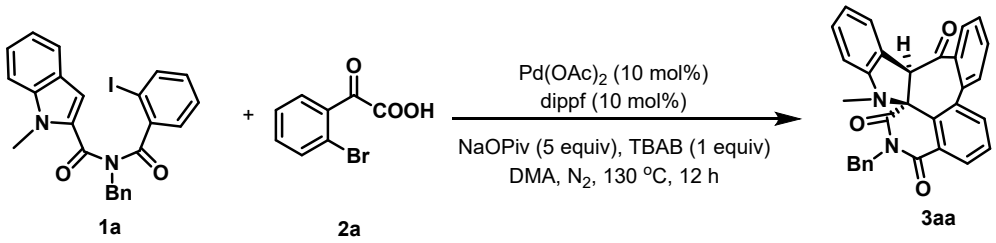
1-(2-bromophenyl)ethan-1-one (5.0 mmol, 1.0 equiv, 0.99 g) was dissolved in pyridine (10.0 mL) and SeO_2 (10.0 mmol, 2.0 equiv, 1.1 g) was added. The reaction mixture was heated in an oil bath at 90 °C under nitrogen for 5 h. The reaction was monitored by TLC. Upon completion, the reaction mixture was filtered, and the residue was washed with EtOAc (3 × 20.0 mL). The combined filtrate was treated with 1 M HCl (40.0 mL), the organic layer was separated, and the aqueous layer was re-extracted with EtOAc (3 × 20.0 mL). The organic layers were combined and treated with 1 M NaOH (50.0 mL), and the aqueous layer was separated. The aqueous layer was acidified with 1 M HCl to pH 1.5. The mixture was extracted with EtOAc (3 × 50.0 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The crude products

were further purified by recrystallization (PE/DCM = 10:1) to afford α-oxocarboxylic acids **2a**.

The procedures for **2b-m** were similar to that for **2a**.

4 Typical Procedures

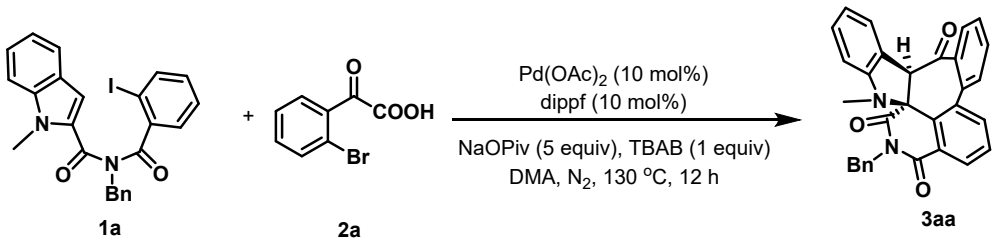
4.1 Typical procedures for the synthesis of hexacyclic fused indolines 3



To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, *N*-benzyl-*N*-(2-iodobenzoyl)-1-methyl-1*H*-indole-2-carboxamide **1a** (0.1 mmol, 1.0 equiv, 49.4 mg), 2-(2-bromoaryl)-2-oxoacetic acid **2a** (0.3 mmol, 3.0 equiv, 68.4 mg), $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.3 mg), dippf (0.01mmol, 10 mol%, 4.2 mg), NaOPiv (0.5 mmol, 5.0 equiv, 71.0 mg) and TBAB (0.1 mmol, 1.0 equiv, 32.2 mg) were added, and dissolved in DMA (2.0 mL). The vessel was evacuated, backfilled with N_2, and stirred at 130 ℃ for 12 h. 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 flash column chromatography (PE/EA = 10:1) to afford the desired products **3aa** (84%, 39.4 mg).

The procedures for **3ba-pa** and **3ab-am** were similar to that for **3aa**.

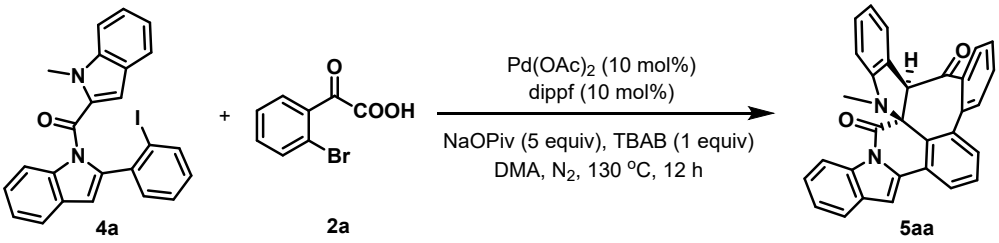
4.2 General procedure for the synthesis of 3aa from 1 mmol scale of 1a



To an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar, *N*-benzyl-*N*-(2-iodobenzoyl)-1-methyl-1*H*-indole-2-carboxamide **1a** (1.0 mmol, 1.0 equiv, 494.0 mg), 2-(2-bromoaryl)-2-oxoacetic acid **2a** (3.0 mmol, 3.0 equiv, 684.0 mg), $Pd(OAc)_2$

(0.1 mmol, 10 mol%, 23.0 mg), dippf (0.1mmol, 10 mol%, 42.0 mg), NaOPiv (5.0 mmol, 5.0 equiv, 710.0 mg) and TBAB (1.0 mmol, 1.0 equiv, 322.0 mg) were added, and dissolved in DMA (20.0 mL). The vessel was evacuated, backfilled with N_2, and stirred at 130 ℃ for 12 h. 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 flash column chromatography (PE/EA = 10:1) to afford the desired products **3aa** (72%, 338.5 mg).

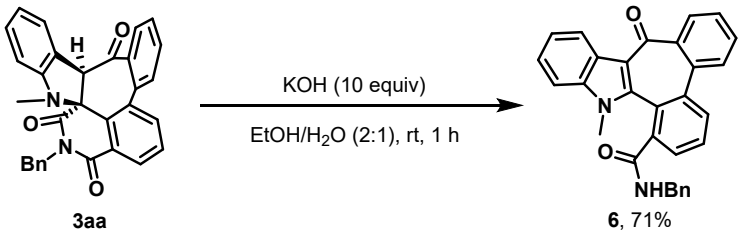
4.3 General procedure for the synthesis of octocyclic fused indolines 5



To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, (2-(2-iodophenyl)-1*H*-indol-1-yl)(1-methyl-1*H*-indol-2-yl)methanone **4a** (0.1 mmol, 1.0 equiv, 47.6 mg), 2-(2-bromoaryl)-2-oxoacetic acid **2a** (0.3 mmol, 3.0 equiv, 68.4 mg), $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.3 mg), dippf (0.01mmol, 10 mol%, 4.2 mg), NaOPiv (0.5 mmol, 5.0 equiv, 71.0 mg) and TBAB (0.1 mmol, 1.0 equiv, 32.2 mg) were added, dissolved in DMA (2.0 mL). The vessel was evacuated, backfilled with N_2, and stirred at 130 ℃ for 12 h. 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 flash column chromatography (PE/EA = 10:1) to afford the desired products **5aa** (79%, 35.7 mg).

The procedures for **5ba-ha**, **5ab-af** and **5ah-am** were similar to **5aa**.

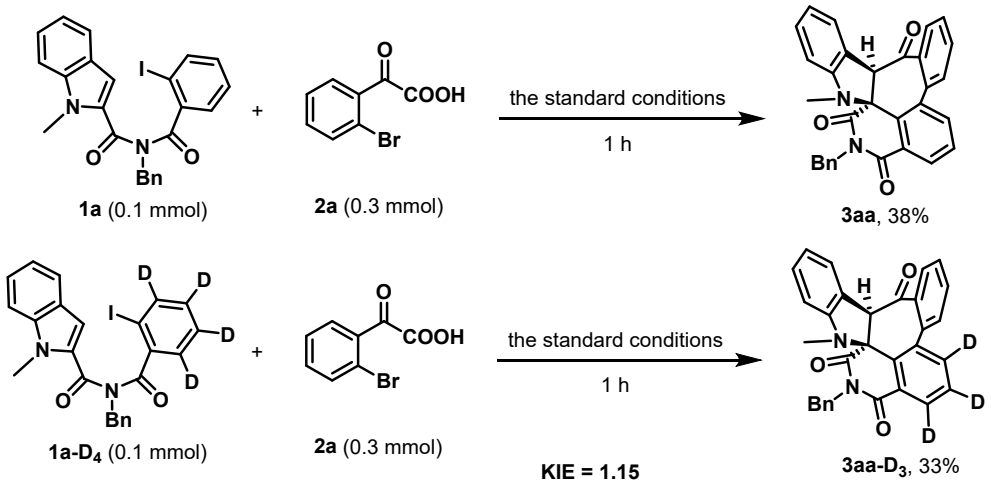
5 Synthetic Transformation of 3aa[3]



To a 25 mL Schlenk tube was added **3aa** (0.2 mmol, 94.0 mg), KOH (2.0 mmol, 112.2 mg), EtOH (2.0 mL) and H_2O (1.0 mL). Then the tube was stirred at room temperature for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography (eluent: petroleum ether/EtOAc = 5:1) to provide the desired product **6** (71%, 62.8 mg).

6 Mechanistic Experiments

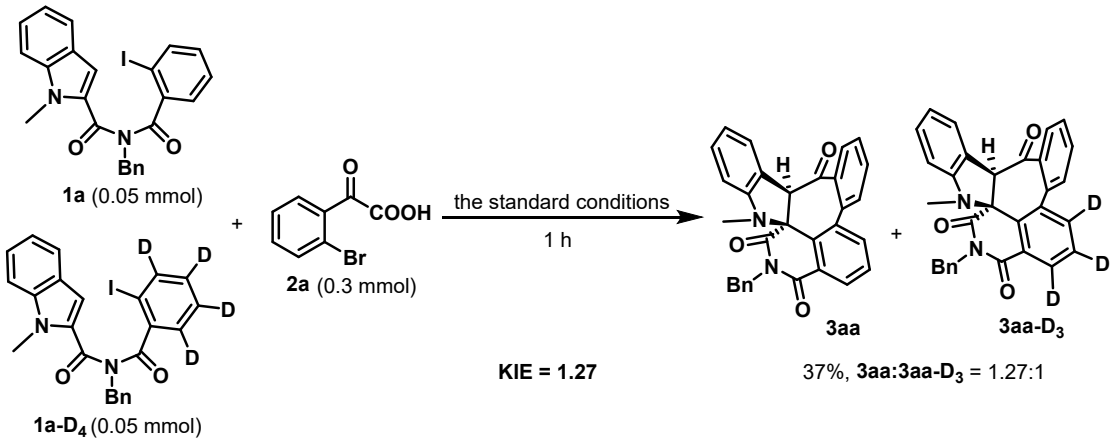
6.1 Parallel experiment



To an oven-dried 25 mL schlenk tube equipped with a magnetic stir bar, **1a** (0.1 mmol, 1.0 equiv, 49.4 mg), **2a** (0.3 mmol, 3.0 equiv, 68.4 mg), $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.3 mg), dippf (0.01mmol, 10 mol%, 4.2 mg), NaOPiv (0.5 mmol, 5.0 equiv, 71.0 mg) and TBAB (0.1 mmol, 1.0 equiv, 32.2 mg) were added, dissolved in DMA (2.0 mL). The other oven-dried Schlenk tube was added **1a-D_4** (0.1 mmol, 1.0 equiv, 49.4 mg), **2a** (0.3 mmol, 3.0 equiv, 68.4 mg), $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.3 mg), dippf (0.01mmol, 10 mol%, 4.2 mg), NaOPiv (0.5 mmol, 5.0 equiv, 71.0 mg), TBAB (0.1 mmol, 1.0 equiv, 32.2 mg) and DMA (2.0 mL). The vessel was evacuated, backfilled with N_2, and stirred at 130 °C for 1 h. 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 flash column chromatography

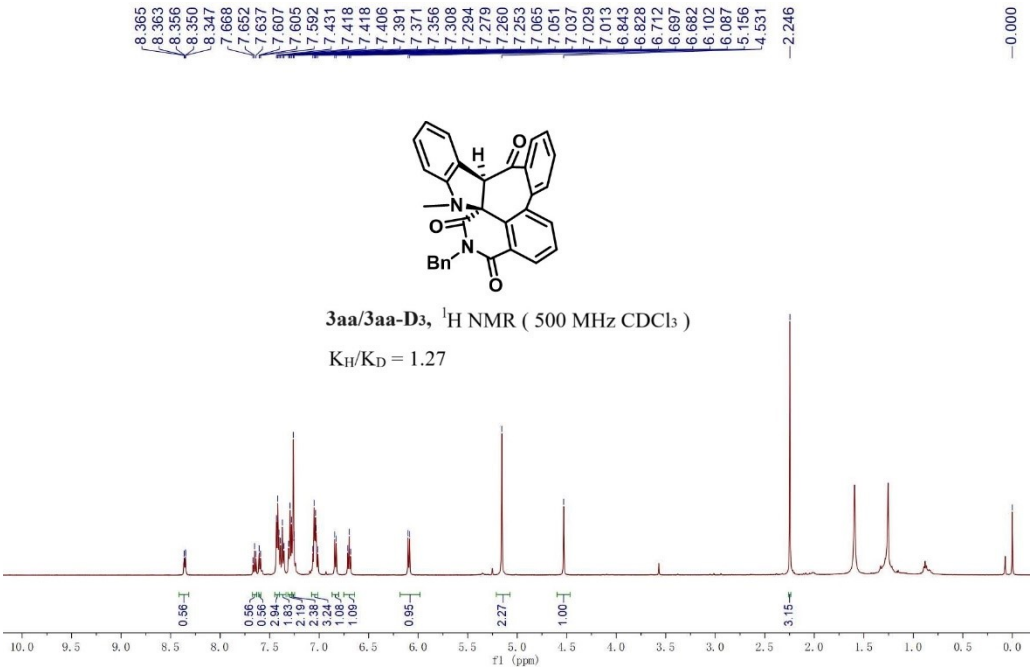
(PE/EA = 10:1) to afford the products **3aa** in 38% yield and **3aa-D$_3$** in 33% yield (K_H/K_D = 1.15).

6.2 Competition experiment



To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, **1a** (0.05 mmol, 1.0 equiv, 29.7 mg), **1a-D$_4$** (0.05 mmol, 1.0 equiv, 29.7 mg), **2a** (0.3 mmol, 3.0 equiv, 68.4 mg), $Pd(OAc)_2$ (0.01 mmol, 10 mol%, 2.3 mg), dippf (0.01mmol, 10 mol%, 4.2 mg), NaOPiv (0.5 mmol, 5.0 equiv, 71.0 mg) and TBAB (0.1 mmol, 1.0 equiv, 32.2 mg) were added, dissolved in DMA (2.0 mL). The vessel was evacuated, backfilled with N_2, and stirred at 130 ℃ for 1 h. 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 flash column chromatography (PE/EA = 10:1) to afford the products **3aa** and **3aa-D$_3$** in 37% yield.

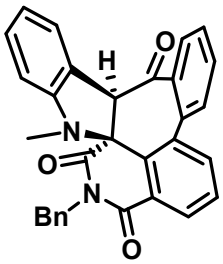
The KIE value for this reaction was estimated to be K_H/K_D = 1.27 by ^{1}H NMR spectra.



7 Crystal Culture Procedure of Product 3af and 5aa

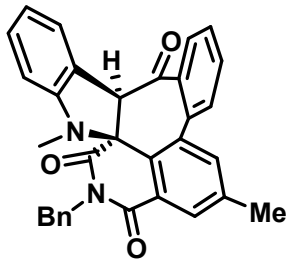
To a round-bottom flask (25 mL) was added **3af** (10.0 mg) or **5aa** (10.0 mg). Dichloromethane (1.0 mL) was added slowly to make it dissolve completely. Then petroleum ether (5.0 mL) was added. Finally, the round-bottom flask was sealed with a rubber stopper, and connected the air with a syringe needle. Putting the flask in a dry and ventilated place to make the organic solvent volatilize slowly. After a few days, the crystal of **3af** and **5aa** were separated out.

8 Characterization Data

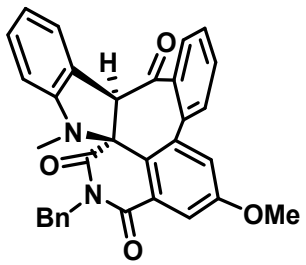


2-benzyl-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3aa): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 84% (39.4 mg) (2-(2-bromophenyl)-2-oxoacetaldehyde acid was used), isolated yield 48% (22.5 mg) (2-(2-iodophenyl)-2-

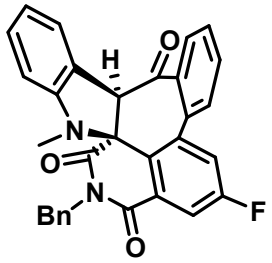
oxoacetic acid was used); mp: 191.5-193.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.35 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0 ,1.5 Hz 1H), 7.44-7.38 (m, 3H), 7.38-7.35 (m, 1H), 7.31-7.27 (m, 2H), 7.25-7.32 (m, 1H), 7.06-7.00 (m, 3H), 6.85-6.80 (m, 1H), 6.72-6.65 (m, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 5.15 (s, 2H), 4.53 (s, 1H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.1, 170.7, 162.8, 153.4, 139.8, 138.5, 137.6, 137.5, 136.5, 133.5, 131.1, 130.1, 129.5, 129.2, 128.9, 128.5, 127.7, 127.5, 127.3, 126.9, 125.2, 124.8, 122.8, 119.2, 105.9, 74.3, 71.9, 44.0, 29.6; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{31}H_{23}N_2O_3^+$ 471.1703; found 471.1706.



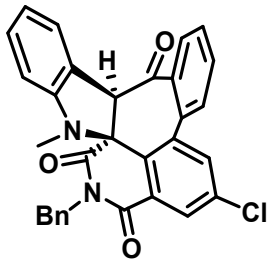
2-benzyl-4,15-dimethyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohep ta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ba): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 75% (36.3 mg); mp: 196.0-197.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.16 (s, 1H), 7.42-7.40 (m, 3H), 7.39-7.35 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.05-7.00 (m, 3H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 4.50 (s, 1H), 2.47 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.3, 170.9, 163.1, 153.4, 140.4, 139.8, 138.7, 138.5, 137.6, 136.6, 131.0, 130.5, 129.5, 128.9, 128.5, 127.7, 127.5, 127.1, 126.8, 125.2, 124.8, 123.0, 119.0, 105.8, 74.1, 71.8, 43.9, 29.5, 21.1; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{25}N_2O_3^+$ 485.1860; found 485.1862.



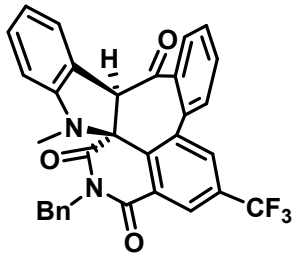
2-benzyl-15-methoxy-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ca): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 78% (39.0 mg); mp: 163.4-165.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 7.82 (d, *J* = 3.0 Hz, 1H), 7.42-7.40 (m, 2H), 7.38-7.34 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.13 (d, *J* = 3.0 Hz, 1H), 7.05-7.00 (m, 3H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 5.14 (s, 2H), 4.50 (s, 1H), 3.91 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.3, 171.0, 162.9, 160.3, 153.3, 141.5, 138.6, 137.3, 136.5, 131.0, 129.4, 128.9, 128.7, 128.5, 127.7, 127.5, 127.0, 125.4, 125.2, 125.1, 124.7, 123.0, 119.0, 111.6, 105.8, 76.7, 73.9, 71.6, 55.8, 44.0, 29.4; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{25}N_2O_4^+$ 501.1809; found 501.1812.



2-benzyl-15-fluoro-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3da): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 66% (32.2 mg); mp: 179.3-182.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.02 (dd, *J* = 8.5, 3.0 Hz, 1H), 7.42-7.39 (m, 3H), 7.35-7.28 (m, 4H), 7.25-7.24 (m, 1H), 7.09-7.01 (m, 3H), 6.85-6.83 (m, 1H), 6.72-6.69 (m, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 5.14 (s, 2H), 4.52 (s, 1H), 2.23 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.6, 170.5, 162.9 (d, C-F, $^1J_{C\text{-}F}$ = 250.8 Hz), 153.2, 142.9 (d, C-F, $^3J_{C\text{-}F}$ = 7.6 Hz), 138.5, 136.4, 136.2, 131.2, 129.7 (d, C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 129.6, 129.4 (d, C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 129.0, 128.6, 127.8, 127.7, 127.5, 125.1, 124.8, 124.6 (d, C-F, $^2J_{C\text{-}F}$ = 22.6 Hz), 122.8, 119.3, 115.3 (d, C-F, $^2J_{C\text{-}F}$ = 23.4 Hz), 106.1, 74.0, 71.7, 44.2, 29.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -109.3; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{31}H_{22}FN_2O_3^+$ 489.1609; found 489.1611.

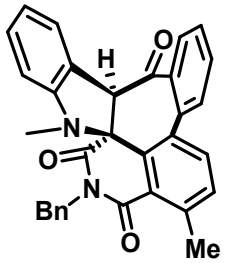


2-benzyl-15-chloro-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cycloheptа[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ea): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 51% (26.9 mg); mp: 218.5-220.2 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.31 (d, *J* = 2.5 Hz, 1H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.43-7.40 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.31-7.27 (m, 2H), 7.25-7.24 (m, 1H), 7.09-7.01 (m, 3H), 6.85-6.83 (m, 1H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 5.14 (s, 2H), 4.52 (s, 1H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.6, 170.3, 161.8, 153.2, 141.8, 138.6, 137.1, 136.5, 136.2, 131.9, 131.2, 129.6, 129.0, 128.8, 128.7, 128.6, 127.9, 127.7, 127.5, 125.1, 124.8, 122.7, 119.4, 106.1, 74.0, 71.7, 44.1, 29.6; HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{31}H_{21}ClN_2NaO_3^+$ 527.1133; found 527.1136.

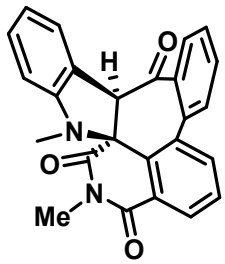


2-benzyl-4-methyl-15-(trifluoromethyl)-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo [2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3fa): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 53% (28.5 mg); mp: 101.4-103.6 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.62 (d, *J* = 1.0 Hz, 1H), 7.80 (d, *J* = 1.5 Hz, 1H), 7.46-7.39 (m, 4H), 7.31-7.25 (m, 3H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 7.06-7.03 (t, *J* = 7.3 Hz, 2H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.12 (d, *J* = 8.0 Hz, 1H), 5.16 (s, 2H), 4.55 (s, 1H), 2.26 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.2, 170.0, 161.7, 153.2, 141.3, 138.5, 137.3, 136.2, 136.1, 133.4 (q, $^{3}J_{C-}$

$_F$ = 3.4 Hz), 132.6 (q, $^2J_{C-F}$ = 33.8 Hz), 131.4, 129.7, 129.0, 128.6, 128.3, 127.9, 127.8, 127.7, 126.1 (q, $^3J_{C-F}$ = 3.6 Hz), 125.1, 124.9, 124.1 (q, $^1J_{C-F}$ = 271.4 Hz), 122.5, 119.6, 106.2, 74.3, 72.0, 44.2, 29.8; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -63.2; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{22}F_3N_2O_3^+$ 539.1577; found 539.1580.

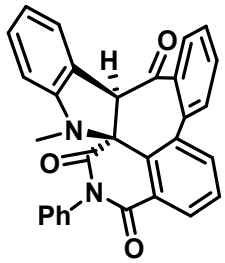


2-benzyl-4,16-dimethyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohept a[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ga) column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 51% (24.7 mg); mp: 195.7-198.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 7.42-7.41 (m, 4H), 7.39-7.34 (m, 2H), 7.31-7.28 (m, 2H), 7.27-7.24 (m, 1H), 7.03-6.98 (m, 3H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.67 (t, *J* = 7.0 Hz, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 5.16-5.09 (m, 2H), 4.41 (s, 1H), 2.80 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.16, 169.95, 163.30, 153.49, 142.63, 138.53, 138.15, 137.77, 136.70, 136.17, 134.16, 134.06, 131.05, 129.54, 128.92, 128.51, 127.62, 127.44, 126.42, 125.68, 124.92, 124.49, 122.06, 118.97, 105.49, 75.02, 71.69, 43.88, 29.46, 23.98. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{25}N_2O_3^+$ 485.1860; found 485.1866.

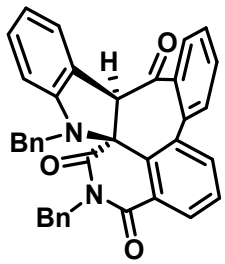


2,4-dimethyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*] isoquinoline-1,3,9(2*H*)-trione (3ia): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 59% (23.2 mg); mp: > 230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.36 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43-7.38 (m, 2H), 7.07-7.01 (m, 3H), 6.85-6.84 (m, 1H), 6.69 (t, *J* = 7.5 Hz,

1H), 6.10 (d, *J* = 8.0 Hz, 1H), 4.60 (s, 1H), 3.36 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.2, 171.1, 163.2, 153.4, 139.8, 138.6, 137.5, 137.5, 133.4, 131.1, 130.1, 129.5, 129.0, 127.5, 127.3, 126.9, 125.1, 124.8, 122.7, 119.1, 105.8, 74.4, 71.9, 29.6, 27.4. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{25}H_{19}N_2O_3^+$ 395.1390; found 395.1391.

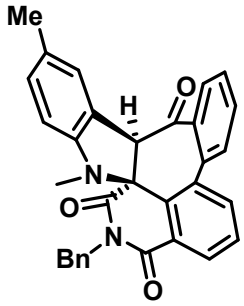


4-methyl-2-phenyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1, 2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ja): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 55% (25.1 mg); mp > 230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.39 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.71-7.66 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.44-7.39 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.09-7.03 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.08 (d, *J* = 7.5 Hz, 1H), 4.76 (s, 1H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.2, 170.7, 163.0, 153.3, 140.0, 138.6, 137.8, 137.6, 134.3, 133.5, 131.2, 130.3, 129.4, 129.4, 129.3, 128.9, 128.3, 127.6, 127.4, 127.0, 125.2, 124.9, 122.6, 119.2, 106.0, 75.0, 72.1, 29.6. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{30}H_{21}N_2O_3^+$ 457.1547; found 457.1549.

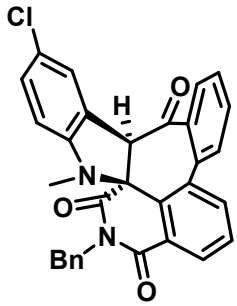


2,4-dibenzyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*] isoquinoline-1,3,9(2*H*)-trione (3ka) : column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 60% (32.8 mg); mp: 117.5-119.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.29 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.51-

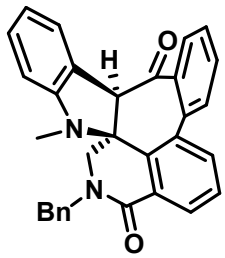
7.50 (m, 1H), 7.47-7.44 (m, 3H), 7.33-7.28 (m, 3H), 7.25-7.23 (m, 1H), 7.15-7.08 (m, 3H), 7.04-7.01 (m, 2H), 6.98-6.95 (m, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.5 Hz, 2H), 6.10 (d, *J* = 8.0 Hz, 1H), 5.09 (s, 2H), 4.65 (s, 1H), 3.95 (d, *J* = 15.0 Hz, 1H), 3.73 (d, *J* = 15.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.2, 171.1, 162.6, 153.4, 139.9, 138.7, 137.9, 137.2, 136.4, 135.9, 133.8, 130.9, 130.1, 129.3, 129.3, 129.2, 128.5, 128.1, 127.8, 127.7, 127.6, 127.5, 127.2, 127.0, 126.9, 124.8, 123.9, 120.0, 108.0, 73.9, 72.4, 50.9, 43.9. HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{37}H_{27}N_2O_3^+$ 547.2016; found 547.2023.



2-benzyl-4,7-dimethyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta [1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3la): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 85% (41.2 mg); mp: 196.0-197.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.35-8.33 (m, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.59-7.58 (m, 1H), 7.43-7.42 (m, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.30-7.27 (m, 2H), 7.25-7.23 (s, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.87-6.81 (m, 3H), 5.99 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 4.50 (s, 1H), 2.22 (s, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.3, 170.8, 162.9, 151.3, 139.9, 138.6, 137.6, 137.5, 136.5, 133.7, 131.1, 130.0, 129.8, 129.1, 129.0, 128.5, 127.7, 127.6, 127.2, 126.9, 125.6, 125.2, 122.9, 105.7, 74.4, 71.9, 43.9, 29.8, 20.7; HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{32}H_{24}N_2NaO_3^+$ 507.1679; found 507.1681.

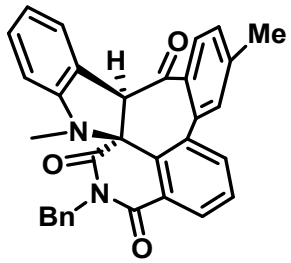


2-benzyl-7-chloro-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclo hepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ma): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 61% (30.8 mg); mp: 148.4-150.1 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.37-8.35 (m, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.60-7.59 (m, 1H), 7.42-7.41 (m, 3H), 7.38-7.36 (m, 1H), 7.31-7.28 (m, 2H), 7.25-7.24 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01-7.00 (s, 1H), 6.97 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.00 (d, *J* = 8.5 Hz, 1H), 5.15 (s, 2H), 4.48 (s, 1H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.6, 170.6, 162.7, 152.1, 139.8, 138.3, 137.7, 137.5, 136.3, 132.8, 131.4, 130.3, 129.4, 129.3, 128.9, 128.6, 127.8, 127.7, 127.3, 127.2, 125.3, 124.9, 123.5, 106.5, 74.5, 71.4, 44.0, 29.7; HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{31}H_{21}ClN_2NaO_3^+$ 527.1133; found 527.1136.

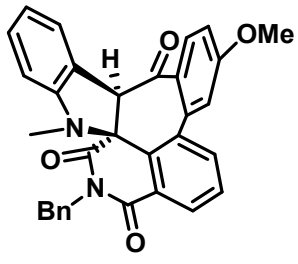


2-benzyl-4-methyl-2,3,4,8b-tetrahydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohe pta[1,2,3-*de*]isoquinoline-1,9-dione (3na): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 26% (11.9 mg, dr = 3.3:1); mp: 83.7-85.5 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ =7.68 (d, *J* = 7.0 Hz, 0.23H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.54-7.45 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 0.77H), 7.37-7.25 (m, 6H), 7.17-7.09 (m, 3H), 6.43 (s, 0.23H), 6.35 (s, 0.77H), 5.49 (d, *J* = 15.0 Hz, 0.77H), 5.36 (d, *J* = 15.0 Hz, 0.23H), 4.55 (d, *J* = 15.0 Hz, 0.77H), 4.49-4.44 (m, 0.46H), 4.40-4.33 (m, 1H), 4.24 (d, *J* = 16.0 Hz, 0.77H), 3.99 (s, 2.30H), 3.29 (s, 0.70H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ

= 192.0, 168.5, 144.7(2C), 143.7, 143.6, 138.1, 138.7, 135.8, 135.0(2C), 134.9, 134.8, 134.2, 134.0, 133.7, 133.6, 133.3, 129. 6, 128.9, 128.7, 128.5, 127.6, 127.4, 127.3, 127.2, 124.6, 124.5, 121.7, 121.6, 120.9, 120.8, 120.5, 120.4(2C), 119.7, 119.4, 109.7, 108.9, 104.0, 101.9, 50.1, 47.1, 44.3, 38.3, 30.4, 29.7; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{31}H_{25}N_2O_2^+$ 457.1911; found 457.1918.

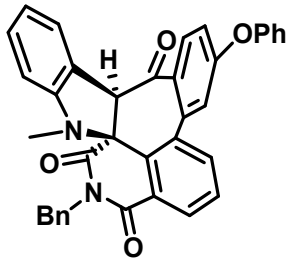


2-benzyl-4,12-dimethyl-4,8b-dihydro-1H,9H-benzo[4,5]indolo[2',3':1,7]cyclohep ta[1,2,3-*de*]isoquinoline-1,3,9(2H)-trione (3ab): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 75% (36.3 mg); mp: 194.5-196.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.34 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.43-7.41 (m, 2H), 7.30-7.27 (m, 3H), 7.25-7.23 (m, 2H), 7.17 (s, 1H), 7.05-7.02 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.12 (d, J = 8.0 Hz, 1H), 5.15 (s, 2H), 4.52 (s, 1H), 2.35 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.3, 170.9, 162.9, 153.4, 141.4, 140.0, 137.6, 137.5, 136.5, 135.9, 133.4, 130.0, 129.4, 129.1, 128.9, 128.5, 127.8, 127.7, 127.3, 125.9, 124.8, 123.2, 119.1, 105.9, 74.3, 71.8, 44.0, 29.6, 21.6; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{25}N_2O_3^+$ 485.1860; found 485.1862.

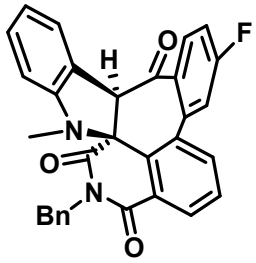


2-benzyl-12-methoxy-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cy clohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ac): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 80% (40.0 mg); mp: 223.6-225.8

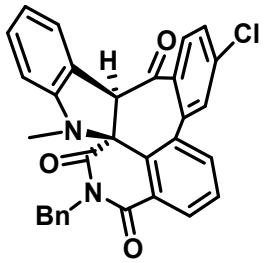
°C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.34 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.59 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.43-7.41 (m, 2H), 7.30-7.24 (m, 3H), 7.04-7.02 (m, 2H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.56 (dd, J = 8.5, 1.5 Hz 1H), 6.14 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 4.49 (s, 1H), 3.80 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.4, 170.8, 162.8, 161.7, 153.3, 139.7, 139.5, 137.5, 136.5, 133.5, 131.4, 130.0, 129.7, 129.3, 129.3, 128.9, 128.5, 127.7, 127.2, 124.7, 123.4, 119.1, 111.5, 111.4, 106.0, 74.2, 71.6, 55.3, 43.9, 29.7; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{25}N_2O_4^+$ 501.1809; found 501.1812.



2-benzyl-4-methyl-12-phenoxy-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ad): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 73% (41.1 mg); mp: 194.2-197.9 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.34 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45-7.39 (m, 2H), 7.39-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.25-7.24 (m, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.09-7.02 (m, 2H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.99-6.95 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 4.51 (s, 1H), 2.28 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.3, 170.7, 162.7, 159.6, 156.3, 153.4, 139.8, 139.3, 137.4, 136.4, 133.6, 133.5, 130.1, 129.9, 129.7, 129.5, 129.4, 128.9, 128.5, 127.7, 127.3, 124.9, 124.0, 123.0, 119.3, 119.1, 116.7, 115.2, 105.9, 74.3, 71.7, 44.0, 29.7; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{37}H_{27}N_2O_4^+$ 563.1965; found 563.1969.

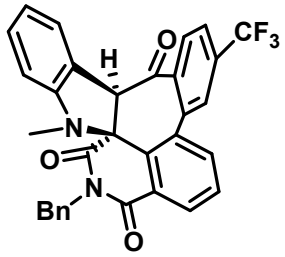


2-benzyl-12-fluoro-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cycloh epta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ae): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 64% (31.3 mg); mp: 174.7-178.7 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.37 (d, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.30-7.24 (m, 3H), 7.08-7.03 (m, 3H), 6.84 (dd, J = 8.5, 6.0 Hz, 1H), 6.77-6.68 (m, 2H), 6.15 (d, *J* = 7.5 Hz, 1H), 5.15 (s, 2H), 4.52 (s, 1H), 2.27 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.9, 170.5, 164.1 (d, C-F, $^{1}J_{C\text{-}F}$ = 249.5 Hz), 162.6, 153.3, 140.0 (d, C-F, $^{4}J_{C\text{-}F}$ = 8.5 Hz) 138.6, 137.3, 136.4, 134.9 (d, C-F, $^{4}J_{C\text{-}F}$ = 3.3 H z), 133.7, 130.3, 130.0 (d, C-F, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 129.7 (d, C-F, $^{3}J_{C\text{-}F}$ = 11.9 Hz), 128.9, 128.5, 127.8, 127.4, 124.9, 122.7, 119.4, 114.0 (d, C-F, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 112.2 (d, C-F, $^{2}J_{C\text{-}F}$ = 22.8 Hz), 106.2, 74.2, 71.6, 44.0, 29.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -108.2; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{31}H_{22}FN_2O_3^+$ 489.1609; found 489.1612.

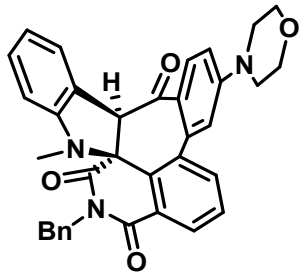


2-benzyl-12-chloro-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cycloh epta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3af): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 79% (39.9 mg); mp: 210.1-212.8 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.38 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43-7.41 (m, 2H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.32-7.27 (m, 2H), 7.25-7.24 (m, 1H), 7.08-7.01 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J*

= 7.5 Hz, 1H), 6.16 (d, *J* = 7.5 Hz, 1H), 5.15 (s, 2H), 4.52 (s, 1H), 2.27 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.9, 170.5, 162.6, 153.3, 139.2, 138.4, 137.4, 137.1, 137.0, 136.4, 133.7, 130.3, 129.8, 129.7, 129.1, 129.0, 128.6, 127.8, 127.5, 127.0, 125.2, 124.9, 122.5, 119.5, 106.3, 74.3, 71.6, 44.0, 29.7; HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{31}H_{21}ClN_2NaO_3^+$ 527.1133; found 527.1136.

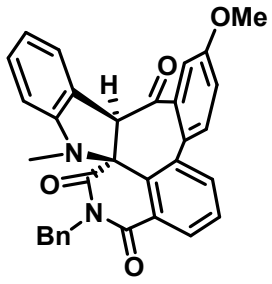


2-benzyl-4-methyl-12-(trifluoromethyl)-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ag): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 74% (39.8 mg); mp: 95.8-97.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.31-7.27 (m, 4H), 7.06 (t, *J* = 7.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.12 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 4.55 (s, 1H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.6, 170.3, 162.5, 153.3, 141.8, 138.2 (2C), 137.4, 136.3, 133.7, 132.9 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 130.1, 130.0, 129.9, 129.0, 128.6, 128.1, 127.8, 127.5, 125.0, 123.5 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.4 (q, $^{1}J_{C\text{-}F}$ = 271.4 Hz), 121.9, 121.9 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 119.6, 106.3, 74.3, 71.6, 44.0, 29.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -62.8; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{22}F_3N_2O_3^+$ 539.1577; found 539.1575.

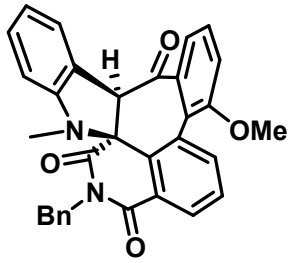


2-benzyl-4-methyl-12-morpholino-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ah): column chromatoghraphy

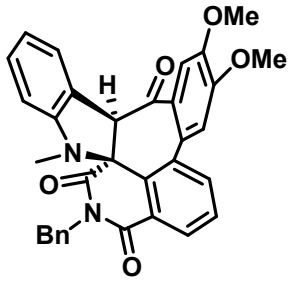
(silica gel; PE/EA = 3:1); yellow solid, isolated yield 71% (39.4 mg); mp: 185.2-188.7 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.34 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.64-7.59 (m, 2H), 7.43-7.41 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.23 (m 1H), 7.03 (t, *J* = 6.5 Hz, 2H), 6.84-6.81 (m, 2H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.54 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 5.14 (s, 2H), 4.48 (s, 1H), 3.84 (t, *J* = 5.0 Hz, 4H), 3.27-3.18 (m, 4H), 2.29 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.3, 170.9, 162.9, 153.4, 153.2, 140.5, 139.3, 137.5, 136.5, 133.5, 129.9, 129.8, 129.5, 129.2, 129.1, 129.0, 128.5, 127.7, 127.3, 124.7, 123.8, 119.1, 112.9, 111.0, 105.9, 74.3, 71.5, 66.5, 48.0, 43.9, 29.8; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{35}H_{30}N_3O_4^+$ 556.2231; found 556.2234.



2-benzyl-11-methoxy-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ai): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 66% (33.0 mg); mp: 218.2-219.8 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.32 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.43-7.42 (m, 2H), 7.31-7.27 (m, 3H), 7.25-7.24 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 2H), 6.93 (dd, J = 8.5, 3.0 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.34 (d, *J* = 3.0 Hz, 1H), 6.12 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 4.54 (s, 1H), 3.61 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.0, 170.9, 162.9, 158.3, 153.5, 139.7, 137.3, 136.5, 133.1, 130.2, 130.0, 129.6, 128.9, 128.8, 128.5, 127.7, 127.3, 126.8, 124.8, 123.0, 119.0, 117.9, 111.8, 106.0, 74.2, 71.9, 55.5, 43.9, 29.5; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{25}N_2O_4^+$ 501.1809; found 501.1812.

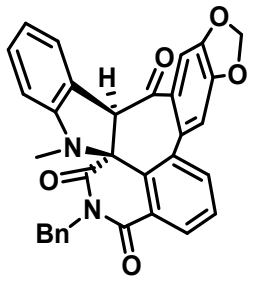


2-benzyl-13-methoxy-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3aj): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 36% (18.0 mg); mp: 222.1-224.2 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.32 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.42-7.40 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.22 (m, 1H), 7.03-6.97 (m, 2H), 6.96-6.94 (m, 2H), 6.68-6.64 (m, 1H), 6.43-6.40 (m, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 2H), 4.42 (s, 1H), 3.81 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.9, 170.6, 162.9, 153.9, 153.6, 140.3, 139.0, 136.6, 135.8, 133.5, 129.5, 129.1, 129.1, 128.9, 128.5, 127.7, 127.7, 127.0, 126.2, 124.8, 122.7, 120.0, 118.9, 113.5, 105.7, 74.6, 72.0, 55.9, 43.9, 29.7; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{25}N_2O_4^+$ 501.1809; found 501.1811.

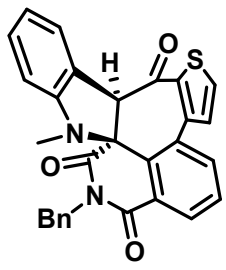


2-benzyl-11,12-dimethoxy-4-methyl-4,8b-dihydro-1*H*,9*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3ak): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 70% (37.1 mg); mp: 192.6-194.5 ^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.33-8.32 (m, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.60-7.58 (m, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.31-7.28 (m, 2H), 7.25-7.24 (m, 1H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.36 (s, 1H), 6.14 (d, *J* = 7.5 Hz, 1H), 5.15 (s, 2H), 4.53 (s, 1H), 3.94 (s, 3H), 3.64 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.5, 170.8, 162.9, 153.4, 151.2, 147.8, 139.9,

137.1, 136.5, 133.3, 131.3, 131.2, 129.9, 129.4, 129.0, 128.8, 128.5, 127.7, 127.3, 124.7, 123.3, 119.0, 110.6, 108.2, 106.1, 74.0, 72.1, 56.1, 56.0, 43.9, 29.7; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{33}H_{27}N_2O_5^+$ 531.1914; found 531.1917.

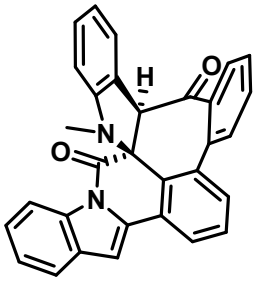


2-benzyl-4-methyl-4,8b-dihydro-1*H*,9*H*-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':4,5] indolo[2',3':1,7]cyclohepta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3al): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 73% (37.5 mg); mp: 244.1-246.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.32 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.42-7.41 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.22 (m, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 6.70 (t, J = 7.5 Hz, 1H), 6.37 (s, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 5.93 (dd, *J* = 7.5, 1.5 Hz, 2H), 5.14 (s, 2H), 4.51 (s, 1H), 2.29 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.0, 170.7, 162.8, 153.4, 150.1, 146.5, 139.6, 137.4, 136.5, 133.2, 133.0, 132.9, 130.0, 129.5, 128.9, 128.5, 127.7, 127.2, 124.8, 123.2, 119.3, 108.1, 106.1, 105.9, 101.7, 74.2, 71.9, 43.9, 29.8; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{32}H_{23}N_2O_5^+$ 515.1601; found 515.1605.

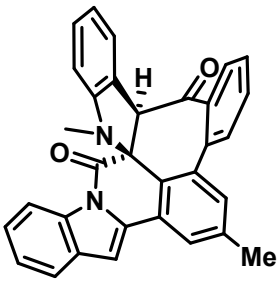


2-benzyl-4-methyl-4,8b-dihydro-1*H*,9*H*-indolo[2',3':1,7]thieno[3',2':4,5]cyclohep ta[1,2,3-*de*]isoquinoline-1,3,9(2*H*)-trione (3am): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 21% (10.0 mg); mp: 120.1-121.4 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.34 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.66-7.61 (m, 2H),

7.43-7.42 (m, 3H), 7.31-7.27 (m, 2H), 7.25-7.24 (m, 1H), 7.18 (d, *J* = 5.0 Hz, 1H), 7.12-7.08 (m, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.25 (d, *J* = 7.5 Hz, 1H), 5.16 (s, 2H), 4.66 (s, 1H), 2.30 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 191.0, 171.1, 162.8, 153.5, 142.1, 138.2, 136.5, 135.9, 135.5, 133.0, 131.1, 130.0, 129.4, 129.05, 129.00, 128.6, 128.0, 127.8, 125.7, 125.3, 124.2, 120.0, 106.3, 74.1, 71.7, 44.0, 30.1; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{29}H_{21}N_2O_3S^+$ 477.1267; found 477.1269.

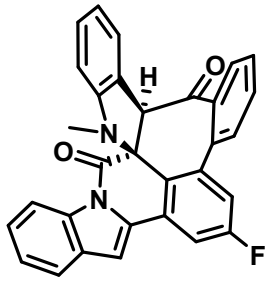


20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*] indolo[2,1-*a*]isoquinoline-5,19-dione (5aa): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 79% (35.7 mg); mp: 180.4-181.9 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.41-8.38 (m, 1H), 7.90 (d, *J* =8.0 Hz, 1H), 7.62-7.58 (m, 1H), 7.54 (t, *J* =8.0 Hz, 1H), 7.39-7.37 (m, 2H), 7.33-7.28 (m, 3H), 7.13 (s, 1H), 7.08 (d, *J* =7.0 Hz, 1H), 7.06-7.01 (m, 2H), 6.84 (d, *J* =7.5 Hz, 1H), 6.70 (t, *J* =7.0 Hz, 1H), 6.11 (d, *J* =7.5 Hz, 1H), 4.70 (s, 1H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.7, 166.8, 153.6, 140.8, 138.6, 138.5, 135.3, 134.2, 132.8, 130.9, 130.8, 129.9, 129.5, 128.4, 127.3, 127.3, 126.5, 125.8, 125.1, 125.0, 124.8, 123.7, 123.5, 120.8, 118.8, 117.0, 105.6, 105.2, 75.7, 71.5, 29.6; HRMS (ESI) m/z calcd for $C_{31}H_{21}N_2O_2^+$ $(M+H)^+$ 453.1598, Found 453.1601.

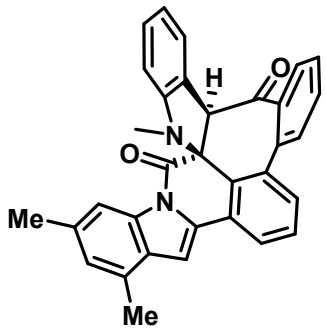


11,20-dimethyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1, 2, 3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ba): column chromatoghraphy (silica

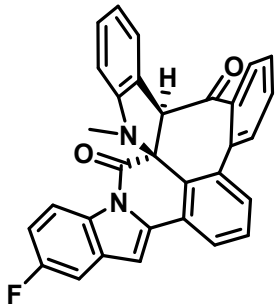
gel; PE/EA = 10:1); yellow solid, isolated yield 74% (34.5 mg); mp: 162.1-164.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.41-8.38 (m, 1H), 7.70 (s, 1H), 7.61-7.58 (m, 1H), 7.38 (d, *J* = 4.0 Hz, 2H), 7.32-7.29 (m, 2H), 7.12-7.10 (m, 2H), 7.08 (d, *J* = 7.0 Hz, 1H), 7.04-7.00 (m, 2H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 4.68 (s, 1H), 2.45 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.9, 167.0, 153.5, 140.5, 139.8, 138.7, 138.5, 135.2, 134.3, 133.9, 130.8, 130.8, 129.4, 127.2, 127.1, 126.3, 125.7, 125.5, 125.0, 125.0, 124.7, 124.0, 123.5, 120.7, 118.7, 116.9, 105.6, 104.9, 75.5, 71.4, 29.5, 21.2; HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O_2^+$ $(M+H)^+$ 467.1754, Found 467.1776.



11-fluoro-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta [1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ca): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 50% (23.5 mg); mp: 188.4-190.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.41-8.37 (m, 1H), 7.64-7.61 (m, 1H), 7.57 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.43-7.40 (m, 1H), 7.37-7.32 (m, 3H), 7.13 (s, 1H), 7.09-7.03 (m, 4H), 6.86-6.83 (m, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.12 (d, *J* = 8.0 Hz, 1H), 4.69 (s, 1H), 2.35 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.3, 166.5, 162.9 (d, C-F, $^1J_{C\text{-}F}$ = 248.0 Hz), 153.4, 143.7 (d, C-F, $^3J_{C\text{-}F}$ = 8.3 Hz), 138.5, 137.4, 135.3, 133.1 (d, C-F, $^3J_{C\text{-}F}$ = 3.3 Hz), 131.0, 130.5, 129.5, 127.4, 127.0, 126.3, 125.3, 124.9, 124.8, 123.4, 121.1, 119.8 (d, C-F, $^2J_{C\text{-}F}$ = 22.6 Hz), 119.0, 117.0, 109.7 (d, C-F, $^2J_{C\text{-}F}$ = 23 Hz), 106.2, 105.8, 75.4, 71.3, 29.6; **^{19}F NMR** (471 MHz, $CDCl_3$): δ = -111.3; HRMS (ESI) m/z calcd for $C_{31}H_{20}FN_2O_2^+$ $(M+H)^+$ 471.1503, Found 471.1504.

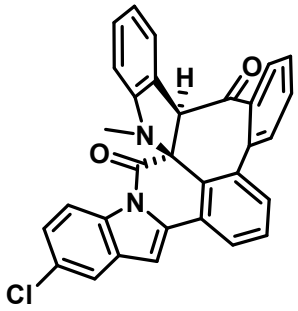


14,16,20-trimethyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta [1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5da): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 69% (33.2 mg); mp: 180.5-182.3 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.10 (s, 1H), 7.91 (d, *J* =7.0 Hz, 1H), 7.53 (t, *J* =7.5 Hz, 1H), 7.41-7.37 (m, 2H), 7.27 (d, *J* =8.0 Hz, 1H), 7.13 (s, 1H), 7.08 (d, *J* =7.5 Hz, 1H), 7.06-7.02 (m, 2H), 6.97 (s, 1H), 6.84 (d, *J* =7.0 Hz, 1H), 6.70 (t, *J* =7.5 Hz, 1H), 6.11 (d, *J* =8.0 Hz, 1H), 4.68 (s, 1H), 2.55 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.9, 166.9, 153.6, 140.7, 138.6, 136.4, 135.4, 132.9, 132.4, 130.9, 129.9, 129.8, 129.4, 128.0, 128.0, 127.6, 127.2, 127.0, 126.4, 125.0, 124.7, 123.5, 123.5, 118.7, 114.8, 105.6, 103.8, 75.7, 71.5, 29.5, 21.7, 18.4; HRMS (ESI) m/z calcd for $C_{33}H_{25}N_2O_2^+$ $(M+H)^+$ 481.1911, Found 481.1931.

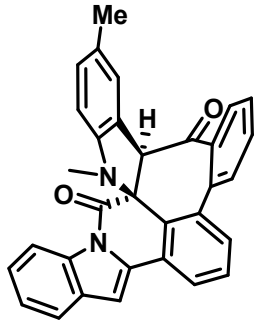


15-fluoro-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta [1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ea): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 73% (34.3 mg); mp: 206.3-208.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.35-8.33 (m, 1H), 7.90 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.32 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.27-7.25 (m, 1H), 7.09-7.00 (m, 5H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.73-6.70 (m, 1H), 6.12 (d, *J* =

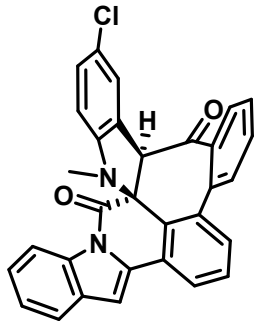
8.0 Hz, 1H), 4.69 (s, 1H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.6, 166.7, 160.4 (d, C-F, $^1J_{C\text{-}F}$ = 240.8 Hz), 153.5, 140.8, 138.5, 138.3, 135.7, 133.1, 132.0 (d, C-F, $^3J_{C\text{-}F}$ = 10.3 Hz), 131.5, 130.9, 130.0, 129.5, 128.6, 127.2, 126.9, 126.5, 125.0, 124.8, 123.8, 123.3, 118.0 (d, C-F, $^3J_{C\text{-}F}$ = 9.1 Hz), 113.3 (d, C-F, $^2J_{C\text{-}F}$ = 24.6 Hz), 106.5 (d, C-F, $^2J_{C\text{-}F}$ = 24.1 Hz), 105.7, 104.6 (d, C-F, $^4J_{C\text{-}F}$ = 4.0 Hz), 75.6, 71.5, 29.6; **^{19}F NMR** (471 MHz, $CDCl_3$): δ = -117.0; HRMS (ESI) m/z calcd for $C_{31}H_{20}FN_2O_2^+$ $(M+H)^+$ 471.1503, Found 471.1494.



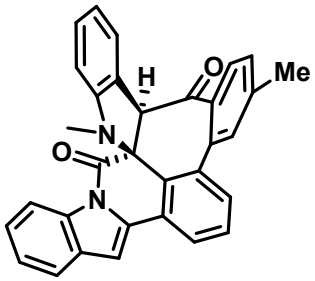
15-chloro-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5fa): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 45% (21.9 mg); mp: 213.1-215.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.30 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.56-7.52 (m, 2H), 7.42-7.37 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.28-7.25 (m, 1H), 7.09 (d, *J* = 7.0 Hz, 1H), 7.06-7.02 (m, 3H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.12 (d, *J* = 8.0, 1H), 4.69 (s, 1H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.5, 166.8, 153.4, 140.8, 138.5, 138.3, 135.5, 133.5, 133.2, 132.1, 131.0, 130.7, 130.0, 129.5, 128.6, 127.3, 126.8, 126.6, 125.9, 125.0, 124.8, 123.9, 123.3, 120.4, 118.9, 117.9, 105.7, 104.2, 75.7, 71.5, 29.6; HRMS (ESI) m/z calcd for $C_{31}H_{20}ClN_2O_2^+$ $(M+H)^+$ 487.1208, Found 487.1211.



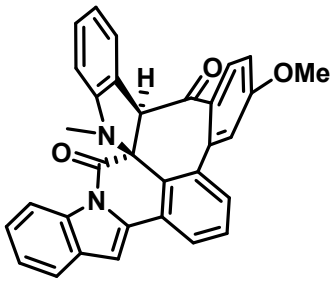
3,20-dimethyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ga): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 51% (23.8 mg); mp: 201.1-203.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.42-8.40 (m, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.61-7.59 (m, 1H), 7.55-7.52 (m, 1H), 7.41-7.36 (m, 2H), 7.32-7.28 (m, 3H), 7.12 (s, 1H), 7.05-7.02 (m, 1H), 6.91 (s, 1H), 6.86-6.83 (m, 2H), 6.02 (d, *J* = 8.0 Hz, 1H), 4.66 (s, 1H), 2.32 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.9, 166.9, 151.5, 140.8, 138.7, 138.6, 135.3, 134.2, 132.8, 130.9, 130.8, 129.8, 129.8, 128.7, 128.2, 127.34, 127.25, 126.5, 125.8, 125.5, 125.1, 125.0, 123.7, 123.6, 120.8, 117.0, 105.5, 105.1, 75.9, 71.6, 29.8, 20.8; HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O_2^+$ $(M+H)^+$ 467.1754, Found 467.1776.



3-chloro-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ha): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 65% (31.6 mg); mp: 168.5-170.4 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40-8.36 (m, 2H), 7.91 (d, *J* =8.0 Hz, 1H), 7.63-7.60 (m, 1H), 7.56 (t, *J* =8.0 Hz, 1H), 7.43-7.38 (m, 2H), 7.34-7.32 (m, 2H), 7.28 (d, *J* =7.5 Hz, 1H), 7.13 (s, 1H), 7.09-7.05 (m, 2H), 6.99 (dd, *J* =8.5, 2.0 Hz, 1H), 6.91 (d, *J* =7.5 Hz, 1H), 6.03 (d, *J* =8.0 Hz, 1H), 4.66 (s, 1H), 2.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.2, 166.6, 152.2, 140.7, 138.4, 138.3, 135.2, 133.9, 132.8, 131.1, 130.8, 130.1, 129.2, 127.7, 127.4, 127.2, 126.7, 125.9, 125.4, 125.2, 125.1, 124.8, 123.9, 123.0, 120.9, 116.9, 106.2, 105.5, 75.9, 71.0, 29.6; HRMS (ESI) m/z calcd for $C_{31}H_{20}ClN_2O_2^+$ $(M+H)^+$ 487.1208, Found 487.1192.

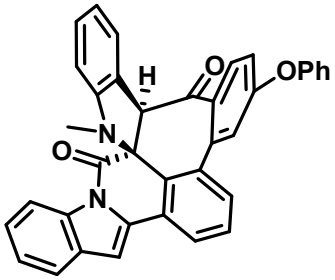


8,20-dimethyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ab): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 84% (39.2 mg); mp: >230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.41-8.38 (m, 1H), 7.91-7.89 (m, 1H), 7.62-7.60 (m, 1H), 7.54 (t, *J* =7.5 Hz, 1H), 7.34-7.29 (m, 3H), 7.19 (s, 1H), 7.13 (s, 1H), 7.09-7.05 (m, 2H), 6.85 (d, *J* =7.5 Hz, 1H), 6.77 (d, *J* =7.5 Hz, 1H), 6.70 (t, *J* =7.5 Hz, 1H), 6.15 (d, *J* =8.0 Hz, 1H), 4.69 (s, 1H), 2.37 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.8, 166.9, 153.6, 141.1, 140.9, 138.5, 136.0, 135.2, 134.2, 132.8, 130.8, 129.8, 129.3, 128.4, 127.4, 127.3, 127.2, 125.8, 125.7, 125.1, 124.7, 123.8, 123.6, 120.8, 118.7, 117.0, 105.7, 105.1, 75.7, 71.4, 29.6, 21.6; HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O_2^+$ $(M+H)^+$ 467.1754, Found 467.1756.

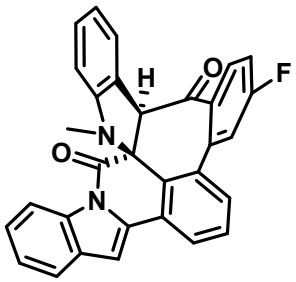


8-methoxy-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ac): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 64% (30.9 mg); mp: 180.0-181.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40-8.37 (m, 1H), 7.91-7.89 (m, 1H), 7.62-7.59 (m, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.32-7.29 (m, 3H), 7.25 (s, 1H), 7.12 (s, 1H), 7.08-7.04 (m, 2H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.55 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 4.66 (s, 1H), 3.82 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.1, 166.9, 161.6, 153.5, 140.7, 140.5,

135.3, 134.1, 132.7, 131.6, 130.8, 129.9, 129.4, 129.3, 128.5, 127.3, 125.8, 125.1, 124.7, 124.0, 123.8, 120.8, 118.8, 117.0, 111.2, 111.1, 105.8, 105.1, 75.7, 71.3, 55.3, 29.7; HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O_3^+$ $(M+H)^+$ 483.1703, Found 483.1704.

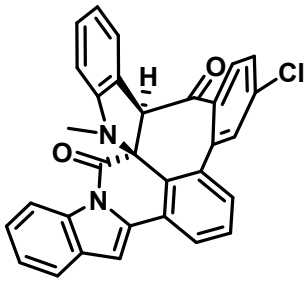


20-methyl-8-phenoxy-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohep ta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ad): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 58% (31.6 mg); mp: > 230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40-8.39 (m, 1H), 7.90-7.89 (m, 1H), 7.61-7.59 (mz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.37-7.31 (m, 4H), 7.24 (s, 1H), 7.15-7.11 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.03 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 4.68 (s, 1H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.9, 166.7, 159.4, 156.6, 153.6, 140.8, 140.2, 135.3, 134.0, 133.8, 132.5, 130.7, 129.9, 129.9, 129.5, 129.4, 128.5, 127.3, 125.9, 125.1, 124.8, 123.9, 123.8, 123.6, 120.8, 118.9, 116.95, 116.5, 115.2, 105.6, 105.3, 75.6, 71.3, 29.7; HRMS (ESI) m/z calcd for $C_{37}H_{25}N_2O_3^+$ $(M+H)^+$ 545.1860, Found 545.1883.

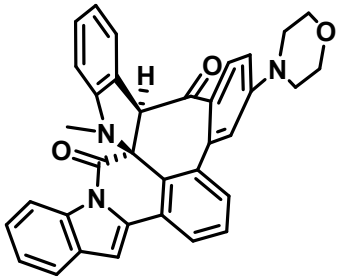


8-fluoro-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta [1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ae): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 66% (31.0 mg); mp: 195.0-196.7 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40-8.38 (m, 1H), 7.93-7.92 (m, 1H), 7.62-7.60

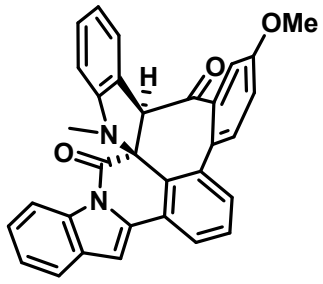
(m, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.33-7.32 (m, 2H), 7.28-7.25 (m, 1H), 7.14 (s, 1H), 7.10-7.06 (m, 3H), 6.86-6.83 (m, 1H), 6.73-6.60 (m, 2H), 6.17 (d, J = 8.0, 1H), 4.68 (s, 1H), 2.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.5, 166.5, 164.1 (d, C-F, $^1J_{C\text{-}F}$ = 248.9 Hz), 153.5, 141.0 (d, C-F, $^3J_{C\text{-}F}$ = 8.5 Hz), 139.6, 135.3, 134.9, 133.9, 132.5, 130.7, 130.0, 129.7 (d, C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 129.6, 128.6, 127.5, 125.9, 125.2, 124.8, 124.2, 123.3, 120.9, 119.1, 117.0, 113.5 (d, C-F, $^2J_{C\text{-}F}$ = 21.6 Hz), 112.0 (d, C-F, $^2J_{C\text{-}F}$ = 22.6 Hz), 105.9, 105.4, 75.7, 71.3, 29.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -108.7; HRMS (ESI) m/z calcd for $C_{31}H_{20}FN_2O_2^+$ $(M+H)^+$ 471.1503, Found 471.1539.



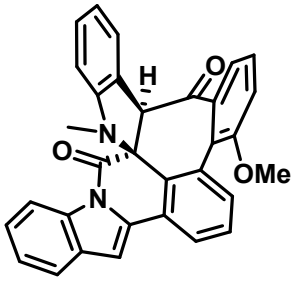
8-chloro-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohepta [1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5af): column chromatoghraphy (silica gel; PE/EA = 10:1); yellow solid, isolated yield 40% (19.5 mg); mp: 162.3-163.9 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.41-8.37 (m, 1H), 7.95-7.93 (m, 1H), 7.62-7.61 (m, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 2.0 Hz, 1H), 7.35-7.32 (m, 2H), 7.30 (dd, J = 7.5, 1.0 Hz, 1H), 7.15 (s, 1H), 7.10-7.07 (m, 2H), 7.00 (dd, J = 8.0, 2.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.74-6.71 (m, 1H), 6.19 (d, J = 8.0 Hz, 1H), 4.69 (s, 1H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.5, 166.5, 153.5, 140.2, 139.4, 137.1, 136.8, 135.3, 133.9, 132.6, 130.7, 130.1, 129.7, 128.8, 128.6, 127.5, 126.5, 126.0, 125.2, 125.0, 124.8, 124.2, 123.1, 120.9, 119.1, 117.0, 106.1, 105.5, 75.7, 71.2, 29.7; HRMS (ESI) m/z calcd for $C_{31}H_{20}ClN_2O_2^+$ $(M+H)^+$ 487.1208, Found 487.1237.



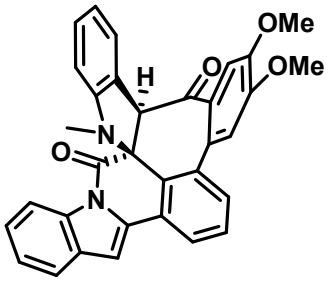
20-methyl-8-(morpholinooxy)-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7] cyclohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ah): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 56% (30.1 mg,); mp: 215.7-217.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40-8.38 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.60-7.58 (m, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.32-7.20 (m, 3H), 7.25 (s, 1H), 7.11 (s, 1H), 7.09-7.04 (m, 2H), 6.85-6.83 (m, 2H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.54-6.52 (m, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 4.65 (s, 1H), 3.87-3.84 (m, 4H), 3.27-3.17 (m, 4H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.9, 167.0, 153.5, 153.1, 141.4, 140.2, 135.2, 134.2, 132.7, 130.7, 130.0, 129.7, 129.2, 129.1, 128.5, 127.2, 125.7, 125.0, 124.6, 124.3, 123.6, 120.7, 118.7, 116.9, 112.6, 110.9, 105.7, 105.0, 75.6, 71.1, 66.6, 48.1, 29.8; HRMS (ESI) m/z calcd for $C_{35}H_{28}N_3O_3^+$ $(M+H)^+$ 538.2125, Found 538.2127.



7-methoxy-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohep ta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (**5ai**): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 41% (19.8 mg); mp: > 230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.41-8.39 (m, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.61-7.59 (m, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.33-7.30 (m, 2H), 7.28-7.25 (m, 2H), 7.12 (s, 1H), 7.08-7.03 (m, 2H), 6.94-6.92 (m, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.36-6.35 (m, 1H), 6.14 (d, *J* = 7.5 Hz, 1H), 4.71 (s, 1H), 3.61 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.58, 166.96, 158.00, 153.65, 140.58, 139.68, 135.25, 134.27, 132.50, 131.21, 130.81, 129.84, 129.58, 128.16, 127.29, 126.55, 125.77, 125.08, 124.68, 123.60, 123.26, 120.79, 118.63, 117.73, 116.97, 111.51, 105.74, 105.07, 75.61, 71.54, 55.46, 29.54; HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O_3^+$ $(M+H)^+$ 483.1703, Found 483.1707.

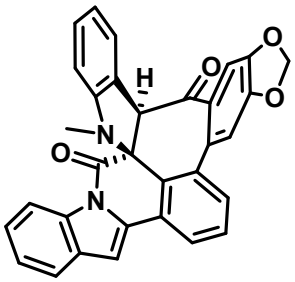


9-methoxy-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cyclohep ta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5aj): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 46% (22.2 mg); mp: > 230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40-8.38 (m, 1H), 7.87 (dd, *J* =7.0, 2.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.50-7.45 (m, 2H), 7.33-7.30 (m, 2H), 7.10 (s, 1H), 7.06-7.02 (m, 2H), 6.96-6.91 (m, 2H), 6.68 (t, *J* =7.5 Hz, 1H), 6.44 (dd, *J* =6.5, 1.5 Hz, 1H), 6.14 (d, *J* =8.0 Hz, 1H), 4.60 (s, 1H), 3.82 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.4, 166.6, 153.8, 140.3, 136.6, 135.2, 134.4, 133.9, 130.8, 129.4, 129.0, 128.5, 127.2, 127.0, 125.6, 125.0, 124.7, 123.4, 123.2, 120.7, 119.8, 118.5, 116.9, 113.4, 105.4, 104.6, 75.9, 71.5, 55.9, 29.7; HRMS (ESI) m/z calcd for $C_{32}H_{23}N_2O_3^+$ $(M+H)^+$ 483.1703, Found 483.1704.

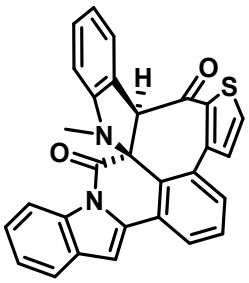


7,8-dimethoxy-20-methyl-4b,20-dihydro-5*H*,19*H*-benzo[4,5]indolo[2',3':1,7]cycl ohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-5,19-dione (5ak): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 55% (28.2 mg); mp: > 230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.41-8.40 (m, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.60-7.59 (m, 1H), 7.52 (t, *J* = 5 Hz, 1H), 7.32-7.28 (m, 3H), 7.25 (s, 1H), 7.12 (s, 1H), 7.08-7.02 (m, 2H), 6.86 (s, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.38 (s, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 4.70 (s, 1H), 3.95 (s, 3H), 3.65 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.1, 166.9, 153.6, 151.0, 147.5, 140.8, 135.2, 134.2, 132.3, 132.2,

131.4, 130.8, 129.8, 129.4, 128.3, 127.3, 125.8, 125.1, 124.6, 123.9, 123.3, 120.8, 118.7, 117.0, 110.4, 108.1, 105.9, 105.1, 75.5, 71.8, 56.0, 56.0, 29.7; HRMS (ESI) m/z calcd for $C_{33}H_{25}N_2O_4^+$ $(M+H)^+$ 513.1809, Found 513.1827.

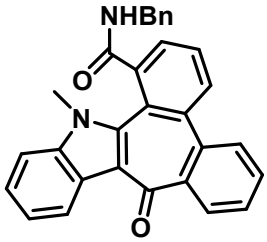


5-methyl-5,21a-dihydro-6*H*,21*H*-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':4,5]indolo [2',3':1,7]cyclohepta[1,2,3-*de*]indolo[2,1-*a*]isoquinoline-6,21-dione (5al): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 42% (20.9 mg); mp: > 230 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.40-8.39 (m, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.61-7.59 (m, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.33-7.31 (m, 2H), 7.25-7.22 (m, 2H), 7.12-7.06 (m, 3H), 6.84 (s, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 6.23 (d, *J* = 8.0 Hz, 1H), 5.94 (d, *J* = 10.0 Hz, 2H), 4.68 (s, 1H), 2.40 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 199.6, 166.8, 153.6, 149.9, 146.1, 140.5, 135.2, 134.1, 134.0, 132.8, 132.6, 130.7, 129.9, 129.5, 128.2, 127.2, 125.8, 125.1, 124.8, 123.7, 123.4, 120.8, 119.0, 117.0, 107.9, 105.9, 105.8, 105.1, 101.5, 75.6, 71.5, 29.8; HRMS (ESI) m/z calcd for $C_{32}H_{21}N_2O_4^+$ $(M+H)^+$ 497.1496, Found 497.1497.



19-methyl-4b,19-dihydro-5*H*,18*H*-indolo[2,1-*a*]indolo[2',3':1,7]thieno[3',2':4,5] cyclohepta[1,2,3-*de*]isoquinoline-5,18-dione (5am): column chromatoghraphy (silica gel; PE/EA = 5:1); yellow solid, isolated yield 38% (17.4 mg); mp: 168.5-170.3 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.42-8.39 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.62-7.59 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 5.0 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H),

7.34-7.31 (m, 2H), 7.19 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.13-7.10 (m, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 4.85 (s, 1H), 2.41 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 191.6, 167.1, 153.6, 143.0, 137.6, 136.4, 135.2, 134.0, 131.1, 130.7, 129.8, 129.3, 127.9, 125.9, 125.8, 125.2, 125.1, 124.8, 123.6, 120.8, 119.6, 117.0, 106.1, 105.3, 75.5, 71.5, 30.2; HRMS (ESI) m/z calcd for $C_{29}H_{19}N_2O_2S^+$ $(M+H)^+$ 459.1162, Found 459.1164.



***N*-benzyl-14-methyl-9-oxo-9,14-dihydrodibenzo[4,5:6,7]cyclohepta[1,2-b]indole-1-carboxamide (6) :** column chromatoghraphy (silica gel; PE/EA = 5:1); white solid, isolated yield 71% (62.8 mg); mp: 217.5-219.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.05 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.81 (dd, *J* = 12.5, 8.0 Hz, 2H), 7.59-7.52 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.36-7.29 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.11-7.10 (m, 1H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.70-6.68 (m, 2H), 5.72 (t, *J* = 5, 1H), 4.25 (dd, *J* = 14.0, 6.0 Hz, 1H), 4.14 (dd, *J* = 14.0, 5.5 Hz, 1H), 3.58 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 189.11, 169.01, 143.58, 138.06, 137.98, 137.82, 137.21, 136.62, 135.75, 134.06, 130.65, 130.17, 129.64, 129.00, 128.53, 128.51, 128.02, 127.83, 127.45, 124.63, 123.79, 123.26, 122.80, 120.53, 110.23, 44.59, 32.62; HRMS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{30}H_{23}N_2O_2^+$ 443.1754; found 443.1759.

9 References

[1] S. Guo, W. Deng, X. Xiao, J. Xia, X. Yang, Y. Liang and Y. Yang, Palladium-Catalyzed Dearomative Heck/C(sp^2)-H Activation/Decarboxylative Cyclization of C2-Tethered Indoles. *Org. Lett*., 2024, **26**, 9389-9394..

[2] L. Zhou, S. Qiao, F. Zhou, X. Xuchen, G. Deng, Y. Yang and Y. Liang, *α*-Oxocarboxylic Acids as Three-Carbon Insertion Units for Palladium-Catalyzed Decarboxylative Cascade Synthesis of Diverse Fused Heteropolycycles. *Org. Lett*.,

2021, **23**, 2878-2883.

[3] L. Zhou, X. Chen, Q. Peng, Z. Li, S. Qiao, G. Deng, Y. Liang, M. Lei and Y.Yang, A Cascade C(sp^3)-H Annulation Involving *C*(alkyl), *C*(alkyl)-Palladacycle Intermediates. *Angew. Chem., Int. Ed.,* 2024, **63**, e202412336.

10 The X-ray Single-Crystal Diffraction Analysis of 3af and 5aa

10.1 The X-ray single-crystal diffraction analysis of 3af

A suitable crystal of **3af** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the olex2.solve3 structure solution program using Charge Flipping and refined with the ShelXL4 refinement package using Least Squares minimisation.

Crystallographic data for **3af** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 2340392, respectively.

Table S2. Crystallographic data details of **3af**

CCDC deposition No.	2340392
Empirical formula	$C_{31}H_{21}ClN_2O_3$
Formula weight	504.19
Temperature/K	293
Crystal system	orthorhombic
Space group	Pb ca
a/Å	11.7884(3)
b/Å	17.5725(4)
c/Å	24.1043(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4993.2(2)
Z	8

ρ_{calc}g/cm^3	1.341
μ/mm^{-1}	1.629
F(000)	2093.0
Crystal size/mm^3	0.3 × 0.2 × 0.05
Radiation	CuKα (λ = 1.54184)
The range for data collection/°	7.334 to 133.184
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -28 ≤ l ≤ 28
Reflections collected	66096
Independent reflections	4401 [Rint = 0.0948, Rsigma = 0.0327]
Data/restraints/parameters	4401/7/346
Goodness-of-fit on F2	1.054
Final R indexes [I>=2σ (I)]	R1 = 0.0736, wR2 = 0.2059
Final R indexes [all data]	R1 = 0.0827, wR2 = 0.2138
Largest diff. peak/hole / e Å-3	0.74/-0.25

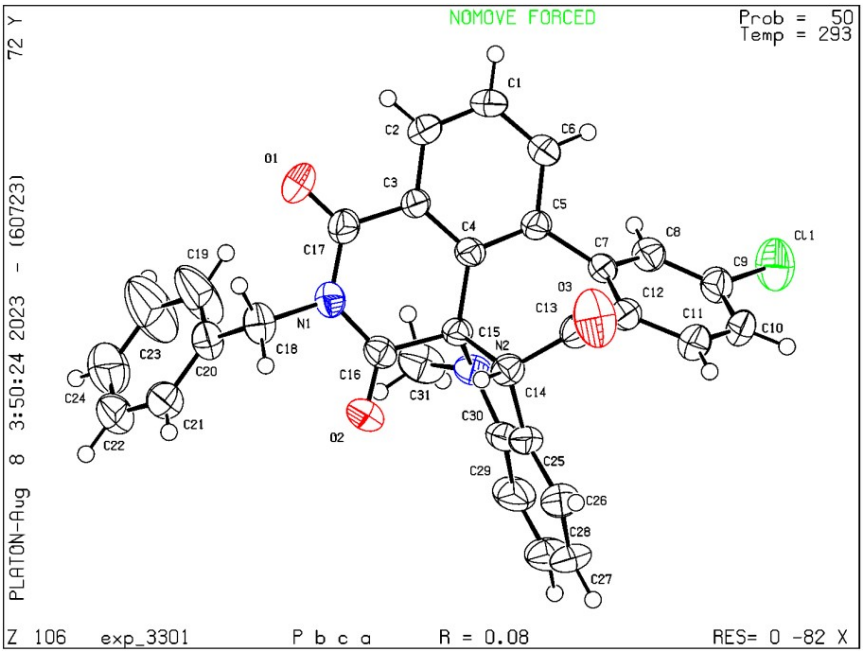


Fig. S1 X-ray structure of **3af**. The thermal ellipsoids are 50% probability level

10.2 The X-ray single-crystal diffraction analysis of 5aa

A suitable crystal of **5aa** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 293(10) K during data collection.

Using Olex2, the structure was solved with the olex2.solve3 structure solution program using Charge Flipping and refined with the ShelXL4 refinement package using Least Squares minimisation.

Crystallographic data for **5aa** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 2359843, respectively.

Table S3. Crystallographic data details of **5aa**

CCDC deposition No.	2359843
Empirical formula	$C_{31}H_{20}N_2O_2$
Formula weight	452.49
Temperature/K	293(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	23.3443(12)
b/Å	9.3993(3)
c/Å	23.0066(11)
α/°	90
β/°	117.957(7)
γ/°	90
Volume/Å^3	4459.0(4)
Z	8
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.674
F(000)	1888.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
The range for data collection/°	4.286 to 133.196
Index ranges	-27 ≤ h ≤ 26, -10 ≤ k ≤ 11, -24 ≤ l ≤ 27
Reflections collected	16302
Independent reflections	7877 [R_{int} = 0.0339, R_{sigma} = 0.0525]

Data/restraints/parameters	7877/0/633
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	$R_1 = 0.0586$, $wR_2 = 0.1401$
Final R indexes [all data]	$R_1 = 0.0911$, $wR_2 = 0.1619$
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.19

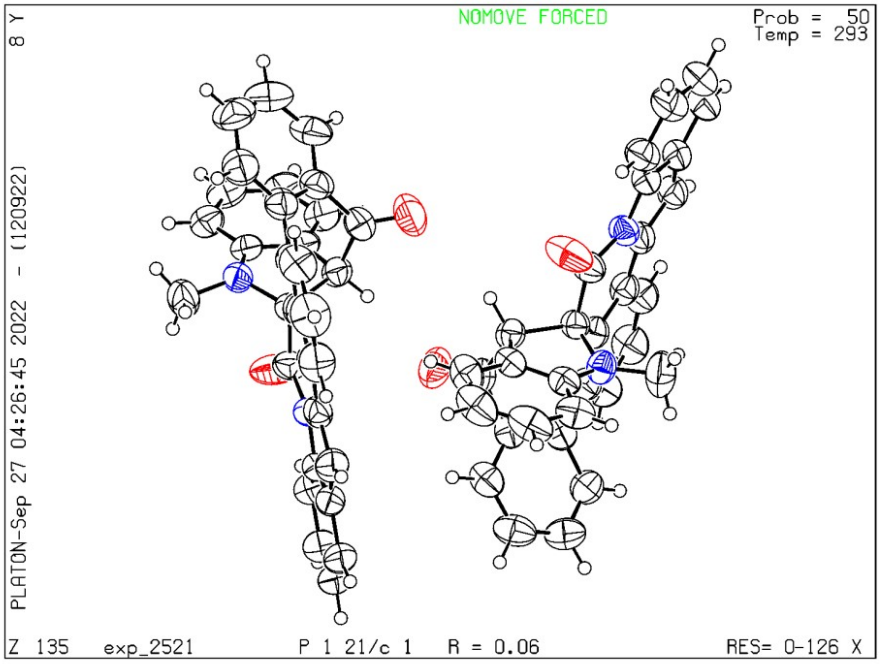
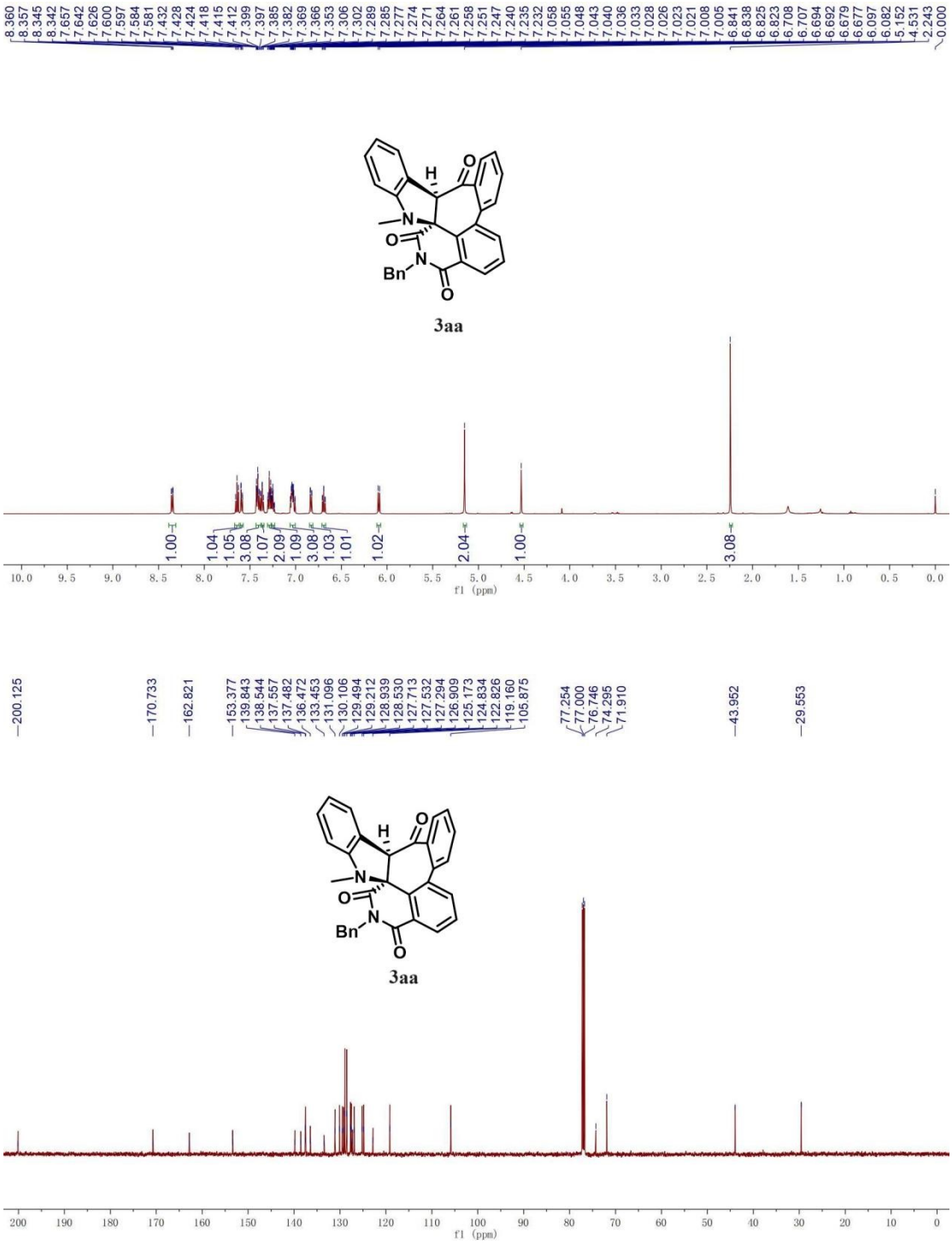


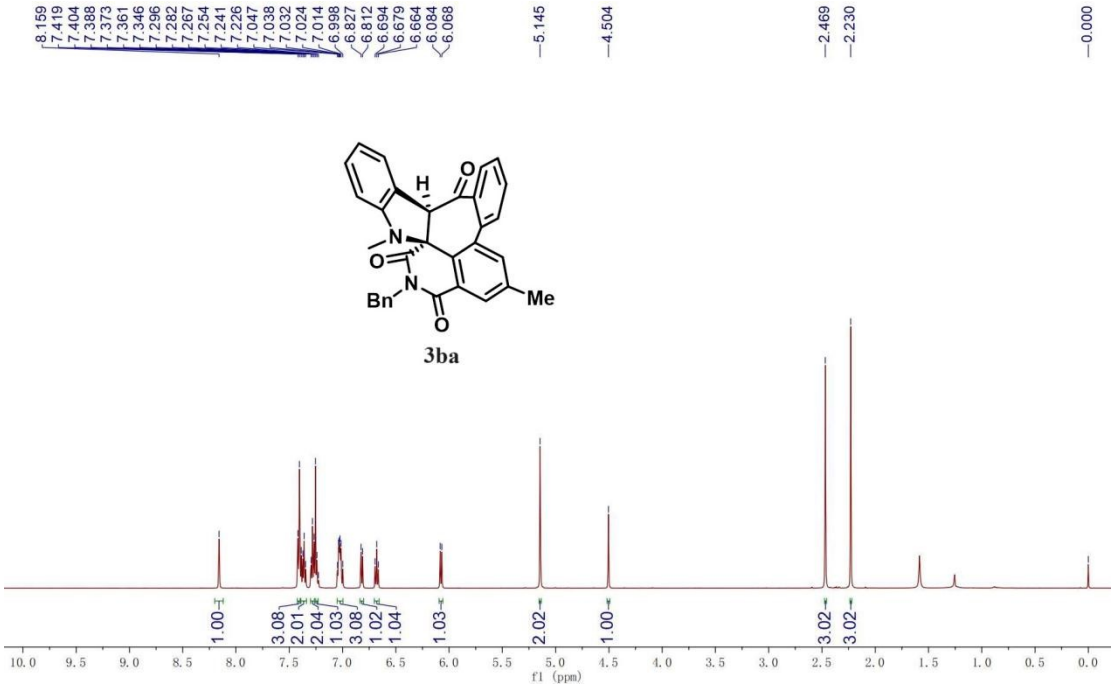
Fig. S2 X-ray structure of **5aa**. The thermal ellipsoids are 50% probability level

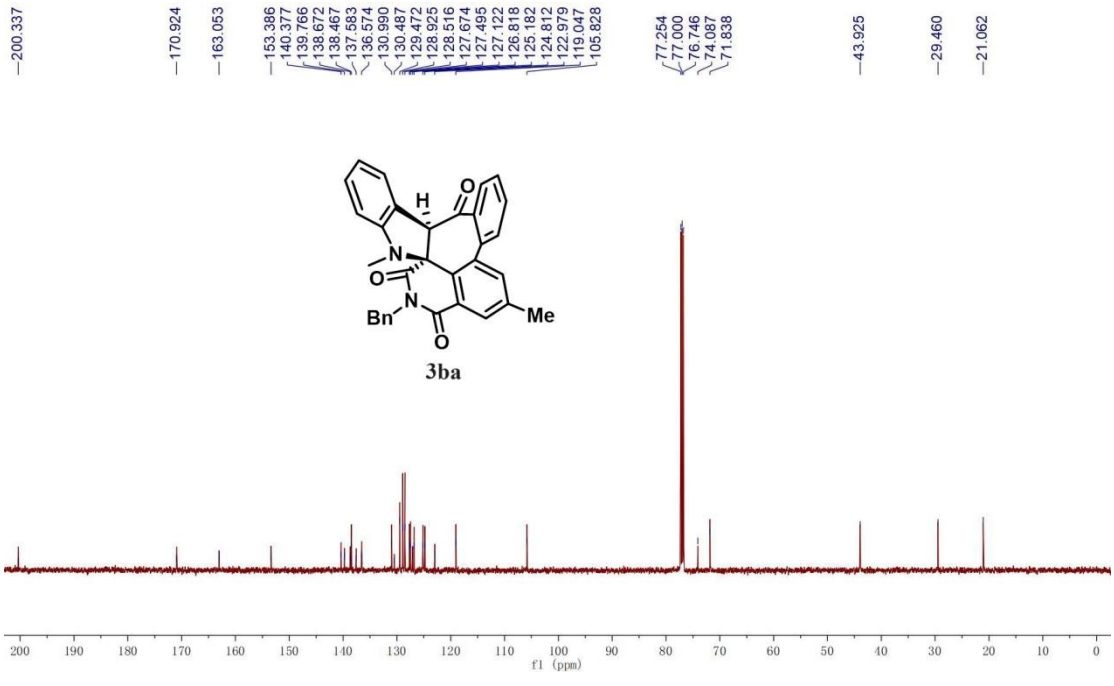
11 NMR Spectra of Products

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

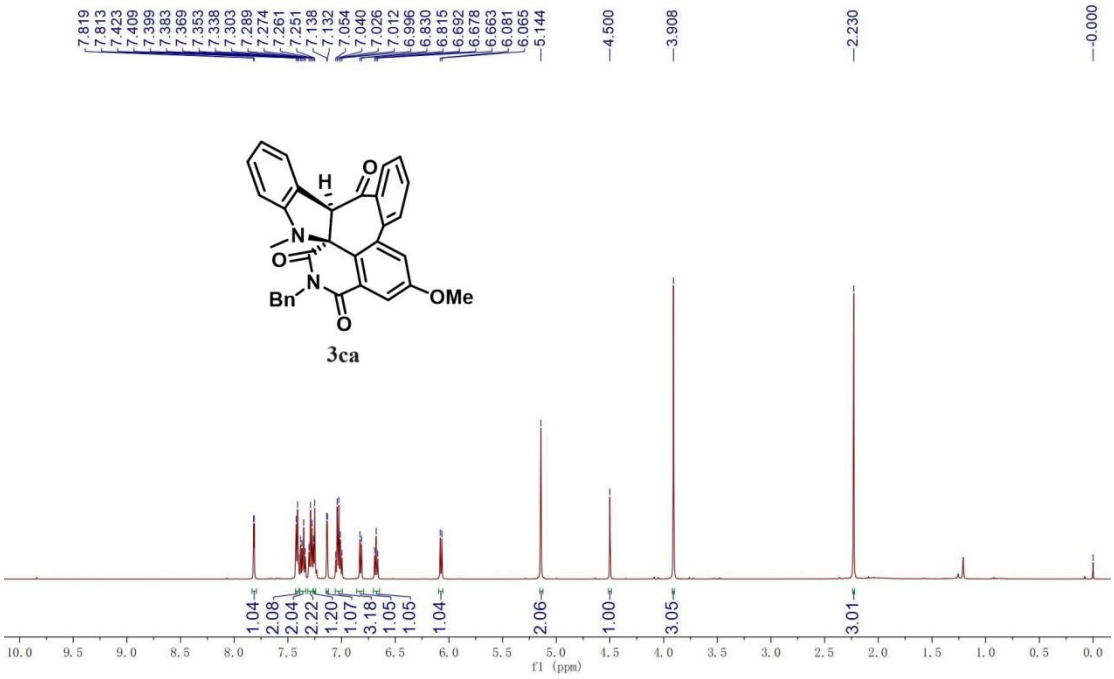


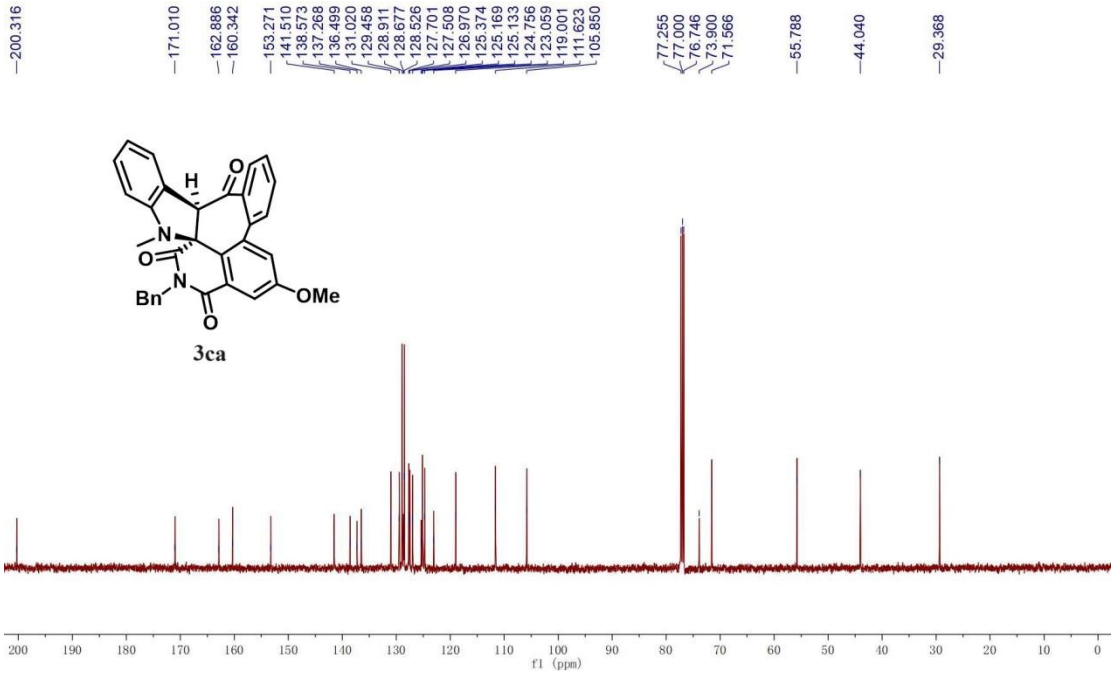
^{1}H NMR of **3ba** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ba** (125 MHz, $CDCl_3$)



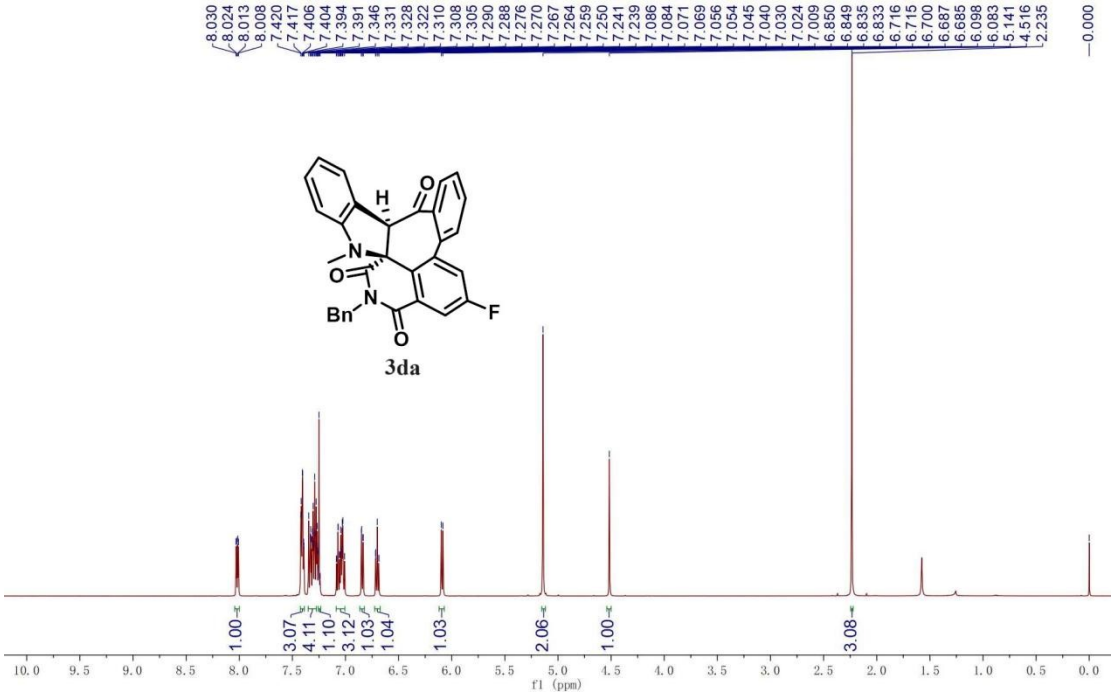


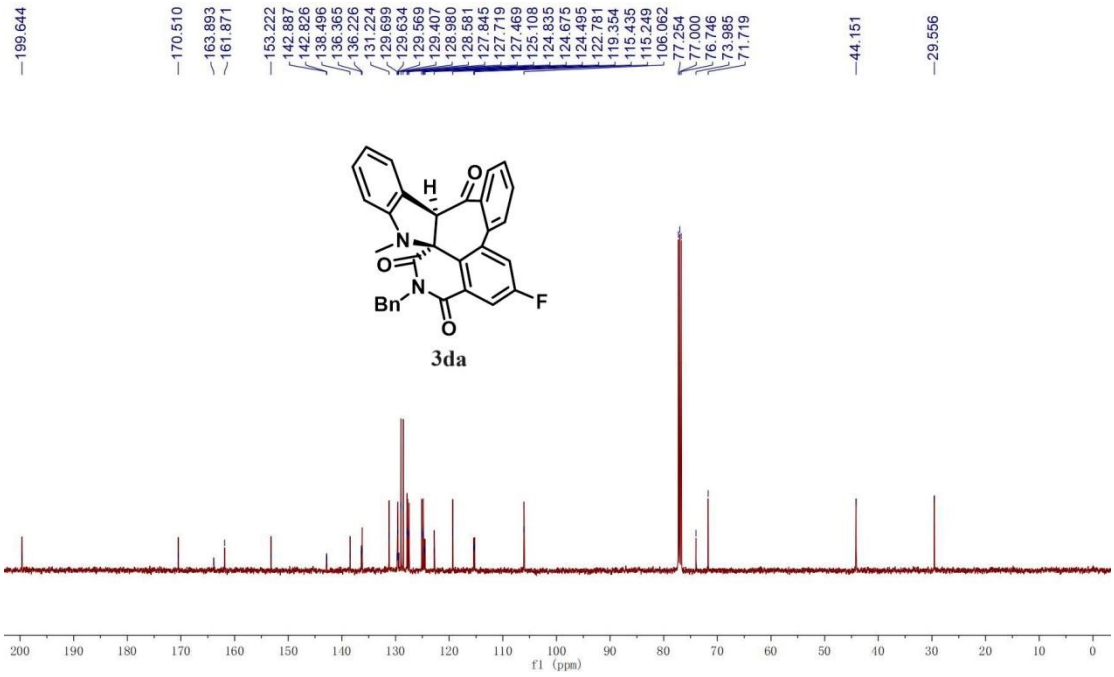
^{1}H NMR of **3ca** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ca** (125 MHz, $CDCl_3$)

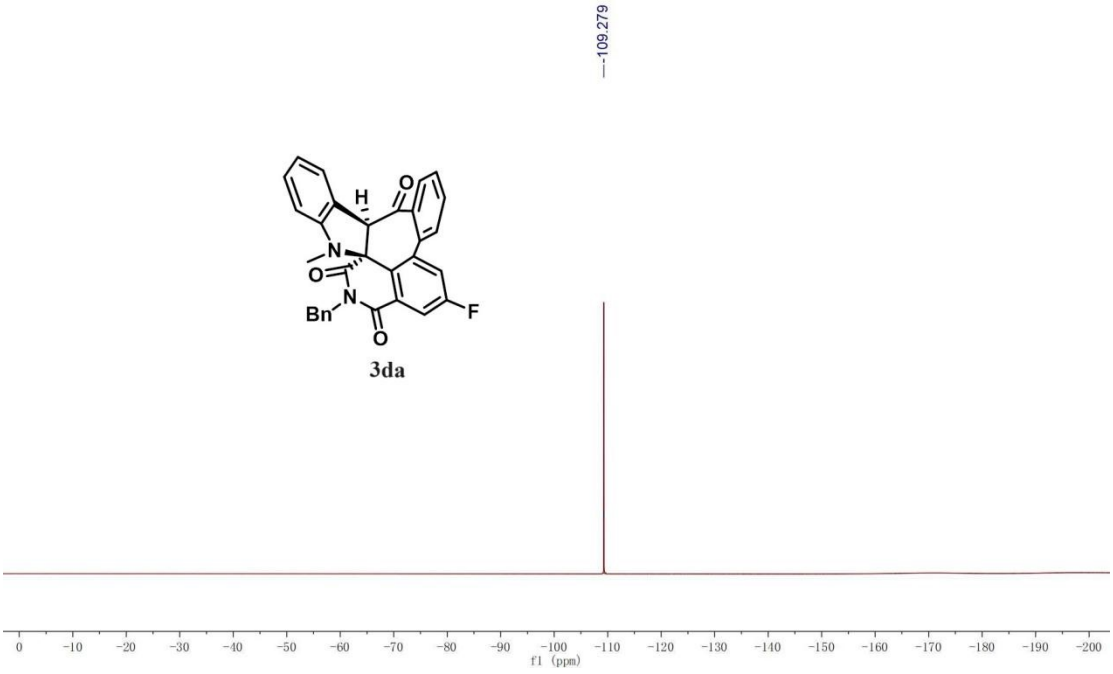




^{1}H NMR of **3da** (500 MHz, $CDCl_3$), ^{13}C NMR of **3da** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3da** (471 MHz, $CDCl_3$)



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H
O
N
O
N
Bn
O
F
0
-10
-20
-30
-40
-50
-60
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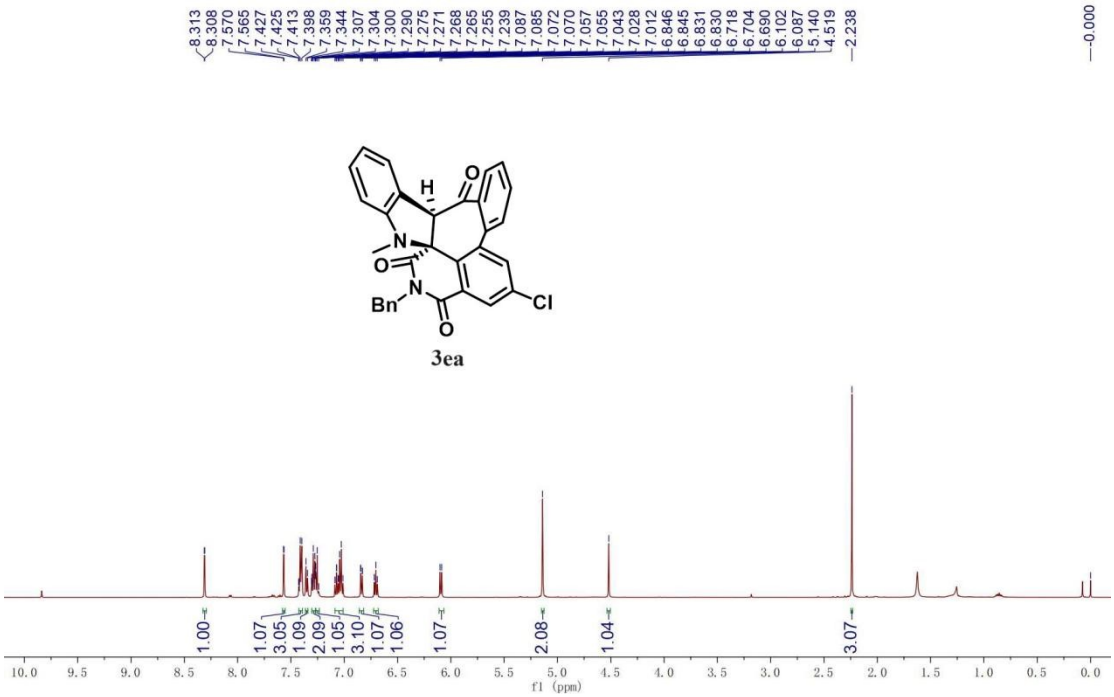
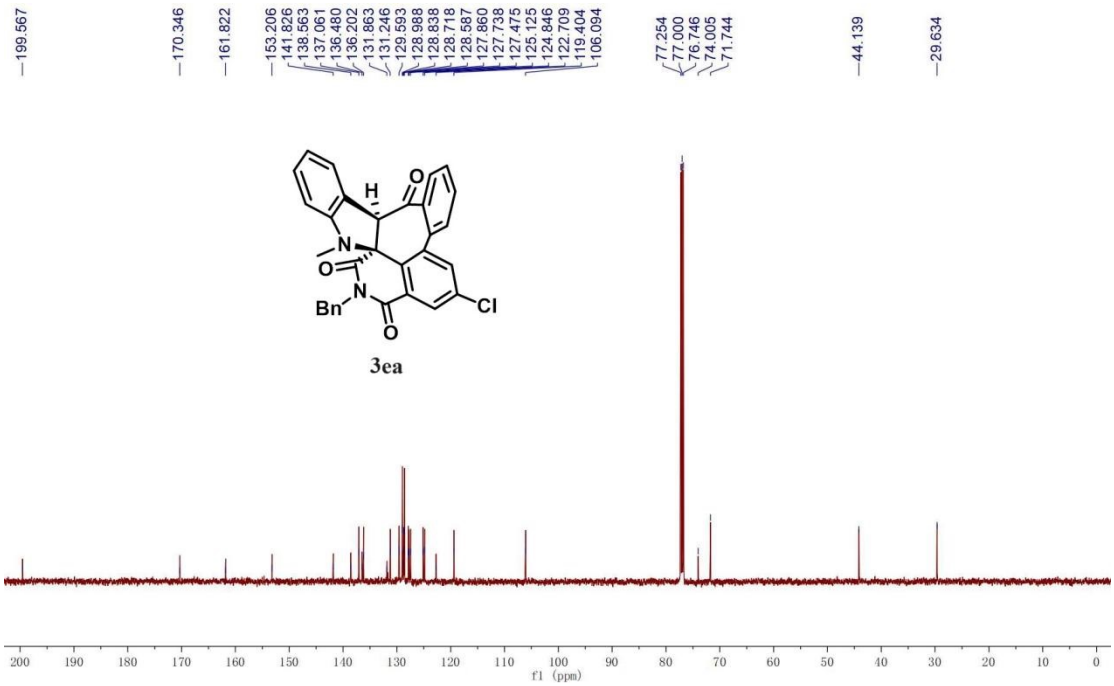
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

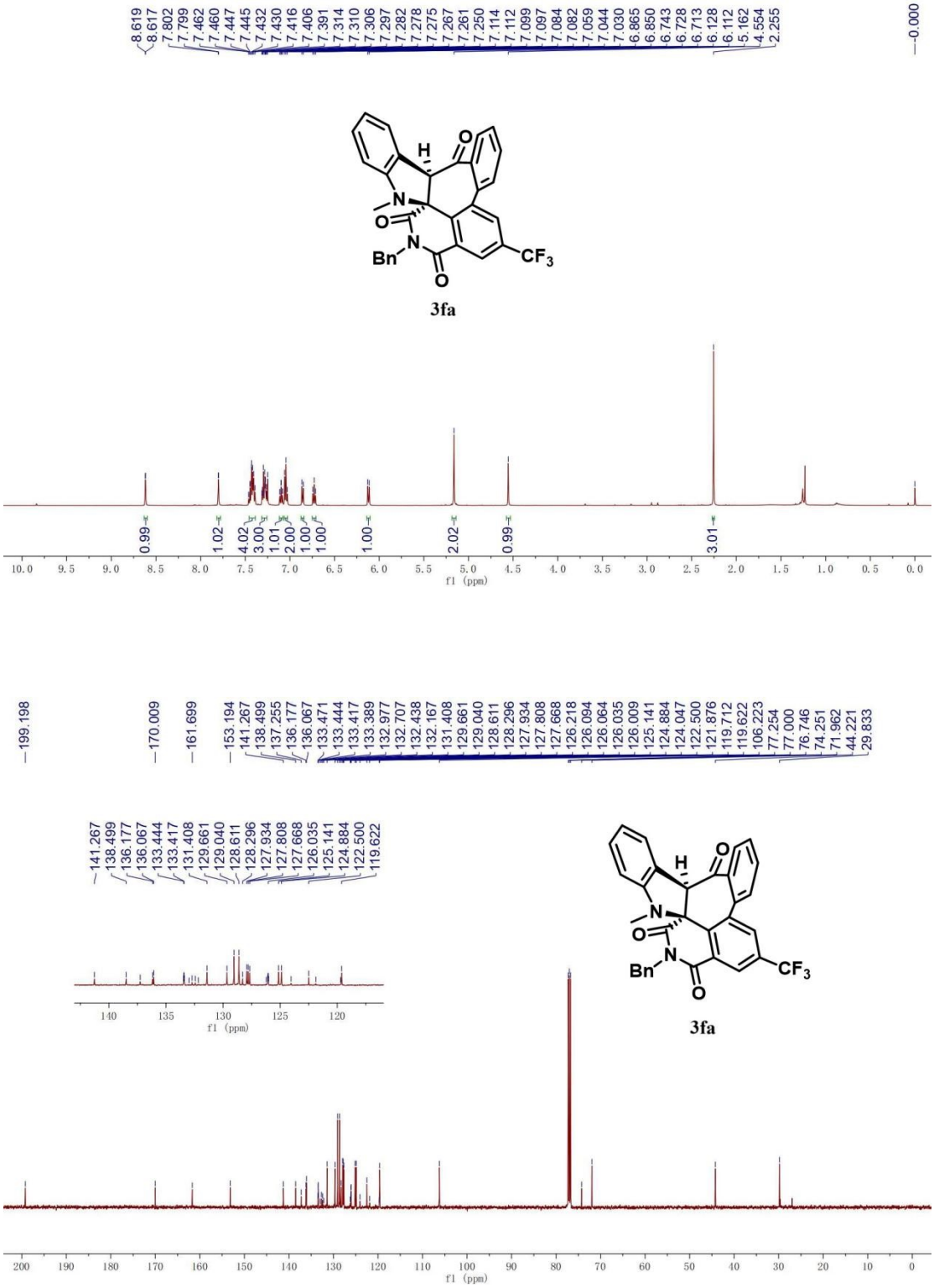
3da

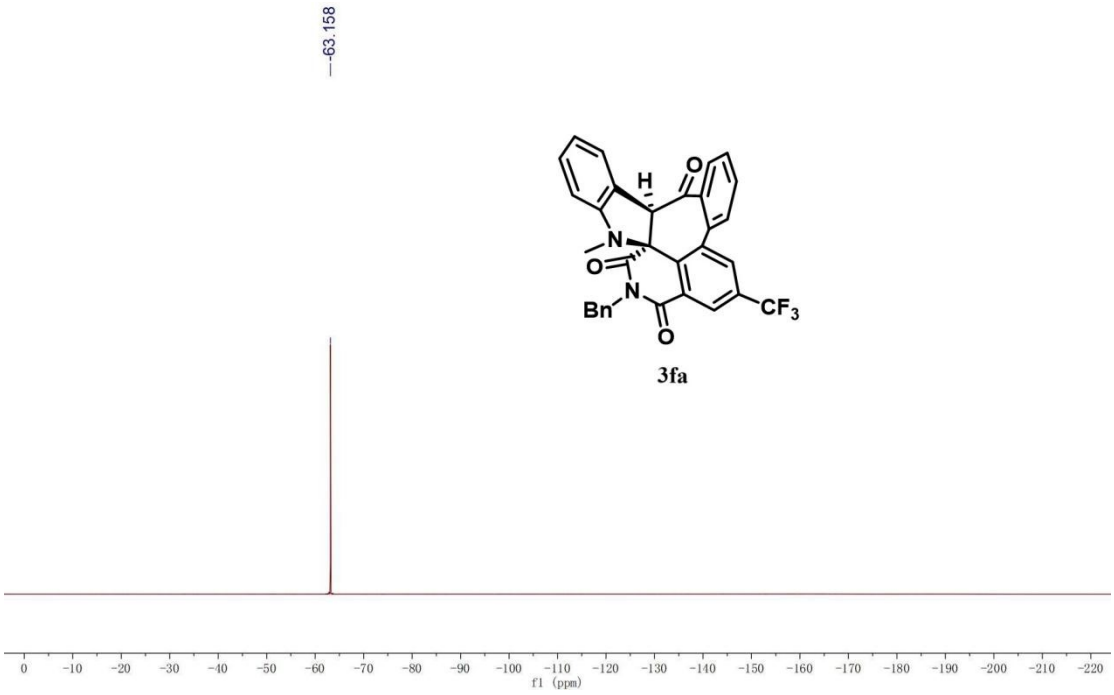
^{1}H NMR of **3ea** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ea** (125 MHz, $CDCl_3$)





^{1}H NMR of **3fa** (500 MHz, $CDCl_3$), ^{13}C NMR of **3fa** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3fa** (471 MHz, $CDCl_3$)




-63.158
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O
N
Bn
O
CF3
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-10
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-30
-40
-50
-60
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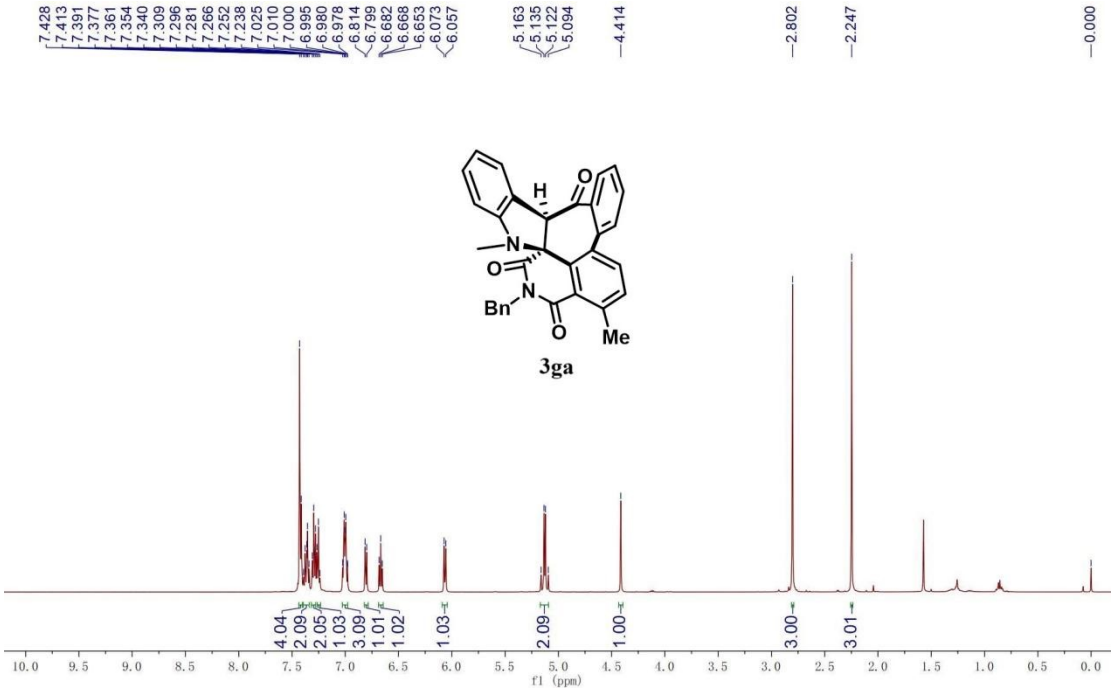
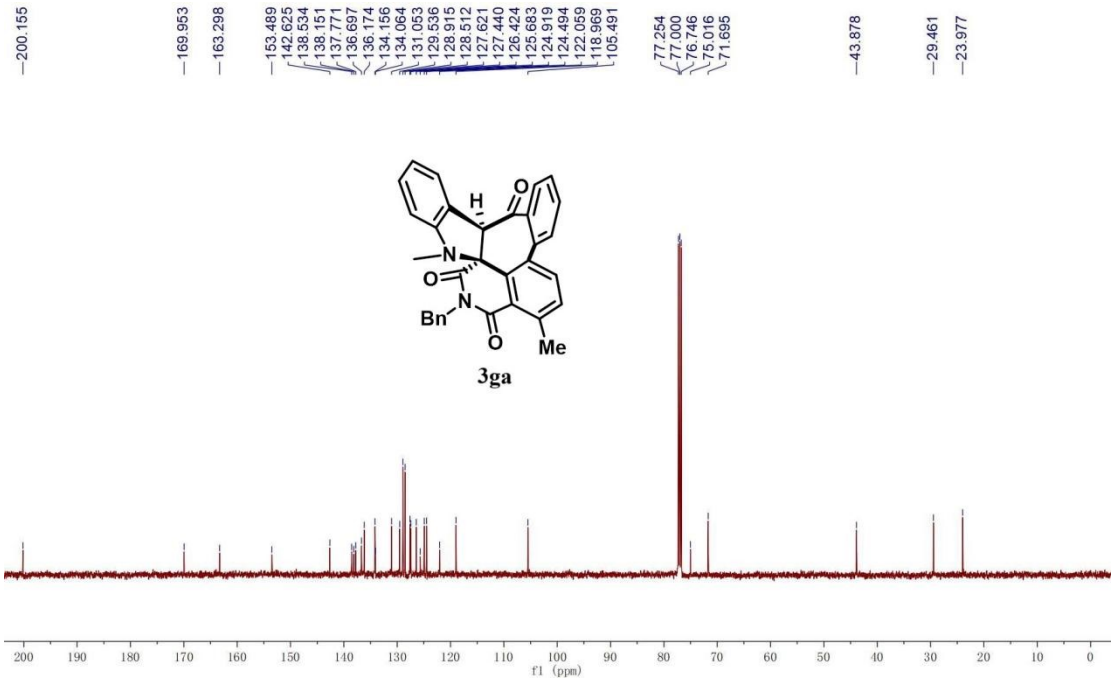
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

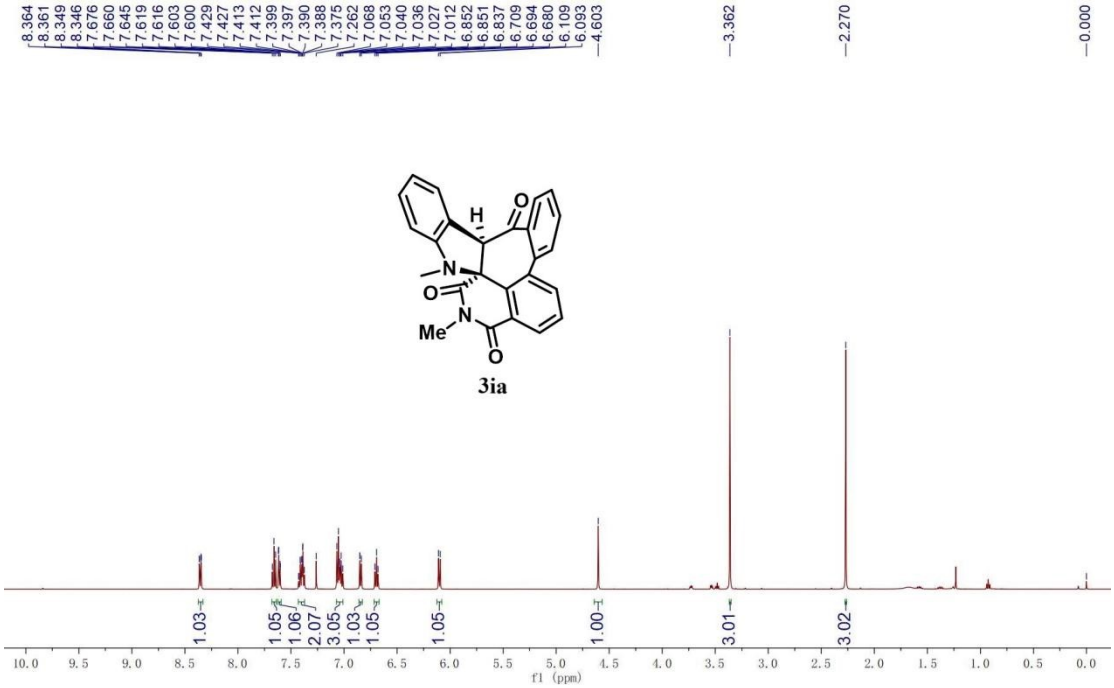
3fa

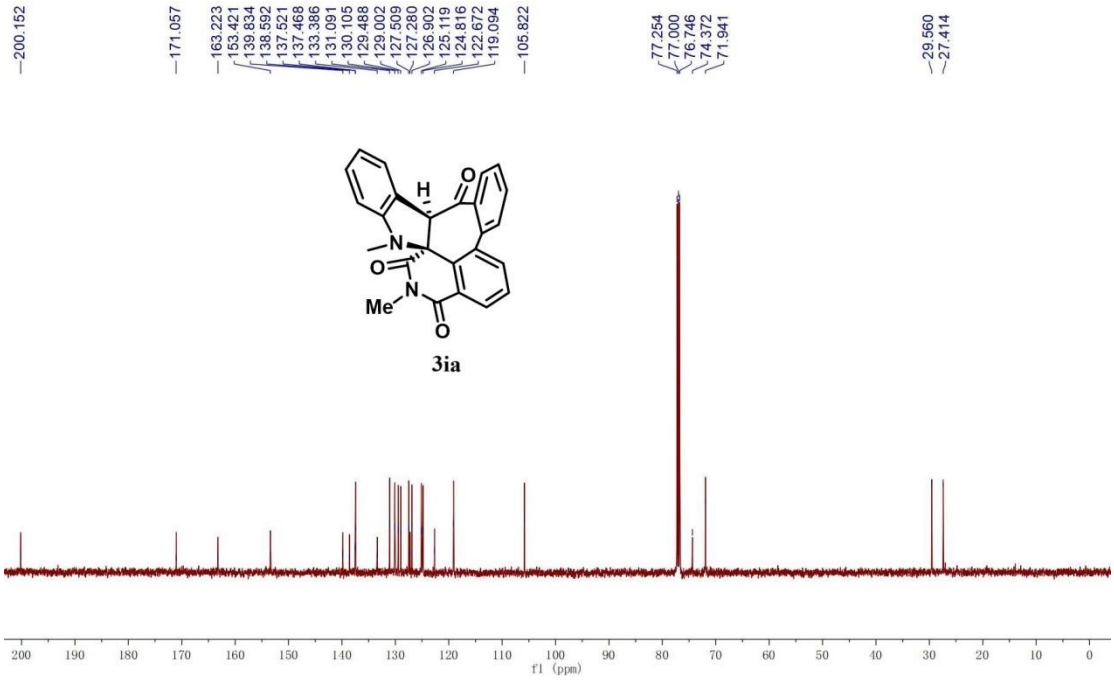
^{1}H NMR of **3ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ga** (125 MHz, $CDCl_3$)



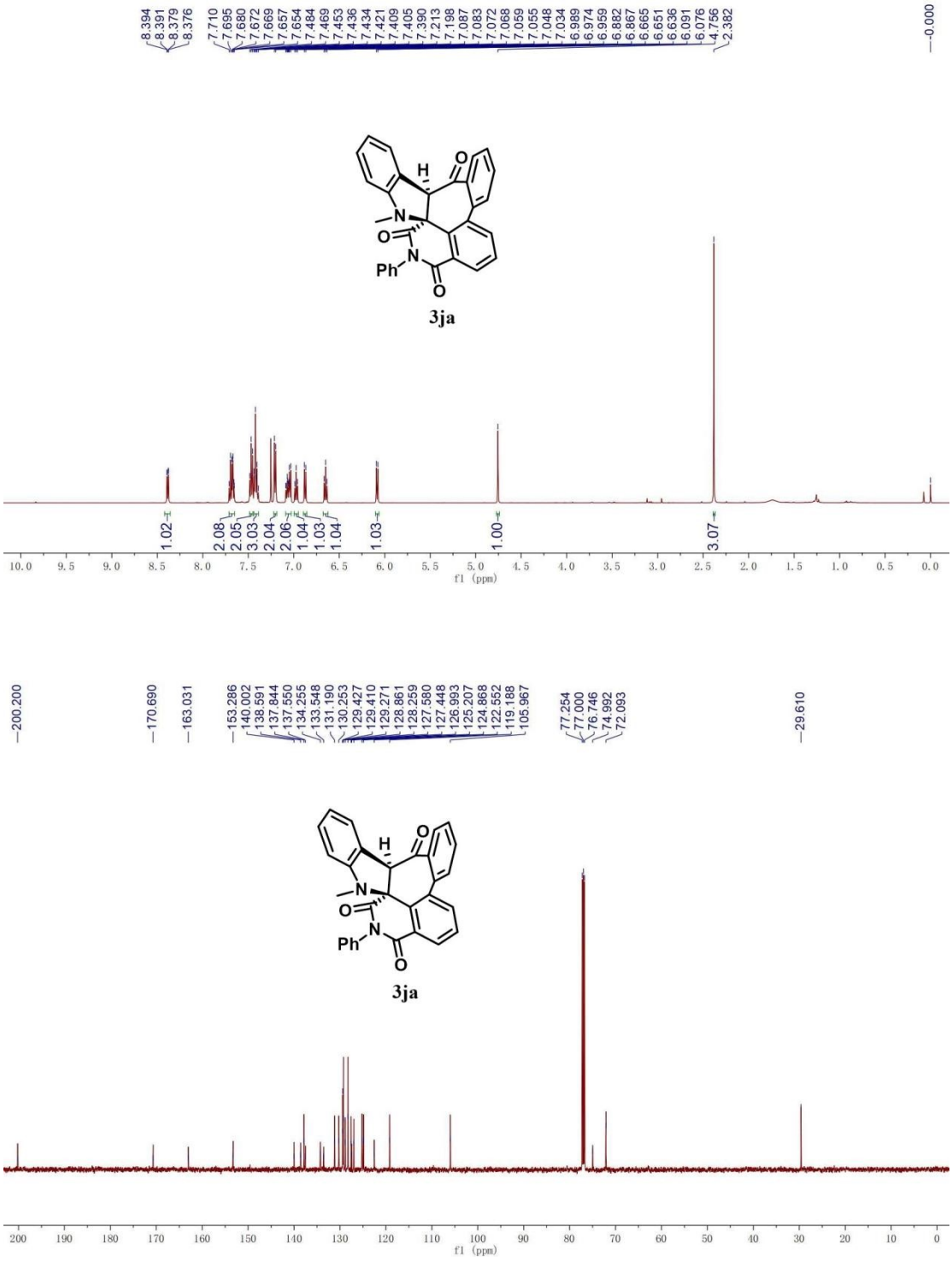


^{1}H NMR of **3ia** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ia** (125 MHz, $CDCl_3$)

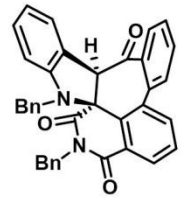




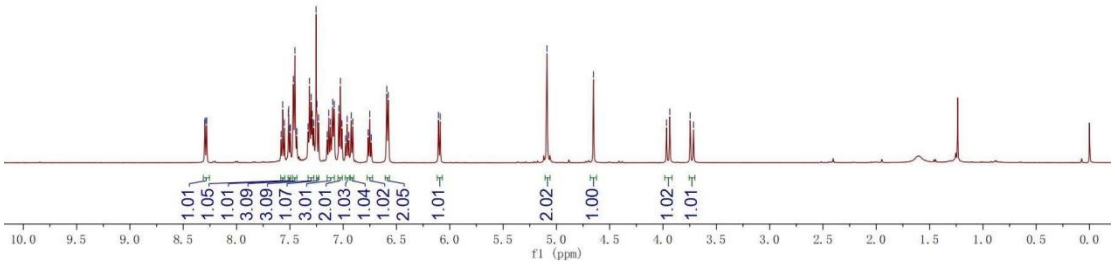
^{1}H NMR of **3ja** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ja** (125 MHz, $CDCl_3$)

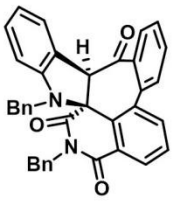


^{1}H NMR of **3ka** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ka** (125 MHz, $CDCl_3$)

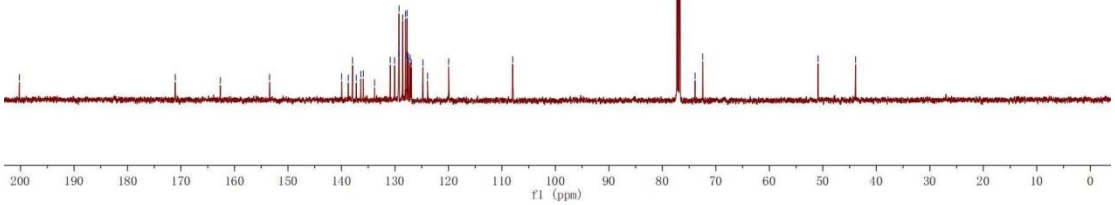


3ka

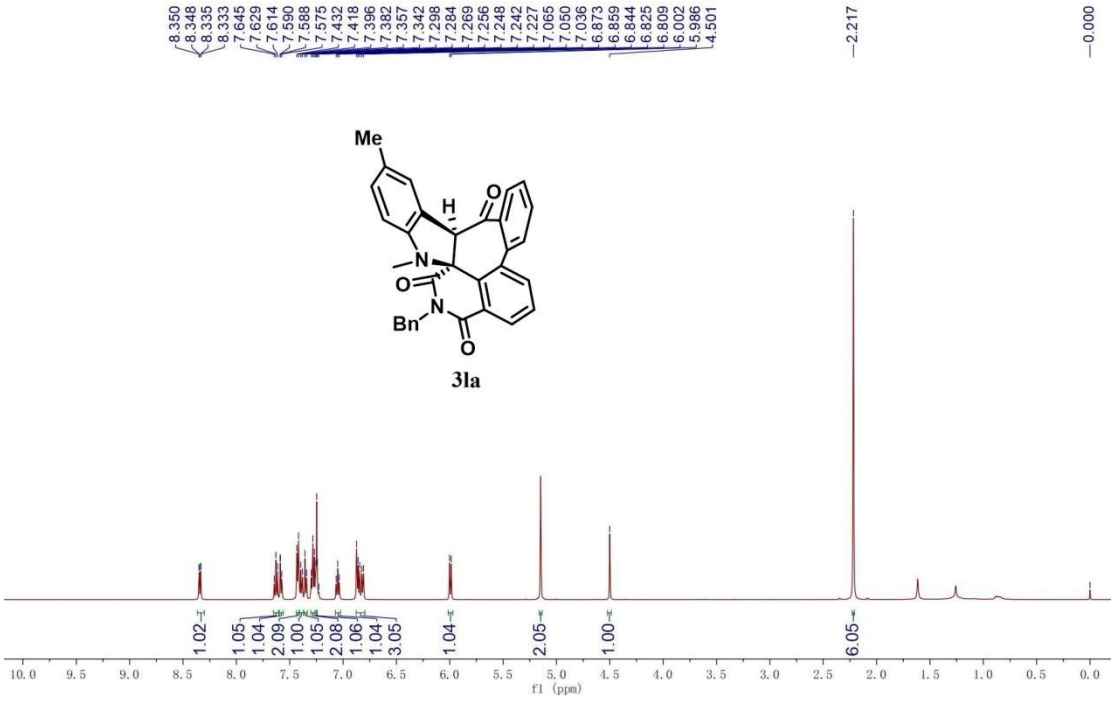


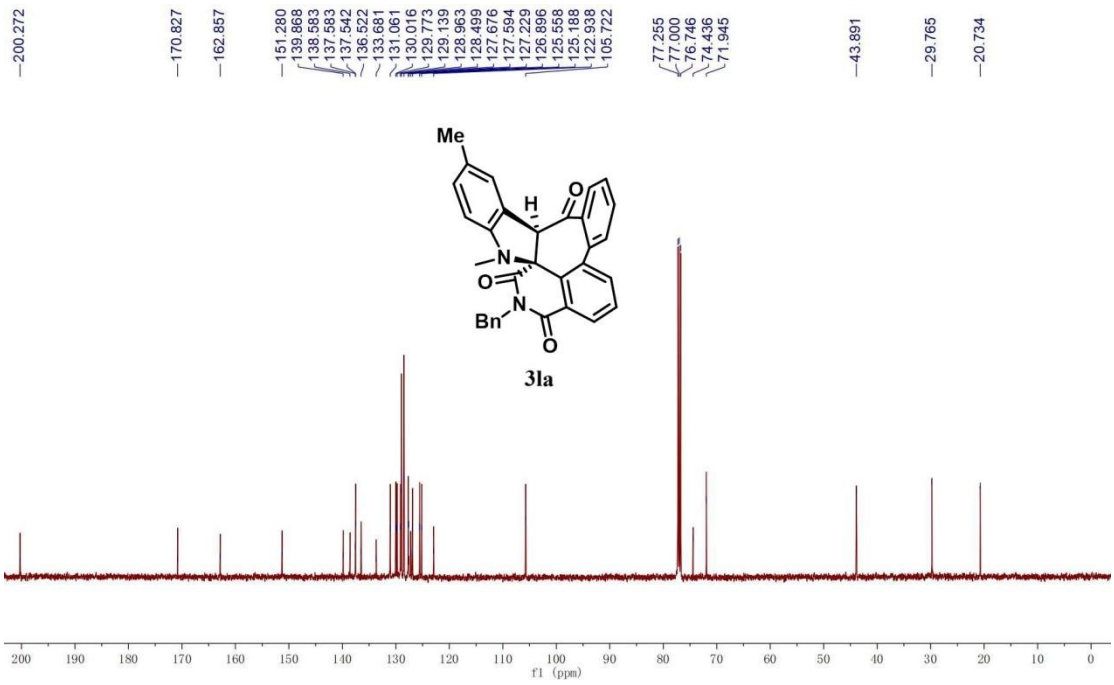


3ka

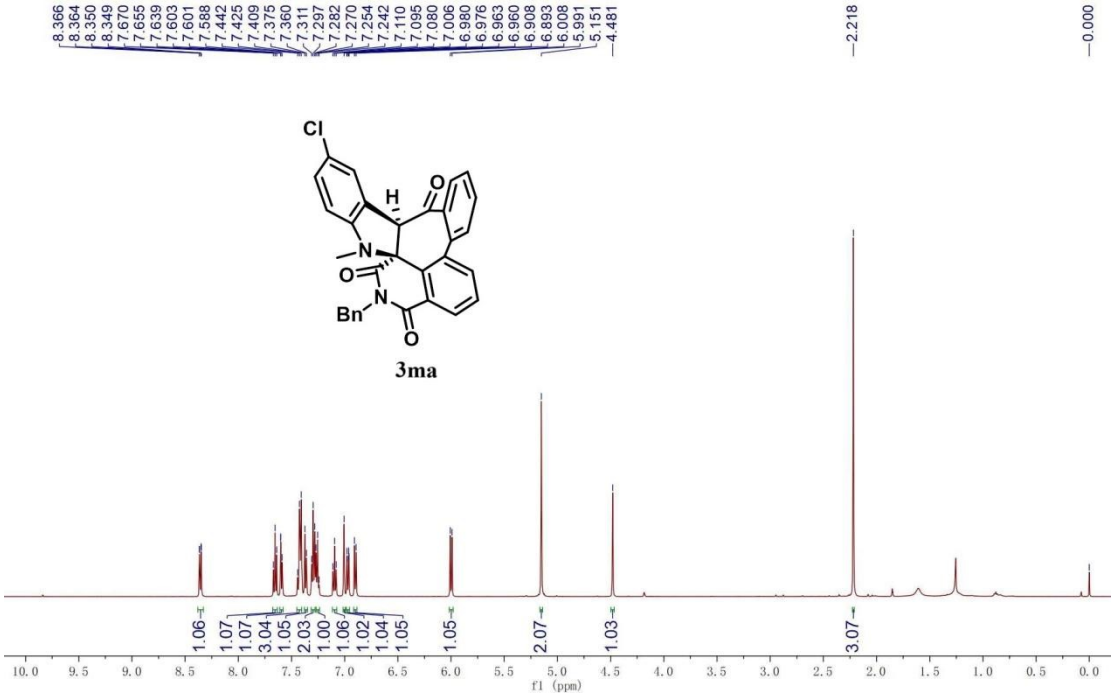


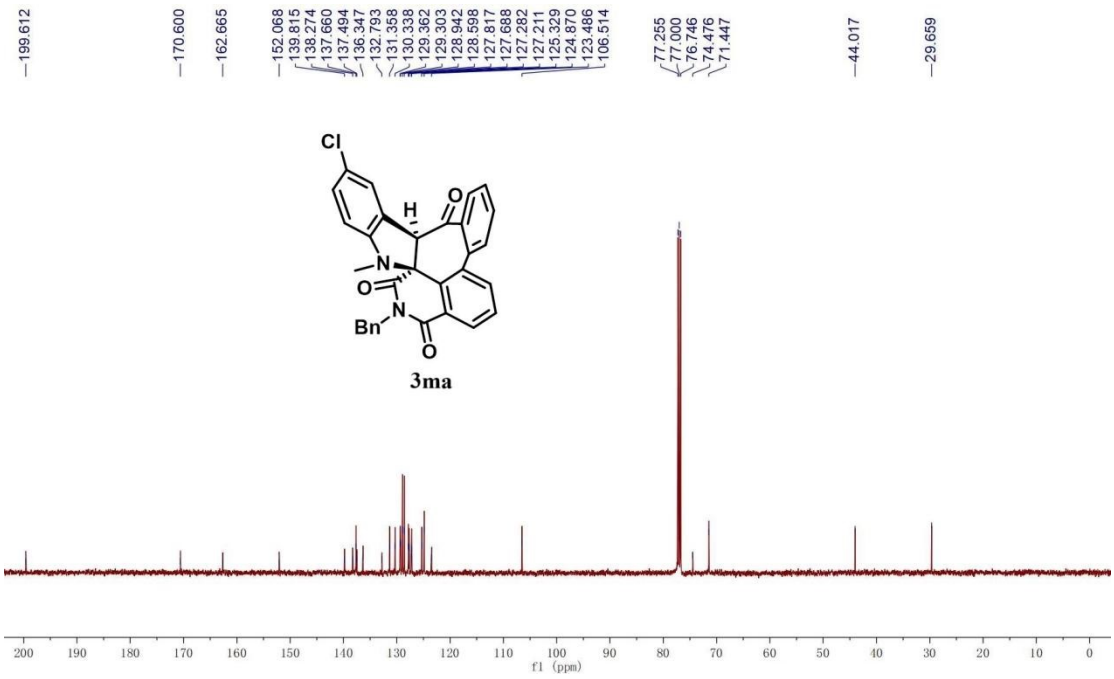
^{1}H NMR of **3la** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3la** (125 MHz, $CDCl_3$)



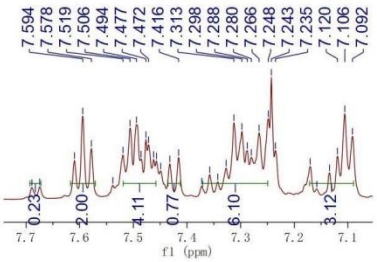


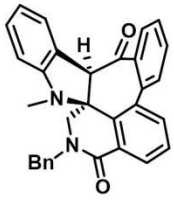
^{1}H NMR of **3ma** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ma** (125 MHz, $CDCl_3$)



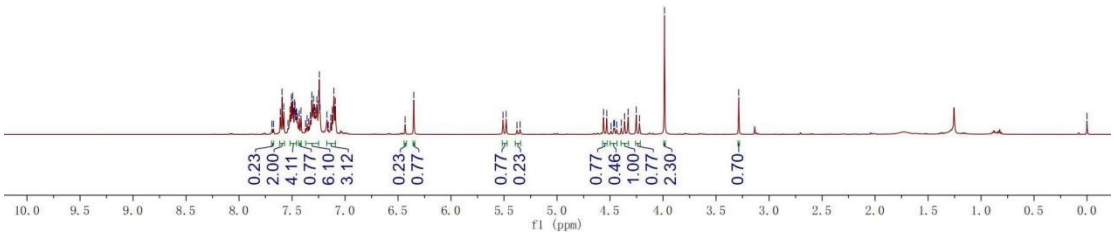


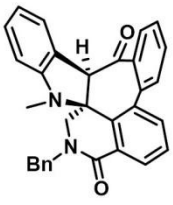
^{1}H NMR of **3na** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3na** (125 MHz, $CDCl_3$)





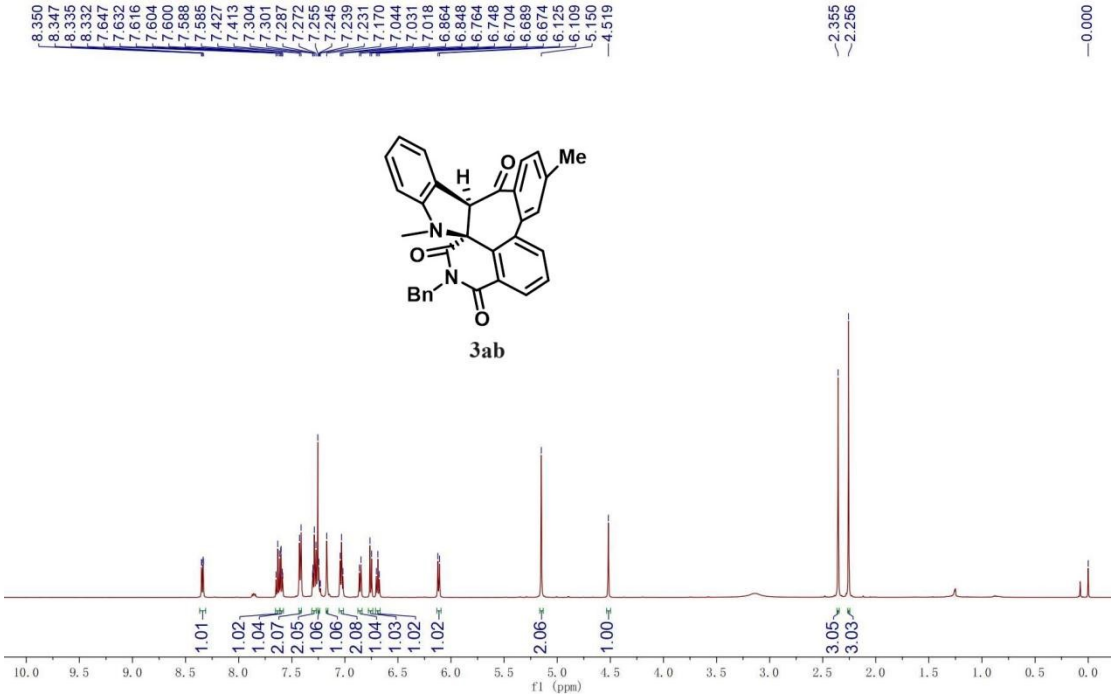
3na

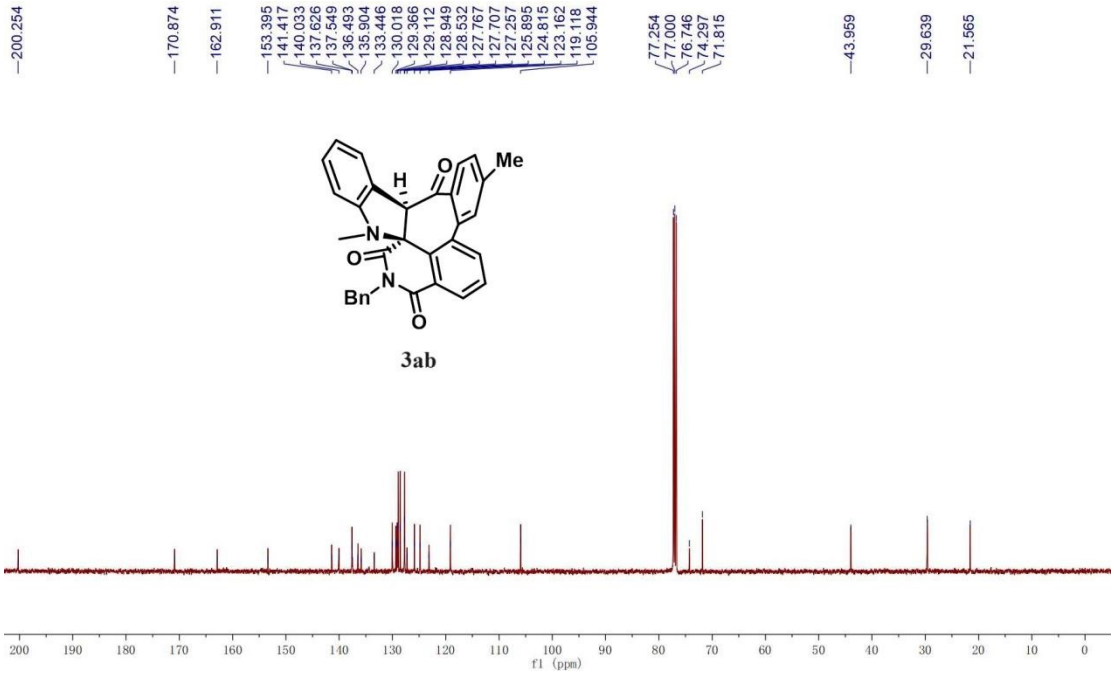




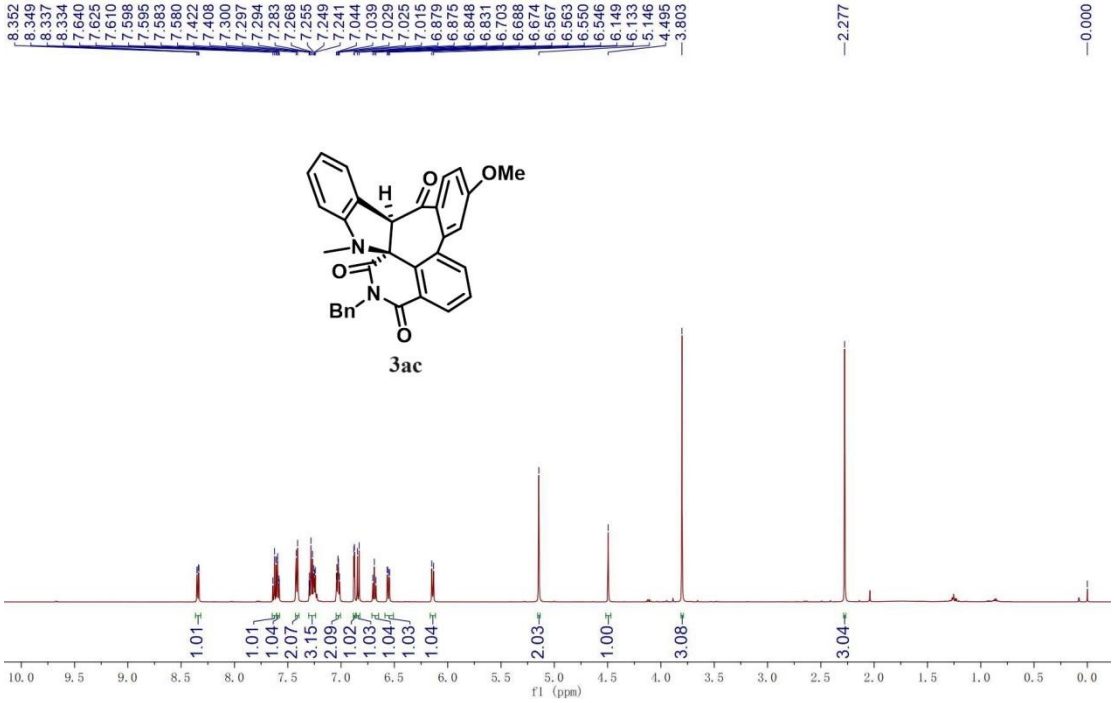
3na

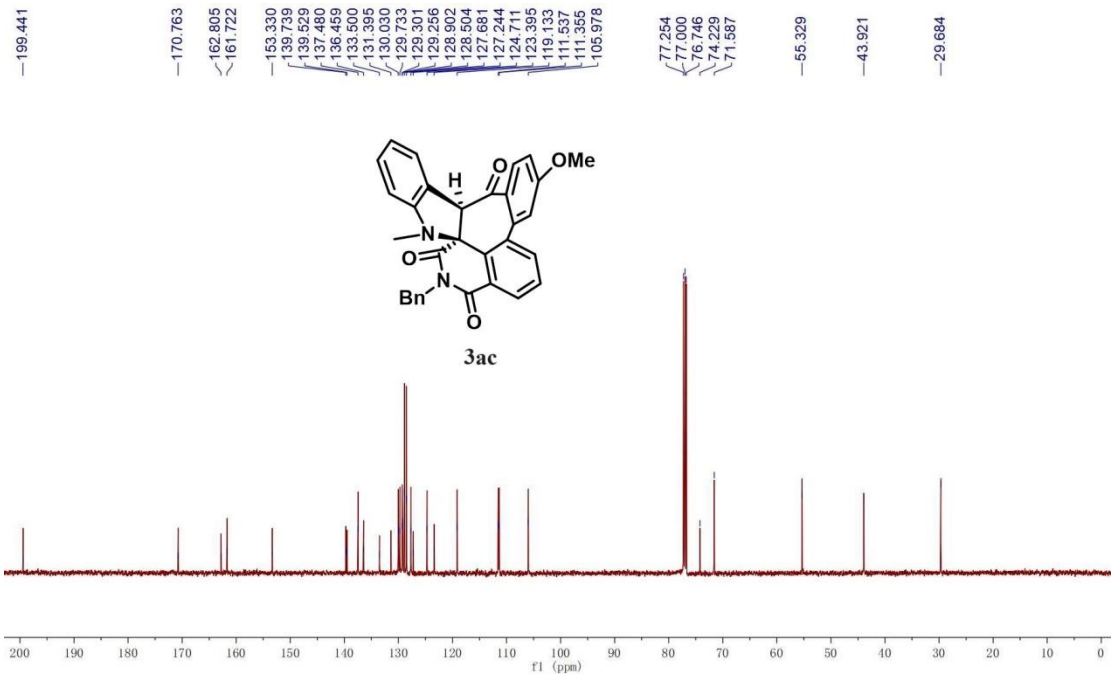
^{1}H NMR of **3ab** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ab** (125 MHz, $CDCl_3$)



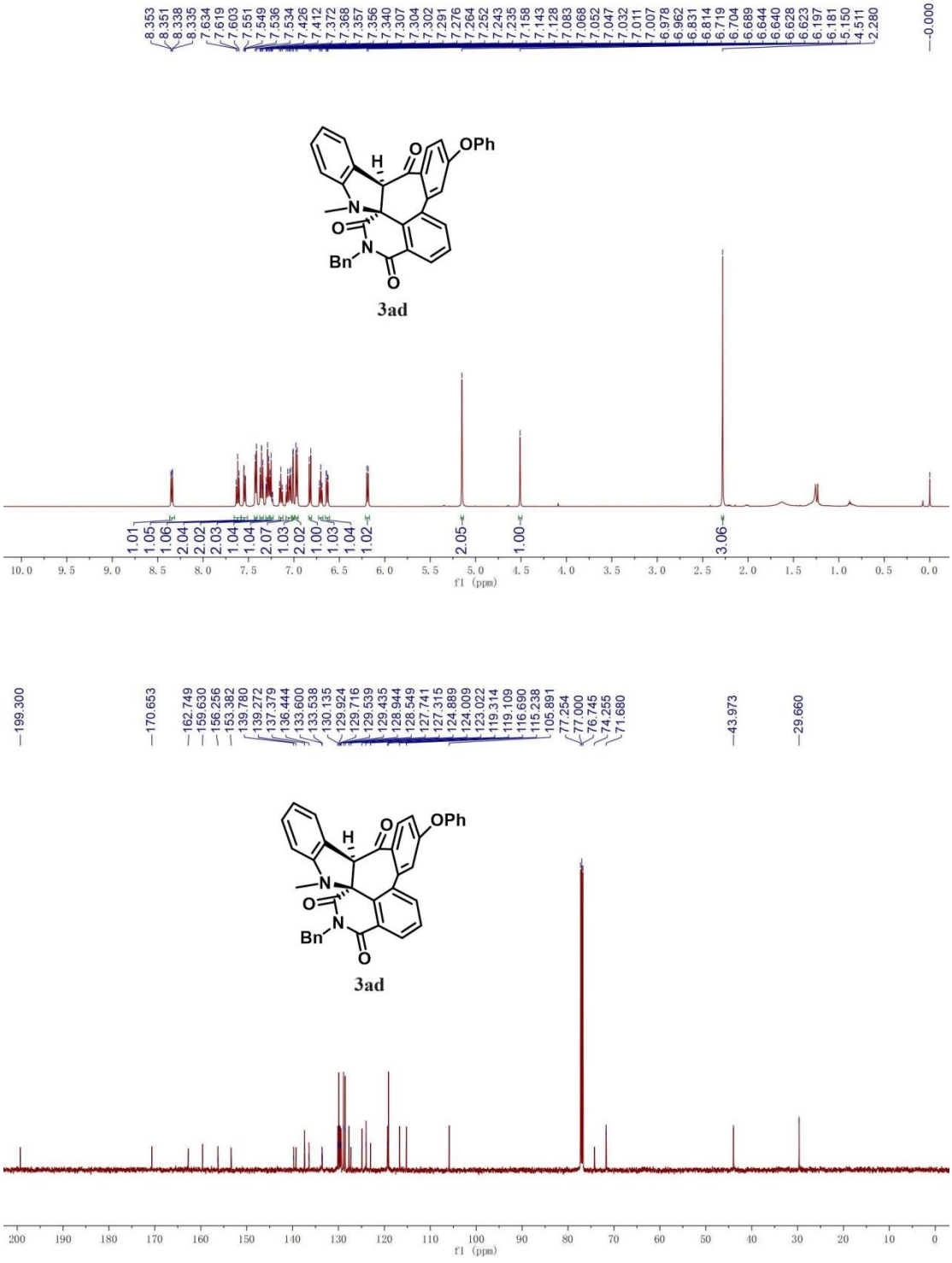


^{1}H NMR of **3ac** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ac** (125 MHz, $CDCl_3$)

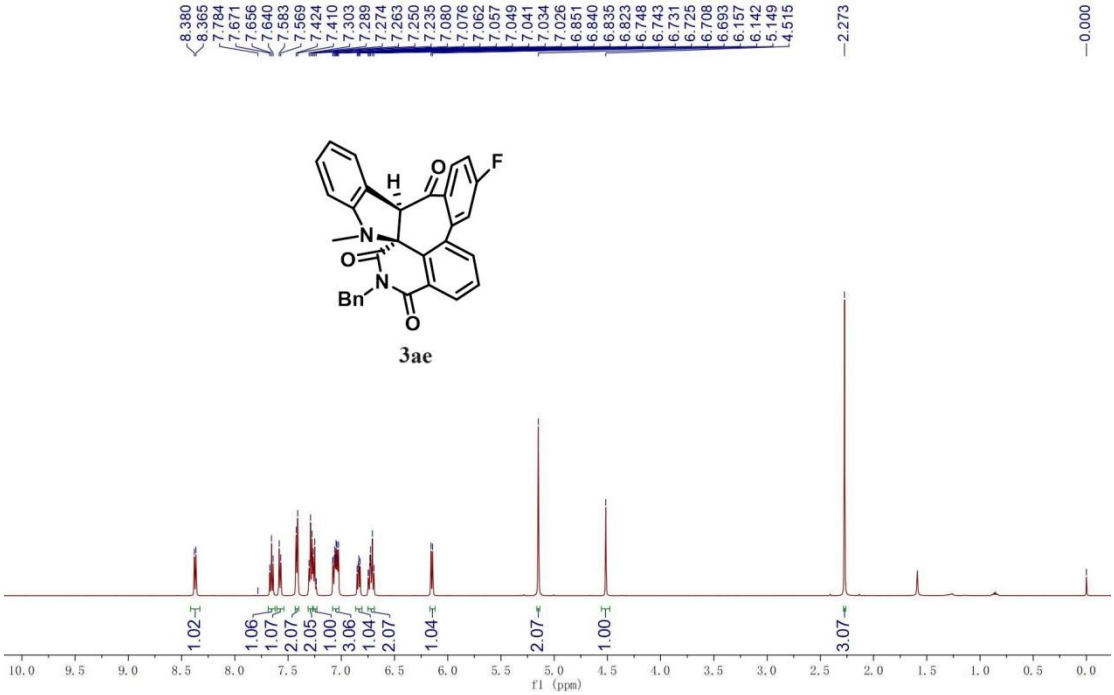


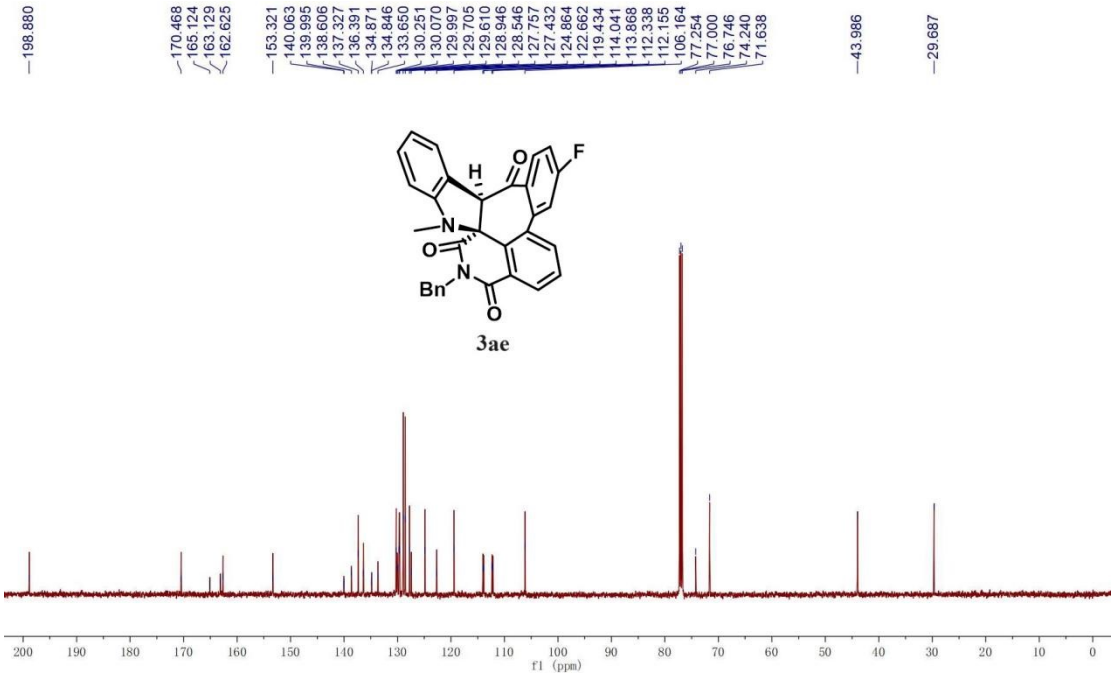


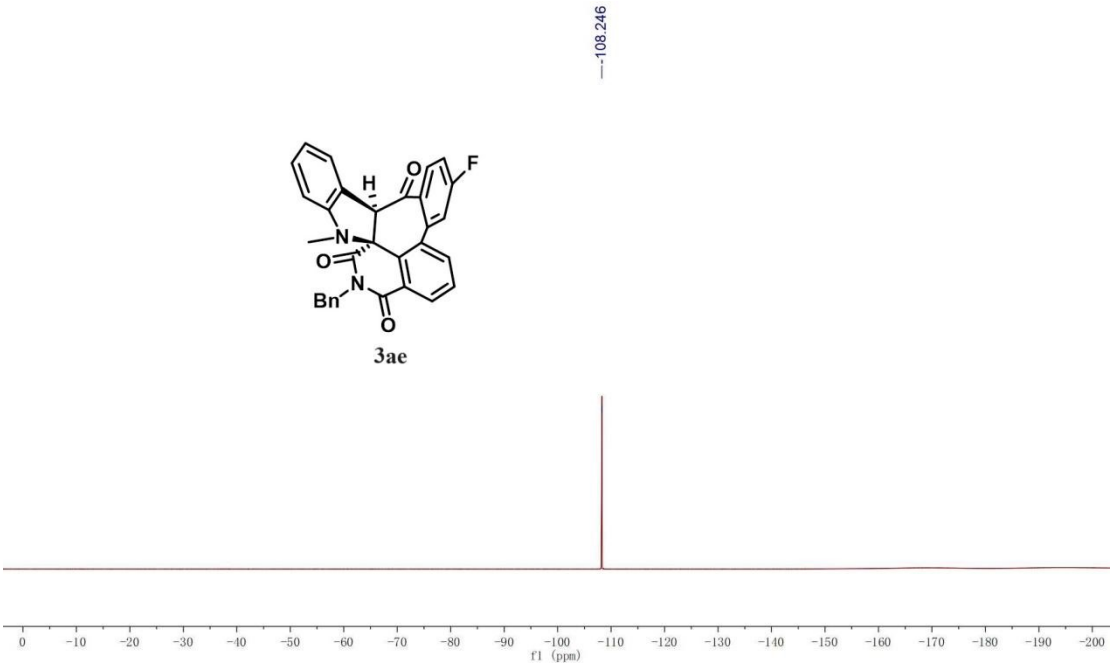
^{1}H NMR of **3ad** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ad** (125 MHz, $CDCl_3$)



^{1}H NMR of **3ae** (500 MHz, $CDCl_3$), ^{13}C NMR of **3ae** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3ae** (471 MHz, $CDCl_3$)

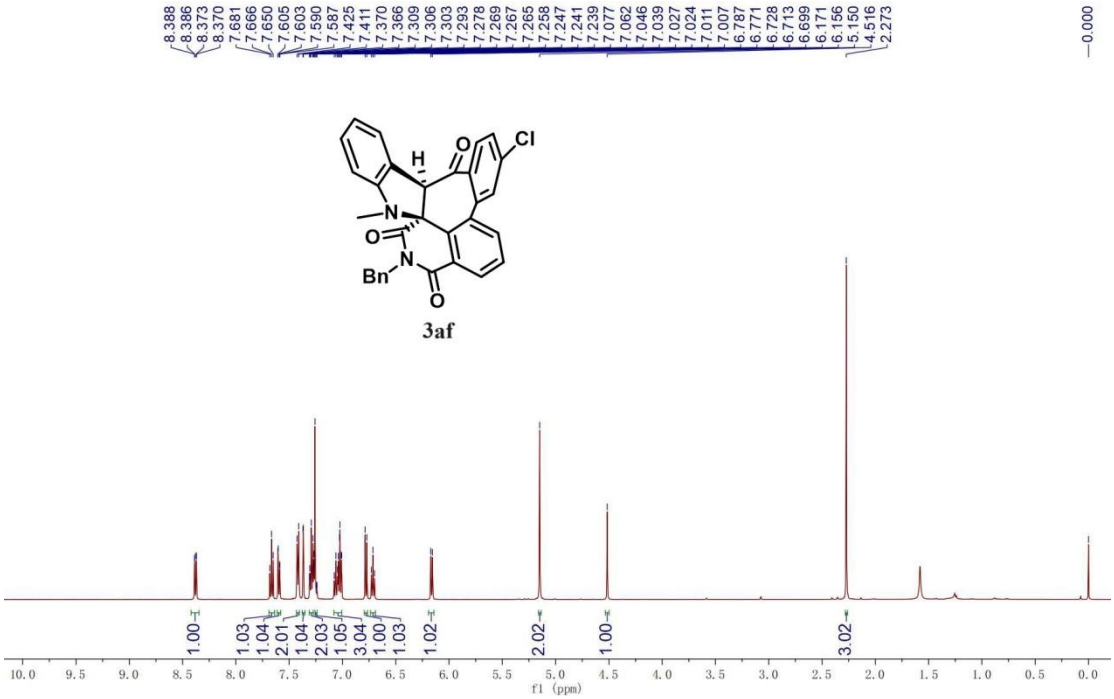


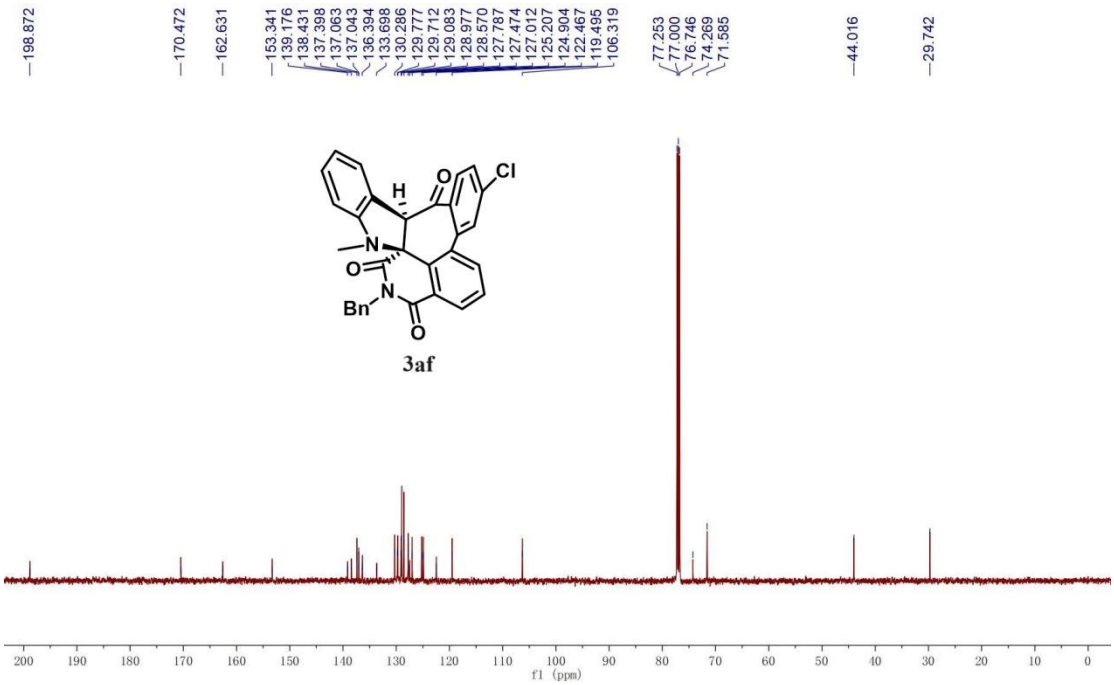



-108.246
F
O
H
N
O
N
Bn
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

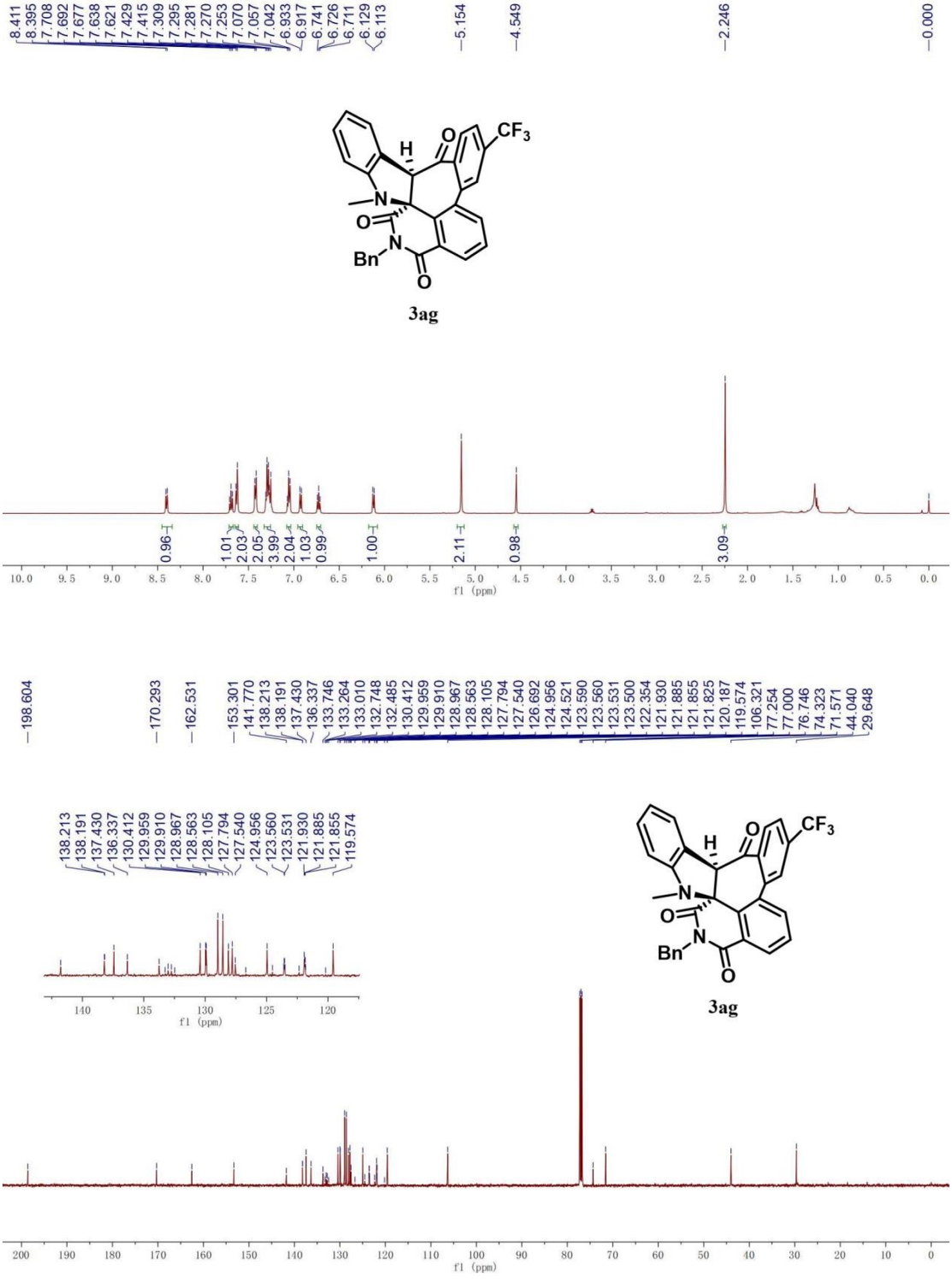
3ae

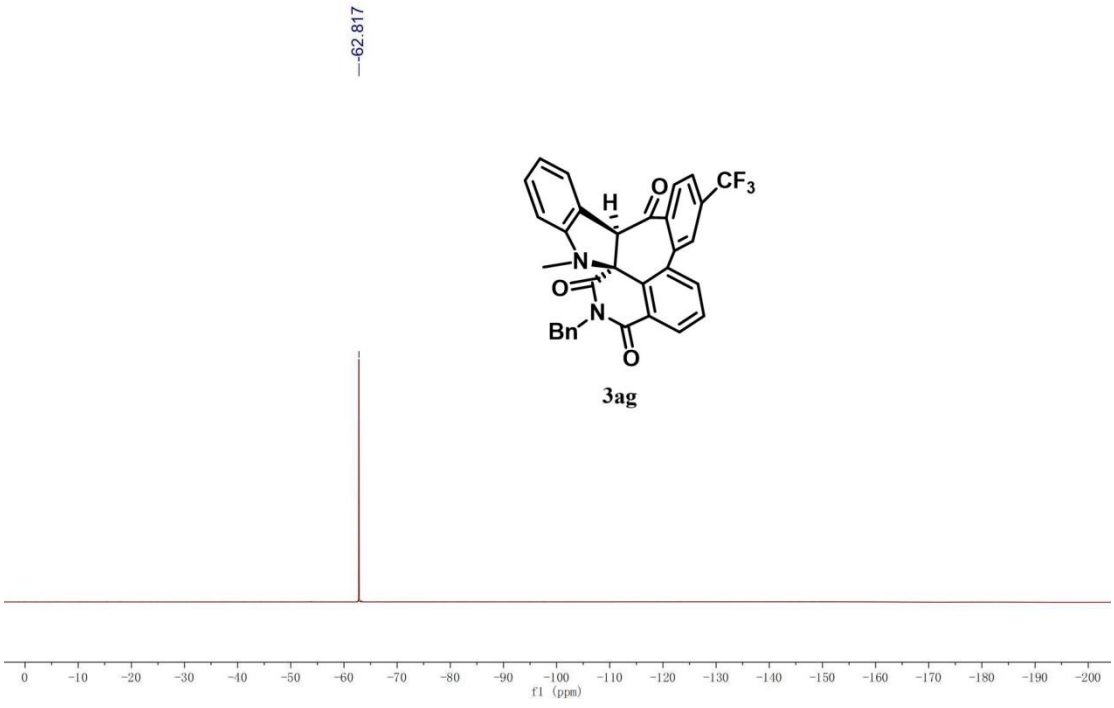
^{1}H NMR of **3af** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3af** (125 MHz, $CDCl_3$)





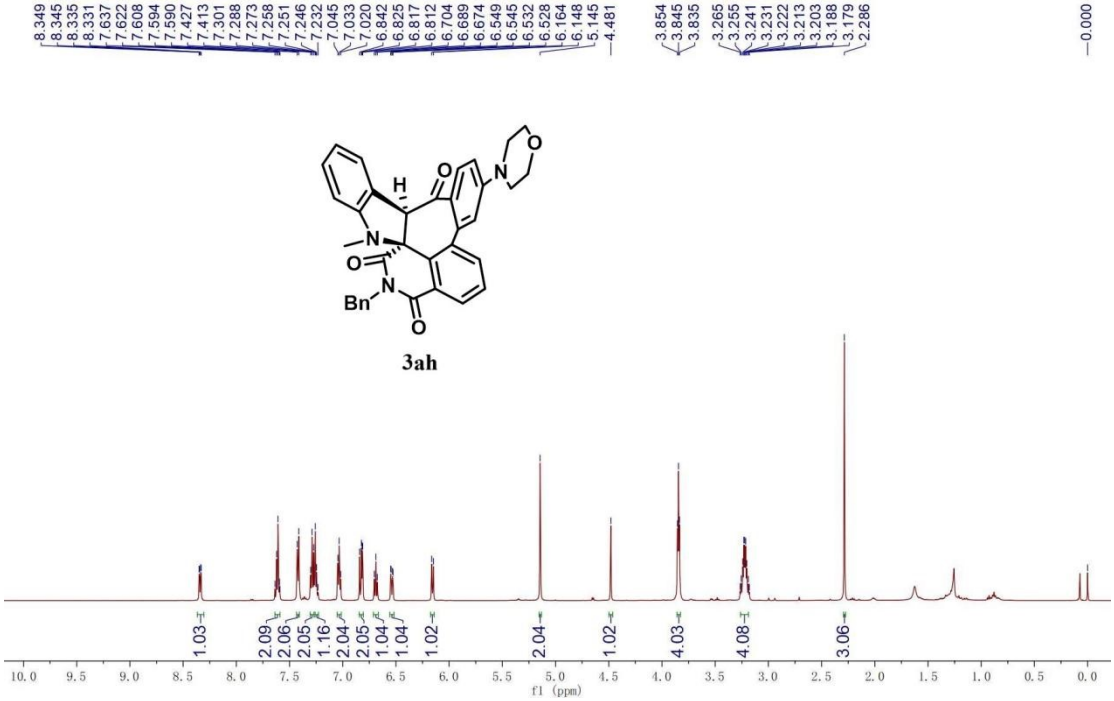
^{1}H NMR of **3ag** (500 MHz, $CDCl_3$), ^{13}C NMR of **3ag** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3ag** (471 MHz, $CDCl_3$)

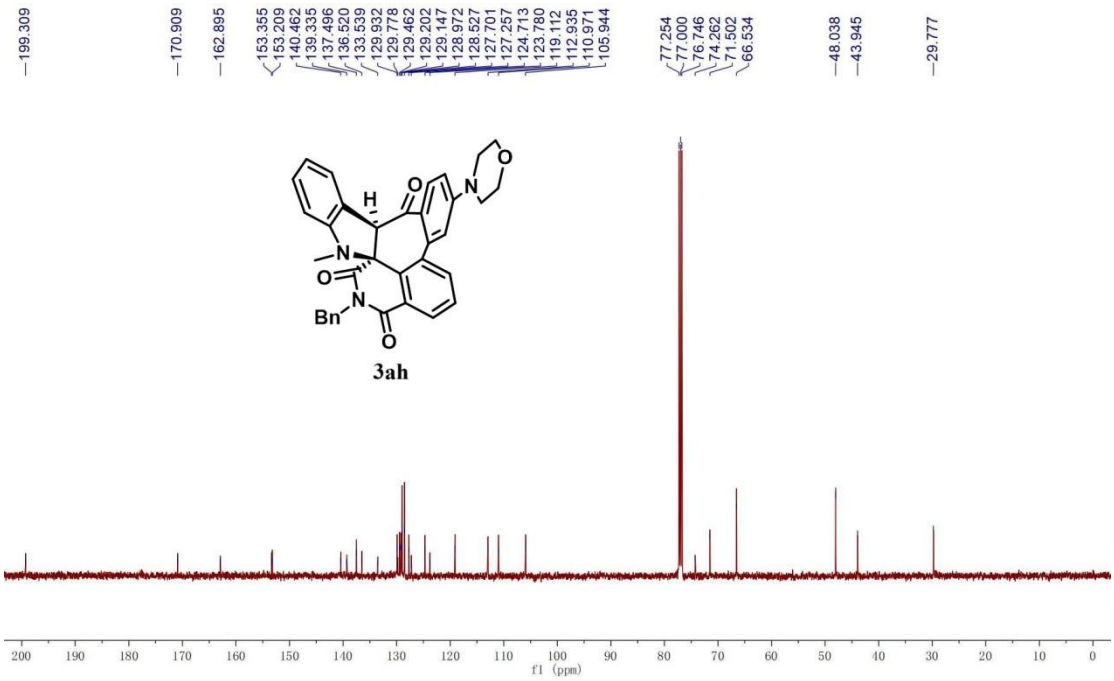



-62.817
H
O
CF3
N
O
N
Bn
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

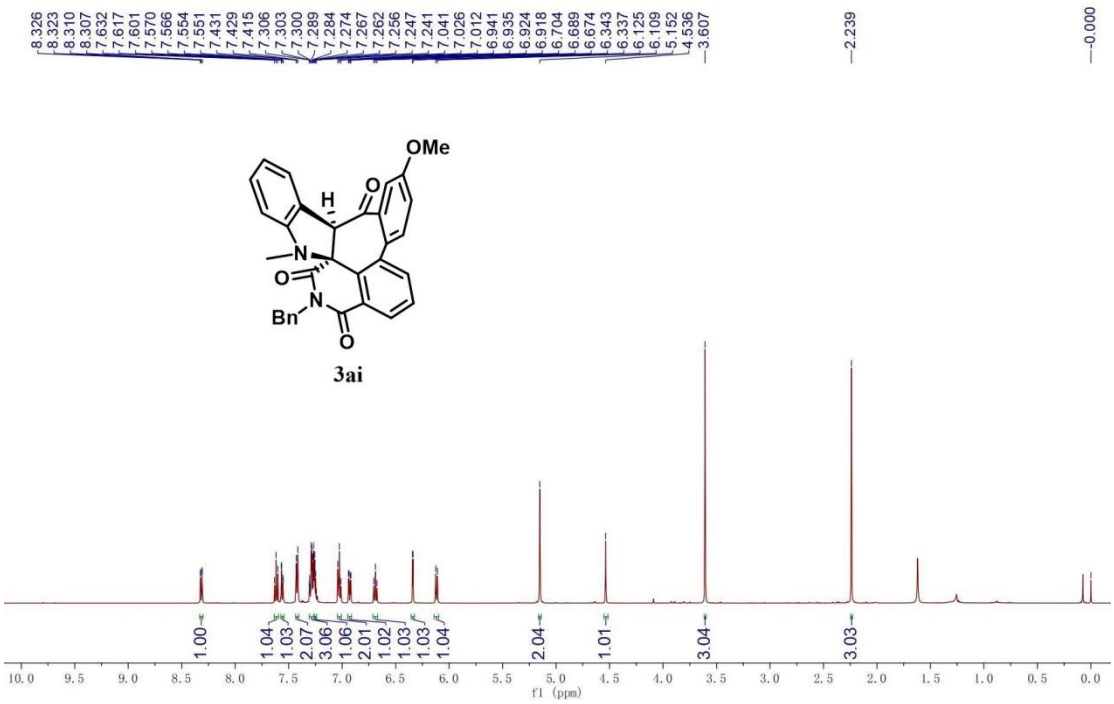
3ag

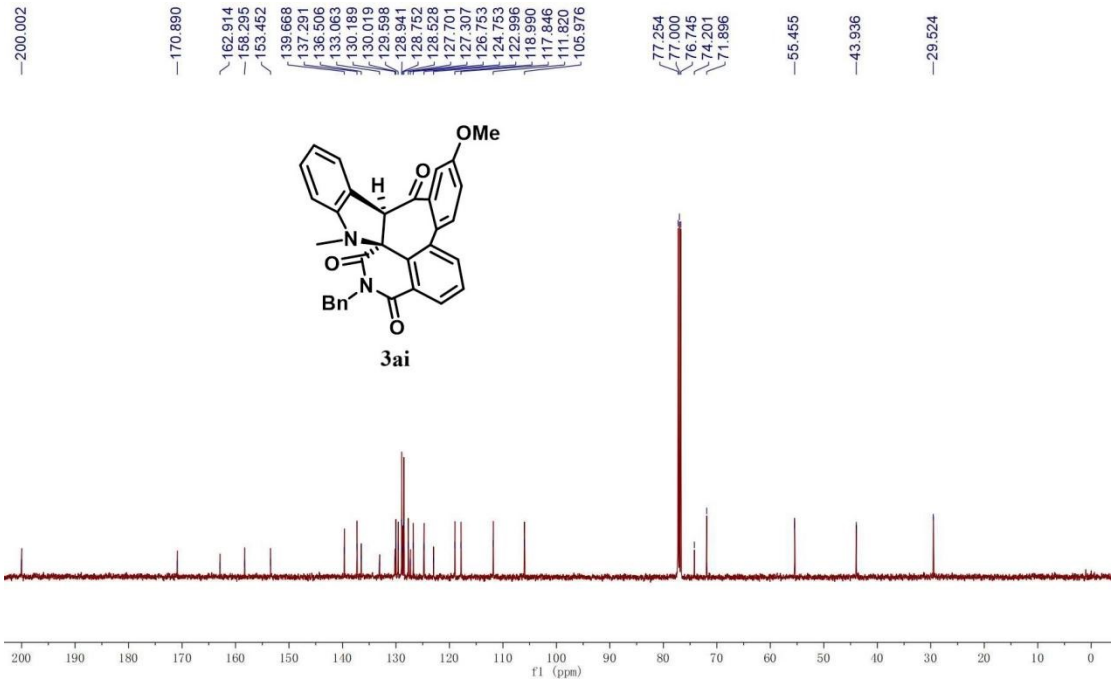
^{1}H NMR of **3ah** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ah** (125 MHz, $CDCl_3$)



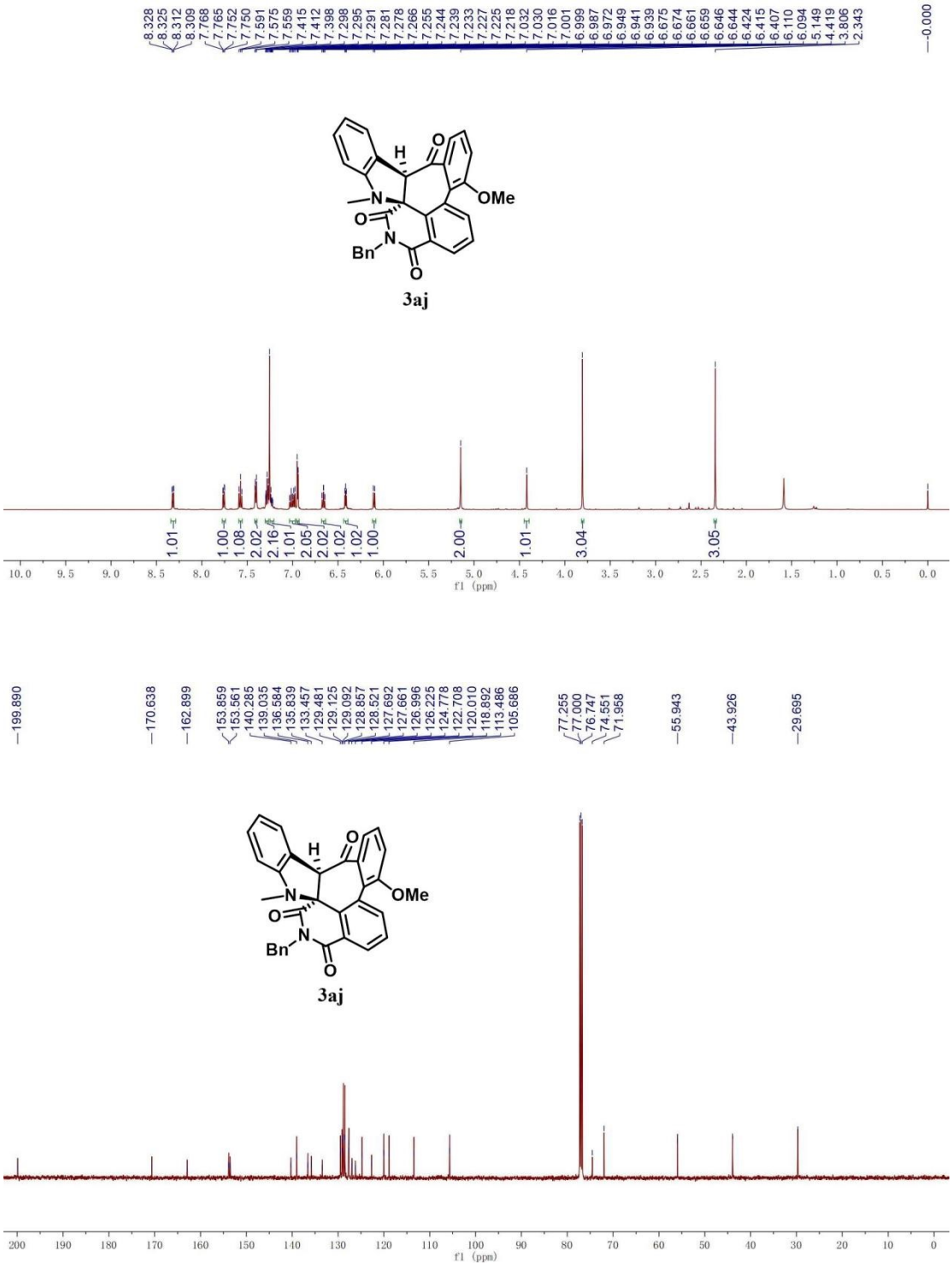


^{1}H NMR of **3ai** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ai** (125 MHz, $CDCl_3$)

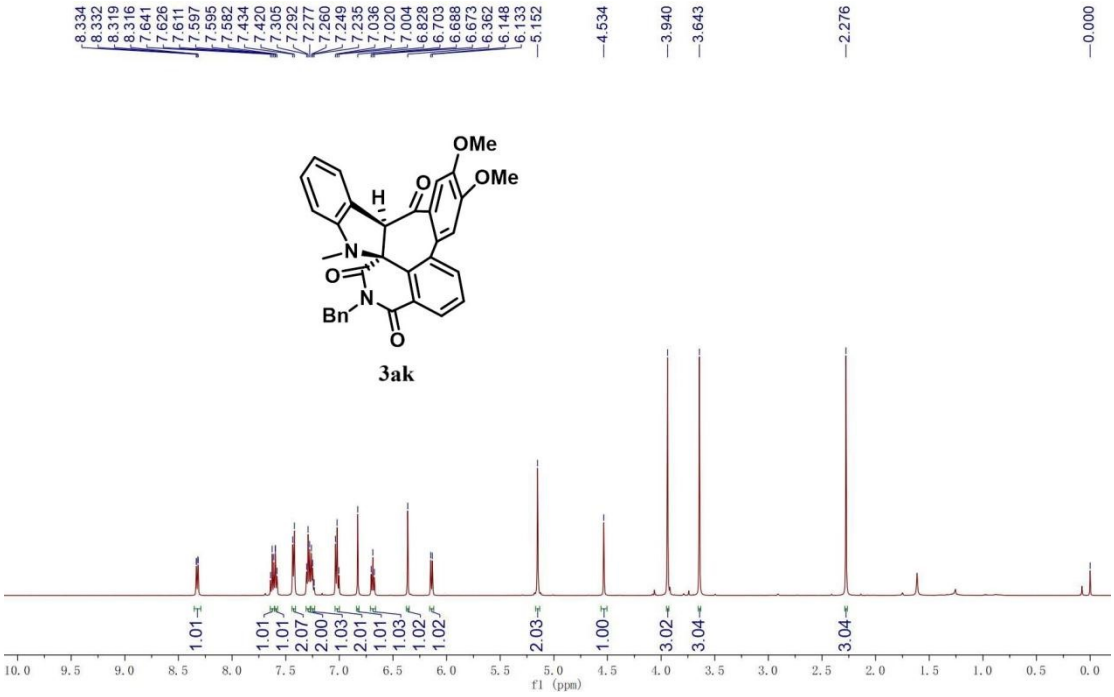


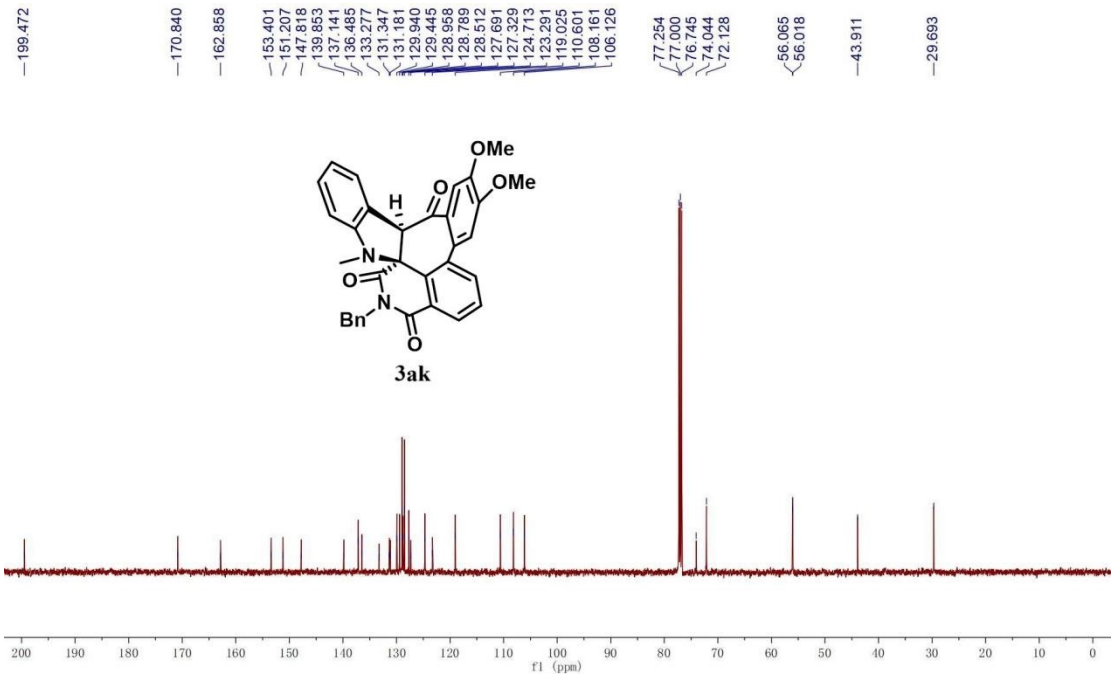


^{1}H NMR of **3aj** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aj** (125 MHz, $CDCl_3$)

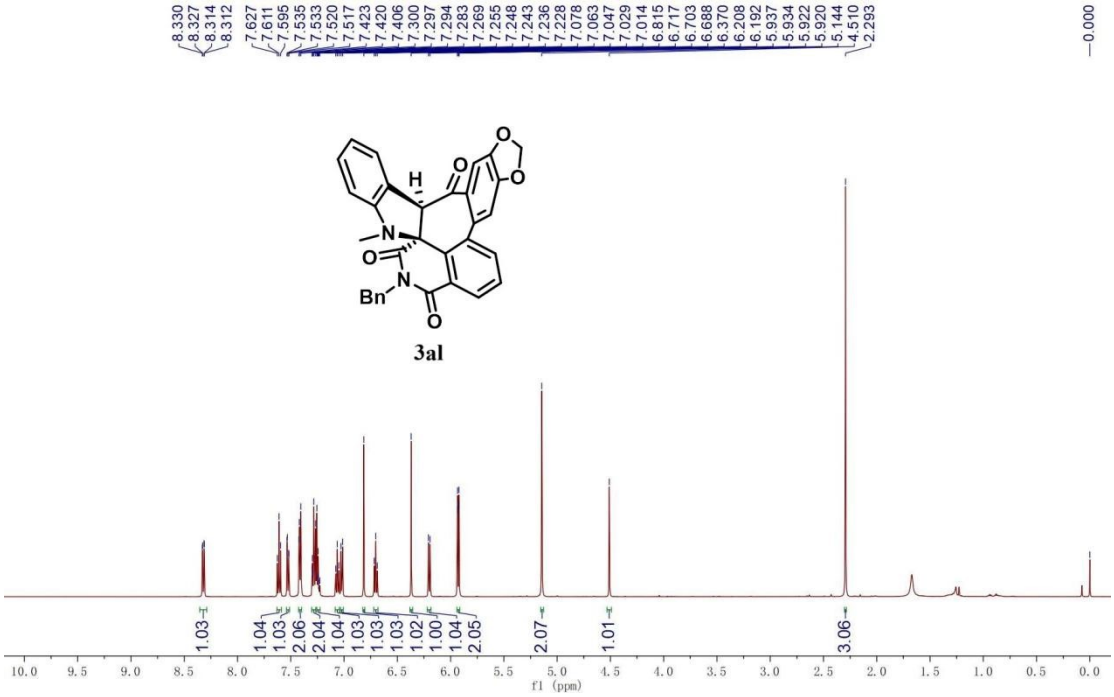


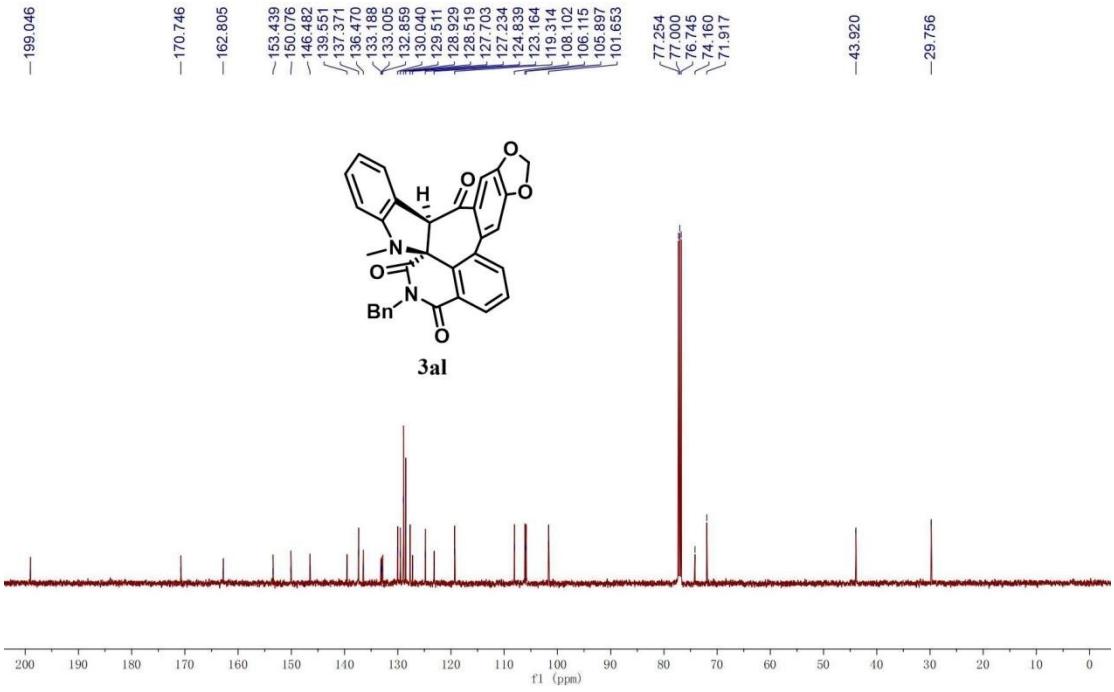
^{1}H NMR of **3ak** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ak** (125 MHz, $CDCl_3$)



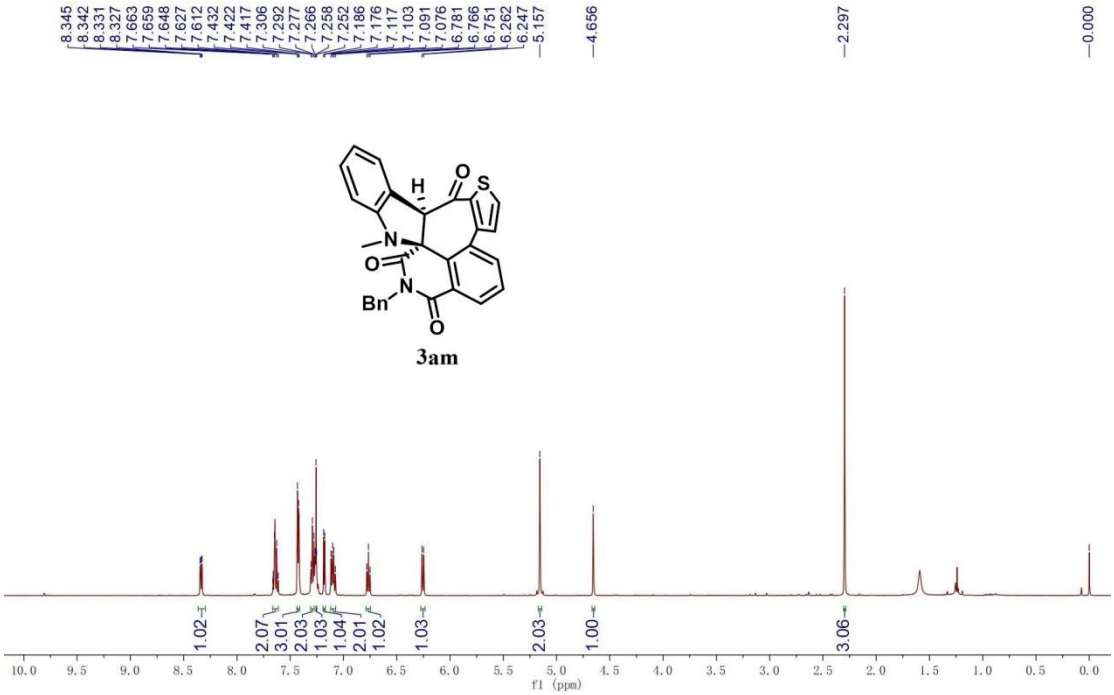


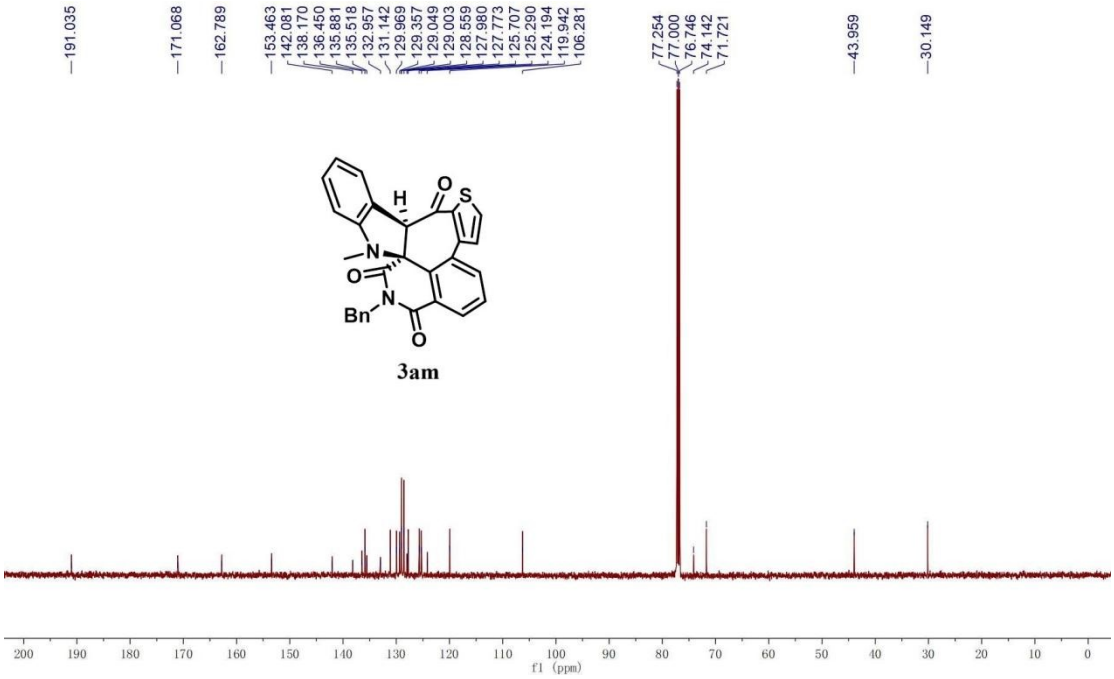
^{1}H NMR of **3al** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3al** (125 MHz, $CDCl_3$)



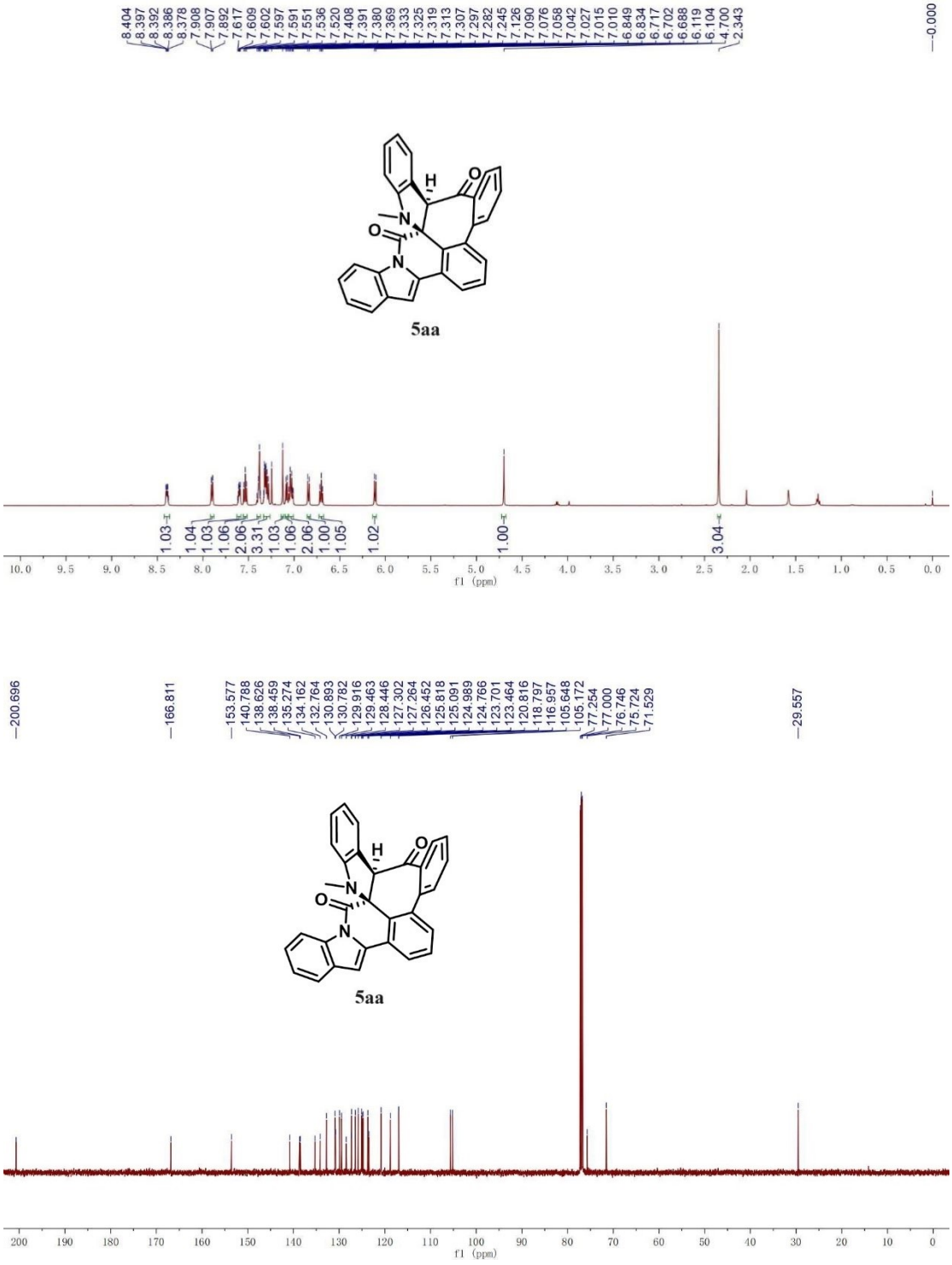


^{1}H NMR of **3am** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3am** (125 MHz, $CDCl_3$)

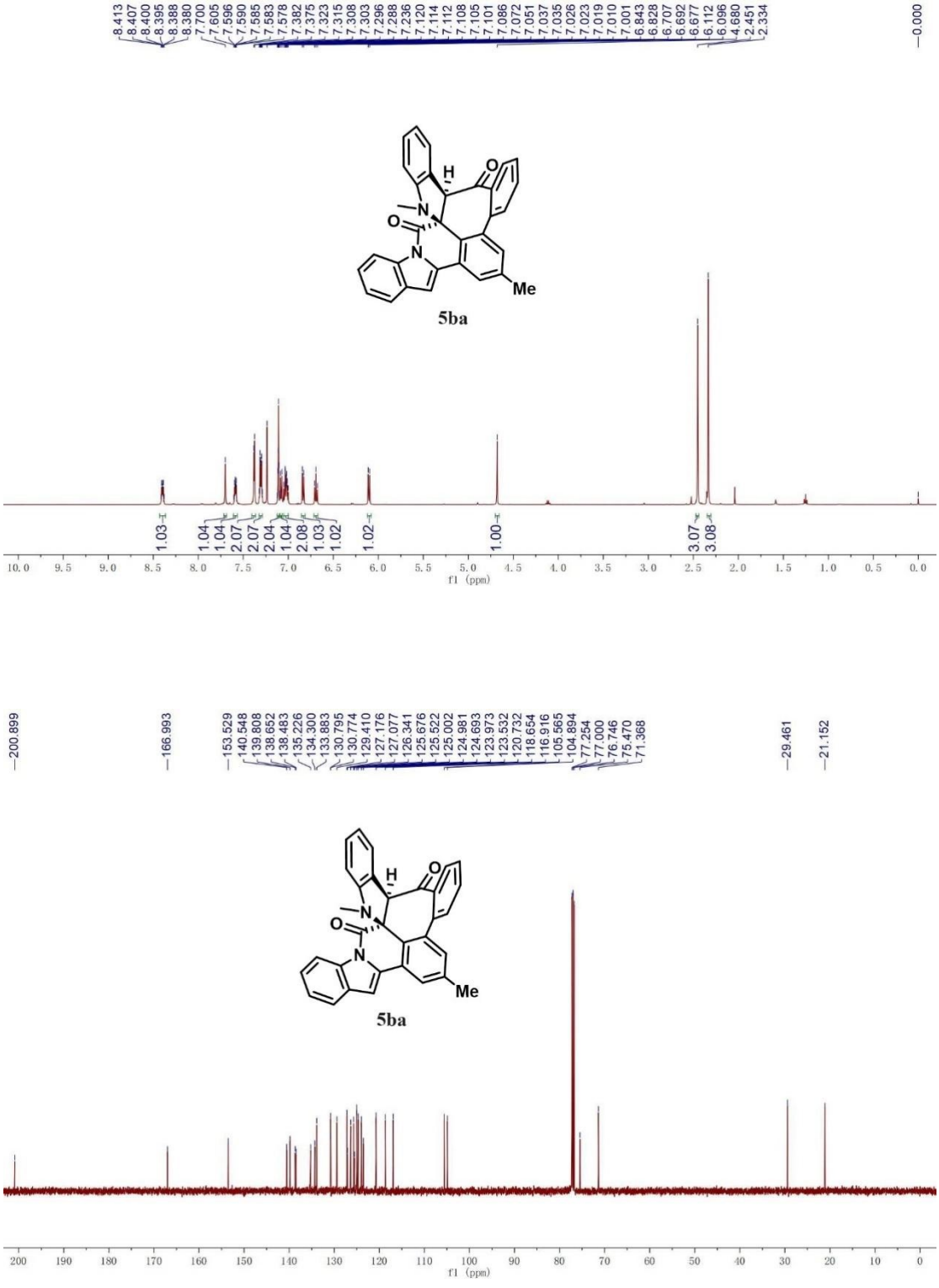




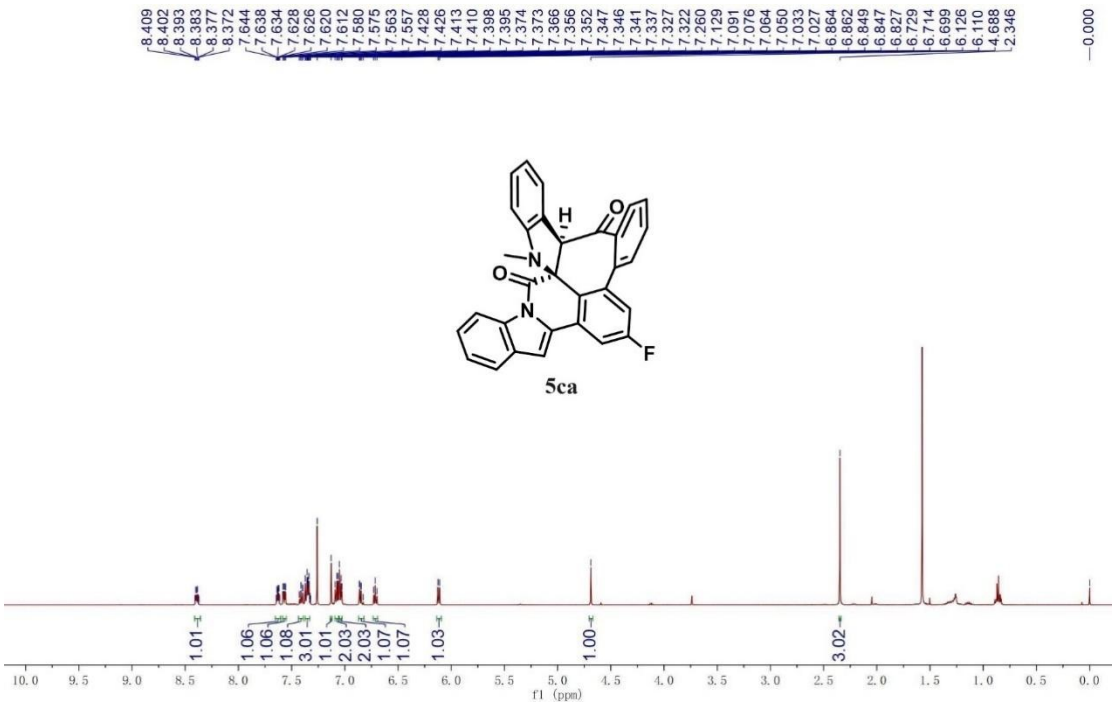
^{1}H NMR of **5aa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5aa** (125 MHz, $CDCl_3$)

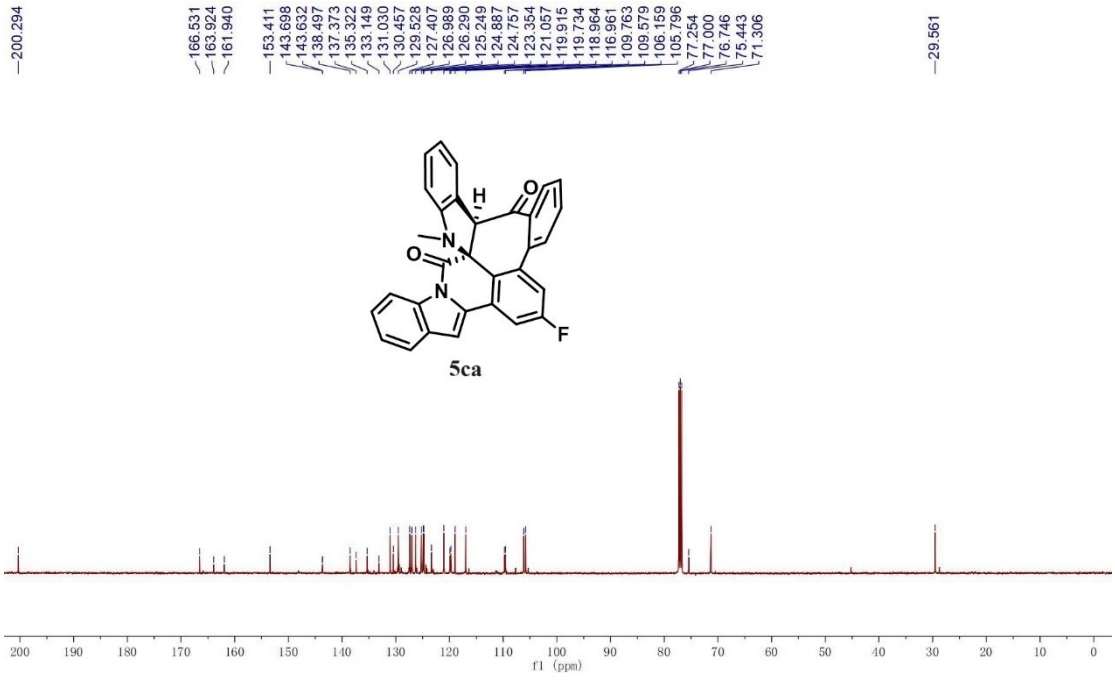


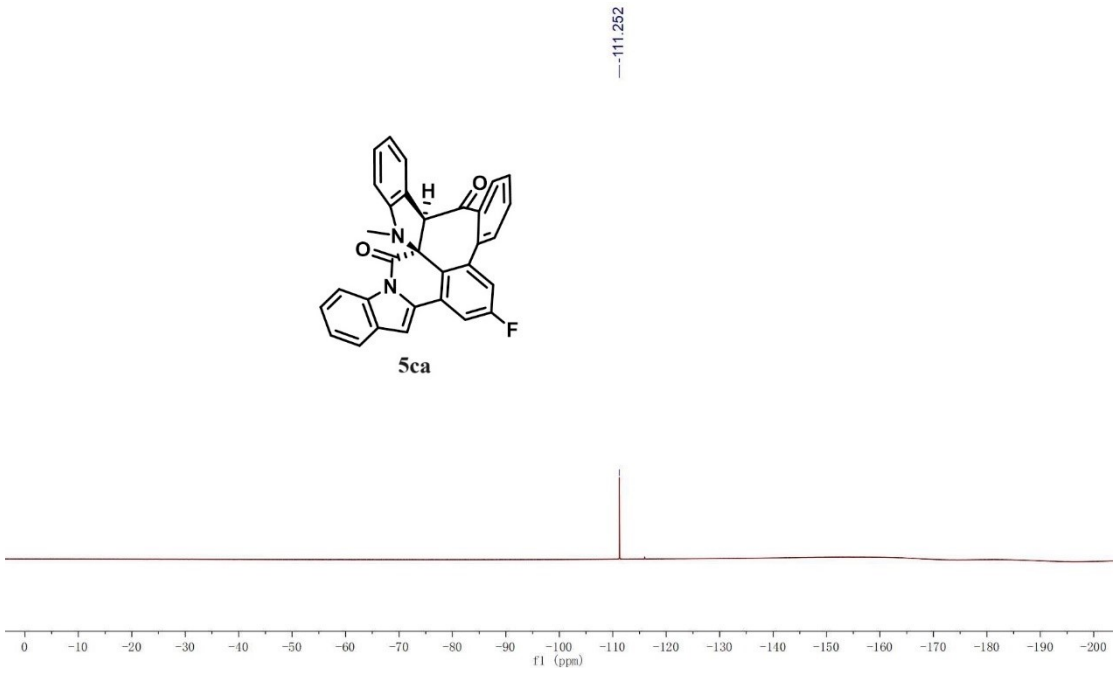
^{1}H NMR of **5ba** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ba** (125 MHz, $CDCl_3$)



^{1}H NMR of **5ca** (500 MHz, $CDCl_3$), ^{13}C NMR of **5ca** (125 MHz, $CDCl_3$) and ^{19}F NMR of **5ca** (471 MHz, $CDCl_3$)

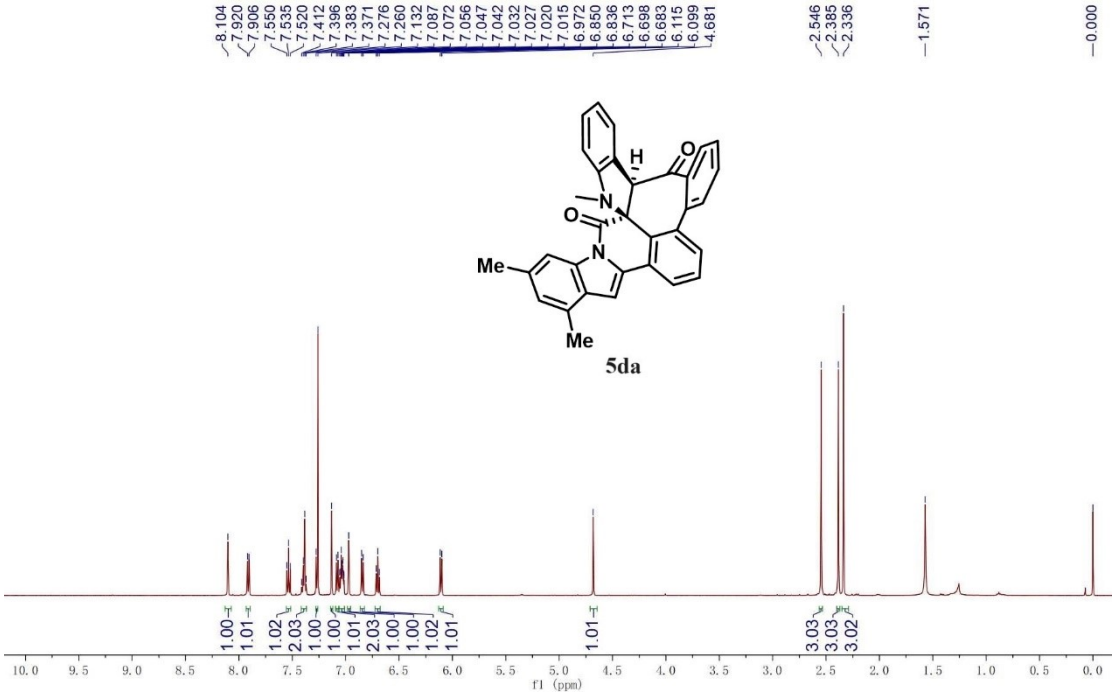


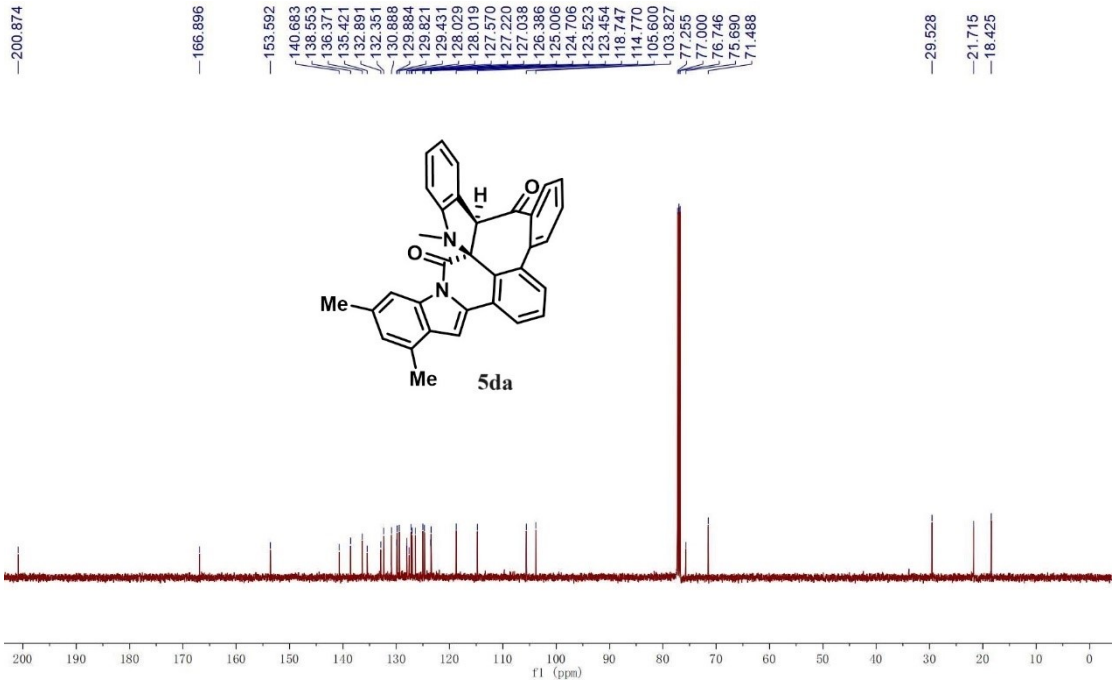



-111.252
H
O
N
O
N
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

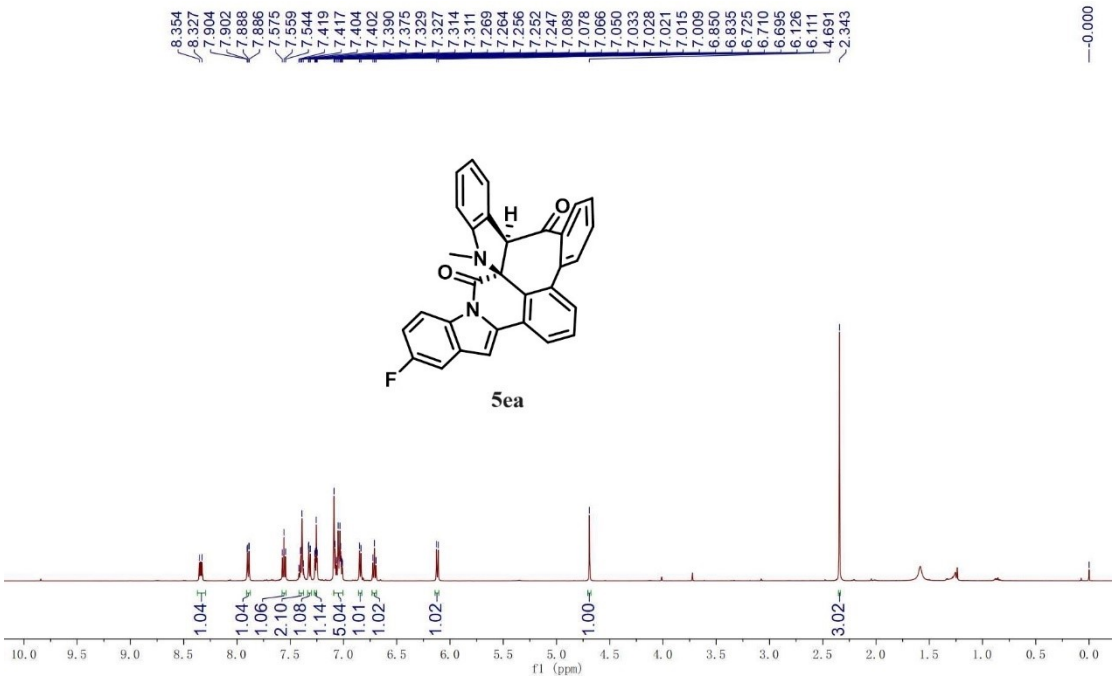
5ca

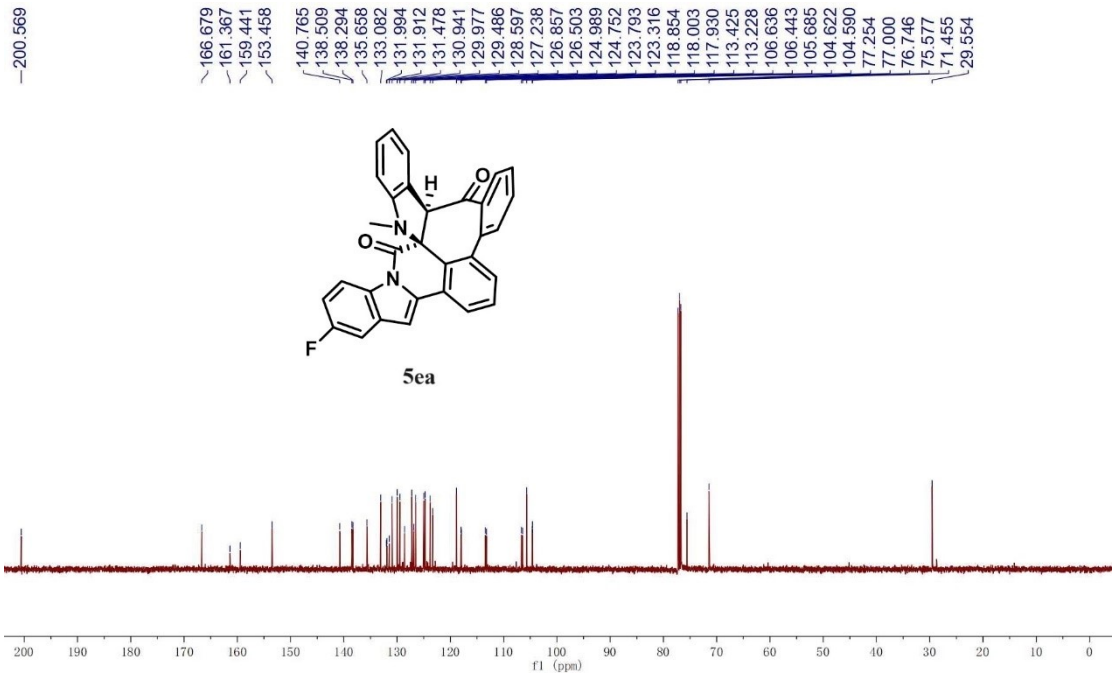
^{1}H NMR of **5da** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5da** (125 MHz, $CDCl_3$)

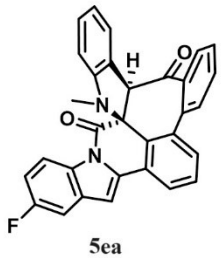




^{1}H NMR of **5ea** (500 MHz, $CDCl_3$), ^{13}C NMR of **5ea** (125 MHz, $CDCl_3$) and ^{19}F NMR of **5ea** (471 MHz, $CDCl_3$)



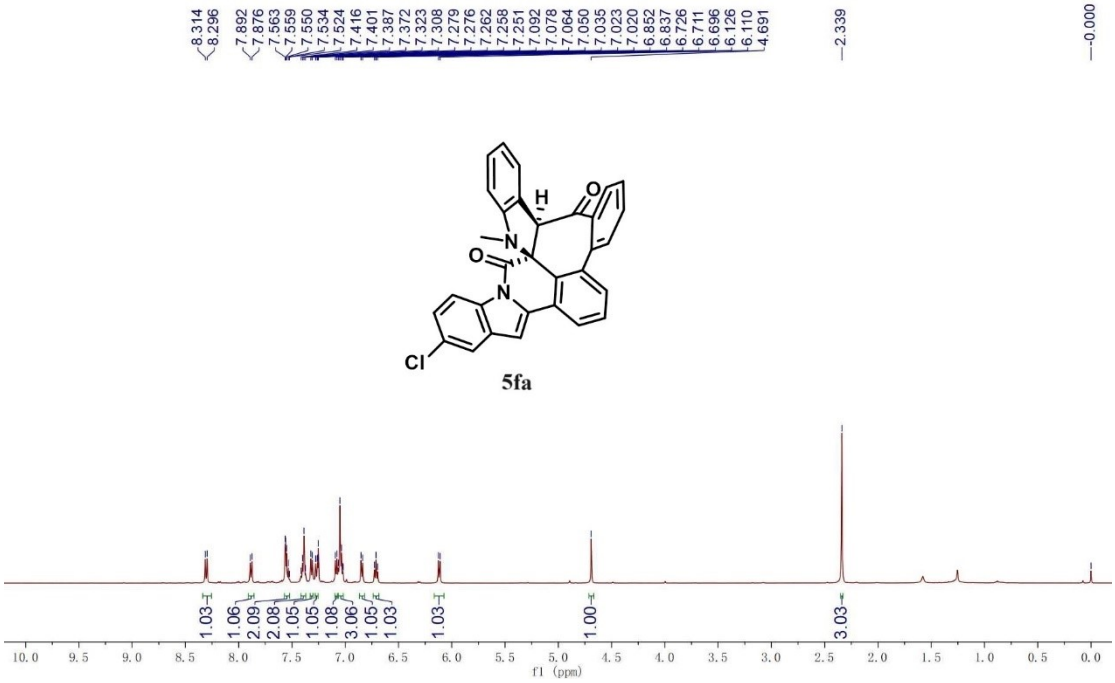


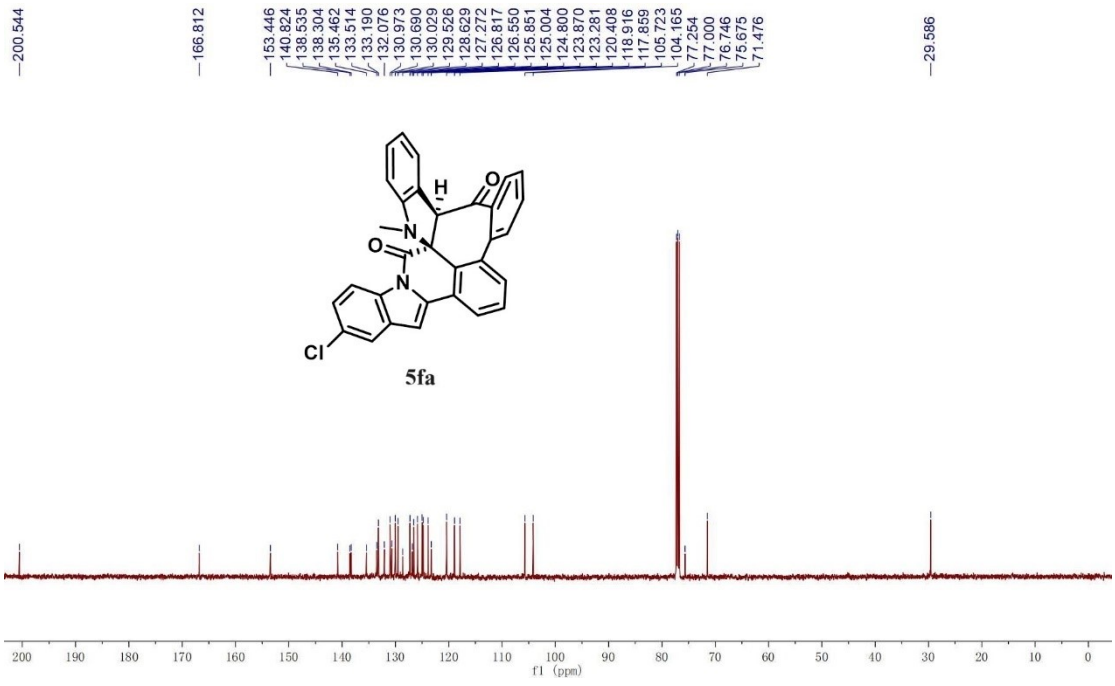

H
O
N
O
N
F

5ea

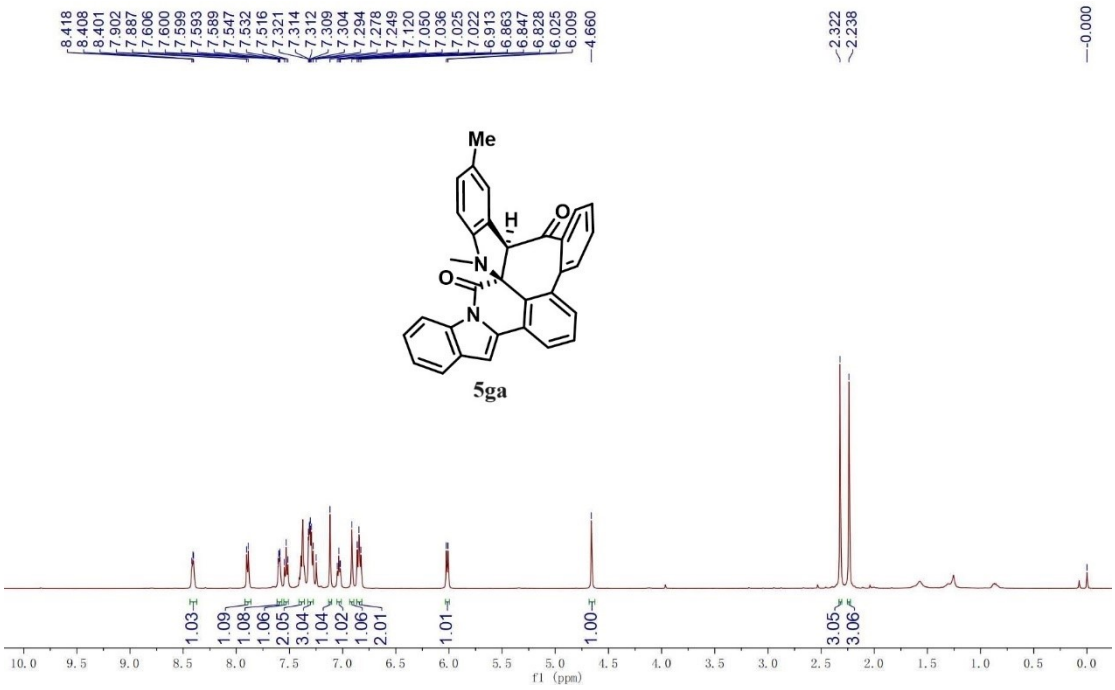
-116.991
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

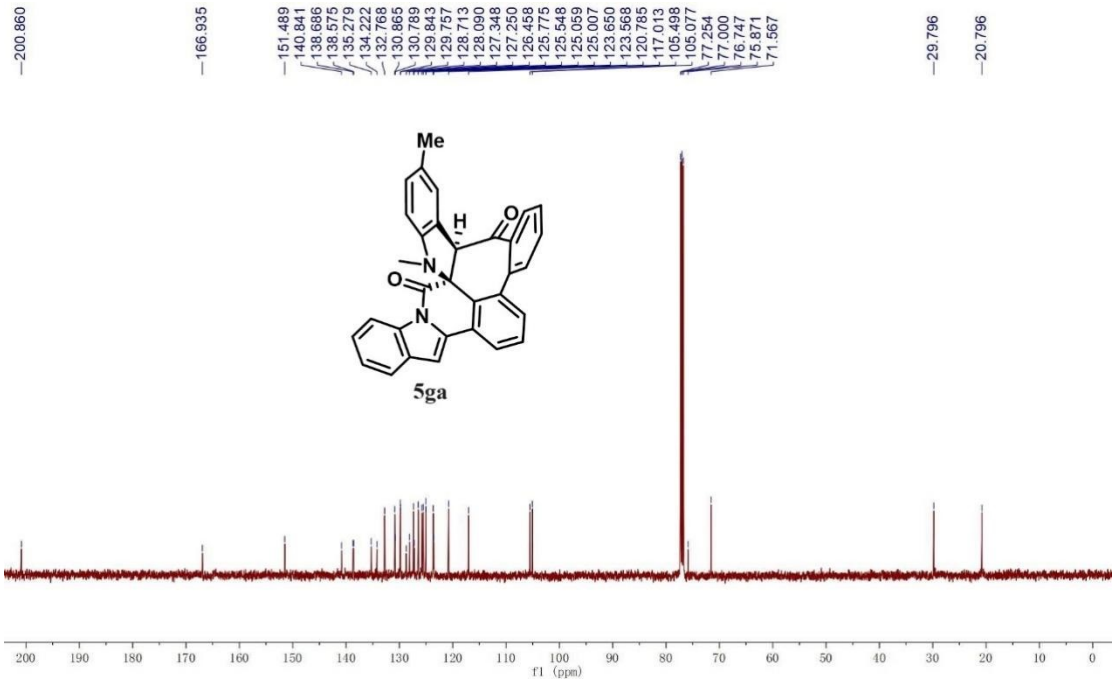
^{1}H NMR of **5fa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5fa** (125 MHz, $CDCl_3$)



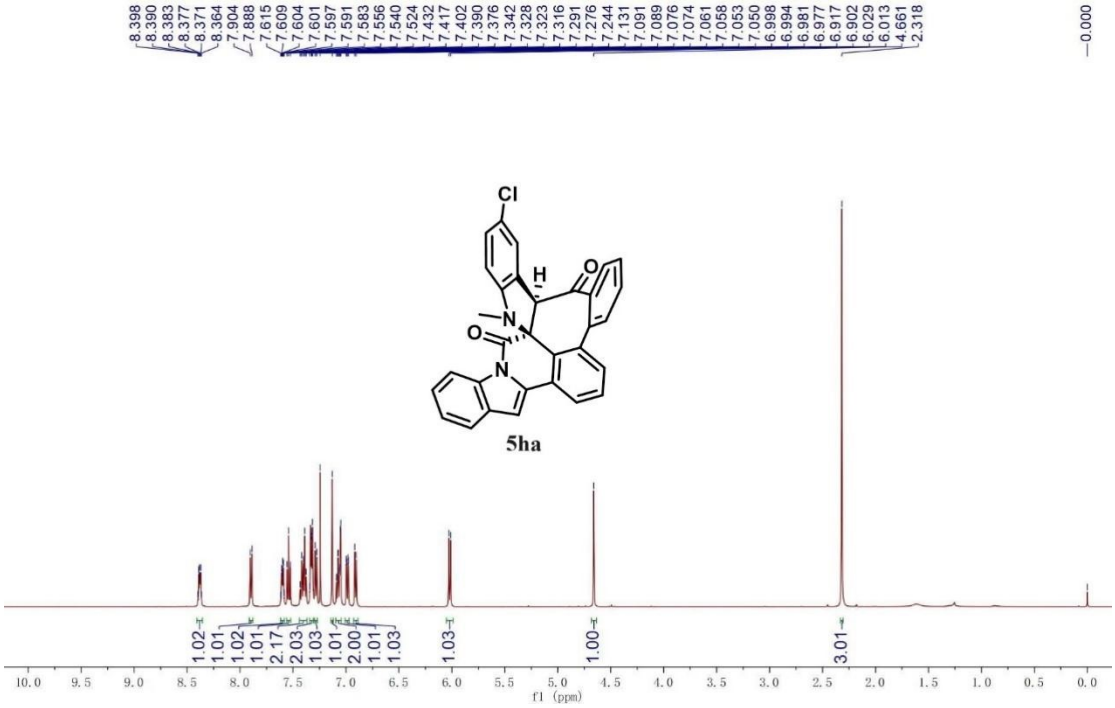


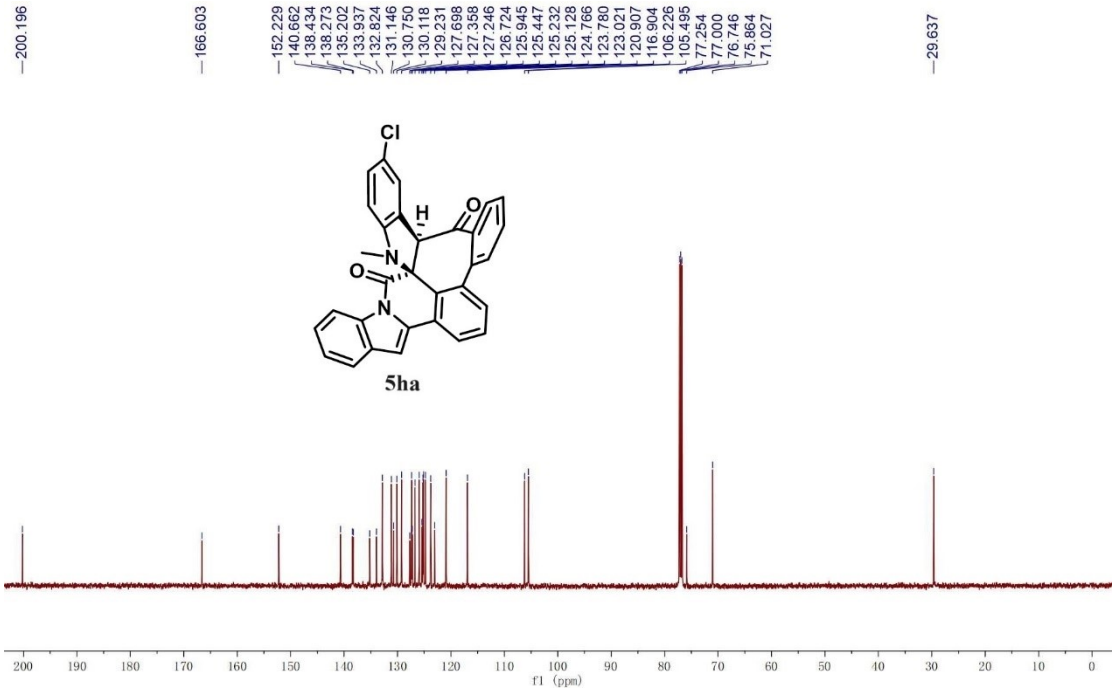
^{1}H NMR of **5ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ga** (125 MHz, $CDCl_3$)



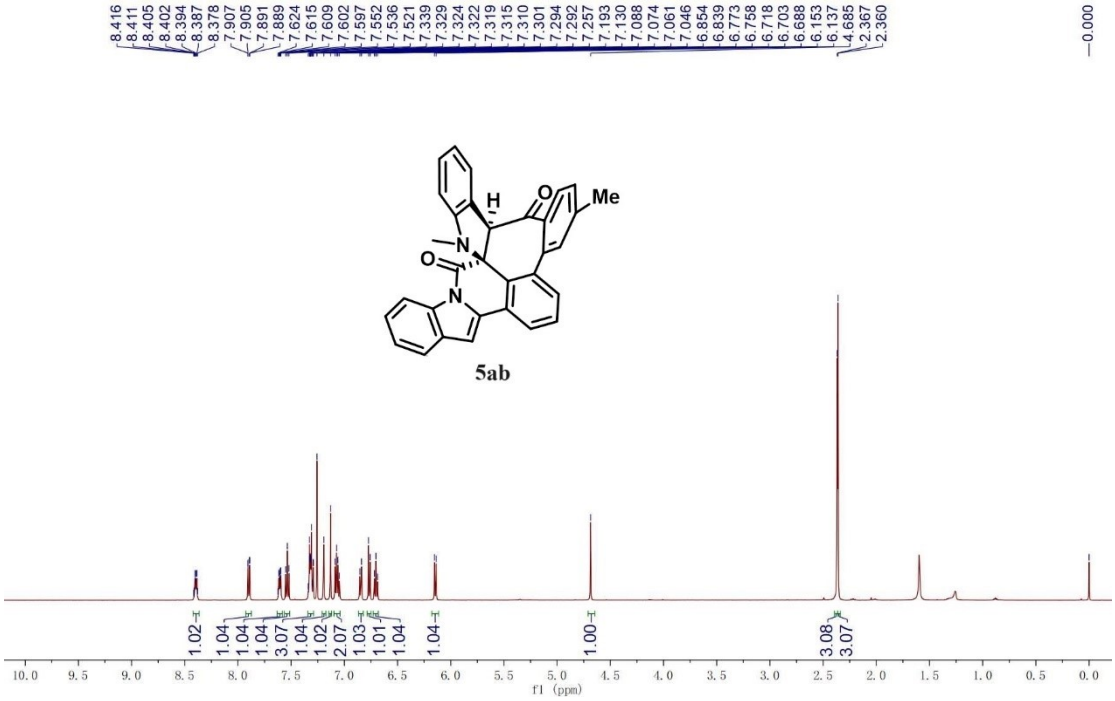


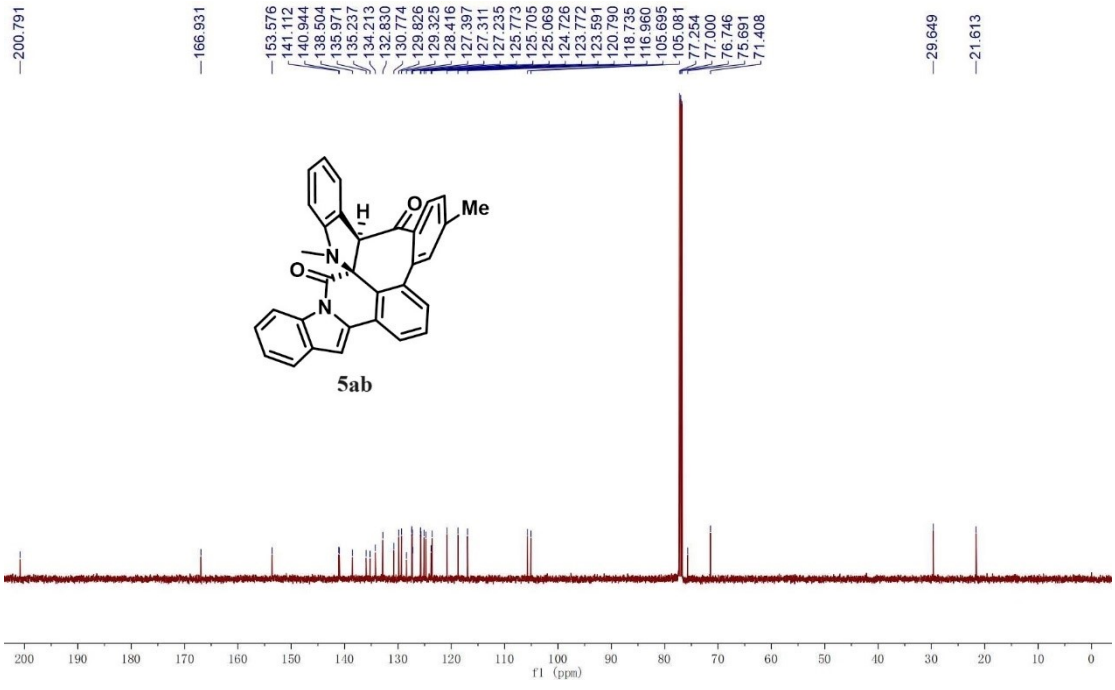
^{1}H NMR of **5ha** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ha** (125 MHz, $CDCl_3$)



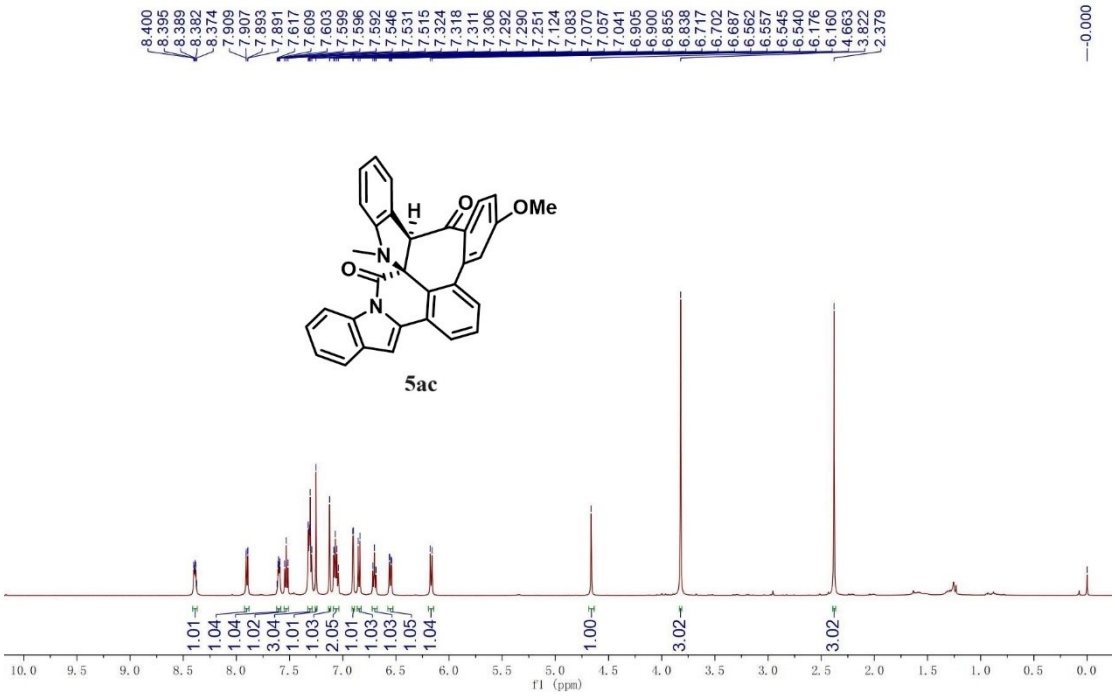


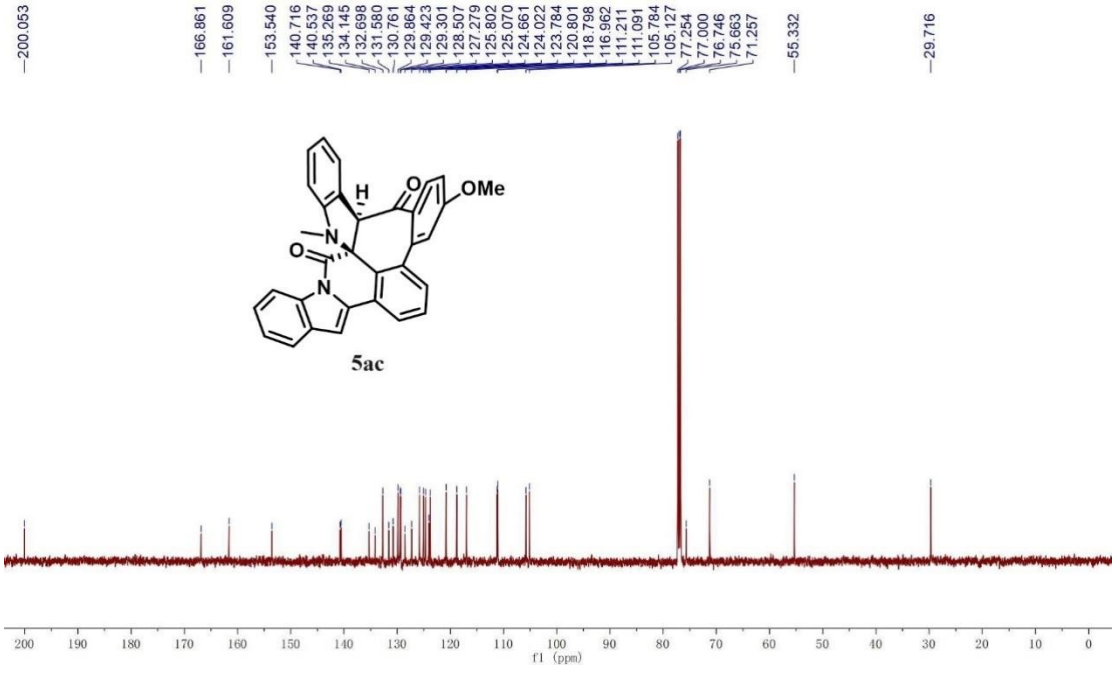
^{1}H NMR of **5ab** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ab** (125 MHz, $CDCl_3$)



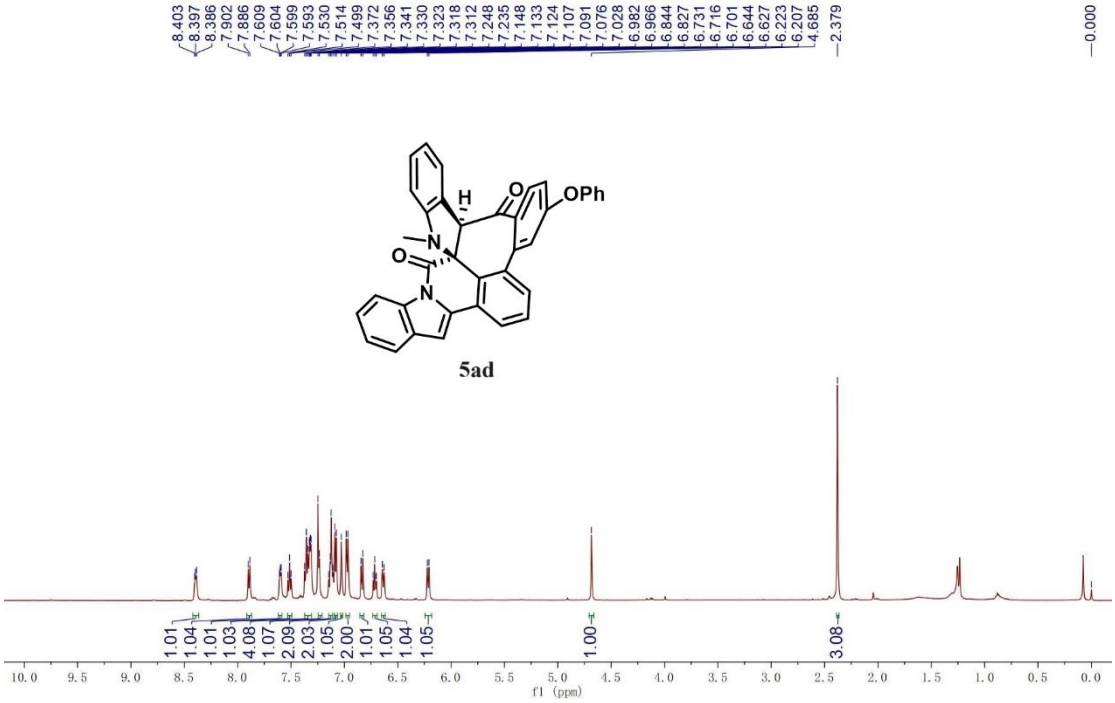


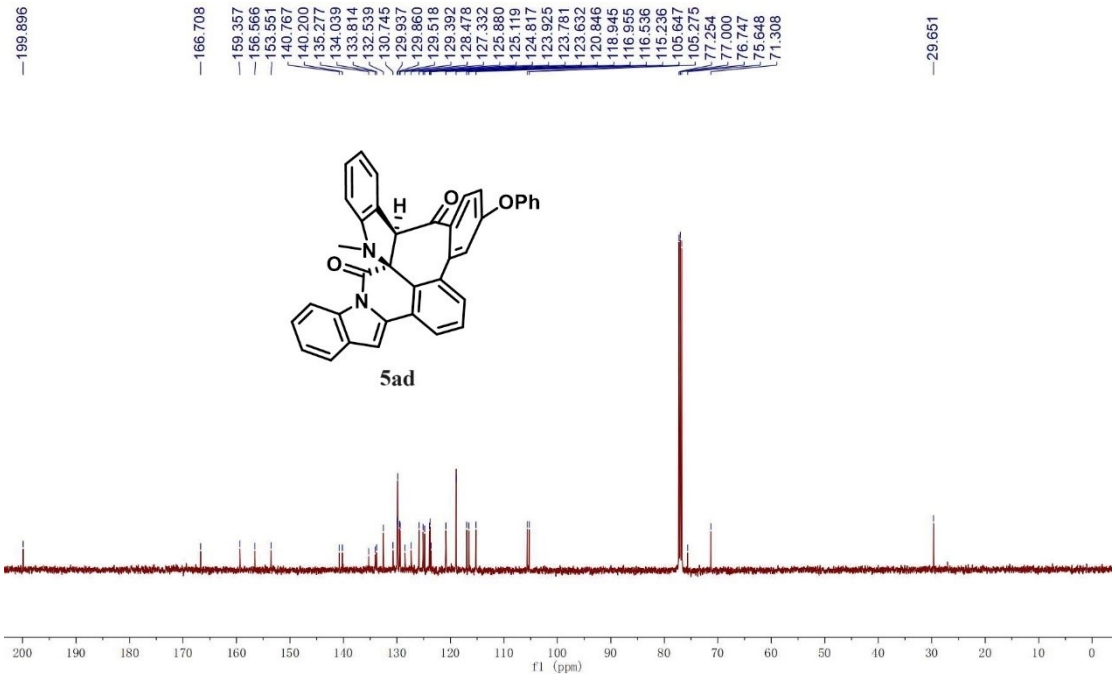
^{1}H NMR of **5ac** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ac** (125 MHz, $CDCl_3$)



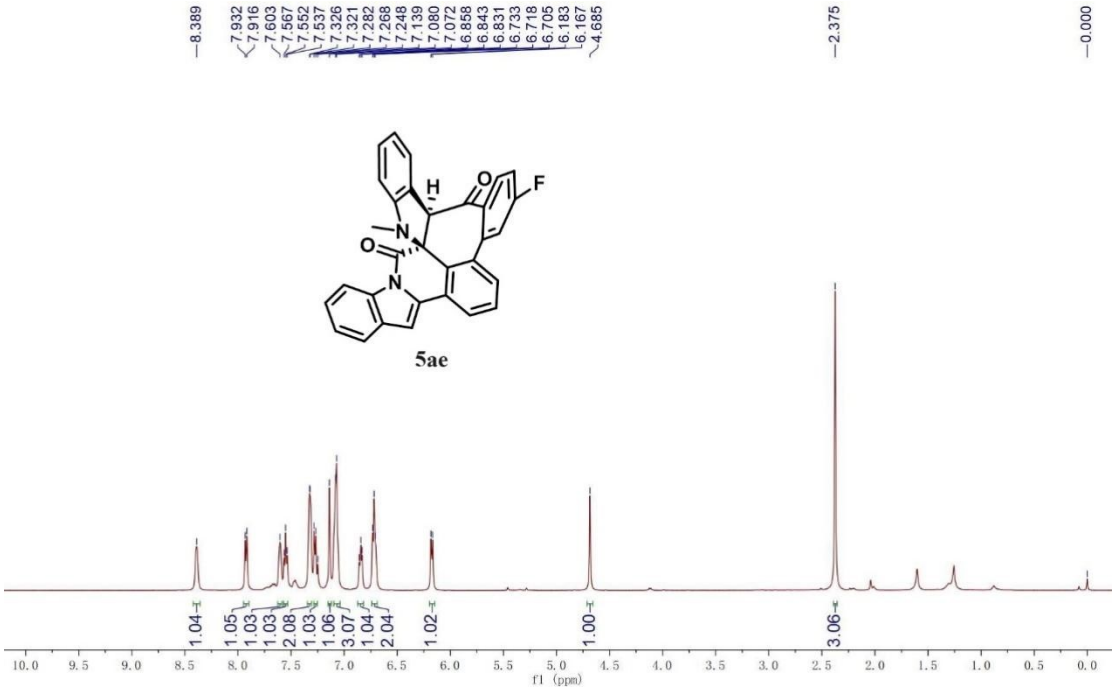


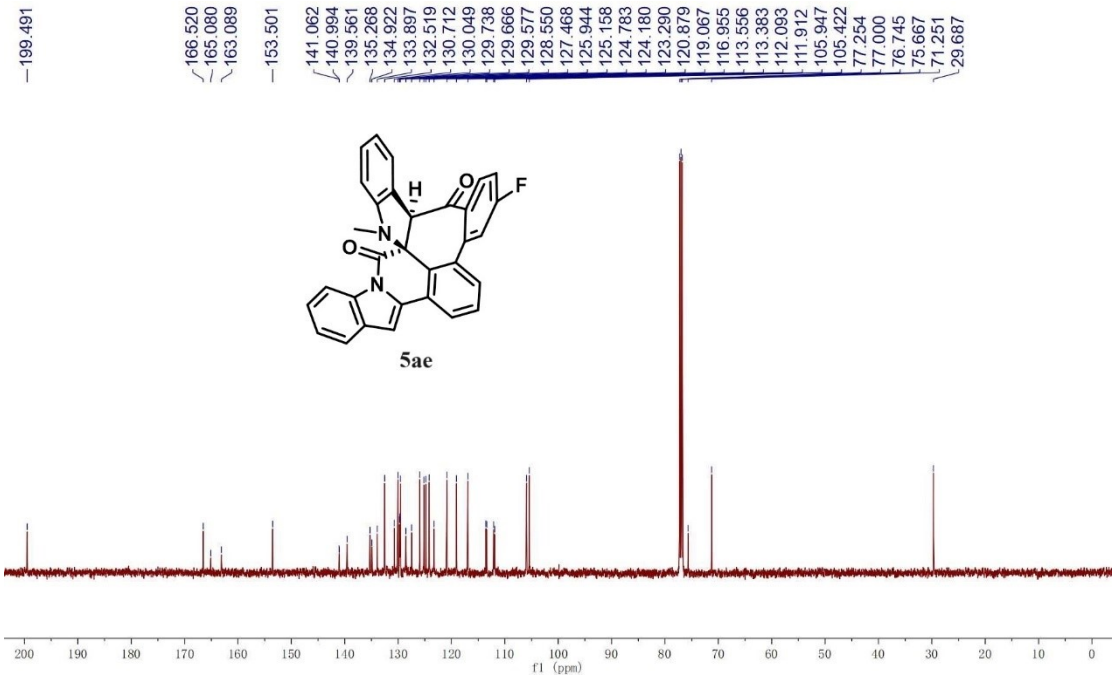
^{1}H NMR of **5ad** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ad** (125 MHz, $CDCl_3$)

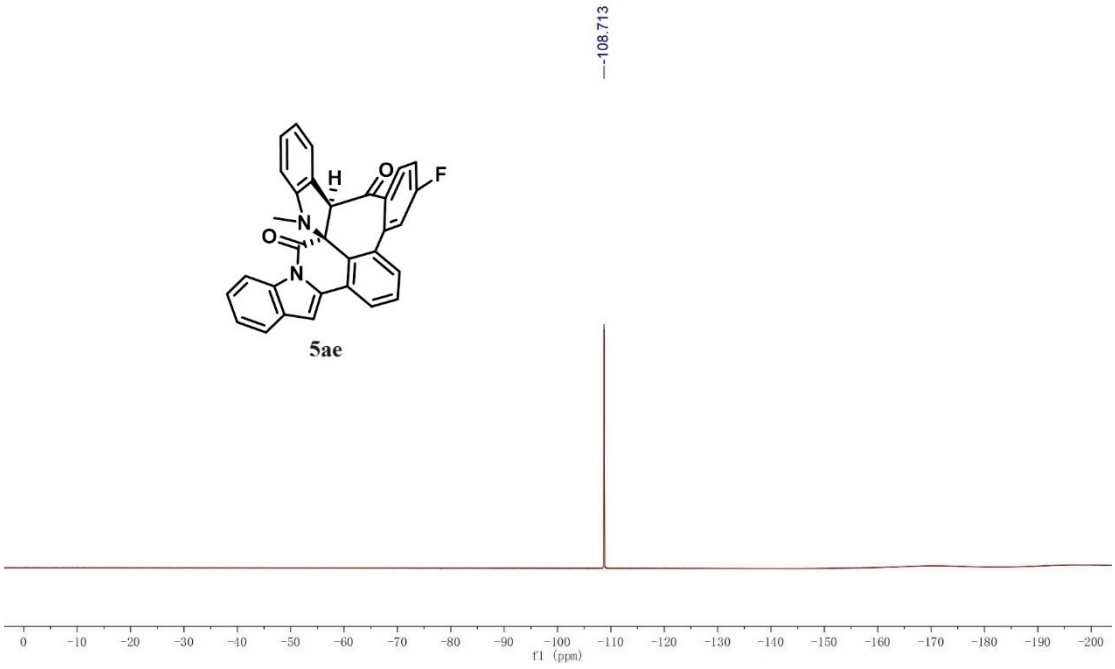




^{1}H NMR of **5ae** (500 MHz, $CDCl_3$), ^{13}C NMR of **5ae** (125 MHz, $CDCl_3$) and ^{19}F NMR of **5ae** (471 MHz, $CDCl_3$)

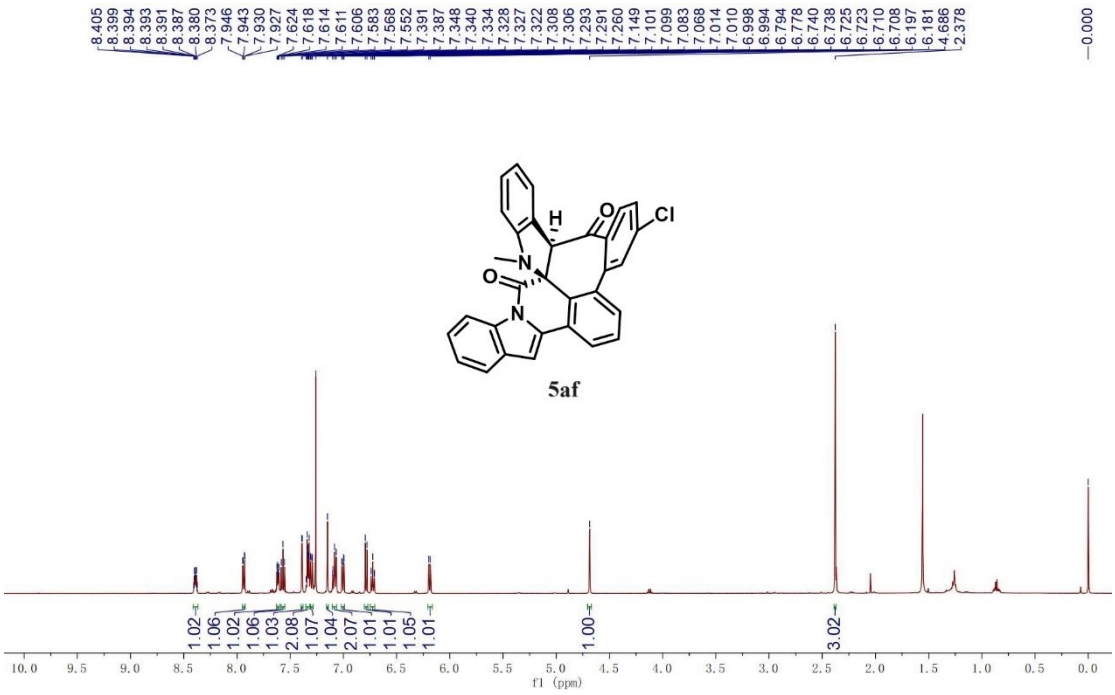


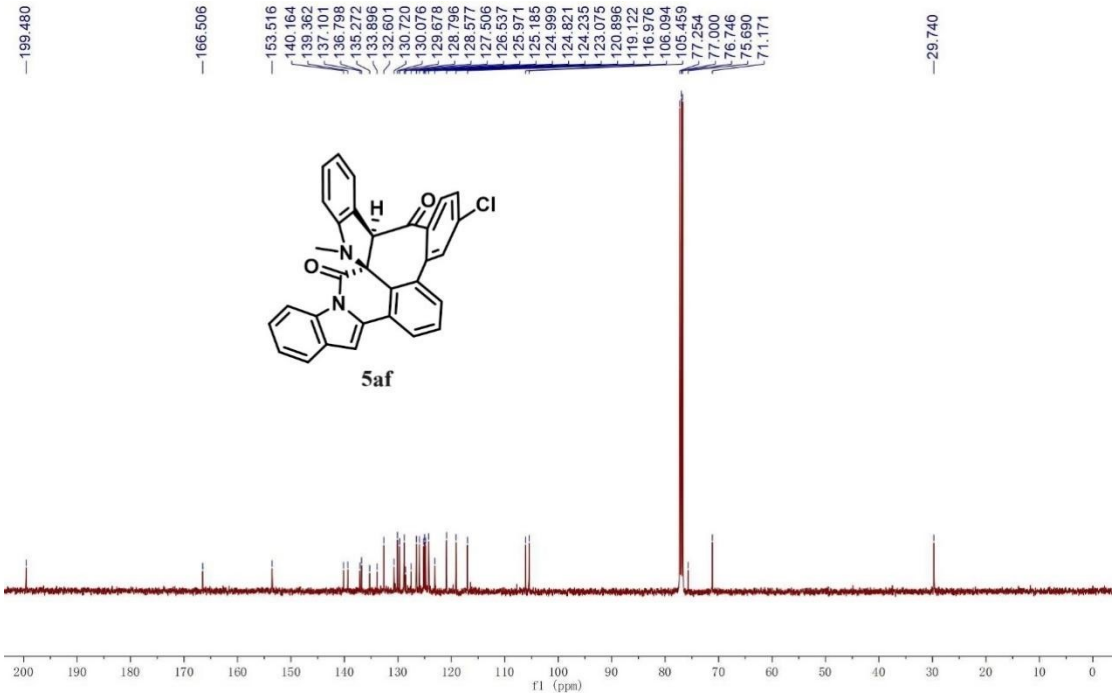



-108.713
H
O
F
N
O
N
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

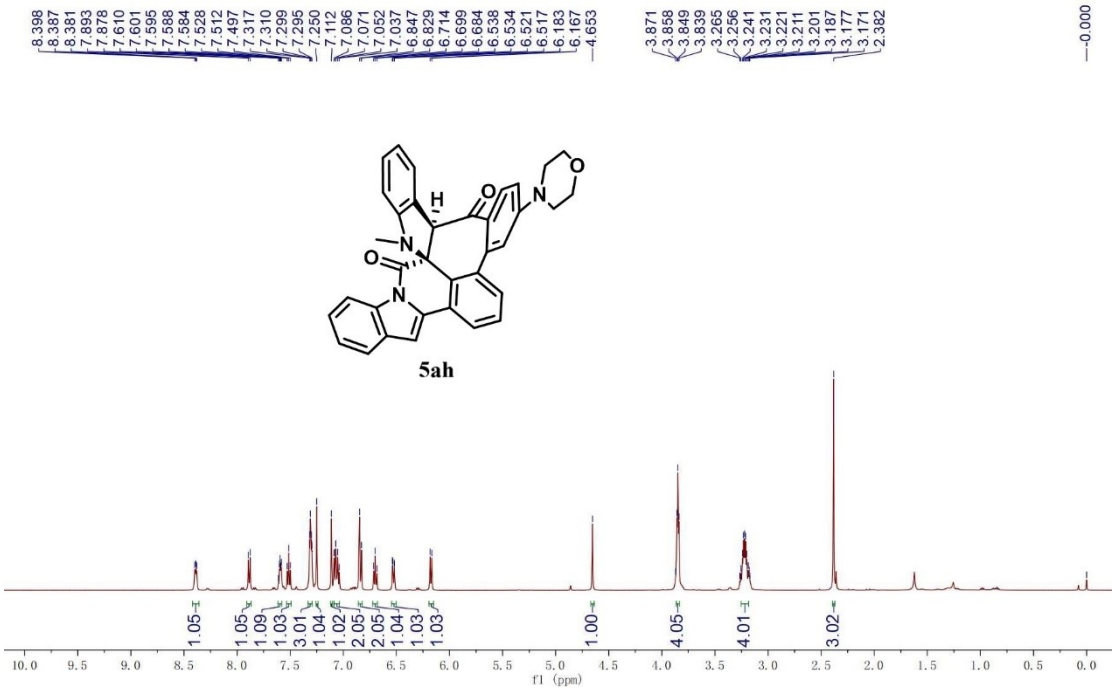
5ae

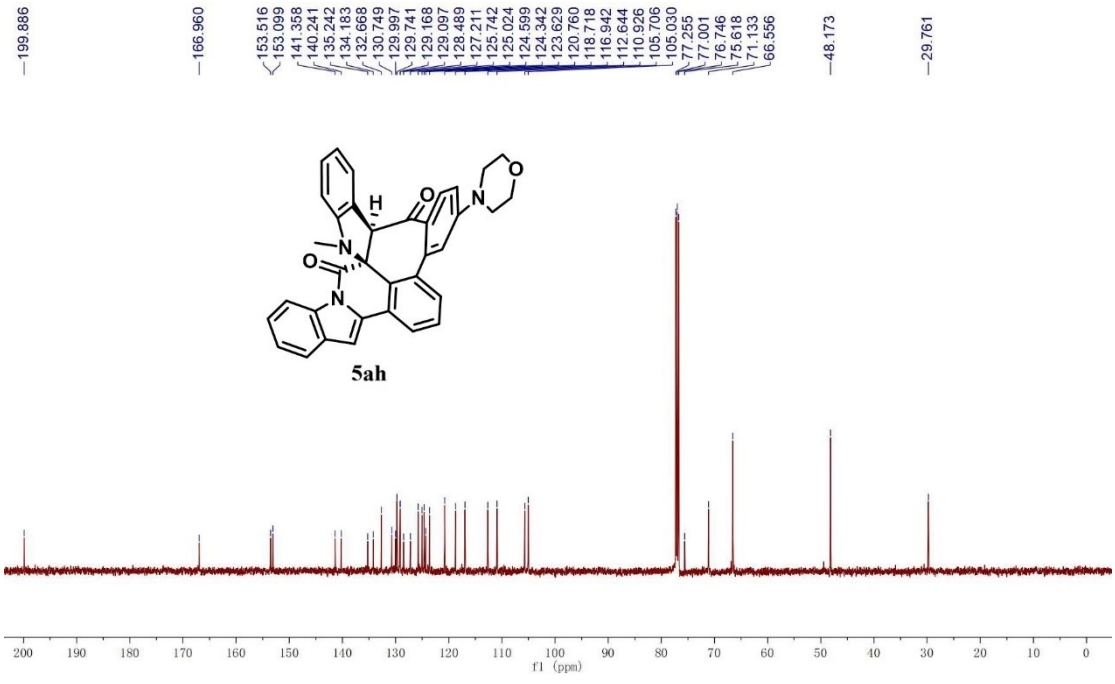
^{1}H NMR of **5af** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5af** (125 MHz, $CDCl_3$)



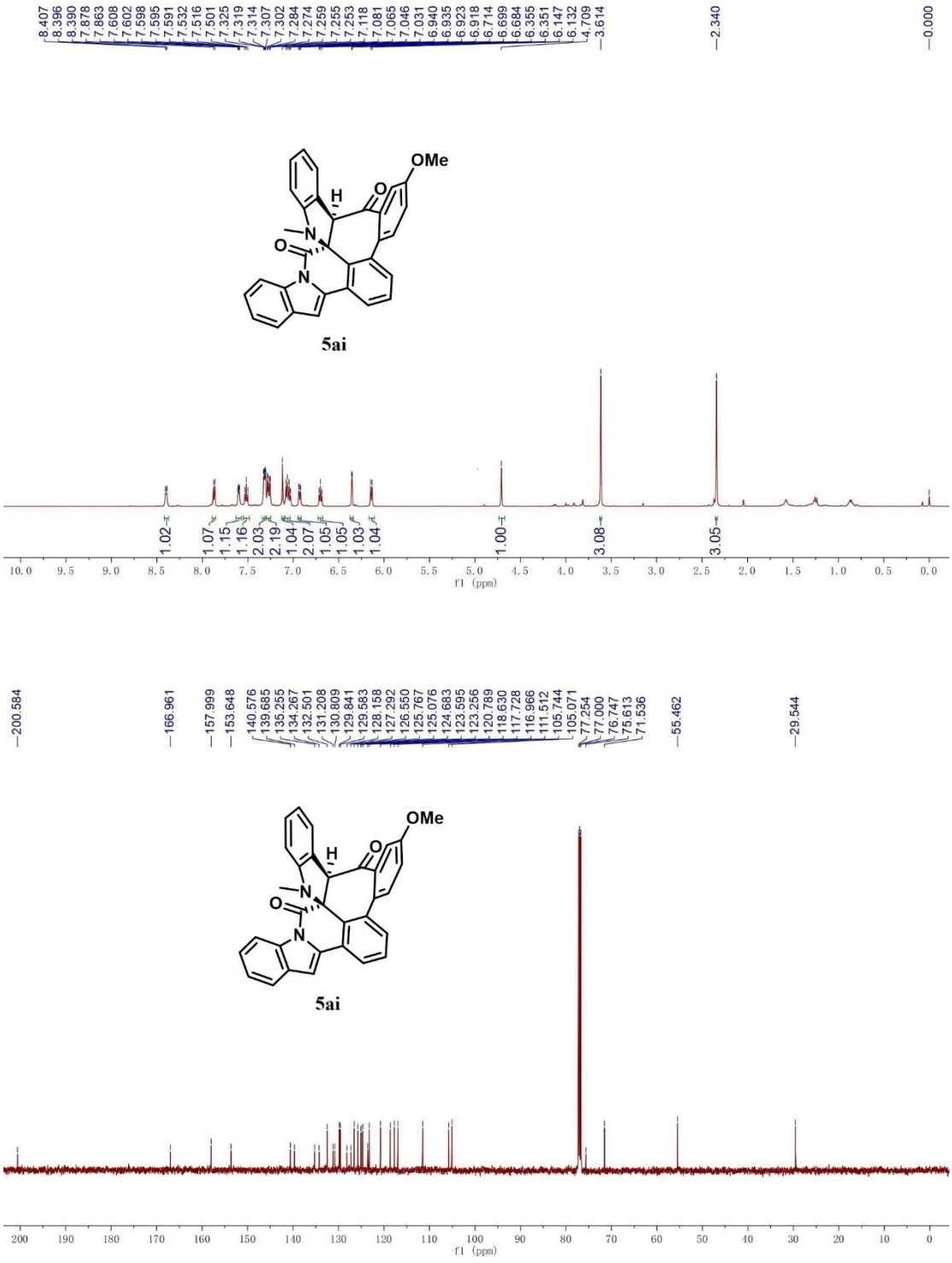


^{1}H NMR of **5ah** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ah** (125 MHz, $CDCl_3$)

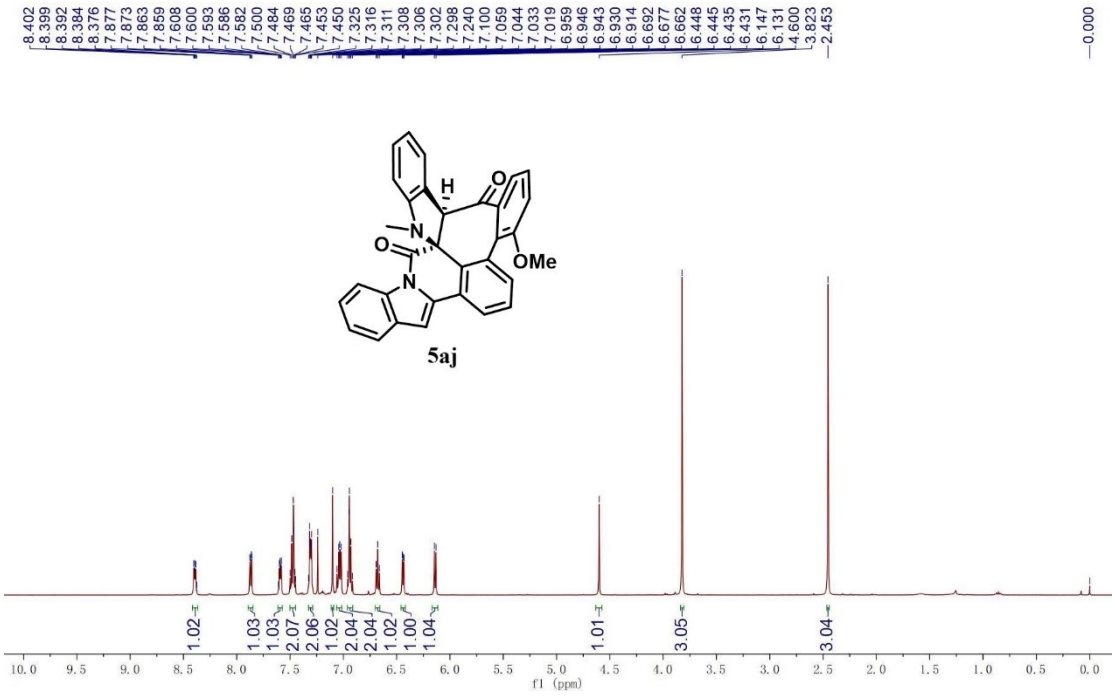


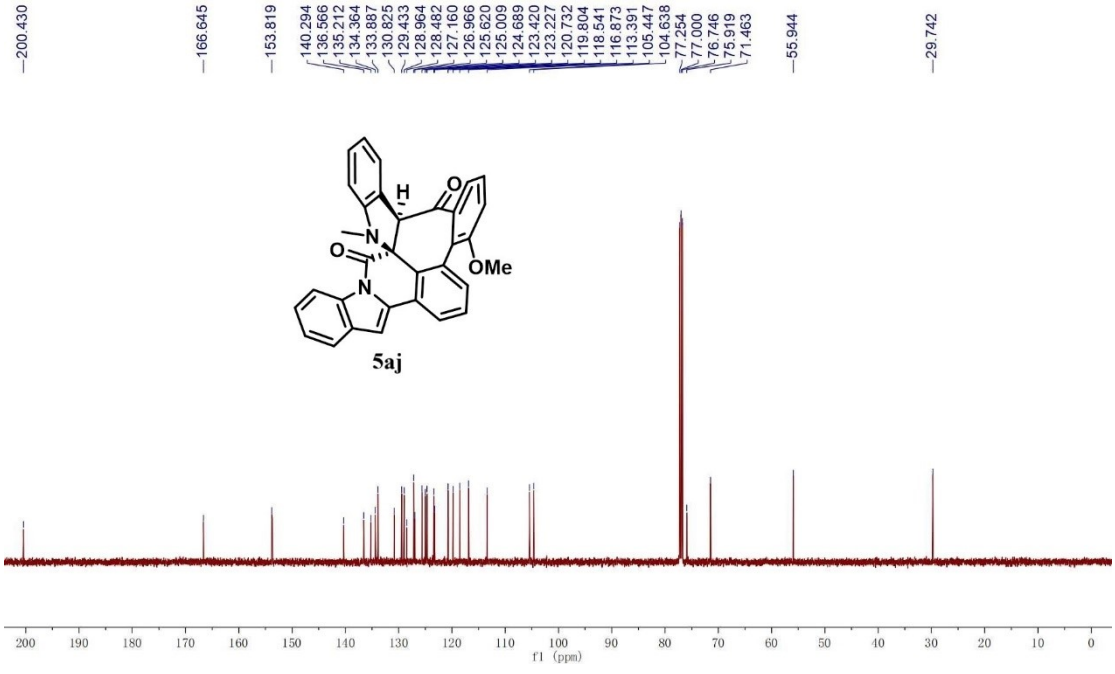


^{1}H NMR of **5ai** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ai** (125 MHz, $CDCl_3$)

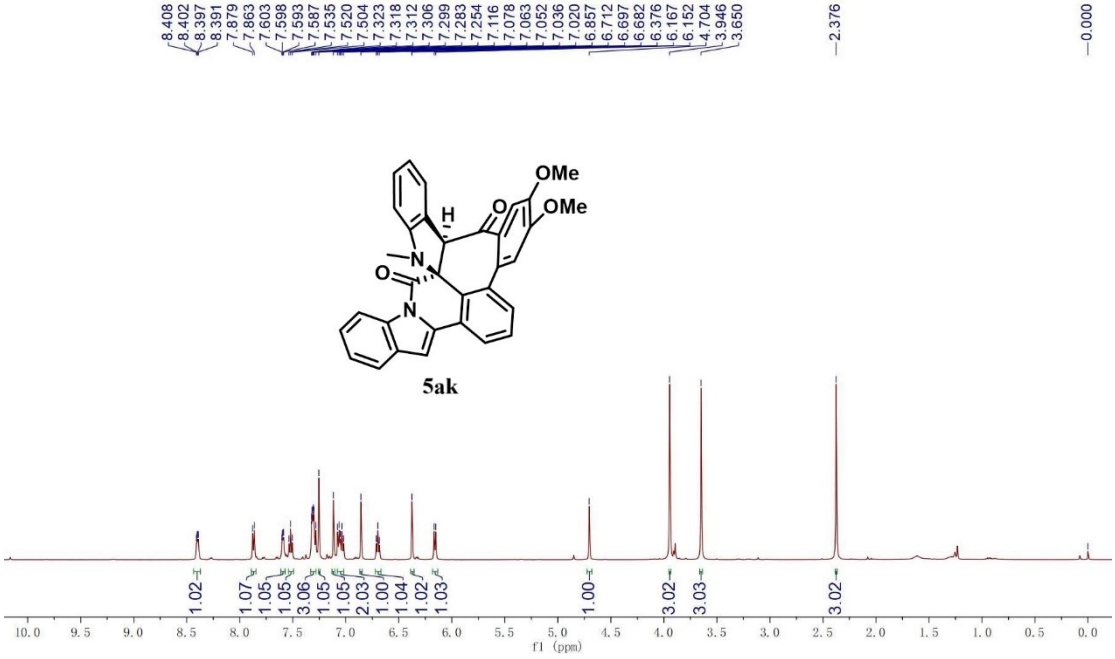


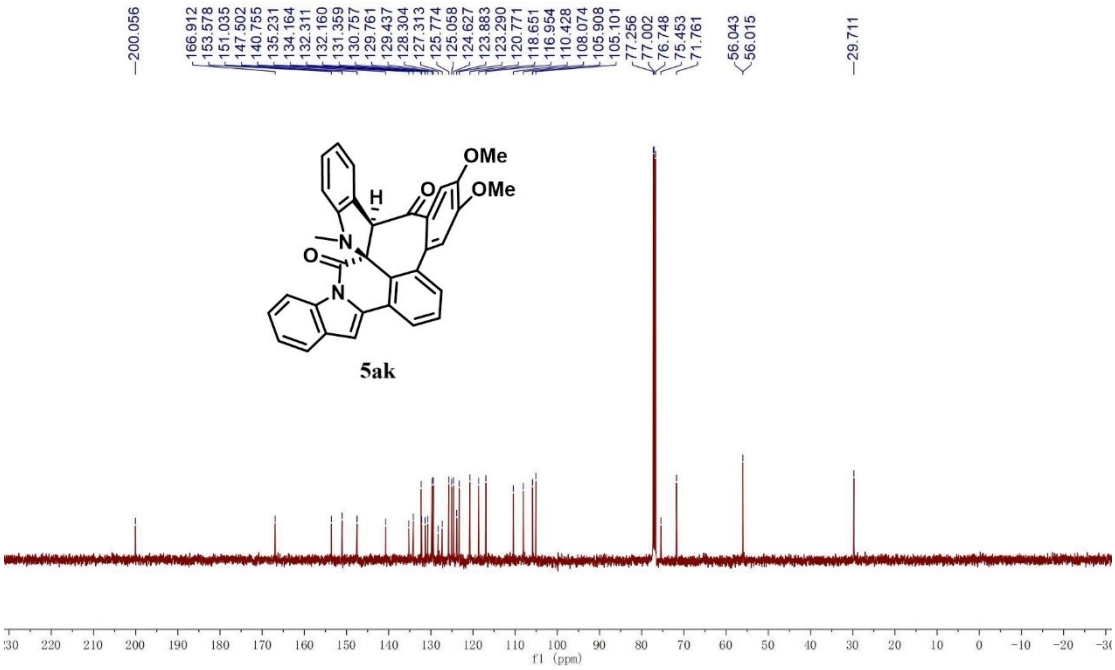
^{1}H NMR of **5aj** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5aj** (125 MHz, $CDCl_3$)



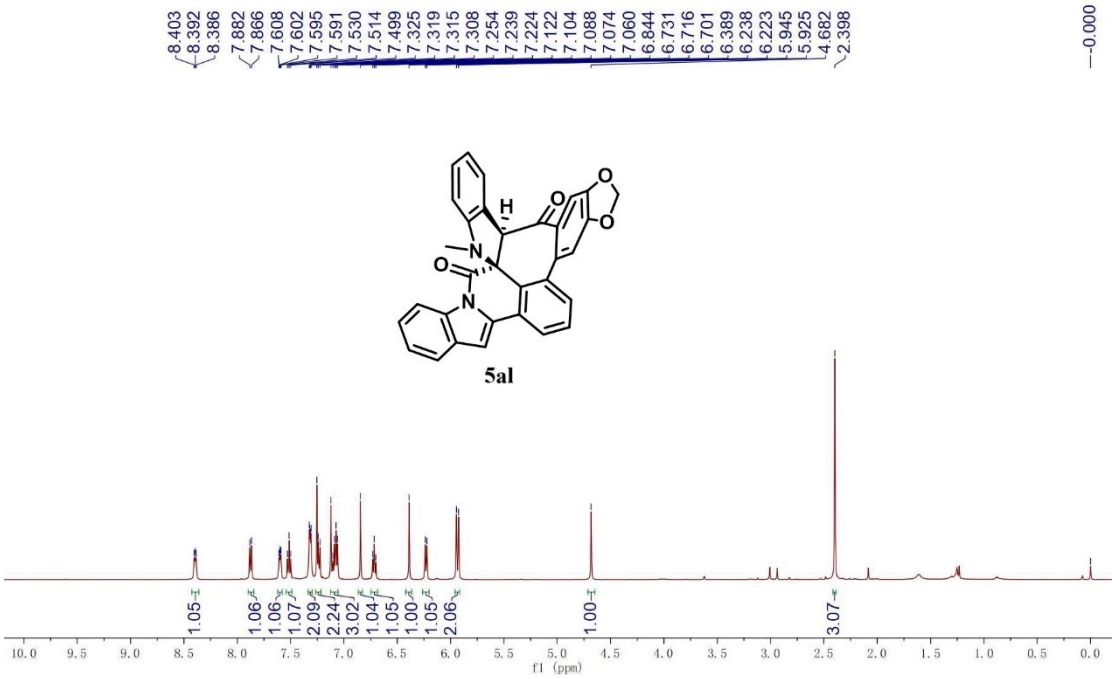


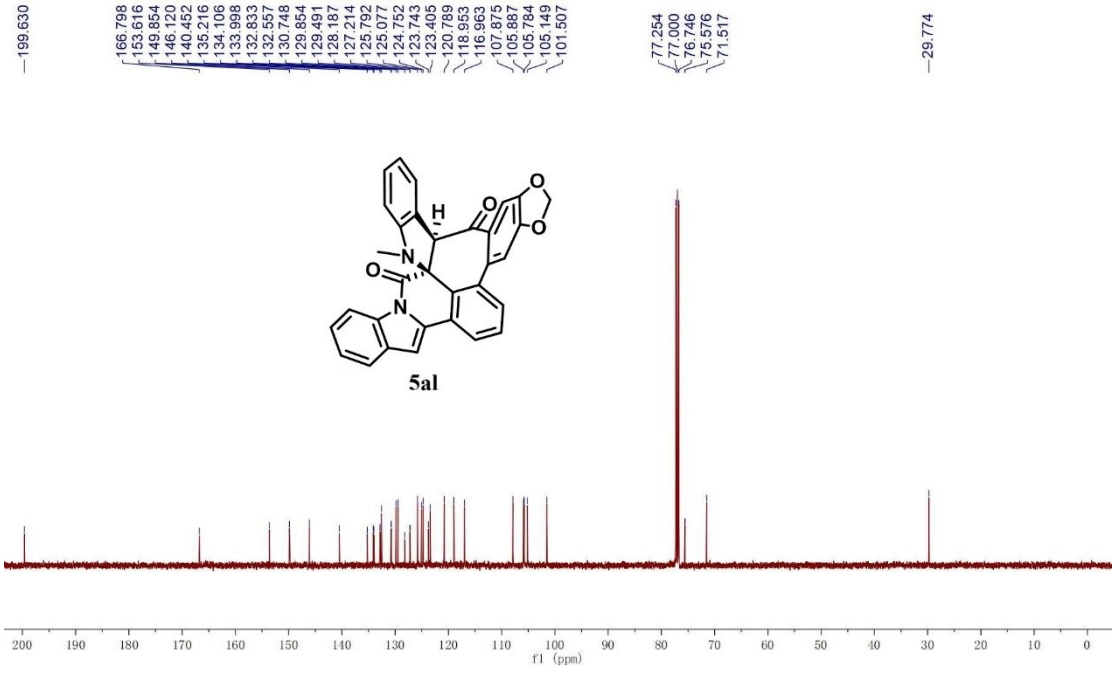
^{1}H NMR of **5ak** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5ak** (125 MHz, $CDCl_3$)



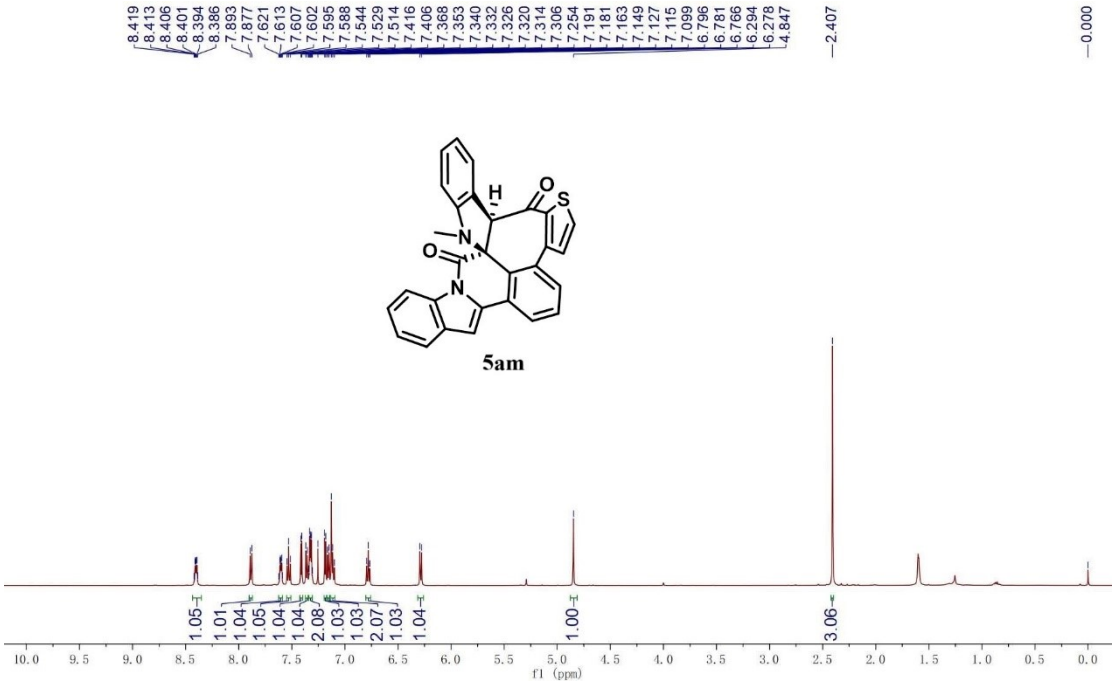


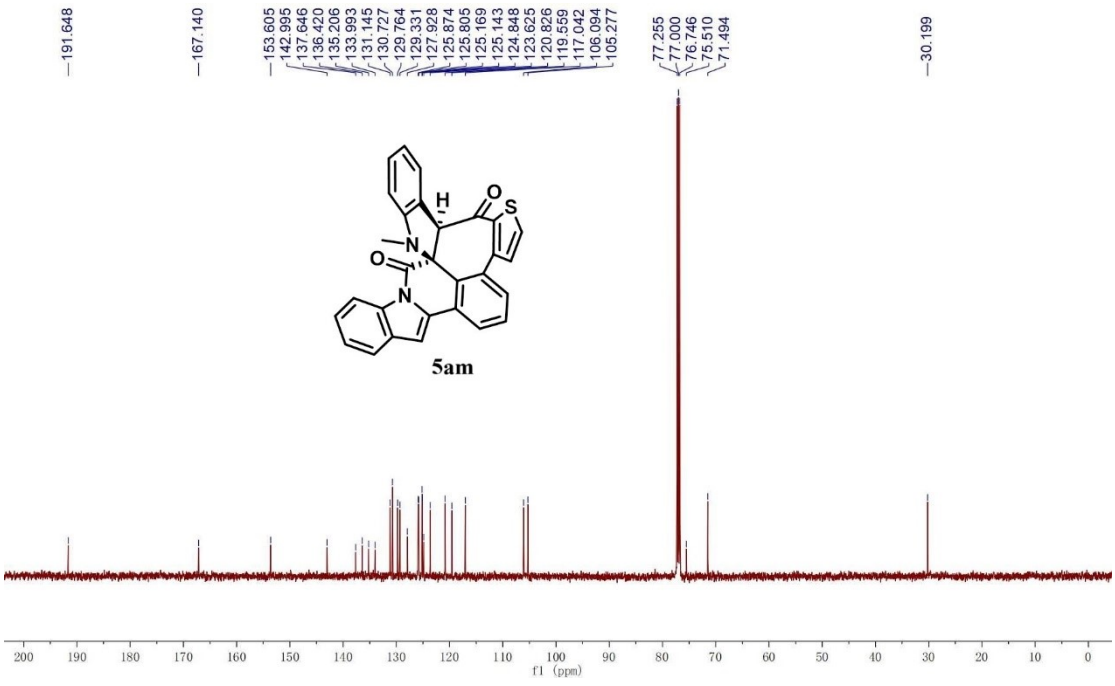
^{1}H NMR of **5al** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5al** (125 MHz, $CDCl_3$)





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





^{1}H NMR of **6** (500 MHz, $CDCl_3$) and ^{13}C NMR of **6** (125 MHz, $CDCl_3$)