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Electronic Supplementary Information (ESI) for

Visible-light-driven reductive dearomatization of *N*-arylformyl indoles in EDA complexes with a thiophenol via a HAT pathway

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Contents

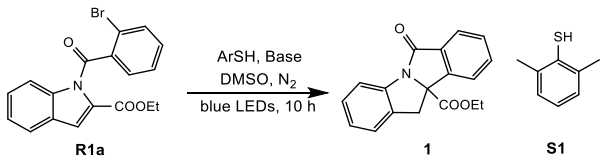
1. Materials and general methods

All aryl thiols and solvents were obtained from commercial suppliers and used without further purification unless otherwise stated. Anhydrous DMSO was purchased from Energy Chemical, and added to molecular sieves during use and stored at room temperature. The ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on a Bruker Ascend 400MHz spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) or on a Bruker Ascend 500MHz spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR). The chemical shifts (δ) for ^{1}H and ^{13}C are reported in ppm and are referenced to Me_4Si (TMS) and the residual undeuterated solvent resonances (TMS at 0.00 ppm; $CHCl_3$ at 7.26 ppm ^{1}H NMR and 77.16 ppm ^{13}C NMR respectively; DMSO at 2.50 ppm ^{1}H NMR and 39.52 ppm ^{13}C NMR respectively). All UV/Vis absorption spectra were recorded in 1 cm path quartz cuvettes on a Shimadzu UV-2450 UV-VIS spectrophotometer. High resolution mass spectra (HRMS) were acquired using a Q-Exactive plus hybrid quadrupole-orbitrap mass spectrometer (Q-Orbitrap MS) (Thermo Scientific, San Jose, USA) with electrospray ionization (ESI) source. A 40 W Kessil PR160L-456 nm LED photoreaction lighting (max frequency, max intensity) was employed as a visible light source without the use of filters.

Figure S1. The photo reaction setup with a 40 W Kessil PR160L-456 nm LED photoreaction lighting and a fan.

2. Condition optimization and all substrates of the dearomatization reaction

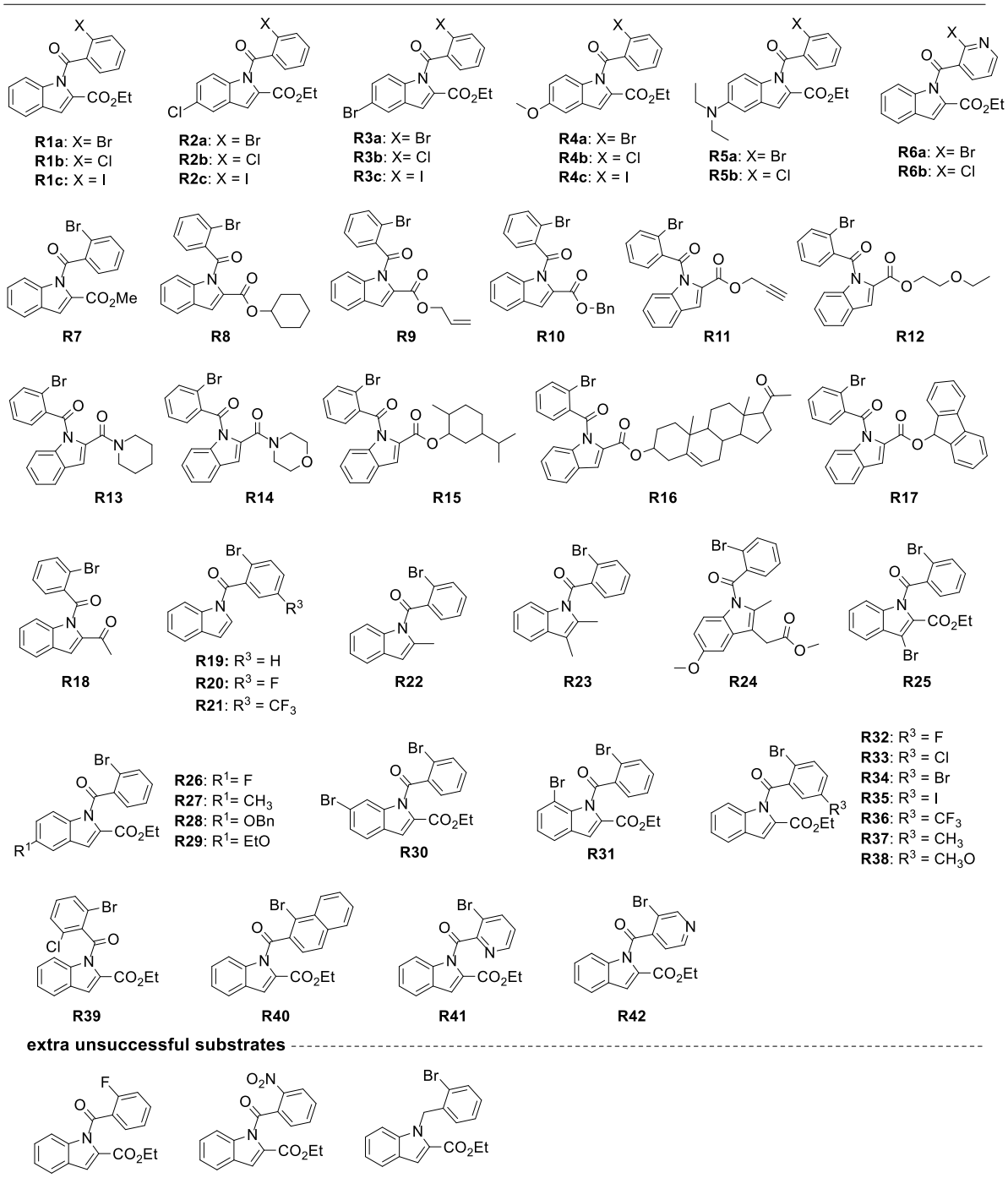
Table S1. Optimization of the conditions



Entry	ArSH (equiv)	Base (equiv)	Yield %[a]
1	**S1** (1.5)	Cs_2CO_3 (1.5)	54
2	**S1** (1.5)	K_2CO_3 (1.5)	60
3	**S1** (1.5)	Na_2CO_3 (1.5)	54
4	**S1** (1.5)	DBU (1.5)	22
5	**S1** (1.5)	DBU (0.5)	45
6	**S1** (1.5)	DBU (0.2)	25
7	**S1** (1.5)	NEt_3 (1.5)	96
8	**S1** (1.5)	DIPEA (1.5)	96
9	**S1** (1.5)	DIPEA (1.0)	83
10	**S1** (1.5)	DIPEA (0.8)	80
11	**S1** (1.0)	DIPEA (1.5)	79
12	**S1** (0.8)	DIPEA (1.5)	77
13	**S1** (0.4)	DIPEA (1.5)	68
14	1.5 eq *p*-Me-	1.5 eq DIPEA	97
15	1.5 eq *p*-MeO-	1.5 eq DIPEA	85
16	1.5 eq *p*-H-	1.5 eq DIPEA	97
17	1.5 eq *p*-F-	1.5 eq DIPEA	94
18	1.5 eq *p*-CF_3-	1.5 eq DIPEA	92
19	None	DIPEA (1.5)	ND
20	**S1** (1.5)	None	ND
21 [b]	**S1** (1.5)	DIPEA (1.5)	ND

[a] Reaction conditions: 0.1 mmol **R1a** in 1.0 mL of DMSO (0.1M), irradiation with a blue LED (456 nm, 40W, Kessil® lighting) for 10 h at room temperature, and yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standards. [b] In dark. ND, not detected.

Table S2. Structures of all substrates in the dearomatization reaction.



3. Mechanistic investigations

3.1 Cyclic voltammetry (CV) measurements

CV measurements were carried out under nitrogen atmosphere in DMSO solutions with 0.1 M of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as a supporting electrolyte. Measurements were made with a glassy carbon electrode, saturated calomel electrode (SCE) as reference electrode, and a Pt wire counter electrode. The concentration of the sample solution was fixed at 10 mM and the sweep rates were set to 100 mV/s. The redox potential of ferrocenium/ferrocene (Fc^+/Fc) was measured under same experimental conditions.

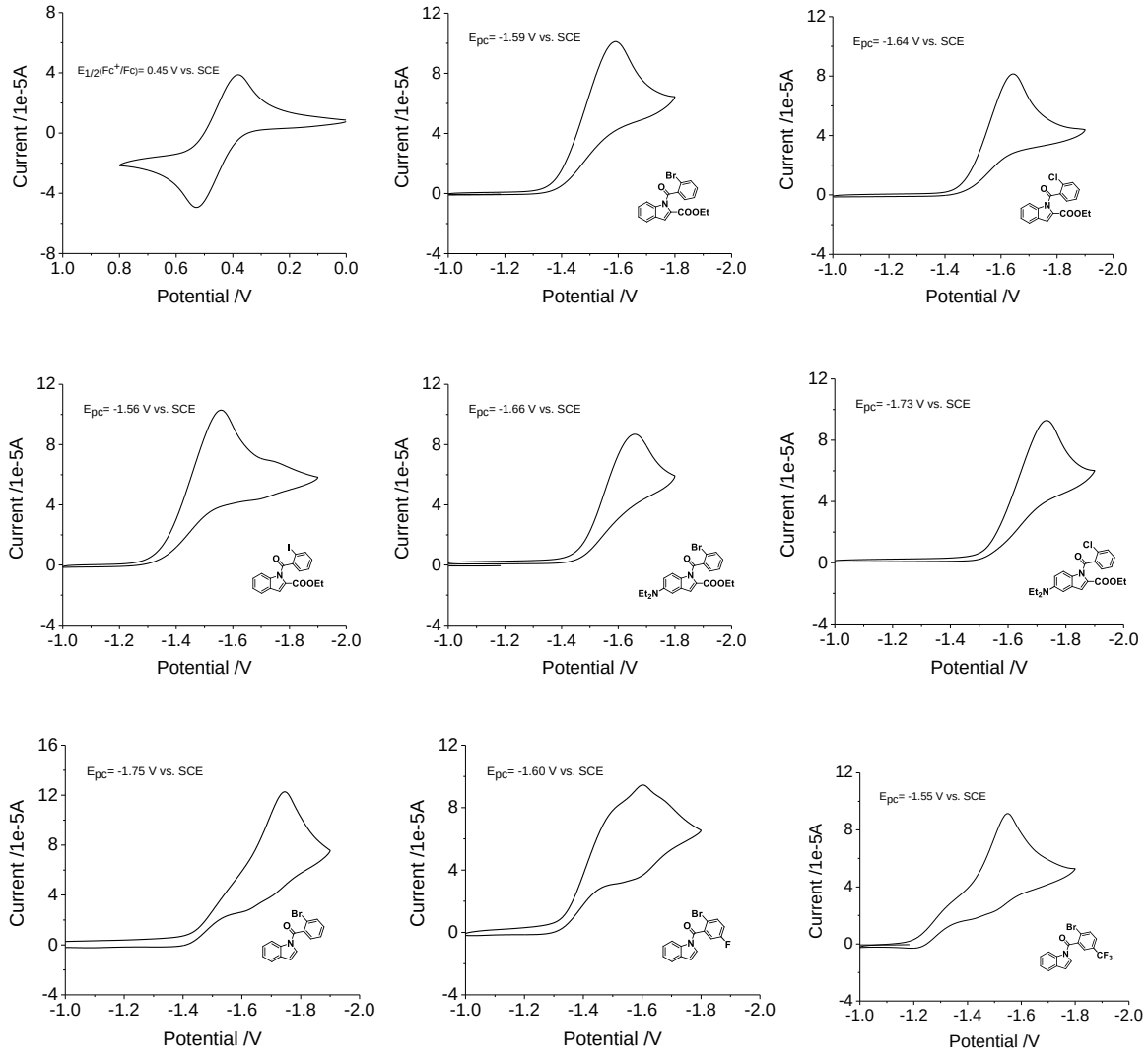


Figure S2. Cyclic voltammograms of ferrocene, **R1a**, **R1b**, **R1c**, **R5a**, **R5b**, **R19**, **R20** and **R21**. $E_{1/2}$ (Fc^+/Fc) (V vs. SCE) = 0.45 V.

3.2 UV-vis absorption spectra as evidence of the EDA complex

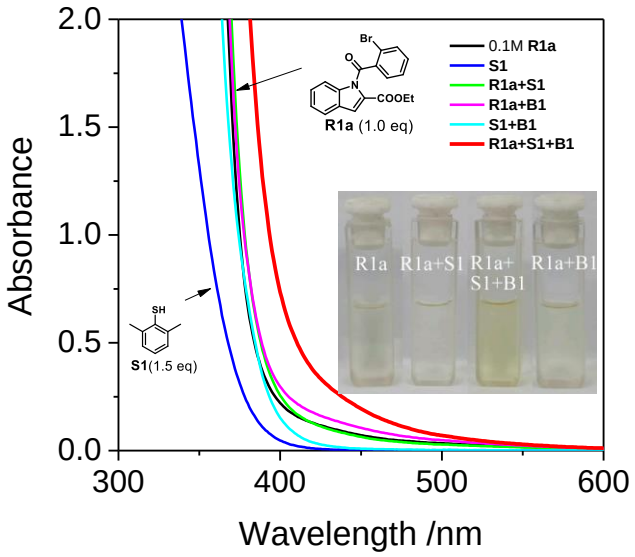


Figure S3. UV/Vis absorption spectra of **R1a**, **S1** (1.5 equiv) and DIPEA (**B1**, 1.5 equiv) in DMSO (0.1M). Inset: photos of above solutions.

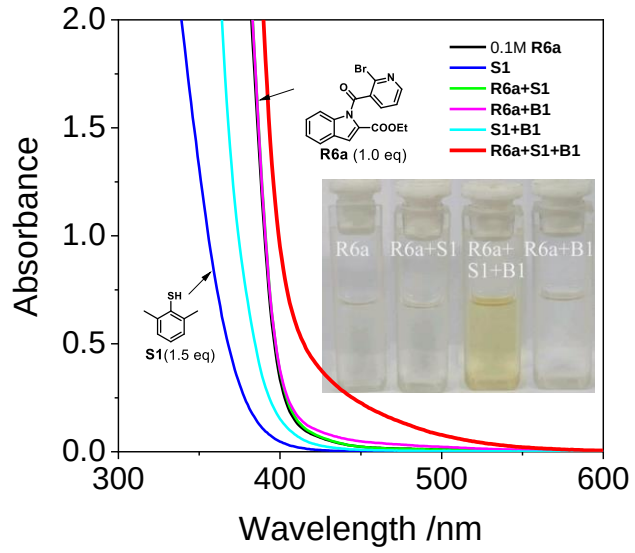


Figure S4. UV/Vis absorption spectra of **R6a**, **S1** (1.5 equiv) and DIPEA (**B1**, 1.5 equiv) in DMSO (0.1M). Inset: photos of above solutions.

3.3 NMR measurements

Mixture of a certain amount of substrate **R32** with increasing amount of thiophenol and the corresponding concentration of DIPEA is analyzed in DMSO-d_6 by ^{19}F-NMR. The chemical shift δ (Ar-F) of the F atom of substrate **R32** gradually moved downfield with the increase of ArS- concentration, indicating that there was an interaction between **R32** and thiophenol anion.[S1]

Table S3. ^{19}F-NMR measurements of **R32** with **S1** and DIPEA.

Entry	**R32** /mmol	**S1** /mmol	DIPEA /mmol	**R32** : **S1** : DIPEA	δ (Ar-F)/ppm
1	0.01	0	0	1:0:0	-113.5027
2	0.01	0.02	0.02	1:2:2	-113.4923
3	0.01	0.04	0.04	1:4:4	-113.4888
4	0.01	0.06	0.06	1:6:6	-113.4849
5	0.01	0.08	0.08	1:8:8	-113.4808
6	0.01	0.10	0.10	1:10:10	-113.4779

Mixture of a certain amount of substrate **R38** with increasing amount of thiophenol and the corresponding concentration of DIPEA is analyzed in DMSO-d_6 by ^{1}H-NMR. The chemical shift δ (MeO-) of the H atom of substrate **R38** gradually moved upfield with the increase of ArS- concentration, indicating that there was an interaction between **R38** and thiophenol anion, which further supported the formation of EDA in this system.[S2]

Table S4. ^{1}H-NMR measurements of **R38** with **S1** and DIPEA.

Entry	**R38** /mmol	**S1** /mmol	DIPEA /mmol	**R38** : **S1** : DIPEA	δ (MeO-)/ppm
1	0.01	0	0	1:0:0	3.7720
2	0.01	0.02	0.02	1:2:2	3.7692
3	0.01	0.04	0.04	1:4:4	3.7663
4	0.01	0.06	0.06	1:6:6	3.7642
5	0.01	0.08	0.08	1:8:8	3.7618
6	0.01	0.10	0.10	1:10:10	3.7597
7	0.01	0.12	0.12	1:12:12	3.7575

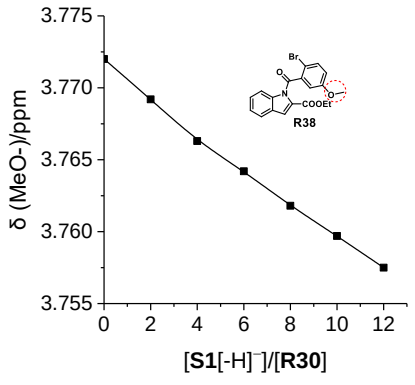


Figure S5. The plot of the chemical shift of H atom in CH_3O group of the concentration ratio of **R38** and **S1**[-H]$^-$.

3.4 Free radical-trapping experiments

The substrate **R1a** (0.2 mmol, 1.0 eq.) and TEMPO (3.0 eq.) were added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N_2) three times. Then DMSO (2 mL), DIPEA (1.5 eq.), and **S2** (1.5 eq.) were added via a gastight syringe under nitrogen atmosphere. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LED (456 nm, distance approximately 3.0 cm from the bulb) with a fan at room temperature for 10 h. The reaction mixture was analyzed by HRMS with ESI source, no desired product **1** was detected, indicating that the reaction was completely inhibited by TEMPO. Meanwhile, free radical-trapping adduct of benzyl radical intermediate with TEMPO was observed with HRMS analysis of the reaction solution at *m/z* 449.2433 (Figure S6). The reaction mixture was extracted with DCM (3×10 mL) and washed with water to remove DMSO. The organic layers were combined and concentrated under vacuum. The free radical-trapping adduct **43**[S3] of benzyl radical intermediate with TEMPO was purified by flash column chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a colorless oil in 11%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.65 (td, *J* =7.5 Hz, 1.1 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 1H), 7.54 (td, *J* =7.6 Hz, 0.9 Hz, 1H), 7.43 (td, *J* =7.7 Hz, 1.2 Hz, 1H), 5.73 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 3H), 1.40-1.37 (m, 2H), 1.25 (d, *J* = 5.8 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.09-1.07 (m, 2H), 1.00 (s, 3H), 0.19 (s, 3H), -0.29 (s, 3H). HRMS (ESI): *m/z* calcd for $C_{27}H_{33}N_2O_4$: 449.2435 [M+H$^+$], found: 449.2433.

The free radical-trapping adduct **44**[S4] of ArS$^\bullet$ with TEMPO was purified by flash column chromatography (petroleum ether/ethyl acetate v/v =50:1) yielding a yellow oil in 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H), 1.66-1.49 (m, 15H), 0.92 (s, 3H). Above data are consistent with the reported literature. [S3, S4]

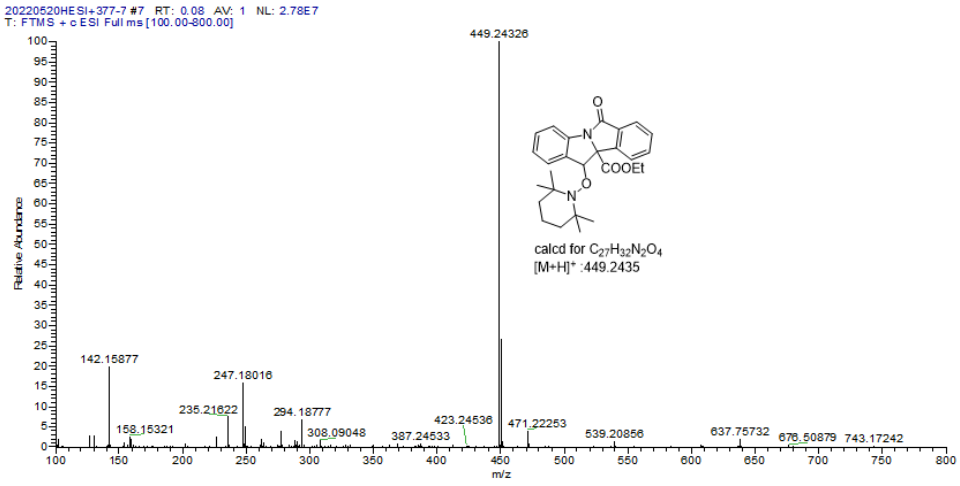


Figure S6. HRMS analysis of free radical-trapping adducts with TEMPO.

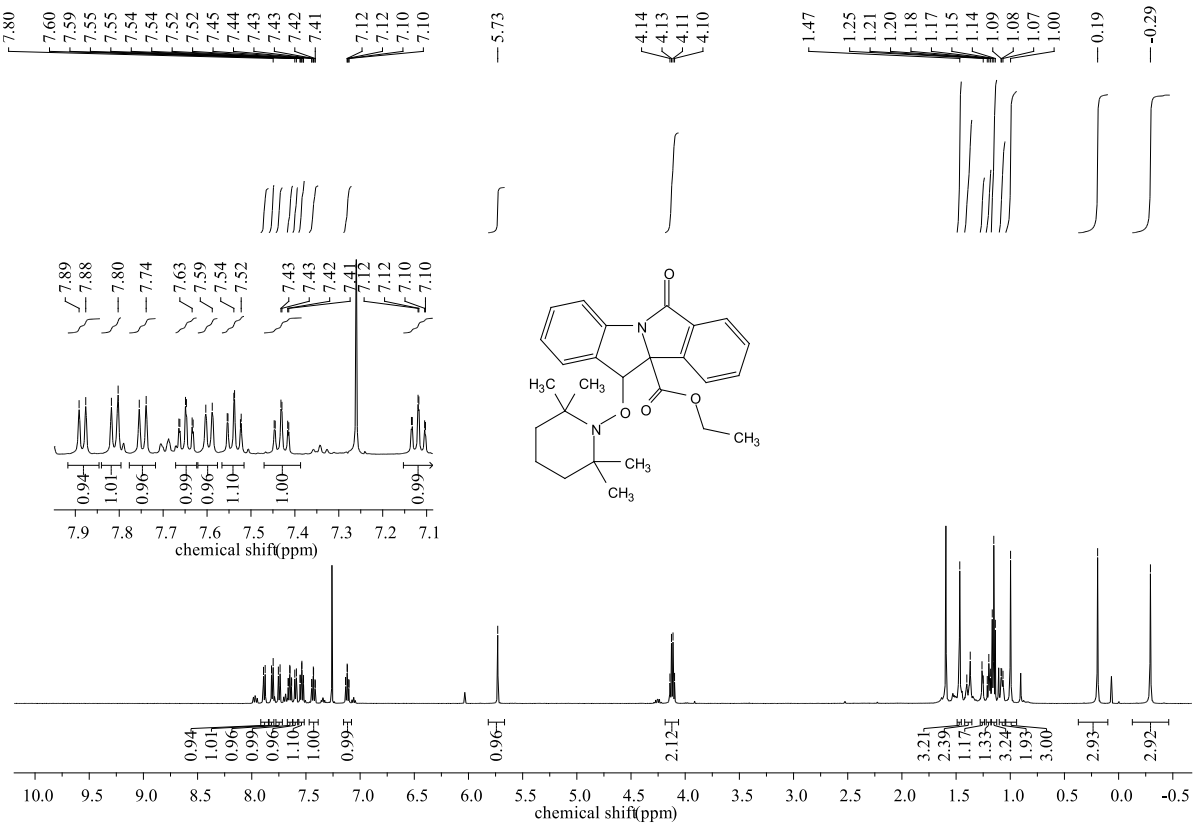


Figure S7. ^{1}H NMR Spectra of the free radical-trapping adduct **43** of benzyl radical intermediate with TEMPO.

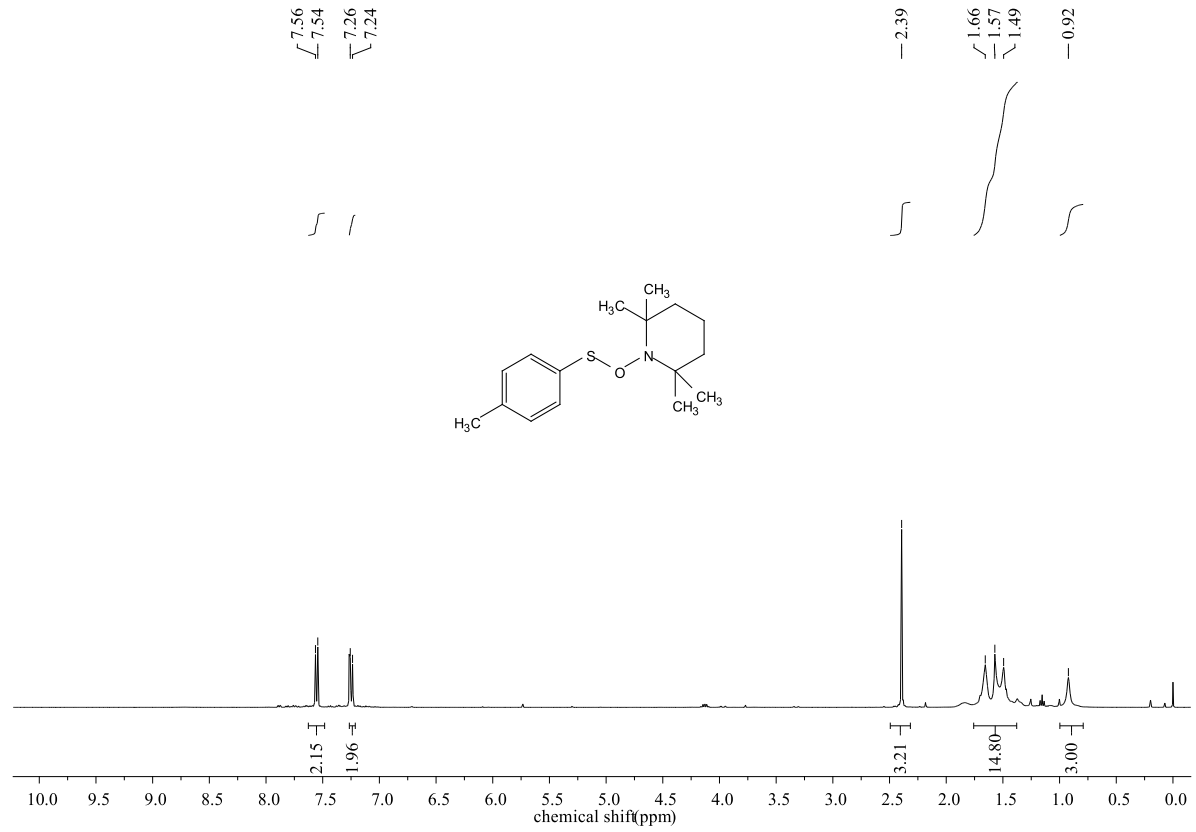
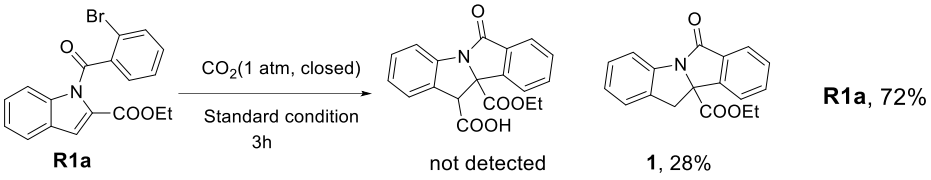
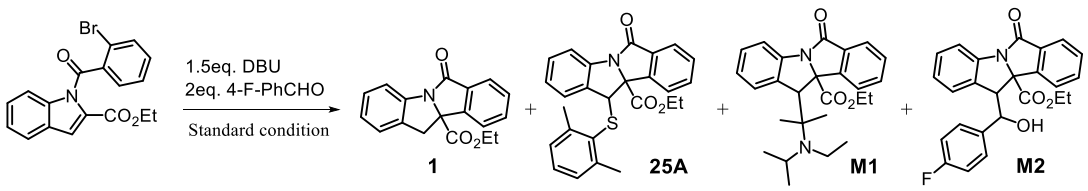


Figure S8. ^{1}H NMR Spectra of the free radical-trapping adduct **44** of ArS• with TEMPO.

3.5 Benzyl anion-trapping experiments



The substrate **R1a** (0.2 mmol, 1.0 eq.) was added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with CO_2 three times. Then DMSO (0.1 M), DIPEA (1.5 eq.) and **S1** (1.5 eq.) were added via a gastight syring. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LED (456 nm, distance approximately 3.0 cm from the bulb) with a fan at room temperature for 3 h. Then, the mixture was quenched with 1 mL of H_2O and 2 mL of HCl (2 N), extracted with DCM (3×10 mL) and washed with water to remove DMSO. The organic layers were combined and concentrated under vacuum, and the yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standards.



The substrate **R1a** (0.2 mmol, 1.0 eq.) was added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N_2) three times. Then DMSO (0.1 M), DIPEA (1.5 equiv), **S1** (1.5 equiv), DBU (1.5 equiv) and 4-F-PhCHO (2 equiv) were added via a gastight syringe under nitrogen atmosphere. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LED (456 nm, distance approximately 3.0 cm from the bulb) with a fan at room temperature for 10 h. The reaction mixture was analyzed by HRMS with ESI source, the *m/z* peaks of adduct product **M2** of the benzyl anion with the aldehyde was found at 440.1272, and the mass spectrum shown in Fig. S9. Meanwhile, the coupling products **25A** and **M1** of benzyl radical with ArS• and DIPEA[-H]• were observed at *m/z* 452.1290 and 421.2485, respectively.

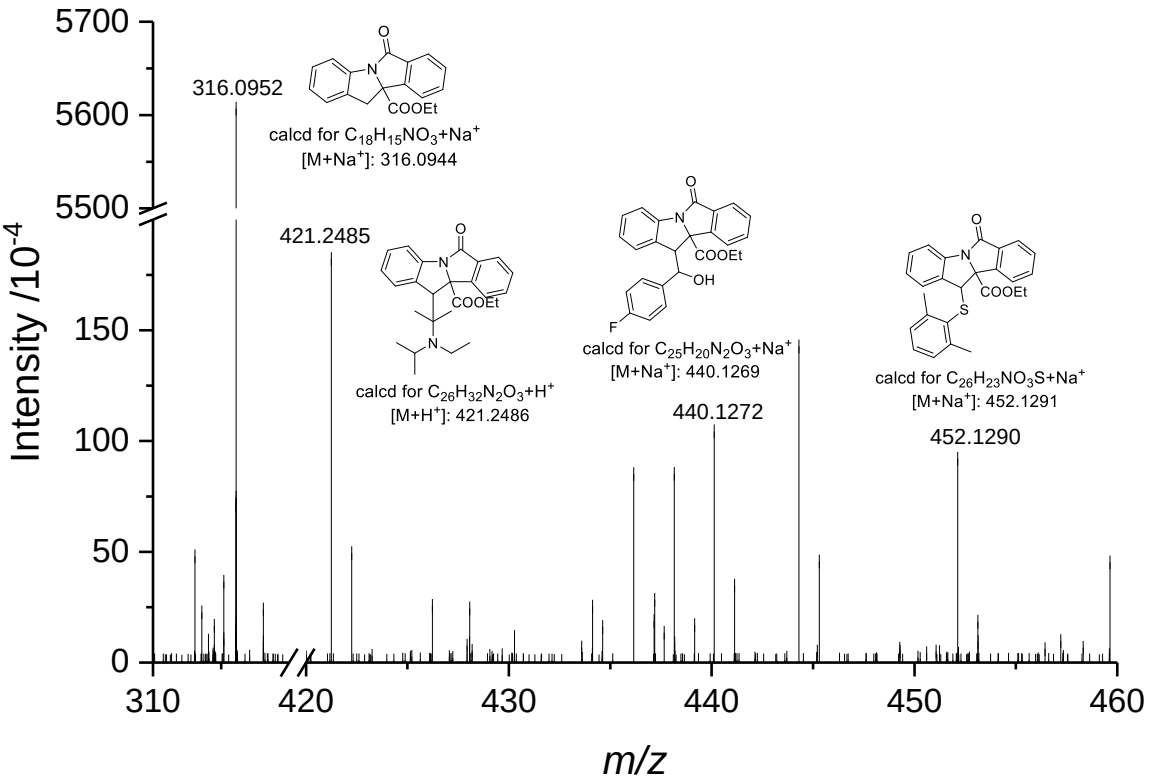
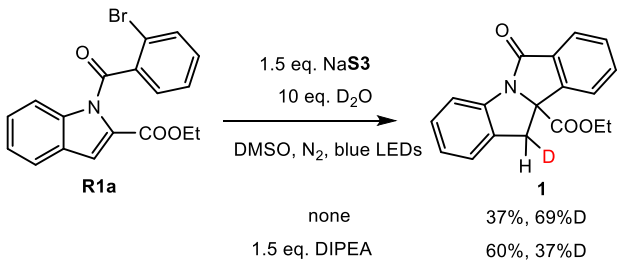


Figure S9. HRMS analysis of the reaction with aldehyde.

3.6 Deuterium labeling experiments



In a glovebox, to a Schlenk tube with a stirring bar was added **R1a** (0.1 mmol, 1.0 eq.), Na**S3** (sodium benzenethiolate) (1.5 eq.), DMSO (1 mL), D_2O (10 eq.) with or without DIPEA (1.5 eq.). Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LED (456 nm, distance approximately 3.0 cm from the bulb) with a fan at room temperature for 10 h. The reaction mixture was extracted with DCM (3×10 mL) and washed with water to remove DMSO. The yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standards. The desired product was purified by flash column chromatography (petroleum ether/ethyl acetate v/v =10:1) to give **1**. As shown in Fig. S10, the deuterium incorporation of the isolated product was determined by integration of the peak areas of ^{1}H NMR spectroscopy. The deuterium incorporation of the other deuterium labeling experiments were analyzed by analogy.

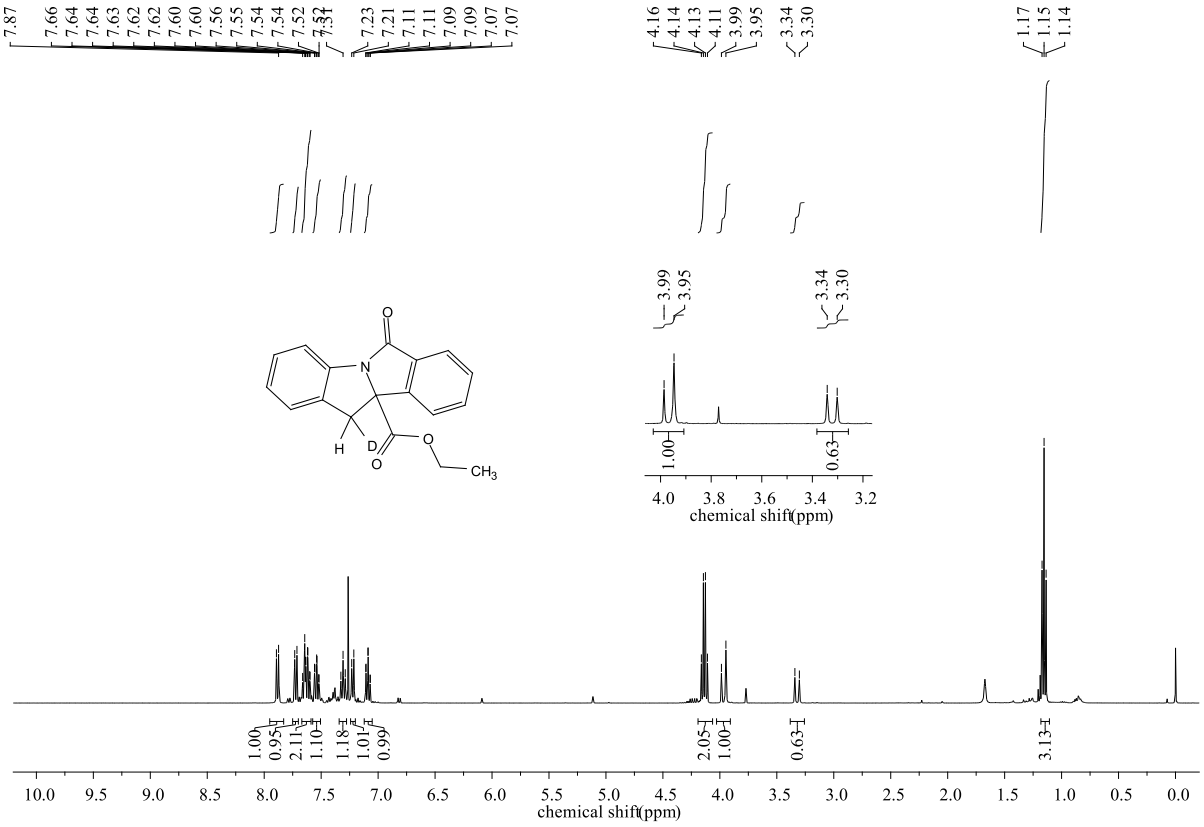
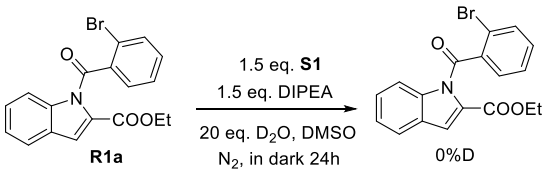


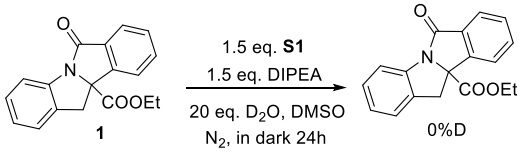
Figure S10. ^{1}H NMR Spectra of compound **1** with 37% deuterium incorporation.

Control experiments with D_2O

The reactant **R1a** was stirred with deuterated water under the reaction condition in dark, there were no deuterated trace in **R1a**. Therefore, we could rule out the possibility that the direct H/D exchange of **R1a** with D_2O.



The dearomatization product **1** was stirred with deuterated water under the reaction condition in dark, there were no deuterated trace in **1**. Therefore, we could rule out the possibility that the direct H/D exchange of **1** with D_2O.



3.7 NOE analysis of the major isomer of **24**

The stereochemistry of the major isomer of **24** was analyzed by NOESY spectroscopy. The methyl (δ=1.52 ppm) at C2 of indole was determined to be *syn* to C3-substituent group based on a cross signal between the methyl hydrogen and methylene hydrogen of -CH_2CO_2Me at C3 of indole at 2.96 ppm, while there is no cross signal between the methyl and benzylic hydrogen at 3.73 ppm. The both evidences indicated the *syn*-relationship between the newly generated C–C bond and C-H bond. The *syn*-form stereochemistry of the other disubstituted products was surmised by analogy while **25A** could be opposite as a nucleophilic substitution product of **25**.

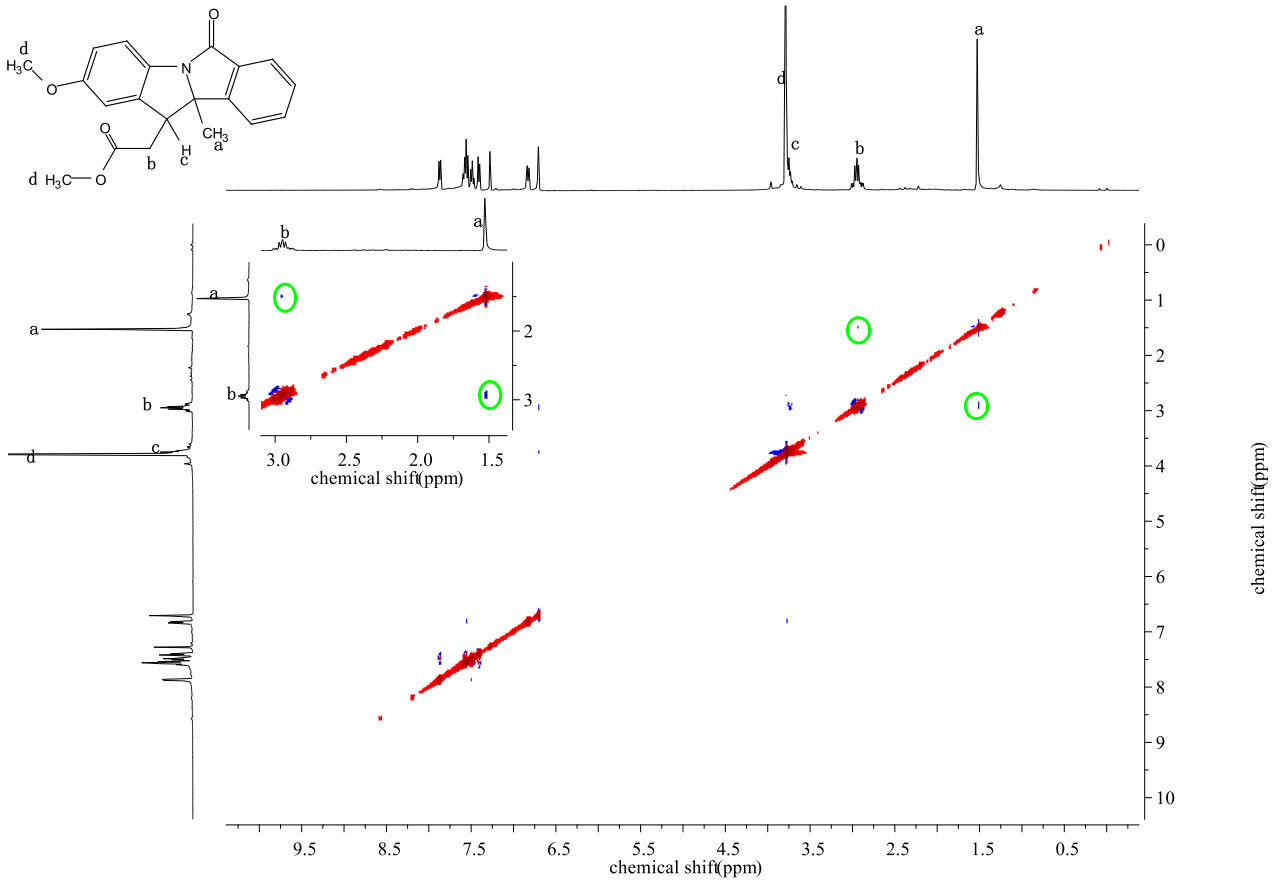
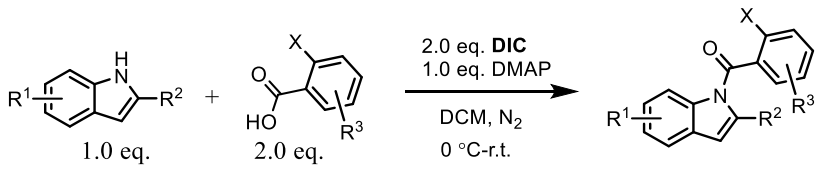


Figure S11. NOESY spectra of compound **24**.

4. Experimental procedure

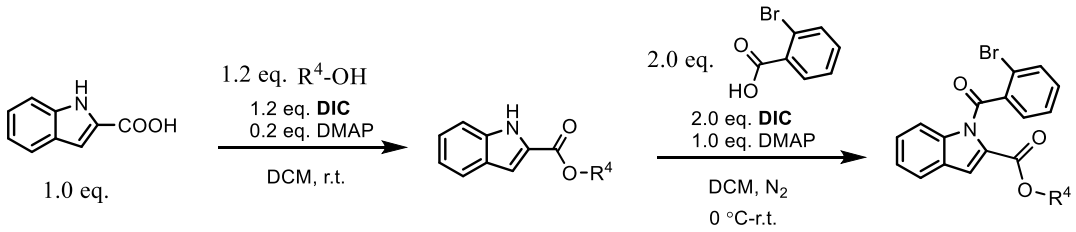
4.1 Synthesis of substrates

General Procedure 1



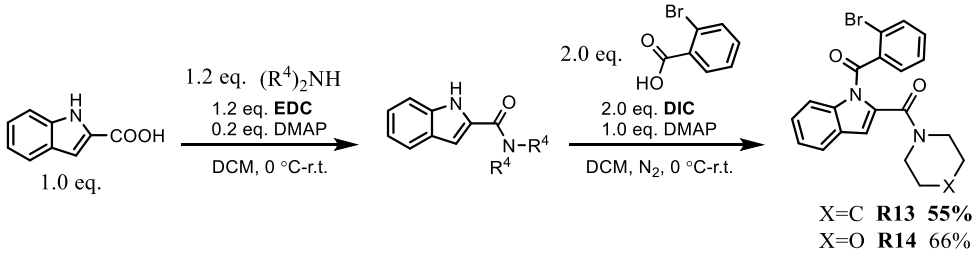
The solution of indole derivative (1.0 eq.), dimethylaminopyridine (DMAP) (1.0 eq.), carboxylic acid (2.0 eq.) and DCM (0.1 M) were stirred at 0 ℃ under a nitrogen atmosphere for 30 mins. After that, N, N'-diisopropylcarbodiimide (DIC) (2.0 eq.) was added dropwise via syringe and the solution was warmed to room temperature until the indole derivative was consumed (monitored by TLC). After the reaction was completed, then the precipitate was filtered off and the solution was concentrated under vacuum. Corresponding substrates were further purified by column chromatography.

General Procedure 2



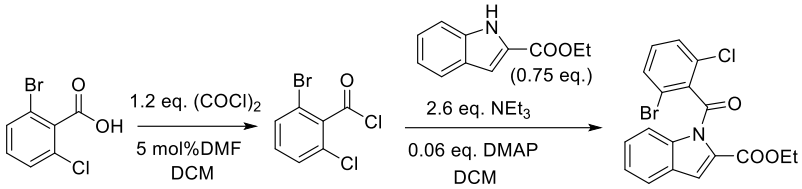
1H-indole-2-carboxylic acid (1.0 eq.), hydroxyl compound R^4-OH (1.2 eq.), DMAP (0.2 eq.) and dichloromethane (0.1 M) were placed in a 100 mL round-bottomed flask equipped with a stirring bar. After that, DIC (1.2 eq.) was added dropwise via syringe and the mixture was stirred at room temperature until the acid was consumed. After the reaction was completed, the precipitate was filtered off and the solution was concentrated under vacuum. Corresponding 2-formiate indole derivatives were purified by short column chromatography (petroleum ether/ethyl acetate v/v =5:1) and used for the following step which is the same as **General Procedure 1**.

Synthesis of Substrates R13 and R14



1H-indole-2-carboxylic acid (1.0 eq.), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), (1.2 eq.), DMAP (0.2 eq.) and dichloromethane 0.1 M) were stirred at 0 ℃ under a nitrogen atmosphere for 10 mins. After that, secondary amines $(R^4)_2NH$ (1.2 eq.) was added dropwise via syringe and the mixture was stirred at room temperature overnight. Upon completion the reaction was extracted with DCM and washed with saturated $NaHCO_3$ solution. The combined organic phases was concentrated under vacuum. Corresponding 2-amide indole derivatives were further purified by short column chromatography (petroleum ether/ethyl acetate v/v =2:1) and used for the following step which is the same as **General Procedure 1**.

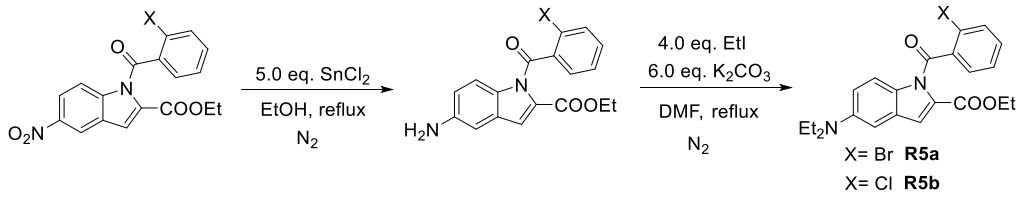
Synthesis of Substrates R39



R39, 91%

To a 100 mL oven-dried flask added 2-bromo-6-chlorobenzoic acid (1 eq.) and solvent DCM (0.5 M) with 5 mol% DMF. Then oxalyl chloride (1.2 eq.) was slowly added to the solution. After 2 h, the solvent was removed in vacuo. The obtained product 2-bromo-6-chlorobenzoyl chloride used for next step without further purification. In a separate flame dried flask, to a solution of ethyl 1H-indole-2-carboxylate and DMAP (0.06 eq.) in DCM (0.1 M) was added NEt_3 (2.6 eq.) at 0 ℃ under a nitrogen atmosphere for 30 mins. Later, the acyl chloride was diluted by DCM and added dropwise to the reaction mixture. The reaction was warmed to room temperature and stirred overnight. Upon completion the reaction was quenched with saturated NH_4Cl solution and extracted with DCM. The organic layers were combined and concentrated under vacuum. The residue was purified via silica gel column chromatography (petroleum ether/ethyl acetate v/v =5:1) to give the corresponding substrates.

Synthesis of substrates R5a and R5b



Indole derivative (1 eq.) and $SnCl_2$-$2H_2O$ (5 eq.) were placed in a 100 mL round-bottomed flask equipped with a stirring bar under a nitrogen atmosphere. Then anhydrous ethanol (0.3 M) was added and the mixture was heated to reflux overnight. Upon completion the reaction mixture was poured into ice 2 M NaOH. Later, the mixture was extracted with DCM, washed with brine. The solvent was removed under reduced pressure and purified with flash

column chromatography (petroleum ether/ethyl acetate v/v =10:3) to obtain the reduction product.

To a mixture of the above reduction product (1 eq.) and K_2CO_3 (6 eq.) in DMF (0.3 M) under a nitrogen atmosphere, iodoethane (4 eq.) was added in drop wise manner. The reaction was stirred at reflux for 16 hours. After cooling down to room temperature, the mixture was treated with water and extracted with ethyl acetate. The organic solvent was dried over anhydrous Na_2SO_4. After removal of the solvent in vacuum, the residue was purified via column chromatography (petroleum ether/ethyl acetate v/v =10:1).

4.2 Photomediated dearomatization reaction

General Procedure 3

The substrate (1.0 eq.) was added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N_2) three times. Then DMSO (0.1 M), DIPEA (1.5 eq.), and aryl thiol (1.5 eq.) were added via a gastight syringe under nitrogen atmosphere. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LED (456 nm, distance approximately 3.0 cm from the bulb) with a fan at room temperature for 10 h. The reaction mixture was extracted with DCM (3×10 mL) and washed with water to remove DMSO. The organic layers were combined and concentrated under vacuum. The desired product was purified by flash column chromatography.

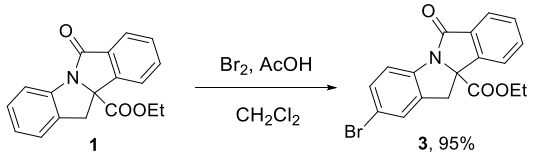
General Procedure 4

The substrate (1.0 eq.) was added to a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N_2) three times. Then DMSO (0.033 M), DIPEA (1.5 eq.), and aryl thiol (1.5 eq.) were added via a gastight syringe under nitrogen atmosphere. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LED (456 nm, distance approximately 3.0 cm from the bulb) with a fan at room temperature for 24 h. The reaction mixture was extracted with DCM (3×10 mL) and washed with water to remove DMSO. The organic layers were combined and concentrated under vacuum. The desired product was purified by flash column chromatography.

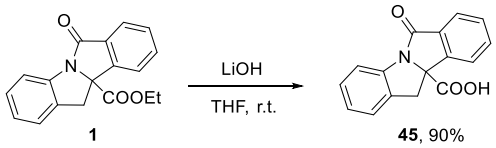
Gram-scale experiment

The substrate **R1a** (1.0 g, 2.69 mmol) was added to a 100 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N_2) three times. Then DMSO (27 mL), DIPEA (4.03 mmol, 702 μL, 1.5 eq.), and **S1** (4.03 mmol, 533 μL, 1.5 eq.) were added via a gastight syringe under nitrogen atmosphere. Afterwards, the tube was sealed, and the reaction mixture was stirred under irradiation with blue LED (456 nm, distance approximately 3.0 cm from the bulb) with a fan at room temperature for 24 h. The reaction mixture was extracted with DCM (3×50 mL) and washed with water to remove DMSO. The organic layers were combined and concentrated under vacuum. The desired product was purified by flash column chromatography (petroleum ether/ethyl acetate v/v =10:1) to obtain a white solid in 81% yield (639 mg).

4.3 Product derivatization

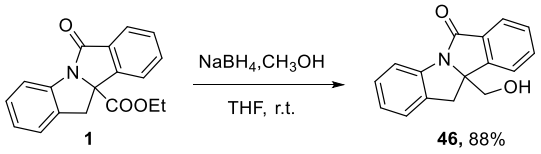


The brominated rea**c**tion was conducted according to a reported procedure.[S5] To a suspension of **1** (58.6 mg, 0.2 mmol) in AcOH (2 mL) was added liquid Br_2 (103μL, 2 mmol) at room temperature. The mixture was stirred for 0.5 h and then CH_2Cl_2 (2 mL) was added to the mixture. After stirring overnight at room temperature, the reaction was quenched with saturated $Na_2S_2O_3$ solution and extracted with CH_2Cl_2 (10 mL x 3). The organic layers were washed with brine and then concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) to obtain **3** as a white solid in 95% yield (70.2 mg).

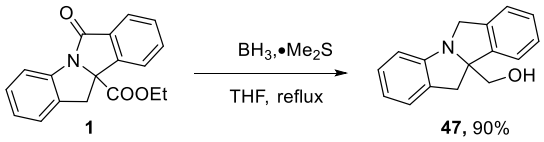


The ester hydrolysis was conducted according to a reported procedure.[S5] **1** (58.6 mg, 0.2 mmol) were dissolved in 2 mL of THF and 1 M LiOH (0.5 mL, 0.5 mmol) was added at room temperature. After 2 h, THF was evaporated and 2 mL of water was added to the mixture. The pH was adjusted to 3 with 1 M HCl and extracted with ethyl acetate. The organic layers were combined and evaporated under reduced pressure to obtain **45** as a white solid in 90% yield (47.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 4.4 Hz, 1H), 7.67 (d, *J* = 4.2 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.94 (d, *J* = 15.8Hz, 1H), 3.34 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 168.6, 143.8, 139.7, 133.9, 133.5, 133.0, 130.1, 128.4, 125.3, 125.2, 125.1, 123.4, 116.9, 76.5, 38.1. HRMS (ESI): *m/z* calcd for

$C_{16}H_{11}NO_3$+H^+ 266.0812 [*M*+H^+]; found: 266.0817.

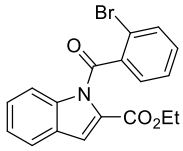


The reduction was conducted according to a reported procedure.[S6] A dry 50 mL round bottomed flask under nitrogen was charged with **1** (58.6 mg, 0.2 mmol), $NaBH_4$ (45.6 mg, 6.00 mmol, 1.2 equiv), methanol (2 mL) and THF (8 mL). The reaction was stirred under a nitrogen atmosphere for 12 hours after which it was quenched with NH_4Cl (sat. aq.) (2 mL) The reaction was diluted with ethyl acetate and the phases were separated. The aqueous phase was extracted with ethyl acetate. The organic layers were rinsed with water and then dried over anhydrous Na_2SO_4. After filtration and concentration under vacuum, the residue was purified by flash chromatography (petroleum ether/ethyl acetate v/v =5:2) to obtain **46** as a white solid in 88% yield (44.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 7.5 Hz, 0.8 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 3.93 (dd, *J* = 11.4 Hz, 7.5 Hz, 1H), 3.93 (dd, *J* = 11.4 Hz, 5.1 Hz, 1H) , 3.27-3.20 (m, 2H), 2.08 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 148.2, 140.0, 135.3, 133.6, 133.1, 129.1, 128.1, 125.6, 125.1, 124.7, 122.4, 117.0, 75.1, 67.3, 35.6. HRMS (ESI): *m/z* calcd for $C_{16}H_{13}NO_2$+H^+ 252.1019 [*M*+H^+]; found: 252.1023.



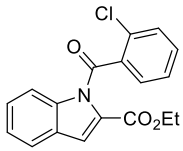
The reduction was conducted according to a reported procedure.[S7] BH_3·Me_2S (200 μL, 0.48 mol, 2.4 equiv., 2.0 M in THF) was added dropwisely to a solution of **1** (58.6 mg, 0.2 mmol) in anhydrous THF (2 mL). The solution was refluxed overnight. Then the mixture was cooled to 0 ℃ and MeOH (4 mL) was added. After stirred for 30 min, organic solvent were removed under vacuum, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) to obtain **47** as a white solid in 90% yield (42.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.16 (m, 3H), 7.13-7.12 (m, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.75-6.72 (m, 2H), 4.58 (d, *J* = 15.0 Hz, 1H), 4.37 (d, *J* = 15.0 Hz, 1H), 3.58 (d, *J* = 11.2 Hz, 1H), 3.52 (d, *J* = 11.2 Hz, 1H), 3.47 (d, *J* = 15.9 Hz, 1H), 3.29(d, *J* = 15.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 143.7, 139.8, 130.1, 128.2, 127.7, 127.6, 124.8, 122.9, 122.2, 121.1, 112.5, 81.6, 67.5, 58.5, 37.3. HRMS (ESI): *m/z* calcd for $C_{16}H_{15}NO$+H^+ 238.1226 [*M*+H^+]; found: 238.1222.

5. Synthesis and characterization of starting materials



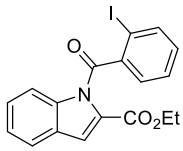
Ethyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R1a**)

R1a was synthesized by **General Procedure 1** on a 10 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (3350.0 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.98 (dd, *J* = 8.4 Hz, 0.7 Hz, 1H), 7.68-7.66 (m, 2H), 7.46-7.43 (m, 1H), 7.35-7.34 (m, 4H), 7.31 (s, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 160.9, 138.8, 137.1, 134.0, 132.4, 130.9, 130.6, 127.8, 127.6, 127.1, 124.2, 122.5, 121.7, 117.4, 115.0, 61.5, 14.1. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}BrNO_3$+Na^+: 394.0049 [*M*+Na^+]; found: 394.0036.



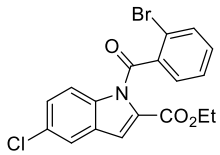
Ethyl 1-(2-chlorobenzoyl)-1H-indole-2-carboxylate (**R1b**)

R1b was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =1:1) yielding a white solid (297.6 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.5 Hz, 0.5 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.49-7.42 (m, 3H), 7.35-7.28 (m, 4H), 7.23(s, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 160.9, 138.8, 135.3. 133.3, 132.4, 130.9, 130.7, 130.3, 127.8, 127.5, 126.6, 124.2, 122.5, 117.3, 115.0, 61.5, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}ClNO_3$+H^+: 328.0735 [*M*+H^+]; found: 328.0743.



Ethyl 1-(2-iodobenzoyl)-1H-indole-2-carboxylate (**R1c**) [S8]

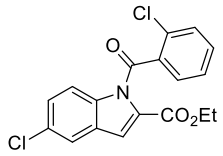
R1c was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (406.6 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.45-7.41 ((td, *J* = 8.2 Hz, 1.2 Hz, 1H), 7.38-7.28 (m, 4H), 7.16 (td, *J* = 7.7 Hz, 1.4 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H).



Ethyl 1-(2-bromobenzoyl)-5-chloro-1H-indole-2-carboxylate (**R2a**)

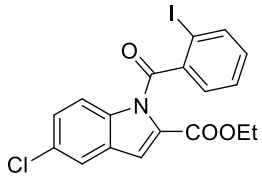
R2a was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =1:1) yielding a white solid (366.0 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J*

= 8.9 Hz, 1H), 7.68-7.66 (m, 1H), 7.65 (d, *J* = 2.0 Hz,, 1H), 7.40 (dd, *J* = 8.9 Hz, 2.1 Hz, 1H), 7.38-7.35 (m, 3H), 7.23(s, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 160.6, 137.0, 136.8, 134.0, 132.6, 132.1, 130.7, 129.8, 128.6, 128.0, 127.2, 121.8, 121.6, 116.2, 116.1, 61.7, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}ClBrNO_3$: 405.9840 [*M*+H^+]; found: 405.9845.



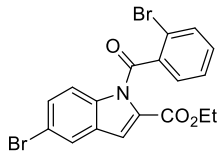
Ethyl 5-chloro-1-(2-chlorobenzoyl)-1H-indole-2-carboxylate (**R2b**)

R2b was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =1:1) yielding a white solid (279.9 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 1.8 Hz, 1H), 7.49-7.44 (m, 2H), 7.98 (dd, *J* = 9.0 Hz, 2.2 Hz, 1H), 7.36-7.29 (m, 2H), 7.23 (d, *J* = 0.6 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 160.6, 137.0, 134.9, 133.3, 132.6, 132.0, 130.7, 130.4, 129.8, 128.6, 128.0, 126.6, 121.8, 116.1, 116.0, 61.7, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}Cl_2NO_3$: 362.0345 [*M*+H^+]; found: 362.0375.



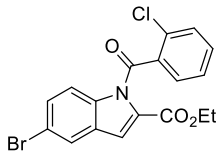
Ethyl 5-chloro-1-(2-iodobenzoyl)-1H-indole-2-carboxylate (**R2c**)

R2c was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (340.2 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.53 (dd, *J* = 8.9 Hz, 1.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.22 (s, 1H), 7.18 (td, *J* = 7.8 Hz, 1.5 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 160.5, 140.8, 140.1, 137.5, 132.6, 132.0, 130.6, 130.4, 129.2, 127.8, 125.0, 117.4, 116.6, 116.0, 94.3, 61.7, 14.1. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}ClINO_3$: 453.9701 [*M*+H^+]; found: 453.9708.



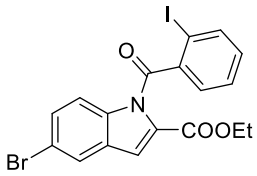
Ethyl 5-bromo-1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R3a**)

R3a was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =15:1) yielding a white solid (297.7 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 1H), 7.80 (m, 1H), 7.67-7.65 (m, 1H), 7.55-7.52 (m, 1H), 7.37-7.35 (m, 3H), 7.22(s, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 159.4, 136.3, 135.7, 132.9, 131.6, 130.8, 129.6, 129.5, 128.1, 126.1, 123.9, 120.5, 116.3, 115.3, 114.9, 60.6, 13.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}Br_2NO_3$: 449.9335 [*M*+H^+]; found: 449.9336.



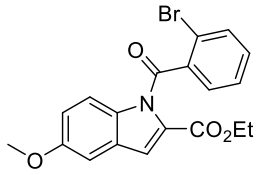
Ethyl 5-bromo-1-(2-chlorobenzoyl)-1H-indole-2-carboxylate (**R3b**)

R3b was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =4:1) yielding a white solid (300.9 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.53 (dd, *J* = 8.9 Hz, 2.0 Hz, 1H), 7.47-7.42 (m, 2H), 7.35-7.28 (m, 2H), 7.23 (d, *J* = 0.6 Hz, 1H),7.22 (s, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ166.3, 160.5, 137.3, 134.9, 133.2, 132.7, 131.8, 130.7, 130.6, 130.4, 129.1, 126.7, 125.0, 117.4, 116.4, 115.8, 61.7, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}ClBrNO_3$: 405.9840 [*M*+H^+]; found: 405.9839.



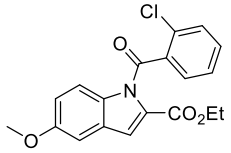
Ethyl 5-bromo-1-(2-iodobenzoyl)-1H-indole-2-carboxylate (**R3c**)

R3c was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (448.3 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.34-7.30 (m, 2H), 7.21 (dd, *J* = 7.6 Hz, 1.4 Hz, 1H), 7.16 (s, 1H), 7.11 (td, *J* = 7.8 Hz, 1.5 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 160.5, 140.8, 140.1, 137.2, 132.6, 132.1, 130.4, 129.8, 128.7, 128.0, 127.8, 121.8, 116.2, 116.1, 94.3, 61.7, 14.1. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}BrINO_3$+Na^+: 519.9016 [*M*+Na^+]; found: 519.9010.



Ethyl 1-(2-bromobenzoyl)-5-methoxy-1H-indole-2-carboxylate (**R4a**)

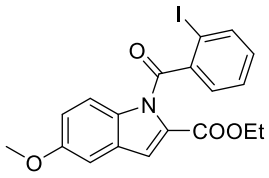
R4a was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (341.9 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* =8.8 Hz, 1H), 7.67-7.65 (m, 1H), 7.35-7.34 (m, 3H), 7.23 (s, 1H), 7.08-7.05 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ167.0, 160.9, 156.8, 137.2, 133.9, 133.7, 132.3, 131.4, 130.5, 128.4, 127.1, 121.6, 117.3, 117.2, 116.1, 104.0, 61.4, 55.7, 14.0. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}BrNO_4$+H^+: 402.0335 [*M*+H^+]; found: 402.0340.



Ethyl 1-(2-chlorobenzoyl)-5-methoxy-1H-indole-2-carboxylate (**R4b**)

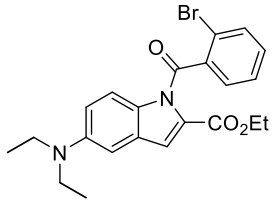
R4b was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum

ether/ethyl acetate v/v =5:1) yielding a white solid (196.8 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.8 Hz, 1H), 7.48-7.40 (m, 2H), 7.36-7.27 (m, 2H), 7.23 (s, 1H), 7.08-7.06 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ166.3, 160.9, 156.9, 135.4, 133.6, 133.2, 132.3, 131.3, 130.6, 130.3, 128.3, 126.5, 117.2, 117.1, 116.0, 104.0, 61.4, 55.7, 14.0. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}ClNO_4$+H^+: 358.0841 [*M*+H^+]; found: 358.0838.



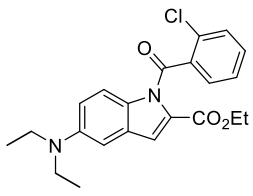
Ethyl 1-(2-iodobenzoyl)-5-methoxy-1H-indole-2-carboxylate (**R4c**)

R4c was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (377.4 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.37 (td, *J* = 7.0 Hz, 1.0 Hz, 1H), 7.28 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.23 (s, 1H), 7.16 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 7.06 (dd, *J* = 9.0 Hz, 2.6 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 160.9, 156.8, 140.6, 140.5, 133.8, 132.3, 131.4, 130.2, 128.4, 127.7, 117.3, 117.3, 117.2, 116.2, 104.0, 94.4, 61.5, 55.7, 14.1. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}INO_4$+H^+: 450.0197 [*M*+H^+]; found: 450.0195.



Ethyl 1-(2-bromobenzoyl)-5-(diethylamino)-1H-indole-2-carboxylate (**R5a**)

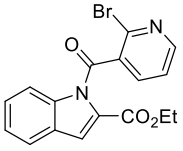
R5a was isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding bright yellow oil (226.1 mg, 51 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.66-7.65 (m, 1H), 7.34-7.32 (m, 3H), 7.17(s, 1H), 6.91 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 3.94 (q, *J* = 7.2 Hz, 4H), 3.38 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ165.7, 160.1, 144.6, 136.5, 132.7, 131.0, 130.3, 129.9, 129.3, 128.0, 126.0, 120.6, 116.9, 114.9, 114.2, 102.5, 60.2, 43.9, 13.0, 11.5. HRMS (ESI): *m/z* calcd for $C_{22}H_{23}BrN_2O_3$+H^+: 443.0965 [*M*+H^+]; found: 443.0969.



Ethyl 1-(2-chlorobenzoyl)-5-(diethylamino)-1H-indole-2-carboxylate (**R5b**)

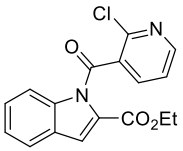
R5b was isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding bright yellow oil (172.9 mg, 43 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.2 Hz, 1H), 7.39 (dd, *J* = 8.1 Hz, 0.7 Hz, 1H), 7.33 (td, *J* = 7.4 Hz, 1.8 Hz, 1H), 7.26 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.21 (dd, *J* = 8.1 Hz, 0.9 Hz, 1H), 7.10 (s, 1H), 6.85 (dd, *J* = 9.2 Hz, 2.1 Hz, 1H), 6.76 (d, *J* = 1.8 Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 4H), 3.32 (q, *J* = 7.1 Hz, 4H), 1.11 (t, *J* = 7.1 Hz, 6H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ166.1, 161.1, 145.6, 135.7, 133.2, 132.0,

131.3, 130.8, 130.5, 130.1, 129.0, 126.5, 117.8, 115.9, 115.3, 103.5, 61.3, 45.0, 14.0, 12.5. HRMS (ESI): *m/z* calcd for $C_{22}H_{23}ClN_2O_3+H^+$: 399.1470 [*M*+H^+]; found: 399.1471.



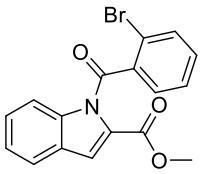
Ethyl 1-(2-bromonicotinoyl)-1H-indole-2-carboxylate (**R6a**)

R6a was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (369.5 mg, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.7 Hz, 1.8 Hz, 1H), 8.15 (d, *J* =8.4 Hz, 1H), 7.75 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 7.70 (d, *J* =7.8 Hz, 1H), 7.52 (dd, *J* =7.3 Hz, 1.1 Hz, 1H), 7.40-7.36 (m, 3H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ166.3, 160.7, 151.6, 139.6, 139.1, 134.9, 130.3, 128.3, 128.3, 127.5, 124.7, 122.7, 122.1, 118.7, 115.2, 61.6, 14.1. HRMS (ESI): *m/z* calcd for $C_{17}H_{13}BrN_2O_3+H^+$: 373.0182 [*M*+H^+]; found: 373.0189.



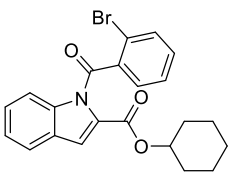
Ethyl 1-(2-chloronicotinoyl)-1H-indole-2-carboxylate (**R6b**)

R6b was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (263.0 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 4.8 Hz, 1.8 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 7.6 Hz, 1.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.50 (td, *J* = 7.8 Hz, 0.9 Hz, 1H), 7.38-7.31(m, 3H), 4.01 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.7, 151.5, 148.8, 139.2, 138.9, 132.3, 130.2, 128.3, 127.5, 124.6, 122.7, 122.0, 118.5, 115.1. HRMS (ESI): *m/z* calcd for $C_{17}H_{13}ClN_2O_3+Na^+$: 351.0507 [*M*+$Na^+$]; found: 351.0494.



Methyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R7**) [S9]

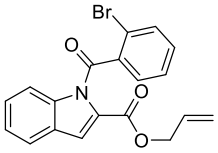
R7 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (293.7 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* =8.4 Hz, 1H), 7.68-7.66 (m, 2H), 7.45 (ddd, *J* =8.4 Hz, 7.2 Hz, 1.1 Hz, 1H), 7.35-7.28 (m, 5H), 3.52 (s, 3H).



Cyclohexyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R8**)

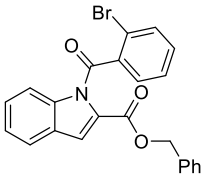
R8 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum

ether/ethyl acetate v/v =5:1) yielding a white solid (359.5 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.4 Hz, 0.5 Hz, 1H), 7.67-7.65 (m, 2H), 7.43 (ddd, *J* = 8.4 Hz, 7.2 Hz, 1.2 Hz, 1H), 7.37-7.31 (m, 4H), 7.28 (d, *J* = 0.3 Hz, 1H), 4.66-4.61 (m, 1H), 1.68-1.61 (m, 4H), 1.51-1.48 (m, 1H), 1.34-1.23 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 160.3, 138.8, 137.3, 133.9, 133.0, 132.3, 131.4, 130.7, 127.6, 127.1, 124.2, 122.4, 121.7, 73.9, 31.2, 25.3, 23.5. HRMS (ESI): *m/z* calcd for $C_{22}H_{20}BrNO_3$+H^+: 426.0699 [*M*+H^+]; found: 426.0709.



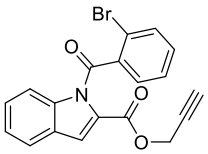
Allyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R9**)

R9 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (315.1 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 2H), 7.45 (td, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.35-7.32 (m, 5H), 5.80-5.72 (m, 1H), 5.27-5.17 (m, 2H), 4.43 (d, *J* = 5.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 138.9, 137.1, 134.0, 132.4, 131.4, 130.6, 130.5, 127.9, 127.5, 127.1, 124.2, 122.5, 121.6, 118.9, 117.8, 115.0, 65.9. HRMS (ESI): *m/z* calcd for $C_{19}H_{14}BrNO_3$+H^+: 384.0230 [*M*+H^+]; found: 384.0226.



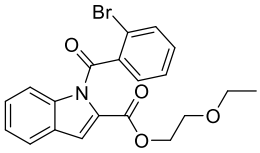
Benzyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R10**)

R10 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (373.5 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62-7.60 (m, 1H), 7.45 (ddd, *J* = 8.4 Hz, 7.4 Hz, 1.0 Hz, 1H), 7.36-7.31 (m, 6H), 7.30-7.28 (m, 2H), 7.26-7.24 (m, 2H), 4.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 160.6, 138.9, 137.1, 135.3, 133.9, 132.4, 130.6, 130.4, 128.6, 128.4, 128.3, 128.0, 127.5, 127.1, 124.3, 122.6, 121.6, 117.9, 115.0, 66.9. HRMS (ESI): *m/z* calcd for $C_{23}H_{16}BrNO_3$+Na^+: 456.0206 [*M*+Na^+]; found: 456.0226.



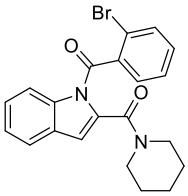
Ethynyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R11**)

R11 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (267.5 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.70-7.66 (m, 2H), 7.46 (ddd, *J* = 8.4 Hz, 7.3 Hz, 1.1 Hz, 1H), 7.41 (s, 1H), 7.38-7.33 (m, 4H), 4.53 (d, *J* = 2.4 Hz, 2H), 2.43 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 159.9, 139.0, 137.0, 134.0, 132.5, 130.7, 129.6, 128.2, 127.4, 127.2, 124.3, 122.7, 121.6, 118.6, 115.0, 76.9, 75.4, 52.7. HRMS (ESI): *m/z* calcd for $C_{19}H_{12}BrNO_3$+H^+: 382.0073 [*M*+H^+]; found: 382.0070.



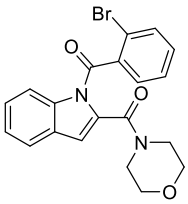
2-Ethoxyethyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R12**)

R12 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (279.7 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.4 Hz,, 0.5 Hz, 1H), 7.68-7.64 (m, 2H), 7.44 (ddd, *J* = 8.5 Hz, 7.2 Hz, 1.2 Hz, 1H), 7.39-7.32 (m, 5H), 4.09 (t, *J* = 5.0, 2H), 3.52 (t, *J* = 5.0, 2H), 3.48 (q, *J* = 7.0 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 160.9, 138.8, 137.1, 133.9, 132.4, 130.7, 130.5, 127.9, 127.6, 127.1, 124.2, 122.6, 121.6, 117.8, 114.9, 67.9, 66.6, 64.5, 15.1. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}BrNO_4$+H^+: 416.0492 [*M*+H^+]; found: 416.0496



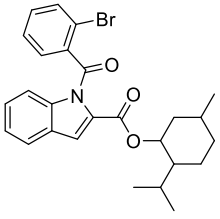
(1-(2-Bromobenzoyl)-1H-indol-2-yl)(piperidin-1-yl) methanone (**R13**)

R13 was synthesized on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:2) yielding a white solid (226.2 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.58-7.55 (m, 2H), 7.49 (br, 1H), 7.43 (td, *J* = 7.4 Hz, 1.3 Hz, 1H), 7.38 (td, *J* = 7.5 Hz, 1.8 Hz, 1H), 7.29-7.25 (m, 2H), 3.52 (t, *J* = 5.2 Hz, 2H), 3.39 (t, *J* = 5.2 Hz, 2H), 1.64-1.48 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.5, 137.1, 136.5, 133.2, 132.9, 132.1, 130.8, 128.8, 127.4, 126.0, 124.1, 121.6, 120.4, 114.9, 111.1, 48.4, 42.6, 25.9, 25.2, 24.5. HRMS (ESI): *m/z* calcd for $C_{21}H_{19}BrN_2O_2$+H^+: 411.0703 [*M*+H^+]; found: 411.0703.



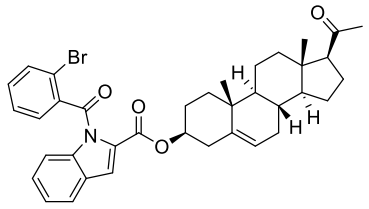
(1-(2-Bromobenzoyl)-1H-indol-2-yl)(morpholino)methanone (**R14**)

R14 was synthesized on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =2:1) yielding a white solid (272.8 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.59 (q, *J* = 3.6, 1H), 7.57 (d, *J* = 2.0, 1H) 7.47-7.40 (m, 3H), 7.30-7.27 (m, 2H), 6.76 (s, 1H), 3.64 (s, 4H), 3.64 (s, 2H), 3.64 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 161.9, 137.1, 136.6, 133.1, 132.3, 132.2, 130.9, 128.6, 127.6, 126.4, 124.2, 121.8, 120.3, 114.8, 111.9, 66.4, 66.2, 47.8, 42.1. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}BrN_2O_3$+H^+: 413.0495 [*M*+H^+]; found: 413.0494.



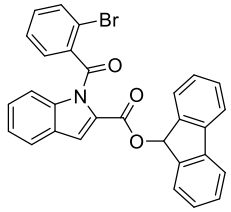
2-Isopropyl-5-methylcyclohexyl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R15**)

R15 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (207.4 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* =8.4 Hz, 1H), 7.67 (d, *J* =7.8 Hz, 1H), 7.65-7.63 (m, 1H), 7.46 (td, *J* =7.8 Hz, 1.0 Hz, 1H), 7.35-7.30 (m, 4H), 7.29 (s, 1H), 1.77 (quintd, *J* =7.8 Hz, 4.4 Hz, 1H), 1.66-1.57 (m, 3H), 1.46-1.38 (m, 2H), 0.97 (qd, *J* =12.6 Hz, 2.4 Hz, 1H), 0.87-0.77 (m, 8H), 0.63 (d, *J* =7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ167.5, 160.3, 139.1, 137.4, 133.9, 132.3, 131.2, 130.6, 127.8, 127.5, 127.1, 124.2, 122.5, 121.7, 117.2, 115.0, 75.5, 46.8, 40.3, 34.1, 31.2, 26.3, 23.4, 22.0, 20.7, 16.4. HRMS (ESI): *m/z* calcd for $C_{26}H_{28}BrNO_3$+H^+: 482.1325 [*M*+H^+]; found: 482.13192.



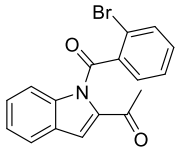
(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R16**)

R16 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (289.2 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.68-7.66 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.36-7.31 (m, 5H), 5.30-5.29 (m, 1H), 4.53-4.45 (m, 1H), 2.53 (t, *J* = 8.8 Hz, 1H), 2.24-2.17 (m, 2H), 2.12 (s, 3H), 2.08-1.97 (m, 3H), 1.82 (dt, *J* = 13.4 Hz, 3.4 Hz, 1H), 1.68-1.43 (m, 10H), 1.26-1.06 (m, 3H), 1.01 (s, 3H), 0.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 167.2, 160.3, 139.4, 138.9, 137.2, 134.0, 132.4, 131.2, 130.8, 127.7, 127.6, 127.2, 124.2, 122.6, 122.5, 121.8, 117.3, 114.9, 75.2, 63.7, 56.8, 49.8, 44.0, 38.8, 37.6, 36.9, 36.6, 31.8, 31.7, 31.6, 27.3, 24.5, 22.8, 21.0, 19.3, 13.2. HRMS (ESI): *m/z* calcd for $C_{37}H_{40}BrNO_4$+H^+: 642.2213 [*M*+H^+]; found: 642.22106.



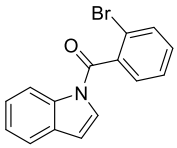
9H-Fluoren-9-yl 1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R17**)

R17 was synthesized by **General Procedure 2** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (320.3 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* =8.5 Hz, 1H), 7.61 (d, *J* =7.5 Hz, 3H), 7.55 (d, *J* =7.7 Hz, 1H), 7.43 (t, *J* =7.8 Hz, 1H), 7.37-7.34 (m, 3H), 7.30-7.23 (m, 4H), 7.21-7.15 (m, 4H), 6.59 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 161.4, 141.4. 141.1, 139.4, 137.3, 134.0, 132.4, 130.5, 130.0, 129.6, 128.2, 127.9, 127.4, 127.1, 126.1, 124.3, 122.7, 121.9, 120.0, 118.8, 114.9, 76.0. HRMS (ESI): *m/z* calcd for $C_{29}H_{18}BrNO_3$+H^+: 508.0543 [*M*+H^+]; found: 508.05361.



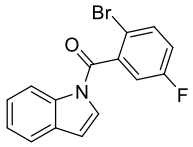
1-(1-(2-Bromobenzoyl)-1H-indol-2-yl)ethan-1-one (**R18**)

R18 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (147.1 mg, 43% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.58-7.56 (m, 1H), 7.41 (ddd, *J* = 8.4 Hz, 7.3 Hz, 1.1 Hz, 1H), 7.29-7.26 (m, 5H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 167.0, 138.4, 137.5, 136.4, 132.8, 131.3, 129.5, 127.5, 126.3, 126.0, 123.1, 121.9, 120.2, 116.6, 113.6, 26.1. HRMS (ESI): *m/z* calcd for $C_{17}H_{12}BrNO_2$+H^+: 342.0124 [*M*+H^+]; found: 342.0123.



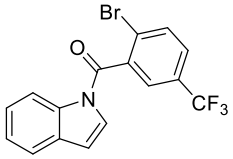
(2-Bromophenyl)(1H-indol-1-yl)methanone (**R19**) [S10]

R19 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a colorless oil (249.1 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.50-7.47 (m, 2H), 7.44-7.38 (m, 2H), 7.33 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.96 (s (br), 1H), 6.61 (d, *J* = 3.8 Hz, 1H).



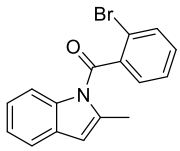
(2-Bromo-5-fluorophenyl)(1H-indol-1-yl)methanone (**R20**)

R20was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =40:1) yielding a white solid (286.3 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s (br), 1H), 7.64 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24-7.20 (m, 1H), 7.13 (td, *J* = 8.5 Hz, 3.0 Hz, 1H), 6.92 (s (br), 1H), 6.62 (d, *J* = 3.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.19, 161.68 (d, *J* =249.4 Hz), 138.40 (d, *J* =27.4 Hz), 135.40, 134.93 (d, *J* =32.2 Hz), 131.09, 126.33, 125.51, 124.66, 121.24, 119.18 (d, *J* =89.4 Hz), 116.58, 116.33 (d, *J* =96.7 Hz), 114.07 (d, *J* =14.3 Hz), 110.35. ^{19}F NMR (375 MHz, $CDCl_3$) δ -112.5. HRMS (ESI): *m/z* calcd for $C_{15}H_9BrFNO$+H^+: 317.9924 [*M*+H^+]; found: 317.9926.



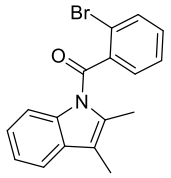
(2-Bromo-5-(trifluoromethyl)phenyl)(1H-indol-1-yl)methanone (**R21**)

R21 was synthesized by **General Procedure 1** on a 2 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =50:1) yielding colorless oil (221.4 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.58 (dd, *J* = 8.4 Hz, 1.9 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.34 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.77 (s, 1H), 6.57 (d, *J* = 3.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 137.9, 135.5, 134.1, 131.2, 130.6 (q, *J* = 3.4 Hz), 128.4 (q, *J* = 3.4 Hz), 126.2, 126.0 (q, *J* = 3.7 Hz), 125.7, 124.9, 123.9, 123.1 (q, *J* = 270.8 Hz), 121.3, 116.8, 110.7. ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.8. HRMS (ESI): *m/z* calcd for $C_{16}H_9BrF_3NO$+H^+: 367.9892 [*M*+H^+]; found: 367.9894.



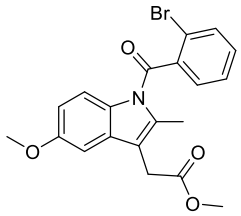
(2-Bromophenyl)(2-methyl-1H-indol-1-yl) methanone **R22**[S9]

R22 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =40:1) yielding colorless oil (94.3 mg, 30% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.48-7.40 (m, 4H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.20 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.11 (td, *J* = 7.8 Hz, 1.2 Hz, 1H), 6.41 (s, 1H), 3.39 (d, *J* = 0.9 Hz, 3H).



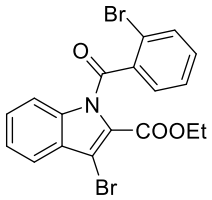
(2-Bromophenyl)(2,3-dimethyl-1H-indol-1-yl) methanone (**R23**) [S10]

R23 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =100:1) yielding colorless oil (98.5 mg, 30% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.45 (m, 2H), 7.43 – 7.38 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.24 (ddd, *J* = 7.8, 7.2, 0.7 Hz, 1H), 7.11 (ddd, *J* = 8.4, 7.2, 1.1 Hz, 1H), 2.20 (s, 6H).



Methyl 2-(1-(2-bromobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**R24**)

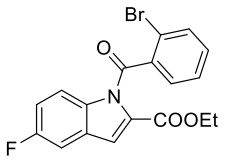
R24 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a yellow oil (149.8 mg, 36% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* =7.8 Hz, 1H), 7.46-7.43 (m, 2H), 7.41-7.38 (m, 1H), 7.21 (d, *J* =9.0 Hz, 1H), 7.94 (d, *J* =2.5 Hz, 1H), 6.72 (dd, *J* =9.0 Hz, 2.5 Hz, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 3.64 (s, 2H), 2.22 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 167.2, 156.6, 138.5, 135.4, 133.5, 132.0, 131.3, 130.4, 129.3, 127.9, 120.2, 115.7, 113.8, 112.0, 101.5, 55.7, 52.2, 30.2, 13.7. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}BrNO_4$+H^+: 416.0492 [*M*+H^+]; found: 416.0492.



Ethyl 3-bromo-1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R25**)

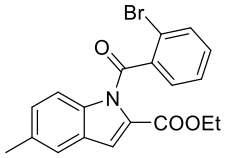
R25 was synthesized by **General Procedure 1** on a 0.9 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a colorless oil (337.0 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.70-7.66 (m, 2H), 7.45 (td, *J* = 7.2 Hz, 1.4 Hz, 1H), 7.41-7.38 (m, 4H), 4.04 (q, *J* = 7.1

Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 160.3, 136.4, 136.3, 134.0, 132.8, 130.7, 128.6, 128.3, 128.2, 127.4, 124.8, 121.6, 121.4, 114.8, 107.1, 62.0, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}Br_2NO_3$+Na^+: 471.9154 [*M*+Na^+]; found: 471.9162



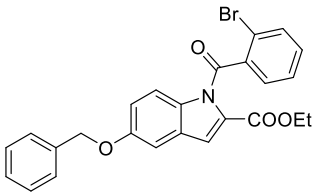
Ethyl 1-(2-bromobenzoyl)-5-fluoro-1H-indole-2-carboxylate (**R26**)

R26 was synthesized by **General Procedure 1** on a 0.6 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (215.4 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 9.2 Hz, 4.6 Hz, 1H), 7.67-7.66 (m, 1H), 7.37-7.34 (m, 3H), 7.32 (dd, *J* = 8.4 Hz, 2.6 Hz, 1H), 7.25 (s, 1H), 7.19 (td, *J* = 9.1 Hz, 2.6 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 160.6, 159.9 (d, *J* = 240.0 Hz), 136.9, 135.1, 134.0, 132.5, 132.3, 130.6, 128.3 (d, *J* = 10.1 Hz), 127.1, 121.6, 116.6 (d, *J* = 4.1 Hz), 116.4 (d, *J* = 9.1 Hz), 116.0 (d, *J* = 25.0 Hz), 107.6 (d, *J* = 23.7 Hz), 61.6, 14.0. ^{19}F NMR (375 MHz, $CDCl_3$) δ -118.3. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}FBrNO_3$+H^+: 390.0136 [*M*+H^+]; found: 390.0131.



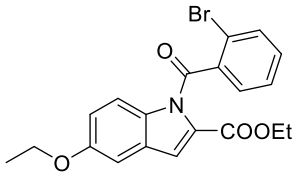
Ethyl 1-(2-bromobenzoyl)-5-methyl-1H-indole-2-carboxylate (**R27**)

R27 was synthesized by **General Procedure 1** on a 0.6 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (171.5 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 1H), 7.67-7.65 (m, 1H), 7.44 (s, 1H), 7.34-7.32 (m, 3H), 7.26 (dd, *J* = 8.4 Hz, 1.0 Hz, 1H), 7.23 (s, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 161.0, 137.2, 137.1, 133.9, 133.9, 132.3, 130.9, 130.5, 129.4, 127.8, 127.1, 122.1, 121.6, 117.3, 114.7, 61.4, 21.3, 14.1. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}BrNO_3$+H^+: 386.0386 [*M*+H^+]; found: 386.0388.



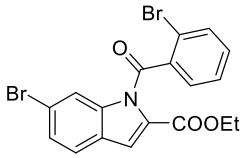
Ethyl 5-(benzyloxy)-1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R28**)

R28 was synthesized by **General Procedure 1** on a 0.8 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (306.2 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.9 Hz, 1H), 7.67-7.65 (m, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.36-7.33 (m, 4H), 7.22 (s, 1H), 7.16-7.15 (m, 2H), 5.13 (s, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.9, 156.0, 137.2, 136.9, 133.9, 133.8, 132.3, 131.4, 130.5, 128.7, 128.4, 128.1, 127.5, 127.1, 121.6, 117.9, 117.3, 116.2, 105.4, 70.6, 61.5, 14.0. HRMS (ESI): *m/z* calcd for $C_{25}H_{20}BrNO_4$+H^+: 478.0648 [*M*+H^+]; found: 478.0645



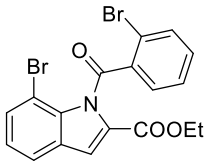
Ethyl 1-(2-bromobenzoyl)-5-ethoxy-1H-indole-2-carboxylate (**R29**)

R29 was synthesized by **General Procedure 1** on a 0.7 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (273.9 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.8 Hz, 1H), 7.67-7.65 (m, 1H), 7.34 (m, 3H), 7.22 (s, 1H), 7.07-7.05 (m, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.9, 156.2, 137.2, 133.9, 133.6, 132.3, 131.3, 130.5, 128.4, 127.1, 121.6, 117.6, 117.3, 116.1, 104.8, 64.0, 61.4, 14.9, 14.0. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}BrNO_4$+H^+: 416.0492 [*M*+H^+]; found: 416.0499.



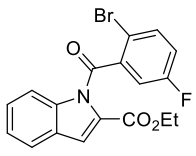
Ethyl 6-bromo-1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R30**)

R30 was synthesized by **General Procedure 1** on a 0.9 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (373.5 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.67-7.65 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.4 Hz, 1.7 Hz, 1H), 7.36-7.32 (m, 3H), 7.25 (s, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 160.5, 139.3, 136.8, 134.0, 132.6, 131.3, 130.6, 127.8, 127.1, 126.3, 123.5, 121.8, 121.7, 118.3, 116.8, 61.6, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}Br_2NO_3$+H^+: 449.9335 [*M*+H^+]; found: 449.9327.



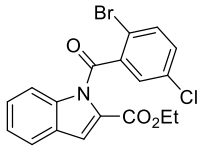
Ethyl 7-bromo-1-(2-bromobenzoyl)-1H-indole-2-carboxylate (**R31**)

R31 was synthesized by **General Procedure 1** on a 2 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (117.3 mg, 13% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.40 (s, 1H), 7.38 (td, *J* = 7.5 Hz, 1.2 Hz, 1H),7.30 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 160.6, 136.2, 135.6, 135.1, 134.0, 133.4, 131.0, 130.6, 129.4, 127.4, 124.2, 123.2, 122.0, 112.6, 105.2, 61.6, 14.1. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}Br_2NO_3$+Na^+: 471.9154 [*M*+Na^+]; found: 471.9156.



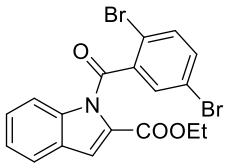
Ethyl 1-(2-bromo-5-fluorobenzoyl)-1H-indole-2-carboxylate (**R32**)

R32 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (296.6 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.5 Hz, 0.6 Hz, 1H), 7.67 (d, *J* =7.9 Hz, 1H), 7.60 (dd, *J* =8.8 Hz, 5.0 Hz, 1H), 7.46 (ddd, *J* =8.4 Hz, 7.3 Hz, 1.2 Hz, 1H), 7.36-7.33 (m, 2H), 7.11 (dd, *J* = 8.2 Hz, 3.0 Hz, 1H), 7.07 (dd, *J* =8.7 Hz, 7.7 Hz, 3.0 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ166.10 (d, *J* =1.0 Hz), 162.45, 161.21 (d, *J* =249 Hz), 160.73, 138.79, 138.67 (d, *J* =6.8 Hz), 135.28 (d, *J* =7.7 Hz), 130.58, 128.07, 127.57, 124.48, 122.62, 119.64 (d, *J* =22.1 Hz), 118.04 (d, *J* =2.8 Hz), 117.78, 115.86 (d, *J* =3.4 Hz), 115.04, 61.55, 14.06. ^{19}F NMR (300 MHz, $CDCl_3$) δ -113.48. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}FBrNO_3$+H^+: 390.0136 [*M*+H^+]; found: 390.0136.



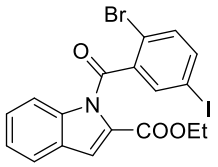
Ethyl 1-(2-bromo-5-chlorobenzoyl)-1H-indole-2-carboxylate (**R33**)

R33 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =2:1) yielding a white solid (394.5 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.5 Hz, 0.6 Hz, 1H), 7.68 (d, *J* =7.8 Hz, 1H), 7.58 (d, *J* =8.5 Hz, 1H), 7.47 (ddd, *J* =8.5 Hz, 7.3 Hz, 1.2 Hz, 1H), 7.37-7.30 (m, 4H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ166.0, 160.8, 138.8, 138.6, 135.0, 133.4, 132.2, 130.6, 130.4, 128.1, 127.6, 124.5, 122.6, 119.5, 118.0, 115.1, 61.6, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}ClBrNO_3$+Na^+: 427.9660 [*M*+Na^+]; found: 427.9669.



Ethyl 1-(2,5-dibromobenzoyl)-1H-indole-2-carboxylate (**R34**)

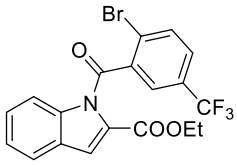
R34 was synthesized by **General Procedure 1** on a 0.5 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (176.0 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.4 Hz, 0.6 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.43-7.37 (m, 3H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.85, 160.78, 138.80, 138.77, 135.21, 135.18, 133.12, 130.61, 128.10, 127.59, 124.54, 122.62, 120.89, 120.32, 118.04, 115.14, 61.62, 14.06. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}Br_2NO_3$+Na^+: 471.9154 [*M*+Na^+]; found: 471.9160.



Ethyl 1-(2-bromo-5-iodobenzoyl)-1H-indole-2-carboxylate (**R35**)

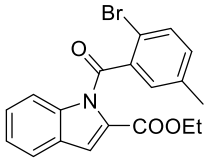
R35 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (433.4 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.65-7.62 (m, 2H), 7.47 (ddd, *J* = 8.4 Hz, 7.3 Hz, 1.2 Hz, 1H), 7.38-7.34 (m, 2H), 7.33 (s, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 160.8, 141.1, 138.9, 138.8, 138.8, 135.4, 130.7, 128.1, 127.6, 124.5, 122.6, 121.5, 118.0, 115.2, 91.4, 61.6, 14.1. HRMS

(ESI): *m/z* calcd for $C_{18}H_{13}BrINO_3$+Na^+: 519.9016 [*M*+Na^+]; found: 519.9017.



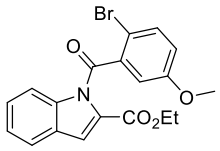
Ethyl 1-(2-bromo-5-(trifluoromethyl)benzoyl)-1H-indole-2-carboxylate (**R36**)

R36 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (220.1 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.4 Hz, 0.7 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.58-7.57 (m, 2H), 7.50 (ddd, *J* = 8.5 Hz, 7.3 Hz, 1.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 0.5 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ166.0, 160.7, 138.9, 138.1, 134.5, 130.4, 129.5, 128.5 (q, *J* =3.2 Hz), 128.3, 127.6, 127.1 (q, *J* =3.7 Hz), 125.9 (q, *J* =270.7 Hz), 125.7, 124.7, 122.7, 118.4, 115.3. ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.9. HRMS (ESI): *m/z* calcd for $C_{19}H_{13}F_3BrNO_3$+H^+: 440.0104 [*M*+H^+]; found: 440.0110.



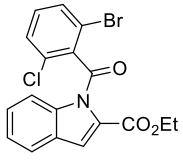
Ethyl 1-(2-bromo-5-methylbenzoyl)-1H-indole-2-carboxylate (**R37**)

R37 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (297.4 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.30 (s, 1H), 7.16-7.15 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 161.0, 138.7, 137.4, 136.7, 133.8, 133.3, 131.1, 131.0, 127.7, 127.6, 124.2, 122.5, 118.4, 117.1, 115.0, 61.5, 20.7, 14.0. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}BrNO_3$+H^+: 386.0386 [*M*+H^+]; found: 386.0379.



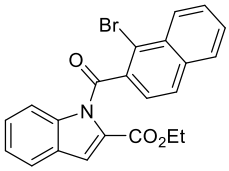
Ethyl 1-(2-bromo-5-methoxybenzoyl)-1H-indole-2-carboxylate (**R38**)

R38 was synthesized by **General Procedure 1** on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (360.0 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 9.6 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 6.89-6.87(m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 160.9, 158.6, 138.6, 137.6, 134.7, 131.1, 127.7, 127.6, 124.3, 122.5, 118.8, 117.2, 115.9, 111.9, 61.5, 55.7, 14.1. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}BrNO_4$+H^+: 402.0335 [*M*+H^+]; found: 402.0330.



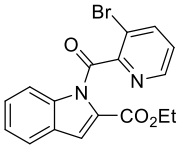
Ethyl 1-(2-bromo-6-chlorobenzoyl)-1H-indole-2-carboxylate (**R39**)

R39 was synthesized on a 1 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =5:1) yielding a white solid (370.1 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.55 (ddd, *J* = 8.4 Hz, 7.3 Hz, 1.1 Hz, 1H), 7.38-7.30 (m, 4H), 4.04 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ166.0, 160.8, 138.8, 138.5, 135.0, 133.4, 132.3, 130.6, 130.3, 128.1, 127.6, 124.5, 122.6, 119.5, 118.1, 115.1, 61.6, 14.0. HRMS (ESI): *m/z* calcd for $C_{18}H_{13}ClBrNO_3$+H^+: 405.9840 [*M*+H^+]; found: 405.9829.



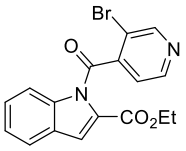
Ethyl 1-(1-bromo-2-naphthoyl)-1H-indole-2-carboxylate (**R40**)

R40 was synthesized by **General Procedure 1** on a 0.5 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =4:1) yielding a white solid (204.8 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* =8.3 Hz, 1H), 8.02 (d, *J* =8.5 Hz, 1H), 7.89-7.86 (m, 2H), 7.69-7.62 (m, 3H), 7.56 (d, *J* =8.4 Hz, 1H), 7.45 (t, *J* =7.8 Hz, 1H), 7.35 (t, *J* =7.6 Hz, 1H), 7.30 (s, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 161.0, 138.6, 135.3, 135.0, 131.8, 131.1, 128.5, 128.3, 128.2, 127.9, 127.9, 127.8, 126.6, 124.3, 122.5, 117.6, 115.3, 61.4, 13.8. HRMS (ESI): *m/z* calcd for $C_{22}H_{17}BrNO_3^+$: 422.0386; found: 422.0394.



Ethyl 1-(3-bromopicolinoyl)-1H-indole-2-carboxylate (**R41**)

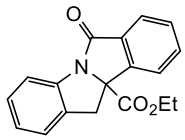
R41 was synthesized by **General Procedure 1** on a 0.5 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =4:1) yielding a white solid (108.2 mg, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* =3.5 Hz, 1H), 8.35 (d, *J* =8.5 Hz, 1H), 8.08 (d, *J* =7.8 Hz, 1H), 7.67 (d, *J* =7.8 Hz, 1H), 7.50 (t, *J* =7.8 Hz, 1H), 7.36-7.33 (m, 2H), 7.27-7.25 (m, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 161.1, 152.0, 146.4, 142.1, 139.3, 131.1, 128.1, 127.6, 126.1, 124.5, 122.5, 120.9, 117.4, 115.8, 61.3, 14.1.HRMS (ESI): *m/z* calcd for $C_{17}H_{13}BrN_2O_3$+H^+: 373.0182 [*M*+H^+]; found: 373.0188.



Ethyl 1-(3-bromoisonicotinoyl)-1H-indole-2-carboxylate (**R42**)

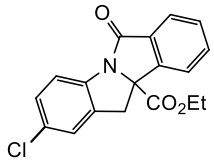
R42 was synthesized by **General Procedure 1** on a 0.5 mmol scale and isolated by flash chromatography (petroleum ether/ethyl acetate v/v =4:1) yielding a white solid (76.5 mg, 41% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.59 (d, *J* =4.9 Hz, 1H), 8.16 (d, *J* =8.5 Hz, 1H), 7.69 (d, *J* =8.5 Hz, 1H), 7.51 (ddd, *J* =8.5 Hz, 7.3 Hz, 1.2 Hz, 1H), 7.39-7.37 (m, 2H), 7.25 (d, *J* =4.9 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 160.6, 153.1, 148.2, 144.0, 138.9, 130.2, 128.5, 127.6, 124.8, 123.5, 122.7, 118.8, 118.7, 115.3, 61.7, 14.0. HRMS (ESI): *m/z* calcd for $C_{17}H_{13}BrN_2O_3$+H^+: 373.0182 [*M*+H^+]; found: 373.0178..

6. Synthesis and characterization of dearomative products



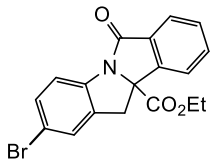
Ethyl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**1**)[S11]

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (X = Br, 56.9 mg, 97%; X = Cl, 77%; X = I, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.67-7.60 (m, 2H), 7.56-7.52 (td, *J* = 7.4 Hz, 1.4 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.23-7.21 (d, *J* = 7.5 Hz, 1H), 7.07 (td, *J* = 7.5 Hz, 0.6 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 15.8 Hz, 1H), 3.32 (d, *J* = 15.8 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).



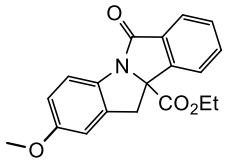
Ethyl 2-chloro-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**2**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (X = Br, 64.9 mg, 99%; X = Cl, 75%; X = I, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 0.9 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.61-7.56 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.30 (d, *J* = 15.8 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ170.8, 166.8, 142.6, 139.7, 136.2, 135.2, 134.0, 133.2, 128.4, 125.3, 125.1, 125.1, 124.3, 116.7, 76.5, 62.8, 38.0, 13.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}ClNO_3$+H^+: 328.0735 [*M*+H^+]; found: 328.0745.



Ethyl 2-bromo-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**3**)

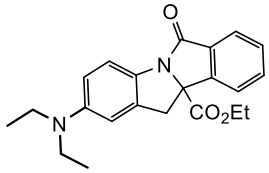
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding colorless oil (X = Br, 68.5 mg, 92%; X = Cl, 80%; X = I, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.65-7.62 (m, 2H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.55 (ddd, *J* = 7.8 Hz, 6.0 Hz, 2.5 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.36 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 16 Hz, 1H), 3.32 (d, *J* = 16 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 168.2, 144.3, 139.1, 136.4, 133.4, 133.0, 131.2, 129.9, 128.3, 125.2, 123.1, 118.0, 117.7, 76.8, 62.8, 37.8, 13.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}BrNO_3$+H^+: 372.0230 [*M*+H^+]; found: 372.0235.



Ethyl 2-methoxy-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**4**)

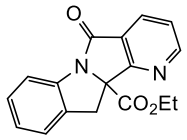
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (X = Br, 59.5 mg, 92%; X = Cl, 71%; X = I, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.64-7.58 (m, 3H), 7.52 (td, *J* = 7.2 Hz, 1.4 Hz, 1H), 6.83-6.80 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.92 (d, *J* = 15.8 Hz, 1H), 3.78 (s, 3H), 3.29 (d, *J* = 15.8 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 168.3, 157.3, 144.4, 135.8, 133.6,

133.4, 132.9, 129.7, 124.9, 122.9, 117.2, 112.7, 111.8, 77.2, 62.5, 55.7, 38.2, 13.9. HRMS (ESI): *m/z* calcd for $C_{19}H_{17}NO_4+H^+$: 324.1230 [*M*+H^+]; found: 324.1238.



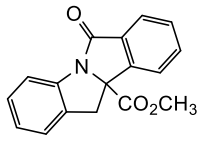
Ethyl 2-(diethylamino)-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**5**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (51.0 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.59-7.54 (m, 2H), 7.51 (td, *J* = 7.5 Hz, 1.2 Hz, 1H), 6.60-6.57 (m, 2H), 4.11 (qd, *J* = 7.1 Hz, 1.6 Hz, 2H), 3.88 (d, *J* = 15.6 Hz, 1H), 3.31 (q, *J* = 7.1 Hz, 4H), 3.25 (d, *J* = 15.6 Hz, 1H), 1.12-1.16 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 168.2, 146.0, 144.4, 135.8, 133.8, 132.6, 129.6, 124.7, 122.7, 117.4, 111.4, 109.3, 77.1, 62.5, 44.8, 38.4, 13.9, 12.5. HRMS (ESI): *m/z* calcd for $C_{22}H_{24}N_2O_3+H^+$: 365.1860 [*M*+H^+]; found: 365.1856.



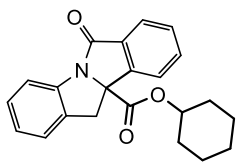
Ethyl 5-oxo-5H-pyrido[2',3':3,4]pyrrolo[1,2-a]indole-11a(11H)-carboxylate (**6**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (X = Br, 50.4 mg, 86%; X = Cl, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.9 Hz, 1.5 Hz, 1H), 8.17 (dd, *J* = 7.7 Hz, 1.5 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 7.7 Hz, 5.0 Hz, 1H), 7.32-7.27 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.19-4.12 (m, 3H), 3.38 (d, *J* = 16.0 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 166.9, 164.2, 153.8, 139.5, 134.3, 133.3, 128.2, 127.6, 125.5, 125.3, 124.5, 116.9, 77.6, 62.9, 35.4, 13.9. HRMS (ESI): *m/z* calcd for $C_{17}H_{14}N_2O_3+H^+$: 295.1077 [*M*+H^+]; found: 295.10779.



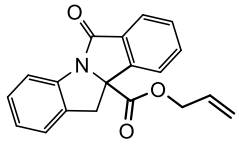
Methyl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**7**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a yellow solid (38.5 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.54 (td, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.09 (td, *J* = 7.5 Hz, 0.8 Hz, 1H), 3.97 (d, *J* = 15.8 Hz, 1H), 3.68 (s, 3H), 3.32 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 168.3, 144.5, 140.0, 134.1, 133.3, 133.2, 129.8, 128.3, 125.2, 125.1, 124.9, 123.1, 116.8, 76.7, 53.5, 38.0. HRMS (ESI): *m/z* calcd for $C_{17}H_{13}NO_3+H^+$: 280.0968 [*M*+H^+]; found: 280.0969.



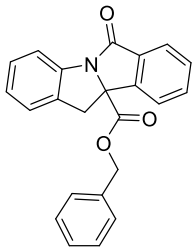
Cyclohexyl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**8**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (64.6 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.6 Hz, 1.1 Hz, 1H), 7.53 (td, *J* = 7.5 Hz, 1.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.08 (td, *J* = 7.5 Hz, 0.8 Hz, 1H), 4.77-4.74 (m, 1H), 3.93 (d, *J* = 15.8 Hz, 1H), 3.33 (d, *J* = 15.8 Hz, 1H), 1.66-1.63 (m, 2H), 1.54-1.48 (m, 2H), 1.43-1.36 (m, 2H), 1.35-1.24 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 168.2, 144.7, 140.1, 134.2, 133.4, 133.0, 129.6, 128.2, 125.1, 125.0, 124.7, 123.0, 116.7, 74.7, 37.9, 30.9, 25.2, 23.0. HRMS (ESI): *m/z* calcd for $C_{22}H_{21}NO_3$+H^+: 348.1594 [*M*+H^+]; found: 348.1594.



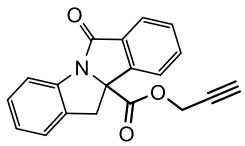
Allyl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**9**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding colorless oil (52.0 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.62 (td, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.54 (td, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.09 (td, *J* = 7.6 Hz, 0.9 Hz, 1H), 5.79-5.71 (m, 1H), 5.13-5.06 (m, 2H), 4.57 (dt, *J* = 5.5 Hz, 1.5 Hz, 1H), 3.98 (d, *J* = 15.8 Hz, 1H), 3.34 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 168.3, 144.4, 140.0, 134.1, 133.3, 133.2, 131.0, 129.8, 128.3, 125.2, 125.1, 124.9, 123.1, 118.4, 116.8, 76.8, 66.6, 38.0. HRMS (ESI): *m/z* calcd for $C_{19}H_{15}NO_3$+H^+: 306.1125 [*M*+H^+]; found: 306.1130.



Benzyl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**10**)

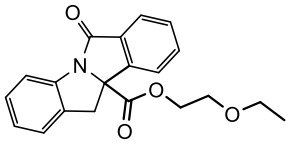
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (59.0 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 3.9 Hz, 2H), 7.55-7.52 (m, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.26-7.23 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.11-7.06 (m, 3H), 5.11 (d, *J* = 3.2 Hz, 2H), 3.96 (d, *J* = 15.8 Hz, 1H), 3.34 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 168.2, 144.2, 140.0, 135.0, 134.1, 133.4, 133.1, 129.8, 128.5, 128.3, 128.3, 127.5, 125.2, 125.1, 124.9, 123.1, 116.8, 76.9, 67.8, 37.9. HRMS (ESI): *m/z* calcd for $C_{23}H_{17}NO_3$+H^+: 356.1281 [*M*+H^+]; found: 356.1273.



Prop-2-yn-1-yl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**11**)

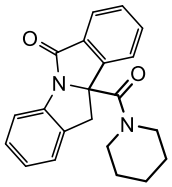
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (34.6 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.63 (td, *J* = 7.2 Hz, 1.0 Hz, 1H), 7.55 (td, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.09 (td, *J* = 7.5 Hz, 0.6 Hz, 1H), 4.72-4.62 (m, 2H), 3.98 (d, *J* = 15.9 Hz, 1H), 3.35 (d, *J* = 15.9 Hz, 1H), 2.42 (t, *J*

= 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 168.3, 144.0, 140.0, 133.9, 133.3, 133.2, 130.0, 128.4, 125.2, 125.2, 124.9, 123.2, 116.9, 76.7, 76.5, 75.8, 53.8, 38.0. HRMS (ESI): *m/z* calcd for $C_{19}H_{13}NO_3$+H^+: 304.0968 [*M*+H^+]; found: 304.0962.



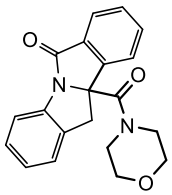
2-Ethoxyethyl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**12**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (60.0 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.62 (td, *J* = 7.5 Hz, 1.1 Hz, 1H), 7.54 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.09 (td, *J* = 7.5 Hz, 1.1 Hz, 1H), 4.29-4.20 (m, 2H), 3.98 (d, *J* = 15.8 Hz, 1H), 3.56-3.47 (m, 2H), 3.36-3.29 (m, 3H), 1.05 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 168.3, 144.4, 140.0, 134.2, 133.3, 133.1, 129.8, 128.3, 125.2, 125.0, 124.8, 123.3, 116.8, 76.9, 67.8, 66.6, 65.6, 38.1, 15.1. HRMS (ESI): *m/z* calcd for $C_{20}H_{19}NO_4$+H^+: 338.1387 [*M*+H^+]; found: 338.1387.



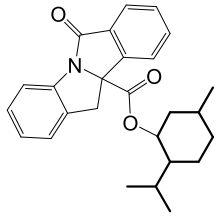
10b-(Piperidine-1-carbonyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (1**3**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (50.5 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.67-7.62 (m, 3H), 7.54 (td, *J* = 7.0 Hz, 1.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.55 (d, *J* = 15.5 Hz, 1H), 3.44 (br, 2H), 3.34 (br, 2H), 3.03 (d, *J* = 15.5 Hz, 1H), 1.45-1.43 (quint, *J* = 0.8 Hz, 2H), 1.32-1.26 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 167.2, 146.8, 139.9, 136.8, 133.7, 132.0, 129.5, 127.7, 125.4, 125.2, 125.1, 123.1, 117.5, 79.7, 46.6, 41.0, 26.0, 24.4. HRMS (ESI): *m/z* calcd for $C_{21}H_{20}N_2O_2$+H^+: 333.1598 [*M*+H^+]; found: 333.1603.



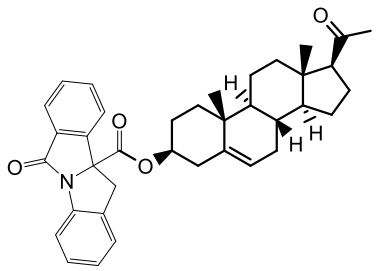
10b-(Morpholine-4-carbonyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**14**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (60.2 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 4.0, 2H), 7.63 (d, J = 7.8, 1H) 7.58-7.55 (m, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 7.7, 1H), 7.14 (t, J = 7.4, 1H), 4.50 (d, J = 15.5, 1H), 3.62-3.58 (m, 2H), 3.41 (m, 6H), 3.07 (d, J = 15.5, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 168.0, 146.4, 139.7, 136.6, 134.0, 131.8, 129.8, 127.9, 125.6, 125.3, 125.2, 123.2, 117.5, 79.5, 66.7, 45.9, 41.0. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}N_2O_3$+H^+: 335.1390 [*M*+H^+]; found: 335.1397.



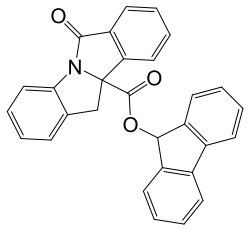
2-Isopropyl-5-methylcyclohexyl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**15**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (37.1mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.68 (dd, *J* = 7.5 Hz, 4.0 Hz, 1H), 7.61 (td, *J* = 7.4 Hz, 0.9 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.57 (td, *J* = 10.9 Hz, 4.4 Hz, 1H), 3.88 (d, *J* =15.6 Hz, 1H), 3.30 (d, *J* =15.6 Hz, 1H), 1.77 (d, *J* =12.2 Hz, 1H), 1.62-1.55 (m, 3H), 1.41-1.37 (m, 1H), 1.31-1.24 (m, 2H), 0.98-0.87 (m, 1H), 0.84-0.79 (m, 4H), 0.66 (d, *J* =6.8 Hz, 3H), 0.45 (d, *J* =6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 167.8, 144.1, 140.0, 134.3, 133.5, 132.9, 129.6, 128.2, 125.1, 124.9, 124.7, 123.2, 116.7, 76.9, 46.8, 40.0, 38.7, 34.0, 31.3,25.8, 23.2, 21.9, 20.5, 15.8. HRMS (ESI): *m/z* calcd for $C_{26}H_{29}NO_3$+H^+: 404.2220 [*M*+H^+]; found: 404.2223.



(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 6-oxo-6H-isoindolo[2,1-a]indole-10b (11H)- carboxylate (**16**)

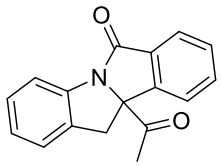
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (99.2 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65-7.60 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.30 (s, 1H), 7.60-7.56 (m, 1H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.32 (d, *J* = 15.8 Hz, 1H), 2.51 (t, *J* = 8.7 Hz, 1H), 2.25-2.16 (m, 3H), 2.11 (s, 3H), 2.03-1.94 (m, 2H), 1.82-1.79 (m, 1H), 1.71-1.60 (m, 5H), 1.58-1.53 (m, 2H), 1.50-1.41 (m, 3H), 1.26-1.18 (m, 1H), 1.15-1.07 (m, 2H), 0.97 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 170.5, 168.3, 144.6, 140.0, 139.1, 134.2, 133.4, 133.1, 129.7, 128.2, 125.1, 125.0, 124.8, 122.9, 122.7, 116.7, 76.9, 76.1, 63.6, 56.8, 49.8, 44.0, 38.7, 37.9, 37.6, 37.5, 36.8, 36.5, 31.7, 31.6, 27.3, 24.5, 22.8, 21.0, 19.3, 13.2. HRMS (ESI): *m/z* calcd for $C_{37}H_{41}NO_4$+H^+: 564.3108 [*M*+H^+]; found: 564.31049.



9H-Fluoren-9-yl 6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**17**)

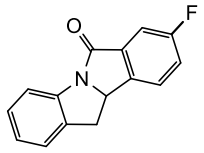
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a yellow solid (43.8 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 7.5 Hz,

3.0 Hz, 2H), 7.61-7.56 (m, 2H), 7.53 (td, *J* = 7.0 Hz, 1.6 Hz, 1H), 7.40-7.37 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.25-7.15 (m, 5H), 7.11 (td, *J* = 7.5 Hz, 0.7 Hz, 1H), 6.72 (s, 1H), 3.93 (d, *J* =15.8 Hz, 1H), 3.34 (d, *J* =15.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 168.1, 144.0, 141.2, 141.0, 141.0, 140.9, 140.0, 133.9, 133.4, 133.1, 129.9, 129.8, 129.7, 128.4, 128.0, 127.9, 125.6, 125.5, 125.2, 124.9, 123.3, 120.2, 116.9, 77.3, 76.9, 38.2. HRMS (ESI): *m/z* calcd for $C_{29}H_{19}NO_3$+H^+: 430.1438 [*M*+H^+]; found: 430.1442.



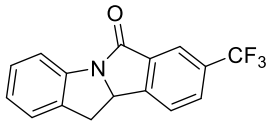
10b-Acetyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**18**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (37.9mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.62 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.56 (td, *J* = 7.5 Hz, 0.7 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.07 (d, *J* = 15.7 Hz, 1H), 3.05 (d, *J* = 15.7 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 169.4, 143.8, 139.5, 135.0, 133.6, 133.3, 129.9, 128.2, 125.4, 125.3, 125.2, 123.2, 116.8, 82.1, 36.0, 24.5. HRMS (ESI): *m/z* calcd for $C_{17}H_{13}NO_2$+H^+ 264.1019 [*M*+H^+]; found: 264.1015.



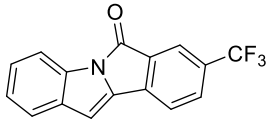
8-Fluoro-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**20**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a yellow solid (47.4 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 7.6 Hz, 2.3 Hz, 1H), 7.49 (dd, *J* = 8.2 Hz, 4.4 Hz, 1H), 7.33-7.25 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 5.59 (t, *J* = 9.4 Hz, 1H), 3.45 (dd, *J* = 15.1Hz, 8.6 Hz, 1H), 3.03 (dd, *J* = 15.1Hz, 10.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.41, 140.38, 136.50, 136.41, 135.90, 128.12, 125.46, 124.75, 124.41, 124.32, 120.16, 119.93, 116.52, 111.66, 111.43, 65.11, 33.85. ^{19}F NMR (300 MHz, $CDCl_3$) δ -112.07. HRMS (ESI): *m/z* calcd for $C_{15}H_{10}FNO$+H^+ 240.0819 [*M*+H^+]; found: 240.0824.



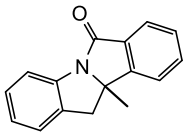
8-(Trifluoromethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**21**)[S12]

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a yellow solid (23.7 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 5.67 (t, *J* = 9.5 Hz, 1H), 3.51 (dd, *J* = 15.1 Hz, 8.7 Hz, 1H), 3.08 (dd, *J* = 15.0 Hz, 10.4 Hz, 1H). ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.4. HRMS (ESI): *m/z* calcd for $C_{16}H_{10}F_3NO$+H^+ 290.0787 [*M*+H^+]; found: 290.0797.



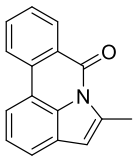
8-(Trifluoromethyl)-6H-isoindolo[2,1-a]indol-6-one (**21A**).

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a yellow solid (18.4 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.31 (td, *J* = 7.7 Hz, 0.9 Hz, 1H), 7.18 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.71 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 137.5, 137.3, 134.3, 134.2, 133.8, 131.0 (q, *J* = 33.0 Hz), 130.7 (q, *J* = 3.6 Hz), 127.2, 124.4, 123.5 (q, *J* = 270.6 Hz), 122.8, 122.4 (q, *J* = 3.7 Hz), 121.4, 113.6, 105.6. ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.7. HRMS (ESI): *m/z* calcd for $C_{16}H_8F_3NO+H^+$ 288.0631 [*M*+H^+]; found: 288.0638.



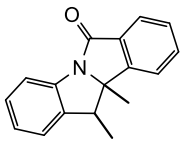
10b-Methyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**22**) [S9]

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a yellow solid (25.4 mg, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.86 (m, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.60 (td, *J* = 7.5 Hz, 1.1 Hz, 1H), 7.49-7.46 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.08 (td, *J* = 7.5 Hz, 0.9 Hz, 1H), 3.10 (d, *J* = 15.1 Hz, 1H), 3.18 (d, *J* = 15.1 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 151.3, 139.5, 135.8, 132.8, 132.7, 128.6, 128.0, 125.7, 125.0, 124.5, 121.9, 117.3, 71.9, 40.4, 27.2.



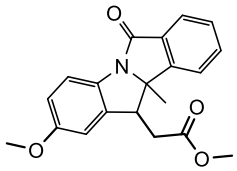
5-Methyl-7H-pyrrolo[3,2,1-de]phenanthridin-7-one (**22A**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a yellow solid (17.6 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.58-7.54 (m, 2H), 7.39 (td, *J* = 7.7 Hz, 0.6 Hz, 1H), 6.51 (s, 1H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 139.2, 132.9, 132.2, 129.3, 127.9, 127.6, 123.8, 122.3, 121.1, 117.1, 116.2, 109.5, 16.0. HRMS (ESI): *m/z* calcd for $C_{16}H_{11}NO+H^+$ 234.0913 [*M*+H^+]; found: 234.0920.



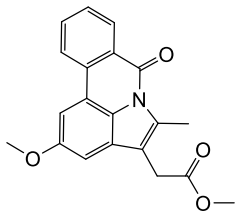
10b, 11-Dimethyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**23**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding yellow oil (21.9 mg, 44% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 1H), 7.63-7.57 (m, 2H), 7.49 (t, *J* = 9.4 Hz, 2H), 7.32-7.27 (m, 1H), 7.16-7.10 (m, 2H), 3.31 (q, *J* = 8.9 Hz, 1H), 1.56 (d, *J* = 8.9 Hz, 3H), 1.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 151.1, 141.1, 138.9, 132.6, 128.7, 128.0, 125.1, 124.7, 123.6, 121.5, 117.2, 75.4, 44.3, 20.8, 11.6. HRMS (ESI): *m/z* calcd for $C_{17}H_{15}NO+H^+$ 250.1226 [*M*+H^+]; found: 250.1234.



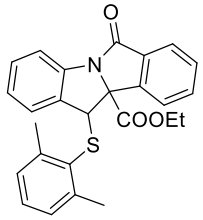
Methyl 2-(2-methoxy-10b-methyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)acetate (**24**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a white solid (19.5 mg, 0.15 mmol, 29% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 7.6 Hz, 1H), 7.59-7.53 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 8.4 Hz, 2.2 Hz, 1H), 6.69 (s, 1H), 3.79-3.78 (m, 6H), 3.75-3.70 (m, 1H), 3.00-2.87 (m, 2H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 167.3, 157.4, 150.0, 140.2, 132.7, 132.5, 132.2, 128.9, 124.9, 122.1, 117.9, 112.2, 111.3, 75.2, 55.7, 52.2, 46.4, 33.0, 21.3. HRMS (ESI): *m/z* calcd for $C_{20}H_{19}NO_4$+H^+ 338.1387 [*M*+H^+]; found: 338.1388.



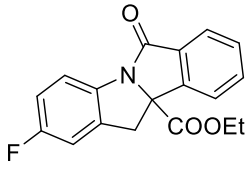
Methyl 2-(2-methoxy-5-methyl-7-oxo-7H-pyrrolo[3,2,1-de]phenanthridin-4-yl)acetate (**24A**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a yellow solid (20.8 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.47 (s, 1H), 7.15 (s, 1H), 3.95 (s, 3H), 3.72 (s, 5H), 2.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 160.0, 157.4, 137.0, 133.9, 132.8, 129.5, 128.6, 128.1, 128.0, 126.4, 122.4, 116.5, 113.8, 105.0, 104.4, 56.2, 52.3, 30.0, 13.3. HRMS (ESI): *m/z* calcd for $C_{20}H_{17}NO_4$+H^+ 336.1230 [*M*+H^+]; found: 336.1232.



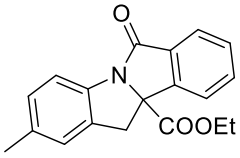
Ethyl 11-((2,6-dimethylphenyl)thio)-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**25A**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a white solid (29.2 mg, 34% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 6.7 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.60-7.58 (m, 3H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.18 (d, *J* = 7.2 Hz, 1H), 5.22 (s, 1H), 4.12 (q, *J* = 6.7 Hz, 2H), 2.11 (s, 6H), 1.13 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 167.6, 144.2, 140.2, 138.9, 134.7, 134.5, 132.4, 130.2, 129.4, 129.0, 128.1, 125.2, 124.7, 124.6, 124.0, 116.7, 80.4, 62.8, 50.8, 21.6, 13.8. HRMS (ESI): *m/z* calcd for $C_{26}H_{23}NO_3S$+H^+ 430.1471 [*M*+H^+]; found: 430.1475.



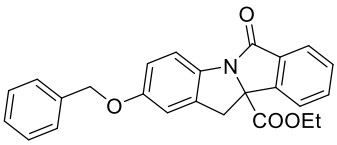
Ethyl 2-fluoro-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**26**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (61.6 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.59-7.53 (m, 3H), 7.81 (ddd, *J* = 7.6 Hz, 6.0 Hz, 2.5 Hz, 1H), 6.93 (td, *J* = 8.8 Hz, 2.5 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.88 (d, *J* = 16.0 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 168.4, 160.3 (d, *J* = 241.6 Hz), 144.4, 136.2, 136.1, 133.3, 133.0, 129.9, 125.1, 123.0, 117.5 (d, *J* = 8.7 Hz), 114.7 (d, *J* = 23.4 Hz), 112.8 (d, *J* = 24.6 Hz), 77.2, 62.7, 38.1(d, *J* = 1.5 Hz), 13.9. ^{19}F NMR (300 MHz, $CDCl_3$) δ -117.8. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}FNO_3$+H^+: 312.1030 [*M*+H^+]; found: 312.1030.



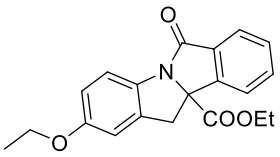
Ethyl 2-methyl-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**27**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (52.8 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.64-7.58 (m, 3H), 7.52 (td, *J* = 7.3 Hz, 1.1 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.03 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.92 (d, *J* = 15.8 Hz, 1H), 3.28 (d, *J* = 15.8 Hz, 1H), 2.31(s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 168.3, 144.5, 137.6, 134.6, 134.3, 133.4, 133.0, 129.7, 128.6, 125.9, 125.0, 122.9, 116.4, 77.0, 62.5, 38.0, 21.1, 13.9. HRMS (ESI): *m/z* calcd for $C_{19}H_{17}NO_3$+H^+: 308.1281 [*M*+H^+]; found: 308.1291.



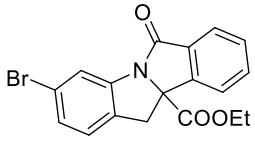
Ethyl 2-(benzyloxy)-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**28**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (69.5 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.63-7.58 (m, 3H), 7.53 (td, *J* = 7.6 Hz, 1.4 Hz, 1H), 7.42-7.37 (m, 4H), 7.32 (t, *J* = 7.1 Hz, 1H), 6.91-6.87 (m, 2H), 5.03(s, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.92 (d, *J* = 15.8 Hz, 1H), 3.29 (d, *J* = 15.8 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 168.4, 156.5, 144.5, 136.9, 135.8, 133.8, 133.4, 133.0, 129.7, 128.6, 128.0, 127.4, 125.0, 122.9, 117.2, 113.8, 112.8, 77.2, 70.6, 62.6, 38.2, 13.9. HRMS (ESI): *m/z* calcd for $C_{25}H_{21}NO_4$+H^+: 400.1543 [*M*+H^+]; found: 400.1541.



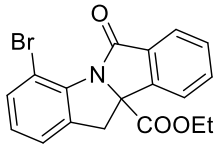
Ethyl 2-ethoxy-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**29**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (58.7 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.62-7.57 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 6.81-6.78 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 15.8 Hz, 1H), 3.27 (d, *J* = 15.8 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 168.3, 156.7, 144.4, 135.8, 133.4, 133.4, 132.9, 129.7, 124.9, 122.9, 117.2, 113.4, 112.4, 77.2, 64.0, 62.5, 38.2, 14.9, 13.9. HRMS (ESI): *m/z* calcd for $C_{20}H_{19}NO_4$+H^+: 338.1387 [*M*+H^+]; found: 338.1386.



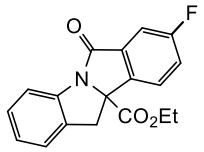
Ethyl 3-bromo-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**30**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (70.7 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.86 (m, 2H), 7.65-7.63 (m, 2H), 7.57-7.53 (m, 1H), 7.20 (dd, *J* = 8.0 Hz, 1.7 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.91 (d, *J* = 16.0 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 168.2, 144.4, 141.2, 133.4, 133.2, 132.8, 129.9, 127.7, 126.3, 125.2, 123.1, 121.6, 120.0, 77.0, 62.8, 37.6, 13.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}BrNO_3$+H^+: 372.0230 [*M*+H^+]; found: 372.0221.



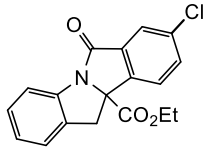
Ethyl 4-bromo-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**31**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (35.0 mg, 0.15 mmol, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.60-7.55 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 4.09-4.04 (m, 2H), 3.81 (d, *J* = 15.7 Hz, 1H), 3.22 (d, *J* = 15.7 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 168.0, 143.7, 140.5, 138.2, 133.3, 132.7, 132.7, 129.9, 126.9, 125.3, 123.9, 122.9, 112.2, 77.8, 62.6, 39.5, 13.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}BrNO_3$+H^+: 372.0230 [*M*+H^+]; found: 372.0233.



Ethyl 8-fluoro-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**32**)

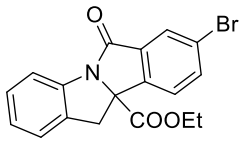
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding colorless oil (61.6 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 7.54 (dd, *J* = 7.4 Hz, 2.4 Hz, 1H), 7.31 (td, *J* = 8.4 Hz, 2.2 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.10 (td, *J* = 7.5 Hz, 0.8 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.31 (d, *J* = 15.8 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.96, 166.92, 163.74 (d, *J* =248.8 Hz), 140.02 (d, *J* =2.4 Hz), 139.76, 135.70 (d, *J* =8.4 Hz), 134.10, 128.33, 125.15 (d, *J* =23.8 Hz), 124.74, 124.67, 120.53 (d, *J* =23.8 Hz), 116.73, 111.79 (d, *J* =23.8 Hz), 76.44, 62.69, 38.03, 13.89. ^{19}F NMR (375 MHz, $CDCl_3$) δ 110.38. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}FNO_3$+H^+: 312.1030 [*M*+H^+]; found: 312.1035.



Ethyl 8-chloro-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**33**)

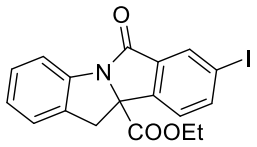
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding colorless oil (60.9 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.83 (m, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.61-7.56 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.09 (td, *J* = 7.5 Hz, 0.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.30 (d, *J* = 15.8 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 166.7, 142.6, 136.2, 139.7, 135.2, 134.0, 133.2, 128.3, 125.3, 125.1, 125.0, 124.3, 116.7, 76.5, 62.8, 38.0, 13.9. HRMS (ESI): *m/z* calcd for

$C_{18}H_{14}ClNO_3$+H^+: 328.0735 [*M*+H^+]; found: 328.0742.



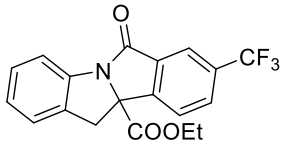
Ethyl 8-bromo-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**34**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (72.2 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.0 (d, *J* = 1.7 Hz, 1H), 7.73 (dd, *J* = 8.1 Hz, 1.8 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.10 (td, *J* = 7.5 Hz, 0.7 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.31 (d, *J* = 15.8 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 165.6, 142.1, 138.6, 135.0, 134.3, 133.0, 127.3, 127.1, 124.2, 124.1, 123.5, 123.0, 114.7, 75.6, 61.8, 36.9, 12.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}BrNO_3$+H^+: 372.0230 [*M*+H^+]; found: 372.0222.



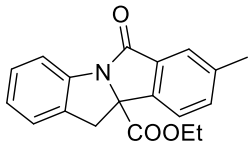
Ethyl 8-iodo-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**35**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =20:1) yielding a white solid (29.3 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (m, 1H), 7.86 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.86 (d, *J* = 15.7 Hz, 1H), 3.23 (d, *J* = 15.7 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 166.5, 143.8, 141.8, 139.6, 135.3, 134.1, 134.0, 128.4, 125.3, 125.1, 124.8, 116.8, 95.2, 76.7, 62.8, 37.9, 13.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}INO_3$+H^+: 420.0091 [*M*+H^+]; found: 420.0092.



Ethyl 6-oxo-8-(trifluoromethyl)-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**36**)

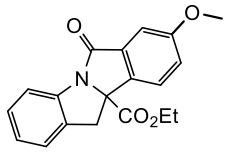
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (52.0 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.98 (d, *J* = 15.8 Hz, 1H), 3.35 (d, *J* = 15.8 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.48, 166.60, 147.57, 139.59, 134.33, 133.80, 132.55 (q, *J* = 33.5 Hz, 1H), 129.97 (q, *J* = 3.5 Hz), 128.48, 125.29, 125.25, 123.83, 123.49 (q, *J* = 271.0 Hz), 122.29 (q, *J* = 3.8 Hz), 116.84, 76.84, 62.98, 37.95, 13.88. ^{19}F NMR (300 MHz, $CDCl_3$) δ -62.5. HRMS (ESI): *m/z* calcd for $C_{19}H_{14}F_3NO_3$+H^+: 362.0999 [*M*+H^+]; found: 290.0797.



Ethyl 8-methyl-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**37**)

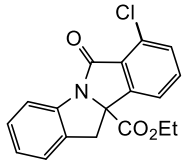
Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (60.8 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.68 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.30

(t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.28 (d, *J* = 15.8 Hz, 1H), 2.45 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 168.5, 141.9, 140.1, 140.0, 134.3, 134.1, 133.4, 128.2, 125.2, 125.1, 124.7, 122.7, 116.7, 76.6, 62.5, 38.0, 21.4, 13.9. HRMS (ESI): *m/z* calcd for $C_{19}H_{17}NO_3$+H^+: 308.1281 [*M*+H^+]; found: 308.1278.



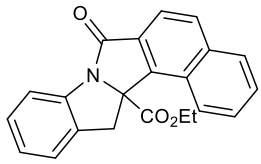
Ethyl 8-methoxy-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**38**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding colorless oil (50.4 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.15 (dd, *J* = 8.4 Hz, 2.5 Hz, 1H), 7.08 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.92 (d, *J* = 15.7 Hz, 1H), 3.87 (s, 3H), 3.28 (d, *J* = 15.7 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 168.2, 161.2, 140.0, 136.8, 134.9, 134.4, 128.2, 125.2, 124.8, 123.9, 121.1, 116.7, 107.7, 76.4, 62.5, 55.8, 38.0, 13.9. HRMS (ESI): *m/z* calcd for $C_{19}H_{17}NO_4$+H^+: 324.1230 [*M*+H^+]; found: 324.1235.



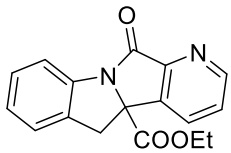
Ethyl 7-chloro-6-oxo-6H-isoindolo[2,1-a]indole-10b(11H)-carboxylate (**39**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding colorless oil (56.3 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 0.9 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.61-7.56 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.30 (d, *J* = 15.8 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ170.8, 166.8, 142.6, 139.7, 136.2, 135.2, 134.0, 133.2, 128.4, 125.3, 125.1, 125.1, 124.3, 116.7, 76.5, 62.8, 38.0, 13.9. HRMS (ESI): *m/z* calcd for $C_{18}H_{14}ClNO_3$+H^+: 328.0735 [*M*+H^+]; found: 328.07343.



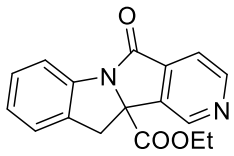
Ethyl 7-oxo-7H-benzo[6,7]isoindolo[2,1-a]indole-13a(13H)-carboxylate (**40**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding yellow oil (58.4 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.14 (m, 1H), 8.01-7.99 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.68-7.65 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.11 (td, *J* = 7.5 Hz, 0.8 Hz, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 4.08-4.00 (m, 2H), 3.41 (d, *J* = 15.6 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 169.4, 144.1, 139.4, 136.0, 134.0, 131.4, 130.7, 129.3, 128.4, 128.2, 127.9, 127.3, 125.4, 124.8, 124.4, 62.7, 36.4, 13.8. HRMS (ESI): *m/z* calcd for $C_{22}H_{17}NO_3$+H^+: 344.1281 [*M*+H^+]; found: 344.1290.



Ethyl 11-oxo-5H-pyrido[3',2':3,4]pyrrolo[1,2-a]indole-4b(11H)-carboxylate (**41**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (31.1 mg, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.6 Hz, 1H), 8.04 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.51 (dd, *J* = 7.8 Hz, 4.8 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 15.7 Hz, 1H), 3.34 (d, *J* = 15.7 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 165.8, 152.4, 151.2, 139.6, 139.0, 133.5, 131.5, 128.5, 126.4, 125.3, 125.2, 117.1, 74.5, 63.0, 38.1, 13.9. HRMS (ESI): *m/z* calcd for $C_{17}H_{14}N_2O_3+H^+$ 295.1077 [*M*+H^+]; found: 295.1076.



Ethyl 5-oxo-5H-pyrido[3',4':3,4]pyrrolo[1,2-a]indole-11a(11H)-carboxylate (**42**)

Purification by flash chromatography (petroleum ether/ethyl acetate v/v =10:1) yielding a white solid (34.6 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.87 (d, *J* = 4.8 Hz, 1H), 7.78 (d, *J* = 4.8 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.26-7.25 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 15.8 Hz, 1H), 3.39 (d, *J* = 15.8 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 165.9, 151.0, 145.3, 141.4, 139.2, 138.6, 134.0, 128.5, 125.5, 125.4, 118.5, 116.9, 76.4, 63.1, 37.9, 13.9. HRMS (ESI): *m/z* calcd for $C_{17}H_{14}N_2O_3+H^+$ 295.1077 [*M*+H^+]; found: 295.1078.

7. Supplementary References

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[S9] Shen, C.; Liu, R.-R.; Fan, R.-J.; Li, Y.-L.; Xu, T.-F.; Gao, J.-R.; Jia, Y.-X. Enantioselective Arylative Dearomatization of Indoles via Pd-Catalyzed Intramolecular Reductive Heck Reactions. *J. Am. Chem. Soc*. **2015**, 137, 4936– 4939.

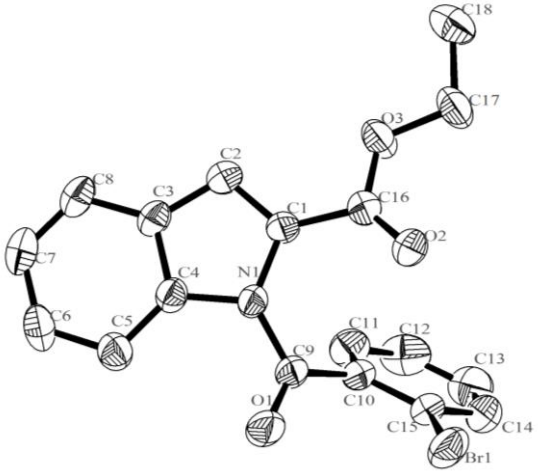
[S10] Petrone, D. A.; Yen, A.; Zeidan, N.; Lautens, M. Dearomative Indole Bisfunctionalization via a Diastereoselective Palladium-Catalyzed Arylcyanation. *Org. Lett.* **2015**, 17, 4838– 4841.

[S11] Qin, X.; Lee, M. W. Y.; Zhou, J. S. Nickel-Catalyzed Asymmetric Reductive Heck Cyclization of Aryl Halides to Afford Indolines. *Angew. Chem., Int. Ed*. **2017**, 56, 12723– 12726.

[S12] Yu, D.; To, W.-P.; Liu, Y.; Wu, L.-L.; You, T.; Ling, J.; Che, C.-M. Direct Photo-Induced Reductive Heck Cyclization of Indoles for the Efficient Preparation of Polycyclic Indolinyl Compoounds. *Chem. Sci.* **2021**, 12, 14050– 14058.

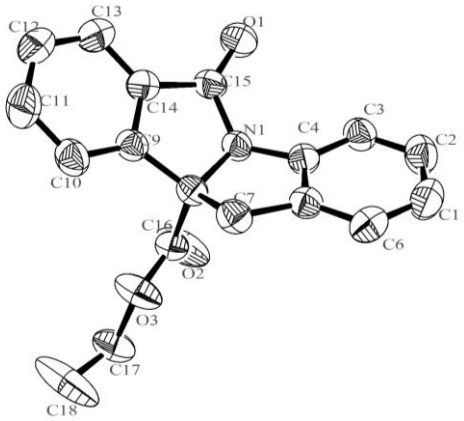
8. X-ray crystal structure data of compounds R1a and 1

8.1 X-ray crystallographic data of **R1a** (CCDC 2183419)



Bond precision:	C-C = 0.0069Å	Wavelength=1.54184	
Cell:	a=7.8811(6)	b=10.3618(5)	c=10.9560(8)
	alpha=66.055(6)	beta=78.039(6)	gamma=88.232(5)
Temperature:	293 K		
	Calculated	Reported	
Volume	798.52(10)	798.52(10)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	$C_{18}H_{14}BrNO_3$	$C_{18}H_{14}BrNO_3$	
Sum formula	$C_{18}H_{14}BrNO_3$	$C_{18}H_{14}BrNO_3$	
Mr	372.20	372.21	
Dx,g cm^{-3}	1.548	1.548	
Z	2	2	
Mu (mm^{-1})	3.635	3.635	
F000	376.0	376.0	
F000	375.61		
h, k, lmax	9, 12, 13	9, 12, 13	
Nref	3199	3096	
Tmin, Tmax	0.489, 0.559	0.460, 1.000	
Tmin’	0.444		
Correction method= # Reported T Limits: Tmin=0.460 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.968		heta(max)= 73.234	
R(reflections)= 0.0673(2967)		wR2(reflections)= 0.1707(3096)	
S = 1.029		Npar= 209	
Displacement ellipsoids are drawn at 50% probability level			

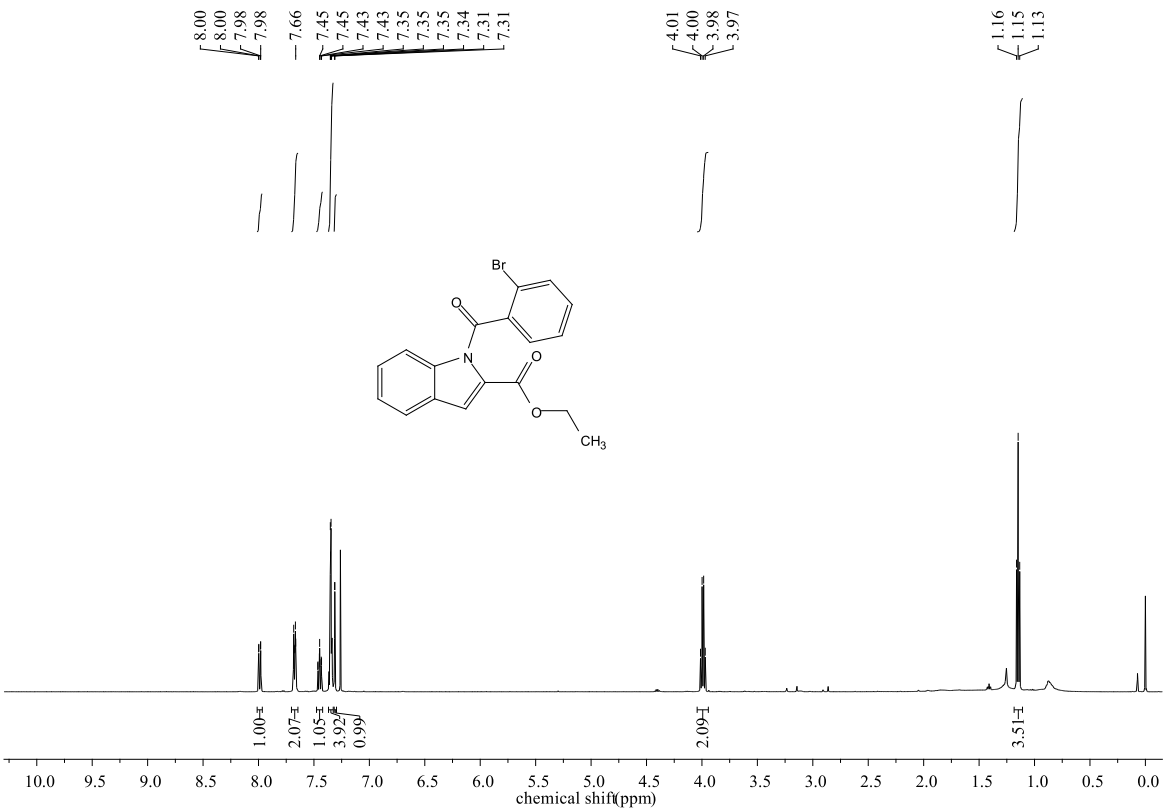
8.2 X-ray crystallographic data of **1** (CCDC 2162244)



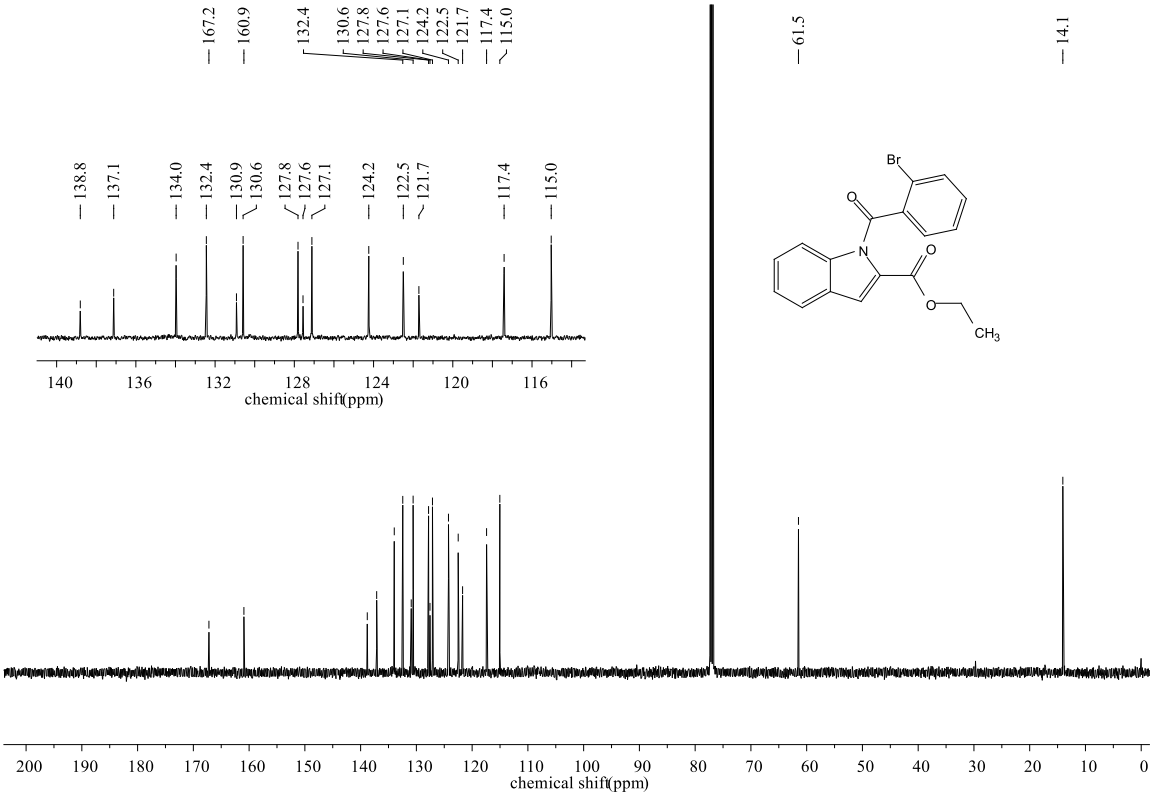
Bond precision:	C-C = 0.0078Å	Wavelength=1.54184	
Cell:	a=8.9025(3)	b=5.6087(2)	c=15.0571(5)
	alpha=90	beta=100.429(3)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	739.40(4)	739.40(5)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	$C_{18}H_{15}NO_3$	$C_{18}H_{15}NO_3$	
Sum formula	$C_{18}H_{15}NO_3$	$C_{18}H_{15}NO_3$	
Mr	293.31	293.31	
Dx,g cm^{-3}	1.317	1.317	
Z	2	2	
Mu (mm^{-1})	0.734	0.734	
F000	308.0	308.0	
F000	308.96		
h, k, lmax	11, 6, 18	10, 6, 18	
Nref	2925 [1620]	2660	
Tmin, Tmax	0.845,0.870	0.829, 1.000	
Tmin’	0.845		
Correction method= # Reported T Limits: Tmin= 0.829 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 1.64/0.91		heta(max)= 72.752	
R(reflections)= 0.0621(2612)		wR2(reflections)= 0.1862(2660)	
S = 1.043		Npar= 200	
Displacement ellipsoids are drawn at 50% probability level			

9. NMR Spectra of related compounds

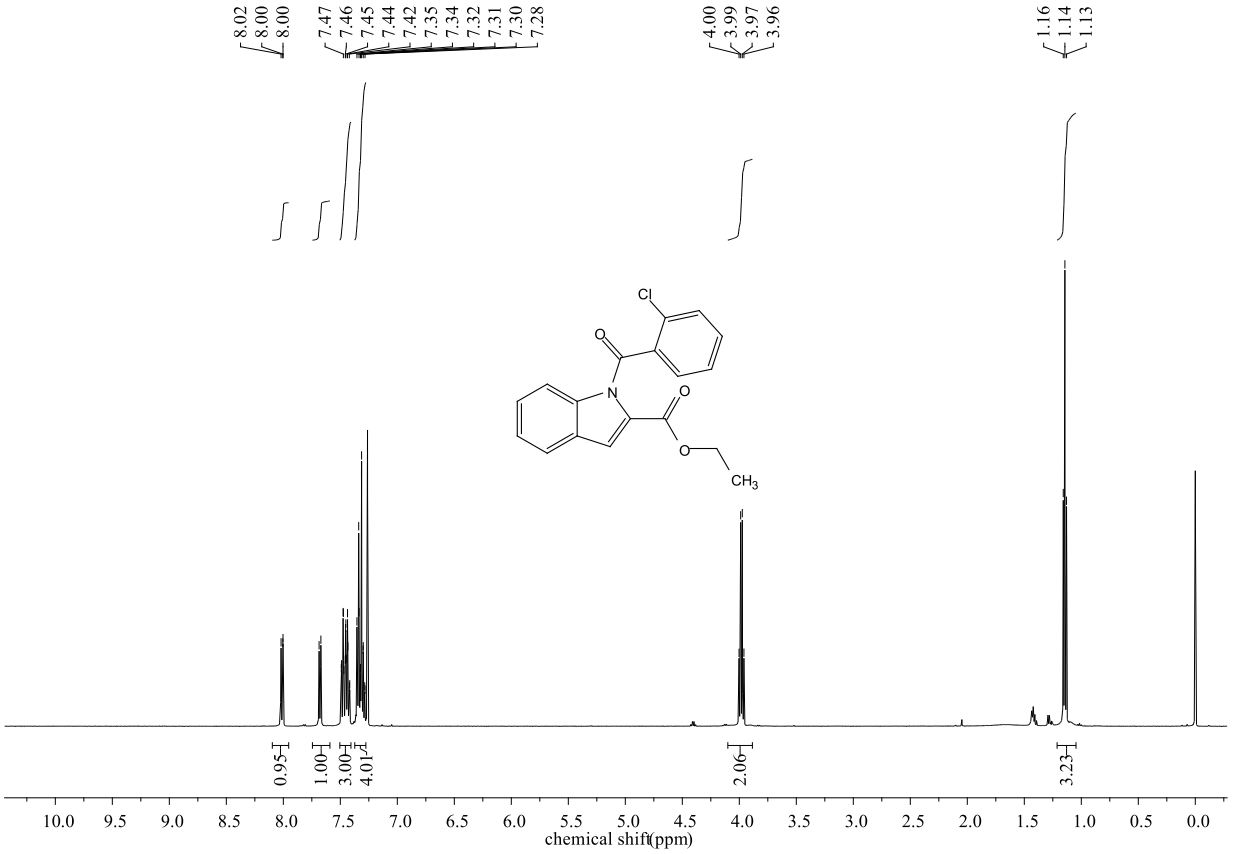
^{1}H NMR Spectra of compound **R1a** (500 MHz, $CDCl_3$)



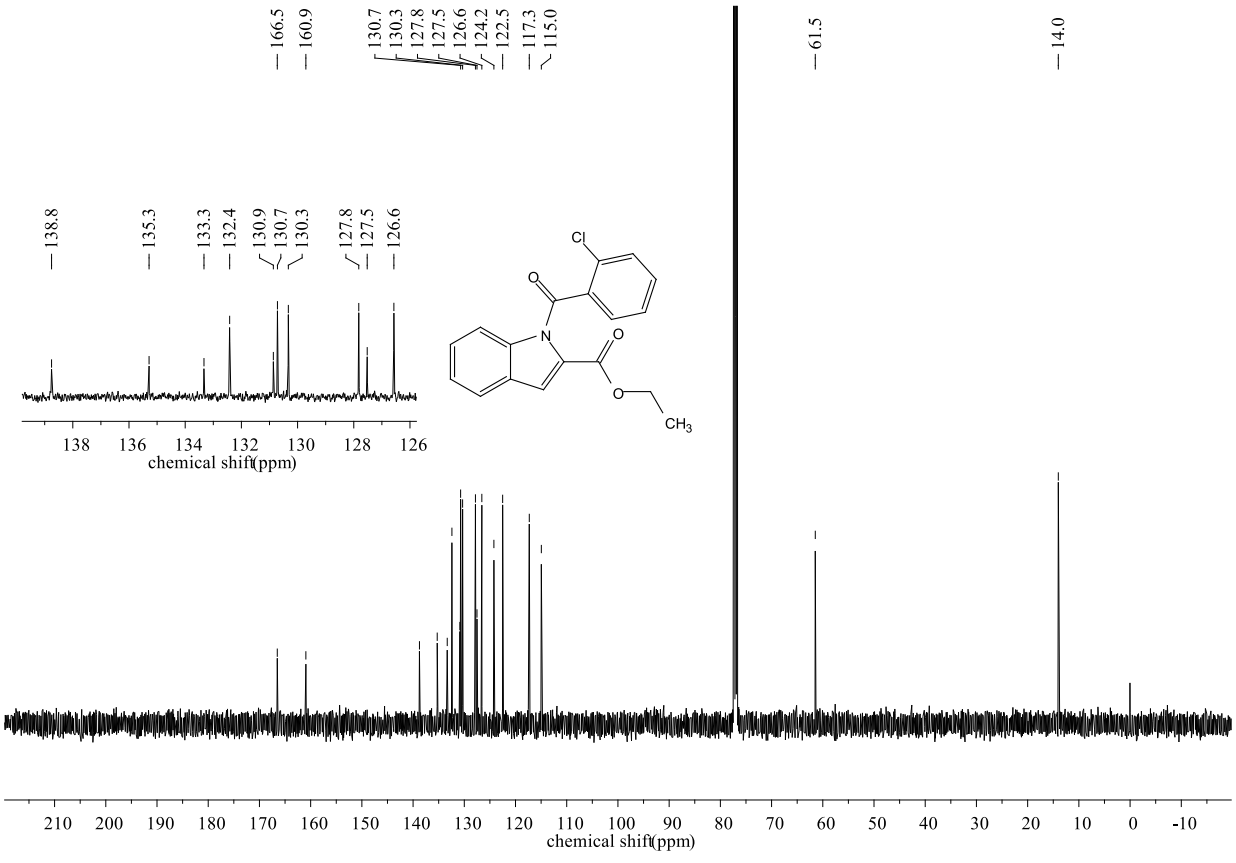
^{13}C NMR Spectra of compound **R1a** (125 MHz, $CDCl_3$)



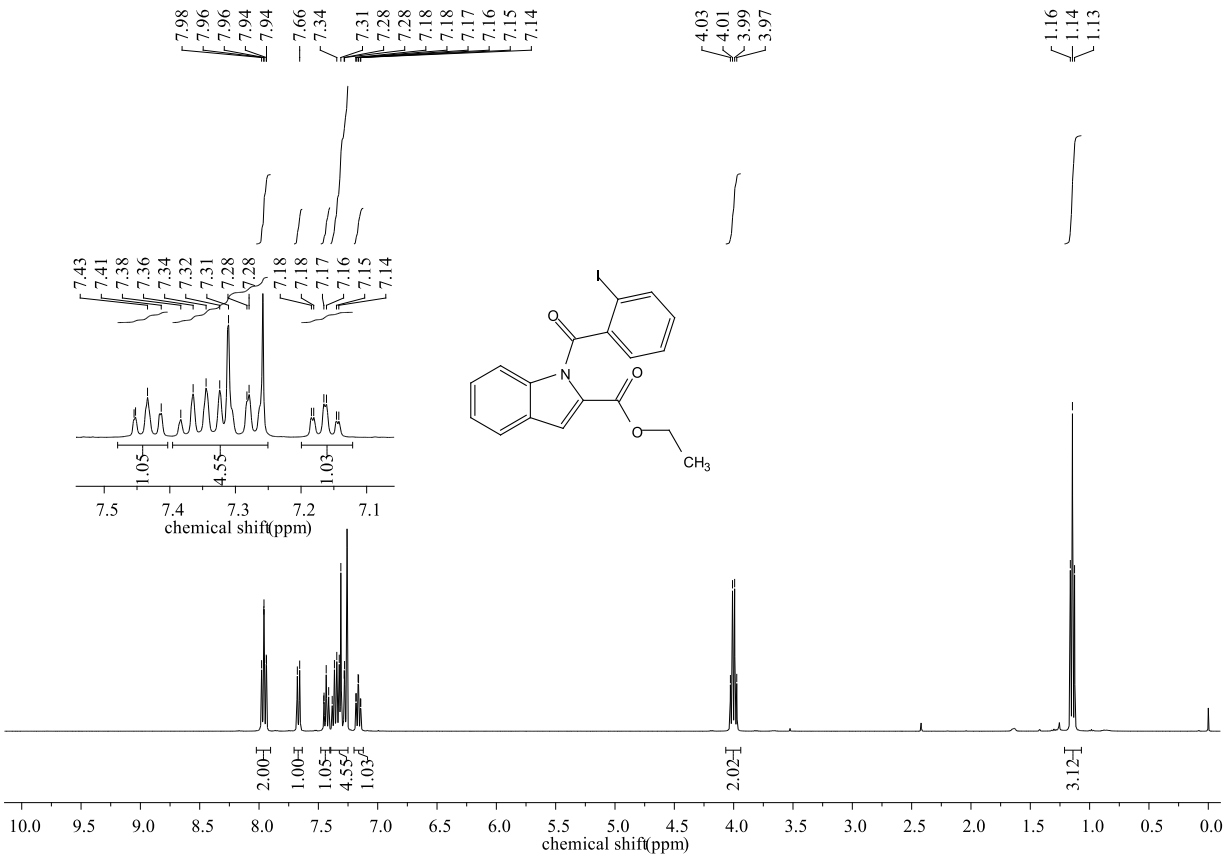
^{1}H NMR Spectra of compound **R1b** (500 MHz, $CDCl_3$)



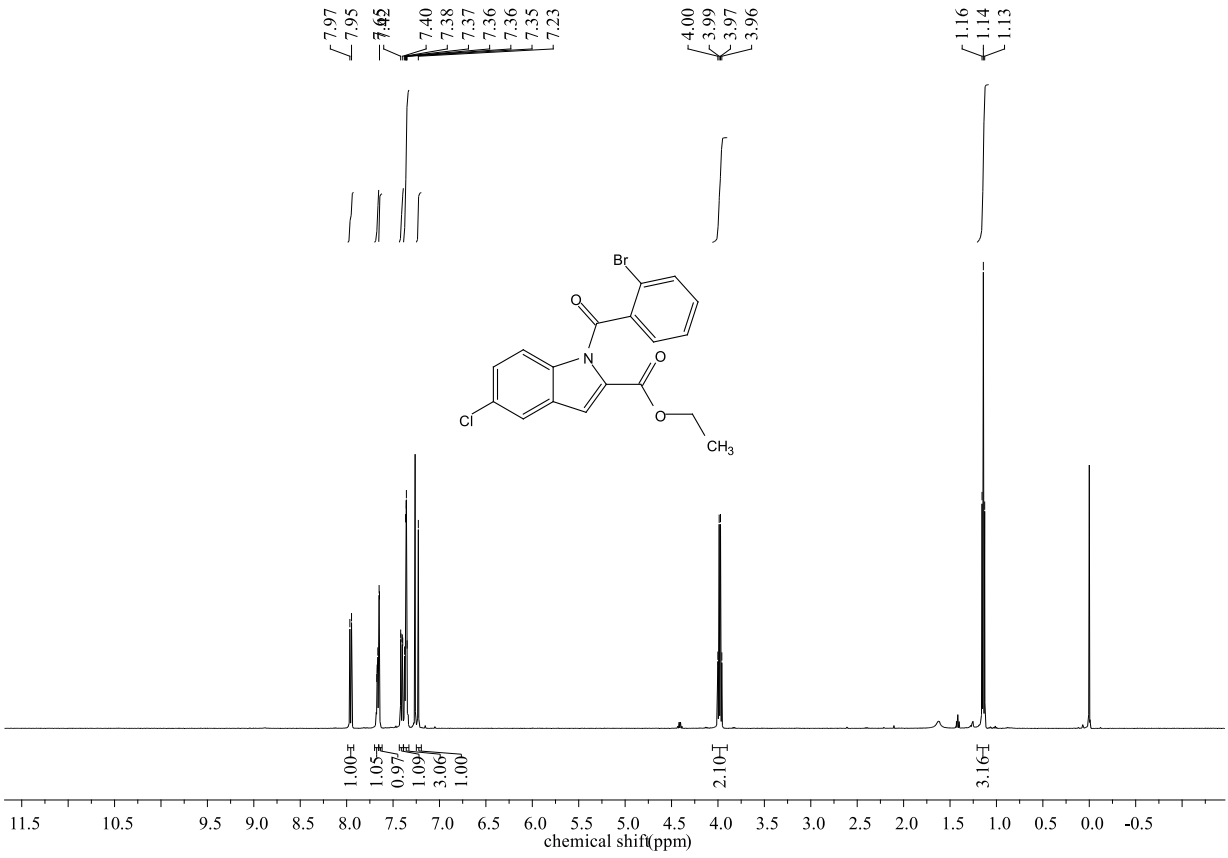
^{13}C NMR Spectra of compound **R1b** (125 MHz, $CDCl_3$)



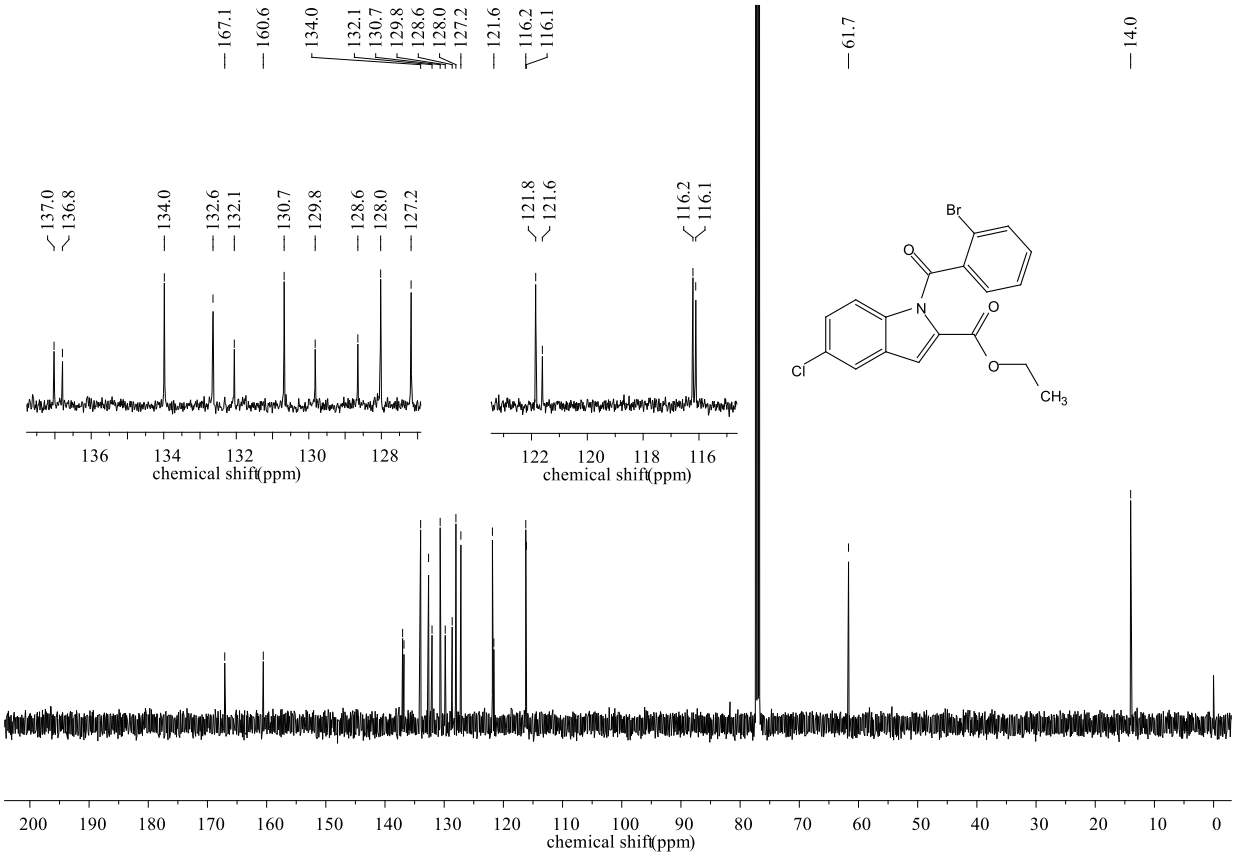
^{1}H NMR Spectra of compound **R1c** (400 MHz, $CDCl_3$)



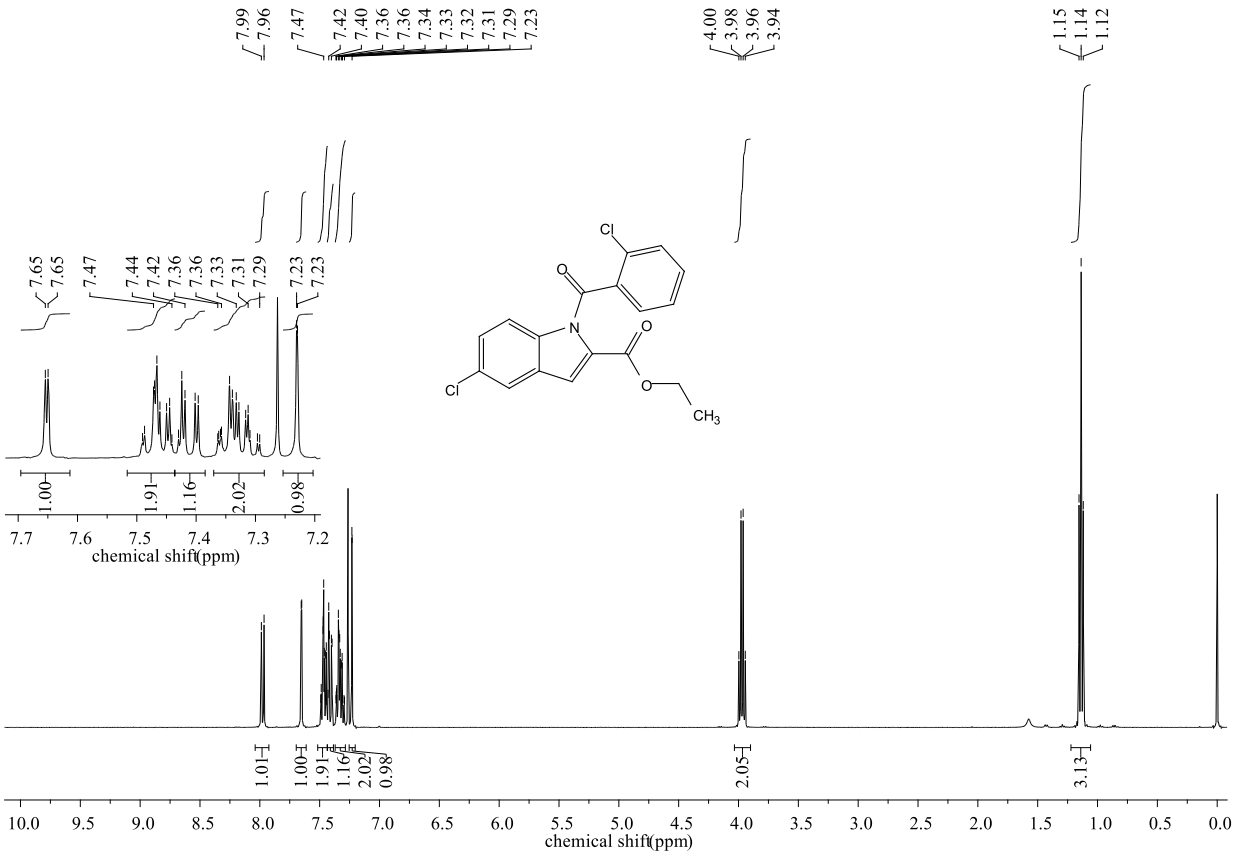
^{1}H NMR Spectra of compound **R2a** (500 MHz, $CDCl_3$)



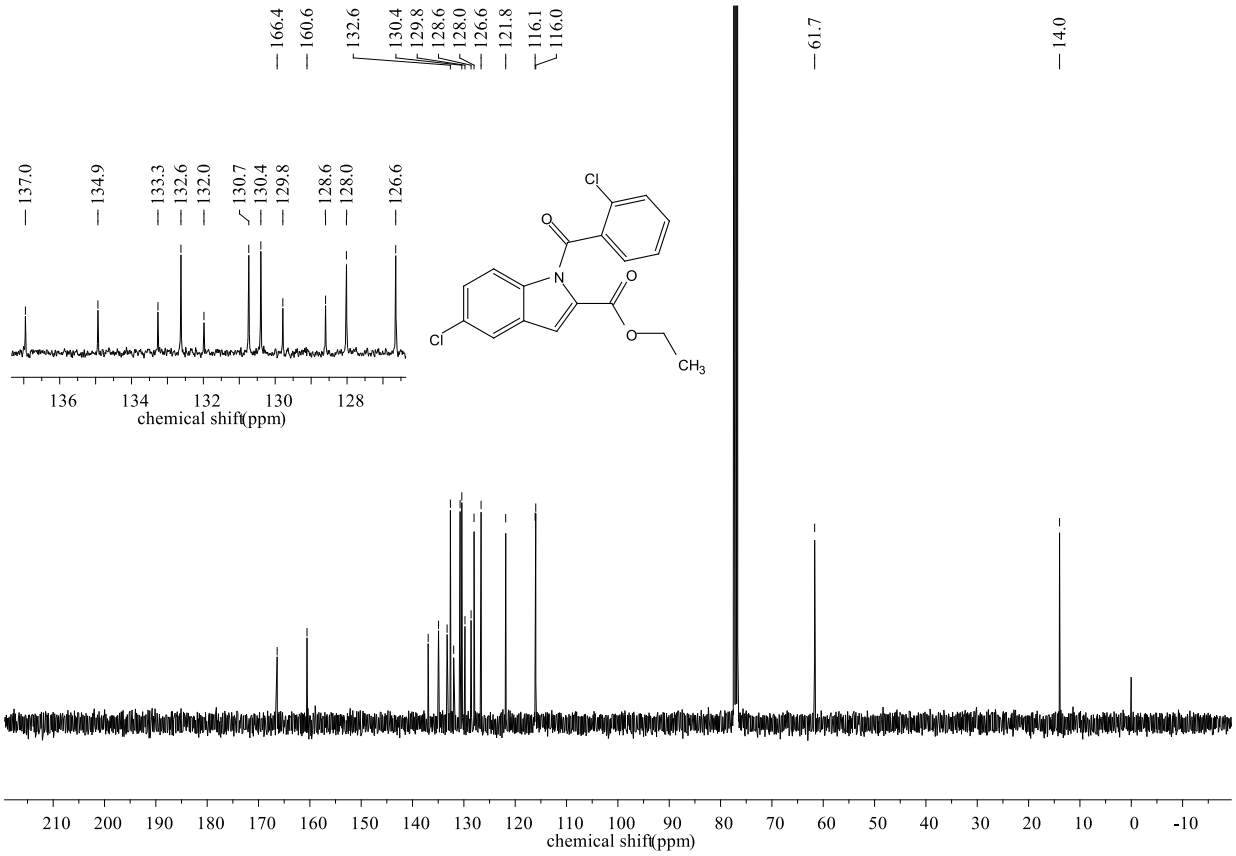
^{13}C NMR Spectra of compound **R2a** (125 MHz, $CDCl_3$)



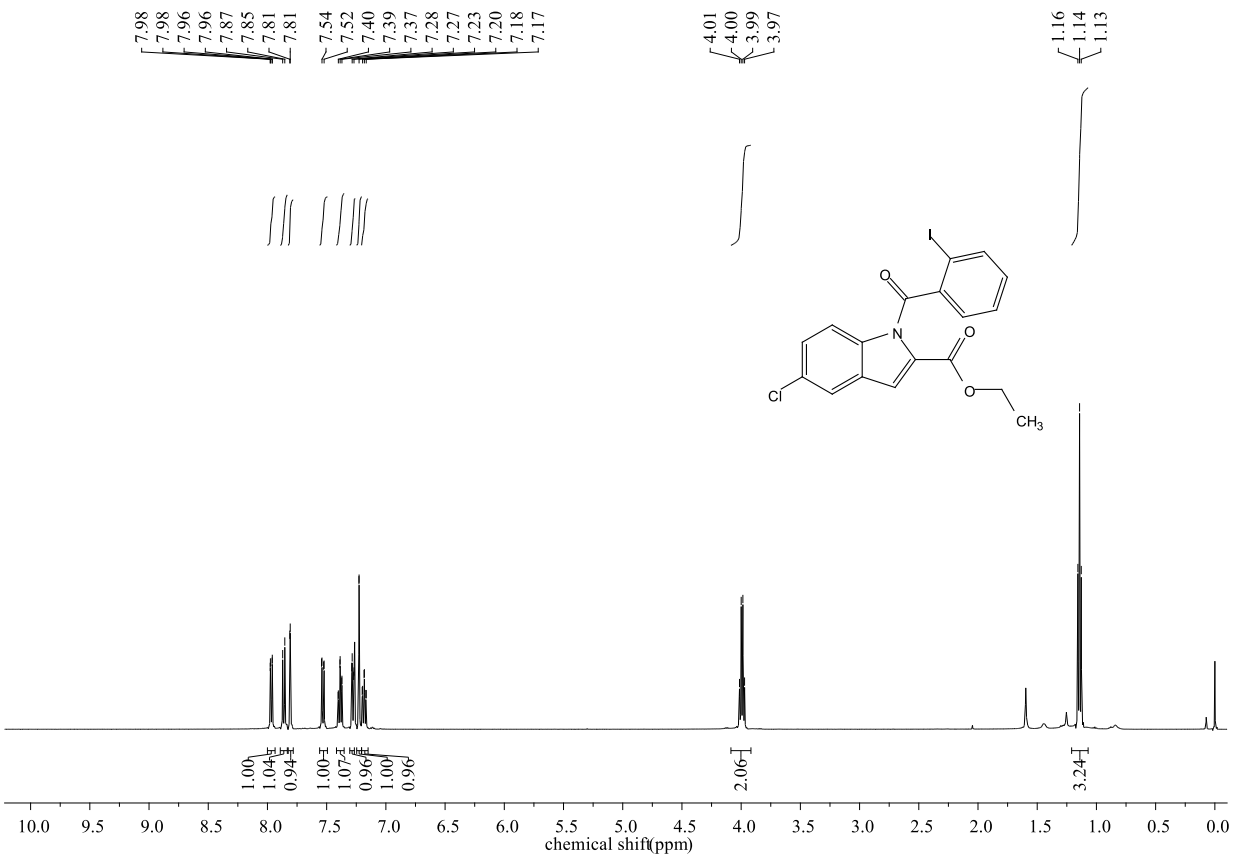
^{1}H NMR Spectra of compound **R2b** (400 MHz, $CDCl_3$)



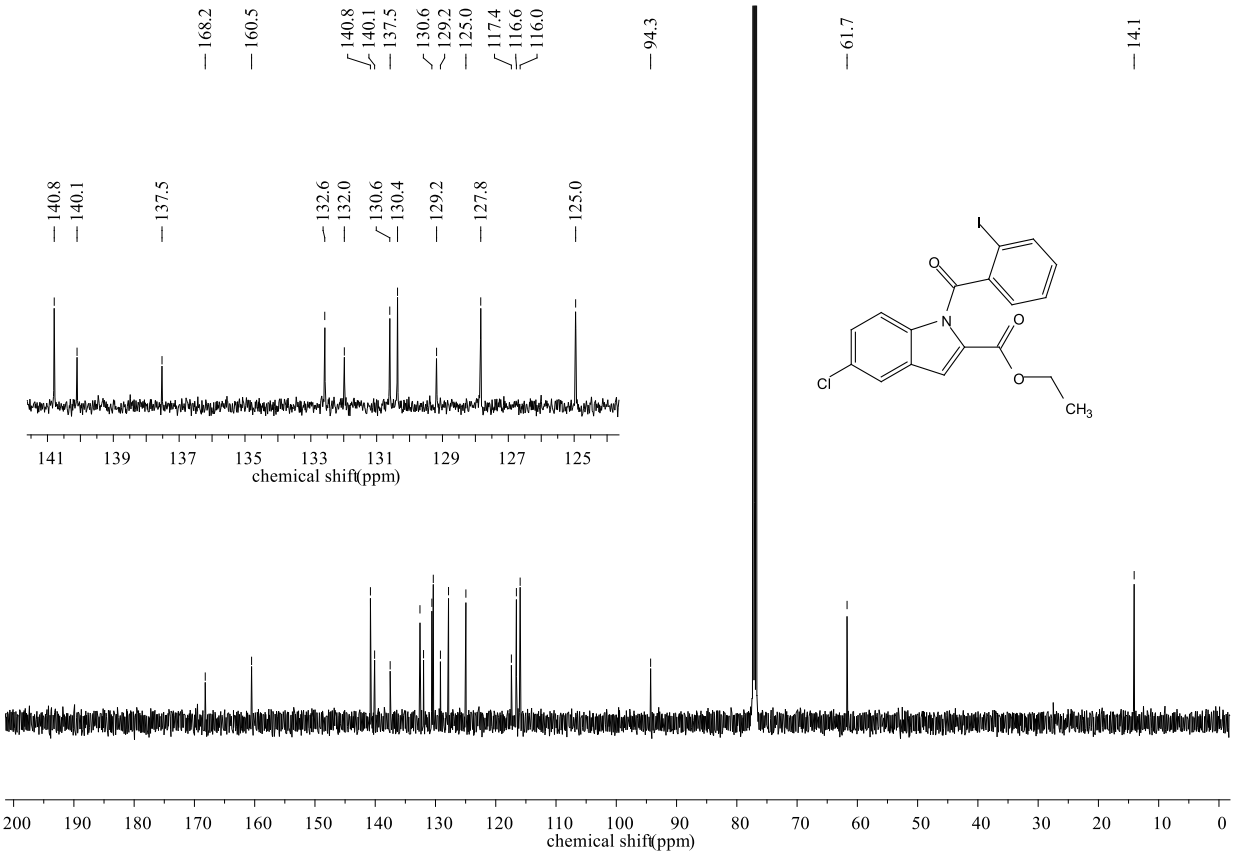
^{13}C NMR Spectra of compound **R2b** (100 MHz, $CDCl_3$)



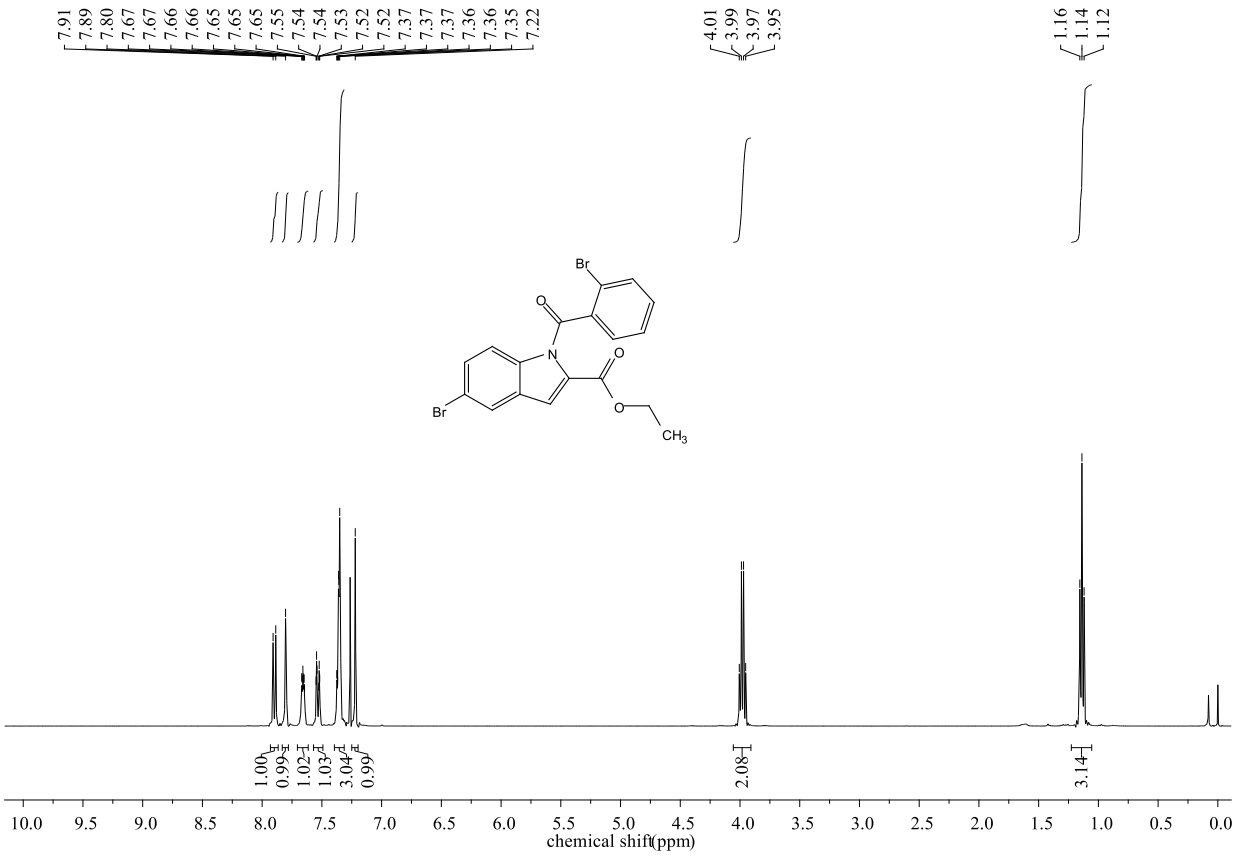
^{1}H NMR Spectra of compound **R2c** (500 MHz, $CDCl_3$)



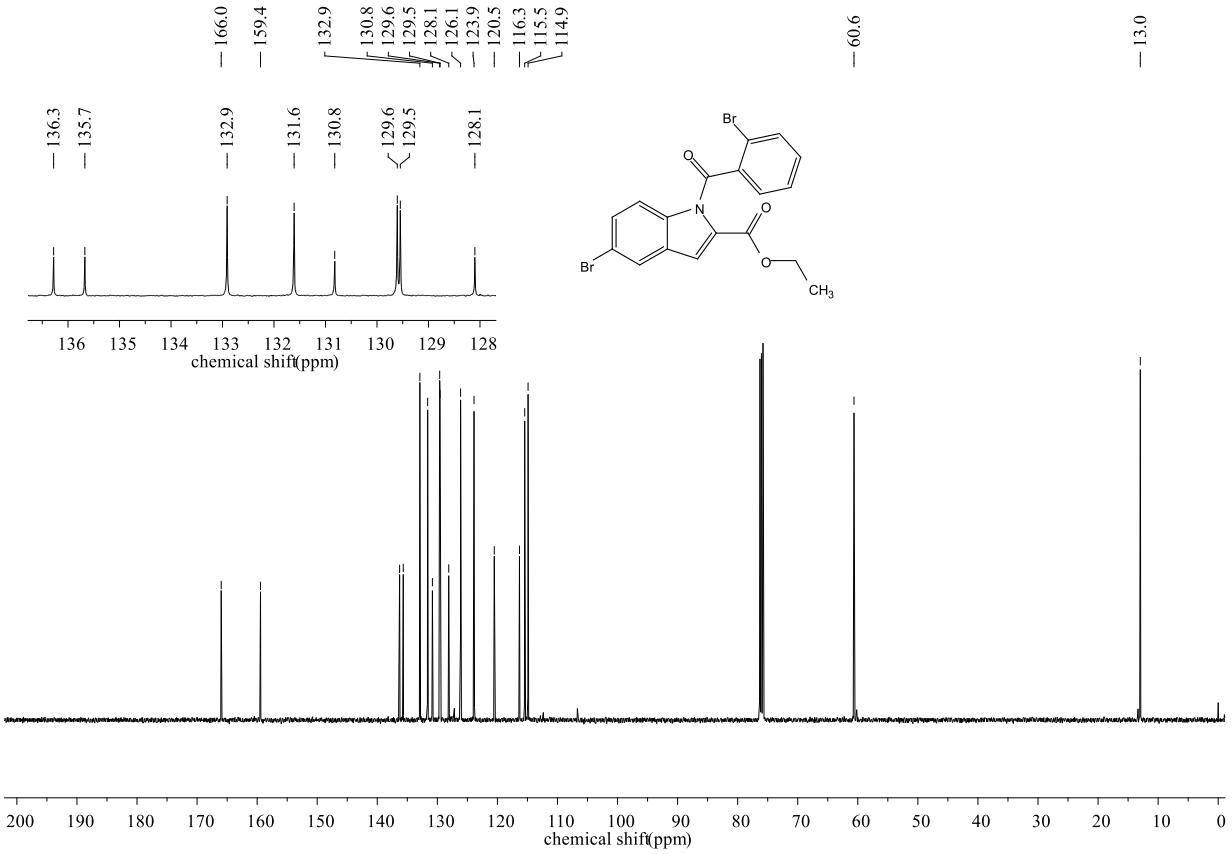
^{13}C NMR Spectra of compound **R2c** (125 MHz, $CDCl_3$)



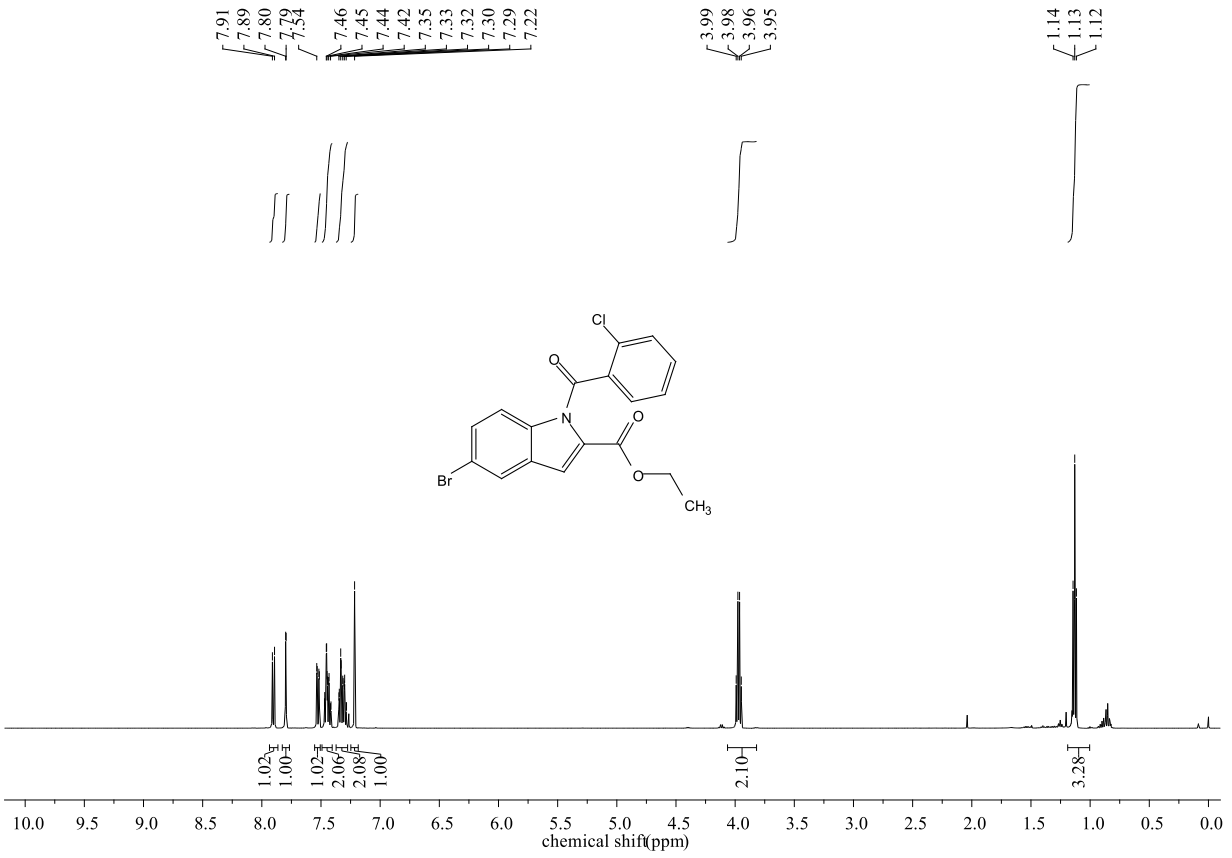
^{1}H NMR Spectra of compound **R3a** (400 MHz, $CDCl_3$)



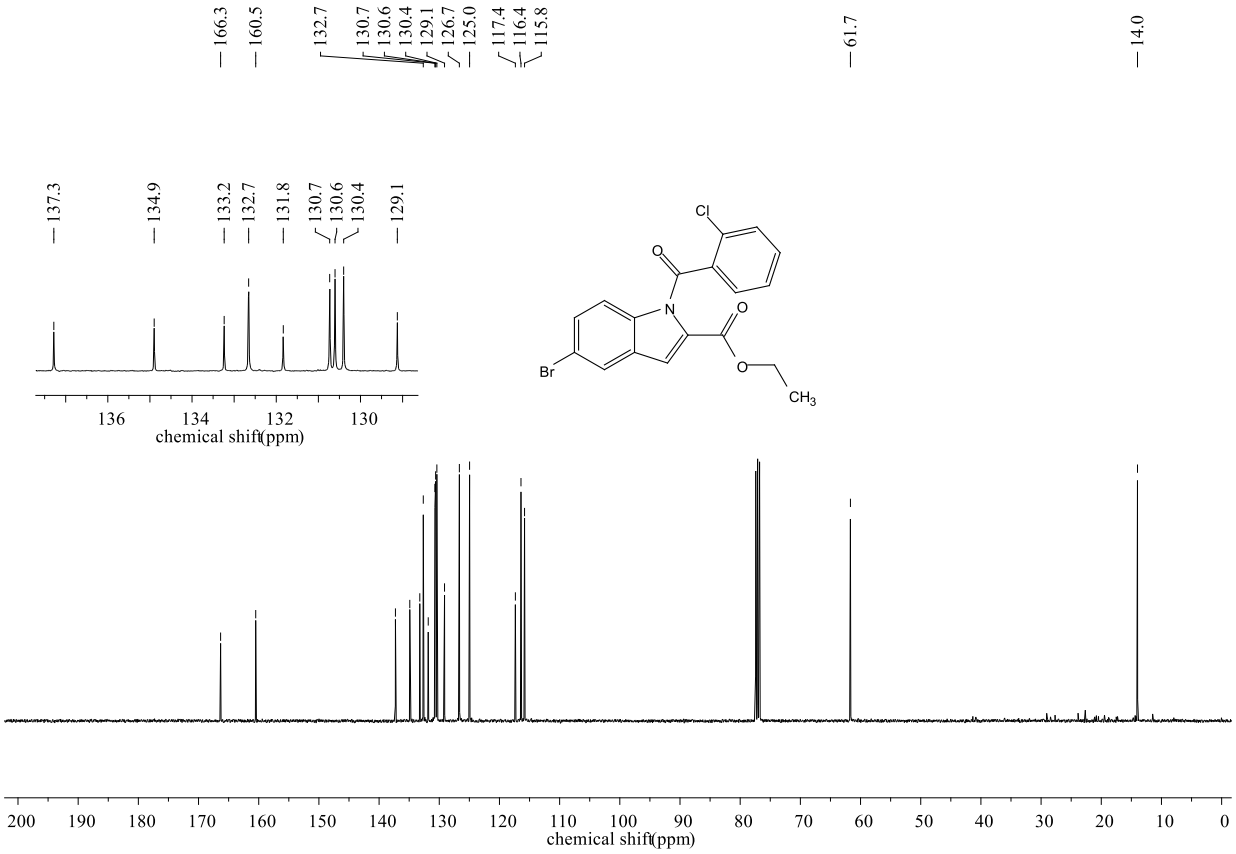
^{13}C NMR Spectra of compound **R3a** (125 MHz, $CDCl_3$)



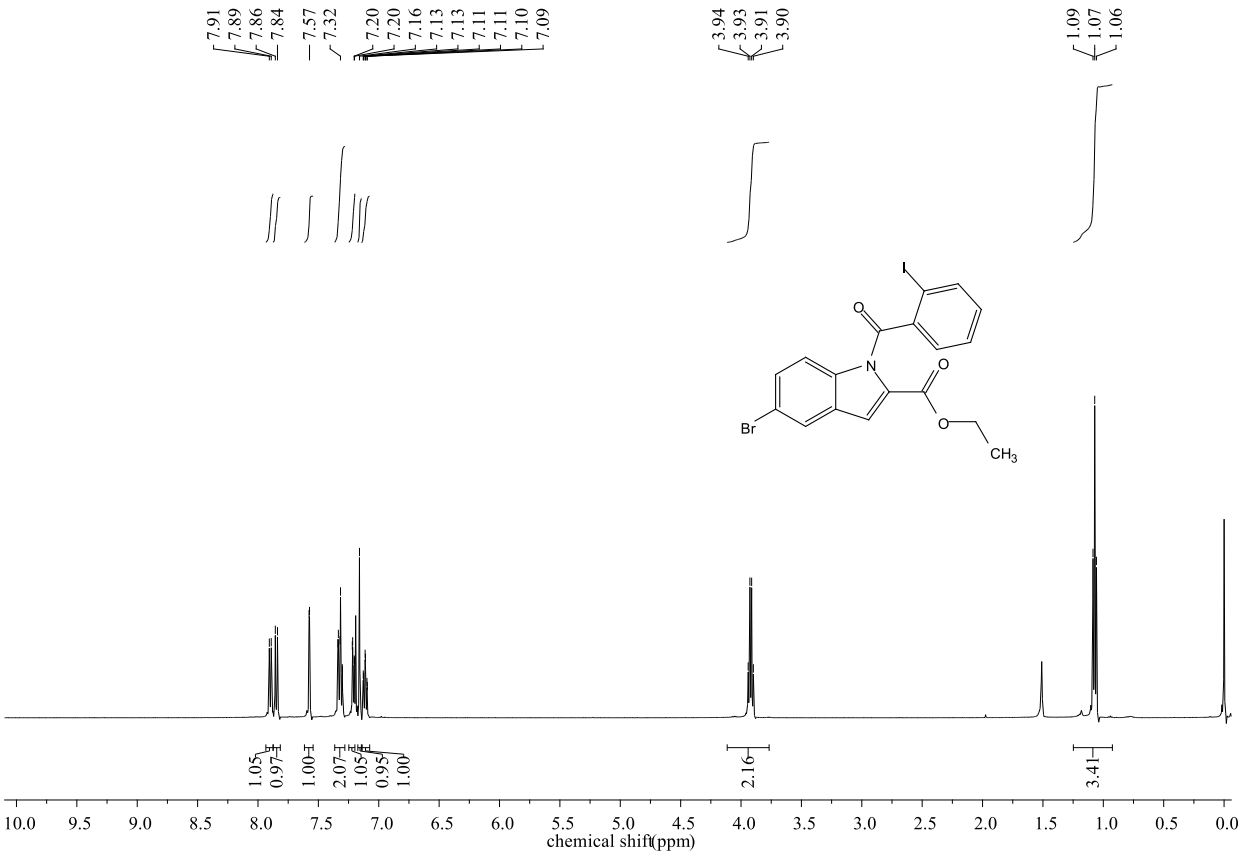
^{1}H NMR Spectra of compound **R3b** (500 MHz, $CDCl_3$)



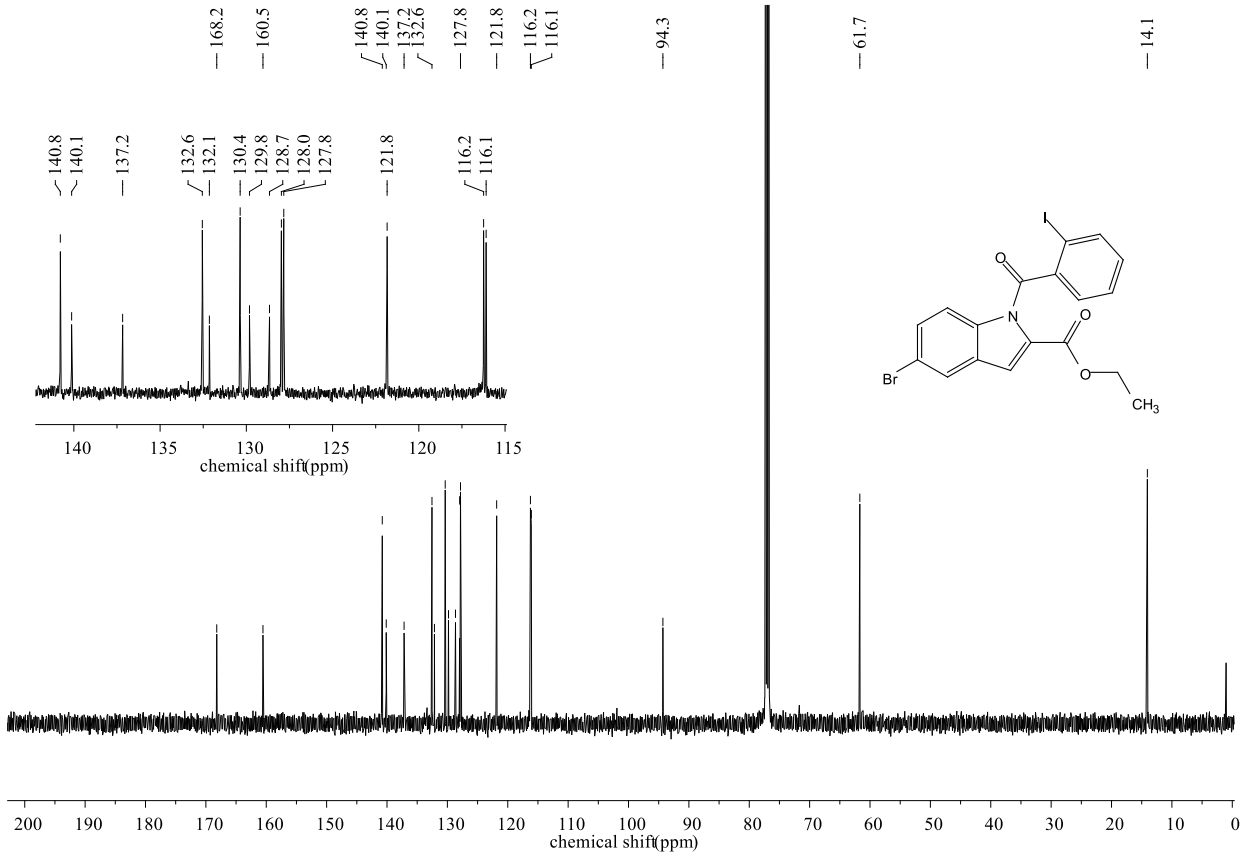
^{13}C NMR Spectra of compound **R3b** (100 MHz, $CDCl_3$)



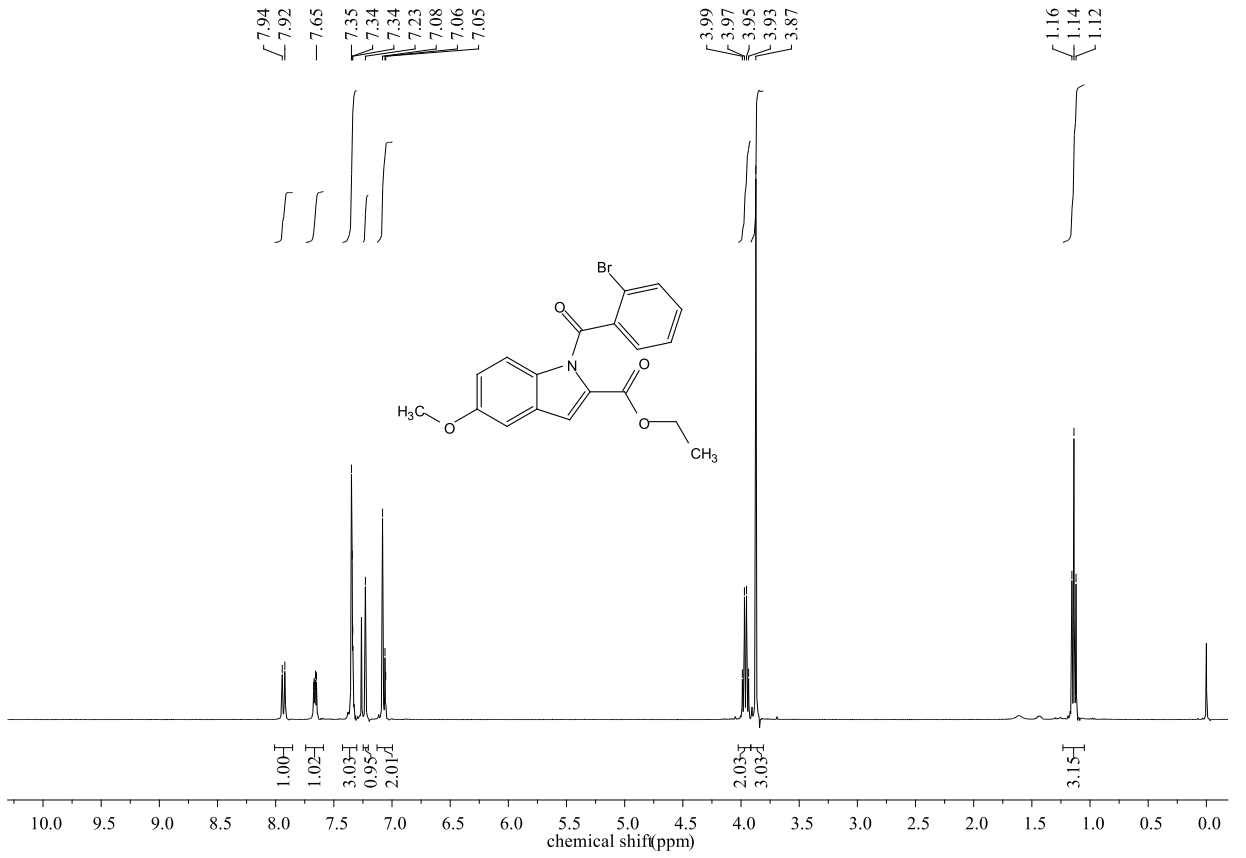
^{1}H NMR Spectra of compound **R3c** (500 MHz, $CDCl_3$)



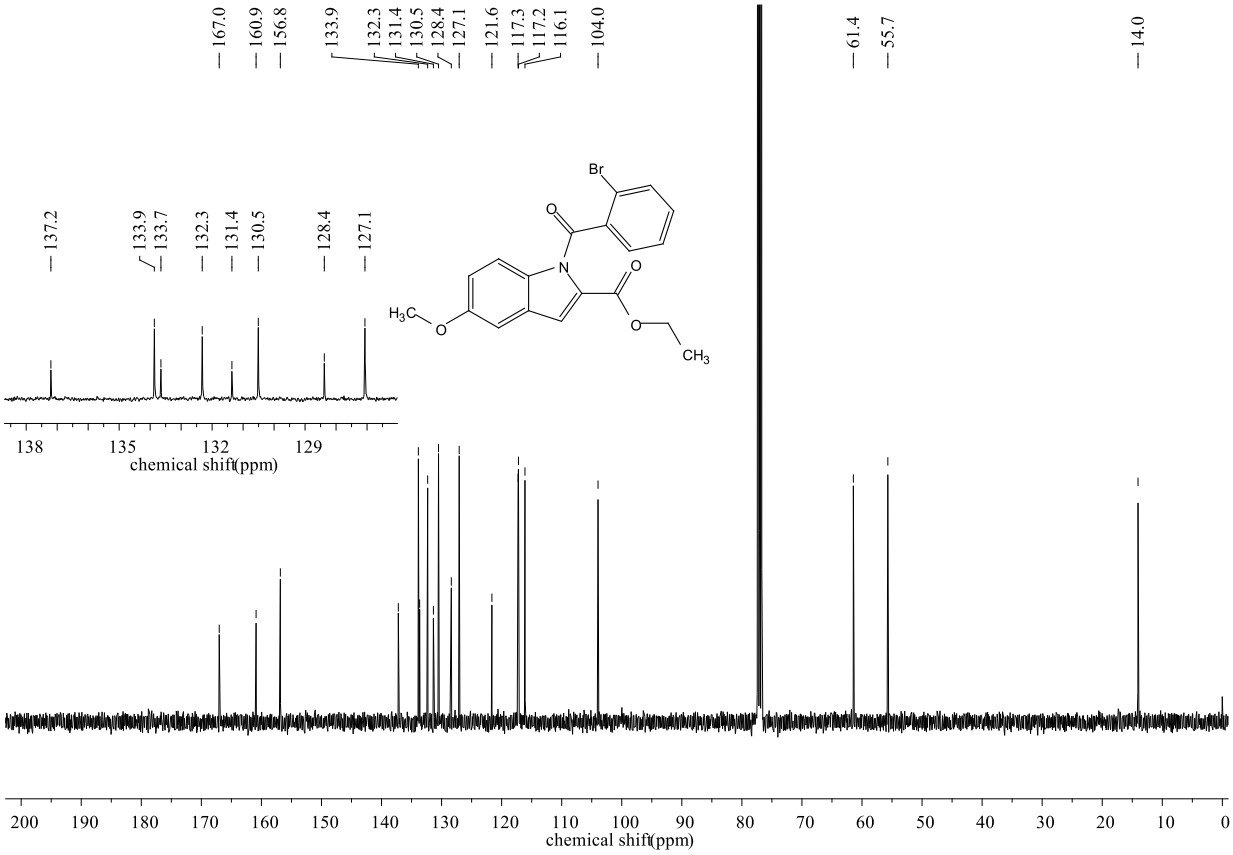
^{13}C NMR Spectra of compound **R3c** (125 MHz, $CDCl_3$)



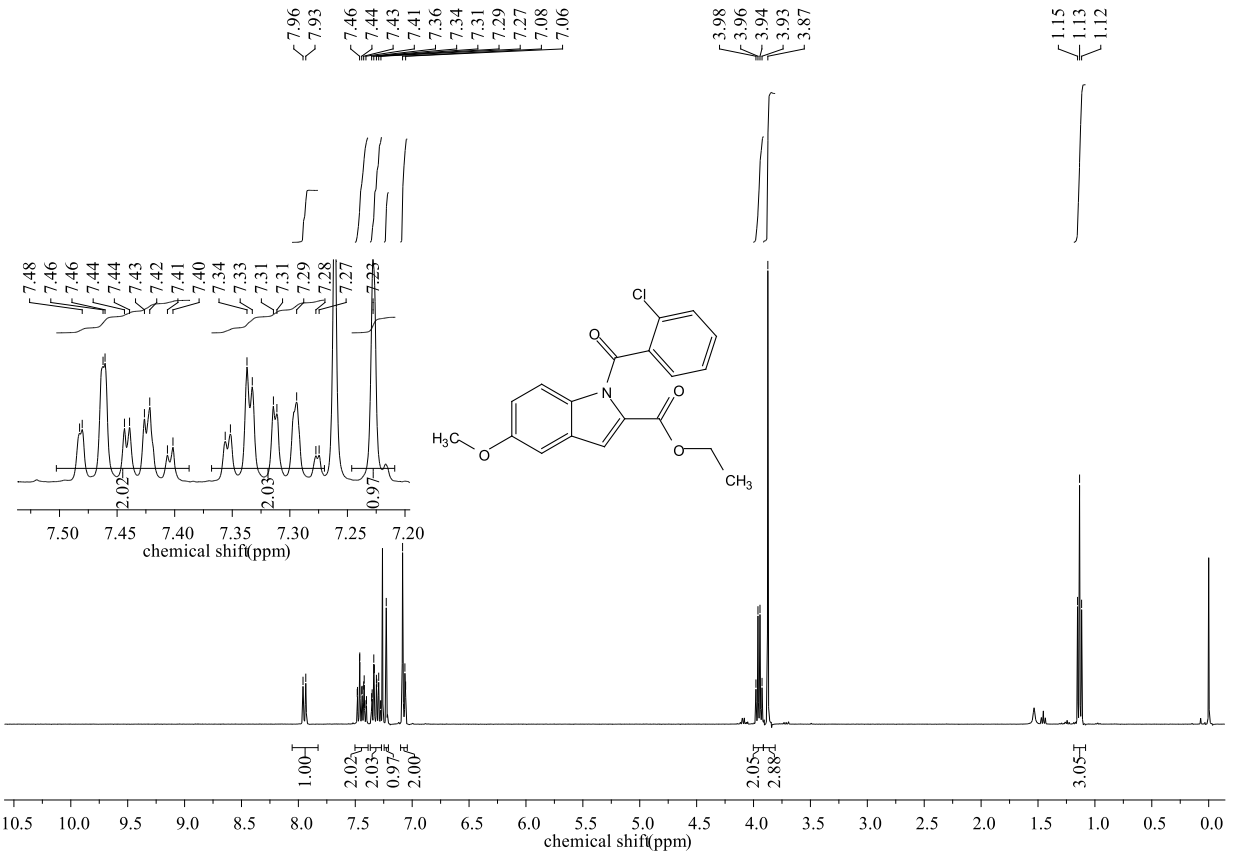
^{1}H NMR Spectra of compound **R4a** (400 MHz, $CDCl_3$)



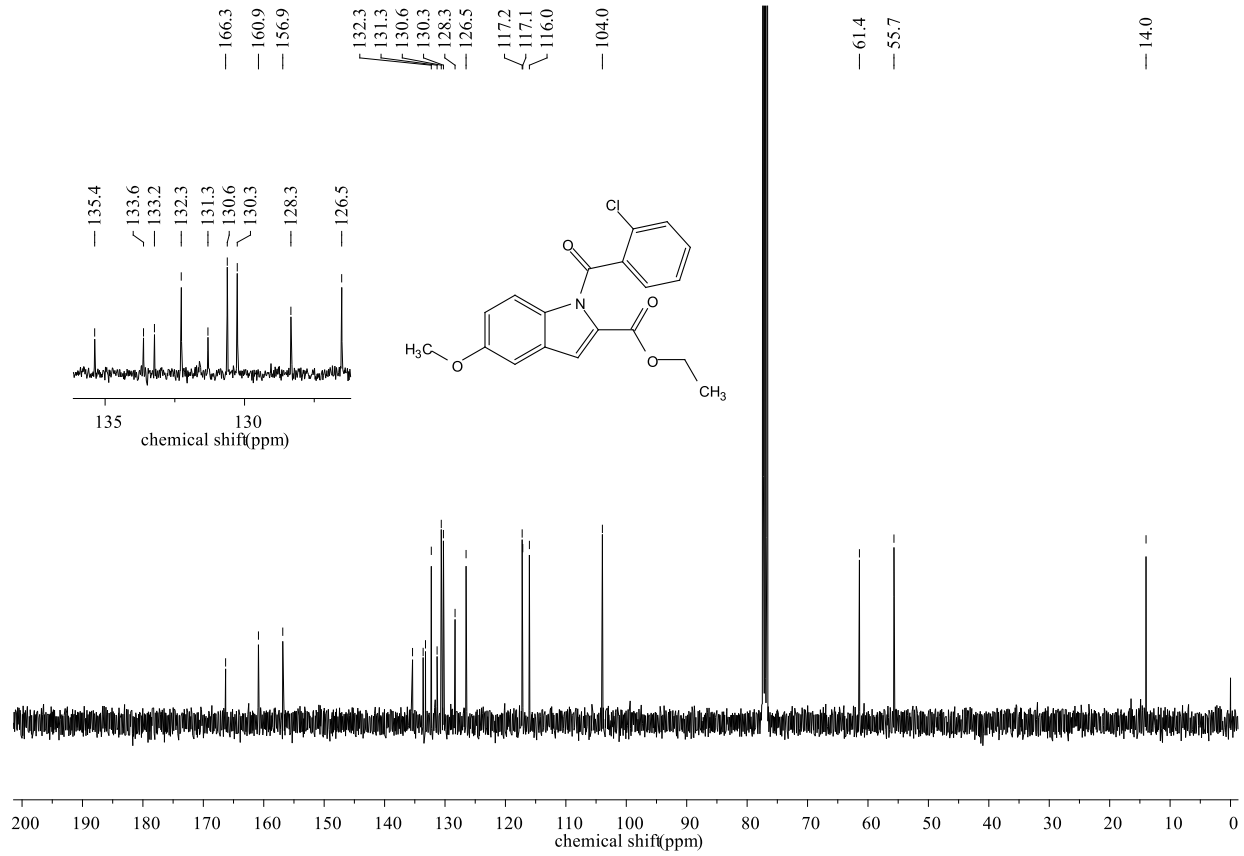
^{13}C NMR Spectra of compound **R4a** (100 MHz, $CDCl_3$)



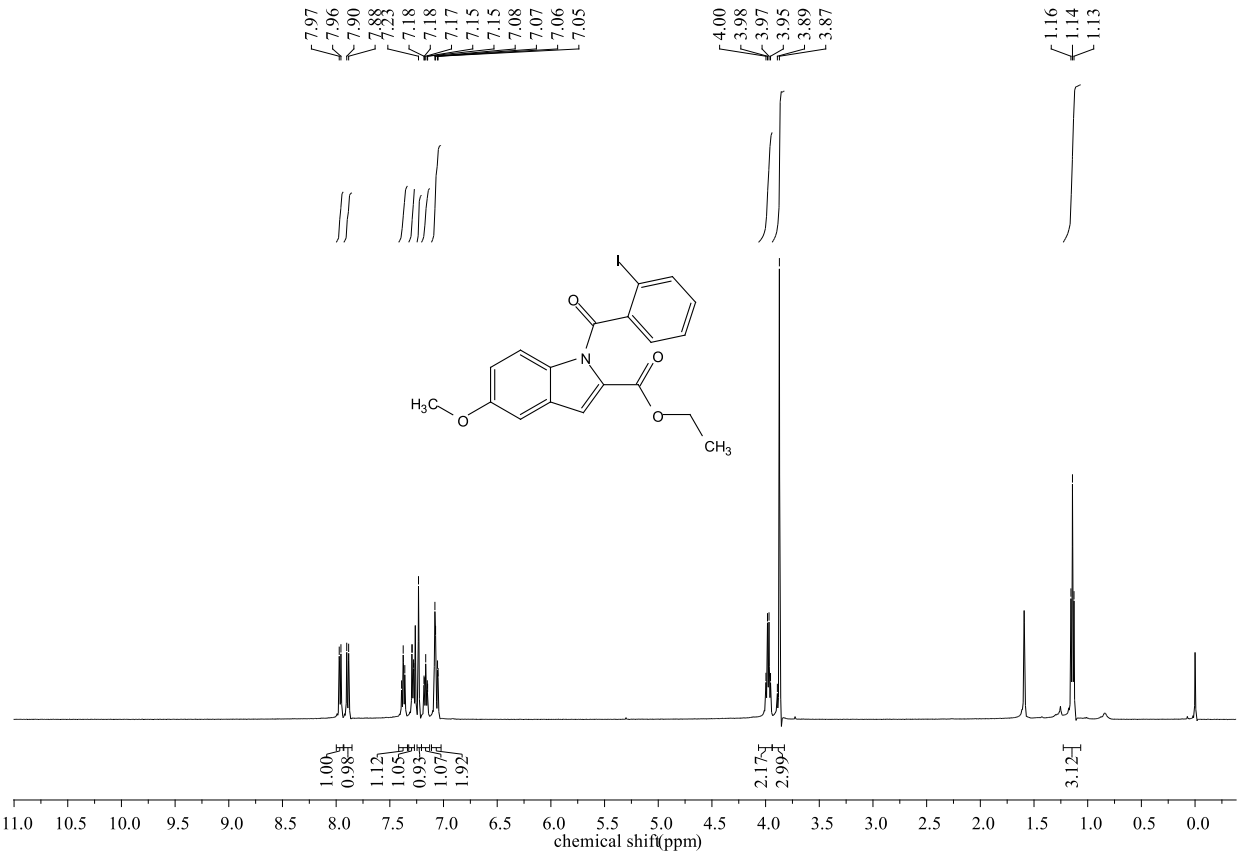
^{1}H NMR Spectra of compound **R4b** (400 MHz, $CDCl_3$)



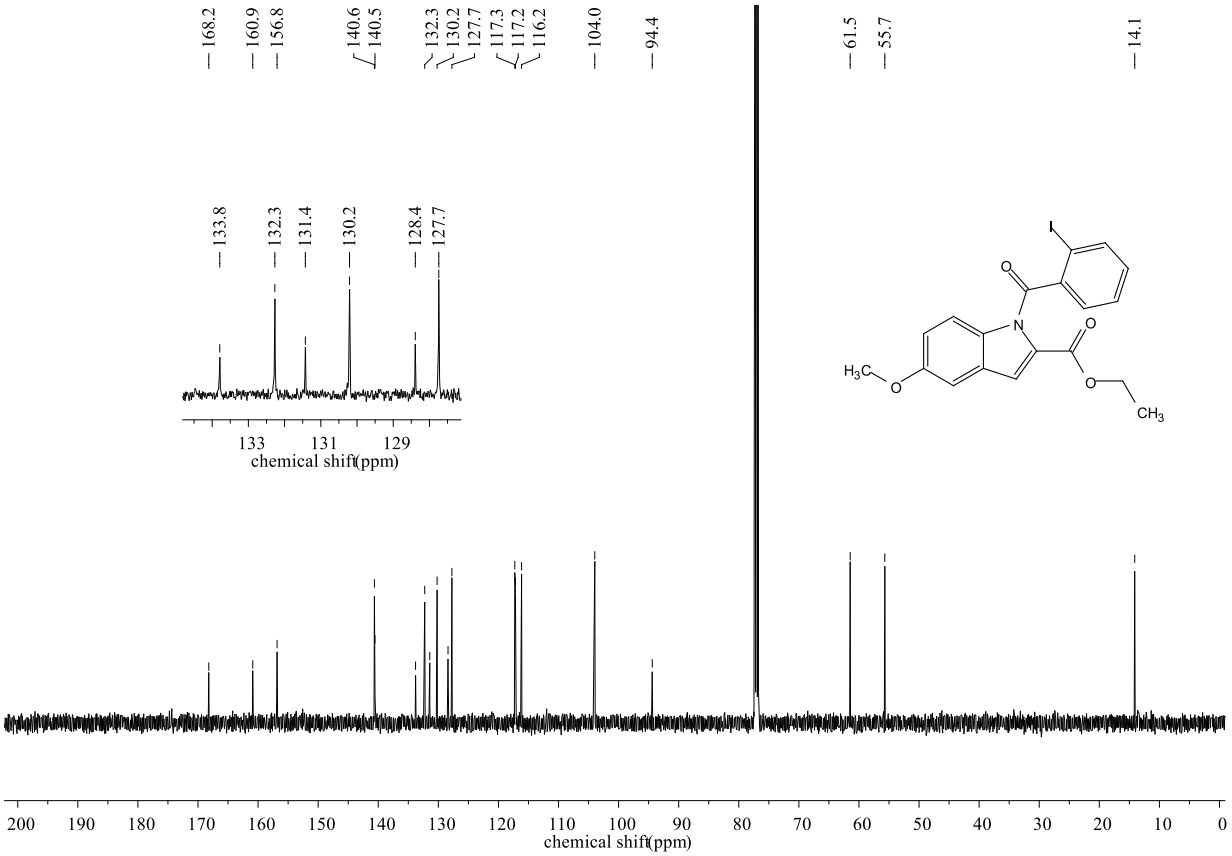
^{13}C NMR Spectra of compound **R4b** (100 MHz, $CDCl_3$)



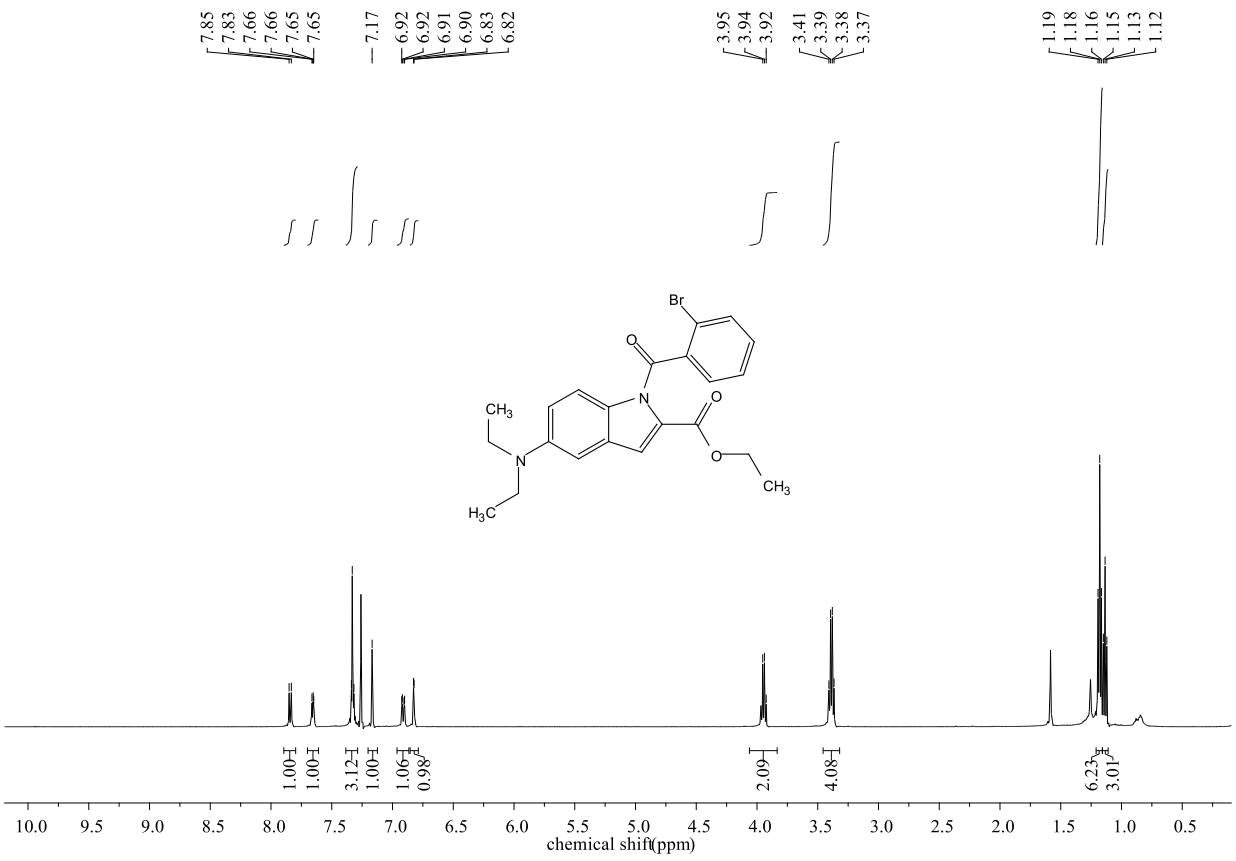
^{1}H NMR Spectra of compound **R4c** (500 MHz, $CDCl_3$)



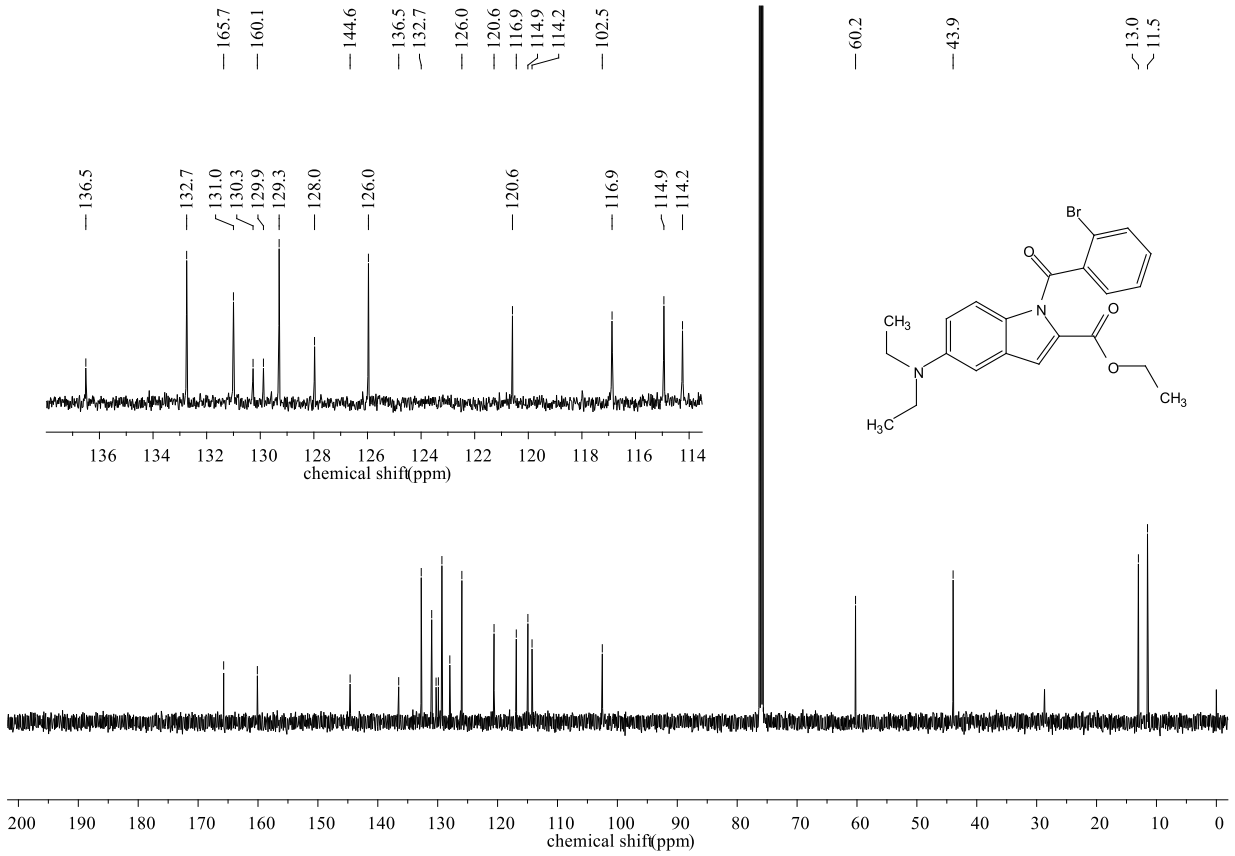
^{13}C NMR Spectra of compound **R4c** (125 MHz, $CDCl_3$)



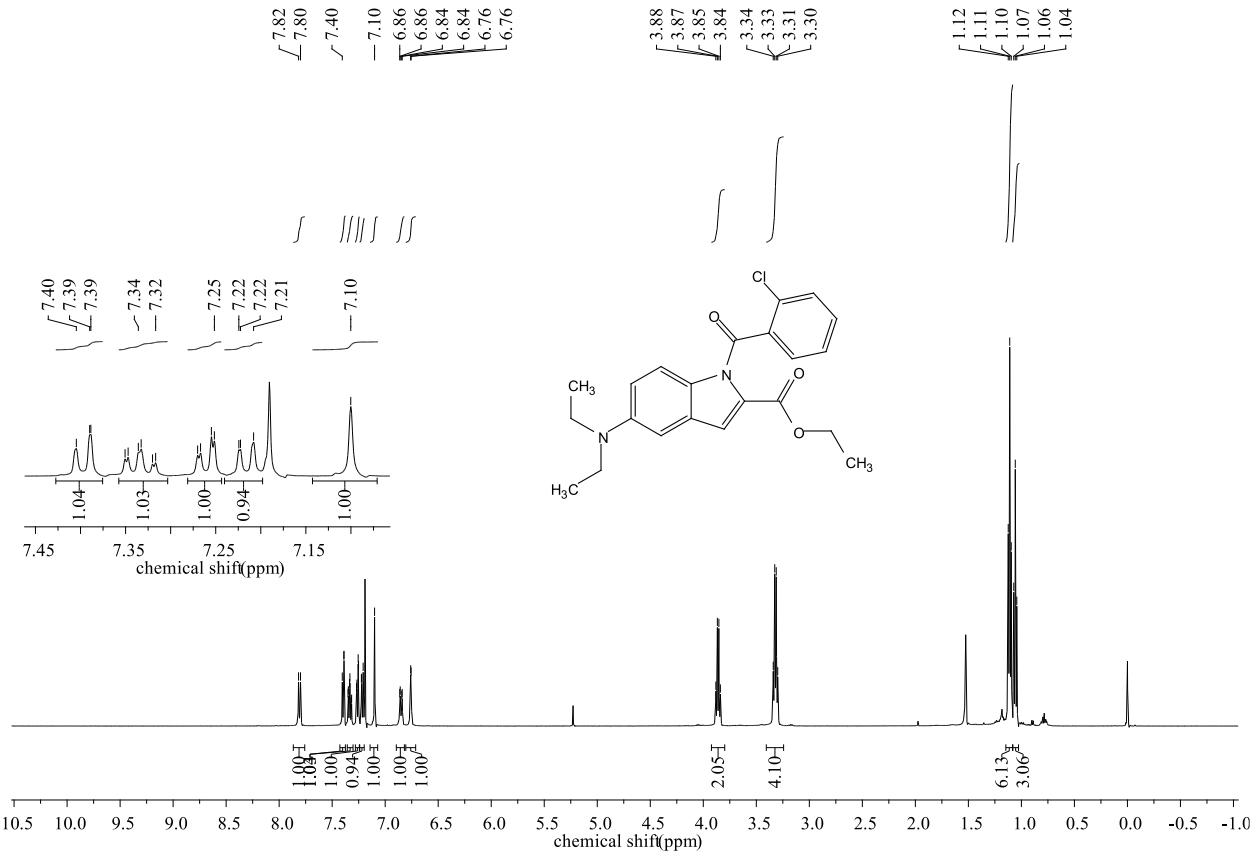
^{1}H NMR Spectra of compound **R5a** (500 MHz, $CDCl_3$)



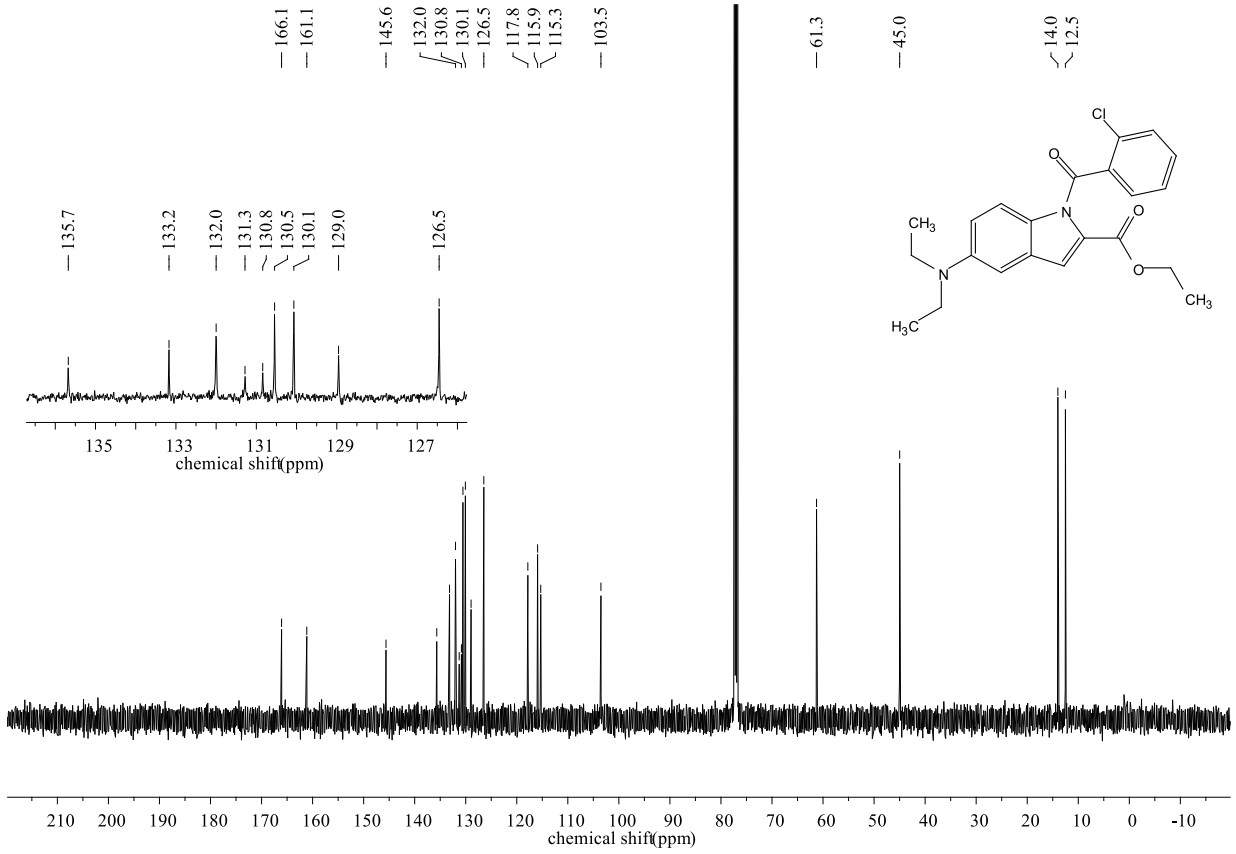
^{13}C NMR Spectra of compound **R5a** (125 MHz, $CDCl_3$)



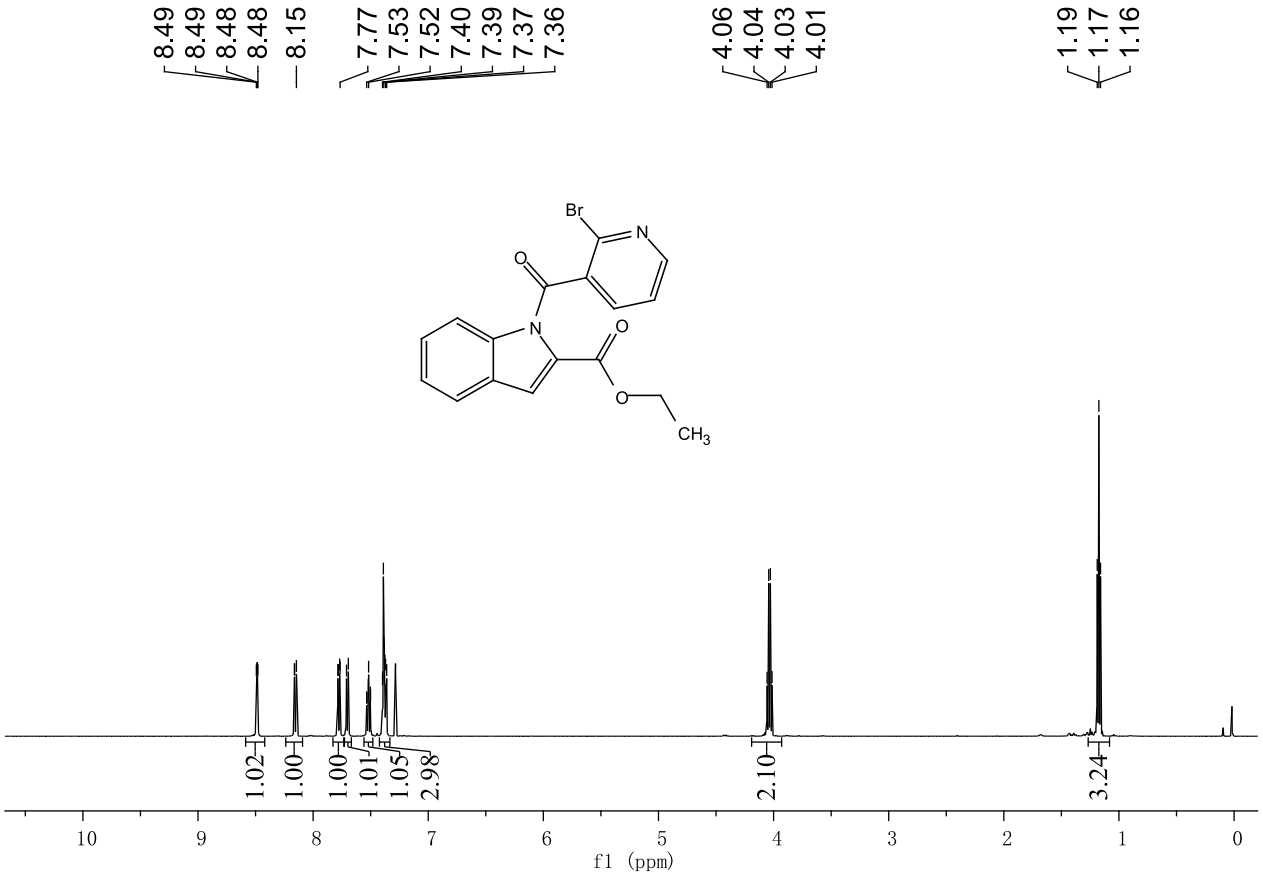
^{1}H NMR Spectra of compound **R5b** (500 MHz, $CDCl_3$)



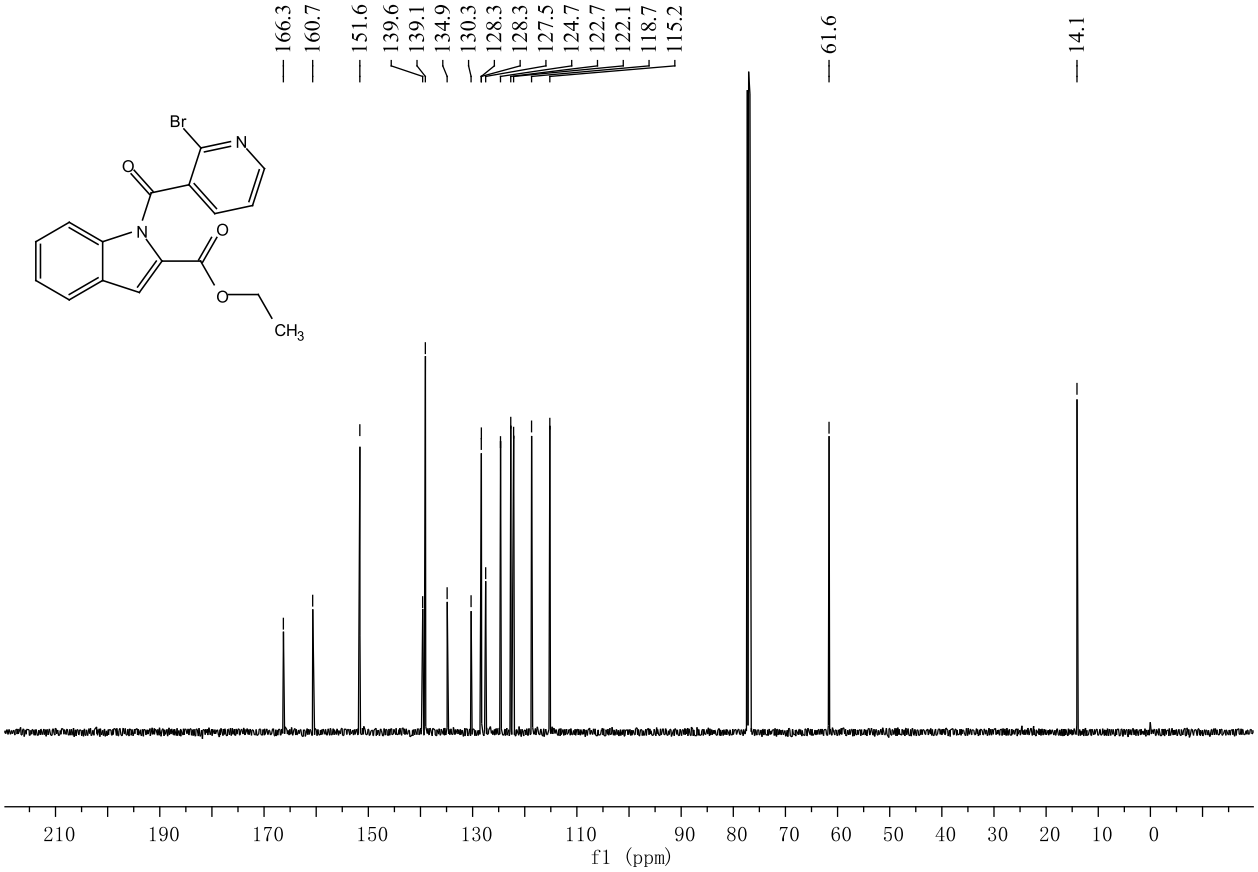
^{13}C NMR Spectra of compound **R5b** (125 MHz, $CDCl_3$)



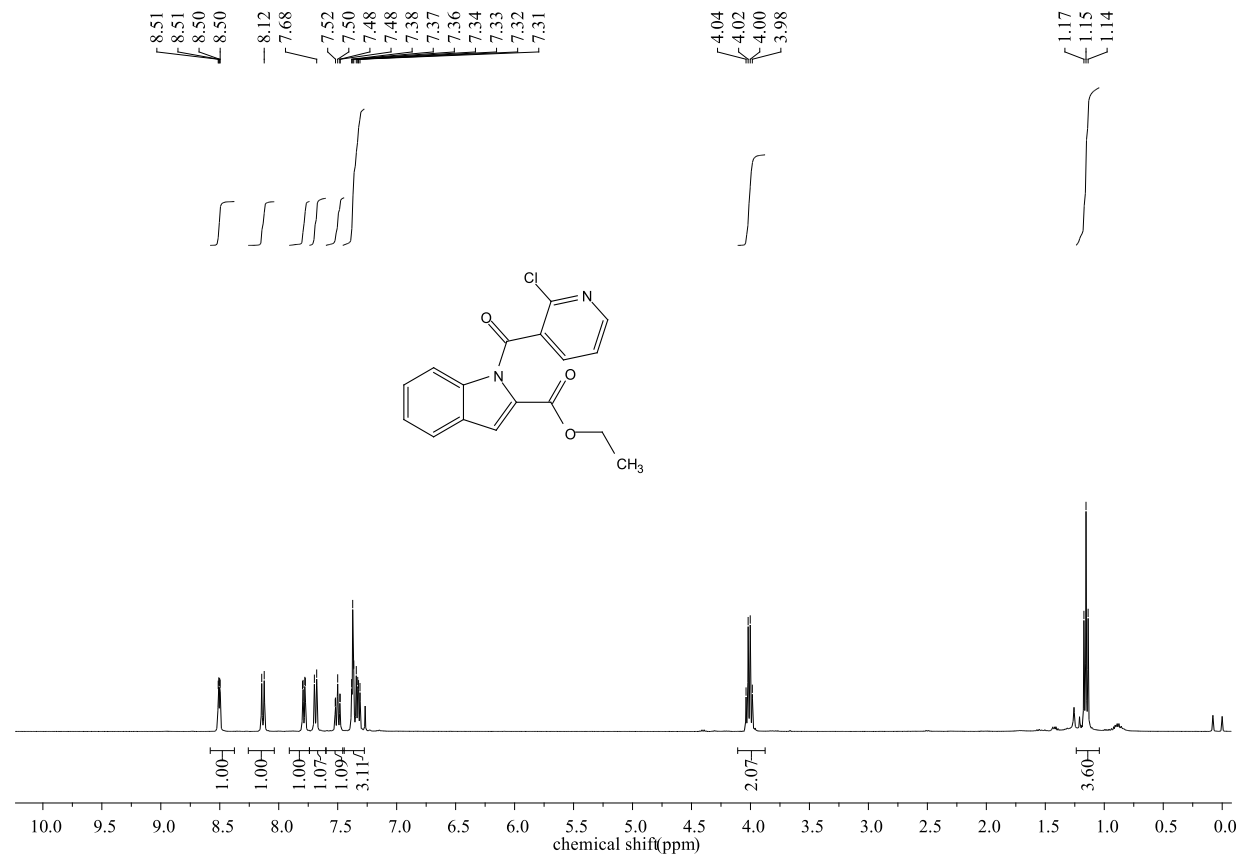
^{1}H NMR Spectra of compound **R6a** (500 MHz, $CDCl_3$)



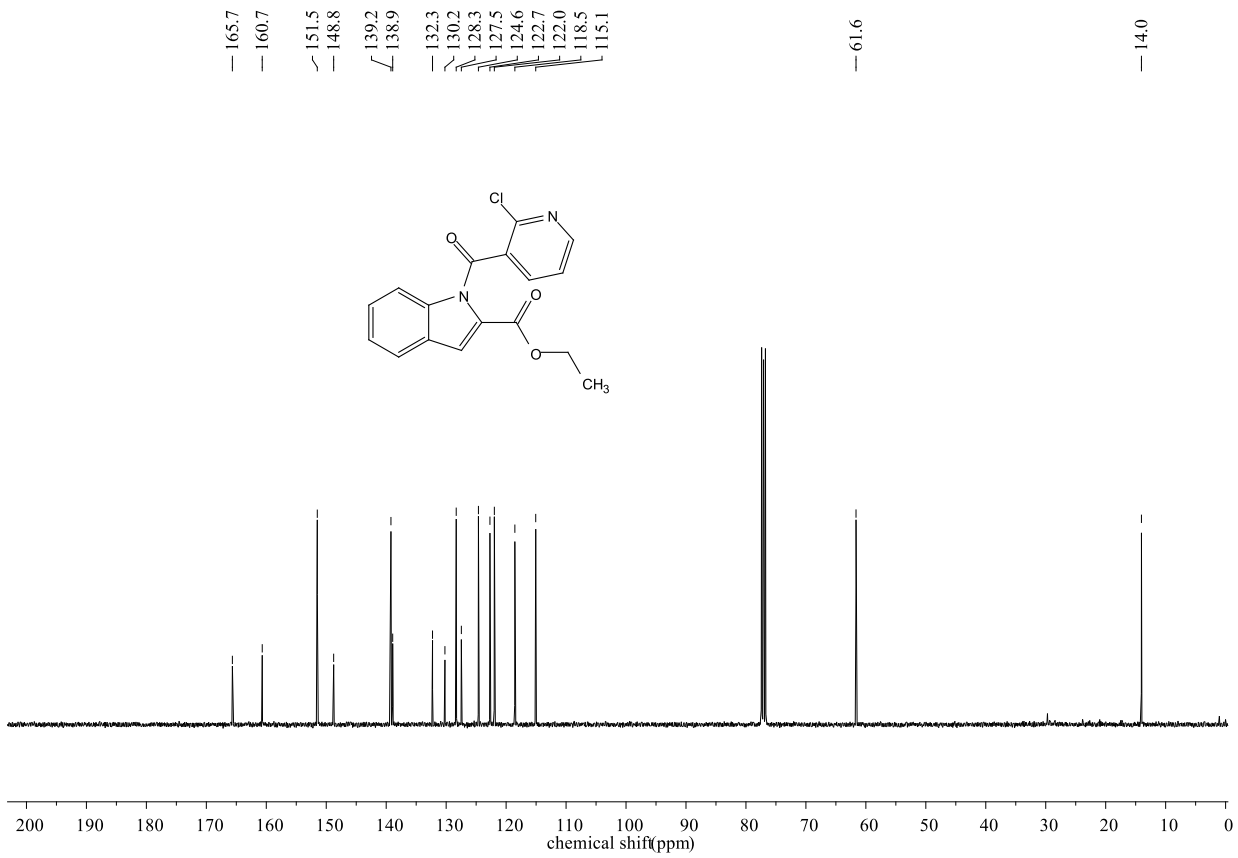
^{13}C NMR Spectra of compound **R6a** (125 MHz, $CDCl_3$)



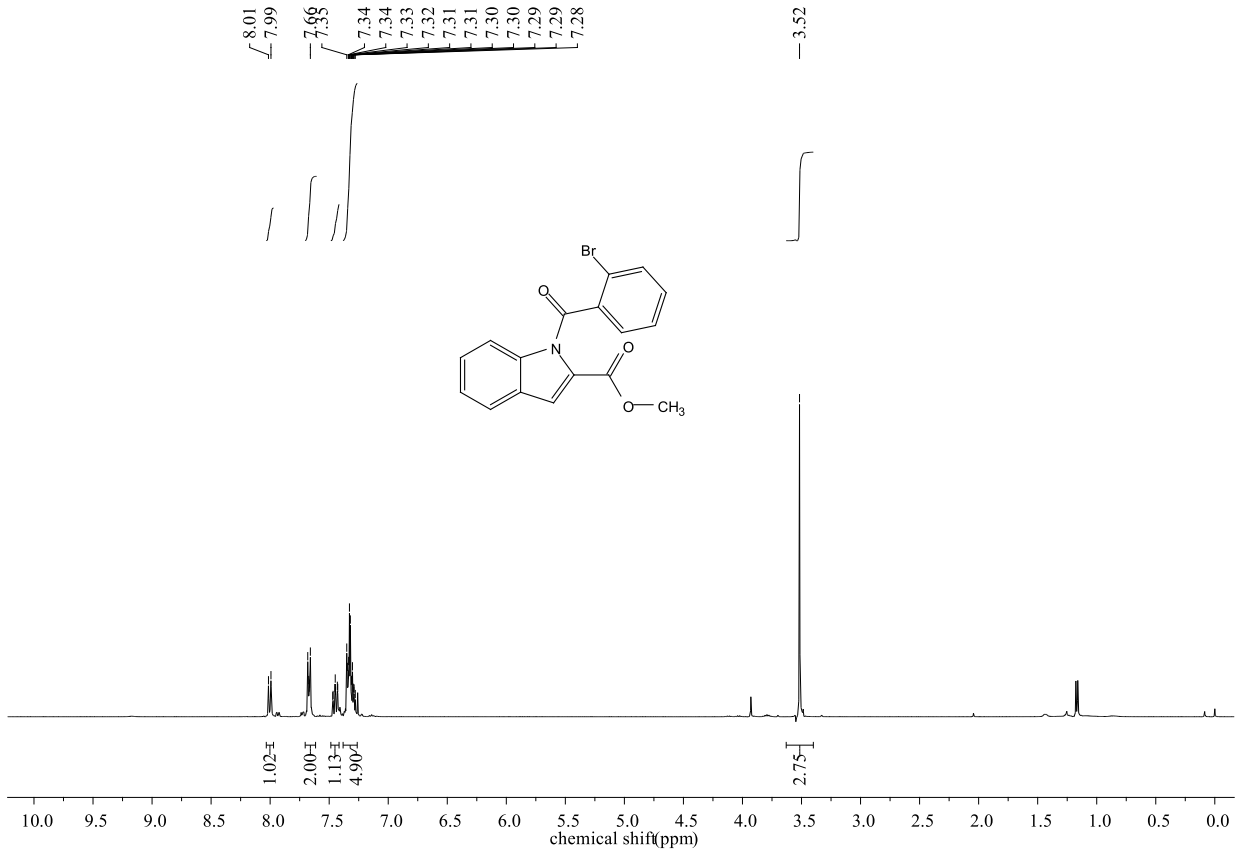
^{1}H NMR Spectra of compound **R6b** (400 MHz, $CDCl_3$)



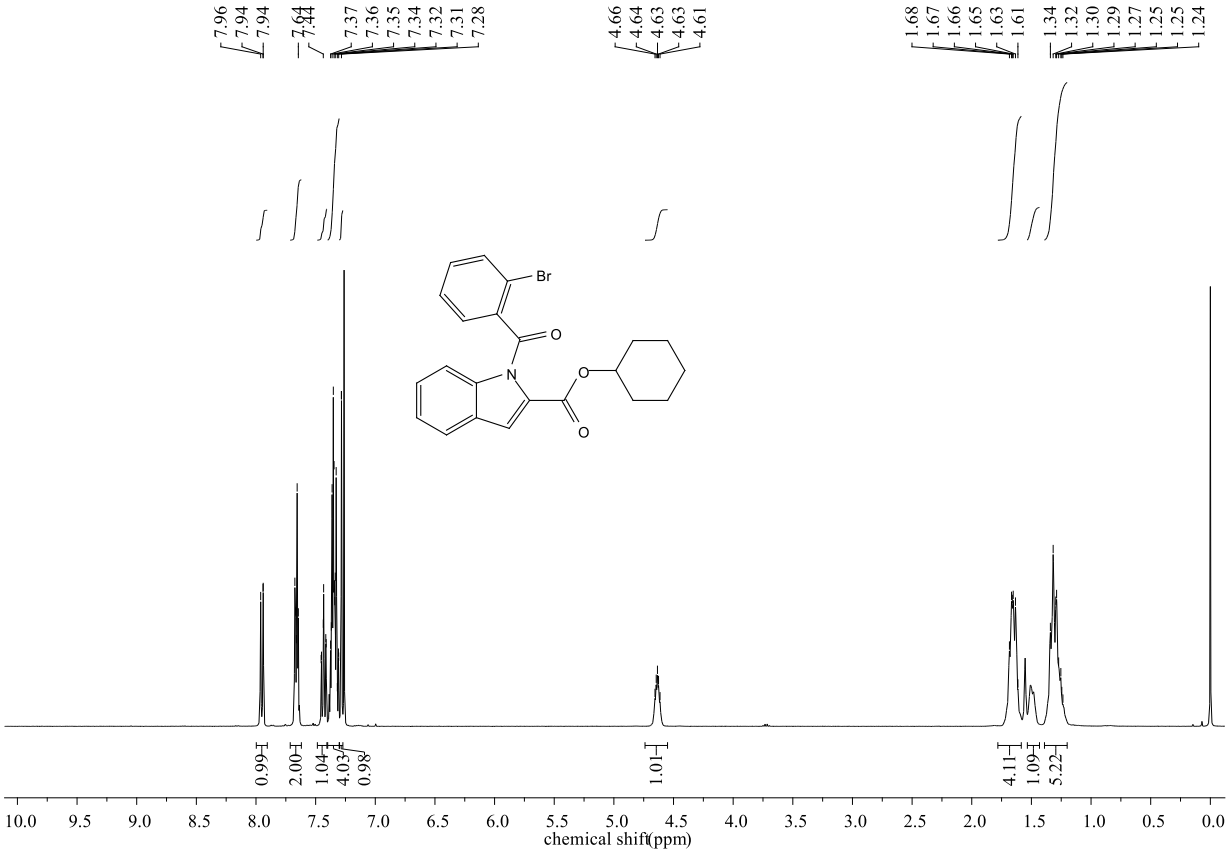
^{13}C NMR Spectra of compound **R6b** (100 MHz, $CDCl_3$)



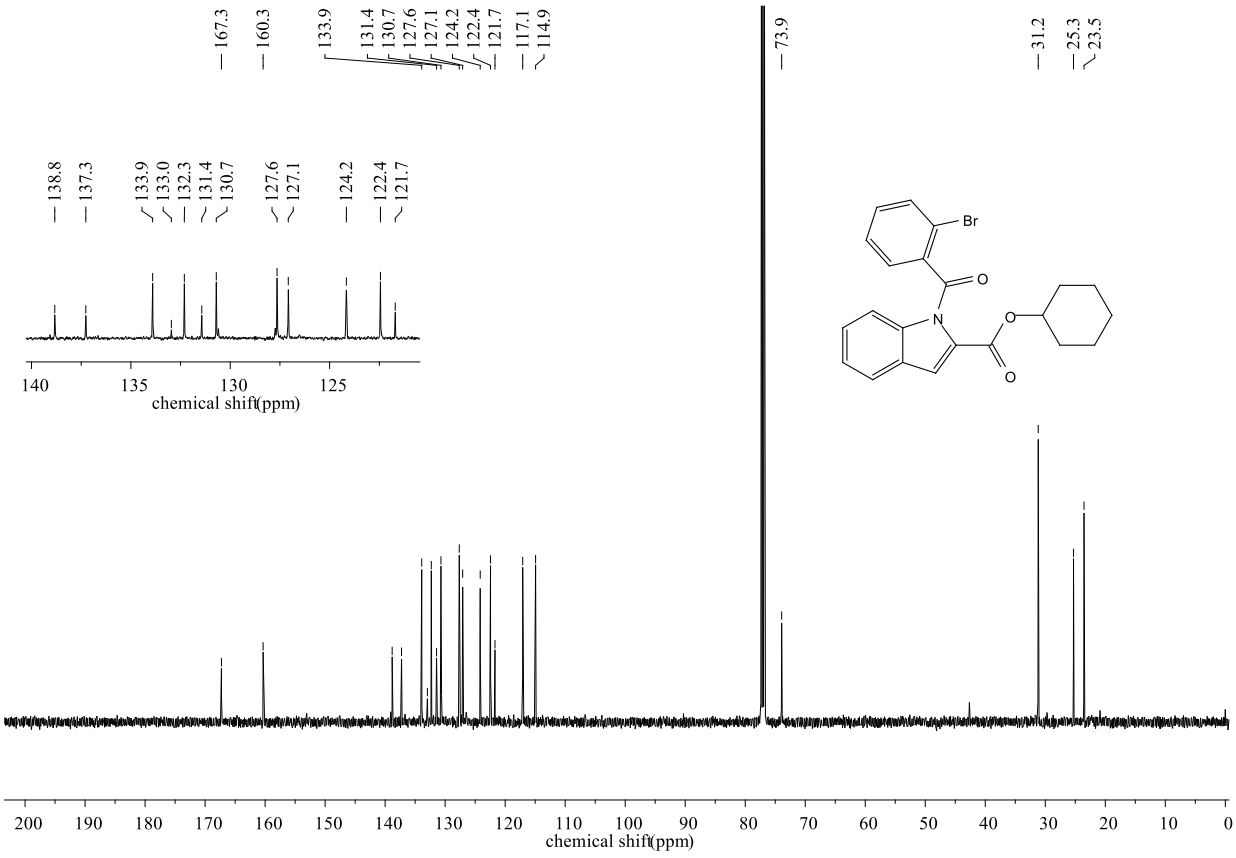
^{1}H NMR Spectra of compound **R7** (400 MHz, $CDCl_3$)



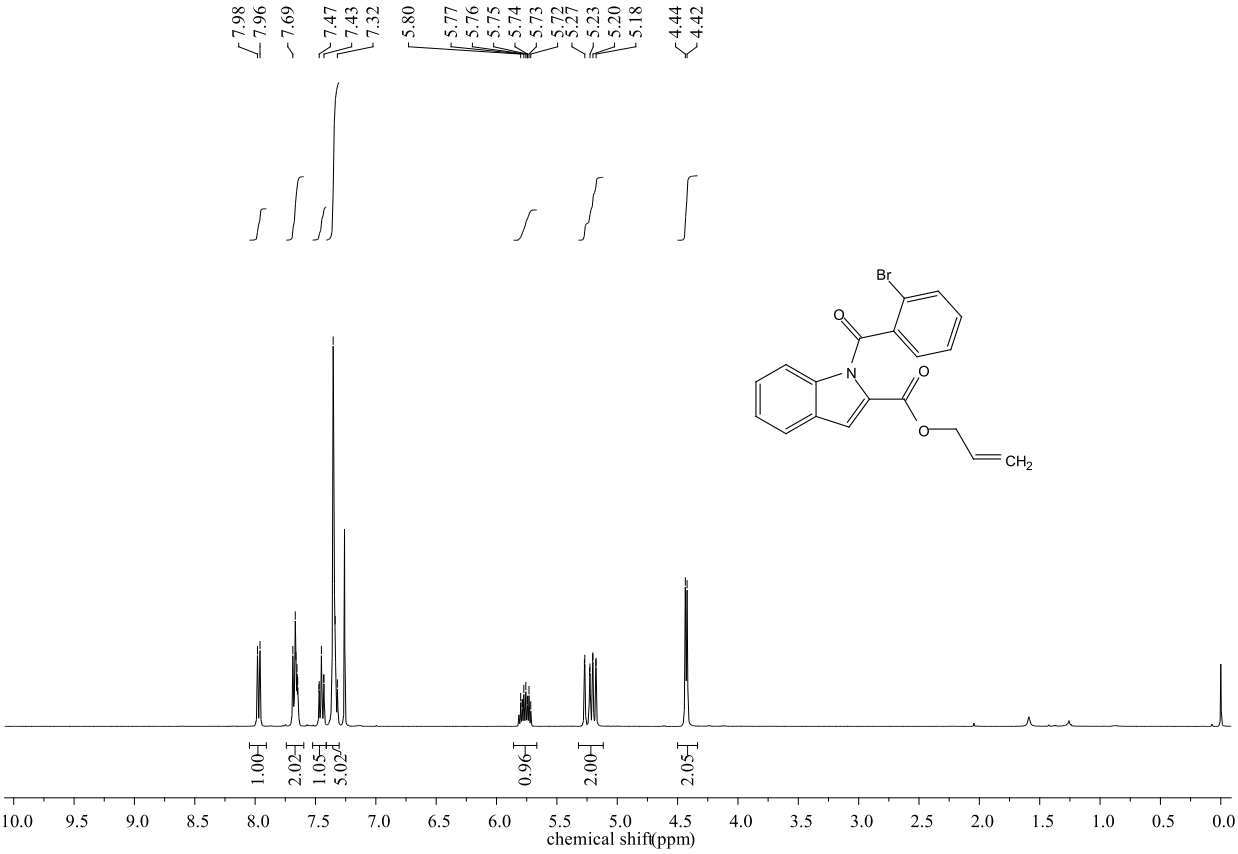
^{1}H NMR Spectra of compound **R8** (400 MHz, $CDCl_3$)



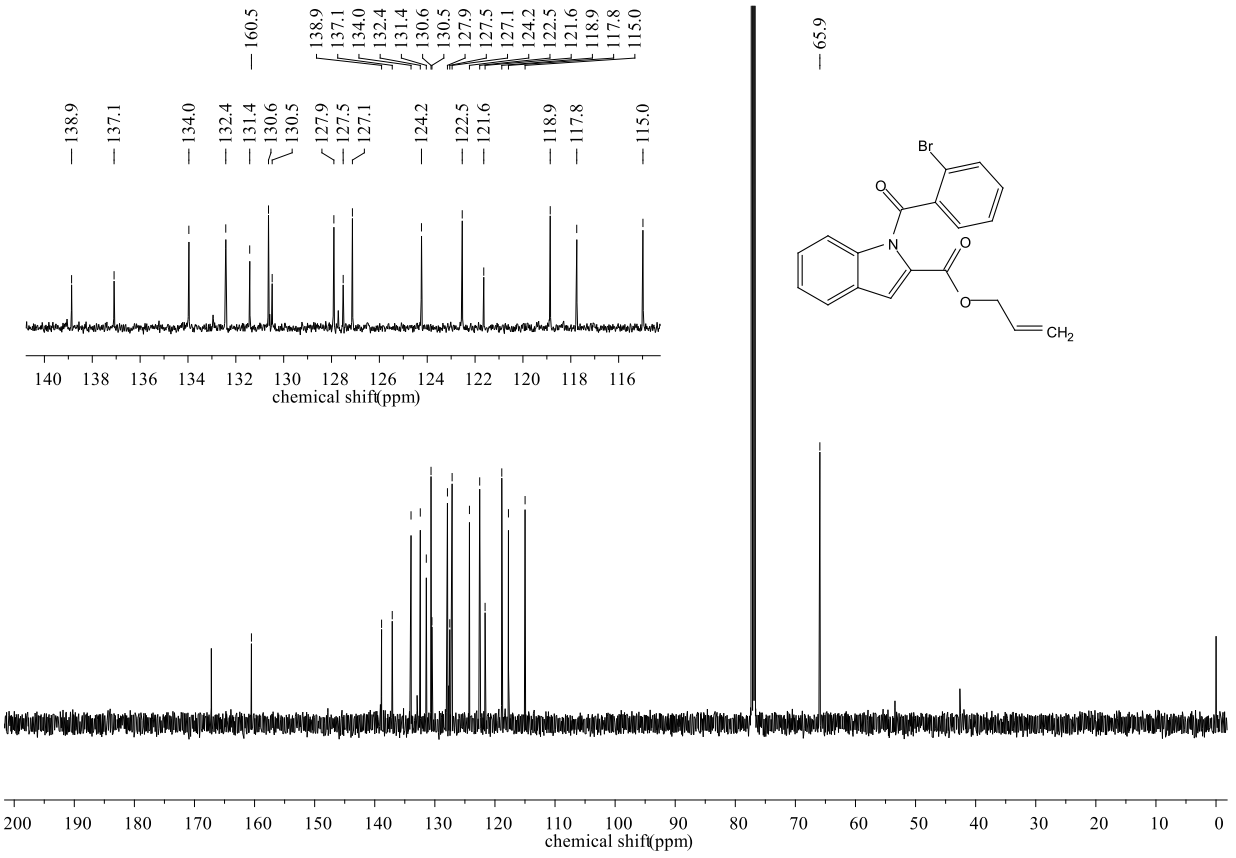
^{13}C NMR Spectra of compound **R8** (125 MHz, $CDCl_3$)



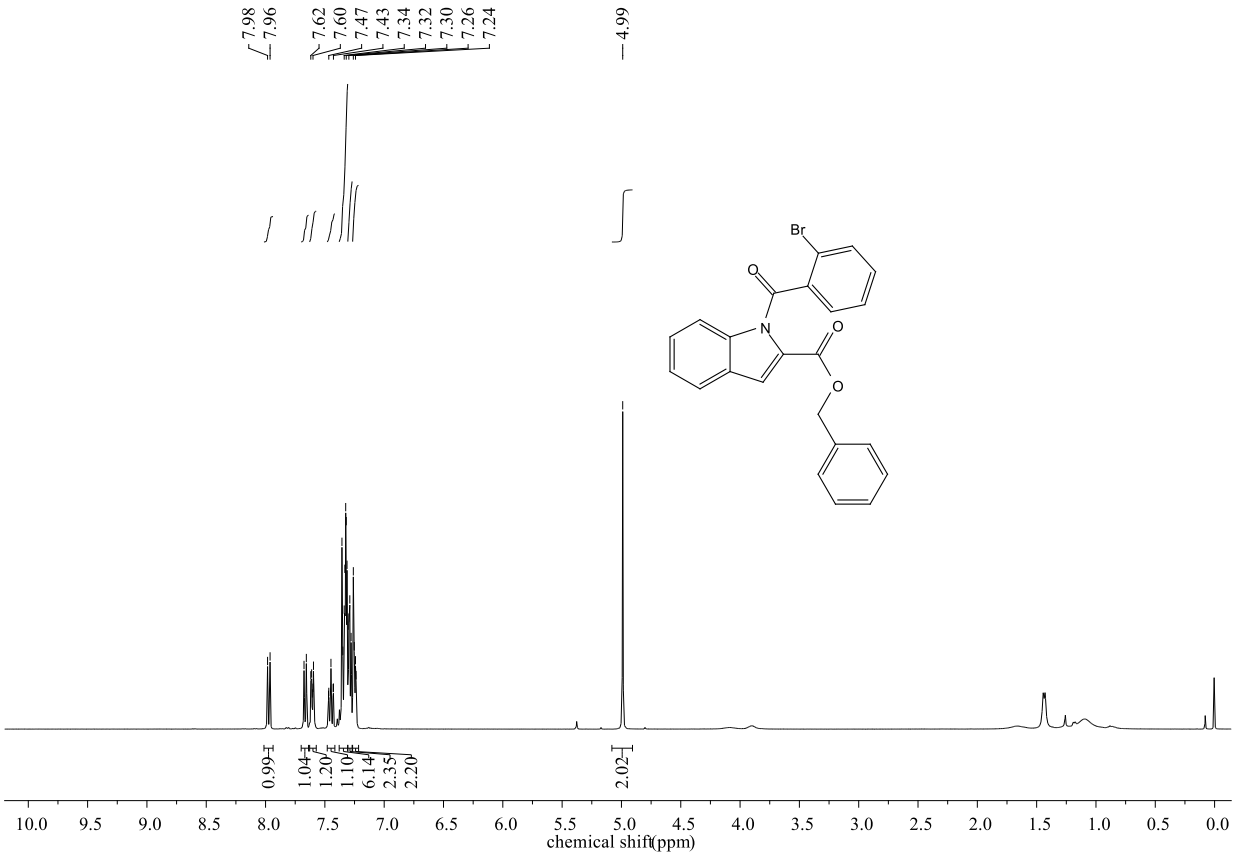
^{1}H NMR Spectra of compound **R9** (400 MHz, $CDCl_3$)



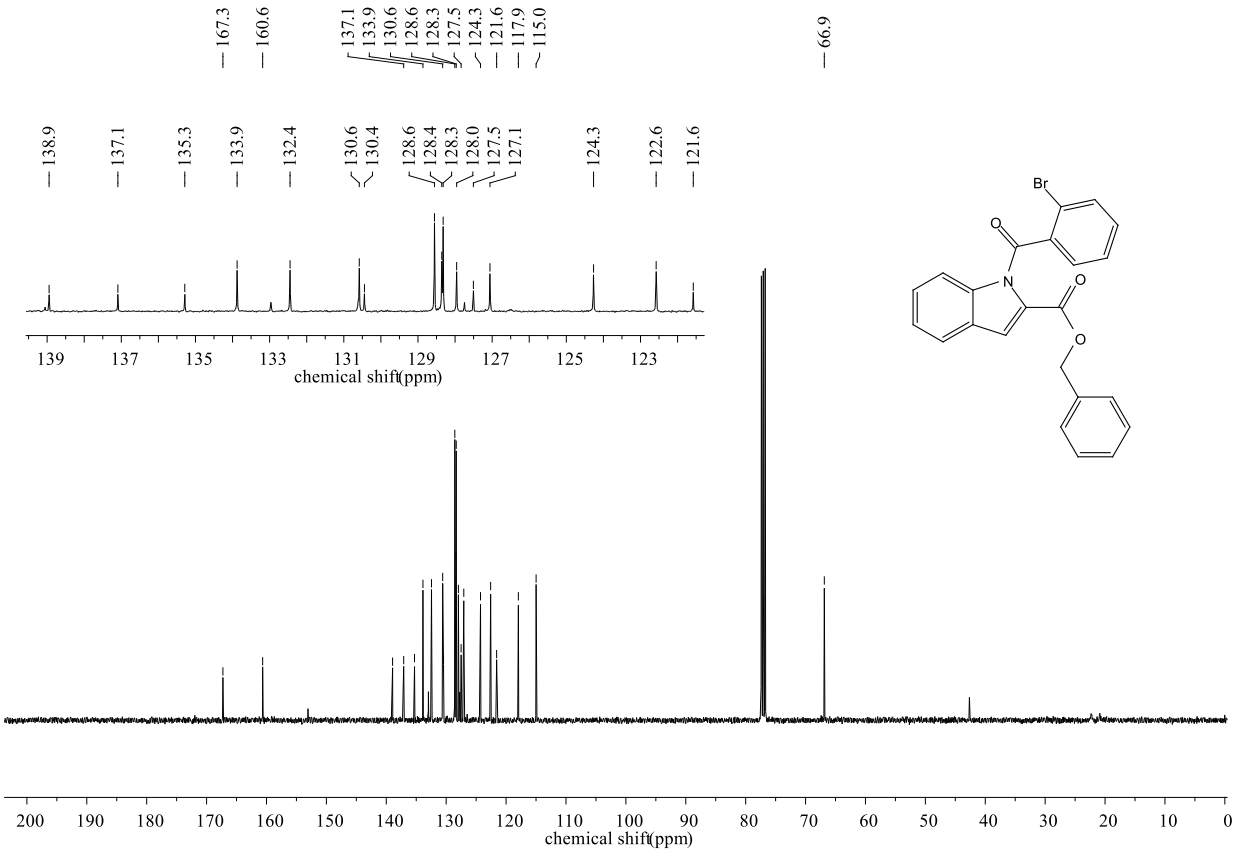
^{13}C NMR Spectra of compound **R9** (125 MHz, $CDCl_3$)



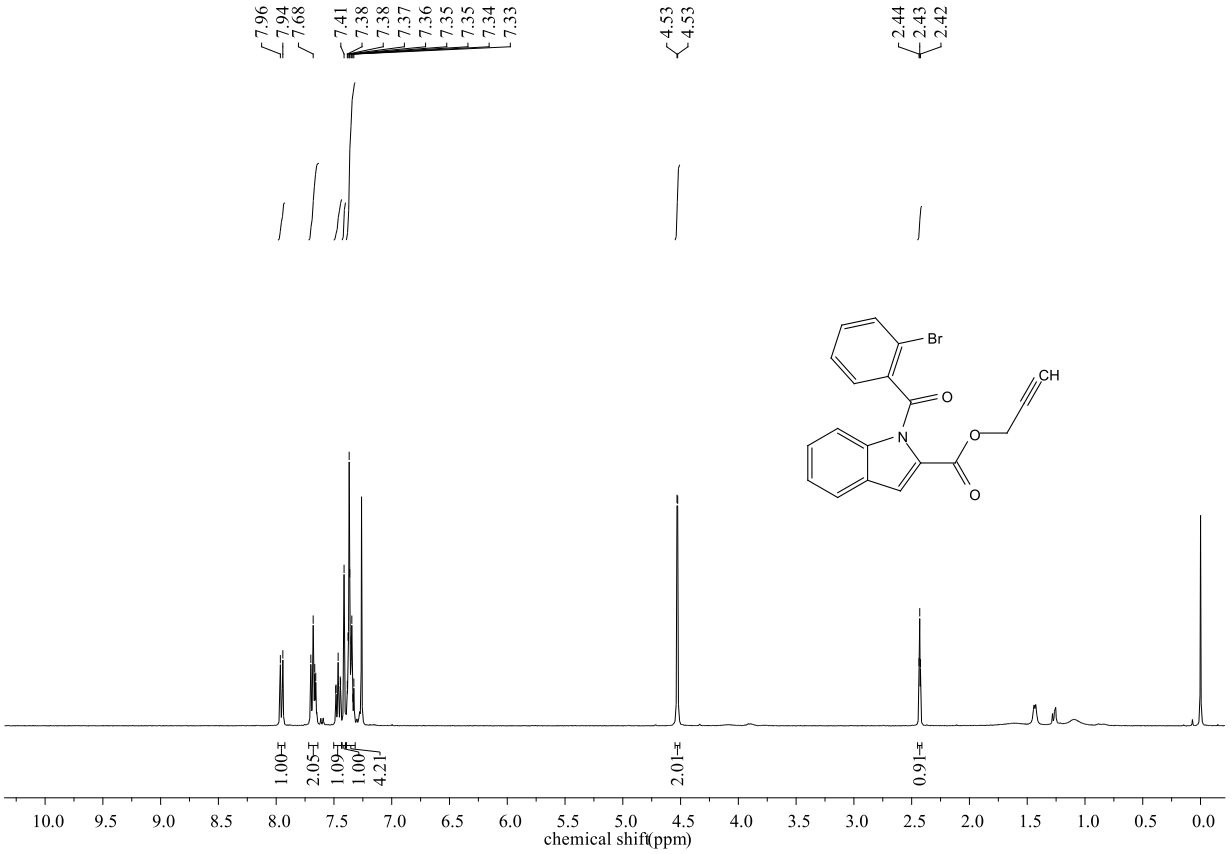
^{1}H NMR Spectra of compound **R10** (400 MHz, $CDCl_3$)



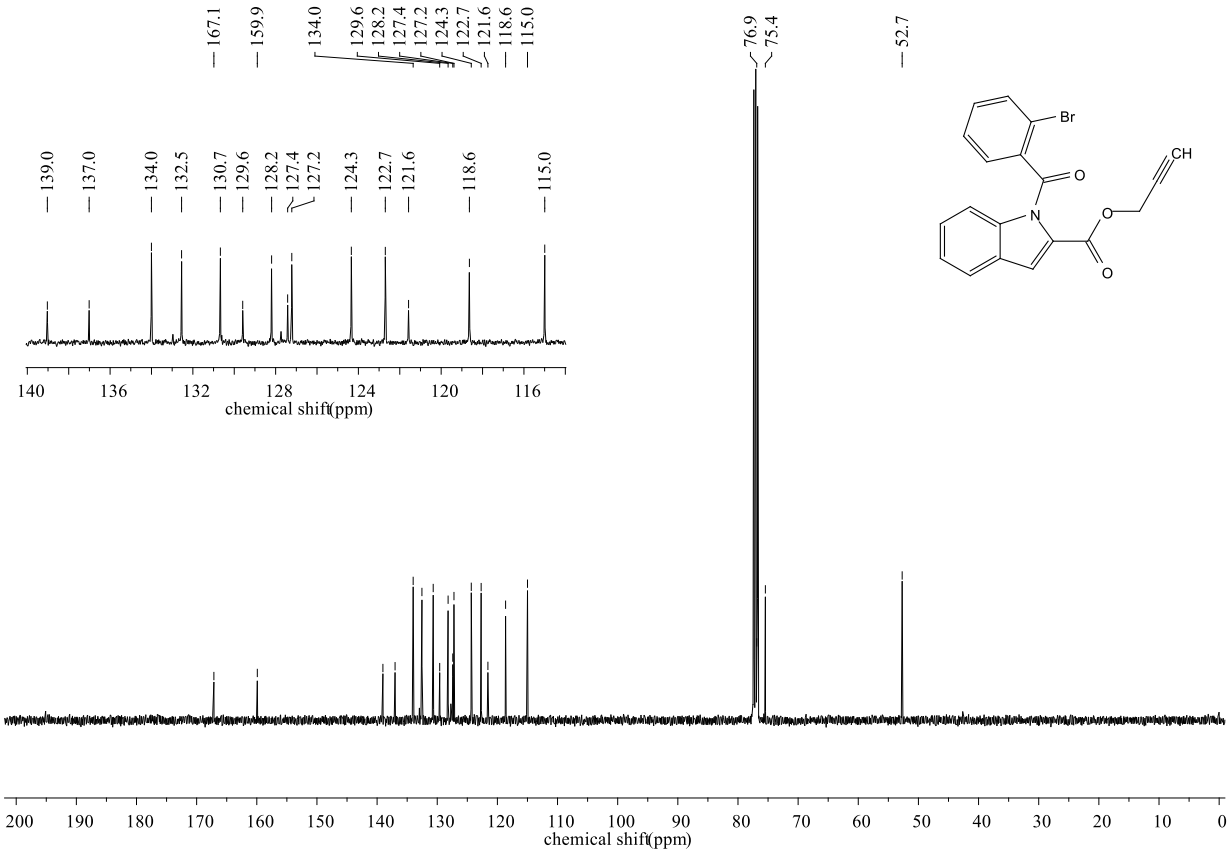
^{13}C NMR Spectra of compound **R10** (100 MHz, $CDCl_3$)



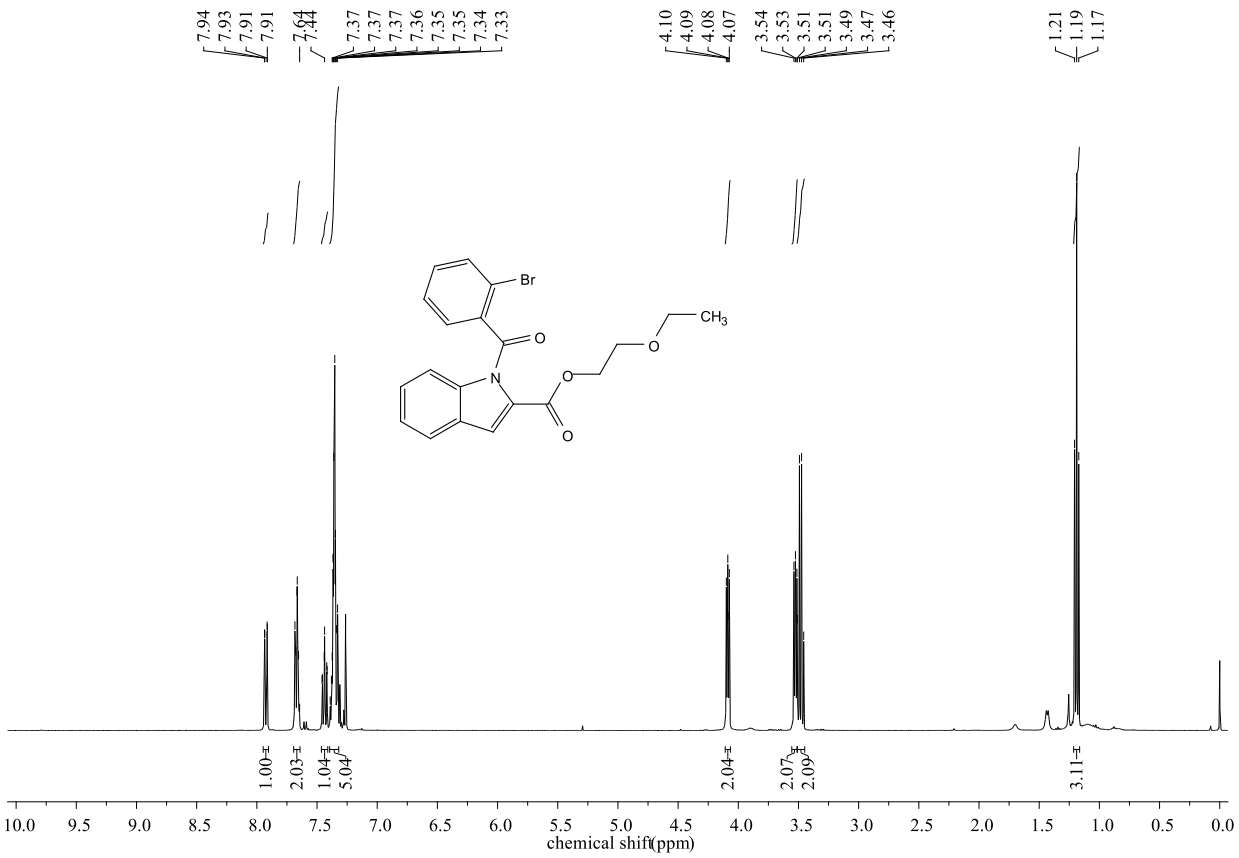
^{1}H NMR Spectra of compound **R11** (400 MHz, $CDCl_3$)



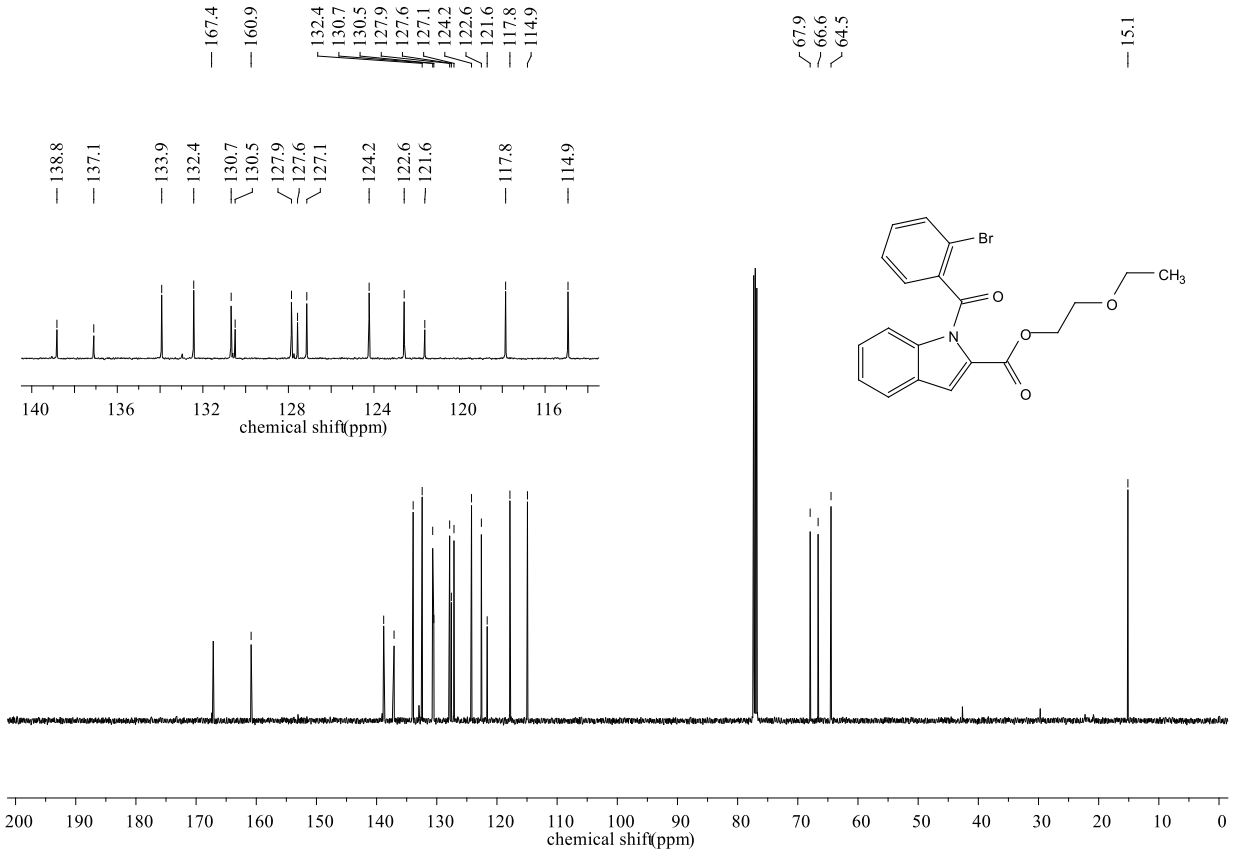
^{13}C NMR Spectra of compound **R11** (100 MHz, $CDCl_3$)



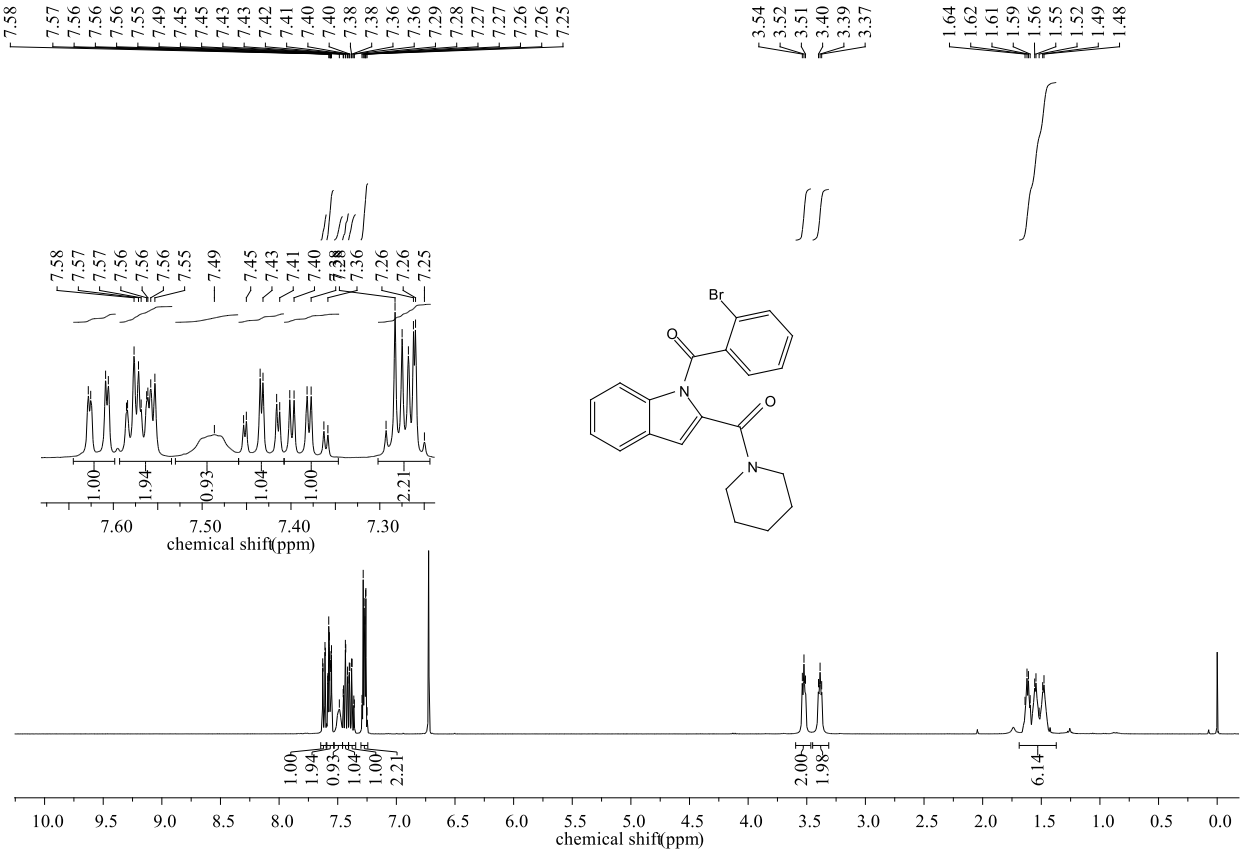
^{1}H NMR Spectra of compound **R12** (400 MHz, $CDCl_3$)



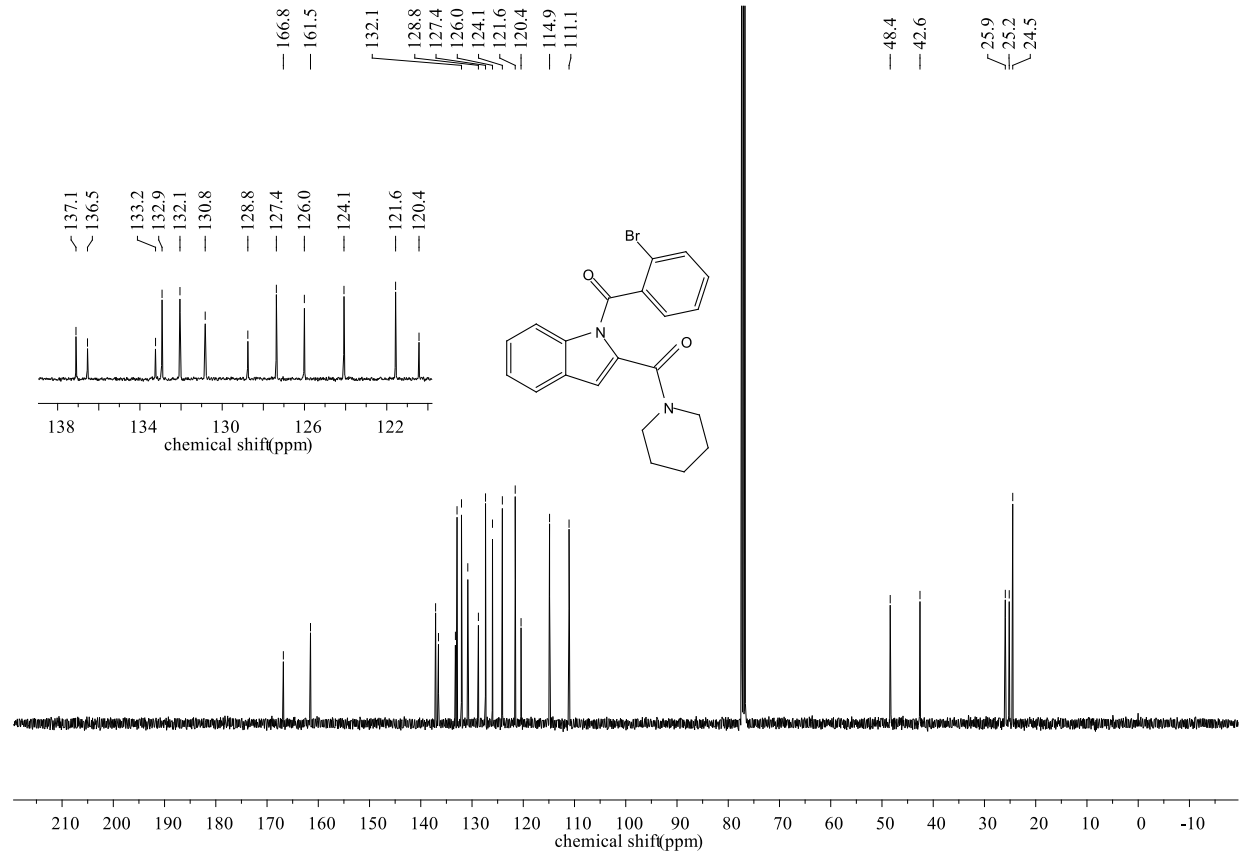
^{13}C NMR Spectra of compound **R12** (125 MHz, $CDCl_3$)



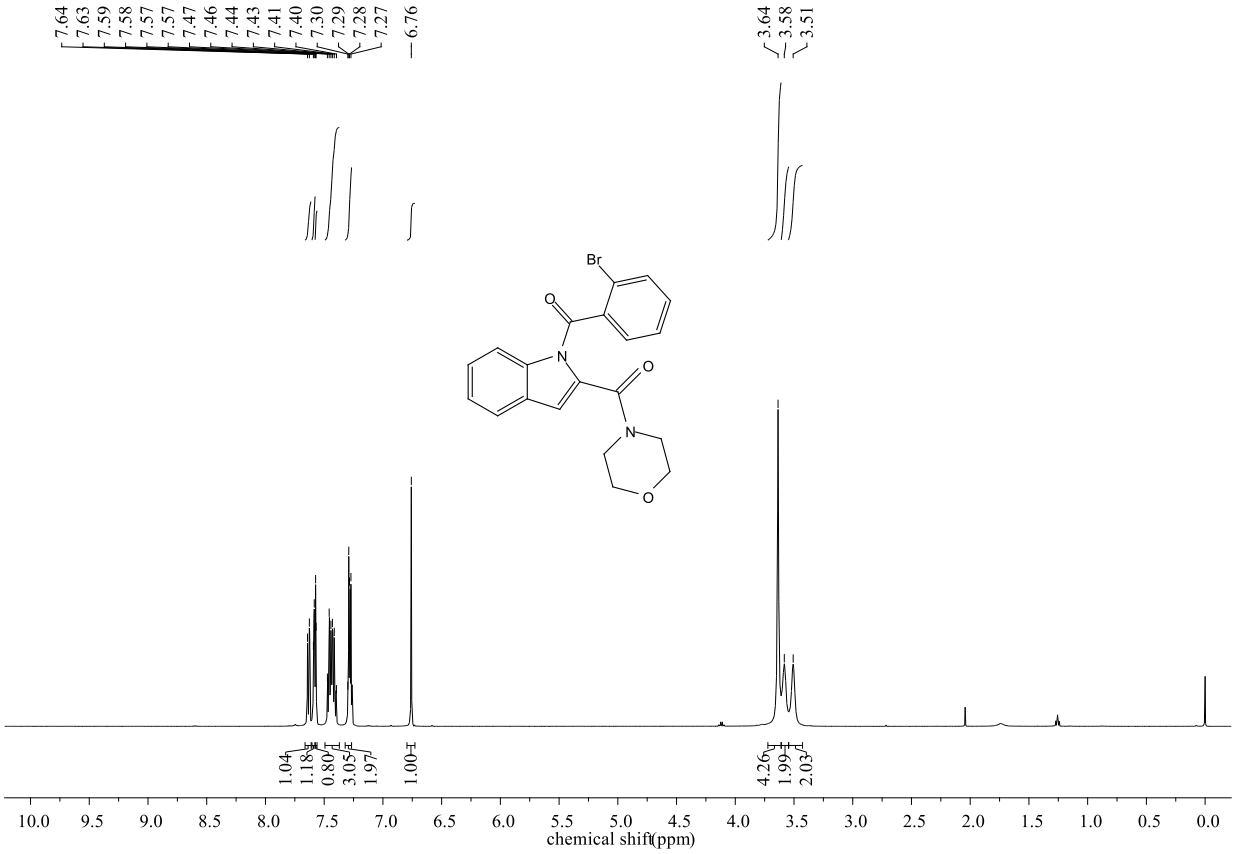
^{1}H NMR Spectra of compound **R13** (400 MHz, $CDCl_3$)



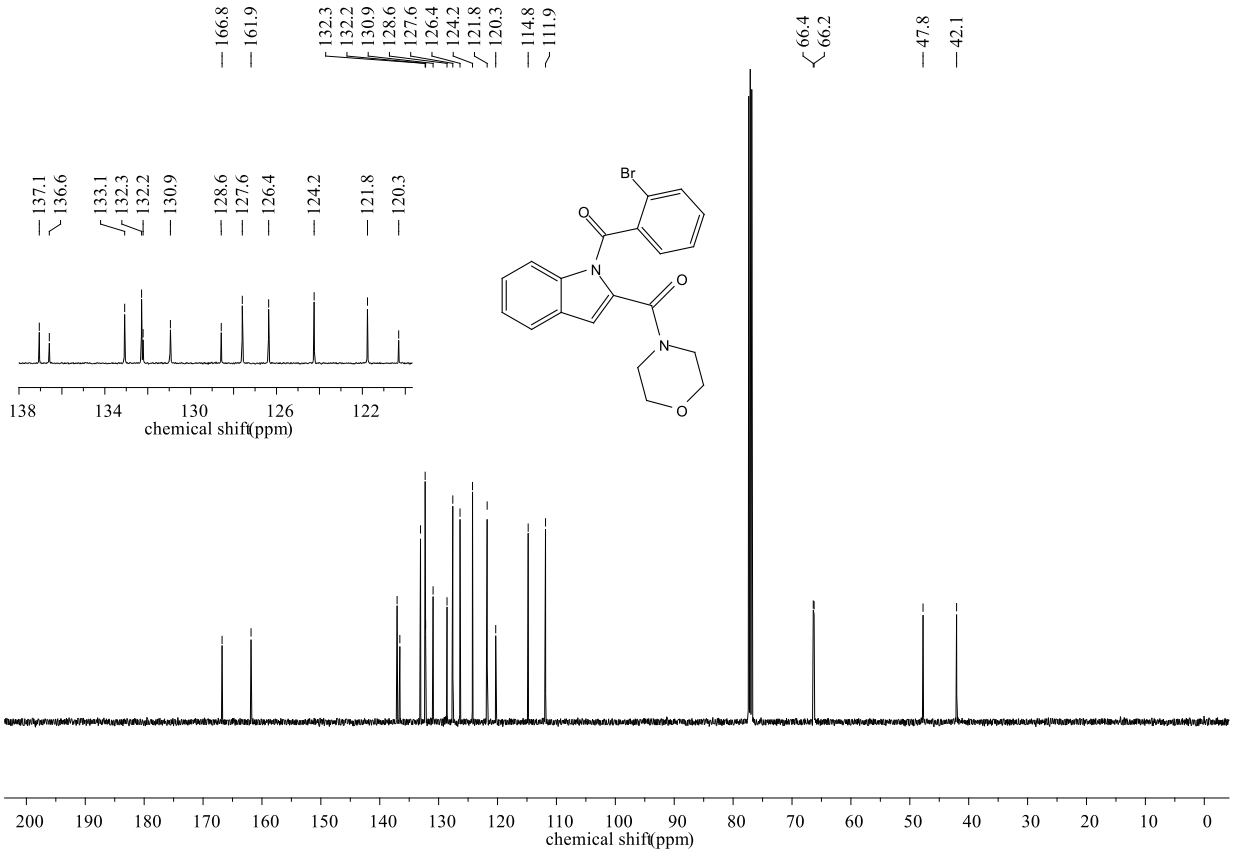
^{13}C NMR Spectra of compound **R13** (100 MHz, $CDCl_3$)



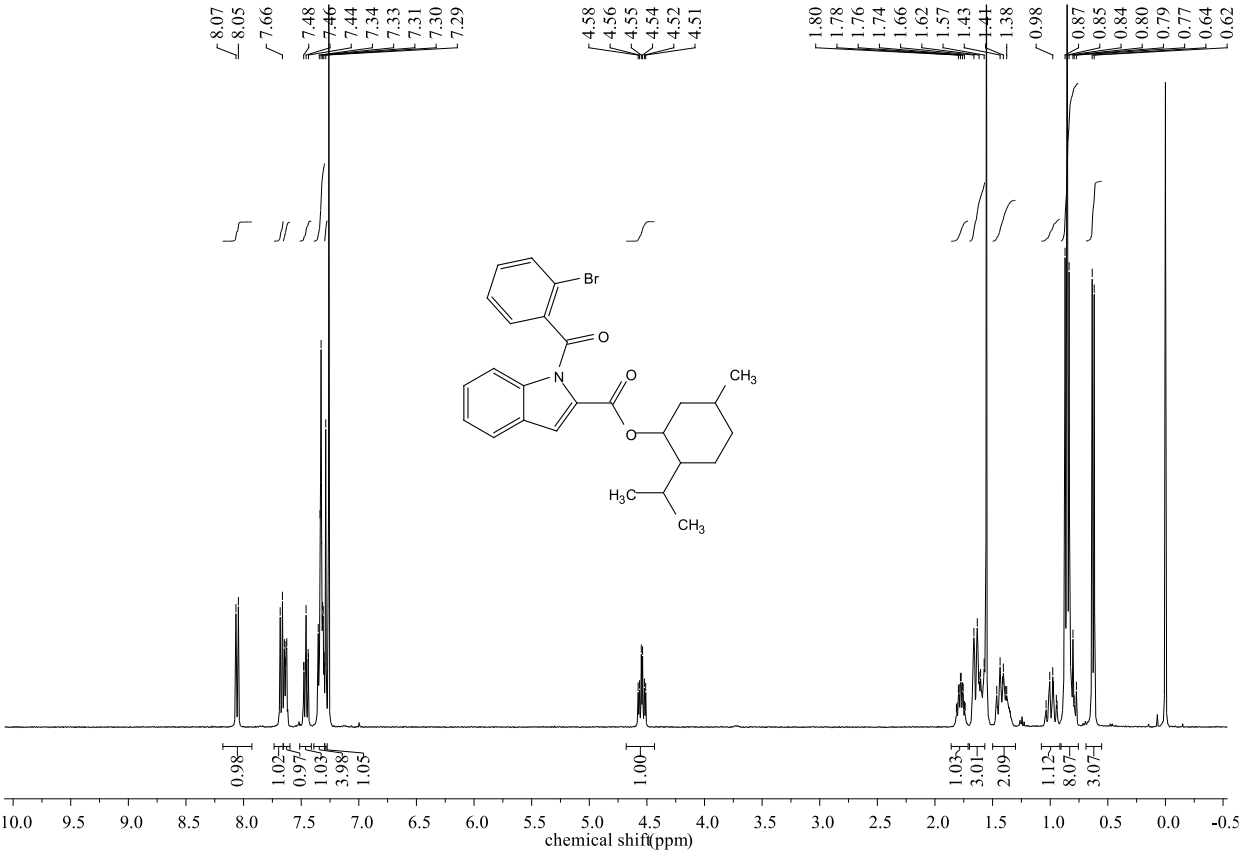
^{1}H NMR Spectra of compound **R14** (500 MHz, $CDCl_3$)



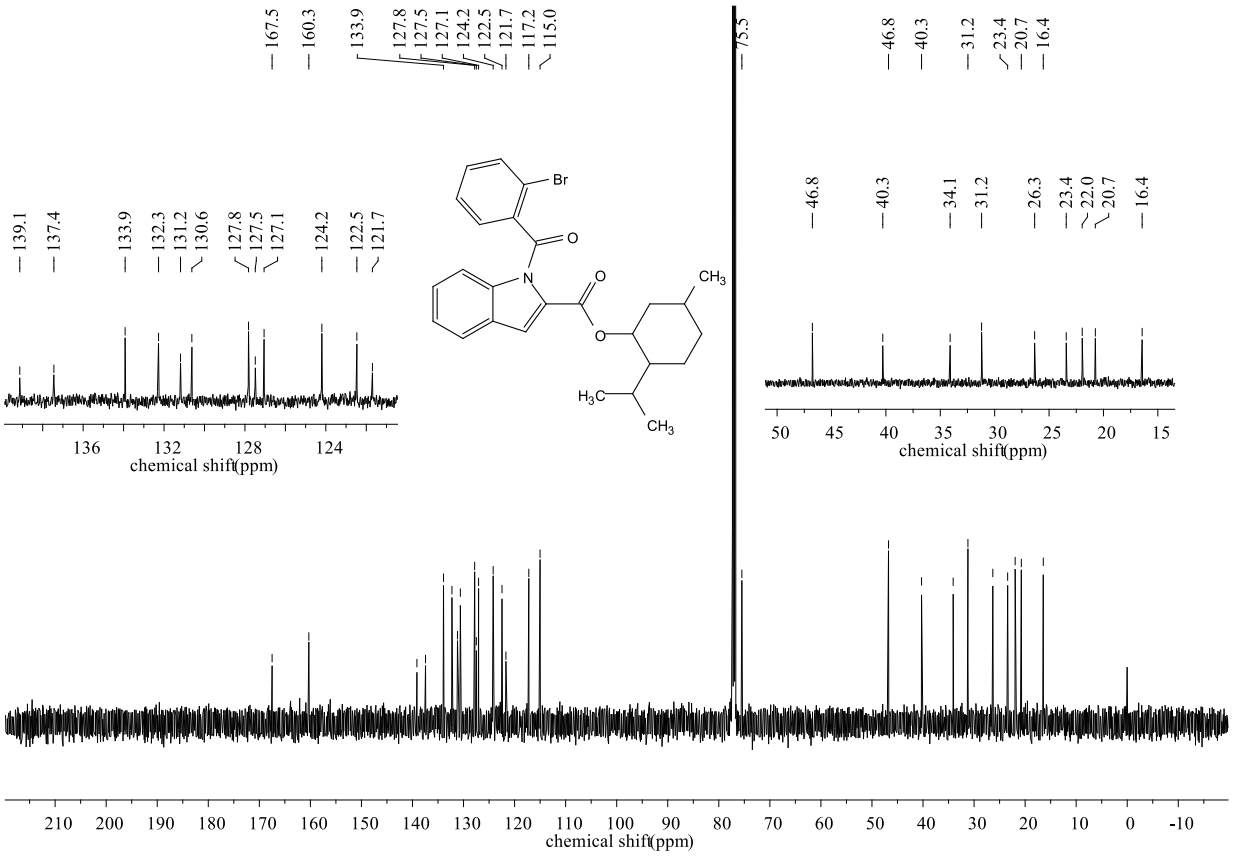
^{13}C NMR Spectra of compound **R14** (125 MHz, $CDCl_3$)



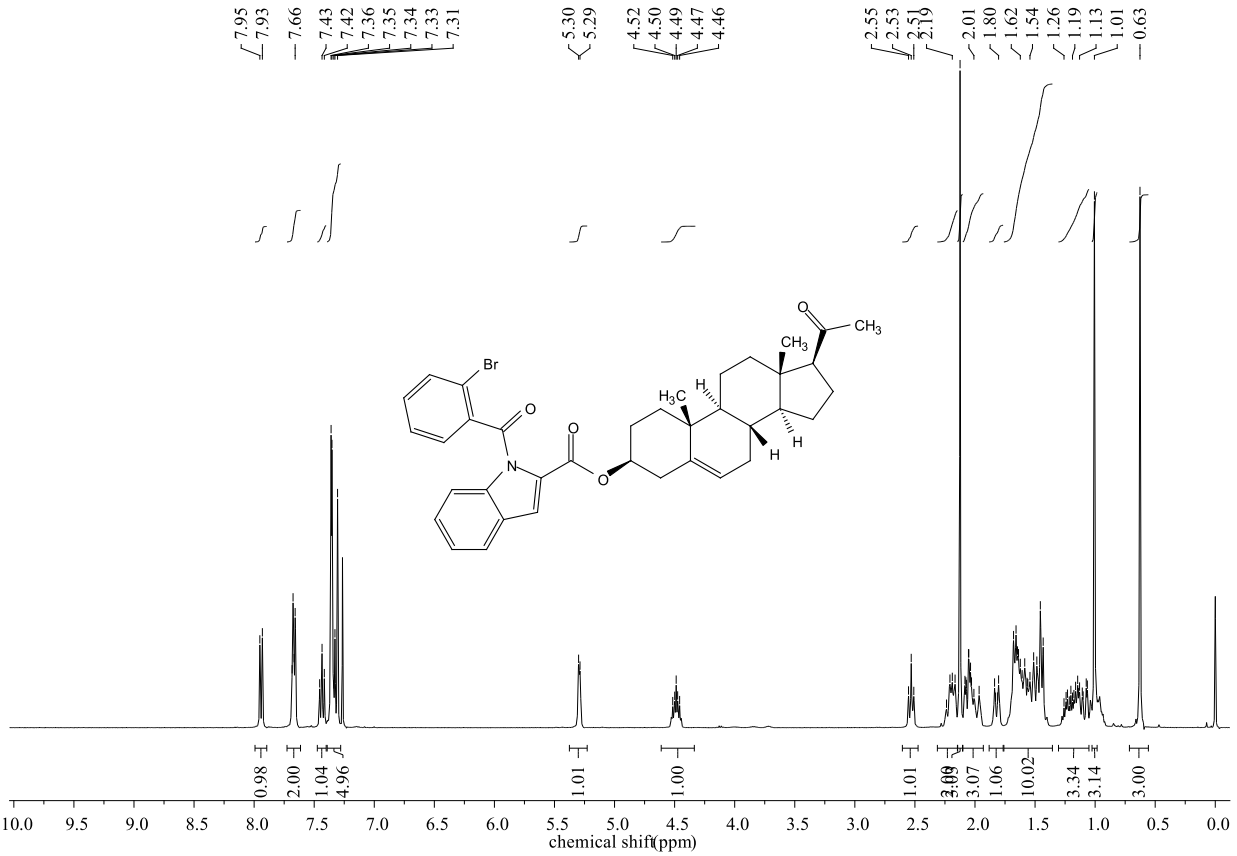
^{1}H NMR Spectra of compound **R15** (400 MHz, $CDCl_3$)



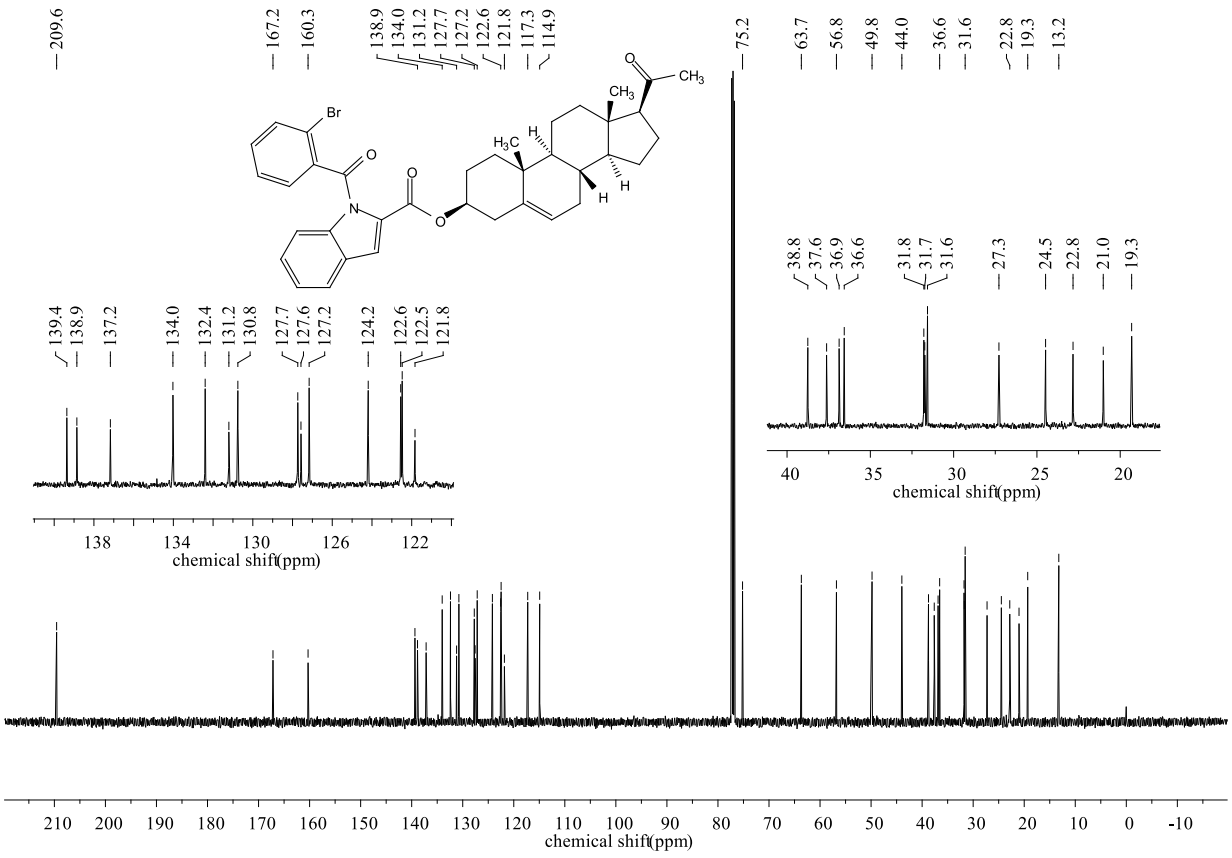
^{13}C NMR Spectra of compound **R15** (125 MHz, $CDCl_3$)



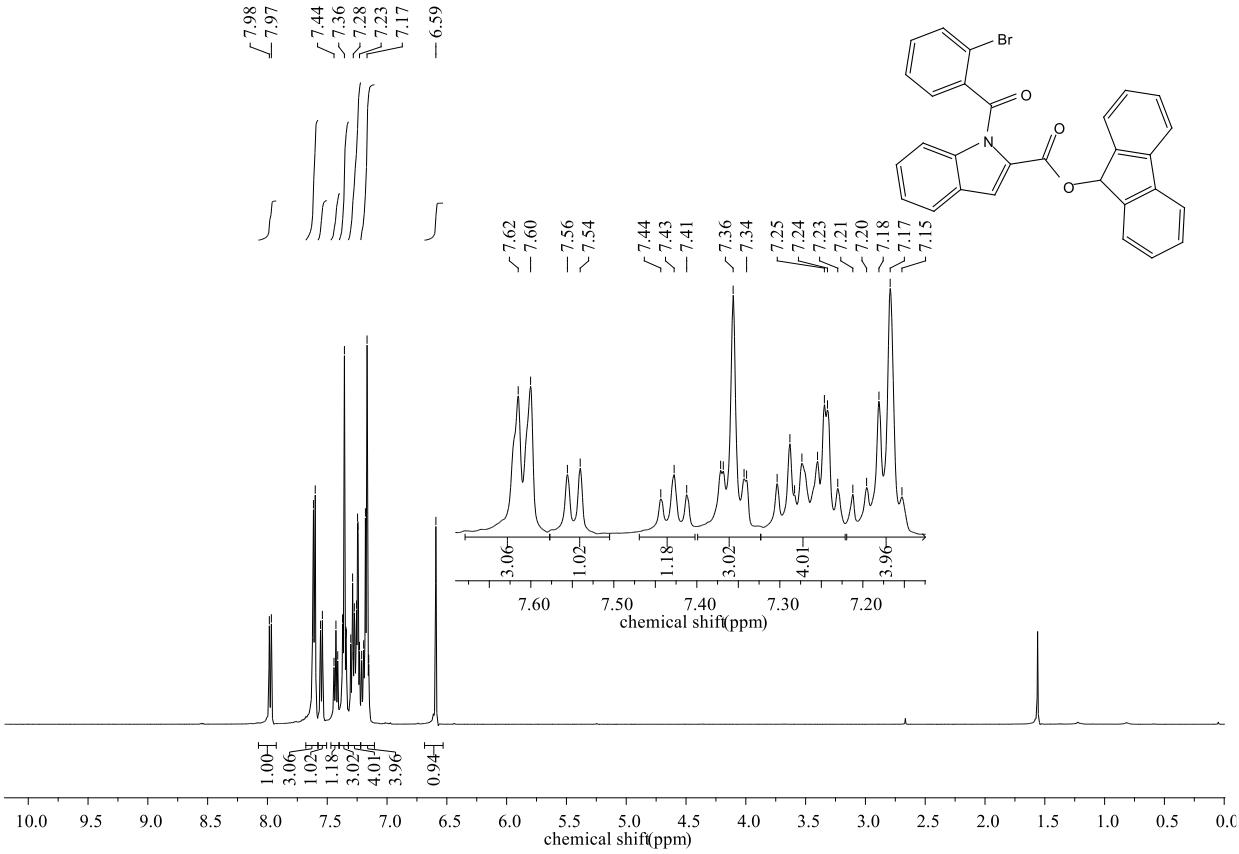
^{1}H NMR Spectra of compound **R16** (400 MHz, $CDCl_3$)



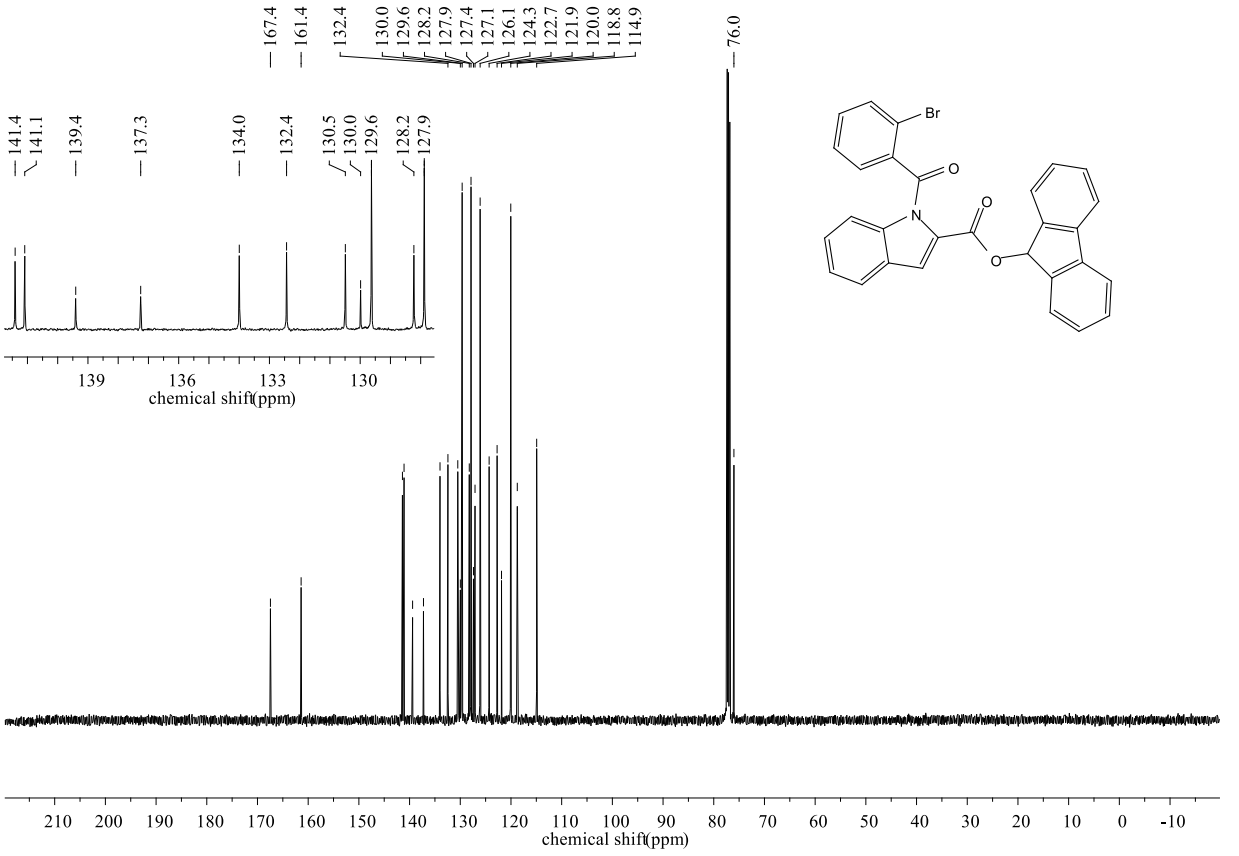
^{13}C NMR Spectra of compound **R16** (125 MHz, $CDCl_3$)



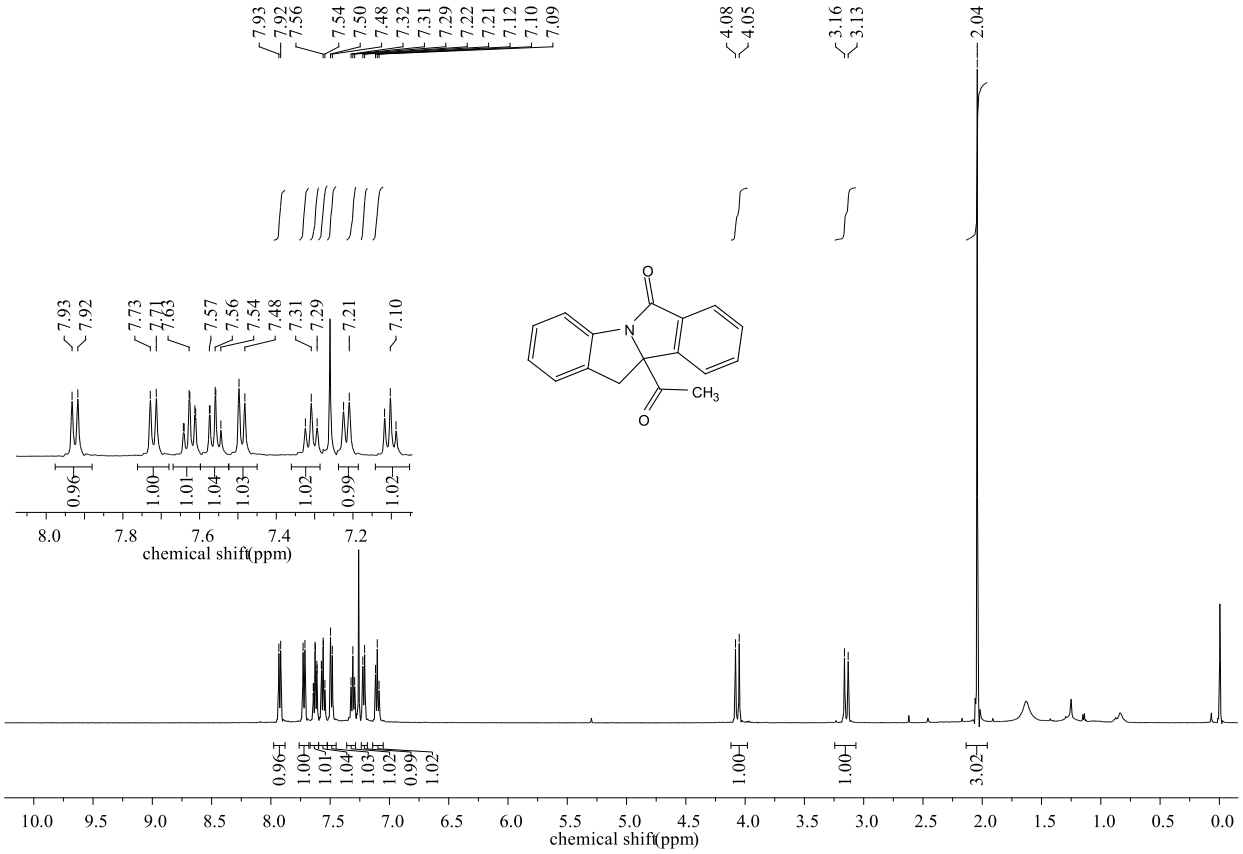
^{1}H NMR Spectra of compound **R7** (500 MHz, $CDCl_3$)



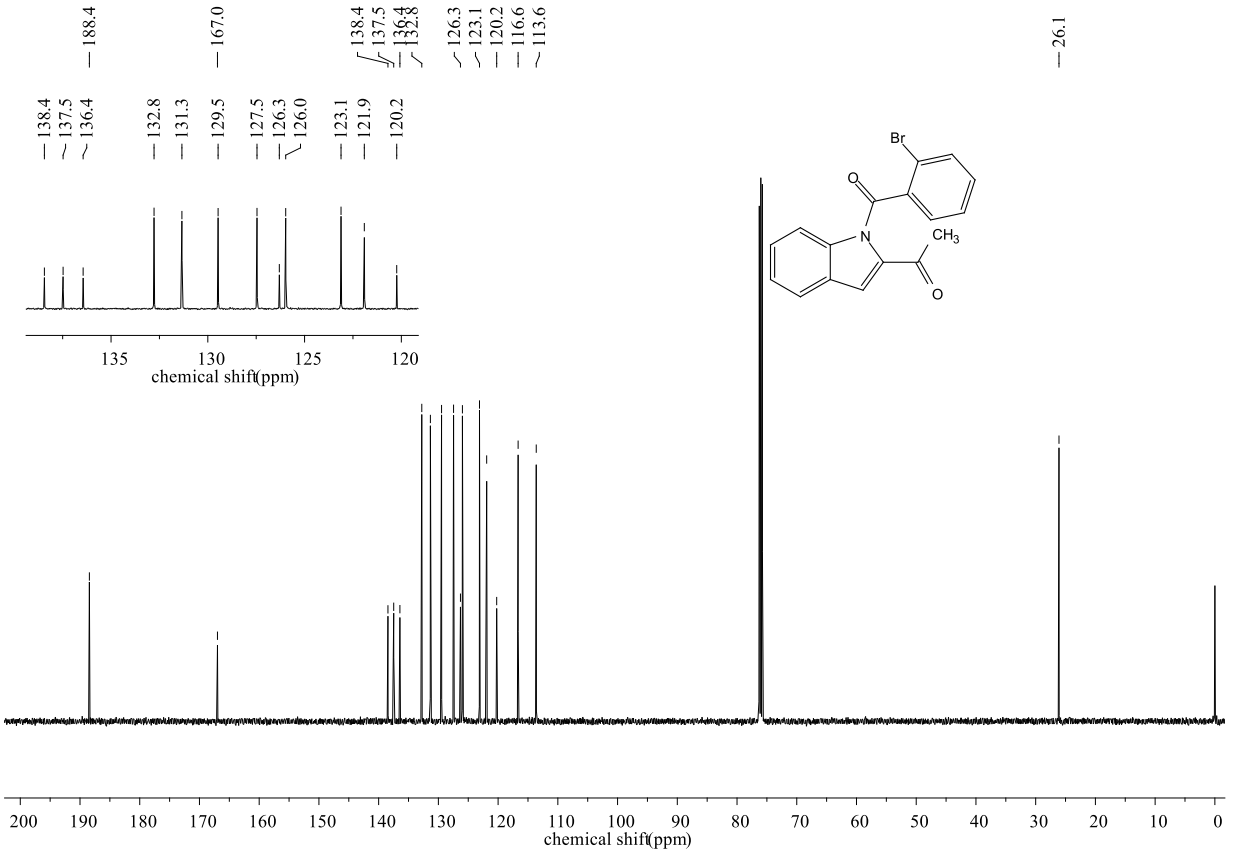
^{13}C NMR Spectra of compound **R17** (125 MHz, $CDCl_3$)



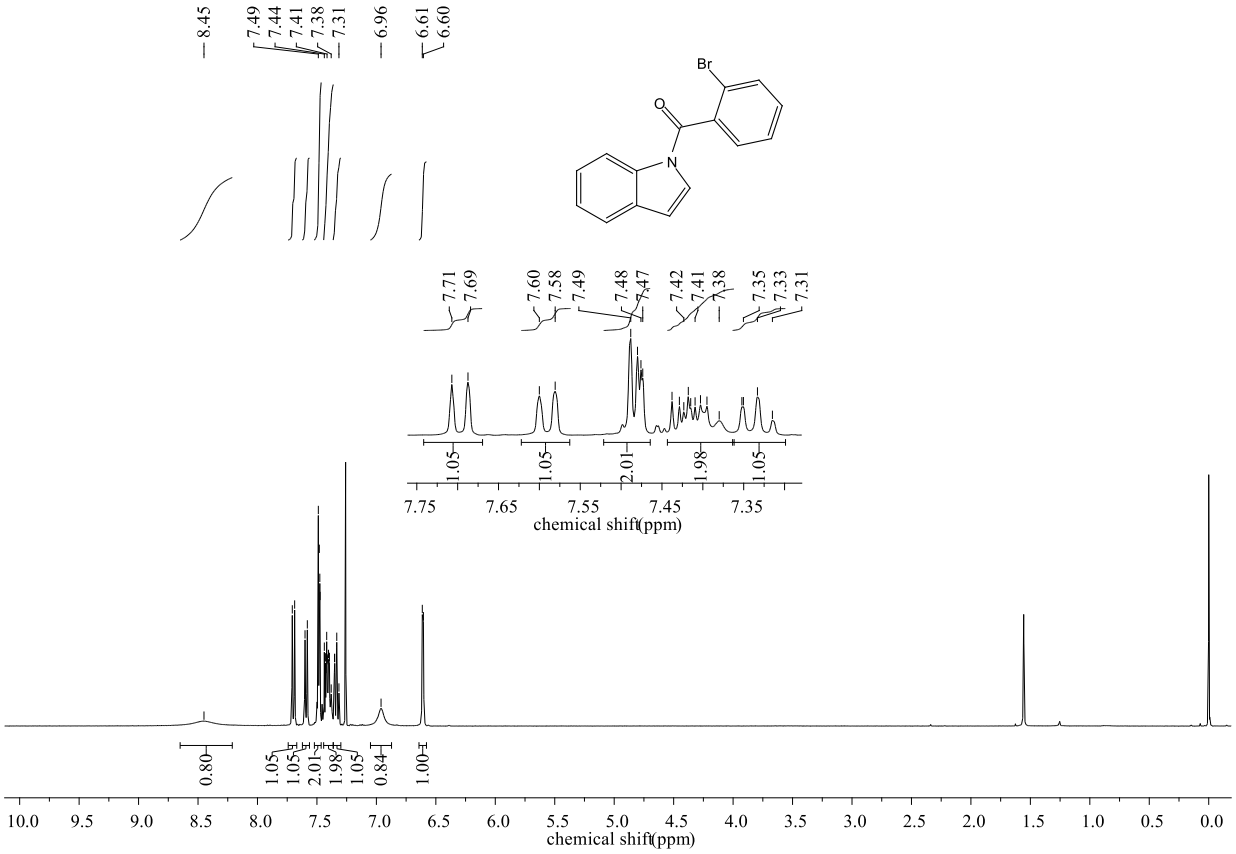
^{1}H NMR Spectra of compound **R18** (500 MHz, $CDCl_3$)



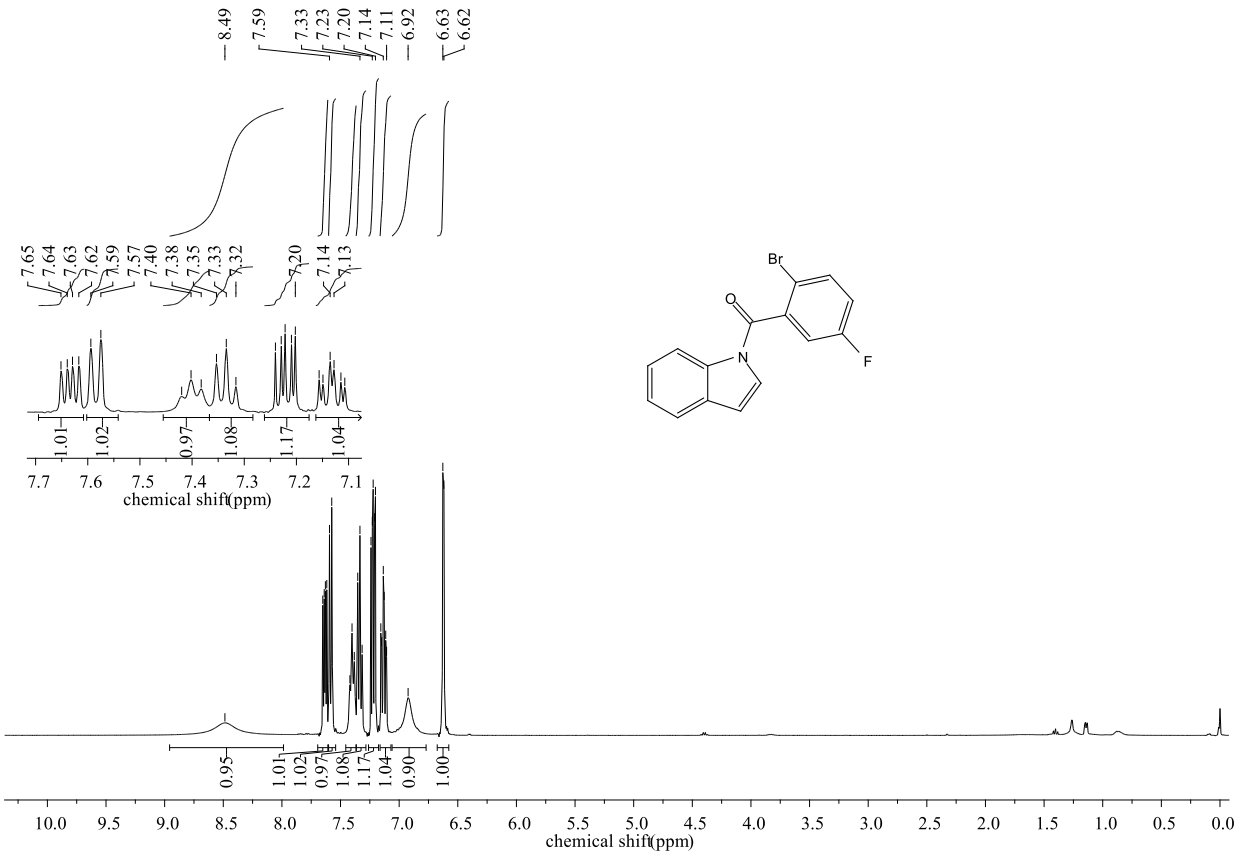
^{13}C NMR Spectra of compound **R18** (125 MHz, $CDCl_3$)



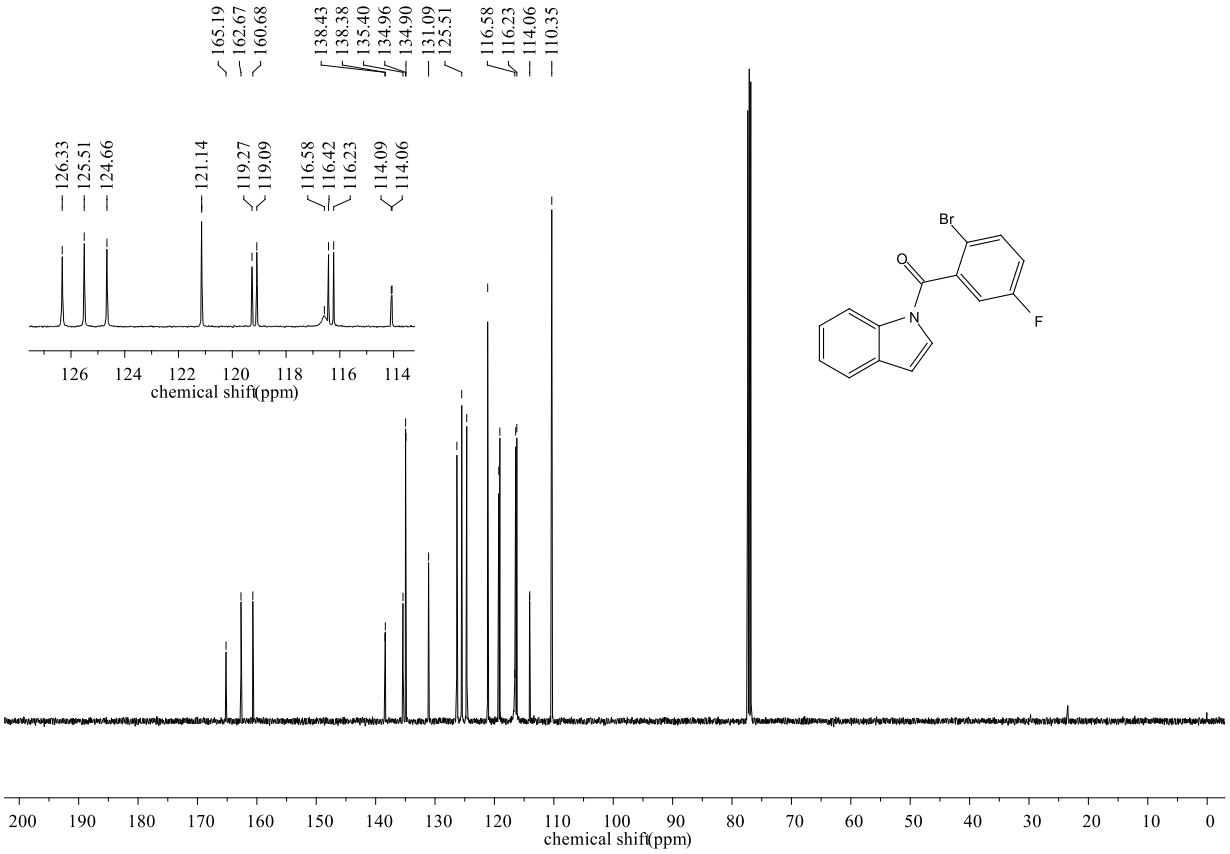
^{1}H NMR Spectra of compound **R19** (400 MHz, $CDCl_3$)



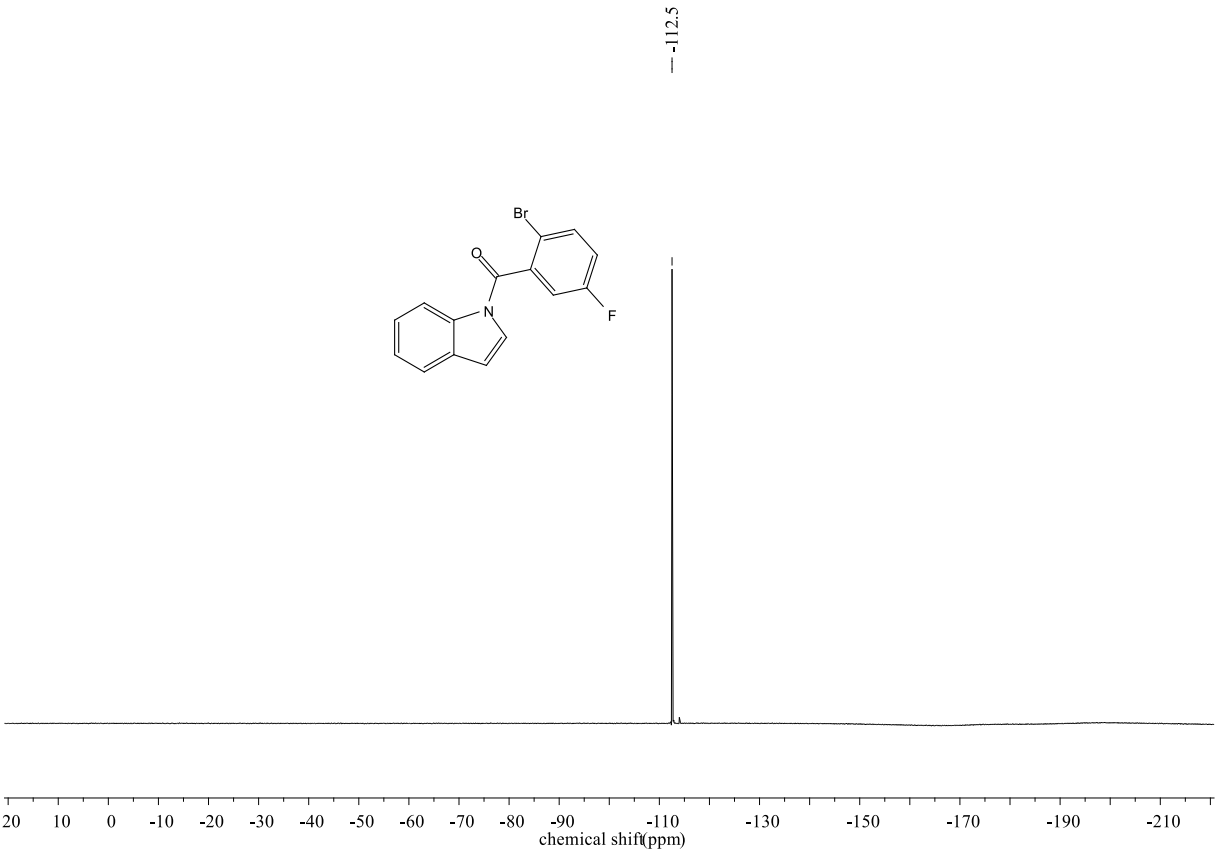
^{1}H NMR Spectra of compound **R20** (400 MHz, $CDCl_3$)



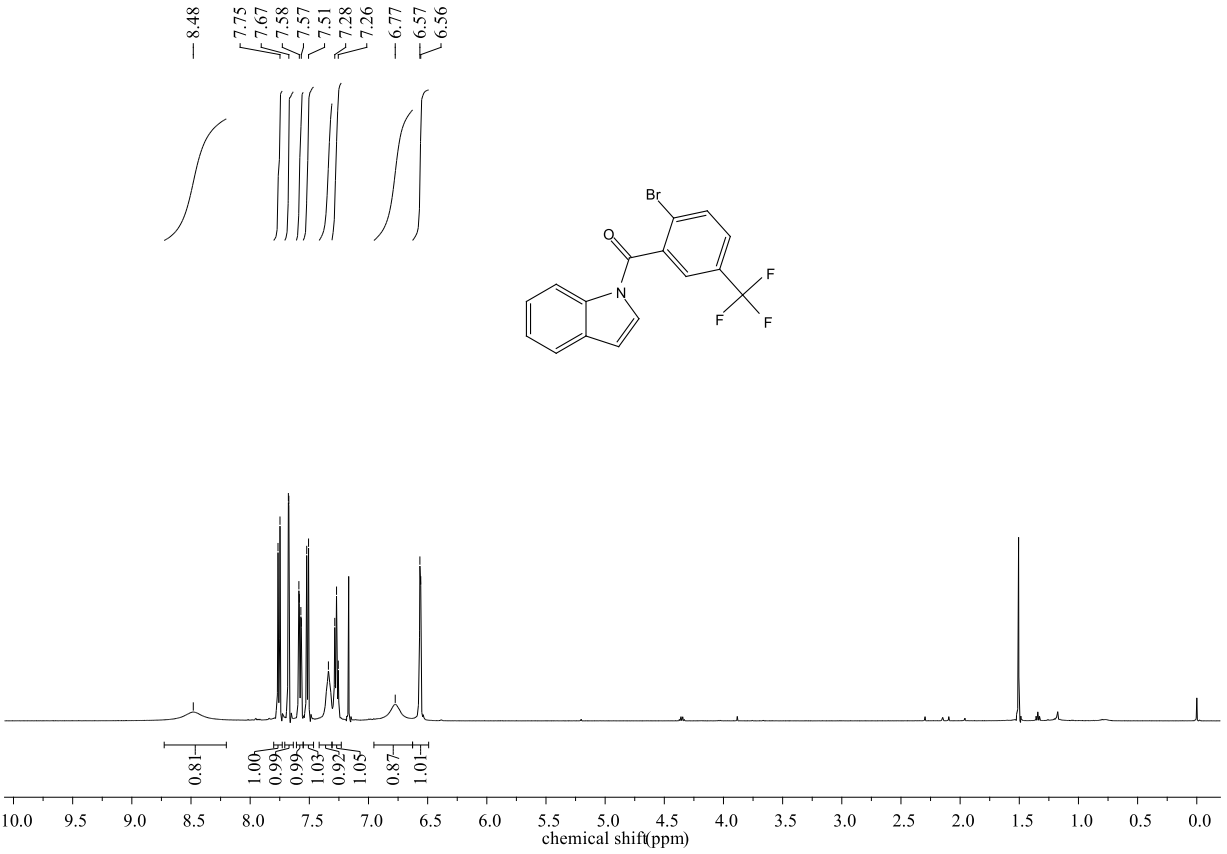
^{13}C NMR Spectra of compound **R20** (125 MHz, $CDCl_3$)



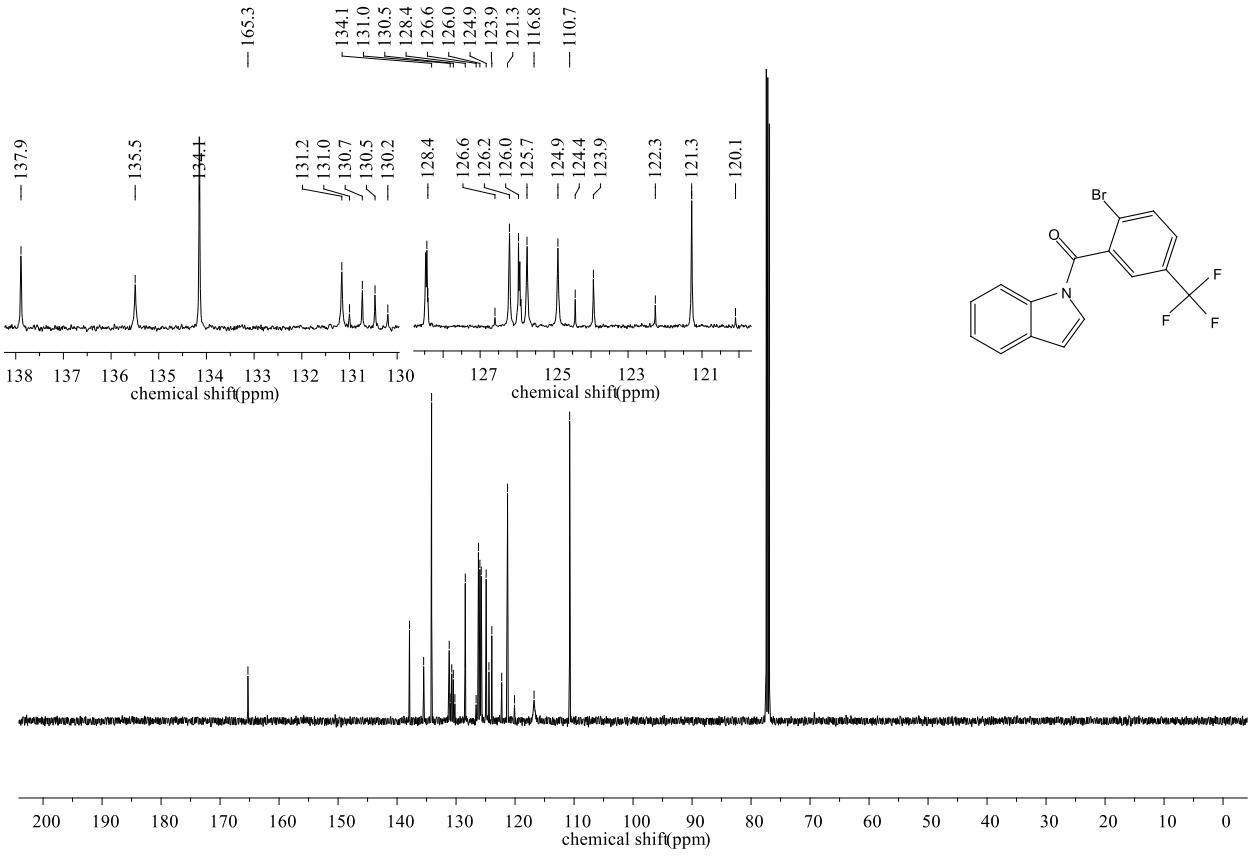
^{19}F NMR Spectra of compound **R20** (375 MHz, $CDCl_3$)



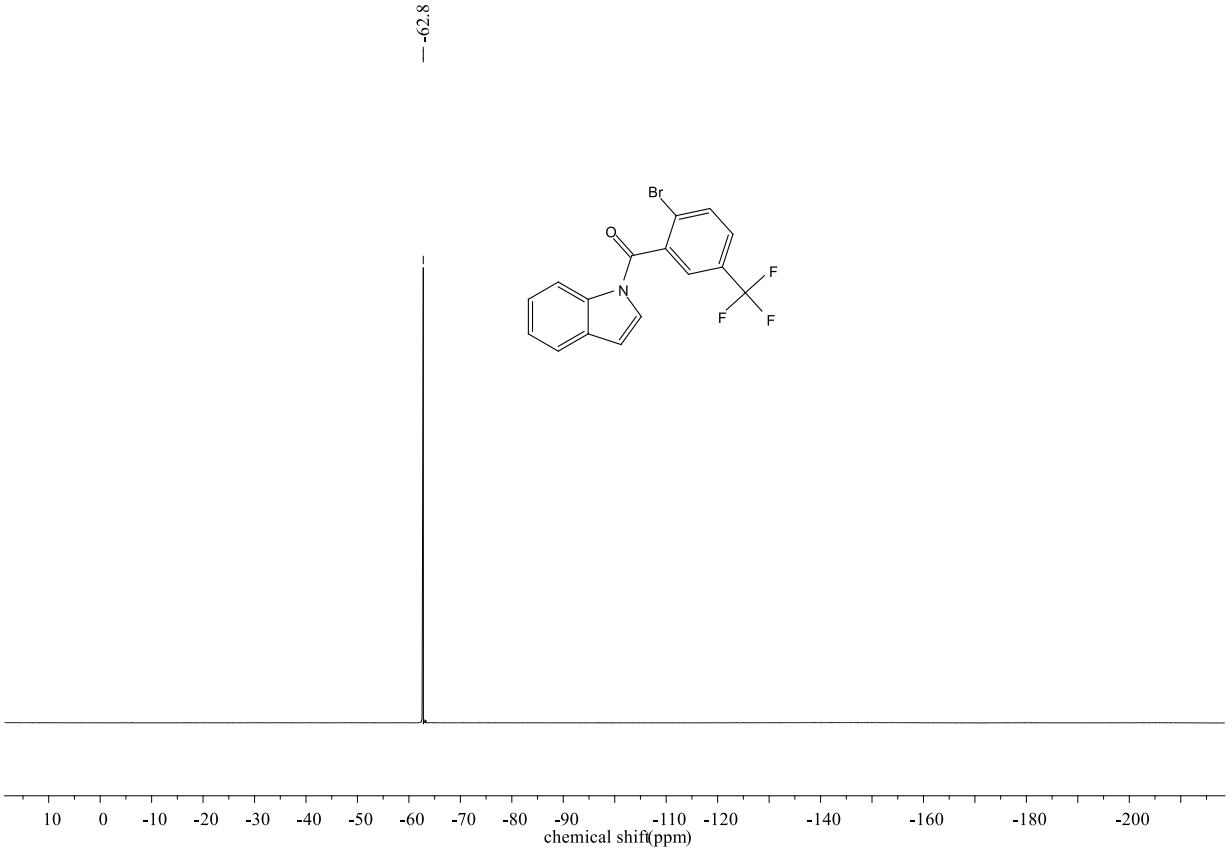
^{1}H NMR Spectra of compound **R21** (500 MHz, $CDCl_3$)



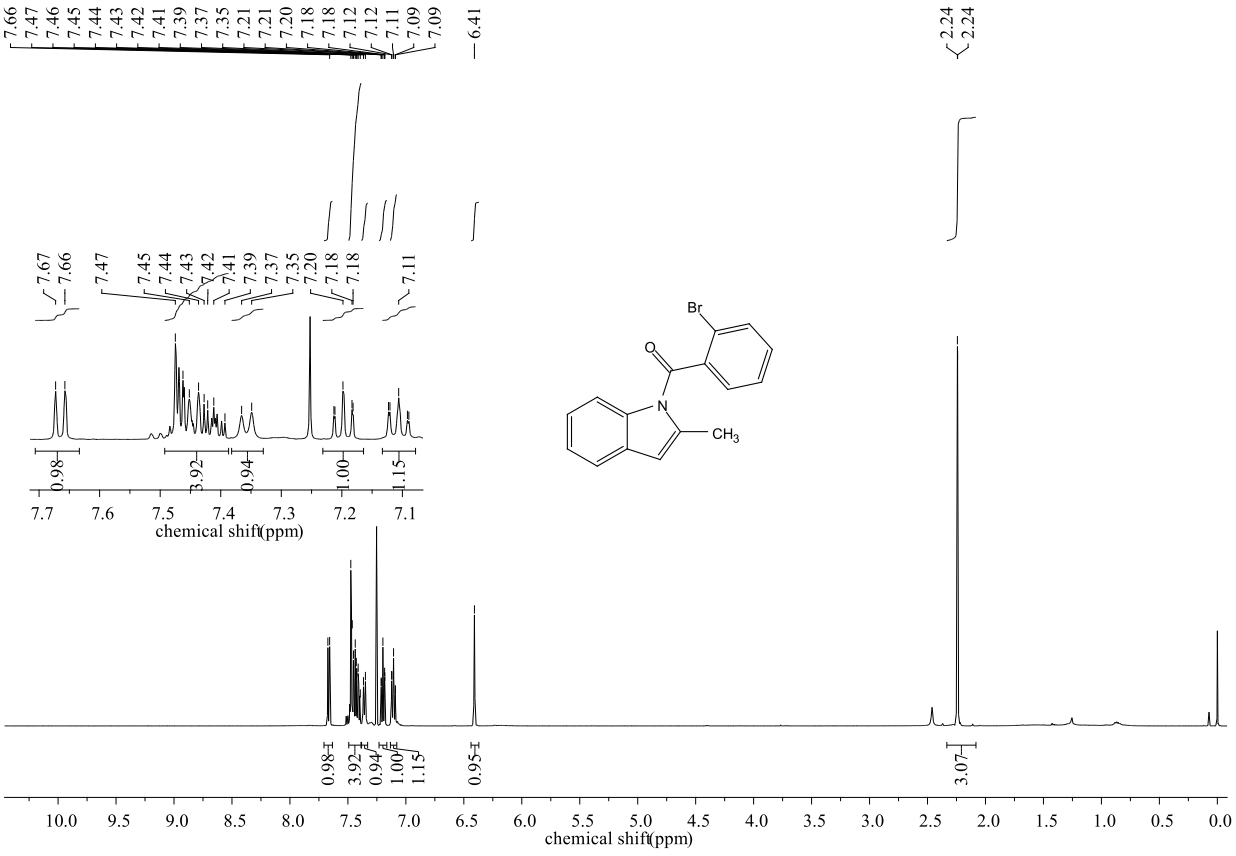
^{13}C NMR Spectra of compound **R21** (125 MHz, $CDCl_3$)



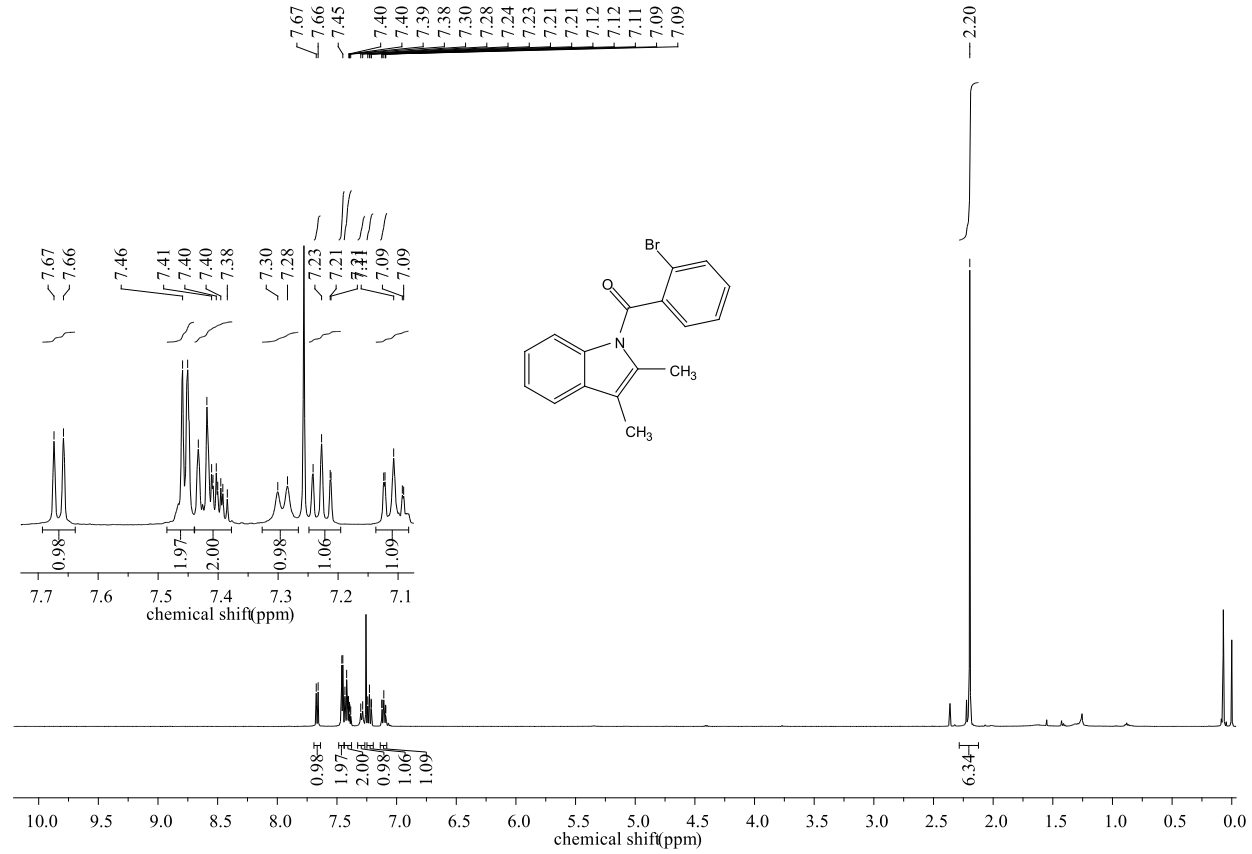
^{19}F NMR Spectra of compound **R21** (300 MHz, $CDCl_3$)



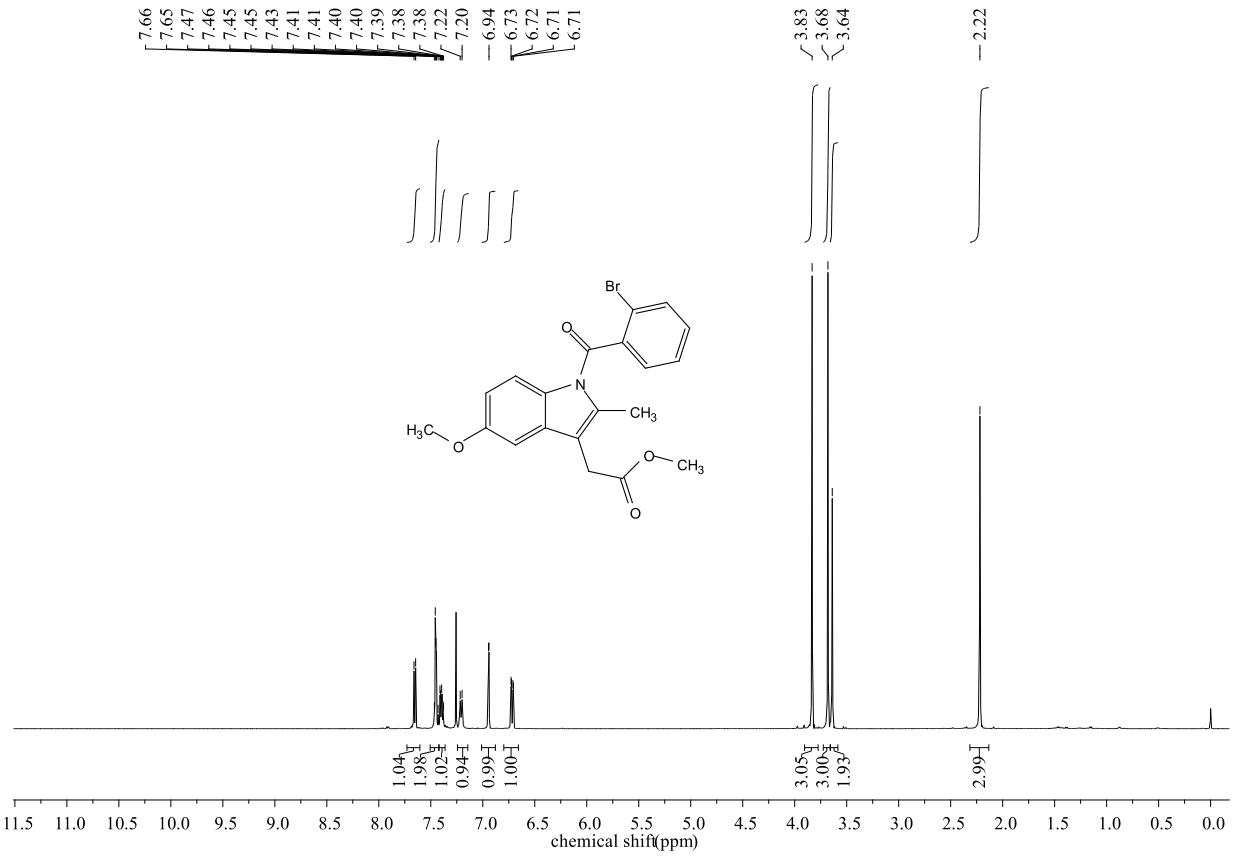
^{1}H NMR Spectra of compound **R22** (500 MHz, $CDCl_3$)



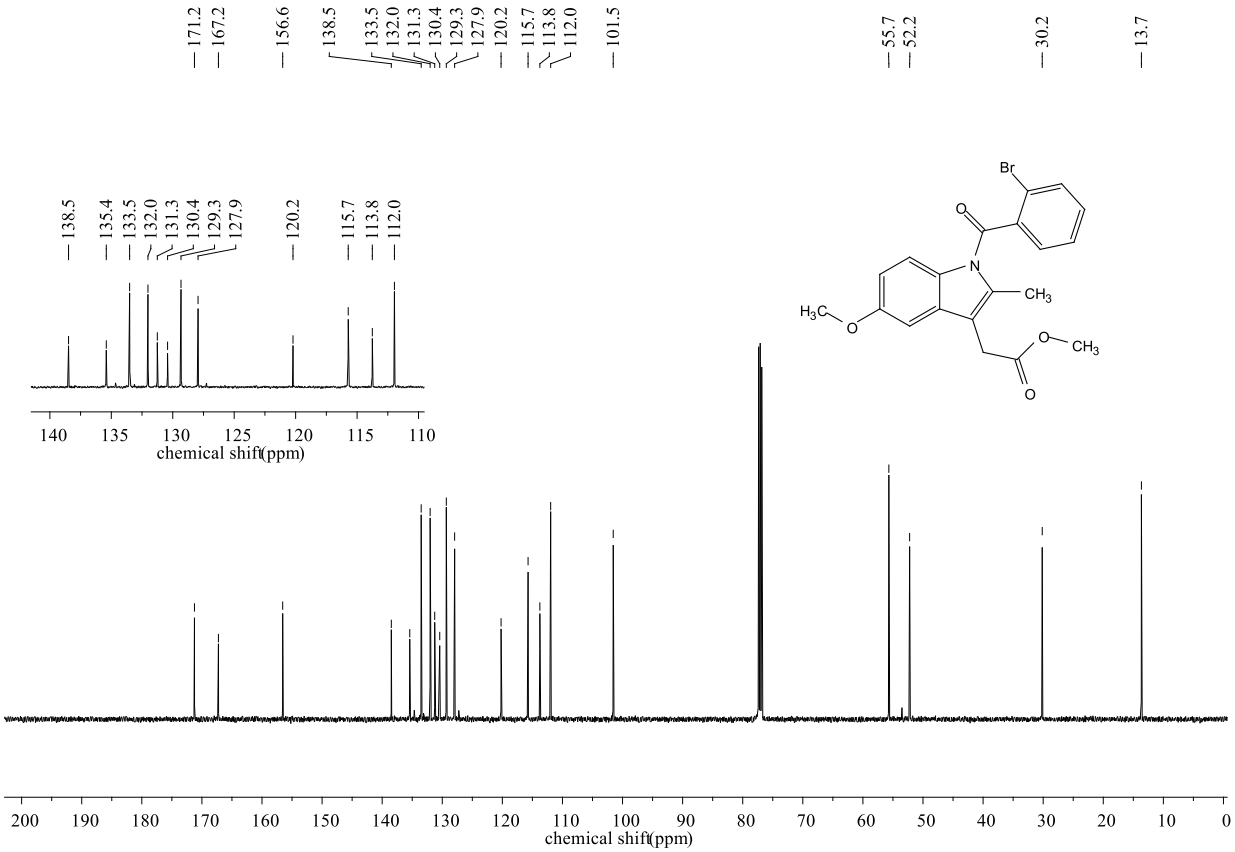
^{1}H NMR Spectra of compound **R23** (500 MHz, $CDCl_3$)



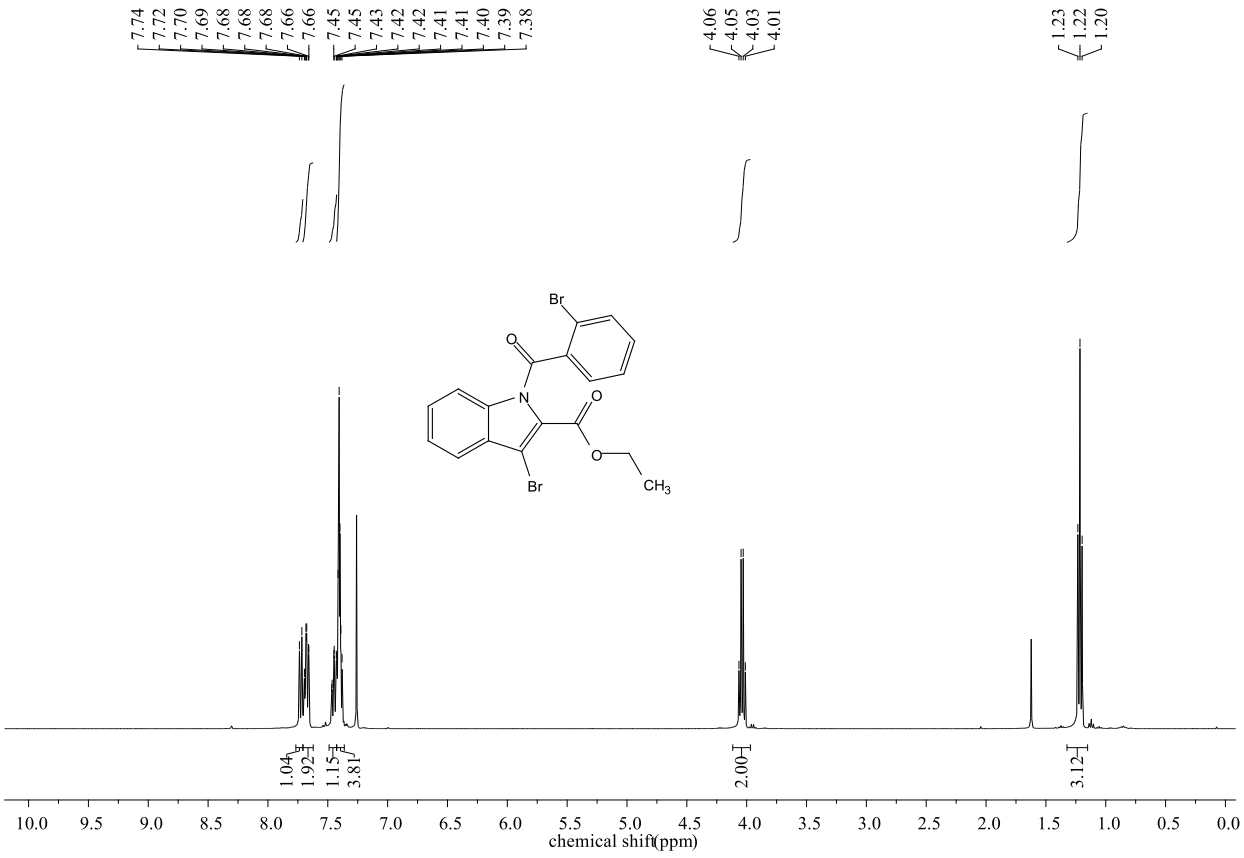
^{1}H NMR Spectra of compound **R24** (500 MHz, $CDCl_3$)



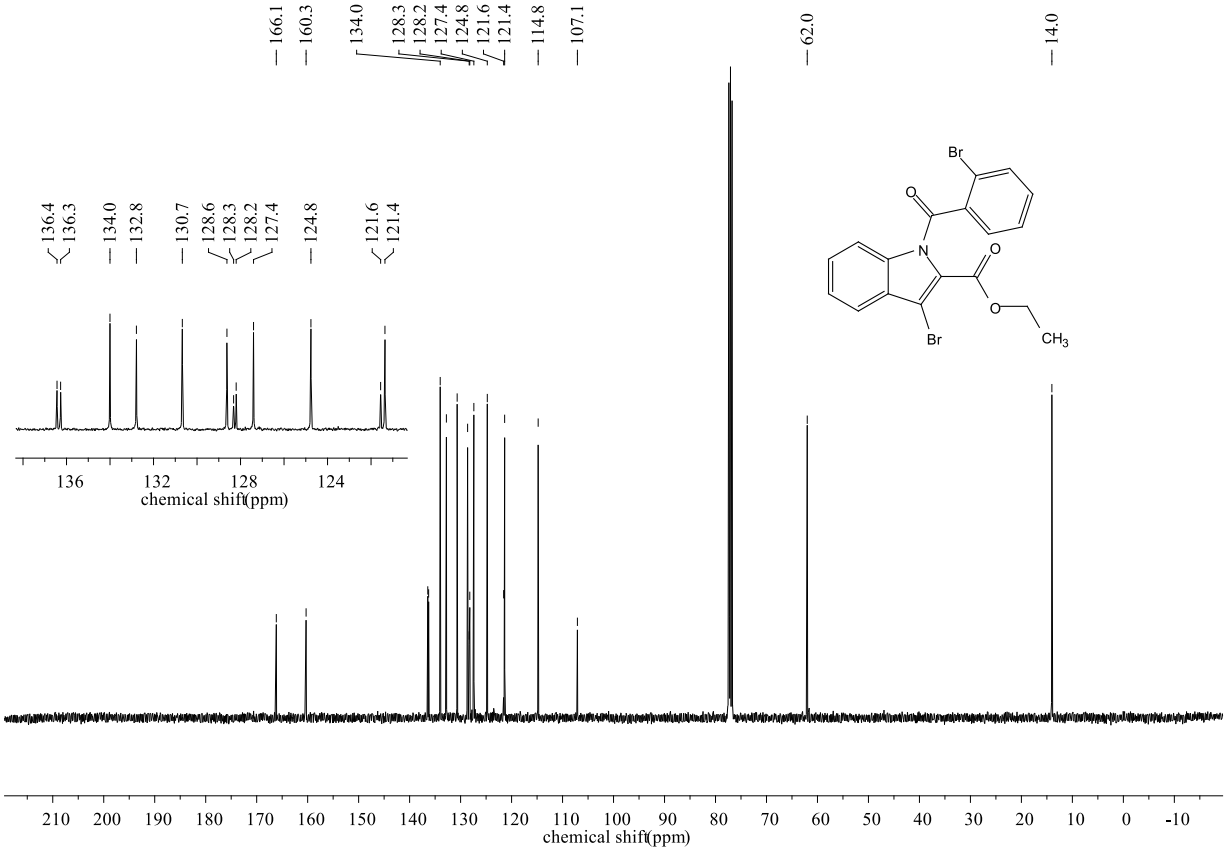
^{13}C NMR Spectra of compound **R24** (125 MHz, $CDCl_3$)



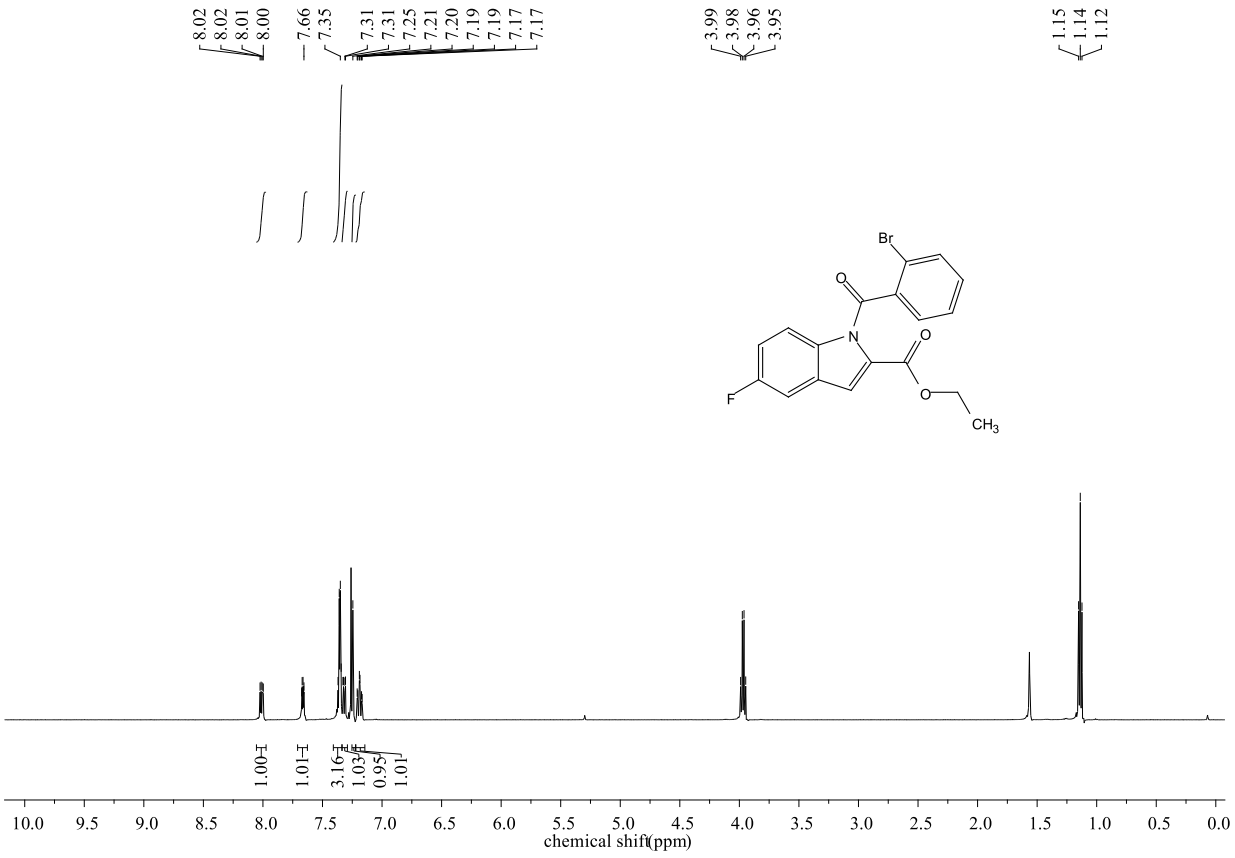
^{1}H NMR Spectra of compound **R25** (400 MHz, $CDCl_3$)



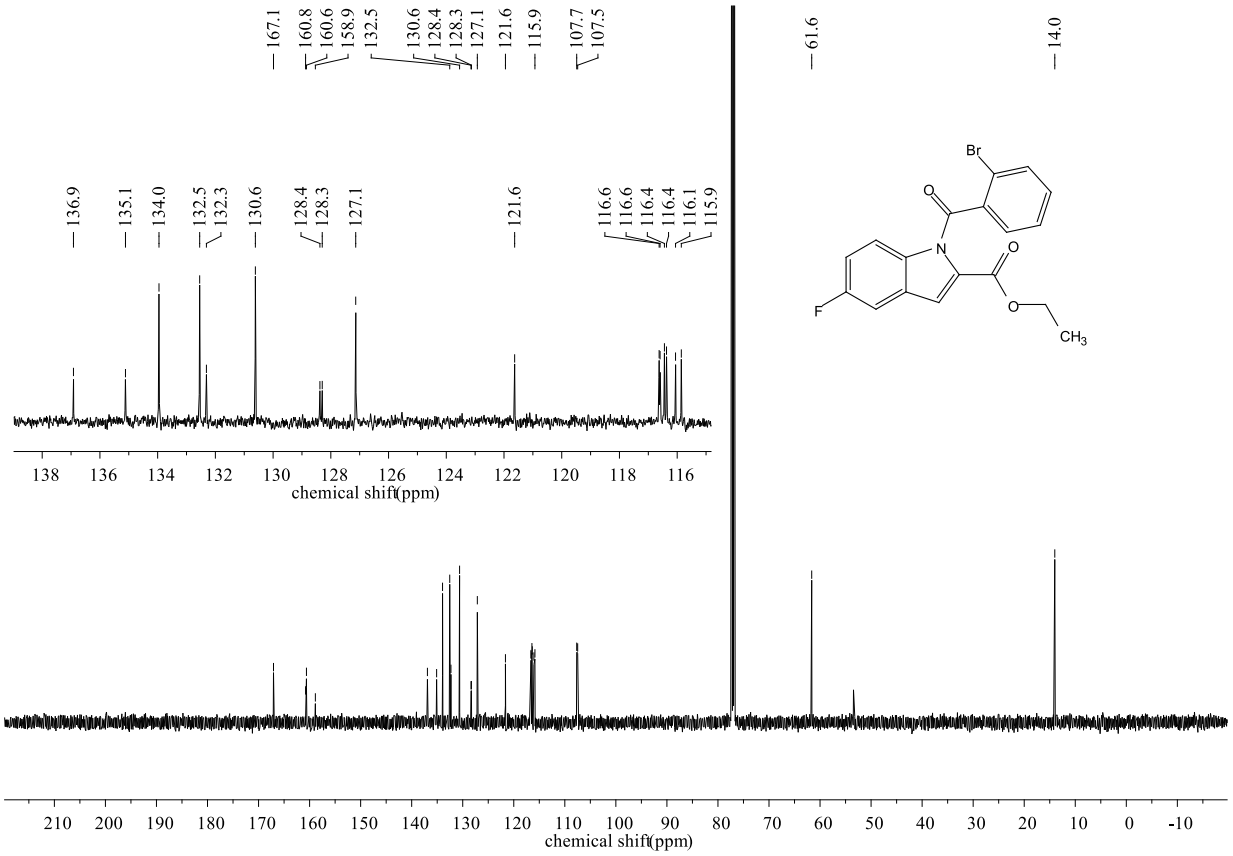
^{13}C NMR Spectra of compound **R25** (100 MHz, $CDCl_3$)



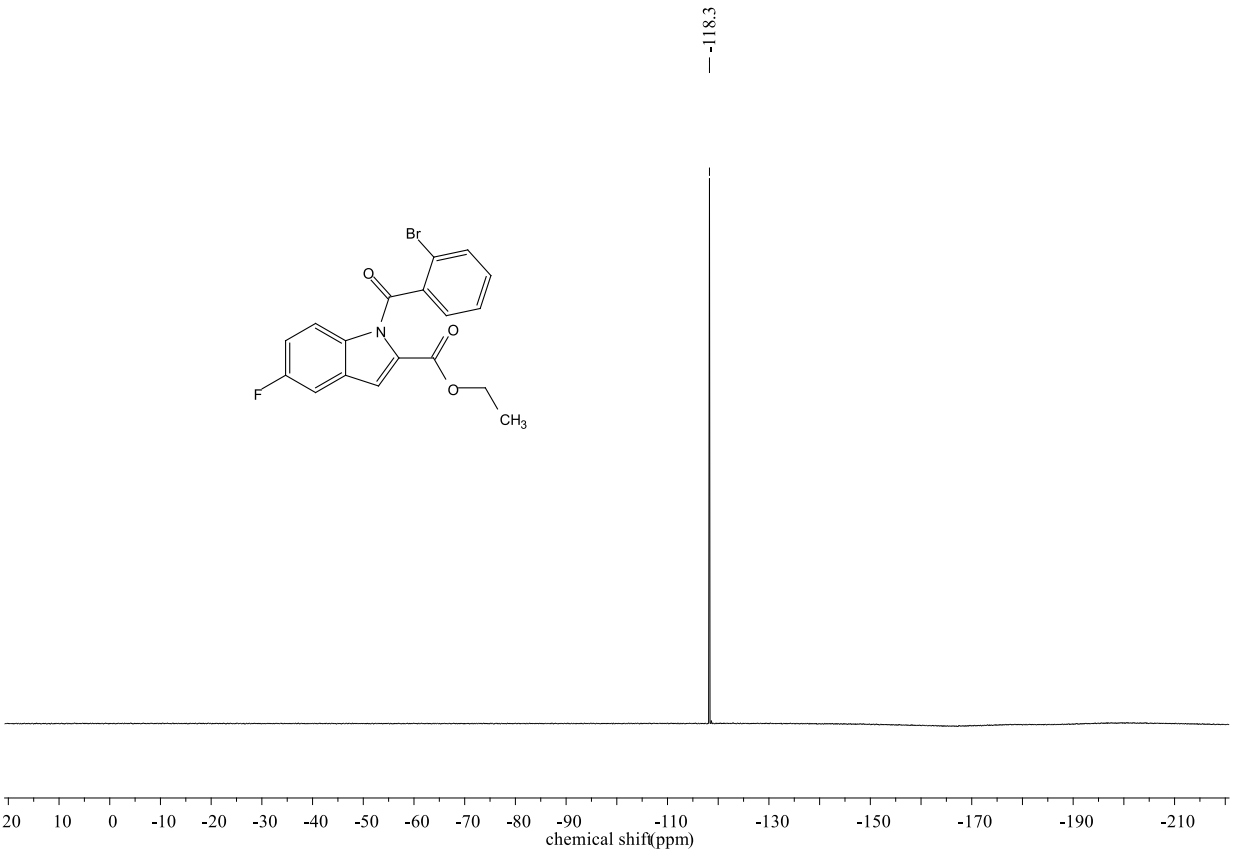
^{1}H NMR Spectra of compound **R26** (500 MHz, $CDCl_3$)



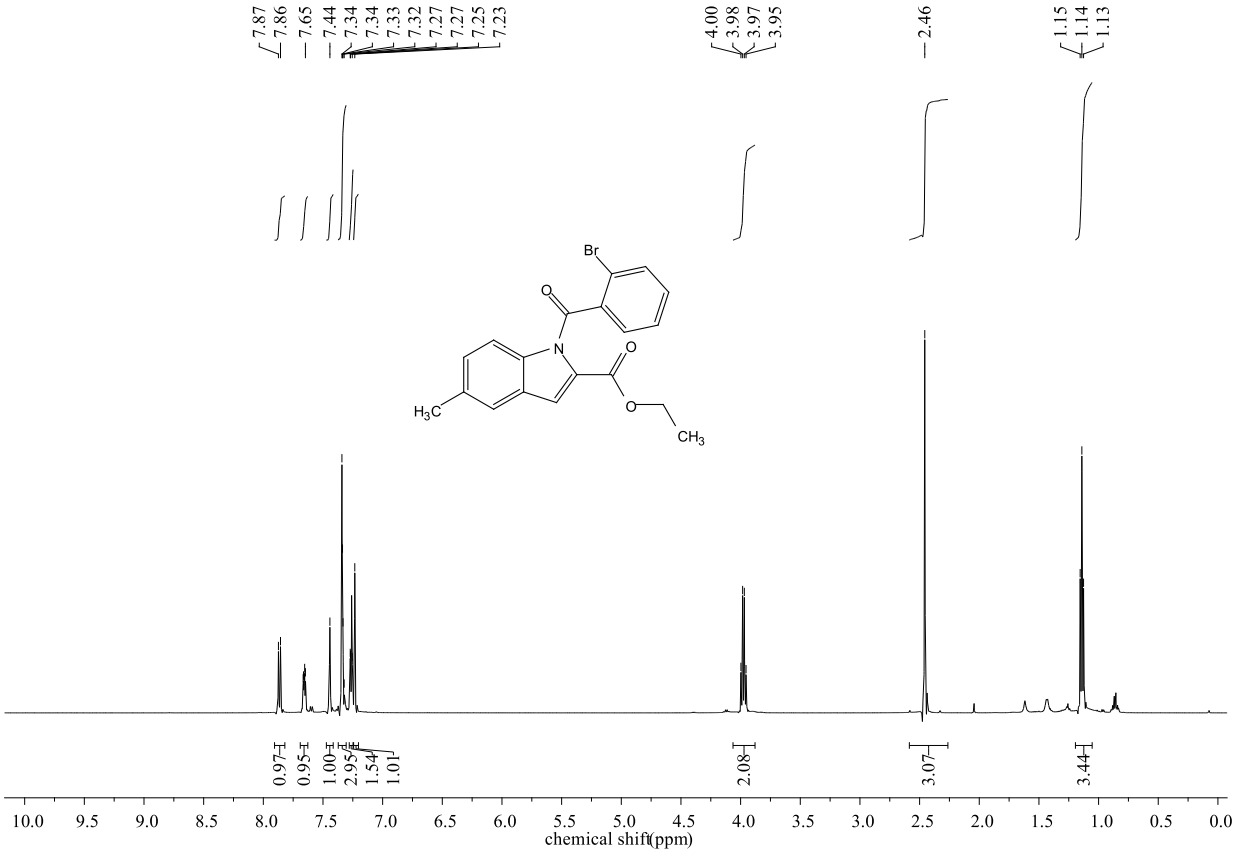
^{13}C NMR Spectra of compound **R26** (125 MHz, $CDCl_3$)



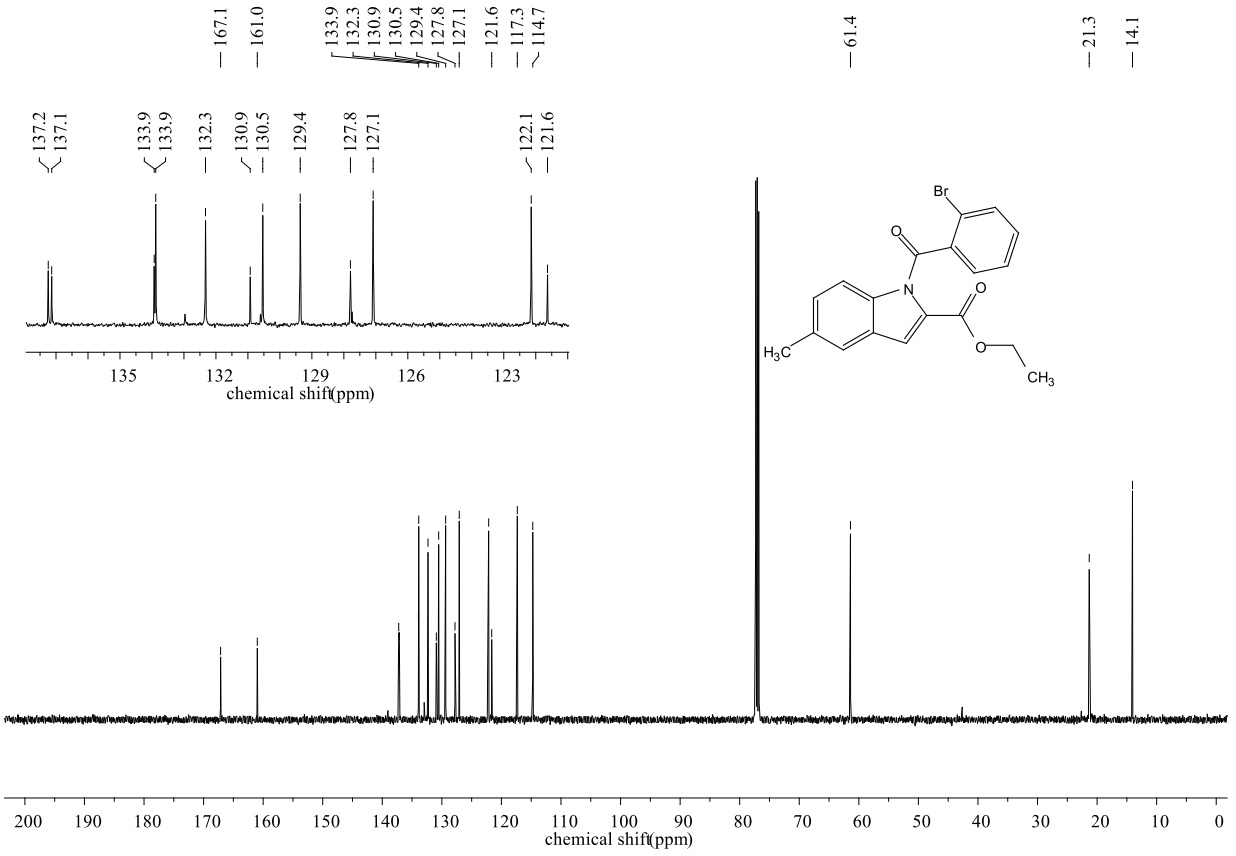
^{19}F NMR Spectra of compound **R26** (375 MHz, $CDCl_3$).



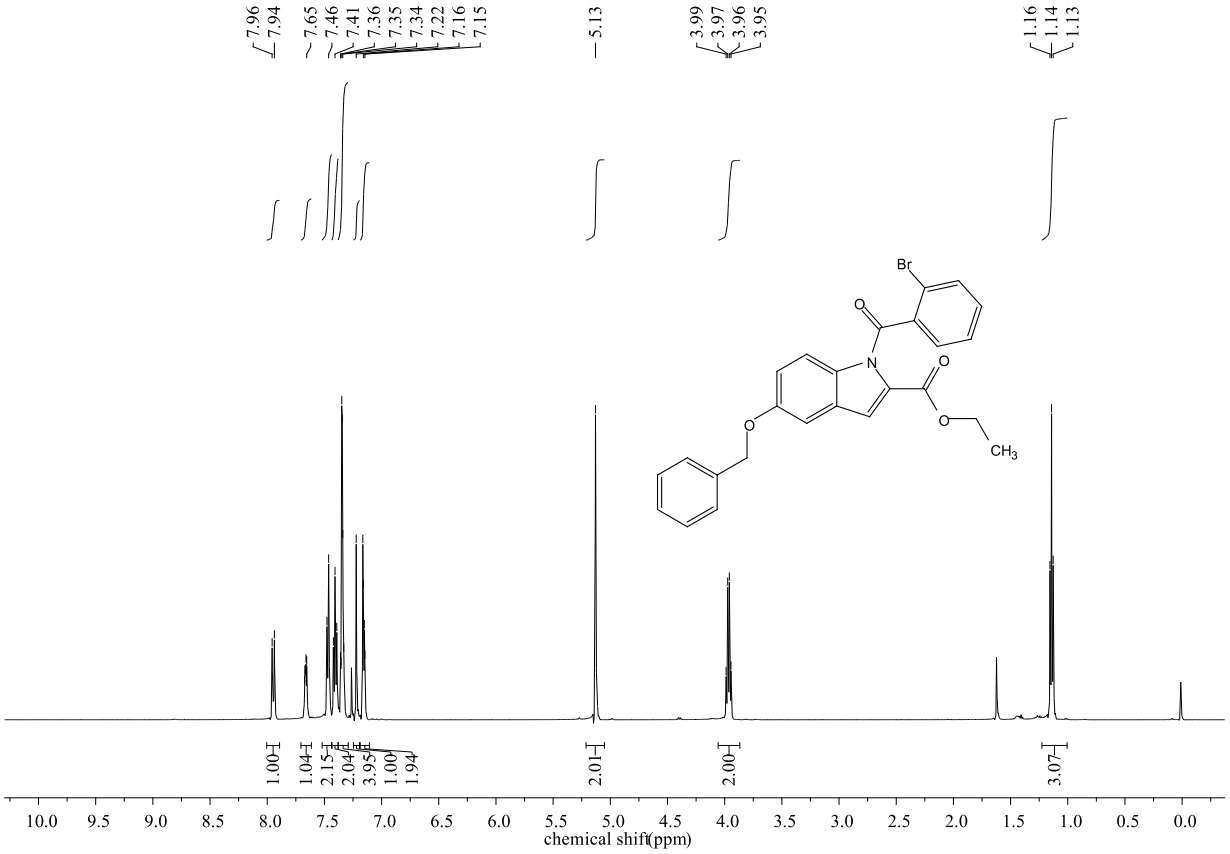
^{1}H NMR Spectra of compound **R27** (500 MHz, $CDCl_3$)



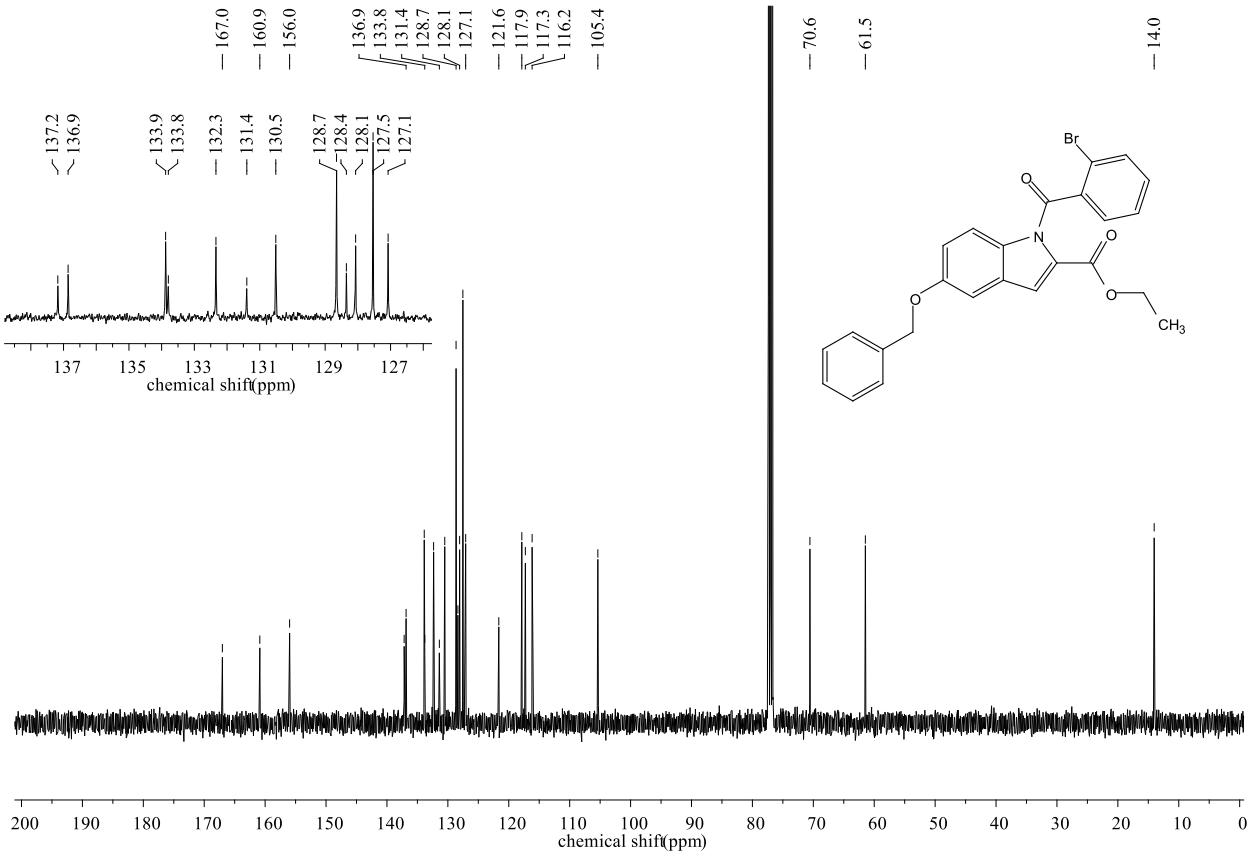
^{13}C NMR Spectra of compound **R27** (125 MHz, $CDCl_3$)



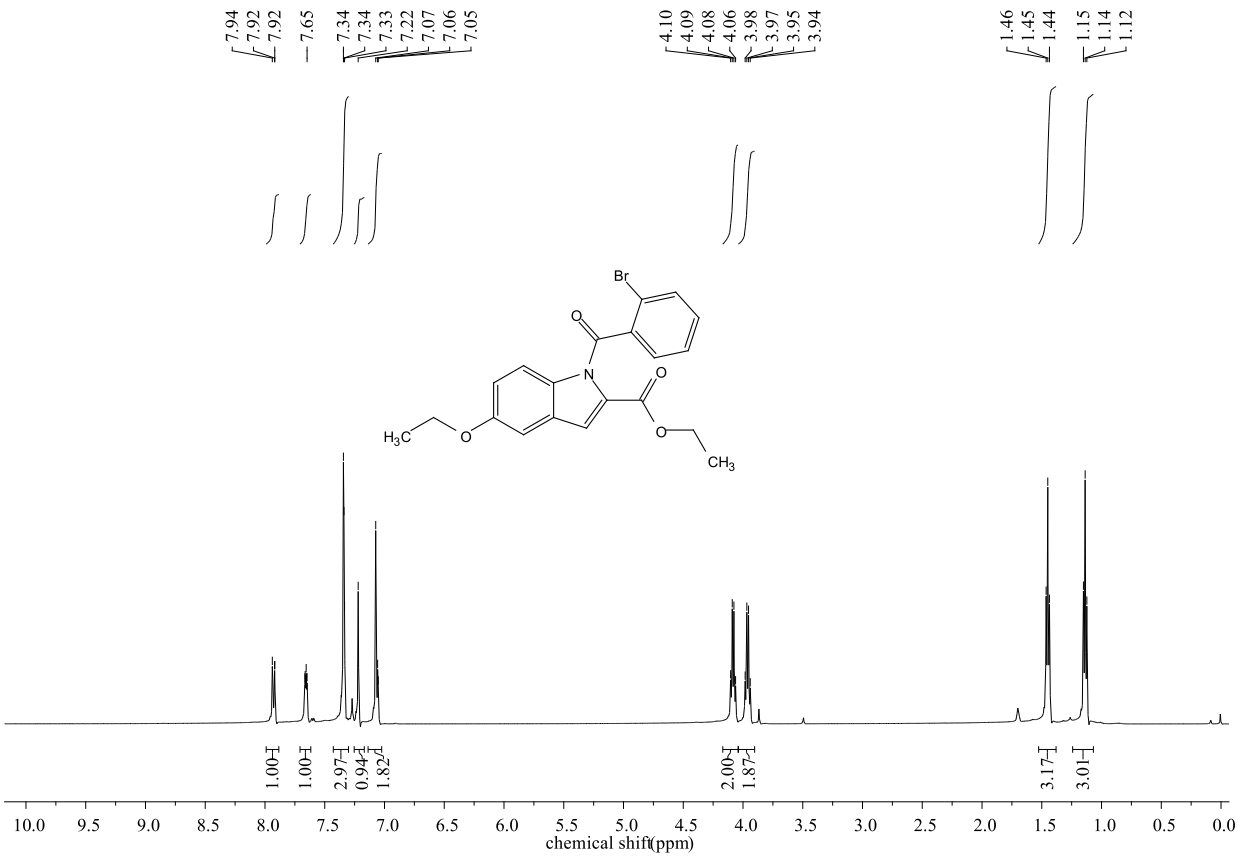
^{1}H NMR Spectra of compound **R28** (500 MHz, $CDCl_3$)



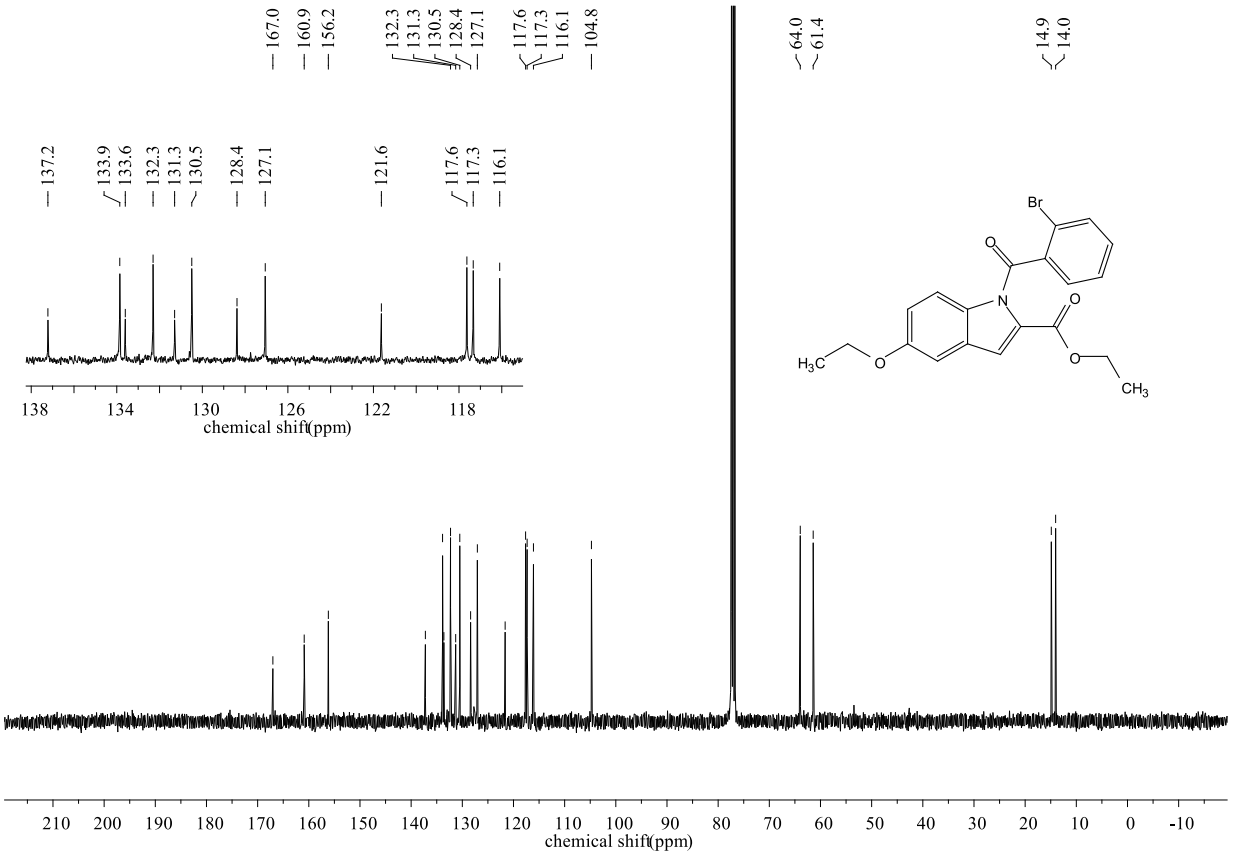
^{13}C NMR Spectra of compound **R28** (100 MHz, $CDCl_3$)



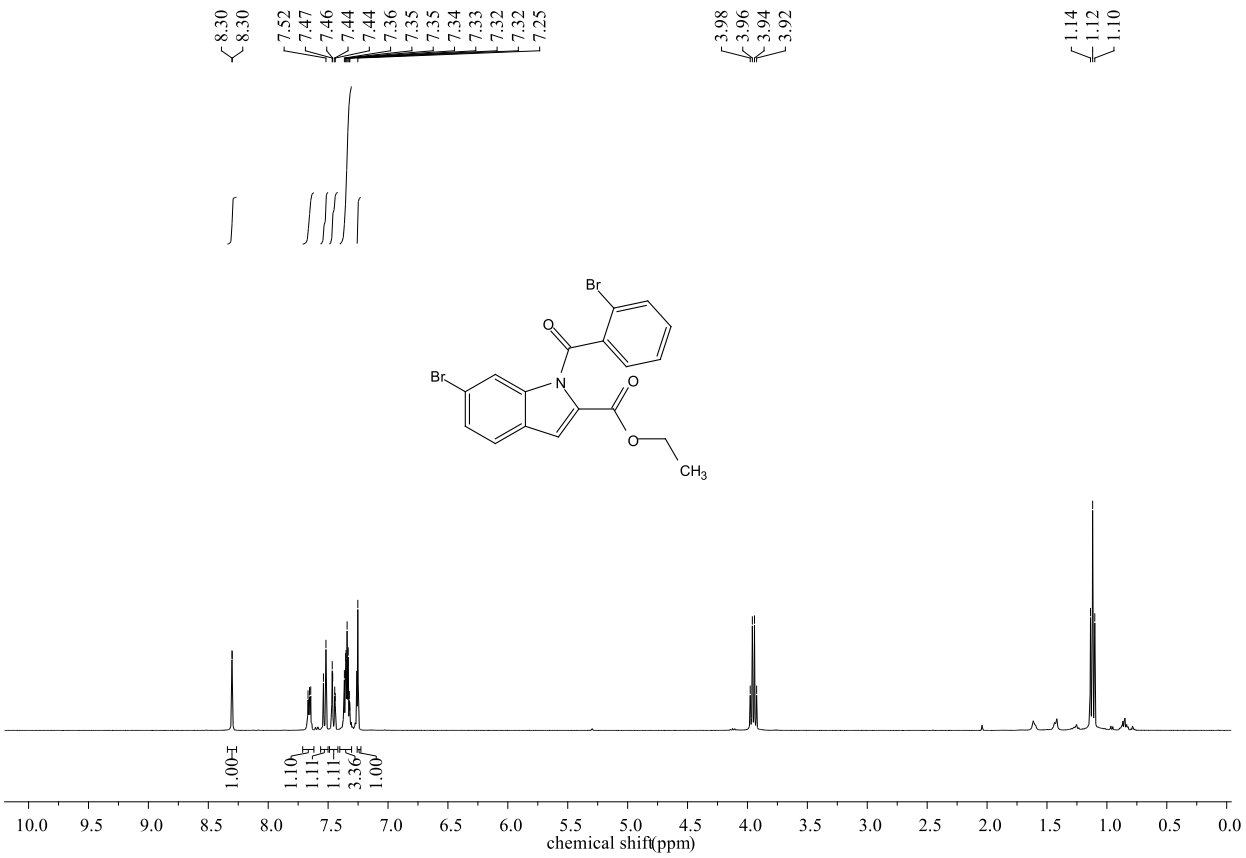
^{1}H NMR Spectra of compound **R29** (500 MHz, $CDCl_3$)



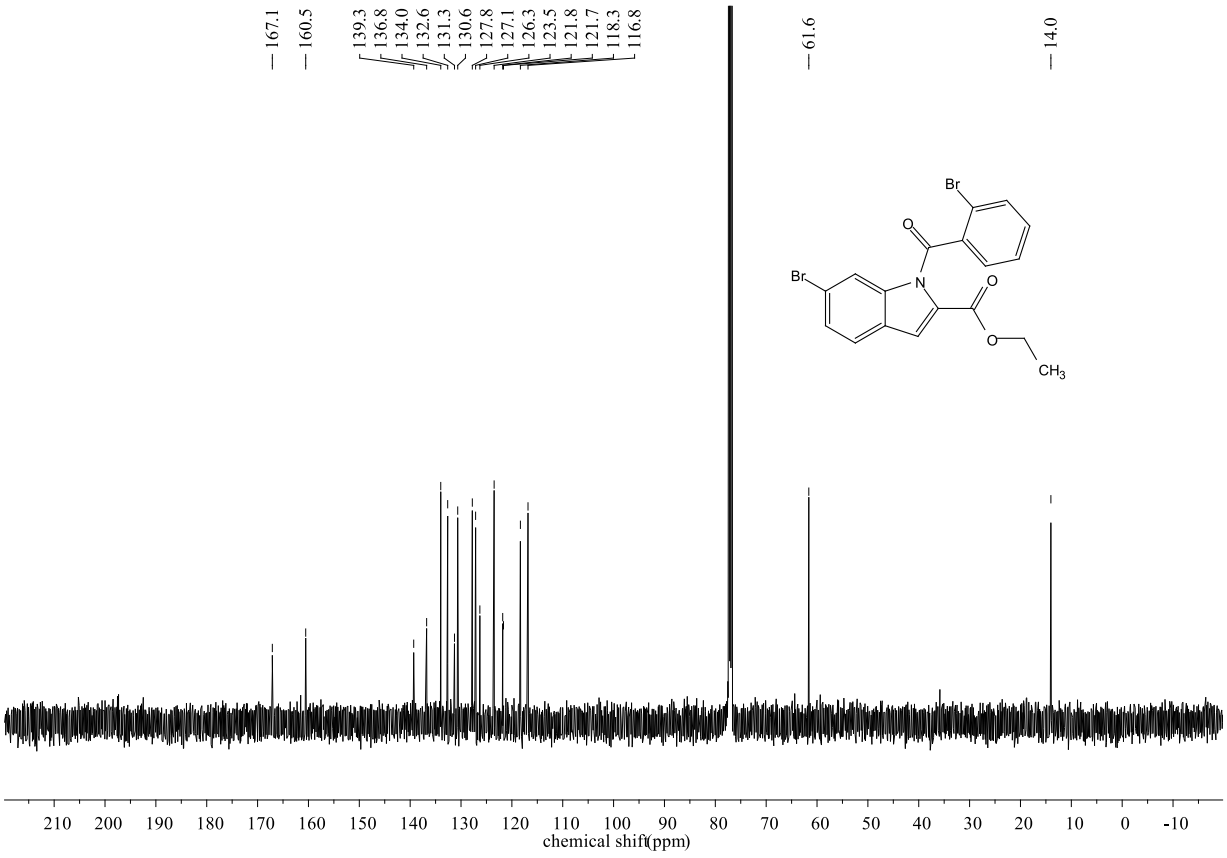
^{13}C NMR Spectra of compound **R29** (100 MHz, $CDCl_3$)



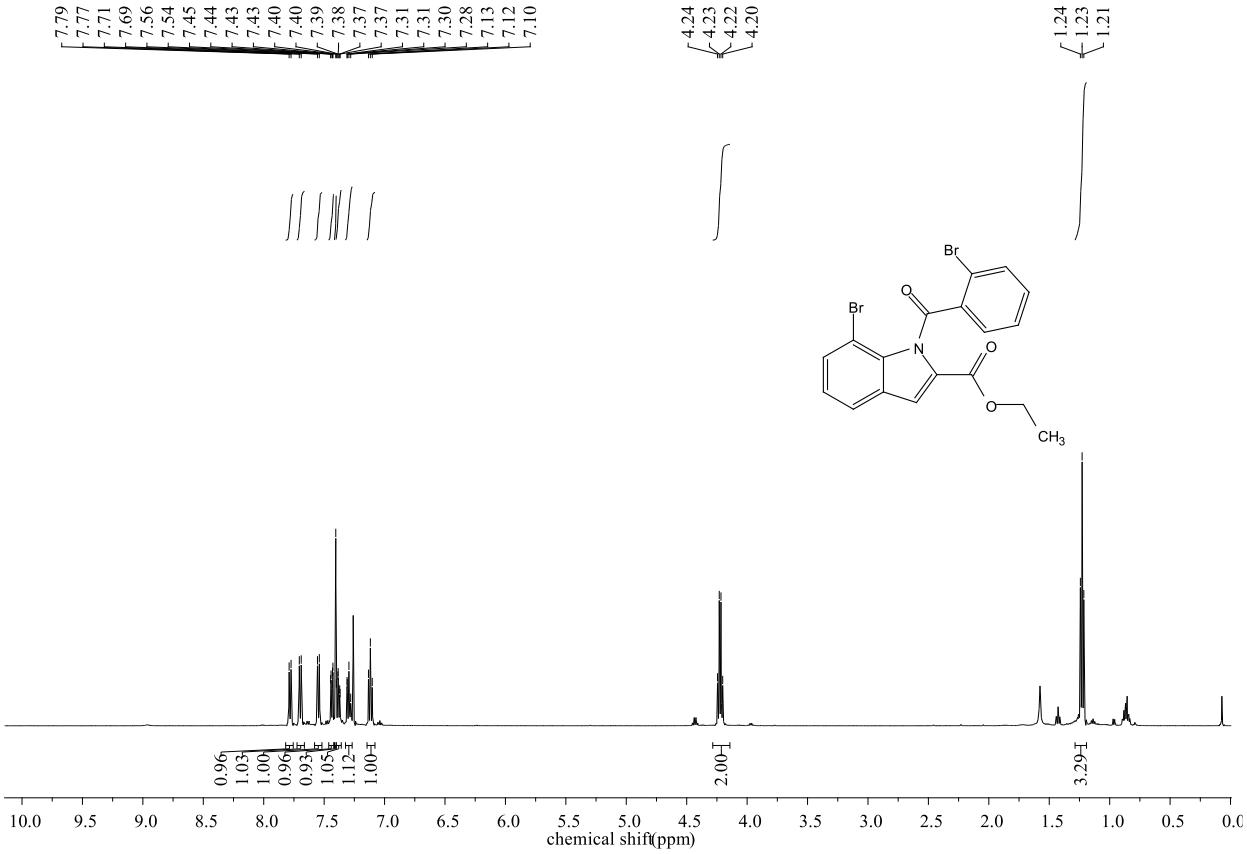
^{1}H NMR Spectra of compound **R30** (400 MHz, $CDCl_3$)



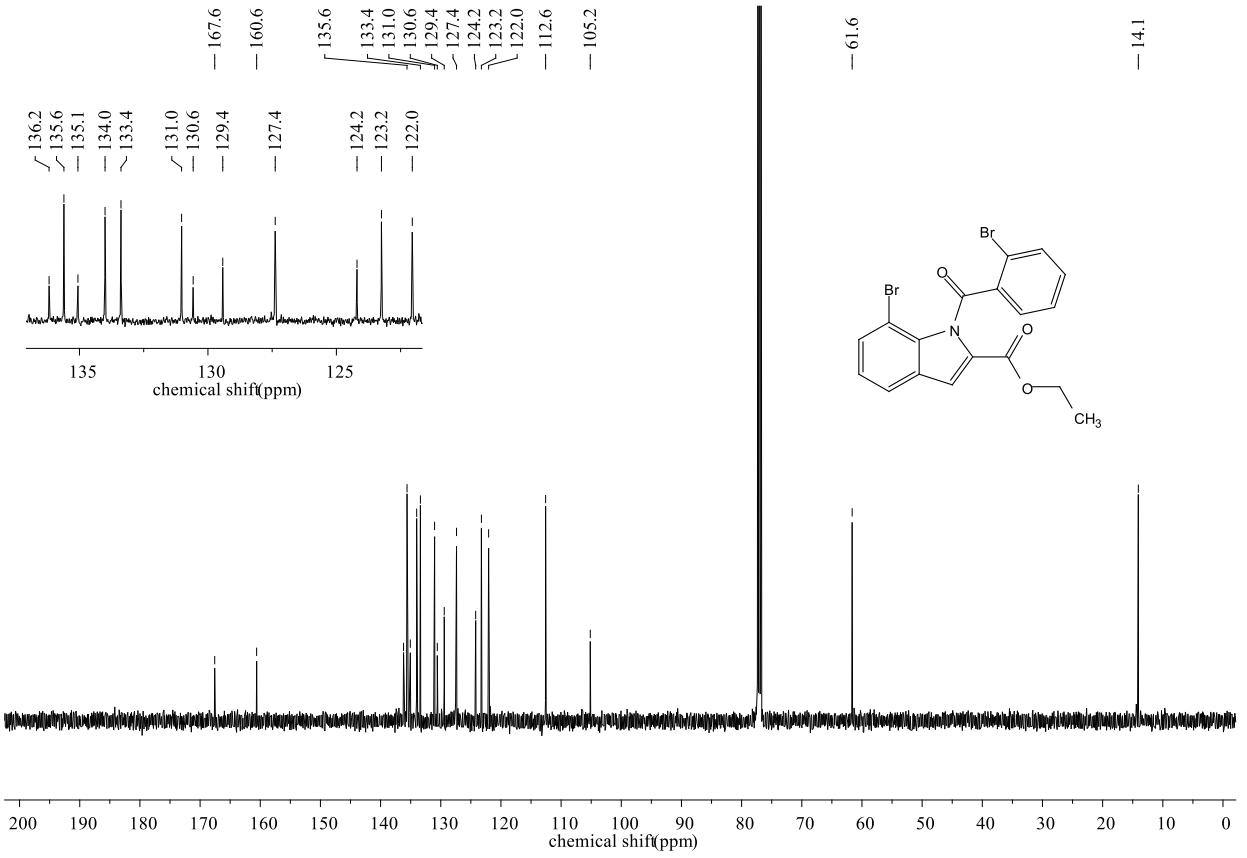
^{13}C NMR Spectra of compound **R30** (125 MHz, $CDCl_3$)



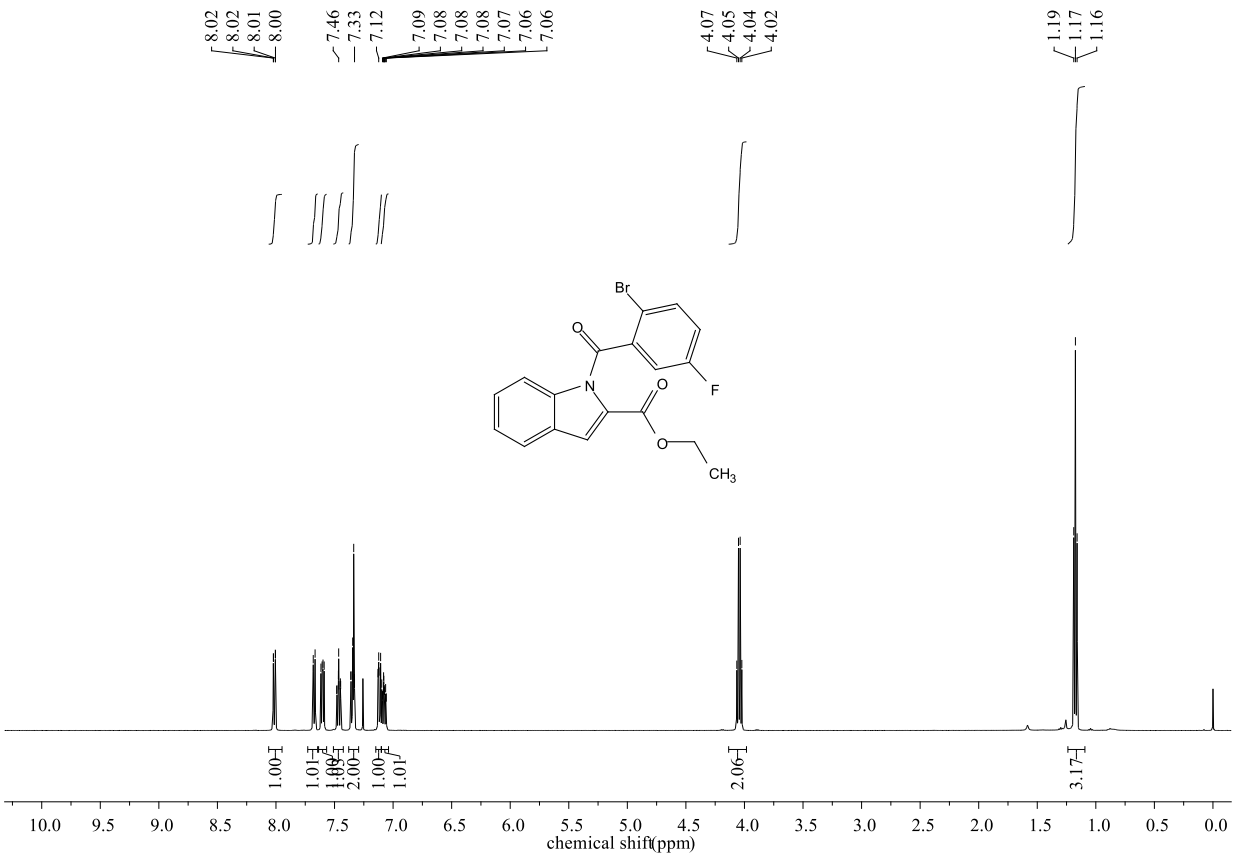
^{1}H NMR Spectra of compound **R31** (500 MHz, $CDCl_3$)



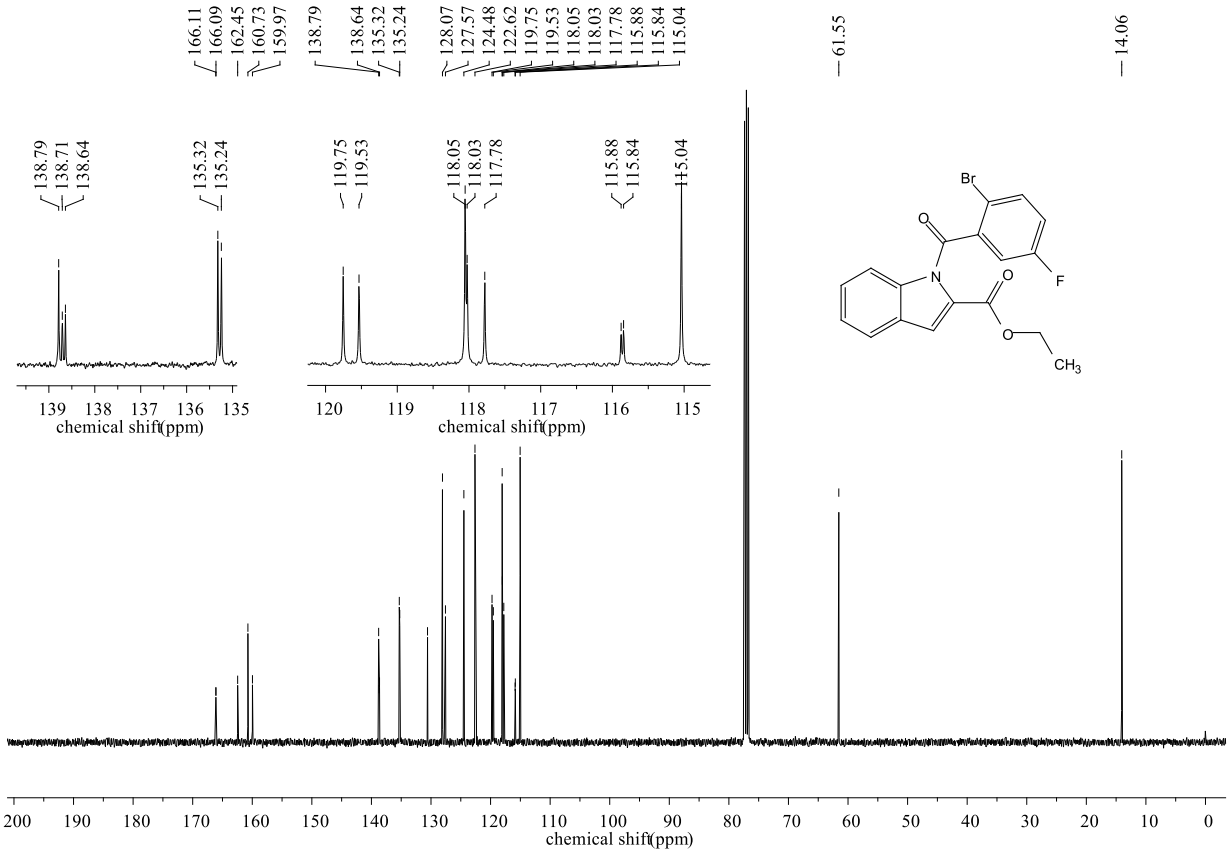
^{13}C NMR Spectra of compound **R31** (125 MHz, $CDCl_3$)



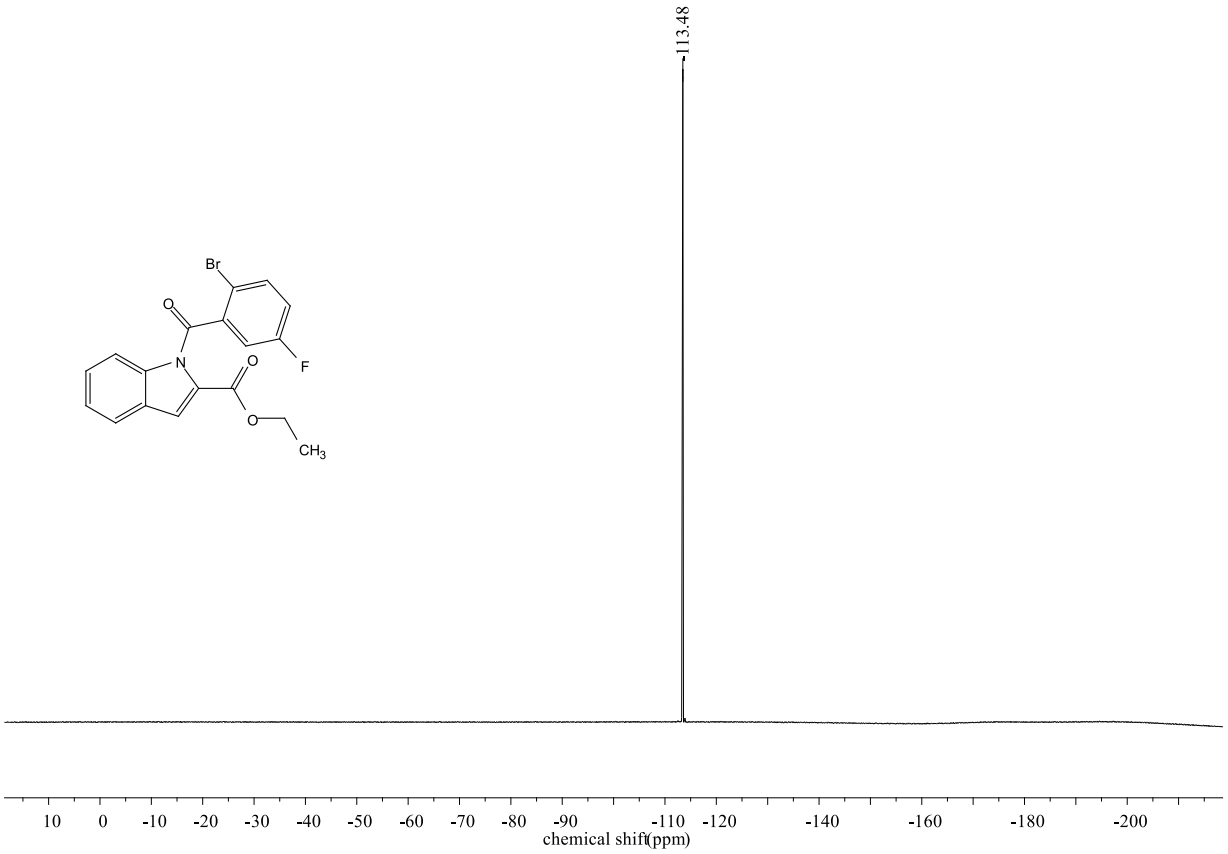
^{1}H NMR Spectra of compound **R32** (500 MHz, $CDCl_3$)



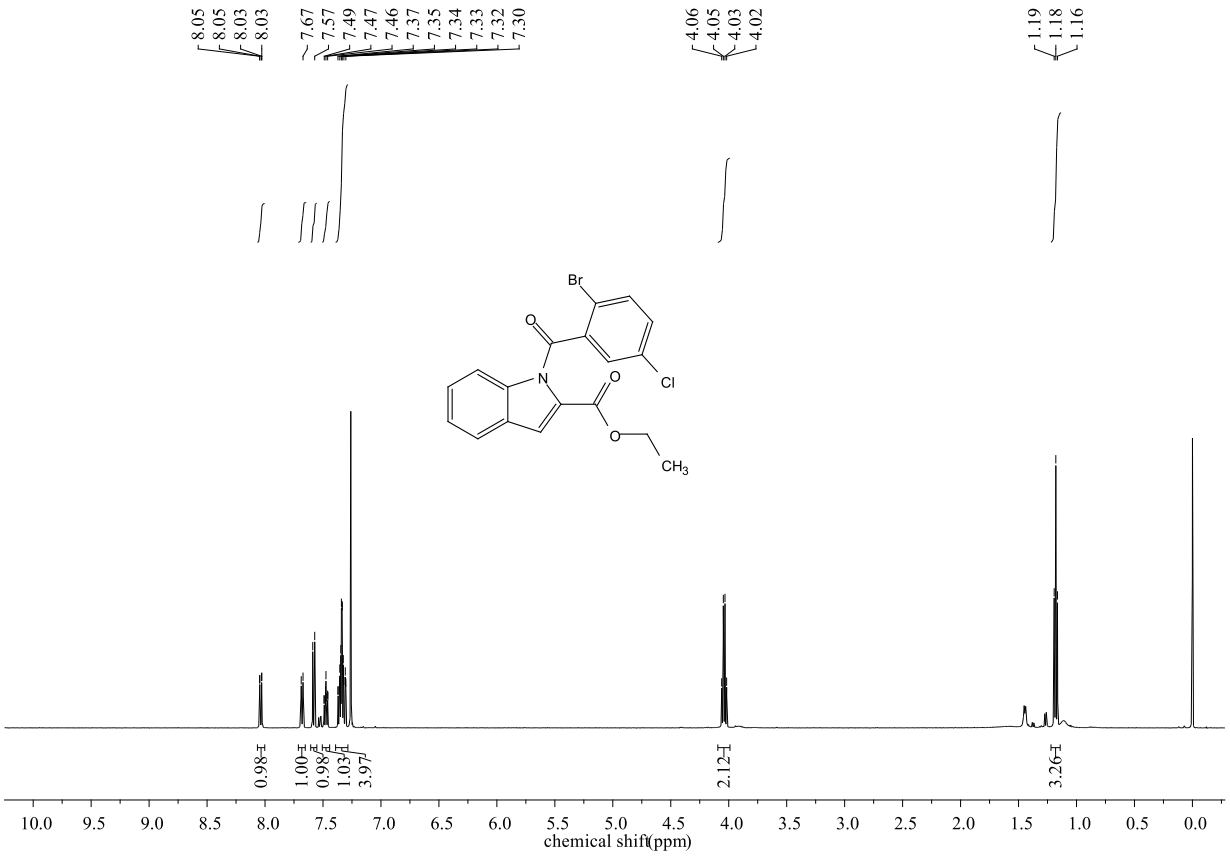
^{13}C NMR Spectra of compound **R32** (100 MHz, $CDCl_3$)



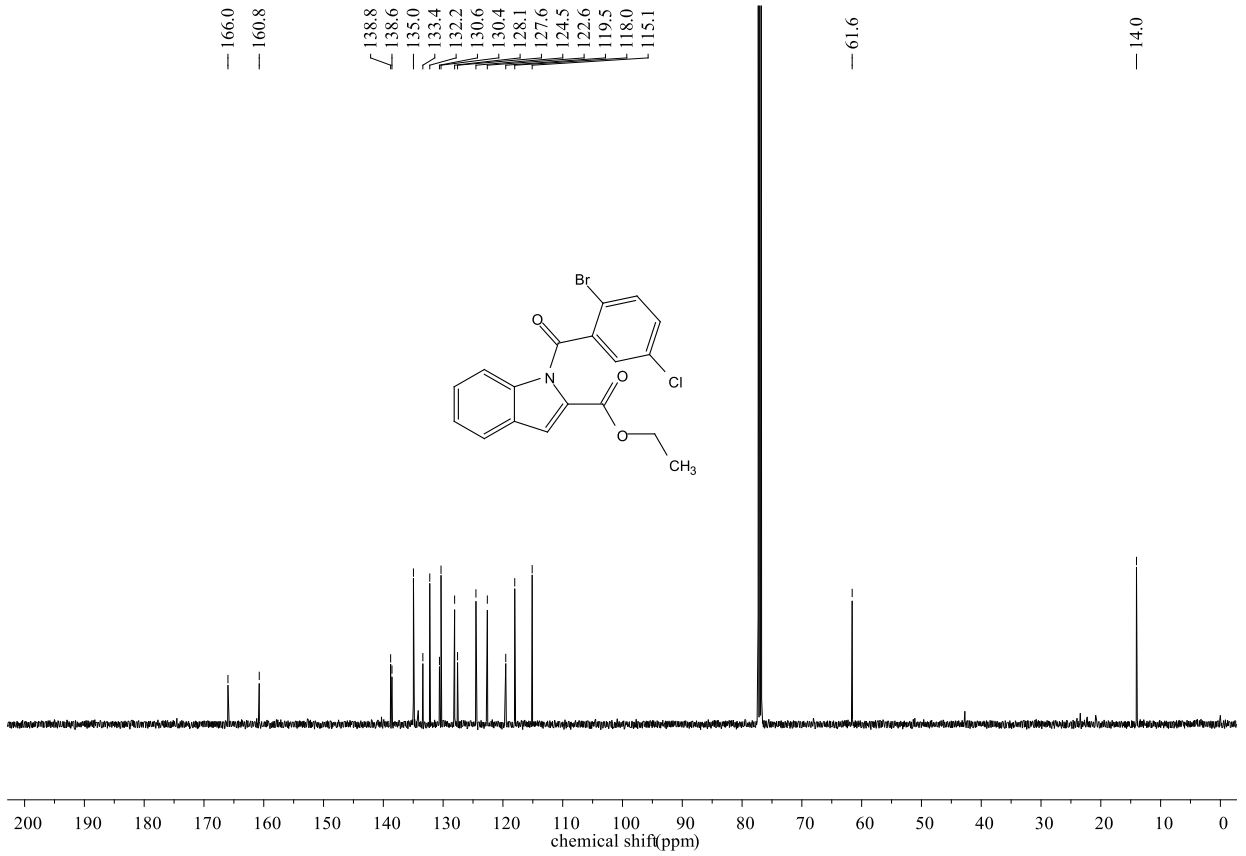
^{19}F NMR Spectra of compound **R32** (300 MHz, $CDCl_3$)



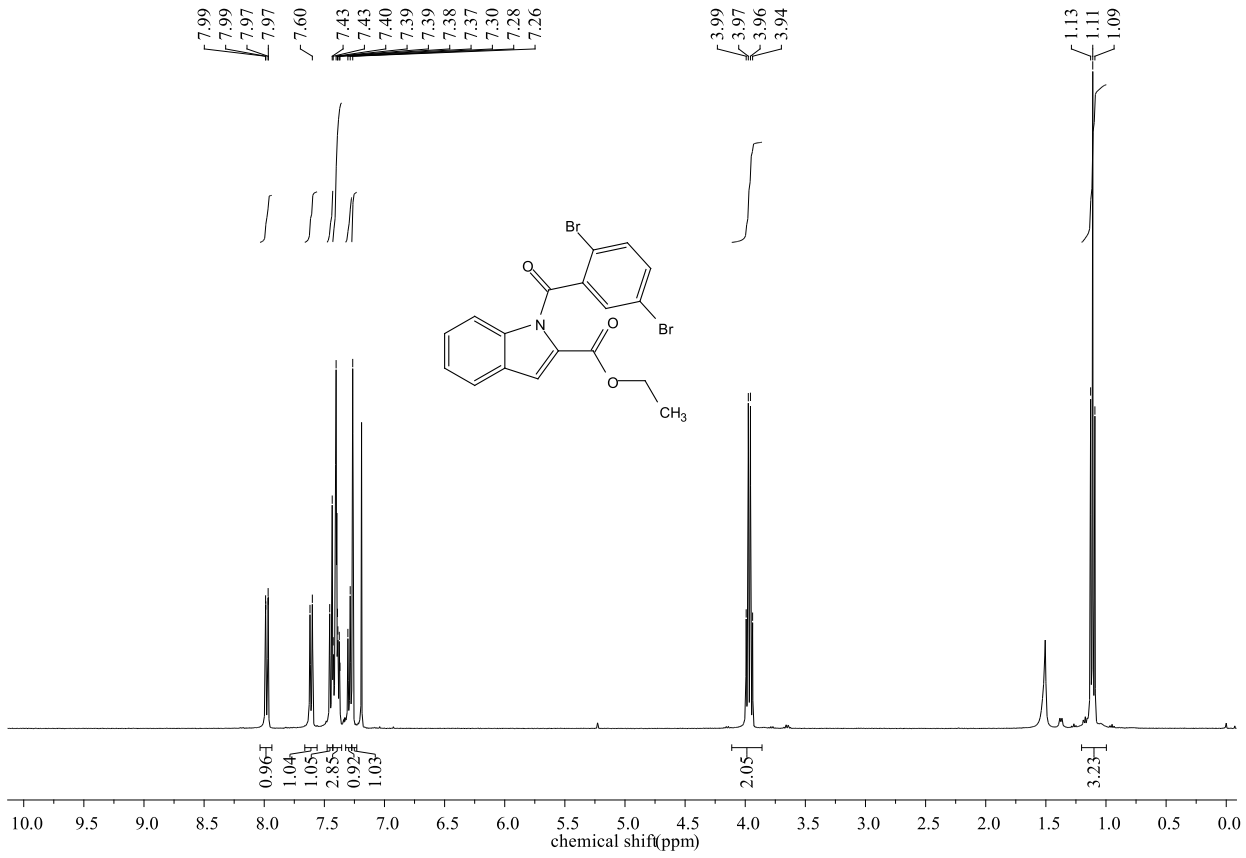
^{1}H NMR Spectra of compound **R33** (500 MHz, $CDCl_3$)



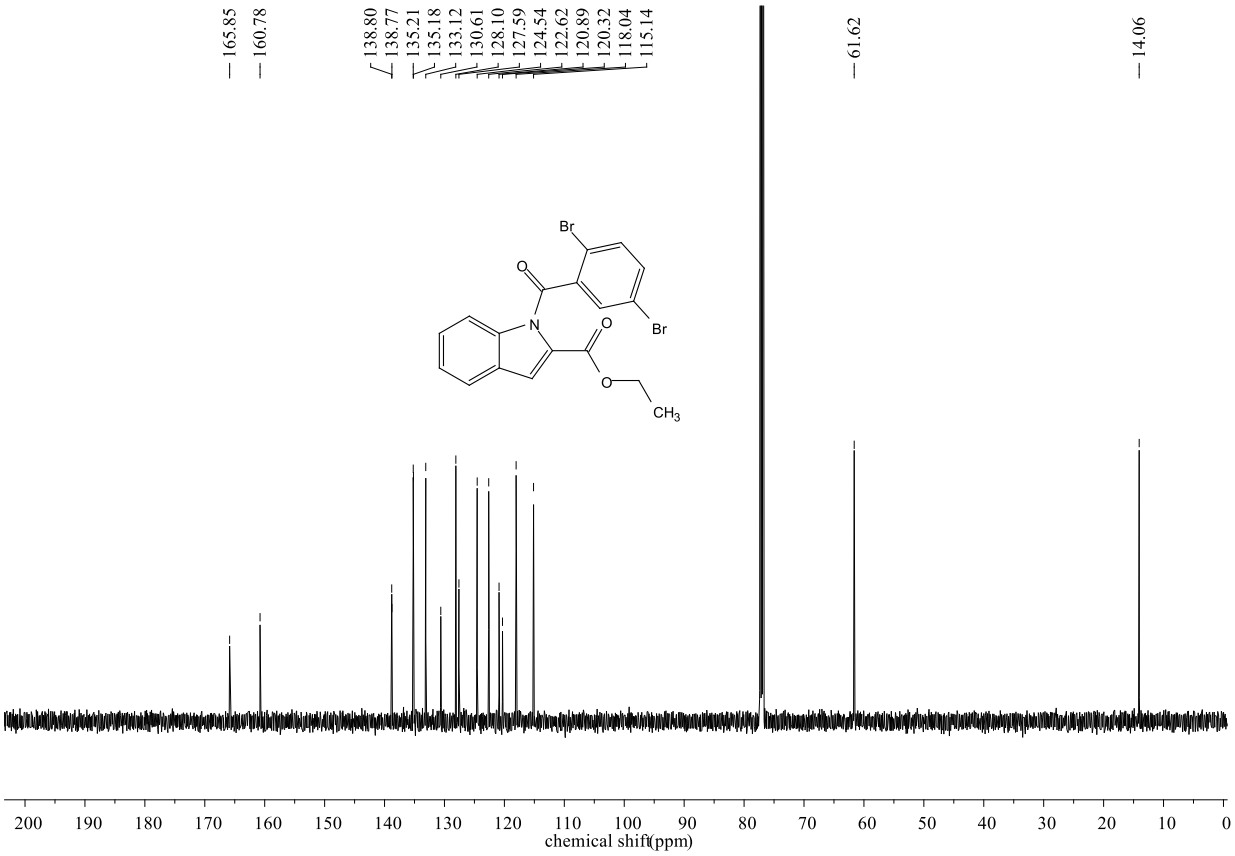
^{13}C NMR Spectra of compound **R33** (125 MHz, $CDCl_3$)



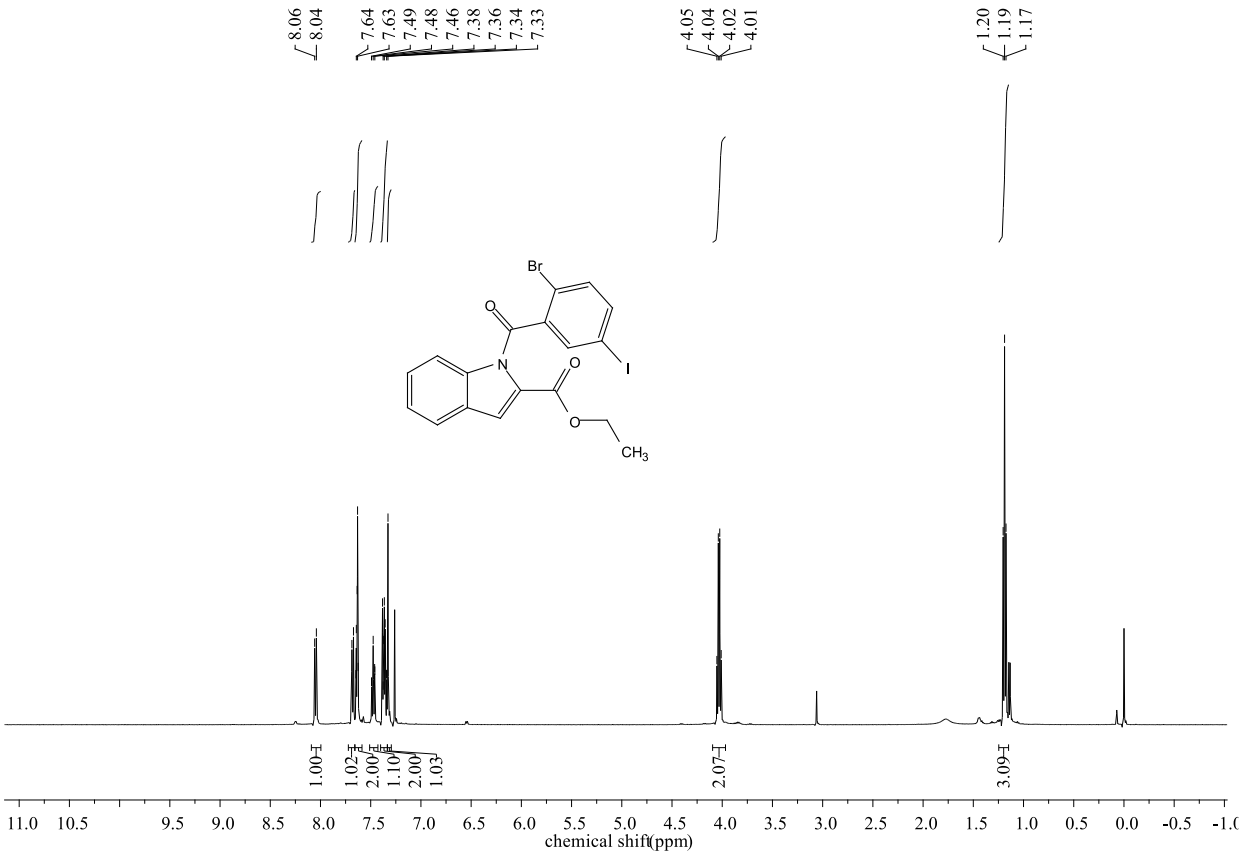
^{1}H NMR Spectra of compound **R34** (400 MHz, $CDCl_3$)



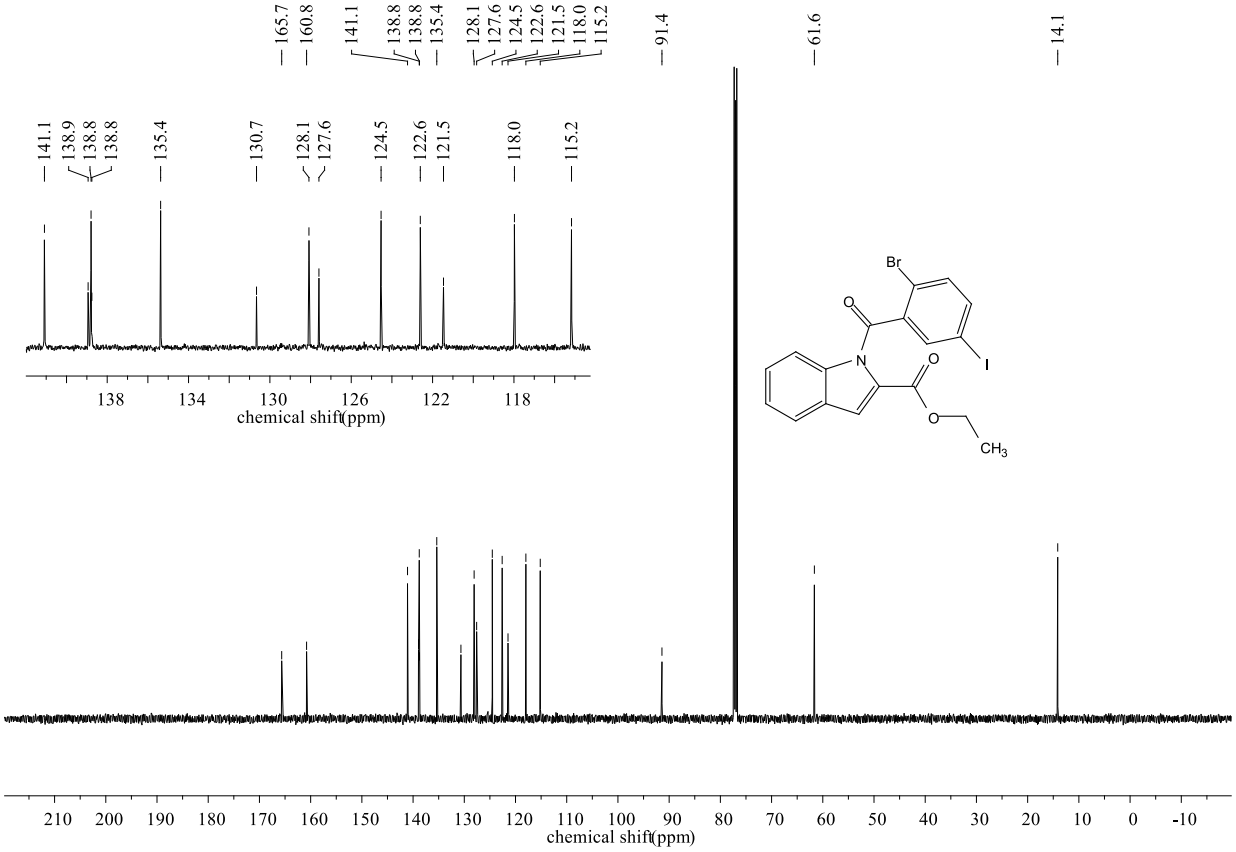
^{13}C NMR Spectra of compound **R34** (125 MHz, $CDCl_3$)



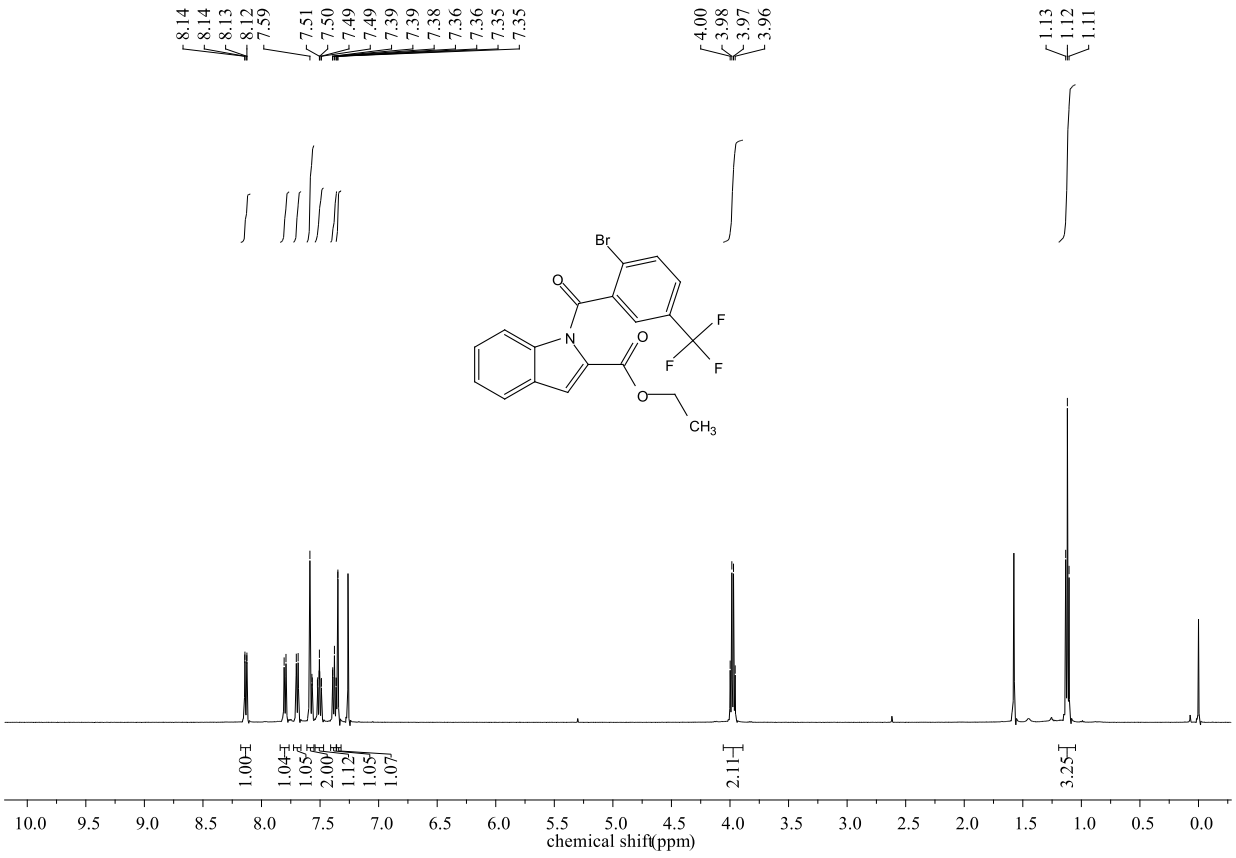
^{1}H NMR Spectra of compound **R35** (500 MHz, $CDCl_3$)



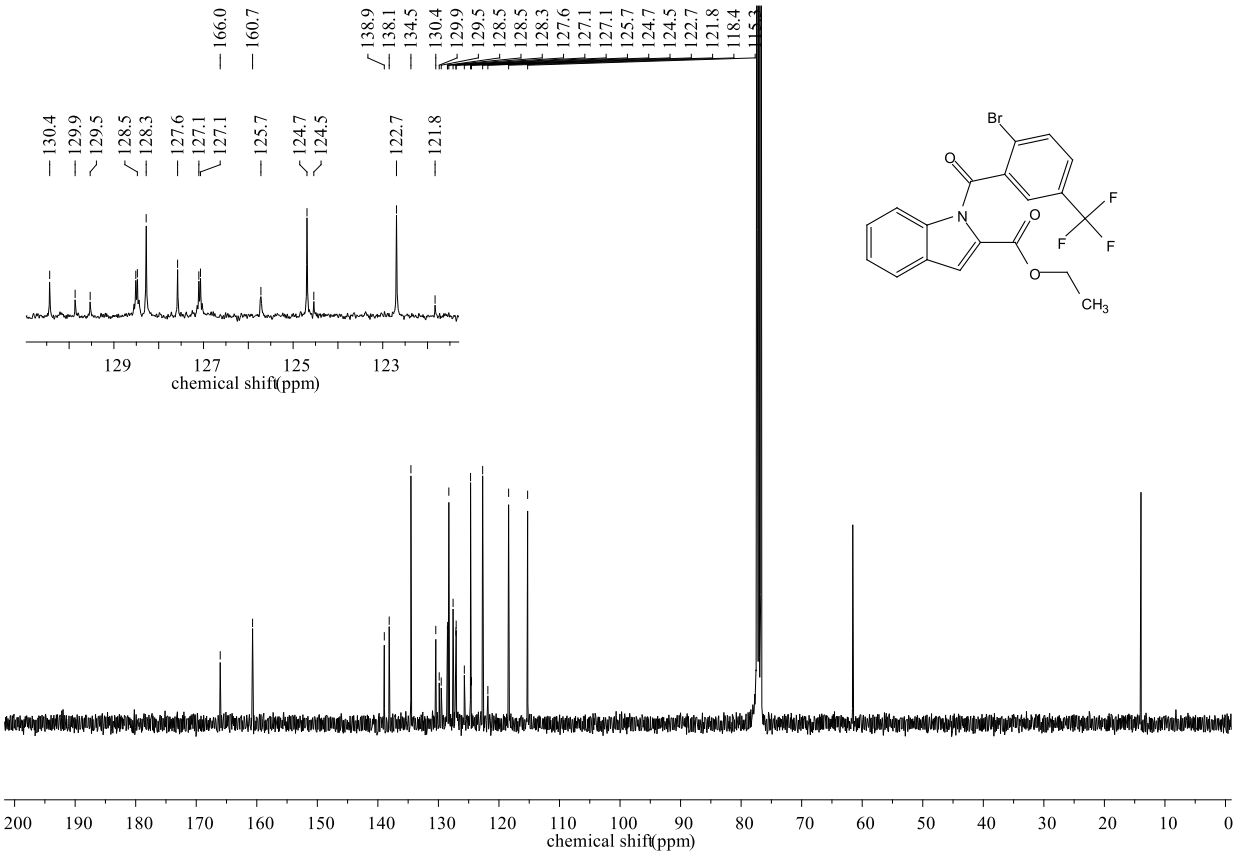
^{13}C NMR Spectra of compound **R35** (125 MHz, $CDCl_3$)



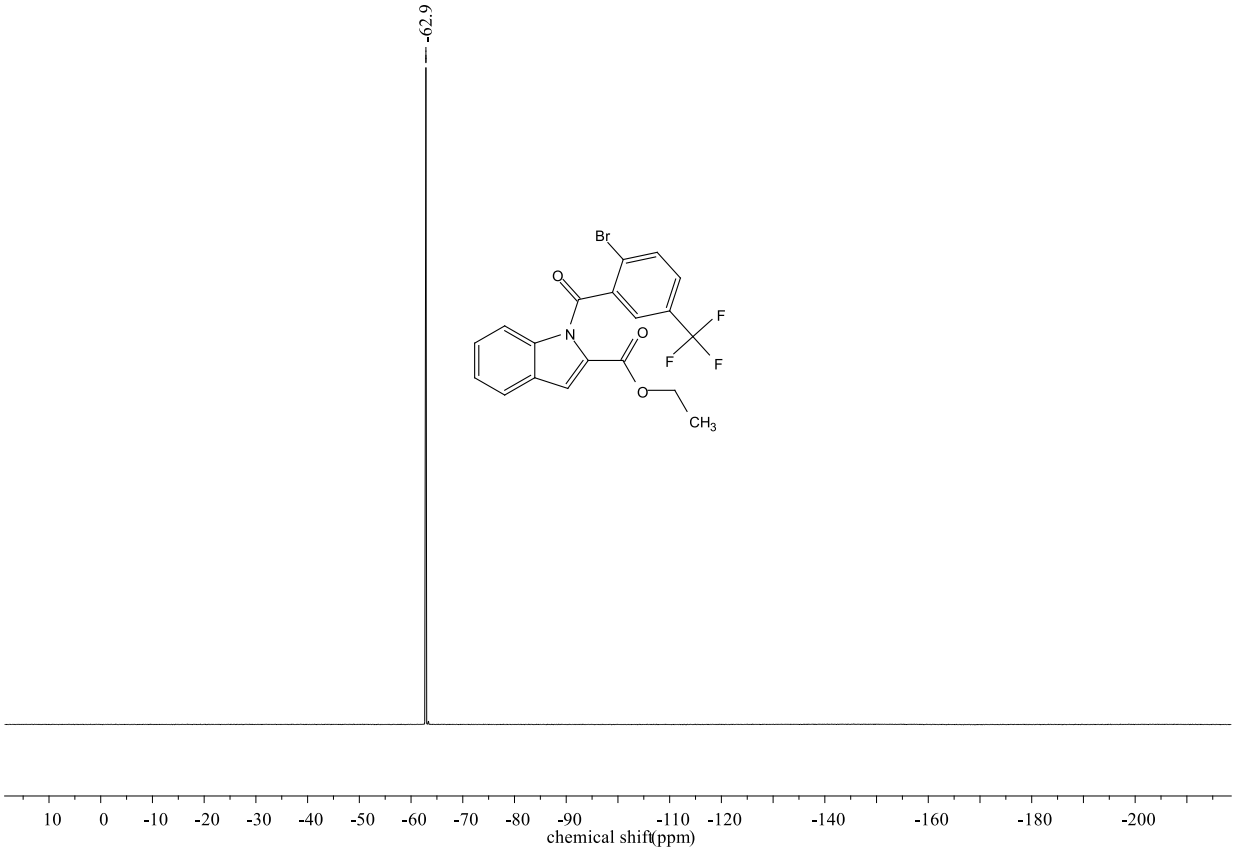
^{1}H NMR Spectra of compound **R36** (500 MHz, $CDCl_3$)



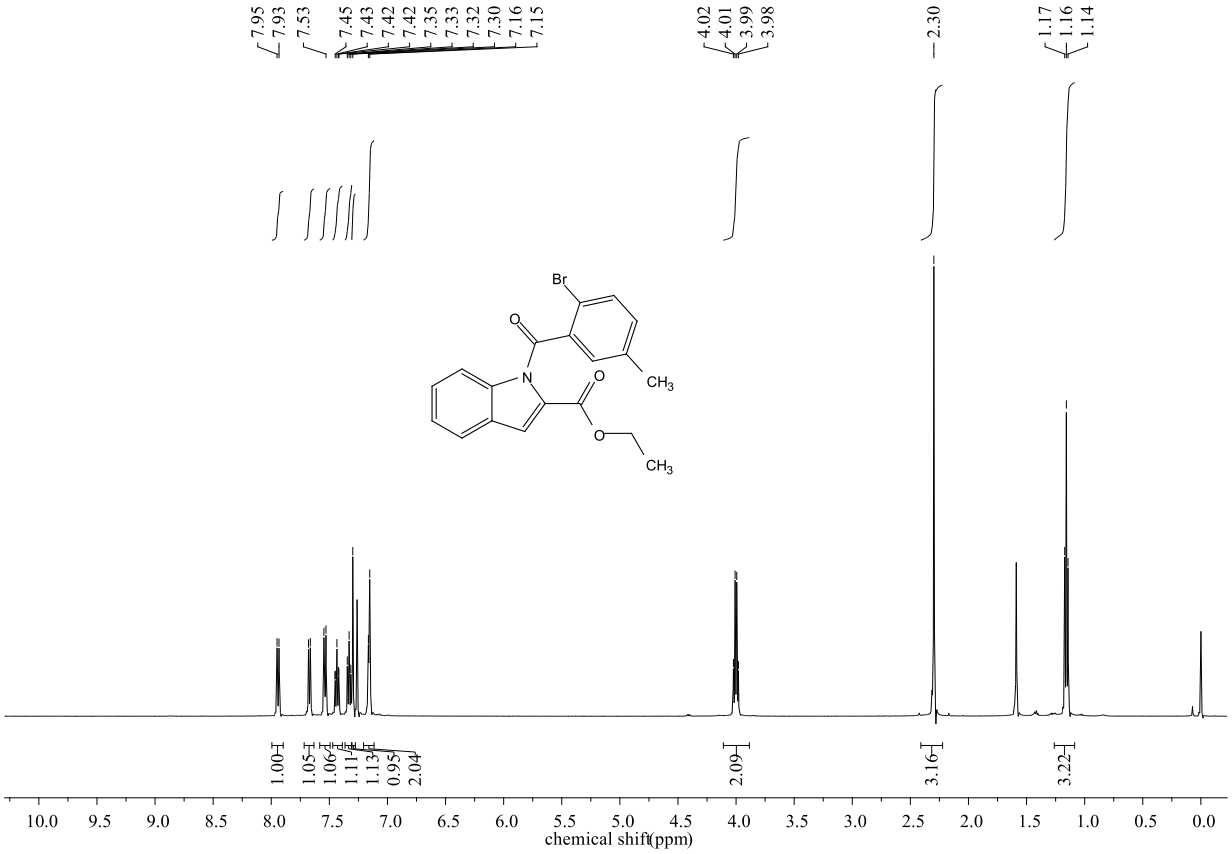
^{13}C NMR Spectra of compound **R36** (100 MHz, $CDCl_3$)



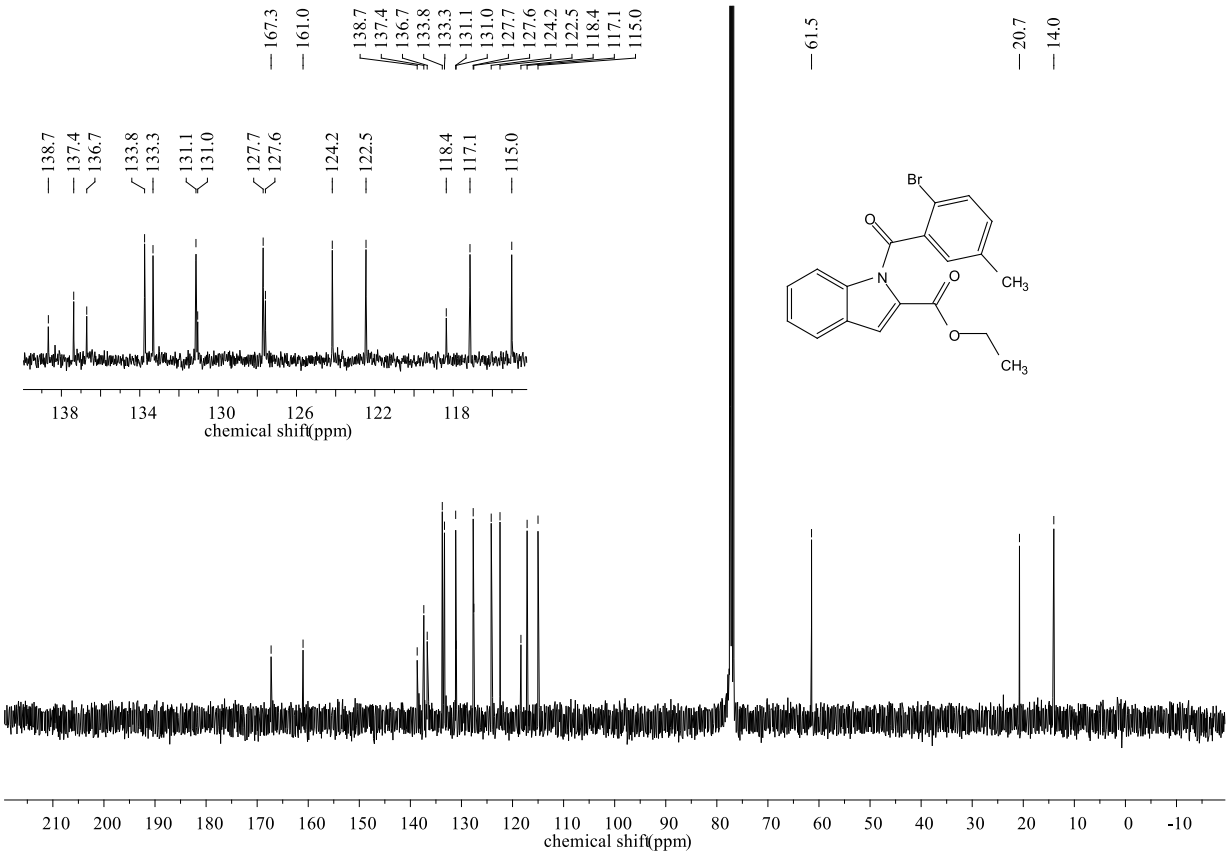
^{19}F NMR Spectra of compound **R36** (300 MHz, $CDCl_3$)



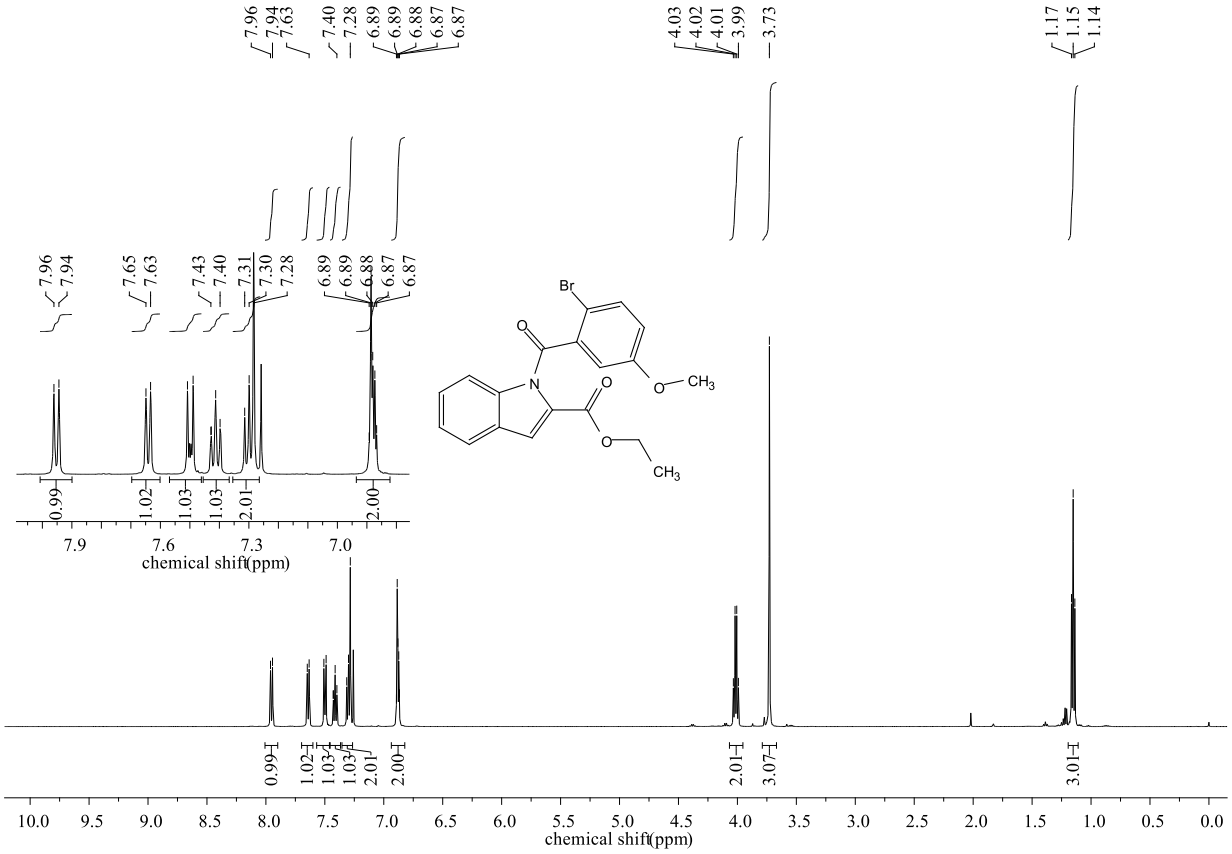
^{1}H NMR Spectra of compound **R37** (500 MHz, $CDCl_3$)



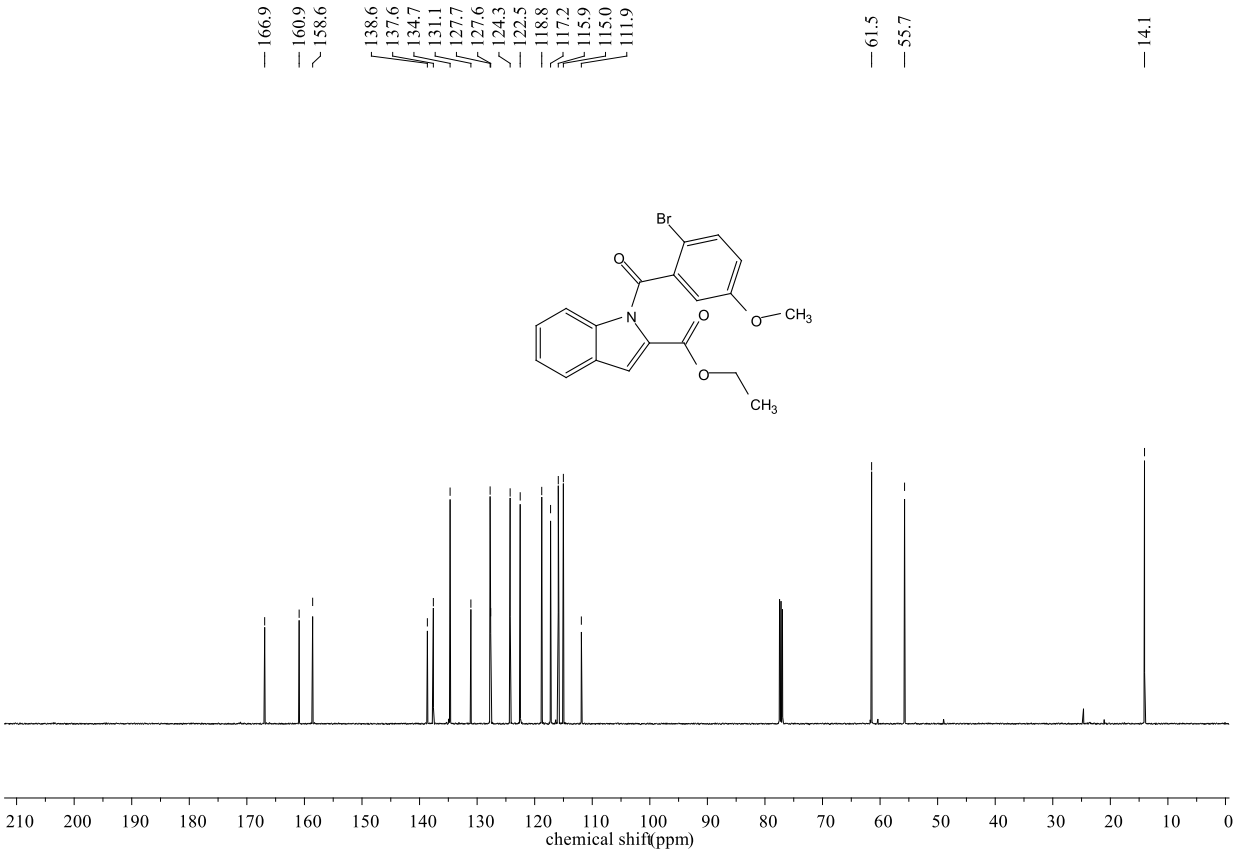
^{13}C NMR Spectra of compound **R37** (100 MHz, $CDCl_3$)



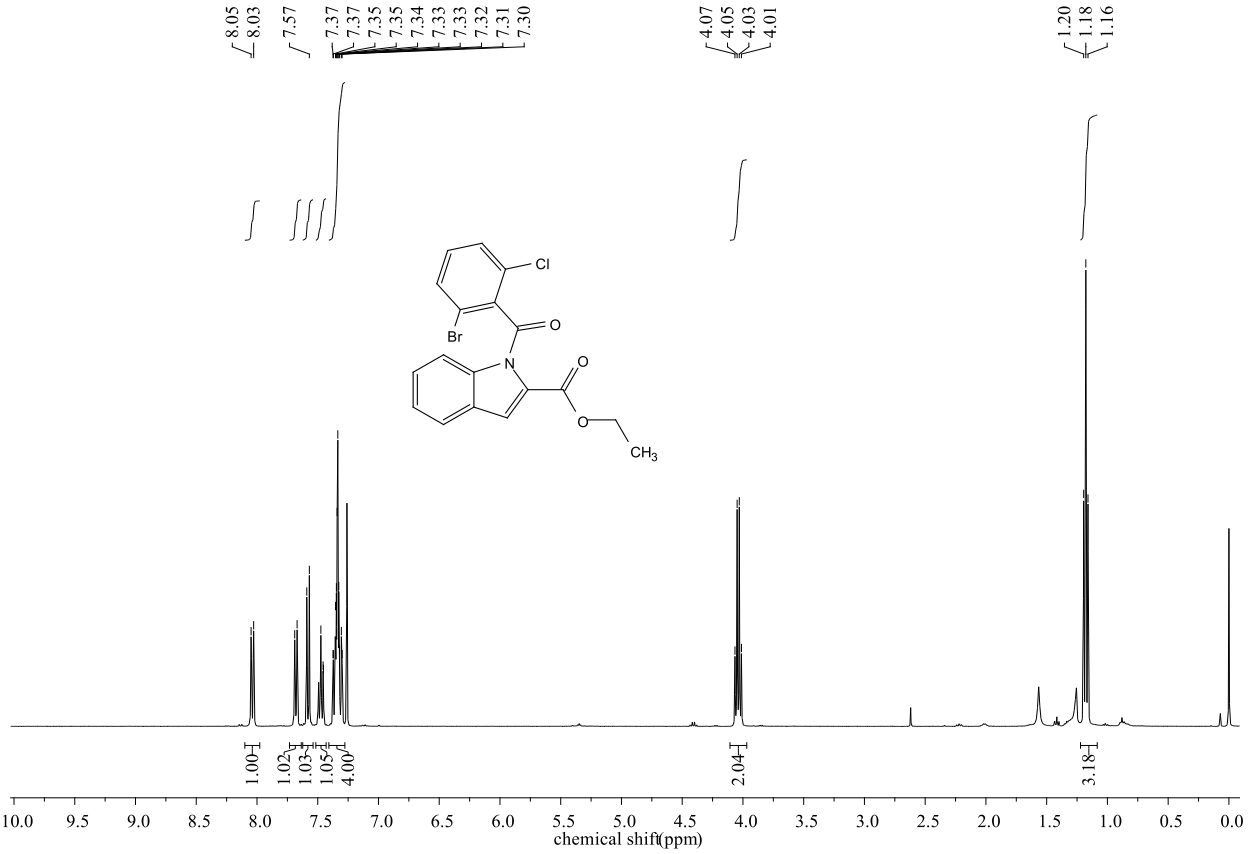
^{1}H NMR Spectra of compound **R38** (500 MHz, $CDCl_3$)



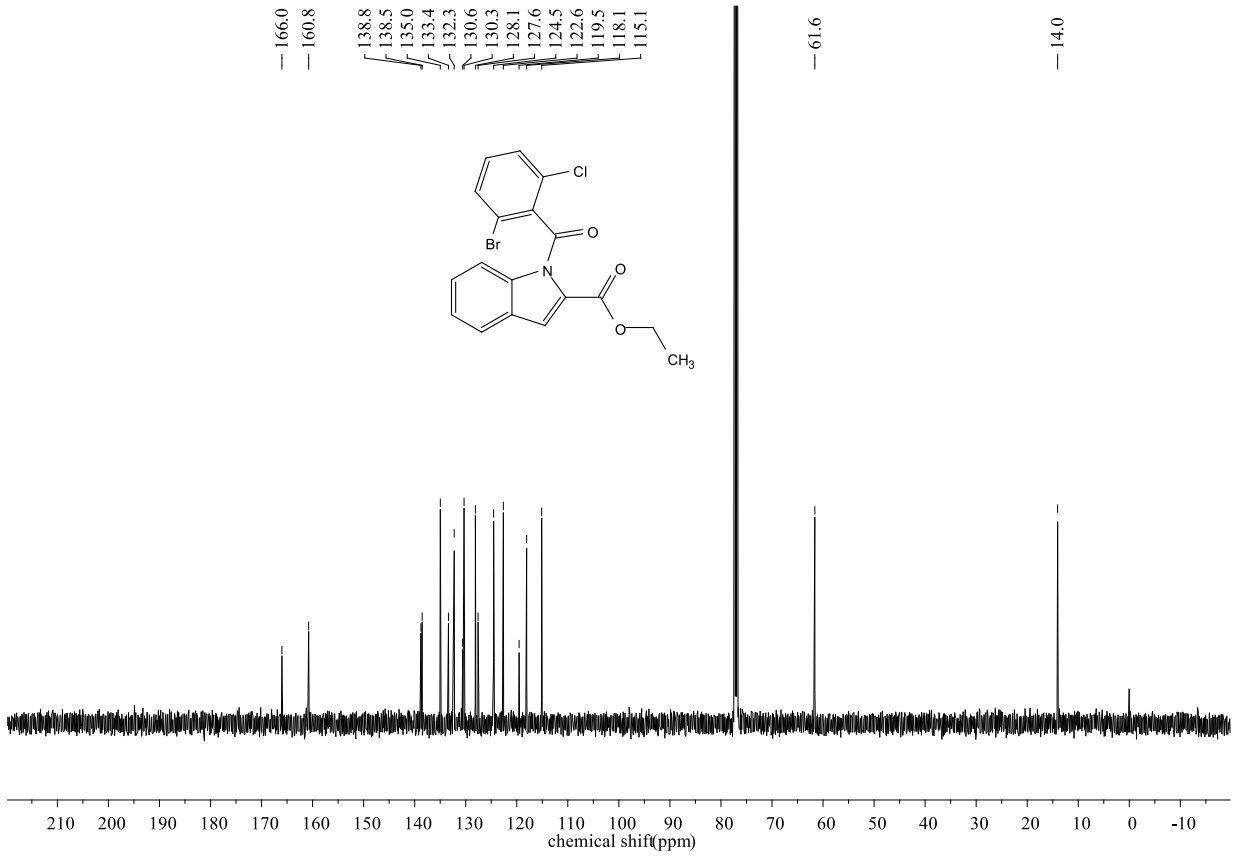
^{13}C NMR Spectra of compound **R38** (125 MHz, $CDCl_3$)



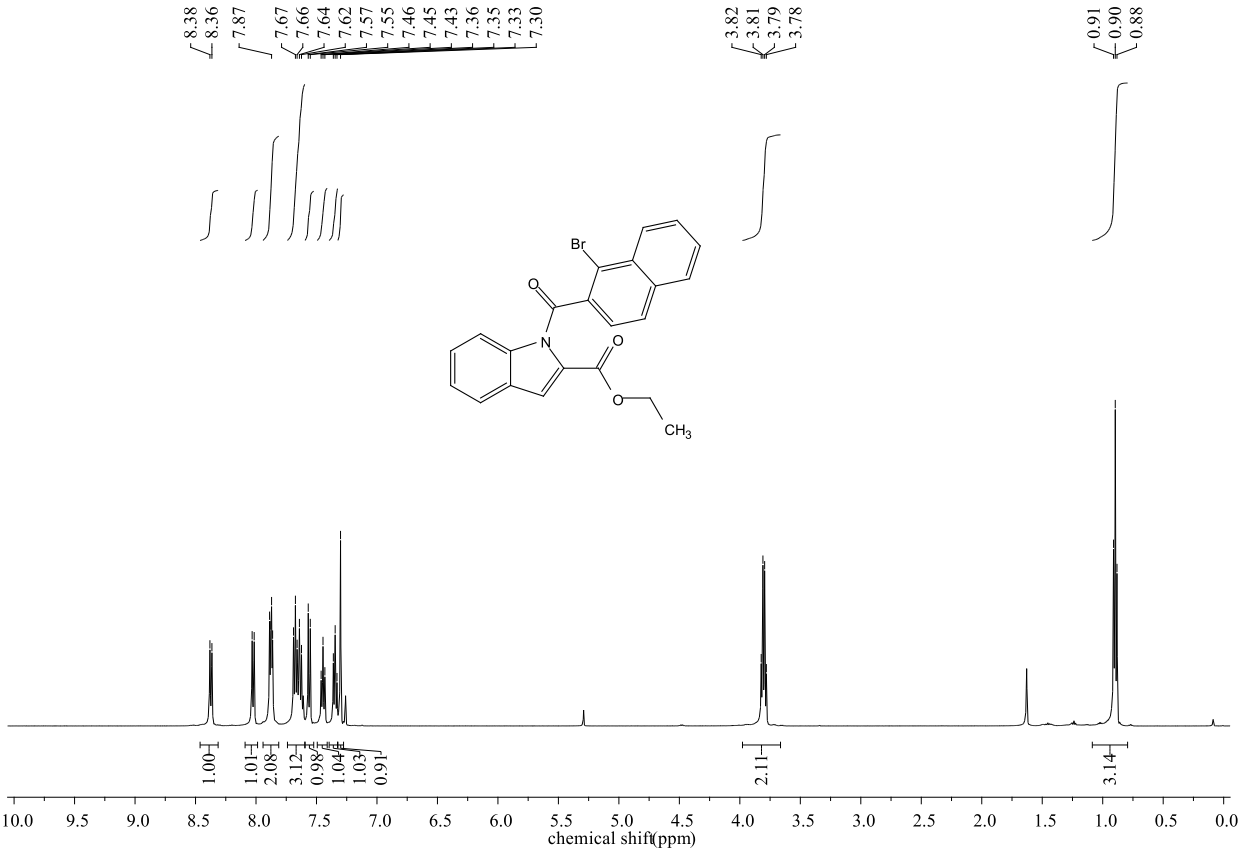
^{1}H NMR Spectra of compound **R39** (400 MHz, $CDCl_3$)



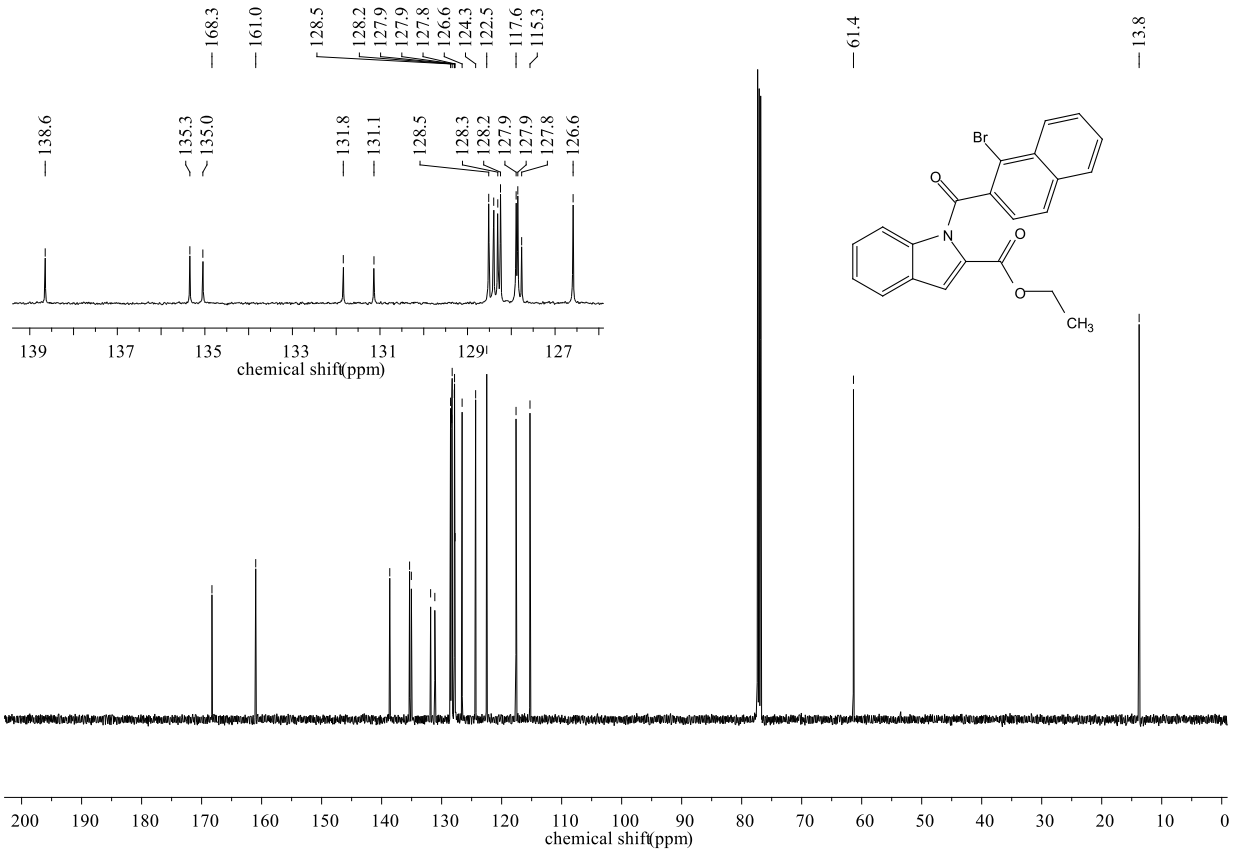
^{13}C NMR Spectra of compound **R39** (125 MHz, $CDCl_3$)



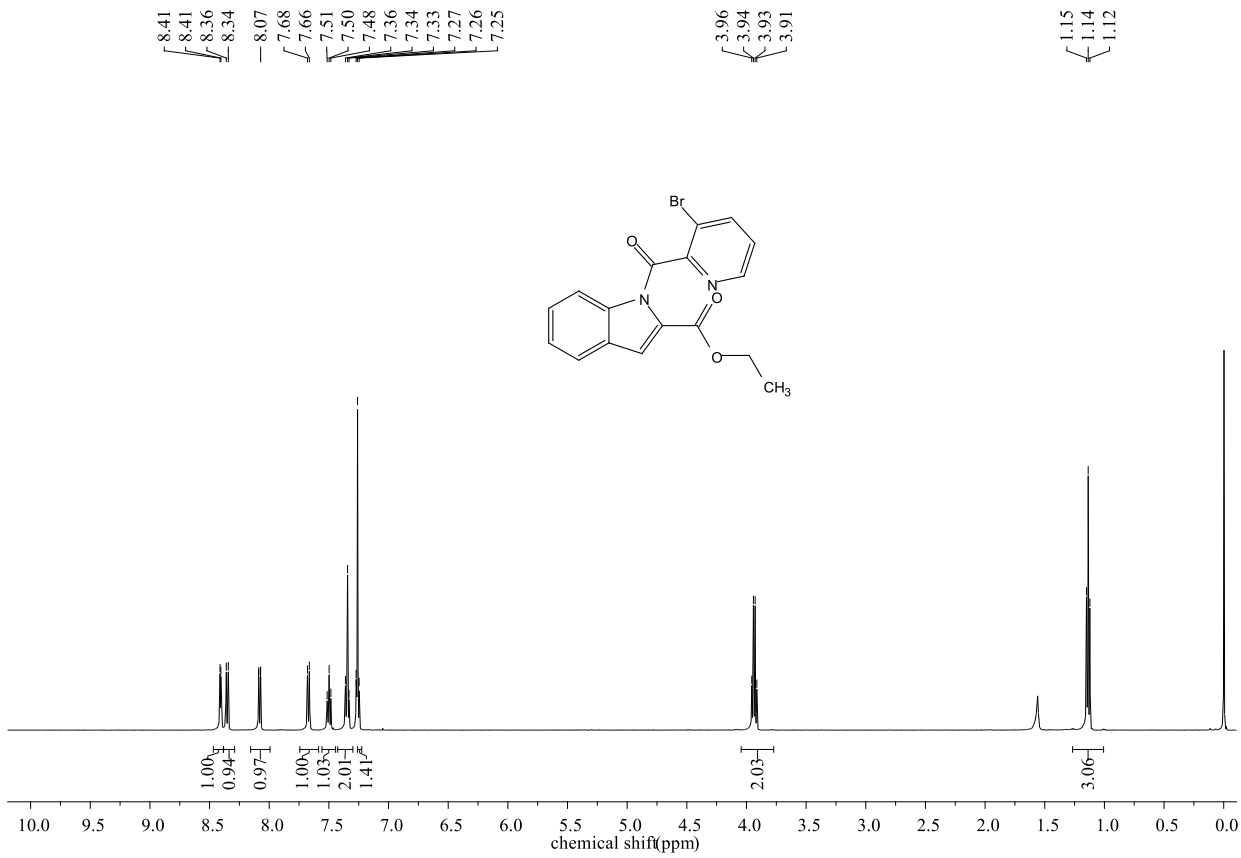
^{1}H NMR Spectra of compound **R40** (500 MHz, $CDCl_3$)



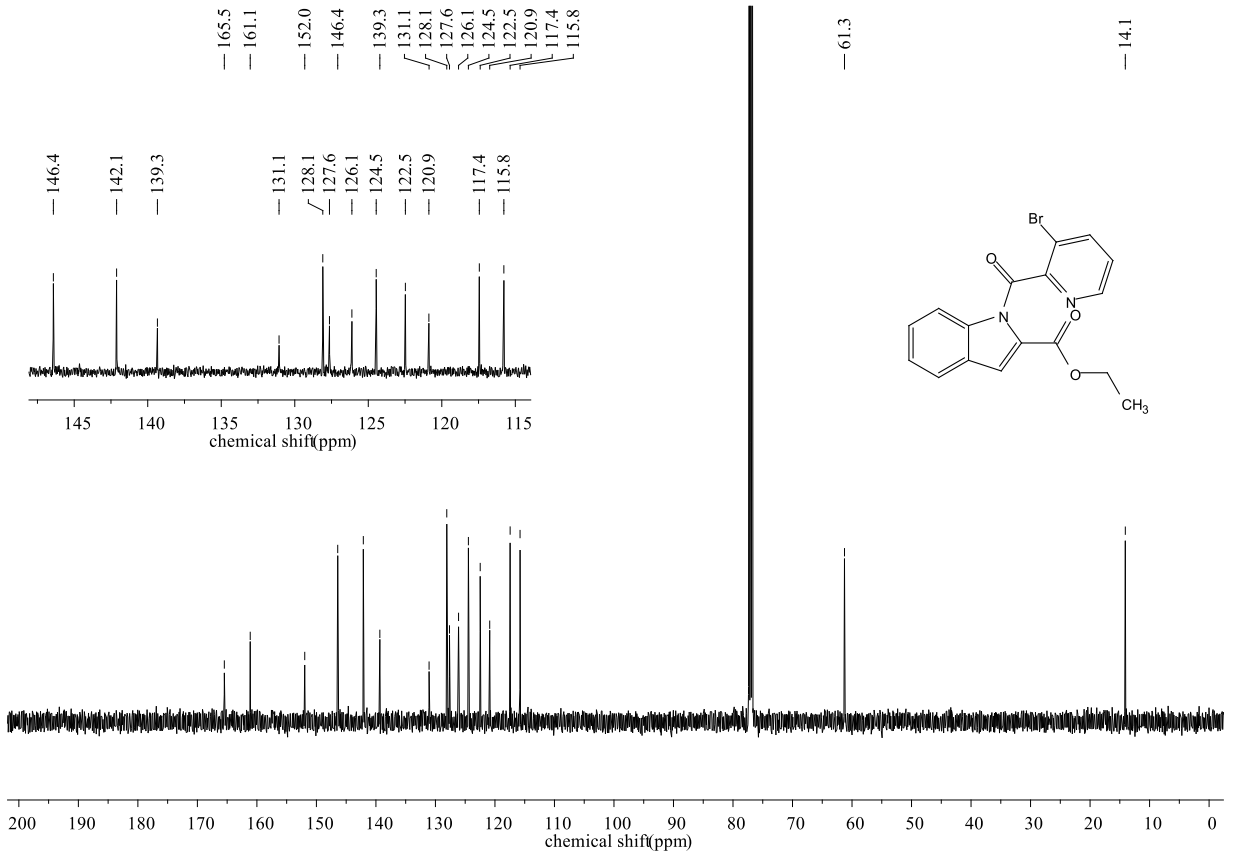
^{13}C NMR Spectra of compound **R40** (125 MHz, $CDCl_3$)



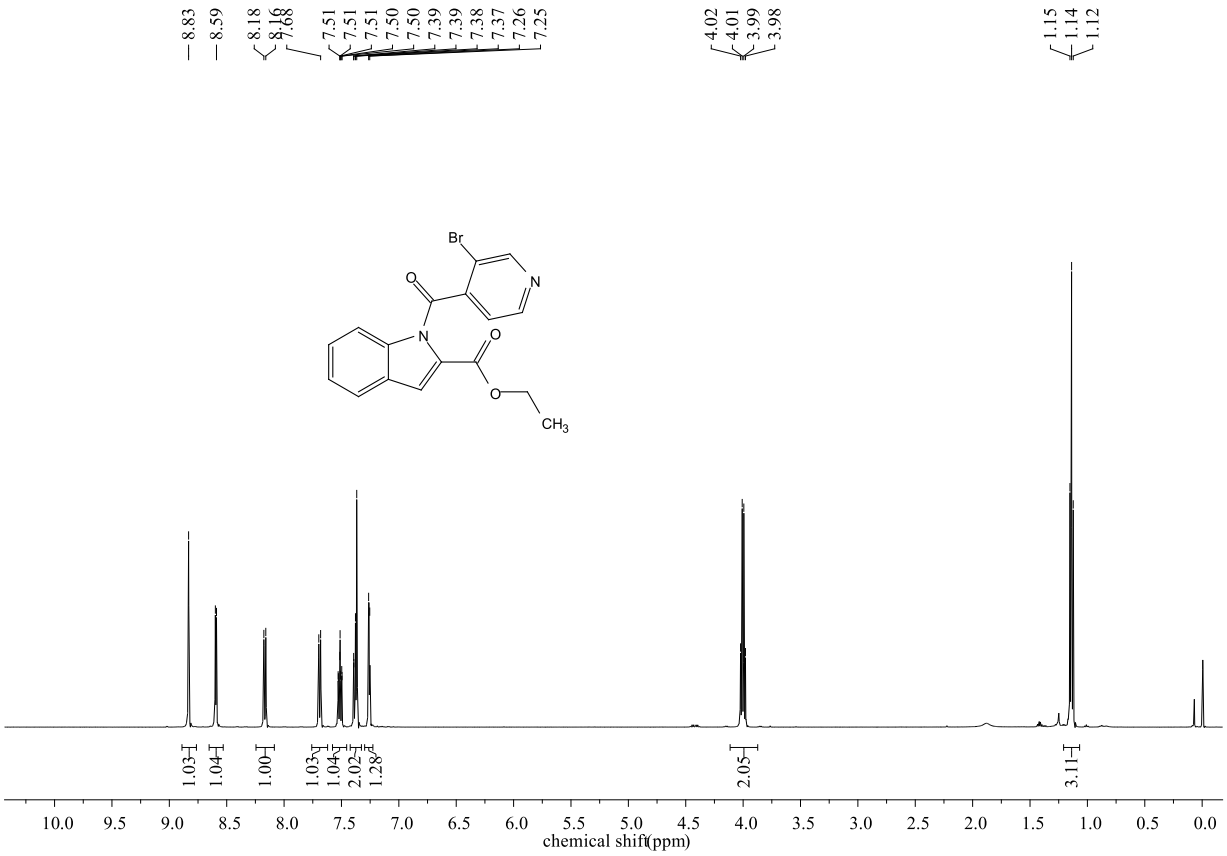
^{1}H NMR Spectra of compound **R41** (500 MHz, $CDCl_3$)



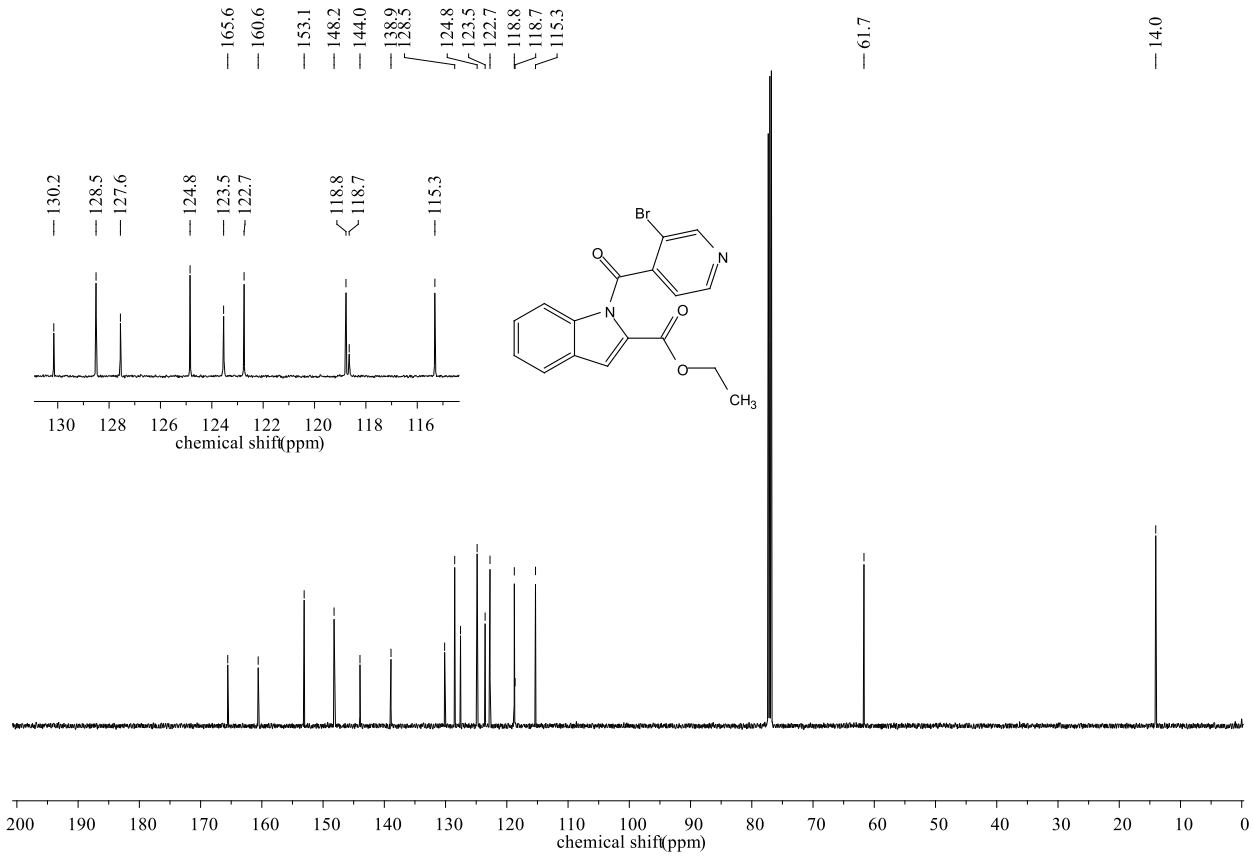
^{13}C NMR Spectra of compound **R41** (125 MHz, $CDCl_3$)



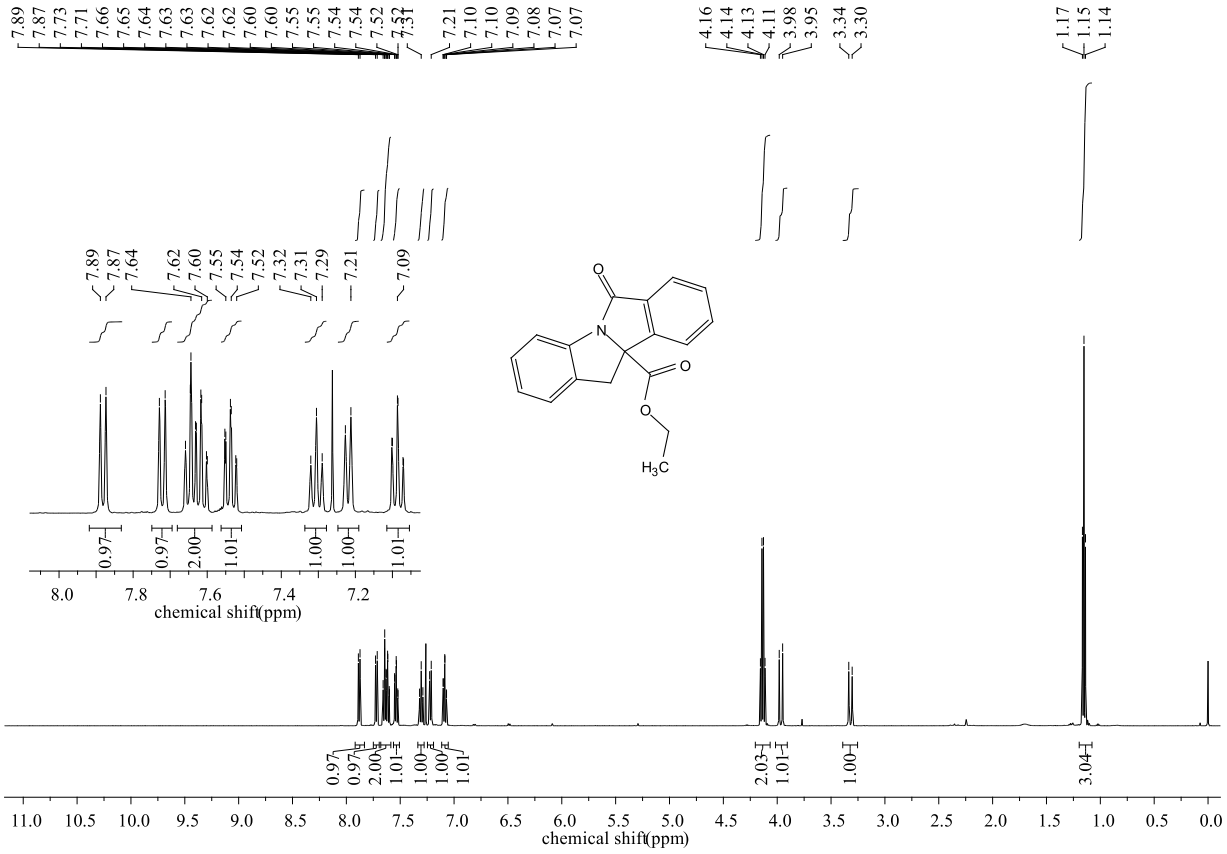
^{1}H NMR Spectra of compound **R42** (500 MHz, $CDCl_3$)



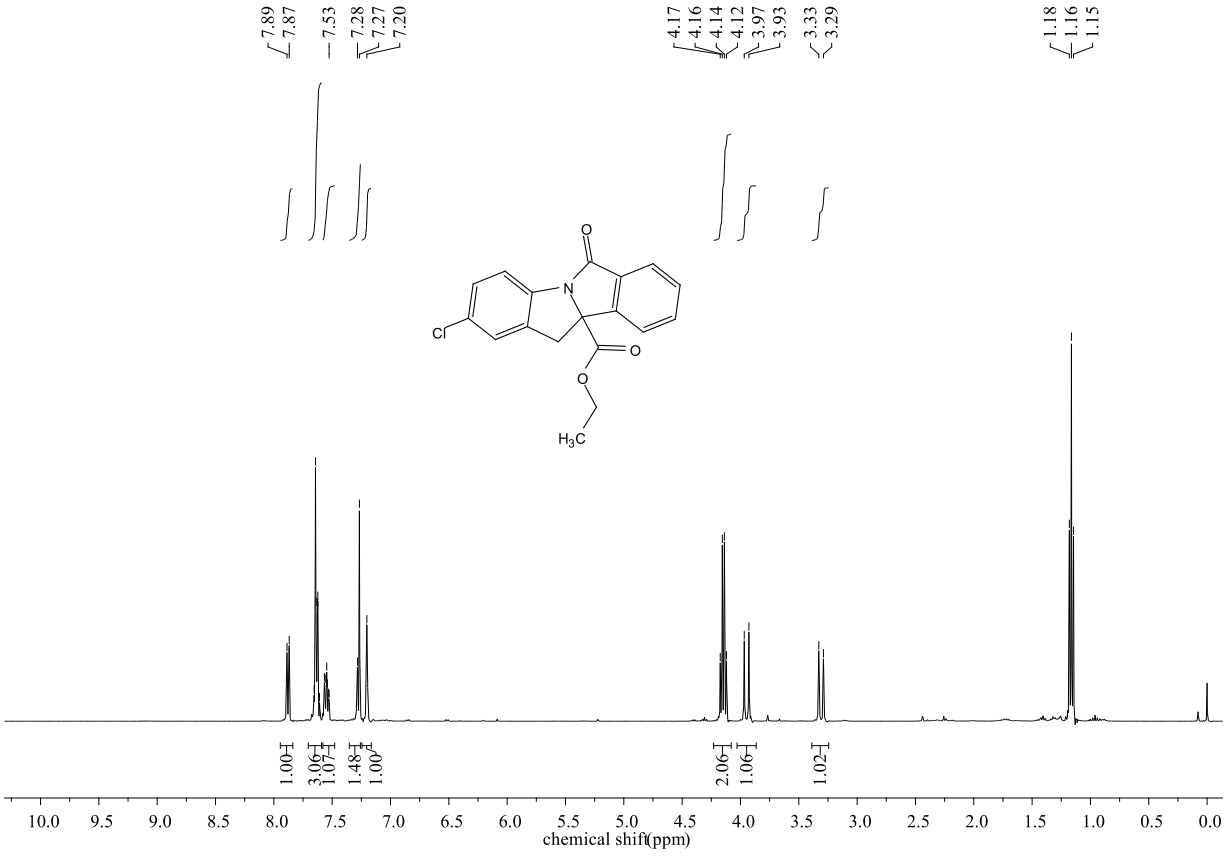
^{13}C NMR Spectra of compound **R42** (125 MHz, $CDCl_3$)



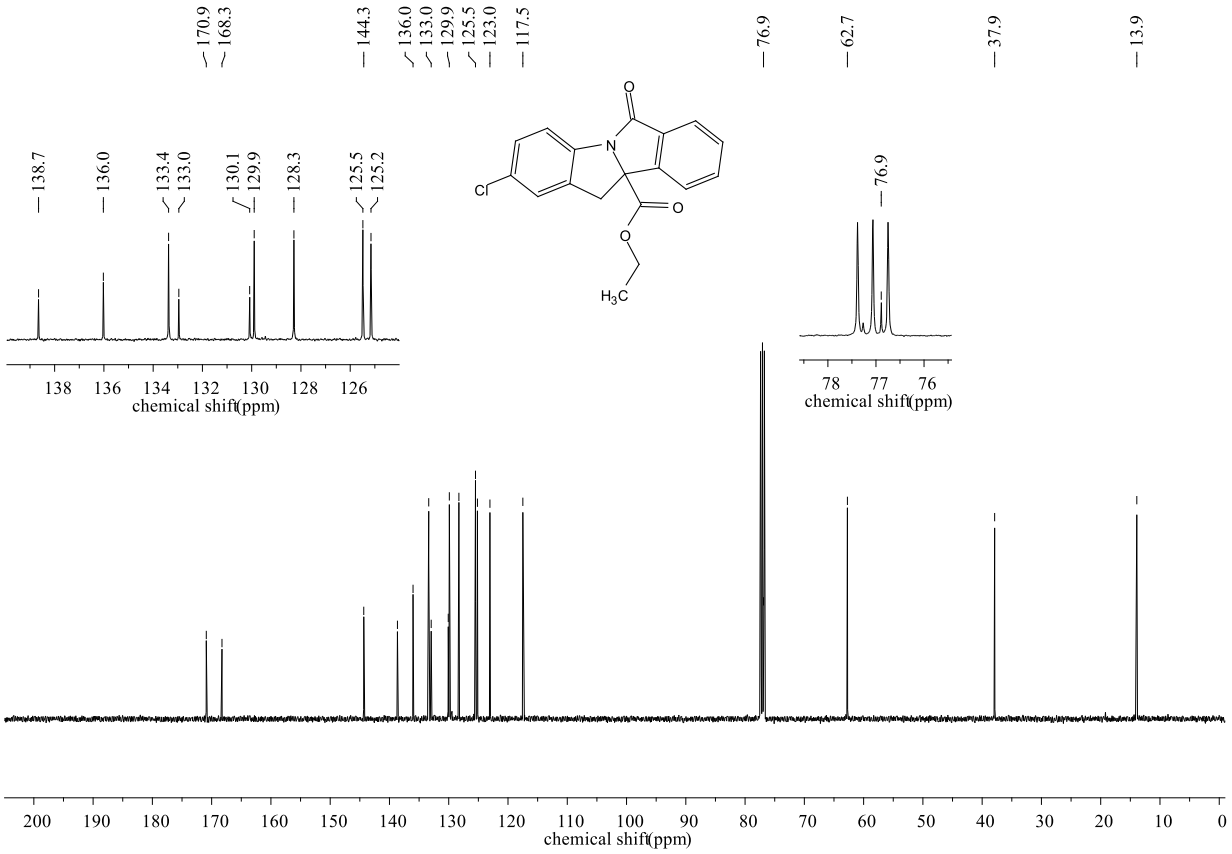
^{1}H NMR Spectra of compound **1** (500 MHz, $CDCl_3$)



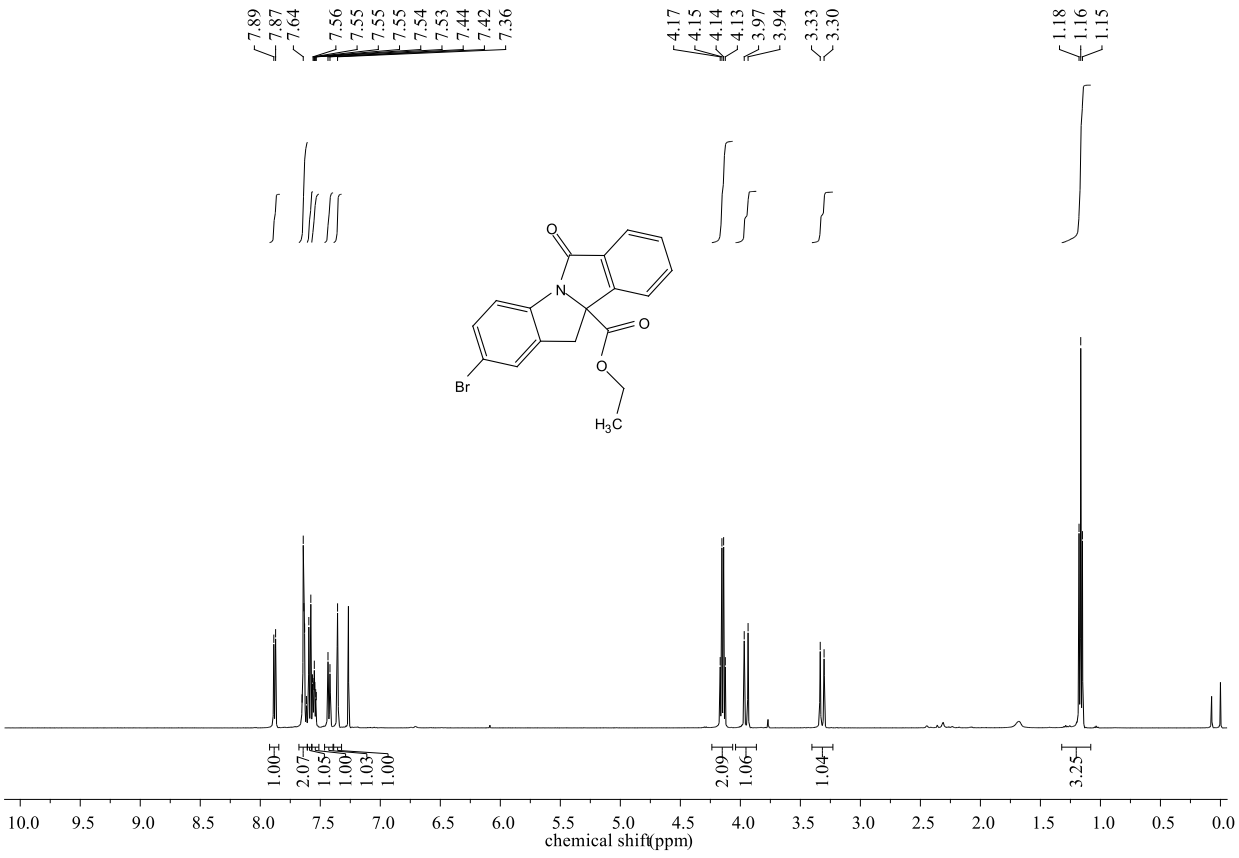
^{1}H NMR Spectra of compound **2** (400 MHz, $CDCl_3$)



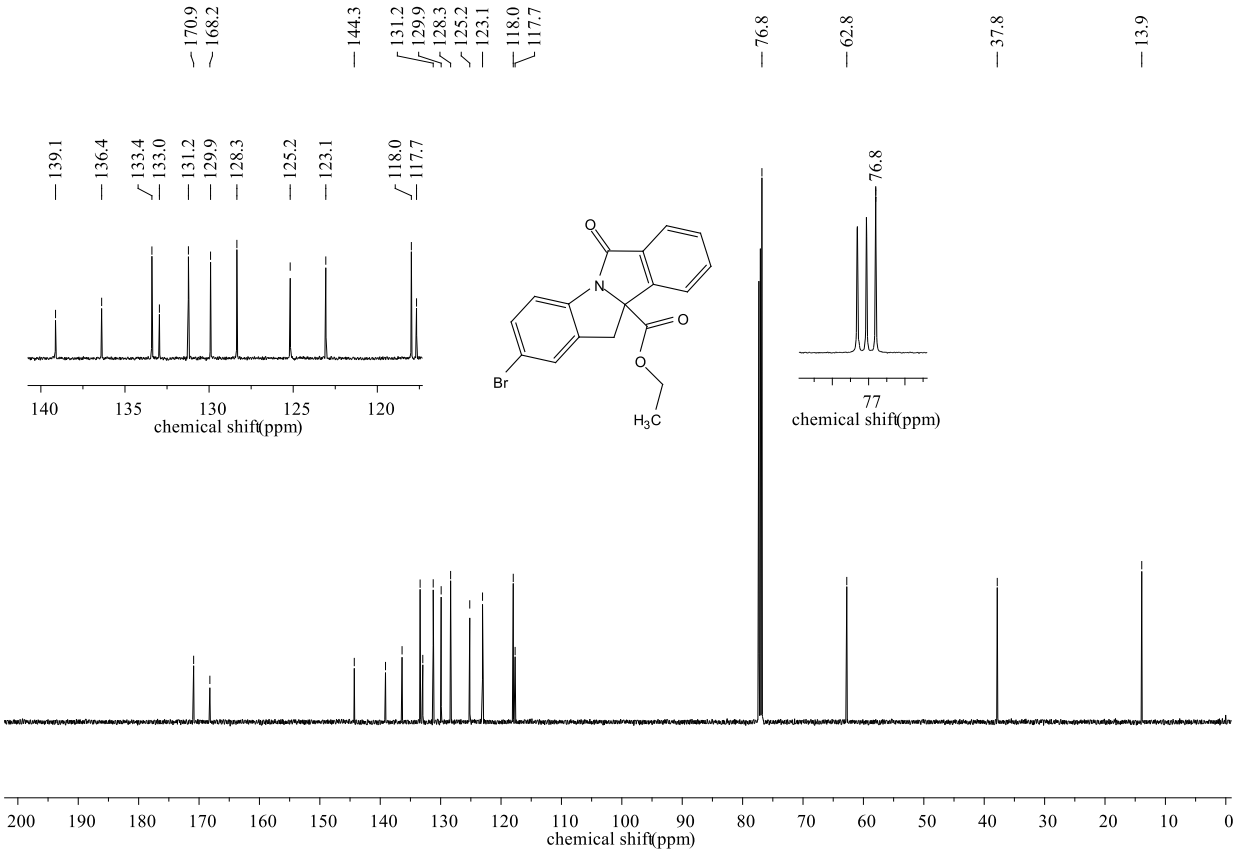
^{13}C NMR Spectra of compound **2** (100 MHz, $CDCl_3$)



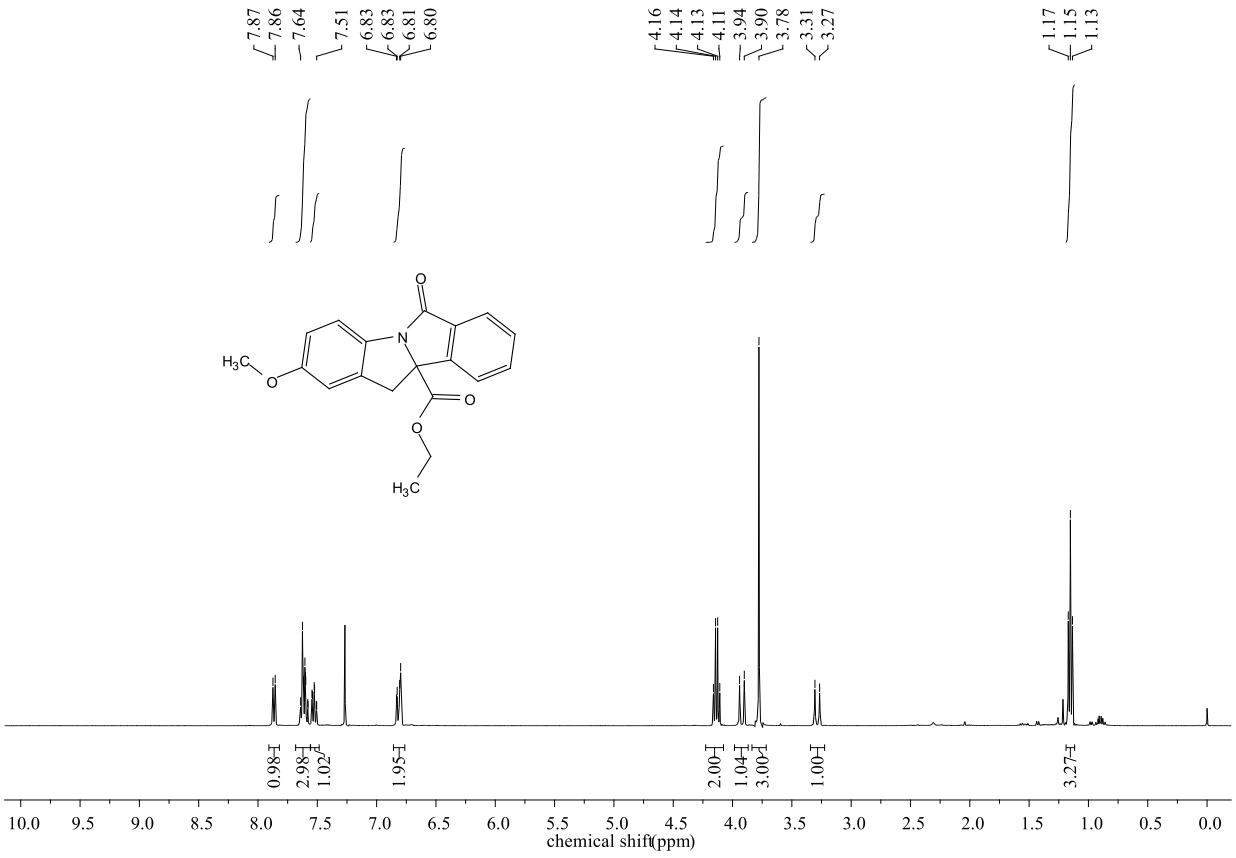
^{1}H NMR Spectra of compound **3** (400 MHz, $CDCl_3$)



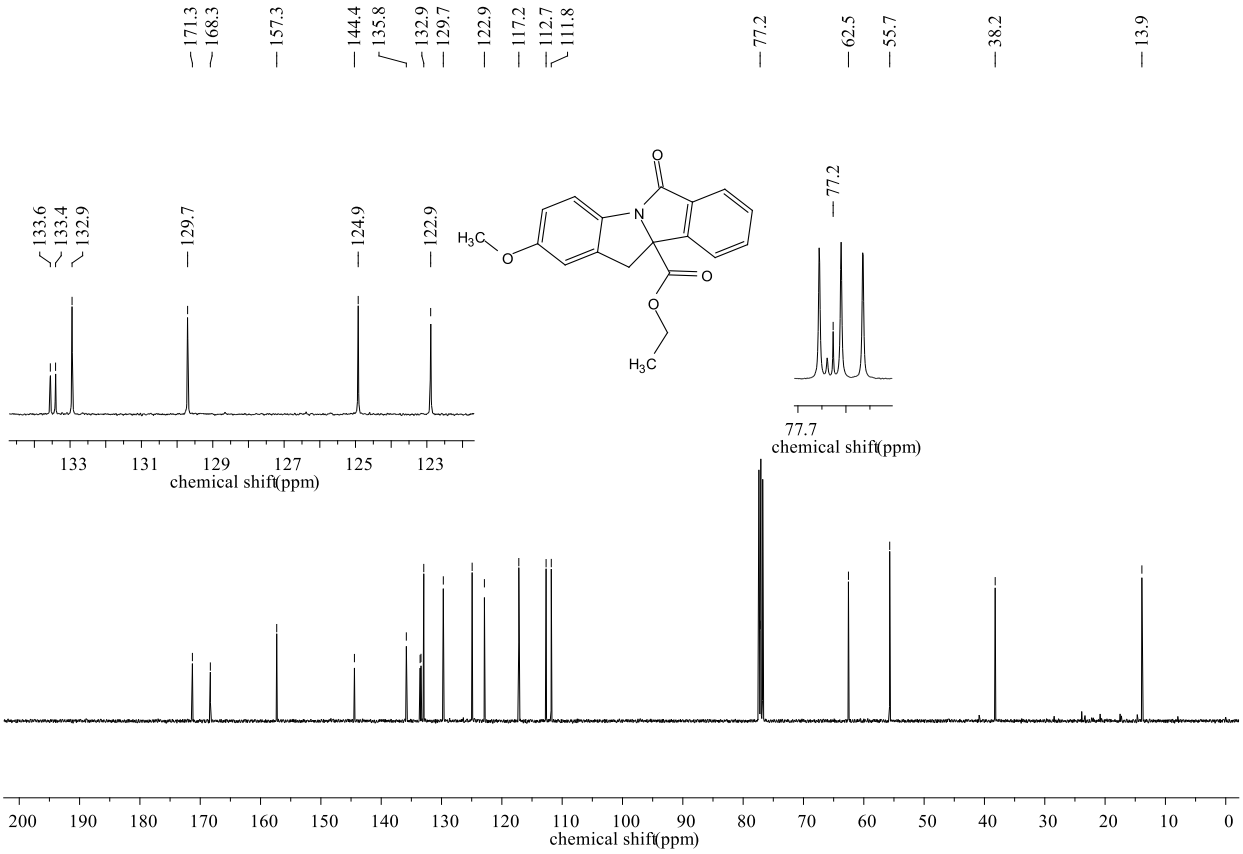
^{13}C NMR Spectra of compound **3** (125 MHz, $CDCl_3$)



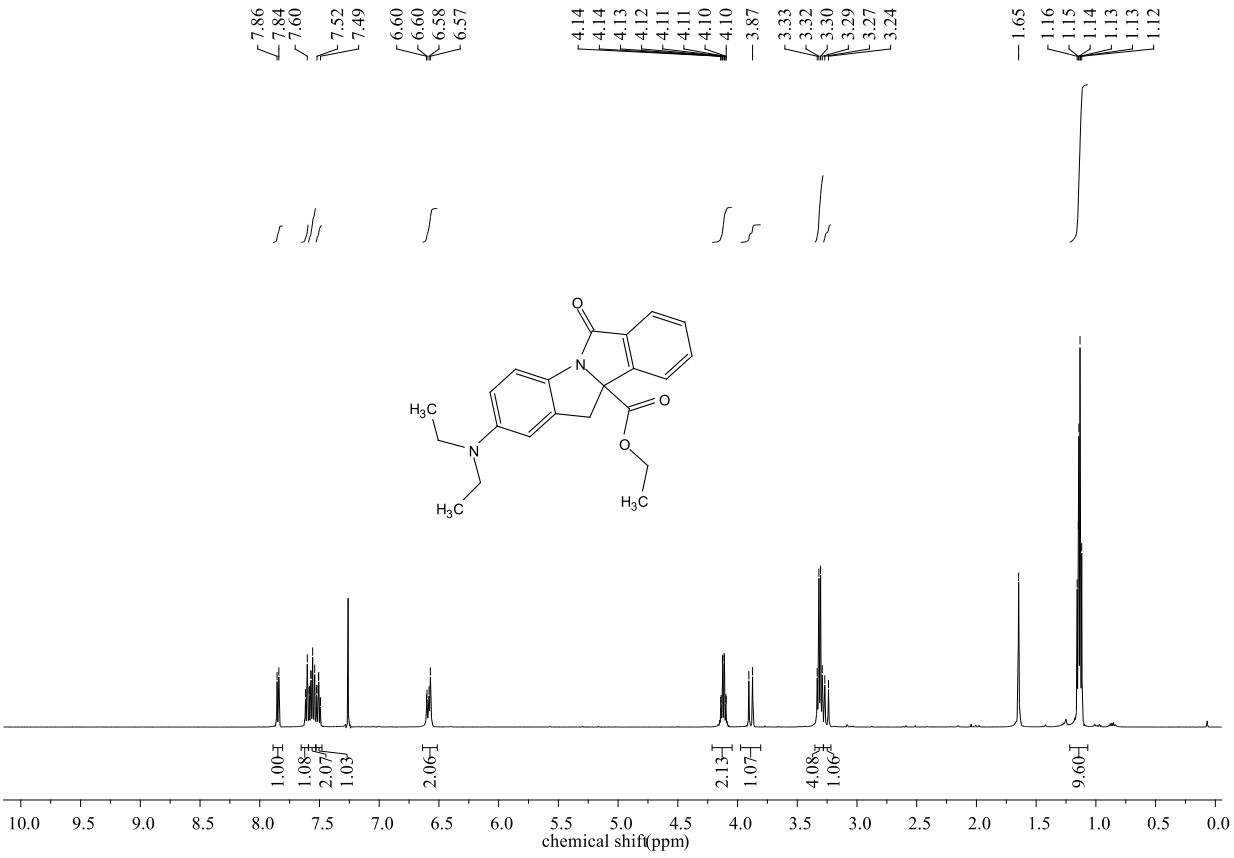
^{1}H NMR Spectra of compound **4** (400 MHz, $CDCl_3$)



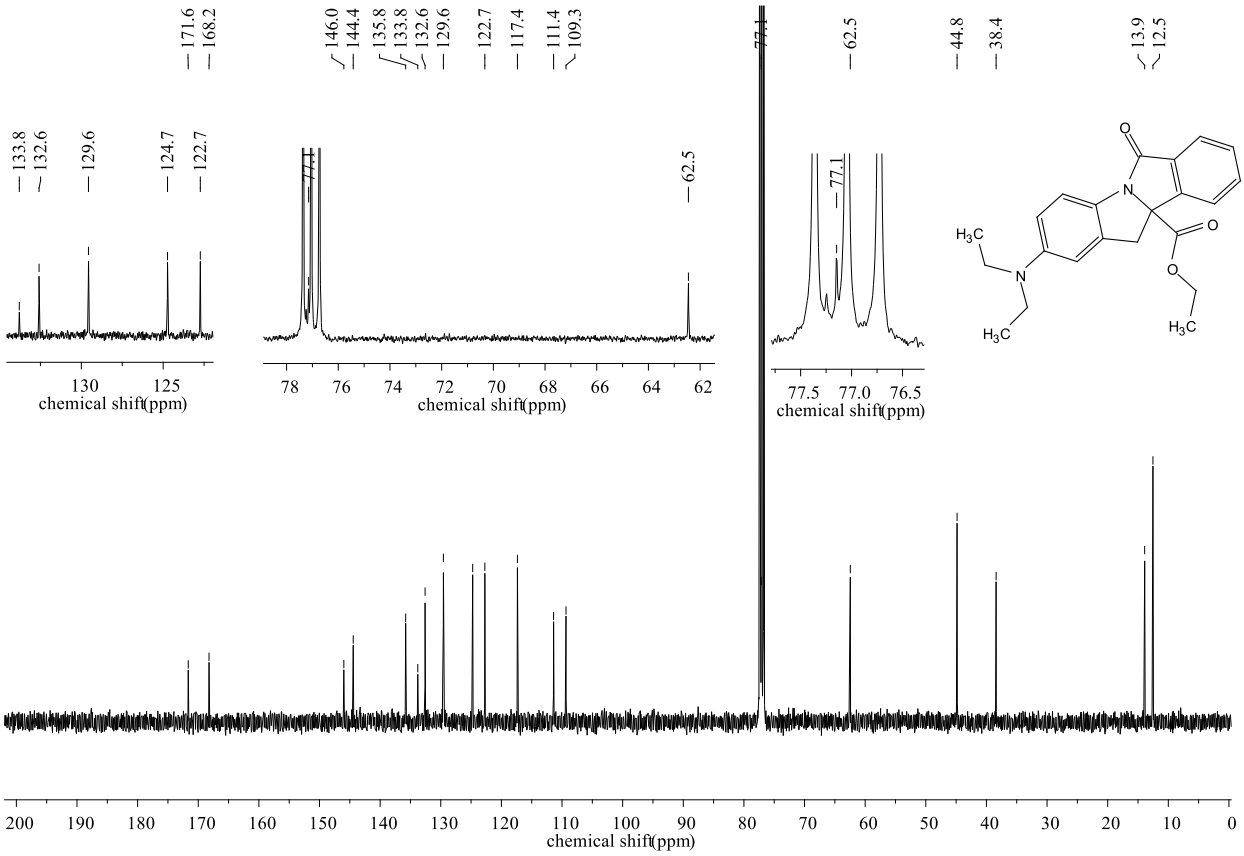
^{13}C NMR Spectra of compound **4** (100 MHz, $CDCl_3$)



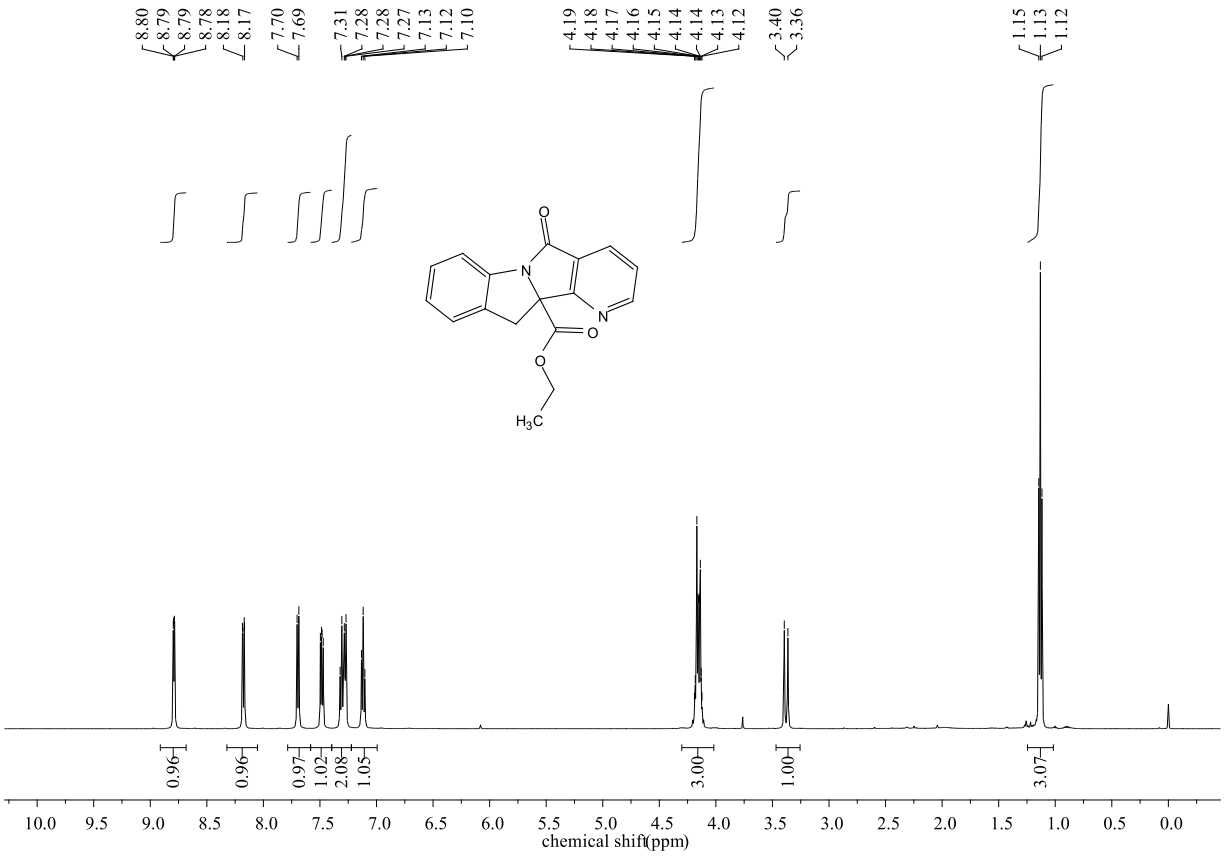
^{1}H NMR Spectra of compound **5** (500 MHz, $CDCl_3$)



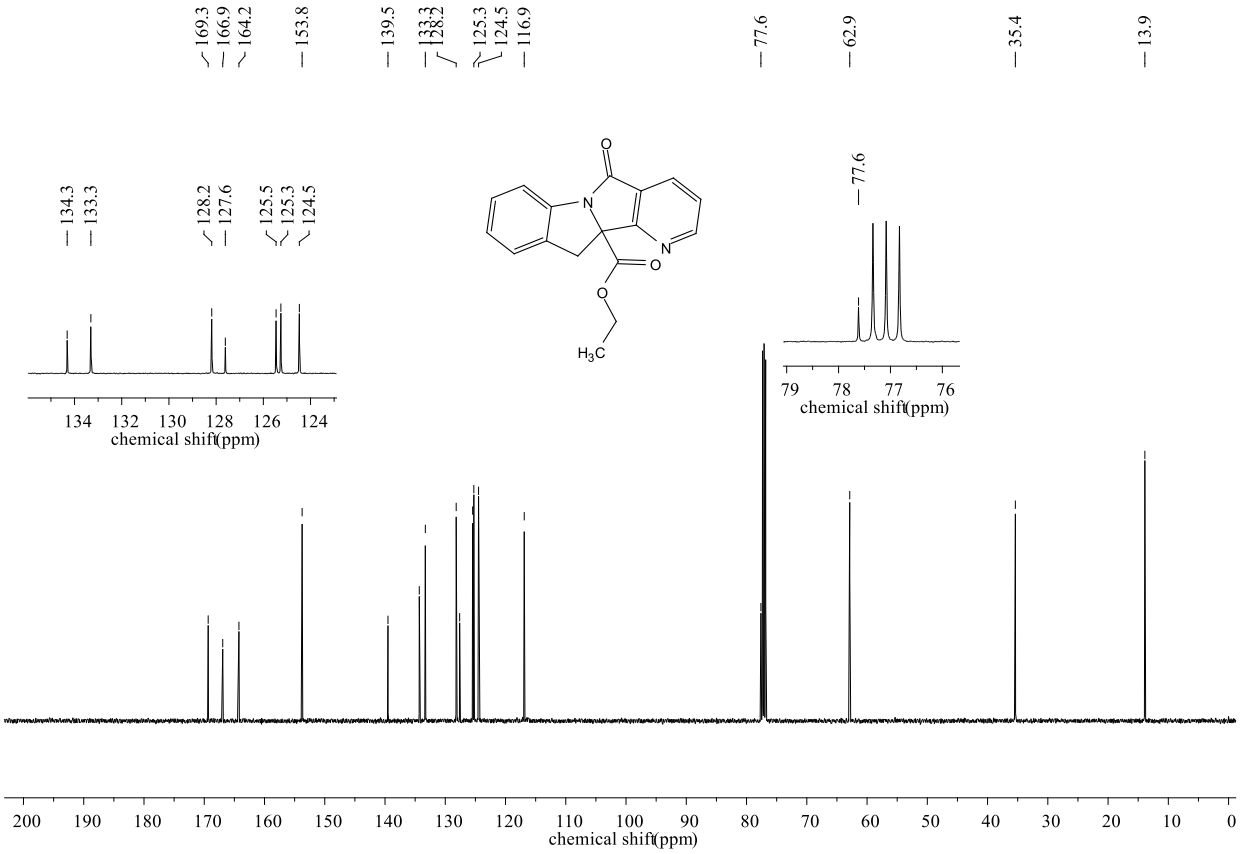
^{13}C NMR Spectra of compound **5** (100 MHz, $CDCl_3$)



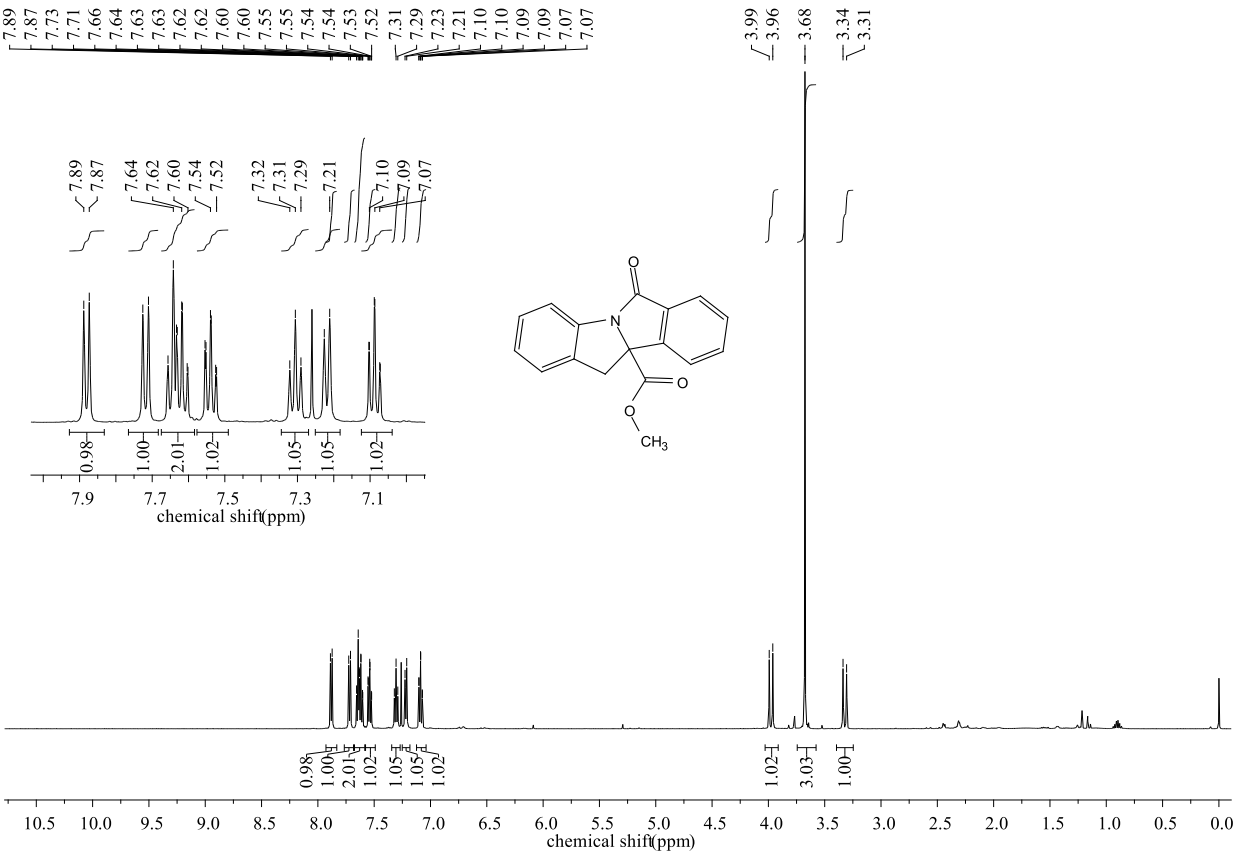
^{1}H NMR Spectra of compound **6** (500 MHz, $CDCl_3$)



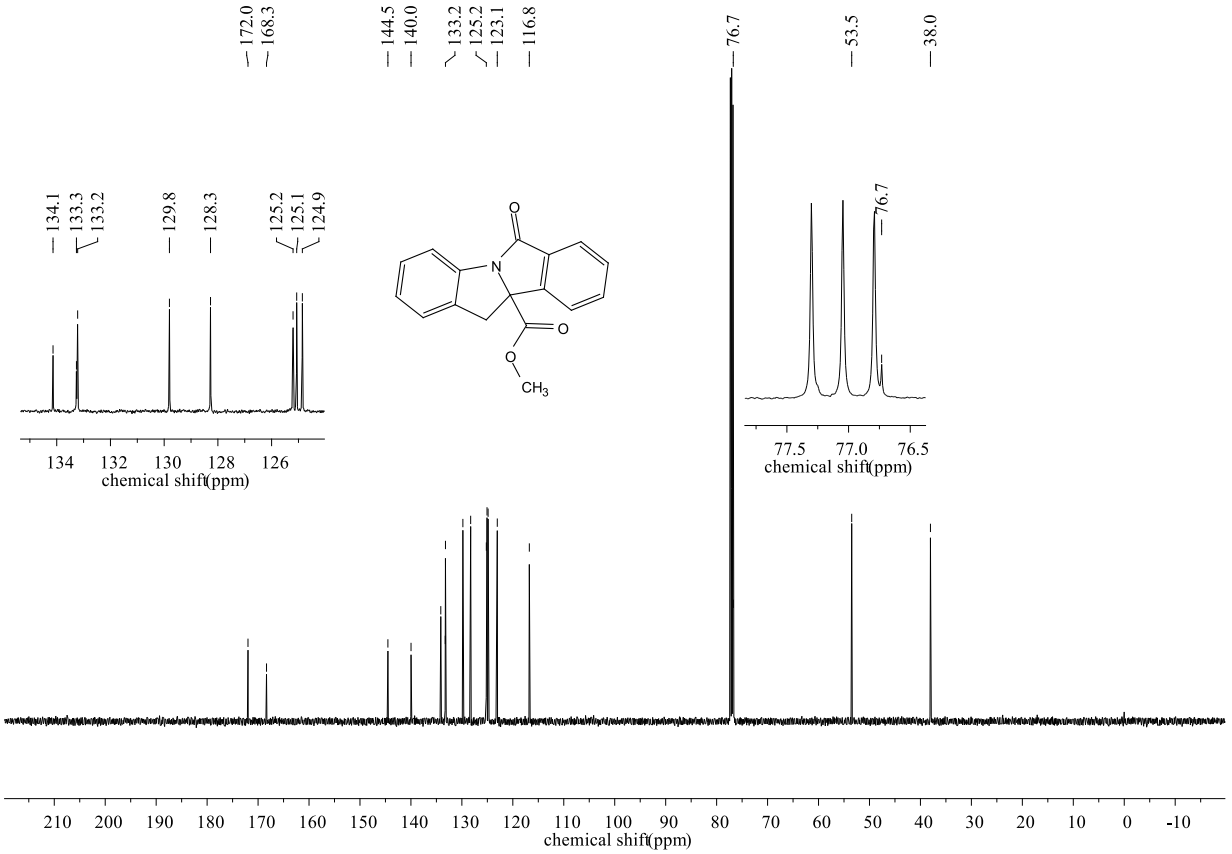
^{13}C NMR Spectra of compound **6** (125 MHz, $CDCl_3$)



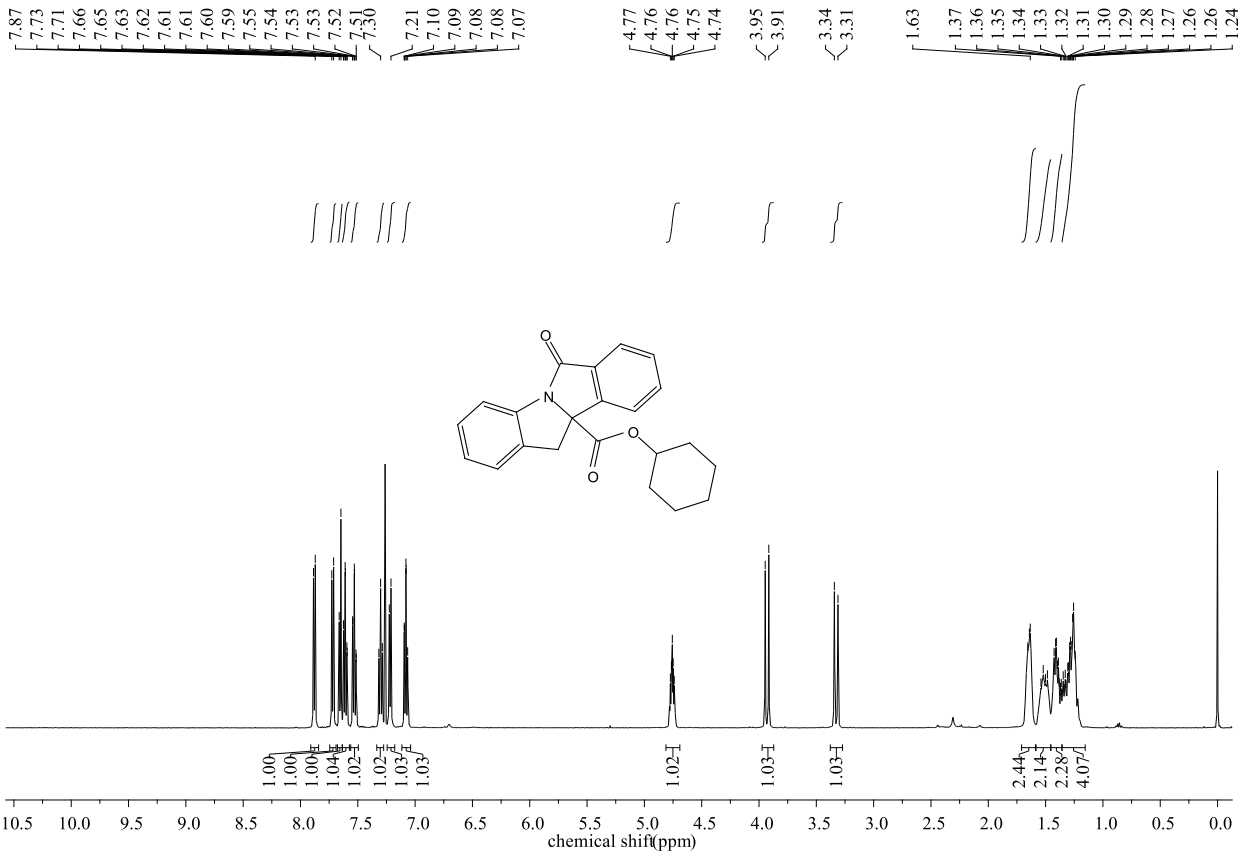
^{1}H NMR Spectra of compound **7** (500 MHz, $CDCl_3$)



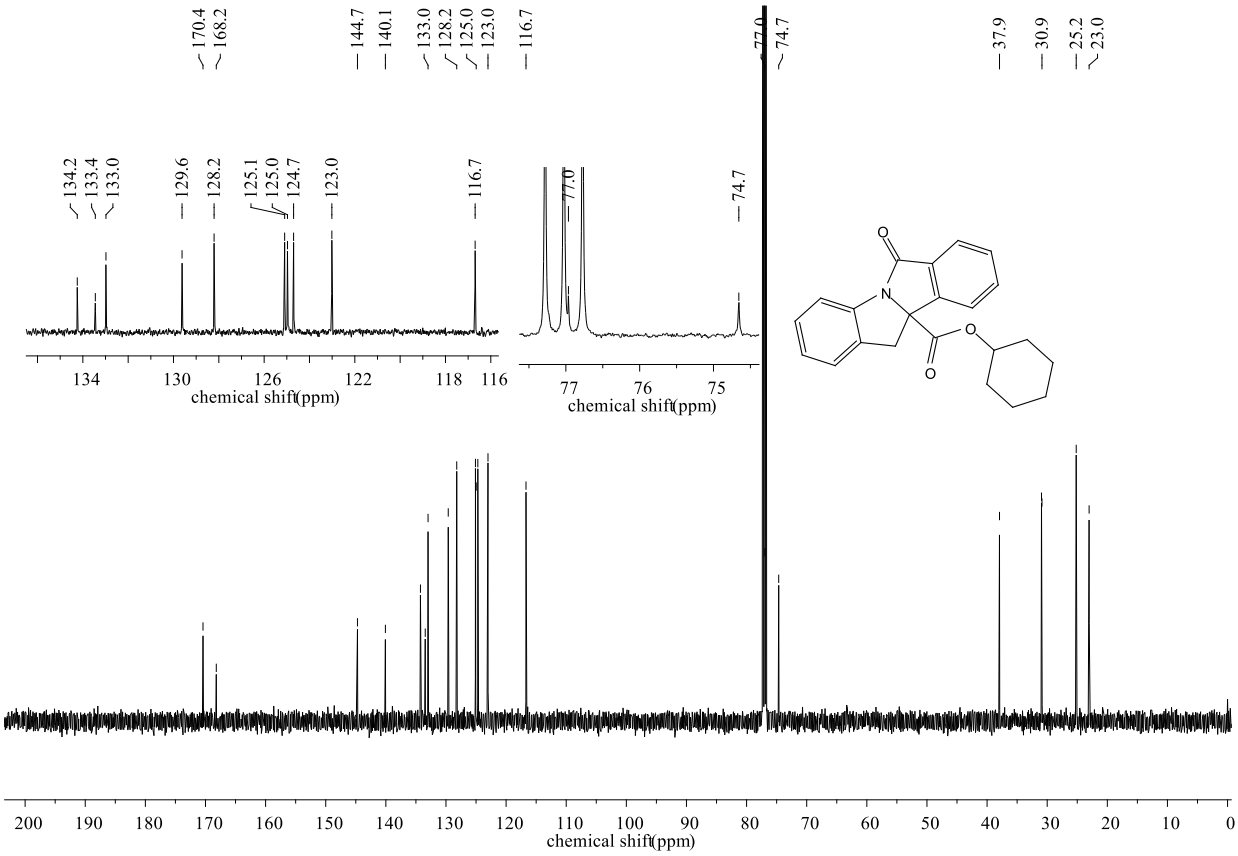
^{13}C NMR Spectra of compound **7** (125 MHz, $CDCl_3$)



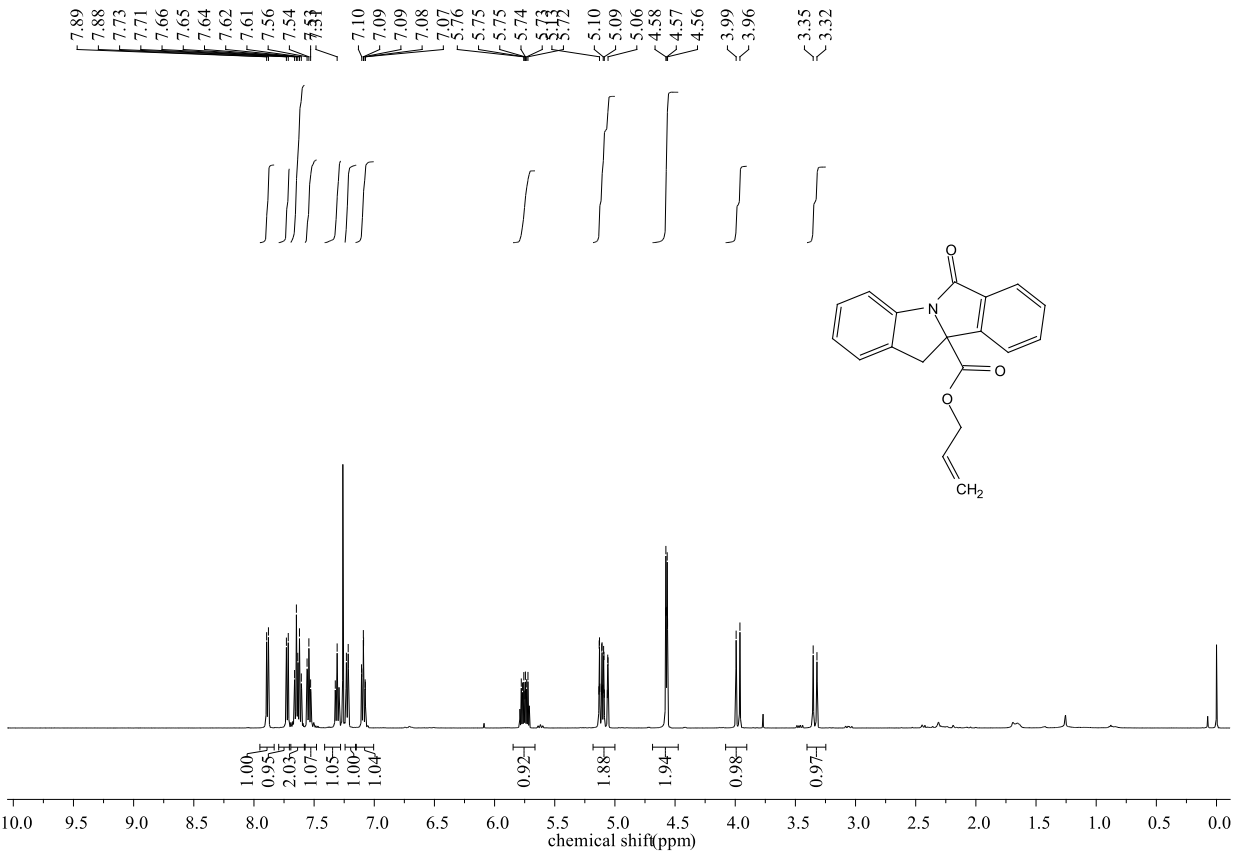
^{1}H NMR Spectra of compound **8** (500 MHz, $CDCl_3$)



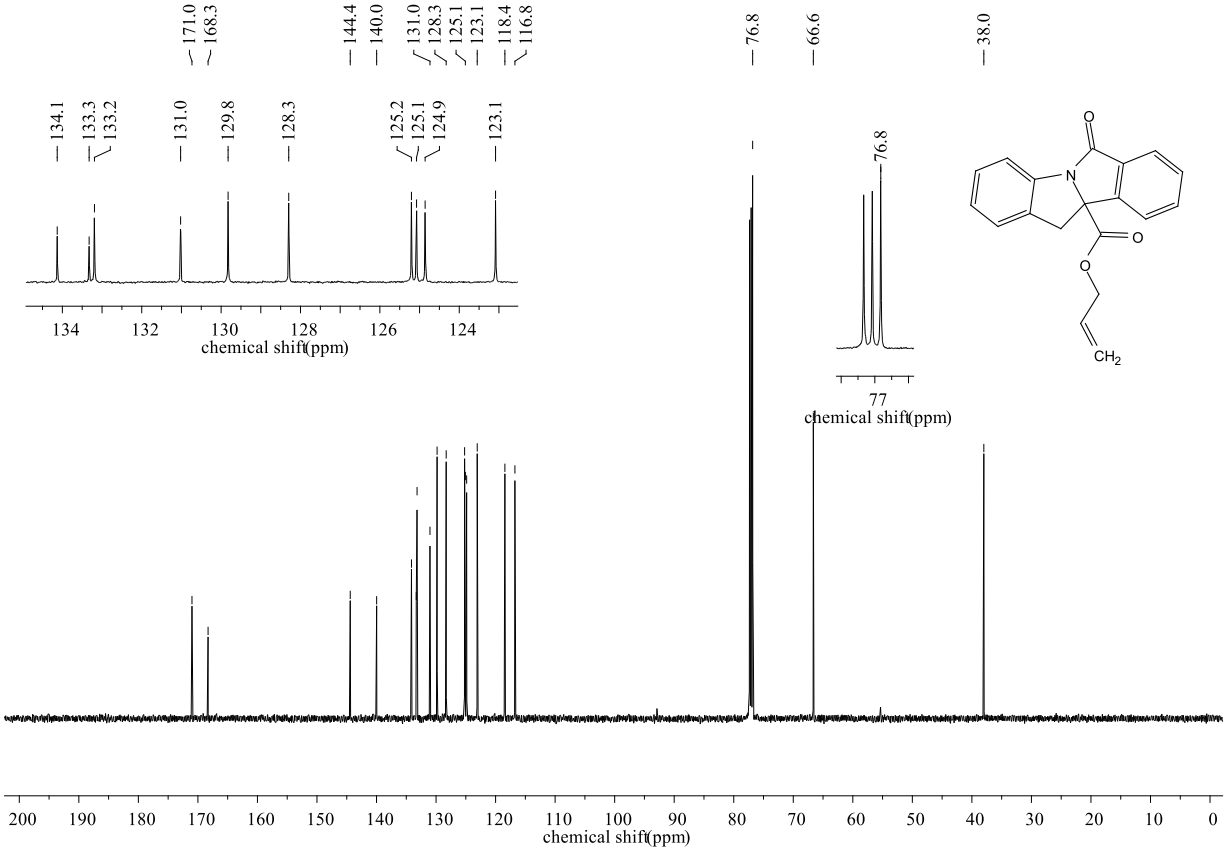
^{13}C NMR Spectra of compound **8** (125 MHz, $CDCl_3$)



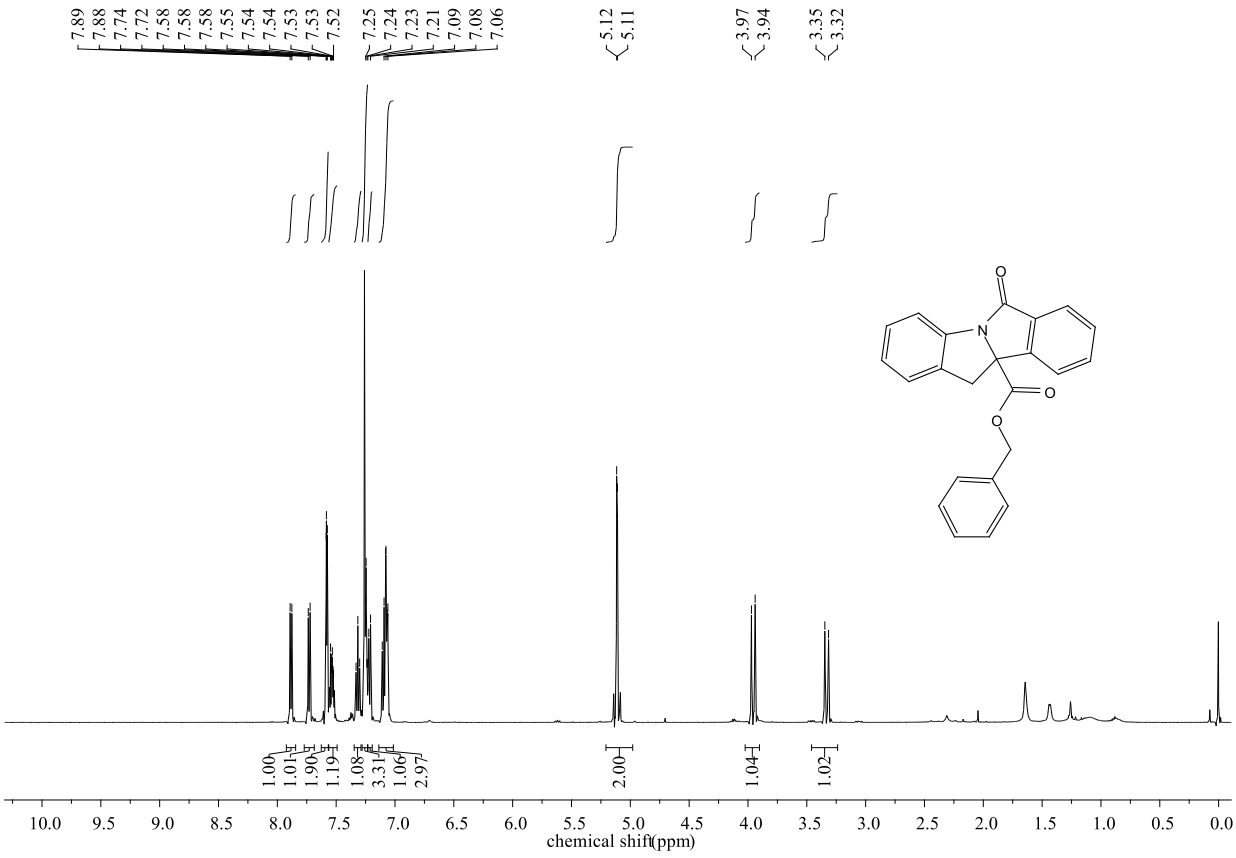
^{1}H NMR Spectra of compound **9** (500 MHz, $CDCl_3$)



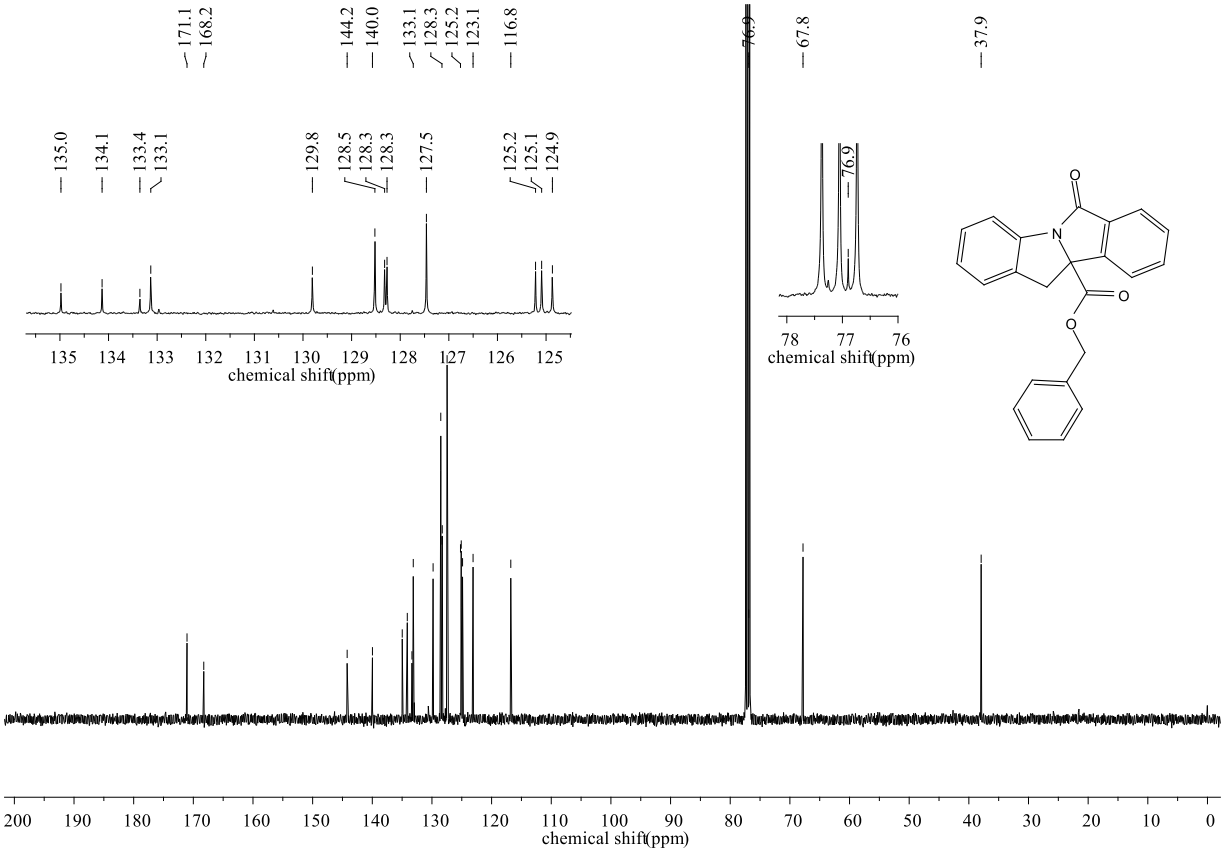
^{13}C NMR Spectra of compound **9** (125 MHz, $CDCl_3$)



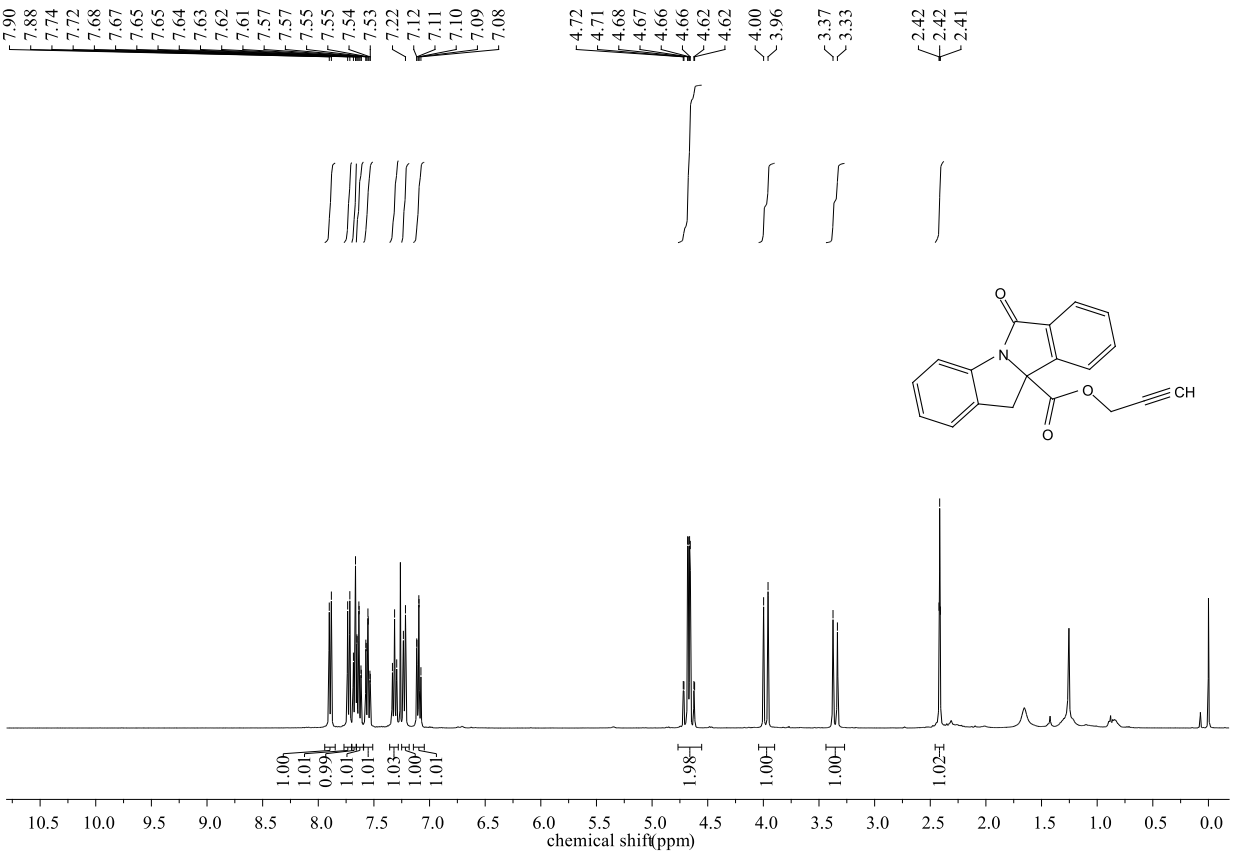
^{1}H NMR Spectra of compound **10** (400 MHz, $CDCl_3$)



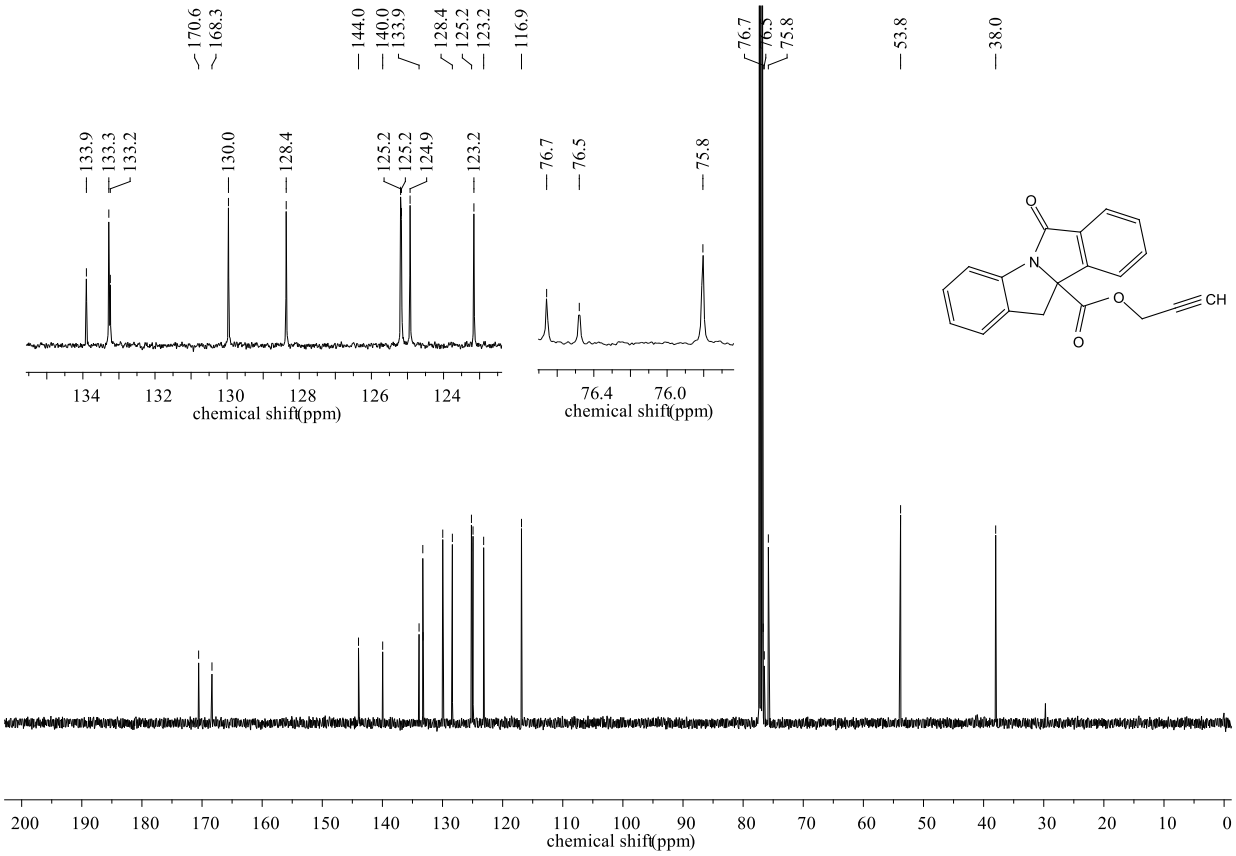
^{13}C NMR Spectra of compound **10** (100 MHz, $CDCl_3$)



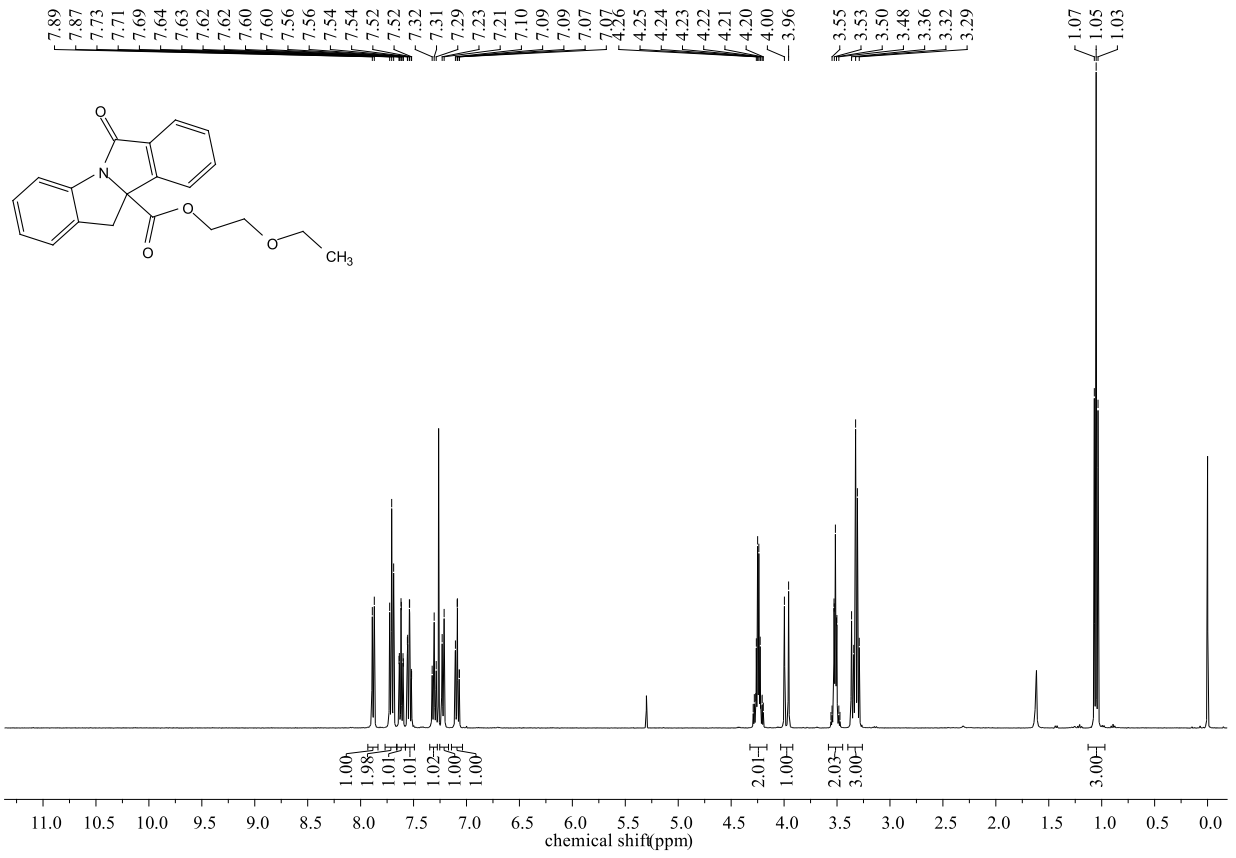
^{1}H NMR Spectra of compound **11** (400 MHz, $CDCl_3$)



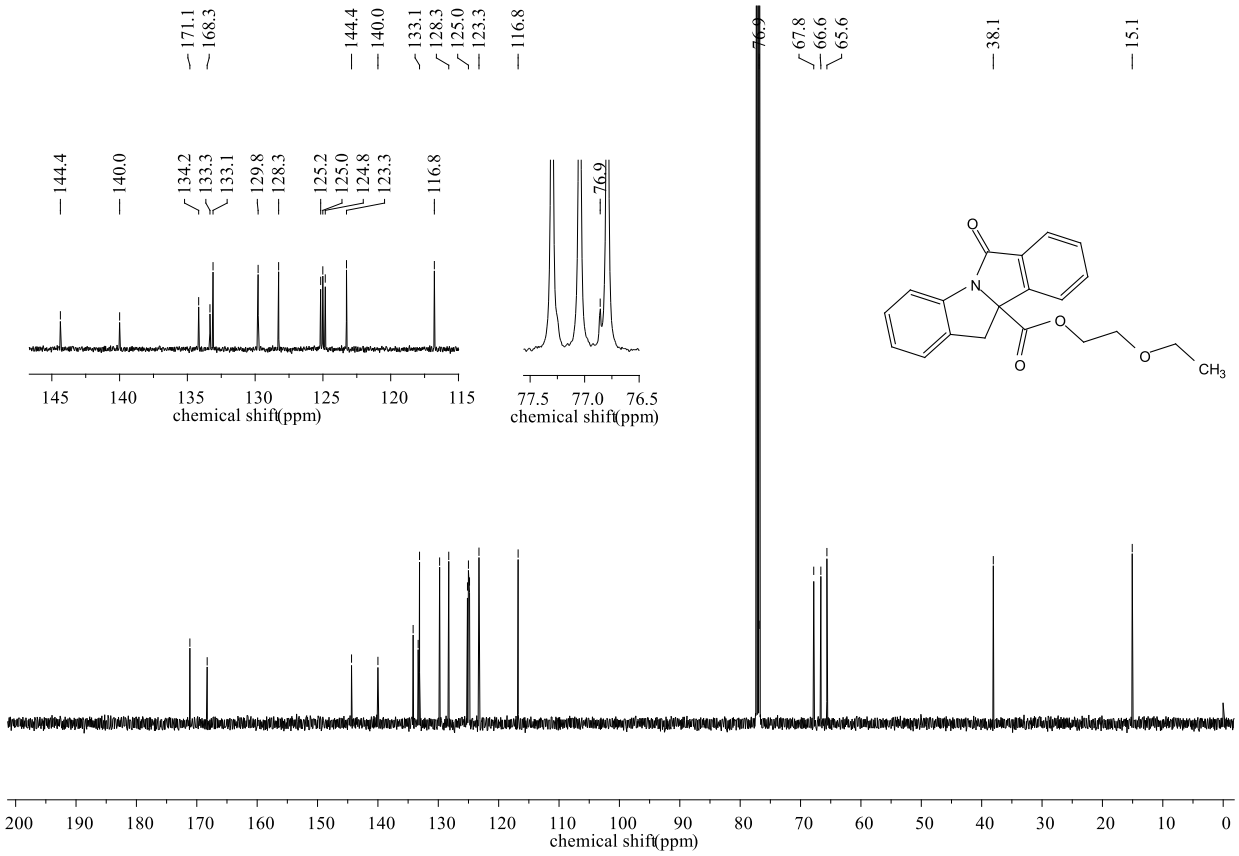
^{13}C NMR Spectra of compound **11** (125 MHz, $CDCl_3$)



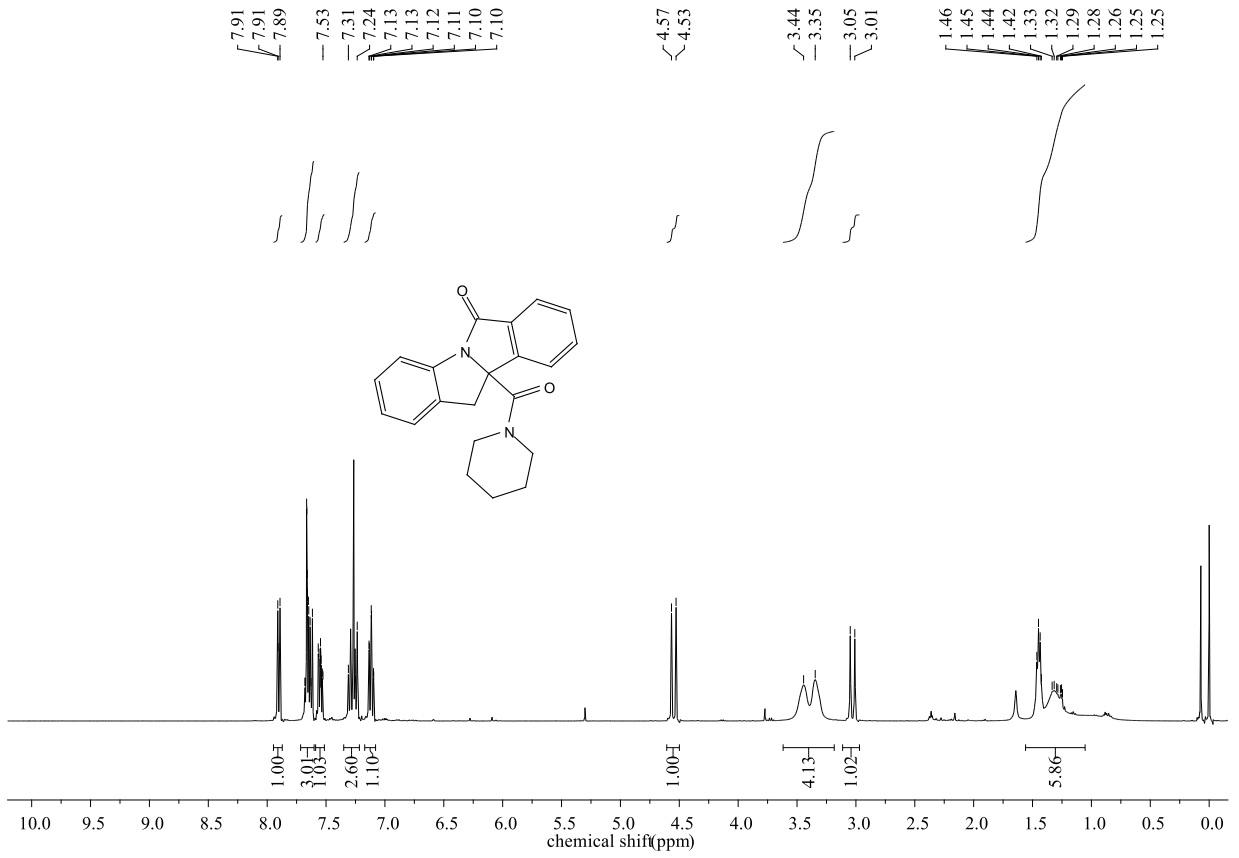
^{1}H NMR Spectra of compound **12** (400 MHz, $CDCl_3$)



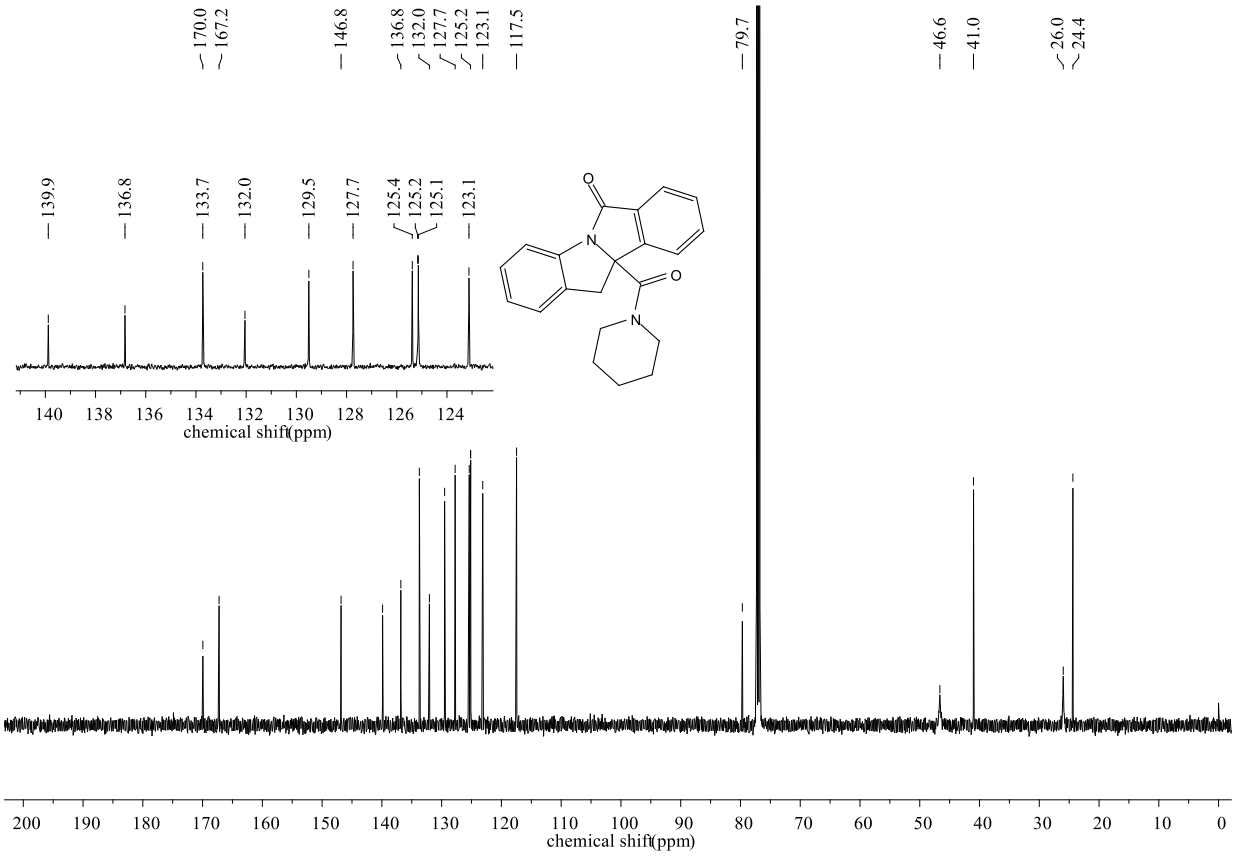
^{13}C NMR Spectra of compound **12** (125 MHz, $CDCl_3$)



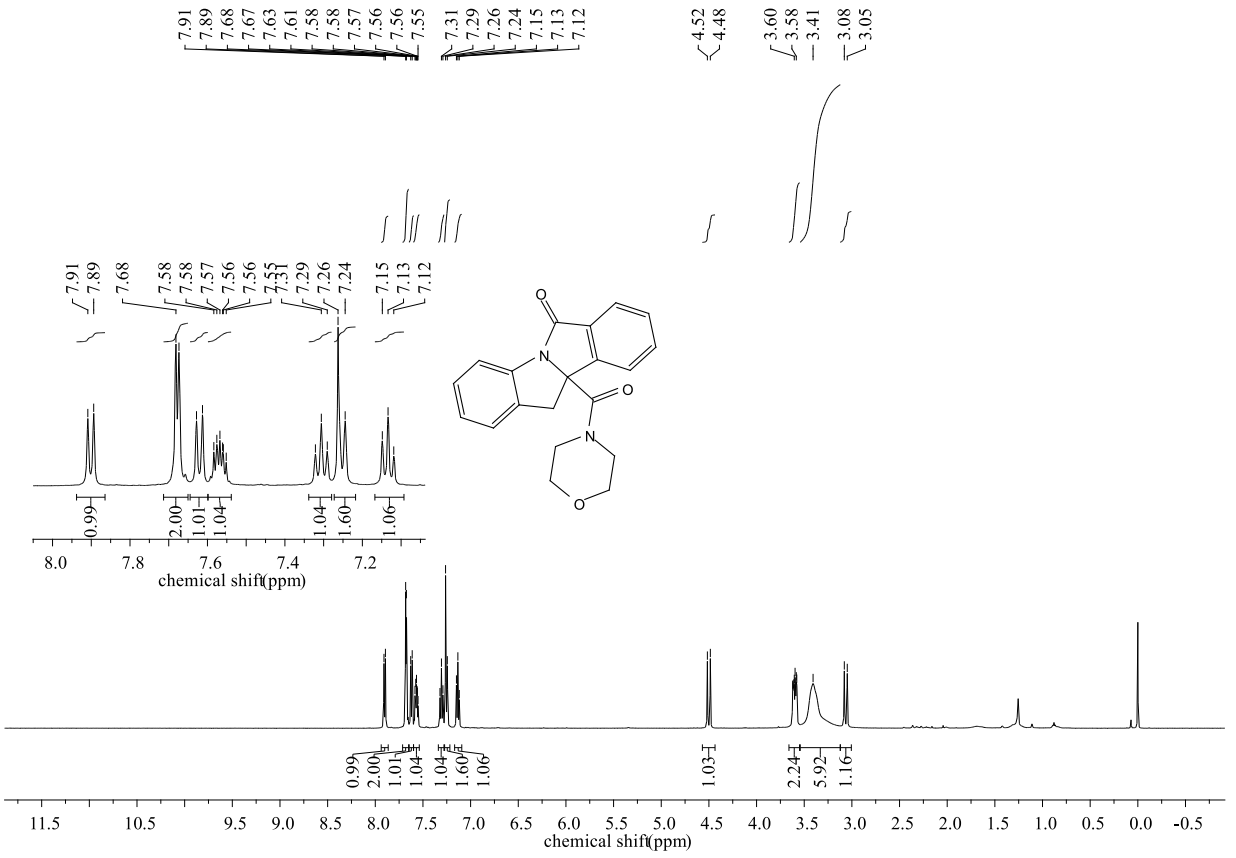
^{1}H NMR Spectra of compound **13** (500 MHz, $CDCl_3$)



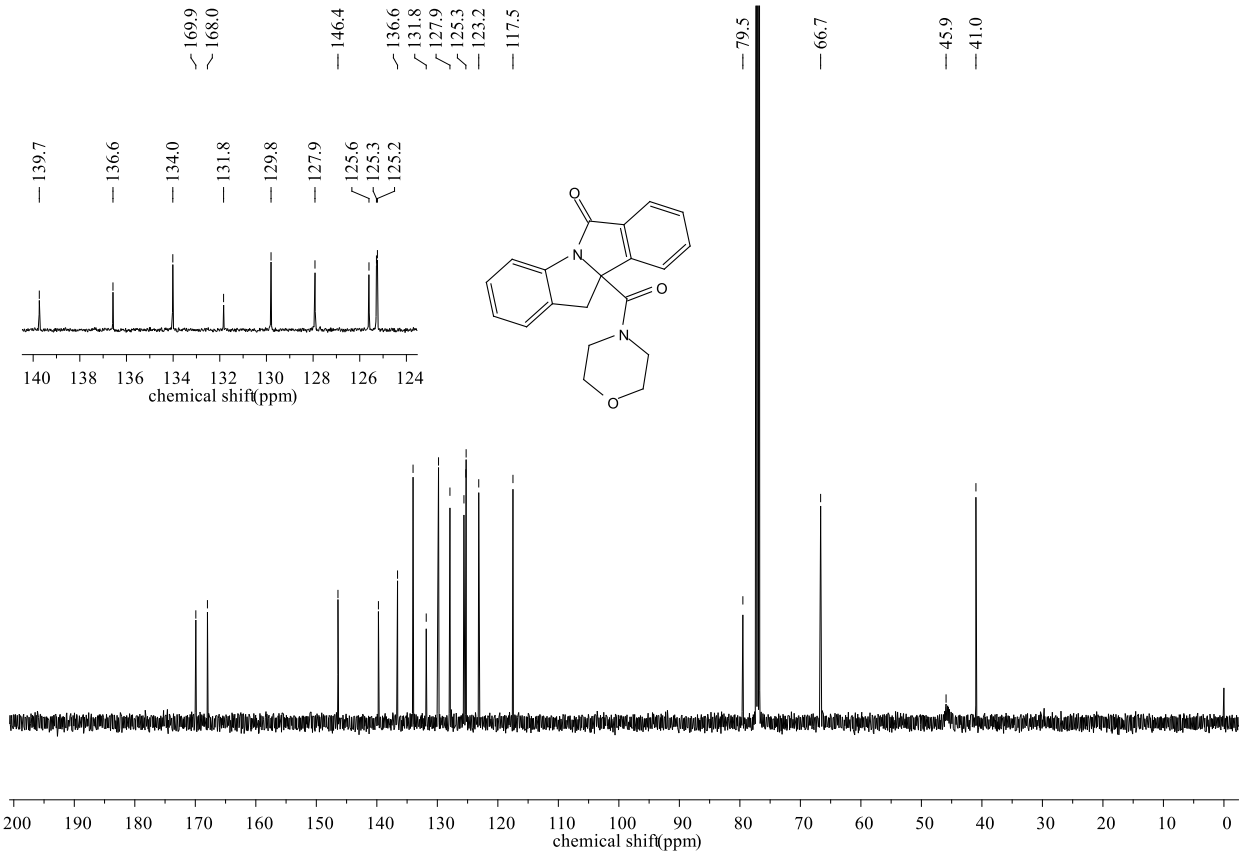
^{13}C NMR Spectra of compound **13** (125 MHz, $CDCl_3$)



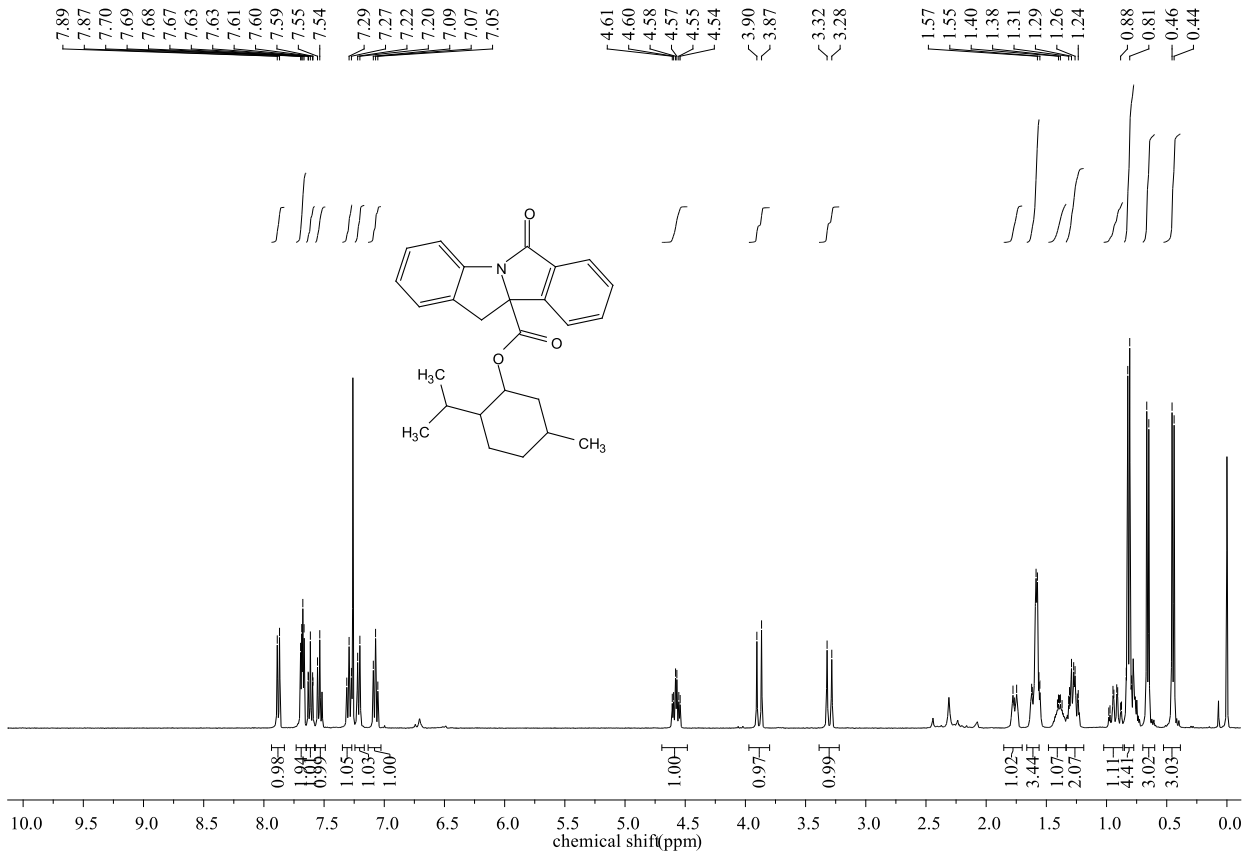
^{1}H NMR Spectra of compound **14** (500 MHz, $CDCl_3$)



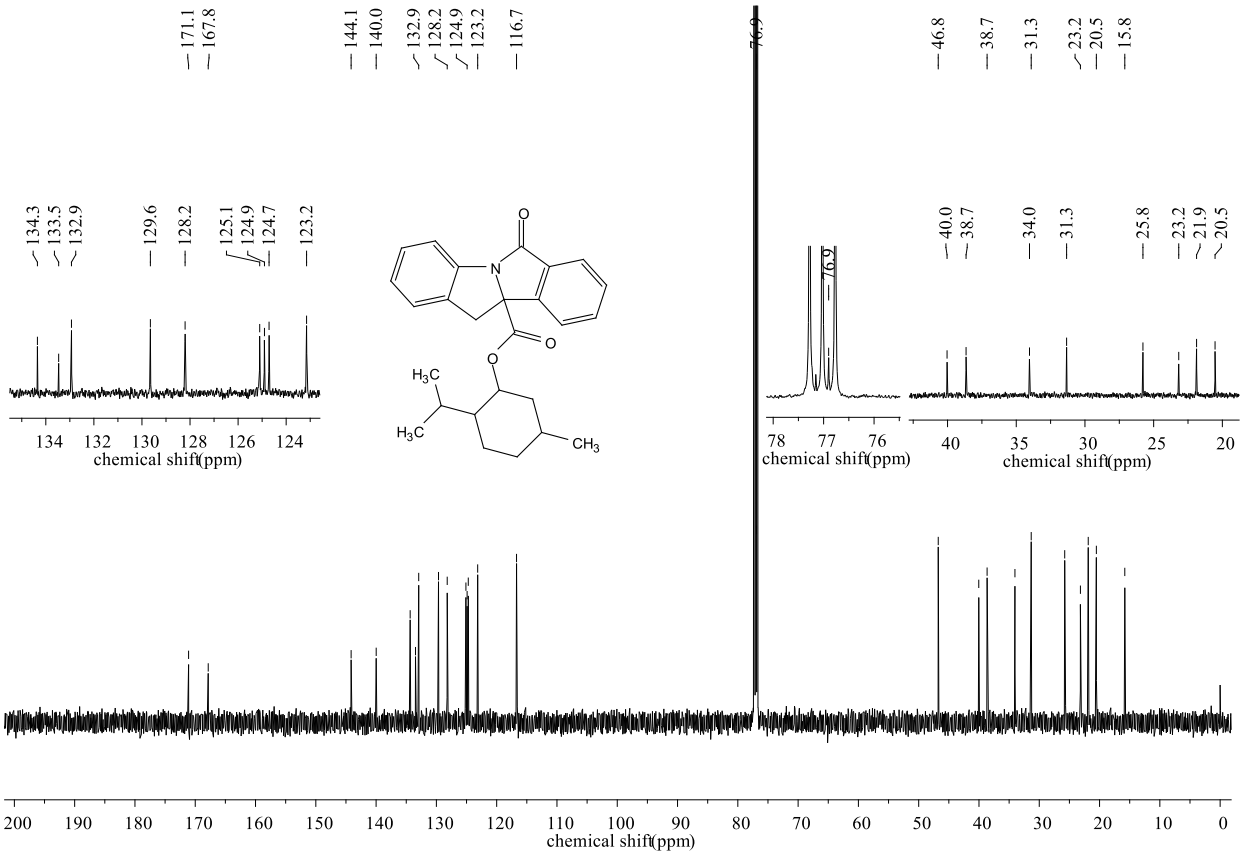
^{13}C NMR Spectra of compound **14** (125 MHz, $CDCl_3$)



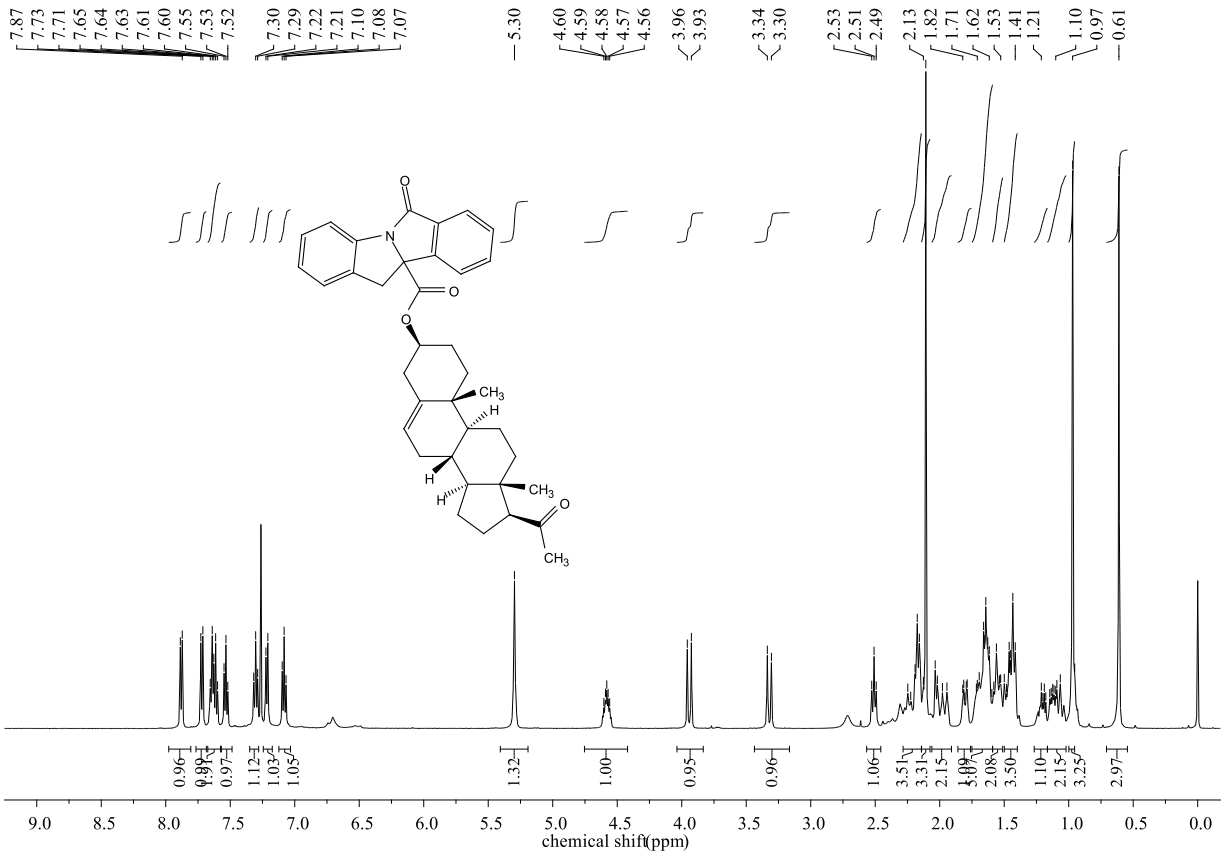
^{1}H NMR Spectra of compound **15** (400 MHz, $CDCl_3$)



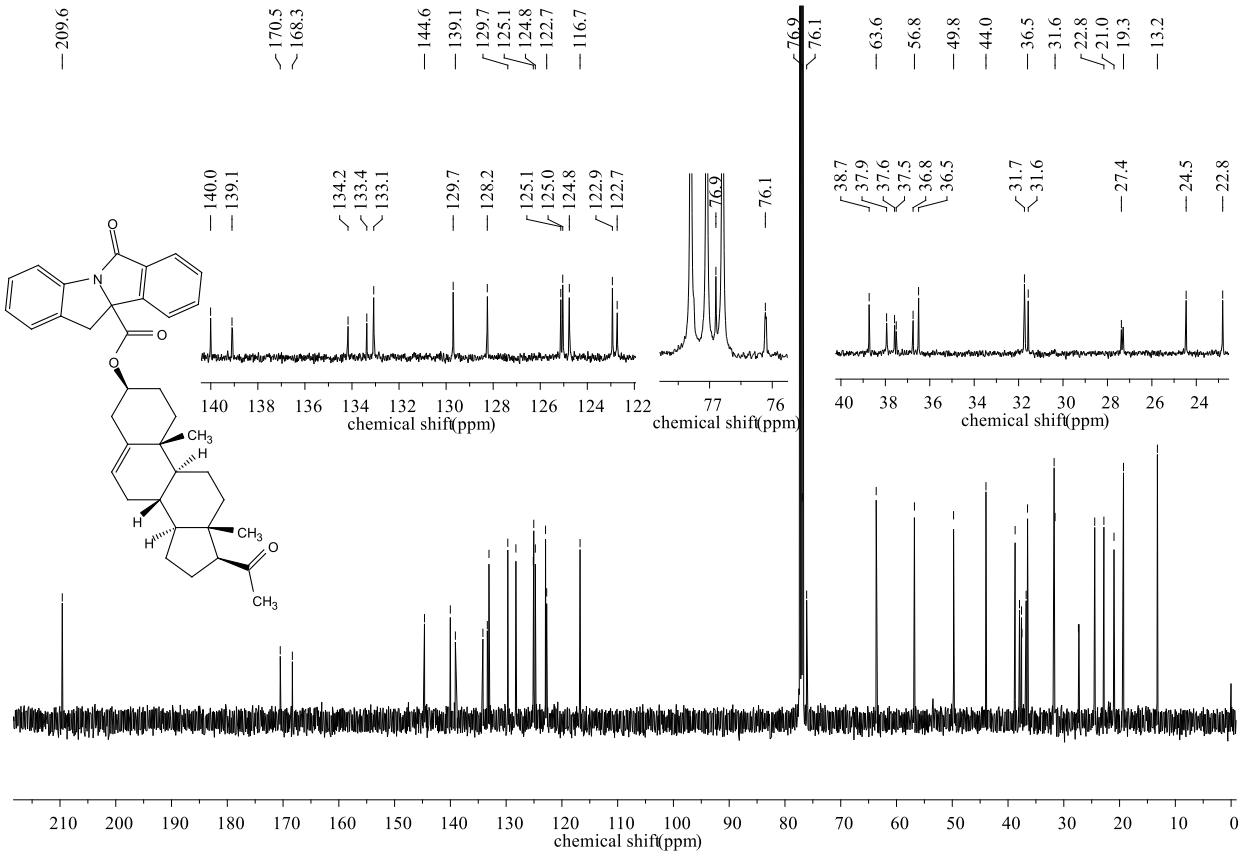
^{13}C NMR Spectra of compound **15** (100 MHz, $CDCl_3$)



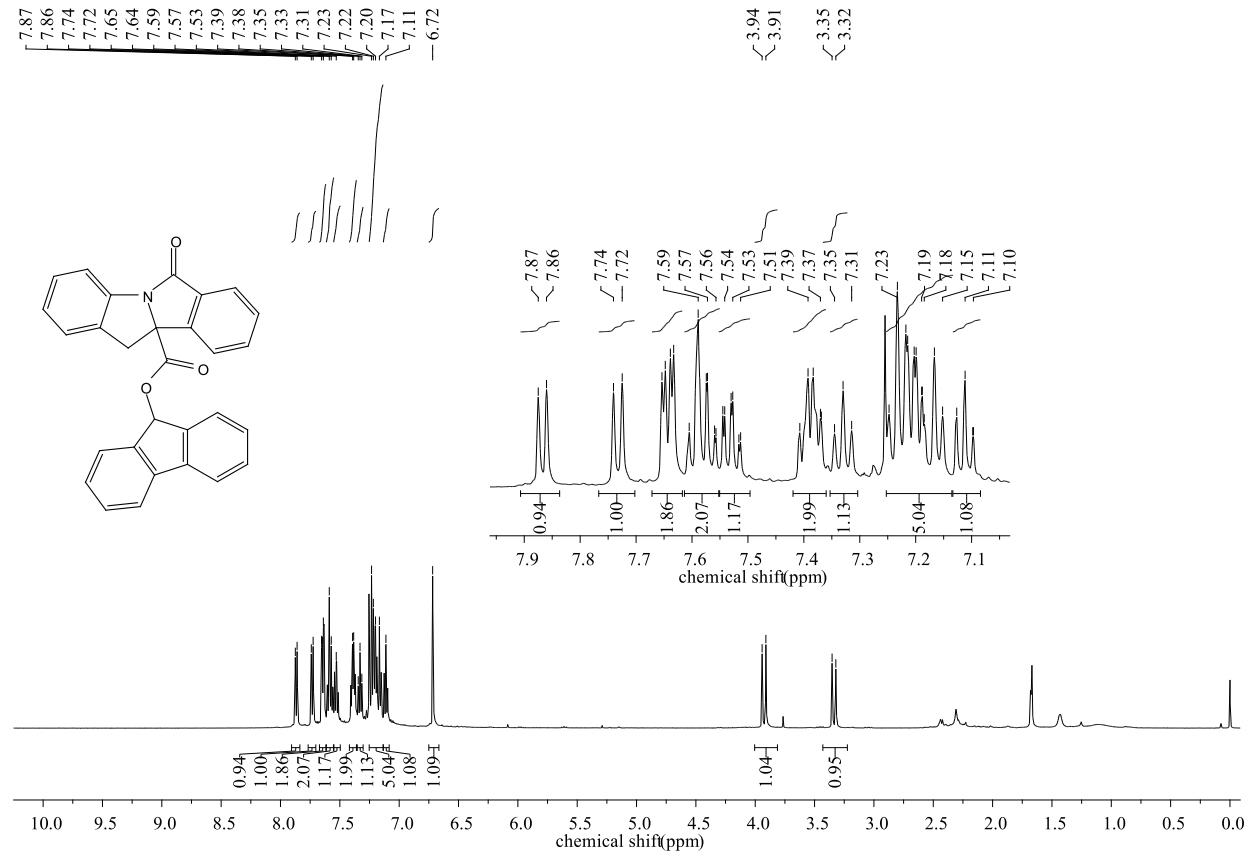
^{1}H NMR Spectra of compound **16** (500 MHz, $CDCl_3$)



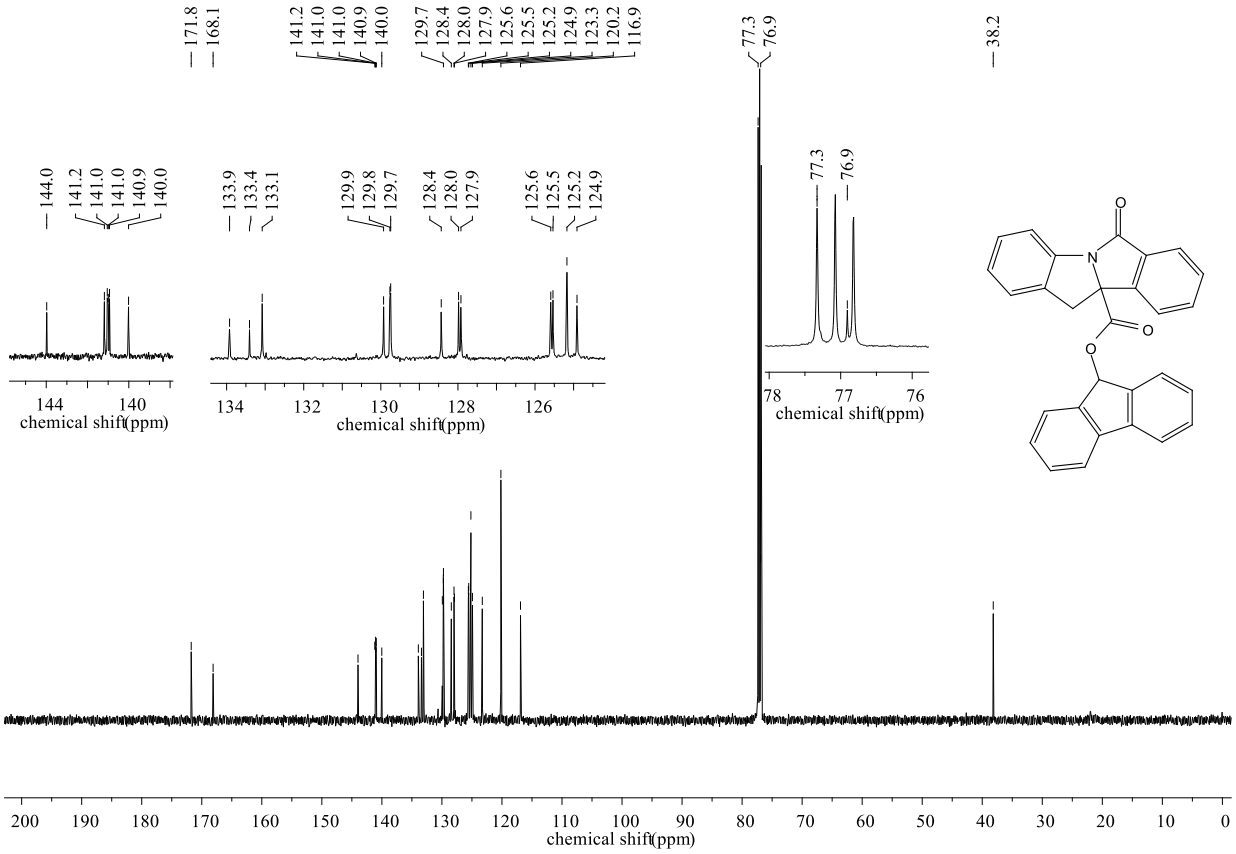
^{13}C NMR Spectra of compound **16** (125 MHz, $CDCl_3$)



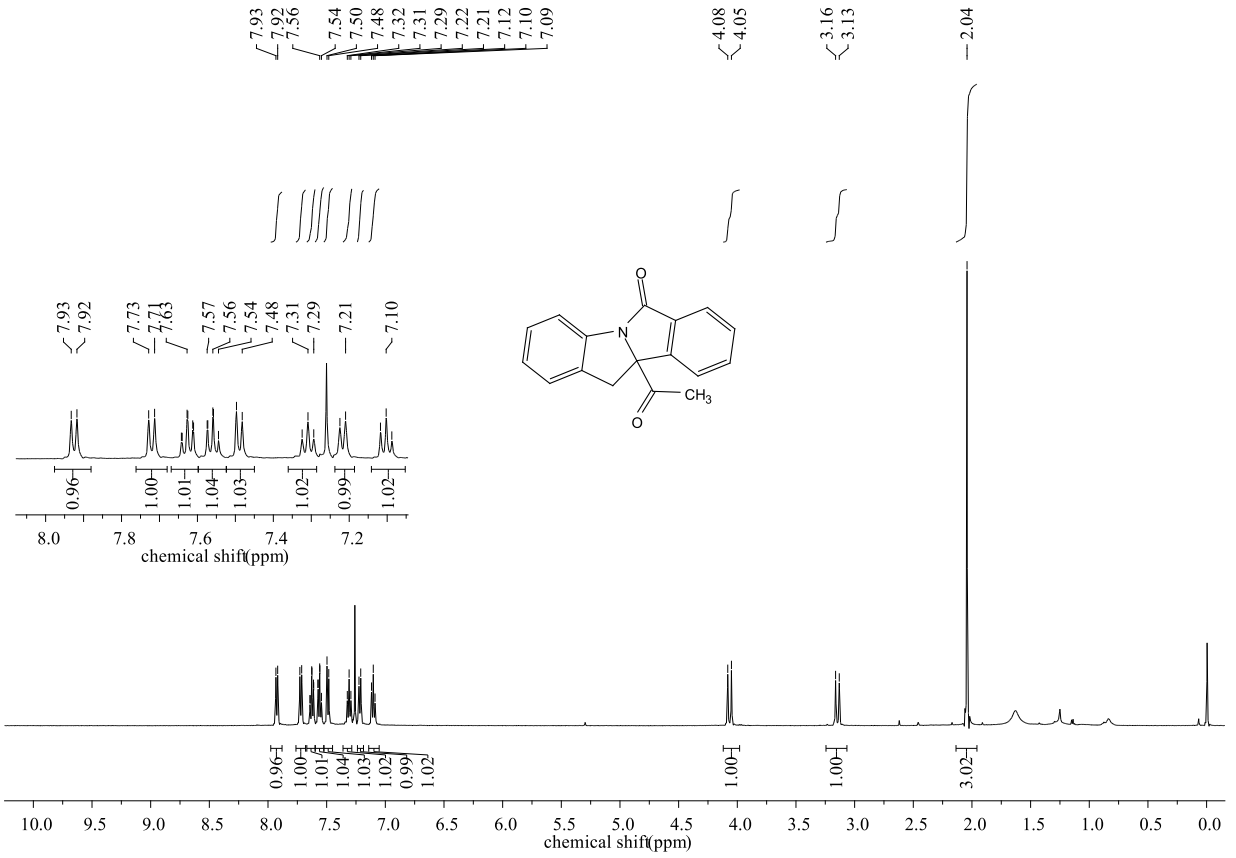
^{1}H NMR Spectra of compound **17**(500 MHz, $CDCl_3$)



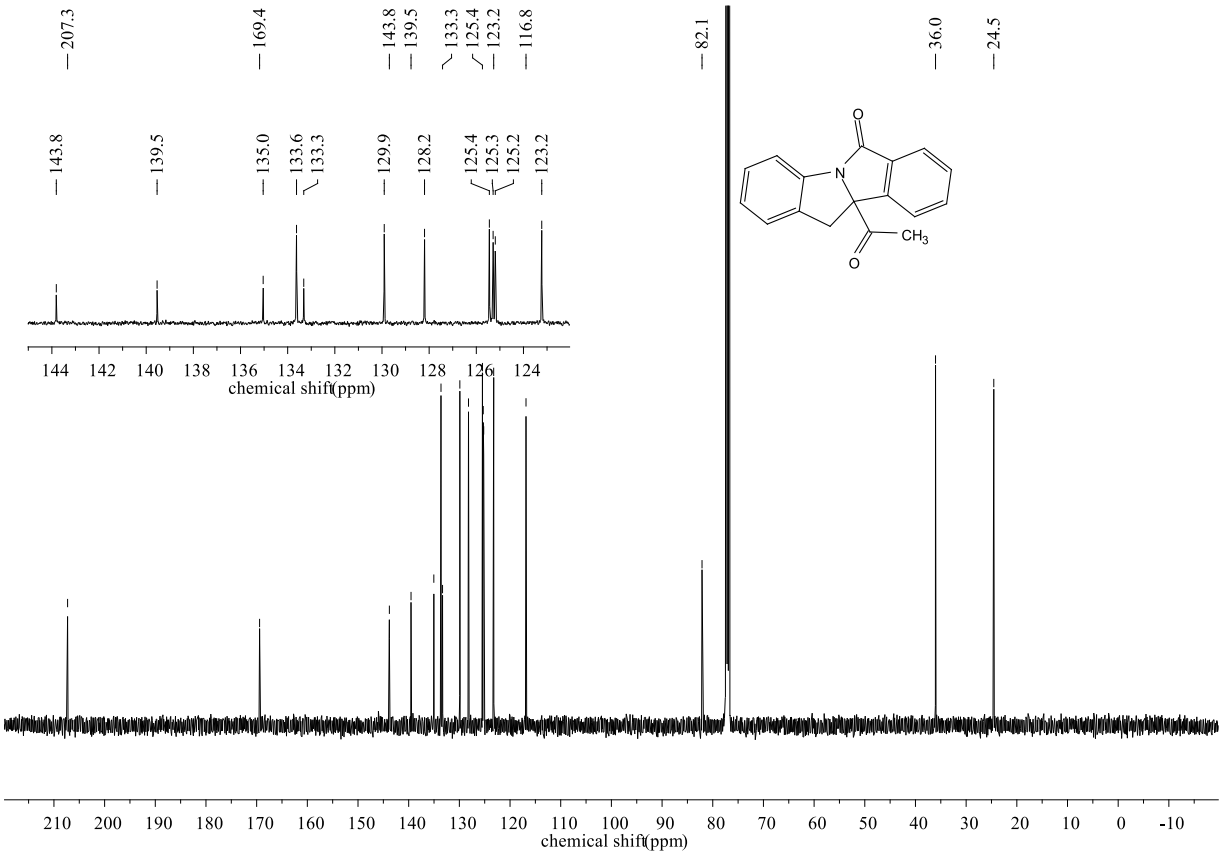
^{13}C NMR Spectra of compound **17** (125 MHz, $CDCl_3$)



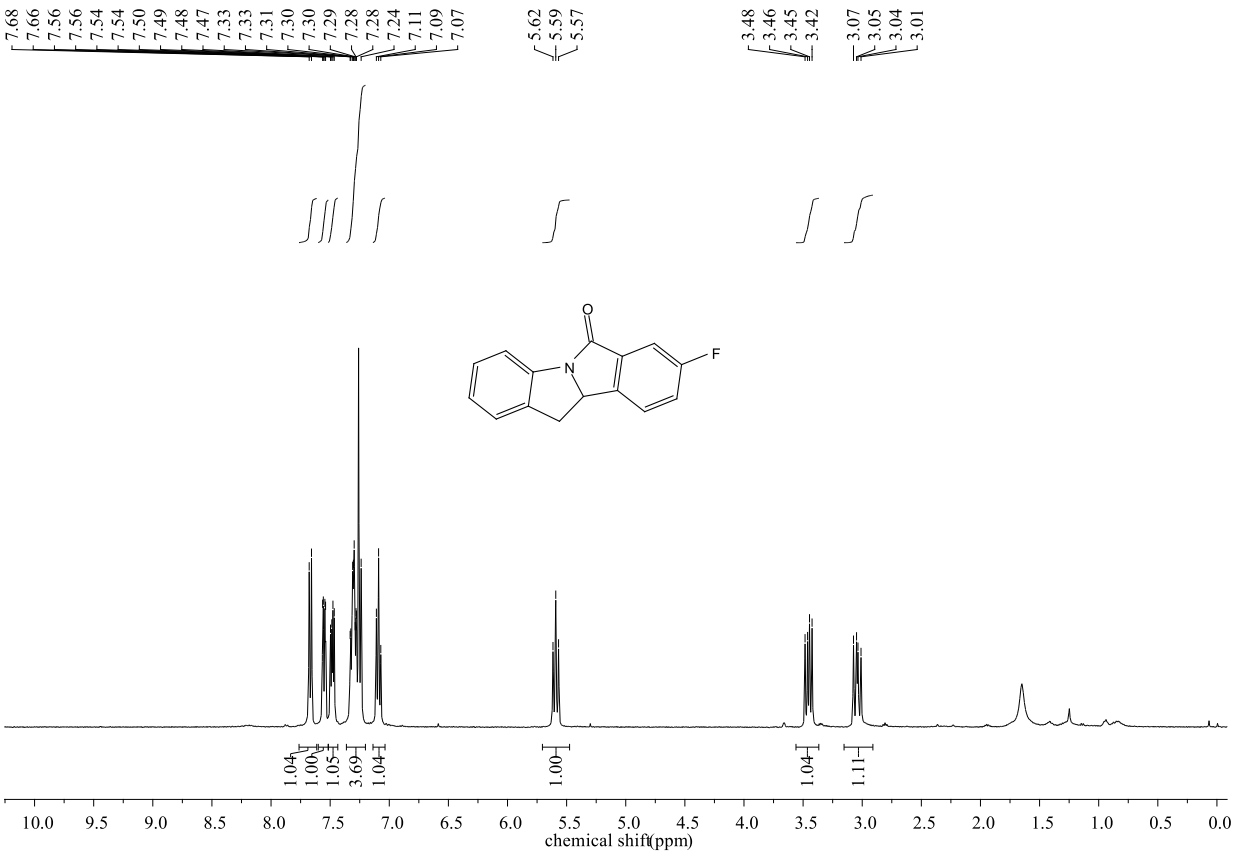
^{1}H NMR Spectra of compound **18** (500 MHz, $CDCl_3$)



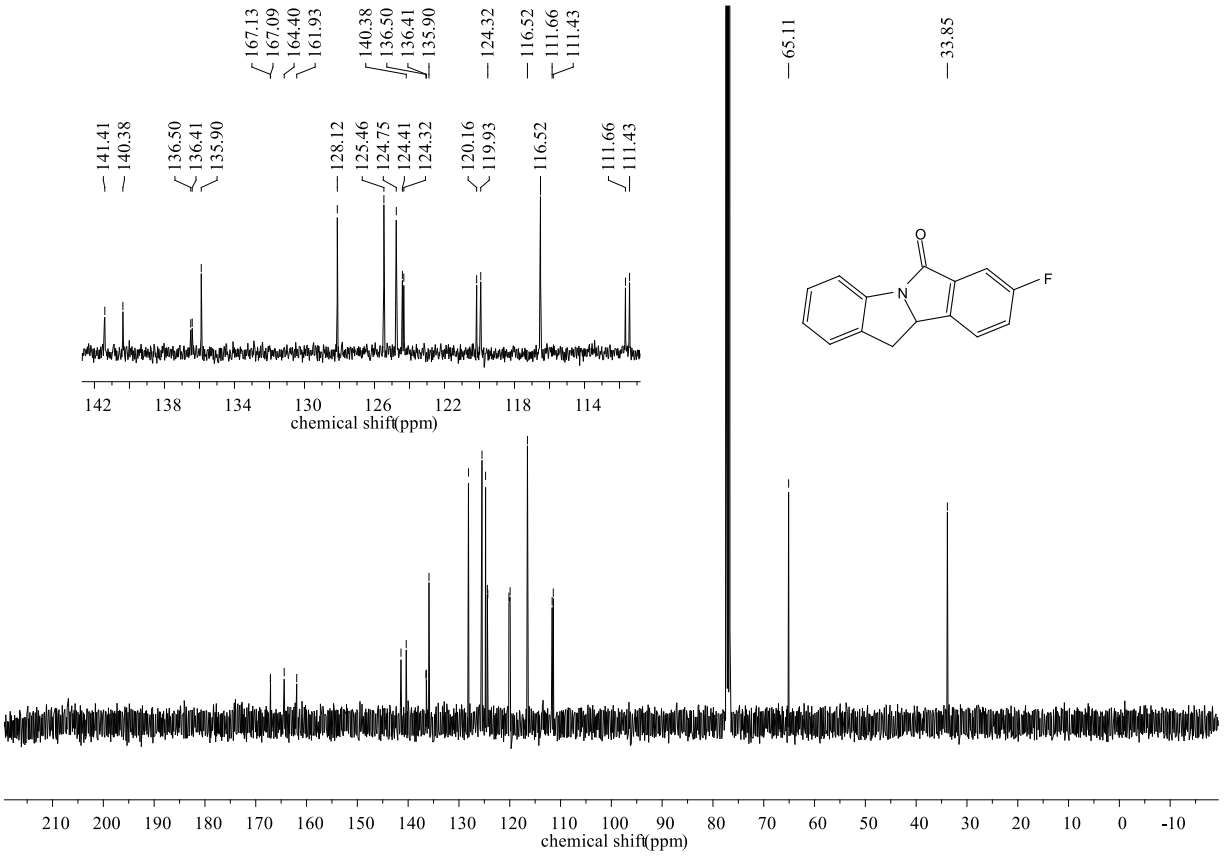
^{13}C NMR Spectra of compound **18** (125 MHz, $CDCl_3$)



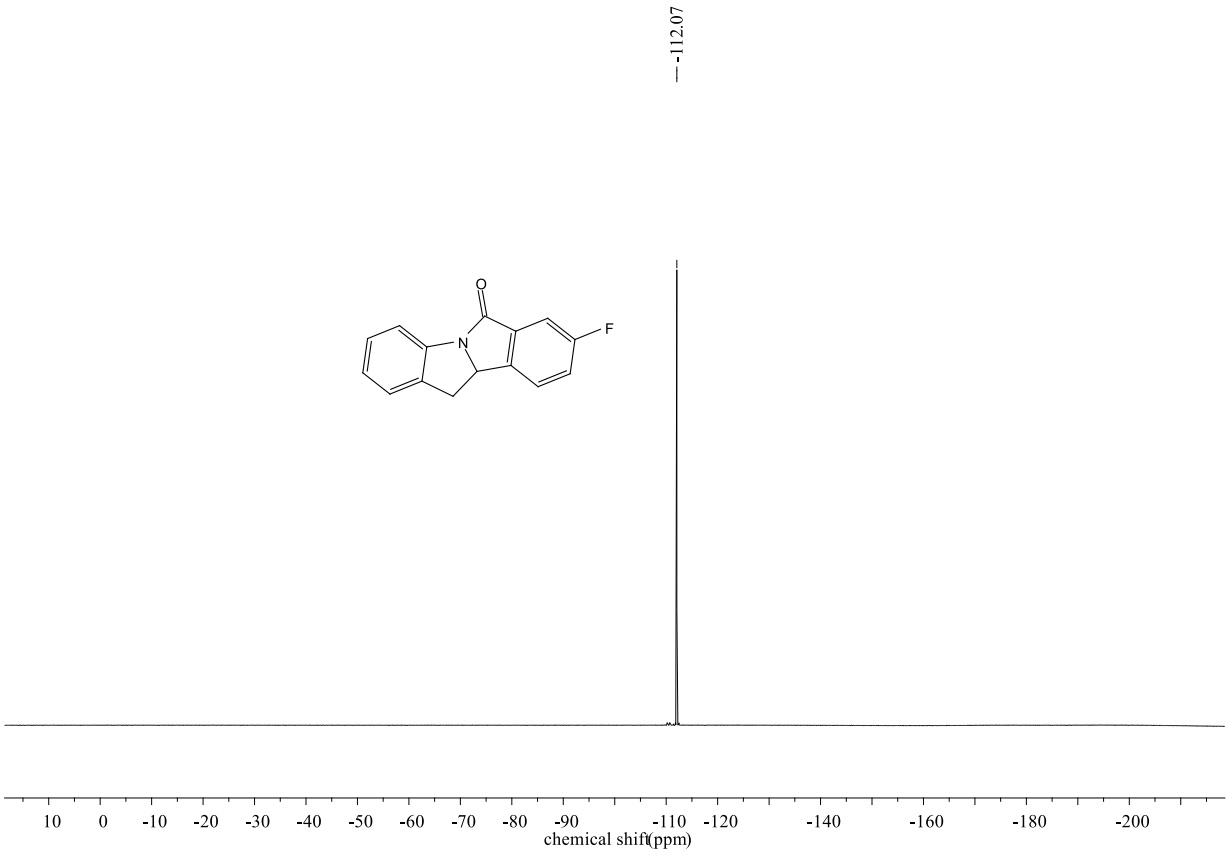
^{1}H NMR Spectra of compound **20** (400 MHz, $CDCl_3$)



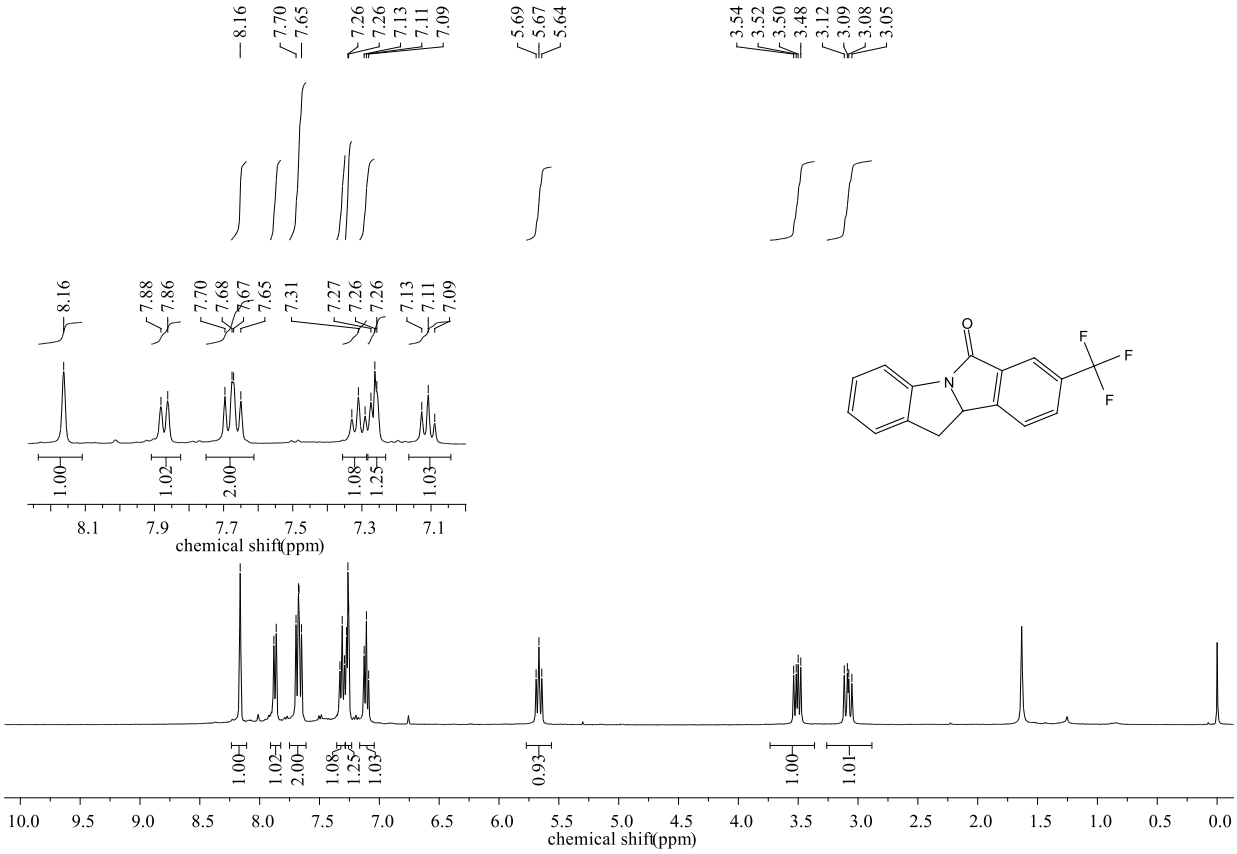
^{13}C NMR Spectra of compound **20** (100 MHz, $CDCl_3$)



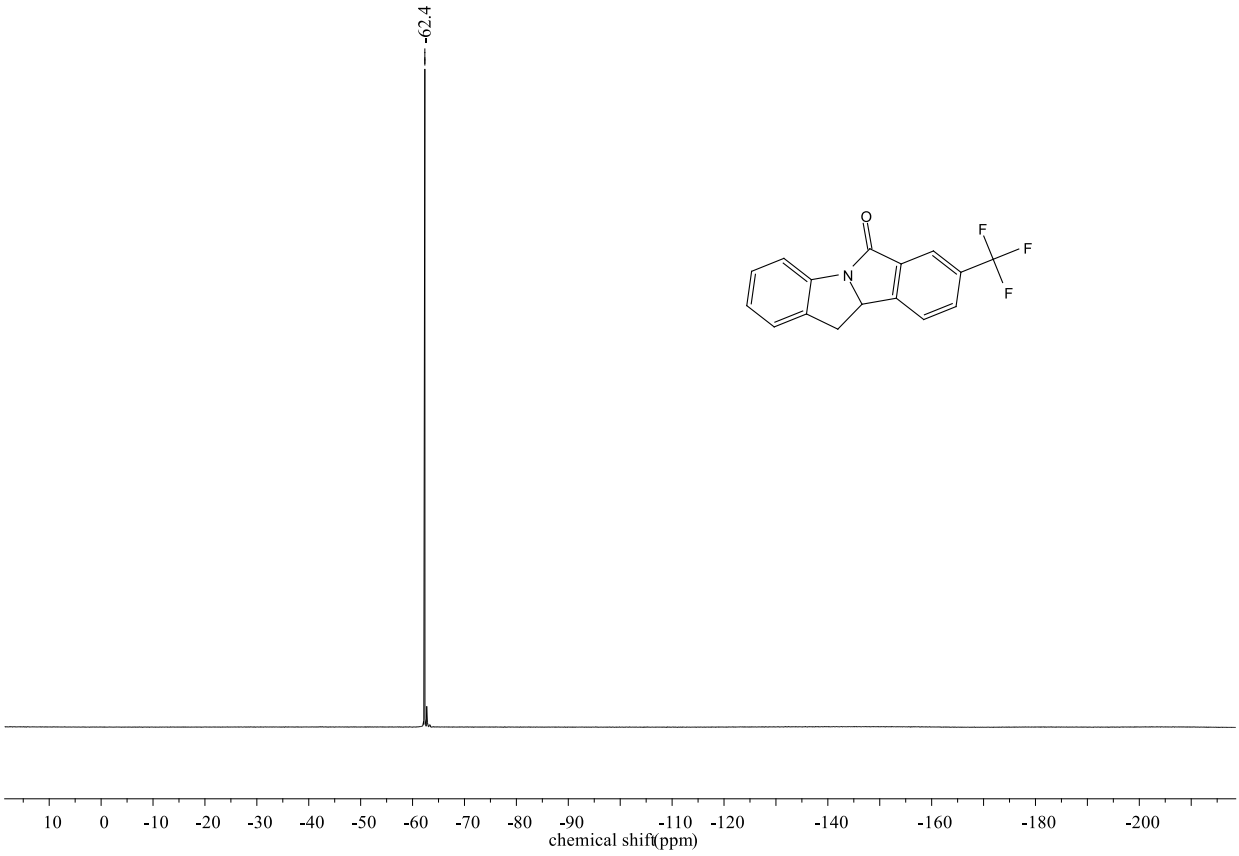
^{19}F NMR Spectra of compound **20** (300 MHz, $CDCl_3$)



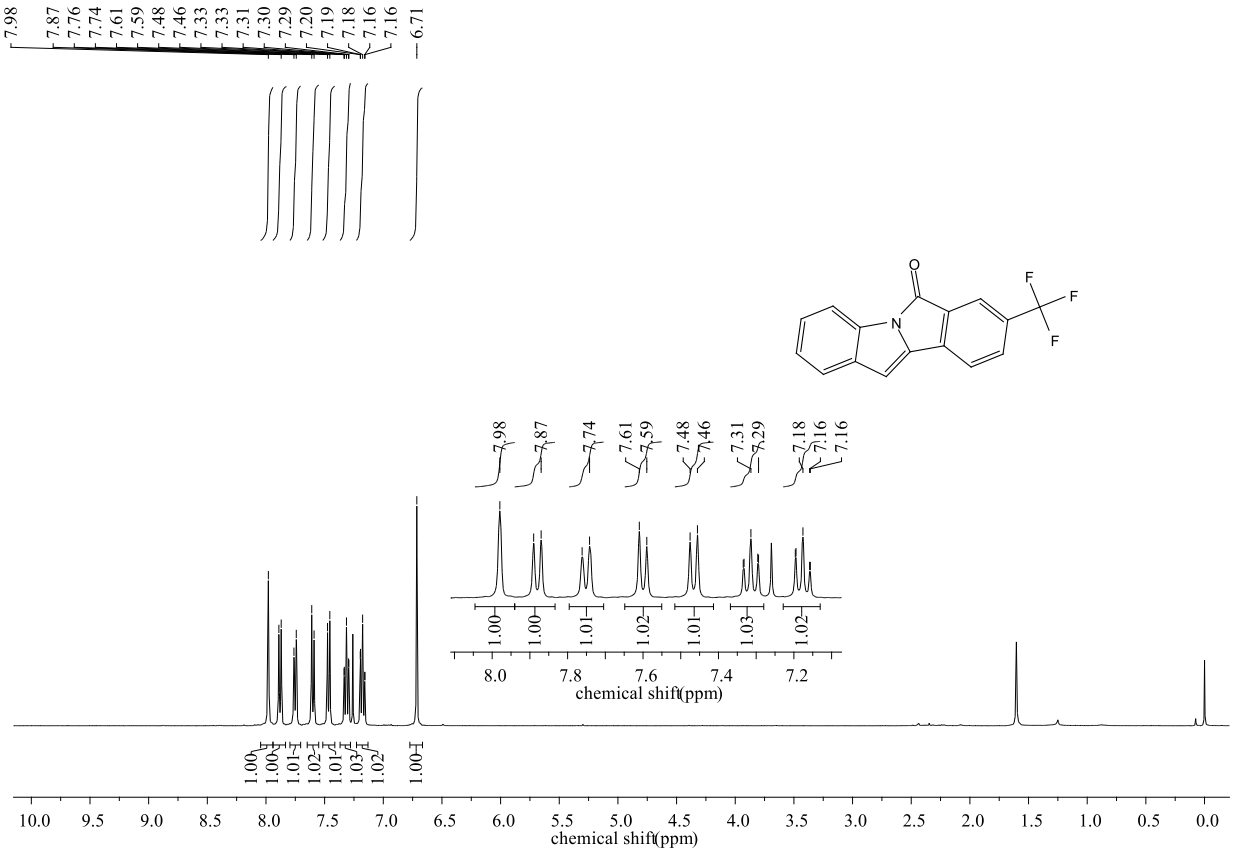
^{1}H NMR Spectra of compound **21** (400 MHz, $CDCl_3$)



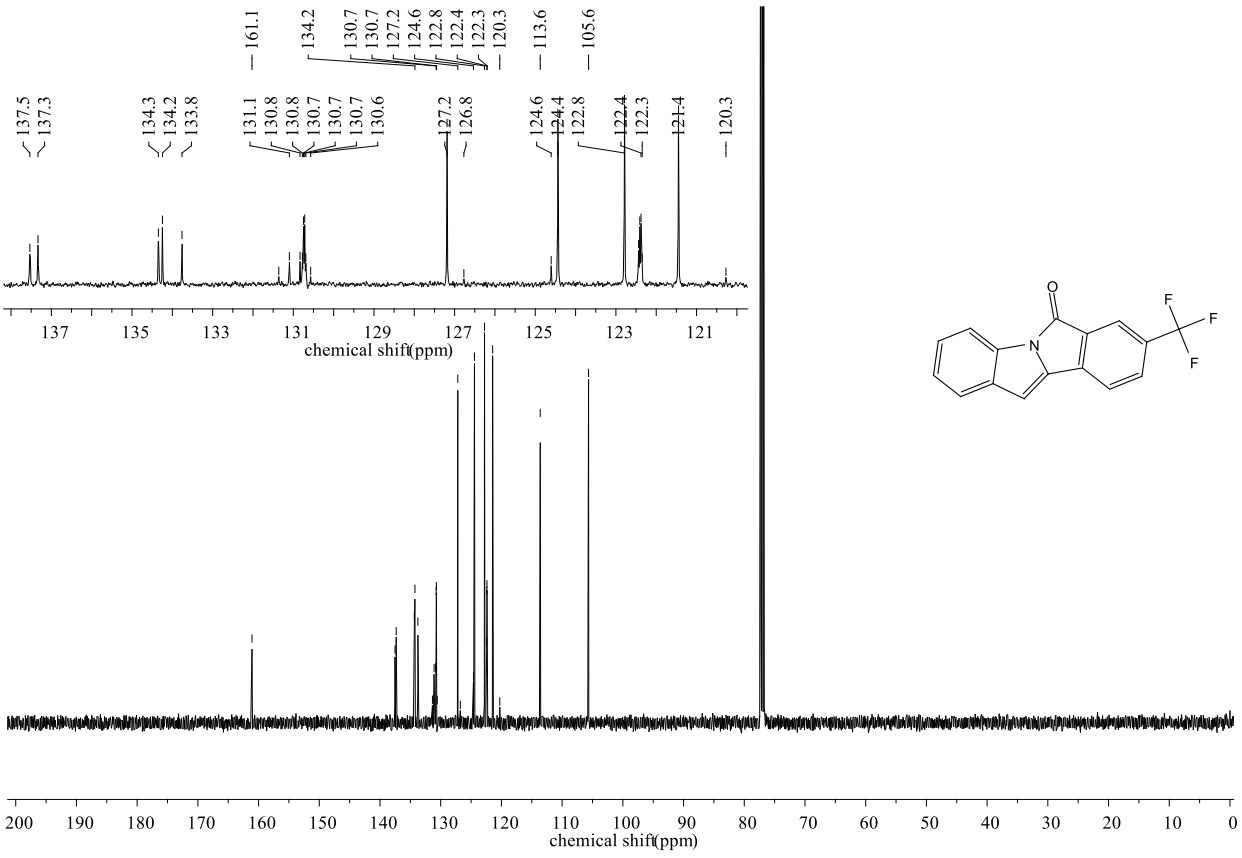
^{19}F NMR Spectra of compound **21** (300 MHz, $CDCl_3$)



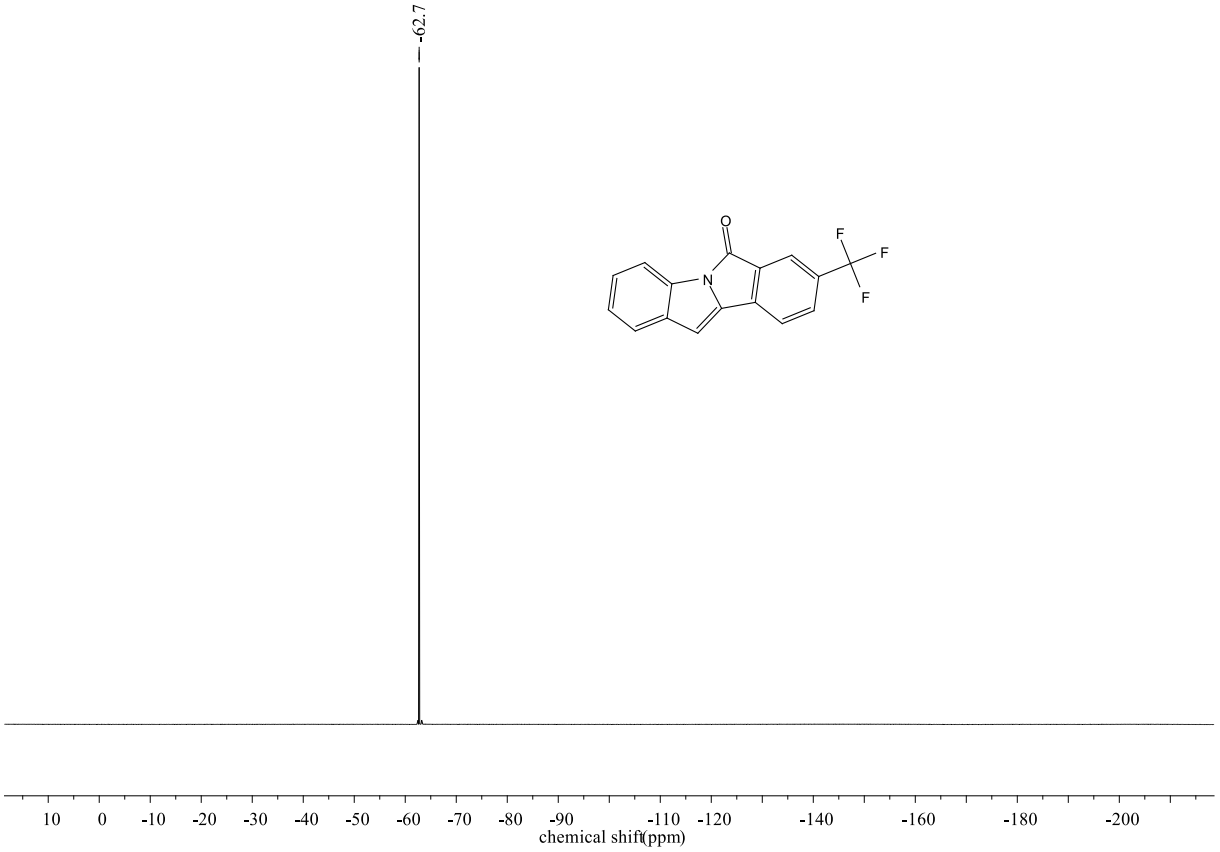
^{1}H NMR Spectra of compound **21A** (400 MHz, $CDCl_3$)



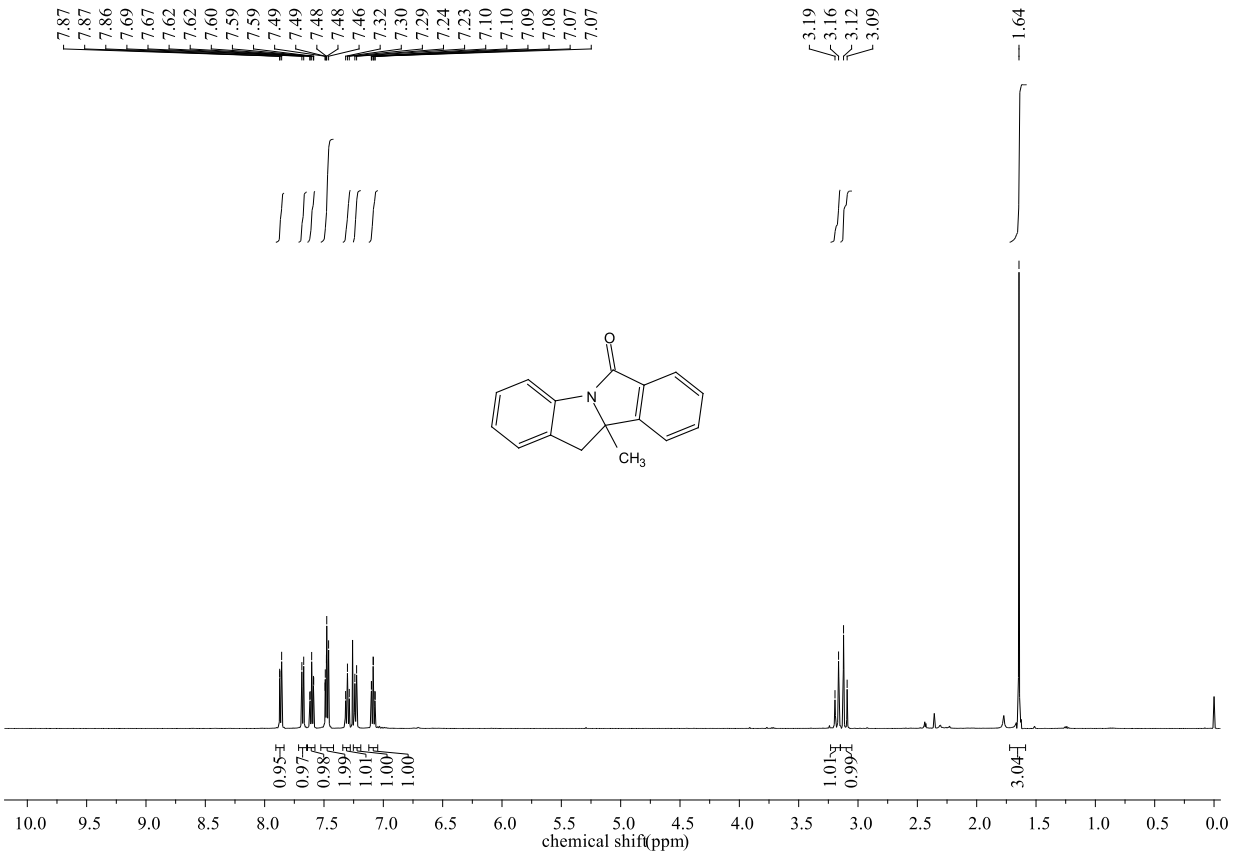
^{13}C NMR Spectra of compound **21A** (125 MHz, $CDCl_3$)



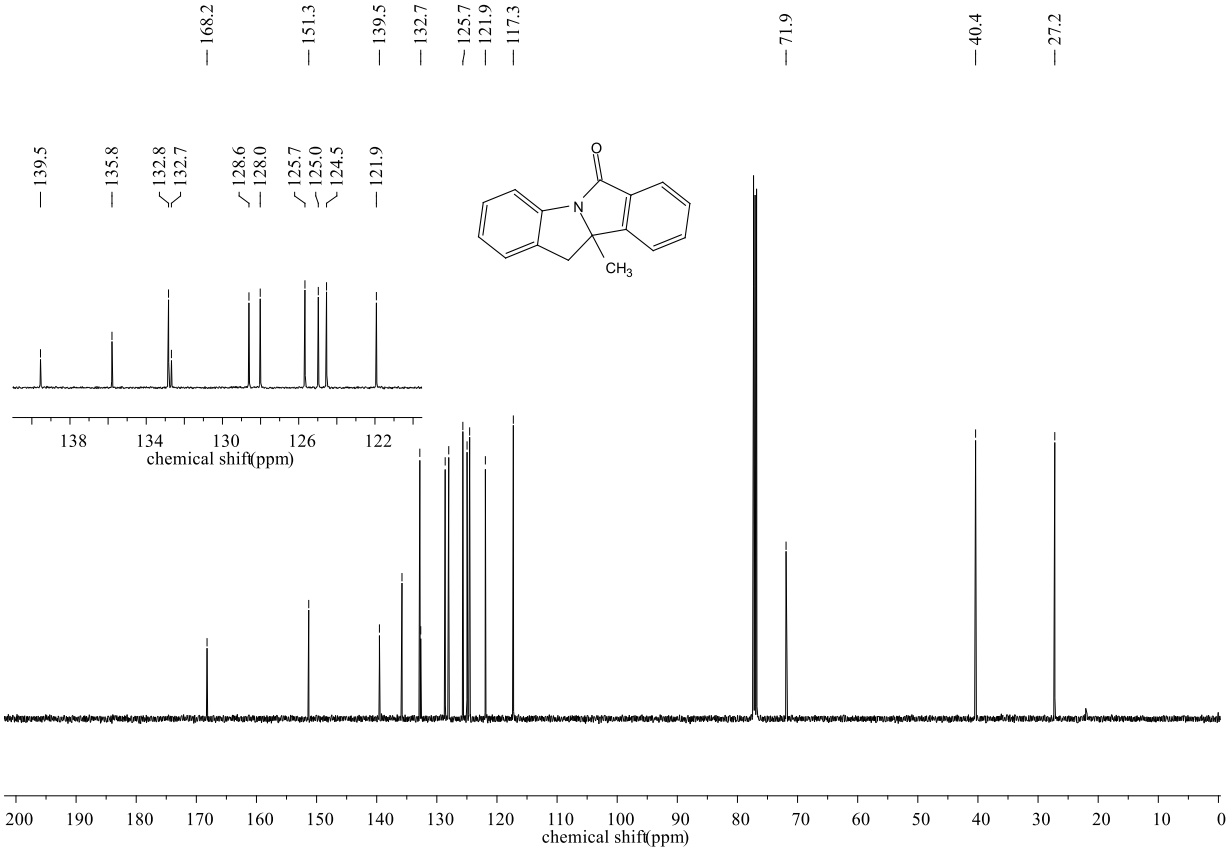
^{19}F NMR Spectra of compound **21A** (300 MHz, $CDCl_3$)



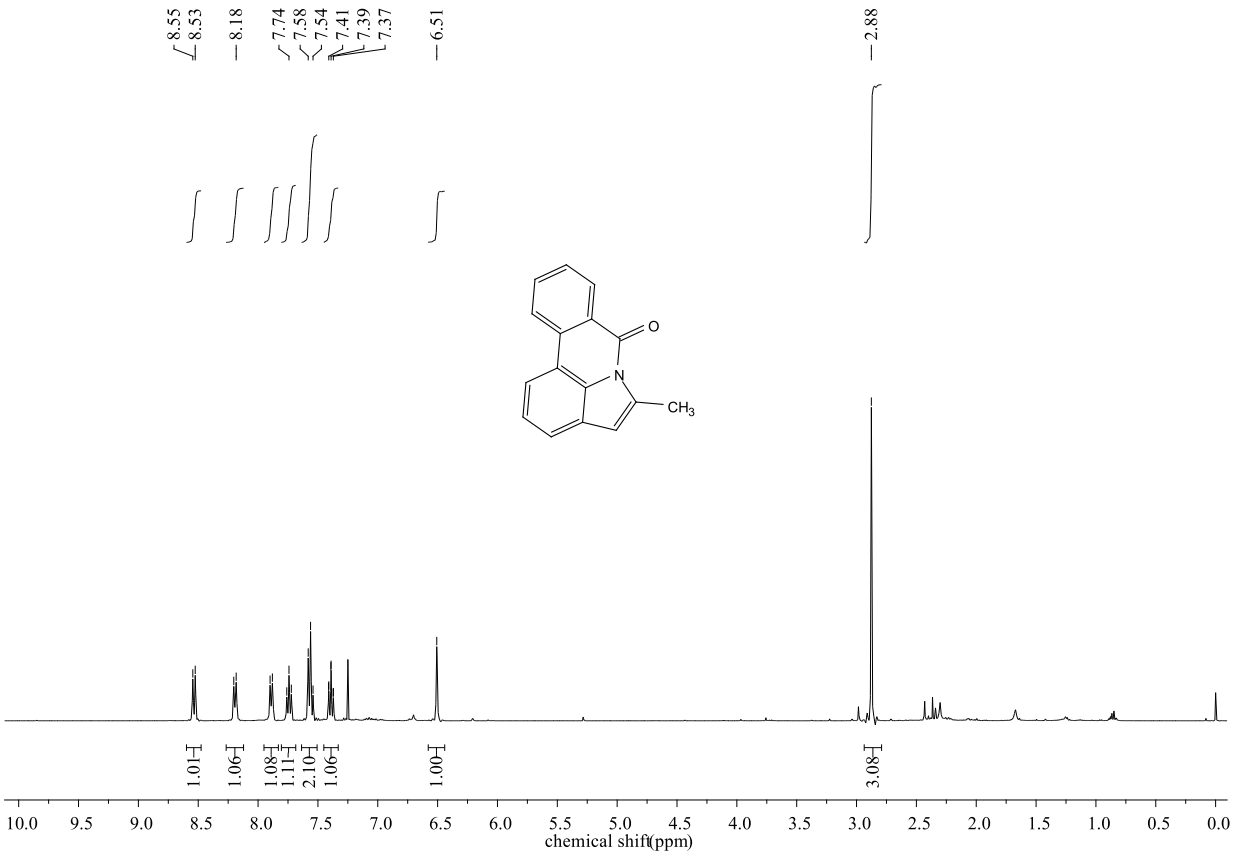
^{1}H NMR Spectra of compound **22** (500 MHz, $CDCl_3$)



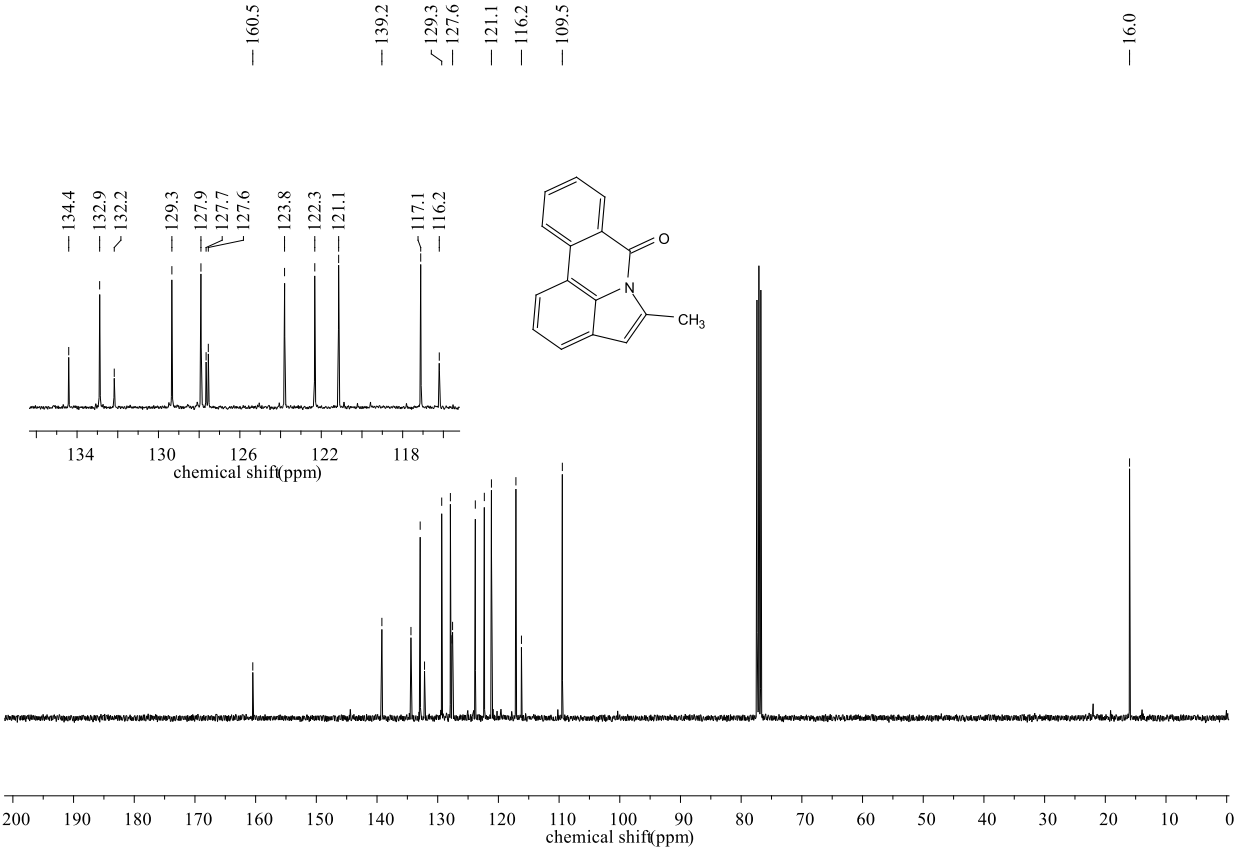
^{13}C NMR Spectra of compound **22** (125 MHz, $CDCl_3$)



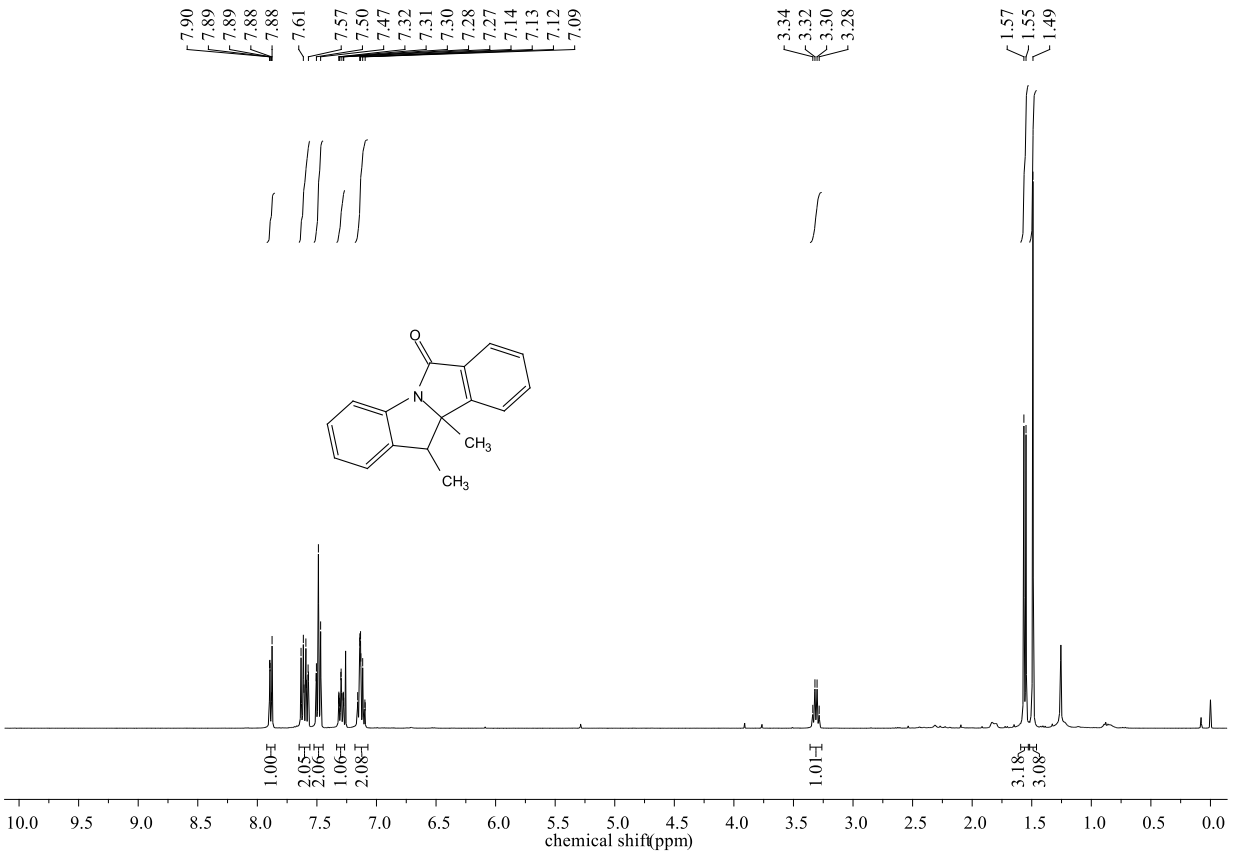
^{1}H NMR Spectra of compound **22A** (400 MHz, $CDCl_3$)



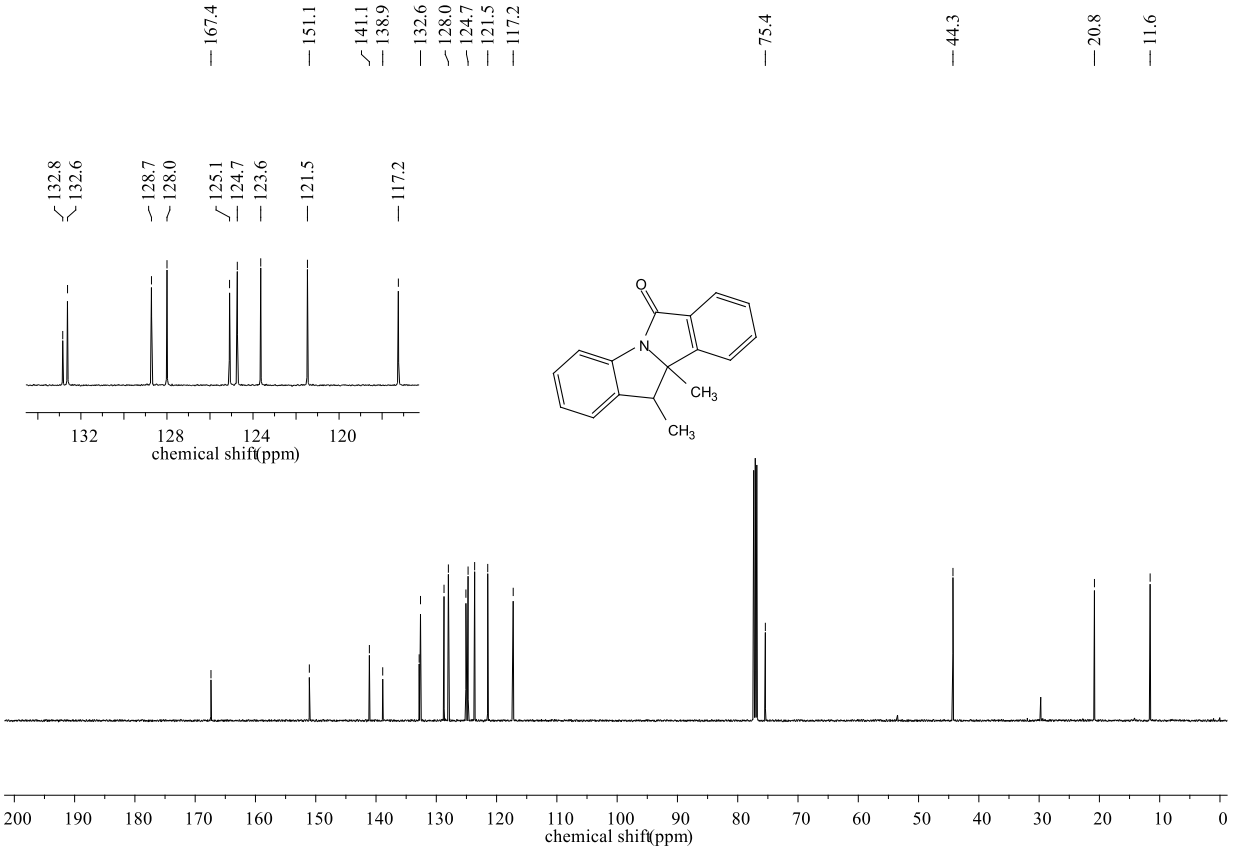
^{13}C NMR Spectra of compound **22A** (100 MHz, $CDCl_3$)



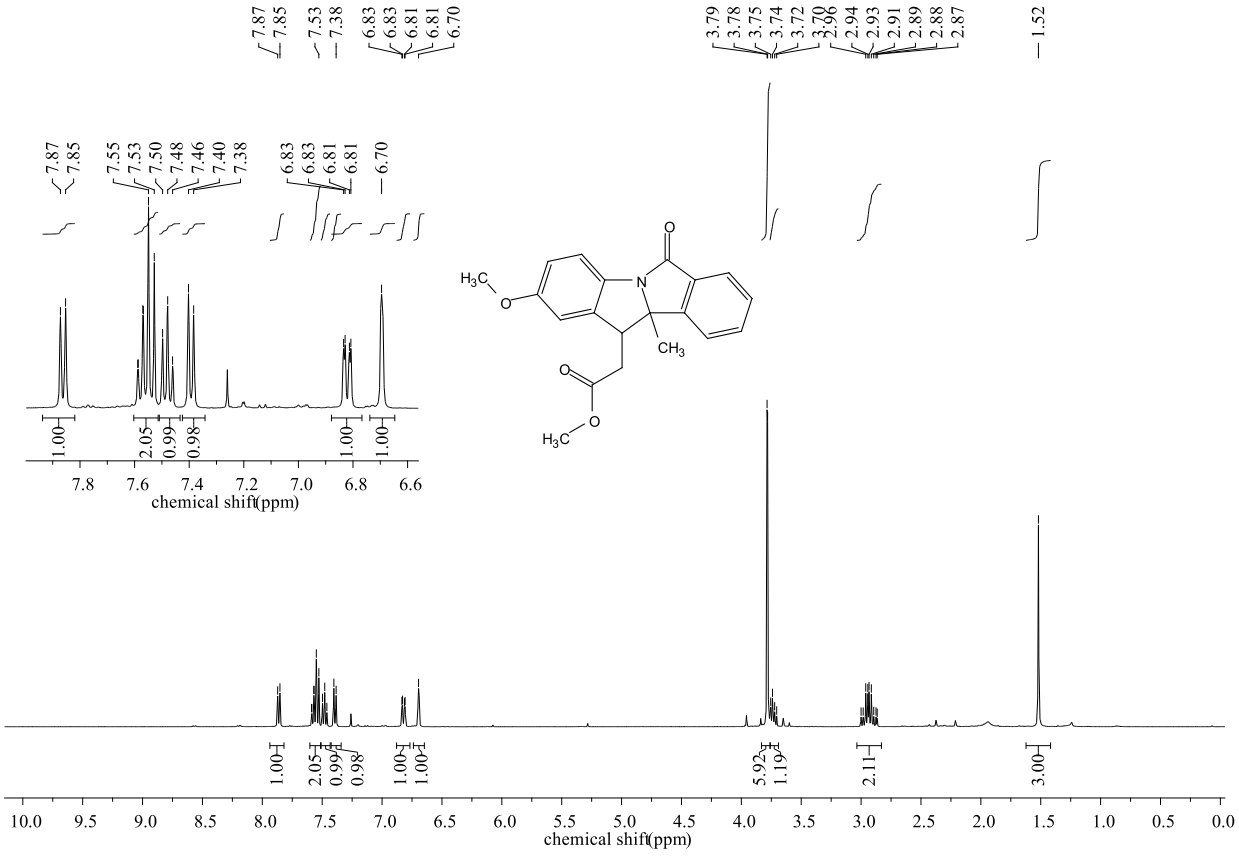
^{1}H NMR Spectra of compound **23** (500 MHz, $CDCl_3$)



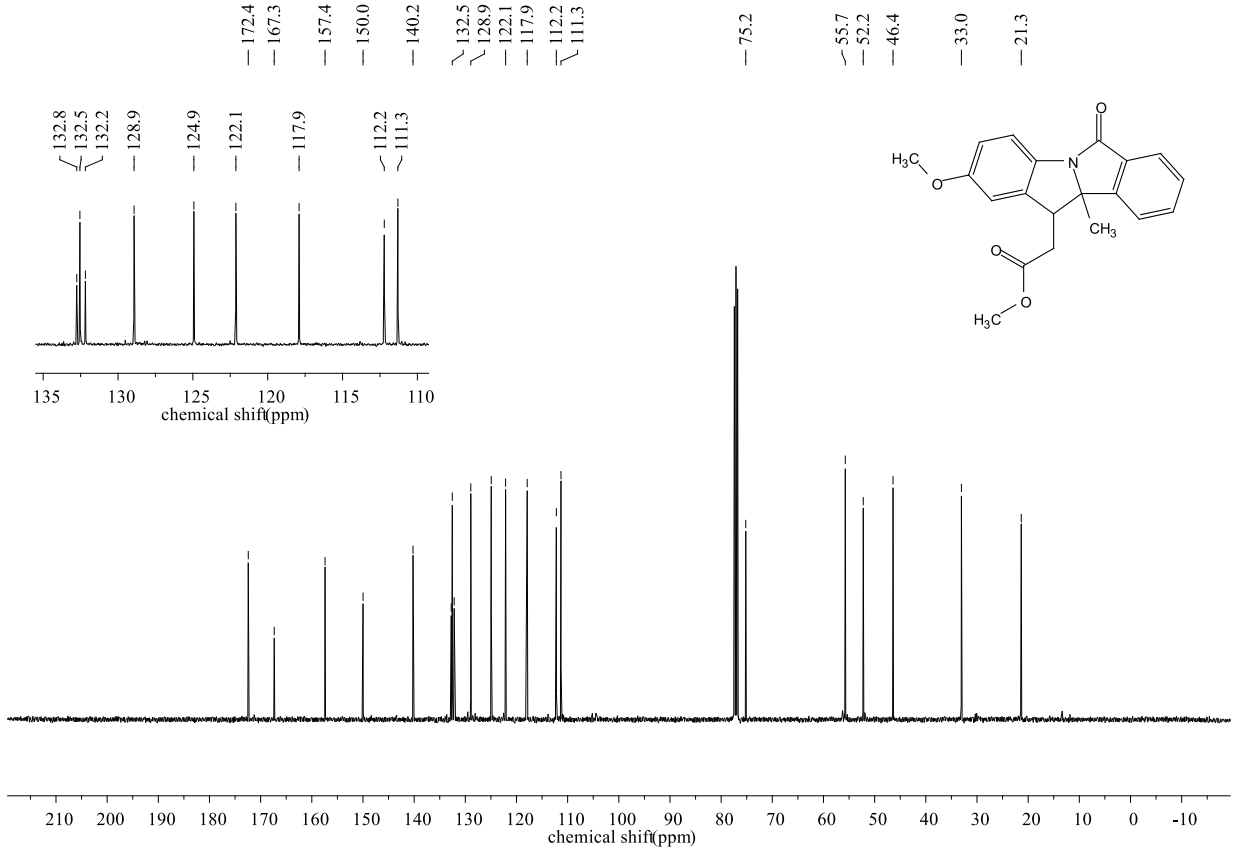
^{13}C NMR Spectra of compound **23** (125 MHz, $CDCl_3$)



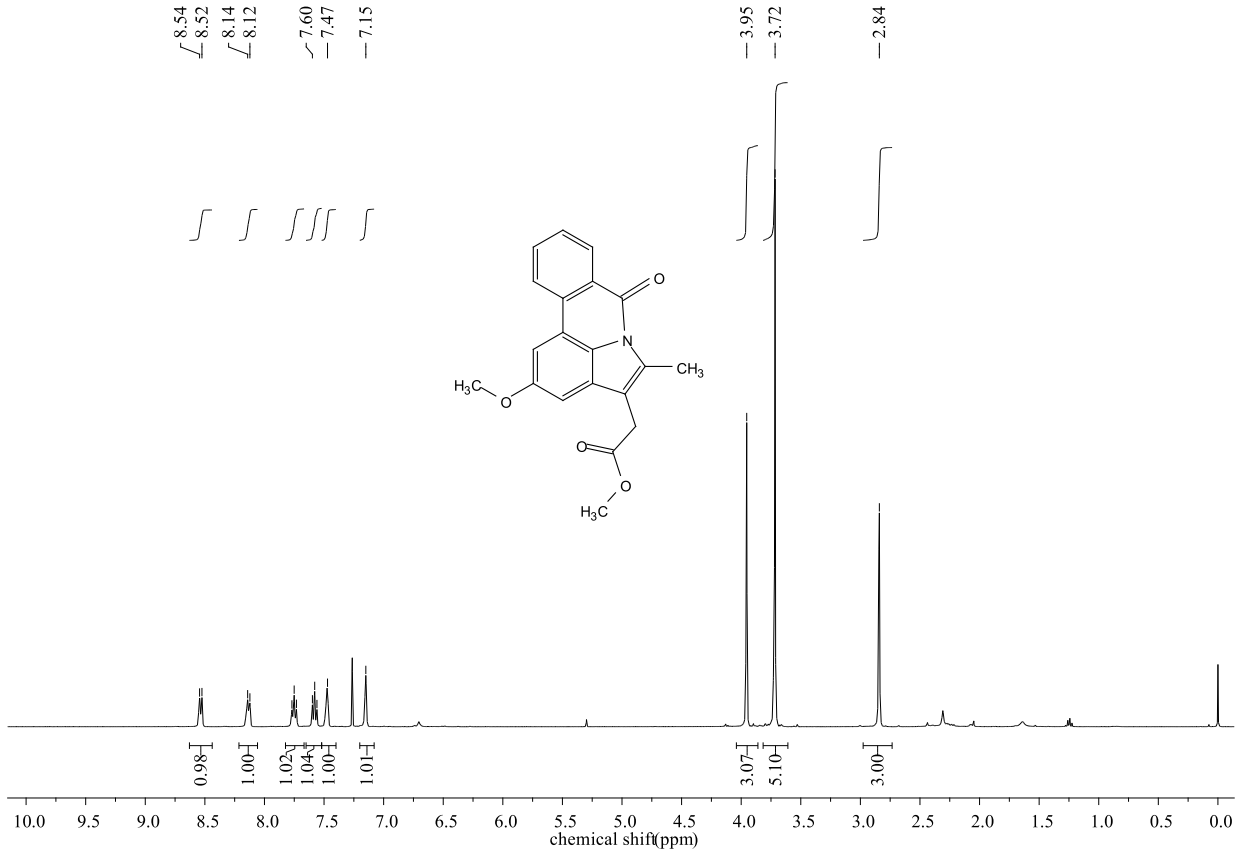
^{1}H NMR Spectra of compound **24** (400 MHz, $CDCl_3$)



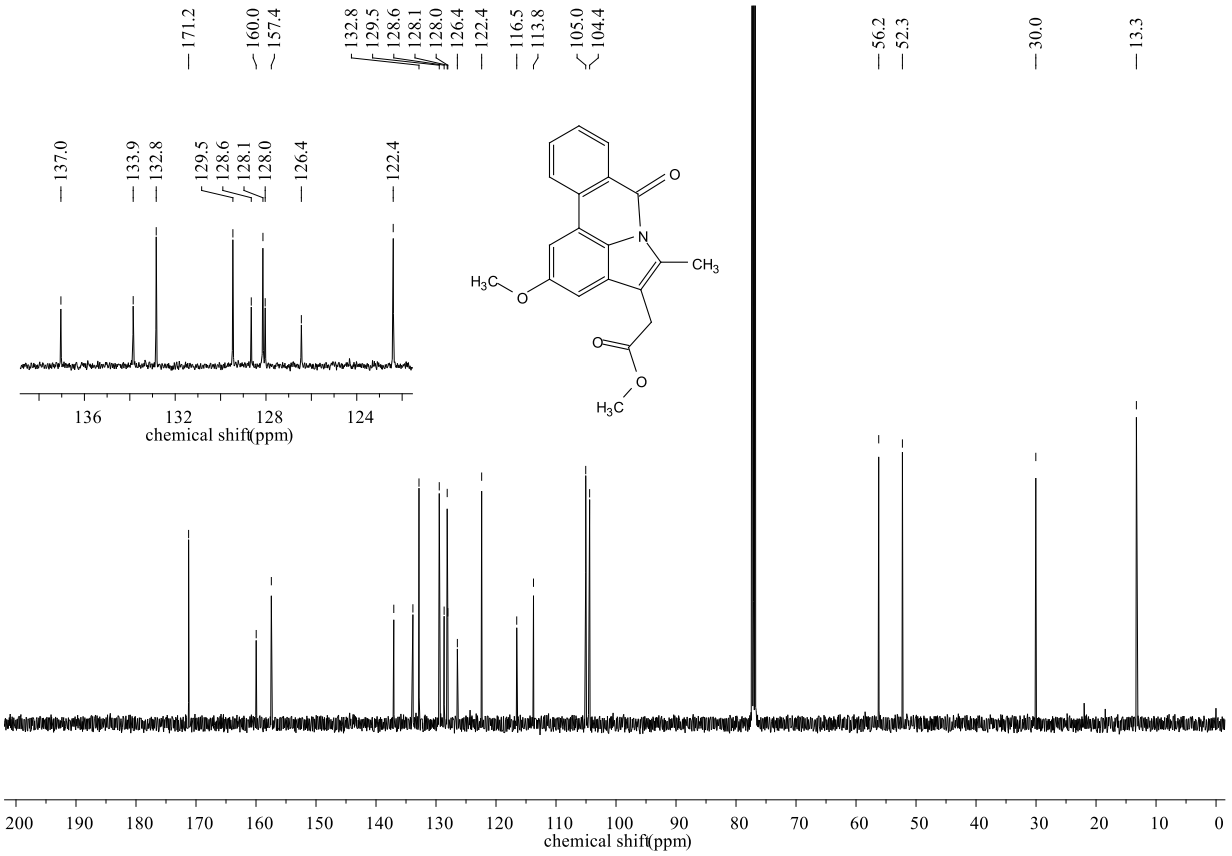
^{13}C NMR Spectra of compound **24** (100 MHz, $CDCl_3$)



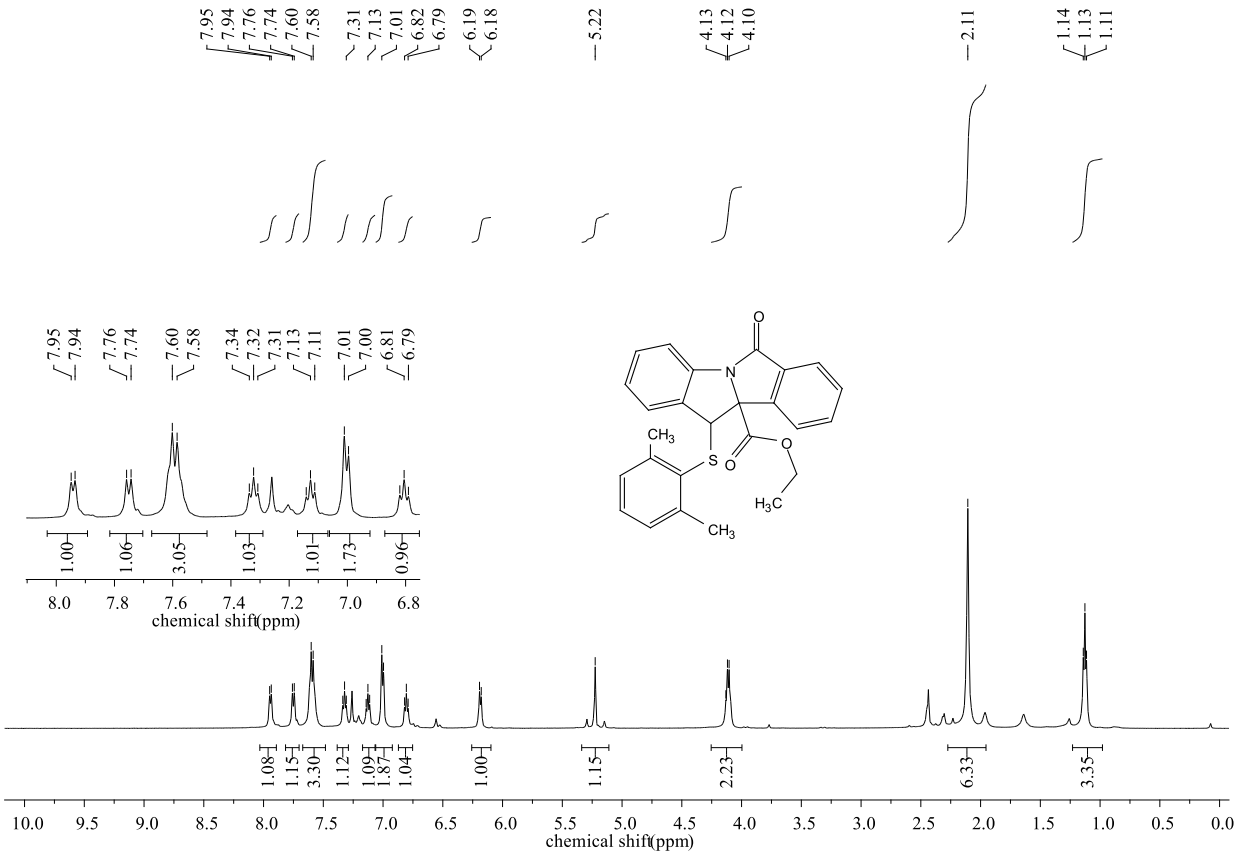
^{1}H NMR Spectra of compound **24A** (400 MHz, $CDCl_3$)



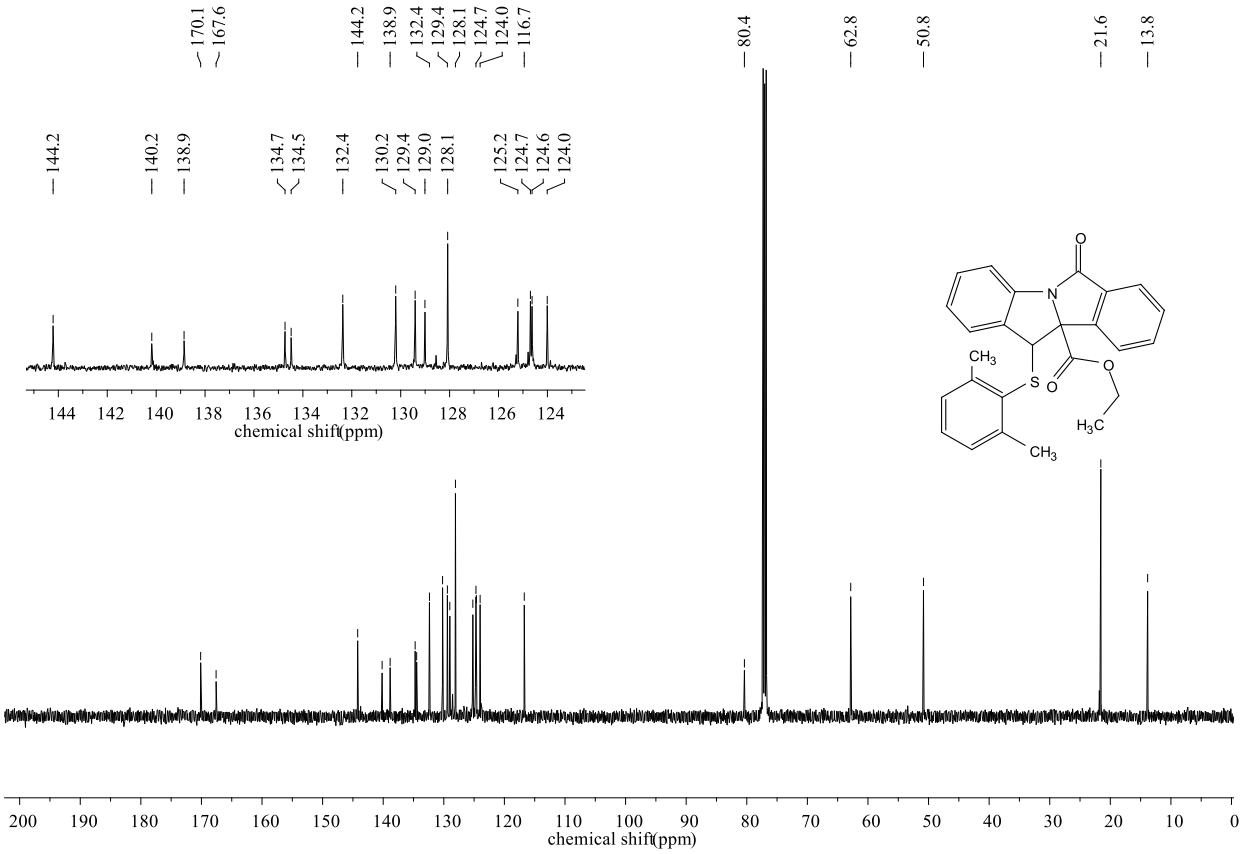
^{13}C NMR Spectra of compound **24A** (125 MHz, $CDCl_3$)



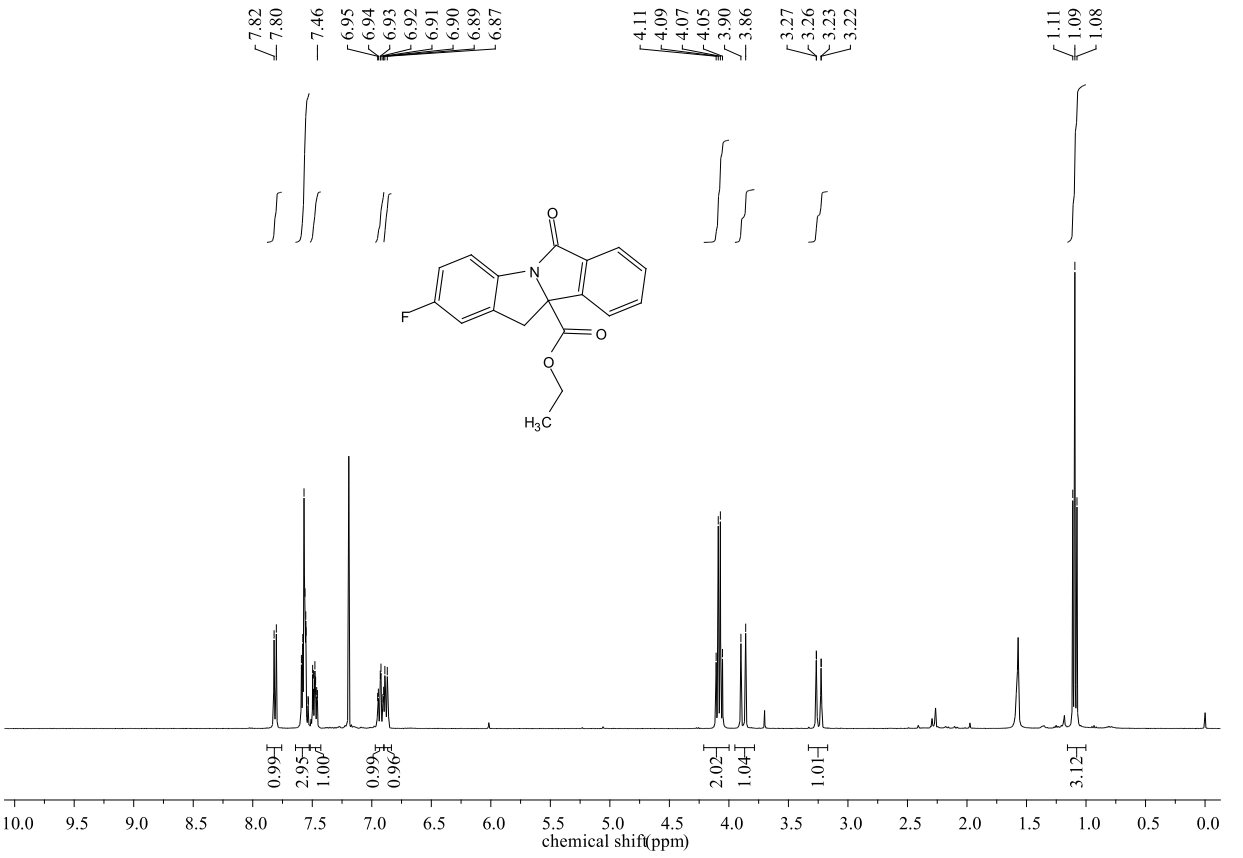
^{1}H NMR Spectra of compound **25A** (500 MHz, $CDCl_3$)



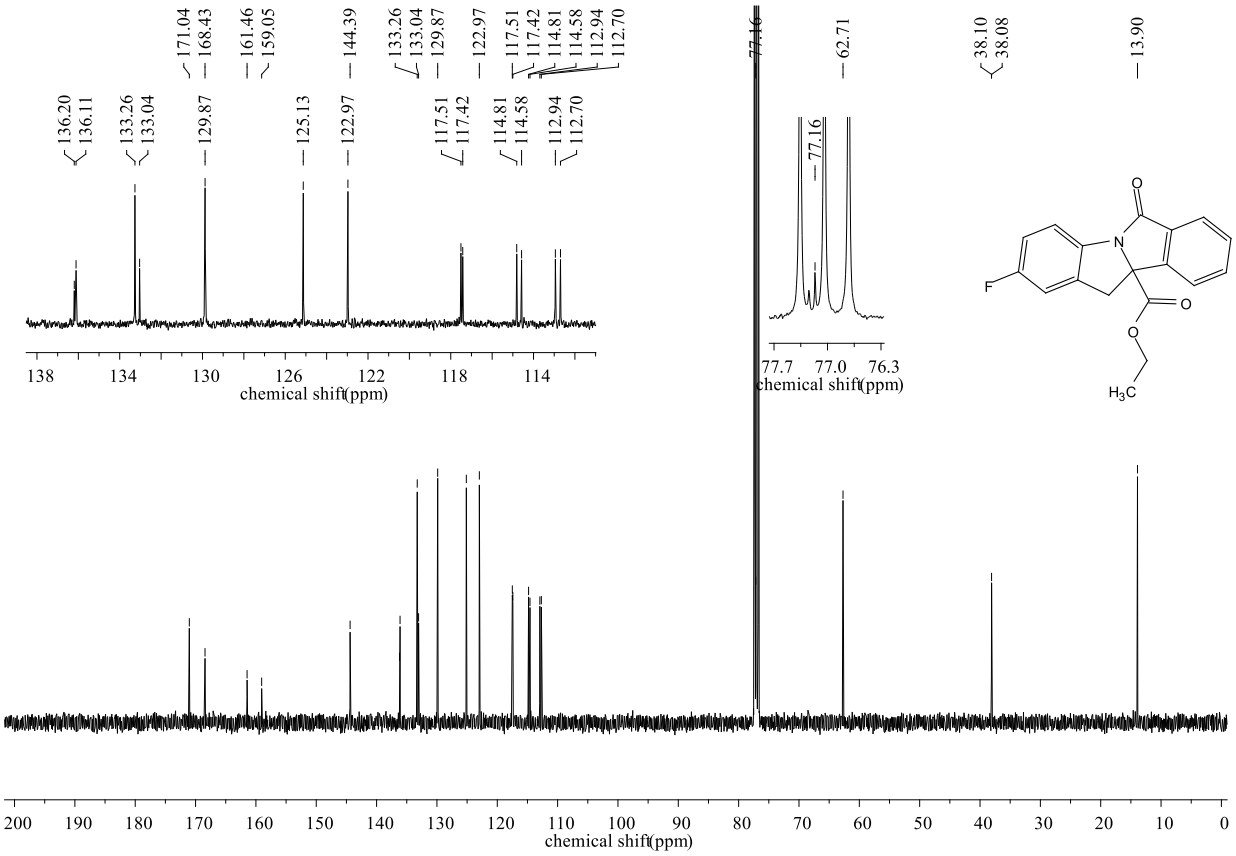
^{13}C NMR Spectra of compound **25A** (125 MHz, $CDCl_3$)



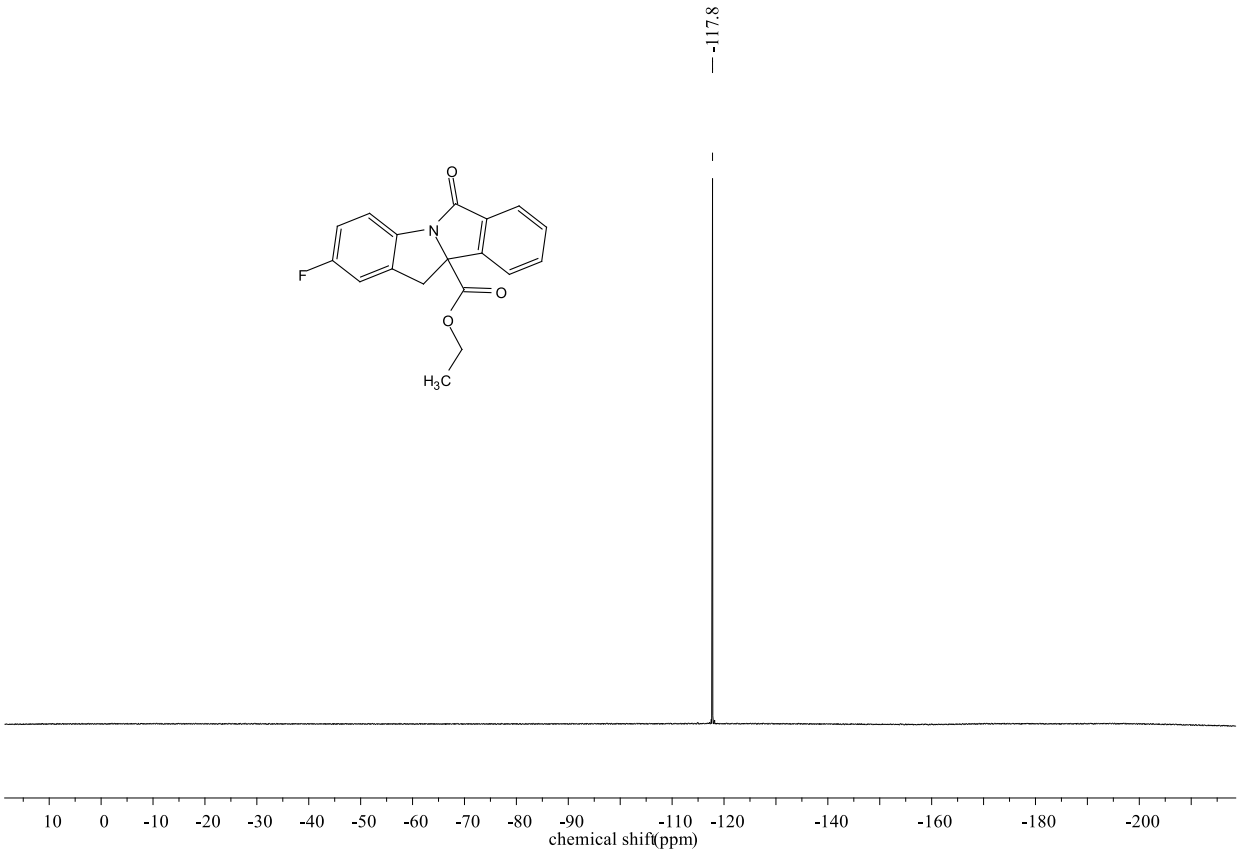
^{1}H NMR Spectra of compound **26** (400 MHz, $CDCl_3$)



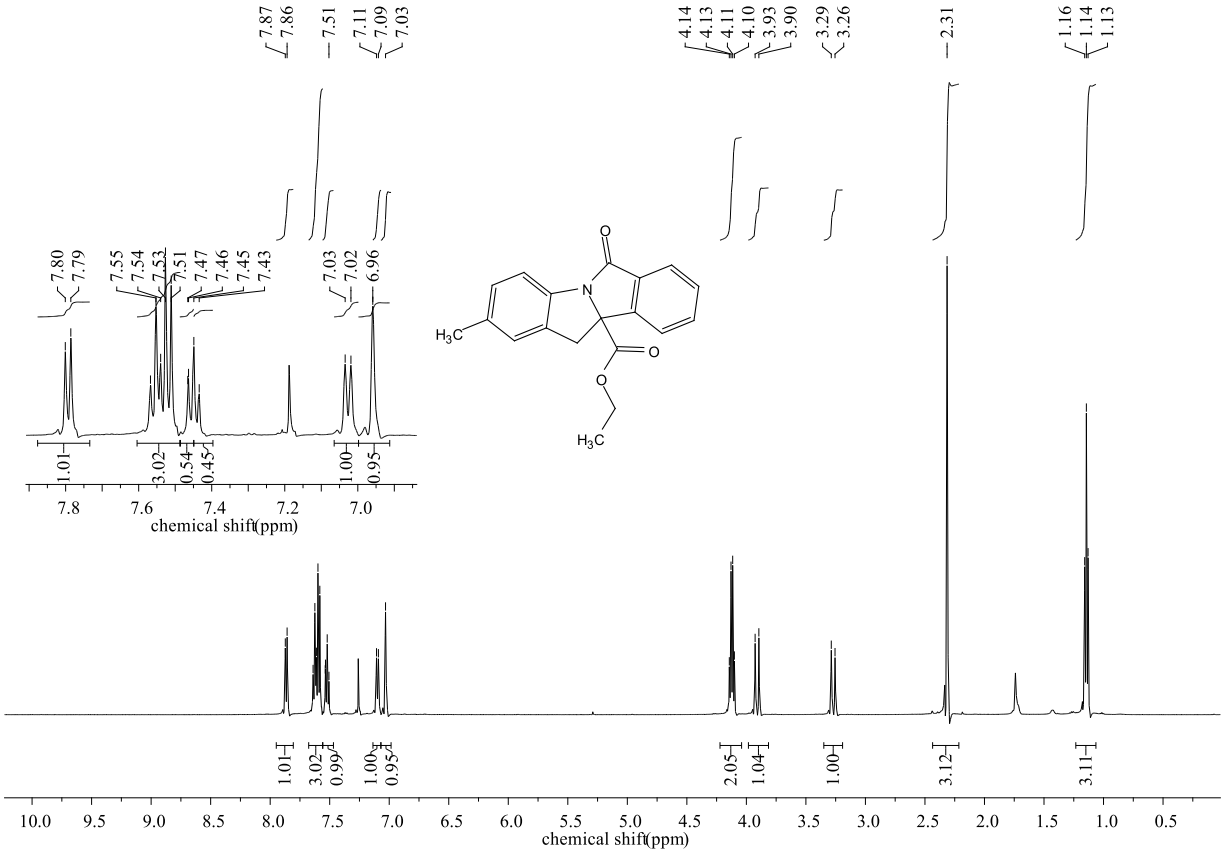
^{13}C NMR Spectra of compound **26** (100 MHz, $CDCl_3$)



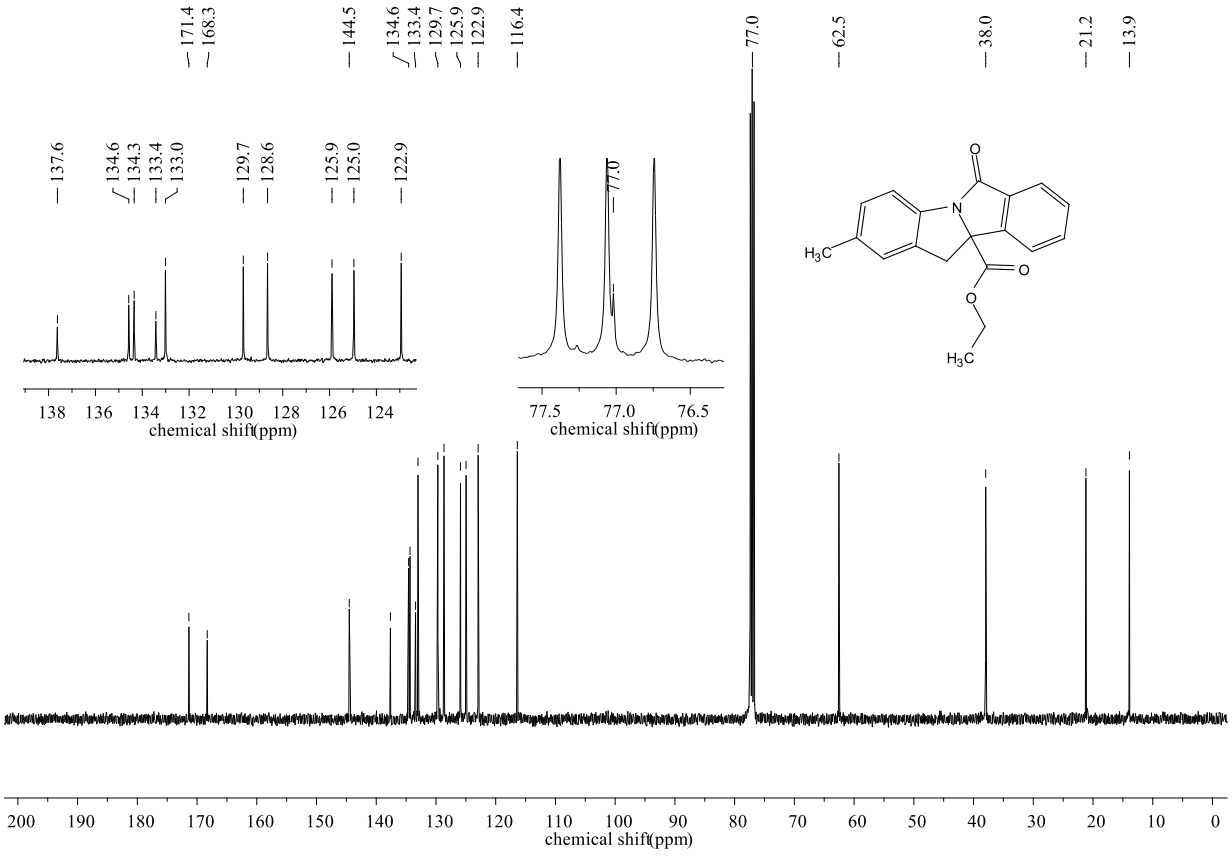
^{19}F NMR Spectra of compound **26** (300 MHz, $CDCl_3$)



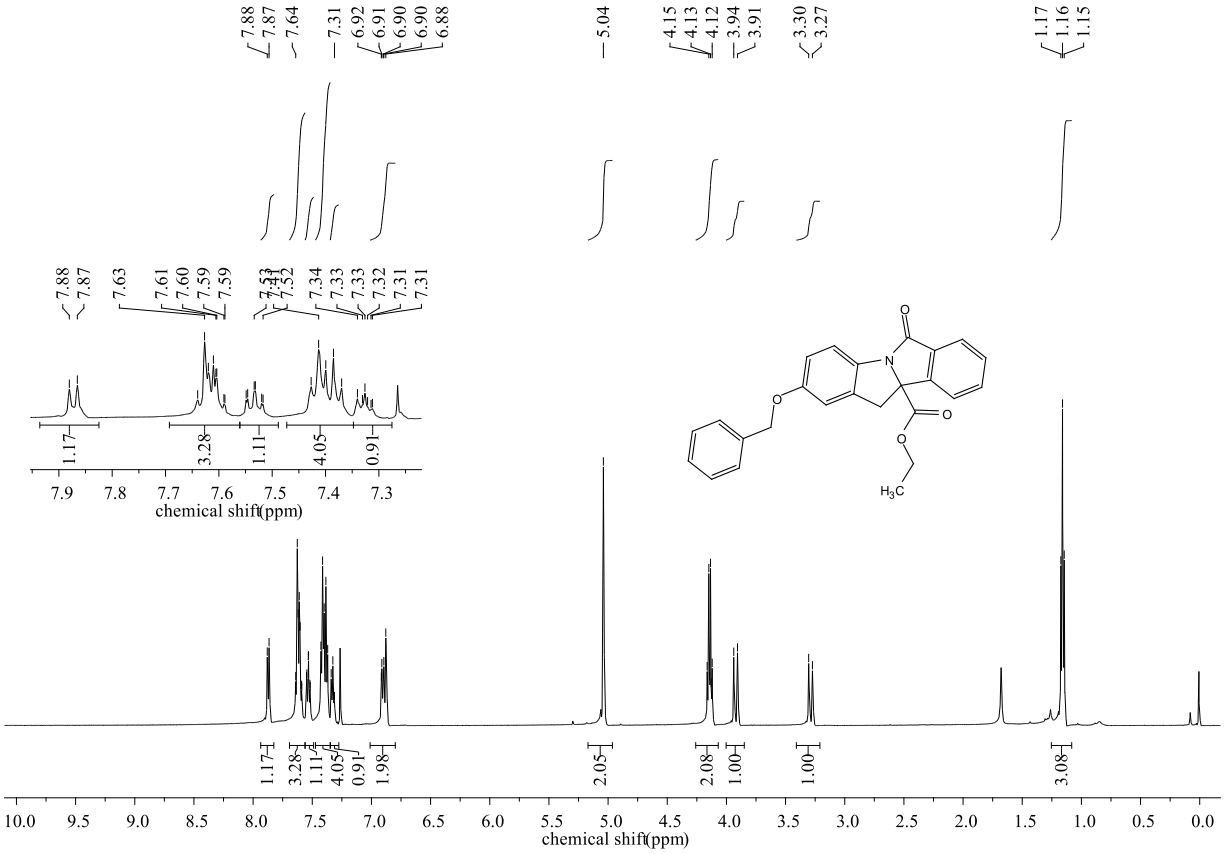
^{1}H NMR Spectra of compound **27** (500 MHz, $CDCl_3$)



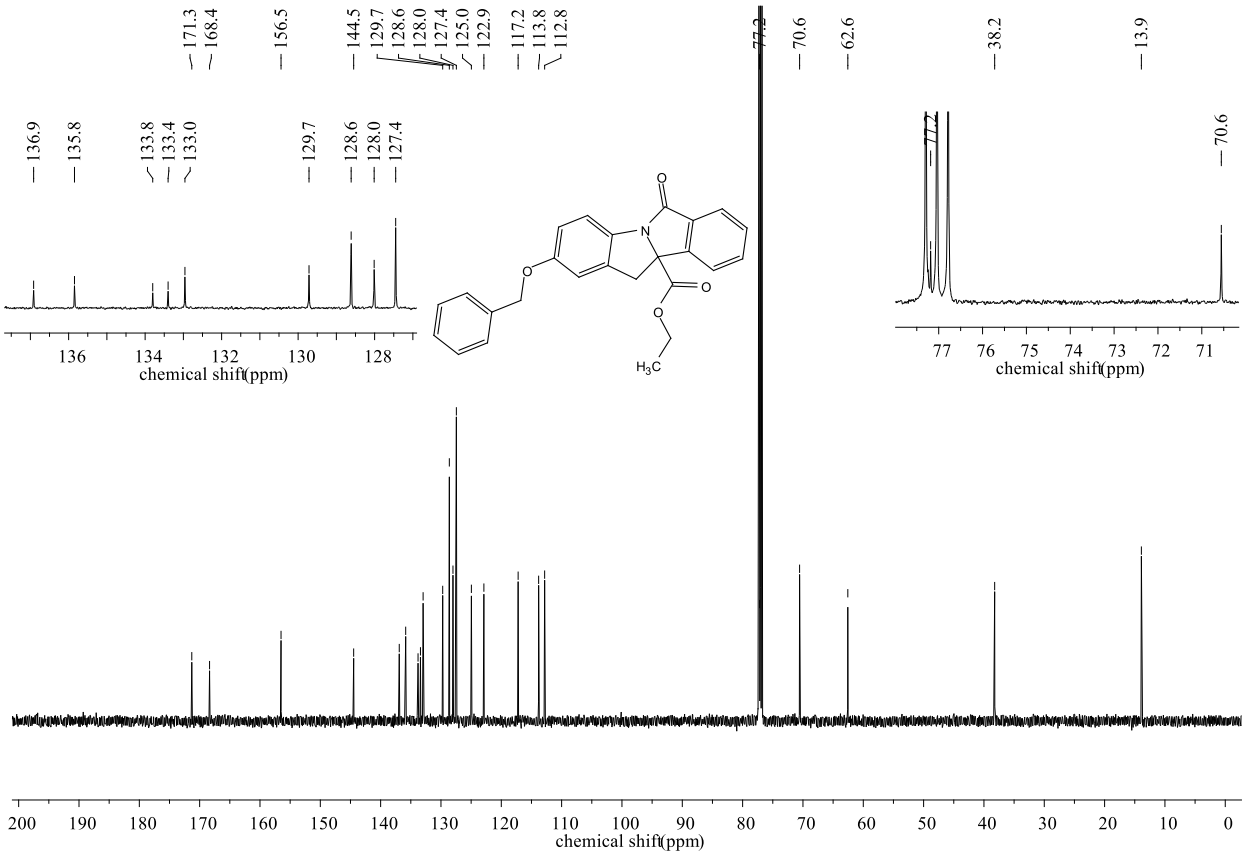
^{13}C NMR Spectra of compound **27** (125 MHz, $CDCl_3$)



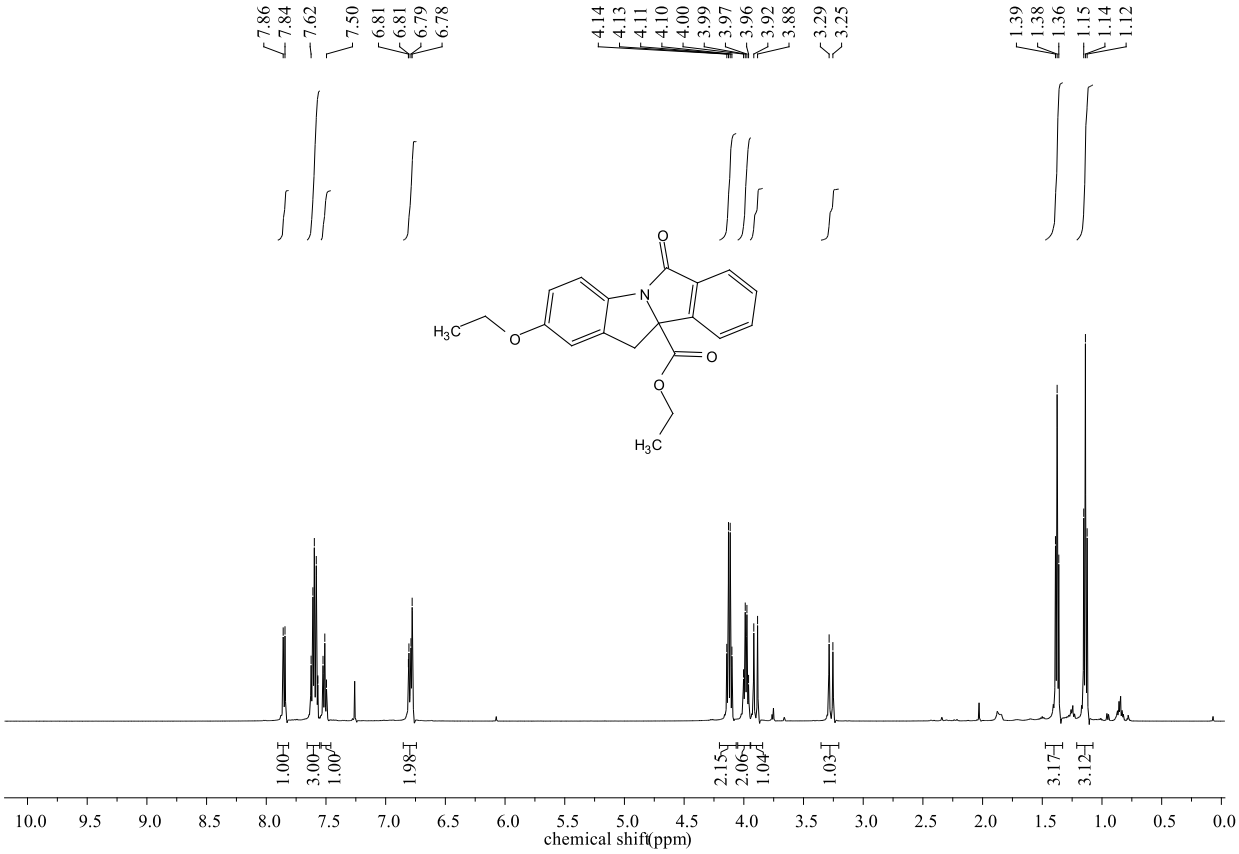
^{1}H NMR Spectra of compound **28** (500 MHz, $CDCl_3$)



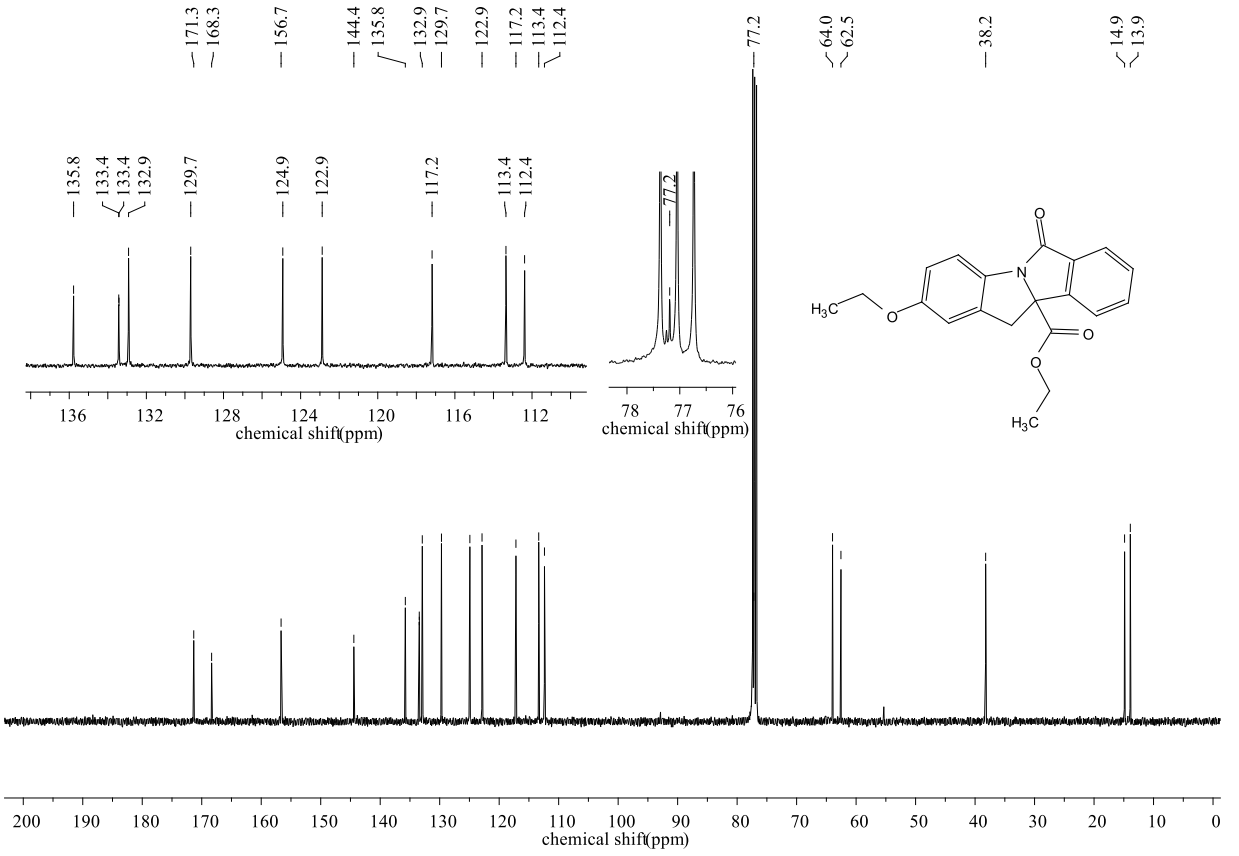
^{13}C NMR Spectra of compound **28** (125 MHz, $CDCl_3$)



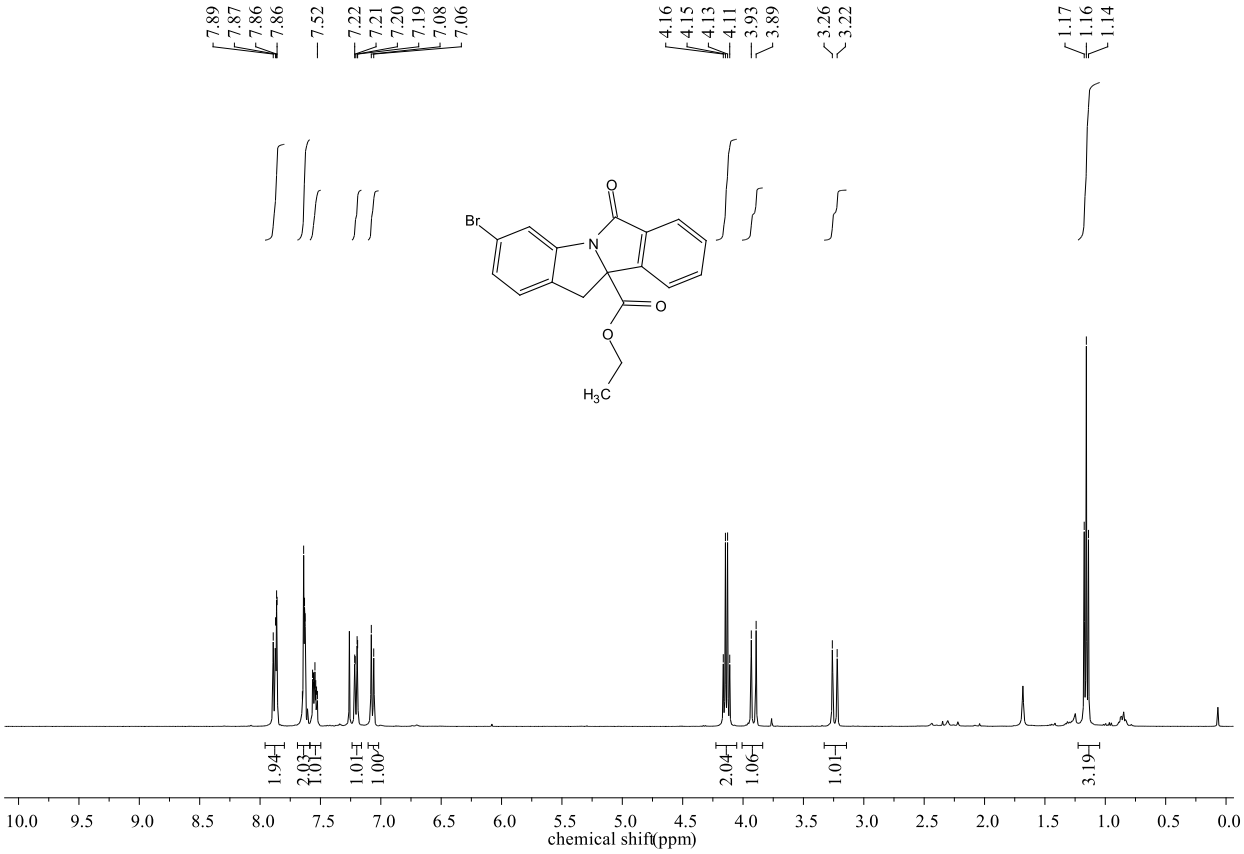
^{1}H NMR Spectra of compound **29** (500 MHz, $CDCl_3$)



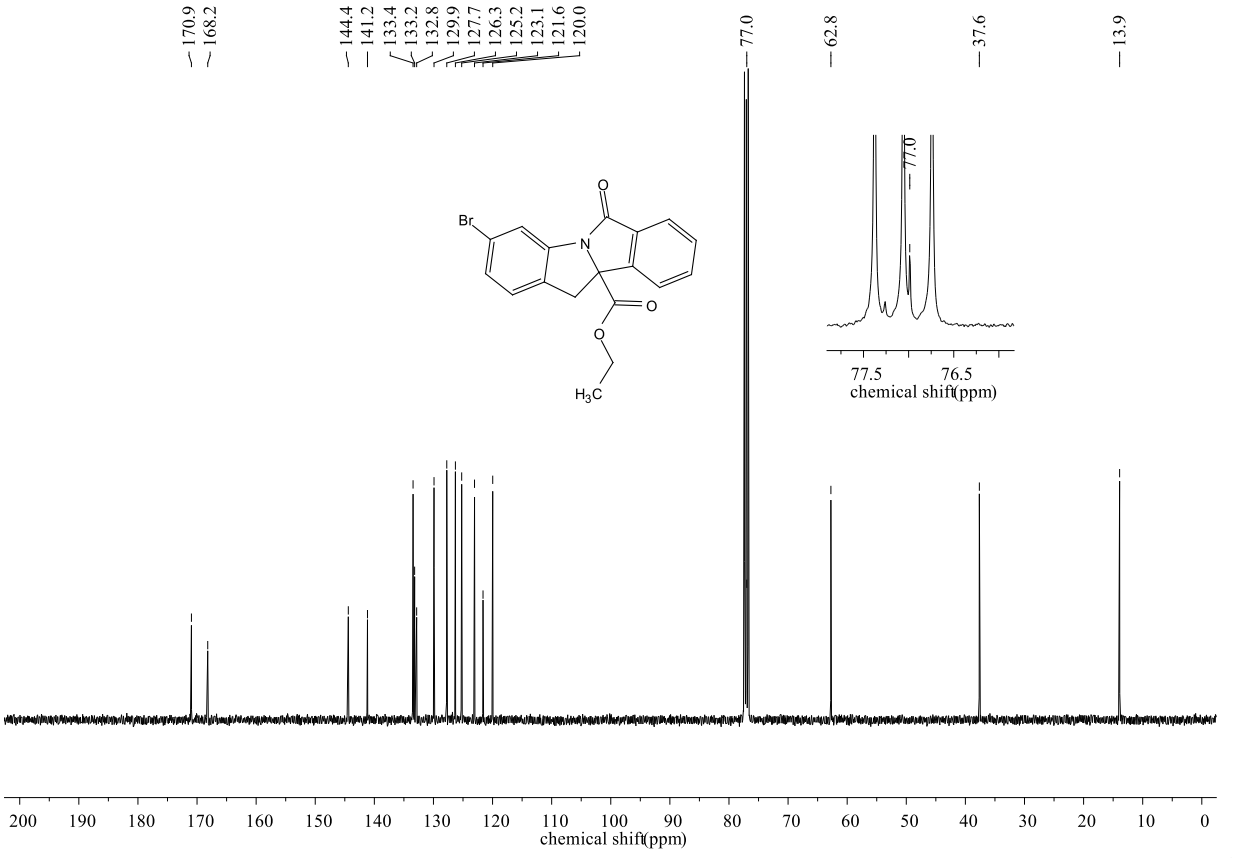
^{13}C NMR Spectra of compound **29** (100 MHz, $CDCl_3$)



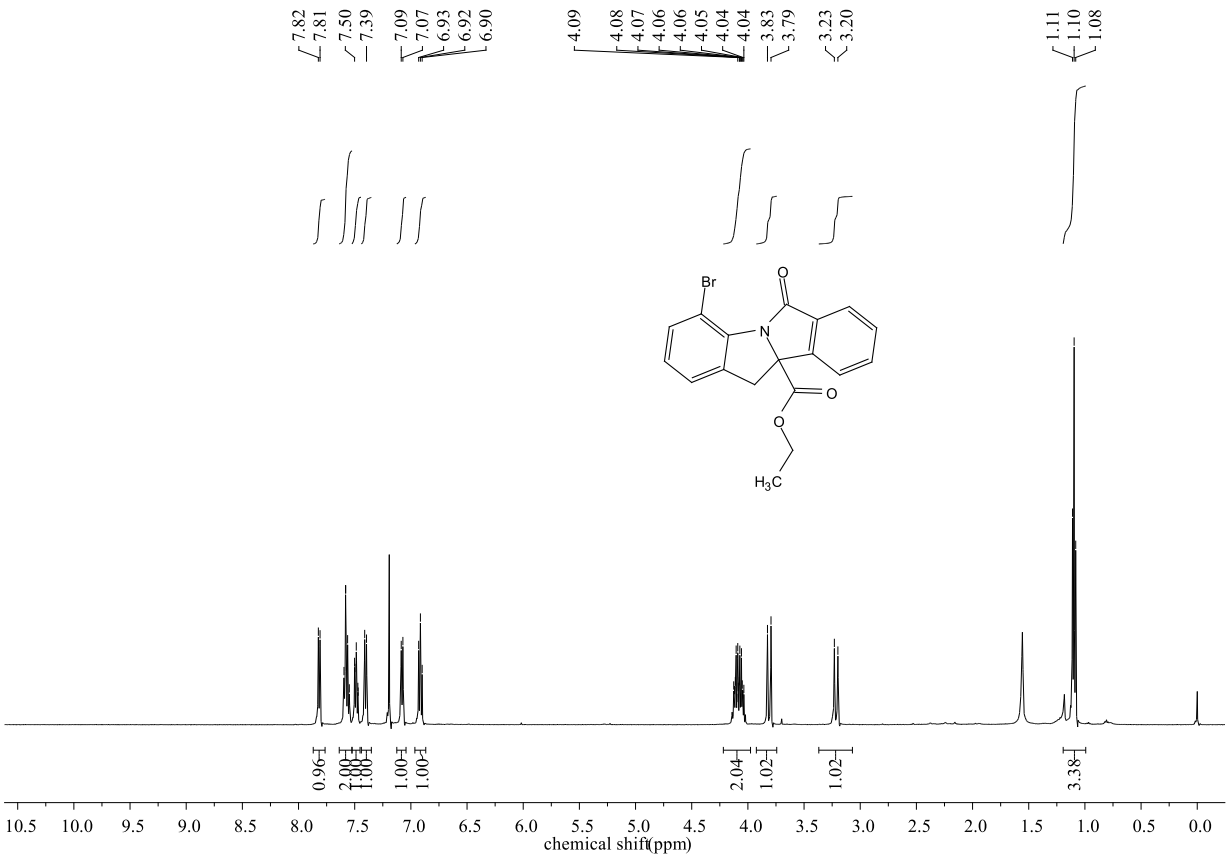
^{1}H NMR Spectra of compound **30** (400 MHz, $CDCl_3$)



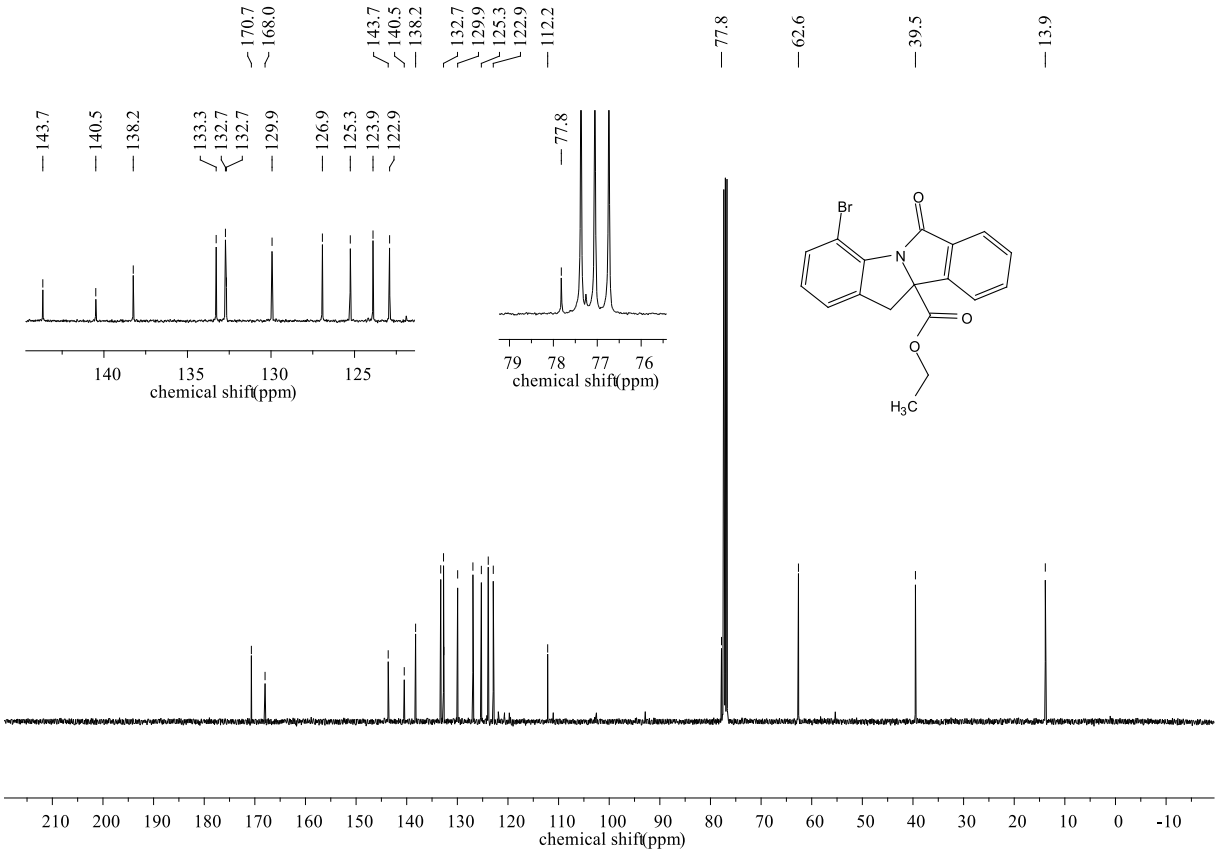
^{13}C NMR Spectra of compound **30** (100 MHz, $CDCl_3$)



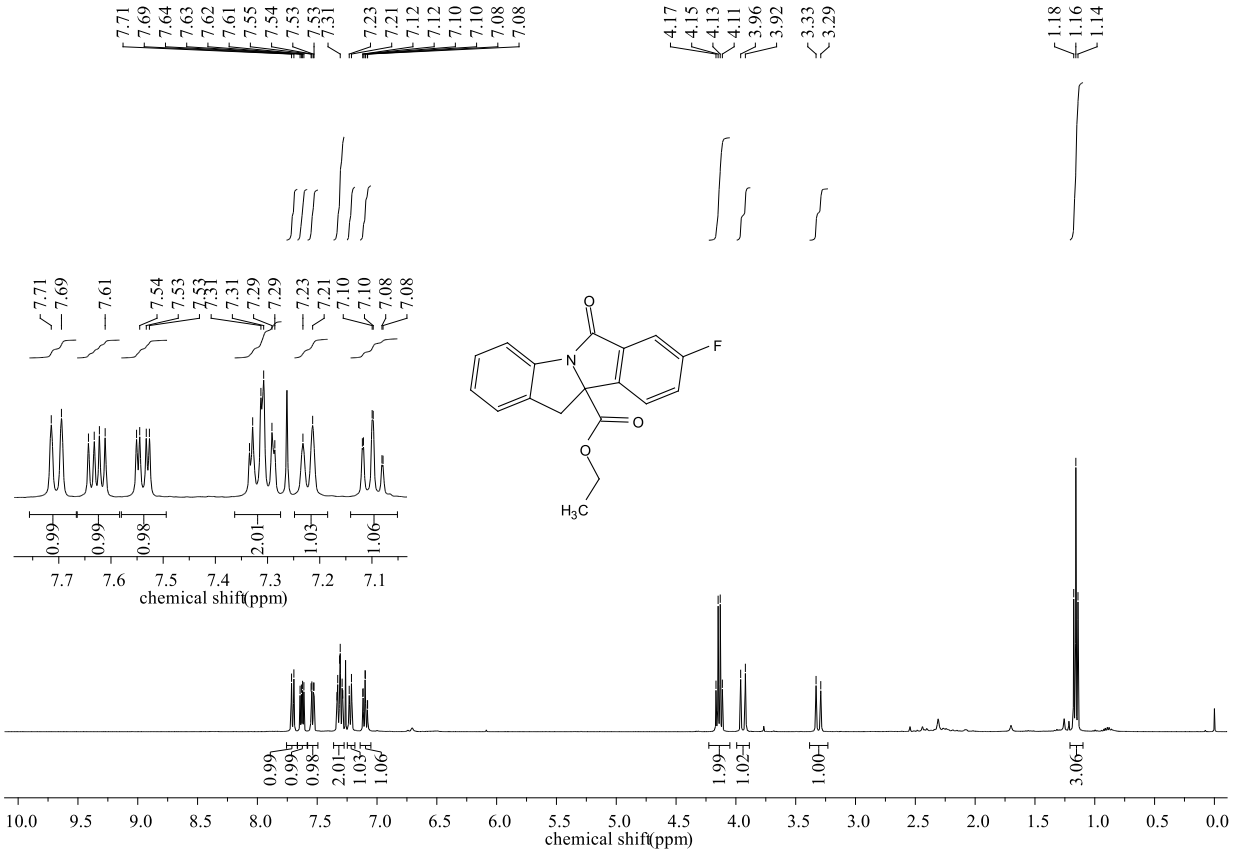
^{1}H NMR Spectra of compound **31** (500 MHz, $CDCl_3$)



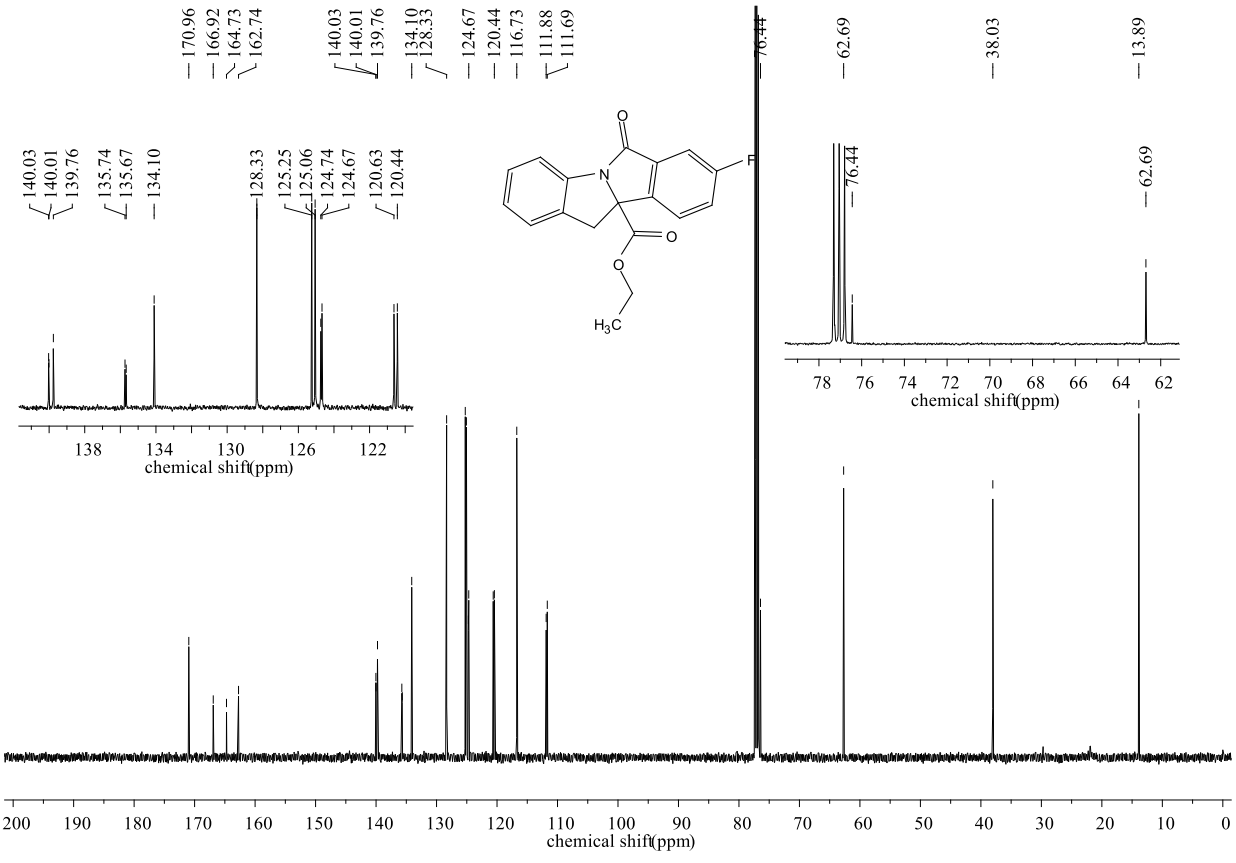
^{13}C NMR Spectra of compound **31** (100 MHz, $CDCl_3$)



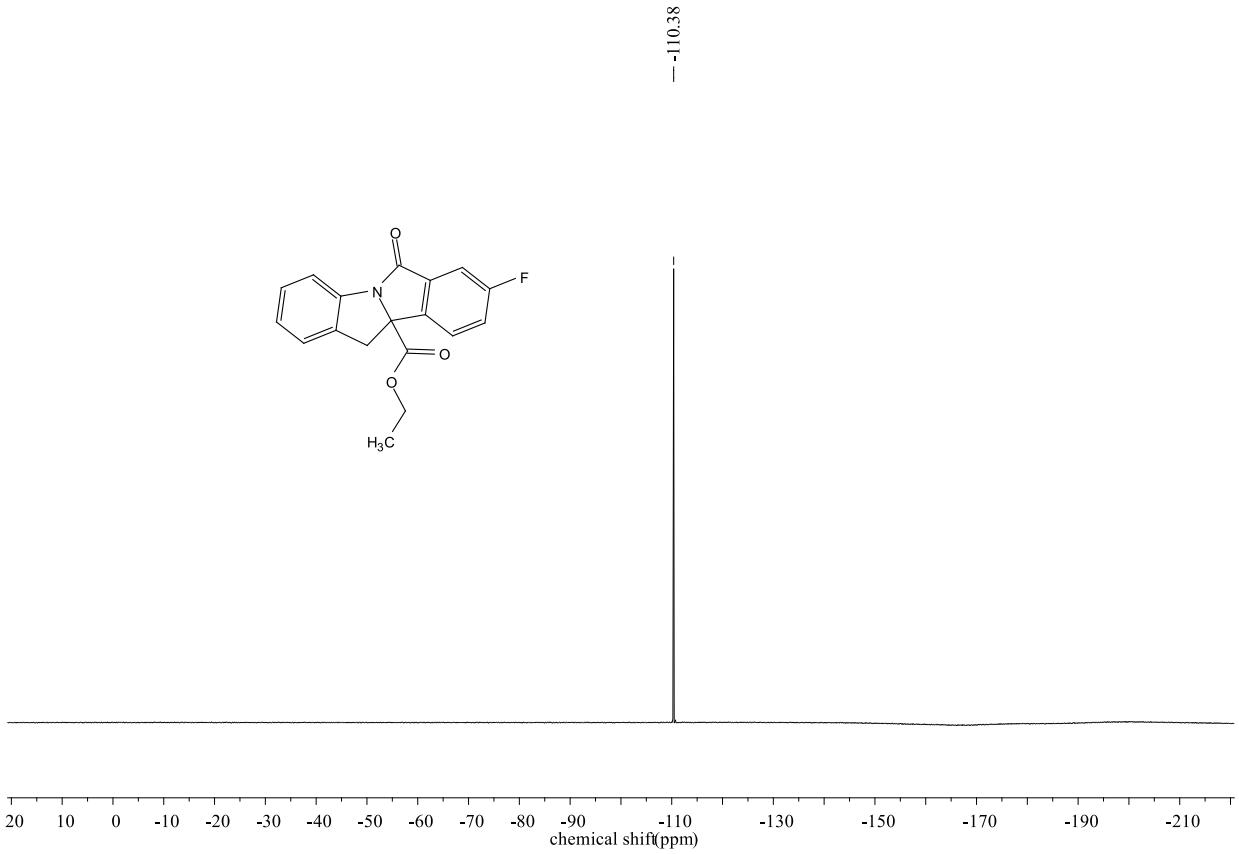
^{1}H NMR Spectra of compound **32** (400 MHz, $CDCl_3$)



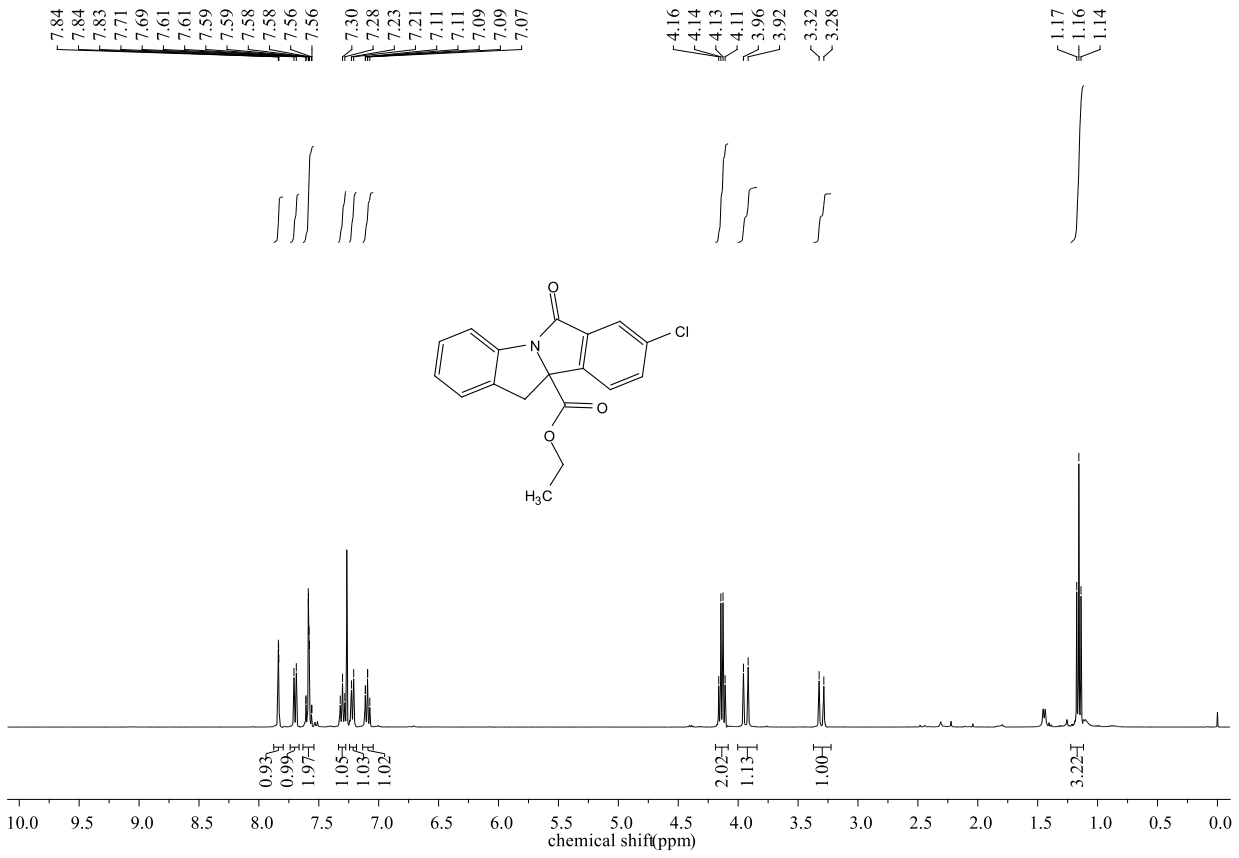
^{13}C NMR Spectra of compound **32** (125 MHz, $CDCl_3$)



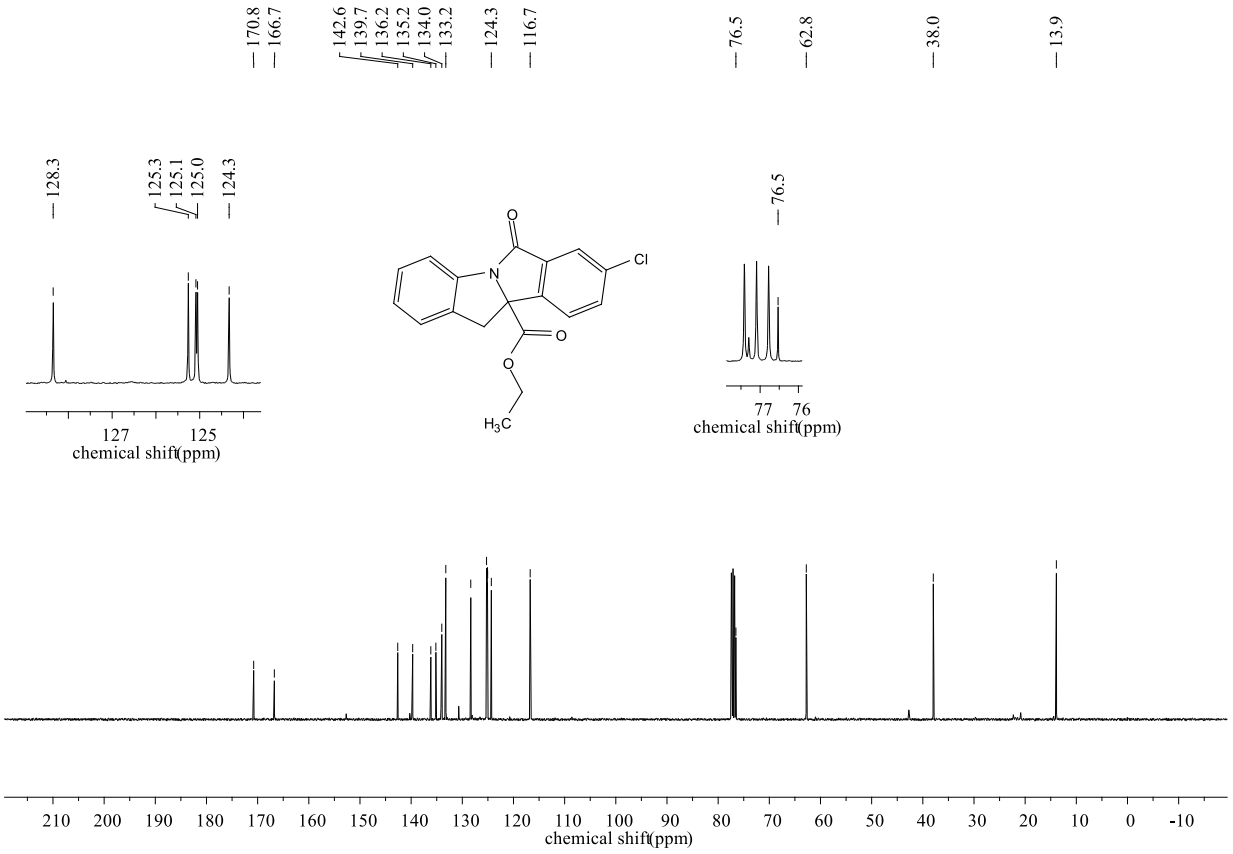
^{19}F NMR Spectra of compound **32** (375 MHz, $CDCl_3$)



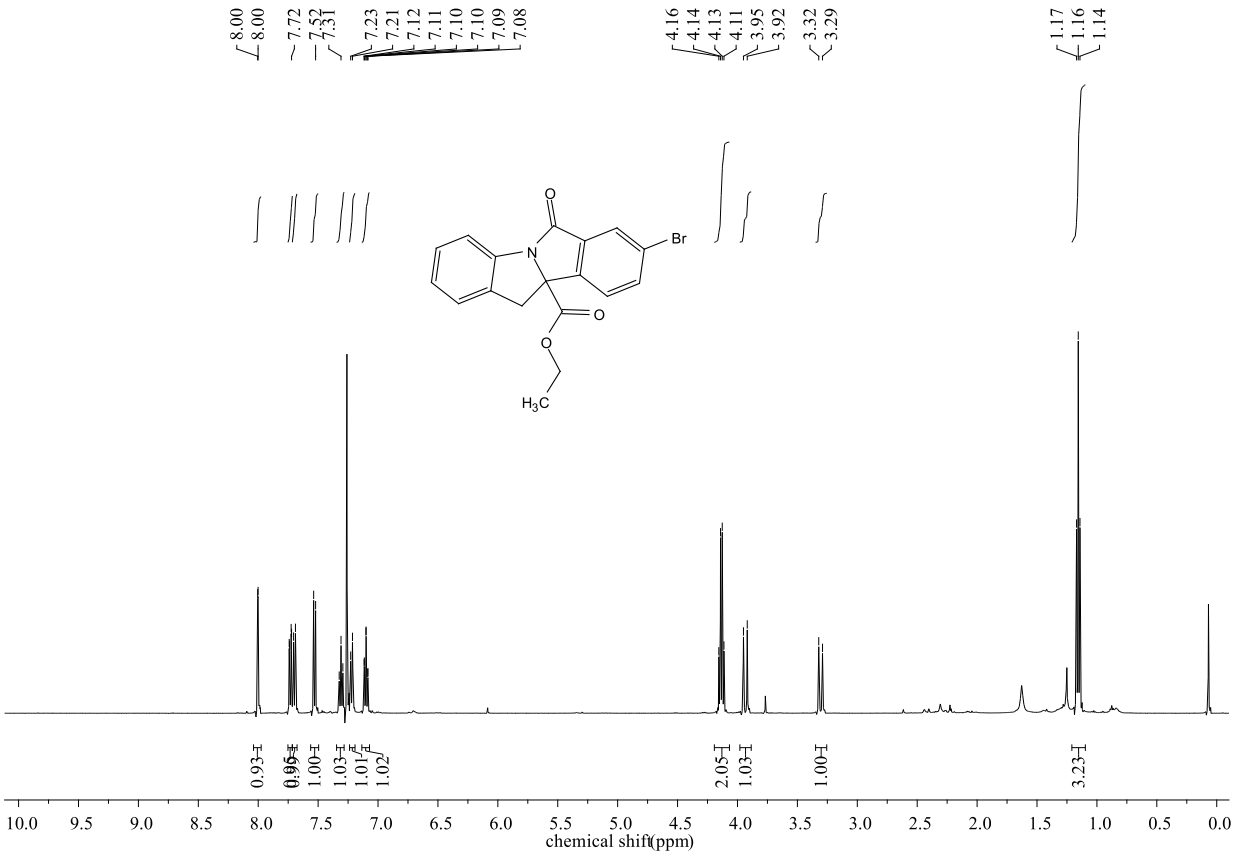
^{1}H NMR Spectra of compound **33** (400 MHz, $CDCl_3$)



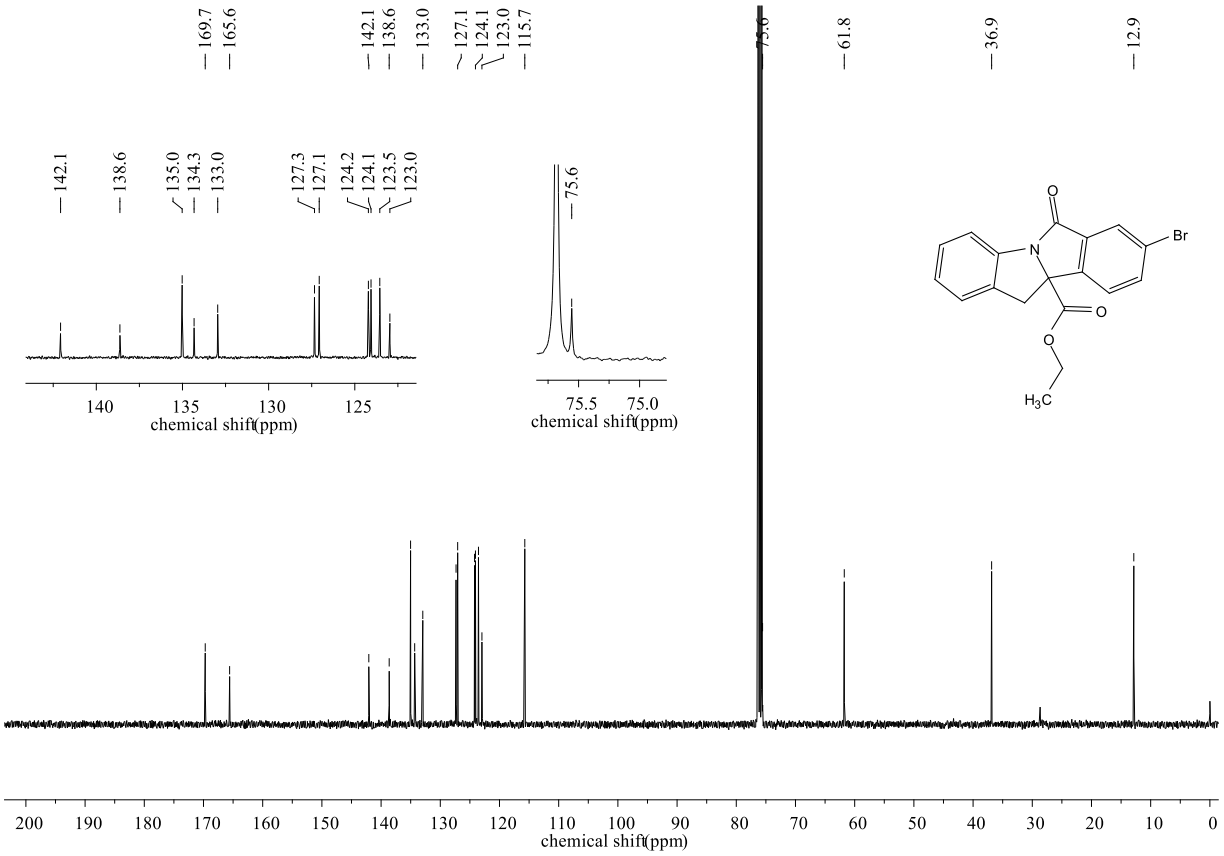
^{13}C NMR Spectra of compound **33** (100 MHz, $CDCl_3$)



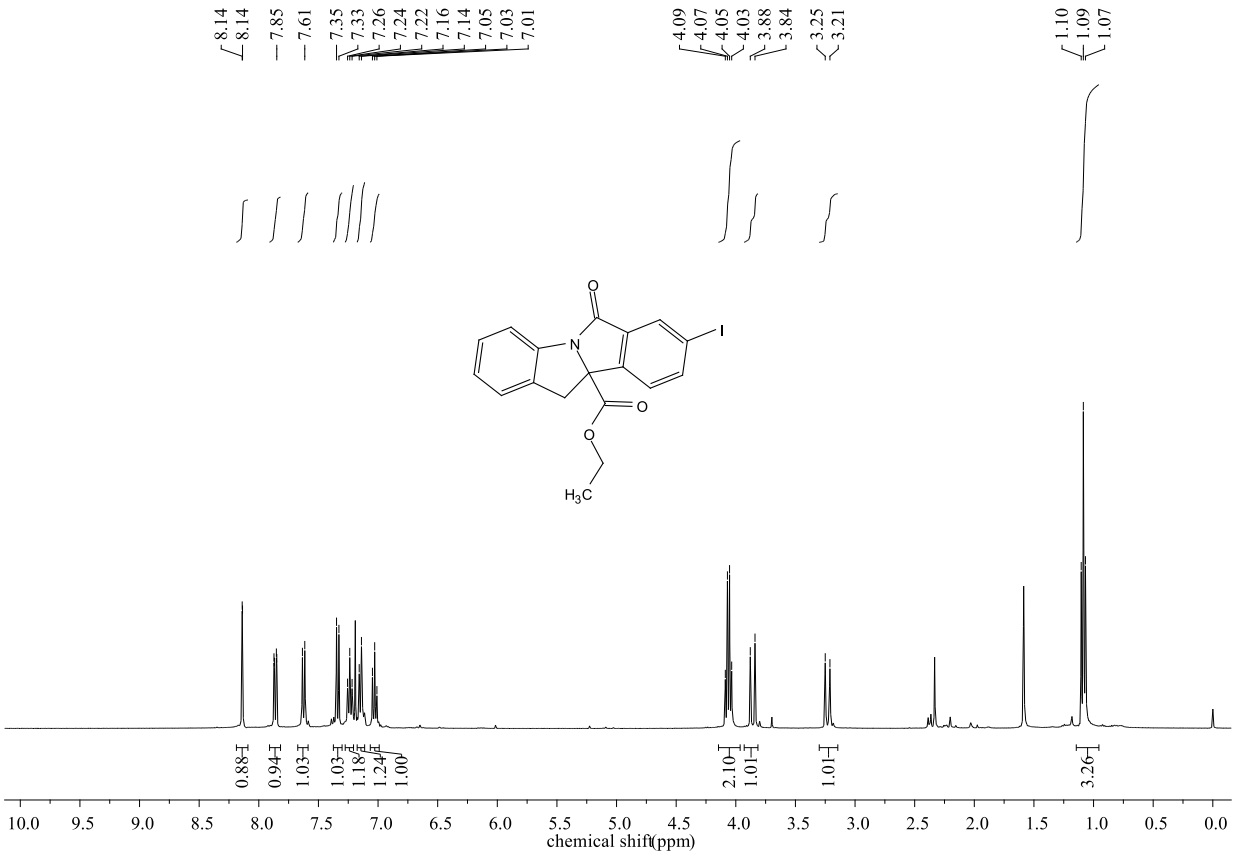
^{1}H NMR Spectra of compound **34** (500 MHz, $CDCl_3$)



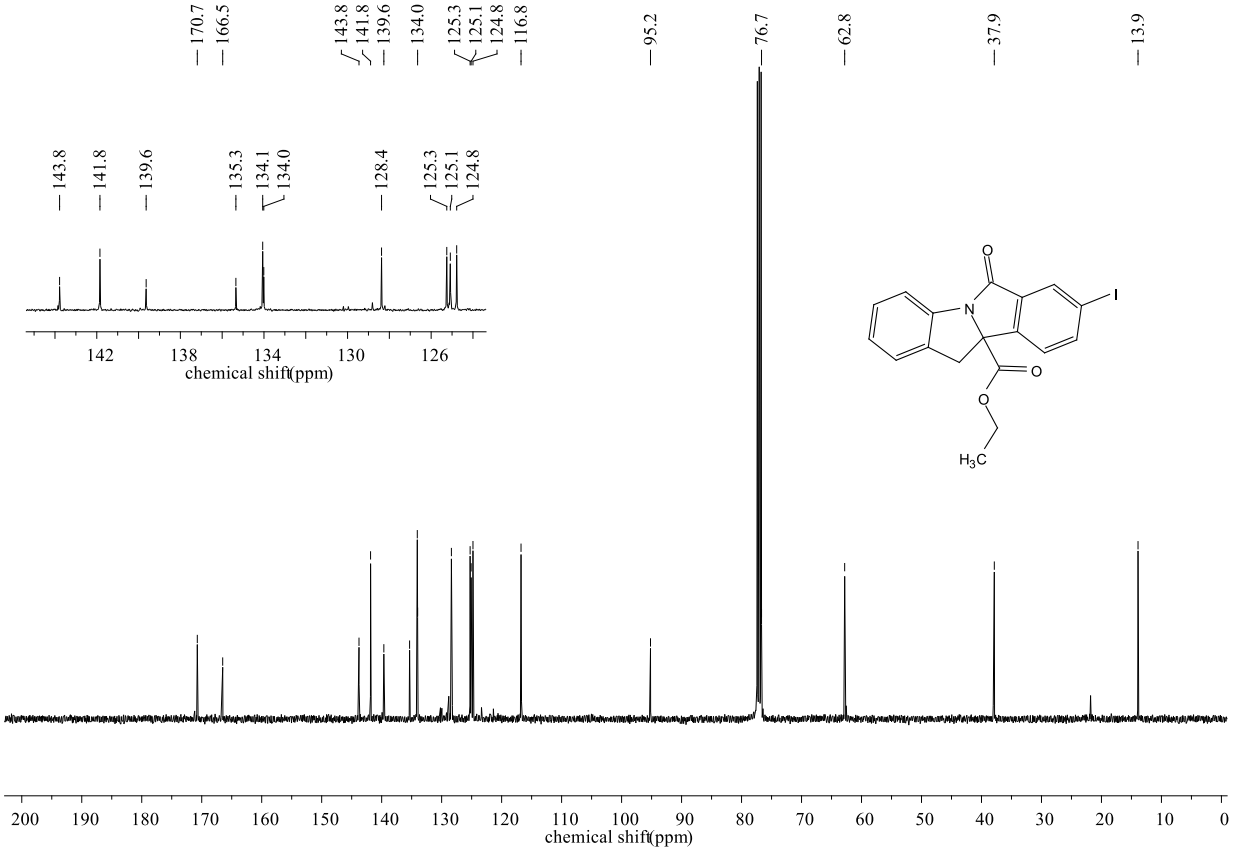
^{13}C NMR Spectra of compound **34** (100 MHz, $CDCl_3$)



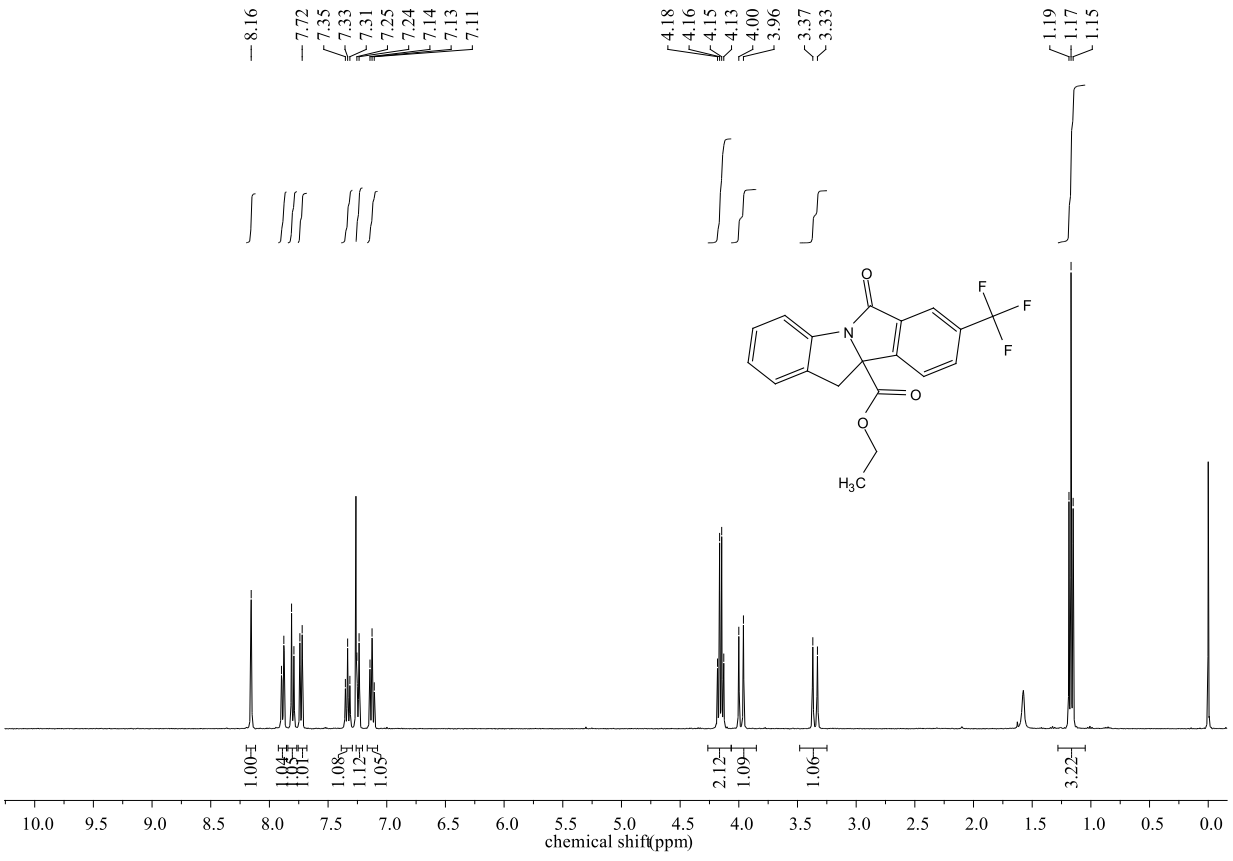
^{1}H NMR Spectra of compound **35** (400 MHz, $CDCl_3$)



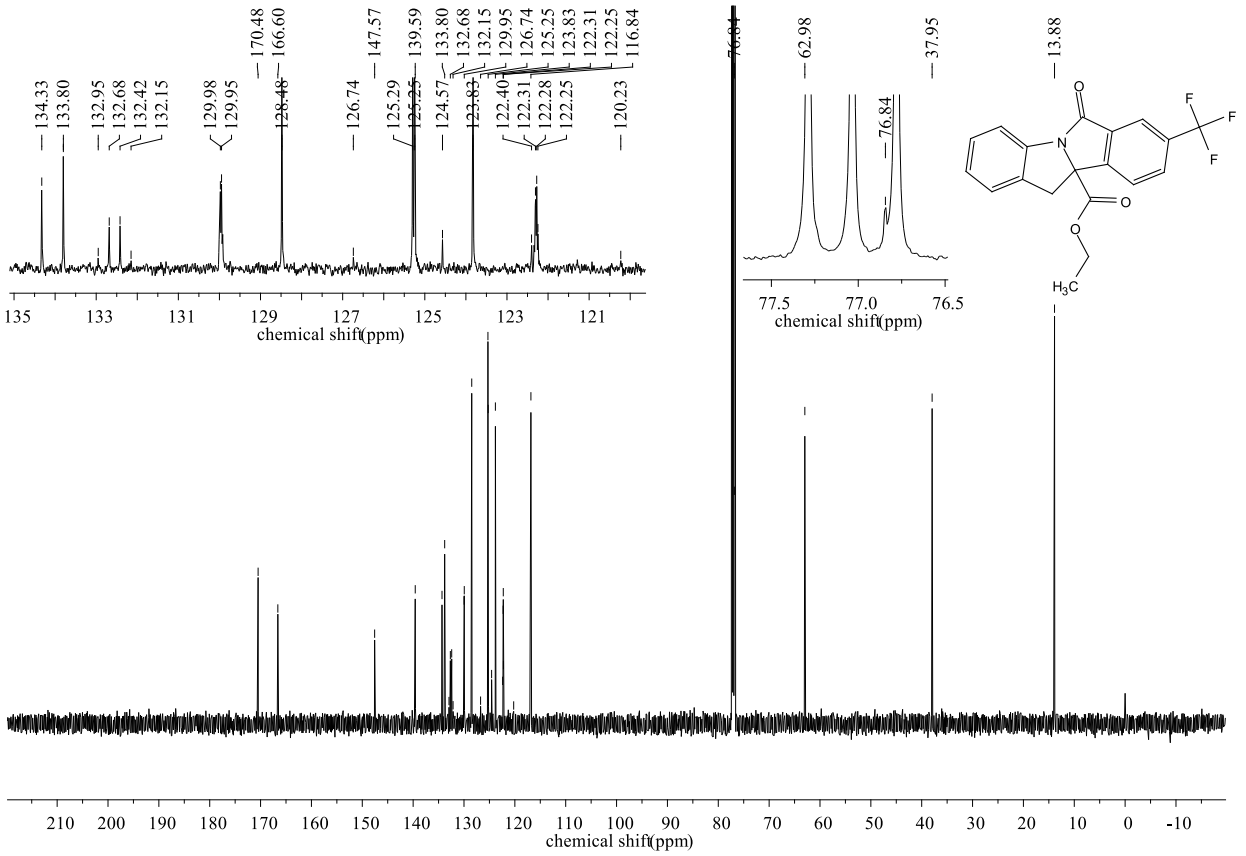
^{13}C NMR Spectra of compound **35** (100 MHz, $CDCl_3$)



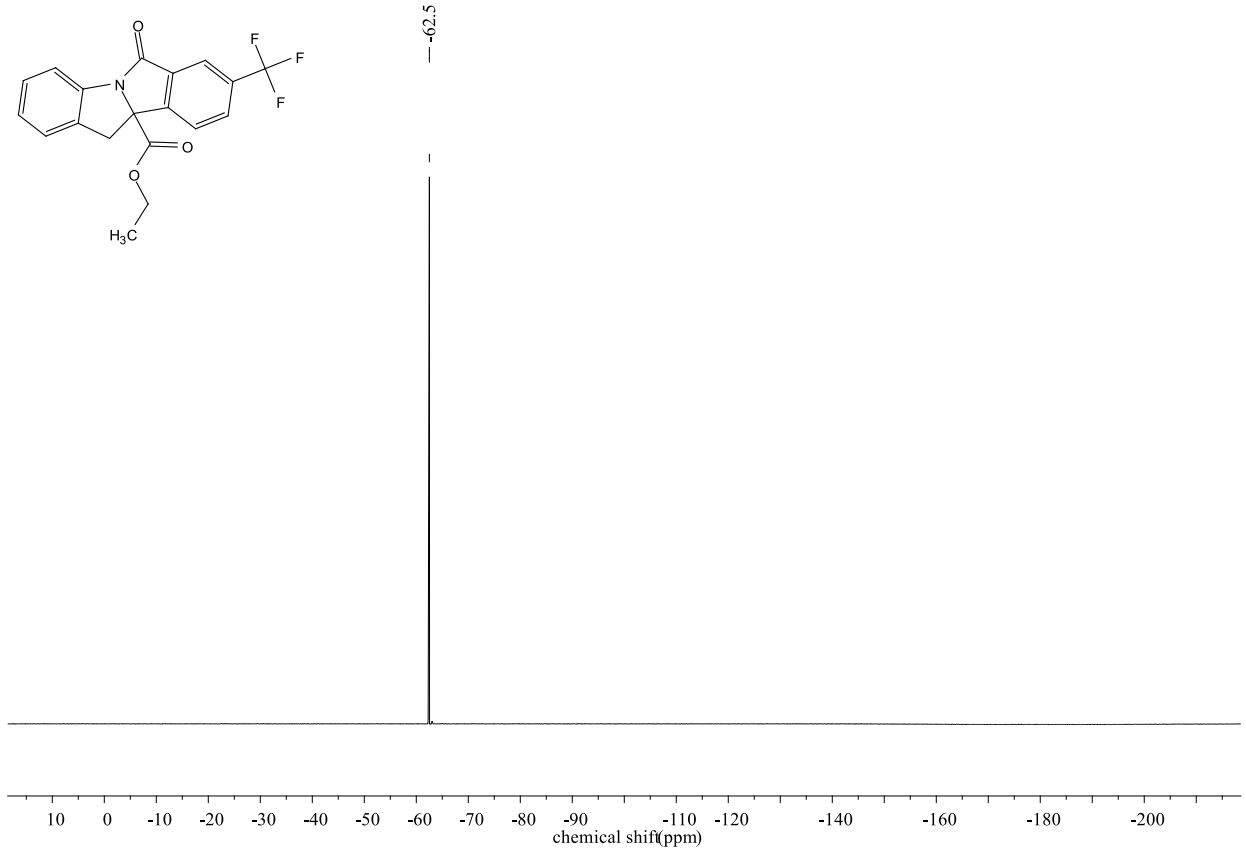
^{1}H NMR Spectra of compound **36** (400 MHz, $CDCl_3$)



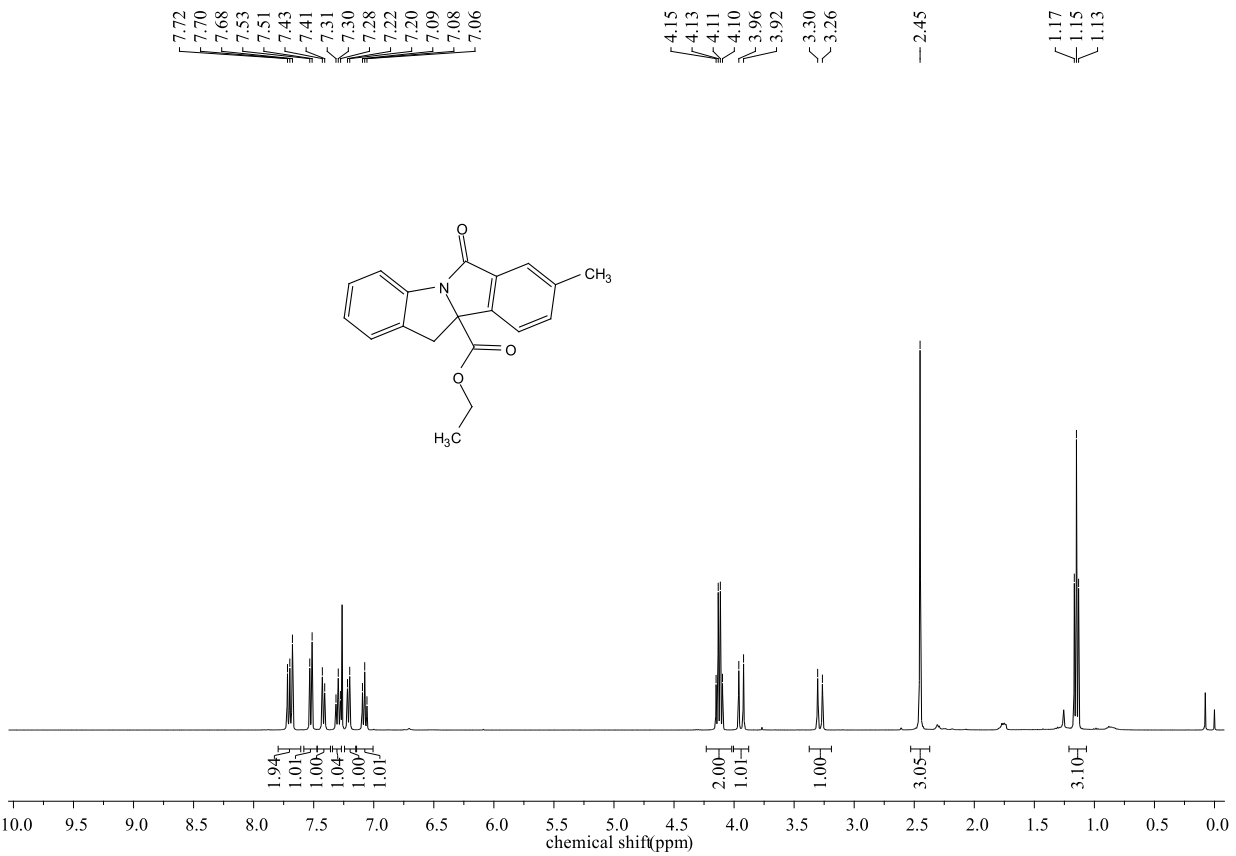
^{13}C NMR Spectra of compound **36** (125 MHz, $CDCl_3$)



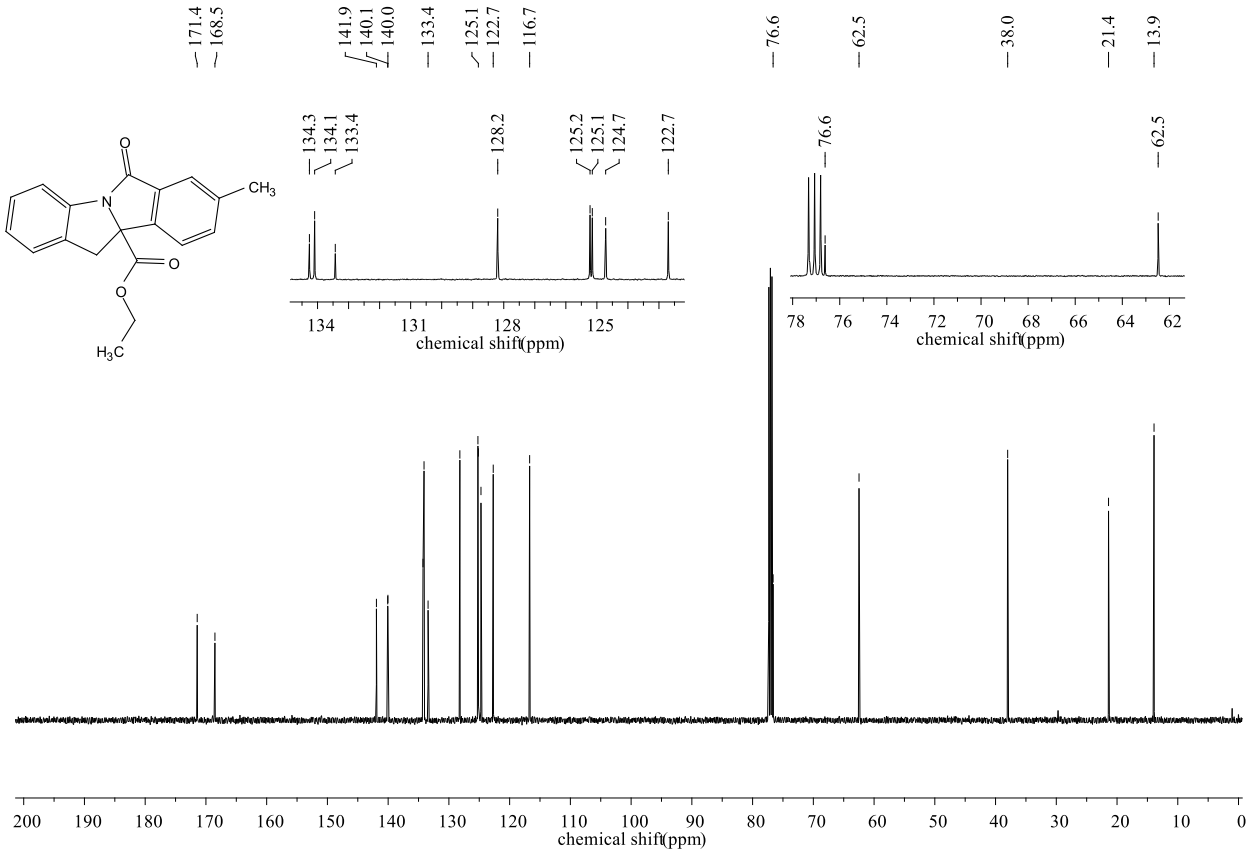
^{19}F NMR Spectra of compound **36** (300 MHz, $CDCl_3$)



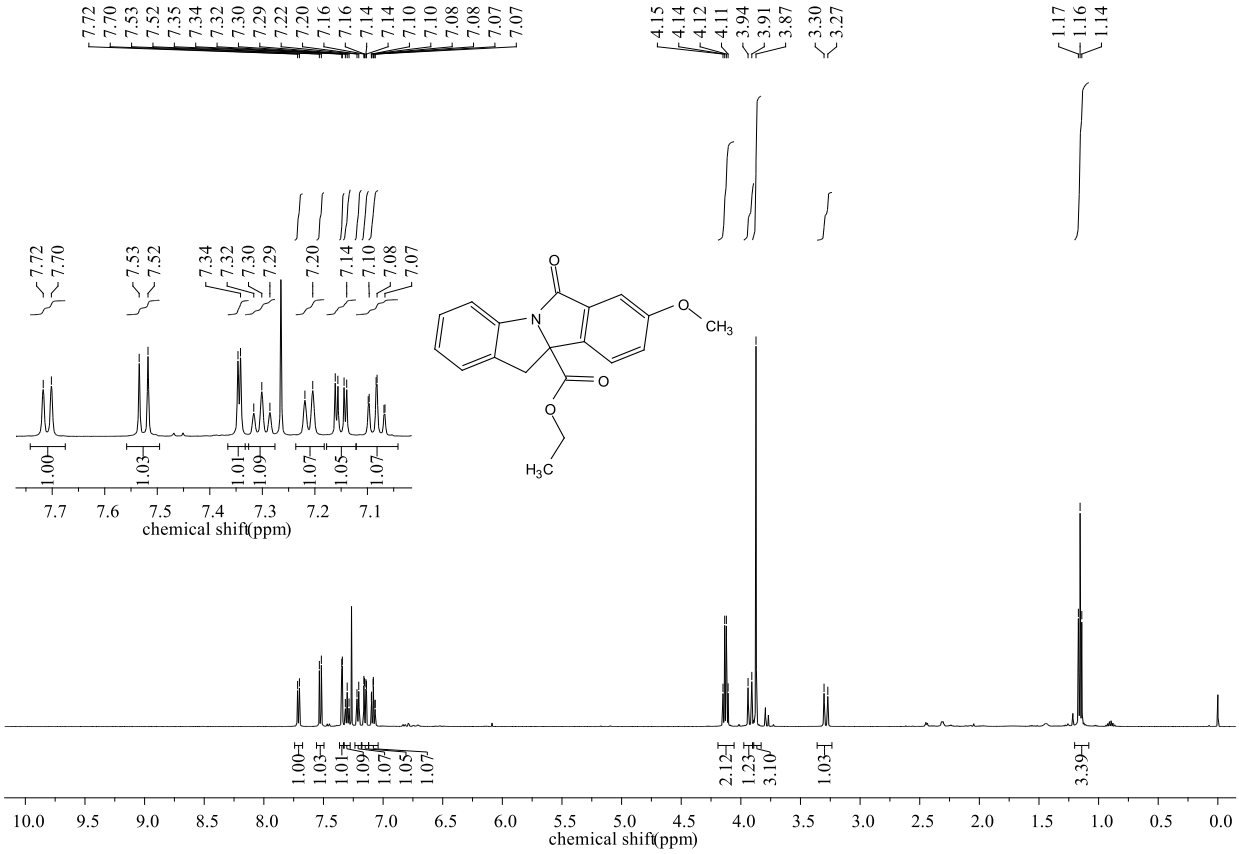
^{1}H NMR Spectra of compound **37** (400 MHz, $CDCl_3$)



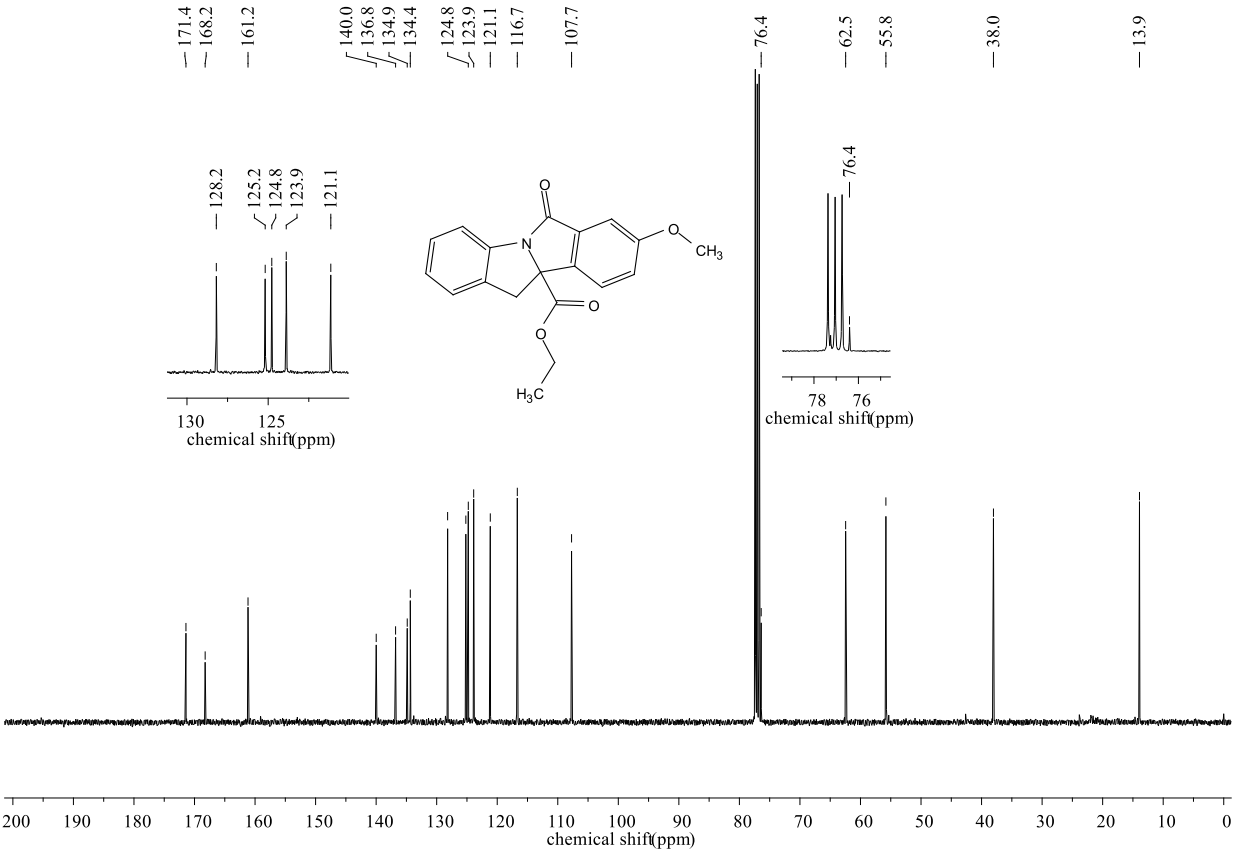
^{13}C NMR Spectra of compound **37** (125 MHz, $CDCl_3$)



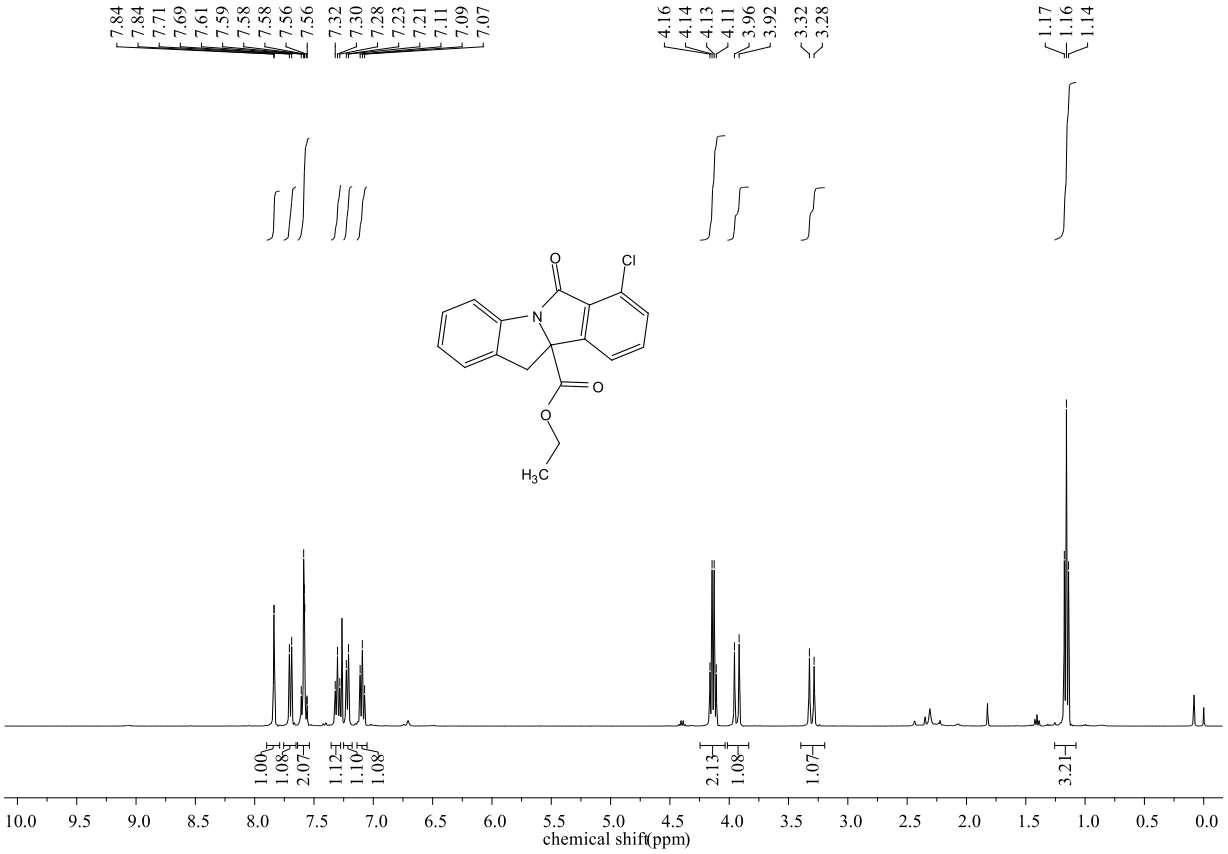
^{1}H NMR Spectra of compound **38** (500 MHz, $CDCl_3$)



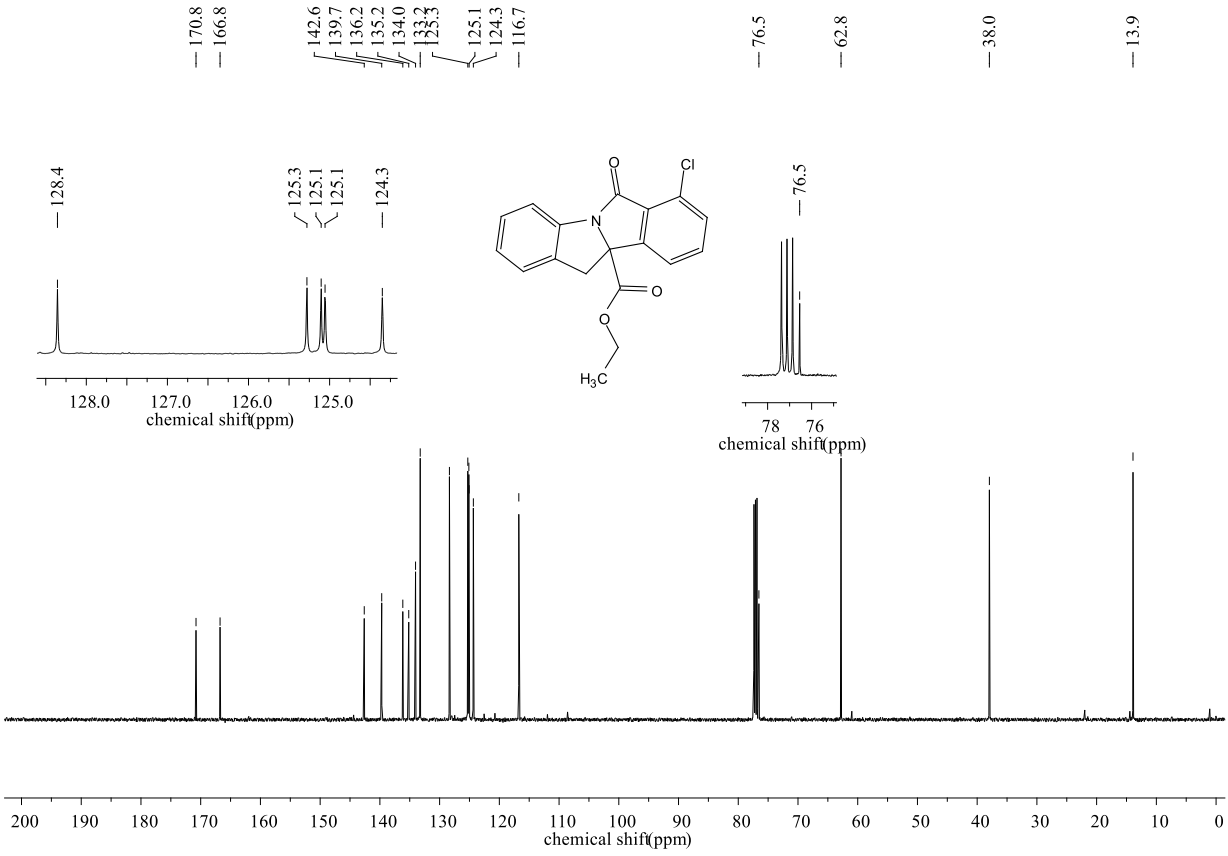
^{13}C NMR Spectra of compound **38** (100 MHz, $CDCl_3$)



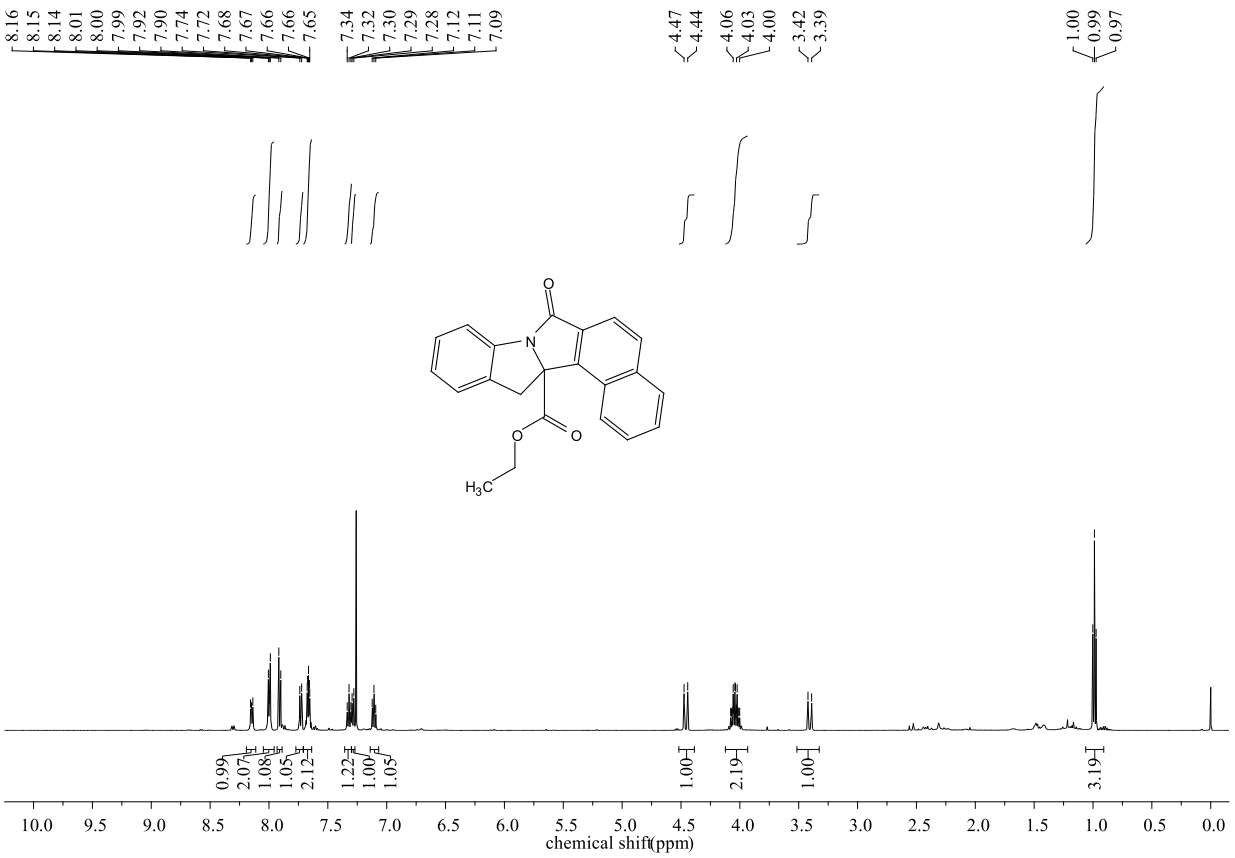
^{1}H NMR Spectra of compound **39** (400 MHz, $CDCl_3$)



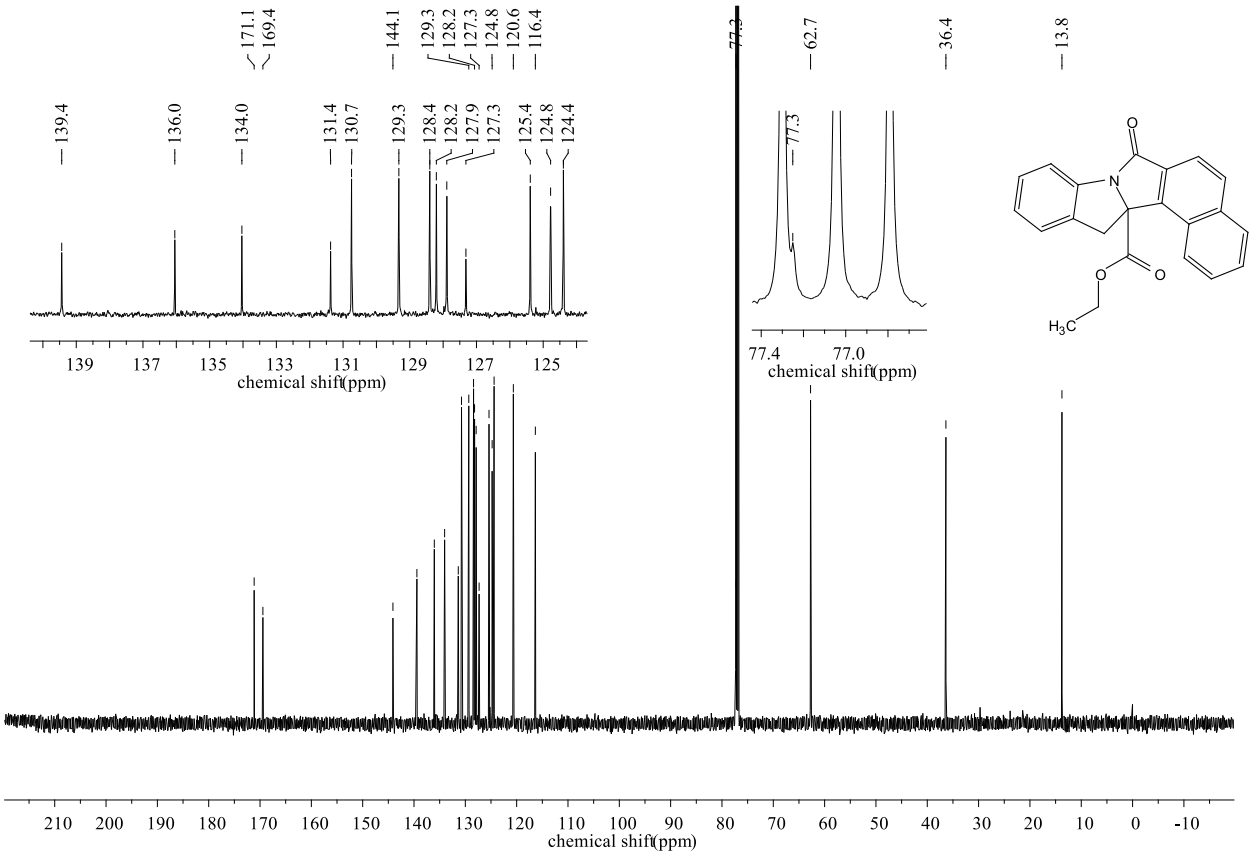
^{13}C NMR Spectra of compound **39** (125 MHz, $CDCl_3$)



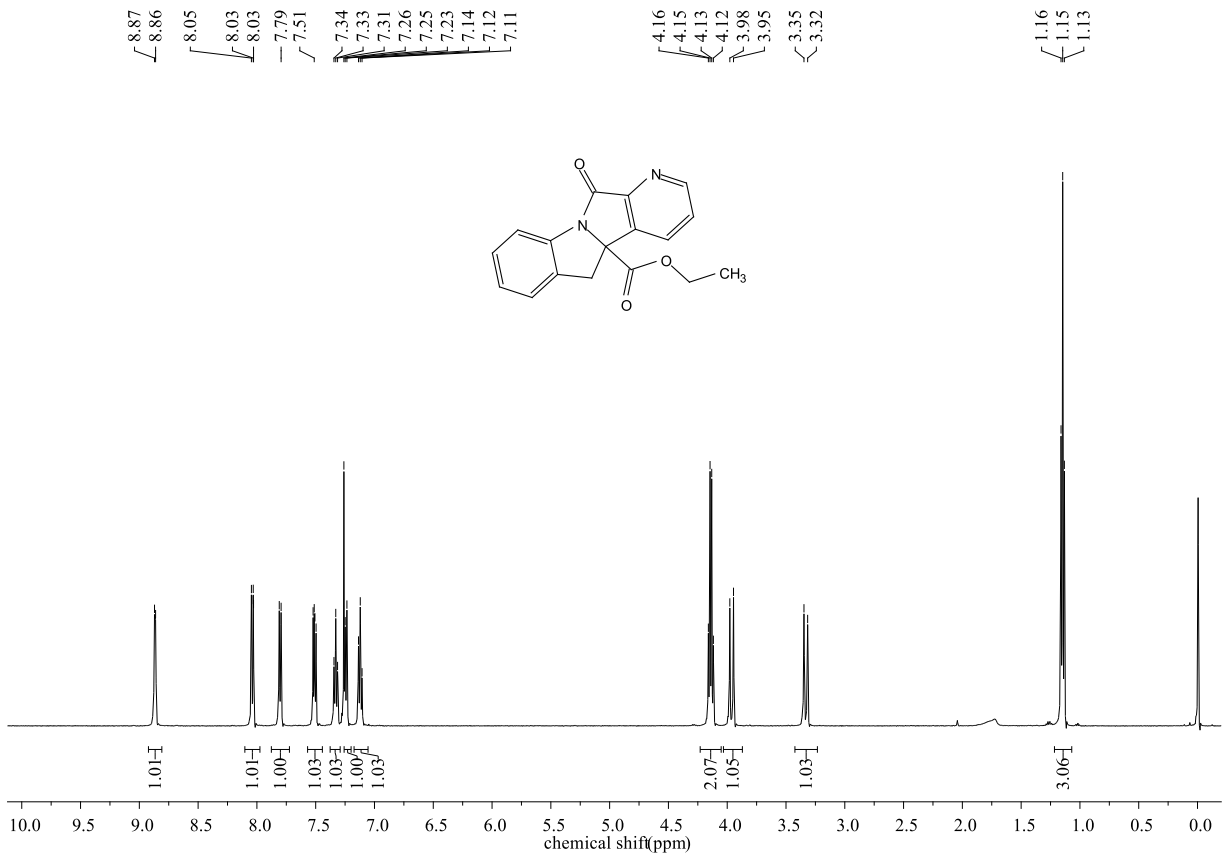
^{1}H NMR Spectra of compound **40** (500 MHz, $CDCl_3$)



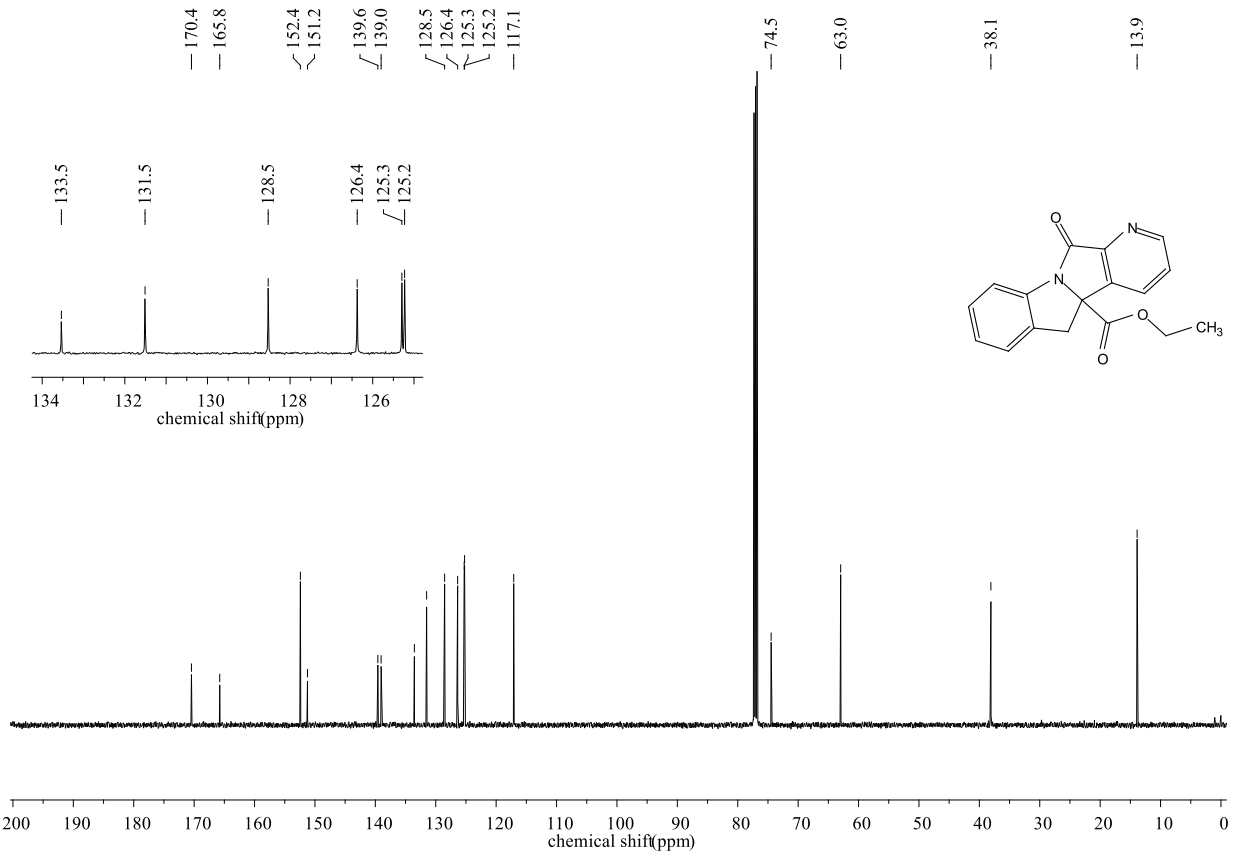
^{13}C NMR Spectra of compound **40** (125 MHz, $CDCl_3$)



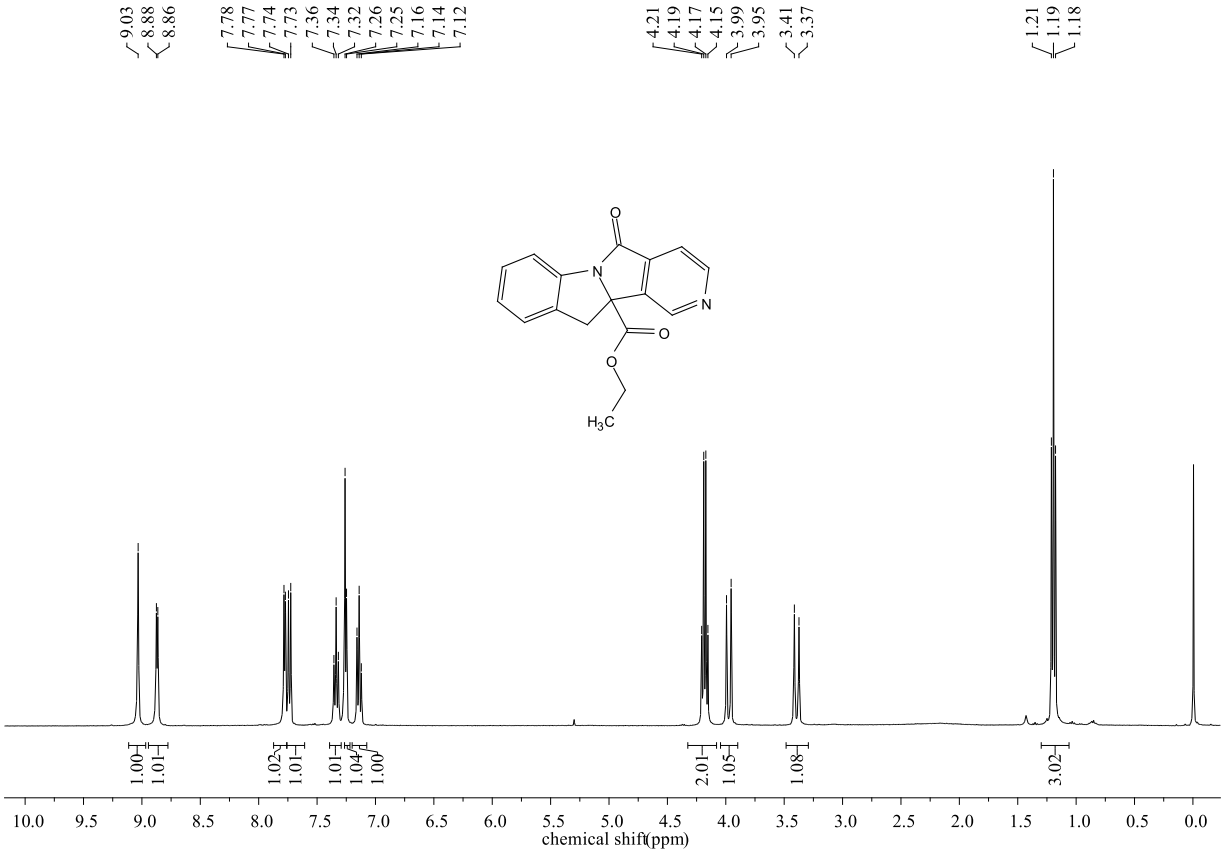
^{1}H NMR Spectra of compound **41** (500 MHz, $CDCl_3$)



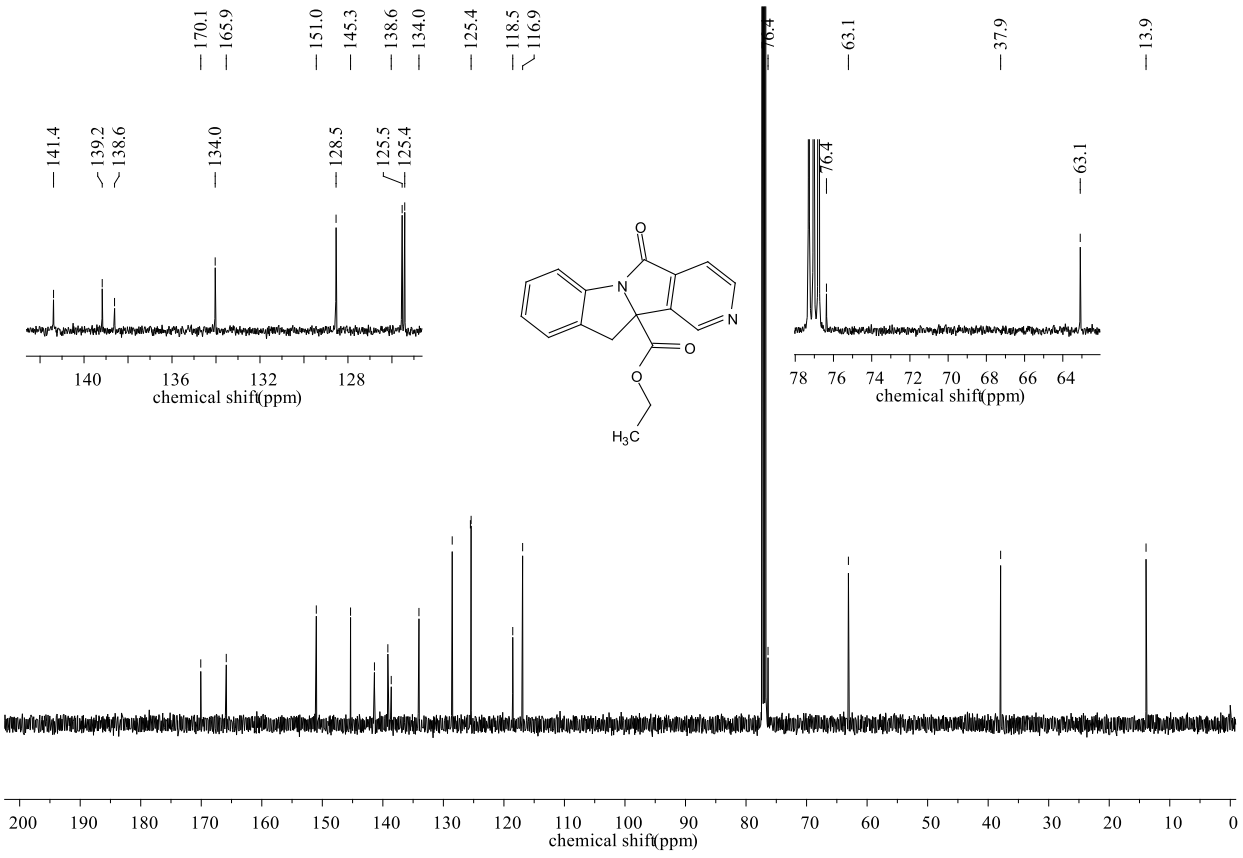
^{13}C NMR Spectra of compound **41** (125 MHz, $CDCl_3$)



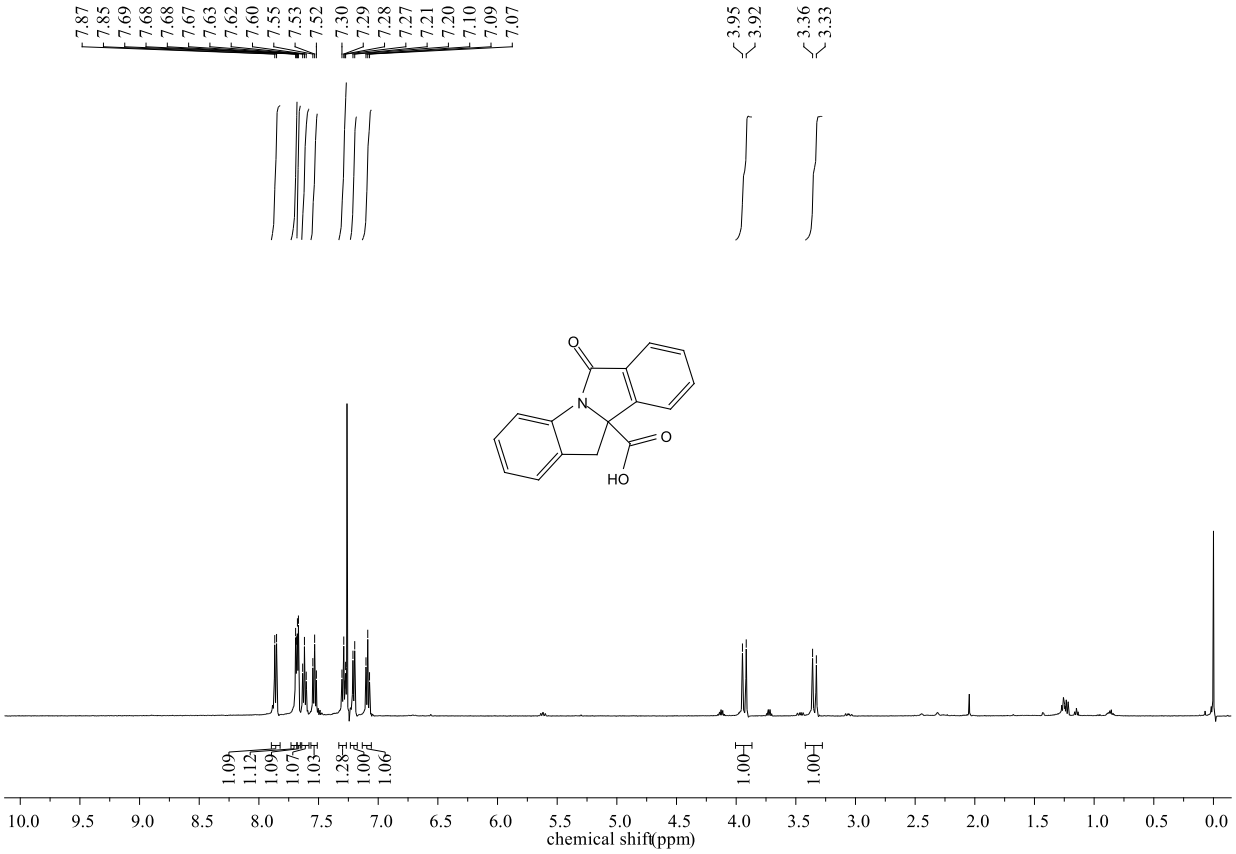
^{1}H NMR Spectra of compound **42** (400 MHz, $CDCl_3$)



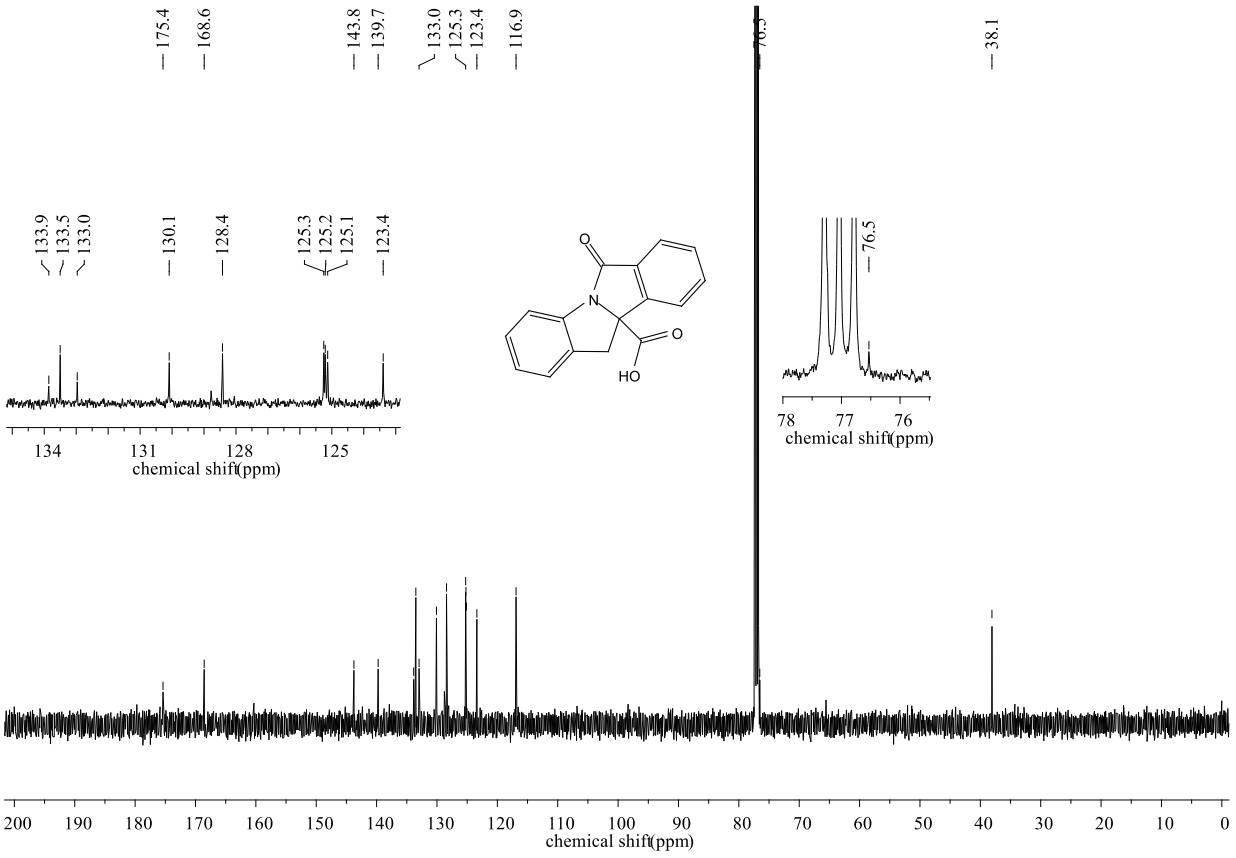
^{13}C NMR Spectra of compound **42** (125 MHz, $CDCl_3$)



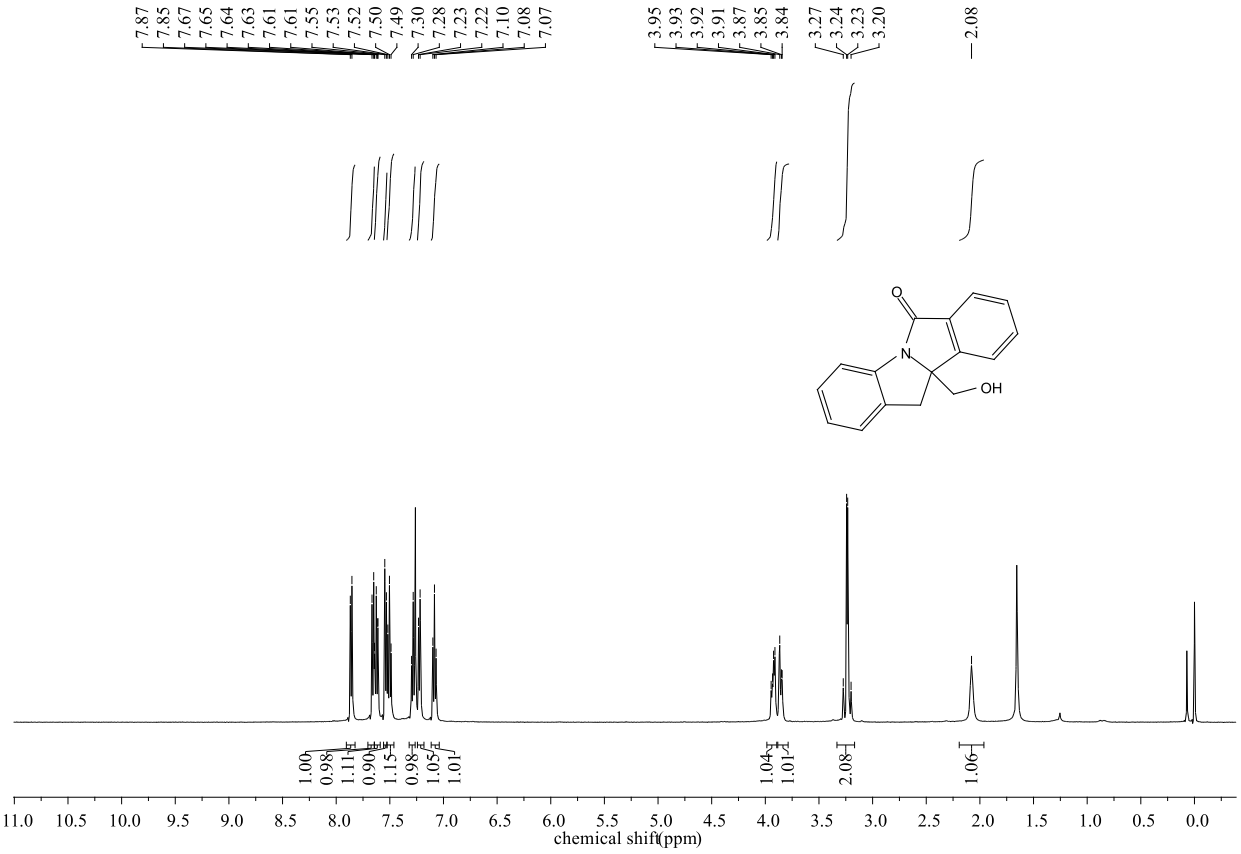
^{1}H NMR Spectra of compound **45** (500 MHz, $CDCl_3$)



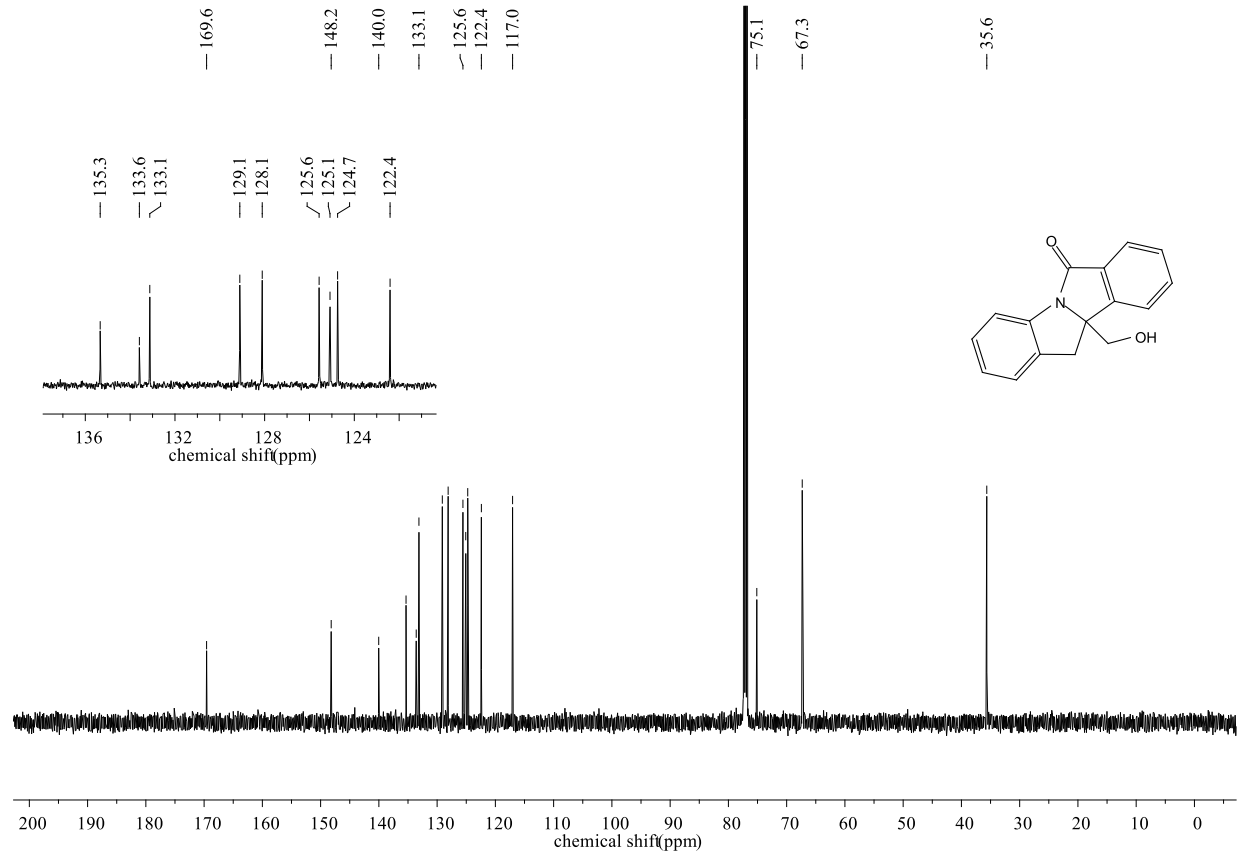
^{13}C NMR Spectra of compound **45** (125 MHz, $CDCl_3$)



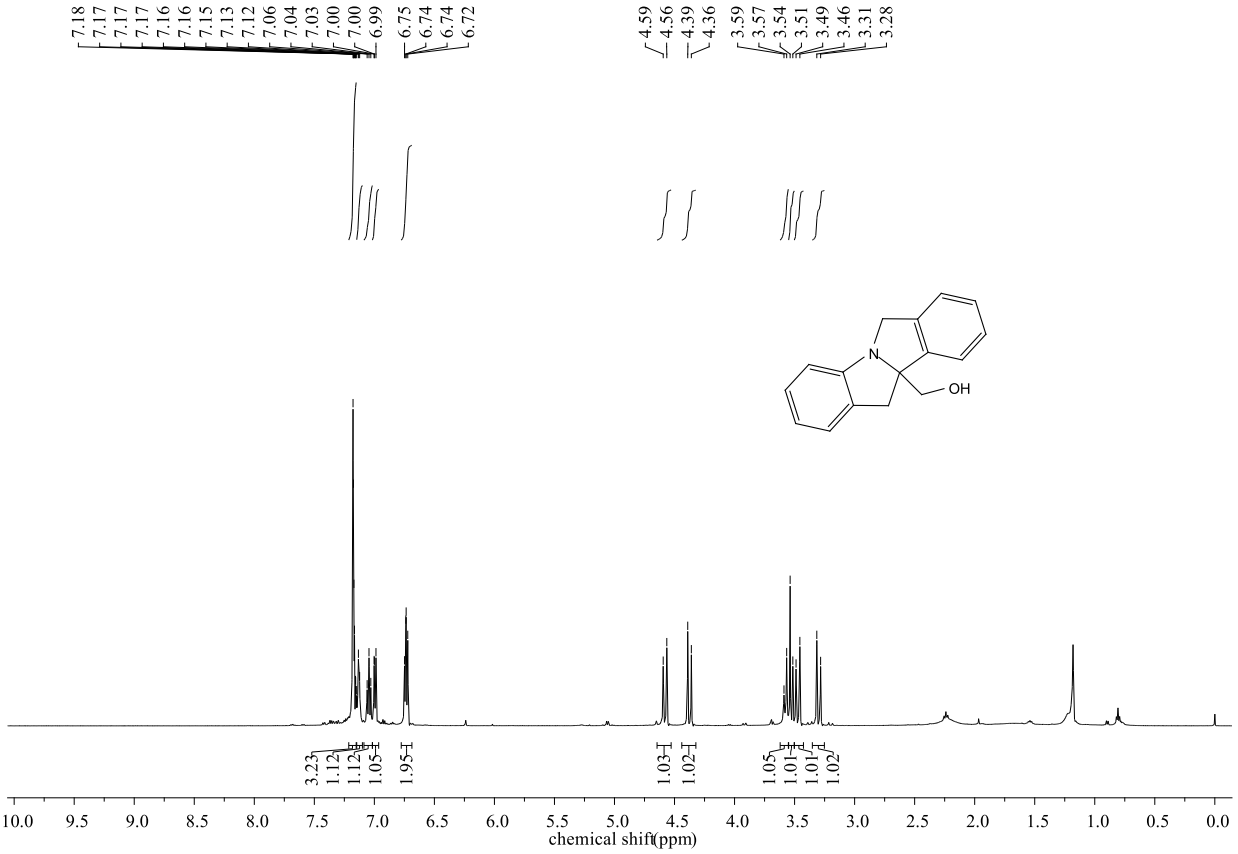
^{1}H NMR Spectra of compound **46** (500 MHz, $CDCl_3$)



^{13}C NMR Spectra of compound **46** (125 MHz, $CDCl_3$)



^{1}H NMR Spectra of compound **47** (500 MHz, $CDCl_3$)



^{13}C NMR Spectra of compound **47** (125 MHz, $CDCl_3$)