

Supplementary Information

Dearomative Difunctionalization of arenes via Highly Selective Radical Relay Reactions

Ning Lei^{1,4}, Qian Zhang^{2,4}, Pan Tao¹, Cong Lu¹, Qian Lei³, Ke Zheng^{1,*}

¹ Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China.

² Department of Obstetrics and Gynecology, Key Laboratory of Birth Defects and Related Diseases of Women and Children of MOE, State Key Laboratory of Biotherapy, West China Second Hospital, Sichuan University and Collaborative Innovation Center, Chengdu, P. R. China.

³ Department of Respiratory and Critical Care Medicine, West China Hospital and Targeted Tracer Research and Development Laboratory, Precision Medicine Key Laboratory of Sichuan Province & Precision Medicine Center, West China Hospital, Sichuan University, Chengdu, P. R. China

⁴ These authors contributed equally to this work

*Correspondence author: E-mail: kzheng@scu.edu.cn (K.Z.)

Table of content

1 General Experiment Details	3
2 Standard Reaction Setup	3
3 Reaction Optimization and General Procedure	4
General procedure for dearomative reaction	4
4 The Application of the Reaction	5
4.1 General procedure for batch photoreactions.	5
4.2 Biological verification.....	6
4.3 Attempts at stereoselectivity of the reaction	8
4.4 Unsuccessful substrate	11
5 Mechanistic Studies	11
5.1 UV-vis absorption spectrum.....	11
5.2 Control Experiments	12
5.2.1 Reaction in dark	12
5.2.2 Reaction in dark at 90 °C	12
5.2.3 Reaction in the presence of TEMPO as the radical scavengers (evidence for the formation of alkyl or benzyl radical via SET).....	13
6 Substrate Synthesis	15
6.1 Synthetic route to <i>N</i> -Boc-3-Arylindolin-2-one ^[2]	15
6.2 Synthetic route to 3-Phenylbenzofuran-2(3H)-one ^[3]	16
6.3 Synthetic route to oxazolone.....	17
6.4 Synthetic route to acids.....	17
6.5 Synthetic route to redox-active esters (RAEs)	18
7 X-ray crystallography	19
8 Analytical Data of Compounds	23
9 NMR spectra	52
10 References.....	132

1 General Experiment Details

All required fine chemicals were used directly without purification unless stated otherwise. All air and moisture sensitive reactions were carried out under nitrogen atmosphere using standard Schlenk manifold technique. All solvents were bought from *J&K Scientific* as 99.9% purity under 4 Å molecular sieves. Other commercial reagents were purchased from Adamas, TCI, Aldrich, Bidepharm and Alfa. Reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F-254 plates. Flash chromatography columns were packed with 200-300 mesh silica gel. NMR-spectra were recorded on BRUKER AVANCE III HD 400 or 600 spectrometers. All spectral data was acquired at 295 K. Deuterated solvents were purchased from Adamas. ^1H and ^{13}C chemicals shifts (δ) are quoted in parts per million (ppm) against tetramethylsilane (TMS, $\delta = 0.00$ ppm) and were internally referenced to residual CHCl_3 (7.26 ppm for ^1H , 77.16 ppm for ^{13}C) or DMSO (2.50 ppm for ^1H , 39.52 ppm for ^{13}C). ^{19}F chemicals shifts (δ) are quoted in parts per million (ppm) and were calibrated using absolute referencing to the ^1H NMR spectrum. Coupling constants (J) are reported in Hertz (Hz) to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, br = broad, m = multiplet. High-resolution mass spectra (HRMS) were recorded on a UPLC of Thermo Q Exactive Focus. UV-Vis absorption spectra were recorded using 1 cm quartz cuvettes on a Thermo NANODROP 2000C Spectrophotometer. Fluorescence spectra were recorded using 1 cm quartz cuvettes on a HORIBA Fluoromax-4 Spectrofluorometer at 25 °C.

2 Standard Reaction Setup

The setup (shown below **Figure S1**) is employed to photochemical organic synthesis reaction, which is made up of separable base and reaction hole. The integrated light panel with certain wavelength can be embedded into the sliding groove of the base. Due to the hollow design, the reaction can be kept at an ideal temperature through cold or hot medium. In a typical reaction, Schlenk tube was inserted into the hole and the reaction mixture is irradiated under 10 W LEDs light with 1.0 cm distance.

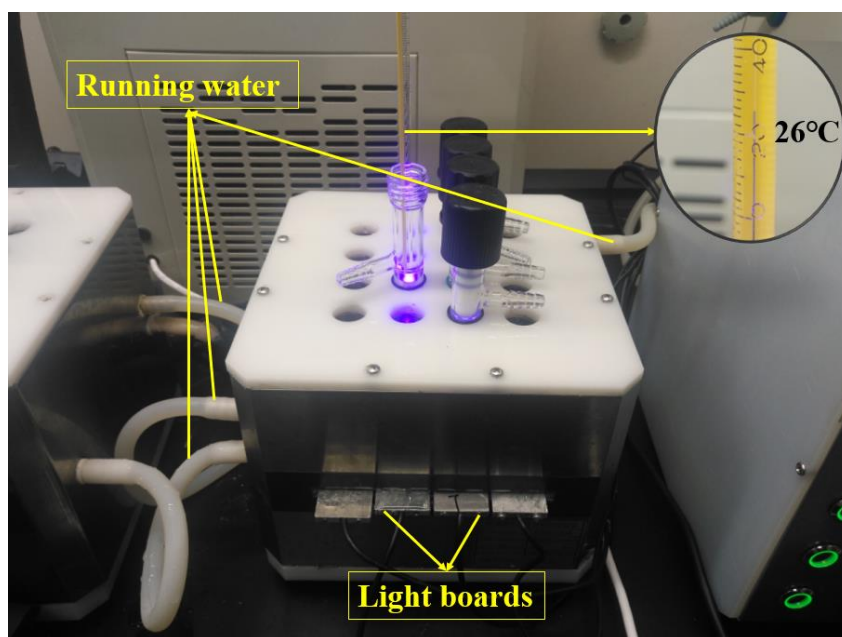
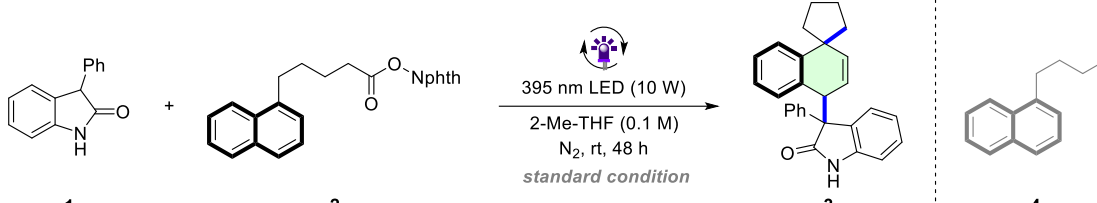


Figure S1. 16-hole parallel photoreactor (PhotoSyn 3.0)

3 Reaction Optimization and General Procedure

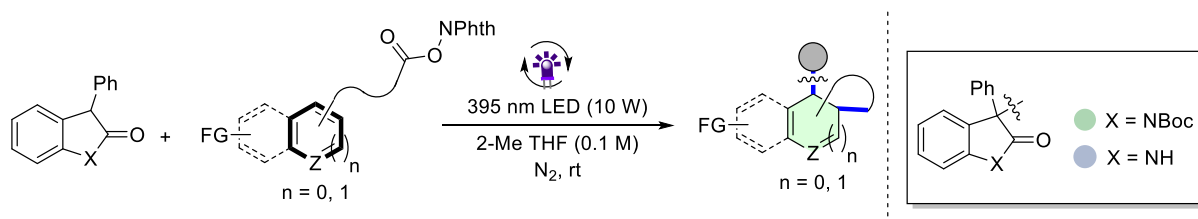
Table S1. Additional optimization of reaction conditions.^[a]



Entry	Deviation from standard conditions	Yield ^[b] (%) 3	Yield ^[b] (%) 4
1	no change	91	48
2	CH ₂ Cl ₂ instead of 2-Me-THF	trace	trace
3	THF instead of 2-Me-THF	84	50
4	CH ₃ CN instead of 2-Me-THF	79	54
5	DMSO instead of 2-Me-THF	32	43
6	410 nm instead of 395 nm	82	45
7	415 nm instead of 395 nm	74	57
8	440 nm instead of 395 nm	trace	trace
9	10 °C instead of 25 °C	78	51
10	40 °C instead of 25 °C	85	50
11	2-Me-THF (0.05) instead of 2-Me-THF (0.1)	61	53
12	2-Me-THF (0.2) instead of 2-Me-THF (0.1)	86	50
13	1.5 equiv instead of 2.0 equiv 2	76	46
14	no light, in dark	0	0
15	no light, 60 °C	0	0
16	Air instead of N ₂	82	48

[a] Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol) in 2-Me-THF (0.1 M), irradiation with a 10 W purple LED (395 nm) under N₂ atmosphere at room temperature for 48 h. [b] Isolated yield.

General procedure for dearomative reaction



Procedure A: An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the oxindoles (0.1mmol, 1.0 equiv.) and the appropriate redox-active esters (0.2 mmol, 2.0 equiv). Then, the mixture of anhydrous 2-Me-THF (0.1M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10 W LED lamp (395 nm) for 48 h. After complete consumption of oxindole, the mixture was diluted with ethyl acetate (EA, 20 mL), then washed with 2 M NaOH aqueous solution (20 mL x 3) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash

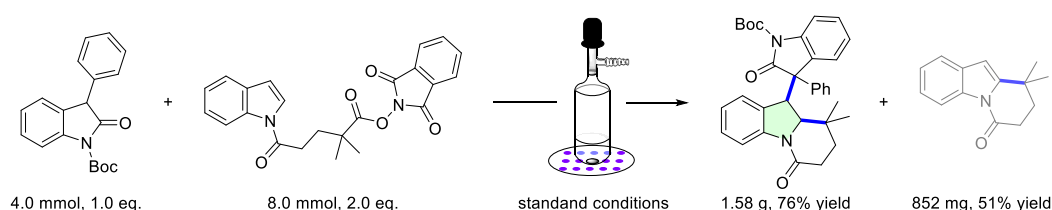
chromatography (petroleum ether/ EA = 5/1) to afford the product.

Procedure B: An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the oxindoles (0.3mmol, 1.0 equiv.) and the appropriate redox-active esters (0.6 mmol, 2.0 equiv). Then, the mixture of anhydrous 2-Me-THF (3.0 ml, 0.1M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10 W LED lamp (395 nm) for 48 h. After complete consumption of oxindole, the mixture was diluted with ethyl acetate (EA, 20 mL), then washed with 2 M NaOH aqueous solution (20 mL x 3) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ EA = 5/1) to afford the product.

Note: if the NPhth was contained in product, pretreatment was employed upon completion according to reported literature. After completion, diluted with ethyl acetate (EA) (15 mL), and then washed with NaOH (10% in water) for three times (ACS Catal. 2018, 8, 9537)¹ Organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography.

4 The Application of the Reaction

4.1 General procedure for batch photoreactions.



An oven-dried 100-mL Schlenk tube equipped with a stirrer was charged with the oxindole (4.0 mmol, 1.0 equiv.) and the appropriate redox-active esters (8.0 mmol, 2.0 equiv). Then, the mixture of anhydrous 2-Me-THF (0.1M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction mixture was inserted into the photo-large-scale reactor and irradiated using a 60 W LED lamp (395 nm) for 48 h. After complete consumption of oxindole, the mixture was diluted with ethyl acetate (EA, 100 mL), then washed with 2 M NaOH aqueous solution (80 mL x 3) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/EA = 5/1) to afford the product.

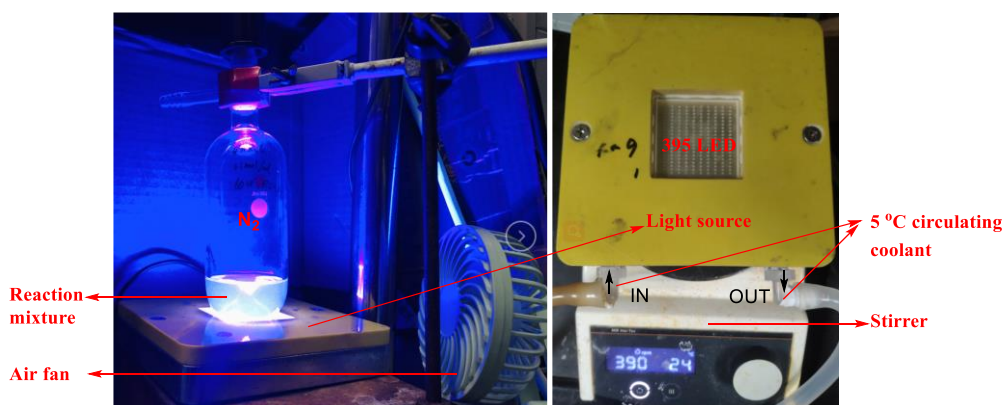


Figure S2. Photo-large-scale reactor

4.2 Biological verification

Cell lines and cell culture:

Murine MC38 colorectal cancer, human HCT116 colorectal cancer and human 293T renal epithelial cell line were obtained from the state key laboratory of biotherapy Sichuan university. 293T and MC38 cells were maintained in DMEM (Life Technologies, Gibco) supplemented with 10% fetal bovine serum (Life Technologies, Gibco), 100 U/mL of penicillin, and 100 mg/mL of streptomycin (Life Technologies). HCT116 cells were maintained in RPMI-1640 Medium (Life Technologies) supplemented with 10% fetal bovine serum (Life Technologies, Gibco), 100 U/mL of penicillin, and 100 mg/mL of streptomycin (Life Technologies, Gibco).

Mouse strains:

All animal studies were reviewed and approved by the Institutional Ethics Committee of Sichuan University. Female C57BL/6J (Six- to eight-week-old) mice and BALB/c nude (Six- to eight-week-old) mice were purchased from Gempharmatech Co., Ltd (Chengdu, China). These mice were housed in a specific-pathogen-free (SPF) environment with a consistent room temperature and humidity.

CCK8 assay:

Cell growth was assessed using the CCK8 assay. Briefly, HCT116 cells (2×10^3 cells/well) were seeded in 96-well plates. The next day, each compound tested was serially diluted in the appropriate medium, and 10 μ L of the diluted solution containing the tested compound was added to the appropriate wells of the cell plate. After 36 h, 10 μ L of CCK8 solution was added to each well and incubated for 1.5 h. The absorbance was measured at a wavelength of 450 nm with a microplate reader. The inhibition rate was calculated as follows: cell viability % = $(A_{\text{treated}} - A_{\text{blank}}) / (A_{\text{control}} - A_{\text{blank}}) \times 100\%$. Numerical IC₅₀ values were generated using non-linear best-fit regression analysis using Prism 6 software (GraphPad; San Diego, CA). Antitumor activity of compounds **34**, **53a** and **53b** was shown in table S2. Excitingly, compound **53b** showed the most impressive antitumor activity. We also determined the inhibitory effect of **53b** on human 293T (2×10^3 cells/well). **53b** exhibits a side effect on these tumor cells with 36 μ M IC₅₀ values. Compared with HCT116 cells (at 22 μ M of **53b**, the viability of normal cells exceeds 80%), 293T cells were less sensitive to **53b**, indicating that the concentration of **53b** used for tumor suppression had less effect on normal cells and no significant hepatotoxicity.

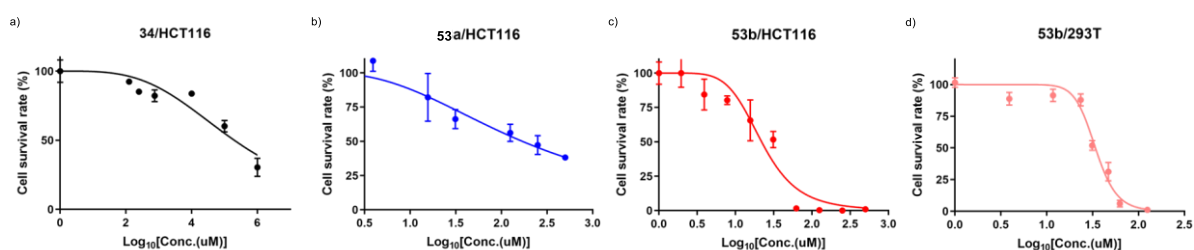


Figure S3. IC₅₀ values of **34**, **53a**, **53b** for HCT116 and 293T cells

Antitumor activity of HCT116

Compounds	34	isomer 53a	isomer 53b
Antitumor activity of HCT 116 (μ M)	>500	>150	21.98 ± 0.52

Table S2. Antitumor activity of HCT116

Antitumor effect of **53b** in mice. Detail information of mouse experiment details: Mice were randomly

divided into two groups (n = 6). MC38 cells were prepared as 5×10^6 /mL cell suspension under aseptic conditions. Then cells were injected subcutaneously into the right subcutaneous area of each mouse (0.1 mL). After 5 days (the average tumor size was 50 mm³), every mouse was orally administered with 0.3 mg **53b** in 0.1 mL PBS every other day in experiment group. And every mouse was orally administered with 0.1 mL PBS every two days in blank group. Tumor volume was assessed every two days. When all animals were euthanized, the tumor weight and volume were measured.

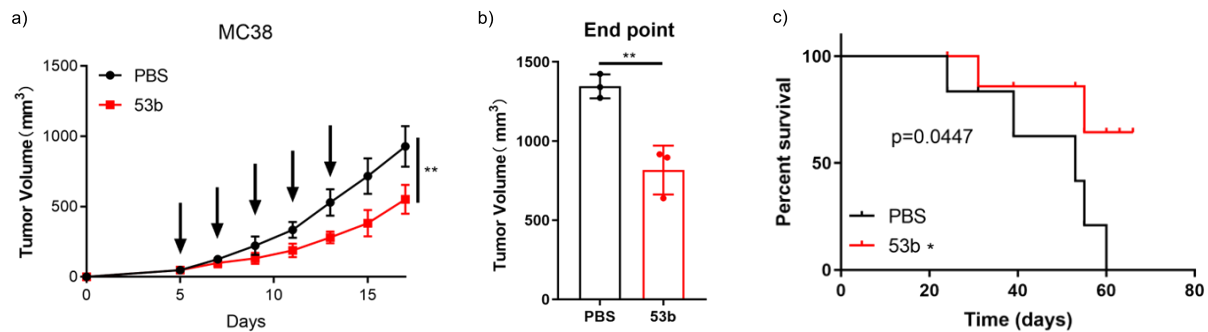


Figure S4. Tumor growth curves and survival cycles of mice with cancer in experimental and control groups

On the thirteen days after tumor vaccination, every mouse was orally administered with 0.3 mg **53b** in 0.1 mL PBS every other day for 5 consecutive times. Fortunately, tumor growth was significantly reduced and survival was better compared to control tumors.

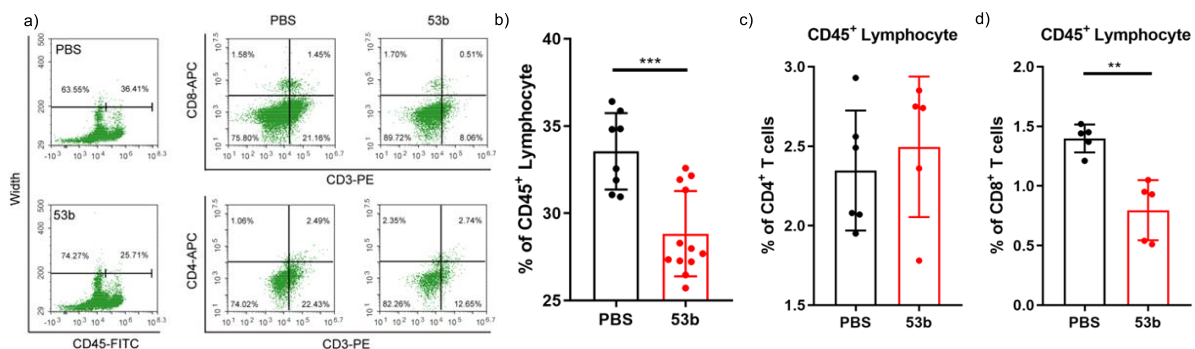


Figure S5. the number of tumor-infiltrating lymphocytes (TILs) after the last dose

We analyzed the number of tumor-infiltrating lymphocytes (TILs) after the last dose. We found that after **53b** treatment, the number of intratumor lymphocytes decreased, and there was no significant difference in the number of CD4⁺ T cells in TILs, but the number of CD8⁺ T cells decreased. Typical CD8⁺ T cells have significant anti-tumor effects, yet despite their presence, the tumor continues to grow. At present, we have only preliminarily detected a decrease in the total number of CD8⁺ T cells in the tumors treated with 49b. Recent studies have found that CD8⁺ T cells include a variety of subtypes, each with different effector functions and cytotoxic potential. We speculated that **53b** may inhibit tumor growth by changing the composition of immune cells in the tumor microenvironment or the anti-tumor function.

53b toxicity analysis

We evaluated the toxicity of **53b** by immunohistochemical analysis of the kidneys and liver of tumor-bearing mice. The kidneys of sacrificed mice were fixed and paraffin embedded, and subsequently used for HE staining. HE staining showed no significant changes in the morphology and distribution of liver and kidney tissue cells in PBS group and **53b** group, indicating that **53b** had no obvious toxic effects on the liver and kidney of mice.

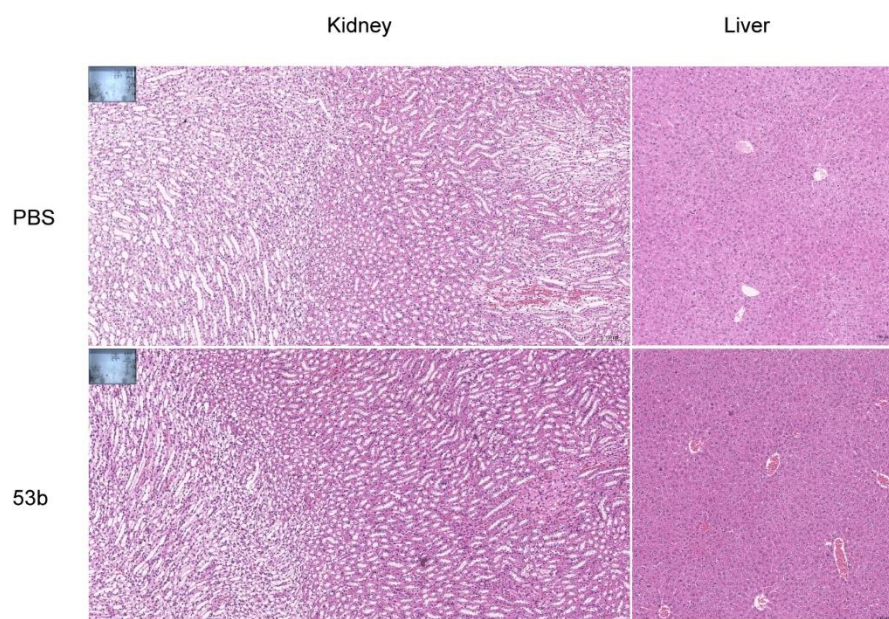
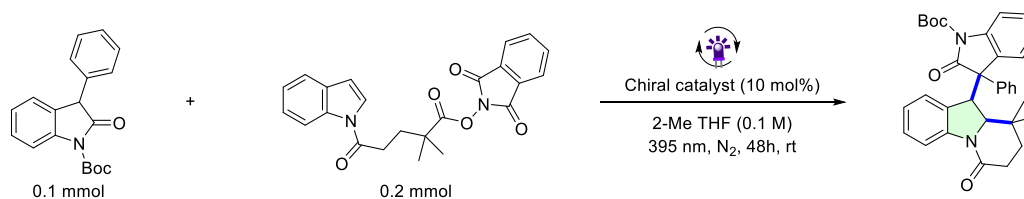
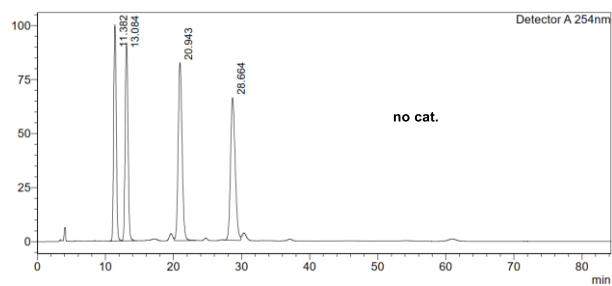


Figure S6. immunohistochemical analysis of the kidneys and liver of tumor-bearing mice for the toxicity of **53b**

4.3 Attempts at stereoselectivity of the reaction

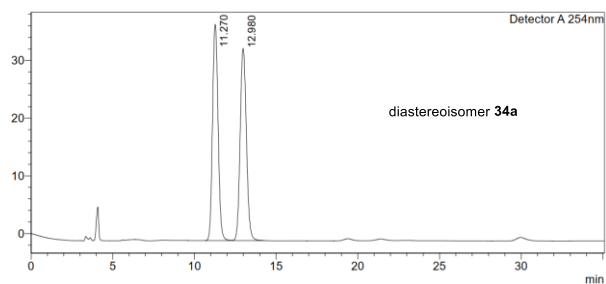


An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the oxindoles (0.1mmol, 1.0 equiv.), chiral catalyst (10 mol%) and the appropriate redox-active esters (0.2 mmol, 2.0 equiv). Then, the mixture of anhydrous 2-Me-THF (0.1M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10W LED lamp (395 nm) for 48 h. After complete consumption of indolone, the mixture was diluted with ethyl acetate (EA, 20 mL), then washed with 2 M NaOH aqueous solution (20 mL x 3) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ EA = 5/1) to afford the product. The enantiomeric excess of **34** was by HPLC analysis (Chiralpak IA column, hexane/ i-PrOH, 95: 5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 37 °C), tR1 (major) = 11.144 min, tR2 (major) = 12.834 min, tR1 (minor) = 20.699 min, tR2 (minor) = 28.202 min.



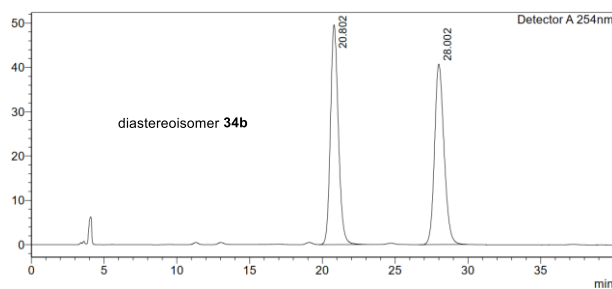
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Conc.	Unit	Mark
1	11.382	2677729	100114	22.732	0.000		M
2	13.084	2698301	91305	22.906	0.000		V M
3	20.943	3291849	82171	27.945	0.000		M
4	28.664	3111830	65952	26.417	0.000		M
Total		11779709	339543	100.000			



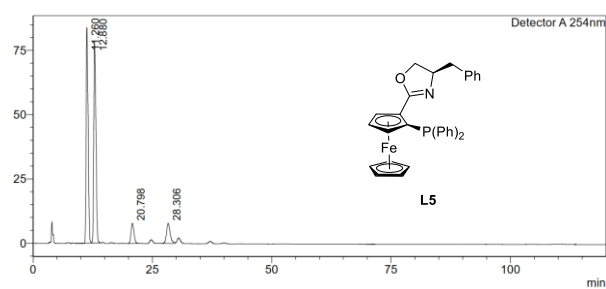
<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Conc.	Unit	Mark
1	11.270	886185	37467	49.980	0.000		
2	12.980	886898	33277	50.020	0.000		V
Total		1773083	70744	100.000			



<Peak Table>

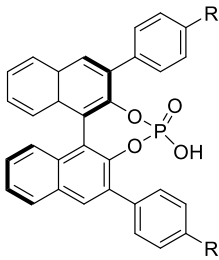
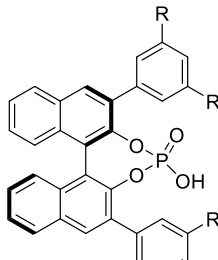
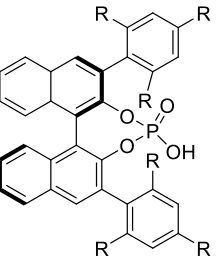
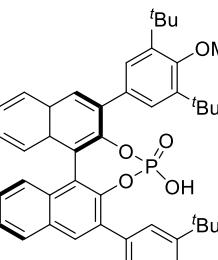
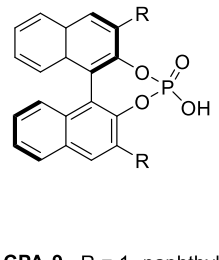
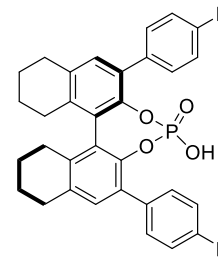
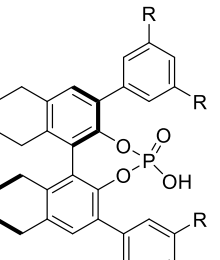
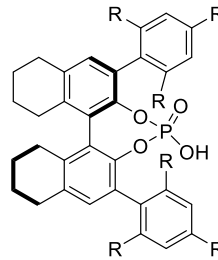
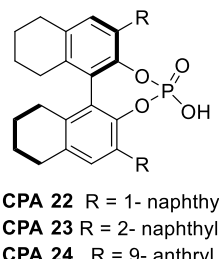
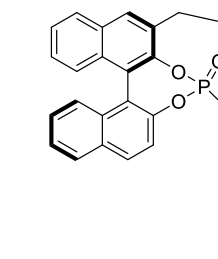
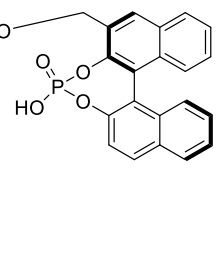
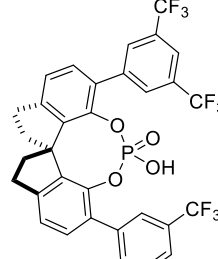
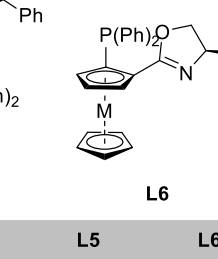
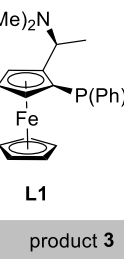
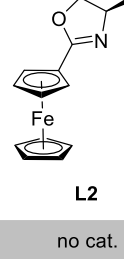
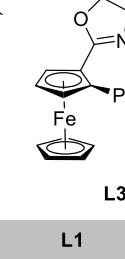
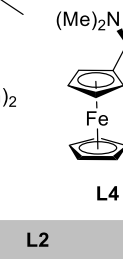
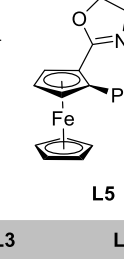
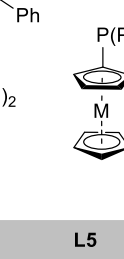
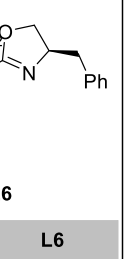
Peak#	Ret. Time	Area	Height	Area%	Conc.	Unit	Mark
1	20.802	1882103	49581	50.366	50.366		
2	28.002	1854786	40752	49.634	49.634		
Total		3736889	90333	100.000			



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Conc.	Unit	Mark
1	11.260	2409684	83733	42.651	42.651		M
2	12.880	2490130	78466	44.075	44.075		V M
3	20.798	328398	7796	5.813	5.813		
4	28.306	421601	7865	7.462	7.462		
Total		5649813	177860	100.000			

Figure S7. HPLC analysis of **34**, isomer **34a**, isomer **34b**

							
CPA 1 R = CF ₃ CPA 2 R = ^t Bu	CPA 3 R = CF ₃ CPA 4 R = Me	CPA 5 R = CH ₃ CPA 6 R = <i>ipr</i> CPA 7 R = Cy	CPA 8				
							
CPA 9 R = 1- naphthyl CPA 10 R = 2- naphthyl CPA 11 R = 9- anthryl CPA 12 R = 2- perylene CPA 13 R = Si(Ph) ₃	CPA 14 R = CF ₃ CPA 15 R = ^t Bu CPA 16 R = NO ₂	CPA 17 R = CF ₃ CPA 18 R = Me	CPA 19 R = CH ₃ CPA 20 R = <i>ipr</i> CPA 21 R = Cy				
							
CPA 22 R = 1- naphthyl CPA 23 R = 2- naphthyl CPA 24 R = 9- anthryl CPA 25 R = 2- perylene CPA 26 R = Si(Ph) ₃ CPA 27 R = 3-trifluoromethyl phenyl		CPA 28	 CPA 29				
							
L1	L2	L3	L4	L5	L6	L6	
product 3	no cat.	L1	L2	L3	L4	L5	L6
Yield (%)	88	78	68	53	84	55	60
<i>d.r.</i>	1:1	4:1	4:1	7:1	4:1	7:1	1:3

4.4 Unsuccessful substrate

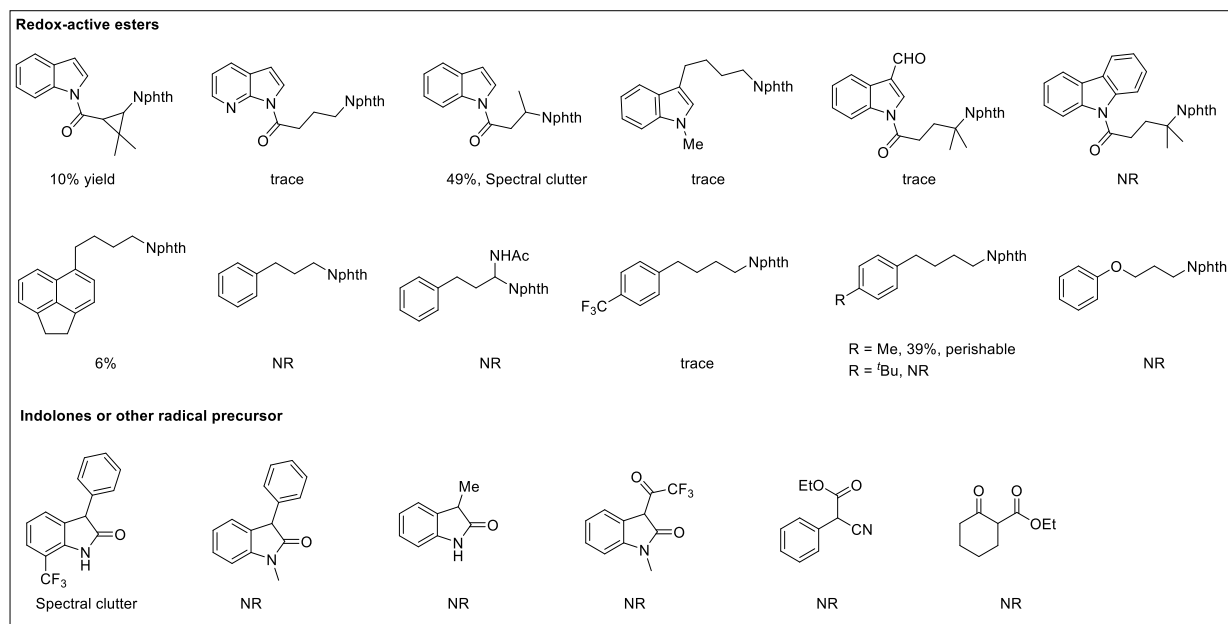


Figure S9. Unsuccessful substrates

5 Mechanistic Studies

5.1 UV-vis absorption spectrum

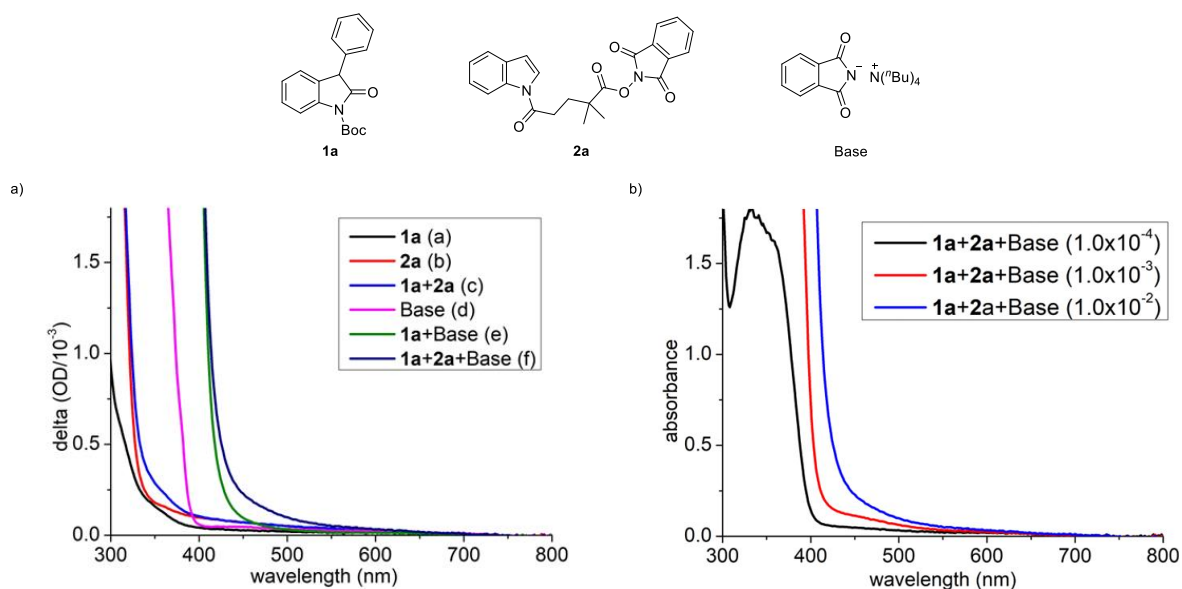


Figure S10. UV- Vis absorption spectra of Indolone **1a**, NHPI ester **2a** and base with 2-Me-THF (0.01 M)

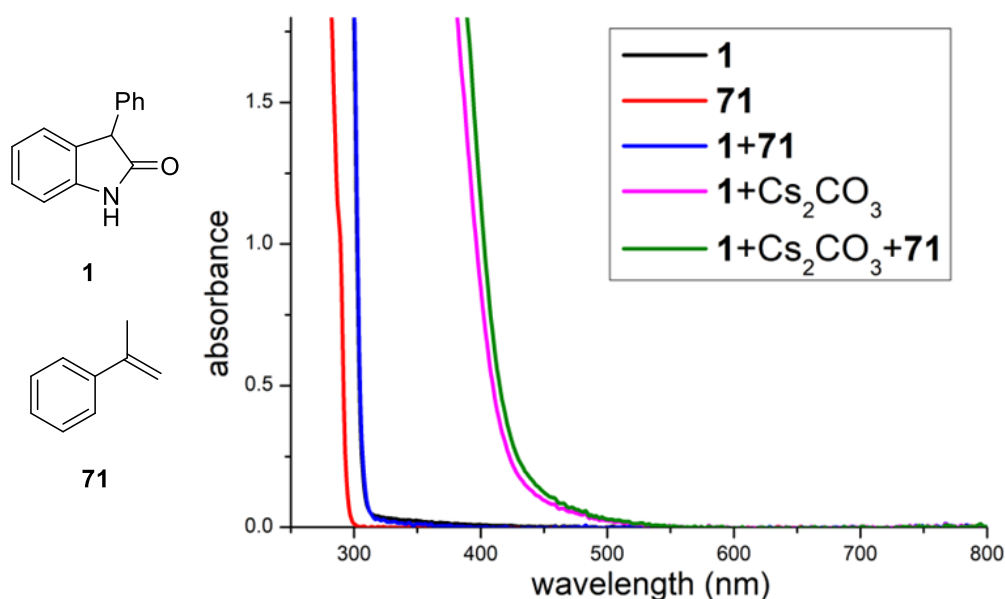
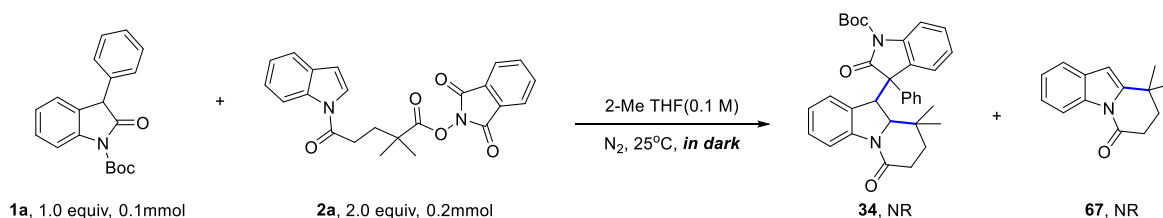


Figure 11. UV- Vis absorption spectra of **1**, **71** and Cs_2CO_3 with $\text{CH}_3\text{CN}:\text{H}_2\text{O} = 9:1$ (V: V) (0.01 M)

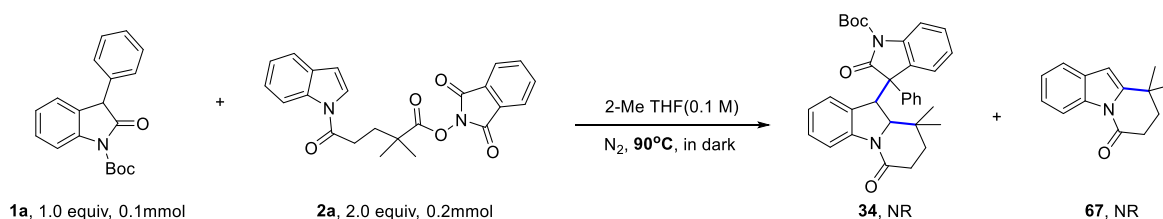
5.2 Control Experiments

5.2.1 Reaction in dark



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1a** (0.1mmol, 1.0 equiv.) and RAE **2a** (0.2 mmol, 2.0 equiv). Then, the solvent anhydrous 2-Me-THF (0.1M) was added in glove box. The tube was sealed with a screw cap and took out form glove box, and stirred in the dark for 24 h. TLC analysis revealed that no reaction occurred.

5.2.2 Reaction in dark at 90 °C

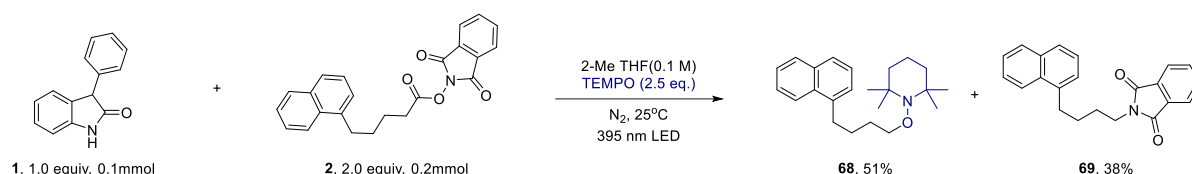


An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1a** (0.1mmol, 1.0 equiv) and RAE **2a** (0.2 mmol, 2.0 equiv). Then, the solvent anhydrous 2-Me-THF (0.1M) was added in glove

box. The tube was sealed with a screw cap and took out from glove box, and stirred in the dark for at 90 °C for 24 h. TLC analysis revealed that no reaction occurred.

5.2.3 Reaction in the presence of TEMPO as the radical scavengers (evidence for the formation of alkyl or benzyl radical via SET)

To verify radical mechanism of this transformation, the radical trapping experiment was carried out as shown in below. When 2.5 equiv. TEMPO was added to this system, no cross-coupling product **3** was detected and the radical trap product **68** were isolated in middle yield, providing direct evidence for the formation of a transient benzyl radical by SET process as a key intermediate in the catalytic cycle. Meanwhile, the amination product **69** was also isolated in 38% yield.



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1** (0.1 mmol, 1.0 equiv), RAE **2** (0.2 mmol, 2.0 equiv) and TEMPO (0.25 mmol, 2.5 equiv). Then, the solvent anhydrous 2-Me-THF (0.1 M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10W LED lamp (395 nm) for 48 h. Then the mixture was diluted with 1 N NaOH aqueous solution (15 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. TLC analysis revealed that no radical-cross-coupling product **3** was formed. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether/ ethyl acetate 20: 1) provided adduct **68** (34.8 mg, 51%) and **69** (25.0 mg, 38%).

2,2,6,6-tetramethyl-1-(4-(naphthalen-1-yl)butoxy)piperidine (**68**)

Physical state: white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 3.14 (q, *J* = 4.5, 4.0 Hz, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 1.94 – 1.80 (m, 4H), 1.79 – 1.37 (m, 7H), 1.11 (d, *J* = 35.2 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 138.19, 133.92, 131.84, 128.79, 126.65, 125.98, 125.78, 125.54, 125.45, 123.79, 59.93, 38.99, 32.92, 32.82, 32.02, 30.51, 25.41, 20.54, 16.99.

HRMS (ESI) calcd for C₂₃H₃₃NO (M+H)⁺: 340.2635, found: 340.2635.

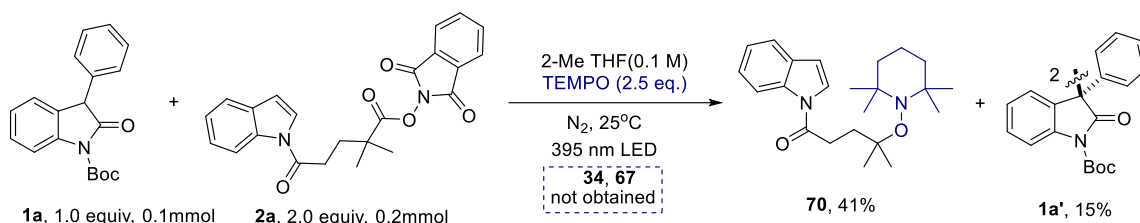
2-(4-(naphthalen-1-yl)butyl)isoindoline-1,3-dione (**69**)

Physical state: white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.53 (dddd, *J* = 19.8, 8.0, 6.8, 1.4 Hz, 2H), 7.47 – 7.40 (m, 1H), 7.37 (d, *J* = 5.7 Hz, 1H), 3.16 (d, *J* = 7.1 Hz, 2H), 2.81 – 2.69 (m, 2H), 2.04 – 1.90 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 169.50, 161.99, 137.79, 134.76, 133.93, 131.81, 128.95, 128.82, 126.76, 126.04, 125.87, 125.57, 125.49, 123.98, 123.73, 32.55, 30.91, 29.80, 24.72.

HRMS (ESI) calcd for C₂₂H₁₉NO₂ (M+H)⁺: 330.1489, found: 330.1490.



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1a** (0.1 mmol, 1.0 equiv), RAE **2a** (0.2 mmol, 2.0 equiv) and TEMPO (0.25 mmol, 2.5 equiv). Then, the solvent anhydrous 2-Me-THF (0.1 M) was added in glove box. The tube was sealed with a screw cap and took out form glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10 W LED lamp (395 nm) for 48 h. Then the mixture was diluted with 1 N NaOH aqueous solution (15 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. TLC analysis revealed that no radical-cross-coupling product **34** was formed. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether/ ethyl acetate 20: 1) provided adduct **70** (30.1 mg, 41%) and **1a'** (9.2 mg, 15%).

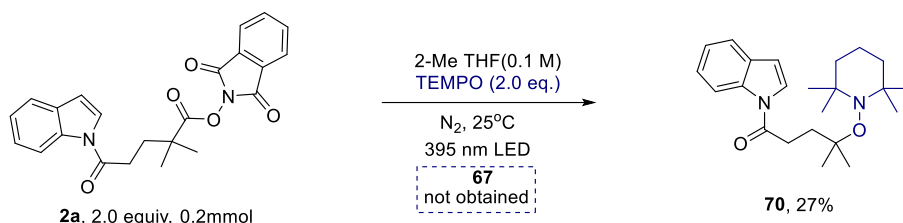
1-(1H-indol-1-yl)-4-methyl-4-((2,2,6,6-tetramethylpiperidin-1-yl) oxy) pentan-1-one (**70**)

Physical state: white solid.

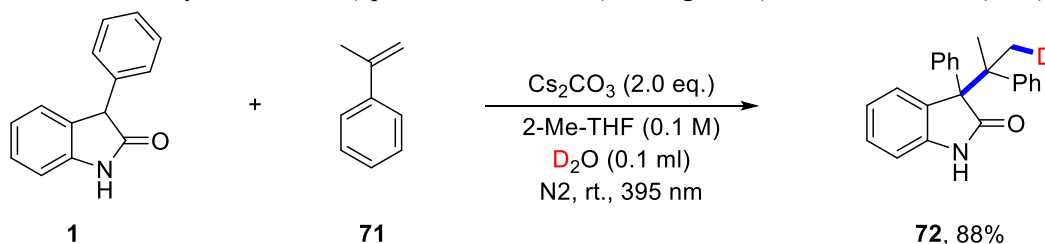
¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 3.8 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 3.08 – 2.89 (m, 2H), 2.21 – 2.03 (m, 2H), 1.87 – 1.49 (m, 6H), 1.37 (s, 6H), 1.18 (s, 6H), 1.07 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 176.38, 171.62, 135.63, 130.49, 125.42, 125.01, 123.64, 120.77, 116.64, 109.32, 60.25, 42.23, 39.07, 35.78, 32.59, 31.98, 25.79, 20.77, 16.93.

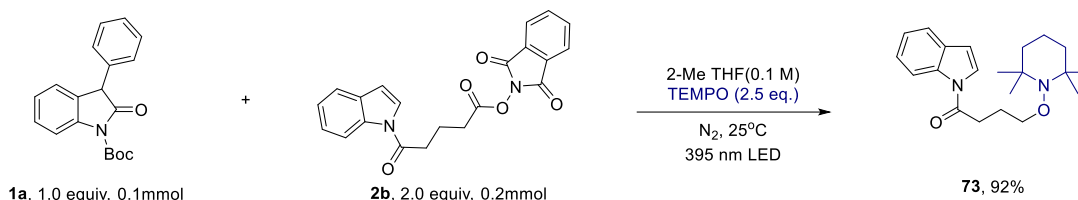
HRMS (ESI) calcd for C₂₃H₃₄N₂O₂ (M+Na)⁺: 371.2693, found: 371.2694.



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with RAE **2a** (0.2 mmol, 1.0 equiv) and TEMPO (0.40 mmol, 2.0 equiv). Then, the solvent anhydrous 2-Me-THF (0.1 M) was added in glove box. The tube was sealed with a screw cap and took out form glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10W LED lamp (395 nm) for 6 days. Then the mixture was diluted with 1 N NaOH aqueous solution (15 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. TLC analysis revealed that no cyclization product **67** was formed. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether/ ethyl acetate 20: 1) provided adduct **70** (10.0 mg, 27%) and recovered **2a** (67%).



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1** (0.1 mmol, 1.0 equiv), 2-Phenyl-1-propene **71** (0.2 mmol, 2.0 equiv) and Cs₂CO₃ (0.2mmol, 2.0 equiv). Then, the solvent anhydrous 2-Me-THF (0.1 M) and D₂O (0.1ml) were added in glove box. The tube was sealed with a screw cap and took out form glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10W LED lamp (395 nm) for 24 h. Then the mixture was diluted with water, then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether/ ethyl acetate 5: 1) provided adduct **72** (28.9 mg, 88%).



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1a** (0.1 mmol, 1.0 equiv), RAE **2b** (0.2 mmol, 2.0 equiv) and TEMPO (0.25 mmol, 2.5 equiv). Then, the solvent anhydrous 2-Me-THF (0.1 M) was added in glove box. The tube was sealed with a screw cap and took out form glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10W LED lamp (395 nm) for 48 h. Then the mixture was diluted with 1 N NaOH aqueous solution (15 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. TLC analysis revealed that no radical-cross-coupling product **28** was formed. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether/ ethyl acetate 20: 1) provided adduct **73** (60.7 mg, 41%).

1-(1H-indol-1-yl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butan-1-one (**73**)

Physical state: white solid.

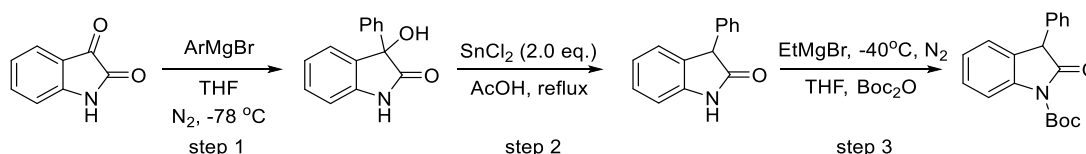
¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 3.8 Hz, 1H), 7.33 (t, J = 7.1 Hz, 1H), 7.30 – 7.22 (m, 1H), 6.63 (d, J = 3.8 Hz, 1H), 3.28 (t, J = 6.7 Hz, 2H), 2.89 (t, J = 6.6 Hz, 2H), 1.75 – 1.58 (m, 1H), 1.53 (m, 2H), 1.40 (m, 1H), 1.13 (d, J = 24.4 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 169.70, 135.65, 130.35, 125.13, 124.40, 123.70, 120.87, 116.55, 109.42, 60.17, 39.08, 31.95, 30.75, 27.06, 20.52, 16.96.

HRMS (ESI) calcd for C₂₁H₃₀N₂O₂ (M+Na)⁺: 343.2380, found: 343.2382.

6 Substrate Synthesis

6.1 Synthetic route to *N*-Boc-3-Arylindolin-2-one ^[2]



According to the reported literature

Step 1: (1) Preparation for Aryl Grignard reagent: a 50 mL round-bottomed flask was equipped with a magnetic stir bar, to a stirring mixture of magnesium (1.2 equiv) and a small piece of iodine in dry THF (1.0 M). A solution of aryl bromide (1.0 equiv) in 2 mL of dry THF was added dropwise to the round-bottom flask and stirred for 3

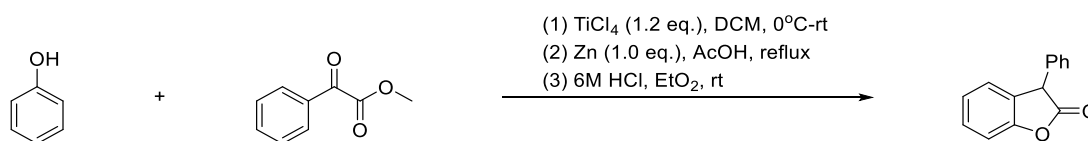
h under N₂ atmosphere. After the formation of Grignard reagent (colorless to brownish-green), the reaction mixture was cooled to 0 °C.

(2) Another 50 mL round-bottomed flask was equipped with a magnetic stir bar, to a stirring isatin (10.0 mmol) in dried THF (20 mL), then cooled to -40 °C for 30 min. Previously obtained Grignard reagent in THF (2.0 equiv) was added dropwise to the reaction mixture under N₂ atmosphere, then the mixture was allowed to warm to room temperature and stirred until isatin was consumed completely. The reaction mixture was diluted with ether, cooled in an ice-bath, and then quenched with HCl (2 M). The aqueous layer was extracted with ether, combined organic layers and washed with water and brine, then dried over with Na₂SO₄, filtered and concentrated in vacuo, 3-hydroxy-3-arylindolin-2-one was obtained as solid and no purification was necessary for further transformation.

Step 2: A 50 mL round-bottomed flask was equipped with a magnetic stir bar, to a stirring the crude product (5.0 mmol) obtained above in AcOH/ HCl (30 mL/ 2 ml), then SnCl₂ (10.0 mmol) was added at room temperature. The mixture was heated to reflux, monitored by TLC until the completely consumption of the starting material. Next, the solution was cooled to room temperature, concentrated in vacuo, and diluted with EtOAc. The residue was washed with water (3x), saturated aqueous NaHCO₃, and brine. The organic layer was dried with anhydrous Na₂SO₄, filtered and concentrated in vacuo. The residue was recrystallized (EtOAc/PE) to afford corresponding product as white solid.

Step 3: a 25 mL round-bottomed flask was equipped with a magnetic stir bar, put the product obtained above (2.0 mmol) into flask and seal, and then replaced with nitrogen (3x), THF (8 mL) was added and stirred under 0 °C for 30 min. EtMgBr Grignard reagent in THF (2.0 equiv) was added dropwise to the reaction mixture, then stirred for 2h under 0°C. A solution of Boc₂O (1.2 equiv) in 5 mL of dry THF was added dropwise to the round-bottom flask and stirred for 30 min. Then stirred at room temperature for 3h. The residue was quenched with water, then washed with DCM, dried over with Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (PE/ EtOAc, 10:1) to afford N-Boc-3-Arylindolin-2-one.

6.2 Synthetic route to 3-Phenylbenzofuran-2(3H)-one ^[3]

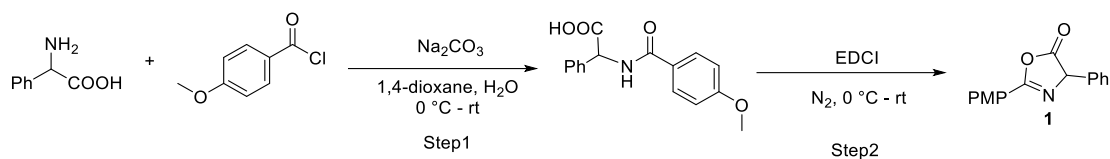


(1) A 50 mL round-bottomed flask was equipped with a magnetic stir bar, to stirring phenol (5.0 mmol, 470 mg) in DCM (20 mL) at room temperature, then TiCl₄ (0.66 mL, 6.0 mmol, 1.2 equiv,) was added dropwise. Methyl phenylglyoxylate (0.54 mL, 6.0 mmol, 1.2 equiv) was added dropwise to the reaction mixture at 0 °C, the mixture was allowed to warm to room temperature and stirred for 2 h.

(2) AcOH (3.0 mL) and Zn (325 mg, 5.0mmol, 1.0 equiv,) were added, and the mixture heated at reflux for 3 h.

(3) The reaction mixture was filtrated in vacuo, the residue was added 6 M HCl (2 mL), Et₂O (3 mL) and stirred at room temperature for 3 h. After the reaction was completed, the reaction mixture was extracted with EtOAc (3x) and the combined organic phases were dried over with Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (PE/EtOAc, 50:1) to afford 3-Phenylbenzofuran-2(3H)-one (*Org. Chem.Front.* **2019**, 6, 3969-3972).

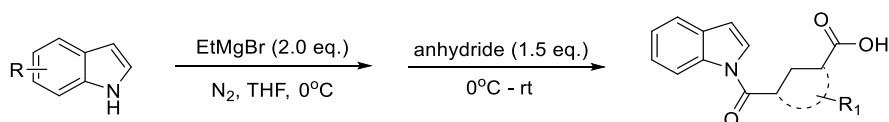
6.3 Synthetic route to oxazolone



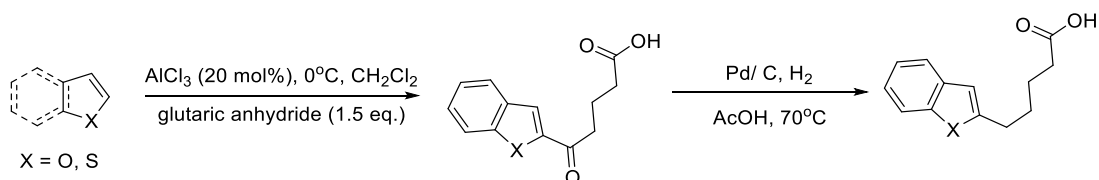
Step 1: 2-Amino-2-phenylacetic acid (1.0 equiv) and Na_2CO_3 (3.4 equiv) was added to round bottom flask equipped with a stirring bar. The reaction mixture was dissolved in 1,4-dioxane (0.50 M) and H_2O (0.18 M). After cooled to 0 °C, 4-methoxybenzoyl chloride (1.1 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at room temperature. After 1 h, the reaction mixture was diluted with H_2O and CH_2Cl_2 . The aqueous layer was separated, and 1 N HCl aq was added to it until cloudy. It was extracted twice with EA, the combined organic layer was dried over Na_2SO_4 , filtered and concentrated to obtain the crude product. The crude product was purified by flash chromatography (petroleum ether/EA = 5/1) to afford the product.

Step 2: To a solution of 2-(4-methoxybenzamido)-2-phenylacetic acid in CH_2Cl_2 (0.072 M) under argon atmosphere was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.2 equiv) at 0 °C. The cooling bath was removed and the reaction mixture was stirred at room temperature. After stirring for 1 h, the reaction mixture was washed with H_2O , sat. NaHCO_3 aq and brine. The combined organic layers were dried over Na_2SO_4 and filtered. After removal of solvent under reduced pressure. The crude product was purified by flash chromatography (*Org. Lett.* **2020**, 22, 4164)¹⁷.

6.4 Synthetic route to acids



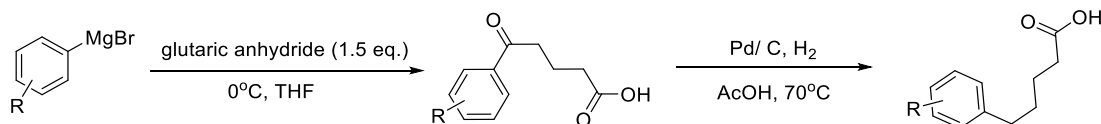
A 25 mL round-bottomed flask was equipped with a magnetic stir bar, put indoles (5.0 mmol) into flask and seal, and then replaced with nitrogen (3x), THF (8 mL) was added and stirred under 0 °C for 30 min. EtMgBr Grignard reagent in THF (2.0 equiv) was added dropwise to the reaction mixture, then stirred for 2h under 0 °C. A solution of anhydride (1.5 equiv) in 5 mL of dry THF was added dropwise to the round-bottom flask and stirred for 30 min, then stirred at room temperature for 3h. The residue was quenched with 2N HCl, then washed with DCM, dried over with Na_2SO_4 , filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (PE/ EtOAc, 5:1) to afford desired products.



Under a nitrogen atmosphere, a mixture of anhydrous aluminum chloride (8.0 g, 60 mmol) in anhydrous dichloromethane (50 mL) was stirred and cooled to -10 °C. A solution of glutaric anhydride (4.8 g, 42 mmol) and substituted arenes (40 mmol) was added dropwise to the cooled mixture with stirring. After 5h at -10 °C, the reaction mixture was poured into ice-cooled 3.5 M HCl (100 mL), and the product

was extracted into dichloromethane. The extract was washed with cold saturated aqueous sodium carbonate, and the aqueous layers were acidified and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous sodium sulfate and evaporated in vacuo without further purification to give intermediate acids as white crystal.

To a three-necked flask was added compound (10 mmol), 30 mL AcOH and Pd/C (10%) and stirred under H₂ balloon atmosphere in 70 °C. The reaction was monitored by TLC. When the reaction was completed, the reaction mixture was filtered through a Celite pad which was washed with acetic acid, then concentrated in vacuo to give the desired acid.

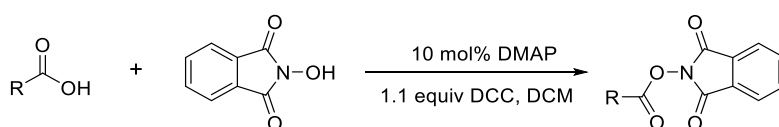


Preparation for Aryl Grignard reagent: same as above 6.1 (Step 1)

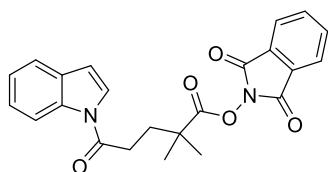
Under a nitrogen atmosphere, a mixture of glutaric anhydride (20 mmol) in anhydrous THF (20 ml) was stirred and cooled to -10 °C. A solution of Aryl Grignard reagent was added dropwise to the cooled mixture with stirring. After 5h at -10 °C, the reaction mixture was poured into ice-cooled 3.5 M HCl (50 mL), and the product was extracted into dichloromethane. The extract was washed with cold saturated aqueous sodium carbonate, and the aqueous layers were acidified and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous sodium sulfate and evaporated in vacuo without further purification to give intermediate acids as white crystal.

To a three-necked flask was added intermediate acid (10 mmol), 30 mL AcOH and Pd/C (10%) and stirred under H₂ balloon atmosphere in 70 °C. The reaction was monitored by TLC. When the reaction was completed, the reaction mixture was filtered through a Celite pad which was washed with acetic acid, then concentrated in vacuo to give the desired acid.

6.5 Synthetic route to redox-active esters (RAEs)



According to the known literature with slight modification, A round-bottom flask was added the carboxylic acid (4.0 mmol), N-hydroxyphthalimide (1.1 equiv), 4-dimethylaminopyridine (DMAP, 10 mol%), Dichloromethane (DCM) was added (15 mL), and the mixture was stirred vigorously. And then the solution of DCC (4.4 mmol in 6 mL DCM) was added dropwise via syringe at room temperature. After completed, the white precipitate was filtered off and the solution was concentrated in vacuo. Corresponding redox active esters were purified rapidly by flash column chromatography. (*Science*, **2017**, 356, 7355; *Org. Lett.* **2018**, 20, 3296)

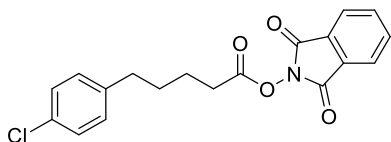


1,3-dioxoisindolin-2-yl 5-(1H-indol-1-yl)-2,2-dimethyl-5-oxopentanoate

¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, *J* = 8.2 Hz, 1H), 7.93 – 7.83 (m, 2H), 7.82 – 7.74 (m, 2H), 7.71 (d, *J* = 3.8 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 3.6 Hz, 1H), 3.30 – 3.05 (m, 2H), 2.38 – 2.23 (m, 2H), 1.52 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 173.36, 170.84, 162.11, 135.68, 134.81, 130.49, 128.91, 125.07, 125.02, 123.98, 123.68, 120.81, 116.65, 109.36, 41.58, 35.37, 31.62, 25.26.

HRMS (ESI) calcd for C₂₃H₂₀N₂O₅ (M+Na)⁺: 427.1264, found: 427.1263.

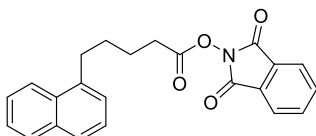


1,3-dioxoisindolin-2-yl 5-(4-chlorophenyl) pentanoate

¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.84 (m, 1H), 7.84 – 7.66 (m, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 2.84 – 2.50 (m, 2H), 1.96 – 1.62 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.41, 161.95, 140.16, 134.78, 131.58, 129.76, 128.89, 128.47, 123.95, 34.70, 30.80, 30.25, 24.17.

HRMS (ESI) calcd for C₁₉H₁₆ClNO₄ (M+Na)⁺: 380.0660, found: 380.0661.

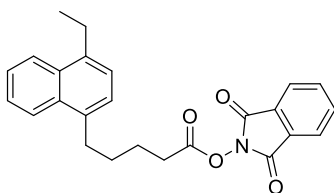


1,3-dioxoisindolin-2-yl 5-(naphthalen-1-yl) pentanoate

¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.75 (m, 1H), 7.74 – 7.68 (m, 2H), 7.67 – 7.64 (m, 1H), 7.55 (s, 1H), 7.39 – 7.29 (m, 1H), 7.26 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.83 – 2.70 (m, 1H), 2.68 – 2.56 (m, 1H), 1.85 – 1.69 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.49, 161.99, 139.24, 134.74, 133.64, 132.06, 128.93, 127.98, 127.62, 127.47, 127.24, 126.46, 125.93, 125.18, 123.95, 35.53, 30.89, 30.28, 24.30.

HRMS (ESI) calcd for C₂₃H₁₉NO₄ (M+H)⁺: 374.1387, found: 374.1391.



1,3-dioxoisindolin-2-yl 5-(4-ethylnaphthalen-1-yl) pentanoate

¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.94 (m, 2H), 7.83 – 7.74 (m, 2H), 7.70 – 7.62 (m, 2H), 7.50 – 7.37 (m, 2H), 7.19 (s, 2H), 3.10 – 2.95 (m, 4H), 2.69 – 2.59 (m, 2H), 1.93 – 1.74 (m, 4H), 1.30 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.52, 161.98, 138.69, 135.81, 134.73, 132.18, 132.07, 128.94, 125.88, 125.38, 125.29, 124.57, 124.51, 124.45, 123.94, 32.57, 30.93, 29.86, 25.90, 24.75, 15.08.

HRMS (ESI) calcd for C₂₅H₂₃NO₄ (M+Na)⁺: 424.1519, found: 424.1518.

7 X-ray crystallography

Single crystal **34a**:

The colourless crystal in block-shape, with approximate dimensions of 0.333 × 0.366 × 0.531 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II

diffractometer at 173(2)K equipped with micro-focus Cu radiation source ($K_{\alpha} = 1.54178\text{\AA}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package. [4-7] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested. [8]

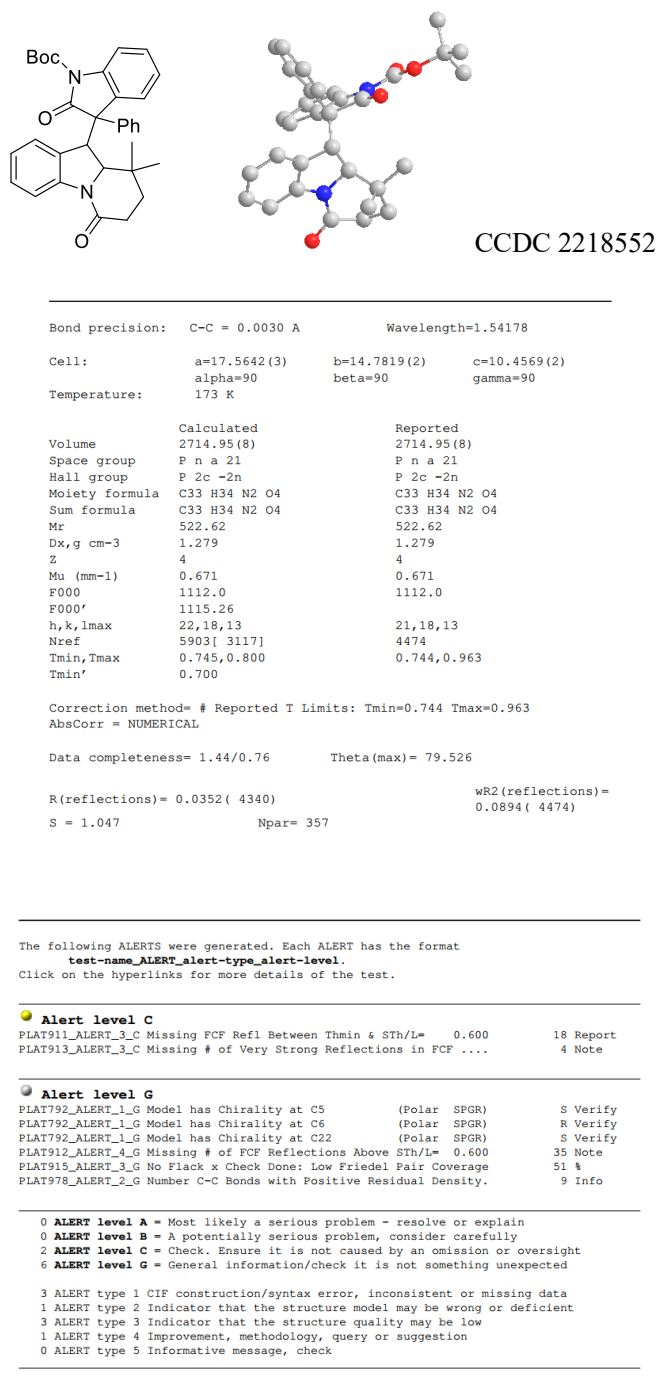
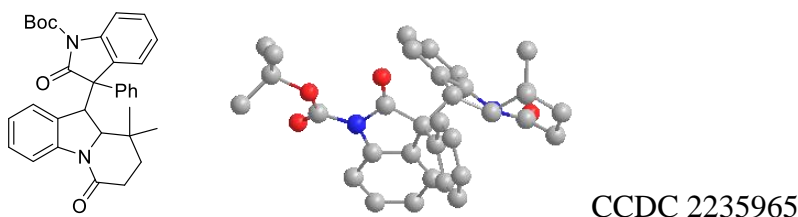


Figure 12. X-ray crystallography data of single crystal **34a**

Single crystal **34b**:

The colourless crystal in block-shape, with approximate dimensions of $0.146 \times 0.282 \times 0.424 \text{ mm}^3$, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source ($K_{\alpha} = 1.54178\text{\AA}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed

by SHELXTL (version 6.14) and OLEX 2.3 program package. [4-7] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested. [8]



Datablock: zhk016

Bond precision:	C-C = 0.0020 Å		Wavelength=1.54178
Cell:	a=18.3540(5)	b=9.4179(2)	c=18.5267(5)
	alpha=90	beta=119.6900	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	2782.03(12)	2781.97(12)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C33 H34 N2 O4	C33 H34 N2 O4	
Sum formula	C33 H34 N2 O4	C33 H34 N2 O4	
Mr	522.62	522.62	
Dx, g cm-3	1.248	1.248	
Z	4	4	
Mu (mm-1)	0.654	0.654	
F000	1112.0	1112.0	
F000'	1115.26		
h, k, lmax	22, 11, 22	22, 11, 22	
Nref	5106	5100	
Tmin, Tmax	0.801, 0.909	0.765, 1.000	
Tmin'	0.758		
Correction method= # Reported T Limits: Tmin=0.765 Tmax=1.000			
AbsCorr = NUMERICAL			
Data completeness=	0.999	Theta(max)= 68.304	
R(reflections)= 0.0390(4637)			
wR2(reflections)=			
S = 1.058	Npar= 358	0.1022(5100)	

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

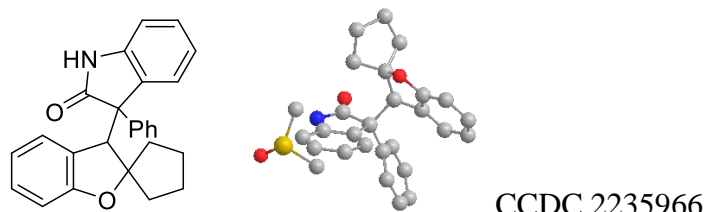
Alert level C			
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	C3 Check	
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	3 Report	
Alert level G			
PLAT145_ALERT_4_G	s.u. on beta Small or Missing	0.0000 Degree	
PLAT793_ALERT_4_G	Model has Chirality at C5 (Centro SPGR)	R Verify	
PLAT793_ALERT_4_G	Model has Chirality at C6 (Centro SPGR)	S Verify	
PLAT793_ALERT_4_G	Model has Chirality at C22 (Centro SPGR)	S Verify	
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	3 Note	
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	16 Info	

0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Figure 13. X-ray crystallography data of single crystal 34b

Single crystal 21:

The colourless crystal in block-shape, with approximate dimensions of $0.187 \times 0.187 \times 0.423$ mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 170(2)K equipped with micro-focus Cu radiation source ($K\alpha = 1.54178\text{\AA}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package. [4-7] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested. [8]



Datablock: zhk013

Bond precision:	C-C = 0.0021 Å	Wavelength=1.54178
Cell:	a=10.7923(2) alpha=90	b=15.0923(3) beta=93.717(1) c=14.4236(3) gamma=90
Temperature:	173 K	
Volume	Calculated 2344.38(8)	Reported 2344.38(8)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C26 H23 N O2, C2 H6 O S	C26 H23 N O2, C2 H6 O S
Sum formula	C28 H29 N O3 S	C28 H29 N O3 S
Mr	459.58	459.58
Dx, g cm ⁻³	1.302	1.302
Z	4	4
Mu (mm ⁻¹)	1.466	1.466
F000	976.0	976.0
F000'	979.96	
h,k,lmax	13,19,18	13,19,18
Nref	5101	4893
Tmin,Tmax	0.756,0.760	0.825,0.980
Tmin'	0.512	
Correction method=	# Reported T Limits: Tmin=0.825 Tmax=0.980	
AbsCorr =	NUMERICAL	
Data completeness=	0.959	Theta(max)= 79.529
R(reflections)=	0.0387(4340)	wR2(reflections)= 0.1171(4893)
S =	1.063	Npar= 304

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C	
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of	S1S Check
PLAT911_ALERT_3_C Missing FCF Refl Between Tmin & Sth/L= 0.600	38 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .	1 Check
PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..	1 Check
Alert level G	
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite	2 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records	1 Report
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O2	106.5 Degree
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels	6 Note
PLAT793_ALERT_4_G Model has Chirality at C2 (Centro SPGR)	R Verify
PLAT793_ALERT_4_G Model has Chirality at C26 (Centro SPGR)	S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints	1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above Sth/L= 0.600	170 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity	3.8 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	14 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by	4 Check

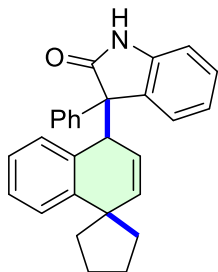
0 **ALERT level A** = Most likely a serious problem - resolve or explain
 0 **ALERT level B** = A potentially serious problem, consider carefully
 4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
 11 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 3 ALERT type 2 Indicator that the structure model may be wrong or deficient
 5 ALERT type 3 Indicator that the structure quality may be low
 6 ALERT type 4 Improvement, methodology, query or suggestion
 1 ALERT type 5 Informative message, check

Figure 14. X-ray crystallography data of single crystal 21

8 Analytical Data of Compounds

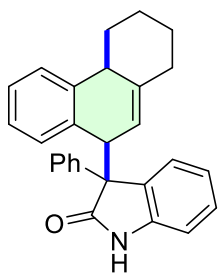
Note: The unknown impurity: Around 1.56 ppm (water peak) and 1.00 ppm – 1.42 ppm in NMR are respectively from the CDCl_3 and eluent (petroleum ether), which do not affect the yield of the product.



^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 0.5H), 8.39 (s, 0.5H), 7.73 – 7.61 (m, 1H), 7.62 – 7.52 (m, 1H), 7.49 – 7.41 (m, 1H), 7.41 – 7.27 (m, 3.5H), 7.24 – 7.12 (m, 1H), 7.12 – 6.81 (m, 3H), 6.81 – 6.70 (m, 1H), 6.66 (d, J = 7.7 Hz, 0.5H), 6.29 (d, J = 7.8 Hz, 0.5H), 5.89 – 5.76 (m, 1H), 5.74 – 5.60 (m, 1H), 5.47 (dd, J = 10.4, 3.9 Hz, 0.5H), 4.82 (d, J = 3.3 Hz, 0.5H), 4.70 (d, J = 4.2 Hz, 0.5H), 2.12 – 1.36 (m, 8H).

^{13}C NMR (101 MHz, CDCl_3) δ 181.07, 180.07, 146.33, 145.43, 141.78, 140.85, 138.74, 138.47, 138.20, 137.82, 133.02, 132.38, 129.10, 128.75, 128.54, 128.37, 128.27, 128.12, 128.10, 127.96, 127.83, 127.50, 127.45, 127.38, 127.33, 127.19, 126.91, 126.71, 126.65, 124.92, 124.40, 121.53, 121.43, 119.23, 118.93, 109.77, 109.60, 62.80, 62.15, 47.75, 47.08, 45.87, 45.83, 45.70, 45.42, 44.44, 44.11, 27.28, 26.60, 26.41, 26.39.

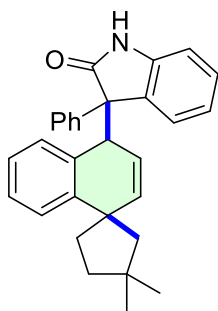
HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}$ ($\text{M}+\text{Na}$) $^+$: 414.1828, found: 414.1833.



^1H NMR (400 MHz, CDCl_3) δ 9.02 (s, 0.25H), 8.98 (s, 0.25H), 8.94 (s, 0.2H), 8.72 (s, 0.25H), 7.76 – 7.47 (m, 2H), 7.46 – 7.39 (m, 0.5H), 7.37 – 7.21 (m, 3.3H), 7.18 – 6.63 (m, 6H), 6.53 (d, J = 7.5 Hz, 0.25H), 6.34 – 6.22 (m, 0.5H), 5.77 – 5.69 (m, 0.5H), 5.65 – 5.58 (m, 0.5H), 5.45 – 5.37 (m, 0.25H), 5.35 – 5.26 (m, 0.2H), 4.87 – 4.79 (m, 0.2H), 4.77 – 4.71 (m, 0.3H), 4.71 – 4.62 (m, 0.2H), 4.60 – 4.53 (m, 0.25H), 4.31 – 3.70 (m, 0.21H), 3.05 – 2.73 (m, 0.8H), 2.40 – 0.86 (m, 8H).

^{13}C NMR (101 MHz, CDCl_3) δ 181.16, 180.74, 180.14, 180.11, 143.28, 142.21, 142.03, 141.65, 141.62, 141.27, 141.16, 141.12, 140.57, 139.67, 139.24, 138.78, 138.59, 138.19, 138.08, 132.78, 132.69, 132.32, 132.22, 129.48, 129.37, 128.74, 128.71, 128.58, 128.53, 128.39, 128.35, 128.30, 128.23, 128.14, 128.10, 127.97, 127.74, 127.71, 127.48, 127.42, 127.36, 127.31, 127.00, 126.92, 126.62, 126.51, 126.37, 126.29, 126.21, 125.44, 124.88, 121.59, 121.41, 121.20, 121.08, 117.07, 115.91, 115.73, 115.34, 109.75, 109.55, 109.47, 63.41, 63.34, 63.02, 62.53, 48.63, 48.26, 46.73, 46.39, 42.14, 41.83, 40.10, 39.12, 36.53, 36.36, 36.10, 35.98, 35.87, 35.70, 35.40, 28.69, 27.64, 27.20, 27.16, 27.05, 26.91, 26.62, 26.40.

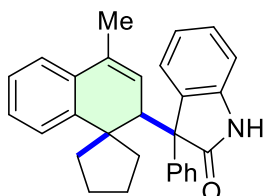
HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{NO}$ ($\text{M}+\text{Na}$) $^+$: 414.1828, found: 414.1832.



^1H NMR (400 MHz, $\text{CDCl}_3/\text{DMSO}-d_6 = 1/1$) δ 10.50 (s, 0.5H), 10.29 (s, 0.5H), 8.06 (dd, $J = 26.5, 9.1$ Hz, 0.5H), 7.73 (dd, $J = 7.5, 1.2$ Hz, 0.25H), 7.66 – 7.55 (m, 0.5H), 7.55 – 7.48 (m, 1.25H), 7.48 – 7.42 (m, 1H), 7.40 – 7.13 (m, 5.5H), 7.03 (m, 1H), 6.98 (m, 1H), 6.92 – 6.86 (m, 0.5H), 6.77 – 6.69 (m, 1H), 6.52 (d, $J = 7.7$ Hz, 0.5H), 6.20 (d, $J = 7.9$ Hz, 0.5H), 5.73 (d, $J = 8.0$ Hz, 0.5H), 5.53 (m, 0.5H), 5.41 – 5.26 (m, 0.5H), 4.62 (m, 0.5H), 4.45 (m, 0.5H), 3.05 – 2.87 (m, 1H), 2.46 – 2.27 (m, 1H), 1.95 (m, 2H), 1.83 – 1.71 (m, 0.5H), 1.42 – 1.35 (m, 0.5H), 1.27 (m, 1H), 1.07 (s, 1.5H), 0.83 (m, 4.5H).

^{13}C NMR (101 MHz, $\text{CDCl}_3/\text{DMSO}-d_6 = 1/1$) δ 179.22, 178.49, 143.13, 142.55, 141.65, 141.38, 141.30, 139.90, 138.93, 138.79, 133.11, 132.90, 129.42, 129.20, 128.88, 128.82, 128.72, 128.61, 128.57, 128.52, 128.32, 128.06, 128.00, 127.94, 127.68, 127.50, 127.34, 127.31, 127.07, 126.75, 126.55, 126.45, 126.38, 126.23, 125.57, 125.04, 121.38, 120.62, 117.40, 116.35, 109.59, 109.56, 62.90, 62.71, 48.84, 48.18, 47.97, 46.07, 44.55, 35.76, 35.01, 32.90, 32.86, 31.72, 31.40, 31.35, 31.22, 24.15, 23.78.

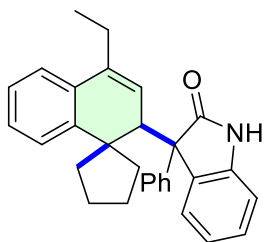
HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{29}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 420.2322, found: 420.2324.



^1H NMR (400 MHz, DMSO) δ 10.44 (s, 0.5H), 10.37 (s, 0.5H), 7.69 – 7.47 (m, 1H), 7.41 – 7.33 (m, 1H), 7.32 – 7.21 (m, 3H), 7.21 – 7.12 (m, 1H), 7.12 – 6.98 (m, 1.5H), 6.97 – 6.80 (m, 1.5H), 6.79 – 6.59 (m, 1.5H), 6.47 – 6.38 (m, 1H), 6.35 (d, $J = 8.1$ Hz, 0.5H), 6.27 – 6.11 (m, 1H), 5.77 (d, $J = 6.0$ Hz, 0.5H), 5.46 (d, $J = 6.1$ Hz, 0.5H), 3.53 – 3.41 (m, 1H), 2.31 – 1.95 (m, 1H), 1.92 (s, 1.5H), 1.84 – 1.75 (m, 1H), 1.72 (s, 1.5H), 1.70 – 0.93 (m, 7H).

^{13}C NMR (101 MHz, DMSO) δ 179.93, 178.72, 143.16, 143.04, 142.53, 141.44, 139.57, 139.45, 134.61, 134.21, 133.84, 133.55, 128.70, 128.56, 128.30, 127.80, 127.60, 127.37, 127.23, 127.01, 126.86, 126.19, 125.95, 125.17, 124.78, 124.19, 123.38, 120.10, 119.48, 109.50, 109.04, 61.04, 58.89, 53.58, 52.21, 50.89, 45.33, 45.27, 32.13, 29.44, 25.44, 24.68, 22.32, 22.09, 19.66, 19.56.

HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{27}\text{NO}$ ($\text{M}+\text{Na}$) $^+$: 428.1985, found: 428.1984.

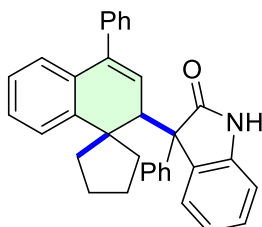


^1H NMR (400 MHz, CDCl_3) δ 8.77 – 8.34 (m, 1H), 7.78 – 7.58 (m, 1H), 7.54 – 7.45 (m, 1H), 7.37 – 7.27 (m, 1.4H), 7.25 – 7.16 (m, 1.6H), 7.16 – 6.72 (m, 5H), 6.69 (d, $J = 7.7$ Hz, 0.5H), 6.50 (d, $J = 7.6$ Hz, 1H), 6.47 – 6.40 (d, $J = 7.3$ Hz, 0.5H), 6.37 – 6.22 (m, 1H), 5.88 (d, $J = 6.1$ Hz, 0.5H), 5.49 (d, $J = 6.2$ Hz, 0.5H), 3.58 (d, $J = 6.3$ Hz, 0.5H),

3.52 (d, $J = 6.1$ Hz, 0.5H), 2.58 – 2.38 (m, 0.5H), 2.39 – 2.22 (m, 0.5H), 2.20 – 1.99 (m, 1H), 1.92 – 1.56 (m, 5H), 1.55 – 1.07 (m, 3H), 1.00 (t, $J = 7.4$ Hz, 1.5H), 0.86 (t, $J = 7.4$ Hz, 1.5H).

^{13}C NMR (101 MHz, CDCl_3) δ 181.27, 180.11, 143.60, 143.56, 141.03, 140.07, 139.73, 139.39, 138.60, 138.54, 133.83, 133.51, 128.94, 128.76, 128.29, 128.23, 128.17, 128.01, 127.55, 127.24, 127.15, 127.08, 126.96, 126.82, 126.78, 126.59, 125.74, 125.43, 125.34, 124.80, 124.39, 123.23, 122.87, 122.70, 120.62, 120.07, 109.19, 108.91, 61.53, 59.11, 53.68, 52.82, 50.79, 45.24, 45.11, 32.34, 29.76, 25.70, 25.56, 25.42, 24.87, 22.38, 22.17, 13.54, 13.15.

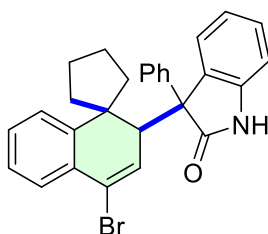
HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{29}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 420.2322, found: 420.2321.



^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.56 (s, 0.5H), 10.43 (s, 0.5H), 7.62 (s, 0.5H), 7.54 (m, 1H), 7.31 (m, 3H), 7.24 (m, 2H), 7.13 (m, 1H), 6.97 (m, 3H), 6.93 – 6.79 (m, 3H), 6.72 (m, 1H), 6.48 (d, $J = 7.8$ Hz, 0.5H), 6.41 (m, 1H), 6.30 (d, $J = 7.8$ Hz, 0.5H), 6.17 (m, 1H), 5.88 (d, $J = 6.1$ Hz, 0.5H), 5.49 (d, $J = 6.3$ Hz, 0.5H), 3.62 (d, $J = 6.4$ Hz, 1H), 3.56 (d, $J = 6.2$ Hz, 1H), 2.11 – 1.44 (m, 9H).

^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 179.83, 178.80, 143.54, 142.56, 141.32, 141.15, 140.60, 140.54, 140.46, 139.03, 138.87, 133.76, 133.35, 129.49, 128.64, 128.56, 128.41, 128.32, 128.16, 127.98, 127.70, 127.66, 127.55, 127.49, 127.41, 127.31, 127.19, 126.43, 125.86, 125.81, 125.72, 125.02, 124.68, 120.07, 119.67, 109.51, 109.04, 60.91, 58.78, 53.84, 52.78, 50.71, 50.67, 45.14, 32.15, 29.50, 25.55, 24.77, 22.52, 22.18.

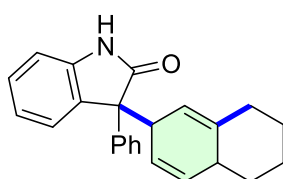
HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{29}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 468.2322, found: 468.2321.



^1H NMR (400 MHz, CDCl_3) δ 8.54 (s, 0.5H), 8.24 (s, 0.5H), 7.63 – 7.53 (m, 1H), 7.53 – 7.46 (m, 1H), 7.39 – 7.32 (m, 1H), 7.32 – 7.18 (m, 3H), 7.17 – 7.03 (m, 1H), 7.02 – 6.62 (m, 3.5H), 6.57 (d, $J = 7.6$ Hz, 0.5H), 6.20 (d, $J = 7.6$ Hz, 0.5H), 5.84 – 5.61 (m, 1H), 5.61 – 5.46 (m, 1H), 5.38 (dd, $J = 10.4, 3.9$ Hz, 0.5H), 4.74 (d, $J = 2.9$ Hz, 0.5H), 4.61 (d, $J = 4.2$ Hz, 0.5H), 2.04 – 1.31 (m, 8H).

^{13}C NMR (101 MHz, CDCl_3) δ 180.65, 179.63, 146.31, 145.45, 141.55, 140.62, 138.67, 138.40, 138.19, 137.81, 132.97, 132.35, 129.02, 128.70, 128.55, 128.37, 128.11, 128.08, 127.91, 127.80, 127.51, 127.39, 127.32, 127.19, 126.89, 126.71, 126.68, 124.89, 124.39, 121.56, 121.46, 119.17, 118.91, 109.55, 109.38, 62.67, 62.02, 47.74, 47.08, 45.86, 45.79, 45.65, 45.39, 44.43, 44.08, 27.27, 26.58, 26.39, 26.36.

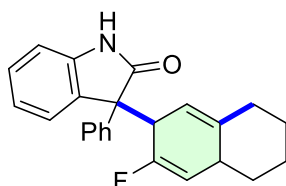
HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{24}\text{BrNO}$ ($\text{M}+\text{Na}$) $^+$: 492.0933, found: 492.0934.



¹H NMR (400 MHz, CDCl₃) δ 9.10 – 8.86 (m, 1H), 7.60 – 7.44 (m, 2H), 7.42 – 7.27 (m, 4H), 7.25 – 7.17 (m, 1H), 7.10 – 6.86 (m, 2H), 5.72 – 5.61 (m, 1H), 5.53 – 5.29 (m, 2H), 5.25 – 5.02 (m, 1H), 4.20 – 4.02 (m, 1H), 2.52 – 0.38 (m, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 180.18, 180.06, 143.04, 142.41, 142.18, 141.95, 141.37, 141.31, 141.20, 137.91, 137.84, 137.77, 137.66, 136.69, 133.44, 132.93, 132.71, 132.21, 130.20, 130.14, 130.02, 129.91, 128.57, 128.51, 128.12, 127.94, 127.91, 127.70, 127.62, 127.51, 127.37, 127.33, 127.30, 127.15, 126.35, 126.29, 122.89, 122.70, 122.34, 121.80, 121.73, 121.64, 121.51, 121.43, 120.96, 120.37, 115.53, 115.15, 114.97, 114.77, 109.89, 109.78, 61.07, 60.82, 60.68, 44.75, 44.66, 44.43, 44.29, 43.87, 43.76, 41.51, 40.94, 38.48, 38.45, 38.23, 35.88, 35.61, 35.32, 35.03, 34.97, 34.66, 28.19, 27.99, 27.78, 26.63, 26.54, 26.35, 24.62.

HRMS (ESI) calcd for C₂₄H₂₃NO (M+H)⁺: 342.1852, found: 342.1858.

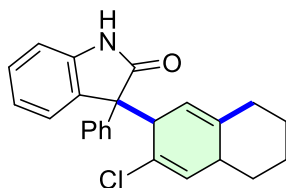


¹H NMR (400 MHz, DMSO-*d*₆) δ 10.57 (s, 0.20H), 10.53 (s, 0.19H), 10.36 (s, 0.25H), 10.34 (s, 0.25H), 7.47 – 6.81 (m, 9H), 5.36 – 4.84 (m, 2H), 4.38 – 4.03 (m, 1H), 2.61 (m, 0.5H), 2.47 – 2.15 (m, 0.6H), 2.13 – 0.80 (m, 8H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 178.64, 178.49, 178.01, 177.91, 143.13, 143.06, 142.75, 142.54, 142.52, 142.42, 142.40, 141.65, 141.63, 139.01, 138.86, 138.54, 138.31, 129.17, 128.98, 128.94, 128.88, 128.72, 128.62, 128.41, 128.32, 127.76, 127.74, 127.72, 127.64, 127.57, 127.31, 127.26, 126.46, 125.97, 121.67, 121.58, 121.33, 121.09, 115.43, 115.39, 115.31, 115.22, 115.05, 114.97, 114.81, 114.73, 114.37, 114.29, 110.18, 109.98, 109.85, 109.64, 109.50, 109.18, 109.04, 107.94, 107.80, 107.69, 107.54, 59.52, 58.67, 58.02, 45.10, 44.96, 44.91, 44.89, 44.68, 44.49, 44.40, 44.27, 44.18, 38.97, 38.89, 38.82, 38.49, 38.42, 38.05, 37.98, 35.34, 34.97, 34.89, 34.70, 34.45, 34.18, 28.40, 27.80, 27.71, 27.62, 26.03, 25.92, 25.69, 25.54.

¹⁹F NMR (377 MHz, DMSO-*d*₆) δ -104.39, -105.14, -110.23, -110.88.

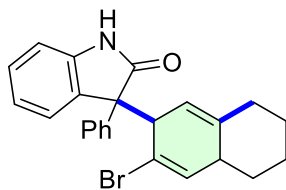
HRMS (ESI) calcd for C₂₄H₂₂FNO (M+H)⁺: 360.1758, found: 360.1759.



¹H NMR (400 MHz, CDCl₃) δ 8.52 – 8.24 (m, 1H), 7.55 – 7.40 (m, 1H), 7.39 – 7.26 (m, 1.7H), 7.25 – 7.16 (m, 3.2H), 7.14 – 6.69 (m, 3.3H), 5.71 (dd, *J* = 16.1, 3.4 Hz, 0.5H), 5.44 (dd, *J* = 28.6, 2.8 Hz, 0.5H), 5.29 – 5.18 (m, 0.5H), 5.03 – 4.87 (m, 0.5H), 4.33 – 4.03 (m, 1H), 2.63 – 2.23 (m, 1H), 2.12 – 1.70 (m, 2H), 1.63 – 0.72 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 180.74, 180.32, 179.21, 179.02, 142.32, 141.98, 141.68, 141.39, 141.16, 140.32, 138.52, 138.07, 137.94, 137.43, 133.01, 132.26, 130.79, 130.37, 129.89, 129.67, 129.13, 129.09, 128.75, 128.68, 128.59, 128.54, 128.40, 128.06, 128.03, 127.96, 127.93, 127.86, 127.68, 127.59, 127.48, 127.44, 127.32, 127.28, 127.02, 125.80, 121.77, 121.75, 121.60, 121.33, 116.90, 116.38, 115.45, 114.98, 110.17, 109.55, 60.99, 60.81, 60.05, 59.33, 50.52, 49.92, 49.44, 48.68, 41.22, 40.88, 40.23, 39.47, 34.96, 34.88, 34.68, 34.62, 34.43, 33.97, 33.72, 33.57, 28.36, 27.64, 27.41, 27.09, 26.22, 26.16, 25.79, 25.49.

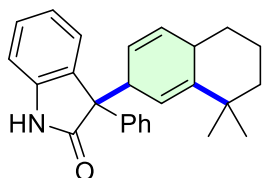
HRMS (ESI) calcd for C₂₄H₂₂ClNO (M+Na)⁺: 376.1463, found: 376.1462.



^1H NMR (400 MHz, CDCl_3) δ 8.31 (s, 0.5H), 8.27 (s, 0.5H), 7.67 – 7.52 (m, 2H), 7.52 – 7.37 (m, 1.3H), 7.36 – 7.15 (m, 4H), 7.18 – 6.97 (m, 1H), 6.87 (m, 1H), 6.11 (d, $J = 4.5$ Hz, 0.5H), 6.05 (d, $J = 2.3$ Hz, 0.5H), 5.37 – 5.22 (m, 1H), 4.37 – 4.15 (m, 1H), 2.49 – 2.23 (m, 0.6H), 2.07 – 1.85 (m, 1H), 1.86 – 1.72 (m, 1H), 1.67 – 1.34 (m, 4.5H), 1.22 – 0.85 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 179.00, 178.82, 142.28, 141.87, 141.61, 141.34, 137.89, 137.66, 137.10, 137.00, 128.71, 128.44, 128.33, 128.14, 127.97, 127.88, 127.53, 127.49, 127.46, 121.77, 121.60, 119.43, 118.42, 115.72, 115.22, 109.46, 61.26, 61.00, 51.79, 51.10, 42.44, 40.53, 34.92, 34.21, 33.98, 33.18, 28.36, 26.96, 26.14, 25.38.

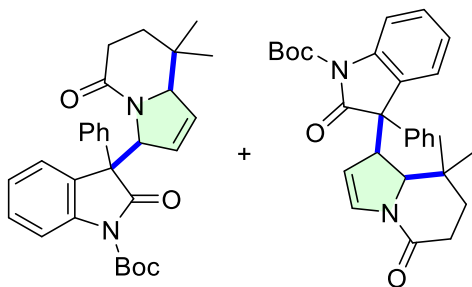
HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{BrNO}$ ($\text{M}+\text{H}$) $^+$: 420.0958, found: 420.0952.



^1H NMR (400 MHz, CDCl_3) δ 8.85 – 8.33 (m, 1H), 7.51 – 7.38 (m, 2H), 7.30 – 7.19 (m, 3.7H), 7.17 – 7.09 (m, 1.3H), 7.00 – 6.72 (m, 2H), 5.82 – 5.68 (m, 0.5H), 5.61 – 5.35 (m, 1.5H), 5.24 – 5.06 (m, 1H), 4.09 – 3.90 (m, 1H), 2.31 – 2.17 (m, 0.5H), 2.11 – 1.97 (m, 1H), 1.97 – 1.77 (m, 1H), 1.73 – 1.57 (m, 1H), 1.55 – 1.41 (m, 0.8H), 1.40 – 1.16 (m, 3.4H), 0.88 (s, 0.75H), 0.87 (s, 0.75H), 0.81 (s, 0.75H), 0.81 (s, 0.75H), 0.58 (s, 0.75H), 0.57 (s, 0.75H), 0.27 (s, 0.75H), 0.23 (s, 0.75H).

^{13}C NMR (101 MHz, CDCl_3) δ 180.24, 179.09, 145.82, 141.81, 141.17, 139.77, 138.95, 138.15, 138.11, 136.52, 136.16, 129.98, 129.86, 129.69, 129.08, 129.01, 128.59, 128.55, 128.43, 128.25, 128.00, 127.94, 127.89, 127.71, 127.66, 127.63, 127.37, 126.67, 125.83, 125.27, 125.24, 124.66, 124.42, 122.73, 121.90, 121.85, 117.46, 110.21, 109.82, 60.37, 60.30, 52.81, 47.07, 47.03, 44.53, 44.28, 41.42, 41.21, 39.33, 35.84, 35.62, 35.16, 35.01, 33.85, 31.91, 30.78, 29.56, 29.51, 22.67, 22.57, 22.27, 21.54, 19.74.

HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{NO}$ ($\text{M}+\text{Na}$) $^+$: 392.1985, found: 392.1986.

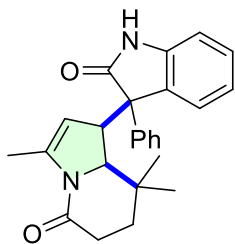


^1H NMR (400 MHz, CDCl_3) δ 8.01 – 7.80 (m, 1H), 7.73 – 7.55 (m, 1H), 7.55 – 7.30 (m, 6H), 7.28 – 6.72 (m, 1H), 6.10 – 5.65 (m, 2H), 2.57 – 2.08 (m, 2H), 1.70 – 1.62 (m, $J = 3.0$ Hz, 9H), 1.59 – 1.28 (m, 2H), 1.05 – 0.22 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 174.52, 174.25, 169.58, 168.90, 149.84, 149.11, 141.40, 139.77, 137.30, 137.05, 131.58, 131.47, 130.48, 130.36, 129.20, 128.84, 128.72, 128.71, 128.59, 128.55, 128.47, 128.43, 128.18, 128.12, 127.99, 127.90, 127.81, 127.61, 127.56, 127.48, 126.74, 126.71, 125.54, 125.06, 124.16, 123.85, 123.17, 115.29, 115.21, 114.59, 109.36, 84.72, 84.37, 83.75, 74.65, 74.00, 72.25, 72.05, 67.21, 66.05, 60.79, 60.08, 59.82, 55.56,

54.71, 35.38, 34.58, 34.48, 34.40, 33.96, 33.52, 32.75, 29.15, 28.93, 28.47, 28.22, 28.13, 28.08, 28.04, 27.34, 26.99, 25.65, 25.38, 25.01, 19.87, 19.43, 18.42, 18.21.

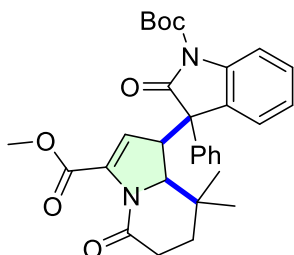
HRMS (ESI) calcd for $C_{29}H_{26}N_2O_4$ ($M+Na$)⁺: 495.2254, found: 495.2253.



¹H NMR (400 MHz, CDCl₃) δ 9.52 (s, 0.7H), 9.32 (s, 0.5H), 7.73 (m, 1.2H), 7.49 – 7.40 (m, 1.4H), 7.37 – 7.27 (m, 5.5H), 7.25 – 7.17 (m, 1.3H), 7.15 – 6.87 (m, 3H), 4.51 (s, 1.2H), 3.94 (s, 0.7H), 3.70 (m, 0.6H), 3.61 (s, 0.5H), 2.84 (m, 0.6H), 2.53 – 2.22 (m, 2H), 2.19 (s, 1.5H), 2.15 – 2.01 (m, 0.8H), 1.91 (s, 1.5H), 1.49 – 1.33 (m, 2.5H), 0.93 (s, 2H), 0.81 (s, 2H), 0.71 (s, 1.7H), 0.27 (s, 1.7H).

¹³C NMR (101 MHz, CDCl₃) δ 179.94, 179.27, 169.45, 169.23, 144.35, 144.29, 141.62, 141.03, 138.23, 136.08, 128.99, 128.95, 128.84, 128.77, 128.60, 128.45, 128.41, 127.78, 127.55, 126.68, 125.84, 122.79, 122.03, 110.41, 110.17, 107.18, 106.93, 67.81, 67.35, 60.41, 59.84, 51.94, 50.12, 34.73, 34.70, 34.33, 34.23, 31.62, 31.04, 25.71, 25.58, 21.85, 15.73, 15.43.

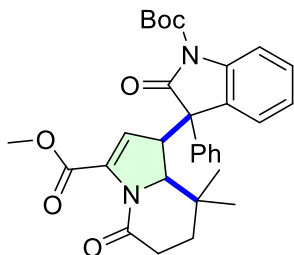
HRMS (ESI) calcd for $C_{25}H_{26}N_2O_2$ ($M+Na$)⁺: 409.1886, found: 409.1884.



¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.2 Hz, 1H), 7.54 – 7.42 (m, 1H), 7.38 – 7.28 (m, 7H), 5.29 (d, J = 2.5 Hz, 1H), 4.40 – 4.30 (m, 1H), 3.80 (s, 3H), 3.13 (d, J = 6.0 Hz, 1H), 2.30 – 2.19 (m, 2H), 1.58 (s, 9H), 1.52 – 1.42 (m, 2H), 0.93 (s, 3H), 0.89 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.71, 168.21, 162.81, 148.97, 140.27, 138.81, 137.99, 129.47, 128.92, 128.14, 127.73, 126.93, 126.55, 125.16, 115.12, 114.91, 84.76, 69.83, 59.01, 53.55, 52.52, 35.27, 33.58, 28.55, 28.02, 25.87, 19.41.

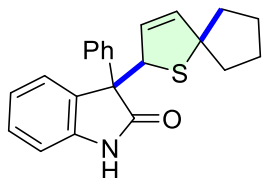
HRMS (ESI) calcd for $C_{31}H_{34}N_2O_6$ ($M+Na$)⁺: 553.2309, found: 553.2308.



¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.79 (m, 1H), 7.78 – 7.58 (m, 2H), 7.50 – 7.29 (m, 4H), 7.25 – 7.02 (m, 2H), 6.17 – 5.15 (m, 1H), 4.04 – 3.87 (m, 1H), 3.72 – 3.53 (m, 3H), 2.60 – 2.23 (m, 1H), 1.73 – 1.56 (m, 9H), 1.56 – 1.36 (m, 2H), 1.19 – 0.82 (m, 2H), 0.71 (s, 1.5H), 0.25 (s, 1.5H).

^{13}C NMR (101 MHz, CDCl_3) δ 175.56, 169.00, 162.47, 148.87, 139.14, 138.86, 134.98, 129.93, 129.04, 128.71, 128.61, 128.36, 127.37, 126.68, 125.68, 124.33, 115.37, 115.00, 84.84, 68.04, 59.68, 54.09, 52.14, 34.85, 34.26, 29.31, 28.17, 28.07, 25.70, 19.60.

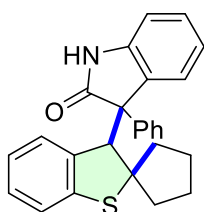
HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_6$ ($\text{M}+\text{Na}$) $^+$: 553.2309, found: 553.2312.



^1H NMR (400 MHz, CDCl_3) δ 8.54 – 8.26 (m, 1H), 7.54 – 7.40 (m, 1H), 7.39 – 7.26 (m, 1.5H), 7.25 – 7.16 (m, 3.0H), 7.14 – 6.72 (m, 3.5H), 5.71 (dd, J = 16.1, 3.4 Hz, 0.5H), 5.44 (dd, J = 29.0, 3.2 Hz, 0.5H), 5.23 (dd, J = 7.7, 1.7 Hz, 0.5H), 4.95 (dd, J = 11.3, 9.5 Hz, 0.5H), 4.41 – 4.00 (m, 1H), 2.74 – 2.20 (m, 1H), 2.16 – 1.70 (m, 2H), 1.63 – 1.23 (m, 3H), 1.12 – 0.76 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 180.74, 180.32, 179.21, 179.02, 142.32, 141.98, 141.68, 141.39, 141.16, 140.32, 138.52, 138.07, 137.94, 137.43, 133.01, 132.26, 130.79, 130.37, 129.89, 129.67, 129.13, 129.09, 128.68, 128.59, 128.54, 128.40, 128.06, 127.96, 127.93, 127.86, 127.68, 127.59, 127.48, 127.44, 127.32, 127.28, 127.02, 125.80, 121.75, 121.60, 121.33, 116.90, 116.38, 115.45, 114.98, 110.17, 109.55, 60.99, 60.81, 60.05, 59.33, 50.52, 49.92, 49.44, 48.68, 41.22, 40.88, 40.23, 39.47, 34.96, 34.88, 34.68, 34.62, 34.43, 33.97, 33.72, 33.57, 28.36, 27.64, 27.41, 27.09, 26.22, 26.16, 25.79, 25.49.

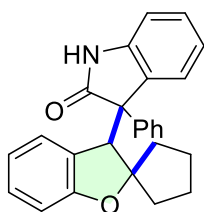
HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{NOS}$ ($\text{M}+\text{Na}$) $^+$: 370.1236, found: 370.1243.



^1H NMR (400 MHz, DMSO) δ 10.58 (s, 0.5H), 10.43 (s, 0.5H), 7.84 (d, J = 7.5 Hz, 0.5H), 7.34 – 6.72 (m, 11H), 6.56 – 6.48 (m, 1H), 5.68 (d, J = 7.7 Hz, 0.5H), 4.34 (s, 0.5H), 4.19 (s, 0.5H), 2.19 – 0.90 (m, 8H).

^{13}C NMR (101 MHz, DMSO) δ 179.28, 142.46, 142.40, 142.05, 139.50, 139.47, 139.09, 129.17, 128.90, 128.85, 128.71, 128.64, 128.52, 128.42, 128.27, 128.12, 127.75, 127.61, 127.14, 126.39, 123.77, 123.28, 122.50, 122.42, 121.09, 120.62, 110.31, 109.51, 71.46, 71.36, 61.34, 59.95, 58.81, 45.58, 34.43, 31.89, 25.05, 24.76, 21.25, 21.00.

HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{NOS}$ ($\text{M}+\text{Na}$) $^+$: 420.1393, found: 420.1391.

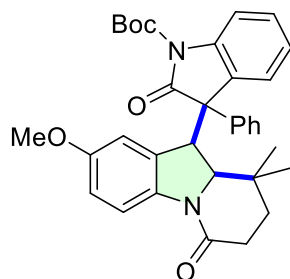


^1H NMR (400 MHz, DMSO) δ 10.66 (s, 0.7H), 10.58 (s, 0.5H), 7.56 (s, 0.7H), 7.49 – 7.23 (m, 5H), 7.23 – 7.08 (m, 1.8H), 7.02 – 6.82 (m, 3H), 6.80 – 6.67 (m, 1.3H), 6.66 – 6.59 (m, 0.5H), 6.59 – 6.47 (m, 1.4H), 5.94 (s, 0.7H), 5.72 (d, J = 7.4 Hz, 0.8H), 4.59 – 4.26 (m, 1H), 1.96 – 1.49 (m, 6.5H), 1.39 – 1.09 (m, 1.5H).

^{13}C NMR (101 MHz, CDCl_3) δ 180.22, 179.72, 159.15, 158.91, 158.06, 140.87, 140.74, 138.77, 138.57, 129.10, 128.66, 128.58, 128.53, 128.37, 128.21, 128.12, 127.89, 127.79, 127.62, 127.05, 126.25, 124.35, 123.17, 122.45,

122.35, 122.03, 120.26, 119.63, 119.35, 110.72, 110.14, 109.85, 109.67, 109.57, 102.16, 99.42, 99.18, 58.42, 55.29, 54.45, 49.77, 42.46, 41.70, 35.46, 33.20, 32.73, 30.95, 30.39, 28.26, 27.24, 26.31, 25.49, 25.32, 24.93, 24.71, 24.25, 23.78, 22.10, 21.54.

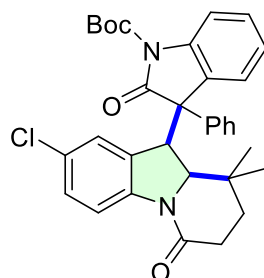
HRMS (ESI) calcd for $C_{26}H_{23}NO_2$ ($M+Na$)⁺: 404.1621, found: 404.1625.



¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.8 Hz, 0.5H), 7.88 (d, *J* = 8.1 Hz, 0.5H), 7.80 (d, *J* = 8.8 Hz, 0.5H), 7.78 – 7.74 (m, 1H), 7.67 – 7.54 (m, 1.5H), 7.46 – 7.30 (m, 4H), 7.19 (t, *J* = 7.9 Hz, 0.5H), 7.09 (t, *J* = 7.6 Hz, 0.5H), 7.00 (t, *J* = 7.2 Hz, 0.5H), 6.78 (dd, *J* = 8.8, 2.6 Hz, 0.5H), 6.72 (d, *J* = 2.5 Hz, 0.5H), 6.55 (dd, *J* = 8.8, 2.6 Hz, 0.5H), 6.01 (d, *J* = 7.5 Hz, 0.5H), 5.52 (d, *J* = 2.6 Hz, 0.5H), 4.47 (d, 0.5H), 4.33 (d, 0.5H), 3.91 (d, 0.5H), 3.67 (s, 1.5H), 3.38 (s, 1.5H), 3.07 (d, *J* = 7.0 Hz, 0.5H), 2.65 – 2.36 (m, 1H), 2.32 – 2.02 (m, 1H), 1.64 (s, 4.5H), 1.64 (s, 4.5H), 1.55 – 1.40 (m, 2H), 1.14 (s, 1.5H), 0.68 (s, 1.5H), 0.57 (s, 1.5H), 0.50 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.34, 174.73, 169.36, 169.16, 155.91, 155.21, 148.89, 148.69, 139.94, 139.34, 138.72, 137.48, 137.12, 135.30, 129.76, 129.30, 129.06, 128.89, 128.63, 128.54, 128.33, 128.22, 126.94, 125.56, 125.42, 124.36, 123.79, 115.85, 115.76, 115.44, 114.75, 114.63, 114.49, 110.00, 108.70, 84.75, 84.68, 68.87, 68.31, 60.90, 59.94, 55.41, 55.05, 51.79, 50.91, 35.38, 35.21, 34.79, 34.36, 31.22, 30.68, 28.09, 28.03, 26.55, 25.64, 24.96, 21.88, 21.86.

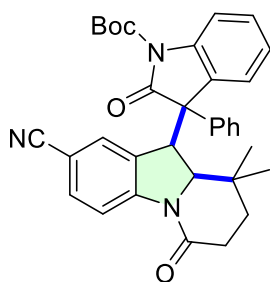
HRMS (ESI) calcd for $C_{34}H_{36}N_2O_5$ ($M+Na$)⁺: 575.2516, found: 575.2519.



¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.6 Hz, 0.5H), 7.87 (d, *J* = 8.1 Hz, 0.5H), 7.77 (d, *J* = 8.7 Hz, 0.5H), 7.76 – 7.71 (m, 1H), 7.63 (d, *J* = 7.8 Hz, 0.5H), 7.60 – 7.49 (m, 1H), 7.46 – 7.27 (m, 4H), 7.23 – 7.15 (m, 1H), 7.14 – 7.11 (d, *J* = 2.0 Hz, 0.5H), 7.08 (t, *J* = 8.1, 7.1 Hz, 0.5H), 7.00 (t, *J* = 7.6 Hz, 0.5H), 6.95 (dd, *J* = 8.6, 2.1 Hz, 0.5H), 6.06 (d, *J* = 7.5 Hz, 0.5H), 5.80 (d, *J* = 1.9 Hz, 0.5H), 4.43 (d, *J* = 2.7 Hz, 0.5H), 4.29 (d, *J* = 2.1 Hz, 0.5H), 3.91 (d, *J* = 2.3 Hz, 0.5H), 3.10 (d, *J* = 2.8 Hz, 0.5H), 2.61 – 2.36 (m, 1H), 2.35 – 2.05 (m, 1H), 1.66 (s, 4.5H), 1.61 (s, 4.5H), 1.55 – 1.38 (m, 2H), 1.11 (s, 1.5H), 0.65 (s, 1.5H), 0.54 (s, 1.5H), 0.52 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 175.96, 174.51, 169.97, 169.87, 148.83, 148.53, 143.38, 142.22, 139.98, 139.46, 136.44, 134.89, 130.22, 130.02, 129.45, 129.15, 129.06, 128.78, 128.74, 128.65, 128.59, 128.55, 128.45, 128.11, 127.65, 126.68, 125.58, 125.33, 125.08, 124.39, 123.79, 123.66, 115.87, 115.78, 114.83, 114.79, 84.97, 84.85, 68.96, 68.47, 60.66, 59.74, 51.64, 50.66, 35.39, 35.22, 34.56, 34.12, 31.30, 30.79, 28.08, 28.05, 26.57, 26.46, 21.95, 21.89.

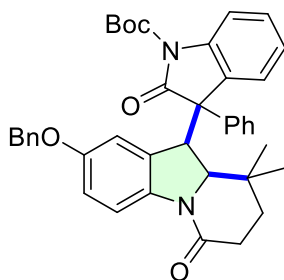
HRMS (ESI) calcd for $C_{33}H_{33}ClN_2O_4$ ($M+Na$)⁺: 579.2021, found: 579.2027.



¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.5 Hz, 0.4H), 7.92 (d, *J* = 8.4 Hz, 0.6H), 7.88 (d, *J* = 8.2 Hz, 0.4H), 7.76 – 7.70 (m, 1.2H), 7.61 (d, *J* = 8.1 Hz, 0.6H), 7.58 – 7.49 (m, 1H), 7.46 – 7.27 (m, 5H), 7.20 (t, *J* = 8.5 Hz, 0.6H), 7.08 (t, *J* = 8.0 Hz, 0.6H), 7.01 (t, *J* = 7.6 Hz, 0.4H), 6.11 (d, 0.4H), 6.02 (d, *J* = 7.5 Hz, 0.4H), 4.45 (d, 0.4H), 4.33 (d, 0.6H), 3.96 (d, *J* = 2.4 Hz, 0.6H), 3.17 (d, *J* = 2.4 Hz, 0.4H), 2.64 – 2.39 (m, 1.2H), 2.35 – 2.09 (m, 0.8H), 1.67 (s, 5.5H), 1.61 (s, 3.5H), 1.58 – 1.40 (m, 2H), 1.11 (s, 1.2H), 0.64 (s, 1.2H), 0.54 (s, 1.8H), 0.48 (s, 1.8H).

¹³C NMR (101 MHz, CDCl₃) δ 175.74, 174.27, 170.61, 170.55, 148.75, 148.39, 148.00, 146.92, 140.04, 139.40, 135.94, 134.48, 134.21, 133.96, 129.69, 129.59, 129.39, 129.01, 128.74, 128.66, 128.58, 127.18, 126.28, 125.21, 124.77, 124.48, 123.90, 118.92, 115.20, 115.05, 114.88, 106.09, 105.72, 85.54, 85.05, 69.08, 68.63, 60.55, 59.60, 51.24, 50.34, 35.33, 35.18, 34.28, 33.84, 31.40, 30.93, 28.08, 28.04, 26.50, 26.38, 21.90.

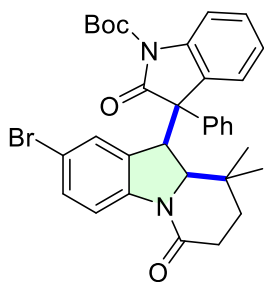
HRMS (ESI) calcd for C₃₄H₃₃N₃O₄ (M+H)⁺: 548.2544, found: 548.2548.



¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.8 Hz, 0.5H), 7.87 (d, *J* = 8.2 Hz, 0.5H), 7.81 – 7.73 (m, 1.5H), 7.69 – 7.48 (m, 1.5 H), 7.47 – 7.27 (m, 9H), 7.19 (t, *J* = 7.8 Hz, 0.5H), 7.08 (t, *J* = 7.5 Hz, 0.5H), 6.98 (t, *J* = 7.6 Hz, 0.5H), 6.86 (dd, *J* = 8.9 Hz, 0.5H), 6.83 (m, 0.5H), 6.60 (dd, *J* = 8.8, 2.0 Hz, 0.5H), 5.98 (d, *J* = 7.5 Hz, 0.5H), 5.60 (d, *J* = 0.9 Hz, 0.5H), 4.95 – 4.78 (m, 1H), 4.58 (d, *J* = 11.6 Hz, 0.5H), 4.52 – 4.39 (m, 1H), 4.33 (s, 0.5H), 3.90 (s, 0.5H), 3.07 (s, 0.5H), 2.61 – 2.35 (m, 1H), 2.29 – 2.01 (m, 1H), 1.62 (s, 5H), 1.57 (s, 4H), 1.54 – 1.38 (m, 2H), 1.13 (s, 1.5H), 0.67 (s, 1.5H), 0.56 (s, 1.5H), 0.49 (s, 1.5H).

¹³C NMR (151 MHz, CDCl₃) δ 176.37, 174.76, 169.45, 169.23, 155.14, 154.37, 148.91, 148.76, 139.95, 139.39, 138.97, 137.71, 137.18, 136.87, 136.84, 135.30, 129.89, 129.34, 129.21, 129.09, 128.94, 128.70, 128.58, 128.48, 128.45, 128.37, 128.26, 127.92, 127.90, 127.63, 127.52, 126.98, 125.58, 125.45, 124.42, 123.84, 116.80, 115.84, 115.81, 115.08, 114.80, 114.66, 111.03, 110.10, 84.79, 84.76, 70.33, 69.96, 68.90, 68.33, 60.90, 59.98, 51.78, 50.90, 35.41, 35.22, 34.78, 34.34, 31.24, 30.70, 28.11, 28.03, 26.58, 21.92, 21.88.

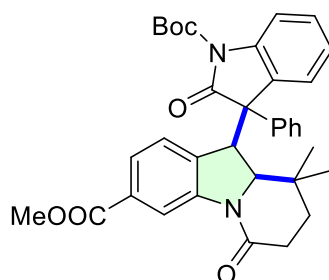
HRMS (ESI) calcd for C₄₀H₄₀N₂O₅ (M+Na)⁺: 651.2829, found: 651.2834.



¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.6 Hz, 0.5H), 7.87 (d, *J* = 8.2 Hz, 0.5H), 7.78 – 7.68 (m, 1.5H), 7.64 (d, *J* = 8.1 Hz, 0.5H), 7.56 (s, 1H), 7.46 – 7.27 (m, 5H), 7.19 (t, *J* = 7.4 Hz, 0.5H), 7.13 – 6.97 (m, 1H), 6.06 (d, *J* = 7.5 Hz, 0.5H), 5.93 (d, *J* = 1.5 Hz, 0.5H), 4.42 (d, *J* = 2.5 Hz, 0.5H), 4.29 (d, *J* = 1.8 Hz, 0.5H), 3.90 (d, *J* = 2.2 Hz, 0.5H), 3.09 (d, *J* = 2.6 Hz, 0.5H), 2.64 – 2.34 (m, 1H), 2.34 – 1.96 (m, 1H), 1.67 (s, 4.5H), 1.61 (s, 4.5H), 1.58 – 1.36 (m, 2H), 1.11 (s, 1.5H), 0.65 (s, 1.5H), 0.54 (s, 1.5H), 0.52 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.03, 174.62, 170.14, 170.03, 148.93, 148.62, 143.91, 142.77, 140.09, 139.57, 136.52, 134.99, 132.12, 131.80, 130.74, 130.50, 129.56, 129.28, 129.17, 128.86, 128.84, 128.77, 128.71, 128.65, 128.56, 126.79, 126.63, 125.42, 125.18, 124.50, 123.89, 116.44, 116.35, 115.72, 115.26, 114.94, 114.91, 85.10, 84.97, 69.04, 68.53, 60.78, 59.84, 51.71, 50.83, 35.49, 35.31, 34.64, 34.20, 31.43, 30.93, 28.24, 28.21, 26.69, 26.57, 22.03, 21.95.

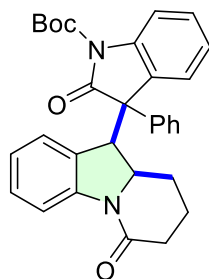
HRMS (ESI) calcd for C₃₃H₃₃BrN₂O₄ (M+Na)⁺: 623.1516, found: 623.1519.



¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, *J* = 1.4 Hz, 0.5H), 8.50 (d, *J* = 1.4 Hz, 0.5H), 7.89 (d, *J* = 8.1 Hz, 0.5H), 7.79 – 7.73 (m, 1H), 7.63 – 7.50 (m, 2H), 7.48 – 7.30 (m, 4.5H), 7.25 – 7.14 (m, 1H), 7.08 (t, *J* = 8.1 Hz, 0.5H), 7.00 (t, *J* = 7.7 Hz, 0.5H), 6.03 (d, *J* = 8.0 Hz, 0.5H), 5.99 (d, *J* = 7.5 Hz, 0.5H), 4.53 (d, *J* = 2.7 Hz, 0.5H), 4.39 (d, *J* = 2.3 Hz, 0.5H), 3.98 (d, *J* = 2.5 Hz, 0.5H), 3.90 (s, 1.5H), 3.84 (s, 1.5H), 3.16 (d, *J* = 2.7 Hz, 0.5H), 2.66 – 2.41 (m, 1H), 2.37 – 2.12 (m, 1H), 1.66 (s, 4.5H), 1.64 (s, 4.5H), 1.58 – 1.45 (m, 1.5H), 1.15 (s, 1.5H), 0.67 (s, 1.5H), 0.55 (s, 1.5H), 0.51 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.25, 174.65, 170.24, 170.08, 167.04, 166.87, 148.96, 145.11, 143.96, 140.09, 139.43, 136.65, 135.11, 133.80, 133.45, 131.38, 130.97, 129.59, 129.27, 129.18, 128.86, 128.76, 128.61, 126.73, 125.36, 125.27, 124.67, 124.57, 124.03, 123.34, 115.86, 115.61, 115.14, 114.93, 85.00, 69.06, 68.53, 60.88, 59.94, 52.28, 52.16, 51.55, 50.82, 35.52, 35.38, 34.67, 34.24, 31.50, 31.02, 28.24, 28.21, 26.58, 22.03, 21.95.

HRMS (ESI) calcd for C₃₅H₃₆N₂O₆ (M+Na)⁺: 603.2466, found: 603.2471.

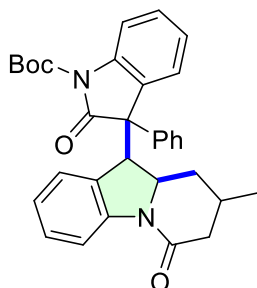


¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.07 (m, 0.6H), 8.02 – 7.81 (m, 1.3H), 7.72 (d, *J* = 8.1 Hz, 0.4H), 7.61 – 7.45 (m, 1.2H), 7.45 – 7.28 (m, 3.7H), 7.25 – 7.12 (m, 2.6H), 7.09 – 6.98 (m, 1.6H), 6.91 – 6.70 (m, 1.2H), 6.55 – 5.71 (m, 1H), 4.72 – 3.31 (m, 2H), 2.69 – 2.07 (m, 2H), 1.76 – 1.65 (m, 1H), 1.66 – 1.57 (m, 9H), 1.57 – 1.48 (m, 1H), 1.48 – 1.36 (m, 1H), 1.30 – 0.95 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 176.01, 175.14, 169.94, 169.00, 167.82, 167.72, 148.87, 148.73, 143.72, 143.29, 142.45, 142.22, 140.15, 139.86, 139.67, 139.08, 137.64, 137.57, 136.54, 133.99, 129.74, 129.28, 129.24, 128.96, 128.92, 128.87, 128.84, 128.65, 128.49, 128.42, 128.24, 128.22, 128.10, 126.76, 126.59, 125.98, 125.82, 125.03,

124.79, 124.76, 124.39, 124.28, 123.76, 123.68, 123.59, 123.54, 123.44, 123.19, 117.47, 117.24, 116.94, 116.29, 115.25, 115.14, 115.10, 114.72, 84.93, 84.81, 84.55, 65.10, 64.48, 62.32, 61.73, 61.50, 60.87, 60.42, 59.81, 58.77, 57.24, 55.12, 54.56, 51.30, 51.12, 36.11, 32.55, 32.24, 32.13, 31.96, 29.80, 29.36, 28.12, 28.08, 27.88, 27.79, 26.66, 23.77, 21.46, 21.10, 20.99, 19.31, 18.08, 14.24.

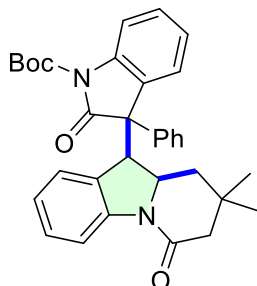
HRMS (ESI) calcd for $C_{31}H_{30}N_2O_4$ ($M+Na$)⁺: 517.2098, found: 517.2101.



¹H NMR (400 MHz, CDCl₃) δ 8.13 – 7.96 (m, 0.8H), 7.95 – 7.72 (m, 0.9H), 7.71 – 7.60 (m, 0.4H), 7.58 – 7.20 (m, 5H), 7.17 – 7.03 (m, 1.2H), 7.03 – 6.60 (m, 3H), 6.54 – 5.70 (m, 1.2H), 4.64 – 3.30 (m, 2H), 2.65 – 2.22 (m, 1H), 2.20 – 1.67 (m, 3.8H), 1.64 – 1.49 (m, 9H), 1.48 – 1.29 (m, 0.7H), 1.03 – 0.63 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.00, 174.88, 170.14, 169.44, 168.23, 148.88, 143.10, 142.05, 139.71, 137.25, 129.33, 129.03, 128.85, 128.78, 128.52, 128.43, 128.37, 128.31, 128.25, 128.16, 126.90, 126.61, 124.93, 124.83, 124.74, 124.35, 124.25, 123.65, 123.48, 123.31, 123.12, 117.62, 117.12, 116.37, 115.98, 115.06, 114.93, 84.85, 84.79, 62.58, 62.23, 60.10, 59.39, 59.05, 58.40, 58.27, 55.03, 54.94, 54.81, 54.39, 51.12, 41.15, 40.59, 40.45, 38.80, 38.62, 37.95, 37.40, 28.12, 28.08, 28.07, 27.71, 26.62, 24.33, 24.02, 22.56, 22.01, 21.95, 21.67, 21.19.

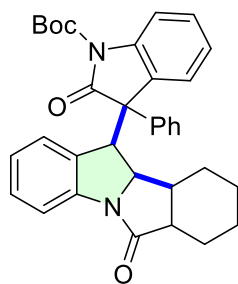
HRMS (ESI) calcd for $C_{32}H_{32}N_2O_4$ ($M+H$)⁺: 509.2435, found: 509.2438.



¹H NMR (400 MHz, CDCl₃) δ 8.14 – 7.94 (m, 0.6H), 7.92 – 7.72 (m, 1.5H), 7.72 – 7.61 (m, 1H), 7.60 – 7.20 (m, 5H), 7.18 – 7.05 (m, 1.3H), 7.02 – 6.88 (m, 1.3H), 6.83 (d, J = 7.6 Hz, 0.4H), 6.68 (m, 1H), 6.42 (d, J = 7.2 Hz, 0.4H), 6.13 – 5.99 (m, 0.6H), 5.80 (d, J = 7.5 Hz, 0.2H), 4.55 – 4.32 (m, 1H), 4.28 (m, 0.2H), 4.09 – 3.93 (m, 0.4H), 3.51 – 3.31 (m, 0.4H), 2.27 – 1.91 (m, 2H), 1.64 – 1.49 (m, 9H), 1.42 – 1.20 (m, 2H), 1.00 – 0.63 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 175.99, 174.86, 169.83, 168.76, 148.87, 143.01, 141.93, 140.20, 139.69, 137.28, 136.55, 134.24, 129.36, 128.92, 128.78, 128.72, 128.38, 128.35, 128.30, 128.20, 126.66, 126.57, 125.97, 124.94, 124.87, 124.74, 124.32, 124.22, 123.54, 123.49, 123.28, 117.60, 116.70, 116.14, 115.08, 114.87, 84.85, 84.80, 60.82, 59.89, 59.22, 58.73, 54.84, 54.56, 51.33, 47.65, 46.93, 45.95, 45.88, 44.11, 36.01, 31.60, 31.44, 30.88, 30.23, 30.12, 30.02, 29.70, 28.48, 28.11, 28.07, 26.92, 24.49.

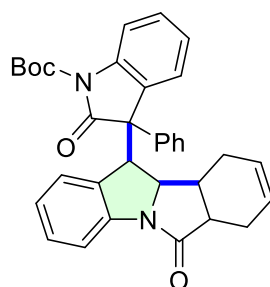
HRMS (ESI) calcd for $C_{33}H_{34}N_2O_4$ ($M+Na$)⁺: 545.2411, found: 545.2410.



¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.1 Hz, 0.5H), 7.81 (d, *J* = 7.8 Hz, 0.5H), 7.61 (d, *J* = 7.8 Hz, 0.5H), 7.51 (d, *J* = 7.9 Hz, 0.5H), 7.49 – 7.45 (m, 1.5H), 7.44 – 7.30 (m, 4.5H), 7.27 – 7.17 (m, 1H), 7.11 – 7.00 (m, 1.5H), 6.82 (d, *J* = 7.6 Hz, 0.5H), 6.79 – 6.71 (m, 1H), 6.62 (s, 0.5H), 6.11 (d, *J* = 7.6 Hz, 0.5H), 4.96 – 4.84 (m, 1H), 4.47 – 4.38 (m, 0.5H), 3.82 (s, 0.5H), 2.89 – 2.74 (m, 1H), 2.42 – 2.04 (m, 2H), 1.88 – 1.68 (m, 2H), 1.67 (s, 4.5H), 1.64 (s, 4.5H), 1.62 – 1.46 (m, 1H), 1.46 – 1.33 (m, 1H) 1.24 – 0.75 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.14, 175.37, 174.60, 173.05, 148.97, 148.84, 141.45, 139.80, 137.71, 137.60, 132.09, 131.63, 129.19, 128.93, 128.85, 128.71, 128.38, 128.31, 128.13, 127.95, 127.35, 125.40, 125.10, 124.64, 124.34, 123.49, 123.45, 123.29, 115.10, 114.52, 114.14, 84.88, 84.80, 66.36, 65.63, 59.43, 58.81, 48.65, 47.98, 46.58, 46.14, 41.33, 39.86, 28.11, 23.99, 23.91, 23.82, 23.34, 22.74, 22.61, 22.47, 22.26.

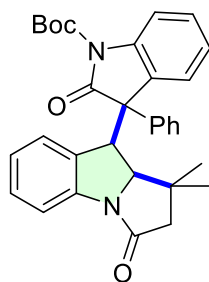
HRMS (ESI) calcd for C₃₄H₃₄N₂O₄₄ (M+Na)⁺: 557.2411, found: 557.2410.



¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.2 Hz, 0.5H), 7.80 (d, *J* = 8.2 Hz, 0.5H), 7.58 (d, *J* = 7.8 Hz, 0.5H), 7.52 – 7.44 (m, 2H), 7.44 – 7.28 (m, 4.5H), 7.24 – 7.14 (m, 1H), 7.11 – 6.97 (m, 1.5H), 6.81 (d, *J* = 7.5 Hz, 0.5H), 6.74 (m, 1H), 6.61 (s, 0.5H), 6.08 (d, *J* = 7.5 Hz, 0.5H), 5.73 – 5.55 (m, 2H), 4.95 – 4.79 (m, 1H), 4.58 – 4.44 (m, 0.5H), 3.90 (s, 0.5H), 2.99 – 2.88 (m, 1H), 2.67 – 2.53 (m, 1H), 2.52 – 2.36 (m, 1H), 2.34 – 1.93 (m, 2H), 1.65 (s, 4.5H), 1.86 – 1.51 (m, 1H), 1.61 (s, 4.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.14, 175.40, 174.79, 173.39, 148.98, 148.88, 141.64, 139.84, 137.57, 131.95, 131.55, 129.27, 128.99, 128.96, 128.80, 128.45, 128.42, 128.39, 128.11, 127.96, 127.29, 125.41, 125.28, 125.09, 124.71, 124.43, 123.91, 123.64, 123.62, 123.46, 123.42, 115.21, 115.18, 114.60, 114.27, 84.93, 84.87, 66.95, 66.24, 59.39, 58.84, 49.16, 48.45, 44.31, 43.90, 37.44, 36.16, 28.12, 28.10, 21.24, 21.19, 21.18, 20.71.

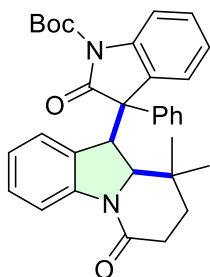
HRMS (ESI) calcd for C₃₄H₃₂N₂O₄ (M+H)⁺: 533.2435, found: 533.2444.



¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.0 Hz, 0.5H), 7.72 – 7.63 (m, 1.5H), 7.57 (d, *J* = 7.8 Hz, 0.5H), 7.48 – 7.29 (m, 5H), 7.23 – 7.14 (m, 1H), 7.10 – 6.94 (m, 2H), 6.81 – 6.65 (m, 1H), 6.26 (d, *J* = 7.5 Hz, 0.5H), 5.97 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 6.7 Hz, 0.5H), 4.62 (d, *J* = 4.9 Hz, 0.5H), 4.30 (d, *J* = 4.9 Hz, 0.5H), 3.51 (d, *J* = 6.6 Hz, 0.5H), 2.62 – 2.46 (m, 1H), 2.17 – 2.00 (m, 1H), 1.64 (s, 4.5H), 1.60 (s, 4.5H), 1.16 (s, 1.5H), 1.09 (s, 1.5H), 0.81 (s, 1.5H), 0.40 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.48, 175.49, 175.39, 172.79, 148.96, 148.82, 142.27, 141.70, 140.42, 139.52, 137.54, 136.57, 131.43, 130.60, 129.31, 128.90, 128.84, 128.81, 128.59, 128.54, 128.50, 128.43, 128.41, 126.71, 126.52, 126.34, 125.61, 125.55, 124.63, 123.98, 123.50, 123.35, 115.20, 115.00, 114.25, 113.90, 84.73, 72.91, 72.80, 59.97, 59.41, 51.27, 50.89, 50.41, 49.60, 42.70, 41.23, 28.12, 28.02, 24.12, 23.07, 22.04, 20.86.

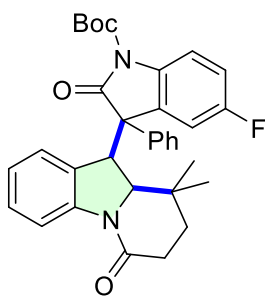
HRMS (ESI) calcd for C₃₂H₃₂N₂O₄ (M+Na)⁺: 531.2254, found: 531.2255.



¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.0 Hz, 0.5H), 7.88 – 7.83 (m, 1H), 7.78 – 7.73 (m, 0.5H), 7.60 – 7.51 (m, 1.5H), 7.41 – 7.28 (m, 4H), 7.24 – 6.92 (m, 3H), 6.81 – 6.74 (m, 0.5H), 6.72 – 6.65 (m, 0.5H), 5.97 (d, *J* = 7.7 Hz, 0.5H), 5.92 (d, *J* = 7.4 Hz, 0.5H), 4.50 (d, *J* = 2.7 Hz, 0.5H), 4.35 (d, *J* = 2.2 Hz, 0.5H), 3.89 (d, *J* = 2.4 Hz, 0.5H), 3.08 (d, *J* = 2.8 Hz, 0.5H), 2.60 – 2.36 (m, 1H), 2.33 – 2.08 (m, 1H), 1.66 (s, 4.5H), 1.64 (s, 4.5H), 1.58 – 1.37 (m, 2H), 1.16 (s, 1.5H), 0.68 (s, 1.5H), 0.57 (s, 11.5H), 0.53 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.32, 174.79, 170.03, 169.89, 148.92, 144.75, 143.54, 139.96, 139.40, 136.98, 135.29, 129.27, 129.21, 129.10, 128.85, 128.79, 128.56, 128.53, 128.45, 128.31, 128.24, 128.12, 126.83, 125.57, 125.36, 125.33, 125.22, 124.32, 123.74, 123.25, 123.13, 122.77, 115.08, 115.04, 114.82, 114.61, 84.73, 84.59, 68.53, 68.06, 60.99, 60.08, 51.70, 50.69, 35.36, 35.23, 34.65, 34.22, 31.49, 30.98, 28.09, 26.60, 26.58, 22.03.

HRMS (ESI) calcd for C₃₃H₃₄N₂O₄ (M+Na)⁺: 545.2411, found: 545.2407.

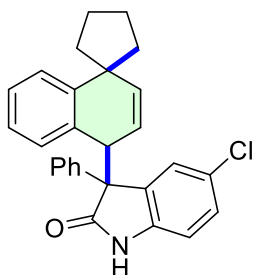


¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.1 Hz, 0.5H), 7.91 (d, *J* = 8.1 Hz, 0.5H), 7.89 – 7.83 (m, 1H), 7.78 – 7.69 (m, 1H), 7.52 (s, 1H), 7.43 – 7.29 (m, 3H), 7.23 (d, *J* = 7.8 Hz, 0.5H), 7.14 – 6.97 (m, 2H), 6.86 (t, *J* = 8.8 Hz, 0.5H), 6.78 (t, *J* = 7.5 Hz, 0.5H), 6.70 (t, *J* = 7.5 Hz, 0.5H), 5.97 (d, *J* = 7.6 Hz, 0.5H), 5.56 (d, *J* = 7.8 Hz, 0.5H), 4.51 (d, *J* = 1.6 Hz, 0.5H), 4.35 (d, *J* = 1.8 Hz, 0.5H), 3.82 (d, *J* = 1.4 Hz, 0.5H), 3.10 (d, *J* = 1.9 Hz, 0.5H), 2.67 – 2.37 (m, 1H), 2.37 – 2.09 (m, 1H), 1.63 (s, 4.5H), 1.60 (s, 4.5H), 1.54 – 1.37 (m, 2H), 1.13 (s, 1.5H), 0.66 (s, 1.5H), 0.54 (s, 1.5H), 0.51 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 175.93, 174.38, 170.06, 169.91, 158.02, 157.85, 148.87, 148.65, 144.75, 143.58, 136.50, 136.02, 135.44, 134.71, 134.30, 132.71, 129.57, 129.10, 128.91, 128.73, 128.70, 128.60, 128.55, 128.46,

128.07, 127.53, 125.07, 123.58, 123.22, 123.20, 122.96, 116.17, 116.11, 116.04, 115.95, 115.88, 115.64, 115.35, 115.31, 114.45, 114.20, 113.03, 112.78, 84.97, 84.83, 68.47, 68.01, 61.29, 60.32, 51.70, 50.68, 35.42, 35.31, 34.64, 34.17, 31.38, 30.97, 28.10, 26.61, 21.89, 21.87.

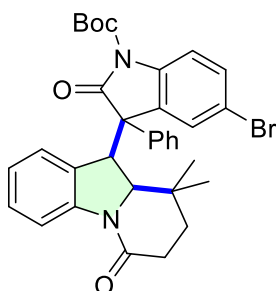
HRMS (ESI) calcd for $C_{33}H_{33}FN_2O_4$ ($M+Na$)⁺: 563.2317, found: 563.2318.



¹H NMR (400 MHz, DMSO-*d*₆) δ 10.64 (d, *J* = 3.6 Hz, 1H), 7.69 – 7.18 (m, 8H), 7.18 – 7.10 (m, 1H), 7.10 – 7.00 (m, 1H), 6.95 (td, *J* = 7.5, 7.1, 1.4 Hz, 0H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.81 – 6.73 (m, 1H), 6.63 (d, *J* = 8.3 Hz, 0H), 6.16 (dd, *J* = 8.0, 1.4 Hz, 1H), 5.89 (dd, *J* = 10.4, 1.6 Hz, 0H), 5.78 – 5.61 (m, 1H), 5.40 – 5.24 (m, 1H), 4.70 (dd, *J* = 4.0, 1.5 Hz, 0H), 4.58 (d, *J* = 3.8 Hz, 1H), 2.18 – 1.37 (m, 8H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 179.32, 178.05, 146.32, 142.03, 138.69, 138.51, 138.32, 138.04, 132.81, 132.39, 131.20, 130.02, 129.07, 128.87, 128.55, 128.47, 128.05, 127.89, 127.84, 127.80, 127.58, 127.51, 127.23, 127.18, 127.13, 126.88, 125.33, 125.26, 124.81, 119.26, 119.05, 111.16, 111.06, 62.67, 61.97, 47.01, 45.89, 45.76, 45.35, 45.11, 44.06, 44.01, 27.12, 26.39, 26.30, 26.24.

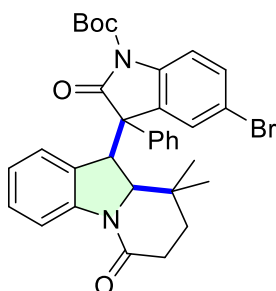
HRMS (ESI) calcd for $C_{28}H_{24}ClNO$ ($M+H$)⁺: 426.1619, found: 426.1620.



¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.45 – 7.32 (m, 4H), 7.28 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.11 – 6.99 (m, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 4.32 (d, *J* = 1.7 Hz, 1H), 3.79 (d, *J* = 2.1 Hz, 1H), 2.68 – 2.35 (m, 2H), 1.62 (s, 9H), 1.57 – 1.33 (m, 2H), 0.53 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 175.49, 169.95, 148.51, 143.58, 138.51, 134.61, 131.77, 129.22, 128.95, 128.76, 128.62, 128.52, 127.91, 127.76, 123.16, 123.12, 116.76, 116.36, 115.29, 85.03, 68.10, 61.18, 51.80, 35.42, 34.17, 31.42, 28.10, 26.71, 22.11.

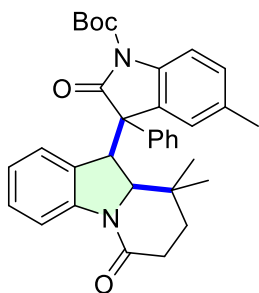
HRMS (ESI) calcd for $C_{33}H_{33}BrN_2O_4$ ($M+Na$)⁺: 623.1516, found: 623.1518.



¹H NMR (600 MHz, CDCl₃) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.42 (s, 2H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.33 – 7.26 (m, *J* = 4.0 Hz, 3H), 7.16 (d, *J* = 15.5 Hz, 1H), 6.61 (t, *J* = 8.2 Hz, 1H), 5.87 (d, *J* = 7.6 Hz, 1H), 5.78 (s, 1H), 4.39 (d, *J* = 2.2 Hz, 1H), 2.98 (d, *J* = 0.7 Hz, 1H), 2.25 – 2.15 (m, 1H), 2.15 – 2.04 (m, 1H), 1.50 (s, 9H), 1.44 – 1.34 (m, 2H), 1.01 (s, 3H), 0.55 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 173.99, 169.82, 148.70, 144.81, 138.99, 136.34, 134.33, 132.22, 129.89, 129.58, 128.79, 128.59, 128.50, 127.49, 124.95, 123.61, 122.99, 117.39, 116.18, 115.29, 85.16, 68.39, 60.28, 50.80, 35.26, 34.60, 31.00, 28.07, 28.07, 26.60, 21.87, 1.04.

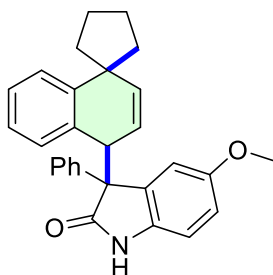
HRMS (ESI) calcd for C₃₃H₃₃BrN₂O₄ (M+Na)⁺: 623.1516, found: 623.1515.



¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 0.4H), 8.08 (d, *J* = 8.1 Hz, 0.5H), 7.94 – 7.80 (m, 1H), 7.80 – 7.67 (m, 2H), 7.55 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 0.5H), 7.41 – 7.29 (m, 2.5H), 7.25 – 7.18 (m, 0.5H), 7.14 – 7.04 (m, 1H), 7.03 – 6.90 (m, 1H), 6.76 (t, *J* = 7.4 Hz, 0.5H), 6.69 (t, *J* = 7.4 Hz, 0.5H), 5.99 (d, *J* = 7.5 Hz, 0.5H), 5.58 (s, 0.5H), 4.49 (d, *J* = 1.5 Hz, 0.5H), 4.33 (d, 0.5H), 3.87 (d, 0.5H), 3.06 (d, *J* = 1.6 Hz, 0.5H), 2.66 – 2.38 (m, 1H), 2.28 (s, 1.5H), 2.26 – 2.12 (m, 1H), 2.09 (s, 1.5H), 1.62 (s, 4.5H), 1.60 (s, 4.5H), 1.54 – 1.38 (m, 2H), 1.13 (s, 1.5H), 0.65 (s, 1.5H), 0.54 (s, 1.5H), 0.53 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 175.37, 173.90, 168.90, 167.08, 147.93, 147.72, 143.83, 142.46, 136.49, 136.03, 135.98, 134.35, 133.25, 132.78, 132.18, 131.66, 128.62, 128.23, 128.10, 127.80, 127.51, 127.47, 127.44, 127.24, 127.14, 126.46, 125.01, 124.41, 124.14, 122.53, 122.27, 122.03, 121.76, 113.88, 113.47, 113.25, 83.50, 83.36, 67.36, 67.05, 60.00, 59.17, 50.66, 49.67, 34.28, 34.15, 33.57, 33.18, 30.45, 29.97, 27.07, 25.63, 25.55, 21.15, 20.99, 20.27, 20.04.

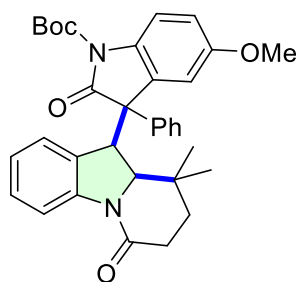
HRMS (ESI) calcd for C₃₄H₃₆N₂O₄ (M+Na)⁺: 559.2567, found: 559.2570.



¹H NMR (400 MHz, DMSO-*d*₆) δ 10.31 (s, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.34 (dd, *J* = 17.6, 8.3 Hz, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.87 – 6.64 (m, 3H), 6.20 (d, *J* = 7.8 Hz, 1H), 5.68 (s, 2H), 5.07 (d, *J* = 2.3 Hz, 1H), 4.56 (d, *J* = 3.1 Hz, 1H), 3.40 (s, 3H), 1.93 – 1.35 (m, 7H), 0.65 – 0.49 (m, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 178.18, 154.07, 146.23, 139.44, 137.89, 136.41, 133.30, 129.06, 128.71, 128.68, 127.79, 127.74, 127.50, 127.15, 124.71, 119.59, 114.46, 113.78, 110.07, 62.71, 55.34, 47.02, 45.94, 45.06, 44.22, 26.11, 26.04.

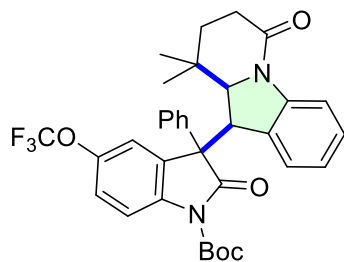
HRMS (ESI) calcd for C₂₉H₂₇NO₂ (M+H)⁺: 422.2115, found: 422.2115.



¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 0.6H), 7.89 (d, *J* = 8.0 Hz, 0.5H), 7.82 – 7.72 (m, 1.5H), 7.69 – 7.45 (m, 1.5H), 7.43 – 7.29 (m, 3.3H), 7.21 (t, *J* = 7.4 Hz, 0.7H), 7.10 (d, *J* = 7.5 Hz, 0.5H), 7.01 (t, *J* = 7.7 Hz, 0.5H), 6.91 – 6.82 (m, 1H), 6.78 (t, *J* = 7.1 Hz, 0.5H), 6.73 – 6.66 (m, 1H), 6.01 (d, *J* = 7.6 Hz, 0.6H), 5.42 (d, *J* = 2.5 Hz, 0.6H), 4.53 (d, *J* = 2.6 Hz, 0.6H), 4.36 (d, *J* = 2.0 Hz, 0.4H), 3.86 (d, *J* = 2.2 Hz, 0.4H), 3.72 (s, 1.3H), 3.45 (s, 1.8H), 3.08 (d, *J* = 2.7 Hz, 0.6H), 2.67 – 2.37 (m, 1H), 2.35 – 2.11 (m, 1.3H), 1.62 (s, 3.6H), 1.60 (s, 5.4H), 1.57 – 1.39 (m, 2H), 1.14 (s, 1.8H), 0.67 (s, 1.8H), 0.55 (s, 1.3H), 0.52 (s, 1.3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.40, 174.85, 169.98, 156.27, 155.99, 148.99, 148.78, 144.87, 143.53, 137.07, 135.26, 133.28, 132.85, 129.19, 129.08, 128.92, 128.77, 128.61, 128.57, 128.35, 128.26, 128.18, 126.74, 126.44, 125.27, 123.30, 123.23, 122.91, 115.86, 115.68, 115.10, 114.38, 111.57, 84.52, 84.41, 68.55, 68.06, 61.36, 60.33, 55.82, 55.50, 51.48, 50.47, 35.40, 35.27, 34.62, 34.15, 31.50, 31.03, 28.12, 26.63, 22.11, 21.99.

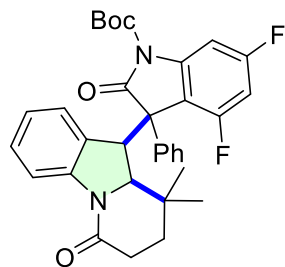
HRMS (ESI) calcd for C₃₄H₃₆N₂O₅ (M+Na)⁺: 575.2516, found: 575.2518.



¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.1 Hz, 0.5H), 7.97 – 7.86 (m, 1H), 7.71 (m, 1H), 7.64 (d, *J* = 8.9 Hz, 0.5H), 7.60 – 7.32 (m, 4H), 7.25 – 7.14 (m, 1.5H), 7.12 – 6.95 (m, 1.5H), 6.74 (m, 1H), 5.95 (d, *J* = 7.6 Hz, 0.5H), 5.75 (s, 0.5H), 4.51 (d, *J* = 1.7 Hz, 0.5H), 4.36 (d, *J* = 1.8 Hz, 0.5H), 3.83 (d, *J* = 2.1 Hz, 0.5H), 3.06 (d, *J* = 2.9 Hz, 0.5H), 2.62 – 2.37 (m, 1H), 2.35 – 2.09 (m, 1H), 1.63 (s, 4.5H), 1.61 (s, 4.5H), 1.56 – 1.40 (m, 2H), 1.13 (s, 1.5H), 0.65 (s, 1.5H), 0.53 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.90, 174.36, 169.97, 169.80, 148.83, 144.80, 143.75, 138.63, 138.10, 136.40, 134.56, 129.64, 129.26, 128.96, 128.92, 128.88, 128.75, 128.66, 128.61, 127.90, 127.35, 125.05, 123.20, 123.11, 123.03, 122.48, 122.11, 120.27, 118.74, 115.98, 115.84, 115.60, 85.35, 85.20, 68.62, 68.16, 61.24, 60.29, 51.94, 50.80, 35.64, 35.42, 34.67, 34.12, 31.39, 31.08, 28.17, 26.83, 26.69, 22.02.

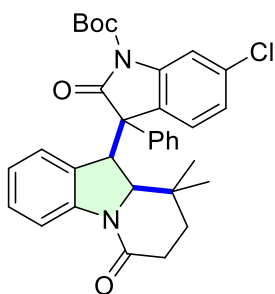
HRMS (ESI) calcd for C₃₄H₃₃F₃N₂O₅ (M+H)⁺: 607.2414, found: 607.2424.



¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.0 Hz, 0.5H), 7.90 (d, *J* = 8.7 Hz, 0.5H), 7.81 – 7.58 (m, 1.5H), 7.54 – 7.48 (m, 0.5H), 7.46 – 7.35 (m, 3H), 7.25 – 7.21 (m, 0.5H), 7.16 (t, *J* = 7.7 Hz, 0.5H), 7.10 – 7.02 (m, 1H), 6.78 (t, *J* = 7.9 Hz, 0.5H), 6.72 – 6.51 (m, 2H), 6.17 (d, *J* = 7.6 Hz, 0.5H), 4.44 (d, *J* = 2.5 Hz, 0.5H), 4.41 (d, *J* = 1.0 Hz, 0.5H), 3.95 (d, *J* = 1.8 Hz, 0.5H), 3.63 (s, 0.5H), 2.52 – 2.22 (m, 2H), 1.64 (s, 5H), 1.56 (s, 4H), 1.53 – 1.36 (m, 2H), 0.78 (s, 1.5H), 0.70 (s, 1.5H), 0.60 (s, 1.5H), 0.52 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 175.18, 173.14, 170.74, 170.00, 148.44, 148.25, 144.21, 143.56, 134.94, 133.61, 129.50, 129.25, 129.05, 128.94, 128.83, 128.72, 128.08, 127.57, 124.78, 123.18, 123.07, 122.87, 115.52, 115.01, 100.98, 100.72, 100.45, 100.28, 100.01, 85.72, 85.63, 68.12, 67.82, 62.55, 61.73, 52.38, 49.55, 35.70, 35.30, 34.65, 34.32, 31.53, 31.26, 28.14, 28.07, 27.22, 26.24, 22.67, 21.86.

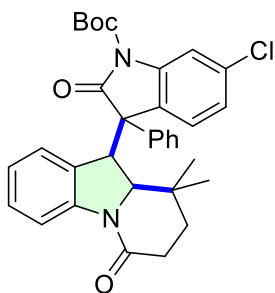
HRMS (ESI) calcd for C₃₃H₃₂F₂N₂O₄ (M+H)⁺: 559.2403, found: 559.2407.



¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.39 (s, 1H), 7.33 – 7.20 (m, 4H), 7.15 – 7.04 (m, 1H), 6.85 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 5.84 (d, *J* = 7.6 Hz, 1H), 5.69 (d, *J* = 8.2 Hz, 1H), 4.40 (d, *J* = 2.5 Hz, 1H), 2.96 (d, *J* = 2.6 Hz, 1H), 2.29 – 2.06 (m, 2H), 1.49 (s, 9H), 1.45 – 1.29 (m, 2H), 1.02 (s, 3H), 0.55 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.34, 168.95, 147.62, 143.70, 139.85, 135.56, 134.17, 128.37, 127.76, 127.67, 127.57, 127.43, 126.69, 126.64, 124.41, 124.14, 123.44, 122.72, 121.87, 114.44, 114.11, 84.26, 67.58, 58.86, 49.60, 34.20, 33.56, 29.89, 27.00, 25.53, 20.80.

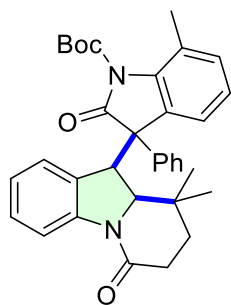
HRMS (ESI) calcd for C₃₃H₃₃ClN₂O₄ (M+H)⁺: 557.2202, found: 557.2205.



¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.75 (m, *J* = 8.3, 5.2 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.31 – 7.20 (m, 3H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.70 (t, *J* = 7.5 Hz, 1H), 4.24 (d, *J* = 2.0 Hz, 1H), 3.73 (d, *J* = 2.3 Hz, 1H), 2.54 – 2.25 (m, 2H), 1.53 (s, 9H), 1.45 – 1.27 (m, 2H), 0.43 (s, 3H), 0.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.92, 170.13, 148.43, 143.50, 140.34, 134.85, 134.68, 134.34, 129.19, 128.92, 128.68, 128.55, 128.16, 126.07, 124.07, 123.89, 123.62, 123.33, 123.13, 115.63, 115.28, 85.16, 68.03, 60.92, 51.57, 35.35, 34.14, 31.43, 28.05, 26.58, 21.94.

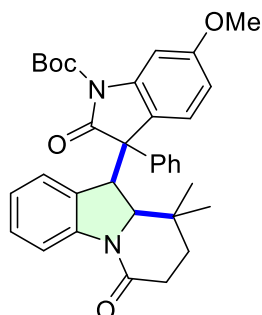
HRMS (ESI) calcd for C₃₃H₃₃ClN₂O₄ (M+H)⁺: 557.2202, found: 557.2205.



¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.0 Hz, 0.5H), 7.88 (d, *J* = 8.3 Hz, 0.5H), 7.77 – 7.70 (m, 1H), 7.60 – 7.49 (m, 1H), 7.40 – 7.28 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 0.5H), 7.15 (dd, *J* = 6.5, 2.2 Hz, 0.5H), 7.09 (m, 1H), 7.05 – 6.98 (m, 0.5H), 6.98 – 6.91 (m, 1H), 6.85 (t, *J* = 7.7 Hz, 0.5H), 6.79 (t, *J* = 8.0 Hz, 0.5H), 6.68 (t, *J* = 8.0 Hz, 0.5H), 6.01 (d, *J* = 7.6 Hz, 0.5H), 5.71 (d, *J* = 7.5 Hz, 0.5H), 4.47 (d, *J* = 2.4 Hz, 0.5H), 4.32 (d, *J* = 2.2 Hz, 0.5H), 3.87 (d, *J* = 2.4 Hz, 0.5H), 3.18 (d, *J* = 2.6 Hz, 0.5H), 2.60 – 2.34 (m, 1H), 2.23 (s, 1.5H), 2.21 – 2.10 (m, 1H), 2.04 (s, 1.5H), 1.64 (s, 4.5H), 1.62 (s, 4.5H), 1.57 – 1.36 (m, 2H), 1.13 (s, 1.5H), 0.64 (s, 1.5H), 0.54 (s, 1.5H), 0.47 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 177.01, 175.94, 170.01, 169.93, 149.48, 149.05, 144.78, 143.54, 138.60, 138.00, 136.68, 135.49, 132.02, 131.59, 129.15, 128.98, 128.80, 128.69, 128.51, 128.41, 128.26, 128.19, 128.11, 126.87, 126.22, 125.15, 124.61, 123.95, 123.76, 123.42, 123.17, 123.08, 122.89, 122.67, 114.96, 85.31, 85.03, 68.04, 67.94, 60.99, 60.27, 51.52, 50.95, 35.34, 35.28, 34.77, 34.24, 31.48, 31.13, 29.71, 27.76, 27.73, 26.55, 26.38, 22.24, 21.98, 19.24, 19.16.

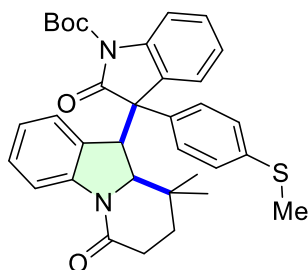
HRMS (ESI) calcd for C₃₄H₃₆N₂O₄ (M+Na)⁺: 559.2567, found: 559.2571.



¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.0 Hz, 0.5H), 7.88 (d, *J* = 8.0 Hz, 0.5H), 7.79 – 7.69 (m, 1H), 7.53 (s, 1H), 7.47 (d, *J* = 2.4 Hz, 0.5H), 7.40 – 7.27 (m, 3H), 7.23 – 7.15 (m, 1.5H), 7.11 (d, *J* = 7.5 Hz, 0.5H), 7.01 (t, *J* = 7.7 Hz, 0.5H), 6.79 (t, *J* = 8.0 Hz, 0.5H), 6.67 (t, *J* = 7.6 Hz, 0.5H), 6.59 (dd, *J* = 8.5, 2.5 Hz, 0.5H), 6.47 (dd, *J* = 8.5, 2.5 Hz, 0.5H), 5.93 (d, *J* = 7.6 Hz, 0.5H), 5.77 (d, *J* = 8.5 Hz, 0.5H), 4.48 (d, *J* = 2.6 Hz, 0.5H), 4.31 (d, *J* = 2.1 Hz, 0.5H), 3.85 (d, *J* = 2.3 Hz, 0.5H), 3.80 (s, 1.5H), 3.71 (s, 1.5H), 3.09 (d, *J* = 2.7 Hz, 0.5H), 2.62 – 2.34 (m, 1H), 2.35 – 2.09 (m, 1H), 1.62 (s, 4.5H), 1.61 (s, 4.5H), 1.59 – 1.37 (m, 2H), 1.13 (s, 1.5H), 0.65 (s, 1.5H), 0.53 (s, 1.5H), 0.47 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.88, 175.38, 170.17, 170.08, 160.39, 160.00, 148.95, 148.74, 144.81, 143.65, 141.08, 140.55, 137.58, 135.91, 129.22, 129.17, 128.94, 128.89, 128.75, 128.62, 128.59, 128.37, 128.33, 128.26, 127.58, 126.00, 125.30, 123.39, 123.27, 122.84, 117.31, 116.97, 115.22, 115.12, 109.59, 109.34, 101.69, 101.65, 84.81, 84.66, 68.71, 68.15, 60.70, 59.79, 55.51, 55.42, 51.71, 50.79, 35.41, 35.28, 34.73, 34.25, 31.59, 31.12, 28.18, 26.70, 26.64, 22.12, 22.09.

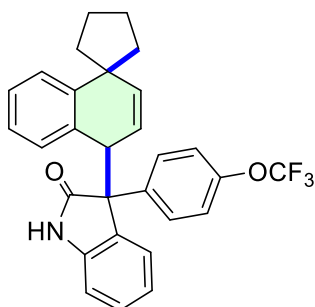
HRMS (ESI) calcd for C₃₄H₃₆N₂O₅ (M+Na)⁺: 559.2567, found: 559.2566.



¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.0 Hz, 0.5H), 7.85 (d, *J* = 2.9 Hz, 0.5H), 7.83 (d, *J* = 2.8 Hz, 0.5H), 7.69 – 7.60 (m, 1H), 7.57 (d, *J* = 7.9 Hz, 0.5H), 7.44 (s, 1H), 7.36 – 7.27 (m, 1H), 7.25 – 7.18 (m, 2.5H), 7.18 – 7.11 (m, 0.5H), 7.11 – 7.02 (m, 1H), 7.01 – 6.90 (m, 1H), 6.83 – 6.66 (m, 1H), 6.09 (d, *J* = 7.6 Hz, 0.5H), 5.87 (d, *J* = 7.5 Hz, 0.5H), 4.46 (d, *J* = 2.5 Hz, 0.5H), 4.32 (d, *J* = 1.9 Hz, 0.5H), 3.88 (d, *J* = 2.2 Hz, 0.5H), 3.05 (d, *J* = 2.6 Hz, 0.5H), 2.62 – 2.37 (m, 4H), 2.34 – 2.01 (m, 1H), 1.63 (s, 4.5H), 1.61 (s, 4.5H), 1.57 – 1.37 (m, 2H), 1.12 (s, 1.5H), 0.65 (s, 1.5H), 0.58 (s, 1.5H), 0.54 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 175.28, 173.74, 169.02, 168.87, 147.84, 147.62, 143.67, 142.46, 138.87, 138.31, 138.18, 137.95, 132.47, 130.77, 128.46, 128.29, 128.22, 128.10, 127.87, 127.83, 127.34, 127.02, 125.65, 125.02, 124.98, 124.45, 124.24, 124.13, 123.35, 122.78, 122.15, 122.11, 121.84, 114.04, 113.82, 113.61, 83.73, 83.59, 67.46, 67.04, 59.59, 58.68, 50.41, 49.36, 34.38, 34.17, 33.54, 33.07, 30.43, 29.92, 27.04, 25.82, 25.53, 20.98, 14.40, 14.38.

HRMS (ESI) calcd for C₃₄H₃₆N₂O₄S (M+Na)⁺: 591.2288, found: 591.2291.

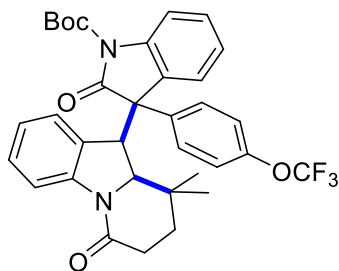


¹H NMR (400 MHz, DMSO-*d*₆) δ 10.59 (s, 1H), 7.65 (m, 1H), 7.59 (m, 1H), 7.42 – 7.28 (m, 4H), 7.27 – 7.14 (m, 1H), 7.13 – 6.81 (m, 3H), 6.74 (m, 1H), 6.64 (m, 0.5H), 6.15 (m, 0.5H), 5.86 (m, 0.5H), 5.68 (s, 1H), 5.52 (m, 0.5H), 4.67 (m, 0.5H), 4.56 (m, 0.5H), 1.97 – 1.38 (m, 8H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 179.24, 177.98, 148.10, 147.94, 147.92, 146.14, 145.38, 143.14, 142.28, 138.80, 138.60, 138.20, 137.89, 132.99, 132.54, 130.65, 129.94, 128.84, 128.69, 127.93, 127.78, 127.65, 127.42, 127.28, 127.19, 127.04, 125.13, 124.68, 121.83, 121.29, 121.23, 121.07, 119.24, 119.18, 110.04, 109.83, 61.88, 61.30, 47.34, 46.73, 45.88, 45.71, 45.43, 45.12, 44.35, 44.04, 26.87, 26.28, 26.09, 26.03.

¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -56.81, -56.83.

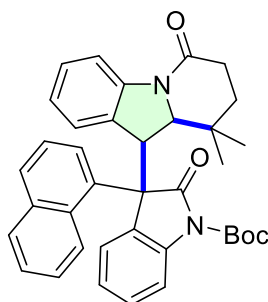
HRMS (ESI) calcd for C₂₉H₂₄F₃NO₂ (M+H)⁺: 476.1832, found: 476.1834.



¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.0 Hz, 0.5H), 7.86 – 7.68 (m, 2H), 7.61 – 7.44 (m, 1.5H), 7.37 – 7.21 (m, 1H), 7.18 – 6.84 (m, 5H), 6.71 (t, *J* = 7.1 Hz, 0.5H), 6.65 (t, *J* = 7.9 Hz, 0.5H), 5.90 (d, *J* = 7.6 Hz, 0.5H), 5.83 (d, *J* = 7.4 Hz, 0.5H), 4.38 (d, *J* = 2.4 Hz, 0.5H), 4.25 (d, *J* = 1.8 Hz, 0.5H), 3.78 (d, *J* = 2.1 Hz, 0.5H), 2.98 (d, *J* = 2.5 Hz, 0.5H), 2.59 – 2.28 (m, 1H), 2.26 – 1.95 (m, 1H), 1.57 (s, 4.5H), 1.55 (s, 4.5H), 1.51 – 1.31 (m, 2H), 1.05 (s, 1.8H), 0.58 (s, 1.7H), 0.53 – 0.40 (m, 2.4H).

¹³C NMR (101 MHz, CDCl₃) δ 175.02, 173.53, 168.95, 168.83, 148.06, 147.71, 147.50, 143.72, 142.46, 138.88, 138.37, 134.57, 132.97, 129.68, 129.31, 128.55, 128.40, 128.15, 128.01, 126.92, 126.65, 125.64, 124.09, 124.02, 123.93, 123.83, 123.51, 122.96, 122.15, 121.84, 119.72, 114.14, 114.08, 113.97, 113.77, 83.98, 83.82, 67.46, 67.06, 59.39, 58.54, 50.86, 49.78, 34.29, 34.14, 33.52, 33.07, 30.41, 29.90, 27.03, 25.59, 25.48, 20.95.

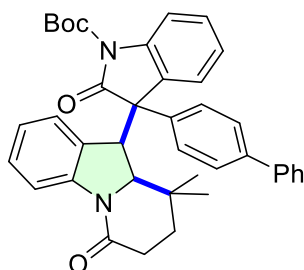
HRMS (ESI) calcd for C₃₄H₃₃F₃N₂O₅ (M+Na)⁺: 629.2234, found: 629.2237.



¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.21 (m, 8.5H), 7.15 – 6.60 (m, 5H), 6.43 (t, *J* = 6.7 Hz, 0.5H), 5.73 (s, 0.5H), 5.40 (s, 1H), 4.81 (s, 0.5H), 3.75 (s, 0.5H), 3.17 (s, 0.5H), 2.44 – 1.97 (m, 2H), 1.51 (s, 9H), 1.44 – 1.25 (m, 2H), 1.20 (s, 1.6H), 0.60 (s, 1.8H), 0.52 – 0.07 (m, 2.6H).

¹³C NMR (101 MHz, CDCl₃) δ 173.26, 169.01, 168.78, 147.93, 143.84, 142.86, 138.60, 138.05, 134.30, 131.96, 130.92, 129.34, 129.21, 128.68, 128.39, 128.28, 128.06, 128.00, 127.01, 125.26, 125.05, 124.58, 124.11, 123.58, 123.36, 123.23, 121.90, 121.75, 113.84, 113.71, 113.55, 113.32, 83.75, 83.52, 66.75, 48.17, 35.02, 34.52, 33.50, 30.59, 29.98, 27.02, 26.99, 26.11, 21.74, 21.34, -0.01.

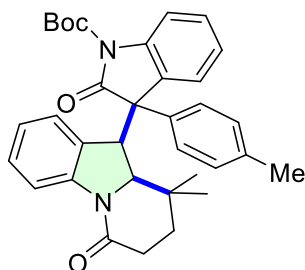
HRMS (ESI) calcd for C₃₇H₃₆N₂O₄ (M+Na)⁺: 595.2567, found: 595.2572.



¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.0 Hz, 0.5H), 7.92 – 7.85 (m, 1H), 7.84 – 7.78 (m, 1H), 7.69 – 7.55 (m, 5.5H), 7.51 – 7.41 (m, 2H), 7.41 – 7.30 (m, 2H), 7.24 – 7.05 (m, 2H), 7.05 – 6.94 (m, 1H), 6.79 (t, *J* = 7.0 Hz, 0.5H), 6.71 (t, *J* = 7.1 Hz, 0.5H), 6.11 (d, *J* = 7.6 Hz, 0.5H), 5.95 (d, *J* = 7.5 Hz, 0.5H), 4.55 (d, *J* = 2.6 Hz, 0.5H), 4.40 (d, *J* = 2.0 Hz, 0.5H), 3.95 (d, *J* = 2.3 Hz, 0.5H), 3.10 (d, *J* = 2.6 Hz, 0.5H), 2.64 – 2.38 (m, 1H), 2.33 – 2.09 (m, 1H), 1.64 (s, 4.5H), 1.63 (s, 4.5H), 1.58 – 1.37 (m, 2H), 1.16 (s, 1.5H), 0.68 (s, 1.5H), 0.58 (s, 1.5H), 0.56 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 176.36, 174.83, 170.09, 169.94, 148.93, 148.71, 144.77, 143.56, 141.07, 140.90, 140.15, 139.98, 139.43, 136.00, 134.29, 129.56, 129.37, 129.29, 129.23, 128.92, 128.42, 128.12, 127.71, 127.12, 127.08, 127.05, 126.81, 125.59, 125.30, 124.44, 123.86, 123.26, 123.18, 122.89, 115.11, 114.89, 114.69, 84.81, 84.66, 68.54, 68.14, 60.87, 59.97, 51.67, 50.60, 35.43, 35.25, 34.64, 34.16, 31.52, 31.01, 28.12, 26.79, 26.61, 22.09.

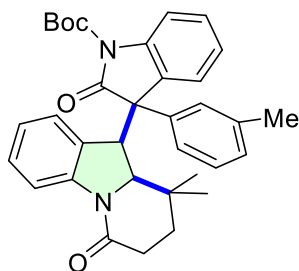
HRMS (ESI) calcd for C₃₉H₃₈N₂O₄ (M+Na)⁺: 621.2724, found: 621.2725.



¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.0 Hz, 0.5H), 7.89 – 7.81 (m, 1H), 7.64 – 7.58 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 0.5H), 7.41 (s, 1H), 7.35 – 7.27 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 0.5H), 7.19 – 7.13 (m, 2H), 7.13 – 6.90 (m, 2.5H), 6.76 (t, *J* = 7.5 Hz, 0.5H), 6.71 (t, *J* = 7.1 Hz, 0.5H), 6.04 (d, *J* = 7.6 Hz, 0.5H), 5.89 (d, *J* = 7.6 Hz, 0.5H), 4.48 (d, *J* = 2.6 Hz, 0.5H), 4.33 (d, *J* = 2.0 Hz, 0.5H), 3.90 (d, *J* = 2.3 Hz, 0.5H), 3.07 (d, *J* = 2.6 Hz, 0.5H), 2.61 – 2.40 (m, 1H), 2.37 (s, 1.5H), 2.33 (s, 1.5H), 2.29 – 2.06 (m, 1H), 1.62 (s, 4.5H), 1.60 (s, 4.5H), 1.55 – 1.38 (m, 2H), 1.12 (s, 1.5H), 0.65 (s, 1.5H), 0.60 – 0.44 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.60, 175.05, 170.17, 170.02, 149.05, 148.83, 144.81, 143.60, 140.02, 139.45, 138.27, 138.16, 134.05, 132.33, 129.37, 129.29, 129.25, 129.07, 128.88, 128.71, 128.35, 126.85, 125.90, 125.67, 125.42, 125.34, 124.39, 123.82, 123.33, 123.23, 122.88, 115.16, 115.11, 114.87, 114.66, 84.73, 84.59, 68.60, 68.13, 60.86, 59.92, 51.54, 50.54, 35.49, 35.31, 34.71, 34.25, 31.59, 31.08, 28.18, 26.83, 26.68, 22.14, 21.21, 21.11.

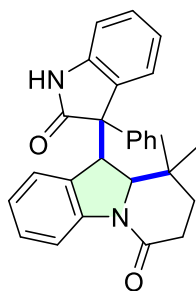
HRMS (ESI) calcd for C₃₄H₃₆N₂O₄ (M+Na)⁺: 559.2567, found: 559.2570.



¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.0 Hz, 0.5H), 7.86 (d, *J* = 3.0 Hz, 0.5H), 7.84 (d, *J* = 3.0 Hz, 0.5H), 7.63 (s, 0.5H), 7.57 (d, *J* = 7.7 Hz, 0.5H), 7.39 (d, *J* = 7.8 Hz, 0.5H), 7.37 – 7.27 (m, 2H), 7.24 – 6.90 (m, 5H), 6.77 (t, *J* = 8.0 Hz, 0.5H), 6.70 (t, *J* = 8.0 Hz, 0.5H), 6.01 (d, *J* = 7.6 Hz, 0.5H), 5.90 (d, *J* = 7.5 Hz, 0.5H), 4.50 (d, *J* = 2.6 Hz, 0.5H), 4.36 (d, *J* = 2.0 Hz, 0.5H), 3.88 (d, *J* = 2.3 Hz, 0.5H), 3.06 (d, *J* = 2.6 Hz, 0.5H), 2.60 – 2.39 (m, 1H), 2.39 – 2.32 (m, 3H), 2.30 – 2.06 (m, 1H), 1.63 (s, 4.5H), 1.61 (s, 4.5H), 1.57 – 1.37 (m, 2H), 1.13 (s, 1.5H), 0.66 (s, 1.5H), 0.61 – 0.50 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 176.42, 174.83, 170.08, 169.93, 148.96, 148.73, 144.74, 143.53, 139.93, 139.38, 138.23, 136.88, 135.19, 129.90, 129.31, 129.21, 129.03, 128.83, 128.53, 128.37, 128.27, 128.21, 126.83, 126.12, 125.94, 125.71, 125.56, 125.33, 124.32, 123.75, 123.22, 123.13, 122.78, 115.07, 115.03, 114.78, 114.58, 84.69, 84.56, 68.53, 68.08, 60.97, 60.03, 51.65, 50.55, 35.46, 35.24, 34.63, 34.20, 31.51, 30.99, 28.11, 26.62, 22.10, 22.07, 21.74, 21.68.

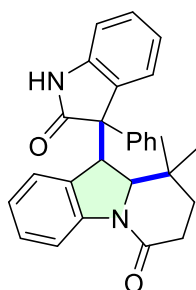
HRMS (ESI) calcd for C₃₄H₃₆N₂O₄ (M+Na)⁺: 559.2567, found: 559.2571.



^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.4 Hz, 2H), 7.47 – 7.30 (m, 5H), 7.24 (d, J = 7.5 Hz, 1H), 7.08 (t, J = 7.1 Hz, 1H), 7.05 – 6.91 (m, 2H), 6.82 – 6.66 (m, 2H), 4.28 (d, J = 2.5 Hz, 1H), 3.98 (d, J = 2.5 Hz, 1H), 2.68 – 2.39 (m, 2H), 1.67 – 1.37 (m, 2H), 0.57 (s, 3H), 0.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 179.53, 170.18, 143.52, 140.46, 135.75, 128.94, 128.72, 128.60, 128.47, 128.12, 127.29, 125.89, 123.61, 123.17, 122.00, 114.95, 110.07, 68.15, 61.19, 50.75, 35.24, 34.22, 31.48, 26.34, 21.91.

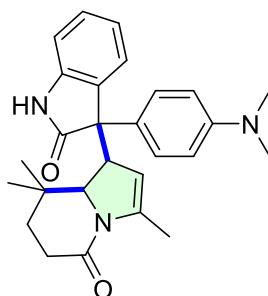
HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 423.2067, found: 423.2065.



^1H NMR (400 MHz, CDCl_3) δ 9.17 (d, J = 61.2 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.62 (s, 2H), 7.40 (m, 3H), 7.24 (dd, J = 17.5, 8.2 Hz, 2H), 6.96 (d, J = 7.8 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 6.71 (t, J = 7.5 Hz, 1H), 5.98 (d, J = 7.5 Hz, 2H), 4.44 (d, J = 1.5 Hz, 1H), 3.16 (s, 1H), 2.39 – 2.09 (m, 2H), 1.75 – 1.37 (m, 2H), 1.13 (s, 3H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 178.79, 169.99, 144.55, 141.06, 137.16, 129.06, 129.01, 128.69, 128.60, 128.49, 128.03, 127.25, 125.23, 122.74, 122.56, 114.98, 110.08, 68.33, 60.49, 49.88, 35.24, 34.53, 31.06, 26.45, 22.19.

HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 423.2067, found: 423.2068.

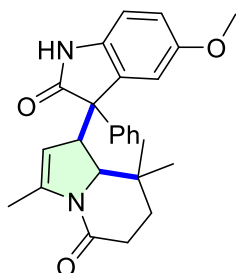


^1H NMR (400 MHz, CDCl_3) δ 9.14 (s, 0.5H), 8.89 (s, 0.5H), 7.50 – 7.41 (m, 1H), 7.27 – 7.09 (m, 3H), 7.02 – 6.91 (m, 1H), 6.88 (d, J = 7.5 Hz, 0.5H), 6.81 (d, J = 7.6 Hz, 0.5H), 6.65 – 6.55 (m, 2H), 4.53 (d, J = 0.6 Hz, 0.5H), 4.43 (d, J = 0.9 Hz, 0.5H), 3.82 (d, J = 1.4 Hz, 0.5H), 3.68 (d, J = 3.0 Hz, 0.5H), 3.49 (d, J = 1.5 Hz, 0.5H), 2.85 (s, 3H), 2.83 (s, 3H), 2.75 (d, J = 3.6 Hz, 0.5H), 2.41 – 2.16 (m, 1.5H), 2.12 (s, 1.5H), 2.08 – 1.95 (m, 0.5H), 1.83 (s, 1.5H), 1.44 – 1.25 (m, 2H), 0.87 (s, 1.5H), 0.74 (s, 1.5H), 0.65 (s, 1.5H), 0.31 (s, 1.5H).

^{13}C NMR (101 MHz, CDCl_3) δ 180.53, 179.87, 169.42, 169.17, 149.99, 149.72, 144.01, 143.92, 141.57, 140.95, 129.58, 129.38, 129.22, 128.53, 128.40, 128.13, 126.63, 125.70, 125.63, 123.26, 122.62, 121.85, 112.39, 112.22,

110.20, 109.96, 107.65, 107.31, 67.80, 67.40, 59.76, 59.07, 51.52, 49.71, 40.48, 40.44, 34.90, 34.77, 34.37, 34.26, 31.69, 31.09, 26.09, 25.67, 21.90, 15.72, 15.42.

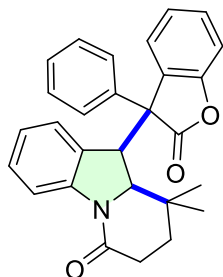
HRMS (ESI) calcd for $C_{27}H_{31}N_3O_2$ ($M+Na$)⁺: 452.2308, found: 452.2309.



1H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 0.6H), 9.04 (s, 0.4H), 7.84 – 7.74 (m, 0.8H), 7.52 – 7.43 (m, 1.2H), 7.42 – 7.32 (m, 3H), 7.02 – 6.81 (m, 3H), 4.62 – 4.55 (m, 1H), 4.00 (d, J = 3.0 Hz, 0.6H), 3.85 – 3.79 (m, 3H), 3.72 (d, J = 3.0 Hz, 0.4H), 3.66 (d, J = 1.6 Hz, 0.4H), 2.90 (d, J = 3.6 Hz, 0.6H), 2.48 – 2.31 (m, 1H), 2.26 (s, 1.6H), 2.23 – 2.11 (m, 0.6H), 2.06 – 2.01 (m, 0.4H), 2.00 (s, 1.4H), 1.54 – 1.40 (m, 2H), 1.00 (s, 1.8H), 0.87 (s, 1.8H), 0.77 (s, 1.2H), 0.34 (s, 1.2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.79, 179.17, 169.28, 169.23, 155.69, 155.23, 144.40, 144.34, 138.25, 136.06, 134.91, 134.40, 130.26, 130.15, 128.63, 128.44, 128.38, 127.76, 127.56, 114.27, 113.36, 113.26, 113.06, 110.55, 110.50, 106.94, 106.87, 67.80, 67.33, 60.83, 60.20, 56.06, 55.83, 51.79, 49.87, 34.74, 34.28, 31.62, 31.12, 25.76, 25.58, 21.89, 21.84, 15.80, 15.47.

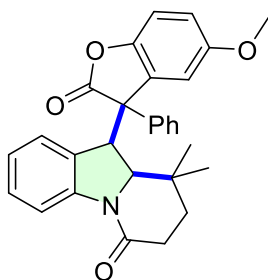
HRMS (ESI) calcd for $C_{26}H_{28}N_2O_3$ ($M+Na$)⁺: 439.1992, found: 439.1994.



1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.1 Hz, 0.5H), 7.88 (d, J = 8.1 Hz, 0.5H), 7.83 – 7.72 (m, 1H), 7.68 – 7.48 (m, 1H), 7.47 – 7.29 (m, 4H), 7.25 – 7.10 (m, 2H), 7.10 – 6.93 (m, 1.5H), 6.92 – 6.78 (m, 1H), 6.72 (t, J = 7.1 Hz, 0.5H), 6.00 – 5.85 (m, 1H), 4.43 (d, J = 2.2 Hz, 0.5H), 4.26 (d, J = 2.2 Hz, 0.5H), 3.91 (d, J = 2.4 Hz, 0.5H), 3.17 (d, J = 2.4 Hz, 0.5H), 2.65 – 2.36 (m, 1H), 2.34 – 2.07 (m, 1H), 1.79 – 1.59 (m, 1H), 1.58 – 1.40 (m, 1H), 1.17 (s, 1.5H), 0.63 (s, 1.5H), 0.55 (s, 1.5H), 0.39 (s, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.60, 176.43, 170.05, 153.27, 152.69, 144.76, 143.59, 136.08, 134.67, 130.09, 129.73, 129.63, 129.23, 128.95, 128.79, 128.72, 128.47, 128.08, 127.46, 127.35, 125.79, 125.31, 125.16, 124.94, 124.46, 123.97, 123.75, 123.47, 122.93, 115.31, 115.23, 111.02, 110.90, 68.99, 68.02, 60.59, 59.47, 51.94, 51.10, 35.49, 35.23, 34.39, 34.24, 31.51, 31.11, 26.42, 26.25, 22.20, 21.90.

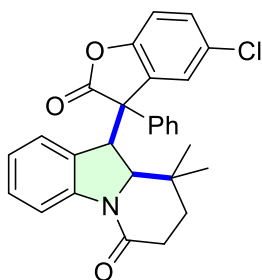
HRMS (ESI) calcd for $C_{28}H_{25}NO_3$ ($M+H$)⁺: 424.1907, found: 424.1907.



^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.0$ Hz, 0.5H), 7.84 (d, $J = 8.0$ Hz, 0.5H), 7.72 (m, 1H), 7.48 (m, 1H), 7.42 – 7.24 (m, 4H), 7.18 – 7.09 (m, 1H), 7.00 – 6.96 (m, 1H), 6.83 – 6.75 (m, 1.5H), 6.73 – 6.57 (m, 1.5H), 5.88 (d, $J = 7.6$ Hz, 0.5H), 5.33 (d, $J = 2.5$ Hz, 0.5H), 4.39 (d, $J = 2.3$ Hz, 0.5H), 4.19 (d, $J = 2.1$ Hz, 0.5H), 3.80 (d, $J = 2.3$ Hz, 0.5H), 3.65 (s, 1.5H), 3.42 (s, 1.5H), 3.10 (d, $J = 2.5$ Hz, 0.5H), 2.52 – 2.33 (m, 1H), 2.28 – 2.13 (m, 1H), 1.71 – 1.56 (m, 1H), 1.52 – 1.34 (m, 1H), 1.12 (s, 1.5H), 0.58 (s, 1.5H), 0.48 (s, 1.5H), 0.34 (s, 1.5H).

^{13}C NMR (101 MHz, CDCl_3) δ 177.82, 176.69, 170.02, 169.88, 156.19, 155.98, 146.96, 146.51, 144.78, 143.47, 136.10, 134.56, 129.48, 129.18, 128.86, 128.70, 128.63, 128.59, 128.32, 128.04, 127.43, 125.84, 125.45, 125.23, 123.67, 123.44, 122.92, 116.52, 115.19, 115.05, 111.86, 111.32, 111.24, 68.90, 67.91, 61.16, 59.96, 56.08, 55.74, 51.68, 50.81, 35.43, 35.14, 34.29, 34.12, 31.42, 31.04, 26.35, 26.20, 22.06, 21.89.

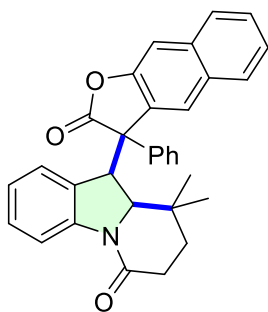
HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{27}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$: 454.2013, found: 454.2012.



^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.1$ Hz, 0.5H), 7.88 (d, $J = 8.1$ Hz, 0.5H), 7.68 (m, 1H), 7.54 – 7.28 (m, 4H), 7.24 (m, 1.5H), 7.14 – 7.05 (m, 1H), 7.05 – 6.94 (m, 1H), 6.85 – 6.71 (m, 1H), 6.68 (t, $J = 7.5$ Hz, 0.5H), 5.86 (d, $J = 7.6$ Hz, 0.5H), 5.72 (s, 0.5H), 4.37 (d, $J = 1.9$ Hz, 0.5H), 4.18 (d, $J = 1.9$ Hz, 0.5H), 3.76 (d, $J = 2.3$ Hz, 0.5H), 3.12 (d, $J = 2.1$ Hz, 0.5H), 2.60 – 2.34 (m, 1H), 2.34 – 2.07 (m, 1H), 1.74 – 1.54 (m, 1H), 1.53 – 1.33 (m, 1H), 1.09 (s, 1.5H), 0.57 (s, 1.5H), 0.47 (s, 1.5H), 0.34 (s, 1.5H).

^{13}C NMR (101 MHz, CDCl_3) δ 176.80, 175.63, 169.88, 151.55, 151.04, 144.70, 143.52, 135.32, 133.84, 130.12, 129.87, 129.72, 129.68, 129.44, 129.19, 129.03, 128.96, 128.89, 128.43, 128.15, 127.45, 126.79, 126.62, 125.89, 124.97, 123.67, 123.27, 123.00, 115.40, 115.35, 111.98, 111.86, 68.81, 67.89, 60.97, 59.88, 51.88, 51.11, 35.46, 35.15, 34.26, 34.11, 31.31, 31.02, 26.32, 26.17, 21.94, 21.71.

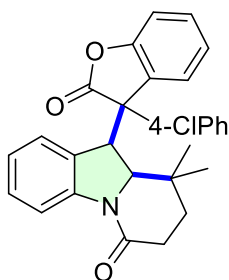
HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{24}\text{ClNO}_3$ ($\text{M}+\text{H}$) $^+$: 458.1517, found: 458.1518.



¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.8 Hz, 0.5H), 7.83 – 7.74 (m, 1H), 7.73 – 7.56 (m, 3.5H), 7.48 – 7.34 (m, 5H), 7.25 – 7.16 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 0.5H), 7.06 (d, *J* = 8.8 Hz, 0.5H), 6.90 – 6.79 (m, 1.5H), 6.75 (t, *J* = 7.0 Hz, 0.5H), 6.66 (d, *J* = 7.6 Hz, 0.5H), 5.83 (d, *J* = 8.5 Hz, 0.5H), 4.73 (d, *J* = 2.0 Hz, 0.5H), 4.61 (s, 0.5H), 4.08 (d, *J* = 1.2 Hz, 0.5H), 3.16 (d, *J* = 1.8 Hz, 0.5H), 2.51 – 1.88 (m, 2H), 1.75 – 1.36 (m, 2H), 1.16 (s, 1.5H), 1.03 (s, 1.5H), 0.62 (s, 1.5H), 0.53 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 178.19, 177.01, 169.75, 169.70, 151.68, 151.12, 144.68, 142.85, 135.06, 134.43, 132.23, 131.63, 131.32, 131.10, 130.50, 130.13, 129.76, 129.73, 129.63, 129.15, 129.10, 129.03, 128.83, 128.69, 128.65, 128.45, 127.68, 126.69, 125.62, 124.70, 124.67, 124.29, 123.44, 123.16, 123.03, 119.16, 118.47, 116.05, 114.40, 111.09, 110.89, 68.95, 68.44, 64.02, 63.07, 51.77, 50.01, 36.33, 35.36, 34.29, 34.20, 31.77, 31.09, 27.77, 26.11, 22.96, 22.27.

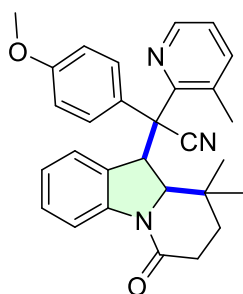
HRMS (ESI) calcd for C₃₂H₂₇NO₃ (M+H)⁺: 474.2064, found: 474.2063.



¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.1 Hz, 0.5H), 7.80 (d, *J* = 8.0 Hz, 0.5H), 7.71 – 7.61 (m, 1H), 7.50 – 7.37 (m, 1H), 7.37 – 7.29 (m, 2H), 7.29 – 7.21 (m, 1H), 7.15 – 7.06 (m, 1.5H), 7.04 – 6.88 (m, 1.5H), 6.85 – 6.73 (m, 1.5H), 6.70 (t, *J* = 7.5 Hz, 0.5H), 5.92 (d, *J* = 7.6 Hz, 0.5H), 5.83 (d, *J* = 7.5 Hz, 0.5H), 4.31 (d, *J* = 2.4 Hz, 0.5H), 4.15 (d, *J* = 2.3 Hz, 0.5H), 3.79 (d, *J* = 2.4 Hz, 0.5H), 3.06 (d, *J* = 2.5 Hz, 0.5H), 2.57 – 2.31 (m, 1H), 2.29 – 1.96 (m, 1H), 1.69 – 1.34 (m, 2H), 1.10 (s, 1.5H), 0.56 (s, 1.5H), 0.48 (s, 1.5H), 0.40 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 177.20, 176.05, 169.93, 153.12, 152.56, 144.67, 143.45, 134.95, 134.82, 134.57, 133.21, 130.26, 130.07, 129.90, 129.78, 129.72, 129.28, 129.02, 128.98, 127.60, 127.09, 127.03, 125.48, 125.07, 124.64, 124.55, 124.38, 124.07, 123.69, 123.31, 122.94, 115.24, 111.07, 110.95, 68.88, 67.99, 60.04, 58.97, 51.80, 50.95, 35.38, 35.16, 34.25, 34.07, 31.37, 30.97, 26.41, 26.28, 22.09, 21.78.

HRMS (ESI) calcd for C₂₂H₂₀NO₃ (M+ Na)⁺: 369.1335, found: 369.1336.

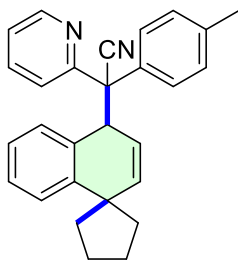


¹H NMR (400 MHz, CDCl₃) δ 8.67 (dd, *J* = 4.6, 1.2 Hz, 0.5H), 8.51 (s, 0.5H), 8.25 (d, *J* = 8.0 Hz, 0.5H), 7.96 (t, *J* = 11.4 Hz, 0.5H), 7.49 – 7.39 (m, 1H), 7.37 – 7.25 (m, 1.5H), 7.22 – 7.03 (m, 1.5H), 6.93 – 6.55 (m, 5H), 5.29 (d, *J* = 9.2 Hz, 0.5H), 5.00 (s, 0.5H), 4.14 (d, *J* = 2.1 Hz, 0.5H), 3.82 (d, *J* = 3.1 Hz, 0.5H), 3.77 (s, 1.5H), 3.72 (s, 1.5H), 2.66 – 2.30 (m, 2H), 2.13 (s, 1.5H), 1.95 (s, 1.5H), 1.83 – 1.61 (m, 1.5H), 1.57 – 1.36 (m, 2H), 0.67 – 0.54 (m, 3H), 0.23 (s, 1.5H).

¹H NMR (400 MHz, CDCl₃) δ 170.15, 169.87, 159.56, 159.25, 153.68, 145.18, 145.03, 144.72, 140.98, 140.88, 134.38, 129.76, 129.18, 128.93, 128.85, 128.06, 126.15, 123.71, 123.17, 122.38, 118.55, 115.59, 114.79, 113.92,

113.52, 69.29, 67.06, 58.57, 55.37, 55.25, 49.46, 36.41, 35.20, 34.71, 34.35, 31.53, 31.27, 26.10, 23.22, 21.84, 20.15, 20.07.

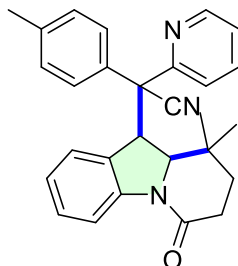
HRMS (ESI) calcd for $C_{29}H_{29}N_3O_2$ ($M+Na$)⁺: 474.2152, found: 474.2153.



¹H NMR (400 MHz, DMSO-*d*₆) δ 8.76 (dd, *J* = 10.3, 4.1 Hz, 1H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 6.9 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 9.1 Hz, 0H), 7.38 (dd, *J* = 14.3, 7.6 Hz, 3H), 7.29 – 7.11 (m, 3H), 6.66 (dt, *J* = 21.0, 7.0 Hz, 1H), 6.10 – 5.85 (m, 2H), 5.50 (dd, *J* = 10.3, 4.3 Hz, 0H), 5.35 (dd, *J* = 10.3, 4.3 Hz, 1H), 5.25 (d, *J* = 4.4 Hz, 1H), 5.05 (d, *J* = 4.3 Hz, 0H), 2.28 (s, 3H), 2.17 – 1.62 (m, 8H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 157.59, 157.55, 149.83, 149.67, 146.34, 146.28, 138.91, 138.67, 138.47, 138.28, 137.94, 137.71, 135.26, 135.03, 132.79, 131.79, 129.73, 129.55, 127.97, 127.91, 127.84, 127.46, 127.20, 124.79, 124.29, 123.77, 123.56, 122.78, 120.78, 120.66, 120.05, 119.84, 63.29, 62.93, 46.76, 46.48, 46.43, 46.26, 46.00, 45.42, 45.36, 45.21, 26.33, 26.30, 26.24, 20.98, 20.93.

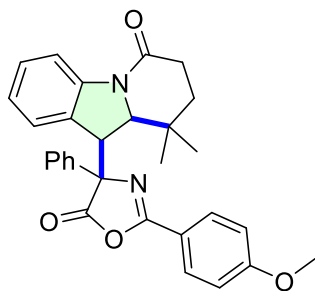
HRMS (ESI) calcd for $C_{28}H_{26}N_2$ ($M+H$)⁺: 391.2169, found: 391.2172.



¹H NMR (400 MHz, CDCl₃) δ 8.82 (d, *J* = 5.6 Hz, 0.5H), 8.70 (d, *J* = 5.6 Hz, 0.5H), 8.23 (d, *J* = 8.1 Hz, 0.5H), 8.11 (d, *J* = 8.1 Hz, 0.5H), 7.80 – 7.70 (m, 1H), 7.68 – 7.58 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 0.5H), 7.50 (d, *J* = 8.0 Hz, 0.5H), 7.45 – 7.37 (m, 1H), 7.35 – 7.28 (m, 0.5H), 7.28 – 7.24 (m, 0.5H), 7.21 – 7.11 (m, 2H), 7.11 – 7.04 (m, 1H), 6.69 – 6.58 (m, 1H), 6.09 (d, *J* = 7.6 Hz, 0.5H), 6.04 (d, *J* = 7.7 Hz, 0.5H), 4.94 (d, *J* = 2.6 Hz, 0.5H), 4.84 (d, *J* = 2.1 Hz, 0.5H), 3.80 (d, *J* = 2.3 Hz, 0.5H), 3.78 (d, *J* = 2.8 Hz, 0.5H), 2.64 – 2.33 (m, 2H), 2.33 – 2.27 (m, 3H), 1.63 – 1.33 (m, 2H), 0.77 (s, 1.5H), 0.58 (s, 1.5H), 0.57 (s, 1.5H), 0.30 (s, 1.5H).

¹³C NMR (101 MHz, CDCl₃) δ 170.19, 170.10, 156.57, 156.29, 149.53, 148.95, 144.78, 144.53, 138.73, 138.67, 137.69, 137.38, 133.15, 132.33, 129.50, 129.20, 128.70, 128.45, 128.29, 127.88, 125.61, 124.89, 123.94, 123.54, 123.41, 123.39, 123.06, 122.78, 120.26, 119.48, 115.82, 115.42, 69.56, 68.24, 60.96, 60.23, 50.99, 50.66, 35.78, 35.24, 34.58, 34.34, 31.43, 31.32, 26.95, 26.15, 22.56, 21.97, 21.16, 21.08.

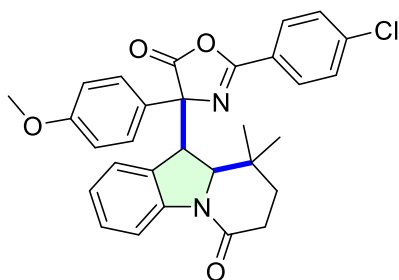
HRMS (ESI) calcd for $C_{28}H_{27}N_3O$ ($M+Na$)⁺: 444.2046, found: 444.2050.



¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.1 Hz, 0.5H), 7.98 (d, *J* = 8.1 Hz, 0.5H), 7.88 – 7.79 (m, 1H), 7.79 – 7.74 (m, 1H), 7.72 – 7.66 (m, 1H), 7.62 – 7.55 (m, 1H), 7.38 – 7.23 (m, 3H), 7.16 – 7.06 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 0.5H), 6.90 – 6.84 (m, 1H), 6.82 – 6.76 (m, 1H), 6.76 – 6.70 (m, 1H), 6.65 (t, *J* = 7.5 Hz, 0.5H), 4.00 (d, *J* = 3.1 Hz, 0.5H), 3.99 (d, *J* = 2.8 Hz, 0.5H), 3.90 (d, *J* = 2.5 Hz, 0.5H), 3.82 (d, *J* = 2.9 Hz, 0.5H), 3.77 (s, 1.5H), 3.71 (s, 1.5H), 2.57 – 2.22 (m, 2H), 1.57 – 1.29 (m, 2H), 0.50 – 0.41 (m, 3H), 0.32 (s, 1.5H), 0.12 (s, 1.5H).

¹³C NMR (151 MHz, CDCl₃) δ 178.65, 176.24, 170.06, 169.78, 163.43, 163.21, 160.41, 160.06, 144.36, 144.09, 136.17, 135.57, 130.00, 129.83, 129.43, 129.39, 128.88, 128.82, 128.76, 128.71, 127.28, 127.18, 126.75, 126.64, 125.76, 123.76, 123.33, 122.78, 117.74, 117.46, 115.57, 115.28, 114.33, 114.02, 67.33, 66.47, 55.52, 55.43, 52.29, 52.05, 34.84, 34.41, 34.30, 33.96, 31.11, 25.64, 25.32, 25.14, 24.97, 21.42.

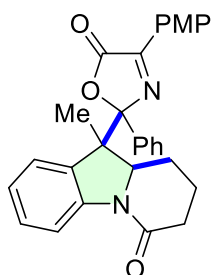
HRMS (ESI) calcd for C₃₀H₂₈N₂O₄ (M+H)⁺: 481.2122, found: 481.2123.



¹H NMR (400 MHz, CDCl₃) δ 8.19 – 7.95 (m, 1H), 7.89 – 7.80 (m, 1H), 7.78 – 7.70 (m, 0.7H), 7.69 – 7.56 (m, 1.5H), 7.54 – 7.44 (m, 0.6H), 7.39 – 7.23 (m, 2H), 7.21 – 7.19 (m, 0.7H), 7.17 – 7.10 (m, 0.9H), 7.08 – 6.65 (m, 4H), 4.62 – 3.87 (m, 1.6H), 3.87 – 3.56 (m, 4.3H), 2.66 – 2.17 (m, 2H), 1.64 – 1.31 (m, 2H), 1.10 – 0.17 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 178.32, 176.14, 169.99, 169.73, 163.57, 163.35, 160.63, 144.35, 144.11, 135.06, 134.96, 134.67, 134.07, 130.07, 129.89, 129.57, 128.87, 128.84, 128.71, 128.63, 128.56, 128.28, 126.38, 126.25, 125.74, 123.74, 123.54, 123.36, 122.84, 117.47, 117.19, 115.59, 115.31, 114.40, 114.08, 76.74, 76.45, 68.82, 67.34, 66.59, 55.55, 55.50, 55.45, 53.00, 52.25, 51.95, 49.48, 35.74, 34.87, 34.42, 34.25, 31.08, 26.15, 25.63, 25.46, 22.70, 21.43, 21.39.

HRMS (ESI) calcd for C₃₀H₂₇ClN₂O₄ (M+H)⁺: 515.1732, found: 515.1730.

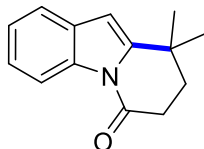


¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.03 (m, 1H), 8.00 – 7.92 (m, 1H), 7.75 (m, 3H), 7.35 – 7.20 (m, 4H), 7.16 – 7.01 (m, 1H), 6.98 – 6.78 (m, 3H), 4.79 (dd, *J* = 11.7, 2.6 Hz, 0.5H), 4.70 (dd, *J* = 11.9, 2.8 Hz, 0.5H), 3.82 (s, 1.5H),

3.75 (s, 1.5H), 2.62 – 2.21 (m, 2H), 1.85 – 1.67 (m, 2H), 1.67 – 1.50 (m, 1H), 1.42 (s, 1.5H), 1.37 (s, 1.5H), 1.31 – 1.20 (m, 2H), 1.05 – 0.67 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 177.43, 176.96, 168.92, 168.75, 163.54, 163.27, 160.11, 159.25, 141.74, 141.51, 134.55, 134.37, 134.15, 130.12, 129.88, 128.79, 128.48, 128.25, 128.21, 127.77, 127.63, 124.25, 124.08, 123.27, 117.87, 117.68, 117.20, 116.99, 114.42, 114.12, 64.68, 63.34, 55.57, 55.47, 54.78, 53.49, 32.23, 24.91, 24.79, 20.21, 20.15, 19.69, 18.43.

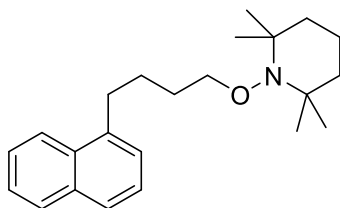
HRMS (ESI) calcd for C₂₉H₂₆N₂O₄ (M+H)⁺: 467.1965, found: 467.1963.



¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.32 – 7.21 (m, 2H), 6.36 (s, 1H), 2.87 (t, *J* = 6.7 Hz, 2H), 1.95 (t, *J* = 6.7 Hz, 2H), 1.43 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 169.30, 147.40, 135.20, 129.83, 124.33, 124.05, 119.97, 116.59, 103.29, 35.29, 31.61, 31.23, 28.76.

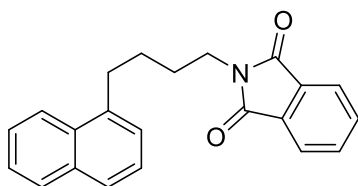
HRMS (ESI) calcd for C₁₄H₁₅NO (M+H)⁺: 214.1226, found: 214.1228.



¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 3.14 (q, *J* = 4.5, 4.0 Hz, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 1.94 – 1.80 (m, 4H), 1.79 – 1.37 (m, 7H), 1.11 (d, *J* = 35.2 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 138.19, 133.92, 131.84, 128.79, 126.65, 125.98, 125.78, 125.54, 125.45, 123.79, 59.93, 38.99, 32.92, 32.82, 32.02, 30.51, 25.41, 20.54, 16.99.

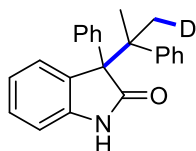
HRMS (ESI) calcd for C₂₃H₃₃NO (M+H)⁺: 214.1226, found: 214.1228.



¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.53 (dddd, *J* = 19.8, 8.0, 6.8, 1.4 Hz, 2H), 7.47 – 7.40 (m, 1H), 7.37 (d, *J* = 5.7 Hz, 1H), 3.16 (d, *J* = 7.1 Hz, 2H), 2.81 – 2.69 (m, 2H), 2.04 – 1.90 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 169.50, 161.99, 137.79, 134.76, 133.93, 131.81, 128.95, 128.82, 126.76, 126.04, 125.87, 125.57, 125.49, 123.98, 123.73, 32.55, 30.91, 29.80, 24.72.

HRMS (ESI) calcd for C₂₂H₁₉NO₂ (M+H)⁺: 214.1226, found: 214.1228.

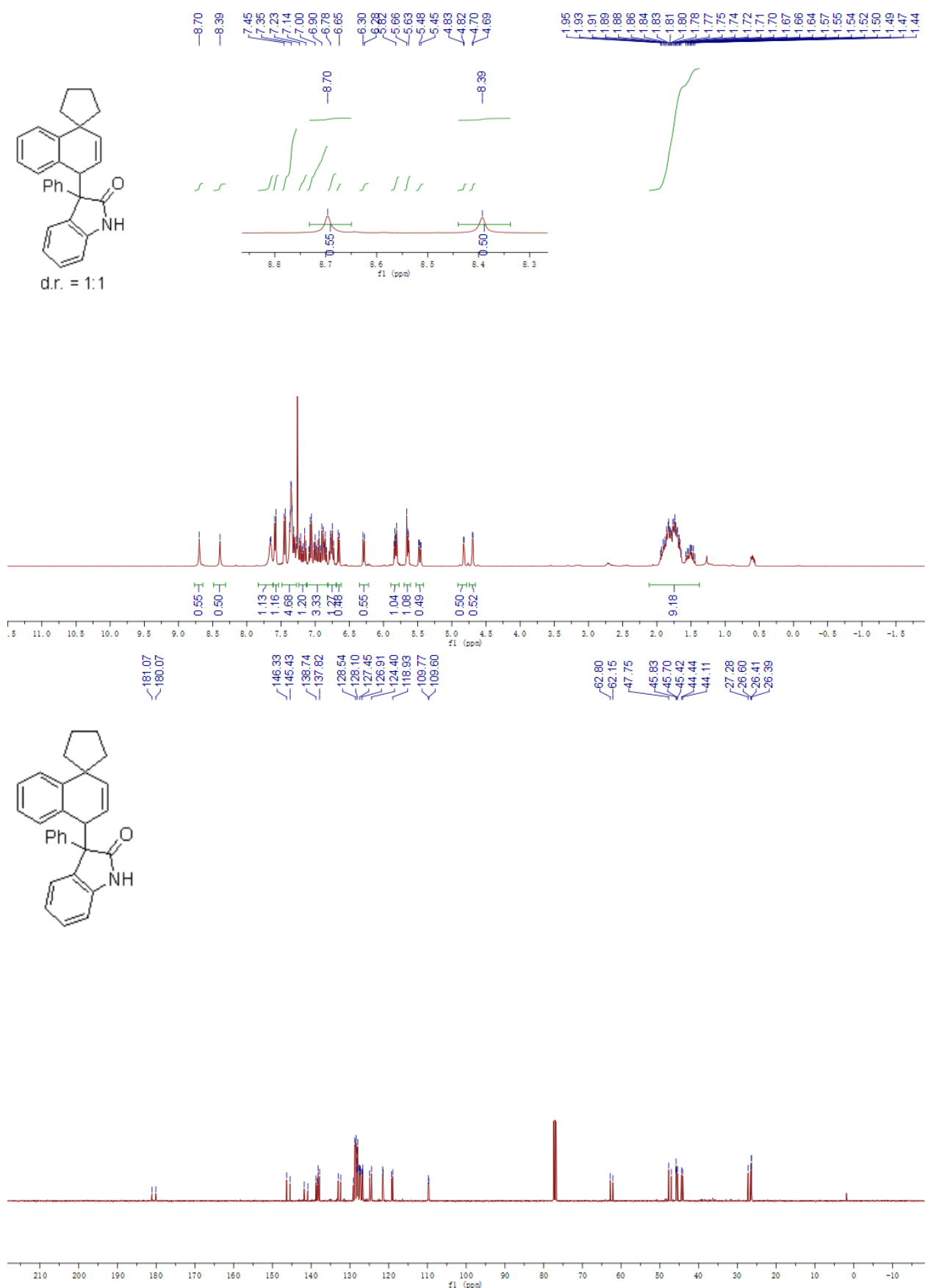


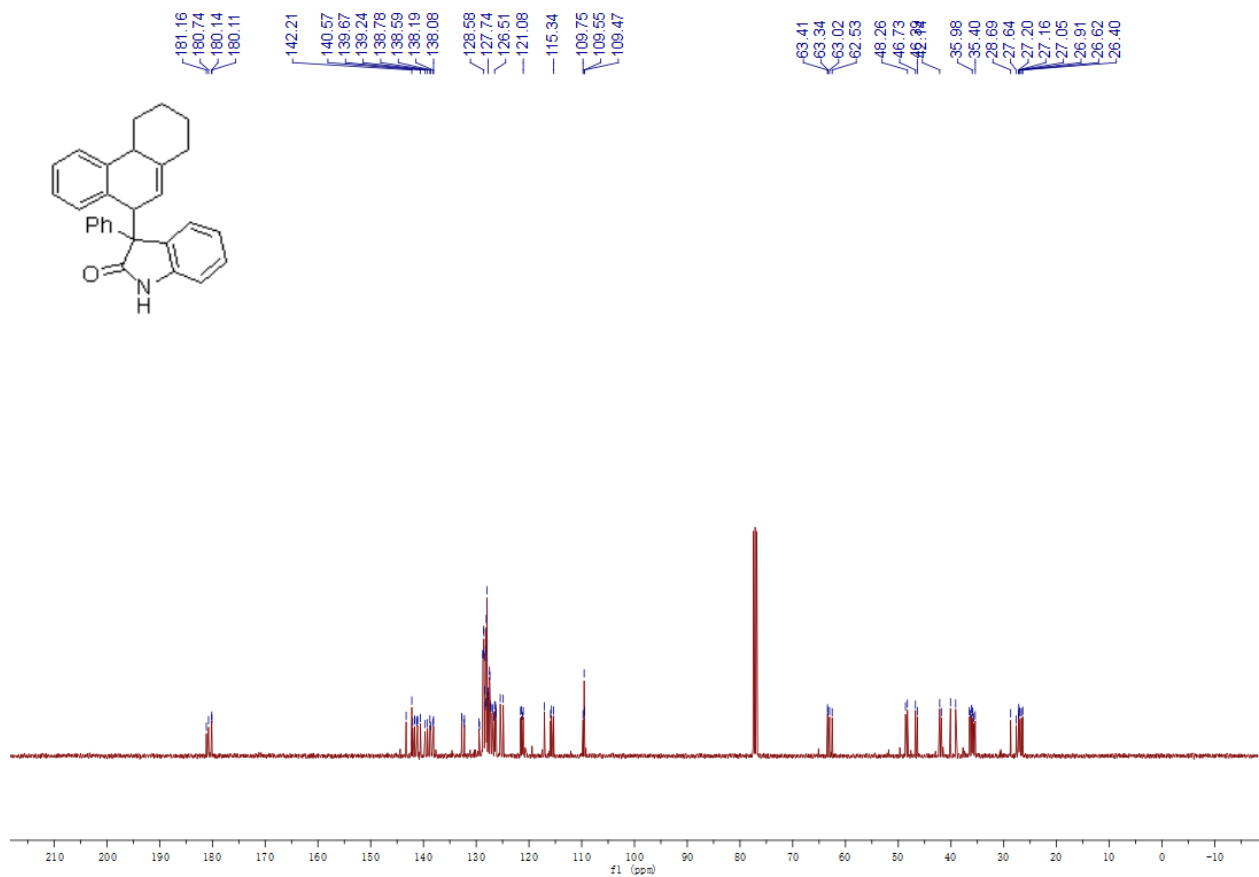
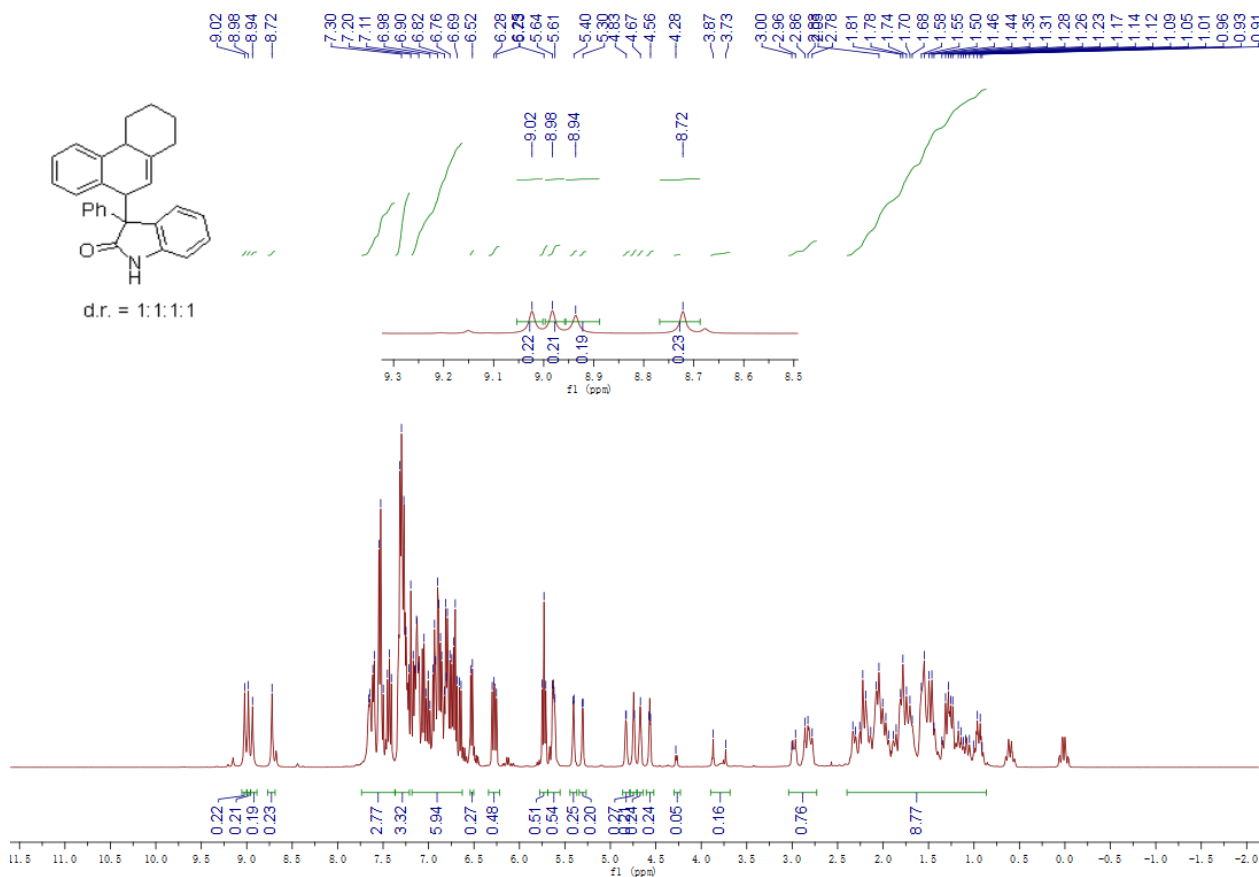
^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 7.90 – 7.78 (m, 2H), 7.35 – 7.30 (m, 3H), 7.23 – 7.12 (m, 4H), 7.07 – 6.95 (m, 7H), 6.86 (m, 1H), 6.71 (d, J = 7.4 Hz, 1H), 6.56 (d, J = 7.2 Hz, 1H), 2.30 – 2.10 (m, 2H).

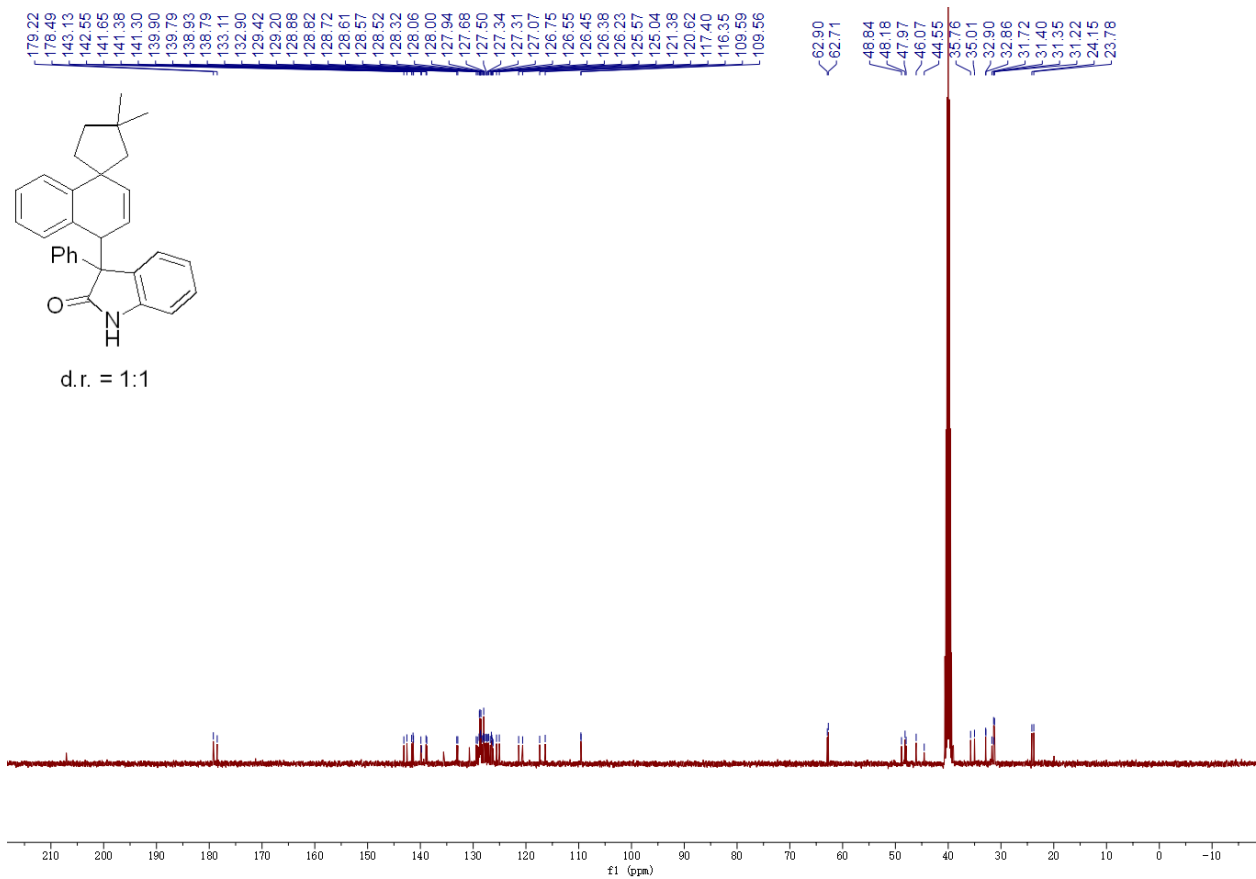
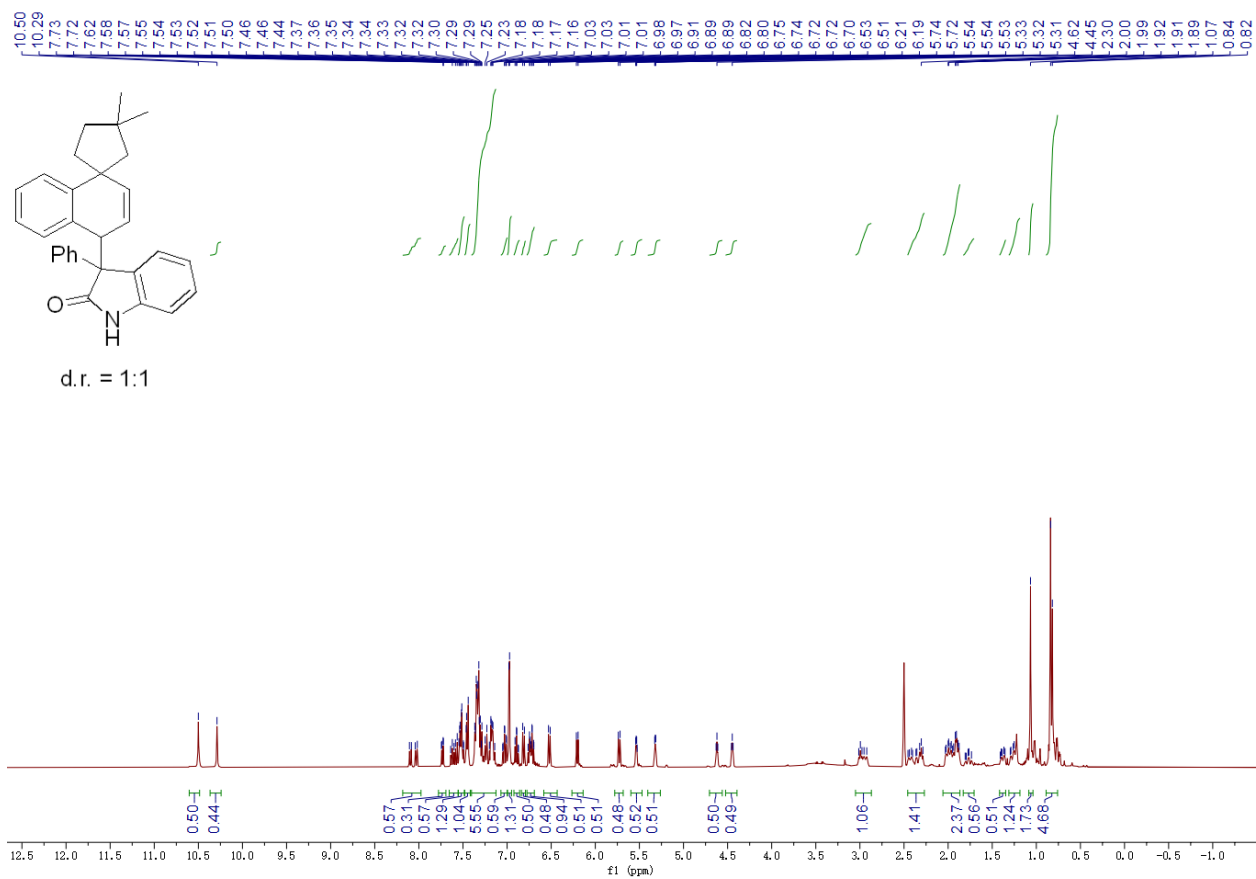
^{13}C NMR (101 MHz, CDCl_3) δ 179.42, 146.41, 143.40, 141.16, 136.29, 132.07, 131.56, 129.69, 129.35, 128.45, 128.08, 127.48, 127.41, 127.25, 127.15, 126.53, 126.49, 121.24, 110.04, 63.45, 53.50, 28.10 – 27.58 (m, 1C).

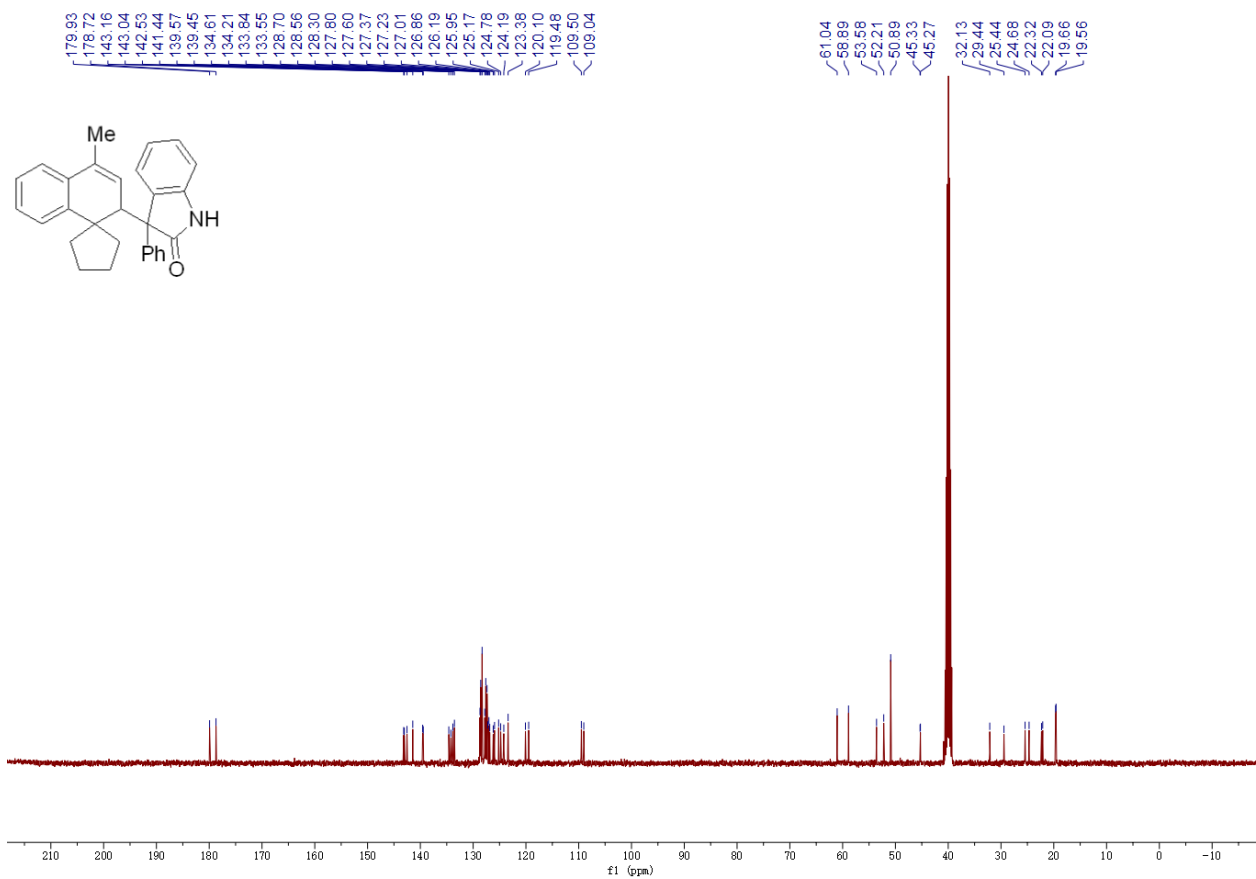
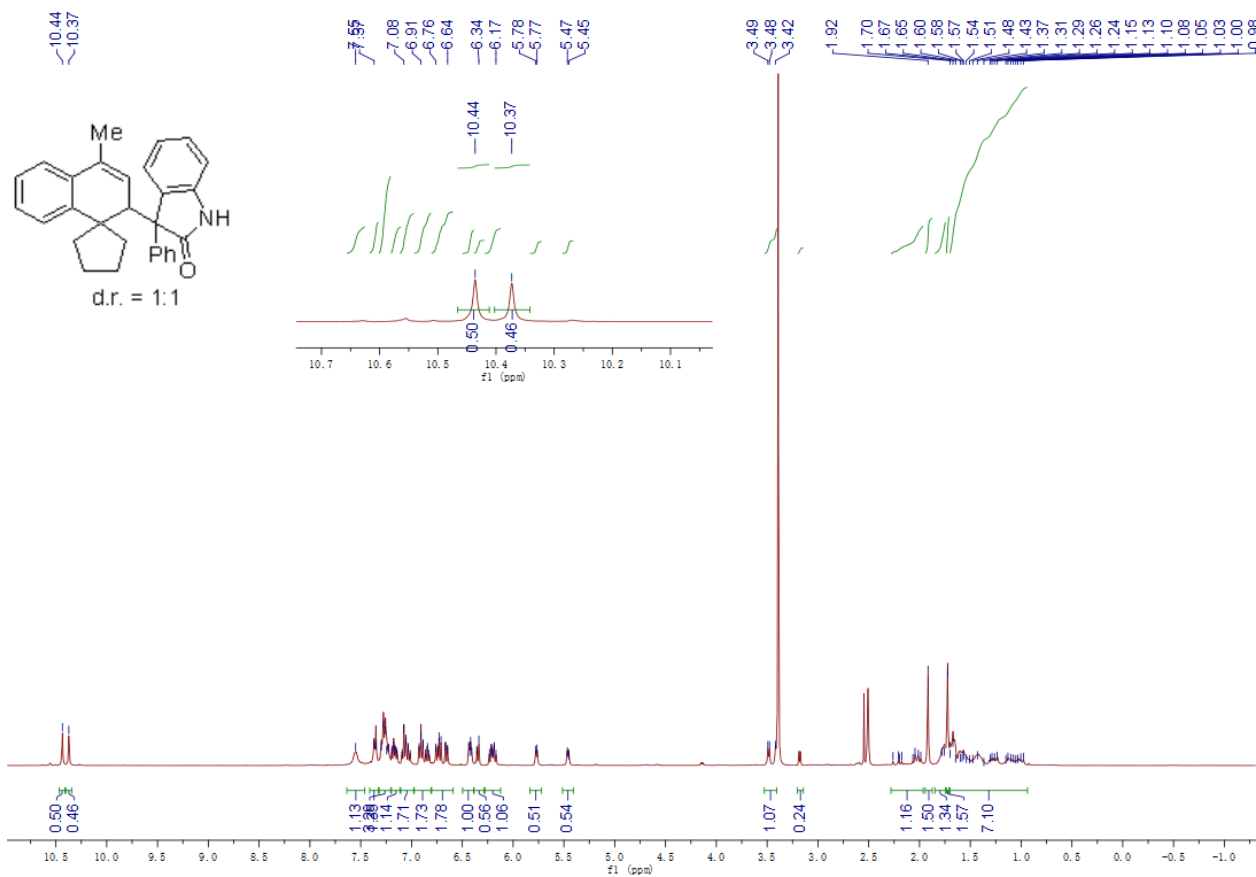
HRMS HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{22}\text{DNO}$ ($\text{M} + \text{Na}$) $^+$ 413.1735, found 413.1738.

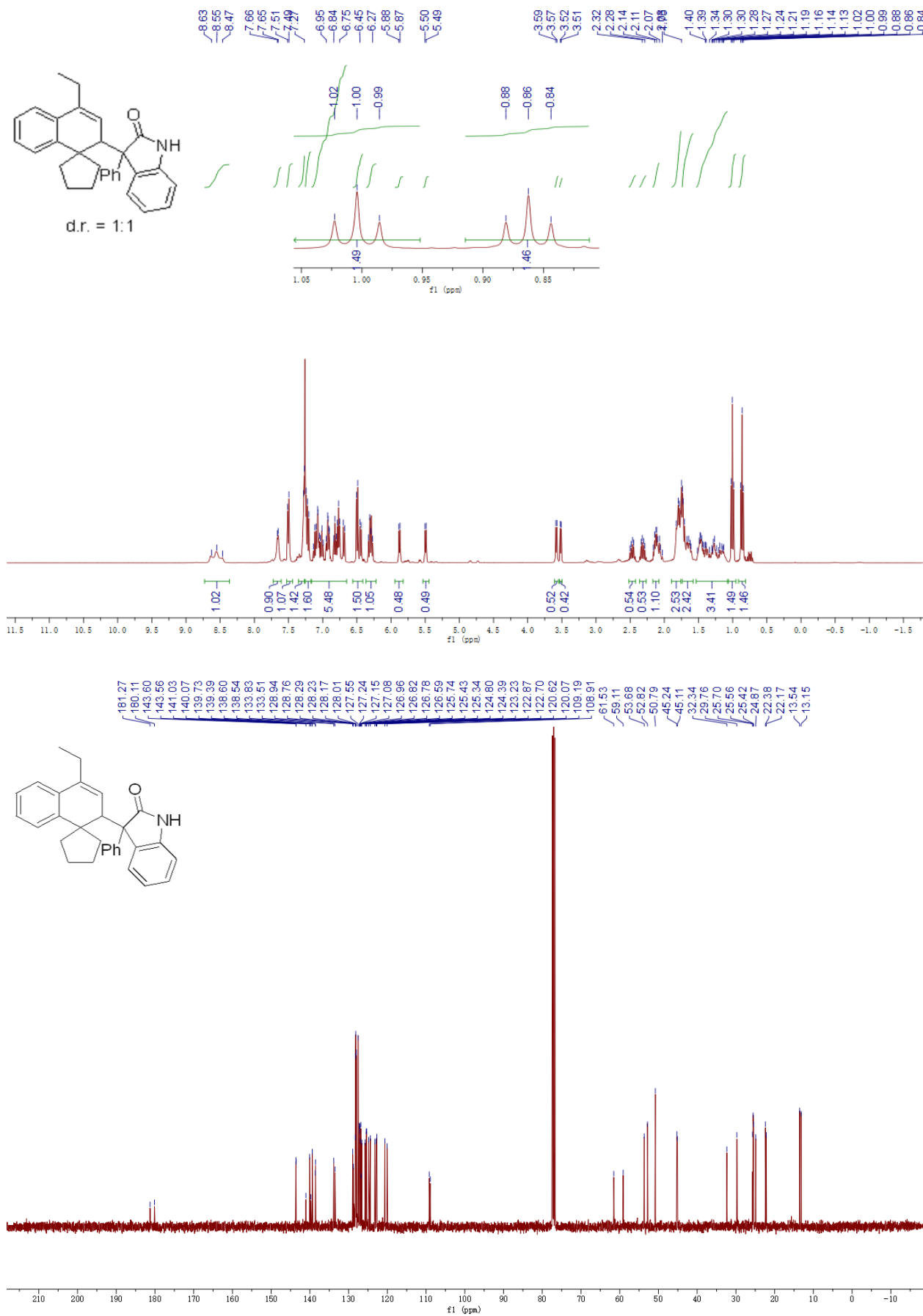
9 NMR spectra

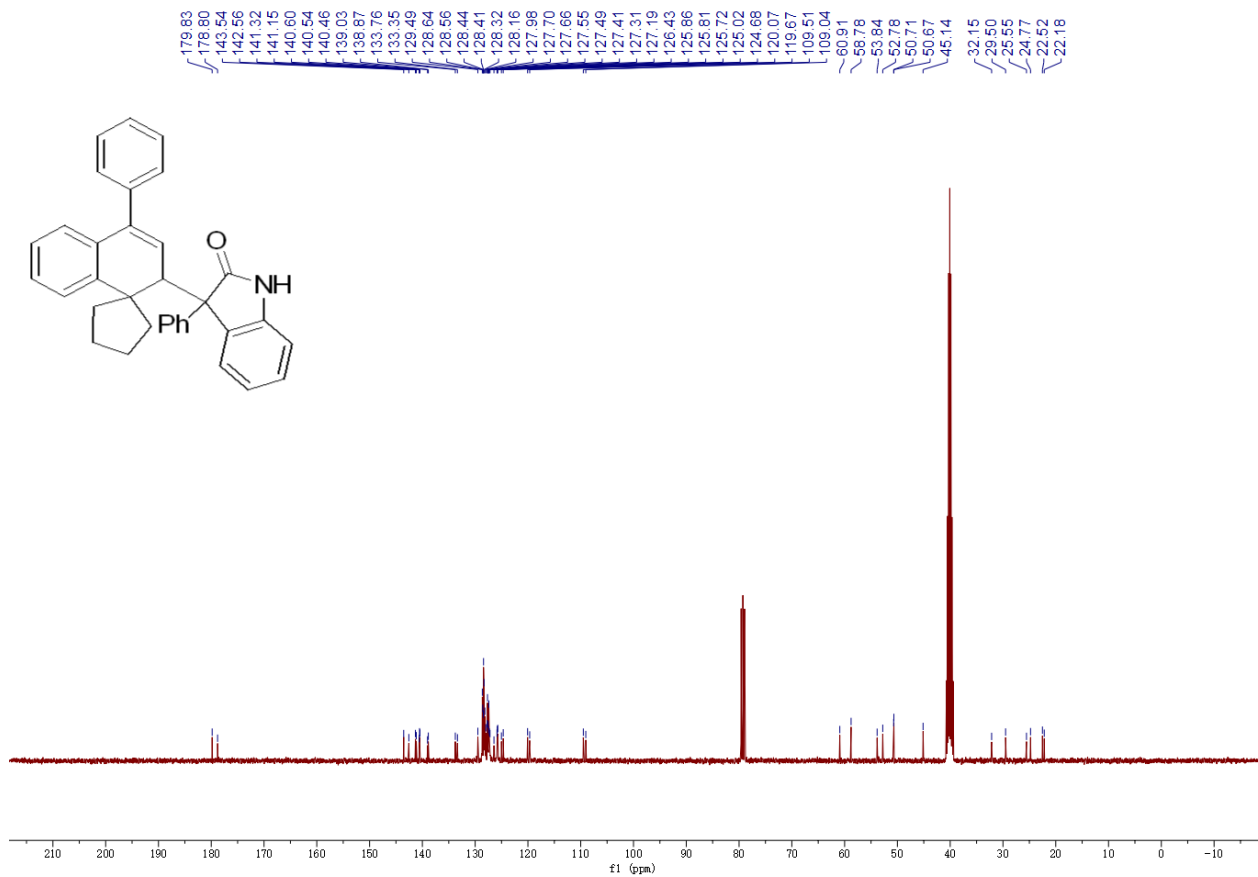
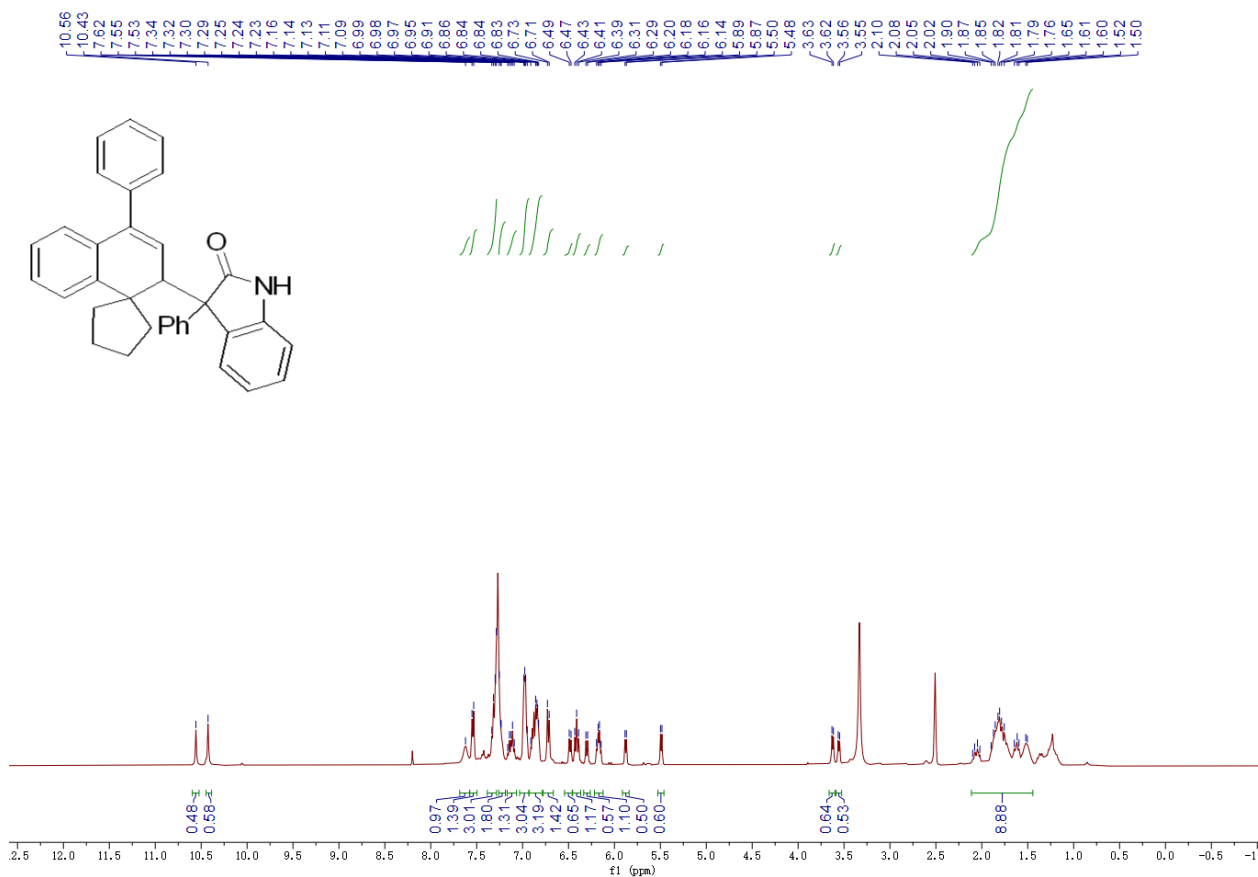


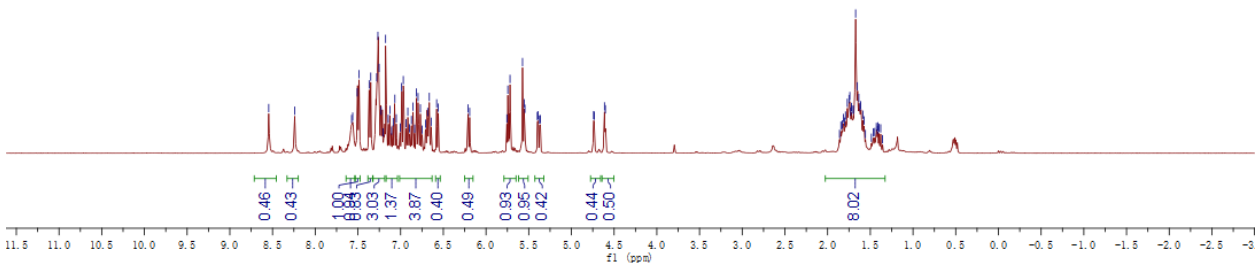


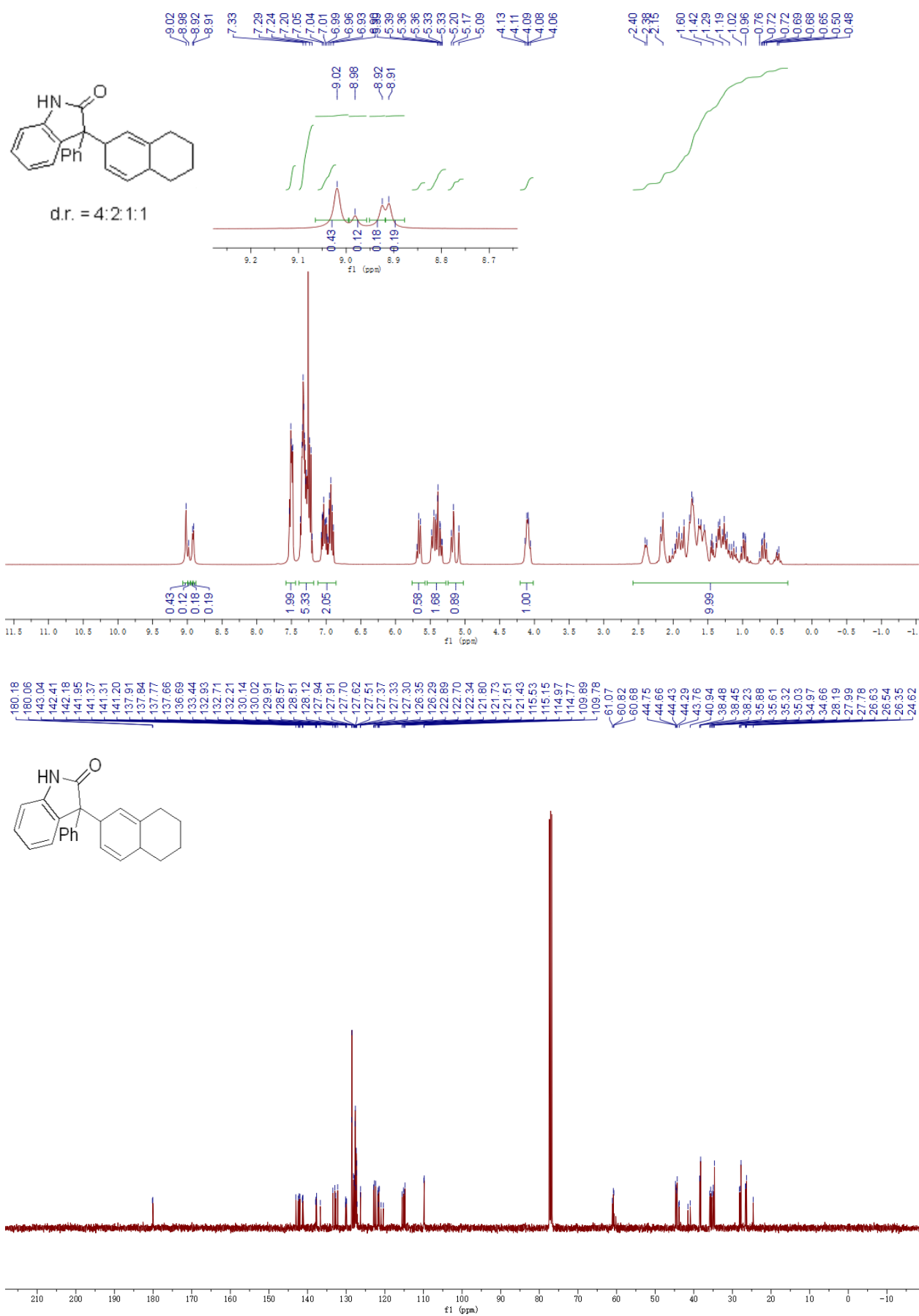


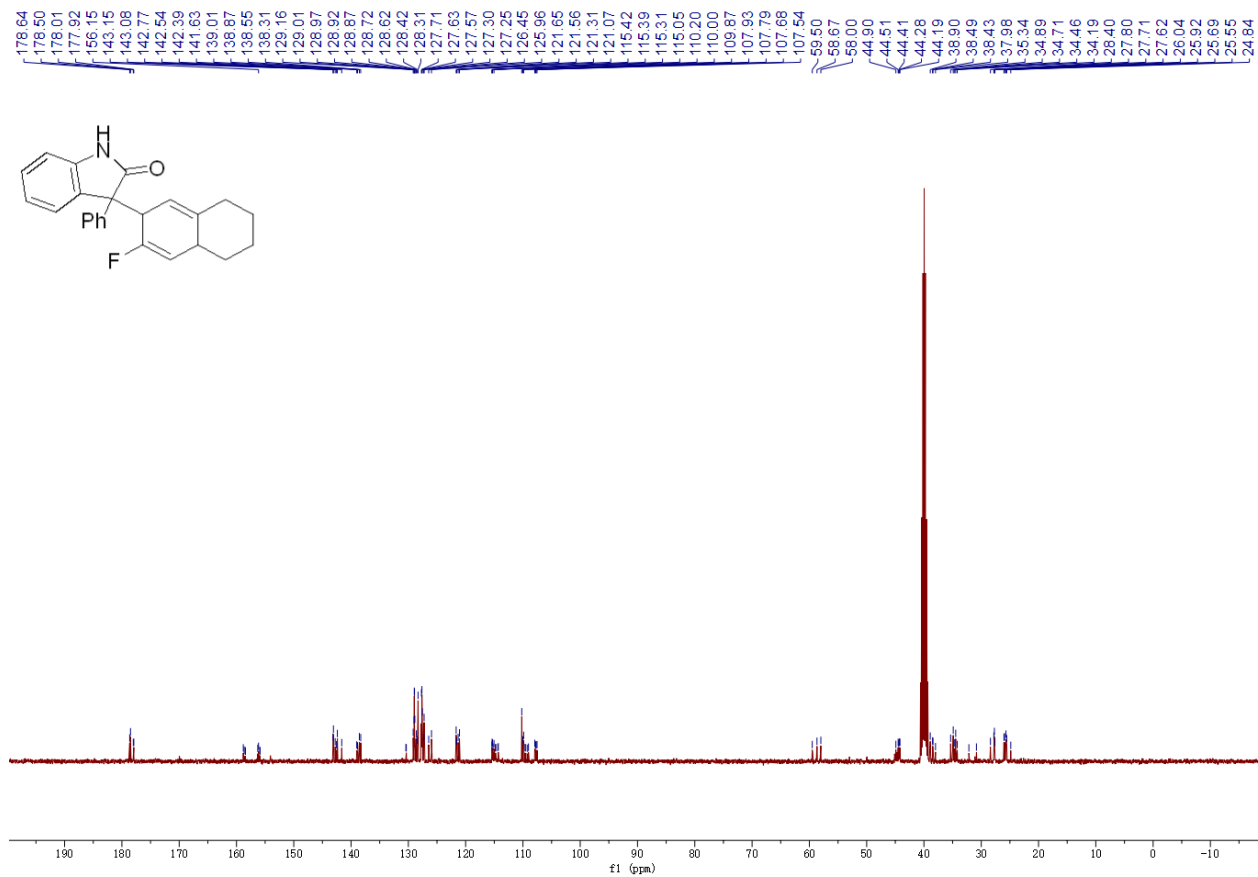
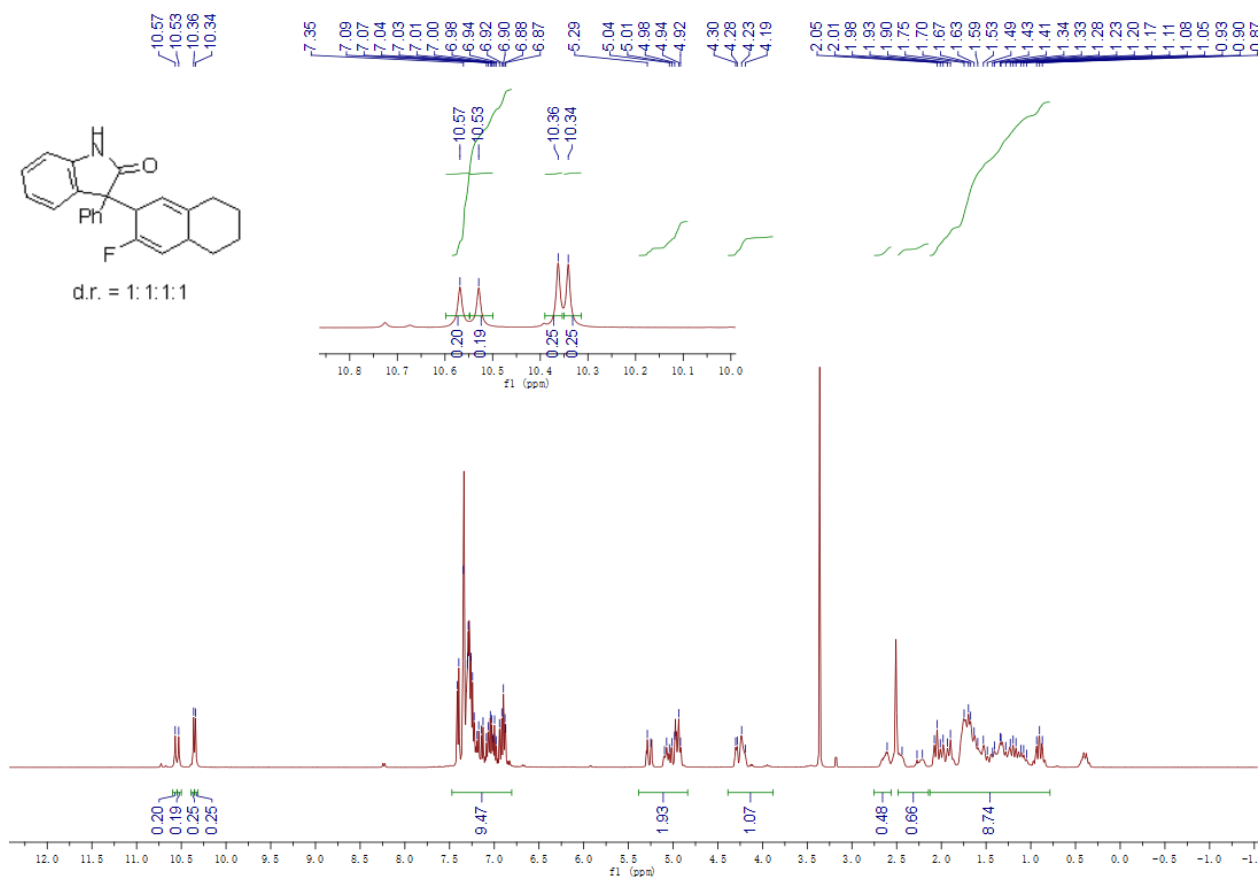


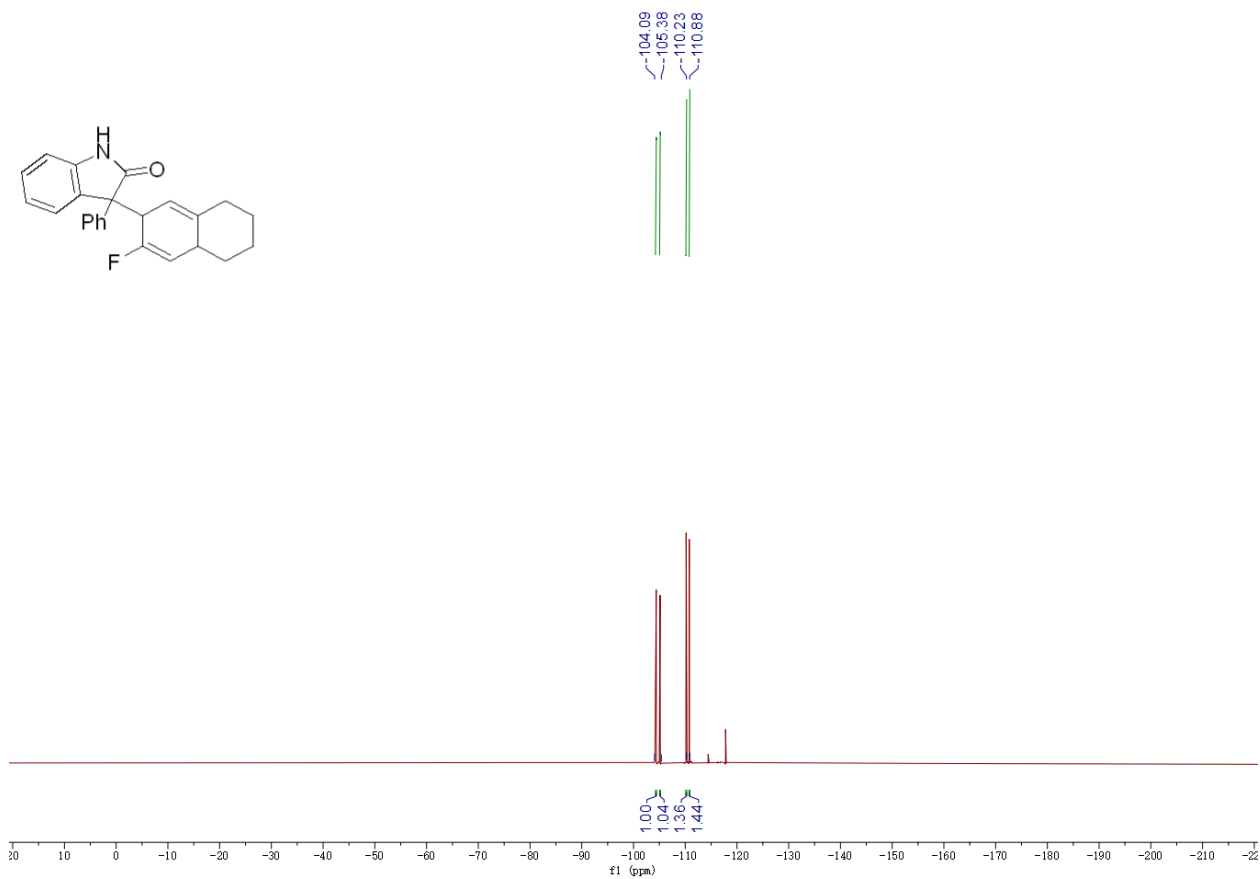


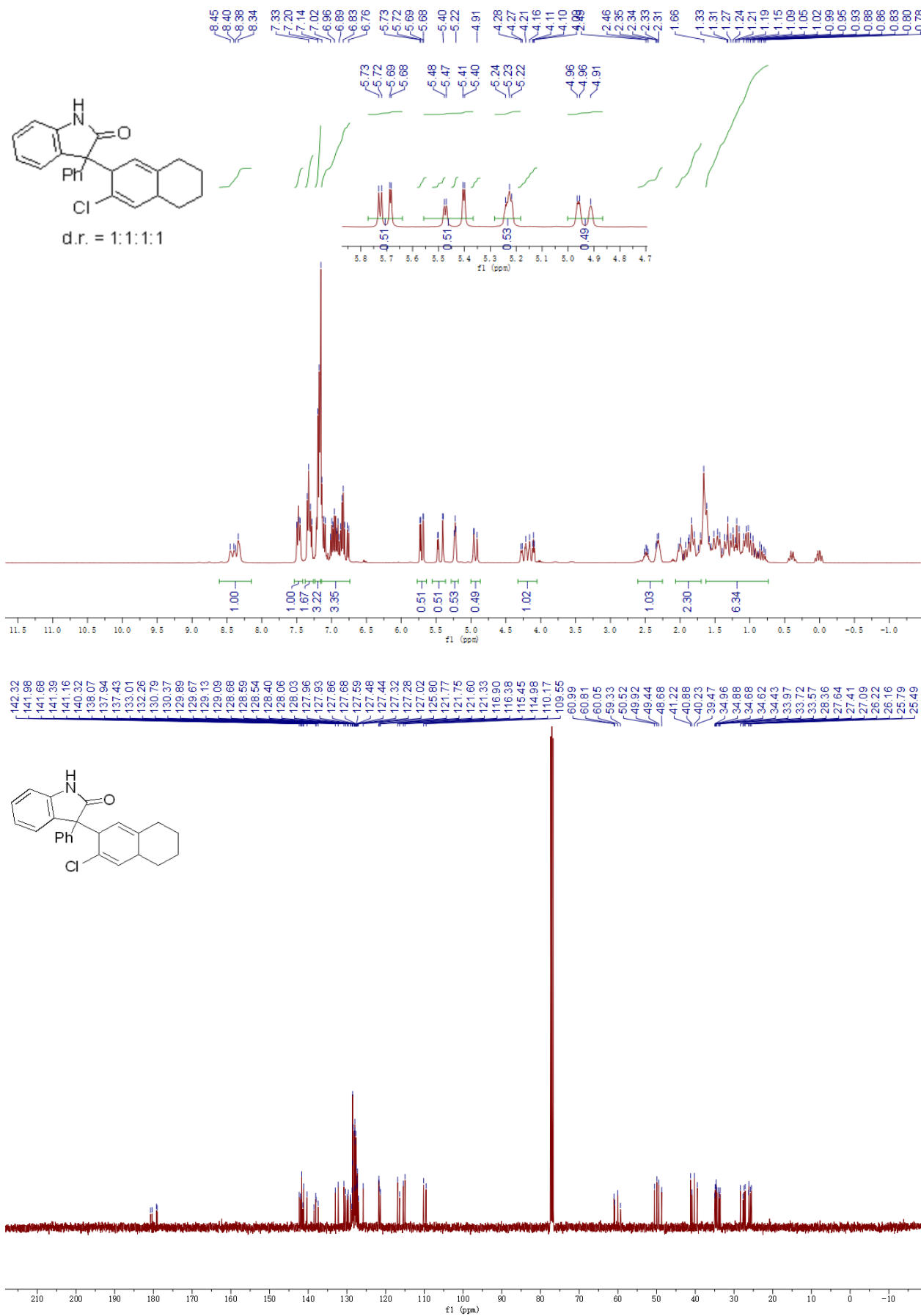


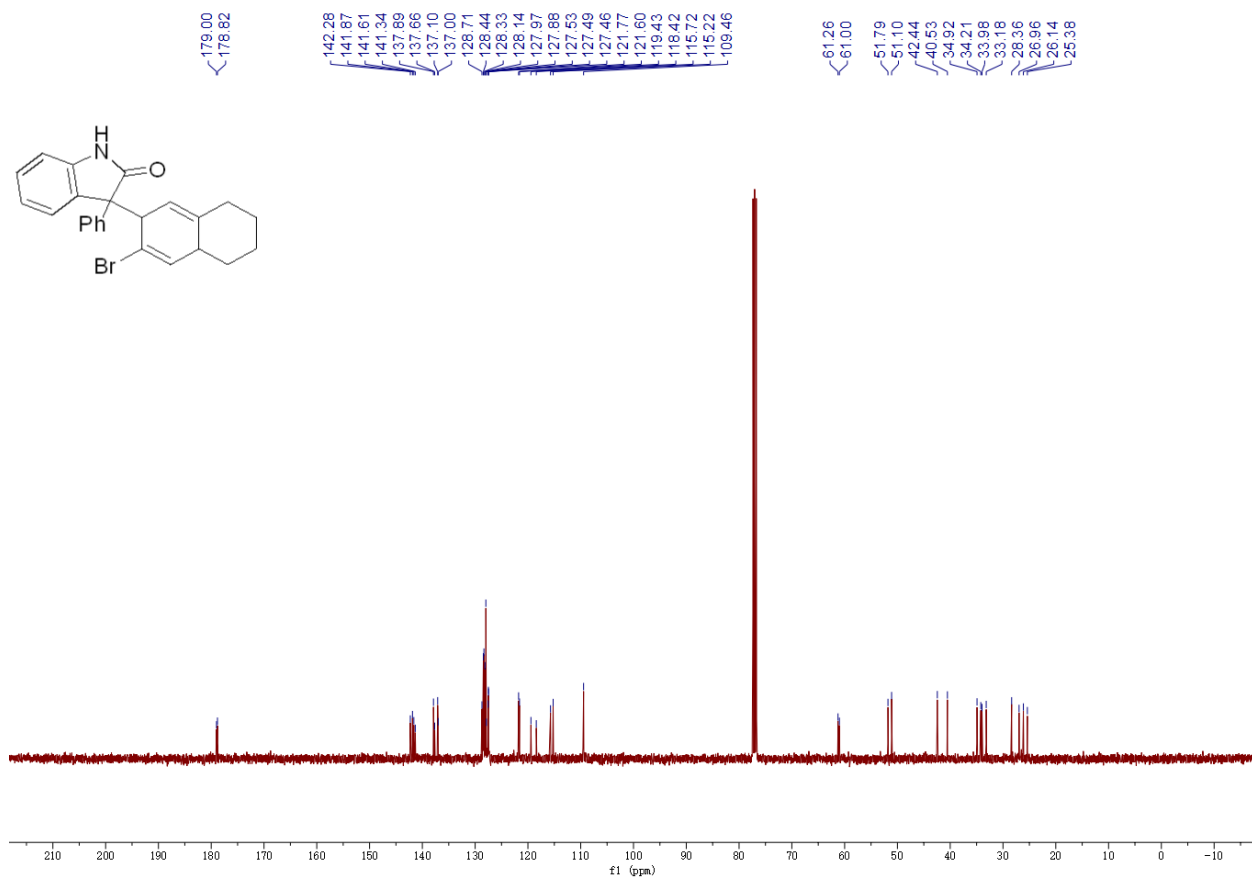
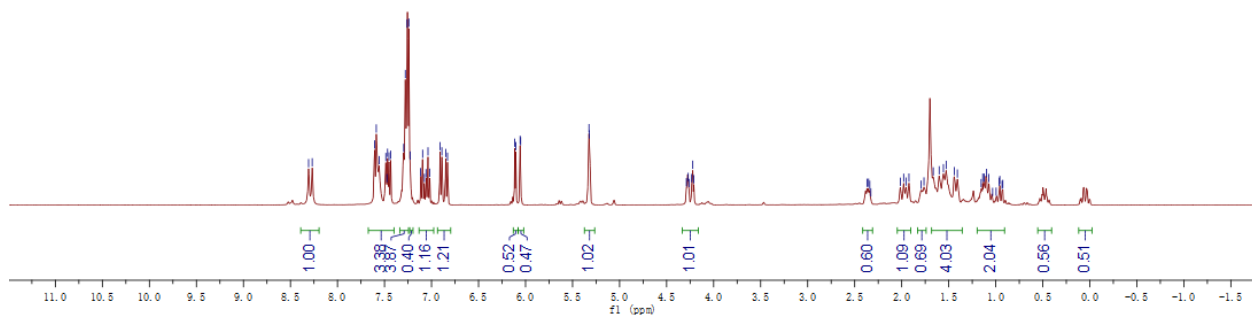
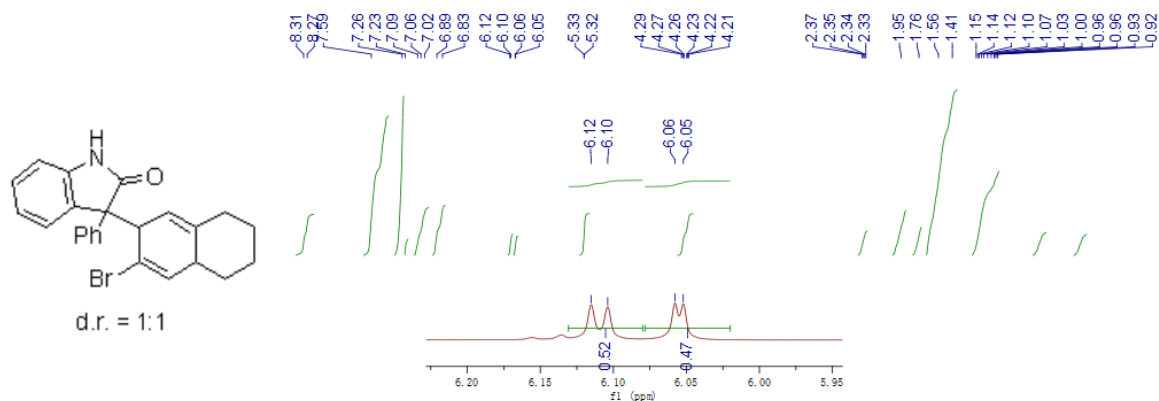


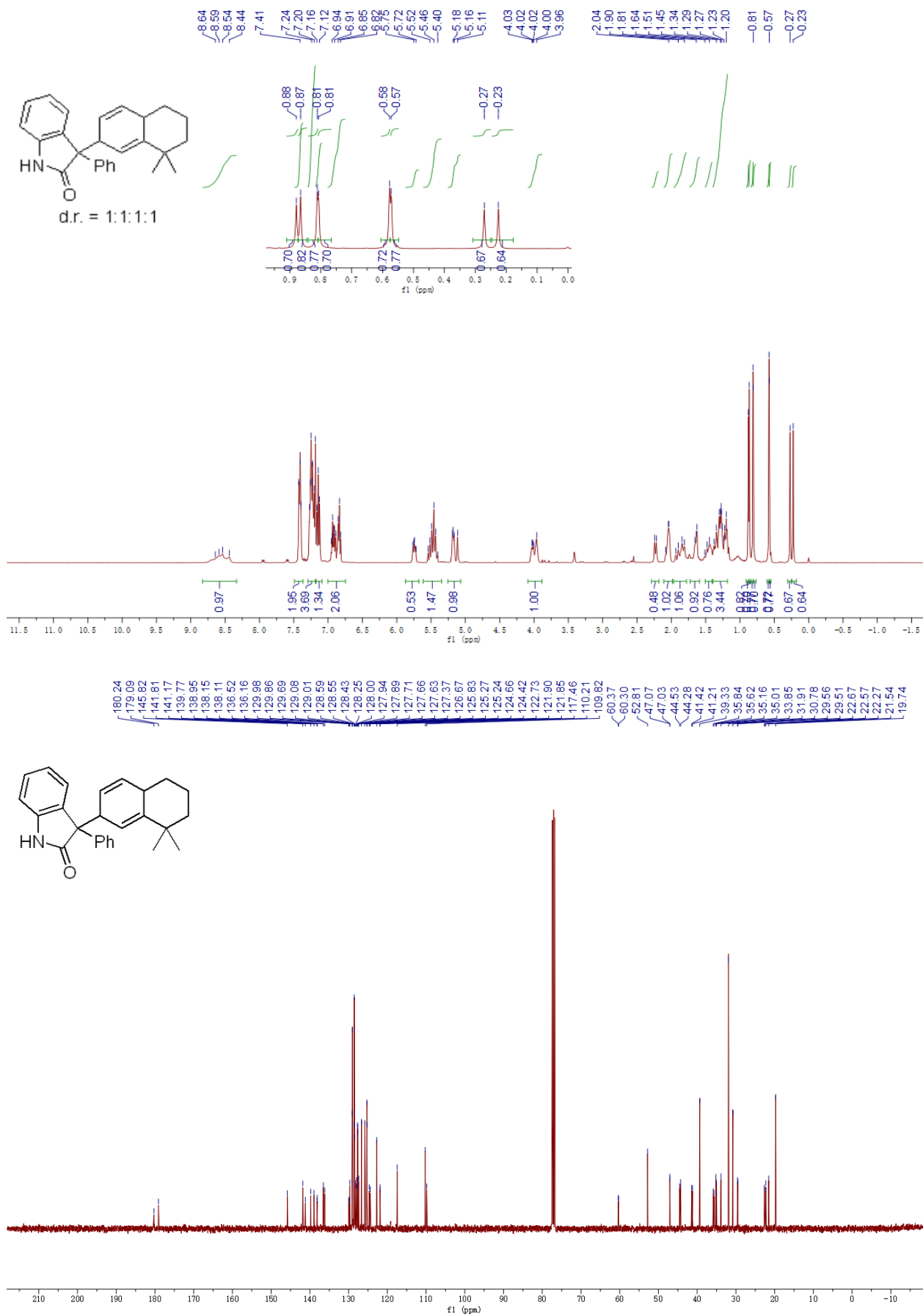


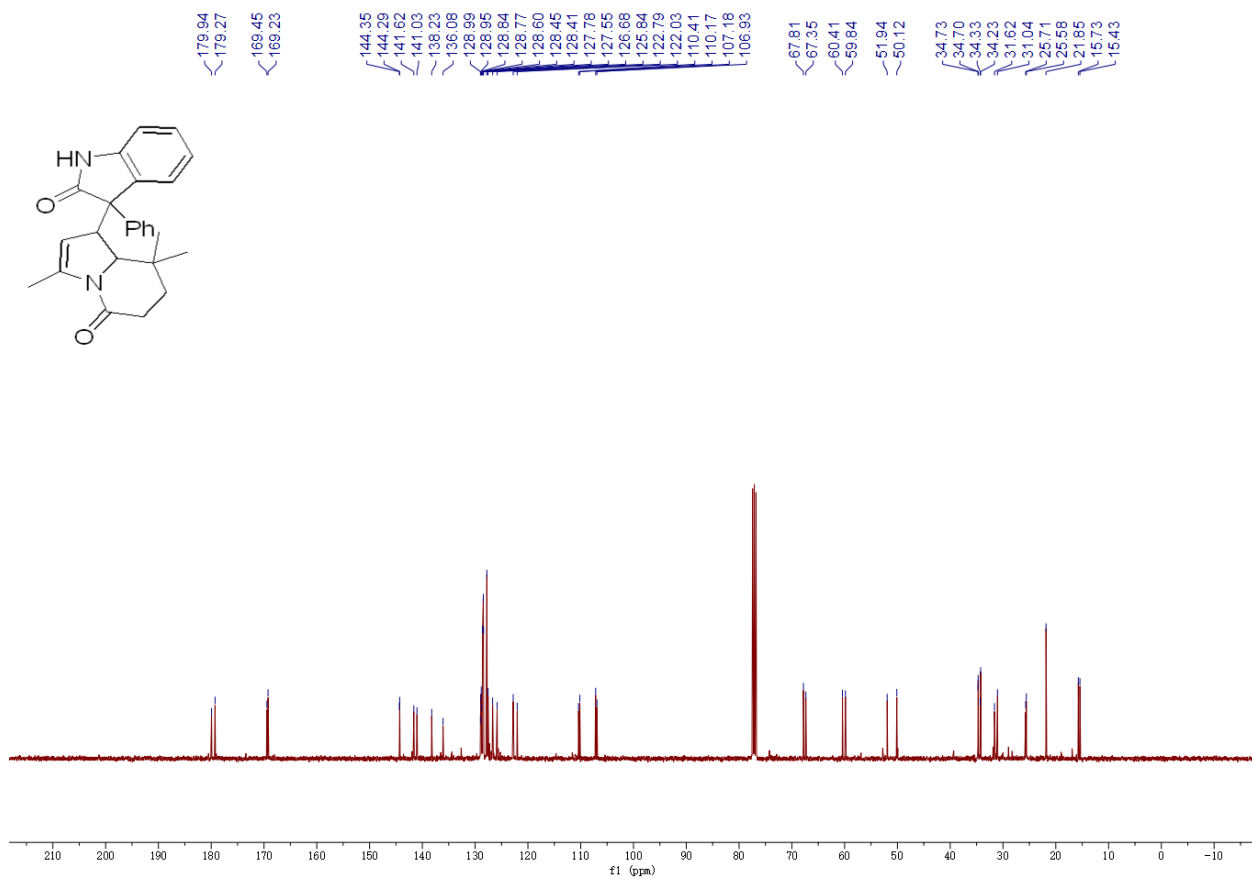
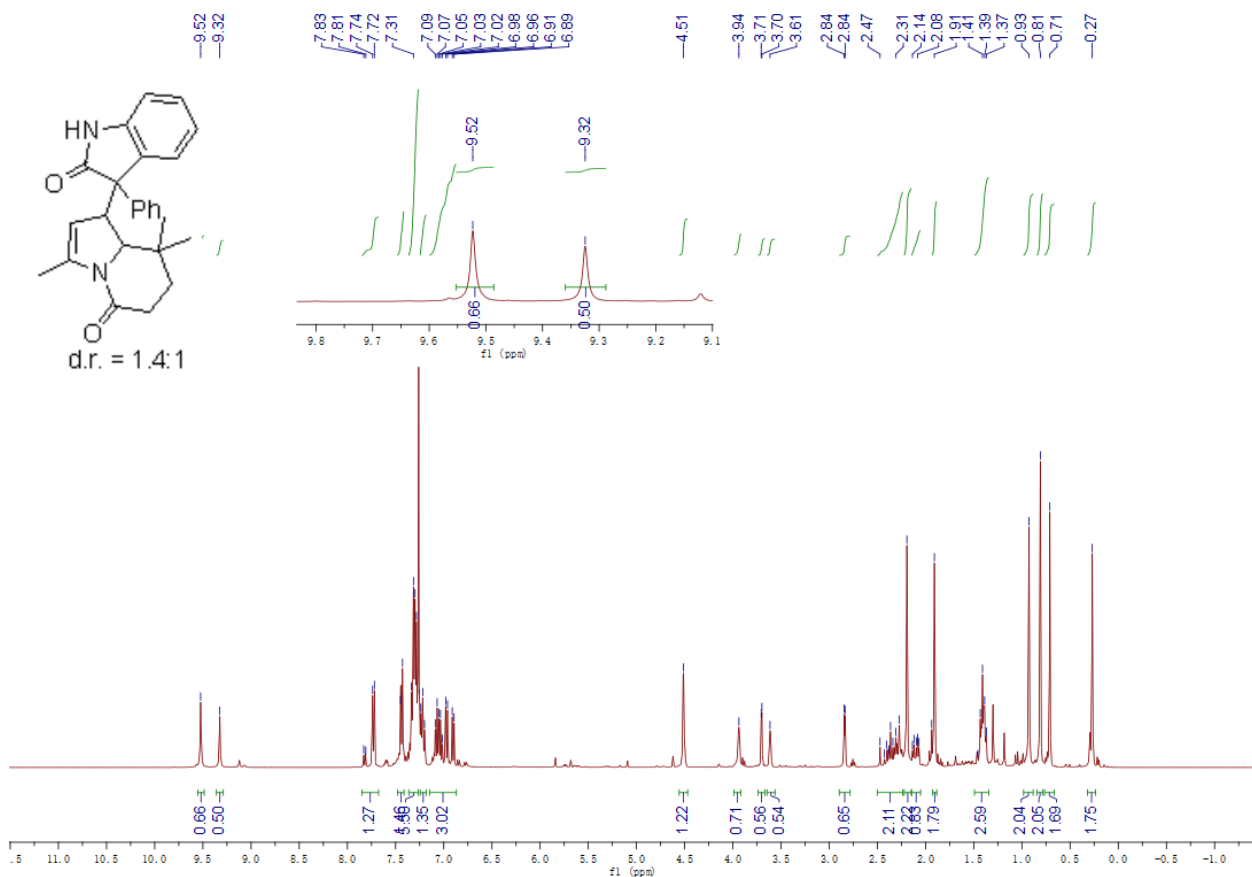


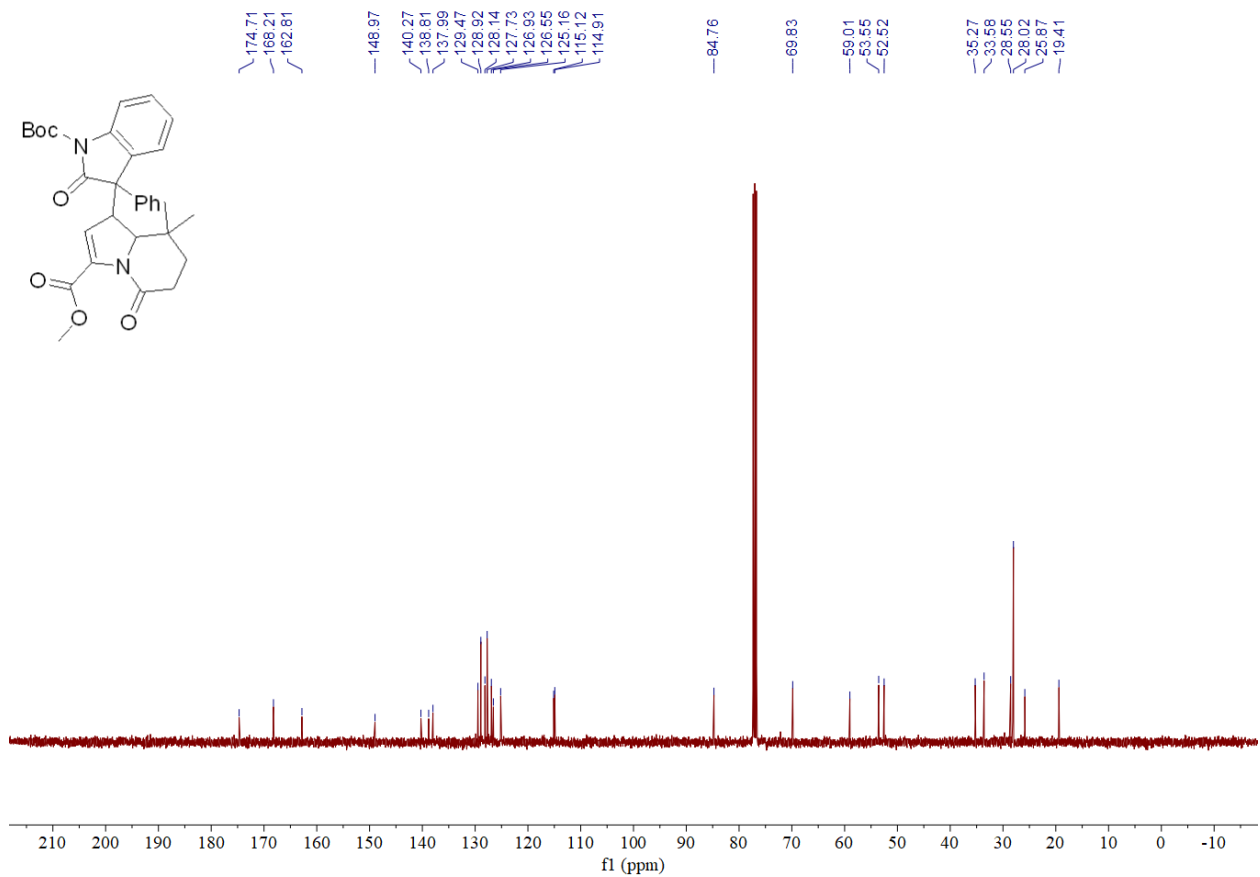
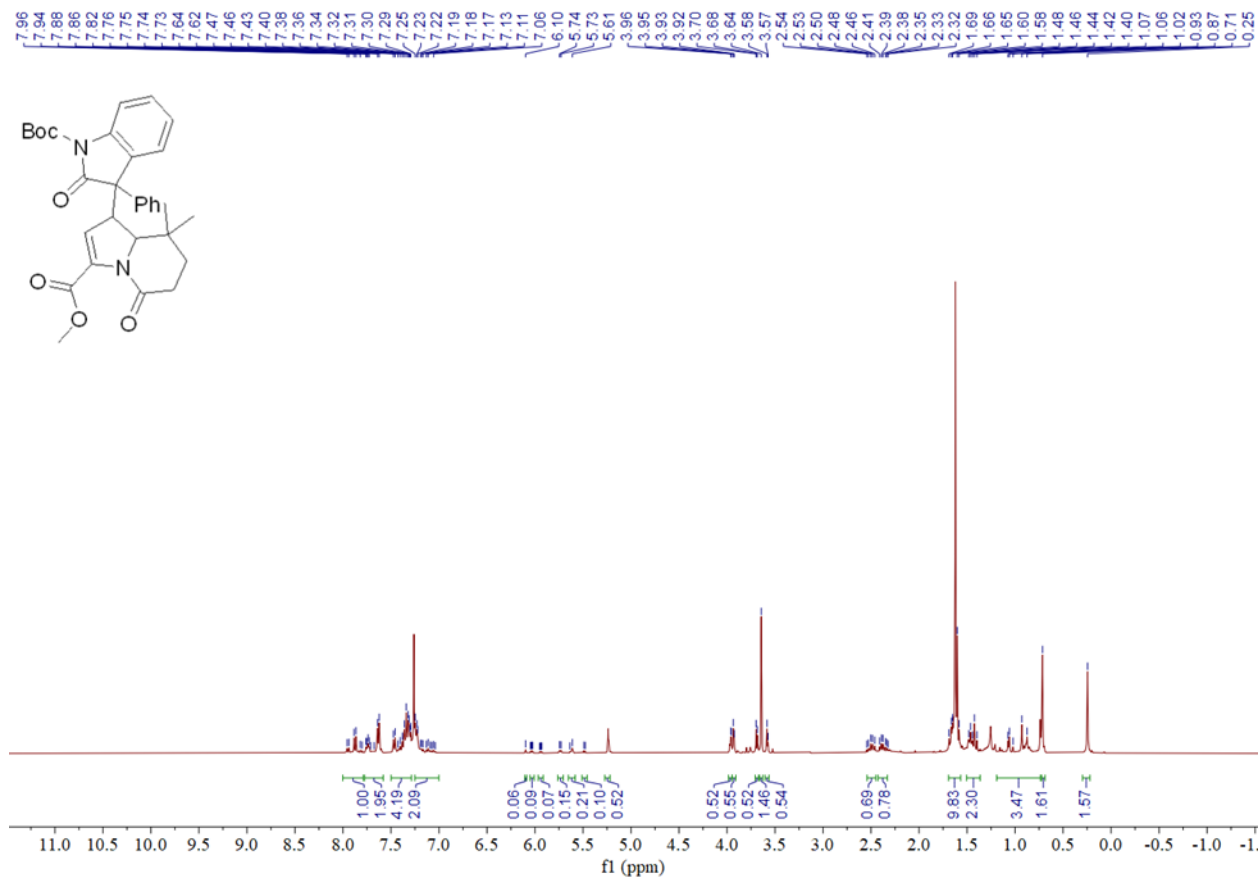


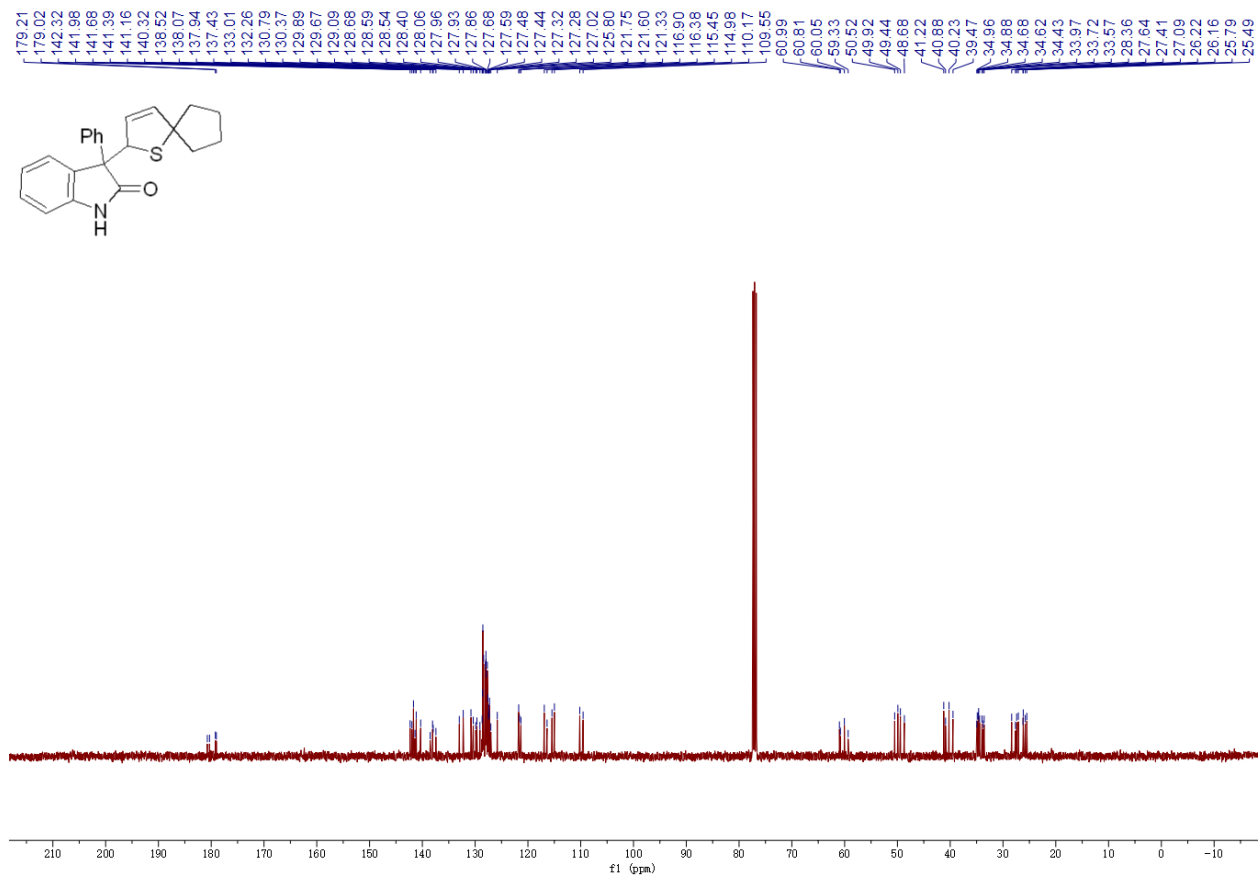
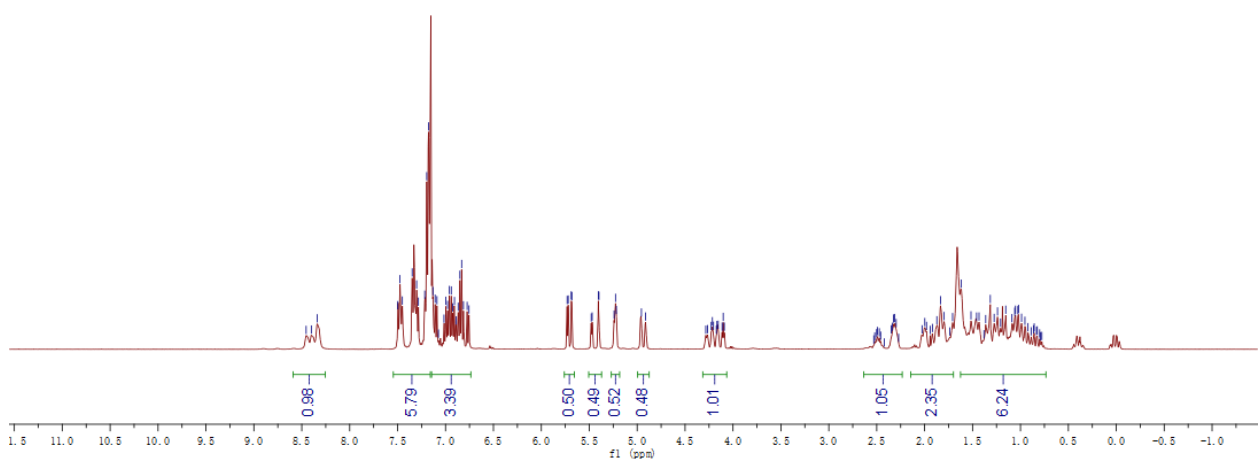
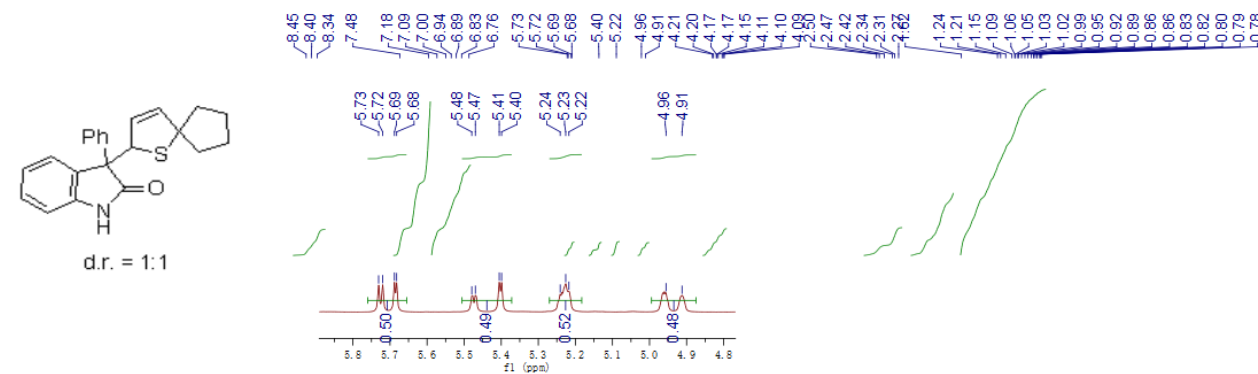


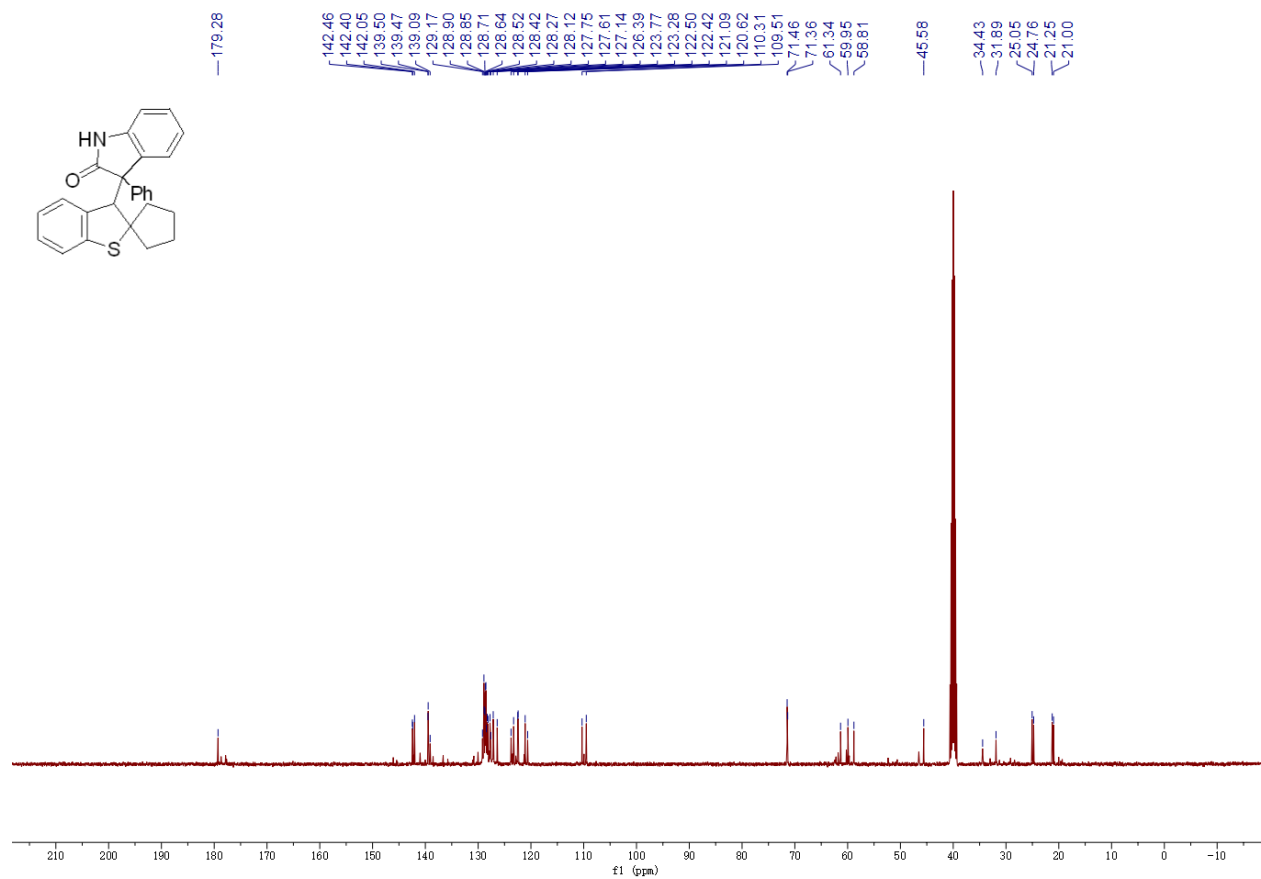
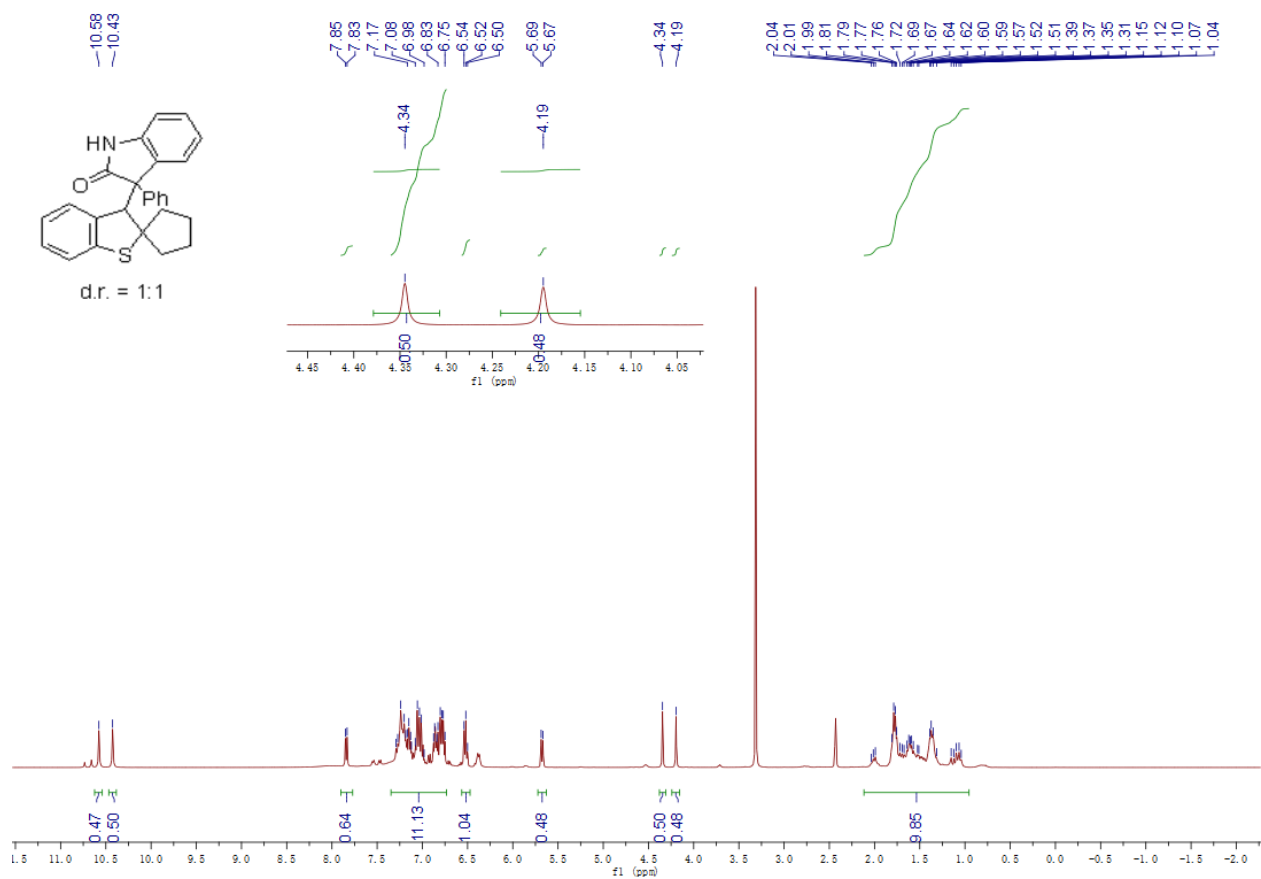


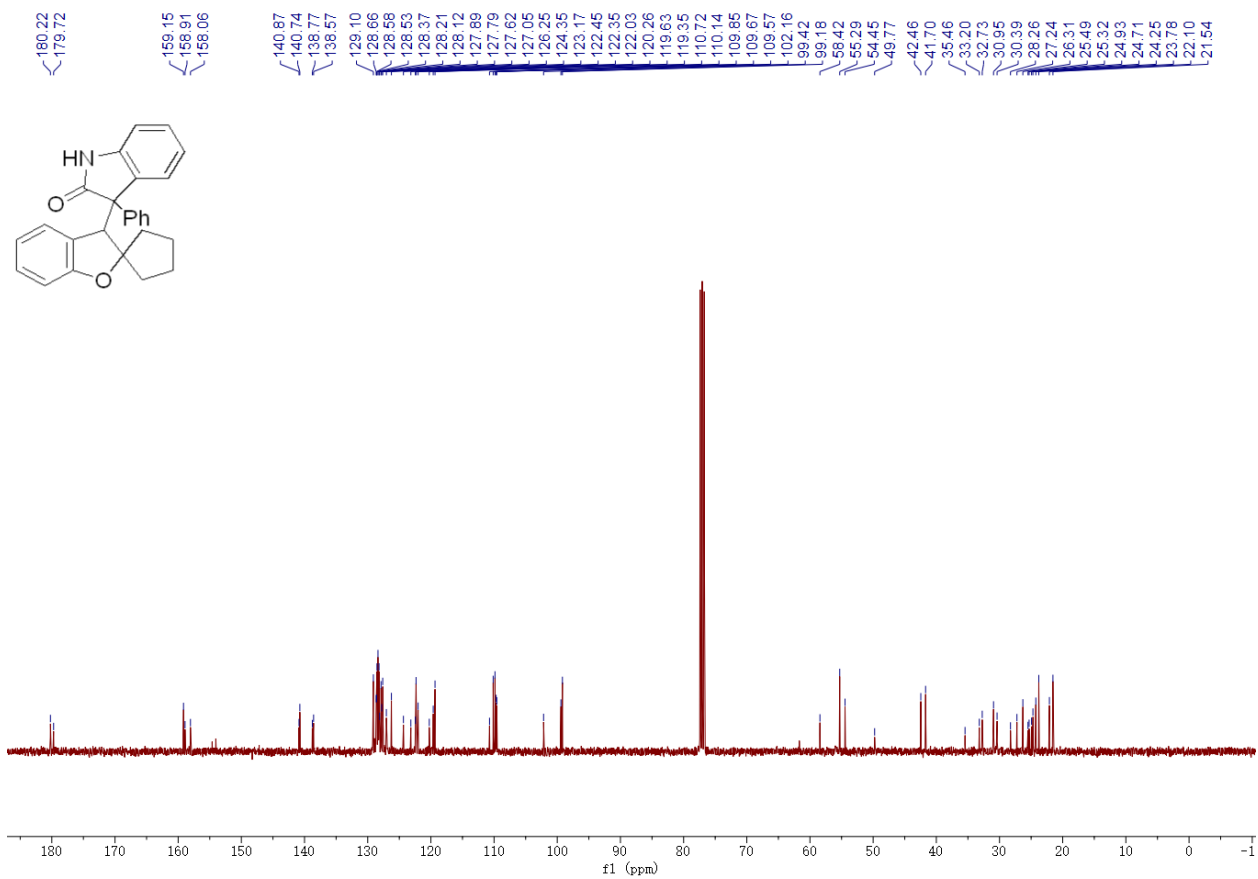
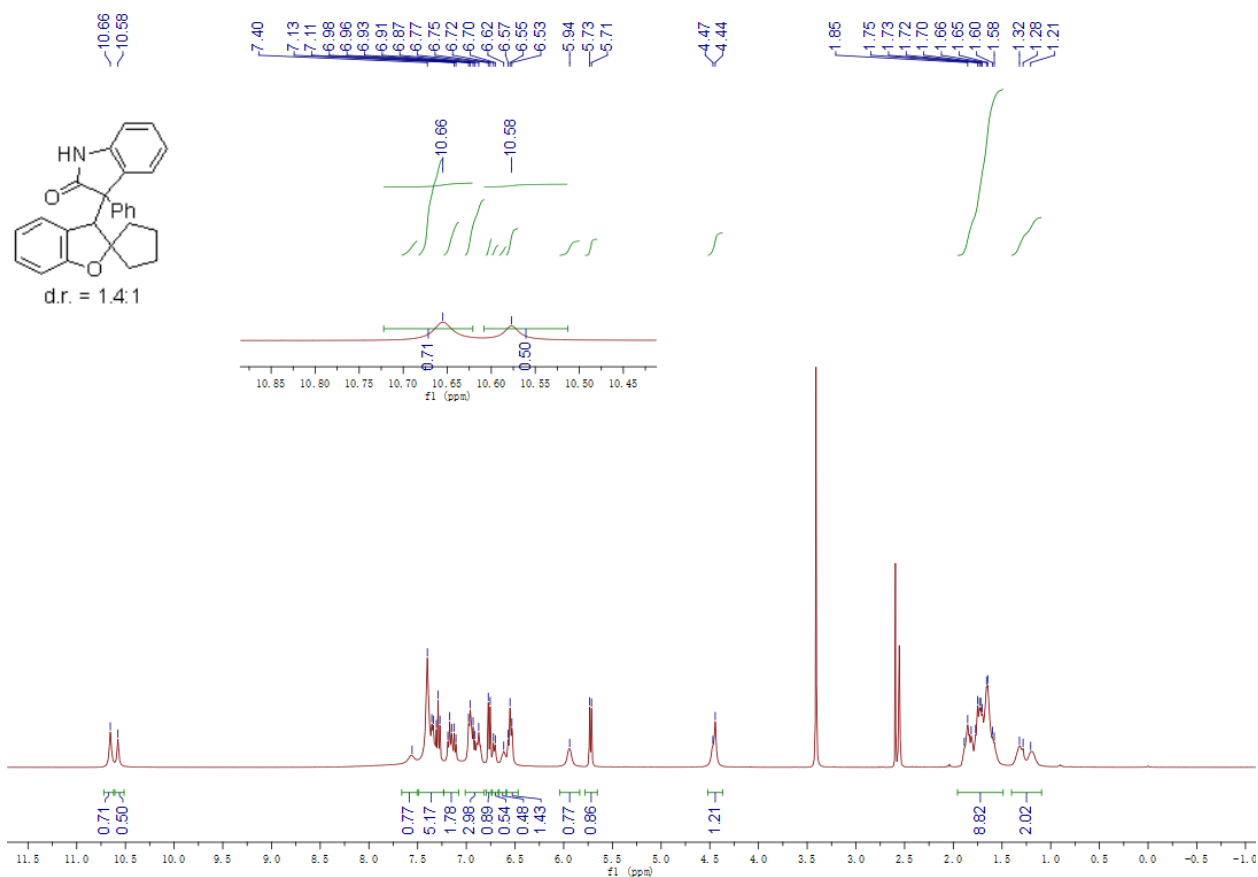


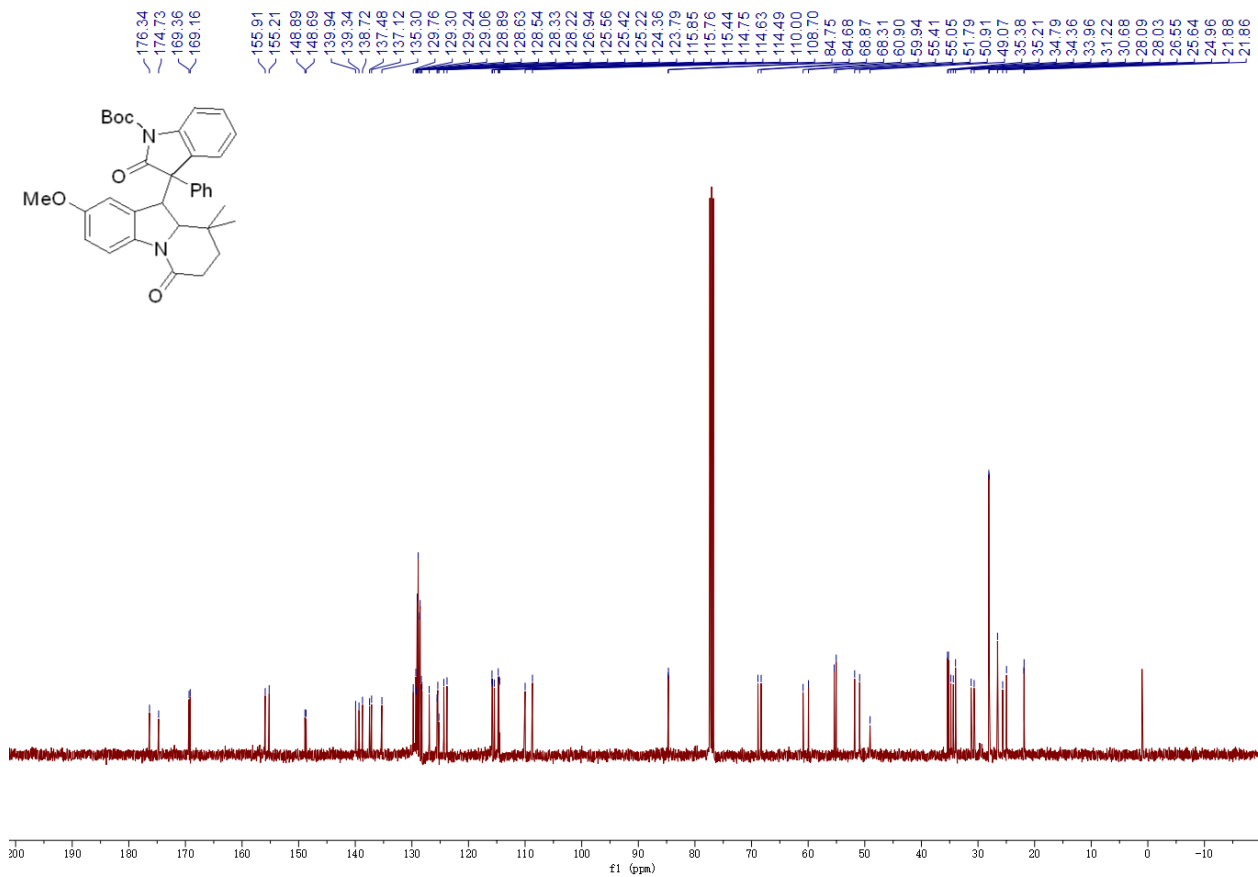
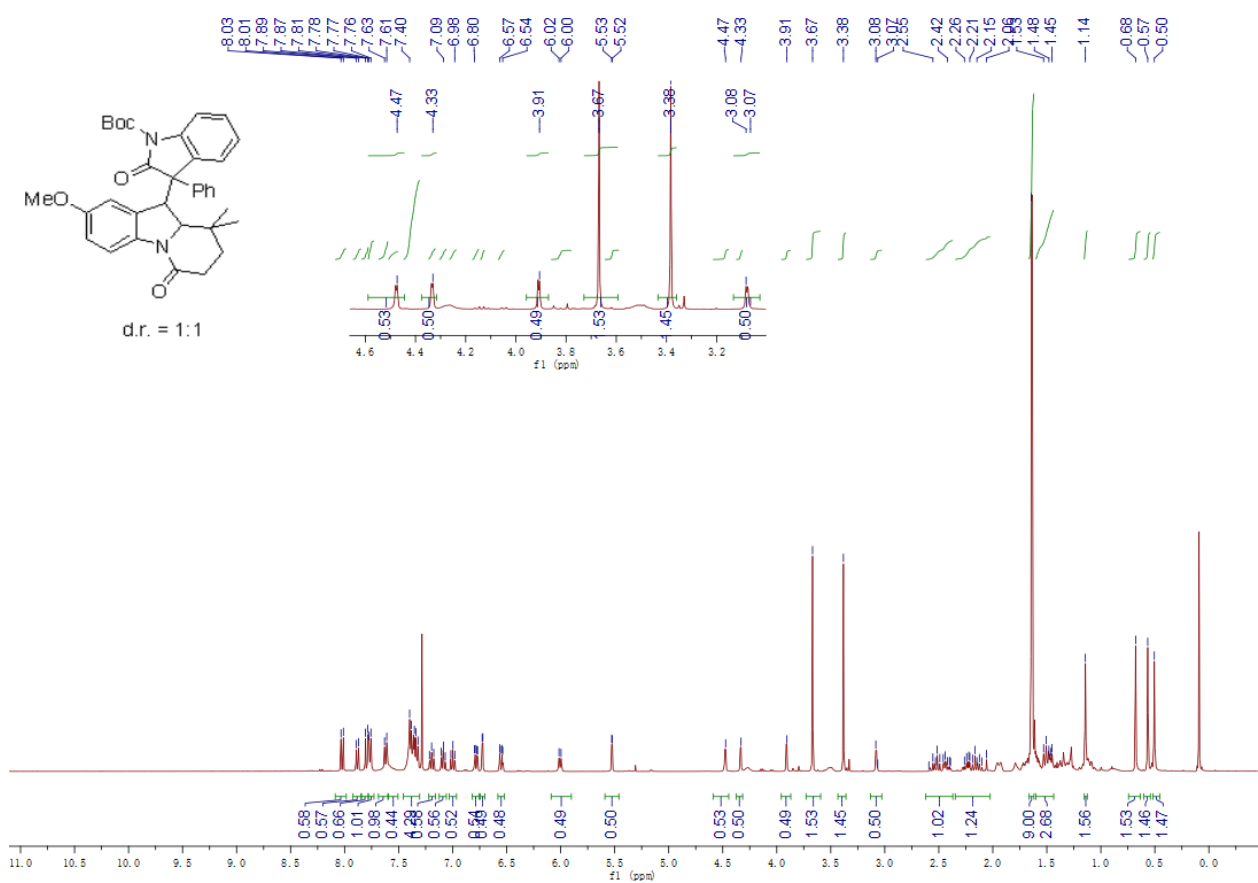


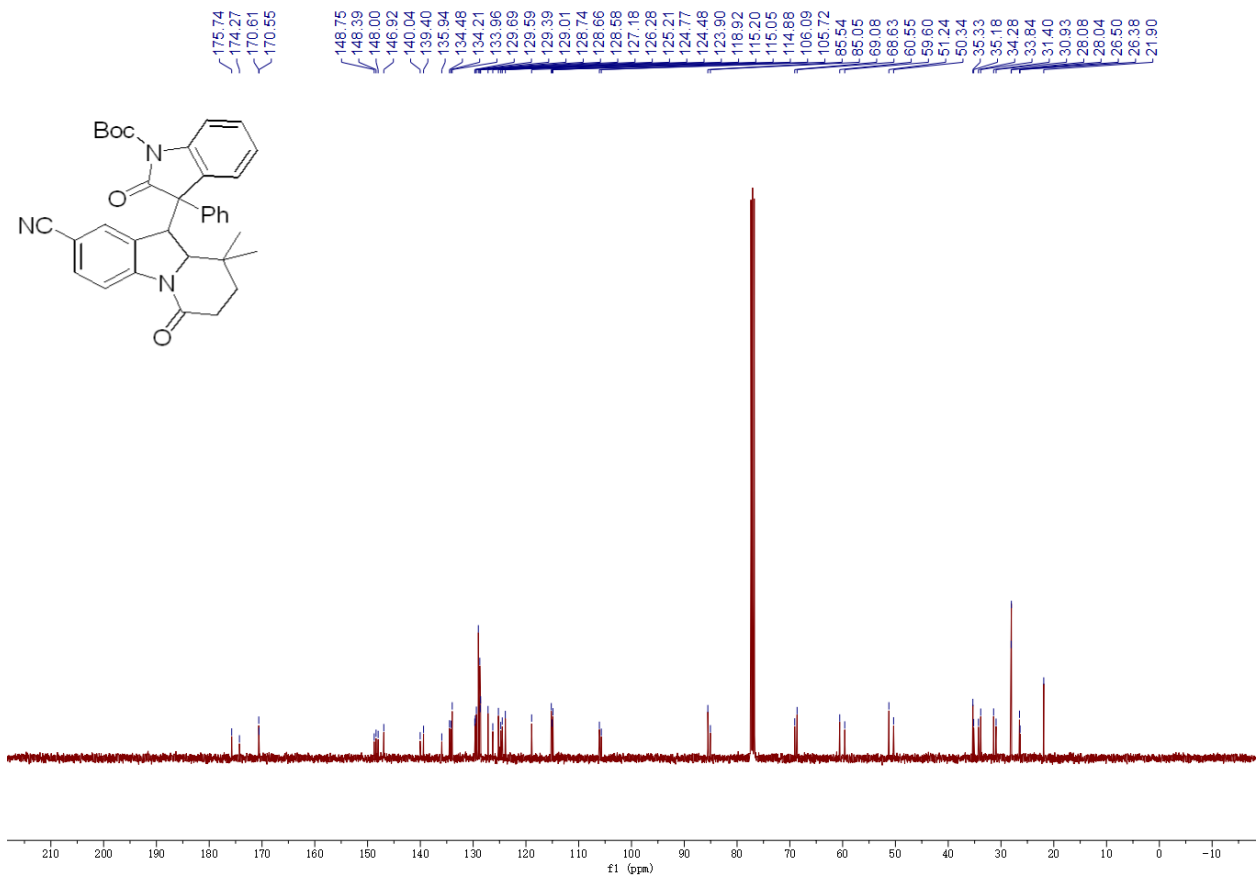
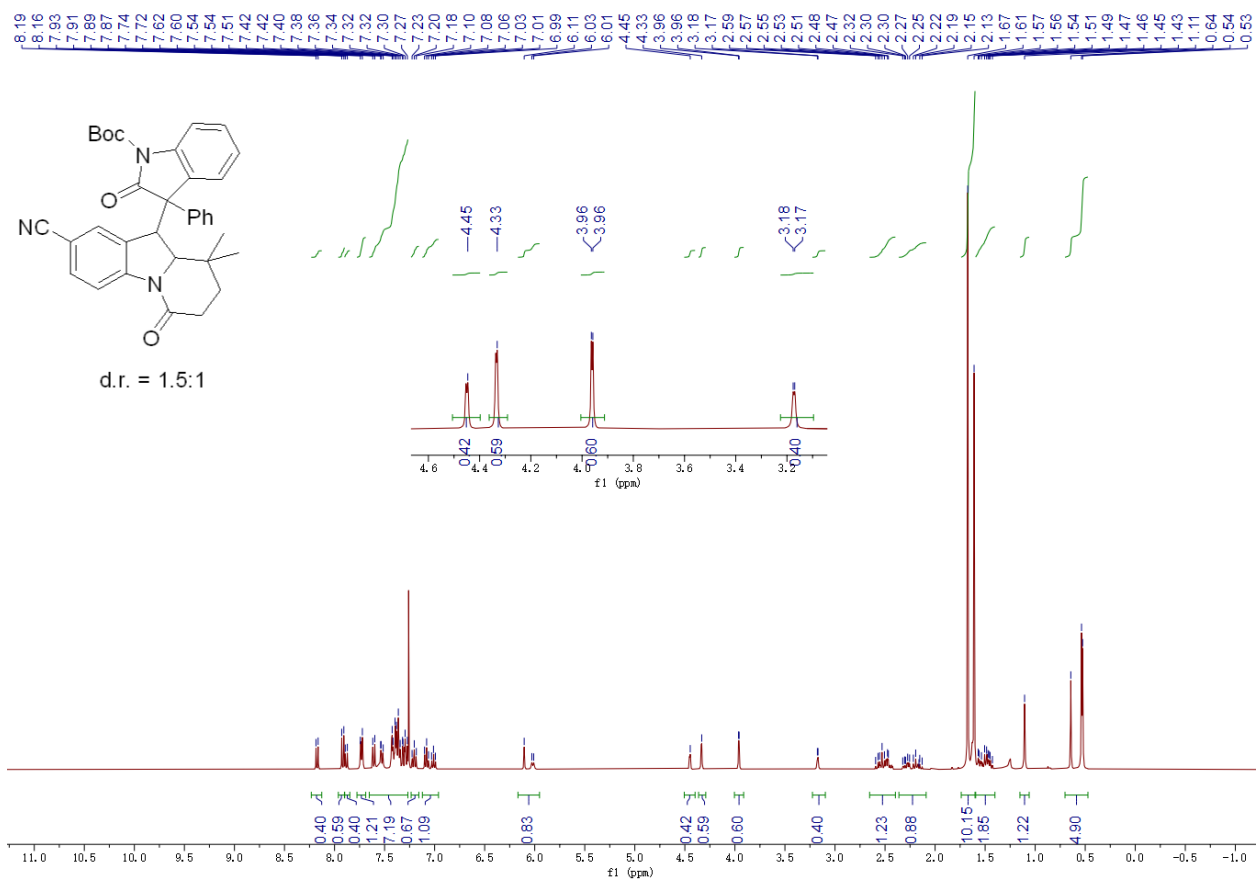


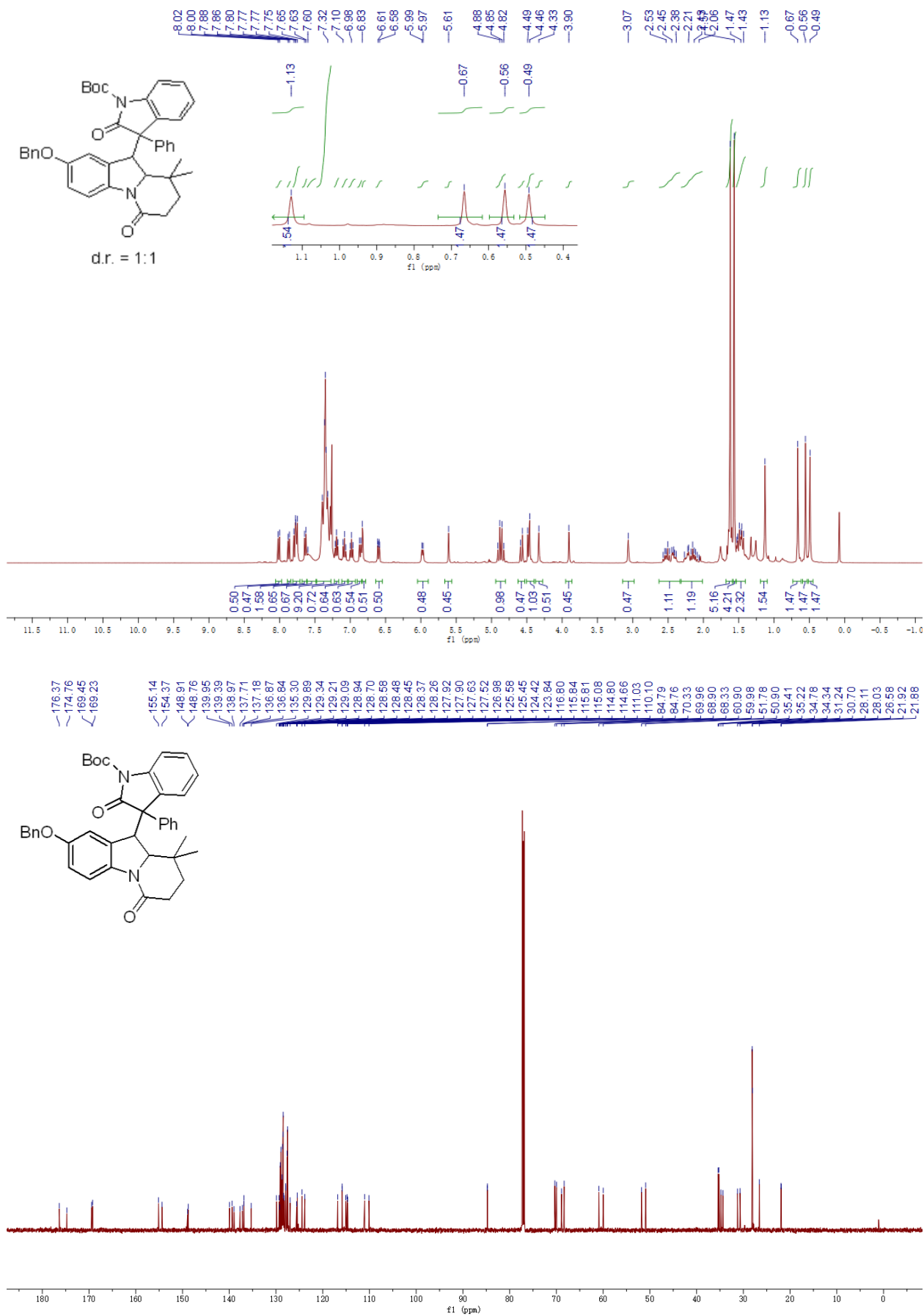


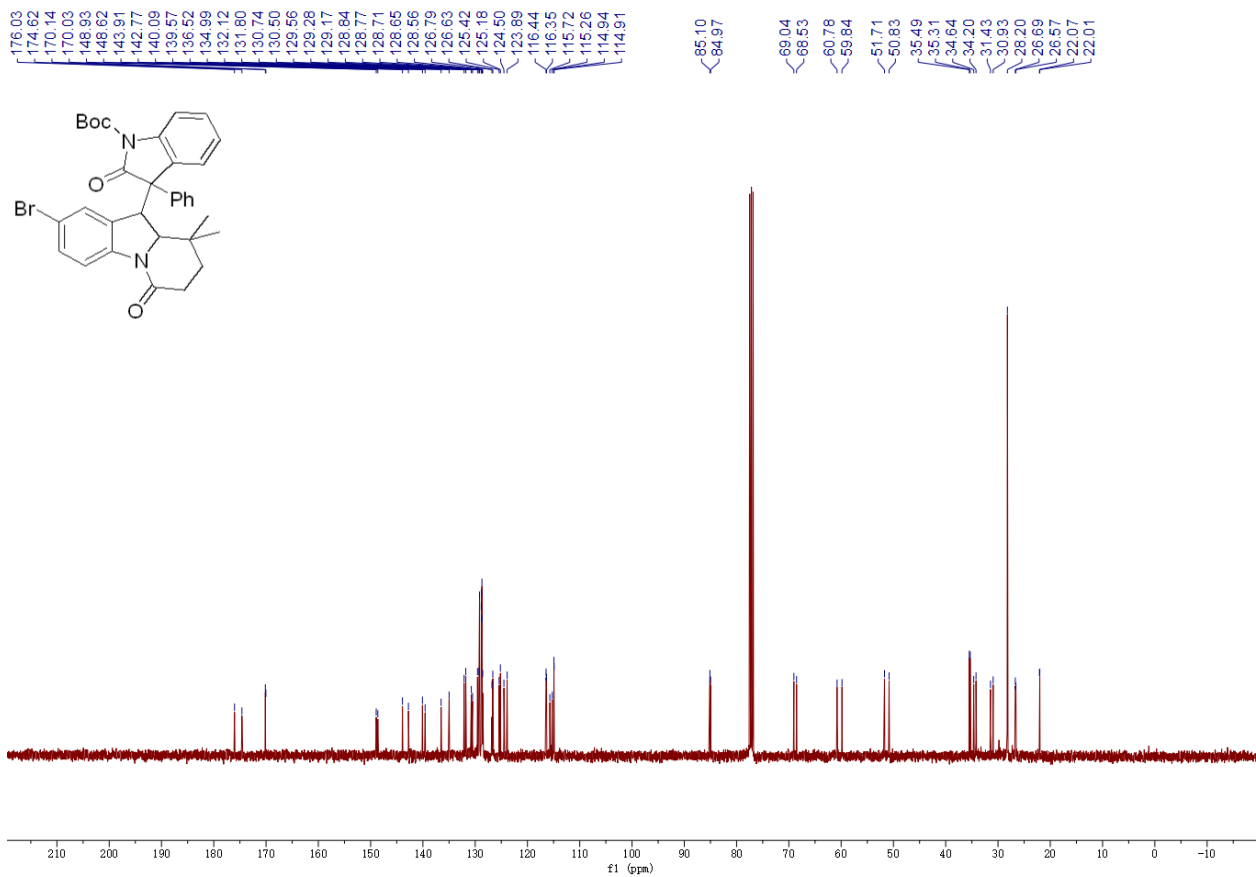
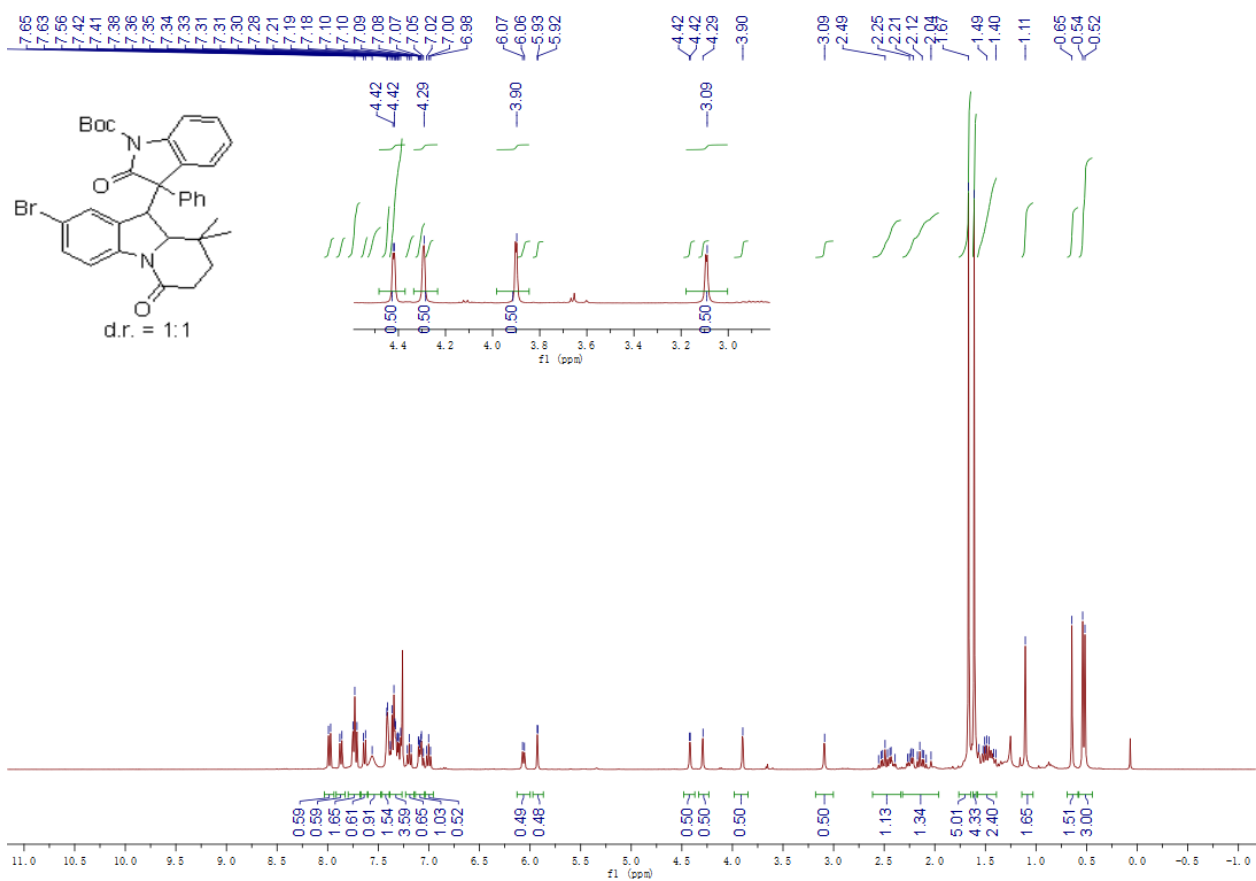


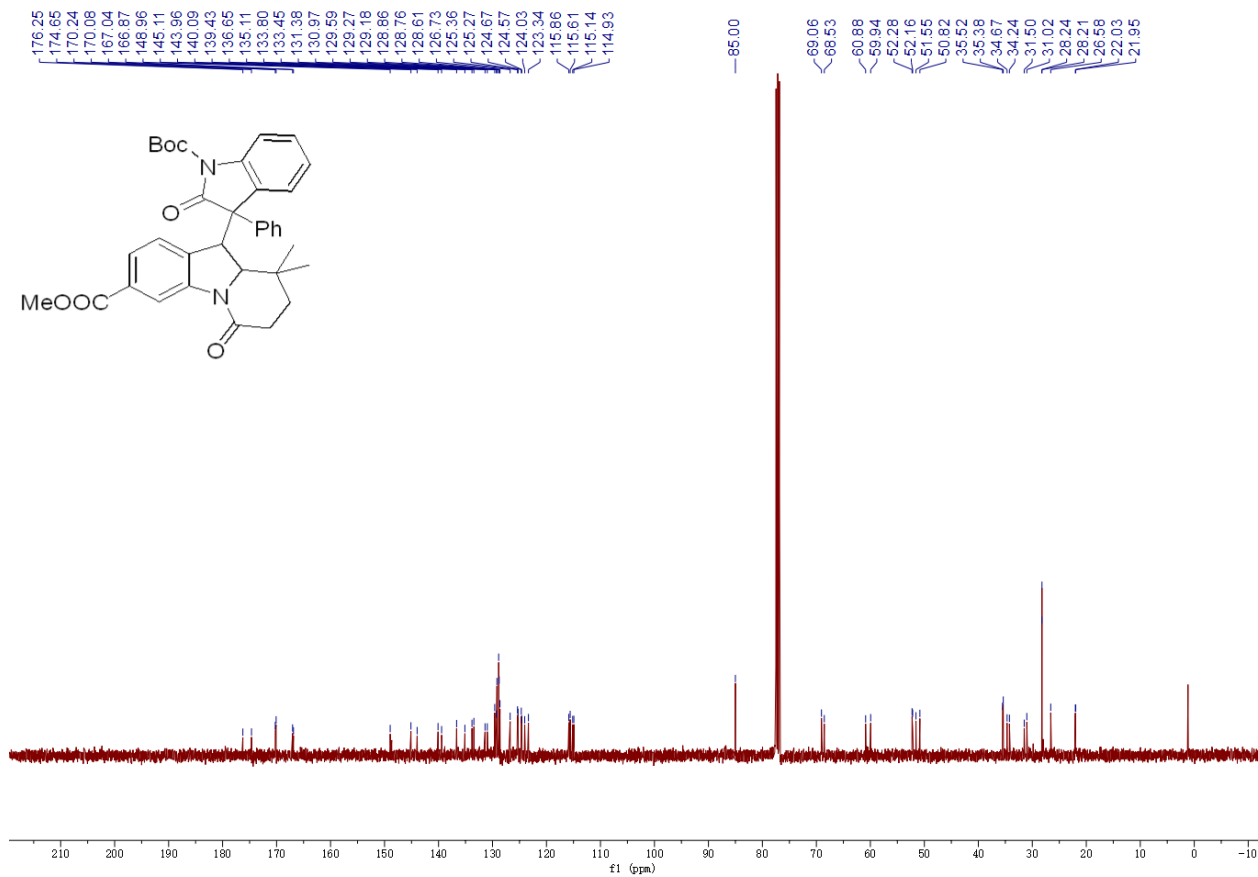
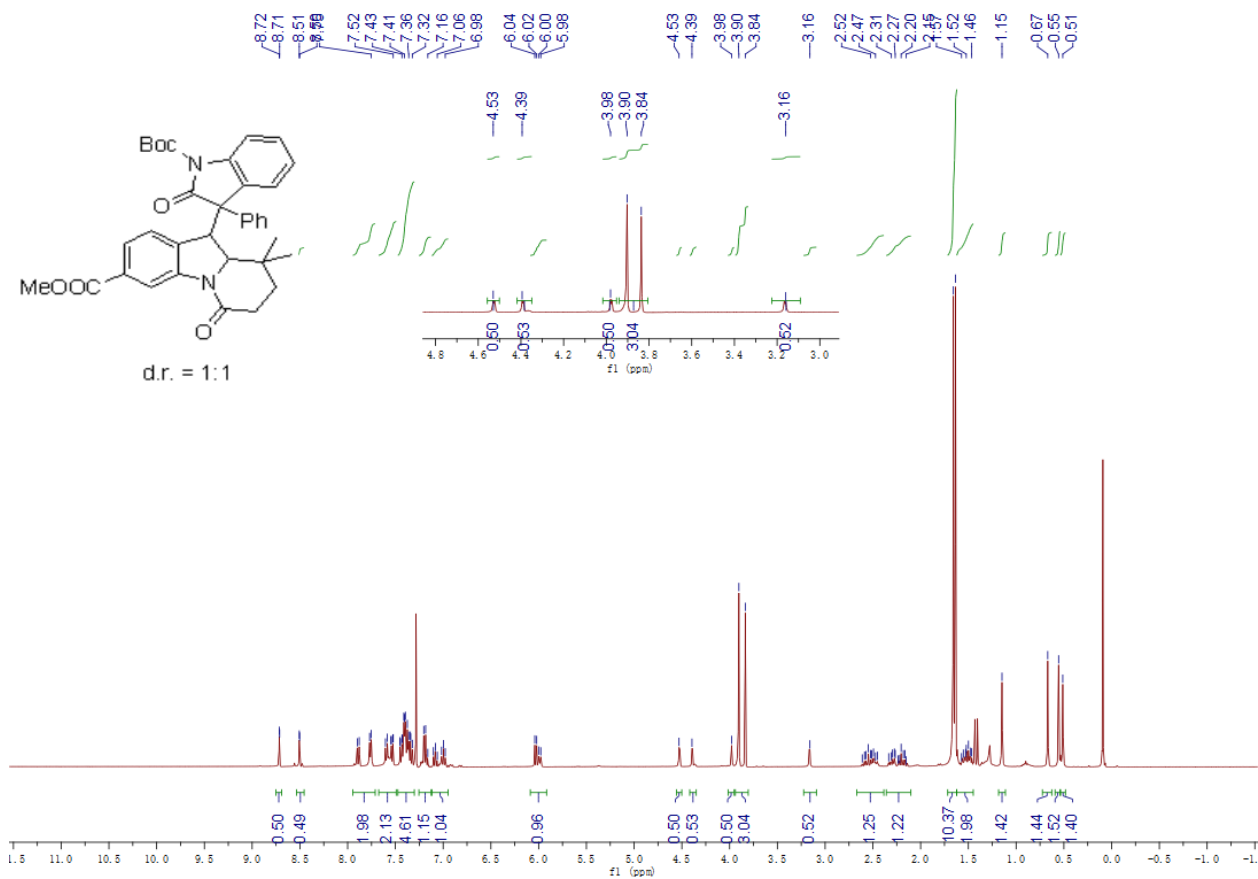


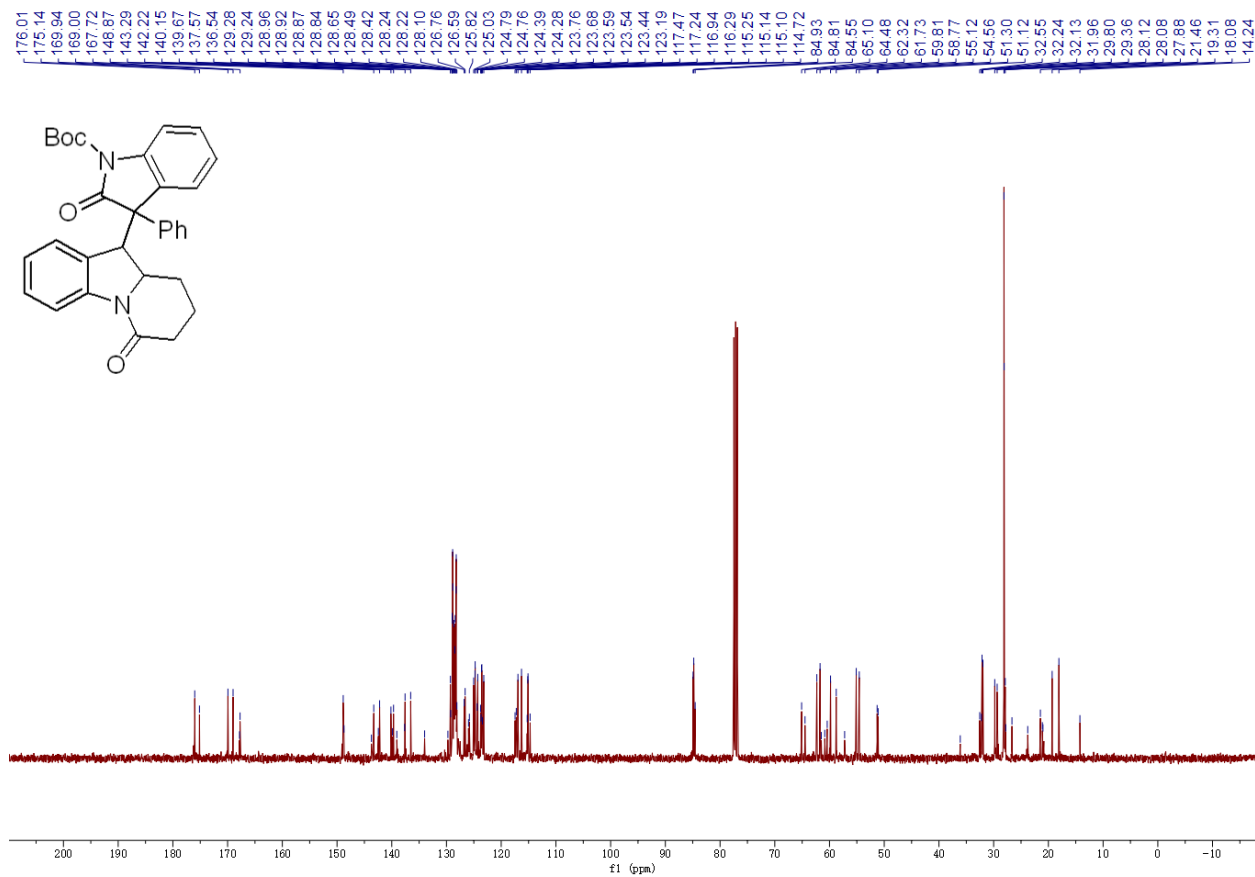
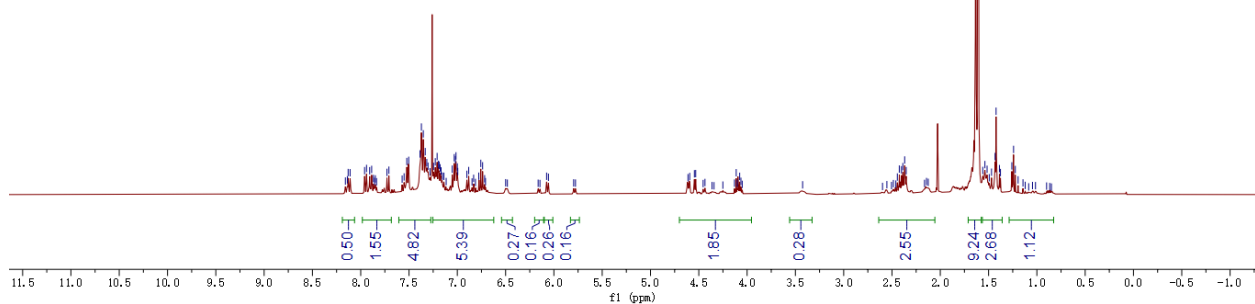
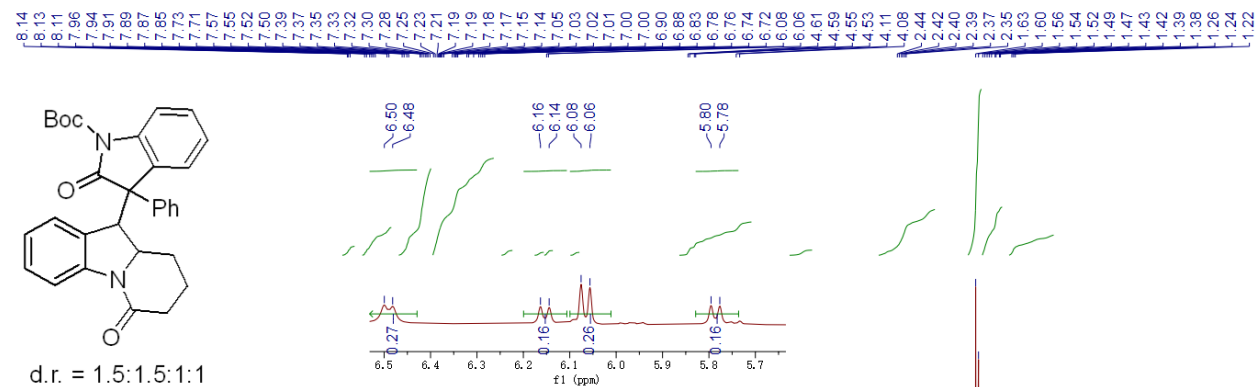


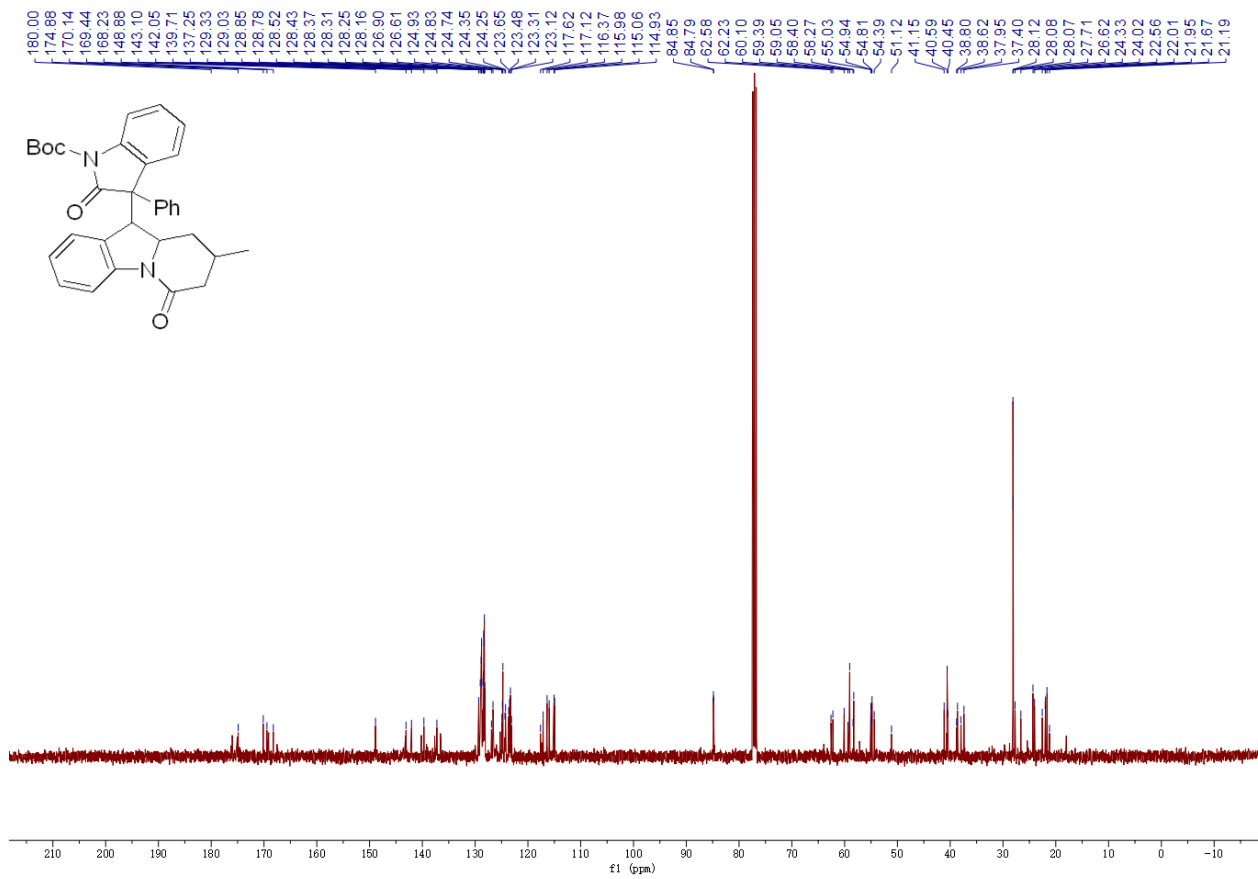
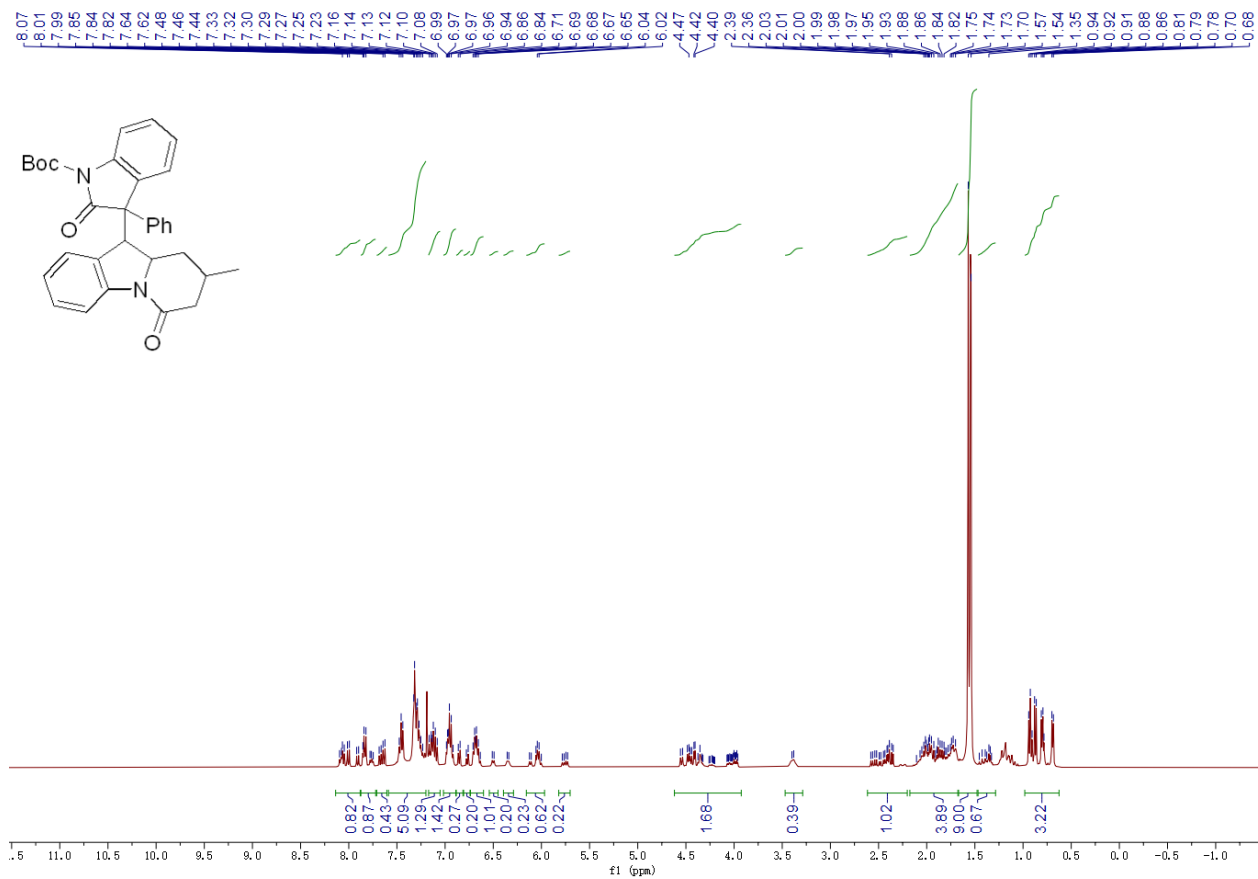


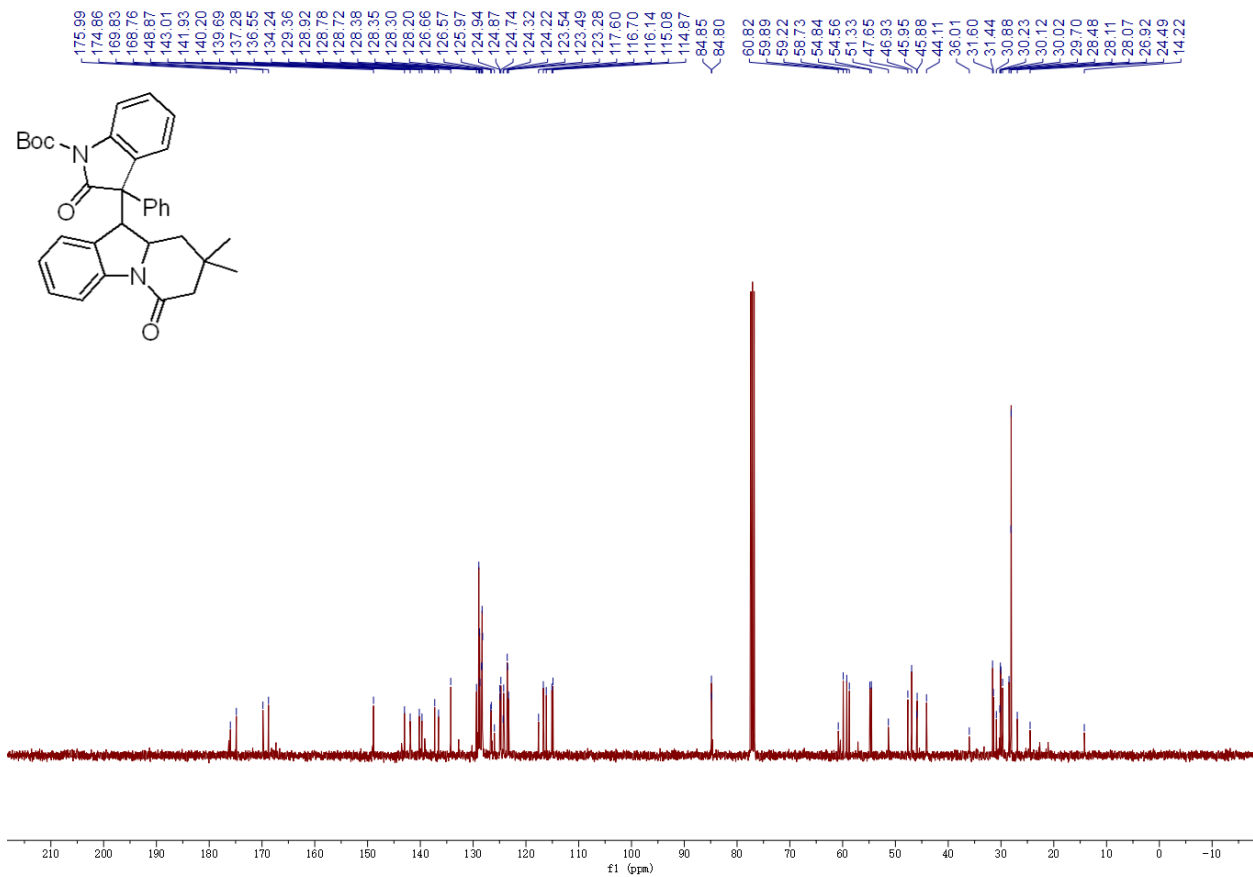
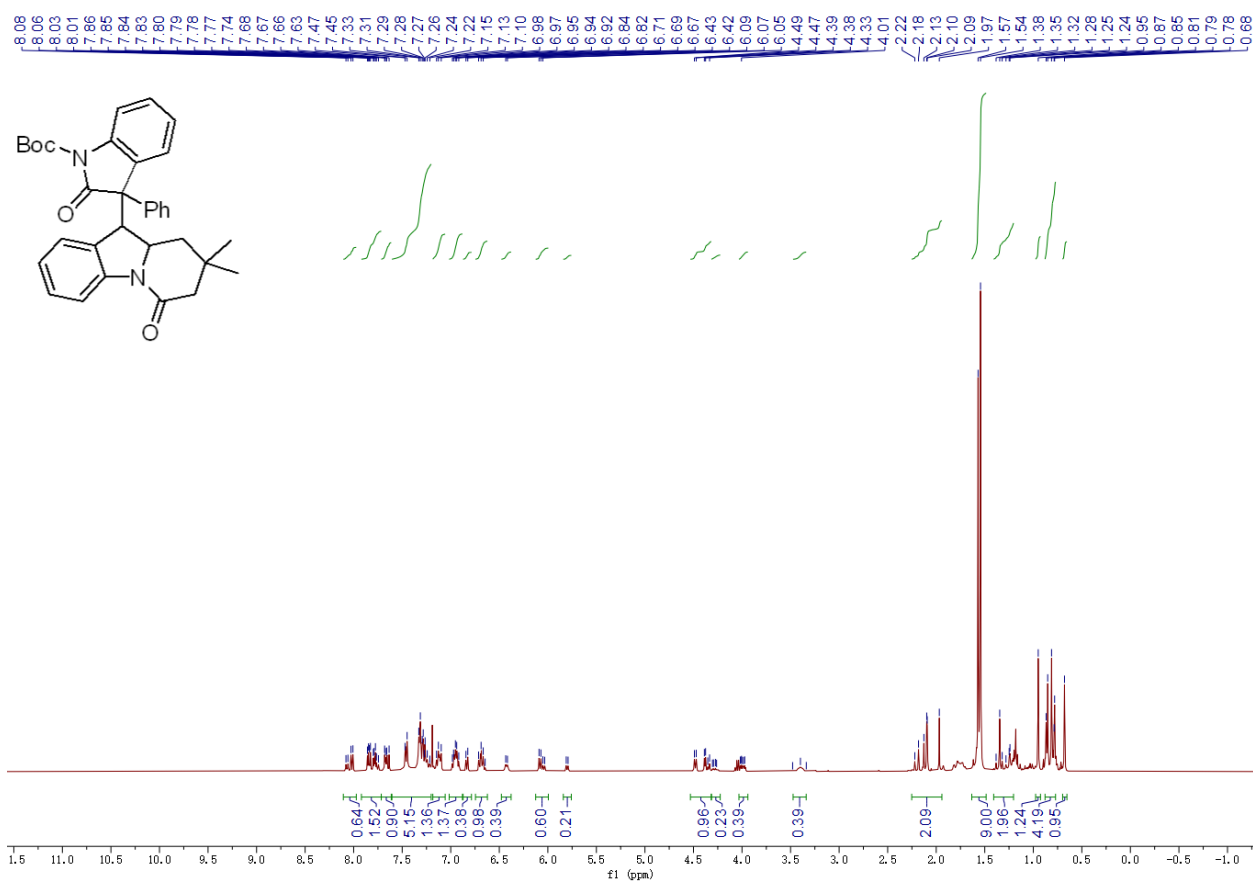


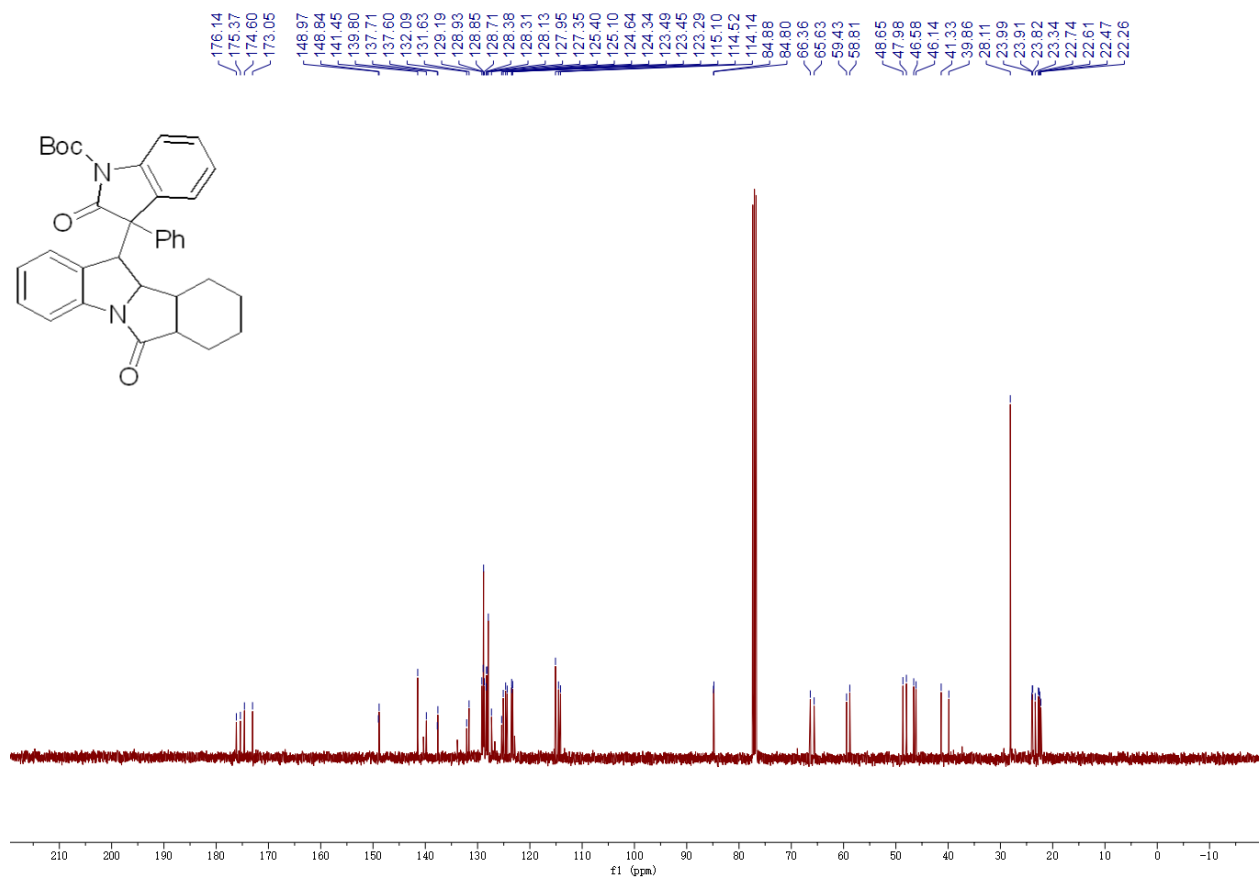
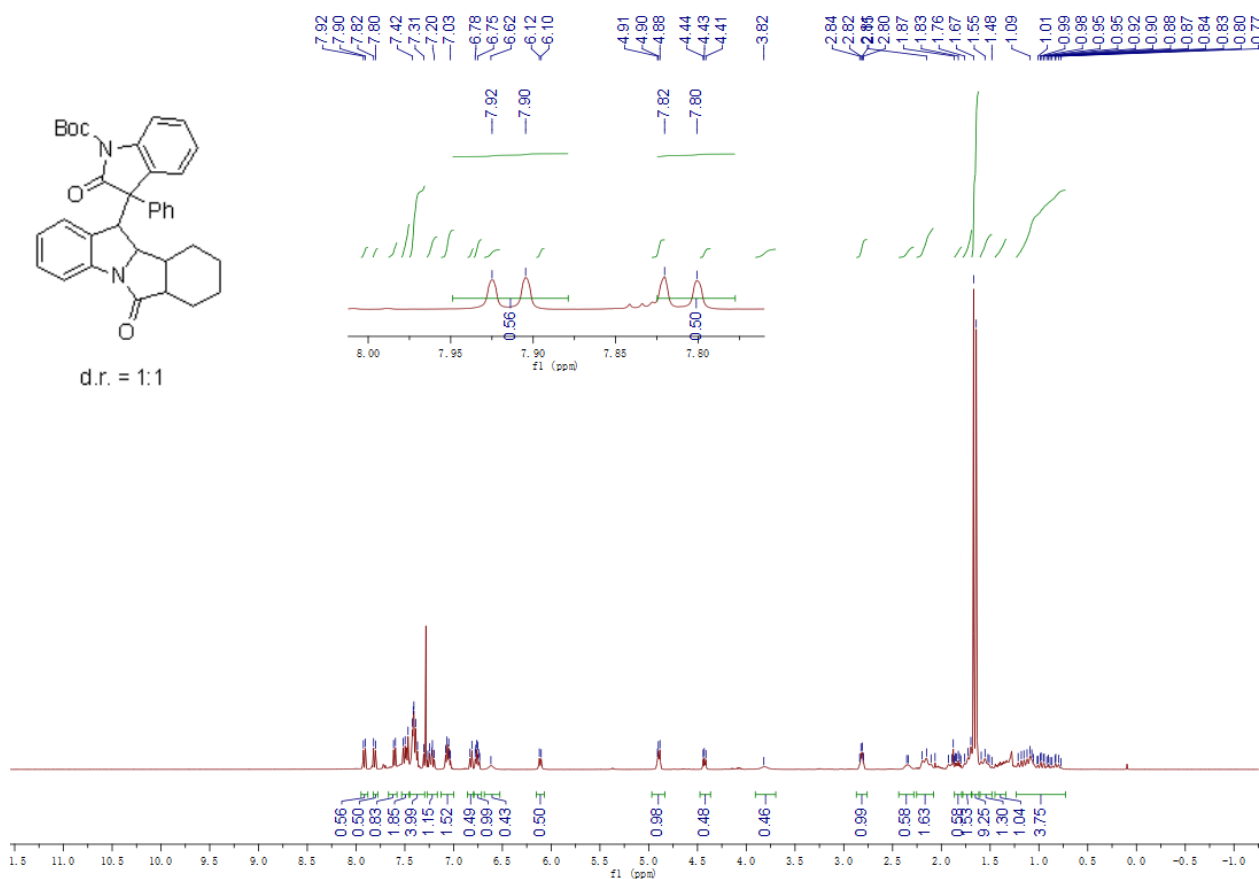


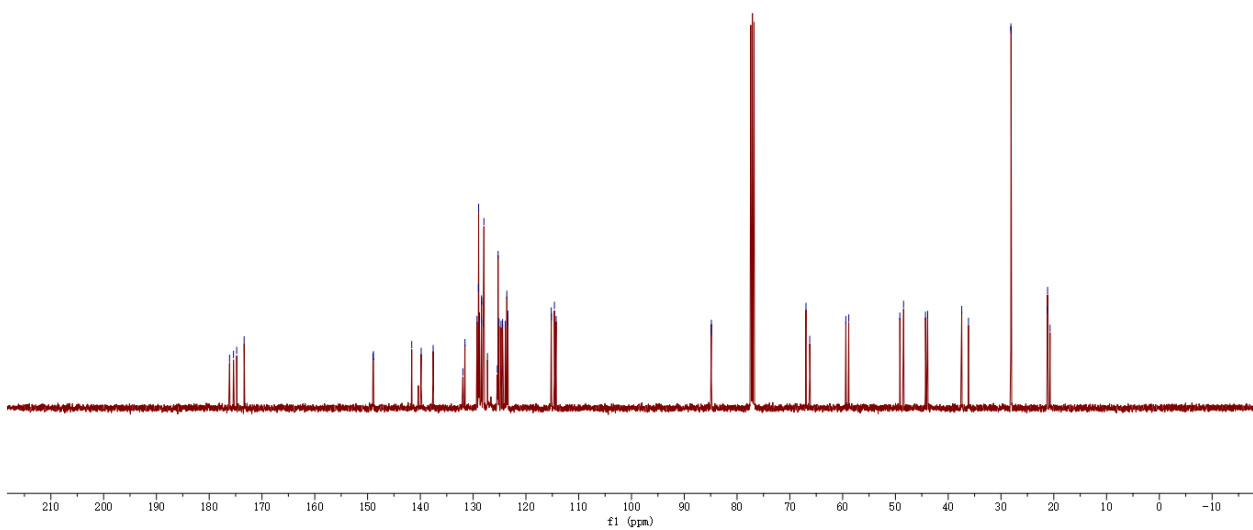
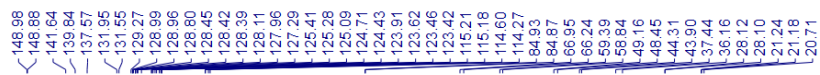
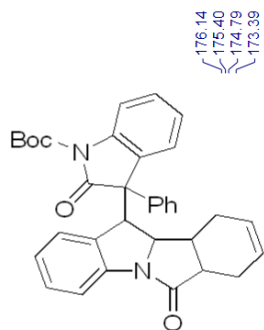
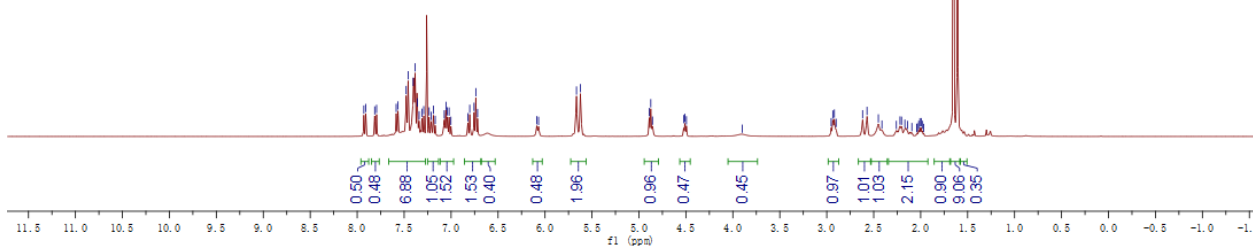
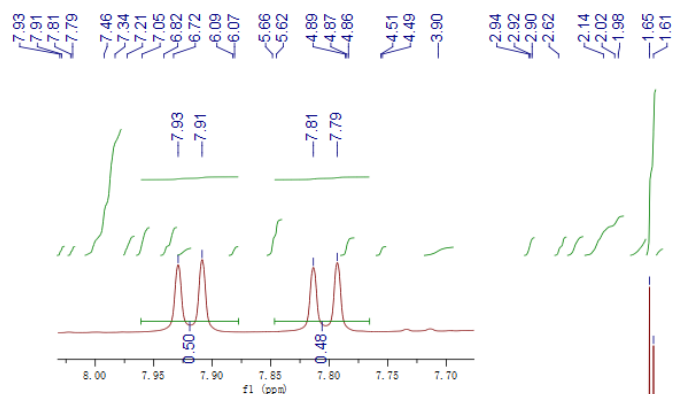
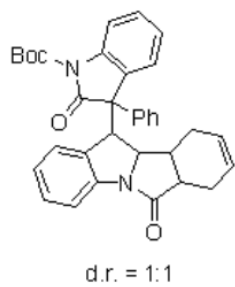


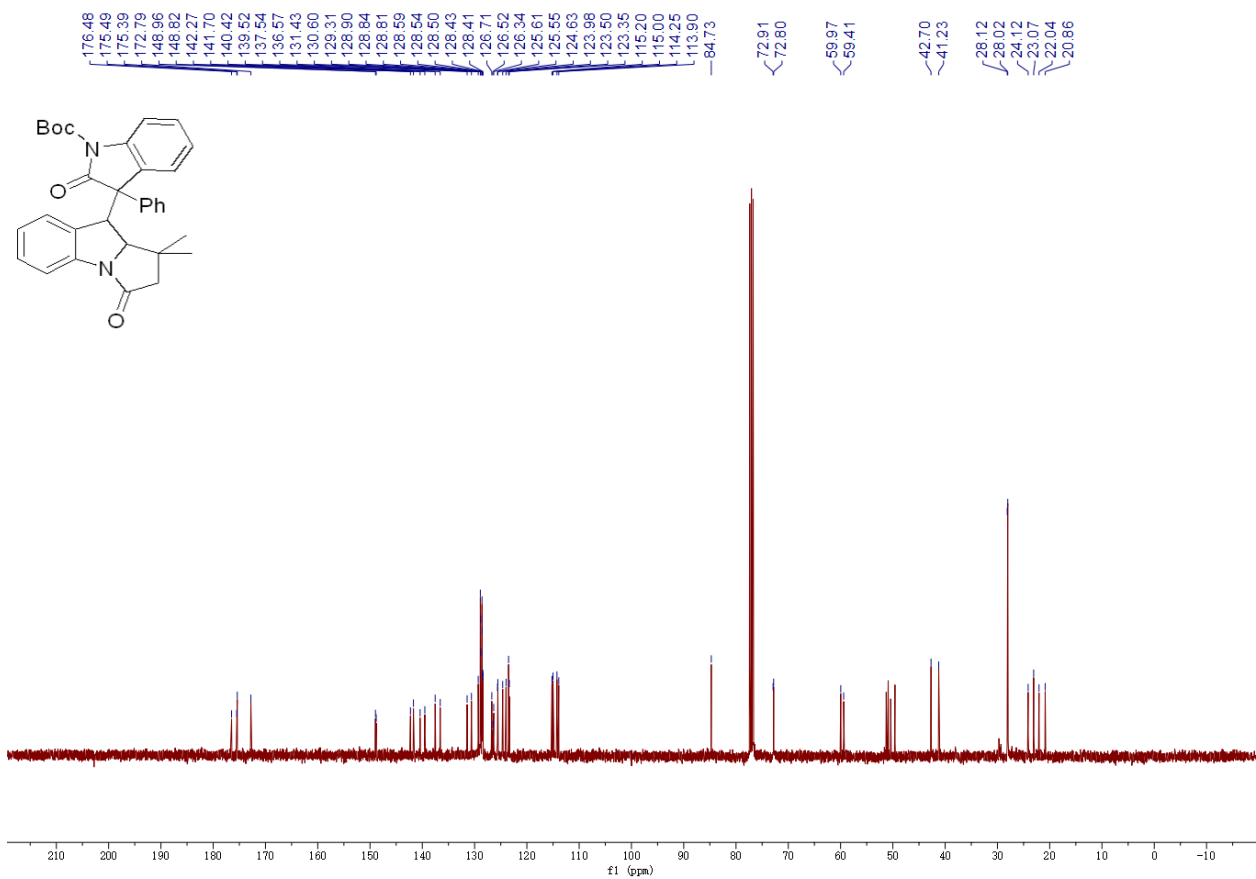
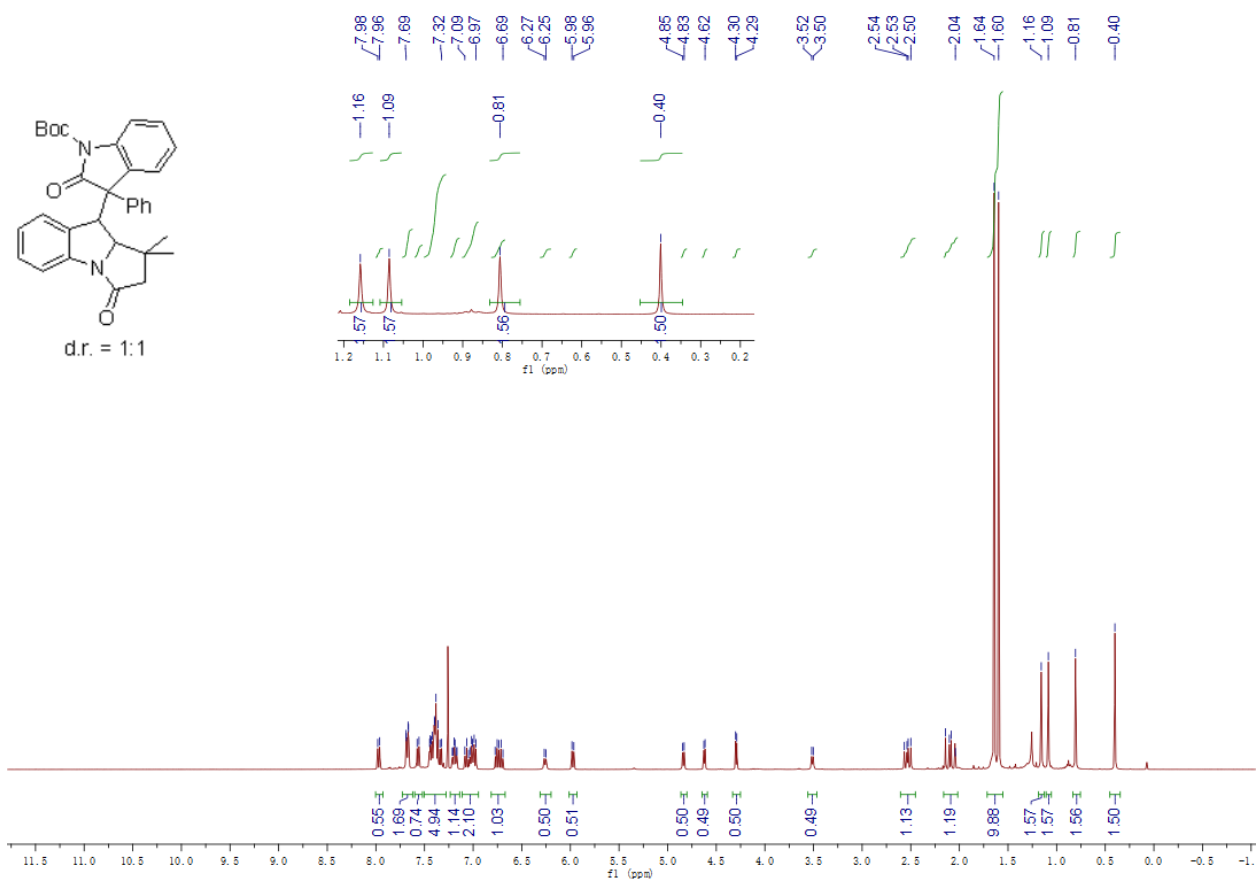


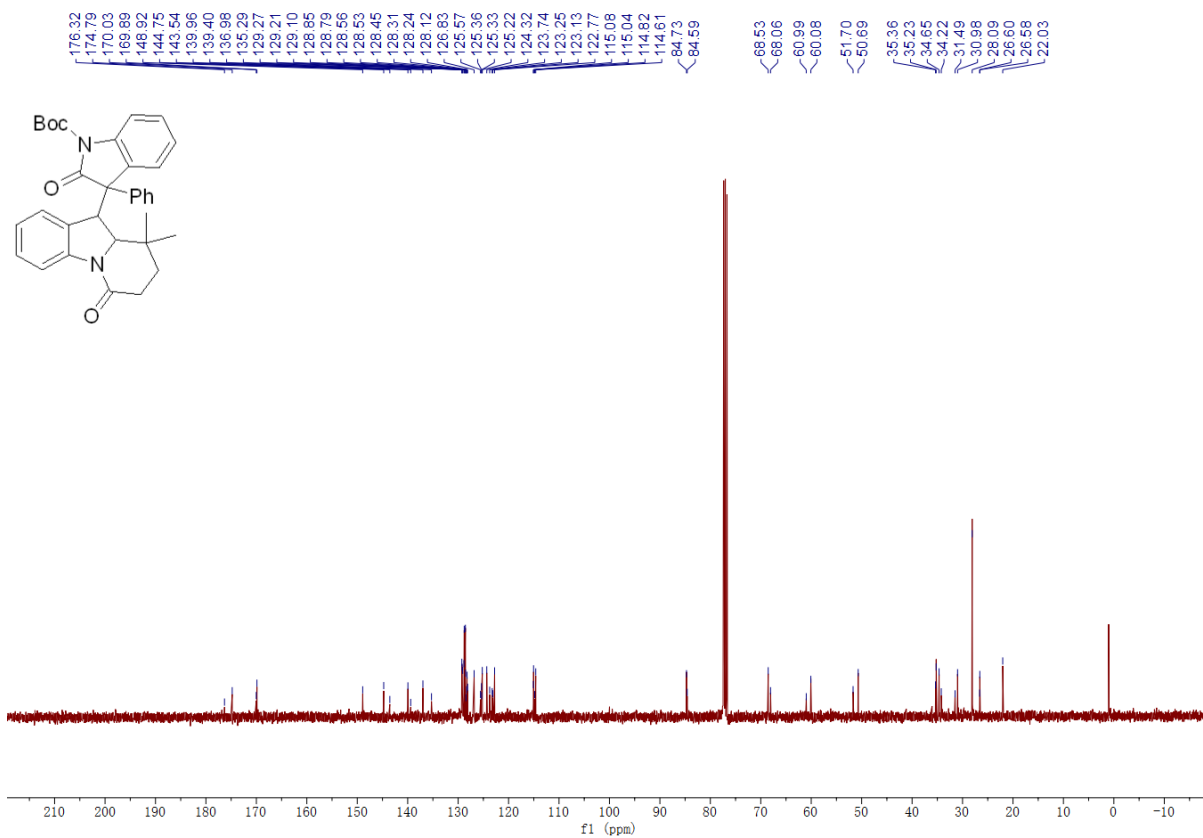
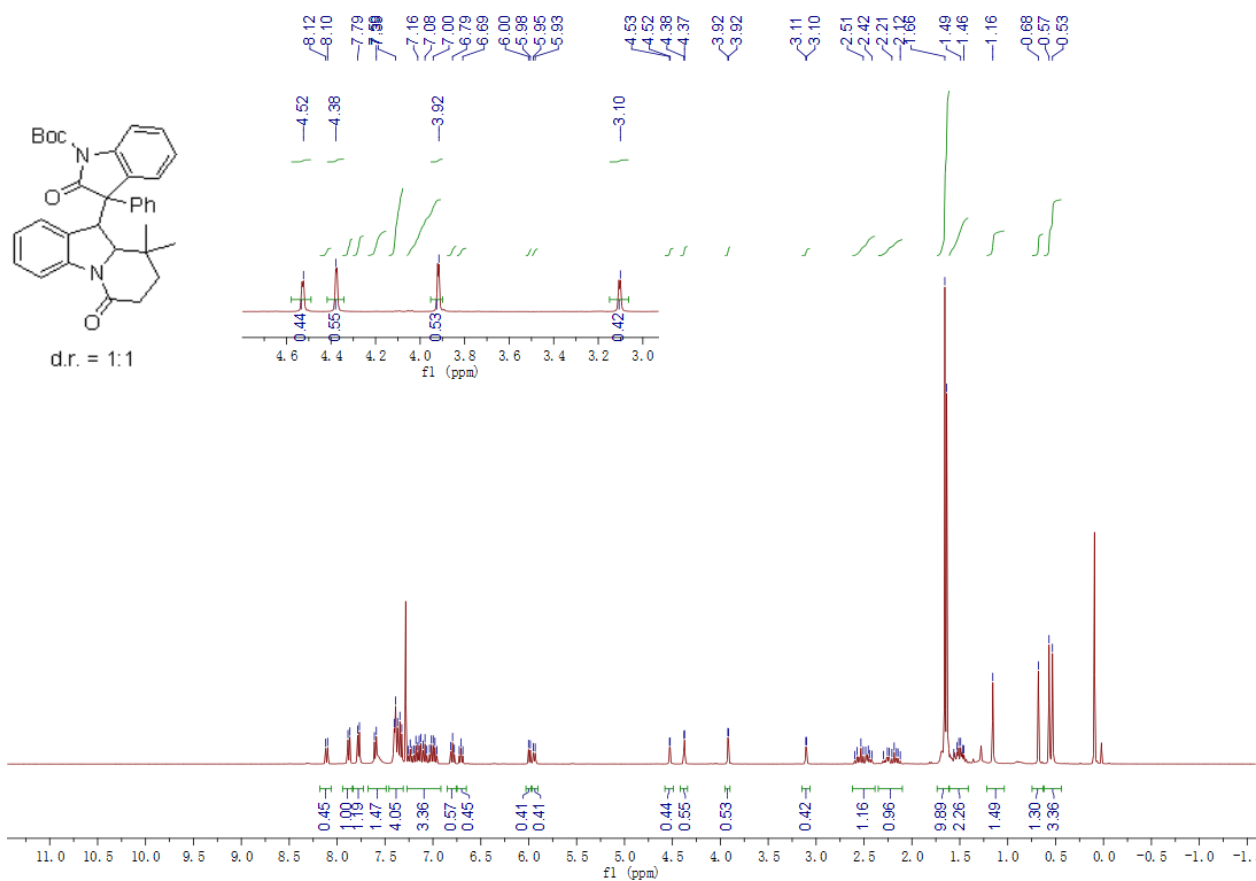


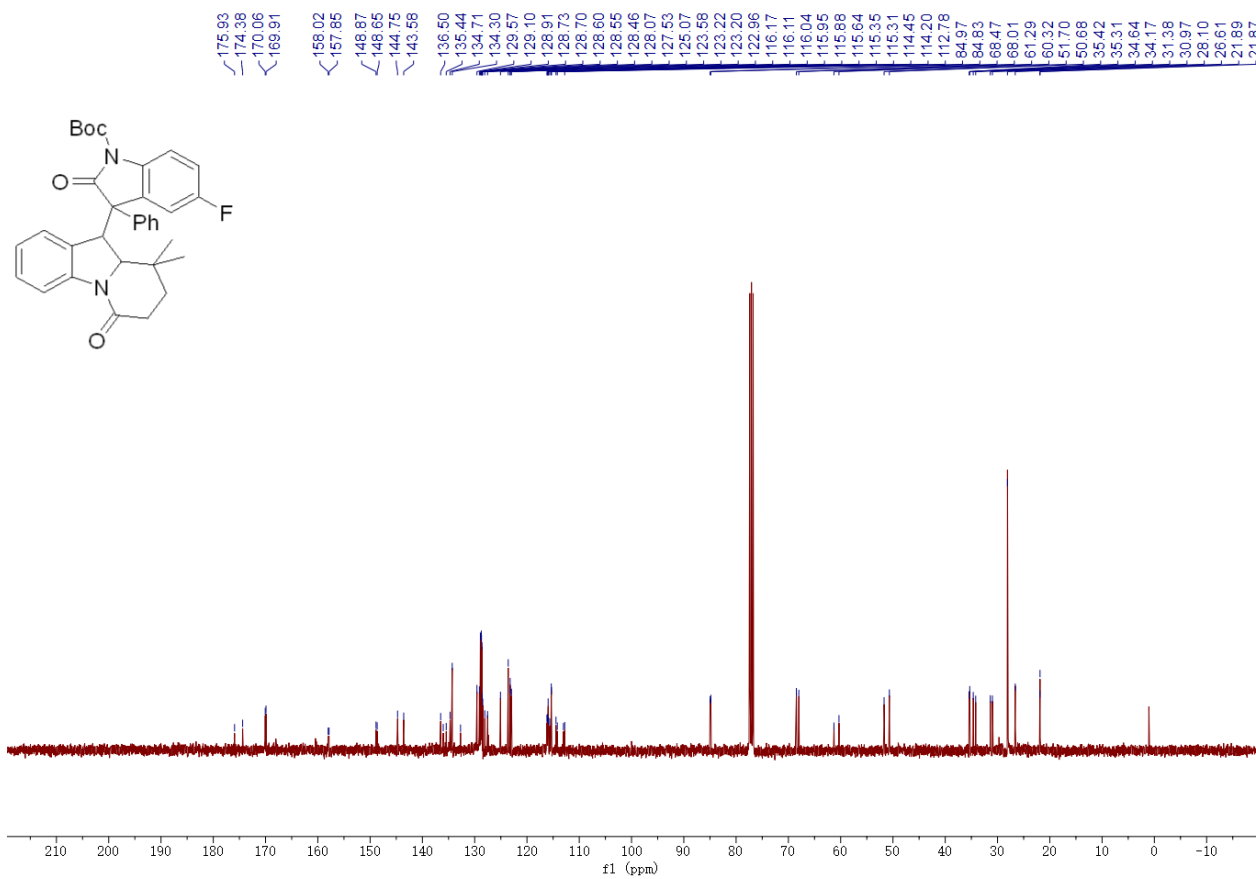
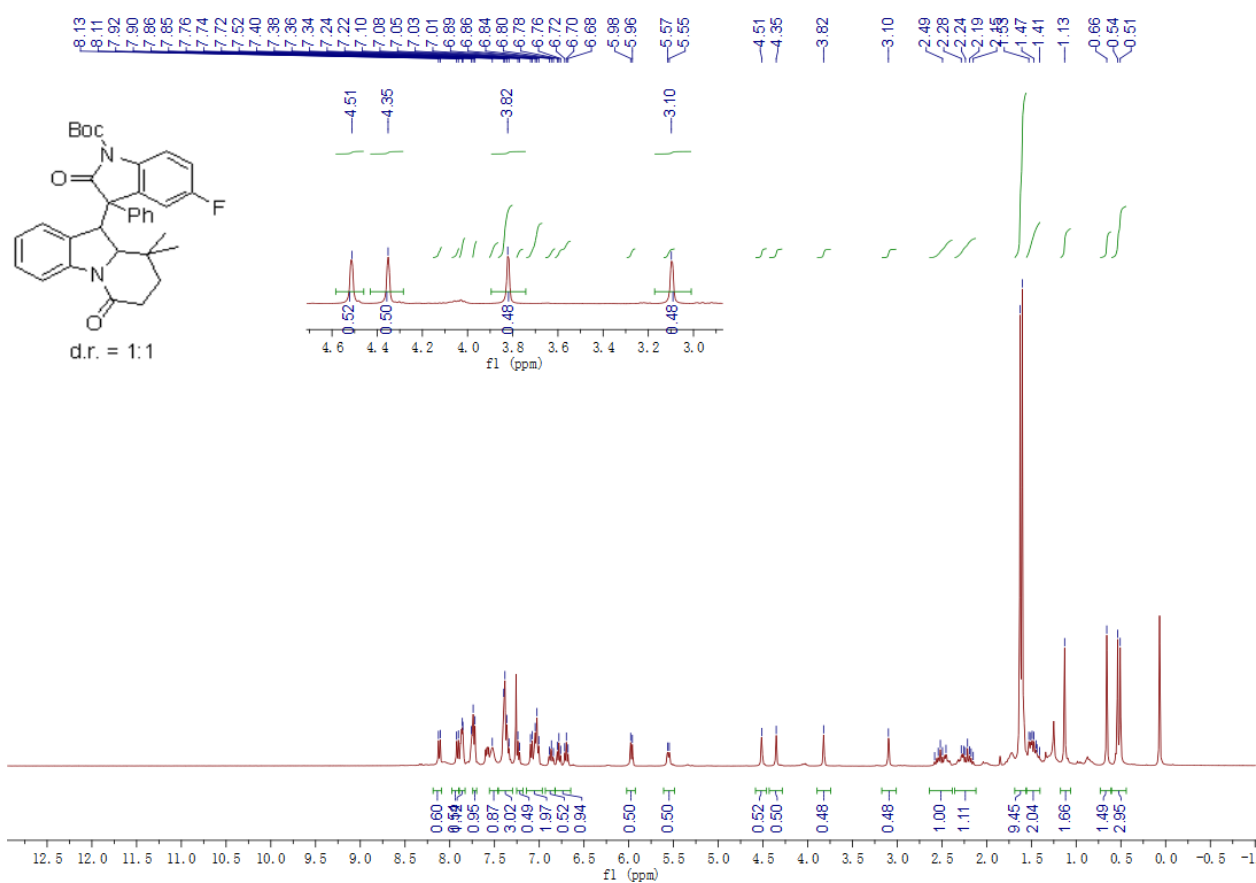


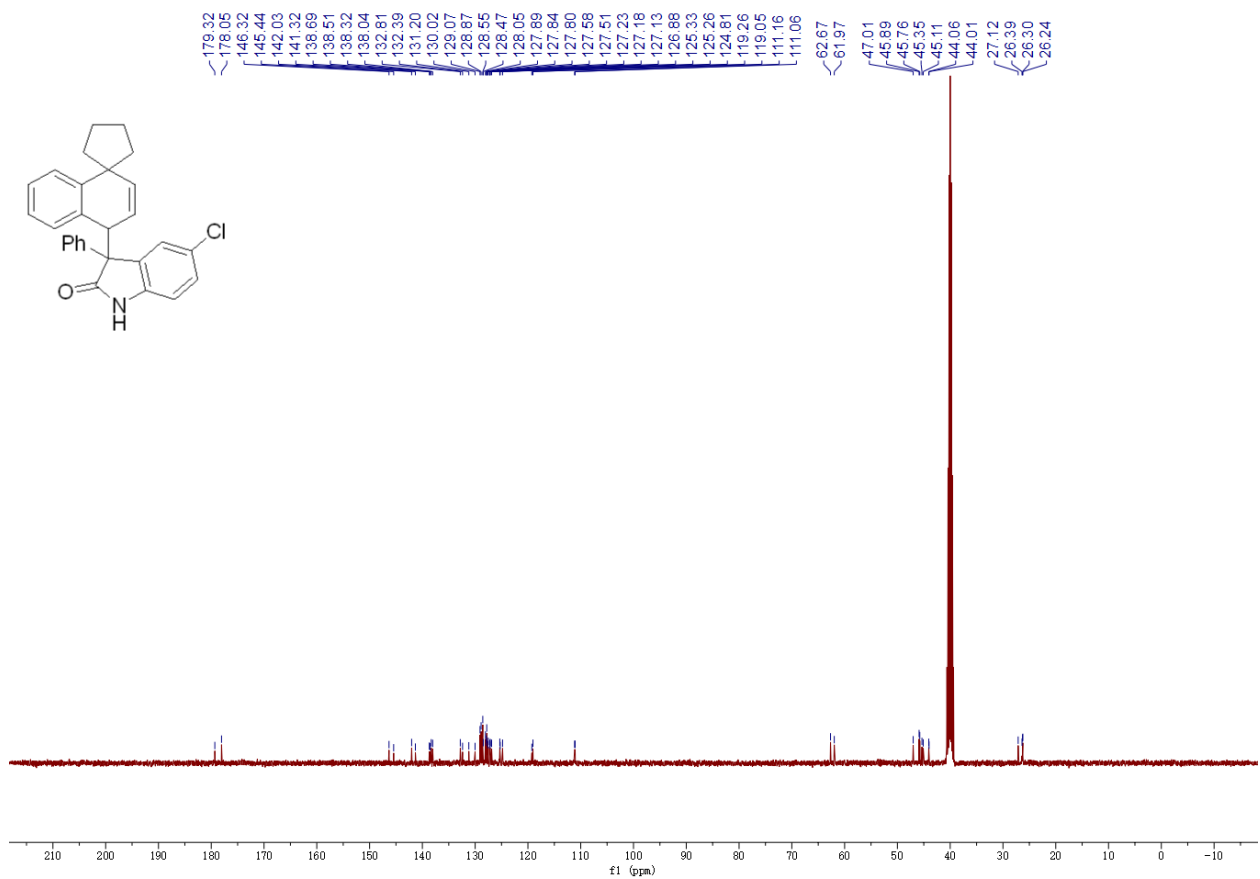
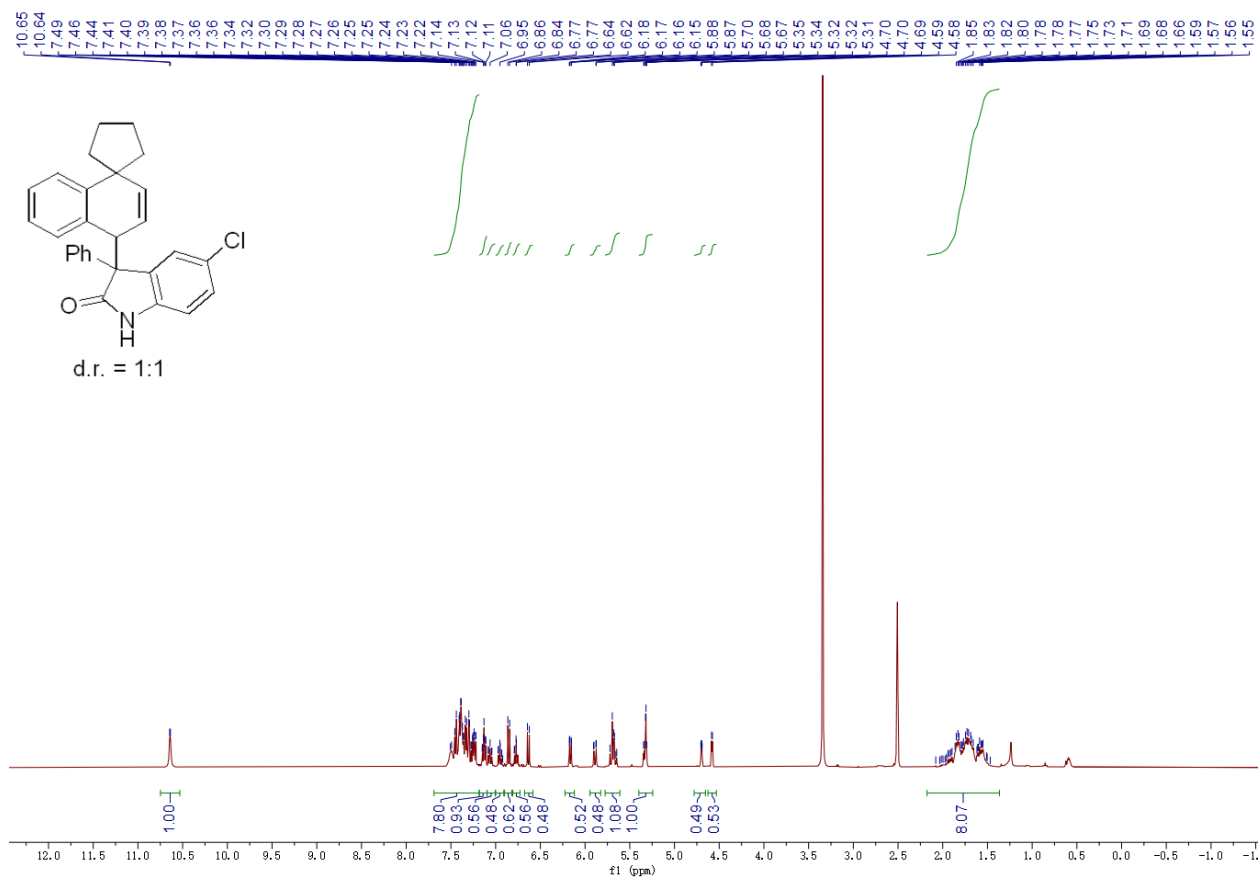


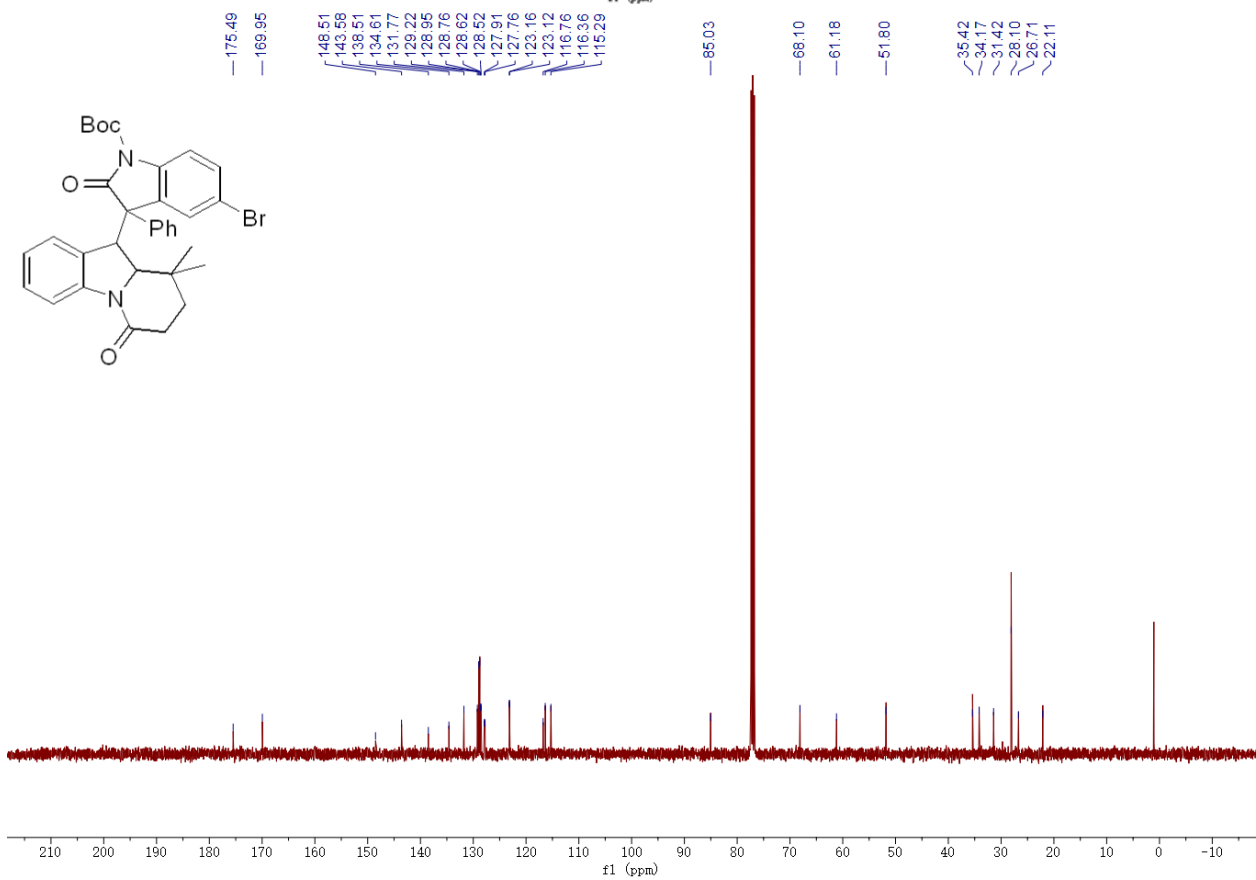
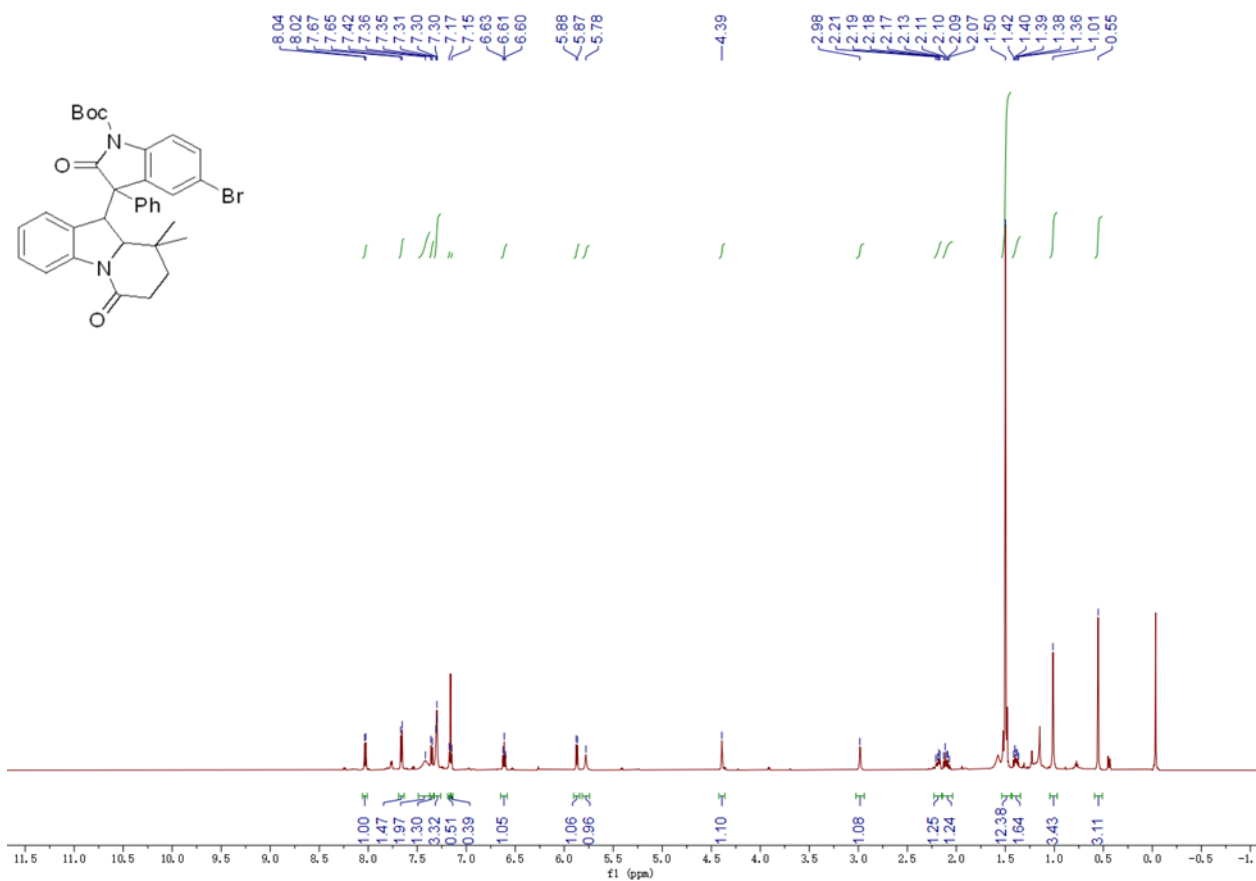


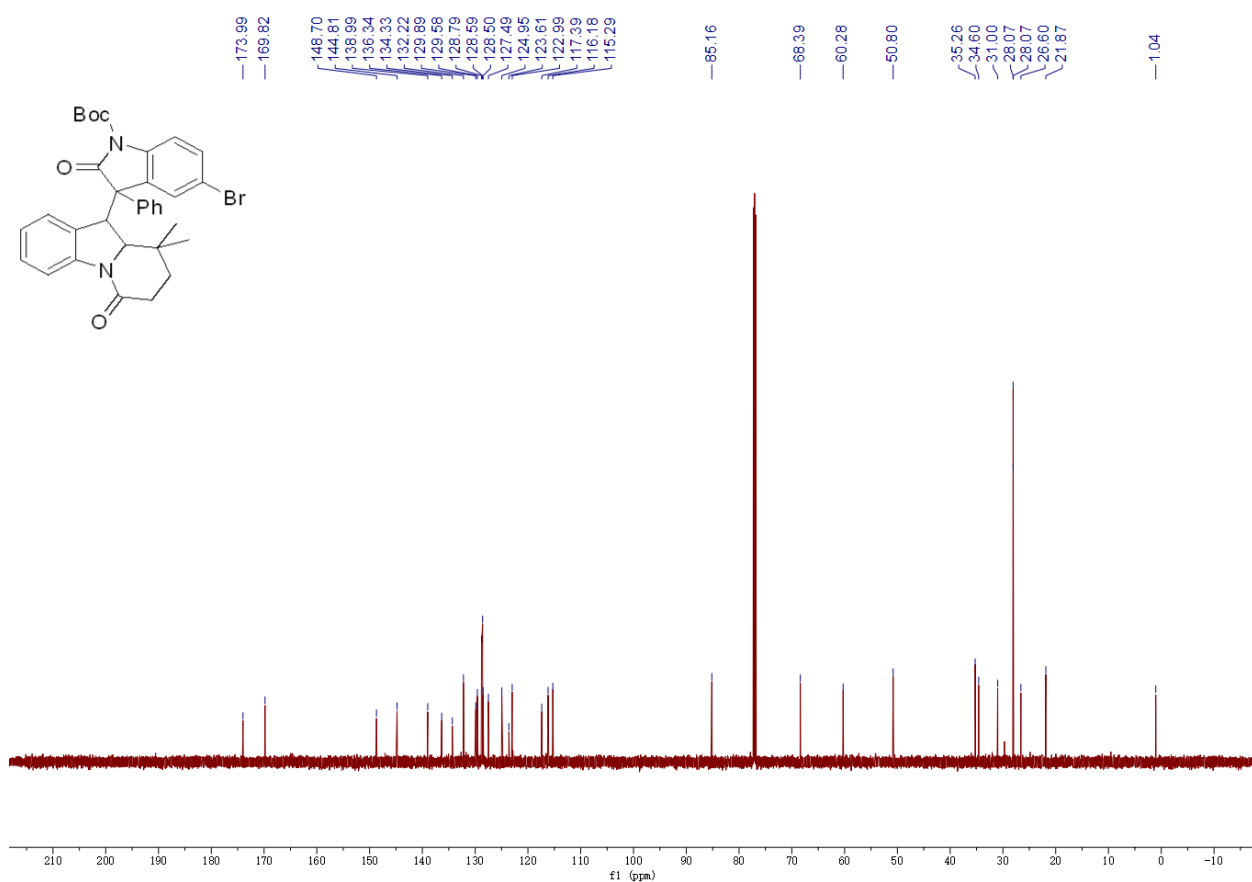
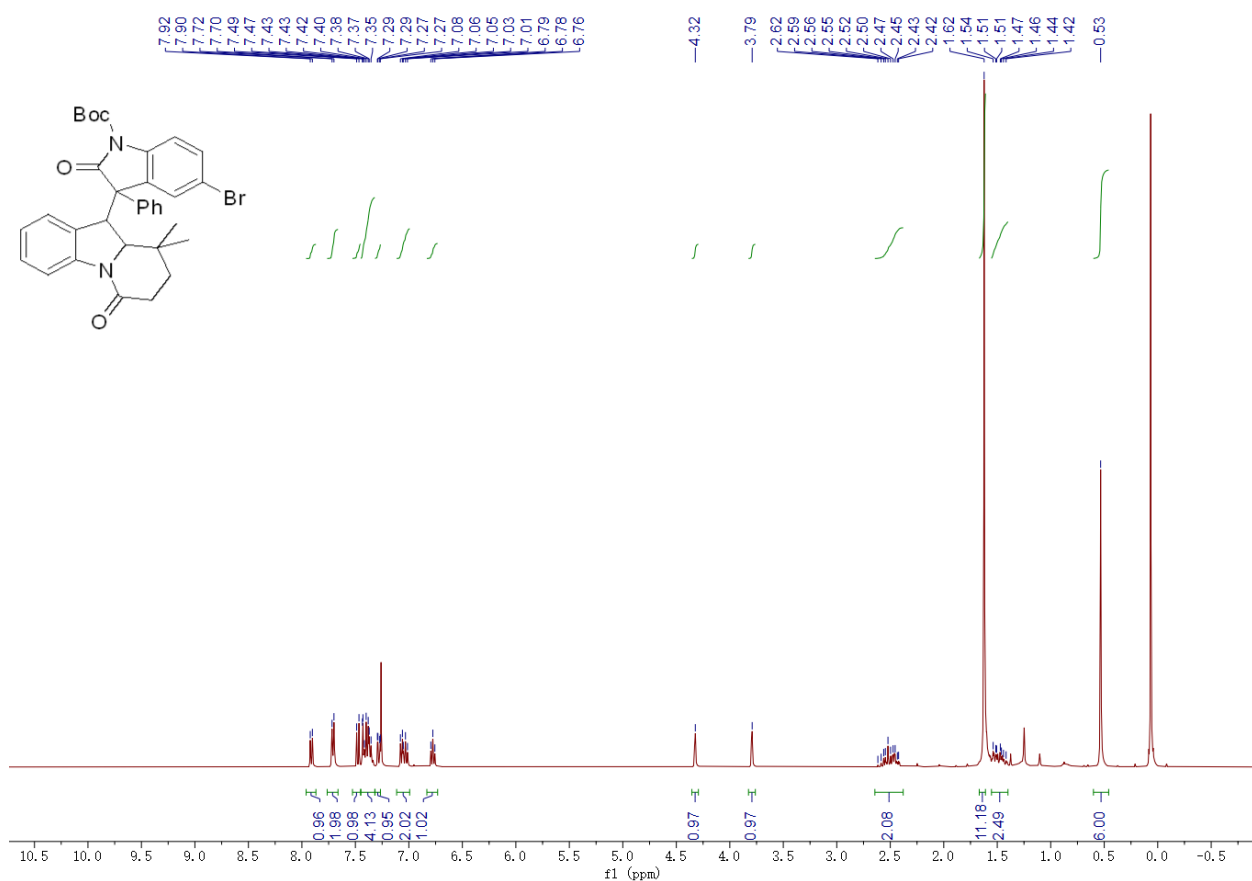


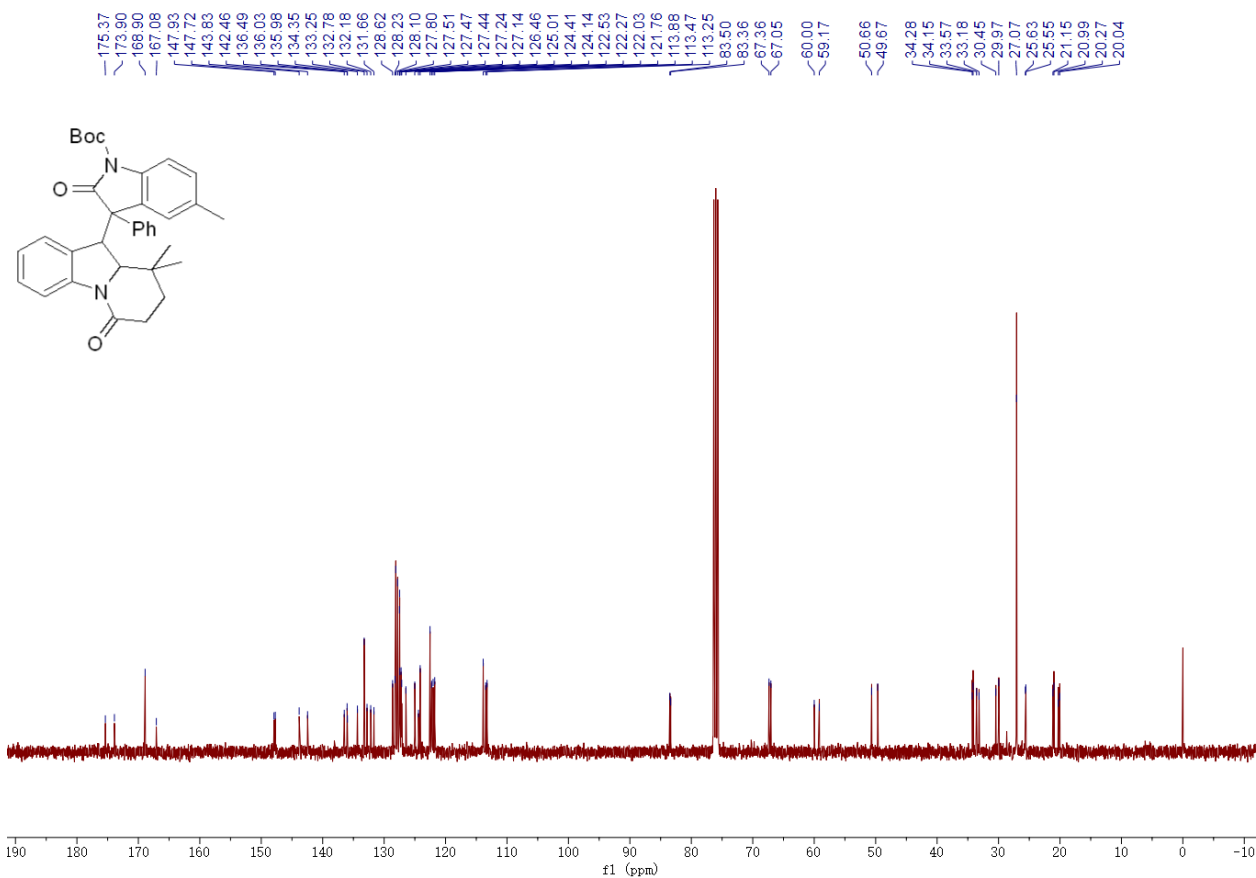
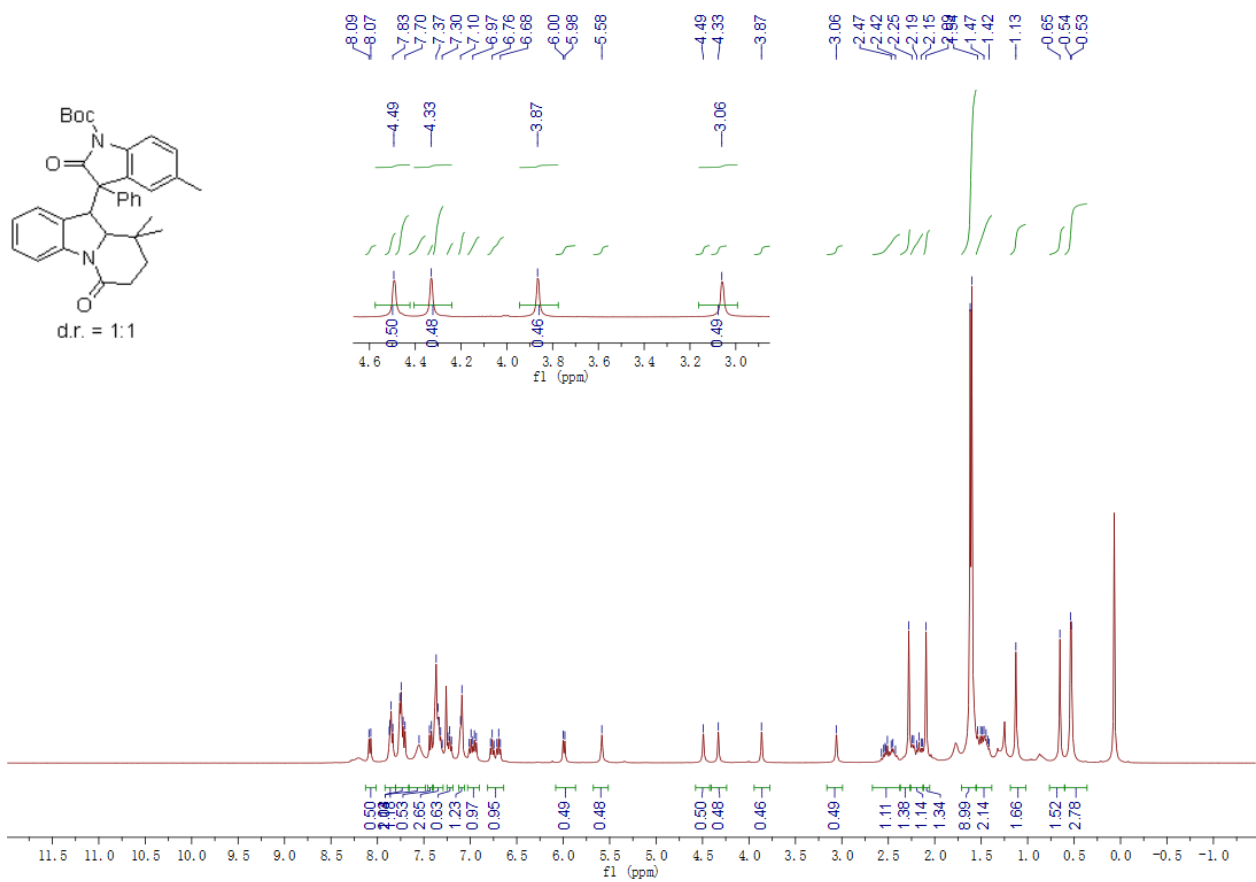


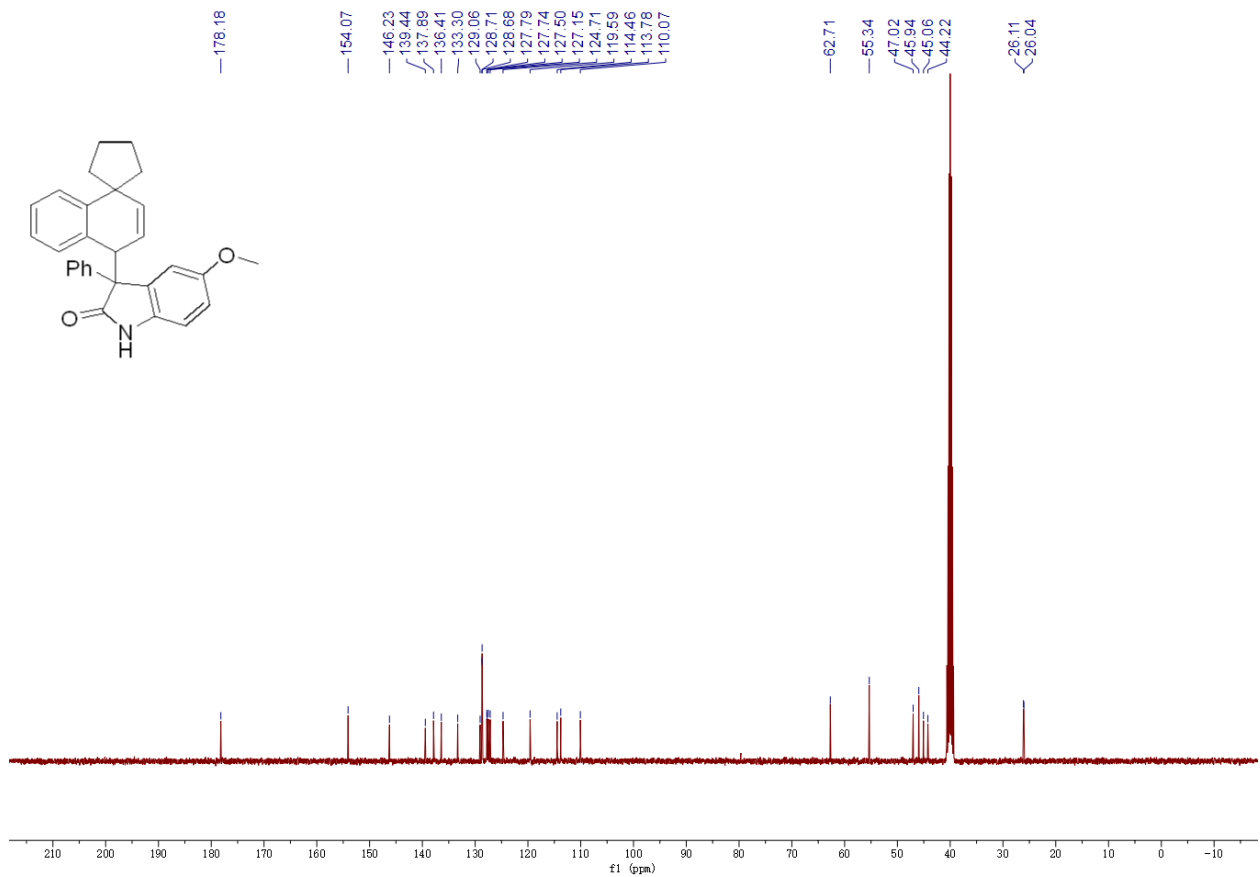
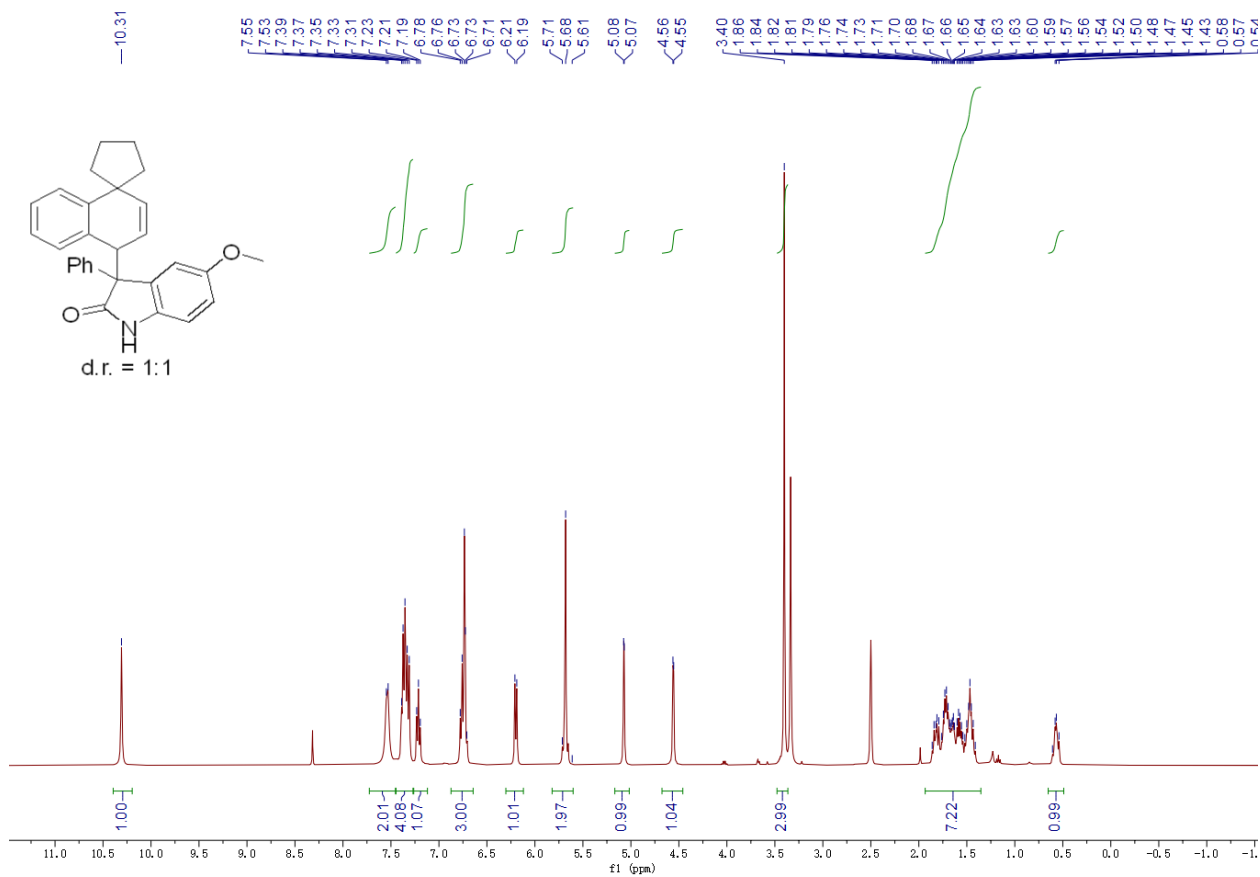


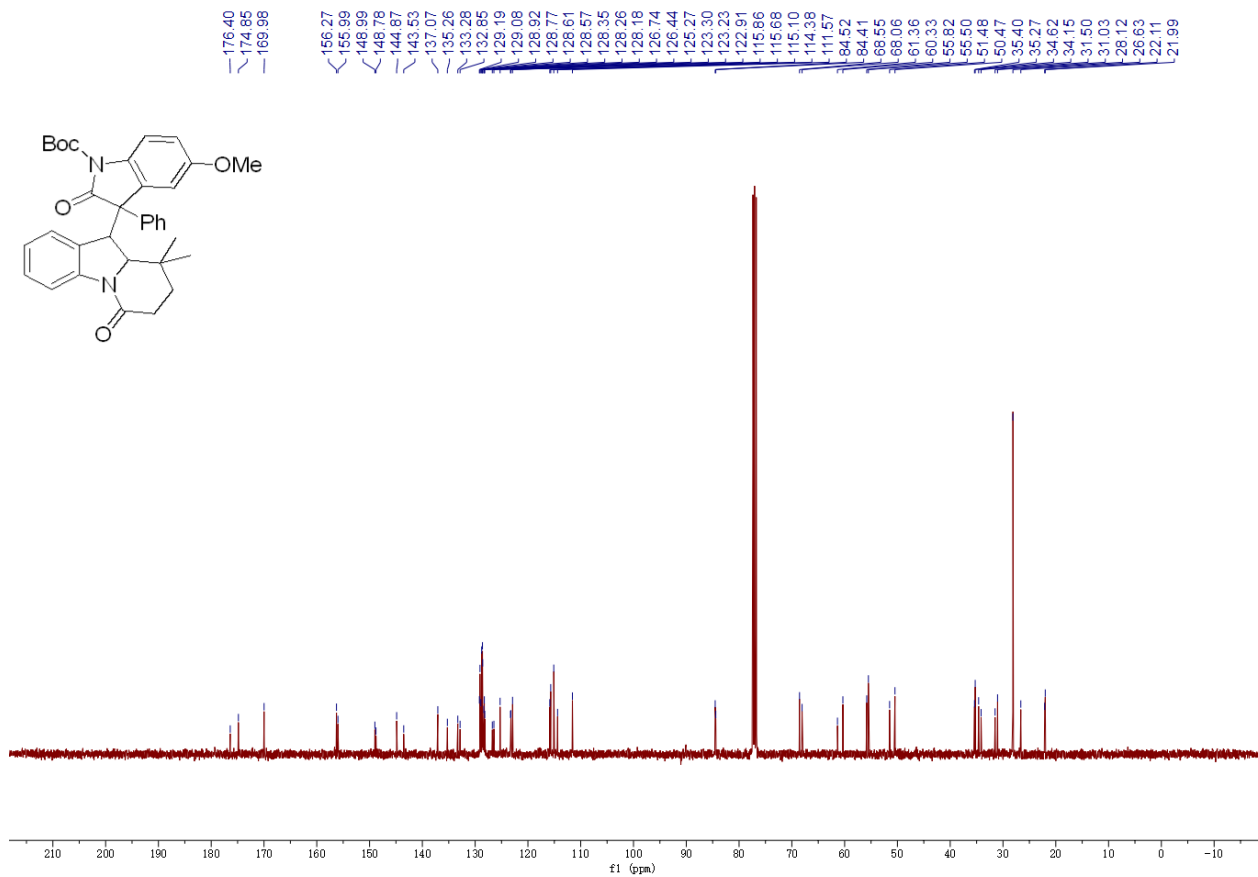
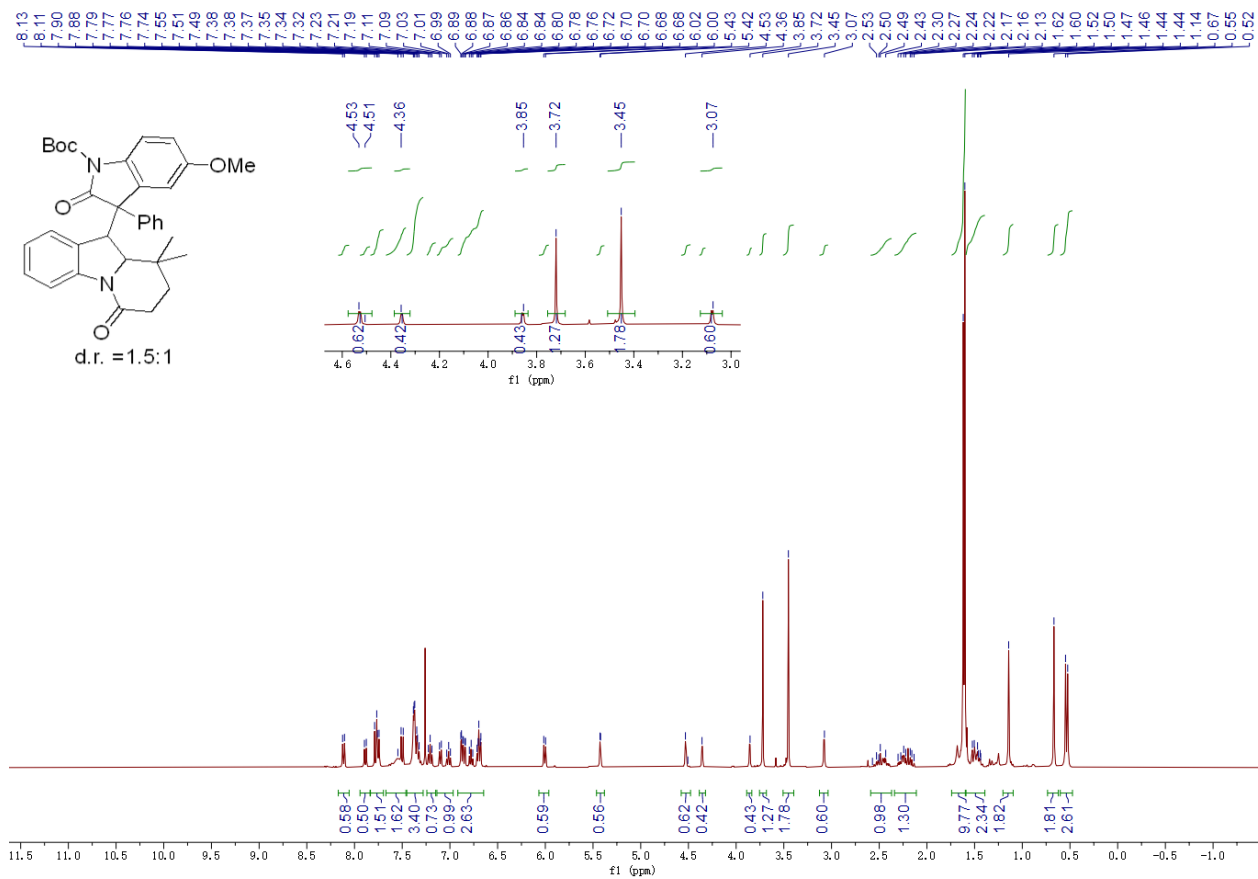


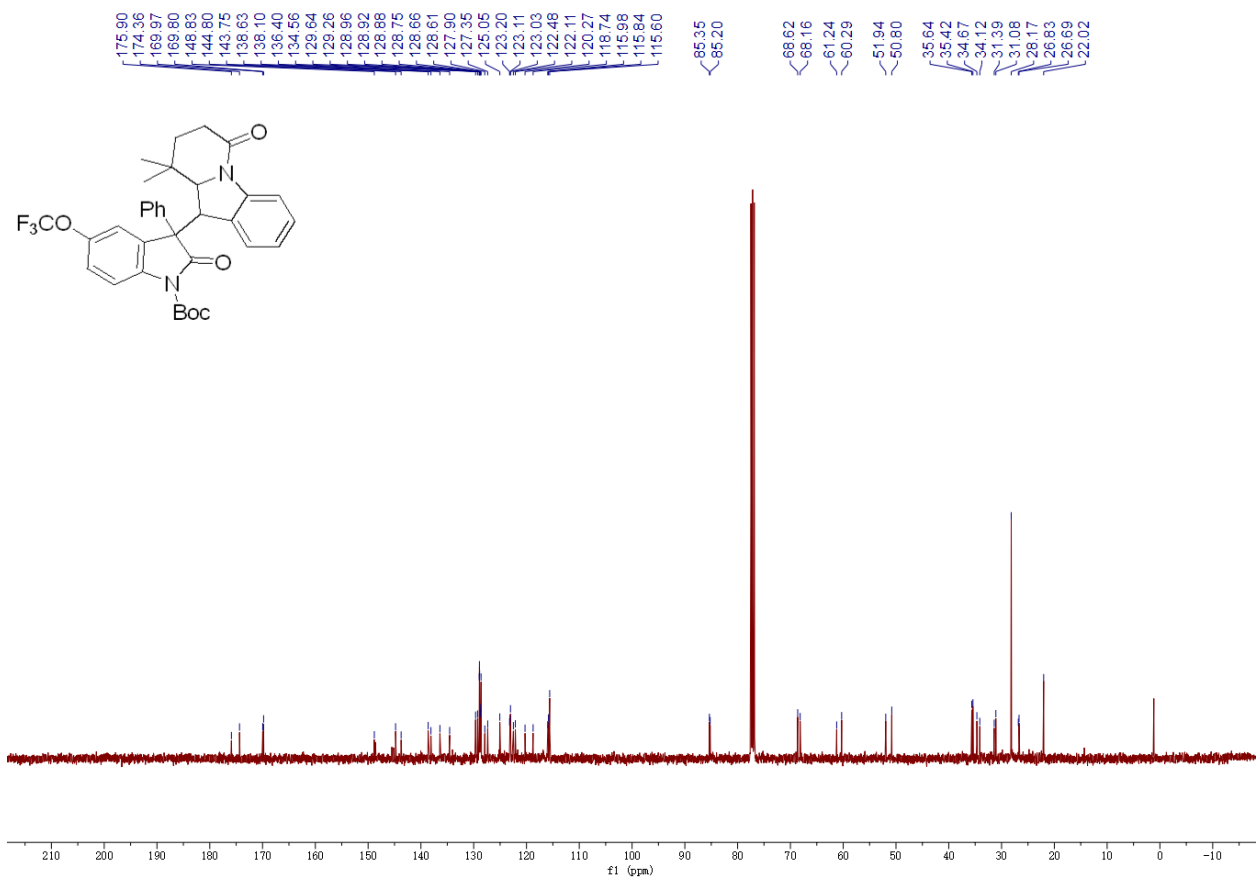
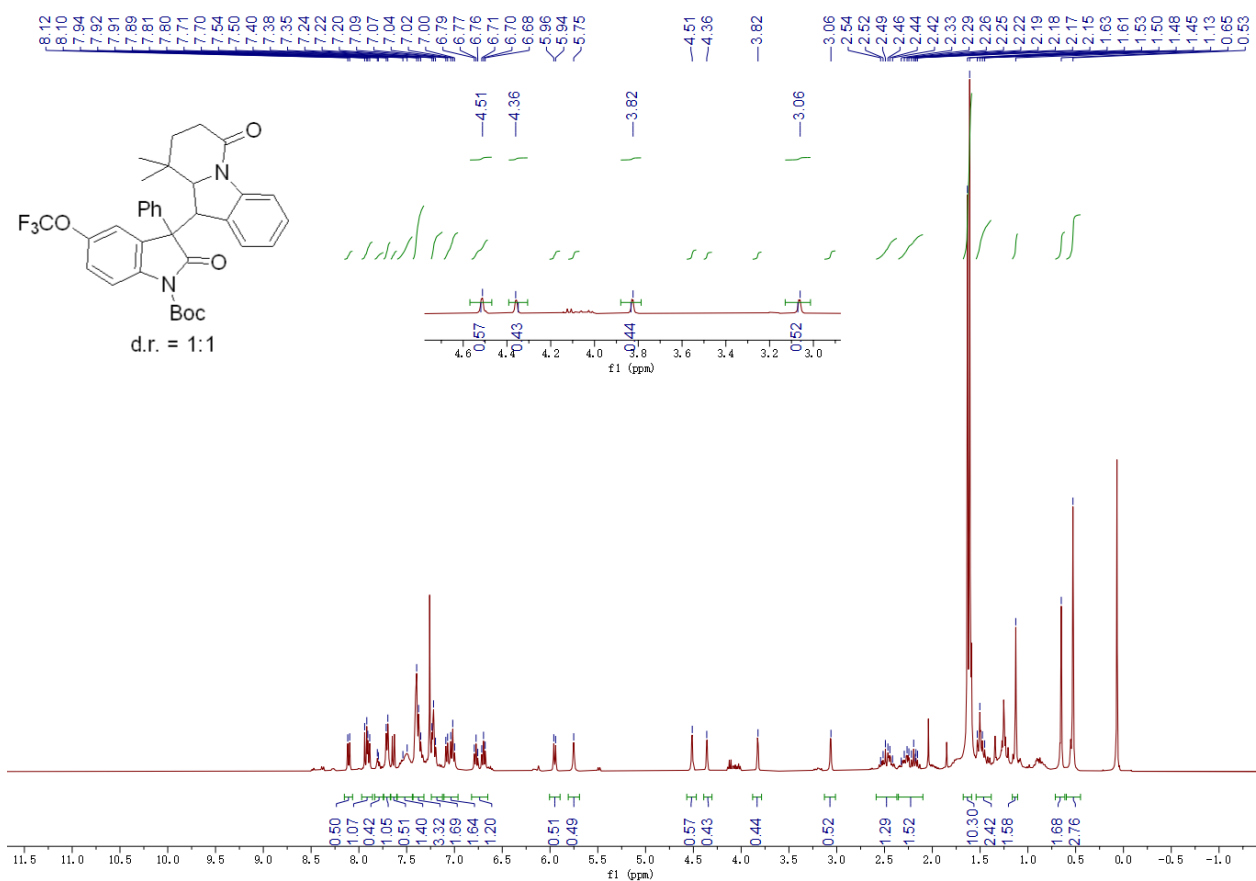


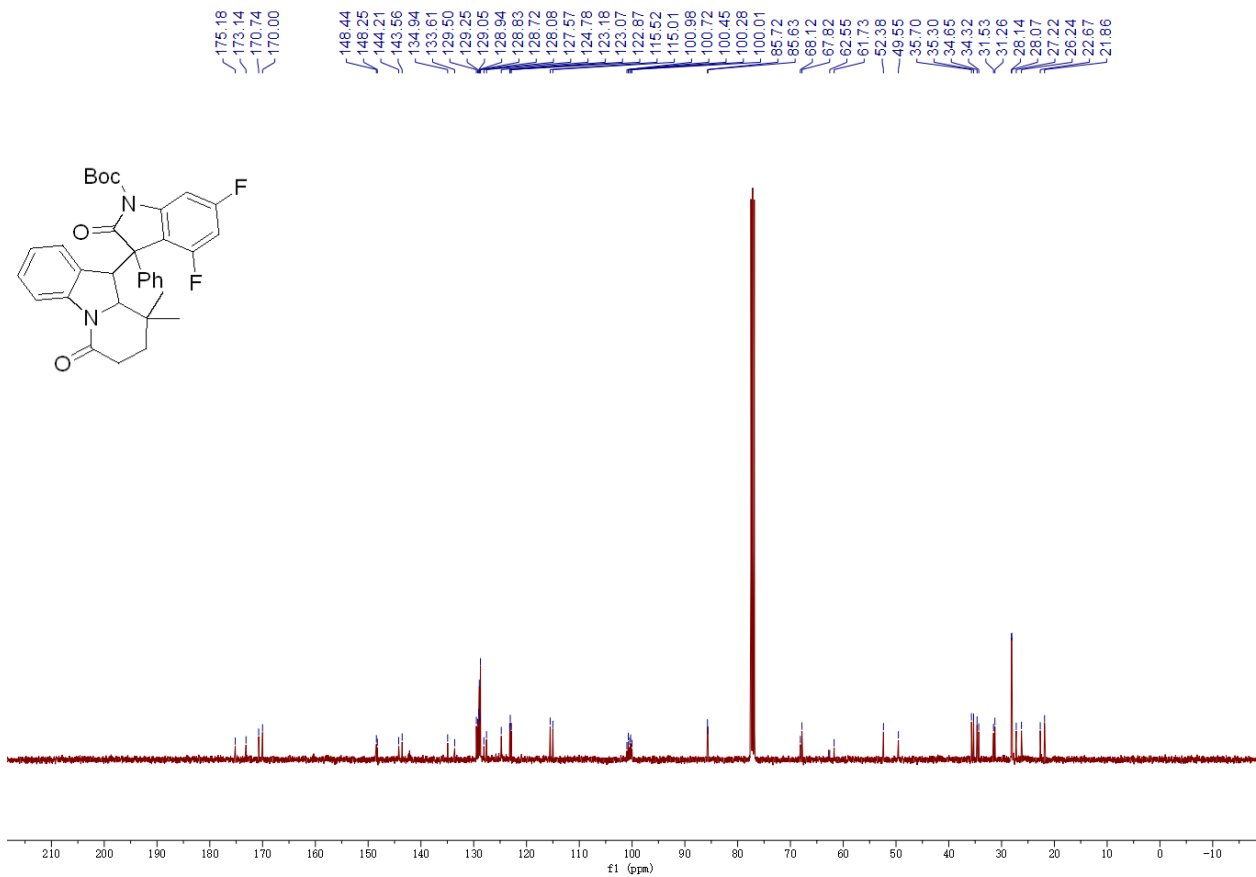
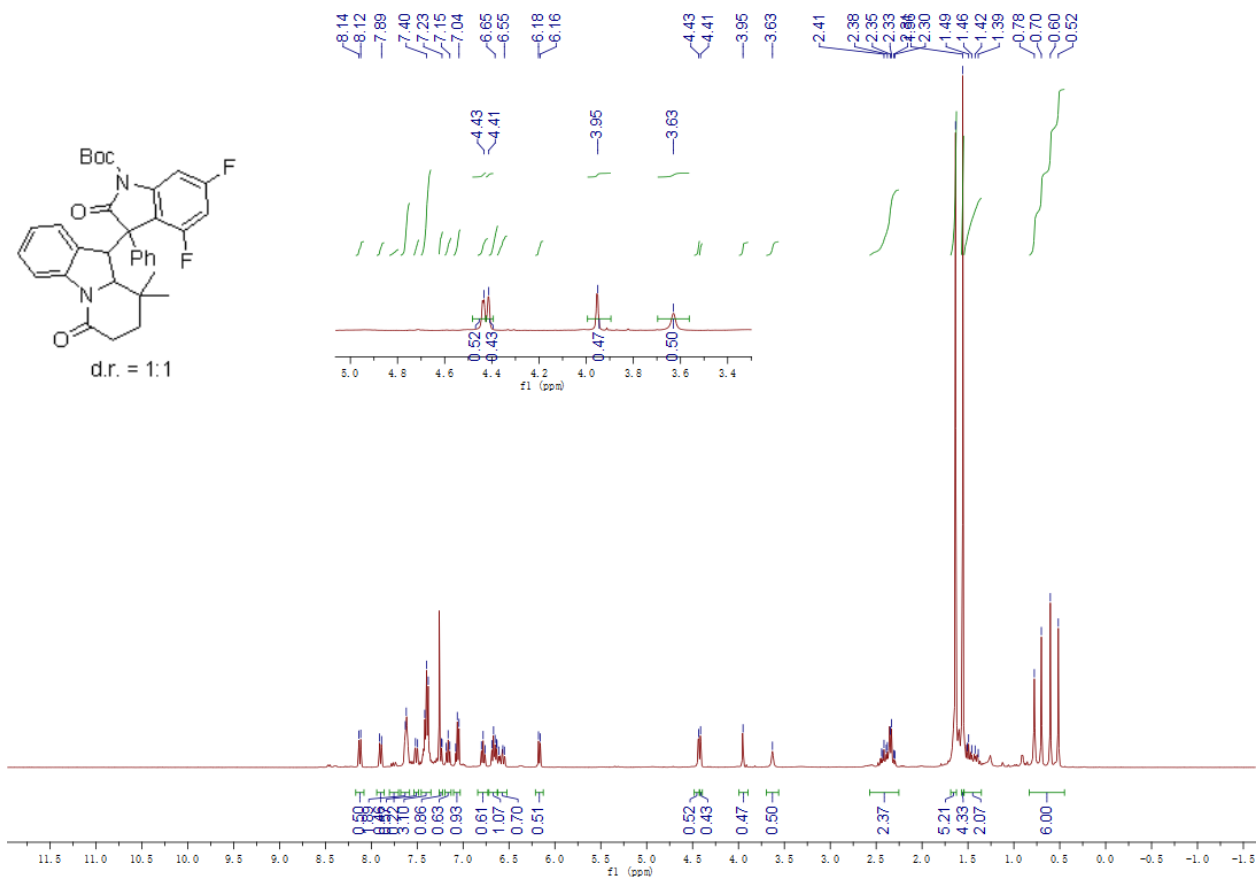


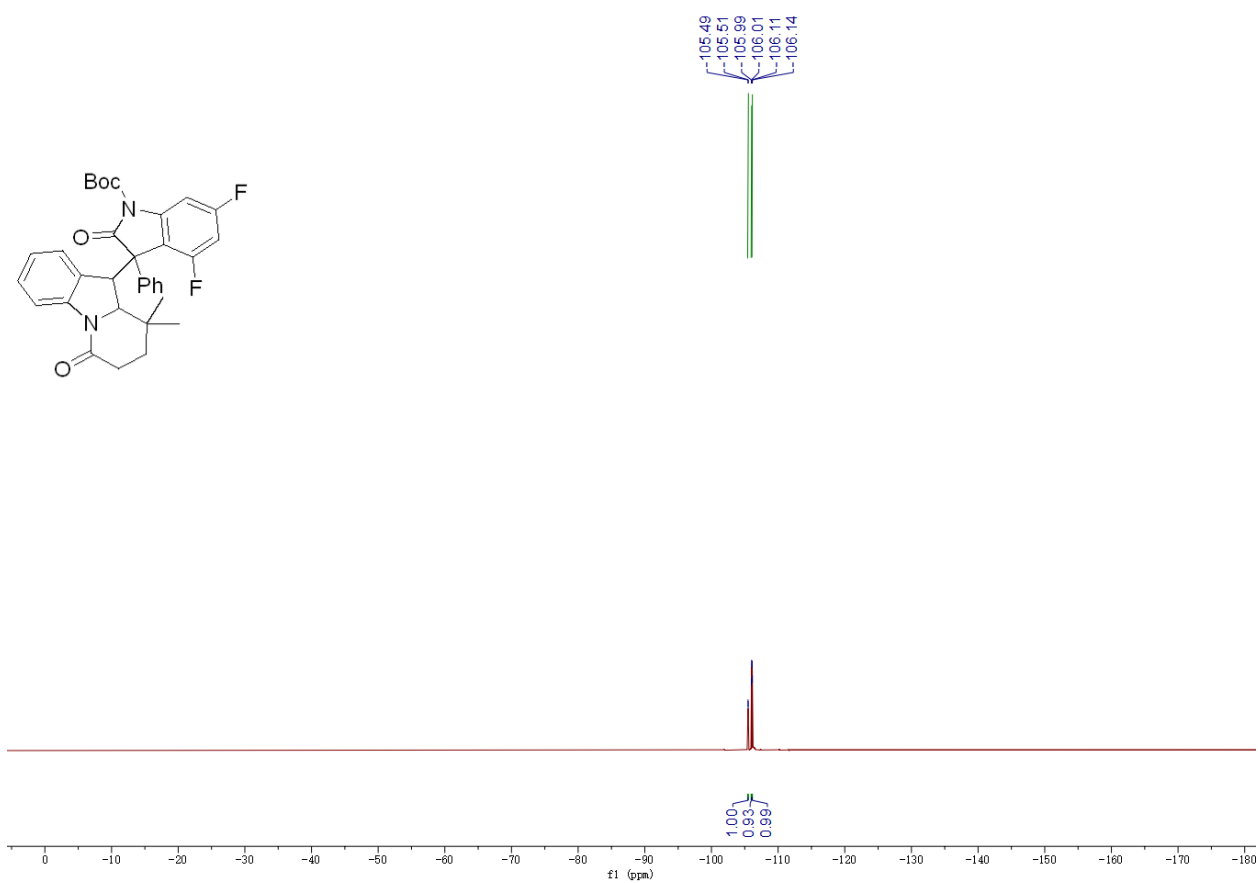


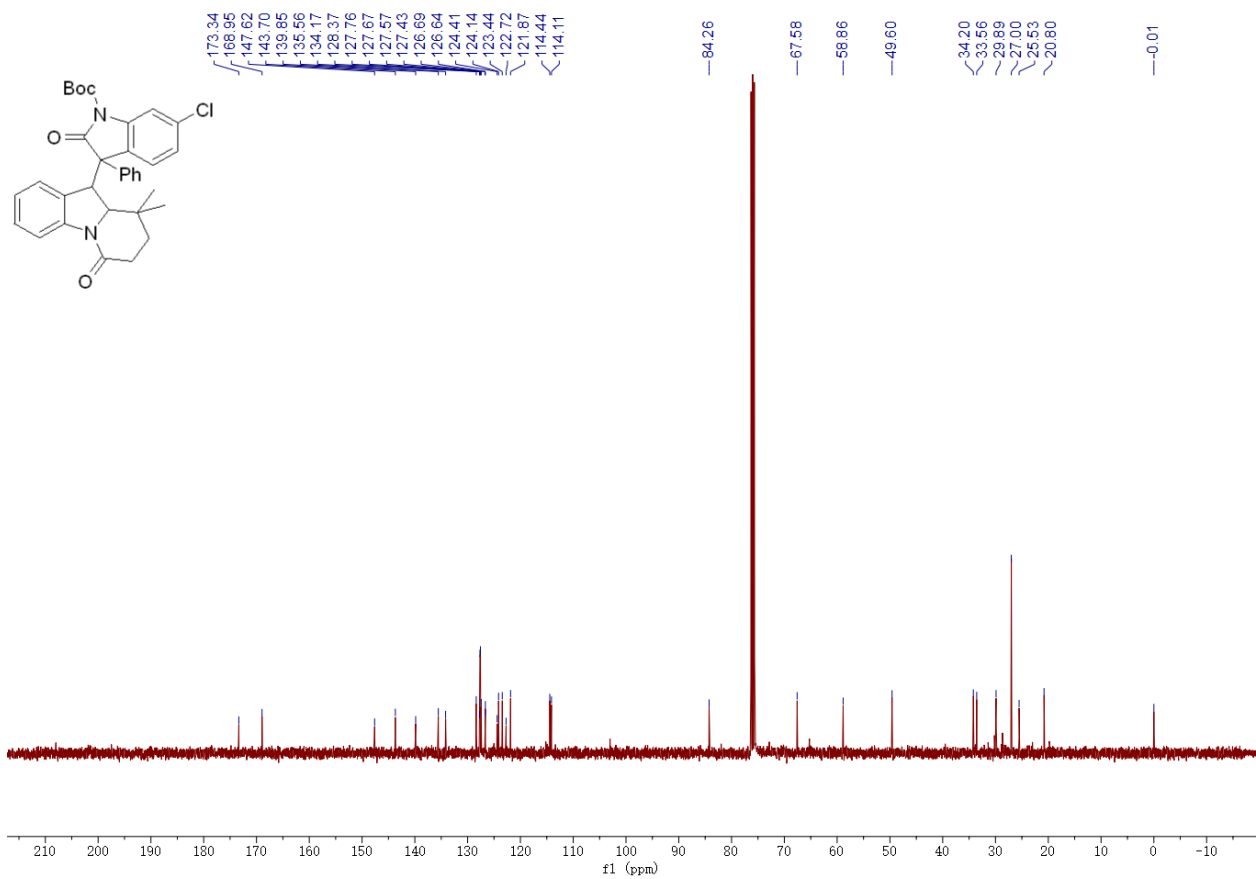
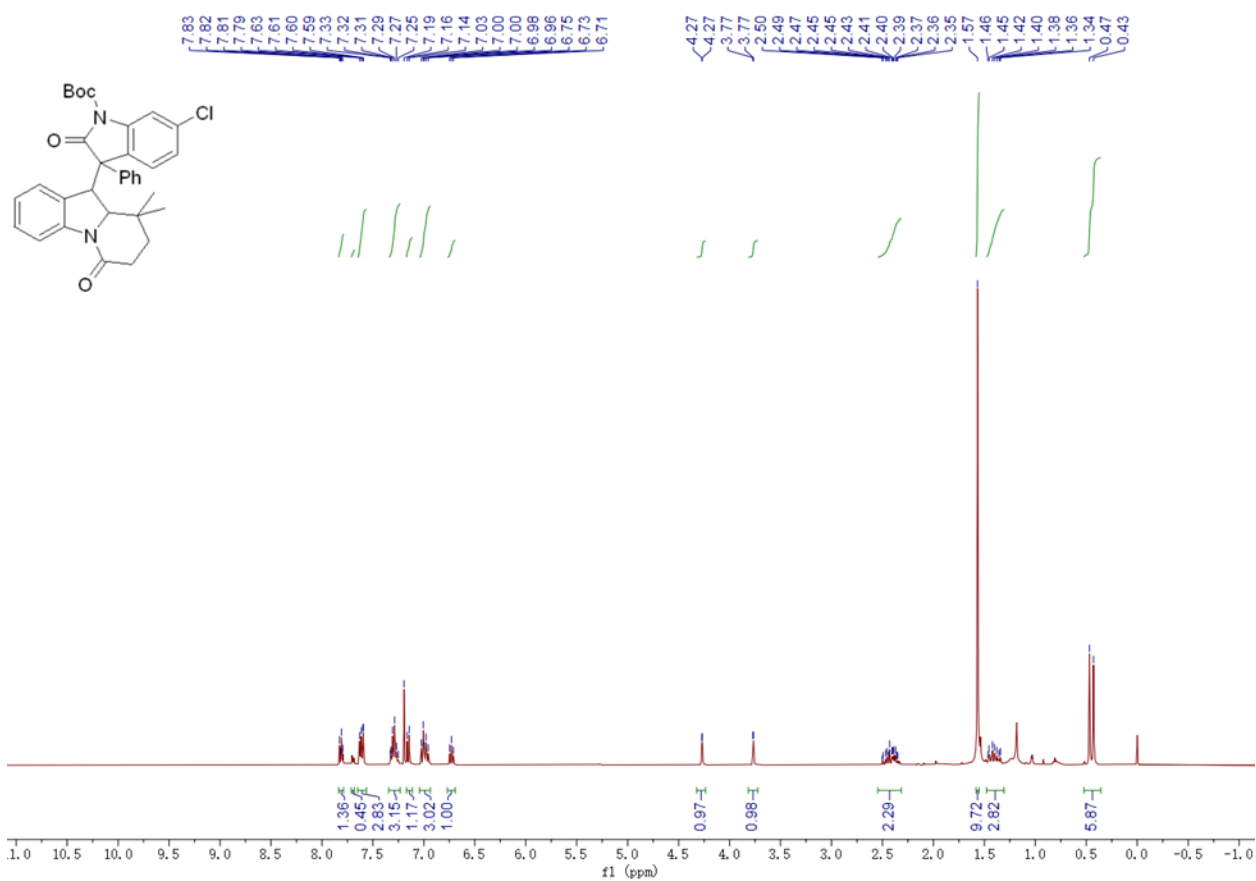


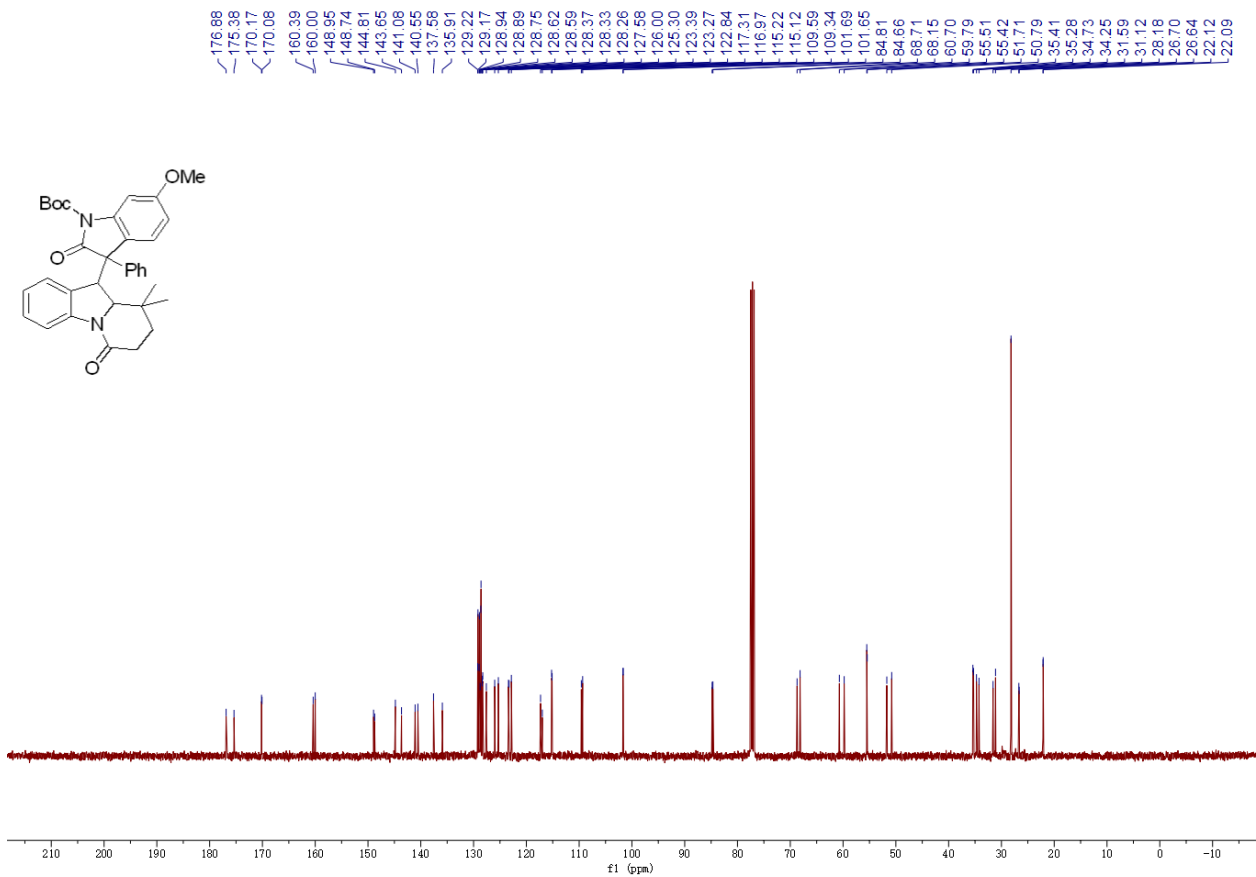
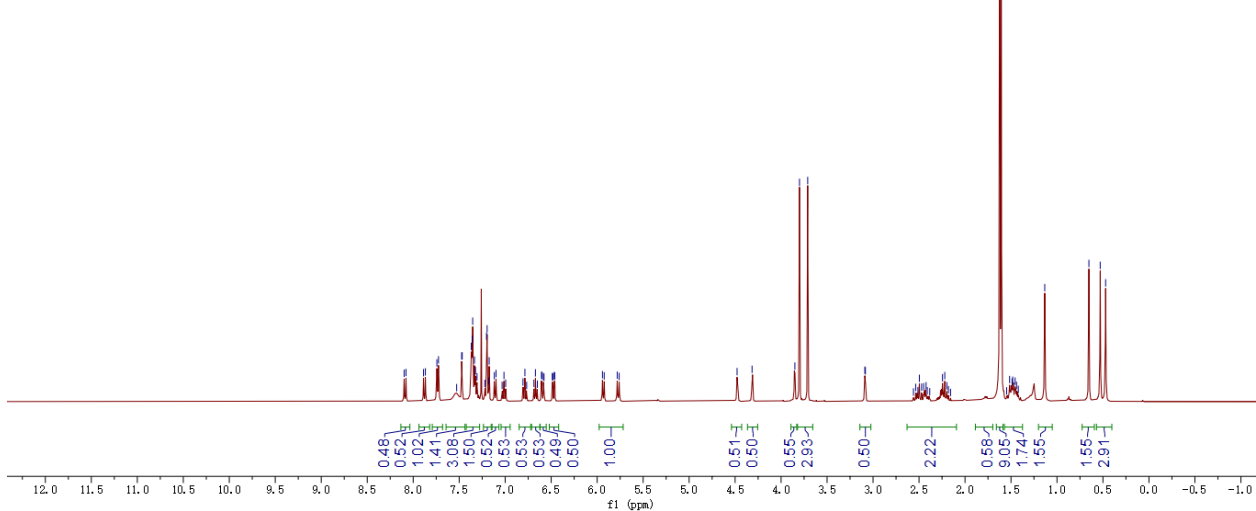
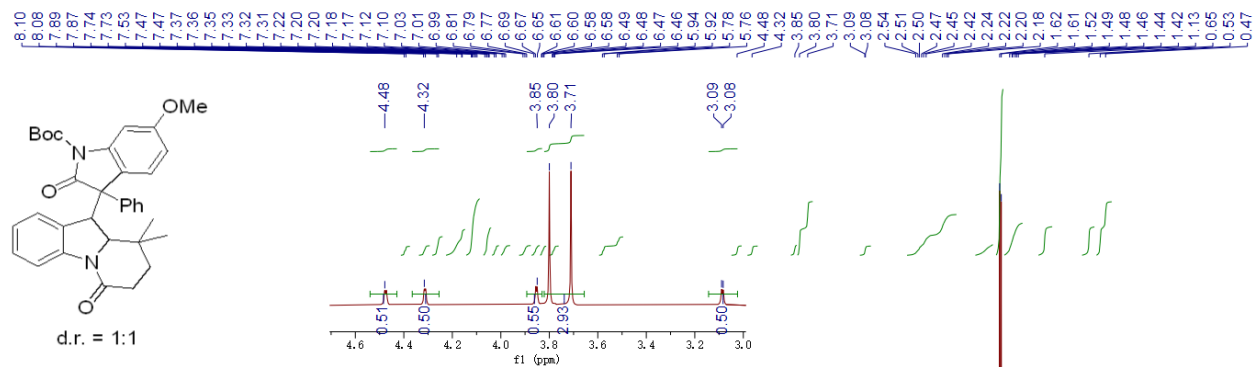


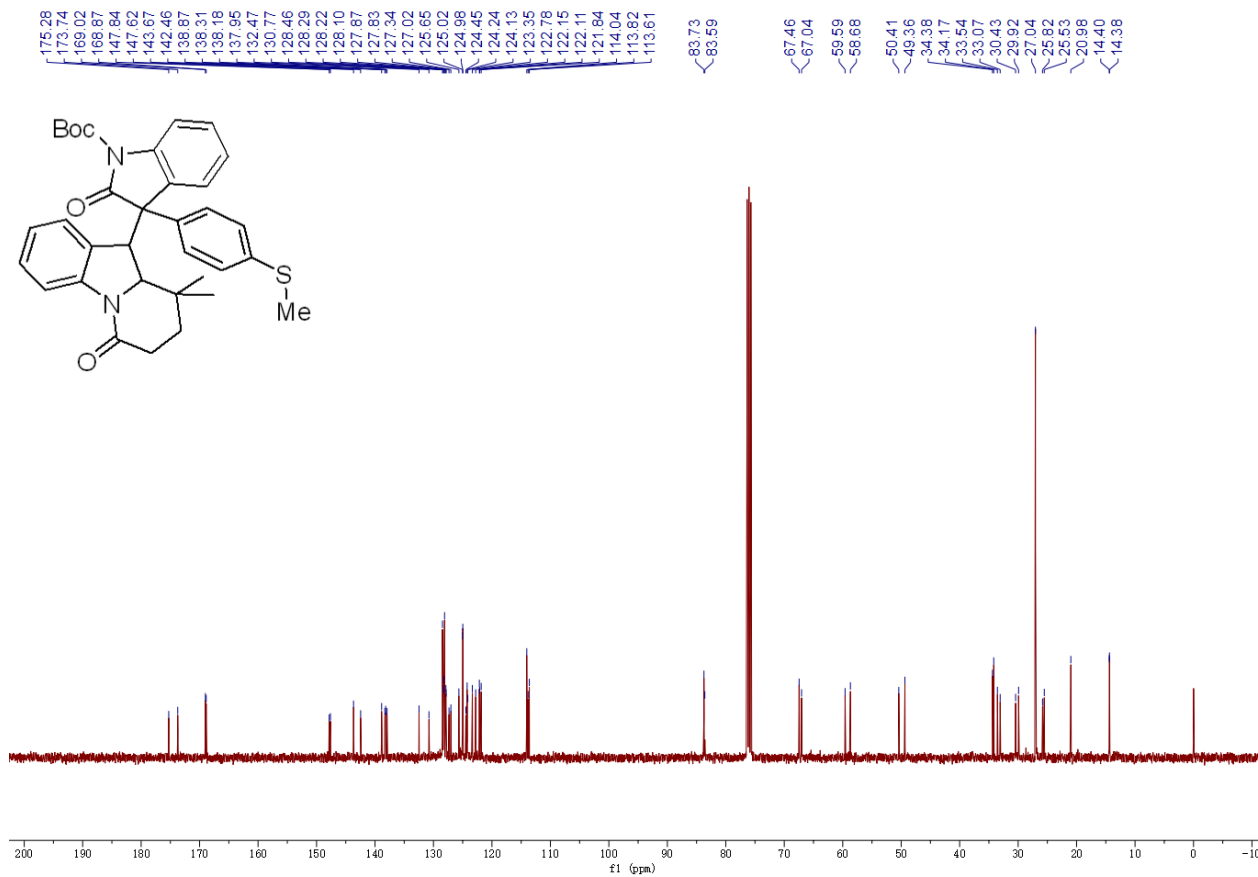
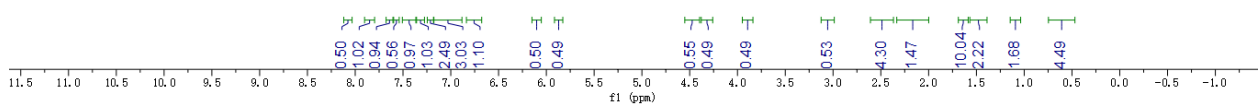
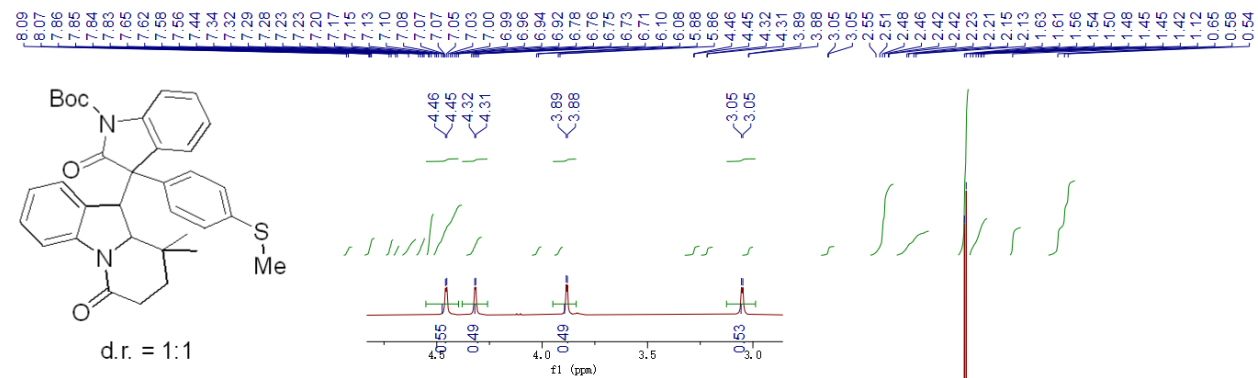


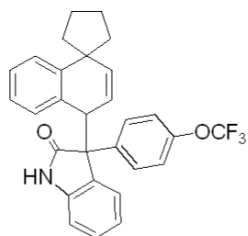
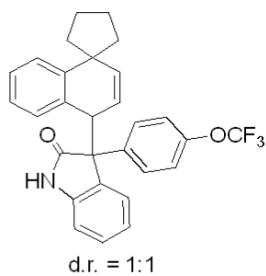


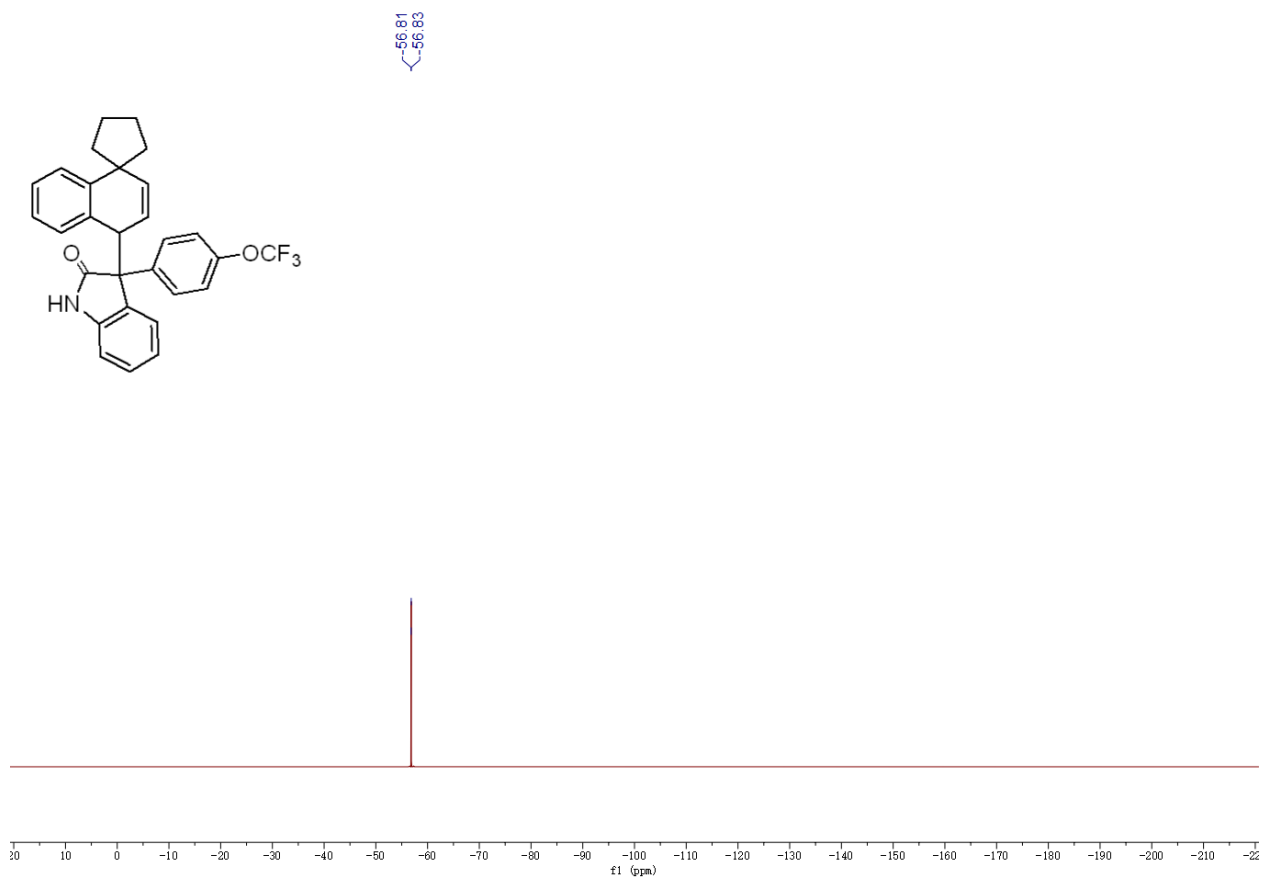


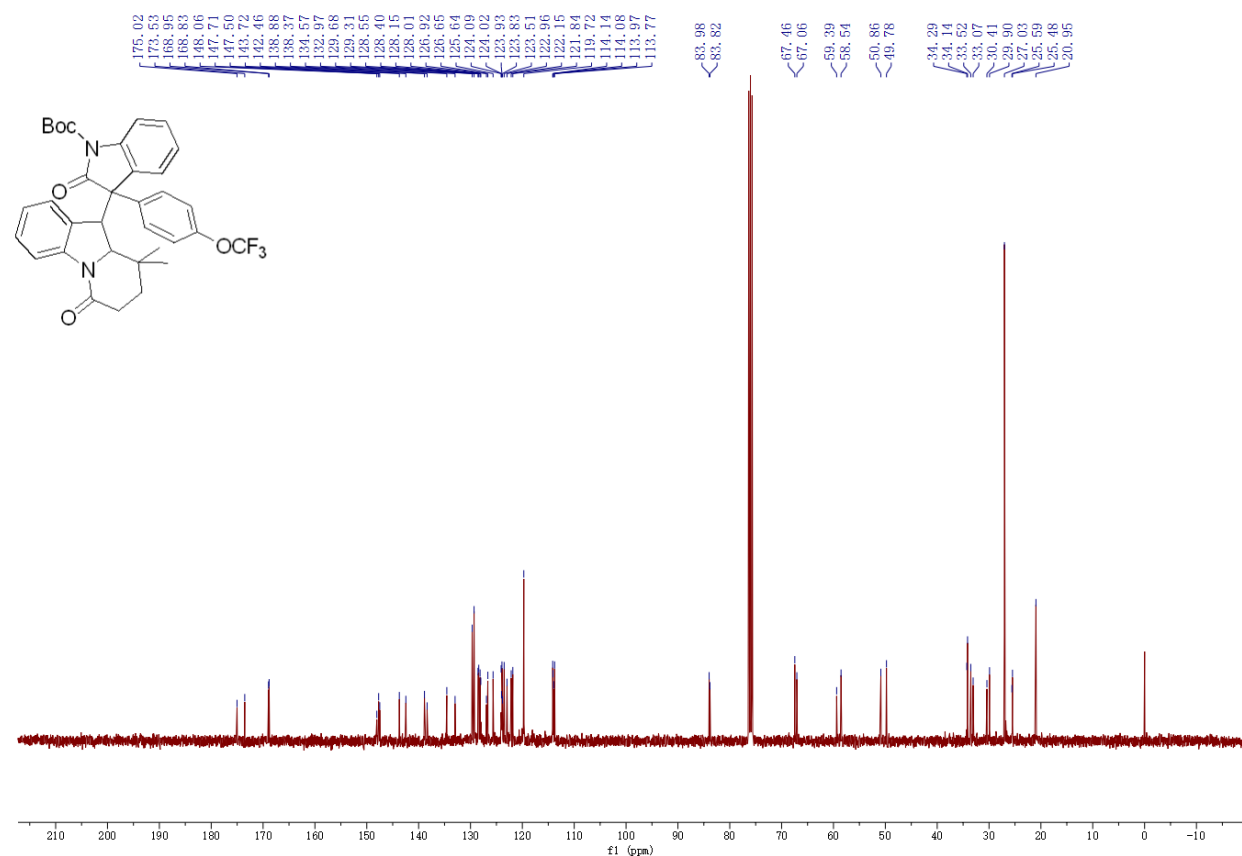
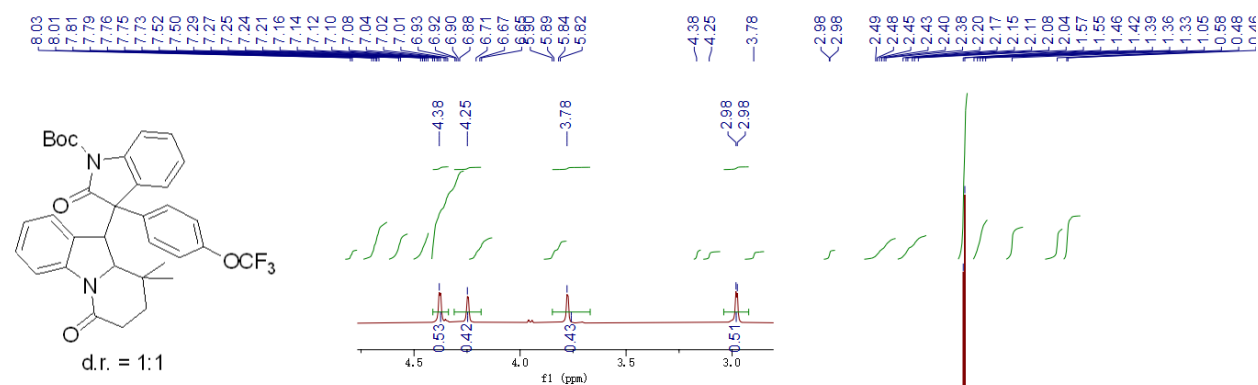


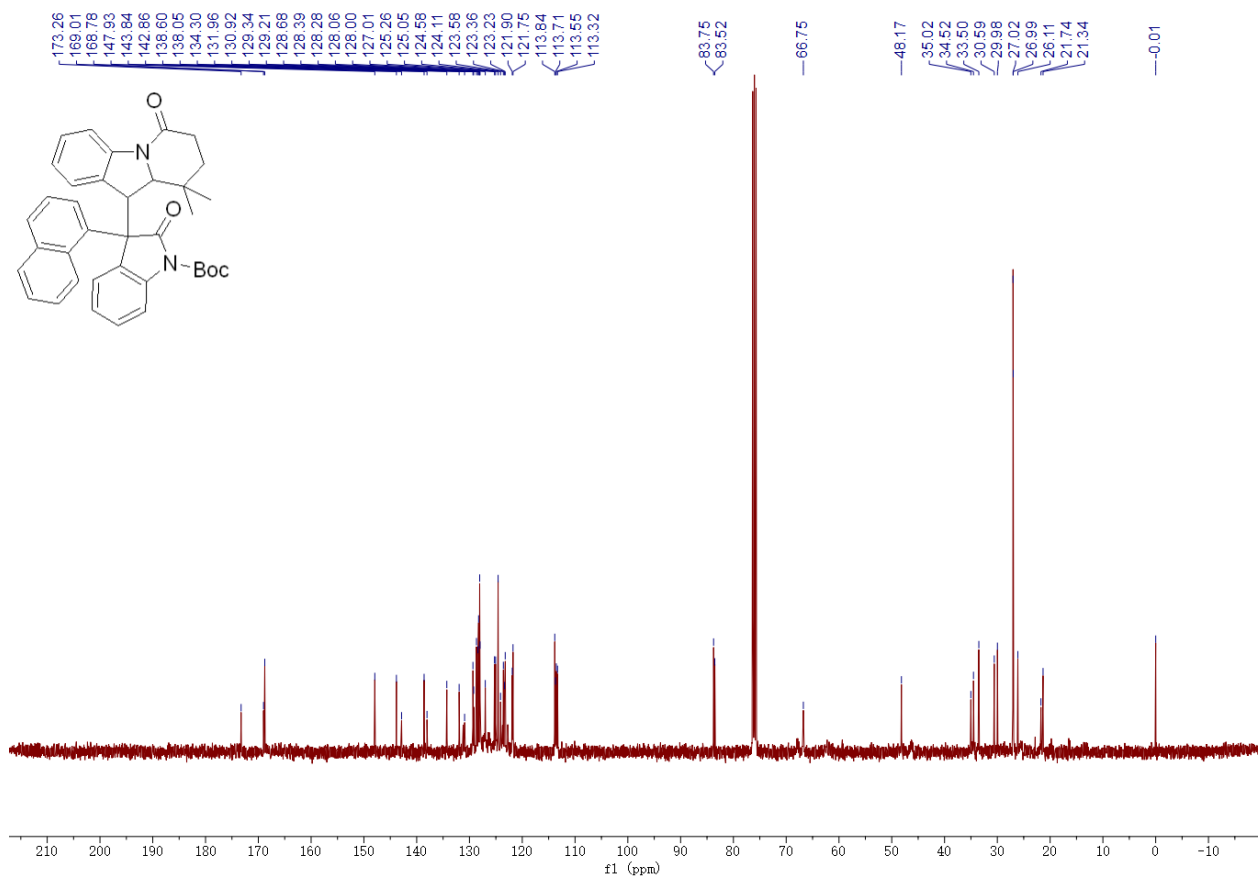
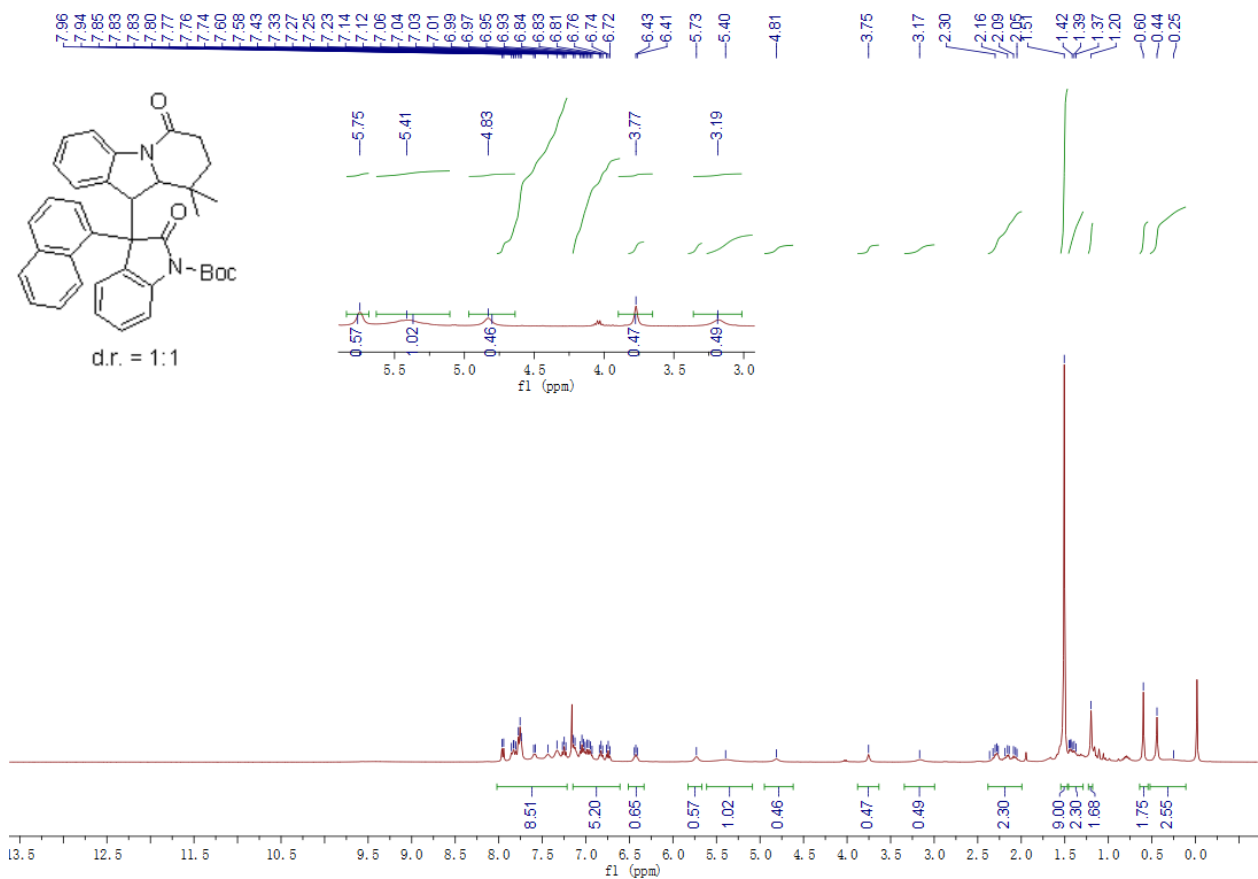


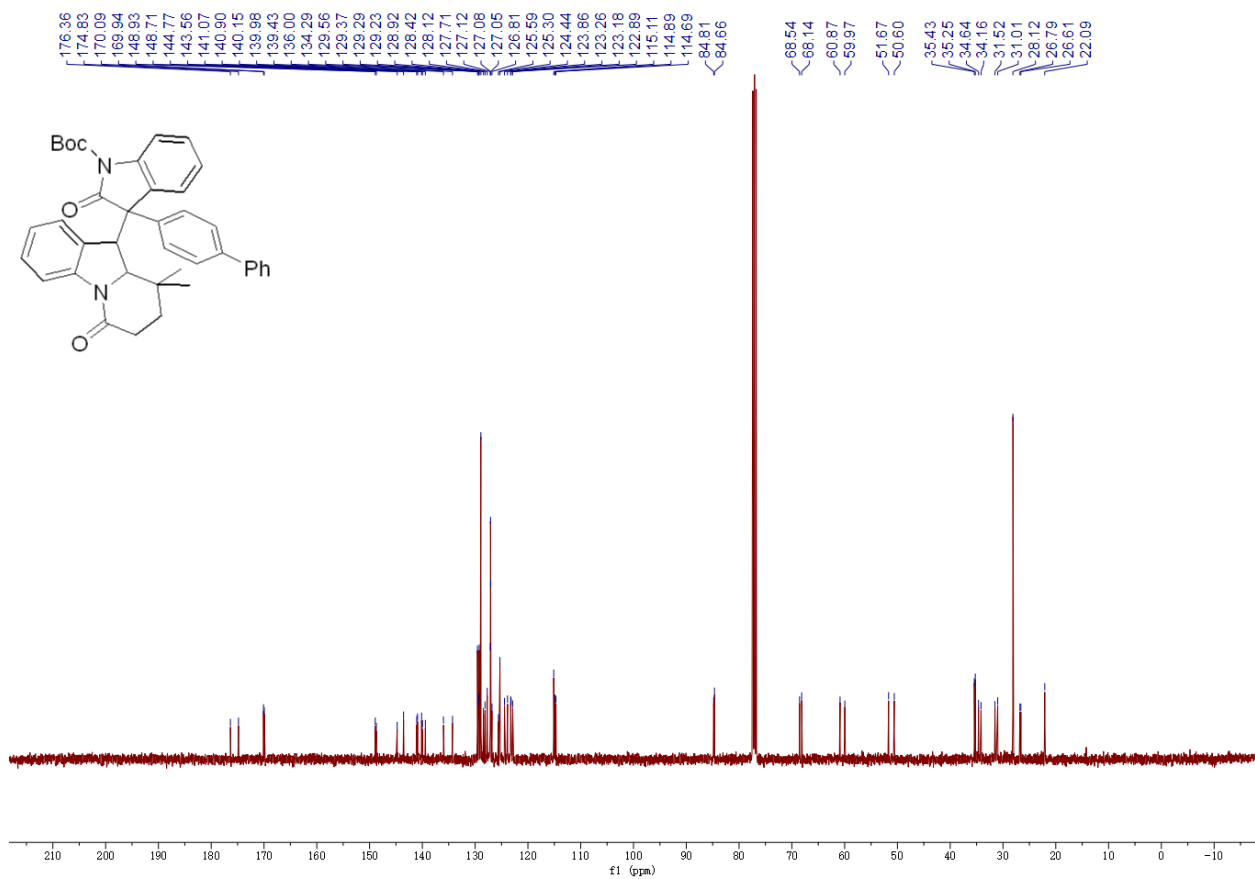
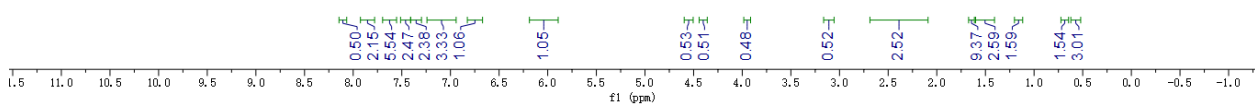
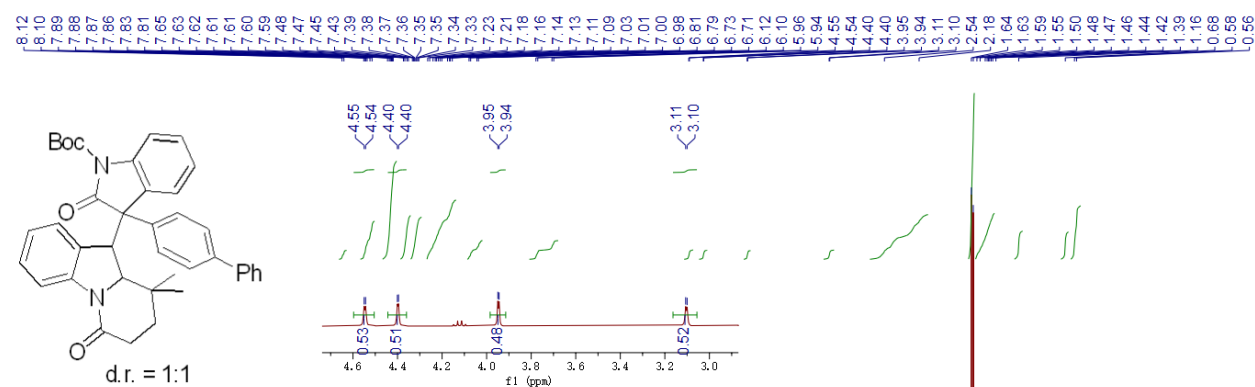


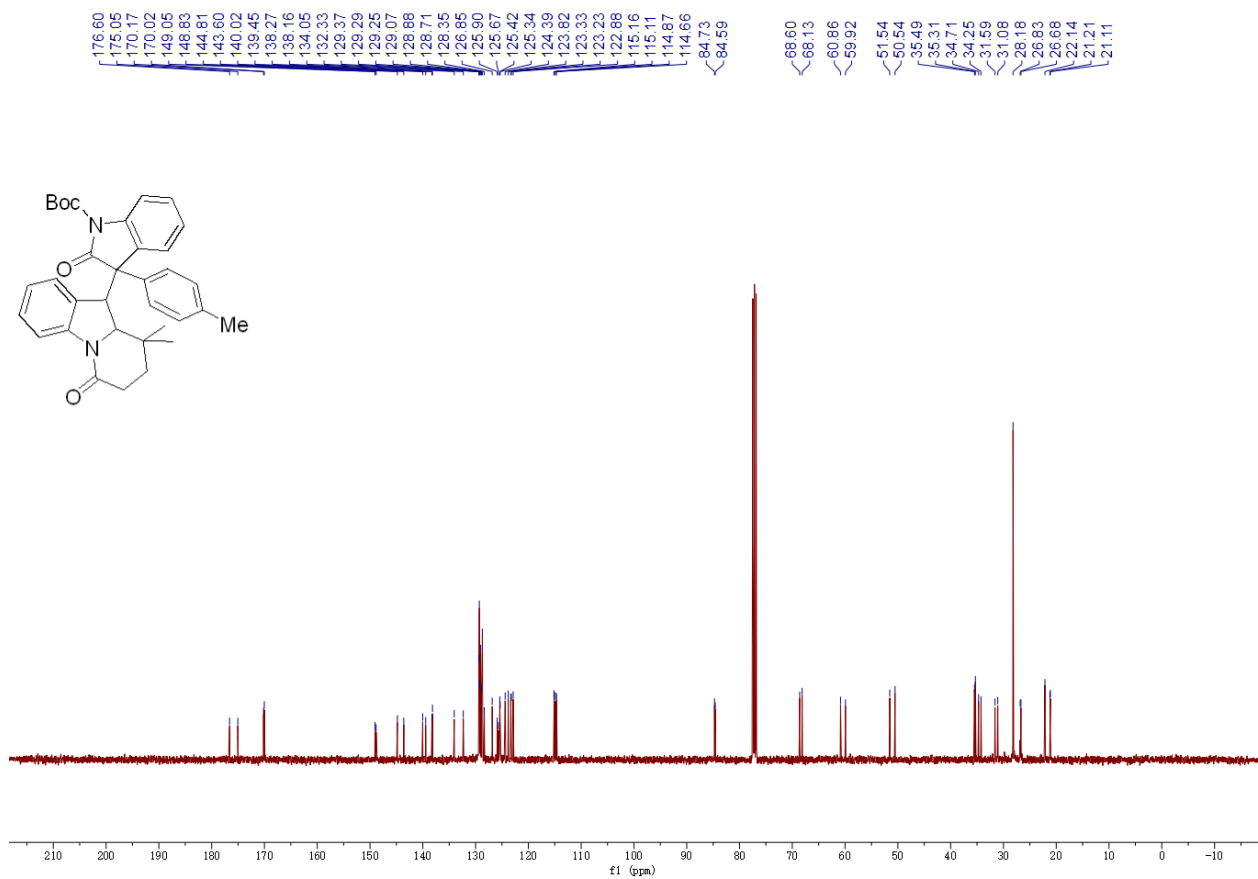


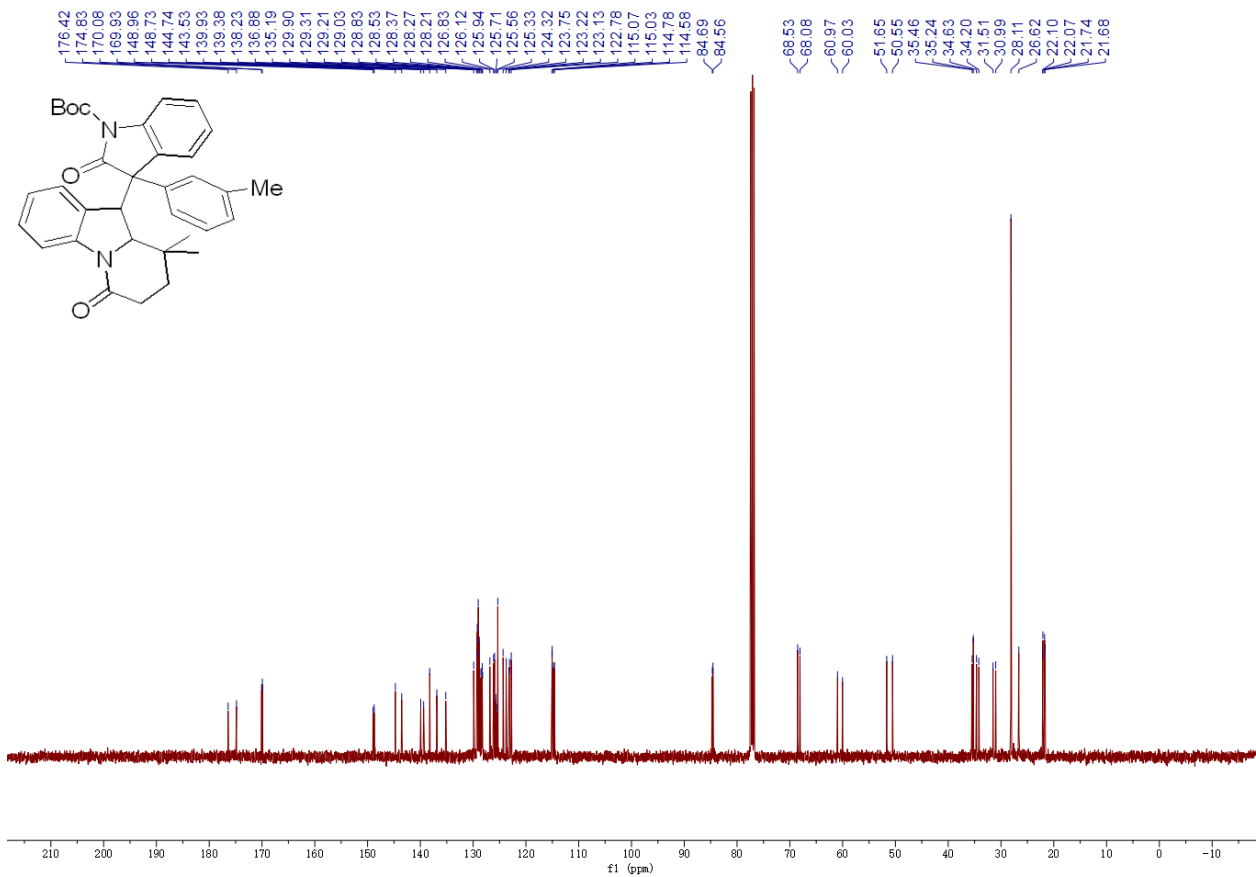
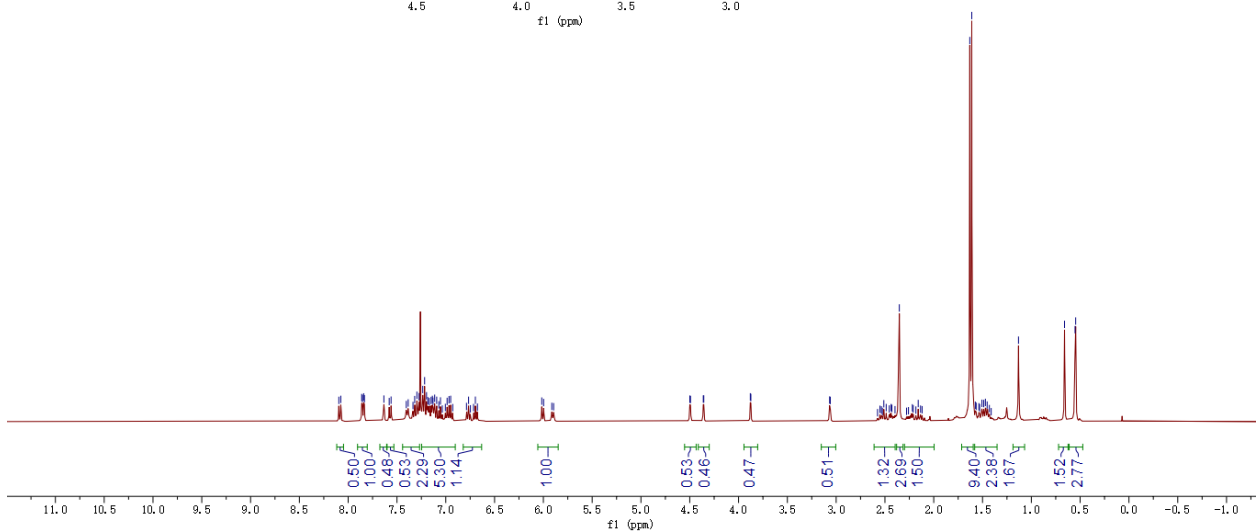
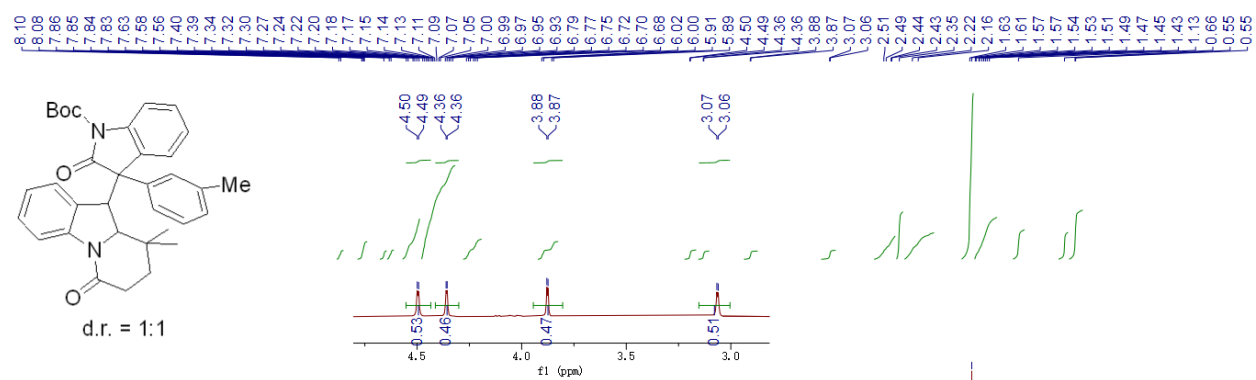


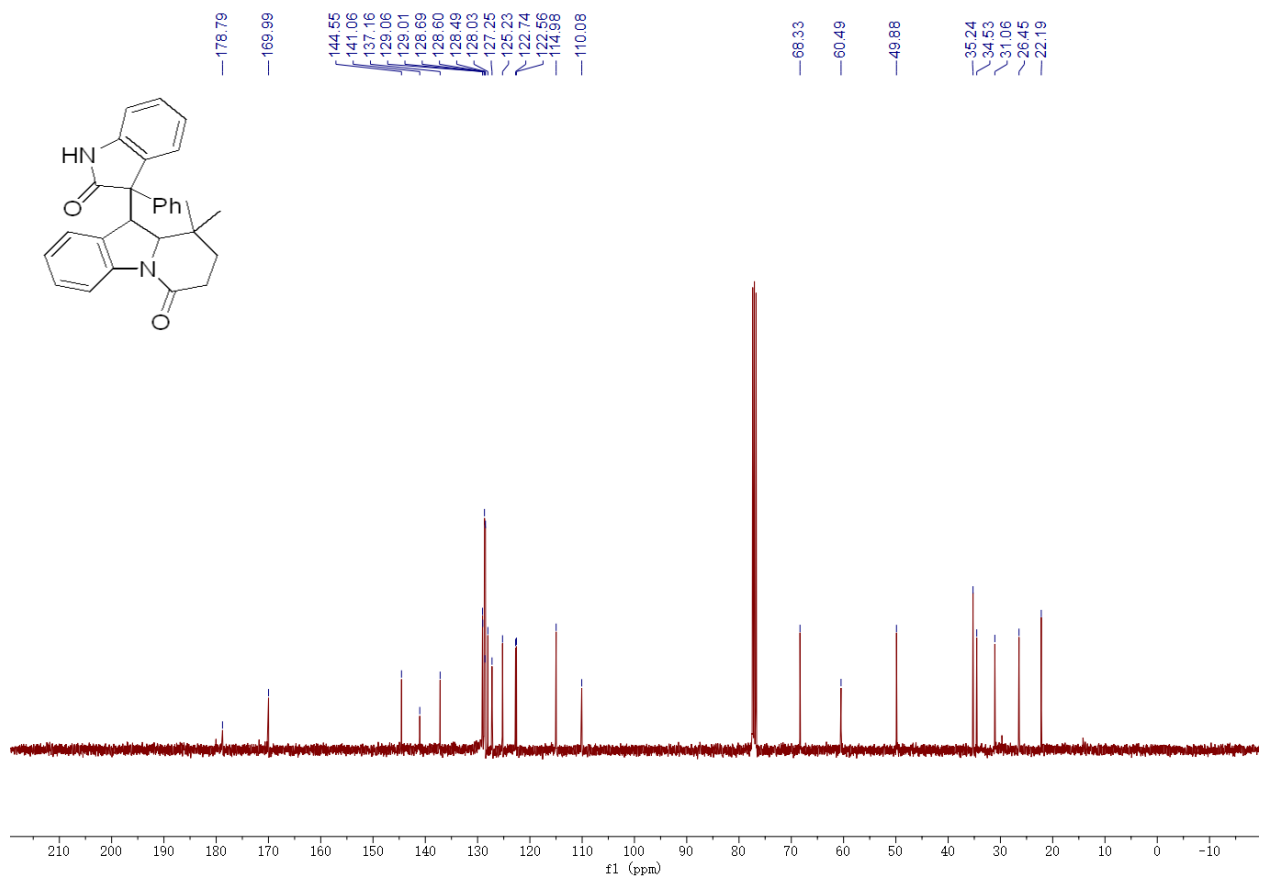
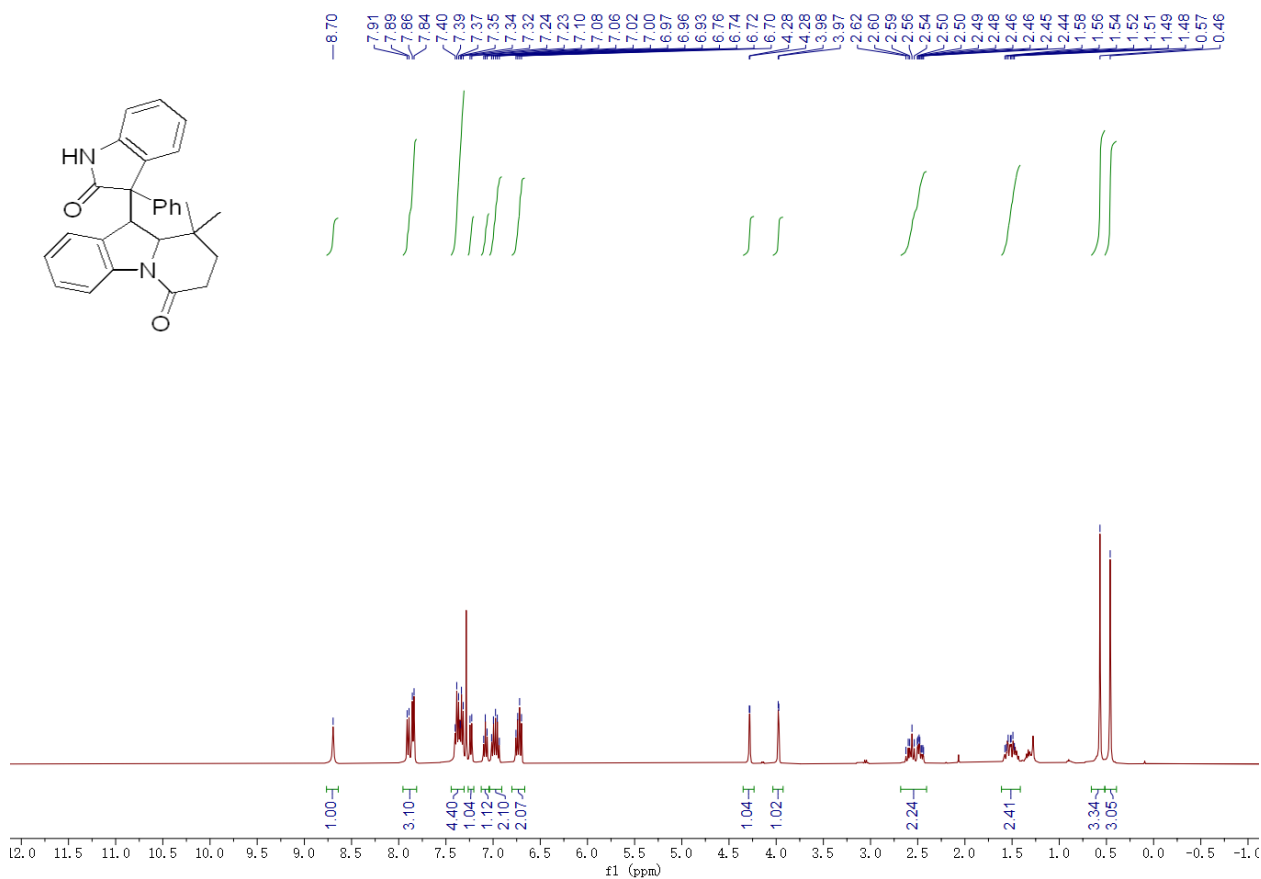


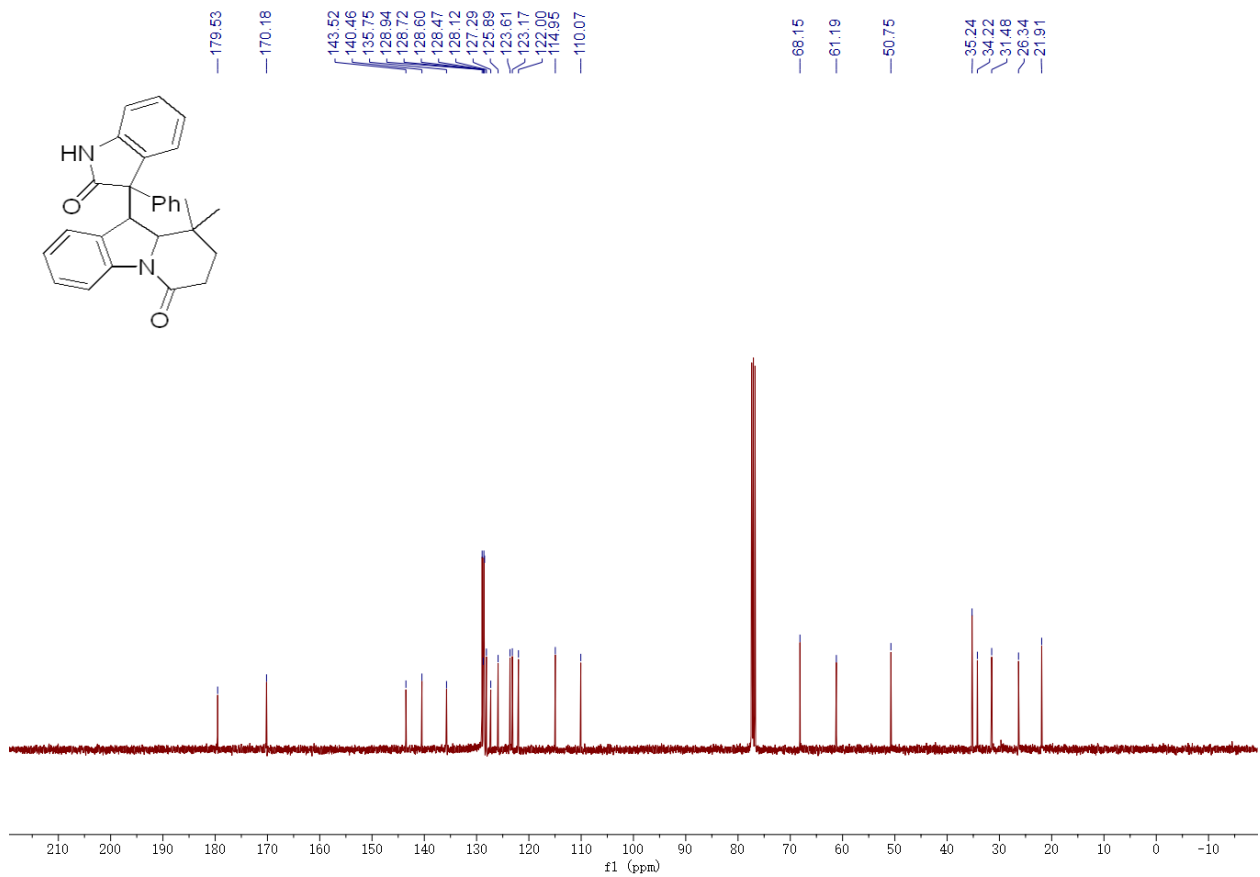
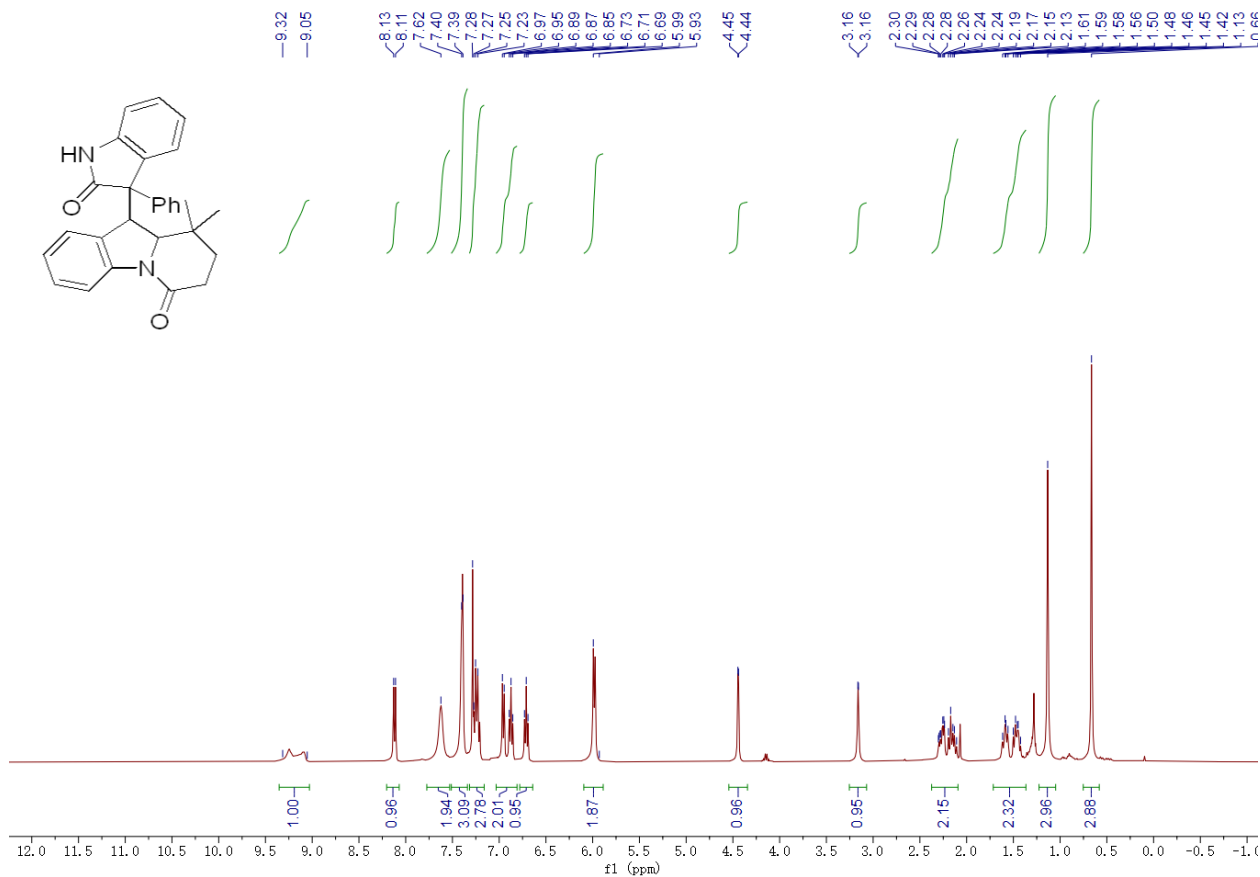


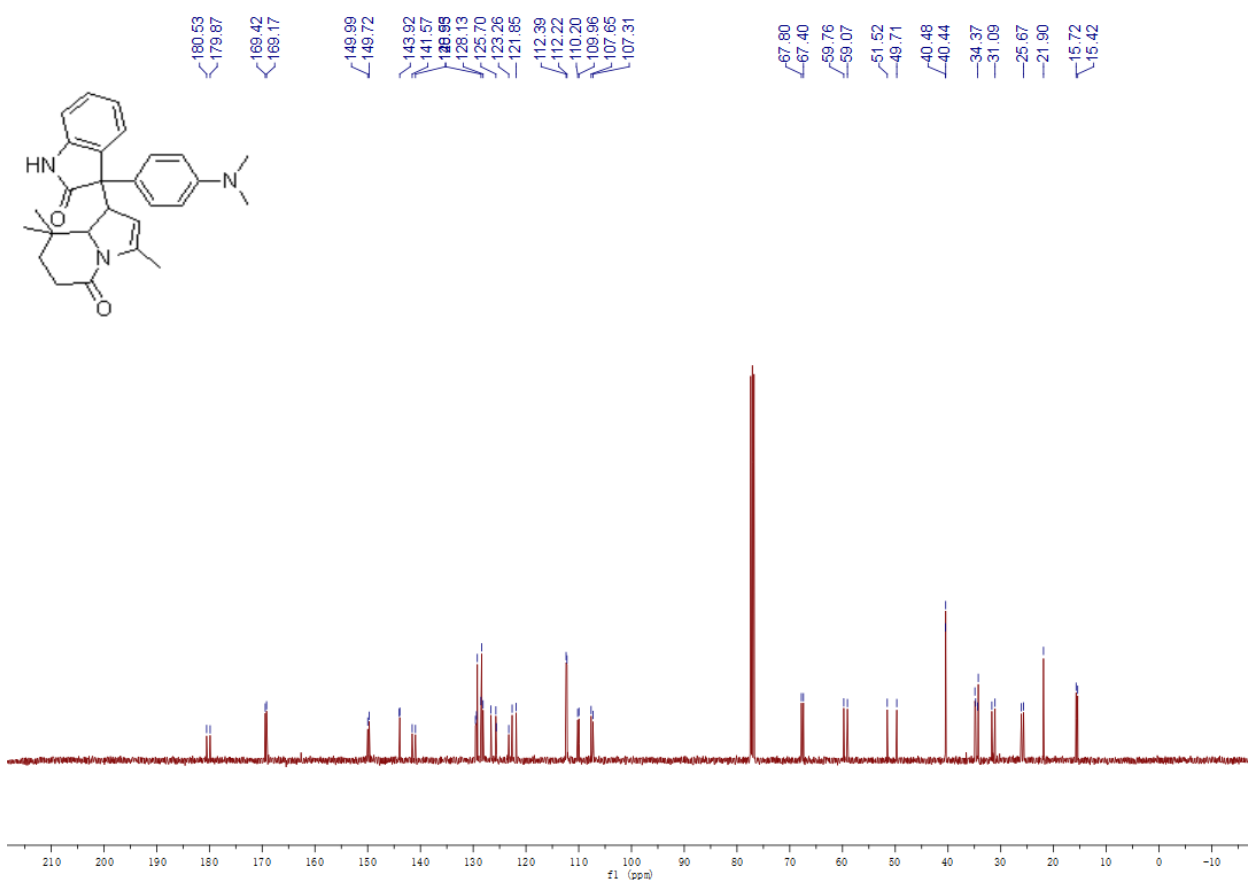
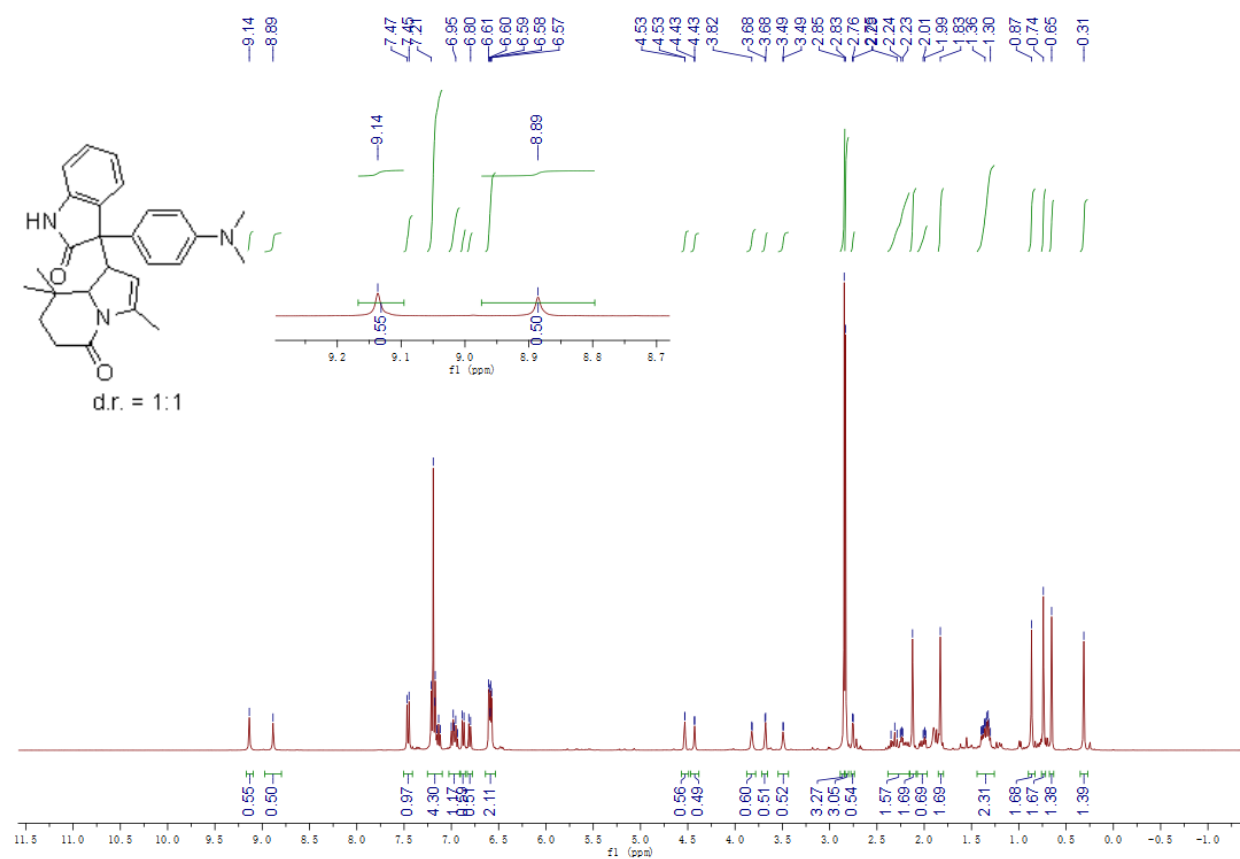


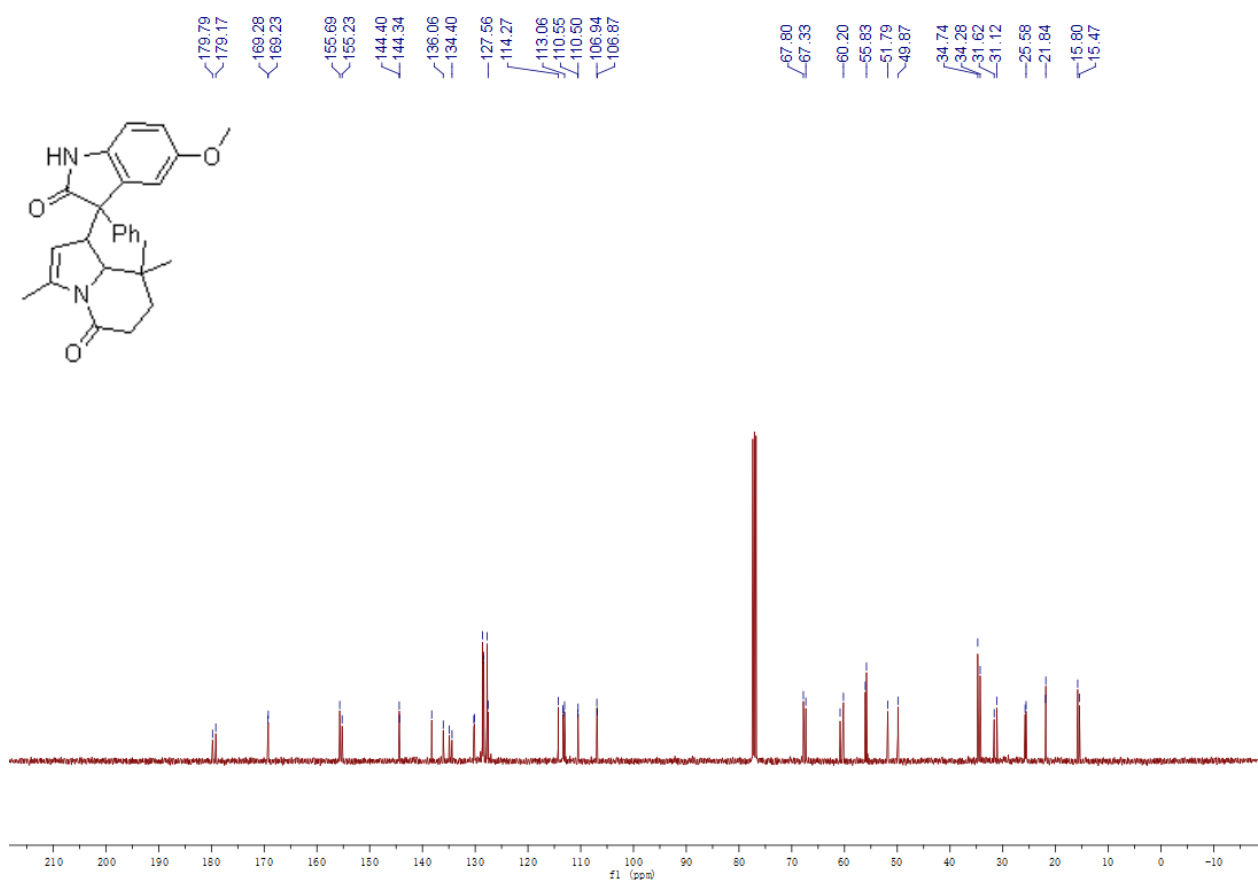
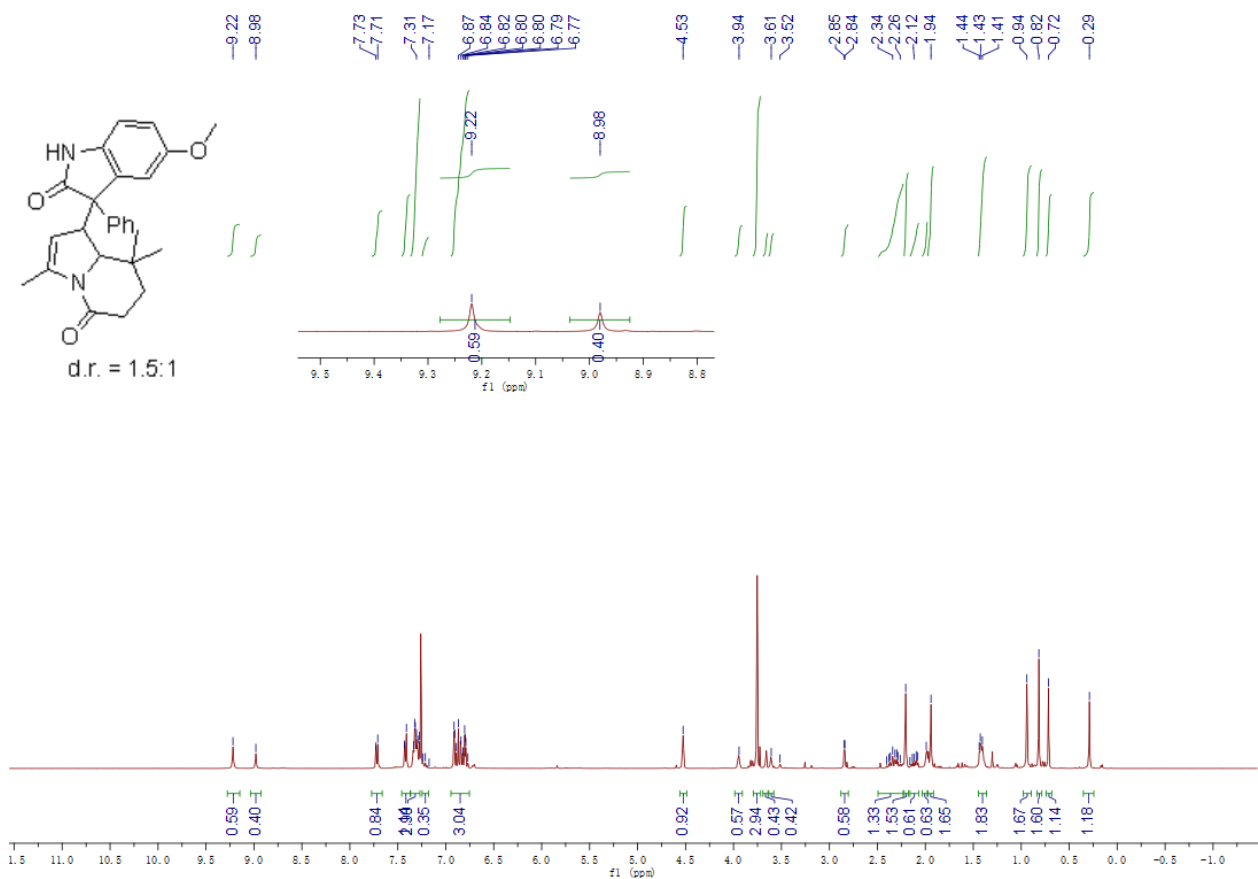


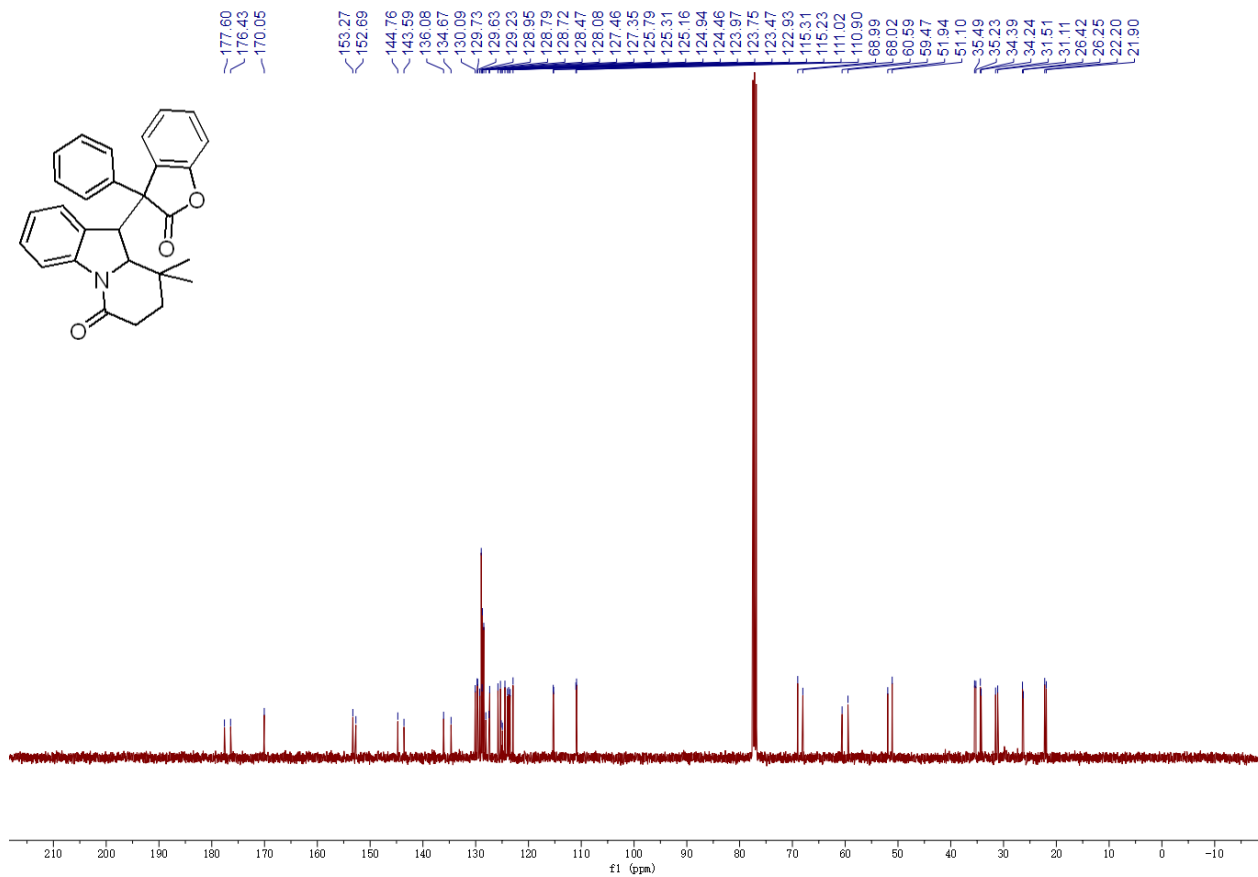
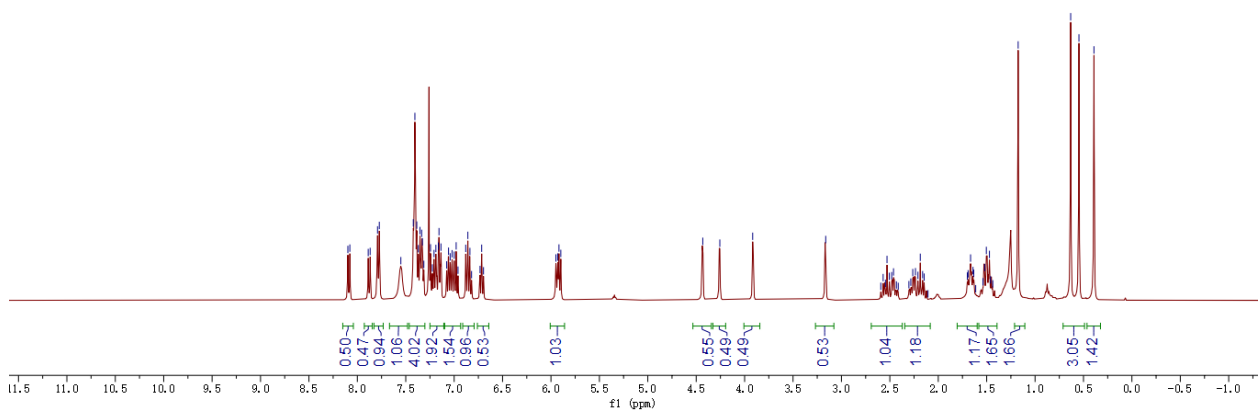
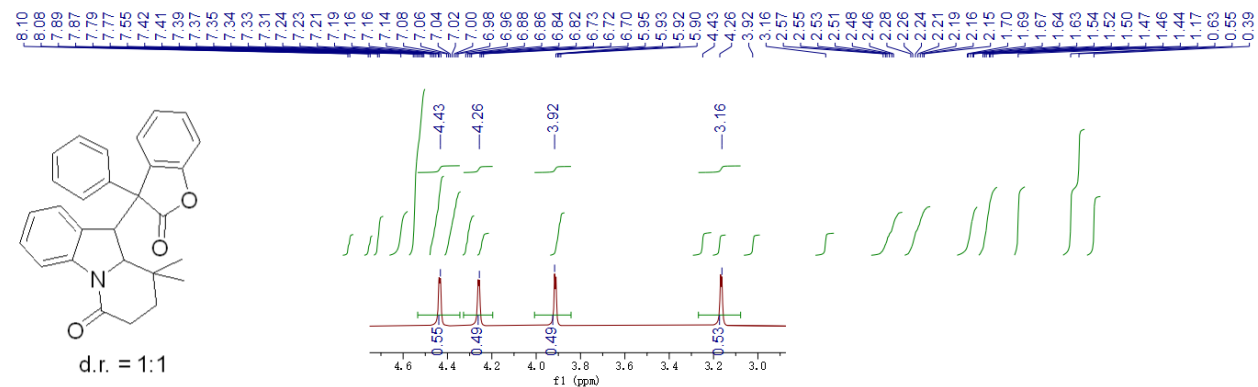


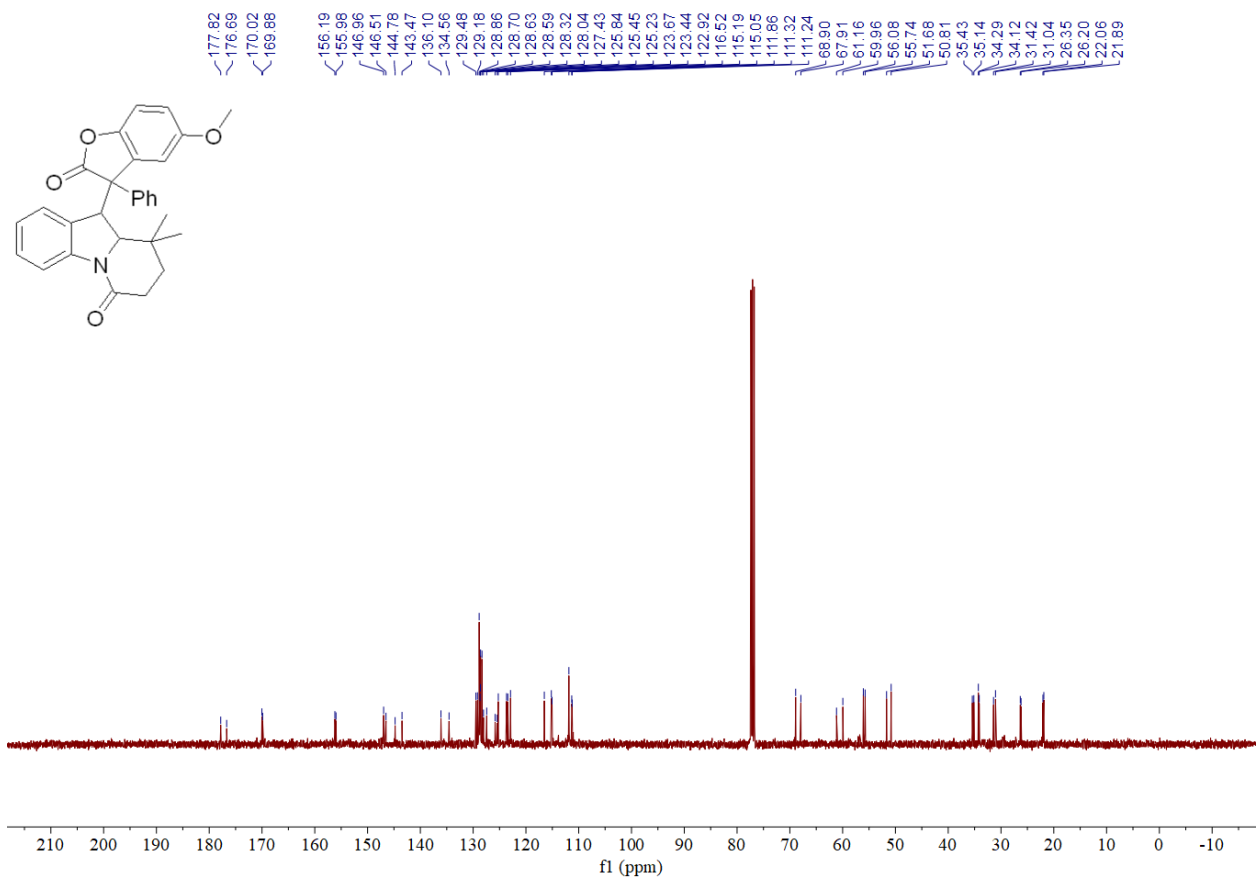
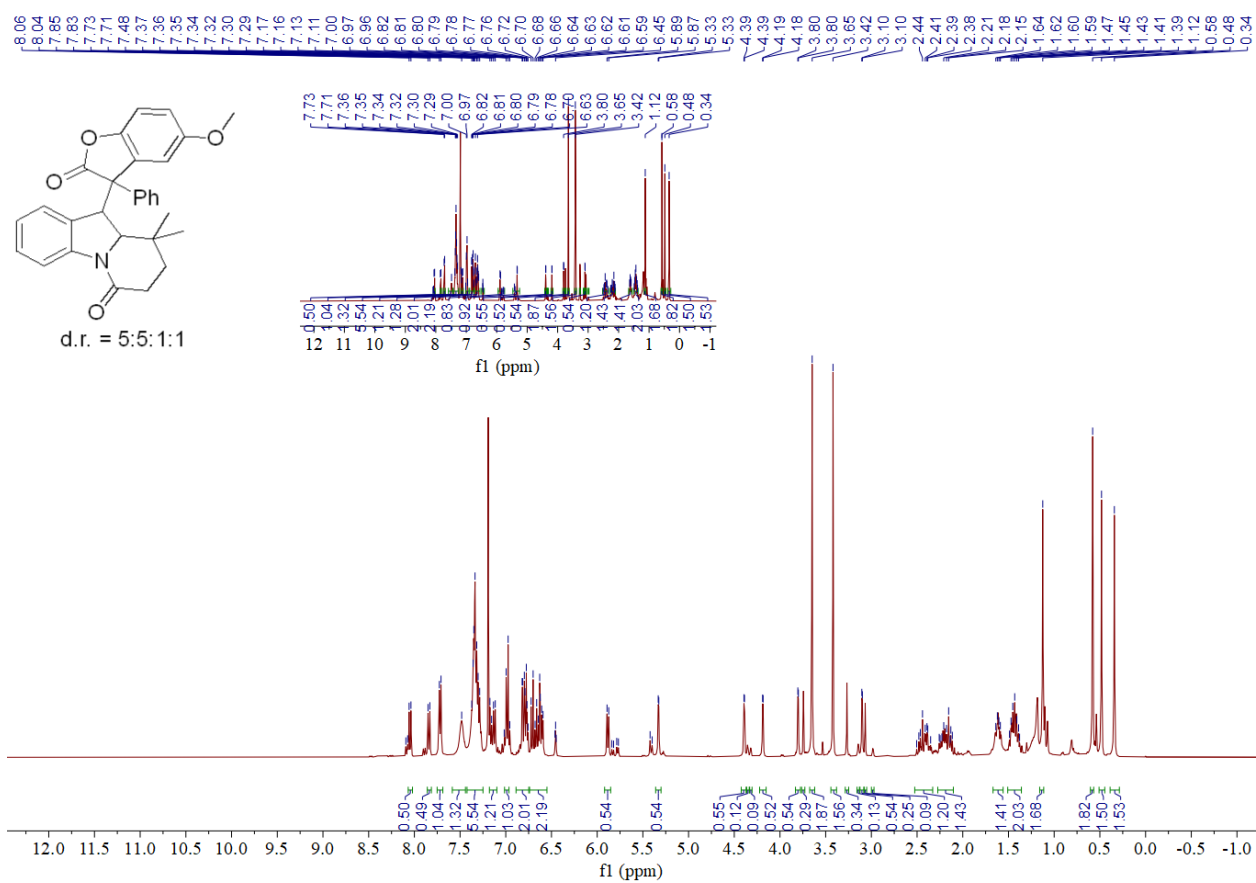


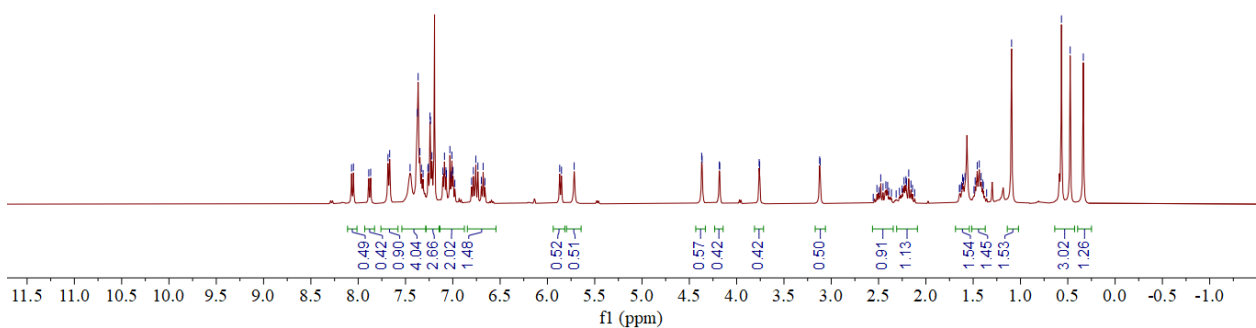


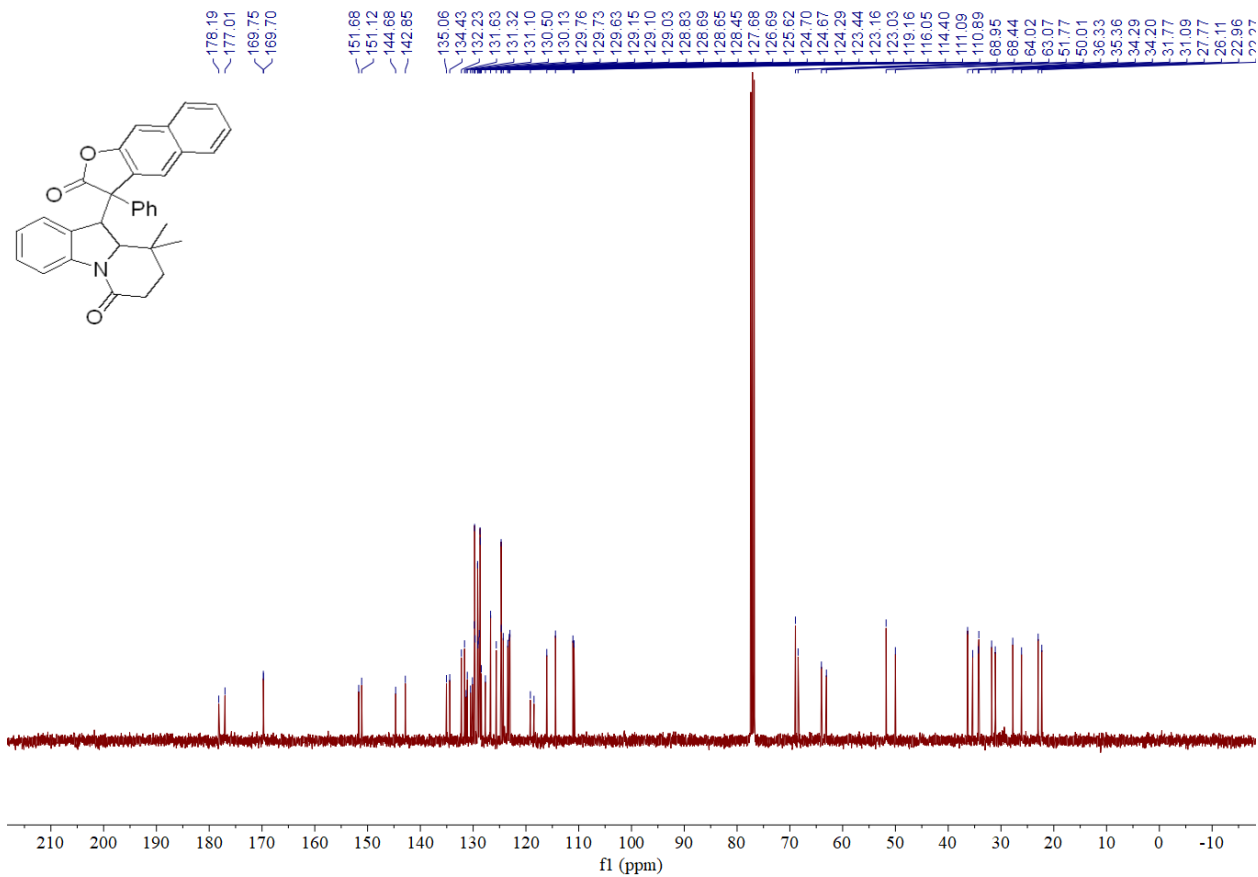
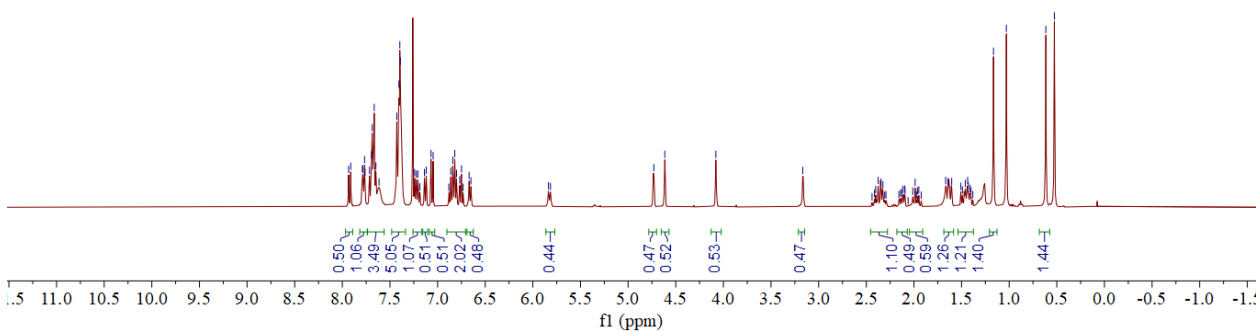
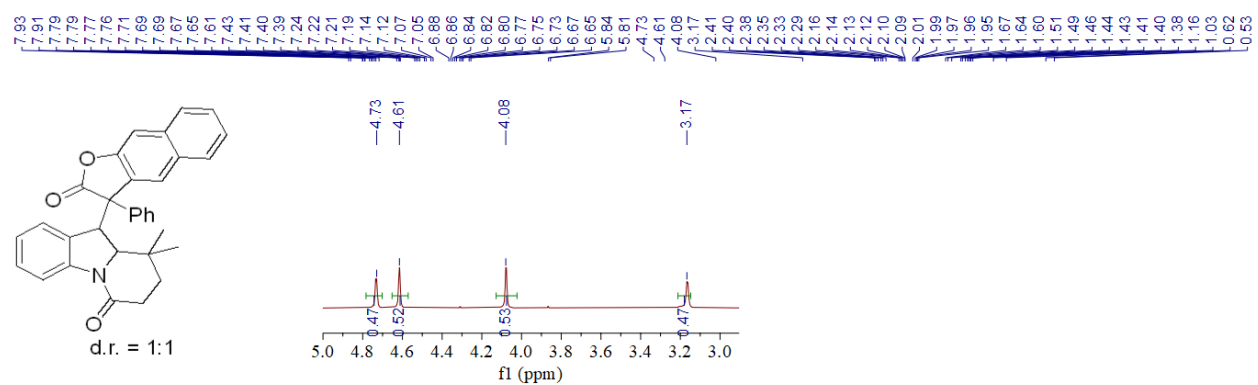


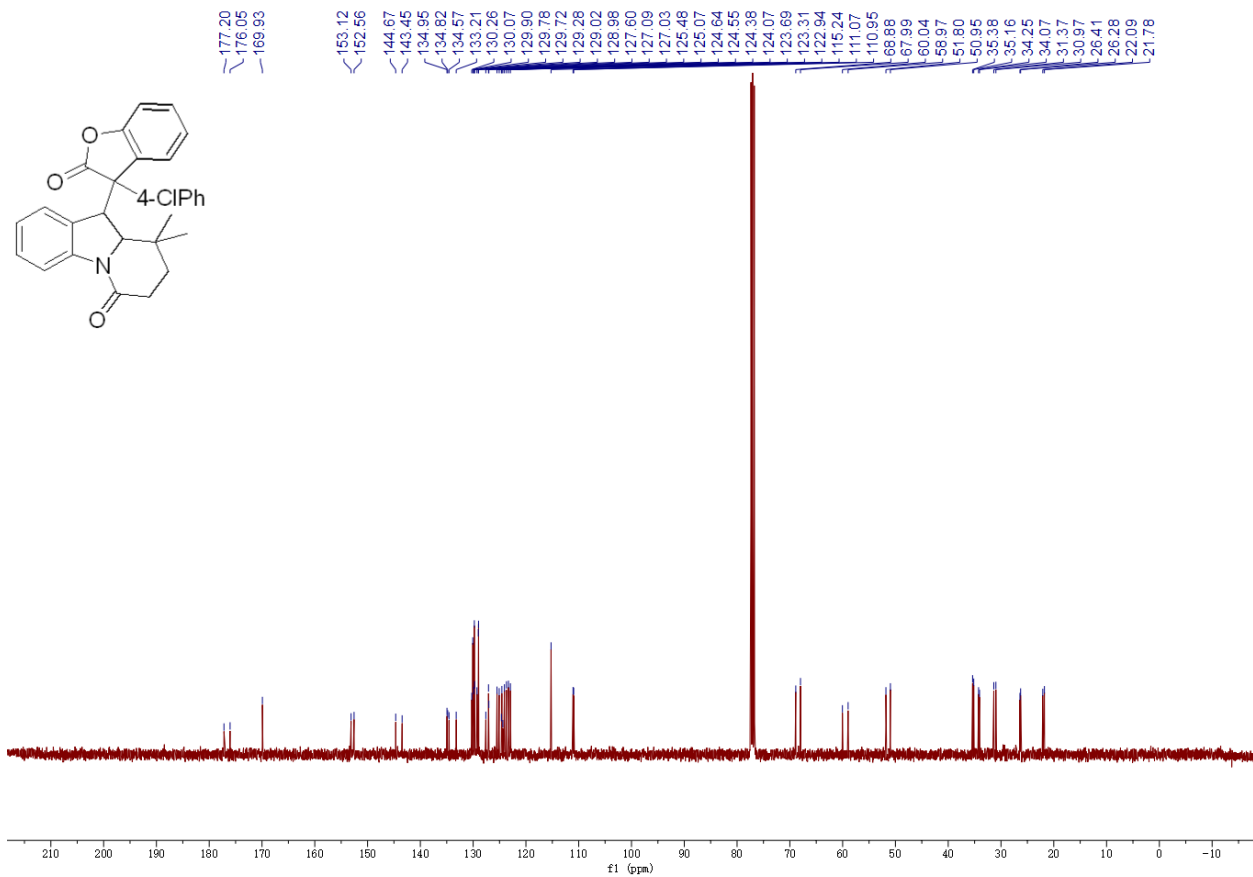
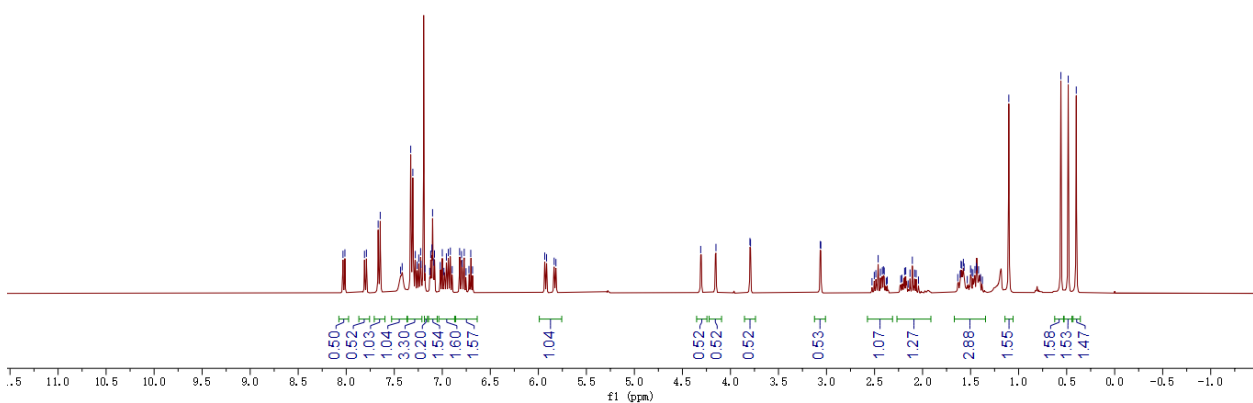
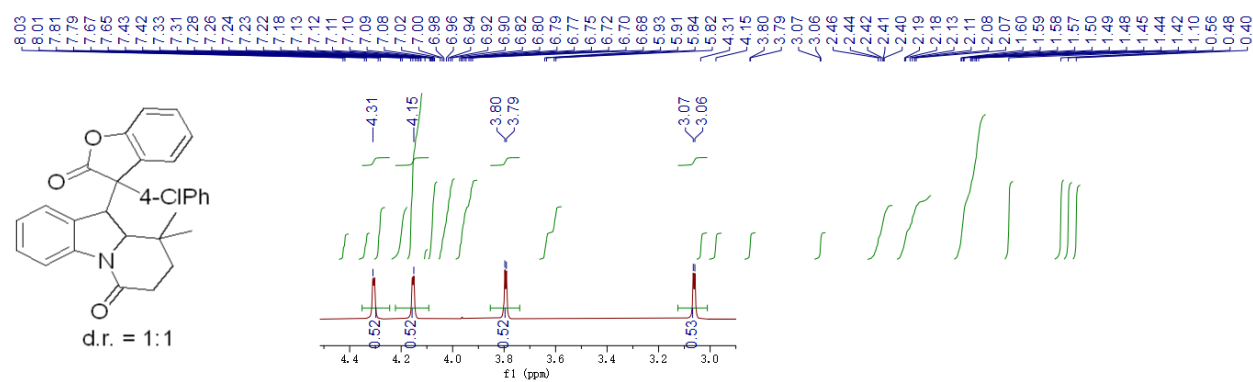


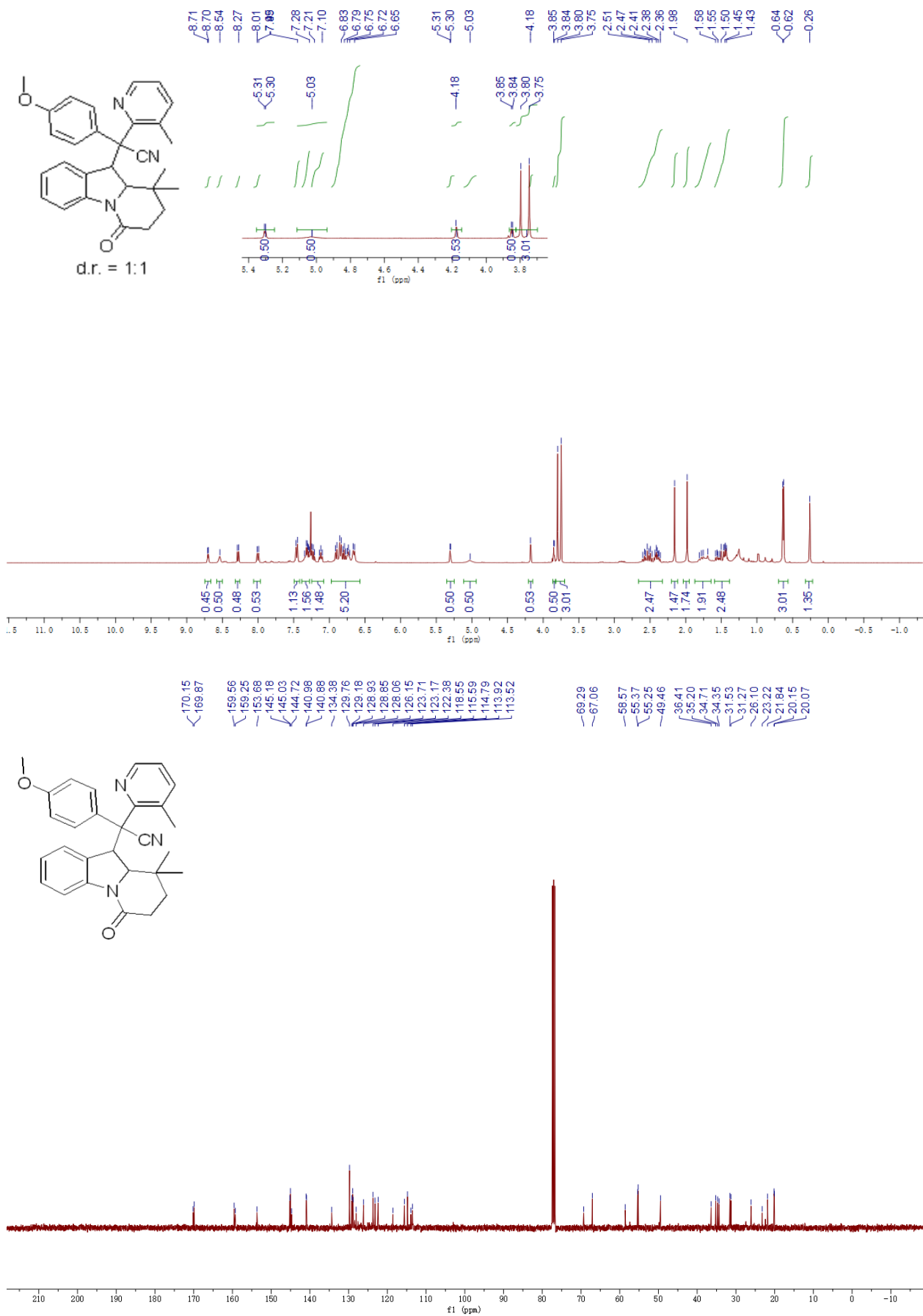


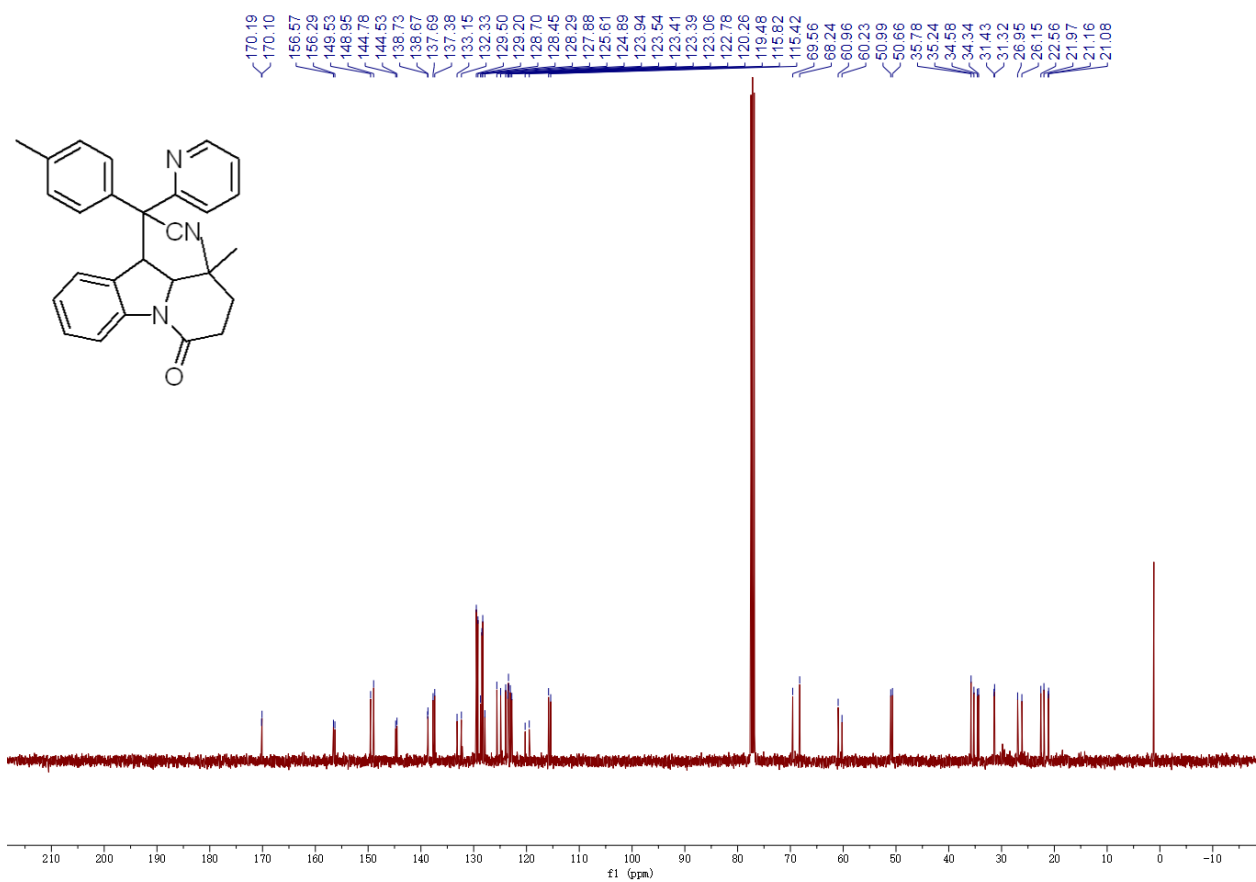
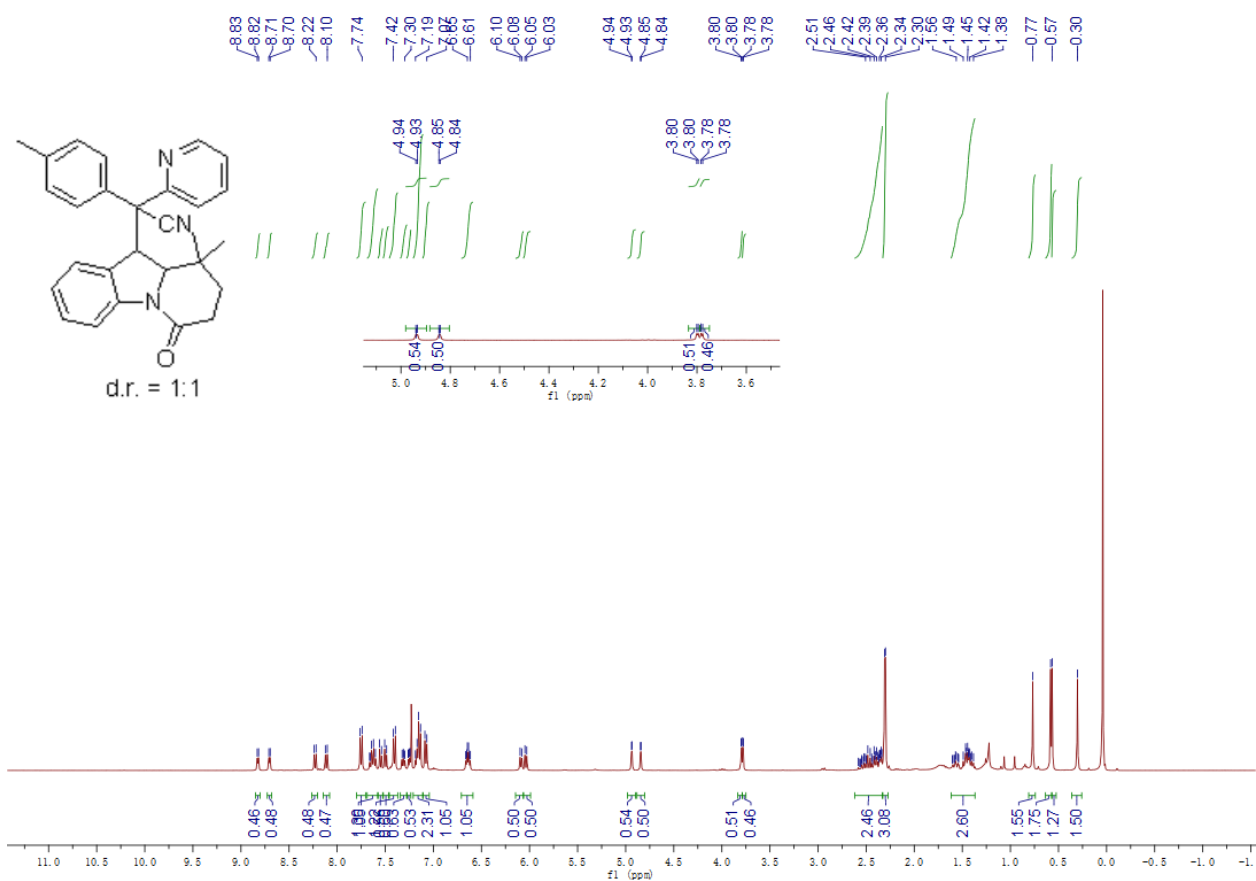


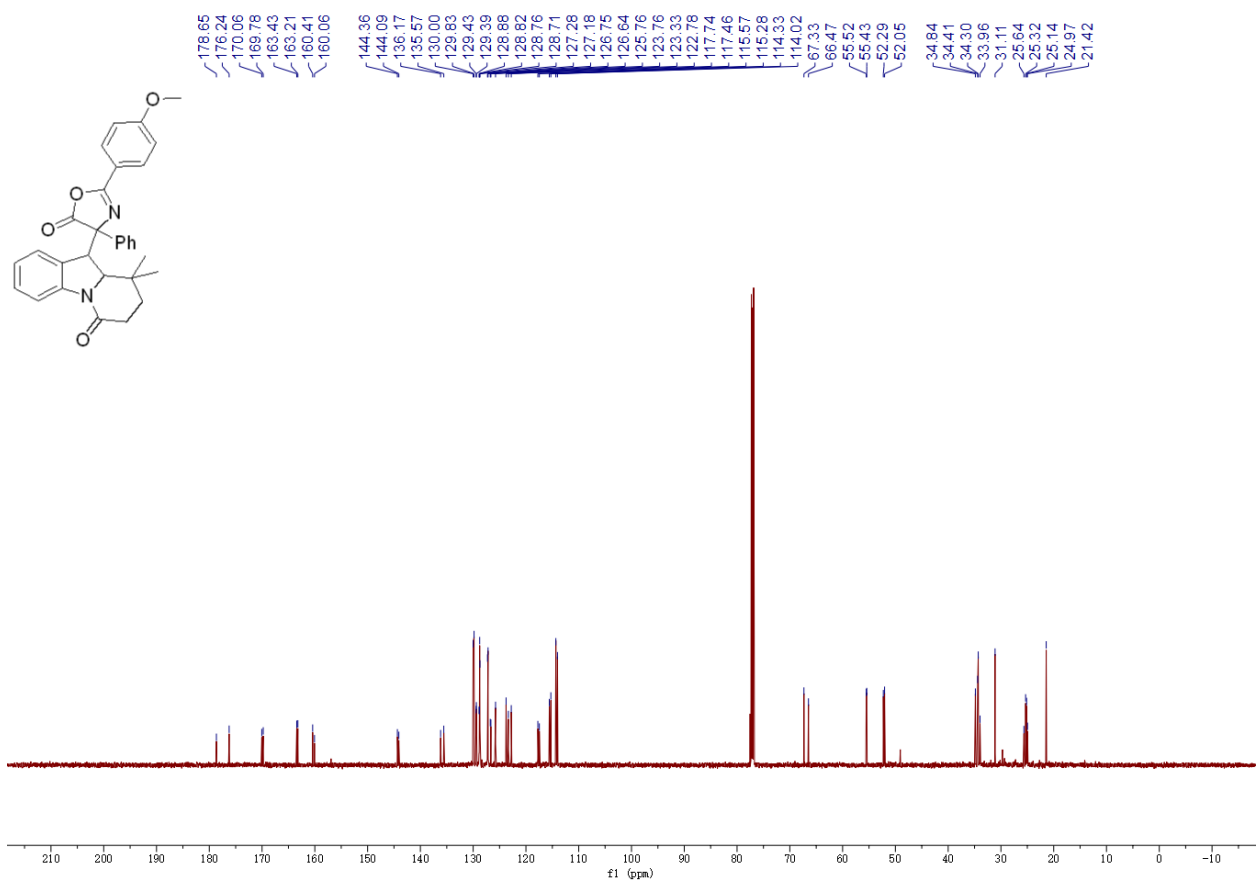
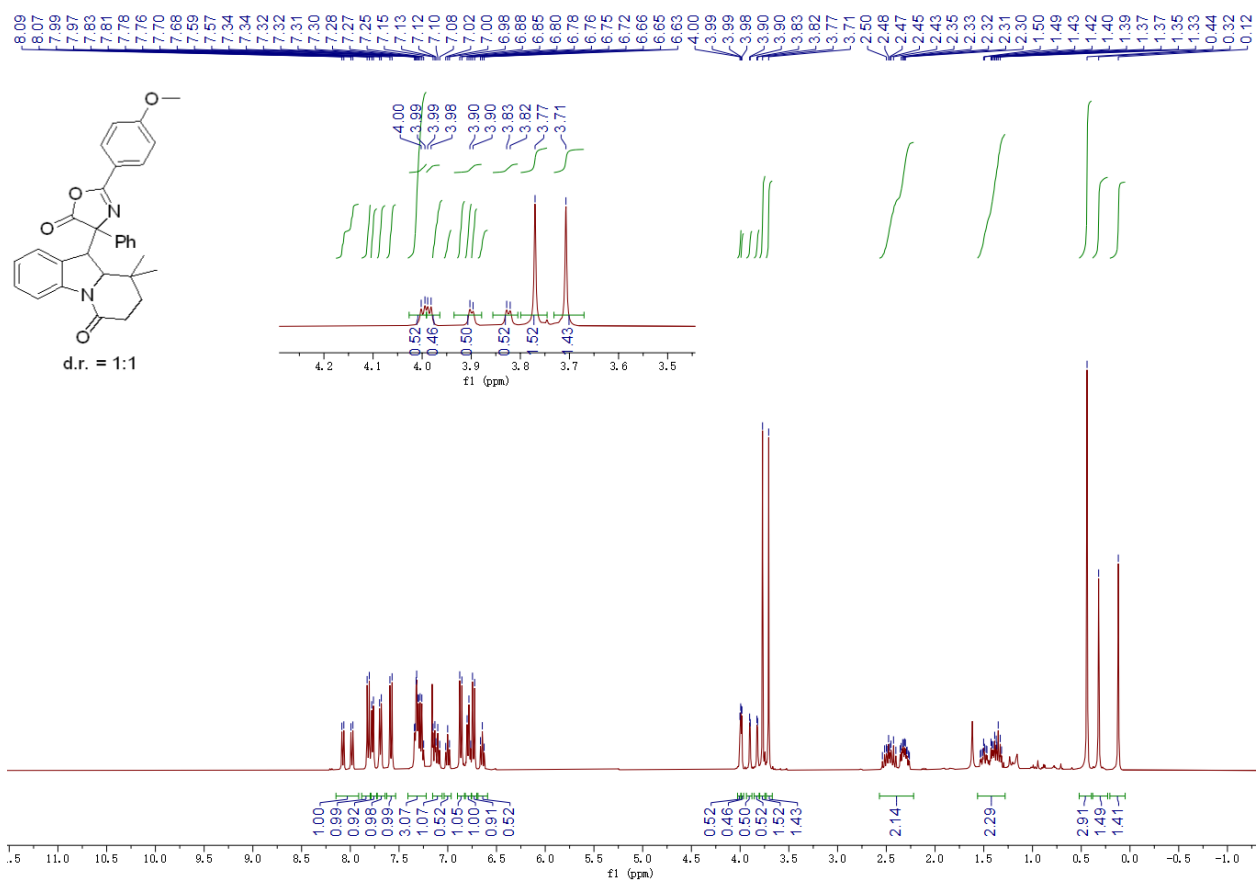


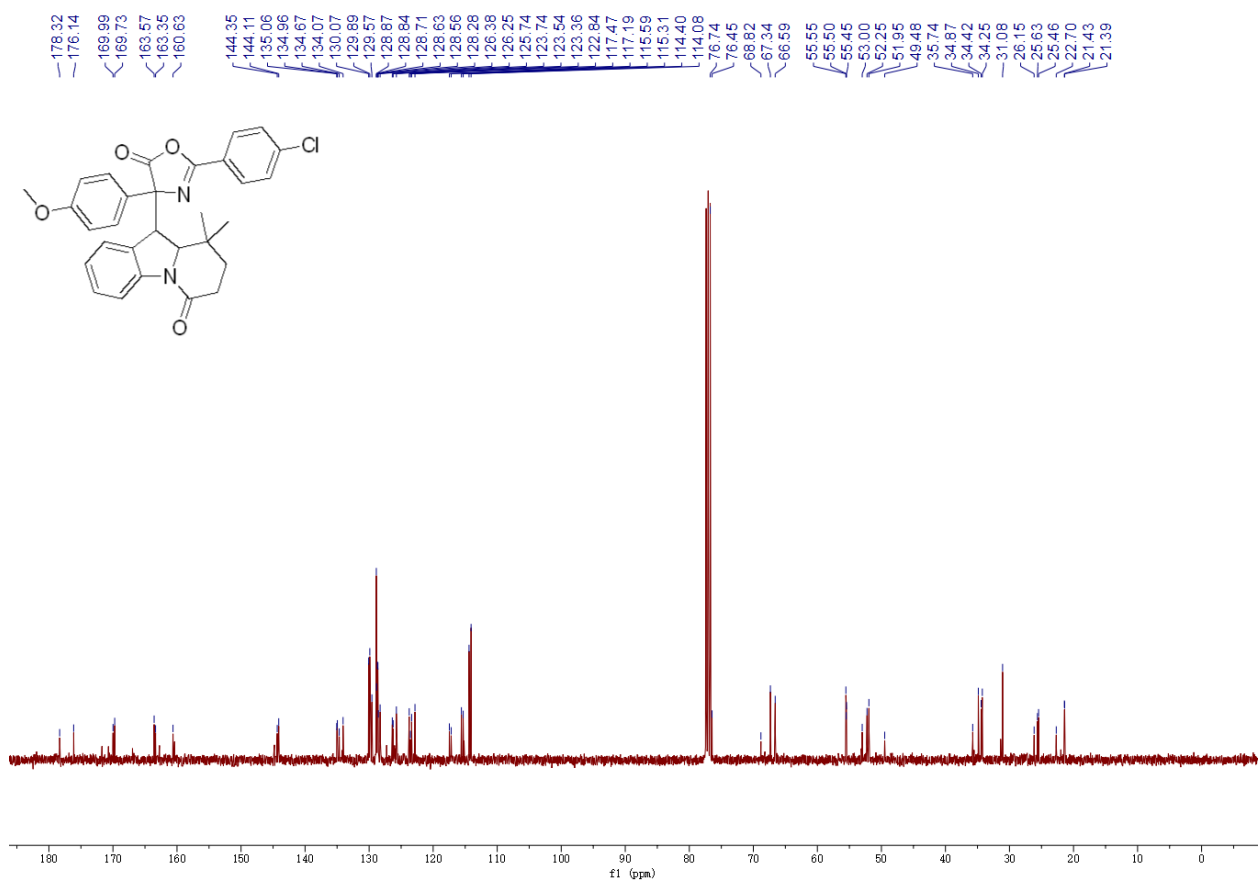
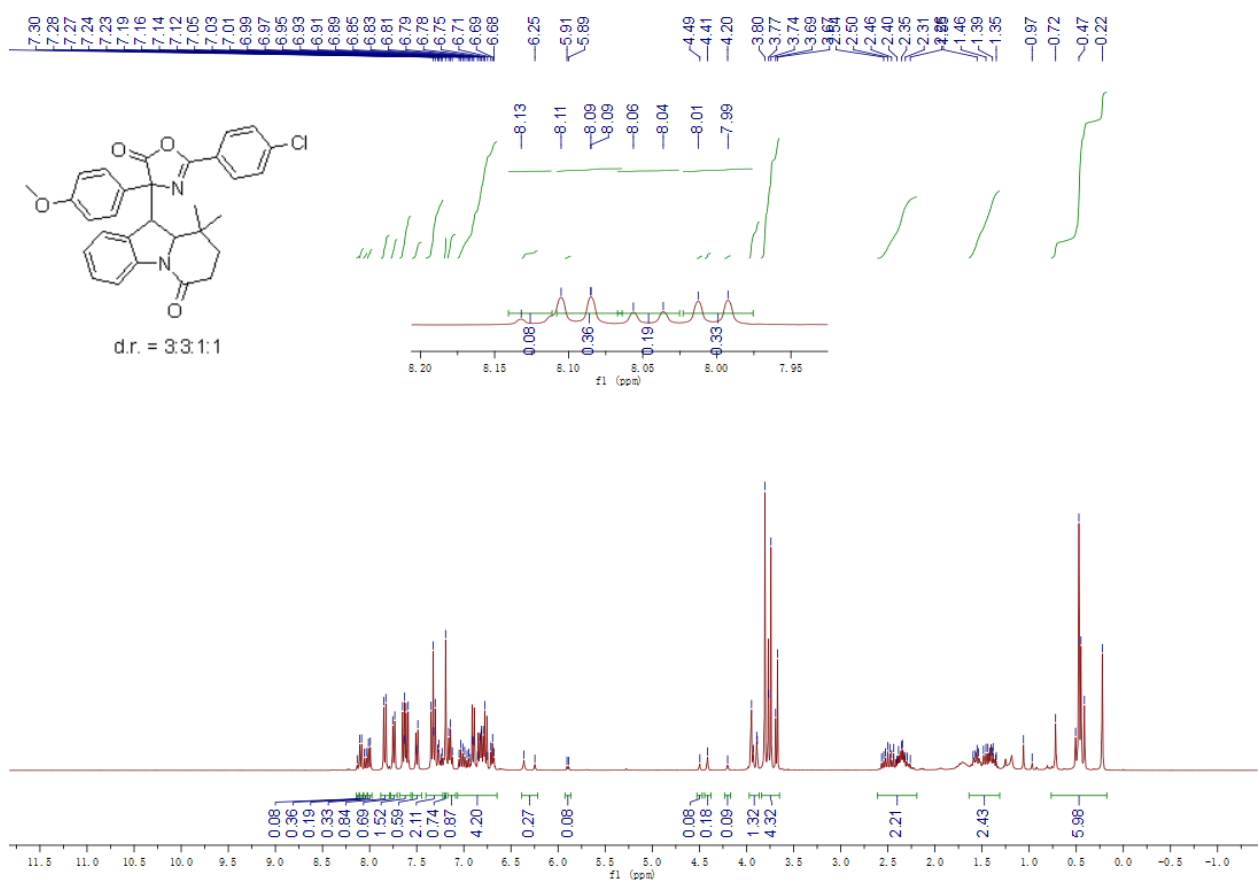


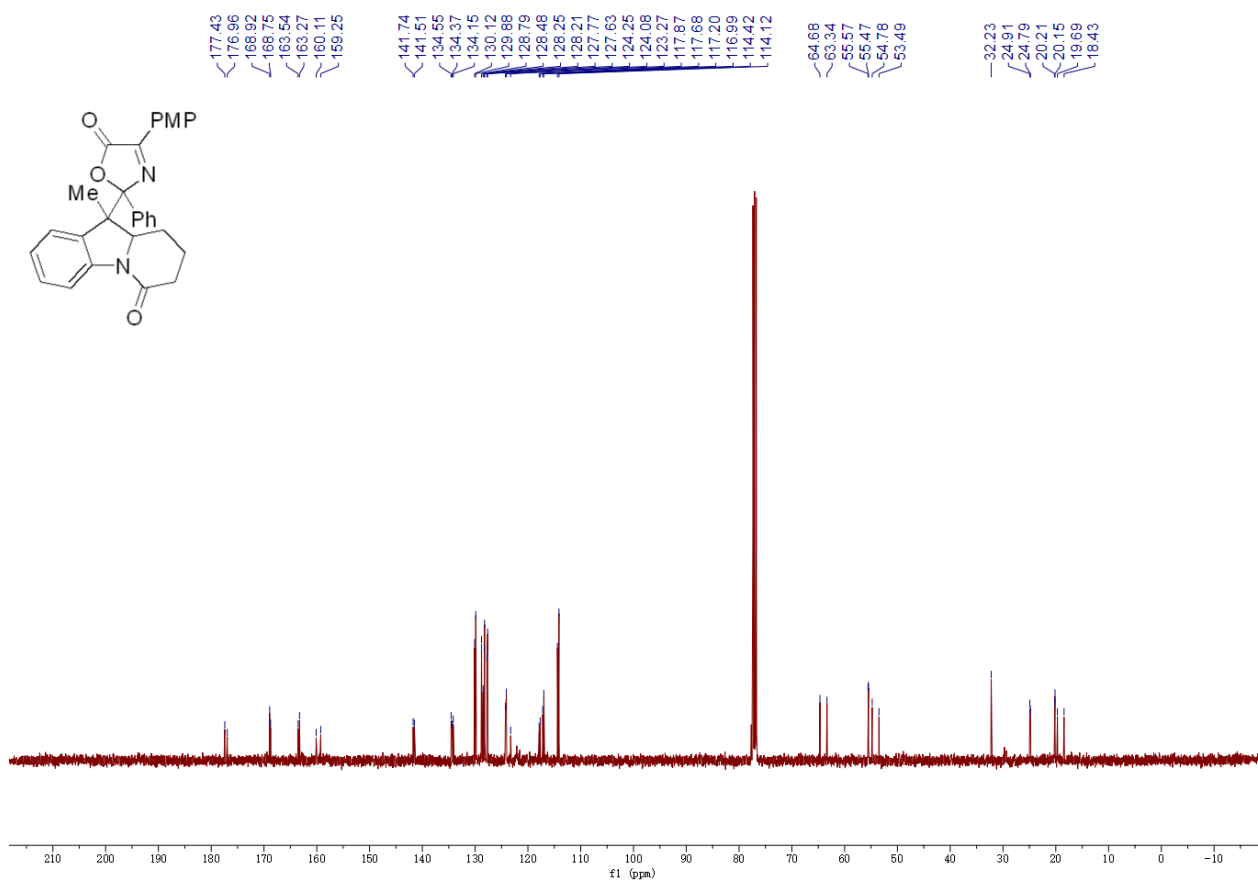
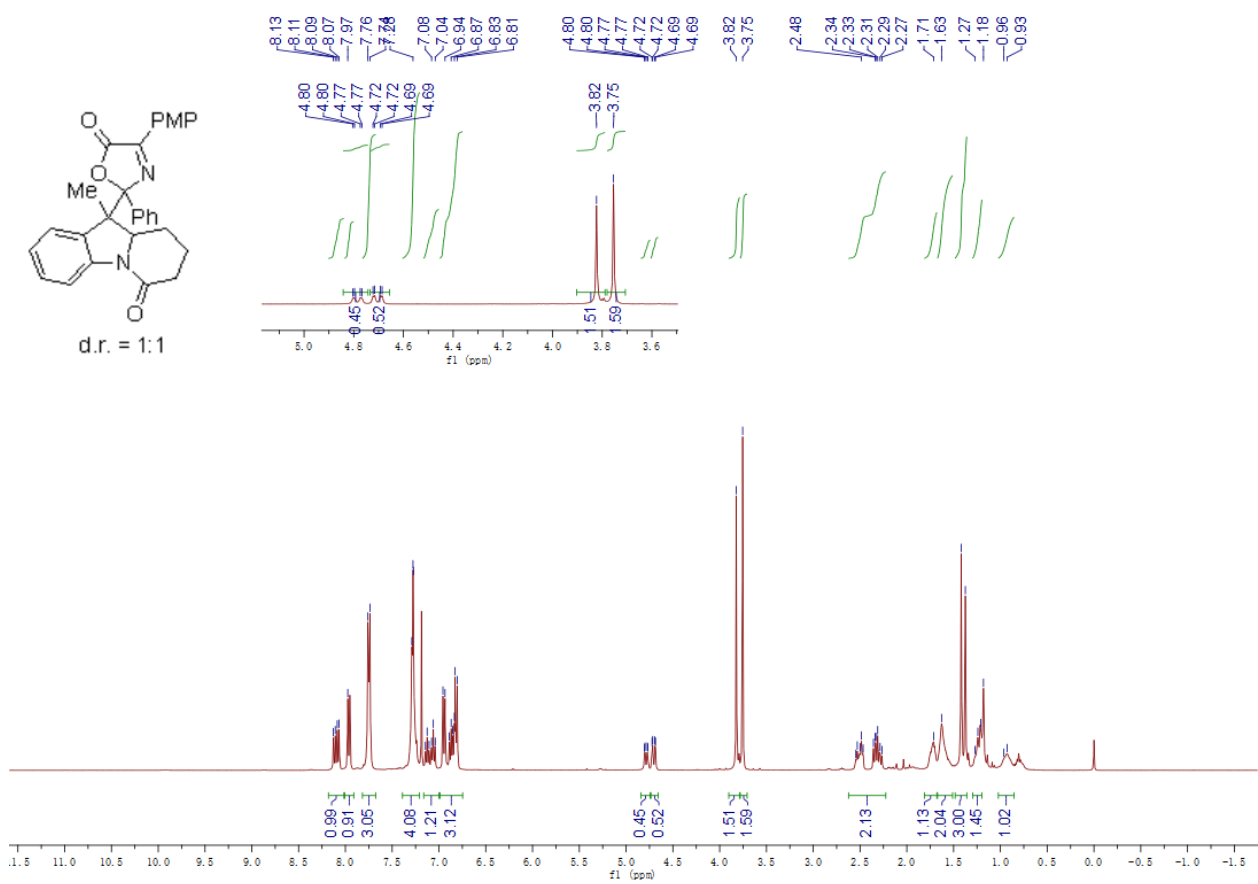


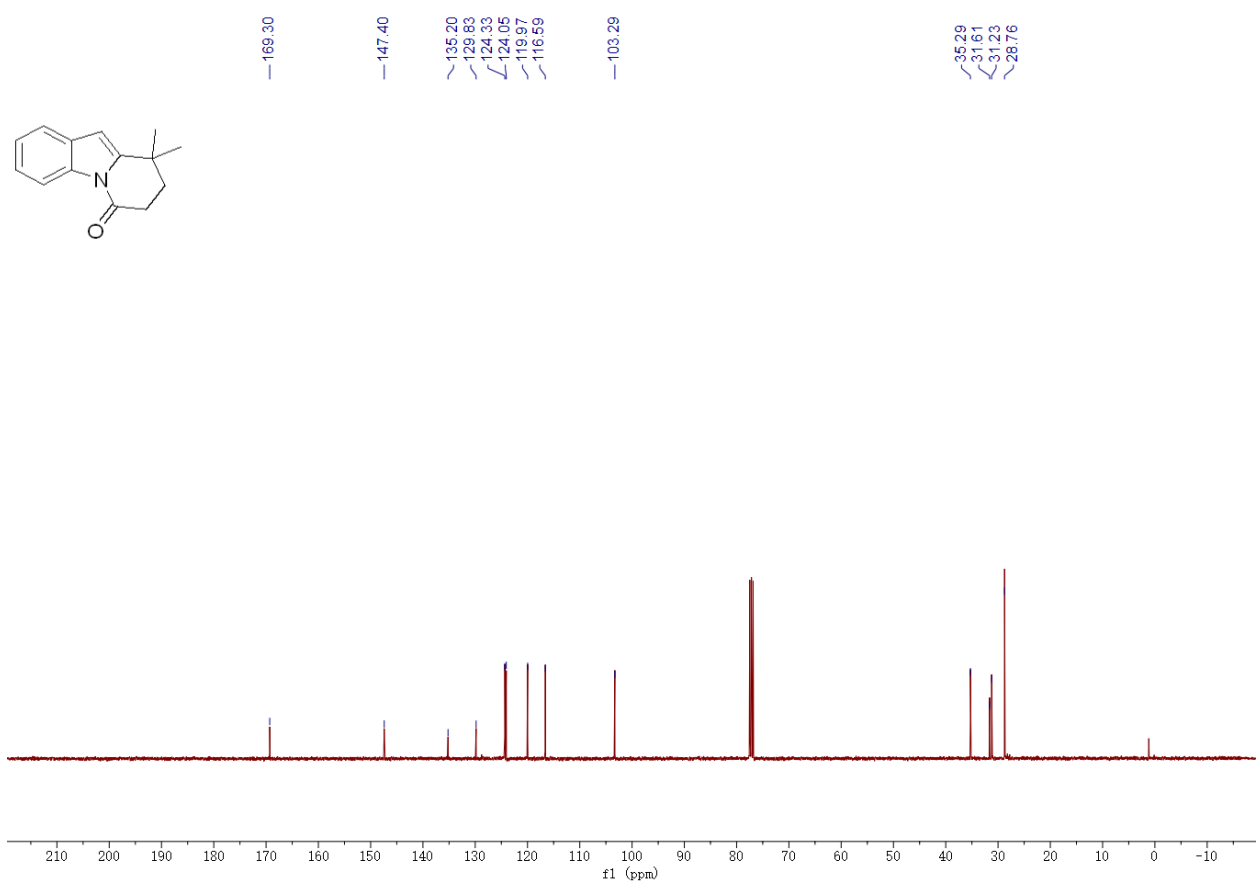
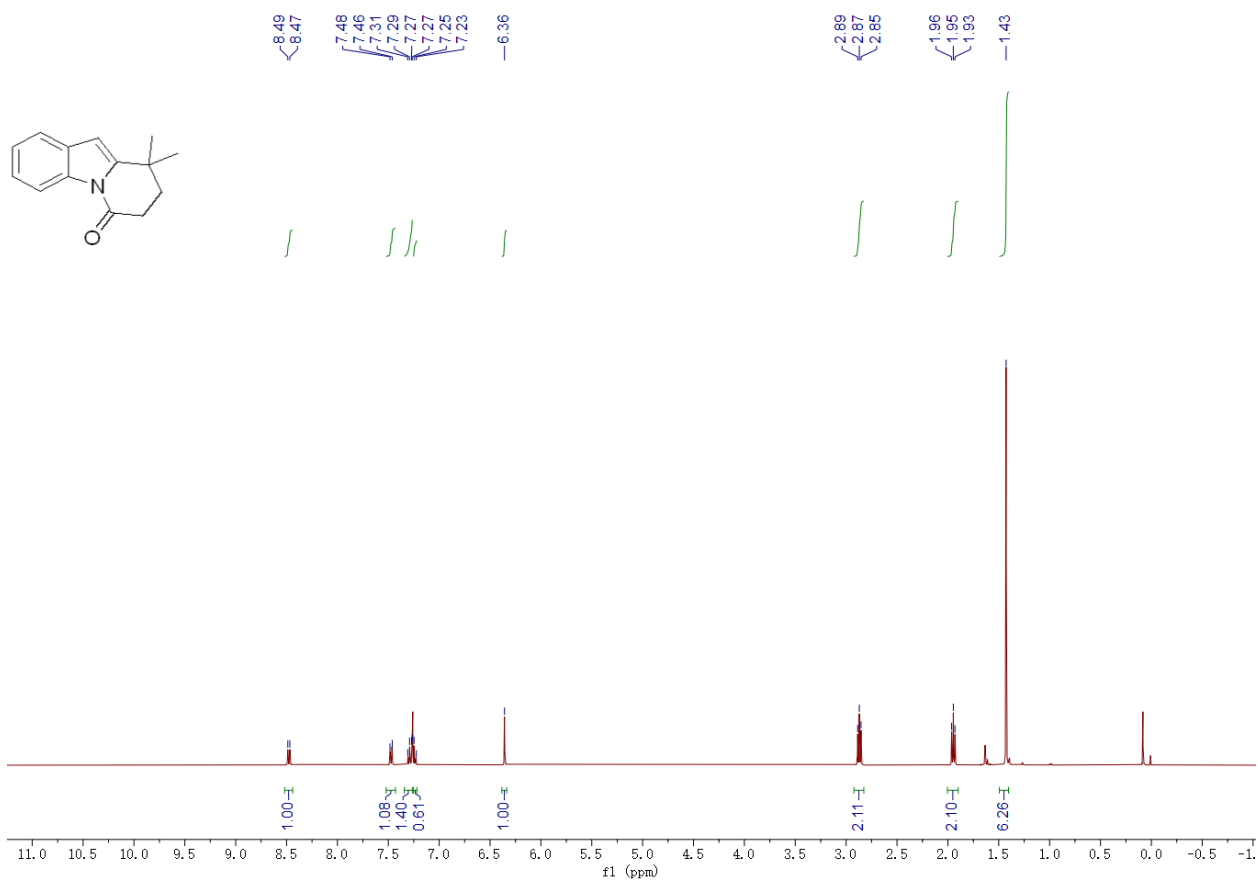


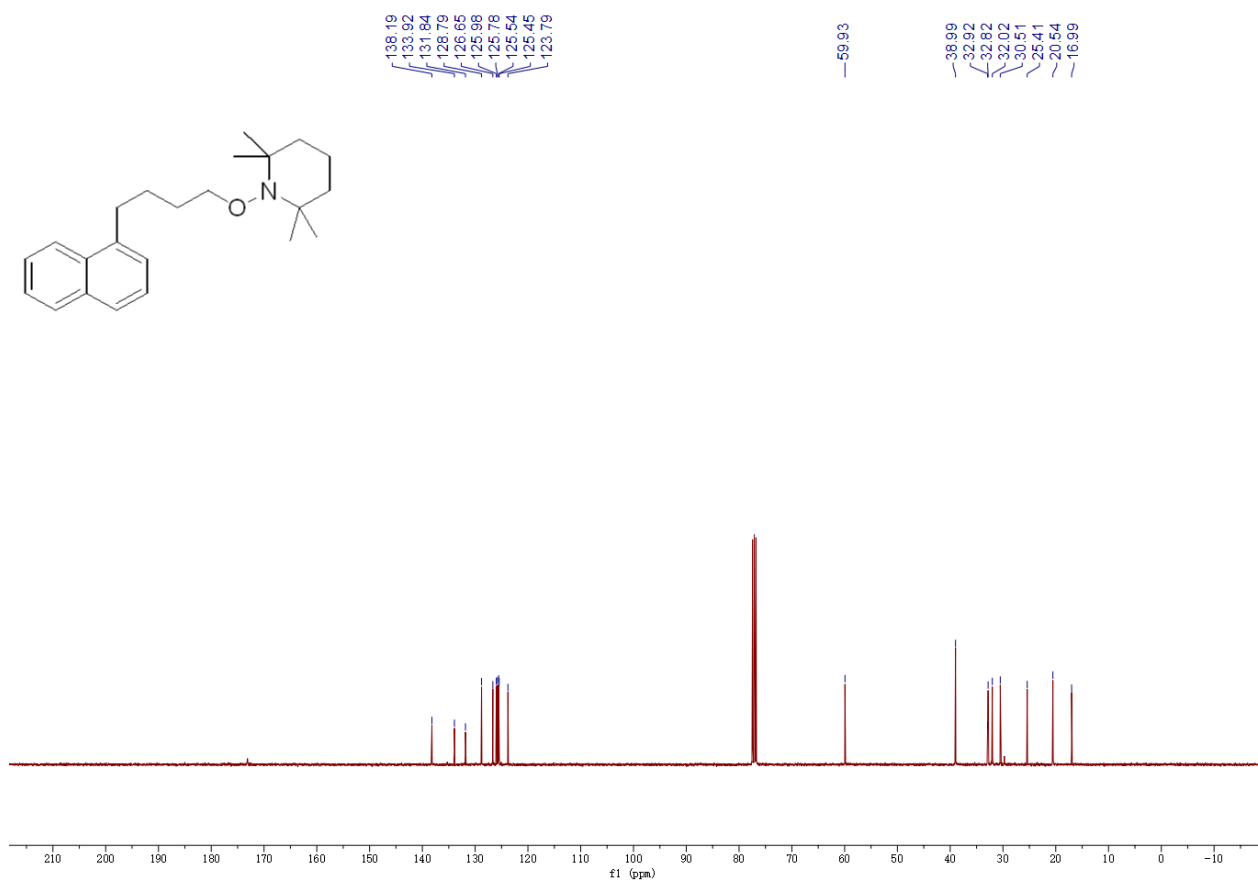
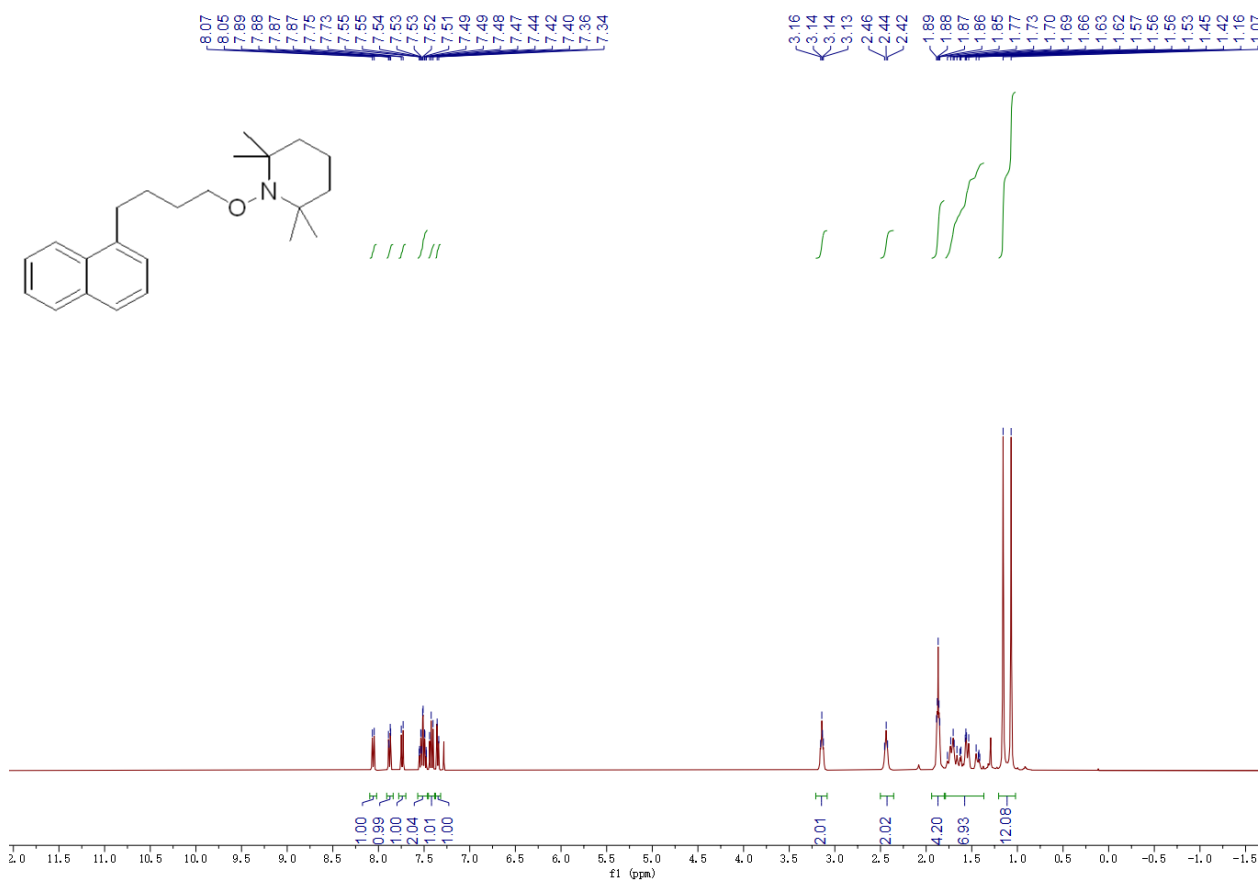


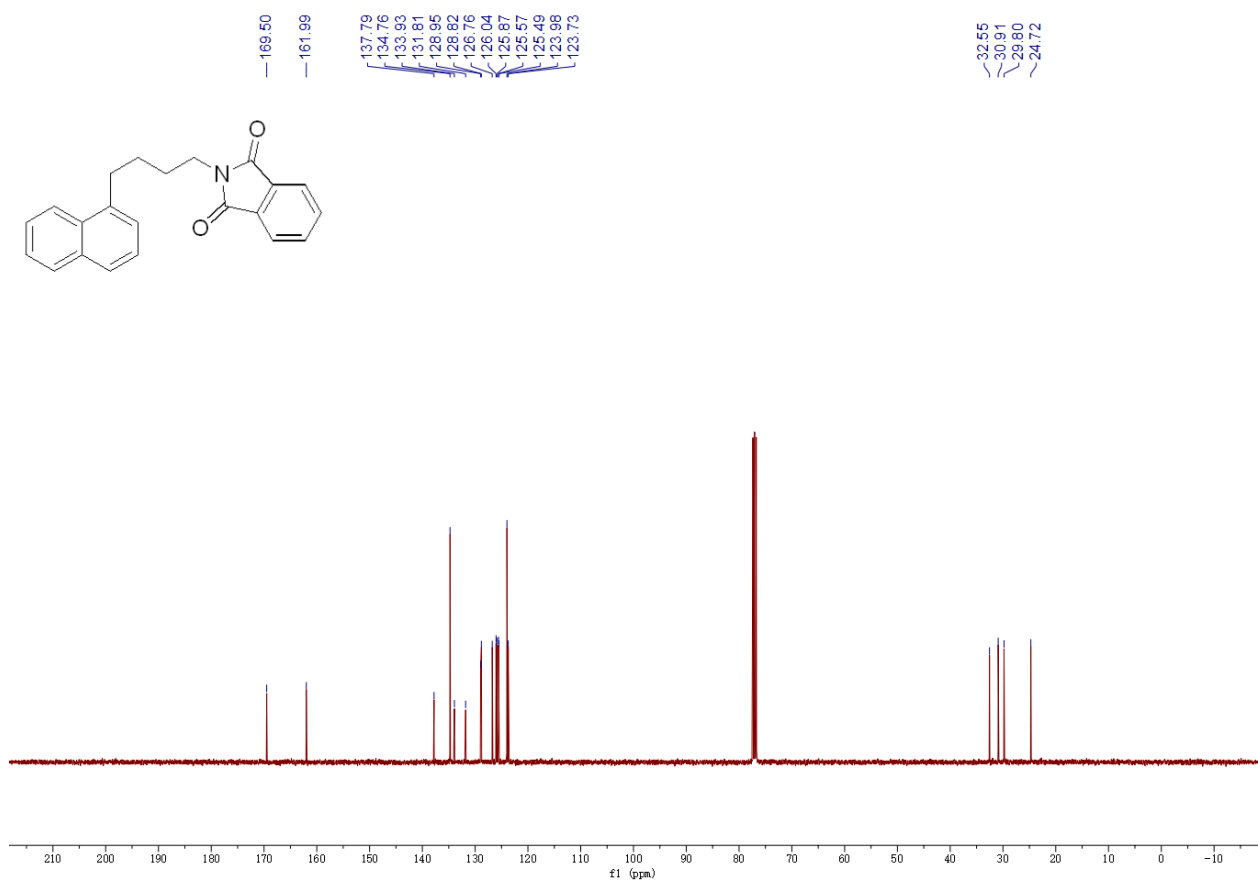
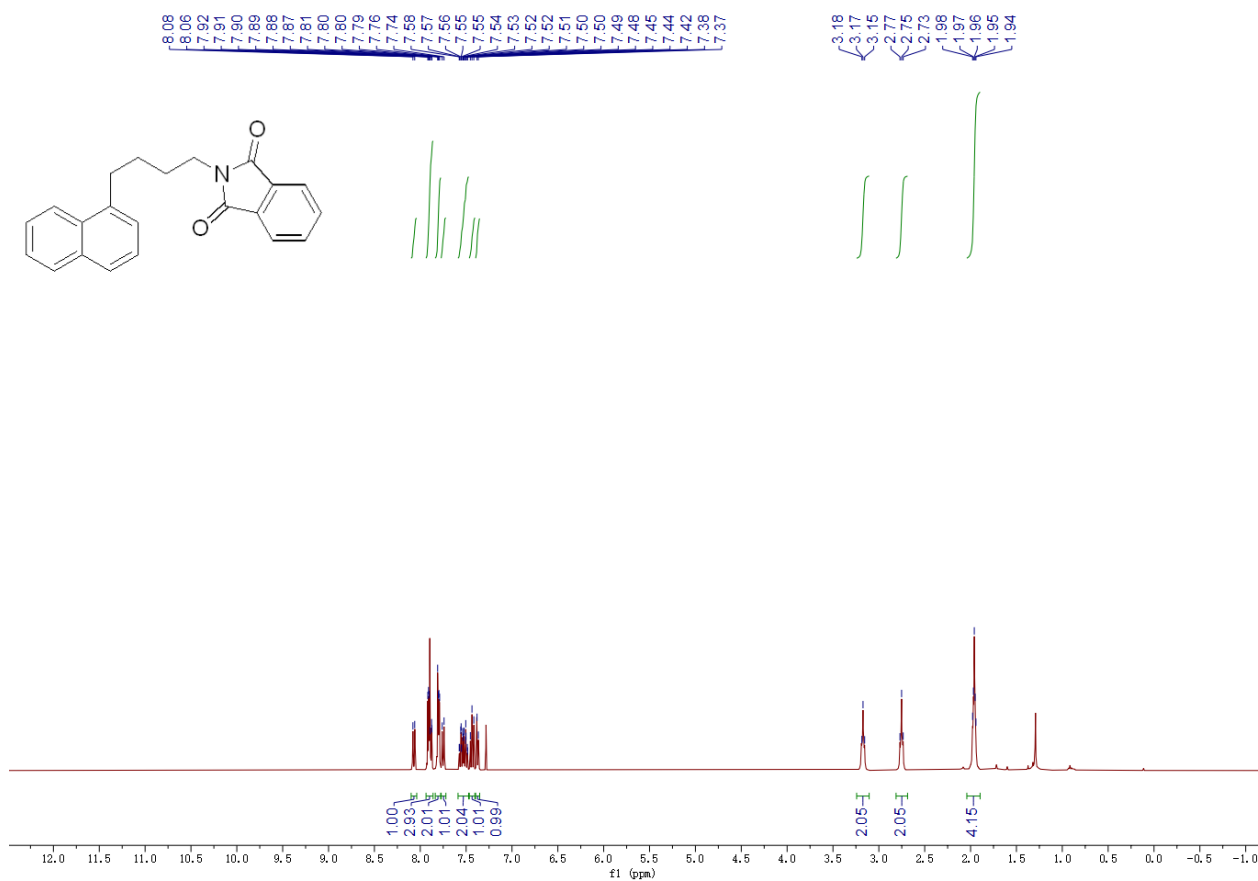


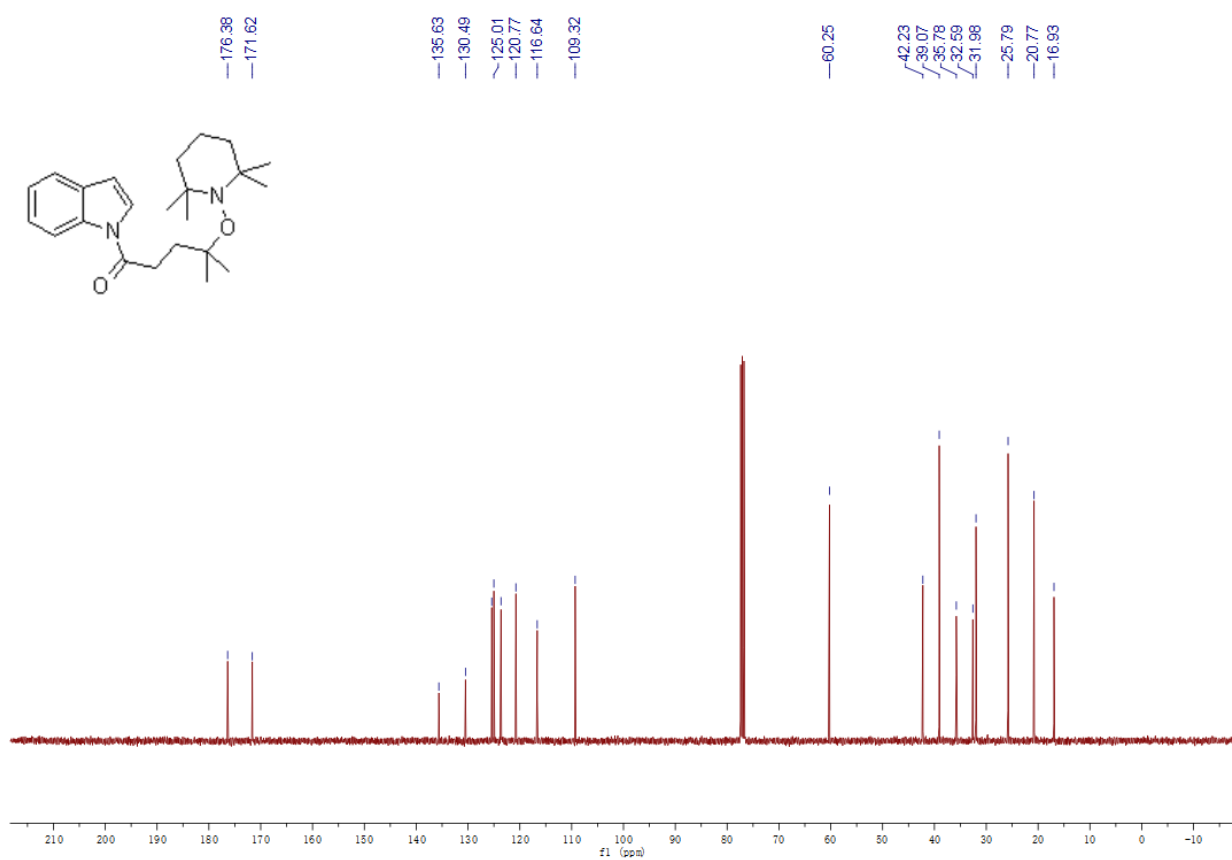
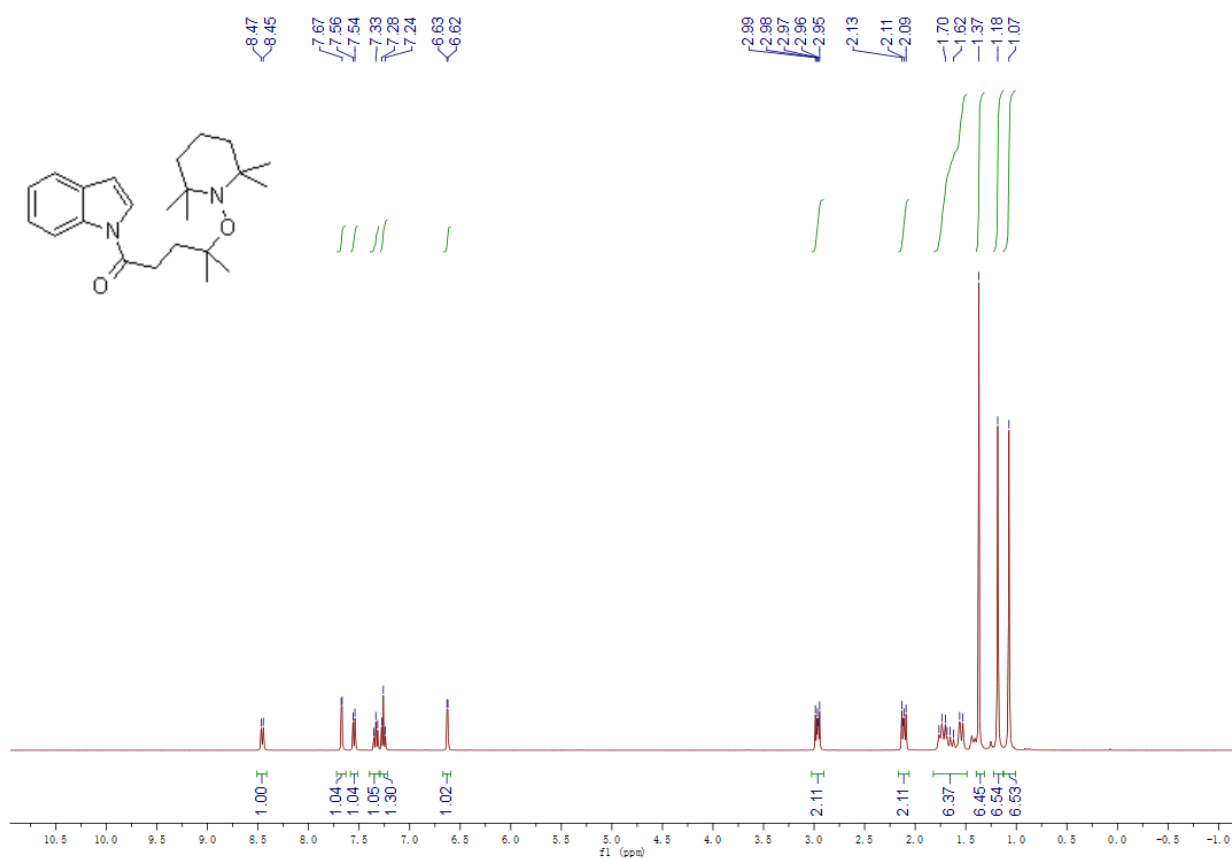


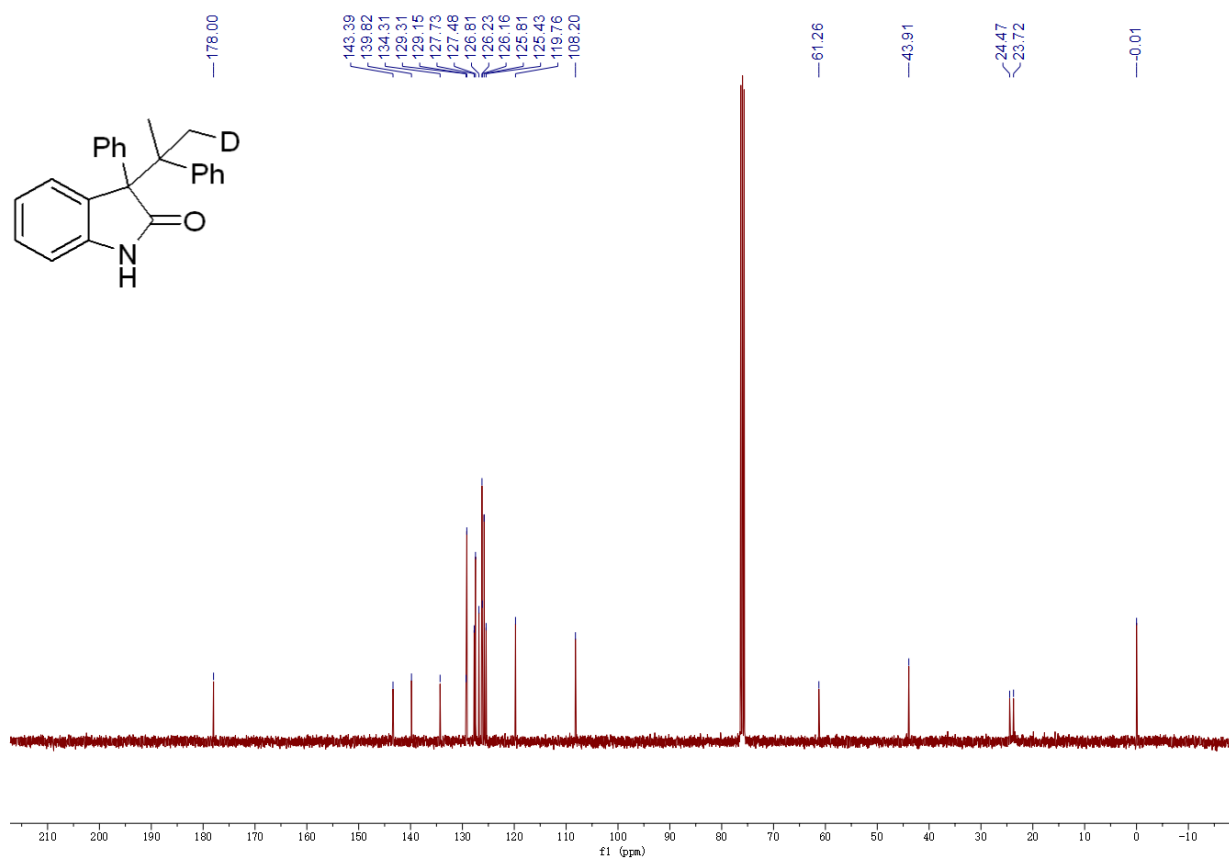
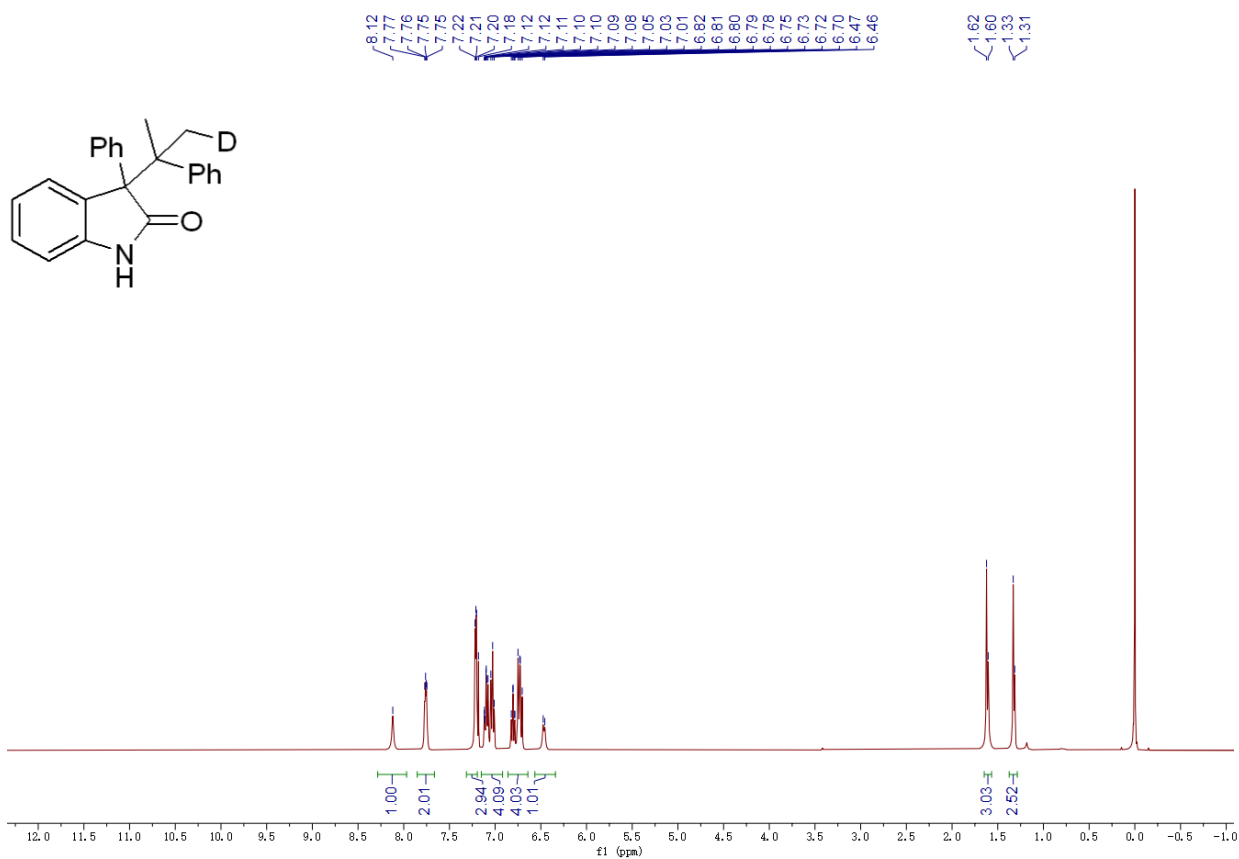


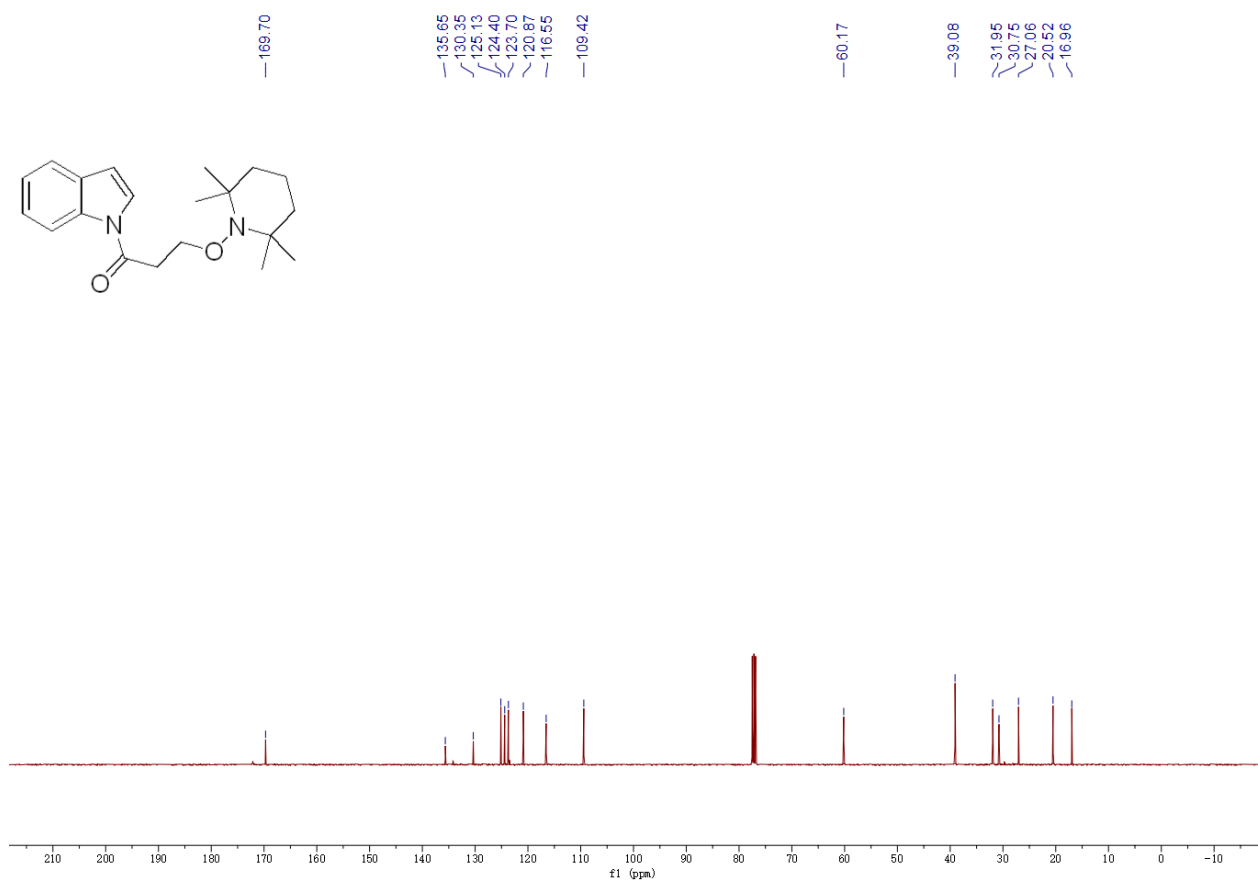
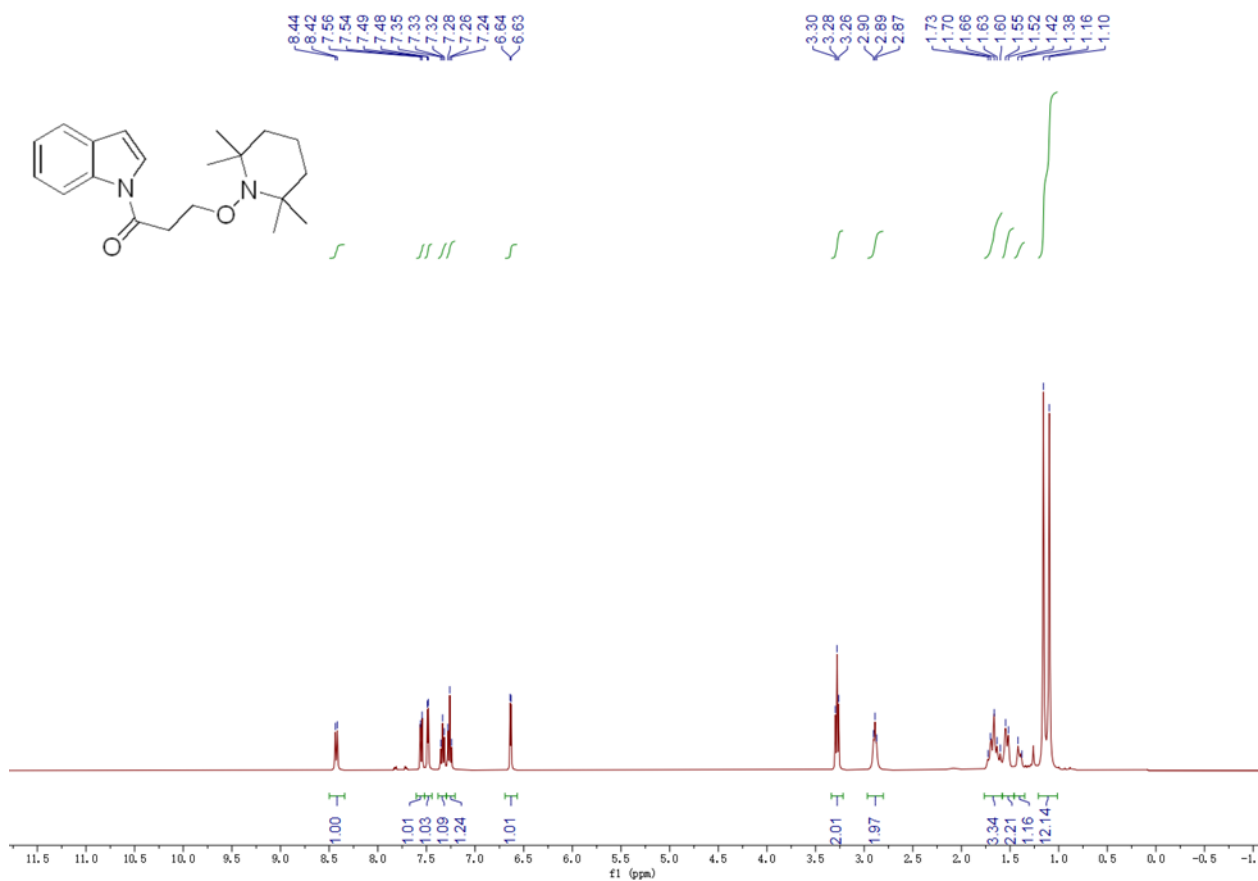


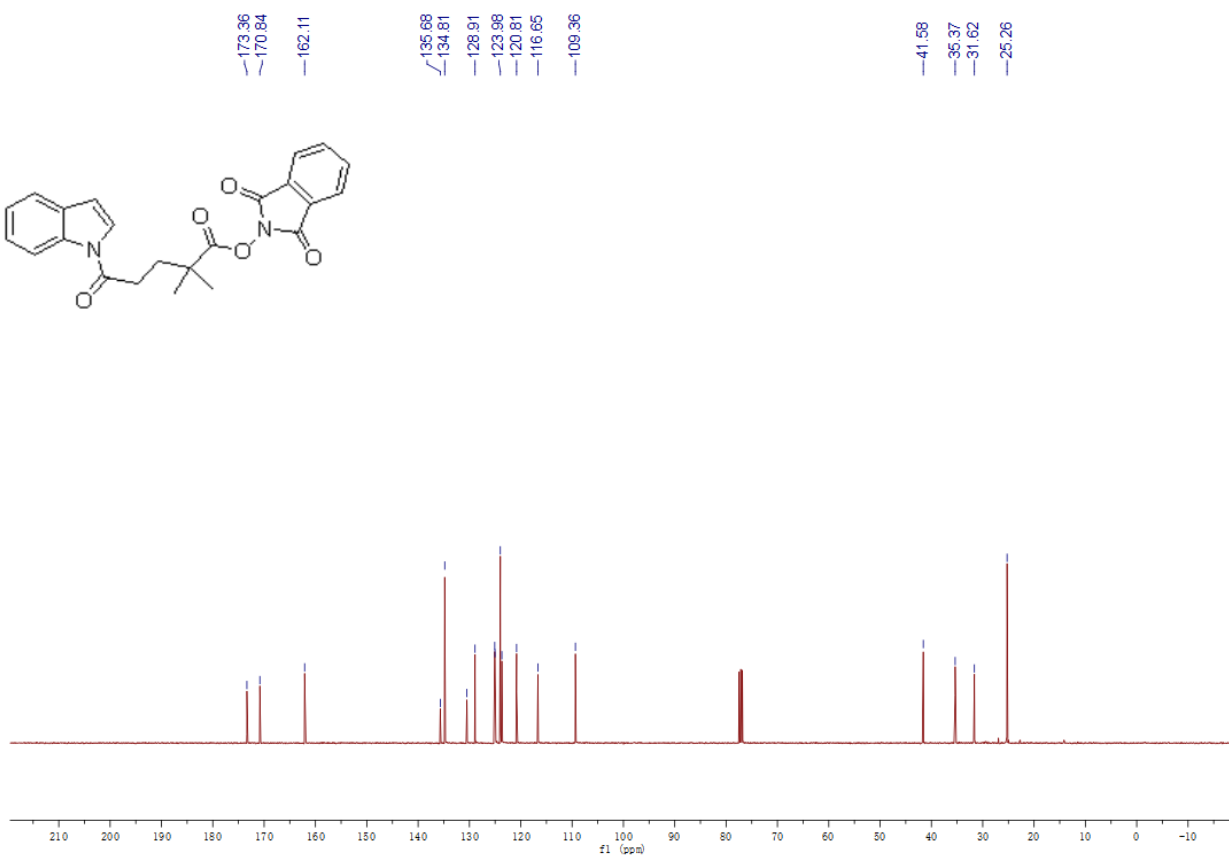
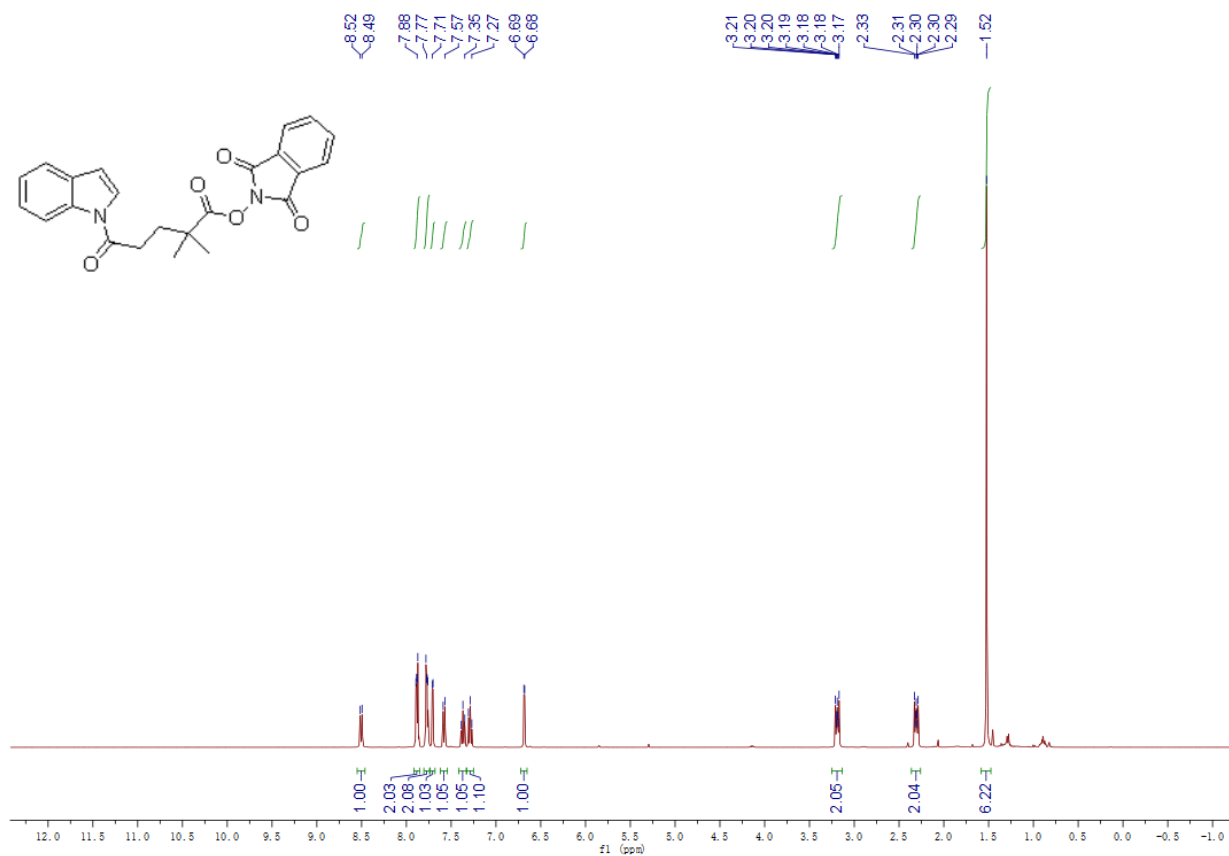


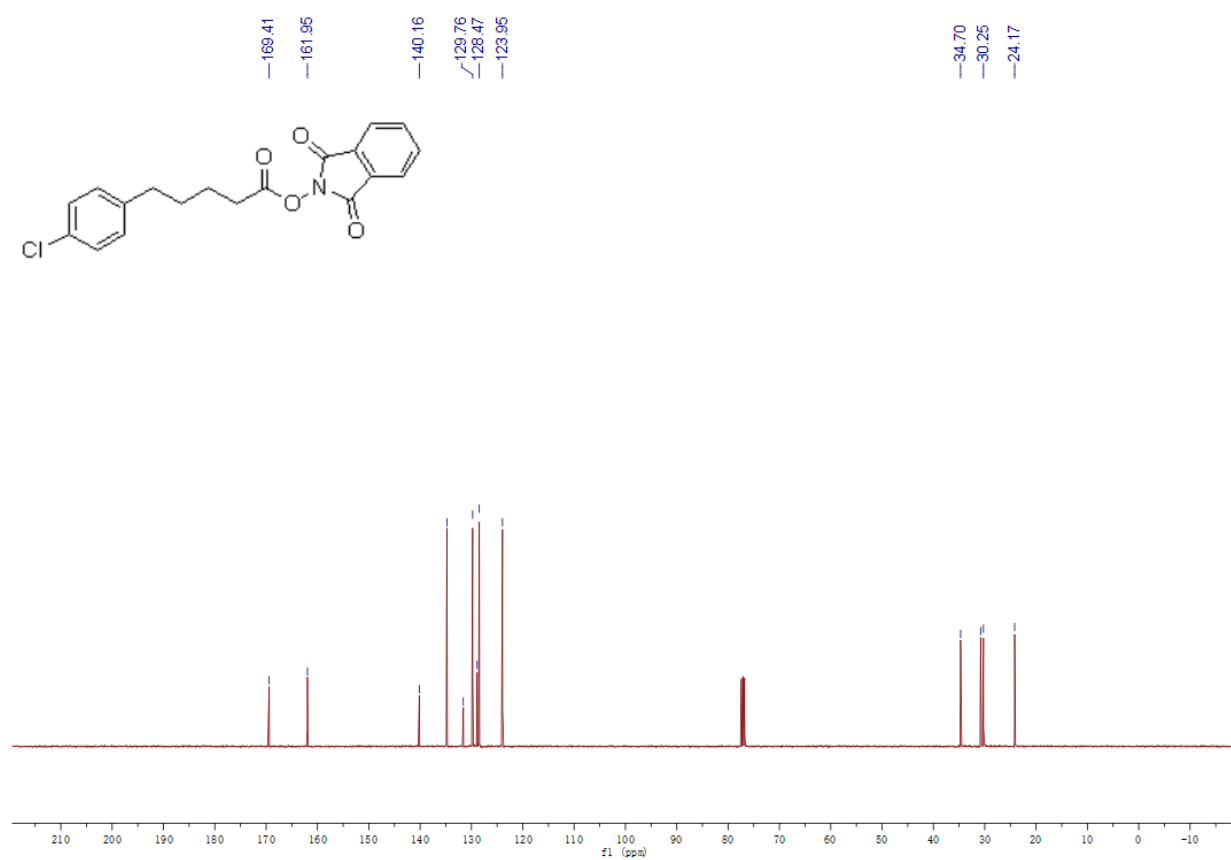
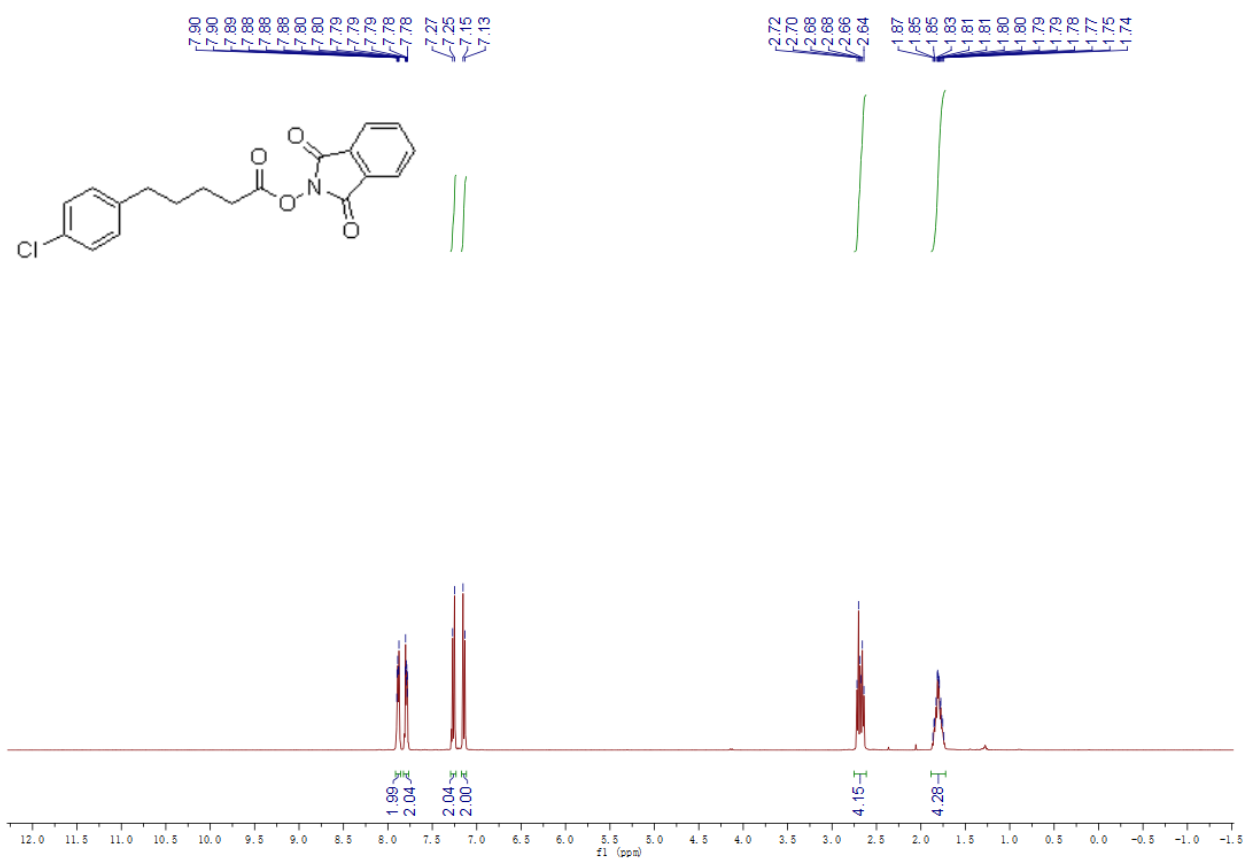


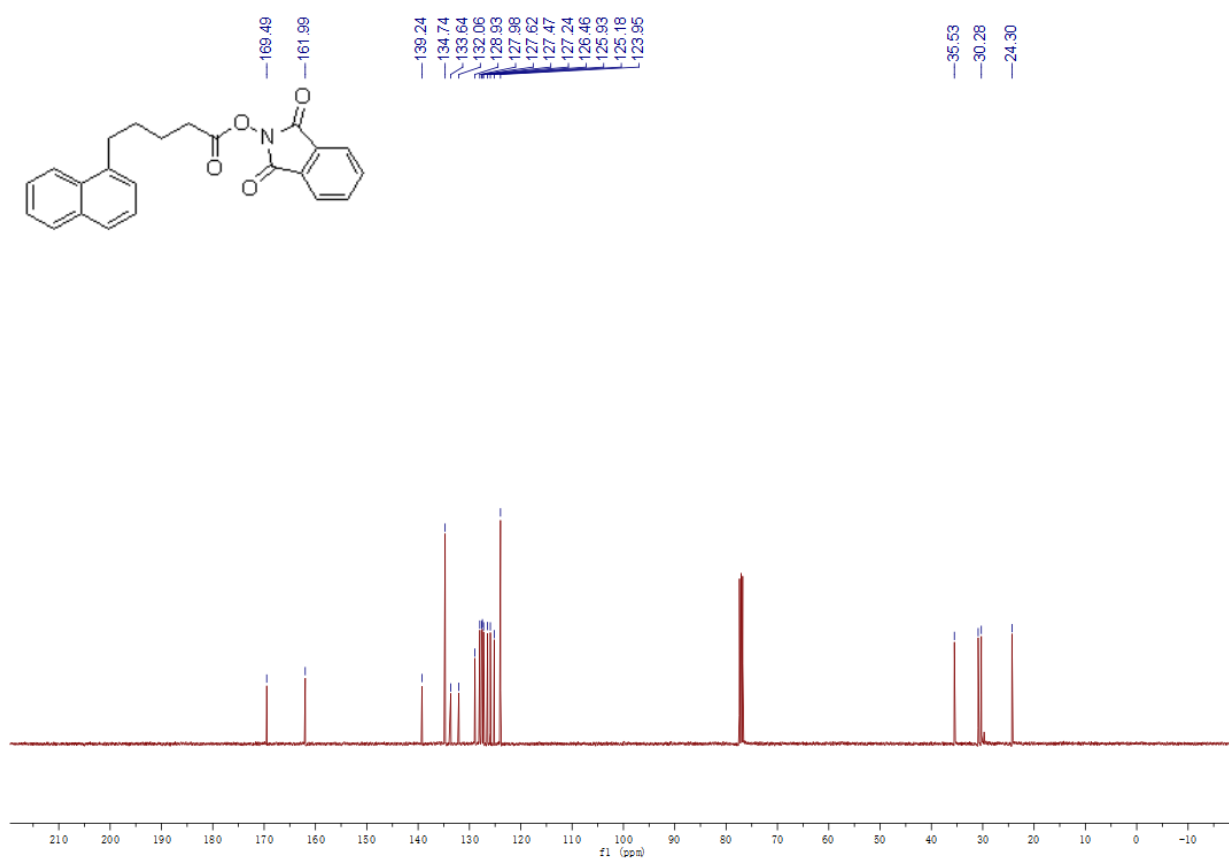
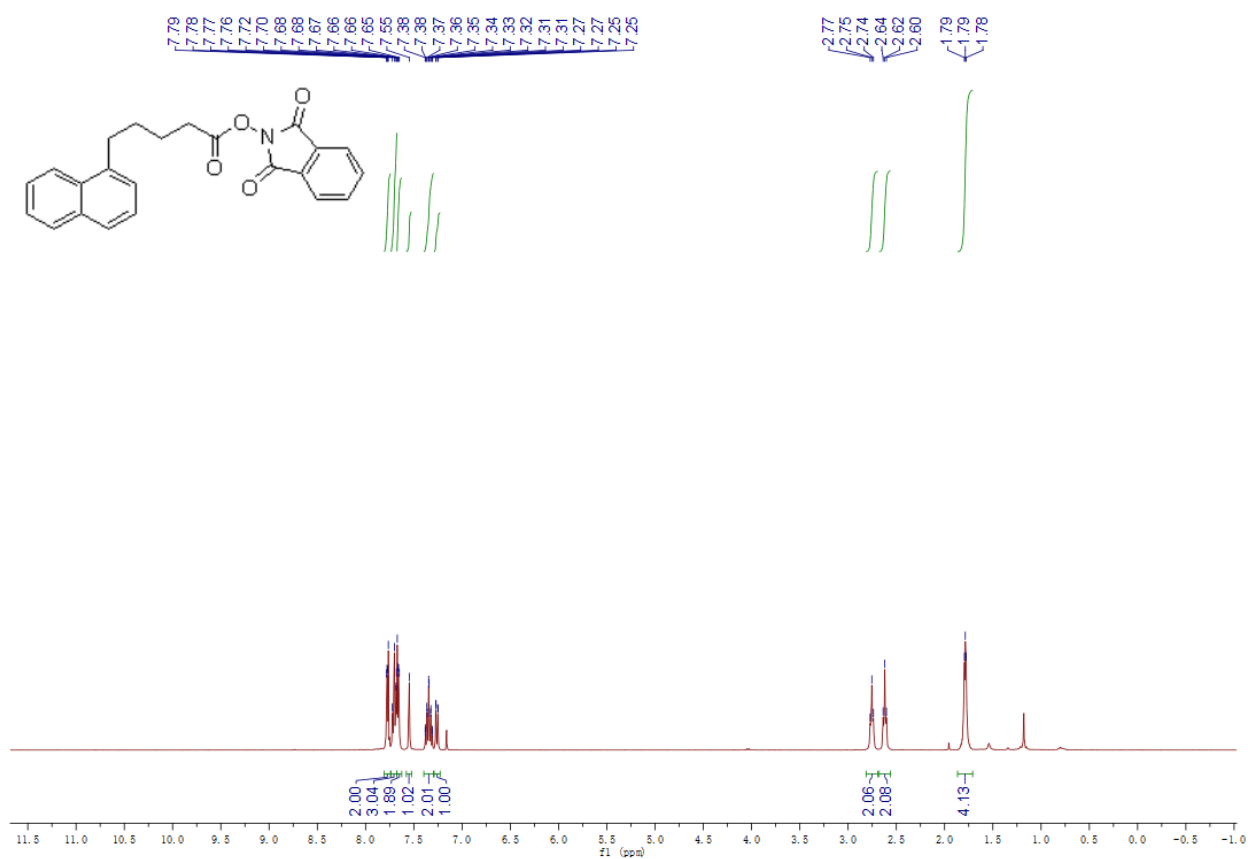


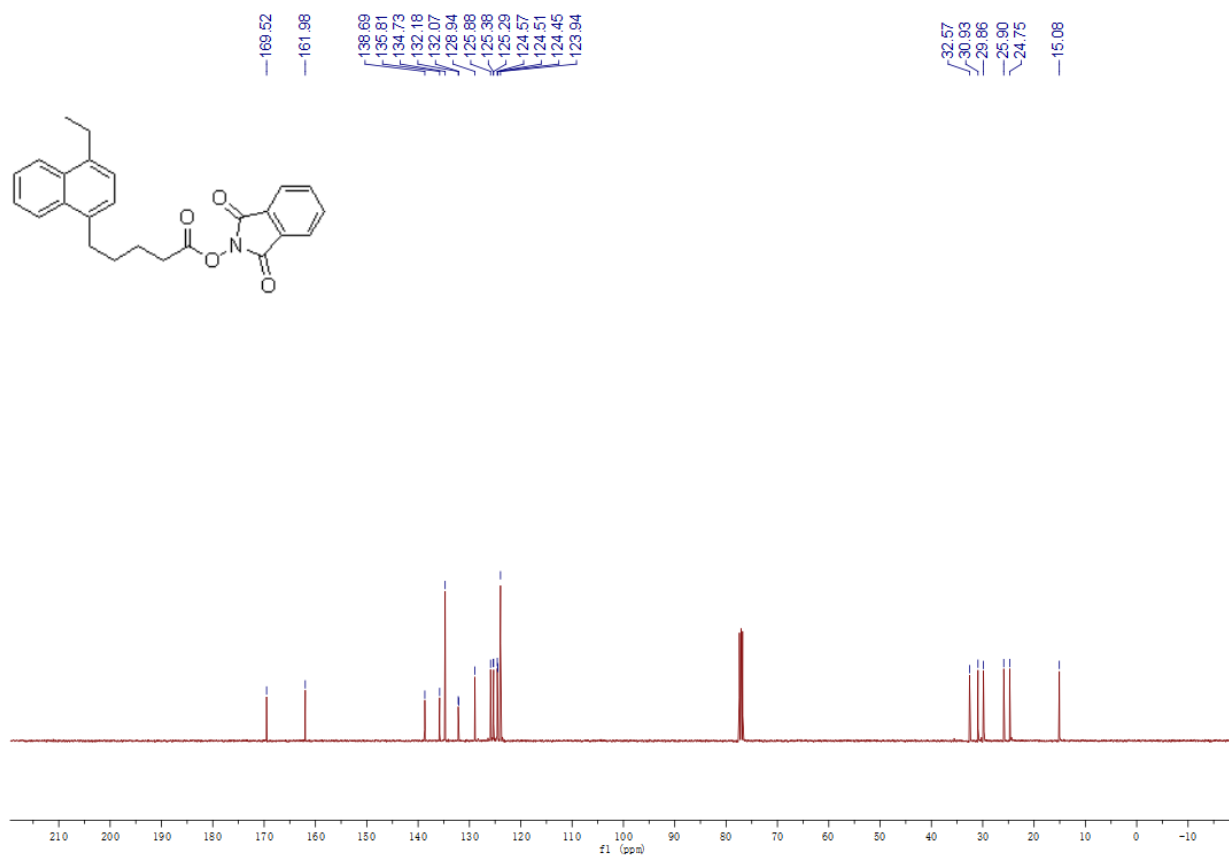
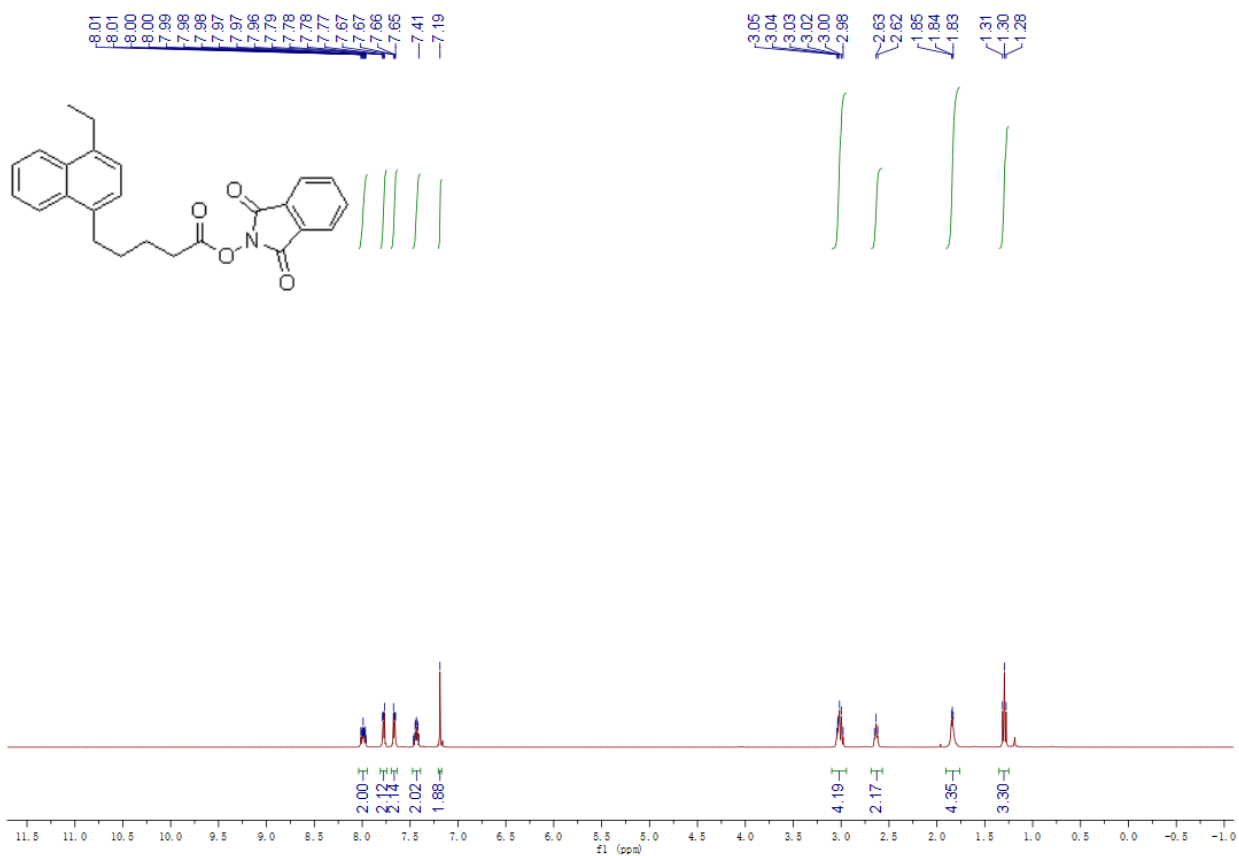












10 References

1. J. Wang, M. Shang, H. Lundberg, K. S. Feu, S. J. Hecker, T. Qin, D. G. Blackmond, P. S. Baran, *ACS Catal.* **2018**, *8*, 9537-9542.
2. J. T. Xia, X. P. Hu, *Org. Lett.* **2020**, *22*, 1102-1107.
3. M. Zhou, E. He, L. Zhang, J. Chen, Z. Zhang, Y. Liu, W. Zhang, *Org. Chem.Front.* **2019**, *6*, 3969-3972.
4. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.
5. Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8.
6. Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3–8.
7. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
8. Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7–13.