Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Dearomative Difunctionalization of arenes via Highly Selective Radical Relay Reactions

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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. ^{1}H and ^{13}C chemicals shifts (δ) are quoted in parts per million (ppm) against tetramethylsilane (TMS, δ = 0.00 ppm) and were internally referenced to residual $CHCl_3$ (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C) or DMSO (2.50 ppm for ^{1}H, 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 ^{1}H 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 ºC.

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.

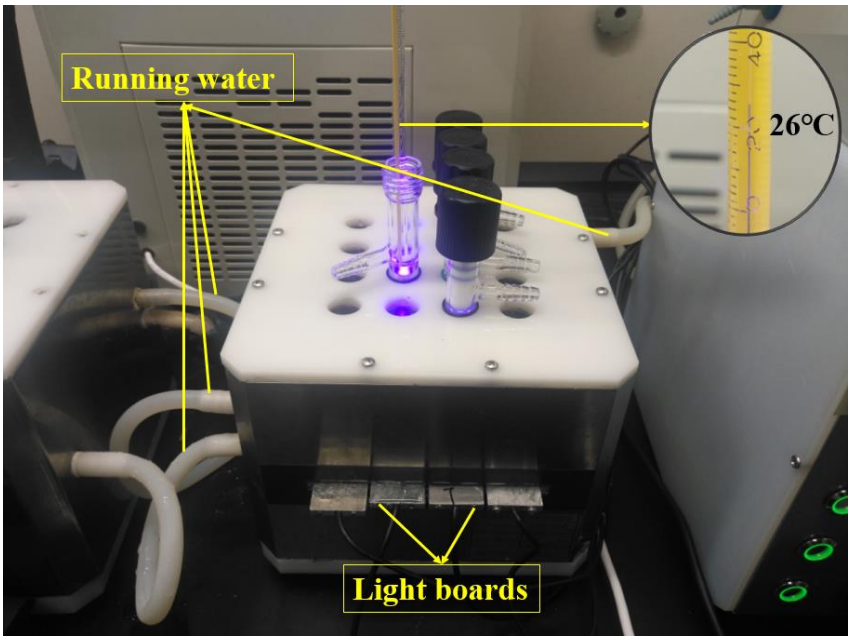
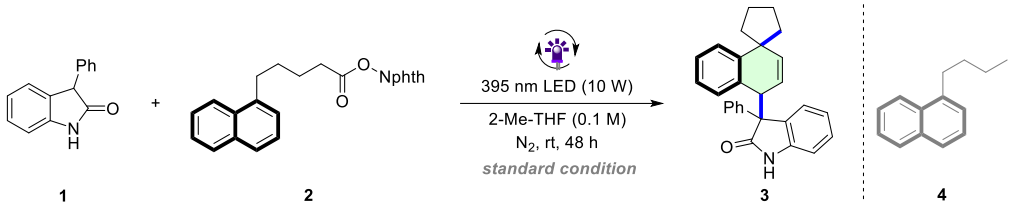


Figure S1. 16-hole parallel photoreactor (PhotoSyn 3.0)

3 Reaction Optimization and General Procedure

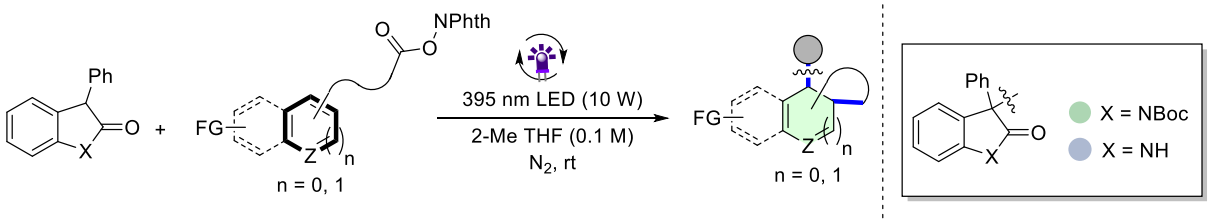
Table S1. Additional optimization of reaction conditions.[a]



Entry	Deviation from standard conditions	Yield[b] (%) **3**	Yield[b] (%) **4**
1[c]	no change	91	48
2[c]	CH_2Cl_2 instead of 2-Me-THF	trace	trace
3[c]	THF instead of 2-Me-THF	84	50
4[c]	CH_3CN instead of 2-Me-THF	79	54
5[c]	DMSO instead of 2-Me-THF	32	43
6[c]	410 nm instead of 395 nm	82	45
7[c]	415 nm instead of 395 nm	74	57
8[c]	440 nm instead of 395 nm	trace	trace
9[c]	10 °C instead of 25 °C	78	51
10[c]	40 °C instead of 25 °C	85	50
11[c]	2-Me-THF (0.05) instead of 2-Me-THF (0.1)	61	53
12[c]	2-Me-THF (0.2) instead of 2-Me-THF (0.1)	86	50
13[d]	3.0 equiv instead of 2.0 equiv **2**	88	34
14[e]	1.5 equiv instead of 2.0 equiv **2**	76	46
15[f]	1.0 equiv instead of 2.0 equiv **2**	62	33
16[f, g]	2.0 equiv **1**, 1.0 equiv **2**	54	36
17	no light, in dark	0	0
18	no light, 60 °C	0	0
19	Air instead of N_2	82	48

[a] Reactions were performed on 0.1 mmol scale in dry 2-Me-THF (1.0 mL) at room temperature for 48 h under nitrogen. [b] Isolated yield (**3** and **4**). NR = no reaction. w/o = without. [c] The yield of **3** is based on 0.1 mmol and the yield of **4** is based on 0.2 mmol. [d] the yield of **4** is based on 0.3 mmol, there's still **2** left until the reaction is complete. [e] the yield of **4** is based on 0.15 mmol. [f] the yield of **4** is based on 0.1 mmol. [g] There's still **1** left until the reaction is complete.

General procedure for dearomative reaction



Procedure A: An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the oxindoles

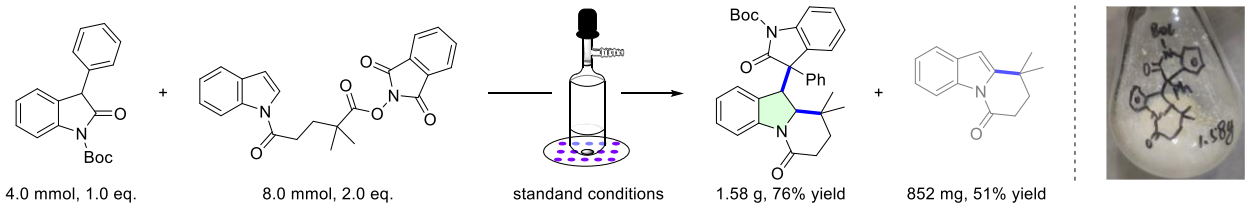
(0.1mmol, 1.0 equiv.) and the appropriate redox-active esters (0.2 mmol, 2.0 equiv). Then, the mixture of anhydrous 2-Me-THF (0.1M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated 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 Na_2SO_4, 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 Na_2SO_4, 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 Na_2SO_4, 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 Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/EA = 5/1) to afford the product.

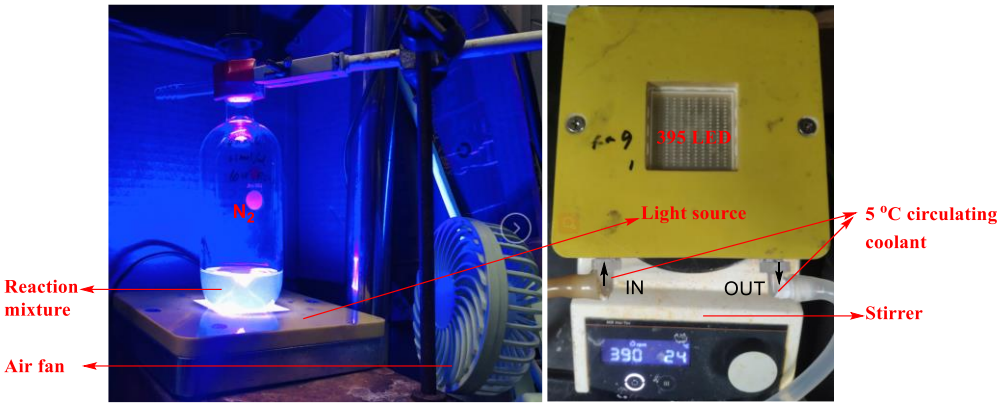


Figure S2. Photo-large-scale reactor

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 libratory 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 (2×103 cells/well) were seeded in 96-well plates. The next day, each compound tested was serially diluted in the appropriate medium, and 10 μL of the diluted solution containing the tested compound was added to the appropriate wells of the cell plate. After 36 h, 10 μl 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 % = (Atreated – Ablank) / (Acontrol – Ablank) × 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**, **53b**, **40**, **40a**, **40b**, **41**, **41a**, **41b**, **46**, **46a**, **46b** was shown in Table S2. Excitingly, compound **53b**, **40b**, **41b**, **46b** showed the most impressive antitumor activity. We also determined the inhibitory effect of **53b**, **40b**, **41b**, **46b** on human 293T (2×103 cells/well) was shown in Table S3. **53b** exhibits a side effect on these tumor cells with 36 μM IC_{50} values. Compared with HCT116 cells (at 22 μM 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.

Antitumor activity of HCT116 cells

Compounds	**34**	**53a**	**53b**	**40**	**40a**	**40b**
IC_{50} (μM)	>500	>150	22 ± 1.1	86 ± 1.0	>150	27 ± 1.0

Compounds	**41**	**41a**	**41b**	**46**	**46a**	**46b**
IC_{50} (μM)	>150	>150	19 ± 1.0	67 ± 1.0	>150	16 ± 1.0

Table S2. Antitumor activity of HCT116 cells

Antitumor activity of 293T cells

Compounds	**53b**	**40b**	**41b**	**46b**
IC_{50} (μM)	36 ± 1.1	14 ± 1.0	14 ± 1.0	15 ± 1.0

Table S3. Antitumor activity of 293T cells

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 mm^3), 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.

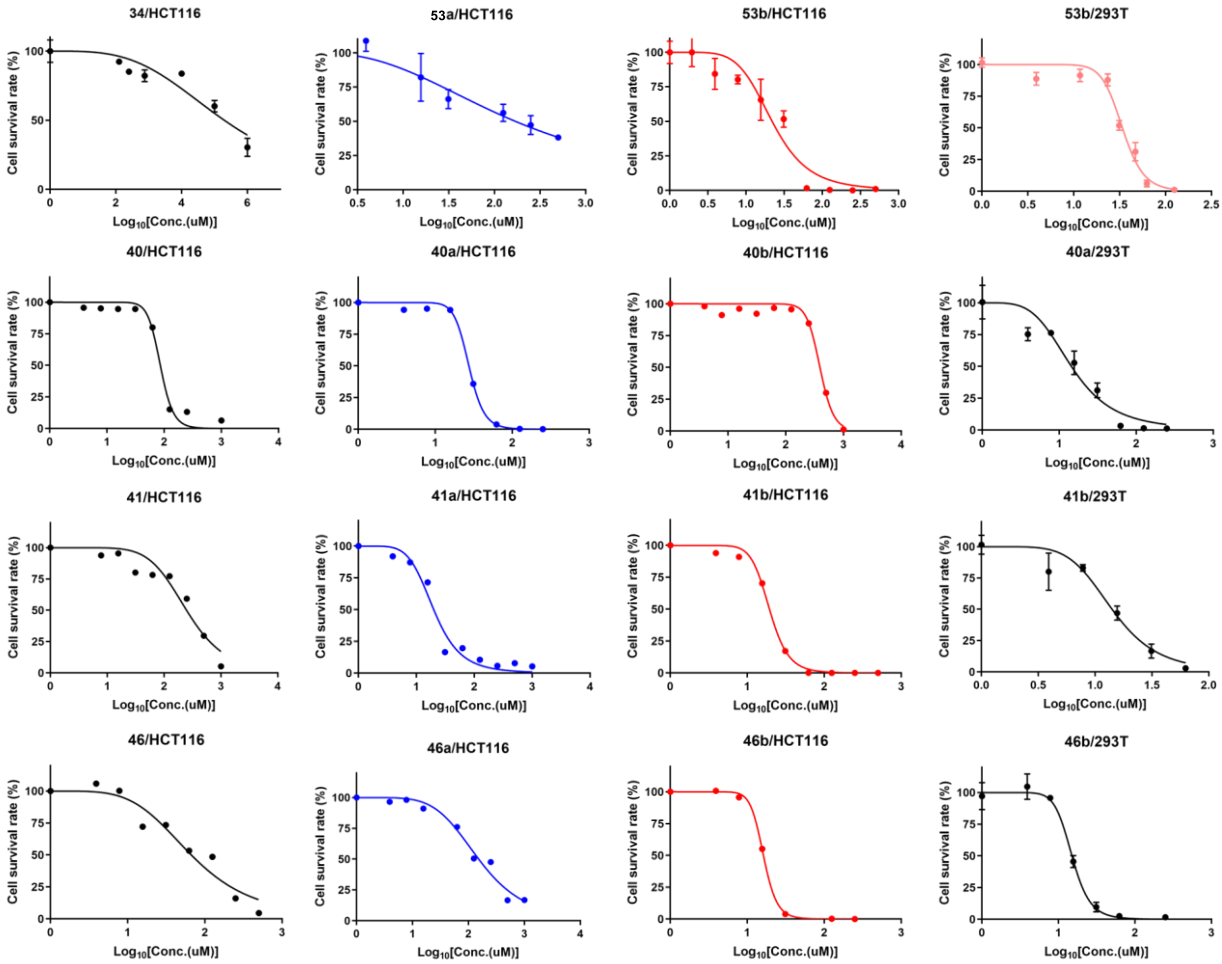


Figure S3. IC_{50} values of **34**, **53a**, **53b** for HCT116 and 293T cells

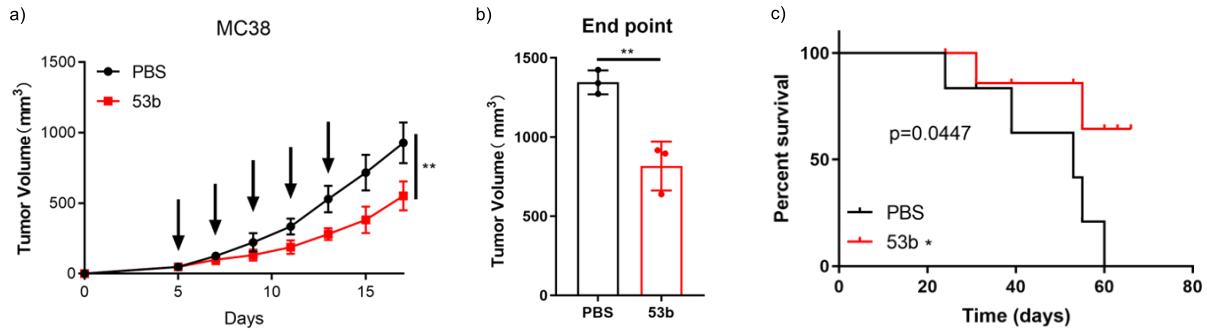


Figure S4. Tumor growth curves and survival cycles of mice with cancer in experimental and control groups

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.

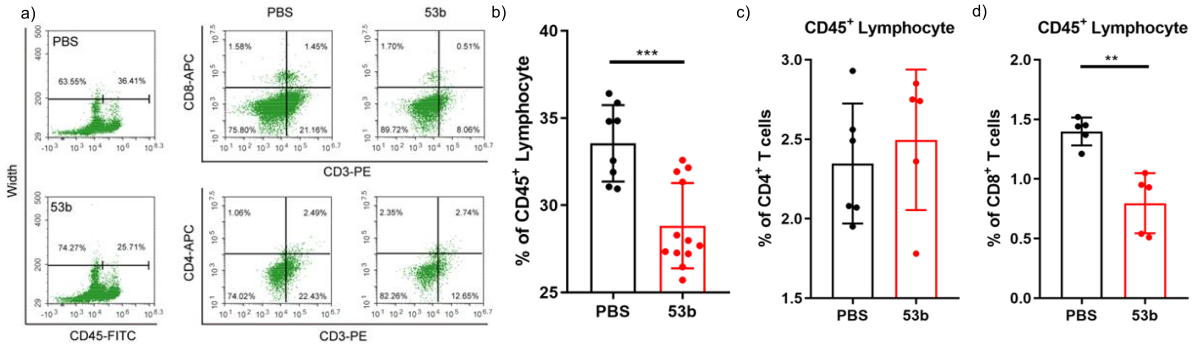


Figure S5. the number of tumor-infiltrating lymphocytes (TILs) after the last dose

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.

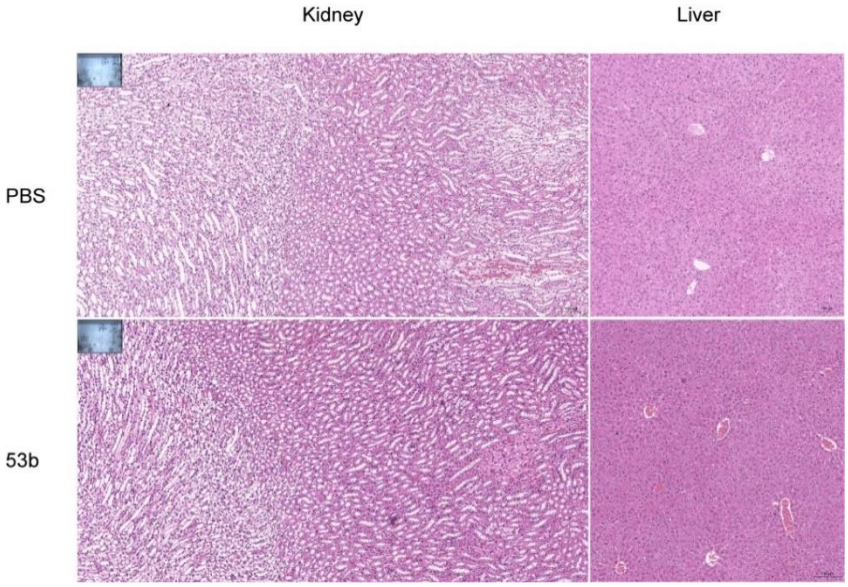
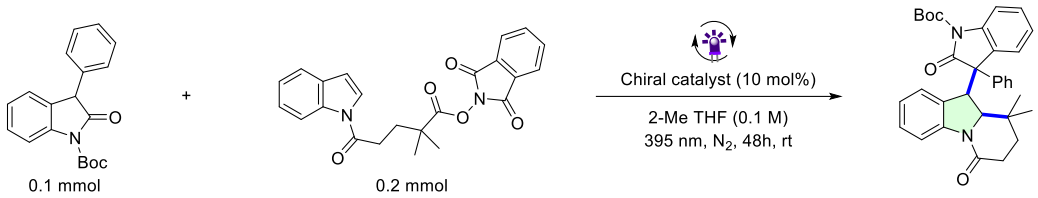
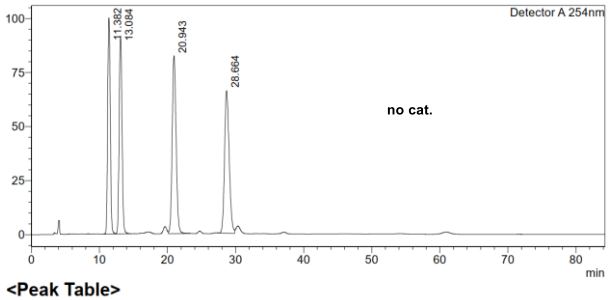


Figure S6. immunohistochemical analysis of the kidneys and liver of tumor-bearing mice for the toxicity of **53b**

4.3 Attempts at stereoselectivity of the reaction



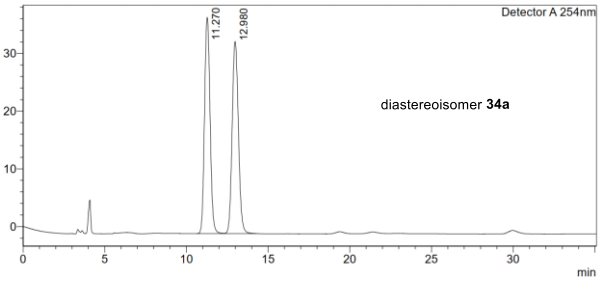
An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the oxindoles (0.1mmol, 1.0 equiv.), chiral catalyst (10 mol%) and the appropriate redox-active esters (0.2 mmol, 2.0 equiv). Then, the mixture of anhydrous 2-Me-THF (0.1M) was added in glove box. The tube was sealed with a screw 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 Na_2SO_4, 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>

Detector A 254nm

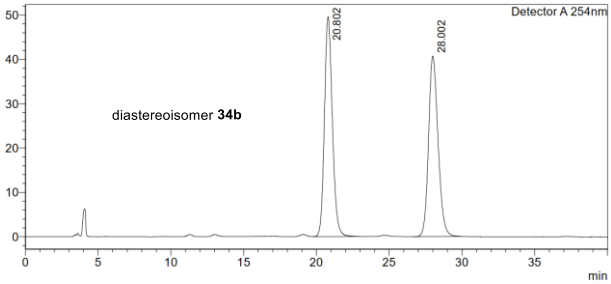
Peak#	Ret. Time	Area	Height	Area%	Conc.	Unit	Mark
1	11.382	2677729	100114	22.732	0.000		M
2	13.084	2698301	91305	22.906	0.000		V M
3	20.943	3291849	82171	27.945	0.000		M
4	28.664	3111830	65952	26.417	0.000		M
Total		11779709	339543	100.000			



<Peak Table>

Detector A 254nm

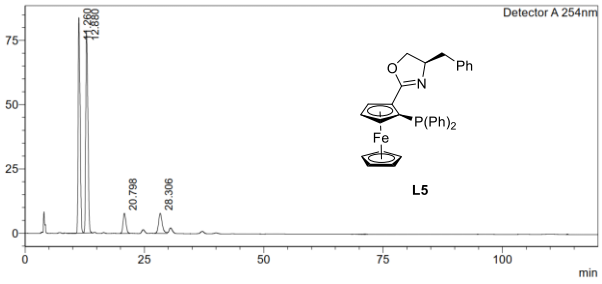
Peak#	Ret. Time	Area	Height	Area%	Conc.	Unit	Mark
1	11.270	886185	37467	49.980	0.000		
2	12.980	886898	33277	50.020	0.000		V
Total		1773083	70744	100.000			



<Peak Table>

Detector A 254nm

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			

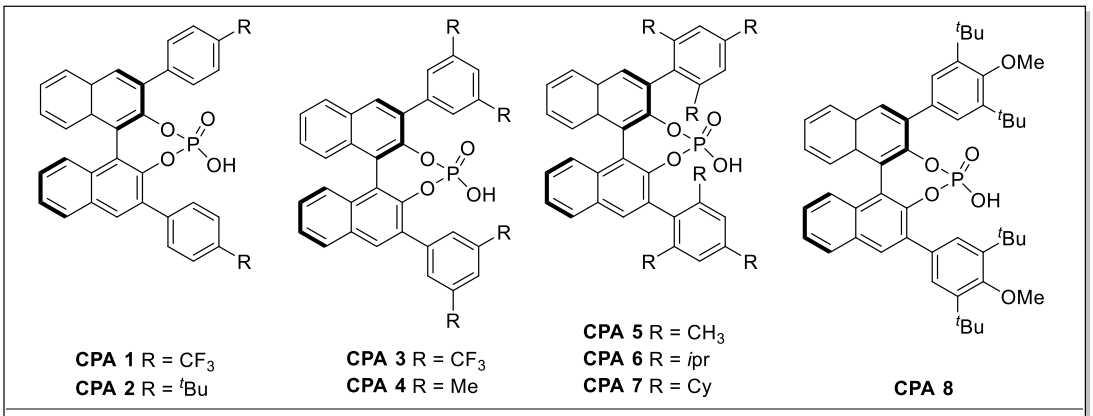


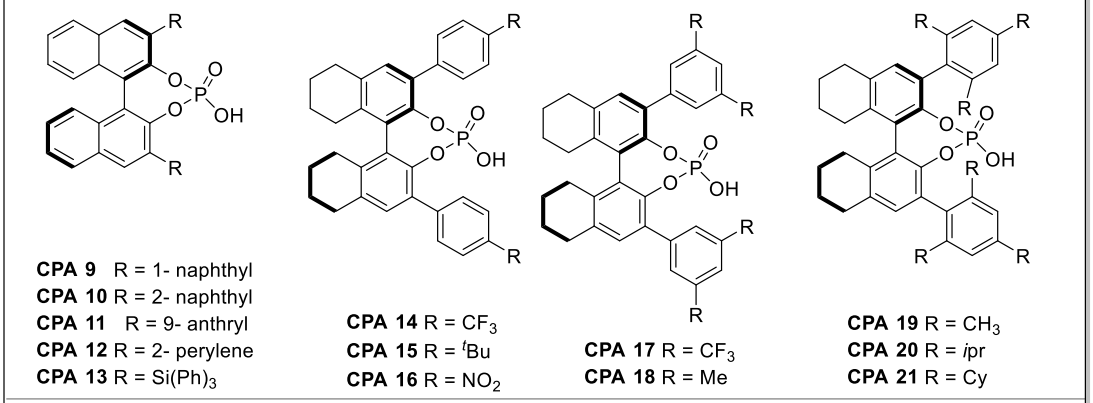
<Peak Table>

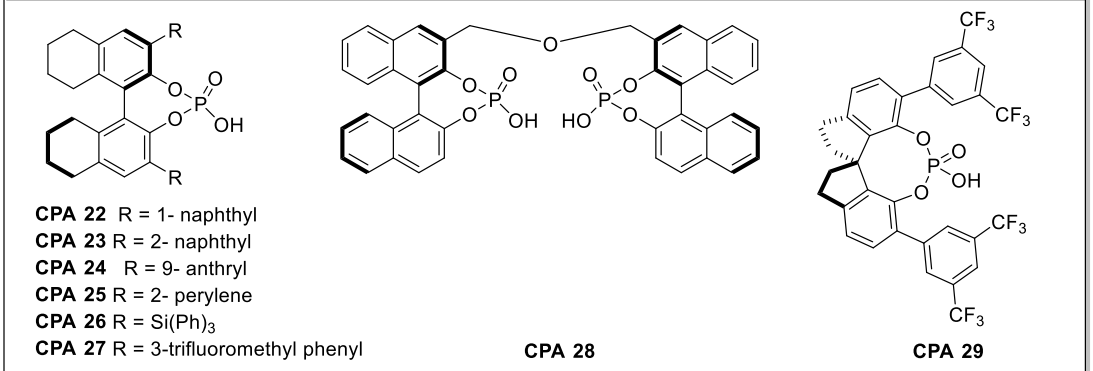
Detector A 254nm

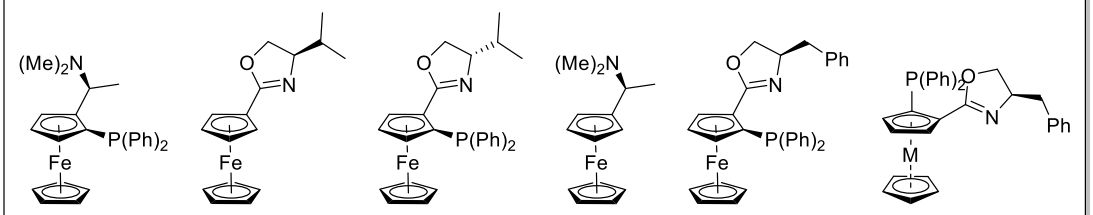
Peak#	Ret. Time	Area	Height	Area%	Conc.	Unit	Mark
1	11.260	2409684	83733	42.651	42.651		M
2	12.880	2490130	78466	44.075	44.075		V M
3	20.798	328398	7796	5.813	5.813		
4	28.306	421601	7865	7.462	7.462		
Total		5649813	177860	100.000			

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









product **3**	no cat.	**L1**	**L2**	**L3**	**L4**	**L5**	**L6**
Yield (%)	88	78	68	53	84	55	60
d.r.	1:1	4:1	1:1	7:1	4:1	7:1	1:3

Figure S8. Chiral ligand screening table

No *ee* value was obtained when the chiral phosphate catalysts (**CPA 1-29**) were added. However, the diastereoselectivity could be controlled when the chiral catalysts ferrocenes (**L1**-**L6**) were added, and **L3** and **L5** gave the best results, and the diastereoselectivity was reversed when **L6** was used. Diastereoisomers are isolated by flash chromatography (petroleum ether/EA = 8/1).

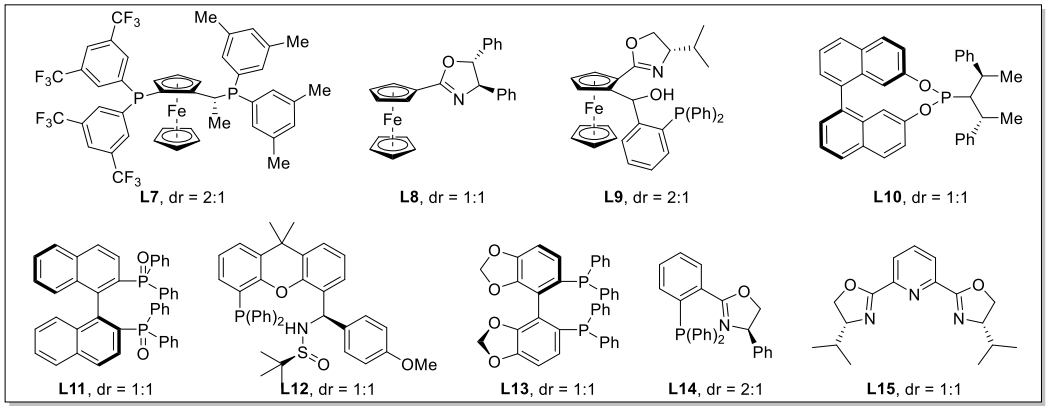


Figure S9. Other chiral ligand screening table

Based on **L3** and **L5**, we also added other ligand (**L7-L15**) into the reaction. Unfortunately, there is no better results than **L3** or **L5**.

4.4 Unsuccessful substrate

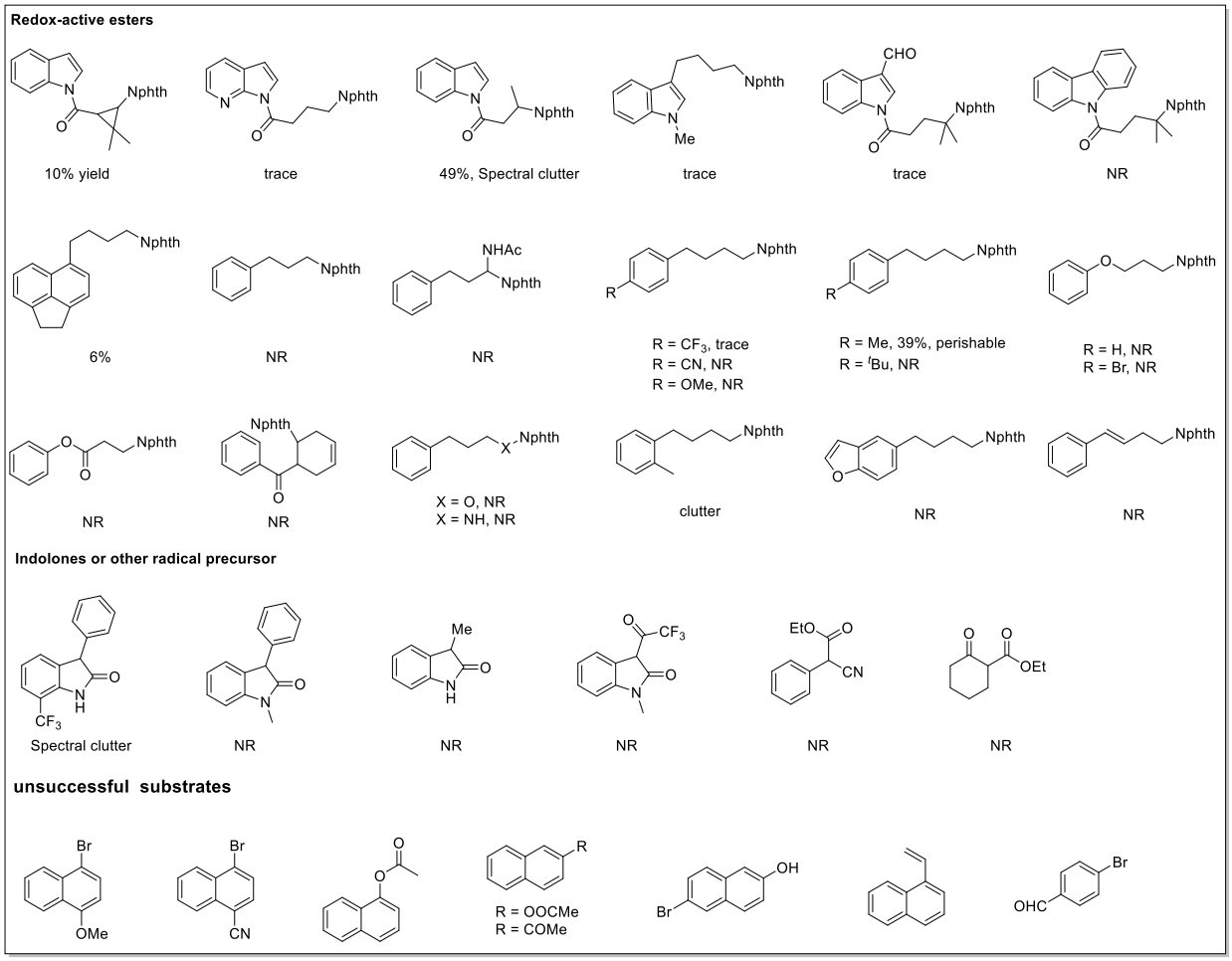


Figure S10. Unsuccessful substrates

5 Mechanistic Studies

5.1 UV-vis absorption spectrum

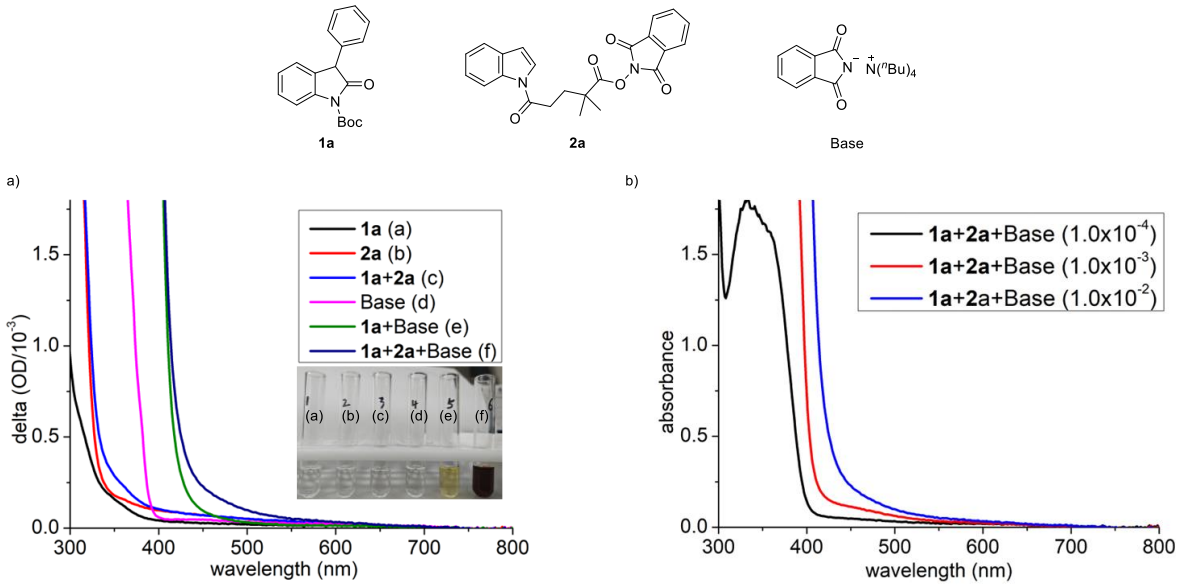
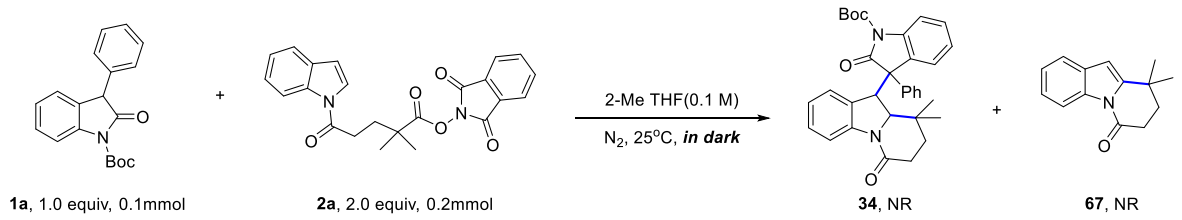


Figure S11. UV- Vis absorption spectra of Indolone **1a**, NHPI ester **2a** and base with 2-Me-THF (0.01 M)

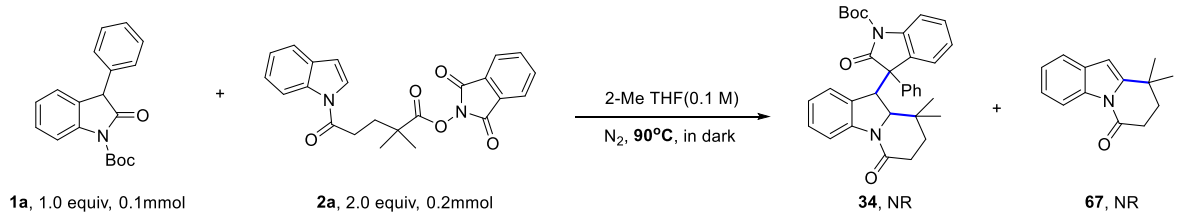
5.2 Control Experiments

5.2.1 Reaction in dark



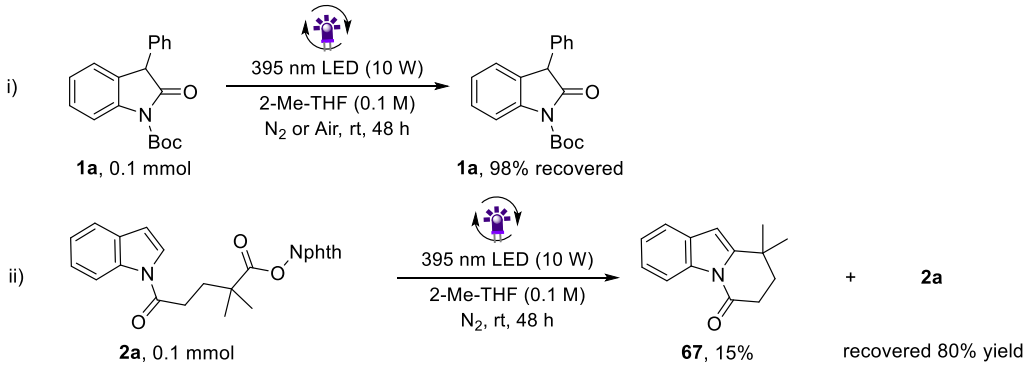
An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1a** (0.1mmol, 1.0 equiv.) and RAE **2a** (0.2 mmol, 2.0 equiv). Then, the solvent anhydrous 2-Me-THF (0.1M) was added in glove box. The tube was sealed with a screw cap and took out form glove box, and stirred in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

5.2.2 Reaction in dark at 90 ºC



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 at 90 ºC for 24 h. TLC analysis revealed that no reaction occurred.

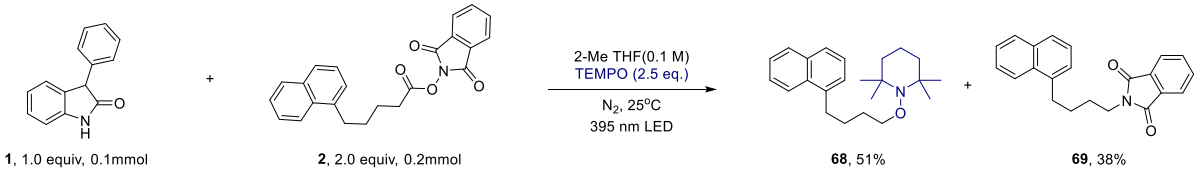
5.2.3 the photosensitivity of the two substrates



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the indolone **1a** (0.1mmol, 1.0 equiv) or only RAE **2a** (0.1 mmol, 1.0 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 was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10W LED lamp (395 nm) for 48 h. TLC analysis revealed that no reaction occurred.

5.2.4 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 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 Na_2SO_4, 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.

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{23}H_{33}NO$ $(M+H)^+$: 340.2635, found: 340.2635.

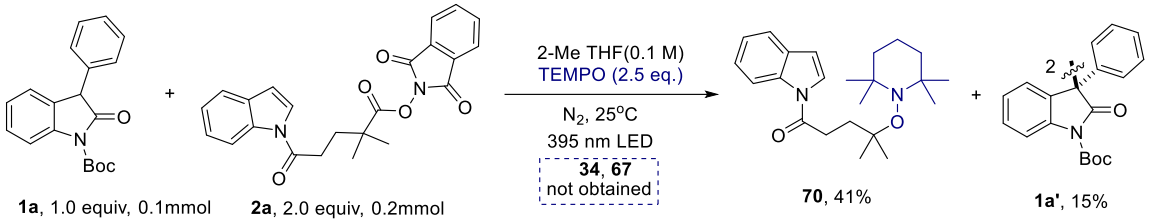
2-(4-(naphthalen-1-yl)butyl)isoindoline-1,3-dione (69)

Physical state: white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{22}H_{19}NO_2$ $(M+H)^+$: 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 Na_2SO_4, 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%).

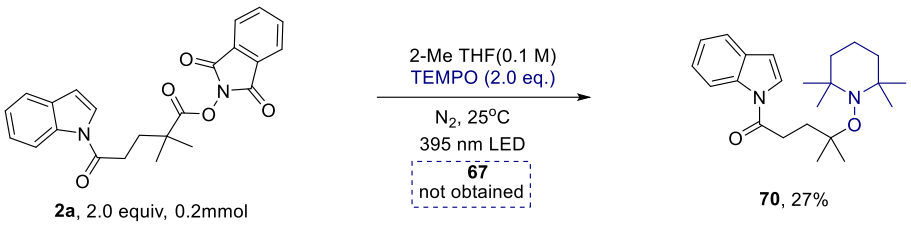
1-(1H-indol-1-yl)-4-methyl-4-((2,2,6,6-tetramethylpiperidin-1-yl) oxy) pentan-1-one (70)

Physical state: white solid.

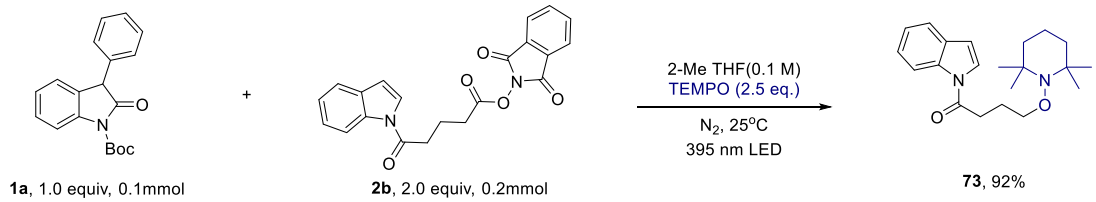
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 3.8 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 3.08 – 2.89 (m, 2H), 2.21 – 2.03 (m, 2H), 1.87 – 1.49 (m, 6H), 1.37 (s, 6H), 1.18 (s, 6H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{23}H_{34}N_2O_2$ $(M+Na)^+$: 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 Na_2SO_4, 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 **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 Na_2SO_4, 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, 92%).

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

Physical state: white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{21}H_{30}N_2O_2$ $(M+Na)^+$: 343.2380, found: 343.2382.

5.3 Adding catalytic base to the reaction

In order to indirectly prove the presence of base in the system, we added an additional catalytic amount of base to verify the reaction time and the change of the situation.

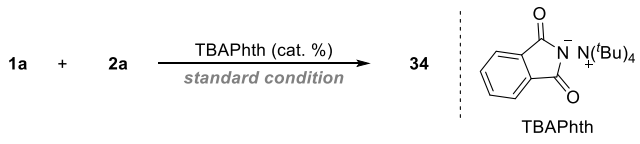
An oven-dried 10-mL Schlenk tube equipped with a stir was charged with the indolone **1** (0.1 mmol, 1.0 equiv), RAE **2** (0.2 mmol, 2.0 equiv) and catalytic base (TBAPhth). Then, the solvent anhydrous 2-Me-THF (0.1 M) was added in glove box. The tube was sealed with a screw cap and took out form glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10 W LED lamp (395 nm). 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 Na_2SO_4, filtered, and concentrated in vacuo. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether/ ethyl acetate 10: 1) provided adduct **3** and **4**.

Base (%)	1	2	5	10
Time (h)	40	33	25	16.5
3 (%)	84	73	58	52
4 (%)	46	43	42	40

Table S4 The time and yield of **3** and **4** adding catalytic base to the reaction

Figure S12 Pre - and post-reaction photos

Similar to the above steps, we performed the reaction of **1a** and **2a** with catalytic base.



base (%)	1	2	5	10
time (h)	36	29	21	14
34 (%)	82	75	61	56

Figure S13 The time and yield of **34** adding catalytic base to the reaction

5.4 Cyclic voltammogram

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line at room temperature. The working electrode was a platinum disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge.

5 mL of CH_3CN containing 0.1 M $^nBu_4NPF_6$ were poured into the electrochemical cell in all experiments. Concentration of a sample: 0.05 M. The scan rate is 0.1 V/s, ranging from 0 V to 3.0 V. The peak potentials vs. Ag/AgCl for used.

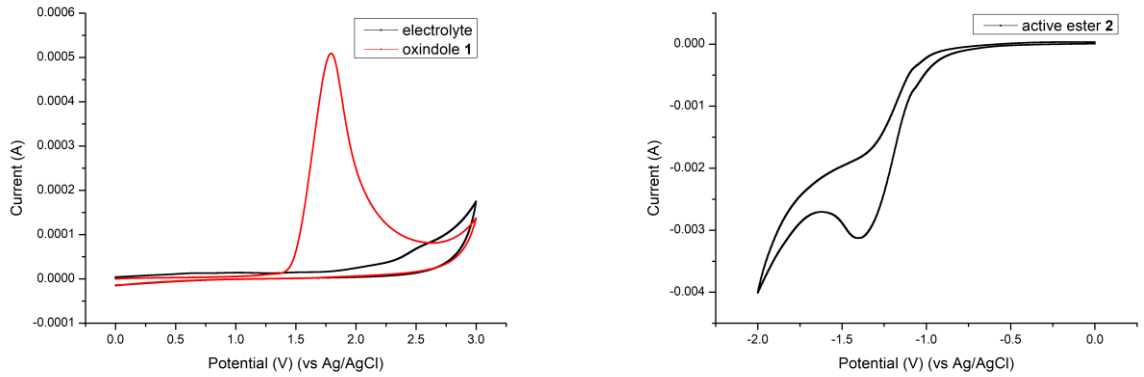
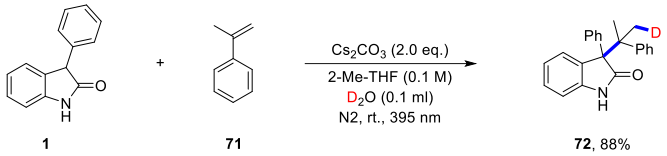


Figure 13. Cyclic voltammogram for oxindole **1** and active ester **2** (0.05 M) in (0.1 M) $TBAPF_6$ in CH_3CN

5.5 Proposed mechanism (evidence for the excited state enalate B* as a strong reducing reagent)



1 **71** **72**, 88%

An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the oxindole **1** (0.1 mmol, 1.0 equiv), 2-Phenyl-1-propene **71** (0.2 mmol, 2.0 equiv) and Cs_2CO_3 (0.2mmol, 2.0 equiv). Then, the solvent anhydrous 2-Me-THF (0.1 M) and D_2O (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 Na_2SO_4, 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%).

when we using the phenylethylene **71** instead of substrate **2** under standard conditions with 2.0 equiv. base, the reaction can still proceed and the product **72** was obtained in 88% yield.

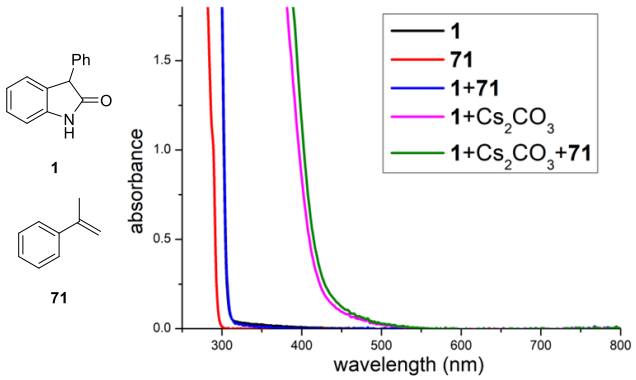


Figure S14. UV- Vis absorption spectra of **1**, **71** and Cs_2CO_3 with CH_3CN: H_2O = 9: 1 (V: V) (0.01 M)

UV-vis spectroscopic measurements on various combinations of **1**, **71** were performed. Oxindole **1** has no terminal absorption of 395 nm, also **71** does (Figure S12, dark and red line). Red-shift of the UV-vis absorption were not obviously observed for the mixture of oxindole **1** and alkene **71** (Figure S12, blue line), and there's no colour change. These results determined that no EDA complex is formed between **1** and **71**. Interestingly, colour change and terminal absorption redshift can be observed by adding base (TBAPhth) to the 2-MeTHF solution of **1** (Figure S12, pink line). The solution of **1**, **71** and base is darker and redshift more pronounced (Figure S12, green line).

Therefore, based on above control experiments and previous reports (*Angew. Chem. Int. Ed.* **2022**, *61*, e202210755.), In our study, we can't rule out another reaction path that is outlined in Figure S13. We speculated the $Phth^-$ acts as a base, abstracting the hydrogen atom from oxindole **A** to form the corresponding enolate **B**, and then upon visible light irradiation, enolate intermediate **B** is directly excited by light and generates the excited state **B*** as a strong reducing reagent that transfers an electron to the electron acceptor RAE **C**, leading to the radical pair of **E** and **F**. The intramolecular cyclization of transient alkyl radical **F** generates the cyclohexadienyl radical intermediates **G**. The longer-lived persistent oxindole radical **E** selectively couples with cyclohexadienyl radical intermediates **G** to afford the dearomatization product **H**.

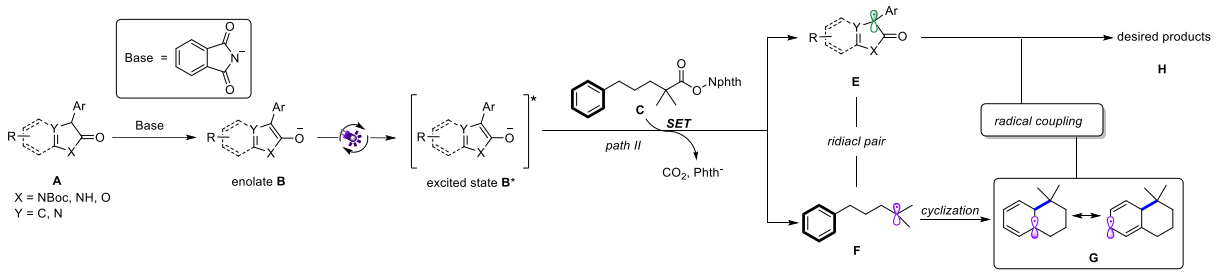
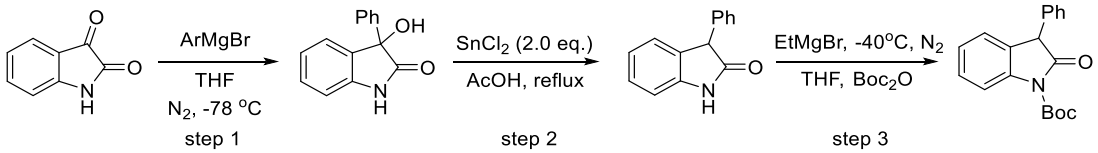


Figure S15. Proposed mechanism of the excited state enalate **B*** as a strong reducing reagent

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 N_2 atmosphere. After the formation of Grignard reagent (colorless to brownish-green), the reaction mixture was cooled to 0 ºC.

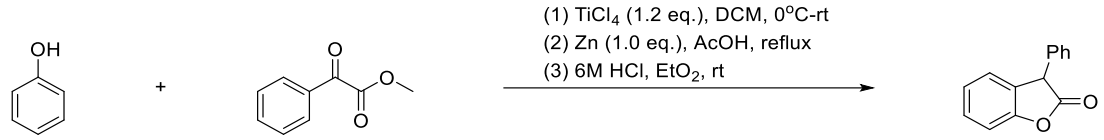
(2) Another 50 mL round-bottomed flask was equipped with a magnetic stir bar, to a stirring isatin (10.0 mmol) in dried THF (20 mL), then cooled to -40 ºC for 30 min. Previously obtained Grignard reagent in THF (2.0 equiv) was added dropwise to the reaction mixture under N_2 atmosphere, then the mixture 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 Na_2SO_4, 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 $SnCl_2$ (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 $NaHCO_3$, and brine. The organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was recrystallized (EtOAc/PE) to afford corresponding product as white solid.

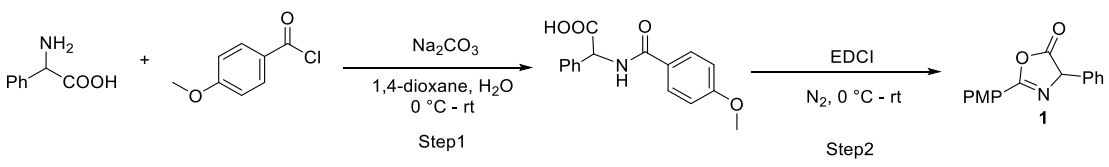
Step 3: a 25 mL round-bottomed flask was equipped with a magnetic stir bar, put the product obtained above (2.0 mmol) into flask and seal, and then replaced with nitrogen (3x), THF (8 mL) was added and stirred under 0 ^oC for 30 min. EtMgBr Grignard reagent in THF (2.0 equiv) was added dropwise to the reaction mixture, then stirred for 2h under 0^oC. A solution of Boc_2O (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 Na_2SO_4, 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 $TiCl_4$ (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 ºC, 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), Et_2O (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 Na_2SO_4, 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).

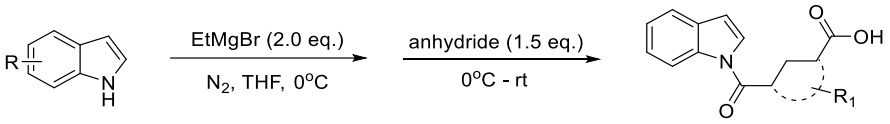
6.3 Synthetic route to oxazolone



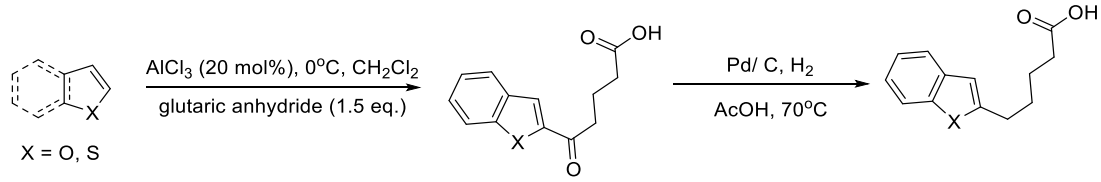
Step 1: 2-Amino-2-phenylacetic acid (1.0 equiv) and Na_2CO_3 (3.4 equiv) was added to round bottom flask equipped with a stirring bar. The reaction mixture was dissolved in 1,4-dioxane (0.50 M) and H_2O (0.18 M). After cooled to 0 °C, 4-methoxybenzoyl chloride (1.1 equiv) was added dropwise. The cooling 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



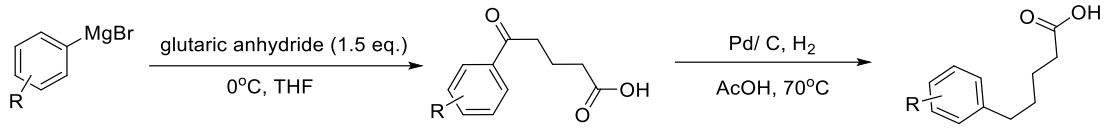
A 25 mL round-bottomed flask was equipped with a magnetic stir bar, put indoles (5.0 mmol) into flask and seal, and then replaced with nitrogen (3x), THF (8 mL) was added and stirred under 0 ºC for 30 min. EtMgBr Grignard reagent in THF (2.0 equiv) was added dropwise to the reaction mixture, then stirred for 2h under 0ºC. 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 H_2 ballon 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.

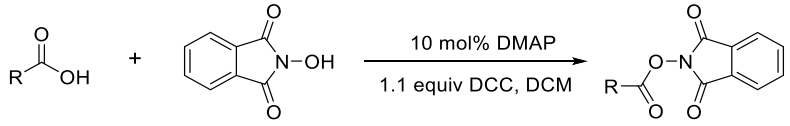


Preparation for Aryl Grignard reagent: same as above 6.1 (Step 1)

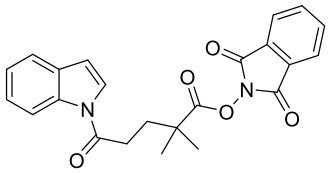
Under a nitrogen atmosphere, a mixture of glutaric anhydride (20 mmol) in anhydrous THF (20 ml) was stirred and cooled to -10 °C. A solution of Aryl Grignard reagent was added dropwise to the cooled mixture with stirring. After 5h at -10 °C, the reaction mixture was poured into ice-cooled 3.5 M HCl (50 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 H_2 ballon 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 addded 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)

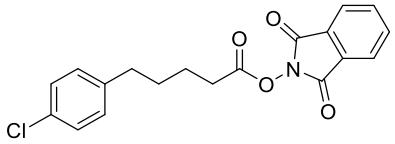


1,3-dioxoisoindolin-2-yl 5-(1H-indol-1-yl)-2,2-dimethyl-5-oxopentanoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{23}H_{20}N_2O_5$ $(M+Na)^+$: 427.1264, found: 427.1263.

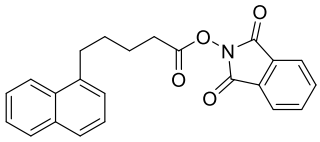


1,3-dioxoisoindolin-2-yl 5-(4-chlorophenyl) pentanoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{19}H_{16}ClNO_4$ $(M+Na)^+$: 380.0660, found: 380.0661.

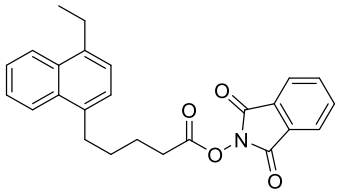


1,3-dioxoisoindolin-2-yl 5-(naphthalen-1-yl) pentanoate

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{23}H_{19}NO_4$ $(M+H)^+$: 374.1387, found: 374.1391.



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

^{1}H NMR (400 MHz, $CDCl_3$) 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).

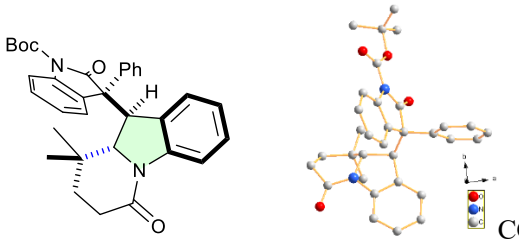
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.52, 161.98, 138.69, 135.81, 134.73, 132.18, 132.07, 128.94, 125.88, 125.38, 125.29, 124.57, 124.51, 124.45, 123.94, 32.57, 30.93, 29.86, 25.90, 24.75, 15.08.

HRMS (ESI) calcd for $C_{25}H_{23}NO_4$ $(M+Na)^+$: 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 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_α = 1.54178Å). 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]



CCDC 2218552

Bond precision: C-C = 0.0030 A Wavelength=1.54178

Cell: a=17.5642(3) b=14.7819(2) c=10.4569(2)
alpha=90 beta=90 gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	2714.95(8)	2714.95(8)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
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	1.279	1.279
Z	4	4
Mu (mm-1)	0.671	0.671
F000	1112.0	1112.0
F000'	1115.26	
h,k,lmax	22,18,13	21,18,13
Nref	5903[3117]	4474
Tmin,Tmax	0.745,0.800	0.744,0.963
Tmin'	0.700	

Correction method= # Reported T Limits: Tmin=0.744 Tmax=0.963
AbsCorr = NUMERICAL

Data completeness= 1.44/0.76 Theta(max)= 79.526

R(reflections)= 0.0352(4340) wR2(reflections)= 0.0894(4474)
S = 1.047 Npar= 357

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
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 18 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 4 Note

Alert level G
PLAT792_ALERT_1_G Model has Chirality at C5 (Polar SPGR) S Verify
PLAT792_ALERT_1_G Model has Chirality at C6 (Polar SPGR) R Verify
PLAT792_ALERT_1_G Model has Chirality at C22 (Polar SPGR) S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 35 Note
PLAT915_ALERT_3_G No Flack x Check Done: Low Friedel Pair Coverage 51 %
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 9 Info

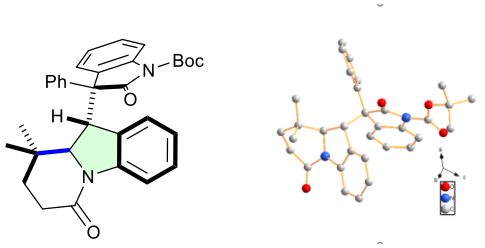
0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

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

Figure 16. X-ray crystallography data of single crystal **34a**

Single crystal **34b**:

The colourless crystal in block-shape, with approximate dimensions of 0.146 × 0.282 × 0.424 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 (Kα = 1.54178Å). 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]



CCDC 2235965

Datablock: zhk016

Bond precision: C-C = 0.0020 A 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)= 0.1022(5100)

S = 1.058 Npar= 358

The following ALERTS were generated. Each ALERT has the format
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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
0 **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

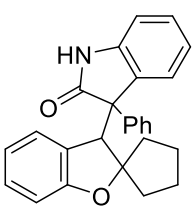
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative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

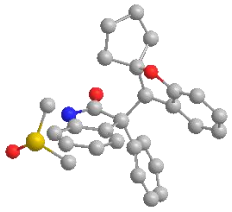
Figure 17. X-ray crystallography data of single crystal **34b**

Single crystal **21**:

The colourless crystal in block-shape, with approximate dimensions of 0.187 × 0.187 × 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 (Kα = 1.54178Å). 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]





CCDC 2235966

Datablock: zhk013

```
Bond precision:   C-C = 0.0021 A          Wavelength=1.54178

Cell:             a=10.7923(2)     b=15.0923(3)      c=14.4236(3)
                  alpha=90         beta=93.717(1)    gamma=90
Temperature:      173 K

                  Calculated                  Reported
Volume            2344.38(8)                  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
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The following ALERTS were generated. Each ALERT has the format
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Click on the hyperlinks for more details of the test.
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Alert level C

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PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of        S1S Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & 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
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Alert level G

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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
```
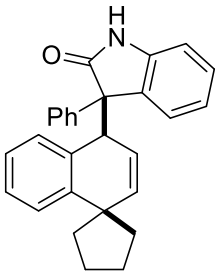

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  11 ALERT level G = General information/check it is not something unexpected

   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 18. X-ray crystallography data of single crystal **21**

8 Analytical Data of Compounds

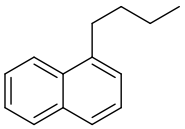
***Note**: The unknown impurity: Around 1.56 ppm (water peak) and 1.00 ppm –1.42 ppm in NMR are respectively from the $CDCl_3$ and eluent (petroleum ether), which do not affect the yield of the product.*

3-phenyl-3-(4'H-spiro[cyclopentane-1,1'-naphthalen]-4'-yl)indolin-2-one (**3**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 35.2 mg (91%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, CDCl3)** 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, CDCl3)** 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 $C_{28}H_{25}NO$ $(M+Na)^+$: 414.1828, found: 414.1833.

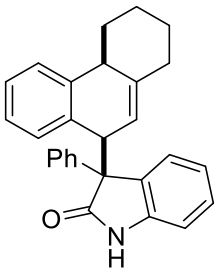
1-butylnaphthalene (4)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.3, 1H), 7.88 (d, J = 8.1, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H), 7.35 (d, J = 5.7 Hz, 1H), 3.10 (t, 2H), 1.83 – 1.71 (m, 2H), 1.54 – 1.34 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.03, 133.93, 131.96, 128.77, 126.41, 125.88, 125.63, 125.56, 125.38, 123.95, 33.06, 32.86, 22.93, 14.06.

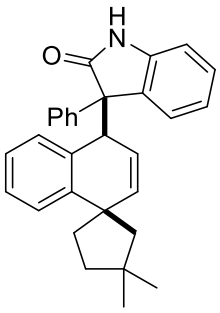
This data is consistent with those reported in the literature (*Angew. Chem. Int. Ed.*, **2021**, 60, 10632–10636).

3-(1,2,3,4,4a,9-hexahydrophenanthren-9-yl)-3-phenylindolin-2-one (**5**)



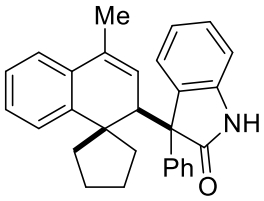
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 33.6 mg (86%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.02 (s, 0.25H), 8.98 (s, 0.25H), 8.94 (s, 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 $C_{28}H_{25}NO$ $(M+Na)^+$: 414.1828, found: 414.1832.

3-(3,3-dimethyl-4'H-spiro[cyclopentane-1,1'-naphthalen]-4'-yl)-3-phenylindolin-2-one (**6**)



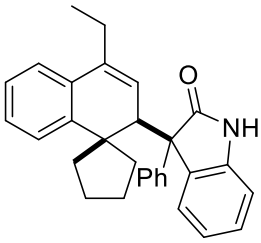
Following the **procedure B** or **C** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 26.0 mg (62%) or 49% of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6** = 1/1**)** δ 10.50 (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, $CDCl_3$/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 $C_{30}H_{29}NO$ $(M+H)^+$: 420.2322, found: 420.2324.

3-(4'-methyl-2'H-spiro[cyclopentane-1,1'-naphthalen]-2'-yl)-3-phenylindolin-2-one (**7**)



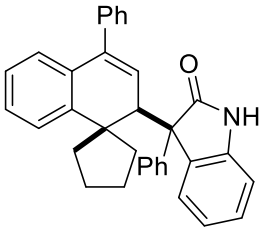
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 25.1 mg (62%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, DMSO)** δ 10.44 (s, 0.5H), 10.37 (s, 0.5H), 7.69 – 7.47 (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 $C_{29}H_{27}NO$ $(M+Na)^+$: 428.1985, found: 428.1984.

3-(4'-ethyl-2'H-spiro[cyclopentane-1,1'-naphthalen]-2'-yl)-3-phenylindolin-2-one (**8**)



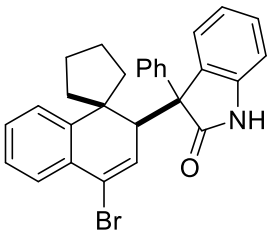
Following the **procedure B** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 21.0 mg (50%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.77 – 8.34 (m, 1H), 7.78 – 7.58 (m, 1H), 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 $C_{30}H_{29}NO$ $(M+H)^+$: 420.2322, found: 420.2321.

3-phenyl-3-(4'-phenyl-2'H-spiro[cyclopentane-1,1'-naphthalen]-2'-yl)indolin-2-one (**9**)



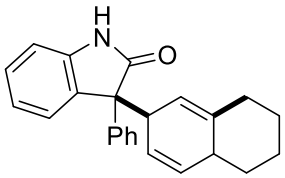
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 24.8 mg (53%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.56 (s, 0.5H), 10.43 (s, 0.5H), 7.62 (s, 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, 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 $C_{34}H_{29}NO$ $(M+H)^+$: 468.2322, found: 468.2321.

3-(4'-bromo-2'H-spiro[cyclopentane-1,1'-naphthalen]-2'-yl)-3-phenylindolin-2-one (**10**)



Following the **procedure B** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 20.0 mg (42%) of the title compound. **Physical state:** white solid. **^{1}H 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 $C_{28}H_{24}BrNO$ $(M+Na)^+$: 492.0933, found: 492.0934.

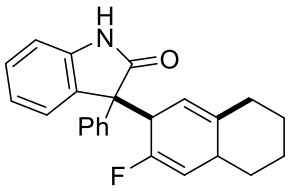
3-(2,4a,5,6,7,8-hexahydronaphthalen-2-yl)-3-phenylindolin-2-one (**11**)



Following the **procedure B** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 16.7 mg (49%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{24}H_{23}NO$ $(M+H)^+$: 342.1852, found: 342.1858.

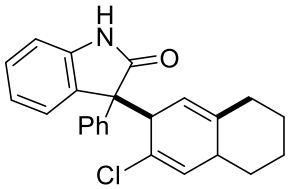
3-(3-fluoro-2,4a,5,6,7,8-hexahydronaphthalen-2-yl)-3-phenylindolin-2-one (**12**)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.7 mg (52%) of the title compound. **Physical state:**



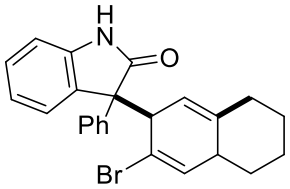
white solid. **^{1}H NMR (400 MHz, DMSO)** δ 10.57 (s, 0.20H), 10.53 (s, 0.19H), 10.36 (s, 0.25H), 10.34 (s, 0.25H), 7.47 – 6.81 (m, 9H), 5.36 – 4.84 (m, 2H), 4.38 – 4.03 (m, 1H), 2.61 (m, 0.5H), 2.47 – 2.15 (m, 0.6H), 2.13 – 0.80 (m, 8H). **^{13}C NMR (101 MHz, DMSO)** δ 178.64, 178.49, 178.01, 177.91, 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. **HRMS (ESI)** calcd for $C_{24}H_{22}FNO$ $(M+H)^+$: 360.1758, found: 360.1759.

3-(3-chloro-2,4a,5,6,7,8-hexahydronaphthalen-2-yl)-3-phenylindolin-2-one (**13**)



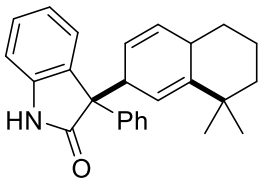
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 20.3 mg (54%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 – 8.24 (m, 1H), 7.55 – 7.40 (m, 1H), 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). **^{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, 128.75, 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 $C_{24}H_{22}ClNO$ $(M+Na)^+$: 376.1463, found: 376.1462.

3-(3-bromo-2,4a,5,6,7,8-hexahydronaphthalen-2-yl)-3-phenylindolin-2-one (**14**)



Following the **procedure B** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 17.2 mg (41%) of the title compound. **Physical state:** white solid. **^{1}H 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 $C_{24}H_{22}BrNO$ $(M+H)^+$: 420.0958, found: 420.0952.

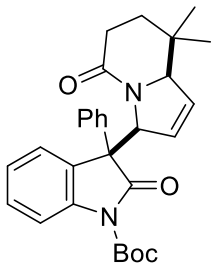
3-(8,8-dimethyl-2,4a,5,6,7,8-hexahydronaphthalen-2-yl)-3-phenylindolin-2-one (**15**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 20.7 mg (56%) of the title compound. **Physical state:** white solid. **^{1}H 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

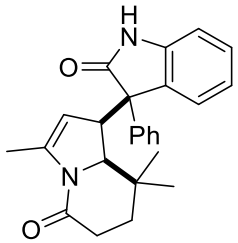
– 3.90 (m, 1H), 2.31 – 2.17 (m, 0.5H), 2.11 – 1.97 (m, 1H), 1.97 – 1.77 (m, 1H), 1.73 – 1.57 (m, 1H), 1.55 – 1.41 (m, 0.8H), 1.40 – 1.16 (m, 3.4H), 0.88 (s, 0.75H), 0.87 (s, 0.75H), 0.81 (s, 0.75H), 0.81 (s, 0.75H), 0.58 (s, 0.75H), 0.57 (s, 0.75H), 0.27 (s, 0.75H), 0.23 (s, 0.75H). **^{13}C NMR (101 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 $C_{26}H_{27}NO$ $(M+Na)^+$: 392.1985, found: 392.1986.

tert-butyl 3-(8,8-dimethyl-5-oxo-3,5,6,7,8,8a-hexahydroindolizin-3-yl)-2-oxo-3-phenylindoline-1-carboxylate (**16**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 43.0 mg (91%) of the title compound. **Physical state:** white solid. **^{1}H 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.

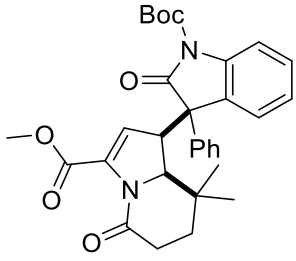
3-phenyl-3-(3,8,8-trimethyl-5-oxo-1,5,6,7,8,8a-hexahydroindolizin-1-yl) indolin-2-one (**17**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 14.4 mg (39%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

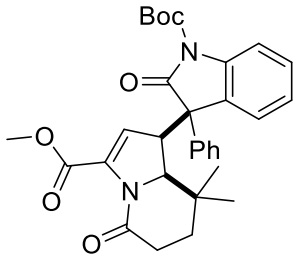
tert-butyl 3-(3-(methoxycarbonyl)-8,8-dimethyl-5-oxo-1,5,6,7,8,8a-hexahydroindolizin-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (**18**)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.0 mg (34%) of the title compound. **Physical state:**



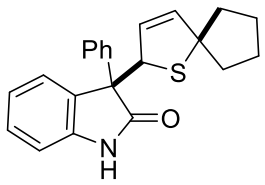
white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.42 (m, 1H), 7.38 – 7.28 (m, 7H), 5.29 (d, *J* = 2.5 Hz, 1H), 4.40 – 4.30 (m, 1H), 3.80 (s, 3H), 3.13 (d, *J* = 6.0 Hz, 1H), 2.30 – 2.19 (m, 2H), 1.58 (s, 9H), 1.52 – 1.42 (m, 2H), 0.93 (s, 3H), 0.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

tert-butyl 3-(3-(methoxycarbonyl)-8,8-dimethyl-5-oxo-1,5,6,7,8,8a-hexahydroindolizin-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (**18**)



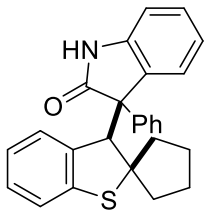
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.0 mg (34%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 – 7.79 (m, 1H), 7.78 – 7.58 (m, 2H), 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 $C_{31}H_{34}N_2O_6$ $(M+Na)^+$: 553.2309, found: 553.2312.

3-phenyl-3-(1-thiaspiro[4.4]non-3-en-2-yl)indolin-2-one (**19**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 25.6 mg (74%) of the title compound. **Physical state:** white solid. **^{1}H 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 $C_{22}H_{21}NOS$ $(M+Na)^+$: 370.1236, found: 370.1243.

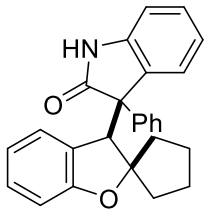
3-phenyl-3-(3H-spiro[benzo[b]thiophene-2,1'-cyclopentan]-3-yl)indolin-2-one (**20**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 25.5 mg (64%) of the title compound. **Physical state:** white solid. **^{1}H 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,

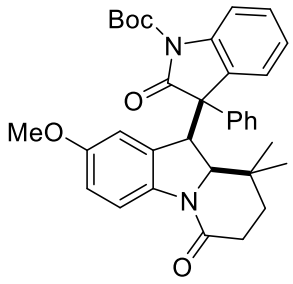
128.85, 128.71, 128.64, 128.52, 128.42, 128.27, 128.12, 127.75, 127.61, 127.14, 126.39, 123.77, 123.28, 122.50, 122.42, 121.09, 120.62, 110.31, 109.51, 71.46, 71.36, 61.34, 59.95, 58.81, 45.58, 34.43, 31.89, 25.05, 24.76, 21.25, 21.00. **HRMS (ESI)** calcd for $C_{26}H_{23}NOS$ $(M+Na)^+$: 420.1393, found: 420.1391.

3-phenyl-3-(3H-spiro[benzofuran-2,1'-cyclopentan]-3-yl)indolin-2-one (**21**)



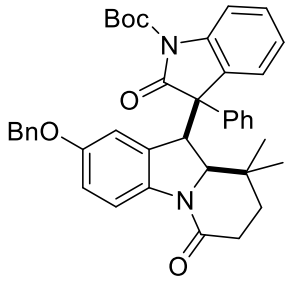
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 29.1 mg (76%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, DMSO)** δ 10.66 (s, 0.7H), 10.58 (s, 0.5H), 7.56 (s, 0.7H), 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.

tert-butyl 3-(2-methoxy-9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydro-pyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**22**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 47.0 mg (85%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

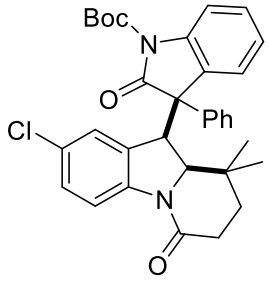
tert-butyl 3-(2-(benzyloxy)-9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**23**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 53.3 mg (85%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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,

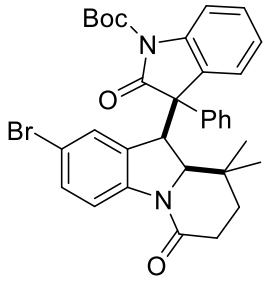
1.5H), 0.67 (s, 1.5H), 0.56 (s, 1.5H), 0.49 (s, 1.5H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.37, 174.76, 169.45, 169.23, 155.14, 154.37, 148.91, 148.76, 139.95, 139.39, 138.97, 137.71, 137.18, 136.87, 136.84, 135.30, 129.89, 129.34, 129.21, 129.09, 128.94, 128.70, 128.58, 128.48, 128.45, 128.37, 128.26, 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 $C_{40}H_{40}N_2O_5$ $(M+Na)^+$: 651.2829, found: 651.2834.

tert-butyl 3-(2-chloro-9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**24**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 49.7 mg (89%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

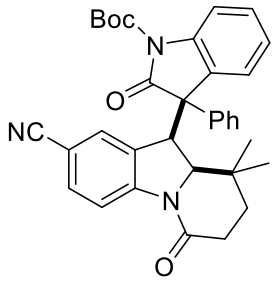
tert-butyl 3-(2-bromo-9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**25**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 48.1 mg (80%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{33}H_{33}BrN_2O_4$ $(M+Na)^+$: 623.1516, found: 623.1519.

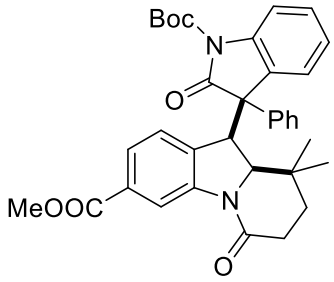
tert-butyl 3-(2-cyano-9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**26**)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 50.9 mg (93%) of the title compound. **Physical state:**



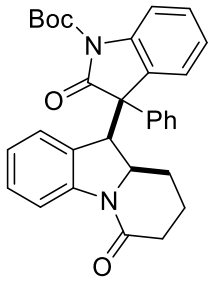
white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 8.5 Hz, 0.4H), 7.92 (d, *J* = 8.4 Hz, 0.6H), 7.88 (d, *J* = 8.2 Hz, 0.4H), 7.76 – 7.70 (m, 1.2H), 7.61 (d, *J* = 8.1 Hz, 0.6H), 7.58 – 7.49 (m, 1H), 7.46 – 7.27 (m, 5H), 7.20 (t, *J* = 8.5 Hz, 0.6H), 7.08 (t, *J* = 8.0 Hz, 0.6H), 7.01 (t, *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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{333}N_3O_4$ $(M+H)^+$: 548.2544, found: 548.2548.

methyl 10-(1-(tert-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl)-9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indole-3-carboxylate (**27**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 48.6 mg (84%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{35}H_{36}N_2O_6$ $(M+Na)^+$: 603.2466, found: 603.2471.

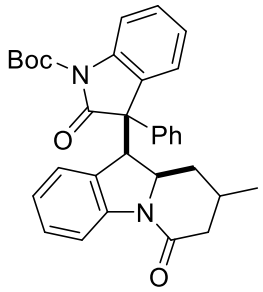
tert-butyl 2-oxo-3-(6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-3-phenylindoline-1-carboxylate (**28**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 37.5 mg (76%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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,

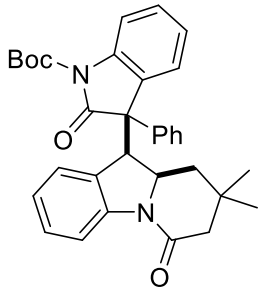
54.56, 51.30, 51.12, 36.11, 32.55, 32.24, 32.13, 31.96, 29.80, 29.36, 28.12, 28.08, 27.88, 27.79, 26.66, 23.77, 21.46, 21.10, 20.99, 19.31, 18.08, 14.24. **HRMS (ESI)** calcd for $C_{31}H_{30}N_2O_4$ $(M+Na)^+$: 517.2098, found: 517.2101.

tert-butyl 3-(8-methyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**29**)



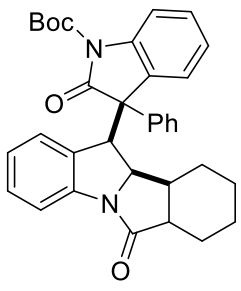
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 28.2 mg (55%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 – 7.96 (m, 0.8H), 7.95 – 7.72 (m, 0.9H), 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

tert-butyl 3-(8,8-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**30**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 32.9 mg (63%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

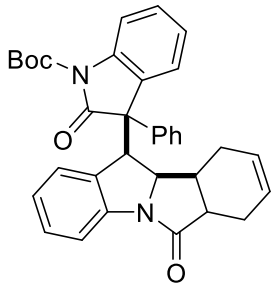
tert-butyl 2-oxo-3-(6-oxo-6a,7,8,9,10,10a,10b,11-octahydro-6H-isoindolo[2,1-a]indol-11-yl)-3-phenylindoline-1-carboxylate (**31**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 33.0 mg (62%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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,

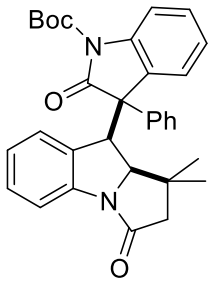
1H), 2.42 – 2.04 (m, 2H), 1.88 – 1.68 (m, 2H), 1.67 (s, 4.5H), 1.64 (s, 4.5H), 1.62 – 1.46 (m, 1H), 1.46 – 1.33 (m, 1H) 1.24 – 0.75 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.14, 175.37, 174.60, 173.05, 148.97, 148.84, 141.45, 139.80, 137.71, 137.60, 132.09, 131.63, 129.19, 128.93, 128.85, 128.71, 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 $C_{34}H_{34}N_2O_{44}$ $(M+Na)^+$: 557.2411, found: 557.2410.

tert-butyl 2-oxo-3-(6-oxo-6a,7,10,10a,10b,11-hexahydro-6H-isoindolo[2,1-a]indol-11-yl)-3-phenylindoline-1-carboxylate (**32**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 27.4 mg (51%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{32}N_2O_4$ $(M+H)^+$: 533.2435, found: 533.2444.

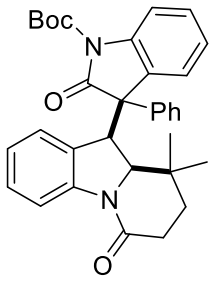
tert-butyl 3-(1,1-dimethyl-3-oxo-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-oxo-3-phenylindoline-1-carboxylate (**33**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 30.2 mg (59%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{32}H_{32}N_2O_4$ $(M+Na)^+$: 531.2254, found: 531.2255.

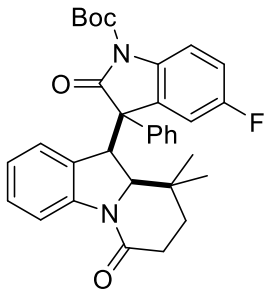
tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1, 2-a] indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**34**)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 46.0 mg (88%) of the title compound. **Physical state:**



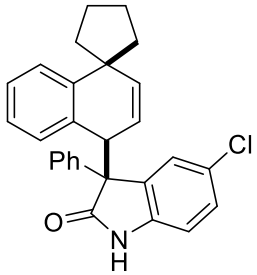
white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.0 Hz, 0.5H), 7.88 – 7.83 (m, 1H), 7.78 – 7.73 (m, 0.5H), 7.60 – 7.51 (m, 1.5H), 7.41 – 7.28 (m, 4H), 7.24 – 6.92 (m, 3H), 6.81 – 6.74 (m, 0.5H), 6.72 – 6.65 (m, 0.5H), 5.97 (d, *J* = 7.7 Hz, 0.5H), 5.92 (d, *J* = 7.4 Hz, 0.5H), 4.50 (d, *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, H), 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{33}H_{34}N_2O_4$ $(M+Na)^+$: 545.2411, found: 545.2407.

tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-5-fluoro-2-oxo-3-phenylindoline-1-carboxylate (35)



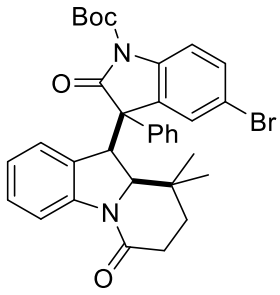
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 35.7 mg (66%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 8.1 Hz, 0.5H), 7.91 (d, *J* = 8.1 Hz, 0.5H), 7.89 – 7.83 (m, 1H), 7.78 – 7.69 (m, 1 H), 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

5-chloro-3-phenyl-3-(4'H-spiro[cyclopentane-1,1'-naphthalen]-4'-yl)indolin-2-one (36)



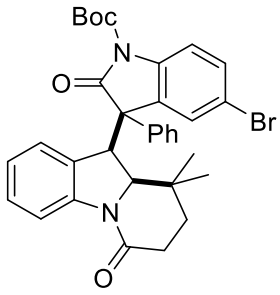
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 33.2 mg (78%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.64 (d, *J* = 3.6 Hz, 1H), 7.69 – 7.18 (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). **^{13}C 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.

tert-butyl 5-bromo-3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (37)



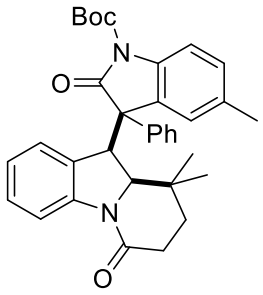
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.2 mg (31%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 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). **^{13}C NMR (101 MHz, CDCl$_3$)** 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.

tert-butyl 5-bromo-3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**37**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.9 mg (32%) of the title compound. **Physical state:** white solid. **^{1}H NMR (600 MHz, CDCl$_3$)** 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). **^{13}C NMR (151 MHz, CDCl$_3$)** 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 $C_{33}H_{33}BrN_2O_4$ (M+Na)$^+$: 623.1516, found: 623.1515.

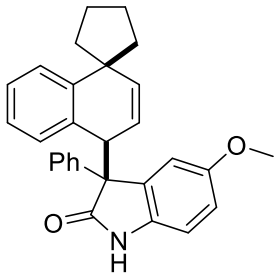
tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (**38**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 38.6 mg (72%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, CDCl$_3$)** 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). **^{13}C NMR (101 MHz, CDCl$_3$)** 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 $C_{34}H_{36}N_2O_4$ (M+Na)$^+$: 559.2567, found: 559.2570.

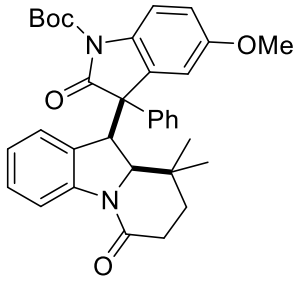
5-methoxy-3-phenyl-3-(4'H-spiro[cyclopentane-1,1'-naphthalen]-4'-yl)indolin-2-one (**39**)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 34.6 mg (82%) of the title compound. **Physical state:**



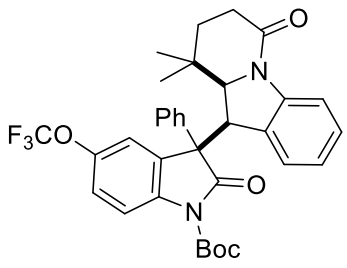
white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.31 (s, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.34 (dd, *J* = 17.6, 8.3 Hz, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.87 – 6.64 (m, 3H), 6.20 (d, *J* = 7.8 Hz, 1H), 5.68 (s, 2H), 5.07 (d, *J* = 2.3 Hz, 1H), 4.56 (d, *J* = 3.1 Hz, 1H), 3.40 (s, 3H), 1.93 – 1.35 (m, 7H), 0.65 – 0.49 (m, 1H). **^{13}C 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 $C_{29}H_{27}NO_2$ $(M+H)^+$: 422.2115, found: 422.2115.

tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-5-methoxy-2-oxo-3-phenylindoline-1-carboxylate (40)



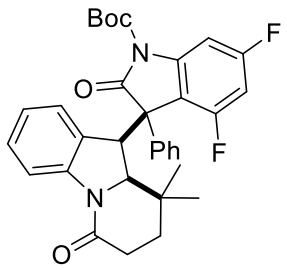
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 46.0 mg (83%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 8.0 Hz, 0.6H), 7.89 (d, *J* = 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{36}N_2O_5$ $(M+Na)^+$: 575.2516, found: 575.2518.

tert-butyl 3-(-9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenyl-5-(trifluoromethoxy)indoline-1-carboxylate (41)



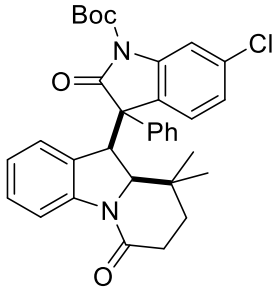
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 30.8 mg (51%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 8.1 Hz, 0.5H), 7.97 – 7.86 (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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{33}F_3N_2O_5$ $(M+H)^+$: 607.2414, found: 607.2424.

tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-4,6-difluoro-2-oxo-3-phenylindoline-1-carboxylate (42)



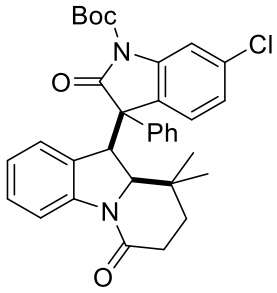
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 42.0 mg (75%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.0 Hz, 0.5H), 7.90 (d, *J* = 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{33}H_{32}F_2N_2O_4$ $(M+H)^+$: 559.2403, found: 559.2407.

tert-butyl 6-chloro-3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**43**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.0 mg (35%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{33}H_{33}ClN_2O_4$ $(M+H)^+$: 557.2202, found: 557.2205.

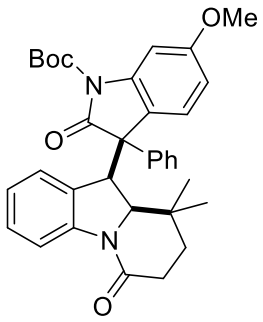
tert-butyl 6-chloro-3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-phenylindoline-1-carboxylate (**43**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.0 mg (35%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{33}H_{33}ClN_2O_4$ $(M+H)^+$: 557.2202, found: 557.2205.

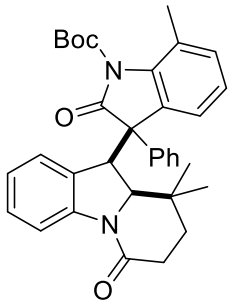
tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-6-methoxy-2-oxo-3-phenylindoline-1-carboxylate (**44**)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 41.0 mg (74%) of the title compound. **Physical state:**



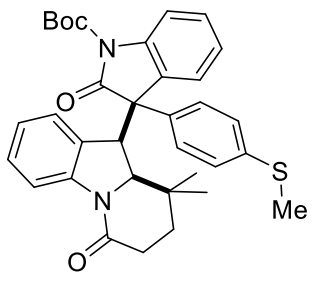
white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.0 Hz, 0.5H), 7.88 (d, *J* = 8.0 Hz, 0.5H), 7.79 – 7.69 (m, 1H), 7.53 (s, 1H), 7.47 (d, *J* = 2.4 Hz, 0.5H), 7.40 – 7.27 (m, 3H), 7.23 – 7.15 (m, 1.5H), 7.11 (d, *J* = 7.5 Hz, 0.5H), 7.01 (t, *J* = 7.7 Hz, 0.5H), 6.79 (t, *J* = 8.0 Hz, 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{36}N_2O_5$ $(M+Na)^+$: 559.2567, found: 559.2566.

tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-7-methyl-2-oxo-3-phenylindoline-1-carboxylate (45)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 34.0 mg (64%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{36}N_2O_4$ $(M+Na)^+$: 559.2567, found: 559.2571.

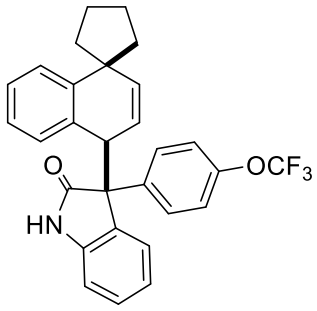
tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-3-(4-(methylthio)phenyl)-2-oxoindoline-1-carboxylate (46)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 49.0 mg (86%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.28, 173.74, 169.02,

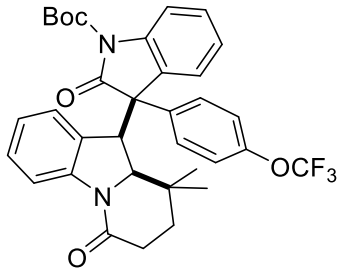
168.87, 147.84, 147.62, 143.67, 142.46, 138.87, 138.31, 138.18, 137.95, 132.47, 130.77, 128.46, 128.29, 128.22, 128.10, 127.87, 127.83, 127.34, 127.02, 125.65, 125.02, 124.98, 124.45, 124.24, 124.13, 123.35, 122.78, 122.15, 122.11, 121.84, 114.04, 113.82, 113.61, 83.73, 83.59, 67.46, 67.04, 59.59, 58.68, 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 $C_{34}H_{36}N_2O_4S$ $(M+Na)^+$: 591.2288, found: 591.2291.

3-(4'H-spiro[cyclopentane-1,1'-naphthalen]-4'-yl)-3-(4-(trifluoromethoxy) phenyl)indolin-2-one (**47**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 41.4 mg (87%) of the title compound. **Physical state:** white solid. **^{1}H 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). **^{13}C 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. **^{19}F NMR (376 MHz, DMSO-d_6)** δ -56.81, -56.83. **HRMS (ESI)** calcd for $C_{29}H_{24}F_3NO_2$ $(M+H)^+$: 476.1832, found: 476.1834.

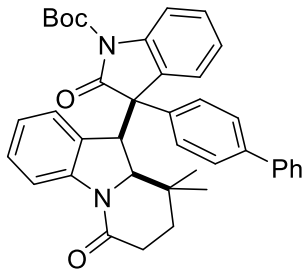
tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-(4 (trifluoromethoxy)phenyl)indoline-1-carboxylate (**48**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 37.9 mg (72%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{33}F_3N_2O_5$ $(M+Na)^+$: 629.2234, found: 629.2237.

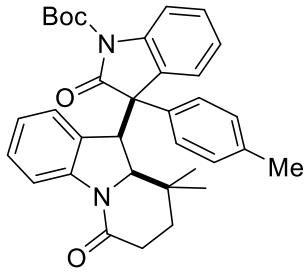
tert-butyl 3-([1,1'-biphenyl]-4-yl)-3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxoindoline-1-carboxylate (**49**)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 39.6 mg (66%) of the title compound. **Physical state:**



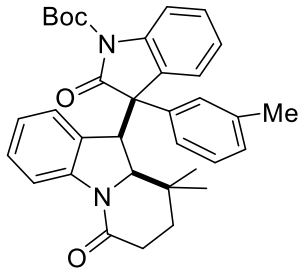
white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 8.0 Hz, 0.5H), 7.92 – 7.85 (m, 1H), 7.84 – 7.78 (m, 1H), 7.69 – 7.55 (m, 5.5H), 7.51 – 7.41 (m, 2H), 7.41 – 7.30 (m, 2H), 7.24 – 7.05 (m, 2H), 7.05 – 6.94 (m, 1H), 6.79 (t, *J* = 7.0 Hz, 0.5H), 6.71 (t, *J* = 7.1 Hz, 0.5H), 6.11 (d, *J* = 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{39}H_{38}N_2O_4$ $(M+Na)^+$: 621.2724, found: 621.2725.

tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-(p-tolyl)indoline-1-carboxylate (**50**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 38.7 mg (72%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{34}H_{36}N_2O_4$ $(M+Na)^+$: 559.2567, found: 559.2570.

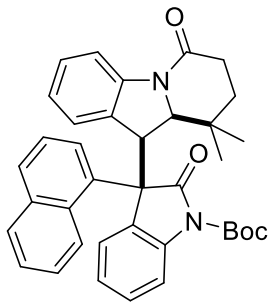
tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-oxo-3-(m-tolyl)indoline-1-carboxylate (**51**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 42.3 mg (79%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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,

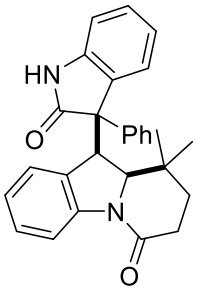
115.03, 114.78, 114.58, 84.69, 84.56, 68.53, 68.08, 60.97, 60.03, 51.65, 50.55, 35.46, 35.24, 34.63, 34.20, 31.51, 30.99, 28.11, 26.62, 22.10, 22.07, 21.74, 21.68. **HRMS (ESI)** calcd for $C_{34}H_{36}N_2O_4$ $(M+Na)^+$: 559.2567, found: 559.2571.

tert-butyl 3-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-3-(naphthalen-1-yl)-2-oxoindoline-1-carboxylate (52)



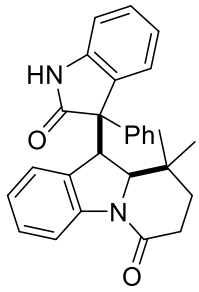
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 51.1 mg (89%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 – 7.21 (m, 8.5H), 7.15 – 6.60 (m, 5H), 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{37}H_{36}N_2O_4$ $(M+Na)^+$: 595.2567, found: 595.2572.

9,9-dimethyl-10-(2-oxo-3-phenylindolin-3-yl)-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (53)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 15.2 mg (36%) of the title compound. **Physical state:** white solid. **^{1}H 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 $C_{28}H_{26}N_2O_2$ $(M+H)^+$: 423.2067, found: 423.2065.

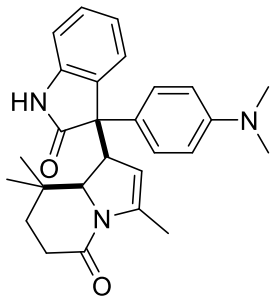
9,9-dimethyl-10-(2-oxo-3-phenylindolin-3-yl)-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (53)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 14.4 mg (34%) of the title compound. **Physical state:** white solid. **^{1}H 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 $C_{28}H_{26}N_2O_2$ $(M+H)^+$: 423.2067, found: 423.2068.

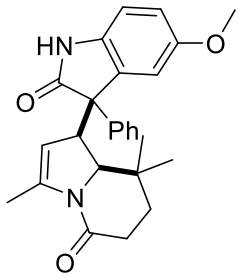
3-(4-(dimethylamino)phenyl)-3-(3,8,8-trimethyl-5-oxo-1,5,6,7,8,8a-hexahydroindolizin-1-yl)indolin-2-one (54)

Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 24.5 mg (57%) of the title compound. **Physical state:**



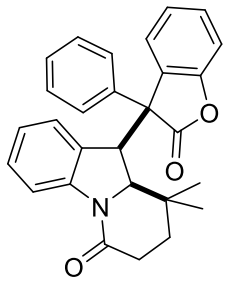
white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.14 (s, 0.5H), 8.89 (s, 0.5H), 7.50 – 7.41 (m, 1H), 7.27 – 7.09 (m, 3H), 7.02 – 6.91 (m, 1H), 6.88 (d, *J* = 7.5 Hz, 0.5H), 6.81 (d, *J* = 7.6 Hz, 0.5H), 6.65 – 6.55 (m, 2H), 4.53 (d, *J* = 0.6 Hz, 0.5H), 4.43 (d, *J* = 0.9 Hz, 0.5H), 3.82 (d, *J* = 1.4 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.

5-methoxy-3-phenyl-3-(3,8,8-trimethyl-5-oxo-1,5,6,7,8,8a-hexahydroindolizin-1-yl)indolin-2-one (**55**)



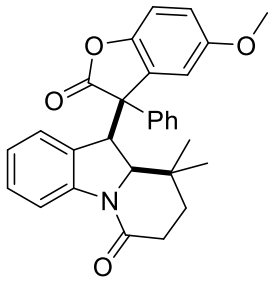
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 22.0 mg (53%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.27 (s, 0.6H), 9.04 (s, 0.4H), 7.84 – 7.74 (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.

9,9-dimethyl-10-(2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (**56**)



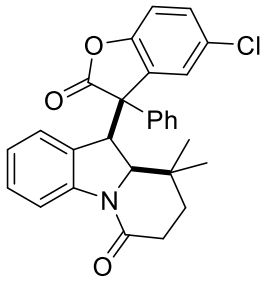
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 30.1 mg (71%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.1 Hz, 0.5H), 7.88 (d, *J* = 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.

10-(5-methoxy-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)-9,9-dimethyl-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (**57**)



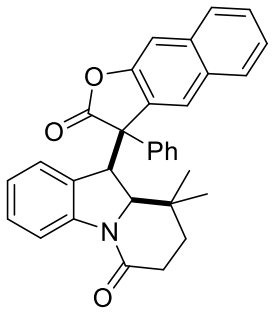
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 23.2 mg (51%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 8.0 Hz, 0.5H), 7.84 (d, *J* = 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 $C_{29}H_{27}NO_4$ $(M+H)^+$: 454.2013, found: 454.2012.

10-(5-chloro-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)-9,9-dimethyl-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (58)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 25.2 mg (55%) of the title compound. **Physical state:** white solid. **^{1}H 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 $C_{28}H_{24}ClNO_3$ $(M+H)^+$: 458.1517, found: 458.1518.

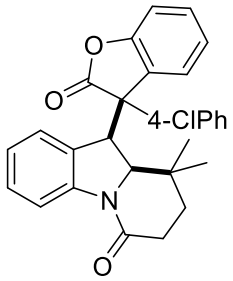
9,9-dimethyl-10-(2-oxo-3-phenyl-2,3-dihydronaphtho[2,3-b]furan-3-yl)-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (59)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 40.0 mg (85%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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,

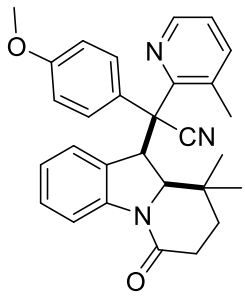
36.33, 35.36, 34.29, 34.20, 31.77, 31.09, 27.77, 26.11, 22.96, 22.27. **HRMS (ESI)** calcd for $C_{32}H_{27}NO_3$ $(M+H)^+$: 474.2064, found: 474.2063.

10-(3-(4-chlorophenyl)-2-oxo-2,3-dihydrobenzofuran-3-yl)-9,9-dimethyl-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (**60**)



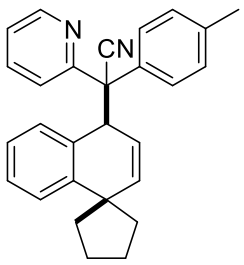
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 18.0 mg (39%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.1 Hz, 0.5H), 7.80 (d, *J* = 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{22}H_{20}NO_3$ $(M+Na)^+$: 369.1335, found: 369.1336.

9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-(4-methoxyphenyl)-2-(3-methylpyridin-2-yl)acetonitrile (**61**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 33.0 mg (74%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

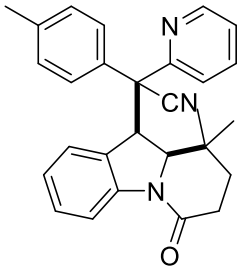
2-(pyridin-2-yl)-2-(4'H-spiro[cyclopentane-1,1'-naphthalen]-4'-yl)-2-(p-tolyl)acetonitrile (**62**)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 29.6 mg (76%) of the title compound. **Physical state:** white solid. **^{1}H 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). **^{13}C 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,

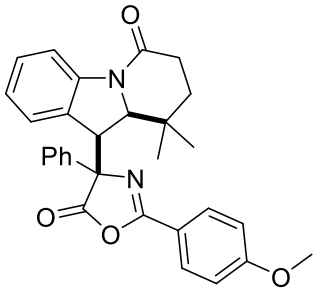
119.84, 63.29, 62.93, 46.76, 46.48, 46.43, 46.26, 46.00, 45.42, 45.36, 45.21, 26.33, 26.30, 26.24, 20.98, 20.93. **HRMS (ESI)** calcd for $C_{28}H_{26}N_2$ $(M+H)^+$: 391.2169, found: 391.2172.

9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-(pyridin-2-yl)-2-(p-tolyl)acetonitrile (63)



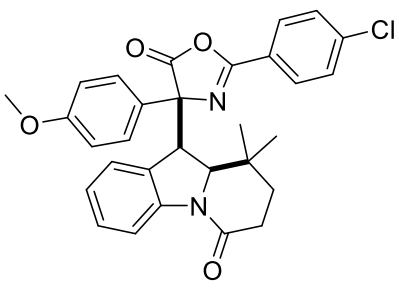
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 30.0 mg (71%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82 (d, *J* = 5.6 Hz, 0.5H), 8.70 (d, *J* = 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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.

4-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-(4-methoxyphenyl)-4-phenyloxazol-5(4H)-one (64)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 20:1) afforded 42.0 mg (88%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (151 MHz, $CDCl_3$)** 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 $C_{30}H_{28}N_2O_4$ $(M+H)^+$: 481.2122, found: 481.2123.

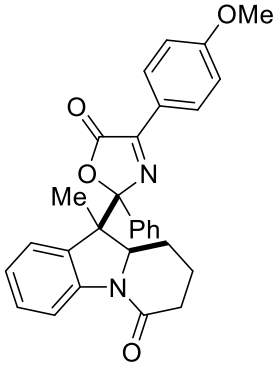
2-(4-chlorophenyl)-4-(9,9-dimethyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-4-(4-methoxyphenyl)oxazol-5(4H)-one (65)



Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 20:1) afforded 45.0 mg (88%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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,

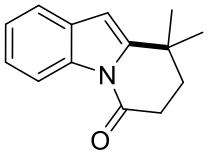
2H), 1.64 – 1.31 (m, 2H), 1.10 – 0.17 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.32, 176.14, 169.99, 169.73, 163.57, 163.35, 160.63, 144.35, 144.11, 135.06, 134.96, 134.67, 134.07, 130.07, 129.89, 129.57, 128.87, 128.84, 128.71, 128.63, 128.56, 128.28, 126.38, 126.25, 125.74, 123.74, 123.54, 123.36, 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 $C_{30}H_{27}ClN_2O_4$ $(M+H)^+$: 515.1732, found: 515.1730.

4-(4-methoxyphenyl)-2-(10-methyl-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indol-10-yl)-2-phenyloxazol-5(2H)-one (**66**)



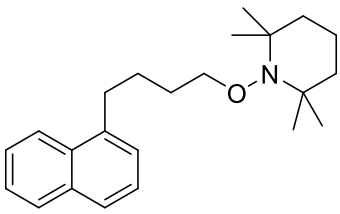
Following the **procedure A** on 0.1 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 20:1) afforded 29.0 mg (62%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 – 8.03 (m, 1H), 8.00 – 7.92 (m, 1H), 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{29}H_{26}N_2O_4$ $(M+H)^+$: 467.1965, found: 467.1963.

9,9-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one (**67**)



Following the **procedure A** on 0.2 mmol scale. Purification via Silica gel (200-300 mesh) column chromatography (hexane/ ethyl acetate = 10:1) afforded 13.8 mg (33%) of the title compound. **Physical state:** white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C NMR (101 MHz, $CDCl_3$)** 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 $C_{14}H_{15}NO$ $(M+H)^+$: 214.1226, found: 214.1228.

2,2,6,6-tetramethyl-1-(4-(naphthalen-1-yl)butoxy)piperidine (69)

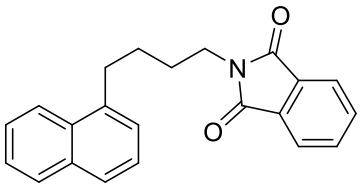


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 3.14 (q, *J* = 4.5, 4.0 Hz, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 1.94 – 1.80 (m, 4H), 1.79 – 1.37 (m, 7H), 1.11 (d, *J* = 35.2 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{23}H_{33}NO$ $(M+H)^+$: 340.2635, found: 340.2635.

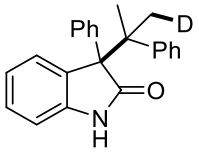
2-(4-(naphthalen-1-yl)butyl)isoindoline-1,3-dione (70)



^{1}H NMR (400 MHz, $CDCl_3$) 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).

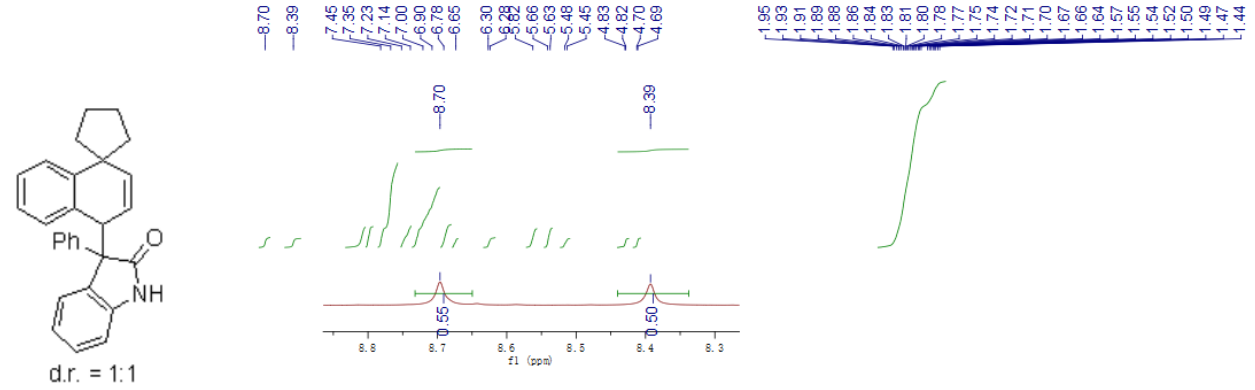
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.50, 161.99, 137.79, 134.76, 133.93, 131.81, 128.95, 128.82, 126.76, 126.04, 125.87, 125.57, 125.49, 123.98, 123.73, 32.55, 30.91, 29.80, 24.72. **HRMS (ESI)** calcd for $C_{22}H_{19}NO_2$ $(M+H)^+$: 330.1489, found: 330.1490.

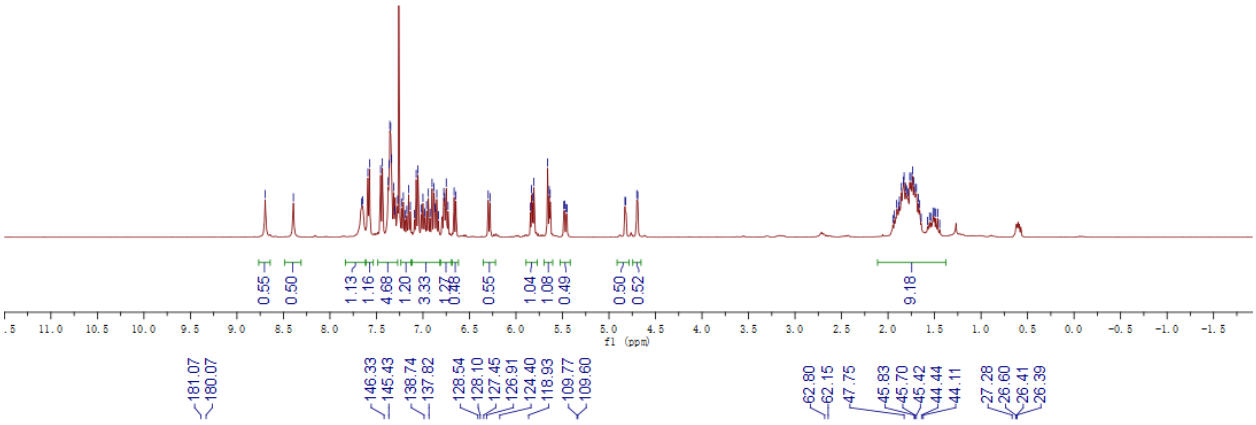
3-phenyl-3-(2-phenylpropan-2-yl-1-d)indolin-2-one ()

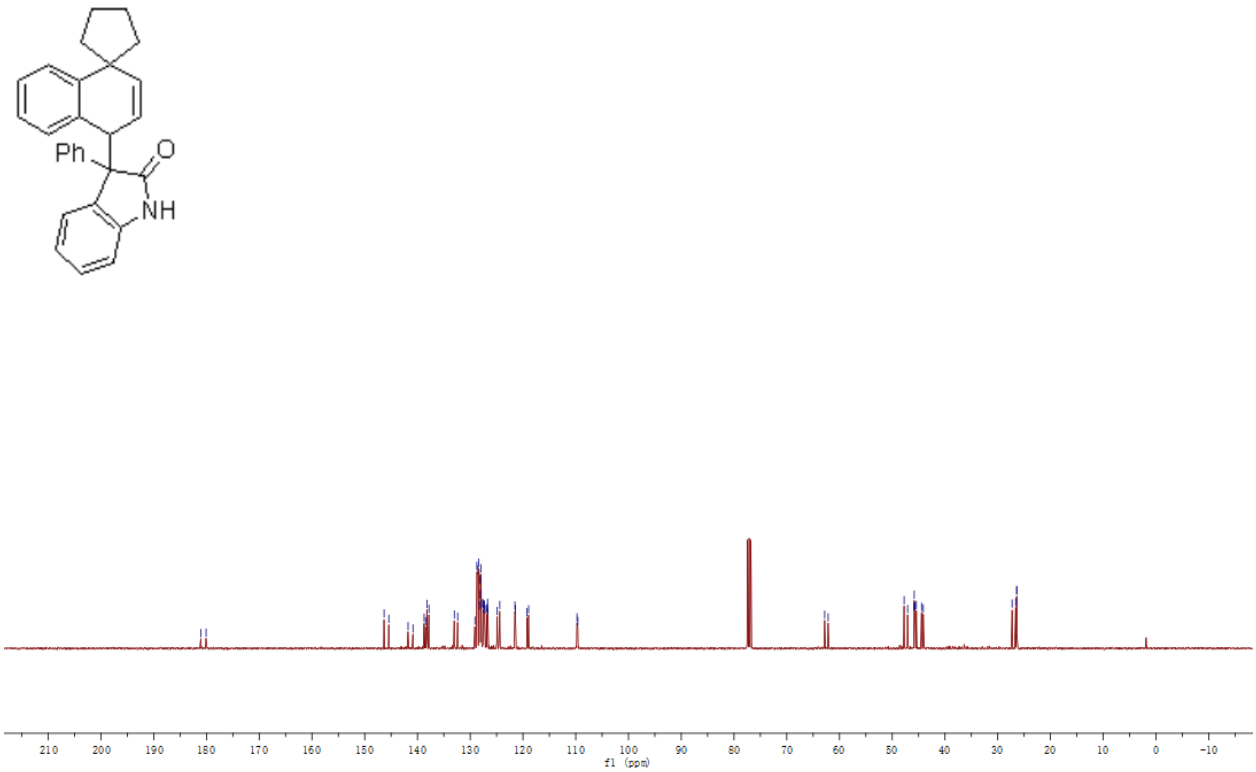


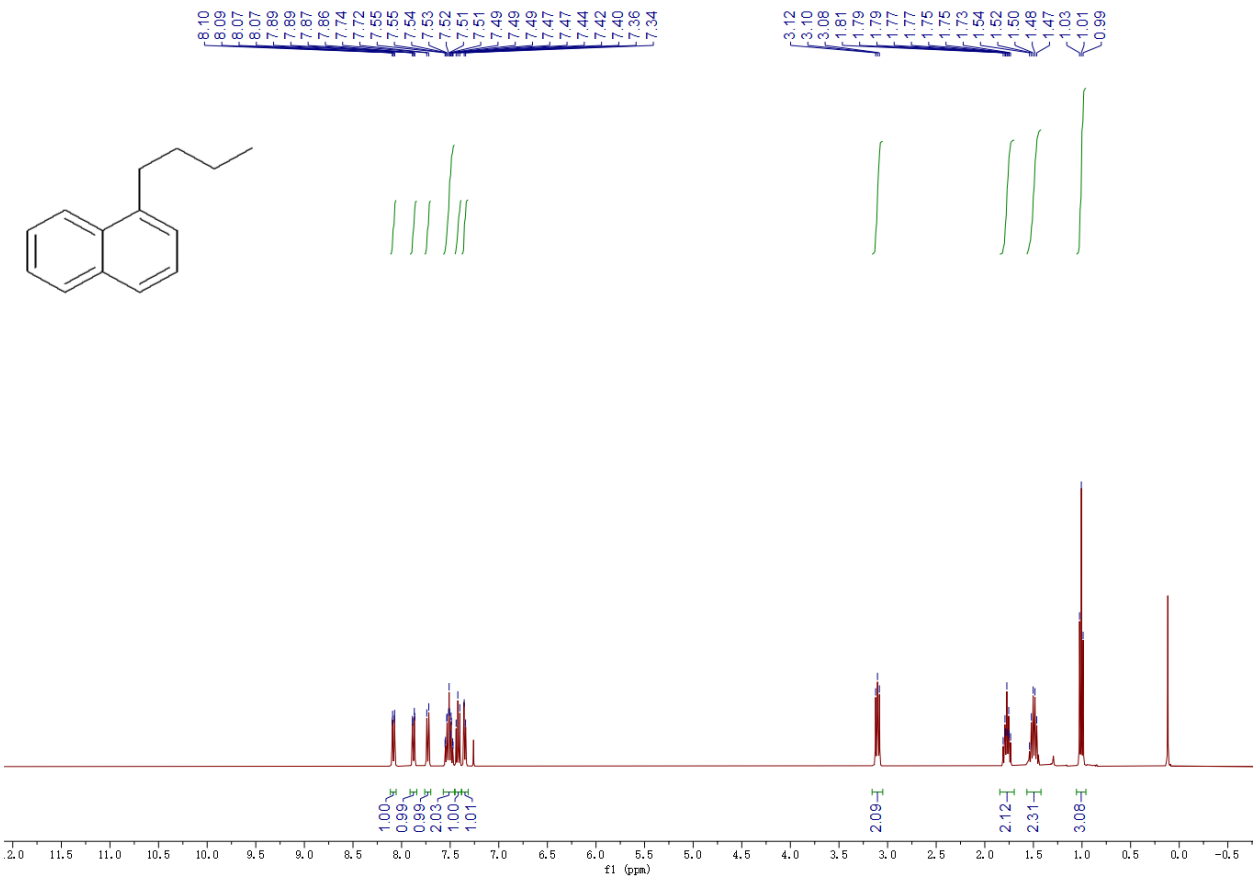
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.40 (s, 1H), 7.90 – 7.78 (m, 2H), 7.35 – 7.30 (m, 3H), 7.23 – 7.12 (m, 4H), 7.07 – 6.95 (m, 7H), 6.86 (m, 1H), 6.71 (d, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.2 Hz, 1H), 2.30 – 2.10 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 179.42, 146.41, 143.40, 141.16, 136.29, 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 $C_{28}H_{22}DNO$ $(M + Na)^+$ 413.1735, found 413.1738.

9 **NMR spectra**





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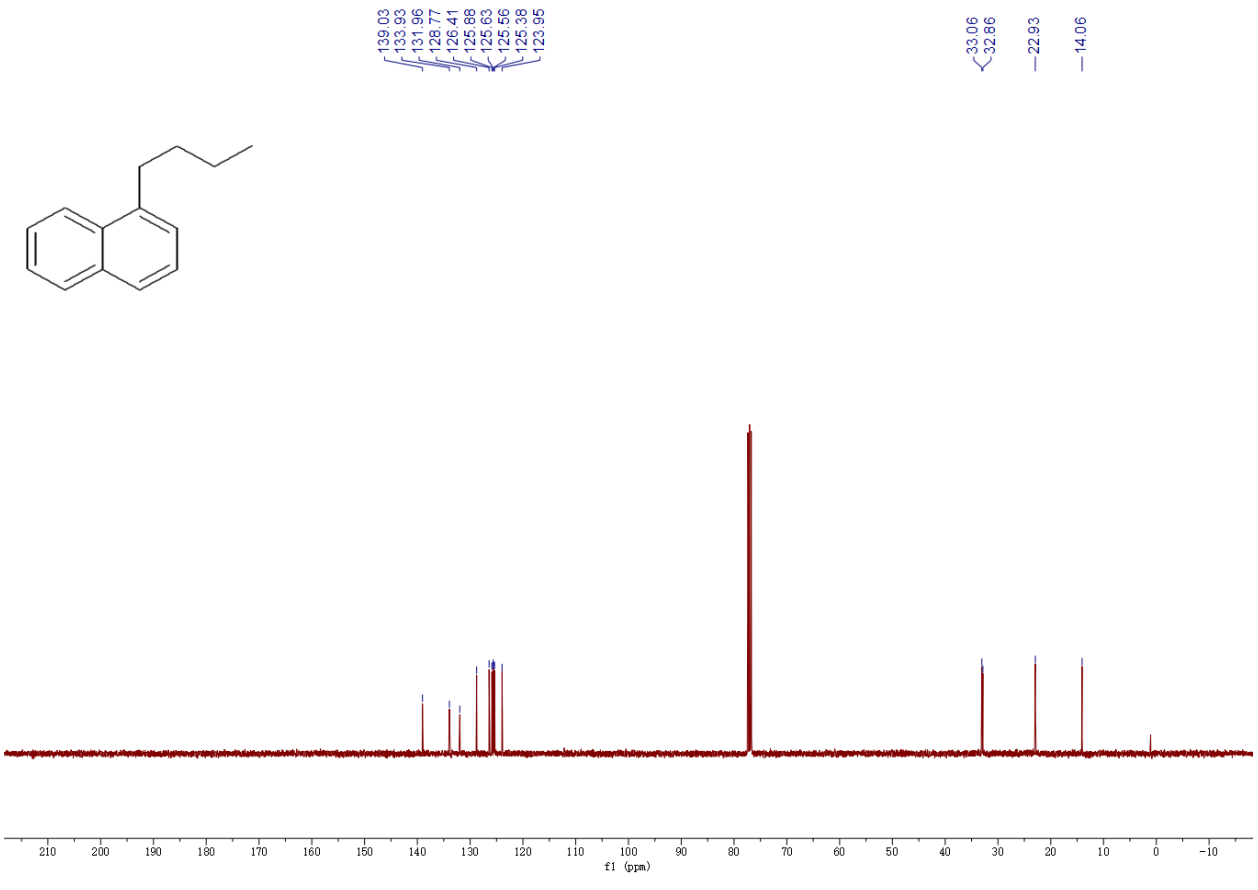
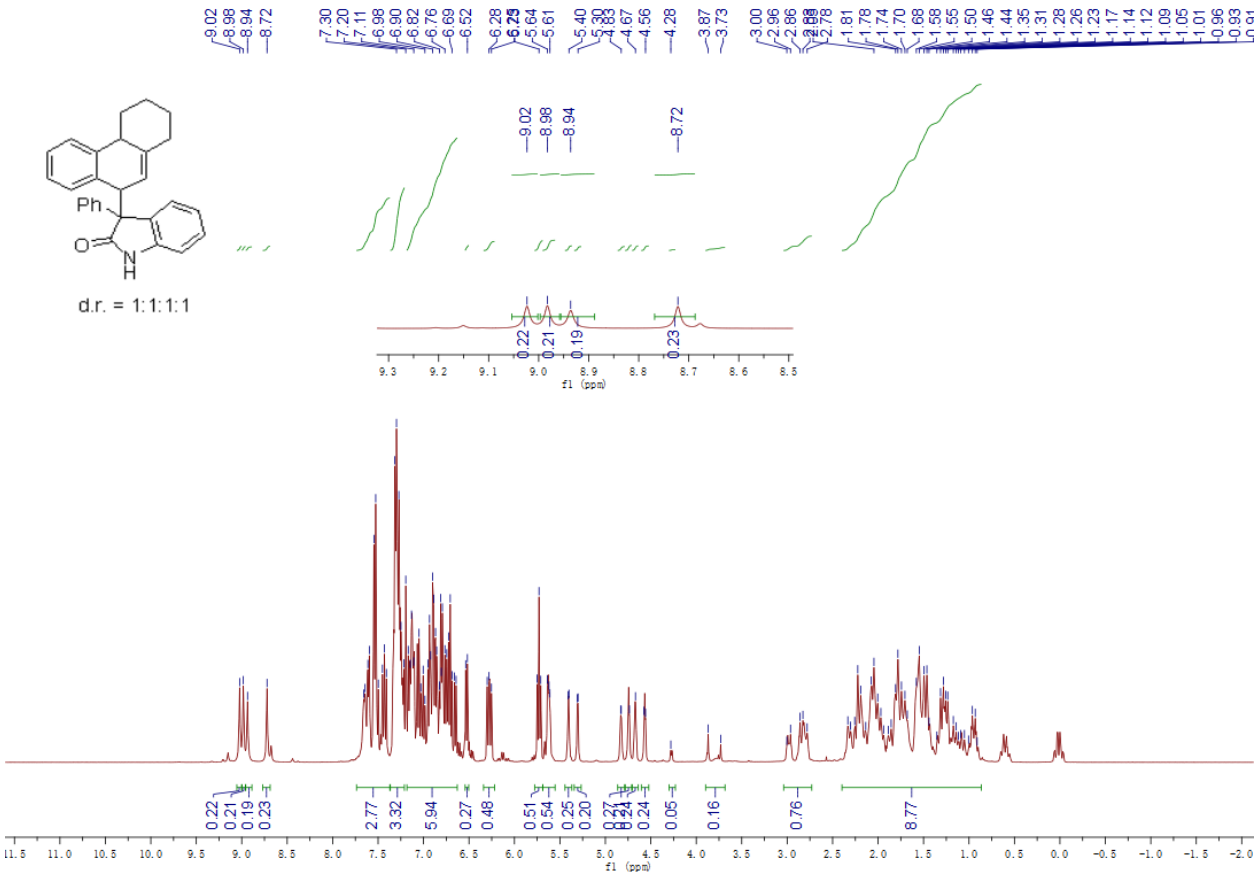
8.09
8.07
8.07
7.89
7.89
7.87
7.86
7.74
7.72
7.55
7.55
7.54
7.53
7.52
7.51
7.51
7.49
7.49
7.49
7.47
7.44
7.42
7.40
7.36
7.34
3.12
3.10
3.08
1.81
1.79
1.77
1.77
1.75
1.75
1.73
1.54
1.52
1.50
1.48
1.47
1.03
1.01
0.99
1.00
0.99
0.99
2.03
1.00
1.01
2.09
2.12
2.31
3.08
f1 (ppm)


139.03
133.93
131.96
128.77
126.41
125.88
125.63
125.56
125.38
123.95
33.06
32.86
22.93
14.06
f1 (ppm)


Ph
O
N
H
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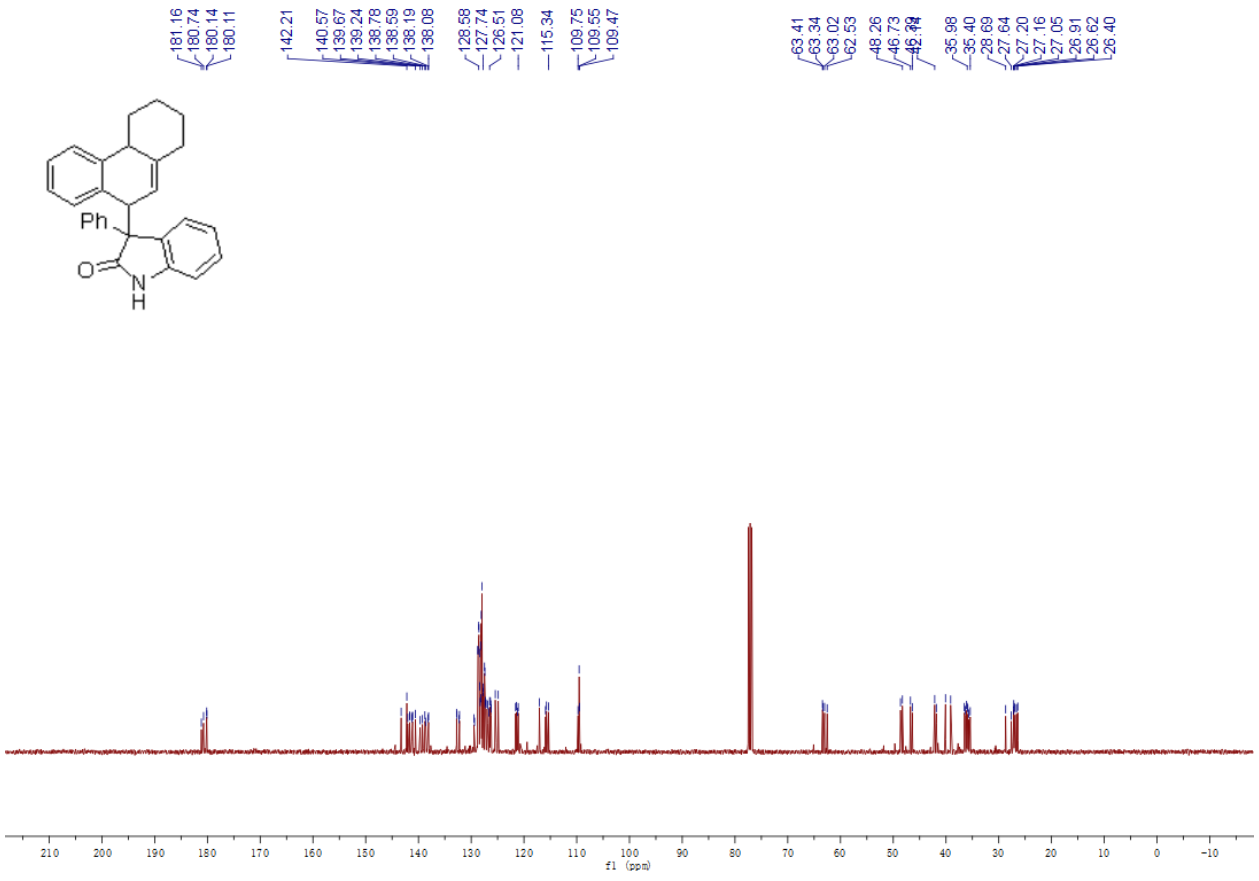
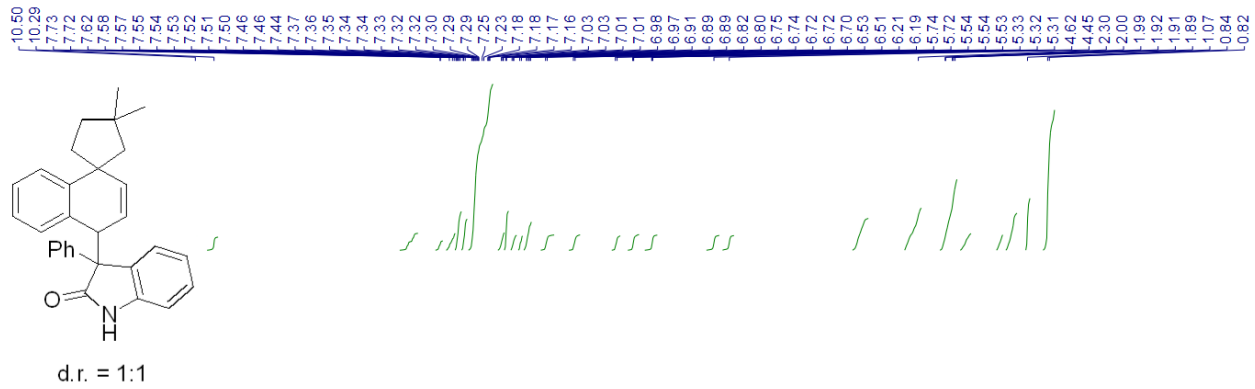
f1 (ppm)


Ph
O
N
H
f1 (ppm)



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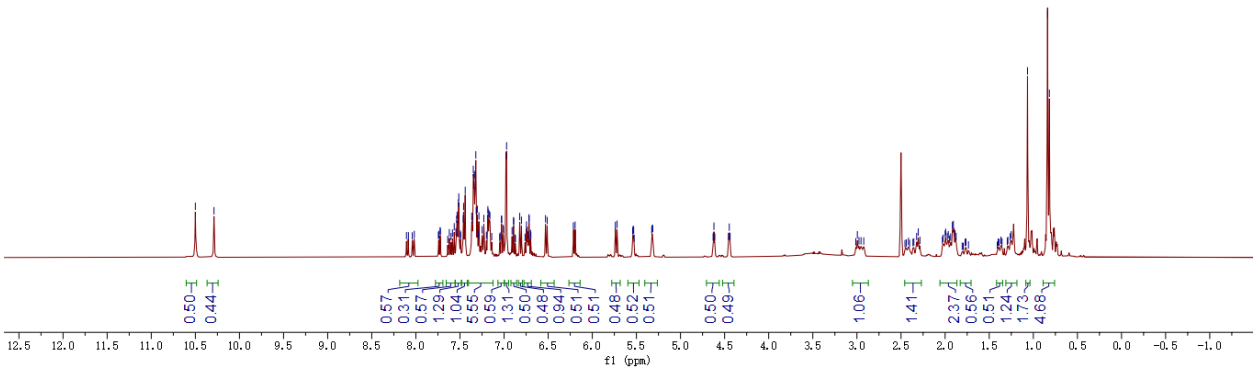

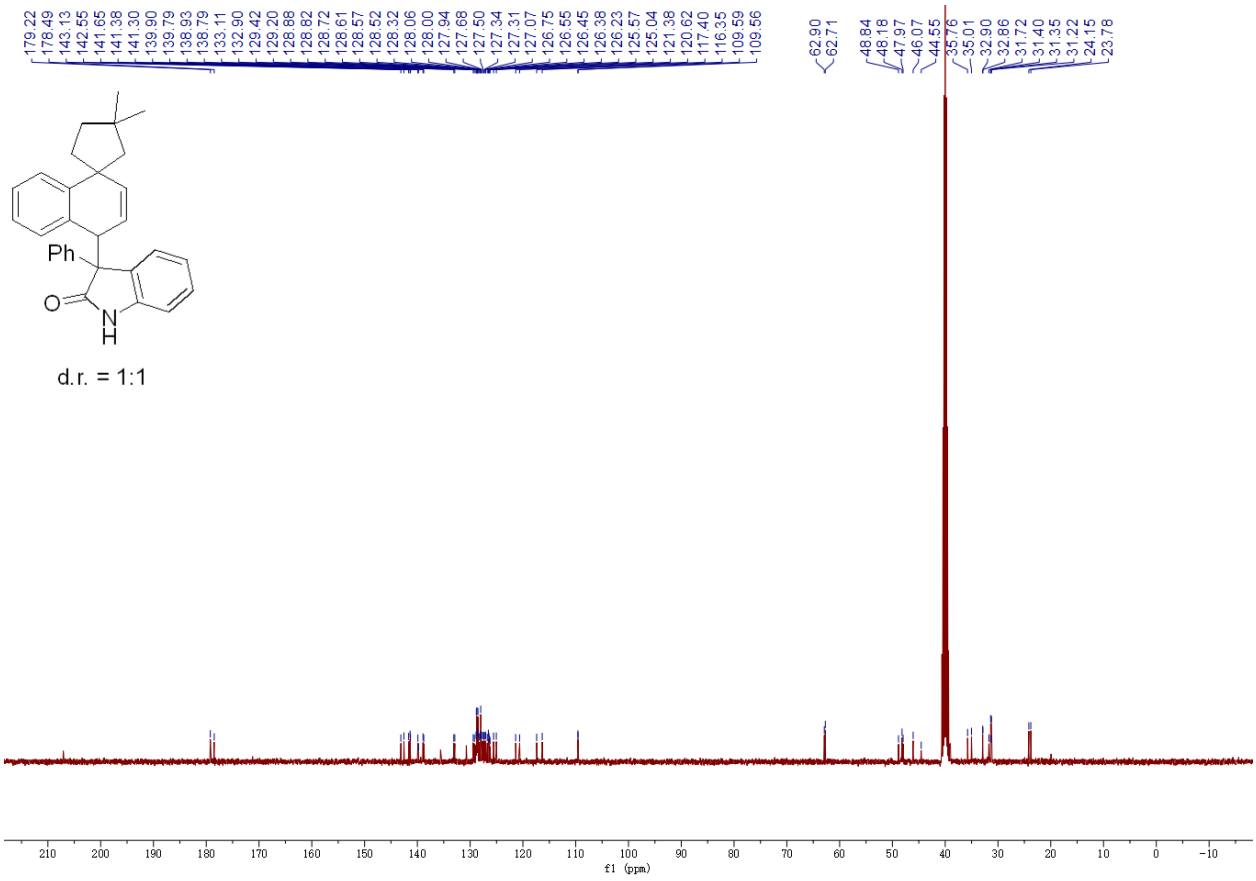

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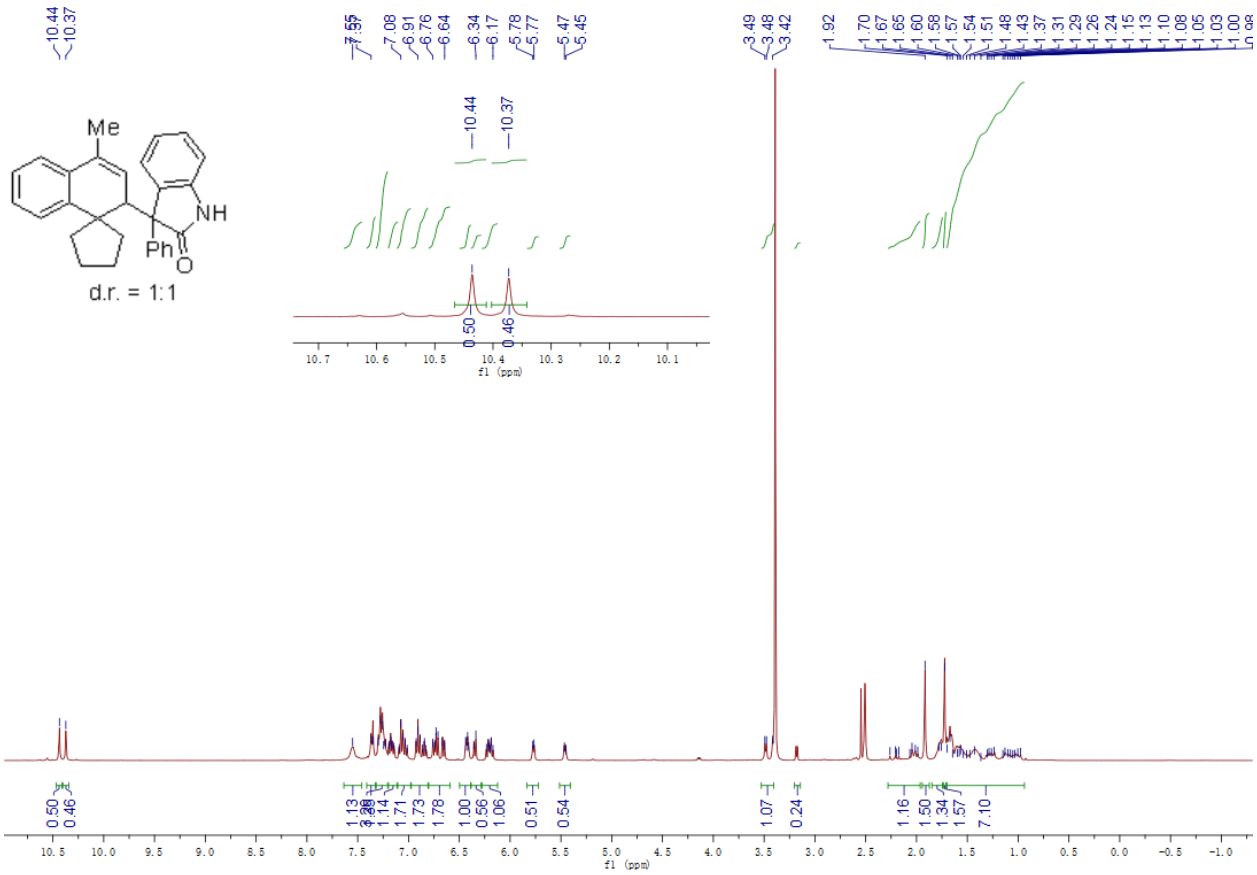
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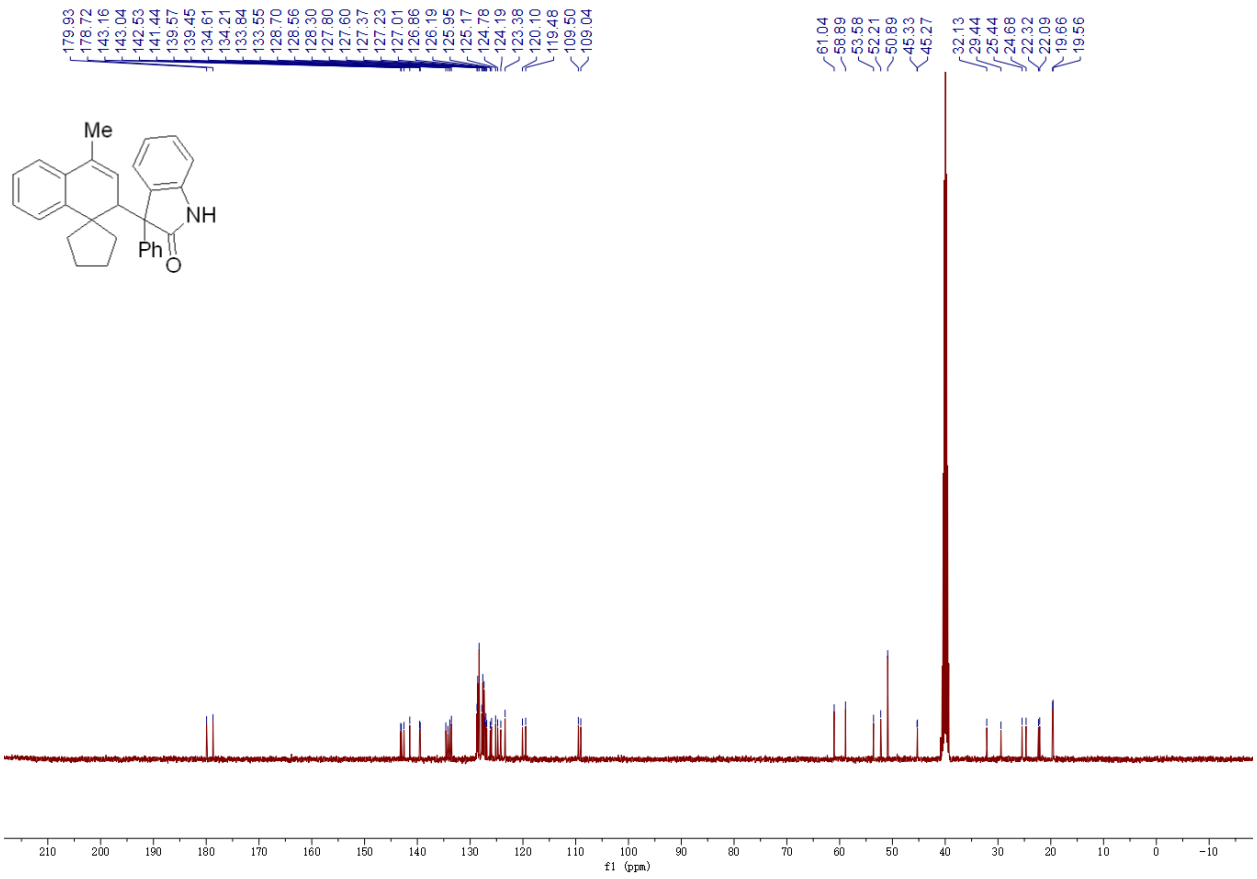
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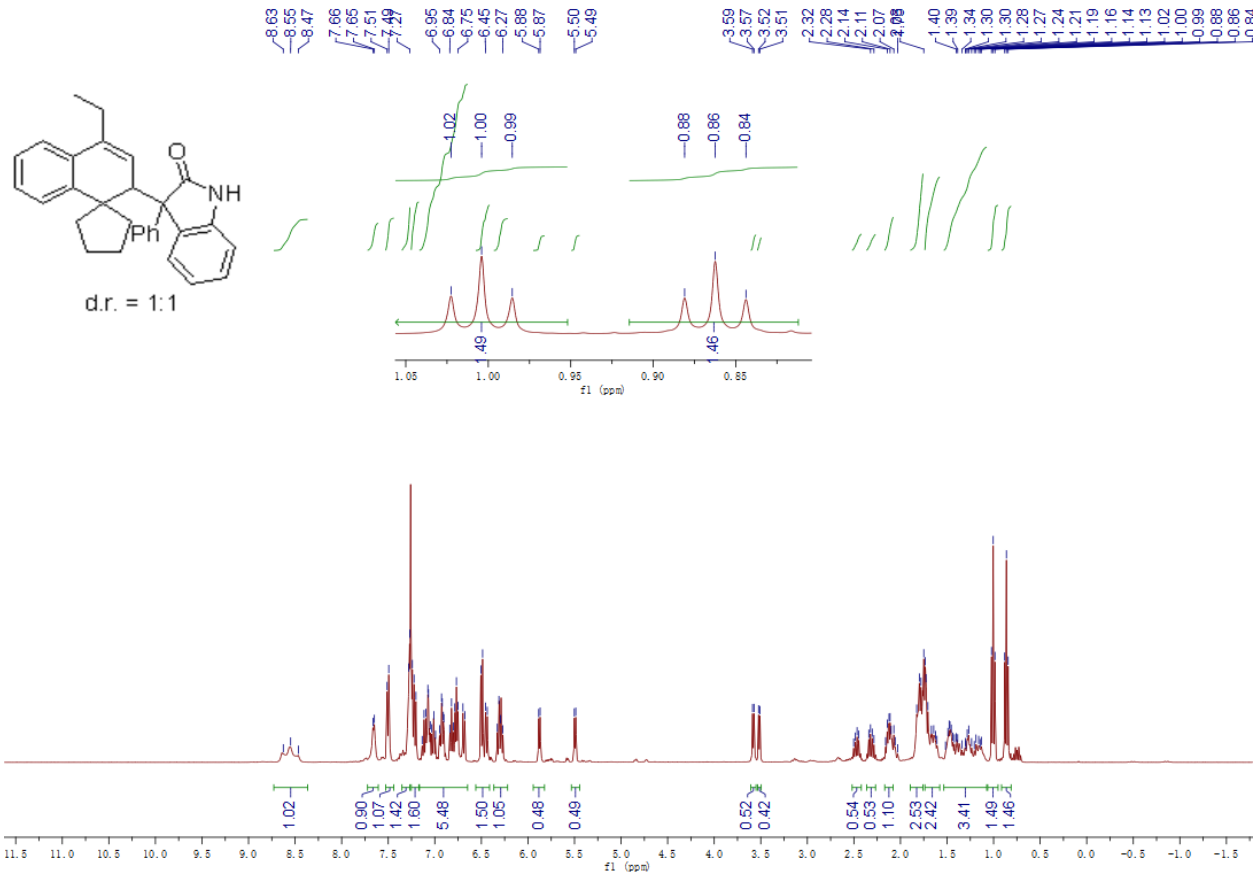
NH
Ph
O
f1 (ppm)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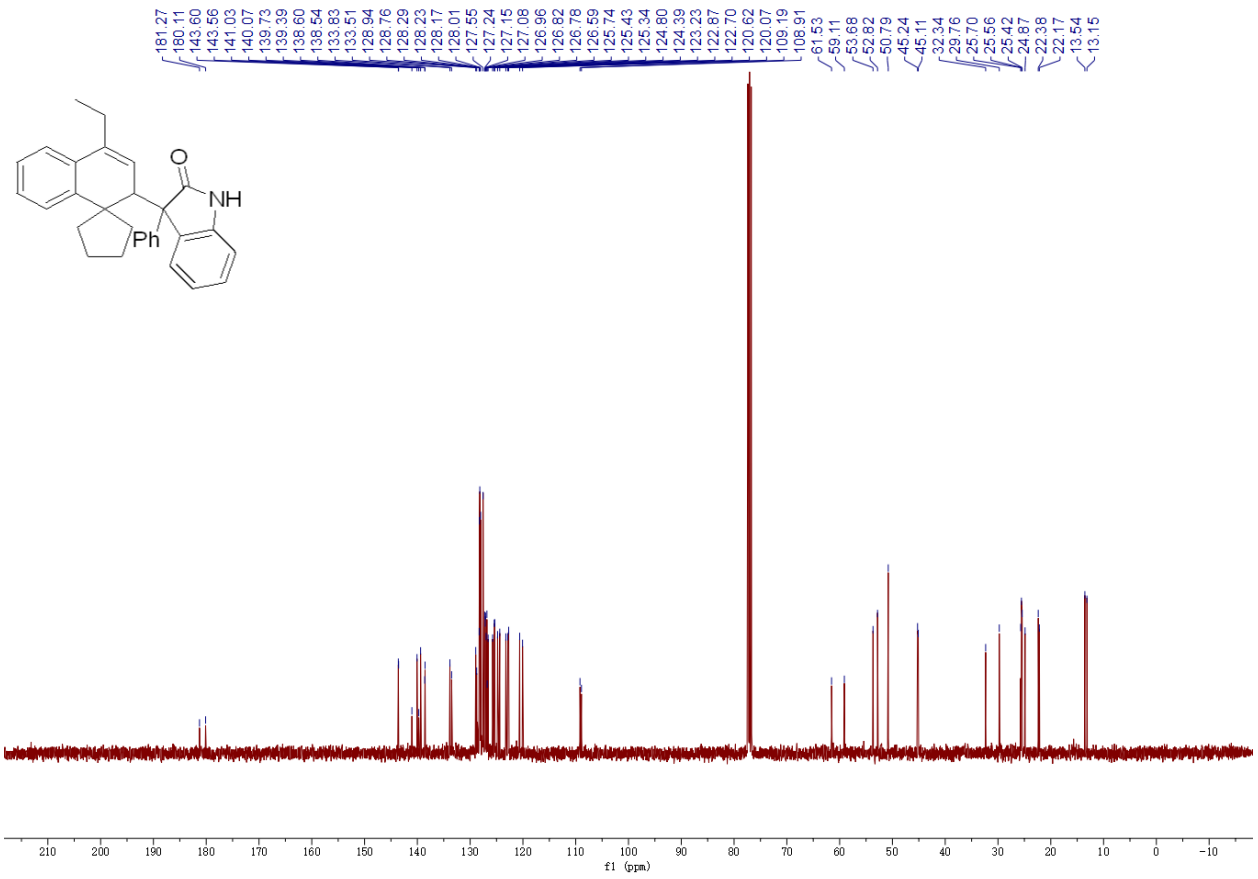
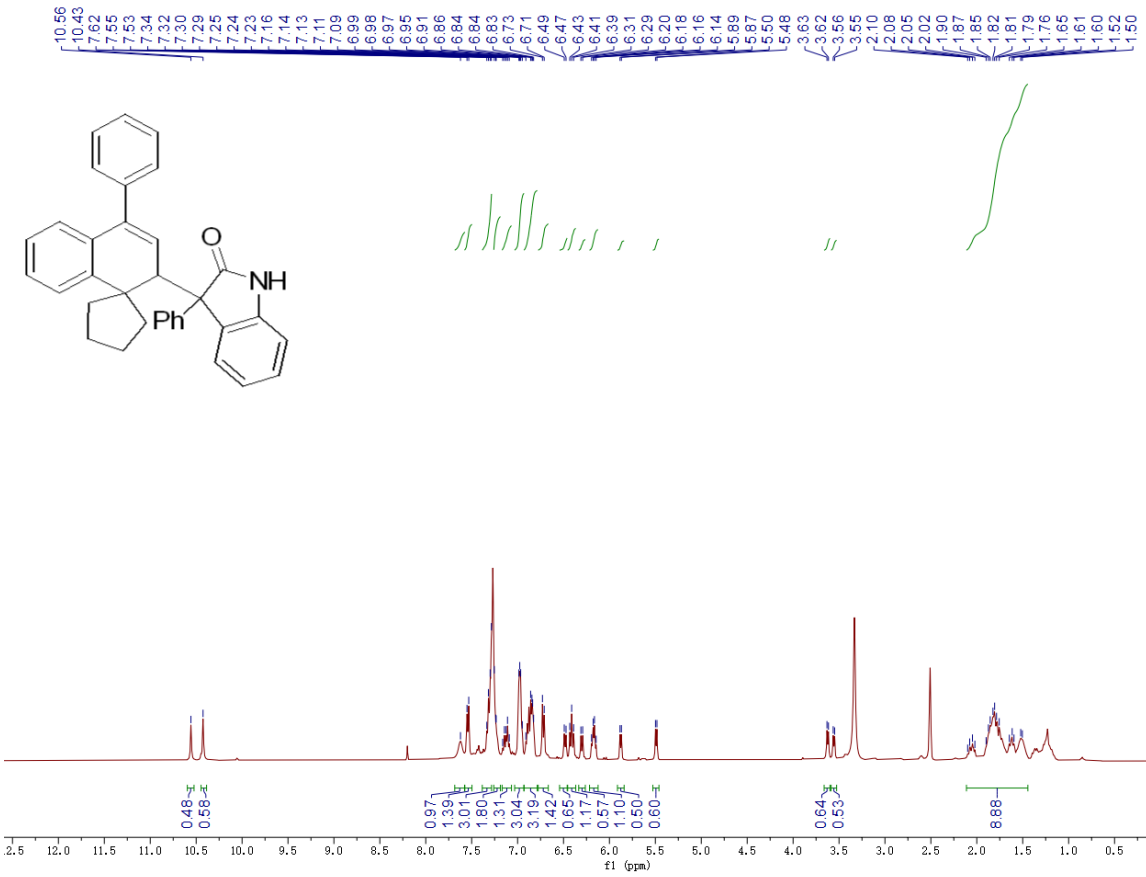
NH
Ph
d.r. = 1:1
f1 (ppm)

f1 (ppm)


O
NH
Ph
f1 (ppm)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6.83
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6.71
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6.14
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5.48
3.63
3.62
3.56
3.55
2.10
2.08
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1.79
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1.60
1.52
1.50
O
NH
Ph
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0.58
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3.01
1.80
1.31
3.04
3.19
1.42
0.65
1.17
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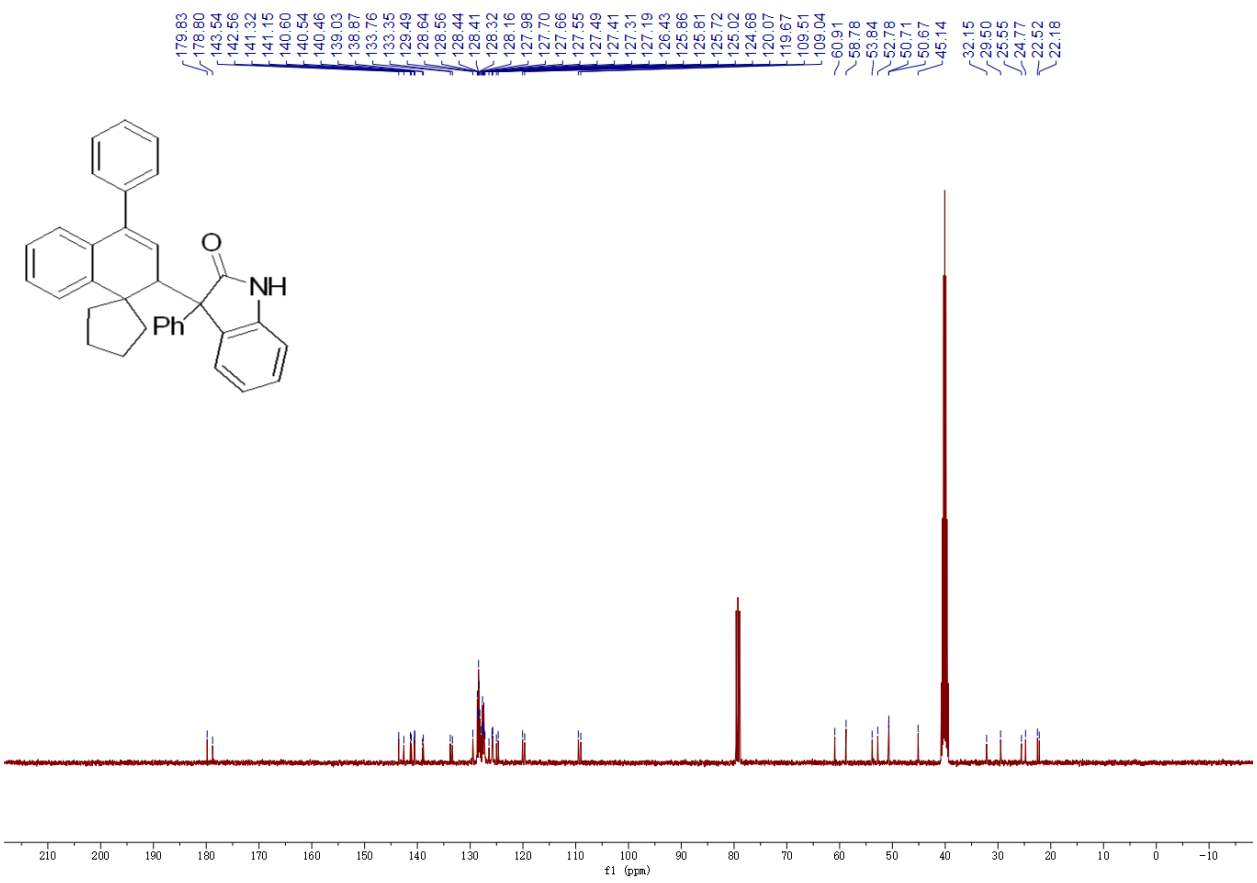
0.50
0.60
0.64
0.53
8.88
f1 (ppm)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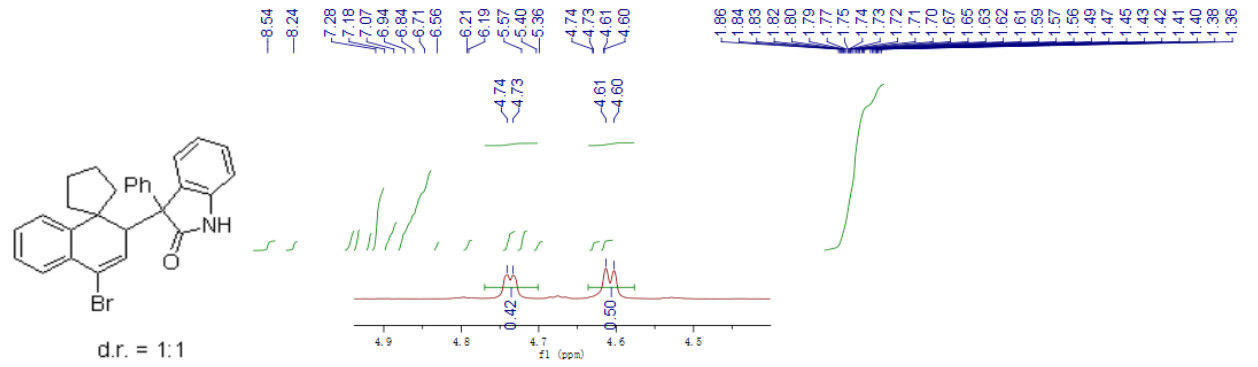
22.52
22.18
O
NH
Ph
f1 (ppm)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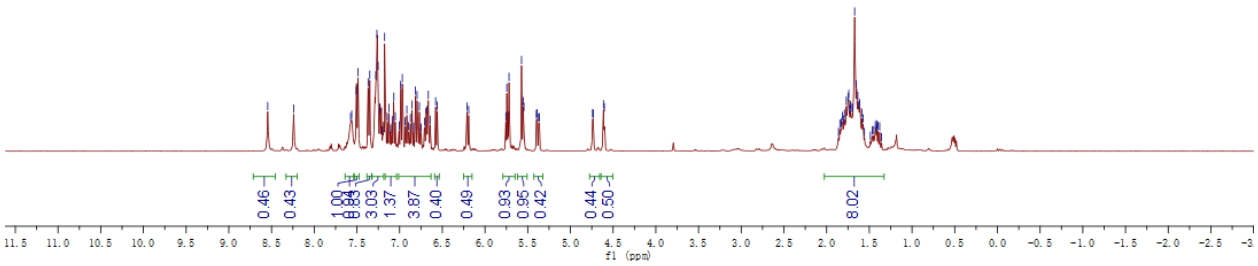
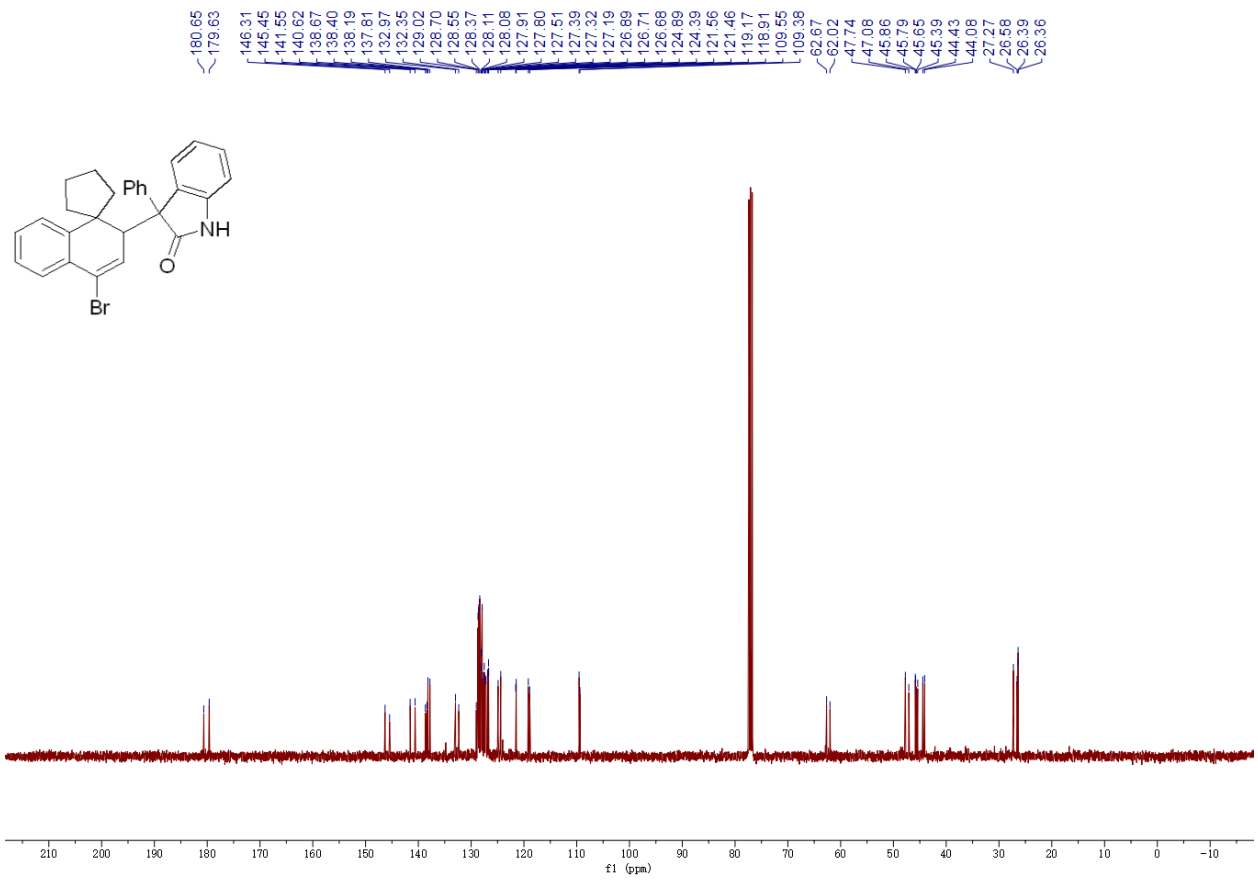
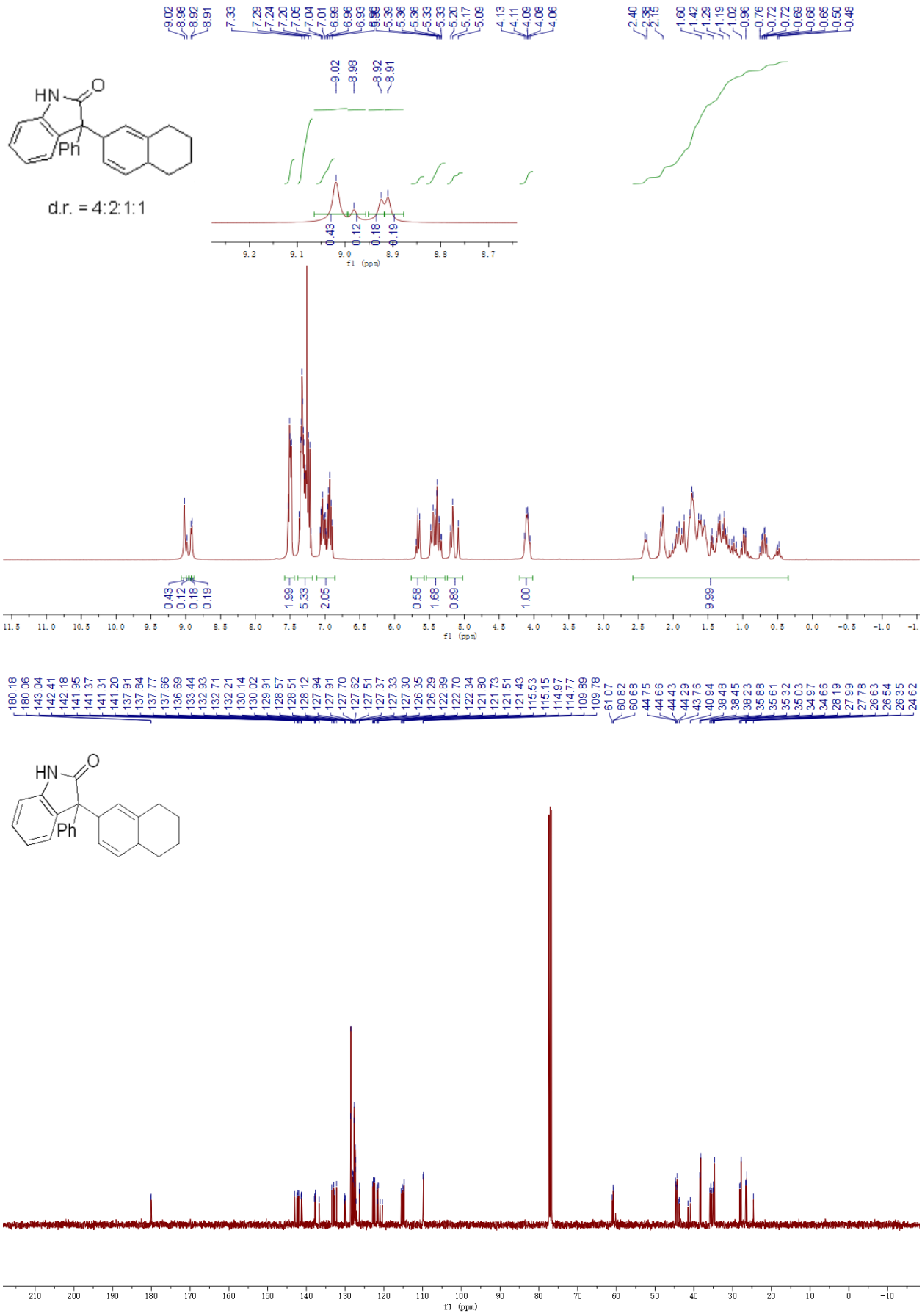
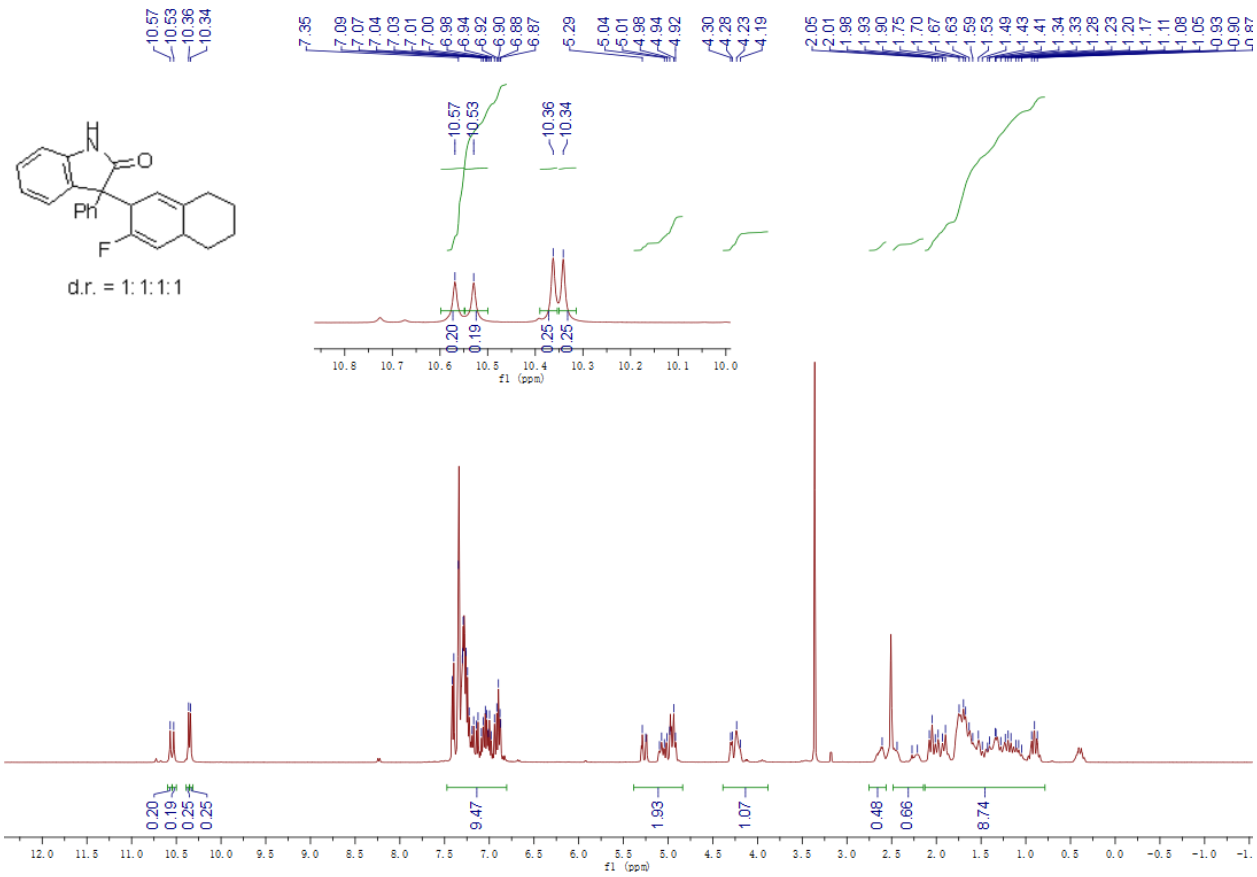
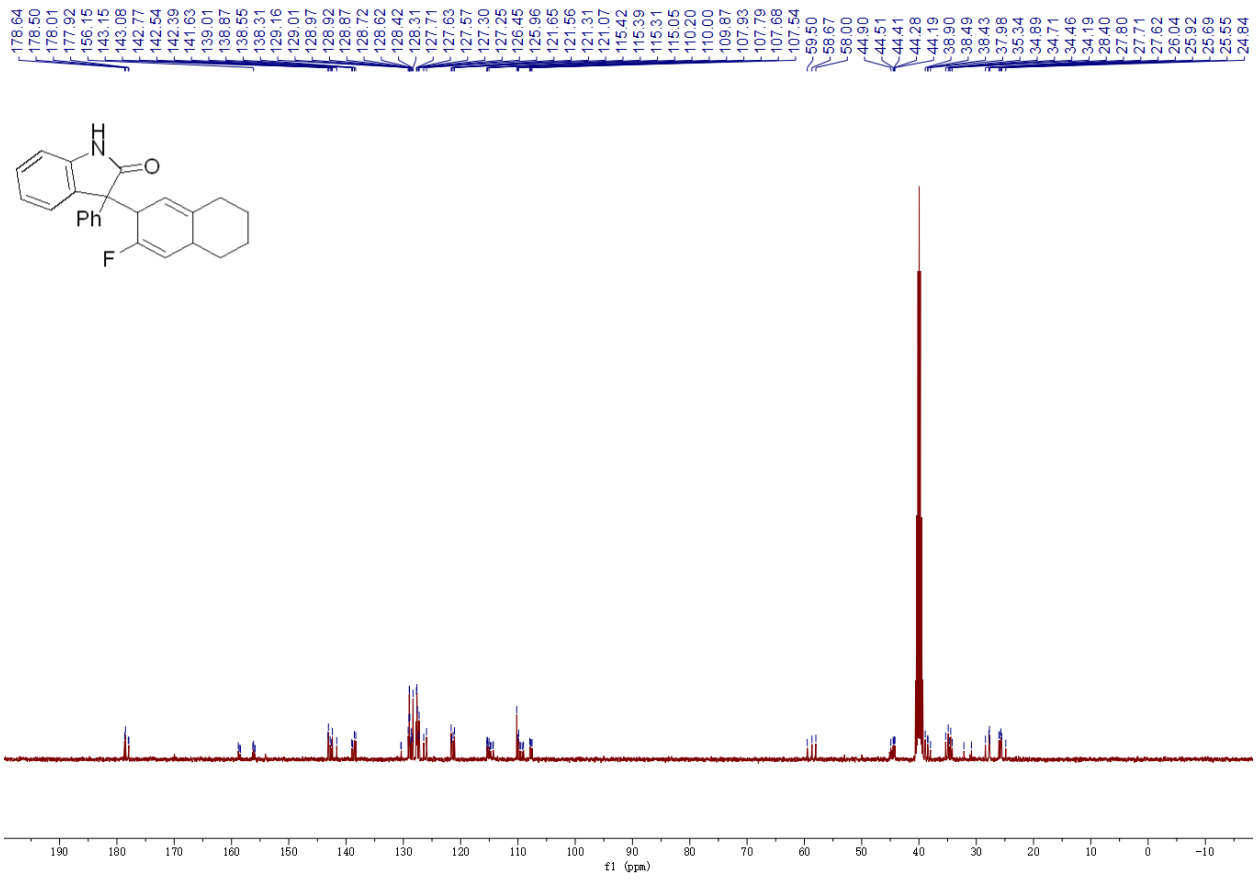
O
Br
d.r. = 1:1
f1 (ppm)

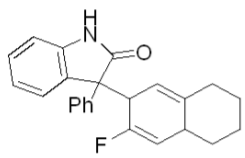

f1 (ppm)


Ph
NH
O
Br
f1 (ppm)

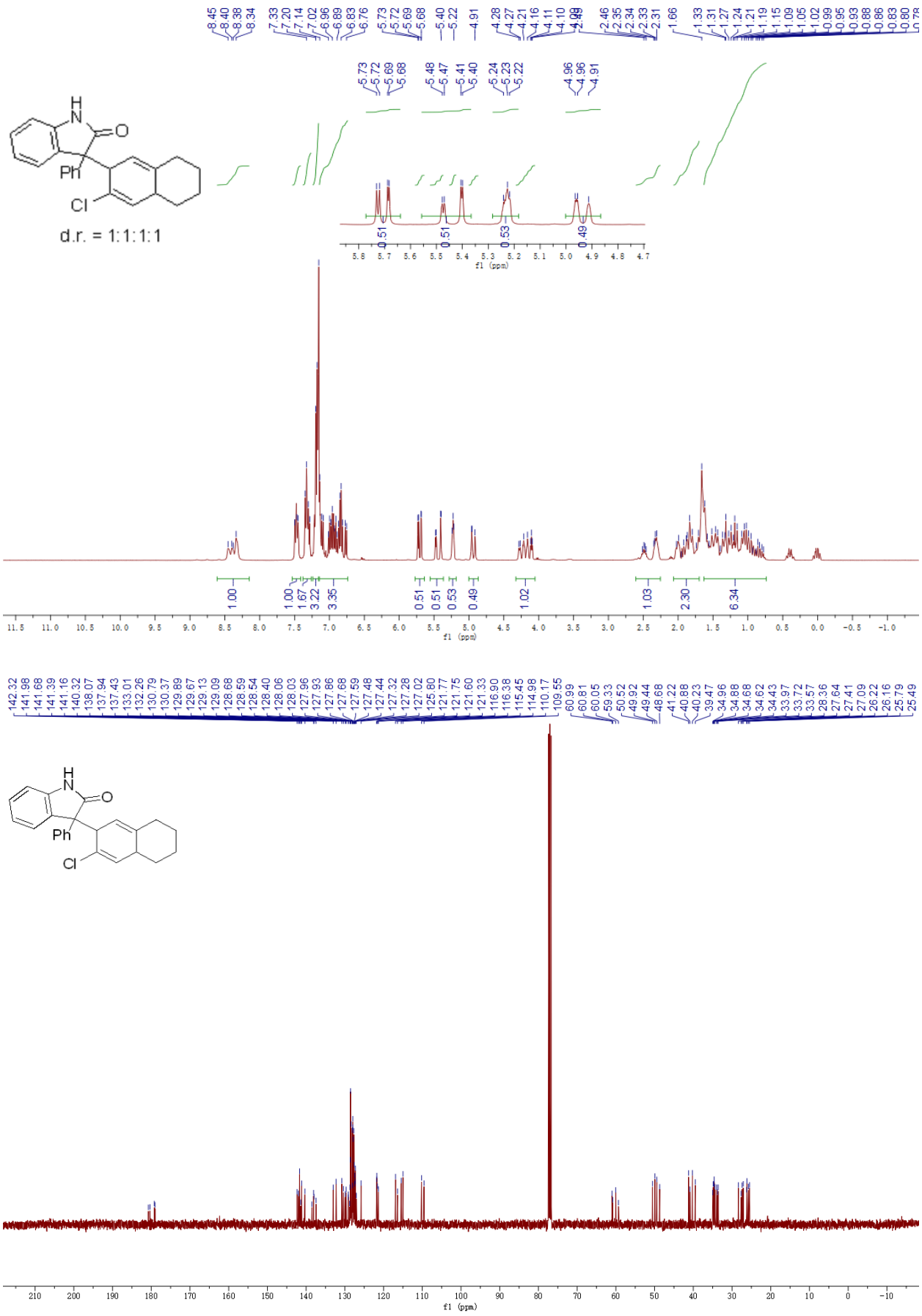

HN
O
Ph
d.r. = 4:2:1:1
f1 (ppm)

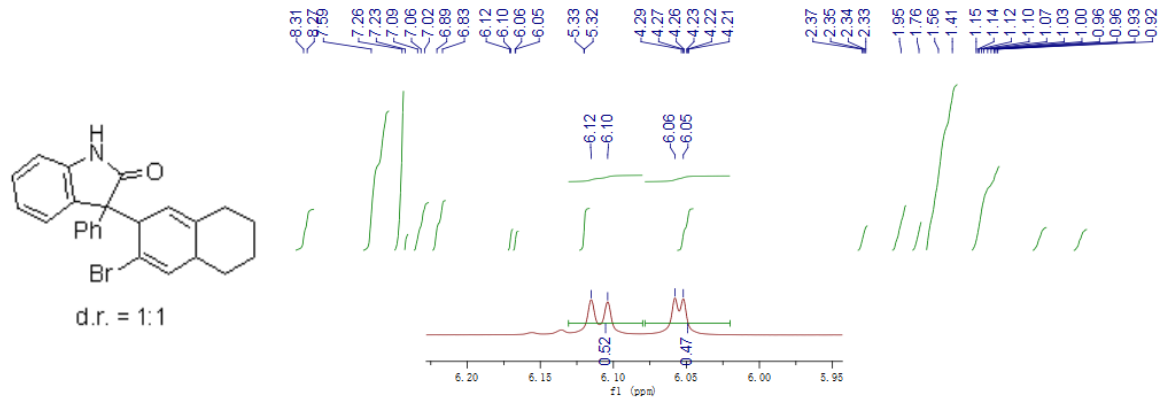

d.r. = 1:1:1:1
f1 (ppm)

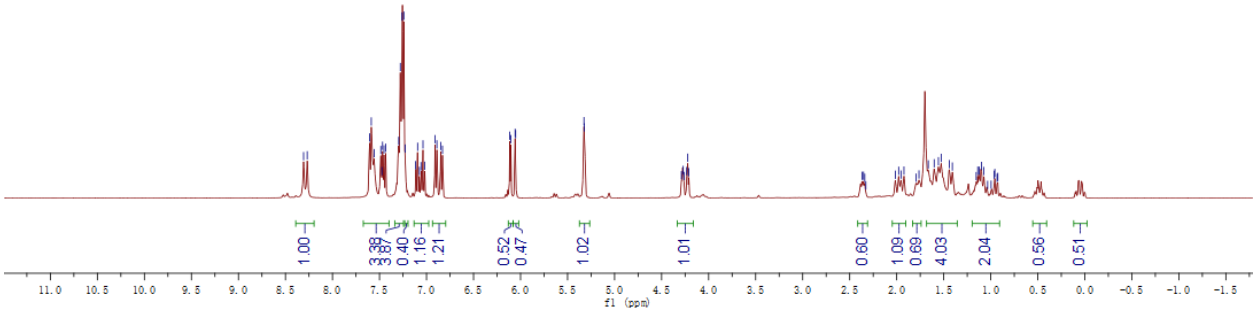

f1 (ppm)

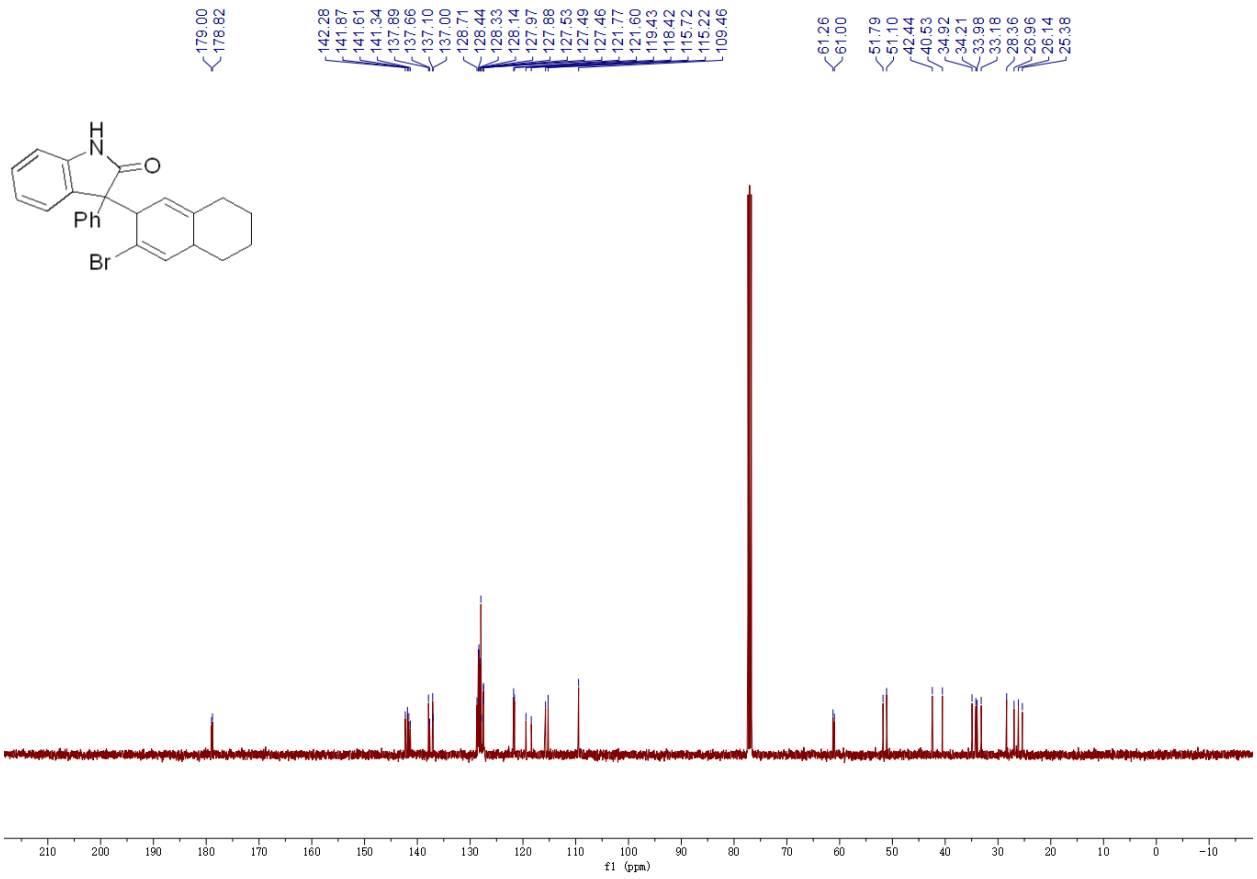

H
N
O
Ph
F

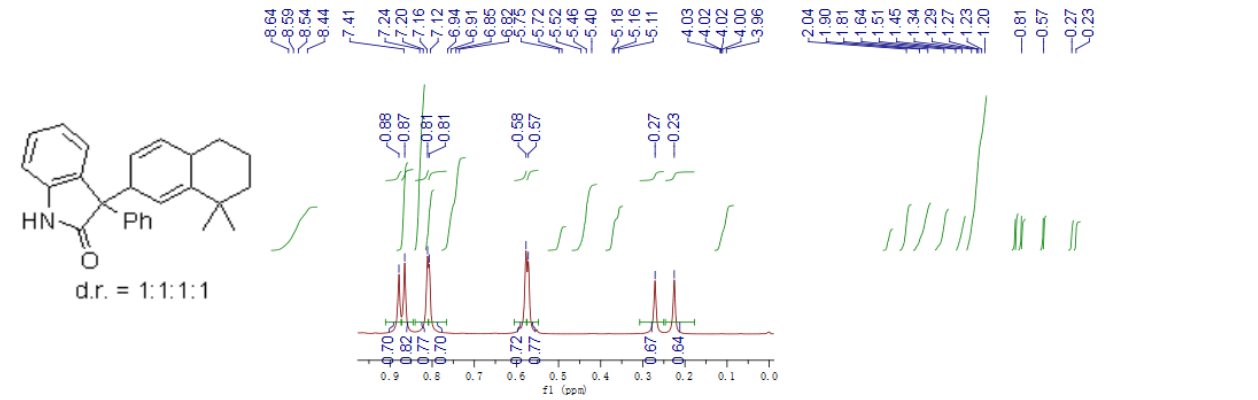
-104.09
-105.38
-110.23
-110.88
1.00
1.04
1.36
1.44
f1 (ppm)


d.r. = 1:1:1:1
fl (ppm)


8.31
7.69
7.26
7.23
7.09
7.06
7.02
6.89
6.83
6.12
6.10
6.06
6.05
5.33
5.32
4.29
4.27
4.26
4.23
4.22
4.21
2.37
2.35
2.34
2.33
1.95
1.76
1.56
1.41
1.15
1.14
1.12
1.10
1.07
1.03
1.00
0.96
0.96
0.93
0.92
6.12
6.10
6.06
6.05
0.52
0.47
6.20
6.15
6.10
6.05
6.00
5.95
f1 (ppm)

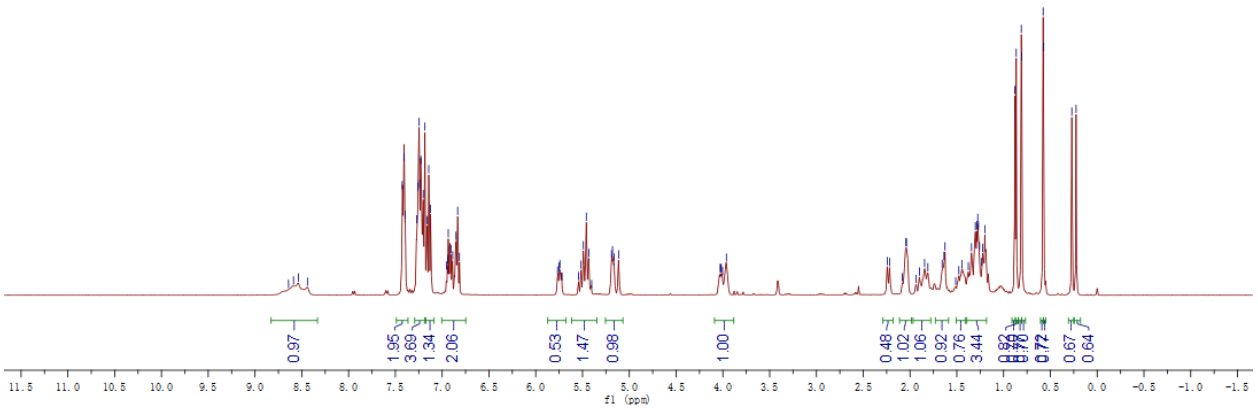

1.00
3.38
3.87
0.40
1.16
1.21
0.52
0.47
1.02
1.01
0.60
1.09
0.69
4.03
2.04
0.56
0.51
f1 (ppm)


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
f1 (ppm)

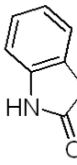

8.64
8.59
8.54
8.44
7.41
7.24
7.20
7.16
7.12
6.94
6.91
6.85
6.82
5.75
5.72
5.52
5.46
5.40
5.18
5.16
5.11
4.03
4.02
4.02
4.00
3.96
2.04
1.90
1.81
1.64
1.51
1.45
1.34
1.29
1.27
1.23
1.20
0.81
0.57
0.27
0.23
0.88
0.87
0.81
0.81
0.58
0.57
0.27
0.23
0.70
0.82
0.77
0.70
0.72
0.77
0.67
0.64
f1 (ppm)

HN
Ph
O

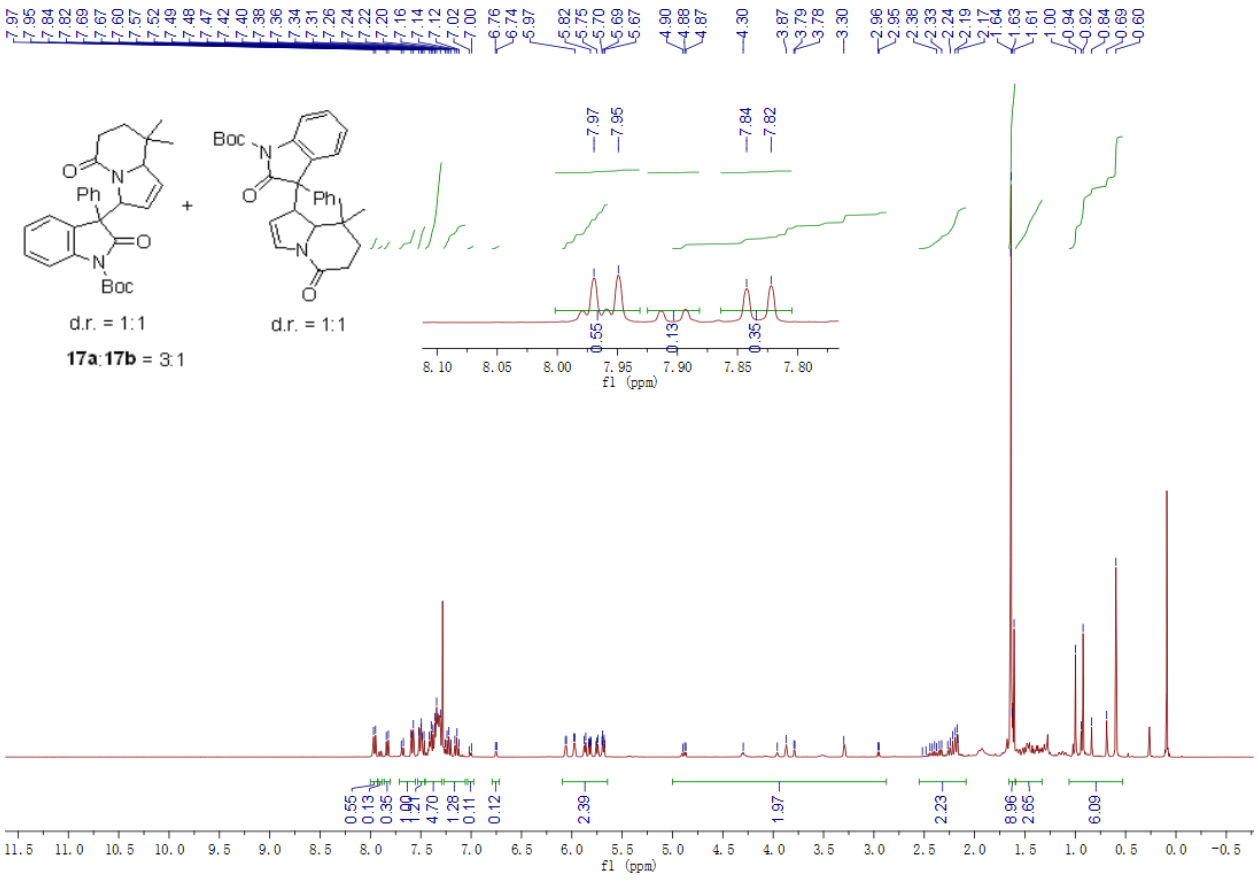
d.r. = 1:1:1:1

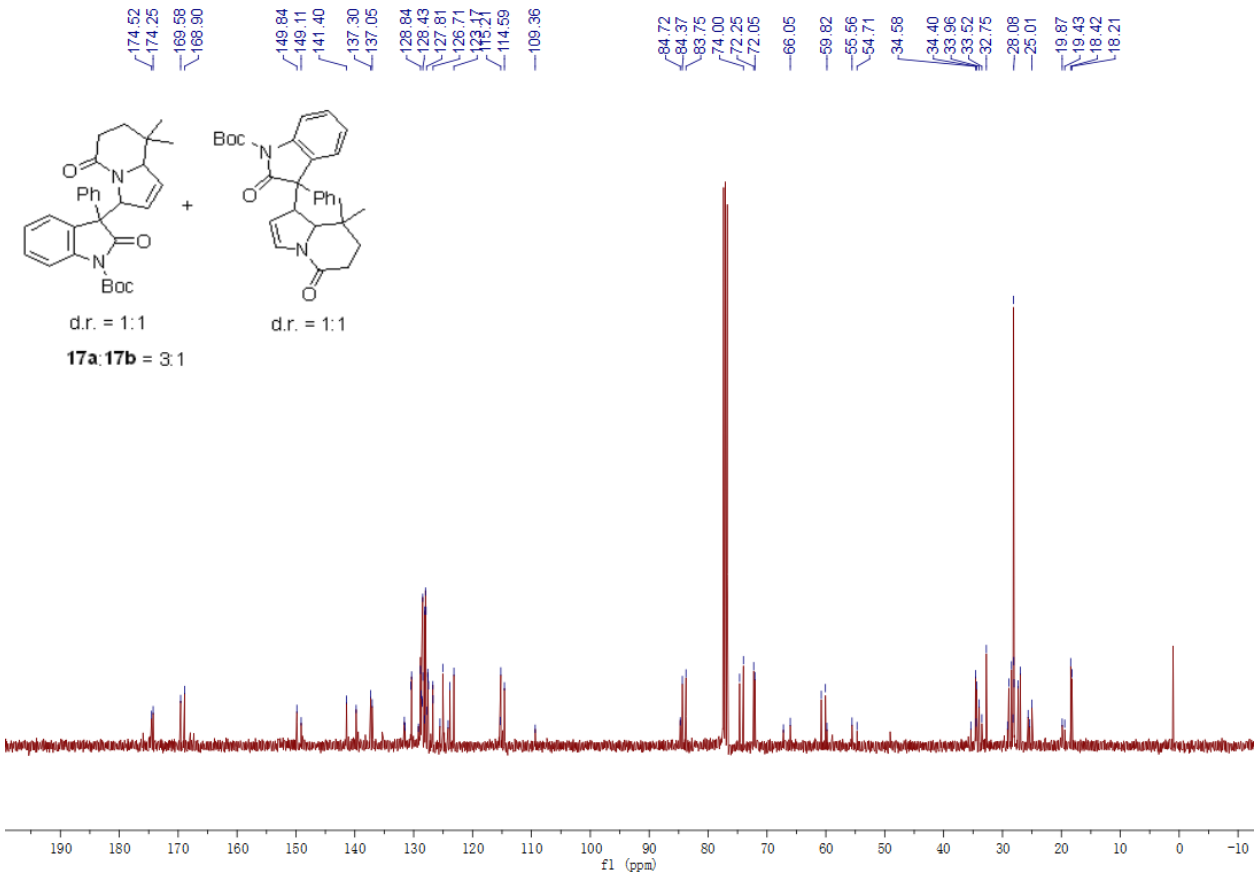

0.97
1.95
3.69
1.34
2.06
0.53
1.47
0.98
1.00
0.48
1.02
1.06
0.92
0.76
3.44
0.67
0.64
f1 (ppm)

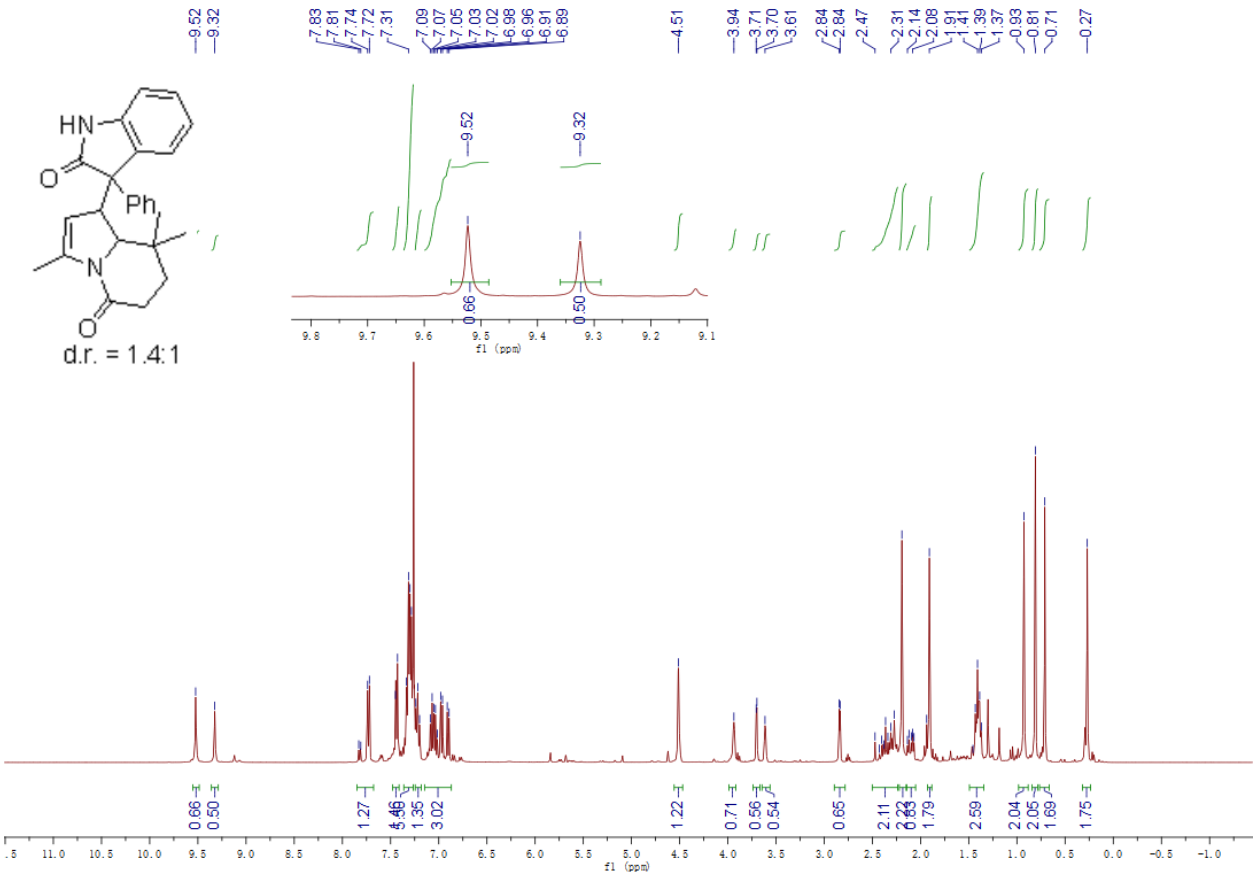

180.24
179.09
145.82
141.81
141.17
139.77
138.95
138.15
138.11
136.52
136.16
129.98
129.86
129.69
129.08
129.01
128.59
128.55
128.43
128.25
128.00
127.94
127.89
127.71
127.66
127.63
127.37
126.67
125.83
125.27
125.24
124.66
124.42
122.73
121.90
121.85
117.46
110.21
109.82
60.37
60.30
52.81
47.07
47.03
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

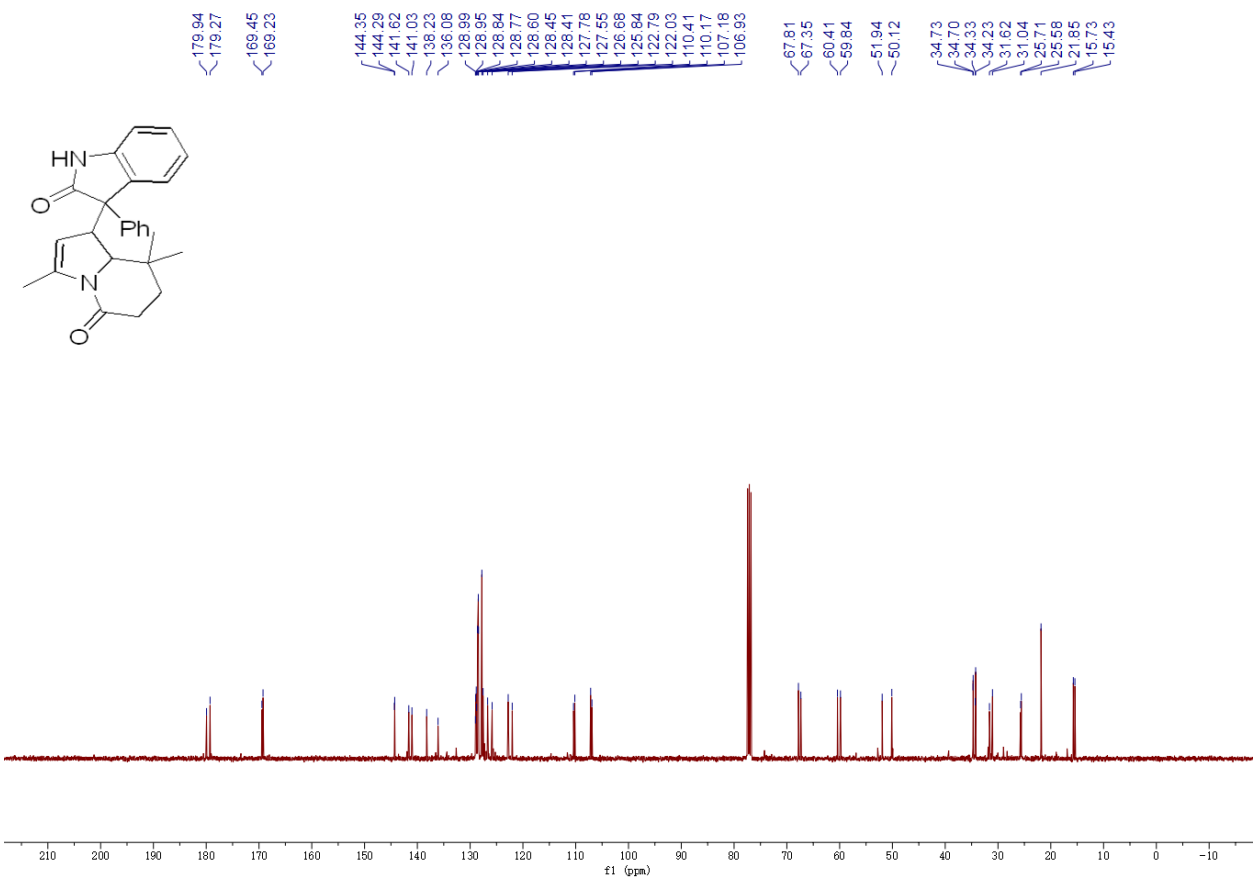

HN
Ph
O

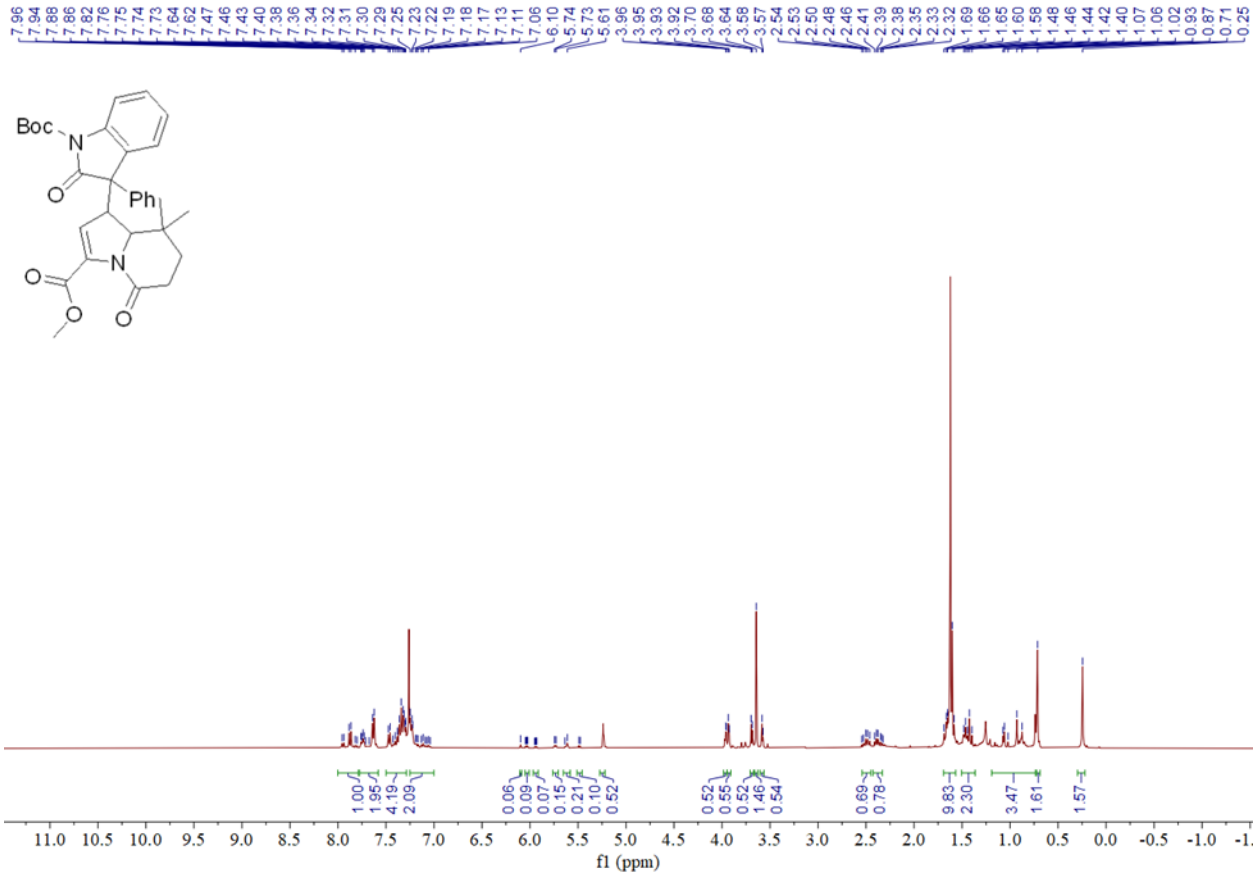
f1 (ppm)

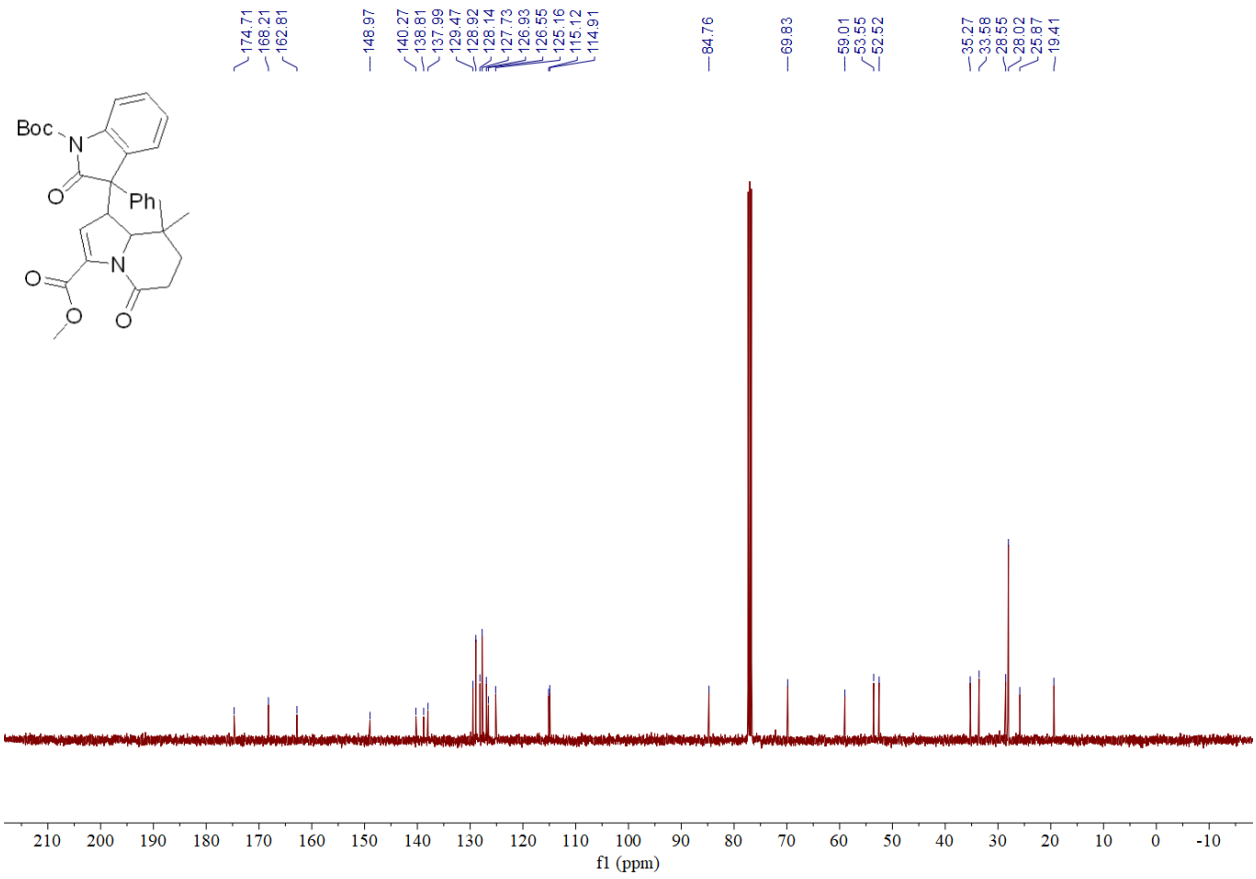

Boc
Ph
d.r. = 1:1
d.r. = 1:1
17a:17b = 3:1
f1 (ppm)

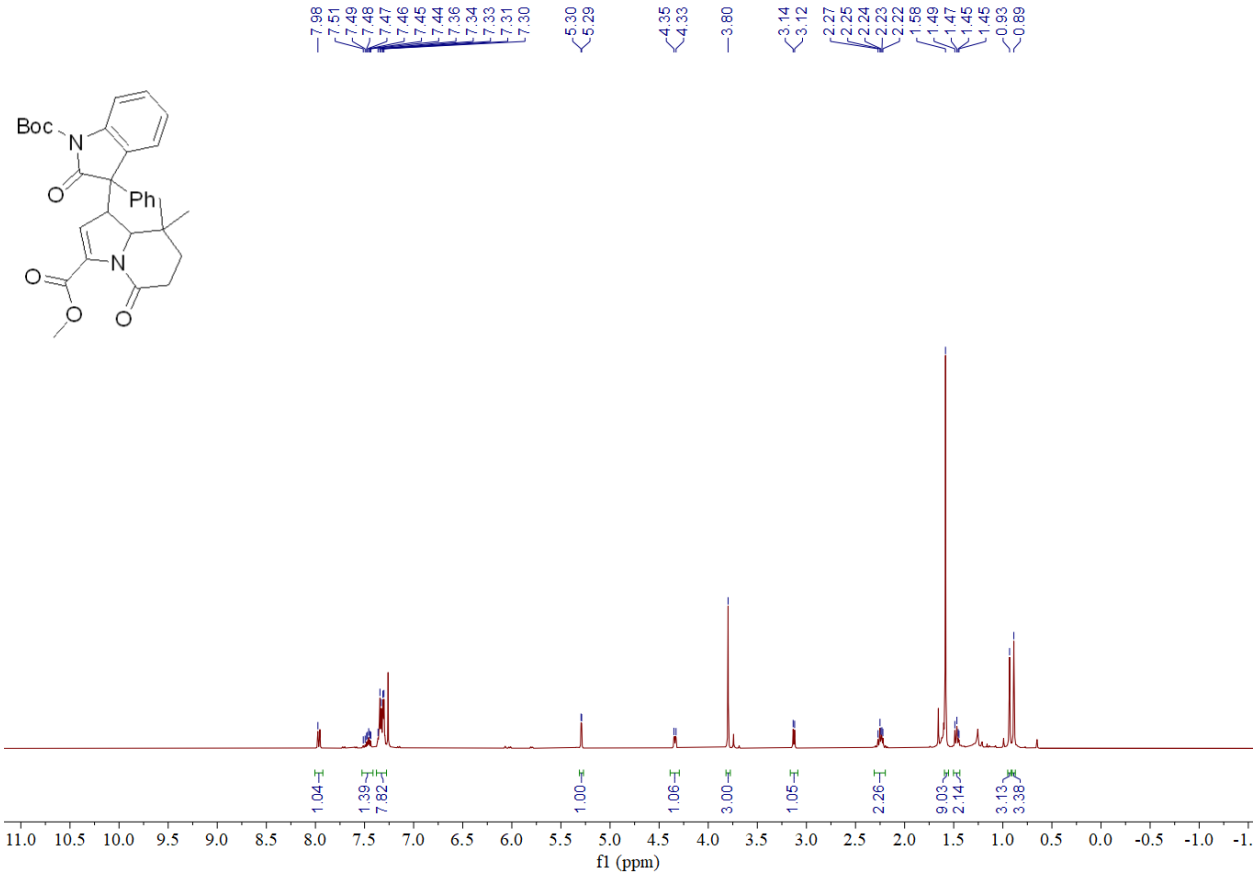

Boc
Ph
d.r. = 1:1
d.r. = 1:1
17a:17b = 3:1
f1 (ppm)

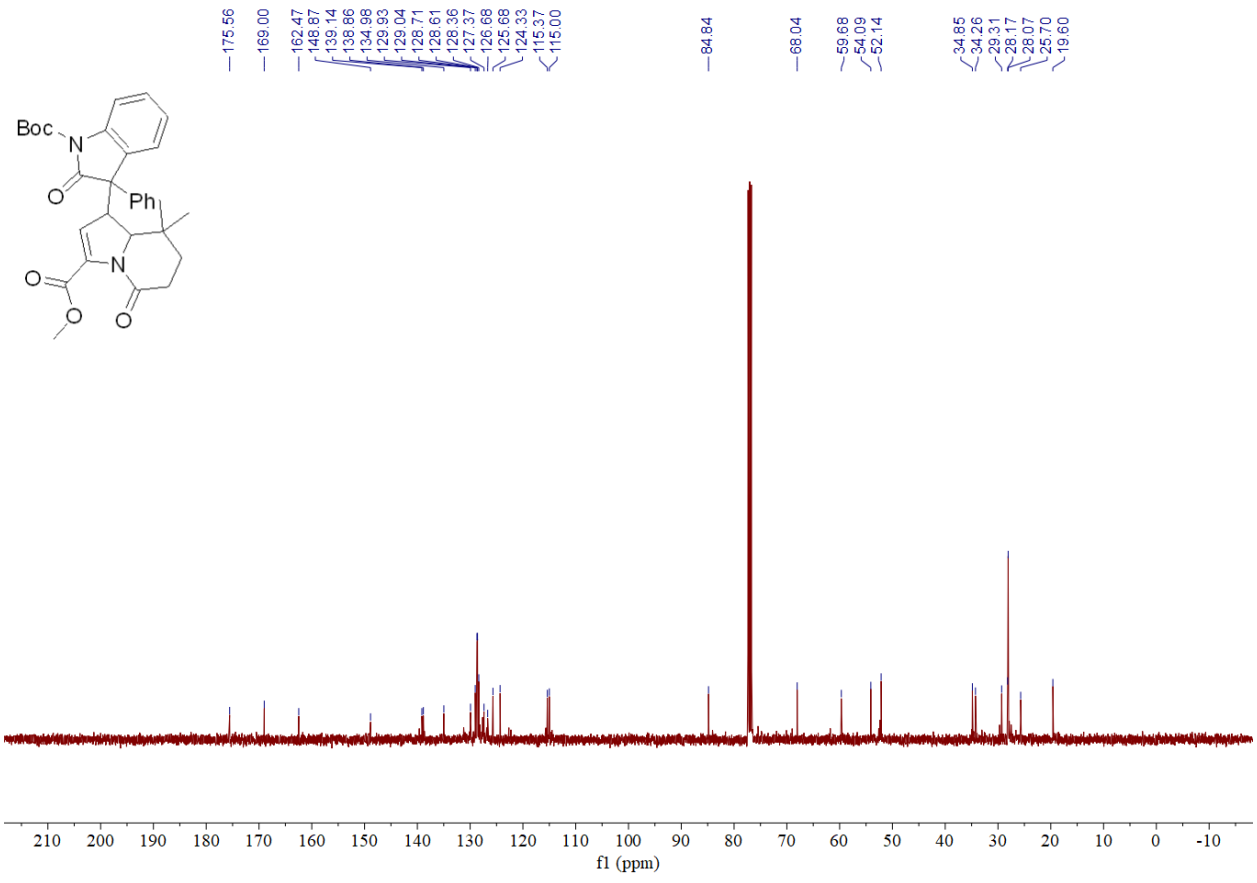

HN
O
Ph
N
O
d.r. = 1.4:1
9.52
9.32
0.66
0.50
f1 (ppm)

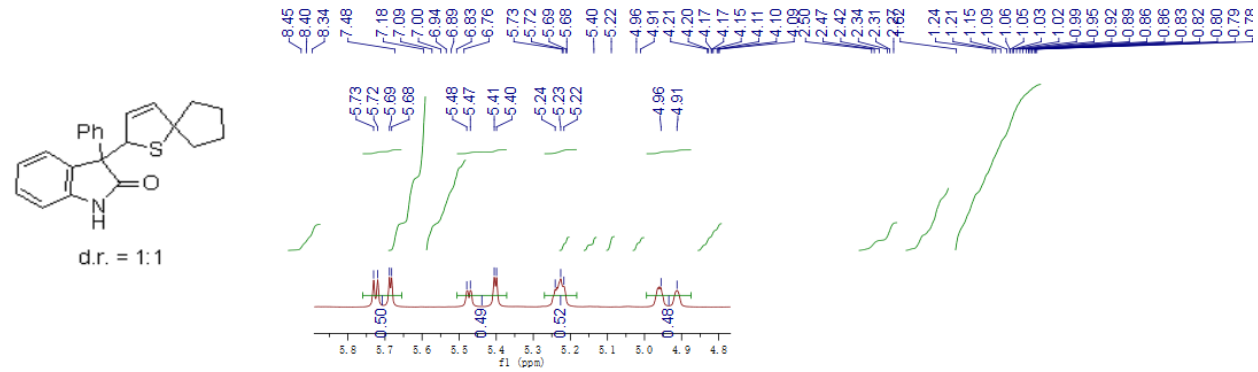

HN
O
Ph
N
O
f1 (ppm)

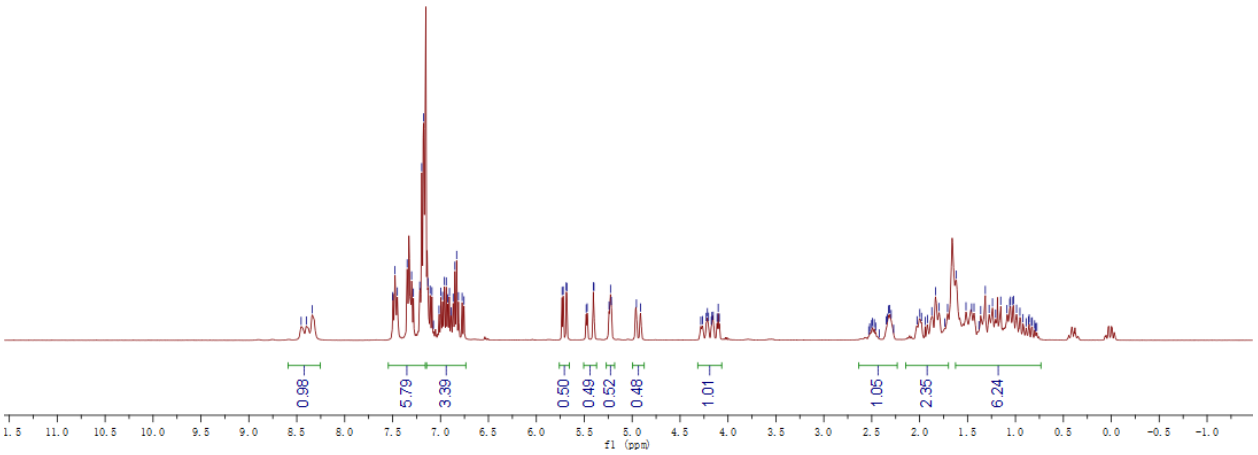

Boc
N
O
Ph
N
O
O
O
f1 (ppm)

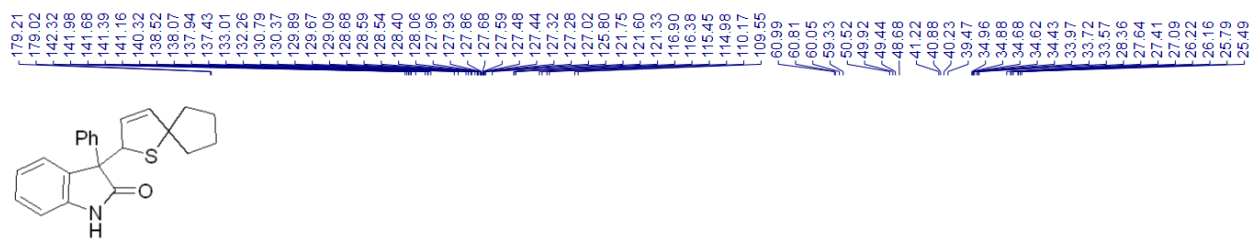

Boc
N
O
Ph
N
O
O
O
f1 (ppm)


7.98
7.51
7.49
7.48
7.47
7.46
7.45
7.44
7.36
7.34
7.33
7.31
7.30
5.30
5.29
4.35
4.33
3.80
3.14
3.12
2.27
2.25
2.24
2.23
2.22
1.58
1.49
1.47
1.45
0.93
0.89
Boc
N
O
Ph
N
O
O
O
1.04
1.39
7.82
1.00
1.06
3.00
1.05
2.26
9.03
2.14
3.13
3.38
f1 (ppm)

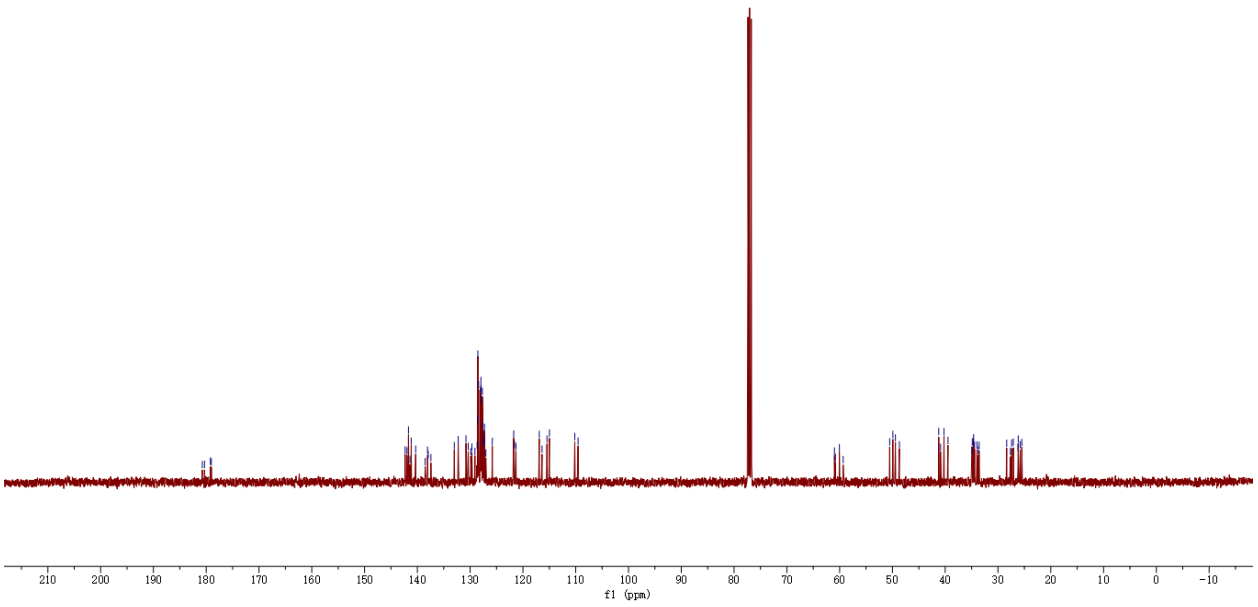

175.56
169.00
162.47
148.87
139.14
138.86
134.98
129.93
129.04
128.71
128.61
128.36
127.37
126.68
125.68
124.33
115.37
115.00
84.84
68.04
59.68
54.09
52.14
34.85
34.26
29.31
28.17
28.07
25.70
19.60
Boc
N
O
Ph
N
O
O
O
f1 (ppm)

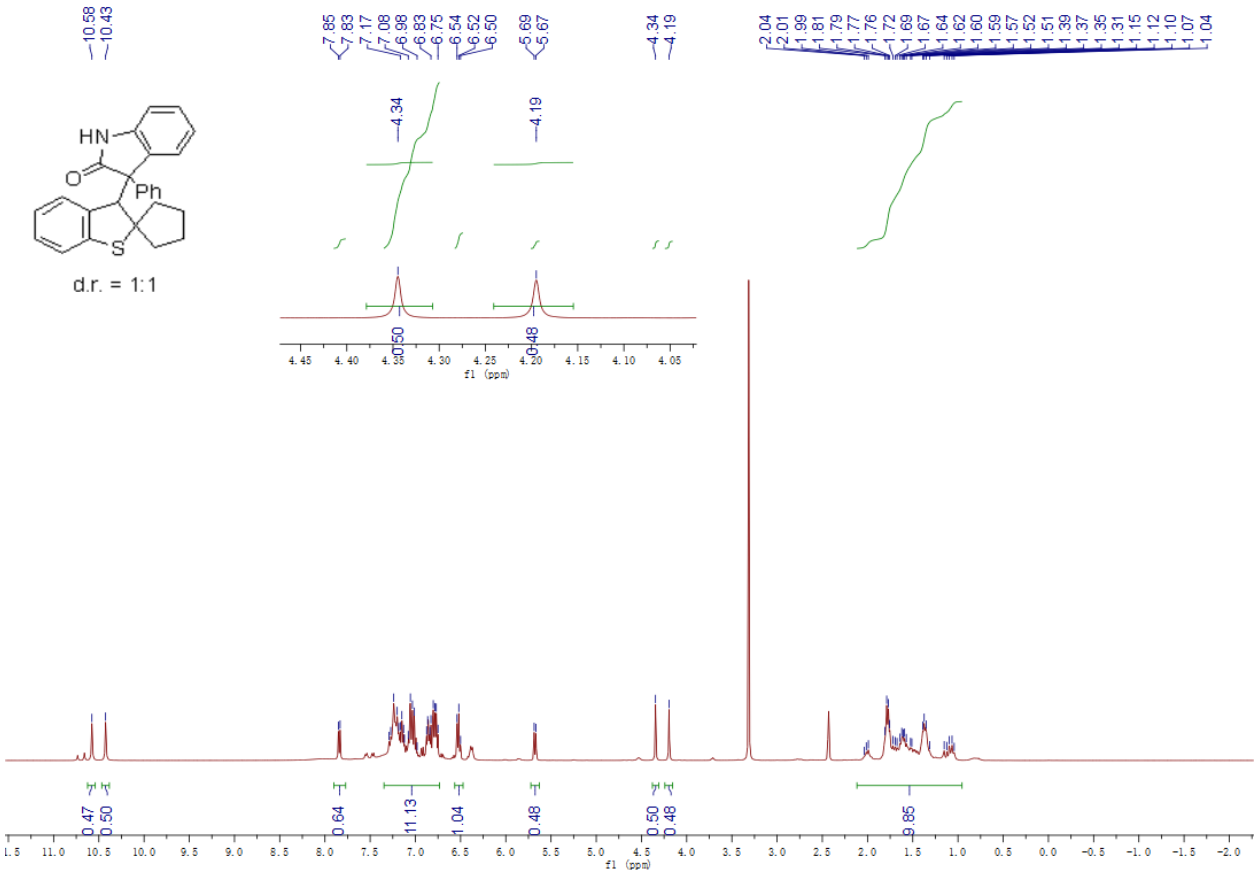

Ph
S
O
N
H
d.r. = 1:1

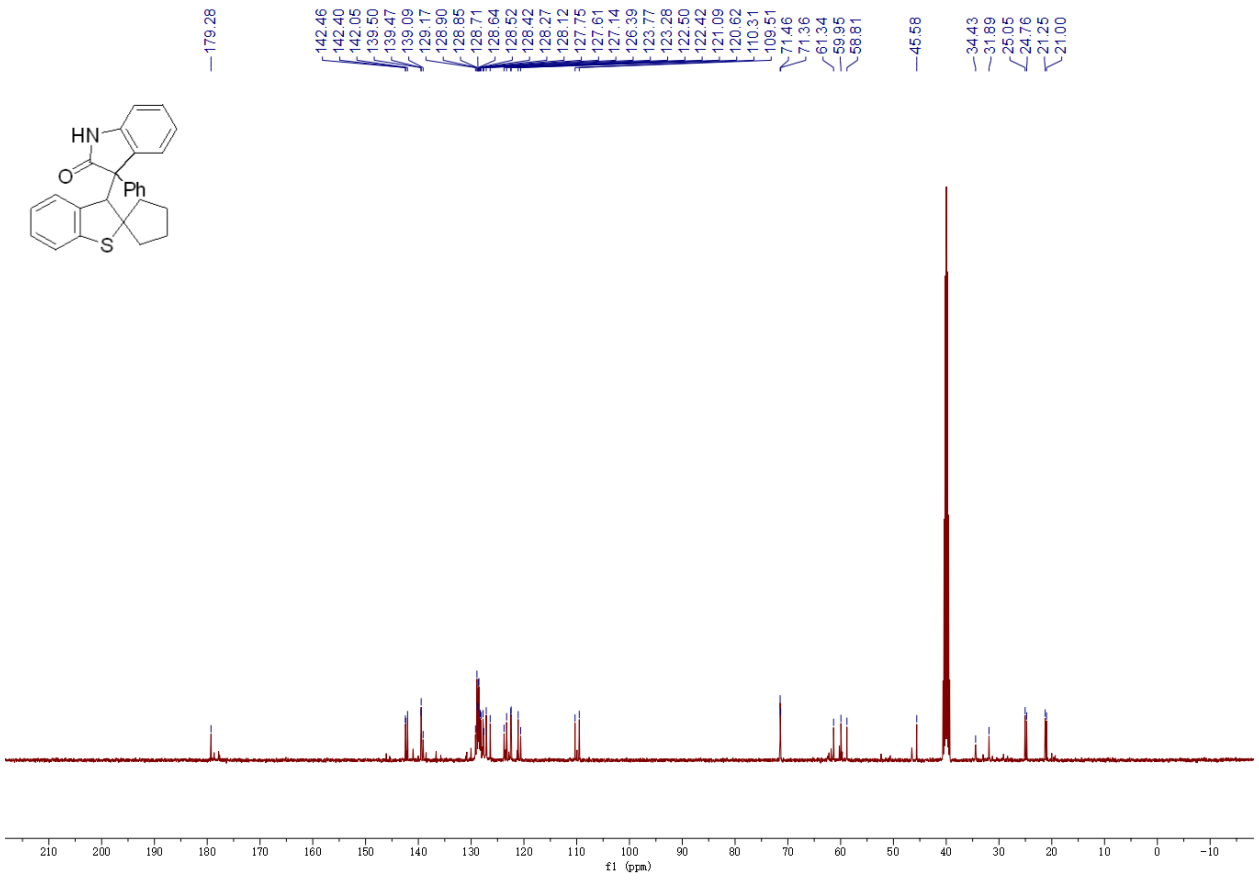

0.98
5.79
3.39
0.50
0.49
0.52
0.48
1.01
1.05
2.35
6.24
f1 (ppm)

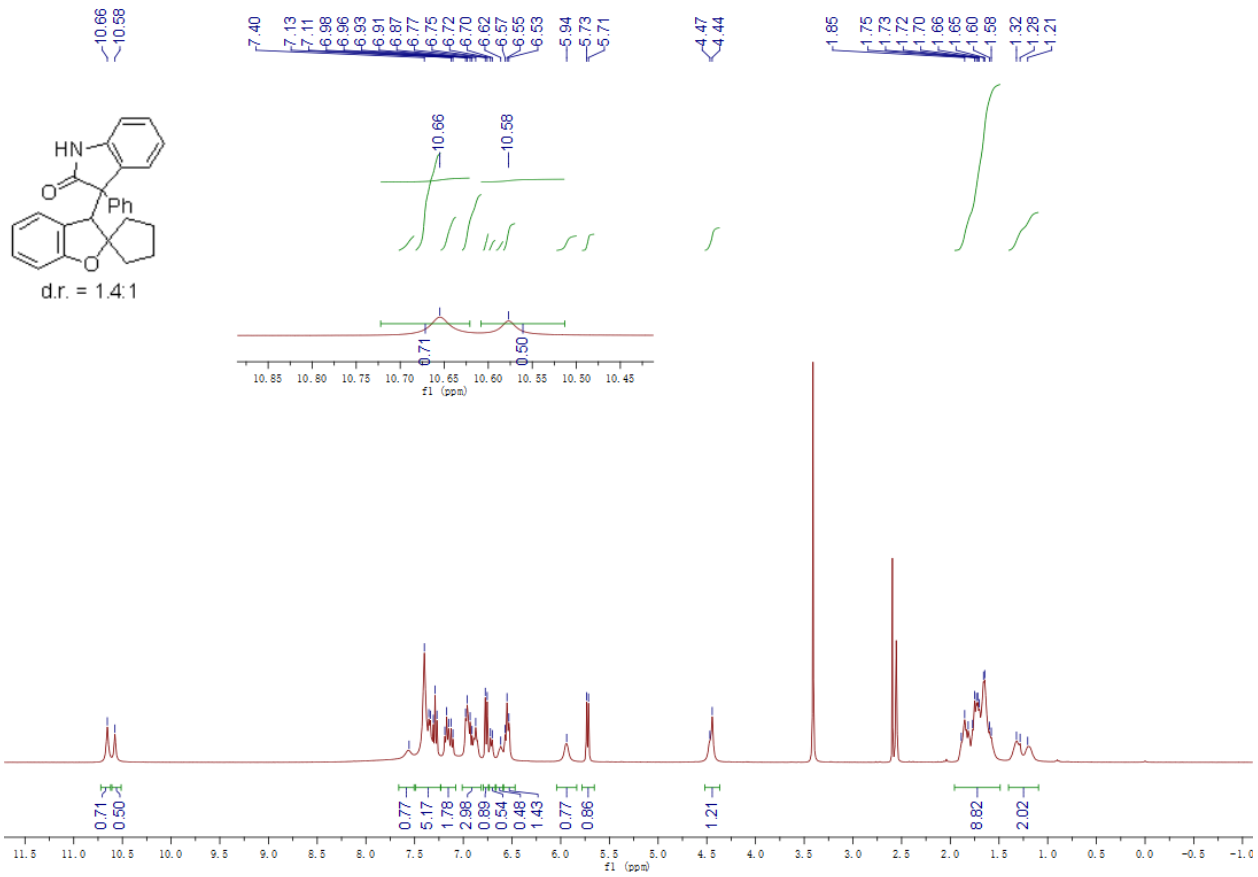


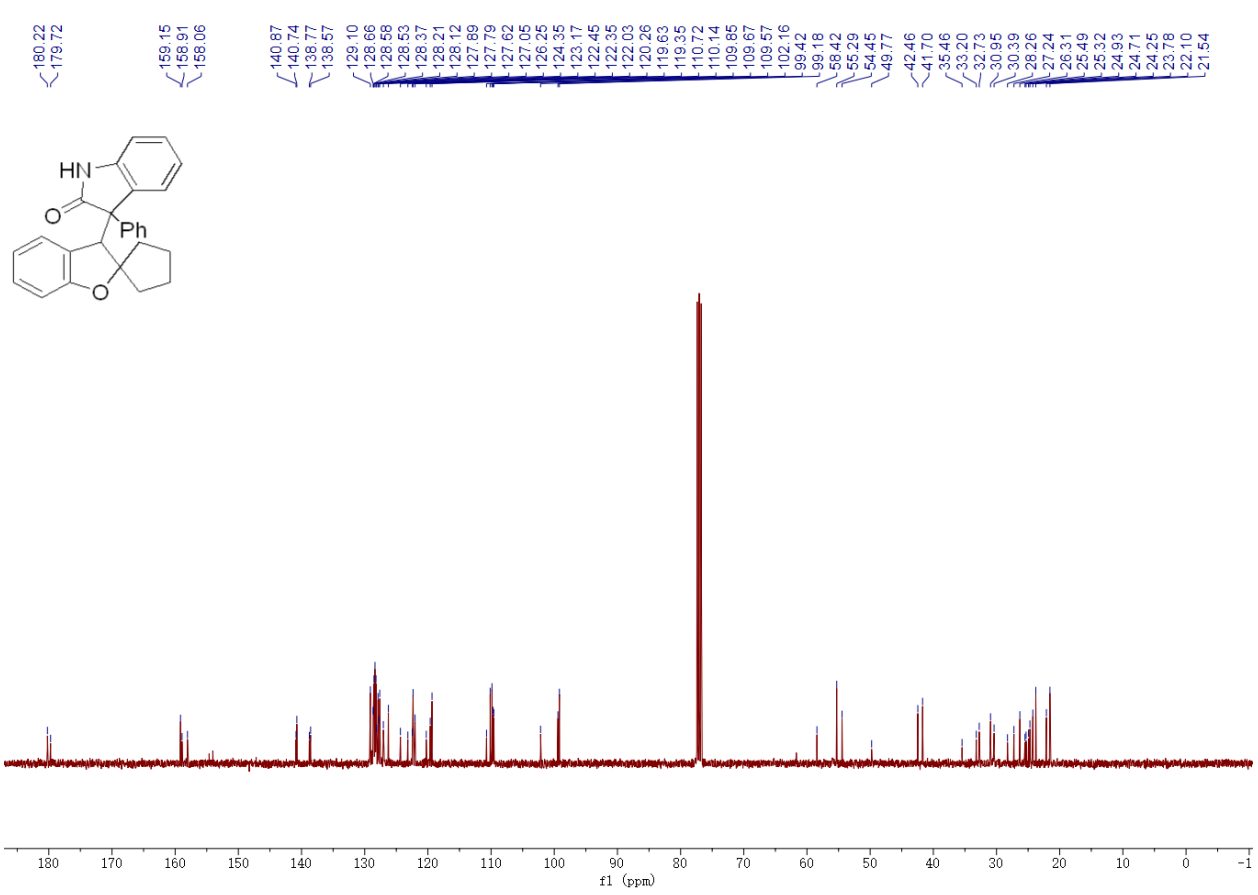
Ph
S
O
N
H

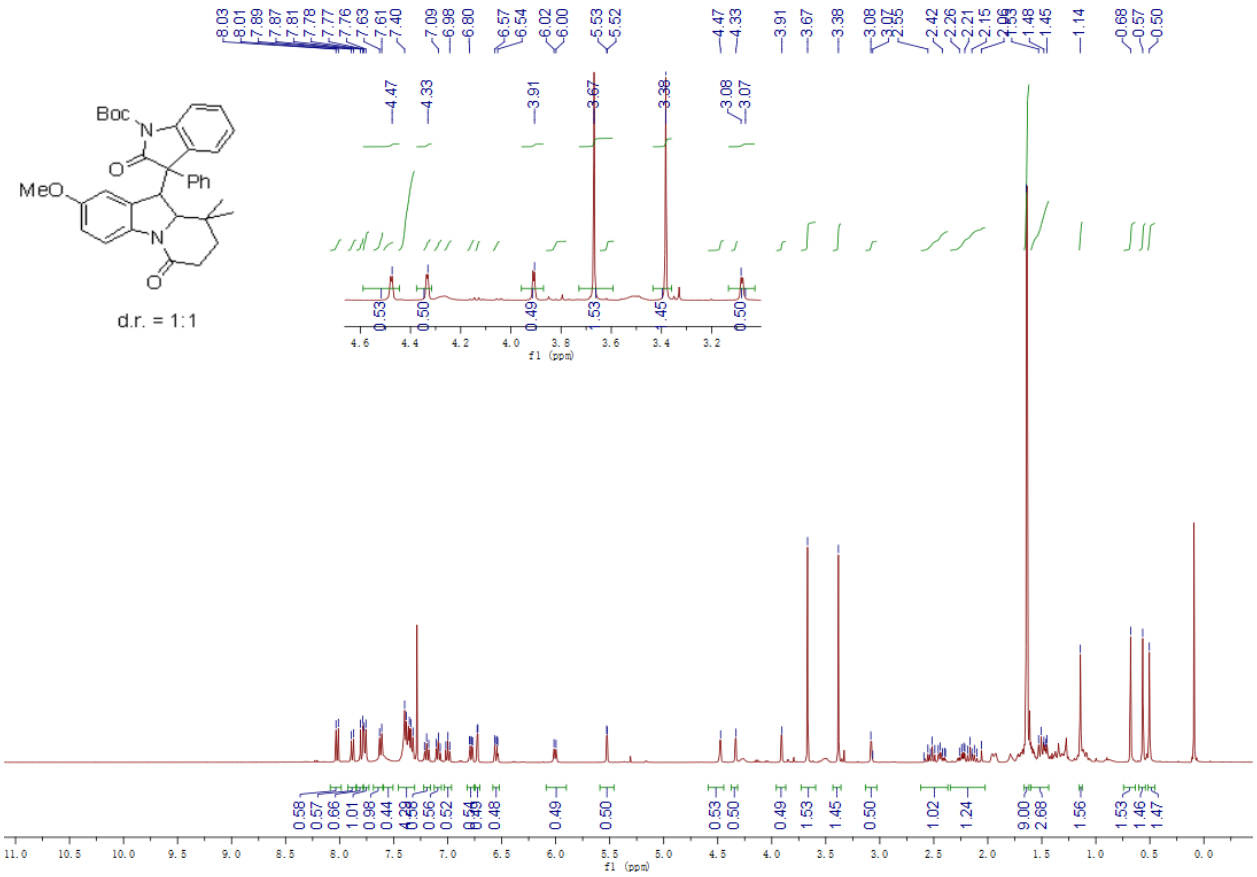

f1 (ppm)

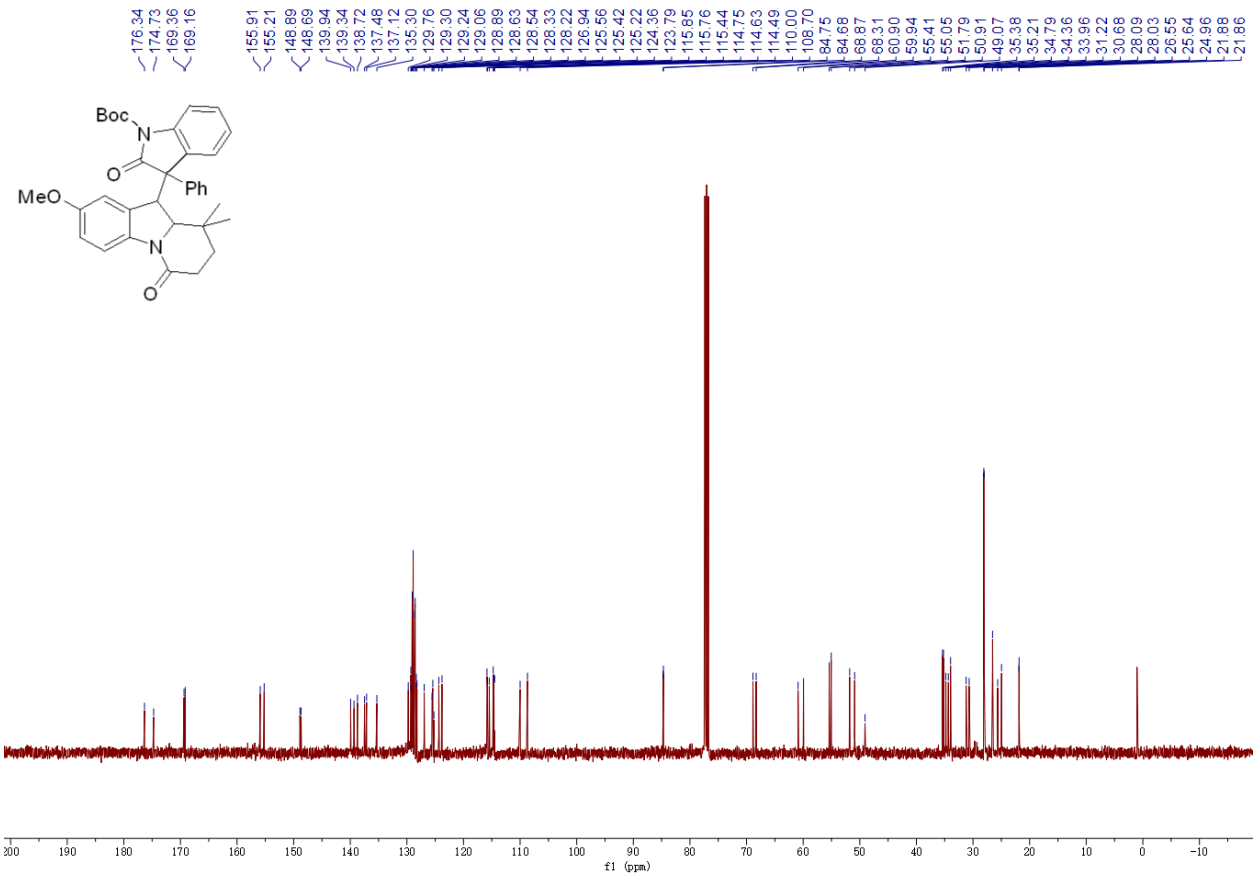

10.58
10.43
7.85
7.83
7.17
7.08
6.98
6.83
6.75
6.54
6.52
6.50
5.69
5.67
4.34
4.19
2.04
2.01
1.99
1.81
1.79
1.77
1.76
1.72
1.69
1.67
1.64
1.62
1.60
1.59
1.57
1.52
1.51
1.39
1.37
1.35
1.31
1.15
1.12
1.10
1.07
1.04
HN
O
Ph
S
d.r. = 1:1
0.50
0.48
f1 (ppm)
0.47
0.50
0.64
11.13
1.04
0.48
0.50
0.48
9.85
f1 (ppm)

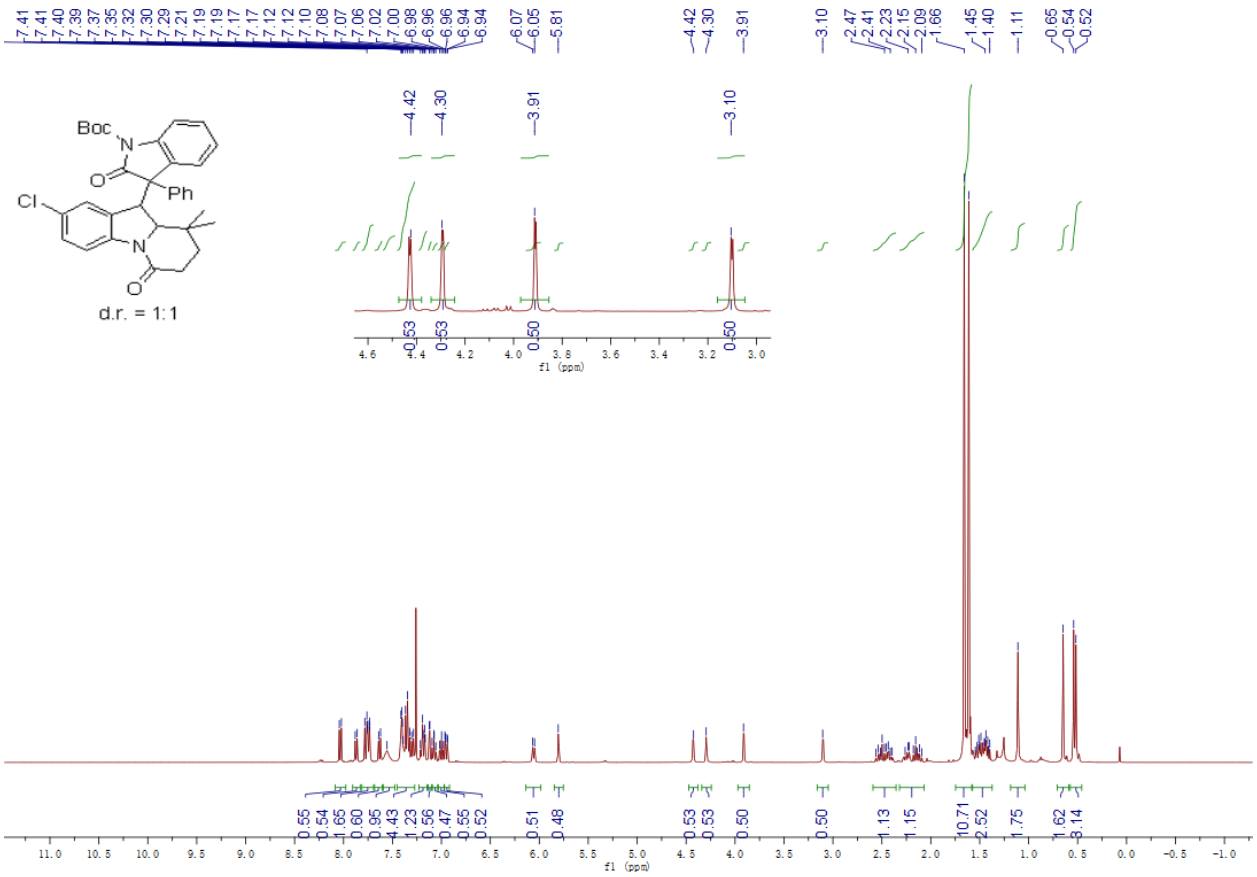

179.28
142.46
142.40
142.05
139.50
139.47
139.09
129.17
128.90
128.85
128.71
128.64
128.52
128.42
128.27
128.12
127.75
127.61
127.14
126.39
123.77
123.28
122.50
122.42
121.09
120.62
110.31
109.51
71.46
71.36
61.34
59.95
58.81
45.58
34.43
31.89
25.05
24.76
21.25
21.00
HN
O
Ph
S
f1 (ppm)

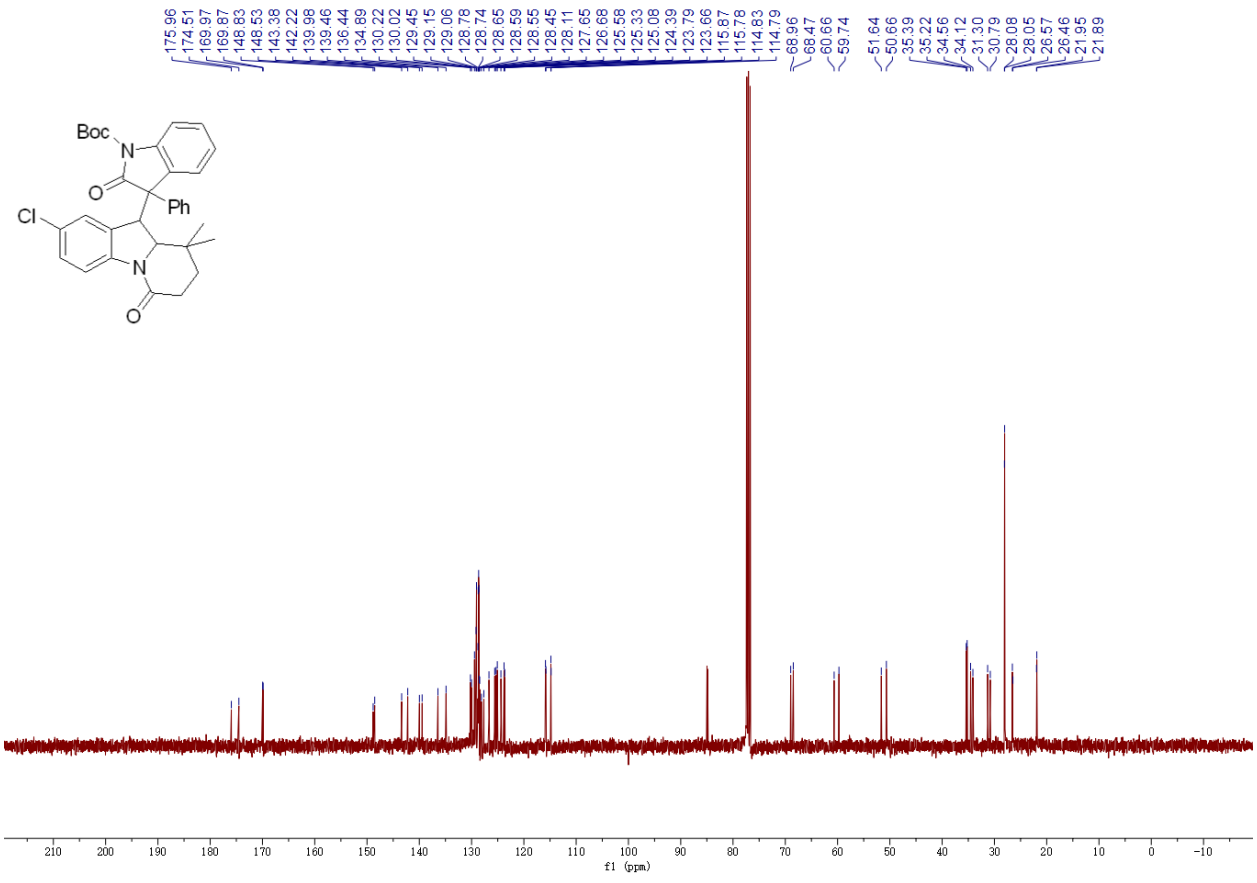

HN
O
Ph
O
d.r. = 1.4:1
f1 (ppm)

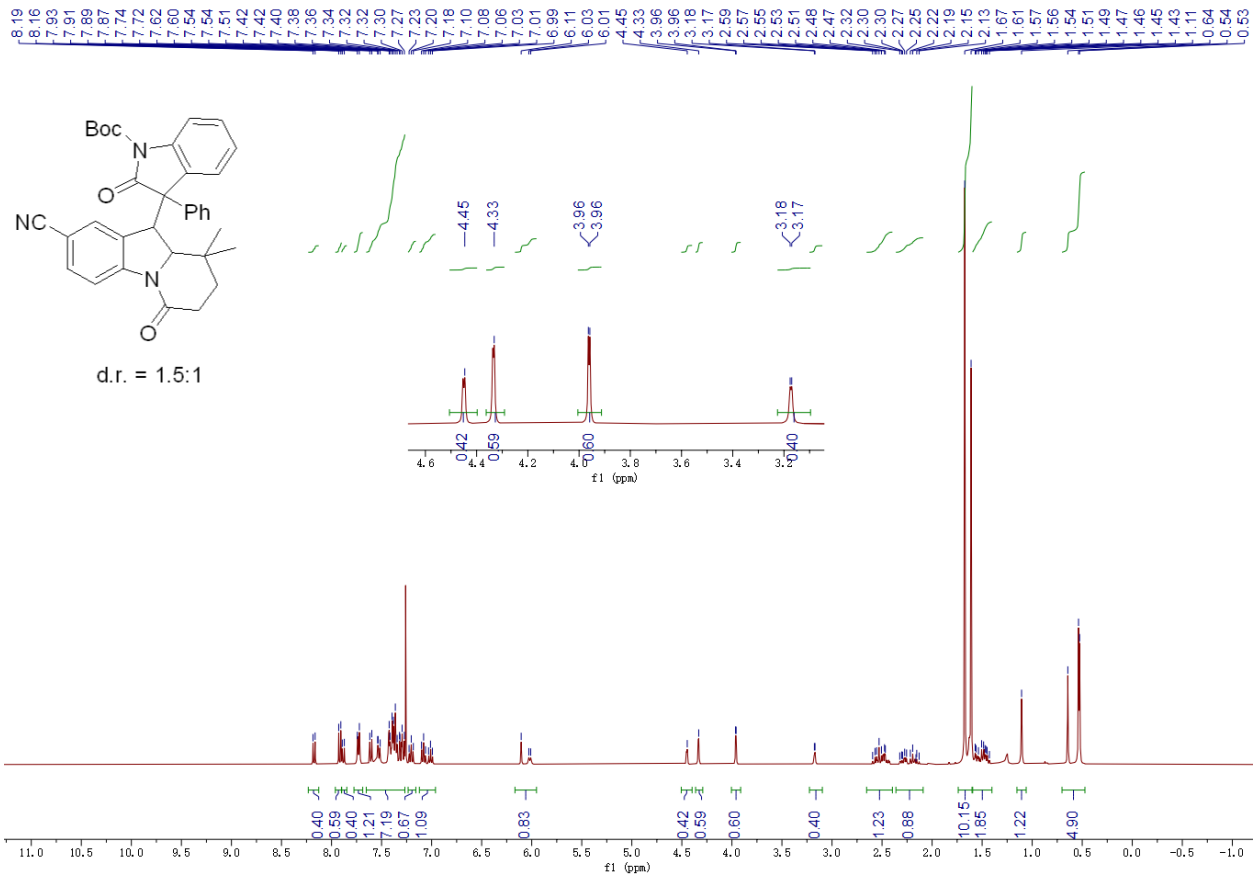

HN
O
Ph
O
f1 (ppm)

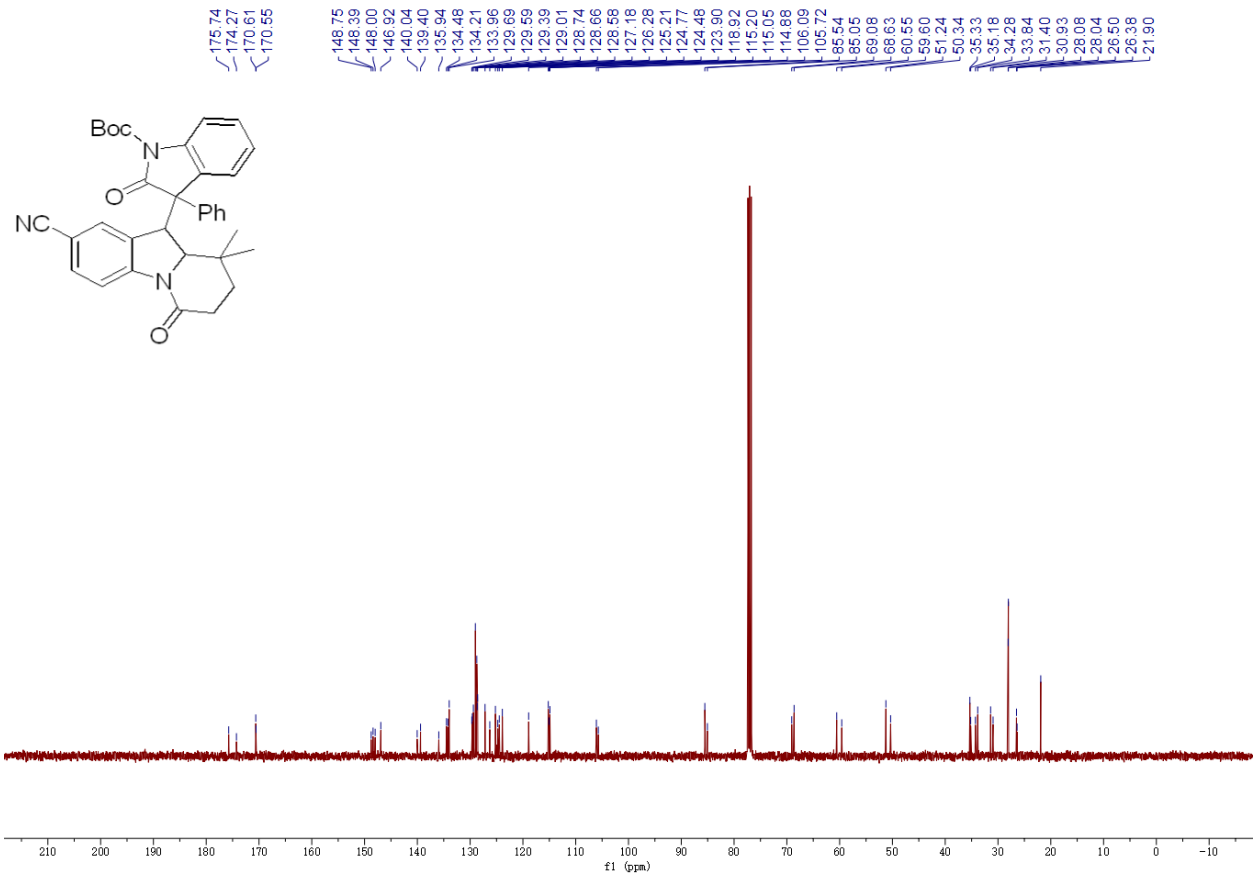

Boc
N
O
Ph
MeO
N
O
d.r. = 1:1
f1 (ppm)

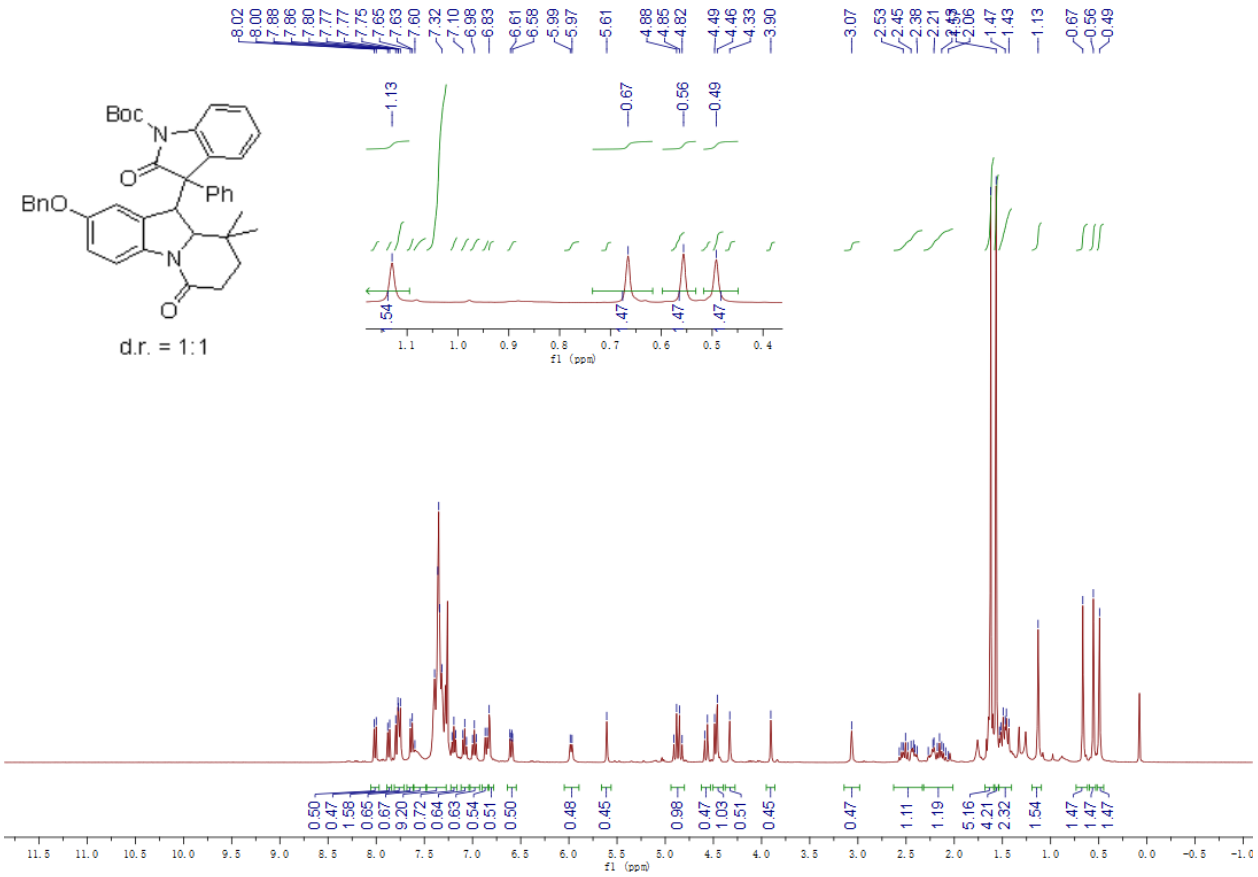

Boc
N
O
Ph
MeO
N
O
f1 (ppm)

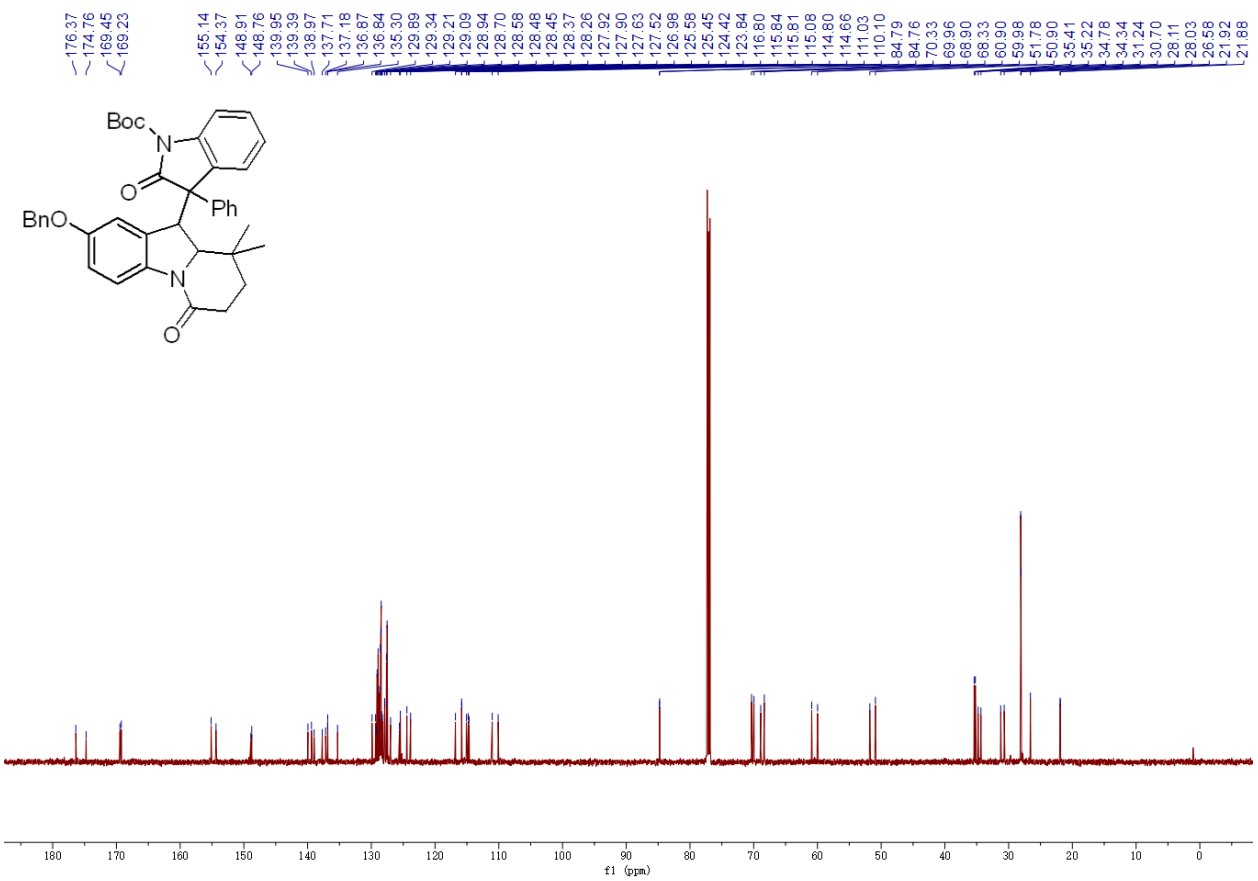

Boc
N
O
Ph
Cl
N
O
d.r. = 1:1
f1 (ppm)

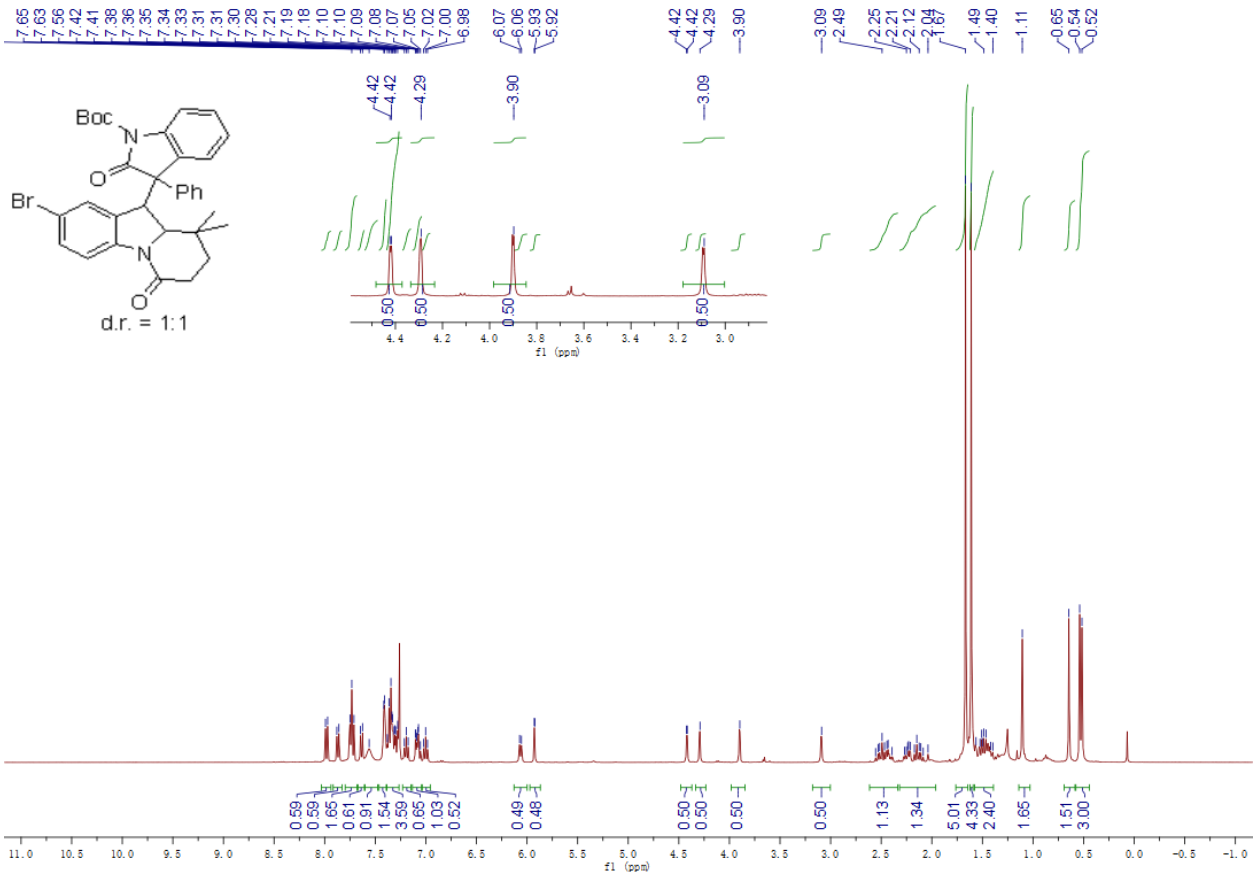

Boc
N
O
Ph
Cl
N
O
f1 (ppm)

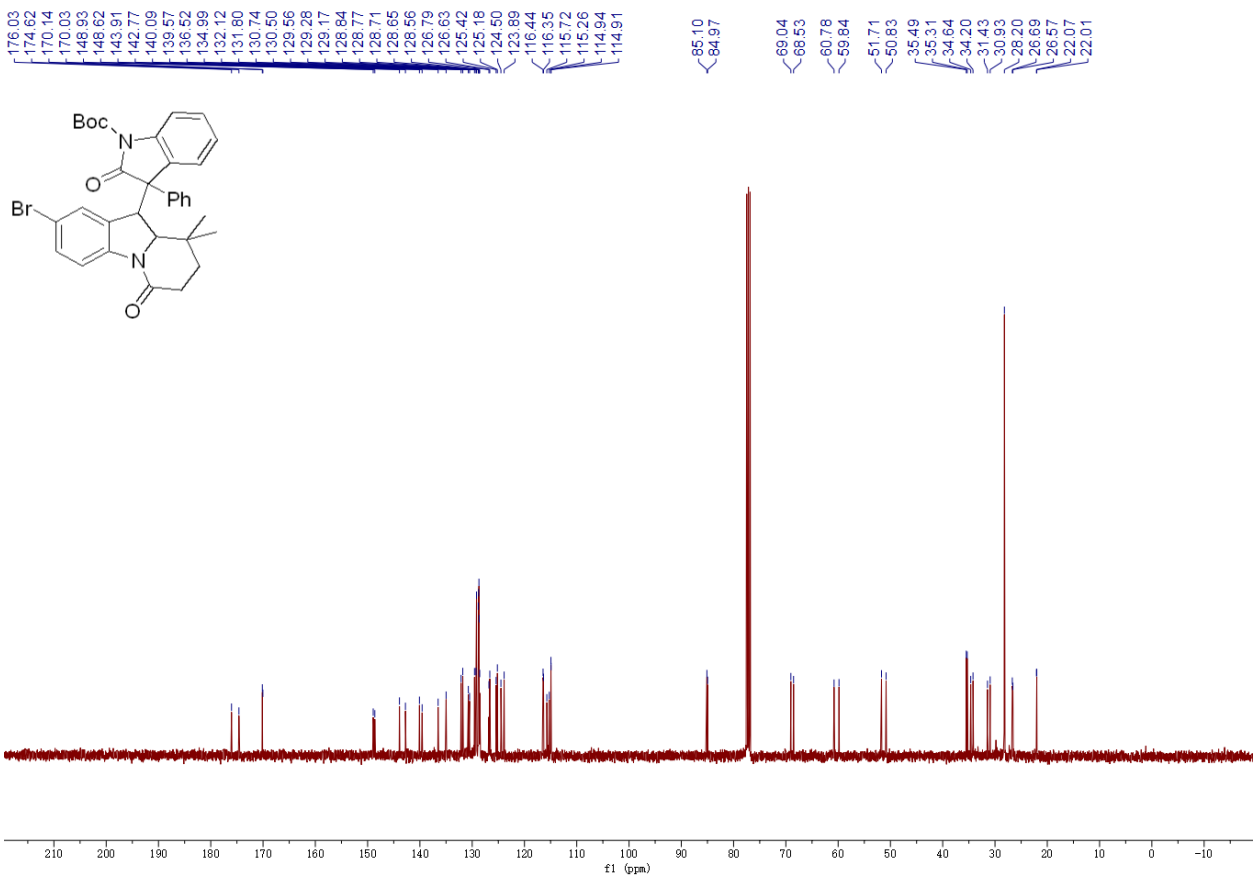

Boc
N
O
Ph
NC
N
O
d.r. = 1.5:1
f1 (ppm)

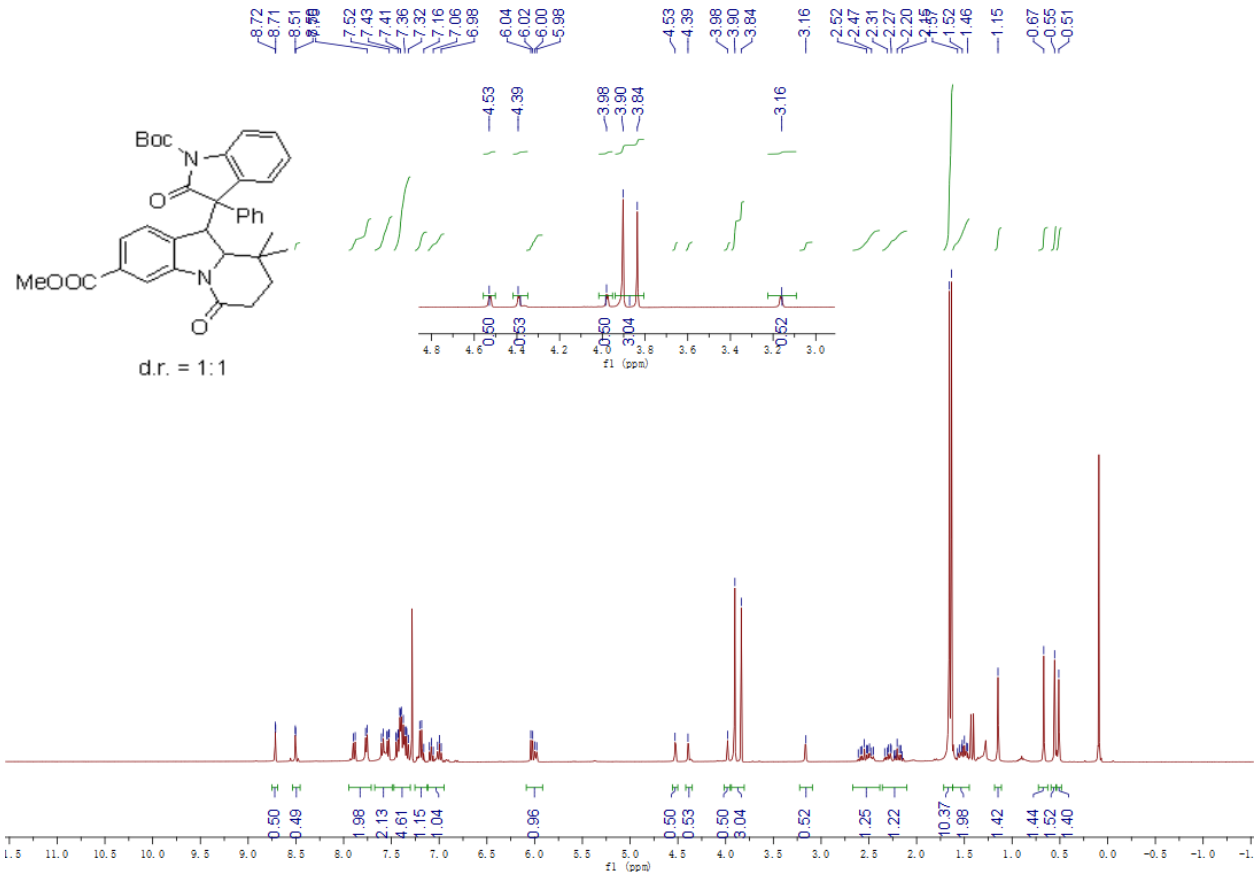

Boc
N
O
Ph
NC
N
O
f1 (ppm)

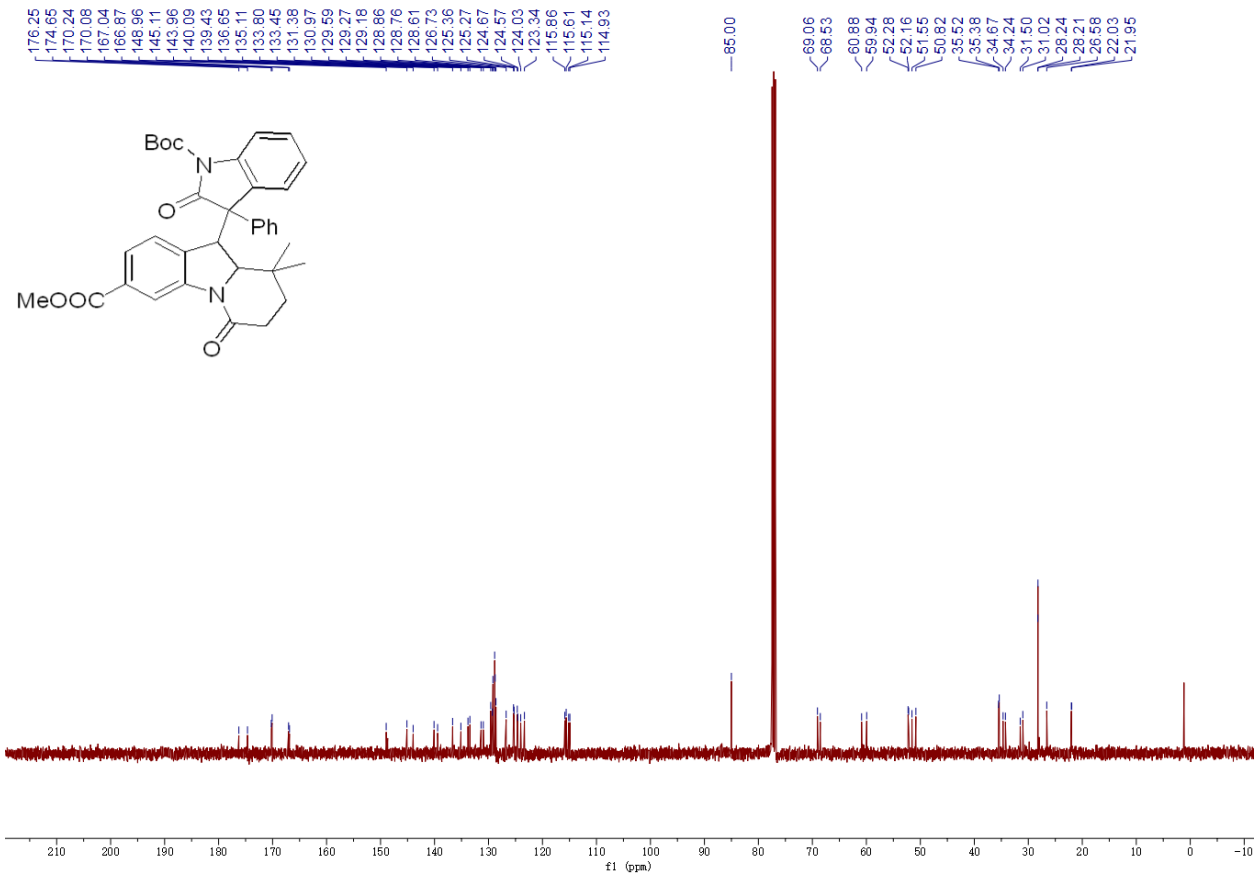

Boc
N
O
Ph
BnO
N
O
d.r. = 1:1
f1 (ppm)

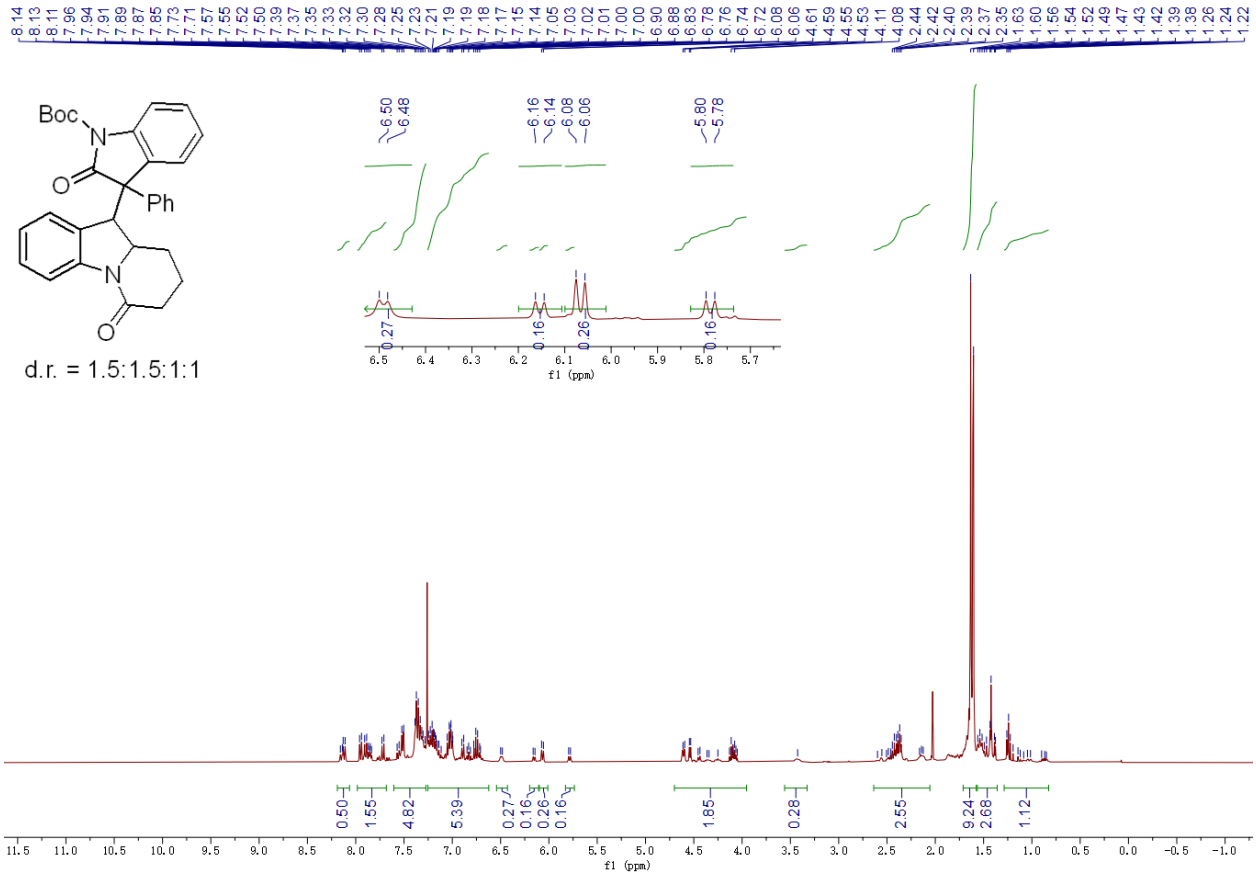

Boc
N
O
Ph
BnO
N
O
f1 (ppm)

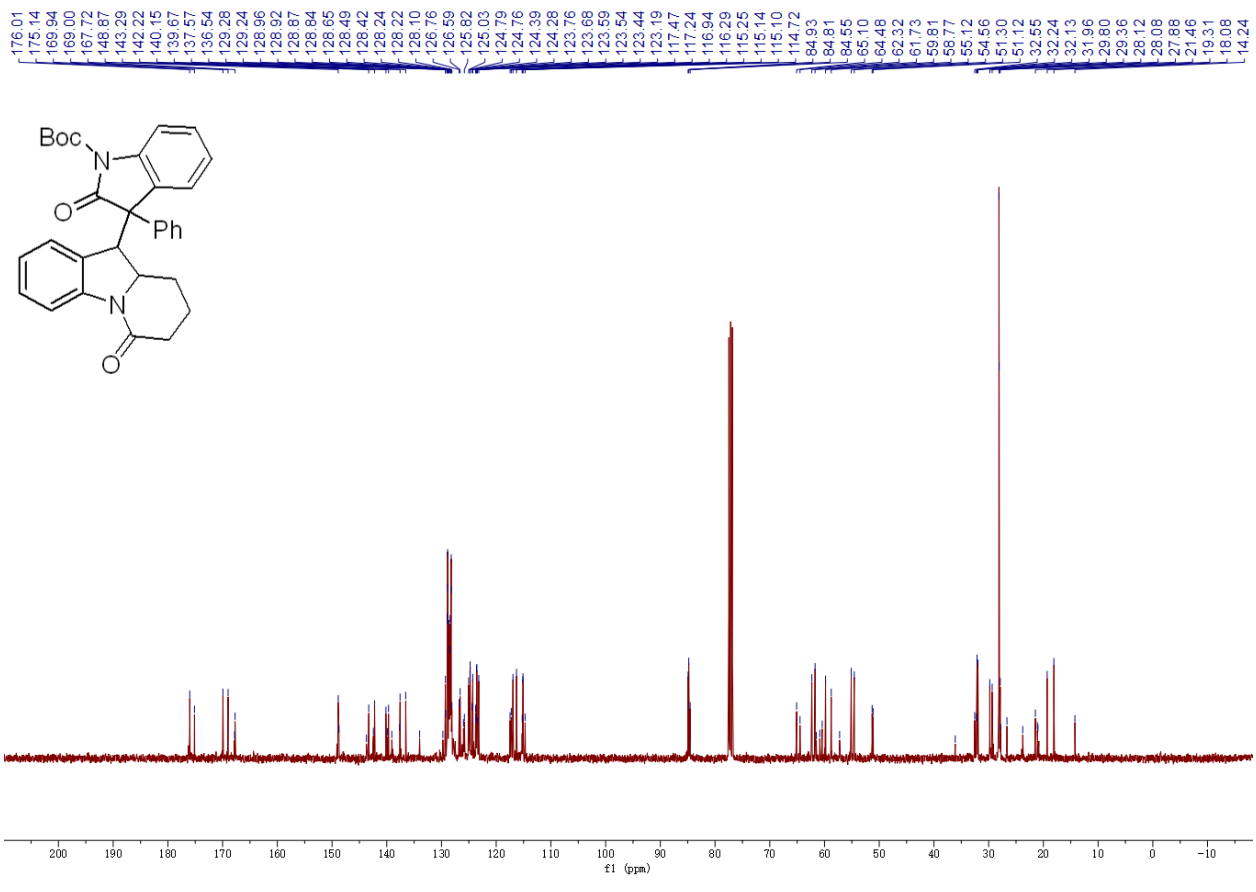

Boc
N
O
Ph
Br
N
O
d.r. = 1:1
f1 (ppm)

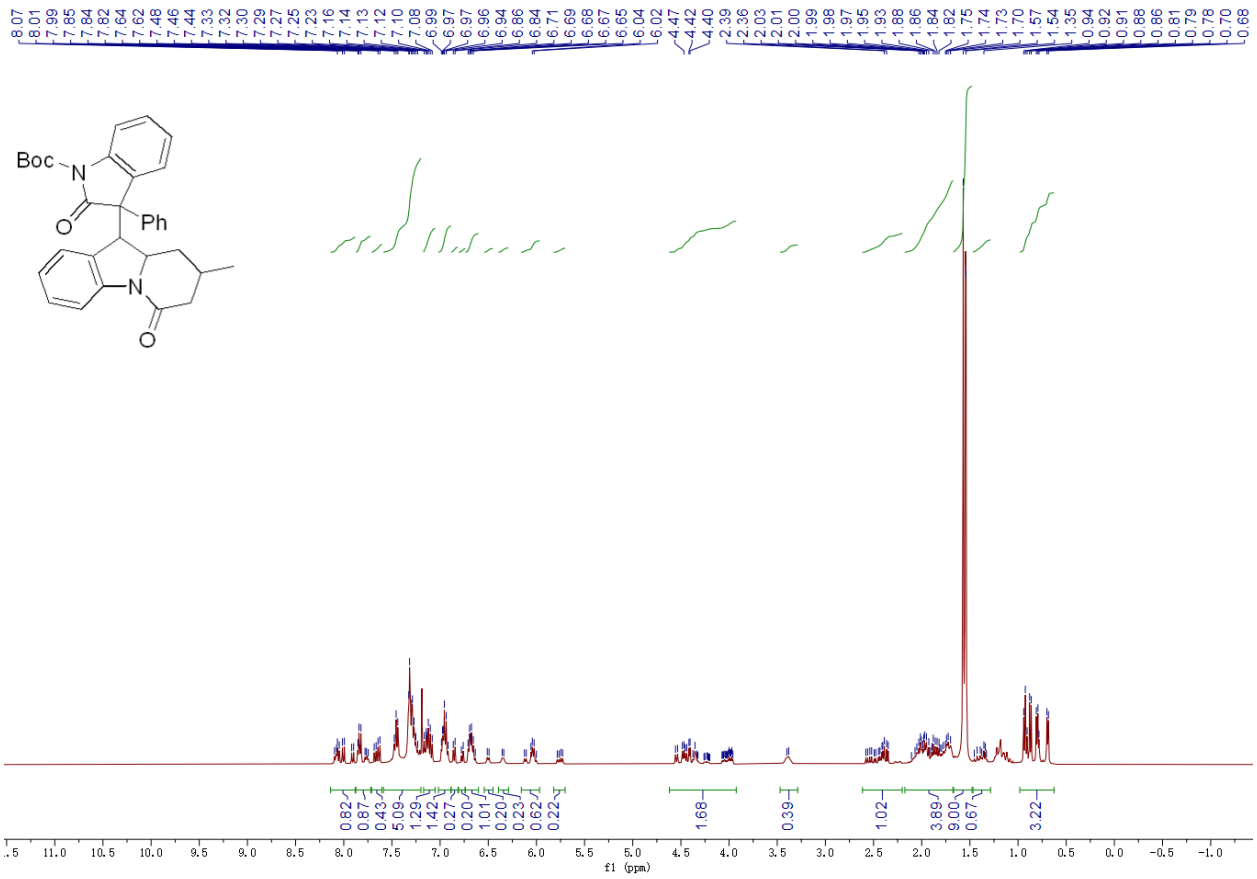

Boc
N
O
Ph
Br
N
O
f1 (ppm)

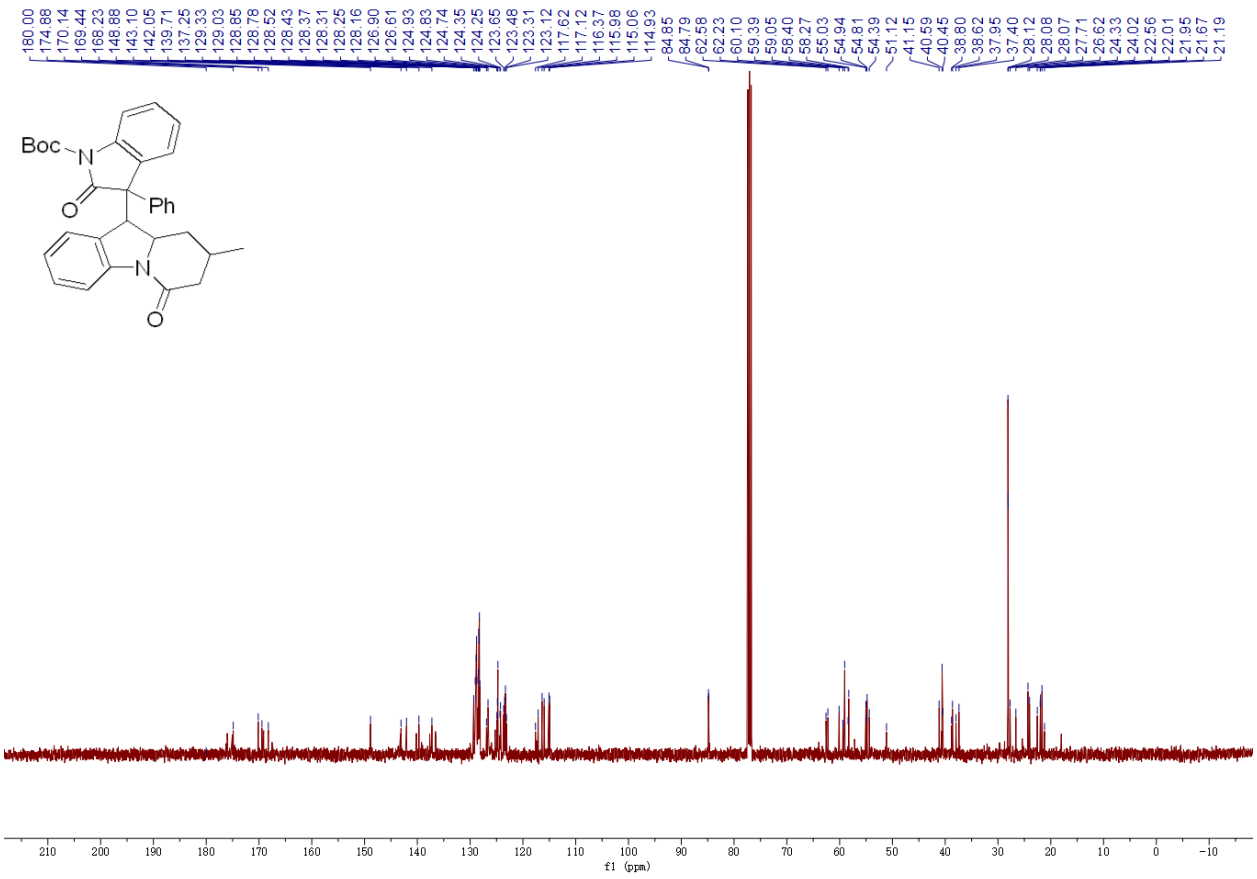

Boc
N
O
Ph
MeOOC
N
O
d.r. = 1:1
f1 (ppm)

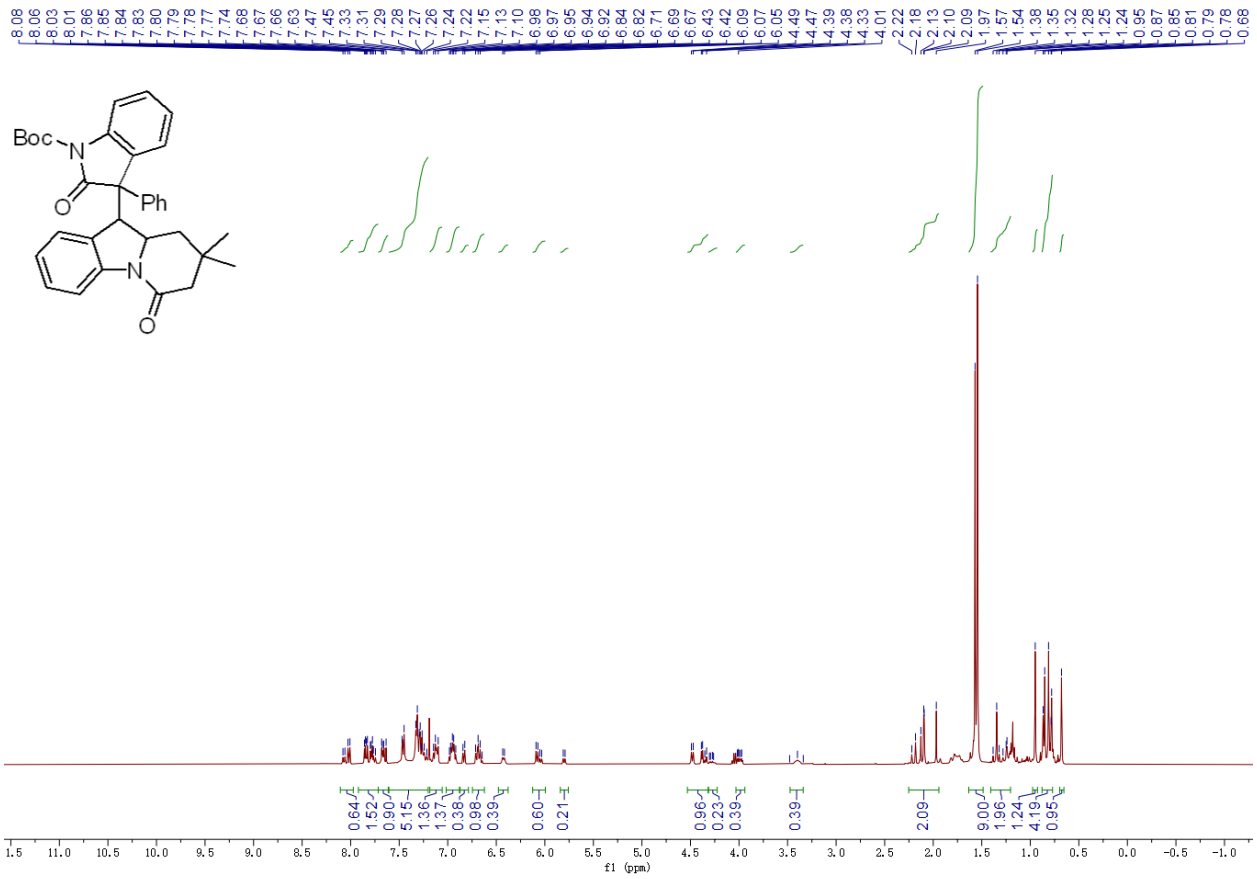

Boc
N
O
Ph
MeOOC
N
O
f1 (ppm)

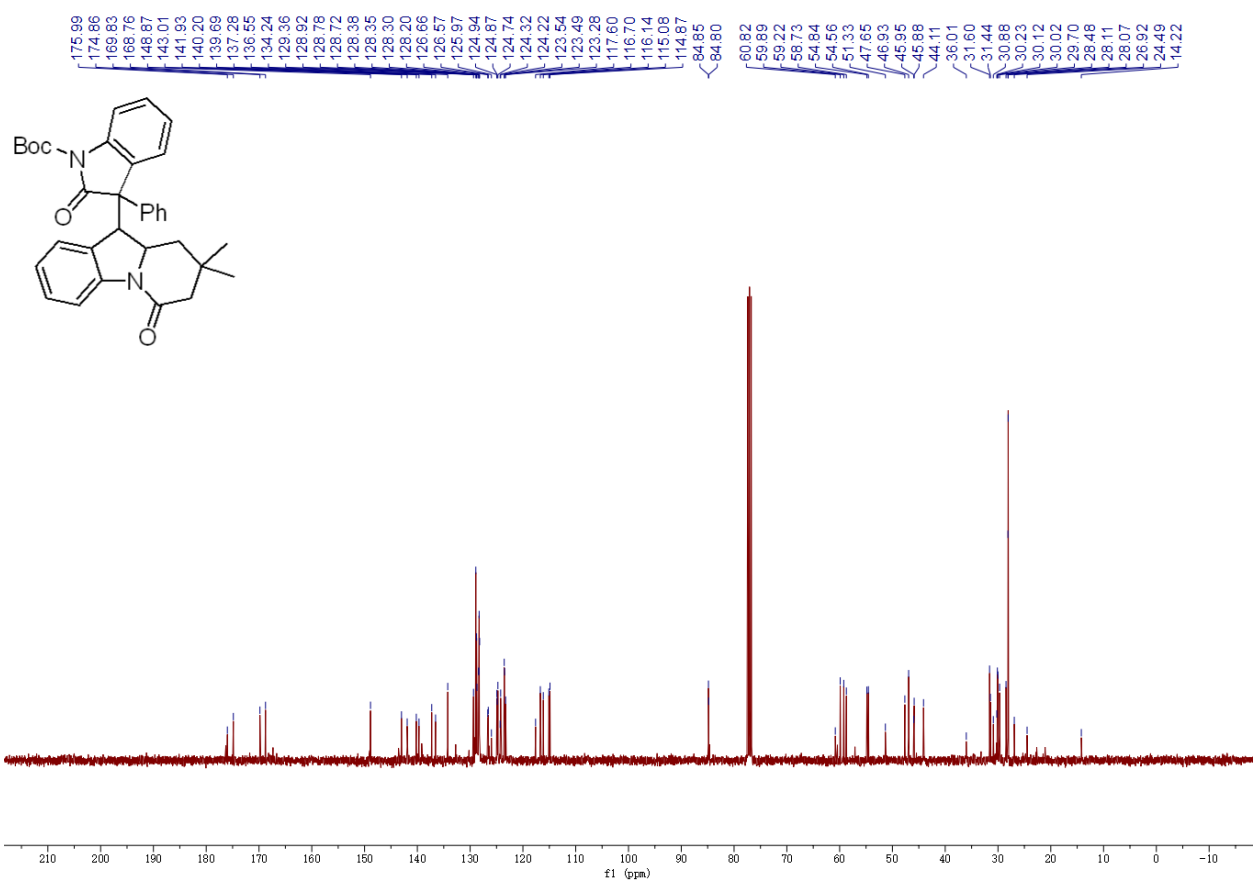

Boc
N
O
Ph
N
O
d.r. = 1.5:1.5:1:1
f1 (ppm)

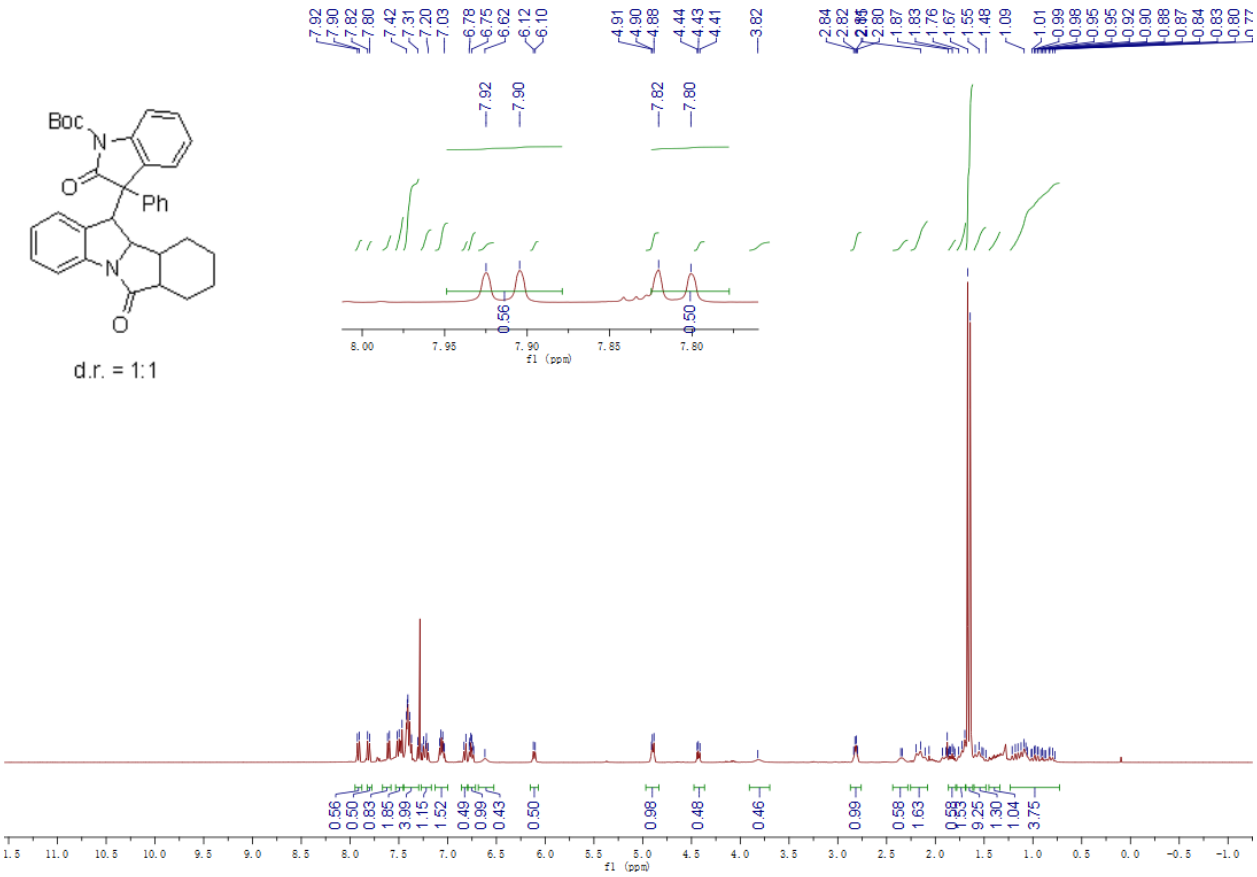

Boc
N
O
Ph
N
O
f1 (ppm)

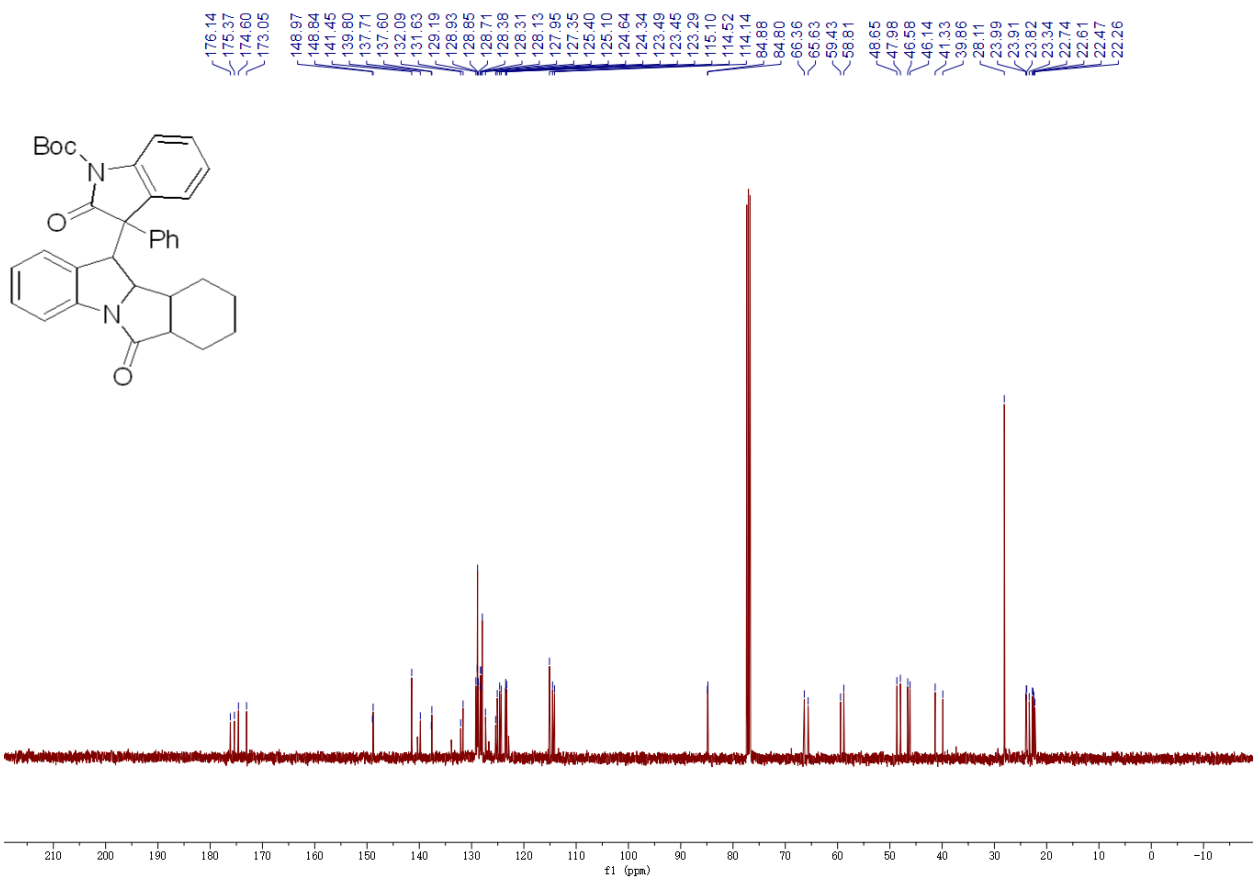

Boc
N
O
Ph
N
O
f1 (ppm)

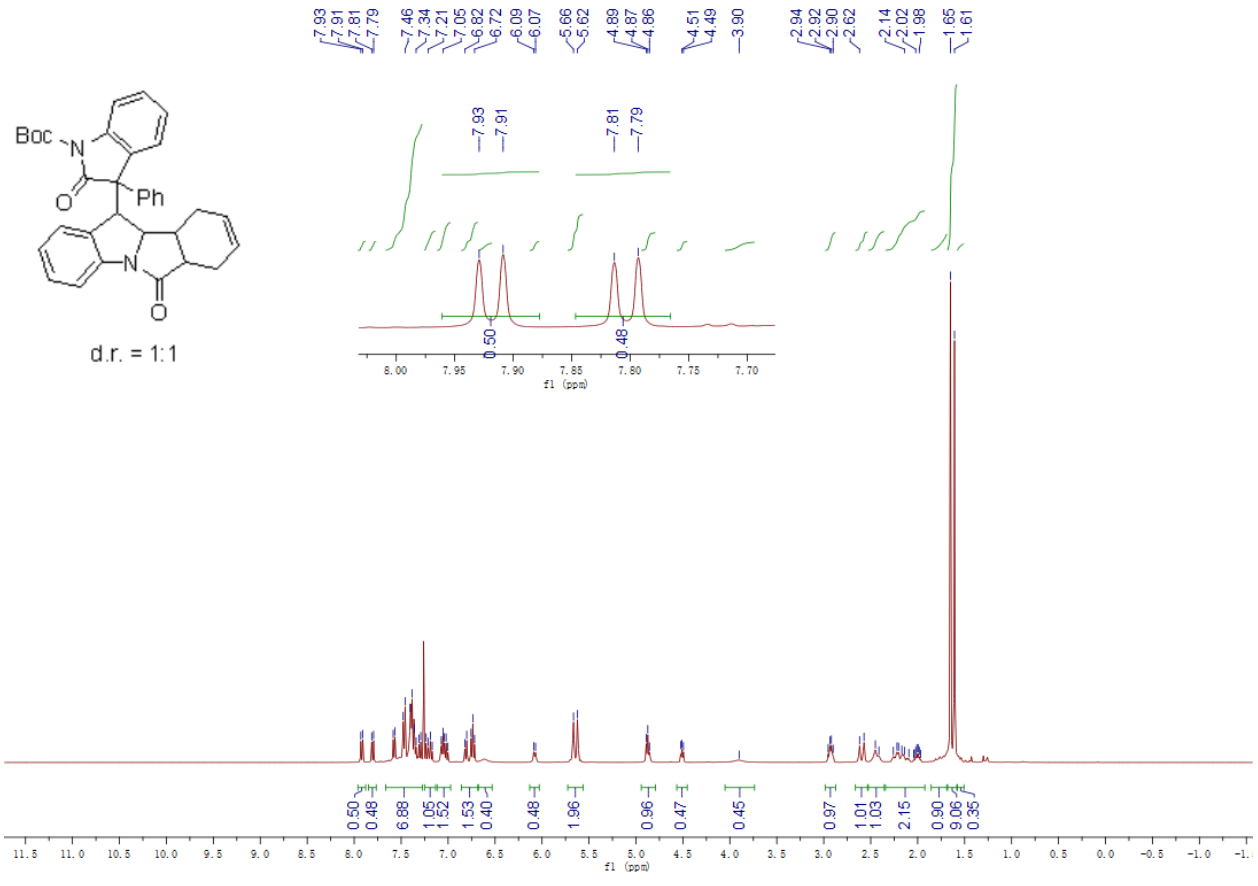

Boc
N
O
Ph
N
O
f1 (ppm)

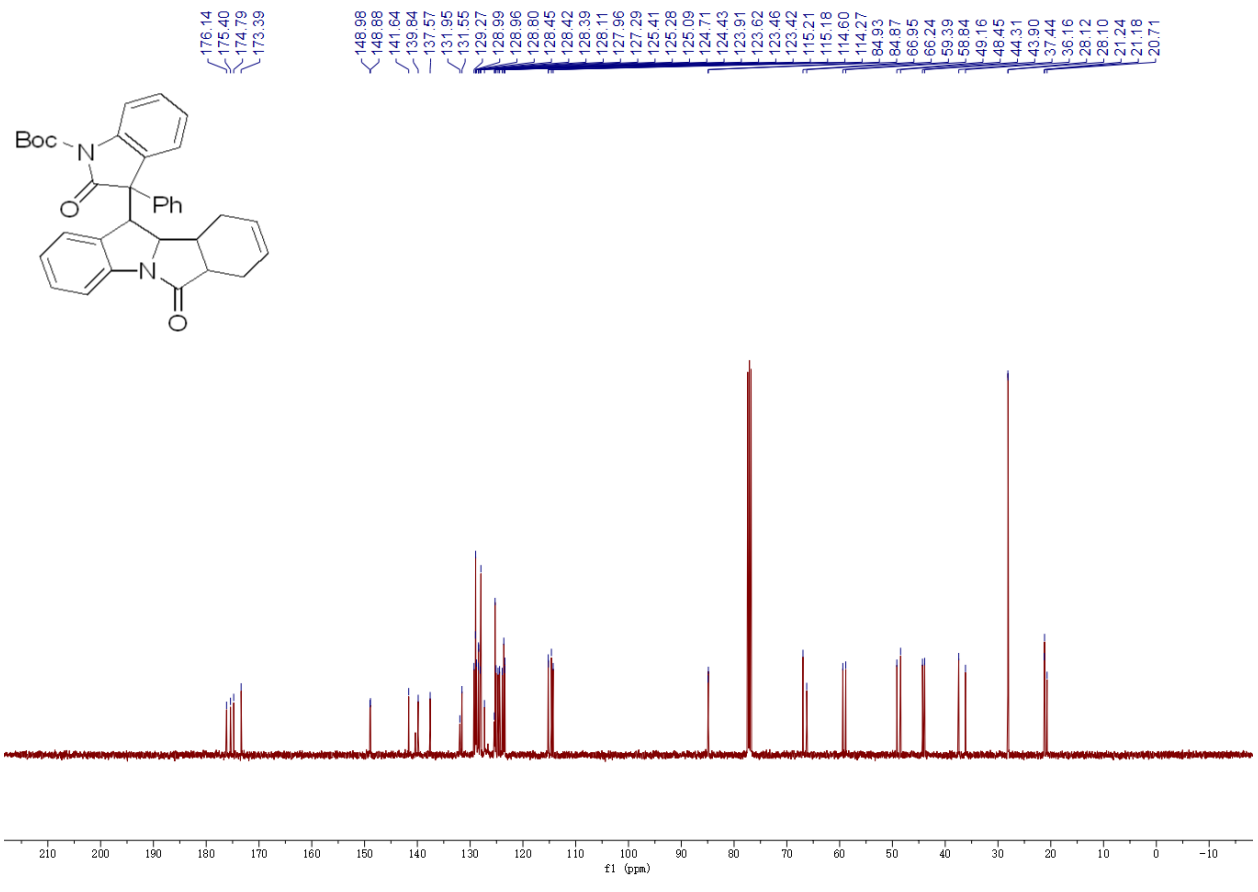

Boc
N
O
Ph
N
O
f1 (ppm)

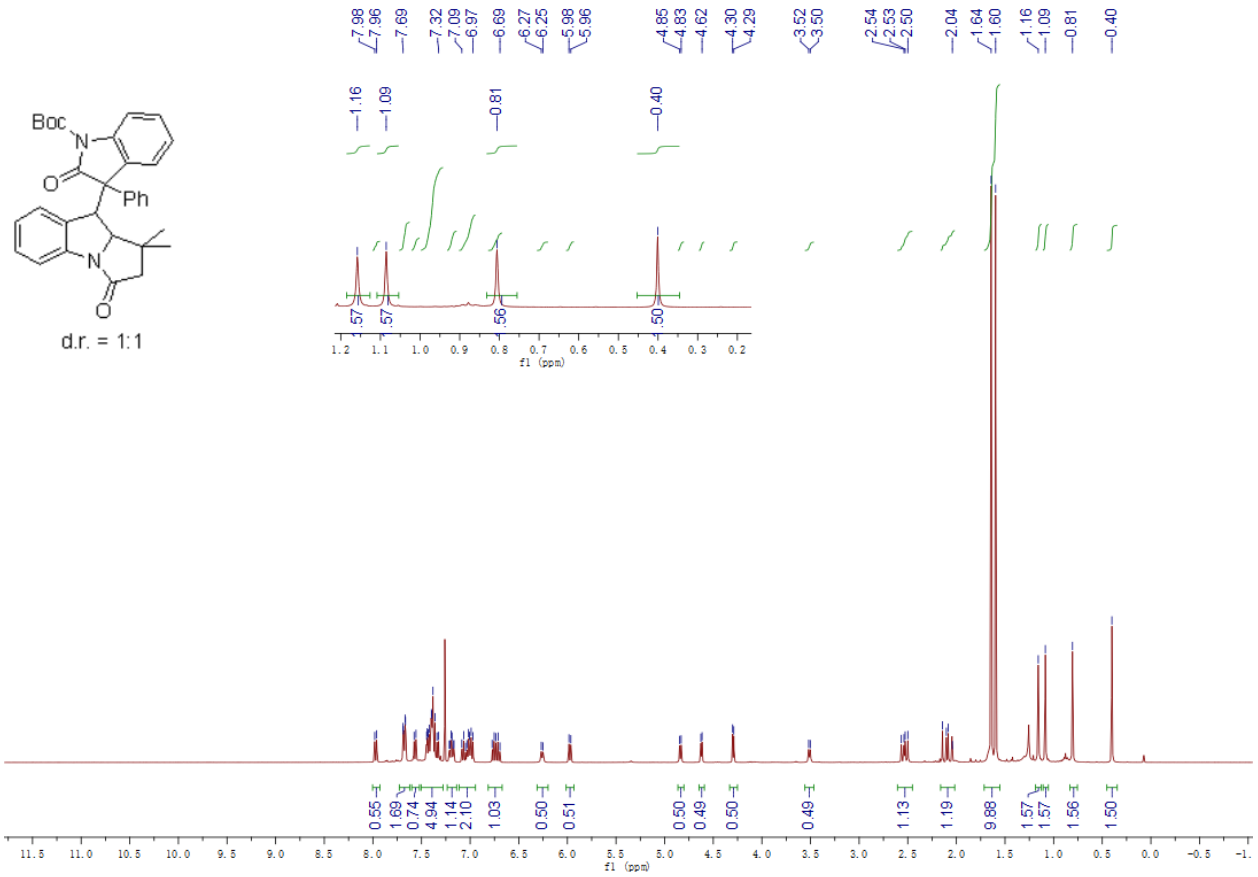

Boc
N
O
Ph
N
O
f1 (ppm)

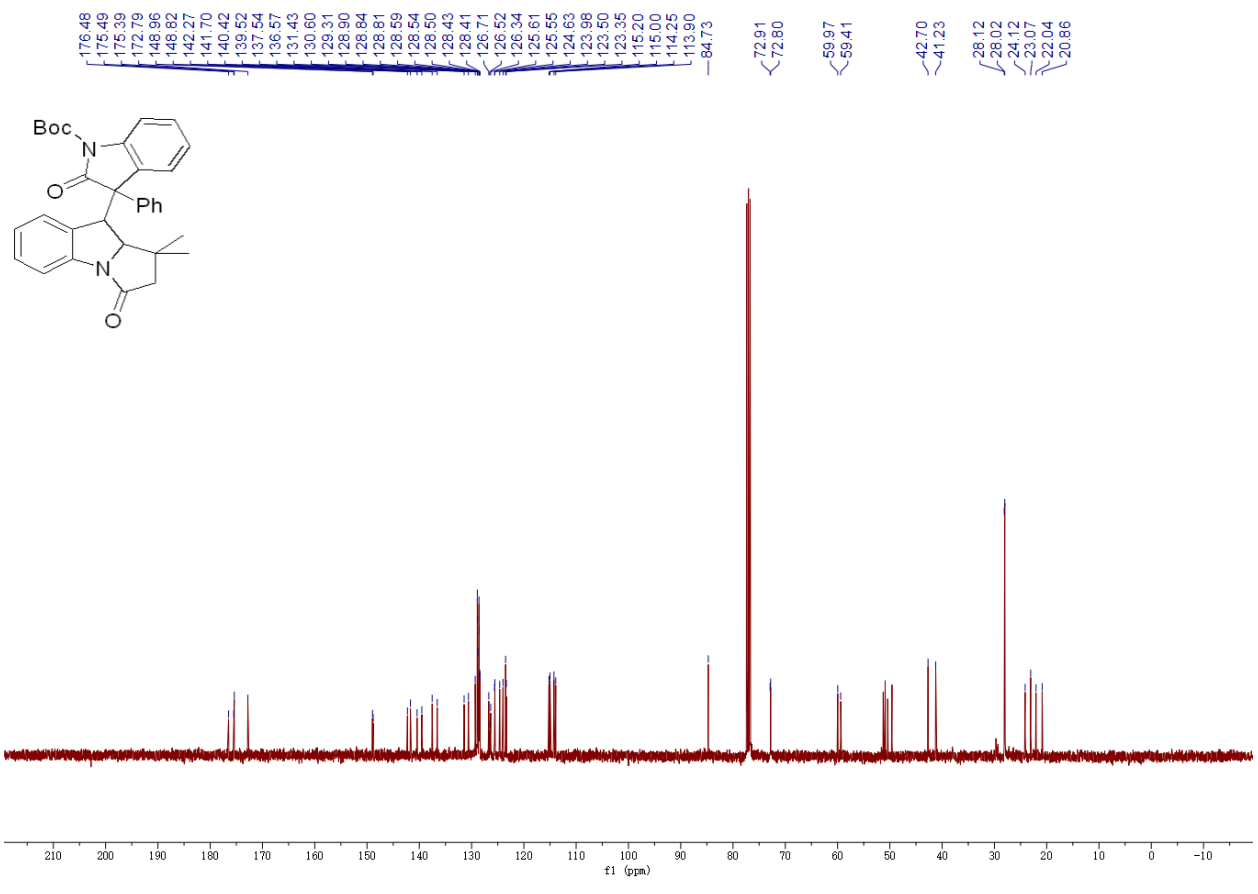

Boc
N
O
Ph
N
O
d.r. = 1:1
f1 (ppm)

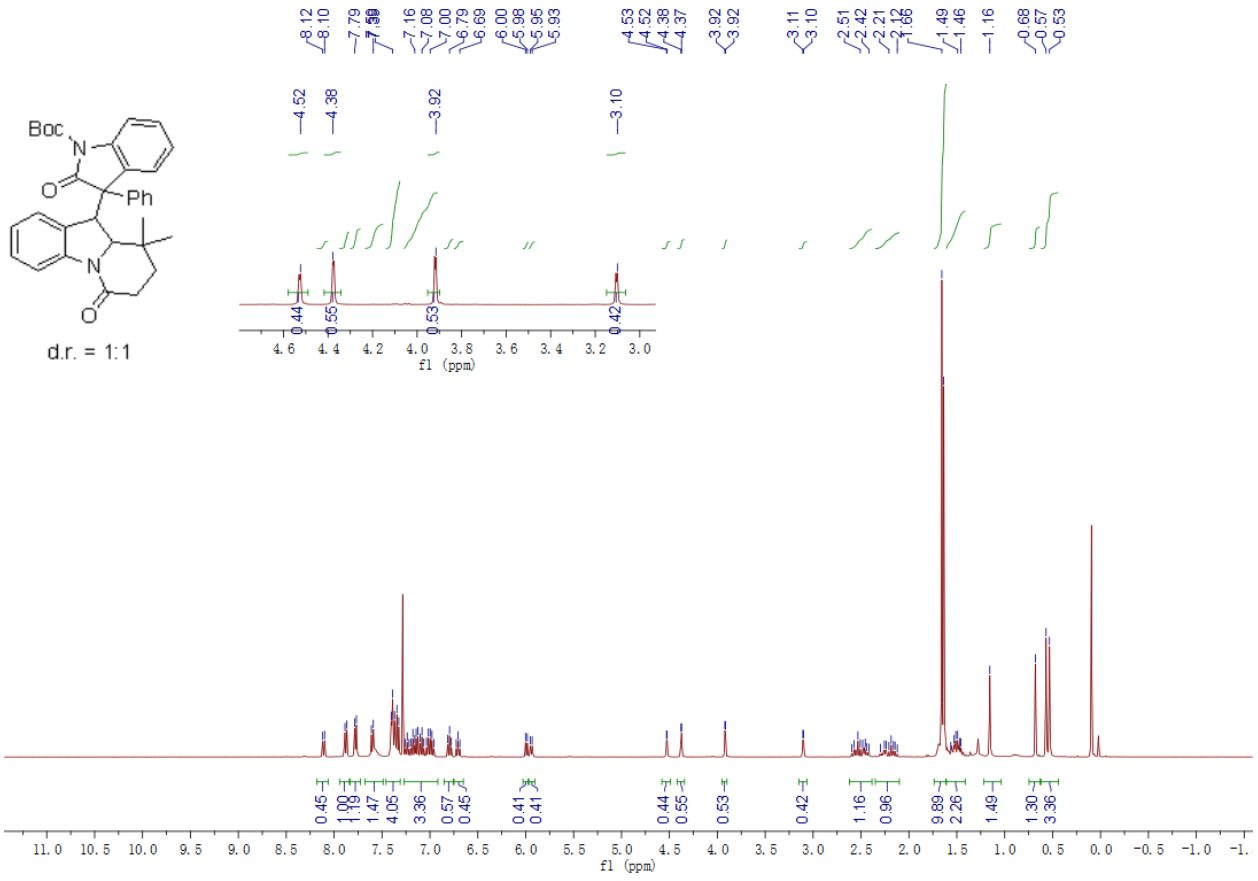

Boc
N
O
Ph
N
O
f1 (ppm)

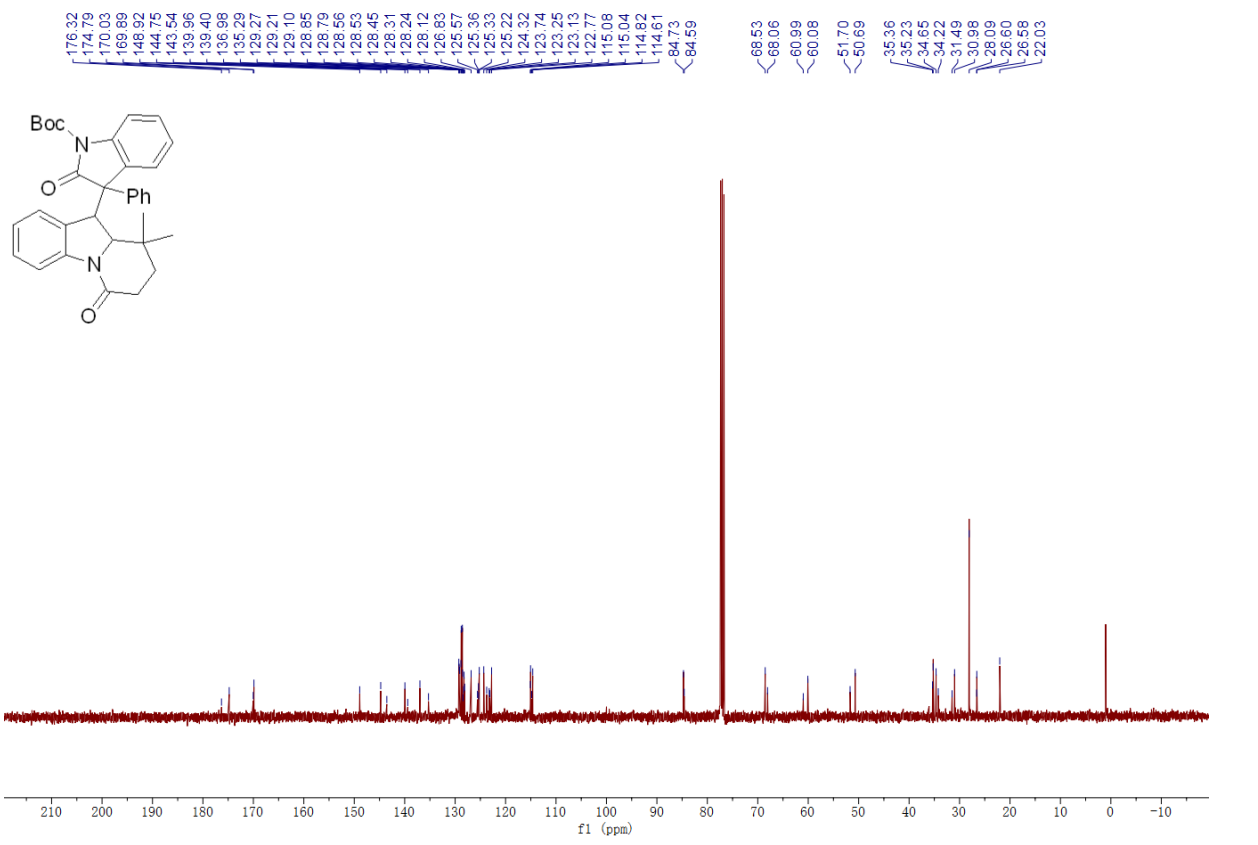

Boc
N
O
Ph
N
O
d.r. = 1:1
7.93
7.91
7.81
7.79
7.46
7.34
7.21
7.05
6.82
6.72
6.09
6.07
5.66
5.62
4.89
4.87
4.86
4.51
4.49
3.90
2.94
2.92
2.90
2.62
2.14
2.02
1.98
1.65
1.61
0.50
0.48
f1 (ppm)
0.50
0.48
6.88
1.05
1.52
1.53
0.40
0.48
1.96
0.96
0.47
0.45
0.97
1.01
1.03
2.15
0.90
9.06
0.35
f1 (ppm)

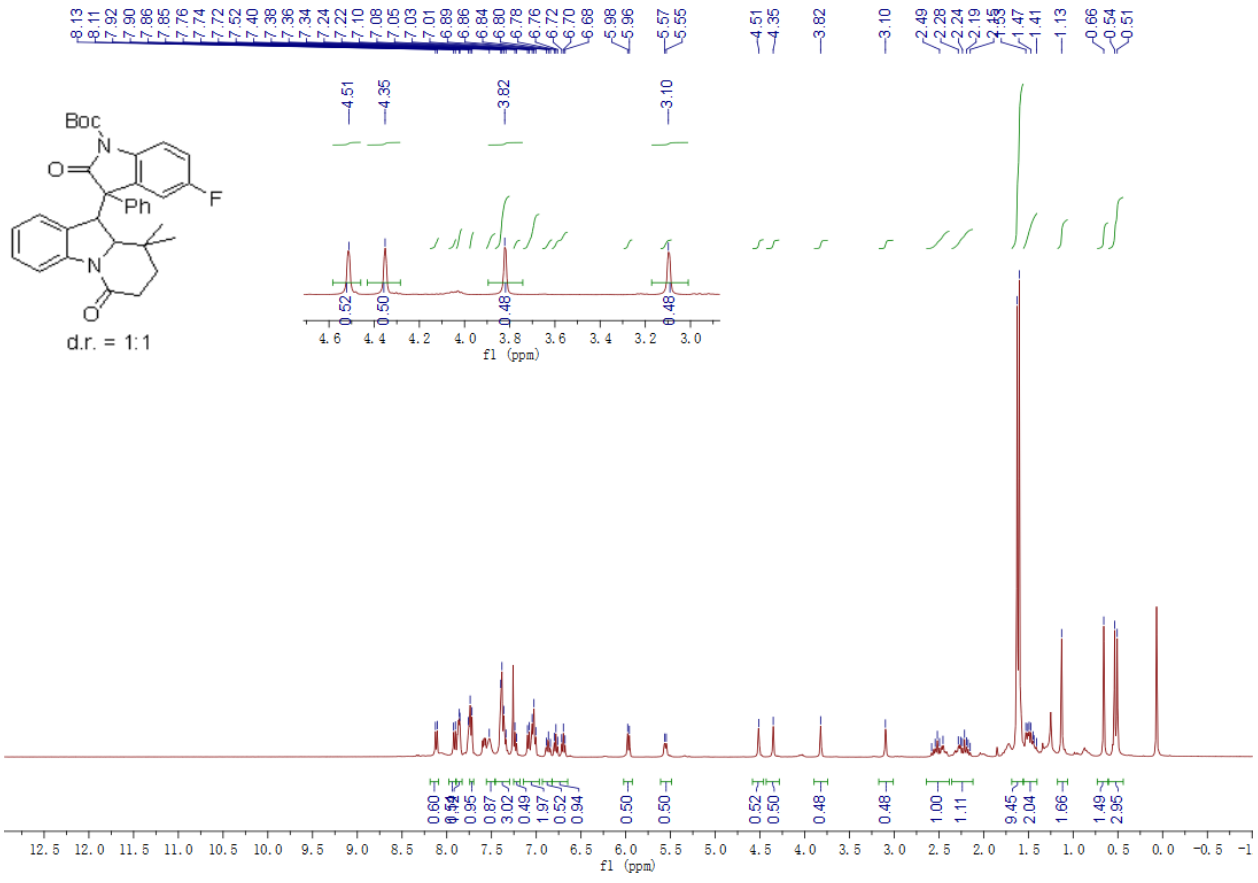

Boc
N
O
Ph
N
O
176.14
175.40
174.79
173.39
148.98
148.88
141.64
139.84
137.57
131.95
131.55
129.27
128.99
128.96
128.80
128.45
128.42
128.39
128.11
127.96
127.29
125.41
125.28
125.09
124.71
124.43
123.91
123.62
123.46
123.42
115.21
115.18
114.60
114.27
84.93
84.87
66.95
66.24
59.39
58.84
49.16
48.45
44.31
43.90
37.44
36.16
28.12
28.10
21.24
21.18
20.71
f1 (ppm)

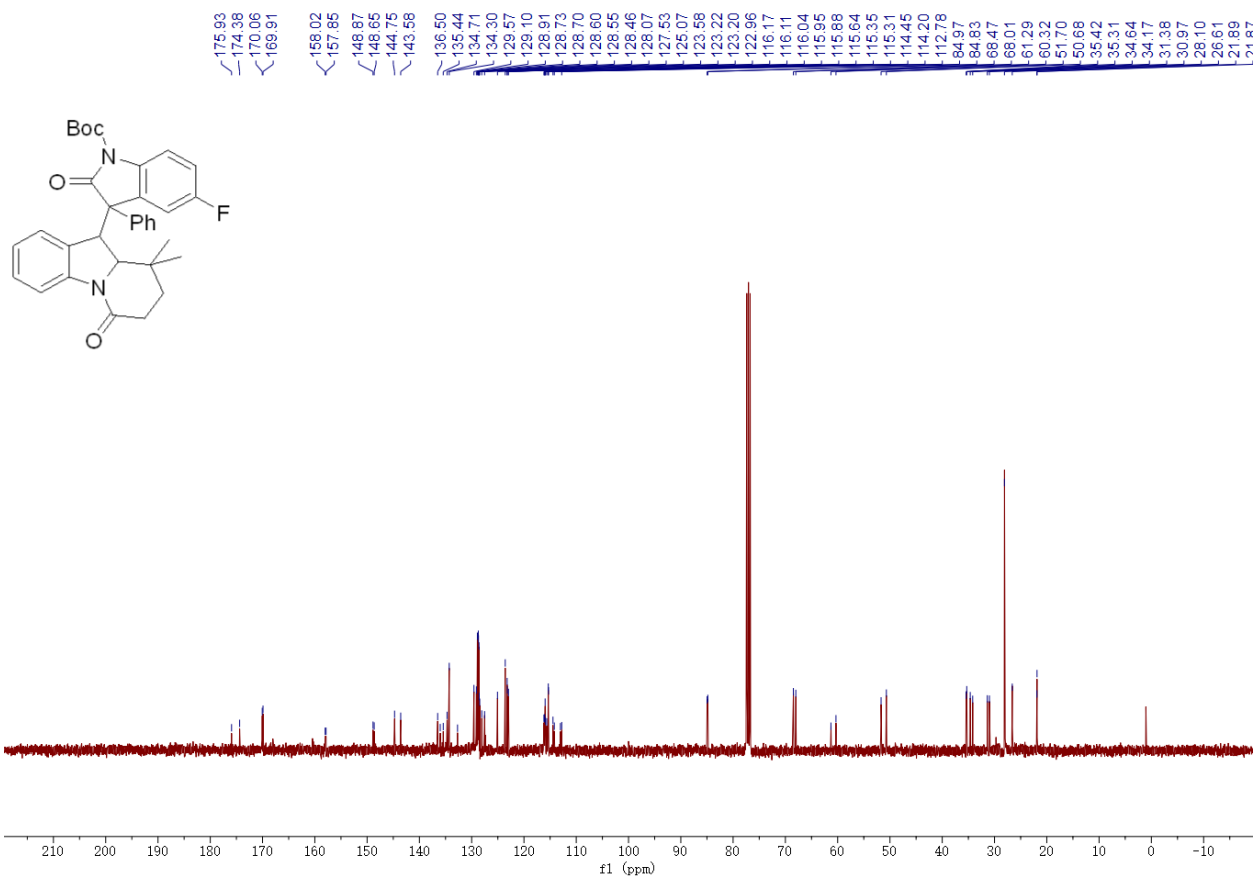

Boc
N
O
Ph
N
O
d.r. = 1:1
7.98
7.96
7.69
7.32
7.09
6.97
6.69
6.27
6.25
5.98
5.96
4.85
4.83
4.62
4.30
4.29
3.52
3.50
2.54
2.53
2.50
2.04
1.64
1.60
1.16
1.09
0.81
0.40
f1 (ppm)

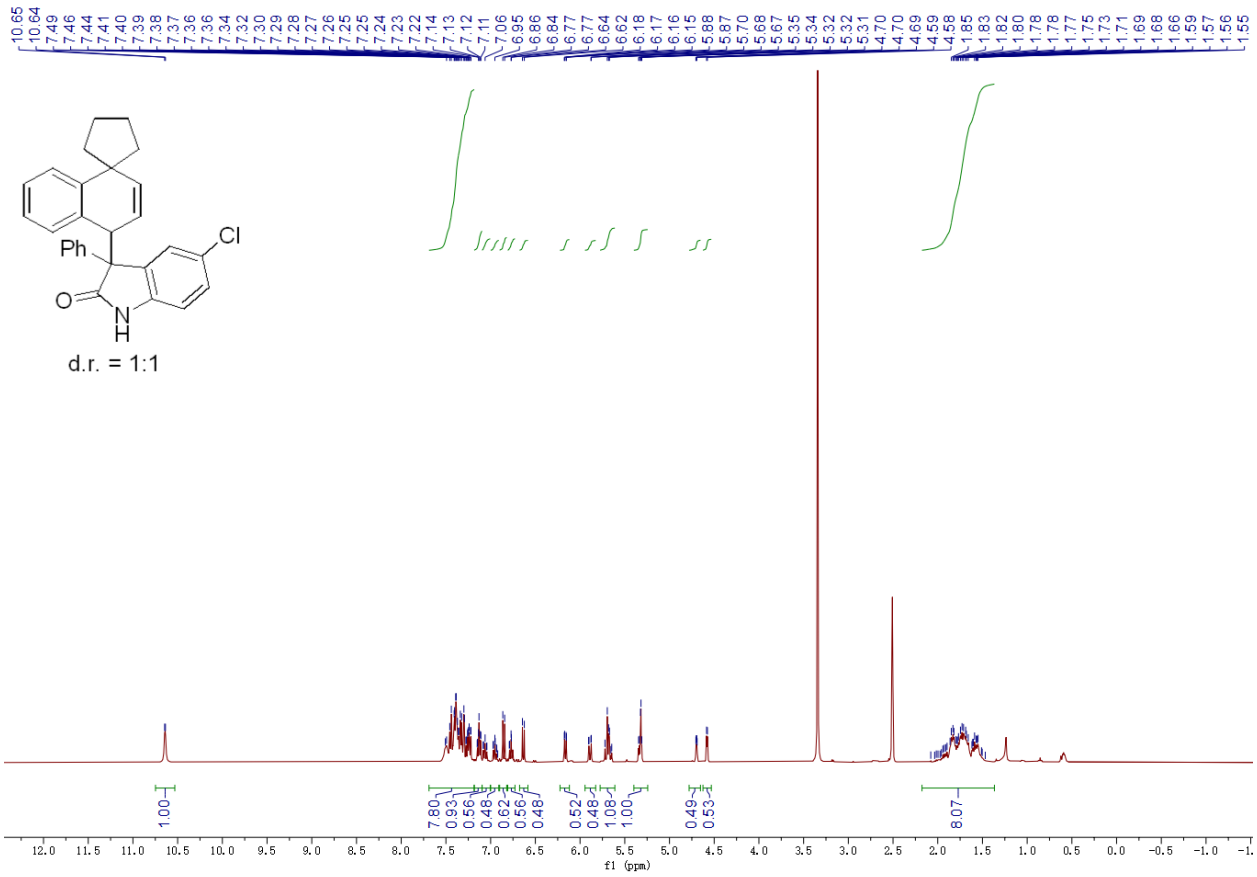

Boc
N
O
Ph
N
O
f1 (ppm)

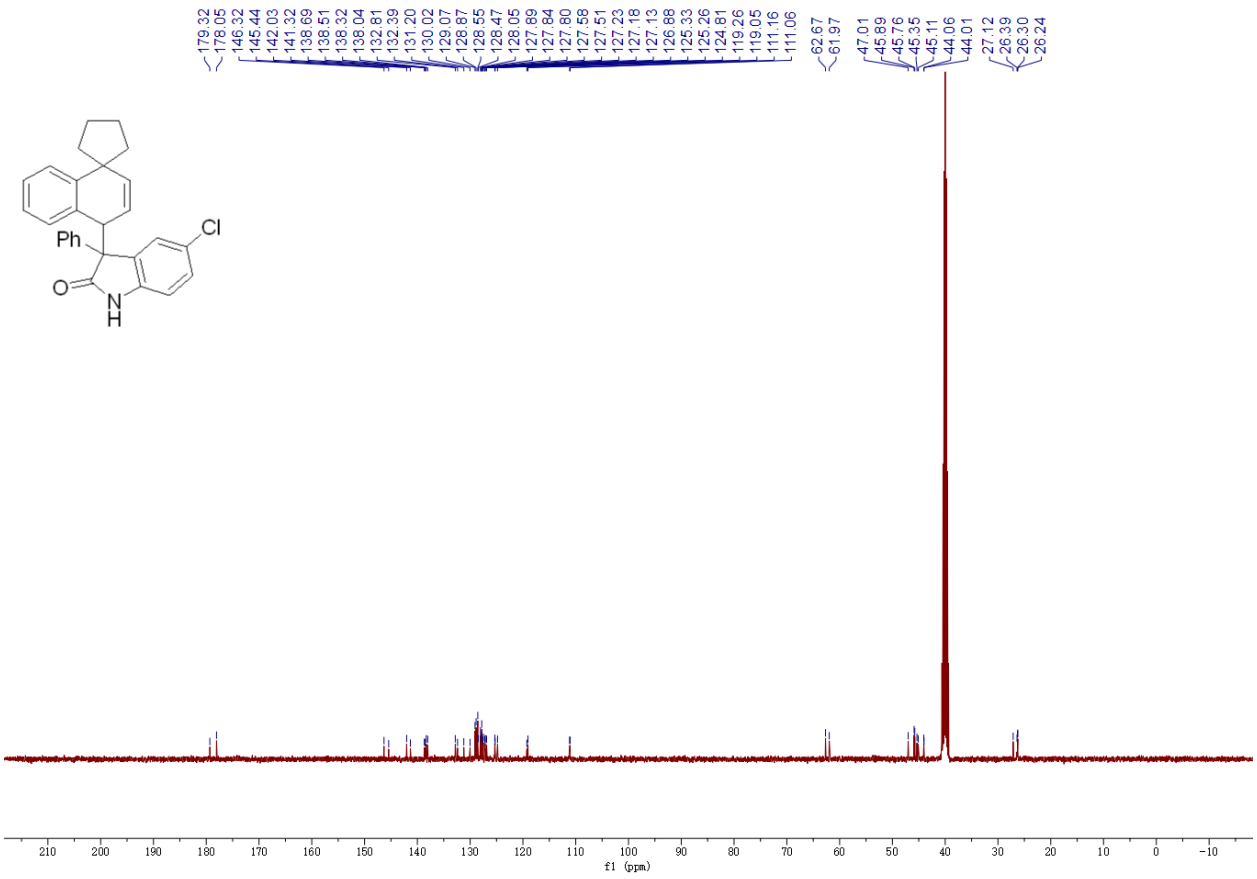

Boc
N
O
Ph
N
O
d.r. = 1:1
f1 (ppm)

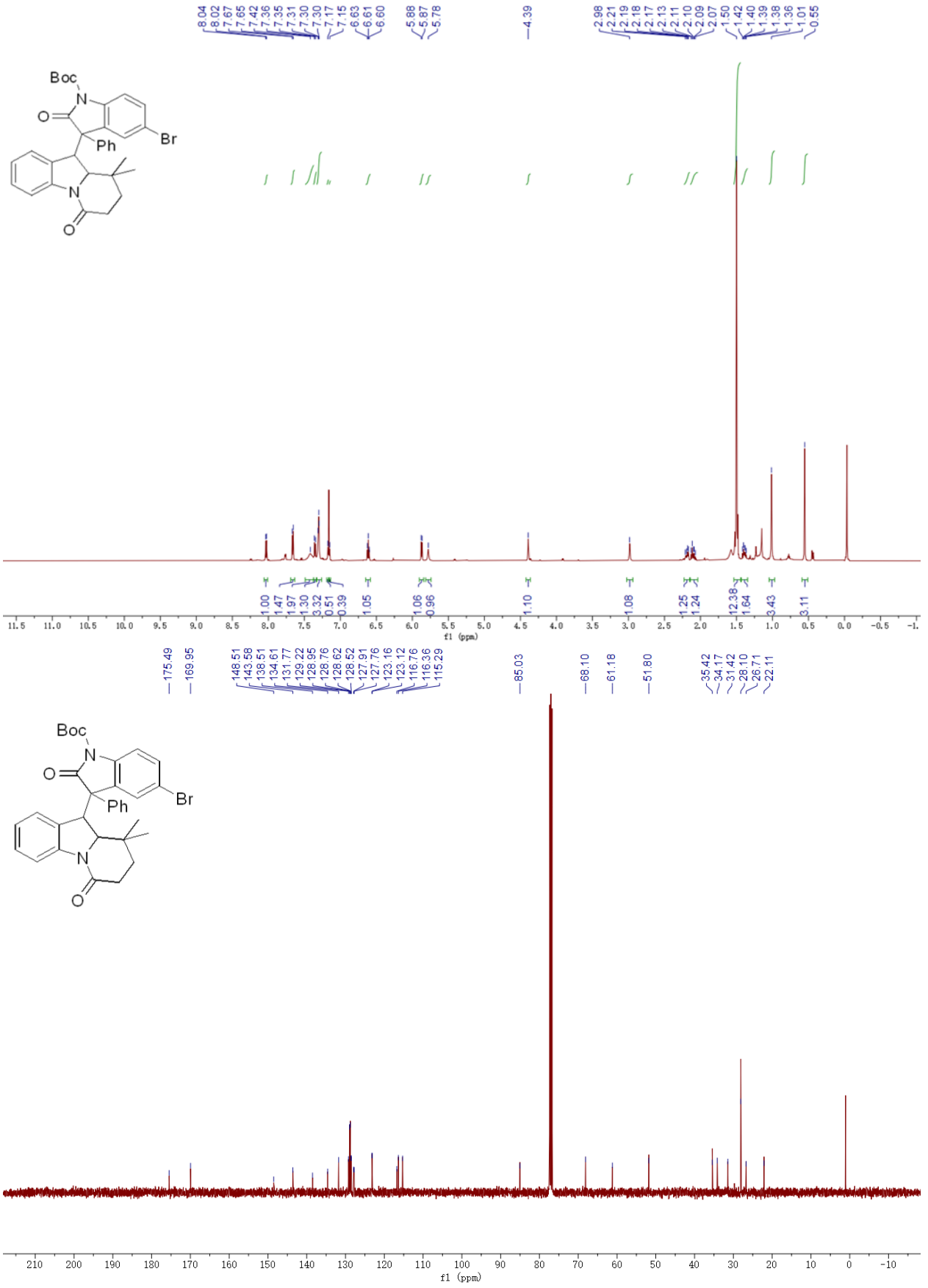

Boc
N
O
Ph
N
O
f1 (ppm)

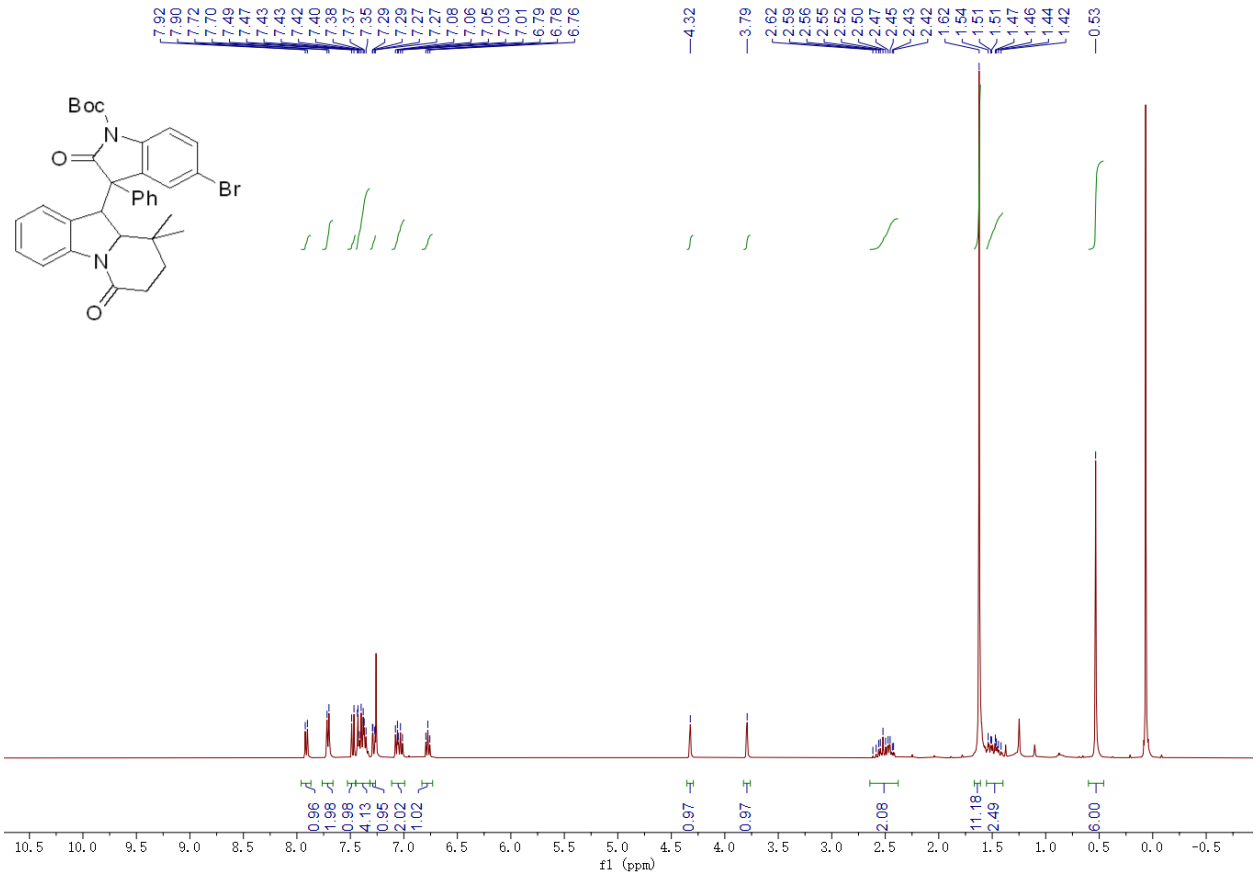

Boc
N
O
Ph
F
N
O
d.r. = 1:1
f1 (ppm)

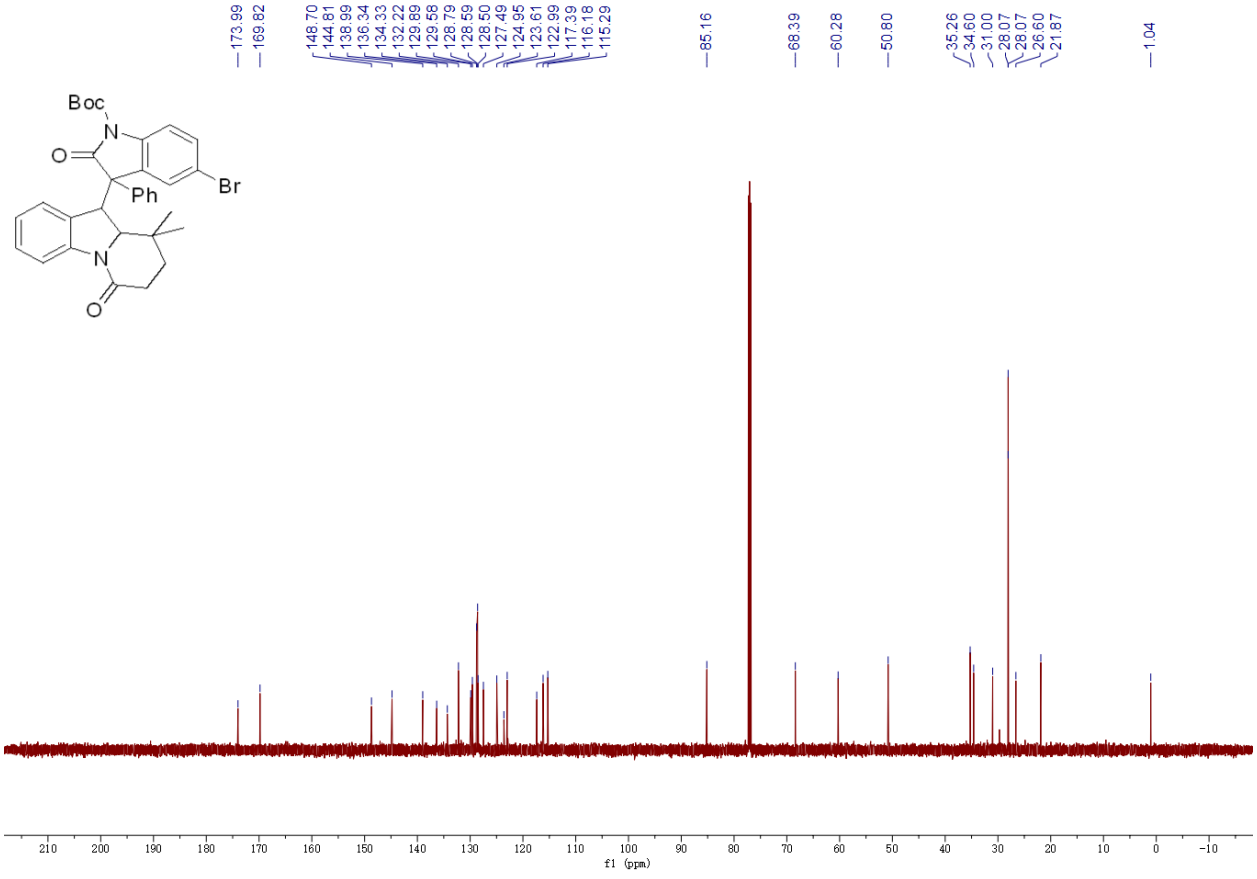

Boc
N
O
Ph
F
N
O
f1 (ppm)

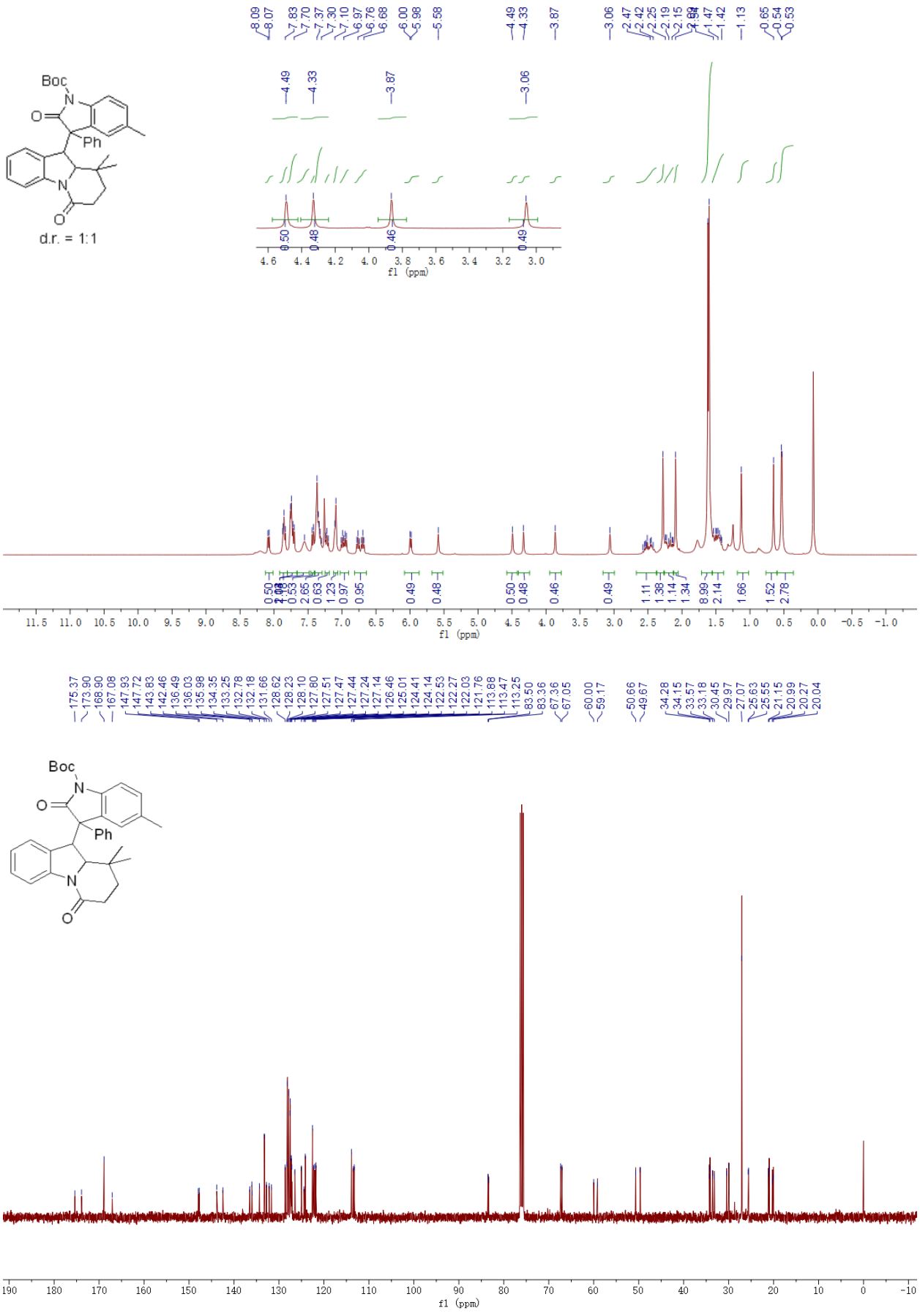

Ph
Cl
O
N
H
d.r. = 1:1
f1 (ppm)

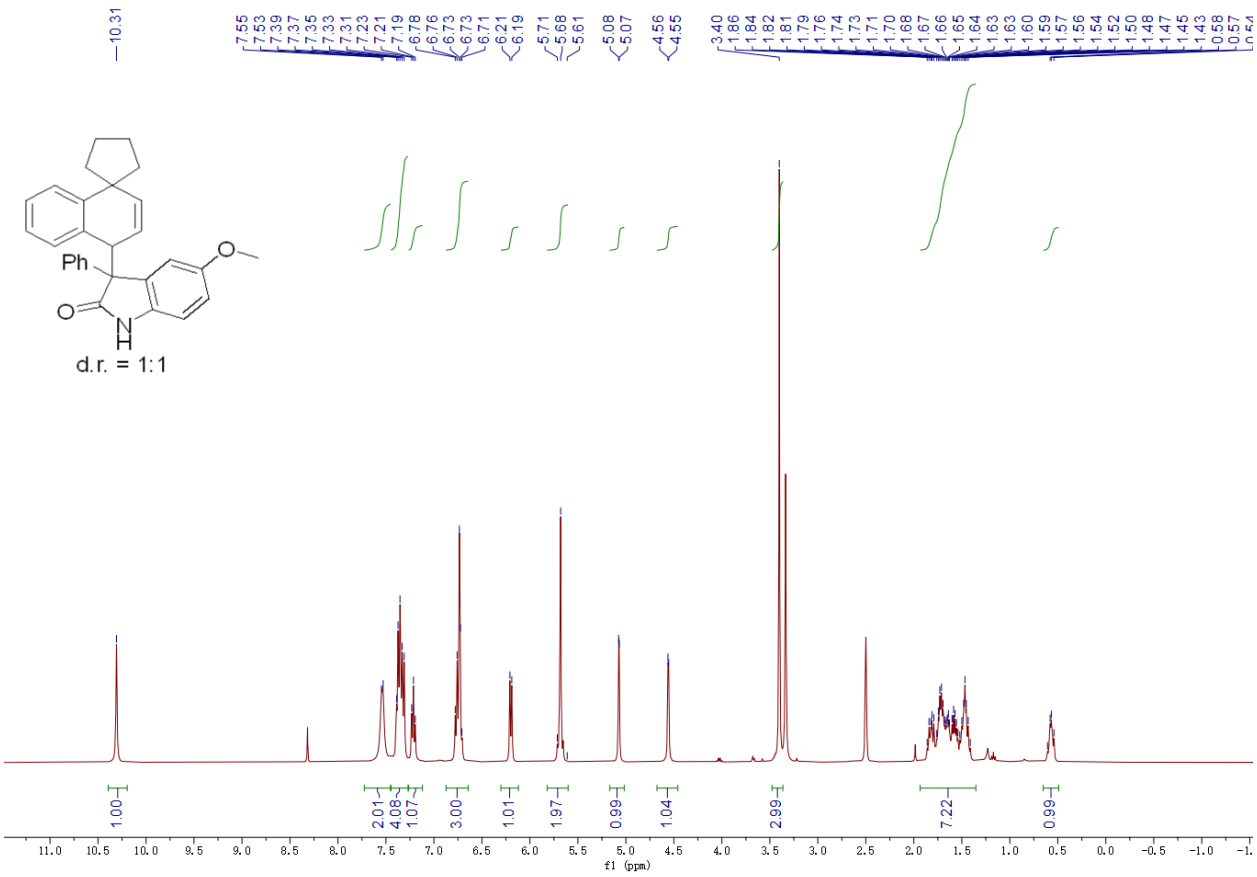

Ph
Cl
O
N
H
f1 (ppm)

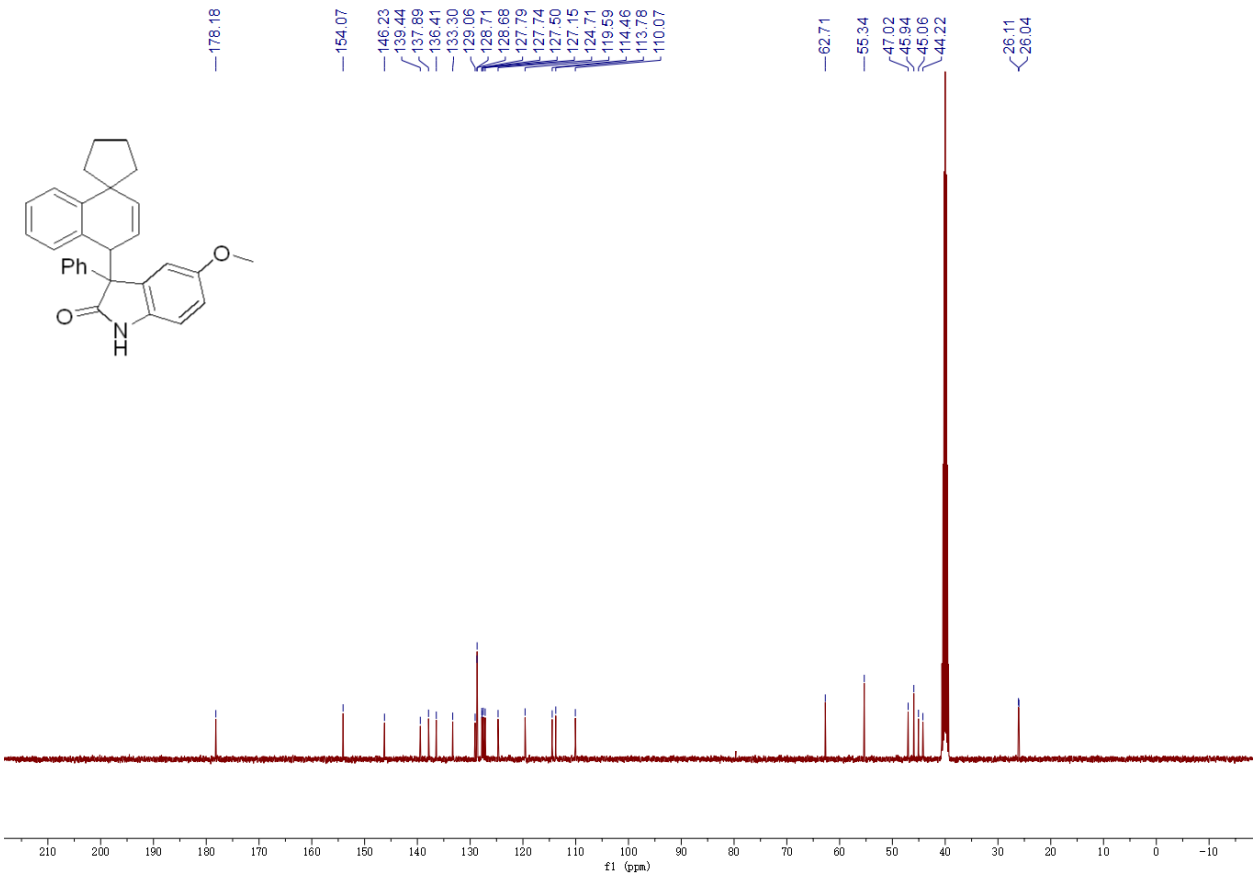

Boc
N
O
Ph
Br
N
O
8.04
8.02
7.67
7.65
7.42
7.36
7.35
7.31
7.30
7.30
7.17
7.15
6.63
6.61
6.60
5.88
5.87
5.78
4.39
2.98
2.21
2.19
2.18
2.17
2.13
2.11
2.10
2.09
2.07
1.50
1.42
1.40
1.39
1.38
1.36
1.01
0.55
1.00
1.47
1.97
1.30
3.32
0.51
0.39
1.05
1.06
0.96
1.10
1.08
1.25
1.24
12.38
1.64
3.43
3.11
f1 (ppm)
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
f1 (ppm)

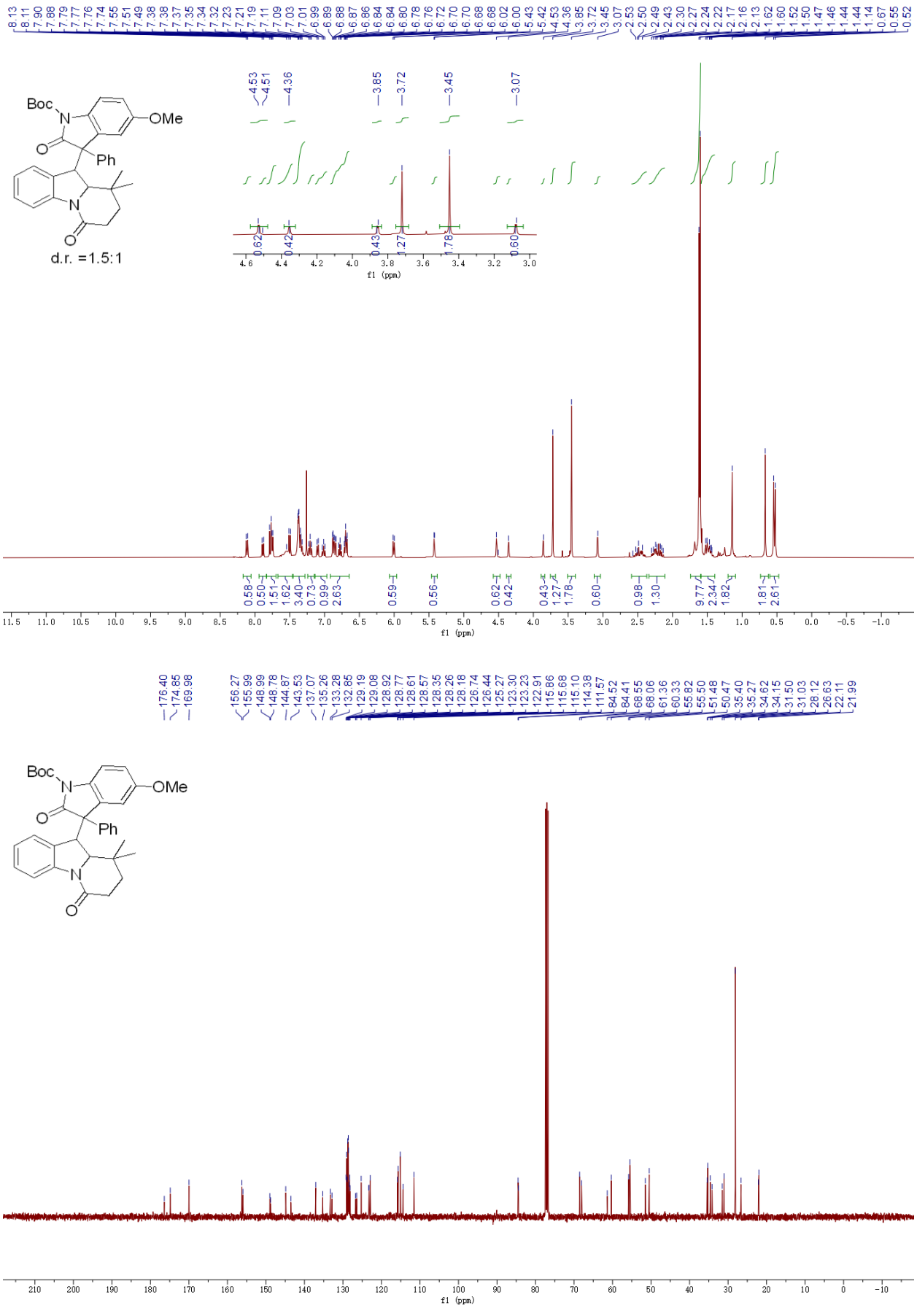

7.92
7.90
7.72
7.70
7.49
7.47
7.43
7.43
7.42
7.40
7.38
7.37
7.35
7.29
7.29
7.27
7.27
7.08
7.06
7.05
7.03
7.01
6.79
6.78
6.76
4.32
3.79
2.62
2.59
2.56
2.55
2.52
2.50
2.47
2.45
2.43
2.42
1.62
1.54
1.51
1.51
1.47
1.46
1.44
1.42
0.53
Boc
N
O
Ph
Br
N
O
0.96
1.98
0.98
4.13
0.95
2.02
1.02
0.97
0.97
2.08
11.18
2.49
6.00
f1 (ppm)

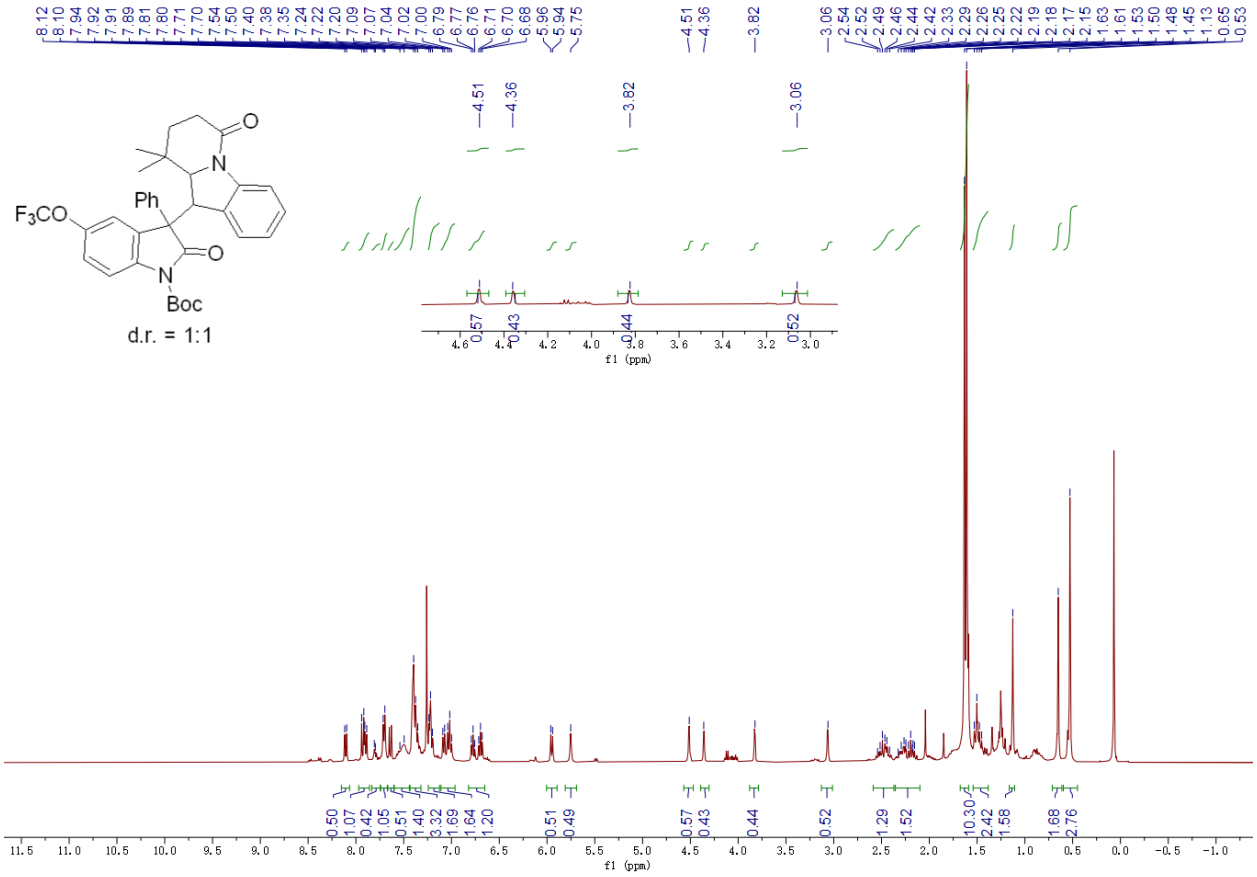

173.99
169.82
148.70
144.81
138.99
136.34
134.33
132.22
129.89
129.58
128.79
128.59
128.50
127.49
124.95
123.61
122.99
117.39
116.18
115.29
85.16
68.39
60.28
50.80
35.26
34.60
31.00
28.07
28.07
26.60
21.87
1.04
Boc
N
O
Ph
Br
N
O
f1 (ppm)

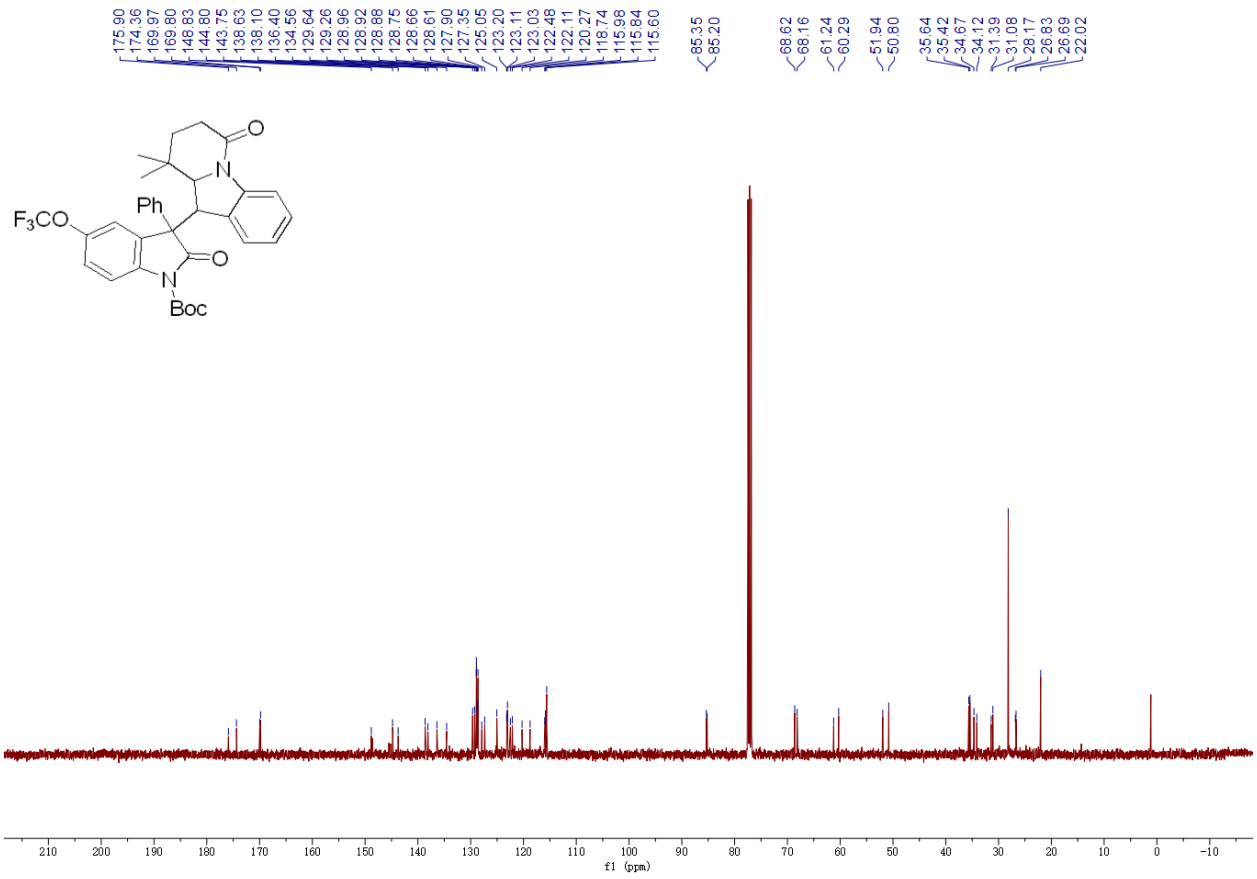

Boc
N
O
Ph
N
O
d.r. = 1:1
f1 (ppm)
f1 (ppm)
f1 (ppm)

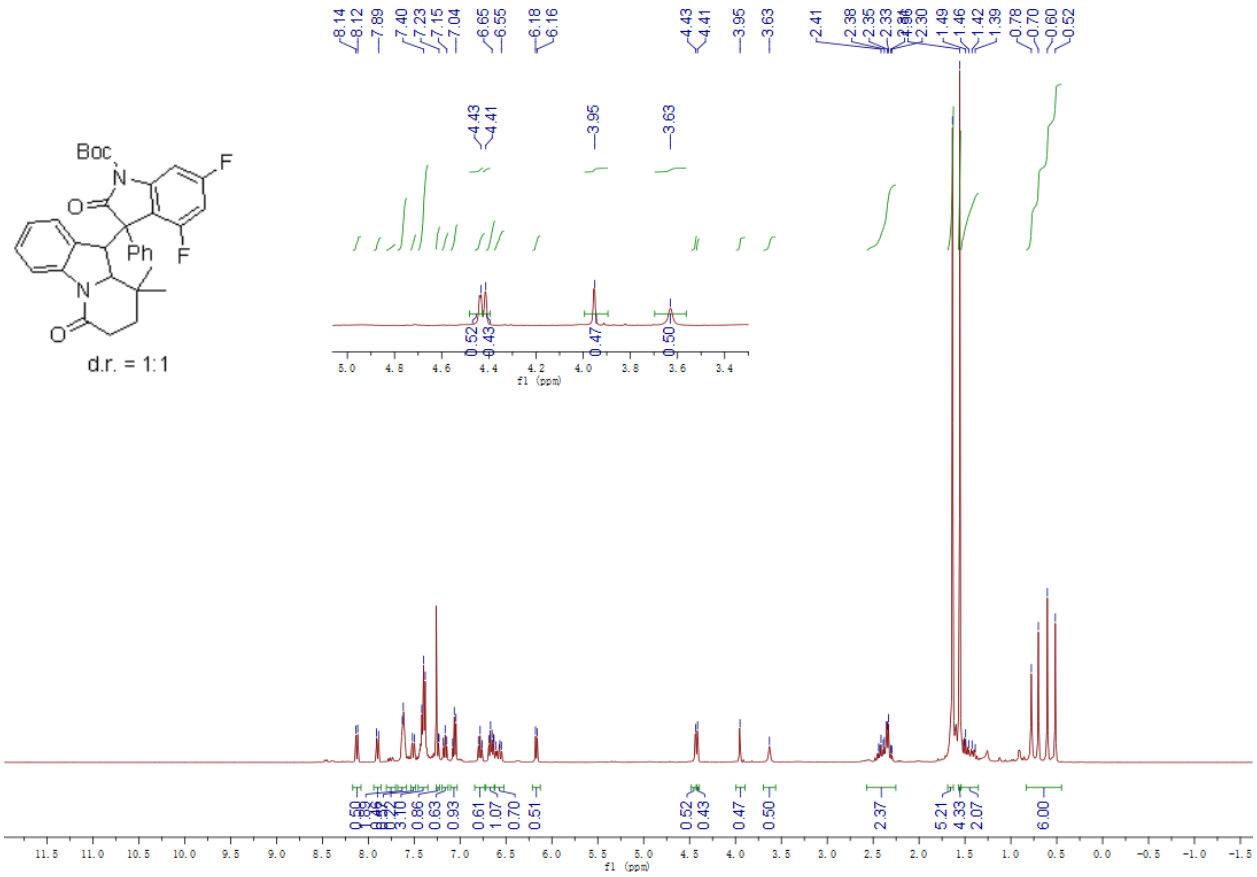

10.31
7.55
7.53
7.39
7.37
7.35
7.33
7.31
7.23
7.21
7.19
6.78
6.76
6.73
6.73
6.71
6.21
6.19
5.71
5.68
5.61
5.08
5.07
4.56
4.55
3.40
1.86
1.84
1.82
1.81
1.79
1.76
1.74
1.73
1.71
1.70
1.68
1.67
1.66
1.65
1.64
1.63
1.60
1.59
1.57
1.56
1.54
1.52
1.50
1.48
1.47
1.45
1.43
0.58
0.57
Ph
O
N
H
d.r. = 1:1
1.00
2.01
4.08
1.07
3.00
1.01
1.97
0.99
1.04
2.99
7.22
0.99
f1 (ppm)

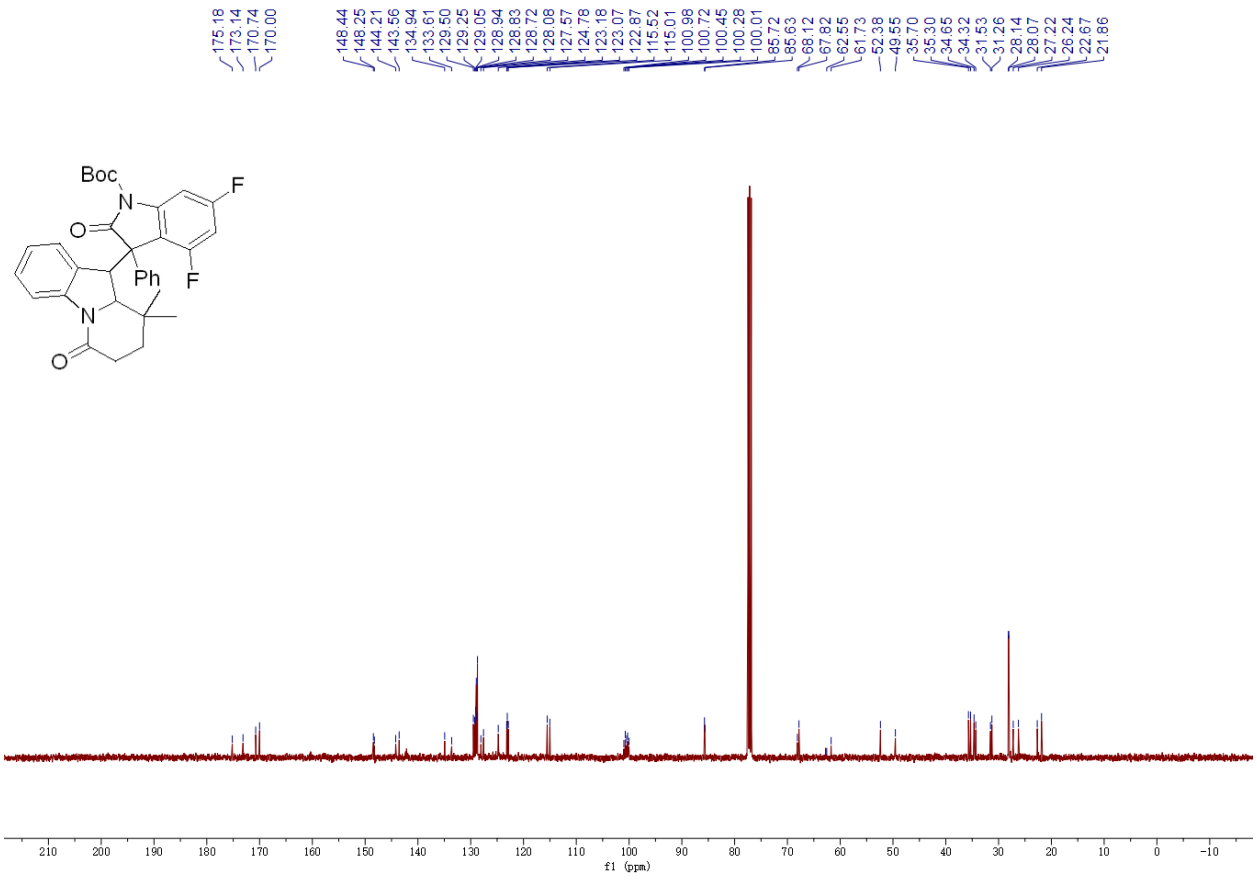

178.18
154.07
146.23
139.44
137.89
136.41
133.30
129.06
128.71
128.68
127.79
127.74
127.50
127.15
124.71
119.59
114.46
113.78
110.07
62.71
55.34
47.02
45.94
45.06
44.22
26.11
26.04
Ph
O
N
H
f1 (ppm)

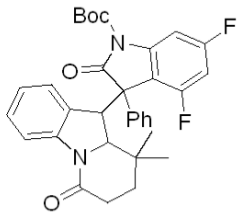

Boc
N
OMe
O
Ph
N
O
d.r. =1.5:1
f1 (ppm)
f1 (ppm)
f1 (ppm)


F3CO
Ph
O
N
O
N
Boc
d.r. = 1:1
f1 (ppm)

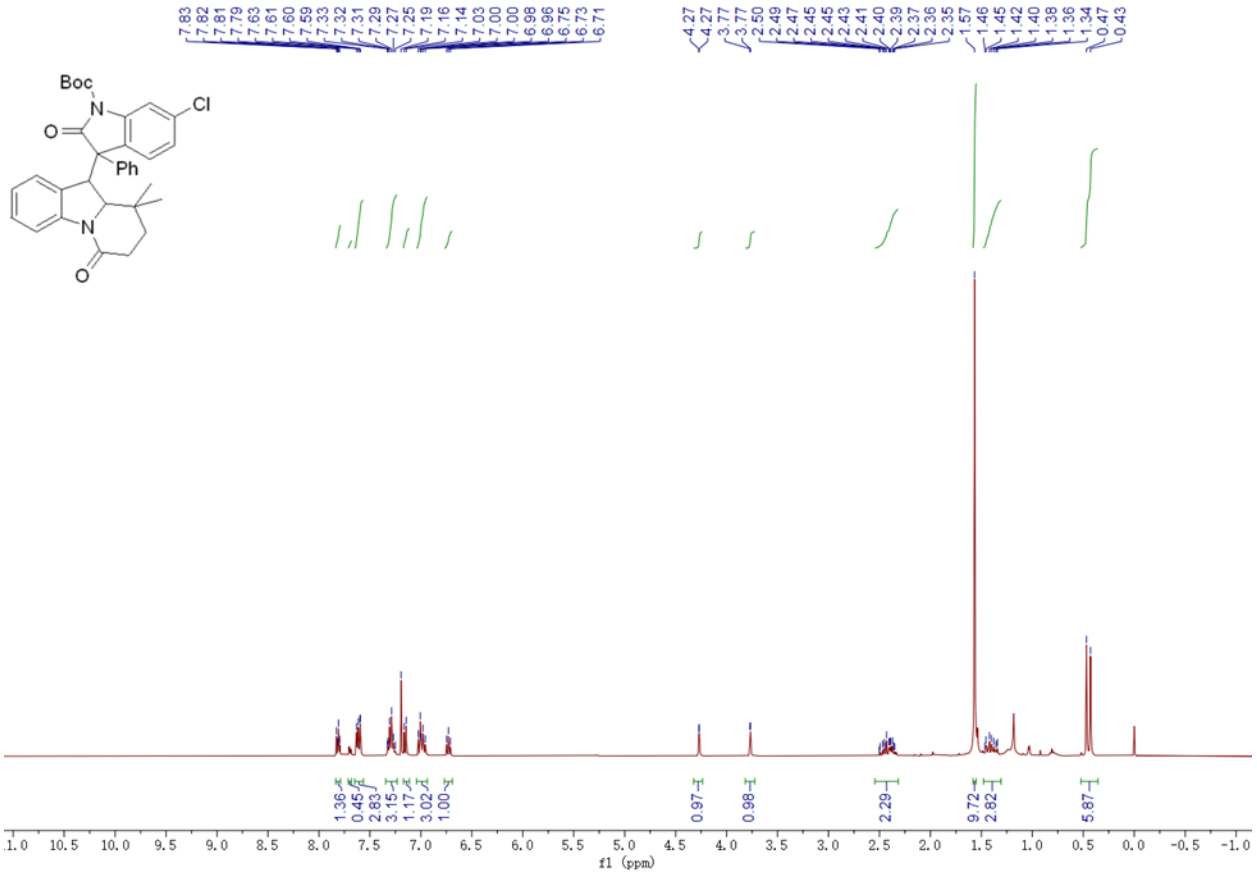

F3CO
Ph
O
N
O
N
Boc
f1 (ppm)

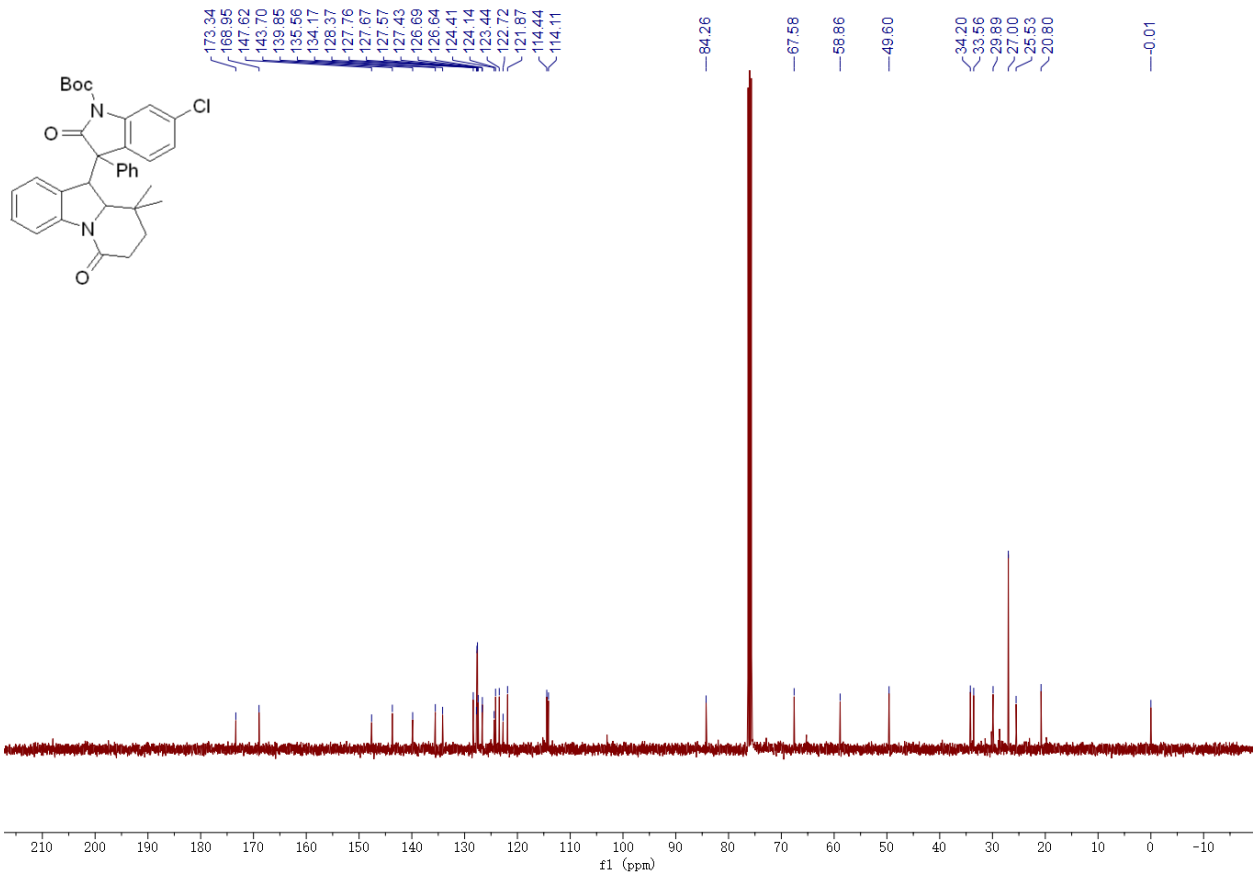

Boc
N
O
F
Ph
F
N
O
d.r. = 1:1
8.14
8.12
7.89
7.40
7.23
7.15
7.04
6.65
6.55
6.18
6.16
4.43
4.41
3.95
3.63
2.41
2.38
2.35
2.33
2.30
1.49
1.46
1.42
1.39
0.78
0.70
0.60
0.52
0.52
0.43
0.47
0.50
f1 (ppm)
0.50
0.86
0.63
0.93
0.61
1.07
0.70
0.51
0.52
0.43
0.47
0.50
2.37
5.21
4.33
2.07
6.00
f1 (ppm)

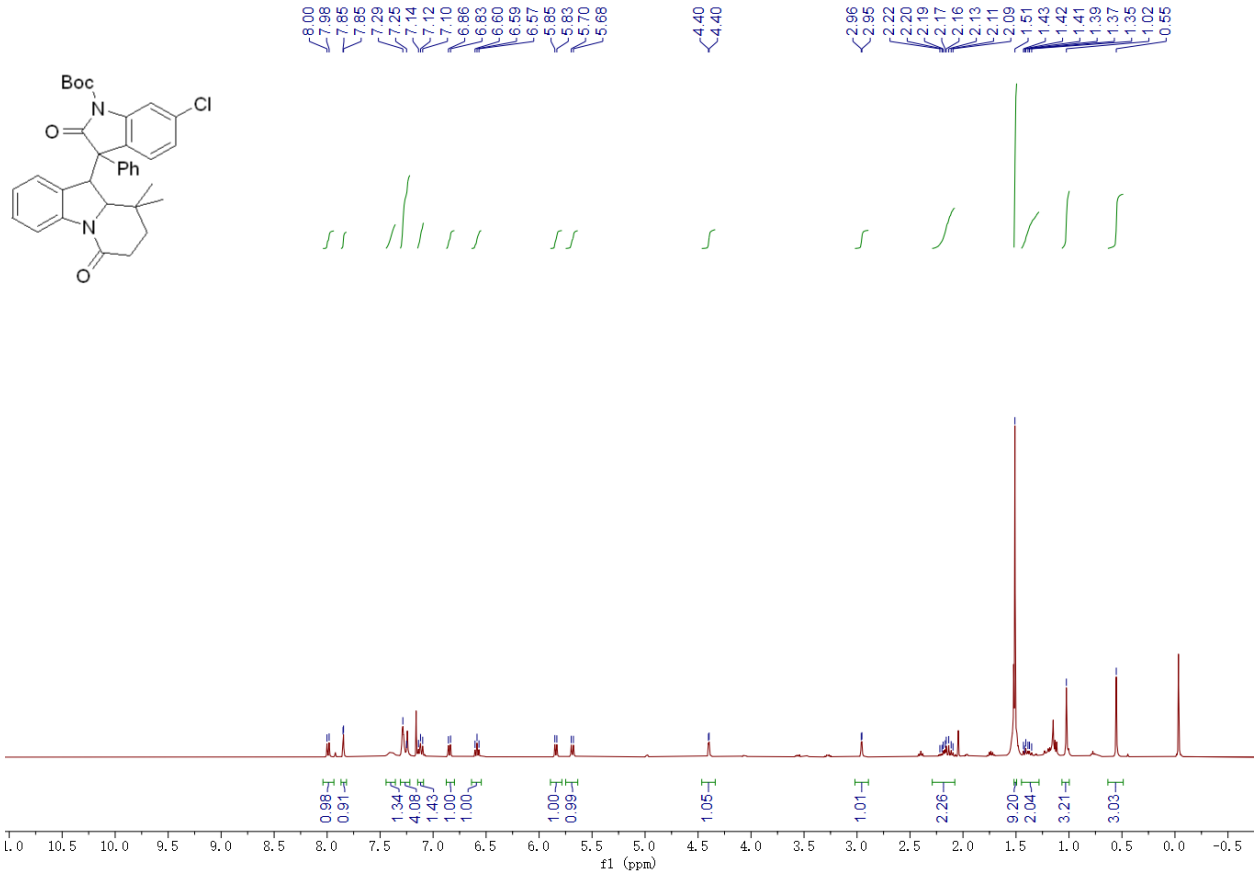

175.18
173.14
170.74
170.00
148.44
148.25
144.21
143.56
134.94
133.61
129.50
129.25
129.05
128.94
128.83
128.72
128.08
127.57
124.78
123.18
123.07
122.87
115.52
115.01
100.98
100.72
100.45
100.28
100.01
85.72
85.63
68.12
67.82
62.55
61.73
52.38
49.55
35.70
35.30
34.65
34.32
31.53
31.26
28.14
28.07
27.22
26.24
22.67
21.86
Boc
N
O
F
Ph
F
N
O
f1 (ppm)

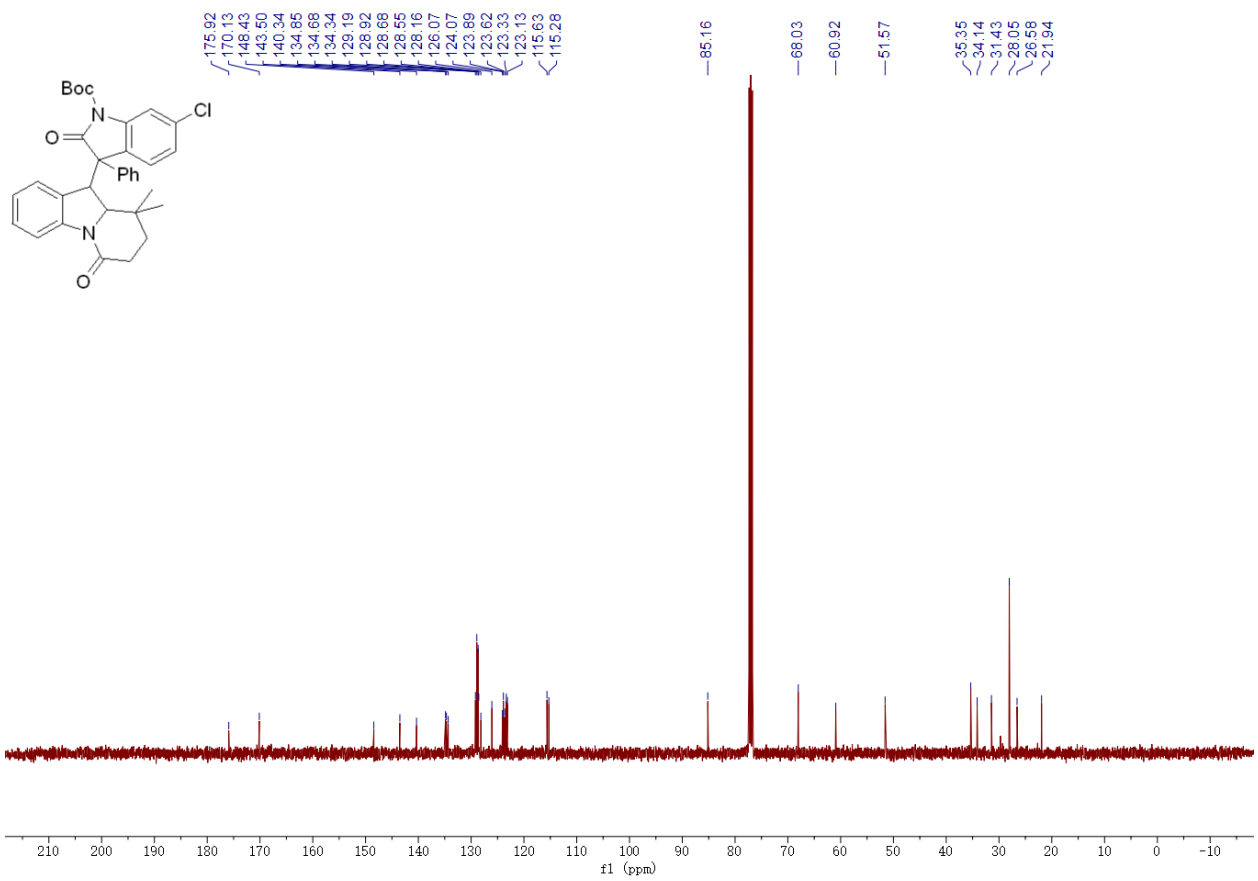

Boc
N
O
F
Ph
F
N
O

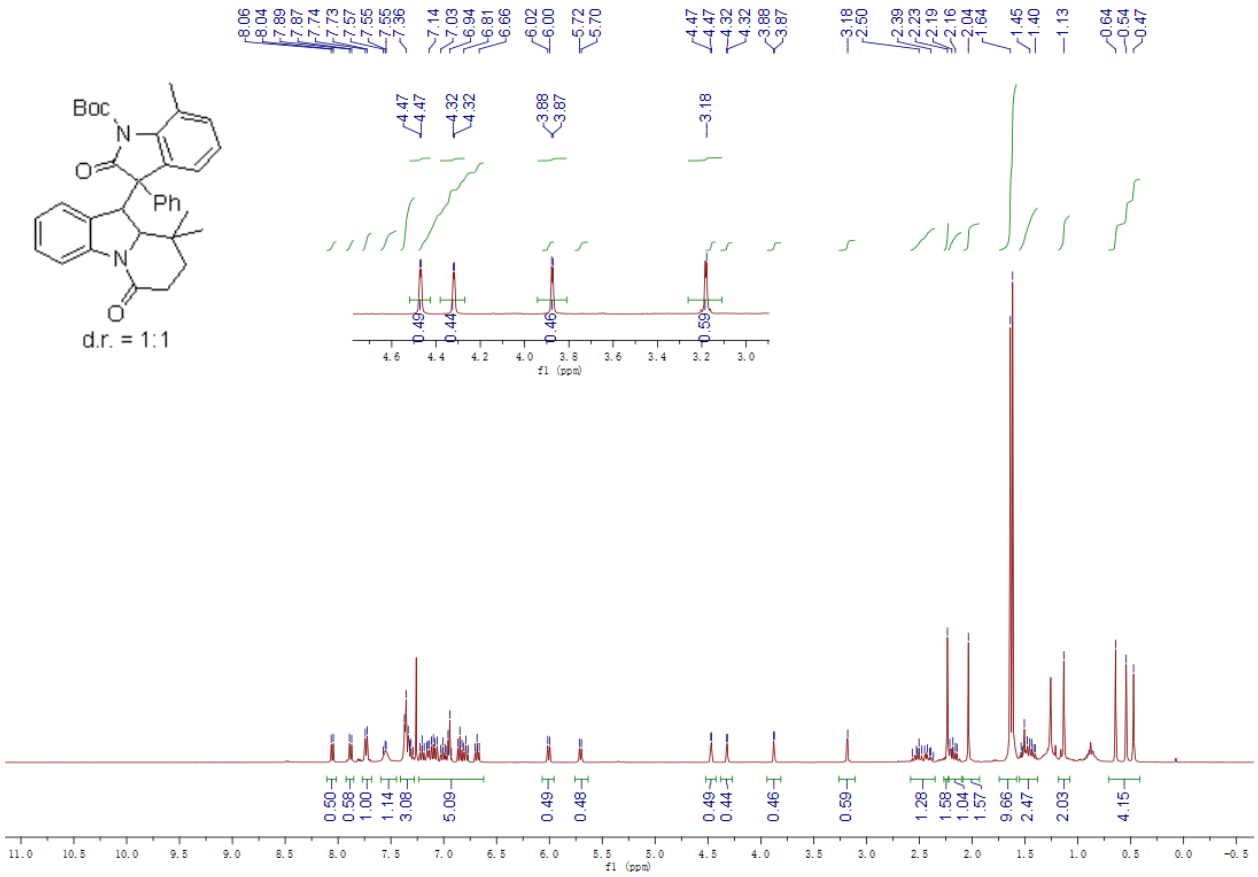
-105.49
-105.51
-105.99
-106.01
-106.11
-106.14
1.00
0.93
0.99
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

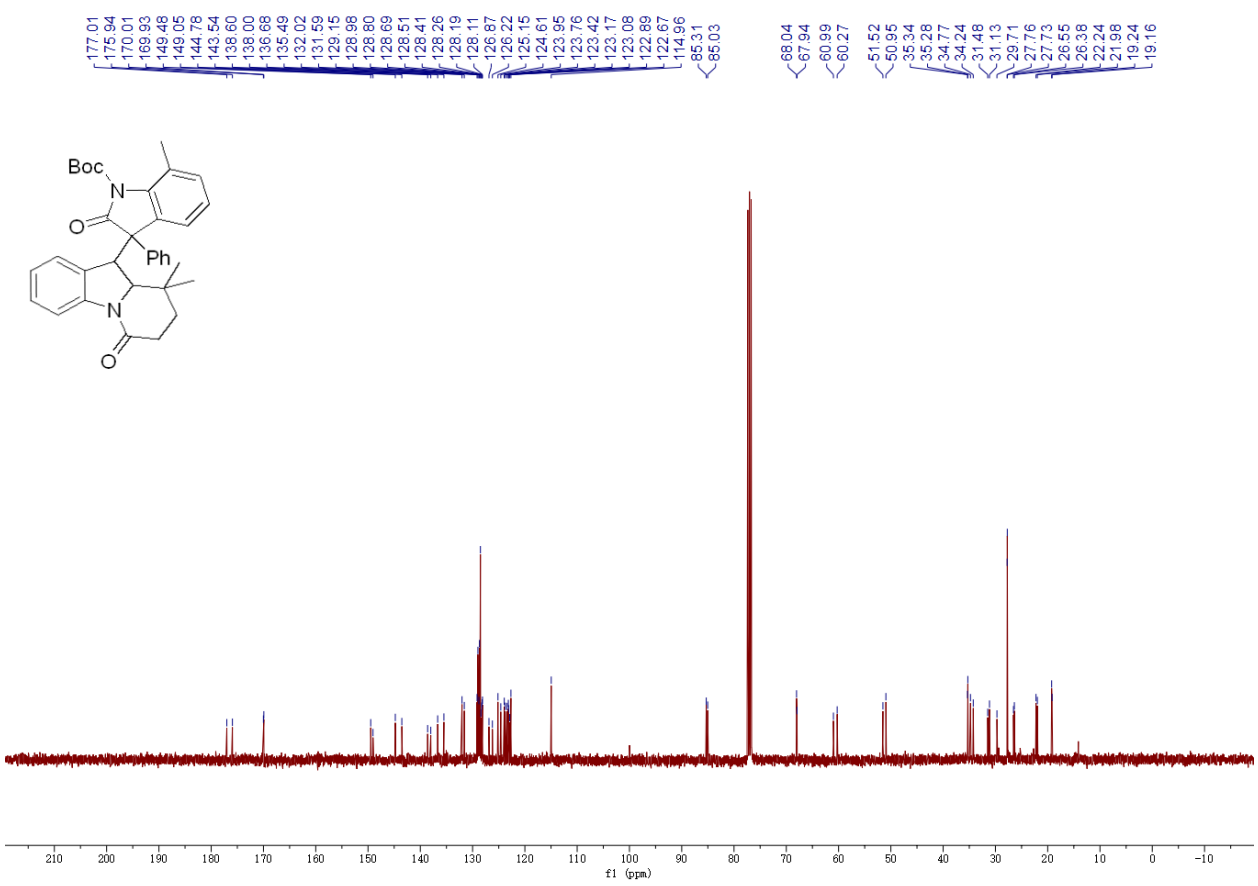

Boc
N
O
Cl
Ph
N
O
f1 (ppm)

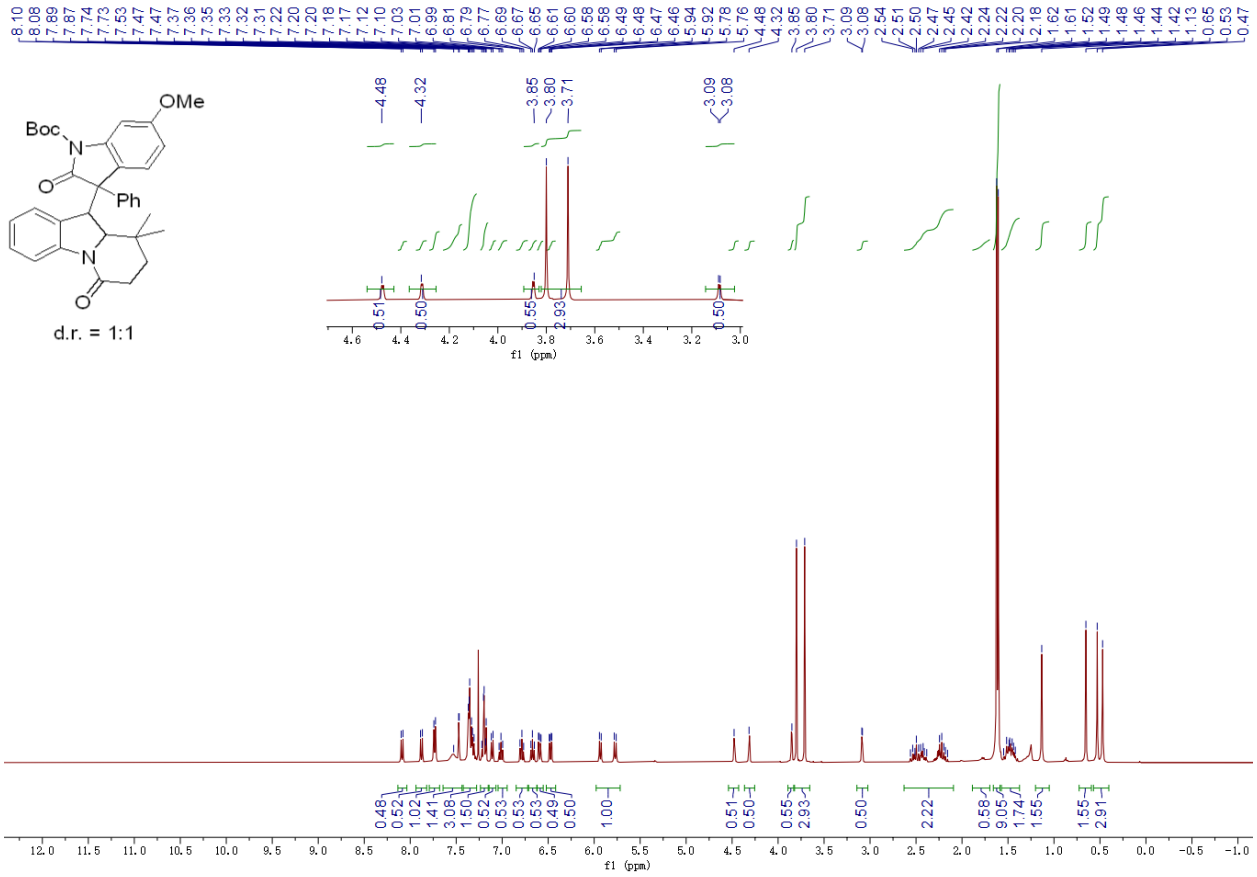

Boc
N
O
Cl
Ph
N
O
f1 (ppm)

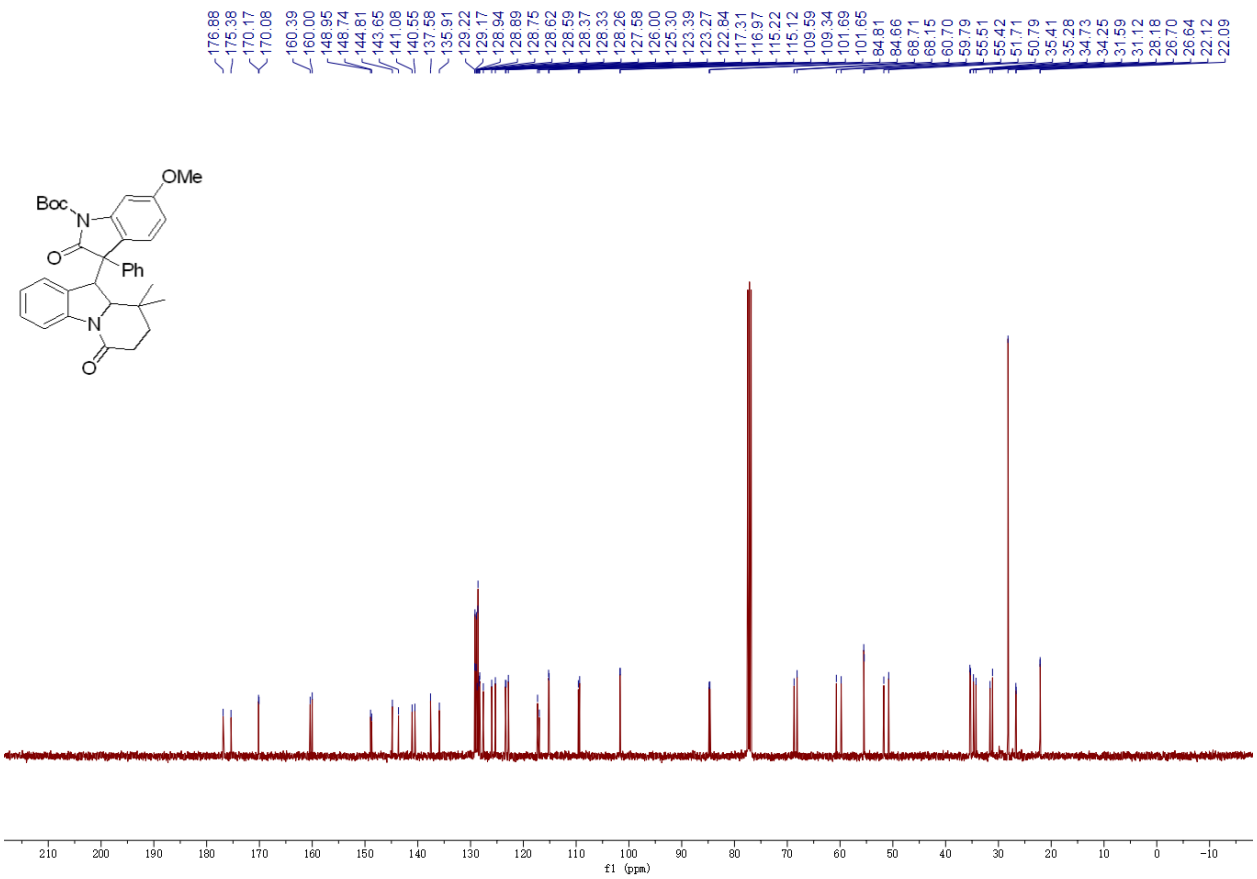

Boc
N
O
Cl
Ph
N
O
8.00
7.98
7.85
7.85
7.29
7.25
7.14
7.12
7.10
6.86
6.83
6.60
6.59
6.57
5.85
5.83
5.70
5.68
4.40
4.40
2.96
2.95
2.22
2.20
2.19
2.17
2.16
2.13
2.11
2.09
1.51
1.43
1.42
1.41
1.39
1.37
1.35
1.02
0.55
0.98
0.91
1.34
4.08
1.43
1.00
1.00
1.00
0.99
1.05
1.01
2.26
9.20
2.04
3.21
3.03
f1 (ppm)

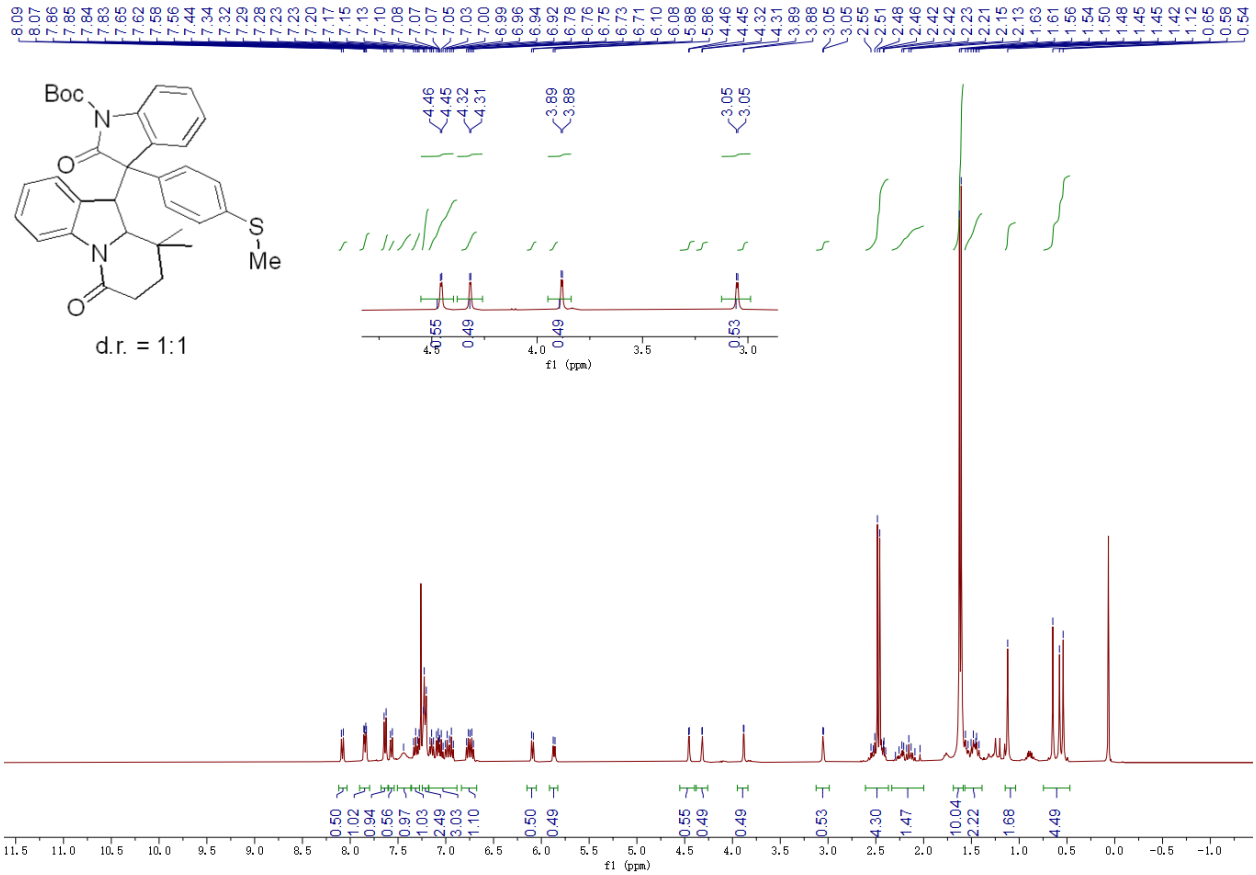

Boc
N
O
Cl
Ph
N
O
175.92
170.13
148.43
143.50
140.34
134.85
134.68
134.34
129.19
128.92
128.68
128.55
128.16
126.07
124.07
123.89
123.62
123.33
123.13
115.63
115.28
85.16
68.03
60.92
51.57
35.35
34.14
31.43
28.05
26.58
21.94
f1 (ppm)

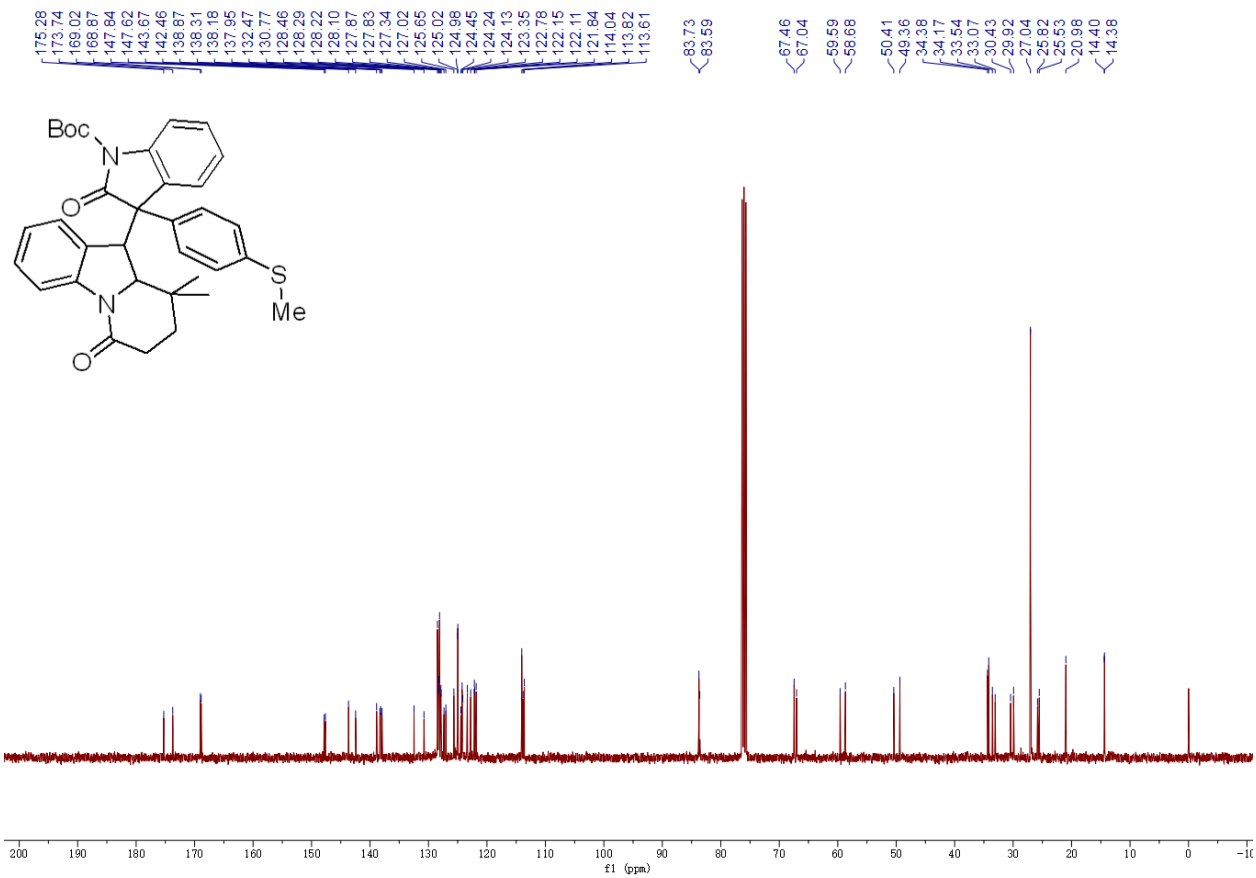

Boc
N
O
Ph
N
O
d.r. = 1:1
f1 (ppm)

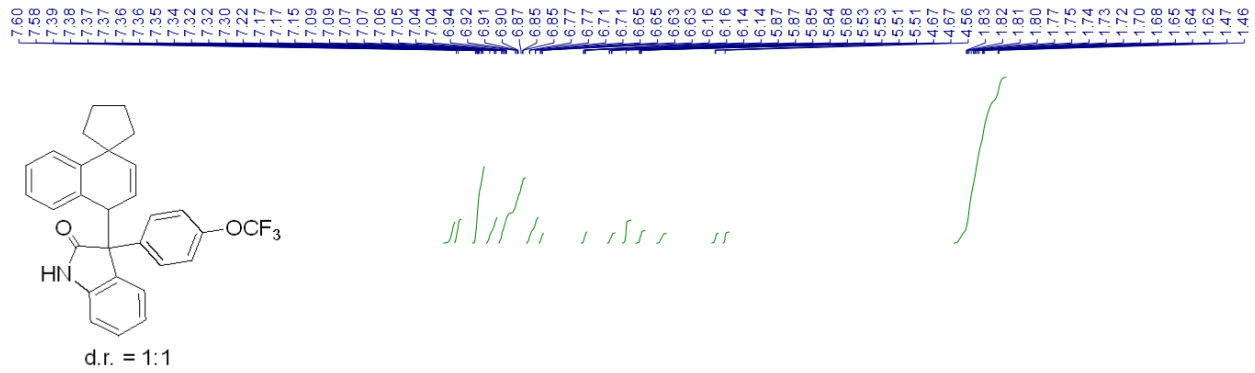

Boc
N
O
Ph
N
O
f1 (ppm)


OMe
Boc
N
O
Ph
N
O
d.r. = 1:1
f1 (ppm)


OMe
Boc
N
O
Ph
N
O
f1 (ppm)

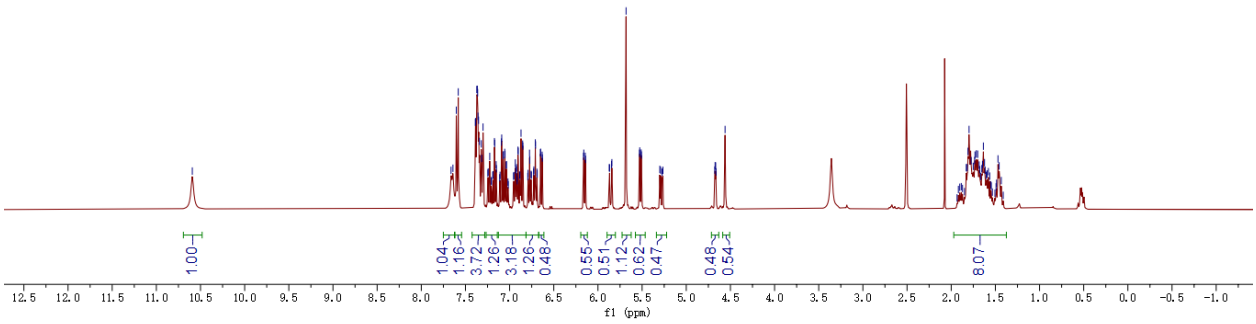

Boc
N
O
S
Me
N
O
d.r. = 1:1
f1 (ppm)

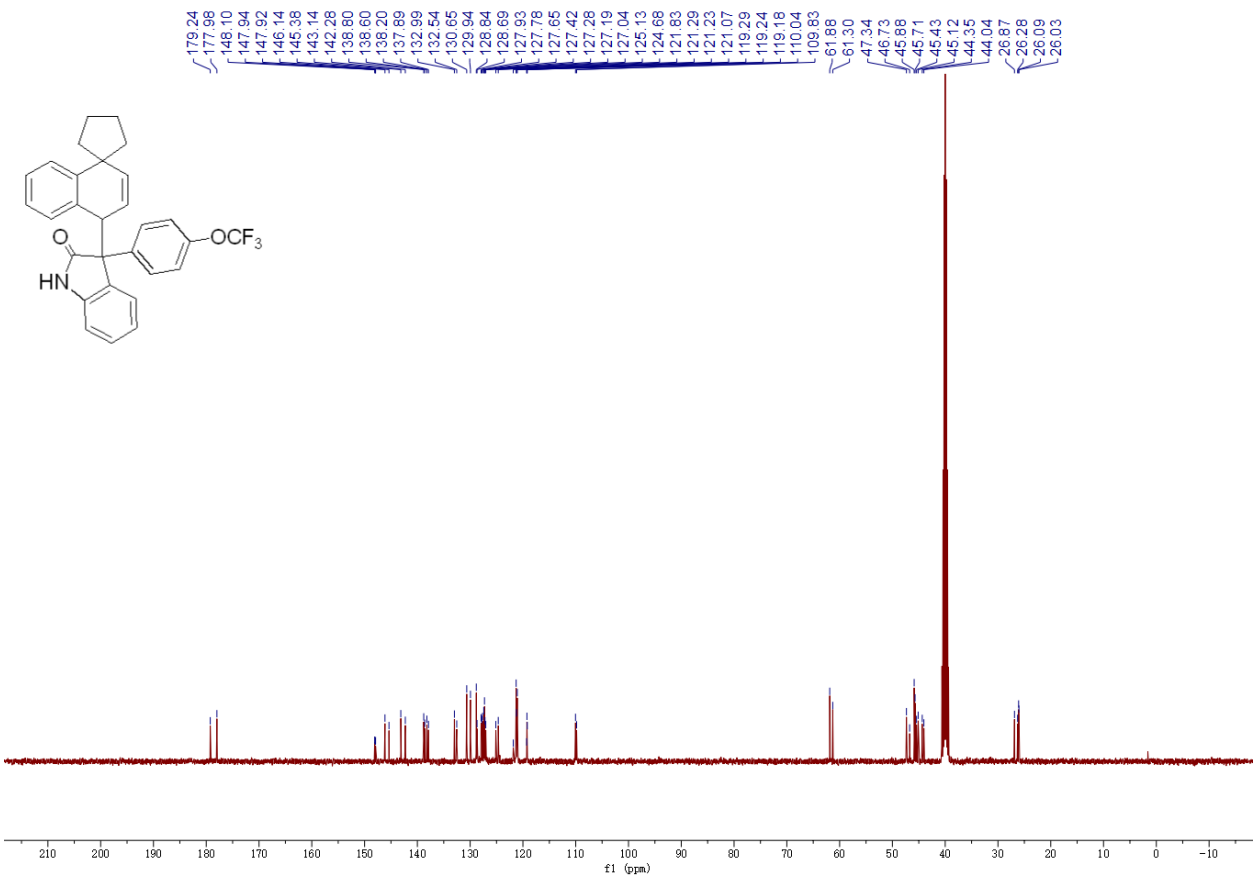

Boc
N
O
S
Me
N
O
f1 (ppm)



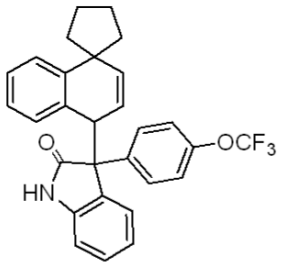
O
HN
OCF3

d.r. = 1:1

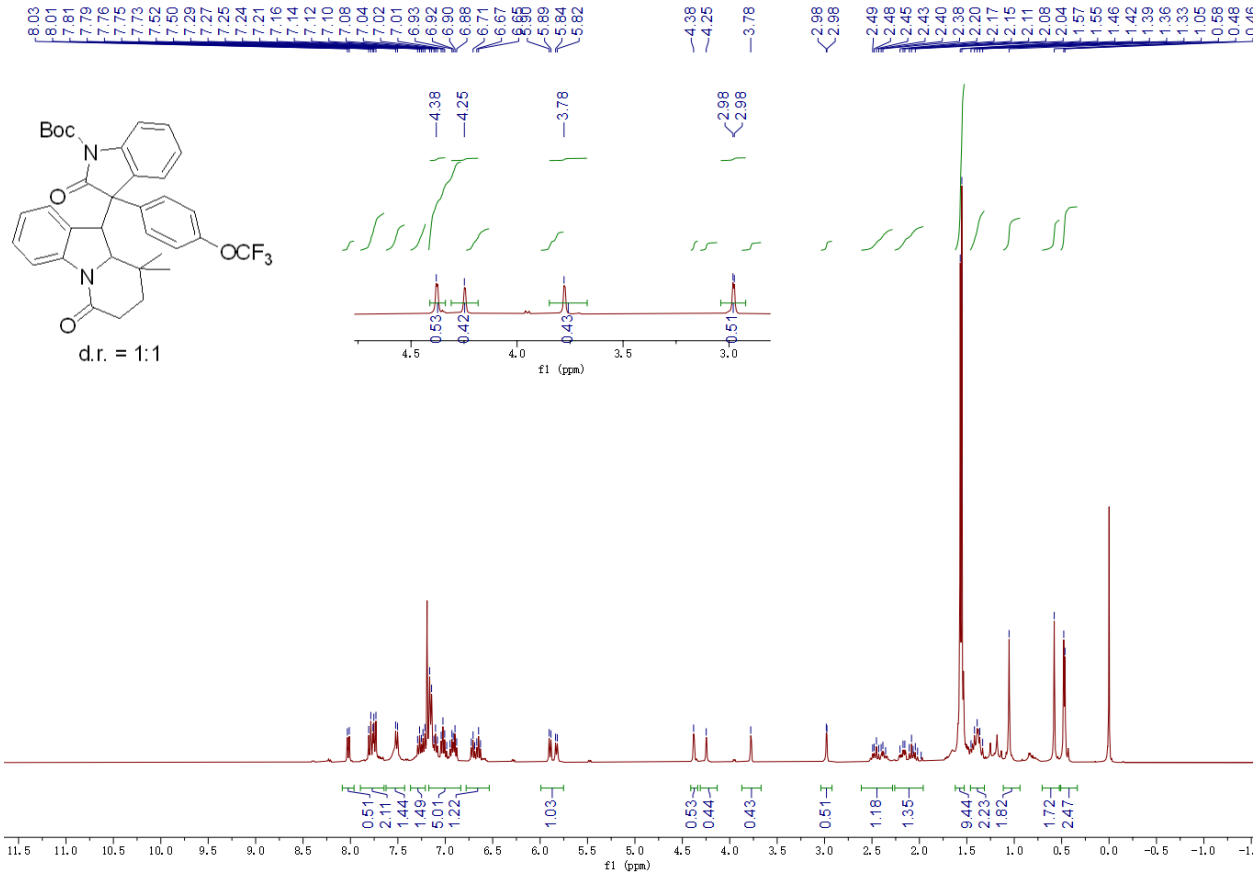

1.00
1.04
1.16
3.72
1.26
3.18
1.26
0.48
0.55
0.51
1.12
0.62
0.47
0.48
0.54
8.07
f1 (ppm)

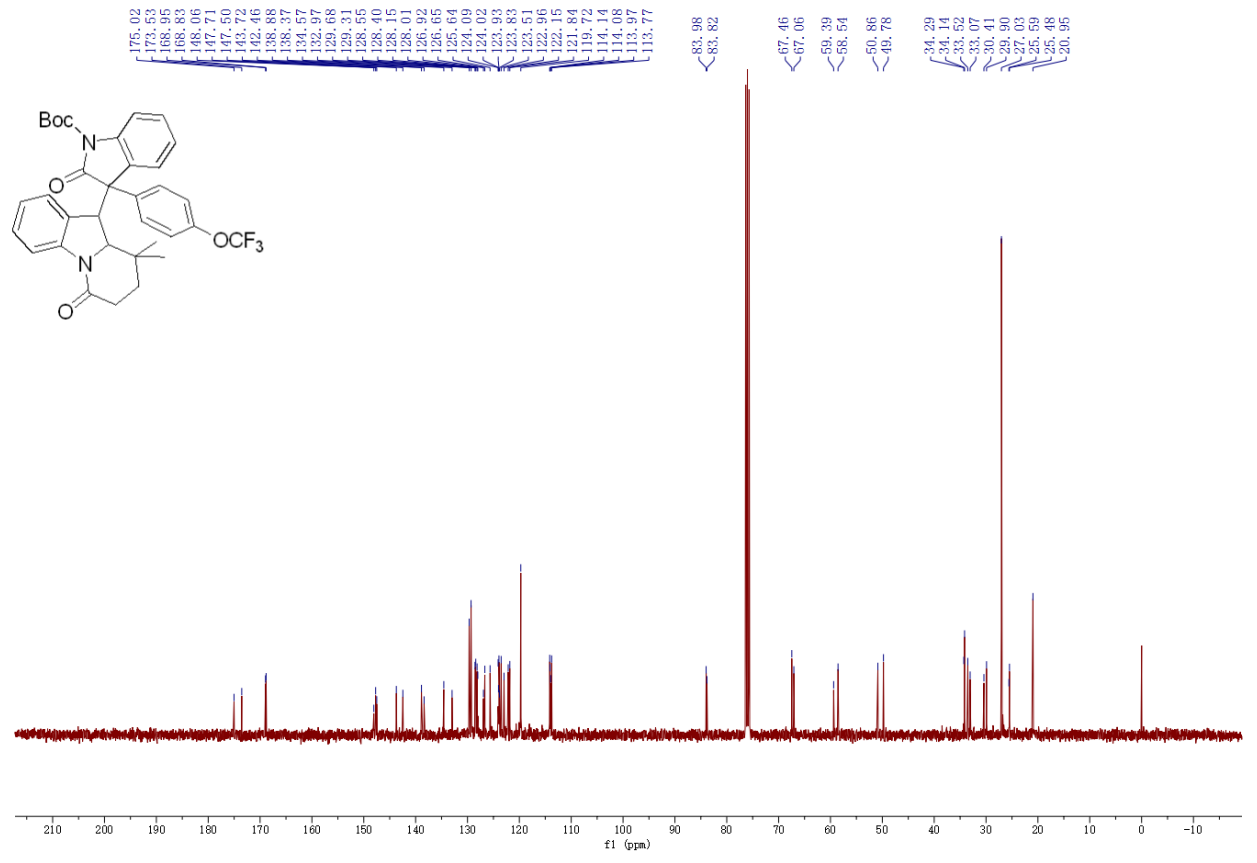

f1 (ppm)

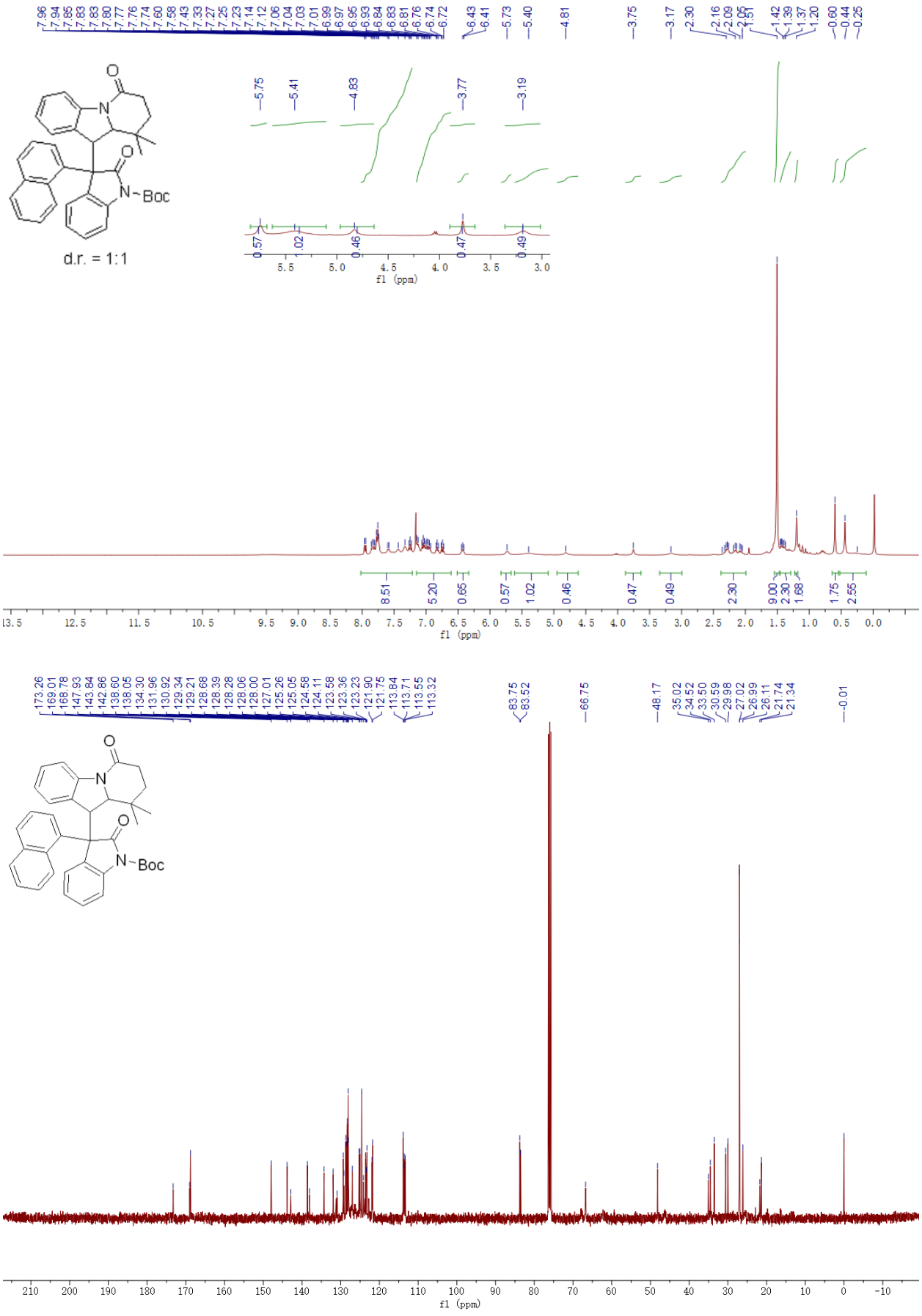
O
HN
OCF3

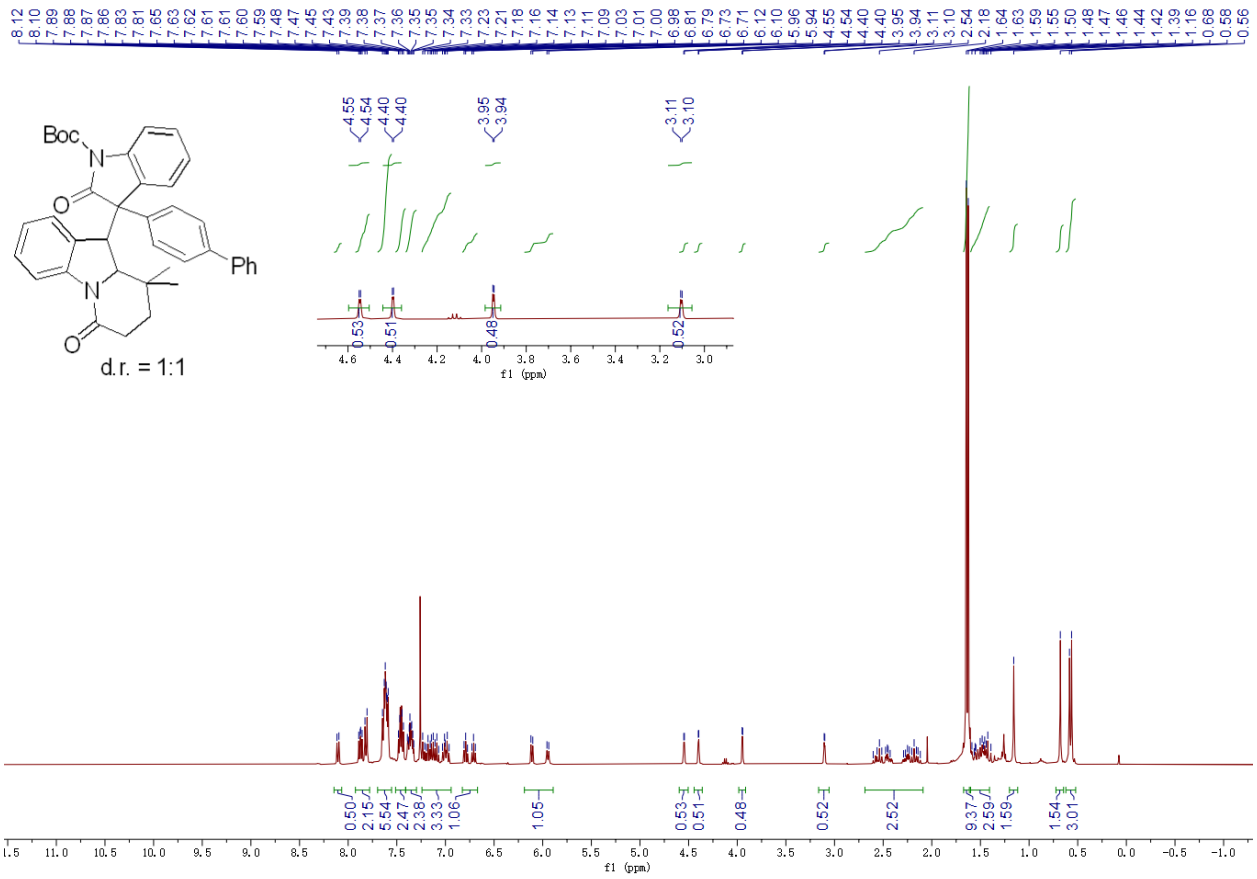

O
HN
OCF3

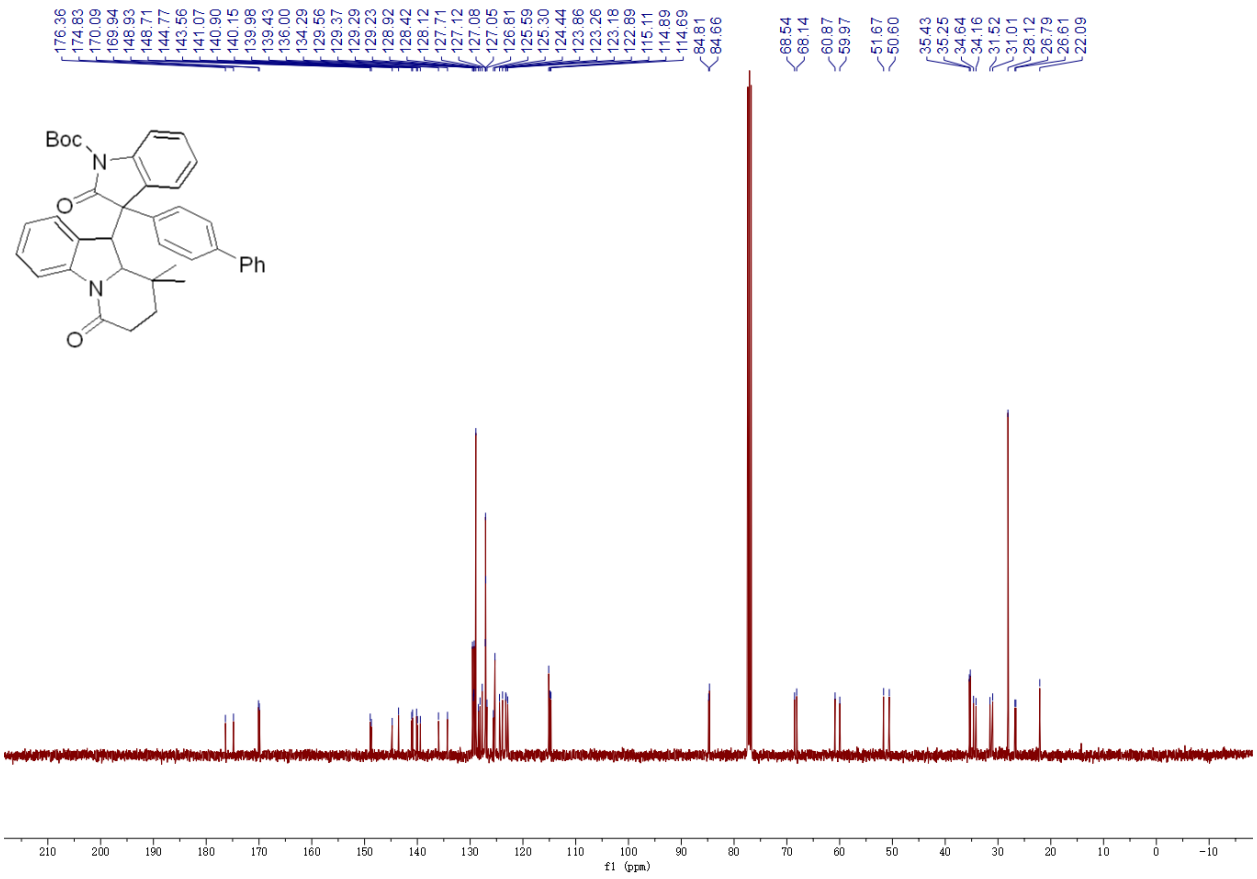
-56.81
-56.83
f1 (ppm)

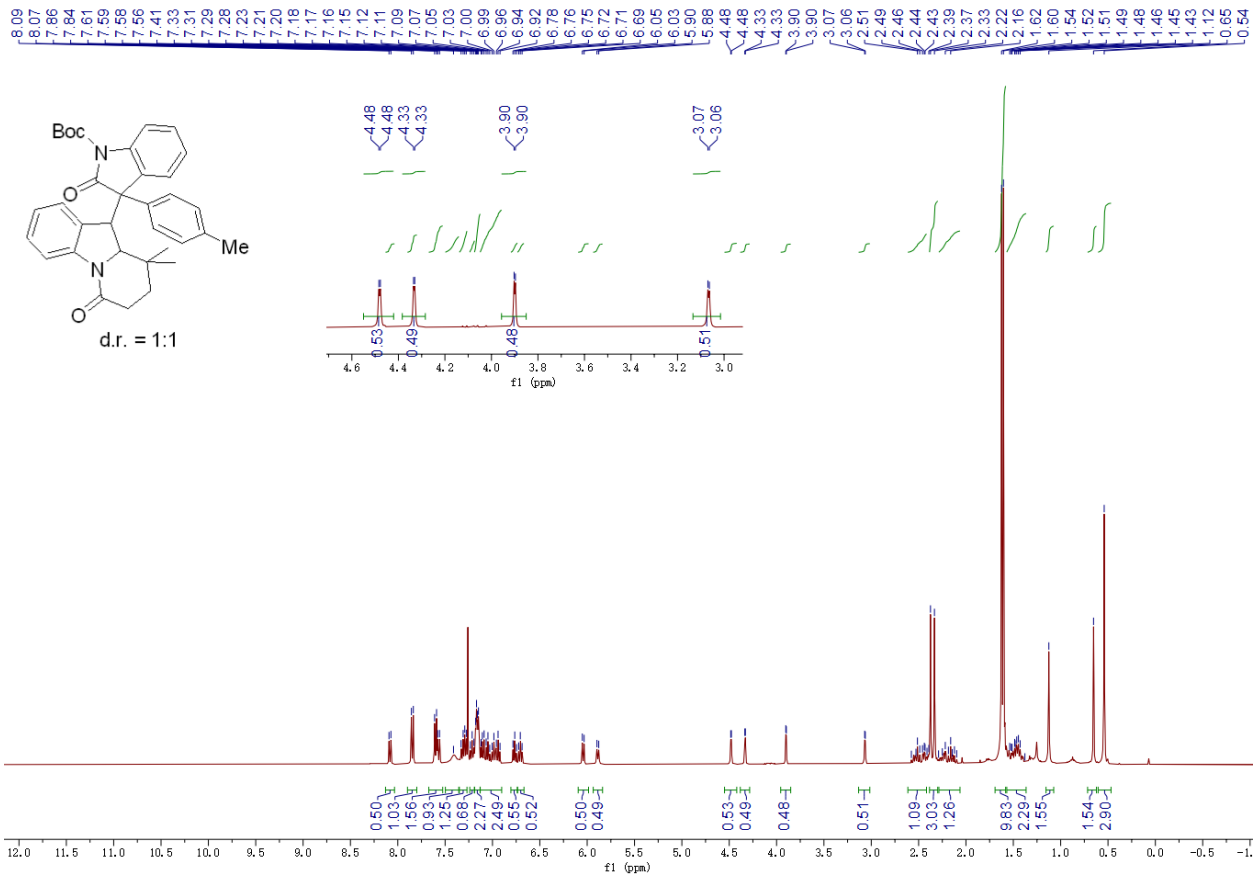

Boc
N
O
N
O
OCF3
d.r. = 1:1
f1 (ppm)

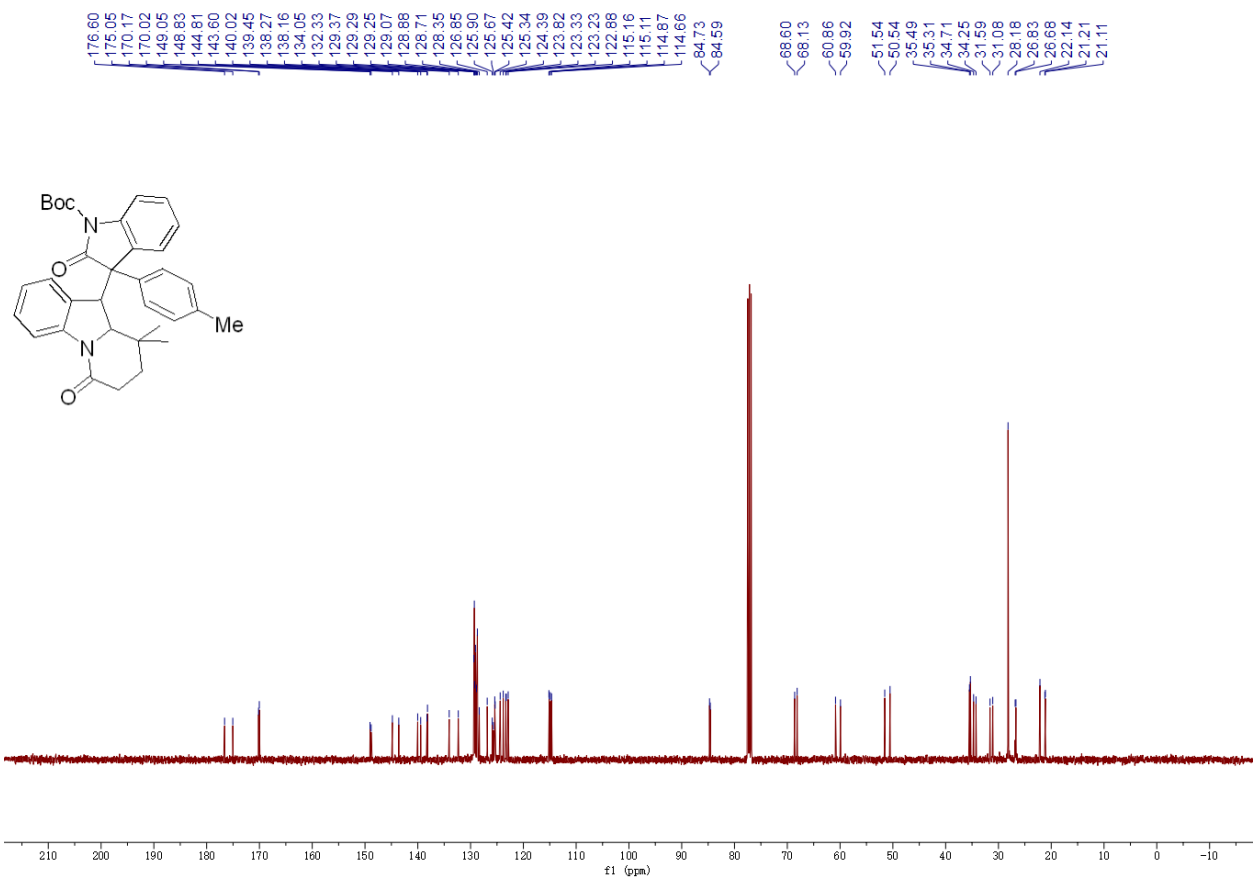

Boc
N
O
N
O
OCF3
f1 (ppm)

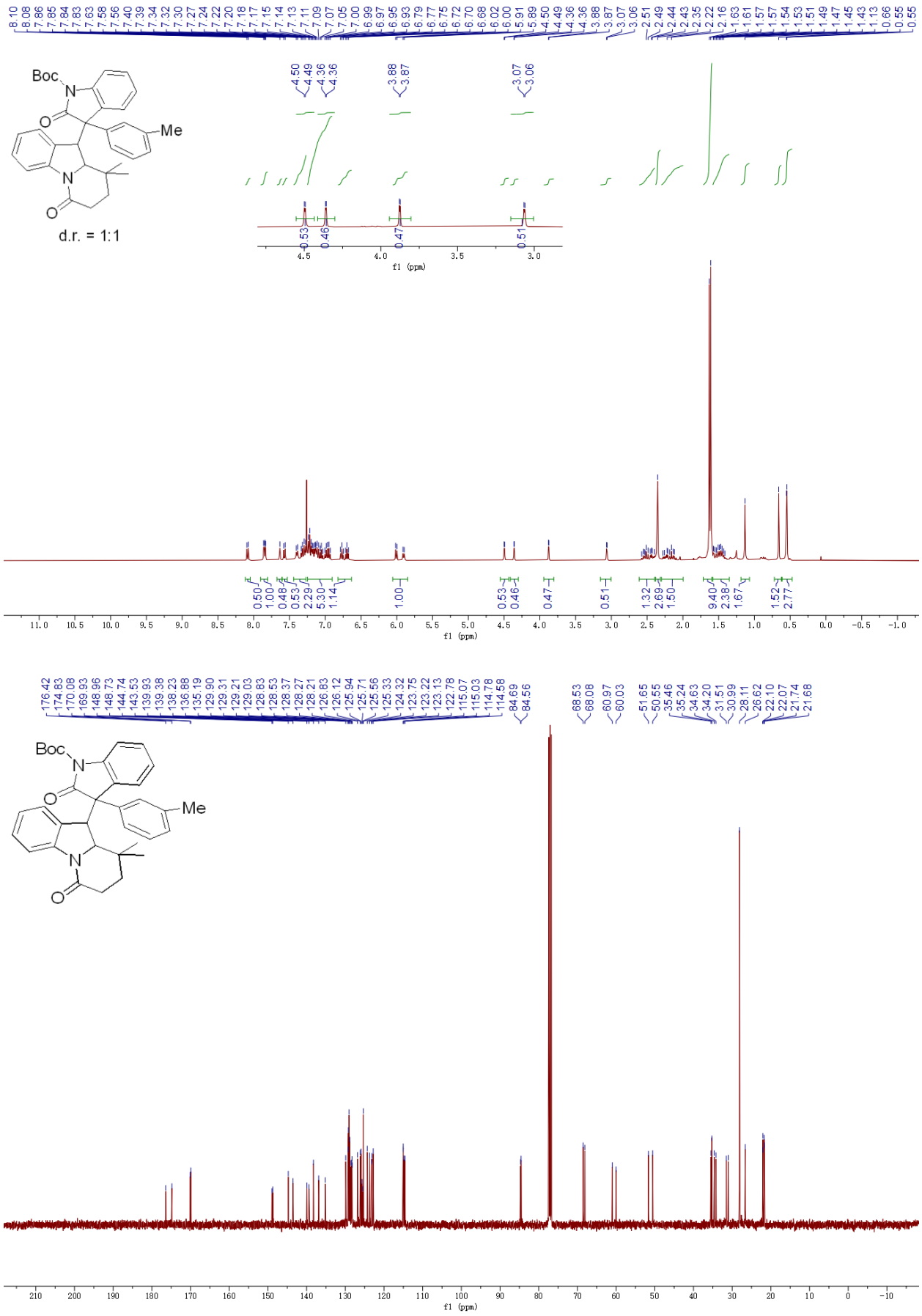

d.r. = 1:1
f1 (ppm)
f1 (ppm)
f1 (ppm)

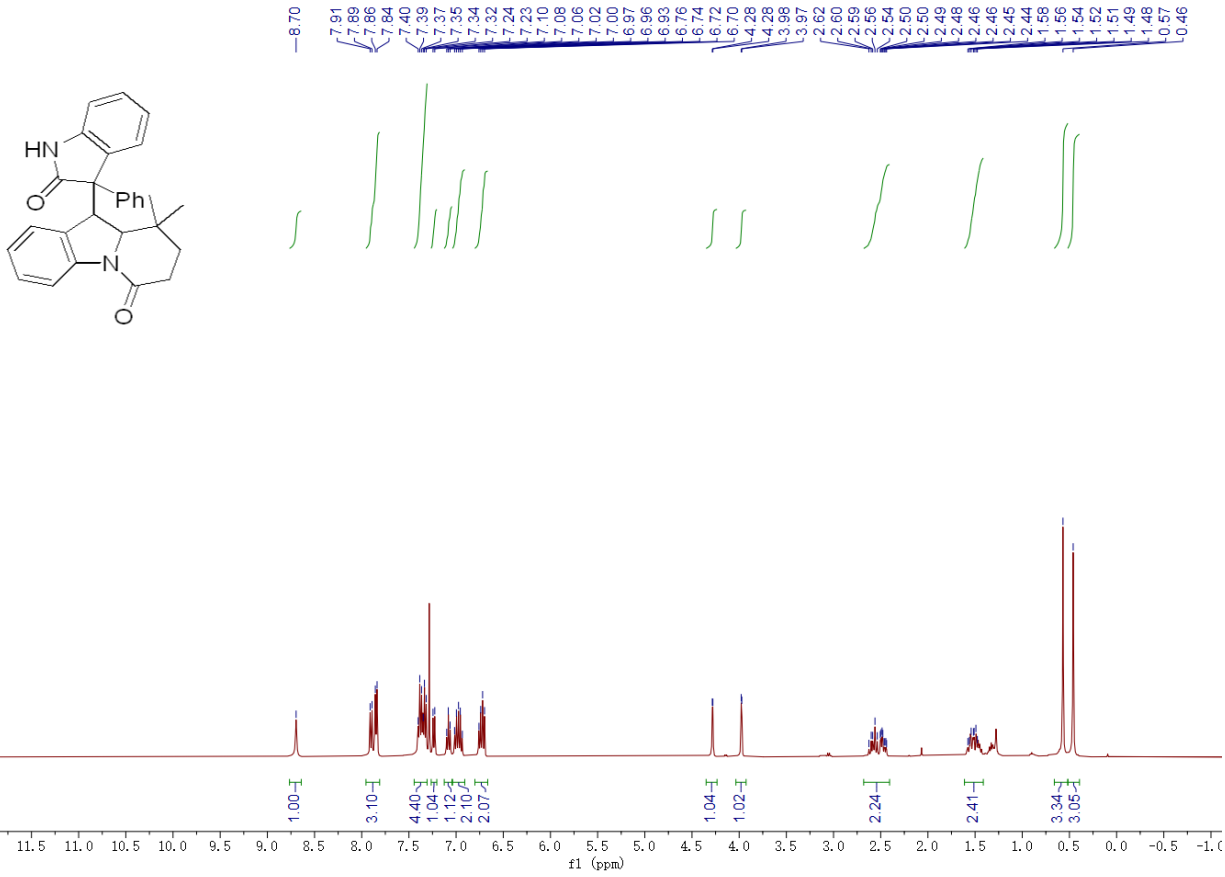

Boc
N
O
Ph
N
O
d.r. = 1:1
f1 (ppm)
f1 (ppm)

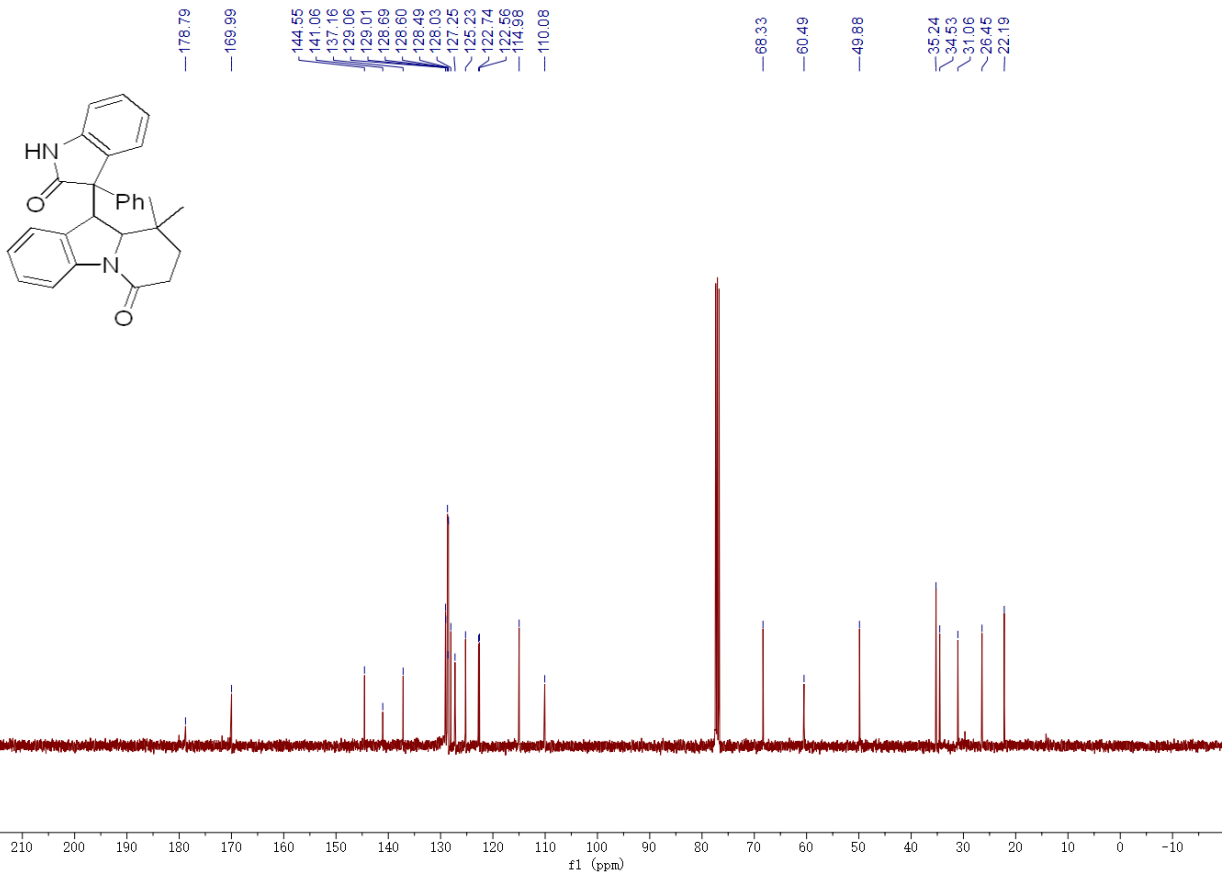

Boc
N
O
Ph
N
O
f1 (ppm)
f1 (ppm)

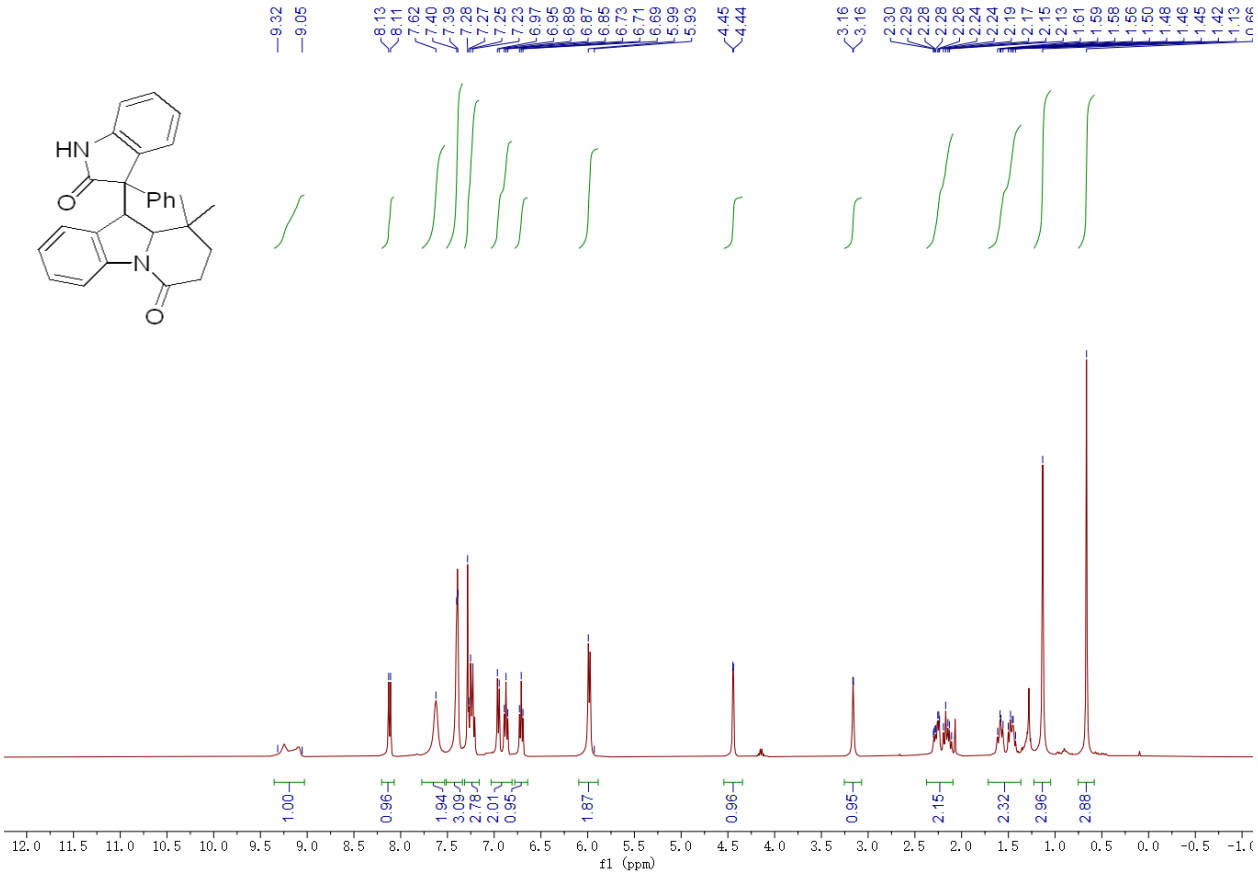

Boc
N
O
N
O
Me
d.r. = 1:1
f1 (ppm)

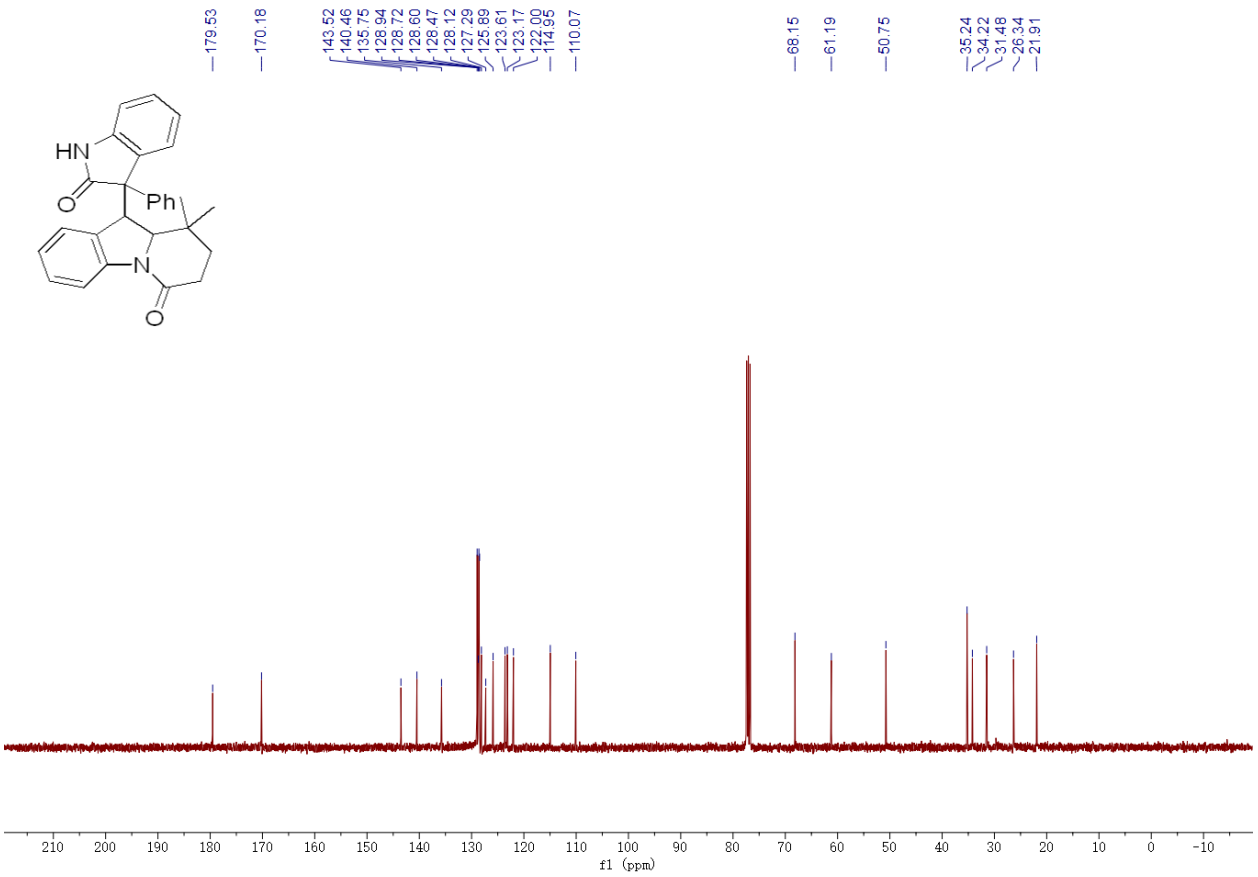

Boc
N
O
N
O
Me
f1 (ppm)

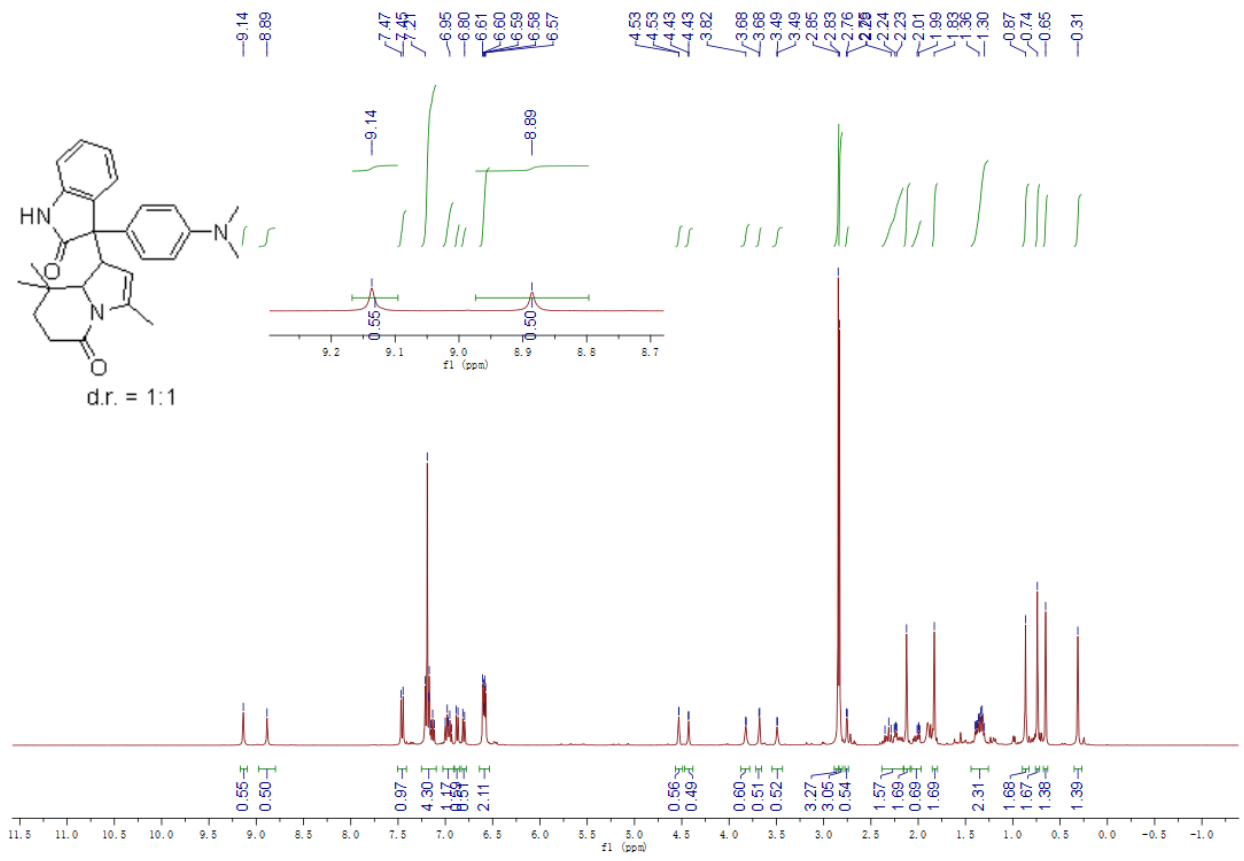

Boc
Me
d.r. = 1:1
f1 (ppm)

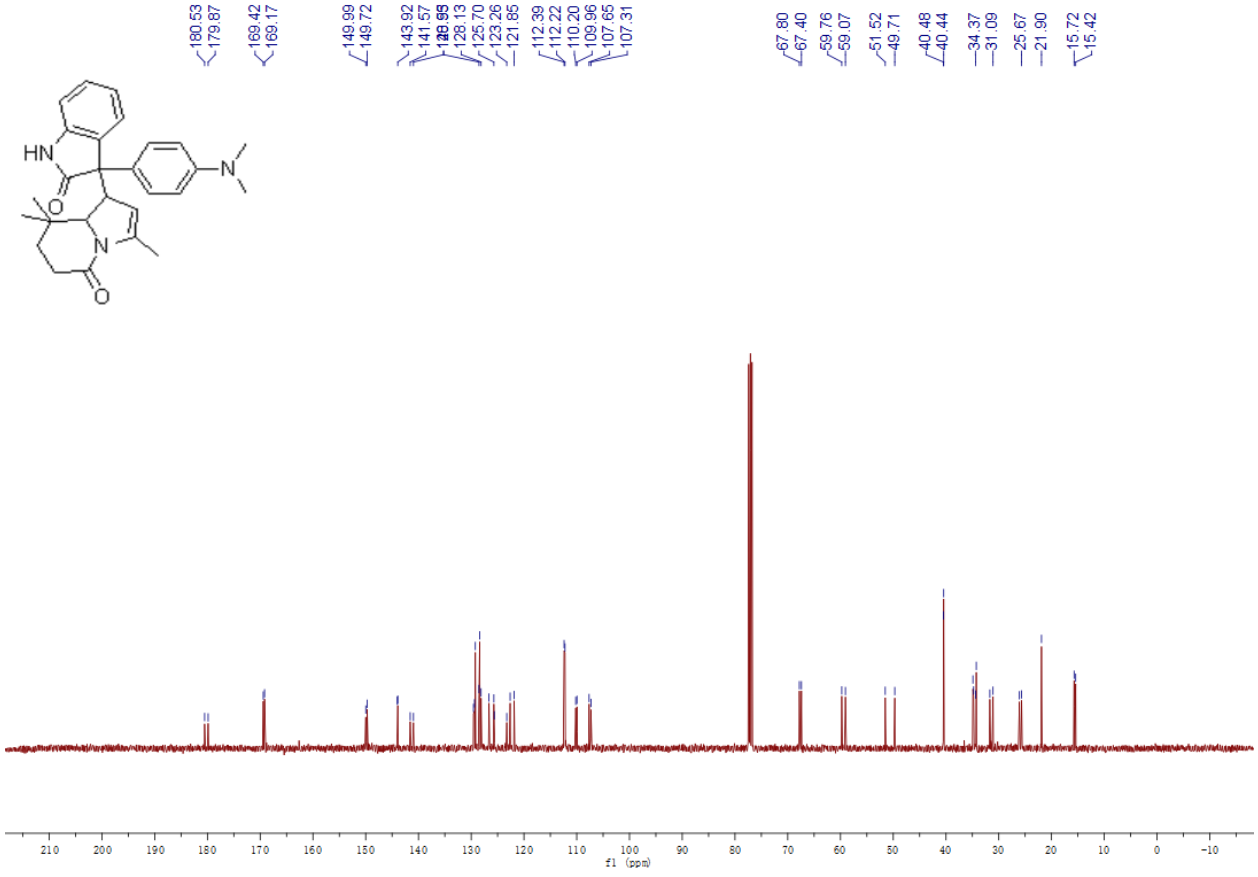

HN
O
Ph
N
O
8.70
7.91
7.89
7.86
7.84
7.40
7.39
7.37
7.35
7.34
7.32
7.24
7.23
7.10
7.08
7.06
7.02
7.00
6.97
6.96
6.93
6.76
6.74
6.72
6.70
4.28
4.28
3.98
3.97
2.62
2.60
2.59
2.56
2.54
2.50
2.50
2.49
2.48
2.46
2.46
2.45
2.44
1.58
1.56
1.54
1.52
1.51
1.49
1.48
0.57
0.46
1.00
3.10
4.40
1.04
1.12
2.10
2.07
1.04
1.02
2.24
2.41
3.34
3.05
f1 (ppm)

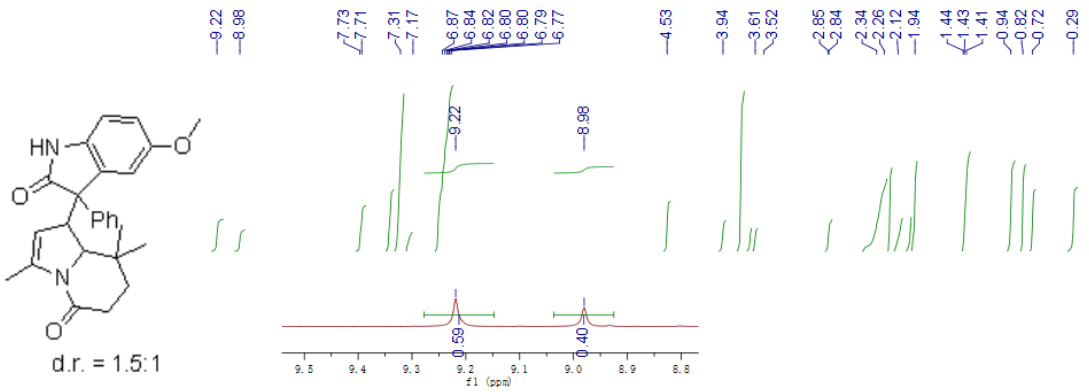

HN
O
Ph
N
O
178.79
169.99
144.55
141.06
137.16
129.06
129.01
128.69
128.60
128.49
128.03
127.25
125.23
122.74
122.56
114.98
110.08
68.33
60.49
49.88
35.24
34.53
31.06
26.45
22.19
f1 (ppm)

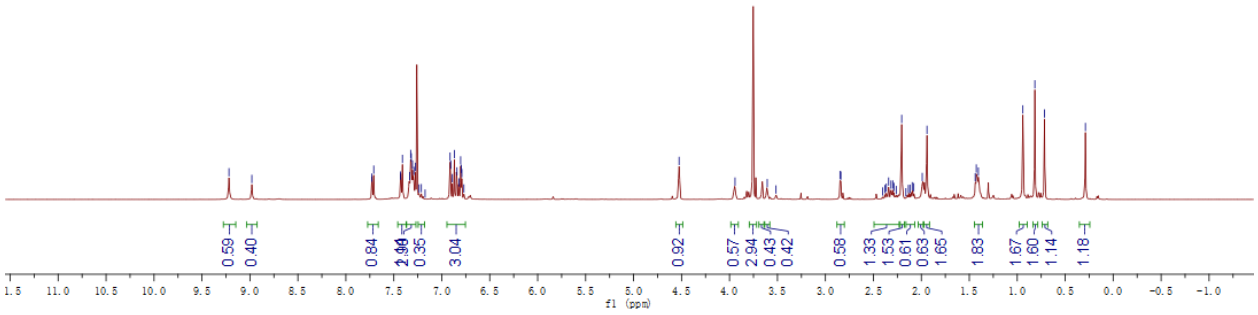

HN
O
Ph
N
O
9.32
9.05
8.13
8.11
7.62
7.40
7.39
7.28
7.27
7.25
7.23
6.97
6.95
6.89
6.87
6.85
6.73
6.71
6.69
5.99
5.93
4.45
4.44
3.16
3.16
2.30
2.29
2.28
2.28
2.26
2.24
2.24
2.19
2.17
2.15
2.13
1.61
1.59
1.58
1.56
1.50
1.48
1.46
1.45
1.42
1.13
1.00
0.96
1.94
3.09
2.78
2.01
0.95
1.87
0.96
0.95
2.15
2.32
2.96
2.88
f1 (ppm)

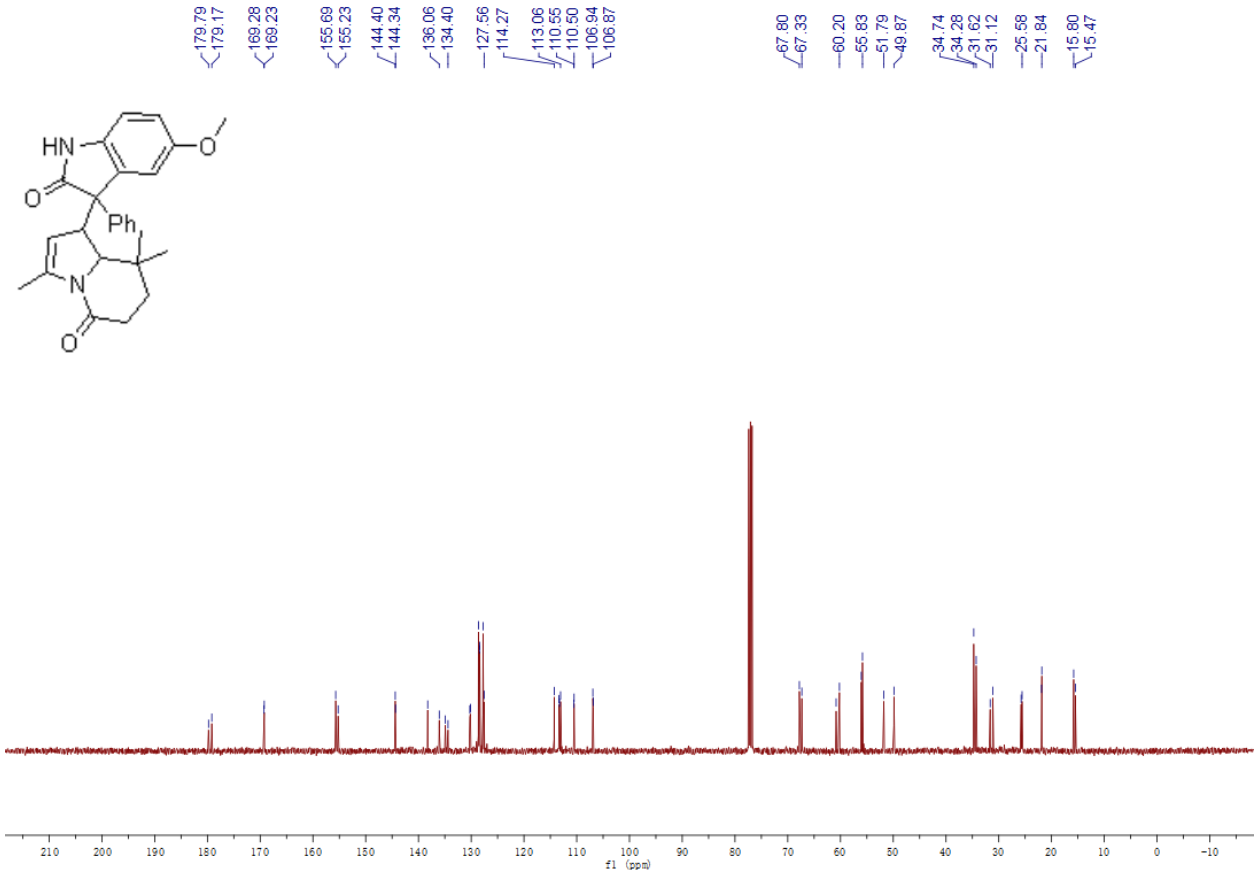

HN
O
Ph
N
O
179.53
170.18
143.52
140.46
135.75
128.94
128.72
128.60
128.47
128.12
127.29
125.89
123.61
123.17
122.00
114.95
110.07
68.15
61.19
50.75
35.24
34.22
31.48
26.34
21.91
f1 (ppm)

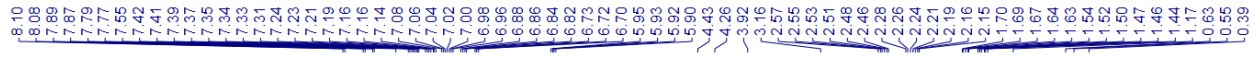

d.r. = 1:1
f1 (ppm)

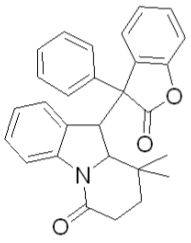

f1 (ppm)


9.22
8.98
7.73
7.71
7.31
7.17
6.87
6.84
6.82
6.80
6.79
6.77
4.53
3.94
3.61
3.52
2.85
2.84
2.34
2.26
2.12
1.94
1.44
1.43
1.41
0.94
0.82
0.72
0.29
HN
O
Ph
N
O
d.r. = 1.5:1
0.59
0.40
f1 (ppm)

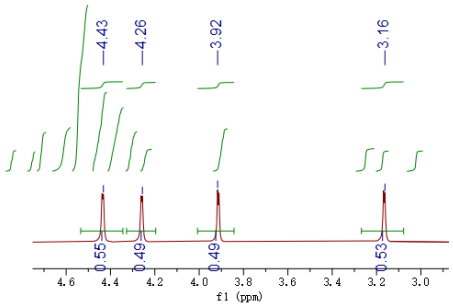

0.59
0.40
0.84
3.04
0.92
0.57
2.94
0.43
0.42
0.58
1.33
1.53
0.61
0.63
1.65
1.83
1.67
1.60
1.14
1.18
f1 (ppm)

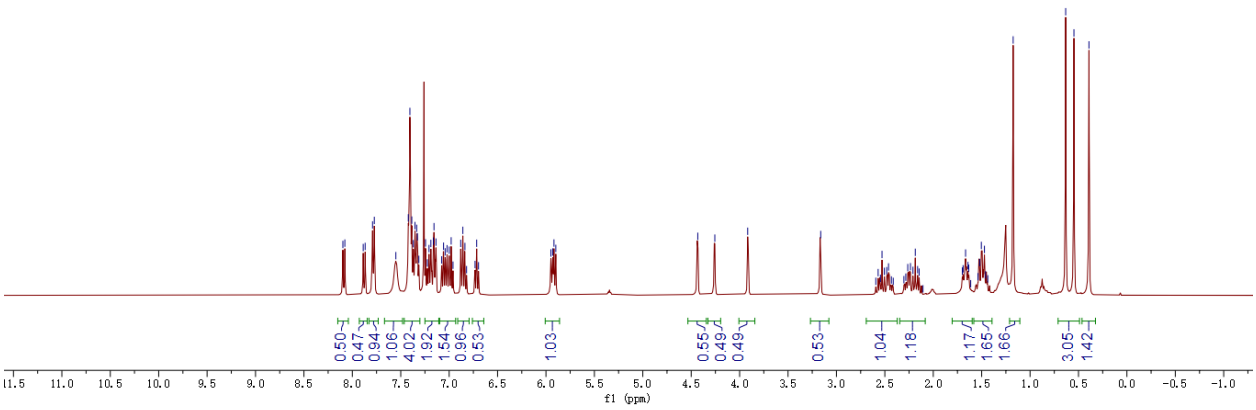

179.79
179.17
169.28
169.23
155.69
155.23
144.40
144.34
136.06
134.40
127.56
114.27
113.06
110.55
110.50
106.94
106.87
67.80
67.33
60.20
55.83
51.79
49.87
34.74
34.28
31.62
31.12
25.58
21.84
15.80
15.47
HN
O
Ph
N
O
f1 (ppm)

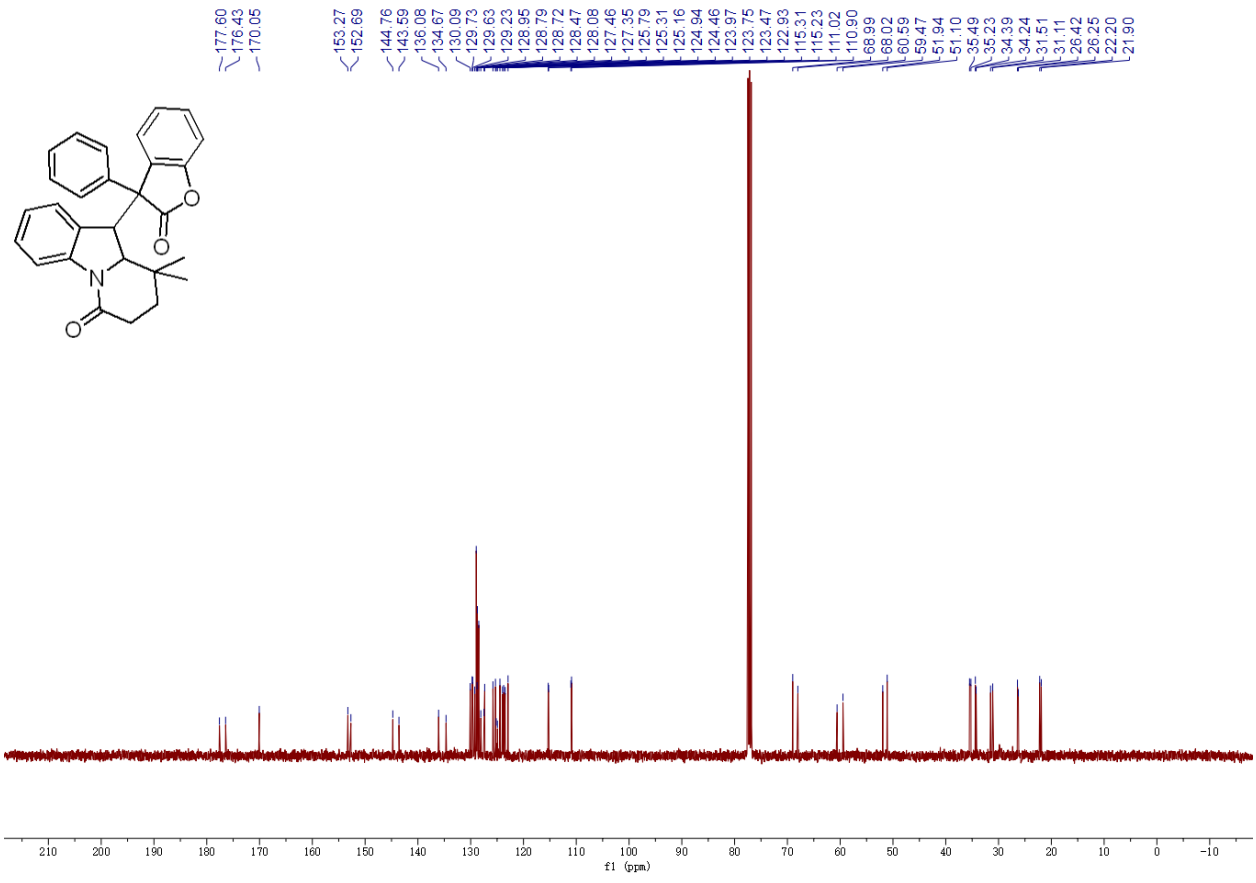


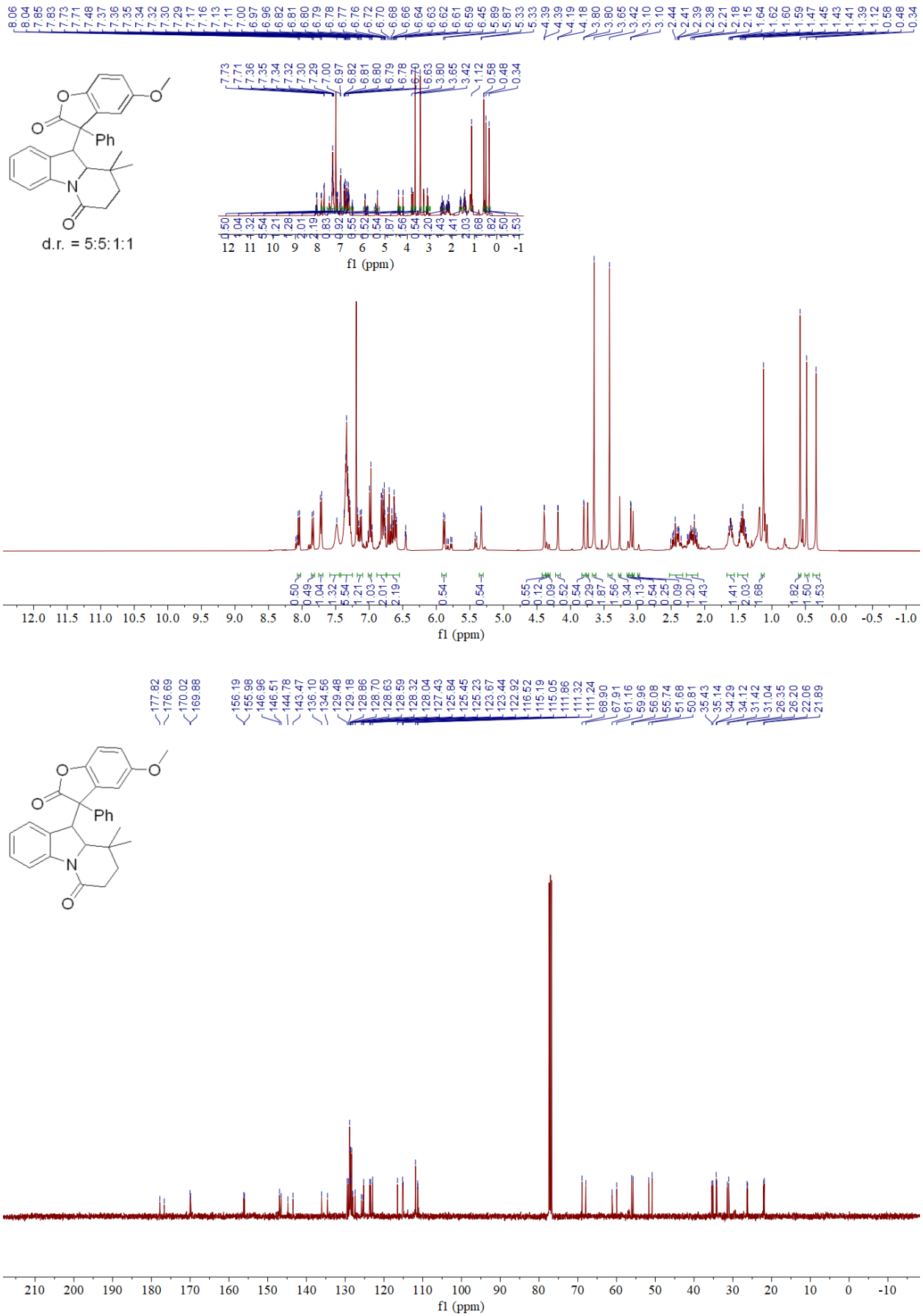


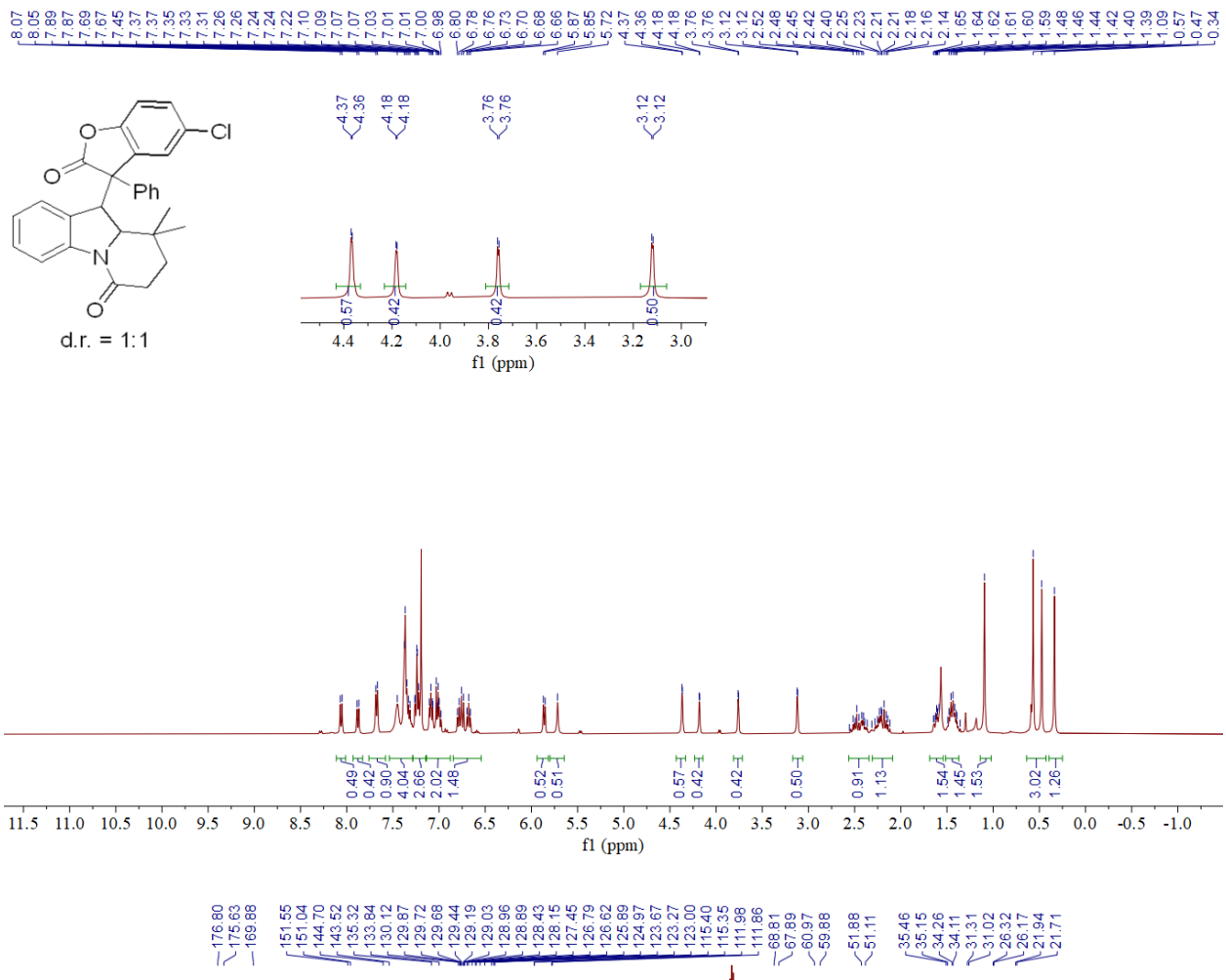
d.r. = 1:1



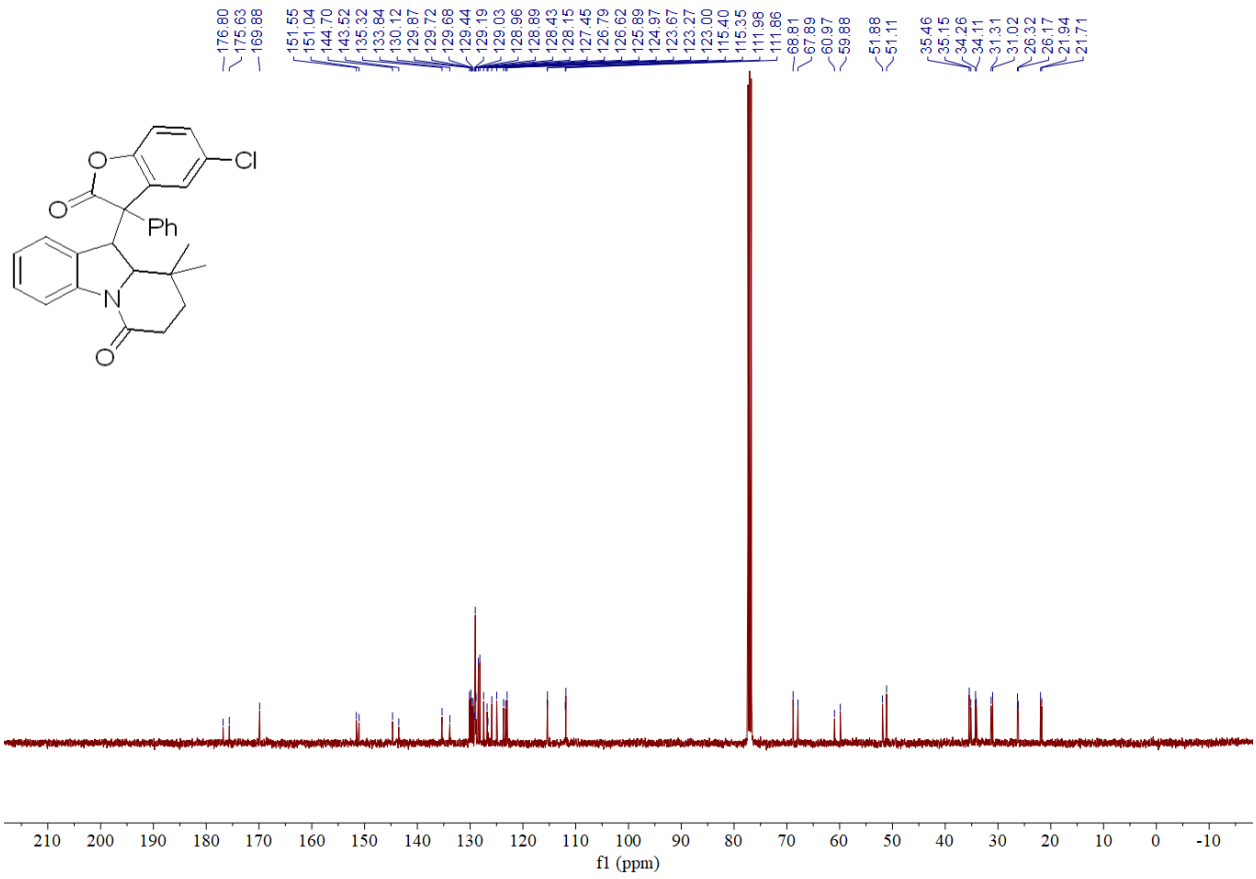


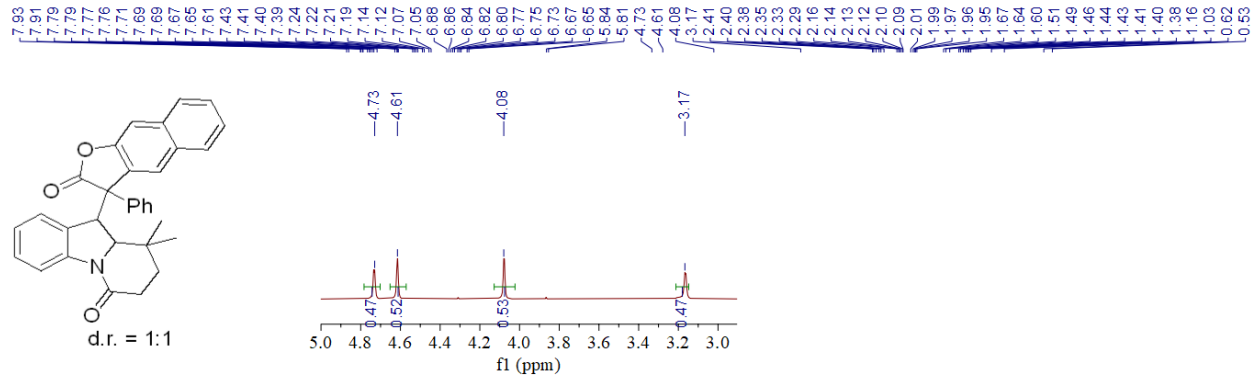


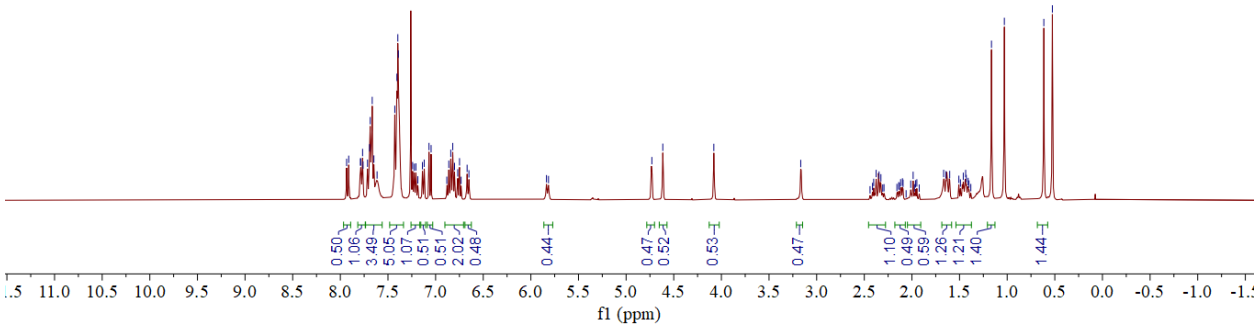

d.r. = 5:5:1:1
f1 (ppm)
f1 (ppm)
f1 (ppm)

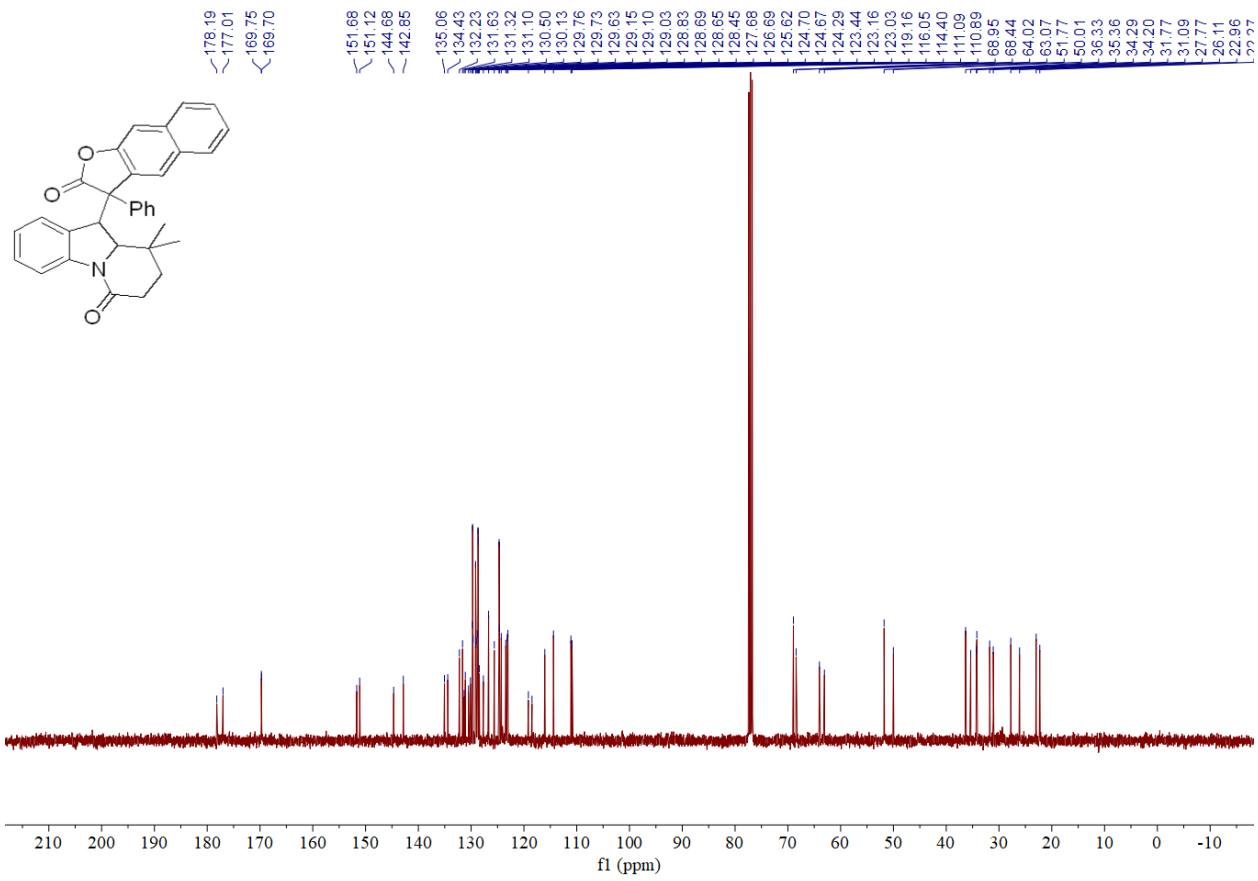

d.r. = 1:1
f1 (ppm)

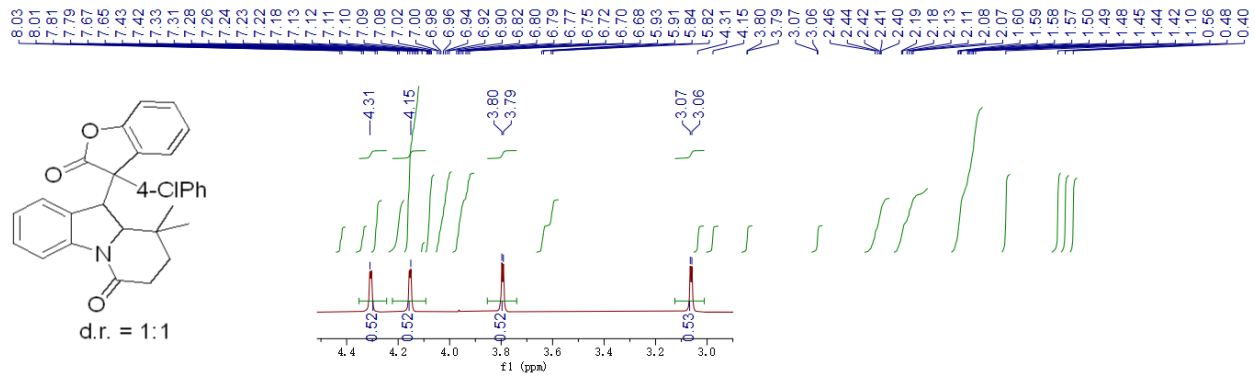
f1 (ppm)


f1 (ppm)


7.93 7.91 7.79 7.79 7.77 7.76 7.71 7.69 7.69 7.67 7.65 7.61 7.43 7.41 7.40 7.39 7.24 7.22 7.21 7.19 7.14 7.12 7.07 7.05 6.88 6.86 6.84 6.82 6.80 6.77 6.75 6.73 6.67 6.65 5.84 5.81 4.73 4.61 4.08 3.17 2.41 2.40 2.38 2.35 2.33 2.29 2.16 2.14 2.13 2.12 2.10 2.09 2.01 1.99 1.97 1.96 1.95 1.67 1.64 1.60 1.51 1.49 1.46 1.44 1.43 1.41 1.40 1.38 1.16 1.03 0.62 0.53
O
O
Ph
N
O
d.r. = 1:1
4.73
4.61
4.08
3.17
0.47
0.52
0.53
0.47
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
f1 (ppm)


0.50 1.06 3.49 5.05 1.07 0.51 0.51 2.02 0.48 0.44 0.47 0.52 0.53 0.47 1.10 0.49 0.59 1.26 1.21 1.40 1.44
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


178.19 177.01 169.75 169.70 151.68 151.12 144.68 142.85 135.06 134.43 132.23 131.63 131.32 131.10 130.50 130.13 129.76 129.73 129.63 129.15 129.10 129.03 128.83 128.69 128.65 128.45 127.68 126.69 125.62 124.70 124.67 124.29 123.44 123.16 123.03 119.16 116.05 114.40 111.09 110.89 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
O
O
Ph
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4-ClPh
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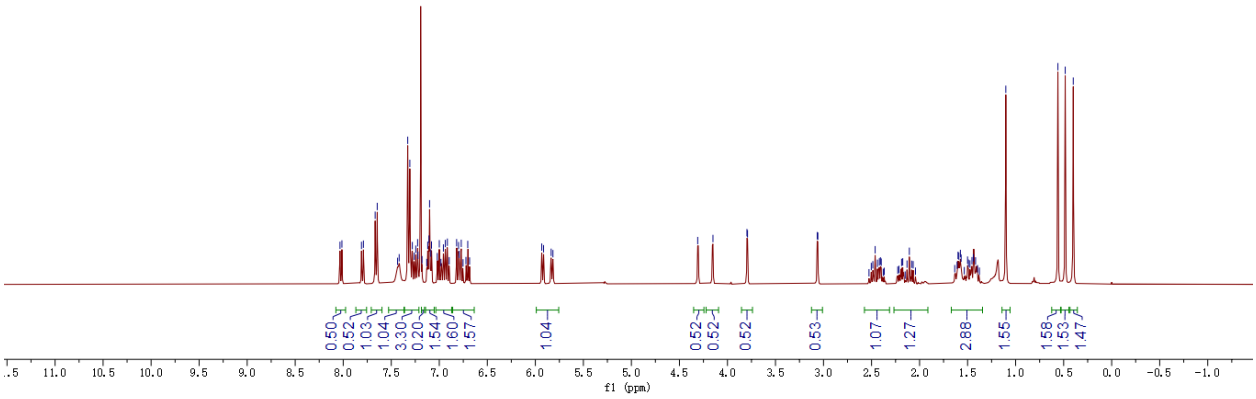
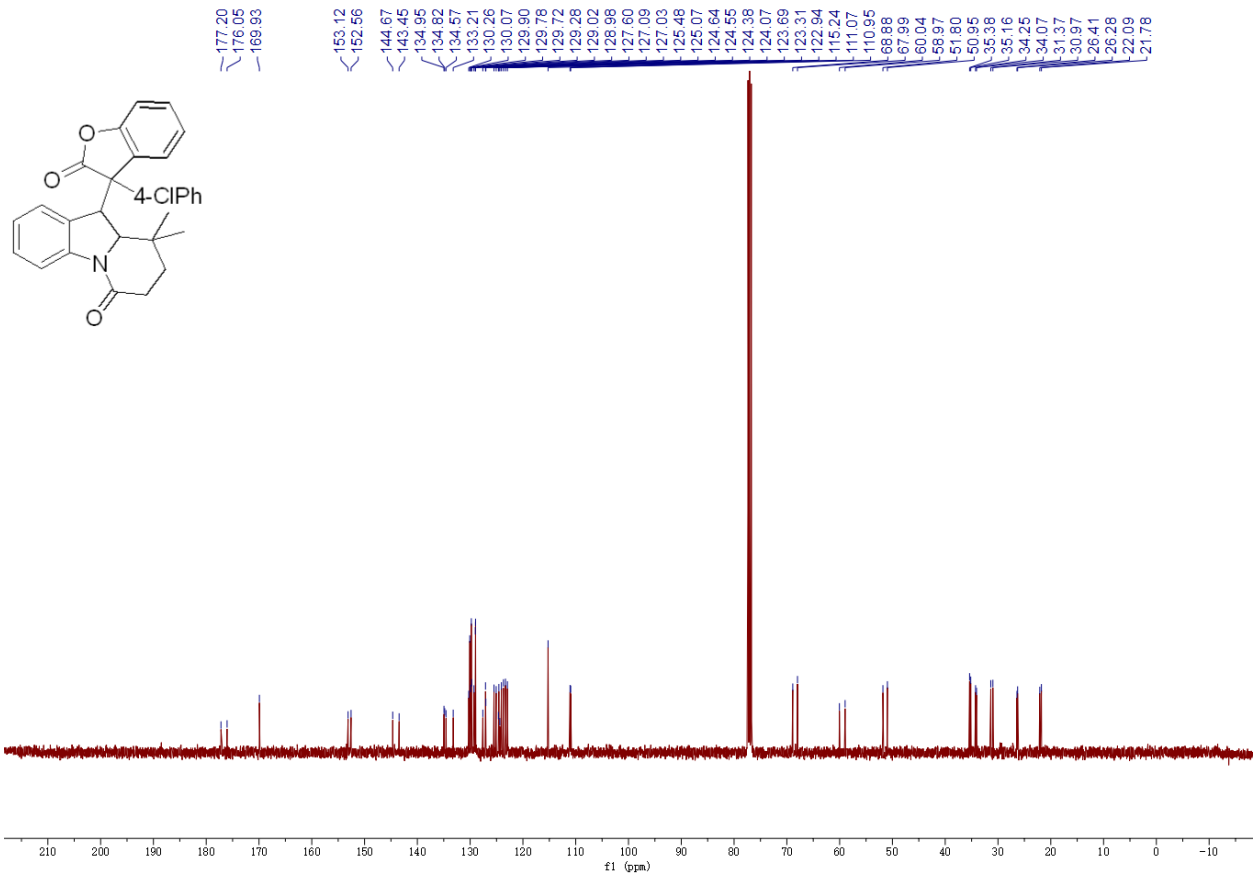
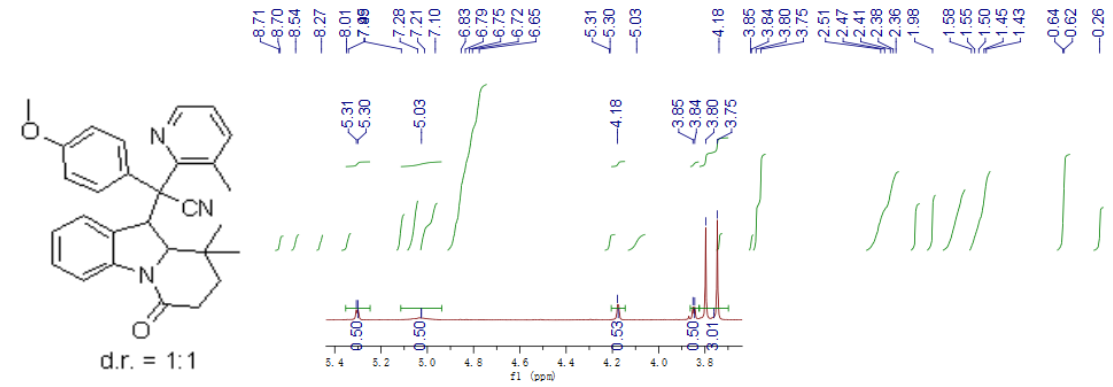
f1 (ppm)


f1 (ppm)


4-ClPh
f1 (ppm)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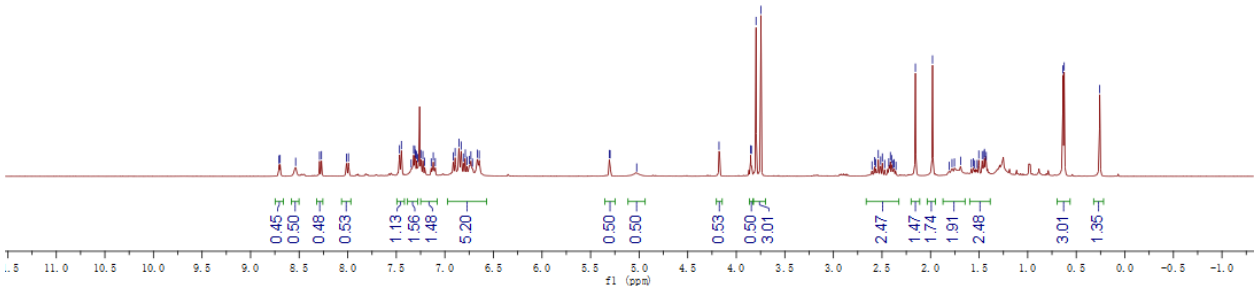
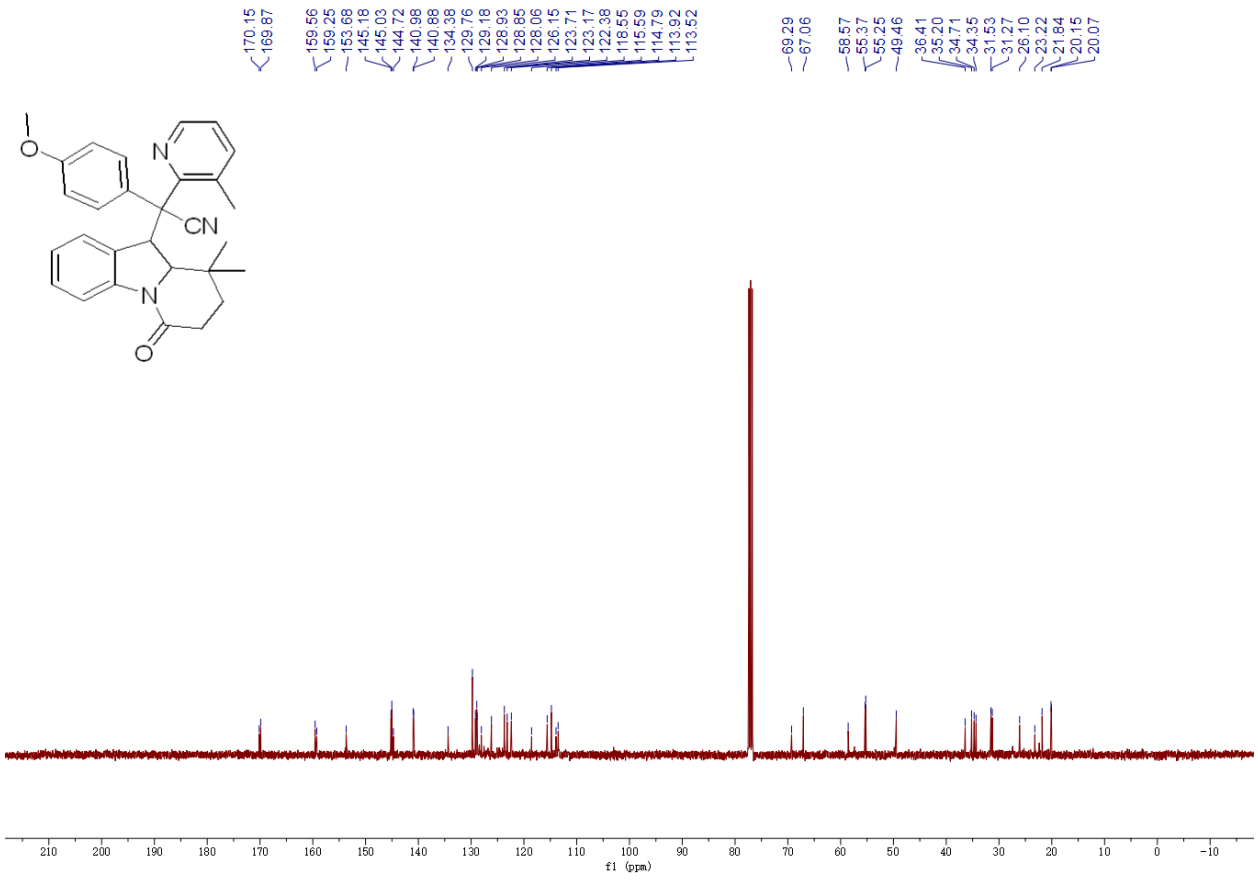

f1 (ppm)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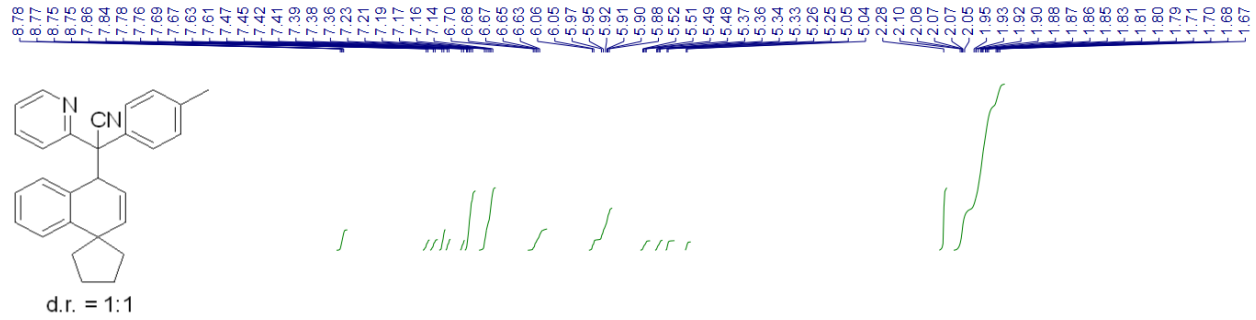

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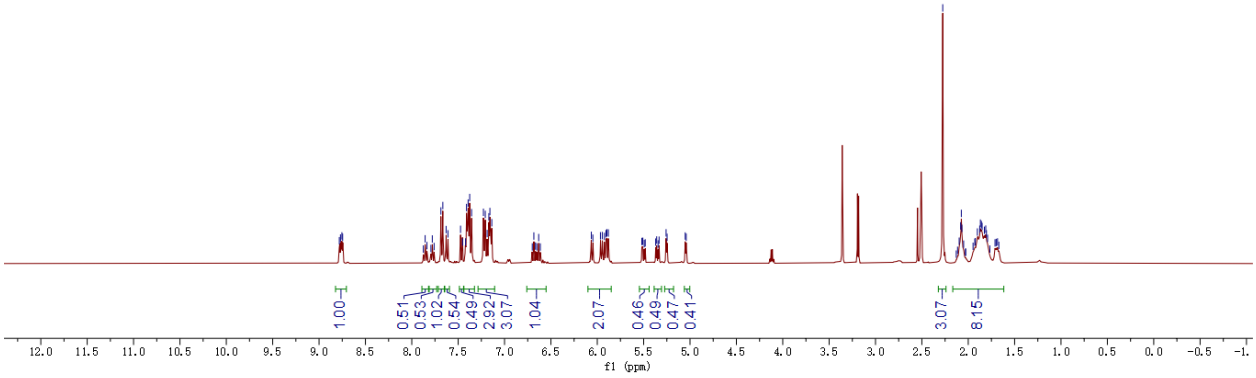

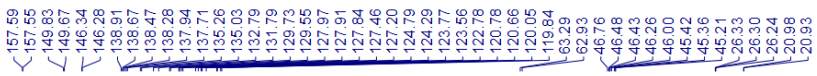

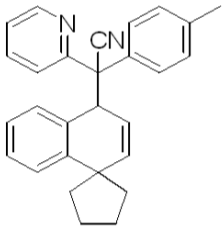

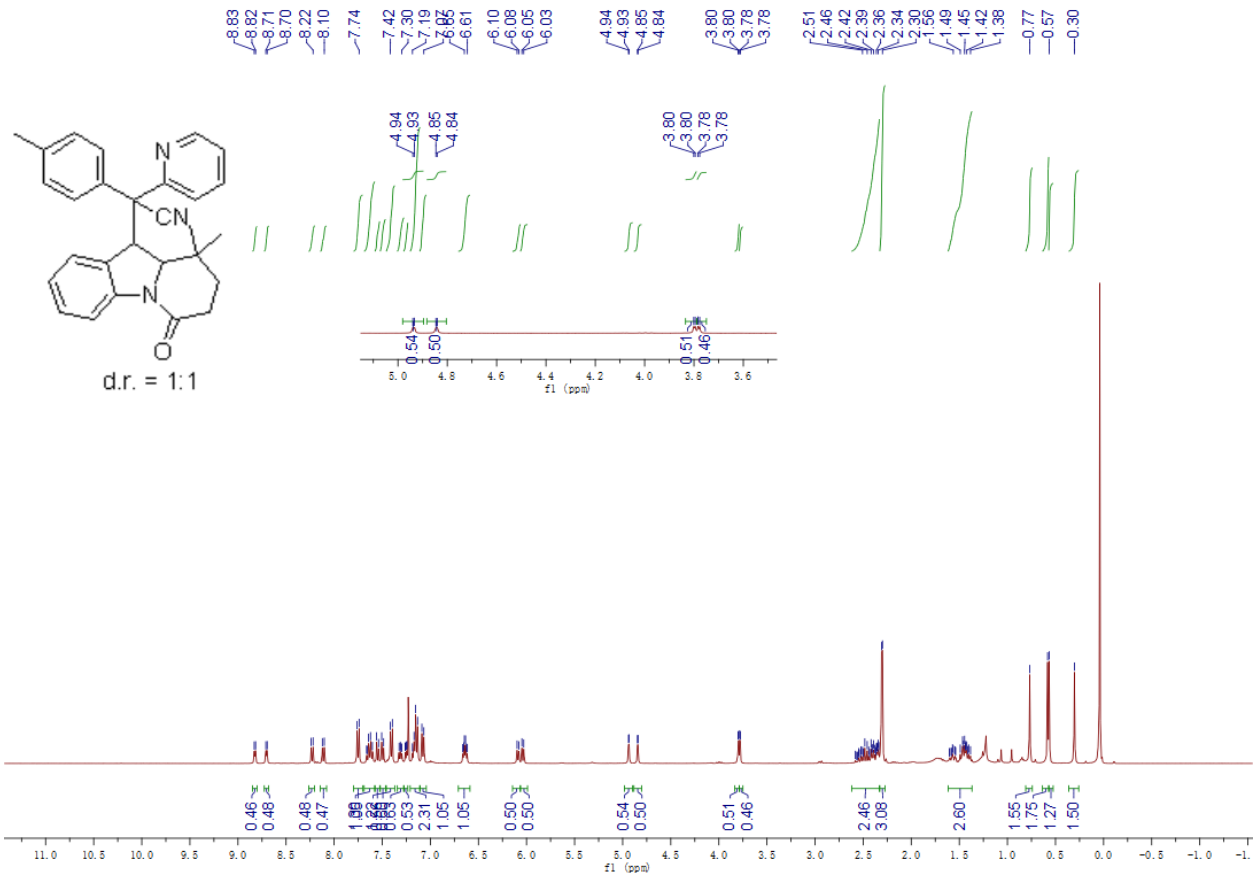
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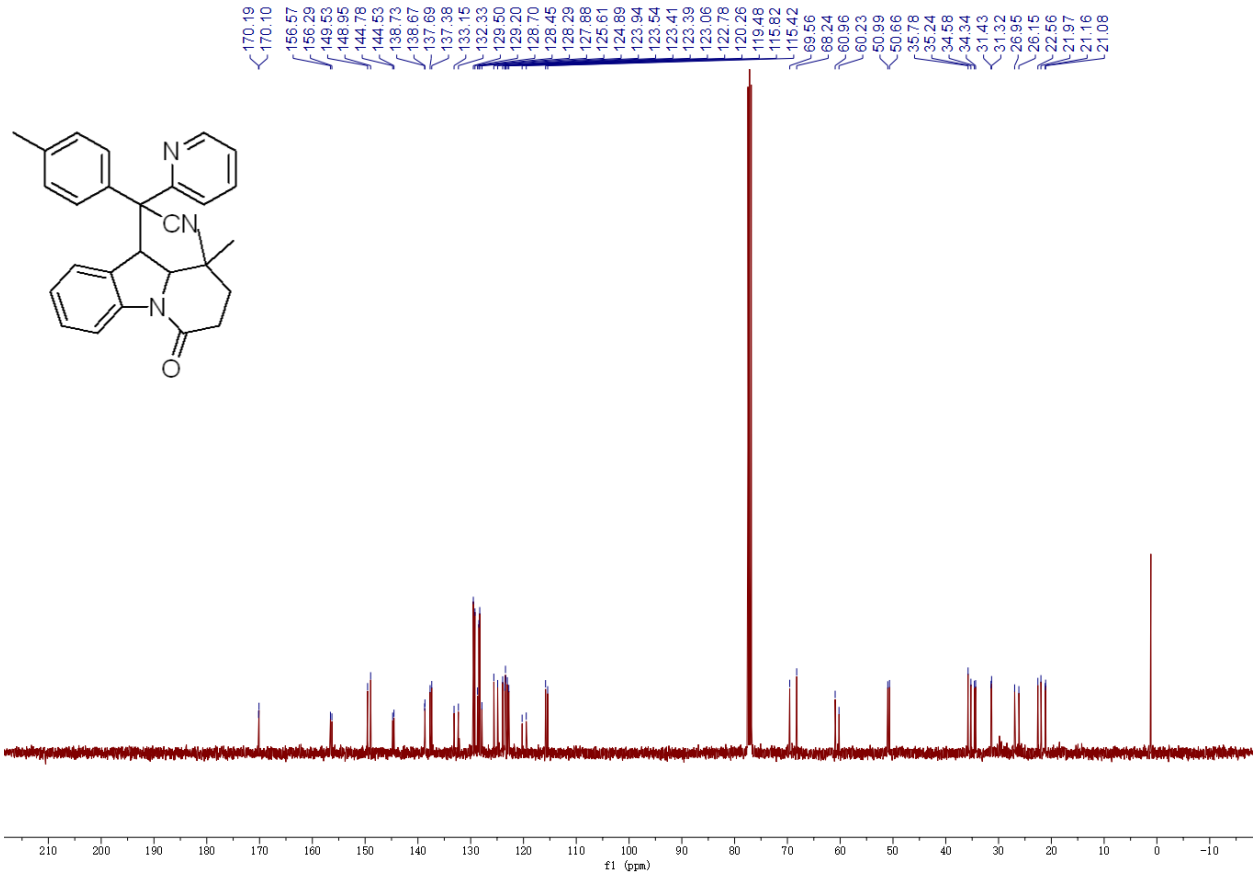
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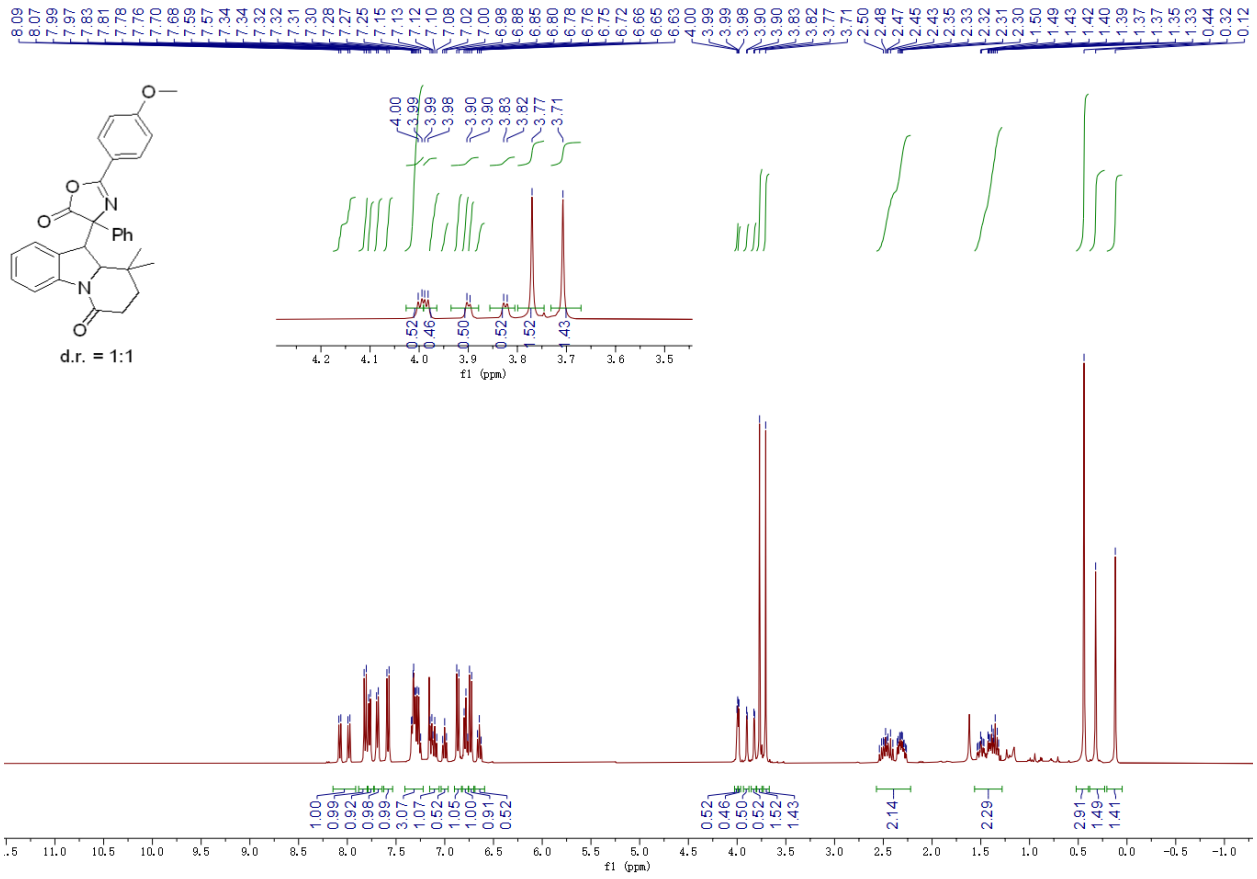
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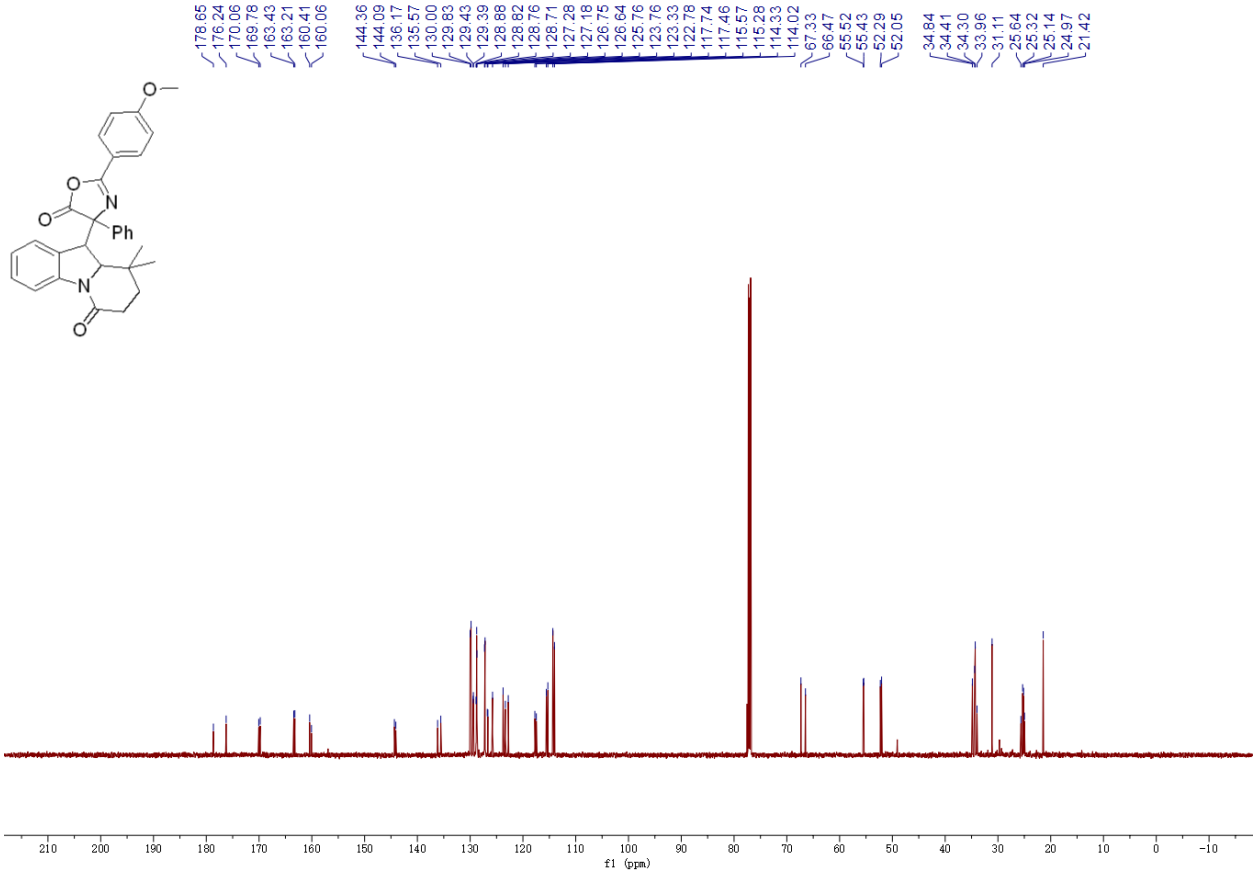
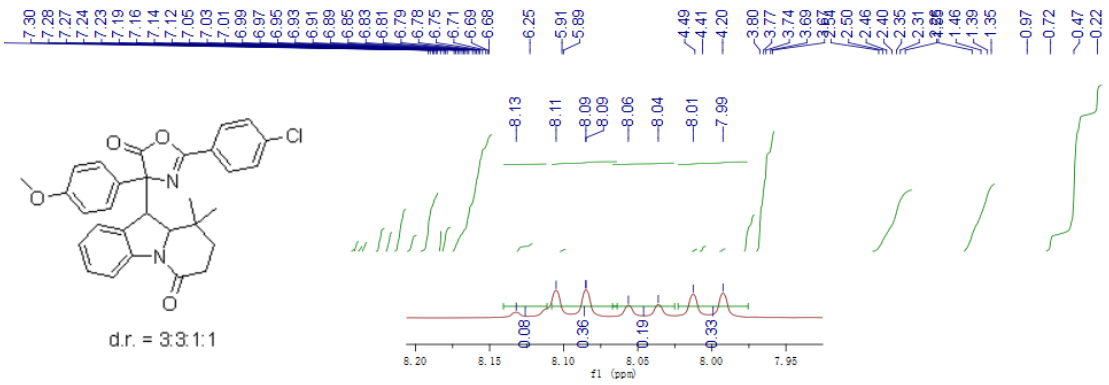

f1 (ppm)



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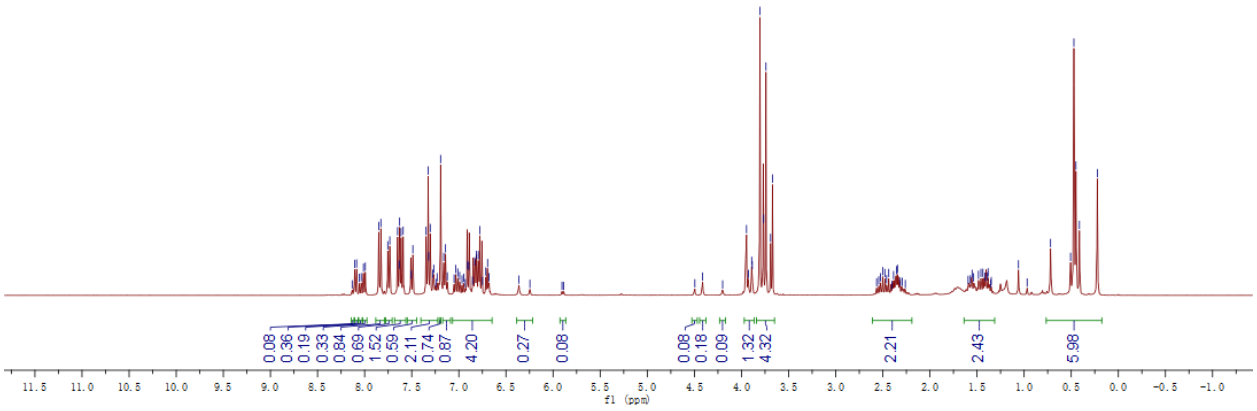
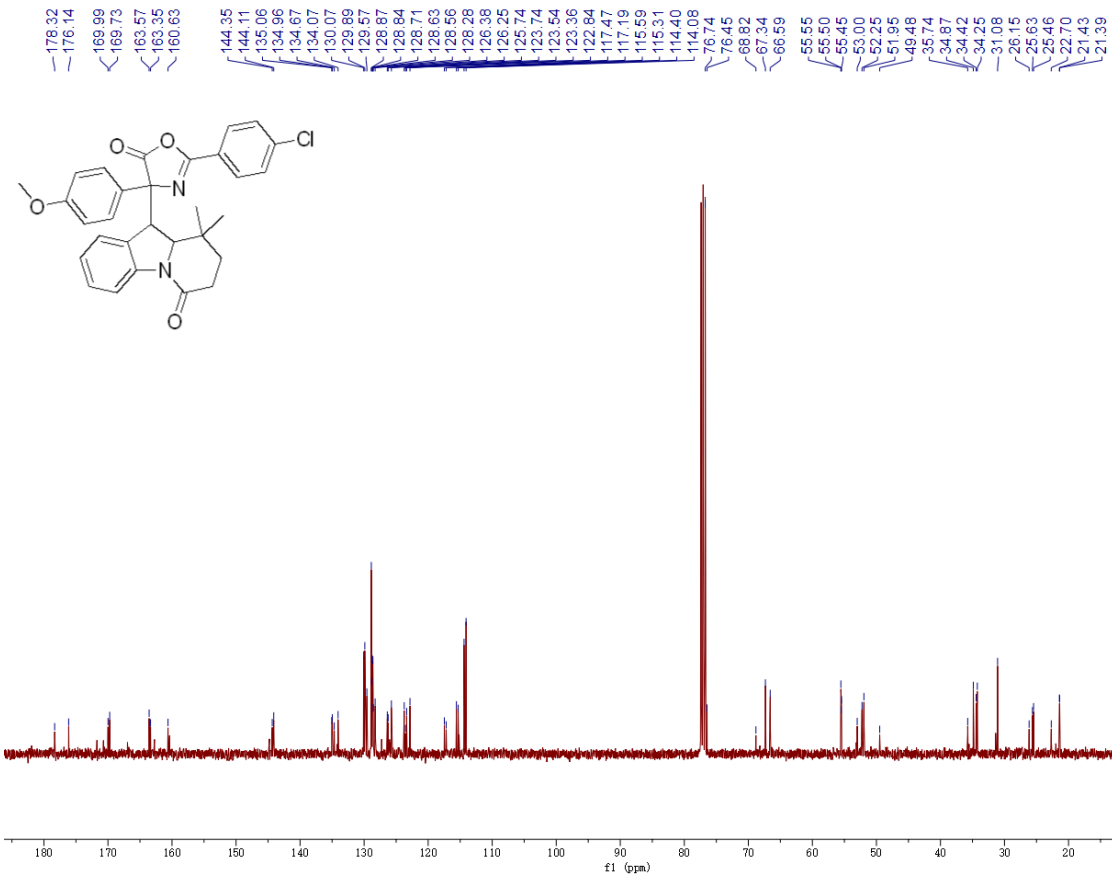
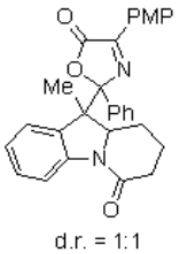
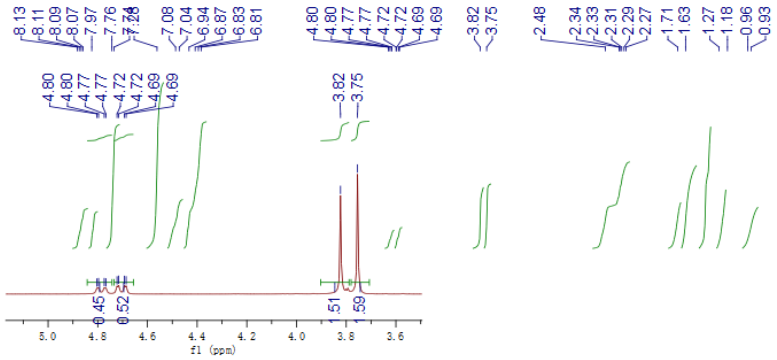





PMP
O
O
N
Me
Ph
N
O

d.r. = 1:1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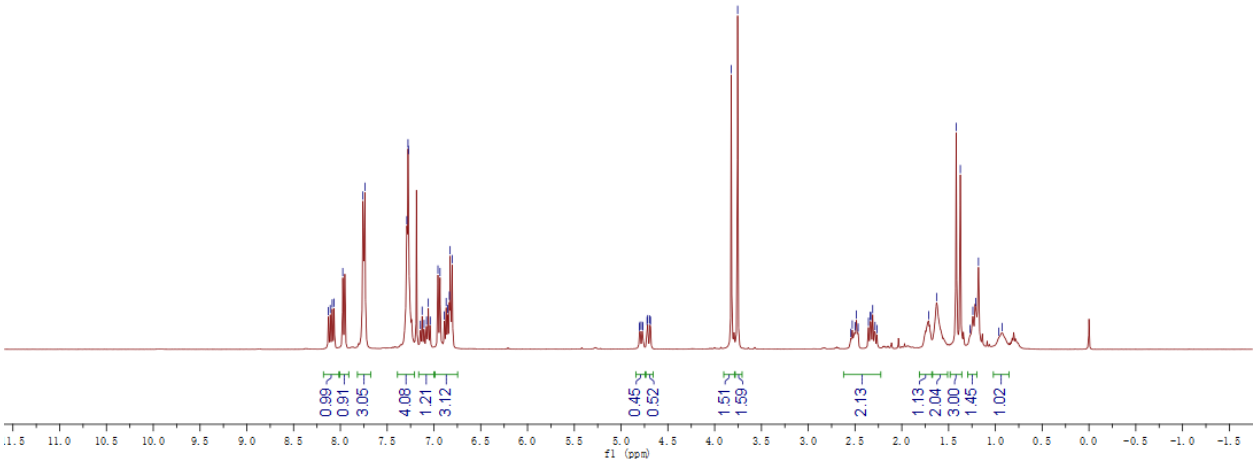
8.09
8.07
7.97
7.76
7.74
7.28
7.08
7.04
6.94
6.87
6.83
6.81
4.80
4.80
4.77
4.77
4.72
4.72
4.69
4.69
3.82
3.75
2.48
2.34
2.33
2.31
2.29
2.27
1.71
1.63
1.27
1.18
0.96
0.93
0.45
0.52
1.51
1.59
f1 (ppm)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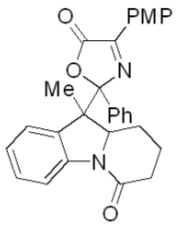
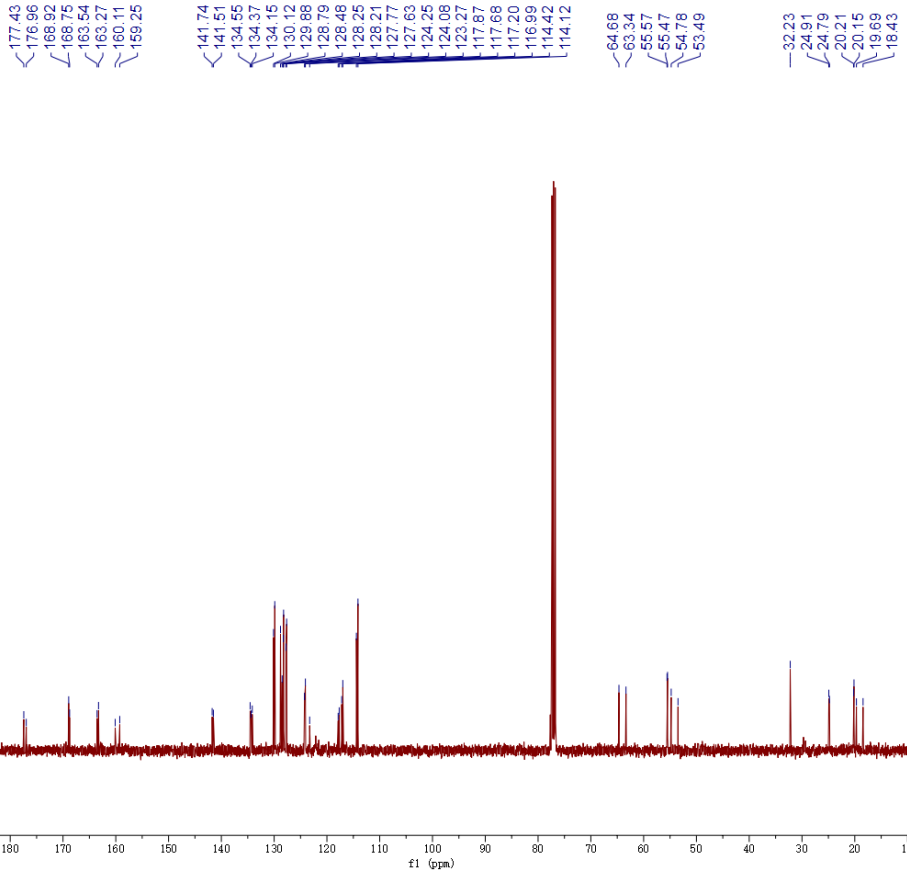
0.91
3.05
4.08
1.21
3.12
0.45
0.52
1.51
1.59
2.13
1.13
2.04
3.00
1.45
1.02
f1 (ppm)


PMP
O
O
N
Me
Ph
N
O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176.96
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163.27
160.11
159.25
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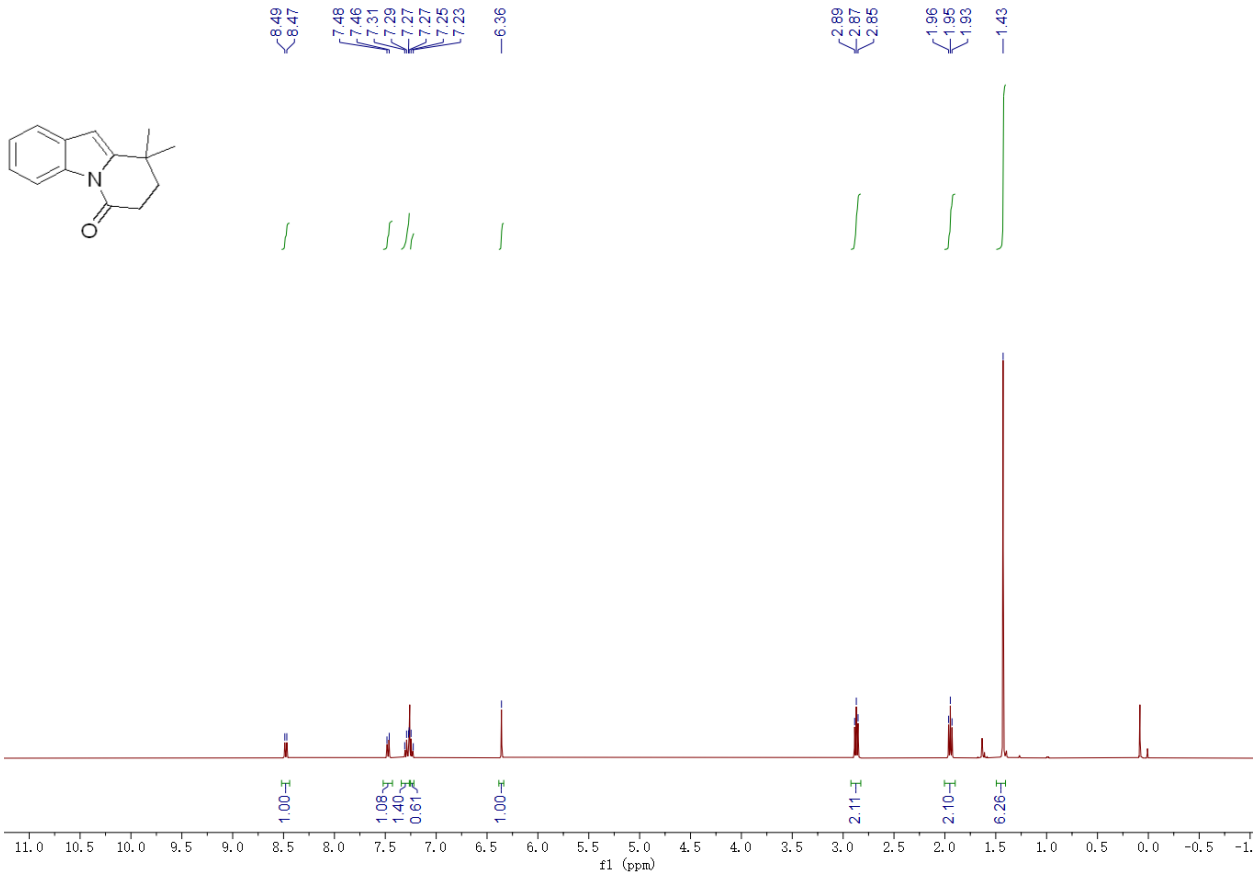
141.51
134.55
134.37
134.15
130.12
129.88
128.79
128.48
128.25
128.21
127.77
127.63
124.25
124.08
123.27
117.87
117.68
117.20
116.99
114.42
114.12
64.68
63.34
55.57
55.47
54.78
53.49
32.23
24.91
24.79
20.21
20.15
19.69
18.43
f1 (ppm)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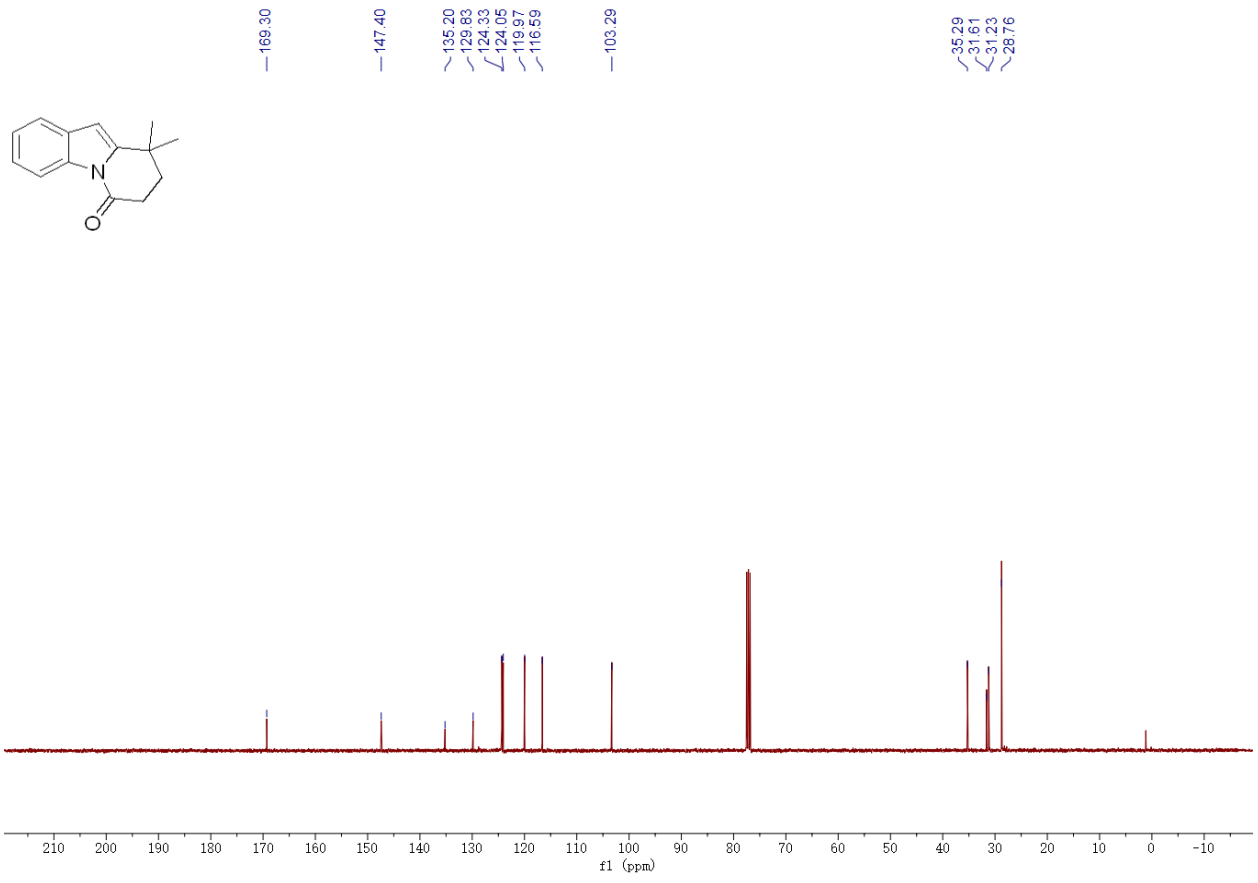
7.48
7.46
7.31
7.29
7.27
7.27
7.25
7.23
6.36
2.89
2.87
2.85
1.96
1.95
1.93
1.43
1.00
1.08
1.40
0.61
1.00
2.11
2.10
6.26
f1 (ppm)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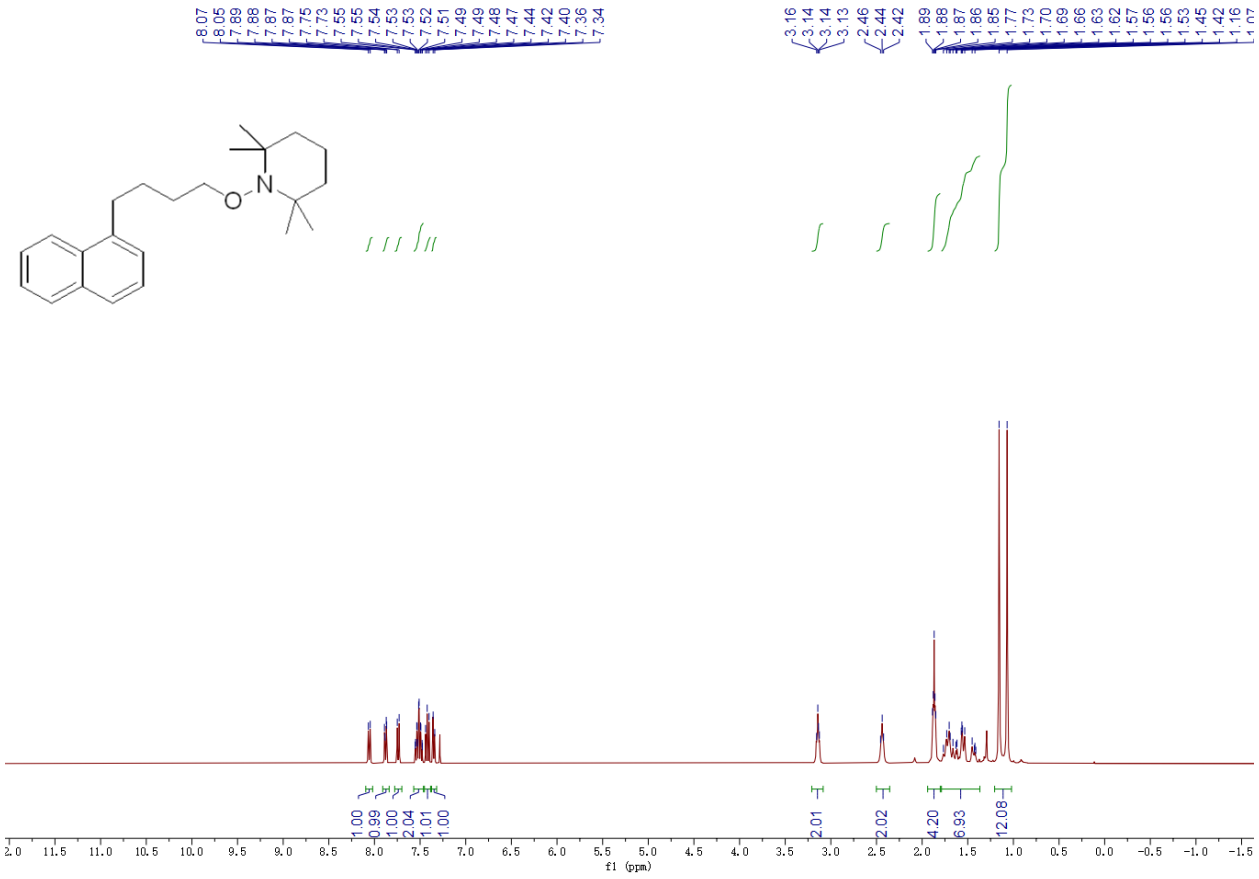
147.40
135.20
129.83
124.33
124.05
119.97
116.59
103.29
35.29
31.61
31.23
28.76
f1 (ppm)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8.05
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7.88
7.87
7.87
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7.73
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.49
7.49
7.48
7.47
7.44
7.42
7.40
7.36
7.34
3.16
3.14
3.14
3.13
2.46
2.44
2.42
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1.88
1.87
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1.85
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1.70
1.69
1.66
1.63
1.62
1.57
1.56
1.56
1.53
1.45
1.42
1.16
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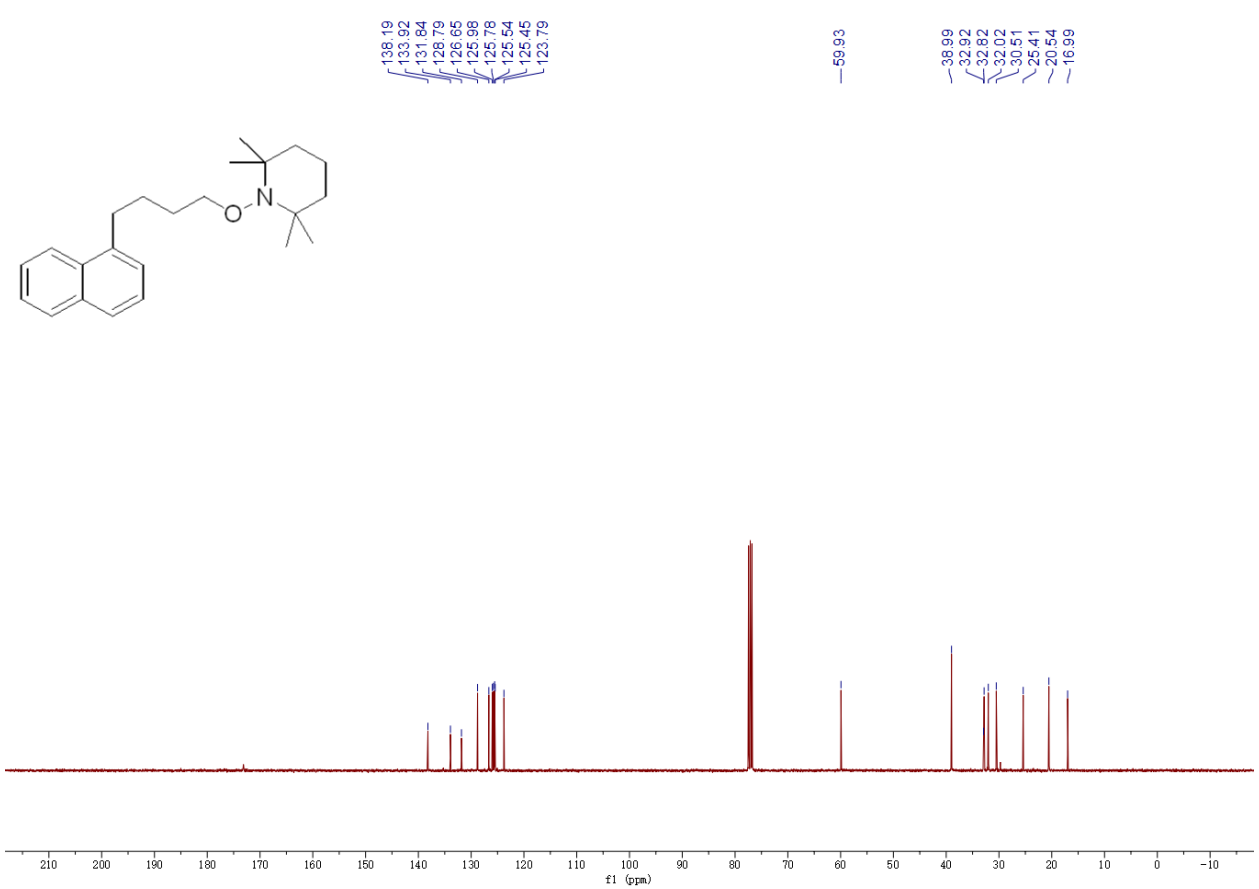
2.04
1.01
1.00
2.01
2.02
4.20
6.93
12.08
f1 (ppm)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125.54
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38.99
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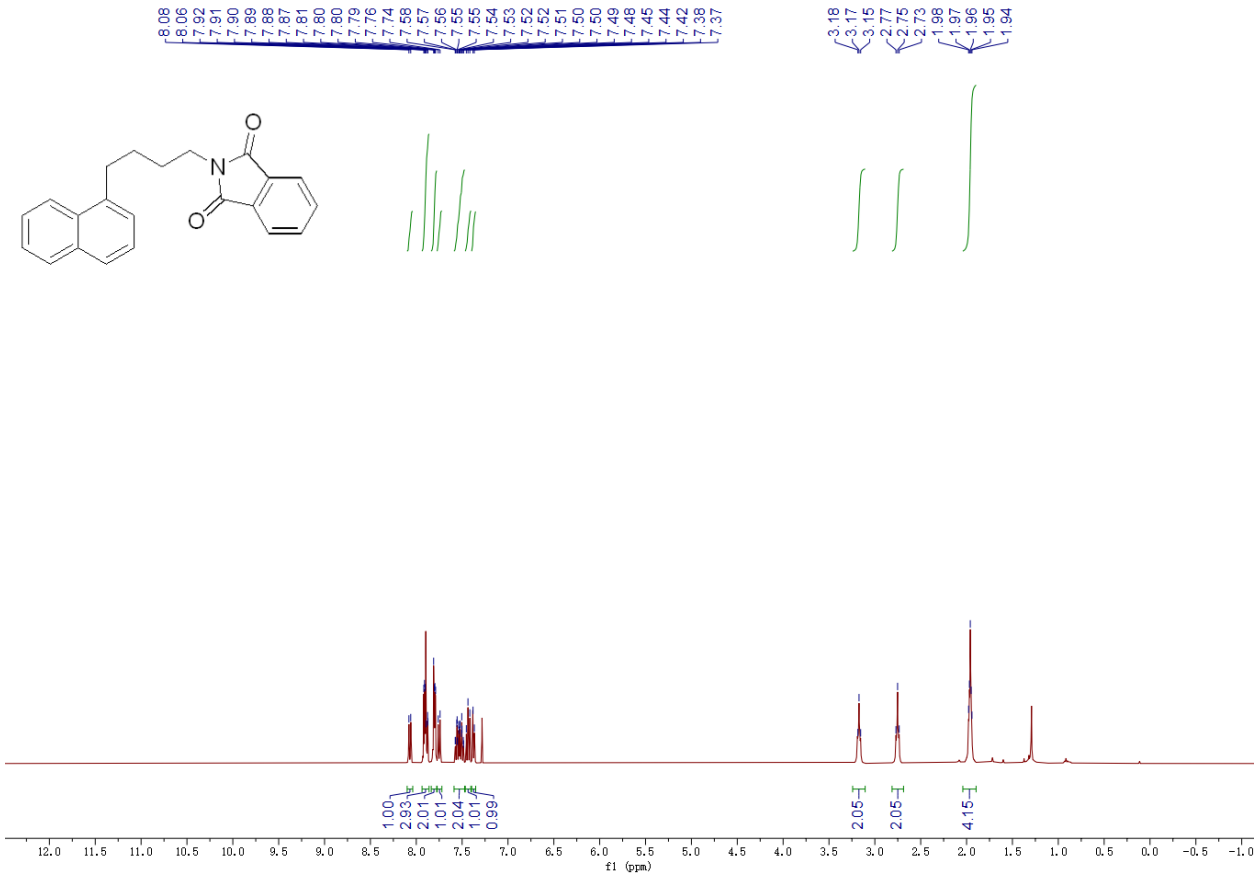
32.82
32.02
30.51
25.41
20.54
16.99
f1 (ppm)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7.74
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7.56
7.55
7.55
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.45
7.44
7.42
7.38
7.37
3.18
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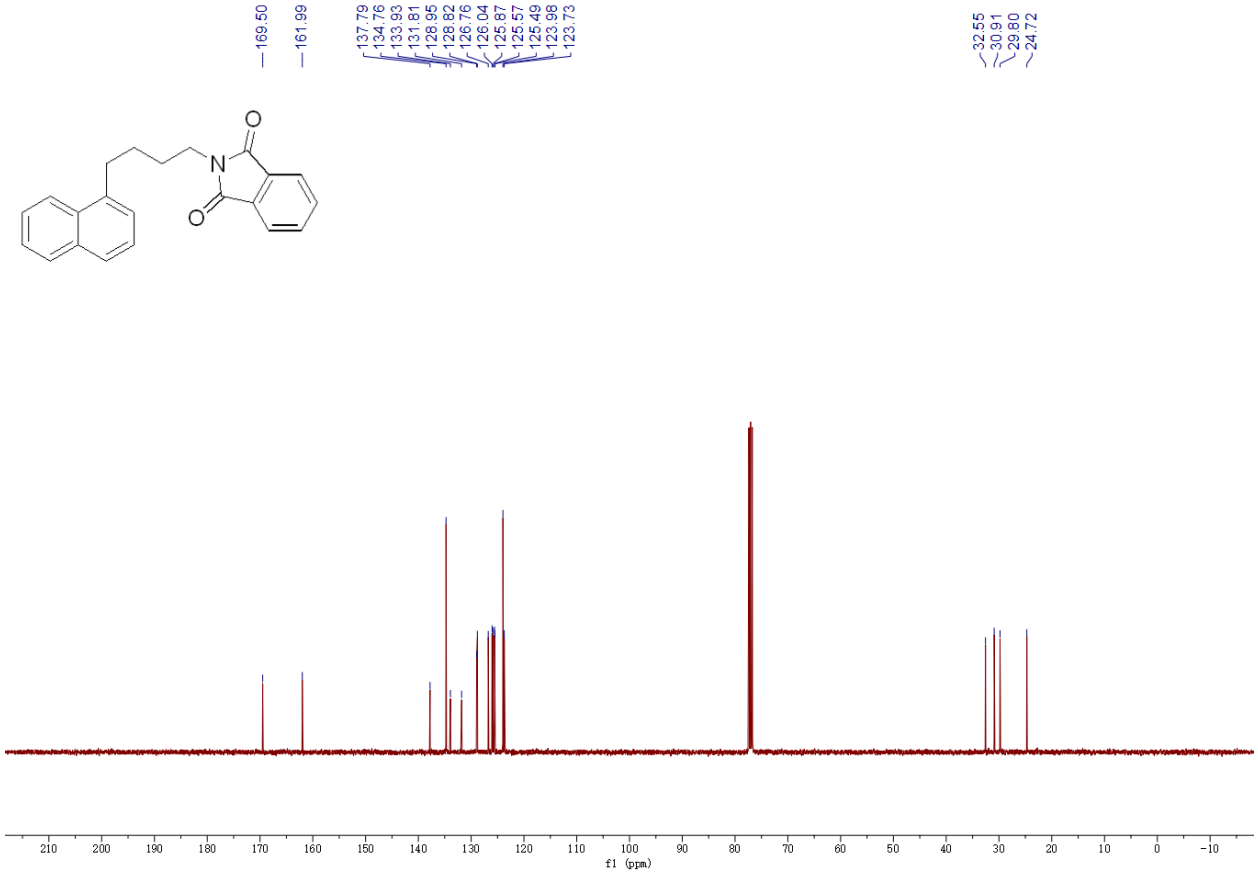
1.97
1.96
1.95
1.94
O
N
O
1.00
2.93
2.01
1.01
2.04
1.01
0.99
2.05
2.05
4.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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125.87
125.57
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123.98
123.73
32.55
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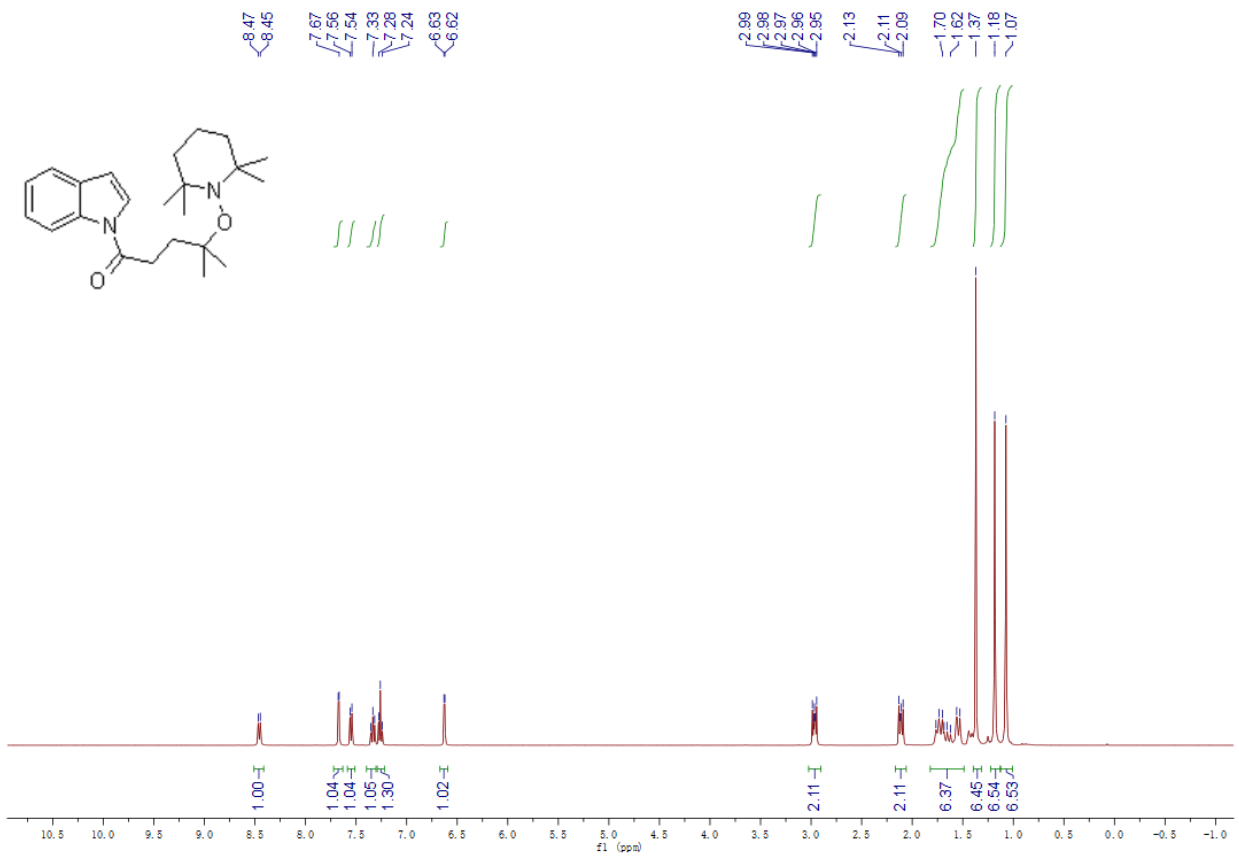
24.72
O
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.28
7.24
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6.62
2.99
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2.97
2.96
2.95
2.13
2.11
2.09
1.70
1.62
1.37
1.18
1.07
1.00
1.04
1.04
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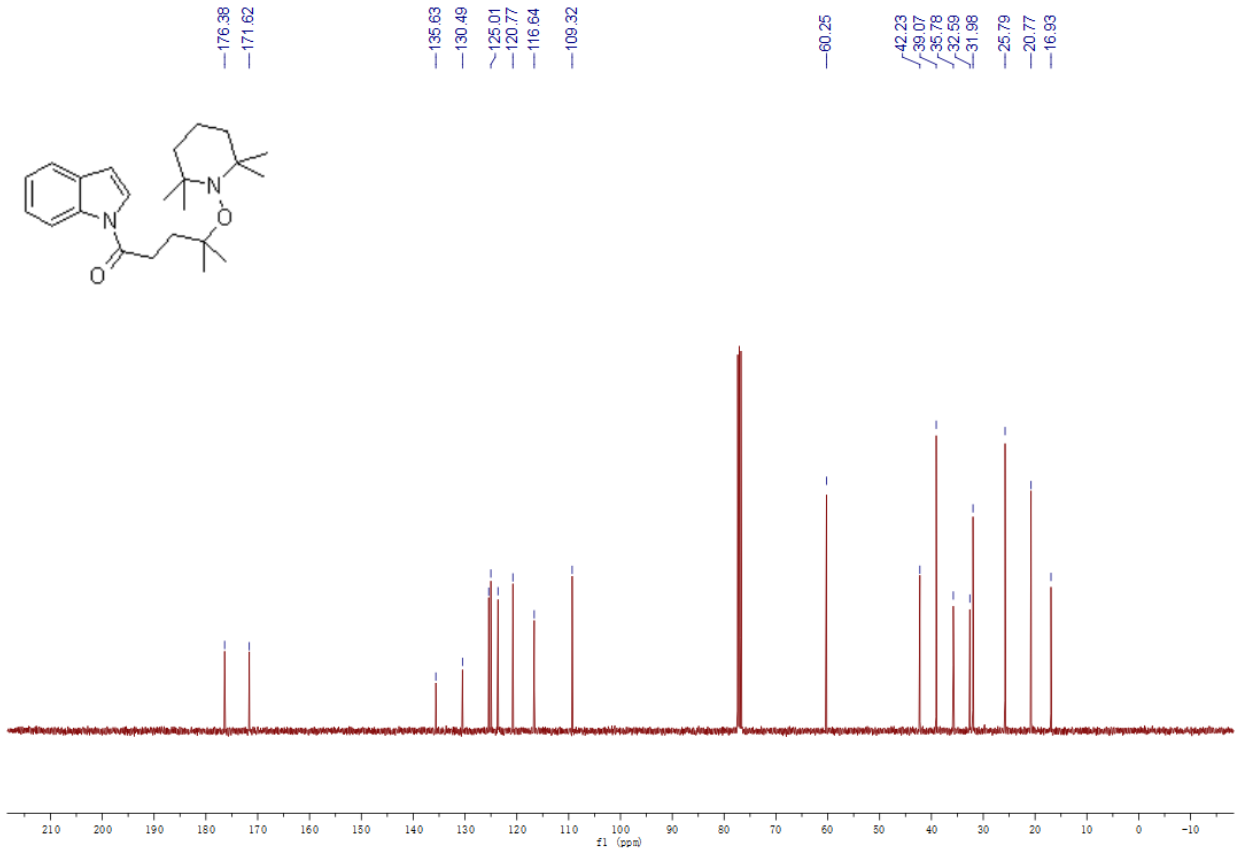
1.30
1.02
2.11
2.11
6.37
6.45
6.54
6.53
f1 (ppm)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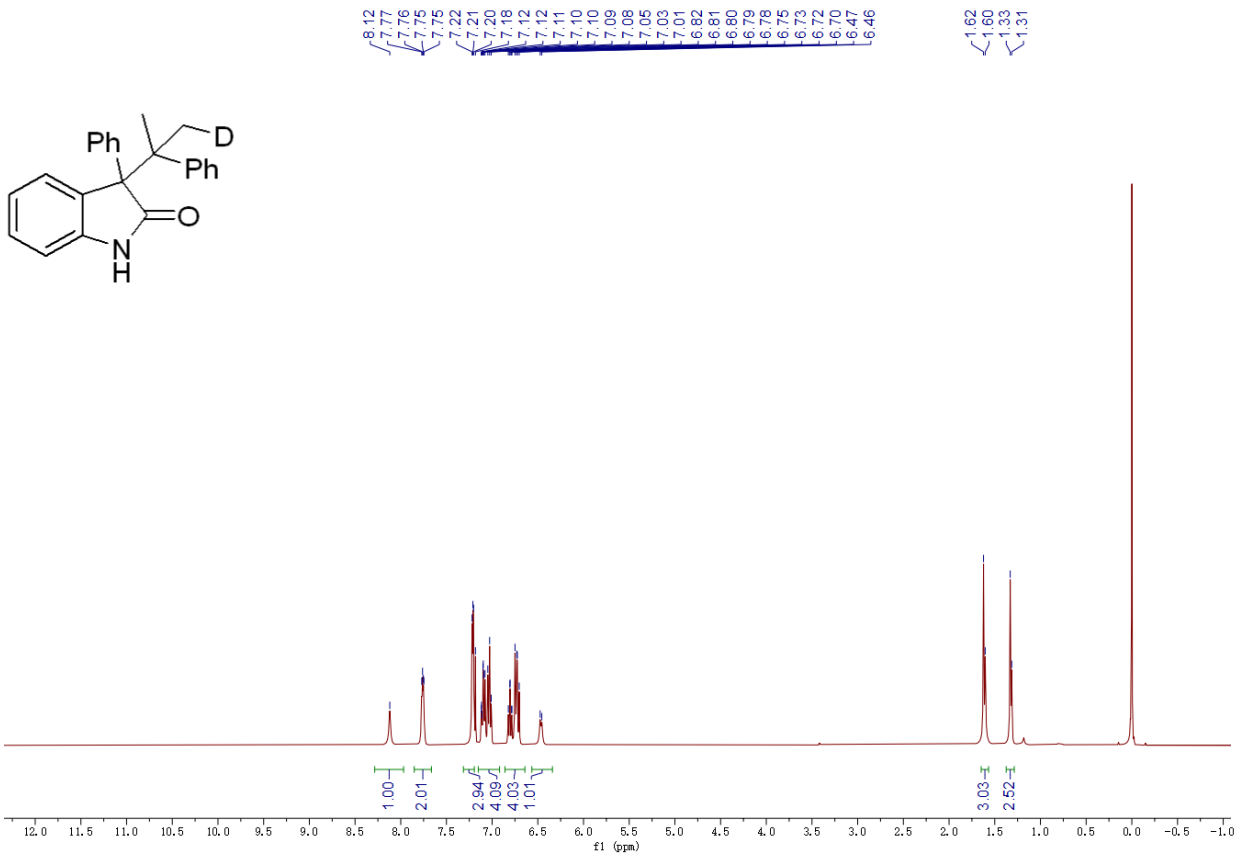
32.59
31.98
25.79
20.77
16.93
f1 (ppm)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7.11
7.10
7.10
7.09
7.08
7.05
7.03
7.01
6.82
6.81
6.80
6.79
6.78
6.75
6.73
6.72
6.70
6.47
6.46
1.62
1.60
1.33
1.31
Ph
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Ph
O
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H
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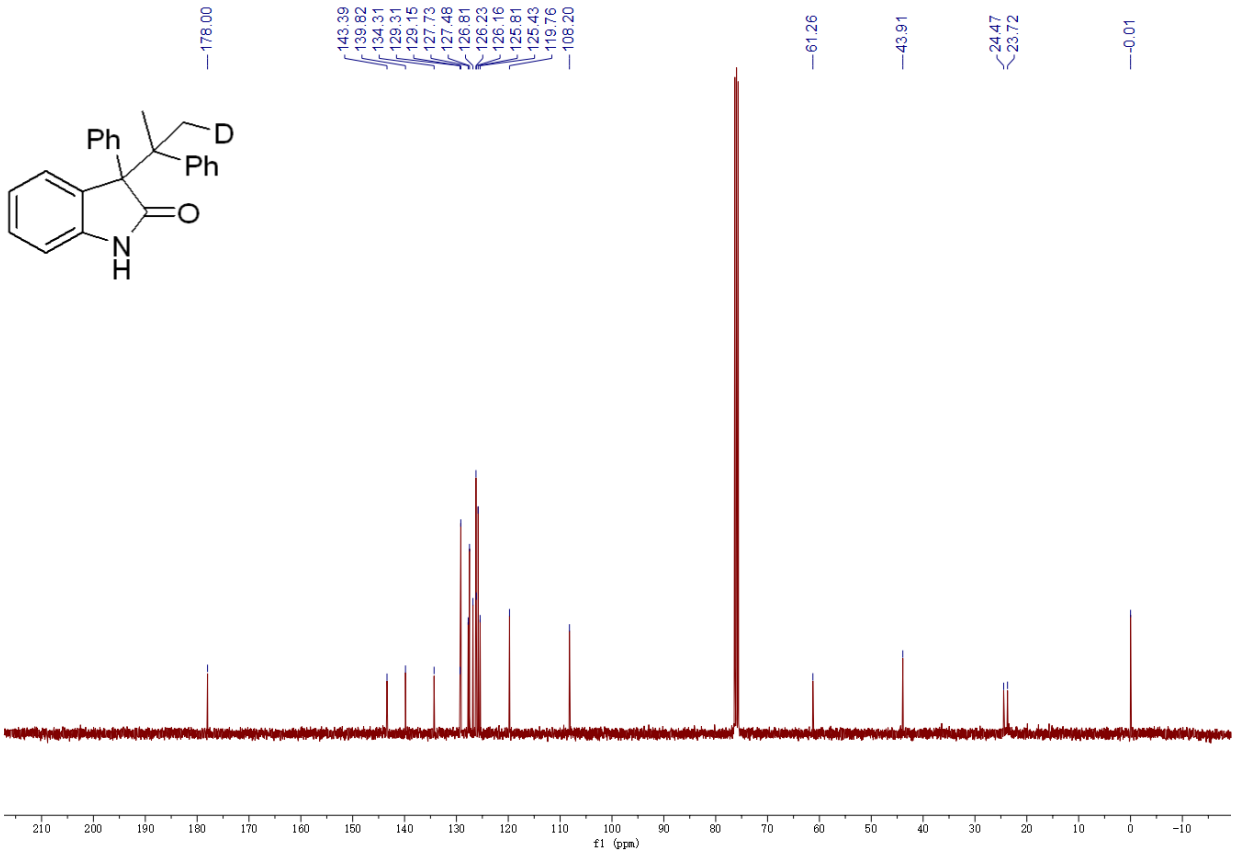
2.94
4.09
4.03
1.01
3.03
2.52
f1 (ppm)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126.16
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125.43
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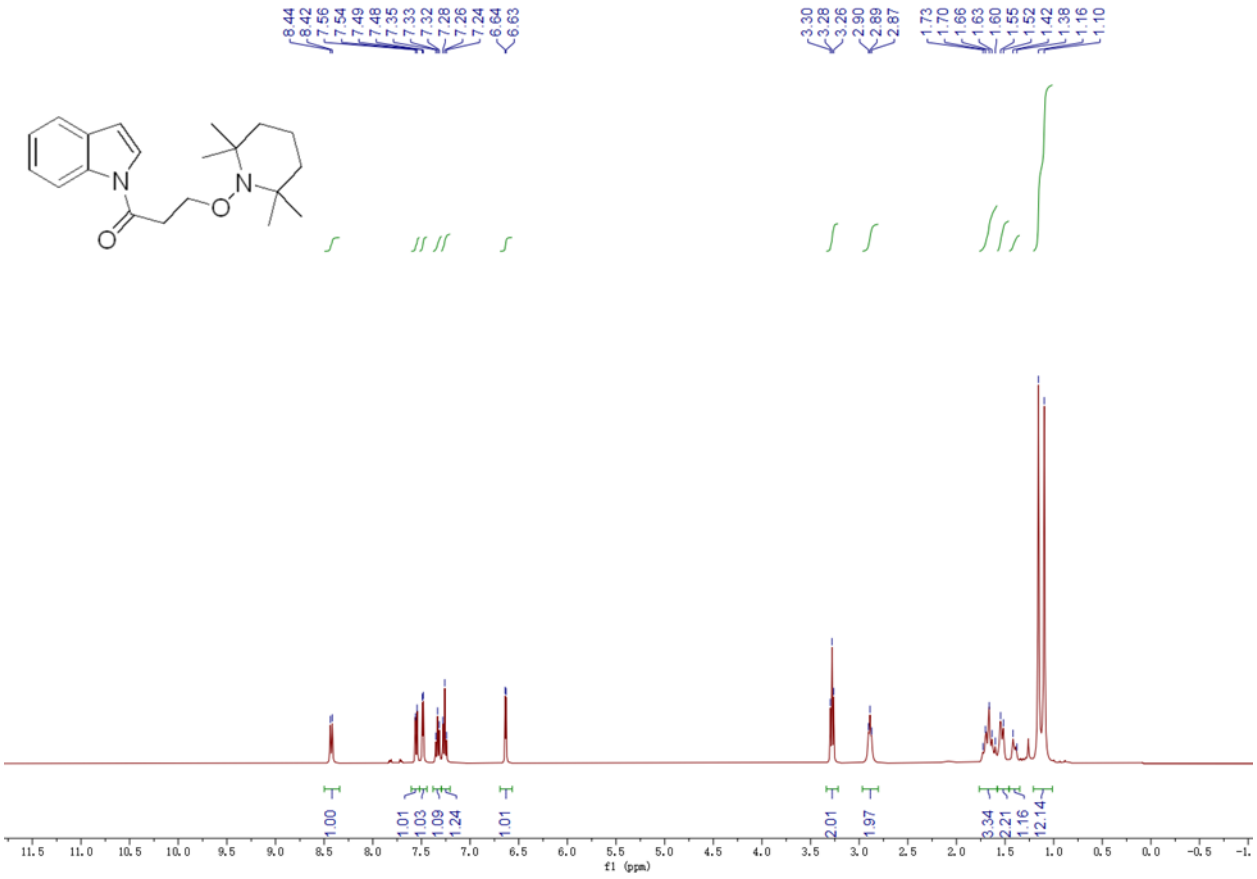
43.91
24.47
23.72
0.01
Ph
D
Ph
O
N
H
f1 (ppm)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7.26
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1.70
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1.60
1.55
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1.42
1.38
1.16
1.10
1.00
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1.03
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1.24
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2.01
1.97
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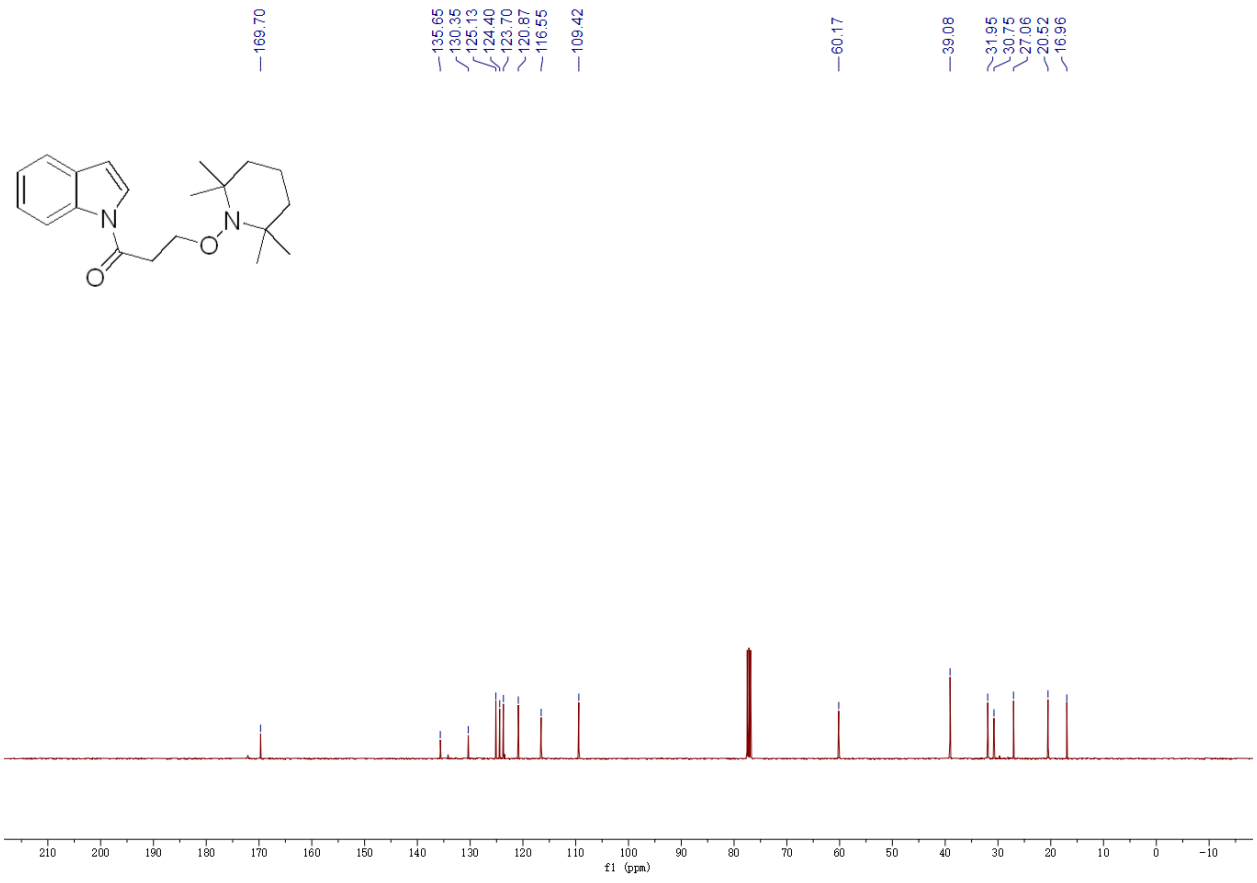
2.21
1.16
12.14
f1 (ppm)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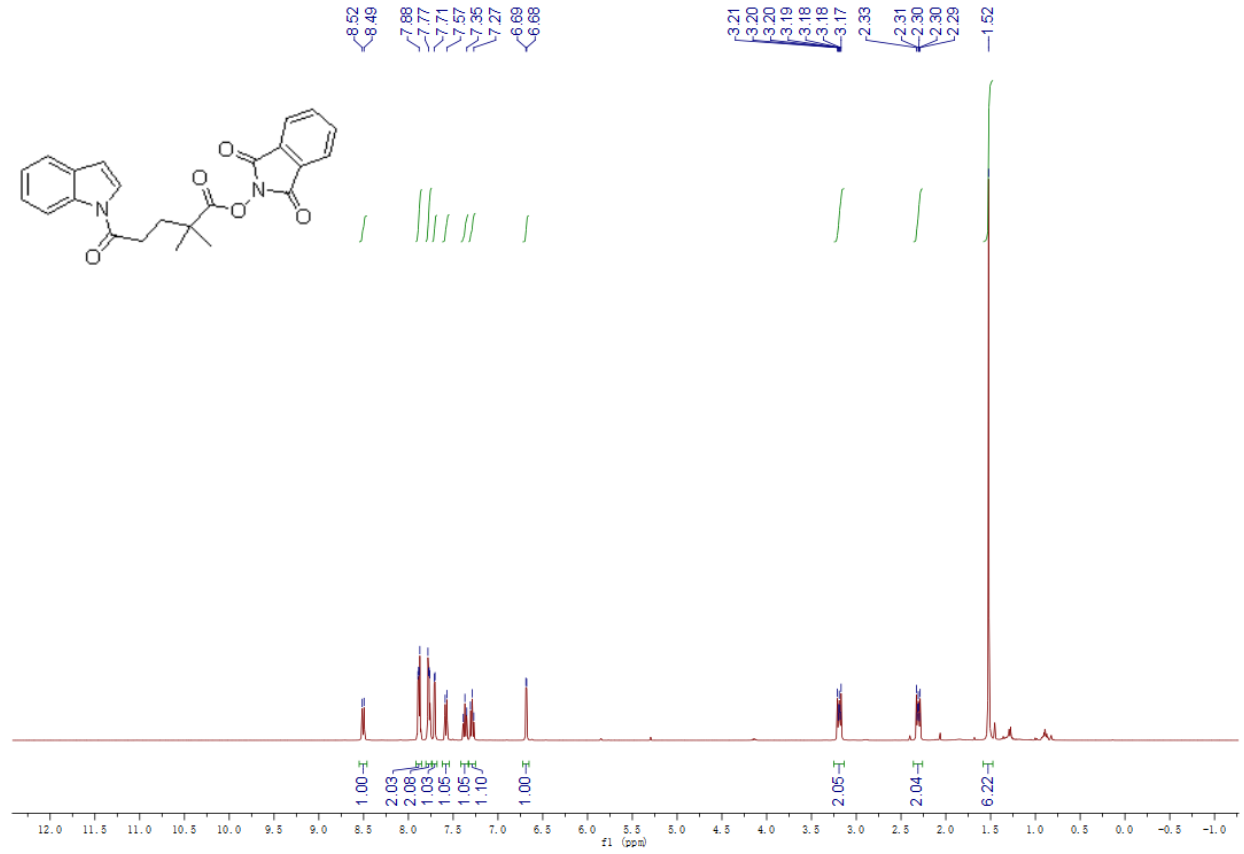
27.06
20.52
16.96
f1 (ppm)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3.21
3.20
3.20
3.19
3.18
3.18
3.17
2.33
2.31
2.30
2.30
2.29
1.52
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2.05
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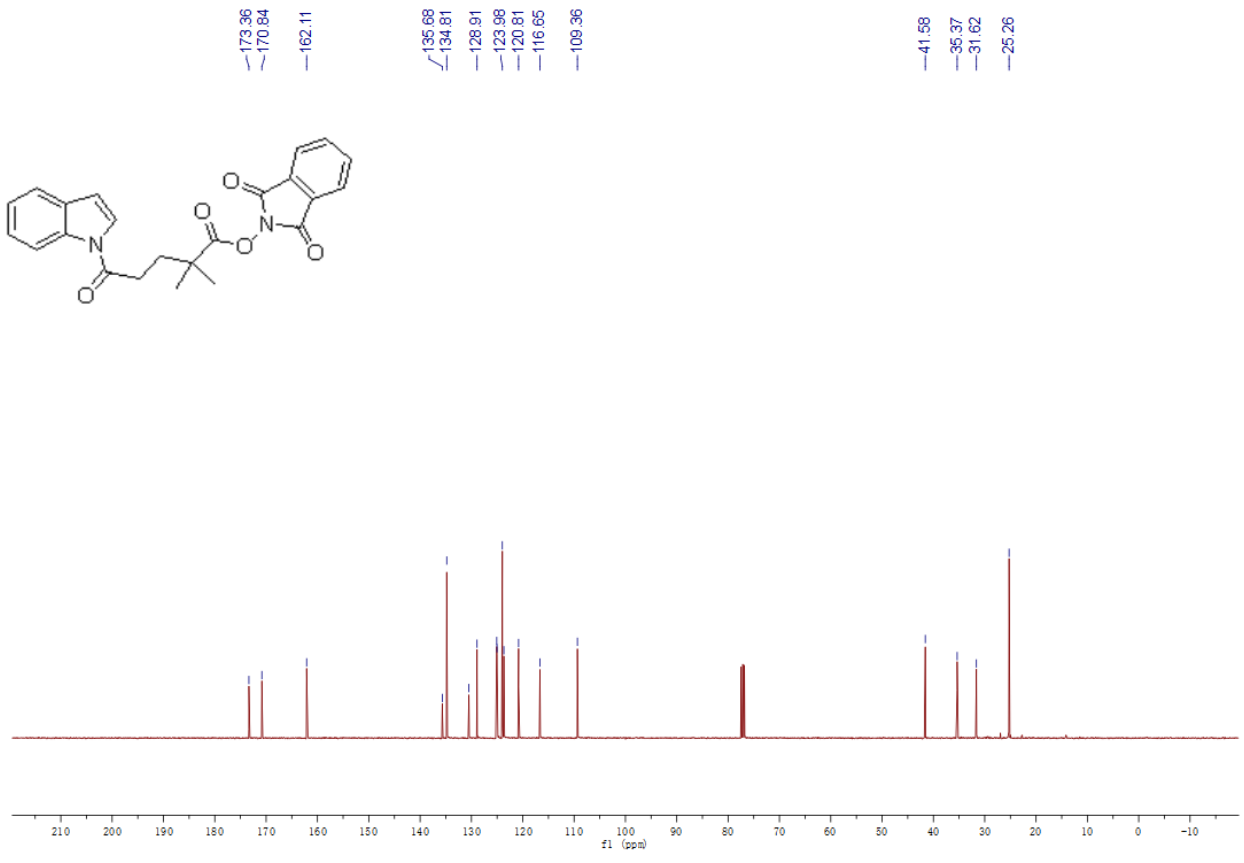
6.22
f1 (ppm)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123.98
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116.65
109.36
41.58
35.37
31.62
25.26
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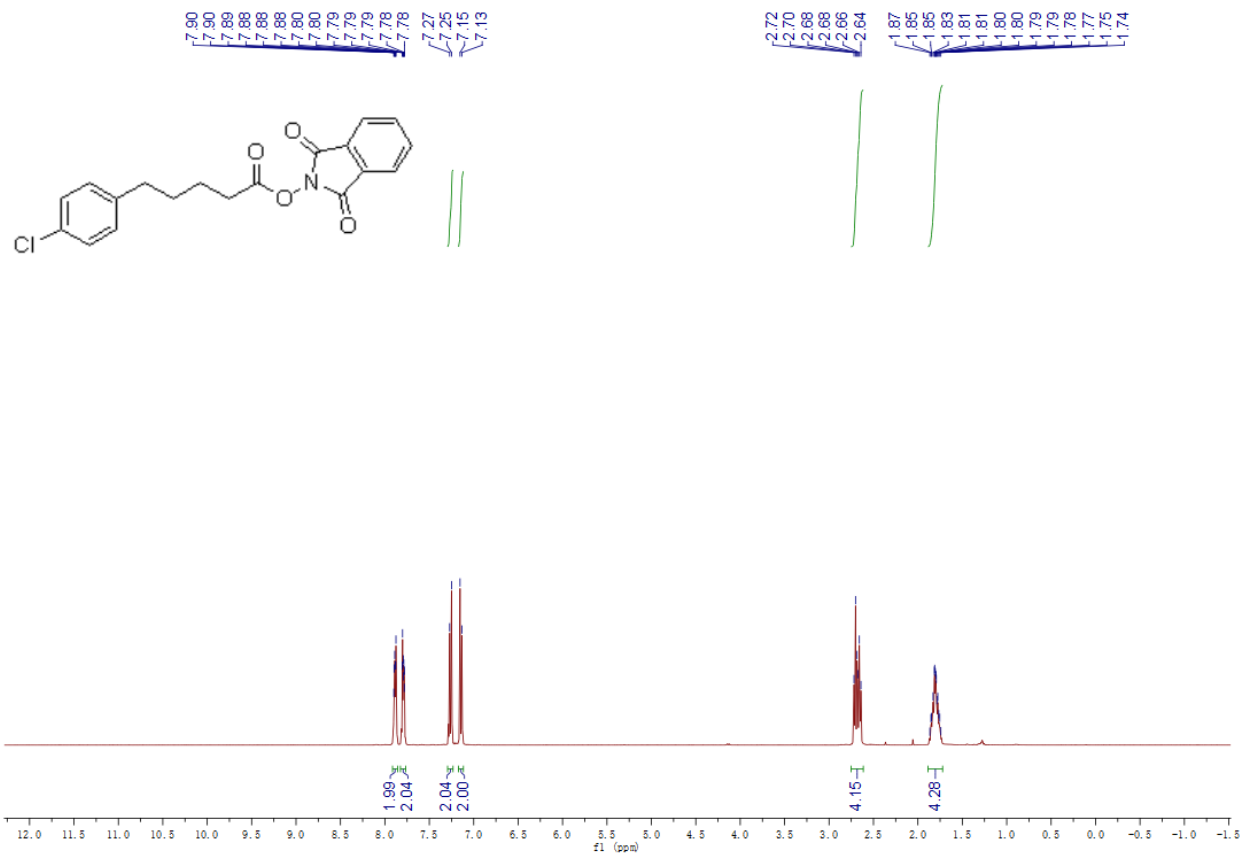
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7.79
7.78
7.78
7.78
7.27
7.25
7.15
7.13
2.72
2.70
2.68
2.68
2.66
2.64
1.87
1.85
1.85
1.83
1.81
1.81
1.80
1.80
1.79
1.79
1.78
1.77
1.75
1.74
O
O
N
O
O
Cl
1.99
2.04
2.04
2.00
4.15
4.28
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
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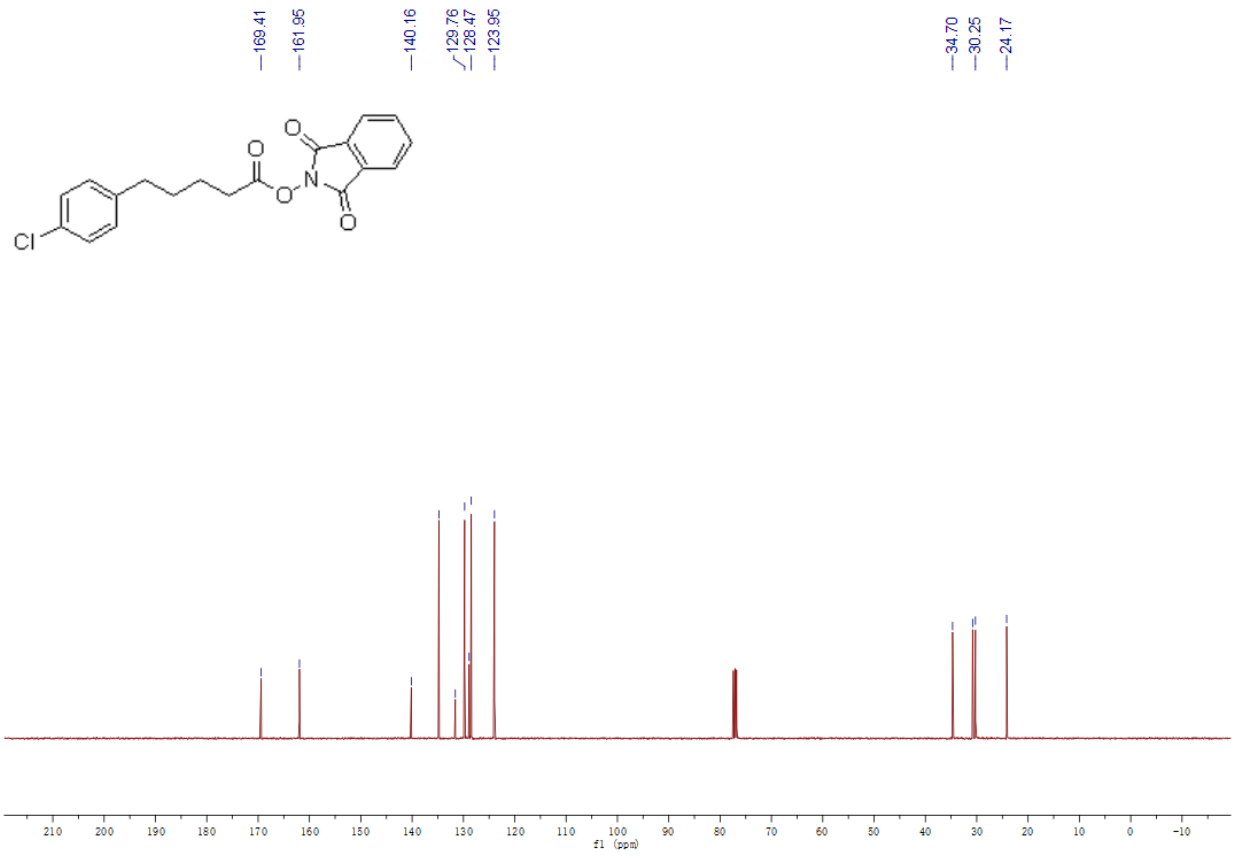
-1.0
-1.5
f1 (ppm)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30.25
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O
N
O
O
Cl
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
50
40
30
20
10
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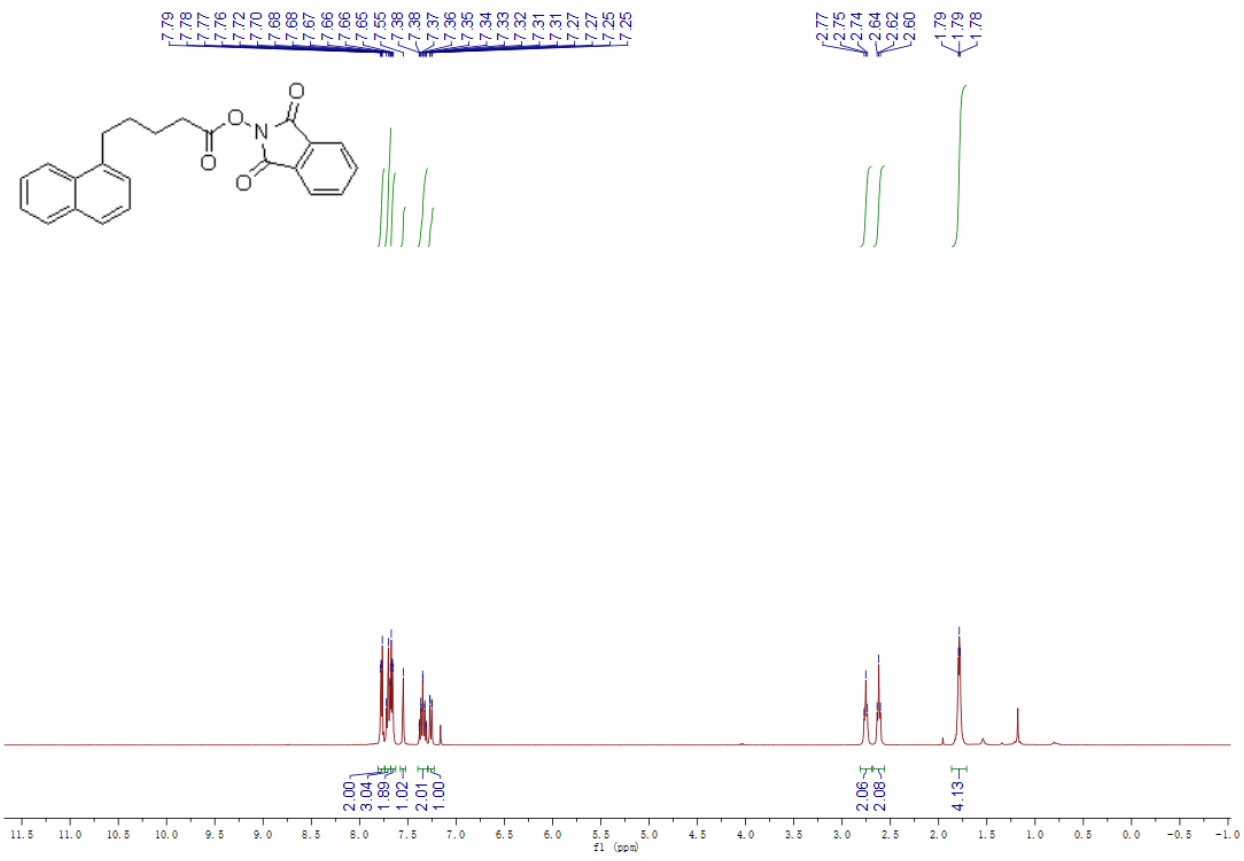
-10
f1 (ppm)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7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.27
7.27
7.25
7.25
2.77
2.75
2.74
2.64
2.62
2.60
1.79
1.79
1.78
O
O
N
O
O
O
2.00
3.04
1.89
1.02
2.01
1.00
2.06
2.08
4.13
11.5
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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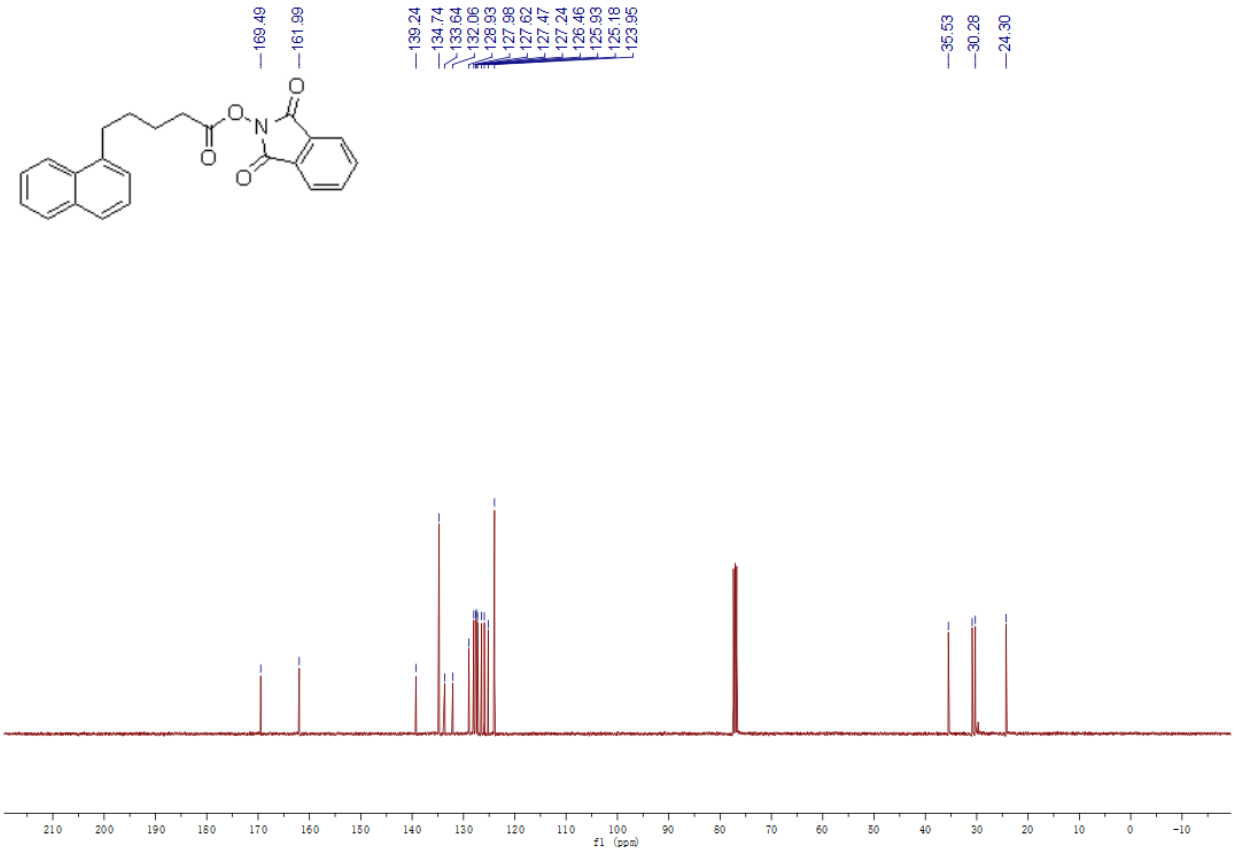
-1.0
f1 (ppm)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127.98
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127.47
127.24
126.46
125.93
125.18
123.95
35.53
30.28
24.30
O
O
N
O
O
O
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200
190
180
170
160
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140
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120
110
100
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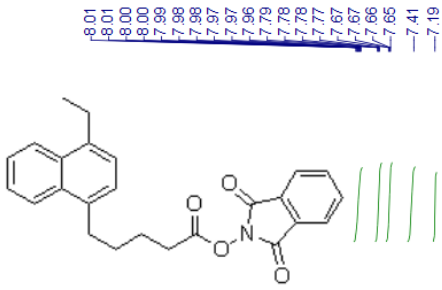
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.00
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7.98
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7.97
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7.67
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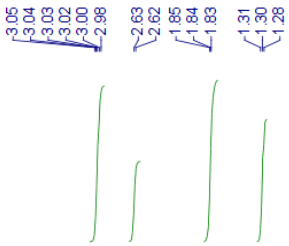
7.65
7.41
7.19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3.04
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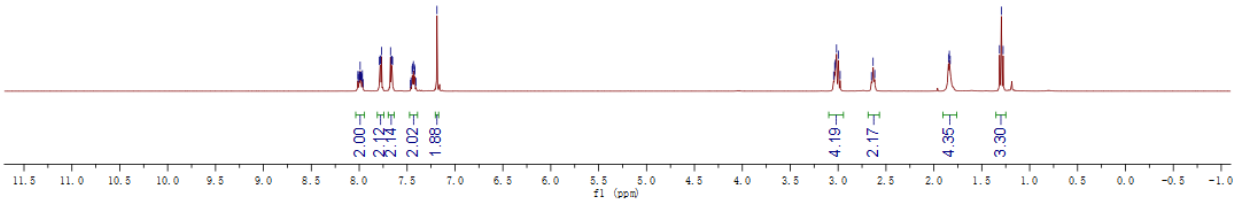
1.31
1.30
1.28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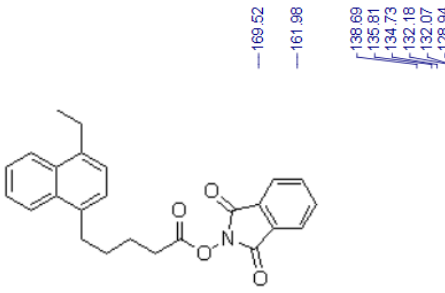
2.02
1.88
4.19
2.17
4.35
3.30
f1 (ppm)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132.18
132.07
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125.38
125.29
124.57
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32.57
30.93
29.86
25.90
24.75
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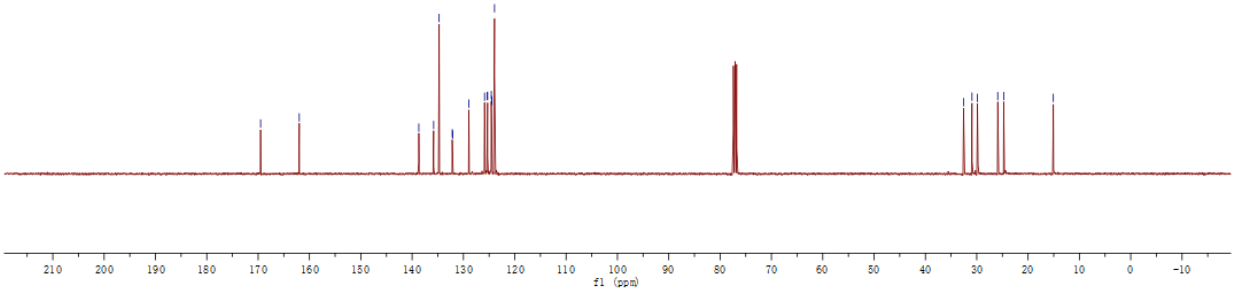
f1 (ppm)

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.