Electronic Supplementary Information

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General information.

All chemicals, unless otherwise noted, were purchased from commercial sources and used without further purification. All solvents for reactions and measurement were purified by standard methods. ^{1}H and ^{13}C NMR spectra were recorded respectively on Bruker 400 M or 500 M spectrometers. ^{19}F NMR spectra were recorded respectively on Bruker 400 M spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{1}H NMR spectroscopy. Flash column chromatography was carried out using 300–400 mesh silica-gel at medium pressure.

High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo

Fisher Scientific, USA. Gas chromatography-mass spectrometry (GC-MS) analyses were performed with an Agilent Technologies 7890A Network GC System equipped with an Agilent Technologies 5975C Network Mass Selective Detector (MSD).

All absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Steady-state emission spectra were recorded on a Horiba Fluorolog-3 spectrophotometer. Solutions for photophysical studies were degassed by using a high vacuum line in a two-compartment cell with five freeze-pump-thaw cycles. Low temperature (77 K) emission spectra for glassy state and solid state samples were recorded in quartz tubes (4 mm internal diameter) placed in a liquid nitrogen Dewar flask with quartz windows. Nanosecond time-resolved emission measurements were performed on a LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd., Livingston, UK). The excitation source was the 355 nm output (third harmonic) of a Nd:YAG laser (Spectra-Physics Quanta-Ray Lab-130 Pulsed Nd:YAG Laser). The signals were processed by a PC plug-in controller with L900 software. Cyclic voltammetry was conducted on a Princeton Applied Research PMC-1000 Potentiostat. The working electrode was glassy carbon; the reference electrode was Ag/AgCl; the counter electrode was a platinum wire. Scan rate: 100 mV/s. All potentials were reported versus Ag/AgCl. Unless stated otherwise, irradiation was performed using 410 nm or 365 nm LEDs (3 W × 4) under argon atmosphere. The illumination instruments were purchased from Shenzhen PURI Materials Technologies Co., LTD (Model: PR-PCR2-365nm, PR-PCR2-410nm). The photon flux received by the reaction tube containing 5 mL of solution in the 365 nm LED photoreactor is estimated to be 3.91×10^{-6} einstein s^{-1}. Large-scale 365 nm LEDs photoreactor (Model: PR-PCRL1-365 nm) was also purchased from Shenzhen Purui Material Technology Co., Ltd.

Photoreactor: (3 W × 4, 410 or 365 nm LEDs)

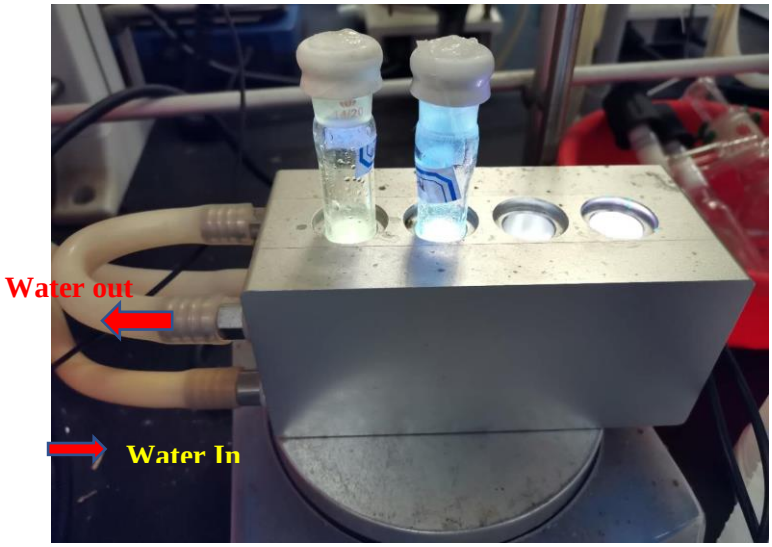


Figure S1. Reaction setup with cooling by running water.

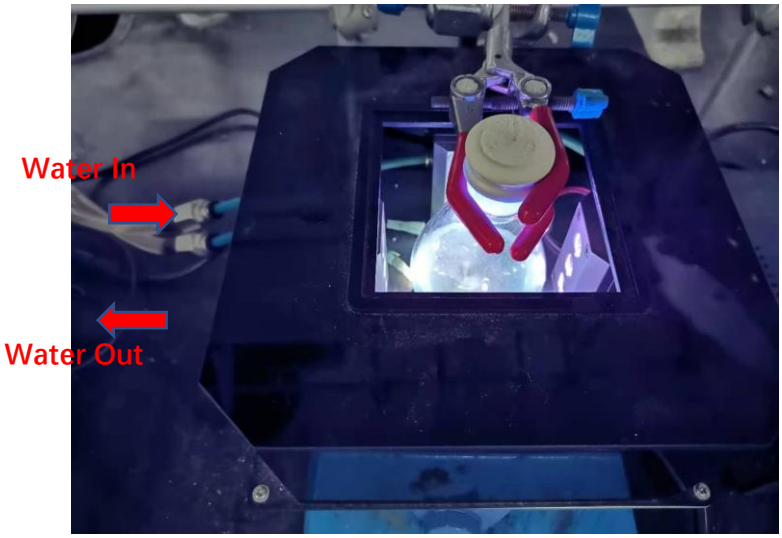
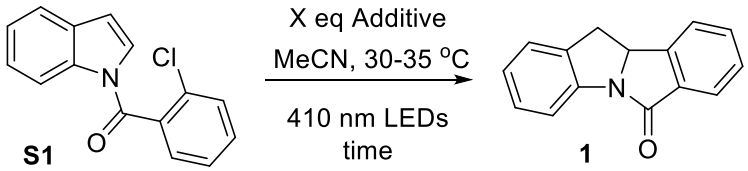


Figure S2: Large-scale photoreactor (25 W, 365 nm LEDs)

Reported compounds:

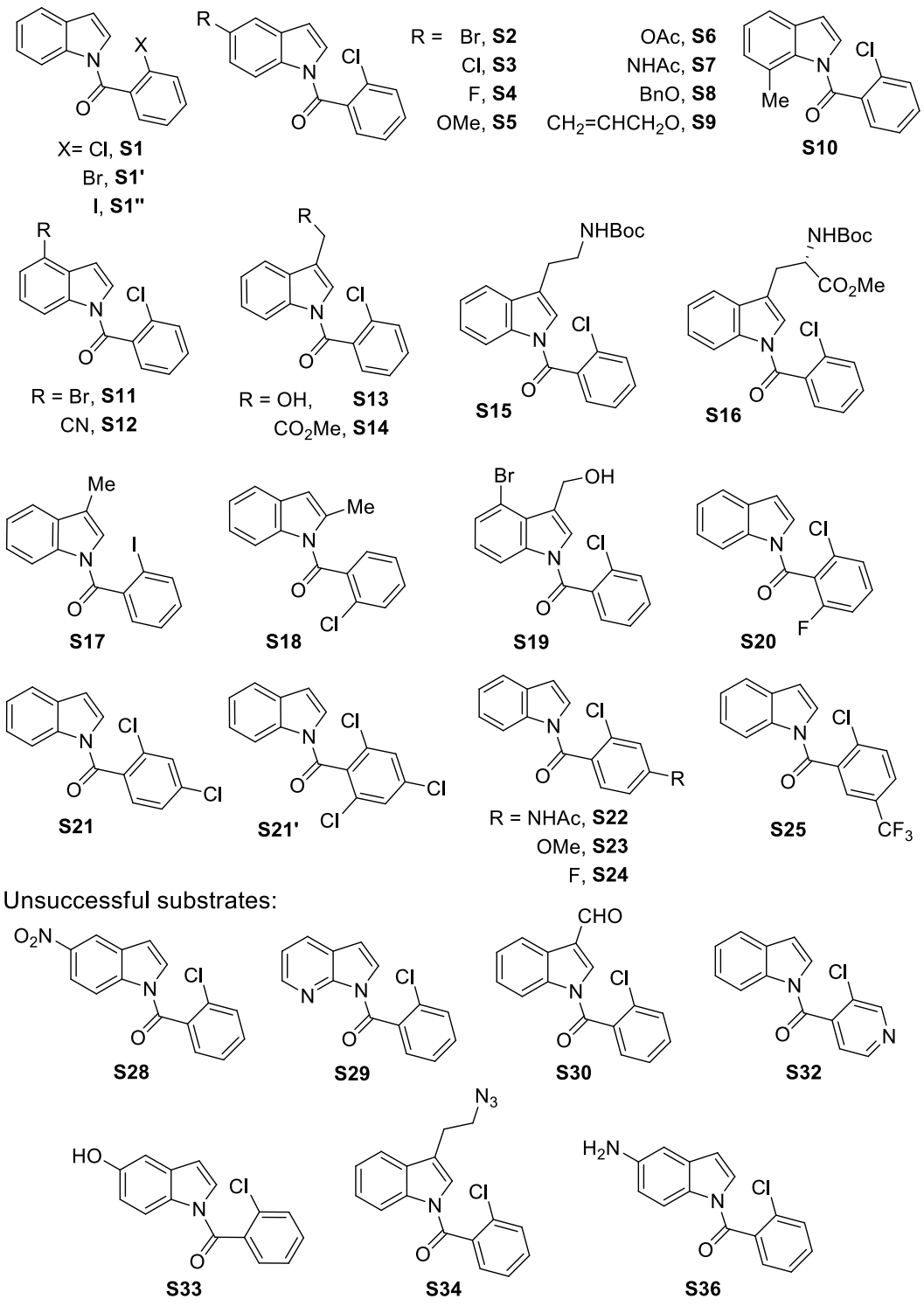
(2-Chlorophenyl)(1H-indol-1-yl)methanone (**S1**),[1] (2-bromophenyl)(1H-indol-1-yl)methanone (**S1′**),[2] (1H-indol-1-yl)(2-iodophenyl)methanone (**S1′′**),[3] *tert*-butyl (2-(1H-indol-3-yl)ethyl)carbamate,[4] (2-iodophenyl)(3-methyl-1H-indol-1-yl)methanone (**S17**),[5] 5-(allyloxy)-1H-indole,[6] (2-chlorophenyl)(2-methyl-1H-indol-1-yl)methanone (**S18**),[7] 1-(2-chlorobenzyl)-1H-indole (**42**).[8]

Table S1: Reaction condition optimization for the dearomatization of **S1**[a]

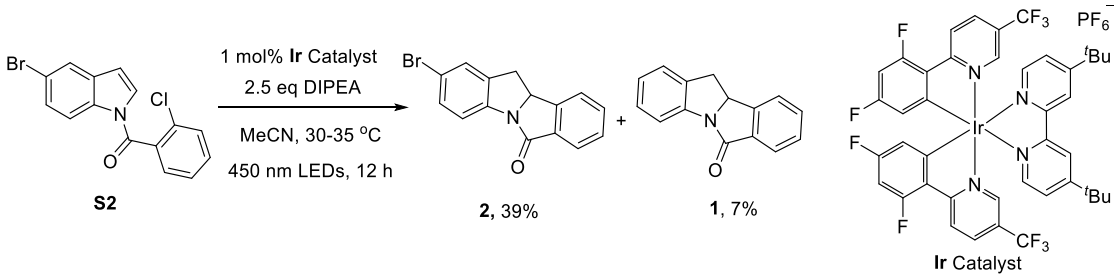


Entry	Additive	X	Solvent	Time / h	Yield (%)
1	DIPEA	2.5	MeCN	2	21
2	DIPEA	2.5	MeCN	4	46
3	DIPEA	2.5	MeCN	6	60
4	DIPEA	2.5	DMF	8	47
5	DIPEA	2.5	DMSO	8	40
6	DIPEA	2.5	Acetone	8	30
7	DIPEA	2.5	THF	8	6
8	DIPEA	2.5	DCE[b]	8	10
9	DIPEA	2.5	Ethyl acetate	8	0
10	DIPEA	2.5	Toluene	8	0
11	DIPEA	2.5	MeOH	8	20
12	DIPEA	0.5	MeCN	8	21
13	DIPEA	1.0	MeCN	8	33
14	TMEDA	2.5	MeCN	8	20[c]
15	Et_3N	2.5	MeCN	8	31[c]
16	DABCO	2.5	MeCN	8	0[c]
17	K_2CO_3	2.5	MeCN	8	0[c]
18	DIPEA $Ir(ppy)_3$[e]	2.5 0.01	MeCN	12	59[c]; 54[d]
19	DIPEA $[Ir(dF(CF_3)ppy)_2(dttbpy)]PF_6$[f]	2.5 0.01	MeCN	12	50[c]; 84[d]

[a] **S1** (0.2 mmol), DIPEA (0.5 mmol) and acetonitrile (2.0 mL), irradiation under 410 nm LEDs at 30-35 °C for 2-12 hours. Yields were determined by ^{1}H NMR using dibromomethane or 1,3,5-trimethoxybenzene as internal standard. [b] DCE: 1,2-dichloroethane. [c] Under 365 nm LEDs irradiation. [d] Under 450 LEDs irradiation. [e] Hppy = 2-phenylpyridine. [f] $HdF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine; dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine.



Scheme S1: Structures of substrates used for examining the scope of photo-induced dearomatization reaction.



Scheme S2: The use of $[Ir(dF(CF_3)ppy)_2(dttbpy)]PF_6$ as photocatalyst in photocyclization of N-(2-chlorobenzoyl)-5-bromoindole. Hydrodebrominated product was also obtained.

Quantum yield determination for photochemical reaction

Determination of light intensity:

The 365 nm LED (FWHM = 8 nm) was used for photochemical quantum yield measurements. The photon flux was determined by ferrioxalate actinometry as follows: 5 mL of 0.15 M solution of potassium ferrioxalate (in 0.05 M H_2SO_4) was placed in a reaction tube and irradiated with stirring. After irradiation, 20 μL of the solution was treated subsequently with 200 μL of 1,10-phenathroline solution (5 mM in water) and 10 μL of buffer solution (0.6 M in NaOAc and 0.18 M in H_2SO_4). The solution was rested in the dark for 10 min, and then made up to 2 mL with water. The absorbance at 510 nm was measured (due to absorption of $[Fe^{II}(phen)_3]^{2+}$). A non-irradiated sample was similarly prepared to analyze the amount of Fe(II) present in the stock 0.15 M ferrioxalate solution. The increase in absorbance of the solution after 3s, 6s and 9s of light irradiation are 0.344, 0.629 and 0.946, respectively, which gives an average increase of absorbance of 0.104 per second. The amount of photo-generated Fe(II) ions per second was calculated using equation (1) to be 4.72 μmol.

$$\text{mol of Fe(II)} = \frac{V \times \Delta A \times DF}{b \times \varepsilon} \qquad (1)$$

where V is the volume of absorbance measurement (0.005 dm^3) , ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples (0.104), DF is the dilution factor (100 times), b is the path length (1 cm), and ε is the molar absorptivity (ε = 11,010 $cm^{-1} M^{-1}$).

The photon flux was calculated using equation (2) to be 3.91×10^{-6} einstein s^{-1}.

$$\text{photon flux} = \frac{\text{mol of Fe(II)}}{\Phi \times t \times f} \qquad (2)$$

where Φ is the quantum yield for the ferrioxalate actinometer (assumed to be 1.21 based on the reported value at 365 nm.[9] t is time of irradiation (1 s), and f is the fraction of light absorbed at 365 nm (> 99.9 %) by the 0.15 M potassium ferrioxalate solution.

Determination of photochemical reaction quantum yield

The reaction mixture (typical reaction condition in Table 2: *N*-(2-chlorobenzoyl)indole (0.5 mmol), *N*,*N*-diisopropylethylamine (1.25 mmol) in CH_3CN (5 mL) at room temperature under argon was prepared in a reaction tube and the absorbance at 365 nm is 0.26 (i.e. ~45 % light absorbed). The reaction tube was then irradiated with 365 nm LED with stirring. After 40 minutes, 89.2 μmol of product were formed (determined by ^{1}H NMR spectroscopy), corresponding to a quantum yield of 2.1%.

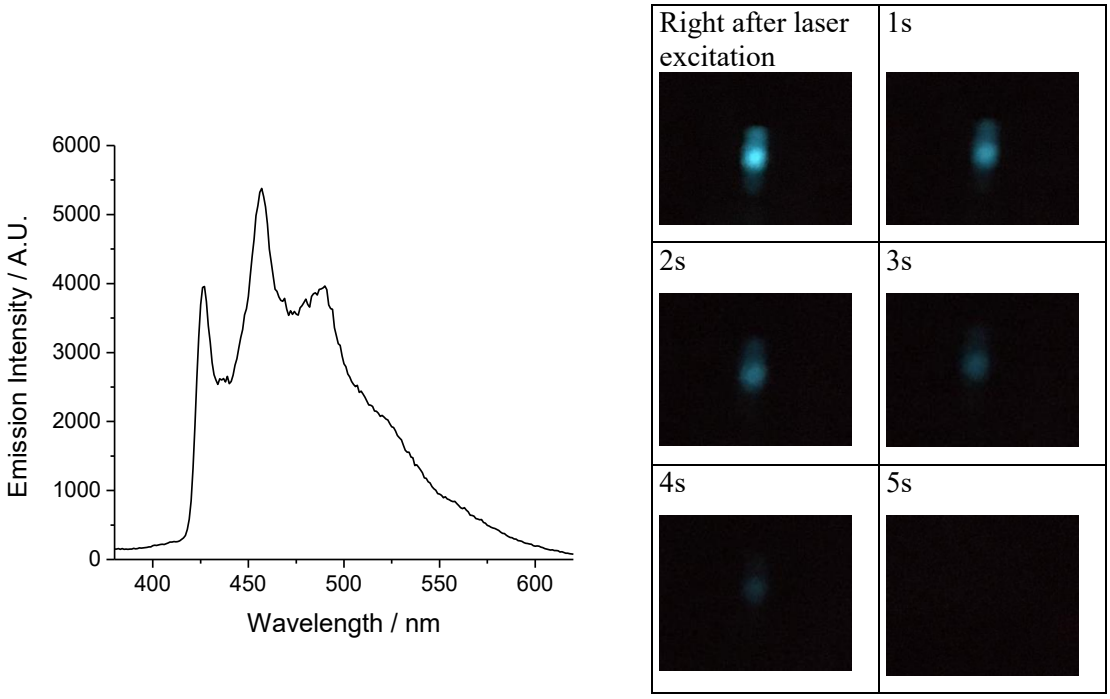


Figure S3: Left: emission spectrum of **S1** in 2-MeTHF at 77 K. (concentration of **S1** = 1×10^{-4} M; excitation at 325 nm); Right: photos showing the afterglow recorded within a few seconds after laser pulse excitation. (photos taken with iPhone 6s)

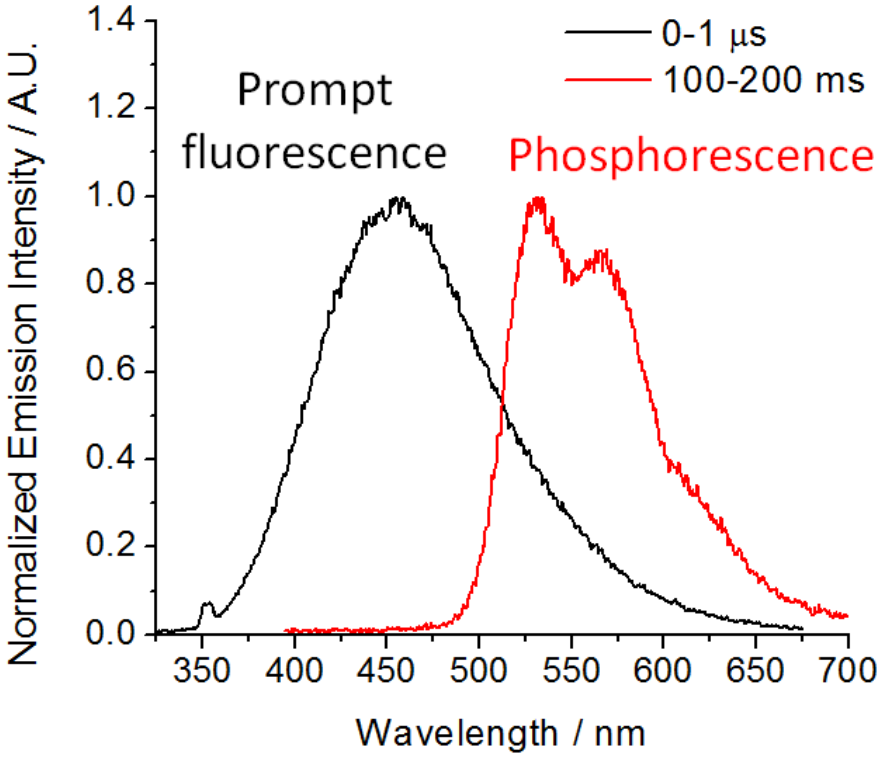


Figure S4: Time-resolved emission spectra of **S3** in the solid state at room temperature. Excitation at 355 nm..

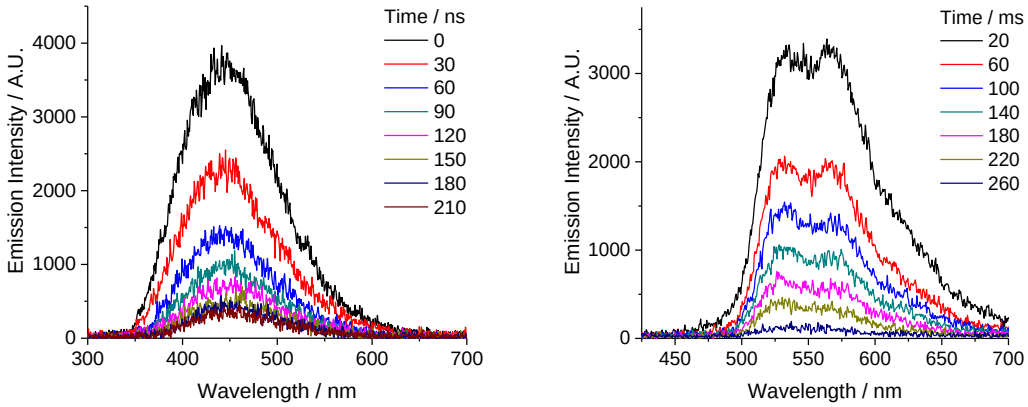


Figure S5. Time-resolved emission spectra of **S3** in the solid state at room temperature. Gate width = 30 ns (left) and 40 ms (right).

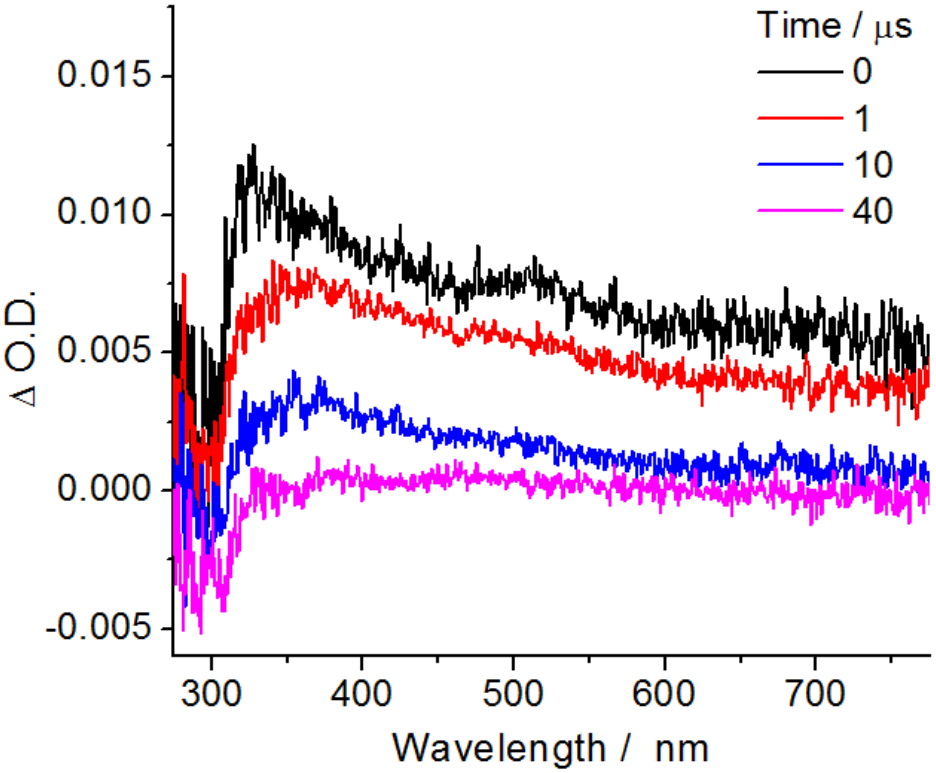


Figure S6: ns-TA spectra of **S3** in degassed MeCN (excitation at 266 nm).

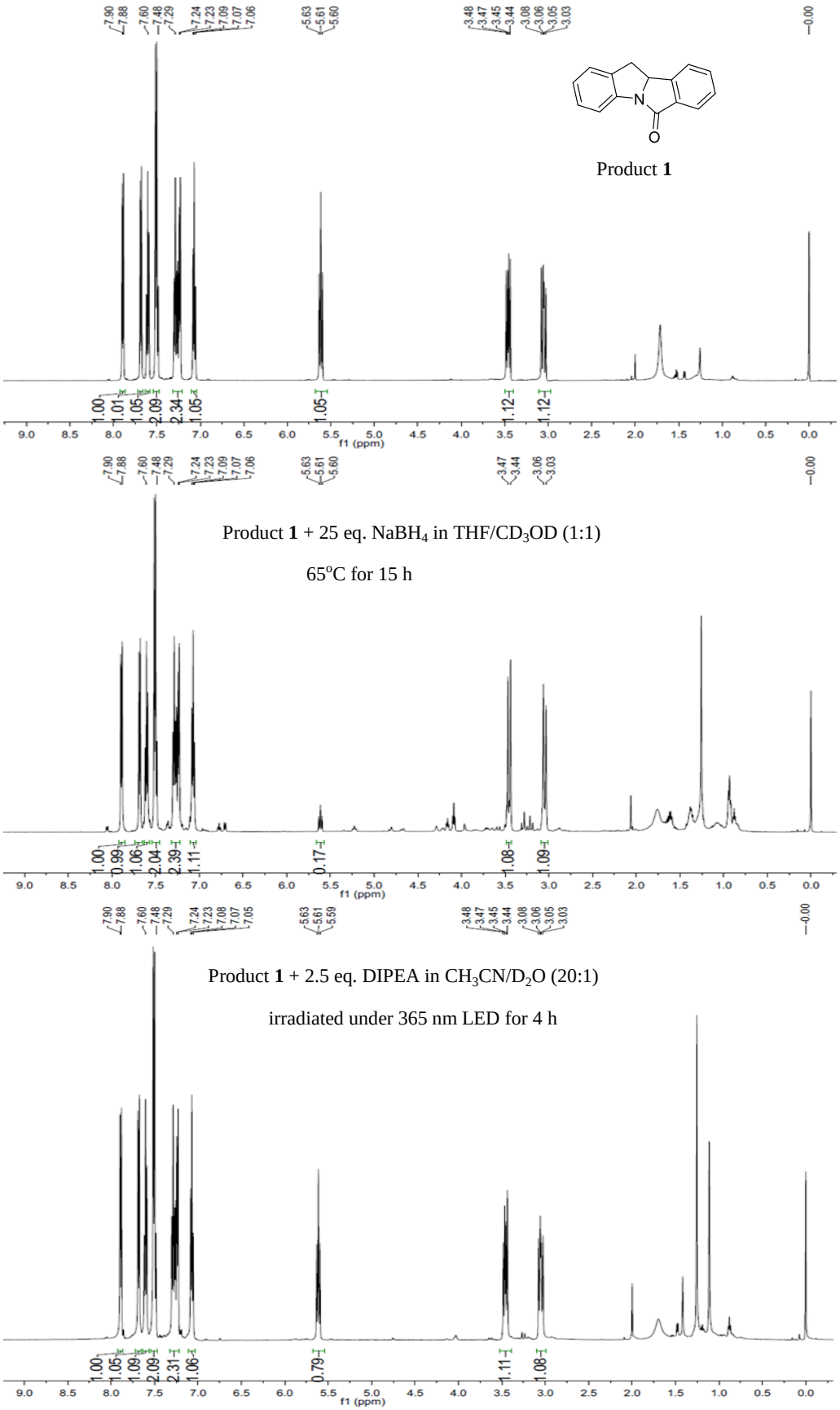


Figure S7. ^{1}H NMR spectra showing the incorporation of deuterium at C2 position (at ~5.6 ppm) upon treatment with $NaBH_4$ or DIPEA in the presence of deuterated protic solvent.

EPR Experiments

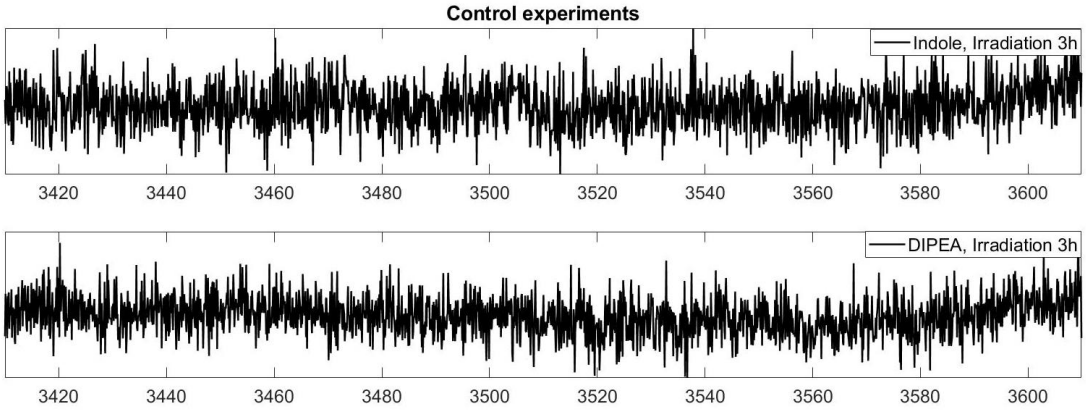


Figure S8: EPR spectra of control experiments. Upper: *N*-benzoyl indole **S1**, irradiated for 3 hours; Bottom: DIPEA, irradiated for 3 hours. Recorded at room temperature. Freq.: 9.841 GHz; Mod. Amp.: 1 G.

In a 10 mL test tube with a magnetic stirring bar, indole derivative **S1** (0.2 mmol) or DIPEA (87 μL) was dissolved in MeCN (2.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes. Then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 3 h. The sample was obtained with a capillary which was inserted into the mixture to obtain a 3 cm long sample solution under the protection of argon balloon. The upper and lower ends of the capillary were sealed with grease. The capillary was put into a small EPR tube, analyzed by EPR spectrometer at room temperature.

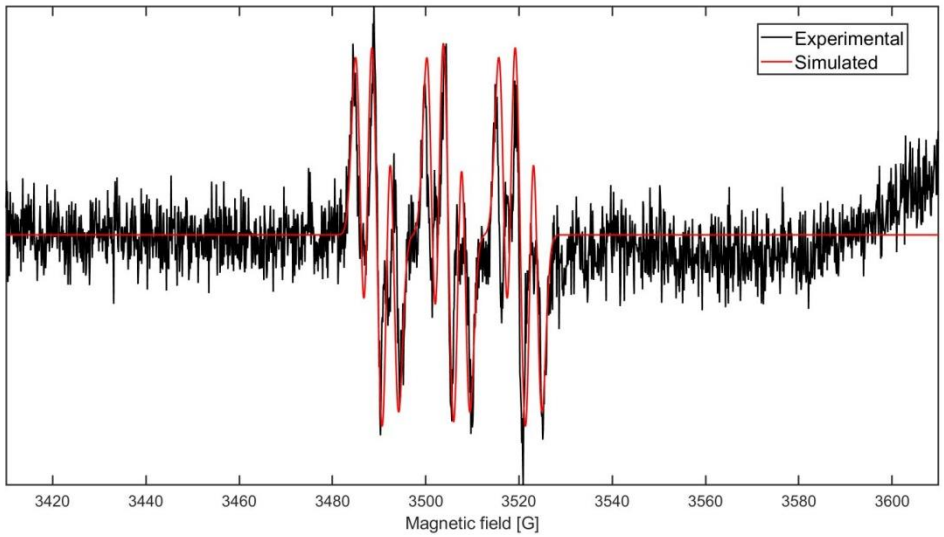


Figure S9: X-band EPR spectrum of the reaction mixture of indole derivative **S1** and DIPEA in MeCN, upon 365 nm LEDs irradiation for 3 hours, recorded at room temperature. Freq.: 9.841 GHz; Mod. Amp.: 1 G.

In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.5 mmol), DIPEA (0.218 mL, 2.5 equiv) were dissolved in MeCN (5.0 mL). The test tube was sealed with a

septum. The mixture was purged with argon for ten minutes. Then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 3 h. The sample was obtained with a capillary which was inserted into the mixture to obtain a 3 cm long sample solution under the protection of argon balloon. The upper and lower ends of the capillary were sealed with grease. The capillary was put into a small EPR tube, analyzed by EPR spectrometer at room temperature.

No signal could be detected when substrate **S1** or DIPEA alone was irradiated for 3 hours (Figure S8). Irradiation of a mixture of **S1** and DIPEA for 3 hours gave a set of triplet signal as shown in Figure S9. The signal could be approximately fitted with g = 2.0060, A_N = 15.2 G, A_{H1} = 4.1 G and A_{H2} = 3.7 G. The g value is higher than those of typical aliphatic amine cation radicals,[10,11] and is comparable to those of nitroxide radicals.[11] The DIPEA radical cation[12] and its deprotonated derivatives has been reported to be very short-lived, especially in basic solutions.[13]

The splitting of the signal mainly arises from one ^{14}N (I = 1) nucleus with A = 15.2 G and two ^{1}H (S = 1/2) nuclei, probably at the α-C atom(s), with A = 4.1 and 3.7 G. It should be noted that contributions from ^{1}H nuclei with smaller A values might also be present, while the associated splittings are, however, not resolved in the recorded spectrum. Possible radical species giving rise to this signal is a tertiary or secondary aliphatic nitroxide radical, which is temporarily accumulated in a decaying process of DIPEA upon photo-oxidation.

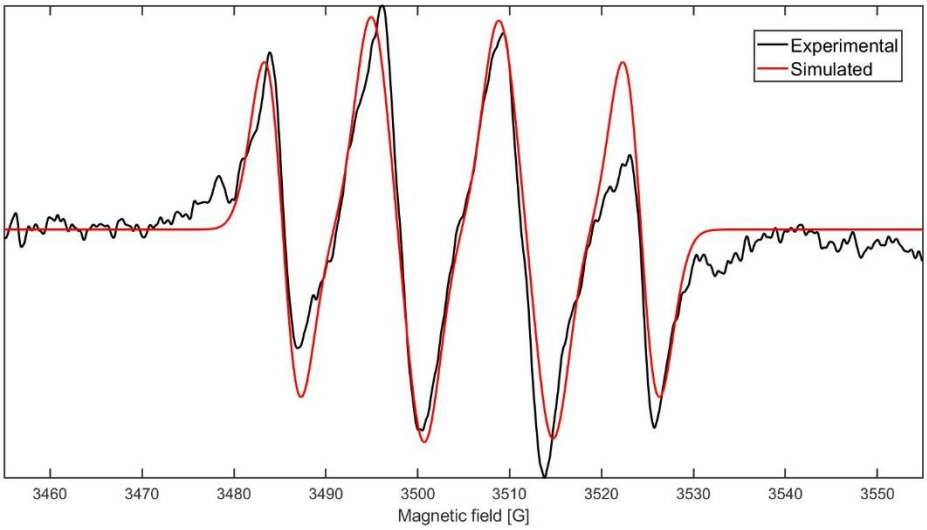


Figure S10: X-band EPR spectrum of the reaction mixture of indole derivative **S1** and DIPEA in MeCN, upon 365 nm LEDs irradiation for 3 hours, then trapped with DMPO, recorded at room temperature. Freq.: 9.841 GHz; Mod. Amp.: 1 G.

In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.2 mmol), DIPEA (87 μL, 2.5 equiv) were dissolved in MeCN (2.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes. Then the mixture was irradiated at 30-35 °C

with 365 nm LEDs for 3 h. 1 mL sample solution was taken out and mixed with DMPO (10 μL) under argon atmosphere. The sample was obtained with a capillary which was inserted into the mixture to obtain a 3 cm long sample solution under the protection of argon balloon. The upper and lower ends of the capillary were sealed with grease. The capillary was put into a small EPR tube, analyzed by EPR spectrometer at room temperature.

The major signal could be fitted with parameters: g = 2.0061, A_N = 14.0 G and A_H = 11. 1 G with a line width of 4 G. The fitting parameters do not correspond to an aryl/alkyl radical, in which case a signal generally spanning a spectral width of ~ 60 gauss or higher would be expected. Instead, they are comparable to typical DMPO-trapped $O_2^{\bullet-}$ or •OOH/R radicals,[14] which might be generated in a trace amount and not significantly interfering with the rapidly preceding intramolecular radical cyclization processes. Hydroxide radical (•OH) might also be present in an even lower concentration, giving the minor overlapping side features in the spectrum. However, broadening of the signals prohibits more detailed analysis of the spectrum.

UV-vis absorption

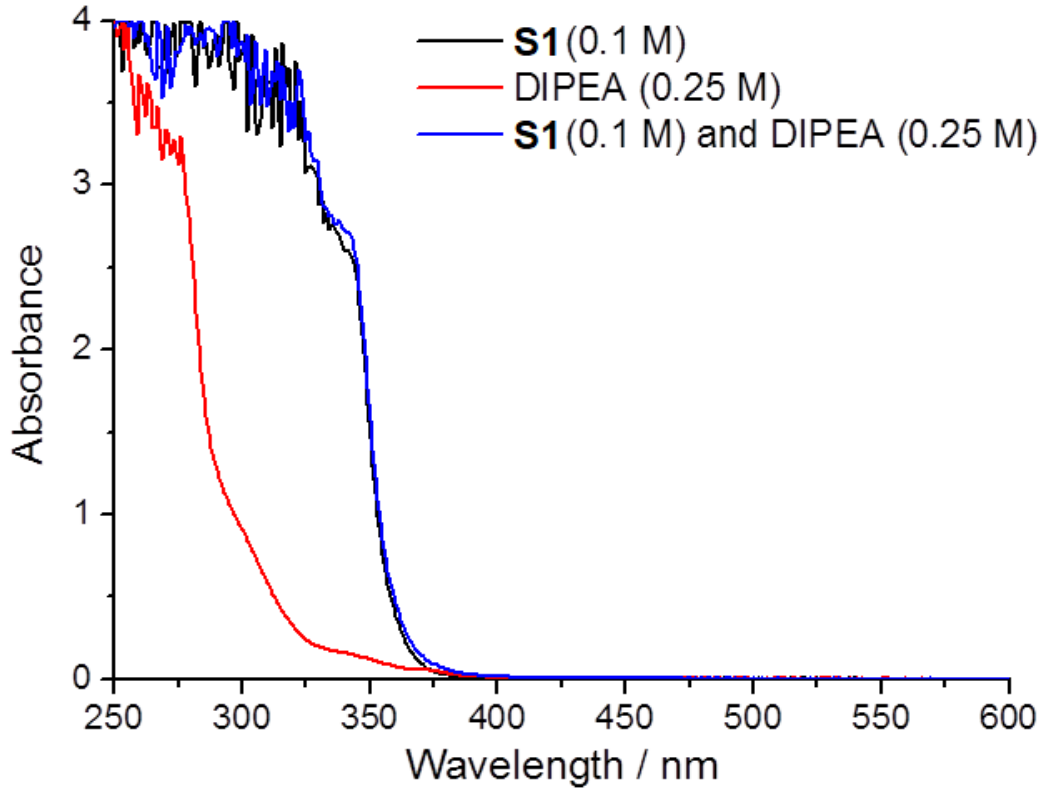


Figure S11. UV-vis absorption spectra of **S1**, DIPEA and their mixture in MeCN at room temperature.

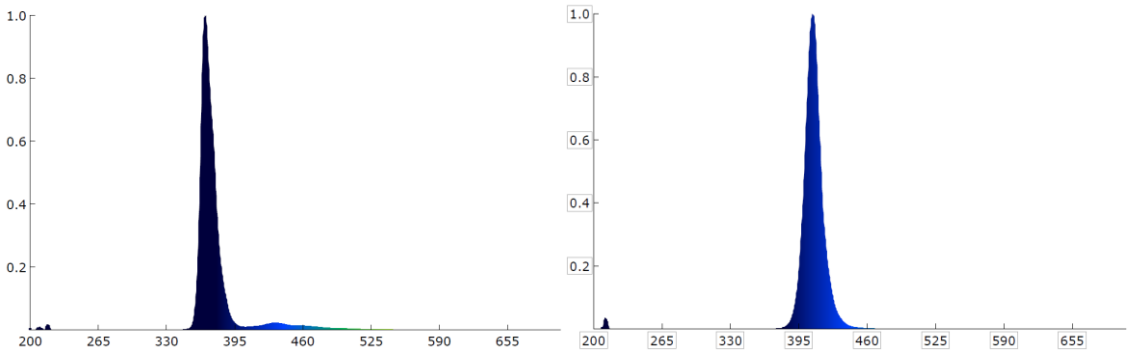
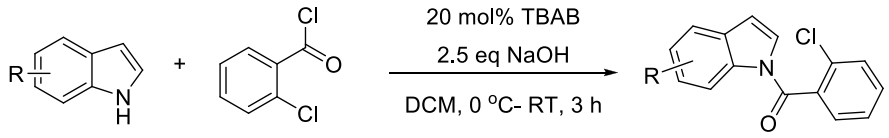
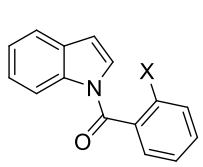


Figure S12. Emission output of 365 (left) and 410 (right) nm LEDs.

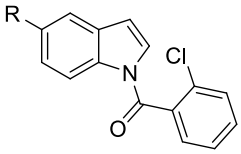
Experimental Procedure

Scheme S3a: Synthesis of substrates.

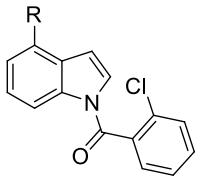




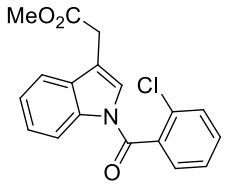
X= Cl, **S1**, 92%
Br, **S1'**, 95%
I, **S1''**, 95%



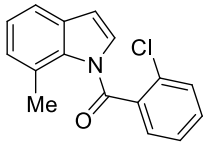
R = Br, **S2**, 98%
Cl, **S3**, 79%
F, **S4**, 74%
OMe, **S5**, 85%
OAc, **S6**, 90%
NHAc, **S7**, 12%
BnO, **S8**, 75%
CH_2=$CHCH_2O$, **S9**, 75%
NO_2, **S28,** 70%



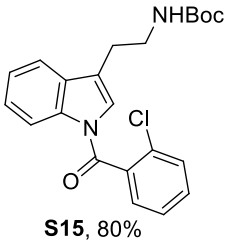
R = Br, **S11**, 90%
CN, **S12**, 90%



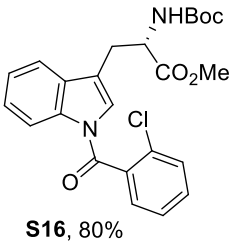
S14, 59%



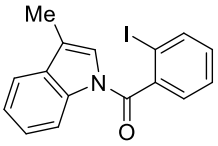
S10, 75%



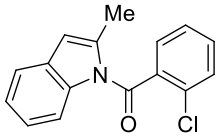
S15, 80%



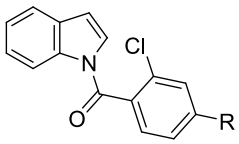
S16, 80%



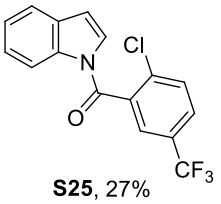
S17, 95%



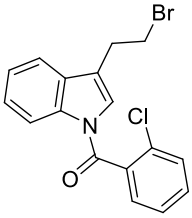
S18, 80%



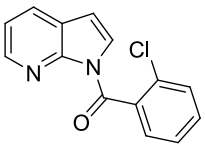
R = OMe, **S23**, 62%
F, **S24**, 94%
NO_2, **S26,** 40%



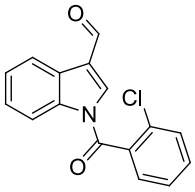
S25, 27%



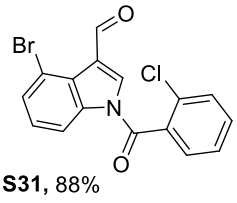
S27, 80%



S29, 56%



S30, 78%



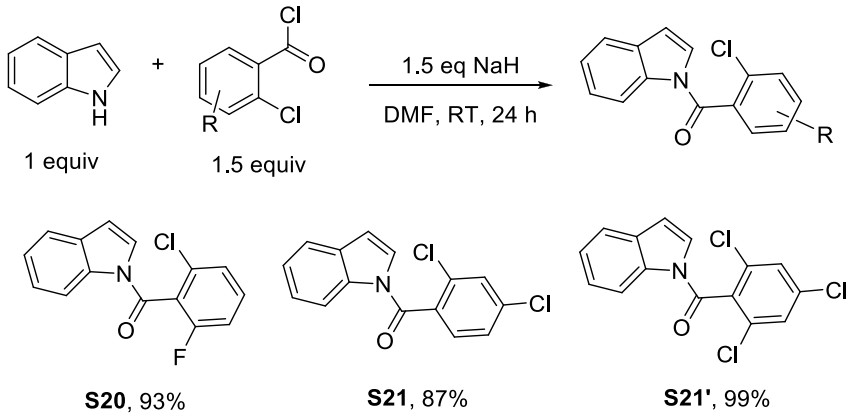
S31, 88%

General Procedure 1: Synthesis of *N*-(2-halidebenzoyl)indole[14]

A CH_2Cl_2 solution of 2-chlorobenzoyl chloride (1.5 equiv) was added dropwise to a solution of the indole derivative (1 equiv), NaOH (2.5 equiv) and tetrabutylammonium bromide (TBAB, 0.2 equiv) in CH_2Cl_2 at 0 ℃. The mixture was stirred at 0 ℃ for 0.5 h. Then the mixture was warmed to room temperature. At this time another 0.5 equivalent of 2-chlorobenzoyl chloride was added. The mixture was stirred at room temperature for 2.5 h. Water was added to quench the reaction and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1).

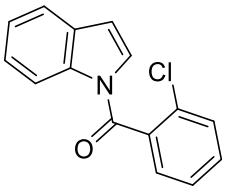
General Procedure 2: Synthesis of *N*-(2-chlorobenzoyl)indole using NaH

Scheme S3b: Synthesis of substrates using NaH



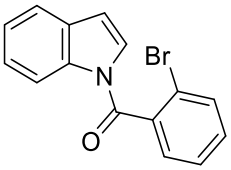
In a 50 mL Schlenk tube with a magnetic stirring bar, indole (1 equiv) was added. The Schlenk tube was evacuated and back-filled with argon for three times. Then anhydrous DMF (10 mL) was added and cooled down to 0 ℃. To this solution, a 60% dispersion of NaH in mineral oil (1.5 equiv) was added and stirred at 0 ℃ for 0.5 h. A solution of the corresponding benzoyl chloride (1.5 equiv) in DMF (5 mL) was added dropwise. Then the mixture was warmed to room temperature and stirred for 24 h. Water was added to quench the reaction and extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1).

(2-Chlorophenyl)(1H-indol-1-yl)methanone (S1)[1]



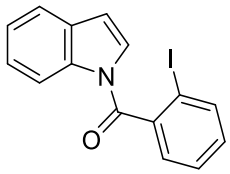
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (br, 1 H), 7.63 (d, *J* = 7.6 Hz, 1 H), 7.56 – 7.50 (m, 3 H), 7.44 (m, 2 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.01 (br, 1 H), 6.63 (d, *J* = 3.8 Hz, 1 H) ppm.

(2-Bromophenyl)(1H-indol-1-yl)methanone (**S1′**)[2]



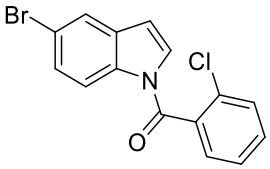
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (br, 1 H), 7.72 (d, *J* = 7.9 Hz, 1 H), 7.65 – 7.57 (m, 1 H), 7.55 – 7.49 (m, 2 H), 7.49 – 7.40 (m, 2 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 6.99 (br, 6.99, 1 H), 6.64 (d, *J* = 3.8 Hz, 1 H) ppm.

(1H-Indol-1-yl)(2-iodophenyl)methanone (S1′′)[3]



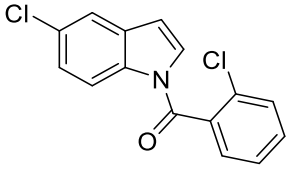
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (br, 1 H), 7.97 (d, *J* = 8.0 Hz, 1 H), 7.62 (d, *J* = 7.4 Hz, 1 H), 7.56 – 7.50 (m, 1 H), 7.49 – 7.39 (m, 2 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 7.30 – 7.20 (m, 1 H), 6.98 (br, 1 H), 6.64 (d, *J* = 3.6 Hz, 1 H) ppm.

(5-Bromo-1H-indol-1-yl)(2-chlorophenyl)methanone (S2)



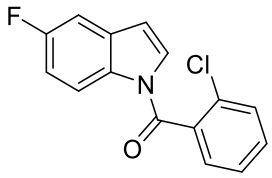
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (br, 1 H), 7.73 (d, *J* = 2.0 Hz, 1 H), 7.55 – 7.48 (m, 4 H), 7.47 – 7.40 (m, 1 H), 7.00 (br, 1 H), 6.56 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.91, 134.36, 134.15, 132.80, 131.96, 131.24, 130.21, 128.93, 128.10, 127.83, 127.26, 123.75, 117.88, 117.70, 108.91 ppm. HRMS (ESI) Calcd for $[C_{15}H_9ClBrNO+H]^+$: 333.9629, Found: 333.9636.

(5-Chloro-1H-indol-1-yl)(2-chlorophenyl)methanone (S3)



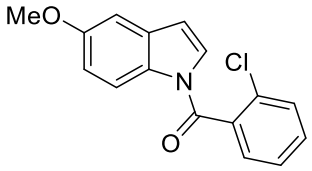
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (br, 1 H), 7.57 (d, *J* = 2.0 Hz, 1 H), 7.56 – 7.51 (m, 3 H), 7.49 – 7.42 (m, 1 H), 7.37 (d, *J* = 8.7 Hz, 1 H), 7.02 (s, 1 H), 6.57 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.88, 134.41, 133.79, 132.29, 131.91, 131.29, 130.20, 129.96, 128.91, 127.92, 127.22, 125.43, 120.66, 117.51, 109.01 ppm. HRMS (ESI) Calcd for $[C_{15}H_9Cl_2NO+H]^+$: 290.0134, Found: 290.0140.

(2-Chlorophenyl)(5-fluoro-1H-indol-1-yl)methanone (S4)



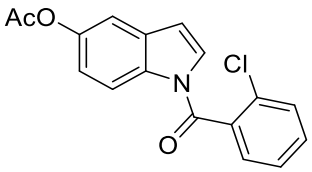
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 7.53 (m, 3 H), 7.49 – 7.41 (m, 1 H), 7.27 (d, *J* = 9.8 Hz, 1 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 7.02 (s, 1 H), 6.59 (br, 1 H); ^{19}F NMR decoupling (376 MHz, $CDCl_3$) δ -118.26; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.76, 160.10 (d, *J* = 241.2 Hz), 134.52, 132.14 (d, *J* = 10.1 Hz), 131.82, 131.29, 130.17, 128.90, 128.19, 127.18, 117.59 (d, *J* = 8.9 Hz), 112.93 (d, *J* = 24.8 Hz), 109.41 (d, *J* = 3.8 Hz), 106.70 (d, *J* = 24.0 Hz) ppm. HRMS (ESI) Calcd for $[C_{15}H_9ClFNO+H]^+$: 274.0429, Found: 274.0434.

(2-Chlorophenyl)(5-methoxy-1H-indol-1-yl)methanone (S5)



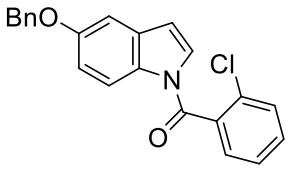
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (br, 1 H), 7.57 – 7.47 (m, 3 H), 7.45 - 7.41 (m, 1 H), 7.08 (d, *J* = 2.4 Hz, 1 H), 7.03 (d, *J* = 8.8 Hz, 1 H), 6.96 (br, 1 H), 6.56 (d, *J* = 3.8 Hz, 1 H), 3.89 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.60, 157.04, 134.82, 132.13, 131.64, 131.28, 130.11, 128.89, 127.35, 127.13, 117.33, 113.49, 109.73, 103.94, 55.72 ppm. HRMS (ESI) Calcd for $[C_{16}H_{12}ClNO_2+H]^+$: 286.0629, Found: 286.0634.

1-(2-Chlorobenzoyl)-1H-indol-5-yl acetate (S6)



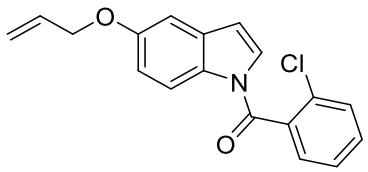
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (br, 1 H), 7.56 – 7.49 (m, 3 H), 7.48 – 7.41 (m, 1 H), 7.33 (d, *J* = 2.3 Hz, 1 H), 7.13 (dd, *J* = 8.8, 2.3 Hz, 1 H), 7.02 (s, 1 H), 6.60 (d, *J* = 3.7 Hz, 1 H), 2.36 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.98, 165.84, 147.44, 134.54, 133.19, 131.85, 131.82, 131.25, 130.17, 128.88, 127.85, 127.20, 118.96, 117.22, 113.66, 109.61, 21.20 ppm. HRMS (ESI) Calcd for $[C_{17}H_{12}ClNO_3+H]^+$: 314.0578, Found: 314.0584.

(5-(Benzyloxy)-1H-indol-1-yl)(2-chlorophenyl)methanone (S8)



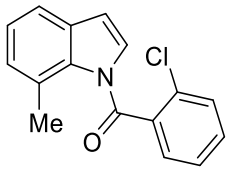
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (br, 1 H), 7.55 – 7.45 (m, 5 H), 7.45 – 7.37 (m, 3 H), 7.34 (t, *J* = 7.3 Hz, 1 H), 7.13 (d, *J* = 2.5 Hz, 1 H), 7.08 (d, *J* = 9.1 Hz, 1 H), 6.93 (br, 1 H), 6.53 (d, *J* = 3.8 Hz, 1 H), 5.14 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.55, 155.12, 136.07, 133.75, 131.02, 130.57, 130.24, 129.22, 129.05, 127.83, 127.57, 126.92, 126.44, 126.30, 126.05, 116.33, 113.22, 108.67, 104.22, 69.50 ppm. HRMS (ESI) Calcd for $[C_{22}H_{16}ClNO_2+H]^+$: 362.0942, Found: 362.0948.

(5-(Allyloxy)-1H-indol-1-yl)(2-chlorophenyl)methanone (S9)



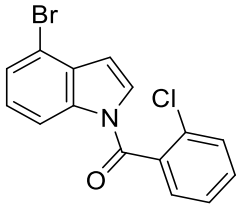
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (br, 1 H), 7.59 – 7.47 (m, 3 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 7.09 (d, *J* = 2.2 Hz, 1 H), 7.05 (d, *J* = 8.3 Hz, 1 H), 6.94 (br, 1 H), 6.55 (d, *J* = 3.6 Hz, 1 H), 6.15 – 6.08 (m, 1 H), 5.48 (d, *J* = 10.5, 1.7 Hz Hz, 1 H), 5.33 (d, *J* = 10.5, 1.5 Hz, 1 H), 4.63 (d, *J* = 5.2 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.60, 155.99, 134.80, 133.42, 132.08, 131.64, 131.27, 130.22, 130.11, 128.89, 127.36, 127.13, 117.69, 117.32, 114.17, 109.73, 105.13, 69.37 ppm. HRMS (ESI) Calcd for $[C_{18}H_{14}ClNO_2+H]^+$: 312.0786, Found：312.0791.

(2-Chlorophenyl)(7-methyl-1H-indol-1-yl)methanone (S10)



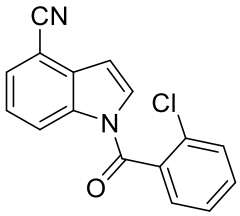
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.9 Hz, 1 H), 7.59 – 7.49 (m, 2 H), 7.48 – 7.38 (m, 2 H), 7.29 (t, *J* = 7.5 Hz, 1 H), 7.24 (d, *J* = 7.2 Hz, 1 H), 6.95 (d, *J* = 3.8 Hz, 1 H), 6.60 (d, *J* = 3.8 Hz, 1 H), 2.68 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.13, 135.05, 134.83, 132.43, 132.35, 132.23, 130.56, 130.31, 128.20, 127.96, 127.10, 126.71, 124.56, 118.65, 109.18, 22.36 ppm. HRMS (ESI) Calcd for $[C_{16}H_{12}ClNO+H]^+$: 270.0680, Found: 270.0684.

(4-Bromo-1H-indol-1-yl)(2-chlorophenyl)methanone (S11)



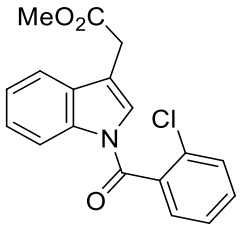
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (br, 1 H), 7.66 – 7.48 (m, 4 H), 7.46 – 7.38 (m, 1 H), 7.26 (t, *J* = 8.0 Hz, 1 H), 7.03 (br, 1 H), 6.68 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.07, 134.74, 133.35, 130.92, 130.65, 130.24, 129.19, 127.87, 126.26, 126.21, 126.17, 125.30, 114.51, 113.67, 108.42 ppm. HRMS (ESI) Calcd for $[C_{15}H_9ClBrNO+H]^+$: 333.9629, Found: 333.9635.

1-(2-Chlorobenzoyl)-1H-indole-4-carbonitrile (S12)



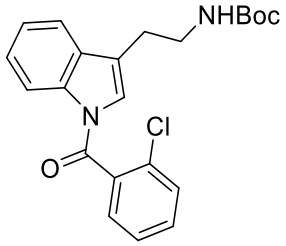
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 6.7 Hz, 1 H), 7.68 (d, *J* = 7.3 Hz, 1 H), 7.57 (s, 1 H), 7.57 – 7.53 (m, 2 H), 7.52 – 7.46 (m, 2 H), 7.18 (d, *J* = 3.9 Hz, 1 H), 6.85 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.09, 135.27, 133.87, 132.92, 132.29, 131.30, 130.34, 129.26, 129.00, 128.69, 127.37, 125.30, 121.07, 117.55, 107.68, 104.01 ppm. HRMS (ESI) Calcd for $[C_{16}H_9ClN_2O+H]^+$: 281.0476, Found: 281.0481.

Methyl 2-(1-(2-chlorobenzoyl)-1H-indol-3-yl)acetate (S14)



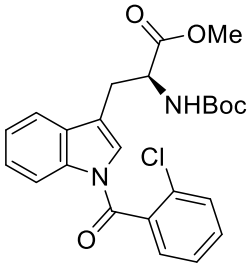
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (br, 1 H), 7.59 (d, *J* = 7.4 Hz, 1 H), 7.55 – 7.50 (m, 3 H), 7.48 – 7.41 (m, 2 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 7.00 (br, 1 H), 3.71 (s, 3 H), 3.70 (s, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.12, 165.75, 135.65, 134.75, 131.77, 131.73, 131.28, 130.74, 130.18, 128.92, 127.17, 125.66, 125.06, 124.41, 119.15, 115.67, 52.23, 30.83 ppm. HRMS (ESI) Calcd for $[C_{18}H_{14}ClNO_3+H]^+$: 328.0735, Found: 328.0741.

***tert*-Butyl (2-(1-(2-chlorobenzoyl)-1H-indol-3-yl)ethyl)carbamate (S15)**



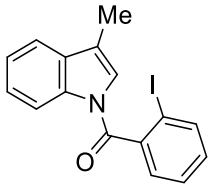
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (br, 1 H), 7.58 (d, *J* = 7.8 Hz, 1 H), 7.56–7.48 (m, 3 H), 7.49 – 7.41 (m, 1 H), 7.42 (t, *J* = 5.0 Hz, 1 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 6.80 (br, 1H), 4.68 (br, 1 H), 3.43–3.38 (m, 2 H), 2.86 (t, *J* = 7.1 Hz, 2 H), 1.43 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.67, 155.87, 135.84, 134.91, 131.69, 131.17, 131.07, 130.15, 128.87, 127.23, 125.57, 124.31, 123.80, 120.44, 119.05, 116.73, 79.34, 39.97, 28.39, 25.53 ppm. HRMS (ESI) Calcd for $[C_{22}H_{23}ClN_2O_3+H]^+$: 399.1470, Found: 399.1464.

(*S*)-Methyl *N*-(*tert*-butoxycarbonyl)-1-(2-chlorobenzoyl)-*L*-tryptophanate (S16)



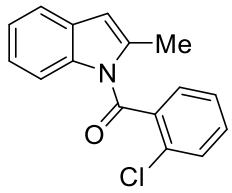
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (br, 1 H), 7.60 – 7.52 (m, 3 H), 7.51 (s, 1 H), 7.49 – 7.43 (m, 1 H), 7.42 (t, *J* = 7.3 Hz, 1 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 6.77 (br, 1 H), 5.12 (d, *J* = 7.5 Hz, 1 H), 4.64 – 4.60 (m, 1 H), 3.63 (s, 3 H), δ 3.23 (dd, *J* = 14.2, 5.0 Hz, 1 H), 3.15 (dd, *J* = 14.4, 4.5 Hz, 1 H), 1.42 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.10, 165.64, 154.97, 135.61, 134.84, 131.75, 131.19, 130.12, 128.91, 127.22, 125.65, 124.68, 124.35, 119.04, 117.83, 116.64, 80.02, 53.47, 52.36, 28.30, 27.75 ppm. HRMS (ESI) Calcd for $[C_{24}H_{25}ClN_2O_5+H]^+$: 457.1525, Found: 457.1518.

(2-Iodophenyl)(3-methyl-1H-indol-1-yl)methanone (S17)[5]



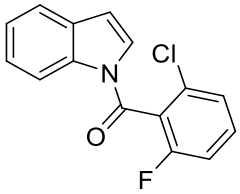
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (br, 1 H), 7.97 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 7.0 Hz, 1 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.44 (dd, *J* = 7.6, 1.7 Hz, 1 H), 7.39 (d, *J* = 7.3 Hz, 2 H), 7.25 (d, *J* = 7.6 Hz, 1 H), 6.68 (br, 1 H), 2.25 (s, 3 H) ppm.

(2-Chlorophenyl)(2-methyl-1H-indol-1-yl)methanone (S18)[7]



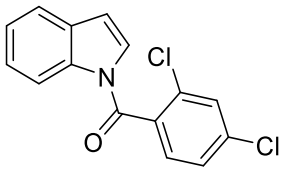
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (br, 1 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 7.60 – 7.49 (m, 2 H), 7.45 – 7.36 (m, 3 H), 7.26 (t, *J* = 7.8 Hz, 1 H), 6.67 (br, 1 H), 2.25 (s, 3 H) ppm.

(2-Chloro-6-fluorophenyl)(1H-indol-1-yl)methanone (S20)



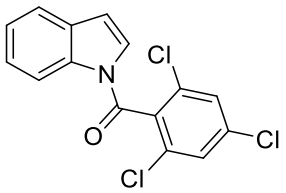
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.3 Hz, 1 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 8.5 Hz, 1 H), 7.48 (t, *J* = 8.1 Hz, 1 H), 7.40 (d, *J* = 7.4 Hz, 1 H), 7.36 (d, *J* = 8.3 Hz, 1 H), 7.19 (t, *J* = 8.4 Hz, 1 H), 6.92 (d, *J* = 3.1 Hz, 1 H), 6.65 (d, *J* = 3.4 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.51 (dd, *J* = 11.3, 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.31, 159.32 (d, *J* = 253.0 Hz), 135.44, 132.48 (d, *J* = 5.2 Hz), 132.19 (d, *J* = 8.8 Hz), 131.08, 125.90, 125.79, 125.57, 124.77, 123.83 (d, *J* = 22.0 Hz), 121.05, 116.91, 114.73 (d, *J* = 21.1 Hz), 110.47 ppm. HRMS (ESI) Calcd for $[C_{15}H_9FClNO+H]^+$: 274.0429, Found: 274.0426.

(2,4-Dichlorophenyl)(1H-indol-1-yl)methanone (S21)



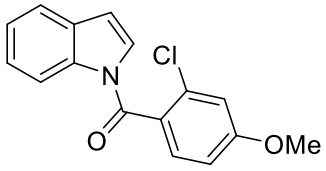
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (br , 1 H), 7.62 (d, *J* = 7.7 Hz, 1 H), 7.57 (d, *J* = 1.8 Hz, 1 H), 7.48 (d, *J* = 8.2 Hz, 1 H), 7.46 (d, *J* = 1.9 Hz, 1 H), 7.44 – 7.40 (m, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 6.98 (br, 1 H), 6.65 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.06, 137.29, 135.41, 133.27, 132.35, 131.03, 130.14, 129.84, 127.64, 126.33, 125.45, 124.58, 121.10, 116.50, 110.15 ppm. HRMS (ESI) Calcd for $[C_{15}H_9Cl_2NO+H]^+$: 290.0134, Found: 290.0131.

(1H-Indol-1-yl)(2,4,6-trichlorophenyl)methanone (S21′)



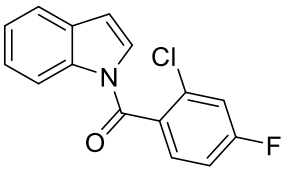
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.63 (d, *J* = 7.7 Hz, 1 H), 7.49 (s, 2 H), 7.47 (t, *J* = 8.4 Hz, 1 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 6.84 (d, *J* = 3.8 Hz, 1 H), 6.67 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.25, 136.97, 135.26, 133.21, 133.14, 132.85, 131.08, 128.43, 128.40, 125.70, 125.35, 124.91, 121.12, 116.91, 110.93 ppm. HRMS (ESI) Calcd for $[C_{15}H_8Cl_3NO+H]^+$: 323.9744, Found: 323.9743.

(2-Chloro-4-methoxyphenyl)(1H-indol-1-yl)methanone (S23)



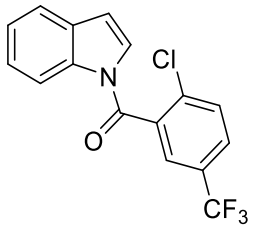
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (br, 1 H), 7.50 (d, *J* = 7.7 Hz, 1 H), 7.36 (d, *J* = 8.5 Hz, 1 H), 7.30 (t, *J* = 7.3 Hz, 1 H), 7.24 (td, *J* = 7.6, 0.9 Hz, 1 H), 6.97 (d, *J* = 3.6 Hz, 1 H), 6.95 (d, *J* = 2.4 Hz, 1 H), 6.85 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.52 (dd, *J* = 3.8, 0.7 Hz, 1 H), 3.80 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.09, 161.74, 135.52, 132.76, 131.06, 130.37, 127.04, 126.93, 125.15, 124.21, 120.95, 116.43, 115.45, 113.12, 109.36, 55.81 ppm. HRMS (ESI) Calcd for $[C_{16}H_{12}ClNO_2+H]^+$: 286.0629, Found: 286.0626.

(2-Chloro-4-fluorophenyl)(1H-indol-1-yl)methanone (S24)



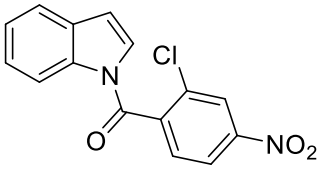
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (br, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.56 – 7.53 (m, 1 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 7.30 (dd, *J* = 8.6, 2.5 Hz, 1 H), 7.18 (td, *J* = 8.2, 2.4 Hz, 1 H), 6.99 (br, 1 H), 6.65 (d, *J* = 3.8 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.53 (m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.19, 163.45 (d, *J* = 254.7 Hz), 135.45, 132.86 (d, *J* = 10.5 Hz), 131.17 (d, *J* = 4.0 Hz), 131.05, 130.56 (d, *J* = 9.4 Hz), 126.45, 125.40, 124.53, 121.09, 117.79 (d, *J* = 25.0 Hz), 116.48, 114.78 (d, *J* = 21.8 Hz), 110.03 ppm. HRMS (ESI) Calcd for $[C_{15}H_9ClFNO+H]^+$: 274.0429, Found: 274.0426.

(2-Chloro-5-(trifluoromethyl)phenyl)(1H-indol-1-yl)methanone (S25)



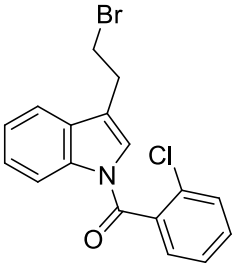
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (br, 1 H), 7.84 (d, *J* = 2.1 Hz, 1 H), 7.78 (dd, *J* = 8.5, 2.3 Hz, 1 H), 7.69 (d, *J* = 8.5 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.45 (t, *J* = 7.9 Hz, 1 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 6.92 (br, 1 H), 6.68 (d, *J* = 3.8 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.65; ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.42, 135.56, 135.42, 135.19 (q, *J* = 1.3 Hz), 131.05, 130.89, 129.95 (q, *J* = 33.8 Hz), 128.43 (q, *J* = 3.7 Hz), 126.05, 126.03 (q, *J* = 4.0 Hz), 125.62, 124.79, 123.18 (q, *J* = 272.6 Hz), 121.19, 116.55, 110.63 ppm. HRMS (ESI) Calcd for $[C_{16}H_9ClF_3NO+H]^+$: 324.0398, Found: 324.0391.

(2-Chloro-4-nitrophenyl)(1H-indol-1-yl)methanone (S26)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (br, 1 H), 8.43 (d, *J* = 1.8 Hz, 1 H), 8.32 (d, *J* = 8.4, 1.7 Hz, 1 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.63 (d, *J* = 7.7 Hz, 1 H), 7.46 (s, 1 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 6.86 (br, 1 H), 6.69 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.88, 149.19, 140.31, 135.34, 132.77, 131.00, 129.75, 125.79, 125.63, 125.44, 125.00, 122.37, 121.29, 116.65, 111.06 ppm. HRMS (ESI) Calcd for $[C_{15}H_9ClN_2O_3+H]^+$: 300.0302, Found: 300.0304

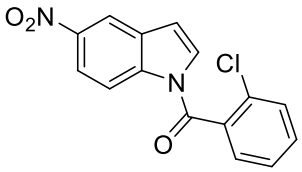
(3-(2-Bromoethyl)-1H-indol-1-yl)(2-chlorophenyl)methanone (S27)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (br, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 7.55 – 7.51 (m, 3 H), 7.49 – 7.33 (m, 3 H), 6.93 (br, 1 H), 3.62 (t, *J* = 7.4 Hz, 2 H), 3.25 (t, *J* = 7.4 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 135.79, 134.82, 131.81, 131.25, 130.64, 130.22, 128.92,

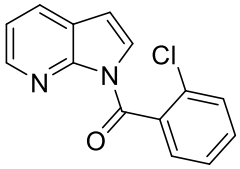
127.27, 125.68, 124.39, 124.15, 120.40, 118.77, 116.79, 31.17, 28.81 ppm. HRMS (ESI) Calcd for $[C_{17}H_{13}BrClNO+H]^+$: 361.9942, Found: 361.9939.

(2-Chlorophenyl)(5-nitro-1H-indol-1-yl)methanone (S28)



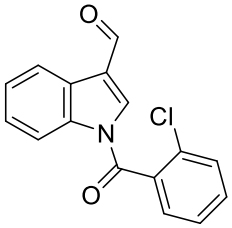
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (br, 1 H), 8.49 (s, 1 H), 8.27 (d, *J* = 8.9 Hz, 1 H), 7.56 (d, *J* = 6.8 Hz, 3 H), 7.50 – 7.46 (m, 1 H), 7.16 (d, *J* = 3.5 Hz, 1 H), 6.75 (d, *J* = 3.5 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.10, 144.70, 138.41, 133.74, 132.40, 131.27, 131.06, 130.35, 129.56, 129.05, 127.44, 120.49, 117.17, 116.62, 109.89 ppm. HRMS (ESI) Calcd for $[C_{15}H_9ClNO_2+H]^+$: 301.0374, Found: 301.0380.

(2-Chlorophenyl)(1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (S29)



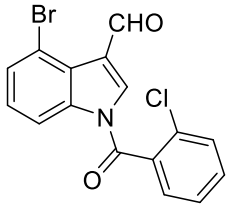
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 4.5, 1.7 Hz, 1 H), 7.87 (dd, *J* = 7.8, 1.7 Hz, 1 H), 7.70 (d, *J* = 4.5 Hz, 1 H), 7.55 – 7.50 (m, 1 H), 7.48 – 7.45 (m, 2 H), 7.41 – 7.39 (m, 1 H), 7.16 (dd, *J* = 7.8, 4.0 Hz, 1 H), 6.65 (d, *J* = 4.0 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.04, 147.98, 144.83, 135.41, 131.57, 131.43, 129.73, 129.25, 128.98, 126.94, 126.07, 123.48, 119.42, 107.21 ppm.

1-(2-Chlorobenzoyl)-1H-indole-3-carbaldehyde (S30)



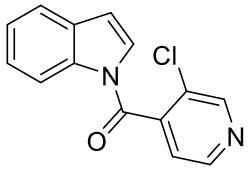
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1 H), 8.42 (d, *J* = 8.1 Hz, 1 H), 8.33 (d, *J* = 7.0 Hz, 1 H), 7.65 (s, 1 H), 7.62 – 7.57 (m, 3 H), 7.53-7.50 (m, 2 H), 7.48 (td, *J* = 7.4, 1.4 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.79, 166.17, 136.68, 136.26, 133.48, 132.60, 131.41, 130.50, 129.19, 127.54, 127.03, 126.56, 126.01, 123.21, 122.18, 116.35 ppm. HRMS (ESI) Calcd for $[C_{16}H_{10}ClNO_2+H]^+$: 284.0473, Found: 284.0479.

4-Bromo-1-(2-chlorobenzoyl)-1H-indole-3-carbaldehyde (S31)

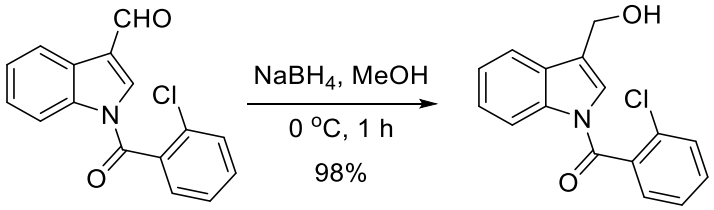


^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1 H), 8.60 (d, *J* = 8.3 Hz, 1 H), 7.78 (s, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.62 – 7.56 (m, 2 H), 7.56 – 7.52 (m, 1 H), 7.52 – 7.46 (m, 1 H), 7.37 (t, *J* = 8.1 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.84, 166.47, 137.39, 133.00, 132.79, 132.41, 131.42, 130.58, 129.90, 129.17, 127.55, 127.37, 127.11, 122.72, 116.01, 113.55 ppm. HRMS (ESI) Calcd for $[C_{16}H_9BrClNO_2+H]^+$: 361.9578, Found: 361.9574.

(3-Chloropyridin-4-yl)(1H-indol-1-yl)methanone (S32)



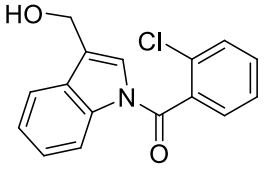
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1 H), 8.72 (d, *J* = 4.9 Hz, 1 H), 8.54 (br, 1 H), 7.62 (d, *J* = 7.7 Hz, 1 H), 7.45 (m, 2 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 6.89 (br, 1 H), 6.68 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.41, 150.45, 148.33, 141.55, 135.32, 131.01, 128.37, 125.74, 124.96, 122.28, 121.24, 116.64, 110.97 ppm. HRMS (ESI) Calcd for $[C_{14}H_9ClN_2O+H]^+$: 257.0476, Found: 257.0470.



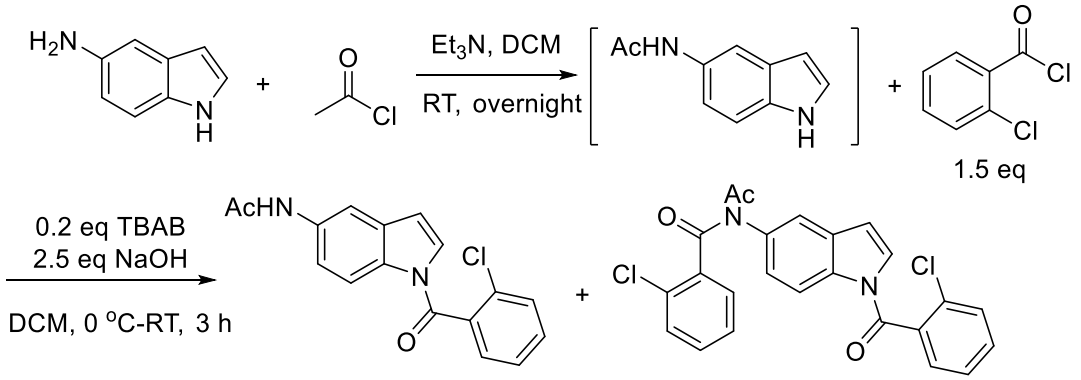
S30 **S13**

In a 50 mL round-bottom flask charged with a magnetic stirring bar, the suspension of indole derivative (2-chlorophenyl)(3-formyl-1H-indol-1-yl) methanone (1 equiv) in MeOH was cooled down to 0 °C with ice bath. $NaBH_4$ (4 equiv) was added slowly. Then the mixture was stirred for 1 h. TLC indicated the substrate was consumed completely. The mixture was quenched with water, extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over sodium sulfate. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 3:1) to afford the product in 98% yield.

(2-Chlorophenyl)(3-(hydroxymethyl)-1H-indol-1-yl)methanone (S13)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (br, 1 H), 7.51 (d, *J* = 7.7 Hz, 1 H), 7.36 (d, *J* = 5.9 Hz, 2 H), 7.33 (d, *J* = 7.4 Hz, 1 H), 7.28 (m, 2 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 6.82 (br, 1 H), 4.63 (s, 2 H), 2.10 (br, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.02, 136.05, 134.66, 131.78, 131.13, 130.16, 129.81, 128.78, 127.22, 125.76, 124.50, 123.95, 123.17, 119.48, 116.73, 57.03 ppm. HRMS (ESI) Calcd for $[C_{16}H_{12}ClNO_2+H]^+$: 286.0629, Found: 286.0636.

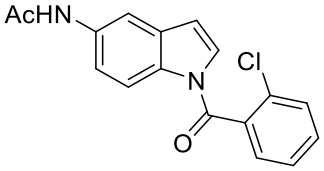


S7, 12% **S7'**, 33%

In a 50 mL round-bottom flask charged with a magnetic stirring bar, to the solution of 5-aminoindole (1 equiv) and triethylamine (1.5 equiv) in CH_2Cl_2 (10 mL), acetyl chloride (1.2 equiv) was added. The mixture was stirred at room temperature overnight. TLC indicated the substrate was consumed completely. The mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over sodium sulfate. The solvent was removed under reduced pressure to afford the product. The product was subjected to next step without further purification.

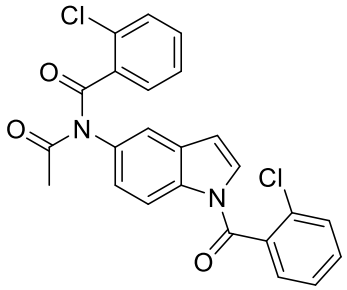
A CH_2Cl_2 solution of 2-chlorobenzoyl chloride (1.5 equiv) was added dropwise to a solution of the above indole derivative (1 equiv), NaOH (2.5 equiv) and tetrabutylammonium bromide (TBAB, 0.2 equiv) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred at 0 °C for 0.5 h. Then the mixture was warmed to room temperature. And another 0.5 equivalent of 2-chlorobenzoyl chloride was added. The mixture was stirred at room temperature for 2.5 h. Water was added to quench the reaction and extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA from 4:1 to 1:1).

***N*-(1-(2-Chlorobenzoyl)-1H-indol-5-yl)acetamide (S7)**

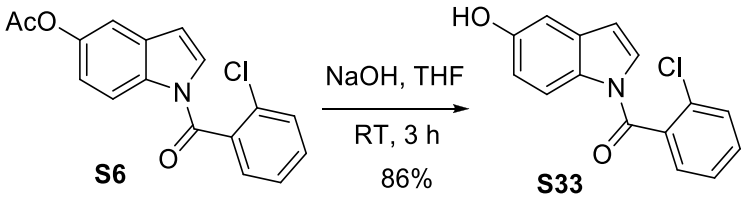


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (br, 1 H), 8.03 (d, *J* = 2.1 Hz, 1 H), 7.52-7.48 (m, 3 H), 7.43 (dd, *J* = 7.0, 1.9 Hz, 1 H), 7.40 (m, 1 H), 7.22 (d, *J* = 8.7 Hz, 1 H), 6.95 (br, 1 H), 6.57 (d, *J* = 3.6 Hz, 1 H), 2.21 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.34, 164.76, 133.61, 133.44, 131.20, 130.70, 130.64, 130.25, 129.11, 127.85, 126.41, 126.11, 116.67, 115.72, 111.46, 108.96, 23.63 ppm. HRMS (ESI) Calcd for $[C_{17}H_{13}ClN_2O_2+H]^+$: 313.0738, Found: 313.0738.

***N*-Acetyl-2-chloro-*N*-(1-(2-chlorobenzoyl)-1H-indol-5-yl)benzamide (S7′)**

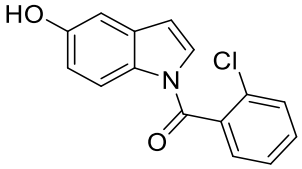


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (br, 1 H), 7.68 – 7.37 (m, 7 H), 7.29 (s, 3 H), 7.03 (s, 1 H), 6.61 (d, *J* = 3.3 Hz, 1 H), 2.40 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.98, 170.02, 165.94, 136.54, 135.15, 134.52, 134.31, 131.96, 131.89, 131.26, 130.73, 130.23, 129.69, 129.57, 128.91, 128.61, 128.02, 127.23, 126.87, 125.56, 121.19, 117.48, 109.49, 26.09 ppm. HRMS (ESI) Calcd for $[C_{24}H_{16}Cl_2N_2O_3+H]^+$: 451.0611, Found: 451.0619.

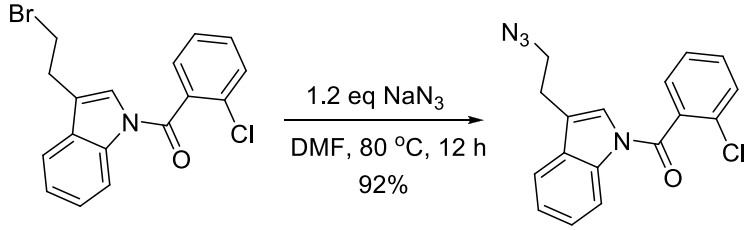


In a 50 mL round-bottom flask, indole derivative **S6** (1.0 mmol) was dissolved in THF (25 mL). A solution of the aqueous NaOH (2 M, 4 mL) was added. The mixture was stirred at room temperature for 3 h. TLC indicated the substrate was consumed. Water (10 mL) was added and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1 – 5:1).

(2-Chlorophenyl)(5-hydroxy-1H-indol-1-yl)methanone (S33)



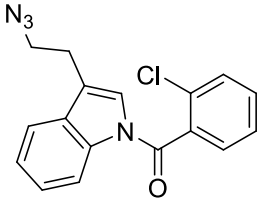
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (br, 1 H), 7.52 (s, 3 H), 7.44 (d, *J* = 6.6 Hz, 1 H), 7.02 (s, 1 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 6.51 (s, 1 H), 5.69 (br, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.86, 153.00, 134.68, 132.40, 131.70, 131.26, 130.13, 128.87, 127.55, 127.15, 117.33, 113.81, 109.71, 106.38 ppm. HRMS (ESI) Calcd for $[C_{15}H_{10}ClNO_2+H]^+$: 272.0473, Found: 272.0478.



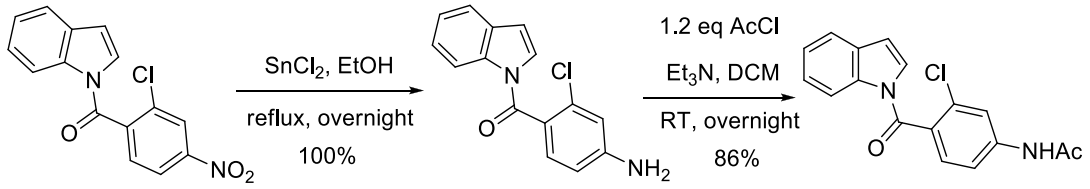
S27 **S34**

In a 50 mL round-bottom flask charged with a magnetic stirring bar, to the solution of (3-(2-bromoethyl)-1H-indol-1-yl)(2-chlorophenyl)methanone (1 equiv) and NaN_3 (1.2 equiv) in DMF (10 mL). The mixture was heated to 80 °C for 12 h. TLC indicated the substrate was consumed completely. The mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over sodium sulfate. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1) to afford the product in 92% yield.

(3-(2-Azidoethyl)-1H-indol-1-yl)(2-chlorophenyl)methanone (S34)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (br, 1 H), 7.74 – 7.50 (m, 4 H), 7.50–7.34 (m, 3 H), 6.89 (br, 1 H), 3.57 (t, *J* = 7.1 Hz, 2 H), 2.97 (t, *J* = 6.9 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.66, 135.80, 134.85, 131.74, 131.26, 130.78, 130.20, 128.89, 127.23, 125.67, 124.35, 124.07, 119.52, 118.77, 116.80, 50.61, 24.87 ppm. HRMS (ESI) Calcd for $[C_{17}H_{13}ClN_4O+H]^+$: 325.0851, Found: 325.0847.

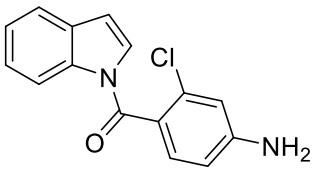


S26 **S35** **S22**

In a 50 mL Schlenk tube charged with a magnetic stirring bar, indole derivative (660 mg) and $SnCl_2$-$2H_2O$ (2.48 g, 5 eq) were added. Then, the Schlenk tube was evacuated and back-filled with argon three times. Anhydrous ethanol (20 mL) was added, the mixture was heated to reflux overnight. TLC indicated the substrate was consumed completely. The solvent was poured into ice-water. 2 M NaOH was added. Filtration over Celite and the filtrate was extracted with CH_2Cl_2, washed with brine, dried with sodium sulfate. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 3:1 to 1:1) to obtain the product in 100% yield.

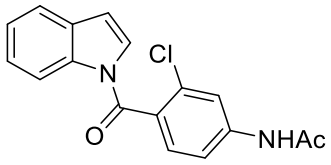
In a 50 mL round-bottom flask charged with a magnetic stirring bar, (4-amino-2-chlorophenyl)(1H-indol-1-yl)methanone (360 mg) was dissolved in DCM (20 mL), acetyl chloride (1.2 eq) and Et_3N (1.5 eq) were added. The mixture was stirred at room temperature overnight. TLC indicated the substrate was consumed completely. The reaction was quenched with water and extracted with CH_2Cl_2 (15 mL × 3), washed with brine and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 3:1 to 1:1) to obtain the product in 86% yield.

(4-Amino-2-chlorophenyl)(1H-indol-1-yl)methanone (S35)

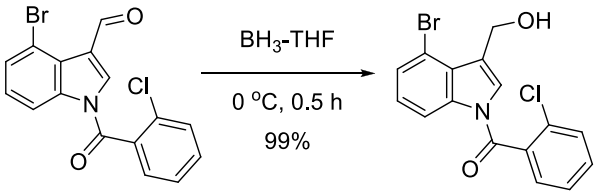


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.39 (t, *J* = 7.7 Hz, 1 H), 7.33 (dd, *J* = 7.5, 1.1 Hz, 1 H), 7.31 (d, *J* = 8.3 Hz, 1 H), 7.16 (d, *J* = 3.8 Hz, 1 H), 6.77 (d, *J* = 2.3 Hz, 1 H), 6.65 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.61 (dd, *J* = 3.8, 0.8 Hz, 1 H), 4.10 (br, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.58, 149.67, 135.57, 133.03, 131.05, 130.92, 127.26, 124.96, 123.99, 123.84, 120.88, 116.35, 115.34, 112.87, 108.90 ppm. HRMS (ESI) Calcd for $[C_{15}H_{11}ClN_2O+H]^+$: 271.0633, Found：271.0629.

***N*-(3-Chloro-4-(1H-indole-1-carbonyl)phenyl)acetamide (S22)**



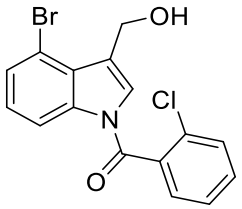
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (br, 1 H), 8.33 (s, 1 H), 7.79 (d, *J* = 2.0 Hz, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.52 (dd, *J* = 8.3, 1.8 Hz, 1 H), 7.42 - 7.39 (m, 2 H), 7.35 (td, *J* = 7.6, 0.9 Hz, 1 H), 7.02 (d, *J* = 3.7 Hz, 1 H), 6.62 (d, *J* = 3.7 Hz, 1 H), 2.24 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.19, 166.19, 141.13, 135.43, 131.96, 131.13, 129.75, 129.48, 126.77, 125.31, 124.49, 121.11, 120.72, 117.93, 116.40, 109.94, 24.60 ppm. HRMS (ESI) Calcd for $[C_{17}H_{13}ClN_2O_2+H]^+$: 313.0738, Found: 313.0732.



S31 **S19**

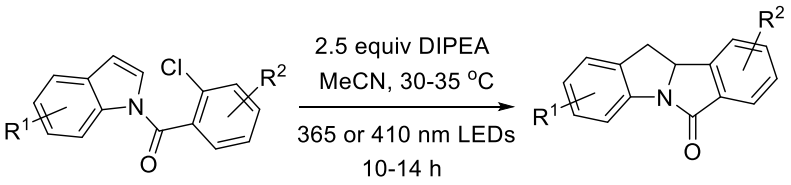
In a 50 mL round-bottom flask charged with a magnetic stirring bar, indole derivative 4-bromo-1-(2-chlorobenzoyl)-1H-indole-3-carbaldehyde (800 mg) was dissolved in THF (15 mL). The mixture was cooled to 0 °C with ice-bath, BH_3-THF (1 M, 6 mL) was added dropwise. After 0.5 h, TLC indicated the substrate was consumed completely. The mixture was quenched with MeOH. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 2:1) to afford the product respectively in 99% yield.

(4-Bromo-3-(hydroxymethyl)-1H-indol-1-yl)(2-chlorophenyl)methanone (S19)



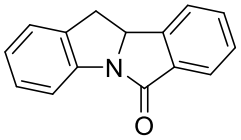
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (br, 1 H), 7.57–7.49 (m, 4 H), 7.47 - 7.44 (m, 1 H), 7.34 – 7.26 (m, 1 H, overlapped with signal of $CHCl_3$ residue), 7.04 (s, 1 H), 4.97 (s, 2 H), 2.09 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.83, 137.53, 134.26, 132.00, 131.24, 130.27, 128.87, 128.74, 128.55, 127.27, 126.65, 126.11, 123.14, 116.05, 113.55, 57.31 ppm. HRMS (ESI) Calcd for $[C_{16}H_{11}ClBrNO_2+H]^+$: 363.9734, Found: 363.9730.

General procedure for metal- and photocatalyst-free photoinduced dearomatization reaction of indole derivatives:



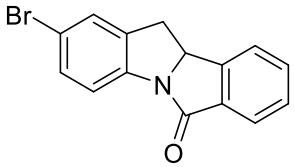
In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.5 mmol) and DIPEA (2.5 equiv) were dissolved in MeCN (5.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes. Then the mixture was irradiated at 30-35 °C with 365 nm or 410 nm LEDs for 10–14 h. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 10:1 – 1:1) to afford the product.

10b,11-Dihydro-6H-isoindolo[2,1-a]indol-6-one (1)



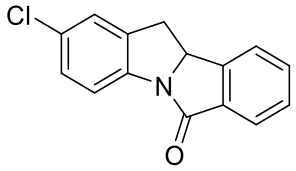
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 1 H), 7.71 (d, *J* = 7.8 Hz, 1 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.54 (d, *J* = 7.7 Hz, 2 H), 7.37–7.27 (m, 2 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 5.64 (dd, *J* = 10.3, 8,7 Hz, 1 H), 3.49 (dd, *J* = 15.1, 8.7 Hz, 1 H), 3.08 (dd, *J* = 15.2, 10.3 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.41, 146.06, 140.66, 135.97, 134.24, 132.58, 128.74, 128.03, 125.37, 124.88, 124.47, 122.87, 116.52, 65.46, 33.82 ppm. HRMS (ESI) Calcd for $[C_{15}H_{11}NO+H]^+$: 222.0913, Found: 222.0912.

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



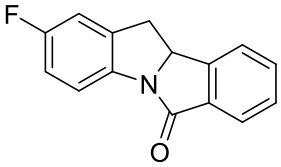
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 1 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.56 (d, *J* = 8.3 Hz, 1 H), 7.53 (t, *J* = 7.1 Hz, 2 H), 7.42 (d, *J* = 8.8 Hz, 1 H), 7.38 (s, 1 H), 5.63 (dd, *J* = 10.3, 8.7 Hz, 1 H), 3.47 (dd, *J* = 15.4, 8.7 Hz, 1 H), 3.07 (dd, *J* = 15.4, 10.4 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.38, 145.77, 139.80, 138.16, 133.82, 132.86, 130.94, 128.93, 128.52, 124.99, 122.93, 117.68, 117.22, 65.43, 33.72 ppm. HRMS (ESI) Calcd for $[C_{15}H_{10}BrNO+H]^+$: 300.0019, Found: 300.0014.

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



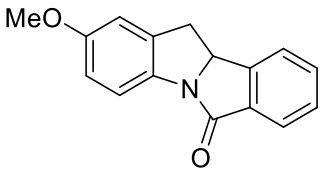
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.58 (d, *J* = 8.3 Hz, 1 H), 7.52 – 7.49 (m, 2 H), 7.24 (d, *J* = 8.3 Hz, 1 H), 7.20 (s, 1 H), 5.61 (dd, *J* = 10.3, 8.7 Hz, 1 H), 3.45 (dd, *J* = 15.4, 8.8 Hz, 1 H), 3.03 (dd, *J* = 15.4, 10.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.41, 145.82, 139.31, 137.81, 133.79, 132.84, 129.61, 128.90, 127.96, 125.66, 124.93, 122.93, 117.15, 65.49, 33.75 ppm. HRMS (ESI) Calcd for $[C_{15}H_{10}ClNO+H]^+$: 256.0524, Found:256.0519.

2-Fluoro-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (4)



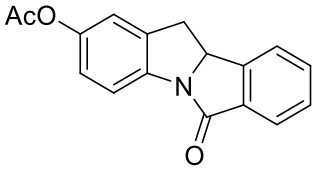
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1 H), 7.62 (d, *J* = 8.3 Hz, 1 H), 7.59 (d, *J* = 7.4 Hz, 1 H), 7.52 (s, 1 H), 7.49 (d, *J* = 7.0 Hz, 1 H), 6.97 (d, *J* = 8.4 Hz, 1 H), 6.94 (s, 1 H), 5.63 (dd, *J* = 10.4, 8.7 Hz, 1 H), 3.45 (dd, *J* = 15.5, 8.7 Hz, 1 H), 3.04 (dd, *J* = 15.3, 10.4 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.20 - 118.26 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.53, 159.99 (d, *J* = 242.8 Hz), 145.88, 137.96 (d, *J* = 8.6 Hz), 136.80 (d, *J* = 2.2 Hz), 133.89, 132.71, 128.86, 124.87, 122.89, 117.05 (d, *J* = 8.8 Hz), 114.31 (d, *J* = 23.4 Hz), 112.98 (d, *J* = 24.3 Hz), 65.76, 33.98 (d, *J* = 1.9 Hz) ppm. HRMS (ESI) Calcd for $[C_{15}H_{10}FNO+H]^+$: 240.0819, Found: 240.0814.

2-Methoxy-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (5)



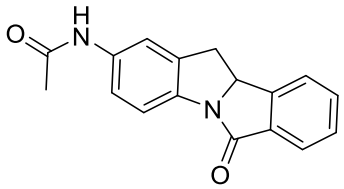
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1 H), 7.60 (t, *J* = 7.9 Hz, 2 H), 7.50 (t, *J* = 7.0 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 5.60 (dd, *J* = 10.3, 8.6 Hz, 1 H), 3.81 (s, 3 H), 3.43 (dd, *J* = 15.2, 8.6 Hz, 1 H), 3.03 (dd, *J* = 15.2, 10.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.37, 157.07, 145.93, 137.62, 134.30, 134.24, 132.38, 128.71, 124.74, 122.80, 116.85, 112.30, 112.13, 65.81, 55.74, 34.10 ppm. HRMS (ESI) Calcd for $[C_{16}H_{13}NO_2+H]^+$: 252.1019, Found:252.1014.

6-Oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-2-yl acetate (6)



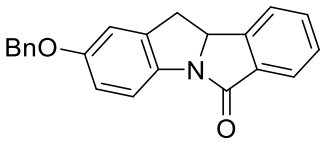
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1 H), 7.67 (d, *J* = 8.6 Hz, 1 H), 7.62 (t, *J* = 7.1 Hz, 1 H), 7.53–7.49 (m, 2 H), 7.00 (d, *J* = 7.6 Hz, 2 H), 5.64 (dd, *J* = 10.3, 8.7 Hz, 1 H), 3.47 (dd, *J* = 15.4, 8.7 Hz, 1 H), 3.07 (dd, *J* = 15.3, 10.3 Hz, 1 H), 2.31 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.84, 168.44, 147.36, 145.93, 138.48, 137.35, 133.94, 132.72, 128.84, 124.91, 122.89, 120.93, 119.22, 116.77, 65.72, 33.90, 21.10 ppm. HRMS (ESI) Calcd for $[C_{17}H_{13}NO_3+H]^+$: 280.0968, Found: 280.0964.

***N*-(6-Oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-2-yl)acetamide (7)**



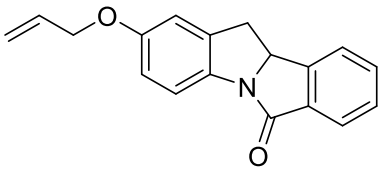
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 1 H), 7.77 (s, 1 H), 7.63-7.61 (m, 2 H), 7.53 (d, *J* = 7.1 Hz, 2 H), 7.37 (s, 1 H), 7.09 (d, *J* = 7.7 Hz, 1 H), 5.63 (dd, *J* = 10.3, 8.6 Hz, 1 H), 3.48 (dd, *J* = 15.3, 8.6 Hz, 1 H), 3.06 (dd, *J* = 15.3, 10.3 Hz, 1 H), 2.20 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.57, 168.47, 146.00, 137.02, 136.92, 134.83, 134.04, 132.65, 128.79, 124.77, 122.94, 119.47, 118.20, 116.36, 65.77, 33.95, 24.50 ppm. HRMS (ESI) Calcd for $[C_{17}H_{14}N_2O_2+H]^+$: 279.1128, Found: 279.1124.

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



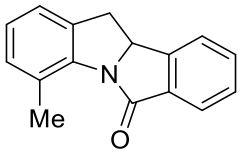
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1 H), 7.65–7.56 (m, 2 H), 7.53–7.49 (m, 2 H), 7.46–7.39 (m, 4 H), 7.35 (d, *J* = 7.0 Hz, 1 H), 6.90 (d, *J* = 7.1 Hz, 2 H), 5.60 (dd, *J* = 10.3, 8.6 Hz, 1 H), 5.06 (s, 2 H), 3.42 (dd, *J* = 15.3, 8.6 Hz, 1 H), 3.03 (dd, *J* = 15.2, 10.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.41, 156.22, 145.94, 137.66, 136.98, 134.45, 134.27, 132.42, 128.73, 128.62, 128.01, 127.46, 124.76, 122.81, 116.86, 113.51, 113.14, 70.56, 65.82, 34.08 ppm. HRMS (ESI) Calcd for $[C_{22}H_{17}NO_2+H]^+$: 328.1332, Found: 328.1326.

2-(Allyloxy)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (9)



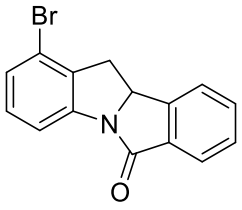
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1 H), 7.61 (t, *J* = 7.1 Hz, 1 H), 7.59 (t, *J* = 8.1 Hz, 1 H), 7.52–7.49 (m, 2 H), 6.88–6.78 (m, 2 H), 6.06 (ddt, *J* = 17.3, 10.5, 2.2 Hz, 1 H), 5.60 (dd, *J* = 10.2, 8.7 Hz, 1 H), 5.42 (dd, *J* = 17.2, 1.7 Hz, 1 H), 5.30 (dd, *J* = 10.4, 1.5 Hz, 1 H), 4.53 (d, *J* = 2.2 Hz, 2 H), 3.43 (dd, *J* = 15.2, 8.6 Hz, 1 H), 3.04 (dd, *J* = 15.2, 10.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.38, 156.03, 145.93, 137.58, 134.39, 134.29, 133.26, 132.39, 128.72, 124.76, 122.79, 117.71, 116.83, 113.37, 113.01, 69.38, 65.80, 34.09 ppm. HRMS (ESI) Calcd for $[C_{18}H_{15}NO_2+H]^+$: 278.1176, Found: 278.1171.

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



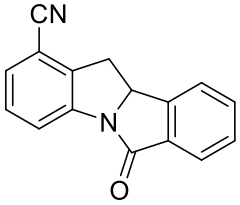
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1 H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.43 – 7.40 (m, 2 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 6.97 (d, *J* = 6.9 Hz, 1 H), 6.92 (d, *J* = 7.4 Hz, 1 H), 5.46 (dd, *J* = 10.4, 8.2 Hz, 1 H), 3.25 (dd, *J* = 14.9, 8.1 Hz, 1 H), 2.87 (dd, *J* = 14.8, 10.7 Hz, 1 H), 2.60 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.09, 144.68, 139.18, 136.50, 133.09, 131.34, 129.07, 127.67, 127.61, 124.26, 123.66, 121.70, 121.36, 65.86, 33.74, 18.65 ppm. HRMS (ESI) Calcd for $[C_{16}H_{13}NO+H]^+$:236.1070, Found: 236.1066.

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



1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1 H), 7.66–7.60 (m, 2 H), 7.54–7.50 (m, 2 H), 7.22 (d, J = 8.0 Hz, 1 H), 7.18 (d, J = 7.8 Hz, 1 H), 5.64 (dd, J = 10.1, 9.0 Hz, 1 H), 3.54 (dd, J = 15.8, 9.0 Hz, 1 H), 3.04 (dd, J = 15.8, 10.1 Hz, 1 H); 13C NMR (126 MHz, $CDCl_3$) δ 168.75, 145.95, 141.76, 136.44, 133.66, 132.96, 129.66, 128.91, 127.36, 125.00, 122.96, 119.50, 115.16, 64.45, 35.13 ppm. HRMS (ESI) Calcd for [C15H10BrNO+H]+: 300.0019, Found: 300.0015.

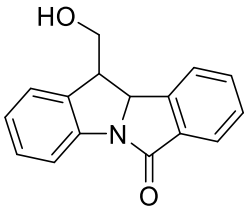
6-Oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indole-1-carbonitrile (12)



.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1 H), 7.86 (d, *J* = 8.1 Hz, 1 H), 7.67 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.56 (t, *J* = 8.0 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 7.33 (dd, *J* = 7.8, 1.1 Hz, 1 H), 5.71 (dd, *J* = 10.2, 8.9 Hz, 1 H), 3.73 (dd, *J* = 16.2, 8.9 Hz, 1 H), 3.21 (dd, *J* = 16.2, 10.2 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.76, 145.67, 141.74, 140.24, 133.36, 133.25, 129.19, 129.11, 127.29, 125.15, 123.14, 120.45, 116.80, 109.60, 64.83, 33.51 ppm. HRMS (ESI) Calcd for $[C_{16}H_{10}N_2O+H]^+$: 247.0866, Found: 247.0862.

11-(Hydroxymethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (13)

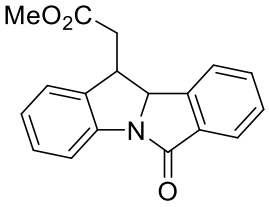


trans :*cis* = 4.0:1

Major (*trans*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.24 (t, *J* = 7.6 Hz, 1 H), 7.14 (d, *J* = 7.4 Hz, 1 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 5.42 (d, *J* = 9.2 Hz,1 H), 4.37 (dd, *J* = 10.7, 4.6 Hz, 1 H), 4.06 (dd, *J* = 10.7, 8.5 Hz, 1 H), 3.47 (td, *J* = 8.9, 4.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.91, 145.99, 140.63, 136.33, 133.69, 132.75, 128.69, 128.44, 124.64, 124.47, 124.30, 124.15, 116.50, 70.39, 63.59, 48.46 ppm.

Minor (*cis*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 7.59 (d, *J* = 6.7 Hz, 2 H), 7.34 (d, *J* = 7.4 Hz, 1 H), 7.29 (d, *J* = 8.5 Hz, 1 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 5.58 (d, *J* = 8.1 Hz, 1 H), 3.69 (dt, *J* = 8.1, 6.1 Hz, 1 H), 3.55 (br, 1 H), 3.45 – 3.40 (m, 1 H), 3.21 (dd, *J* = 11.2, 6.1 Hz, 1 H), 2.44 (s, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.28, 142.66, 139.88, 136.84, 134.86, 132.29, 128.83, 128.78, 126.06, 124.71, 124.68, 124.21, 116.38, 67.60, 62.97, 45.34 ppm. HRMS (ESI) Calcd for $[C_{16}H_{13}NO_2+H]^+$: 252.1019, Found:252.1015.

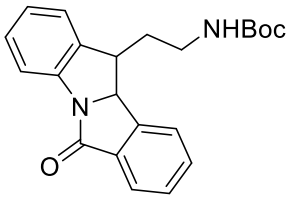
Methyl 2-(6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)acetate (14)



trans :cis = 12.8 :1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.59 (t, *J* = 7.4 Hz, 1 H), 7.55 (d, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.29 (t, *J* = 7.6 Hz, 1 H), 7.16 (d, *J* = 7.5 Hz, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 5.31 (d, *J* = 9.3 Hz, 1 H), 3.81 (s, 3 H), 3.76 (dd, *J* = 7.7, 5.6 Hz, 1 H), 3.12 (dd, *J* = 15.9, 5.6 Hz, 1 H), 2.96 (dd, *J* = 15.9, 7.7 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.15, 168.42, 145.08, 140.27, 138.09, 133.85, 132.74, 128.98, 128.52, 124.79, 124.66, 124.01, 123.26, 116.49, 71.03, 52.15, 42.73, 37.76 ppm. HRMS (ESI) Calcd for $[C_{18}H_{15}NO_3+H]^+$: 294.1125, Found: 294.1119.

***tert*-Butyl (2-(6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)ethyl)carbamate (15)**



trans :cis = 3.3 :1

Major (*trans*):

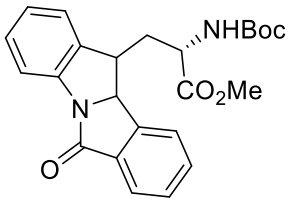
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.52 – 7.49 (m, 2 H), 7.39 (t, *J* = 7.2 Hz, 1 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 7.06 (d, *J* = 7.4 Hz, 1 H), 6.89 (t, *J* = 7.3 Hz, 1 H), 5.12 (d, *J* = 9.4 Hz, 1 H), 5.05 (d, *J* = 6.0 Hz, 1 H), 3.47 – 3.41 (m, 2 H), 3.17 (dt, *J* = 13.9, 6.6 Hz, 1 H), 2.29 – 2.22 (m, 1 H), 2.19 – 1.99 (m, 1 H), 1.38 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.35, 156.06, 145.30, 140.20, 139.27, 134.00, 132.79, 128.88, 128.10, 124.87, 124.65, 124.13, 123.04, 116.40, 79.53, 71.09, 43.69, 39.11, 28.48, 28.42 ppm.

Minor (*cis*):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz,1 H), 7.61 (d, *J* = 7.7 Hz, 1 H), 7.52 – 7.49 (m, 2 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.27 (d, *J* = 7.8 Hz, 1 H), 7.21 (t, *J* = 7.7 Hz, 1 H), 7.00 (t, *J* = 7.2 Hz, 1 H), 5.44 (d, *J* = 7.7 Hz, 1 H), 4.50 (t, *J* = 6.0 Hz, 1 H), 3.07 (q, *J* = 7.2 Hz, 1 H), 2.88 (ddd, *J* = 14.6, 10.6, 5.2 Hz, 1 H), 2.19 – 1.99 (m, 2 H), 1.32 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.29, 155.99, 142.46, 139.06, 138.94, 135.28, 132.26, 128.50, 126.17, 124.77, 124.45, 116.70, 79.33, 69.04, 41.71, 40.49, 37.38, 32.09, 28.42 ppm

HRMS (ESI) Calcd for $[C_{22}H_{24}N_2O_3+H]^+$: 365.1869, Found: 365.1853.

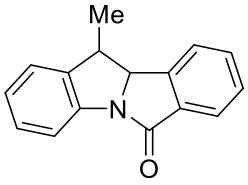
Methyl (2*S*)-2-((tert-butoxycarbonyl)amino)-3-(6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)propanoate (16)



trans :cis = 1.4 :1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.5, 3.0 Hz, 0.5 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.69 (t, *J* = 8.2 Hz, 0.5 H), 7.64 – 7.56 (m, 4.66 H), 7.55 – 7.47 (m, 3 H), 7.43 (p, *J* = 6.2 Hz, 3 H), 7.30 (t, *J* = 8.6 Hz, 0.5 H), 7.24 (t, *J* = 7.7 Hz, 0.5 H), 7.19 (t, *J* = 6.1 Hz, 2 H), 7.13 (t, *J* = 7.5 Hz, 1.5 H), 7.07 (d, *J* = 7.4 Hz, 1 H), 6.97 – 6.90 (m, 2 H), 6.01 (d, *J* = 8.6 Hz, 0.5 H), 5.83 (d, *J* = 8.6 Hz, 1 H), 5.52 (dd, *J* = 7.8, 5.6 Hz, 0.5 H), 5.26 (dd, *J* = 10.0, 6.6 Hz, 2 H), 4.69 (td, *J* = 8.6, 5.8 Hz, 1 H), 4.63 – 4.54 (m, 1 H), 4.32 (t, *J* = 7.4 Hz, 0.5 H), 3.72 (s, 3 H), 3.70 (s, 3 H), 3.64 – 3.54 (m, 0.5 H), 3.50 – 3.38 (m, 1.5 H), 3.38 – 3.30 (m, 1 H), 2.58 (dt, *J* = 12.7, 6.4 Hz, 1.5 H), 2.51 (ddd, *J* = 14.9, 11.0, 4.1 Hz, 1.5 H), 2.40 – 2.31 (m, 2 H), 1.41 (s, 6 H), 1.37 (s, 12 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.19, 172.83, 168.59, 168.31, 155.94, 155.59, 145.23, 145.05, 140.12, 140.08, 139.13, 138.68, 133.85, 133.70, 132.88, 132.68, 128.82, 128.17, 128.07, 124.75, 124.68, 124.56, 124.36, 124.05, 123.48, 123.10, 116.30, 80.18, 80.15, 71.36, 71.01, 68.89, 60.40, 52.60, 52.52, 43.06, 42.72, 36.05, 35.39, 28.32, 28.27, 28.25, 21.01, 14.17 ppm HRMS (ESI) Calcd for $[C_{24}H_{26}N_2O_5+H]^+$: 423.1914, Found: 423.1907. $[\alpha]^{25}_D$ = +24.9 (c 1.0, $CHCl_3$).

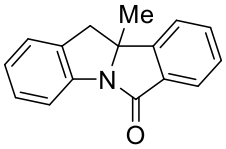
11-Methyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (17)



trans :cis = 5.9 :1

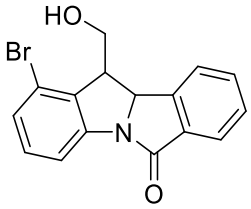
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1 H), 7.56 (d, *J* = 7.7 Hz, 1 H), 7.50 (t, *J* = 7.2 Hz, 1 H), 7.44 (d, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.3 Hz, 1 H), 7.19 (t, *J* = 7.9 Hz, 1 H), 7.09 (d, *J* = 7.4 Hz, 1 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 5.01 (d, *J* = 9.8 Hz, 1 H), 3.27–3.13 (m, 1 H), 1.60 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.85, 144.31, 139.96, 139.08, 133.10, 131.45, 127.79, 126.98, 123.85, 123.56, 122.58, 121.32, 115.43, 71.93, 40.29, 15.70 ppm. HRMS (ESI) Calcd for $[C_{16}H_{13}NO+H]^+$: 236.1070, Found: 236.1066.

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



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 1 H), 7.62 (t, *J* = 8.0 Hz, 1 H), 7.55–7.44 (m, 2 H), 7.32 (t, *J* = 7.7 Hz, 1 H), 7.25 (d, *J* = 7.4 Hz, 1 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 3.19 (d, *J* = 15.2 Hz, 1 H), 3.12 (d, *J* = 15.1 Hz, 1 H), 1.66 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.24, 151.31, 139.52, 135.82, 132.86, 132.65, 128.62, 128.01, 125.70, 124.97, 124.57, 121.95, 117.27, 71.94, 40.38, 27.21 ppm. HRMS (ESI) Calcd for $[C_{16}H_{13}NO+H]^+$: 236.1070, Found: 236.1066.

1-Bromo-11-(hydroxymethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (19)



trans:cis = 2.7:1

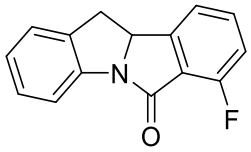
Major (*trans*):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* = 7.5 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.58 (t, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.18 (d, *J* = 7.5 Hz, 1 H), 7.08 (t, *J* = 7.1 Hz, 1 H), 5.48 (d, *J* = 9.2 Hz, 1 H), 4.42 (dd, *J* = 10.6, 4.5 Hz, 1 H), 4.22 – 3.95 (m, 1 H), 3.59 – 3.52 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.80, 145.94, 140.91, 136.03, 133.83, 132.71, 128.71, 128.58, 124.59, 124.57, 124.17, 124.03, 116.65, 70.21, 63.75, 48.53 ppm.

Minor (*cis*):

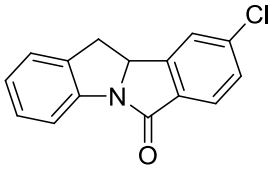
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 7.3 Hz, 1 H), 7.27 (s, 1 H), 7.24 (d, *J* = 7.7 Hz, 1 H), 5.63 (d, *J* = 8.0 Hz, 1 H), 3.80 (ddd, *J* = 8.3, 5.8, 2.8 Hz, 1 H), 3.66 (dd, *J* = 11.5, 2.9 Hz, 1 H), 3.60 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.18, 142.61, 141.75, 135.57, 134.93, 132.44, 130.51, 128.97, 127.93, 124.89, 124.36, 119.68, 115.36, 67.25, 60.56, 47.00 ppm. HRMS (ESI) Calcd for $[C_{16}H_{12}BrNO_2+H]^+$: 330.0124, Found: 330.0121.

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



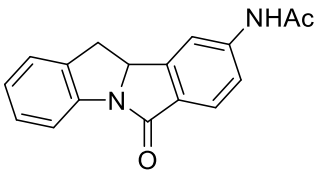
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1 H), 7.60–7.55 (m, 1 H), 7.30 (d, *J* = 7.5 Hz, 1 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 7.11 (t, *J* = 8.8 Hz, 1 H), 7.07(t, *J* = 7.4 Hz, 1 H), 5.58 (dd, *J* = 10.3, 8.8 Hz, 1 H), 3.46 (dd, *J* = 15.2, 8.8 Hz, 1 H), 3.05 (dd, *J* = 15.1, 10.3 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.18 (dd, *J* = 9.0, 4.7 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.24 (d, *J* = 2.3 Hz), 159.36 (d, *J* = 261.9 Hz), 148.68 (d, *J* = 2.7 Hz), 140.43, 135.68 (d, *J* = 2.0 Hz), 134.81 (d, *J* = 7.7 Hz), 128.00 (d, *J* = 2.2 Hz), 125.40, 124.67, 121.23 (d, *J* = 12.2 Hz), 119.00 (d, *J* = 3.8 Hz), 116.56 (d, *J* = 2.5 Hz), 116.04 (d, *J* = 19.3 Hz), 65.09, 33.79 ppm. HRMS (ESI) Calcd for $[C_{15}H_{10}FNO+H]^+$: 240.0819, Found: 240.0814.

9-Chloro-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (21)



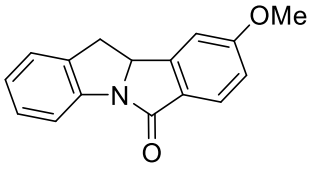
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 7.54 (s, 1 H), 7.51 (d, *J* = 8.1 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.27 (d, *J* = 10.4 Hz, 1 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 5.61 (dd, *J* = 10.4, 8.7 Hz, 1 H), 3.47 (dd, *J* = 15.1, 8.7 Hz, 1 H), 3.09 (dd, *J* = 15.0, 10.4 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.28, 147.48, 140.39, 139.00, 135.57, 132.71, 129.38, 128.14, 126.04, 125.44, 124.71, 123.42, 116.50, 64.99, 33.64 ppm. HRMS (ESI) Calcd for $[C_{15}H_{10}ClNO+H]^+$: 256.0524, Found:256.0519.

***N*-(6-Oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-9-yl)acetamide (22)**



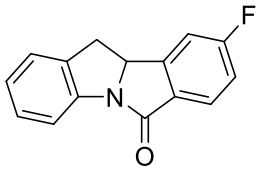
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1 H), 8.07 (s, 1 H), 7.70 (d, *J* = 8.3 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 1 H), 7.46 (d, *J* = 7.8 Hz, 1 H), 7.31 (d, *J* = 7.4 Hz, 1 H), 7.26 (t, *J* = 7.7 Hz, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 5.70 (dd, *J* = 10.1, 8.9 Hz, 1 H), 3.55 (dd, *J* = 15.5, 8.9 Hz, 1 H), 2.96 (dd, *J* = 15.5, 10.1 Hz, 1 H), 2.12 (s, 3 H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.54, 168.29, 148.52, 144.12, 140.98, 136.87, 127.93, 127.69, 126.15, 125.32, 124.67, 119.63, 116.14, 113.38, 65.27, 33.72, 24.67 ppm. HRMS (ESI) Calcd for $[C_{17}H_{14}N_2O_2+H]^+$: 279.1128, Found: 279.1122.

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



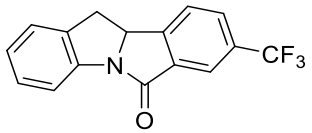
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 7.8 Hz, 1 H), 7.31 (d, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 7.4 Hz, 1 H), 7.08 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.03 (dd, *J* = 8.4, 2.2 Hz, 1 H), 7.00 (d, *J* = 2.3 Hz, 1 H), 5.58 (dd, *J* = 10.3, 8.8 Hz, 1 H), 3.93 (s, 3 H), 3.46 (dd, *J* = 15.2, 8.8 Hz, 1 H), 3.09 (dd, *J* = 15.1, 10.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.65, 163.70, 148.63, 141.03, 135.58, 128.01, 126.47, 126.34, 125.28, 124.22, 116.43, 115.17, 107.80, 65.03, 55.76, 33.85 ppm. HRMS (ESI) Calcd for $[C_{16}H_{13}NO_2+H]^+$: 252.1019, Found: 252.1015.

9-Fluoro-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (24)



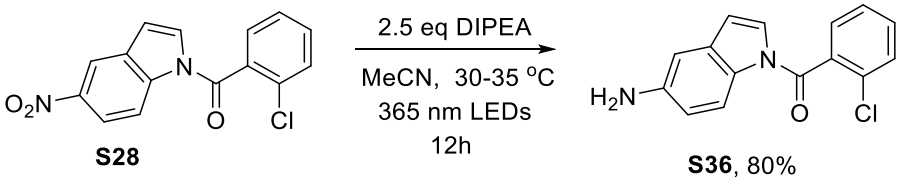
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.84 (m, 1 H), 7.68 (d, *J* = 7.8 Hz, 1 H), 7.32 (d, *J* = 7.7 Hz, 1 H), 7.26 (d, *J* = 7.4 Hz, 1 H), 7.21 (t, *J* = 8.0 Hz, 2 H), 7.09 (td, *J* = 7.5, 1.1 Hz, 1 H), 5.59 (dd, *J* = 10.3, 8.8 Hz, 1 H), 3.47 (dd, *J* = 15.1, 8.8 Hz, 1 H), 3.08 (dd, *J* = 15.1, 10.3 Hz, 1 H); ^{19}F NMR-decoupling (376 MHz, $CDCl_3$) δ -105.56; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.41, 164.73 (d, *J* = 253.2 Hz), 147.45 (d, *J* = 9.8 Hz), 139.49, 134.47, 129.12 (d, *J* = 2.3 Hz), 127.06, 125.90 (d, *J* = 10.0 Hz), 124.36, 123.55, 115.50 (d, *J* = 23.5 Hz), 115.39, 109.35 (d, *J* = 24.0 Hz), 63.91 (d, *J* = 2.7 Hz), 32.60 ppm. HRMS (ESI) Calcd for $[C_{15}H_{10}FNO+H]^+$: 240.0819, Found: 240.0816.

8-(Trifluoromethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (25)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1 H), 7.89 (d, *J* = 7.9 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 1 H), 7.28 (d, *J* = 7.4 Hz, 1 H), 7.12 (td, *J* = 7.5, 1.1 Hz, 1 H), 5.68 (dd, *J* = 10.4, 8.7 Hz, 1 H), 3.53 (dd, *J* = 15.2, 8.7 Hz, 1 H), 3.10 (dd, *J* = 15.1, 10.4 Hz, 1 H); ^{19}F NMR decoupling (376 MHz, $CDCl_3$) δ -62.38; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.64, 148.04, 139.11, 134.52, 134.12, 130.57 (q, *J* = 33.0 Hz), 128.34 (q, *J* = 3.5

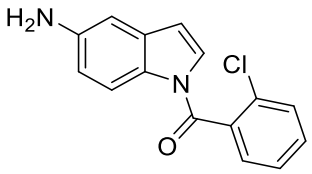
Hz), 127.18, 124.46, 123.89, 122.64 (q, *J* = 272.6 Hz), 122.56, 121.07 (q, *J* = 4.0 Hz), 115.54, 64.40, 32.52 ppm. HRMS (ESI) Calcd for $[C_{16}H_9F_3NO+H]^+$: 290.0787, Found: 290.0783.



S28 **S36**, 80%

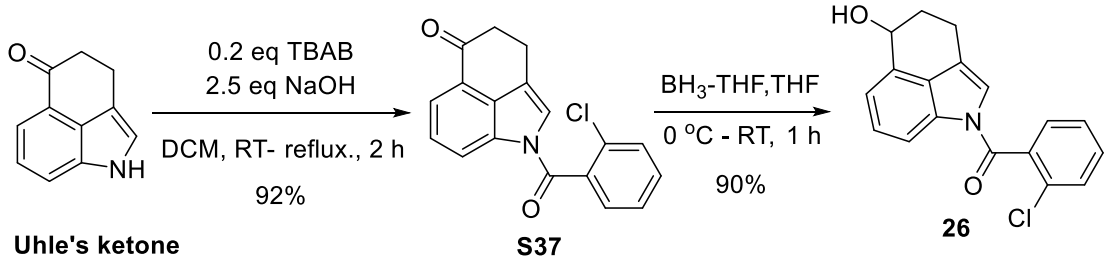
In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.2 mmol) and DIPEA (80 μL, 2.5 equiv) were dissolved in MeCN (2.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 2:1) to give the product (80%).

(5-Amino-1H-indol-1-yl)(2-chlorophenyl)methanone (**S36**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (br, 1 H), 7.51 (t, *J* = 7.2 Hz, 3 H), 7.45 – 7.38 (m, 1 H), 6.86 (d, *J* = 1.8 Hz, 2 H), 6.78 (d, *J* = 7.9 Hz, 1 H), 6.45 (d, *J* = 3.5 Hz, 1 H), 3.50 (br, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.43, 143.57, 134.96, 132.32, 131.52, 131.26, 130.06, 129.26, 128.87, 127.15, 127.08, 117.23, 114.10, 109.50, 105.97 ppm. HRMS (ESI) Calcd for $[C_{15}H_{11}ClN_2O+H]^+$: 271.0633, Found: 271.0630.

Modification of complex molecules

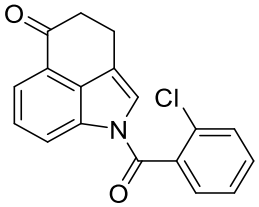


Scheme S4: Synthesis of compound 26

A CH_2Cl_2 solution of 2-chlorobenzoyl chloride (1.5 equiv) was added dropwise to a solution of the Uhle's ketone (1 equiv), which was synthesized accord to the reported peocedure[11], NaOH (2.5 equiv) and tetrabutylammonium bromide (TBAB, 0.2 equiv) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred at 0 ℃ for 0.5 h. Then the mixture was warmed to room temperature. Another 0.5 equivalent of 2-chlorobenzoyl chloride was added. The mixture was heated to reflux for 1 h. Water was added to quench the reaction and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1) to afford the product in 92% yield.

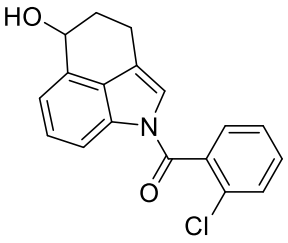
In a 50 mL Schlenk tube charged with a magnetic stirring bar, indole 1-(2-chlorobenzoyl)-3,4-dihydrobenzo[cd]indol-5(1H)-one (190 mg) was dissolved in THF (10 mL). The mixture was cooled to 0 ℃ with ice-bath, BH_3•THF (1 M, 2 mL) was added dropwise. After 0.5 h, TLC indicated the substrate was consumed completely. The mixture was quenched with MeOH. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 2:1) to afford the product respectively in 90% yield.

1-(2-Chlorobenzoyl)-3,4-dihydrobenzo[cd]indol-5(1H)-one (S37)

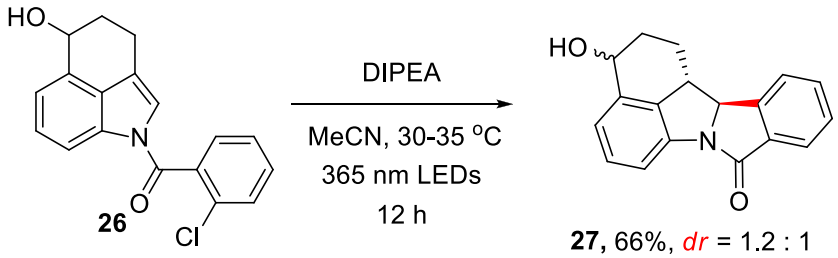


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (br, 1 H), 7.81 (d, *J* = 7.4 Hz, 1 H), 7.65–7.53 (m, 3 H), 7.52–7.44 (m, 2 H), 6.82 (br, 1 H), 3.19 (t, *J* = 7.5 Hz, 2 H), 2.90 (t, *J* = 7.5 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.90, 165.95, 135.40, 134.52, 134.20, 131.94, 131.22, 130.25, 128.82, 127.29, 126.27, 121.90, 120.24, 117.54, 38.31, 20.41 ppm. HRMS (ESI) Calcd for $[C_{18}H_{12}ClNO_2+H]^+$: 310.0629, Found: 310.0627.

(2-Chlorophenyl)(5-hydroxy-4,5-dihydrobenzo[cd]indol-1(3H)-yl)methanone (26)

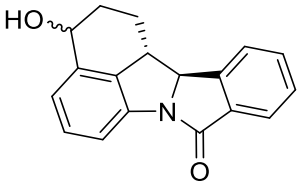


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (br, 1 H), 7.59–7.47 (m, 3 H), 7.48–7.31 (m, 3 H), 6.62 (br, 1 H), 5.09 (d, *J* = 5.1 Hz, 1 H), 2.94 (dt, *J* = 14.3, 6.4 Hz, 1 H), 2.83–2.71 (m, 1 H), 2.14 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.91, 135.03, 133.84, 133.63, 131.59, 131.18, 130.12, 129.54, 129.33, 128.80, 127.15, 126.16, 120.51, 119.75, 116.15, 67.16, 32.65, 18.04 ppm. HRMS (ESI) Calcd for $[C_{18}H_{14}ClNO_2+H]^+$: 312.0786, Found: 312.0790.



In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.5 mmol) and DIPEA (0.2 mL, 2.5 eq) were dissolved in MeCN (5.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes. Then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 3:1, CH_2Cl_2:MeOH = 15:1) to afford the product in 66% yield.

3-Hydroxy-2,3,12b,12c-tetrahydrobenzo[cd]isoindolo[2,1-a]indol-8(1H)-one (27)

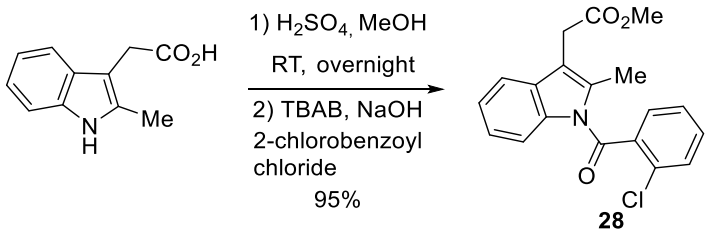


dr = 1.2 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 1 H), 7.61 (t, *J* = 7.4 Hz, 1 H), 7.56–7.47 (m, 2 H), 7.44 (d, *J* = 7.3 Hz, 1 H), 7.32 (d, *J* = 7.4 Hz, 0.6 H), 7.23 (t, *J* = 7.7 Hz, 0.7 H), 7.11 (d, *J* = 7.7 Hz, 0.7 H), 7.08 (d, *J* = 7.7 Hz, 0.55 H), 7.03 (d, *J* = 7.6 Hz, 0.55 H), 5.20 (d, *J* = 10.2 Hz, 0.55 H), 5.11 (d, *J* = 10.2 Hz, 0.5 H), 4.90 – 4.75 (m, 1 H), 2.98 – 2.89 (m, 1 H), 2.65 – 2.36 (m, 1 H), 2.32 – 2.23 (m 1.86 H), 2.09 – 1.66 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.04, 144.59, 138.23, 137.86, 137.77, 137.56, 136.52, 132.49, 128.99, 128.92, 128.85, 128.46, 125.09, 124.97, 124.07, 122.69, 122.60, 122.56, 115.86, 114.94, 73.61, 73.23, 68.05, 64.29, 43.87,

43.66, 33.87, 32.45, 26.83, 21.59 ppm. HRMS (ESI) Calcd for $[C_{28}H_{15}NO_2+H]^+$: 278.1176, Found: 278.1175.

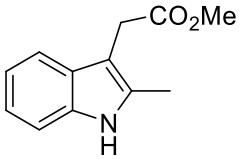
Scheme S5: Synthesis of compound 28



In a 100 mL round-bottom flask charged with a magnetic stirring bar, 2-(2-methyl-1H-indol-3-yl)acetic acid (1.89 g, 10 mmol) was dissolved in MeOH (50 mL). Then a few drops of concentrated H_2SO_4 was added. The mixture was stirred at room temperature overnight. The reaction was quenched with water, extracted with ethyl acetate (20 mL × 3), washed with brine and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was subjected to next step without purification.

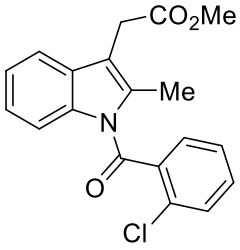
A CH_2Cl_2 solution of 2-chlorobenzoyl chloride (1.5 equiv) was added dropwise to a solution of the above indole derivative 1 equiv), NaOH (2.5 equiv) and tetrabutylammonium bromide (TBAB, 0.2 equiv) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred at 0 °C for 0.5 h. Then the mixture was warmed to room temperature. And another 0.5 equivalent of 2-chlorobenzoyl chloride was added. The mixture was stirred at room temperature for 2.5 h. Water was added to quench the reaction, and extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1, 4:1) to afford the product in 95% overall yield.

Methyl 2-(2-methyl-1H-indol-3-yl)acetate[16]

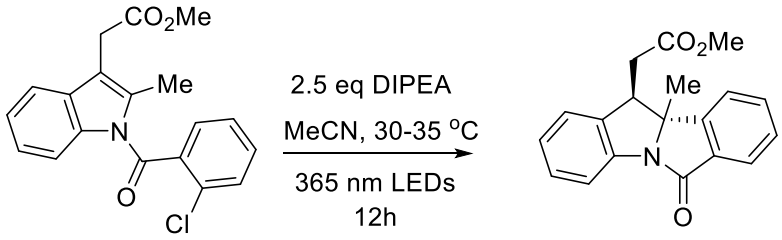


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1 H), 7.56 (dd, *J* = 6.2, 2.5 Hz, 1 H), 7.44 – 7.22 (m, 1 H), 7.21 – 7.09 (m, 2 H), 3.73 (s, 2 H), 3.70 (s, 3 H), 2.41 (s, 3 H) ppm.

Methyl 2-(1-(2-chlorobenzoyl)-2-methyl-1H-indol-3-yl)acetate (28)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61–7.47 (m, 4 H), 7.46–7.38 (m, 1 H), 7.28 (d, *J* = 8.3 Hz, 1 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 7.13 (t, *J* = 7.7 Hz, 1 H), 3.70 (s, 5 H), 2.29 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.18, 166.83, 136.37, 135.89, 134.71, 132.14, 131.79, 130.46, 130.16, 129.42, 127.45, 124.15, 123.62, 118.26, 114.62, 113.71, 52.19, 30.09, 13.45 ppm. HRMS (ESI) Calcd for $[C_{19}H_{16}ClNO_3+H]^+$: 342.0891, Found: 342.0889.

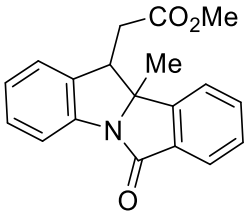


28

29, 32%
dr > 20 :1

In a 10 mL test tube with a magnetic stirring bar, indole derivative (methyl 2-(1-(2-chlorobenzoyl)-2-methyl-1H-indol-3-yl)acetate (160 mg, 0.47 mmol) and DIPEA (0.2 mL, 2.5 eq) were dissolved in MeCN (5 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes. The mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 10:1) to afford the product respectively in 32% yield.

Methyl 2-(10b-methyl-6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)acetate (29)

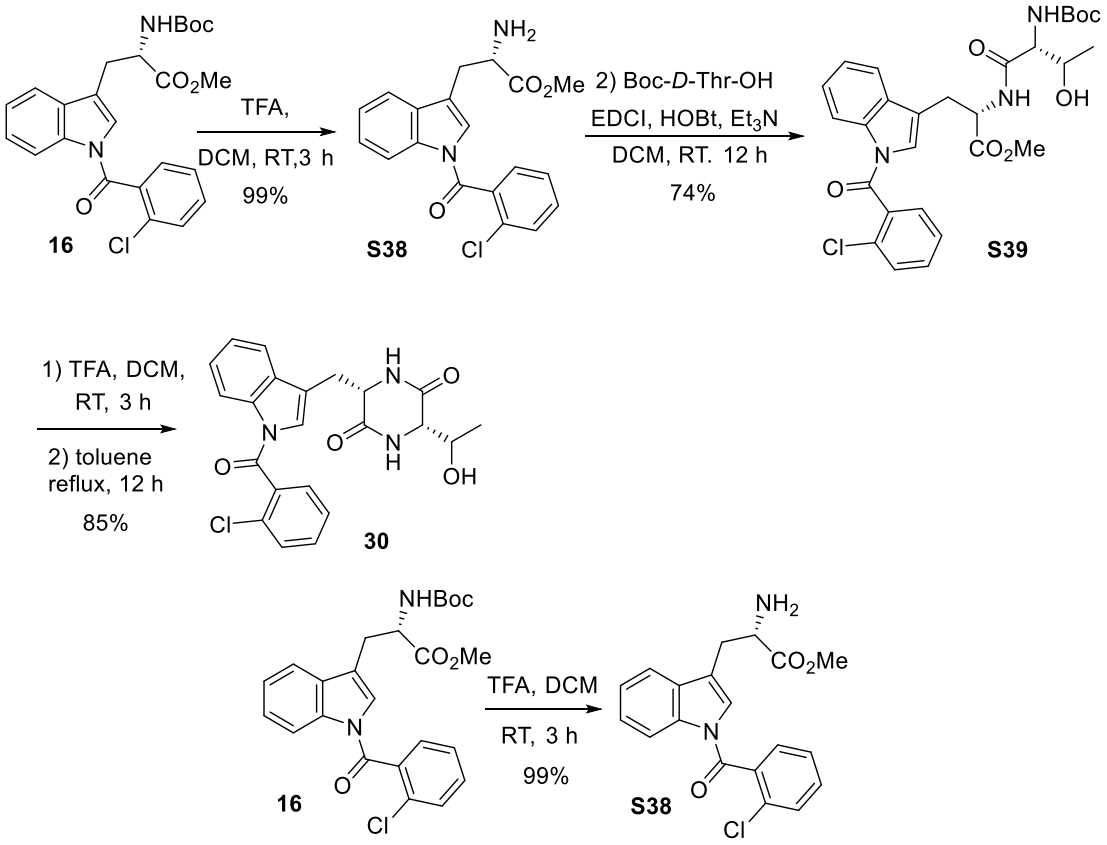


dr > 20:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1 H), 7.66 (d, *J* = 7.7 Hz, 1 H), 7.61 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.36–7.32 (dt, *J* = 7.9, m, 1 H), 7.13 (d, *J* = 4.1 Hz, 2 H), 3.82 (s, 3 H), 3.81 (t, *J* = 7.5 Hz, 1 H), 3.04 (dd, *J* = 15.6, 7.1 Hz, 1 H), 2.95 (dd, *J* = 15.6, 7.7 Hz, 1 H), 1.56 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50,

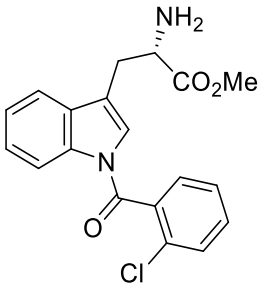
167.31, 150.18, 138.74, 138.47, 132.74, 132.70, 128.93, 128.53, 125.04, 124.83, 123.89, 122.22, 117.46, 74.86, 52.18, 46.25, 33.12, 21.53 ppm. HRMS ESI) Calcd for $[C_{19}H_{17}NO_3+H]^+$: 308.1281, Found: 308.1275.

Scheme S6: Synthesis of glioperazine C analogues

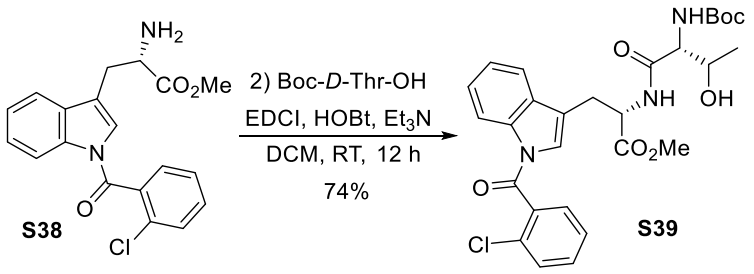


To a stirred solution of compound **16** (400 mg, 0.88 mmol) in CH_2Cl_2 (10 mL) was dropwise added TFA (4.0 mL) at 0 ℃. The solution was stirred at room temperature for 3 h. The reaction mixture was evaporated. The residue was dissolved in DCM (20 mL), washed with $NaHCO_3$, brine, dried over anhydrous Na_2SO_4 and evaporated used in the next step without further purification.

(*L*-)Methyl 1-(2-chlorobenzoyl)tryptophanate (S38)

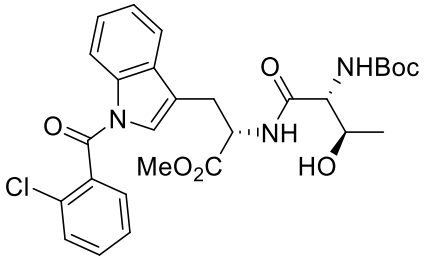


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1 H), 7.60 (d, *J* = 7.7 Hz, 1 H), 7.53–7.50 (m, 3 H), 7.49–7.42 (m, 2 H), 7.40 (d, *J* = 7.3 Hz, 1 H), 7.36 (d, *J* = 7.4 Hz, 1 H), 6.87 (br, 1 H), 3.81 (d, *J* = 6.5 Hz, 1 H), 3.68 (s, 3 H), 3.17 (dd, *J* = 14.4, 4.8 Hz, 1 H), 2.94 (dd, *J* = 14.4, 7.6 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.25, 165.63, 135.76, 134.86, 131.73, 131.17, 131.04, 130.14, 128.89, 127.23, 125.64, 124.71, 124.32, 119.04, 118.72, 116.69, 54.20, 52.10, 30.45 ppm.

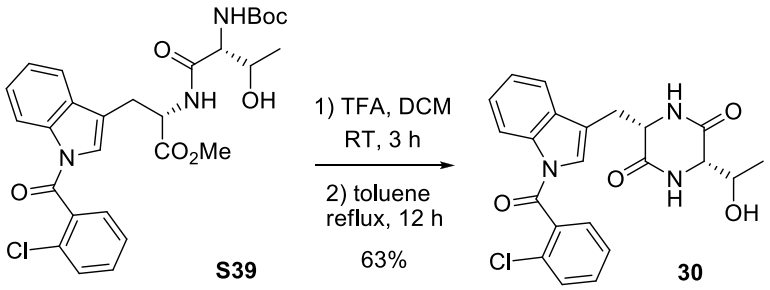


To a solution of indole derivative **S38** (230 mg, 0.64 mmol) in CH_2Cl_2 (10 mL), EDCI (150 mg, 0.77 mmol, 1.2 eq), HOBT (100 mg, 0.77 mmol, 1.2 equiv) and *N*- Boc-*D*-Thr (170 mg, 0.77 mmol, 1.2 equiv) were added at room temperature. The solution was stirred at room temperature overnight. After completion of the reaction, the solution was washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2:MeOH=100:1) to give the desired product (270 mg, 74%) as a white solid.

(*L*)-Methyl *N*-((*tert*-butoxycarbonyl)-*D*-allothreonyl)-1-(2-chlorobenzoyl)-tryptophanate (S39)

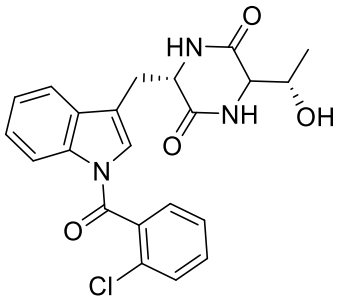


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (br, 1 H), 7.58–7.49 (m, 3 H), 7.46 (dd, *J* = 6.5, 2.2 Hz, 1 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.39 (d, *J* = 4.1 Hz, 1 H), 7.35 (d, *J* = 7.3 Hz, 1 H), 7.18 (d, *J* = 7.2 Hz, 1 H), 6.85 (br, 1 H), 5.45 (d, *J* = 7.7 Hz, 1 H), 4.86 (q, *J* = 6.5 Hz, 1 H), 4.26 (d, *J* = 5.9 Hz, 1 H), 4.01 (d, *J* = 7.5 Hz, 1 H), 3.62 (s, 3 H), 3.39–3.09 (m, 3 H), 1.40 (s, 9 H), 1.10 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.64, 171.59, 165.63, 156.45, 135.66, 134.76, 131.74, 131.17, 130.84, 130.12, 128.93, 127.21, 125.72, 124.70, 124.44, 118.78, 117.53, 116.70, 80.45, 66.68, 58.08, 52.54, 52.24, 28.22, 27.44, 18.26 ppm. HRMS (ESI) Calcd for $[C_{28}H_{32}ClN_3O_7+H]^+$: 558.2002, Found: 558.1996.

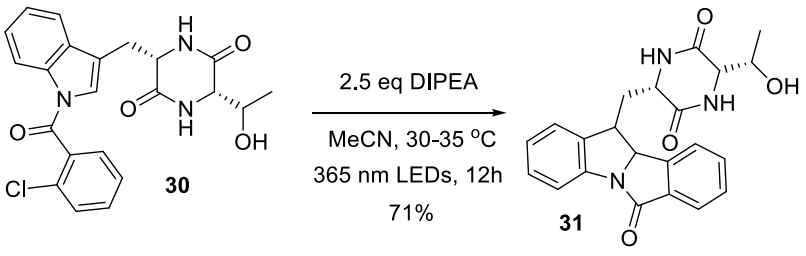


To a stirred solution of **S39** (270 mg, 0.48 mmol) in CH_2Cl_2 (10 mL) was dropwise added TFA (3.0 mL) at 0 ℃. The solution was stirred at room temperature for 3 h. The reaction mixture was evaporated and the residue was dissolved in CH_2Cl_2 (20 mL), washed with $NaHCO_3$, brine, dried over anhydrous Na_2SO_4 and evaporated used in the next step without further purification. The residue was dissolved in toluene (10 mL), and stirred under reflux 12 h with white solid precipitated out of solution. The solid was filtered and washed with Et_2O to give the product (130 mg, 63%) as a white solid.

(3*S*,6*S*)-3-((1-(2-Chlorobenzoyl)-1H-indol-3-yl)methyl)-6-((*R*)-1-hydroxyethyl)piperazine-2,5-dione (30)

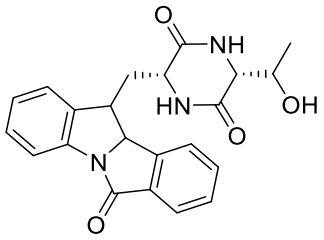


^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28 (br, 1 H), 8.03 (d, *J* = 9.1 Hz, 2 H), 7.77 (d, *J* = 7.3 Hz, 1 H), 7.72–7.65 (m, 3 H), 7.57 (td, *J* = 7.2, 1.9 Hz, 1 H), 7.39–7.33 (m, 2 H), 7.01 (br, 1 H), 4.98 (d, *J* = 5.4 Hz, 1 H), 4.20 (t, *J* = 4.6 Hz, 1 H), 3.97 (td, *J* = 7.3, 3.7 Hz, 1 H), 3.26 (t, *J* = 2.6 Hz, 1 H), 3.17 (dd, *J* = 14.9, 4.4 Hz, 1 H), 3.00 (dd, *J* = 14.8, 4.7 Hz, 1 H), 1.04 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.65, 168.63, 165.65, 135.14, 134.75, 132.75, 131.99, 130.39, 130.29, 129.56, 128.30, 126.03, 125.51, 124.51, 120.64, 118.53, 115.84, 68.65, 61.16, 53.65, 26.67, 20.30 ppm. HRMS (ESI) Calcd for [M+ MeOH+H^+] $C_{23}H_{25}ClN_3O_5$: 458.1477, Found: 458.1473. $[\alpha]^{25}_D$ = +33.5 (c 0.25, MeOH).



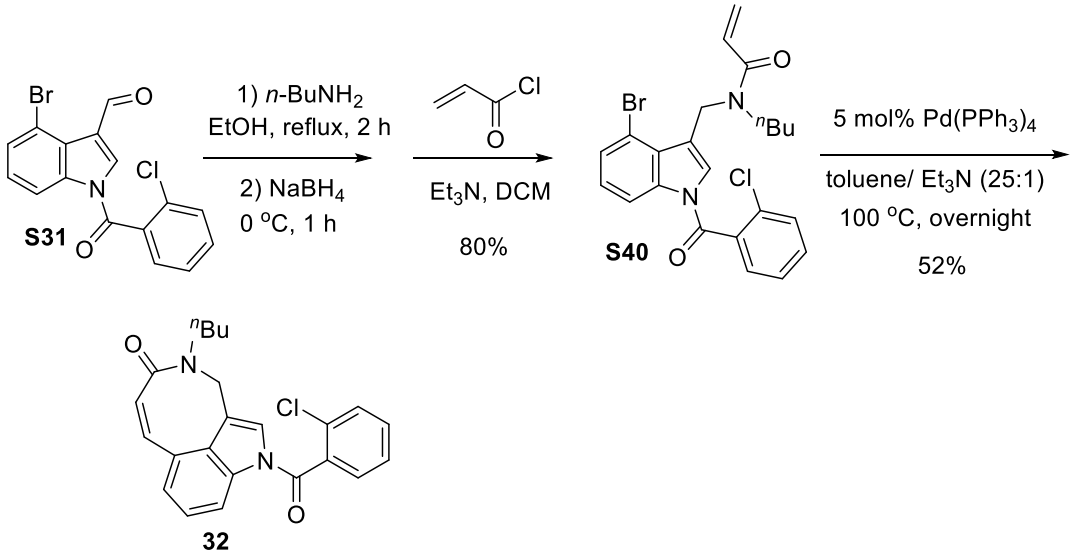
In a 10 mL test tube with a magnetic stirring bar, **30** (85.2 mg, 0.2 mmol) and DIPEA (83 μL, 0.5 mmol, 2.5 equiv) were dissolved in MeCN (4 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (CH_2Cl_2:MeOH = 50:1) to afford the product as a white solid in 71% yield (*trans* only).

(3*R*,6*R*)-3-((*R*)-1-Hydroxyethyl)-6-((6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)methyl)piperazine-2,5-dione (31)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.58 (br, 1 H), 8.39–8.28 (m, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H), 7.78 (d, *J* = 7.4 Hz, 1 H), 7.74 (d, *J* = 7.4 Hz, 1 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.51 (d, *J* = 7.4 Hz, 1 H), 7.39 (d, *J* = 7.5 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 5.46 (d, *J* = 9.4 Hz, 1 H), 4.90 (s, 1 H), 4.54 (s, 1 H), 2.93 (d, *J* = 4.9 Hz, 1 H), 2.59–2.52 (m, 1 H), 1.86 (s, 1 H), 1.16 (m, 1 H), 0.93 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 174.37, 172.59, 168.08, 146.05, 140.53, 140.09, 133.46, 133.36, 129.44, 128.34, 125.38, 125.09, 124.54, 124.14, 116.24, 70.66, 68.20, 61.06, 52.68, 43.04, 35.34, 20.46 ppm. HRMS (ESI) Calcd for $[C_{22}H_{21}N_3O_4+H]^+$: 392.1605, Found: 392.1600. $[\alpha]^{25}_D$ = +19.0 (c 0.25, MeOH).

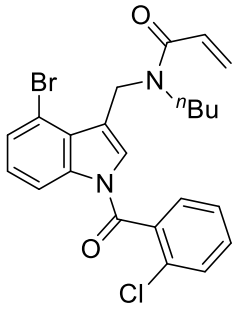
Scheme S7: Synthesis of compound **32**



In a 50 mL round-bottom flask charged with a magnetic stirring bar, to a suspension of indole derivative **S31** (1.0 equiv) in EtOH (20 mL), butan-1-amine (1.0 equiv) was added. The mixture was heated to reflux for 2 h. Then the mixture was cooled down to room temperature. $NaBH_4$ (4 equiv) was added slowly. After 1 h, the mixture was quenched with MeOH. Water was added to quench the reaction and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was subjected to next step without purification

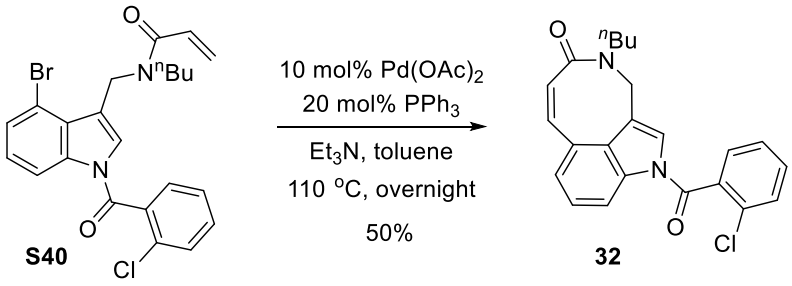
In a 50 mL round-bottom flask charged with a magnetic stirring bar, to above substrate in DCM (20 mL), acryloyl chloride (1.0 equiv) and Et_3N (1.5 equiv) were added. The mixture was stirred at room temperature overnight. The mixture was quenched with water and extracted with CH_2Cl_2 (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 4:1, 1:1) to afford the product in 80% yield.

***N*-((4-Bromo-1-(2-chlorobenzoyl)-1H-indol-3-yl)methyl)-*N*-butylacrylamide (S40)**



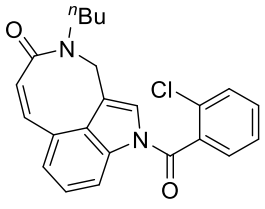
amide's rotamer 3:2

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 0.6 H), 8.36 (s, 0.4 H), 7.56 – 7.41 (m, 5 H), 7.30 (t, *J* = 8.1 Hz, 0.6 H), 7.23 (t, *J* = 8.0 Hz, 0.4 H), 6.86 (s, 0.4 H), 6.71 (s, 0.6 H), 6.55 (dd, *J* = 16.6, 10.6 Hz, 0.4 H), 6.45 (dd, *J* = 16.6, 10.2 Hz, 0.6 H), 6.34 (d, *J* = 13.4 Hz, 0.6 H), 6.30 (d, *J* = 13.4 Hz, 0.4 H), 5.68 (d, *J* = 10.7 Hz, 0.4 H), 5.63 (dd, *J* = 10.1, 3.0 Hz, 0.6 H), 5.03 (s, 2 H), 3.41 (t, *J* = 7.7 Hz, 1.2 H), 3.35 (t, *J* = 7.8 Hz, 0.8 H), 1.57 (m, 2 H), 1.32 (td, *J* = 14.7, 7.3 Hz, 2 H), 0.93 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.57, 166.43, 165.71, 165.54, 137.74, 137.36, 134.25, 132.50, 132.06, 131.20, 131.08, 130.32, 130.11, 129.21, 128.98, 128.85, 128.71, 128.58, 128.32, 128.16, 127.61, 127.46, 127.32, 126.94, 126.42, 125.98, 124.97, 120.75, 119.75, 115.96, 115.69, 113.92, 113.73, 47.57, 47.09, 46.02, 42.26, 31.72, 30.24, 20.30, 19.99, 13.91, 13.80 ppm. HRMS (ESI) Calcd for $[C_{23}H_{22}BrClN_2O_2+H]^+$: 473.0626, Found: 473.0619.



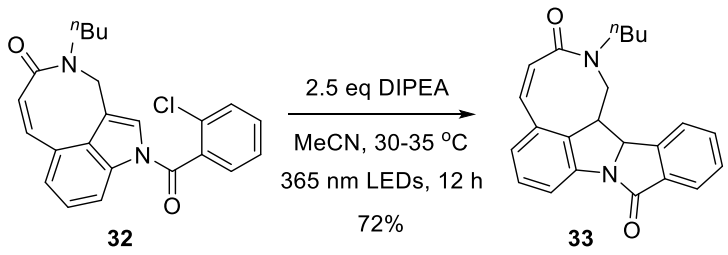
In a 25 mL Schlenk tube charged with a magnetic stirring bar, indole derivative **S40** (1.0 equiv) was added. The Schlenk tube was evacuated and back-filled with argon three times. Then Et_3N (0.2 mL), $Pd(PPh_3)_4$ (16 mg) and toluene (5 mL) were added. The mixture was degassed by freeze-pump-thaw cycle for three times and back-filled with argon. The mixture was heated to reflux overnight. TLC indicated the substrate was consumed completely. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 10:1 to 4:1) to afford the product in 50% yield.

(*Z*)-9-Butyl-2-(2-chlorobenzoyl)-9,10-dihydroazocino[3,4,5-cd]indol-8(2H)-one (32)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 7.63–7.52 (m, 3 H), 7.50–7.47 (m, 1 H), 7.37 (t, *J* = 7.8 Hz, 1 H), 7.17 (d, *J* = 7.6 Hz, 1 H), 6.90 (br, 1 H), 6.83 (d, *J* = 13.3 Hz, 1 H), 6.15 (d, *J* = 13.3 Hz, 1 H), 5.24 (d, *J* = 15.2 Hz, 1 H), 3.85 (d, *J* = 15.2 Hz, 1 H), 3.79 (dd, *J* = 13.6, 7.1 Hz, 1 H), 2.85 (br, 1 H), 1.59–1.52 (m, 2 H), 1.36–1.26 (m, 2 H), 0.91 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.31, 165.69, 136.67, 134.59, 131.98, 131.43, 131.19, 130.25, 129.03,

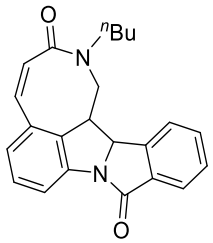
128.98, 127.40, 127.08, 127.03, 125.96, 125.18, 123.46, 120.55, 116.71, 45.23, 43.67, 29.48, 20.20, 13.91 ppm. HRMS (ESI) Calcd for $[C_{23}H_{21}ClN_2O_2+H]^+$: 393.1363, Found: 393.1360.



32 **33**

In a 10 mL test tube with a magnetic stirring bar, indole **32** (100 mg, 0.255 mmol) and DIPEA (0.11 mL, 0.638 mmol, 2.5 eq) were dissolved in MeCN (3 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes. Then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 1:1) to afford the product in 71% yield.

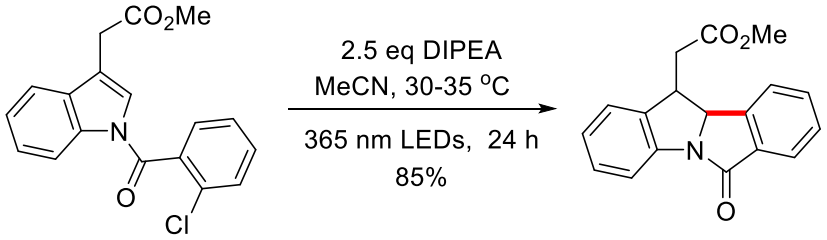
(*Z*)-2-Butyl-1,2,14b,14c-tetrahydroazocino[3,4,5-cd]isoindolo[2,1-a]indole-3,10-dione (33)



trans : cis = 2.0 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 0.5 H), 7.82 (d, *J* = 7.9 Hz, 1 H), 7.75 (d, *J* = 6.9 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 0.5 H), 7.59–7.54 (m, 4 H), 7.51–7.45 (m, 1 H), 7.44–7.32 (m, 2 H), 7.27–7.20 (m, 1 H), 7.20–7.11 (m, 1 H), 6.98 (d, *J* = 7.6 Hz, 0.5 H), 6.90 (s, 0.5 H), 6.83 (dd, *J* = 13.3, 6.3 Hz, 1 H), 6.75 (d, *J* = 13.3 Hz, 0.5 H), 6.17 (d, *J* = 13.2 Hz, 0.5 H), 6.14 (d, *J* = 13.3 Hz, 1 H), 5.25 (dd, *J* = 18.8, 15.4 Hz, 1.5 H), 4.34 (d, *J* = 15.3 Hz, 0.5 H), 3.97–3.75 (m, 2 H), 2.93 (dt, *J* = 14.0, 7.0 Hz, 0.5 H), 2.82 (m, 1 H), 1.69–1.60 (m, 1 H), 1.60–1.48 (m, 2 H), 1.40–1.23 (m, 5 H), 0.96–0.87 (m, 5 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.46, 168.38, 168.31, 165.70, 134.69, 134.27, 134.00, 132.23, 131.98, 131.65, 131.50, 131.40, 131.18, 130.25, 130.19, 129.22, 129.17, 128.98, 128.92, 128.79, 127.40, 127.06, 127.03, 126.81, 126.63, 126.62, 125.95, 125.93, 125.59, 125.29, 125.08, 124.96, 124.52, 123.47, 120.50, 120.45, 116.64, 113.54, 45.64, 45.22, 43.69, 29.46, 20.30, 20.20, 13.89 ppm. HRMS (ESI) Calcd for $[C_{23}H_{22}N_2O_2+H]^+$: 359.1754, Found: 359.1748.

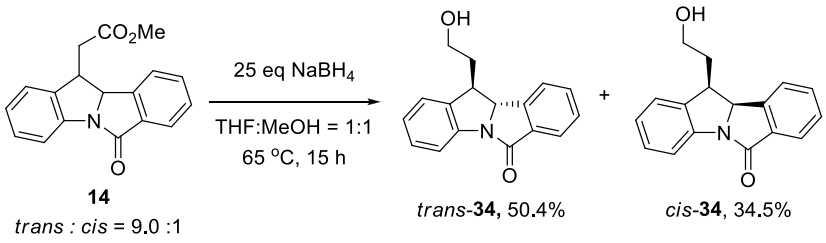
Large-scale reaction and application



S14
1.4 g scale

14
trans :*cis* = 9.0 :1

In a 100 mL round-bottom flask with a magnetic stirring bar, methyl 2-(1-(2-chlorobenzoyl)-1H-indol-3-yl)acetate **S14** (1.40 g, 4.3 mmol) and DIPEA (1.87 mL, 10.7 mmol, 2.5 eq) were dissolved in MeCN (20 mL). The round-bottom flask was sealed with a septum. The mixture was purged with argon for ten minutes. Then the mixture was irradiated with 365 nm LEDs at 30-35 °C for 24 h. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 10:1) to afford the product (1.10 g) in 85% yield.



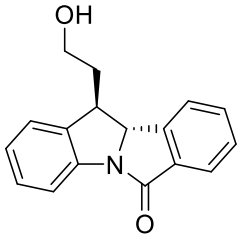
14
trans : *cis* = 9.0 :1

trans-**34**, 50.4%

cis-**34**, 34.5%

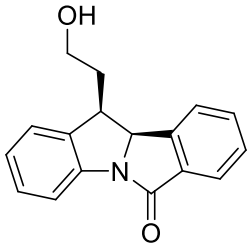
To a 50 mL Schlenk tube was charged with **14** (290 mg, 0.99 mmol), $NaBH_4$ (93.0 mg, 25 mmol) and dry THF (10 mL) under argon. To the stirred mixture, CH_3OH (10 mL) was added slowly. The solution became gradually to reflux. When the bubble ceased to evolve, the mixture was heated to reflux for 15 h. The mixture was then quenched with water. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration under vacuum, the residue was purified by flash column chromatography on silica gel (PE:EA = 2:1) to afford the products as a white solid with an overall yield of 85%. *Trans*-**34** was isolated in pure form in 45% yield.

***Trans*-(11-(2-Hydroxyethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (*trans*-34)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1 H), 7.64 (dd, *J* = 7.6, 3.3 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 5.31 (d, *J* = 9.3 Hz, 1 H), 4.11–4.08 (m, 2 H), 3.46–3.36 (m, 1 H), 3.04 (s, 1 H), 2.64–2.39 (m, 1 H), 2.25–2.09 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.62, 145.73, 140.11, 139.77, 133.88, 132.76, 128.75, 128.00, 124.67, 124.65, 124.23, 123.35, 116.24, 71.33, 60.49, 43.22, 35.71 ppm. HRMS (ESI) Calcd for $[C_{17}H_{15}NO_2+H]^+$: 266.1176, Found: 266.1171.

***Cis*-11-(2-Hydroxyethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (*cis*-34)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* = 7.7 Hz, 1 H), 7.62 (d, *J* = 7.5 Hz, 1 H), 7.60–7.50 (m, 2 H), 7.35 (d, *J* = 7.9 Hz, 2 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 5.60 (d, *J* = 7.7 Hz, 1 H), 3.81–3.76 (m, 1 H), 3.54–3.50 (m, 2 H), 1.85 (br, 1 H), 1.63–1.57 (m, 1 H), 0.93–0.86 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.44, 142.69, 139.04, 135.32, 132.20, 128.84, 128.43, 126.19, 124.77, 124.30, 124.01, 116.74, 69.06, 58.76, 39.32, 33.85 ppm. HRMS (ESI) Calcd for $[C_{17}H_{15}NO_2+H]^+$: 266.1176, Found: 266.1170.

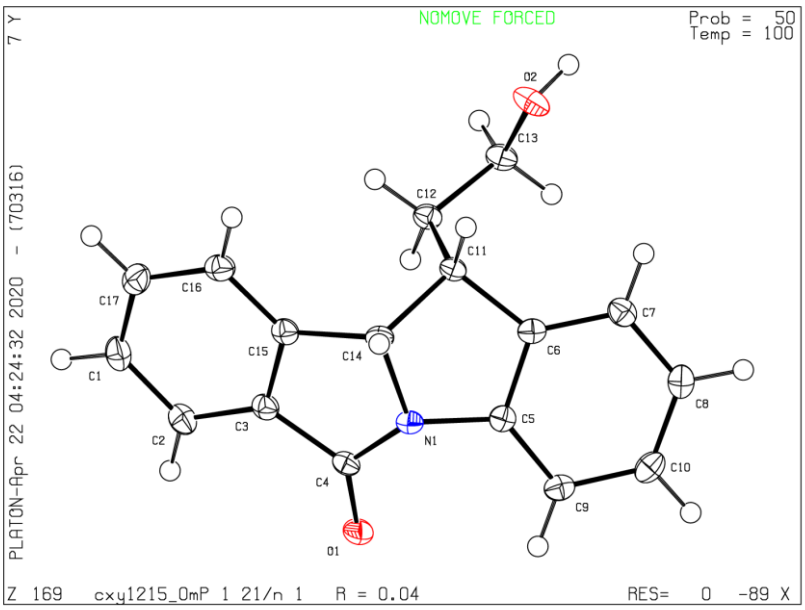
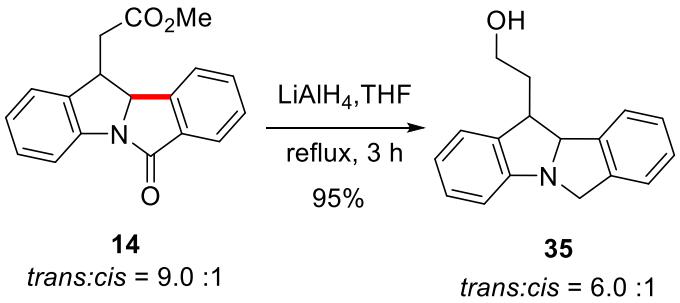


Figure S13: X-ray crystal structure of compound *cis*-**34.**

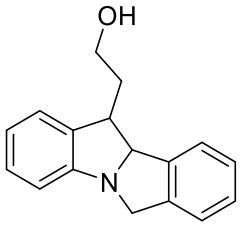


14
trans:cis = 9.0 :1

35
trans:cis = 6.0 :1

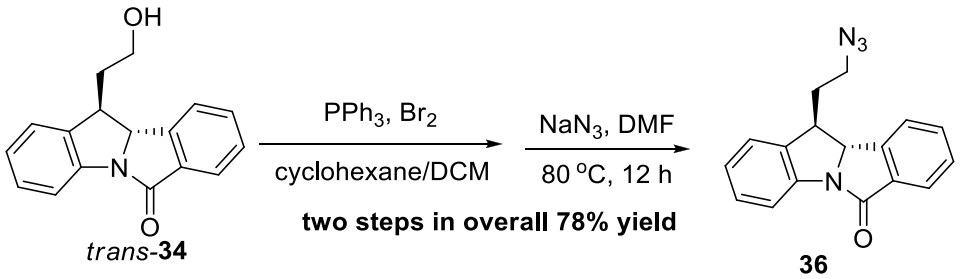
In a 50 mL round-bottom flask charged with a magnetic stirring bar, to a solution of **14** (380 mg, 1.3 mmol) in THF (20 mL), $LiAlH_4$ (250 mg, 4 eq) was added. The mixture was stirred at 80 °C for 5 h. TLC indicated the substrate was consumed completely. The reaction was quenched with water, extracted with ethyl acetate (15 mL × 3), washed with brine and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 4:1 to 1:1) to obtain the product (310 mg) in 95% yield.

2-(10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)ethan-1-ol (35)



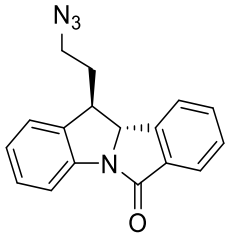
trans : cis = 6.0 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.7 Hz, 1 H), 7.23–7.24 (m, 2 H), 7.24 (d, *J* = 5.7 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 7.09 (d, *J* = 7.3 Hz, 1 H), 6.90–6.79 (m, 2 H), 4.97 (s, 1 H), 4.63 (d, *J* = 14.0 Hz, 1 H), 4.53 (d, *J* = 14.9 Hz, 1 H), 3.98–3.72 (m, 3 H), 3.28 (br, 1 H), 2.25–2.01 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.02, 143.20, 139.65, 133.37, 128.12, 127.74, 127.34, 124.57, 122.72, 122.30, 120.93, 112.37, 76.08, 60.55, 58.74, 44.86, 38.94 ppm. HRMS (ESI) Calcd for $[C_{17}H_{17}NO+H]^+$: 252.1383, Found: 252.1379.

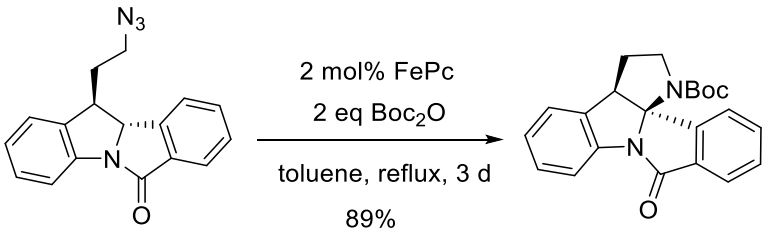


In a 50 mL Schlenk tube charged with a magnetic stirring bar, triphenylphosphine (140 mg) was added. Then the Schlenk tube was evacuated and back-filled with argon three times. Cyclohexane (10 mL), Br_2 (83.0 mg) were added. A yellow solid was formed immediately and stirred for 10 min at room temperature. *Trans*-**34** (110 mg) dissolved in CH_2Cl_2 (2 mL) was added dropwise. The mixture was stirred at room temperature for 5 h. TLC indicated the substrate was consumed completely. The solvent was removed under reduced pressure. Filtration over Celite and concentration of the filtrate in vacuo yielded the corresponding product. To the aforementioned product, DMF (10 mL), NaN_3 (28.0 mg) were added. The mixture was heated to 80 ℃ overnight. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 10:1) to obtain the product 78% yield for two steps.

***Trans*-11-(2-Azidoethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (36)**



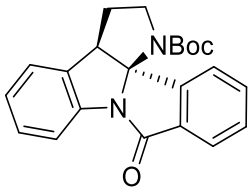
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 7.8 Hz, 1 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.56 (d, *J* = 4.6 Hz, 1 H), 7.55–7.50 (m, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.22 (d, *J* = 7.6 Hz, 1 H), 7.13 (t, *J* = 7.5 Hz, 1 H), 5.32 (d, *J* = 9.3 Hz, 1 H), 3.82–3.69 (m, 2 H), 3.53–3.47 (m, 1 H), 2.55–2.47 (m, 1 H), 2.31–2.22 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.36, 145.22, 140.50, 138.48, 134.03, 132.82, 129.01, 128.47, 125.05, 124.69, 124.02, 122.84, 116.59, 70.69, 49.23, 43.74, 31.85 ppm. HRMS (ESI) Calcd for $[C_{17}H_{14}N_4O+H]^+$: 291.1240, Found: 291.1238.



36 **37**

In a 25 mL Schlenk tube charged with a magnetic stirring bar, iron(II) phthalocyanine (FePc, 1.50 mg) and Boc_2O (44.4 mg) were added. The Schlenk tube was evacuated and back-filled with argon three times. Then **36** (39.4 mg) in toluene (5 mL) was added. The mixture was degassed by freeze-pump-thaw cycle for three times and back-filled with argon. The mixture was heated to reflux for 3 days. TLC indicated the substrate was consumed completely. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE : EA = 10 : 1) to obtain the product (43.7 mg) in 89% yield.

***Tert*-Butyl-8-Oxo-1,13b-dihydro-8H-isoindolo[2,1-a]pyrrolo[2,3-b]indole-3(2H)-carboxylate (37)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 1 H), 7.58 (d, *J* = 7.8 Hz, 1 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 7.36 (d, *J* = 7.5 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.13 (d, *J* = 7.4 Hz, 1 H), 7.06 (t, *J* = 7.4 Hz, 1 H), 3.93 (d, *J* = 6.5 Hz, 1 H), 3.89 (t, *J* = 8.7 Hz, 1 H),

3.29 (td, *J* = 11.2, 5.9 Hz, 1 H), 2.60–2.44 (m, 1 H), 2.35 (dd, *J* = 12.8, 5.8 Hz, 1 H), 0.97 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.06, 152.18, 146.25, 139.80, 135.50, 132.48, 132.07, 128.29, 127.77, 123.86, 123.28, 122.95, 120.53, 116.46, 89.98, 79.51, 51.88, 45.39, 26.78, 26.23 ppm. HRMS (ESI) Calcd for $[C_{22}H_{22}N_2O_3+H]^+$: 363.1703, Found: 363.1696.

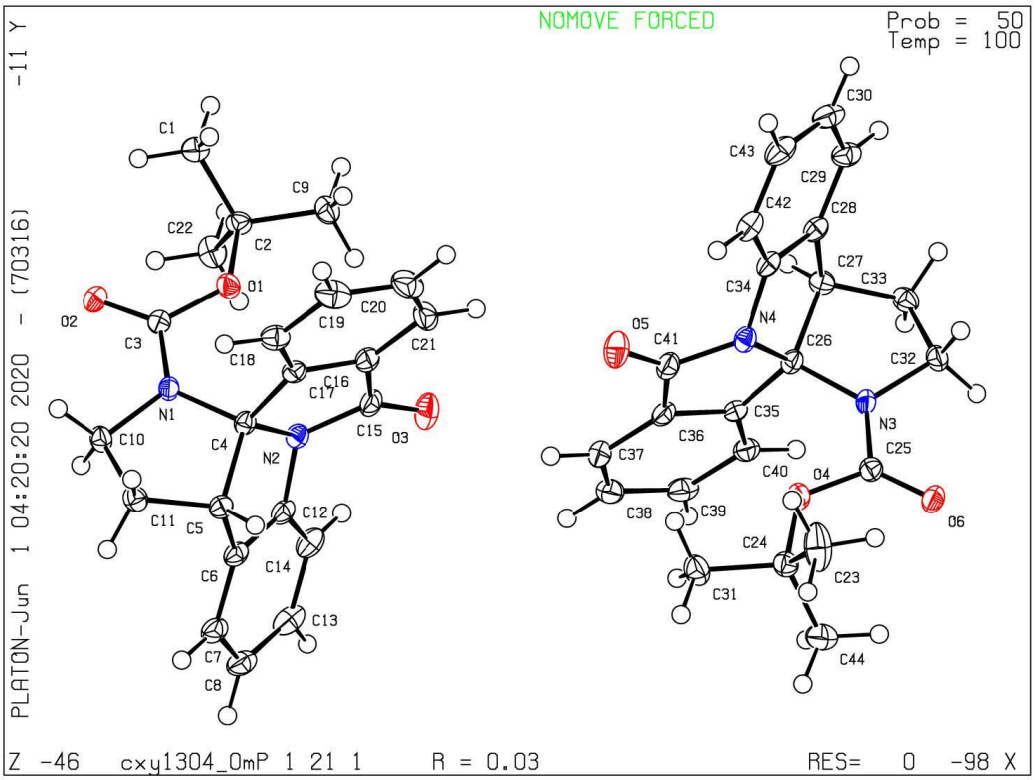
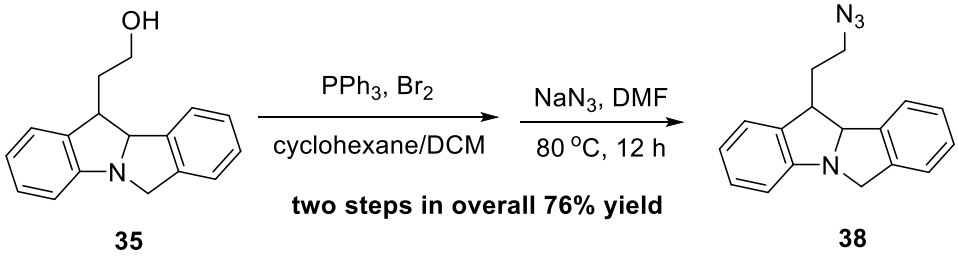


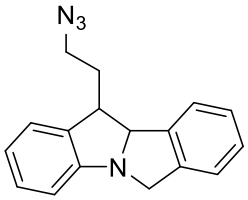
Figure S14: X-ray crystal structure of compound **37**



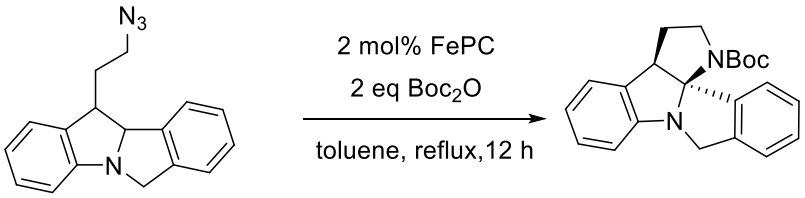
In a 25 mL Schlenk tube charged with a magnetic stirring bar, triphenylphosphine (12.0 mg) was added. Then the Schlenk tube was evacuated and back-filled with argon three times. Cyclohexane (10 mL), Br_2 (25 μL) were added. A yellow solid was formed immediately and stirred for 10 min at room temperature. **35** (96.3 mg) dissolved in CH_2Cl_2 (2 mL) was added dropwise. The mixture was stirred at room temperature for 5 h. TLC indicated the substrate was consumed completely. The solvent was removed under reduced pressure. Filtration over Celite

and concentration of the filtrate in vacuo yielded the corresponding product. To the aforementioned product, DMF (10 mL), NaN_3 (28 mg) were added. The mixture was heated to 80 °C overnight. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 10:1 to 5:1) to obtain the product in 76% yield.

11-(2-Azidoethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indole (38)



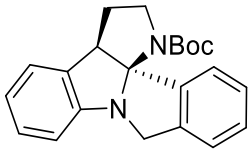
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.3 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 7.24–7.22 (m, 2 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 7.13 (d, *J* = 7.3 Hz, 1 H), 6.84 (d, *J* = 8.1 Hz, 1 H), 6.83 (t, *J* = 7.4 Hz, 1 H), 4.89 (s, 1 H), 4.64 (d, *J* = 15.0 Hz, 1 H), 4.53 (d, *J* = 15.0 Hz, 1 H), 3.90 (t, *J* = 8.5 Hz, 1 H), 3.87–3.79 (m, 2 H), 2.34–2.23 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.18, 142.87, 139.67, 132.59, 128.37, 127.84, 127.41, 124.63, 122.73, 122.37, 120.64, 112.25, 75.58, 58.92, 45.07, 42.87, 38.88 ppm. HRMS (ESI) Calcd for $[C_{17}H_{16}N_4+H]^+$: 277.1448, Found: 277.1442.



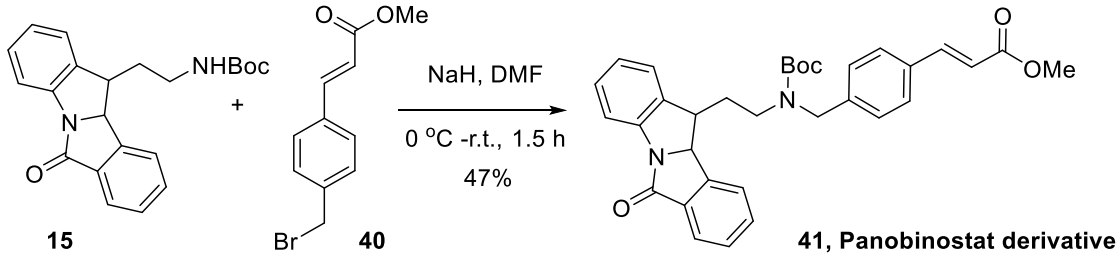
38 **39**, 86%

In a 25 mL Schlenk tube, charged with a magnetic stirring bar, FePc (3.30 mg) and Boc_2O (13.0 mg) were added. The Schlenk tube was evacuated and back-filled with argon three times. Then 11-(2-azidoethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indole **38** (80.0 mg) in toluene (5 mL) was added. The mixture was degassed by freeze-pump-thaw cycle for three times and back-filled with argon. The mixture was heated to reflux for 12 h. TLC indicated the substrate was consumed completely. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 10:1 to 5:1) to obtain the product (87.3 mg) in 86% yield.

***tert*-Butyl 1,13b-dihydro-8H-isoindolo[2,1-a]pyrrolo[2,3-b]indole-3(2H)-carboxylate (39)**

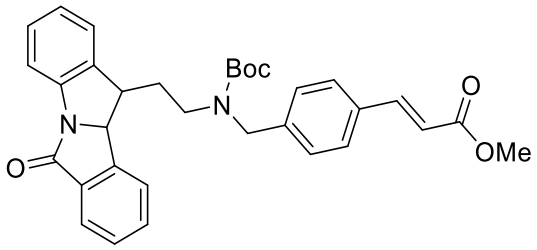


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.3 Hz, 1 H), 7.54 (d, *J* = 7.9 Hz, 1 H), 7.37 (d, *J* = 7.5 Hz, 1 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 7.24 (d, *J* = 8.1 Hz, 1 H), 7.21 (t, *J* = 7.7 Hz, 1 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 7.03 (t, *J* = 7.4 Hz, 1 H), 4.94 (s, 2 H), 4.59 (t, *J* = 6.4 Hz, 1 H), 3.41 (t, *J* = 6.6 Hz, 2 H), 3.15 (t, *J* = 6.7 Hz, 2 H), 1.33 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.14, 141.82, 141.13, 133.85, 133.30, 132.52, 128.37, 126.84, 124.49, 123.68, 121.80, 121.21, 119.71, 119.32, 112.60, 110.59, 109.35, 103.76, 48.29, 41.49, 28.55, 25.28 ppm. HRMS (ESI) Calcd for $[C_{22}H_{24}N_2O_2+H]^+$: 349.1911, Found: 349.1902.



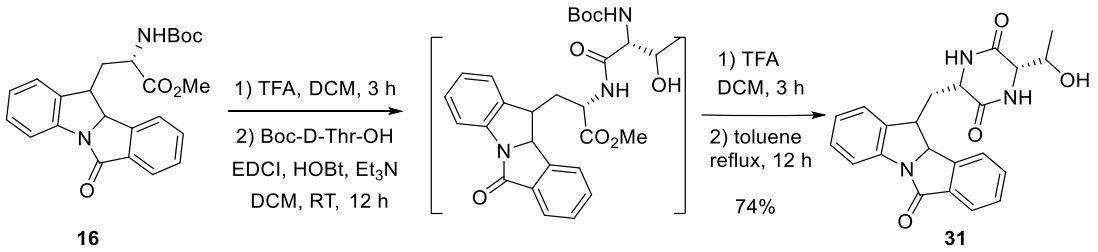
In a 25 mL Schlenk tube charged with a magnetic stirring bar, compound **15** (11.0 mg, 0.30 mmol) was added. The Schlenk tube was evacuated and back-filled with argon three times. Then DMF (5 mL), NaH (24.0 mg, 0.6 mmol) were added. The mixture was stirred at 0 °C for 30 min. methyl (*E*)-3-(4-(bromomethyl)phenyl)acrylate **40** (84.2 mg, 0.33 mmol) was added. The mixture was stirred at room temperature for 1 h. TLC indicated the substrate was consumed completely. The solvent was removed under reduced pressure. The residue was purified with flash column chromatography (PE:EA = 4:1) to afford the product (75.3 mg) in 47% yield.

Methyl (*E*)-3-(4-(((tert-butoxycarbonyl)(2-(6-oxo-10b,11-dihydro-6H-isoindolo[2,1-a]indol-11-yl)ethyl)amino)methyl)phenyl)acrylate (41)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1 H), 7.64 (d, *J* = 7.3 Hz, 3 H), 7.52 (d, *J* = 16.0 Hz, 1 H), 7.42 (m, 4 H), 7.16 (t, *J* = 8.2 Hz, 3 H), 6.69 (d, *J* = 8.0 Hz, 2 H), 6.29 (d, *J* =

16.0 Hz, 1 H), 4.45 (t, *J* = 5.7 Hz, 1 H), 3.87–3.81 (m, 1 H), 3.77 (s, 3 H), 3.34 (dd, *J* = 10.8, 4.5 Hz, 1 H), 3.20 (s, 2 H), 3.00 (m, 1 H), 1.85 (s, 1 H) 1.43 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.46, 166.96, 155.97, 145.14, 144.51, 138.64, 137.74, 136.92, 134.68, 132.67, 131.97, 130.50, 128.95, 128.81, 127.26, 126.55, 124.70, 124.58, 123.74, 117.34, 117.26, 79.43, 78.40, 51.66, 47.01, 44.43, 37.54, 33.36, 28.39 ppm. HRMS (ESI) Calcd for $[C_{33}H_{34}N_2O_5+H]^+$: 539.2540, Found: 539.2553.



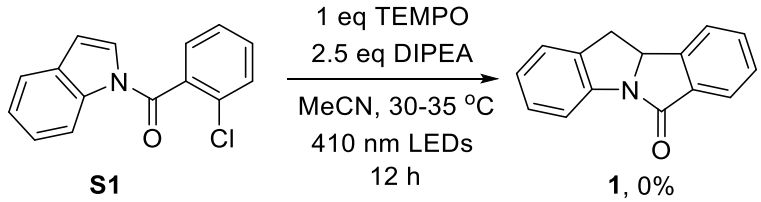
16 **31**

To a stirred solution of compound **16** (400 mg, 0.95 mmol) in CH_2Cl_2 (10 mL) was dropwise added TFA (4.0 mL) at 0 ℃. The solution was stirred at room temperature for 3 h. The reaction mixture was evaporated and the residue was dissolved in CH_2Cl_2 (20 mL), washed with $NaHCO_3$, brine, dried over anhydrous Na_2SO_4 and evaporated. The crude product was used in the next step without further purification.

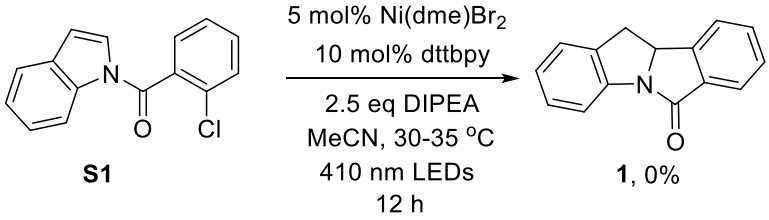
To a solution of indole derivative in CH_2Cl_2 (10 mL), EDCI (210 mg, 1.2 eq), HOBT (150 mg, 1.2 equiv) and *N*-Boc-*D*-Thr (240 mg, 1.2 equiv) were added at room temperature. The solution was stirred at room temperature overnight. After completion of the reaction, the solution was washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by silica gel column chromatography (DCM : MeOH = 100 : 1) to give the desired product.

To a stirred solution of the above obtained product in CH_2Cl_2 (10 mL) was dropwise added TFA (4.0 mL) at 0 ℃. The solution was stirred at room temperature for 3 h. The reaction mixture was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL), washed with $NaHCO_3$, brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was dissolved in toluene (10 mL), and stirred under reflux 12 h. A white solid precipitated out of solution. The solid was filtered and washed with Et_2O to give the solid (276 mg) in 74% yield.

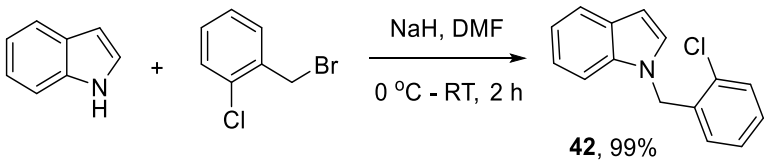
Mechanistic experiments



In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.2 mmol), DIPEA (87 μL, 2.5 equiv) and TEMPO (0.2 mmol, 1.0 equiv) were dissolved in MeCN (2.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 410 nm LEDs for 12 h. The solvent was removed under reduced pressure. 1,3,5-trimethoxylbenzene (0.2 mmol) was added. The mixture was analyzed by ^{1}H NMR and GC-MS.



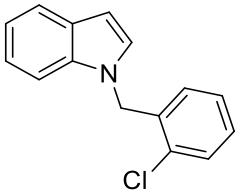
In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.2 mmol), DIPEA (87 μL, 2.5 equiv) Ni(dme)Br_2 (3.1 mg, 0.001 mmol, 5 mol%) and dttbpy (5.4 mg, 0.02 mmol, 10 mol%) were dissolved in MeCN (2.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 410 nm LEDs for 12 h. The solvent was removed under reduced pressure. Dibromomethane (0.2 mmol) was added. The mixture was analyzed by ^{1}H NMR and GC-MS.



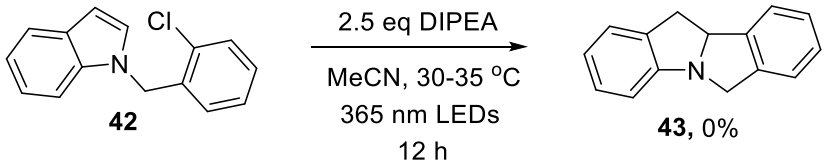
To a Schlenk tube (50 mL) charged with magnetic stirring bar, indole (234 mg, 2 mmol) was added. The Schlenk tube was evacuated and back-filled with argon three times. Anhydrous DMF (10 mL) was added and then cooled down to 0 °C with ice bath. Sodium hydride (60%, 96 mg, 2.4 mmol) was added. The mixture was stirred at 0 °C for 30 min. 2-chlorobenzyl bromide (45.0 mg, 2.2 mmol, 1.1 eq) was added in one portion. The mixture was stirred at room temperature for 1.5 h. TLC showed that the reaction was consumed completely. Water was added to quench the reaction and extracted with DCM (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure.

The residue was purified by flash column chromatography (PE:EA = 50:1) to give the product (48.0 mg, 99%) as a colorless oil.

1-(2-Chlorobenzyl)-1H-indole (42)[8]

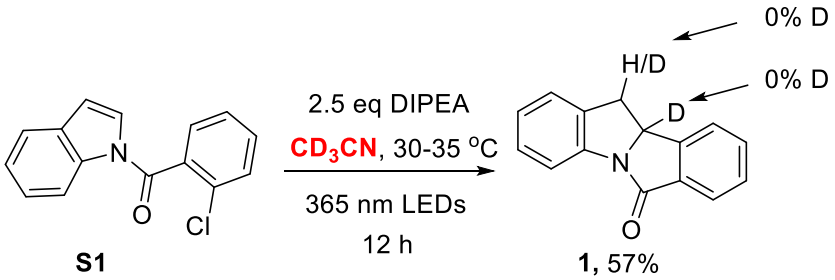


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 7.7 Hz, 1 H), 7.26–7.19 (m, 2 H), 7.20–7.14 (m, 2 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 6.81–6.54 (m, 2 H), 5.46 (s, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.29, 135.16, 132.38, 129.50, 128.81, 128.67, 128.40, 127.98, 127.23, 121.91, 121.07, 119.73, 109.64, 102.06, 47.68 ppm.



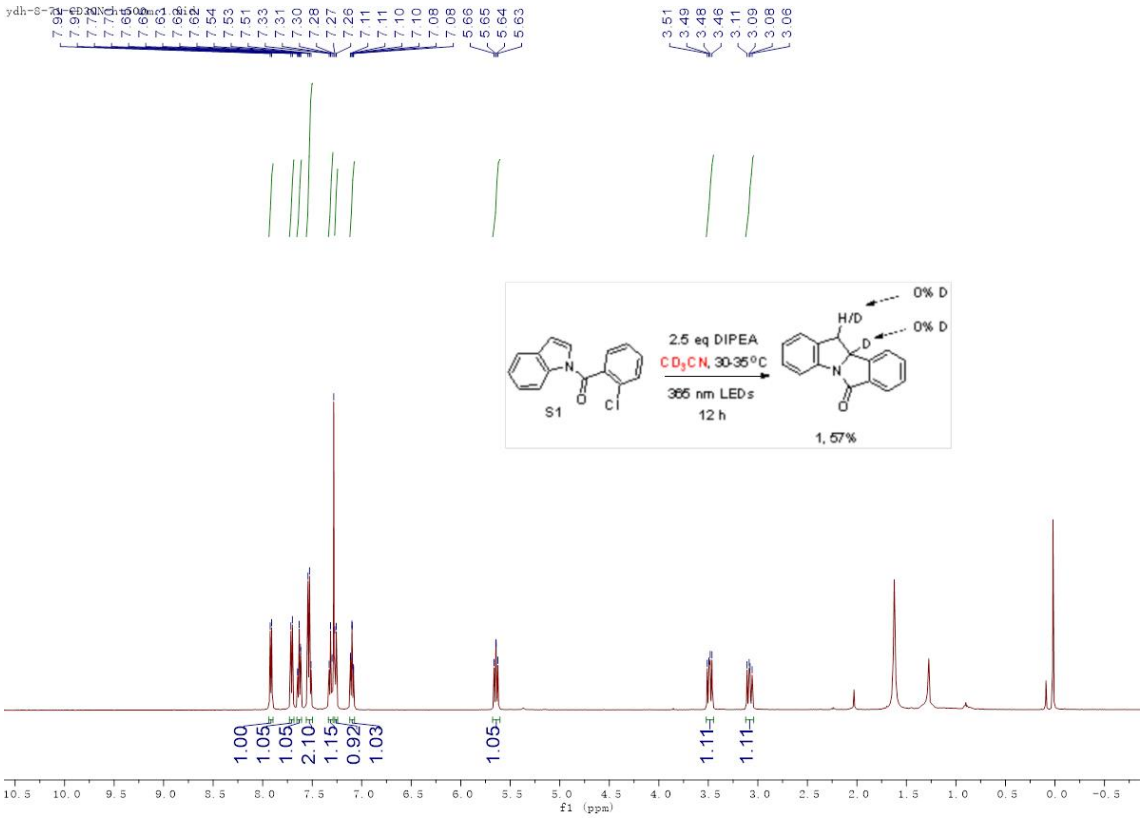
In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.2 mmol) and DIPEA (87 μL, 2.5 equiv) were dissolved in MeCN (2.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. Then the mixture was detected by ^{1}H NMR and GC-MS. Substrate was recovered completely.

Isotope labelling experiments

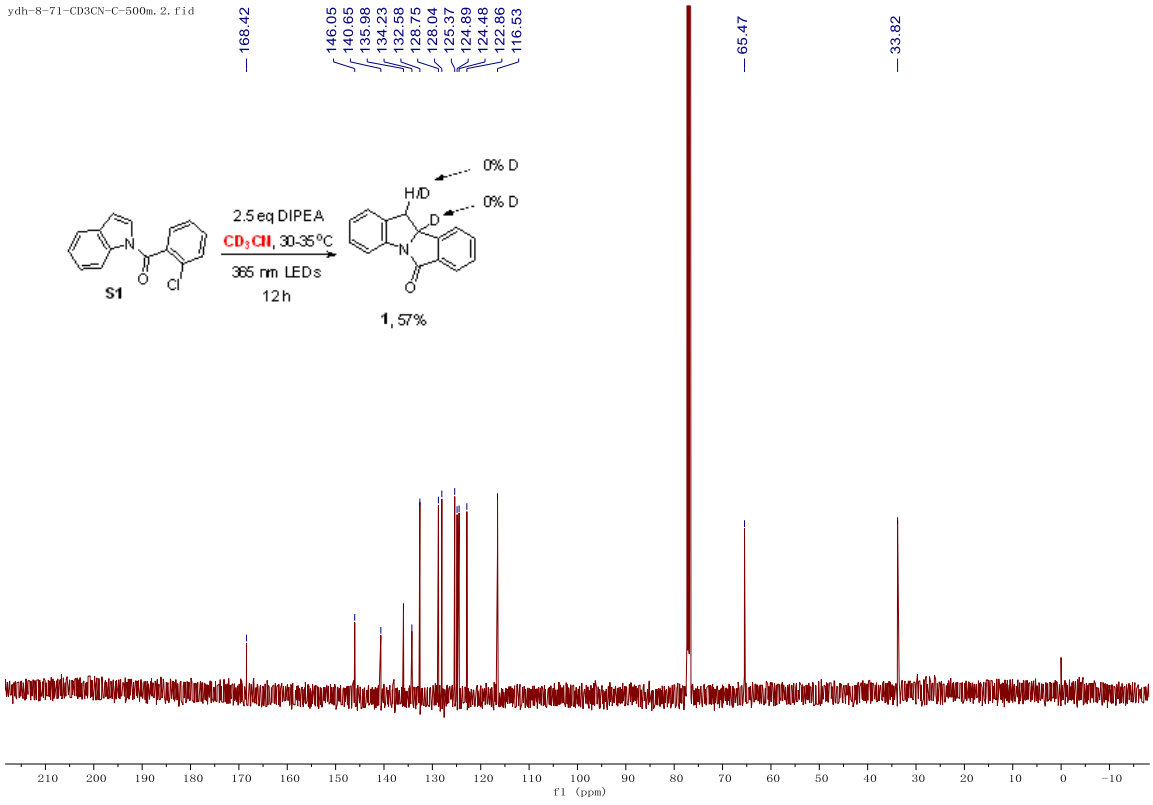


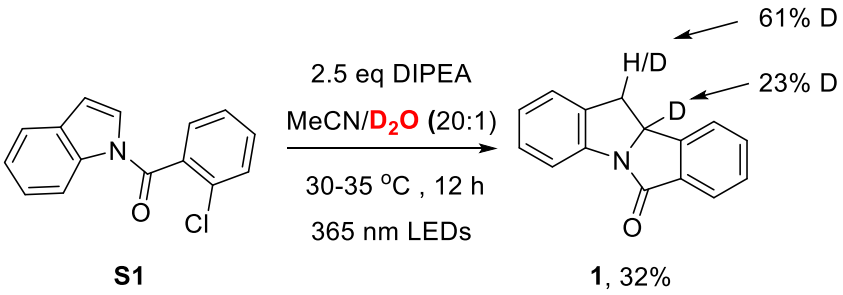
In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.2 mmol) and DIPEA (87 μL, 2.5 equiv) were dissolved in CD_3CN (2.0 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1) to give the product in 57% yield.

^{1}H NMR of 1



^{13}C NMR

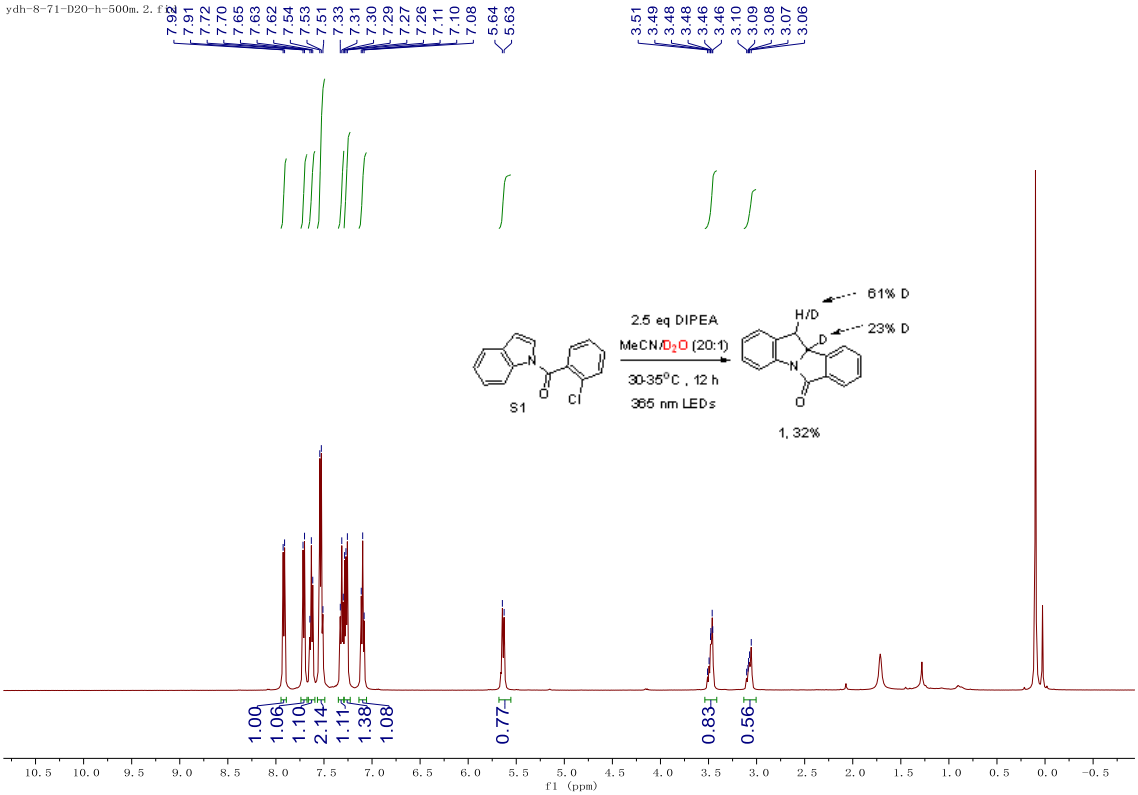




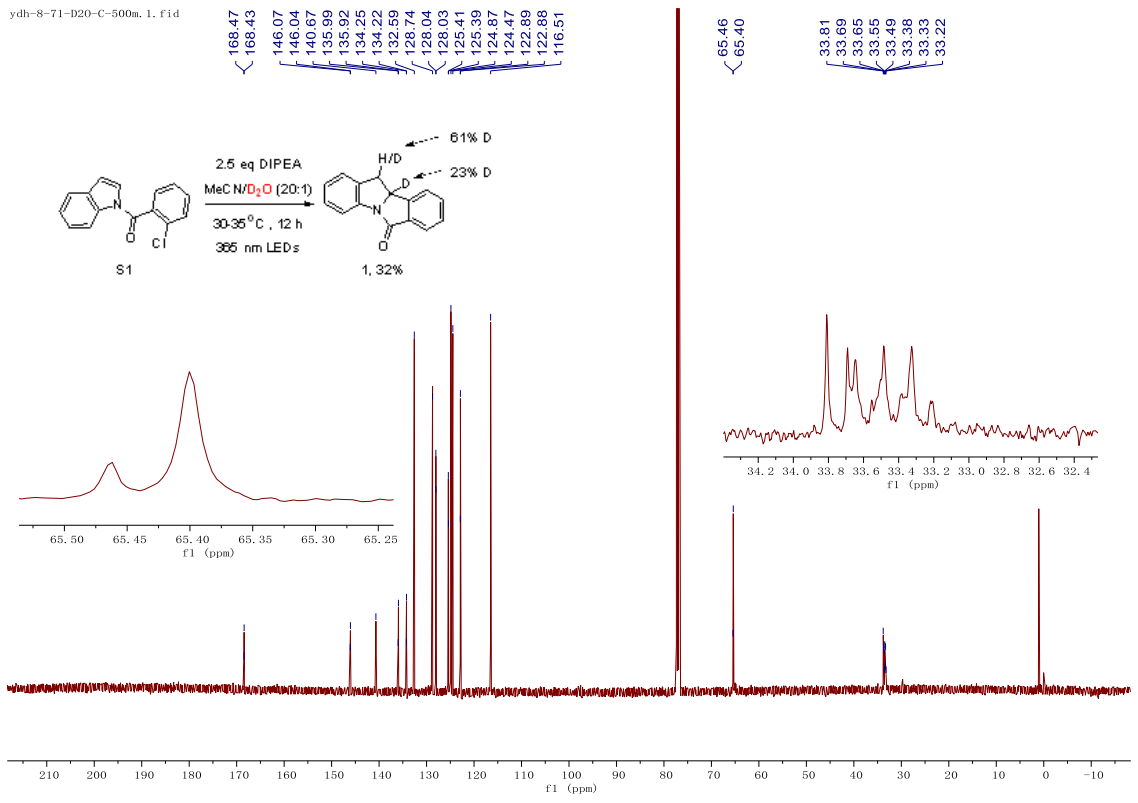
S1 **1**, 32%

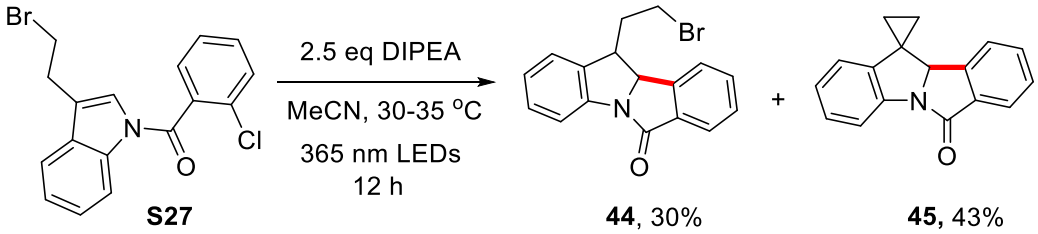
In a 10 mL test tube with a magnetic stirring bar, indole derivative (0.2 mmol) and DIPEA (87 μL, 2.5 equiv) were dissolved in CH_3CN/D_2O (v/v, 2.0/0.10 mL). The test tube was sealed with a septum. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1) to give the product in 32% yield.

^{1}H NMR of 1



^{13}C NMR

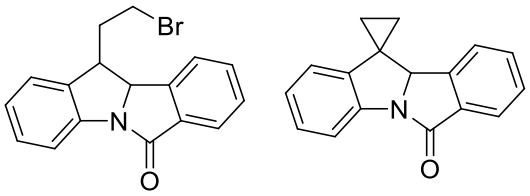




S27 **44**, 30% **45,** 43%

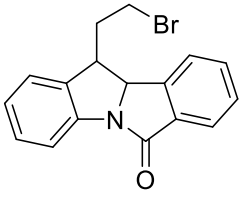
In a 10 mL test tube with a magnetic stirring bar, indole derivative **S27** (0.5 mmol), DIPEA (0.20 mL, 2.5 equiv) were dissolved in MeCN (5.0 mL). The test tube was screwed with a stopper. The mixture was purged with argon for ten minutes, then the mixture was irradiated at 30-35 °C with 365 nm LEDs for 12 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE:EA = 10:1) to give the as a colorless oil product **44** and **45** as a mixture.

11-(2-Bromoethyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (44) and spiro [cyclopropane-1,11'-isoindolo[2,1-a]indol]-6'(10b'H)-one (45)



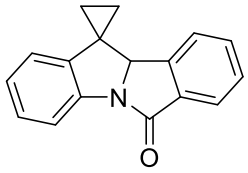
44
trans : cis = 1:1

45



44
trans : cis = 1:1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, 1 H), 7.75 (d, *J* = 7.8 Hz, 1 H), 7.66 – 7.61 (m, 3 H), 7.61 – 7.56 (m, 2 H), 7.53 (t, *J* = 7.3 Hz, 2 H), 7.35 (td, *J* = 7.7, 1.3 Hz, 2 H), 7.28 (d, *J* = 8.9 Hz, 3 H), 7.13 (td, *J* = 5.6, 2.8 Hz, 2 H), 5.55 (d, *J* = 7.8 Hz, 1 H), 5.27 (d, *J* = 9.3 Hz, 1 H), 3.43 (m, 1 H), 3.34 (td, *J* = 8.6, 4.7 Hz, 1 H), 2.27 (m, 1 H), 2.01 (dt, *J* = 14.6, 7.5 Hz, 1 H), 1.55 – 1.47 (m, 2 H), 1.01 – 0.91 (m, 2 H), 0.66 – 0.59 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.52, 167.45, 145.93, 142.99, 140.93, 139.65, 139.41, 139.30, 135.35, 134.18, 132.58, 132.01, 128.72, 128.65, 128.26, 128.00, 126.05, 124.91, 124.73, 124.52, 124.20, 124.06, 123.90, 123.01, 116.52, 116.37, 70.67, 69.21, 47.46, 44.31, 25.25, 24.78, 12.10, 10.39 ppm. HRMS (ESI) Calcd for $[C_{17}H_{14}BrNO+H]^+$: 328.0332, Found: 328.0328.



45

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 1 H), 7.72 (d, *J* = 7.9 Hz, 1 H), 7.62 – 7.56 (m, 1 H), 7.53 (t, *J* = 7.3 Hz, 1 H), 7.28 (d, *J* = 8.9 Hz, 1 H), 7.22 (d, *J* = 7.4 Hz, 1 H), 7.09 (d, *J* = 7.5 Hz, 1 H), 6.77 (d, *J* = 7.5 Hz, 1 H), 5.64 (s, 1 H), 1.34 (t, *J* = 7.6 Hz, 2 H), 0.68 (t, *J* = 7.4 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.19, 143.30, 141.12, 132.41, 128.98, 127.28, 125.19, 124.78, 122.30, 119.19, 116.28, 68.81, 27.27, 18.32, 10.80 ppm. HRMS (ESI) Calcd for $[C_{17}H_{13}NO+H]^+$: 248.1070, Found: 248.1067.

Computational details

DFT/TDDFT calculations were performed using the Gaussian09 program package.[18] The real vibrational frequencies of these optimized structures were computed to confirm that all the optimized structures are potential energy minima. Hybrid functional PBE0[19] with dispersion corrections in revision three (D3BJ)[20] was employed. The 6-31G* basis set[21] was used for all atoms. Unrestricted DFT calculations were performed to optimize the structures of molecules at triplet excited states of T_1.

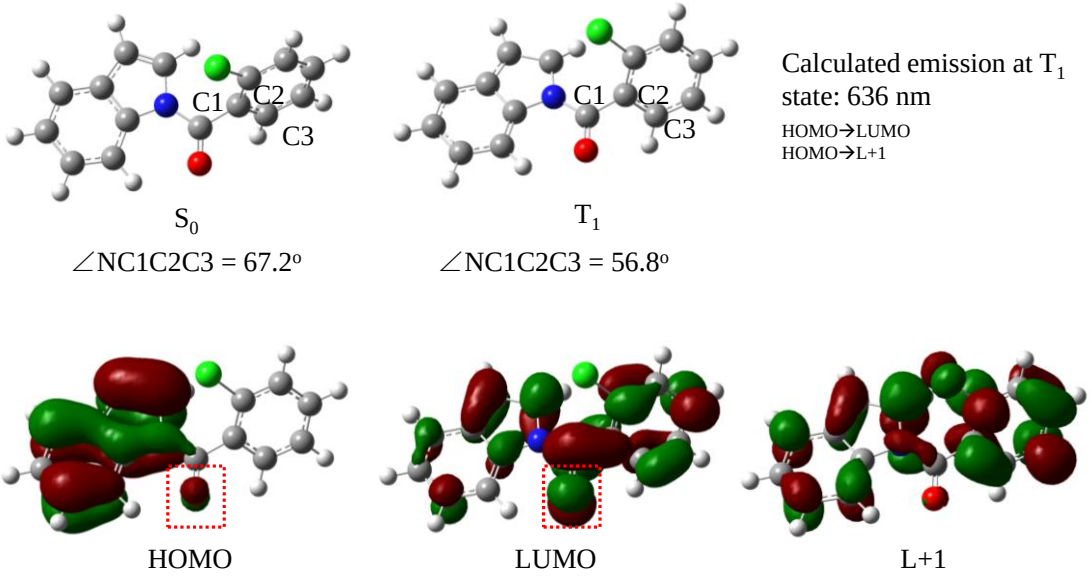


Figure S15. Calculated frontier molecular orbitals of **S1** at T_1 State

Table S2. Mulliken charge distribution of **S1** in the ground state (S_0) and T_1 state.

	indole group	carbonyl group	2-chlorobenzoyl
S_0	-0.04	0.05	-0.01
T_1	0.17	-0.08	-0.09

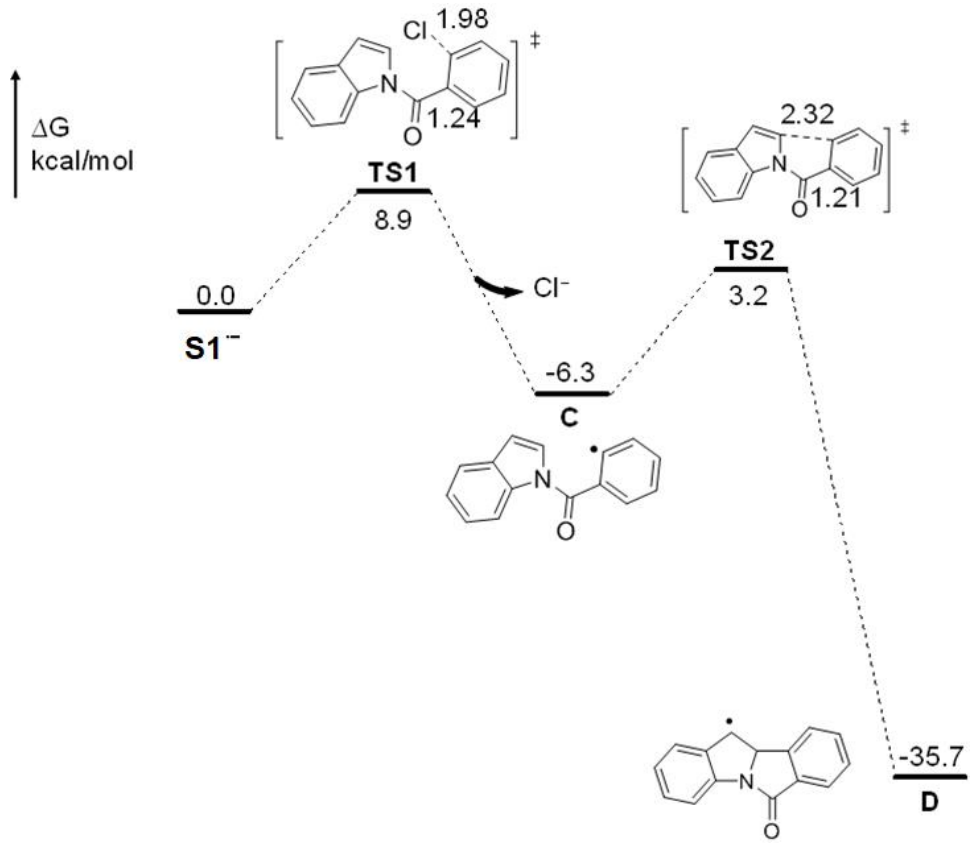


Figure S16. Energy profile for the proposed reaction pathway (in Scheme 2 in manuscript) calculated at the M06-2X-D3/6–311++G**/PCM//B3LYP-D3/6–311G*/PCM level of theory. Critical bond lengths are given in Å.

Calculated coordinates:

S1, S_0

C	2.65052200	-0.72671900	-0.79063200
C	2.01128400	0.28735500	-0.04445700
C	2.71843600	1.17664800	0.75998900
C	4.09968800	1.02642600	0.80460400
C	4.75428500	0.02728100	0.07166300
C	4.04027100	-0.85319100	-0.72848300
C	1.62305000	-1.44894500	-1.49752300
C	0.43374600	-0.89063500	-1.17306500
H	2.20730400	1.95045700	1.31684000
H	4.68280900	1.70385100	1.42194500
H	4.54831600	-1.62824800	-1.29570000
H	1.76682100	-2.28342100	-2.17024700
H	-0.56554700	-1.13439600	-1.50048200
N	0.63476300	0.17153600	-0.28376700
C	-0.34845400	0.98991600	0.24684900
C	-1.76955700	0.60519000	-0.04318500
C	-2.38005300	-0.54755000	0.45814100
C	-2.54315000	1.50586700	-0.77891900
C	-3.72246700	-0.81276700	0.20387600
C	-3.87985200	1.24419600	-1.04784200
H	-2.07450500	2.41830200	-1.13533500
C	-4.46682200	0.08064000	-0.55758200
H	-4.17392200	-1.71087500	0.61201300
H	-4.46367600	1.94928600	-1.63134500
H	-5.51316300	-0.13144800	-0.75683200
Cl	-1.48804300	-1.65970000	1.45117100
O	-0.09029500	1.99441000	0.87790400
H	5.83574700	-0.05690200	0.13177800

S1, T_1

C	2.69388100	-0.79317000	-0.69524200
C	2.00413400	0.30085100	-0.05131600
C	2.66568900	1.27824000	0.63722000
C	4.07994200	1.17421100	0.72414100
C	4.78140300	0.11975700	0.11875900
C	4.11833300	-0.86205200	-0.59018800
C	1.76194100	-1.59342600	-1.30526900
C	0.43268100	-1.00155200	-1.05395800
H	2.12473000	2.09436300	1.09566300
H	4.62475000	1.93231300	1.27784000
H	4.65602600	-1.67644300	-1.06580100
H	1.92904700	-2.50578900	-1.86146500
H	-0.50755300	-1.20307100	-1.54237200
N	0.60766500	0.12778600	-0.27858800
C	-0.36412400	0.99730900	0.18330400
C	-1.78486300	0.60880500	-0.04079200
C	-2.38470700	-0.58126900	0.39203600
C	-2.60601800	1.56673700	-0.65099600
C	-3.73731000	-0.82934400	0.17648700
C	-3.95316500	1.32836600	-0.87517400
H	-2.15076100	2.50862900	-0.94125800
C	-4.51911600	0.12183300	-0.46760300
H	-4.16915600	-1.75901200	0.53229100
H	-4.56333800	2.08276100	-1.36272500
H	-5.57384100	-0.07625000	-0.63450800
Cl	-1.47465600	-1.76840000	1.28163200
O	-0.06872600	2.08481400	0.68096000
H	5.86318900	0.08050900	0.20857500

[S1]$^{-1}$

C	2.69540700	-0.72187300	-0.64993100

C	1.93262400	0.32951200	-0.06833100
C	2.50974000	1.28596800	0.76904900
C	3.86594500	1.17343000	1.03578100
C	4.63846100	0.13696900	0.47847400
C	4.06545300	-0.80510000	-0.36129200
C	1.79071500	-1.48740300	-1.44962200
C	0.55923100	-0.90240500	-1.31801800
H	1.90259800	2.09324400	1.16123100
H	4.34343900	1.90520600	1.68376500
H	4.66873900	-1.60226400	-0.79196200
H	2.02145400	-2.36107000	-2.04525100
H	-0.38971000	-1.16542200	-1.76383700
N	0.62312000	0.18256900	-0.47563000
C	-0.44200900	1.12183200	-0.21214800
C	-1.77550300	0.61981900	-0.07847000
C	-2.23940600	-0.67452200	0.33074400
C	-2.82665900	1.56108800	-0.34328400
C	-3.58012300	-1.01633900	0.33423300
C	-4.15659800	1.21827500	-0.34378700
H	-2.50529200	2.57150400	-0.57670000
C	-4.56495500	-0.09493300	-0.03577700
H	-3.85689700	-2.01296000	0.66942500
H	-4.90175900	1.97485000	-0.58585100
H	-5.61290900	-0.38102500	-0.04169600
Cl	-1.14546600	-1.85439500	1.05094300
O	-0.13667100	2.33485000	-0.18481900
H	5.70086200	0.07996600	0.70707800

S1$^{\cdot-}$

C	-1.465206000	0.085411000	-7.709592000
C	-1.917036000	-0.688469000	-6.627361000
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C	-2.223881000	1.355505000	-5.278092000
C	-1.771195000	2.093463000	-6.364835000
C	-1.394634000	1.465185000	-7.570540000
C	-2.110001000	-2.094503000	-6.412007000
C	-2.564605000	-2.239675000	-5.128287000
N	-2.668664000	-1.007094000	-4.506760000
H	-1.173257000	-0.391573000	-8.640770000
H	-2.536601000	1.830162000	-4.356693000
H	-1.709552000	3.174437000	-6.285790000
H	-1.047161000	2.072861000	-8.400469000
H	-1.935665000	-2.892602000	-7.119519000
H	-2.824533000	-3.131771000	-4.579387000
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O	-4.109389000	0.137000000	-3.106697000
C	-2.802927000	-1.588787000	-2.105071000
C	-1.576825000	-2.321698000	-1.948488000
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C	-1.330207000	-3.147736000	-0.865703000
C	-3.447792000	-2.514603000	0.098148000
C	-2.271461000	-3.287620000	0.162461000
H	-4.601244000	-1.100619000	-1.021510000

H	-0.377768000	-3.663797000	-0.803977000
H	-4.175091000	-2.568812000	0.903729000
H	-2.073786000	-3.948342000	0.998918000
Cl	-0.186655000	-2.049293000	-3.042267000

TS1

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C	-1.860898000	-0.668273000	-6.594414000
C	-2.273141000	0.016874000	-5.418494000
C	-2.331634000	1.413131000	-5.367356000
C	-1.973358000	2.118421000	-6.511373000
C	-1.566512000	1.455788000	-7.685110000
C	-1.904181000	-2.074655000	-6.295544000
C	-2.304904000	-2.198149000	-4.999162000
N	-2.529831000	-0.942868000	-4.439205000
H	-1.188464000	-0.440631000	-8.638607000
H	-2.660447000	1.918869000	-4.470426000
H	-2.012115000	3.203089000	-6.497838000
H	-1.296898000	2.038564000	-8.560337000
H	-1.666416000	-2.888361000	-6.965582000
H	-2.451026000	-3.080299000	-4.398408000
C	-3.086540000	-0.679183000	-3.141901000
O	-3.805428000	0.322752000	-3.018399000
C	-2.757910000	-1.582609000	-2.060722000
C	-1.660597000	-2.497332000	-2.034386000
C	-3.609250000	-1.567315000	-0.912433000

C	-1.499239000	-3.397688000	-0.972188000
C	-3.478877000	-2.493397000	0.094844000
C	-2.436179000	-3.457530000	0.044300000
H	-4.389890000	-0.814347000	-0.873058000
H	-0.632517000	-4.053115000	-0.958343000
H	-4.165586000	-2.483510000	0.935539000
H	-2.361878000	-4.224186000	0.809934000
Cl	0.089796000	-1.878797000	-2.731538000

TS1'

C	-1.425247000	0.102374000	-7.724727000
C	-1.826047000	-0.658845000	-6.602546000
C	-2.309629000	-0.000359000	-5.433347000
C	-2.396020000	1.366988000	-5.350597000
C	-1.985510000	2.105209000	-6.486107000
C	-1.511885000	1.486306000	-7.649508000
C	-1.849152000	-2.036010000	-6.344096000
C	-2.336338000	-2.197852000	-5.016727000
N	-2.606504000	-1.007582000	-4.476229000
H	-1.057658000	-0.391955000	-8.615964000
H	-2.770830000	1.861973000	-4.467060000
H	-2.044315000	3.186546000	-6.445866000
H	-1.211936000	2.094724000	-8.493799000
H	-1.556791000	-2.842398000	-6.999257000
H	-2.493675000	-3.109346000	-4.463561000
C	-3.191627000	-0.744618000	-3.148863000

O	-3.934275000	0.229648000	-3.084569000
C	-2.810983000	-1.617026000	-2.070063000
C	-1.777075000	-2.590632000	-2.108922000
C	-3.564506000	-1.503585000	-0.859431000
C	-1.554219000	-3.445328000	-1.022835000
C	-3.378311000	-2.386225000	0.175889000
C	-2.390099000	-3.398100000	0.078332000
H	-4.303043000	-0.712239000	-0.789170000
H	-0.731968000	-4.153232000	-1.060155000
H	-3.980555000	-2.304892000	1.074467000
H	-2.276736000	-4.125140000	0.876649000
Cl	0.031951000	-2.077220000	-3.002174000

TS1''

C	-1.034833000	-0.142066000	-7.260747000
C	-1.764485000	-0.769425000	-6.231969000
C	-2.552931000	0.023095000	-5.351209000
C	-2.626942000	1.395822000	-5.456214000
C	-1.888561000	1.995821000	-6.490805000
C	-1.107709000	1.239944000	-7.378235000
C	-1.900841000	-2.117965000	-5.832731000
C	-2.749767000	-2.148275000	-4.706242000
N	-3.154521000	-0.849649000	-4.418789000
H	-0.428253000	-0.731529000	-7.938442000
H	-3.232235000	1.981024000	-4.778115000
H	-1.930725000	3.073013000	-6.604854000

H	-0.558026000	1.743963000	-8.164598000
H	-1.482445000	-2.989045000	-6.313588000
H	-3.355611000	-2.985946000	-4.402003000
C	-3.526914000	-0.468657000	-3.101616000
O	-4.092155000	0.574744000	-2.862829000
C	-3.060187000	-1.469327000	-2.120315000
C	-2.065455000	-2.368828000	-2.527796000
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H	-1.826129000	-4.266224000	0.255704000
Cl	0.027346000	-1.072524000	-3.184315000

C

C	-1.531902000	0.054597000	-7.743294000
C	-1.864882000	-0.641637000	-6.575641000
C	-2.268946000	0.073561000	-5.422204000
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C	-2.003589000	2.136850000	-6.584957000
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C	-1.894534000	-2.044938000	-6.243456000
C	-2.282585000	-2.154141000	-4.950187000

N	-2.509699000	-0.874251000	-4.405243000
H	-1.221124000	-0.483944000	-8.632461000
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H	-1.352100000	1.998318000	-8.635525000
H	-1.670396000	-2.869104000	-6.904567000
H	-2.464924000	-3.035608000	-4.360441000
C	-2.950659000	-0.570302000	-3.113176000
O	-3.401651000	0.529825000	-2.848067000
C	-2.827782000	-1.625522000	-2.061668000
C	-1.884806000	-2.632049000	-2.045596000
C	-3.666415000	-1.545378000	-0.931832000
C	-1.702825000	-3.556960000	-1.048574000
C	-3.538195000	-2.463115000	0.104600000
C	-2.564083000	-3.464569000	0.054938000
H	-4.407759000	-0.755026000	-0.890801000
H	-0.935557000	-4.322174000	-1.097405000
H	-4.198762000	-2.397952000	0.961834000
H	-2.466638000	-4.173195000	0.871034000

TS2

C	-1.171967000	0.099112000	-7.541839000
C	-1.789807000	-0.663297000	-6.538275000
C	-2.495755000	-0.003314000	-5.498317000
C	-2.572614000	1.384011000	-5.419407000
C	-1.946219000	2.116535000	-6.426249000

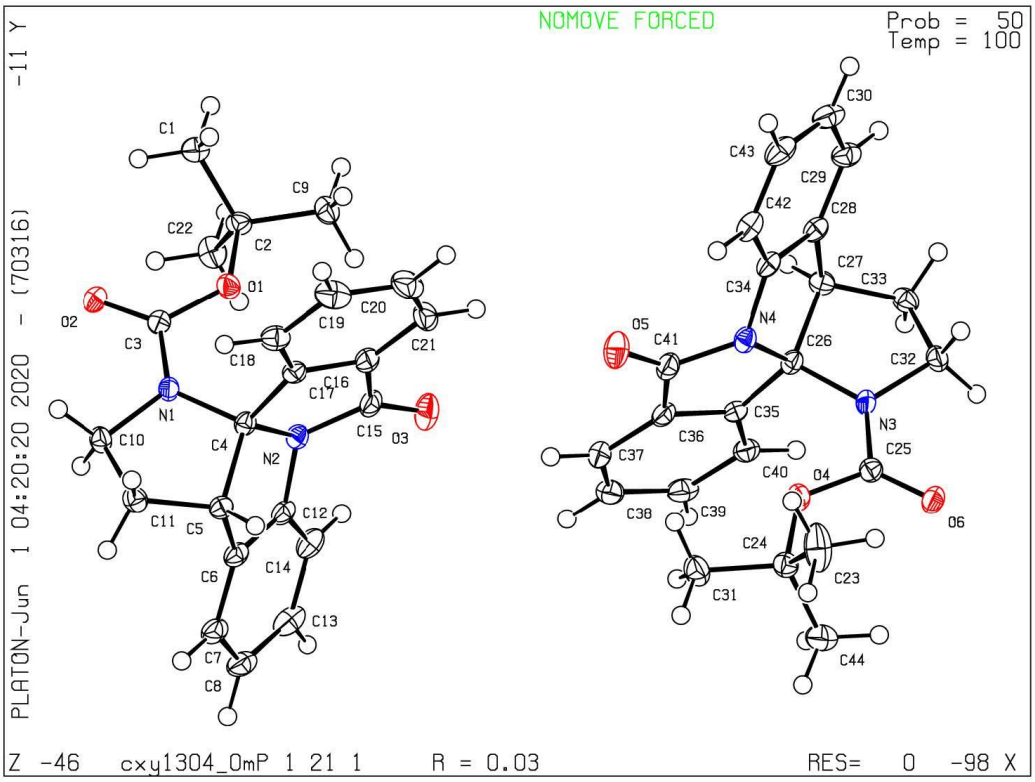
C	-1.258724000	1.483397000	-7.477364000
C	-1.893820000	-2.071648000	-6.299195000
C	-2.601246000	-2.254785000	-5.127810000
N	-2.998976000	-0.988600000	-4.630584000
H	-0.635746000	-0.388903000	-8.348765000
H	-3.111595000	1.866267000	-4.615541000
H	-1.999576000	3.199650000	-6.401359000
H	-0.790844000	2.088423000	-8.246632000
H	-1.550078000	-2.862662000	-6.949475000
H	-3.167568000	-3.131322000	-4.856557000
C	-3.192490000	-0.761570000	-3.250520000
O	-3.721005000	0.246637000	-2.826589000
C	-2.588179000	-1.828805000	-2.419870000
C	-1.764948000	-2.760836000	-3.026462000
C	-2.752969000	-1.877609000	-1.027023000
C	-1.119337000	-3.768426000	-2.344684000
C	-2.100987000	-2.869549000	-0.302598000
C	-1.289137000	-3.807432000	-0.952654000
H	-3.385874000	-1.143898000	-0.538728000
H	-0.492834000	-4.499307000	-2.845721000
H	-2.223098000	-2.920682000	0.773568000
H	-0.782565000	-4.573880000	-0.374115000

D

C	-1.072327000	0.287579000	-7.570997000
C	-1.635480000	-0.531721000	-6.565962000

C	-2.546397000	0.060262000	-5.631302000
C	-2.874199000	1.400808000	-5.664419000
C	-2.292228000	2.190739000	-6.669198000
C	-1.409020000	1.634786000	-7.608793000
C	-1.466431000	-1.888167000	-6.250545000
C	-2.416051000	-2.241278000	-5.139095000
N	-2.946439000	-0.923959000	-4.708853000
H	-0.384211000	-0.135110000	-8.295095000
H	-3.551221000	1.822132000	-4.932896000
H	-2.534533000	3.246434000	-6.721011000
H	-0.983117000	2.271111000	-8.377473000
H	-0.879667000	-2.614935000	-6.793500000
H	-3.245732000	-2.844501000	-5.542149000
C	-2.893566000	-0.760426000	-3.319557000
O	-3.196185000	0.254861000	-2.720272000
C	-2.336578000	-2.025220000	-2.783754000
C	-1.970210000	-2.866023000	-3.836570000
C	-2.099950000	-2.370549000	-1.456332000
C	-1.370008000	-4.091977000	-3.584571000
C	-1.484752000	-3.593606000	-1.199599000
C	-1.122177000	-4.441856000	-2.254446000
H	-2.385850000	-1.699387000	-0.653809000
H	-1.090428000	-4.759209000	-4.392732000
H	-1.282843000	-3.894269000	-0.177432000
H	-0.639492000	-5.387972000	-2.033808000

X-ray crystallographic details of compound 37



cxy1304_0m (CCDC number 2101131)

Table S3 Crystal data and structure refinement for cxy1304_0m.

Identification code	cxy1304_0m
Empirical formula	$C_{22}H_{22}N_2O_3$
Formula weight	362.41
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6179(7)
b/Å	15.5833(12)
c/Å	12.4610(9)
α/°	90
β/°	93.679(3)
γ/°	90
Volume/Å^3	1863.8(2)
Z	4
ρ_{calc}g/cm^3	1.292
μ/mm^{-1}	0.087
F(000)	768.0
Crystal size/mm^3	0.34 × 0.32 × 0.29
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.984 to 55.086

Index ranges	$-12 \le h \le 12, -20 \le k \le 20, -16 \le l \le 16$
Reflections collected	44261
Independent reflections	8583 [R_{int} = 0.0475, R_{sigma} = 0.0345]
Data/restraints/parameters	8583/1/494
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0786
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.0830
Largest diff. peak/hole / e Å $^{-3}$	0.27/-0.18
Flack parameter	0.4(3)

Table S4 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å ^{2}×10^3) for cxy1304_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	1728.5(14)	4098.4(9)	-326.5(11)	19.3(3)
O2	-96.5(15)	3621.0(9)	-1427.9(11)	20.0(3)
O3	2922.7(17)	4266.8(11)	2811.8(13)	29.4(4)
O4	6461.7(14)	5970.7(10)	7013.6(11)	22.0(3)
O5	5690.9(17)	5924.6(11)	3807.1(13)	30.4(4)
O6	8150.8(15)	6340.6(10)	8298.5(11)	20.9(3)
N1	-425.2(17)	4458.8(11)	17.3(13)	15.5(3)
N2	845.2(17)	4280.6(11)	1773.3(13)	16.7(3)
N3	8635.1(17)	5567.3(11)	6830.6(13)	17.3(4)
N4	7622.8(17)	5808.5(11)	4996.7(13)	17.7(4)
C1	3003(2)	3728.8(16)	-1901.9(17)	25.1(5)
C2	2803(2)	3534.7(14)	-731.4(16)	17.7(4)
C3	379(2)	4014.3(12)	-644.7(15)	15.3(4)
C4	79(2)	4871.3(13)	1029.3(15)	15.0(4)
C5	-1303(2)	5058.2(13)	1571.0(16)	16.7(4)
C6	-1390(2)	4287.5(13)	2308.9(16)	18.1(4)
C7	-2483(2)	3997.8(14)	2879.9(16)	21.6(4)
C8	-2254(2)	3306.1(15)	3581.9(17)	25.0(5)
C9	4087(2)	3794.8(15)	-31.4(18)	22.1(4)
C10	-1951(2)	4451.8(14)	-163.2(16)	18.0(4)
C11	-2407(2)	5117.5(13)	635.9(17)	18.6(4)
C12	-105(2)	3877.2(13)	2435.6(16)	18.1(4)
C13	-964(3)	2914.7(14)	3702.7(18)	25.7(5)
C14	143(2)	3186.7(14)	3121.0(17)	23.0(5)
C15	2140(2)	4599.3(14)	2127.8(16)	21.0(4)
C16	2316(2)	5406.8(14)	1534.6(17)	19.2(4)
C17	1113(2)	5579.7(13)	899.1(16)	17.0(4)
C18	998(2)	6304.6(14)	258.4(17)	21.4(4)
C19	2119(3)	6867.5(15)	315(2)	28.5(5)
C20	3314(2)	6706.9(16)	974(2)	29.9(5)
C21	3439(2)	5971.2(16)	1591.6(18)	25.6(5)
C22	2424(2)	2600.2(14)	-556.1(19)	24.2(5)
C23	5641(3)	7390.3(16)	7448(2)	39.0(7)

C24	5322(2)	6443.5(14)	7461.1(17)	19.4(4)
C25	7766(2)	5996.1(14)	7458.5(16)	17.1(4)
C26	8224(2)	5180.7(13)	5784.3(15)	16.0(4)
C27	9654(2)	4937.9(14)	5354.1(16)	18.0(4)
C28	9932(2)	5702.1(13)	4648.2(16)	18.0(4)
C29	11140(2)	5948.4(14)	4189.5(17)	21.8(4)
C30	11099(2)	6664.4(15)	3520.6(18)	24.8(5)
C31	4096(2)	6230.9(15)	6672.3(18)	24.9(5)
C32	10137(2)	5531.6(14)	7117.5(17)	18.9(4)
C33	10630(2)	4838.5(14)	6361.7(17)	19.7(4)
C34	8713(2)	6174.8(13)	4438.3(16)	18.5(4)
C35	7090(2)	4515.5(14)	5811.8(16)	17.0(4)
C36	5990(2)	4746.0(14)	5094.0(16)	19.5(4)
C37	4816(2)	4234.8(15)	4939.3(18)	23.7(5)
C38	4780(2)	3480.7(16)	5529.3(18)	25.7(5)
C39	5873(2)	3258.5(15)	6264.5(17)	24.1(5)
C40	7044(2)	3780.6(14)	6424.1(17)	20.8(4)
C41	6335(2)	5553.7(14)	4536.4(16)	20.5(4)
C42	8652(2)	6880.2(14)	3763.6(17)	22.3(5)
C43	9878(3)	7116.7(14)	3303.0(17)	25.2(5)
C44	5078(3)	6107(2)	8571.2(19)	40.2(7)

Table S5 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for cxy1304_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	14.9(7)	22.2(8)	20.7(7)	-5.7(6)	1.0(6)	0.9(6)
O2	21.8(7)	21.8(8)	16.3(7)	-4.2(6)	0.1(6)	-0.8(6)
O3	29.2(8)	31.9(9)	25.4(8)	-2.1(7)	-10.9(7)	5.3(7)
O4	15.5(7)	28.9(8)	21.4(7)	-9.1(7)	-0.9(6)	2.7(6)
O5	30.9(8)	33.3(9)	25.1(8)	4.4(7)	-11.1(6)	2.8(7)
O6	22.0(7)	24.7(8)	15.7(7)	-3.9(6)	-1.9(6)	0.1(6)
N1	14.1(8)	17.4(8)	14.8(8)	-2.3(7)	-1.3(6)	0.6(7)
N2	17.6(8)	17.4(8)	14.9(8)	1.2(7)	-0.3(6)	0.8(7)
N3	14.3(8)	22.8(9)	14.5(8)	-2.0(7)	-2.5(6)	0.8(7)
N4	18.9(8)	18.4(9)	15.3(8)	0.5(7)	-2.0(6)	2.6(7)
C1	21.6(11)	34.0(13)	20.1(11)	1.8(9)	3.6(8)	-1.5(10)
C2	16.2(9)	18.6(10)	18.5(10)	-0.2(8)	3.0(8)	3.7(8)
C3	17.6(9)	13.1(9)	15.2(10)	1.2(8)	0.5(7)	-1.4(8)
C4	16.3(9)	14.1(9)	14.5(9)	-1.7(7)	-0.2(7)	1.3(8)
C5	17.5(9)	16.6(10)	16.2(9)	-2.5(8)	1.7(7)	0.7(8)
C6	23.2(10)	16.5(10)	14.8(9)	-4.0(8)	2.0(8)	-1.8(8)
C7	26.7(11)	21.1(10)	17.3(10)	-6.1(8)	4.1(8)	-3.6(9)
C8	33.8(12)	23.8(11)	18.3(10)	-4.8(9)	7.8(9)	-9.2(10)
C9	16.3(10)	25.5(11)	24.0(11)	-0.1(9)	-1.3(8)	1.0(9)
C10	14.5(9)	19.8(10)	19.4(10)	-0.8(8)	-2.1(7)	1.3(8)
C11	16.2(9)	18.0(10)	21.5(10)	-0.8(8)	0.6(8)	1.9(8)
C12	23.8(10)	17.1(10)	13.4(9)	-3.8(8)	1.2(8)	-2.0(8)

C13	43.3(14)	16.4(10)	17.5(10)	-0.2(8)	4.2(9)	-4.3(10)
C14	33.6(12)	17.4(10)	17.7(10)	-1.8(8)	-0.1(9)	2.8(9)
C15	21.2(10)	26.0(11)	15.4(10)	-7.4(8)	-1.6(8)	2.1(9)
C16	18.8(10)	21.5(10)	17.4(10)	-7.5(8)	1.9(8)	1.7(8)
C17	17.6(9)	17.6(10)	16.1(10)	-4.5(8)	3.5(7)	0.0(8)
C18	23.7(10)	18.5(10)	22.5(10)	-1.4(9)	5.9(8)	1.2(9)
C19	32.4(13)	18.4(11)	35.9(13)	-0.4(10)	10.9(10)	-2.7(9)
C20	26.3(12)	27.3(12)	37.0(13)	-10.3(10)	9.9(10)	-11.4(10)
C21	18.3(10)	30.6(12)	27.8(11)	-11.5(10)	0.9(8)	-4.6(9)
C22	24.0(11)	19.1(10)	29.0(12)	3.6(9)	-2.1(9)	1.9(9)
C23	38.6(15)	22.0(12)	53.3(16)	-6.5(12)	-20.7(13)	3.8(11)
C24	17.0(10)	20.7(10)	20.6(10)	-2.2(8)	1.1(8)	1.9(8)
C25	17.3(9)	17.8(9)	16.0(9)	2.5(8)	-0.1(7)	-0.8(8)
C26	17.4(9)	17.0(9)	13.5(9)	-0.7(8)	-0.9(7)	3.0(8)
C27	17.7(9)	17.1(10)	19.5(10)	0.1(8)	2.2(8)	1.3(8)
C28	23.3(10)	16.3(10)	14.4(9)	-3.0(8)	1.4(8)	0.2(8)
C29	25.8(11)	19.9(10)	20.5(10)	-3.2(9)	6.6(8)	-0.7(9)
C30	34.4(12)	21.3(11)	19.9(10)	-4.2(9)	10.6(9)	-6.4(10)
C31	17.8(10)	27.1(12)	29.4(12)	-4.3(9)	-1.8(8)	2.2(9)
C32	14.4(9)	22.9(10)	18.9(10)	2.1(8)	-2.2(7)	-1.3(8)
C33	15.9(10)	20.6(10)	22.6(11)	4.6(8)	1.0(8)	1.3(8)
C34	24.0(10)	18.3(10)	13.2(9)	-3.3(8)	0.2(8)	-0.2(8)
C35	16.9(9)	20.5(10)	13.8(9)	-3.8(8)	3.3(7)	0.7(8)
C36	20.7(10)	25.0(11)	12.9(9)	-3.9(8)	0.8(7)	2.2(8)
C37	20.2(10)	32.9(12)	17.7(10)	-5.8(9)	-0.7(8)	-1.9(9)
C38	23.1(11)	31.9(12)	22.9(11)	-6.0(9)	6.5(9)	-8.0(9)
C39	28.4(12)	23.9(11)	21.0(11)	0.9(9)	9.0(9)	-3.1(9)
C40	20.3(10)	25.3(11)	17.1(10)	0.1(8)	3.6(8)	2.6(9)
C41	21.5(10)	23.3(11)	16.4(10)	-4.6(8)	-1.8(8)	2.1(9)
C42	31.8(12)	18.3(11)	16.3(10)	-0.4(8)	-1.5(9)	2.5(9)
C43	40.3(13)	18.8(10)	16.6(10)	2.0(8)	3.1(9)	-3.0(10)
C44	24.4(12)	72(2)	24.7(12)	6.6(13)	5.1(9)	-4.3(13)

Table S6 Bond Lengths for cxy1304_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.470(2)	C10	C11	1.522(3)
O1	C3	1.339(2)	C12	C14	1.385(3)
O2	C3	1.217(2)	C13	C14	1.392(3)
O3	C15	1.216(3)	C15	C16	1.475(3)
O4	C24	1.461(2)	C16	C17	1.386(3)
O4	C25	1.339(2)	C16	C21	1.391(3)
O5	C41	1.213(3)	C17	C18	1.384(3)
O6	C25	1.213(2)	C18	C19	1.389(3)
N1	C3	1.357(3)	C19	C20	1.392(4)
N1	C4	1.470(2)	C20	C21	1.381(4)
N1	C10	1.471(2)	C23	C24	1.507(3)

N2	C4	1.470(3)	C24	C31	1.522(3)
N2	C12	1.417(3)	C24	C44	1.512(3)
N2	C15	1.386(3)	C26	C27	1.555(3)
N3	C25	1.357(3)	C26	C35	1.507(3)
N3	C26	1.467(3)	C27	C28	1.515(3)
N3	C32	1.467(2)	C27	C33	1.526(3)
N4	C26	1.477(2)	C28	C29	1.381(3)
N4	C34	1.415(3)	C28	C34	1.395(3)
N4	C41	1.389(3)	C29	C30	1.392(3)
C1	C2	1.514(3)	C30	C43	1.381(3)
C2	C9	1.521(3)	C32	C33	1.528(3)
C2	C22	1.520(3)	C34	C42	1.383(3)
C4	C5	1.556(3)	C35	C36	1.388(3)
C4	C17	1.502(3)	C35	C40	1.378(3)
C5	C6	1.518(3)	C36	C37	1.385(3)
C5	C11	1.528(3)	C36	C41	1.486(3)
C6	C7	1.383(3)	C37	C38	1.388(3)
C6	C12	1.391(3)	C38	C39	1.393(3)
C7	C8	1.397(3)	C39	C40	1.394(3)
C8	C13	1.382(3)	C42	C43	1.394(3)

Table S7 Bond Angles for cxy1304_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O1	C2	121.96(16)	C16	C17	C4	109.26(18)
C25	O4	C24	122.22(16)	C18	C17	C4	129.29(18)
C3	N1	C4	125.13(16)	C18	C17	C16	121.44(19)
C3	N1	C10	120.38(17)	C17	C18	C19	116.9(2)
C4	N1	C10	113.92(15)	C18	C19	C20	121.7(2)
C12	N2	C4	109.21(16)	C21	C20	C19	121.1(2)
C15	N2	C4	112.34(17)	C20	C21	C16	117.2(2)
C15	N2	C12	124.95(17)	O4	C24	C23	109.33(19)
C25	N3	C26	125.01(16)	O4	C24	C31	102.30(16)
C25	N3	C32	120.76(17)	O4	C24	C44	109.80(18)
C32	N3	C26	113.96(16)	C23	C24	C31	110.86(19)
C34	N4	C26	108.86(16)	C23	C24	C44	113.1(2)
C41	N4	C26	112.68(17)	C44	C24	C31	110.86(19)
C41	N4	C34	125.54(17)	O4	C25	N3	109.99(17)
O1	C2	C1	110.29(17)	O6	C25	O4	126.59(18)
O1	C2	C9	101.94(16)	O6	C25	N3	123.42(18)
O1	C2	C22	110.03(16)	N3	C26	N4	112.97(16)
C1	C2	C9	110.53(17)	N3	C26	C27	102.25(15)
C1	C2	C22	112.10(19)	N3	C26	C35	114.61(16)
C22	C2	C9	111.49(18)	N4	C26	C27	104.44(16)
O1	C3	N1	110.47(16)	N4	C26	C35	102.58(15)
O2	C3	O1	126.46(19)	C35	C26	C27	119.88(17)
O2	C3	N1	123.05(18)	C28	C27	C26	101.66(16)

N1	C4	N2	113.05(16)	C28	C27	C33	115.81(17)
N1	C4	C5	102.14(15)	C33	C27	C26	104.59(16)
N1	C4	C17	114.41(16)	C29	C28	C27	130.05(19)
N2	C4	C5	104.54(15)	C29	C28	C34	119.64(19)
N2	C4	C17	102.68(15)	C34	C28	C27	110.26(17)
C17	C4	C5	119.95(17)	C28	C29	C30	118.6(2)
C6	C5	C4	101.33(16)	C43	C30	C29	121.2(2)
C6	C5	C11	116.56(17)	N3	C32	C33	102.47(16)
C11	C5	C4	104.56(16)	C27	C33	C32	103.69(16)
C7	C6	C5	130.03(19)	C28	C34	N4	109.58(17)
C7	C6	C12	119.4(2)	C42	C34	N4	128.02(19)
C12	C6	C5	110.45(17)	C42	C34	C28	122.39(19)
C6	C7	C8	118.7(2)	C36	C35	C26	109.27(18)
C13	C8	C7	120.9(2)	C40	C35	C26	129.26(19)
N1	C10	C11	102.78(16)	C40	C35	C36	121.5(2)
C10	C11	C5	104.04(16)	C35	C36	C41	109.69(18)
C6	C12	N2	109.34(18)	C37	C36	C35	121.4(2)
C14	C12	N2	127.7(2)	C37	C36	C41	128.8(2)
C14	C12	C6	122.9(2)	C36	C37	C38	117.5(2)
C8	C13	C14	121.4(2)	C37	C38	C39	121.0(2)
C12	C14	C13	116.8(2)	C38	C39	C40	121.2(2)
O3	C15	N2	125.0(2)	C35	C40	C39	117.4(2)
O3	C15	C16	129.0(2)	O5	C41	N4	124.9(2)
N2	C15	C16	106.01(17)	O5	C41	C36	129.4(2)
C17	C16	C15	109.50(18)	N4	C41	C36	105.61(17)
C17	C16	C21	121.5(2)	C34	C42	C43	117.2(2)
C21	C16	C15	128.9(2)	C30	C43	C42	121.0(2)

Table S8 Torsion Angles for cxy1304_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C15	C16	C17	-174.8(2)	C15	C16	C21	C20	-177.5(2)
O3	C15	C16	C21	2.1(4)	C16	C17	C18	C19	-2.6(3)
N1	C4	C5	C6	96.25(17)	C17	C4	C5	C6	-136.03(18)
N1	C4	C5	C11	-25.29(19)	C17	C4	C5	C11	102.4(2)
N1	C4	C17	C16	-124.46(18)	C17	C16	C21	C20	-0.9(3)
N1	C4	C17	C18	54.5(3)	C17	C18	C19	C20	0.8(3)
N1	C10	C11	C5	-31.4(2)	C18	C19	C20	C21	0.8(4)
N2	C4	C5	C6	-21.75(19)	C19	C20	C21	C16	-0.8(3)
N2	C4	C5	C11	-143.29(16)	C21	C16	C17	C4	-178.28(18)
N2	C4	C17	C16	-1.6(2)	C21	C16	C17	C18	2.7(3)
N2	C4	C17	C18	177.4(2)	C24	O4	C25	O6	6.0(3)
N2	C12	C14	C13	179.02(19)	C24	O4	C25	N3	-174.41(17)
N2	C15	C16	C17	3.6(2)	C25	O4	C24	C23	61.0(3)
N2	C15	C16	C21	-179.5(2)	C25	O4	C24	C31	178.55(19)
N3	C26	C27	C28	-96.17(17)	C25	O4	C24	C44	-63.7(3)
N3	C26	C27	C33	24.7(2)	C25	N3	C26	N4	58.3(3)

N3	C26	C35	C36	124.00(18)	C25	N3	C26	C27	169.97(18)
N3	C26	C35	C40	-55.6(3)	C25	N3	C26	C35	-58.7(3)
N3	C32	C33	C27	32.6(2)	C25	N3	C32	C33	167.71(18)
N4	C26	C27	C28	21.75(19)	C26	N3	C25	O4	3.7(3)
N4	C26	C27	C33	142.62(16)	C26	N3	C25	O6	-176.7(2)
N4	C26	C35	C36	1.2(2)	C26	N3	C32	C33	-17.9(2)
N4	C26	C35	C40	-178.4(2)	C26	N4	C34	C28	12.4(2)
N4	C34	C42	C43	-179.85(19)	C26	N4	C34	C42	-168.6(2)
C2	O1	C3	O2	-16.4(3)	C26	N4	C41	O5	-173.6(2)
C2	O1	C3	N1	165.49(16)	C26	N4	C41	C36	4.3(2)
C3	O1	C2	C1	70.3(2)	C26	C27	C28	C29	167.2(2)
C3	O1	C2	C9	-172.33(17)	C26	C27	C28	C34	-15.5(2)
C3	O1	C2	C22	-53.9(2)	C26	C27	C33	C32	-36.0(2)
C3	N1	C4	N2	-53.9(2)	C26	C35	C36	C37	178.53(19)
C3	N1	C4	C5	-165.61(18)	C26	C35	C36	C41	1.3(2)
C3	N1	C4	C17	63.2(2)	C26	C35	C40	C39	-178.0(2)
C3	N1	C10	C11	-172.11(17)	C27	C26	C35	C36	-113.8(2)
C4	N1	C3	O1	-8.3(3)	C27	C26	C35	C40	66.6(3)
C4	N1	C3	O2	173.56(19)	C27	C28	C29	C30	176.7(2)
C4	N1	C10	C11	16.1(2)	C27	C28	C34	N4	2.8(2)
C4	N2	C12	C6	-11.3(2)	C27	C28	C34	C42	-176.32(19)
C4	N2	C12	C14	169.1(2)	C28	C27	C33	C32	74.9(2)
C4	N2	C15	O3	173.70(19)	C28	C29	C30	C43	-0.9(3)
C4	N2	C15	C16	-4.8(2)	C28	C34	C42	C43	-1.0(3)
C4	C5	C6	C7	-168.1(2)	C29	C28	C34	N4	-179.58(18)
C4	C5	C6	C12	16.2(2)	C29	C28	C34	C42	1.3(3)
C4	C5	C11	C10	35.7(2)	C29	C30	C43	C42	1.3(3)
C4	C17	C18	C19	178.6(2)	C32	N3	C25	O4	177.38(18)
C5	C4	C17	C16	113.7(2)	C32	N3	C25	O6	-3.0(3)
C5	C4	C17	C18	-67.4(3)	C32	N3	C26	N4	-115.77(19)
C5	C6	C7	C8	-174.5(2)	C32	N3	C26	C27	-4.1(2)
C5	C6	C12	N2	-3.9(2)	C32	N3	C26	C35	127.20(19)
C5	C6	C12	C14	175.74(18)	C33	C27	C28	C29	54.5(3)
C6	C5	C11	C10	-75.2(2)	C33	C27	C28	C34	-128.17(19)
C6	C7	C8	C13	-0.3(3)	C34	N4	C26	N3	88.63(19)
C6	C12	C14	C13	-0.6(3)	C34	N4	C26	C27	-21.7(2)
C7	C6	C12	N2	179.80(18)	C34	N4	C26	C35	-147.45(16)
C7	C6	C12	C14	-0.5(3)	C34	N4	C41	O5	-36.8(3)
C7	C8	C13	C14	-0.9(3)	C34	N4	C41	C36	141.13(19)
C8	C13	C14	C12	1.3(3)	C34	C28	C29	C30	-0.4(3)
C10	N1	C3	O1	-179.08(17)	C34	C42	C43	C30	-0.3(3)
C10	N1	C3	O2	2.8(3)	C35	C26	C27	C28	135.79(18)
C10	N1	C4	N2	117.46(18)	C35	C26	C27	C33	-103.3(2)
C10	N1	C4	C5	5.7(2)	C35	C36	C37	C38	-0.1(3)
C10	N1	C4	C17	-125.46(18)	C35	C36	C41	O5	174.4(2)
C11	C5	C6	C7	-55.3(3)	C35	C36	C41	N4	-3.4(2)
C11	C5	C6	C12	128.95(19)	C36	C35	C40	C39	2.5(3)
C12	N2	C4	N1	-89.17(19)	C36	C37	C38	C39	1.3(3)

C12	N2	C4	C5	21.1(2)	C37	C36	C41	O5	-2.6(4)
C12	N2	C4	C17	147.05(16)	C37	C36	C41	N4	179.6(2)
C12	N2	C15	O3	37.5(3)	C37	C38	C39	C40	-0.7(3)
C12	N2	C15	C16	-140.92(19)	C38	C39	C40	C35	-1.2(3)
C12	C6	C7	C8	0.9(3)	C40	C35	C36	C37	-1.9(3)
C15	N2	C4	N1	127.78(18)	C40	C35	C36	C41	-179.08(18)
C15	N2	C4	C5	-121.95(17)	C41	N4	C26	N3	-127.42(18)
C15	N2	C4	C17	4.0(2)	C41	N4	C26	C27	122.27(18)
C15	N2	C12	C6	126.0(2)	C41	N4	C26	C35	-3.5(2)
C15	N2	C12	C14	-53.6(3)	C41	N4	C34	C28	-125.8(2)
C15	C16	C17	C4	-1.2(2)	C41	N4	C34	C42	53.2(3)
C15	C16	C17	C18	179.81(18)	C41	C36	C37	C38	176.6(2)

Table S9 Hydrogen Atom Coordinates (Å ×10^4) and Isotropic Displacement Parameters (Å ^{2}×10^3) for cxy1304_0m.

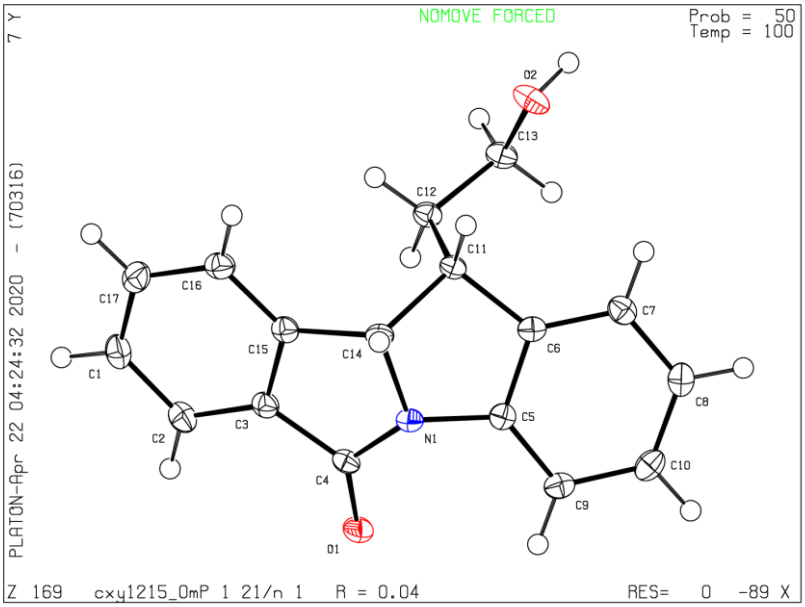
Atom	*x*	*y*	*z*	U(eq)
H1A	2180.24	3539.19	-2343.81	38
H1B	3827.79	3424.88	-2126.2	38
H1C	3129.63	4347.84	-1993.57	38
H5	-1240.35	5605.52	1990.26	20
H7	-3372.09	4263.88	2796.45	26
H8	-2995.05	3101.86	3981.6	30
H9A	4254.53	4410.9	-114.21	33
H9B	4896.75	3472.92	-251.89	33
H9C	3938.69	3668.14	723.01	33
H10A	-2338.88	3879.13	-11.4	22
H10B	-2243.04	4617.67	-910.9	22
H11A	-3342.98	4981.41	876.18	22
H11B	-2425.48	5698.66	314.52	22
H13	-829.55	2450.6	4192.72	31
H14	1026.06	2912.02	3190.77	28
H18	188.62	6412.29	-199.35	26
H19	2069.92	7375.57	-106.9	34
H20	4056.46	7110.08	1000.53	36
H21	4257.68	5855.58	2035.97	31
H22A	2242.73	2510.97	200.87	36
H22B	3196.73	2232.03	-745.71	36
H22C	1587.09	2455.34	-1010.36	36
H23A	6492.04	7503.45	7901.37	59
H23B	4863.45	7710.06	7725.71	59
H23C	5775.41	7572.8	6709.52	59
H27	9590.68	4394.14	4927.57	22
H29	11980.24	5635.69	4327.66	26
H30	11925.65	6845.3	3208.16	30
H31A	4298.35	6425.68	5951	37
H31B	3257.51	6520.95	6895.66	37
H31C	3941.82	5609.19	6662.28	37

H32A	10327.88	5367.11	7880.1	23
H32B	10589.06	6089.45	6987.2	23
H33A	11611.08	4933.9	6197.38	24
H33B	10542.6	4260.42	6680.06	24
H37	4064.51	4394.35	4447.94	28
H38	3997.42	3110.35	5430.33	31
H39	5818.57	2741.76	6664.17	29
H40	7782.73	3635.69	6934.94	25
H42	7810.48	7190.48	3620.11	27
H43	9874.22	7596.26	2832.13	30
H44A	5046.24	5478.45	8554.25	60
H44B	4190.8	6329.19	8800.56	60
H44C	5837.6	6294.92	9078.51	60

Table S10 Crystal data and structure refinement for cxy1304_0m.

Identification code	cxy1304_0m
Empirical formula	$C_{22}H_{22}N_2O_3$
Formula weight	362.41
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6179(7)
b/Å	15.5833(12)
c/Å	12.4610(9)
α/°	90
β/°	93.679(3)
γ/°	90
Volume/Å ^{3}	1863.8(2)
Z	4
ρ_{calc}g/cm^3	1.292
μ/mm^{-1}	0.087
F(000)	768.0
Crystal size/mm^3	0.34 × 0.32 × 0.29
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.984 to 55.086
Index ranges	$-12 \le h \le 12$, $-20 \le k \le 20$, $-16 \le l \le 16$
Reflections collected	44261
Independent reflections	8583 [R_{int} = 0.0475, R_{sigma} = 0.0345]
Data/restraints/parameters	8583/1/494
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0786
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.0830
Largest diff. peak/hole / e Å $^{-3}$	0.27/-0.18
Flack parameter	0.4(3)

X-Ray details of compound *cis*-34



cxy1215_0m (CCDC number 2101130)

Table S11 Crystal data and structure refinement for cxy1215_0m.

Identification code	cxy1215_0m
Empirical formula	$C_{17}H_{15}NO_2$
Formula weight	265.30
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.4073(6)
b/Å	8.7265(5)
c/Å	14.6032(7)
α/°	90
β/°	94.709(2)
γ/°	90
Volume/Å ^{3}	1321.78(12)
Z	4
ρ_{calc}g/cm^3	1.333
μ/mm^{-1}	0.088
F(000)	560.0
Crystal size/mm^3	0.34 × 0.29 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.632 to 55.162
Index ranges	$-13 \leq h \leq 13$, $-11 \leq k \leq 9$, $-18 \leq l \leq 19$
Reflections collected	18279
Independent reflections	3054 [R_{int} = 0.0357, R_{sigma} = 0.0229]
Data/restraints/parameters	3054/0/183
Goodness-of-fit on F^2	1.054

Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0919
Final R indexes [all data]	R_1 = 0.0430, wR_2 = 0.0960
Largest diff. peak/hole / e Å $^{-3}$	0.31/-0.20

Table S12 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å ^{2}×10^3) for cxy1215_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4575.9(8)	2426.3(10)	878.5(5)	21.1(2)
O2	1532.6(8)	3810.9(10)	4907.7(6)	23.8(2)
N1	3831.5(9)	4160.0(10)	1903.4(6)	15.3(2)
C1	7765.9(11)	2381.4(14)	3150.8(8)	22.0(3)
C2	6929.1(11)	2276.5(13)	2358.7(8)	20.2(2)
C3	5794.2(10)	3121.5(12)	2330.2(7)	16.3(2)
C4	4715.5(10)	3154.7(12)	1599.5(7)	15.8(2)
C5	2475.3(10)	4087.4(11)	1758.0(7)	14.9(2)
C6	1941.2(11)	4373.3(12)	2589.3(7)	15.1(2)
C7	613.0(11)	4449.3(12)	2603.4(8)	18.5(2)
C8	-156.1(11)	4202.1(13)	1783.6(8)	20.6(2)
C9	1731.5(11)	3806.3(12)	943.7(7)	17.9(2)
C10	397.2(11)	3861.4(13)	975.0(8)	20.3(2)
C11	2998.3(10)	4486.3(12)	3372.3(7)	14.2(2)
C12	3135.0(11)	2996.1(12)	3937.0(7)	16.3(2)
C13	1925.5(11)	2547.7(12)	4388.3(8)	18.3(2)
C14	4199.1(10)	4799.2(12)	2827.4(7)	14.9(2)
C15	5481.5(10)	4037.6(12)	3063.7(7)	15.9(2)
C16	6340.0(11)	4170.5(13)	3839.7(7)	19.3(2)
C17	7481.9(11)	3326.6(14)	3877.5(8)	21.3(3)

Table S13 Anisotropic Displacement Parameters (Å ^{2}×10^3) for cxy1215_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	20.9(4)	26.1(4)	16.5(4)	-6.1(3)	3.6(3)	0.8(3)
O2	27.2(5)	22.5(4)	23.7(4)	-5.5(3)	13.4(3)	-5.9(3)
N1	17.4(5)	15.9(4)	12.7(4)	-1.1(3)	2.1(3)	-0.3(3)
C1	14.7(5)	22.8(6)	28.6(6)	3.0(5)	3.0(4)	-0.6(4)
C2	17.4(6)	20.3(6)	23.5(6)	-1.7(4)	5.0(4)	-1.6(4)
C3	15.8(5)	16.6(5)	16.8(5)	0.0(4)	3.4(4)	-3.7(4)
C4	16.7(5)	16.1(5)	15.1(5)	0.9(4)	5.0(4)	-1.7(4)
C5	17.1(5)	11.3(5)	16.3(5)	1.6(4)	1.4(4)	1.1(4)
C6	19.5(5)	11.3(5)	14.6(5)	0.9(4)	1.8(4)	0.5(4)
C7	19.5(5)	16.3(5)	20.3(5)	1.0(4)	4.4(4)	1.6(4)
C8	16.3(5)	19.1(5)	26.1(6)	2.7(4)	0.1(4)	-0.1(4)
C9	23.0(6)	15.2(5)	15.4(5)	-0.2(4)	1.0(4)	1.4(4)
C10	22.9(6)	16.3(5)	20.6(5)	1.3(4)	-4.5(4)	-1.7(4)
C11	16.2(5)	12.8(5)	13.8(5)	-0.5(4)	3.2(4)	-0.1(4)
C12	19.3(5)	14.5(5)	15.6(5)	1.4(4)	3.5(4)	0.9(4)

C13	22.4(6)	15.5(5)	17.6(5)	0.2(4)	5.1(4)	-1.8(4)
C14	18.7(5)	13.1(5)	12.9(5)	-1.3(4)	2.1(4)	-1.9(4)
C15	16.3(5)	14.7(5)	17.0(5)	1.7(4)	3.2(4)	-3.7(4)
C16	20.6(5)	20.8(5)	16.8(5)	-0.9(4)	2.8(4)	-5.4(4)
C17	17.7(5)	24.0(6)	21.9(5)	4.1(4)	-1.0(4)	-6.3(4)

Table S14 Bond Lengths for cxy1215_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C4	1.2282(13)	C6	C7	1.3857(15)
O2	C13	1.4172(13)	C6	C11	1.5235(14)
N1	C4	1.3711(14)	C7	C8	1.4011(15)
N1	C5	1.4115(14)	C8	C10	1.3878(17)
N1	C14	1.4810(13)	C9	C10	1.3941(16)
C1	C2	1.3925(16)	C11	C12	1.5402(14)
C1	C17	1.3947(17)	C11	C14	1.5597(14)
C2	C3	1.3901(16)	C12	C13	1.5193(15)
C3	C4	1.4843(15)	C14	C15	1.5054(15)
C3	C15	1.3962(15)	C15	C16	1.3892(15)
C5	C6	1.3984(15)	C16	C17	1.3953(17)
C5	C9	1.3864(14)			

Table S15 Bond Angles for cxy1215_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N1	C5	127.72(9)	C6	C7	C8	118.72(10)
C4	N1	C14	113.95(9)	C10	C8	C7	120.81(10)
C5	N1	C14	109.53(8)	C5	C9	C10	116.96(10)
C2	C1	C17	120.91(11)	C8	C10	C9	121.28(10)
C3	C2	C1	117.51(10)	C6	C11	C12	112.12(8)
C2	C3	C4	128.50(10)	C6	C11	C14	100.83(8)
C2	C3	C15	122.12(10)	C12	C11	C14	112.23(9)
C15	C3	C4	109.27(9)	C13	C12	C11	113.97(9)
O1	C4	N1	124.98(10)	O2	C13	C12	108.52(9)
O1	C4	C3	129.45(10)	N1	C14	C11	103.95(8)
N1	C4	C3	105.53(9)	N1	C14	C15	101.56(8)
C6	C5	N1	108.98(9)	C15	C14	C11	122.56(9)
C9	C5	N1	128.17(10)	C3	C15	C14	109.57(9)
C9	C5	C6	122.85(10)	C16	C15	C3	119.92(10)
C5	C6	C11	110.43(9)	C16	C15	C14	130.46(10)
C7	C6	C5	119.31(10)	C15	C16	C17	118.48(10)
C7	C6	C11	130.20(10)	C1	C17	C16	121.00(10)

Table S16 Torsion Angles for cxy1215_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°

N1	C5	C6	C7	176.29(9)	C6	C5	C9	C10	1.80(16)
N1	C5	C6	C11	-6.19(11)	C6	C7	C8	C10	1.09(16)
N1	C5	C9	C10	-177.27(10)	C6	C11	C12	C13	-60.49(12)
N1	C14	C15	C3	1.79(11)	C6	C11	C14	N1	-24.11(10)
N1	C14	C15	C16	179.14(11)	C6	C11	C14	C15	-137.91(10)
C1	C2	C3	C4	-176.48(10)	C7	C6	C11	C12	76.75(14)
C1	C2	C3	C15	-0.54(16)	C7	C6	C11	C14	-163.68(11)
C2	C1	C17	C16	1.30(17)	C7	C8	C10	C9	-2.25(17)
C2	C3	C4	O1	1.85(19)	C9	C5	C6	C7	-2.93(16)
C2	C3	C4	N1	179.72(11)	C9	C5	C6	C11	174.58(9)
C2	C3	C15	C14	-179.86(10)	C11	C6	C7	C8	-175.55(10)
C2	C3	C15	C16	2.47(16)	C11	C12	C13	O2	-53.34(12)
C3	C15	C16	C17	-2.46(16)	C11	C14	C15	C3	116.78(10)
C4	N1	C5	C6	134.17(10)	C11	C14	C15	C16	-65.87(15)
C4	N1	C5	C9	-46.66(16)	C12	C11	C14	N1	95.38(9)
C4	N1	C14	C11	-127.69(9)	C12	C11	C14	C15	-18.42(13)
C4	N1	C14	C15	0.39(11)	C14	N1	C4	O1	175.74(10)
C4	C3	C15	C14	-3.23(12)	C14	N1	C4	C3	-2.25(11)
C4	C3	C15	C16	179.10(9)	C14	N1	C5	C6	-10.80(11)
C5	N1	C4	O1	32.03(17)	C14	N1	C5	C9	168.37(10)
C5	N1	C4	C3	-145.96(10)	C14	C11	C12	C13	-173.14(9)
C5	N1	C14	C11	22.53(10)	C14	C15	C16	C17	-179.57(11)
C5	N1	C14	C15	150.61(8)	C15	C3	C4	O1	-174.50(11)
C5	C6	C7	C8	1.41(15)	C15	C3	C4	N1	3.37(12)
C5	C6	C11	C12	-100.41(10)	C15	C16	C17	C1	0.63(16)
C5	C6	C11	C14	19.16(11)	C17	C1	C2	C3	-1.33(17)
C5	C9	C10	C8	0.80(16)					

Table S17 Hydrogen Atom Coordinates (Å ×10^4) and Isotropic Displacement Parameters (Å ^{2}×10^3) for cxy1215_0m.

Atom	*x*	*y*	*z*	U(eq)
H2	912.17	3548.26	5206.17	36
H1	8540.79	1801.11	3196.81	26
H2A	7126.52	1650.96	1856.68	24
H7	231.34	4664.83	3158.26	22
H8	-1067.48	4268.49	1781.29	25
H9	2113.8	3586.04	389.73	21
H10	-144	3661.98	432.19	24
H11	2835.66	5375.03	3779.34	17
H12A	3366.85	2152.34	3528.33	20
H12B	3852.23	3118.6	4420.24	20
H13A	1232.15	2266.95	3913.15	22
H13B	2104.31	1651.65	4794.72	22
H14	4329.16	5930.35	2776.15	18
H16	6153.93	4820.99	4333.44	23
H17	8074.99	3397.01	4406.12	26

Experimental details

Single crystals of $C_{17}H_{15}NO_2$ **[cxy1215_0m]** were generated from ethyl acetate and hexane. A suitable crystal was selected on a **BrukerD8 venture microsource** diffractometer. The crystal was kept at 100 K during data collection. Using Olex2,[18] the structure was solved with the ShelXT [19] structure solution program using Intrinsic Phasing and refined with the ShelXL [20] refinement package using Least Squares minimisation.

Crystal structure determination of [cxy1215_0m]

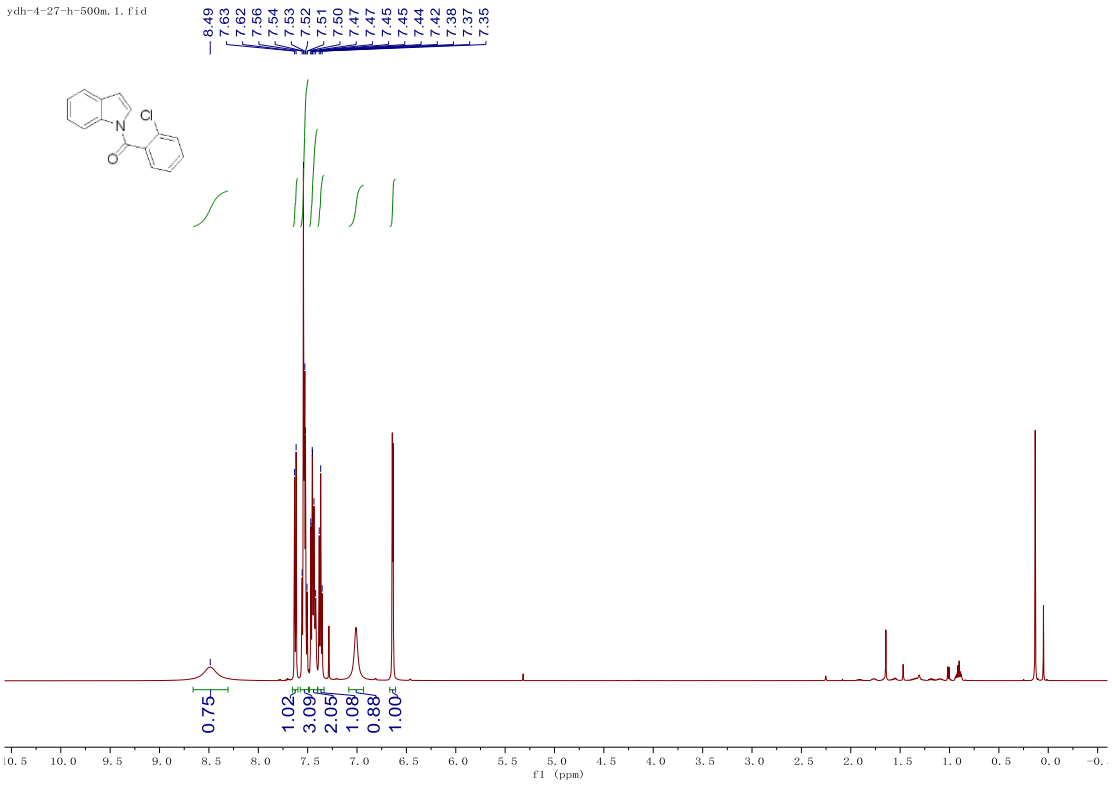
Crystal Data for $C_{17}H_{15}NO_2$ (*M* =265.30 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 10.4073(6) Å , *b* = 8.7265(5)Å , *c* = 14.6032(7)Å , *β* = 94.709(2), *V* = 1321.78(12)Å ^{3}, *Z* = 4, *T* = 100 K, 00MoKαo = 0.088 mm^{-1}, *Dcalc* = 1.333 g/cm^3, 18279 reflections measured (4.632 oup P2-8.Howard, J.A.K. & PusR_{int} = 0.0357, R_{sigma} = 0.0229) which were used in all calculations. The final R_1 was 0.0365 (I > 2asI)) and wR_2 was 0.0960 (all data).

Refinement model description

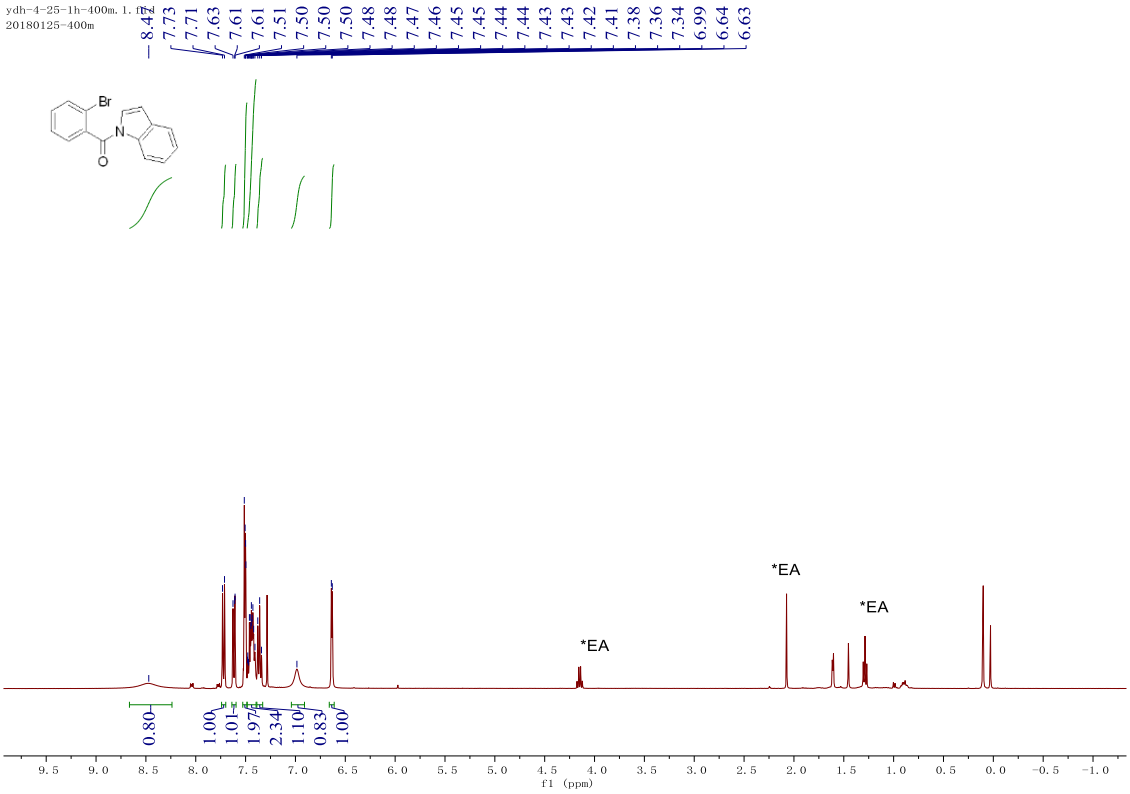
Number of restraints - 0, number of constraints - unknown.
Details:
1. Fixed Uiso
   At 1.2 times of:
   All C(H) groups, All C(H,H) groups
   At 1.5 times of:
   All O(H) groups
   2.a Ternary CH refined with riding coordinates:
   C11(H11), C14(H14)
   2.b Secondary CH2 refined with riding coordinates:
   C12(H12A,H12B), C13(H13A,H13B)
   2.c Aromatic/amide H refined with riding coordinates:
   C1(H1), C2(H2A), C7(H7), C8(H8), C9(H9), C10(H10), C16(H16), C17(H17)
   2.d Idealised tetrahedral OH refined as rotating group:
   O2(H2)

NMR Spectra

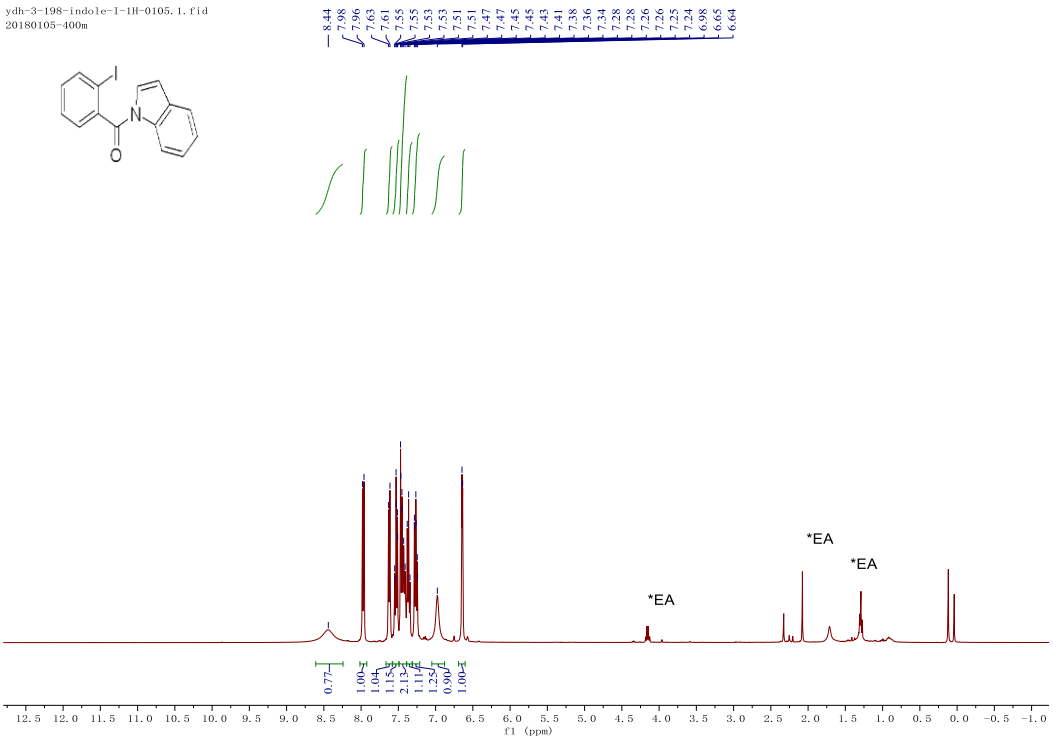
^{1}H NMR of S1



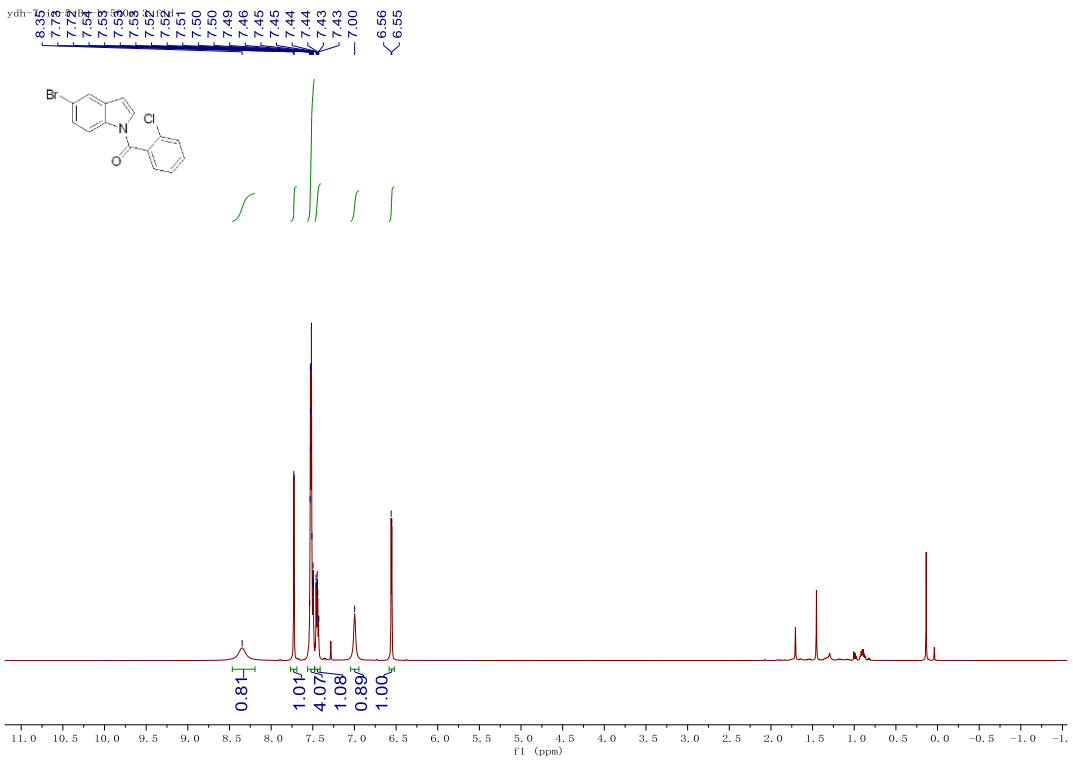
^{1}H NMR of S1′



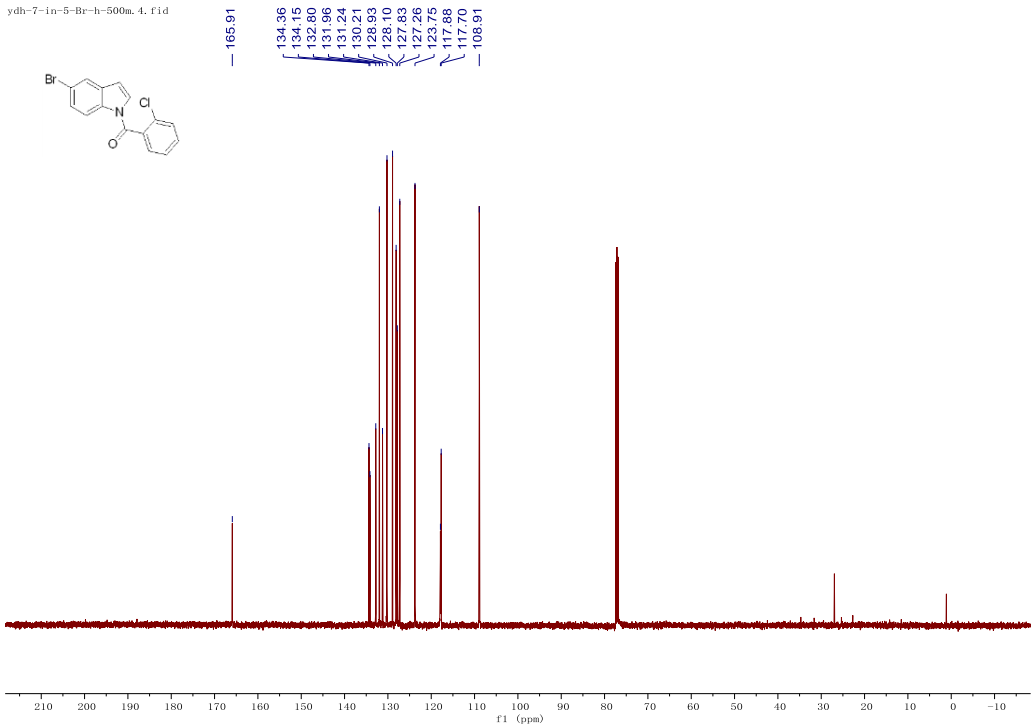
^{1}H NMR of S1''



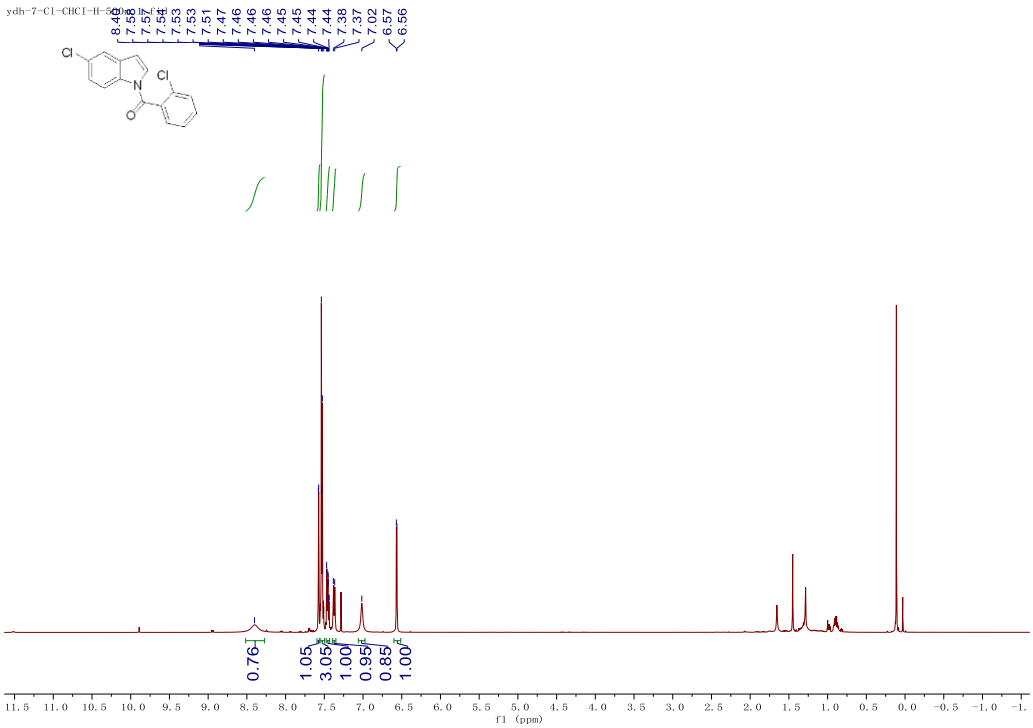
^{1}H NMR of S2



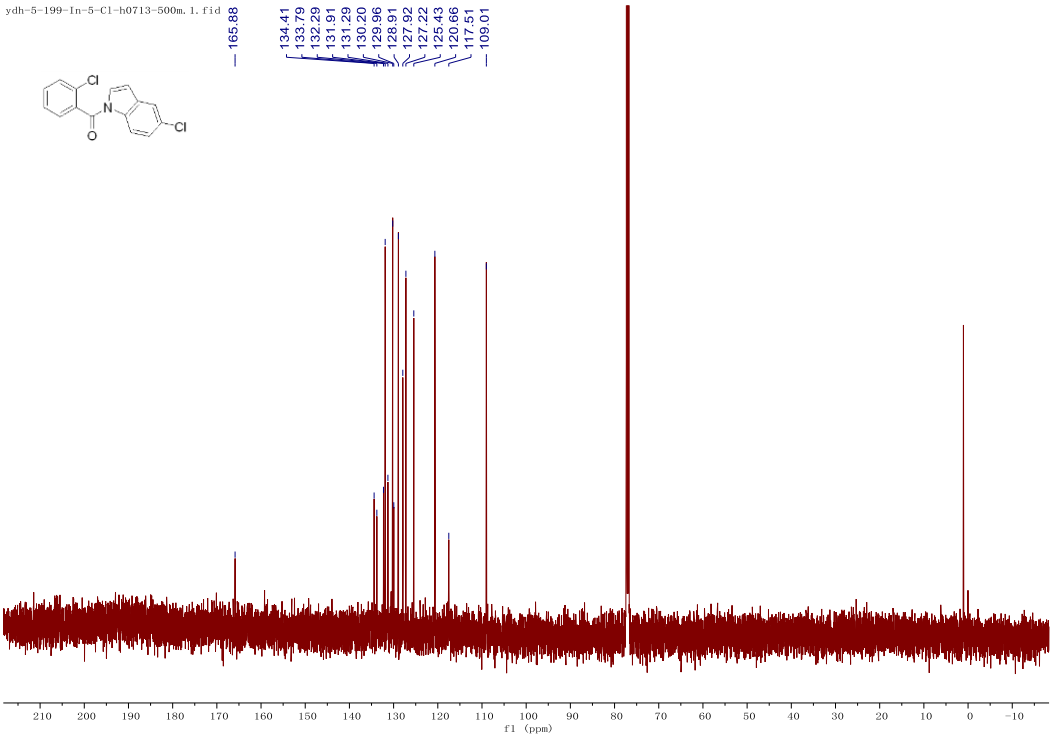
^{13}C NMR of S2



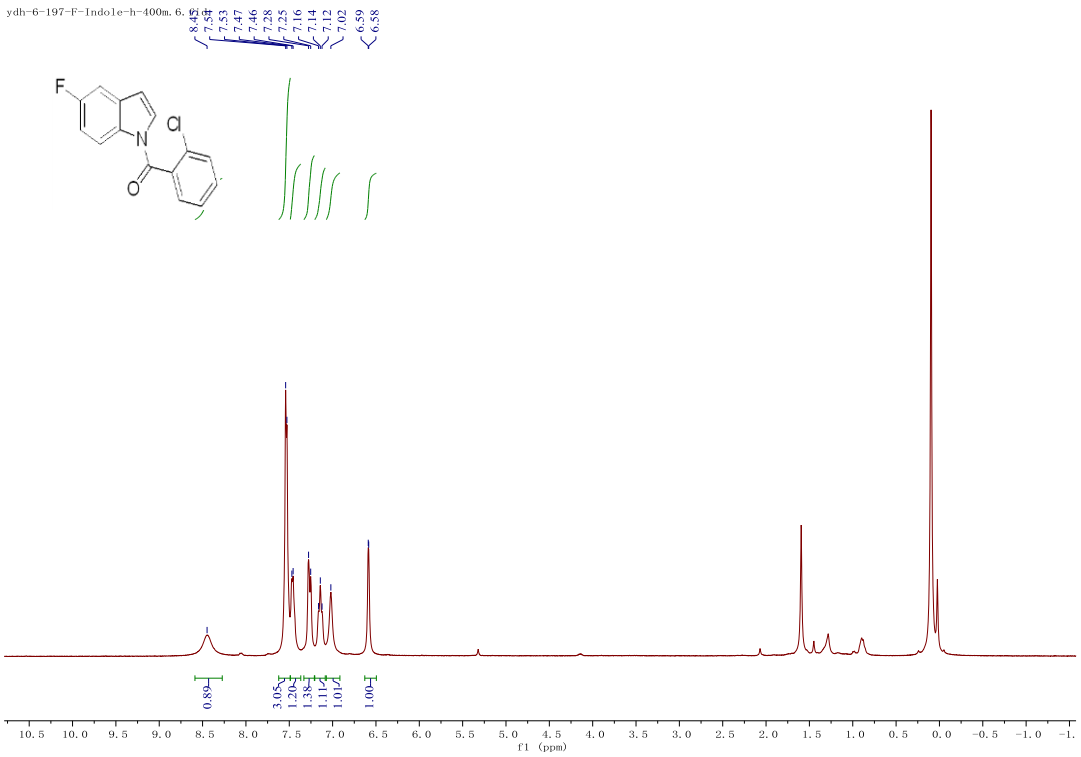
^{1}H NMR of S3



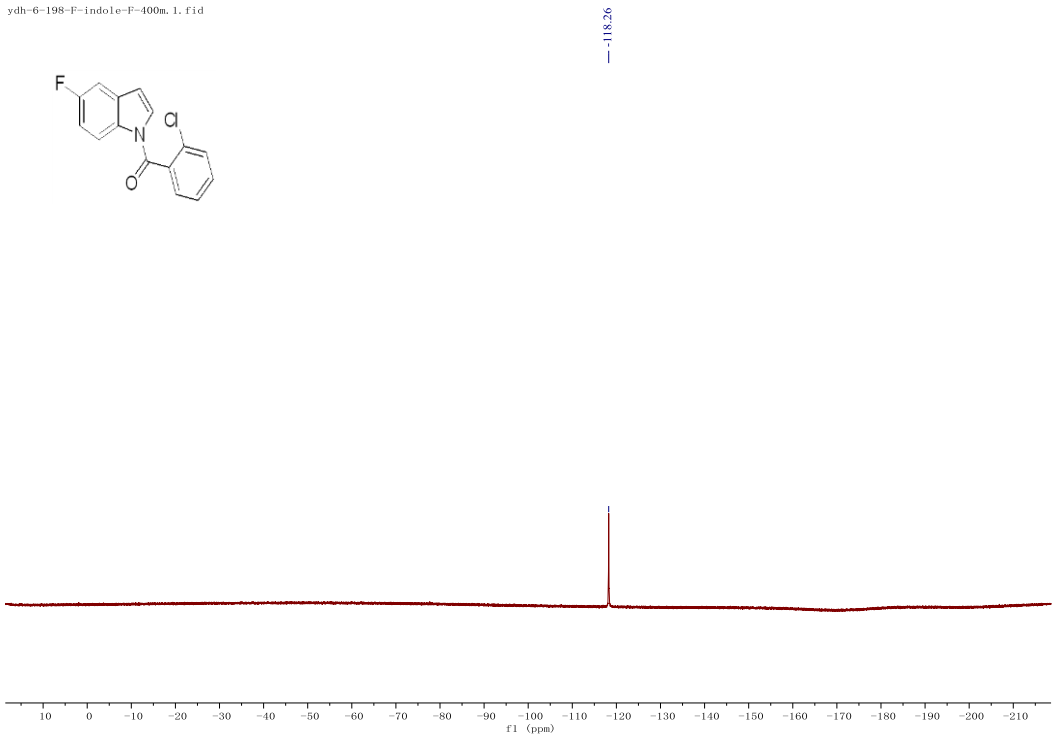
^{13}C NMR of S3



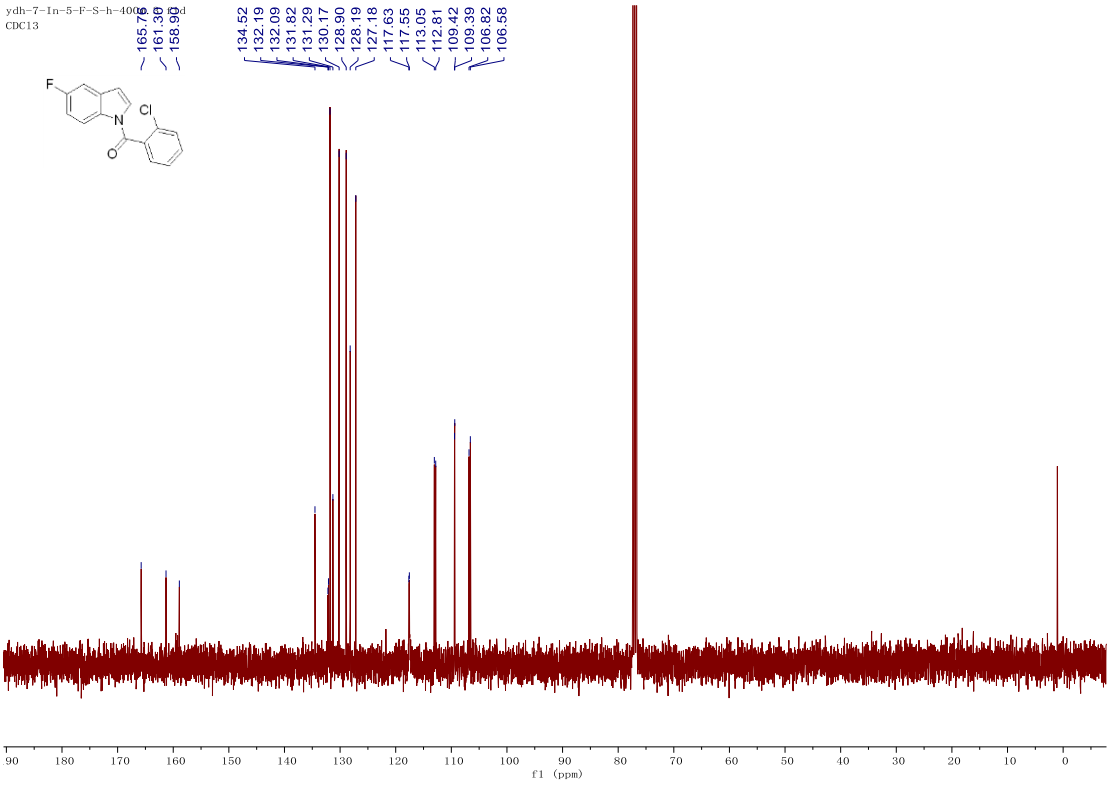
^{1}H NMR of S4



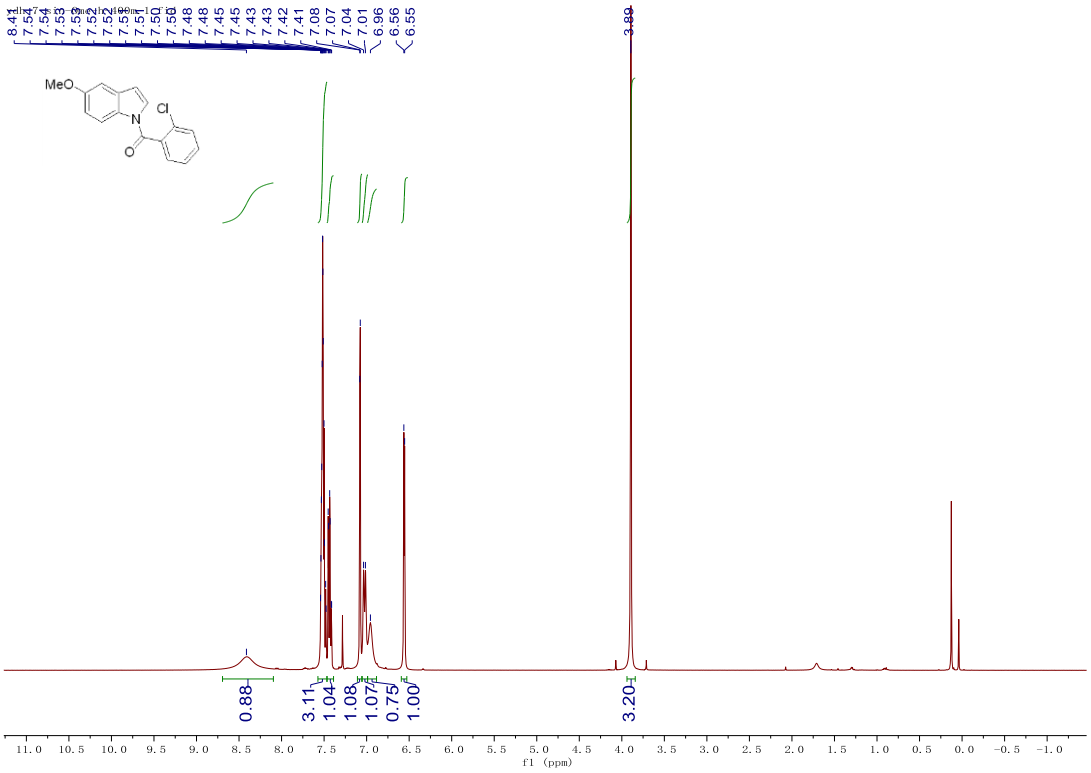
^{19}F NMR of S4



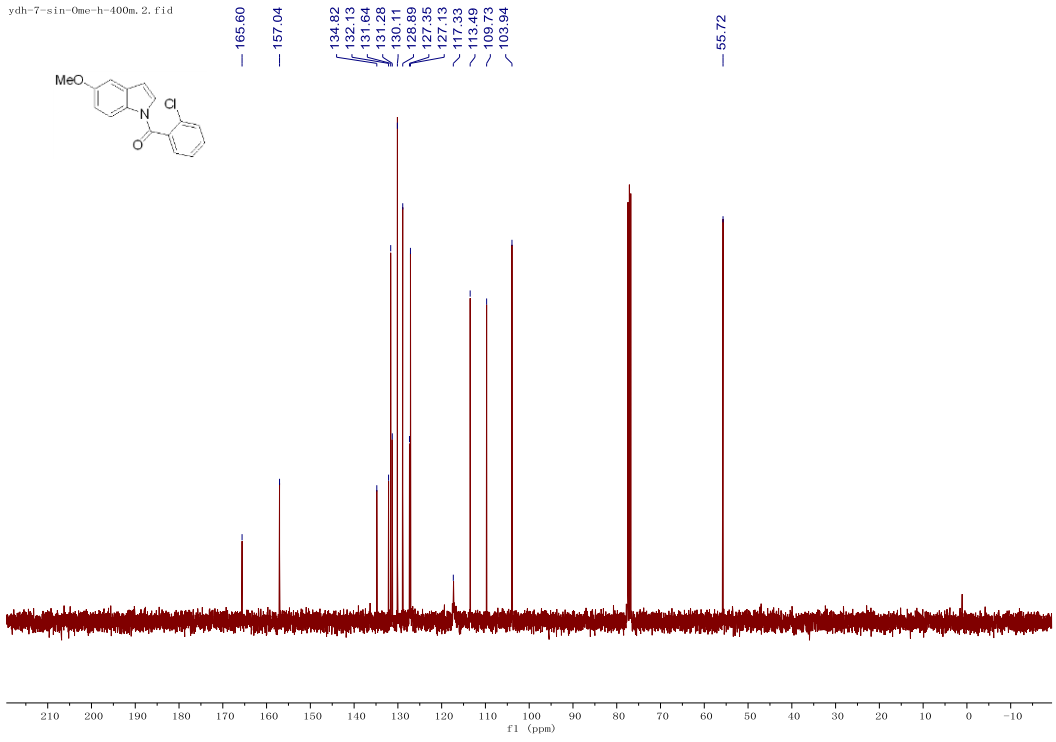
^{13}C NMR of S4



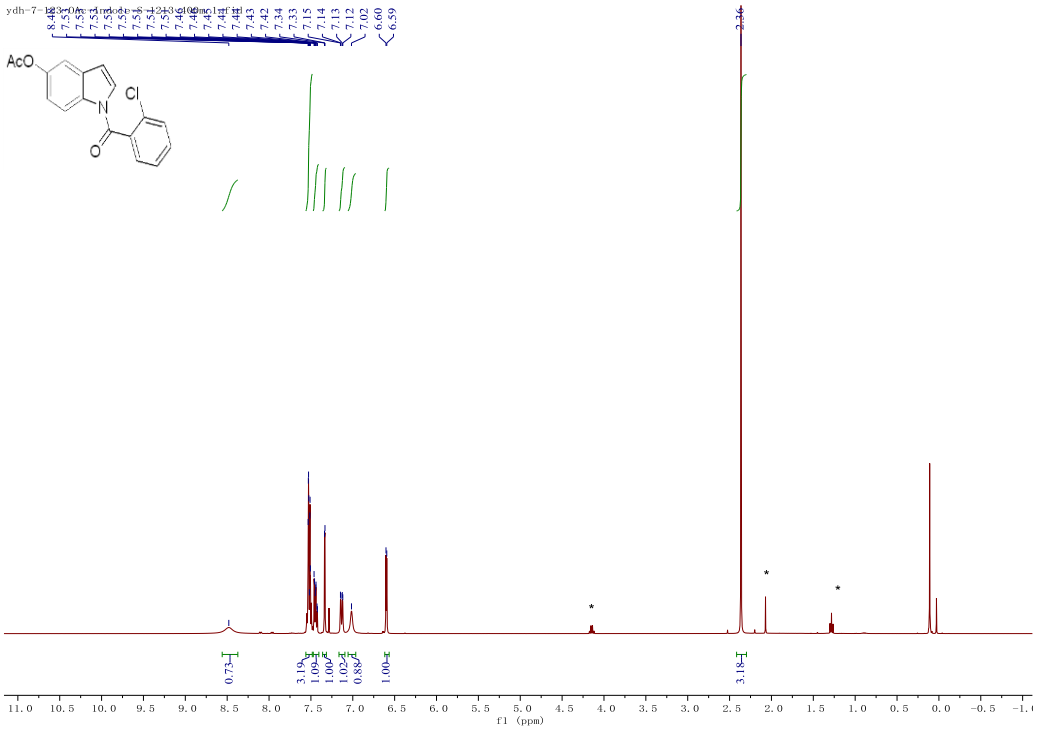
^{1}H NMR of S5



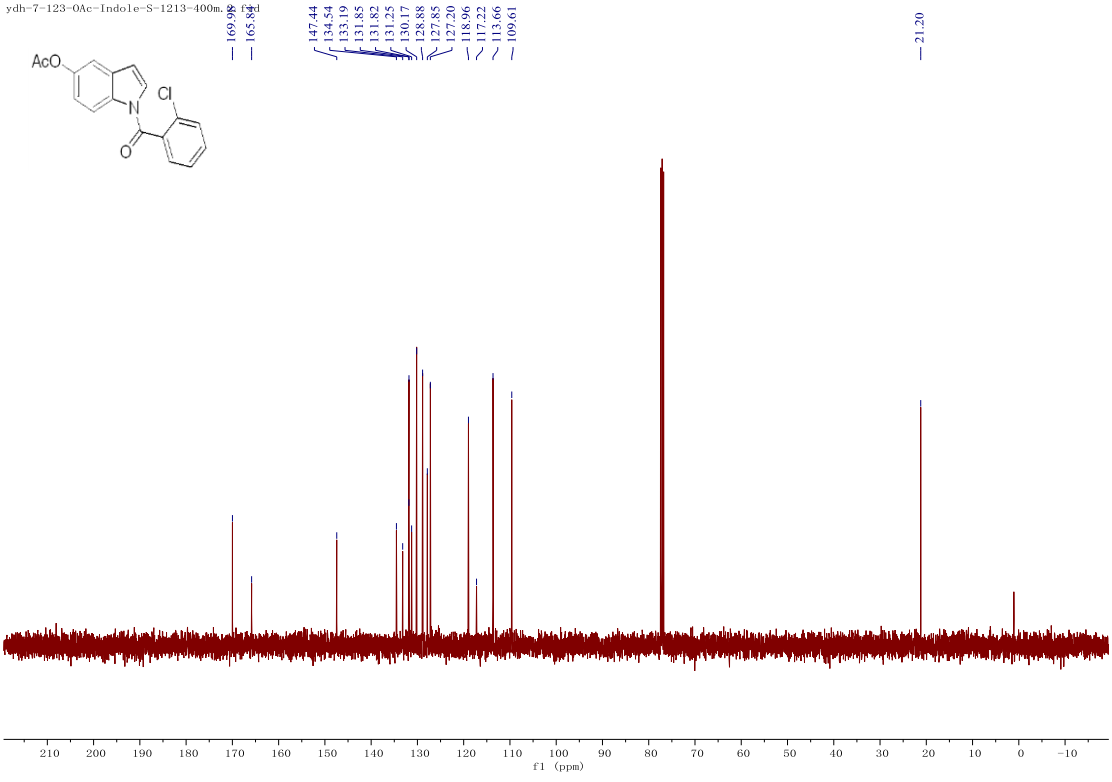
^{13}C NMR of S5



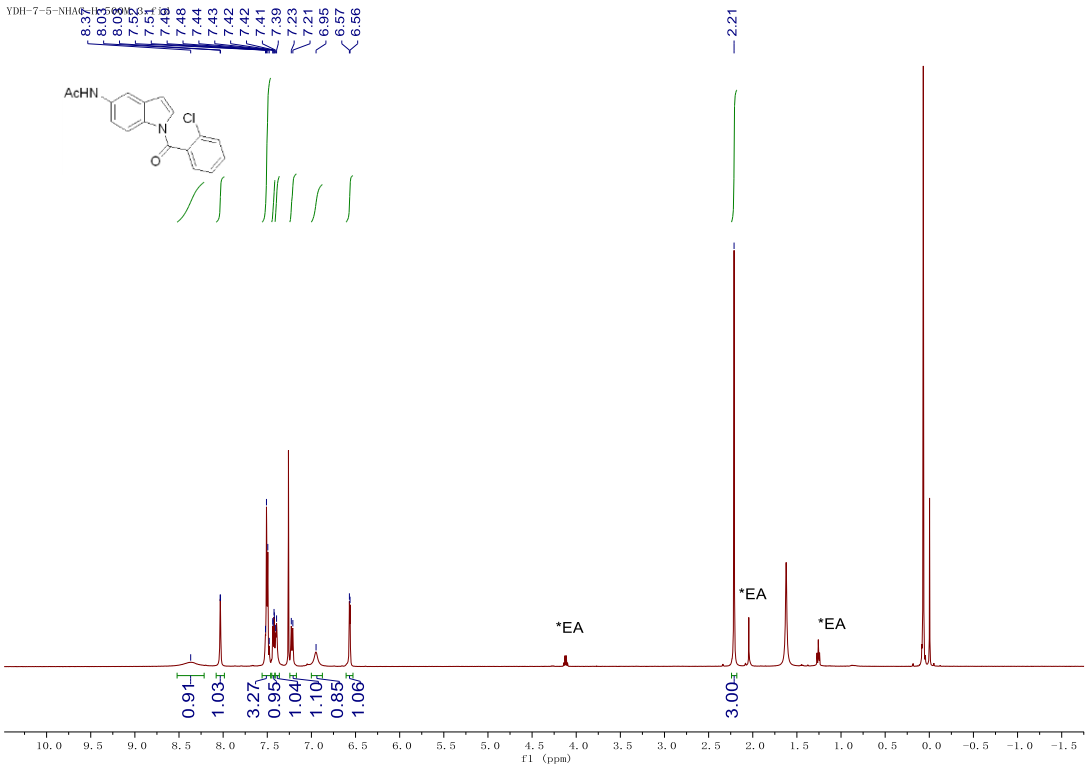
^{1}H NMR of S6



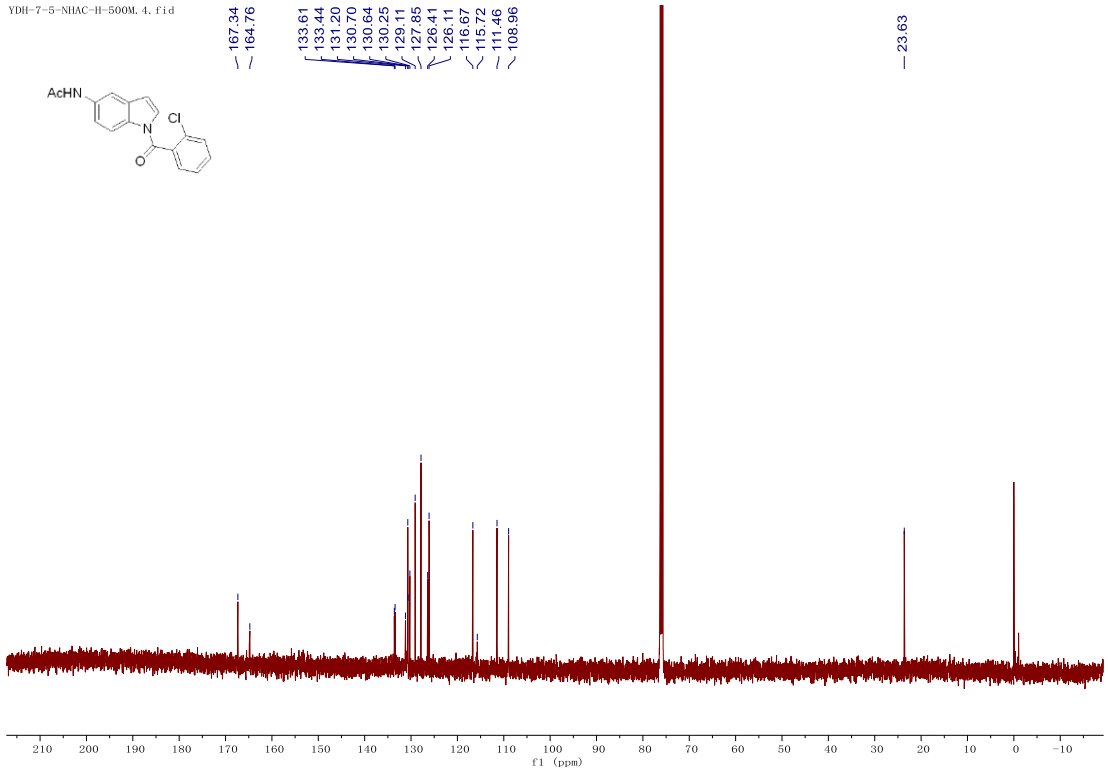
^{13}C NMR of S6



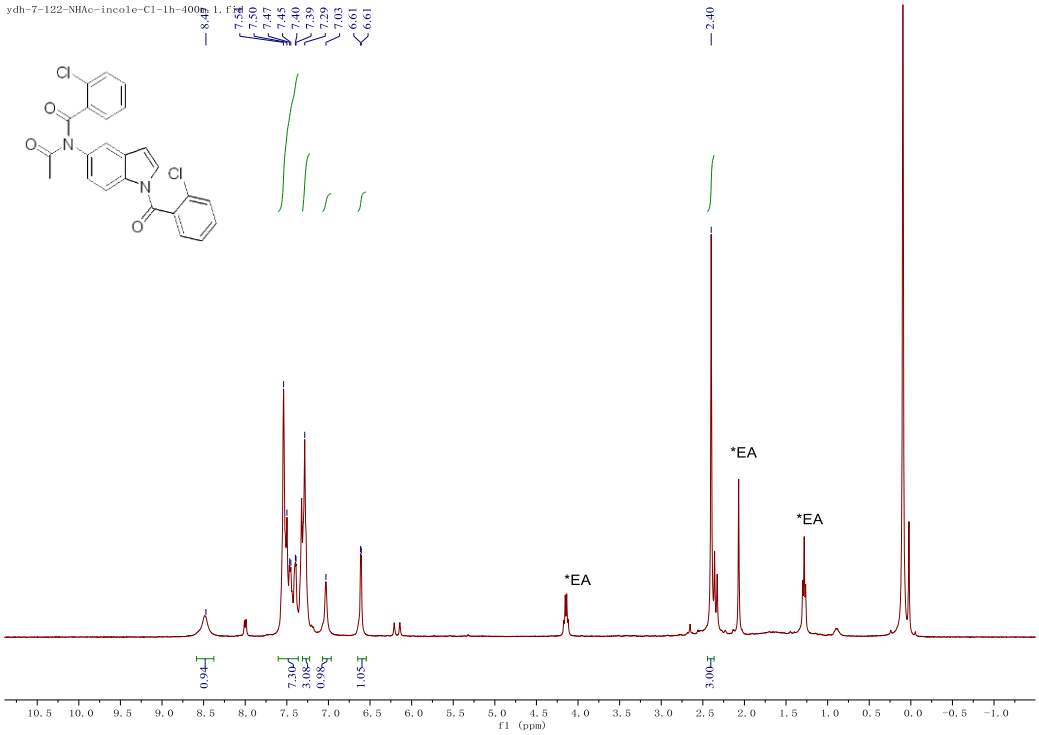
^{1}H NMR of S7



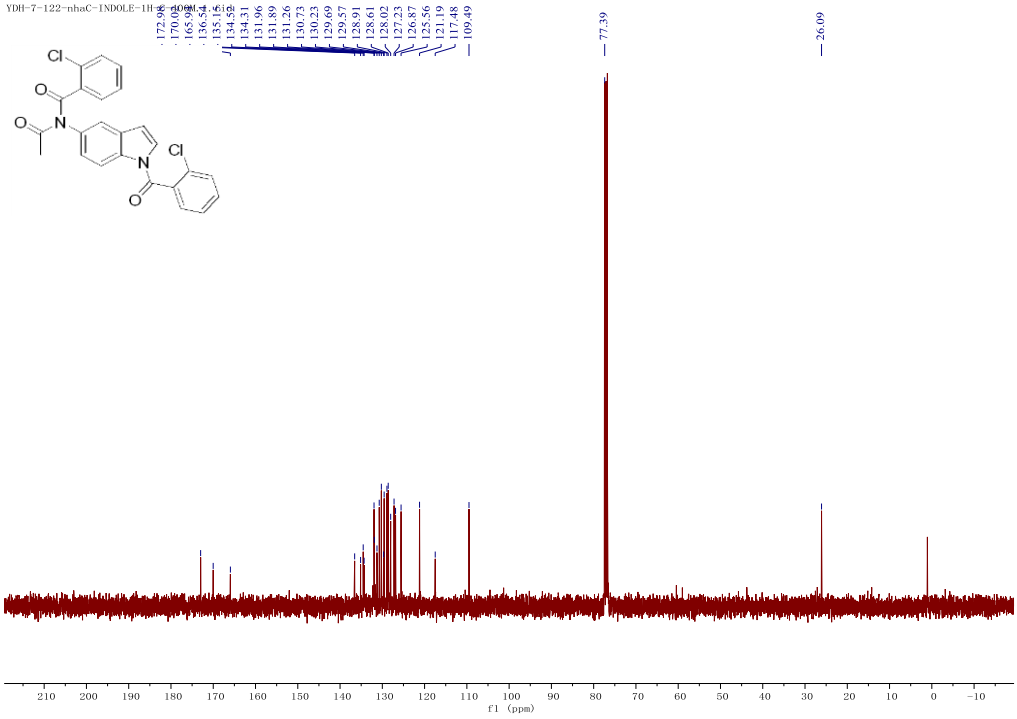
^{13}C NMR of S7



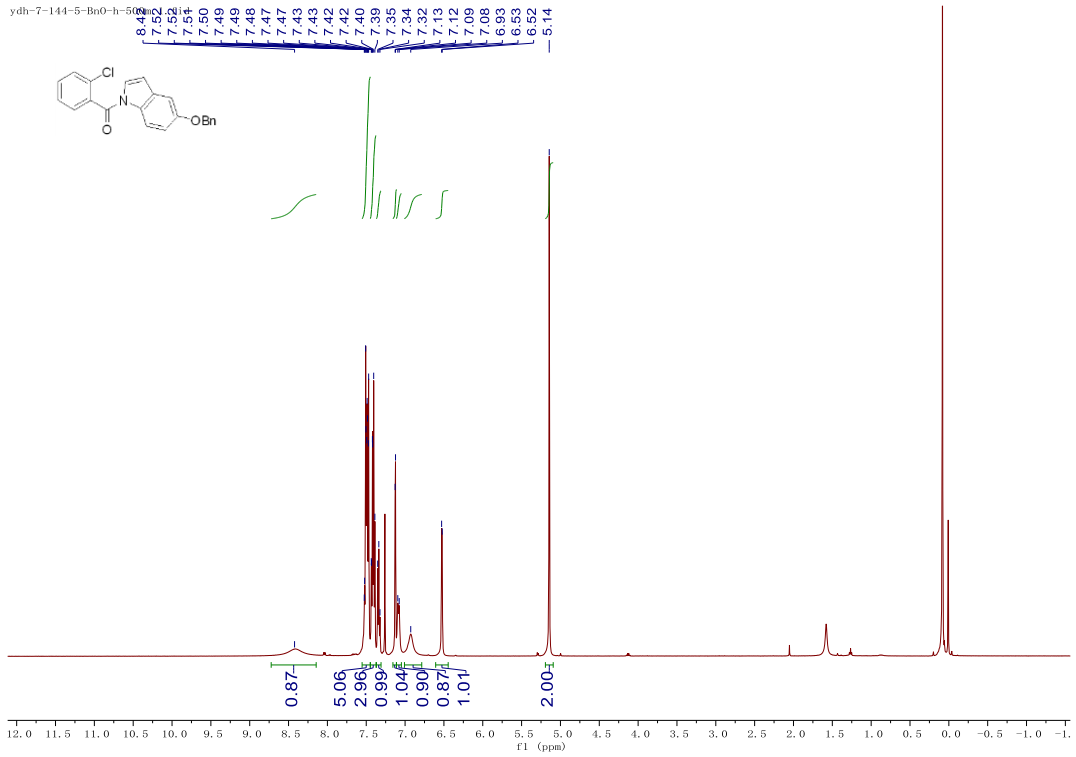
^{1}H NMR of S7′



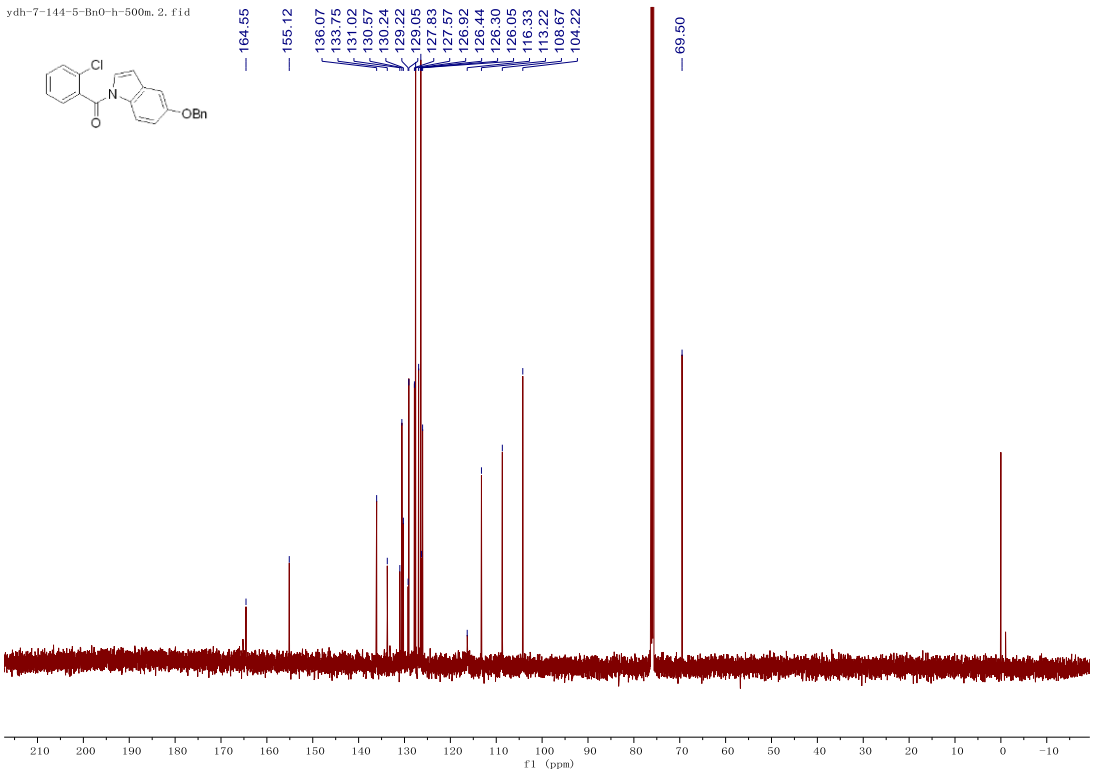
^{13}C NMR of S S7′



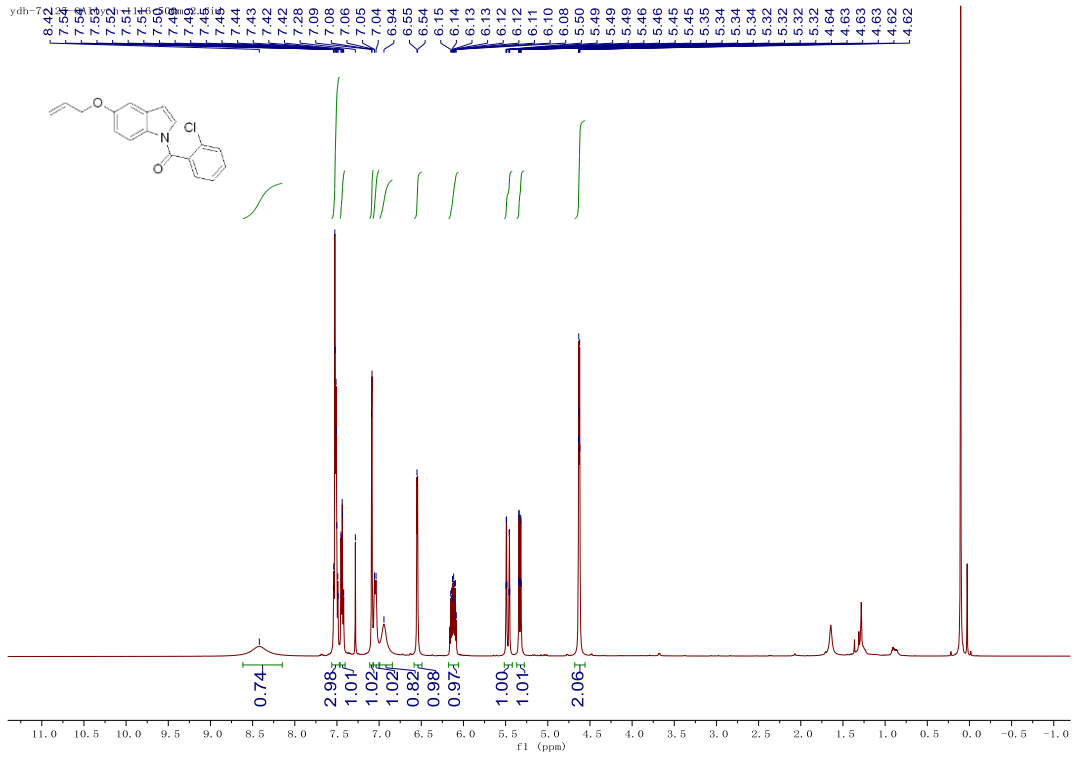
^{1}H NMR of S8



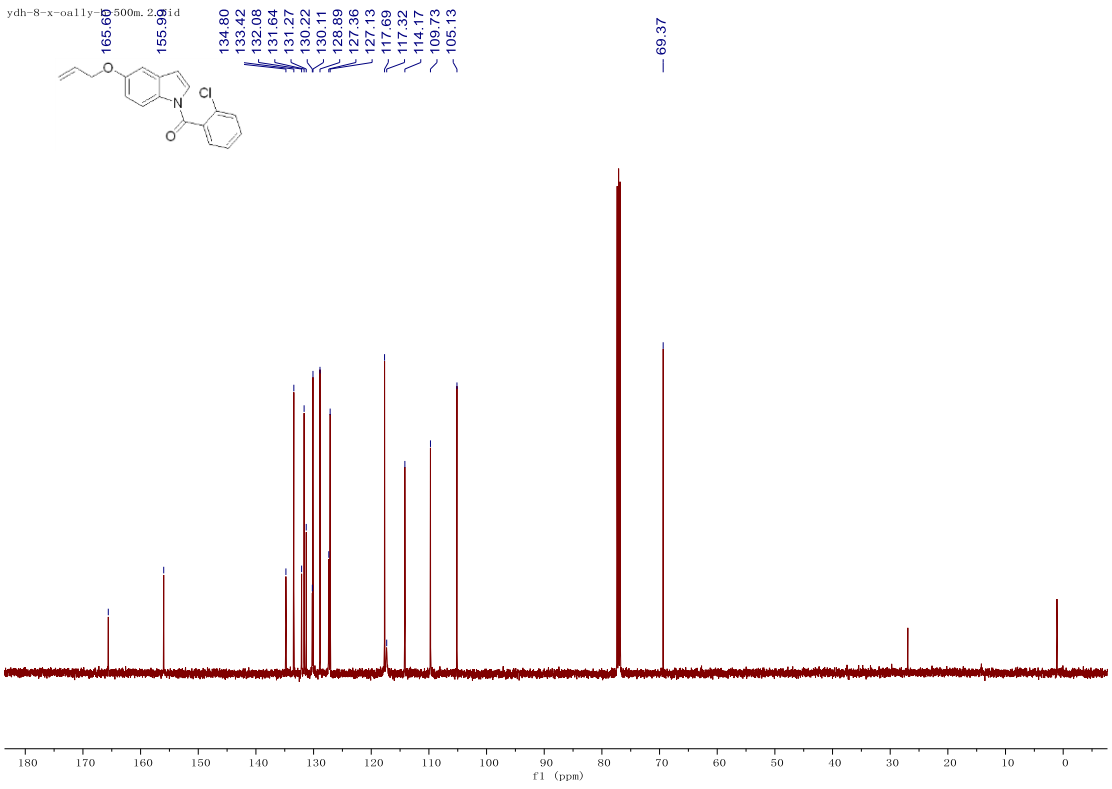
^{13}C NMR of S8



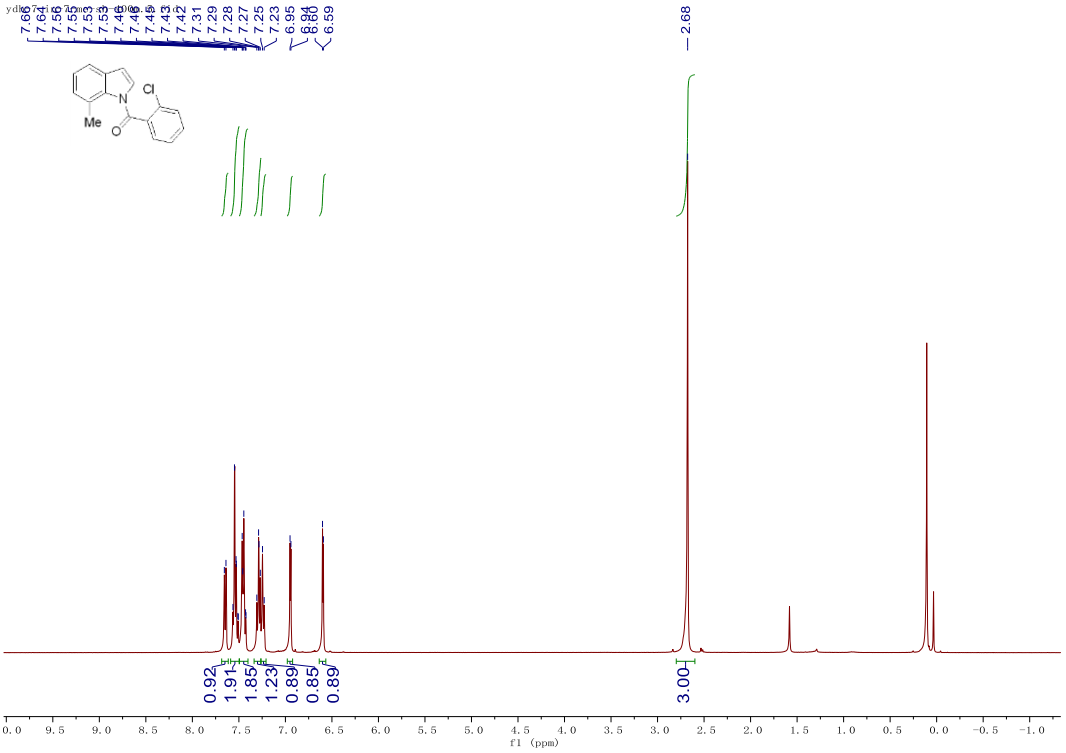
^{1}H NMR of S9



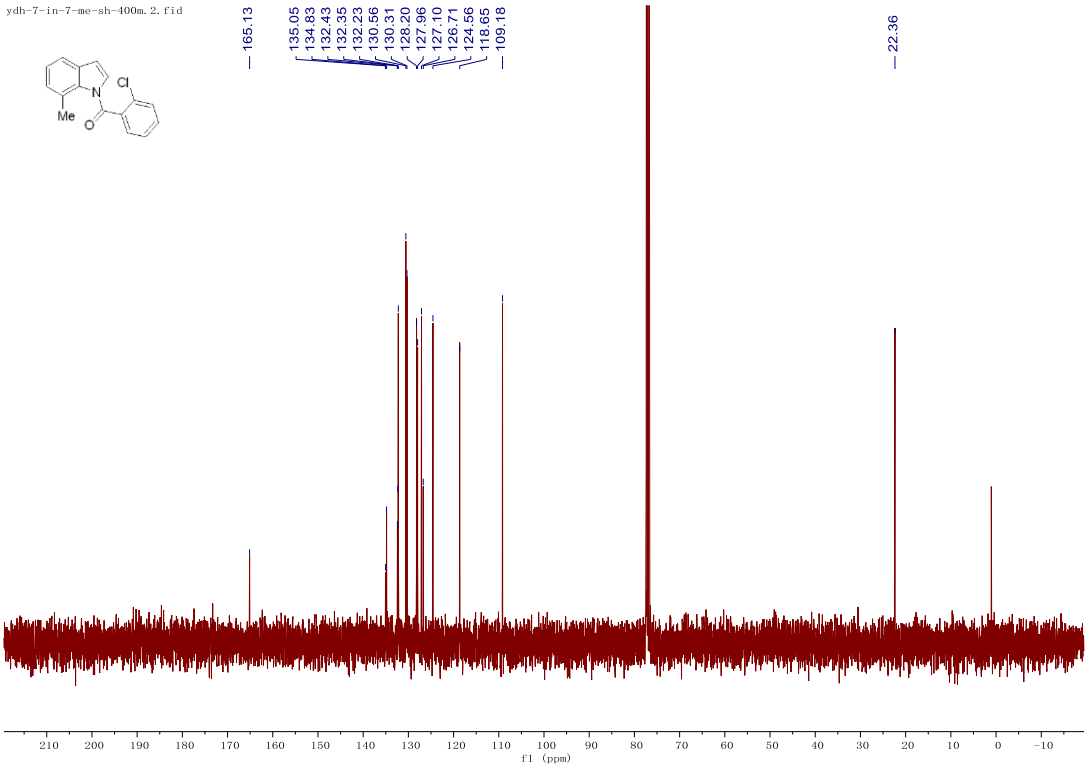
^{13}C NMR of S9



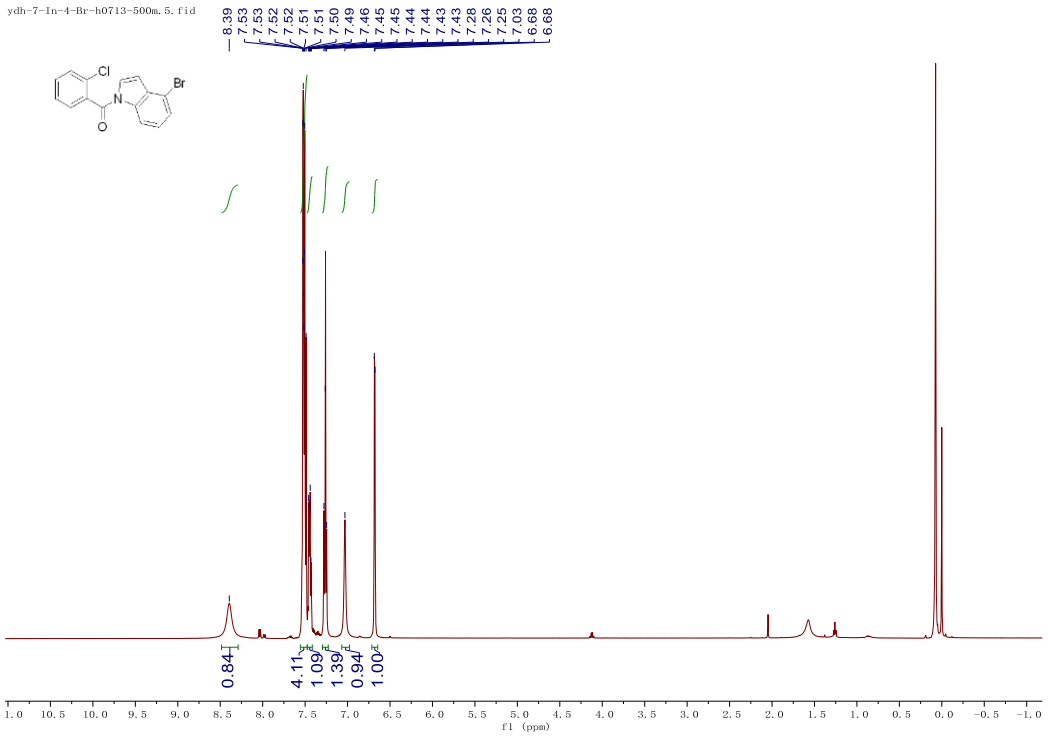
^{1}H NMR of S10



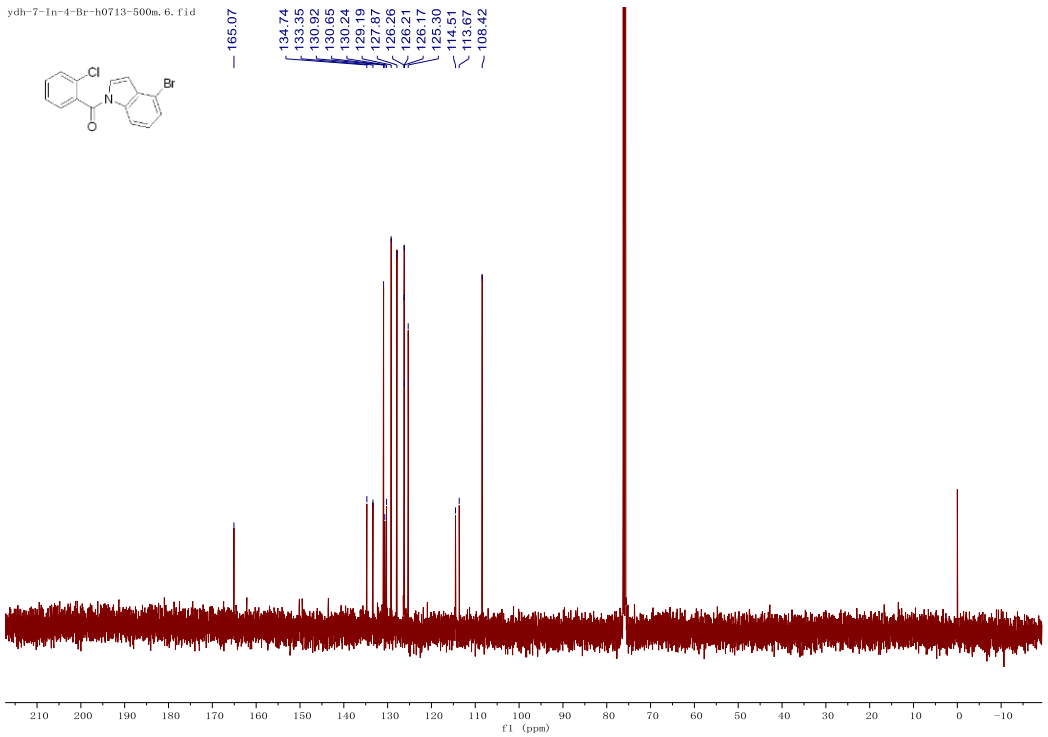
^{13}C NMR of S10



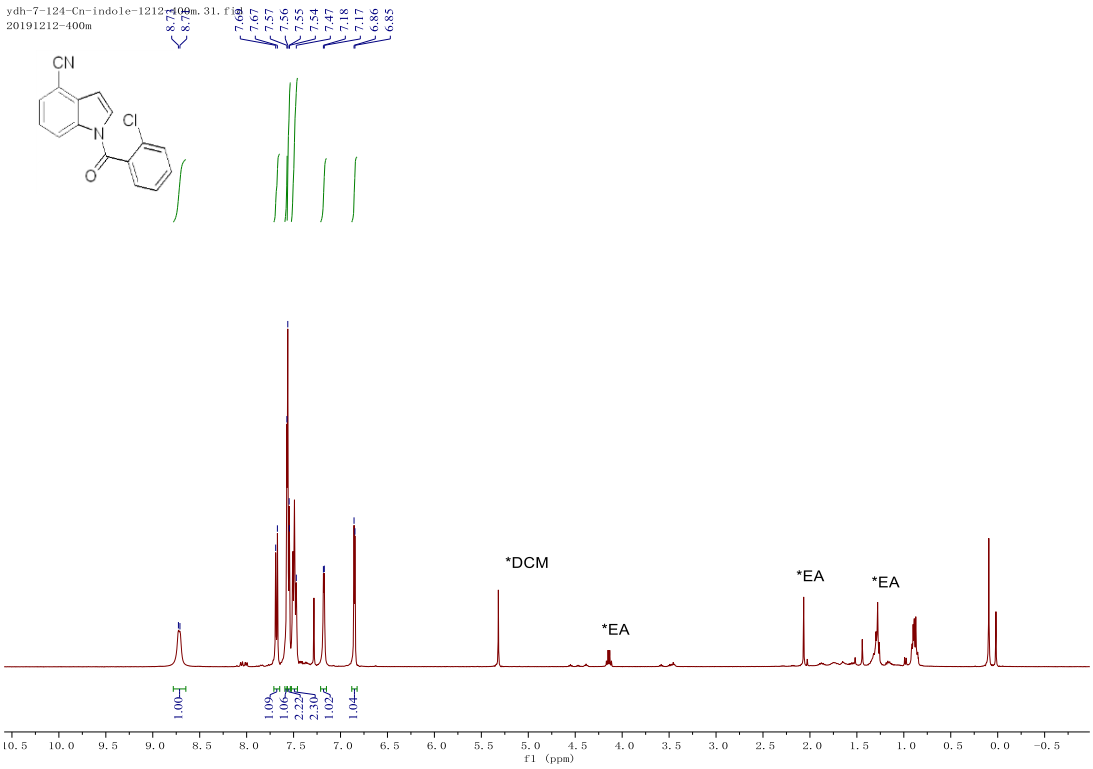
^{1}H NMR of S11



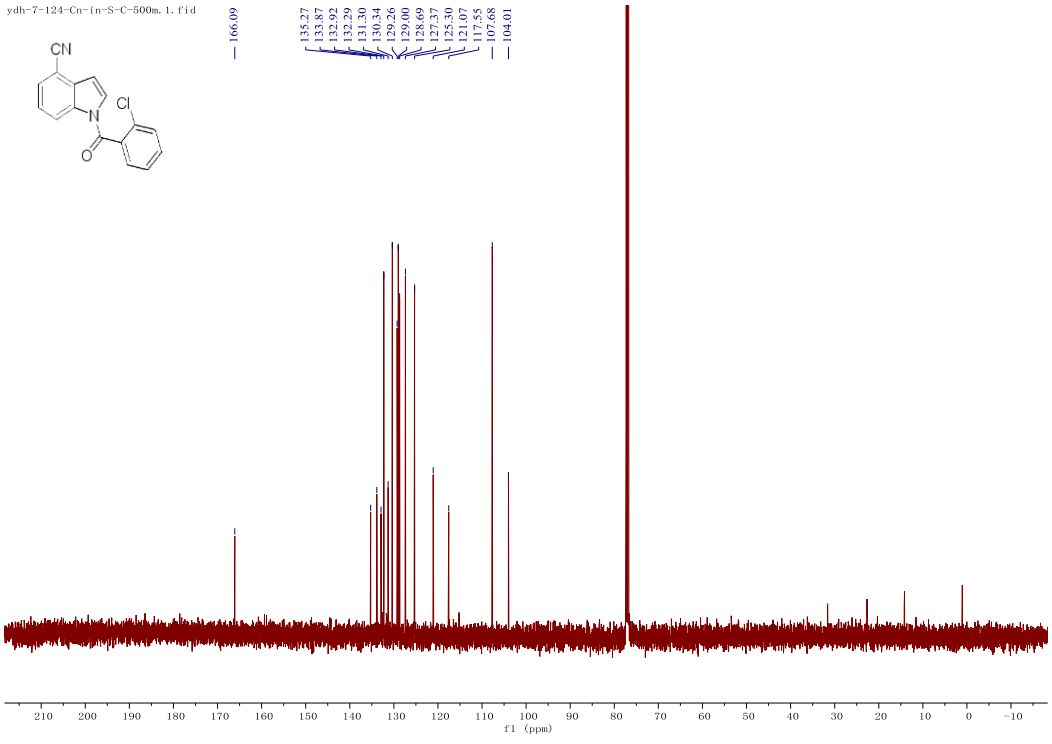
^{13}C NMR of S11



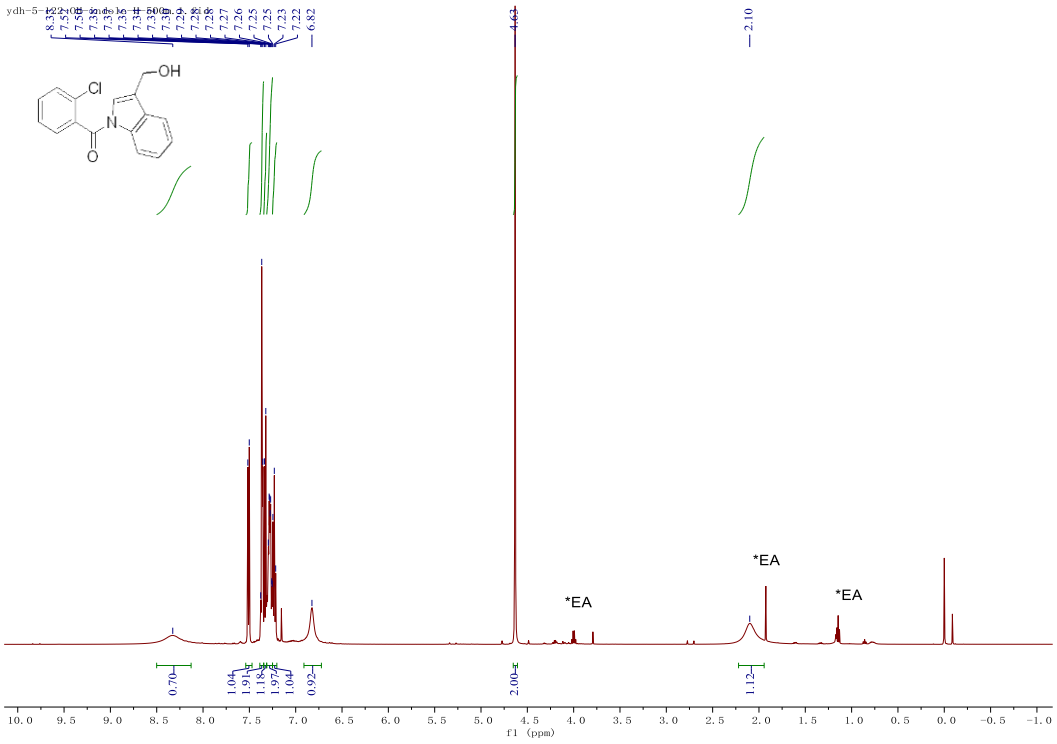
^{1}H NMR of S12



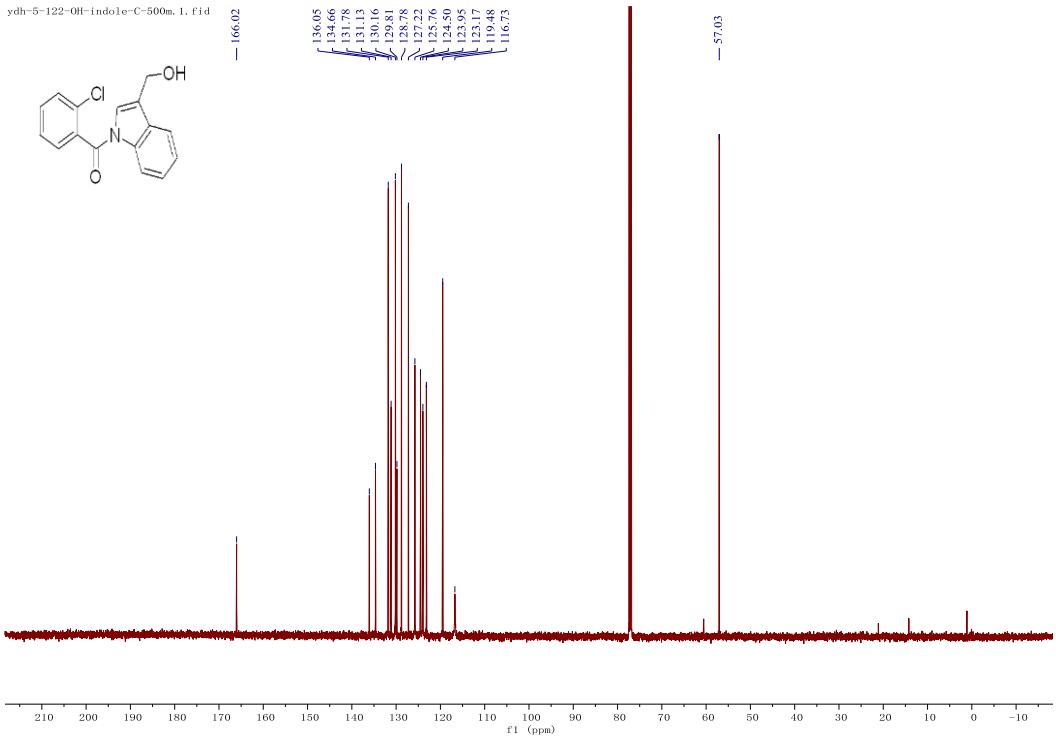
^{13}C NMR of S12



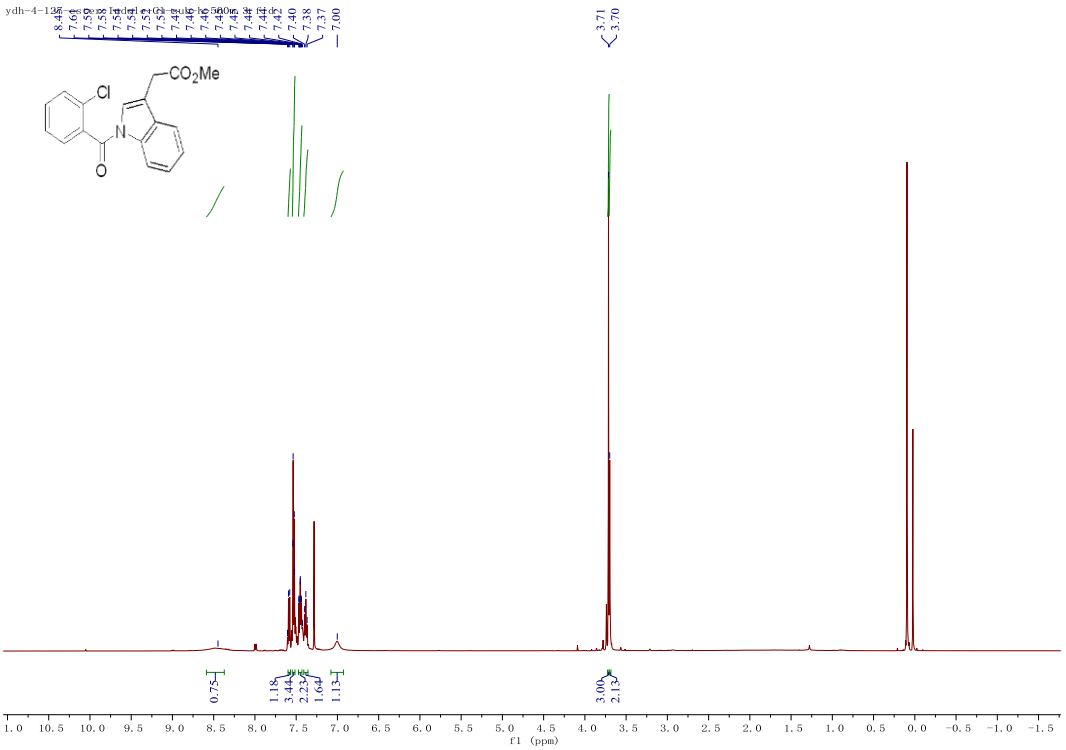
^{1}H NMR of S13



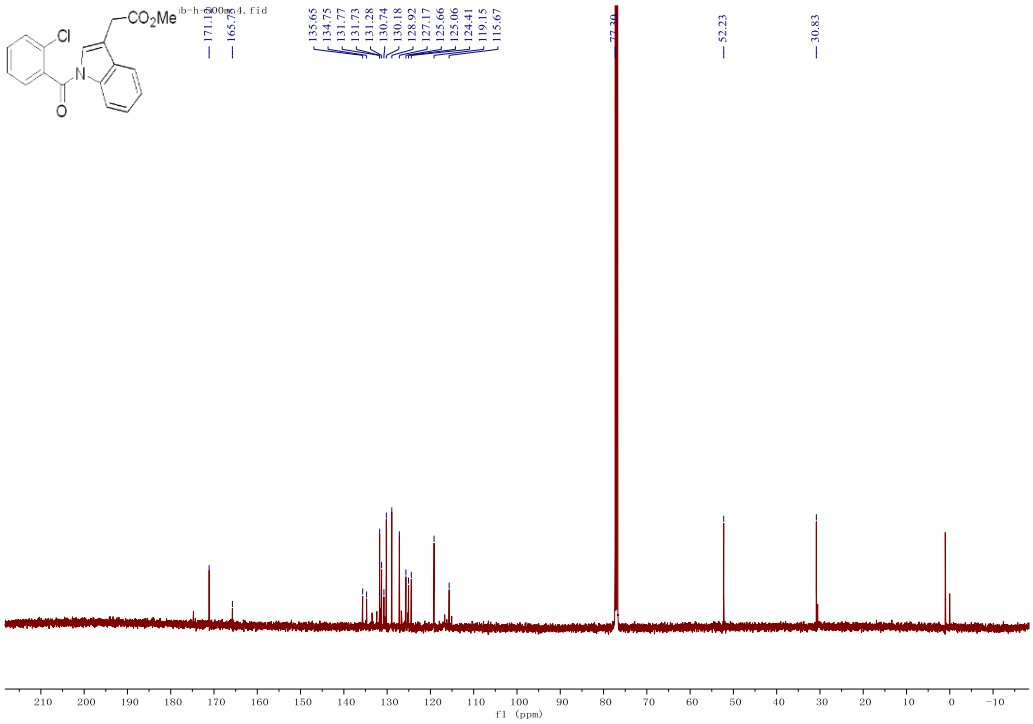
^{13}C NMR of S13



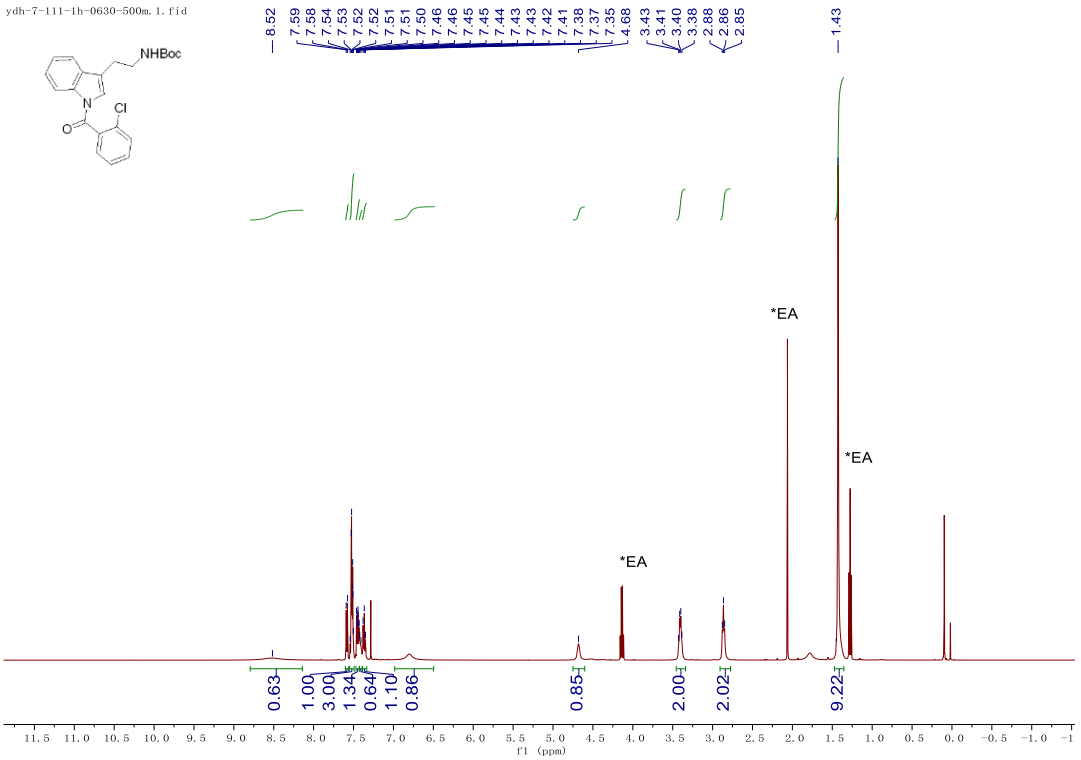
^{1}H NMR of S14



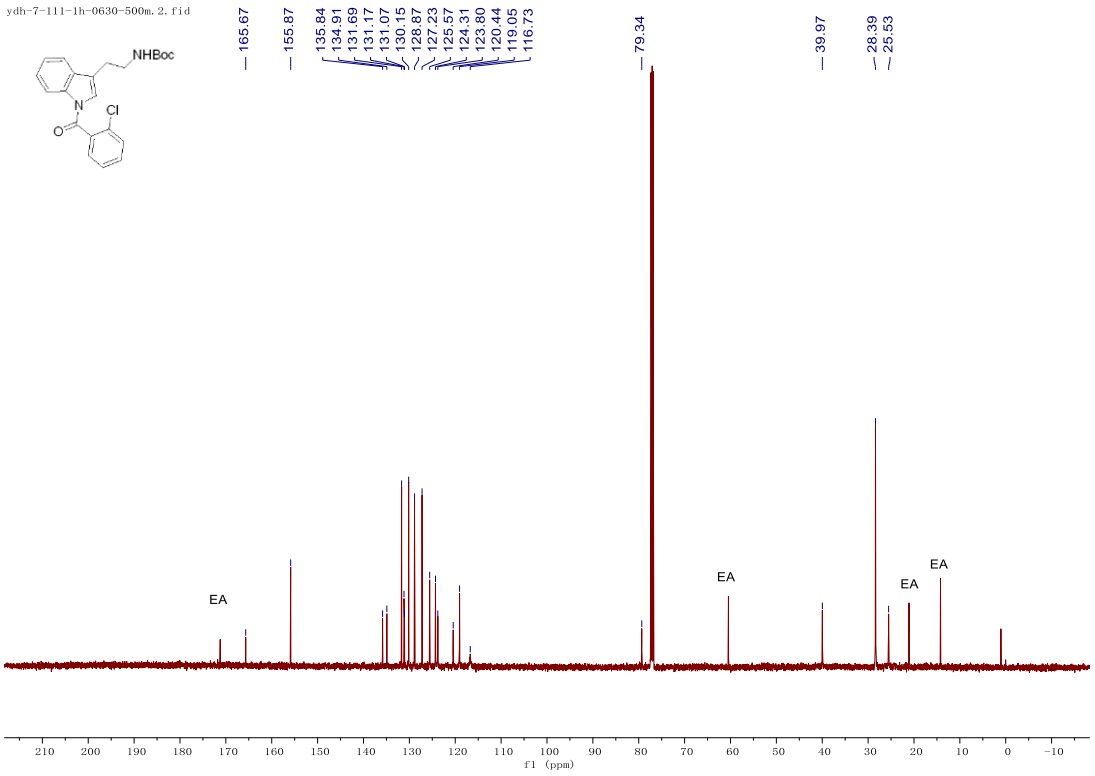
^{13}C NMR of S14



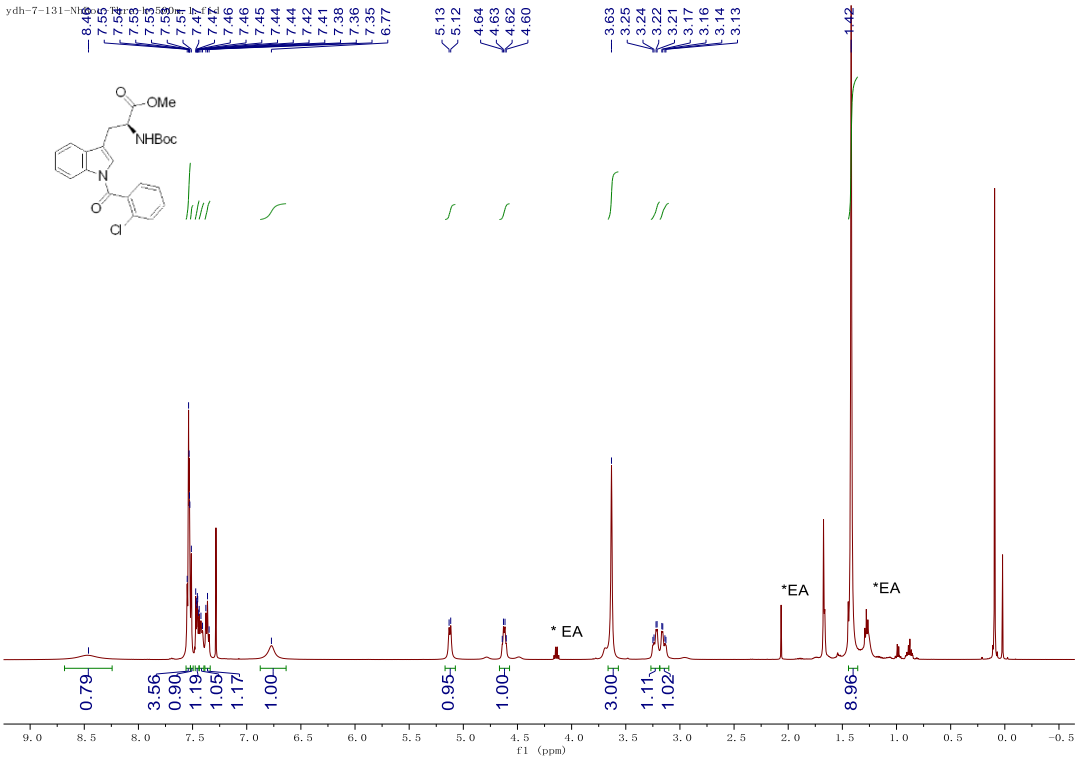
^{1}H NMR of S15



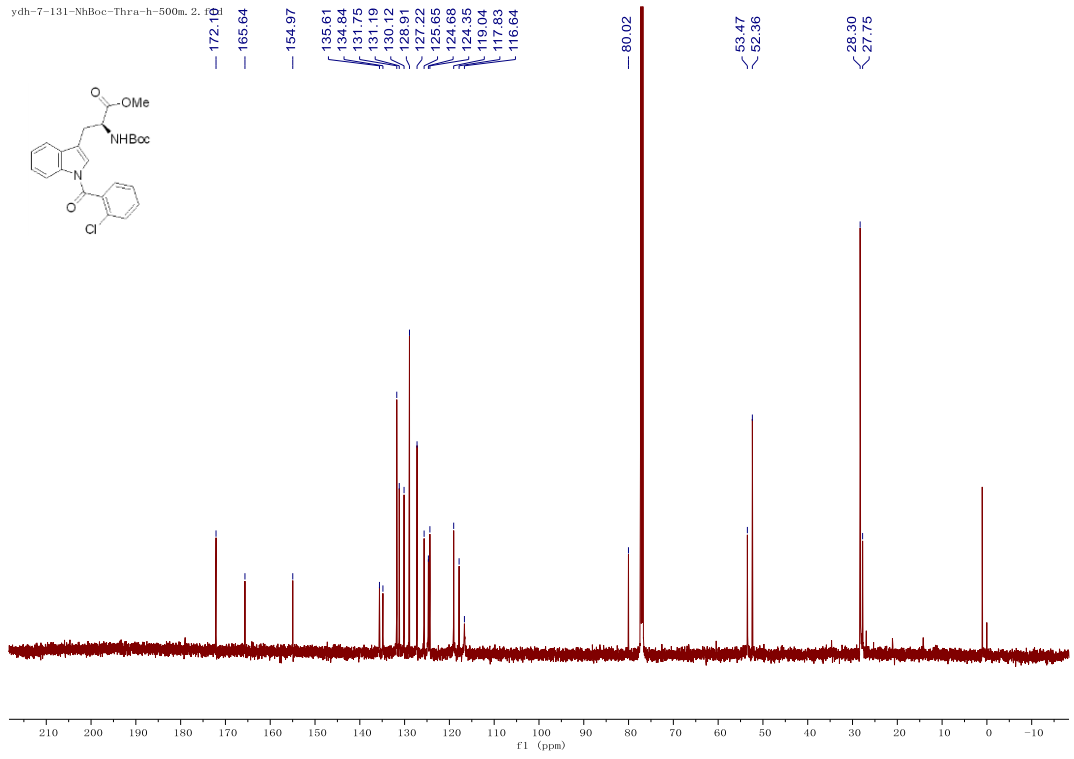
^{13}C NMR of S15



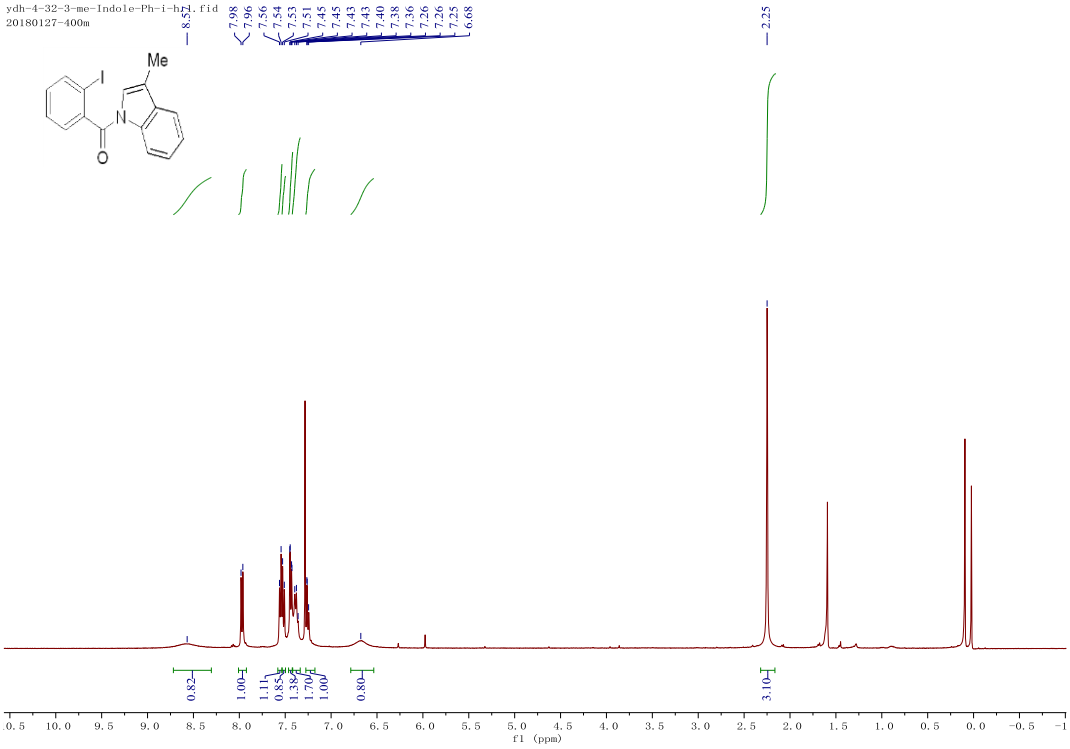
^{1}H NMR of S16



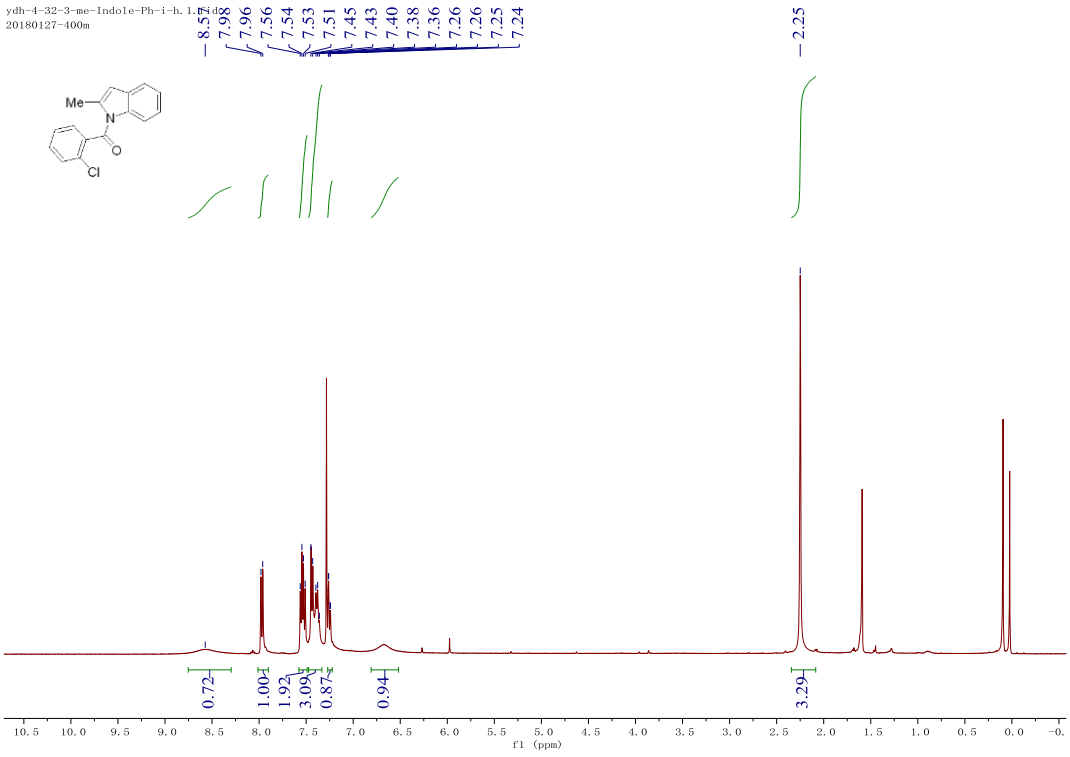
^{13}C NMR of S16



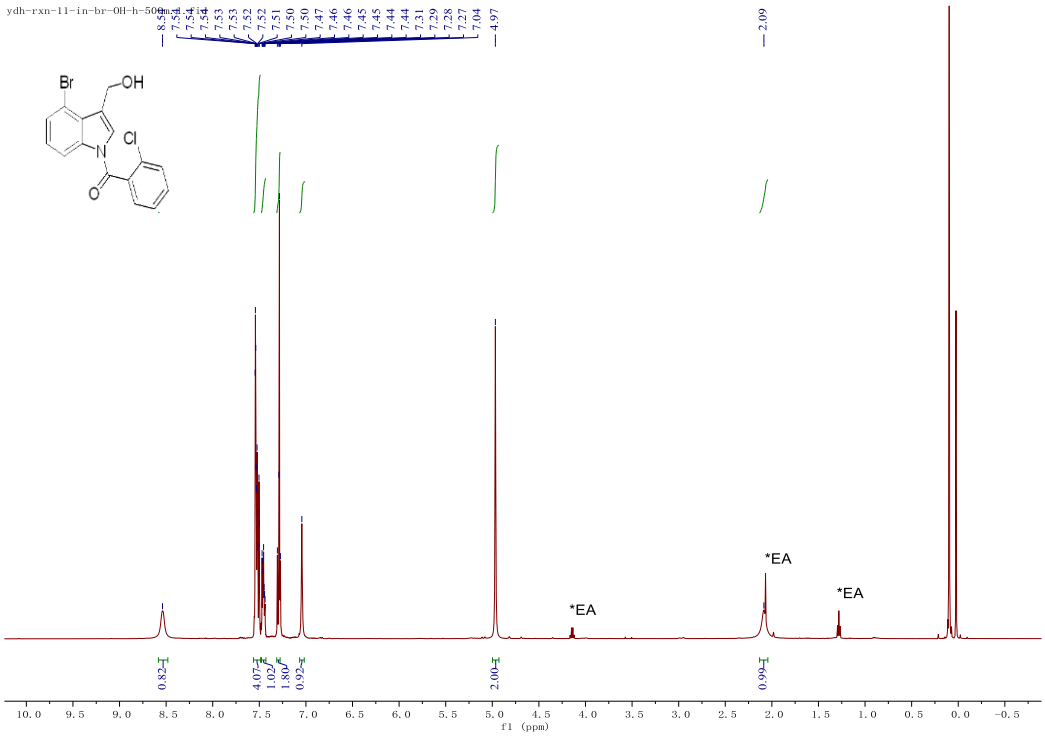
^{1}H NMR of S17



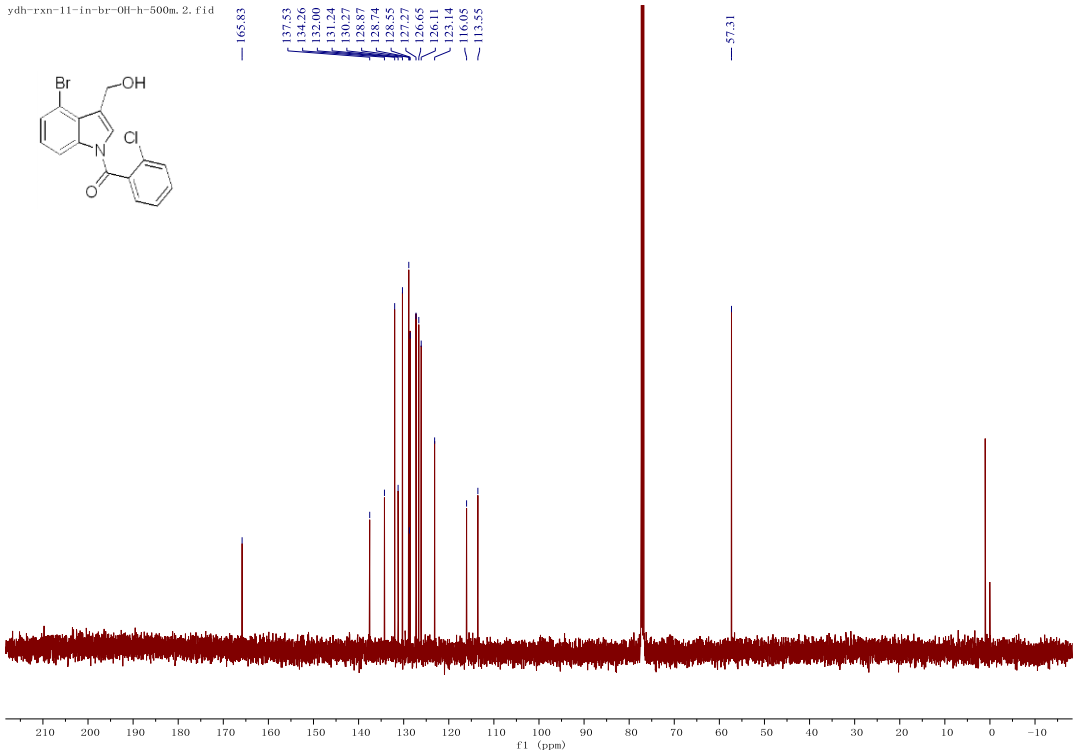
^{1}H NMR of S18



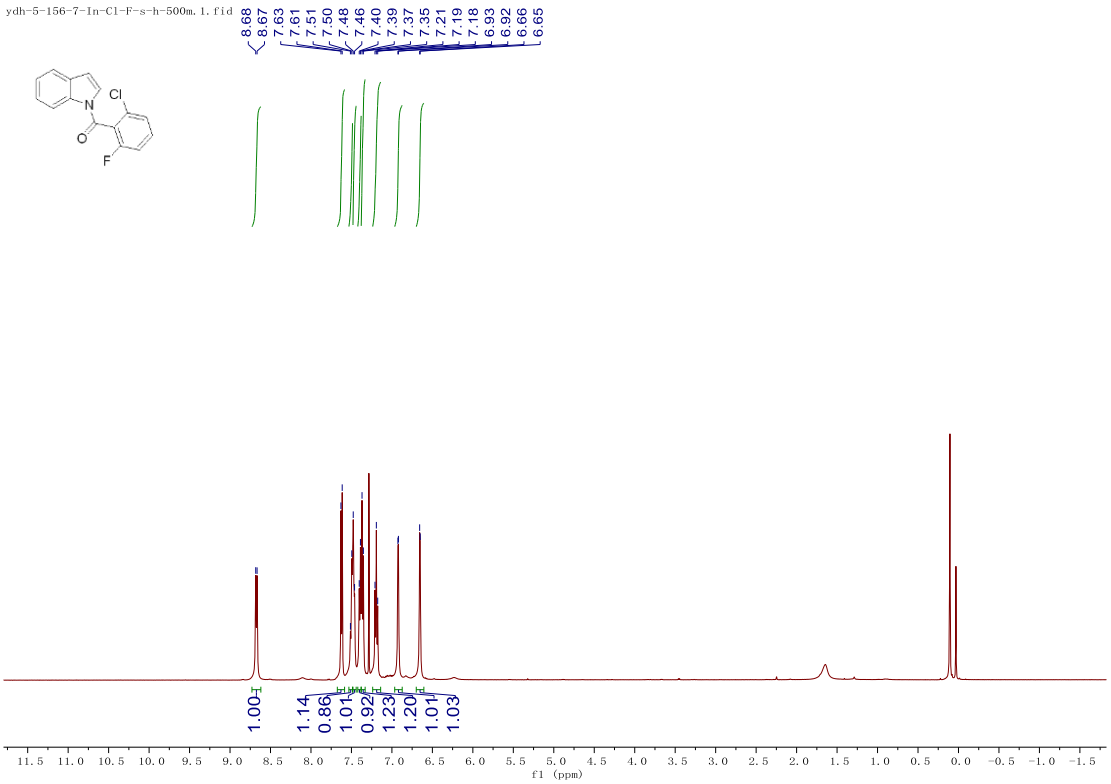
^{1}H NMR of S19



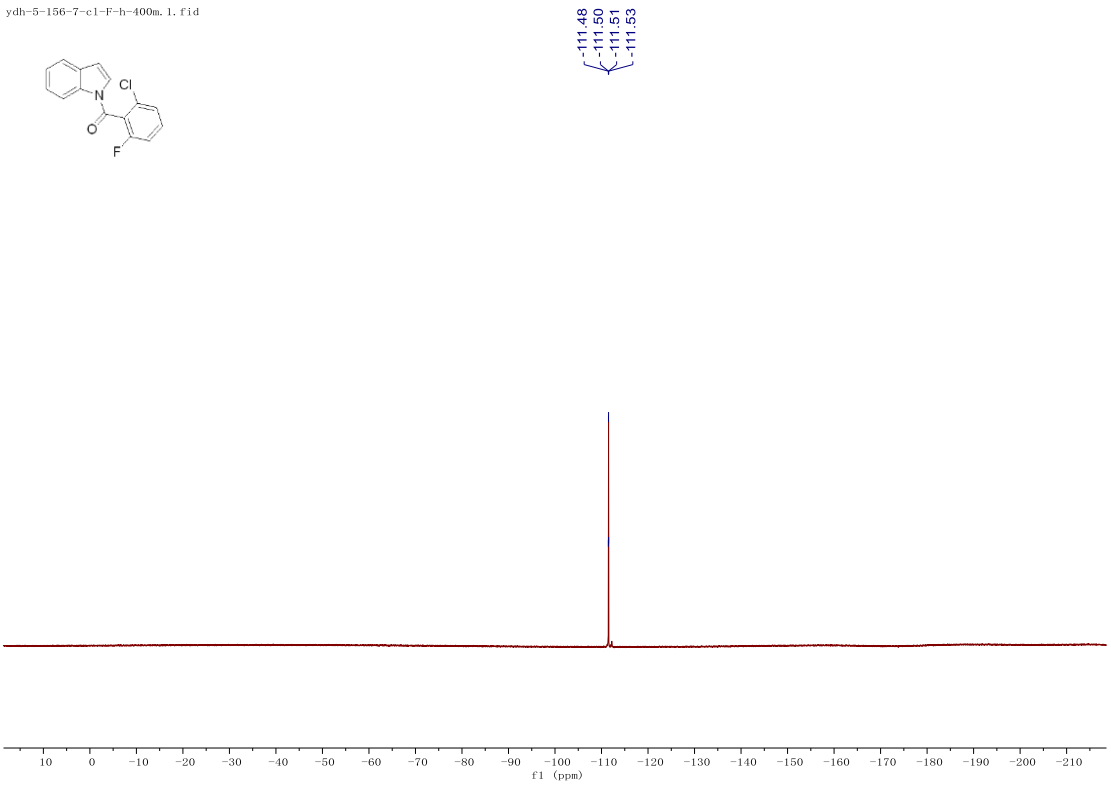
^{13}C NMR of S19



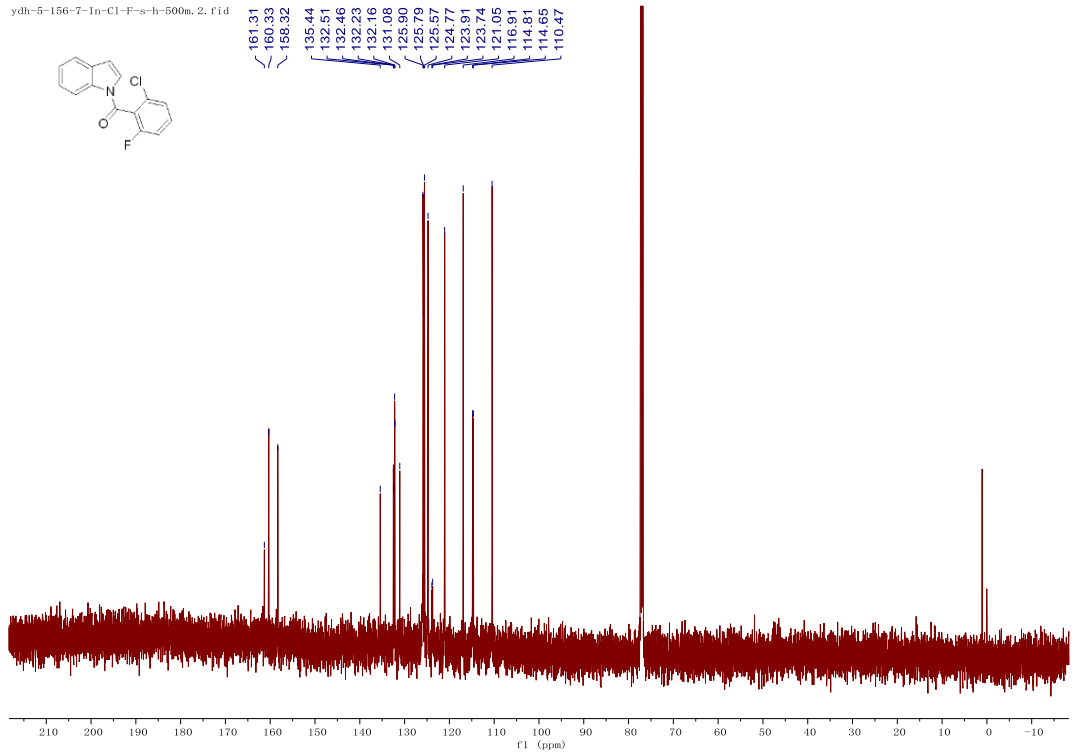
^{1}H NMR of S20



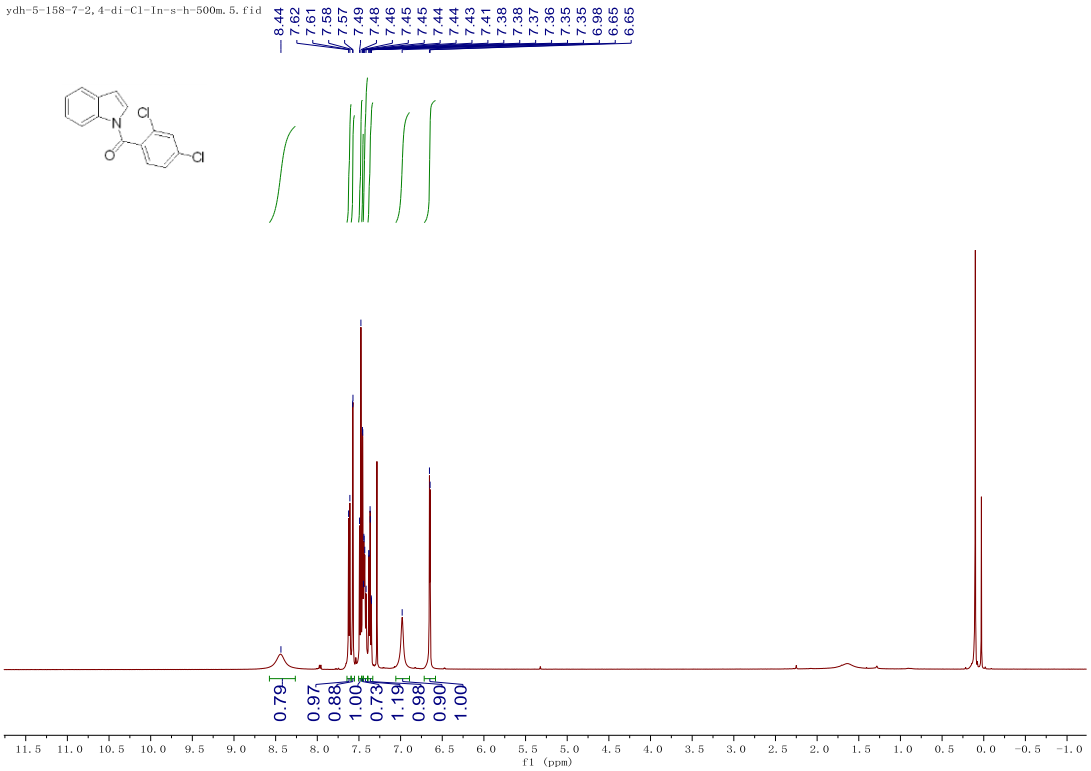
^{19}F NMR of S20



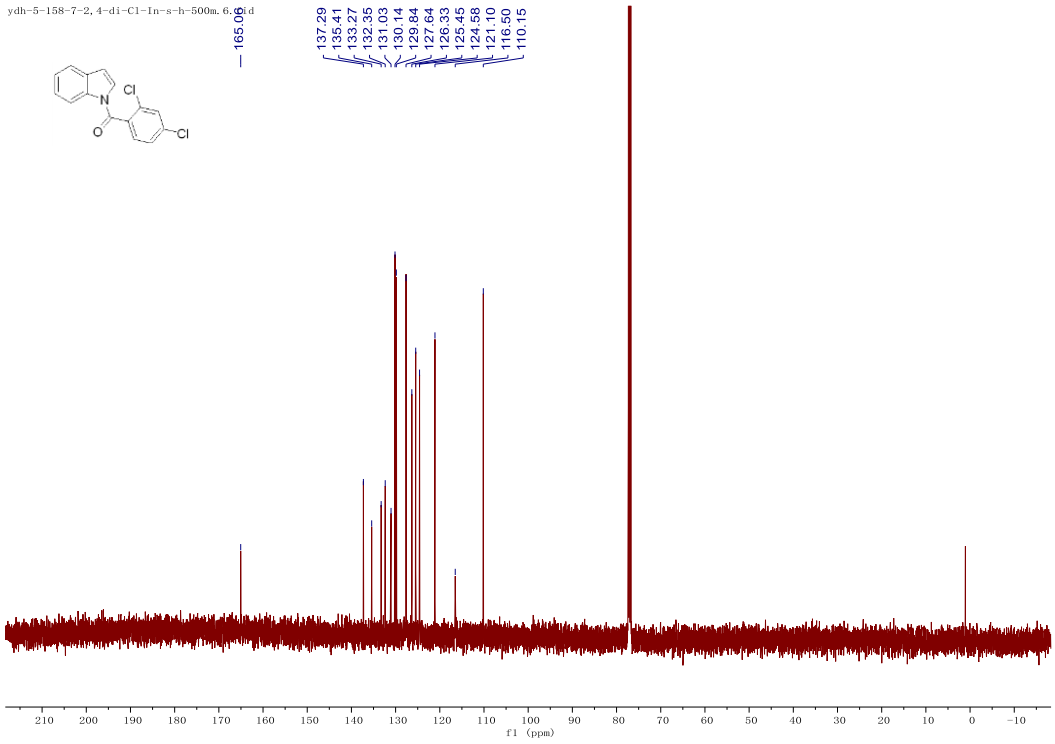
^{13}C NMR of S20



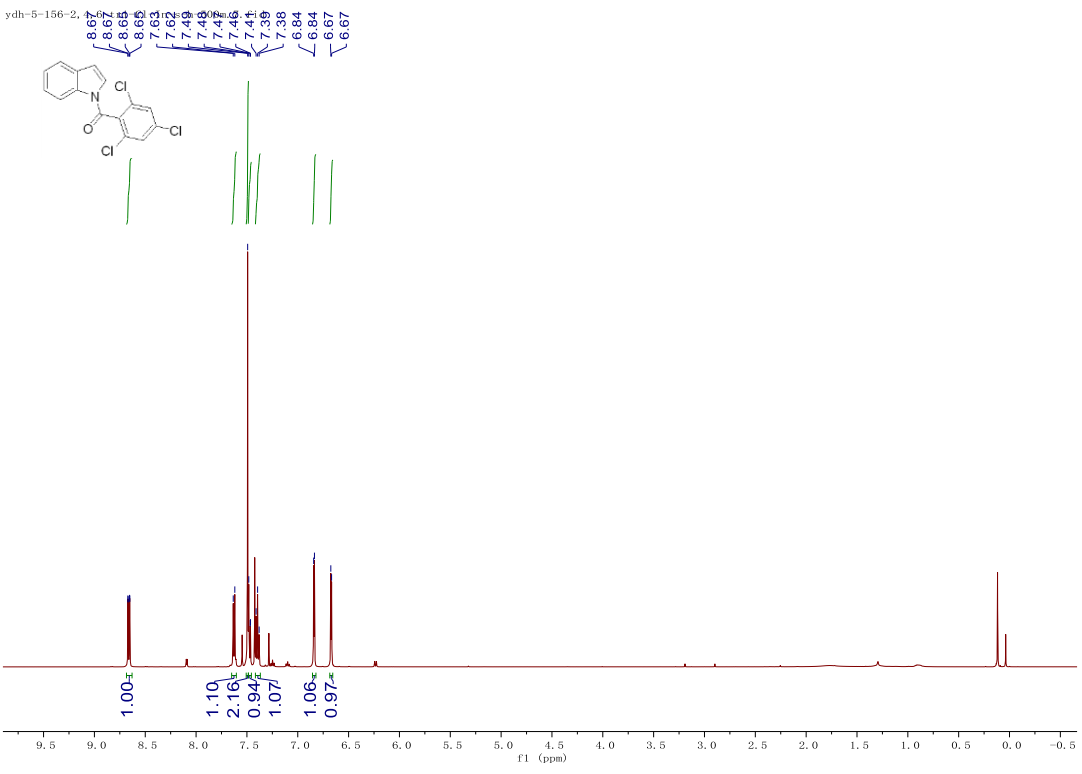
^{1}H NMR of S21



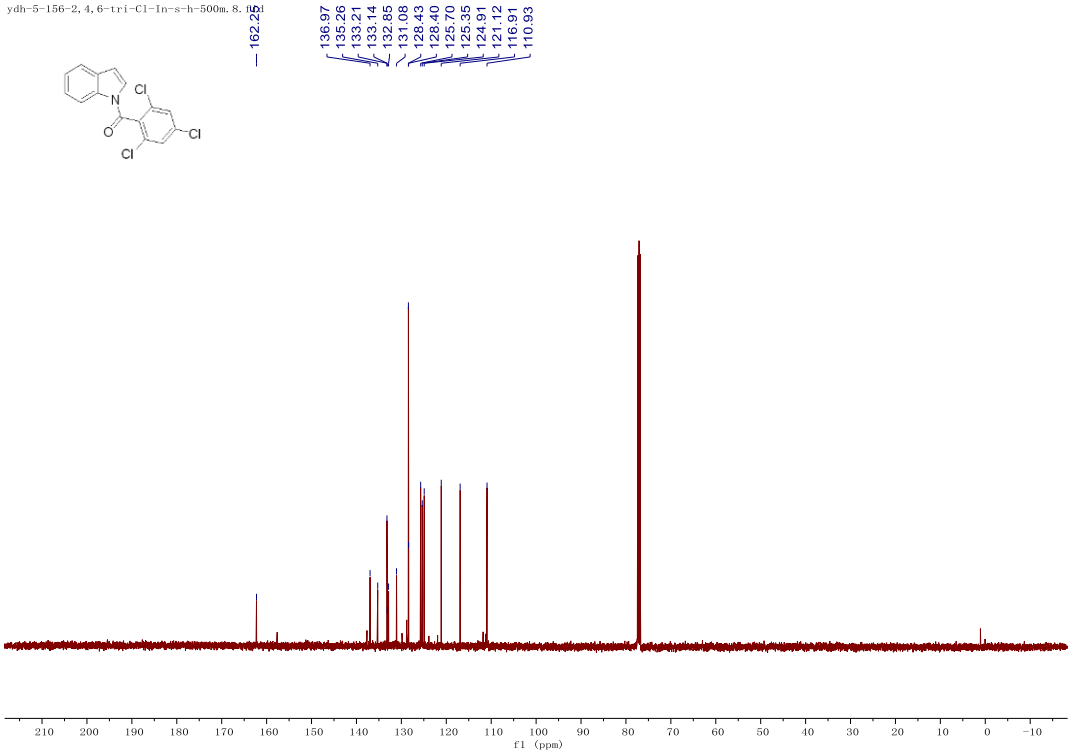
^{13}C NMR of S21



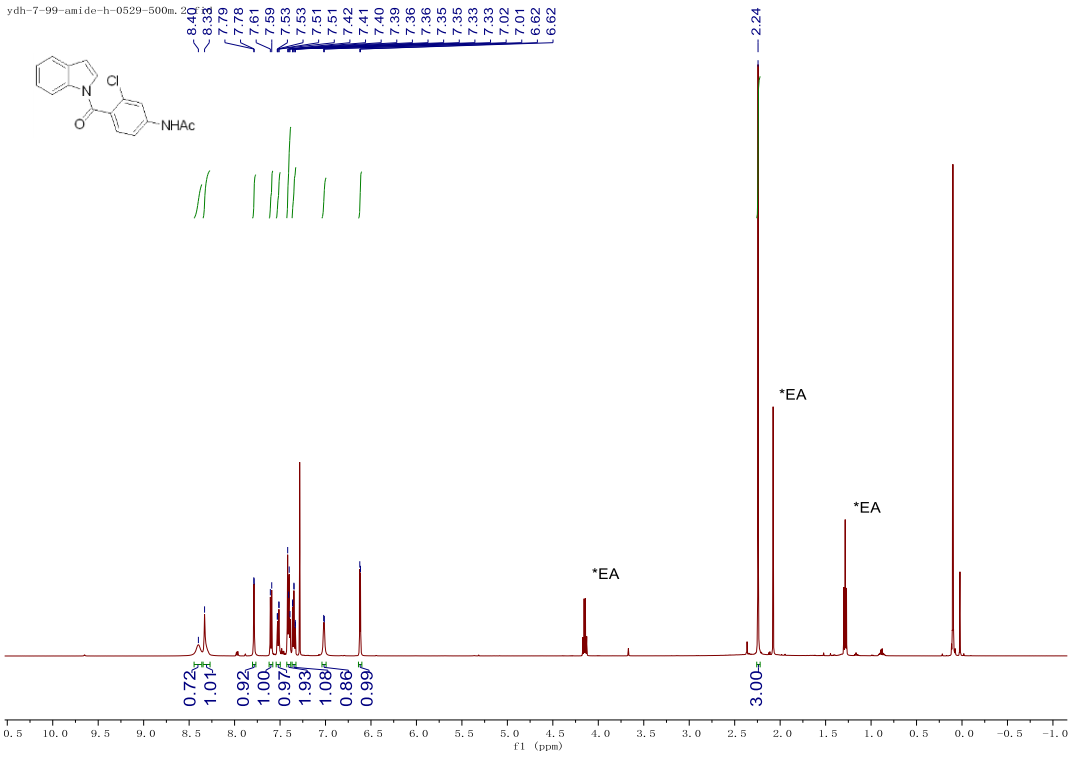
^{1}H NMR of S21'



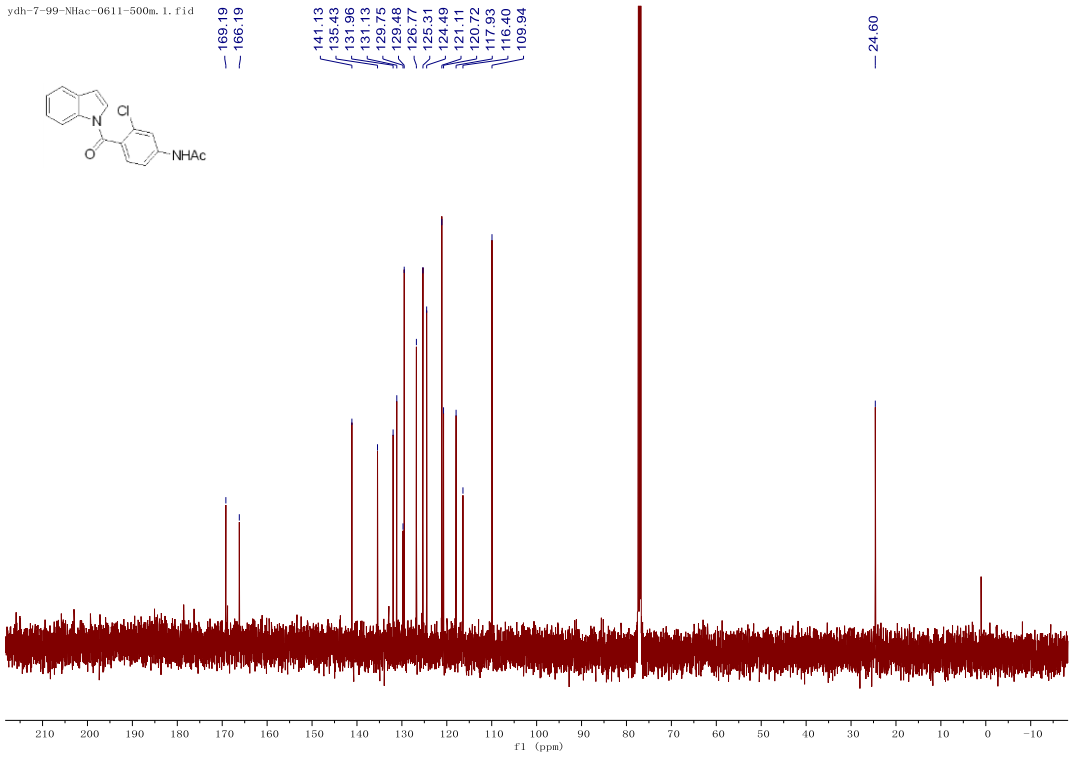
^{13}C NMR of S21'



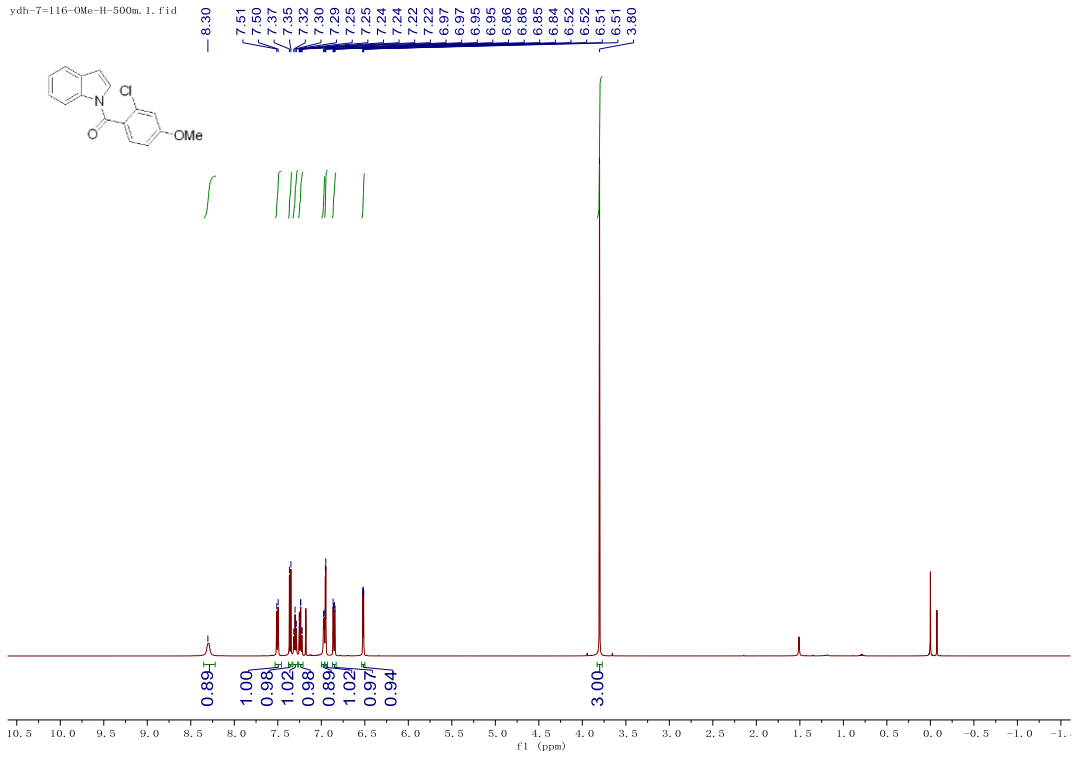
^{1}H NMR of S22



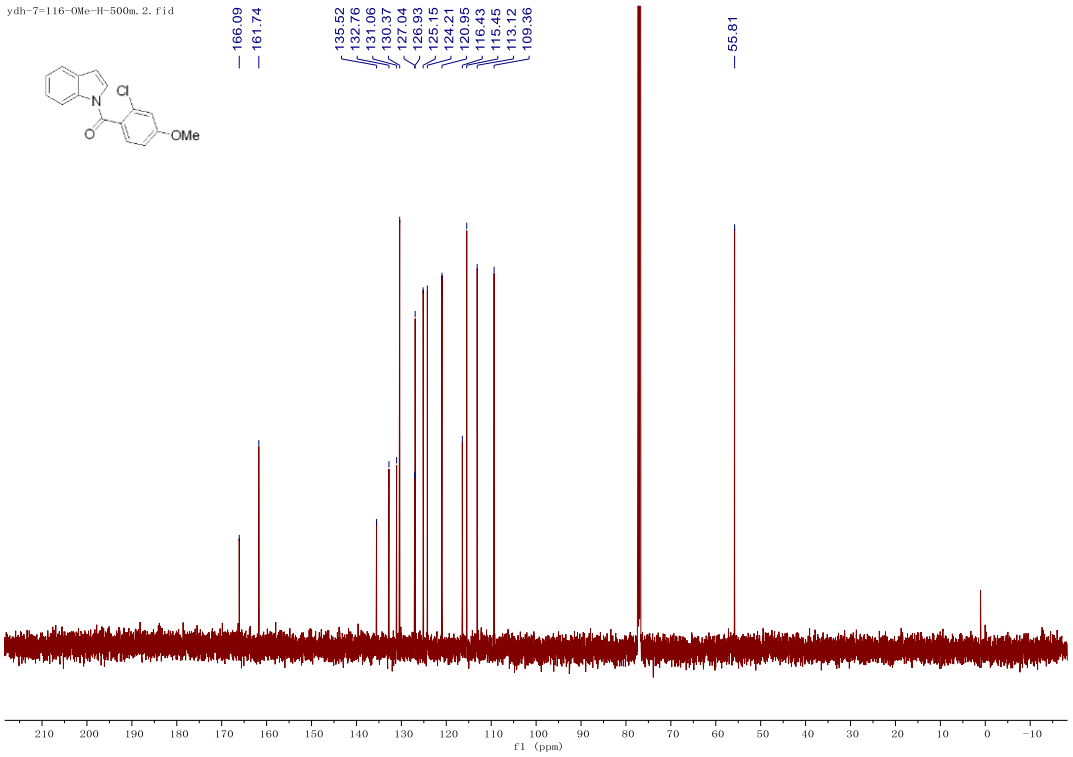
^{13}C NMR of S22



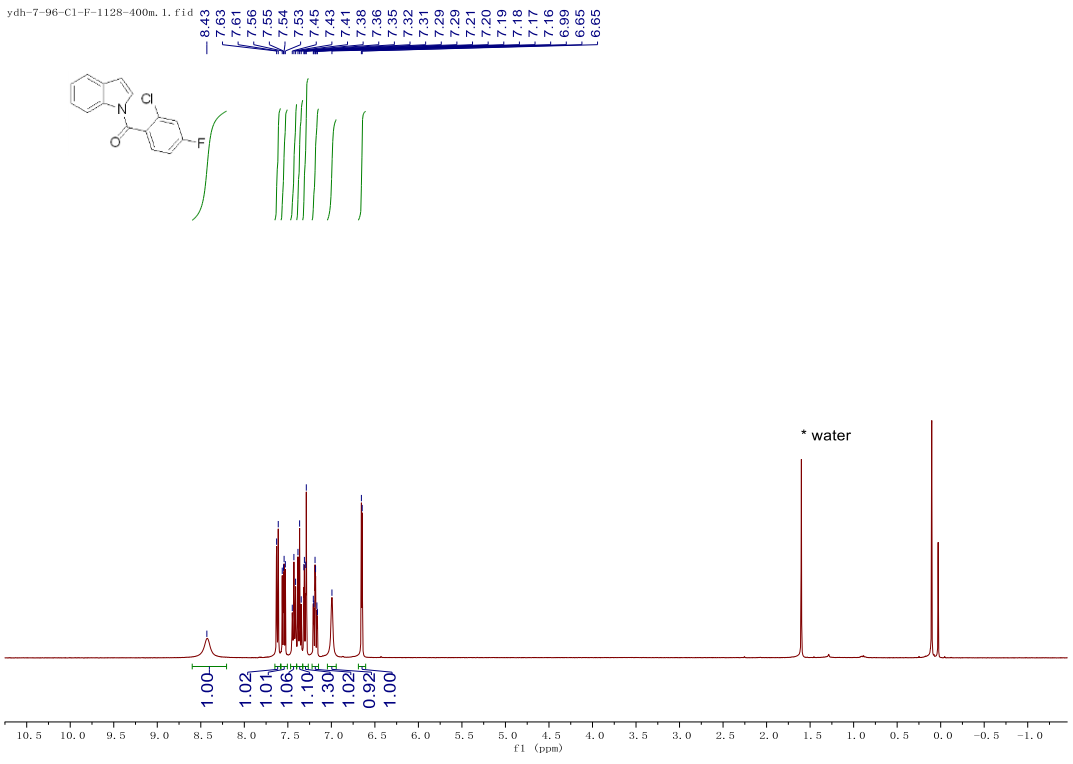
^{1}H NMR of S23



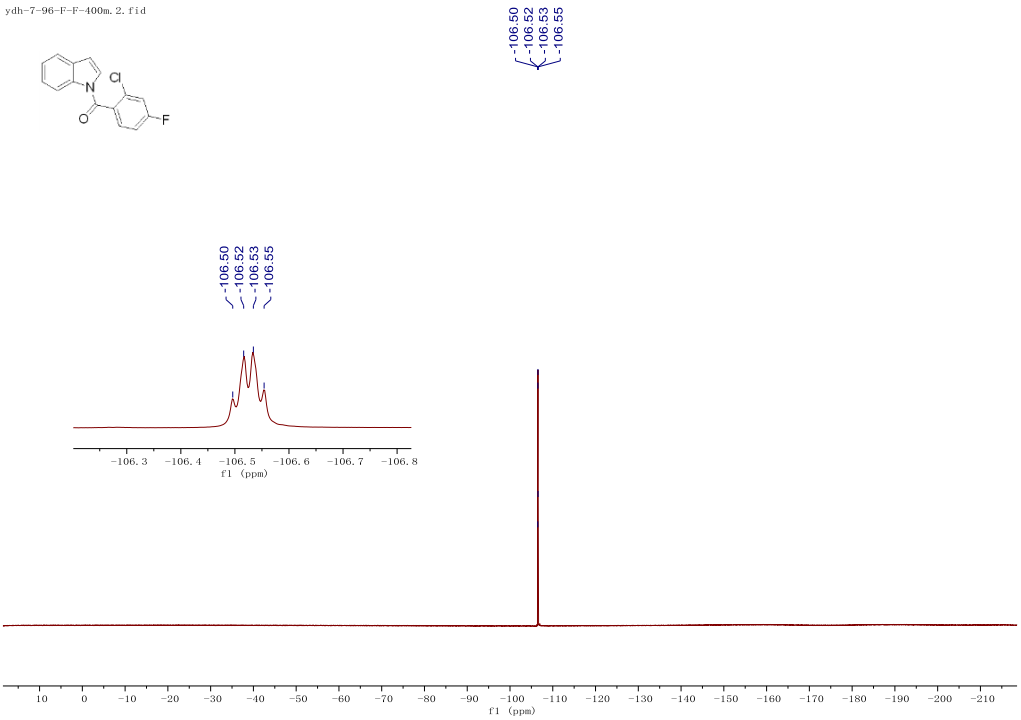
^{13}C NMR of S23



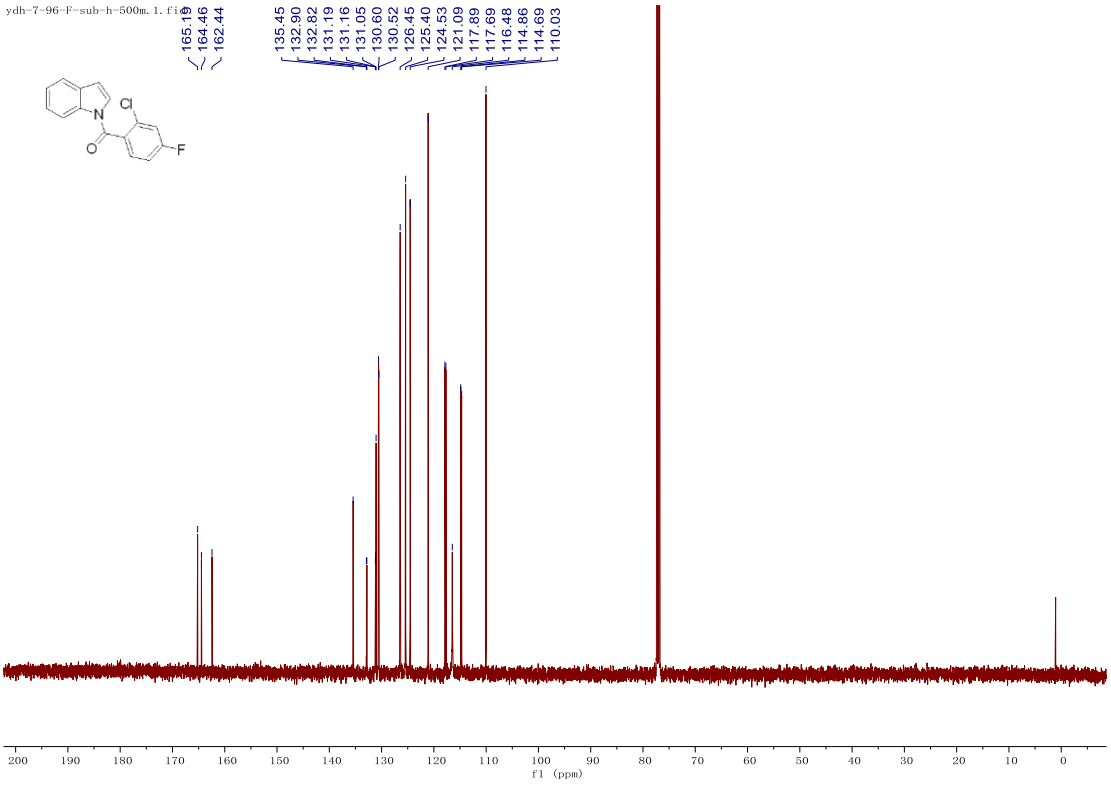
^{1}H NMR of S24



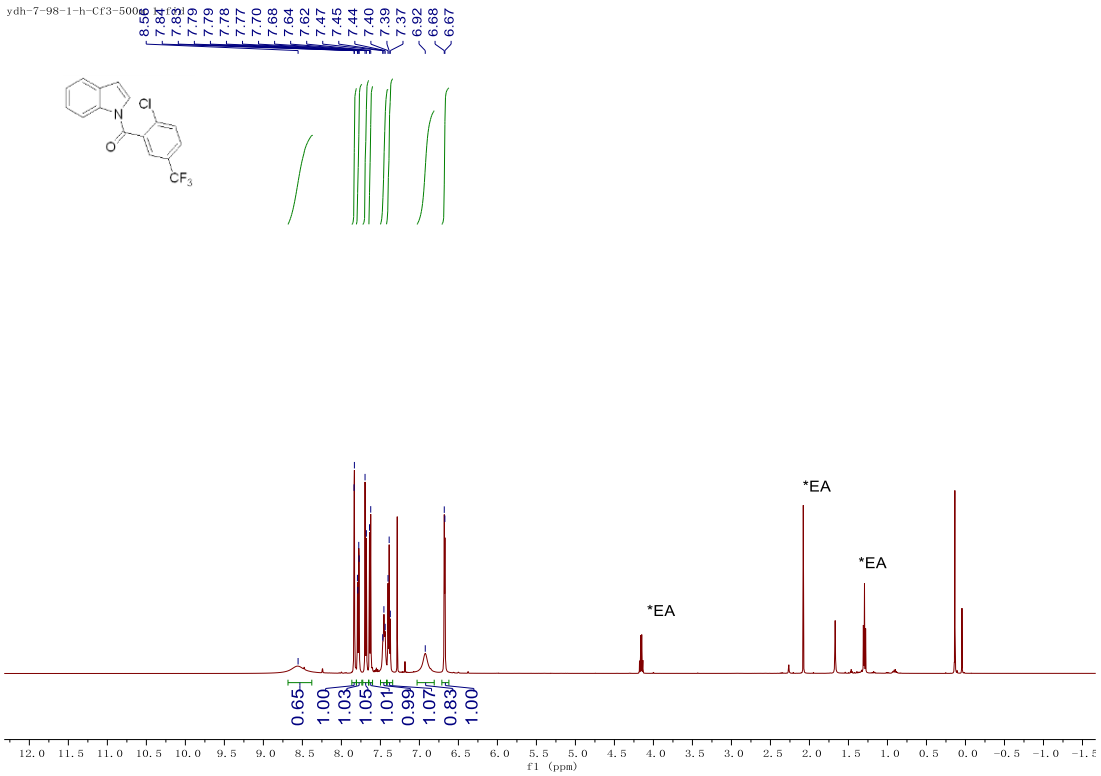
^{19}F NMR of S24



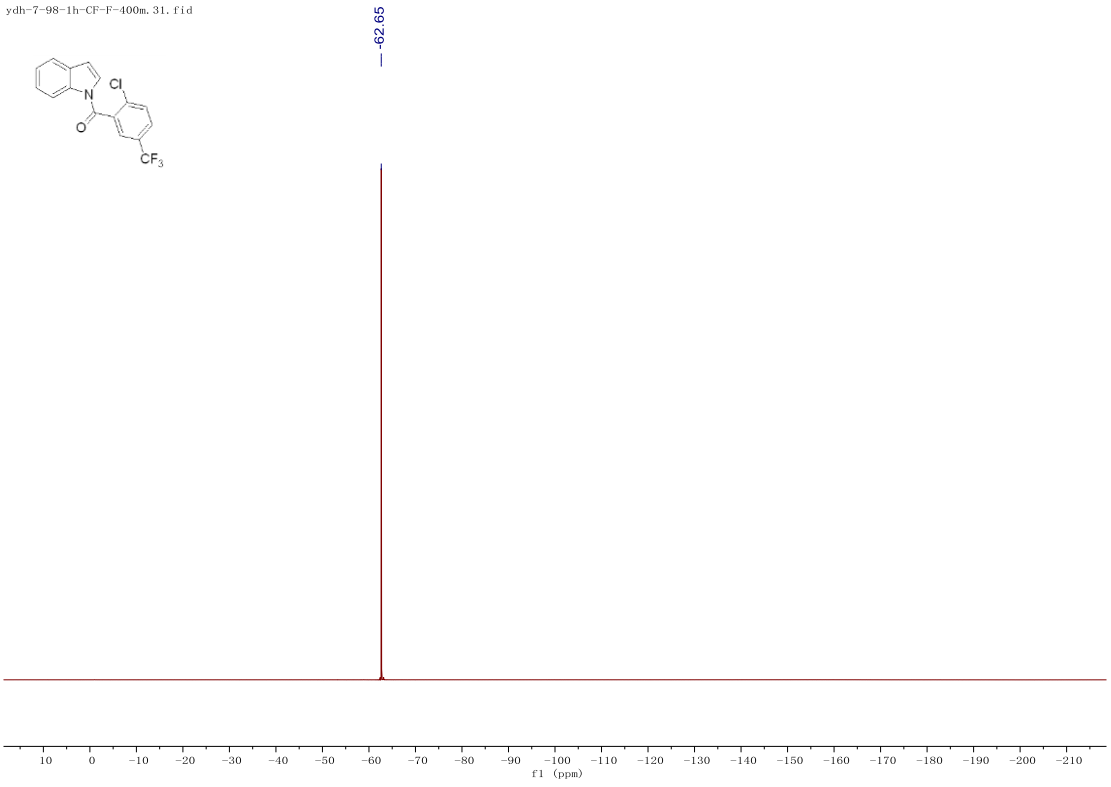
^{13}C NMR of S24



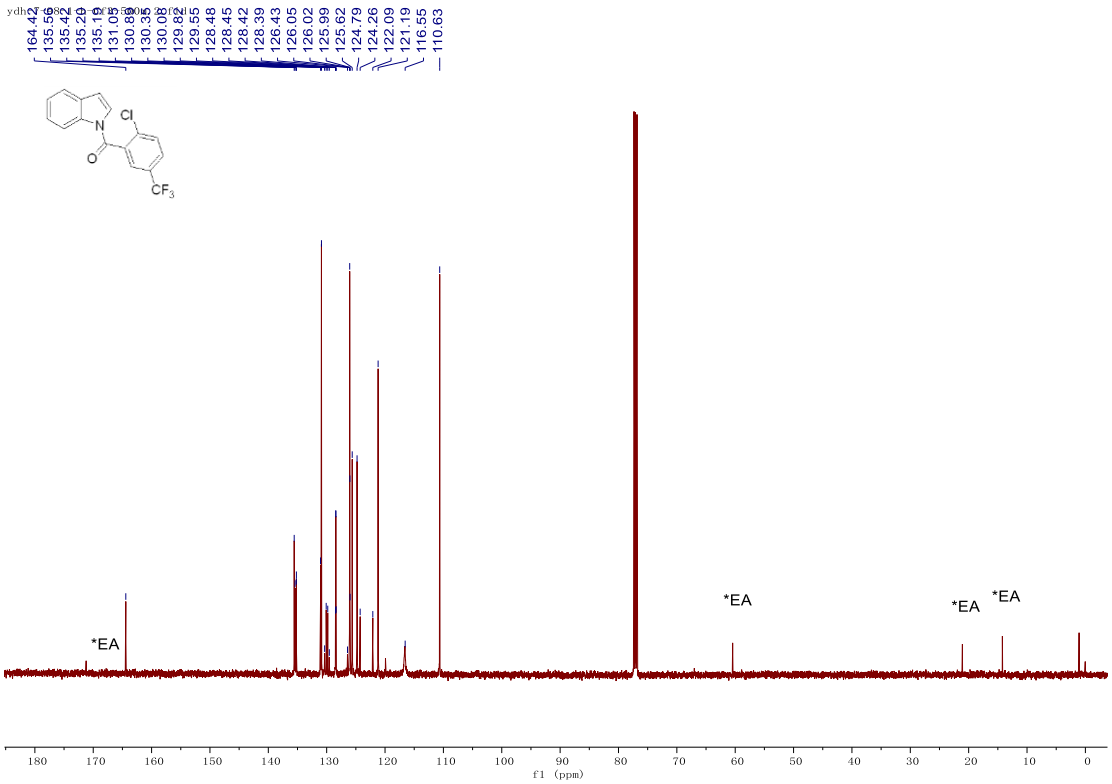
^{1}H NMR of S25



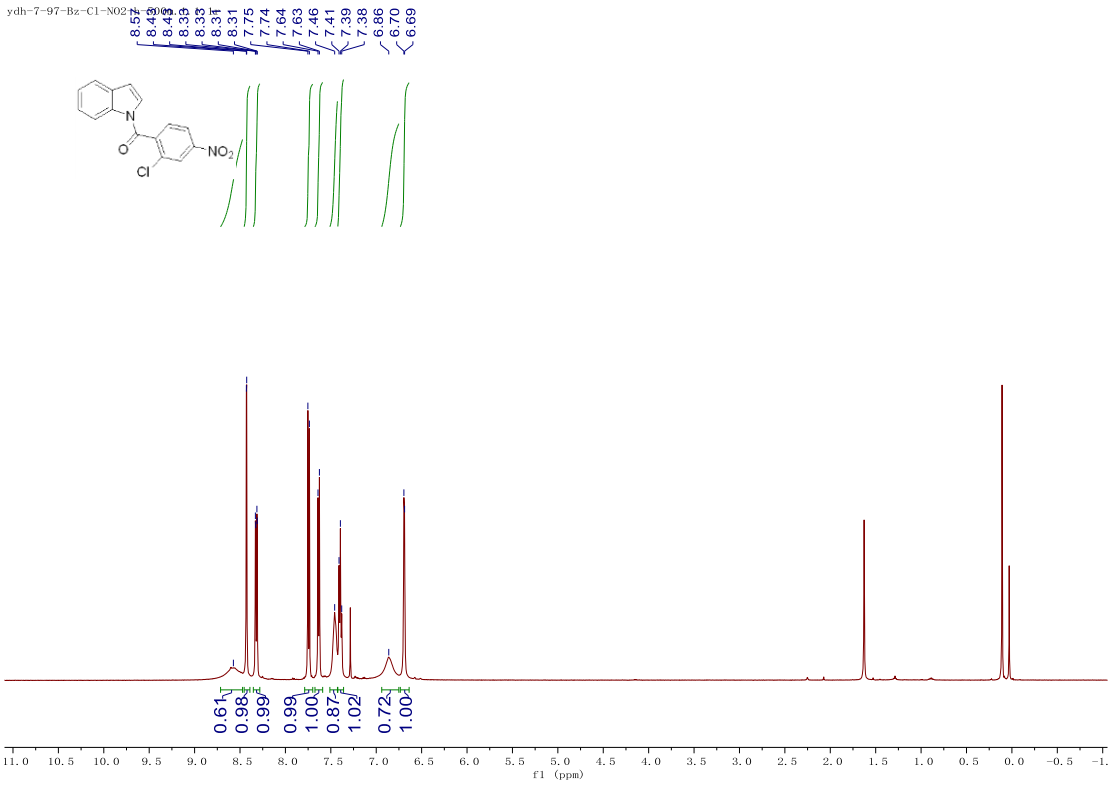
^{19}F NMR of S25



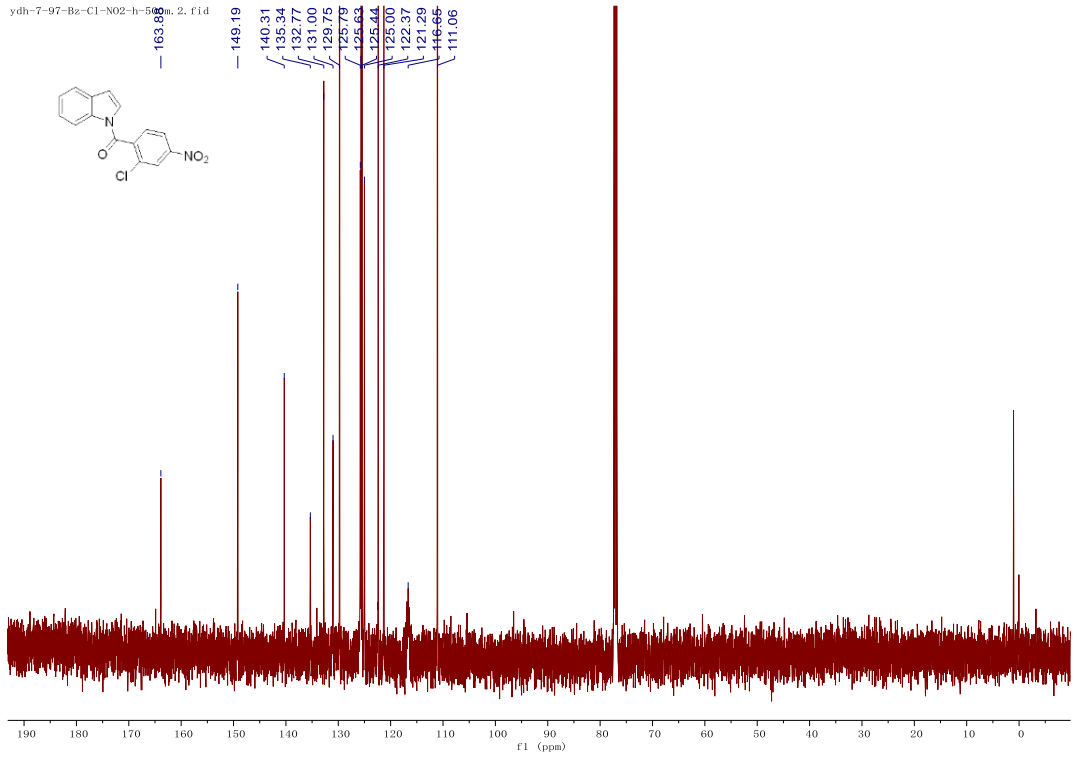
^{13}C NMR of S25



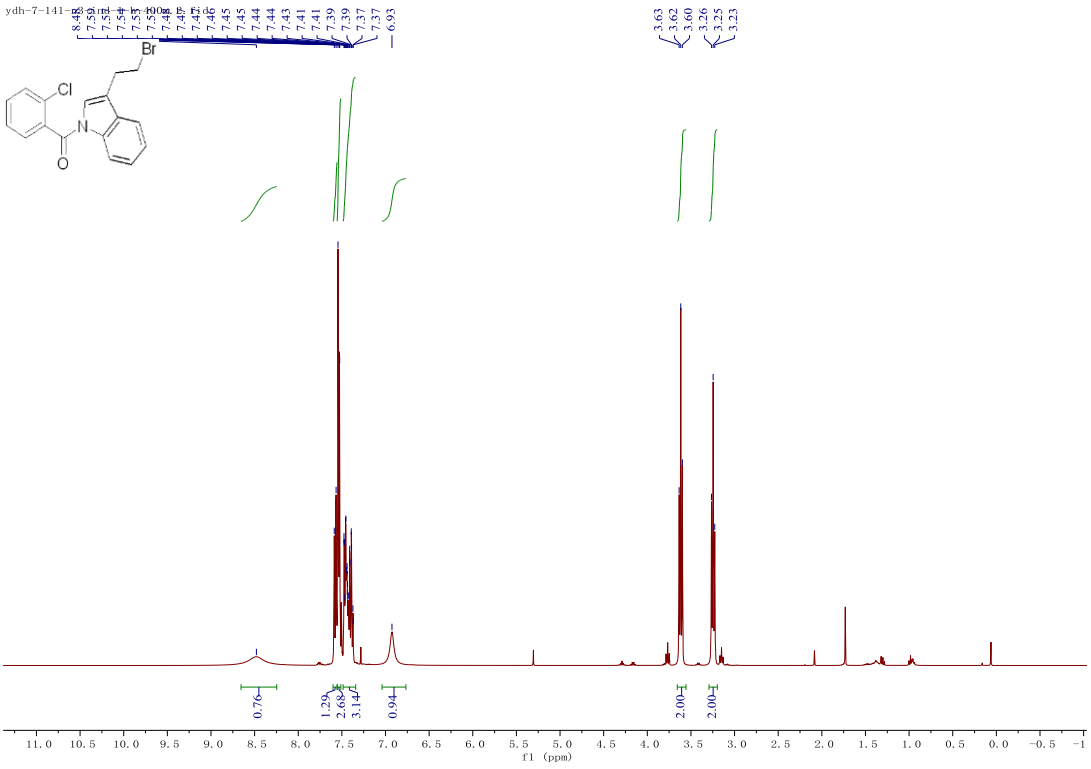
^{1}H NMR of S26



^{13}C NMR of S26



^{1}H NMR of S27



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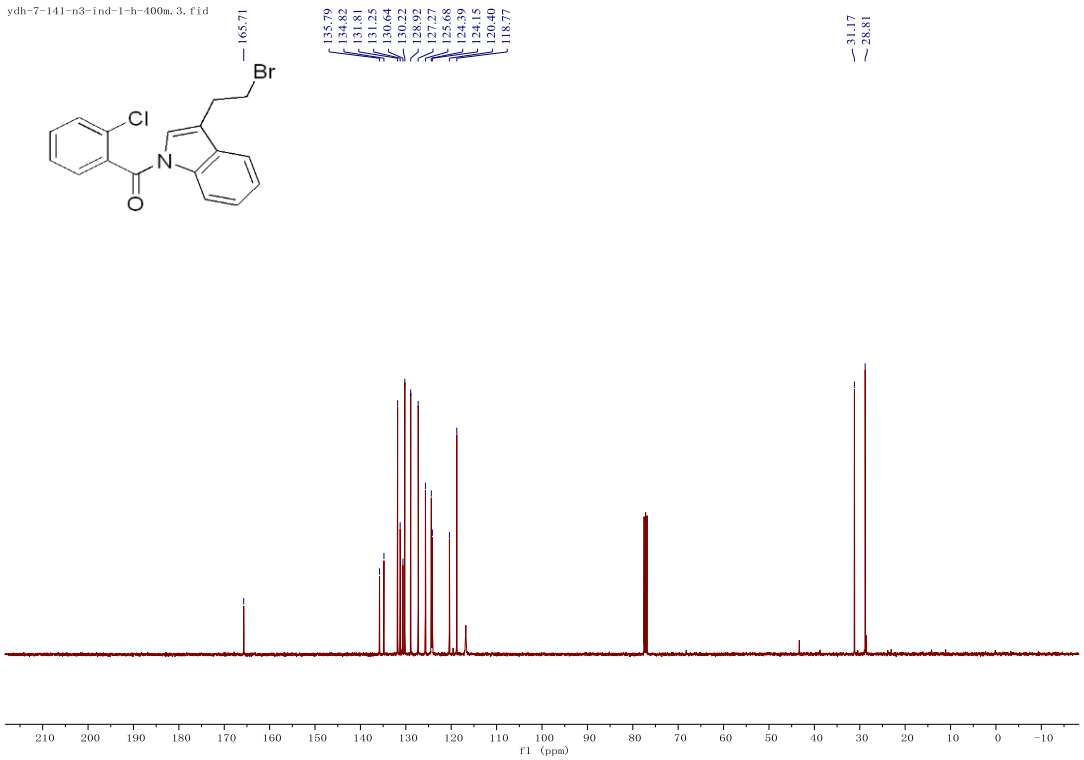
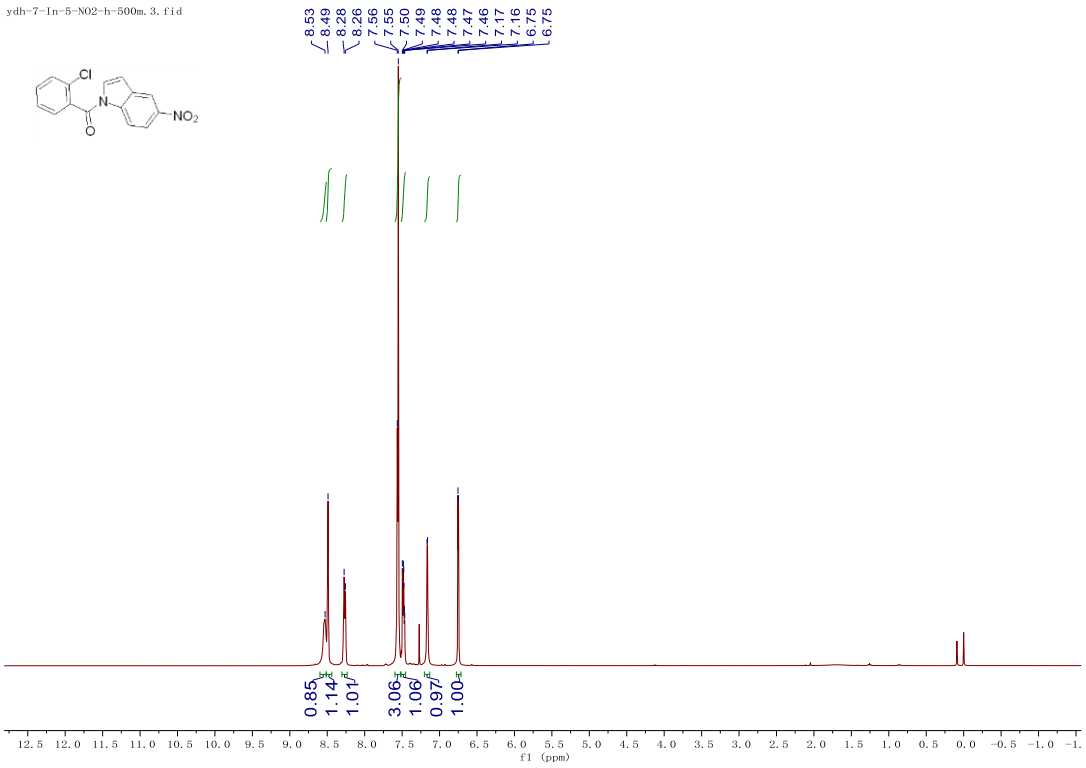
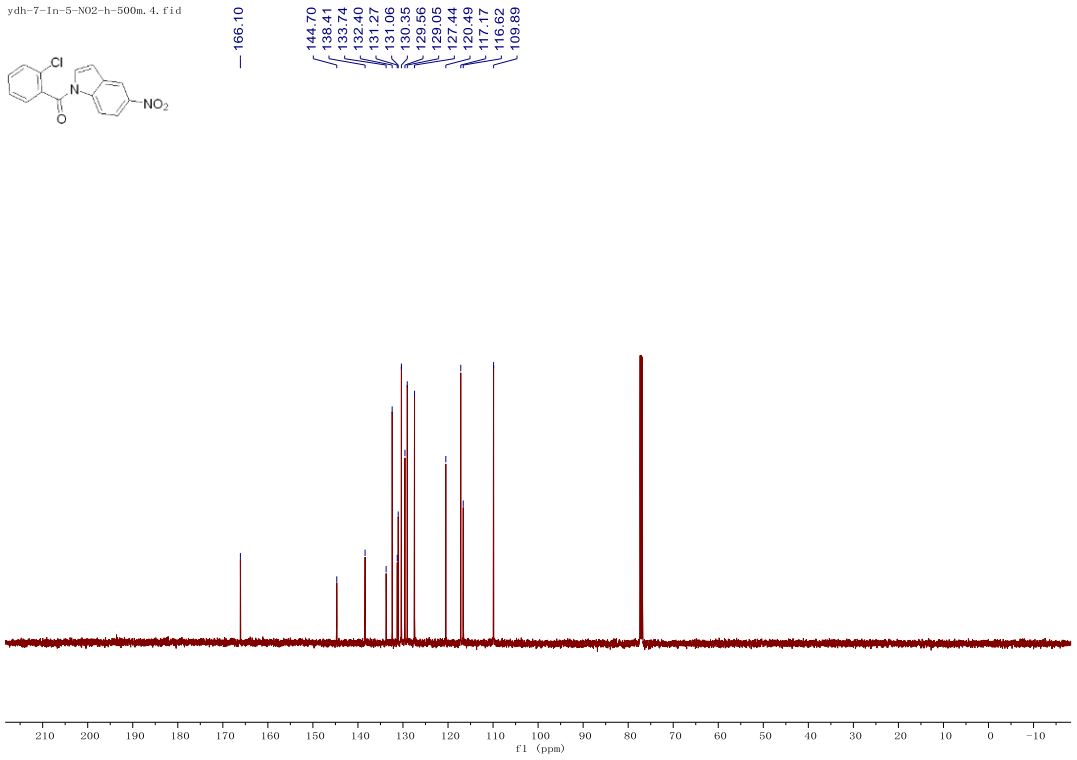


^{1}H NMR of S28



^{13}C NMR of S28



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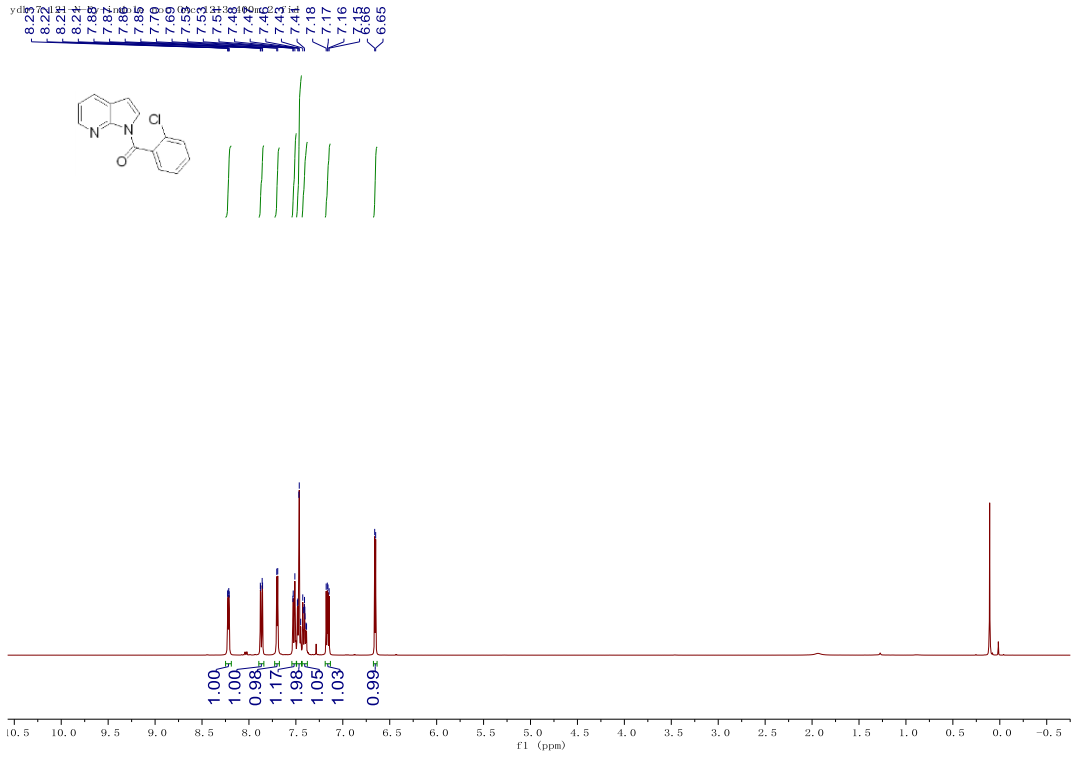
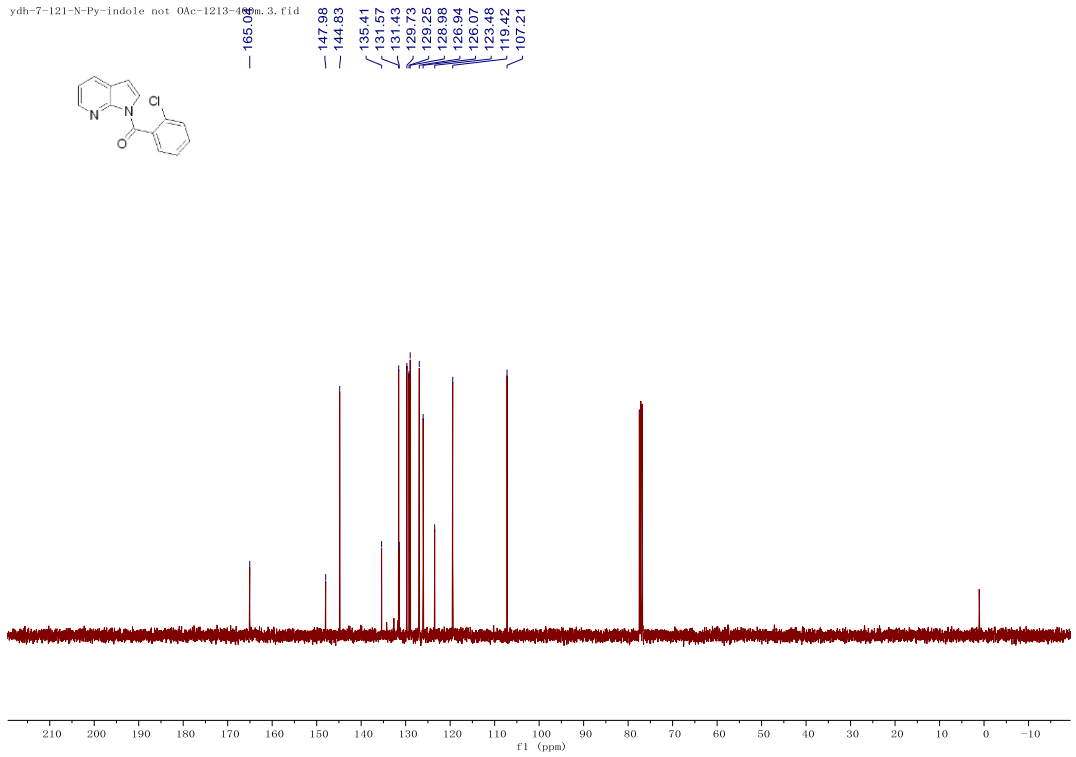
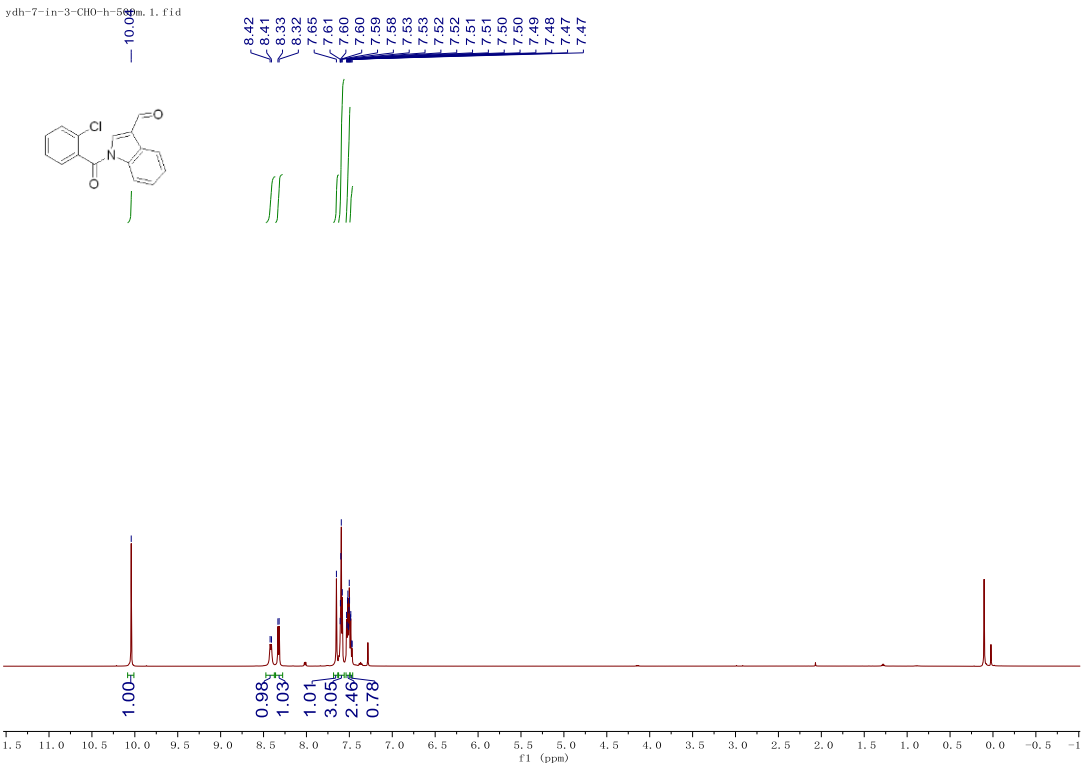


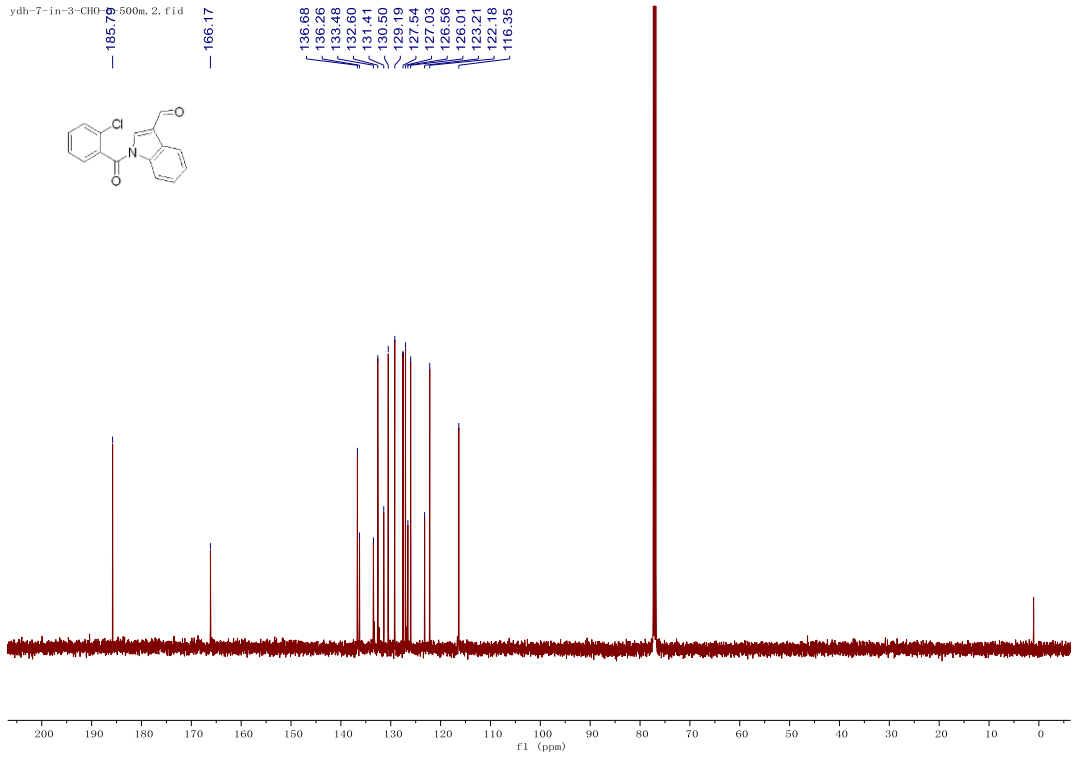
^{13}C NMR of S29



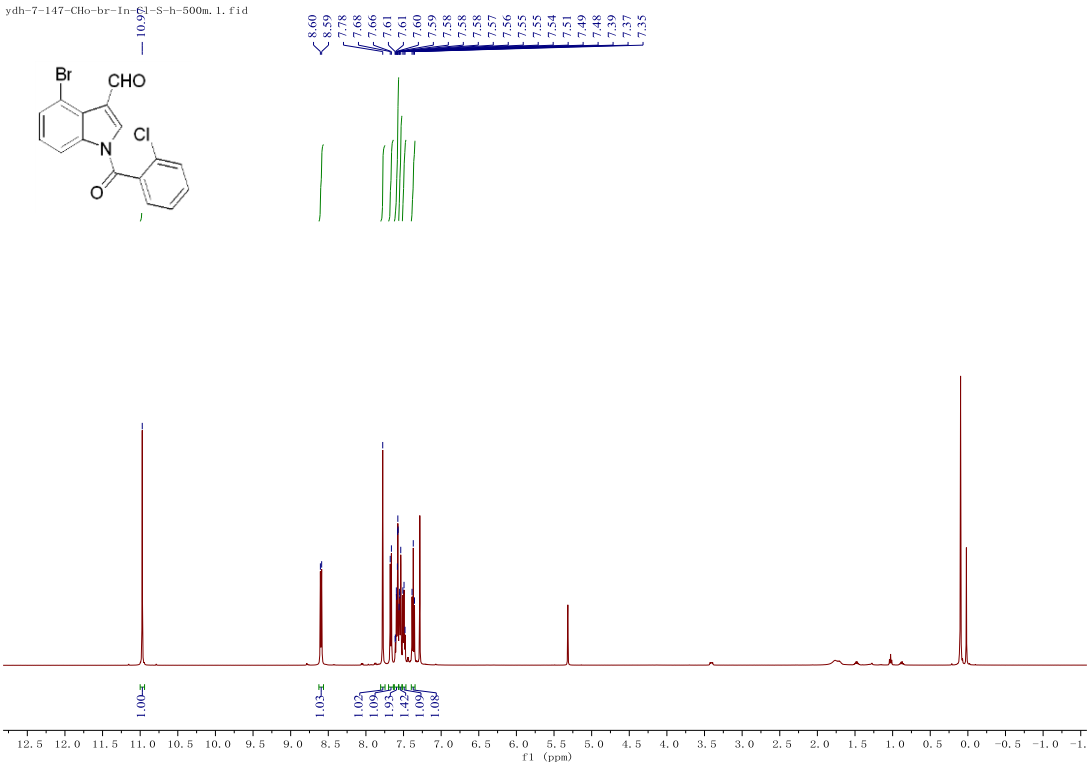
^{1}H NMR of S30



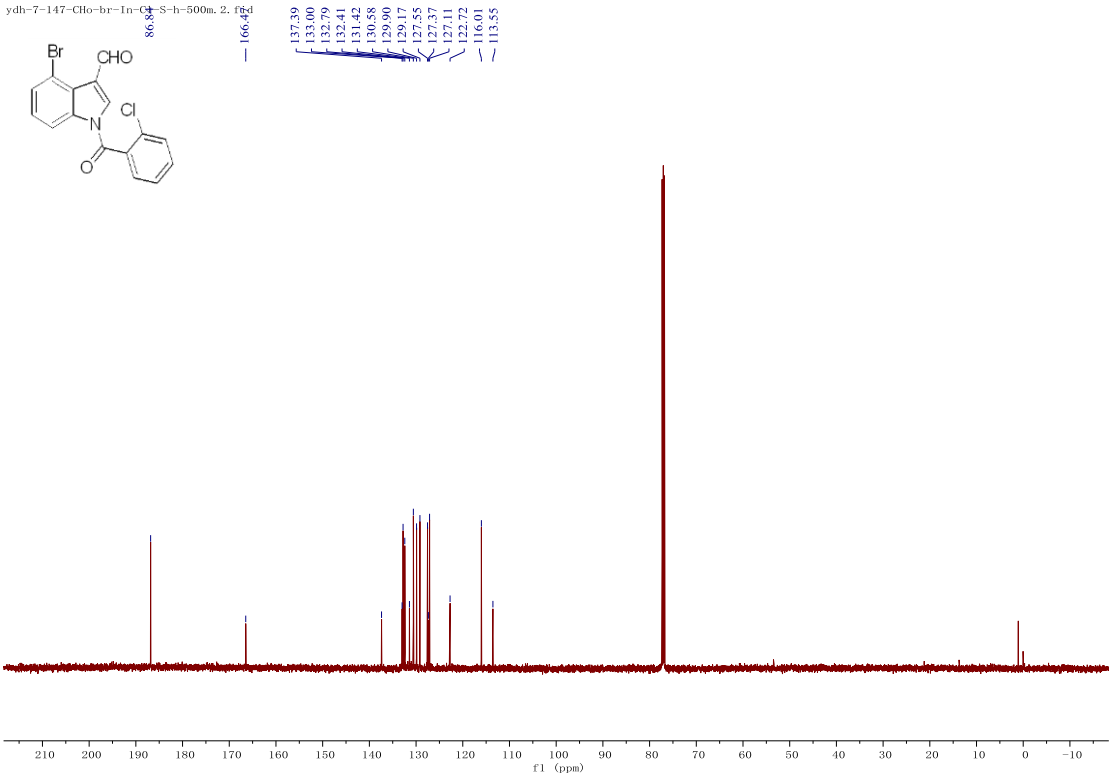
^{13}C NMR of S30



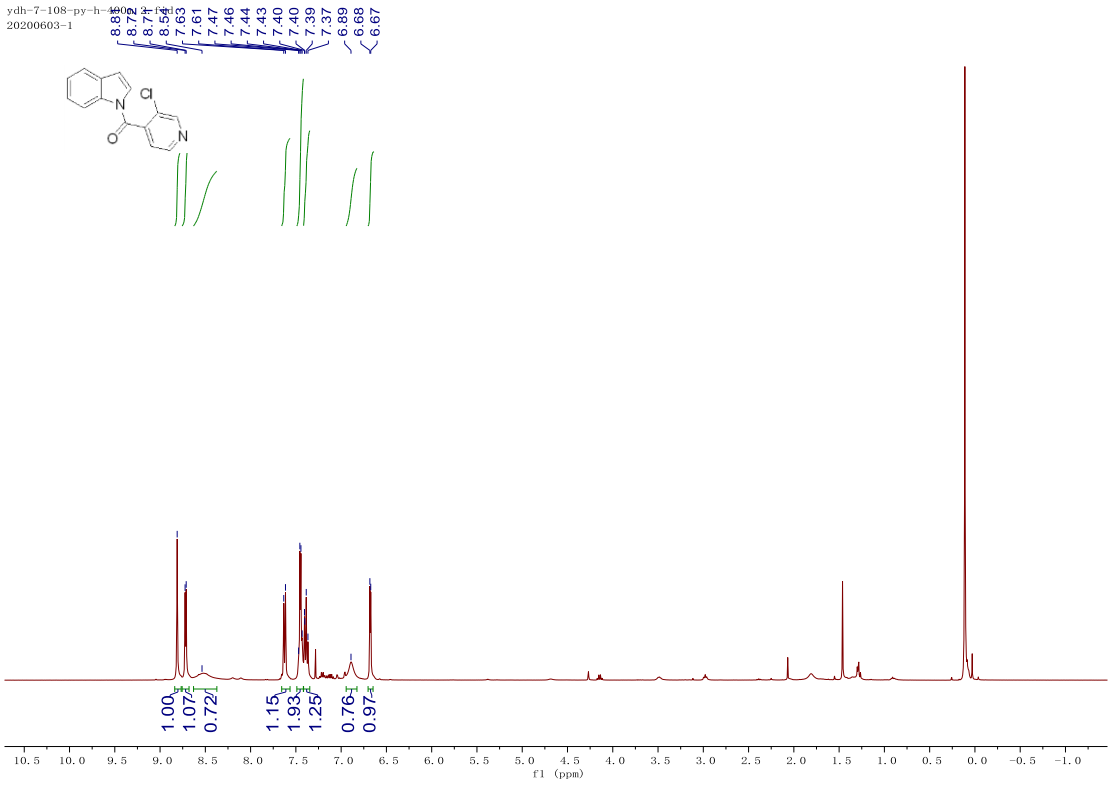
^{1}H NMR of S31



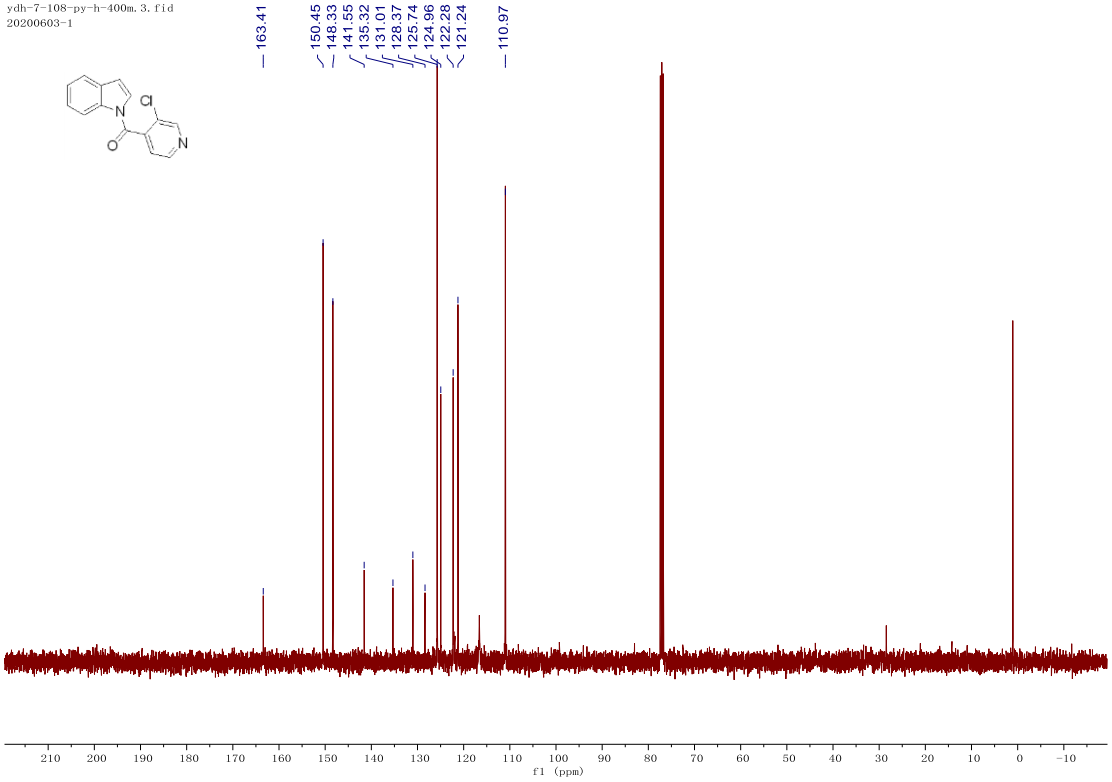
^{13}C NMR of S31



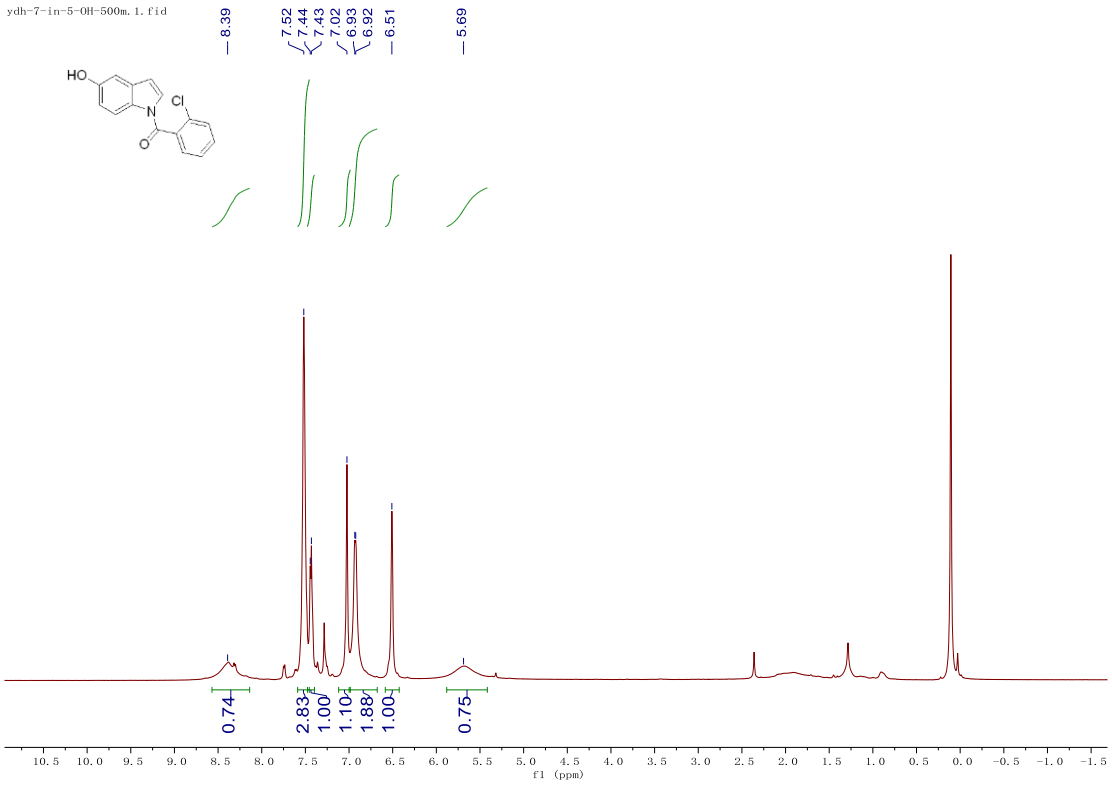
^{1}H NMR of S32



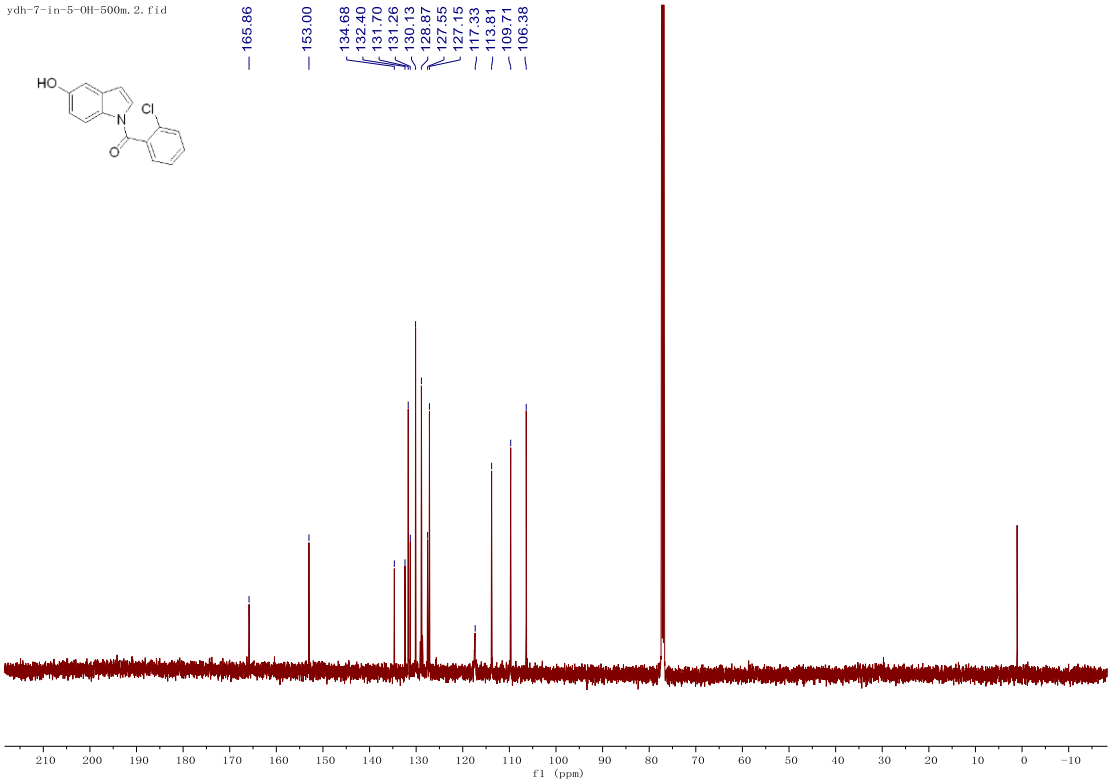
^{13}C NMR of S32



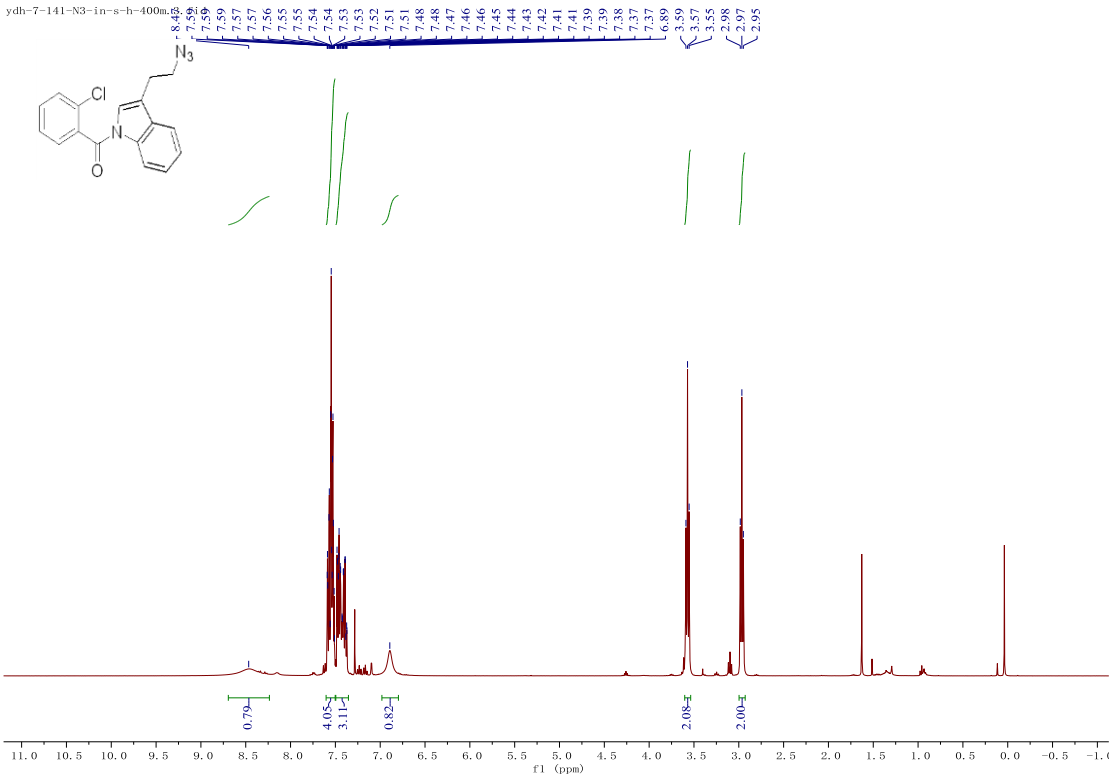
^{1}H NMR of S33



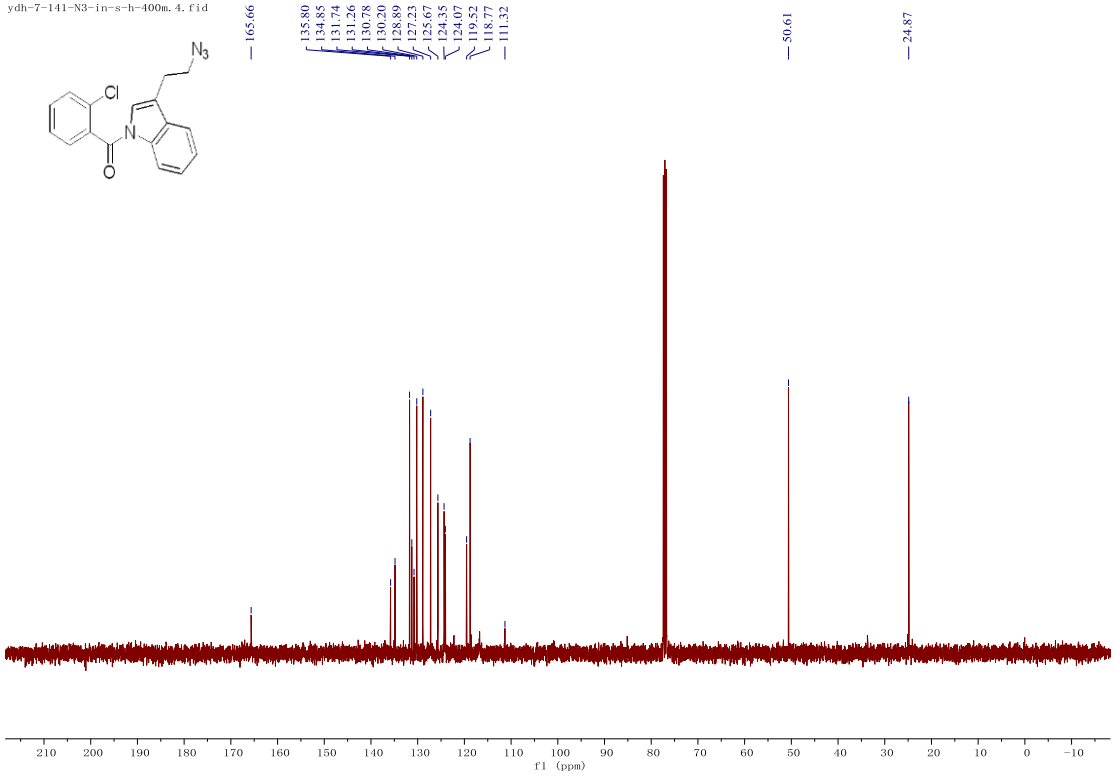
^{13}C NMR of S33



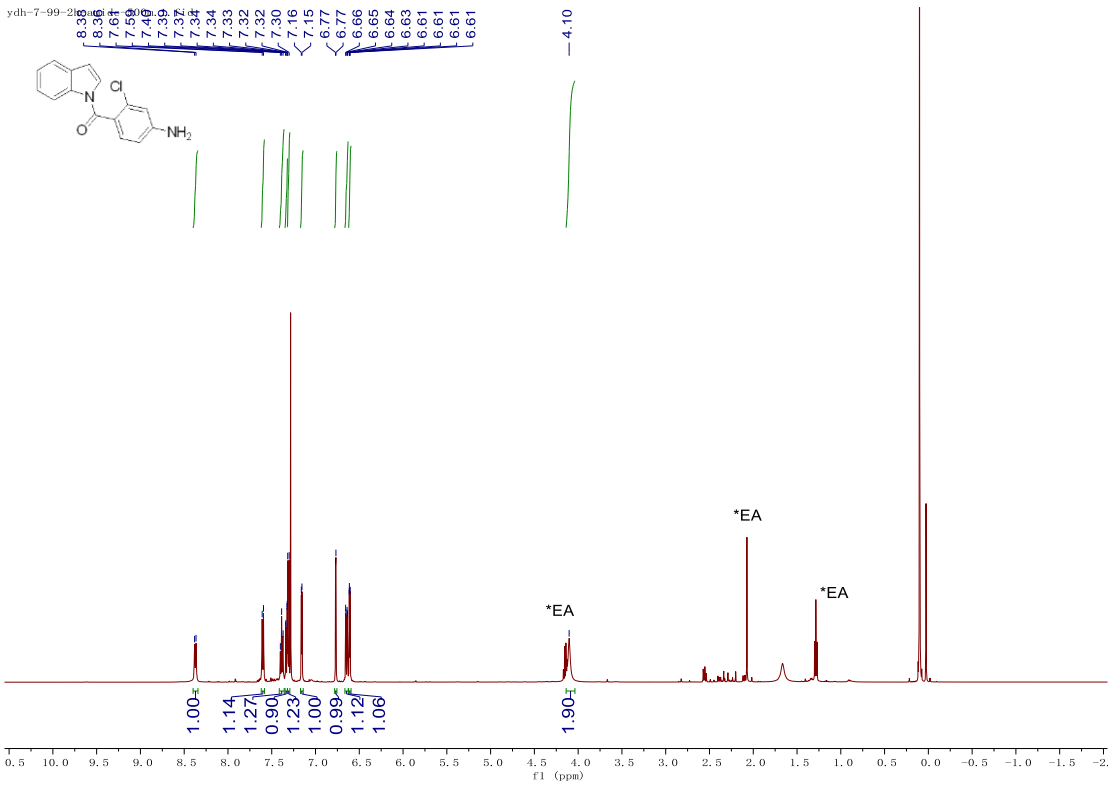
^{1}H NMR of S34



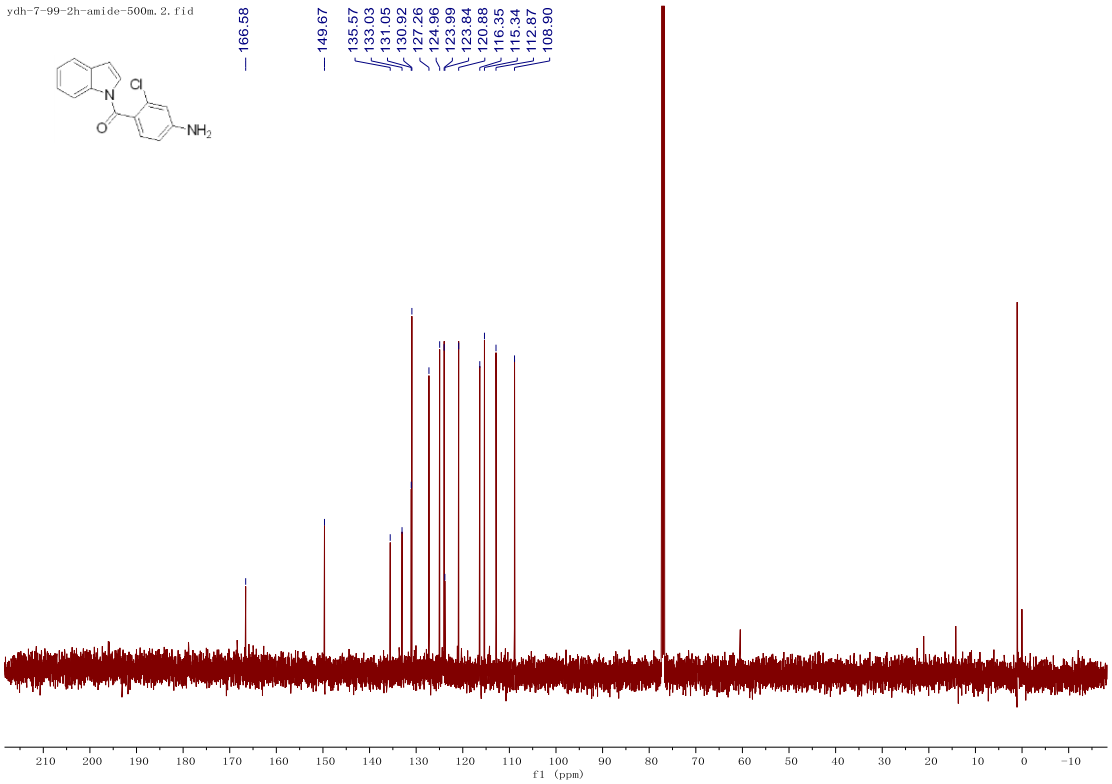
^{13}C NMR of S34



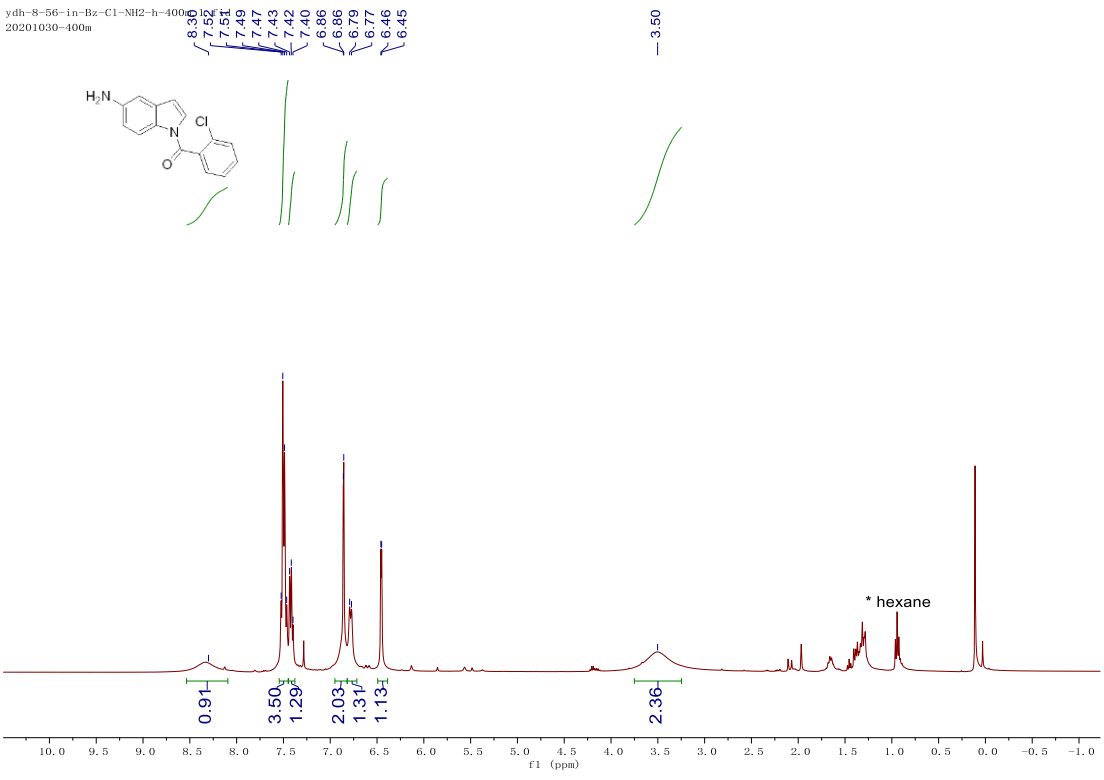
^{1}H NMR of S35



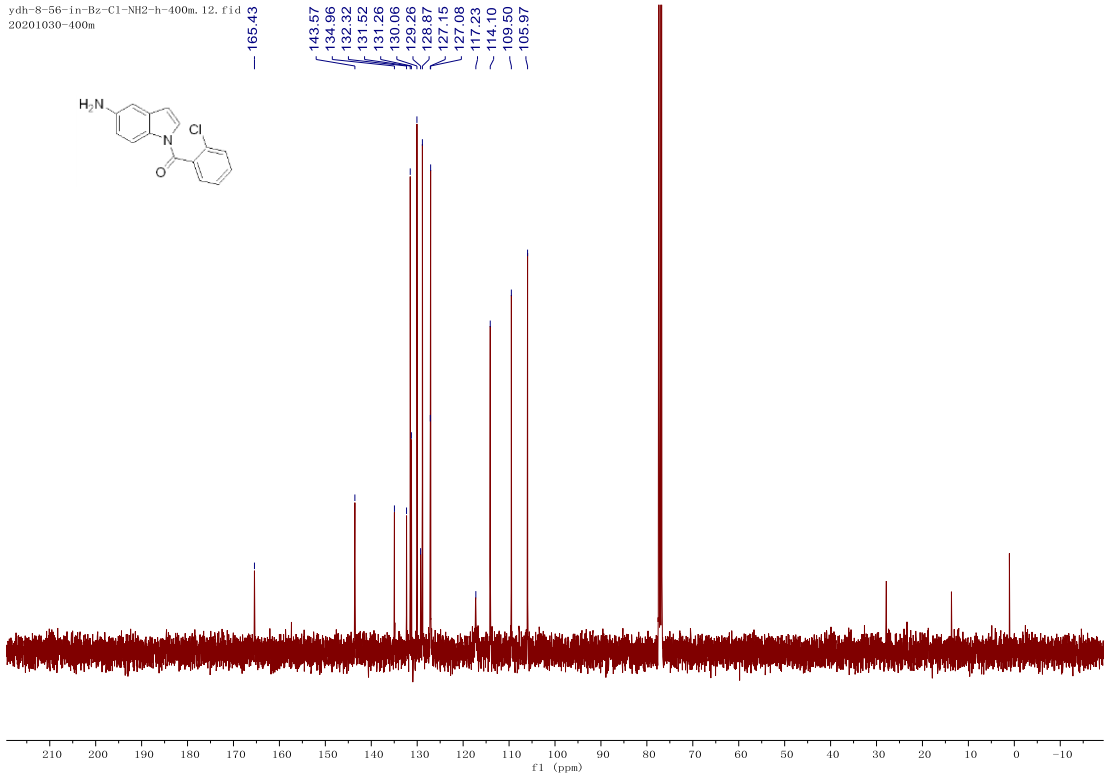
^{13}C NMR of S35



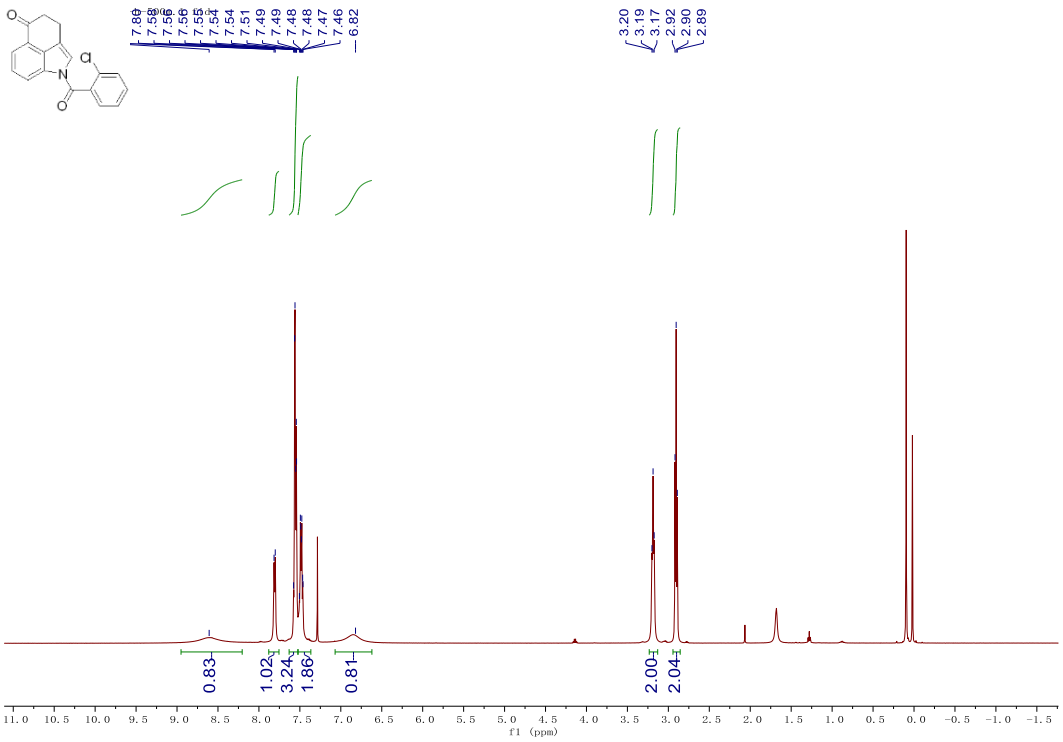
^{1}H NMR of S36



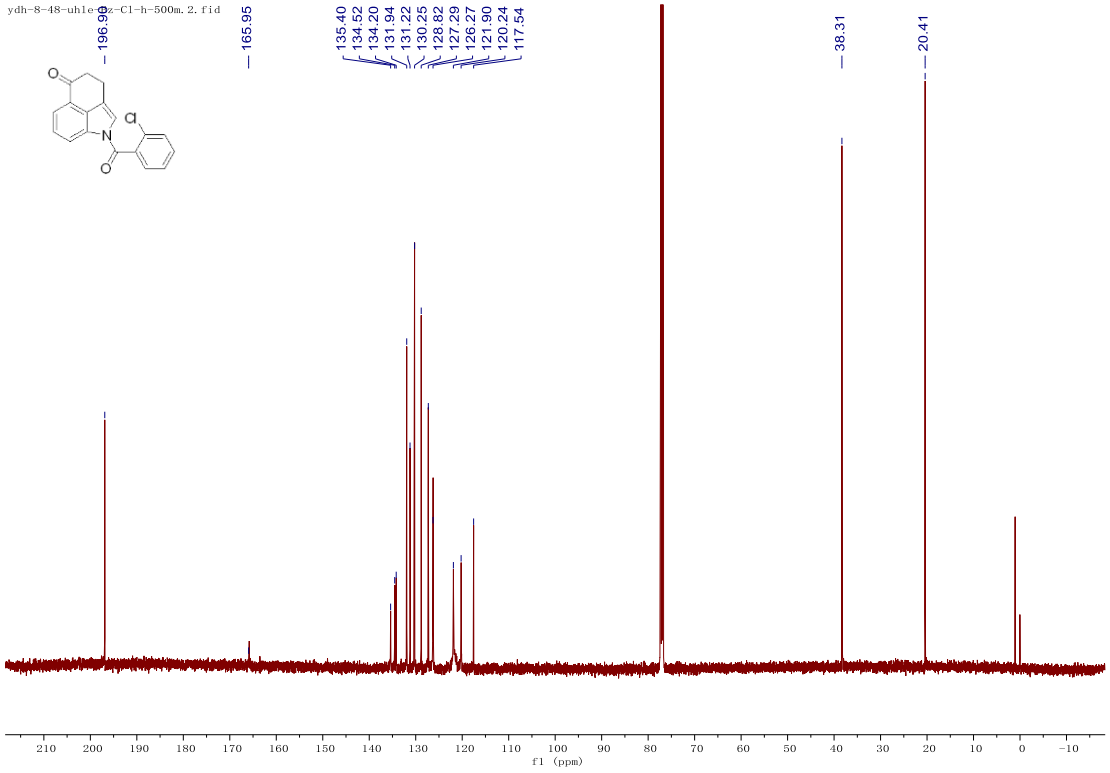
^{13}C NMR of S36



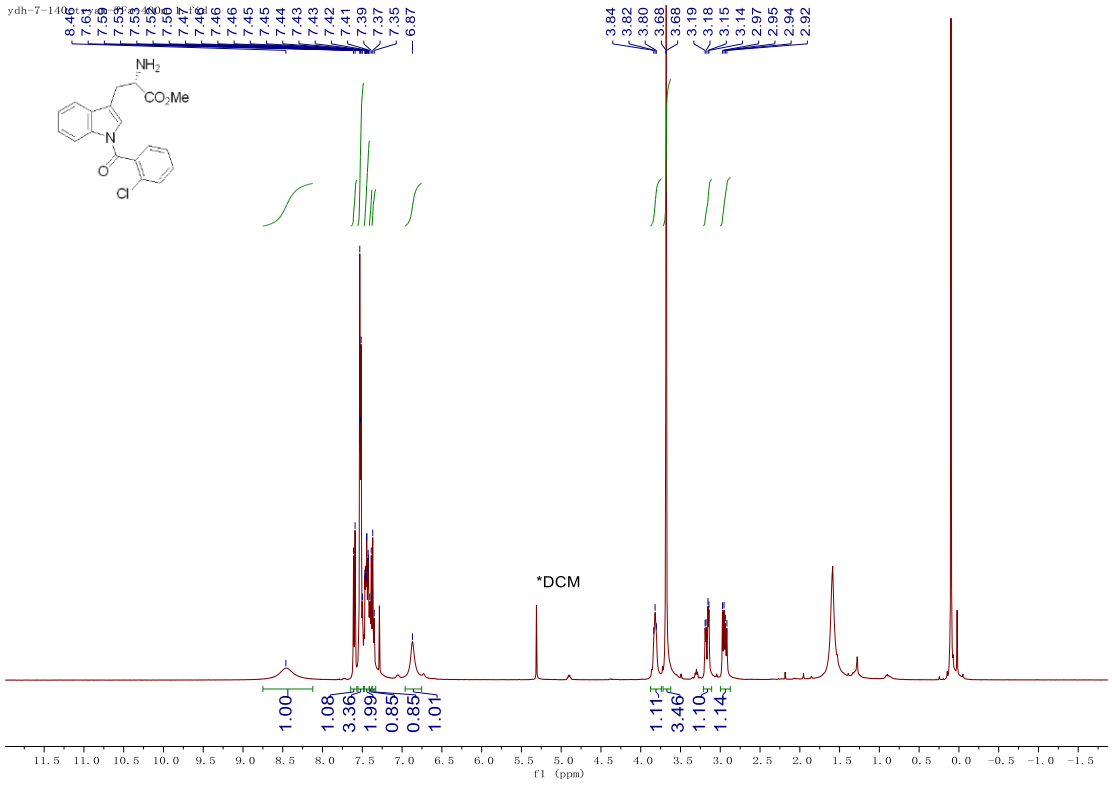
^{1}H NMR of S37



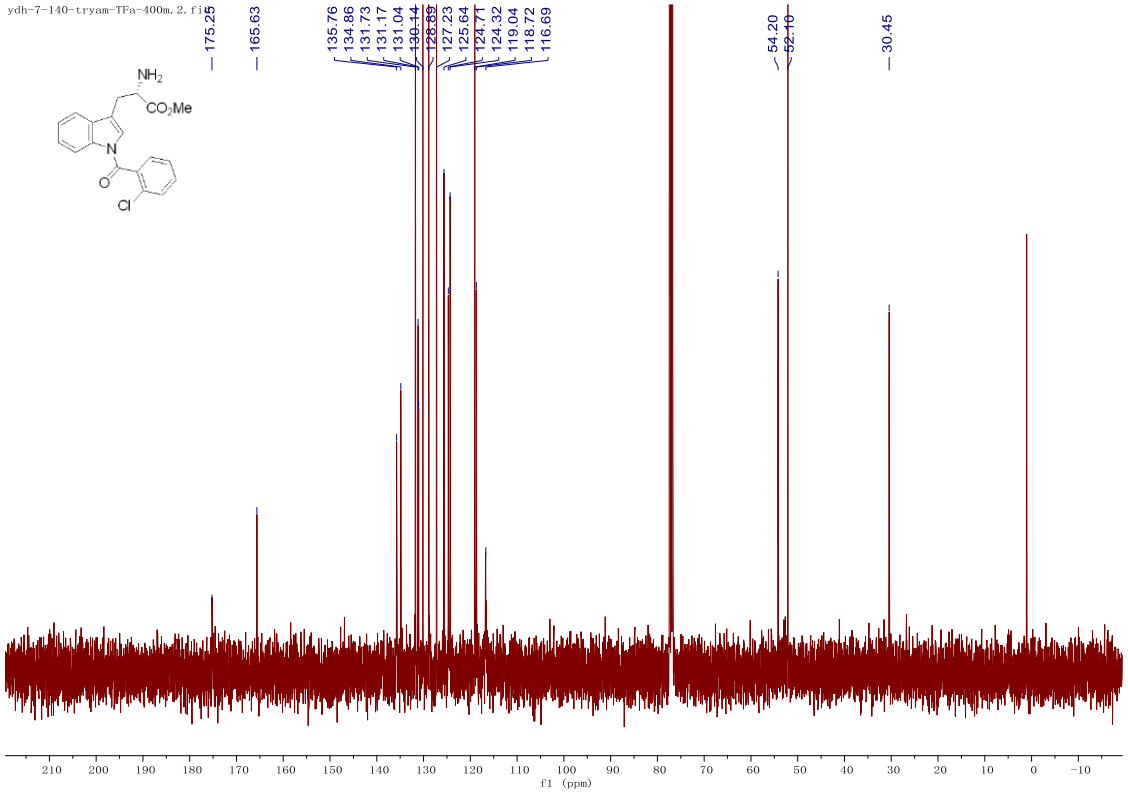
^{13}C NMR of S37



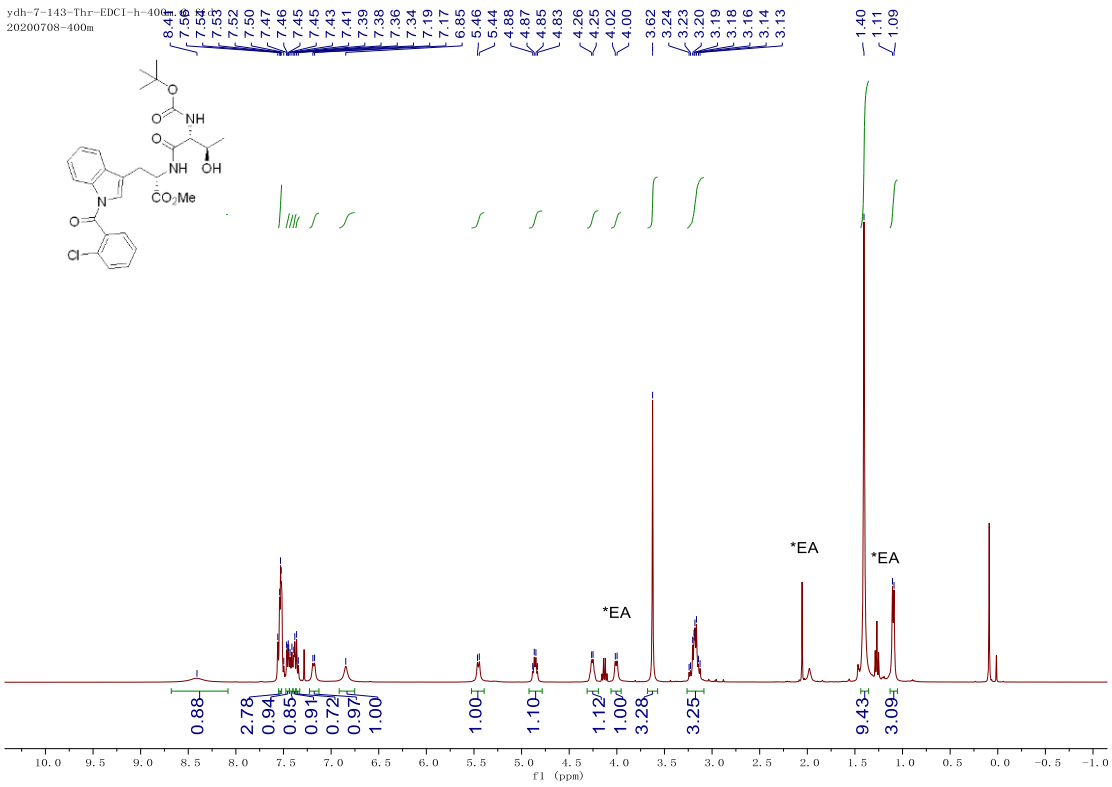
^{1}H NMR of S38



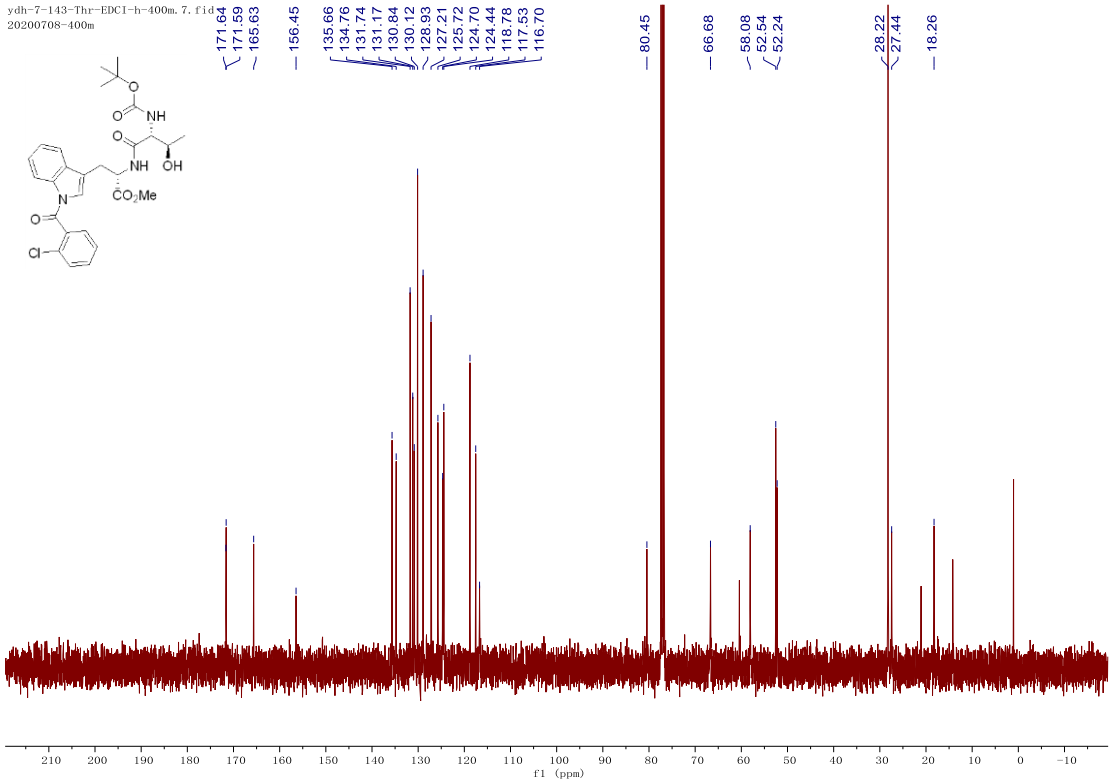
^{13}C NMR of S38



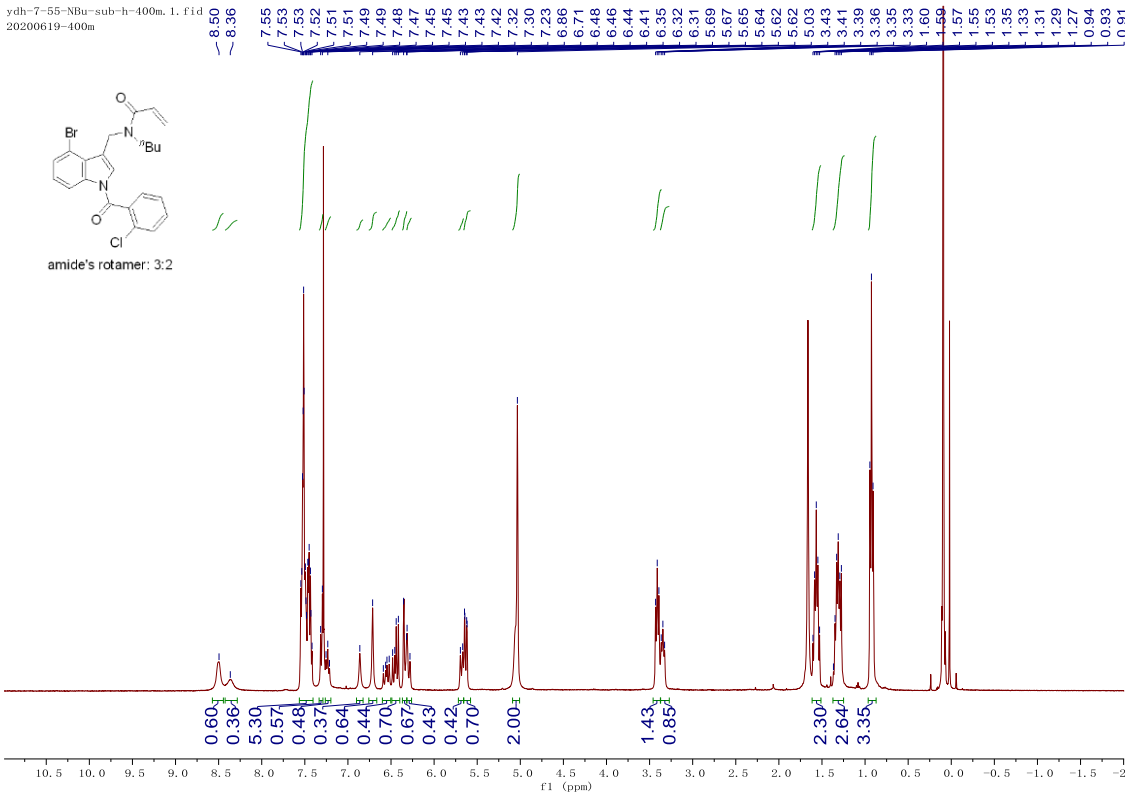
^{1}H NMR of S39



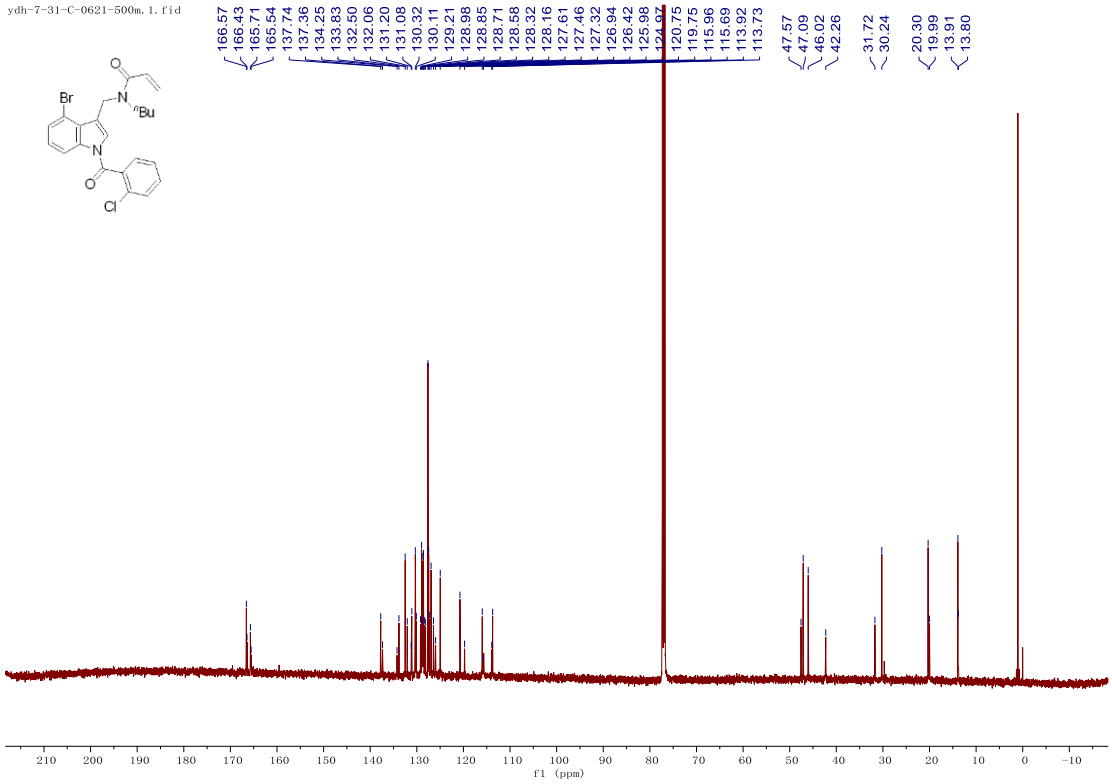
^{13}C NMR of S39



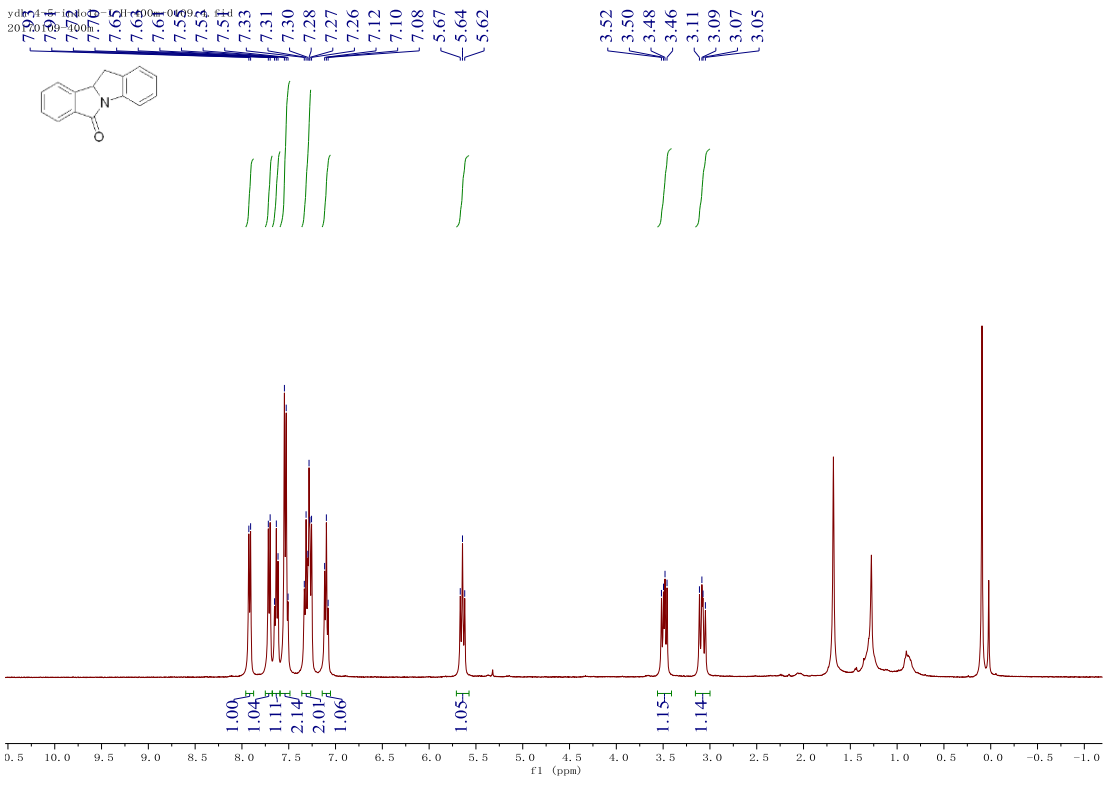
^{1}H NMR of S40



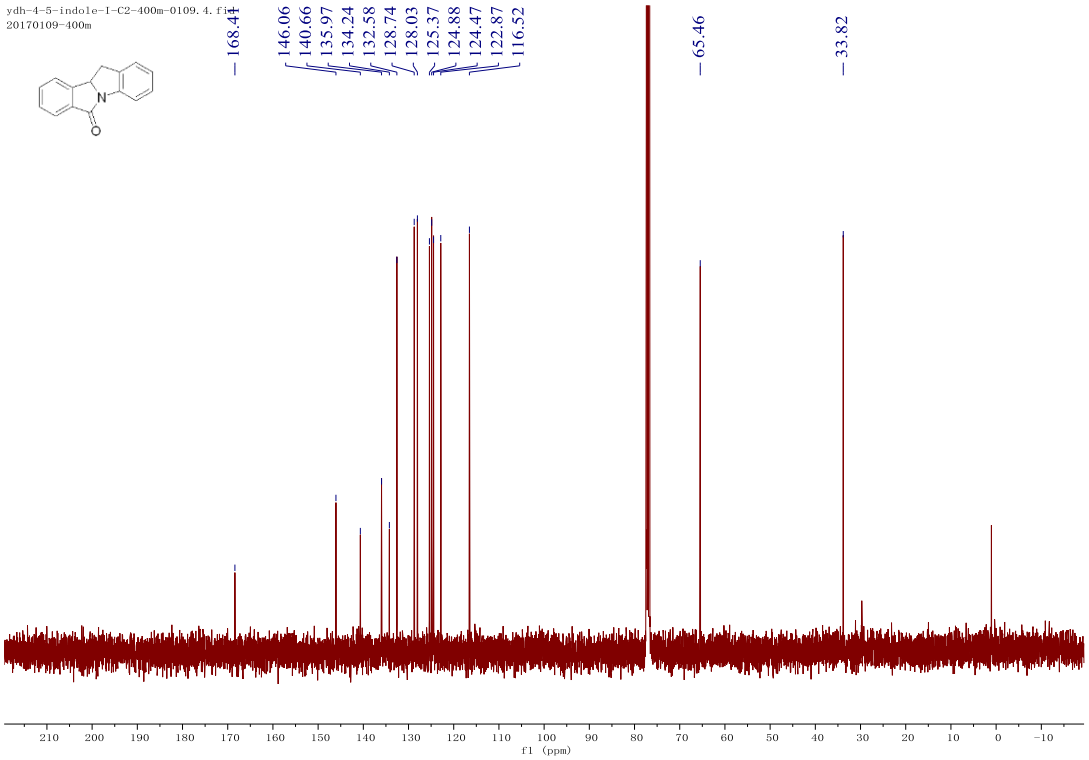
^{13}C NMR of S40



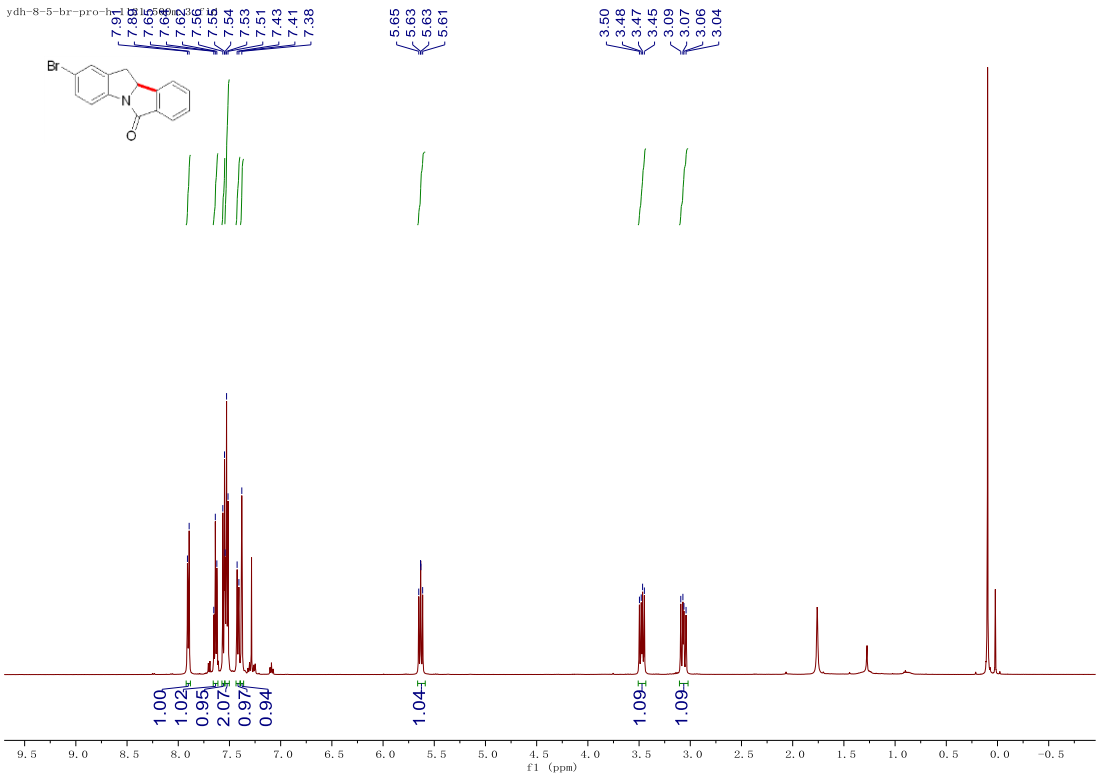
^{1}H NMR of 1



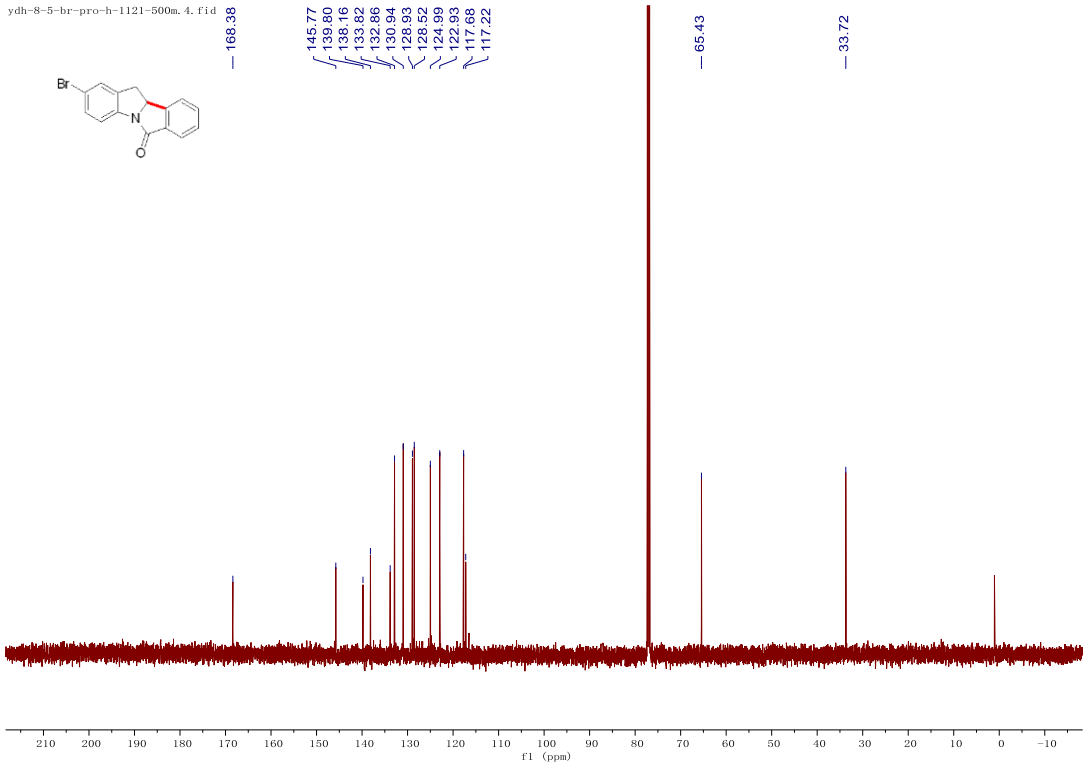
^{13}C NMR of 1



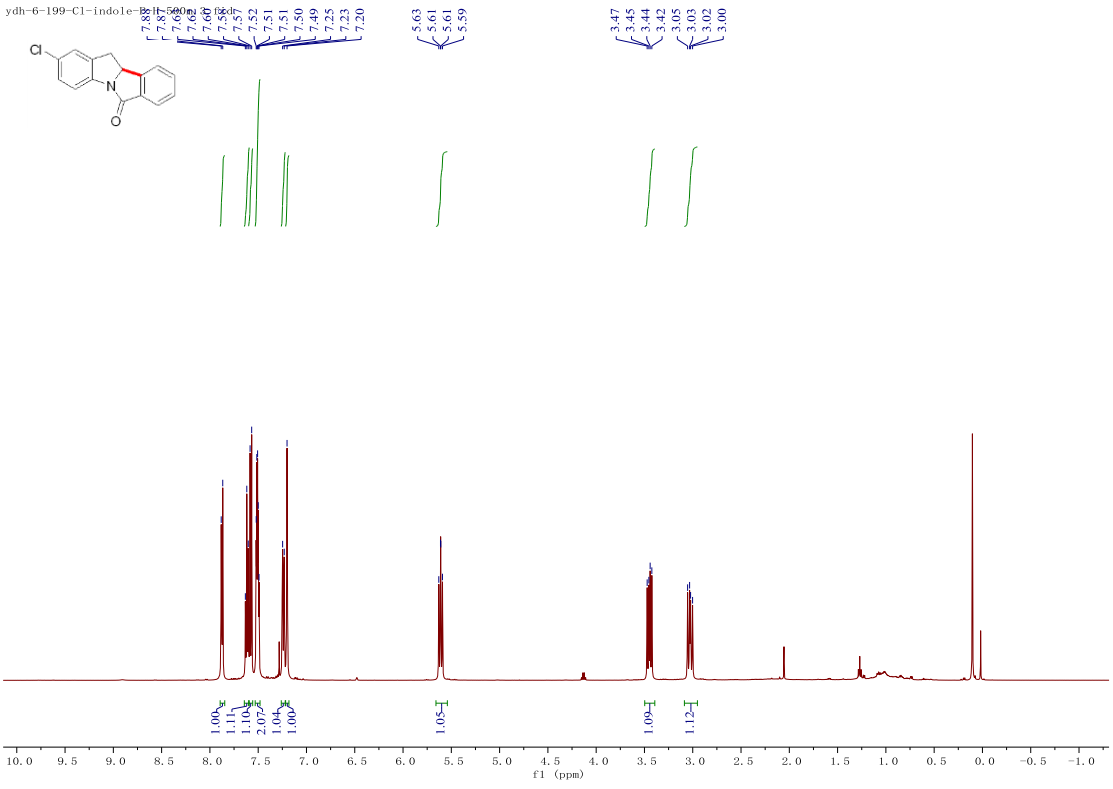
^{1}H NMR of 2



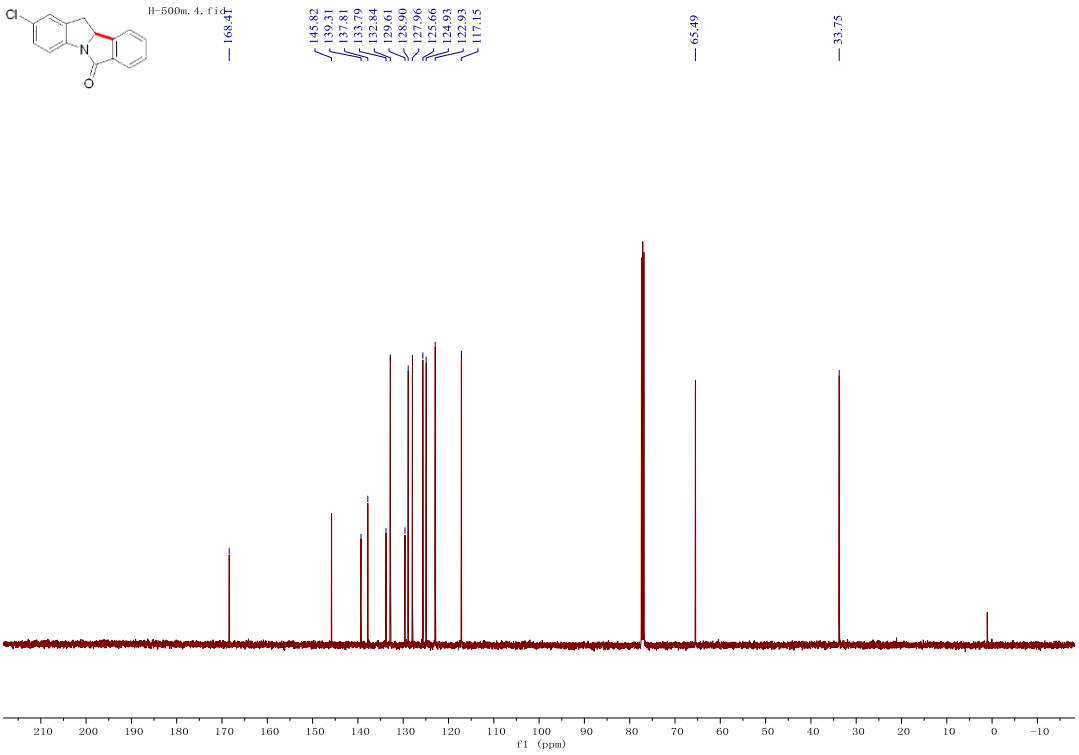
^{13}C NMR of 2



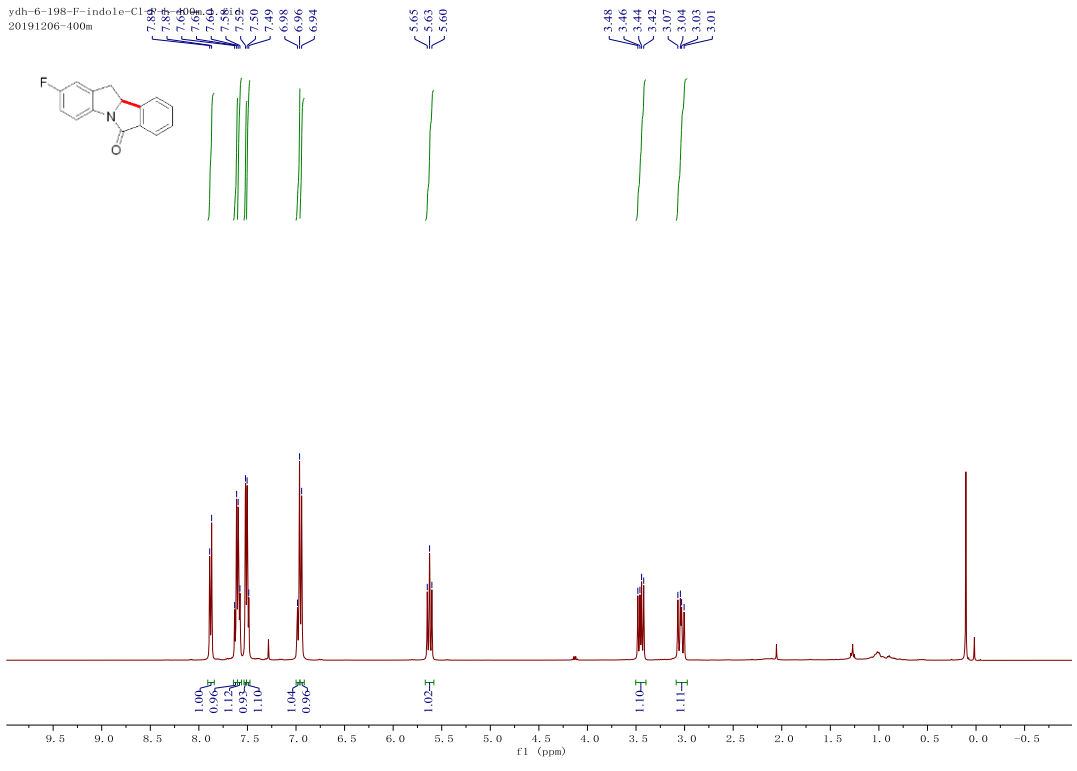
^{1}H NMR of 3



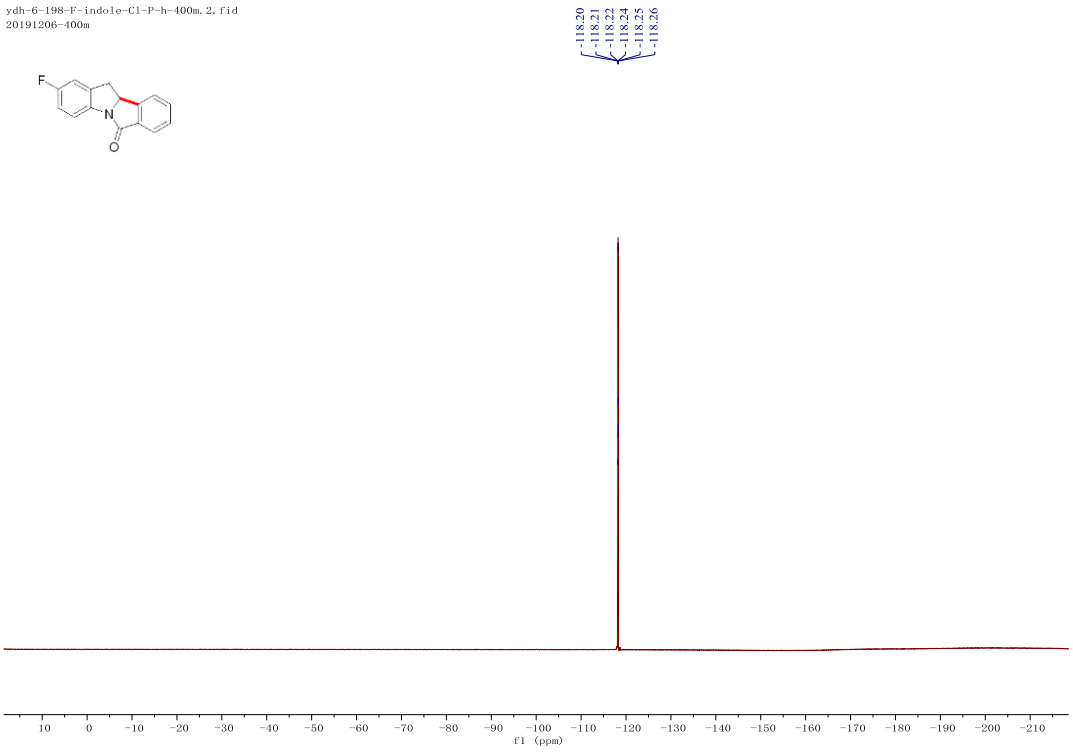
^{13}C NMR of 3



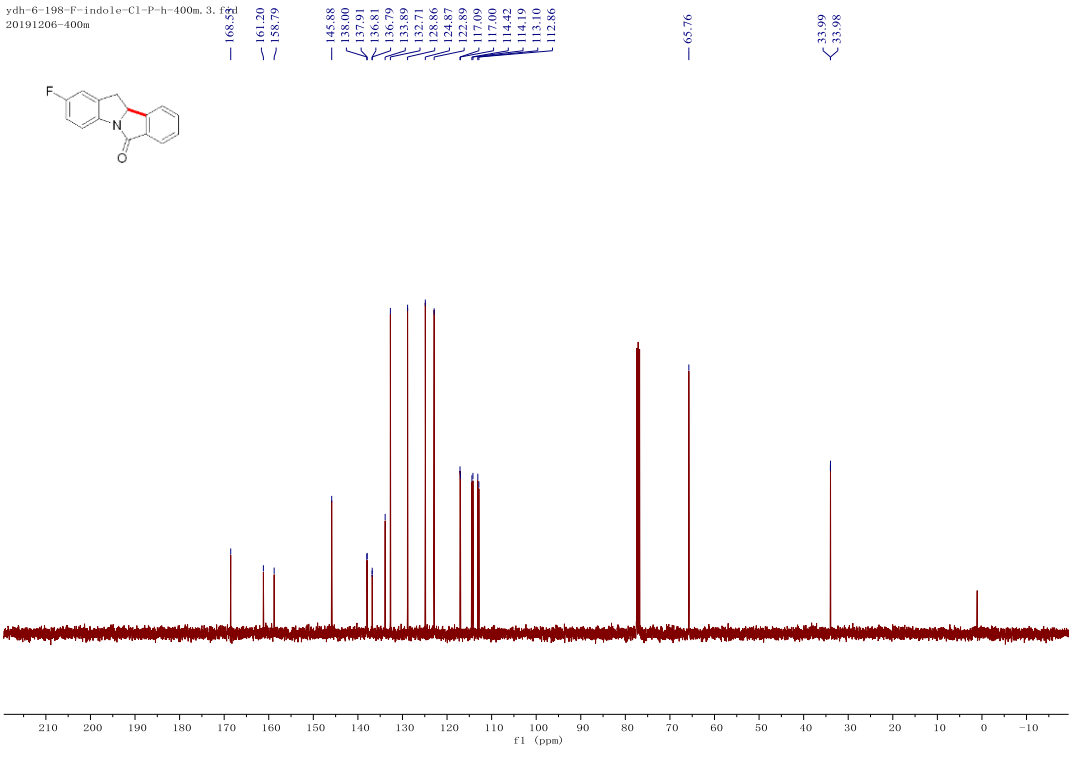
^{1}H NMR of 4



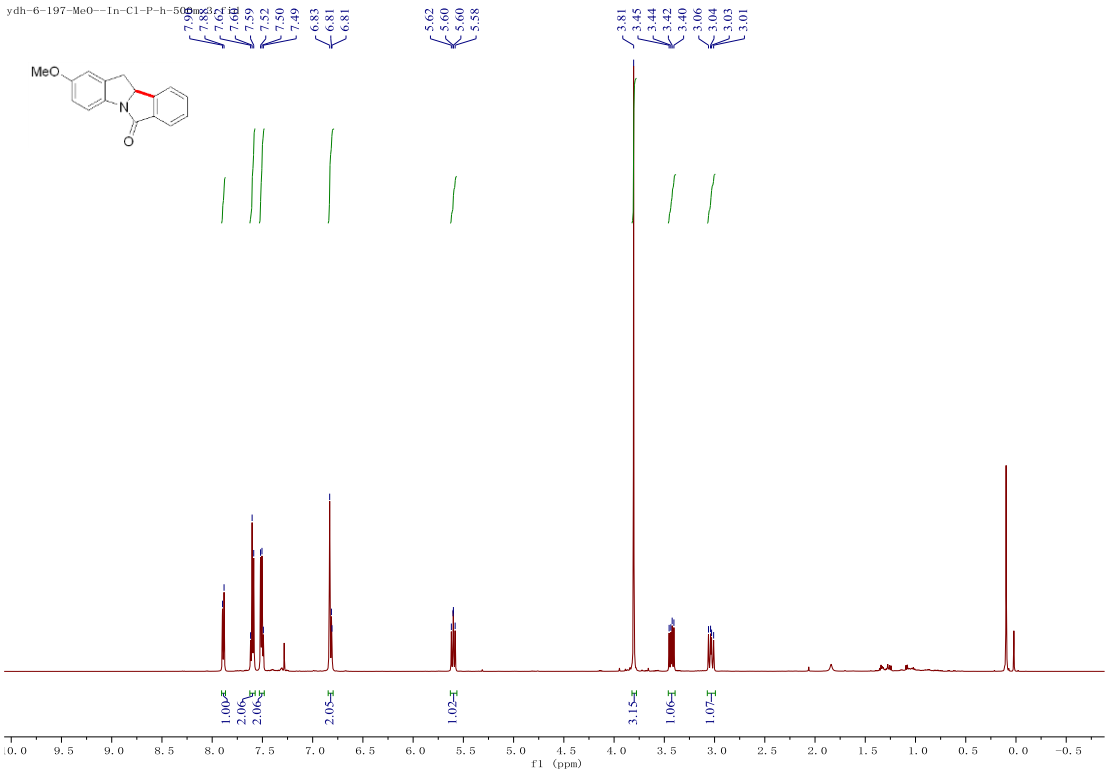
^{19}F NMR of 4



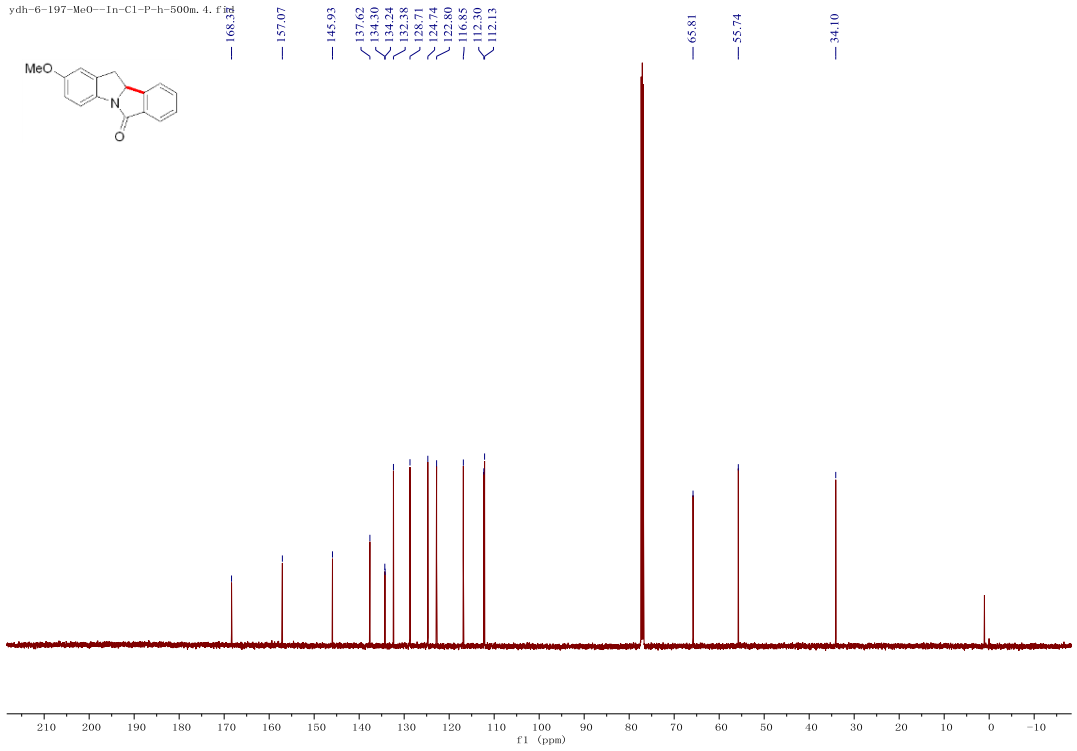
^{13}C NMR of 4



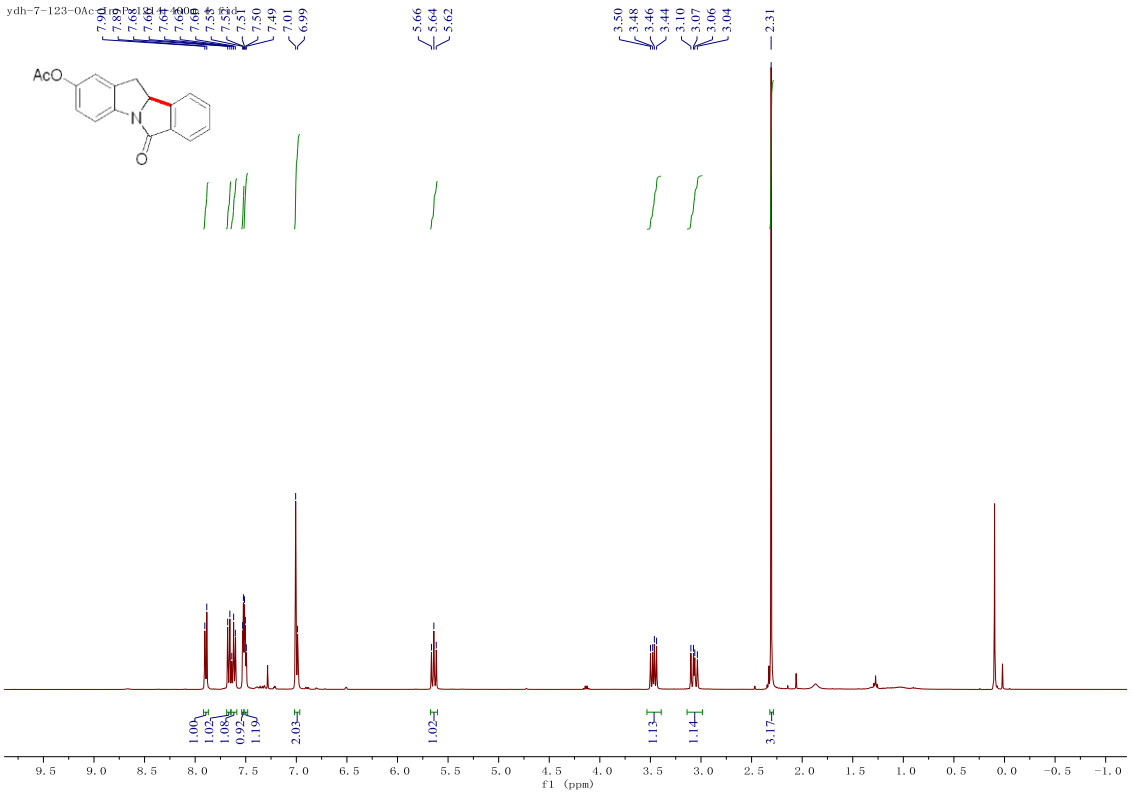
^{1}H NMR of 5



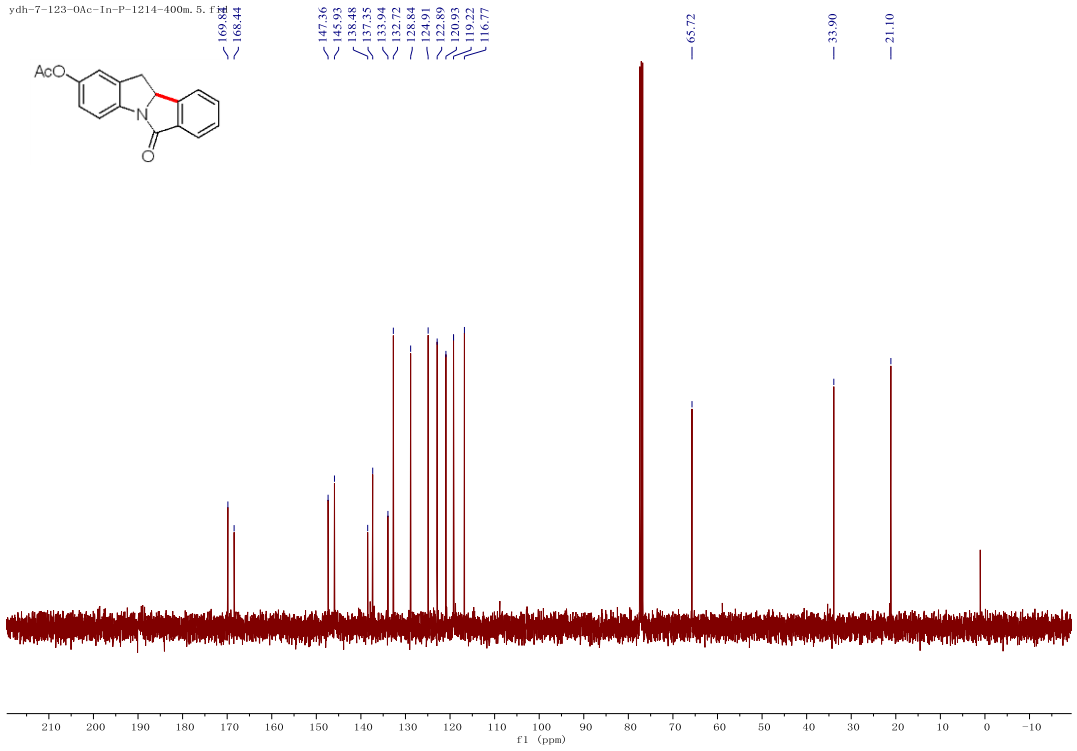
^{13}C NMR of 5



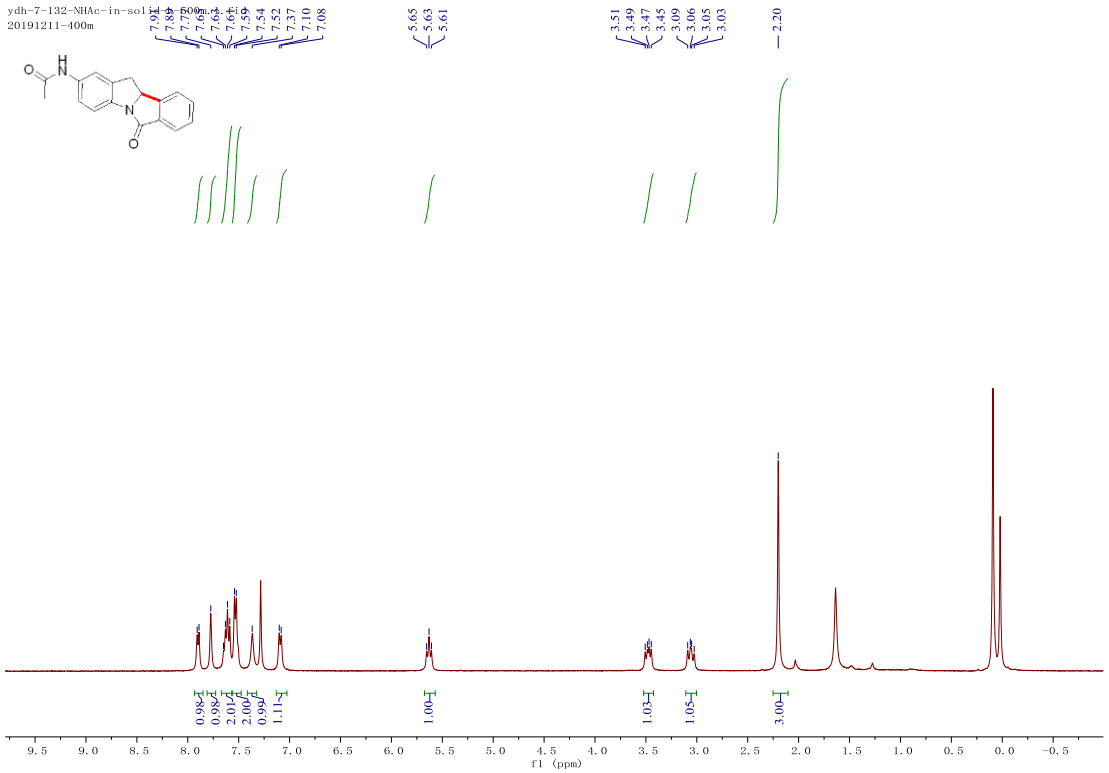
^{1}H NMR of 6



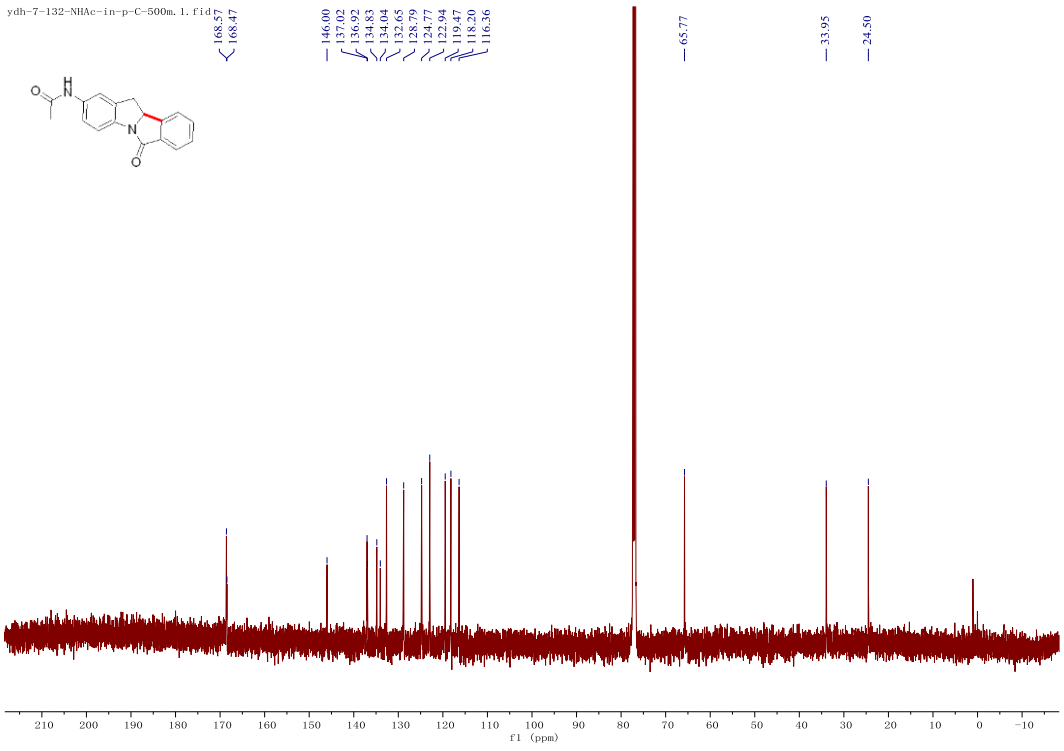
^{13}C NMR of 6



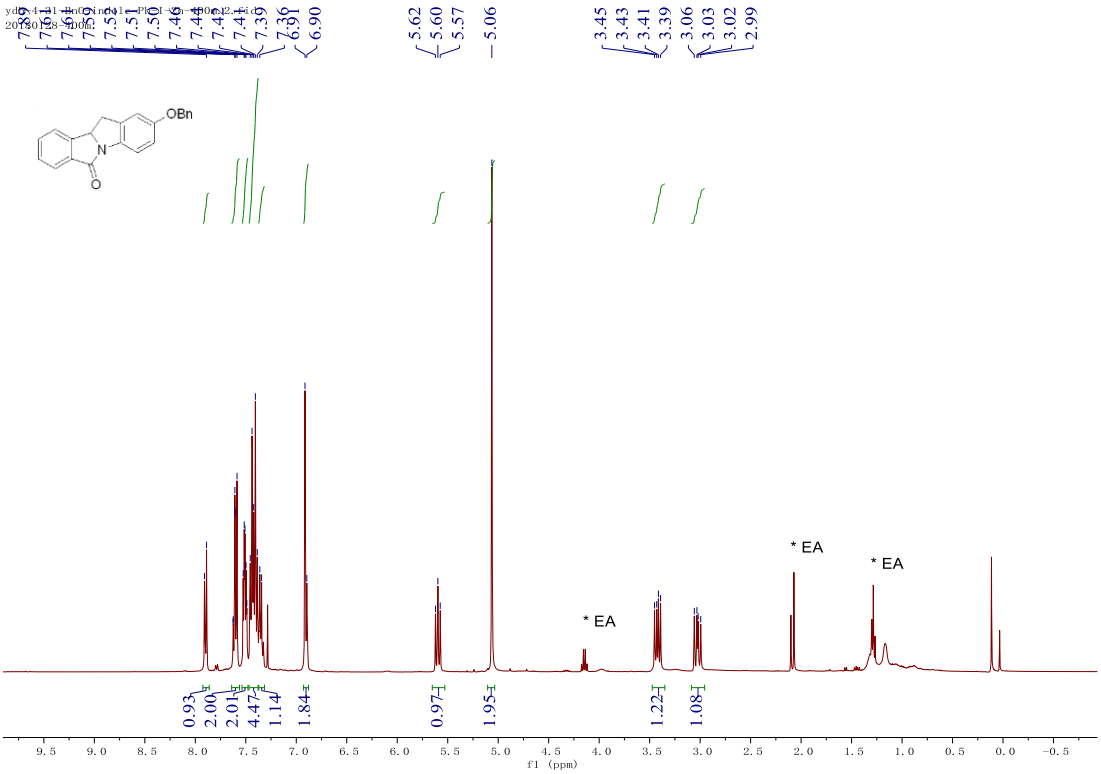
^{1}H NMR of 7



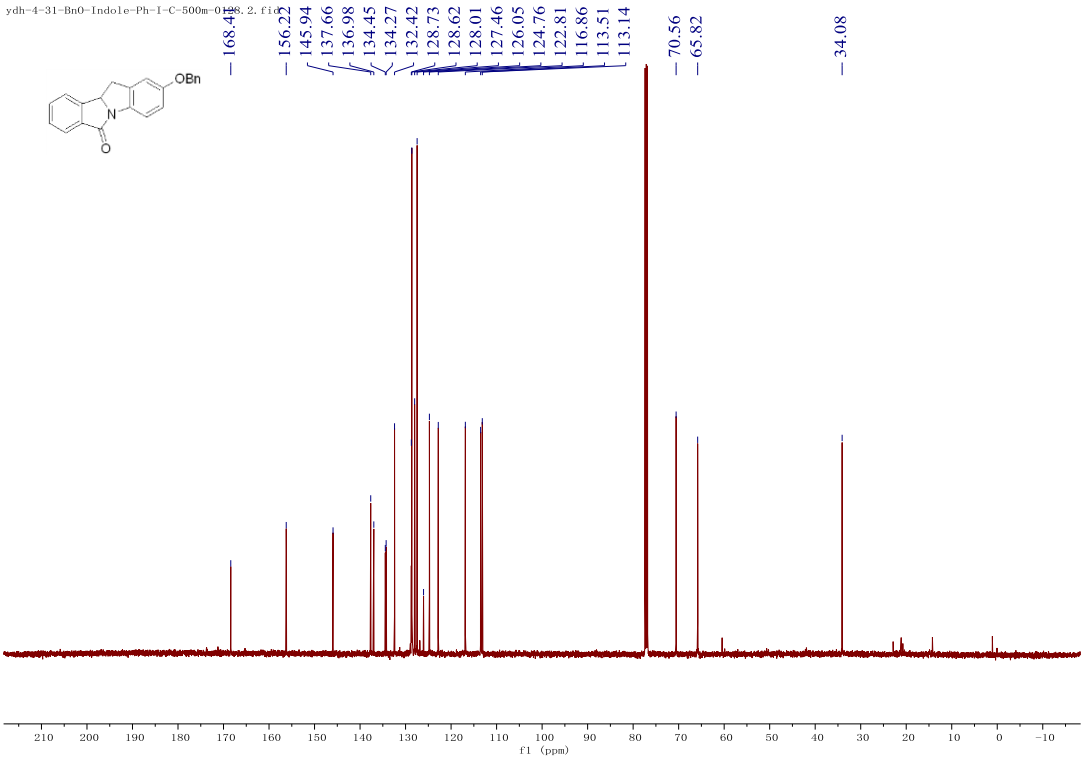
^{13}C NMR of 7



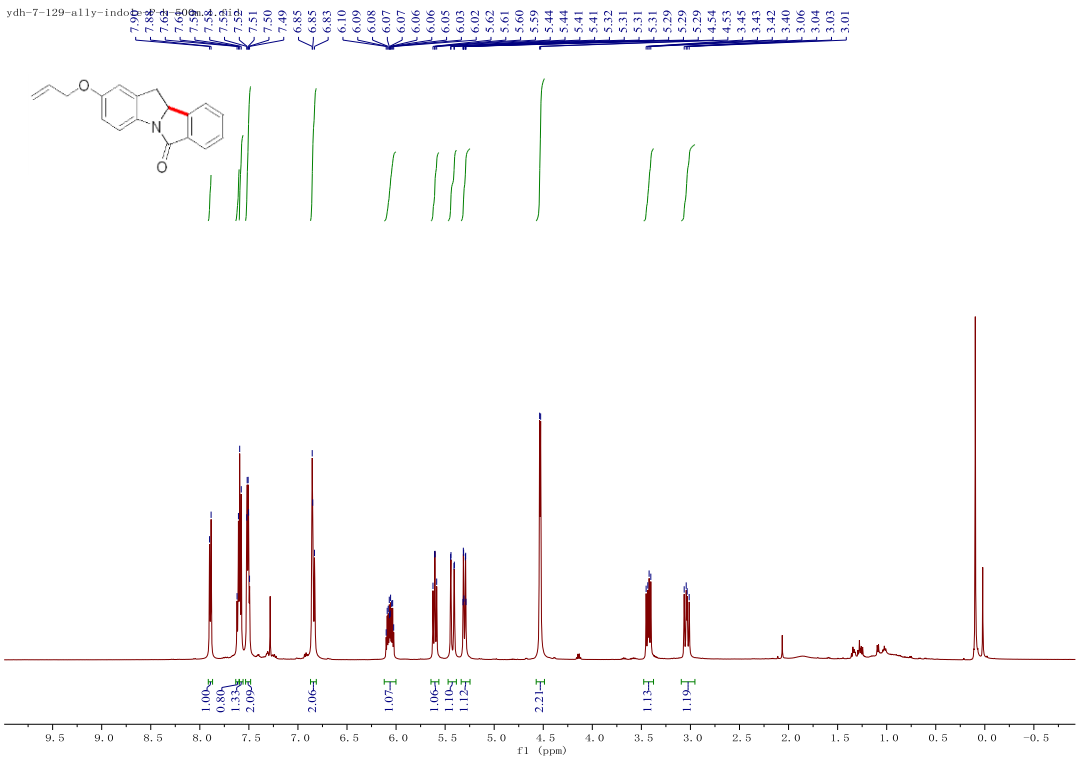
^{1}H NMR of 8



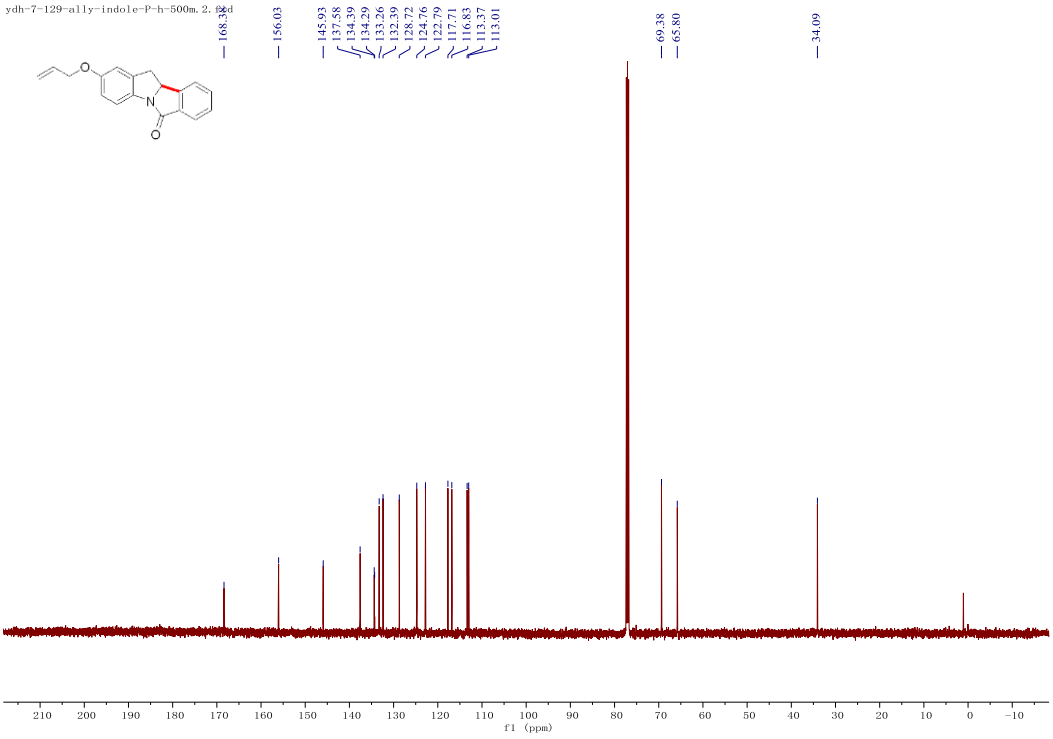
^{13}C NMR of 8



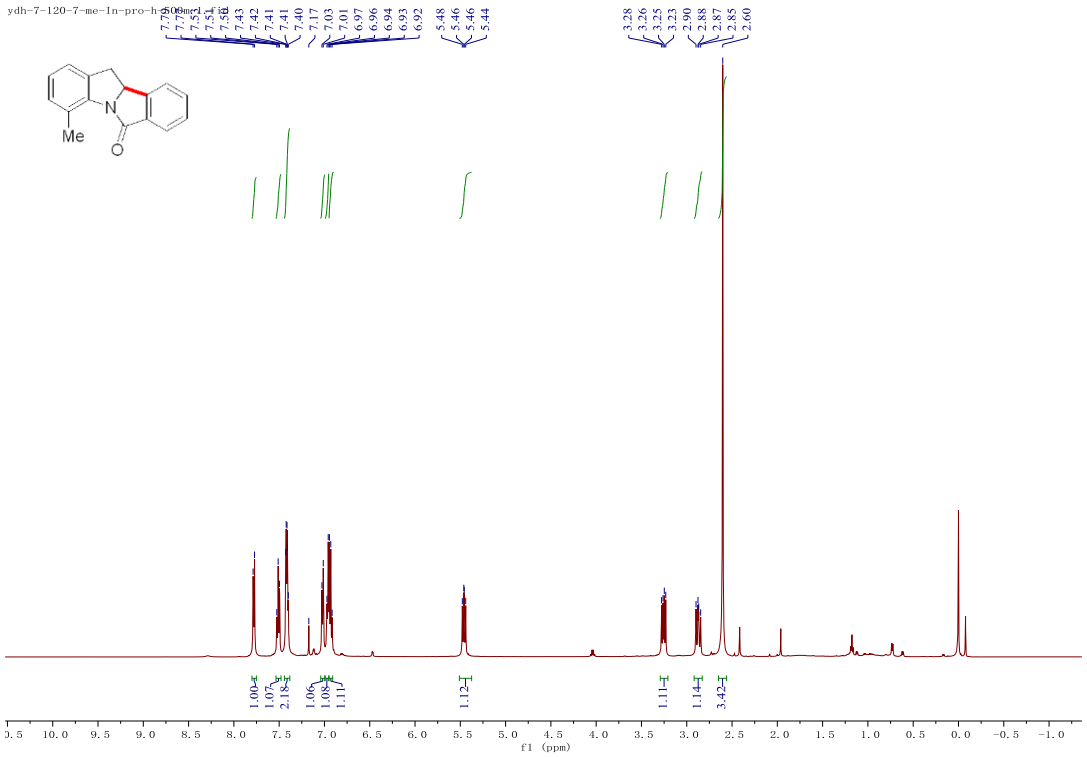
^{1}H NMR of 9



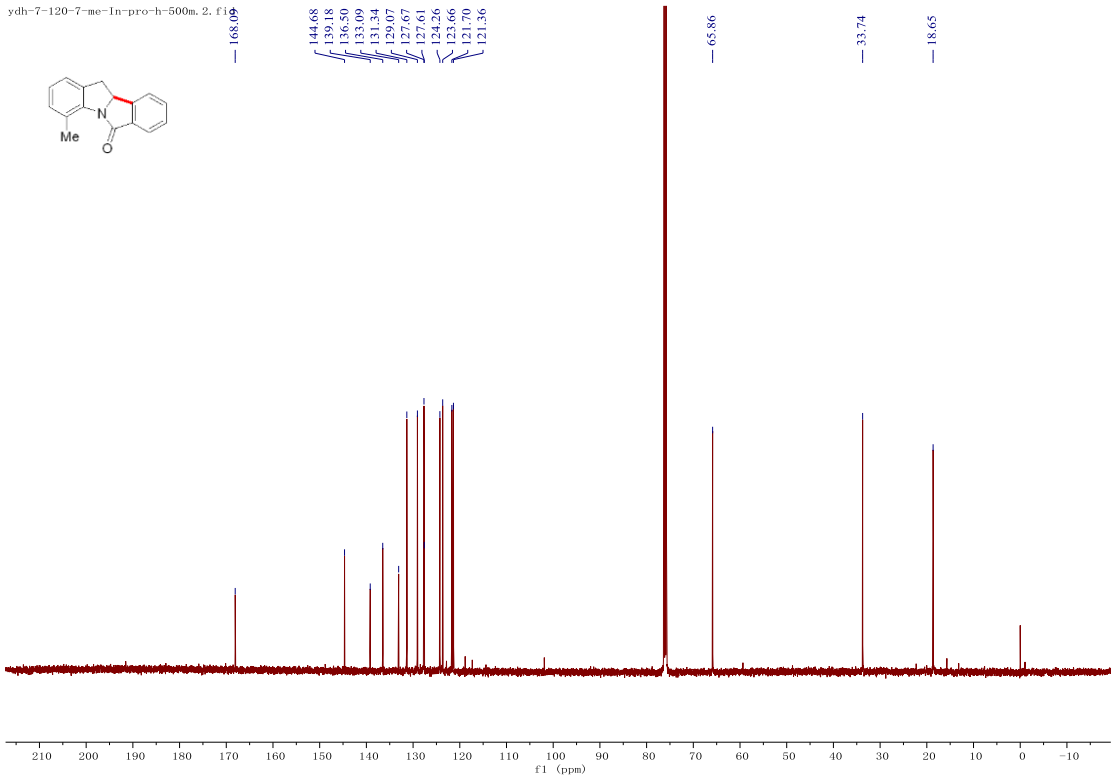
^{13}C NMR of 9



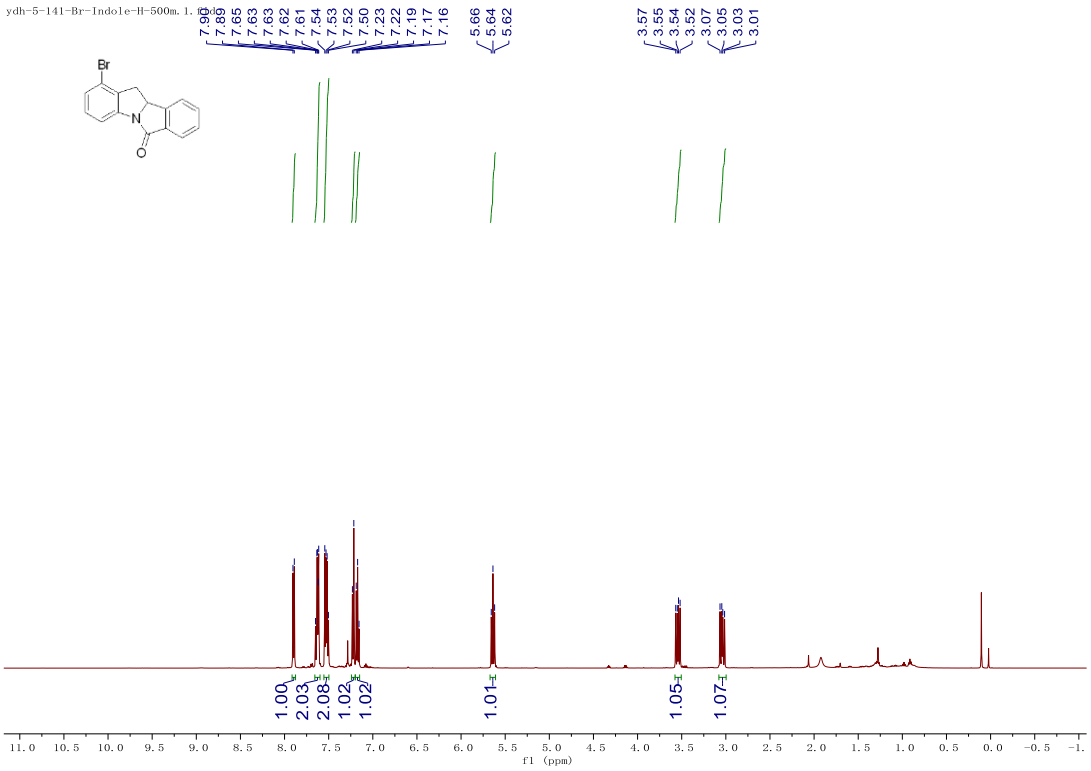
^{1}H NMR of 10



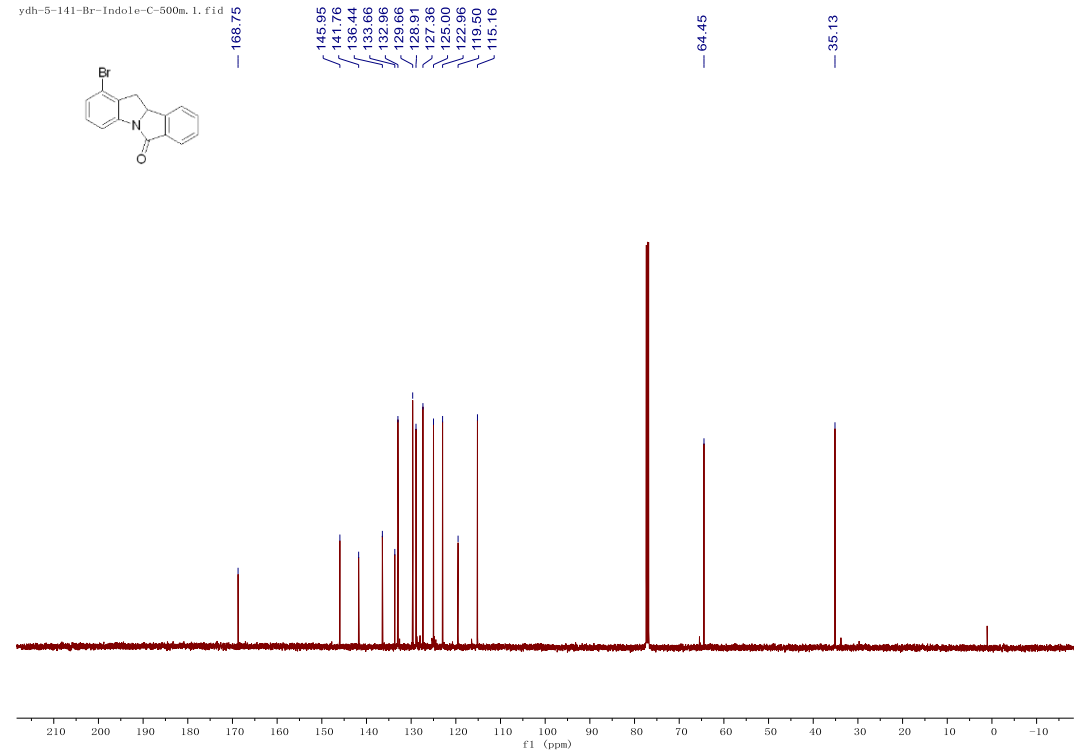
^{13}C NMR of 10



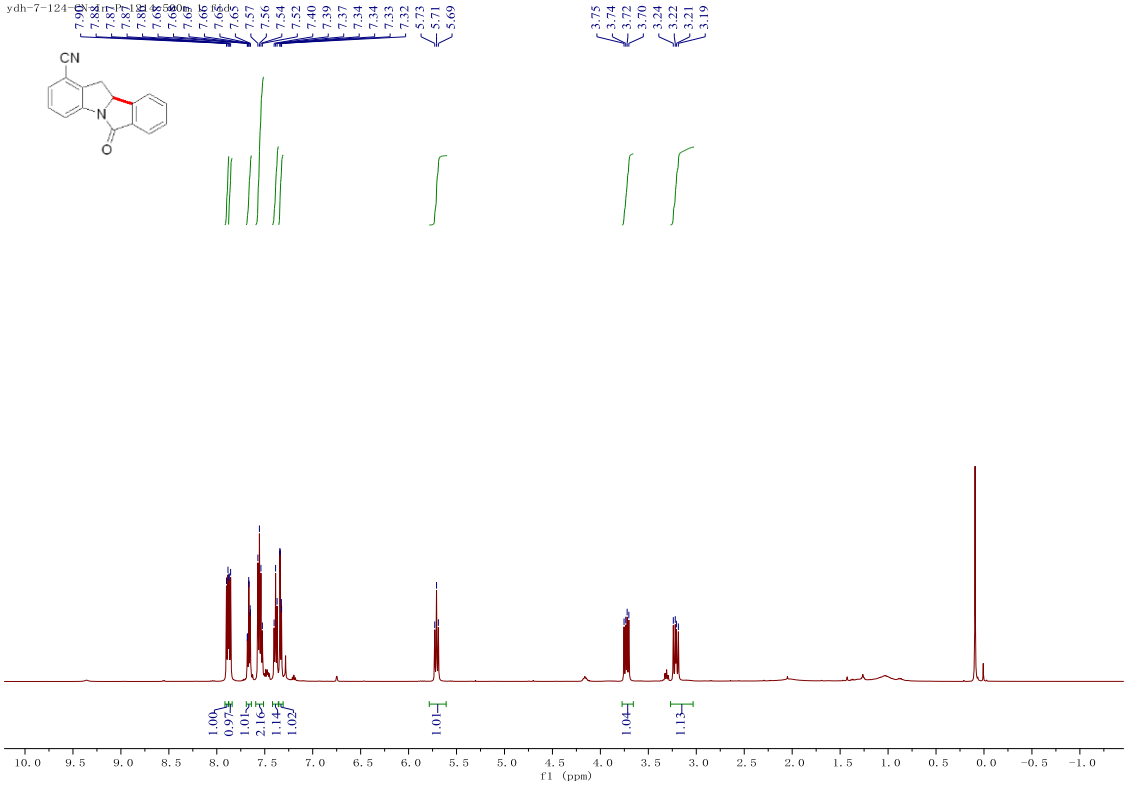
^{1}H NMR of 11



^{13}C NMR of 11



^{1}H NMR of 12



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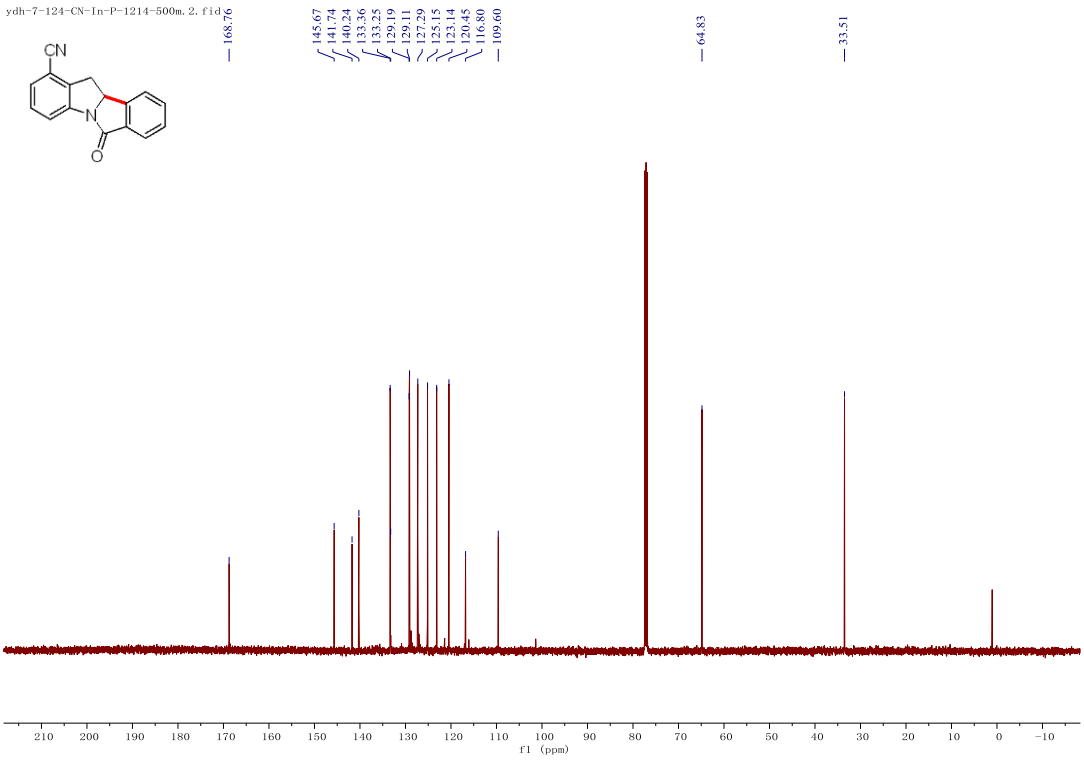
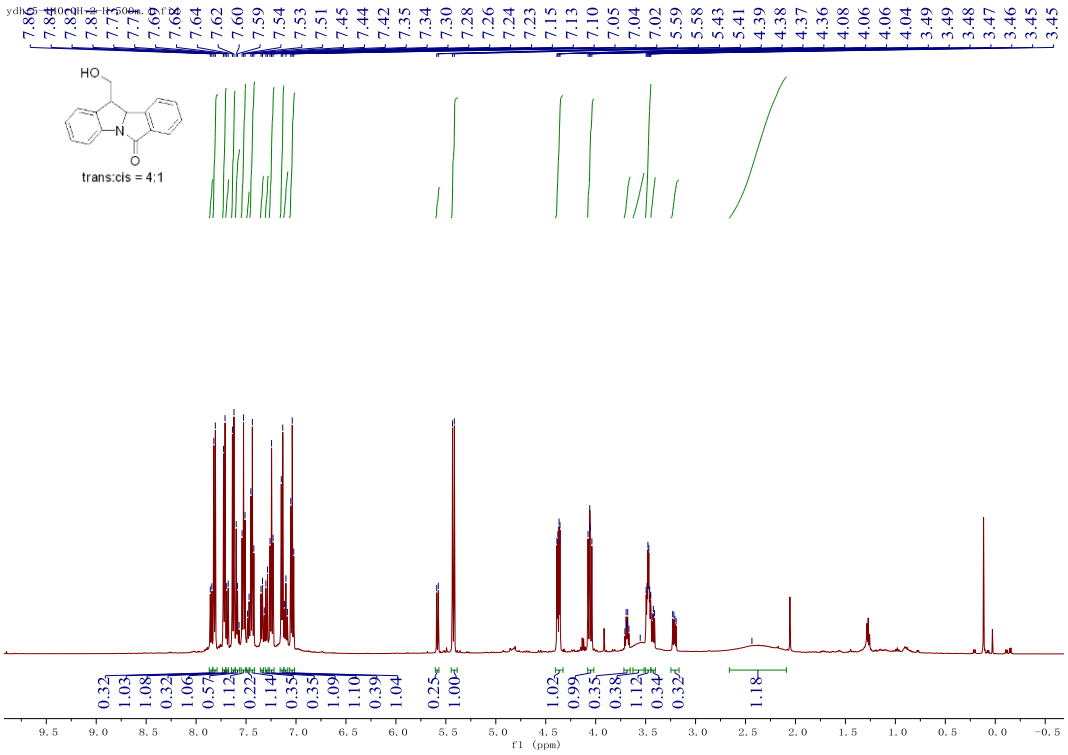


^{1}H NMR of 13



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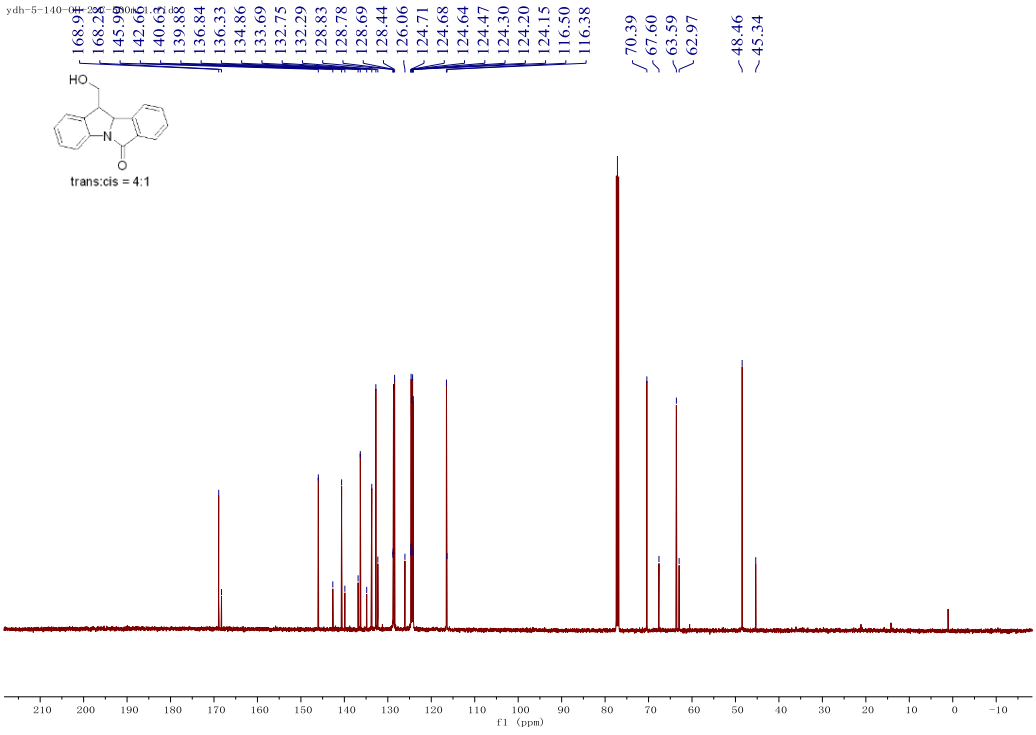
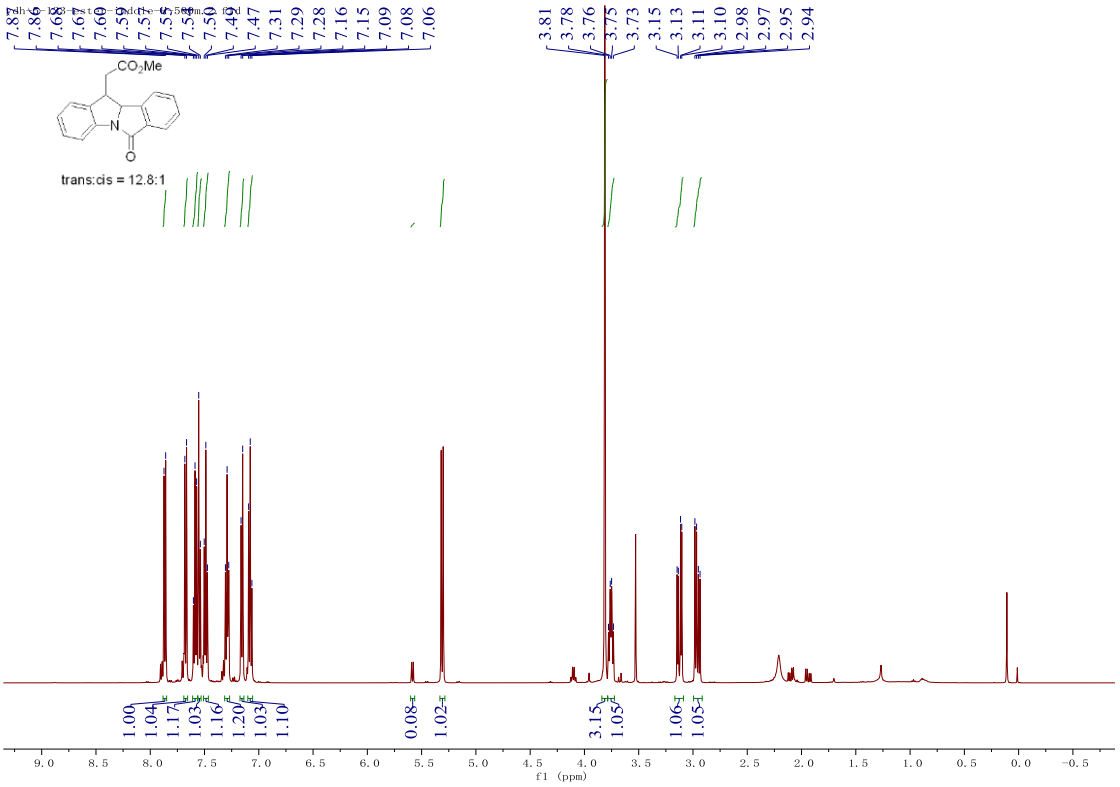


^{1}H NMR of 14



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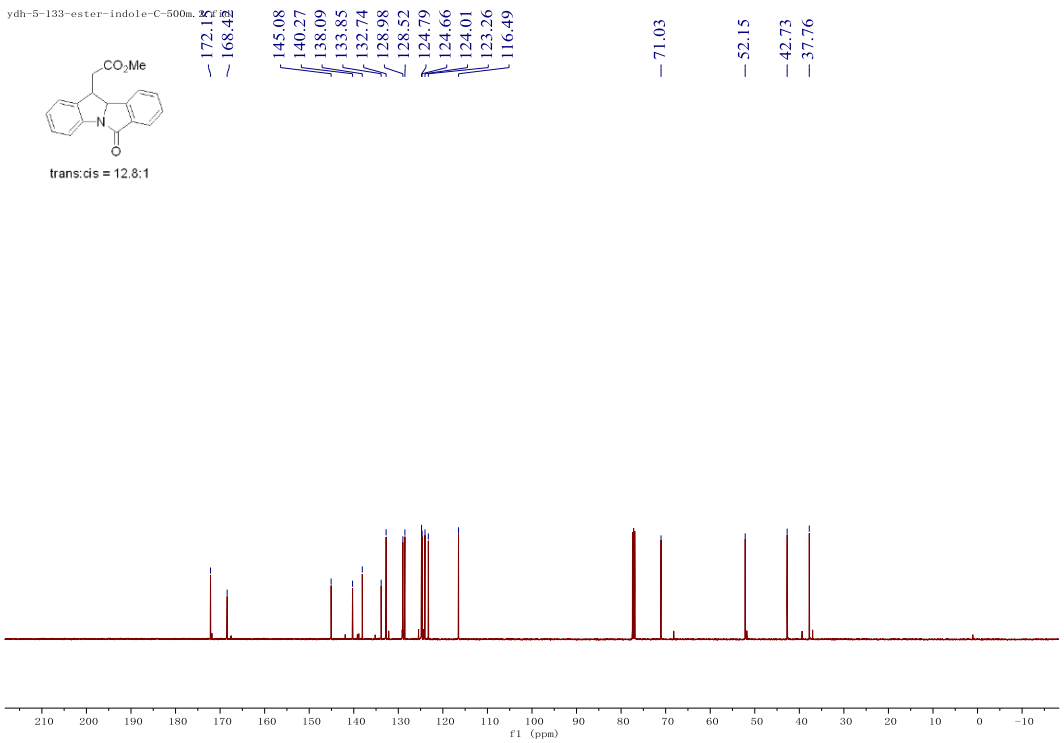
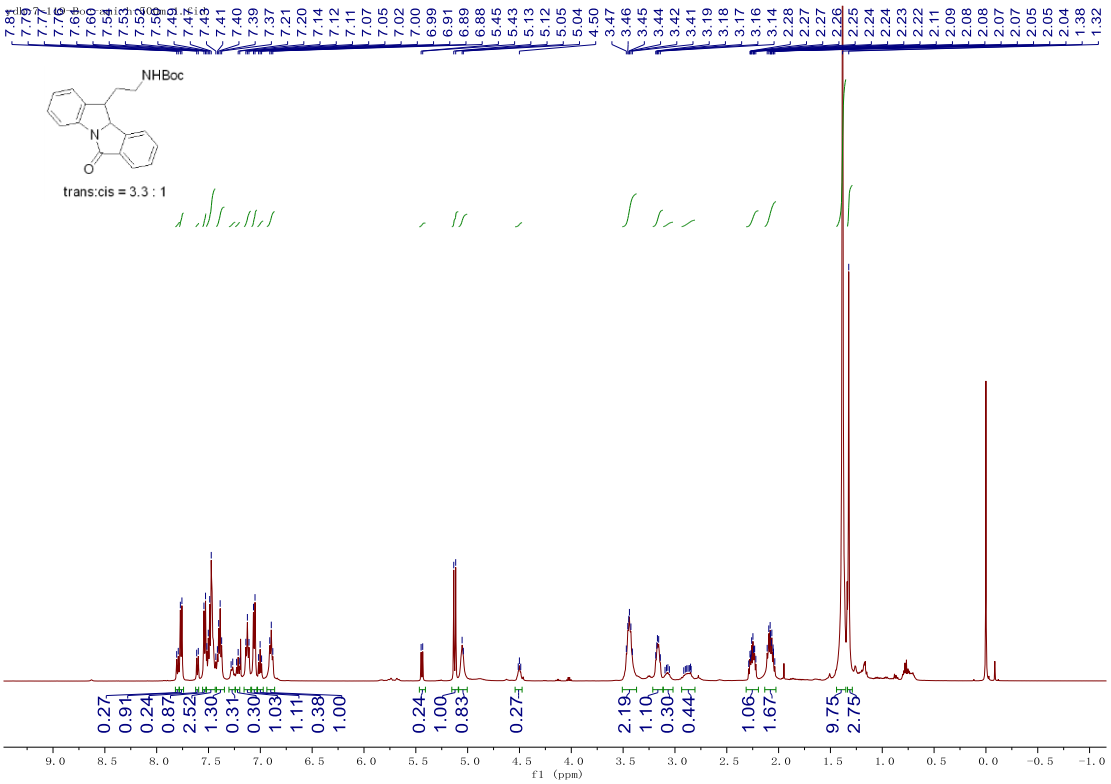


^{1}H NMR of 15



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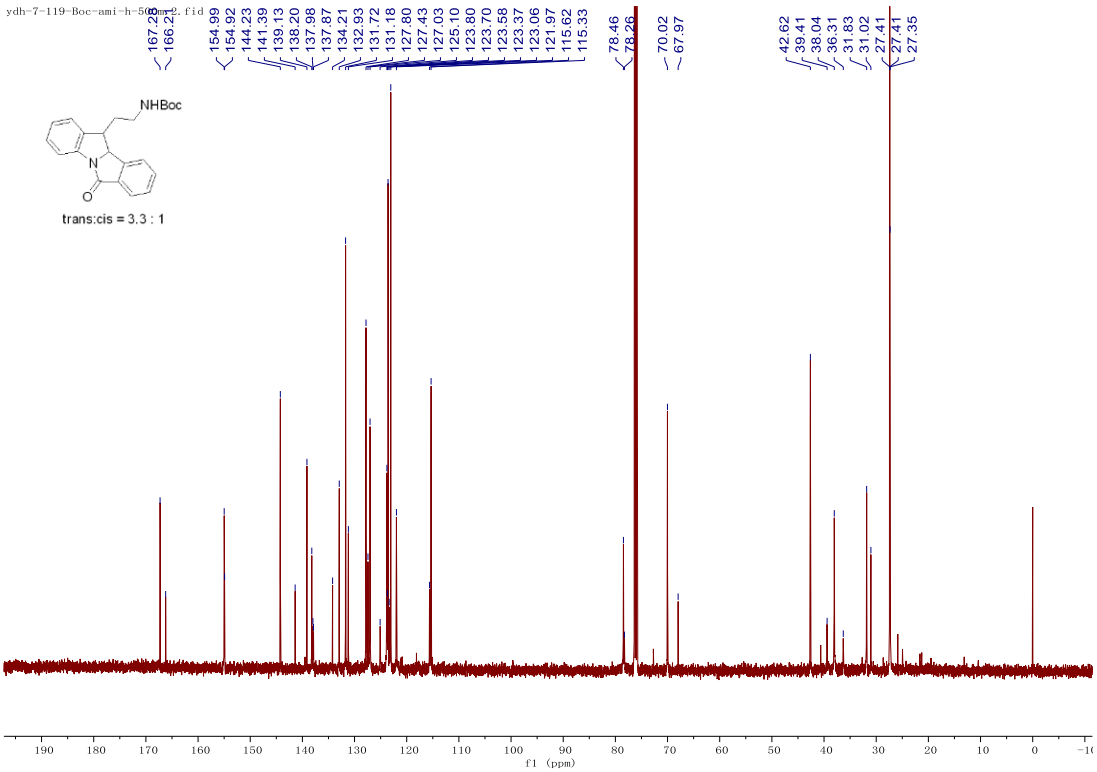
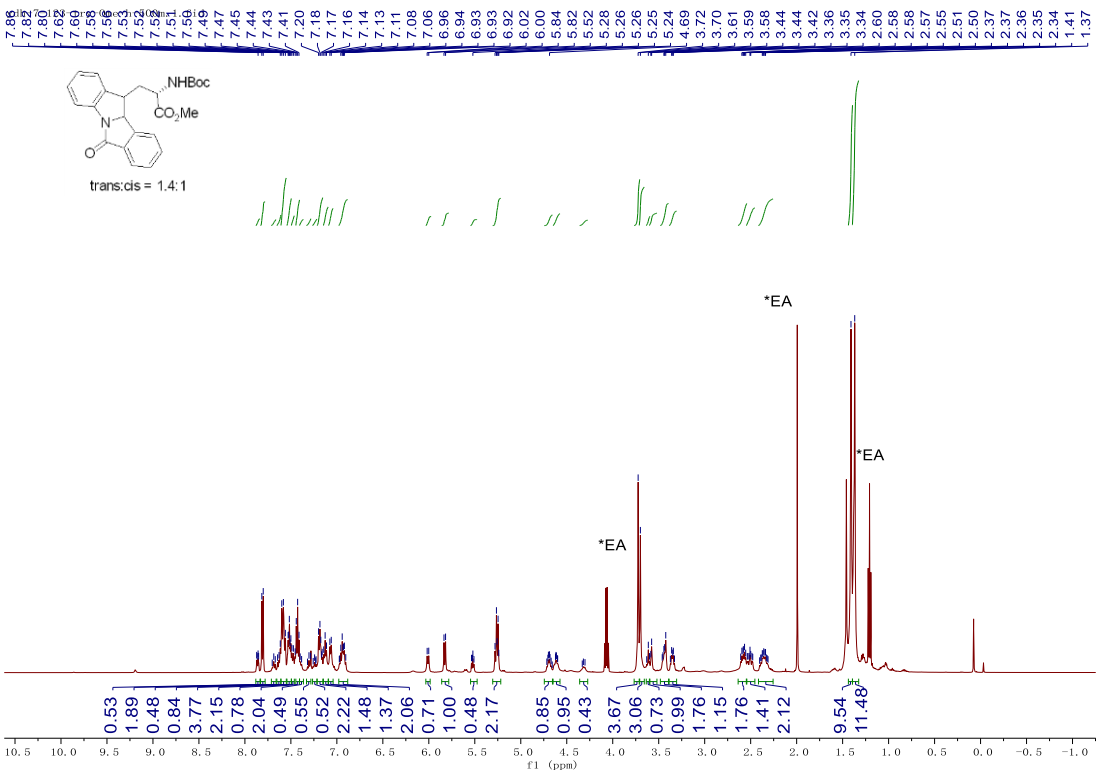
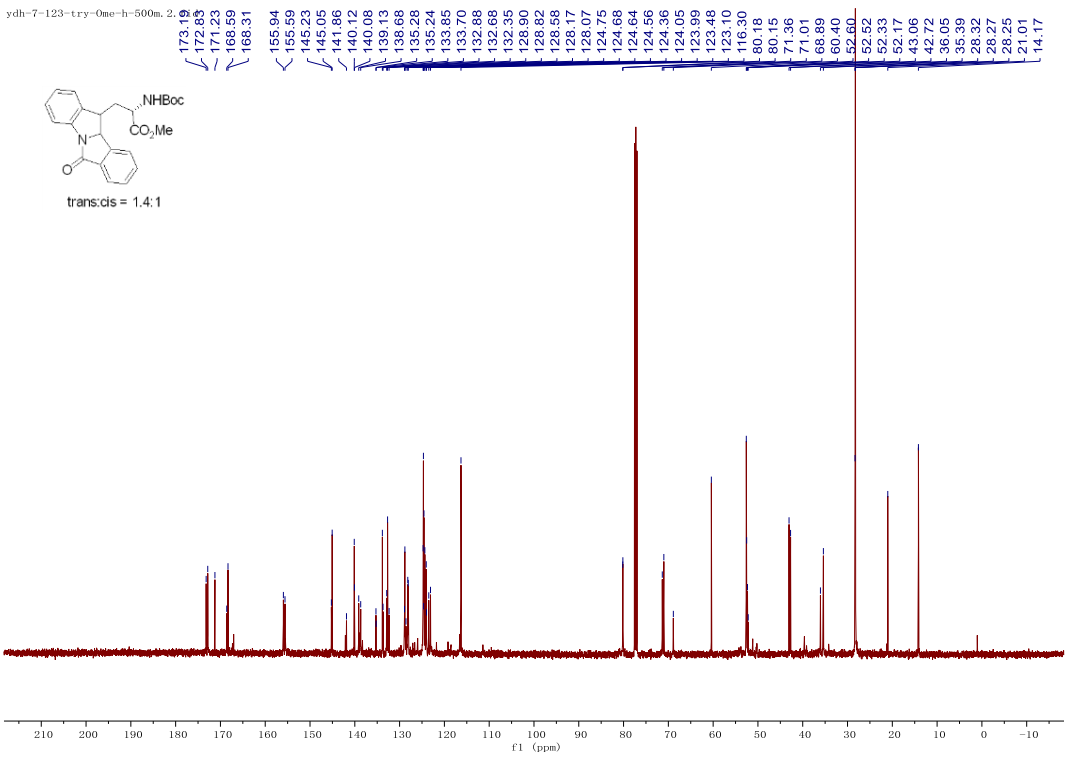


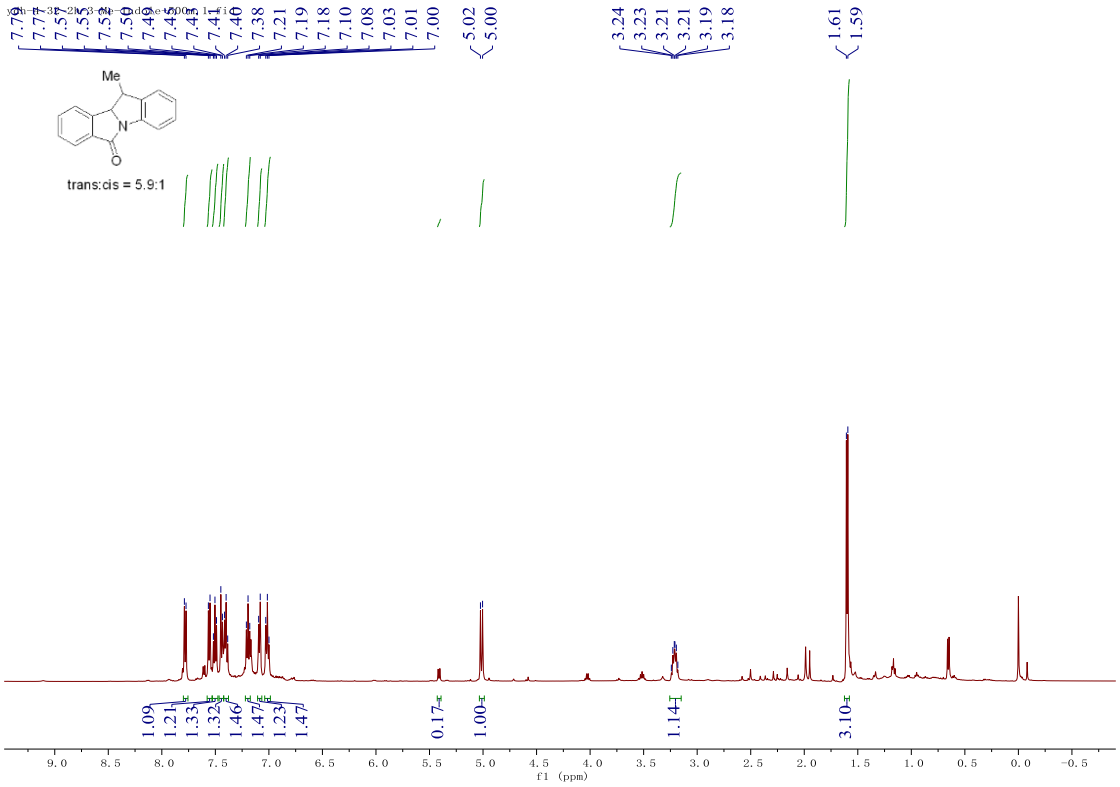
^{1}H NMR of 16



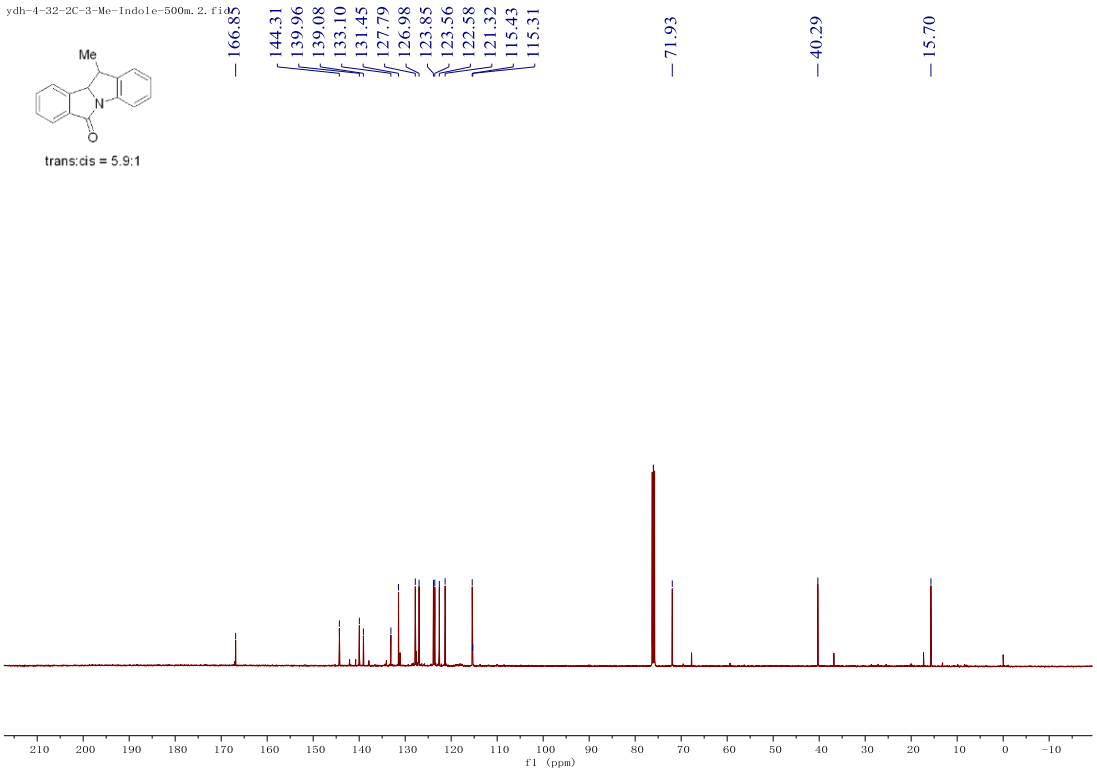
^{13}C NMR of 16



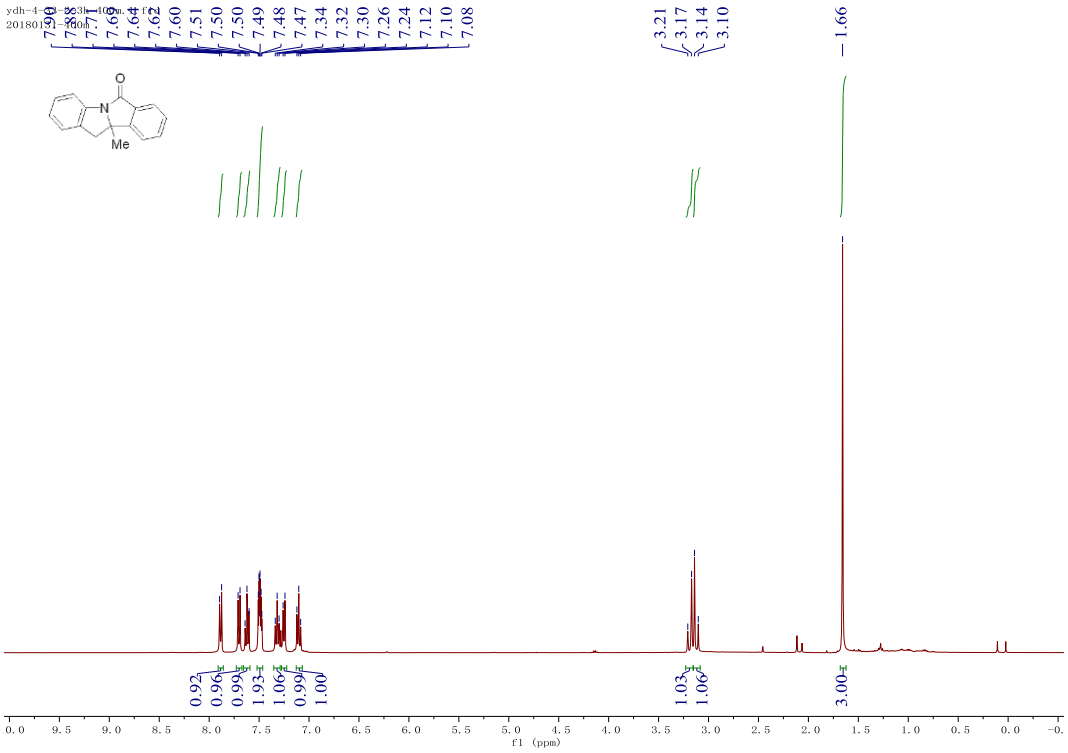
^{1}H NMR of 17



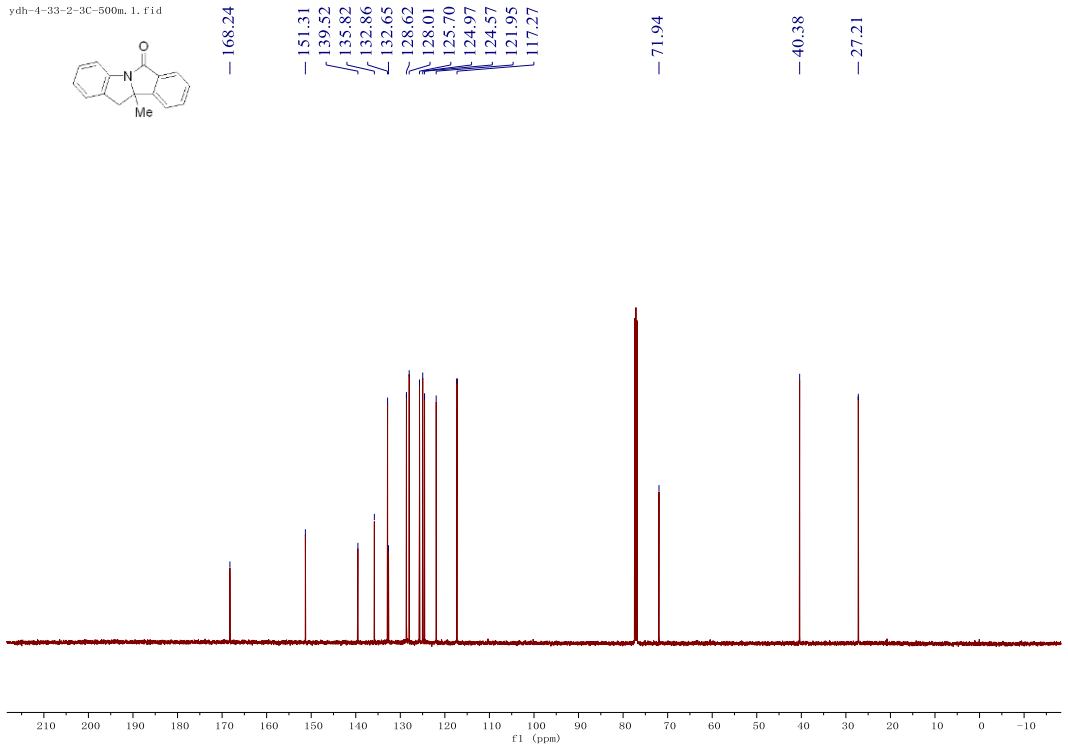
^{13}C NMR of 17



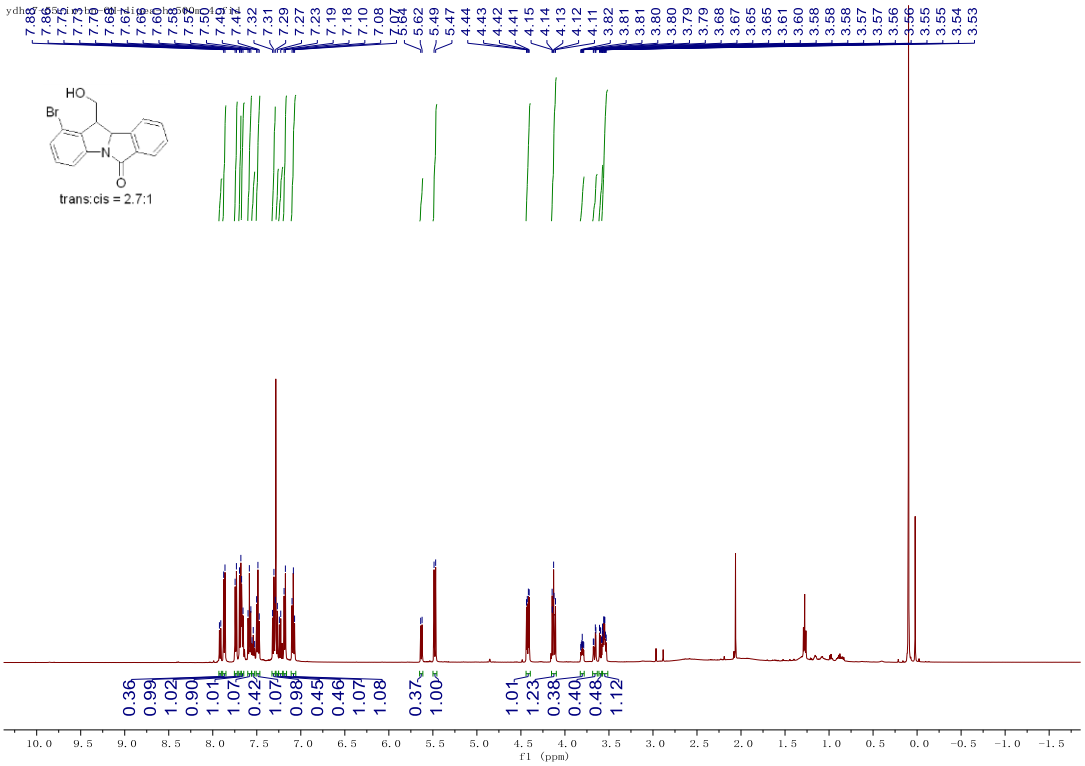
^{1}H NMR of 18



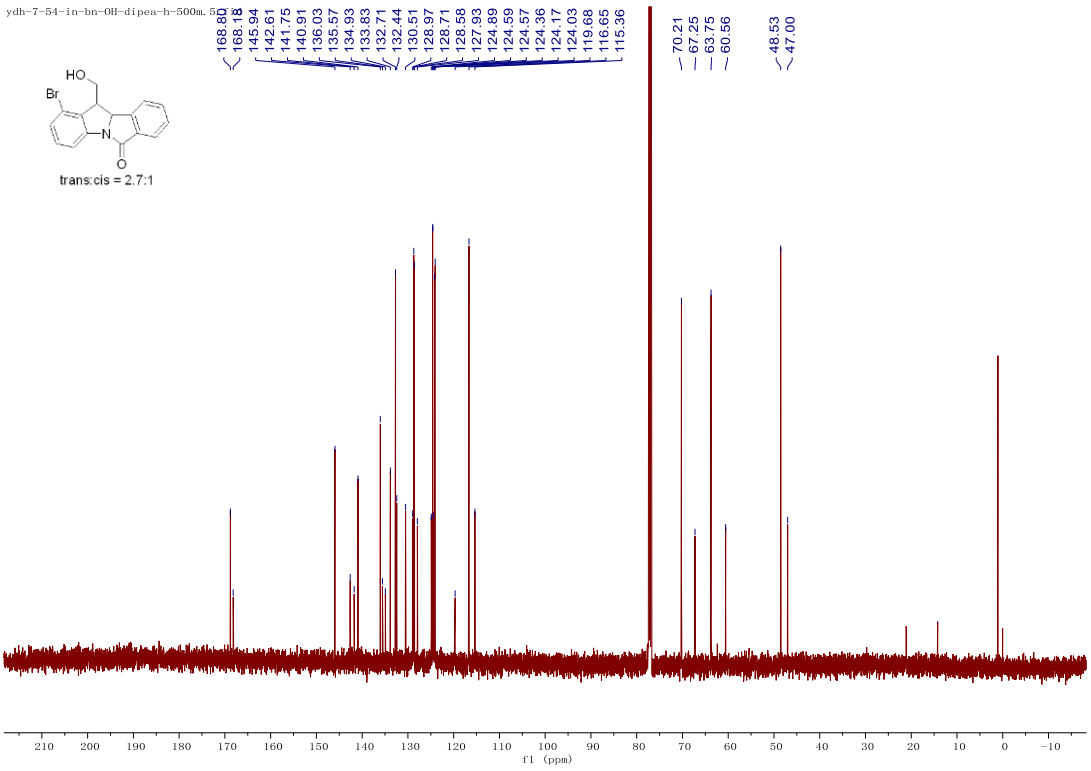
^{13}C NMR of 18



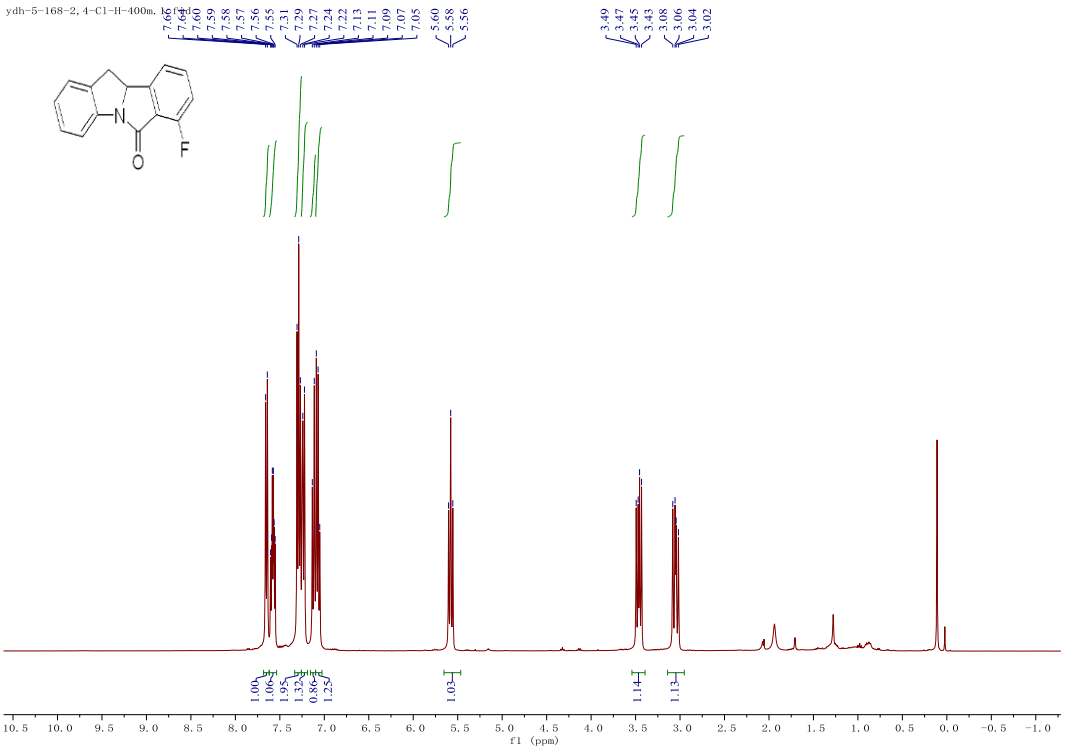
^{1}H NMR of 19



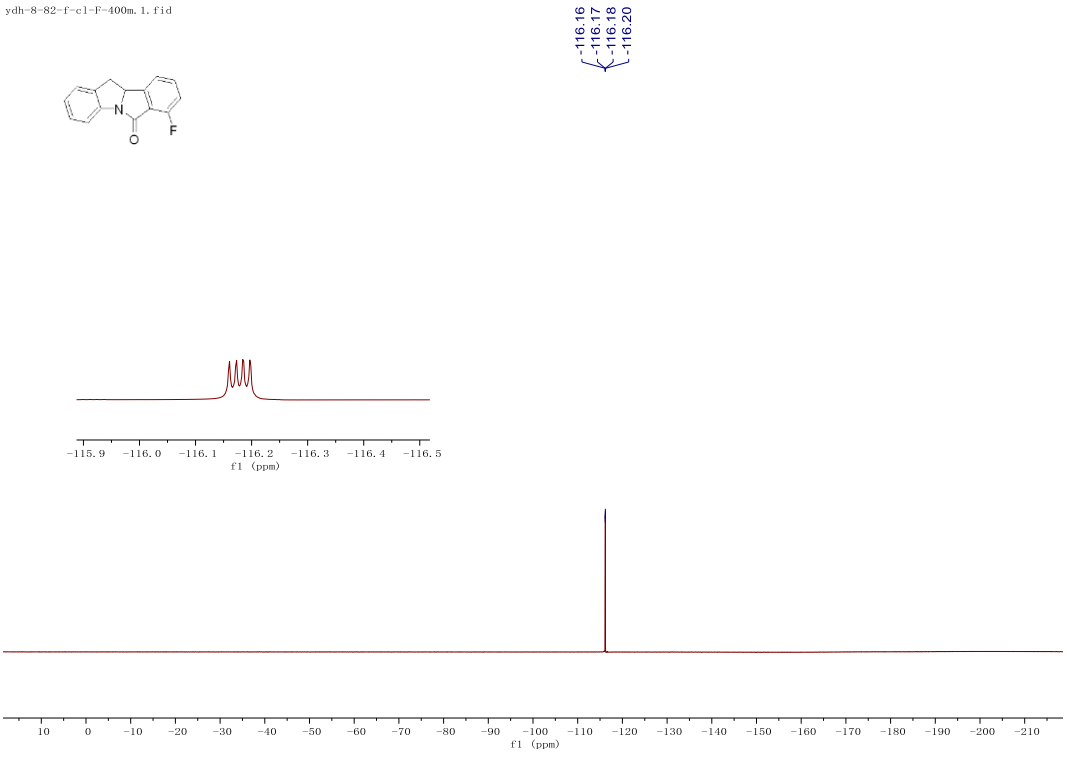
^{13}C NMR of 19



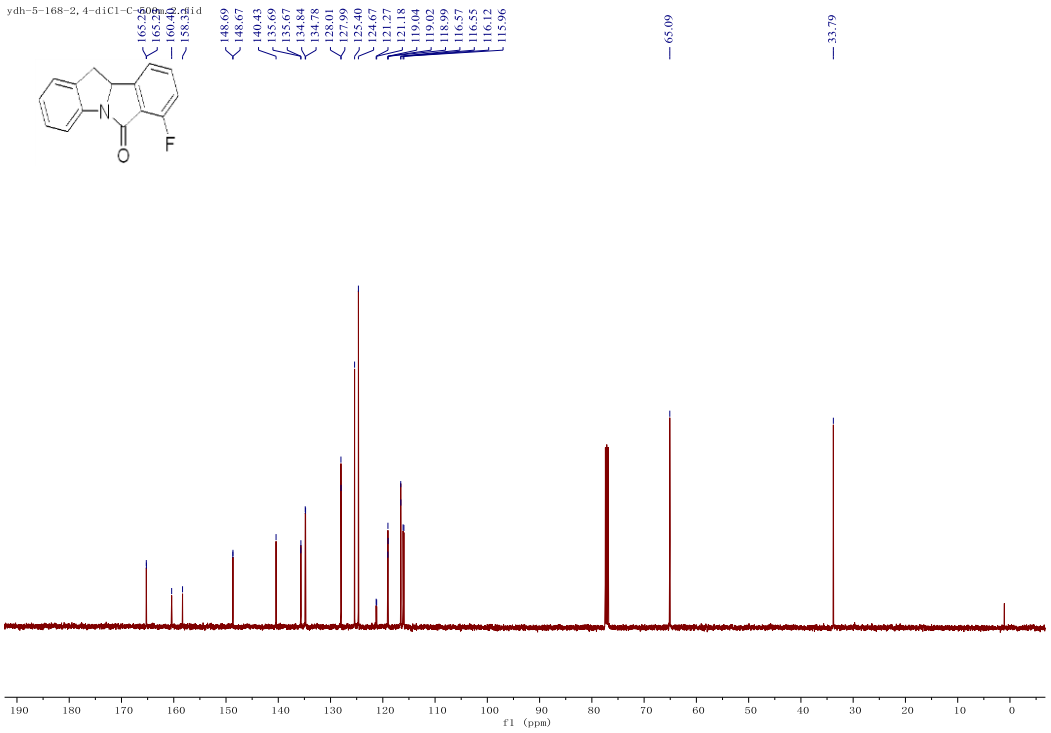
^{1}H NMR of 20



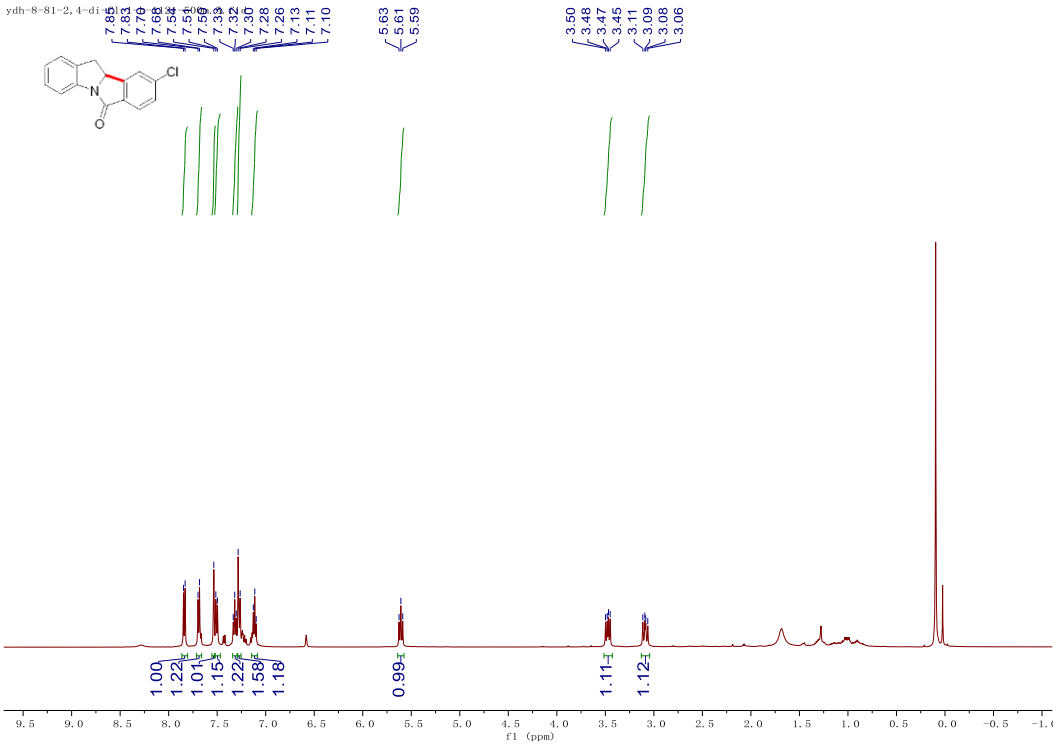
^{19}F NMR of 20



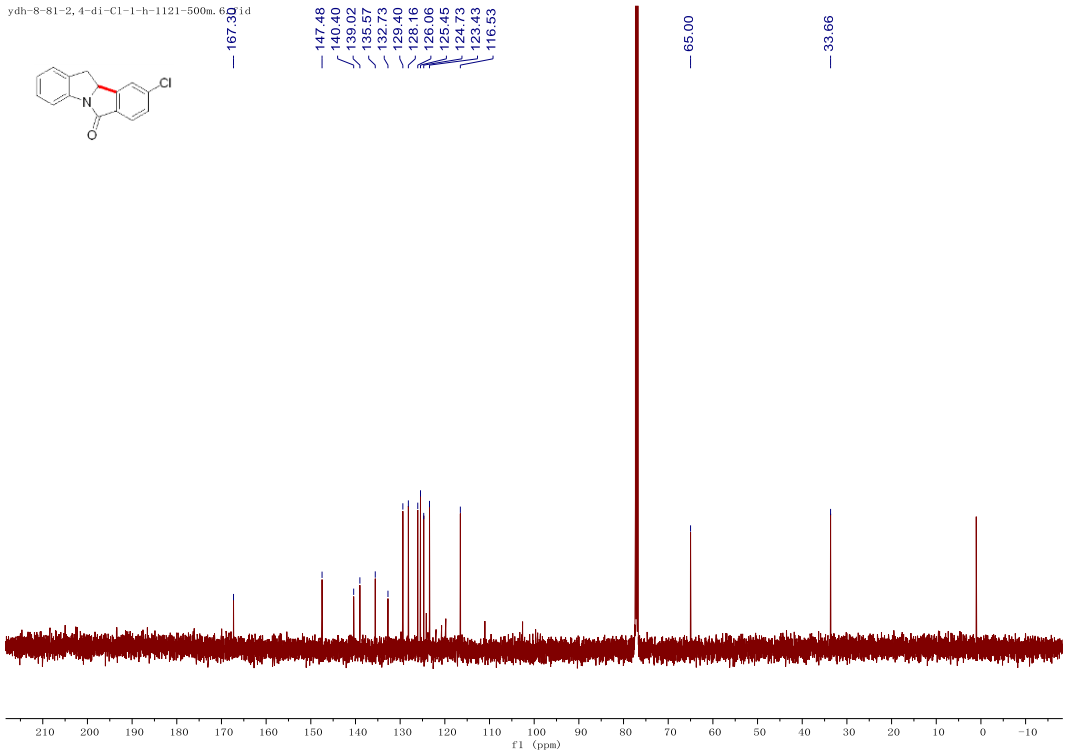
^{13}C NMR of 20



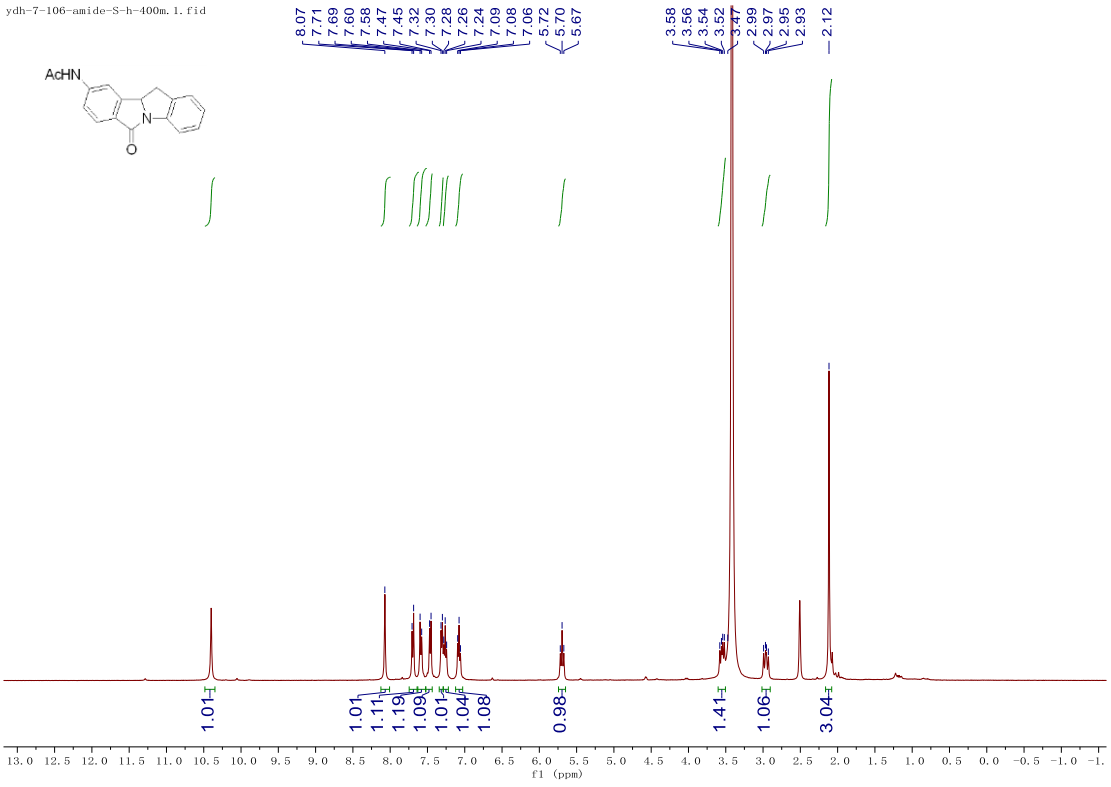
^{1}H NMR of 21



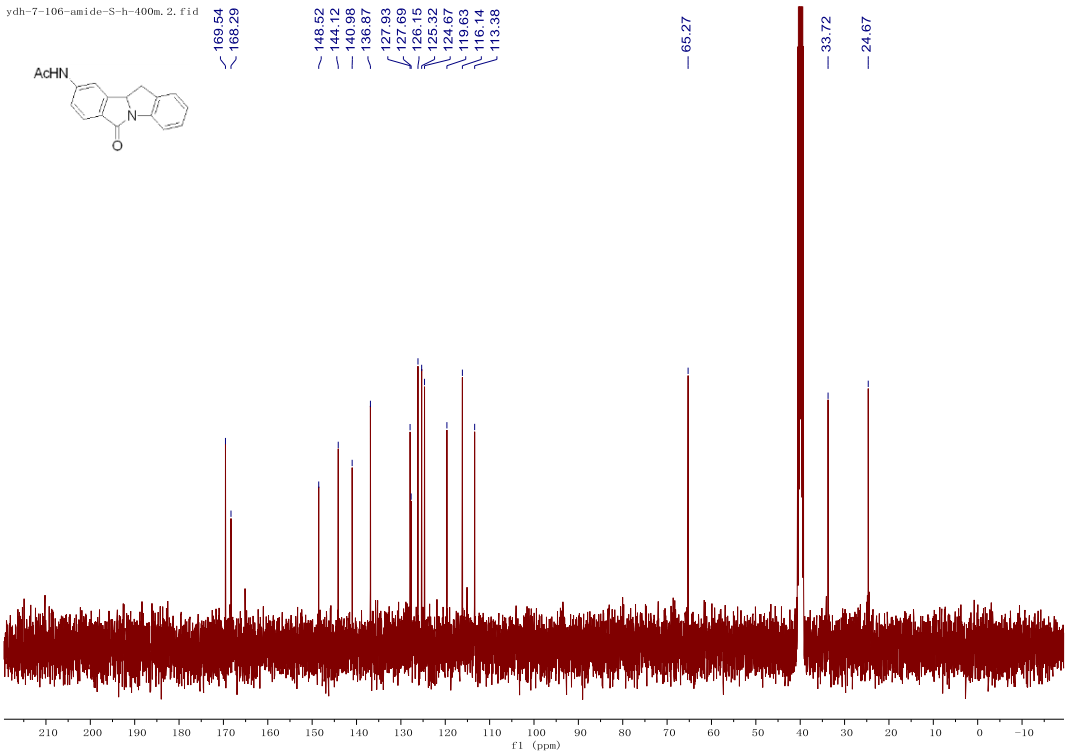
^{13}C NMR of 21



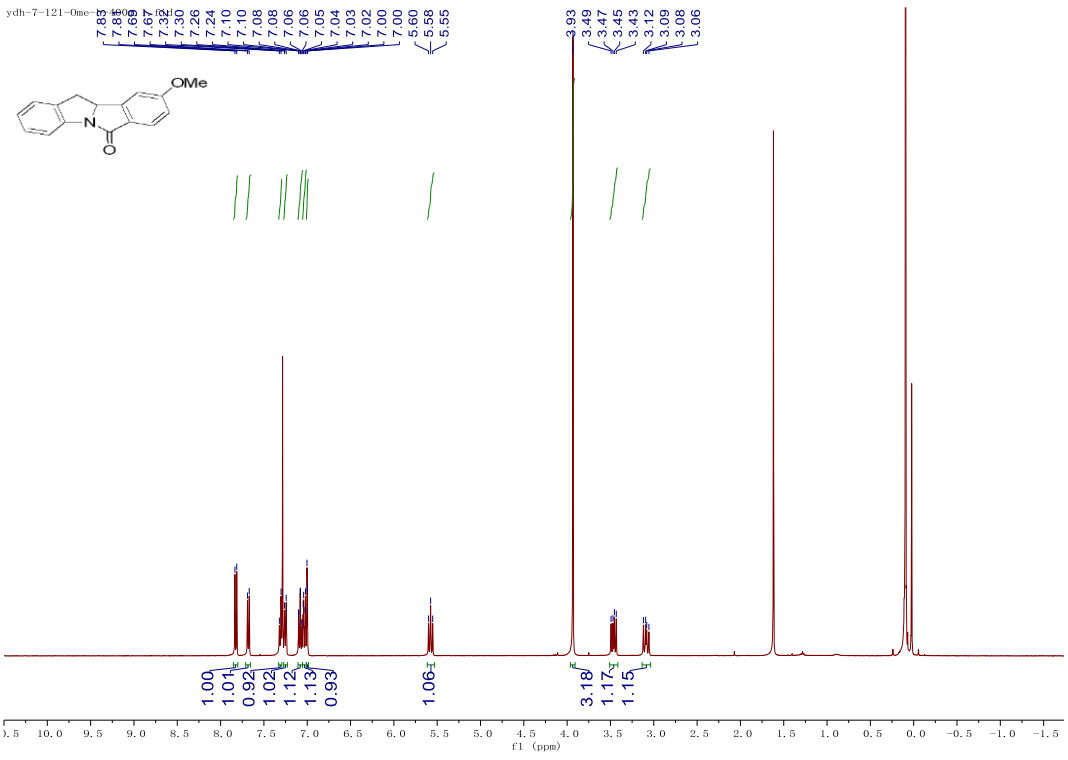
^{1}H NMR of 22



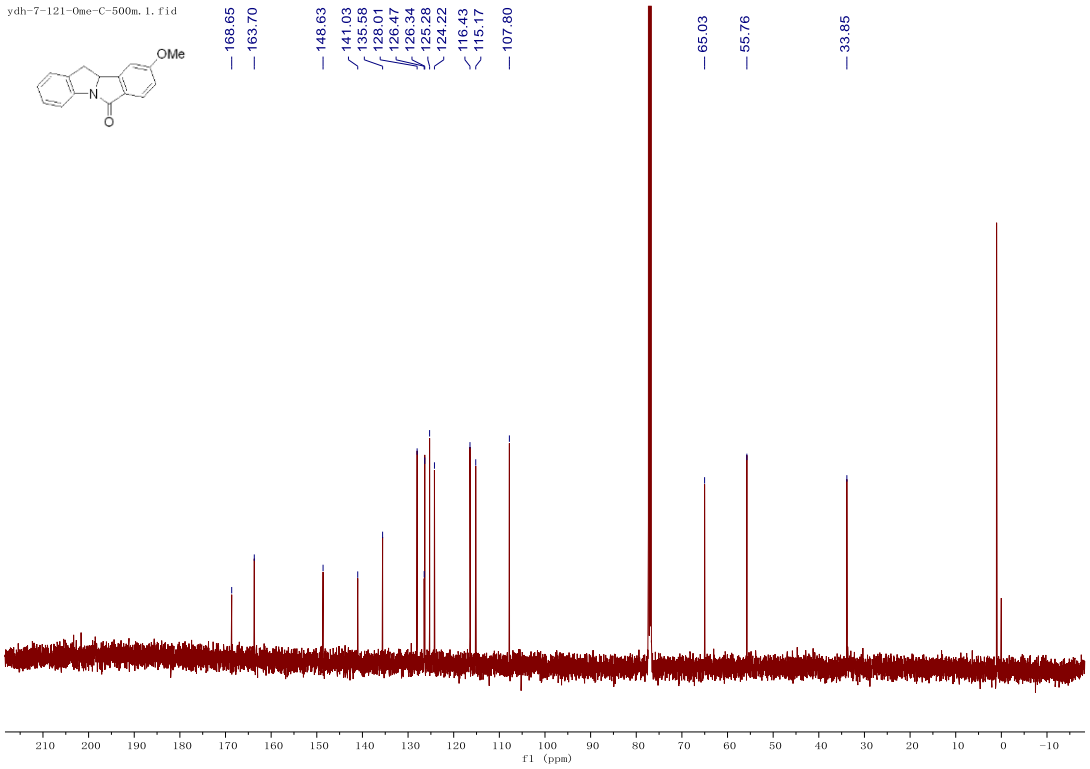
^{13}C NMR of 22



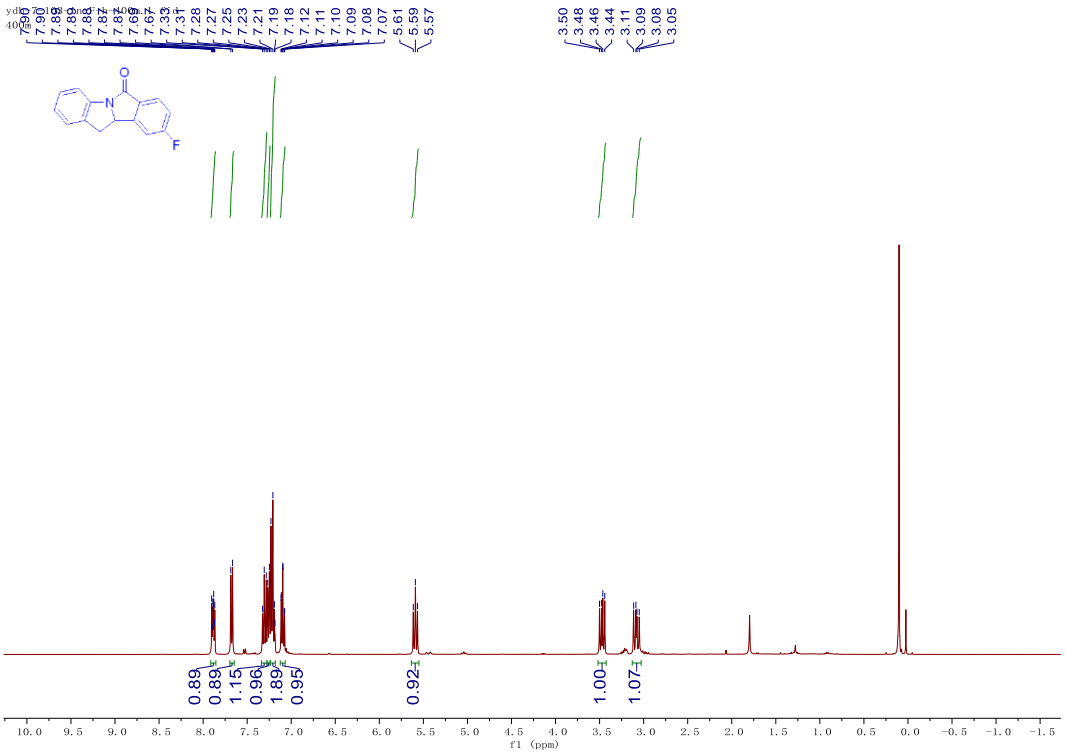
^{1}H NMR of 23



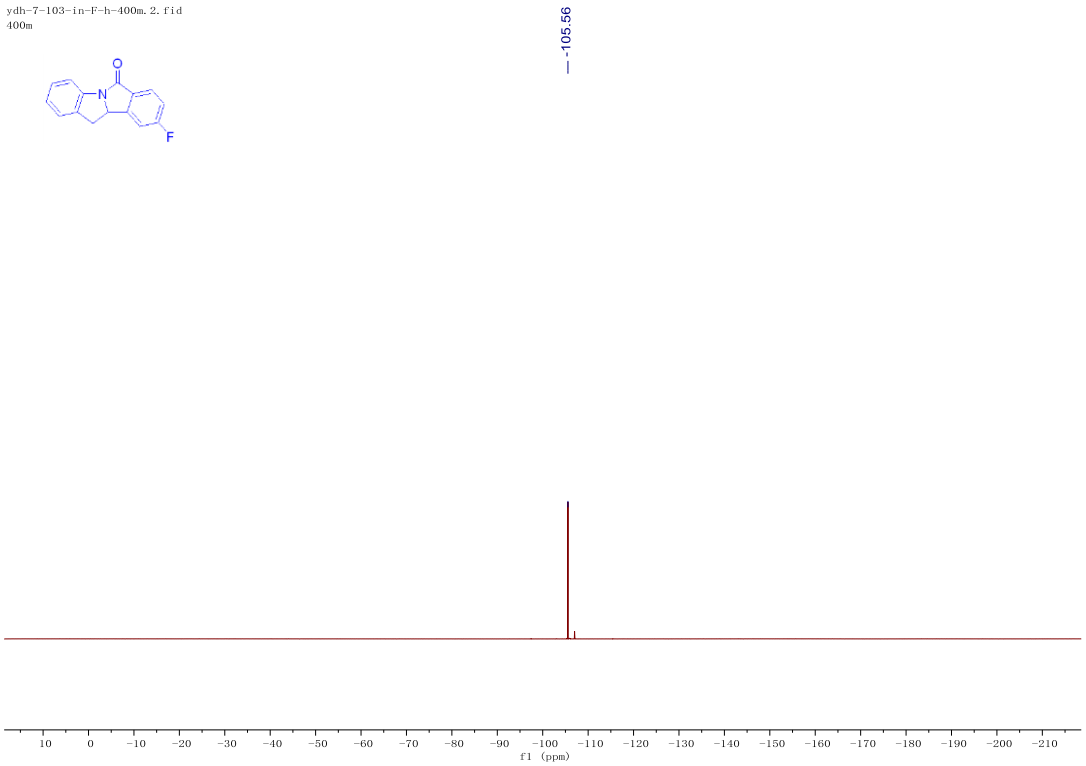
^{13}C NMR of 23



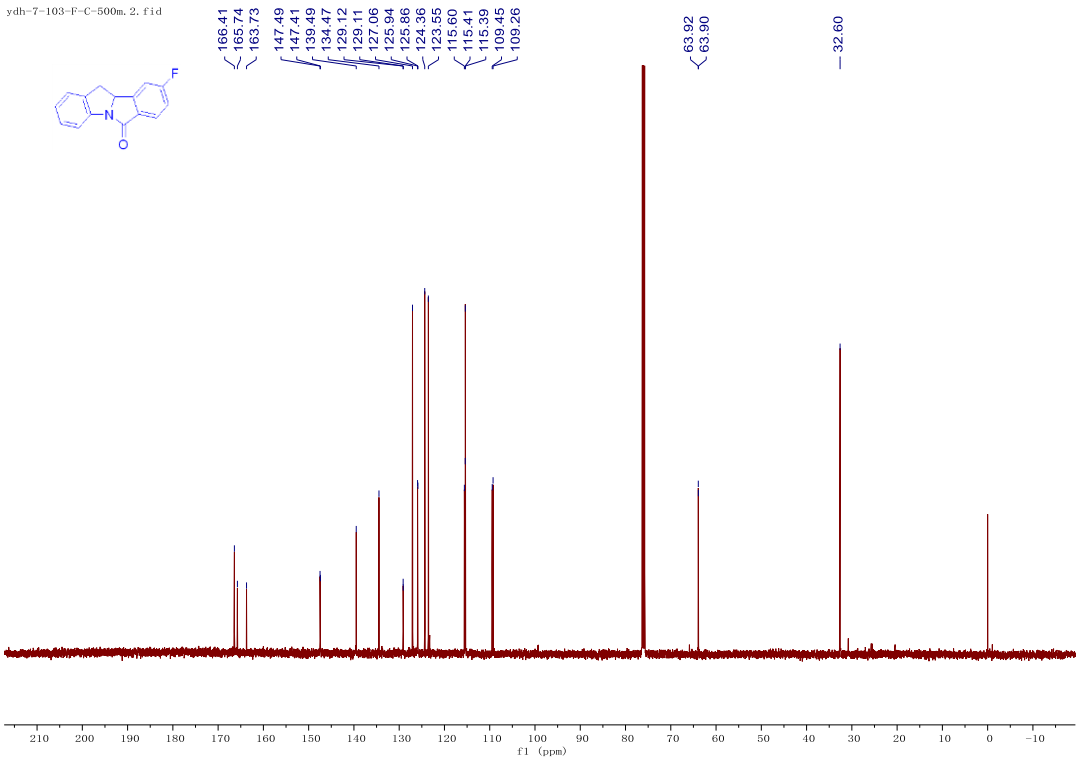
^{1}H NMR of 24



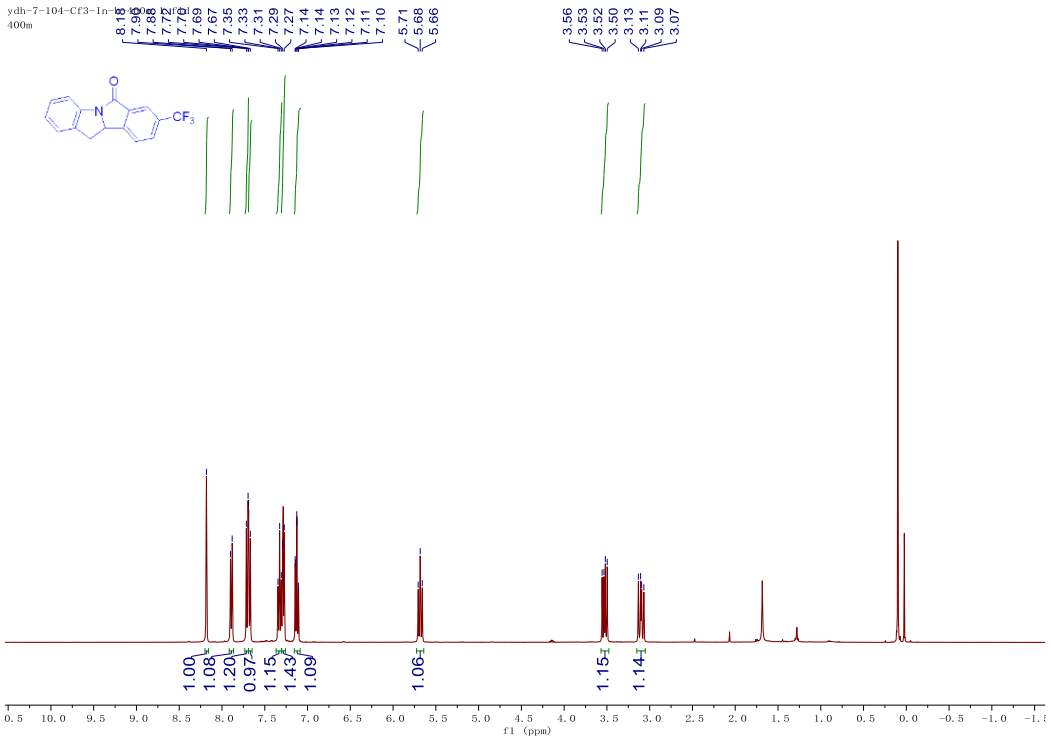
^{19}F NMR of 24



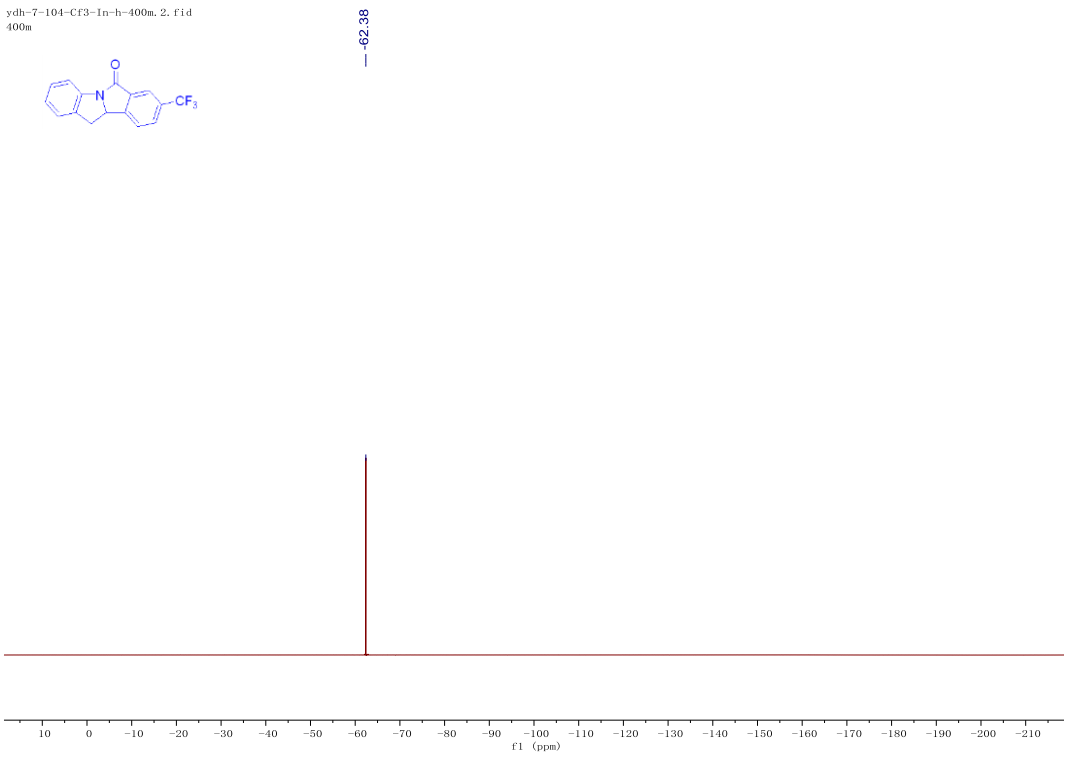
^{13}C NMR of 24



^{1}H NMR of 25



^{19}F NMR of 25



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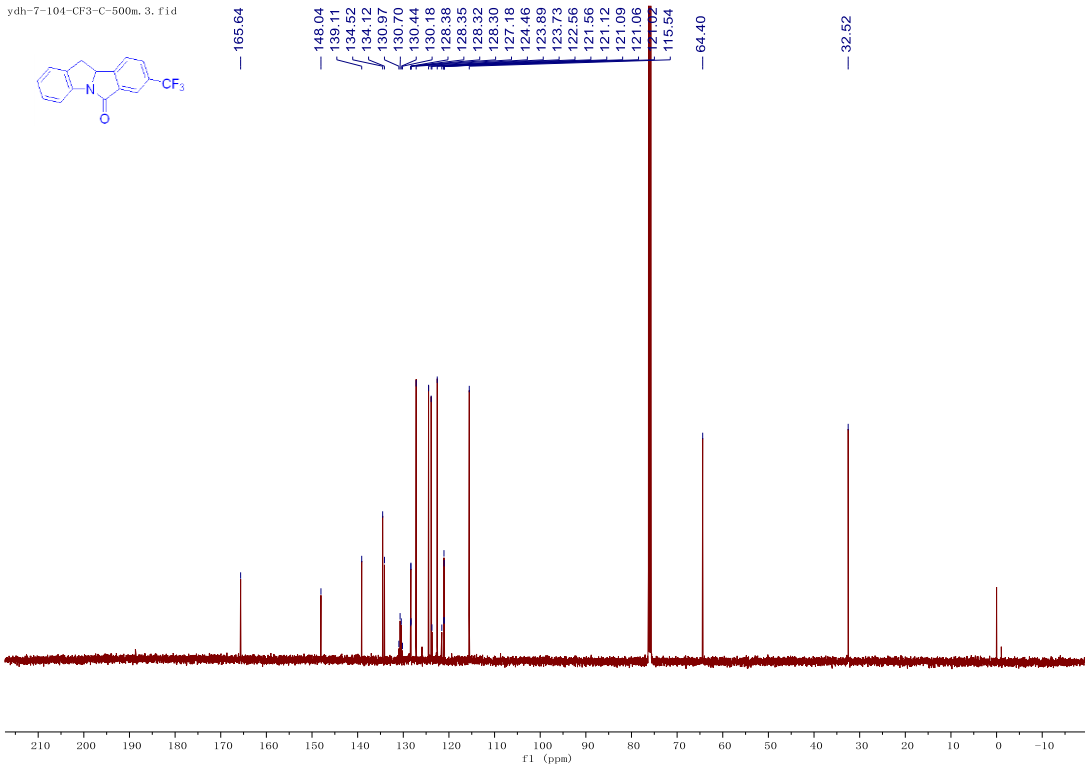
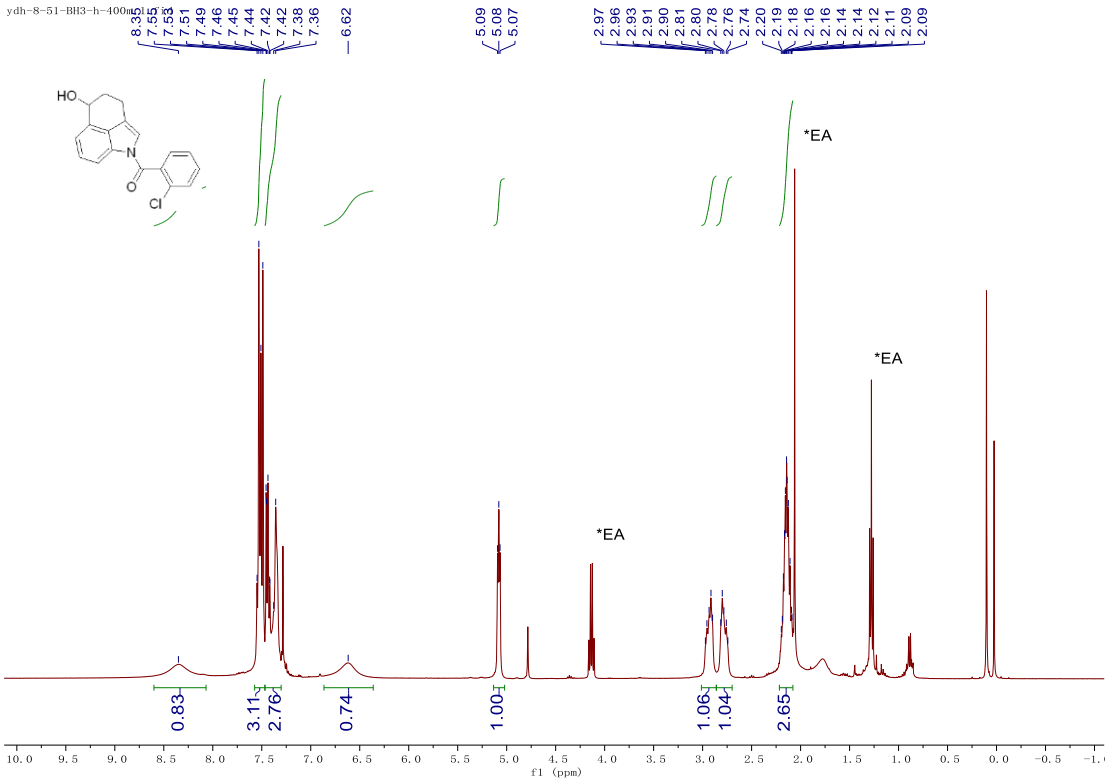
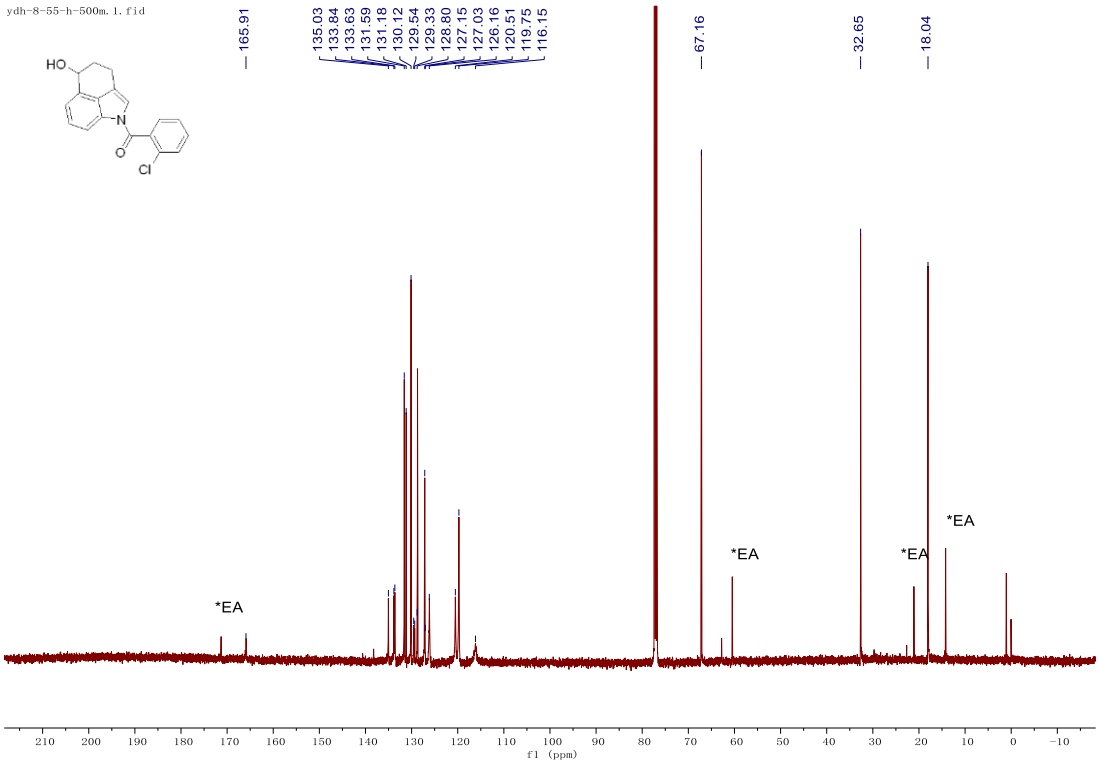


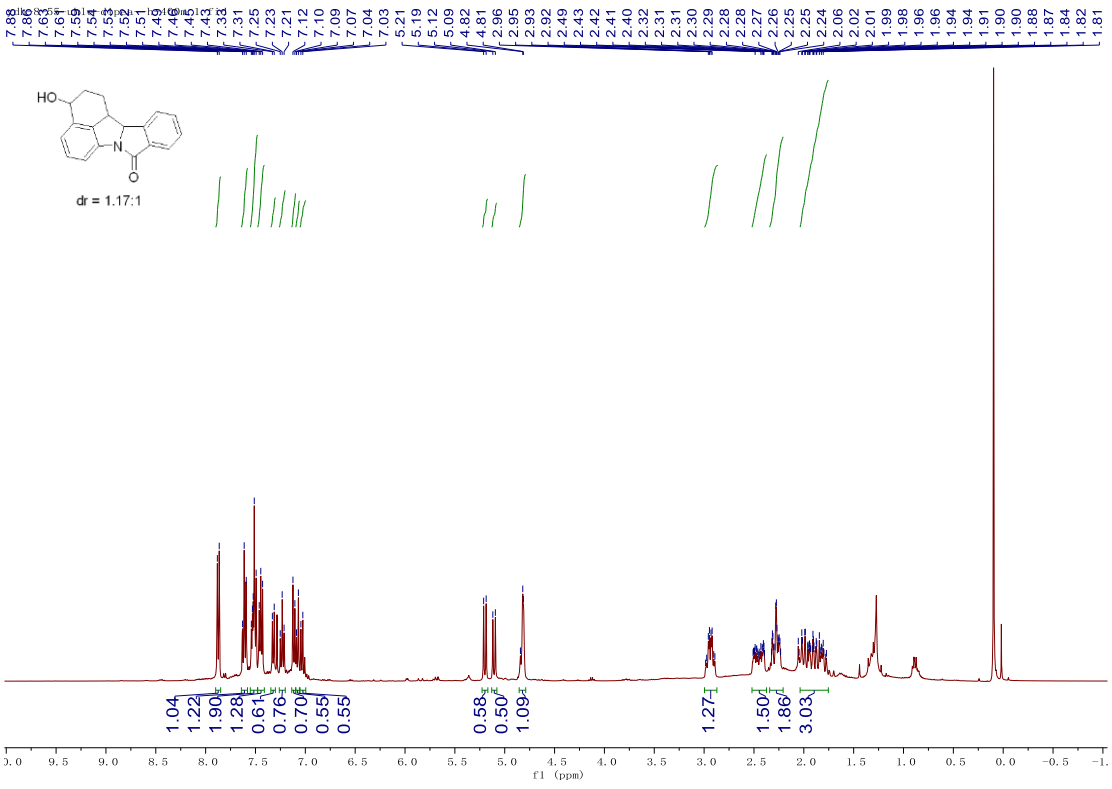
^{1}H NMR of 26



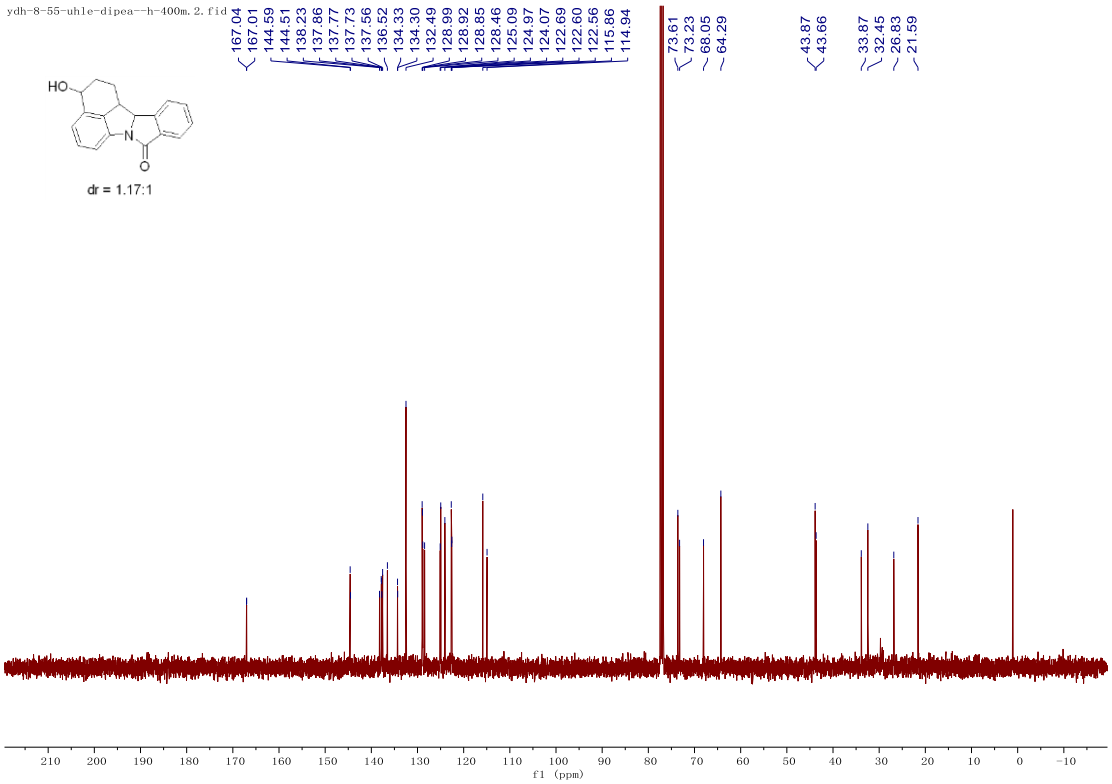
^{13}C NMR of 26



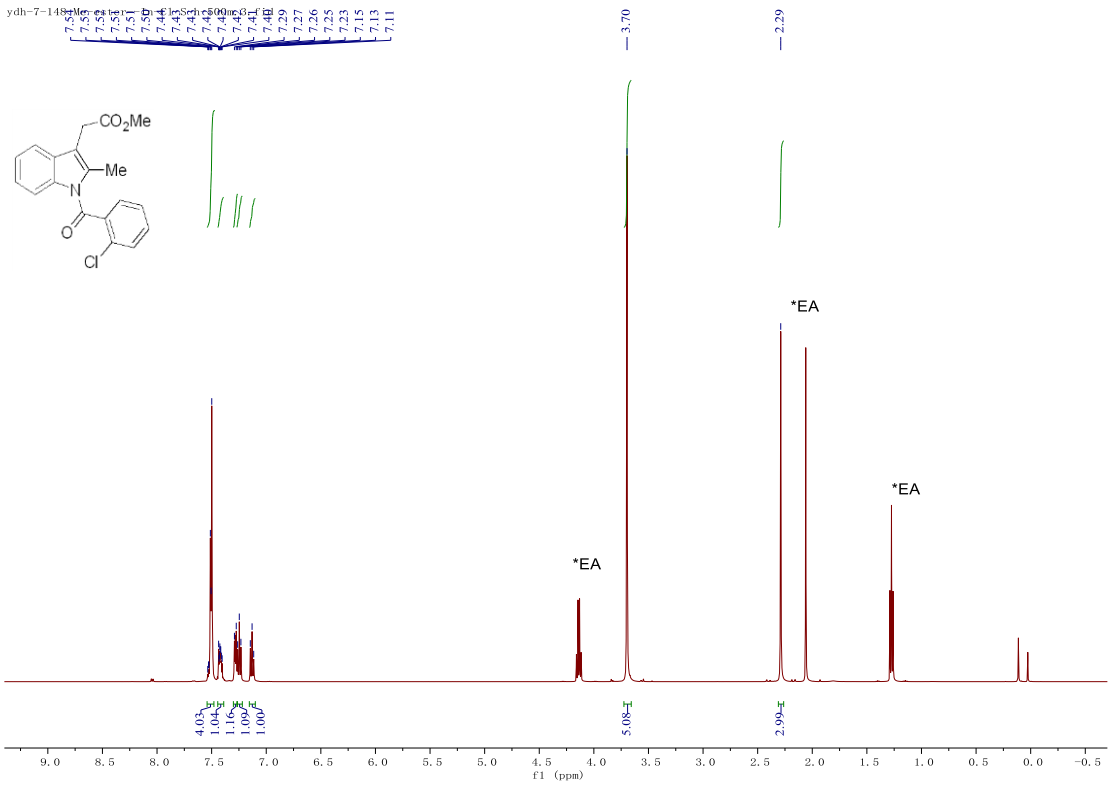
^{1}H NMR of 27



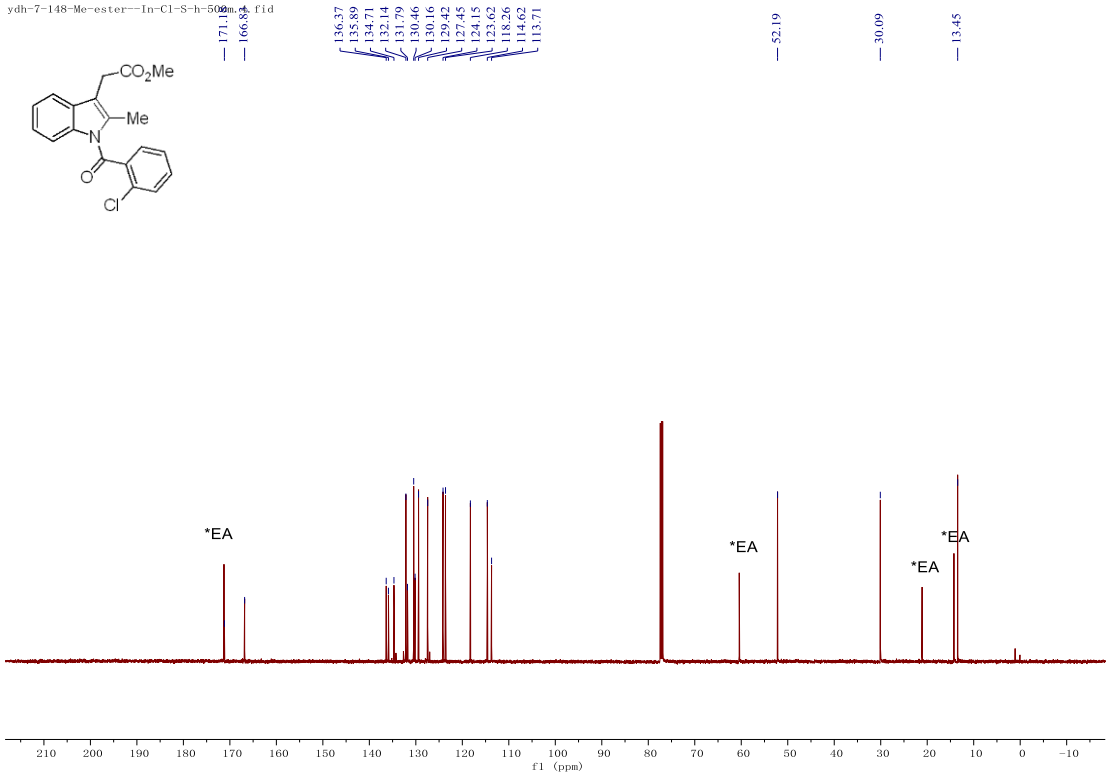
^{13}C NMR of 27



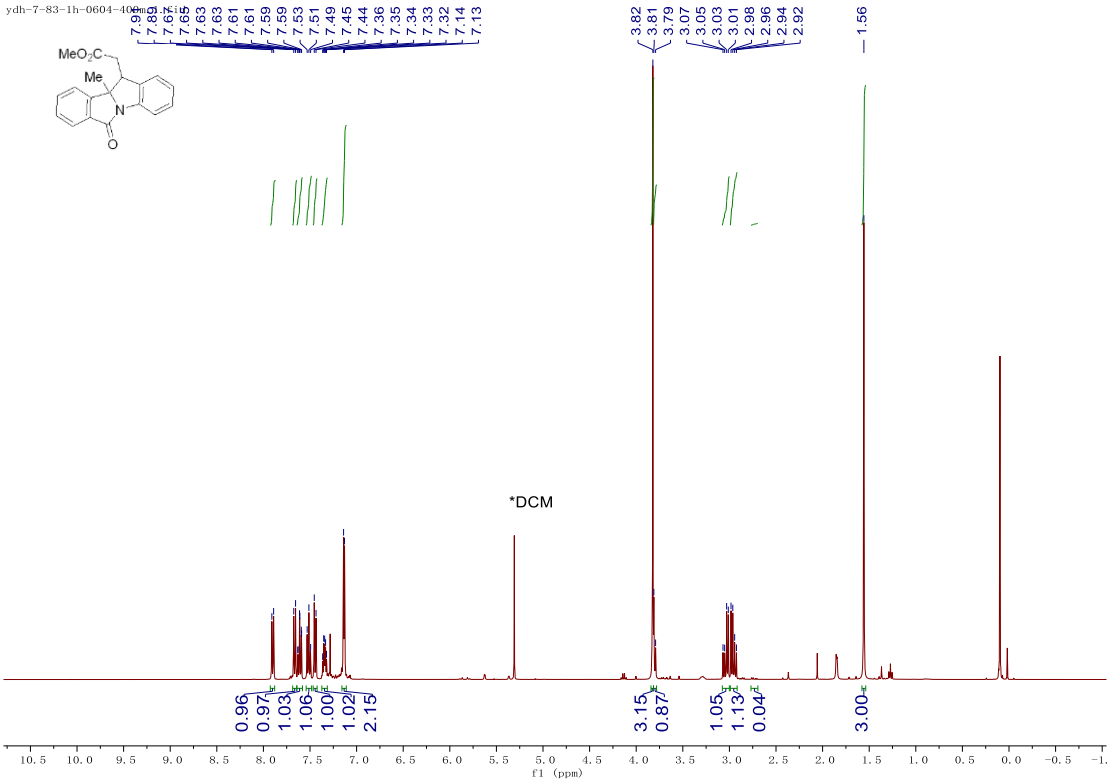
^{1}H NMR of 28



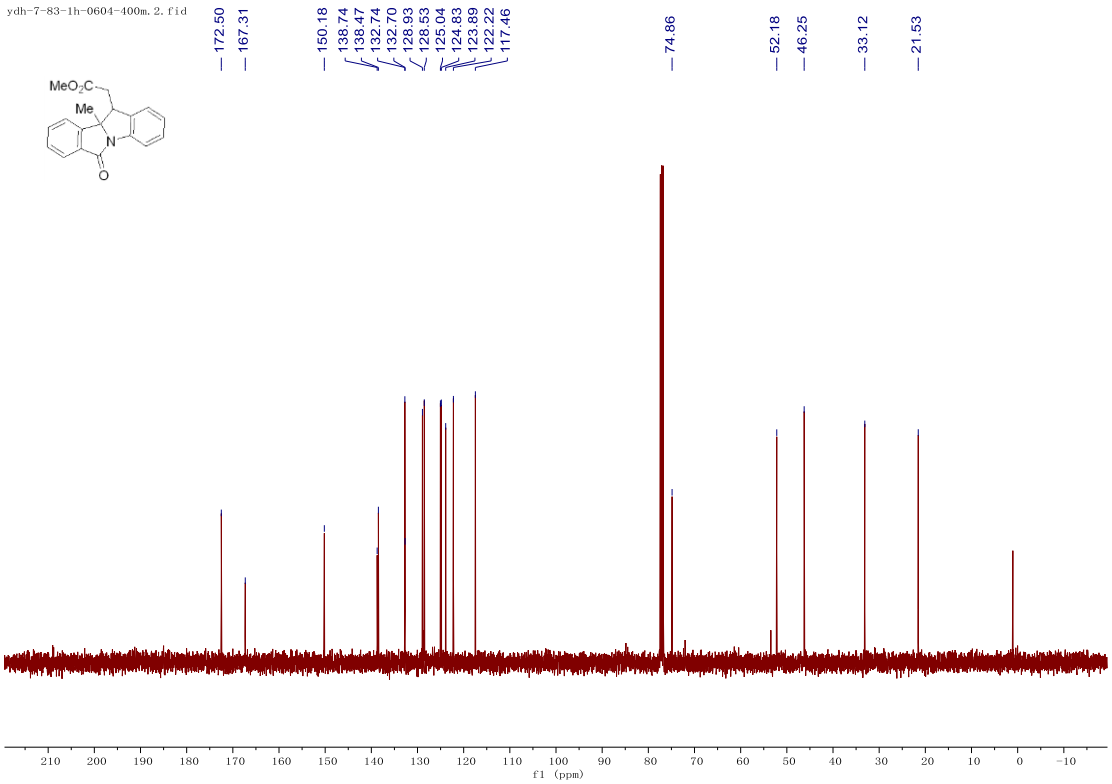
^{13}C NMR of 28



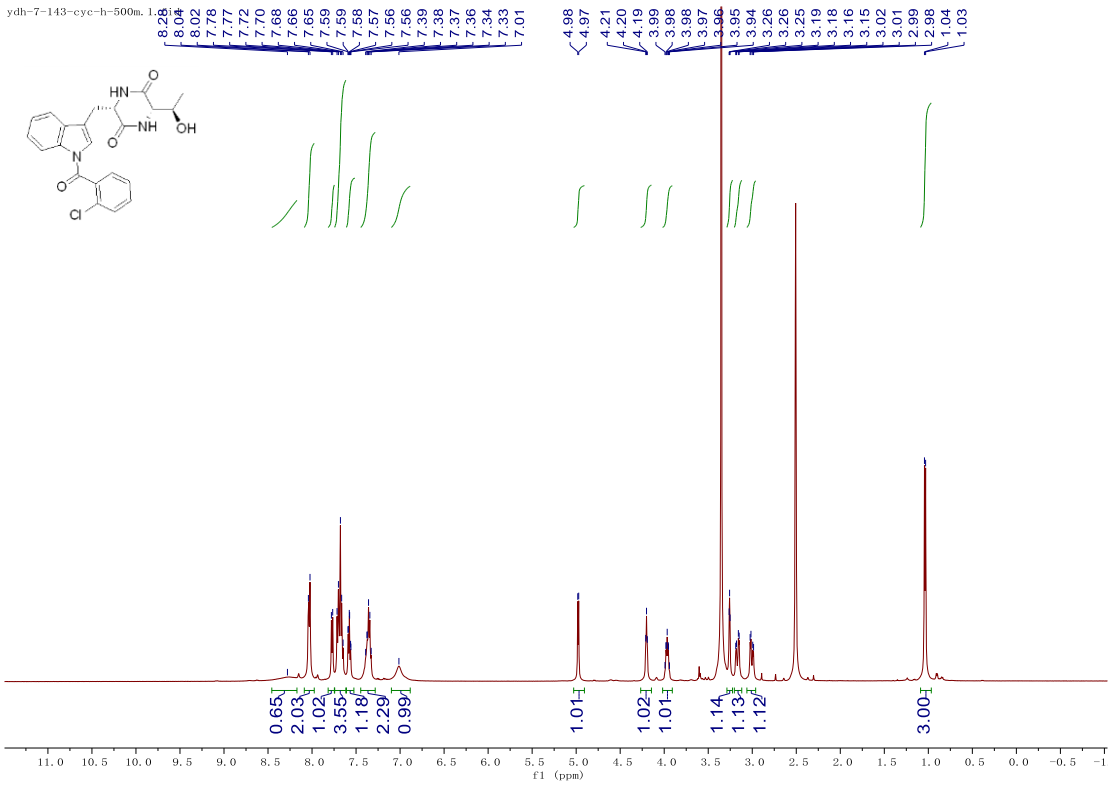
^{1}H NMR of 29



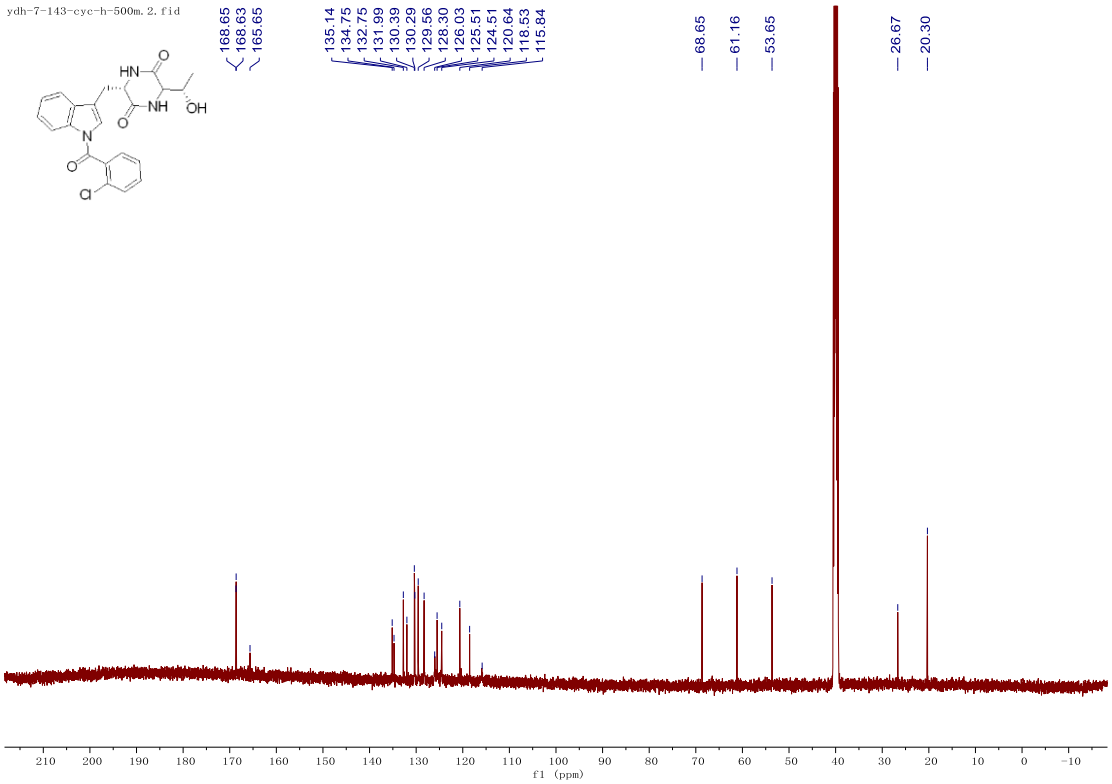
^{13}C NMR of 29



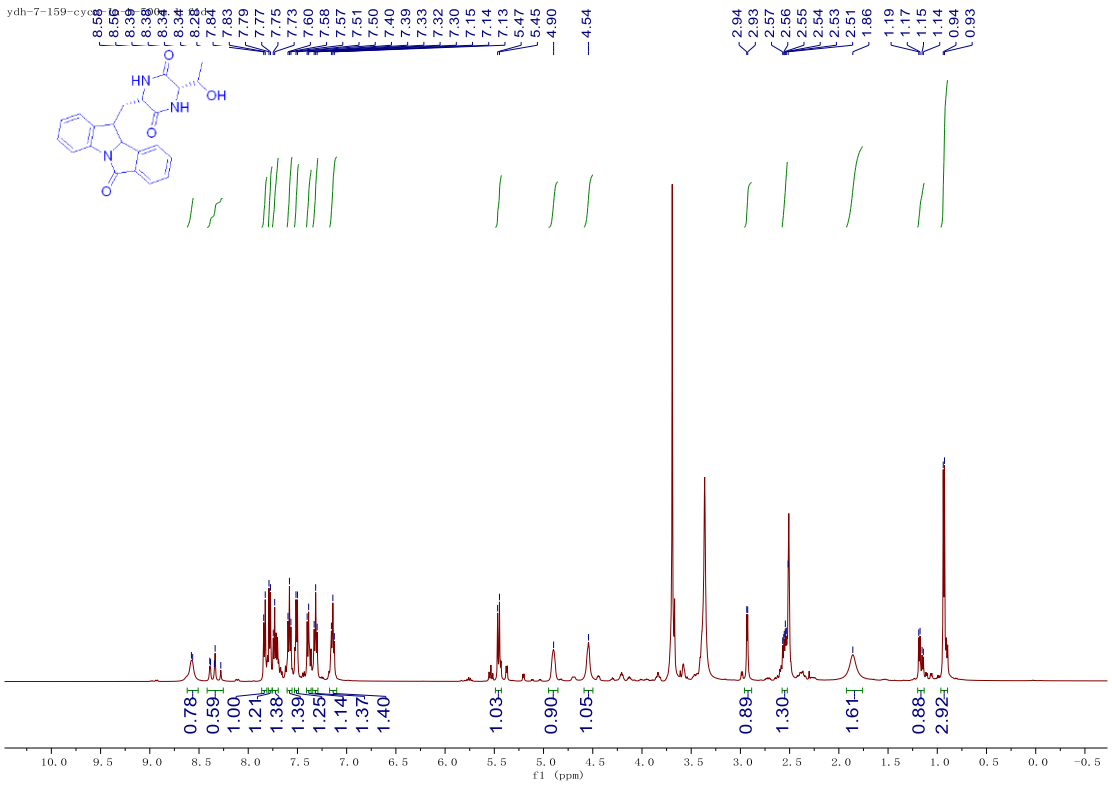
^{1}H NMR of 30



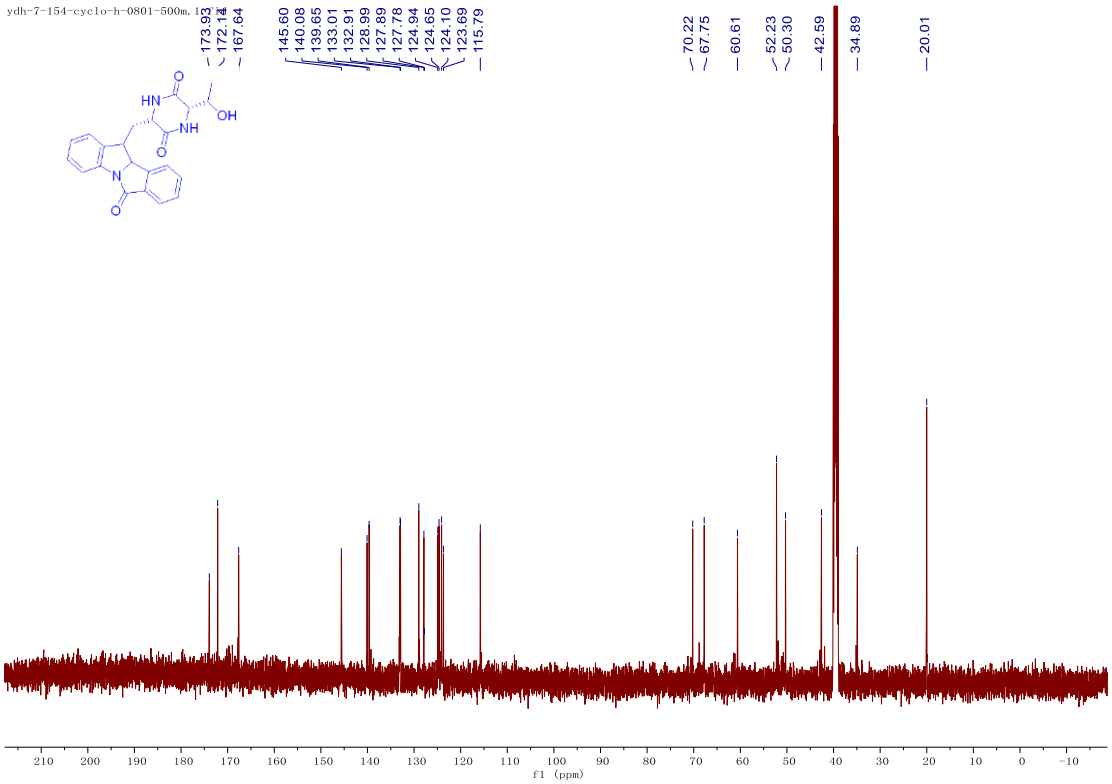
^{13}C NMR of 30



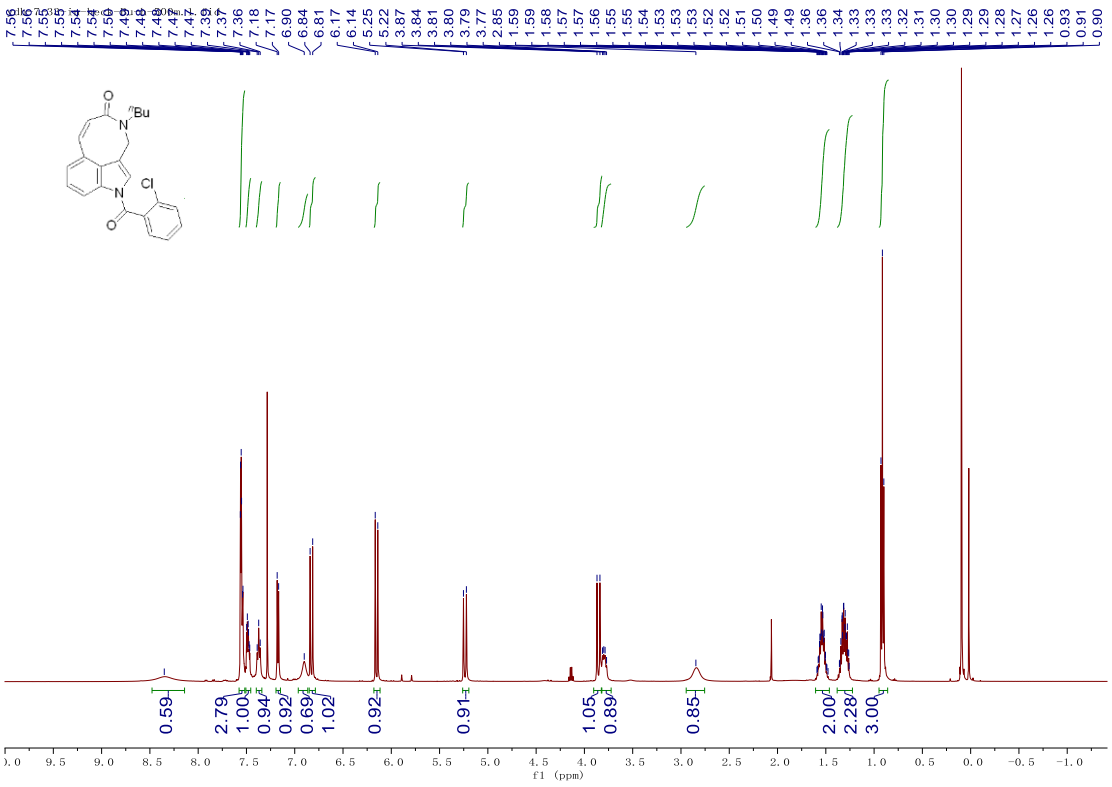
^{1}H NMR of 31



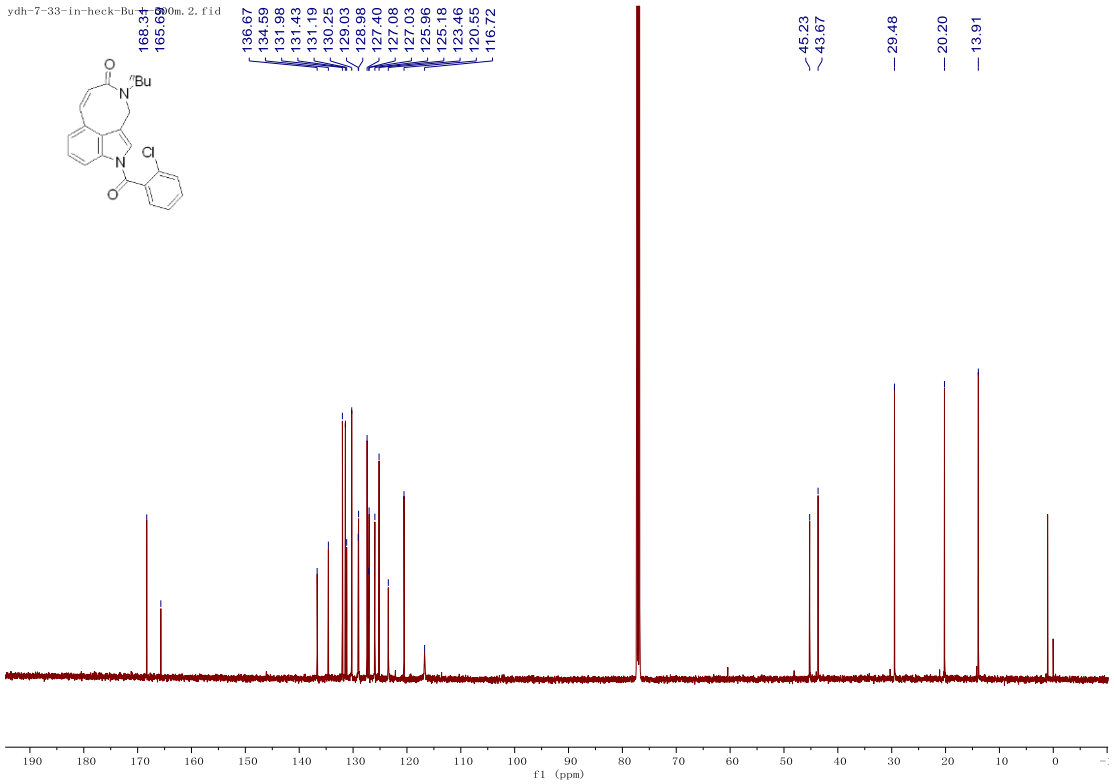
^{13}C NMR of 31



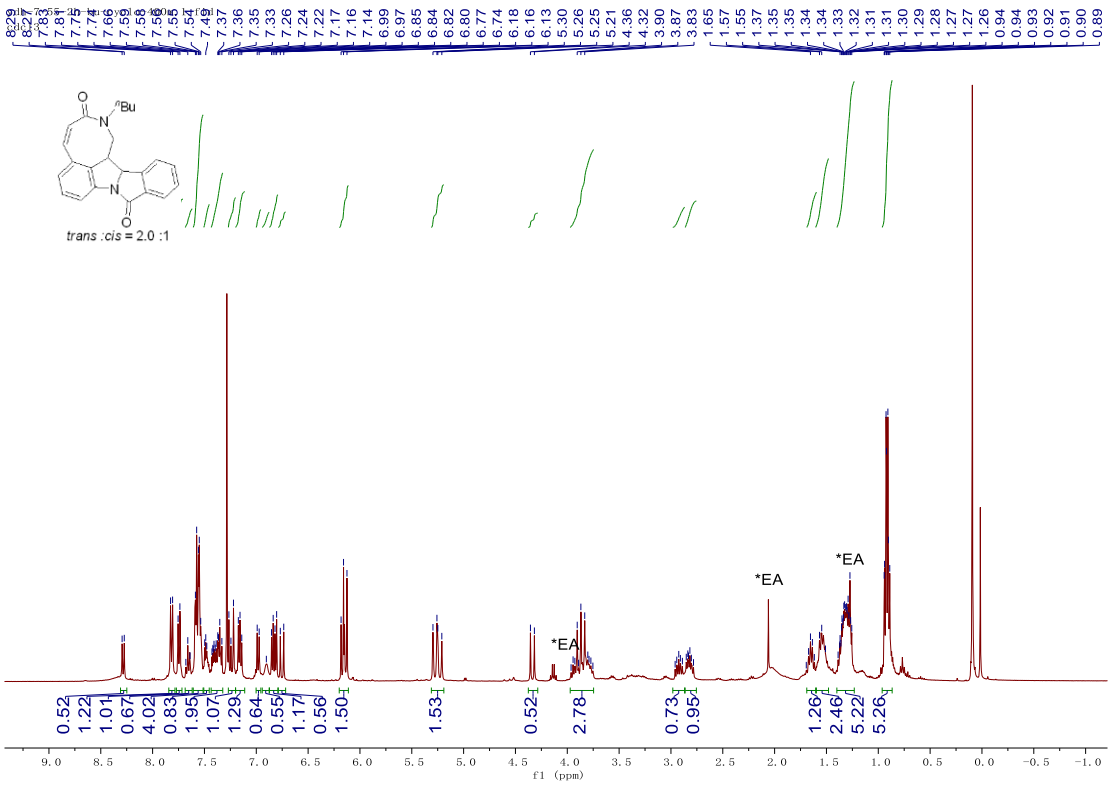
^{1}H NMR of 32



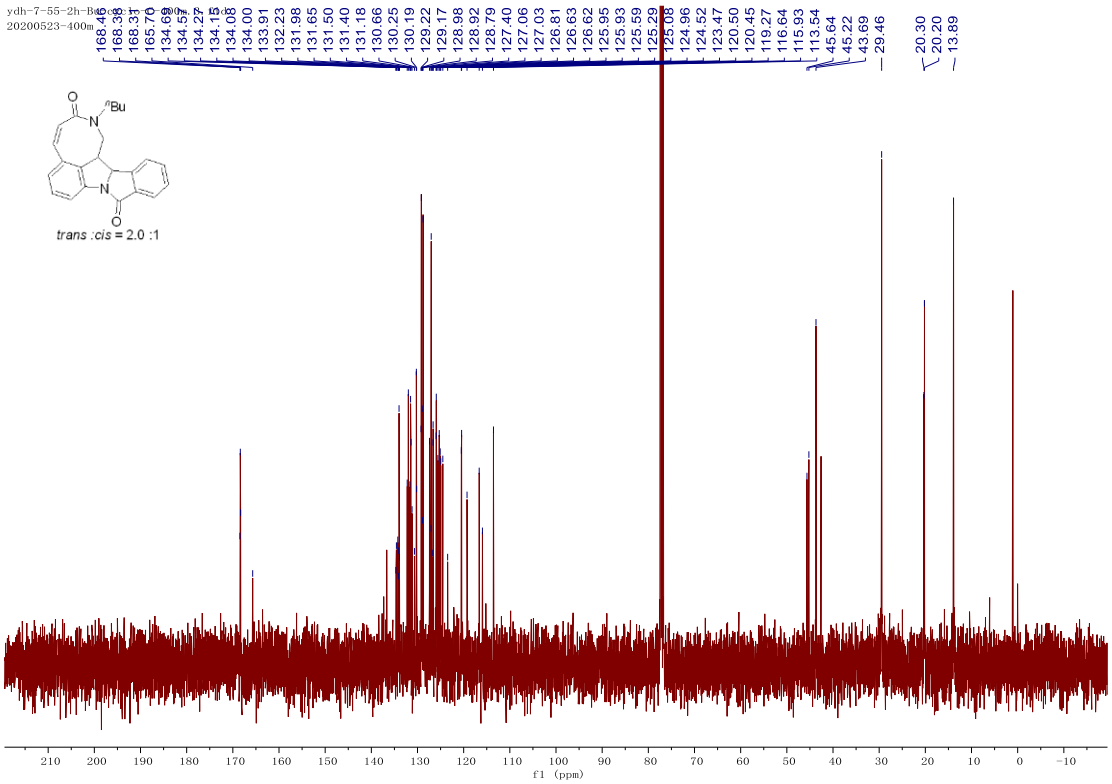
^{13}C NMR of 32



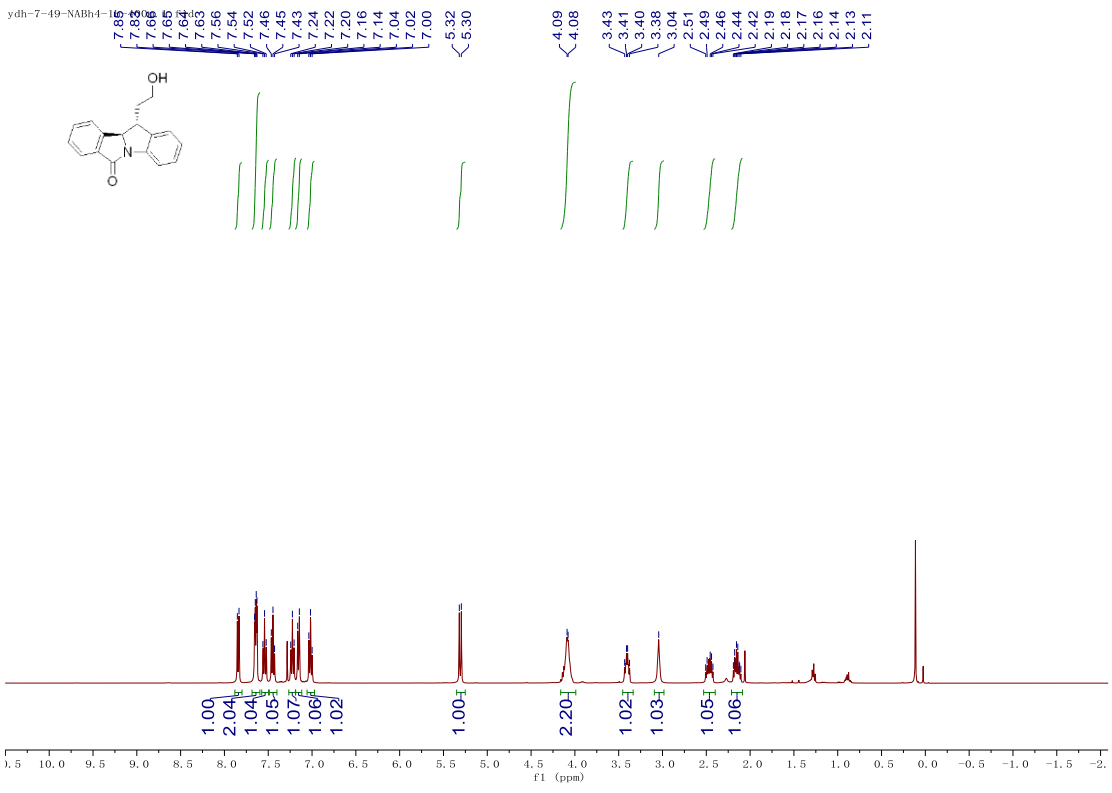
^{1}H NMR of 33



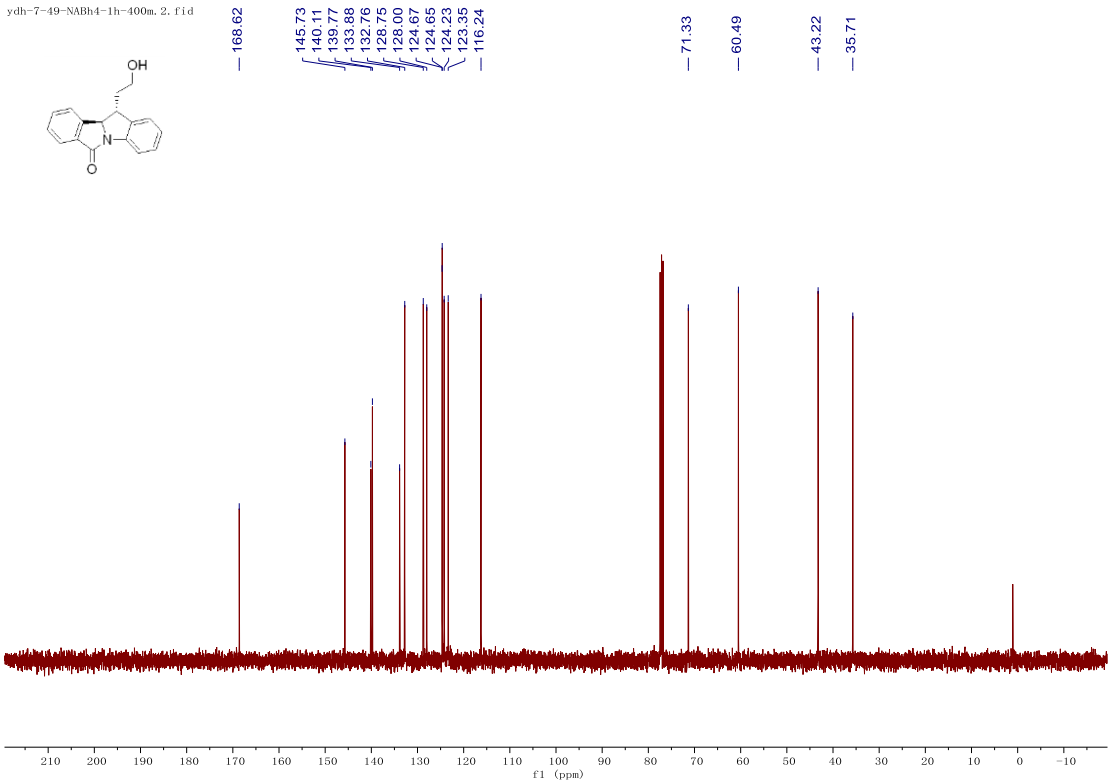
^{13}C NMR of 33



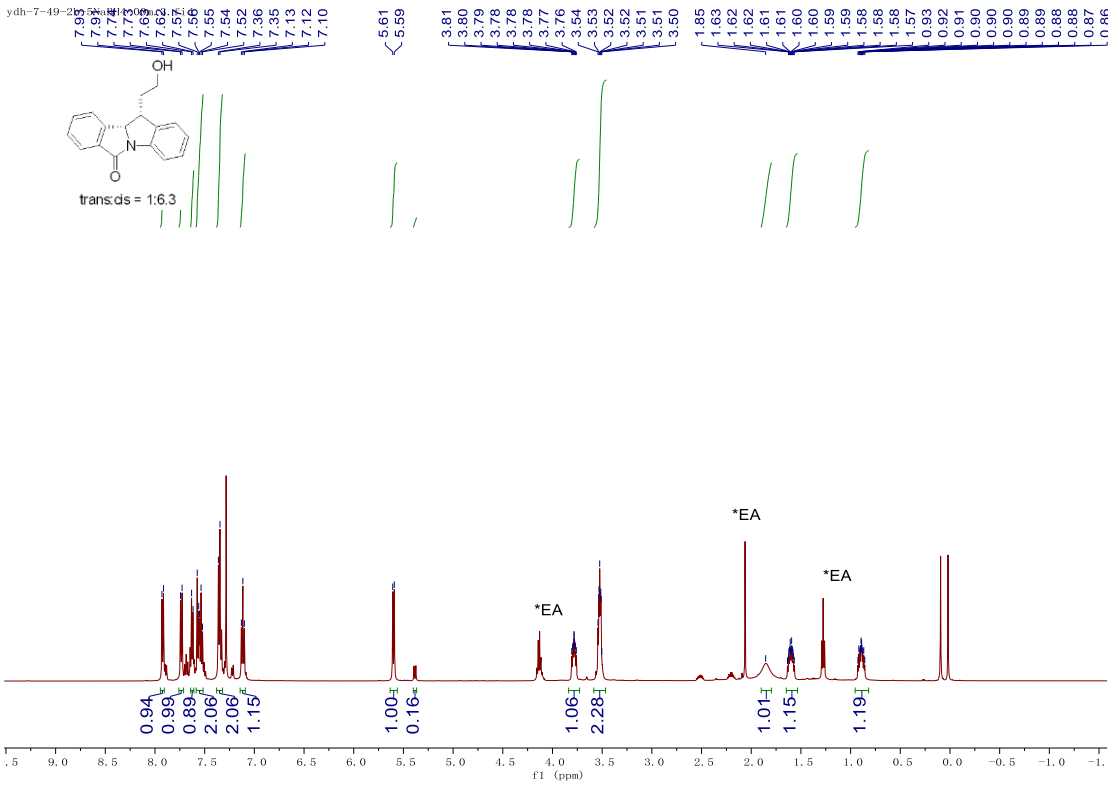
^{1}H NMR of *trans*-34



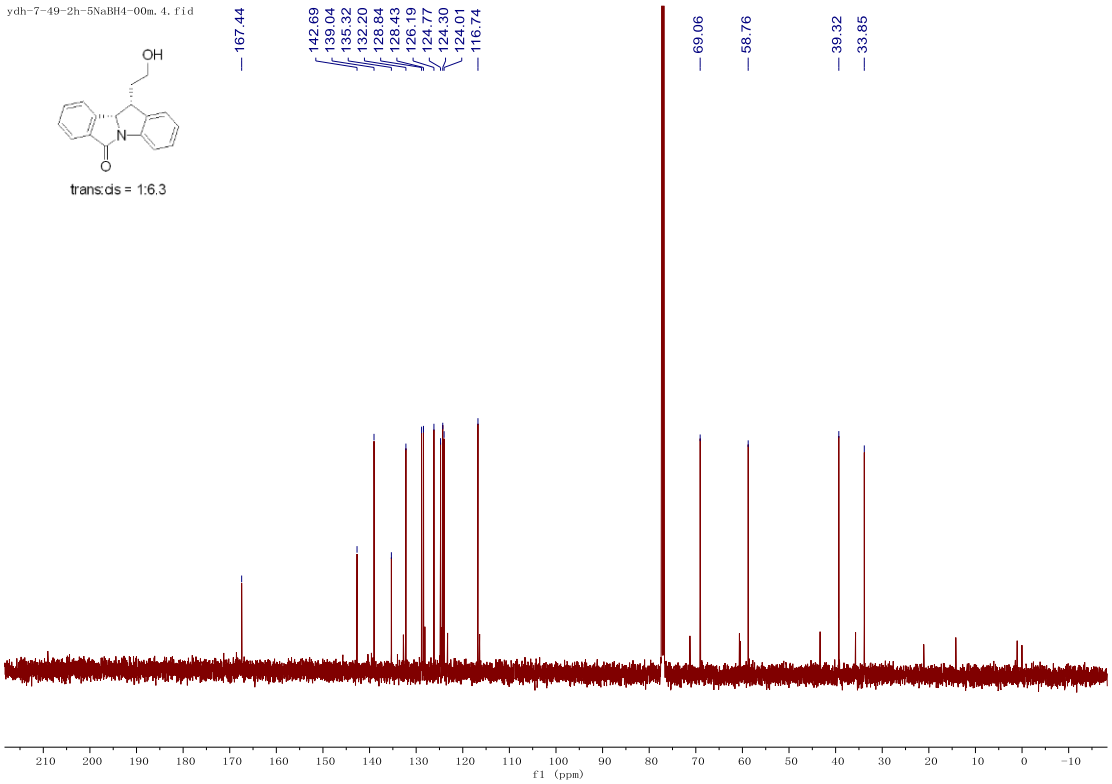
^{13}C NMR of *trans*-34



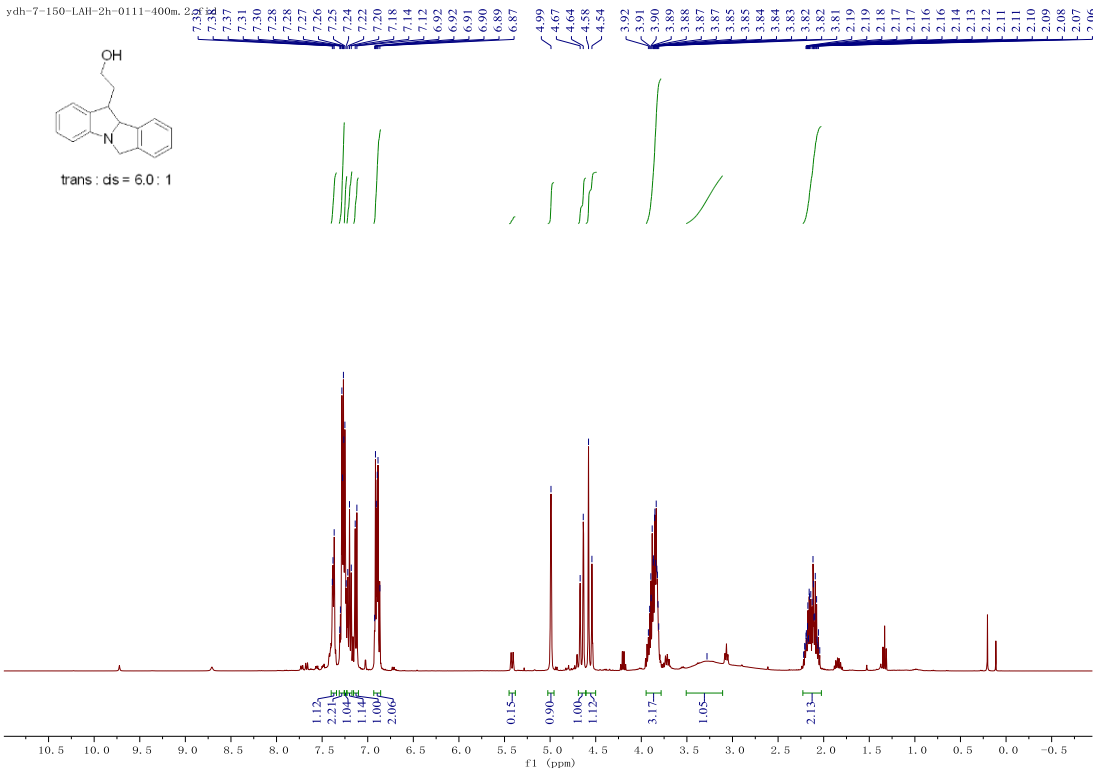
^{1}H NMR of *cis*-34 (contains a minor amount of *trans*-**34**)



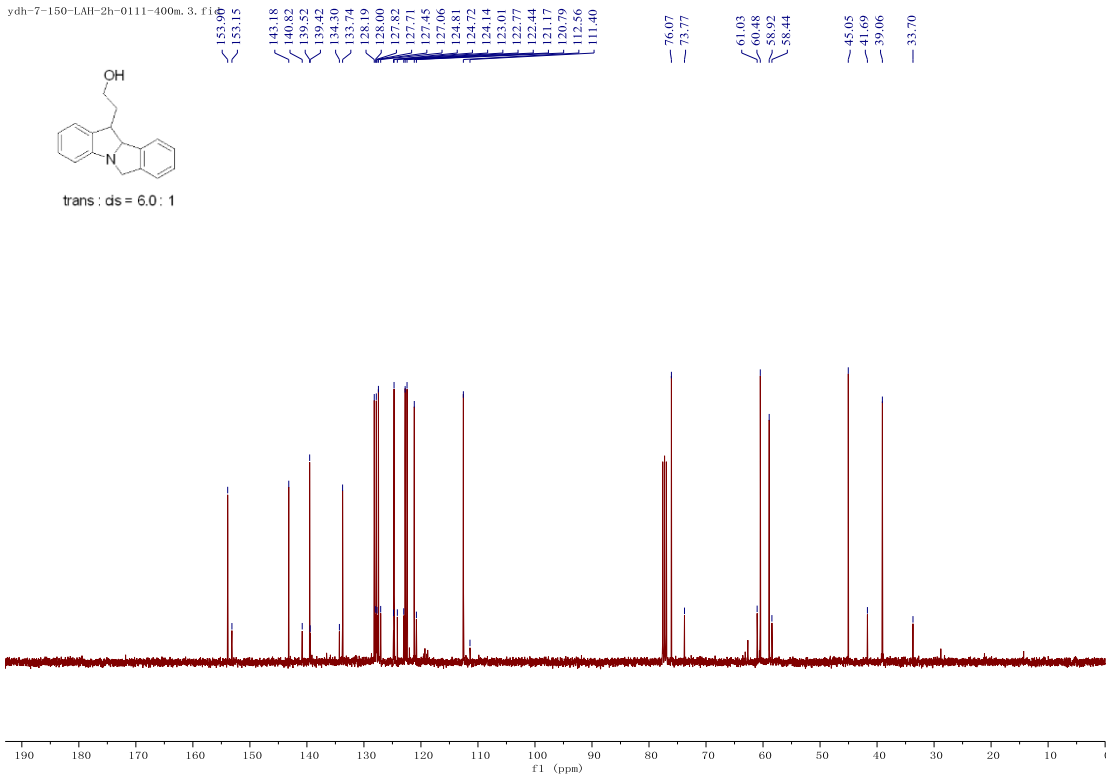
^{13}C NMR of *cis*-34 (contains a minor amount of *trans*-**34**)



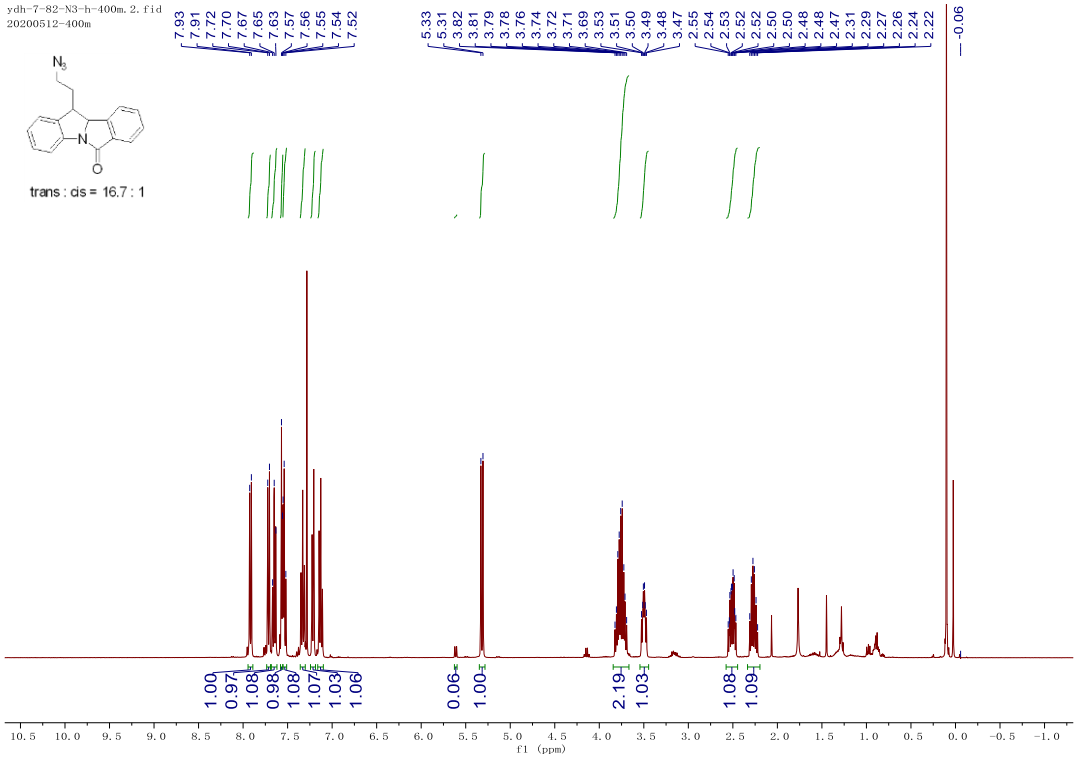
^{1}H NMR of 35



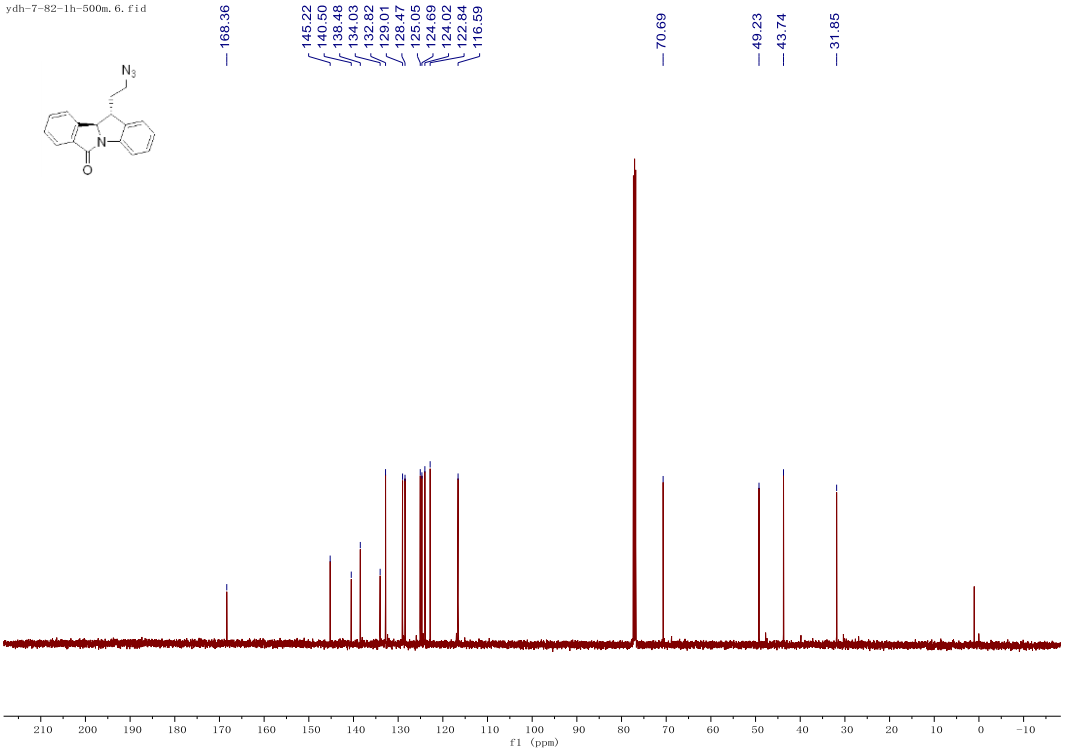
^{13}C NMR of 35



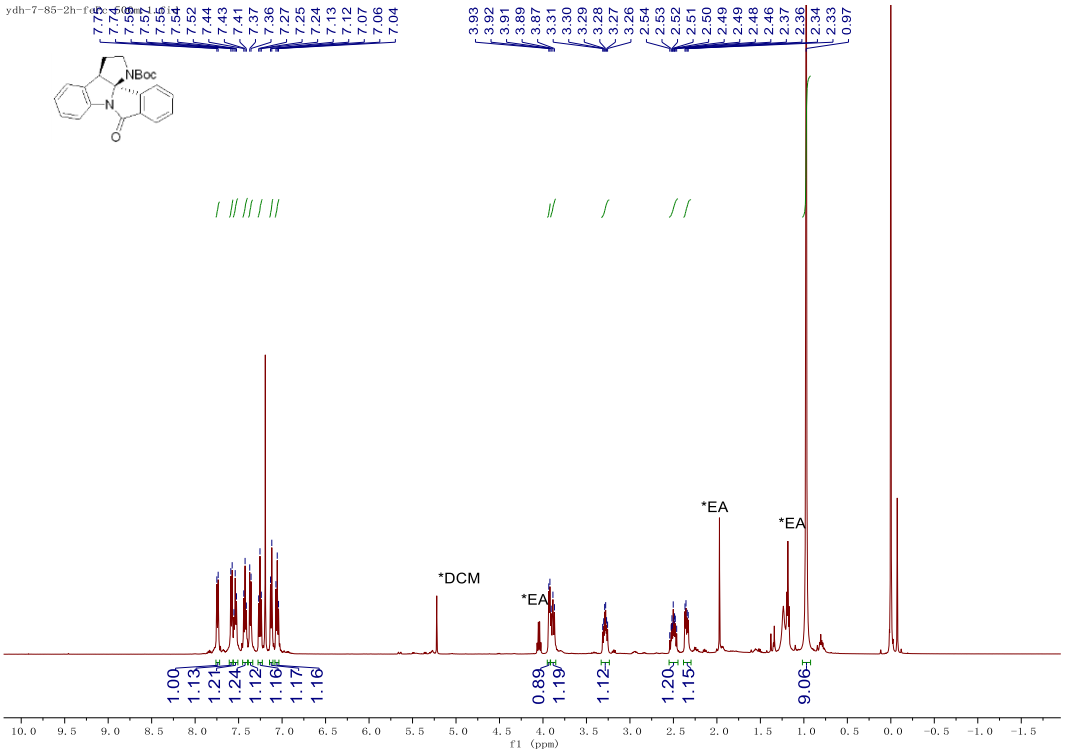
^{1}H NMR of 36



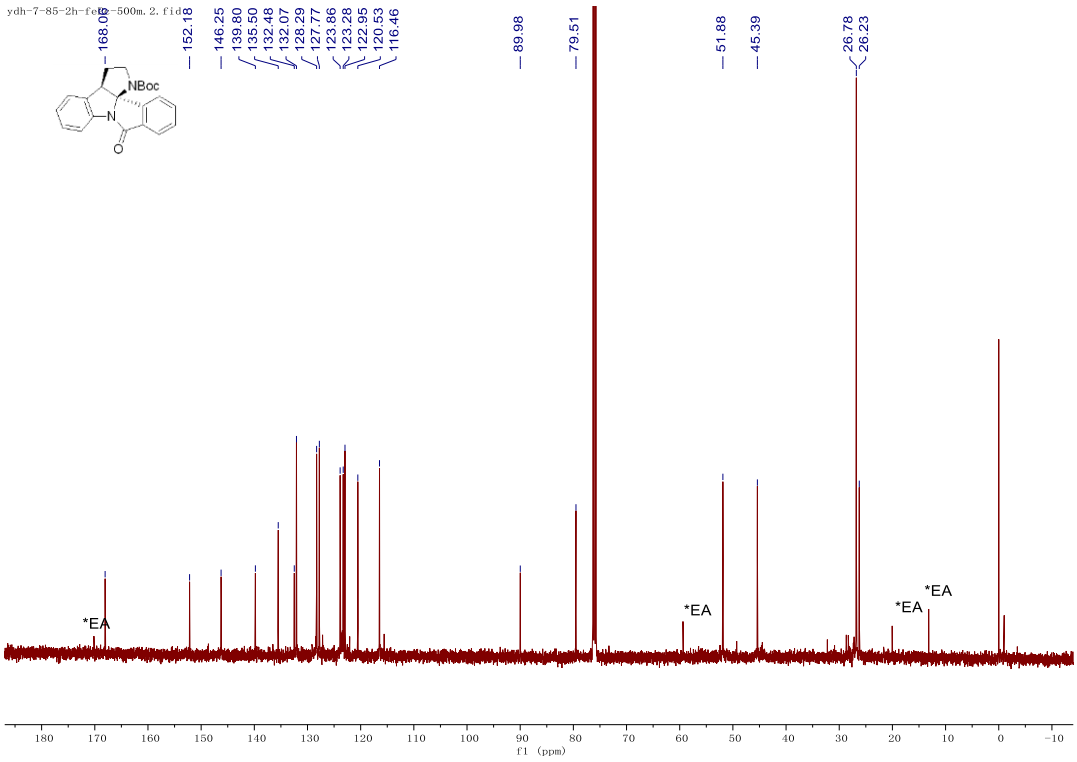
^{13}C NMR of 36



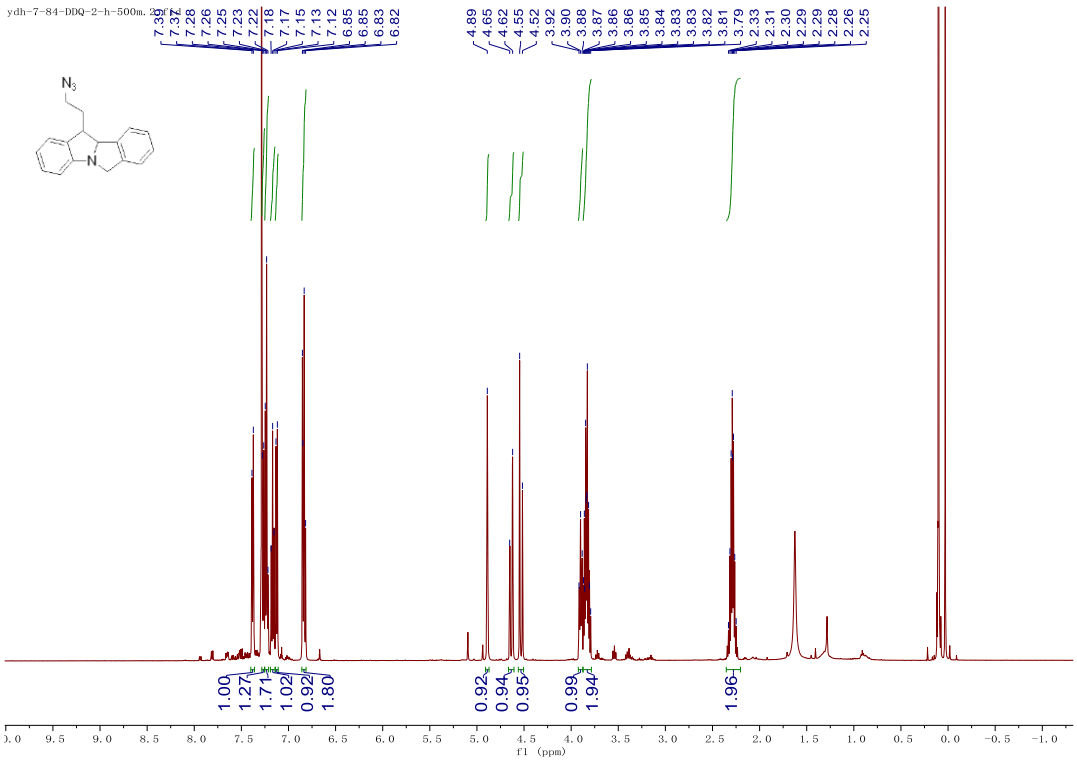
^{1}H NMR of 37



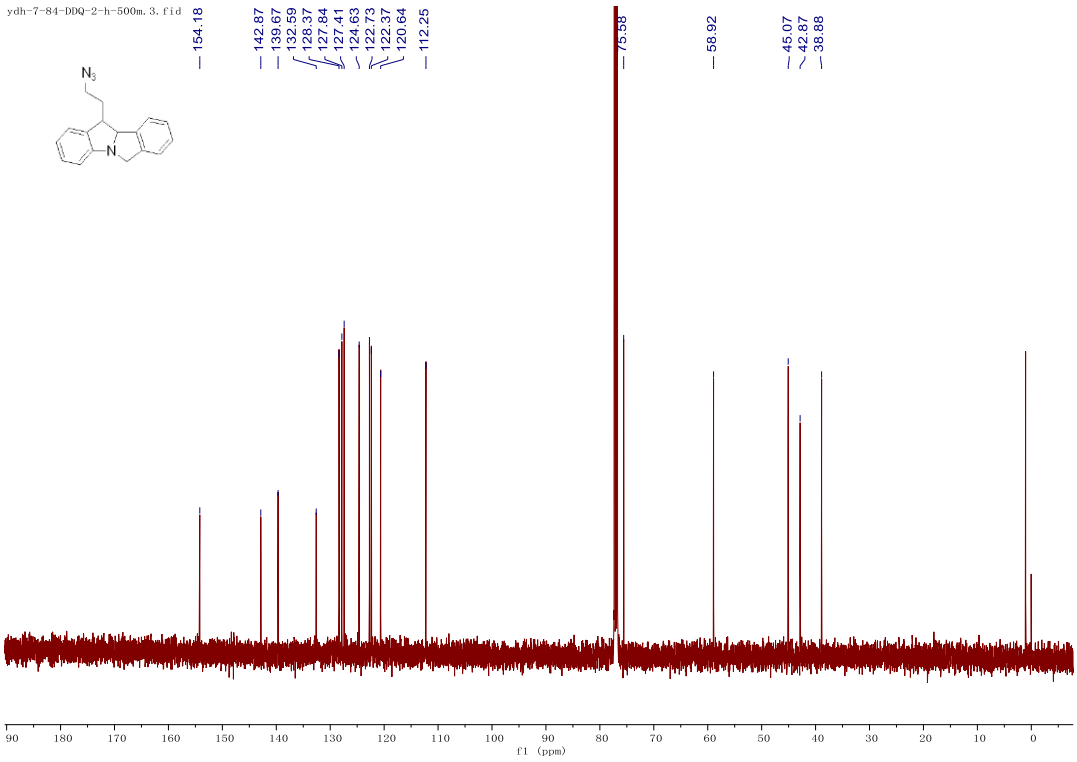
^{13}C NMR of 37



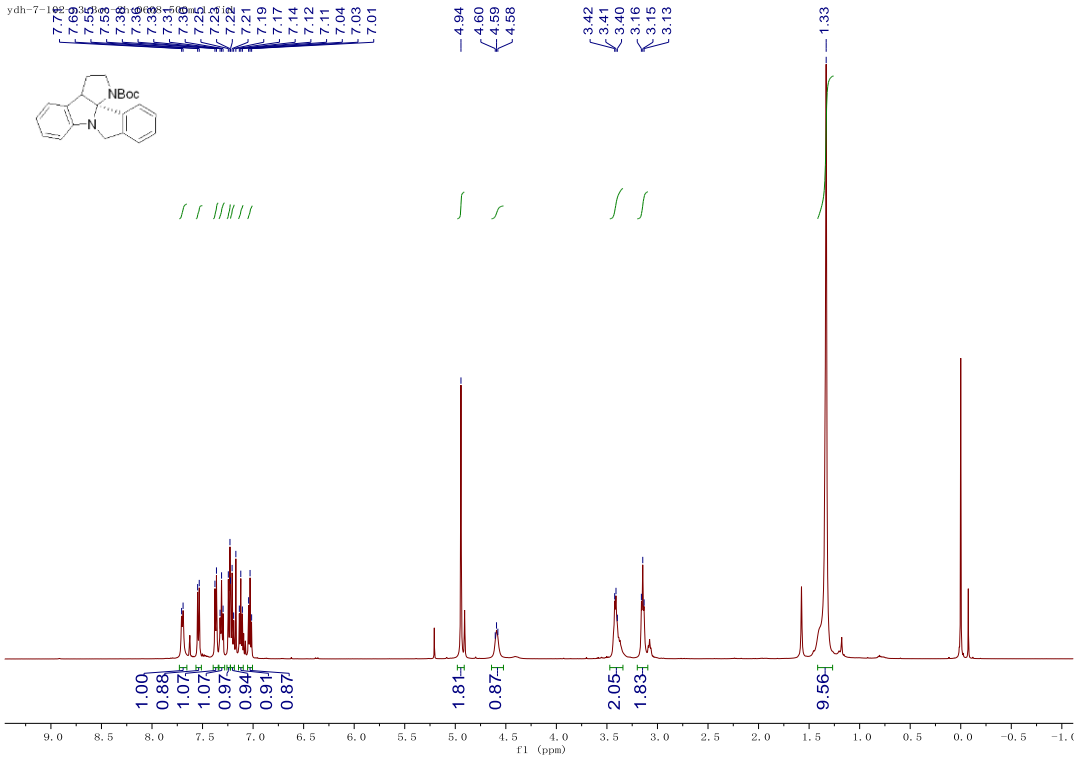
^{1}H NMR of 38



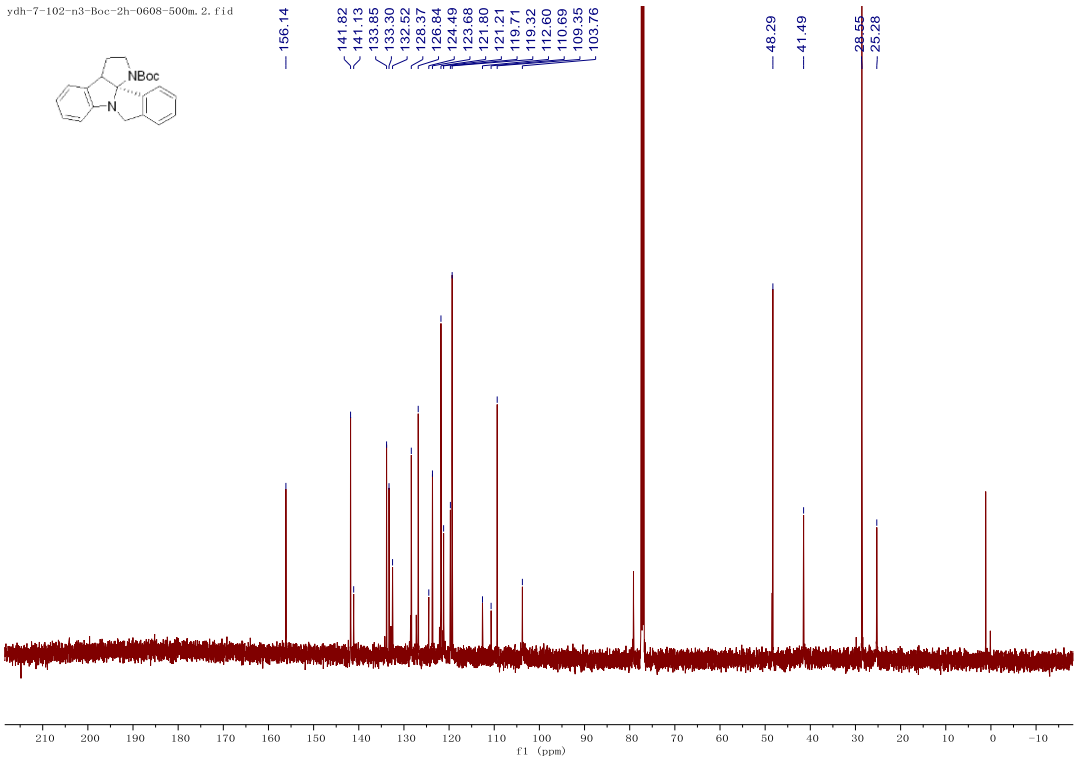
^{13}C NMR of 38



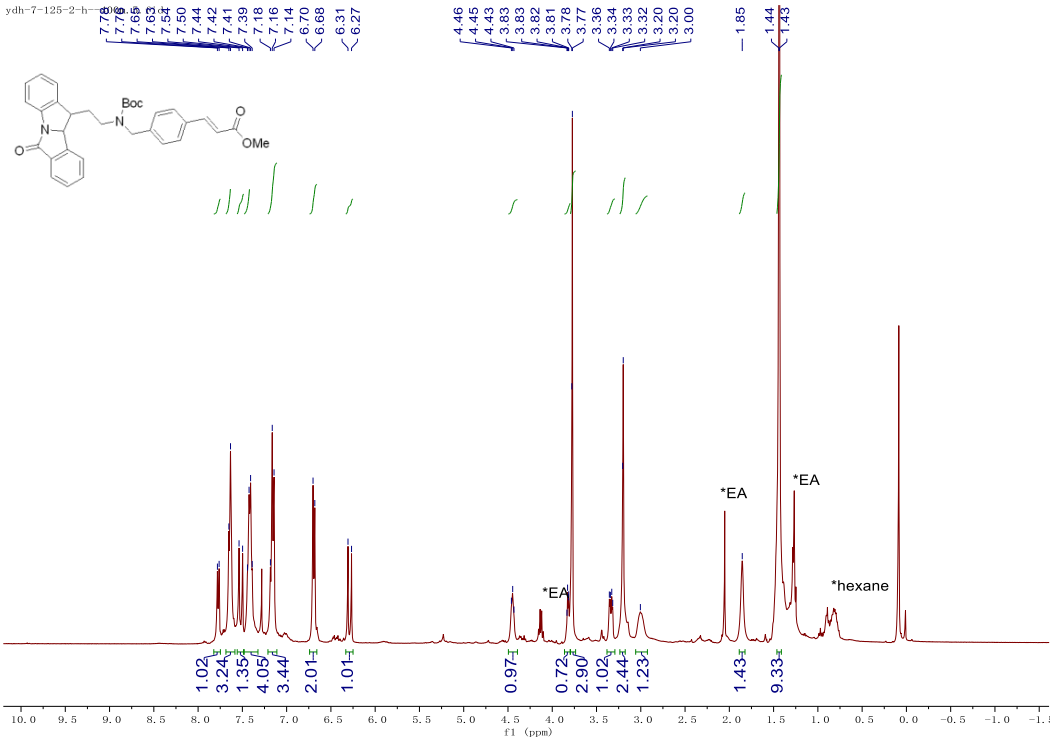
^{1}H NMR of 39



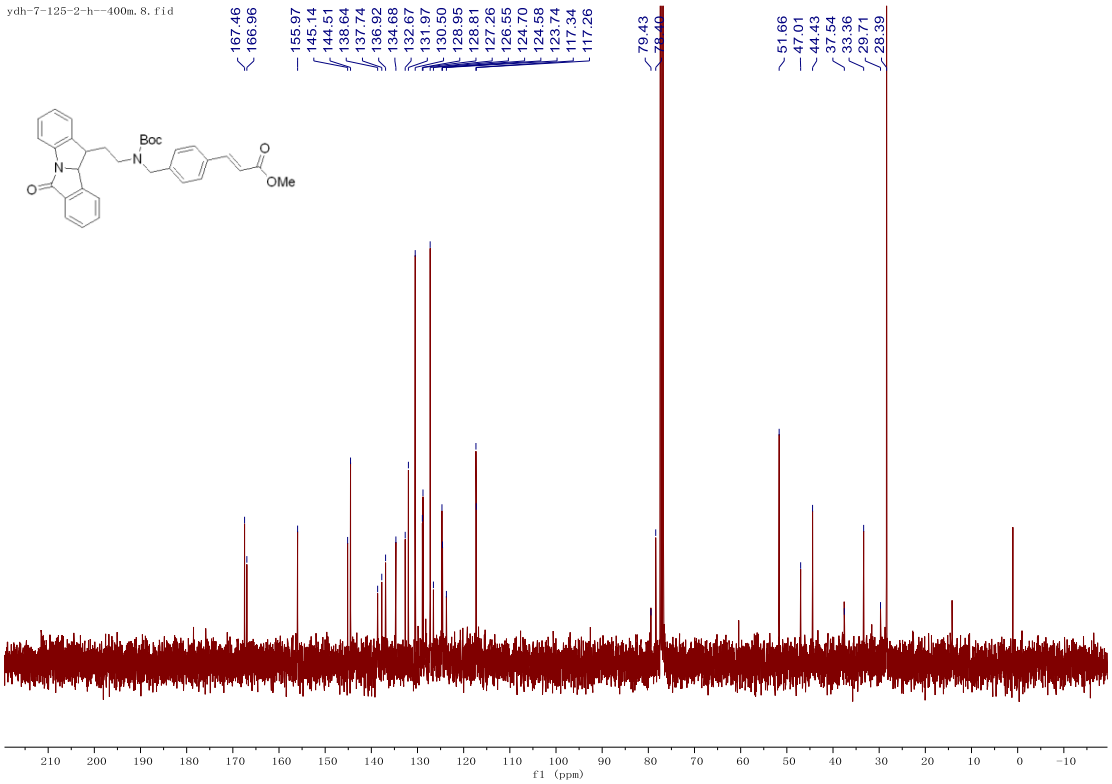
^{13}C NMR of 39



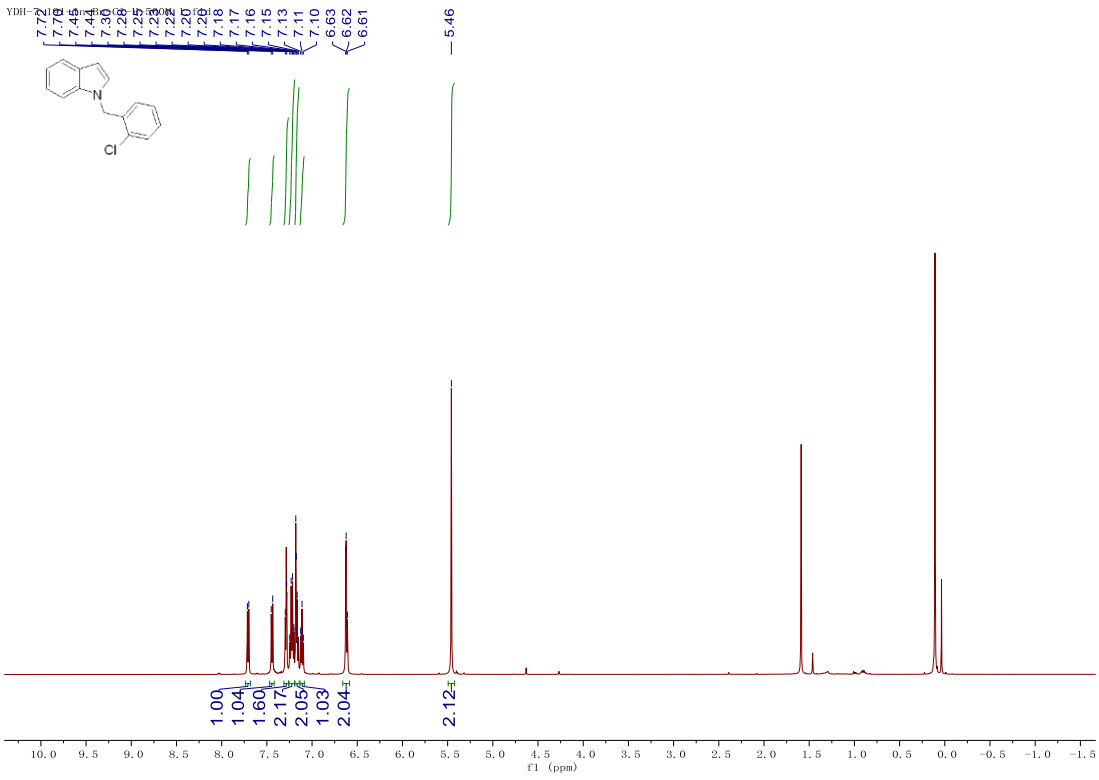
^{1}H NMR of 41



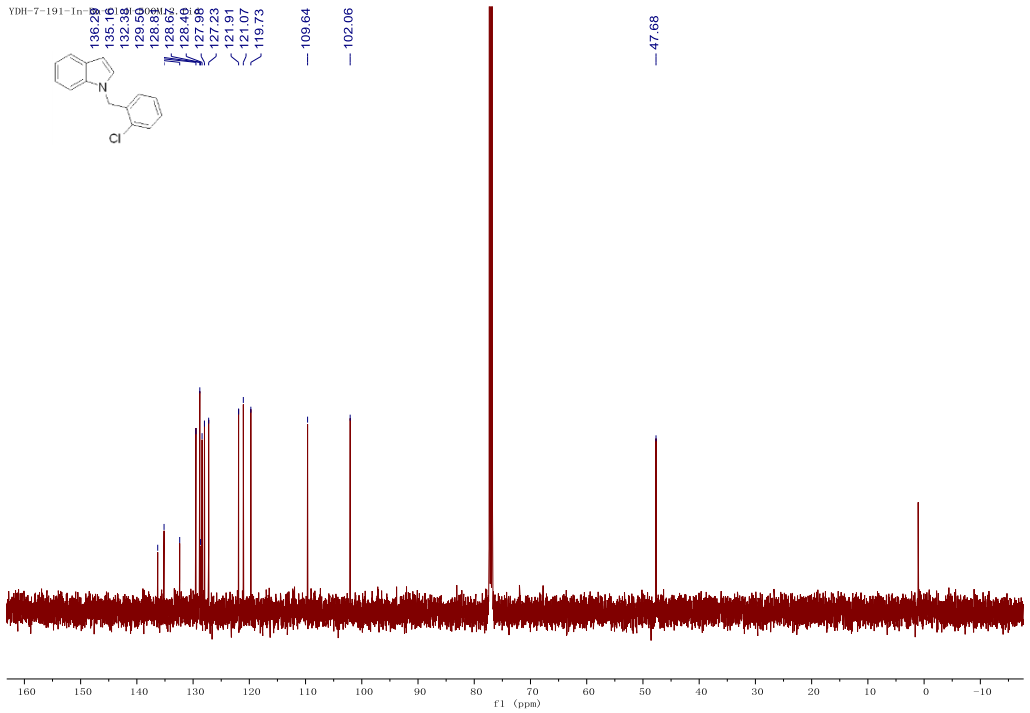
^{13}C NMR of 41



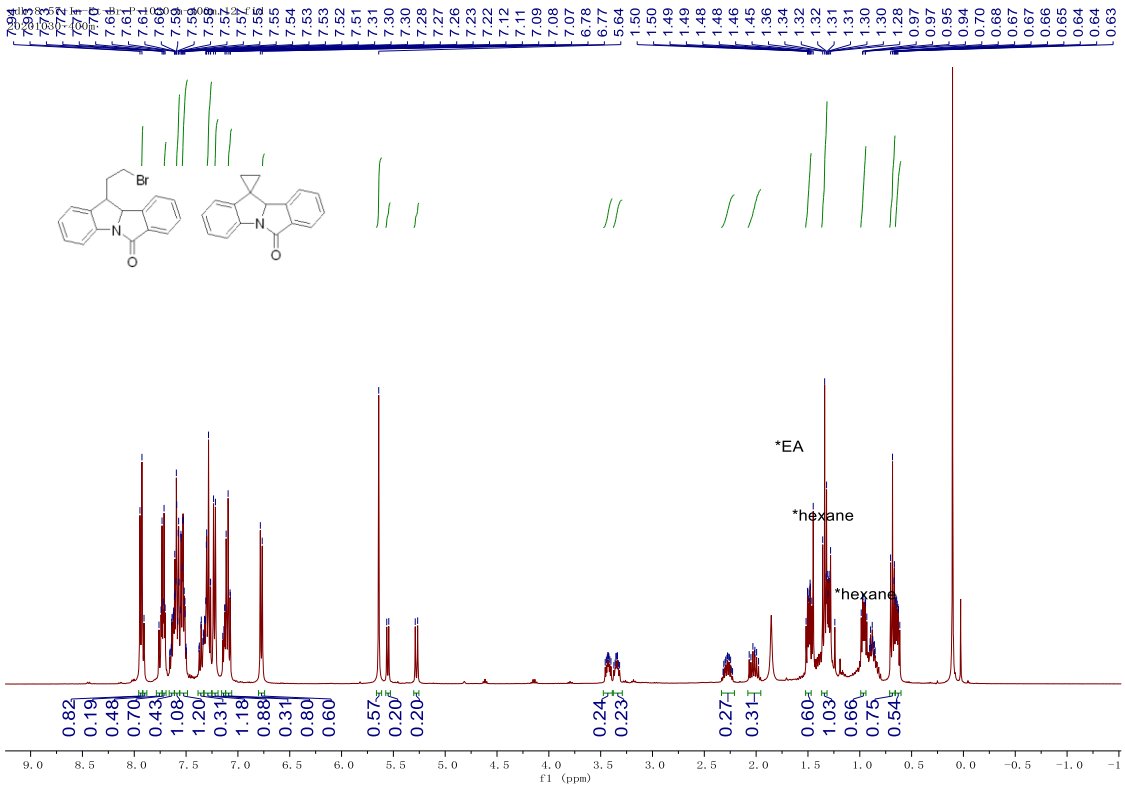
^{1}H NMR of 42



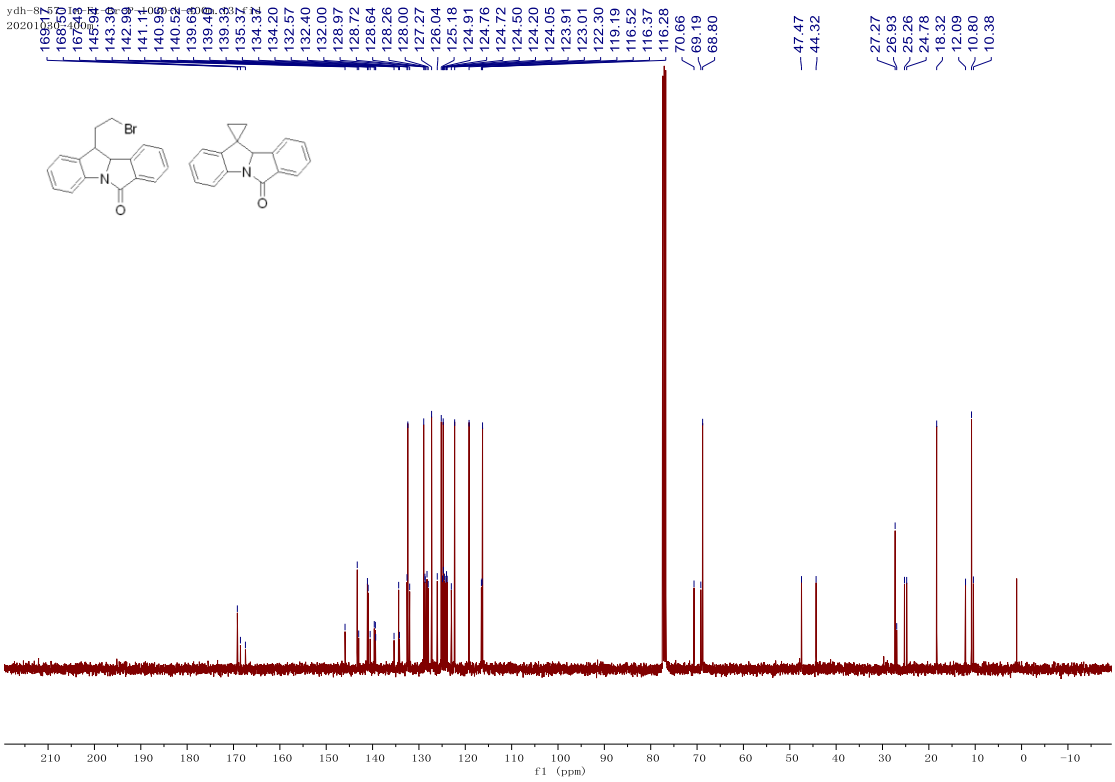
^{13}C NMR of 42



^{1}H NMR of 44 and 45



^{13}C NMR of 44 and 45



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