Supporting Information

Redox-neutral ketyl radical coupling/cyclization of carbonyls with N-aryl acrylamides through consecutive photoinduced electron transfer

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1. General information

The reactions via general procedure was carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AVANCE-III-HD (400 and 100 MHz, respectively) and processed using either MestReNova. ^{1}H NMR chemical shifts are given in ppm with respect to the residual $CDCl_3$ peak (δ 7.26 ppm), residual DMSO-d_6 (δ 2.50 ppm), or an internal TMS standard (δ 0.00 ppm), ^{13}C NMR shifts are given in ppm with respect to $CDCl_3$ (δ 77.00 ppm), DMSO-d_6 (δ 39.52 ppm). Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those in literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Fluorescence quenching experiments were recorded with PTI-QM40 spectrophotometer. A commercially available blue LED (35W, HIPAR30, luminous flux is not less than 3200 lm) was purchased from Shenzhen Jing Feng Times Lighting Technology Co., Ltd as the reaction light source. All irradiation reactions were carried out in borosilicate glass vessel. The distance from the light source to the irradiation vessel is around 4-5 cm. Unless otherwise noted, all other reagents were obtained from commercial suppliers and used without further purification. The organic photocatalysts 4DPAIPN, 3DPAClIPN, 4CzIPN, 4CzPN and 5CzBN were synthesized using reported procedures.[1] The substrates of amides and bioactive molecules were prepared according previous methods from literature.[2]

2. General procedure for the coupling cyclization reaction

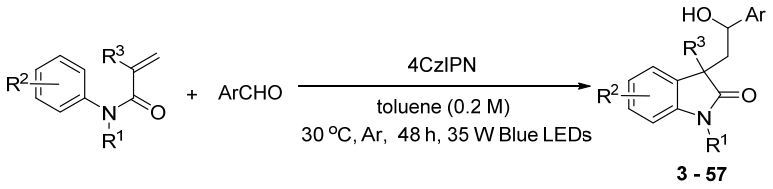


Figure S1

A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), amides (0.24 mmol, 1.2 equiv), and aromatic aldehydes (0.2 mmol, 1.0 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W blue LEDs at 30 ºC. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×10 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give the oxindole products **3-57**.

Scale-up experiment

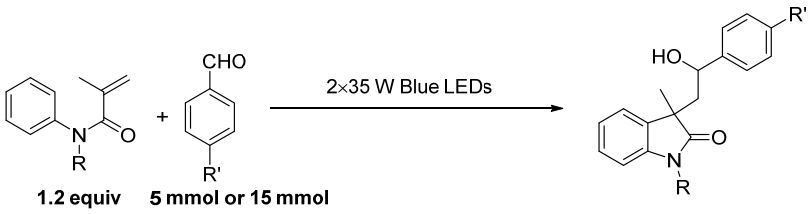


Figure S2

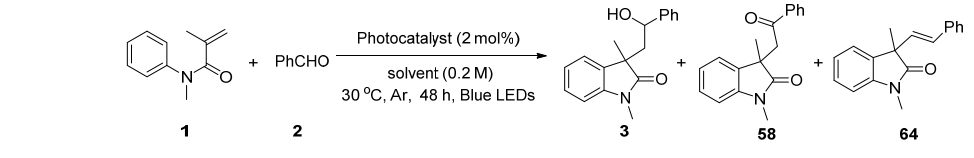
15 mmol scale reaction: A 250 mL oven-dried reaction vessel was charged with 4CzIPN (60 mg, 0.075 mmol, 0.5 mol%), *N*-methly-*N*-phenylmethacrylamide (3.32 g, 18 mmol, 1.2 equiv), PhCHO (1.60 mL, 15 mmol, 1.0 equiv) in 70 mL toluene under Ar atmosphere. The resulting mixture was stirred for 72 h under irradiation with 2 × 35 W blue LEDs at 30 ºC. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×100 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) to give the product **3** (3.329 g, 79% yield, 4.9:1 *dr*).

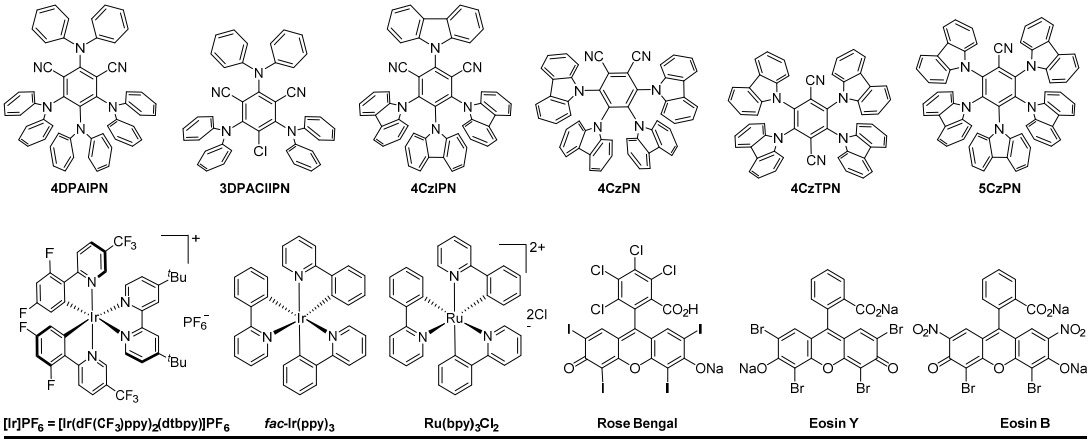
5 mmol scale reaction: A 100 mL oven-dried reaction vessel was charged with 4CzIPN (40 mg, 0.01 mmol, 1.0 mol%), amides (6 mmol, 1.2 equiv), aldehydes (5 mmol, 1.0 equiv) in 20 mL toluene under Ar atmosphere. The resulting mixture was stirred for 60 h under irradiation with 2 × 35 W blue LEDs at 30 ºC. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×50 mL). The

extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) to give products **12** (1.561 g, 91% yield, 4.5:1 *dr*) and **34** (1.314 g, 73% yield, 4.7:1 *dr*), respectivily.

2. Optimization of reaction conditions

Table S1.



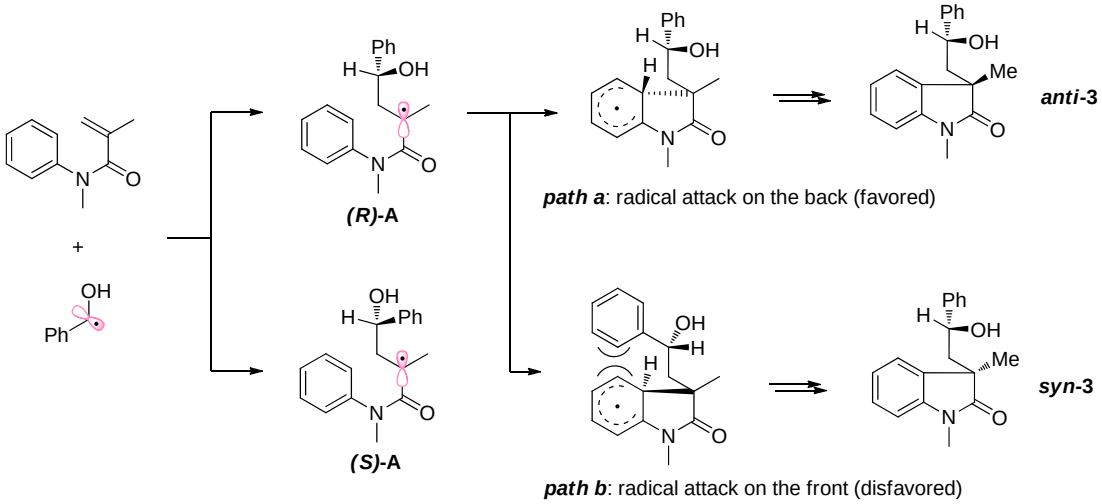


entry	**PC**	solvent	yield (%) [b]		
			3	**58**	**64**
1	**4DPAIPN**	toluene	trace	n.d.	n.d.
2	**3DPAClIPN**	toluene	n.d.	n.d.	n.d.
3	**4CzIPN**	toluene	94% (4.0:1 *dr*)	trace	trace
4	**4CzPN**	toluene	26%	n.d.	trace
5	**4CzTPN**	toluene	trace	8%	n.d.
6	**5CzBN**	toluene	68% (4.0:1 *dr*)	trace	10%
7	**[Ir]PF_6**	toluene	43% (4.0 :1 *dr*)	trace	18%
8	***fac*-Ir(ppy)$_3$**	toluene	trace	n.d.	n.d.
9	**Ru(bpy)$_3$Cl$_2$**	toluene	n.d.	n.d.	n.d.
10	**Rose bengal**	toluene	n.d.	n.d.	n.d.
11	**Eosin Y**	toluene	n.d.	n.d.	n.d.
12	**Eosin B**	toluene	trace	21%	n.d.
13	**4CzIPN**	mesitylene	84% (4.0:1 *dr*)	6%	trace
14	**4CzIPN**	*p*-xylene	87% (4.0:1 *dr*)	trace	trace
15	**4CzIPN**	cumene	trace	46%	n.d.
16	**4CzIPN**	PhCl	24% (4.0:1 *dr*)	trace	n.d.
17	**4CzIPN**	DCM	12%	n.d.	n.d.
18	**4CzIPN**	CH_3CN	n.d.	n.d.	n.d.
19	**4CzIPN**	acetone	19%	n.d.	17%
20	**4CzIPN**	CH_3OH	n.d.	n.d.	14%

21 [c]	**4CzIPN**	toluene	26% (4.0:1 *dr*)	n.d.	n.d.
22 [d]	**4CzIPN**	toluene	65% (4.0:1 *dr*)	trace	n.d.
23	–	toluene	n.d.	n.d.	n.d.
24 [e]	**4CzIPN**	toluene	n.d.	n.d.	n.d.
25 [f]	**4CzIPN**	toluene	93% (4.0:1 *dr*)	trace	trace
26 [g]	**4CzIPN**	toluene	44% (4.0:1 *dr*)	trace	trace

[a] Reaction conditions: **1** (1.2 equiv.), **2** (0.2 mmol), photocatalyst (2 mol%), solvent (0.2 M) at 30 °C under Ar atmosphere and 35 W blue LEDs irradiation for 48 h, *dr* = diastereomeric ratio. [b] Isolated yield. [c] 5 mol% DIPEA was added. [d] 5 mol% HOAc was added. [e] The reaction was carried out in the dark. [f] The reaction was carried out at 60 °C. [g] The reaction was carried out under air atmosphere.

Scheme S1. Analysis for the derivation of diastereomeric ratio (*dr*)



The radical attack of ketyl radical to alkene would form two isomer radical intermediates ***(R)*-A** and ***(S)*-A**. Taking ***(R)*-A** for example, the cyclization of it relies on the radical attack to the benzene ortho position, which would have two directions, on the back and on the front. Obviously, the radical attach on the back has less steric hindrance effect, which would lead to the formation of the isomer of ***anti*-3**.

3. Mechanistic studies

3.1 Radical trapping experiments

(i) The following reaction was carried out under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), *N*-methyl-*N*-phenylmethacrylamide **1** (42 mg, 0.24 mmol, 1.2 equiv), benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.8 mg, 0.4 mmol, 2 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. After completion, the crude residues were analyzed by GC-MS and HRMS. TEMPO-trapped product was not detected by GC-MS and the formation of product **3** was

completely suppressed.

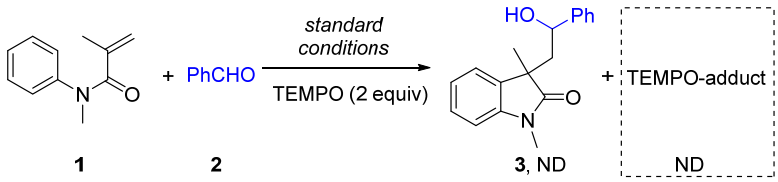
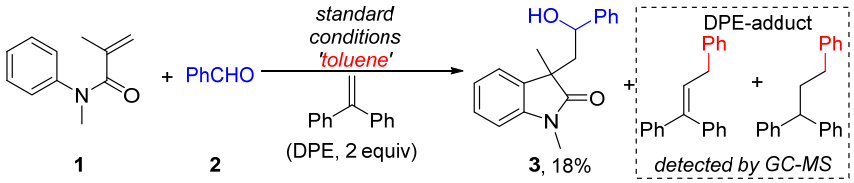
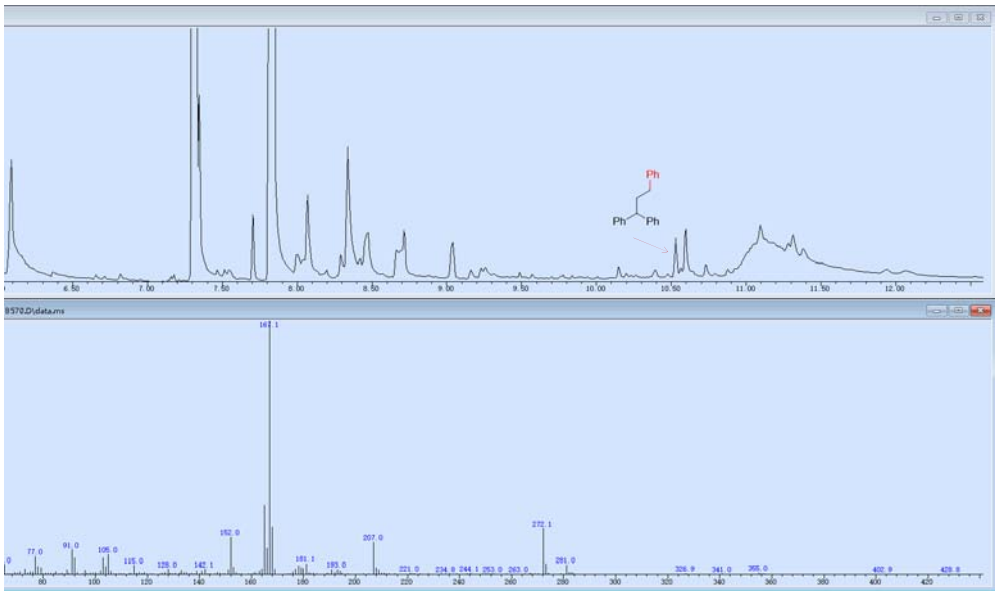


Figure S3

(ii) The following reaction was carried out under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), *N*-methyl-*N*-phenylmethacrylamide **1** (42 mg, 0.24 mmol, 1.2 equiv), benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) and 1,1-diphenylethene (DPE) (71 uL, 0.4 mmol, 2 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. After completion, the crude residues were analyzed by GC-MS. Yield of **3** was reduced to 18% and DPE-trapped products were detected by GC-MS.





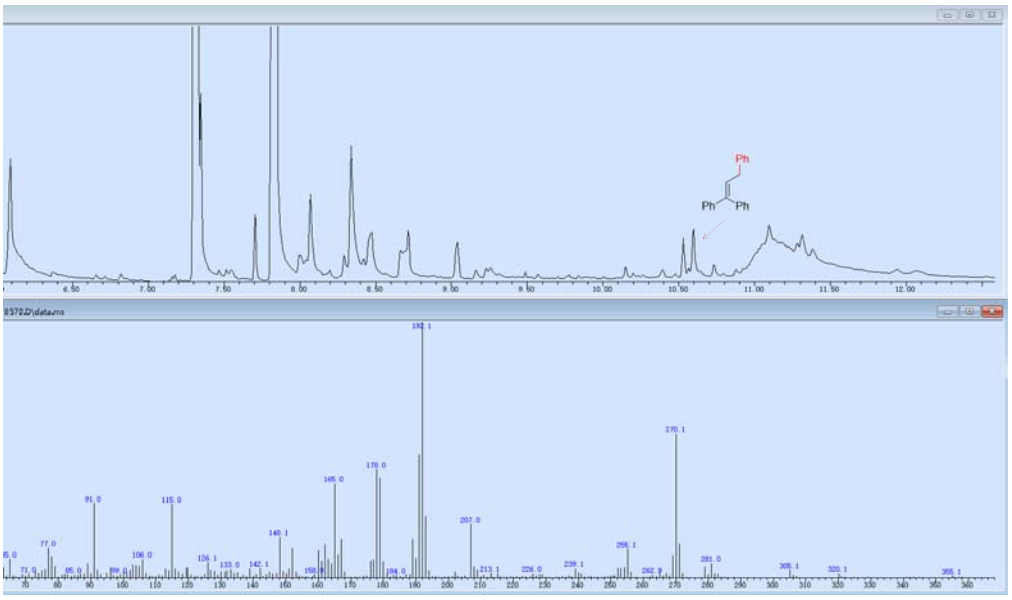
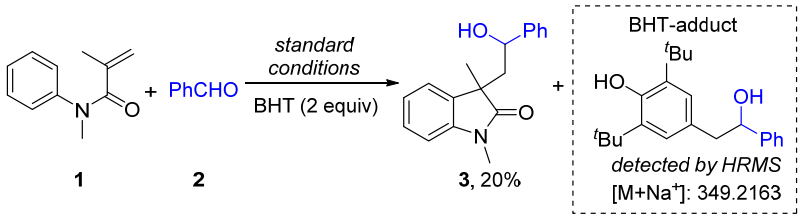


Figure S4

(iii) The following reaction was carried out under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), *N*-methyl-*N*-phenylmethacrylamide **1** (42 mg, 0.24 mmol, 1.2 equiv), benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) and butylated hydroxytoluene (BHT) (88.2 mg, 0.4 mmol, 2 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. After completion, the crude residues were analyzed by GC-MS and HRMS. Yield of **3** was reduced to 20% and BHT-trapped products were detected by HRMS.



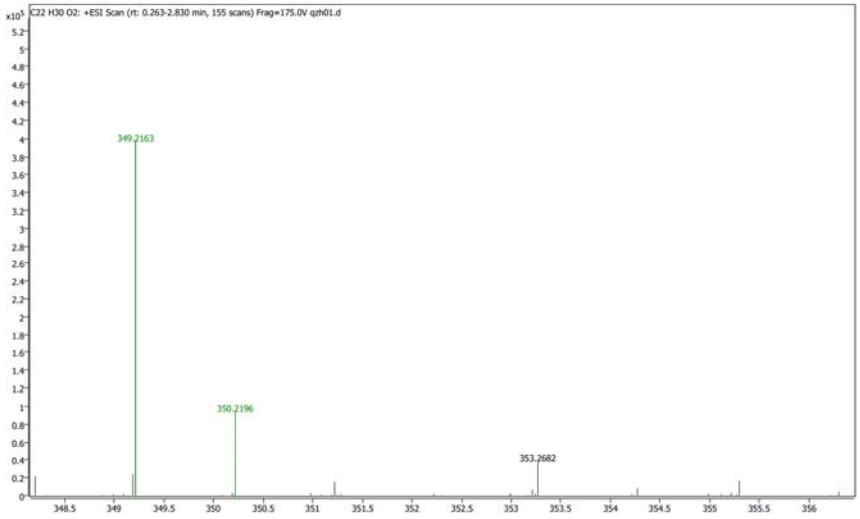
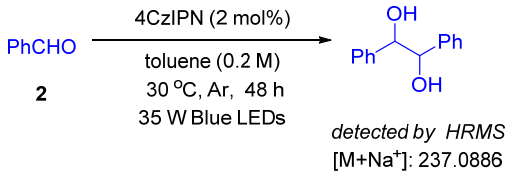


Figure S5

3.2 Control experiments

(i) The following reaction was carried out under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), and benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. After completion, the crude residues were analyzed by GC-MS and HRMS. The homocoupling product 1,2-diphenylethane-1,2-diol was detected by HRMS.



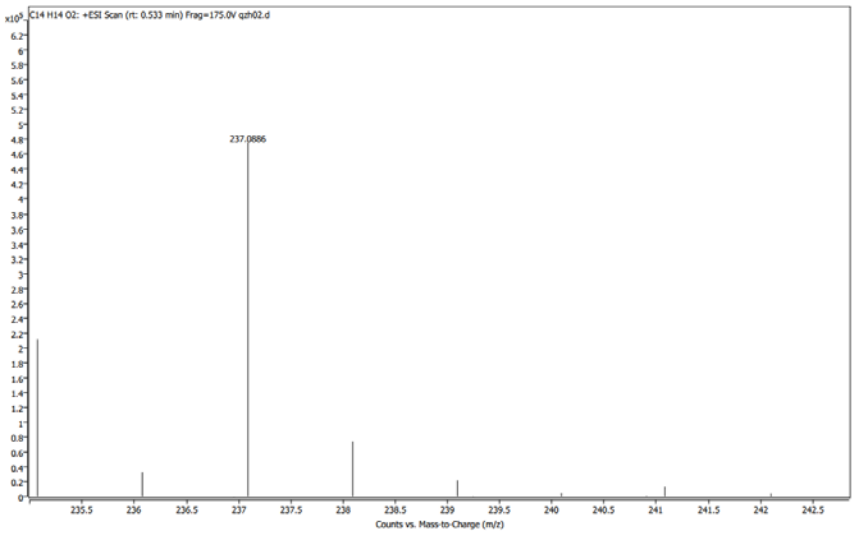
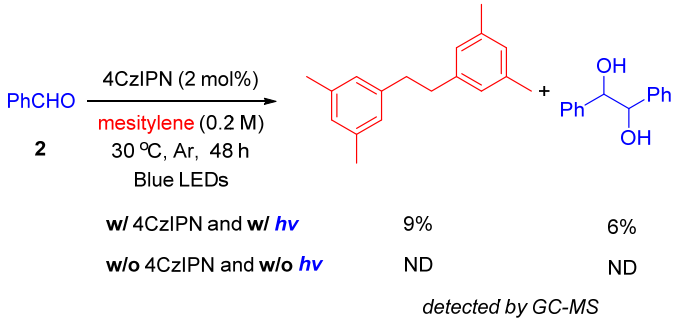


Figure S6

(ii) A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), and benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) in 1.0 mL mesitylene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. After completion, the crude residues were analyzed by GC-MS. The corresponding homocoupling products 1,2-bis(3,5-dimethylphenyl)ethane and 1,2-diphenylethane-1,2-diol were all detected by GC-MS. When the reaction was carried out by using 4CzIPN-free and no light coditions, The corresponding homocoupling products 1,2-bis(3,5-dimethylphenyl)ethane and 1,2-diphenylethane-1,2-diol were not detected by GC-MS.



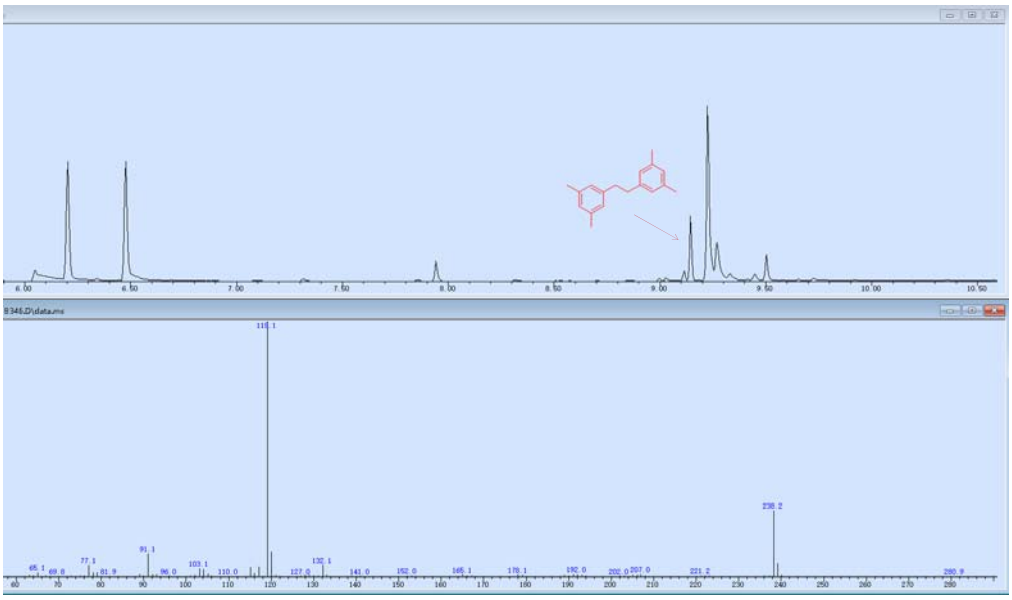
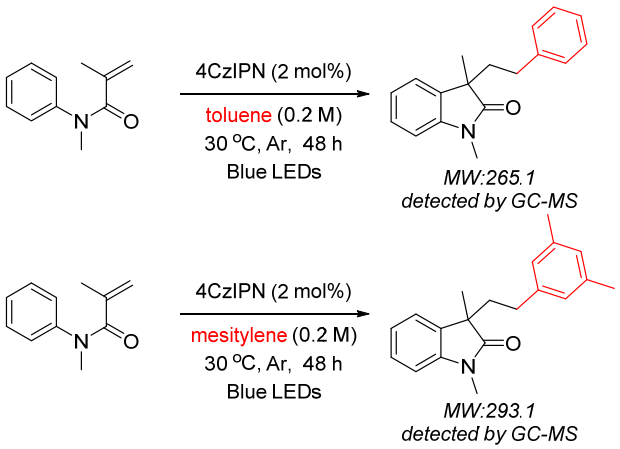


Figure S7

(iii) A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%) and *N*-methyl-*N*-phenylmethacrylamide **1** (35 mg, 0.2 mmol) in 1.0 mL toluene or mesitylene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. After completion, the crude residues were analyzed by GC-MS. The corresponding products of benzyl radical addition to *N*-methyl-*N*-phenylmethacrylamide **1** could be detected by GCMS.



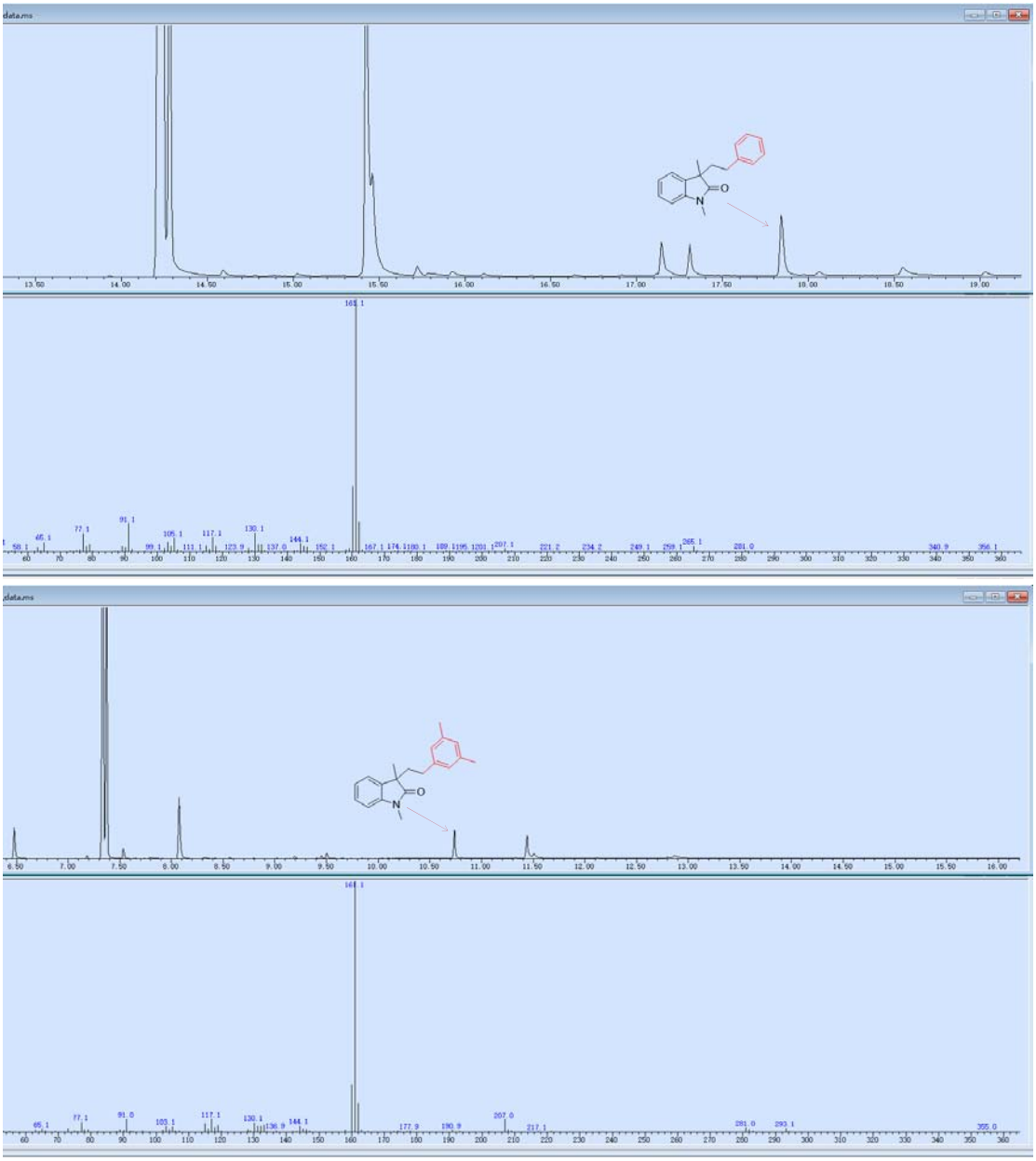
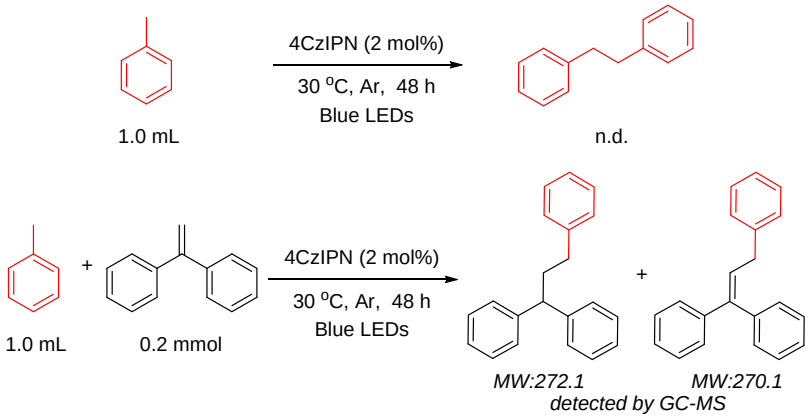
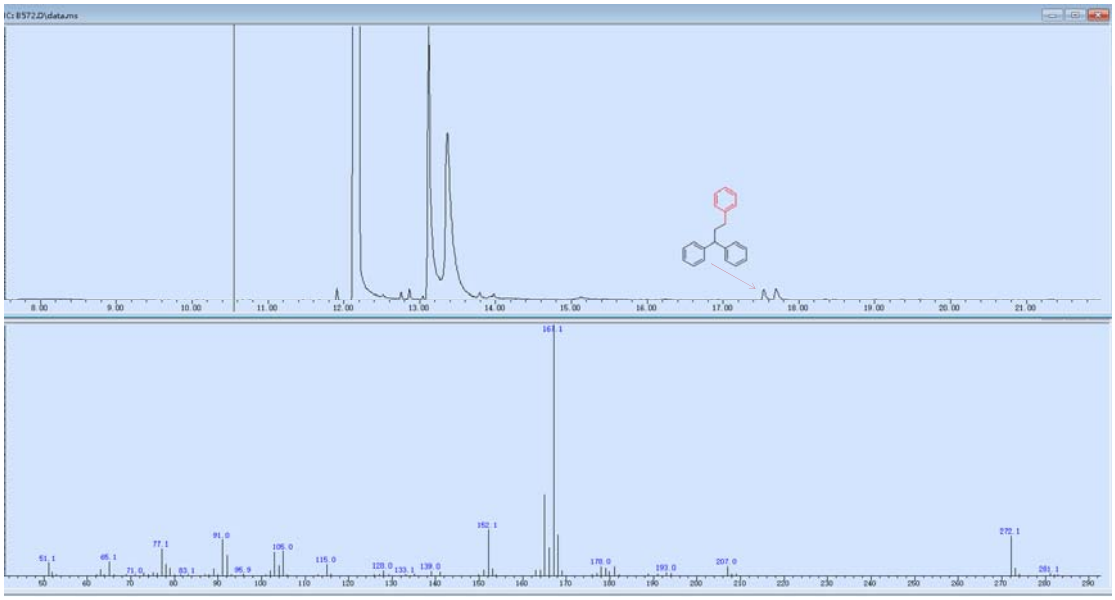


Figure S8

(iv) A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%) and 1.0 mL toluene under Ar atmosphere. Another 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%) and ethene-1,1-diyldibenzene (DPE, 0.2 mmol) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. After completion, the crude residues were analyzed by GC-MS. The coupling product 1,2-diphenylethane was not detected due to the strong activity of the benzyl radical by GC-MS. However, the benzyl radical could be captured by DPE and the experimental results were shown Figure S9.


4CzIPN (2 mol%)
30 °C, Ar, 48 h
Blue LEDs
1.0 mL
n.d.
4CzIPN (2 mol%)
30 °C, Ar, 48 h
Blue LEDs
1.0 mL
0.2 mmol
MW:272.1
MW:270.1
detected by GC-MS



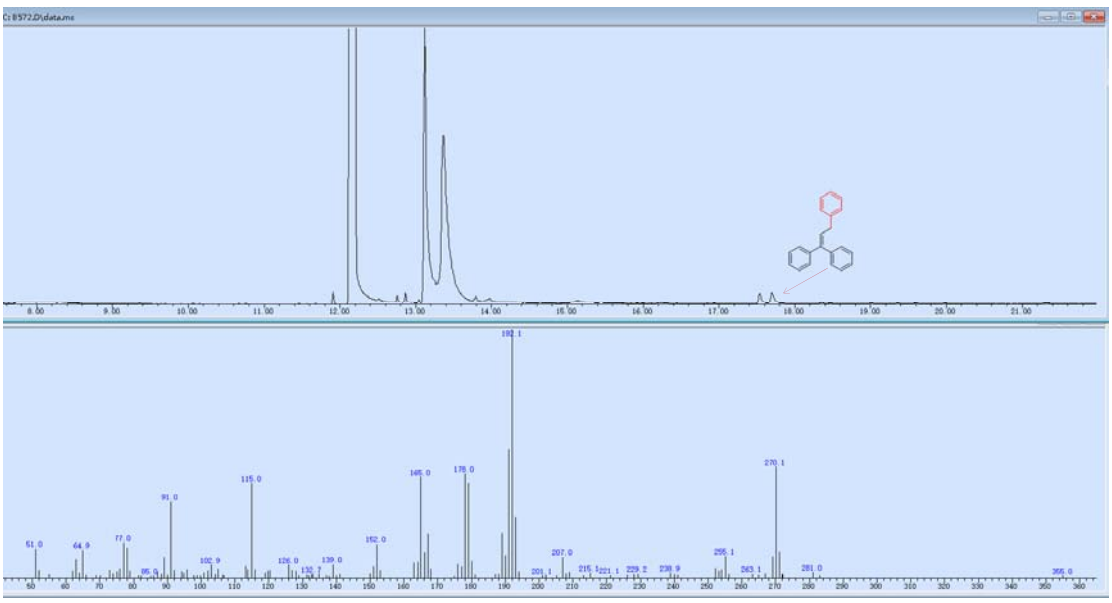


Figure S9

3.3 H/D exchange and KIE experiments

(i) Using **1-D$_5$** under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), **1-D$_5$** (43.2 mg, 0.24 mmol, 1.2 equiv), benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×10 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give hydroxylation product **3-D$_4$** (92% yield, 5:1 *dr*).

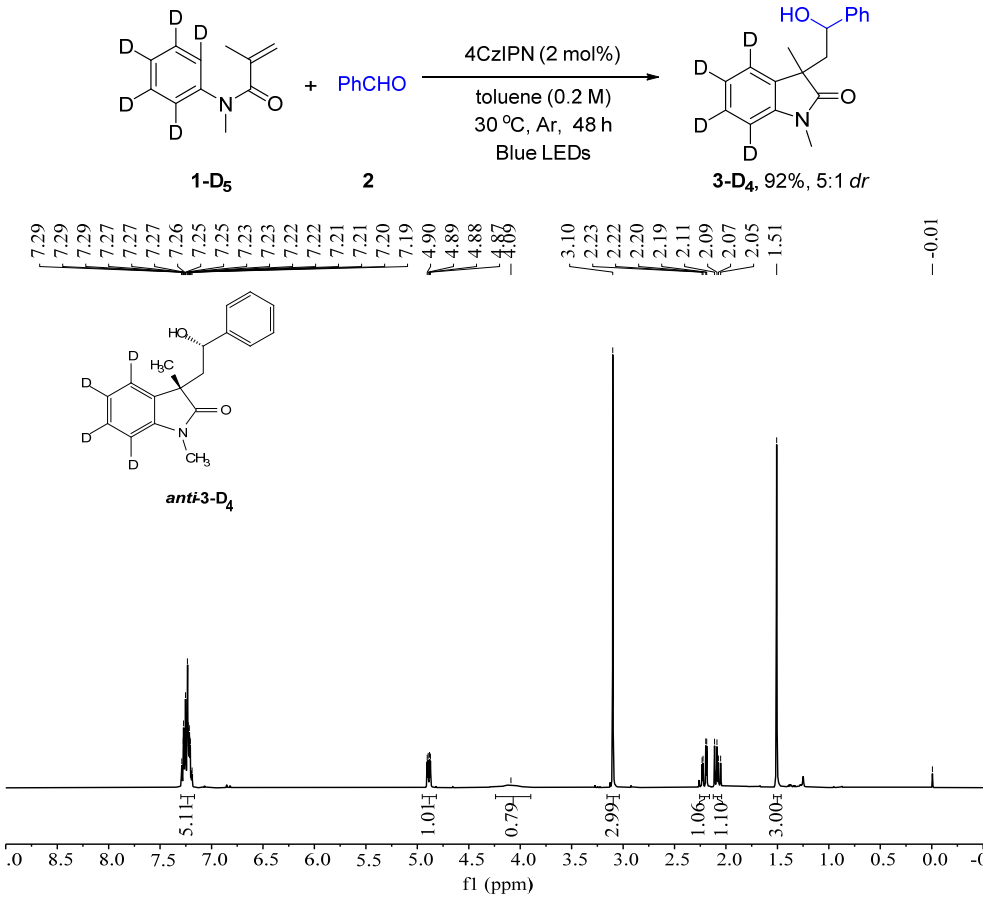


Figure S10

(ii) Using **PhCDO** (**2-D**) under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), *N*-methyl-*N*-phenylmethacrylamide **1** (42.0 mg, 0.24 mmol, 1.2 equiv), deuterated benzaldehyde **2-D** (21 uL, 0.2 mmol, 1.0 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 48 h under irradiation with a 35 W Blue LEDs at 30 ºC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×10 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give hydroxylation product **3-D** (89% yield, 4:1 *dr*).

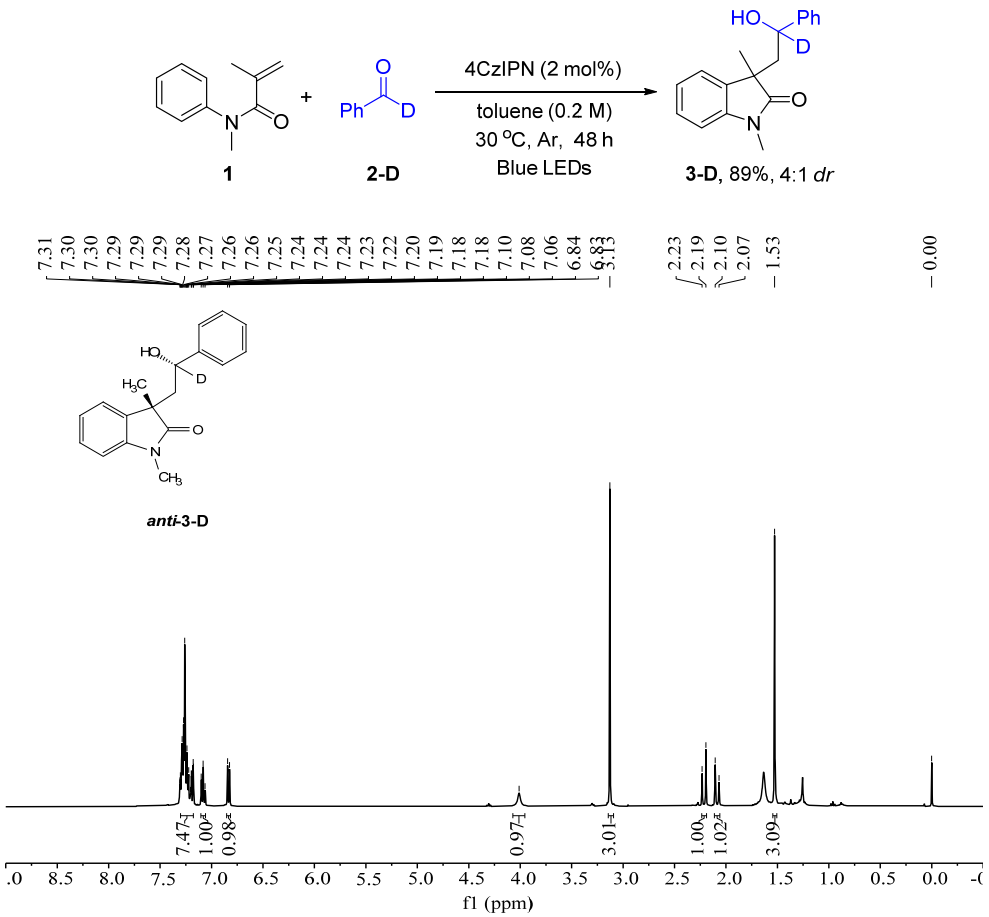


Figure S11

(iii) Two parallel reactions of **1** or **1-D$_5$** were performed under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%), **1** (42.0 mg, 0.24 mmol, 1.2 equiv) or **1-D$_5$** (43.2 mg, 0.24 mmol, 1.2 equiv), benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) in 1.0 mL toluene under Ar atmosphere. The resulting mixture was stirred for 3 h under irradiation with a 35 W Blue LEDs at 30 ºC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×10 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Yield determined by GC analysis of the crude reaction mixture using dodecane as the internal standard, and obtained **3** or **3-D$_4$** in 16% and 13% yields, respectively (k_H/k_D=1.2).

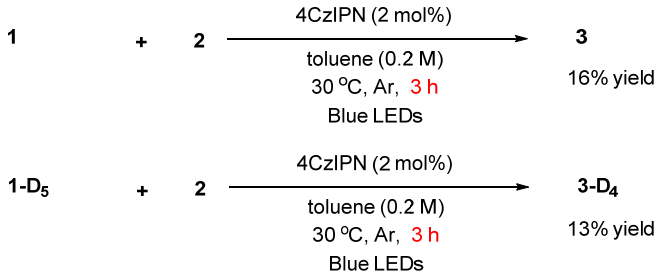


Figure S12

(iv) Two parallel reactions of **toluene** or **toluene-d$_8$** were performed under standard conditions: A 20 mL reaction vessel was charged with 4CzIPN (3.2 mg, 0.004 mmol, 2 mol%),

N-methyl-*N*-phenylmethacrylamide **1** (42.0 mg, 0.24 mmol, 1.2 equiv), benzaldehyde **2** (21 uL, 0.2 mmol, 1.0 equiv) in 1.0 mL **toluene** or **toluene-d_8** under Ar atmosphere. The resulting mixture was stirred for 3 h under irradiation with a 35 W Blue LEDs at 30 ºC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with dichloromethane (3×10 mL). The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. Yield determined by GC analysis of the crude reaction mixture using dodecane as the internal standard, and obtained **3** in 18% and 15% yields, respectively (k_H/k_D=1.2).

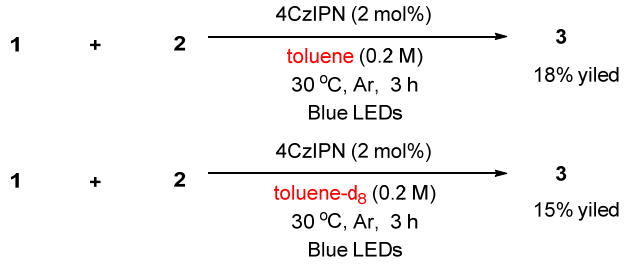


Figure S13

3.4 Spectroscopic experiments.

(i) 4CzIPN photo-degradation: UV-VIS analysis was performed on an Agilent Cary 60 spectrophotometer. Experiments were recorded using a cuvette equipped with septa-lined screw cap. A sample containing 4CzIPN (10 μM) in degassed CH_3CN was placed in the dark while recording UV-VIS spectra (Figure S14, left). Subsequently, the sample was irradiated using a 456 nm LED for 5 min while recording UV-VIS spectra at defined times after start of the irradiation (Figure S14, left). Another sample containing 4CzIPN (10 μM) in degassed toluene was placed in the dark while recording UV-VIS spectra (Figure S14, right). Then, the sample was irradiated using a 456 nm LED for 5 min while recording UV-VIS spectra at defined times after start of the irradiation (Figure S14, right). The data shows, that the photo-degradation of 4CzIPN is existed in the presence of toluene, indicating a photoreaction between 4CzIPN and the toluene.

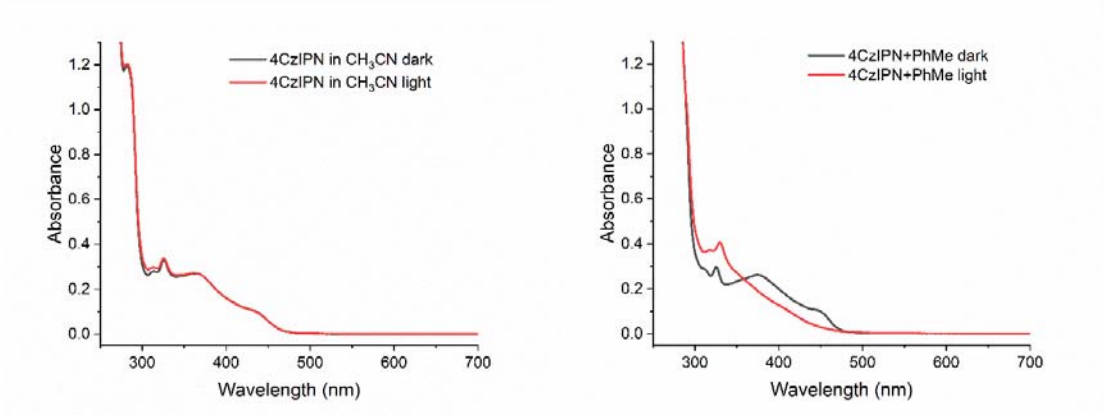


Figure S14. Left: UV-VIS online measurement of a sample containing 4CzIPN (10 μM) in degassed CH_3CN. Right: UV-VIS online measurement of a sample containing 4CzIPN (10 μM) in degassed PhMe. Light: irradiation with 456 nm for 5 min.

(ii) Emission profile for 4CzIPN+toluene in CH_3CN: A sample containing 4CzIPN (10 μM)

and toluene (0.3 M) in degassed CH_3CN was placed in the dark while recording fluorescence emission spectra (Figure S15, left). Subsequently, the sample was irradiated using a 456 nm LED for 5 min, while recording fluorescence emission spectra at defined times after start of the irradiation (Figure S15, left).

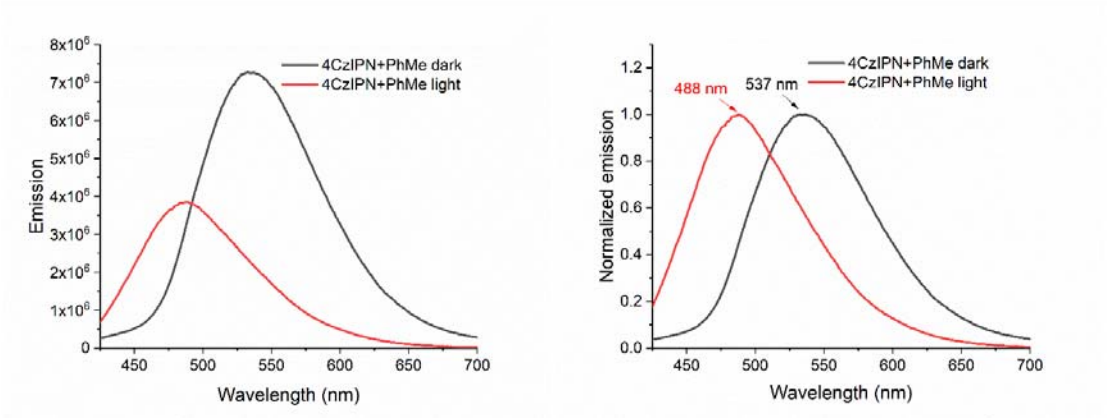


Figure S15. Left: emission profile for 4CzIPN (10 μM) and PhMe (0.3 M) in degassed CH_3CN. Right: normalized emission profile for 4CzIPN (10 μM) and PhMe (0.3 M) in degassed CH_3CN. Light: irradiation with 456 nm for 5 min.

(iii) Emission profile for 4CzIPN in toluene: A sample containing 4CzIPN (2.0×10^{-7} M) in degassed toluene was irradiated using a 456 nm LED for 22 s, while recording fluorescence emission spectra at defined times after start of the irradiation (Figure S16).

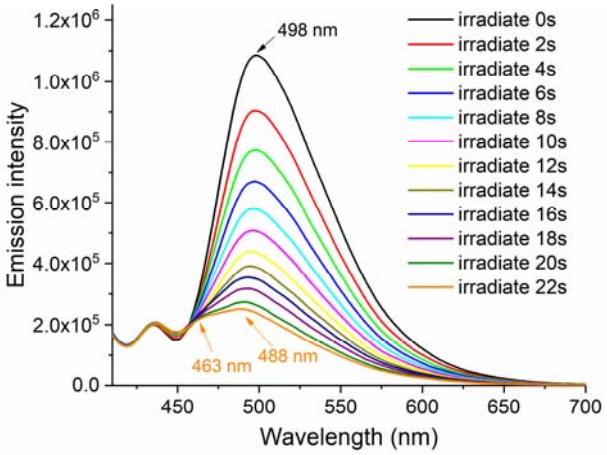


Figure S16. Emission profile for 4CzIPN in toluene

(iv) Emission profile for 4CzIPN in different solvent: A series of sample containing 4CzIPN (2.0×10^{-7} M) in different solvents were formulated and then recorded fluorescence emission spectra, respectively (Figure S17).

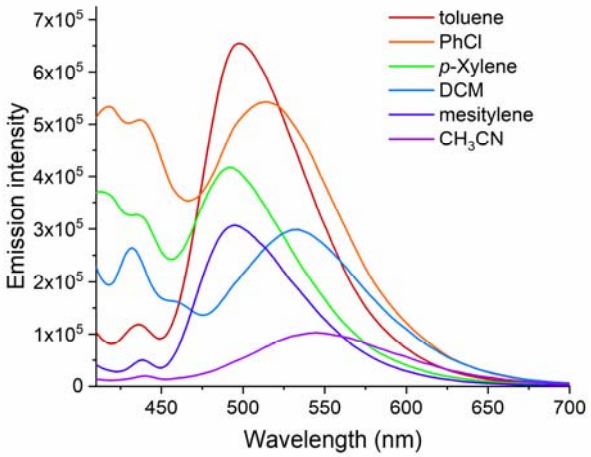


Figure S17. Emission profile of 4CzIPN (2.0×10^{-7} M) in different solvent

(v) Stern-Volmer quenching

Formulation solution: *N*-methyl-*N*-phenylmethacrylamide (**1**, 175 mg) was dissolved in toluene in a 5 mL volumetric flask to set the concentration to be 0.2 M. PhCHO (**2**, 106 mg) was dissolved in toluene in a 5 mL volumetric flask to set the concentration to be 0.2 M. Photocatalyst 4CzIPN (2 mg) was dissolved in toluene (25.0 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 mM solution (4 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding toluene to prepare a 0.2 μM solution. The resulting mixture was sparged with argon for 3 minutes and then irradiated at 390 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 20.0 μL of a *N*-methyl-*N*-phenylmethacrylamide solution was successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 3 minutes and irradiated at 390 nm. Fluorescence emission spectra of 0 μL, 20.0 μL, 40.0 μL, 60.0 μL, 80.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The results were shown in the following figures.

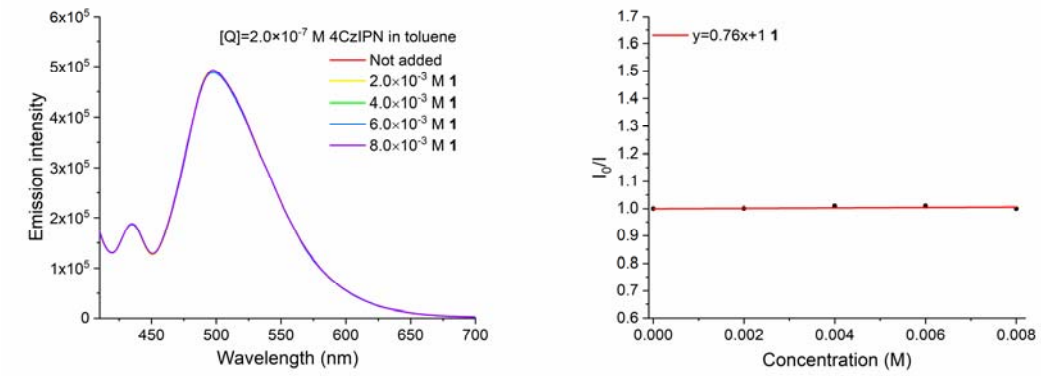


Figure S18. Emission quenching of 4CzIPN with *N*-methyl-*N*-phenylmethacrylamide (**1**) in toluene

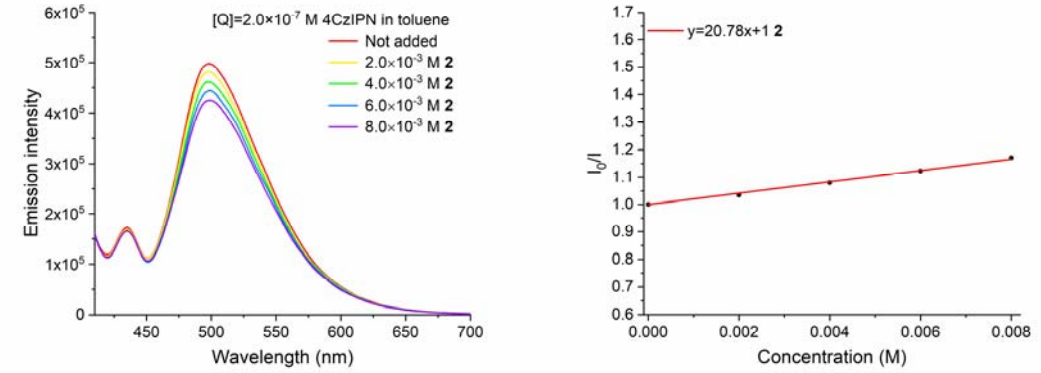


Figure S19. Emission quenching of 4CzIPN with PhCHO (**2**) in toluene

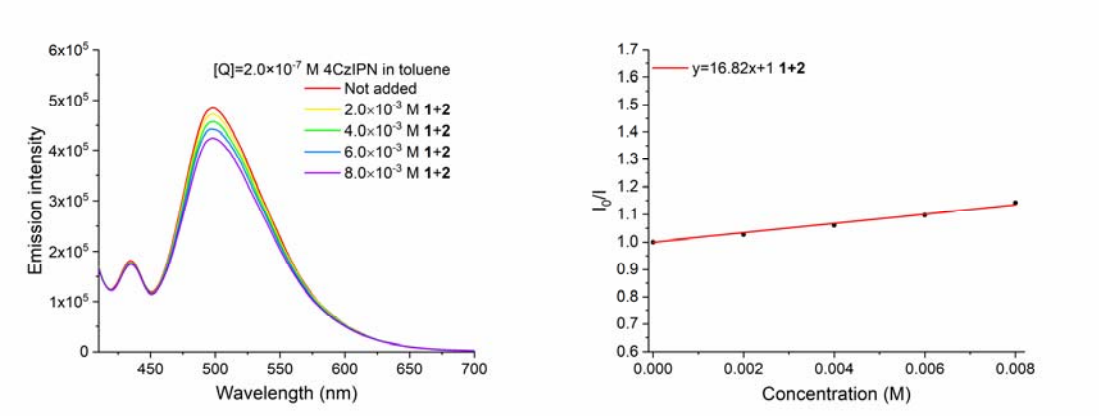


Figure S20. Emission quenching of 4CzIPN with *N*-methyl-*N*-phenylmethacrylamide (**1**) + PhCHO (**2**) in toluene

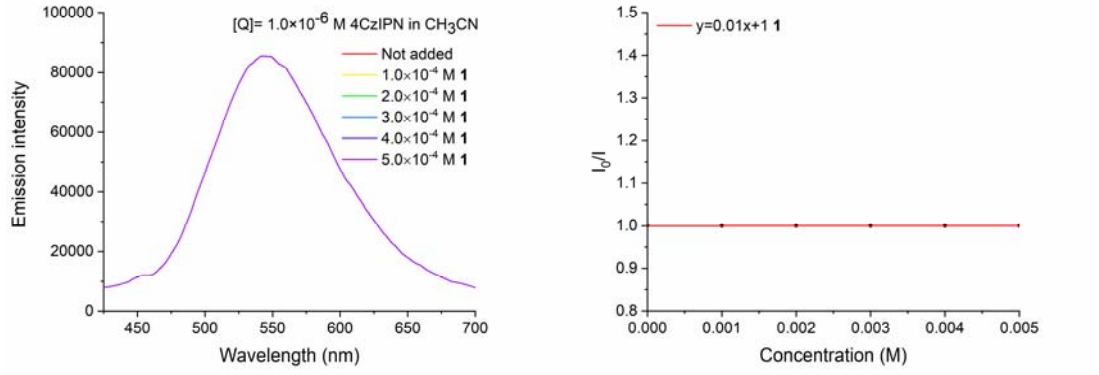


Figure S21. Emission quenching of 4CzIPN with *N*-methyl-*N*-phenylmethacrylamide (**1**) in CH_3CN

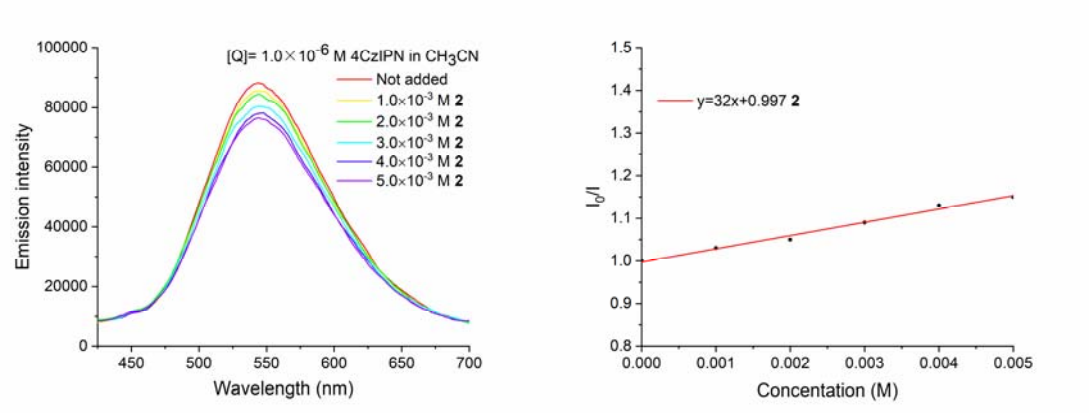


Figure S22. Emission quenching of 4CzIPN with PhCHO (**2**) in CH_3CN

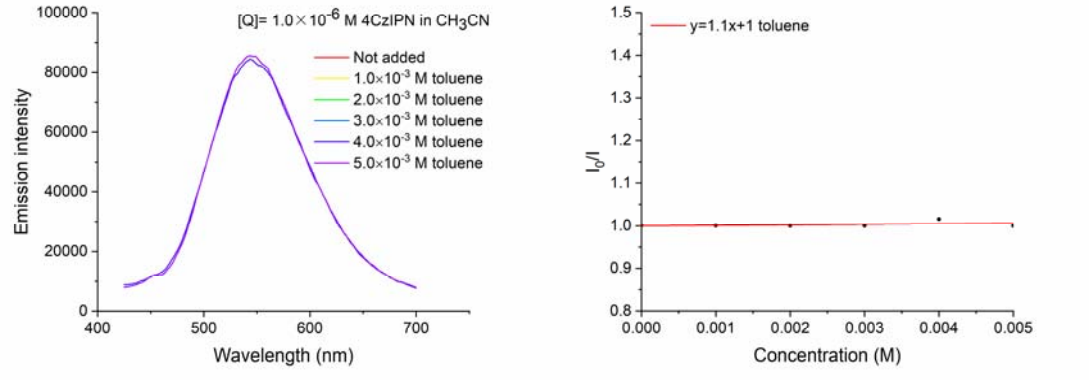


Figure S23. Emission quenching of 4CzIPN with toluene (10^{-3} M) in CH_3CN

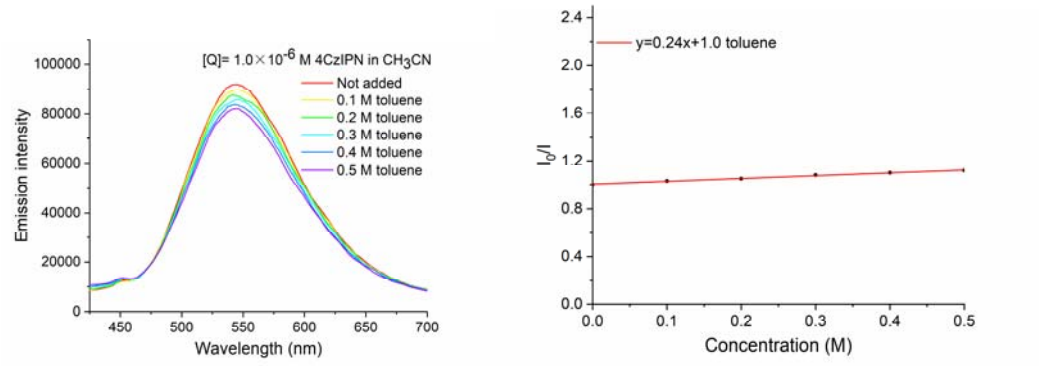


Figure S24. Emission quenching of 4CzIPN with toluene (10^{-1} M) in CH_3CN

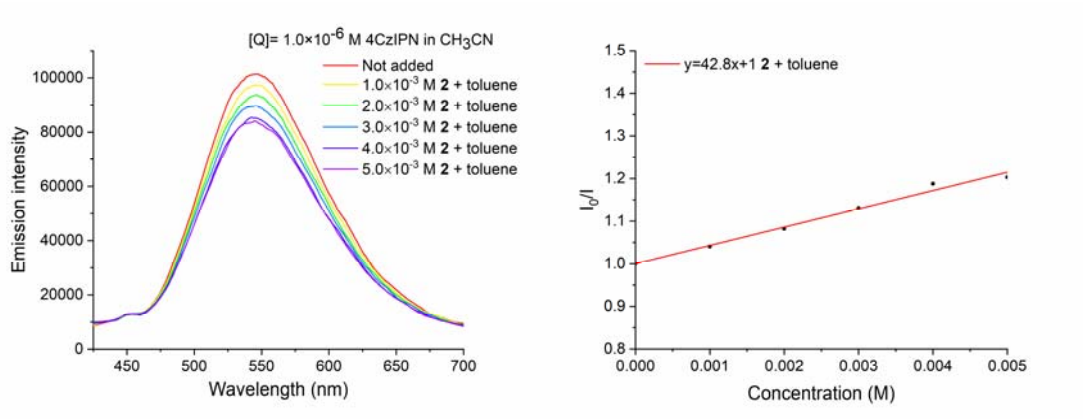


Figure S25. Emission quenching of 4CzIPN with PhCHO (**2**) + toluene (10^{-3} M) in CH_3CN

3.5 Reaction profile

Conducted the relationship of products with reaction time under standard conditions. The remaining of substrate **1** and yield of product **3** were determined by GC analysis with dodecane as the internal standard (Figure S26).

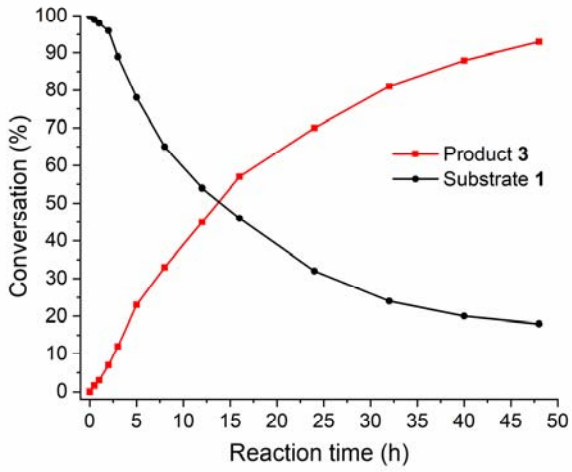


Figure S26. Reaction profile plot

3.6 Switch light experiments

Conducted the relationship of products with light on-off under standard conditions. Subsequent samples (each 20 μL) taken at regular time intervals and determined by GC with dodecane as the internal standard. The corresponding experimental results were constructed in Figure S27.

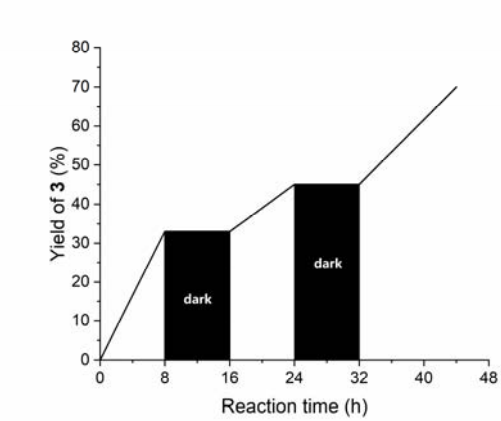
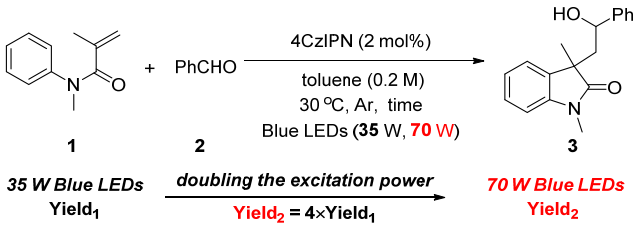


Figure S27 Plot of light on-off experiments

3.7 The dependence of the yield on the excitation power

Conducted the relationship of products with the excitation power under standard conditions. Reactions was stirred under irradiation with a 35 W blue LEDs, two 35 W blue LEDs, respectively. Samples were taken out at 10, 20, 30 and 40 min with syringe (100 uL of reaction mixture of each time). The yield of product **3** was determined by GC analysis with dodecane as the internal standard. The corresponding experimental results were constructed in Figure S28.



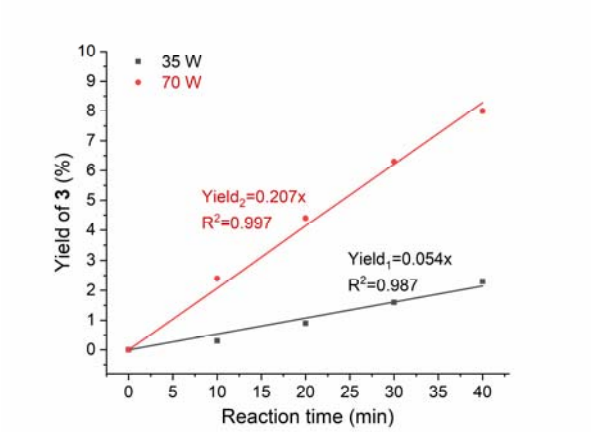
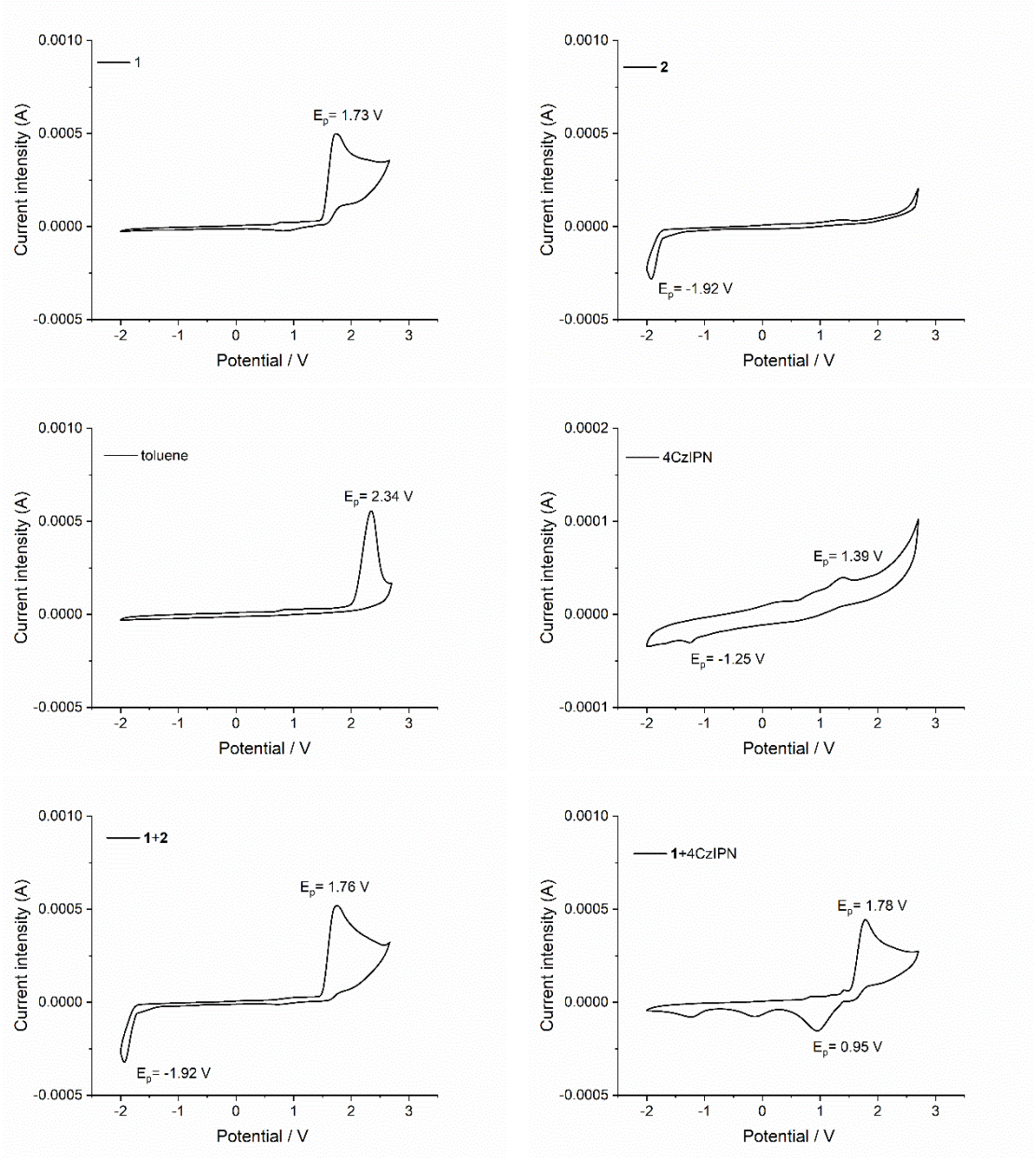


Figure S28 Plot of the yield dependency on the irradiation intensity

3.8 Cyclic voltammetry measurements

Cyclic voltammograms were taken on a CHI660D electrochemical analyzer/workstation (Shanghai Chen Hua Instrument Co., Ltd) in CH_3CN (Energy Chemical, 99.9%, with molecular sieves, water≤50 ppm (by K.F.)) at room temperature using a glass carbon working electrode, a

platinum auxiliary electrode and 0.1 M NBu_4PF_6 as supporting electrolyte. All potentials are referenced against the Ag/AgCl redox couple. 20 mM *N*-methyl-*N*-phenylmethacrylamide (**1**) was dissolved in an anhydrous CH_3CN solution containing 0.1 M NBu_4PF_6. According to the above method, 20.0 mM benzaldehyde (**2**), 20 mM toluene and 2.0 mM 4CzIPN were prepared sequentially. The solution was degassed with nitrogen bubbling for 5 min prior to voltammetric studies. The scan rate was 100 mV/s.



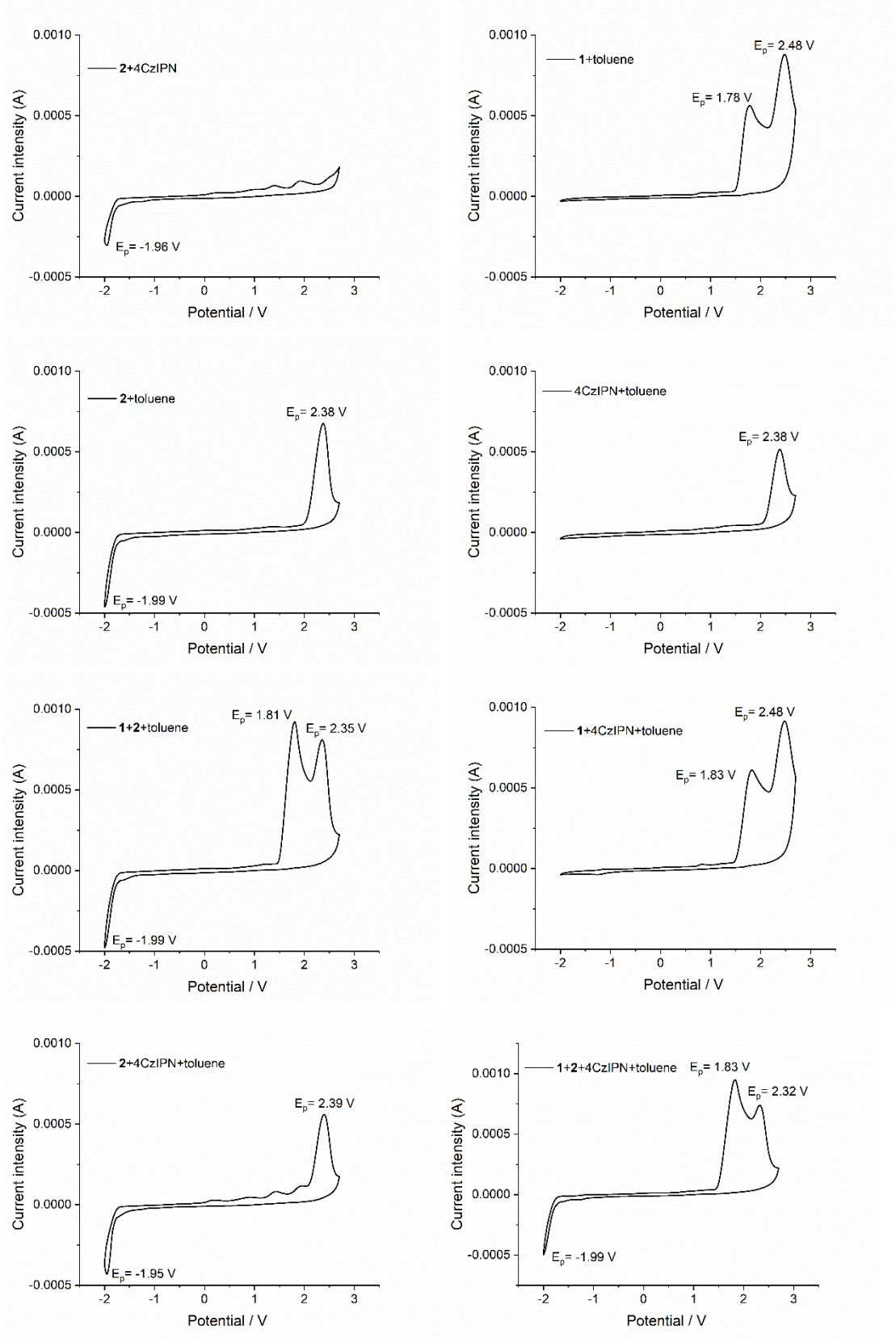


Figure S29 Cyclic Voltammetry of each reaction component

3.9 Additional experiment

In order to confirm the strong photoreduction potential of this catalytic system, we performed

the reaction using *p*-chlorotoluene and pinacol diboronate as starting materials under standard conditions. The results showed that the aryl chloride was reduced under the photocatalytic system, and the boronation product of aryl chloride was obtained with 23% GC yield.

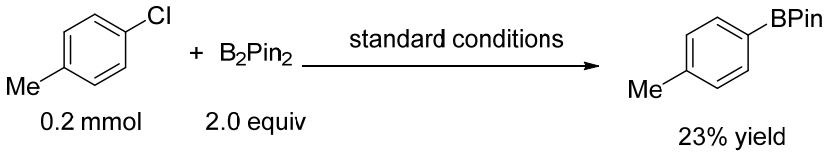


Figure S30

4. Late-stage derivation and application

(a) To a stirred solution of the alcohol ***anti*-3** (56.2 mg, 0.2 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) at room temperature was added Dess-Martin periodinane (DMP) (170 mg, 0.4 mmol, 2.0 equiv), and the mixture was stirred for 1 h.[3] The mixture was quenched by sat. aqueous $Na_2S_2O_3$ and sat. aqueous $NaHCO_3$ successively, and diluted by CH_2Cl_2. The organic phase was collected, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 3:1) to afford product **58** (54.7 mg, 98% yield) as a white solid.

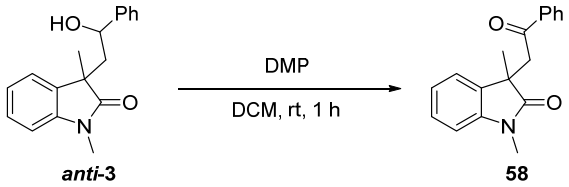


Figure S31

(b) To a stirred solution of the alcohol ***anti*-3** (56.2 mg, 0.2 mmol) in pyridine (0.5 mL, 6.2 mmol) at room temperature was added acetic anhydride (Ac_2O) (0.5 mL, 5.3 mmol), and the mixture was stirred for 24 h.[4] The reactions were stopped by the addition of 10% HCl (1 mL) and the acetate produced was extracted with ethyl acetate (3 x 20 mL). The combined organic phases were dried over Na_2SO_4 and then filtered. The organic solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1) to afford product **59** (60.7 mg, 94% yield) as a white solid (mp 115-117 ^oC).

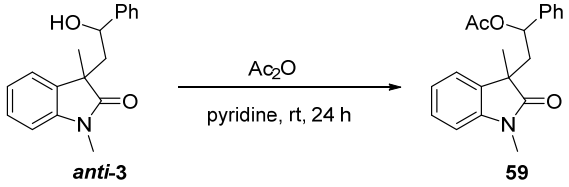
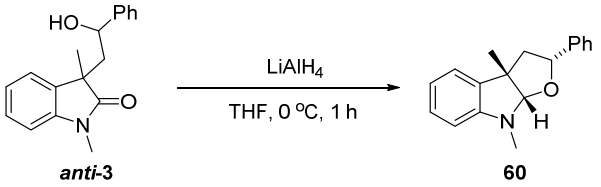


Figure S32

(c) To a stirred solution of the alcohol ***anti*-3** (56.2 mg, 0.2 mmol, 1.0 equiv) in dry THF (4 mL) at 0 ^oC was added $LiAlH_4$ (32 mg, 0.8 mmol, 4.0 equiv), and the mixture was stirred at this

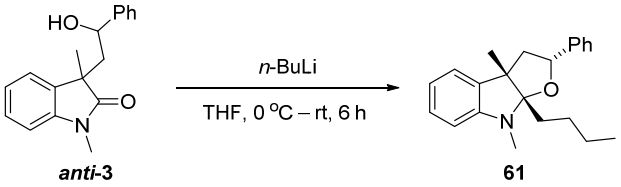
temperature for 1 h.[2a] The mixture was quenched by sat. aqueous $NaHCO_3$, and diluted by EtOAc. The organic phase was collected, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1) to afford product **60** (51.9 mg, 98% yield) as white solid (mp 82-84 ^oC).



***anti*-3** **60**

Figure S33

(d) Under argon atmosphere, to a stirred solution of the alcohol ***anti*-3** (56.2 mg, 0.2 mmol, 1.0 equiv) in dry THF (3 mL) at 0 °C was dropwise added *n*-BuLi (2.5 M in n-hexane, 0.16 mL, 0.4 mmol, 2 equiv), and the mixture was stirred at room temperature for 6 h.[2a] The mixture was quenched by sat. aqueous $NaHCO_3$, and diluted by EtOAc. The organic phase was collected, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1) to afford product **61** (61.6 mg, 96% yield) as colorless liquid.



***anti*-3** **61**

Figure S34

(e) To a stirred solution of the alcohol ***anti*-34** or ***anti*-12** or ***anti*-3** (0.2 mmol, 1.0 equiv) in 1,4-dioxane (2 mL) was added 2-3 drops H_2SO_4, and the mixture was stirred at 120 ^oC for 6 h.[5] The mixture was quenched by sat. aqueous $NaHCO_3$, and diluted by EtOAc. The organic phase was collected, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to afford products **62** (61.6 mg, 90% yield) as light yellow solid (mp 111-113 ^oC), **63** (59.8 mg, 92% yield) as white solid (mp 97-99 ^oC) and **64** (48.9 mg, 93% yield) as white solid (mp 129-131 ^oC), respectively.

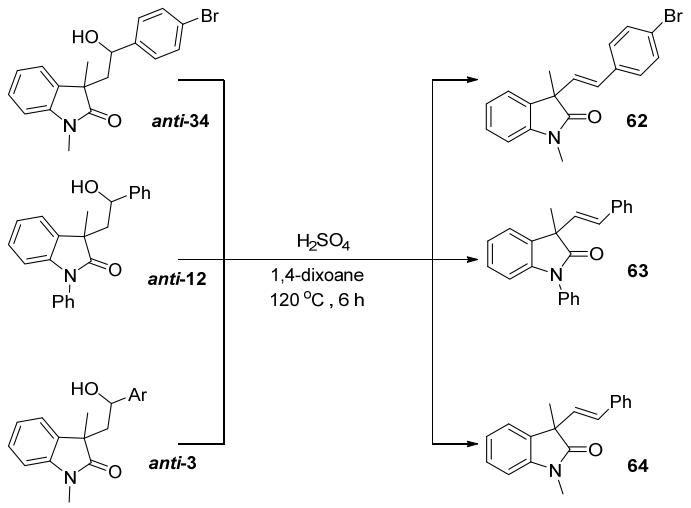


Figure S35

(f) Trifluoroacetic acid (83 uL, 1 mmol, 5 equiv) was added dropwise to Et_2Zn (1.1 M in hexane, 0.9 mL, 1 mmol, 5 equiv) in anhydrous DCM (2 mL) at 0 °C. After stirring for 10 min, CH_2I_2 (80 uL, 1 mmol, 5 equiv) was added dropwise. After stirring for 20 min, alkene **62** (68.0 mg, 0.2 mmol, 1.0 equiv) in DCM (1.0 mL) was added, and the reaction mixture was stirred at room temperature for 20 h,[6] followed by addition of an aqueous solution of HCl. After extraction with Et_2O and ethyl acetate, the combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 2:1) to afford product **65** (67.6 mg, 95% yield) as colorless liquid.

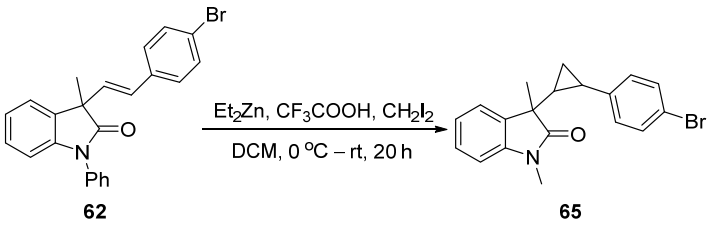


Figure S36

(g) A mixture of *m*-CPBA (39.0 mg, 0.22 mmol, 1.1 equiv), alkene **63** (65.0 mg, 0.2 mmol, 1.0 equiv) and $NaHCO_3$ (26 mg, 0.3 mmol, 1.5 equiv) in DCM (1.0 mL) was stirred at room temperature for 24 h.[7] The mixture was quenched by water, and diluted by EtOAc. The organic phase was collected, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford product **66** in 64% yield (35.7 mg) as colorless liquid.

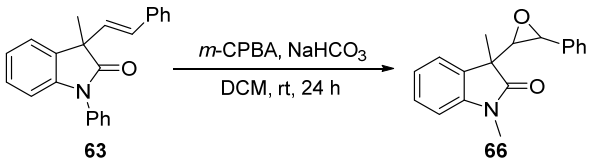


Figure S37

(h) A mixture of $NaNO_2$ (0.7 mg, 0.01 mmol, 5 mol%), alkene **64** (52.6 mg, 0.2 mmol, 1.0 equiv) and 48% aq. HBr (46 uL, 0.4 mmol, 2.0 equiv) in CH_3CN (2.0 mL) was covered with an air filled balloon (1 L) and stirred at 25 ^oC for 12 h. The mixture was quenched by sat. aqueous $NaHCO_3$, and diluted by EtOAc. The organic phase was collected, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 5:1) to afford product **67** in 81% yield (71.1 mg) as white solid (mp 202-204 ^oC).

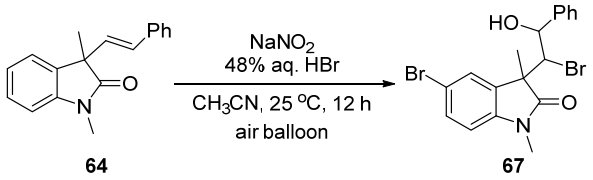


Figure S38

(i) A mixture of $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 5 mol%), AgOAc (33.4 mg, 0.2 mmol, 1.0 equiv), alkene **64** (52.6 mg, 0.2 mmol, 1.0 equiv) and PhI (34 uL, 0.3 mmol, 1.5 equiv) in HOAc (1.5 mL) was stirred at 120 ^oC for 12 h.[8] The mixture was quenched by sat. aqueous $NaHCO_3$, and diluted by EtOAc. The organic phase was collected, and the aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 40:1) to afford product **68** in 52% yield (35.2 mg) as light yellow solid (mp 158-160 ^oC).

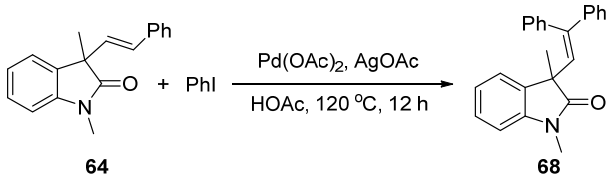


Figure S39

(j) A mixture of BF_3·OEt (25 μL, 0.4 mmol, 2.0 equiv), alcohol **28** (29.5 mg, 0.1 mmol, 1.0 equiv) in DCM (2.0 mL) was stirred at room temperature for 4 h.[9] The mixture was quenched by saturated NH_4Cl solution, and diluted by DCM. The organic phase was collected, and the aqueous phase was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 4:1) to afford product **69** in 89% yield (24.8 mg) as white solid (mp 150-152 ^oC).

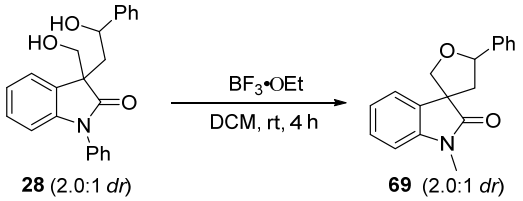
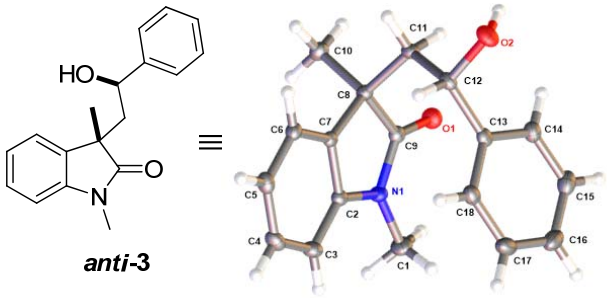


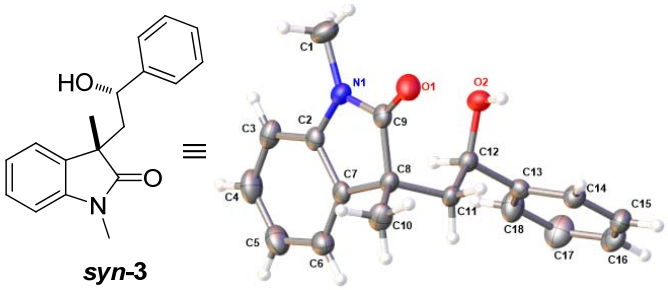
Figure S40

5. Characterization data of all products

3-(2-hydroxy-2-phenylethyl)-1,3-dimethylindolin-2-one (3)



***anti*-3** CCDC No: 2166562



***syn*-3** CCDC No: 2166563

The title compound **3** was synthesized according to General Procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-3** (42.3 mg) as a white solid (mp 100-102 ^{o}C) and ***syn*-3** (10.6 mg) as a white solid (mp 131-133 ^{o}C). Total isolated yield of **3**: 94%, *dr*: 4.0:1.

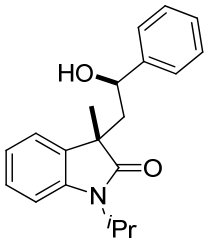
Data of ***anti*-3**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.21 (m, 6H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.93 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.18 (s, 1H), 3.12 (s, 3H), 2.21 (dd, *J* = 14.7, 3.6 Hz, 1H), 2.08 (dd, *J* = 14.6, 9.2 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 143.9, 142.4, 134.5, 128.2, 128.0, 127.4, 126.0, 123.0, 122.5, 108.4, 71.4, 47.3, 46.3, 26.3, 23.2. HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_2^+$ $(M+Na)^+$ 304.1308, found 304.1315.

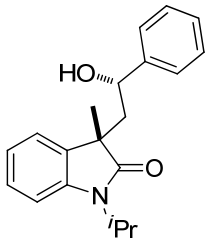
Data of ***syn*-3**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.24 (m, 3H), 7.22 – 7.19 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 4.27 (dd, *J* = 10.7, 2.7 Hz, 1H), 3.24 (s, 3H), 2.53 (dd, *J* = 14.5, 10.7 Hz, 1H), 2.14 (dd, *J* = 14.5, 2.8 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 144.4, 143.6, 133.2, 128.3, 127.9, 127.4, 125.4, 122.5, 122.4, 108.2, 71.7, 47.1, 47.0, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_2^+$ $(M+Na)^+$ 304.1308, found 304.1317

3-(2-hydroxy-2-phenylethyl)-1-isopropyl-3-methylindolin-2-one (4)



***anti*-4**



***syn*-4**

The title compound **4** was synthesized according to General Procedure using *N*-isopropyl-*N*-phenylmethacrylamide (48.7 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 6:1 to 3:1) was performed to give ***anti*-4** (41.1 mg) as a colorless liquid and ***syn*-4** (10.8 mg) as a white solid (mp 73-75 ^{o}C). Total isolated yield of **4**: 84%, *dr*: 3.8:1.

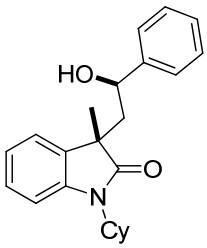
Data of ***anti*-4**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 4H), 7.26 – 7.19 (m, 2H), 7.19 – 7.14 (m, 1H), 7.04 (t, *J* = 7.4 Hz, 2H), 5.01 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.63 (hept, *J* = 7.0 Hz, 1H), 4.40 (s, 1H), 2.15 (dd, *J* = 14.8, 2.7 Hz, 1H), 2.01 (dd, *J* = 14.8, 9.8 Hz, 1H), 1.52 (s, 3H), 1.47 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 144.4, 140.9, 135.2, 128.2, 127.7, 127.2, 125.8, 122.7, 122.4, 110.2, 71.2, 47.2, 46.6, 43.9, 23.2, 19.3, 19.3. HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_2^+$ $(M+Na)^+$ 332.1621, found 332.1629.

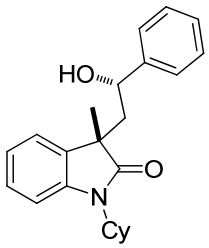
Data of ***syn*-4**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.17 (m, 7H), 7.07 (d, *J* = 7.6 Hz, 2H), 4.71 (hept, *J* = 7.1 Hz, 1H), 4.24 (dd, *J* = 10.8, 2.7 Hz, 1H), 2.51 (dd, *J* = 14.5, 10.7 Hz, 1H), 2.12 (dd, *J* = 14.5, 2.7 Hz, 1H), 1.50 (dd, *J* = 7.0, 5.2 Hz, 6H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.0, 144.6, 142.2, 133.7, 128.3, 127.6, 127.4, 125.4, 122.8, 121.8, 110.1, 71.8, 47.2, 46.8, 43.5, 25.6, 19.3, 18.9. HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_2^+$ $(M+Na)^+$ 332.1621, found 332.1628.

1-cyclohexyl-3-(2-hydroxy-2-phenylethyl)-3-methylindolin-2-one (5)



***anti*-5**



***syn*-5**

The title compound **5** was synthesized according to General Procedure using *N*-cyclohexyl-*N*-phenylmethacrylamide (58.3 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 5:1 to 2:1) was performed to give ***anti*-5** (41.2 mg) as a white solid (mp 128-130 ^{o}C) and ***syn*-5** (15.3 mg) as a white solid (mp 103-105 ^{o}C). Total isolated yield of **5**: 81%, *dr*: 2.7:1.

Data of ***anti*-5**

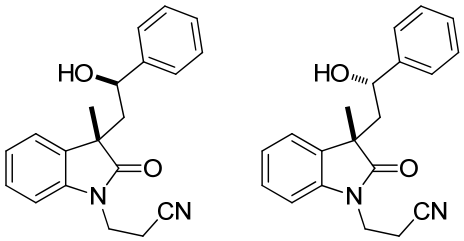
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.25 (m, 4H), 7.25 – 7.18 (m, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.10 – 6.99 (m, 2H), 5.01 (dd, *J* = 9.8, 2.5 Hz, 1H), 4.37 (s, 1H), 4.23 – 4.13 (m, 1H),

2.20 – 2.10 (m, 3H), 2.02 – 1.96 (m, 1H), 1.95 – 1.86 (m, 2H), 1.79 – 1.70 (m, 3H), 1.52 (s, 3H), 1.47 – 1.36 (m, 2H), 1.32 – 1.25 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.7, 144.5, 141.4, 135.2, 128.2, 127.7, 127.2, 125.7, 122.7, 122.4, 110.4, 71.2, 52.3, 47.2, 46.8, 29.1, 29.0, 25.9, 25.3, 23.2. HRMS (ESI) m/z calcd for $C_{23}H_{27}NNaO_2^+$ $(M+Na)^+$ 372.1934, found 372.1941.

Data of ***syn*-5**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.15 (m, 7H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.34 – 4.15 (m, 2H), 2.51 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.18 – 2.10 (m, 2H), 1.92 – 1.72 (m, 6H), 1.49 – 1.40 (m, 2H), 1.36 (s, 3H), 1.32 – 1.27 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.2, 144.6, 142.6, 133.7, 128.3, 127.5, 127.4, 125.4, 122.7, 121.8, 110.3, 71.8, 52.0, 47.3, 46.8, 29.1, 28.7, 26.0, 26.0, 25.7, 25.5. HRMS (ESI) m/z calcd for $C_{23}H_{27}NNaO_2^+$ $(M+Na)^+$ 372.1934, found 372.1942.

3-(3-(2-hydroxy-2-phenylethyl)-3-methyl-2-oxoindolin-1-yl)propanenitrile (6)



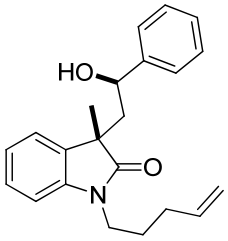
***anti*-6** ***syn*-6**

The title compound **6** was synthesized according to general procedure using *N*-(2-cyanoethyl)-*N*-phenylmethacrylamide (51.4 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give an inseparable mixture of ***anti*-6** (major) and ***syn*-6** (58.2 mg, 91%, *dr*: 3.2:1) as a colorless liquid.

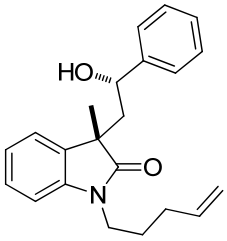
Data of mixture ***anti*-6** (major) and ***syn*-6** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.17 (m, 5.52H), 7.14 – 7.05 (m, 2.48H), 6.95 (d, *J* = 7.9 Hz, 0.24H), 6.85 (d, *J* = 7.8 Hz, 0.76H), 4.72 (dd, *J* = 8.2, 5.0 Hz, 0.76H), 4.16 (dd, *J* = 11.1, 2.5 Hz, 0.24H), 4.12 – 4.05 (m, 0.24H), 3.87 (dt, *J* = 14.3, 7.2 Hz, 0.24H), 3.76 (t, *J* = 7.0 Hz, 1.54H), 3.43 (s, 0.51H), 2.75 – 2.65 (m, 0.48H), 2.56 (td, *J* = 6.9, 3.1 Hz, 1.54H), 2.51 (dd, *J* = 10.6, 3.9 Hz, 0.24H), 2.30 (dd, *J* = 14.5, 5.0 Hz, 0.76H), 2.18 (dd, *J* = 14.5, 8.2 Hz, 0.76H), 2.08 (dd, *J* = 14.4, 2.6 Hz, 0.24H), 1.45 (s, 2.38H), 1.35 (s, 0.72H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.2, 180.9, 144.2, 143.3, 141.6, 140.4, 133.9, 132.8, 128.2, 128.0, 128.0, 127.9, 127.5, 127.4, 126.1, 125.3, 123.2, 123.1, 122.9, 122.7, 117.8, 117.1, 108.0, 108.0, 71.5, 71.3, 47.0, 46.8, 46.7, 45.6, 35.6, 35.6, 25.1, 24.4, 16.0, 15.5. HRMS (ESI) m/z calcd for $C_{20}H_{20}N_2NaO_2^+$ $(M+Na)^+$ 343.1417, found 343.1427.

3-(2-hydroxy-2-phenylethyl)-3-methyl-1-(pent-4-en-1-yl)indolin-2-one (7)



***anti*-7**



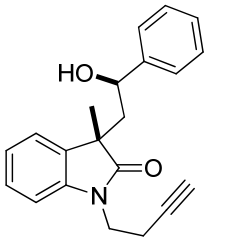
***syn*-7**

The title compound **7** was synthesized according to general procedure using *N*-(pent-4-en-1-yl)-*N*-phenylmethacrylamide (55.0 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give an inseparable mixture of ***anti*-7** (major) and ***syn*-7** (minor) (59.0 mg, 88%, *dr*: 4.5:1) as a colorless liquid.

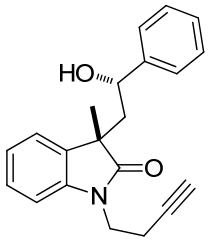
Data of mixture ***anti*-7** (major) and ***syn*-7** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.14 (m, 7H), 7.10 – 7.02 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 0.18H), 6.84 (d, *J* = 7.8 Hz, 0.82H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1.00H), 5.12 – 4.89 (m, 2.82H;), 4.25 (s, 0.62H), 3.79 – 3.55 (m, 2H), 2.51 (dd, *J* = 14.5, 10.6 Hz, 0.18H), 2.23 – 1.98 (m, 4H), 1.82 – 1.71 (m, 2H), 1.52 (s, 2.46H), 1.36 (s, 0.54H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 181.2, 144.5, 144.1, 142.9, 141.7, 137.5, 137.2, 134.7, 133.3, 128.3, 128.1, 127.9, 127.8, 127.3, 127.3, 125.8, 125.4, 122.7, 122.7, 122.6, 122.1, 115.5, 115.3, 108.6, 108.4, 71.6, 71.3, 47.3, 47.0, 46.9, 46.4, 39.4, 39.4, 30.9, 30.8, 26.4, 26.2, 25.6, 23.3. HRMS (ESI) m/z calcd for $C_{22}H_{25}NNaO_2^+$ $(M+Na)^+$ 358.1778, found 358.1789.

1-(but-3-yn-1-yl)-3-(2-hydroxy-2-phenylethyl)-3-methylindolin-2-one (8)



***anti*-8**



***syn*-8**

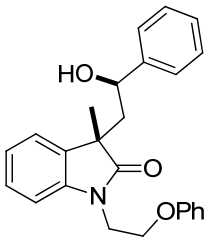
The title compound **8** was synthesized according to general procedure using *N*-(but-3-yn-1-yl)-*N*-phenylmethacrylamide (51.1 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/DCM 5:1 to 4:1) was performed to give an inseparable mixture of ***anti*-8** (major) and ***syn*-8** (minor) (49.8 mg, 78%, *dr*: 3.6:1) as a colorless liquid.

Data of mixture ***anti*-8** (major) and ***syn*-8** (minor)

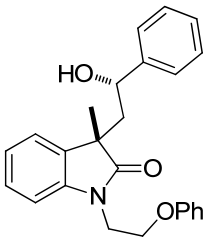
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.15 (m, 7.00H), 7.10 – 7.05 (m, 1.00H), 6.97 (d, *J* = 7.8 Hz, 0.22H), 6.90 (d, *J* = 7.8 Hz, 0.78H), 4.89 (dd, *J* = 9.1, 3.7 Hz, 0.78H), 4.22 (dd, *J* = 10.7, 2.6 Hz, 0.22H), 4.00 – 3.94 (m, 0.22H), 3.89 – 3.82 (m, 0.44H), 3.78 (td, *J* = 7.1, 3.1 Hz, 1.56H), 2.62 – 2.57 (m, 0.44H), 2.55 – 2.49 (m, 1.56H), 2.22 (dd, *J* = 14.7, 3.7 Hz, 0.78H), 2.16 – 2.04 (m, 1.00H), 1.97 – 1.94 (m, 1.00H), 1.51 (s, 2.35H), 1.37 (s, 0.65H); ^{13}C NMR (100 MHz,

Chloroform-*d*) δ 181.4, 181.3, 144.4, 143.9, 142.4, 141.3, 134.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.4, 127.3, 125.9, 125.4, 122.9, 122.8, 122.7, 122.4, 108.6, 108.5, 81.0, 80.3, 71.5, 71.3, 70.5, 70.2, 47.2, 47.1, 46.9, 46.3, 38.6, 38.5, 25.3, 23.6, 17.3, 17.0. HRMS (ESI) m/z calcd for $C_{21}H_{21}NNaO_2^+$ $(M+Na)^+$ 342.1465, found 342.1478.

3-(2-hydroxy-2-phenylethyl)-3-methyl-1-(2-phenoxyethyl)indolin-2-one (9)



***anti*-9**



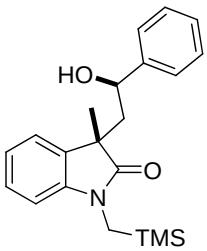
***syn*-9**

The title compound **9** was synthesized according to general procedure using *N*-(2-phenoxyethyl)-*N*-phenylmethacrylamide (67.4 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give an inseparable mixture of ***anti*-9** (major) and ***syn*-9** (minor) (64.2 mg, 83%, *dr*: 4.2:1) as a white solid (mp 109-111 ^oC).

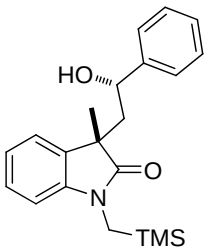
Data of mixture ***anti*-9** (major) and ***syn*-9** (minor)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.11 (m, 9.19H), 7.12 – 7.00 (m, 2.00H), 6.90 (t, *J* = 7.4 Hz, 0.81H), 6.89 – 6.76 (m, 2.00H), 4.86 (dd, *J* = 9.0, 3.8 Hz, 0.81H), 4.26 – 4.17 (m, 0.38H), 4.18 – 4.15 (m, 0.19H), 4.12 (t, *J* = 5.5 Hz, 1.62H), 4.11 – 4.00 (m, 0.38H), 3.97 (t, *J* = 5.5 Hz, 1.62H), 2.51 (dd, *J* = 14.4, 10.7 Hz, 0.19H), 2.21 (dd, *J* = 14.6, 3.8 Hz, 0.81H), 2.14 – 2.03 (m, 1.00H), 1.48 (s, 2.43H), 1.35 (s, 0.57H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.8, 181.6, 158.5, 158.3, 144.7, 144.1, 143.3, 142.1, 134.4, 133.1, 129.6, 128.4, 128.3, 128.0, 127.9, 127.5, 127.5, 126.1, 125.5, 123.0, 122.7, 122.7, 122.4, 121.2, 121.2, 114.6, 114.5, 109.4, 109.2, 71.7, 71.5, 65.4, 65.2, 47.4, 47.3, 47.0, 46.4, 39.9, 39.7, 25.4, 23.7. HRMS (ESI) m/z calcd for $C_{25}H_{25}NNaO_3^+$ $(M+Na)^+$ 410.1727, found 410.1740.

3-(2-hydroxy-2-phenylethyl)-3-methyl-1-((trimethylsilyl)methyl)indolin-2-one (10)



***anti*-10**



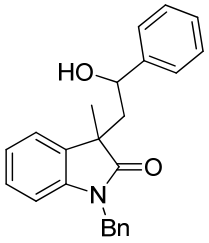
***syn*-10**

The title compound **10** was synthesized according to general procedure using *N*-phenyl-*N*-((trimethylsilyl)methyl)methacrylamide (59.3 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 5:1 to 4:1) was performed to give an inseparable mixture of ***anti*-10** (major) and ***syn*-10** (minor) (45.2 mg, 64%, *dr*: 5.0:1) as a colorless liquid.

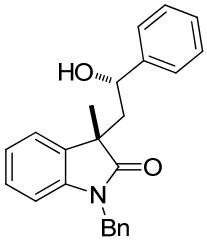
Data of mixture ***anti*-10** (major) and ***syn*-10** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.22 (m, 6H), 7.21 – 7.16 (m, 1H), 7.10 – 7.02 (m, 1H), 6.85 (d, *J* = 7.7 Hz, 0.17H), 6.82 (d, *J* = 7.8 Hz, 0.83H), 5.08 (dd, *J* = 10.0, 2.5 Hz, 0.83H), 4.66 (s, 0.73H), 4.36 (dd, *J* = 10.7, 2.5 Hz, 0.17H), 3.39 – 3.12 (m, 2H), 2.52 (dd, *J* = 14.6, 10.4 Hz, 0.17H), 2.16 (dd, *J* = 14.8, 2.6 Hz, 1.00H), 2.00 (dd, *J* = 14.7, 10.0 Hz, 0.83H), 1.58 (s, 2.49H), 1.41 (s, 0.51H), 0.16 (s, 1.53H), 0.15 (s, 7.47H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.1, 180.7, 144.7, 144.5, 143.8, 142.6, 135.2, 133.8, 128.3, 128.2, 127.8, 127.7, 127.3, 127.2, 125.8, 125.4, 122.7, 122.4, 122.3, 122.0, 108.9, 108.6, 71.6, 71.2, 47.3, 47.0, 46.9, 46.8, 31.5, 31.4, 25.9, 22.9, -1.4, -1.5. HRMS (ESI) m/z calcd for $C_{21}H_{27}NNaO_2Si^+$ $(M+Na)^+$ 376.1703, found 376.1718.

1-benzyl-3-(2-hydroxy-2-phenylethyl)-3-methylindolin-2-one (11)



***anti*-11**



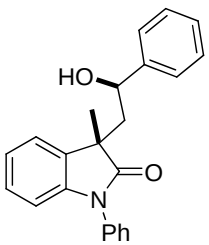
***syn*-11**

The title compound **11** was synthesized according to general procedure using *N*-benzyl-*N*-phenylmethacrylamide (60.2 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give an inseparable mixture of ***anti*-11** (major) and ***syn*-11** (36.4 mg, 51%, *dr*: 3.4:1) as a white solid (mp 124-126 ^{o}C).

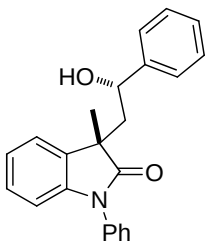
Data of mixture ***anti*-11** (major) and ***syn*-11** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.10 (m, 12H), 7.07 – 7.01 (m, 1H), 6.76 – 6.72 (m, 1H), 5.02 – 4.88 (m, 2H), 4.74 (d, *J* = 15.6 Hz, 0.77H), 4.33 (dd, *J* = 10.7, 2.7 Hz, 0.23H), 3.99 (s, 0.67H), 2.60 (dd, *J* = 14.5, 10.7 Hz, 0.23H), 2.25 (dd, *J* = 14.7, 3.2 Hz, 0.77H), 2.21 – 2.08 (m, 1.00H), 1.58 (s, 2.31H), 1.44 (s, 0.69H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.7, 181.4, 144.5, 144.1, 142.7, 141.5, 136.1, 135.6, 134.6, 133.2, 128.8, 128.7, 128.4, 128.2, 128.0, 127.8, 127.7, 127.5, 127.4, 127.4, 127.4, 127.1, 125.9, 125.4, 123.0, 122.6, 122.4, 109.4, 109.3, 71.7, 71.4, 47.4, 47.2, 46.9, 46.6, 43.9, 43.7, 26.0, 23.5. HRMS (ESI) m/z calcd for $C_{24}H_{23}NNaO_2^+$ $(M+Na)^+$ 380.1621, found 380.1633.

3-(2-hydroxy-2-phenylethyl)-3-methyl-1-phenylindolin-2-one (12)



***anti*-12**



***syn*-12**

The title compound **12** was synthesized according to General Procedure using *N*, *N*-diphenylmethacrylamide (56.9 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give ***anti*-12** (56.1 mg) as a white solid (mp 146-148 ^{o}C) and ***syn*-12** (12.5 mg) as a white solid (mp 148-150 ^{o}C). Total isolated yield of **12**: 83%, *dr*: 4.5:1.

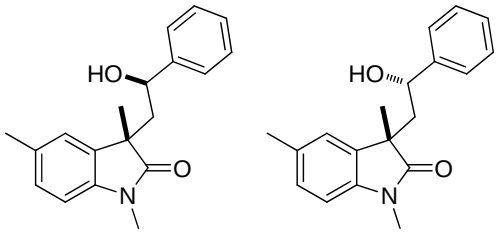
Data of ***anti*-12**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.18 (m, 9H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.98 (dd, *J* = 8.9, 3.7 Hz, 1H), 3.78 (s, 1H), 2.35 (dd, *J* = 14.7, 3.8 Hz, 1H), 2.25 (dd, *J* = 14.7, 8.9 Hz, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.9, 144.0, 142.4, 134.2, 134.0, 129.5, 128.3, 128.1, 127.9, 127.5, 126.4, 126.0, 123.3, 122.9, 109.7, 71.5, 47.4, 46.5, 24.1. HRMS (ESI) m/z calcd for $C_{23}H_{21}NNaO_2^+$ $(M+Na)^+$ 366.1465, found 366.1477.

Data of ***syn*-12**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.44 (m, 4H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.21 (m, 7H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.35 (dd, *J* = 11.1, 2.6 Hz, 1H), 2.64 (dd, *J* = 14.5, 11.0 Hz, 1H), 2.22 (dd, *J* = 14.5, 2.7 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.9, 144.3, 143.7, 134.9, 132.8, 129.5, 128.5, 127.9, 127.8, 127.6, 126.7, 125.5, 122.9, 122.8, 109.5, 72.0, 47.4, 47.2, 25.6. HRMS (ESI) m/z calcd for $C_{23}H_{21}NNaO_2^+$ $(M+Na)^+$ 366.1465, found 366.1476.

3-(2-hydroxy-2-phenylethyl)-1,3,5-trimethylindolin-2-one (13)



***anti*-13** ***syn*-13**

The title compound **13** was synthesized according to General Procedure using *N*-methyl-*N*-(*p*-tolyl)methacrylamide (45.4 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-13** (33.3 mg) as a white solid (mp 124-126 ^{o}C) and ***syn*-13** (9.8 mg) as a white solid (mp 135-137 ^{o}C). Total isolated yield of **13**: 73%, *dr*: 3.4:1.

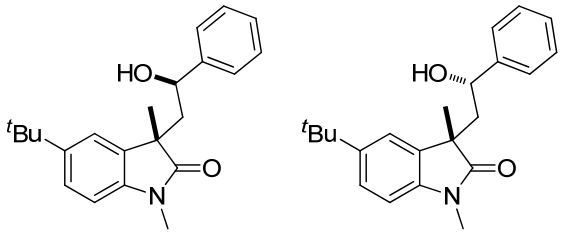
Data of ***anti*-13**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.16 (m, 5H), 7.06 (d, *J* = 6.8 Hz, 1H), 6.99 (s, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.92 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.25 (s, 1H), 3.10 (s, 3H), 2.32 (s, 3H), 2.19 (dd, *J* = 14.6, 3.6 Hz, 1H), 2.05 (dd, *J* = 14.7, 9.2 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 144.0, 140.0, 134.5, 132.5, 128.2, 128.1, 127.3, 125.9, 123.3, 108.1, 71.3, 47.3, 46.5, 26.3, 23.2, 21.0. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_2^+$ $(M+Na)^+$ 318.1465, found 318.1478.

Data of ***syn*-13**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.17 (m, 5H), 7.09 (d, *J* = 7.1 Hz, 1H), 6.98 (s, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 4.28 (dd, *J* = 10.4, 3.0 Hz, 1H), 3.23 (s, 3H), 2.52 (dd, *J* = 14.5, 10.4 Hz, 1H), 2.36 (s, 3H), 2.13 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 144.5, 141.2, 133.3, 132.0, 128.3, 128.1, 127.4, 125.5, 123.4, 108.0, 71.7, 47.2, 47.0, 26.4, 25.5, 21.1. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_2^+$ $(M+Na)^+$ 318.1465, found 318.1479.

5-(*tert*-butyl)-3-(2-hydroxy-2-phenylethyl)-1,3-dimethylindolin-2-one (14)



***anti*-14** ***syn*-14**

The title compound **14** was synthesized according to General Procedure using *N*-(4-(*tert*-butyl)phenyl)-*N*-methylmethacrylamide (55.4 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-14** (34.5 mg) as a white solid (mp 133-135 ^{o}C) and ***syn*-14** (8.6 mg) as a white solid (mp 107-109 ^{o}C). Total isolated yield of **14**: 64%, *dr*: 4.0:1.

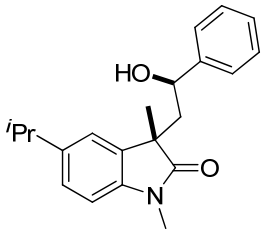
Data of ***anti*-14**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.15 (m, 7H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.97 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.42 (s, 1H), 3.12 (s, 3H), 2.19 (dd, *J* = 14.7, 3.4 Hz, 1H), 2.06 (dd, *J* = 14.7, 9.4 Hz, 1H), 1.54 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.8, 146.4, 144.1, 140.0, 134.2, 128.2, 127.3, 126.0, 124.7, 119.5, 107.8, 71.4, 47.6, 46.5, 34.6, 31.6, 26.3, 23.1. HRMS (ESI) m/z calcd for $C_{22}H_{27}NNaO_2^+$ $(M+Na)^+$ 360.1934, found 360.1946.

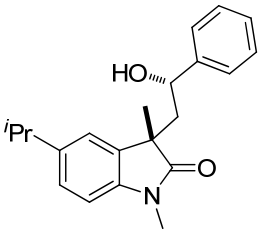
Data of ***syn*-14**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.15 (m, 7H), 6.80 (d, *J* = 8.1 Hz, 1H), 4.27 (dd, *J* = 10.2, 2.9 Hz, 1H), 3.23 (s, 3H), 2.53 (dd, *J* = 14.5, 10.2 Hz, 1H), 2.15 (dd, *J* = 14.5, 2.9 Hz, 1H), 1.40 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 145.8, 144.6, 141.2, 133.1, 128.4, 127.5, 125.4, 124.4, 119.8, 107.6, 71.9, 47.4, 47.3, 34.6, 31.7, 26.4, 25.5. HRMS (ESI) m/z calcd for $C_{22}H_{27}NNaO_2^+$ $(M+Na)^+$ 360.1934, found 360.1948.

3-(2-hydroxy-2-phenylethyl)-5-isopropyl-1,3-dimethylindolin-2-one (15)



***anti*-15**



***syn*-15**

The title compound **15** was synthesized according to General Procedure using *N*-(4-isopropylphenyl)-*N*-methylmethacrylamide (52.1 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-15** (34.1 mg) as a white solid (mp 103-105 ^{o}C) and ***syn*-15** (11.7 mg) as a white solid (mp 92-94 ^{o}C). Total isolated yield of **15**: 71%, *dr*: 2.9:1.

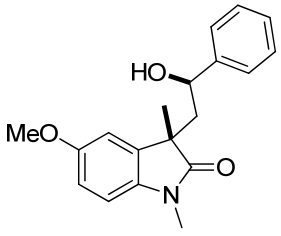
Data of ***anti*-15**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.18 (m, 5H), 7.13 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.03 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.96 (dd, *J* = 9.4, 3.4 Hz, 1H), 4.37 (s, 1H), 3.12 (s, 3H), 2.88 (p, *J* = 6.9 Hz, 1H), 2.19 (dd, *J* = 14.7, 3.4 Hz, 1H), 2.06 (dd, *J* = 14.7, 9.4 Hz, 1H), 1.53 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.7, 144.1, 144.0, 140.3, 134.5, 128.2, 127.3, 126.0, 125.7, 120.7, 108.2, 71.4, 47.5, 46.5, 33.9, 26.3, 24.2, 24.2, 23.0. HRMS (ESI) m/z calcd for $C_{21}H_{25}NNaO_2^+$ $(M+Na)^+$ 346.1778, found 346.1792.

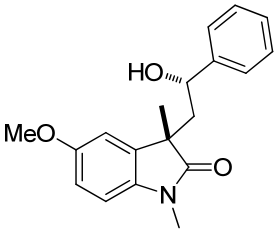
Data of ***syn*-15**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 7.23 – 7.12 (m, 4H), 7.05 (s, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 4.27 (dd, *J* = 10.4, 2.9 Hz, 1H), 3.24 (s, 3H), 2.92 (p, *J* = 6.9 Hz, 1H), 2.53 (dd, *J* = 14.5, 10.4 Hz, 1H), 2.15 (dd, *J* = 14.5, 2.9 Hz, 1H), 1.39 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 144.5, 143.5, 141.4, 133.3, 128.4, 127.4, 125.6, 125.4, 120.8, 108.0, 71.8, 47.3, 47.2, 33.9, 26.4, 25.4, 24.4, 24.3. HRMS (ESI) m/z calcd for $C_{21}H_{25}NNaO_2^+$ $(M+Na)^+$ 346.1778, found 346.1792.

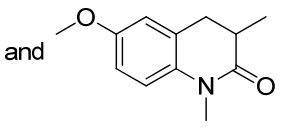
3-(2-hydroxy-2-phenylethyl)-5-methoxy-1,3-dimethylindolin-2-one (16) and 6-methoxy-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (16')



***anti*-16**



***syn*-16**



16'

The title compound **16** and **16'** were synthesized according to General Procedure using *N*-(4-methoxyphenyl)-*N*-methylmethacrylamide (49.2 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) were performed to give ***anti*-16** (8.1 mg) as a white solid

(mp 140-142 °C) and ***syn*-16** (3.1 mg) as a white solid (mp 115-117 °C), and **16'** (32.4 mg, 79% yield) as white solid (mp 75-76 °C). Total isolated yield of **16**: 18%, *dr*: 2.6:1.

Data of ***anti*-16**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.20 (m, 5H), 6.83 – 6.70 (m, 3H), 4.95 (dd, *J* = 9.2, 3.6 Hz, 1H), 3.78 (s, 3H), 3.11 (s, 3H), 2.18 (dd, *J* = 14.7, 3.6 Hz, 1H), 2.07 (dd, *J* = 14.7, 9.2 Hz, 1H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.2, 156.3, 144.0, 135.9, 135.8, 128.2, 127.4, 126.0, 112.2, 110.0, 108.7, 71.3, 55.8, 47.8, 46.4, 26.4, 23.2. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_3^+$ $(M+Na)^+$ 334.1414, found 334.1430.

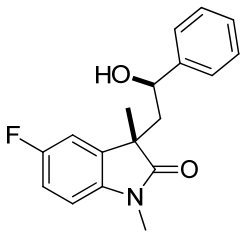
Data of ***syn*-16**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.19 (m, 5H), 6.86 – 6.72 (m, 3H), 4.31 (dd, *J* = 10.5, 2.9 Hz, 1H), 3.81 (s, 3H), 3.23 (s, 3H), 2.53 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.12 (dd, *J* = 14.5, 2.9 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.1, 156.0, 144.4, 137.1, 134.7, 128.4, 127.5, 125.5, 111.7, 110.4, 108.5, 71.7, 55.8, 47.6, 47.0, 26.5, 25.5. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_3^+$ $(M+Na)^+$ 334.1414, found 334.1431.

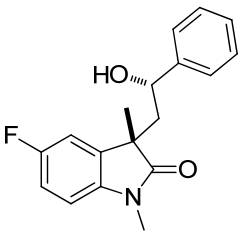
Data of **16'**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (d, *J* = 8.7 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.71 (d, *J* = 2.9 Hz, 1H), 3.77 (s, 3H), 3.31 (s, 3H), 2.87 (dd, *J* = 14.2, 4.4 Hz, 1H), 2.68 – 2.59 (m, 1H), 1.22 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.6, 155.1, 133.9, 127.0, 115.2, 114.0, 111.6, 55.4, 35.4, 33.4, 29.8, 15.6.

5-fluoro-3-(2-hydroxy-2-phenylethyl)-1,3-dimethylindolin-2-one (17)



***anti*-17**



***syn*-17**

The title compound **17** was synthesized according to General Procedure using *N*-(4-fluorophenyl)-*N*-methylmethacrylamide (46.3 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-17** (24.9 mg) as a white solid (mp 170-179 °C) and ***syn*-17** (6.2 mg) as a white solid (mp 154-162 °C). Total isolated yield of **17**: 52%, *dr*: 4.0:1.

Data of ***anti*-17**

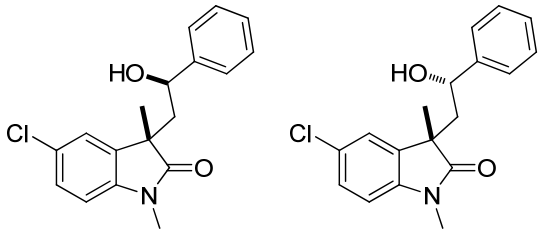
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.18 (m, 5H), 7.01 – 6.90 (m, 2H), 6.73 (dd, *J* = 8.5, 4.1 Hz, 1H), 4.88 (dd, *J* = 8.9, 4.0 Hz, 1H), 3.89 (s, 1H), 3.09 (s, 3H), 2.20 (dd, *J* = 14.6, 4.0 Hz, 1H), 2.09 (dd, *J* = 14.6, 8.9 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.0, 159.5 (d, *J* = 241.3 Hz), 143.7, 138.4 (d, *J* = 2.0 Hz), 136.2 (d, *J* = 7.8 Hz), 128.2, 127.5, 125.9, 114.1 (d, *J* = 23.5 Hz), 110.8 (d, *J* = 24.7 Hz), 108.8 (d, *J* = 8.2 Hz), 71.3, 47.7 (d, *J* = 1.8 Hz),

46.2, 26.4, 23.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.92. HRMS (ESI) m/z calcd for $C_{18}H_{18}FNNaO_2^+$ $(M+Na)^+$ 322.1214, found 322.1230.

Data of ***syn*-17**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.19 (m, 5H), 7.06 – 6.89 (m, 2H), 6.79 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.29 (dd, *J* = 10.6, 2.9 Hz, 1H), 3.23 (s, 3H), 2.55 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.11 (dd, *J* = 14.5, 3.1 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.0, 159.3 (d, *J* = 240.4 Hz), 144.1, 139.5, 134.9 (d, *J* = 7.7 Hz), 128.4, 127.7, 125.5, 114.1 (d, *J* = 23.4 Hz), 110.8 (d, *J* = 24.6 Hz), 108.6 (d, *J* = 8.2 Hz), 71.7, 47.6 (d, *J* = 1.8 Hz), 46.7, 26.5, 25.3; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.92. HRMS (ESI) m/z calcd for $C_{18}H_{18}FNNaO_2^+$ $(M+Na)^+$ 322.1214, found 322.1228.

5-chloro-3-(2-hydroxy-2-phenylethyl)-1,3-dimethylindolin-2-one (18)



***anti*-18** ***syn*-18**

The title compound **18** was synthesized according to General Procedure using *N*-(4-chlorophenyl)-*N*-methylmethacrylamide (50.2 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-18** (41.7 mg) as a white solid (mp 176-178 ^{o}C) and ***syn*-18** (9.9 mg) as a light yellow solid (mp 165-167 ^{o}C). Total isolated yield of **18**: 82%, *dr*: 4.2:1.

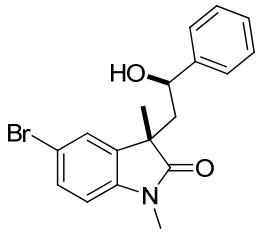
Data of ***anti*-18**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.10 (m, 7H), 6.72 (d, *J* = 8.3 Hz, 1H), 4.81 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.80 (s, 1H), 3.04 (s, 3H), 2.22 (dd, *J* = 14.6, 4.4 Hz, 1H), 2.11 (dd, *J* = 14.5, 8.6 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.7, 143.4, 141.0, 136.0, 128.2, 128.1, 127.8, 127.5, 125.9, 123.2, 109.2, 71.2, 47.3, 45.9, 26.3, 23.5. HRMS (ESI) m/z calcd for $C_{18}H_{18}ClNNaO_2^+$ $(M+Na)^+$ 338.0918, found 338.0930.

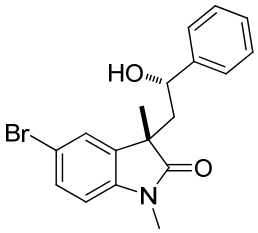
Data of ***syn*-18**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.17 (m, 6H), 7.15 (d, *J* = 2.1 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 4.37 (s, 1H), 4.29 (dd, *J* = 10.7, 3.1 Hz, 1H), 3.22 (s, 3H), 2.54 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.12 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.9, 144.0, 142.2, 134.9, 128.4, 127.8, 127.7, 127.7, 125.5, 123.2, 109.1, 71.7, 47.3, 46.6, 26.5, 25.3. HRMS (ESI) m/z calcd for $C_{18}H_{18}ClNNaO_2^+$ $(M+Na)^+$ 338.0918, found 338.0931.

5-bromo-3-(2-hydroxy-2-phenylethyl)-1,3-dimethylindolin-2-one (19)



***anti*-19**



***syn*-19**

The title compound **19** was synthesized according to General Procedure using *N*-(4-bromophenyl)-*N*-methylmethacrylamide (60.9 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-19** (43.3 mg) as a white solid (mp 148-150 ^{o}C) and ***syn*-19** (11.4 mg) as a white solid (mp 134-136 ^{o}C). Total isolated yield of **19**: 76%, *dr*: 3.8:1.

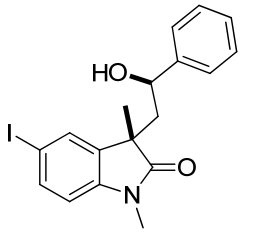
Data of ***anti*-19**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.30 – 7.15 (m, 6H), 6.68 (d, *J* = 8.3 Hz, 1H), 4.83 (dd, *J* = 8.7, 4.3 Hz, 1H), 3.75 (s, 1H), 3.05 (s, 3H), 2.22 (dd, *J* = 14.6, 4.3 Hz, 1H), 2.10 (dd, *J* = 14.6, 8.6 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.6, 143.5, 141.5, 136.4, 130.8, 128.2, 127.6, 126.0, 115.5, 109.7, 71.3, 47.3, 46.0, 26.3, 23.6. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_2^+$ $(M+Na)^+$ 382.0413, found 382.0424.

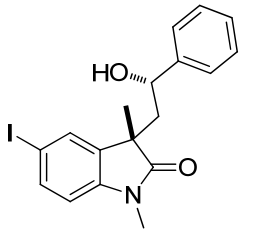
Data of ***syn*-19**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.30 – 7.18 (m, 6H), 6.74 (d, *J* = 8.2 Hz, 1H), 4.28 (dd, *J* = 10.6, 3.2 Hz, 1H), 3.21 (s, 3H), 2.54 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.11 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.7, 144.0, 142.7, 135.3, 130.7, 128.4, 127.7, 125.9, 125.5, 115.0, 109.6, 71.7, 47.3, 46.6, 26.5, 25.3. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_2^+$ $(M+Na)^+$ 382.0413, found 382.0426.

3-(2-hydroxy-2-phenylethyl)-5-iodo-1,3-dimethylindolin-2-one (20)



***anti*-20**



***syn*-20**

The title compound **20** was synthesized according to General Procedure using *N*-(4-iodophenyl)-*N*-methylmethacrylamide (72.2 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-20** (44.9 mg) as a white solid (mp 107-109 ^{o}C) and ***syn*-20** (10.4 mg) as a white solid (mp 115-117 ^{o}C). Total isolated yield of **20**: 68%, *dr*: 4.3:1.

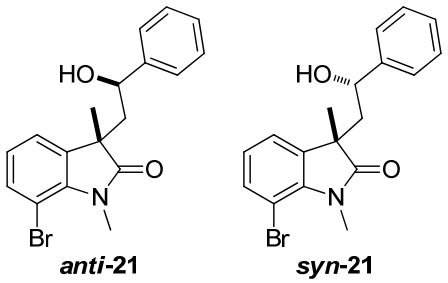
Data of ***anti*-20**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.44 (s, 1H), 7.30 – 7.14 (m, 5H), 6.58 (d, *J* = 8.2 Hz, 1H), 4.82 (dd, *J* = 8.5, 4.4 Hz, 1H), 3.84 (s, 1H), 3.02 (s, 3H), 2.21 (dd, *J* = 14.6, 4.4 Hz, 1H), 2.09 (dd, *J* = 14.5, 8.6 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.4, 143.4, 142.2, 136.7, 136.7, 131.4, 128.1, 127.5, 125.9, 110.3, 85.4, 71.2, 47.1, 45.9, 26.2, 23.5. HRMS (ESI) m/z calcd for $C_{18}H_{18}INNaO_2^+$ $(M+Na)^+$ 430.0274, found 430.0289.

Data of ***syn*-20**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.44 (s, 1H), 7.32 – 7.17 (m, 5H), 6.65 (d, *J* = 8.2 Hz, 1H), 4.28 (dd, *J* = 10.5, 3.3 Hz, 1H), 3.21 (s, 3H), 2.53 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.11 (dd, *J* = 14.5, 3.3 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.6, 143.9, 143.3, 136.7, 135.7, 131.5, 128.4, 127.7, 125.5, 110.3, 84.9, 71.7, 47.1, 46.6, 26.4, 25.3. HRMS (ESI) m/z calcd for $C_{18}H_{18}INNaO_2^+$ $(M+Na)^+$ 430.0274, found 430.0288.

7-bromo-3-(2-hydroxy-2-phenylethyl)-1,3-dimethylindolin-2-one (21)



***anti*-21** ***syn*-21**

The title compound **21** was synthesized according to General Procedure using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (60.9 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-21** (39.7 mg) as a colorless liquid and ***syn*-21** (9.2 mg) as a colorless liquid. Total isolated yield of **21**: 68%, *dr*: 4.3:1.

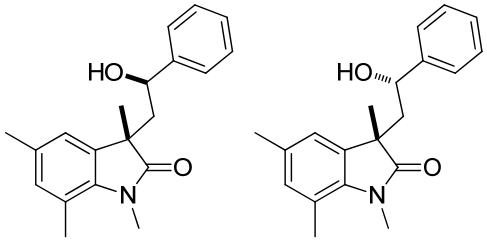
Data of ***anti*-21**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.16 (m, 5H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.94 – 6.87 (m, 1H), 4.79 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.61 (s, 1H), 3.43 (s, 3H), 2.23 (dd, *J* = 14.5, 4.5 Hz, 1H), 2.12 (dd, *J* = 14.5, 8.6 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 143.4, 139.9, 137.4, 133.6, 128.2, 127.6, 126.0, 123.9, 121.7, 102.6, 71.4, 46.8, 46.3, 29.8, 24.0. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_2^+$ $(M+Na)^+$ 382.0413, found 382.0422.

Data of ***syn*-21**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.16 (m, 4H), 7.10 (d, *J* = 6.1 Hz, 1H), 6.95 – 6.87 (m, 1H), 4.28 (dd, *J* = 10.7, 3.0 Hz, 1H), 3.62 (s, 3H), 2.55 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.11 (dd, *J* = 14.4, 3.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.7, 144.1, 141.0, 136.4, 133.6, 128.4, 127.6, 125.5, 123.5, 121.6, 102.7, 71.7, 47.1, 46.8, 30.0, 25.8. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_2^+$ $(M+Na)^+$ 382.0413, found 382.0424.

3-(2-hydroxy-2-phenylethyl)-1,3,5,7-tetramethylindolin-2-one (22)



***anti*-22** ***syn*-22**

The title compound **22** was synthesized according to General Procedure using *N*-(2,4-dimethylphenyl)-*N*-methylmethacrylamide (48.7 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-22** (35.3 mg) as a white solid (mp 151-153 ^{o}C) and ***syn*-22** (8.6 mg) as a white solid (mp 143-145 ^{o}C). Total isolated yield of **22**: 71%, *dr*: 4.1:1.

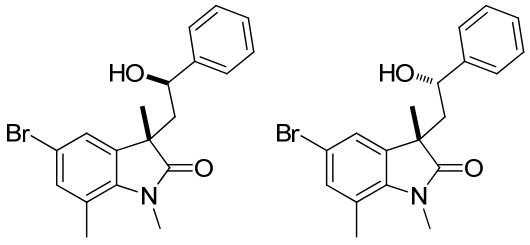
Data of ***anti*-22**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 4H), 7.24 – 7.20 (m, 1H), 6.81 (s, 2H), 4.95 (dd, *J* = 9.4, 3.3 Hz, 1H), 4.42 (s, 1H), 3.39 (s, 3H), 2.51 (s, 3H), 2.26 (s, 3H), 2.14 (dd, *J* = 14.7, 3.3 Hz, 1H), 2.00 (dd, *J* = 14.6, 9.5 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.2, 144.1, 137.6, 135.3, 132.4, 132.2, 128.1, 127.3, 126.0, 121.2, 119.8, 71.3, 46.8, 46.7, 29.6, 23.3, 20.7, 18.7. HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_2^+$ $(M+Na)^+$ 332.1621, found 332.1634.

Data of ***syn*-22**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 6.82 (s, 2H), 4.29 (dd, *J* = 10.5, 2.8 Hz, 1H), 3.50 (s, 3H), 2.56 (s, 3H), 2.51 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.31 (s, 3H), 2.10 (dd, *J* = 14.5, 2.8 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.2, 144.6, 138.9, 134.0, 132.1, 131.9, 128.3, 127.4, 125.5, 121.1, 119.6, 71.7, 47.3, 46.5, 29.7, 26.0, 20.8, 18.9. HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_2^+$ $(M+Na)^+$ 332.1621, found 332.1636.

5-bromo-3-(2-hydroxy-2-phenylethyl)-1,3,7-trimethylindolin-2-one (23)



***anti*-23** ***syn*-23**

The title compound **23** was synthesized according to General Procedure using *N*-(4-bromo-2-methylphenyl)-*N*-methylmethacrylamide (64.3 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give ***anti*-23** (38.2 mg) as a white solid (mp 117-119 ^{o}C) and ***syn*-23** (8.9 mg) as a white solid (mp 126-128 ^{o}C). Total isolated yield of **23**: 63%, *dr*: 4.3:1.

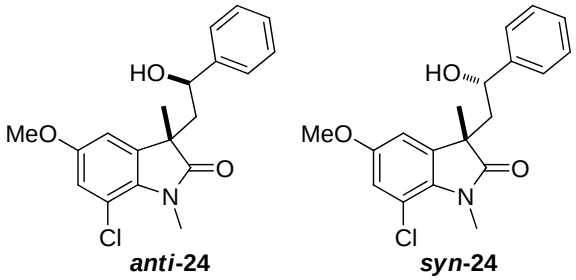
Data of ***anti*-23**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.24 – 7.20 (m, 3H), 7.14 (s, 1H), 7.11 (s, 1H), 4.86 (dd, *J* = 8.9, 4.1 Hz, 1H), 4.01 (s, 1H), 3.32 (s, 3H), 2.51 (s, 3H), 2.17 (dd, *J* = 14.6, 4.1 Hz, 1H), 2.05 (dd, *J* = 14.6, 8.9 Hz, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 143.5, 139.3, 137.0, 134.0, 128.1, 127.5, 126.0, 123.7, 121.9, 115.2, 71.2, 46.7, 46.3, 29.5, 23.7, 18.6. HRMS (ESI) m/z calcd for $C_{19}H_{20}BrNNaO_2^+$ $(M+Na)^+$ 396.0570, found 396.0579.

Data of ***syn*-23**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 1H), 7.26 (s, 1H), 7.25 – 7.18 (m, 3H), 7.15 (s, 1H), 7.11 (s, 1H), 4.28 (dd, *J* = 10.6, 3.1 Hz, 1H), 3.49 (s, 3H), 2.56 (s, 3H), 2.52 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.08 (dd, *J* = 14.5, 3.1 Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.6, 144.0, 140.5, 135.9, 134.0, 128.4, 127.6, 125.5, 123.6, 121.9, 114.8, 71.6, 46.9, 46.6, 29.7, 25.8, 18.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}BrNNaO_2^+$ $(M+Na)^+$ 396.0570, found 396.0577.

7-chloro-3-(2-hydroxy-2-phenylethyl)-5-methoxy-1,3-dimethylindolin-2-one (24)



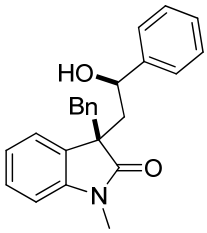
***anti*-24** ***syn*-24**

The title compound **24** was synthesized according to general procedure using *N*-benzyl-*N*-phenylmethacrylamide (60.2 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give an inseparable mixture of ***anti*-24** (major) and ***syn*-24** (minor) (37.9 mg, 55%, *dr*: 3.0:1) as a colorless liquid.

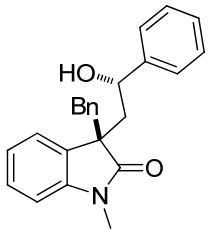
Data of mixture ***anti*-24** (major) and ***syn*-24** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.15 (m, 5.00H), 6.71 (d, *J* = 2.3 Hz, 1.00H), 6.66 (d, *J* = 2.3 Hz, 1.00H), 4.86 (dd, *J* = 8.8, 4.1 Hz, 0.75H), 4.29 (dd, *J* = 10.4, 3.1 Hz, 0.25H), 3.78 (s, 0.75H), 3.76 (s, 2.25H), 3.56 (s, 0.75H), 3.41 (s, 2.25H), 2.52 (dd, *J* = 14.5, 10.4 Hz, 0.25H), 2.18 (dd, *J* = 14.6, 4.2 Hz, 0.75H), 2.13 – 2.03 (m, 1.00H), 1.47 (s, 2.25H), 1.35 (s, 0.75H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.2, 181.1, 156.0, 155.7, 144.1, 143.6, 138.3, 137.1, 133.0, 131.8, 128.3, 128.2, 127.6, 126.0, 125.5, 115.6, 115.5, 114.0, 113.7, 109.4, 109.2, 71.5, 71.3, 55.8, 55.8, 47.4, 47.3, 47.0, 46.4, 29.6, 29.5, 25.8, 23.9. HRMS (ESI) m/z calcd for $C_{19}H_{20}ClNNaO_3^+$ $(M+Na)^+$ 368.1024, found 368.1038.

3-benzyl-3-(2-hydroxy-2-phenylethyl)-1-methylindolin-2-one (25)



***anti*-25**



***syn*-25**

The title compound **25** was synthesized according to General Procedure using 2-benzyl-*N*-methyl-*N*-phenylacrylamide (60.2 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-25** (36.5 mg) as a white solid (mp 121-123 ^{o}C) and ***syn*-25** (13.5 mg) as a white solid (mp 138-140 ^{o}C). Total isolated yield of **25**: 70%, *dr*: 2.7:1.

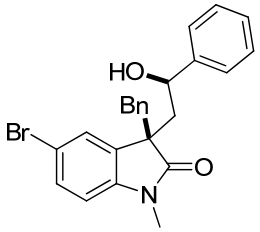
Data of ***anti*-25**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.13 (m, 7H), 7.09 – 6.95 (m, 4H), 6.77 (d, *J* = 7.0 Hz, 2H), 6.51 (d, *J* = 7.7 Hz, 1H), 4.90 (dd, *J* = 8.7, 4.4 Hz, 1H), 3.78 (s, 1H), 3.36 (d, *J* = 12.8 Hz, 1H), 3.05 (d, *J* = 12.8 Hz, 1H), 2.76 (s, 3H), 2.44 (dd, *J* = 14.5, 4.4 Hz, 1H), 2.28 (dd, *J* = 14.4, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.4, 143.7, 143.1, 135.0, 131.2, 129.8, 128.1, 127.5, 127.3, 126.5, 126.1, 123.6, 122.3, 107.9, 71.3, 53.3, 45.1, 43.6, 25.7. HRMS (ESI) m/z calcd for $C_{24}H_{23}NNaO_2^+$ $(M+Na)^+$ 380.1621, found 380.1636.

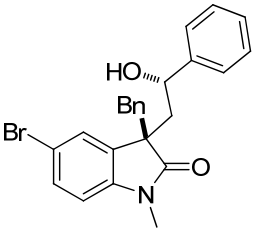
Data of ***syn*-25**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.17 (m, 6H), 7.13 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.08 – 7.00 (m, 4H), 6.81 – 6.73 (m, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 4.32 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.13 (d, *J* = 12.8 Hz, 1H), 3.00 – 2.96 (m, 4H), 2.67 (dd, *J* = 14.5, 10.7 Hz, 1H), 2.27 (dd, *J* = 14.4, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.9, 144.5, 144.1, 135.2, 130.3, 130.0, 128.4, 128.0, 127.5, 127.3, 126.5, 125.5, 123.5, 121.9, 108.0, 71.6, 53.2, 45.5, 45.2, 26.0. HRMS (ESI) m/z calcd for $C_{24}H_{23}NNaO_2^+$ $(M+Na)^+$ 380.1621, found 380.1637.

3-benzyl-5-bromo-3-(2-hydroxy-2-phenylethyl)-1-methylindolin-2-one (26)



***anti*-26**



***syn*-26**

The title compound **26** was synthesized according to General Procedure using 2-benzyl-*N*-(4-bromophenyl)-*N*-methylacrylamide (79.2 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-26** (51.0 mg) as a white solid (mp 128-130 ^{o}C) and ***syn*-26** (19.6 mg) as a white solid (mp 163-165 ^{o}C). Total isolated yield of

26: 81%, *dr*: 2.6:1.

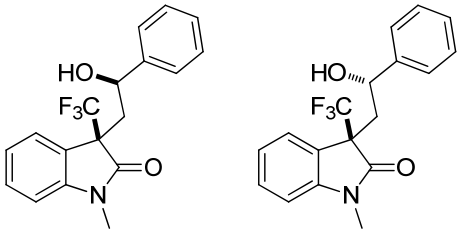
Data of ***anti*-26**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.13 (m, 7H), 7.08 – 6.99 (m, 3H), 6.77 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.36 (d, *J* = 8.7 Hz, 1H), 4.85 (dd, *J* = 8.3, 4.9 Hz, 1H), 3.51 (s, 1H), 3.32 (d, *J* = 12.8 Hz, 1H), 3.02 (d, *J* = 12.9 Hz, 1H), 2.71 (s, 3H), 2.44 (dd, *J* = 14.5, 4.9 Hz, 1H), 2.29 (dd, *J* = 14.5, 8.3 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.8, 143.3, 142.2, 134.6, 133.5, 130.8, 129.8, 128.1, 127.7, 127.5, 126.8, 126.7, 126.1, 114.9, 109.3, 71.2, 53.4, 44.7, 43.9, 25.8. HRMS (ESI) m/z calcd for $C_{24}H_{22}BrNNaO_2^+$ $(M+Na)^+$ 458.0726, found 458.0735.

Data of ***syn*-26**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.17 (m, 7H), 7.11 – 7.01 (m, 3H), 6.78 (d, *J* = 5.8 Hz, 2H), 6.46 (d, *J* = 8.2 Hz, 1H), 4.33 (dd, *J* = 10.5, 3.3 Hz, 1H), 3.11 (d, *J* = 12.9 Hz, 1H), 2.95 (d, *J* = 12.9 Hz, 1H), 2.92 (s, 3H), 2.68 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.25 (dd, *J* = 14.4, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 144.0, 143.2, 134.7, 132.5, 130.8, 129.9, 128.4, 127.7, 127.5, 126.7, 126.7, 125.6, 114.5, 109.3, 71.6, 53.4, 45.2, 45.1, 26.0. HRMS (ESI) m/z calcd for $C_{24}H_{22}BrNNaO_2^+$ $(M+Na)^+$ 458.0726, found 458.0736.

3-(2-hydroxy-2-phenylethyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (27)



***anti*-27** ***syn*-27**

The title compound **27** was synthesized according to General Procedure using *N*-methyl-*N*-phenyl-2-(trifluoromethyl)acrylamide (55.0 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give ***anti*-27** (46.8 mg) as a colorless liquid and ***syn*-27** (16.1 mg) as a colorless liquid. Total isolated yield of **27**: 94%, *dr*: 2.9:1.

Data of ***anti*-27**

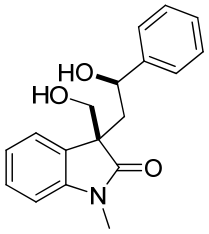
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.24 – 7.20 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.98 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.77 (d, *J* = 9.1 Hz, 1H), 4.55 (t, *J* = 6.9 Hz, 1H), 2.87 (s, 3H), 2.78 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.62 (dd, *J* = 14.2, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.1 (q, *J* = 2.2 Hz), 144.2, 141.8, 130.0, 128.1, 128.1, 126.3, 125.2, 124.6 (q, *J* = 280.8 Hz), 123.9, 123.0, 108.6, 70.9, 54.9 (q, *J* = 26.5 Hz), 38.6, 26.3; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.80. HRMS (ESI) m/z calcd for $C_{18}H_{16}F_3NNaO_2^+$ $(M+Na)^+$ 358.1025, found 358.1045.

Data of ***syn*-27**

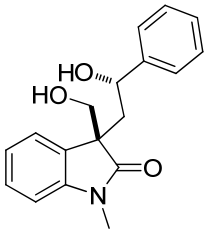
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.36 (m, 2H), 7.32 – 7.19 (m, 5H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.26 (dd, *J* = 11.1, 2.8 Hz, 1H), 3.25 (s, 3H), 2.87 (dd, *J* = 14.3, 11.2

Hz, 1H), 2.46 (dd, *J* = 14.3, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.5, 145.2, 143.2, 130.1, 128.6, 128.0, 125.5, 125.0, 124.8 (q, *J* = 281.0 Hz), 123.2, 122.8, 108.8, 70.7, 55.4 (q, *J* = 26.4 Hz), 39.3, 26.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.07. HRMS (ESI) m/z calcd for $C_{18}H_{16}F_3NNaO_2^+$ $(M+Na)^+$ 358.1025, found 358.1047.

3-(2-hydroxy-2-phenylethyl)-3-(hydroxymethyl)-1-methylindolin-2-one (28)



***anti*-28**



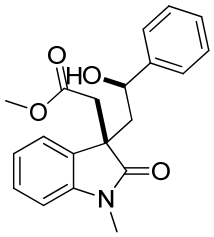
***syn*-28**

The title compound **28** was synthesized according to general procedure using 2-(hydroxymethyl)-*N*-methyl-*N*-phenylacrylamide (45.8 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 1:1 to 2:3) was performed to give an inseparable mixture of ***anti*-28** (major) and ***syn*-28** (minor) (55.8 mg, 94%, *dr*: 2.0:1) as a white solid (mp 108-110 ^{o}C).

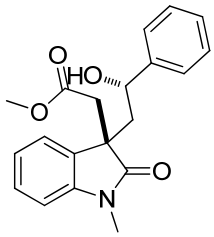
Data of mixture ***anti*-28** (major) and ***syn*-28** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.14 (m, 5.67H), 7.11 – 7.01 (m, 2.33H), 6.84 (d, *J* = 7.8 Hz, 0.33H), 6.77 (d, *J* = 7.5 Hz, 0.67H), 4.64 (t, *J* = 6.8 Hz, 0.67H), 4.48 (dd, *J* = 10.6, 2.6 Hz, 0.33H), 3.81 – 3.68 (m, 2H), 3.16 (s, 0.99H), 2.90 (s, 2.01H), 2.51 (dd, *J* = 14.6, 10.6 Hz, 0.33H), 2.28 (d, *J* = 6.8 Hz, 1.34H), 2.04 (dd, *J* = 14.6, 2.6 Hz, 0.33H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.6, 178.8, 144.3, 143.9, 143.5, 143.1, 130.1, 130.0, 128.4, 128.2, 128.2, 128.0, 127.6, 127.3, 126.1, 125.4, 123.8, 123.2, 122.7, 122.6, 108.3, 108.3, 71.2, 70.6, 67.3, 66.8, 53.1, 52.9, 42.0, 41.3, 26.2, 26.0. HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_3^+$ $(M+Na)^+$ 320.1257, found 320.1272.

methyl 2-(3-(2-hydroxy-2-phenylethyl)-1-methyl-2-oxoindolin-3-yl)acetate (29)



***anti*-29**



***syn*-29**

The title compound **29** was synthesized according to General Procedure using methyl 3-(methyl(phenyl)carbamoyl)but-3-enoate (55.9 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-29** (8.7 mg) as a colorless liquid and ***syn*-29** (3.5 mg) as a colorless liquid. Total isolated yield of **29**: 18%, *dr*: 2.5:1.

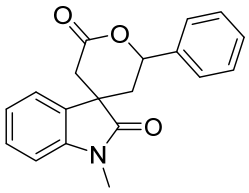
Data of ***anti*-29**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 7H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.89 (dd, *J* = 9.1, 5.9 Hz, 1H), 3.49 (s, 3H), 3.18 (s, 3H), 3.15 – 3.06 (m, 3H), 2.24 (dd, *J* = 14.7, 5.8 Hz, 1H), 2.12 (dd, *J* = 15.0, 9.3 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.0, 170.2, 143.8, 143.5, 131.4, 128.6, 128.3, 127.5, 125.8, 123.0, 122.8, 108.5, 71.2, 51.7, 48.8, 45.8, 40.1, 26.5. HRMS (ESI) m/z calcd for $C_{20}H_{21}NNaO_4^+$ $(M+Na)^+$ 362.1363, found 362.1377.

Data of ***syn*-29**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.18 (m, 7H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.36 (dd, *J* = 10.6, 2.6 Hz, 1H), 3.46 (s, 3H), 3.28 (s, 3H), 3.04 (d, *J* = 16.2 Hz, 1H), 2.86 (d, *J* = 16.2 Hz, 1H), 2.47 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.20 (dd, *J* = 14.3, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.6, 170.1, 144.5, 144.3, 130.5, 128.5, 128.4, 127.6, 125.4, 123.0, 122.4, 108.2, 71.1, 51.6, 48.5, 46.3, 41.8, 26.5. HRMS (ESI) m/z calcd for $C_{20}H_{21}NNaO_4^+$ $(M+Na)^+$ 362.1363, found 362.1375.

1-methyl-6'-phenyl-5',6'-dihydrospiro[indoline-3,4'-pyran]-2,2'(3'*H*)-dione (29')



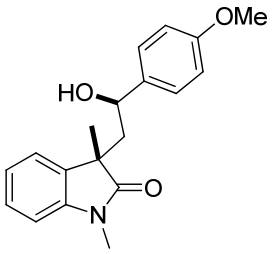
29'

The title compound **29'** was synthesized according to general procedure using 3-(methyl(phenyl)carbamoyl)but-3-enoate (55.9 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give an inseparable mixture of **29'** (30.7 mg, 50%, *dr*: 2.8:1) as a white solid (mp 167-169 ^{o}C).

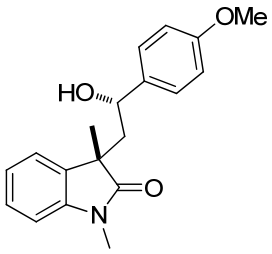
Data of mixture **29'**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.29 (m, 6.74H), 7.25 (d, *J* = 7.9 Hz, 0.26H), 7.16 (t, *J* = 7.5 Hz, 0.74H), 7.11 (t, *J* = 7.5 Hz, 0.26H), 6.96 (d, *J* = 7.8 Hz, 0.74H), 6.89 (d, *J* = 7.8 Hz, 0.26H), 5.90 (dd, *J* = 12.0, 4.0 Hz, 0.26H), 5.74 (dd, *J* = 12.4, 3.7 Hz, 0.74H), 3.25 – 3.24 (m, 3.00H), 3.11 – 3.01 (m, 1.00H), 2.71 – 2.59 (m, 1.00H), 2.43 (dd, *J* = 14.3, 12.4 Hz, 0.74H), 2.33 (dd, *J* = 14.7, 3.3 Hz, 0.26H), 2.19 (dd, *J* = 14.8, 11.8 Hz, 0.26H), 1.98 – 1.97 (m, 0.74H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.5, 177.1, 169.9, 168.8, 142.7, 142.4, 138.5, 138.3, 132.5, 130.9, 129.2, 128.9, 128.6, 128.6, 128.5, 125.9, 125.8, 123.4, 123.3, 123.1, 122.5, 108.9, 108.5, 78.6, 45.9, 44.9, 39.8, 38.4, 36.8, 36.1, 26.5, 26.4. HRMS (ESI) m/z calcd for $C_{19}H_{17}NNaO_3^+$ $(M+Na)^+$ 330.1101, found 330.1122.

3-(2-hydroxy-2-(4-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (30)



***anti*-30**



***syn*-30**

The title compound **30** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-methoxybenzaldehyde (27.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-30** (39.5 mg) as a white solid (mp 115-117 ^{o}C) and ***syn*-30** (9.6 mg) as a white solid (mp 134-136 ^{o}C). Total isolated yield of **30**: 79%, *dr*: 4.1:1.

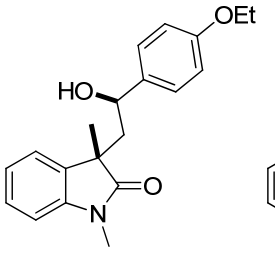
Data of ***anti*-30**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 1H), 7.18 (d, *J* = 6.2 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.84 – 6.77 (m, 3H), 4.79 (dd, *J* = 8.8, 4.3 Hz, 1H), 3.77 (s, 3H), 3.07 (s, 3H), 2.21 (dd, *J* = 14.5, 4.4 Hz, 1H), 2.10 (dd, *J* = 14.5, 8.7 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.2, 158.8, 142.4, 135.9, 134.3, 128.0, 127.2, 122.8, 122.5, 113.4, 108.3, 70.9, 55.2, 47.1, 46.1, 26.2, 23.4. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_3^+$ $(M+Na)^+$ 334.1414, found 334.1429.

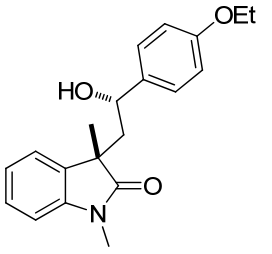
Data of ***syn*-30**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.22 (dd, *J* = 10.7, 2.8 Hz, 1H), 3.77 (s, 3H), 3.25 (s, 3H), 2.55 (dd, *J* = 14.5, 10.7 Hz, 1H), 2.11 (dd, *J* = 14.4, 2.9 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 158.9, 143.6, 136.6, 133.2, 127.9, 126.7, 122.5, 122.4, 113.7, 108.2, 71.3, 55.2, 47.1, 46.9, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_3^+$ $(M+Na)^+$ 334.1414, found 334.1430.

3-(2-(4-ethoxyphenyl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (31)



***anti*-31**



***syn*-31**

The title compound **31** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-ethoxybenzaldehyde (30.0 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica

gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-31** (39.5 mg) as a white solid (mp 110-112 °C) and ***syn*-31** (9.9 mg) as a white solid (mp 123-125 °C). Total isolated yield of **31**: 76%, *dr*: 4.0:1.

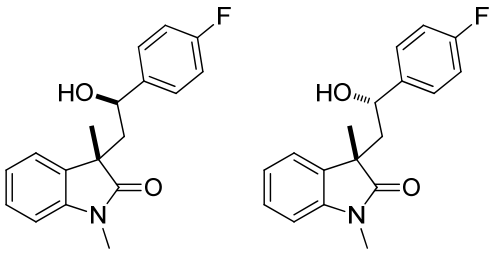
Data of ***anti*-31**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.11 – 7.03 (m, 3H), 6.79 (t, *J* = 9.1 Hz, 3H), 4.74 (dd, *J* = 8.5, 4.6 Hz, 1H), 3.98 (qd, *J* = 7.0, 1.4 Hz, 2H), 3.04 (s, 3H), 2.22 (dd, *J* = 14.5, 4.6 Hz, 1H), 2.11 (dd, *J* = 14.5, 8.5 Hz, 1H), 1.47 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.1, 158.1, 142.4, 135.6, 134.2, 127.9, 127.2, 122.7, 122.5, 113.9, 108.2, 70.9, 63.2, 47.0, 45.9, 26.1, 23.5, 14.7. HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_3^+$ $(M+Na)^+$ 348.1570, found 348.1585.

Data of ***syn*-31**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.13 – 7.05 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.19 (dd, *J* = 10.6, 2.9 Hz, 1H), 3.98 (q, *J* = 7.0 Hz, 2H), 3.23 (s, 3H), 2.54 (dd, *J* = 14.5, 10.7 Hz, 1H), 2.10 (dd, *J* = 14.4, 2.9 Hz, 1H), 1.43 – 1.31 (m, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 158.2, 143.5, 136.4, 133.2, 127.8, 126.7, 122.5, 122.3, 114.2, 108.2, 71.2, 63.3, 47.1, 46.8, 26.3, 25.4, 14.8. HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_3^+$ $(M+Na)^+$ 348.1570, found 348.1587.

3-(2-(4-fluorophenyl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (32)



***anti*-32** ***syn*-32**

The title compound **32** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-fluorobenzaldehyde (24.8 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-32** (39.0 mg) as a white solid (mp 87-89 °C) and ***syn*-32** (10.0 mg) as a white solid (mp 97-99 °C). Total isolated yield of **32**: 82%, *dr*: 3.9:1.

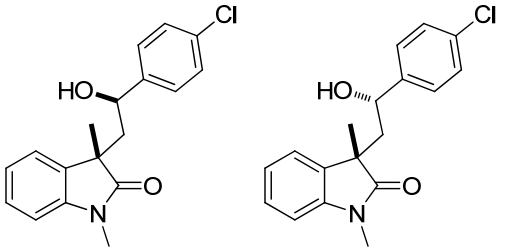
Data of ***anti*-32**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (td, *J* = 7.8, 1.4 Hz, 1H), 7.23 – 7.13 (m, 3H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.87 (dd, *J* = 9.0, 3.9 Hz, 1H), 4.21 (s, 1H), 3.11 (s, 3H), 2.19 (dd, *J* = 14.6, 4.0 Hz, 1H), 2.06 (dd, *J* = 14.6, 9.0 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 162.0 (d, *J* = 245.1 Hz), 142.4, 139.6 (d, *J* = 3.1 Hz), 134.3, 128.1, 127.6 (d, *J* = 8.0 Hz), 123.0, 122.5, 114.9 (d, *J* = 21.3 Hz), 108.4, 70.7, 47.2, 46.2, 26.2, 23.3.; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.24. HRMS (ESI) m/z calcd for $C_{18}H_{18}FNNaO_2^+$ $(M+Na)^+$ 322.1214, found 322.1228.

Data of ***syn*-32**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (td, *J* = 7.7, 1.3 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.25 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.23 (s, 3H), 2.50 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.10 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 162.0 (d, *J* = 245.5 Hz), 143.5, 140.2, 133.1, 128.0, 127.1 (d, *J* = 8.1 Hz), 122.5 (d, *J* = 2.7 Hz), 115.1 (d, *J* = 21.3 Hz), 108.3, 71.1, 47.1, 47.0, 26.4, 25.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.17. HRMS (ESI) m/z calcd for $C_{18}H_{18}FNNaO_2^+$ $(M+Na)^+$ 322.1214, found 322.1230.

3-(2-(4-chlorophenyl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (33)



***anti*-33** ***syn*-33**

The title compound **33** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-chlorobenzaldehyde (28.0 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-33** (42.6 mg) as a white solid (mp 127-129 ^{o}C) and ***syn*-33** (11.5 mg) as a white solid (mp 109-111 ^{o}C). Total isolated yield of **33**: 86%, *dr*: 3.7:1.

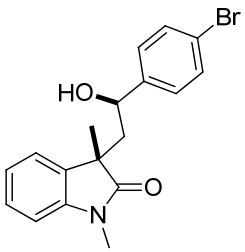
Data of ***anti*-33**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (td, *J* = 7.0, 6.4, 1.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.10 (m, 3H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.83 (dd, *J* = 9.0, 4.0 Hz, 1H), 4.37 (s, 1H), 3.09 (s, 3H), 2.17 (dd, *J* = 14.6, 4.0 Hz, 1H), 2.04 (dd, *J* = 14.6, 9.0 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 142.4, 142.4, 134.2, 133.0, 128.3, 128.2, 127.6, 123.1, 122.6, 108.5, 70.8, 47.3, 46.1, 26.3, 23.5. HRMS (ESI) m/z calcd for $C_{18}H_{18}ClNNaO_2^+$ $(M+Na)^+$ 338.0918, found 338.0931.

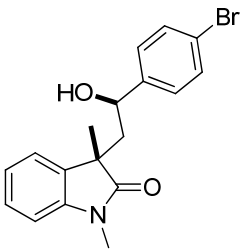
Data of ***syn*-33**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (td, *J* = 7.7, 1.3 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.12 – 7.07 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.24 (dd, *J* = 10.5, 2.9 Hz, 1H), 3.23 (s, 3H), 2.48 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.10 (dd, *J* = 14.5, 2.9 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 143.5, 142.9, 133.1, 133.1, 128.4, 128.0, 126.9, 122.5, 122.5, 108.3, 71.1, 47.1, 46.9, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{18}H_{18}ClNNaO_2^+$ $(M+Na)^+$ 338.0918, found 338.0929.

3-(2-(4-bromophenyl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (34)



***anti*-34**



***syn*-34**

The title compound **34** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-bromobenzaldehyde (37.0 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-34** (53.6 mg) as a white solid (mp 117-119 ^{o}C) and ***syn*-34** (11.9 mg) as a white solid (mp 107-109 ^{o}C). Total isolated yield of **34**: 91%, *dr*: 4.5:1.

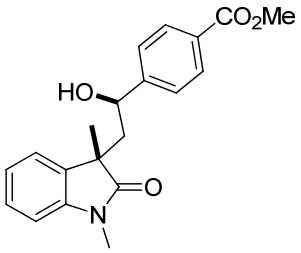
Data of ***anti*-34**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.28 (t, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.13 – 7.06 (m, 3H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.88 (dd, *J* = 9.3, 3.6 Hz, 1H), 3.13 (s, 3H), 2.16 (dd, *J* = 14.7, 3.6 Hz, 1H), 2.02 (dd, *J* = 14.7, 9.3 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 142.9, 142.3, 134.2, 131.1, 128.1, 127.7, 123.0, 122.5, 121.0, 108.5, 70.7, 47.3, 46.1, 26.3, 23.2. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_2^+$ $(M+Na)^+$ 382.0413, found 382.0416.

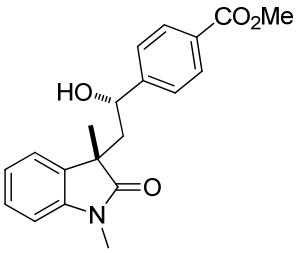
Data of ***syn*-34**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.11 – 7.05 (m, 3H), 6.88 (d, *J* = 7.8 Hz, 1H), 4.22 (dd, *J* = 10.6, 2.9 Hz, 1H), 3.23 (s, 3H), 2.48 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.09 (dd, *J* = 14.5, 2.9 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 143.5, 143.4, 133.0, 131.4, 128.0, 127.2, 122.5, 122.5, 121.2, 108.3, 71.1, 47.0, 46.8, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_2^+$ $(M+Na)^+$ 382.0413, found 382.0417.

methyl 4-(2-(1,3-dimethyl-2-oxoindolin-3-yl)-1-hydroxyethyl)benzoate (35)



***anti*-35**



***syn*-35**

The title compound **35** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 4-formylbenzoate (32.8 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica

gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give ***anti*-35** (29.9 mg) as a white solid (mp 135-137 ^{o}C) and ***syn*-35** (6.0 mg) as a white solid (mp 126-128 ^{o}C). Total isolated yield of **35**: 53%, *dr*: 5.0:1.

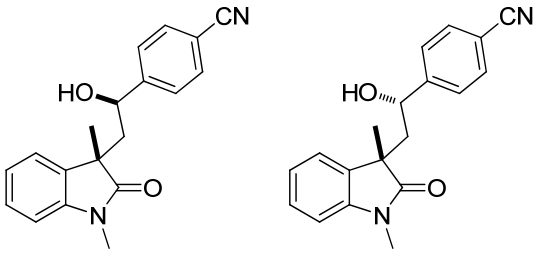
Data of ***anti*-35**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.22 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.08 (td, *J* = 7.5, 0.99 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.98 (dd, *J* = 9.3, 3.50 Hz, 1H), 4.56 (s, 1H), 3.88 (s, 3H), 3.13 (s, 3H), 2.19 (dd, *J* = 14.7, 3.5 Hz, 1H), 2.04 (dd, *J* = 14.7, 9.3 Hz, 1H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 166.9, 149.1, 142.3, 134.2, 129.4, 129.0, 128.1, 125.9, 123.0, 122.4, 108.4, 70.9, 51.9, 47.3, 46.0, 26.2, 23.1. HRMS (ESI) m/z calcd for $C_{20}H_{21}NNaO_4^+$ $(M+Na)^+$ 362.1363, found 362.1372.

Data of ***syn*-35**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.31 (td, *J* = 7.7, 1.3 Hz, 1H), 7.27 (d, *J* = 3.6 Hz, 2H), 7.21 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.33 (dd, *J* = 10.5, 2.8 Hz, 1H), 3.89 (s, 3H), 3.25 (s, 3H;, 2.50 (dd, *J* = 14.6, 10.5 Hz, 1H), 2.14 (dd, *J* = 14.6, 2.8 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 166.8, 149.5, 143.5, 133.1, 129.7, 129.2, 128.1, 125.4, 122.6, 122.5, 108.3, 71.4, 52.0, 47.1, 46.9, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{20}H_{21}NNaO_4^+$ $(M+Na)^+$ 362.1363, found 362.1373.

4-(2-(1,3-dimethyl-2-oxoindolin-3-yl)-1-hydroxyethyl)benzonitrile (36)



***anti*-36** ***syn*-36**

The title compound **36** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 4-formylbenzonitrile (26.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 2:1 to 1:1) was performed to give ***anti*-36** (23.2 mg) as a white solid and ***syn*-36** (4.9 mg) as a white solid (mp 76-78 ^{o}C). Total isolated yield of **36**: 46%, *dr*: 4.7:1.

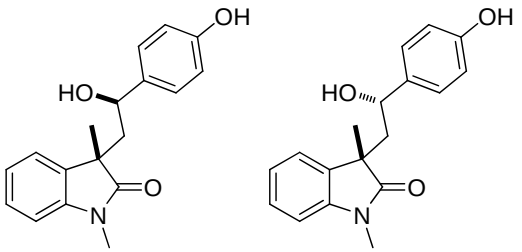
Data of ***anti*-36**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.30 (td, *J* = 7.9, 1.6 Hz, 1H), 7.16 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.04 (dd, *J* = 9.6, 3.0 Hz, 1H), 4.78 (s, 1H), 3.19 (s, 3H), 2.16 (dd, *J* = 14.8, 3.1 Hz, 1H), 1.99 (dd, *J* = 14.7, 9.6 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 149.5, 142.2, 134.1, 132.0, 128.3, 126.6, 123.2, 122.4, 118.8, 110.9, 108.6, 70.7, 47.4, 46.1, 26.4, 23.0. HRMS (ESI) m/z calcd for $C_{19}H_{18}N_2NaO_2^+$ $(M+Na)^+$ 329.1260, found 329.1268.

Data of ***syn*-36**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.18 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.35 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.25 (s, 3H), 2.47 (dd, *J* = 14.6, 10.3 Hz, 1H), 2.12 (dd, *J* = 14.6, 3.0 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.1, 149.7, 143.4, 133.0, 132.2, 128.2, 126.2, 122.7, 122.4, 118.7, 111.1, 108.4, 71.1, 47.1, 46.9, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{19}H_{18}N_2NaO_2^+$ $(M+Na)^+$ 329.1260, found 329.1269.

3-(2-hydroxy-2-(4-hydroxyphenyl)ethyl)-1,3-dimethylindolin-2-one (37)



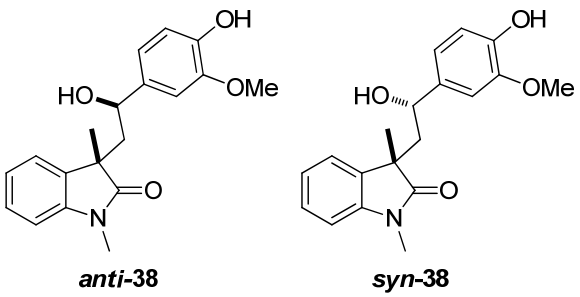
***anti*-37** ***syn*-37**

The title compound **37** was synthesized according to general procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-hydroxybenzaldehyde (24.4 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 1:1 to 2:3) was performed to give an inseparable mixture of ***anti*-37** (major) and ***syn*-37** (minor) (57.6 mg, 97%, *dr*: 3.3:1) as a white solid (mp 152-154 ^{o}C).

Data of mixture ***anti*-37** (major) and ***syn*-37** (minor)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (s, 1.00H), 7.35 (d, *J* = 7.3 Hz, 0.77H), 7.30 – 7.21 (m, 1.23H), 7.06 (t, *J* = 7.4 Hz, 0.77H), 6.99 (d, *J* = 7.4 Hz, 0.23H), 6.93 (t, *J* = 8.2 Hz, 1.00H), 6.87 (d, *J* = 7.7 Hz, 0.77H), 6.62 – 6.52 (m, 3.23H), 4.90 (d, *J* = 4.0 Hz, 0.77H), 4.64 (d, *J* = 4.3 Hz, 0.23H), 4.01 – 3.95 (m, 1.00H), 3.08 (s, 0.69H), 2.72 (s, 2.31H), 2.26 – 2.21 (m, 0.77H), 2.14 – 2.09 (m, 1.00H), 2.03 – 1.93 (m, 0.23H), 1.19 (d, *J* = 3.89 Hz, 3.00H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.4, 179.2, 156.5, 156.2, 143.7, 143.1, 136.6, 134.5, 133.4, 133.3, 127.8, 127.8, 127.6, 126.8, 123.2, 123.1, 122.1, 121.8, 114.8, 114.4, 108.4, 108.3, 70.3, 69.7, 47.0, 46.4, 46.1, 45.8, 26.2, 25.8, 25.5, 25.3. HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_3^+$ $(M+Na)^+$ 320.1257, found 320.1268.

3-(2-hydroxy-2-(4-hydroxy-3-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (38)



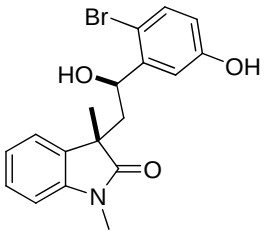
***anti*-38** ***syn*-38**

The title compound **38** was synthesized according to general procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-hydroxy-3-methoxybenzaldehyde (30.4 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 2:1 to 1:1) was performed to give an inseparable mixture of ***anti*-38** (major) and ***syn*-38** (minor) (46.4 mg, 71%, *dr*: 3.3:1) as white solid (mp 142-144 ^{o}C).

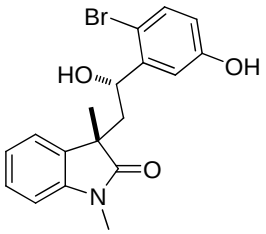
Data of mixture ***anti*-38** (major) and ***syn*-38** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 1.23H), 7.20 – 7.17 (m, 1.00H), 7.10 – 7.06 (m, 1.00H), 6.87 (d, *J* = 7.8 Hz, 0.23H), 6.82 – 6.73 (m, 2.54H), 6.59 (dd, *J* = 8.1, 2.0 Hz, 0.23H), 6.54 (dd, *J* = 8.1, 1.9 Hz, 0.77H), 5.81 (s, 1H), 4.74 (dd, *J* = 8.6, 4.7 Hz, 0.77H), 4.17 (dd, *J* = 10.6, 2.9 Hz, 0.23H), 3.83 – 3.82 (m, 3H), 3.22 (s, 0.69H), 3.05 (s, 2.31H), 2.57 – 2.51 (m, 0.23H), 2.25 (dd, *J* = 14.5, 4.7 Hz, 0.77H), 2.17 – 2.10 (m, 1.00H), 1.48 (s, 2.31H), 1.37 (s, 0.69H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 181.2, 146.5, 146.4, 144.9, 144.9, 143.5, 142.5, 136.4, 135.5, 134.2, 133.2, 127.9, 127.8, 122.8, 122.6, 122.5, 122.3, 119.1, 118.4, 113.9, 113.7, 108.7, 108.3, 108.2, 108.1, 71.5, 71.4, 55.8, 55.8, 47.1, 47.0, 46.7, 45.9, 26.3, 26.1, 25.4, 23.6. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_4^+$ $(M+Na)^+$ 350.1363, found 350.1375.

3-(2-(2-bromo-5-hydroxyphenyl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (39)



***anti*-39**



***syn*-39**

The title compound **39** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 2-bromo-5-hydroxybenzaldehyde (40.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 2:1 to 1:1) was performed to give ***anti*-39** (45.1 mg) as a white solid (mp 170-172 ^{o}C) and ***syn*-39** (18.8 mg) as a light yellow solid (mp 201-203 ^{o}C). Total isolated yield of **39**: 85%, *dr*: 2.4:1.

Data of ***anti*-39**

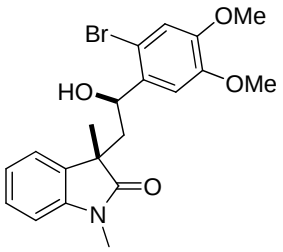
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.30 – 7.12 (m, 4H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.54 (dd, *J* = 8.6, 3.0 Hz, 1H), 5.86 (s, 1H), 5.41 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.20 (s, 3H), 2.28 (dd, *J* = 15.0, 2.4 Hz, 1H), 1.76 (dd, *J* = 15.0, 9.7 Hz, 1H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.8, 156.1, 143.0, 141.9, 134.8, 133.1, 128.2, 123.5, 122.4, 116.6, 114.8, 110.5, 108.7, 70.3, 47.7, 43.4, 26.5, 22.1. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_3^+$ $(M+Na)^+$ 398.0362, found 398.0372.

Data of ***syn*-39**

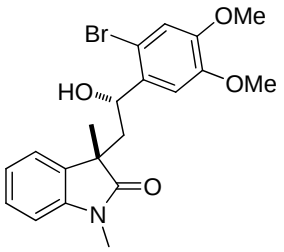
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 3.1 Hz, 1H), 6.87 (d, *J* = 7.8 Hz,

1H), 6.60 (dd, *J* = 8.6, 2.9 Hz, 1H), 4.44 (dd, *J* = 10.1, 3.2 Hz, 1H), 3.05 (s, 3H), 2.26 – 2.17 (m, 2H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.7, 156.5, 144.2, 143.2, 133.3, 132.6, 128.1, 123.2, 122.8, 116.7, 114.1, 110.1, 108.6, 70.9, 47.5, 44.8, 26.3, 25.2. HRMS (ESI) m/z calcd for $C_{18}H_{18}BrNNaO_3^+$ $(M+Na)^+$ 398.0362, found 398.0371.

3-(2-(2-bromo-4,5-dimethoxyphenyl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (40)



***anti*-40**



***syn*-40**

The title compound **40** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 2-bromo-4,5-dimethoxybenzaldehyde (49.0 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-40** (49.0 mg) as a white solid (mp 110-112 ^{o}C) and ***syn*-40** (18.2 mg) as a colorless liquid (mp 97-99 ^{o}C). Total isolated yield of **40**: 80%, *dr*: 2.7:1.

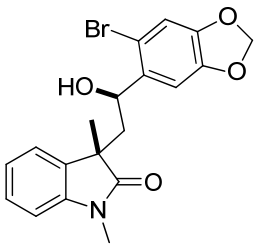
Data of ***anti*-40**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.16 (s, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.46 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.38 (s, 1H), 3.84 (d, *J* = 1.3 Hz, 6H), 3.25 (s, 3H), 2.23 (dd, *J* = 14.8, 1.8 Hz, 1H), 1.72 (dd, *J* = 14.9, 10.0 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.5, 148.5, 148.3, 141.9, 135.4, 135.0, 128.0, 123.2, 122.3, 114.8, 110.6, 109.9, 108.4, 69.7, 56.0, 55.8, 47.6, 44.3, 26.4, 21.8. HRMS (ESI) m/z calcd for $C_{20}H_{22}BrNNaO_4^+$ $(M+Na)^+$ 442.0624, found 442.0633.

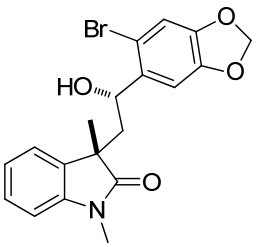
Data of ***syn*-40**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.85 (s, 1H), 4.50 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.23 (s, 3H), 2.31 (dd, *J* = 14.3, 10.7 Hz, 1H), 2.16 (dd, *J* = 14.5, 2.4 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 148.7, 148.5, 143.5, 135.6, 132.7, 127.9, 123.2, 122.2, 114.8, 110.5, 109.4, 108.0, 70.7, 56.1, 56.0, 47.1, 45.0, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{20}H_{22}BrNNaO_4^+$ $(M+Na)^+$ 442.0624, found 442.0635.

3-(2-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (41)



***anti*-41**



***syn*-41**

The title compound **41** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 6-bromobenzo[*d*][1,3]dioxole-5-carbaldehyde (45.8 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-41** (35.8 mg) as a white solid (mp 72-74 ^{o}C) and ***syn*-41** (10.2 mg) as a white solid (mp 90-92 ^{o}C). Total isolated yield of **41**: 57%, *dr*: 3.5:1.

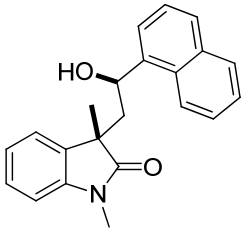
Data of ***anti*-41**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.11 (s, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 8.1 Hz, 2H), 5.43 (d, *J* = 9.8 Hz, 1H), 5.30 (s, 1H), 3.25 (s, 3H), 2.18 (dd, *J* = 14.9, 1.8 Hz, 1H), 1.72 – 1.66 (m, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.5, 147.6, 147.2, 142.0, 136.9, 135.0, 128.0, 123.2, 122.3, 112.0, 111.2, 108.4, 107.6, 101.5, 69.8, 47.6, 44.3, 26.4, 22.0. HRMS (ESI) m/z calcd for $C_{19}H_{18}BrNNaO_4^+$ $(M+Na)^+$ 426.0311, found 426.0316.

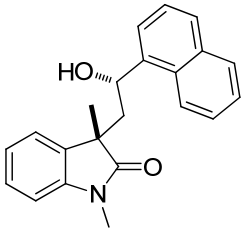
Data of ***syn*-41**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.86 (s, 1H), 5.94 (s, 2H), 4.53 (dd, *J* = 10.7, 2.7 Hz, 1H), 3.25 (s, 3H), 2.29 (dd, *J* = 14.5, 10.7 Hz, 1H), 2.18 (dd, *J* = 14.5, 2.7 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 147.8, 147.5, 143.6, 137.0, 132.7, 128.0, 123.2, 122.2, 112.2, 111.1, 108.1, 107.2, 101.7, 70.8, 47.1, 45.0, 26.4, 25.5. HRMS (ESI) m/z calcd for $C_{19}H_{18}BrNNaO_4^+$ $(M+Na)^+$ 426.0311, found 426.0319.

3-(2-hydroxy-2-(naphthalen-1-yl)ethyl)-1,3-dimethylindolin-2-one (42)



***anti*-42**



***syn*-42**

The title compound **42** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 1-naphthaldehyde (31.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-42** (35.8 mg) as a white solid (mp 105-107 ^{o}C) and ***syn*-42** (7.2 mg) as a white solid (mp 78-80 ^{o}C). Total isolated yield of

42: 65%, *dr*: 5.0:1.

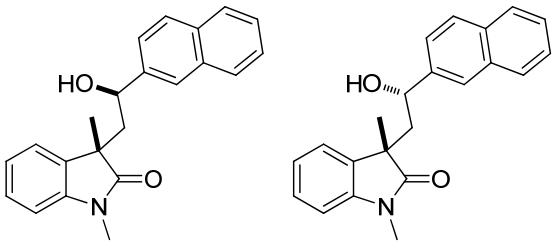
Data of ***anti*-42**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.38 (m, 3H), 7.27 – 7.21 (m, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.80 (dd, *J* = 9.6, 2.6 Hz, 1H), 4.33 (s, 1H), 3.14 (s, 3H), 2.41 (dd, *J* = 14.9, 2.6 Hz, 1H), 2.12 (dd, *J* = 14.9, 9.6 Hz, 1H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.6, 142.3, 139.7, 134.6, 133.6, 129.9, 128.8, 128.0, 127.7, 125.9, 125.5, 125.2, 123.3, 123.0, 122.7, 122.4, 108.5, 67.7, 47.6, 45.7, 26.3, 23.2. HRMS (ESI) m/z calcd for $C_{22}H_{21}NNaO_2^+$ $(M+Na)^+$ 354.1465, found 354.1476.

Data of ***syn*-42**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.79 (m, 1H), 7.76 – 7.69 (m, 2H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.46 – 7.30 (m, 5H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 5.03 (dd, *J* = 10.6, 2.4 Hz, 1H), 3.29 (s, 3H), 2.61 (dd, *J* = 14.7, 10.6 Hz, 1H), 2.32 (dd, *J* = 14.7, 2.4 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 143.8, 140.2, 133.6, 133.2, 129.8, 128.9, 128.1, 127.9, 125.9, 125.5, 125.4, 122.7, 122.5, 122.4, 108.4, 68.5, 47.4, 46.5, 26.5, 25.2. HRMS (ESI) m/z calcd for $C_{22}H_{21}NNaO_2^+$ $(M+Na)^+$ 354.1465, found 354.1477.

3-(2-hydroxy-2-(naphthalen-2-yl)ethyl)-1,3-dimethylindolin-2-one (43)



***anti*-43** ***syn*-43**

The title compound **43** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 2-naphthaldehyde (31.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-43** (46.5 mg) as a colorless liquid and ***syn*-43** (11.1 mg) as a white solid (mp 57-59 ^{o}C). Total isolated yield of **43**: 87%, *dr*: 4.2:1.

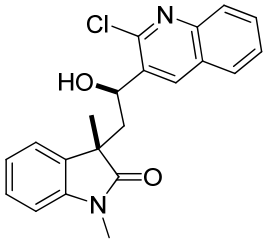
Data of ***anti*-43**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.74 (m, 2H), 7.72 – 7.65 (m, 1H), 7.47 (s, 1H), 7.43 – 7.39 (m, 3H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 4.97 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.17 (s, 1H), 2.87 (s, 3H), 2.31 (dd, *J* = 14.6, 4.4 Hz, 1H), 2.16 (dd, *J* = 14.5, 8.8 Hz, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.1, 142.4, 140.9, 134.1, 132.9, 132.8, 127.9, 127.8, 127.8, 127.5, 125.8, 125.6, 124.7, 124.2, 122.8, 122.5, 108.3, 71.5, 47.1, 45.8, 26.0, 23.6. HRMS (ESI) m/z calcd for $C_{22}H_{21}NNaO_2^+$ $(M+Na)^+$ 354.1465, found 354.1475.

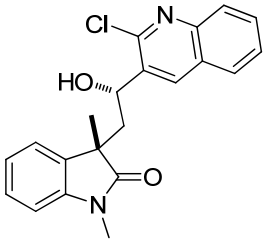
Data of ***syn*-43**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.72 (m, 3H), 7.61 (s, 1H), 7.47 – 7.41 (m, 2H), 7.34 – 7.21 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.43 (dd, *J* = 10.6, 2.9 Hz, 1H), 3.24 (s, 3H), 2.61 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.21 (dd, *J* = 14.5, 2.9 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 143.6, 141.7, 133.2, 133.1, 132.8, 128.1, 127.9, 127.8, 127.6, 126.1, 125.8, 124.0, 123.8, 122.6, 122.4, 108.2, 71.8, 47.1, 46.8, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{22}H_{21}NNaO_2^+$ $(M+Na)^+$ 354.1465, found 354.1476.

3-(2-(2-chloroquinolin-3-yl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (44)



***anti*-44**



***syn*-44**

The title compound **44** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl 2-chloroquinoline-3-carbaldehyde (38.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 2:1) was performed to give ***anti*-44** (35.3 mg) as a white solid (mp 125-127 ^{o}C) and ***syn*-44** (10.1 mg) as a white solid (mp 143-145 ^{o}C). Total isolated yield of **44**: 62%, *dr*: 3.5:1.

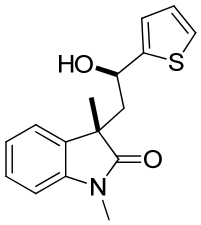
Data of ***anti*-44**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.58 – 7.48 (m, 1H), 7.26 – 7.21 (m, 1H), 7.18 (d, *J* = 6.7 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.87 – 6.83 (m, 1H), 5.68 (s, 1H), 5.66 (d, *J* = 9.8 Hz, 1H), 3.26 (s, 3H), 2.46 (dd, *J* = 14.9, 1.7 Hz, 1H), 1.78 (dd, *J* = 14.9, 9.7 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.6, 148.1, 146.8, 141.9, 136.2, 135.9, 134.7, 130.0, 128.2, 128.0, 127.7, 127.5, 127.0, 123.4, 122.3, 108.5, 67.6, 47.6, 44.0, 26.5, 22.0. HRMS (ESI) m/z calcd for $C_{21}H_{19}ClN_2NaO_2^+$ $(M+Na)^+$ 389.1027, found 389.1036.

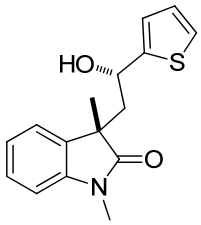
Data of ***syn*-44**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.65 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.30 (m, 2H), 7.20 – 7.11 (m, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 4.75 – 4.71 (m, 2H), 3.28 (s, 3H), 2.49 – 2.35 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 148.0, 146.9, 143.5, 136.2, 135.8, 132.5, 130.3, 128.2, 128.1, 127.6, 127.4, 127.2, 123.1, 122.6, 108.3, 68.5, 47.3, 45.0, 26.5, 25.6. HRMS (ESI) m/z calcd for $C_{21}H_{19}ClN_2NaO_2^+$ $(M+Na)^+$ 389.1027, found 389.1037.

3-(2-hydroxy-2-(thiophen-2-yl)ethyl)-1,3-dimethylindolin-2-one (45)



***anti*-45**



***syn*-45**

The title compound **45** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl thiophene-2-carbaldehyde (22.4 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-45** (16.6 mg) as a colorless liquid and ***syn*-45** (6.4 mg) as a colorless liquid. Total isolated yield of **45**: 40%, *dr*: 2.6:1.

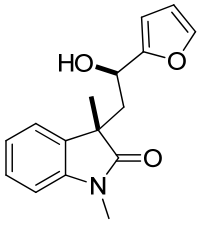
Data of ***anti*-45**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (td, *J* = 7.7, 1.3 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 5.25 (dd, *J* = 9.5, 3.3 Hz, 1H), 4.44 (s, 1H), 3.18 (s, 3H), 2.31 (dd, *J* = 14.6, 3.4 Hz, 1H), 2.17 (dd, *J* = 14.6, 9.5 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 148.2, 142.4, 134.4, 128.1, 126.2, 124.3, 123.1, 123.1, 122.5, 108.5, 67.4, 47.3, 46.5, 26.4, 22.9. HRMS (ESI) m/z calcd for $C_{16}H_{17}NNaO_2S^+$ $(M+Na)^+$ 310.0872, found 310.0885.

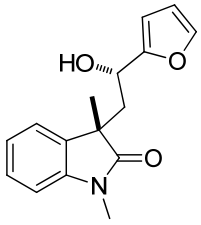
Data of ***syn*-45**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 5.7 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 4.1 Hz, 1H), 4.50 (dd, *J* = 10.9, 2.8 Hz, 1H), 3.23 (s, 3H), 2.66 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.32 (dd, *J* = 14.4, 2.9 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 148.3, 143.6, 132.9, 128.0, 126.6, 124.5, 123.2, 122.6, 122.4, 108.3, 67.5, 47.0, 46.7, 26.4, 25.4. HRMS (ESI) m/z calcd for $C_{16}H_{17}NNaO_2S^+$ $(M+Na)^+$ 310.0872, found 310.0886.

3-(2-(furan-2-yl)-2-hydroxyethyl)-1,3-dimethylindolin-2-one (46)



***anti*-46**



***syn*-46**

The title compound **46** was synthesized according to General Procedure using methyl *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and methyl furan-2-carbaldehyde (19.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 4:1 to 3:1) was performed to give ***anti*-46** (11.4 mg) as a colorless liquid and ***syn*-46** (5.4 mg) as a colorless liquid. Total isolated yield of **46**: 31%, *dr*:

2.1:1.

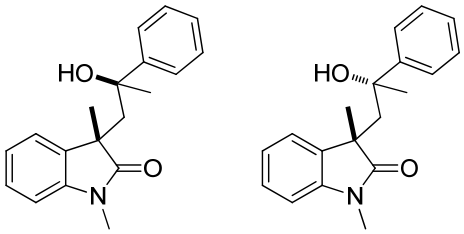
Data of ***anti*-46**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.27 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 4.95 (dd, *J* = 9.2, 3.9 Hz, 1H), 4.13 (s, 1H), 3.17 (s, 3H), 2.38 (dd, *J* = 14.6, 3.9 Hz, 1H), 2.19 (dd, *J* = 14.5, 9.2 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 155.9, 142.4, 141.8, 134.3, 128.1, 123.0, 122.5, 110.0, 108.4, 105.8, 65.1, 47.0, 42.7, 26.3, 23.0. HRMS (ESI) m/z calcd for $C_{16}H_{17}NNaO_3^+$ $(M+Na)^+$ 294.1101, found 294.1115.

Data of ***syn*-46**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.26 (m, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.23 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 4.28 (dd, *J* = 10.8, 3.2 Hz, 1H), 3.22 (s, 3H), 2.63 (dd, *J* = 14.4, 10.7 Hz, 1H), 2.30 (dd, *J* = 14.4, 3.3 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 156.2, 143.5, 141.8, 132.7, 128.0, 122.6, 122.4, 110.1, 108.3, 105.5, 65.2, 46.6, 43.1, 26.4, 25.3. HRMS (ESI) m/z calcd for $C_{16}H_{17}NNaO_3^+$ $(M+Na)^+$ 294.1101, found 294.1119.

3-(2-hydroxy-2-phenylpropyl)-1,3-dimethylindolin-2-one (47)



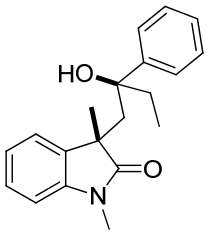
***anti*-47** ***syn*-47**

The title compound **47** was synthesized according to general procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and acetophenone (24.0 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 5:1 to 4:1) was performed to give an inseparable mixture of ***anti*-47** (major) and ***syn*-47** (minor) (30.1 mg, 51%, *dr*: 1.5:1) as a white solid (mp 74-76 ^{o}C).

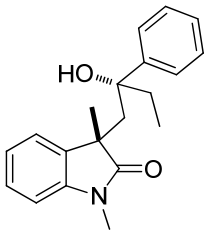
Data of mixture ***anti*-47** (major) and ***syn*-47** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.21 (m, 3.80H), 7.20 – 7.15 (m, 0.60H), 7.10 – 7.03 (m, 1.00H), 6.96 – 6.92 (m, 2.00H), 6.81 – 6.78 (m, 0.60H), 6.75 (d, *J* = 7.8 Hz, 0.60H), 6.53 (d, *J* = 7.8 Hz, 0.40H), 3.53 (s, 0.34H), 3.24 (s, 0.52H), 2.98 (s, 1.20H), 2.93 (s, 1.80H), 2.73 – 2.64 (m, 1.20H), 2.41 – 2.25 (m, 0.80H), 1.42 (s, 1.20H), 1.31 (s, 1.20H), 1.27 (s, 1.80H), 1.16 (s, 1.80H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.8, 181.0, 147.2, 145.9, 142.8, 142.0, 134.2, 133.8, 128.1, 127.7, 127.0, 127.0, 126.4, 125.8, 124.8, 124.7, 122.9, 122.5, 122.5, 122.4, 108.4, 107.9, 74.5, 74.1, 51.0, 49.7, 47.1, 46.9, 33.0, 32.2, 27.8, 26.1, 26.1. HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_2^+$ $(M+Na)^+$ 318.1465, found 318.1484.

3-(2-hydroxy-2-phenylbutyl)-1,3-dimethylindolin-2-one (48)



***anti*-48**



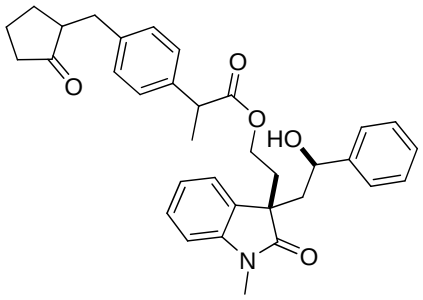
***syn*-48**

The title compound **48** was synthesized according to general procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and acetophenone (26.8 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 5:1 to 4:1) was performed to give an inseparable mixture of ***anti*-48** and ***syn*-48** (29.0 mg, 47%, *dr*: 1.7:1) as a yelleow solid (mp 114-116 ^{o}C).

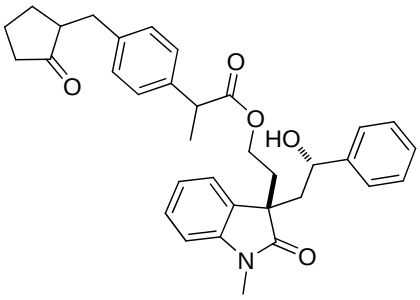
Data of mixture ***anti*-48** and ***syn*-48**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.27 (m, 0.63H), 7.24 – 7.22 (m, 0.74H), 7.19 – 6.99 (m, 2.37H), 6.91 – 6.84 (m, 3.00H), 6.77 – 6.68 (m, 1.63H), 6.50 (d, *J* = 7.8 Hz, 0.63H), 3.42 (s, 0.58H), 3.24 (s, 0.34H), 2.98 (s, 1.89H), 2.82 (s, 1.11H), 2.71 – 2.65 (m, 1.73H), 2.34 (d, *J* = 14.9 Hz, 0.37H), 1.73 (qd, *J* = 7.2, 3.4 Hz, 1.27H), 1.65 (q, *J* = 7.5 Hz, 0.74H), 1.30 (s, 1.89H), 1.14 (s, 1.11H), 0.61 (t, *J* = 7.4 Hz, 1.89H), 0.55 (t, *J* = 7.3 Hz, 1.11H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.1, 181.0, 144.5, 143.9, 142.8, 142.0, 134.5, 133.9, 128.1, 127.5, 126.8, 126.8, 126.3, 125.7, 125.6, 125.4, 122.9, 122.4, 122.4, 122.3, 108.4, 107.8, 77.2, 76.3, 50.4, 48.8, 47.1, 46.8, 37.9, 37.4, 27.9, 26.1, 26.0, 26.0, 7.3, 7.3. HRMS (ESI) m/z calcd for $C_{20}H_{23}NNaO_2^+$ $(M+Na)^+$ 332.1621, found 332.1638.

2-(3-(2-hydroxy-2-phenylethyl)-1-methyl-2-oxoindolin-3-yl)ethyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (49)



***anti*-49**



***syn*-49**

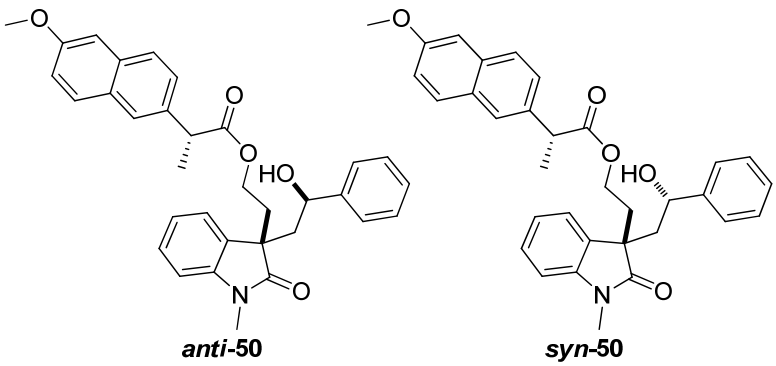
The title compound **49** was synthesized according to general procedure using 3-(methyl(phenyl)carbamoyl)but-3-en-1-yl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (104.0 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give an inseparable mixture of ***anti*-49** and ***syn*-49** (52.8 mg, 49%, *dr*: 1.0:1) as a colorless liquid.

Data of mixture ***anti*-49** and ***syn*-49**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 4H), 7.19 – 7.13 (m, 3H), 7.11 – 7.05 (m,

5H), 6.81 – 6.76 (m, 1H), 4.77 (dt, *J* = 8.7, 4.3 Hz, 1H), 3.97 – 3.91 (m, 0.5H), 3.84 – 3.71 (m, 1H), 3.63 – 3.51 (m, 1H), 3.48 – 3.42 (m, 1.50H), 3.10 (dd, *J* = 13.9, 4.1 Hz, 1H), 3.03 (s, 1.50H), 2.99 (s, 1.50H), 2.54 – 2.40 (m, 2H), 2.36 – 2.20 (m, 4H), 2.17 – 2.04 (m, 3H), 1.98 – 1.90 (m, 1H), 1.76 – 1.66 (m, 1H), 1.58 – 1.48 (m, 1H), 1.36 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.6, 179.6, 174.2, 174.1, 143.5, 143.5, 143.1, 143.0, 138.8, 138.7, 138.1, 137.9, 131.1, 131.0, 129.0, 129.0, 128.4, 128.4, 128.1, 127.5, 127.4, 127.3, 126.0, 125.9, 123.1, 123.1, 122.9, 122.9, 108.4, 71.1, 71.0, 60.7, 60.7, 50.9, 49.6, 49.5, 46.4, 46.2, 44.7, 44.7, 38.1, 35.4, 35.2, 35.1, 29.1, 29.1, 26.1, 26.1, 20.4, 18.5, 18.3. HRMS (ESI) m/z calcd for $C_{34}H_{37}NNaO_5^+$ $(M+Na)^+$ 562.2564, found 562.2591.

2-(3-(2-hydroxy-2-phenylethyl)-1-methyl-2-oxoindolin-3-yl)ethyl (2*R*)-2-(6-methoxynaphthalen-2-yl)propanoate (50)



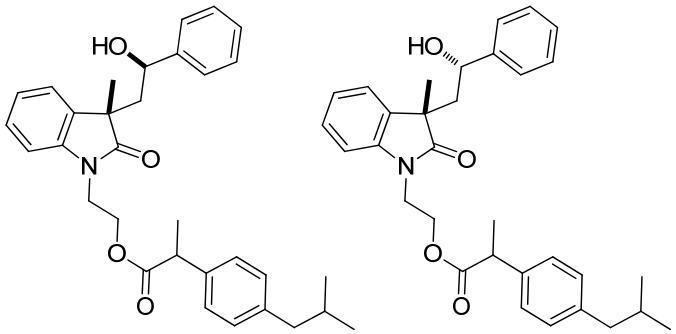
***anti*-50** ***syn*-50**

The title compound **50** was synthesized according to general procedure using 3-(methyl(phenyl)carbamoyl)but-3-en-1-yl (*R*)-2-(6-methoxynaphthalen-2-yl)propanoate (100.1 mg, 0.24 mmol) and PhCHO (21 μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 5:1 to 3:1) was performed to give an inseparable mixture of ***anti*-50** and ***syn*-50** (42.9 mg, 41%, *dr*: 1.0:1) as a white solid (mp 64-66 ^{o}C).

Data of mixture ***anti*-50** and ***syn*-50**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.7, 3.2 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.32 – 7.19 (m, 5H**b**), 7.19 – 7.07 (m, 5H), 7.07 – 6.99 (m, 1H), 6.75 (d, *J* = 7.8 Hz, 0.5H), 6.66 (d, *J* = 7.8 Hz, 0.5H), 4.80 – 4.75 (m, 1H), 4.00 – 3.94 (m, 0.5H), 3.89 (d, *J* = 2.0 Hz, 3H), 3.84 – 3.72 (m, 1H), 3.64 – 3.56 (m, 1.5H), 3.51 (s, 1H), 3.00 (s, 1.5H), 2.92 (s, 1.5H), 2.56 – 2.49 (m, 0.5H), 2.48 – 2.38 (m, 0.5H), 2.28 – 2.16 (m, 2H), 2.14 – 2.08 (m, 1H), 1.45 (dd, *J* = 7.2, 3.3 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.7, 179.6, 174.3, 174.2, 157.5, 143.6, 143.5, 143.1, 143.0, 135.5, 135.3, 133.6, 133.5, 131.1, 131.0, 129.2, 128.8, 128.4, 128.4, 128.1, 127.5, 127.5, 127.1, 127.0, 126.1, 126.1, 126.0, 125.9, 125.8, 125.7, 123.1, 123.1, 122.9, 122.9, 118.9, 108.4, 105.5, 71.1, 71.1, 60.8, 60.8, 55.2, 49.6, 49.5, 46.5, 46.3, 45.1, 45.0, 35.3, 35.1, 26.2, 26.1, 18.7, 18.3. HRMS (ESI) m/z calcd for $C_{33}H_{33}NNaO_5^+$ $(M+Na)^+$ 546.2251, found 546.2274.

2-(3-(2-hydroxy-2-phenylethyl)-3-methyl-2-oxoindolin-1-yl)ethyl 2-(4-isobutylphenyl)propanoate (51)



***anti*-51** ***syn*-51**

The title compound **51** was synthesized according to General Procedure using 2-(*N*-phenylmethacrylamido)ethyl 2-(4-isobutylphenyl)propanoate (94.3 mg, 0.24 mmol) and PhCHO (21μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, DCM/MeOH 200:1 to 100:1) was performed to give ***anti*-51** (51.7 mg) as a colorless liquid and ***syn*-51** (16.1 mg) as a colorless liquid. Total isolated yield of **51**: 68%, *dr*: 3.2:1.

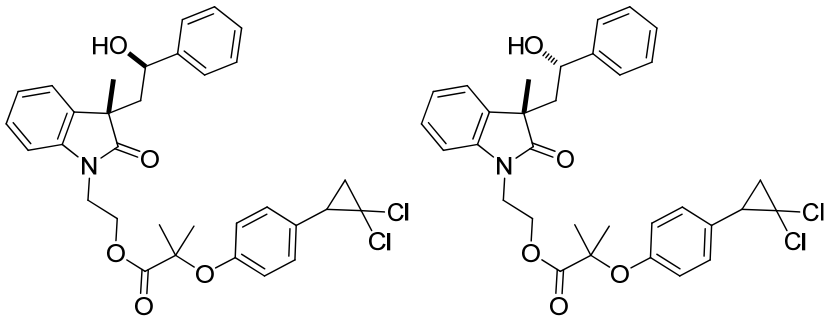
Data of ***anti*-51**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.21 (m, 6H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.07 (td, *J* = 7.6, 2.2 Hz, 3H), 7.00 (dd, *J* = 8.0, 3.8 Hz, 2H), 6.83 (dd, *J* = 7.8, 3.9 Hz, 1H), 4.90 (ddd, *J* = 12.3, 9.2, 3.5 Hz, 1H), 4.34 (dq, *J* = 11.2, 5.2 Hz, 1H), 4.19 (dq, *J* = 11.2, 5.5 Hz, 1H), 3.95 – 3.71 (m, 3H), 3.59 (qd, *J* = 7.1, 3.6 Hz, 1H), 2.39 (dd, *J* = 7.2, 4.3 Hz, 2H), 2.20 (dd, *J* = 14.6, 6.0 Hz, 1H), 2.08 (dd, *J* = 13.7, 9.3 Hz, 1H), 1.84 – 1.77 (m, 1H), 1.47 (d, *J* = 8.4 Hz, 2H), 1.40 – 1.37 (m, 3H), 0.87 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.6, 174.6, 144.1, 141.7, 140.5, 137.2, 134.5, 129.3, 128.2, 127.9, 127.4, 127.1, 125.9, 122.9, 122.7, 108.7, 71.3, 61.5, 47.2, 46.3, 44.9, 39.0, 30.1, 23.5, 22.3, 18.3. HRMS (ESI) m/z calcd for $C_{32}H_{37}NNaO_4^+$ $(M+Na)^+$ 522.2615, found 522.2635.

Data of ***syn*-51**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.15 (m, 6H), 7.13 – 7.03 (m, 3H), 7.02 – 6.95 (m, 2H), 6.94 – 6.87 (m, 2H), 4.40 – 4.31 (m, 1H), 4.28 – 4.14 (m, 2H), 4.12 – 4.03 (m, 1H), 3.94 – 3.84 (m, 1H), 3.59 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.52 – 2.42 (m, 1H), 2.34 (d, *J* = 7.2 Hz, 1H), 2.22 (d, *J* = 7.2 Hz, 1H), 2.07 (td, *J* = 14.8, 2.6 Hz, 1H), 1.93 (dd, *J* = 12.8, 3.9 Hz, 1H), 1.39 – 1.36 (m, 3H), 1.33 (s, 3H), 0.84 (dd, *J* = 13.1, 6.6 Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 174.7, 144.6, 143.2, 140.6, 137.3, 133.0, 129.3, 128.3, 127.8, 127.4, 127.1, 125.4, 122.7, 122.4, 108.6, 71.5, 62.1, 49.2, 47.4, 46.9, 45.0, 39.0, 33.9, 30.1, 25.3, 18.2. HRMS (ESI) m/z calcd for $C_{32}H_{37}NNaO_4^+$ $(M+Na)^+$ 522.2615, found 522.2638.

2-(3-(2-hydroxy-2-phenylethyl)-3-methyl-2-oxoindolin-1-yl)ethyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (52)



***anti*-52** ***syn*-52**

The title compound **52** was synthesized according to General Procedure using 2-(*N*-phenylmethacrylamido)ethyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (114.2 mg, 0.24 mmol) and PhCHO (21μL, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, DCM/MeOH 200:1 to 100:1) was performed to give ***anti*-52** (68.8 mg) as a white solid (mp 113-115 ^{o}C) and ***syn*-52** (19.6 mg) as a c white solid (mp 124-126 ^{o}C). Total isolated yield of **52**: 76%, *dr*: 3.5:1.

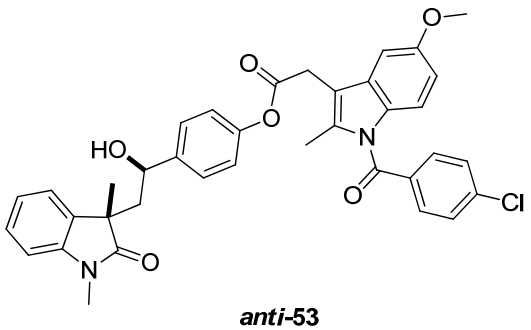
Data of ***anti*-52**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.19 (m, 6H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 6.9 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 6.5 Hz, 2H), 4.86 (dd, *J* = 9.2, 3.7 Hz, 1H), 4.35 (td, *J* = 5.6, 2.8 Hz, 2H), 3.91 – 3.80 (m, 3H), 2.77 (ddd, *J* = 10.7, 8.3, 4.1 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.07 (ddd, *J* = 14.6, 9.2, 3.6 Hz, 1H), 1.90 (ddd, *J* = 10.4, 7.4, 2.2 Hz, 1H), 1.73 (td, *J* = 7.9, 2.0 Hz, 1H), 1.50 (s, 3H), 1.49 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.5, 173.9, 154.5, 143.9, 141.4, 134.3, 129.5, 128.2, 128.1, 127.9, 127.4, 125.9, 123.0, 122.7, 118.8, 108.7, 79.1, 71.3, 62.0, 60.8, 47.1, 46.2, 38.8, 34.7, 25.7, 25.2, 25.2, 23.6. HRMS (ESI) m/z calcd for $C_{32}H_{33}Cl_2NNaO_5^+$ $(M+Na)^+$ 604.1628, found 604.1651.

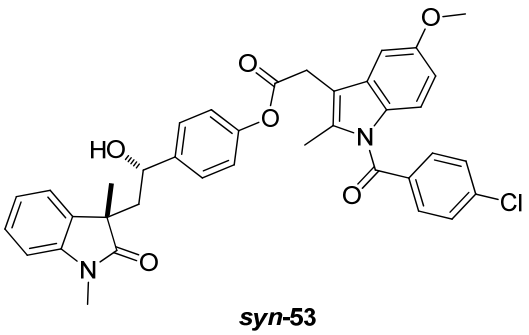
Data of ***syn*-52**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.14 (m, 7H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.99 (dd, *J* = 8.7, 3.3 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 2H), 4.54 – 4.35 (m, 2H), 4.14 (d, *J* = 10.8 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.96 – 3.89 (m, 1H), 2.76 – 2.69 (m, 1H), 2.51 (dd, *J* = 14.5, 11.0 Hz, 1H), 2.08 (dd, *J* = 14.5, 2.5 Hz, 1H), 1.91 – 1.87 (m, 1H), 1.72 (d, *J* = 7.9 Hz, 1H), 1.50 (s, 3H), 1.48 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 174.0, 154.5, 144.5, 142.9, 133.0, 129.6, 128.4, 127.9, 127.4, 125.4, 122.7, 122.4, 119.0, 118.9, 108.7, 79.2, 71.6, 62.5, 60.8, 47.3, 46.9, 38.7, 34.7, 25.8, 25.3, 25.2, 25.2. HRMS (ESI) m/z calcd for $C_{32}H_{33}Cl_2NNaO_5^+$ $(M+Na)^+$ 604.1628, found 604.1653.

4-(2-(1,3-dimethyl-2-oxoindolin-3-yl)-1-hydroxyethyl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (53)



***anti*-53**



***syn*-53**

The title compound **53** was synthesized according to General Procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-formylphenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (92.2 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give ***anti*-53** (60.2 mg) as a white solid (mp 164-166 ^{o}C) and ***syn*-53** (20.1 mg) as a white solid (mp 153-155 ^{o}C). Total isolated yield of **53**: 63%, *dr*: 3.0:1.

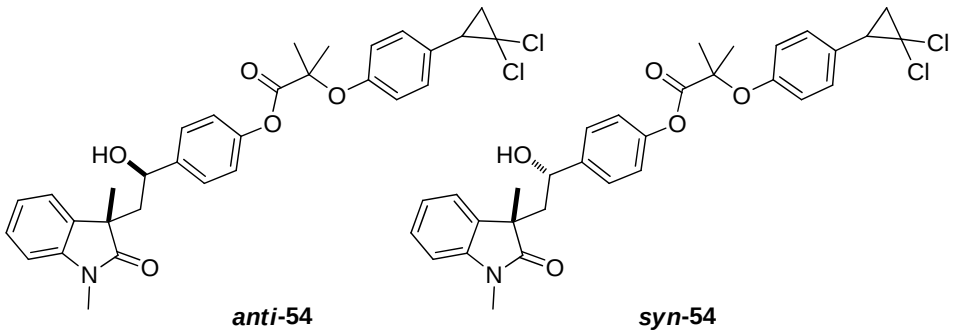
Data of ***anti*-53**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 6.2 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.88 (dd, *J* = 9.1, 3.9 Hz, 1H), 4.17 (s, 1H), 3.88 (s, 2H), 3.82 (s, 3H), 3.10 (s, 3H), 2.43 (s, 3H), 2.20 (dd, *J* = 14.7, 3.9 Hz, 1H), 2.05 (dd, *J* = 14.7, 9.0 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 169.3, 168.2, 156.0, 149.8, 142.4, 141.5, 139.2, 136.1, 134.2, 133.7, 131.1, 130.7, 130.4, 129.1, 128.1, 127.1, 123.0, 122.5, 121.0, 114.9, 111.9, 111.7, 108.4, 101.1, 70.8, 55.6, 47.2, 46.1, 30.4, 26.2, 23.3, 13.4. HRMS (ESI) m/z calcd for $C_{37}H_{33}ClN_2NaO_6^+$ $(M+Na)^+$ 659.1919, found 659.1942.

Data of ***syn*-53**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.87 (s, 1H), 6.69 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.27 (d, *J* = 2.6 Hz, 1H), 3.88 (s, 2H), 3.83 (s, 3H), 3.24 (s, 3H), 2.50 (dd, *J* = 14.6, 10.6 Hz, 1H), 2.44 (s, 3H), 2.11 (dd, *J* = 14.5, 2.7 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.4, 169.3, 168.3, 156.1, 149.8, 143.5, 142.2, 139.3, 136.2, 133.8, 133.1, 131.2, 130.8, 130.4, 129.1, 128.0, 126.6, 122.5, 121.3, 115.0, 111.9, 111.8, 108.3, 101.2, 71.2, 55.7, 47.1, 46.9, 30.5, 26.4, 25.4, 13.4. HRMS (ESI) m/z calcd for $C_{37}H_{33}ClN_2NaO_6^+$ $(M+Na)^+$ 659.1919, found 659.1943.

4-(2-(1,3-dimethyl-2-oxoindolin-3-yl)-1-hydroxyethyl)phenyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (54)



***anti*-54** ***syn*-54**

The title compound **54** was synthesized according to General Procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-formylphenyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (78.6 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give ***anti*-54** (66.7 mg) as a white solid (mp 94-96 ^{o}C) and ***syn*-54** (13.9 mg) as a white solid (mp 110-112 ^{o}C). Total isolated yield of **54**: 71%, *dr*: 4.8:1.

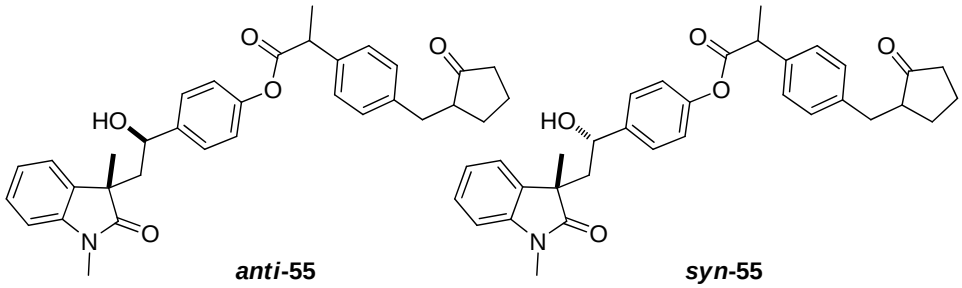
Data of ***anti*-54**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 1H), 7.21 – 7.14 (m, 5H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.87 (dd, *J* = 8.6, 2.0 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.88 (dd, *J* = 9.2, 4.1 Hz, 1H), 4.17 (s, 1H), 3.10 (s, 3H), 2.85 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.19 (dd, *J* = 14.7, 3.9 Hz, 1H), 2.09 – 2.02 (m, 1H), 1.95 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.80 (dd, *J* = 8.3, 7.4 Hz, 1H), 1.74 (s, 6H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 172.8, 154.9, 149.6, 142.4, 141.7, 134.2, 129.7, 128.3, 128.1, 127.1, 123.0, 122.5, 120.9, 118.5, 108.4, 79.2, 70.8, 60.8, 47.2, 46.1, 34.7, 26.3, 25.7, 25.4, 25.4, 23.3. HRMS (ESI) m/z calcd for $C_{31}H_{31}Cl_2NNaO_5^+$ $(M+Na)^+$ 590.1471, found 590.1496.

Data of ***syn*-54**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.7 Hz, 1H), 7.17 (dd, *J* = 12.0, 8.5 Hz, 5H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.95 – 6.83 (m, 5H), 4.26 (dd, *J* = 10.7, 2.7 Hz, 1H), 3.24 (s, 3H), 2.86 (dd, *J* = 10.7, 8.4 Hz, 1H), 2.50 (dd, *J* = 14.5, 10.6 Hz, 1H), 2.11 (dd, *J* = 14.6, 2.8 Hz, 1H), 1.96 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.80 (t, *J* = 7.9 Hz, 1H), 1.74 (s, 6H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 172.8, 154.9, 149.7, 143.5, 142.3, 133.1, 129.8, 128.4, 128.0, 126.6, 122.5, 121.1, 118.5, 118.5, 108.3, 79.3, 71.2, 60.8, 47.1, 47.0, 34.8, 26.4, 25.8, 25.5, 25.4, 25.4. HRMS (ESI) m/z calcd for $C_{31}H_{31}Cl_2NNaO_5^+$ $(M+Na)^+$ 590.1471, found 590.1496.

4-(2-(1,3-dimethyl-2-oxoindolin-3-yl)-1-hydroxyethyl)phenyl 2-(4-((2-oxocyclopentyl)methyl) phenyl)propanoate (55)



***anti*-55** ***syn*-55**

The title compound **55** was synthesized according to General Procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 4-formylphenyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (70.0 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give ***anti*-55** (60.4 mg) as a white solid (mp 134-136 ^{o}C) and ***syn*-55** (13.1 mg) as a white solid (mp 126-128 ^{o}C). Total isolated yield of **55**: 70%, *dr*: 4.6:1.

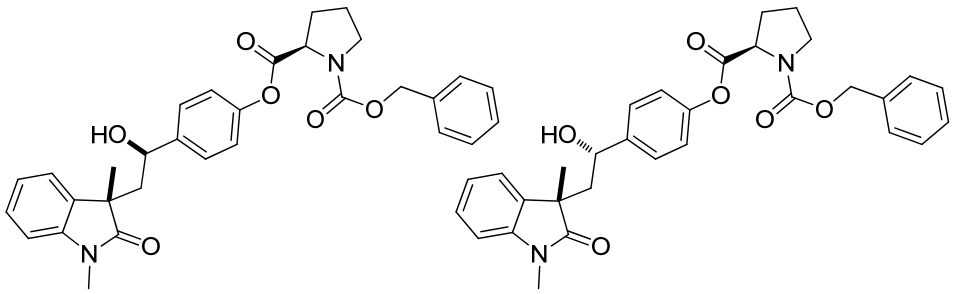
Data of ***anti*-55**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 3H), 7.20 – 7.13 (m, 5H), 7.10 – 7.04 (m, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 7.7 Hz, 1H), 4.84 (dd, *J* = 7.0, 4.2 Hz, 1H), 4.10 (s, 1H), 3.91 (q, *J* = 7.1 Hz, 1H), 3.14 (dd, *J* = 13.9, 4.1 Hz, 1H), 3.08 (s, 3H), 2.52 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.39 – 2.28 (m, 2H), 2.20 (dd, *J* = 14.6, 4.2 Hz, 1H), 2.16 – 2.03 (m, 3H), 1.99 – 1.94 (m, 1H), 1.77 – 1.68 (m, 1H), 1.58 (d, *J* = 5.6 Hz, 3H), 1.56 – 1.52 (m, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.2, 173.0, 149.9, 142.4, 141.2, 139.0, 137.7, 134.2, 129.2, 128.0, 127.5, 127.0, 122.9, 122.5, 120.9, 108.4, 70.8, 50.9, 47.1, 46.0, 45.1, 38.1, 35.1, 29.1, 26.2, 23.4, 20.4, 18.4. HRMS (ESI) m/z calcd for $C_{33}H_{35}NNaO_5^+$ $(M+Na)^+$ 548.2407, found 548.2435.

Data of ***syn*-55**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.28 (m, 3H), 7.18 – 7.15 (m, 5H), 7.09 (t, *J* = 7.0 Hz, 1H), 6.92 – 6.85 (m, 3H), 4.25 (dd, *J* = 10.6, 2.7 Hz, 1H), 3.91 (q, *J* = 7.1 Hz, 1H), 3.23 (s, 3H), 3.14 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.59 – 2.44 (m, 2H), 2.41 – 2.28 (m, 2H), 2.13 – 2.07 (m, 2H), 2.00 – 1.92 (m, 2H), 1.77 – 1.70 (m, 2H), 1.58 (d, *J* = 7.1 Hz, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 173.1, 150.0, 143.6, 142.0, 139.1, 137.8, 133.1, 129.3, 128.0, 127.5, 126.5, 122.5, 122.4, 121.2, 108.3, 71.2, 50.9, 47.1, 46.9, 45.2, 38.2, 35.2, 29.2, 26.4, 25.4, 20.5, 18.5. HRMS (ESI) m/z calcd for $C_{33}H_{35}NNaO_5^+$ $(M+Na)^+$ 548.2407, found 548.2431.

1-benzyl 2-(4-(2-(1,3-dimethyl-2-oxoindolin-3-yl)-1-hydroxyethyl)phenyl) (2*R*)-pyrrolidine-1,2-dicarboxylate (56)



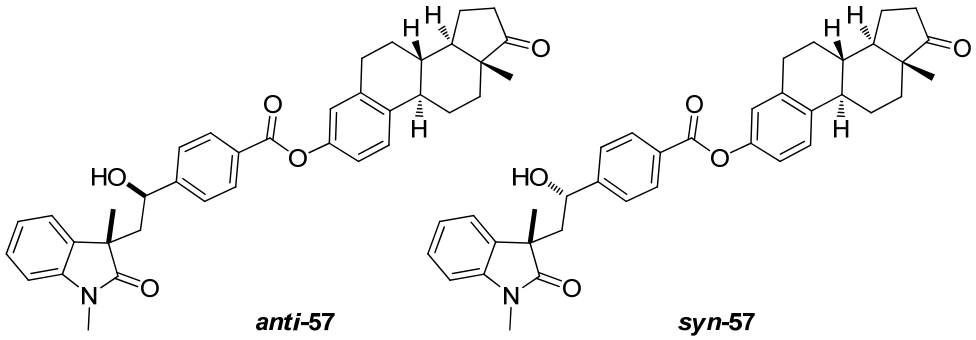
***anti*-56** ***syn*-56**

The title compound **56** was synthesized according to general procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and 1-benzyl 2-(4-formylphenyl) (*R*)-pyrrolidine-1,2-dicarboxylate (70.6 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1 to 2:1) was performed to give an inseparable mixture of ***anti*-56** (major) and ***syn*-56** (minor) (84.5 mg, 80%, *dr*: 4.3:1) as a white solid (mp 143-145 ^{o}C).

Data of mixture ***anti*-56** (major) and ***syn*-56** (minor)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.24 (m, 6.00H), 7.19 – 7.15 (m, 2.00H), 7.14 – 7.05 (m, 2.19H), 6.99 (dd, *J* = 8.3, 4.0 Hz, 0.81H), 6.86 (d, *J* = 7.7 Hz, 0.19H), 6.80 (d, *J* = 7.8 Hz, 0.81H), 6.70 – 6.66 (m, 1.00H), 5.26 – 5.01 (m, 2.00H), 4.86 – 4.76 (m, 0.81H), 4.54 (ddd, *J* = 17.6, 8.6, 4.1 Hz, 1.00H), 4.21 (s, 1.00H), 3.68 – 3.61 (m, 1.00H), 3.59 – 3.49 (m, 1.00H), 3.20 (s, 0.57H), 3.05 (s, 2.43H), 2.54 – 2.44 (m, 0.19H), 2.41 – 2.28 (m, 1.38H), 2.27 – 2.14 (m, 2.00H), 2.12 – 2.05 (m, 1.81H), 1.99 – 1.90 (m, 1.19H), 1.48 (s, 2.43H), 1.36 (s, 0.57H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.1, 171.1, 171.0, 154.7, 154.1, 149.7, 149.4, 142.4, 141.4, 141.3, 141.2, 141.2, 136.4, 136.1, 134.0, 133.0, 128.4, 128.3, 127.9, 127.9, 127.8, 127.8, 127.7, 127.0, 126.4, 122.8, 122.4, 122.3, 121.0, 120.9, 120.7, 108.3, 108.1, 70.8, 70.7, 67.1, 66.9, 59.2, 59.2, 58.7, 47.0, 46.9, 46.9, 46.4, 45.9, 30.9, 29.8, 26.2, 26.1, 25.1, 24.3, 23.5, 23.4. HRMS (ESI) m/z calcd for $C_{31}H_{32}N_2NaO_6^+$ $(M+Na)^+$ 551.2153, found 551.2179.

(8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-(2-(1,3-dimethyl-2-oxoindolin-3-yl)-1-hydroxyethyl)benzoate (57)



***anti*-57** ***syn*-57**

The title compound **57** was synthesized according to General Procedure using *N*-methyl-*N*-phenylmethacrylamide (42.0 mg, 0.24 mmol) and (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-formylbenzoate (80.4 mg, 0.2 mmol) and irradiated with blue LEDs for 48 h. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 2:1 to 1:1) was performed to give ***anti*-57** (56.8 mg) as a white solid (mp 215-217 ^{o}C) and ***syn*-57** (13.5 mg) as a white solid (mp 186-188 ^{o}C). Total isolated yield of **57**: 61%, *dr*: 4.2:1.

Data of ***anti*-57**

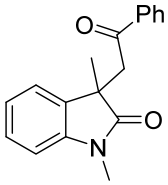
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.10 (dd, *J* = 9.8, 2.8 Hz, 1H), 4.64 (s, 1H), 3.21 (s, 3H), 3.00 – 2.86 (m, 2H), 2.52 (dd, *J* = 18.9, 8.6 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.32 (td, *J* = 10.7, 4.0 Hz, 1H), 2.23 – 2.05 (m, 3H), 2.04 – 1.93 (m, 2H), 1.72 – 1.61 (m, 3H), 1.58 (s, 3H), 1.57 – 1.41 (m, 4H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.7, 165.3, 150.1, 148.8, 142.3, 138.0, 137.3, 134.4, 130.2, 128.5, 128.3, 126.4, 126.0, 123.2, 122.4, 121.7, 118.8, 108.6, 71.0, 50.4, 47.9, 47.5, 46.3, 44.1, 38.0, 35.8, 31.5, 29.4, 26.4, 26.3, 25.7, 23.0, 21.5, 13.8. HRMS (ESI) m/z calcd for $C_{37}H_{39}NNaO_5^+$ $(M+Na)^+$ 600.2720, found 600.2741.

Data of ***syn*-57**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.23 (d, *J* =

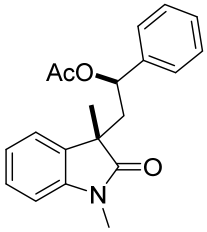
6.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.99 – 6.88 (m, 3H), 4.38 (d, *J* = 9.5 Hz, 1H), 3.27 (s, 3H), 3.00 – 2.90 (m, 2H), 2.57 – 2.47 (m, 2H), 2.45 – 2.41 (m, 1H), 2.36 – 2.28 (m, 1H), 2.22 – 2.08 (m, 3H), 2.04 – 1.94 (m, 2H), 1.64 – 1.46 (m, 6H), 1.41 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.3, 165.2, 150.3, 148.7, 143.5, 138.0, 137.4, 133.0, 130.3, 128.6, 128.1, 126.4, 125.5, 122.6, 122.5, 121.6, 118.8, 108.4, 71.4, 50.4, 47.9, 47.2, 46.9, 44.1, 38.0, 35.8, 31.5, 29.4, 26.4, 26.3, 25.7, 25.4, 21.6, 13.8. HRMS (ESI) m/z calcd for $C_{37}H_{39}NNaO_5^+$ $(M+Na)^+$ 600.2720, found 600.2742.

1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (58)



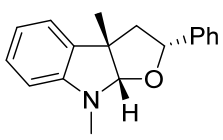
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.76 – 3.62 (m, 2H), 3.32 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 196.1, 180.6, 143.79, 136.2, 133.7, 133.2, 128.5, 127.9, 127.8, 122.1, 121.7, 108.1, 46.0, 45.2, 26.4, 24.9.

(*R*)-2-((*S*)-1,3-dimethyl-2-oxoindolin-3-yl)-1-phenylethyl acetate (59)



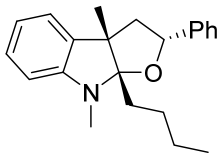
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.21 (m, 5H), 7.15 – 7.09 (m, 1H), 7.08 – 7.02 (m, 2H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.49 (t, *J* = 6.9 Hz, 1H), 2.98 (s, 3H), 2.47 (d, *J* = 7.0 Hz, 2H), 1.58 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 169.6, 143.0, 139.3, 132.9, 128.0, 128.0, 127.8, 126.6, 123.1, 122.4, 108.1, 73.0, 46.8, 43.1, 25.9, 25.5, 20.5. HRMS (ESI) m/z calcd for $C_{20}H_{21}NNaO_3^+$ $(M+Na)^+$ 346.1414, found 346.1433.

(2*R*,3a*S*,8a*S*)-3a,8-dimethyl-2-phenyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (60)



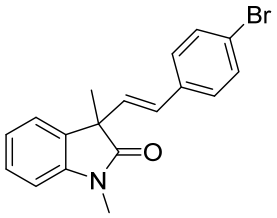
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.18 – 7.06 (m, 5H), 7.00 – 6.92 (m, 2H), 6.53 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 7.7 Hz, 1H), 5.06 – 4.99 (m, 2H), 2.86 (s, 3H), 2.47 – 2.41 (m, 1H), 1.85 (dd, *J* = 12.3, 8.7 Hz, 1H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.6, 142.3, 135.8, 128.0, 127.7, 127.0, 125.6, 122.2, 117.5, 106.0, 78.4, 51.9, 48.5, 31.5, 23.0. HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO^+$ $(M+Na)^+$ 288.1359, found 288.1369.

(2*R*,3a*S*,8a*S*)-8a-butyl-3a,8-dimethyl-2-phenyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (61)



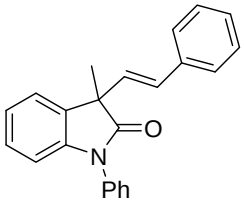
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.07 (m, 6H), 6.98 – 6.90 (m, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 5.21 (t, *J* = 7.5 Hz, 1H), 2.96 (s, 3H), 2.52 (dd, *J* = 12.6, 7.2 Hz, 1H), 2.34 (dd, *J* = 12.6, 7.9 Hz, 1H), 2.08 – 1.92 (m, 2H), 1.50 (s, 3H), 1.34 (p, *J* = 7.1 Hz, 2H), 1.29 – 1.13 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.5, 143.2, 135.1, 127.9, 127.9, 126.9, 125.7, 121.1, 116.7, 110.3, 104.8, 79.2, 53.8, 51.3, 33.4, 28.2, 26.1, 23.2, 19.6, 13.9. HRMS (ESI) m/z calcd for $C_{22}H_{27}NNaO^+$ $(M+Na)^+$ 344.1985, found 344.2000.

(*E*)-3-(4-bromostyryl)-1,3-dimethylindolin-2-one (62)



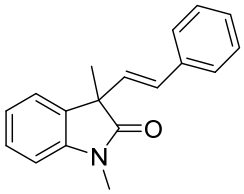
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.32 (td, *J* = 7.7, 1.3 Hz, 1H), 7.26 (d, *J* = 6.3 Hz, 1H), 7.17 (d, *J* = 1.8 Hz, 2H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.40 – 6.28 (m, 2H), 3.23 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.3, 142.8, 135.4, 132.4, 131.4, 130.5, 128.8, 128.2, 127.9, 123.8, 122.6, 121.3, 108.3, 50.6, 26.3, 22.9. HRMS (ESI) m/z calcd for $C_{18}H_{16}BrNNaO^+$ $(M+Na)^+$ 364.0307, found 364.0316.

(*E*)-3-methyl-1-phenyl-3-styrylindolin-2-one (63)



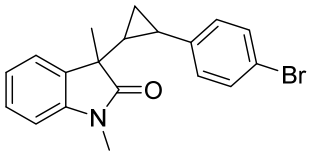
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.45 – 7.32 (m, 6H), 7.30 – 7.12 (m, 5H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.55 – 6.41 (m, 2H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.9, 142.8, 136.4, 134.3, 132.5, 130.2, 129.8, 129.5, 128.4, 128.0, 127.9, 127.6, 126.5, 126.4, 124.2, 123.0, 109.6, 50.7, 23.5. HRMS (ESI) m/z calcd for $C_{23}H_{19}NNaO^+$ $(M+Na)^+$ 348.1359, found 348.1374.

(*E*)-1,3-dimethyl-3-styrylindolin-2-one (64)



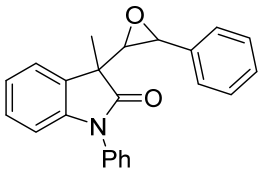
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 3H), 7.29 – 7.23 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.46 – 6.30 (m, 2H), 3.23 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.6, 142.9, 136.4, 132.8, 130.0, 129.8, 128.4, 128.1, 127.6, 126.4, 123.9, 122.6, 108.3, 50.6, 26.3, 23.0. HRMS (ESI) m/z calcd for $C_{18}H_{17}NNaO^+$ $(M+Na)^+$ 286.1202, found 286.1222.

3-(2-(4-bromophenyl)cyclopropyl)-1,3-dimethylindolin-2-one (65)



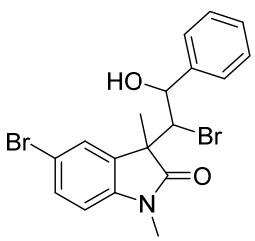
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 3H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.87 (dd, *J* = 16.0, 8.1 Hz, 3H), 3.21 (s, 3H), 1.72 (dt, *J* = 9.5, 5.2 Hz, 1H), 1.53 – 1.48 (m, 1H), 1.46 (s, 3H), 0.99 (dt, *J* = 9.0, 5.7 Hz, 1H), 0.85 (dt, *J* = 8.8, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.5, 143.1, 141.3, 132.5, 131.2, 128.1, 128.1, 122.9, 122.3, 119.1, 108.0, 47.3, 29.0, 26.1, 21.7, 17.9, 11.7. HRMS (ESI) m/z calcd for $C_{19}H_{18}BrNNaO^+$ $(M+Na)^+$ 378.0464, found 378.0483.

3-methyl-1-phenyl-3-(3-phenyloxiran-2-yl)indolin-2-one (66)



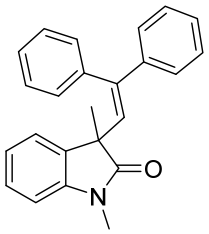
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.46 – 7.40 (m, 4H), 7.36 – 7.27 (m, 5H), 7.27 – 7.23 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.03 (d, *J* = 2.0 Hz, 1H), 3.32 (d, *J* = 2.0 Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.3, 143.4, 136.4, 134.2, 130.5, 129.6, 128.6, 128.4, 128.3, 128.1, 126.5, 125.7, 124.0, 123.0, 109.6, 65.0, 55.4, 48.8, 18.1. HRMS (ESI) m/z calcd for $C_{23}H_{19}NNaO_2^+$ $(M+Na)^+$ 364.1308, found 364.1326.

5-bromo-3-(1-bromo-2-hydroxy-2-phenylethyl)-1,3-dimethylindolin-2-one (67)



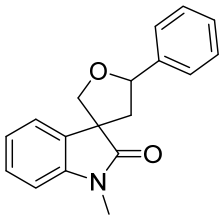
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.29 (m, 5H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.10 (d, *J* = 8.2 Hz, 1H), 4.62 (d, *J* = 8.2 Hz, 1H), 3.17 (s, 3H), 2.74 (s, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.2, 142.6, 141.5, 132.5, 131.4, 128.7, 128.5, 128.1, 126.9, 115.3, 109.5, 77.2, 60.3, 53.1, 26.3, 23.8. HRMS (ESI) m/z calcd for $C_{18}H_{17}Br_2NNaO_2^+$ $(M+Na)^+$ 459.9518, found 459.9533.

3-(2,2-diphenylvinyl)-1,3-dimethylindolin-2-one (68)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.10 (m, 7H), 7.09 – 6.95 (m, 4H), 6.56 (d, *J* = 6.7 Hz, 2H), 6.43 (d, *J* = 7.7 Hz, 1H), 6.40 (s, 1H), 2.70 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.4, 145.2, 142.5, 141.5, 137.7, 136.5, 129.8, 129.5, 128.0, 127.4, 127.4, 127.2, 126.8, 126.7, 122.8, 122.3, 107.8, 48.8, 26.8, 25.8. HRMS (ESI) m/z calcd for $C_{24}H_{21}NNaO^+$ $(M+Na)^+$ 362.1515, found 362.1530.

1'-methyl-5-phenyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one (69, 2.0:1 *dr***)**



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 2.33H), 7.42 – 7.37 (m, 2.00H), 7.37 – 7.28 (m, 2.67H), 7.15 (t, *J* = 7.6 Hz, 0.33H), 7.08 (t, *J* = 7.5 Hz, 0.67H), 6.90 (d, *J* = 7.8 Hz, 0.33H), 6.85 (d, *J* = 7.8 Hz, 0.67H), 5.40 – 5.33 (m, 1.00H), 4.45 (d, *J* = 8.5 Hz, 0.33H), 4.23 (s, 1.34H), 4.05 (d, *J* = 8.5 Hz, 0.33H), 3.25 (s, 3H), 2.84 (dd, *J* = 12.8, 6.6 Hz, 0.67H), 2.57 (dd, *J* = 12.6, 10.0 Hz, 0.33H), 2.47 (dd, *J* = 12.6, 6.3 Hz, 0.33H), 2.17 (dd, *J* = 12.8, 9.5 Hz, 0.67H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.8, 177.4, 143.0, 142.9, 141.3, 140.7, 133.9, 133.4, 128.5, 128.3, 128.1, 127.8, 127.7, 126.1, 125.8, 123.1, 123.0, 122.9, 122.6, 108.2, 108.0, 82.2, 82.0, 77.3, 55.4, 54.9, 46.9, 46.8, 26.5, 26.4. HRMS (ESI) m/z calcd for $C_{18}H_{17}NNaO_2^+$ $(M+Na)^+$ 302.1151, found 302.1155.

6. References

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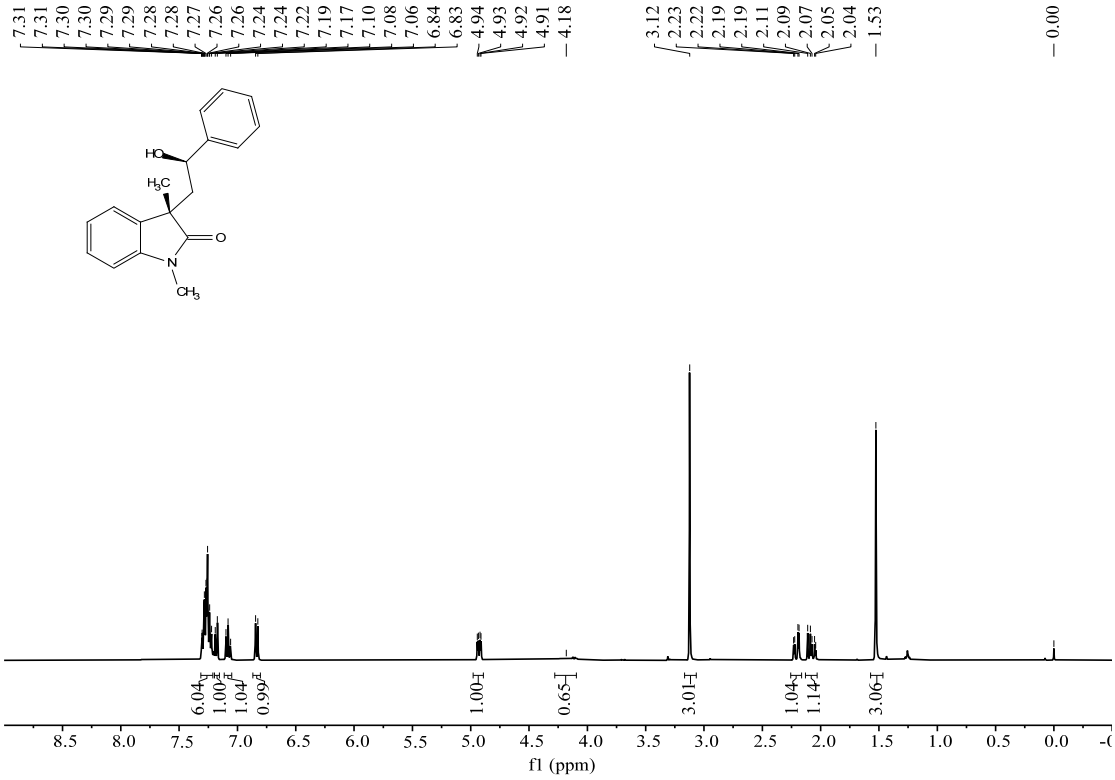
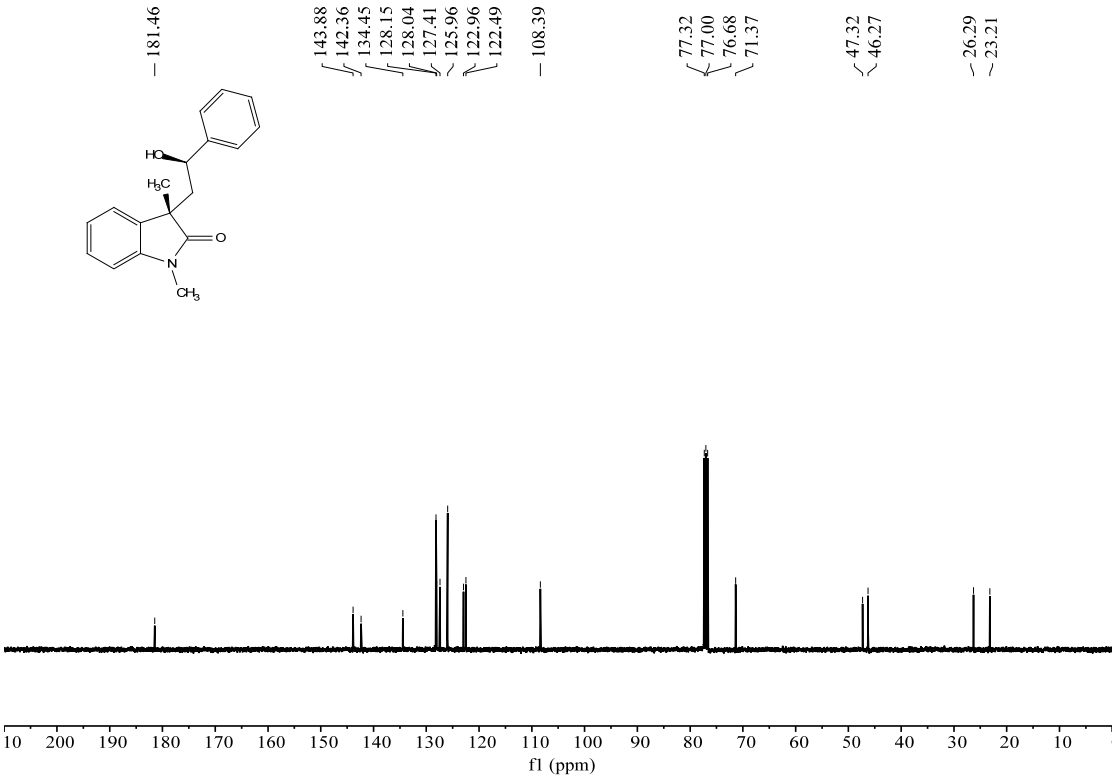
7. Copies of NMR spectra of all products

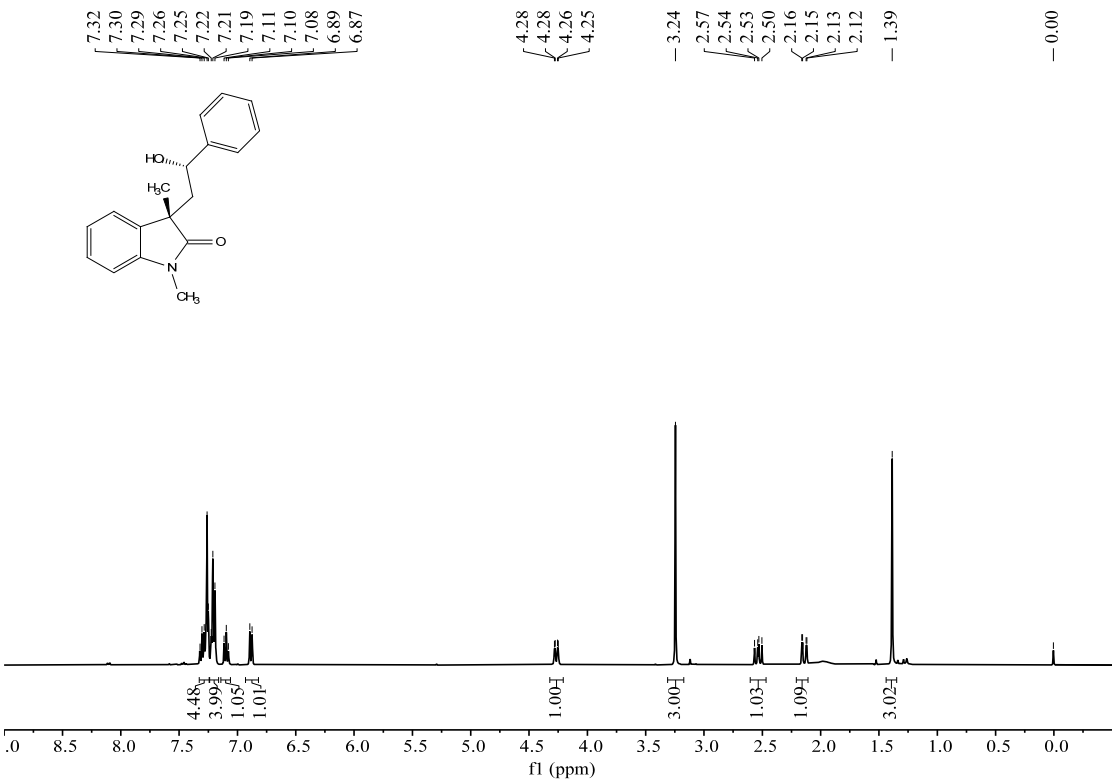
^{1}H NMR spectra of 3a (400 MHz, $CDCl_3$)



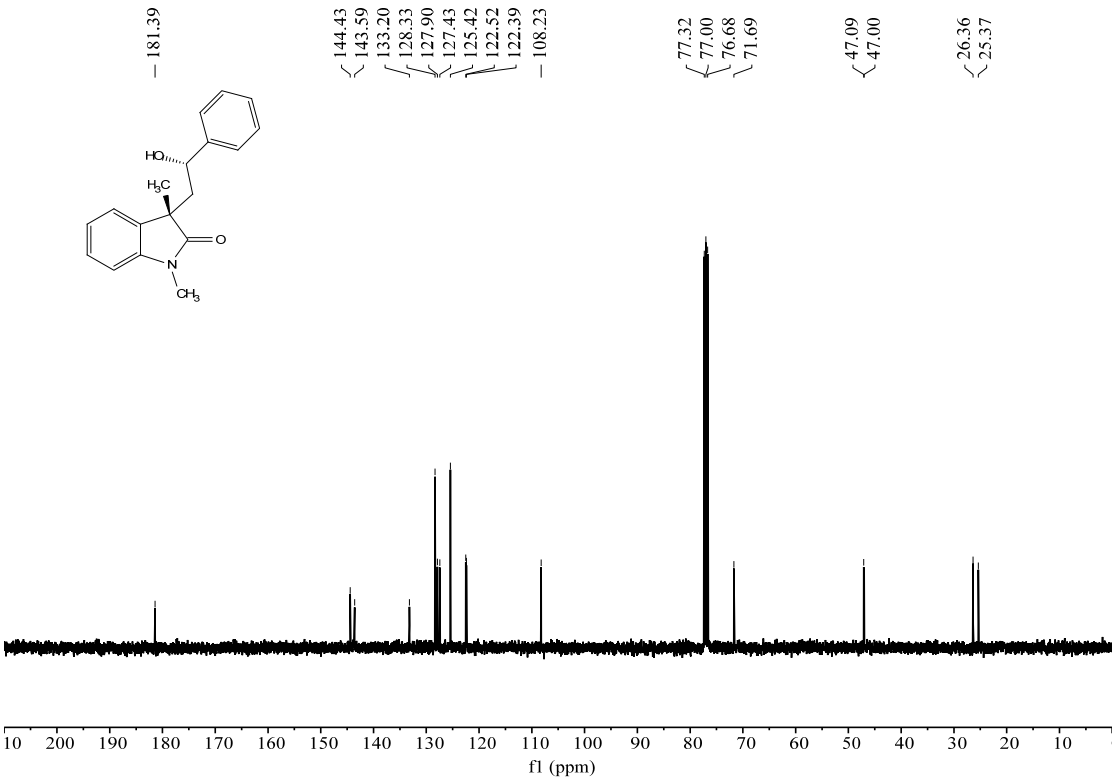
^{13}C NMR spectra of 3a (100 MHz, $CDCl_3$)



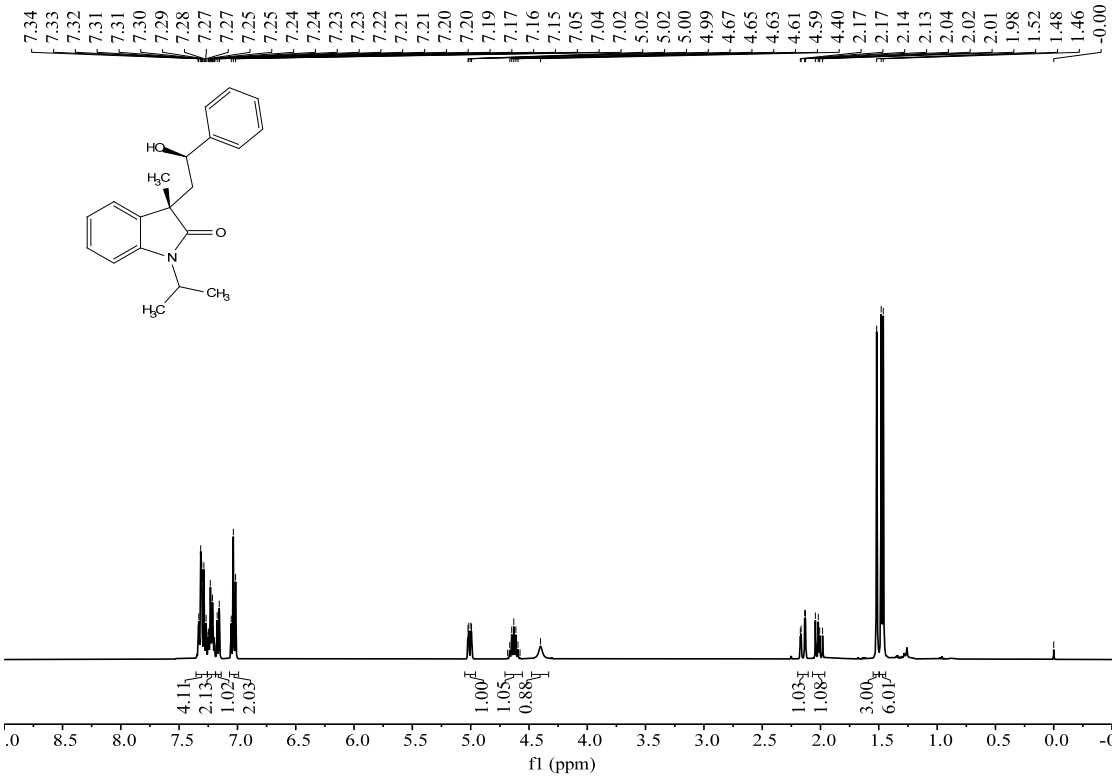
^{1}H NMR spectra of 3b (400 MHz, $CDCl_3$)



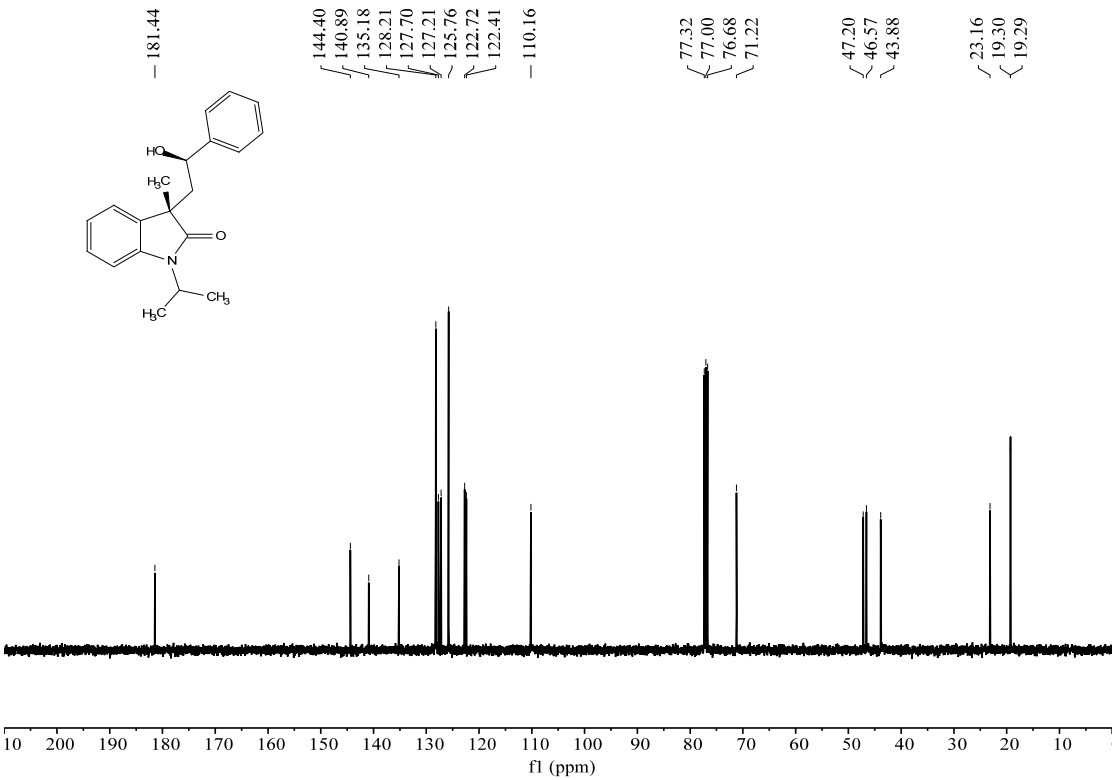
^{13}C NMR spectra of 3b (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 4a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 4a (100 MHz, $CDCl_3$)



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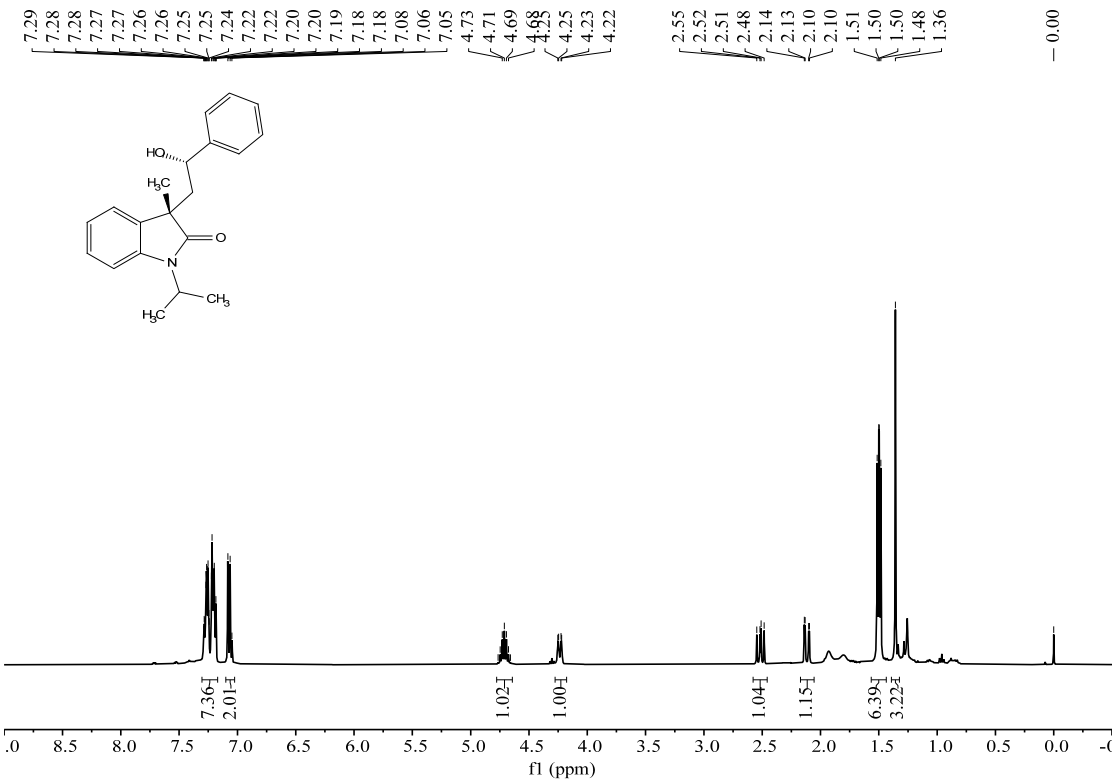

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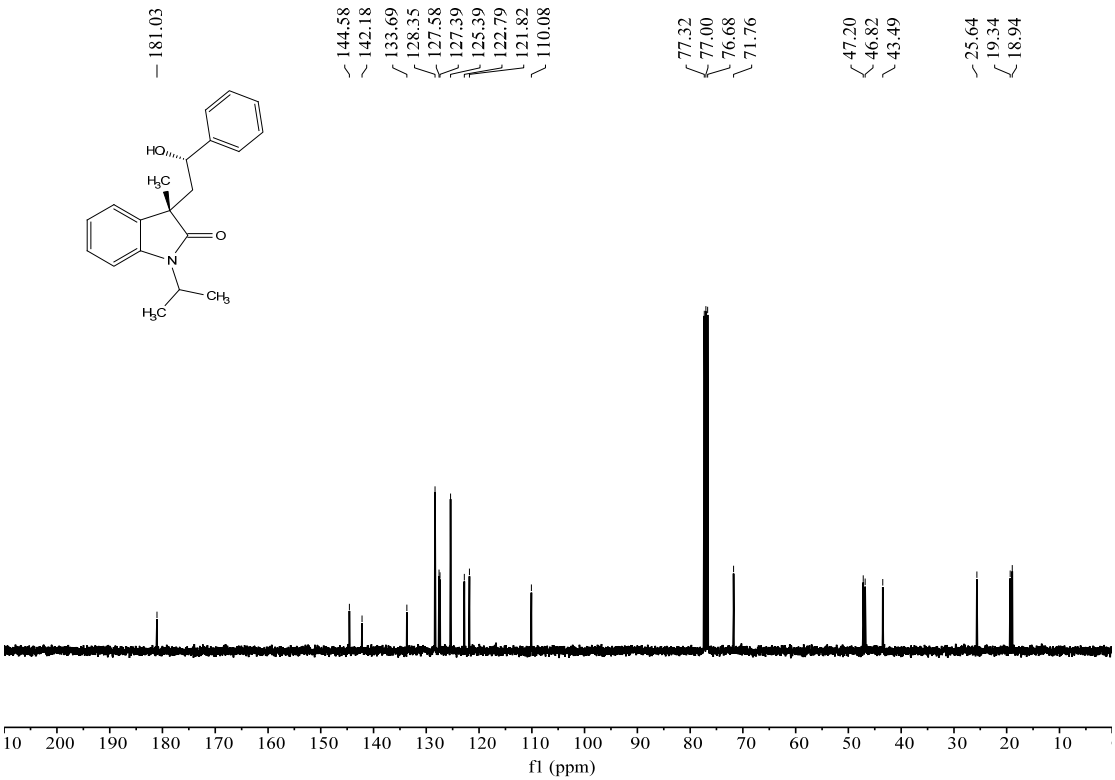
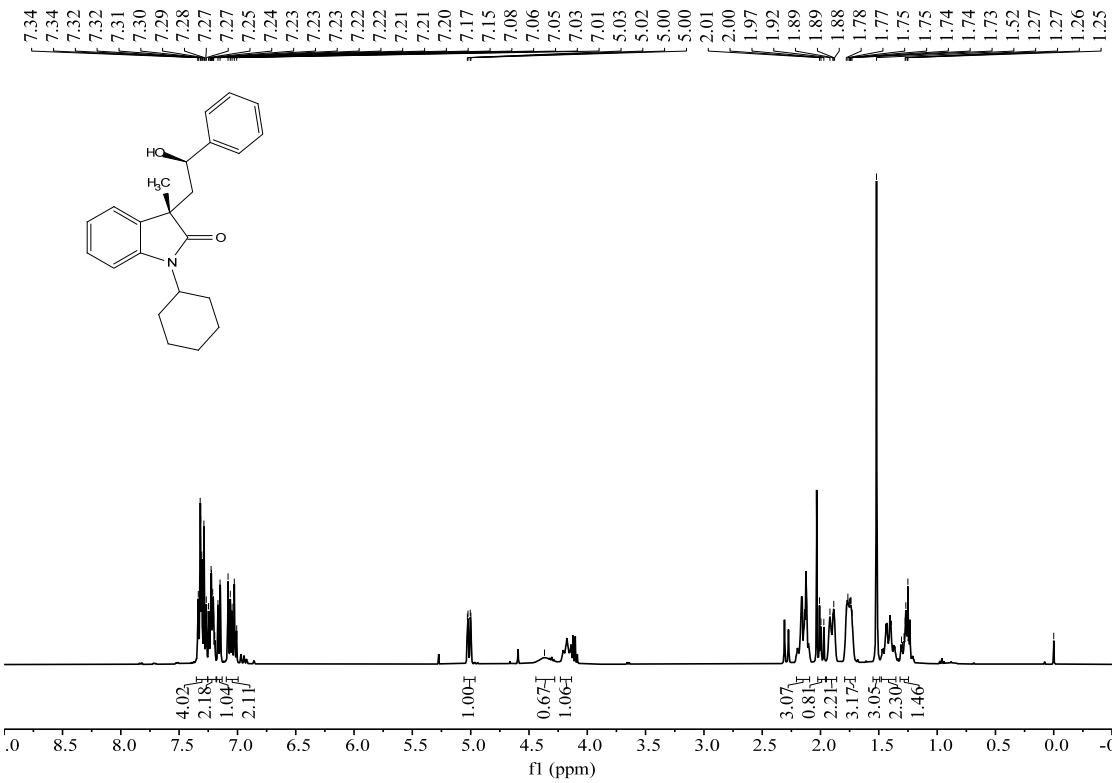
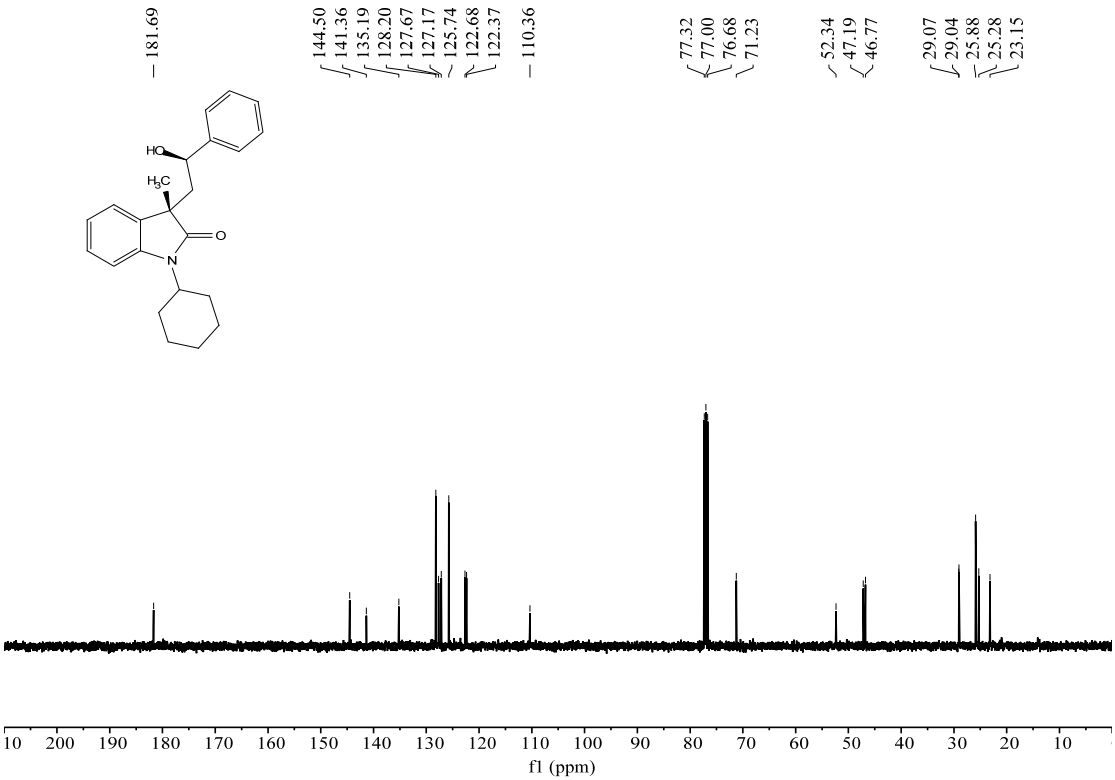


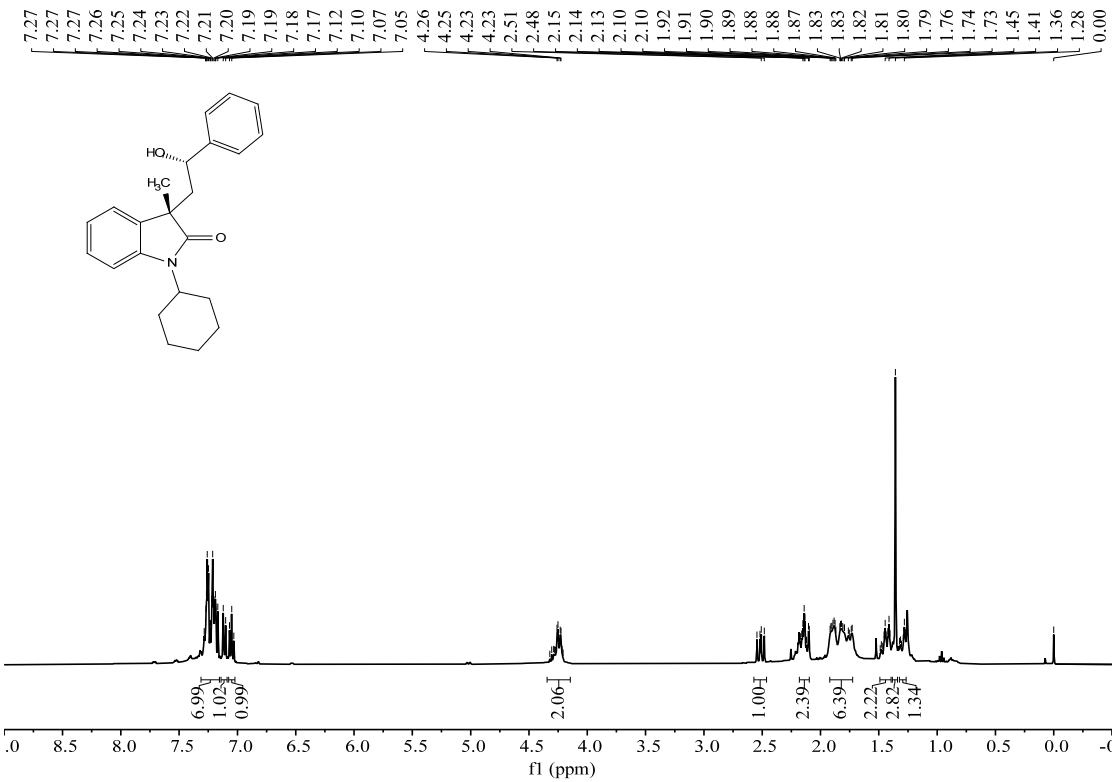
^{1}H NMR spectra of 5a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 5a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 5b (400 MHz, $CDCl_3$)



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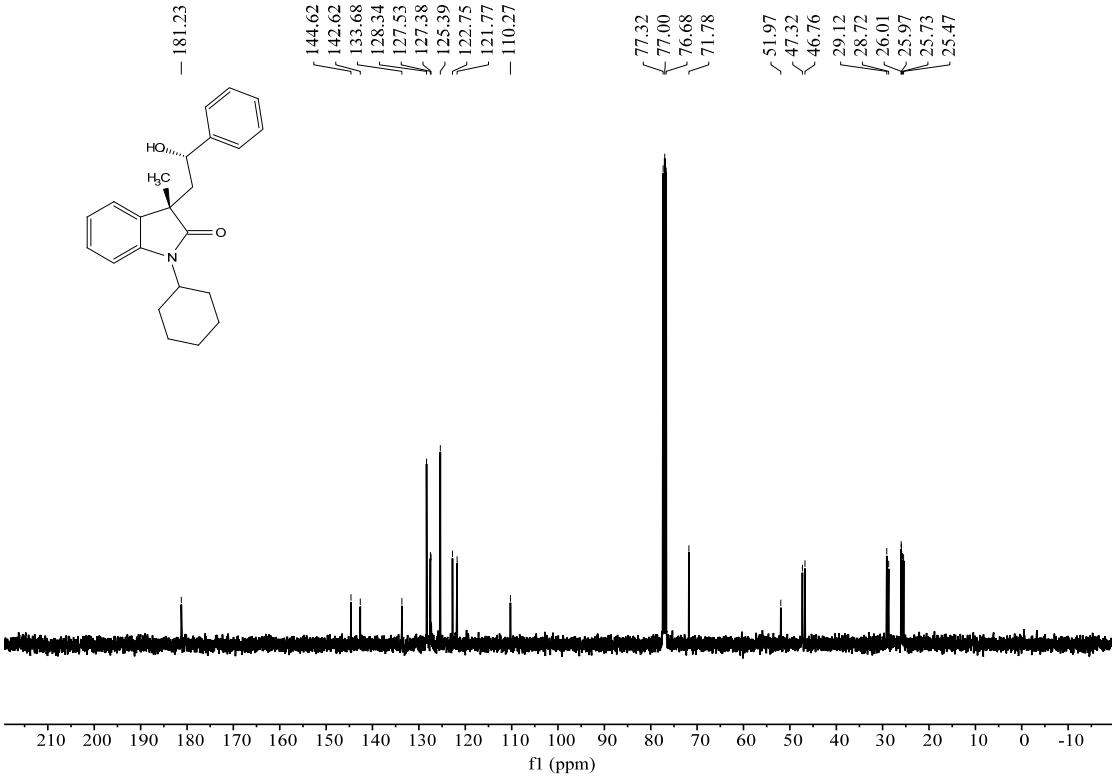
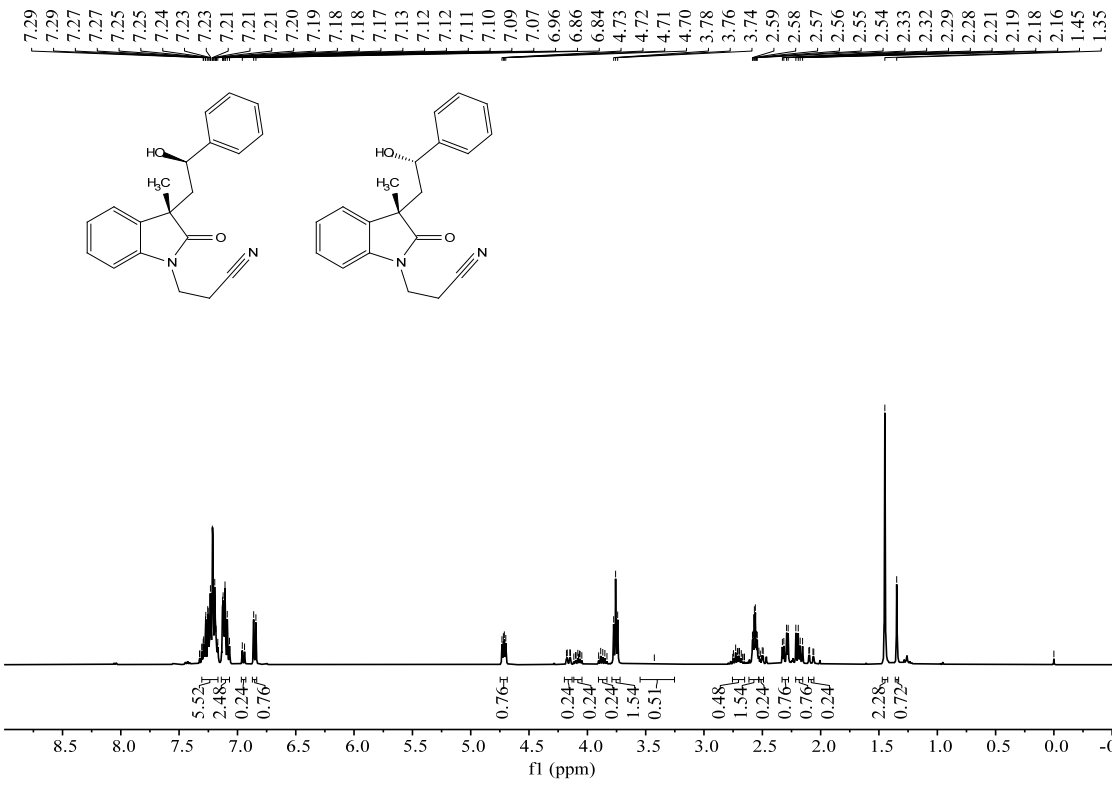


^{1}H NMR spectra of 6ab (400 MHz, $CDCl_3$)



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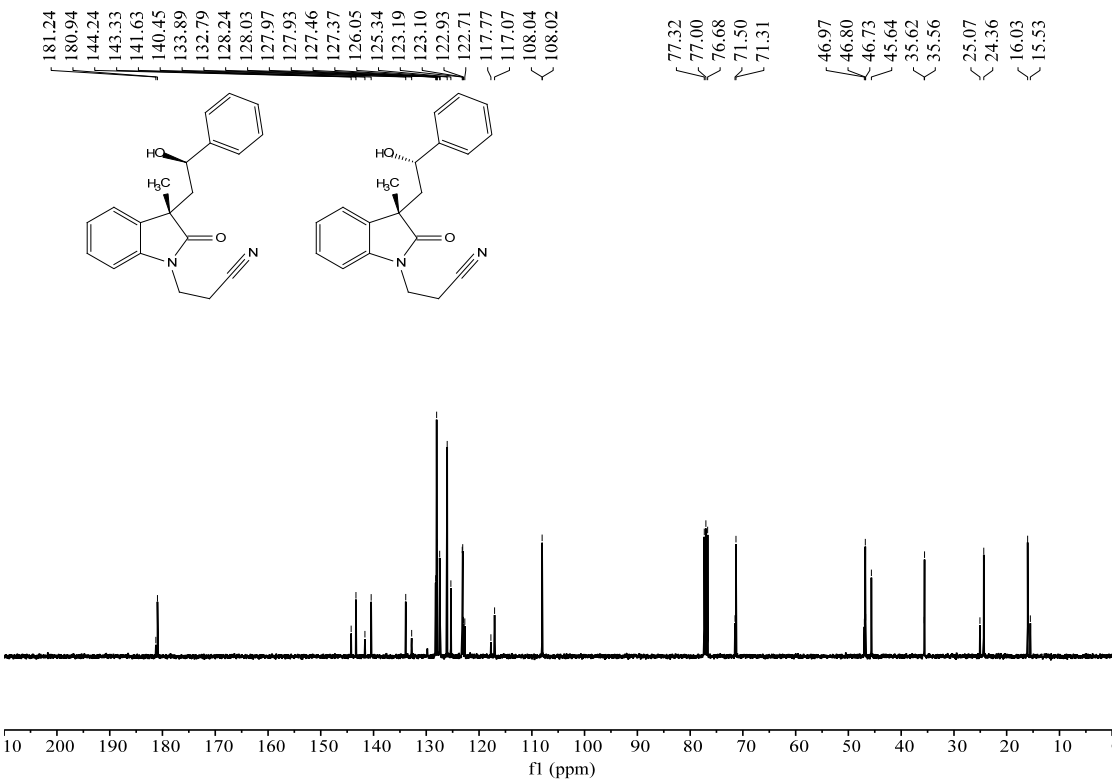
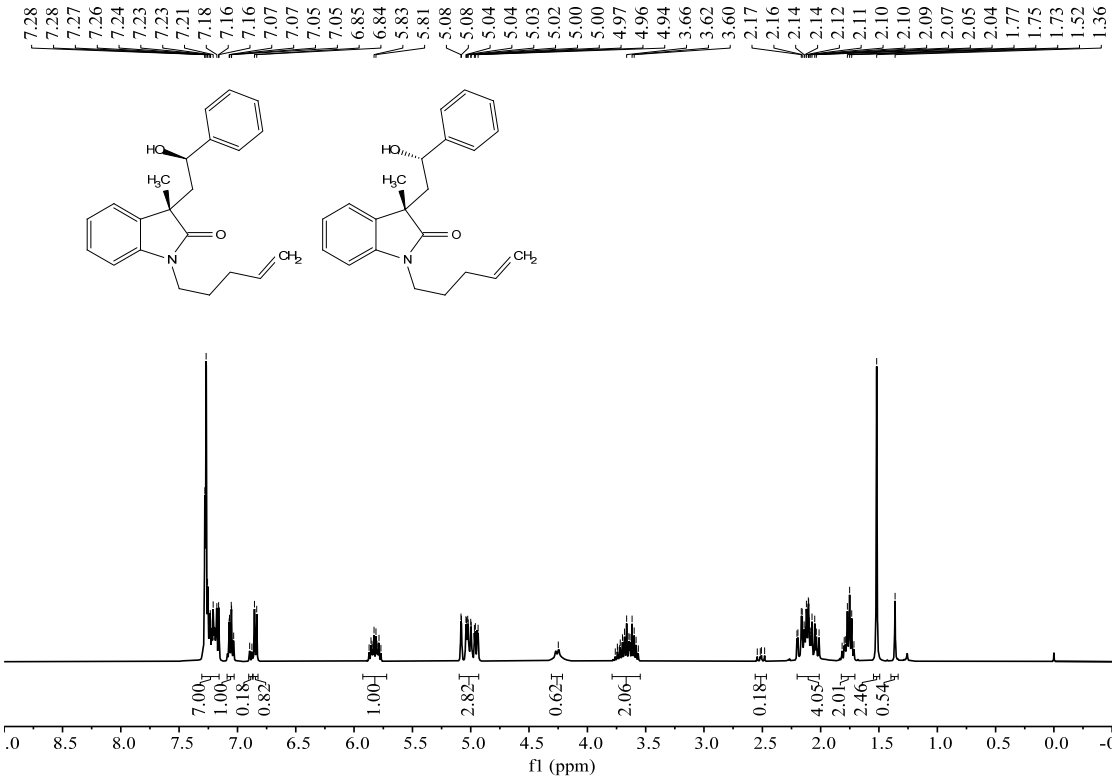
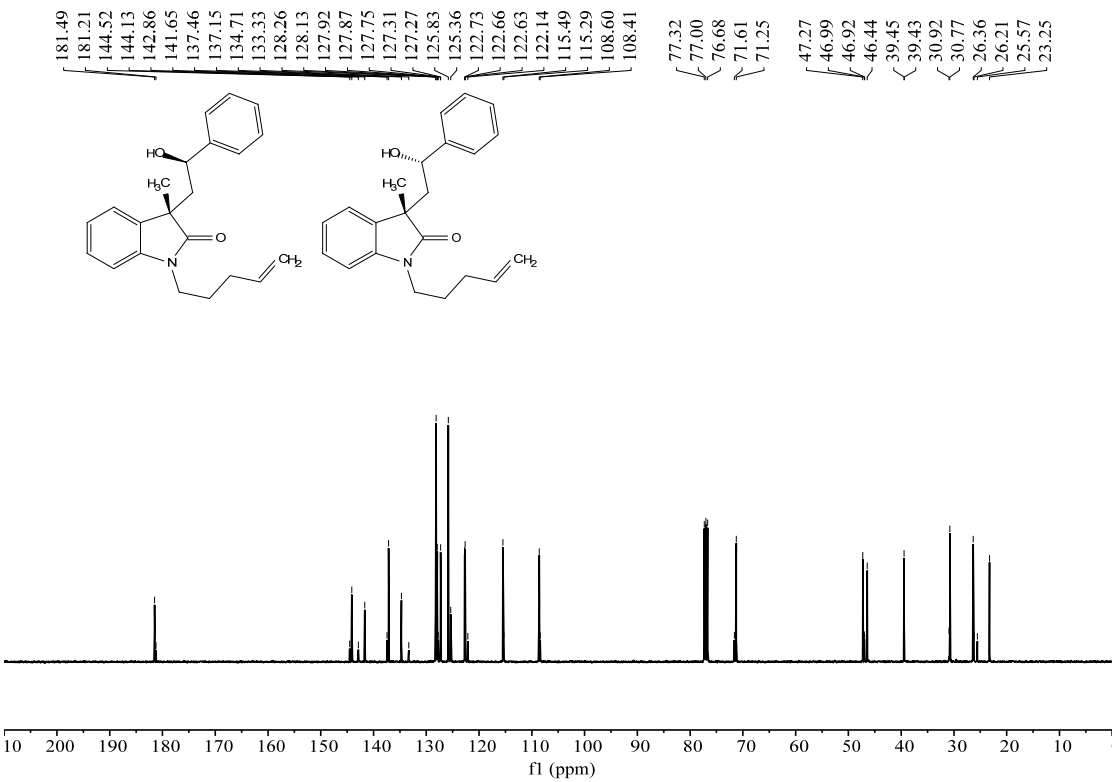


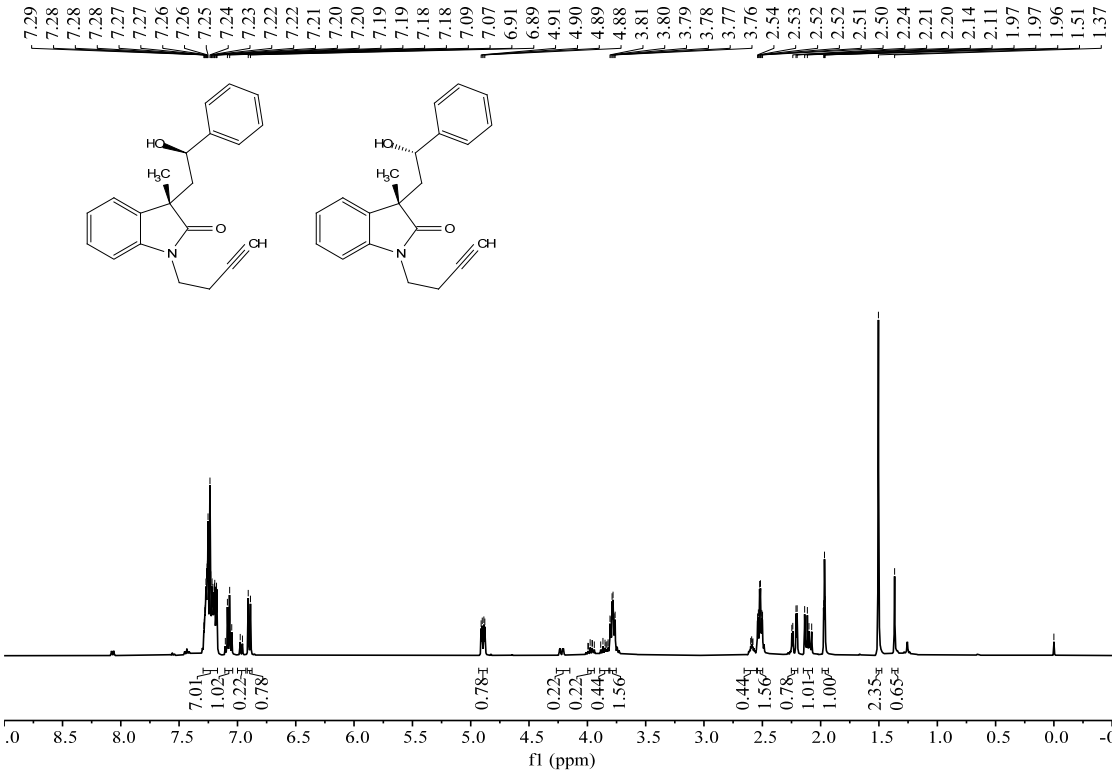
^{1}H NMR spectra of 7ab (400 MHz, $CDCl_3$)



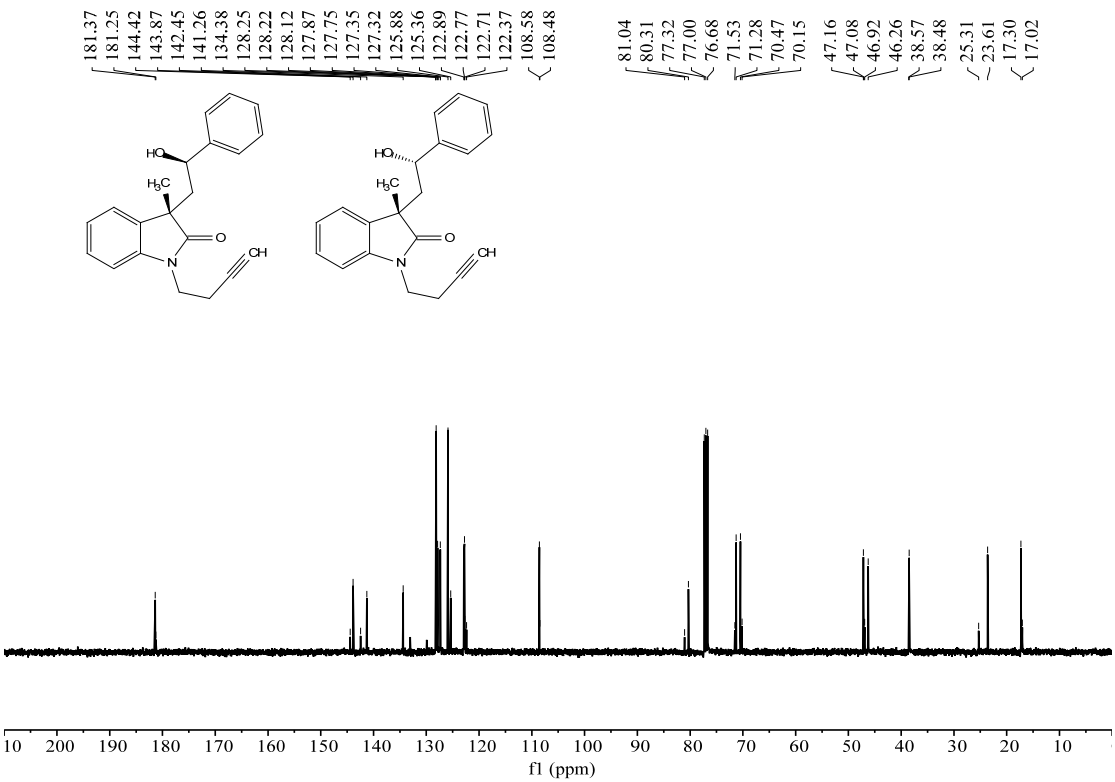
^{13}C NMR spectra of 7ab (100 MHz, $CDCl_3$)



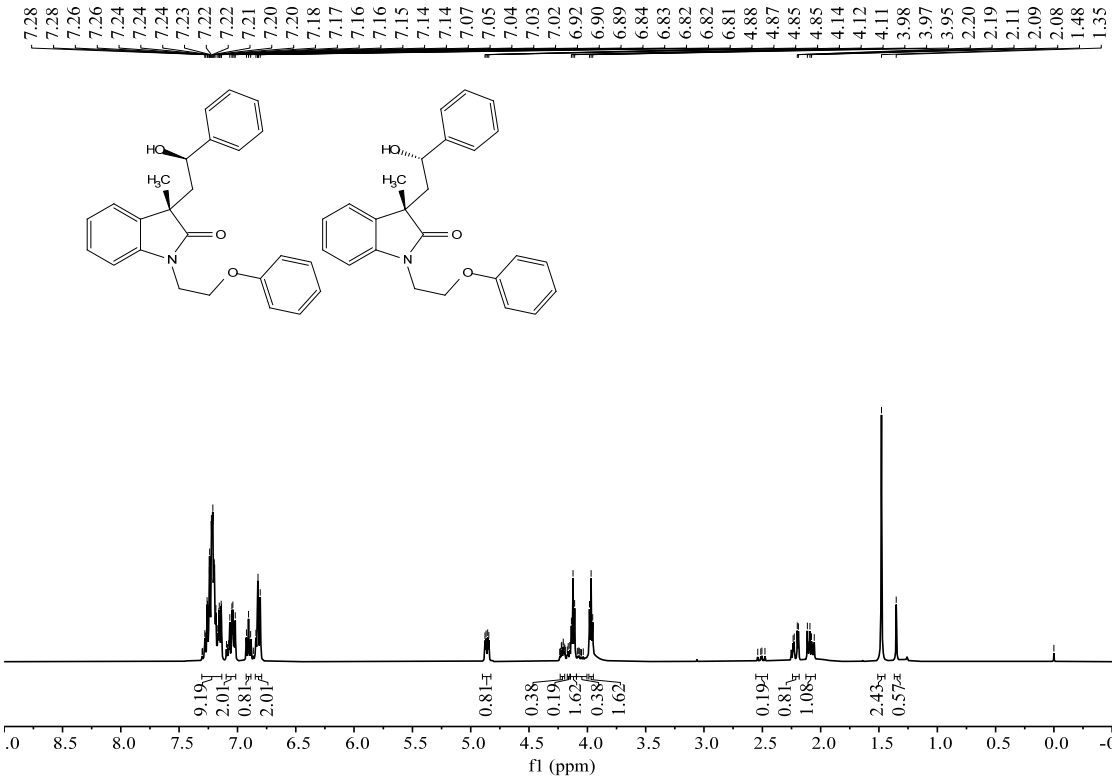
^{1}H NMR spectra of 8ab (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 8ab (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 9ab (400 MHz, $CDCl_3$)



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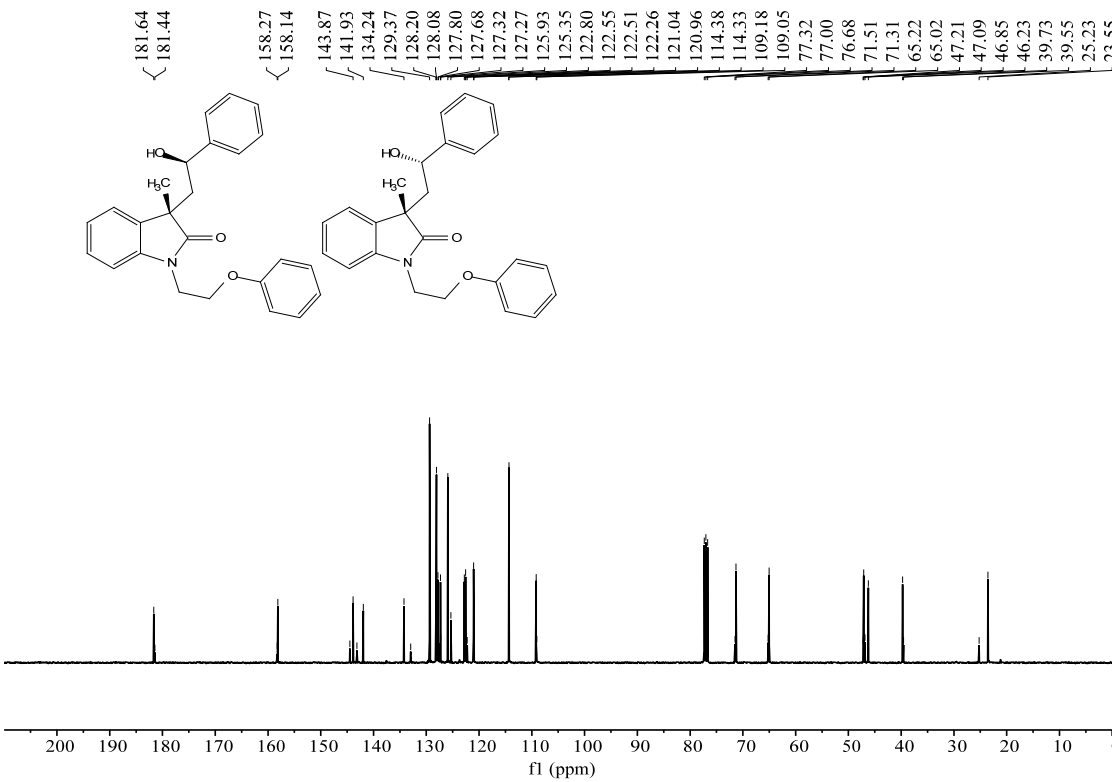

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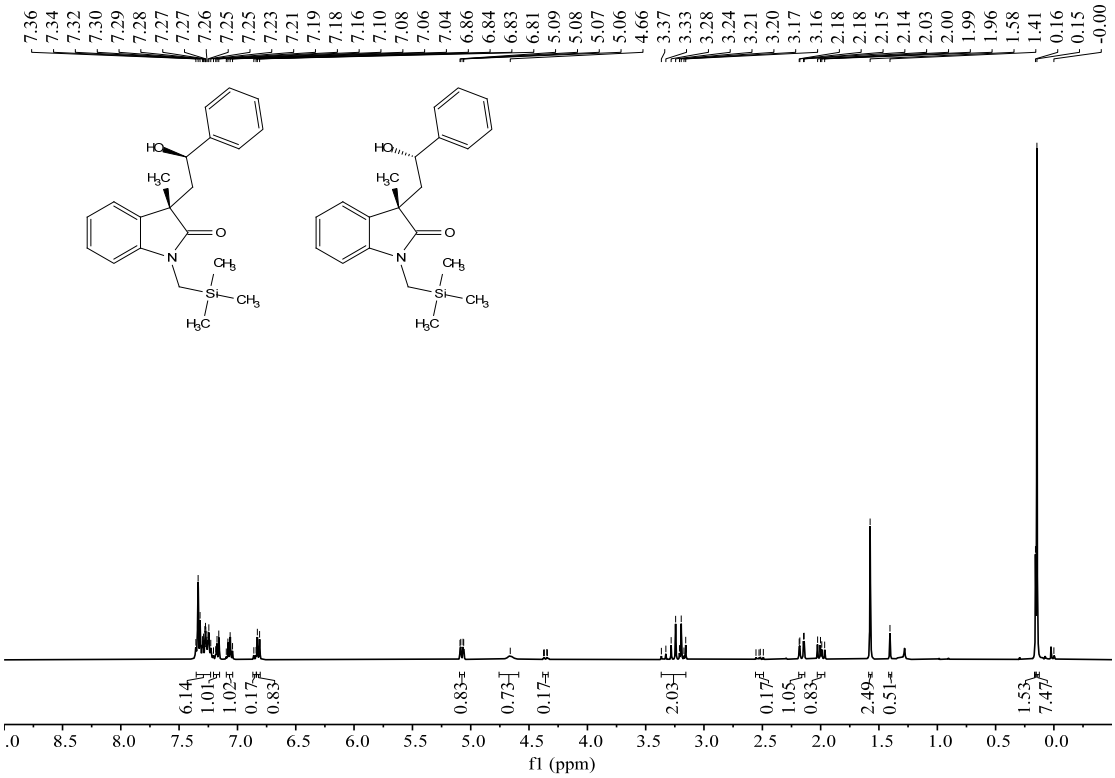

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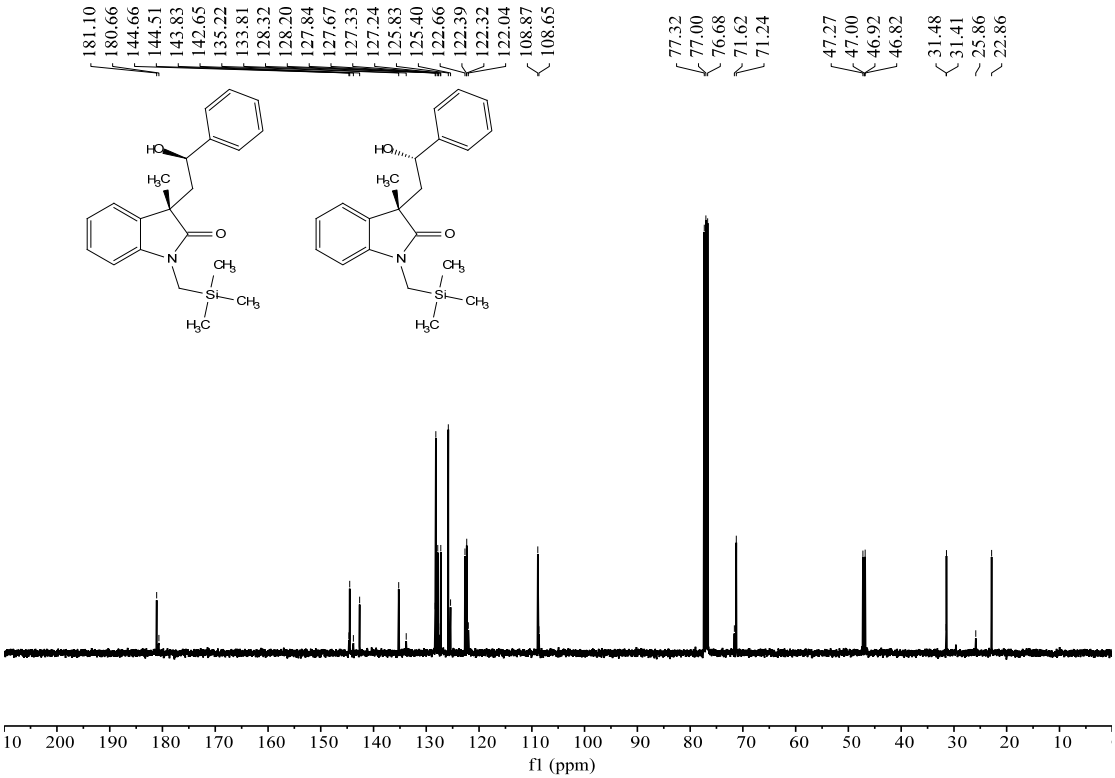
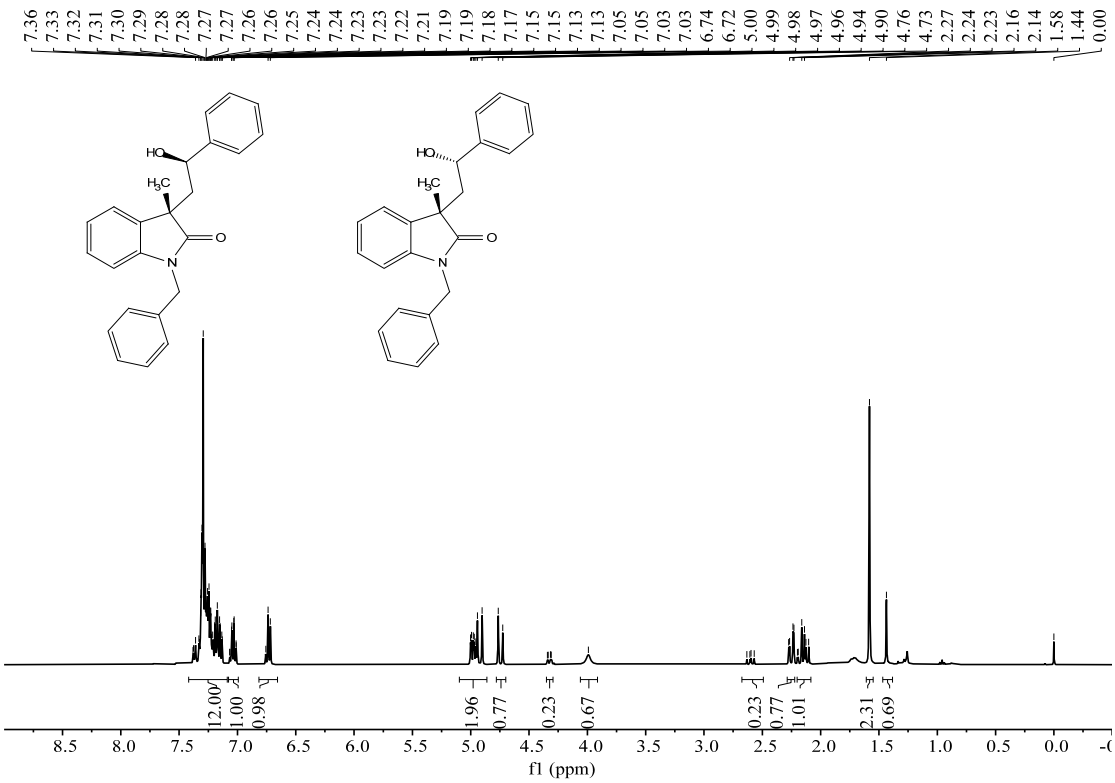


^{1}H NMR spectra of 11ab (400 MHz, $CDCl_3$)



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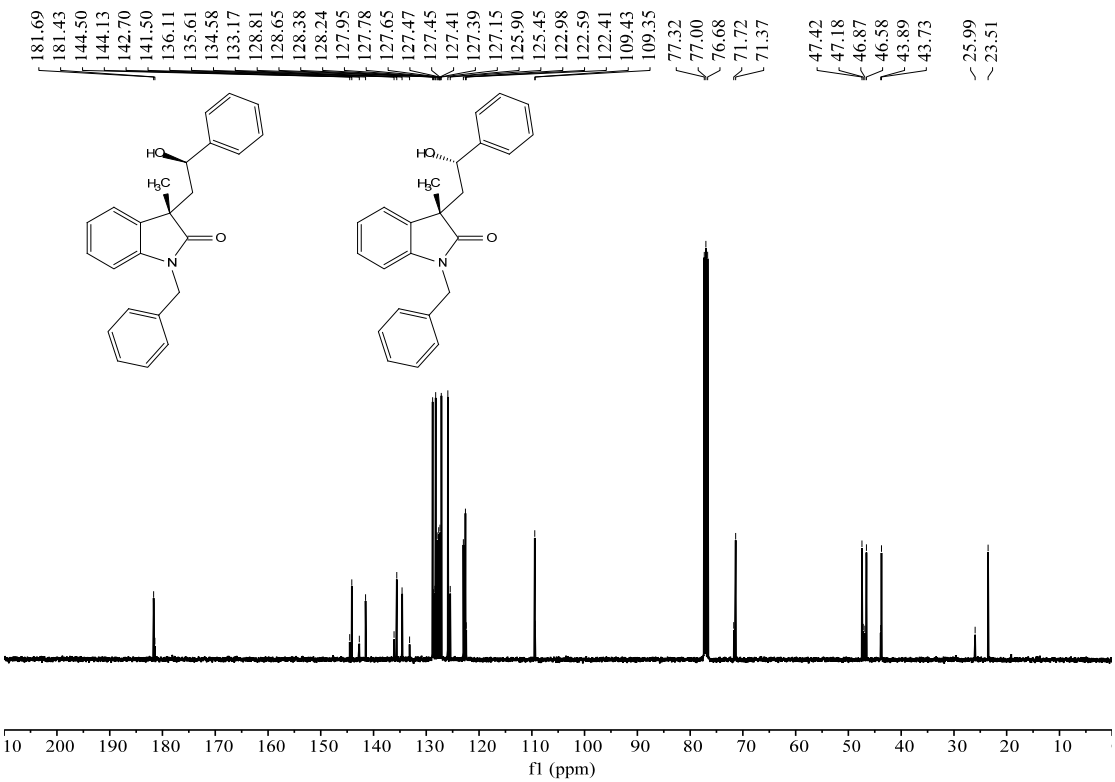
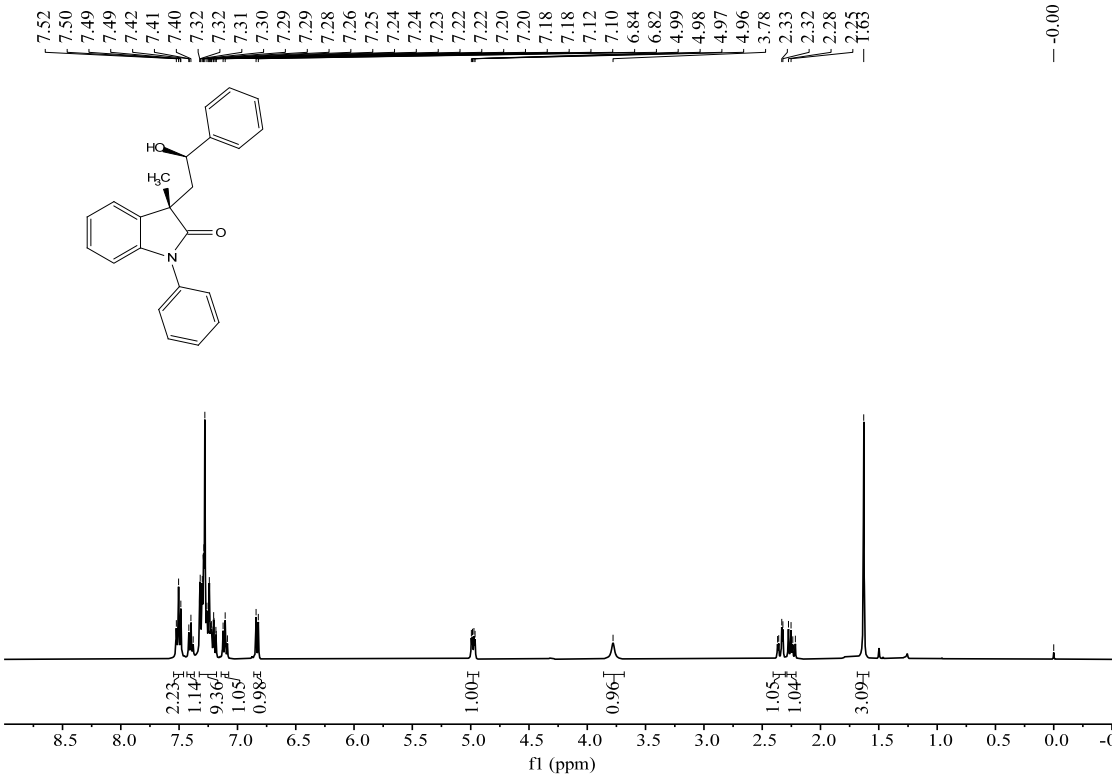
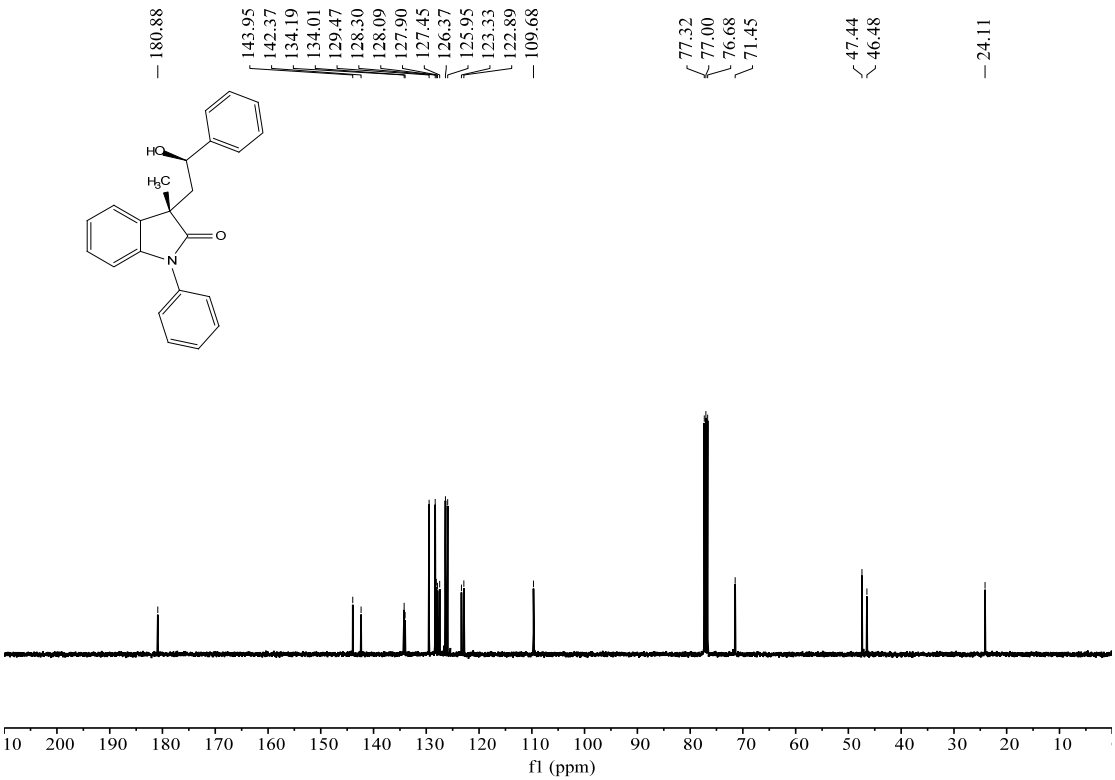


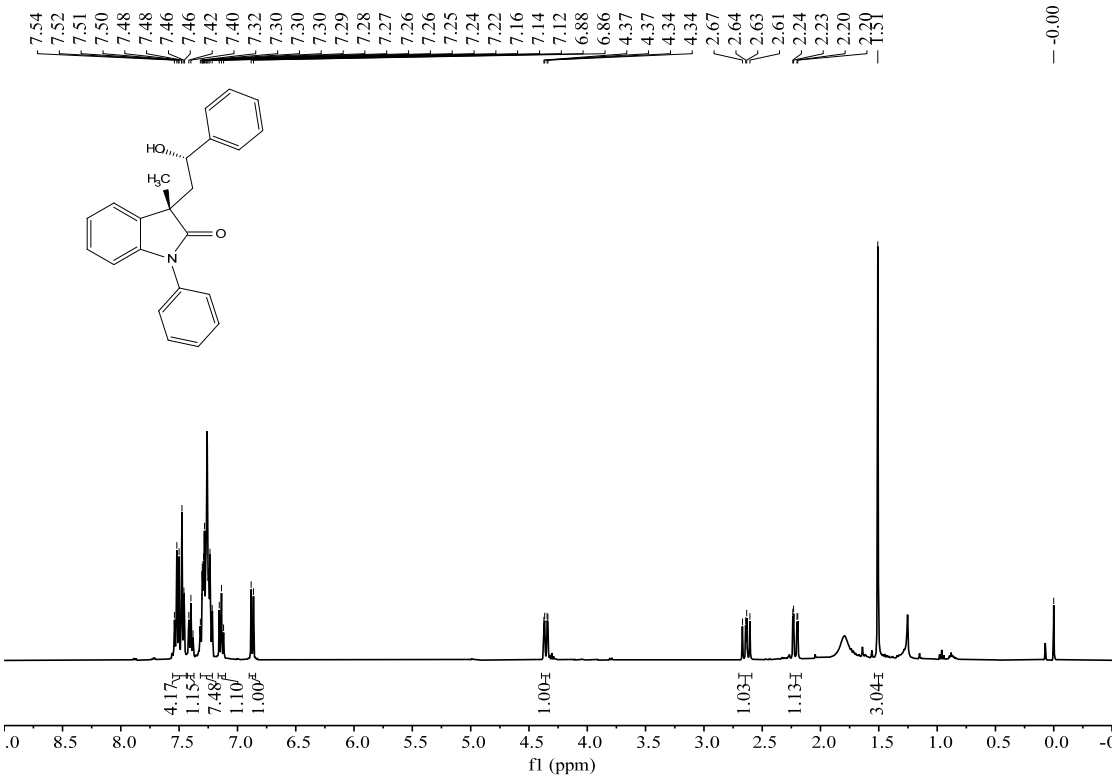
^{1}H NMR spectra of 12a (400 MHz, $CDCl_3$)



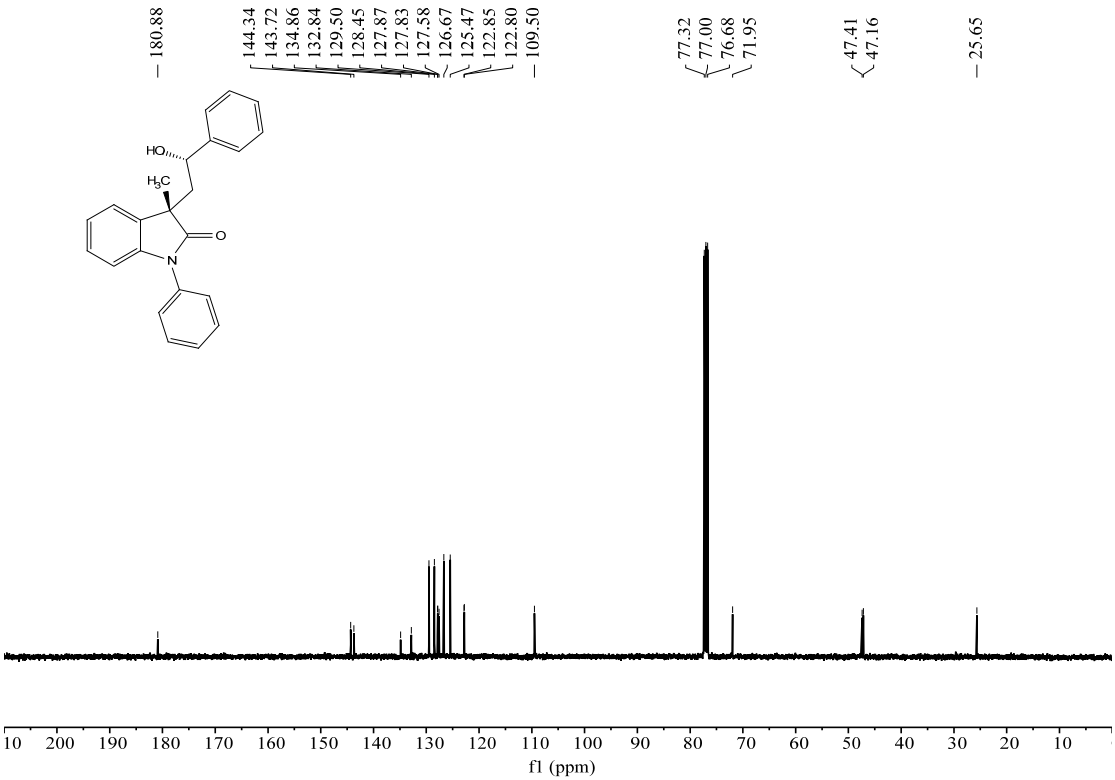
^{13}C NMR spectra of 12a (100 MHz, $CDCl_3$)



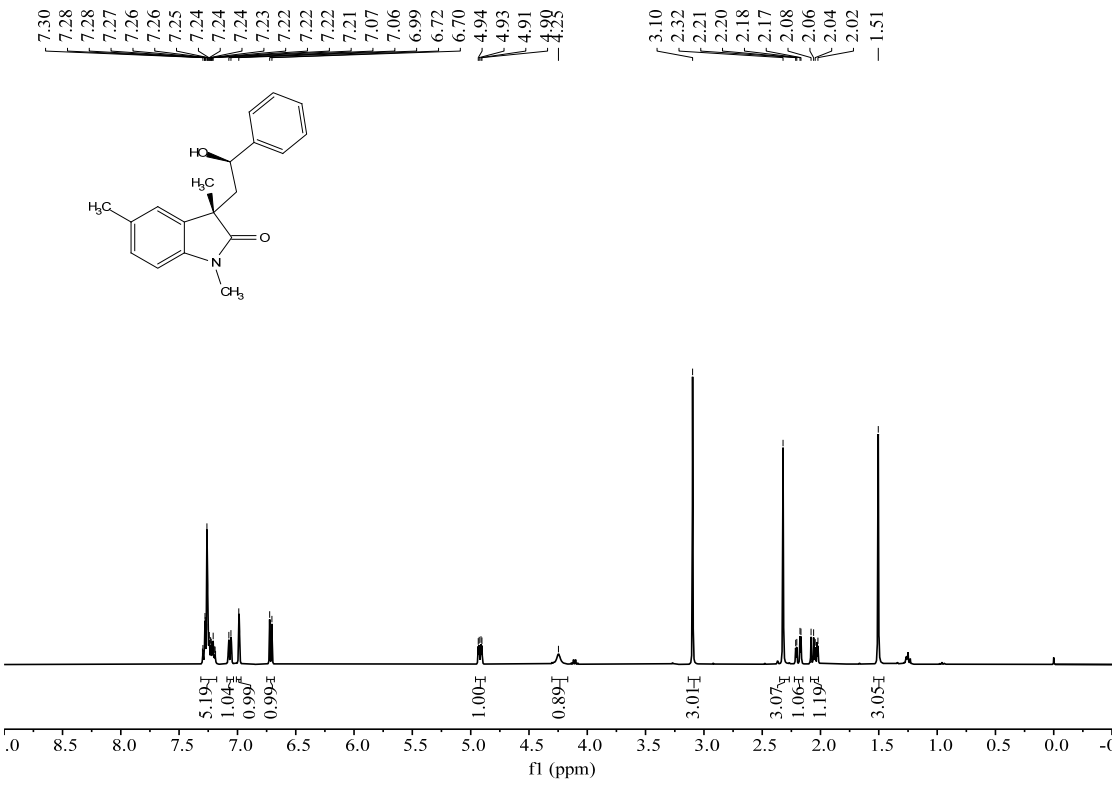
^{1}H NMR spectra of 12b (400 MHz, $CDCl_3$)



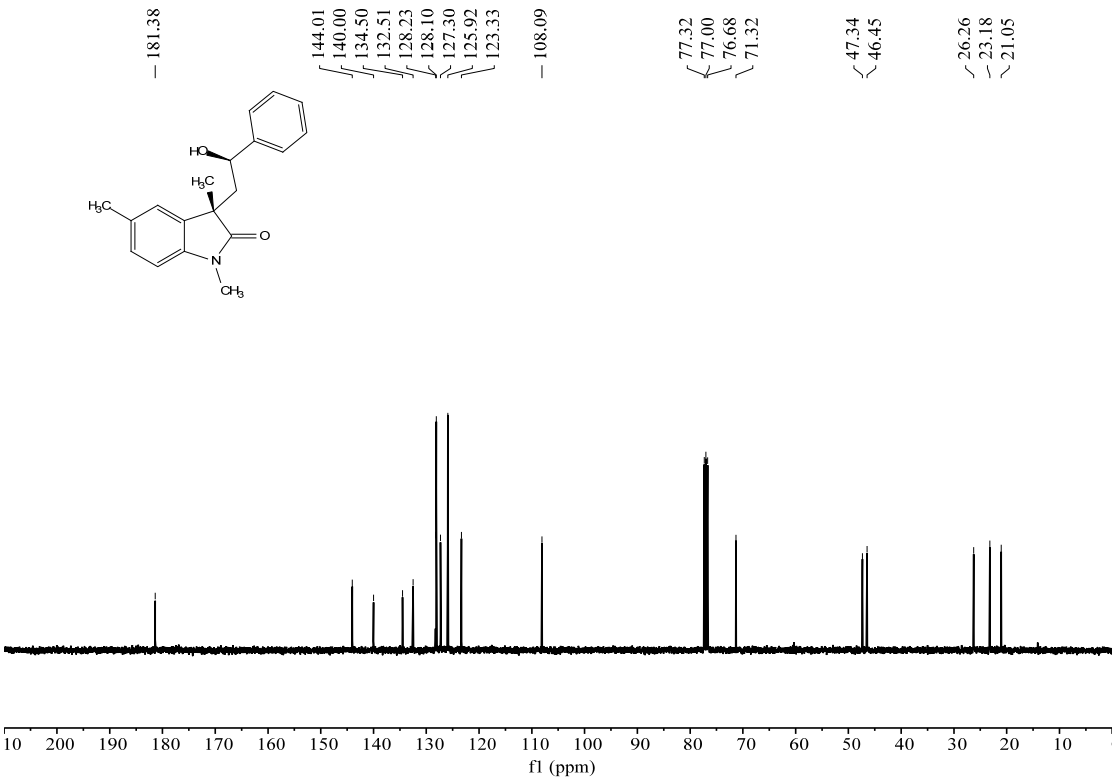
^{13}C NMR spectra of 12b (100 MHz, $CDCl_3$)



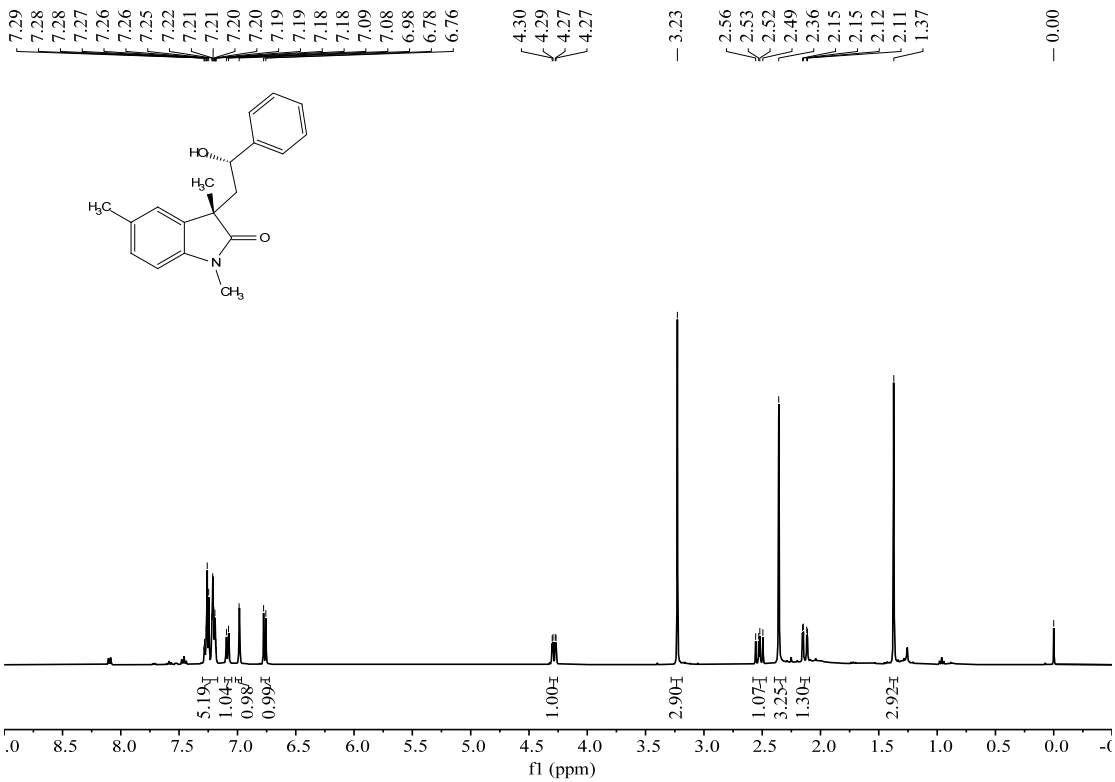
^{1}H NMR spectra of 13a (400 MHz, $CDCl_3$)



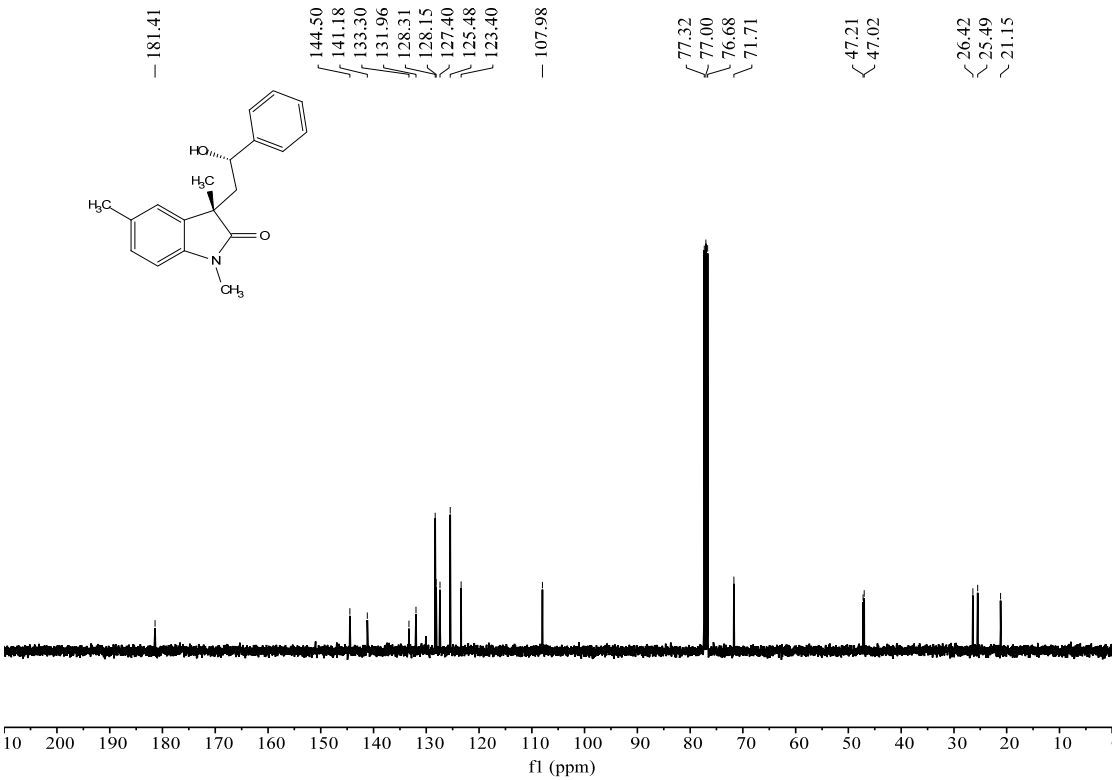
^{13}C NMR spectra of 13a (100 MHz, $CDCl_3$)



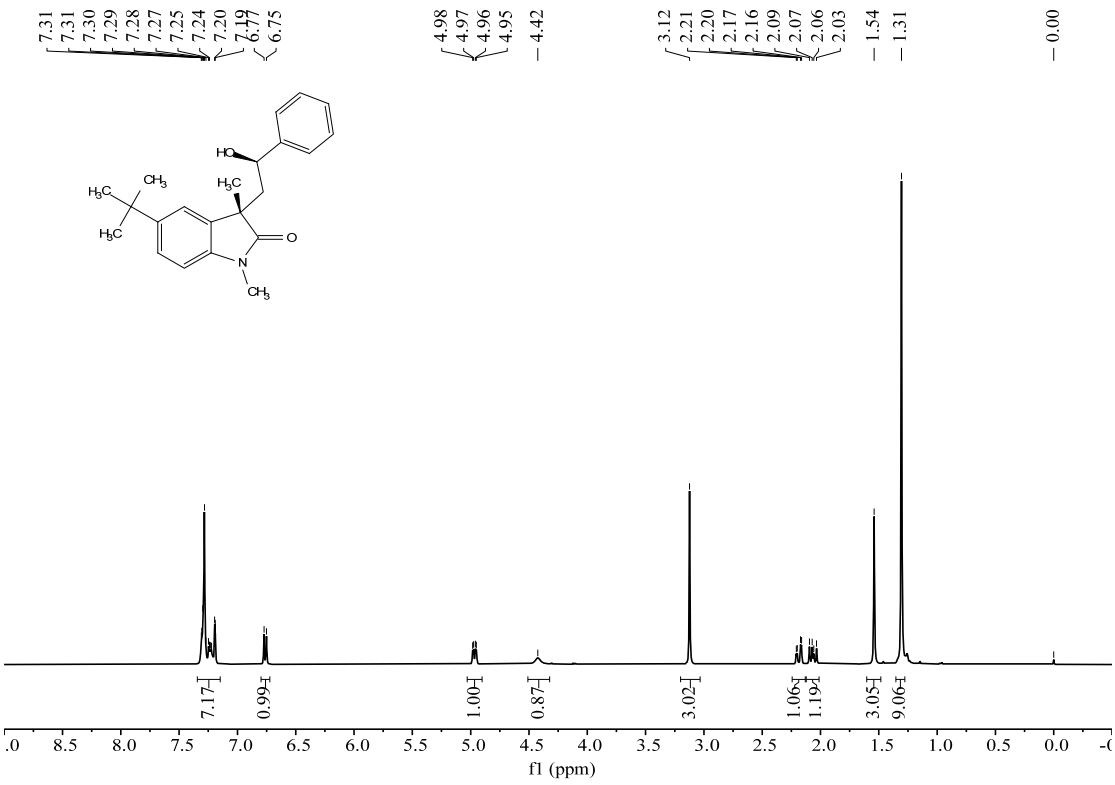
^{1}H NMR spectra of 13b (400 MHz, $CDCl_3$)



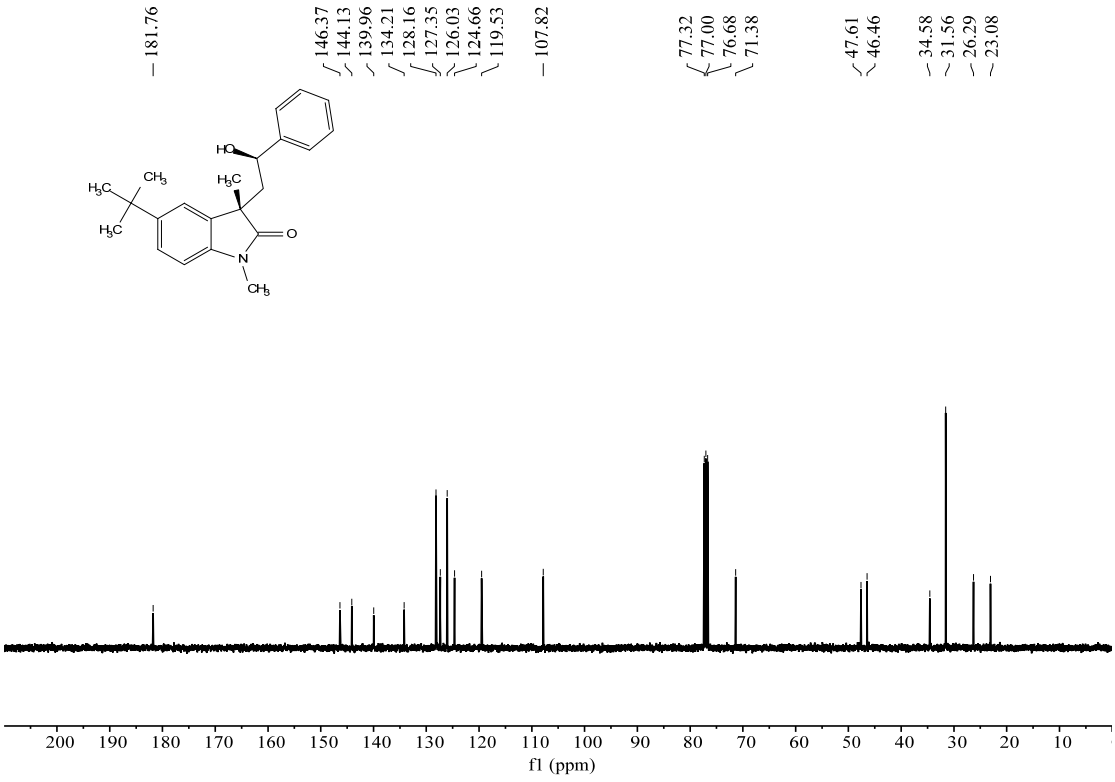
^{13}C NMR spectra of 13b (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 14a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 14a (100 MHz, $CDCl_3$)



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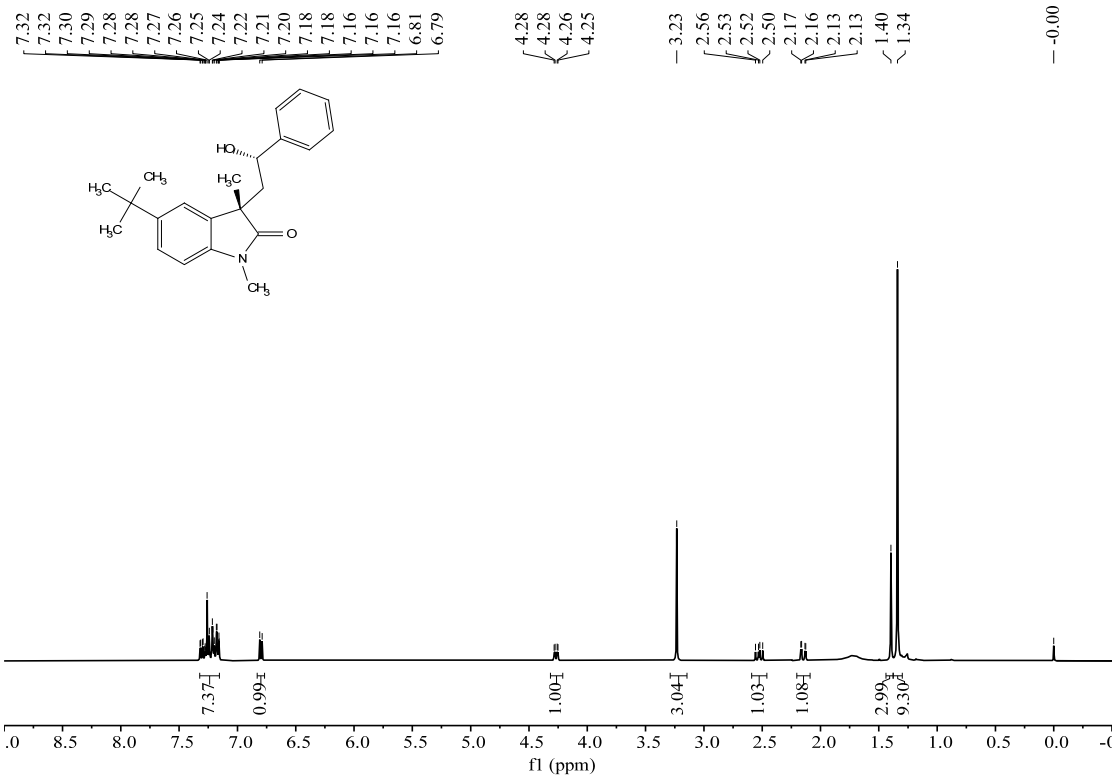
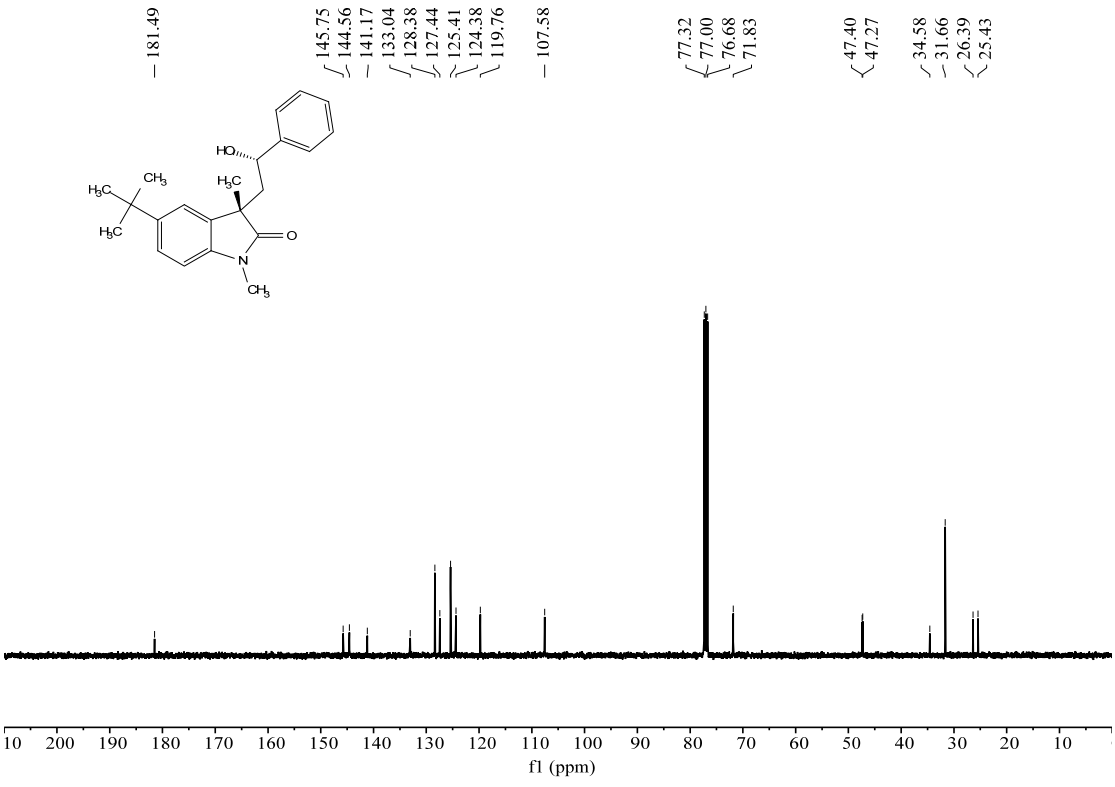
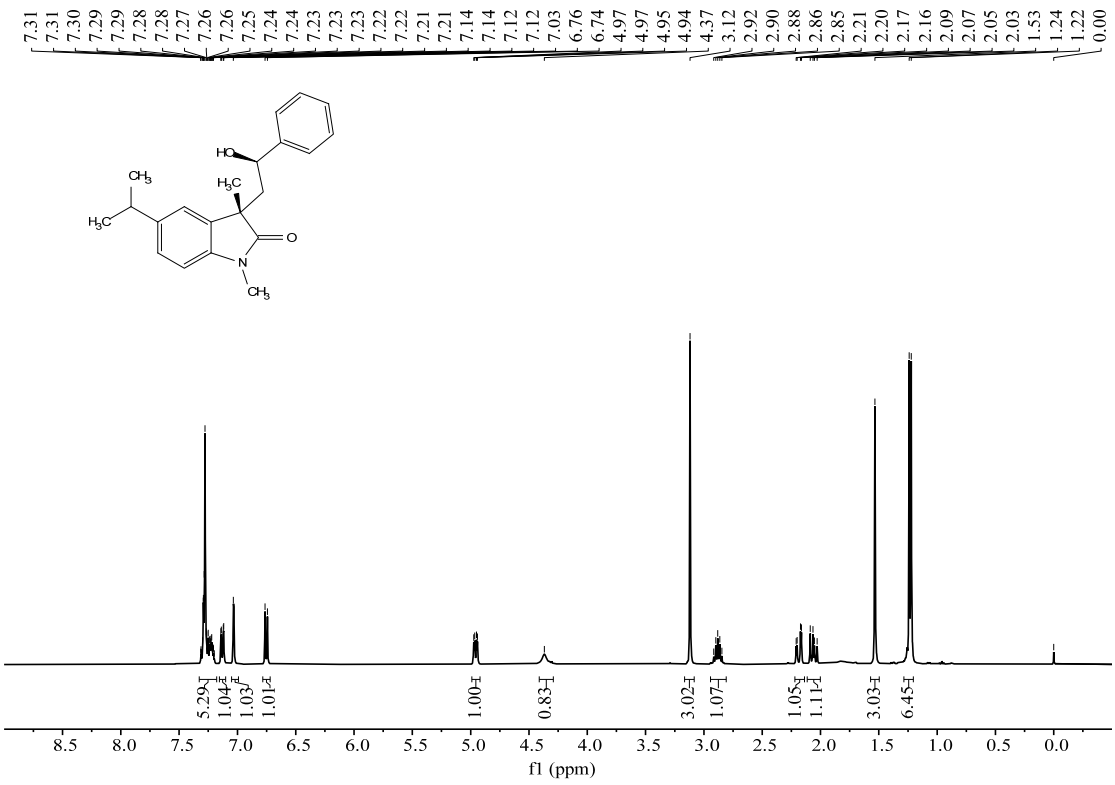


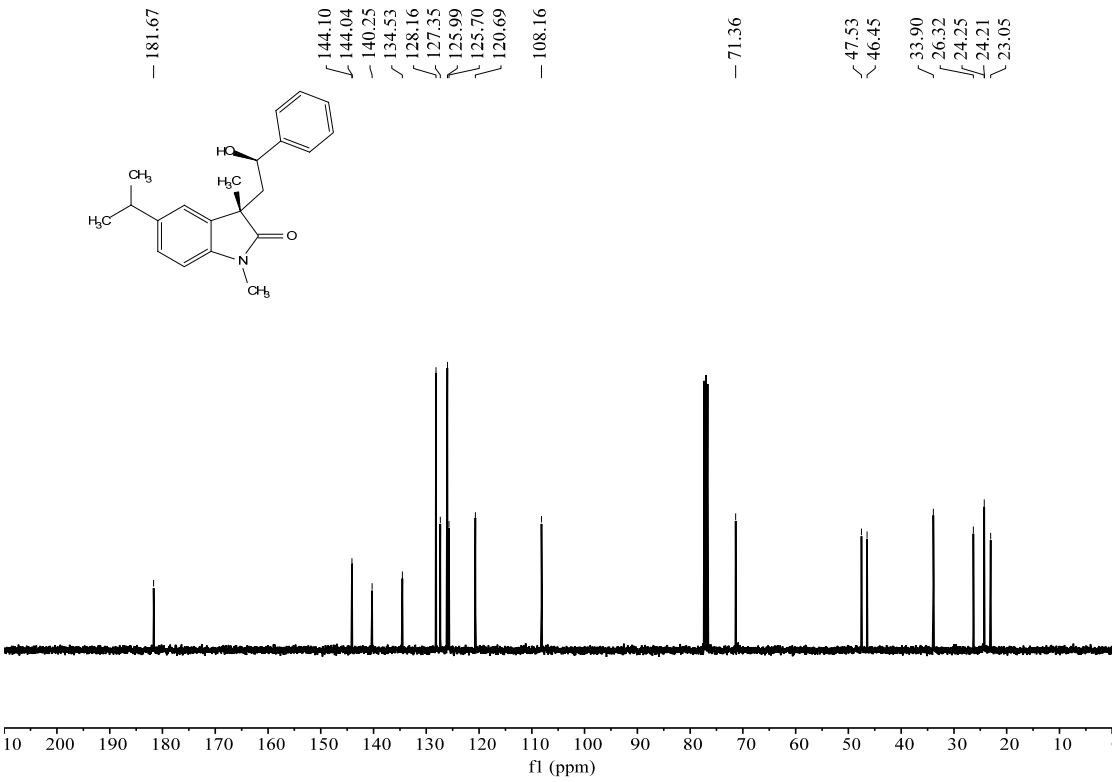
^{13}C NMR spectra of 14b (100 MHz, $CDCl_3$)



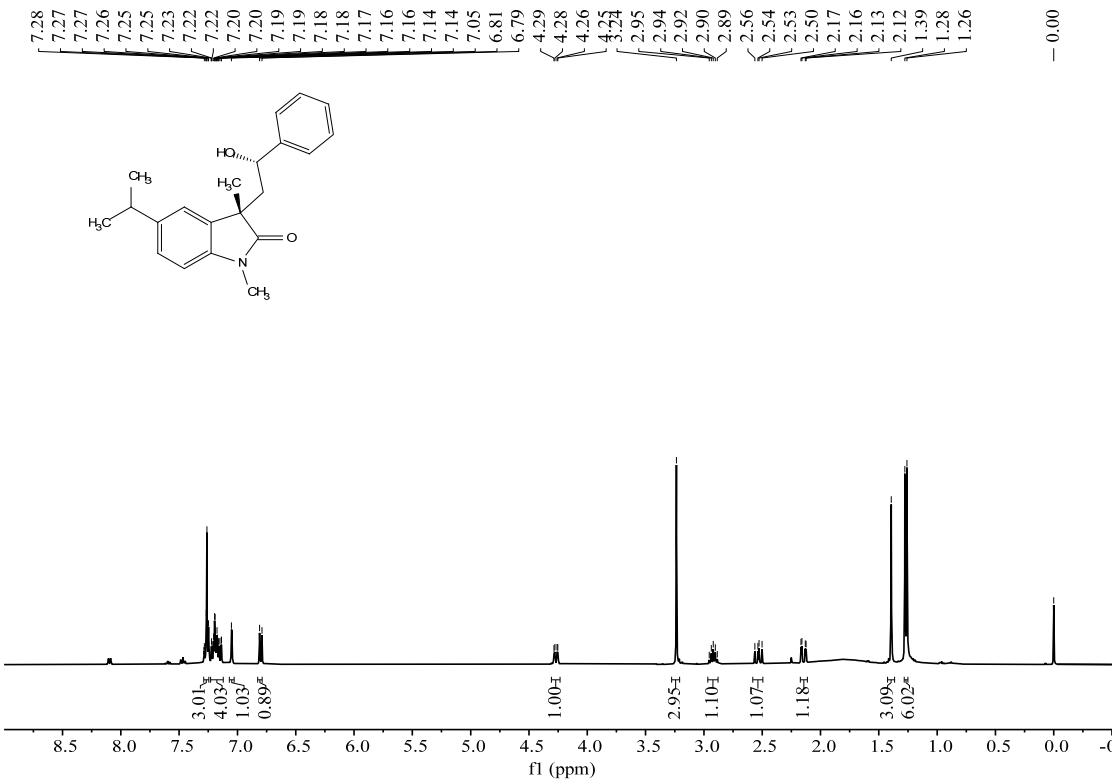
^{1}H NMR spectra of 15a (400 MHz, $CDCl_3$)



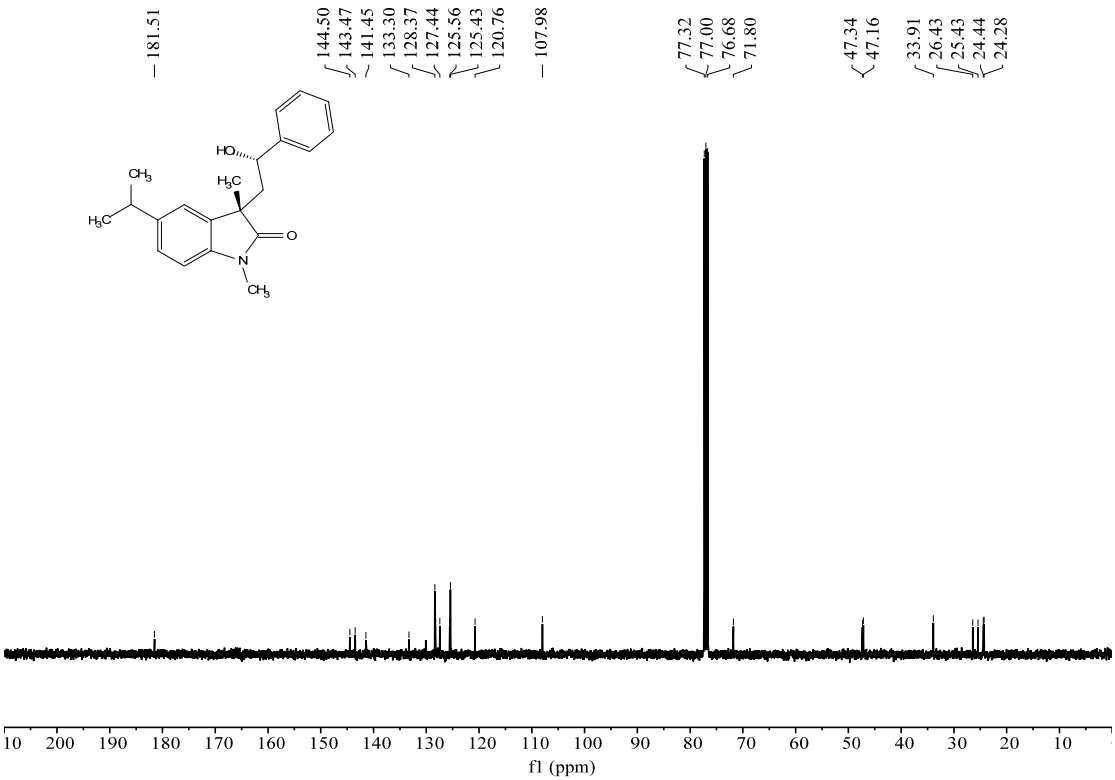
^{13}C NMR spectra of 15a (100 MHz, $CDCl_3$)



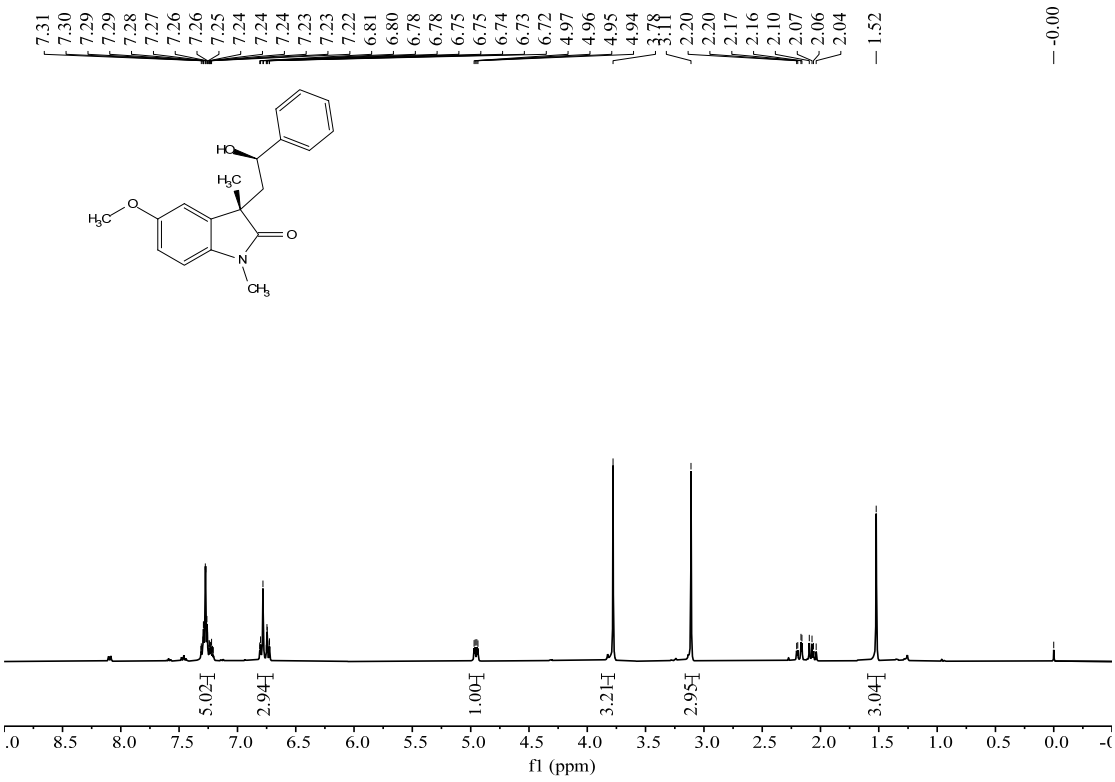
^{1}H NMR spectra of 15b (400 MHz, $CDCl_3$)



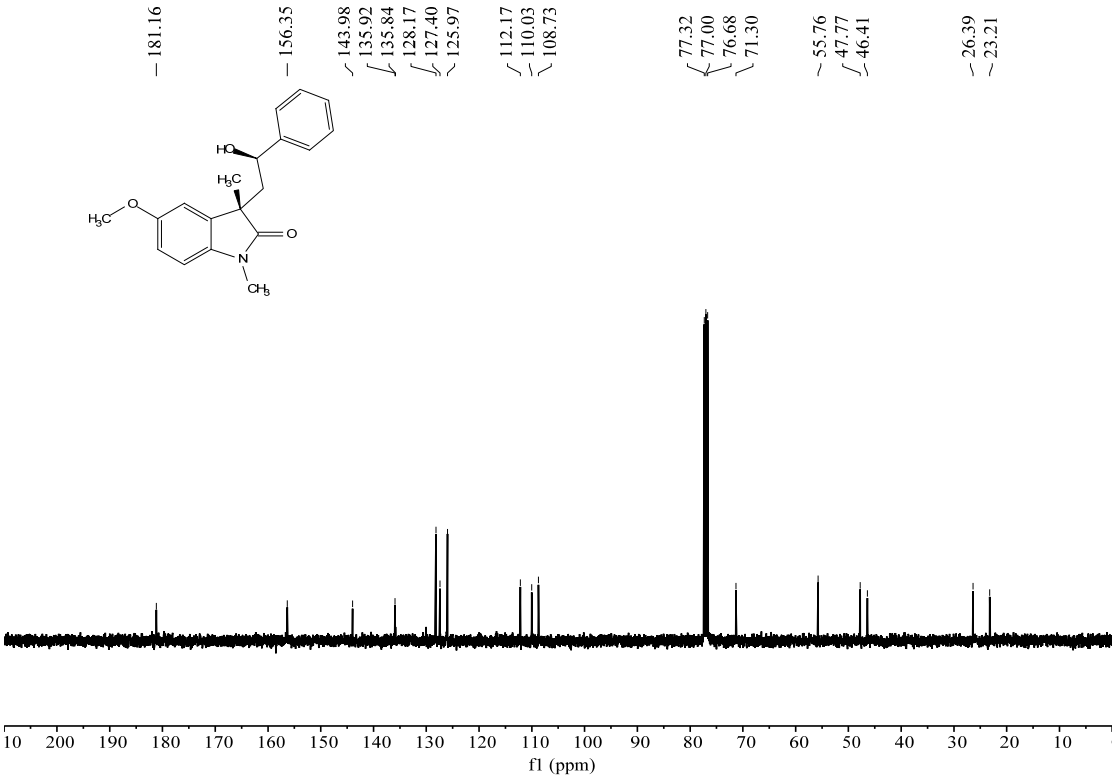
^{13}C NMR spectra of 15b (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 16a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 16a (100 MHz, $CDCl_3$)



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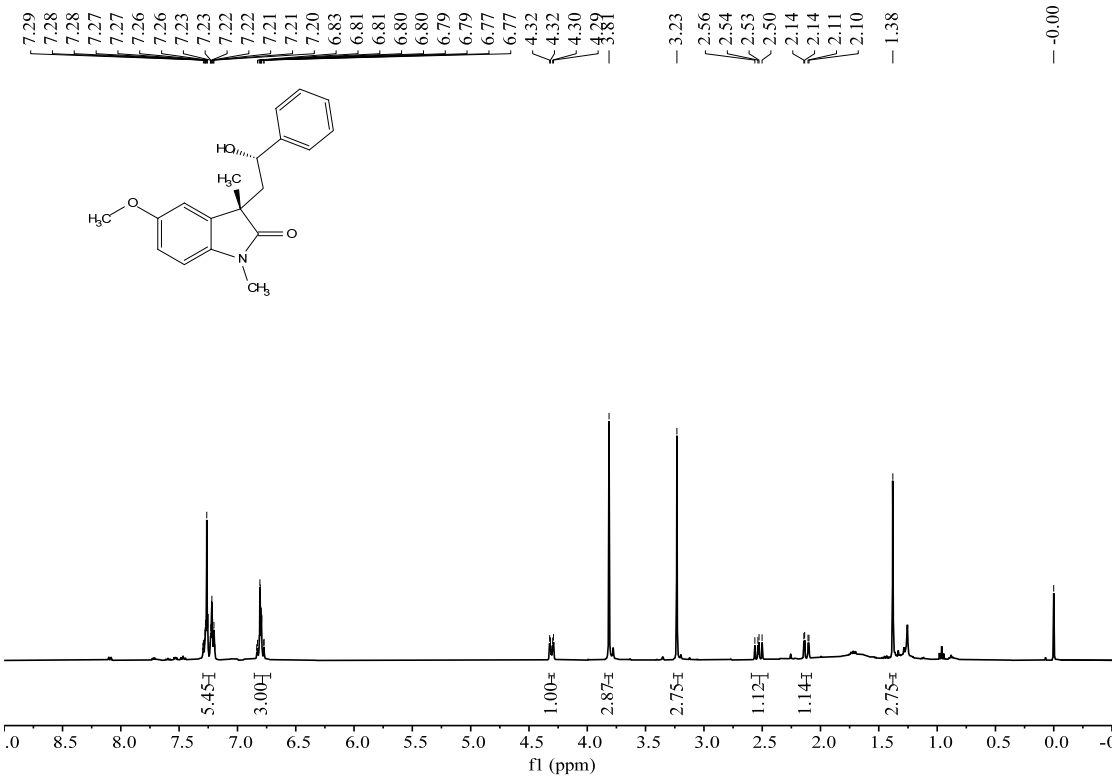
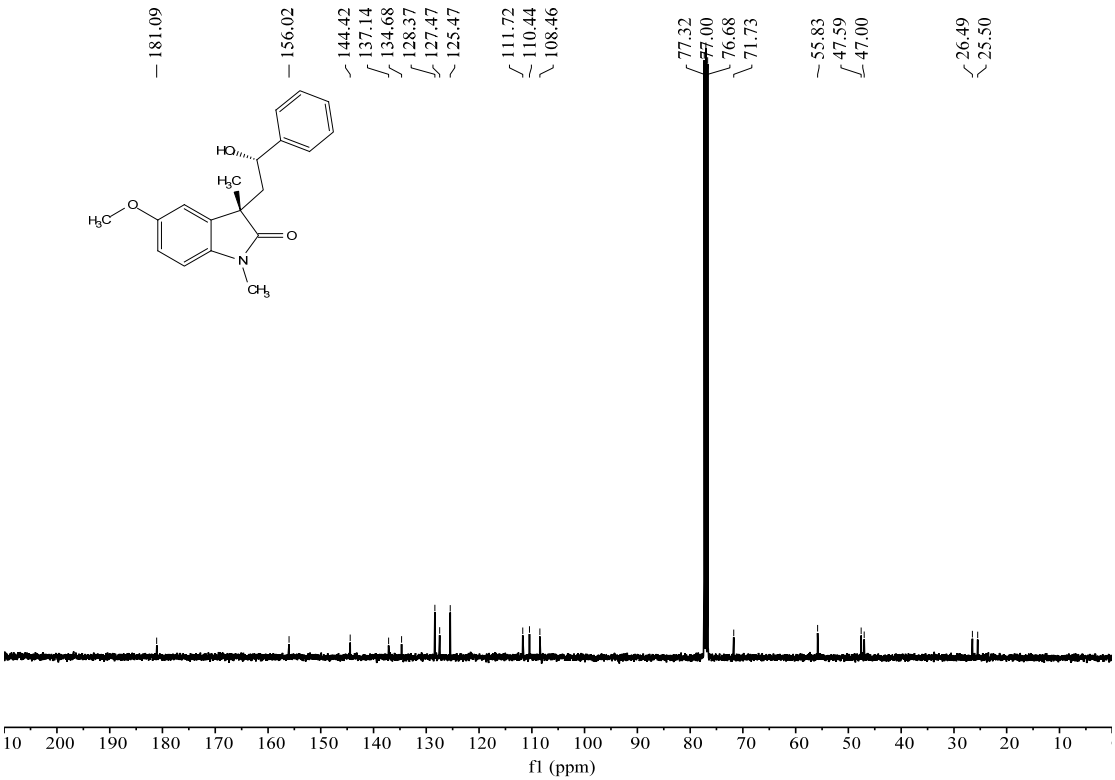
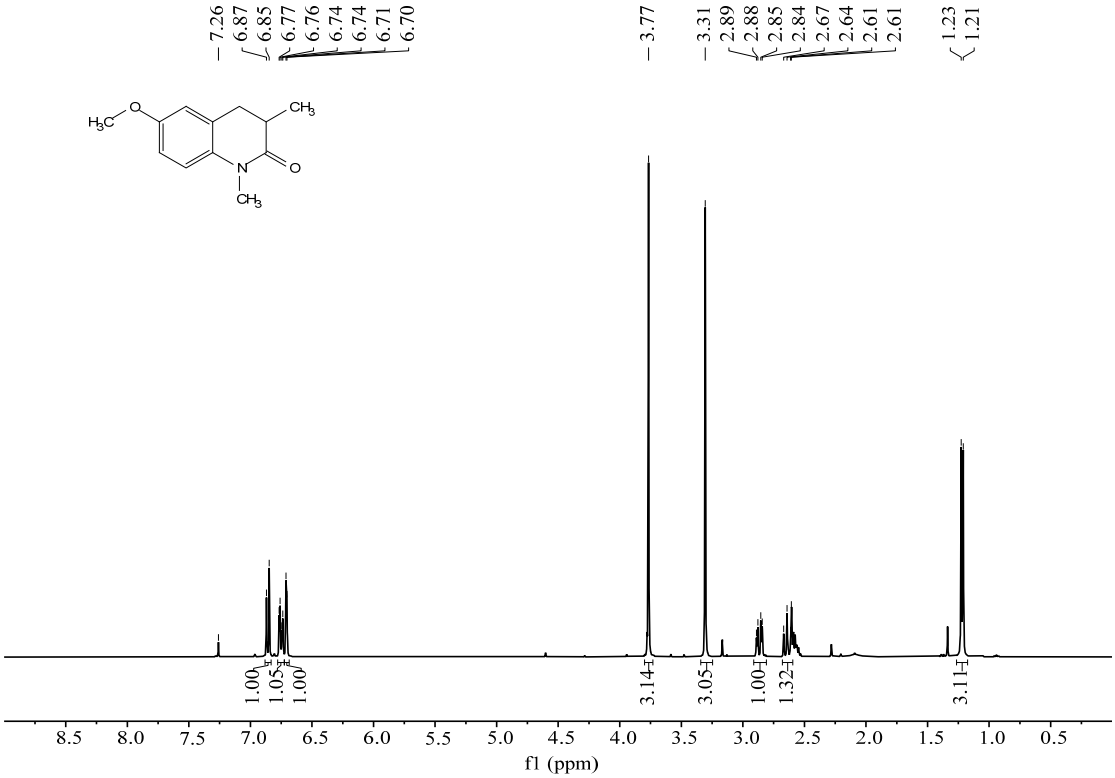


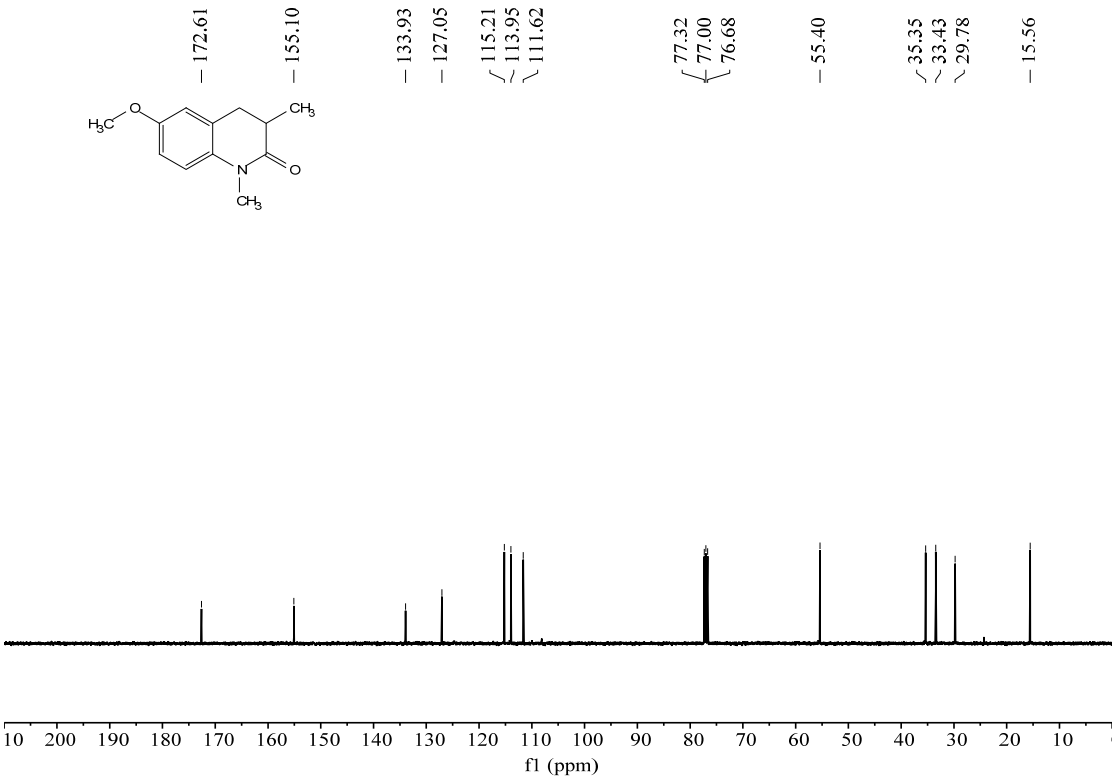
^{13}C NMR spectra of 16b (100 MHz, $CDCl_3$)



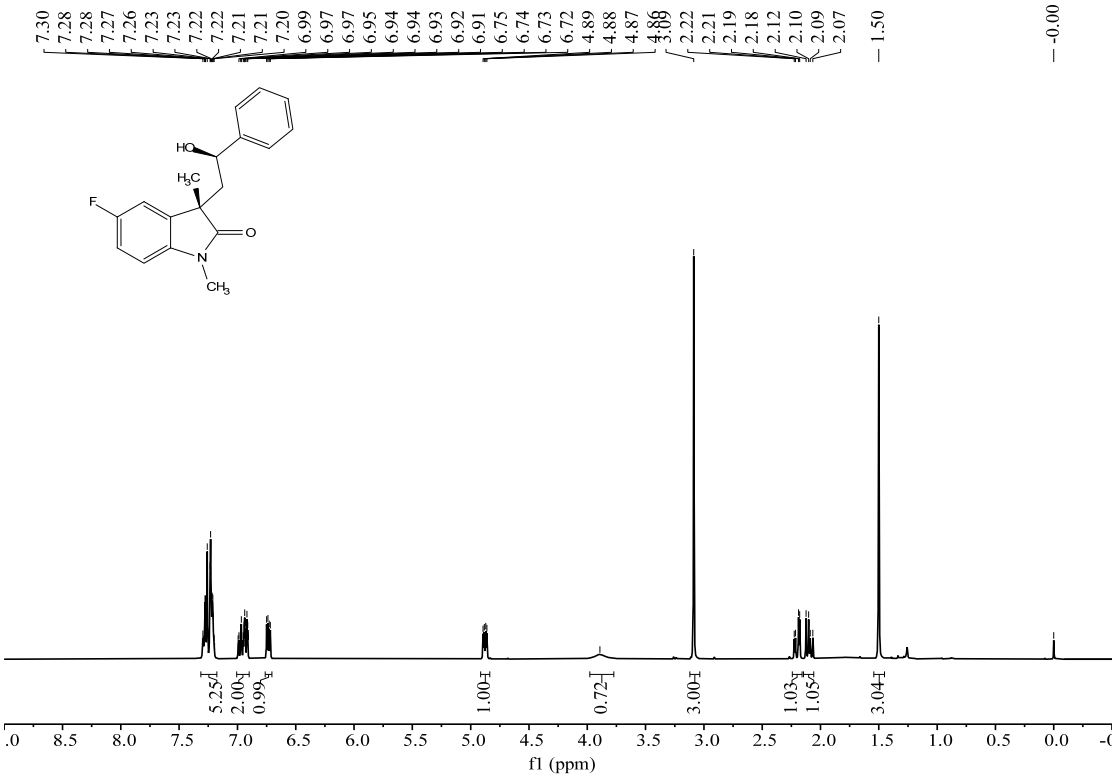
^{1}H NMR spectra of 16’ (400 MHz, $CDCl_3$)



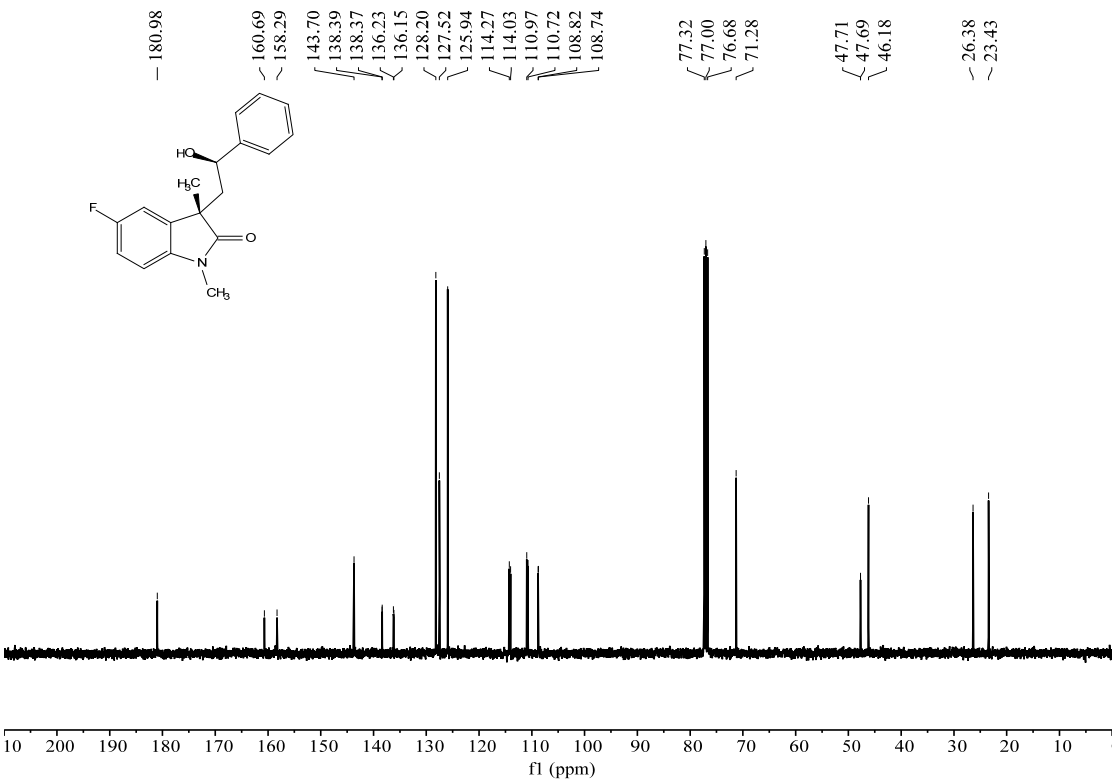
^{13}C NMR spectra of 16’ (100 MHz, $CDCl_3$)



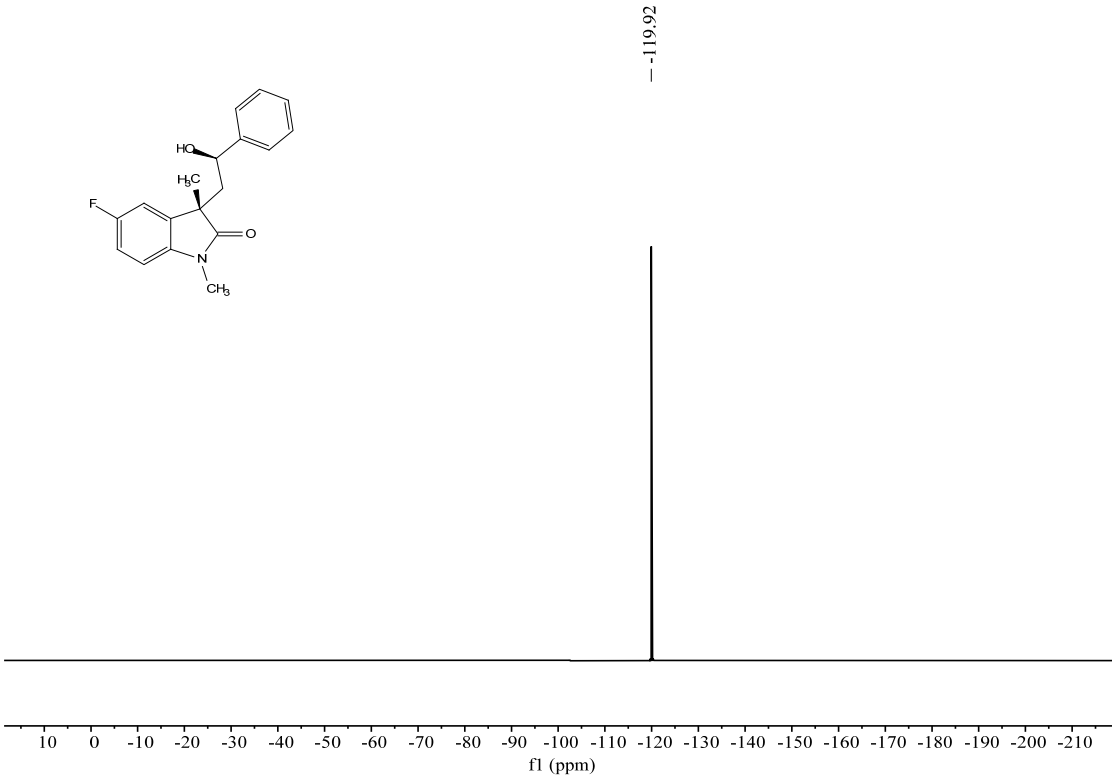
^{1}H NMR spectra of 17a (400 MHz, $CDCl_3$)



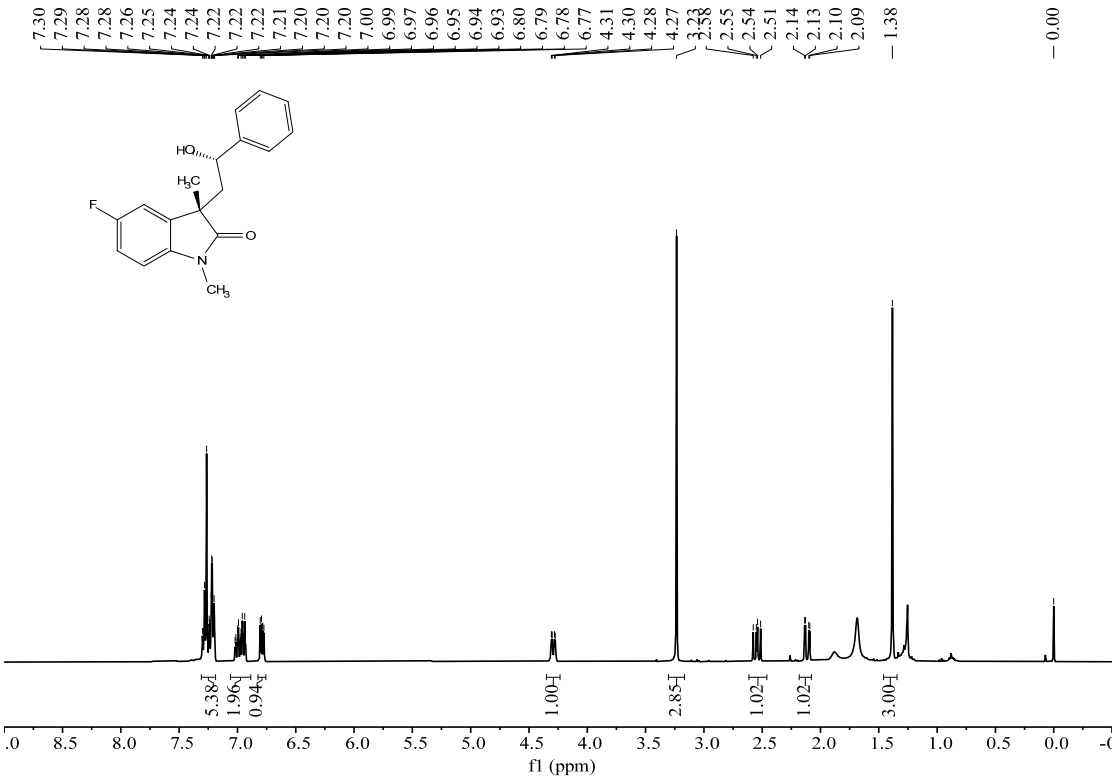
^{13}C NMR spectra of 17a (100 MHz, $CDCl_3$)



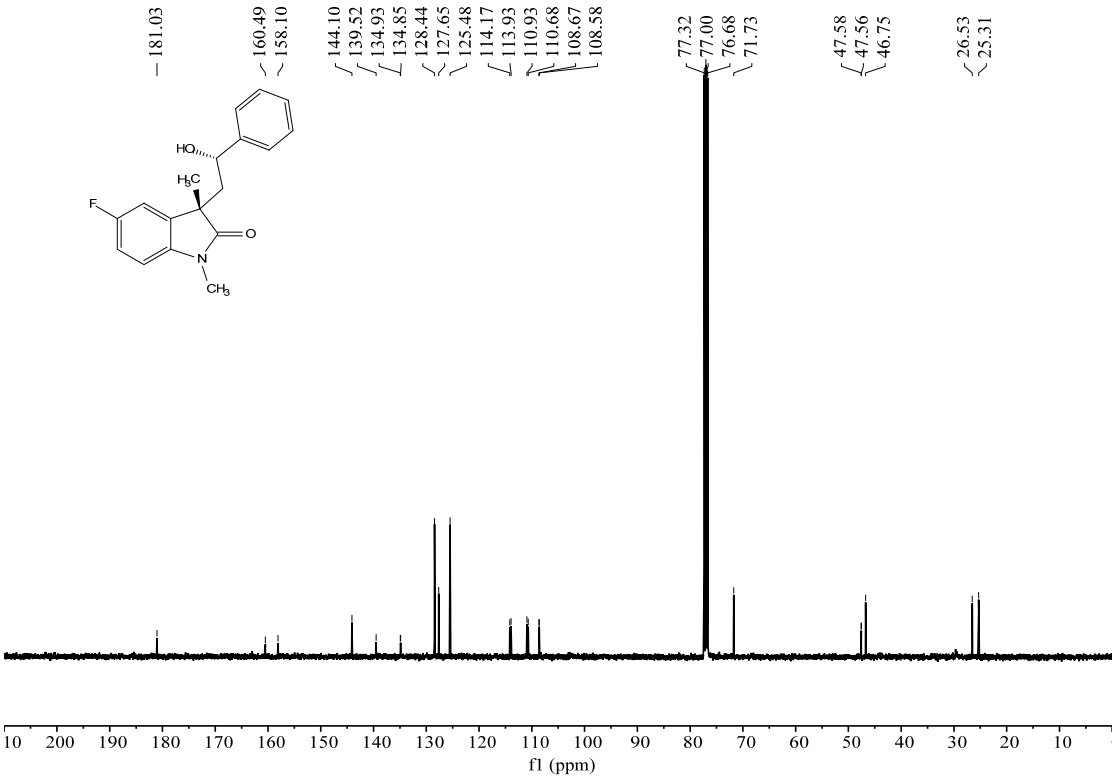
^{19}F NMR spectra of 17a (376 MHz, $CDCl_3$)



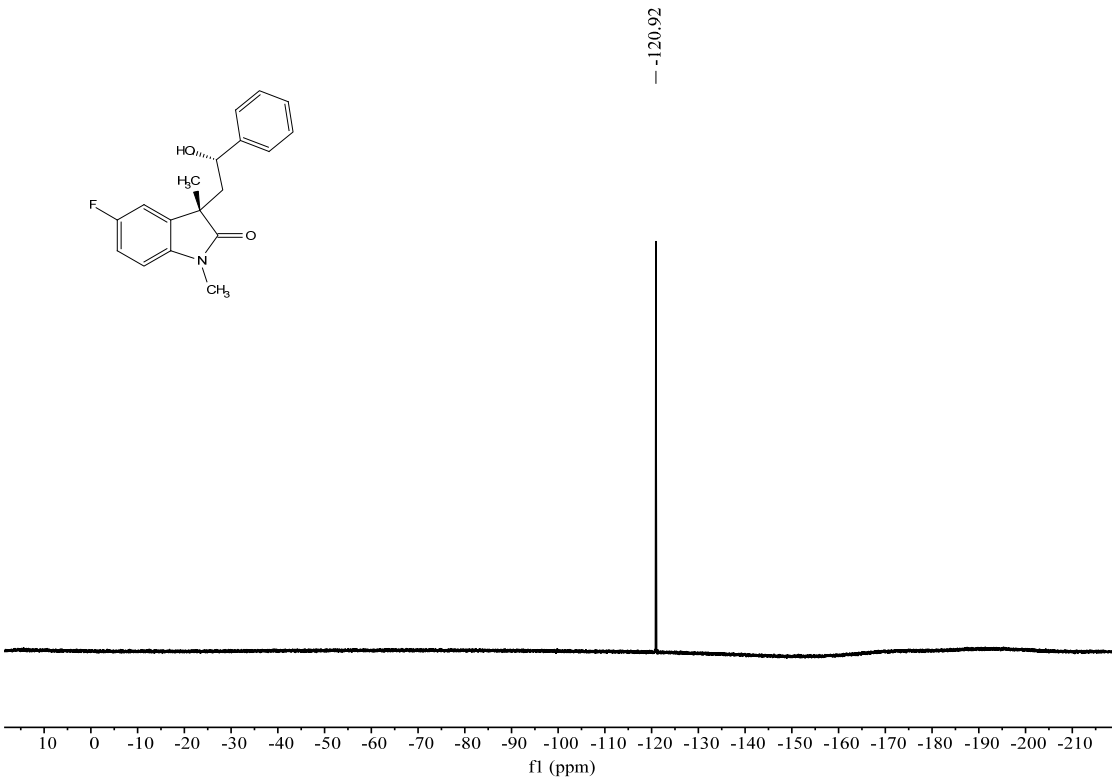
^{1}H NMR spectra of 17b (400 MHz, $CDCl_3$)



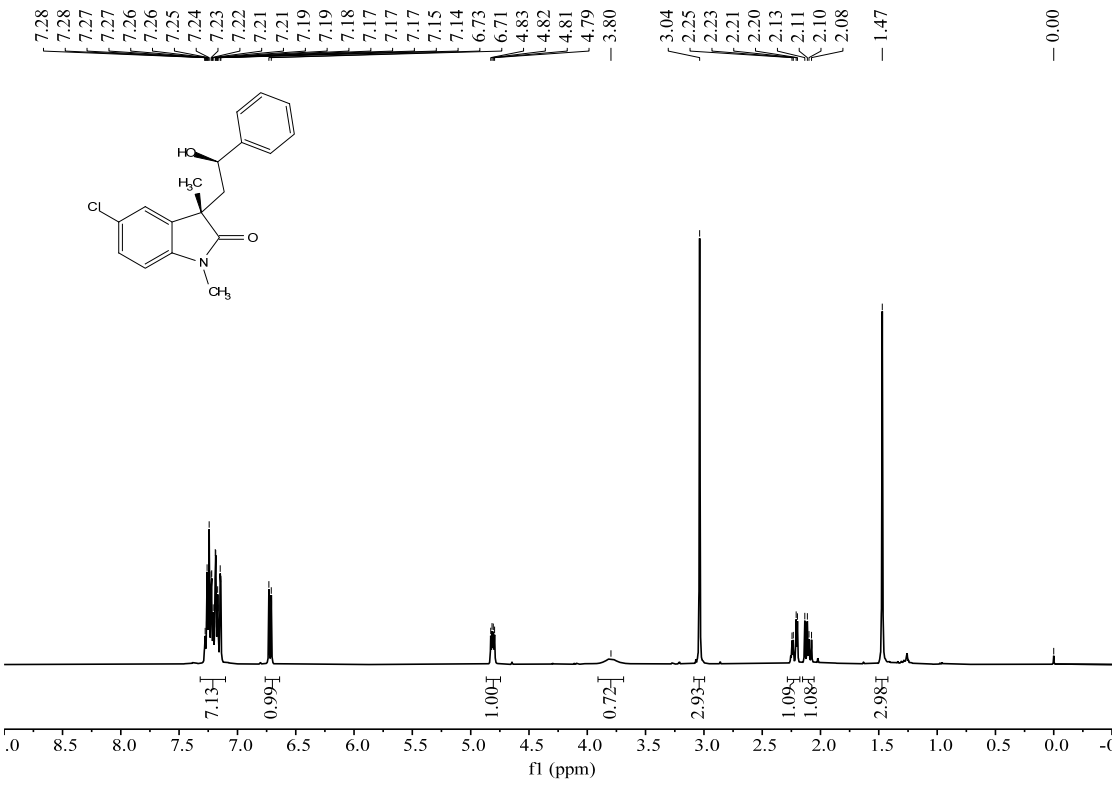
^{13}C NMR spectra of 17b (100 MHz, $CDCl_3$)



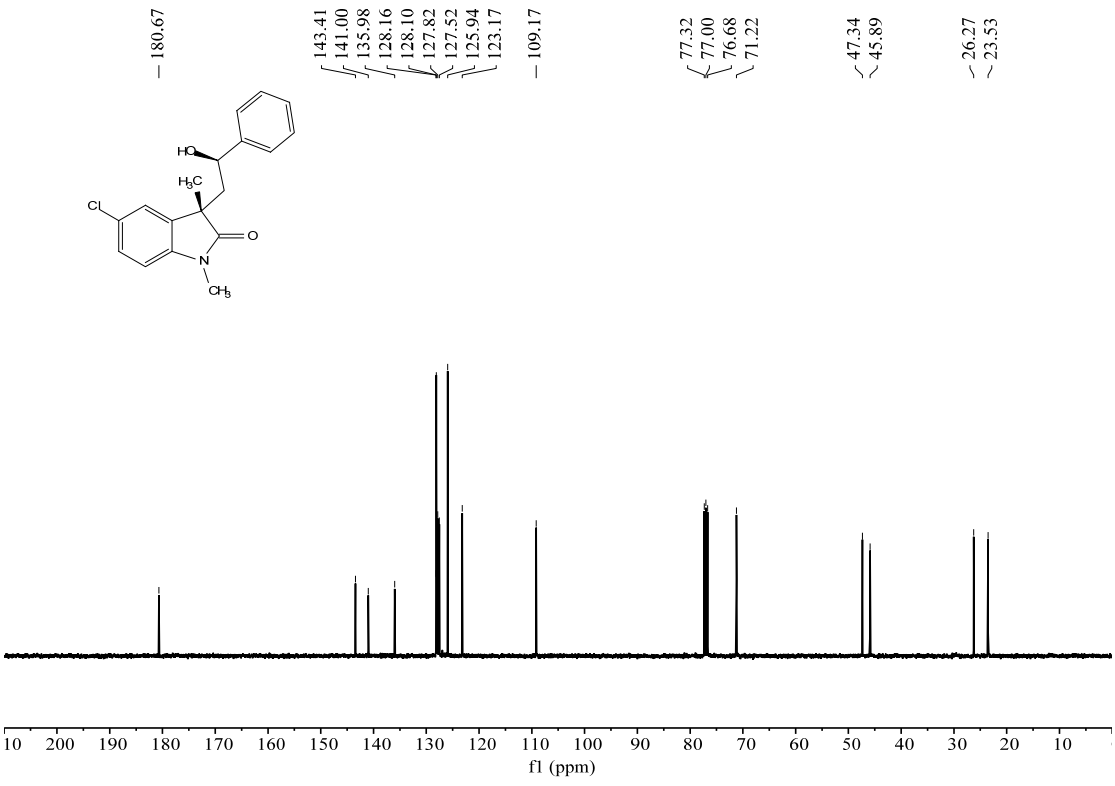
^{19}F NMR spectra of 17b (376 MHz, $CDCl_3$)



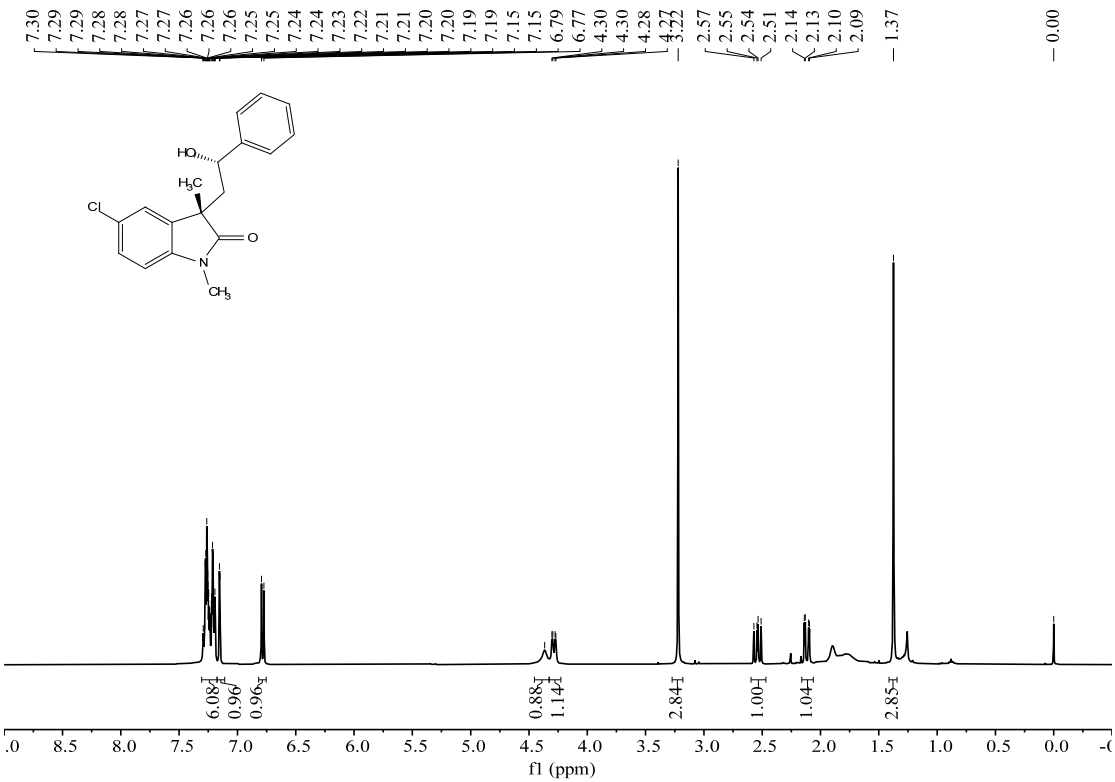
^{1}H NMR spectra of 18a (400 MHz, $CDCl_3$)



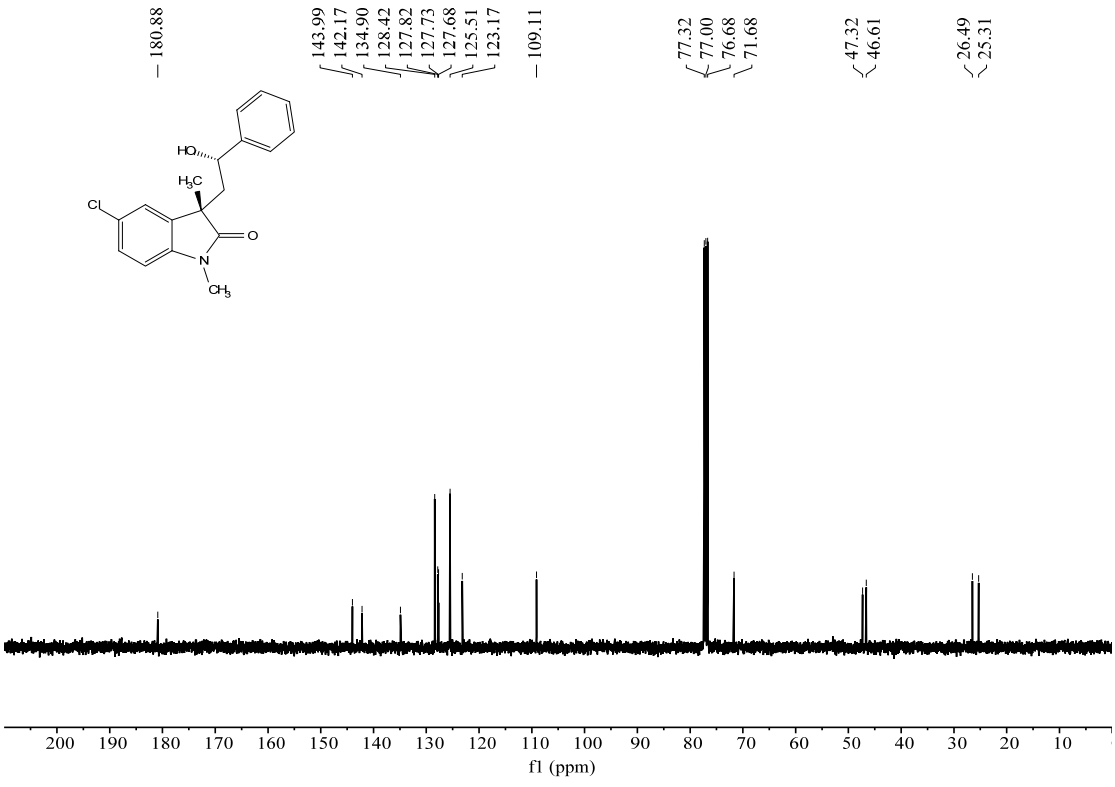
^{13}C NMR spectra of 18a (100 MHz, $CDCl_3$)



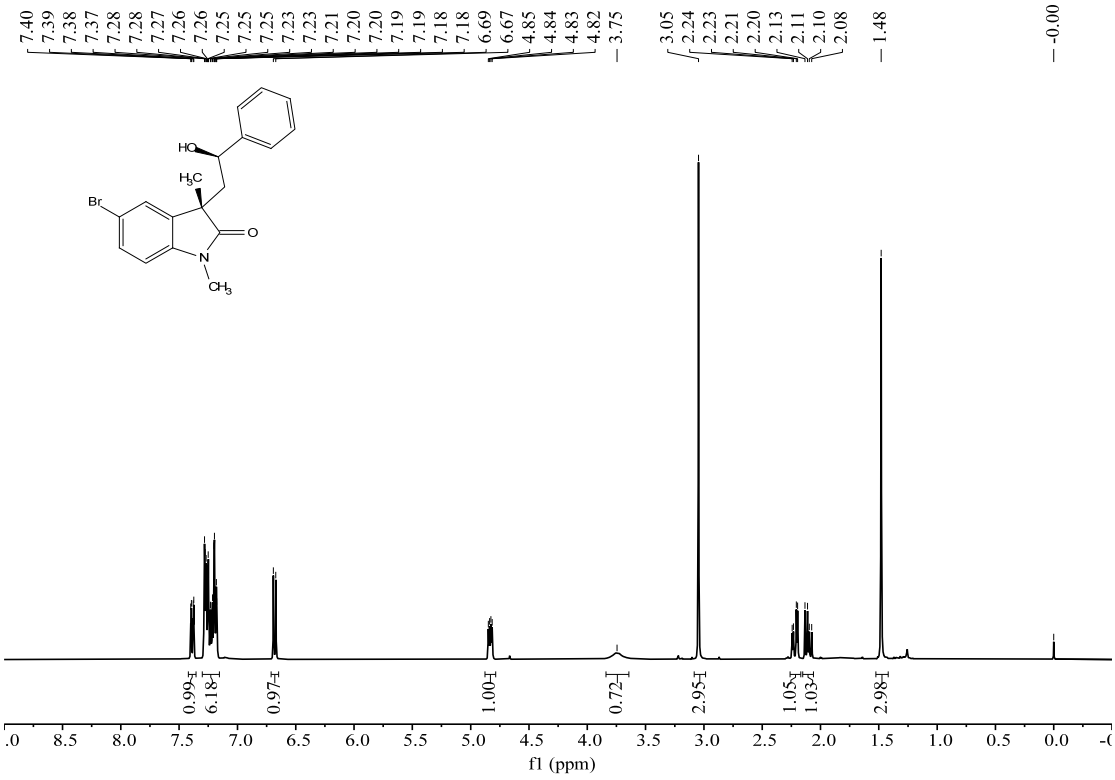
^{1}H NMR spectra of 18b (400 MHz, $CDCl_3$)



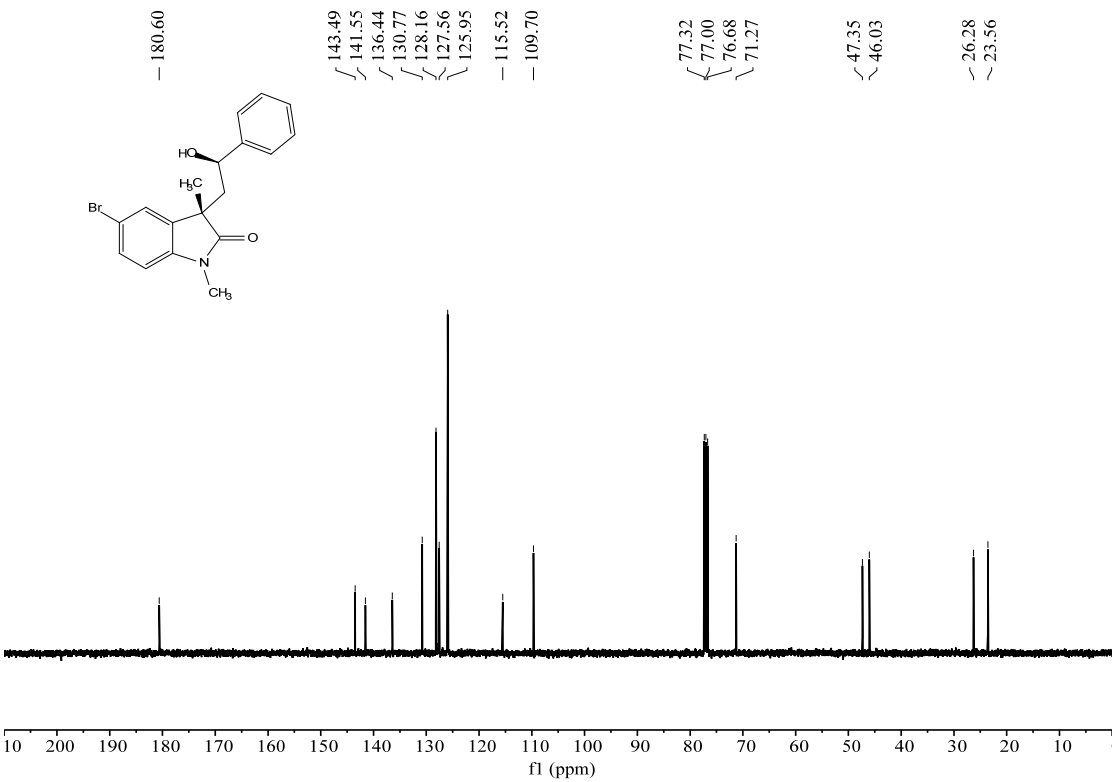
^{13}C NMR spectra of 18b (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 19a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 19a (100 MHz, $CDCl_3$)



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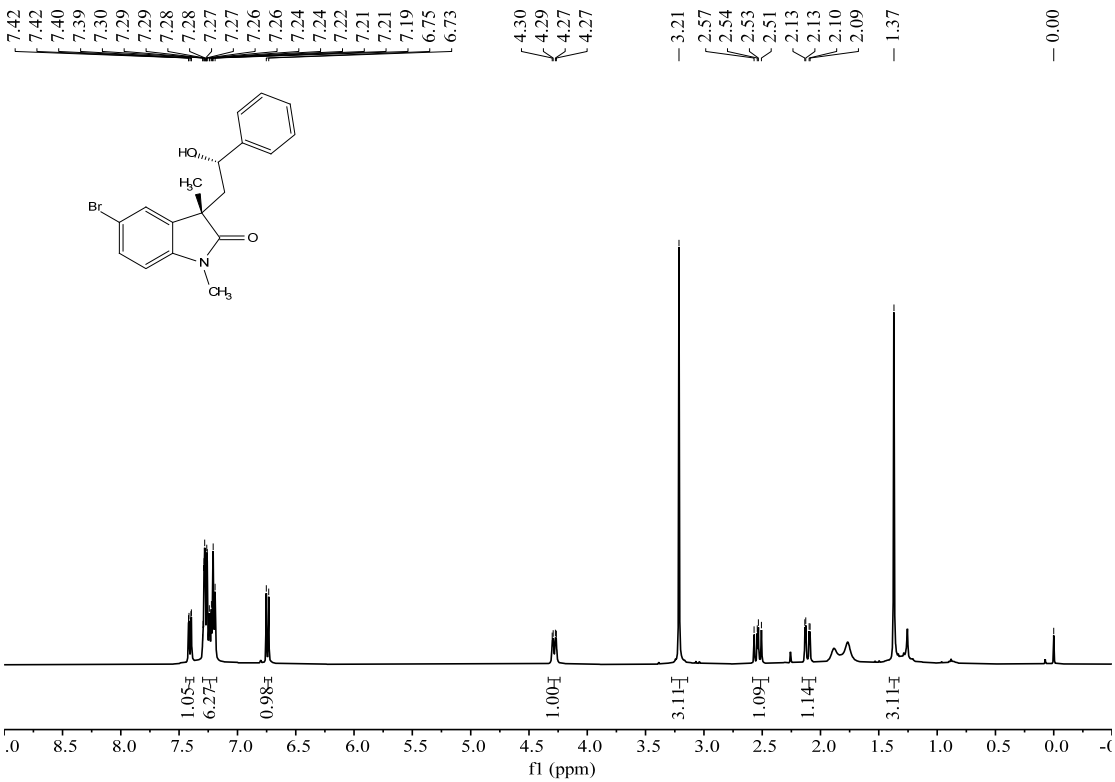

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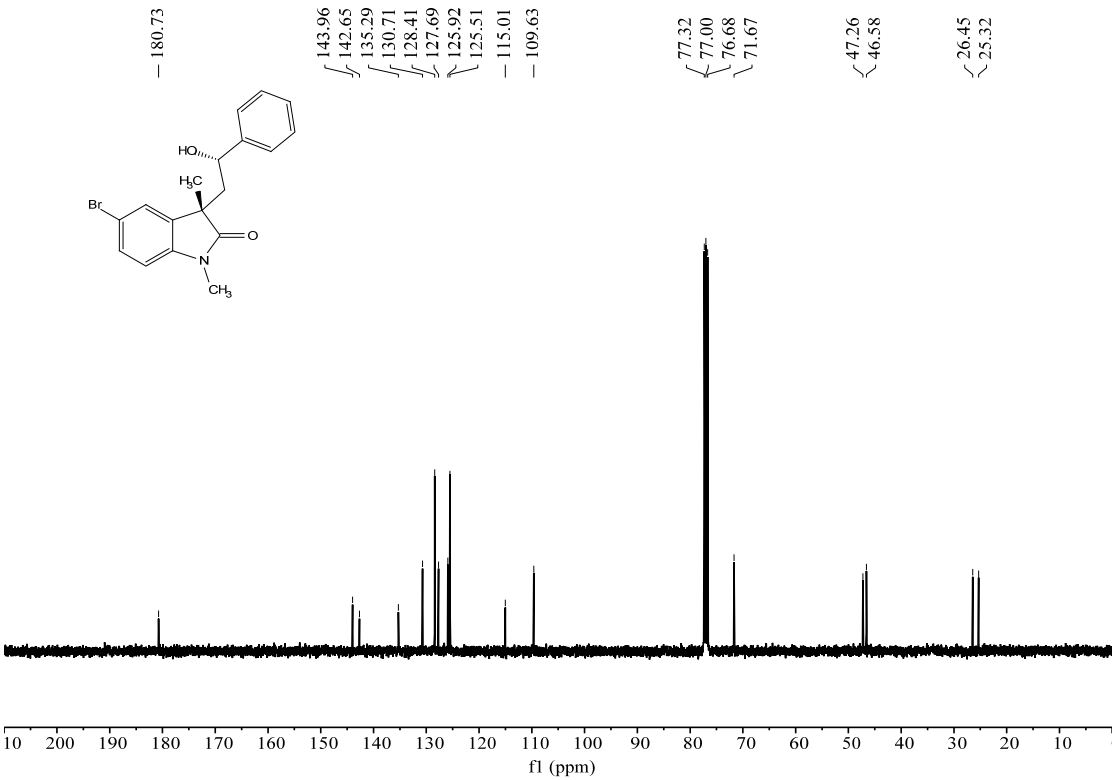
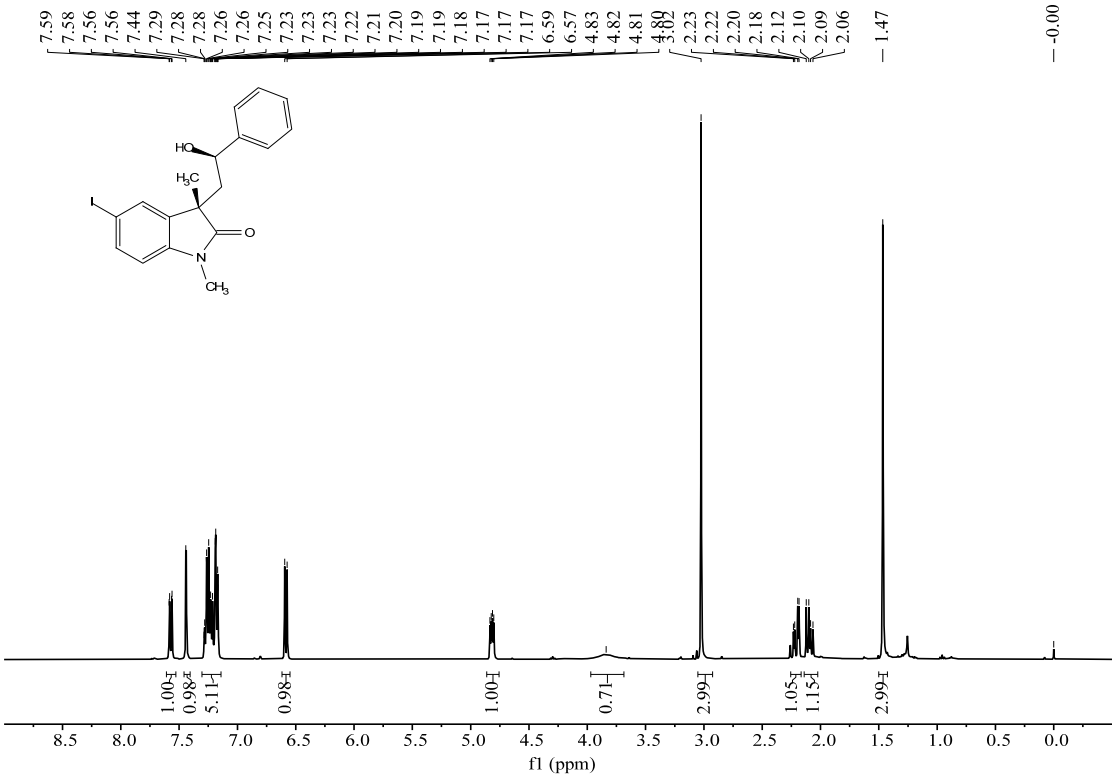
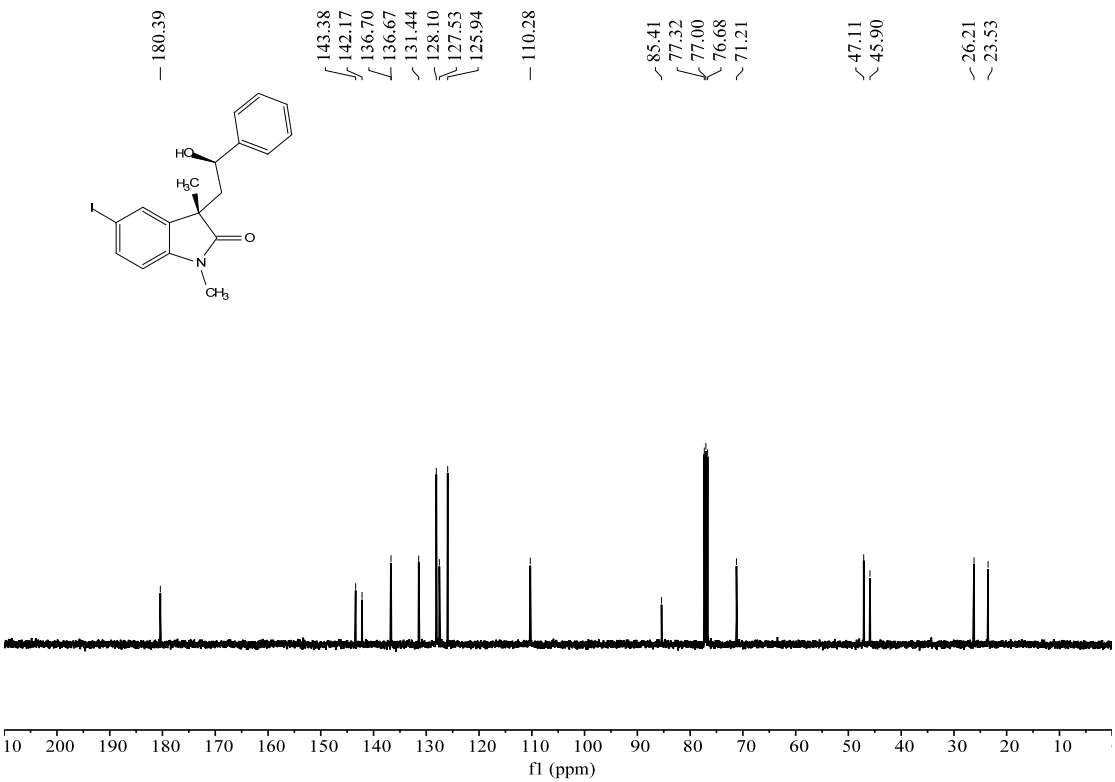


^{1}H NMR spectra of 20a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 20a (100 MHz, $CDCl_3$)



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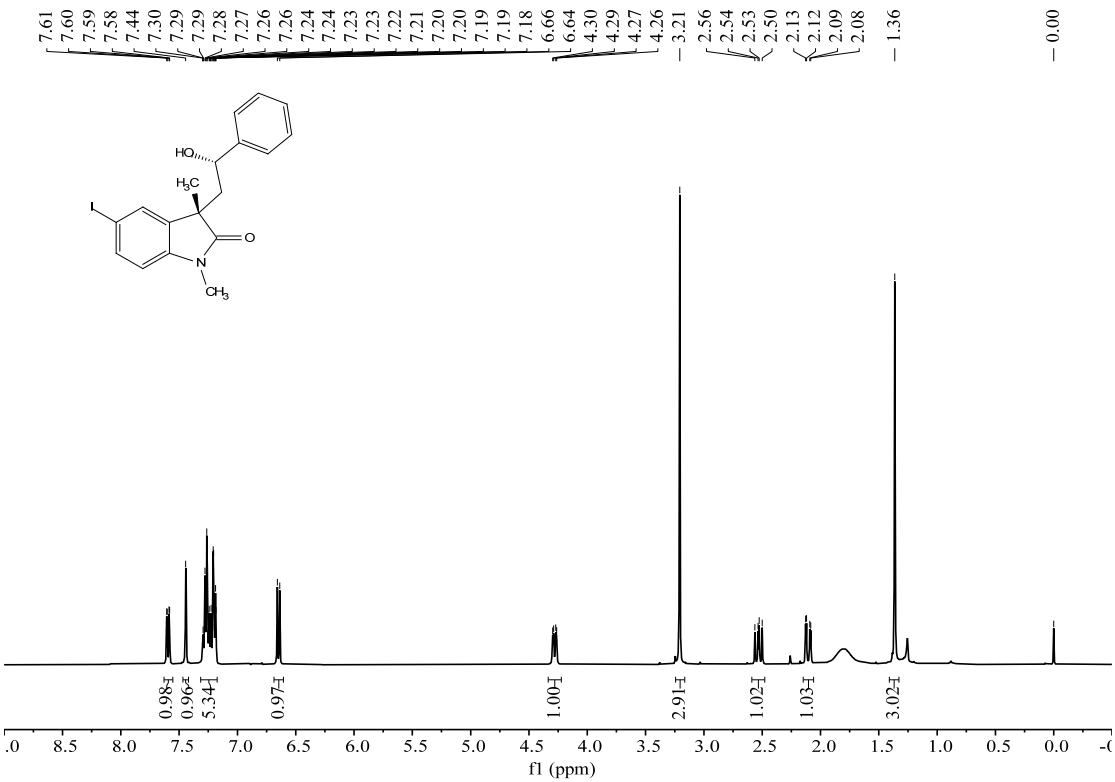

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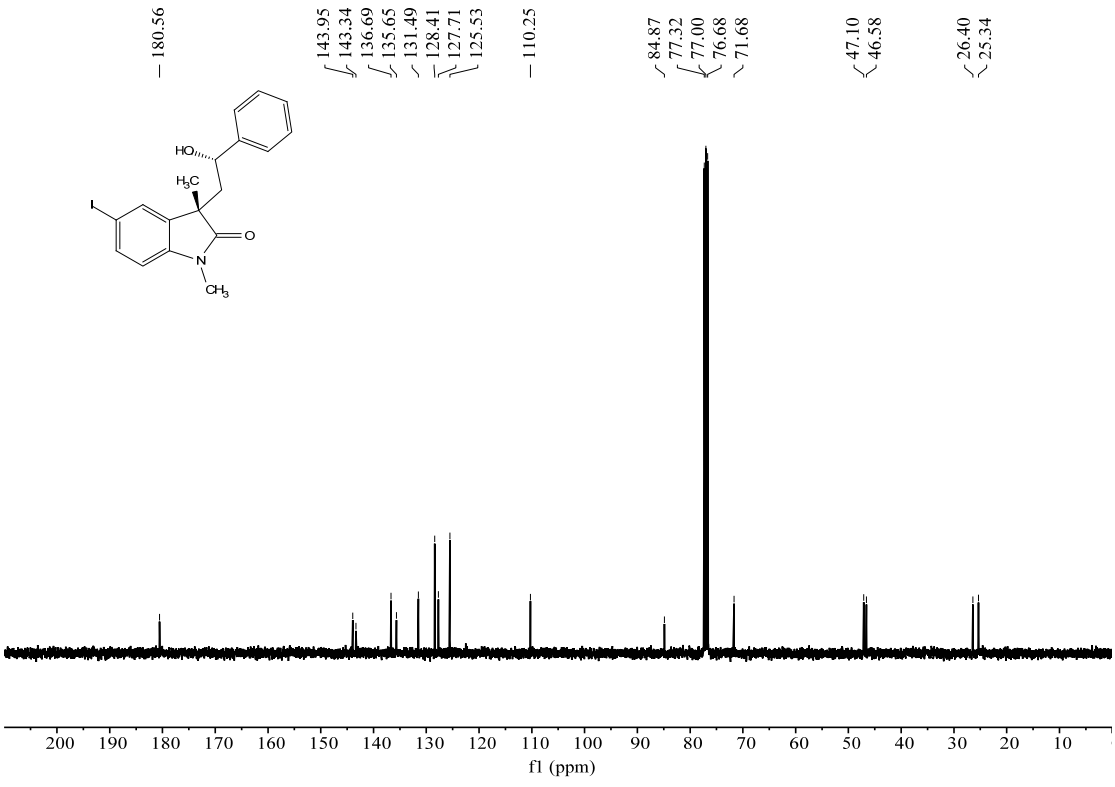
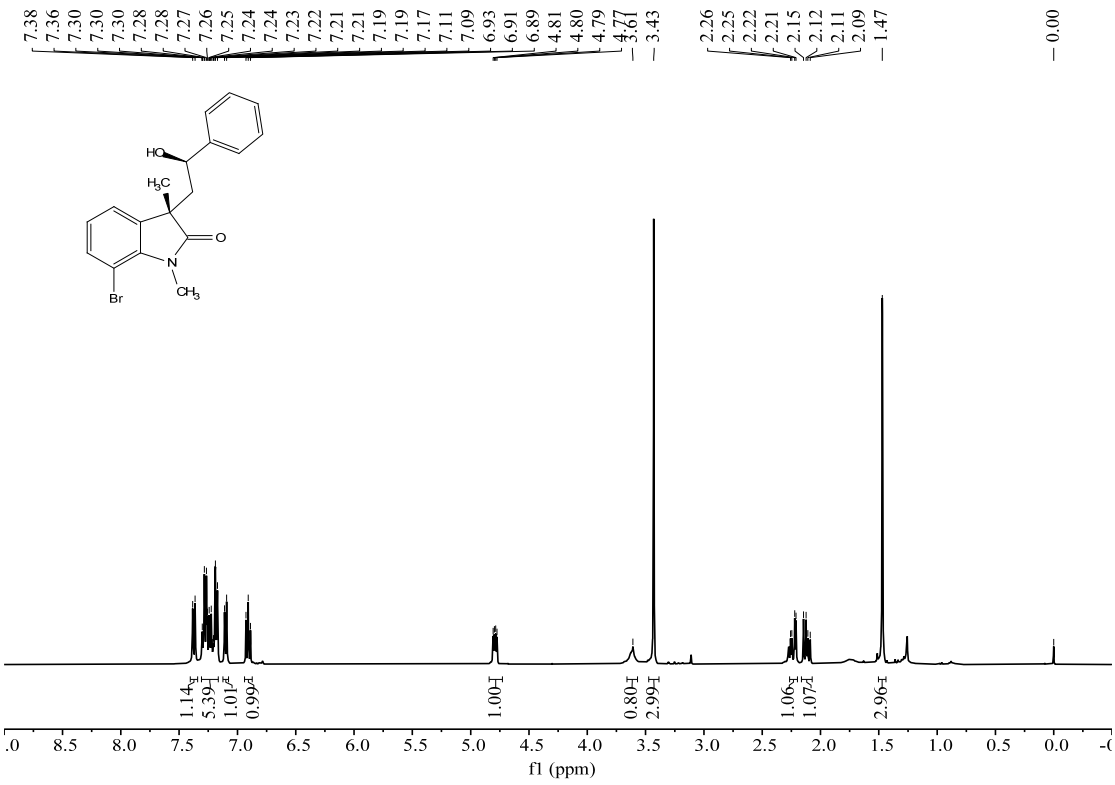
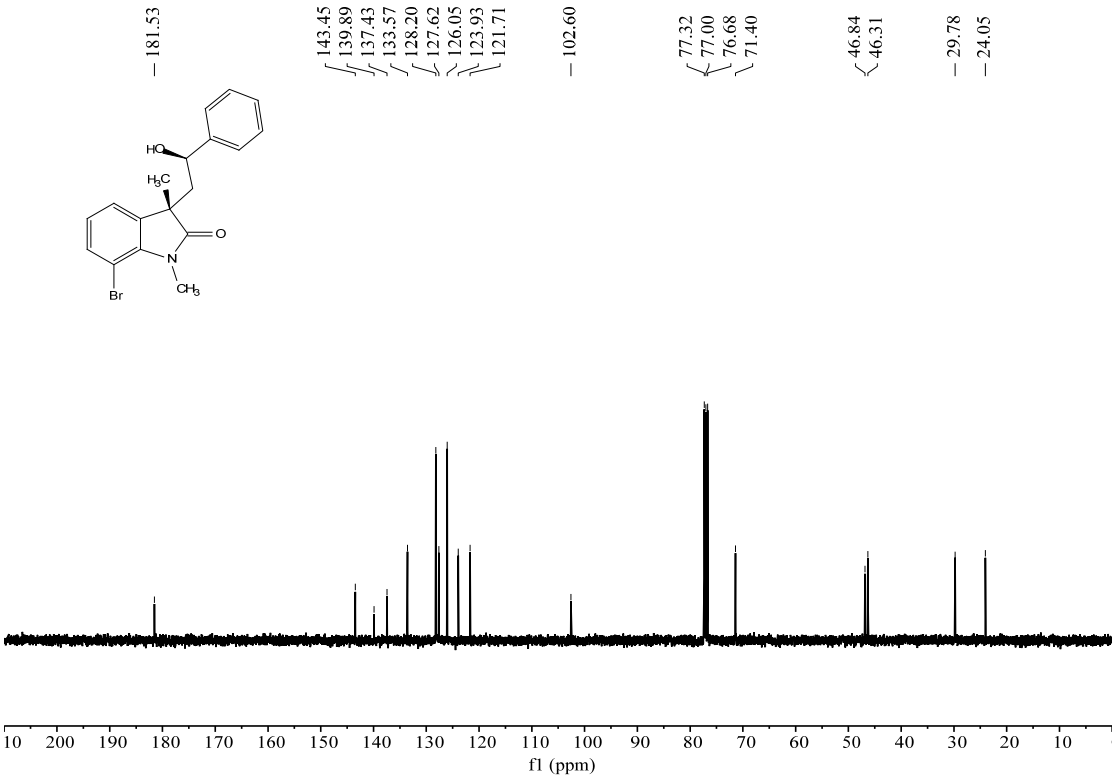


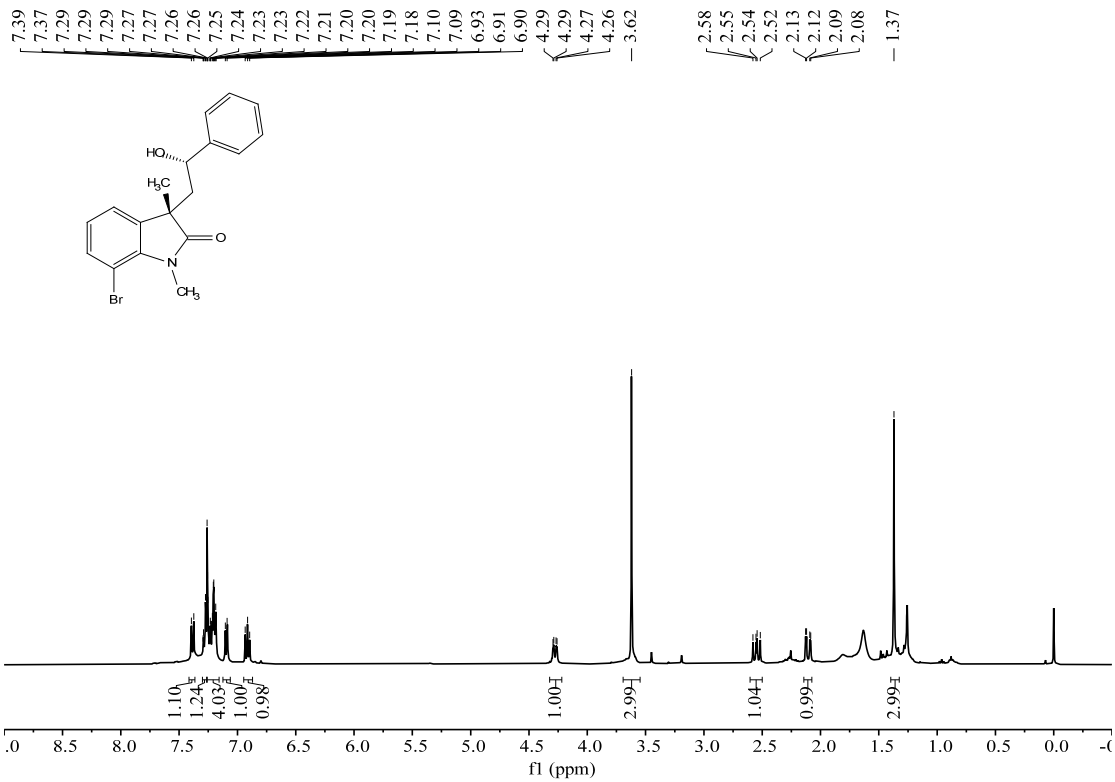
^{1}H NMR spectra of 21a (400 MHz, $CDCl_3$)



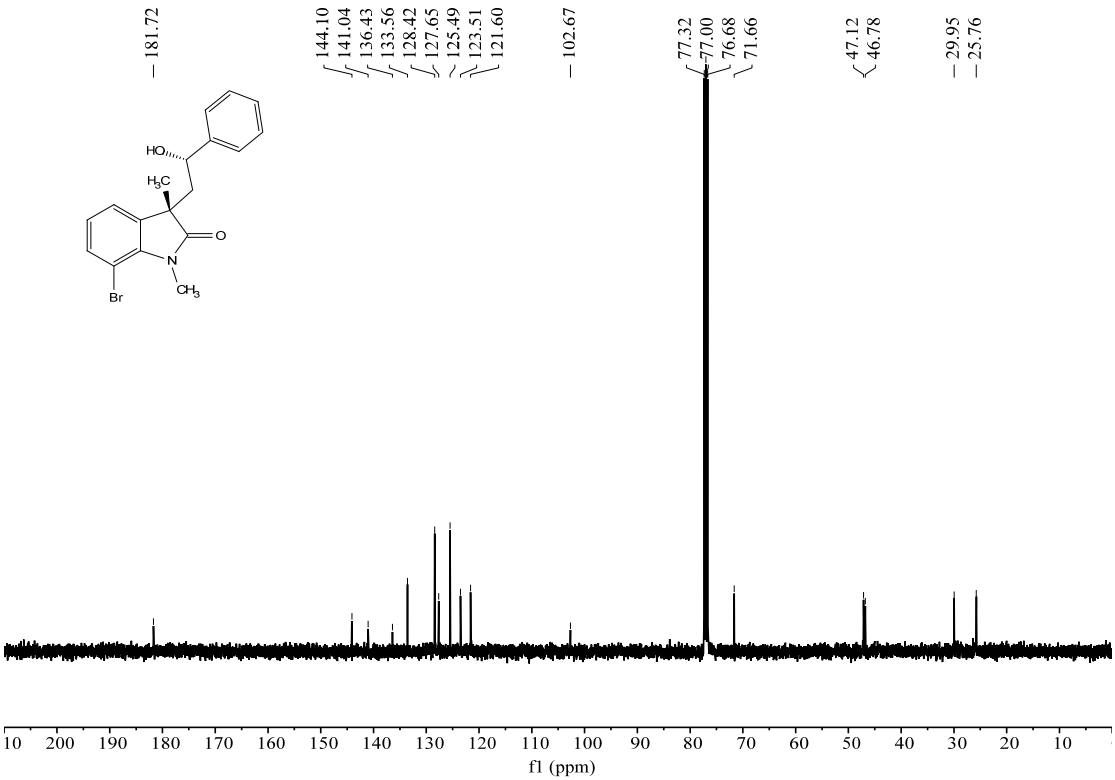
^{13}C NMR spectra of 21a (100 MHz, $CDCl_3$)



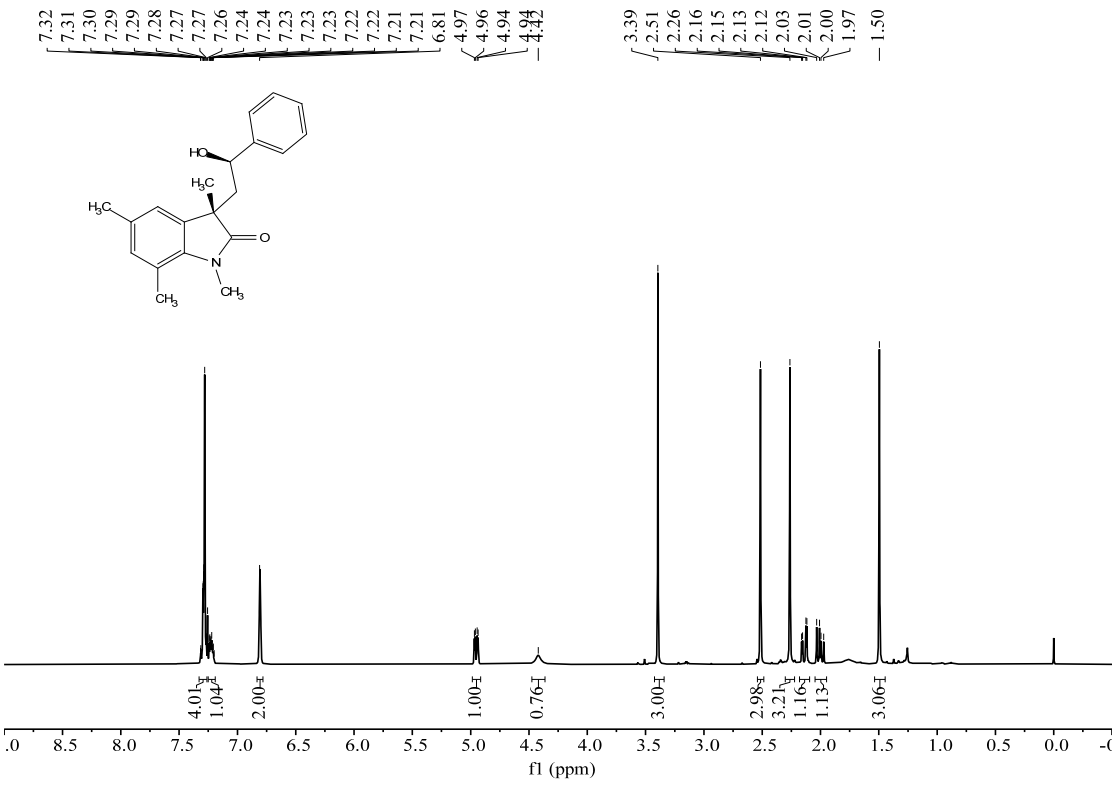
^{1}H NMR spectra of 21b (400 MHz, $CDCl_3$)



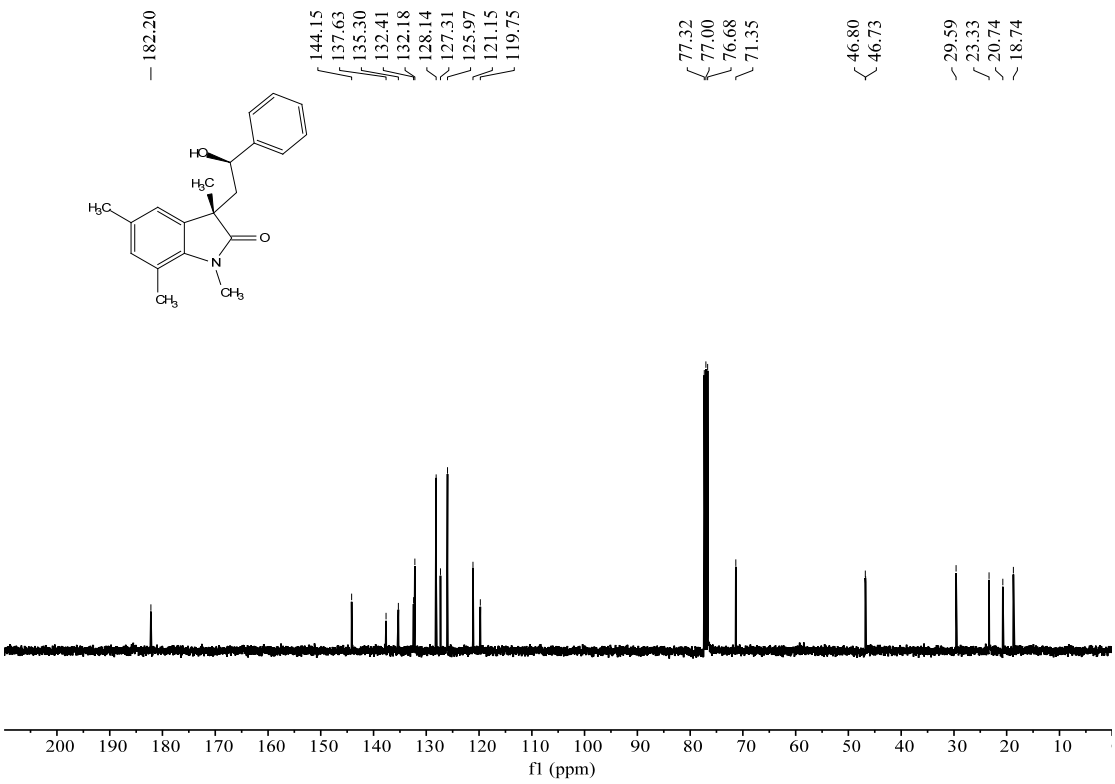
^{13}C NMR spectra of 21b (100 MHz, $CDCl_3$)



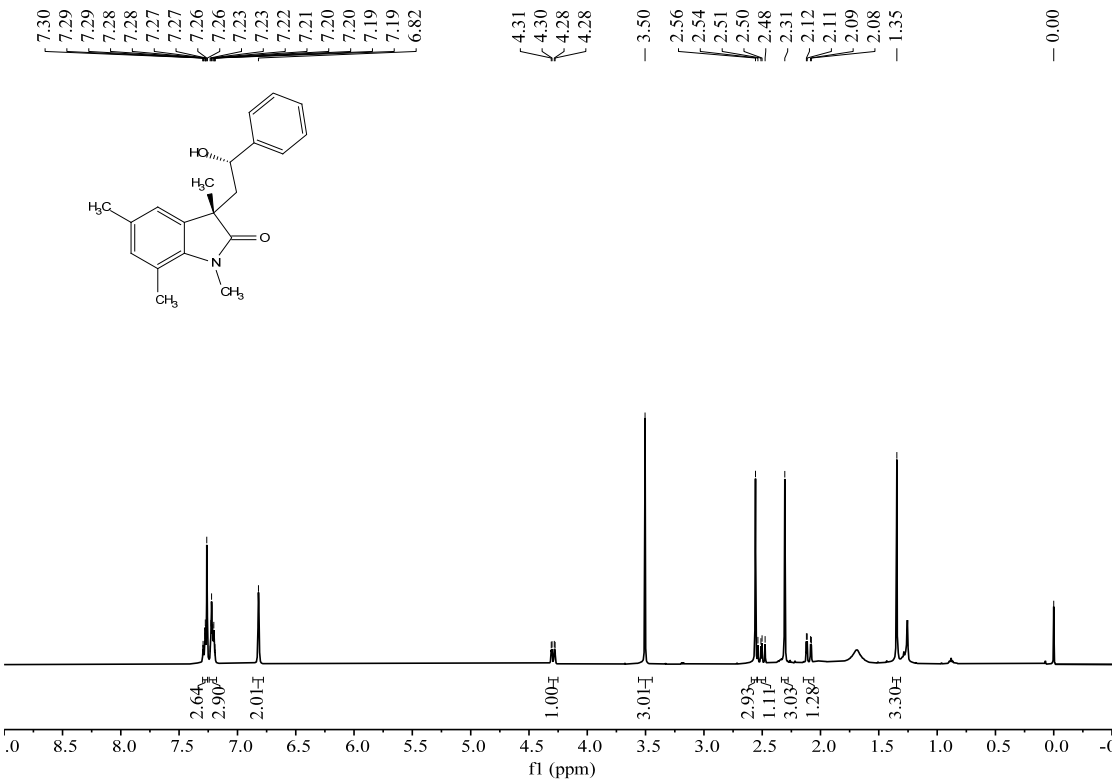
^{1}H NMR spectra of 22a (400 MHz, $CDCl_3$)



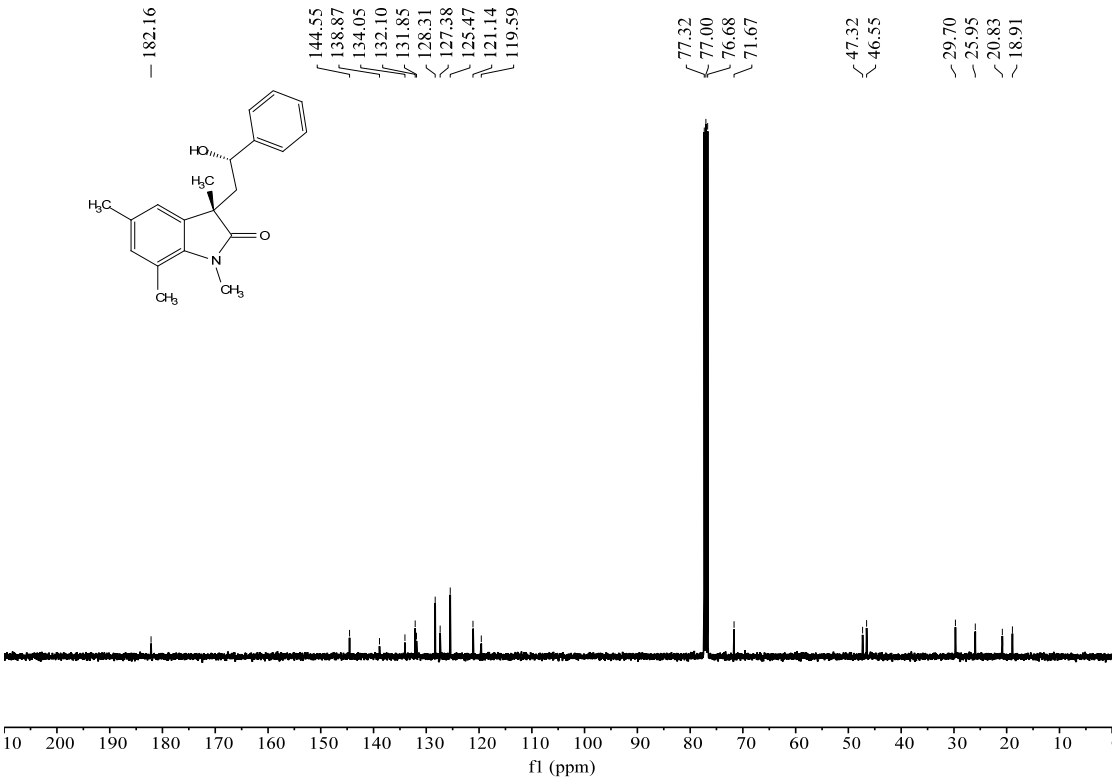
^{13}C NMR spectra of 22a (100 MHz, $CDCl_3$)



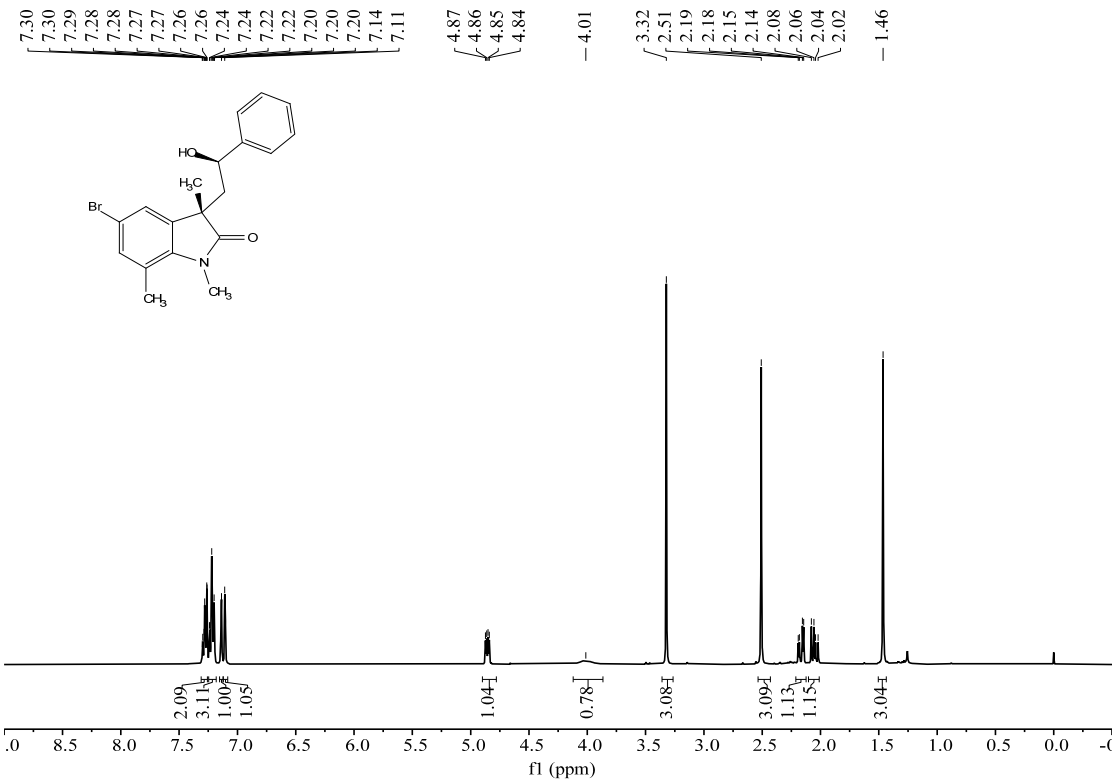
^{1}H NMR spectra of 22b (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 22b (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 23a (400 MHz, $CDCl_3$)



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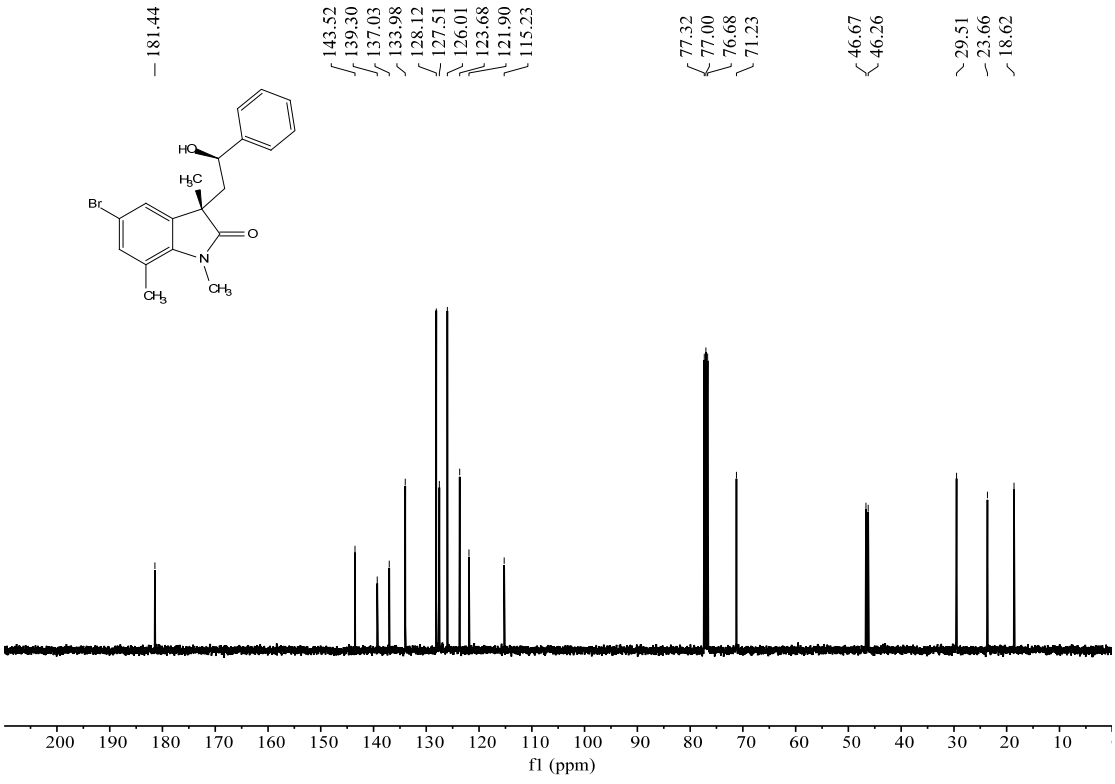

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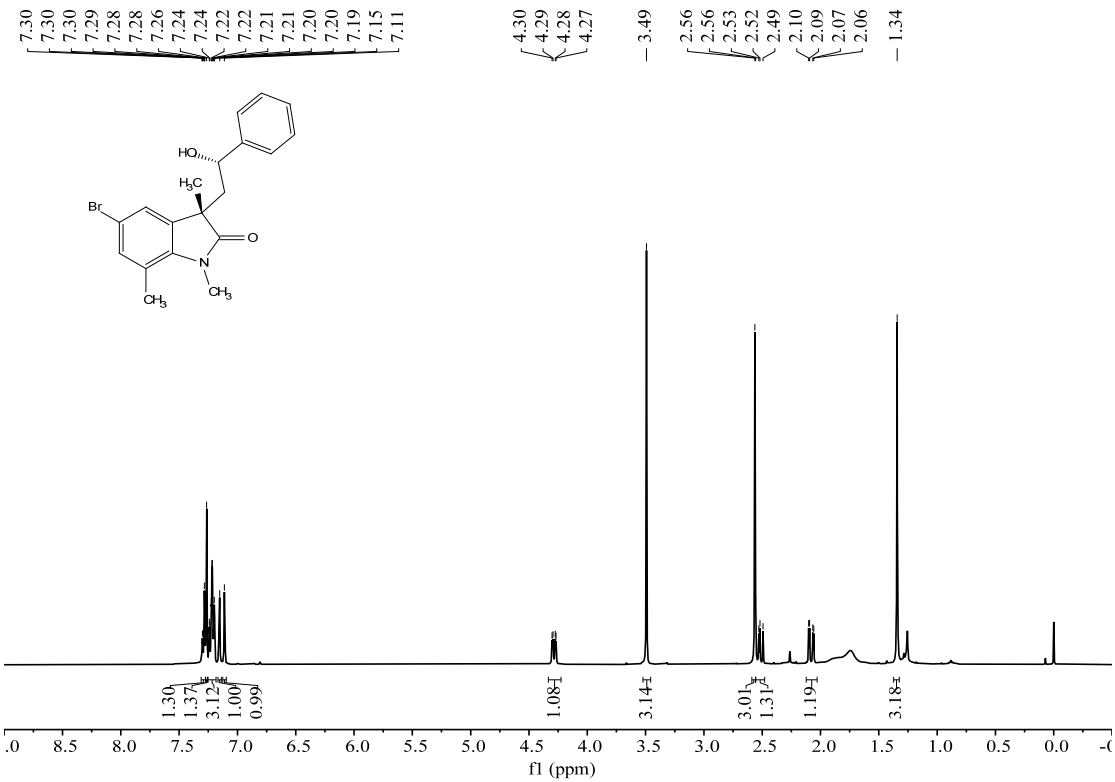
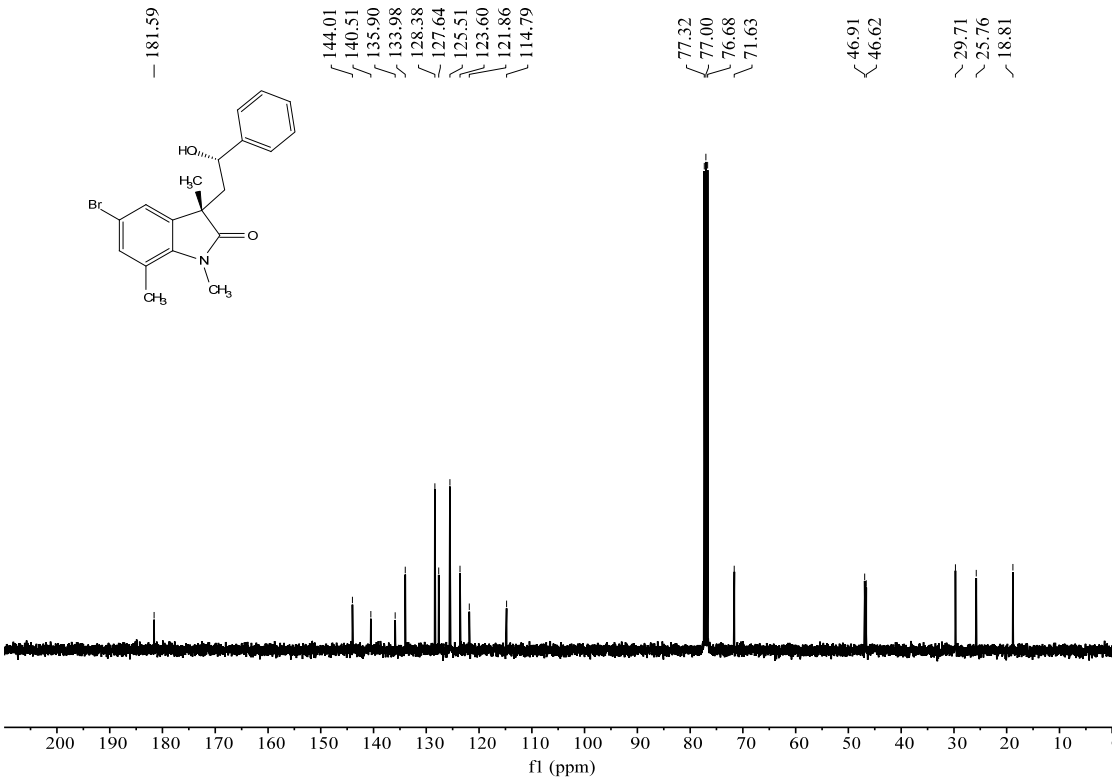
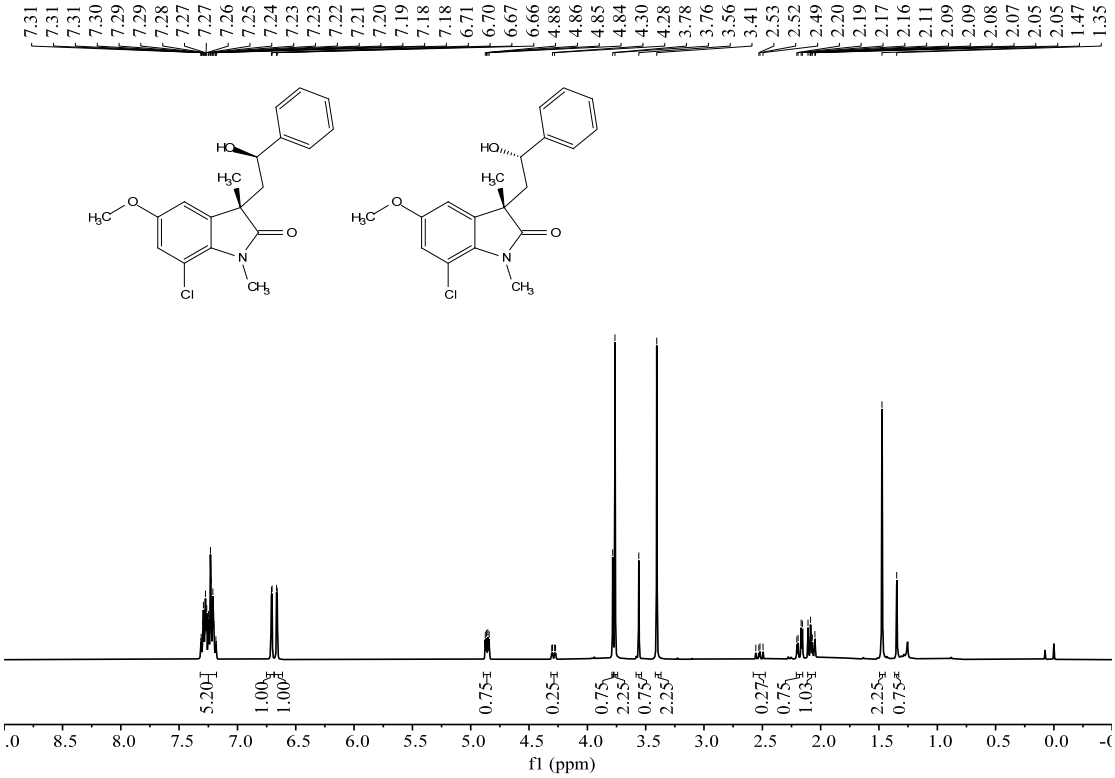


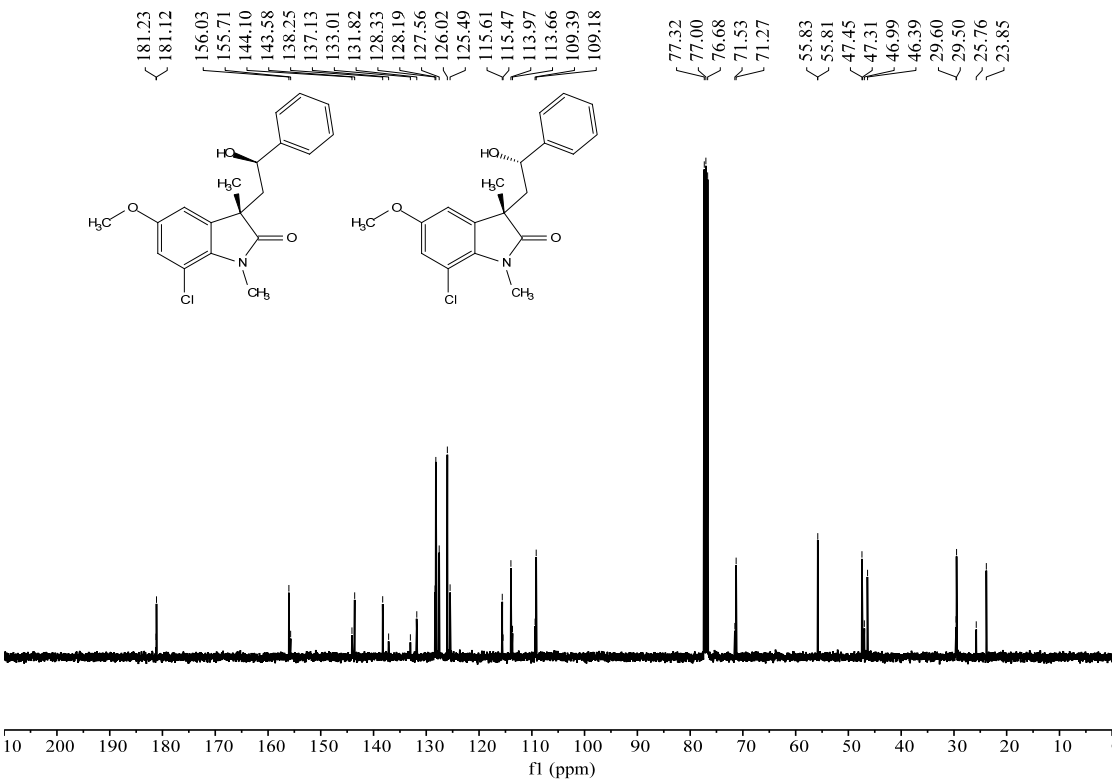
^{13}C NMR spectra of 23b (100 MHz, $CDCl_3$)



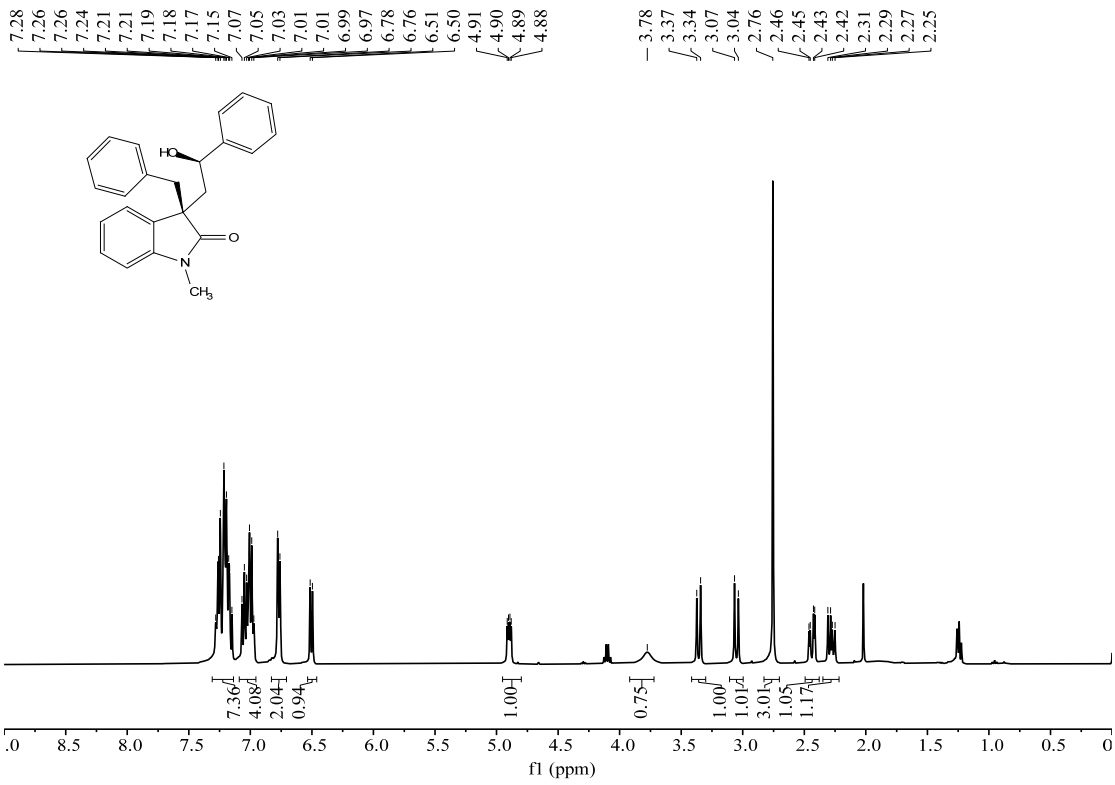
^{1}H NMR spectra of 24ab (400 MHz, $CDCl_3$)



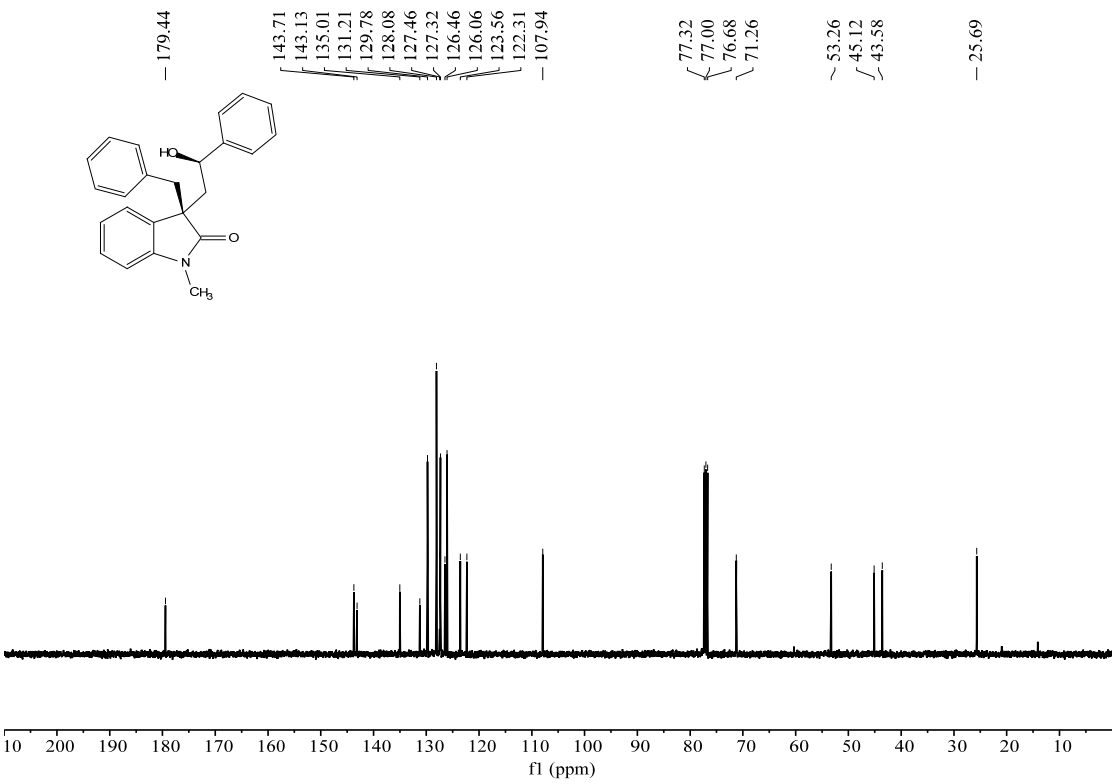
^{13}C NMR spectra of 24ab (100 MHz, $CDCl_3$)



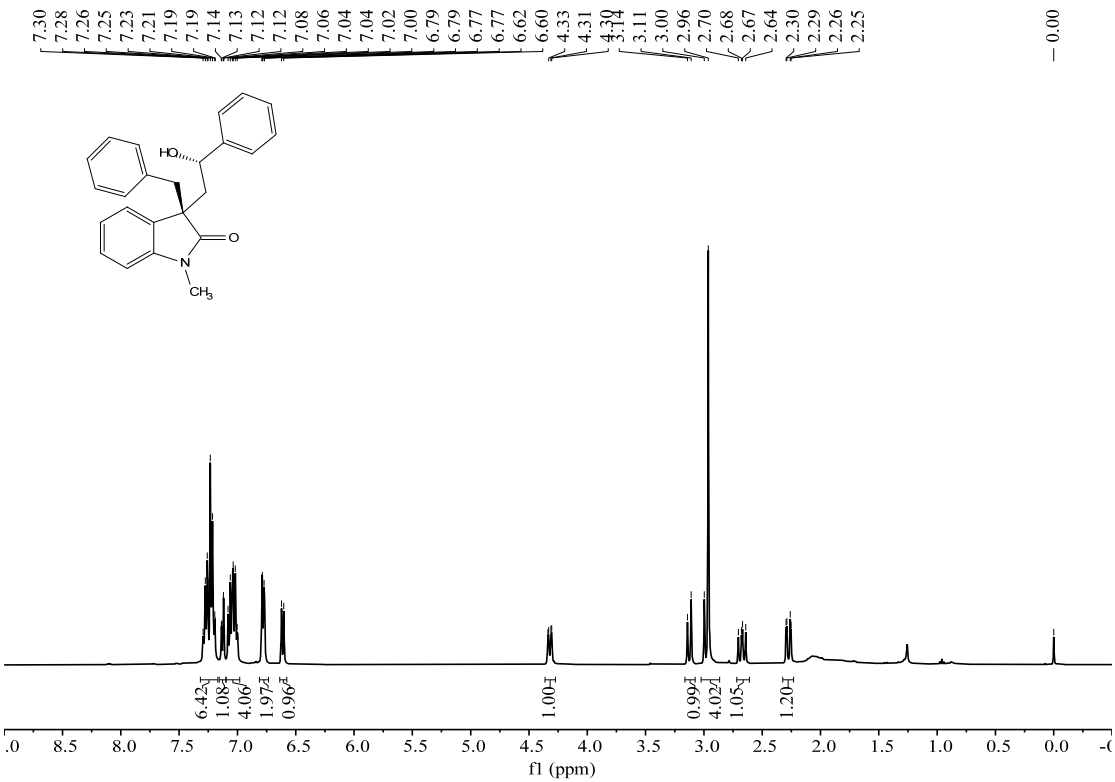
^{1}H NMR spectra of 25a (400 MHz, $CDCl_3$)



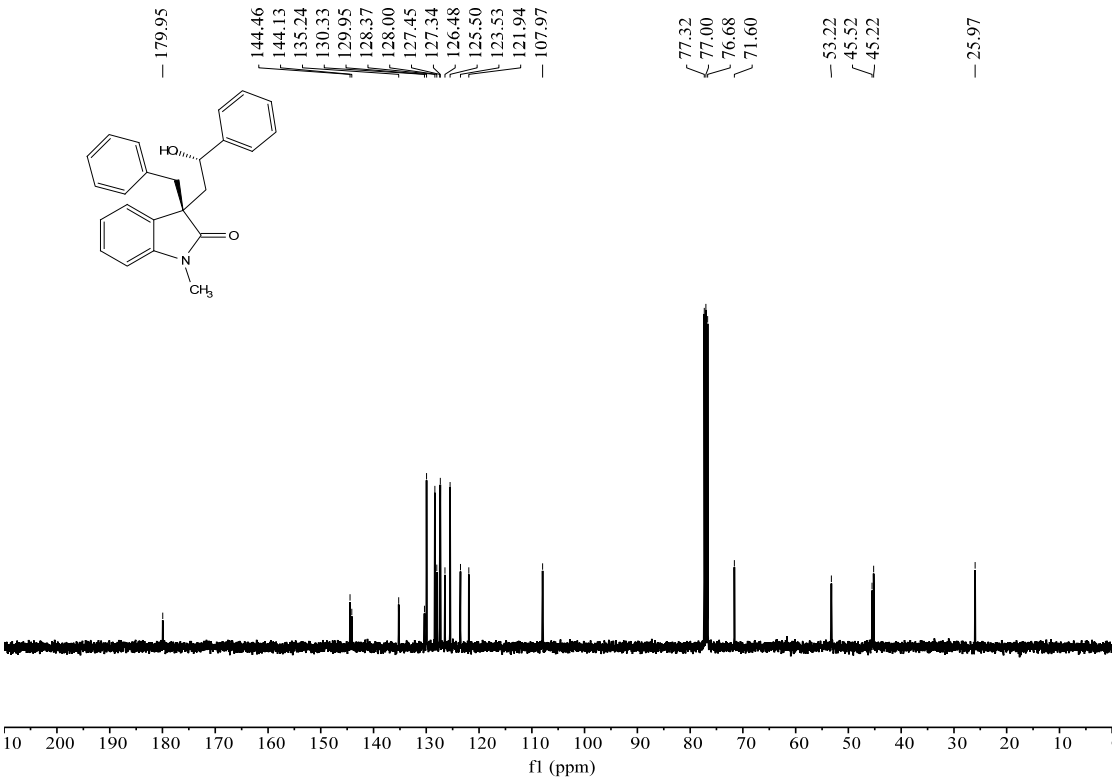
^{13}C NMR spectra of 25a (100 MHz, $CDCl_3$)



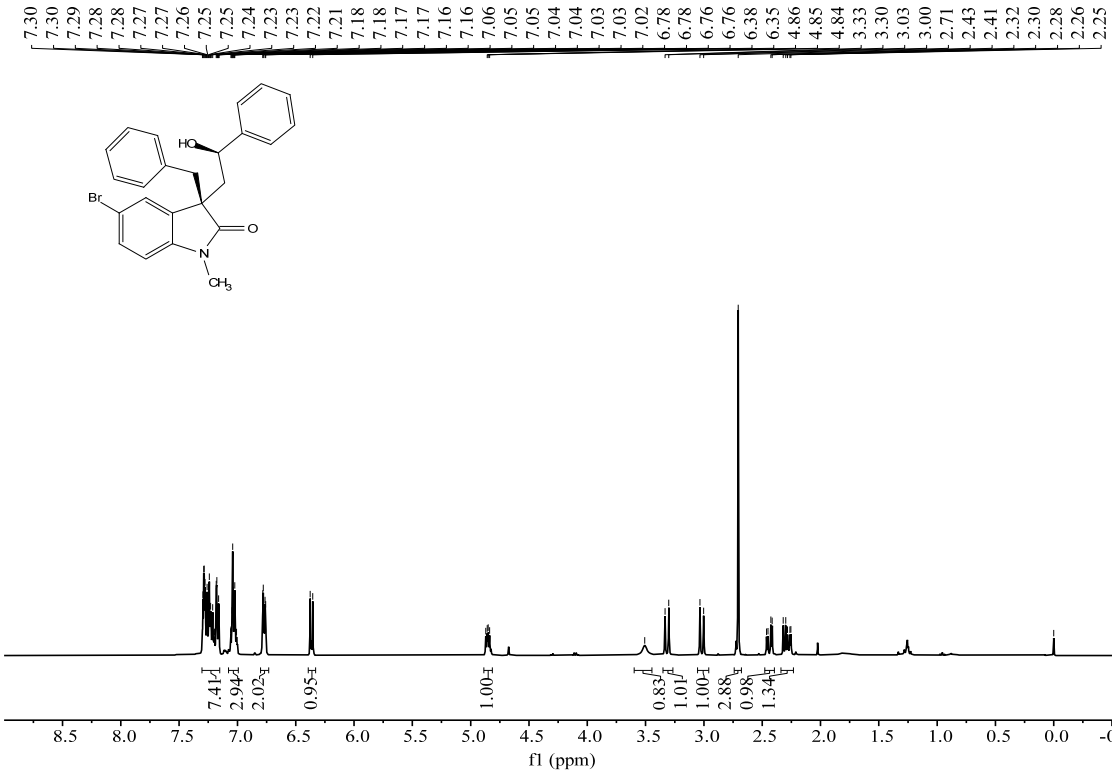
^{1}H NMR spectra of 25b (400 MHz, $CDCl_3$)



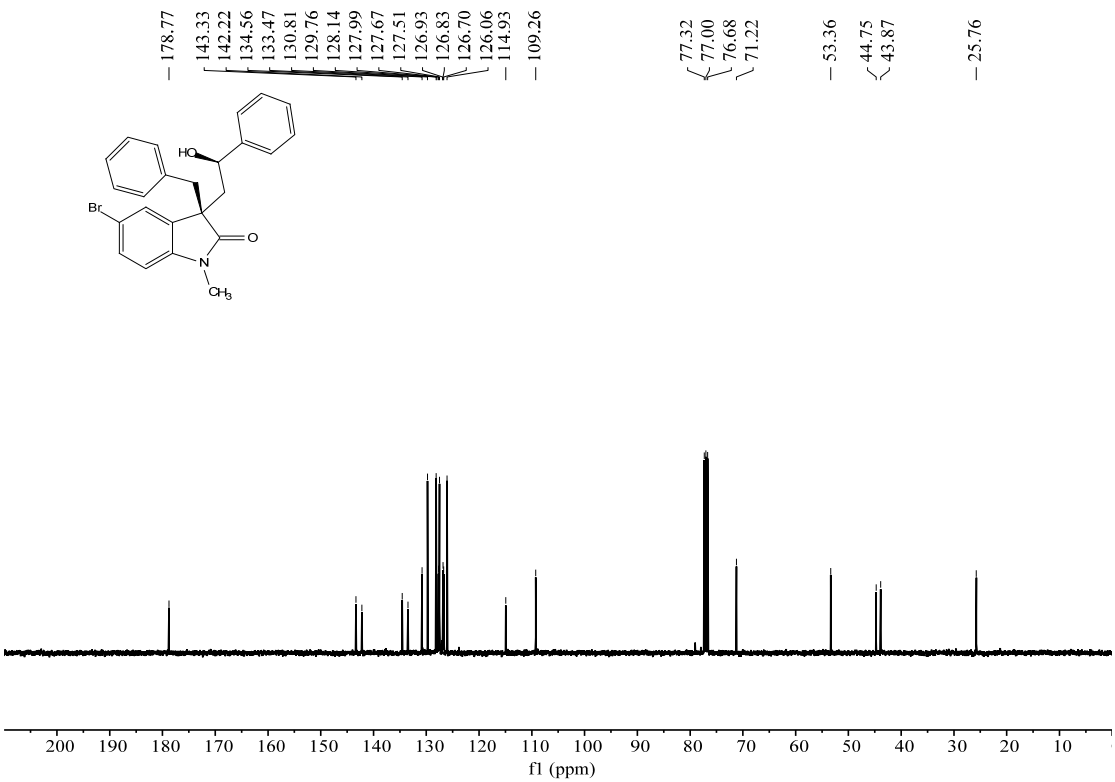
^{13}C NMR spectra of 25b (100 MHz, $CDCl_3$)



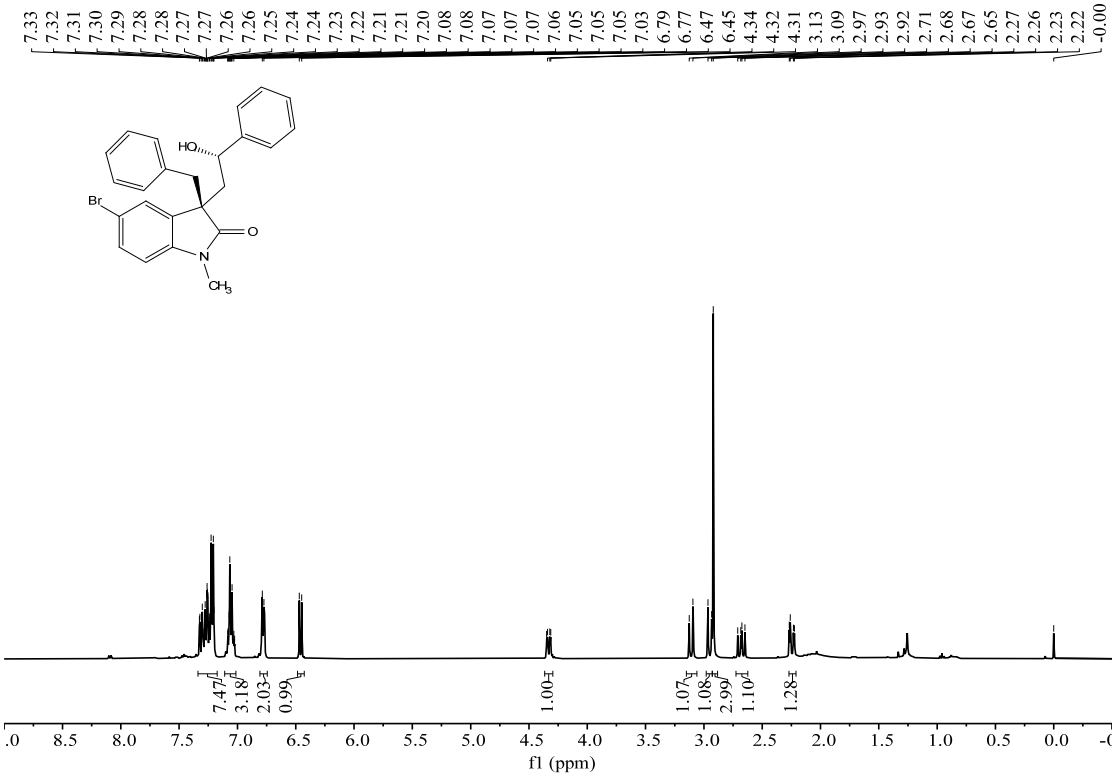
^{1}H NMR spectra of 26a (400 MHz, $CDCl_3$)



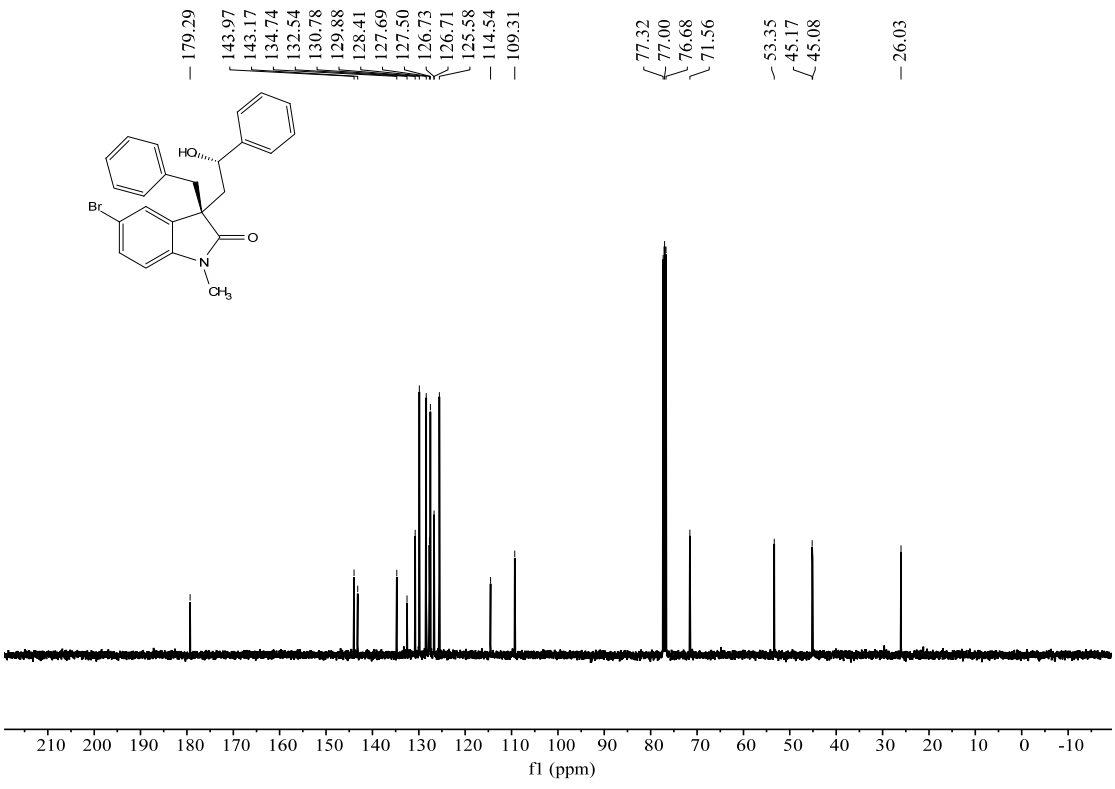
^{13}C NMR spectra of 26a (100 MHz, $CDCl_3$)



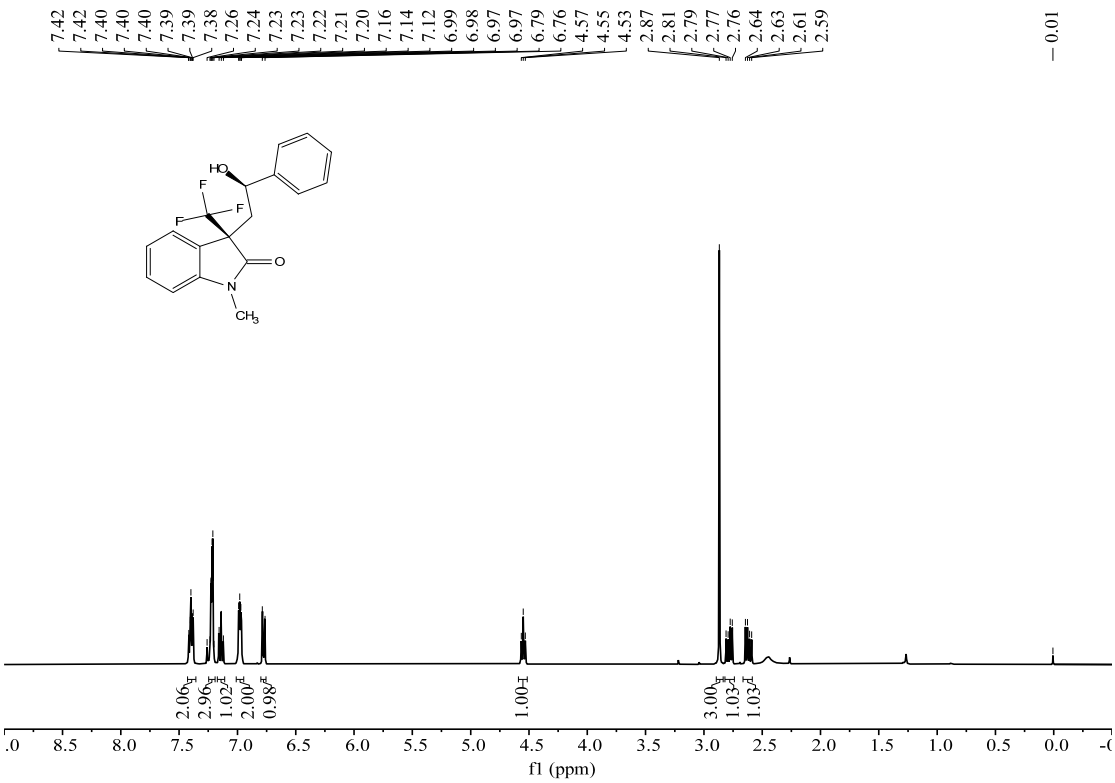
^{1}H NMR spectra of 26b (400 MHz, $CDCl_3$)



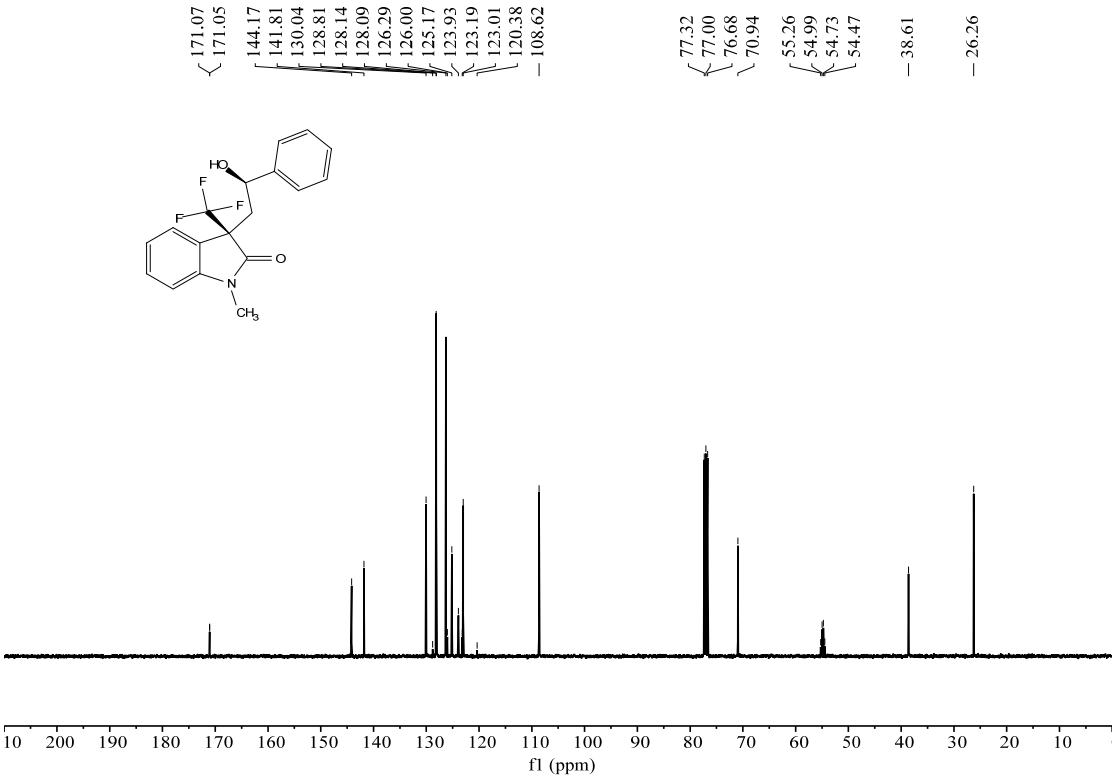
^{13}C NMR spectra of 26b (100 MHz, $CDCl_3$)



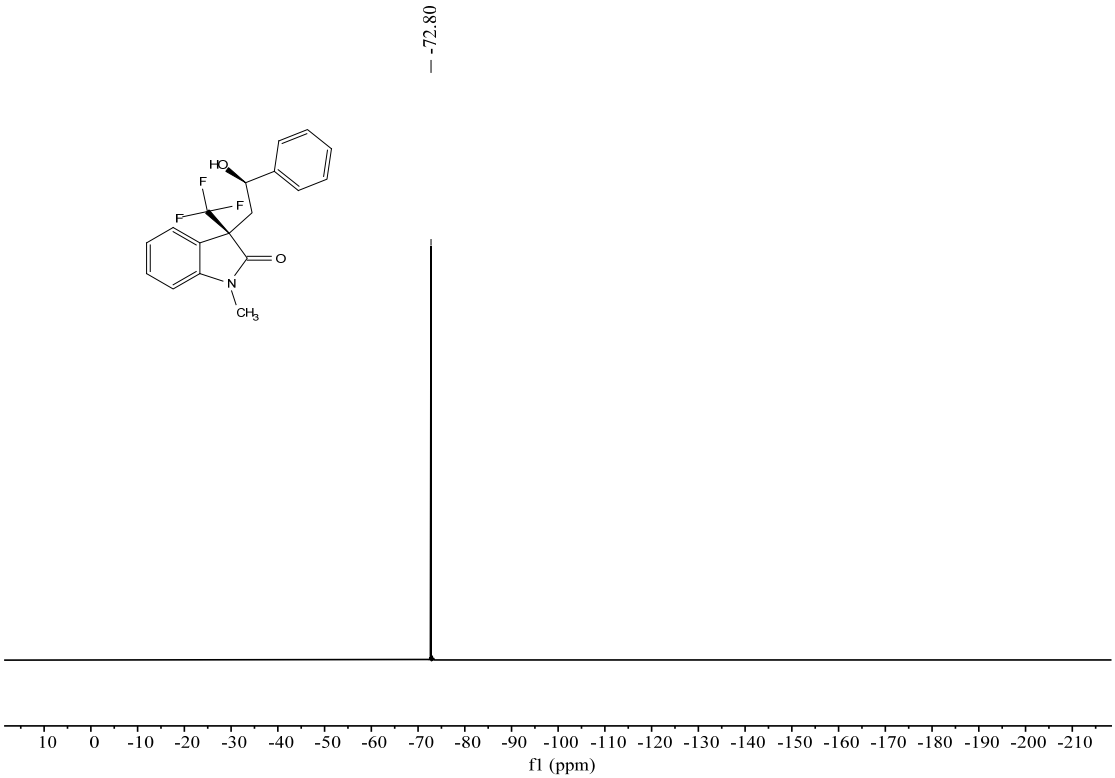
^{1}H NMR spectra of 27a (400 MHz, $CDCl_3$)



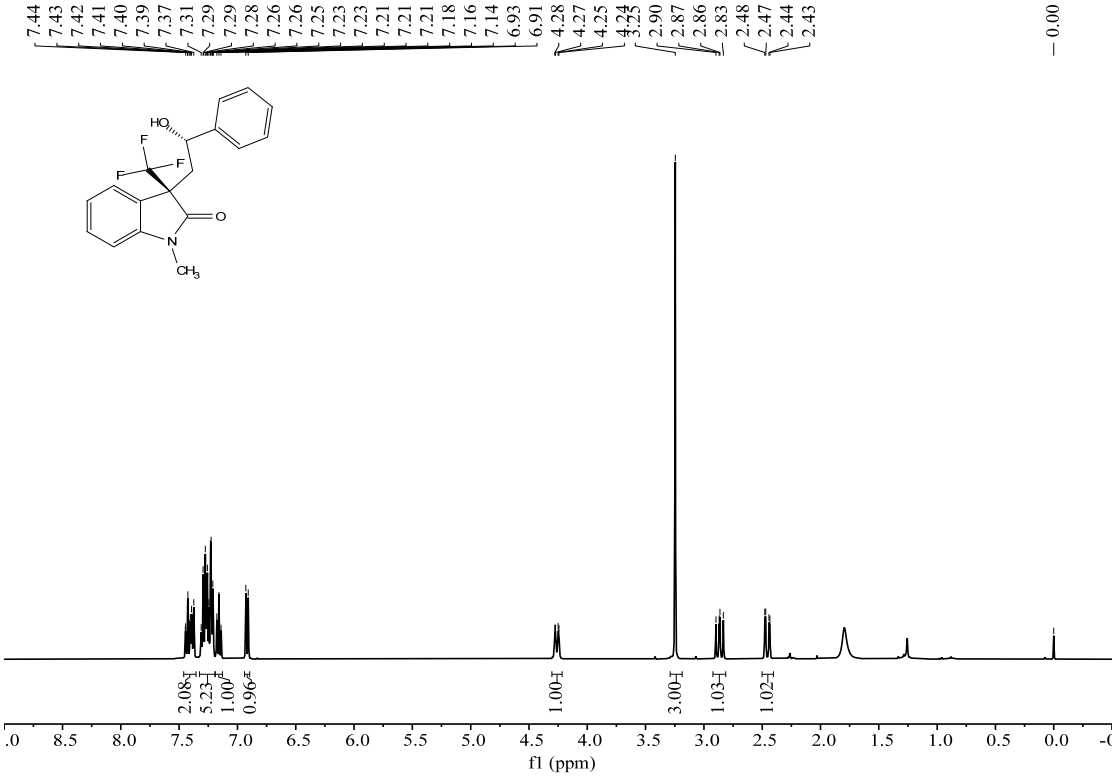
^{13}C NMR spectra of 27a (100 MHz, $CDCl_3$)



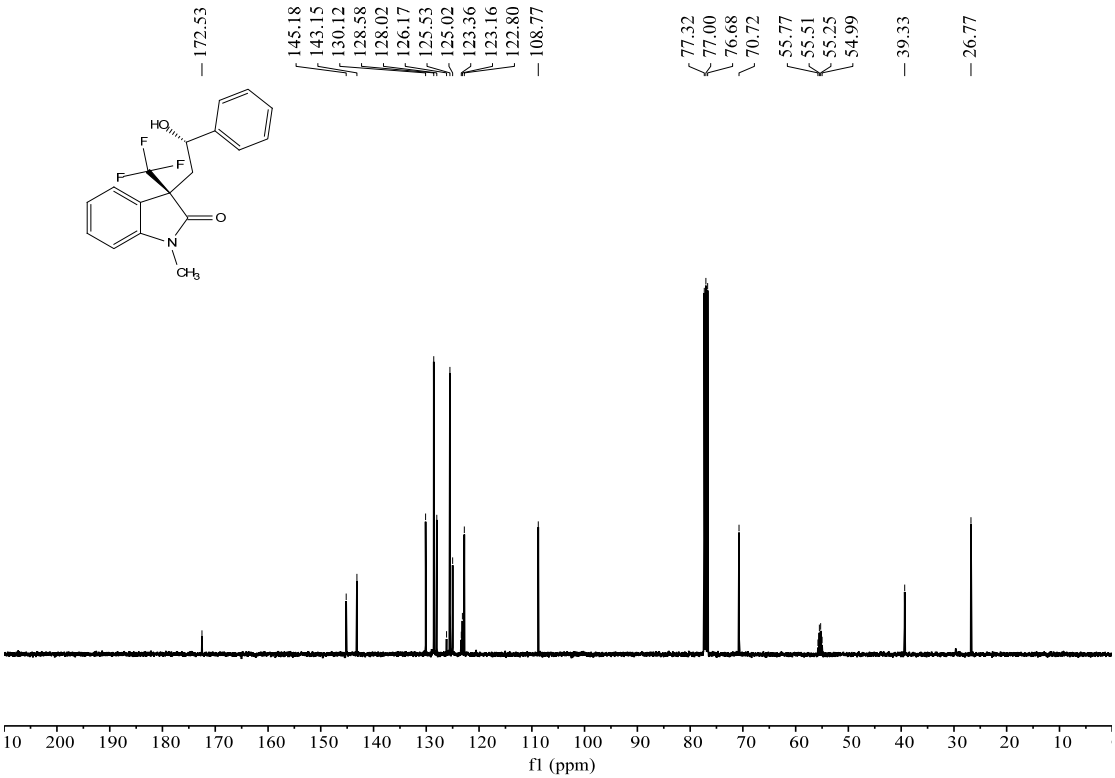
^{19}F NMR spectra of 27a (376 MHz, $CDCl_3$)



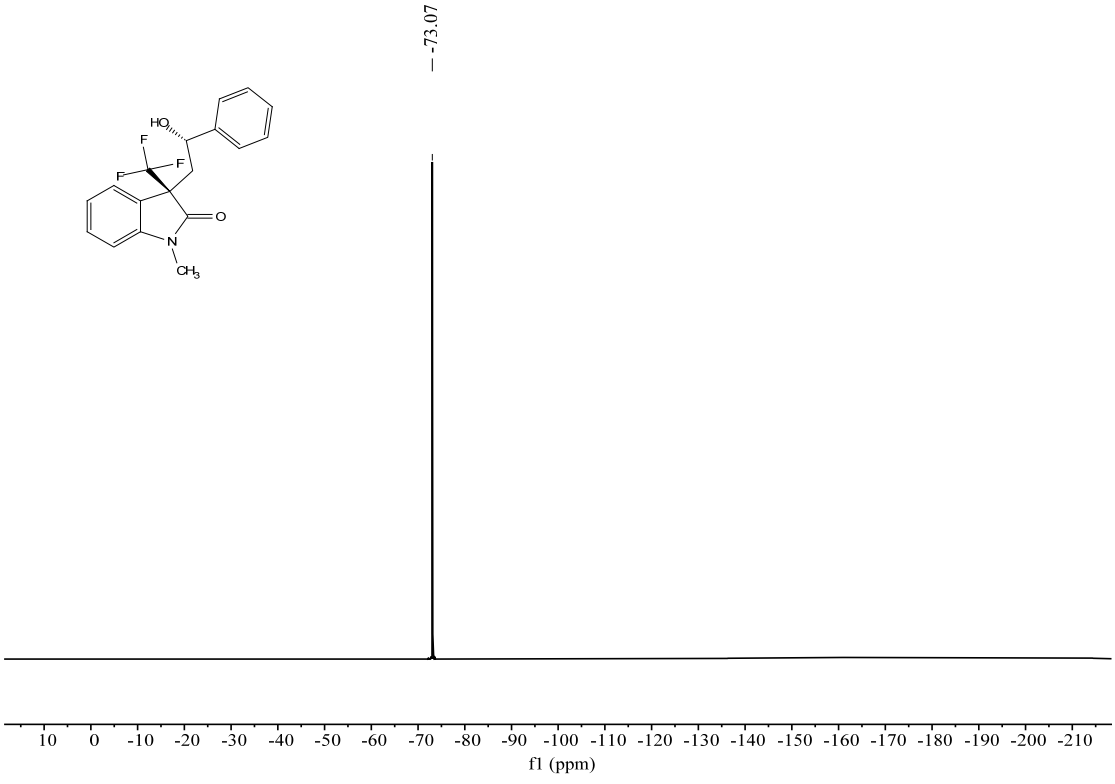
^{1}H NMR spectra of 27b (400 MHz, $CDCl_3$)



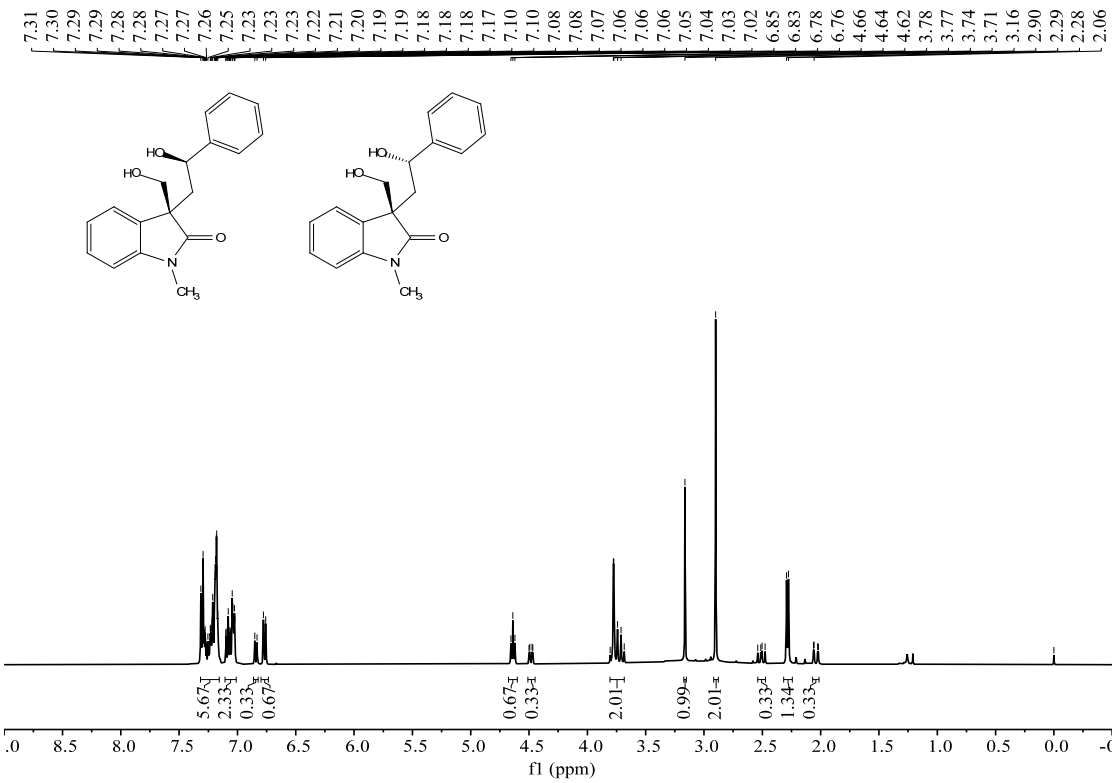
^{13}C NMR spectra of 27b (100 MHz, $CDCl_3$)



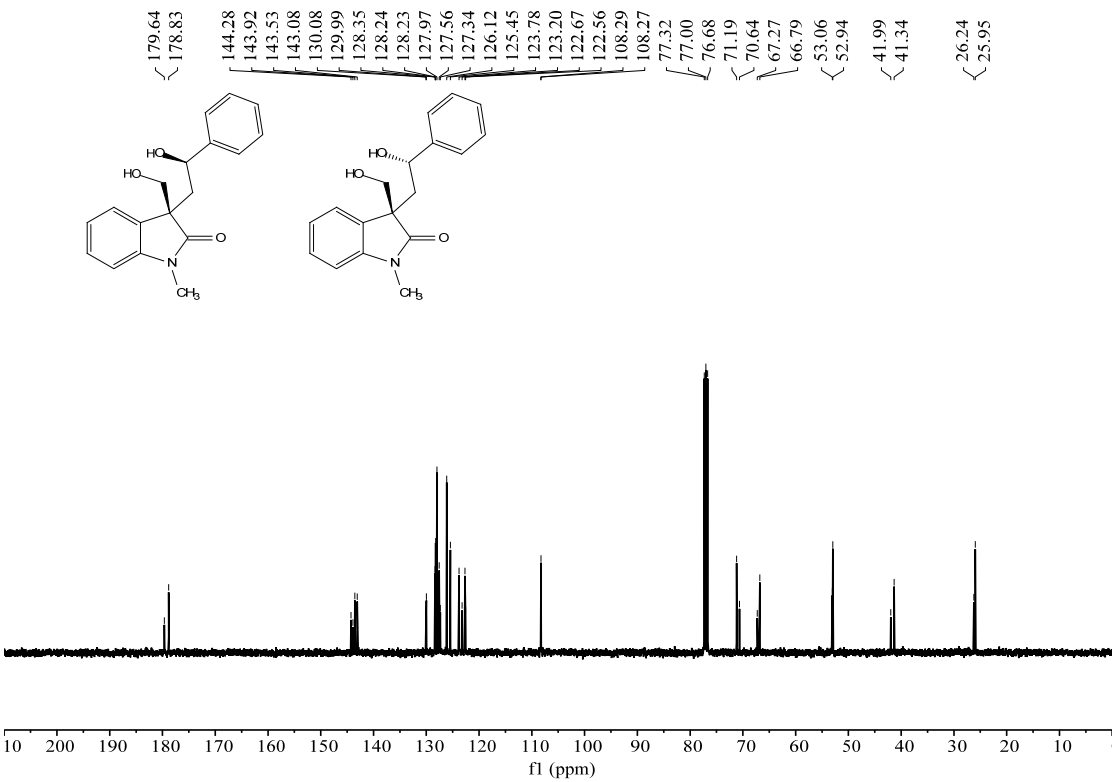
^{19}F NMR spectra of 27b (376 MHz, $CDCl_3$)



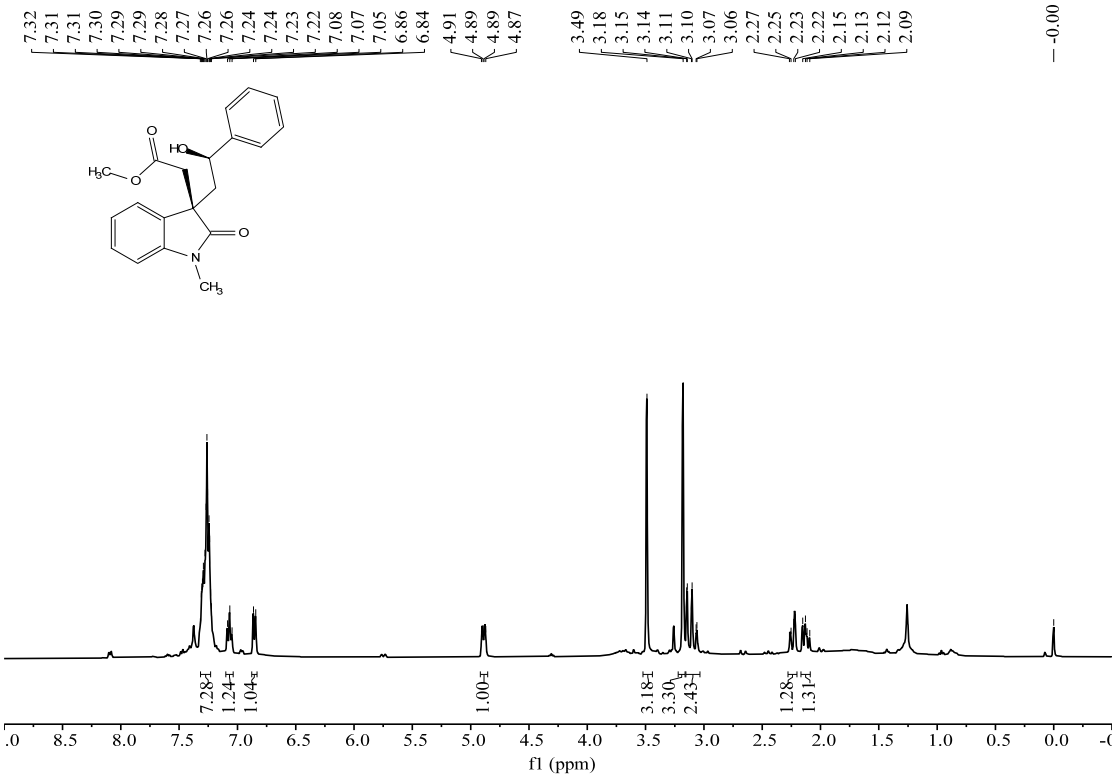
^{1}H NMR spectra of 28ab (400 MHz, $CDCl_3$)



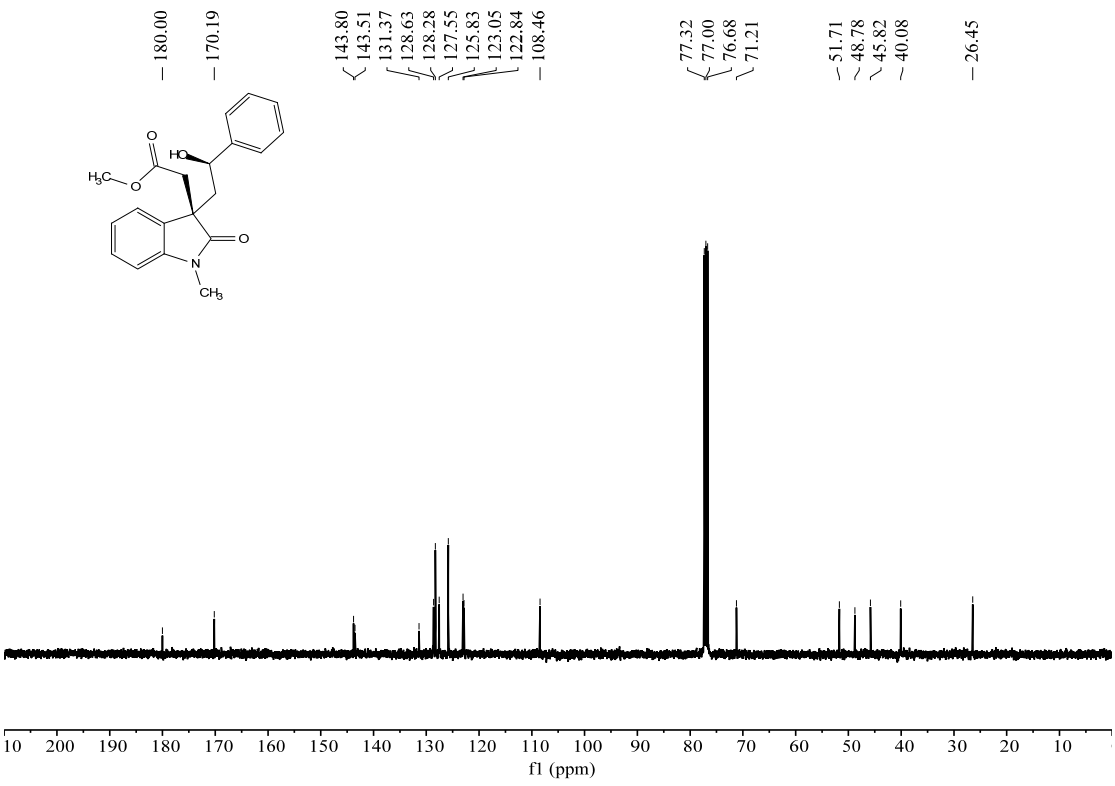
^{13}C NMR spectra of 28ab (100 MHz, $CDCl_3$)



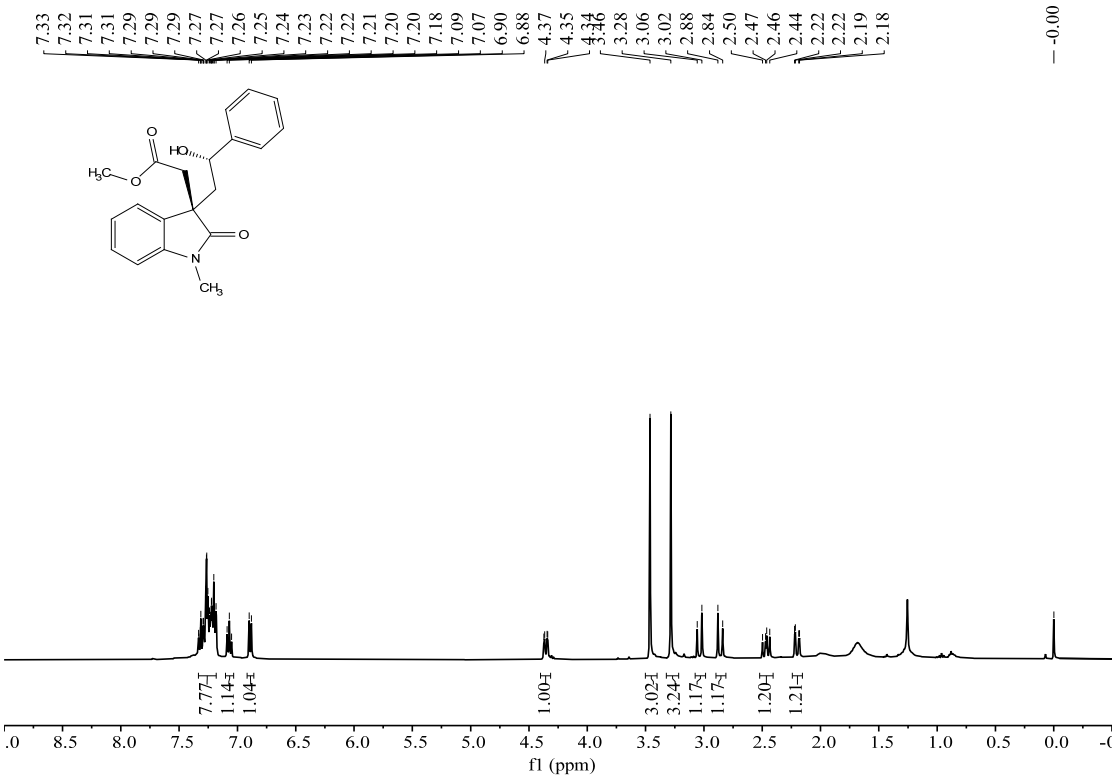
^{1}H NMR spectra of 29a (400 MHz, $CDCl_3$)



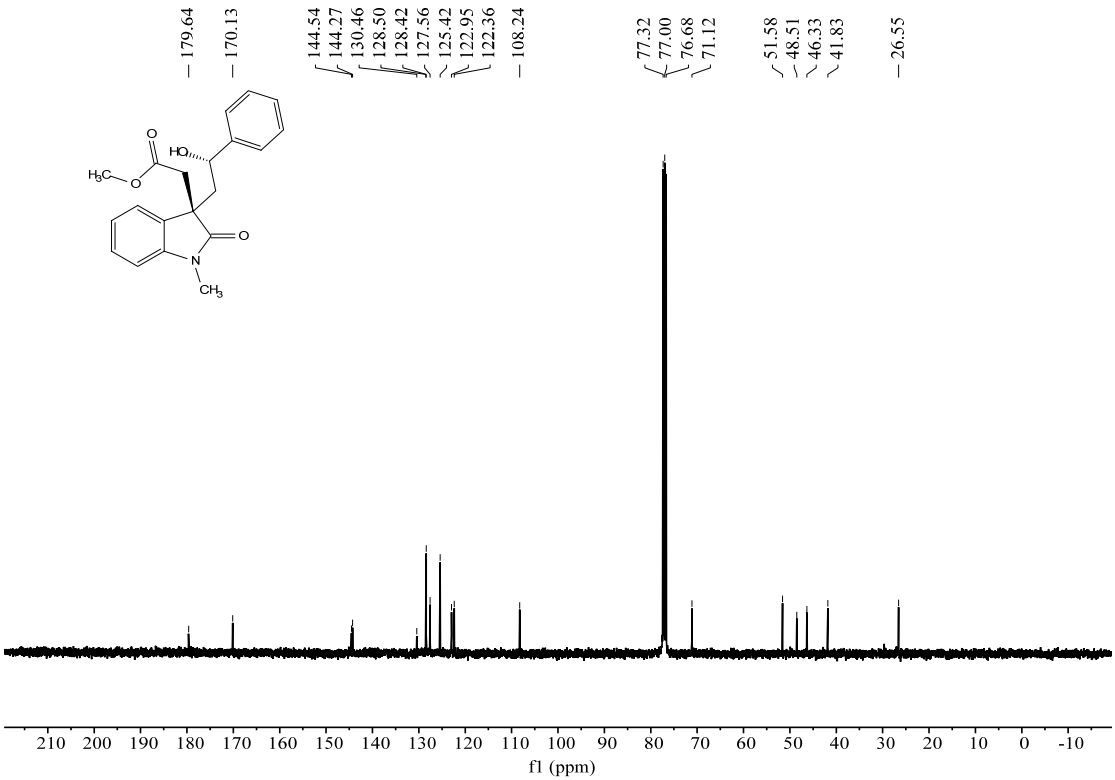
^{13}C NMR spectra of 29a (100 MHz, $CDCl_3$)



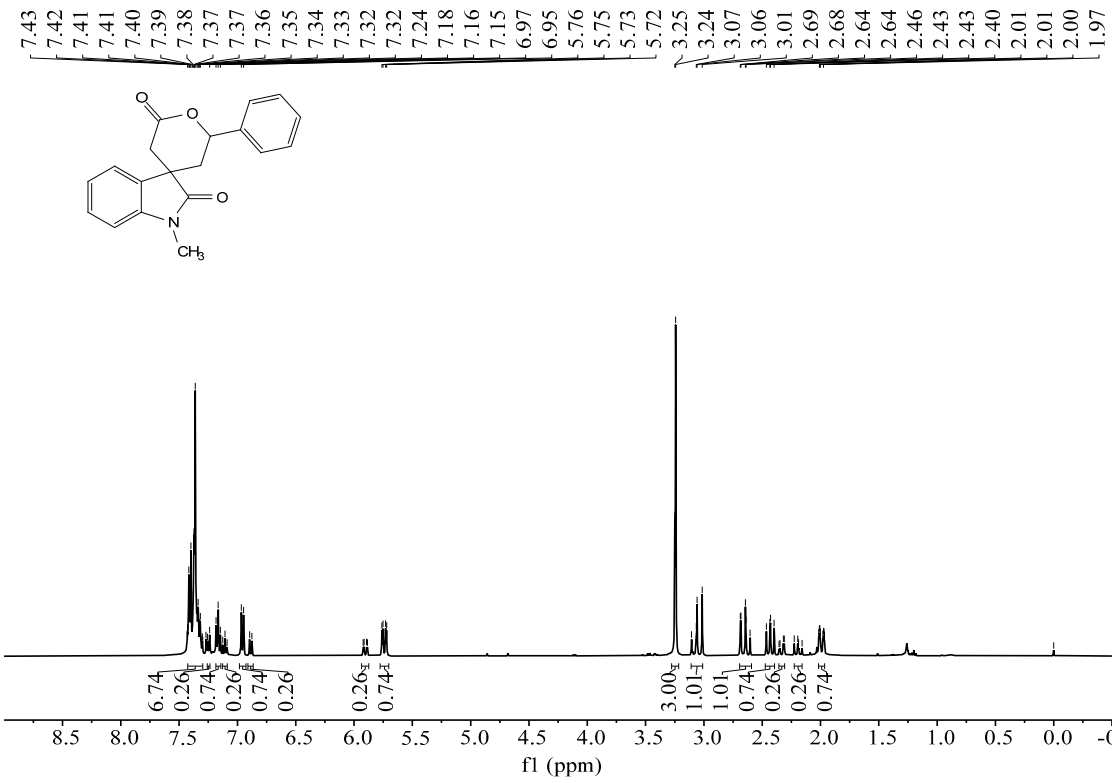
^{1}H NMR spectra of 29b (400 MHz, $CDCl_3$)



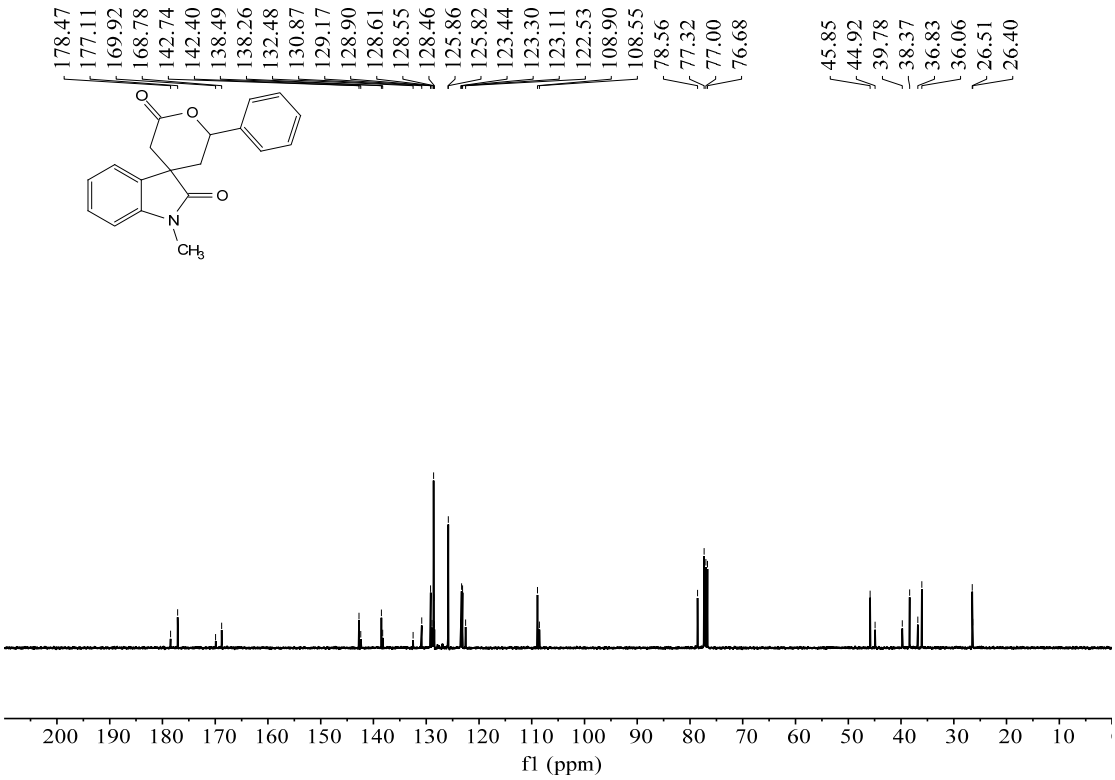
^{13}C NMR spectra of 29b (100 MHz, $CDCl_3$)



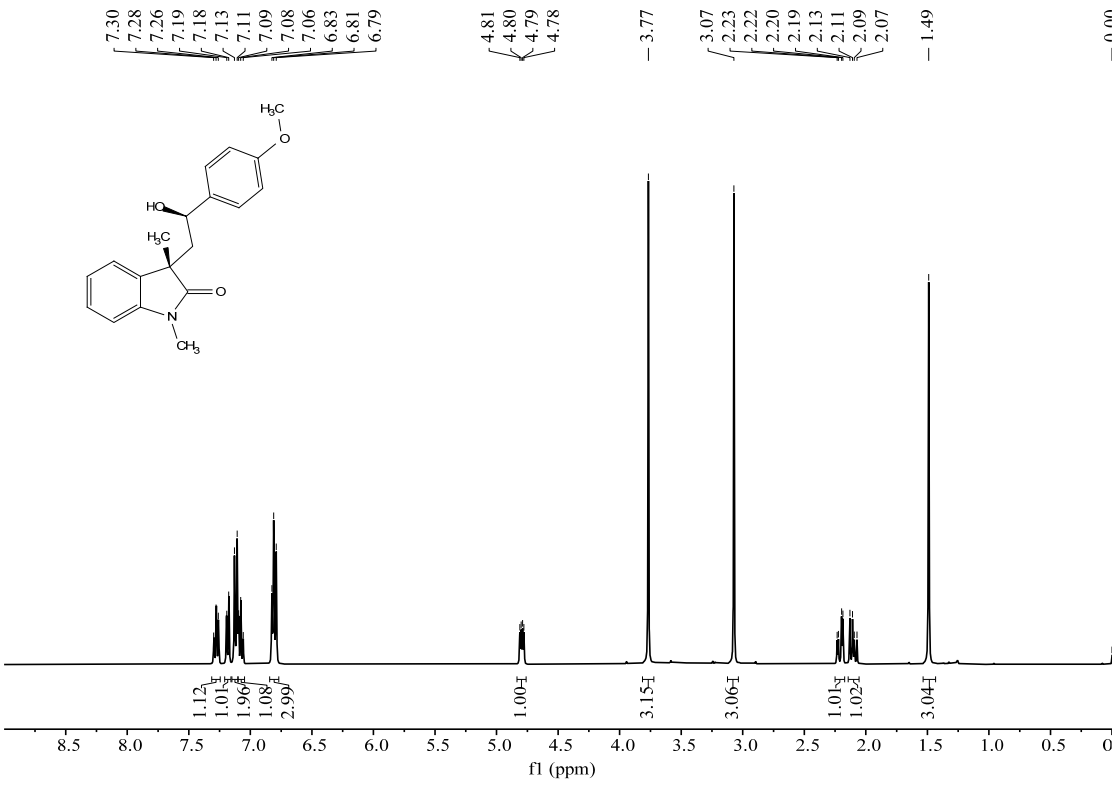
^{1}H NMR spectra of 29’ (400 MHz, $CDCl_3$)



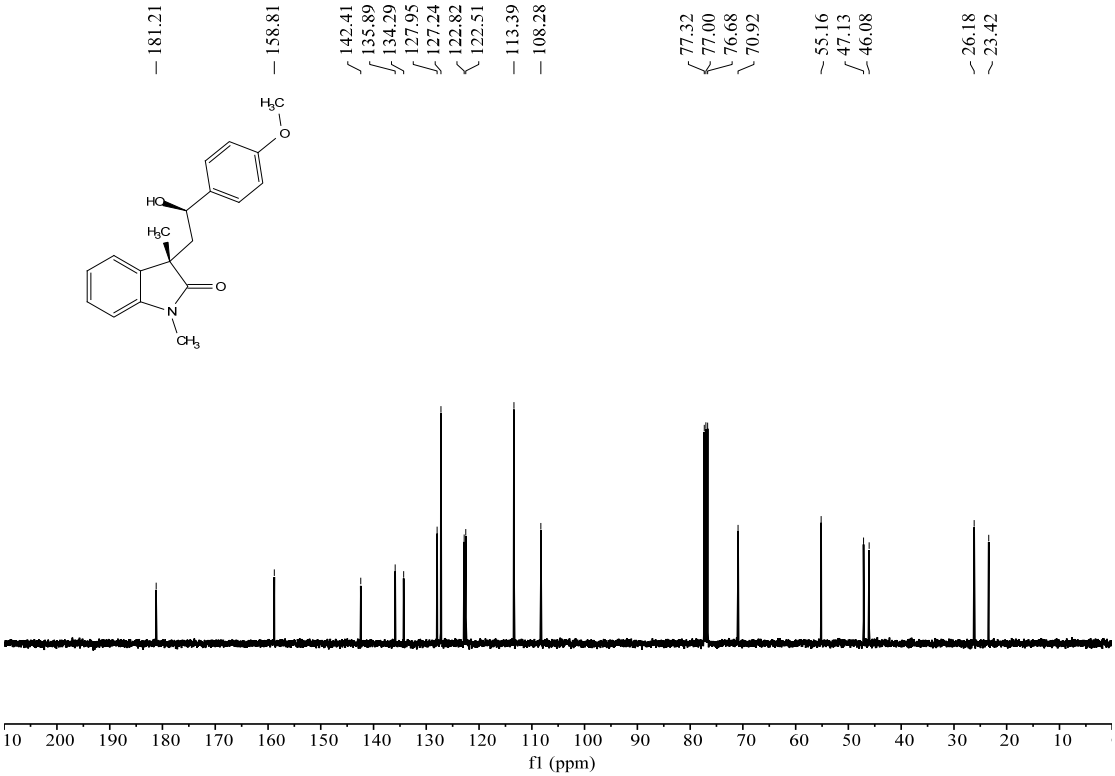
^{13}C NMR spectra of 29’ (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 30a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 30a (100 MHz, $CDCl_3$)



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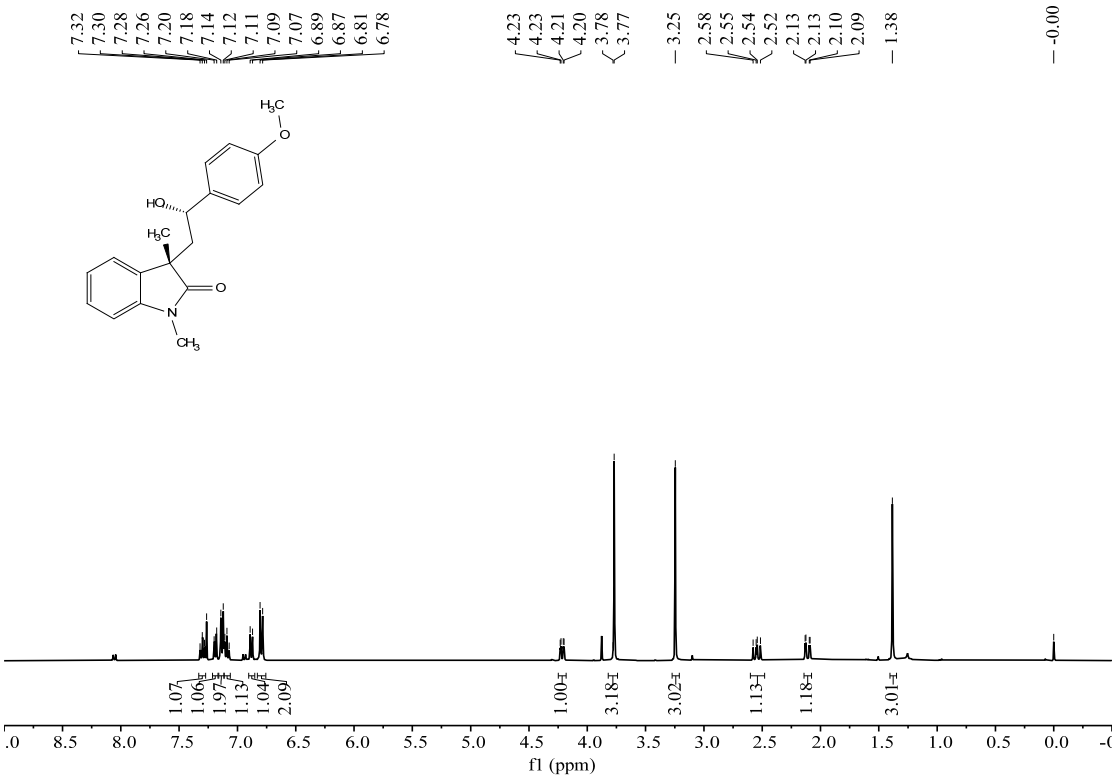

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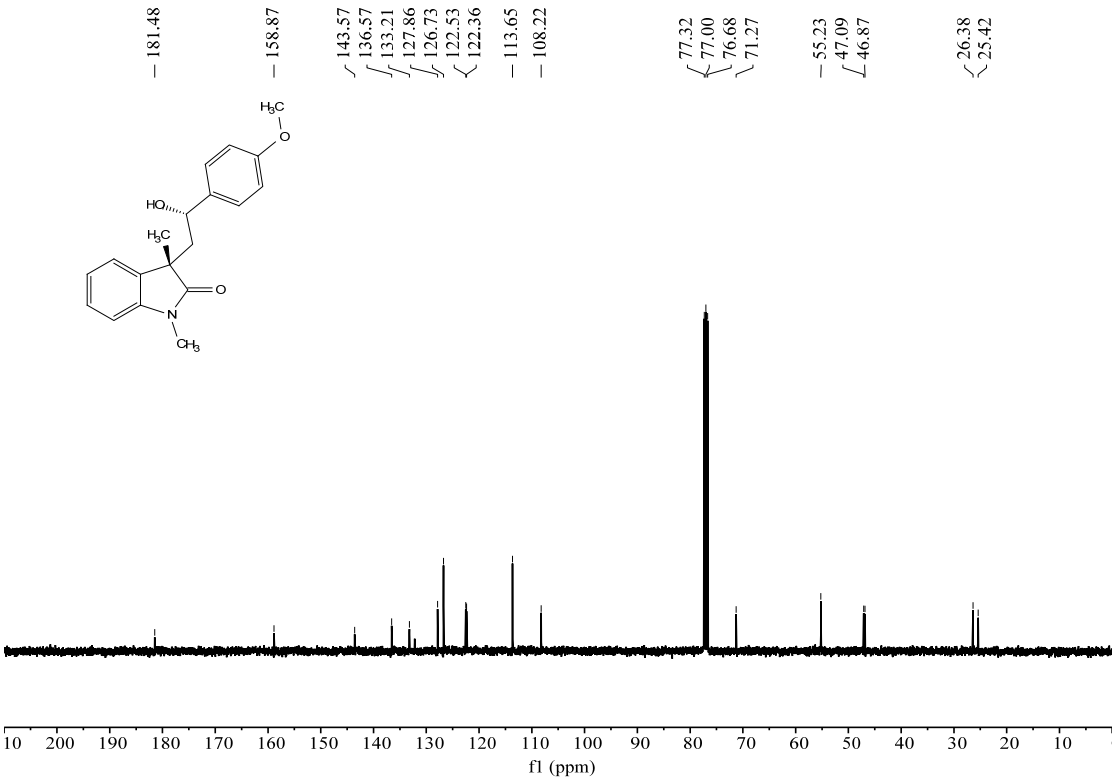
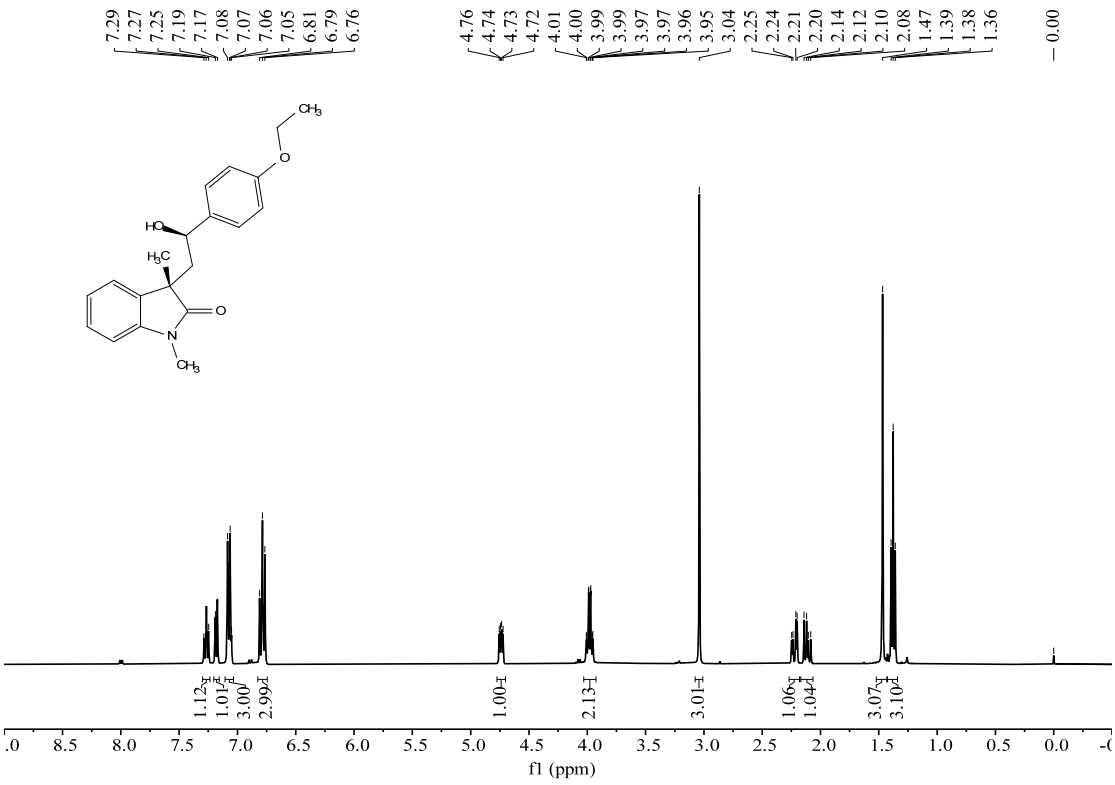


^{1}H NMR spectra of 31a (400 MHz, $CDCl_3$)



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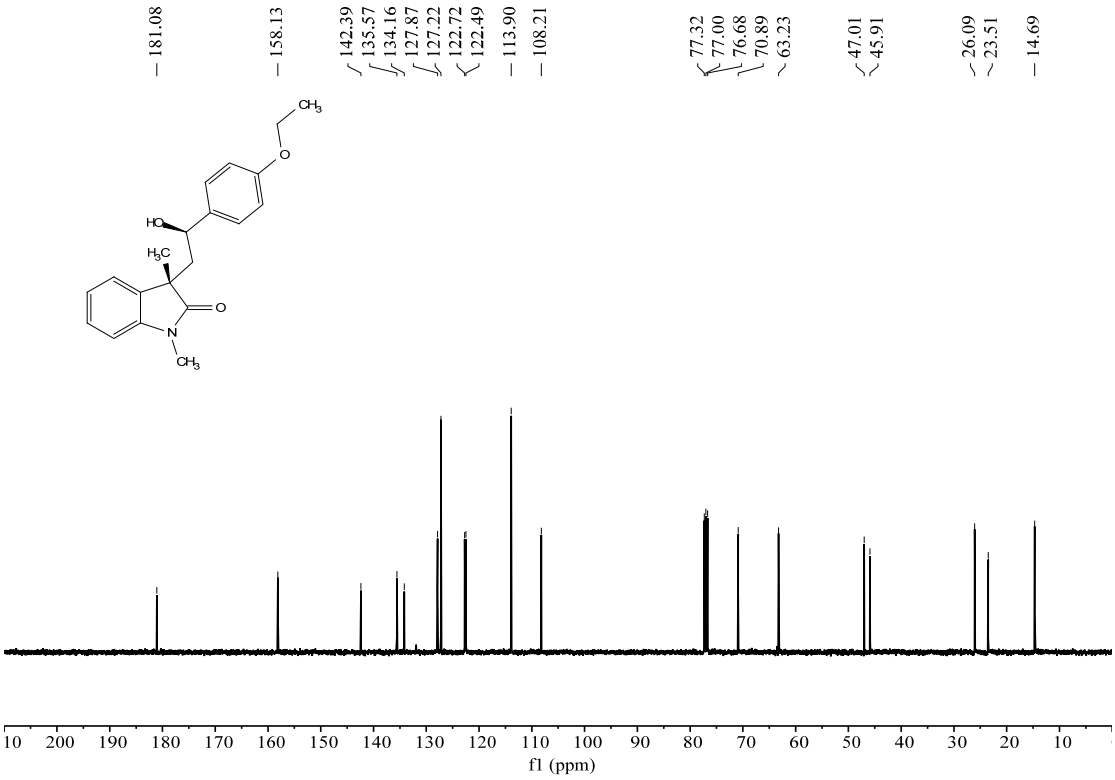

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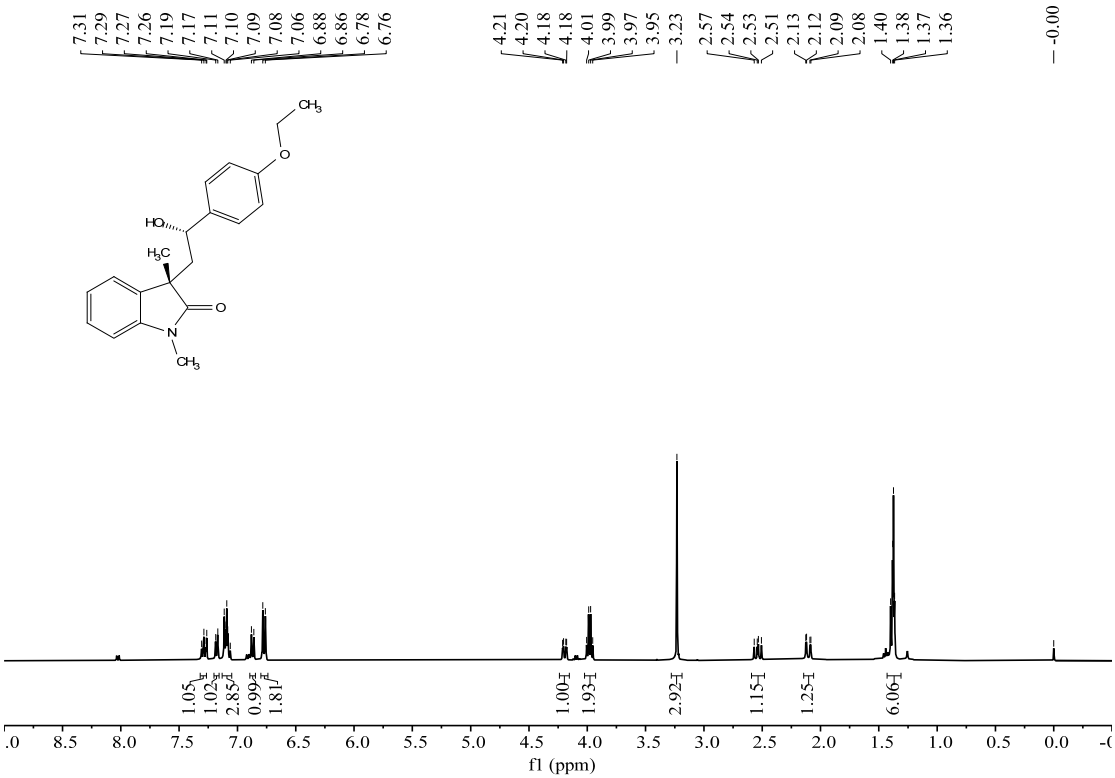

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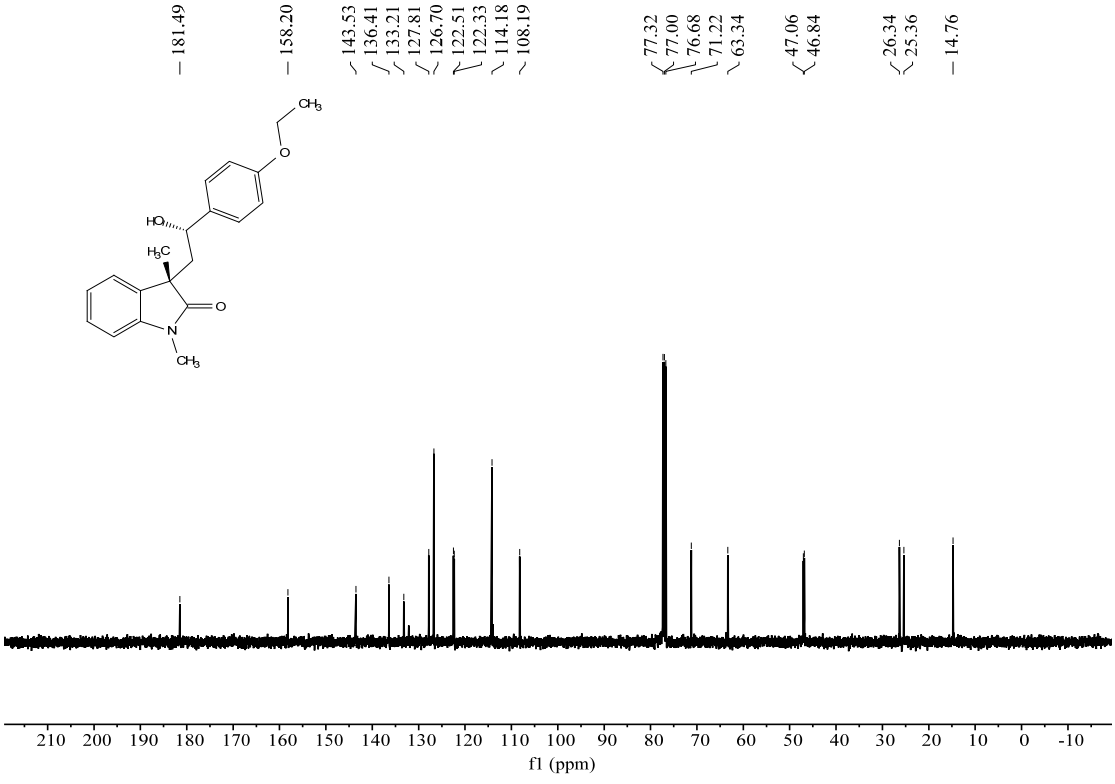

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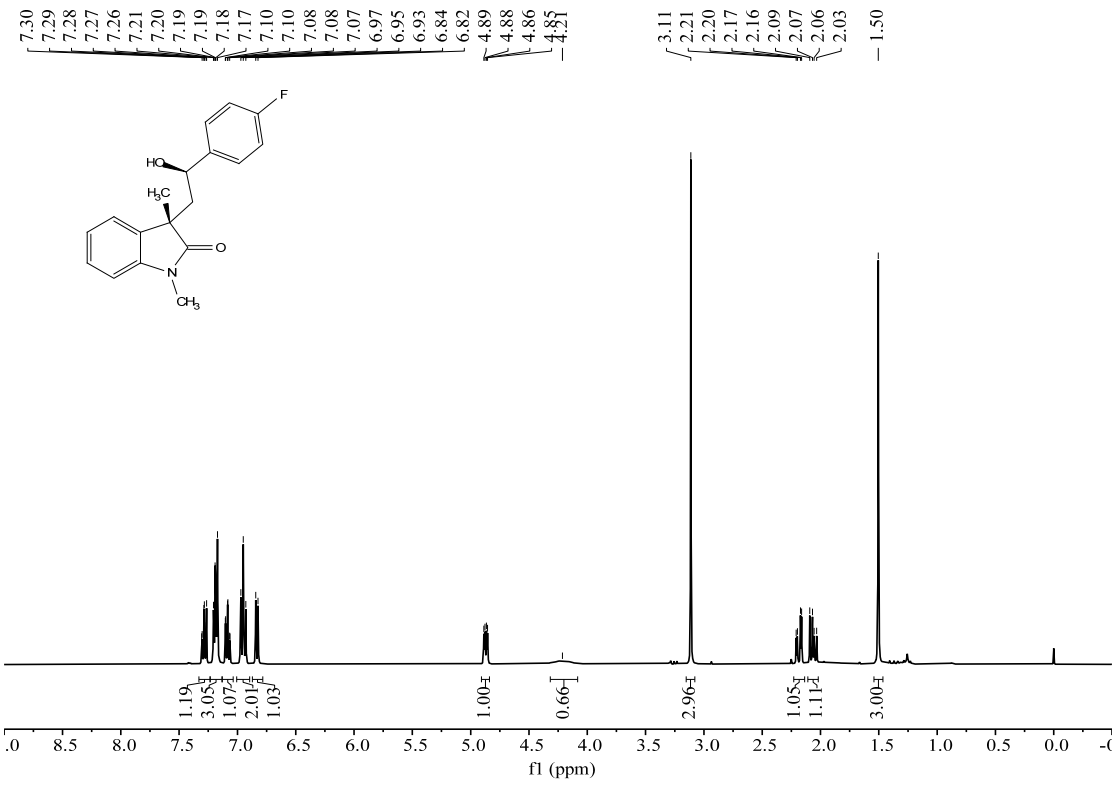
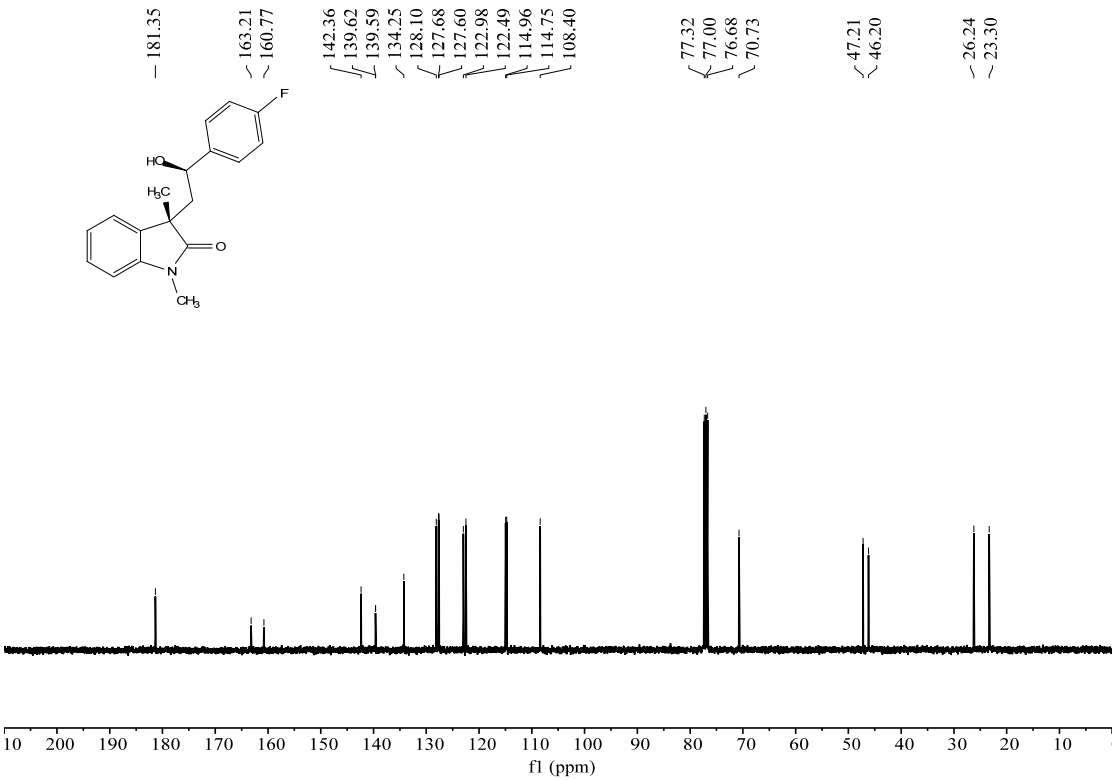
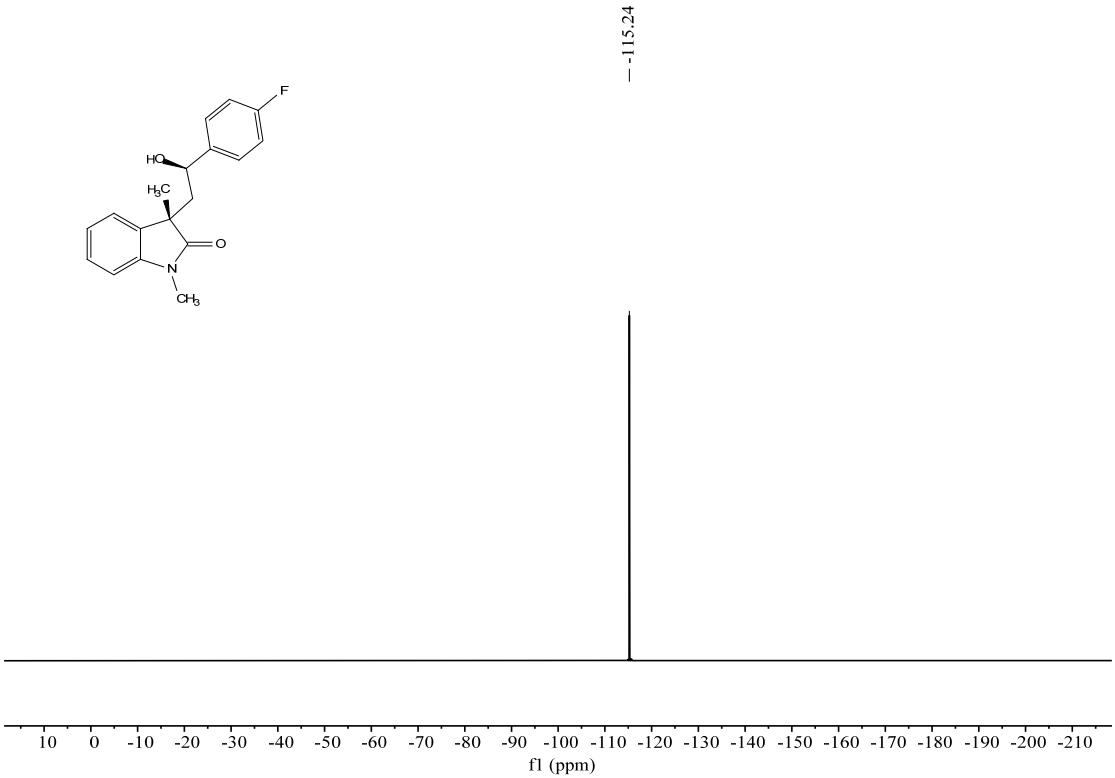


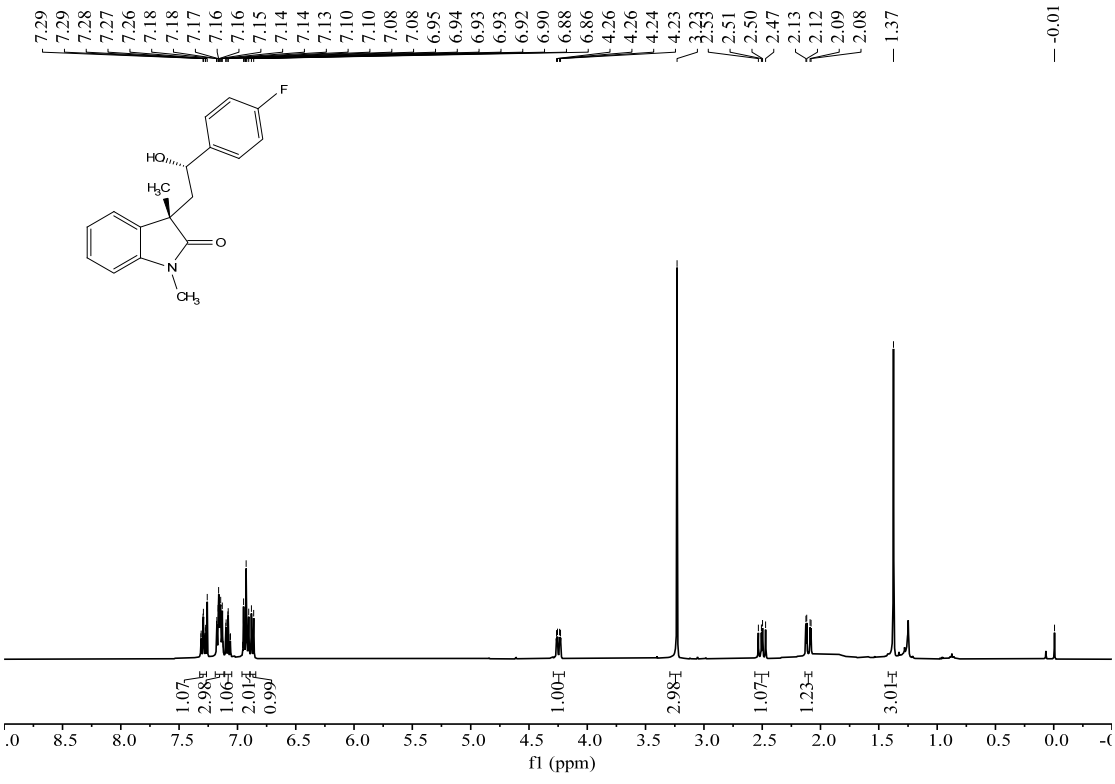
^{13}C NMR spectra of 32a (100 MHz, $CDCl_3$)



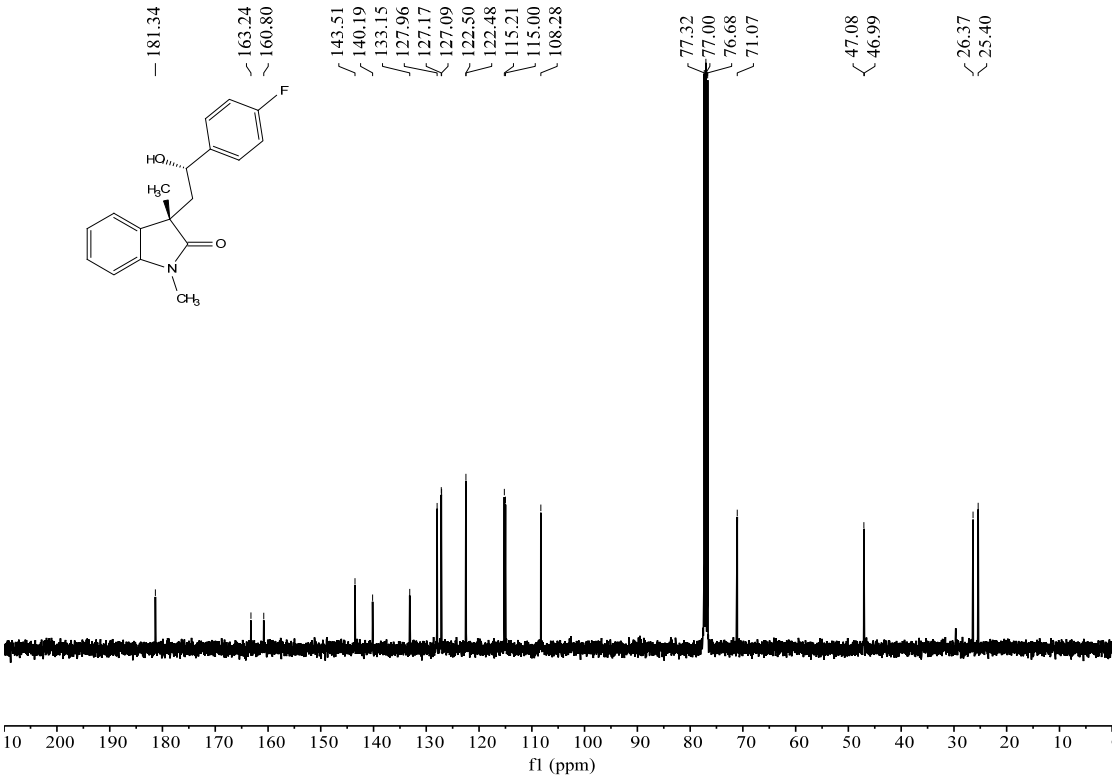
^{19}F NMR spectra of 32a (376 MHz, $CDCl_3$)



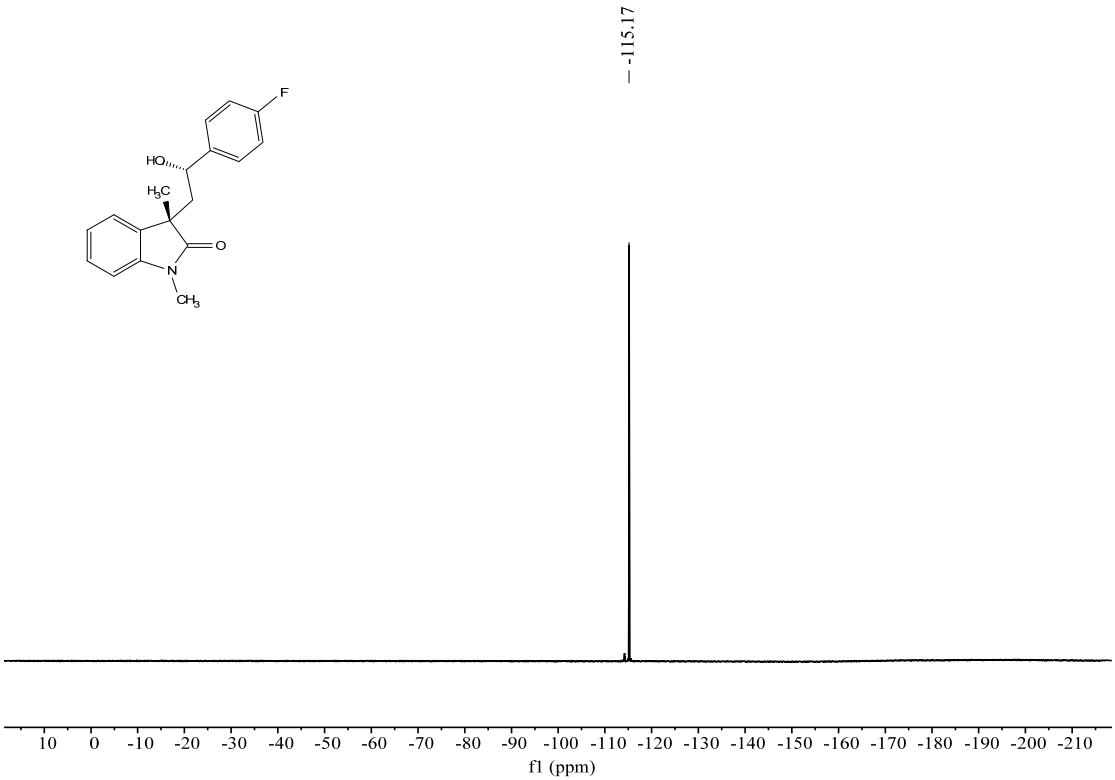
^{1}H NMR spectra of 32b (400 MHz, $CDCl_3$)



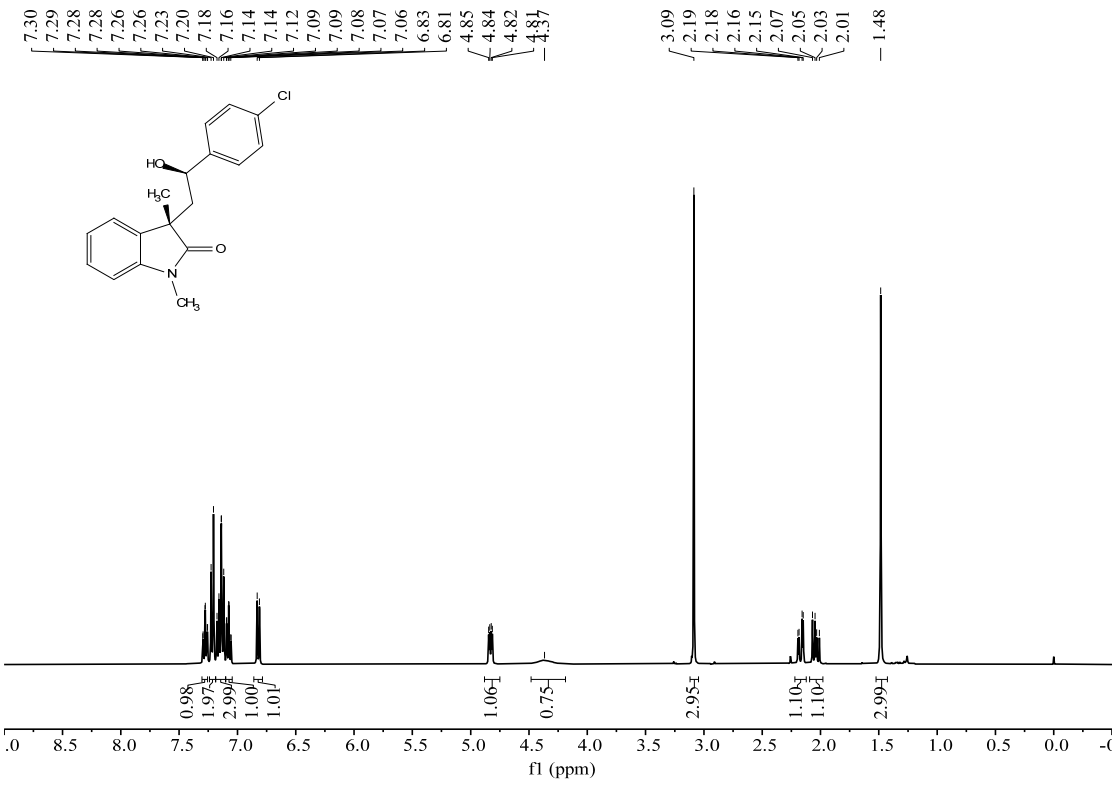
^{13}C NMR spectra of 32b (100 MHz, $CDCl_3$)



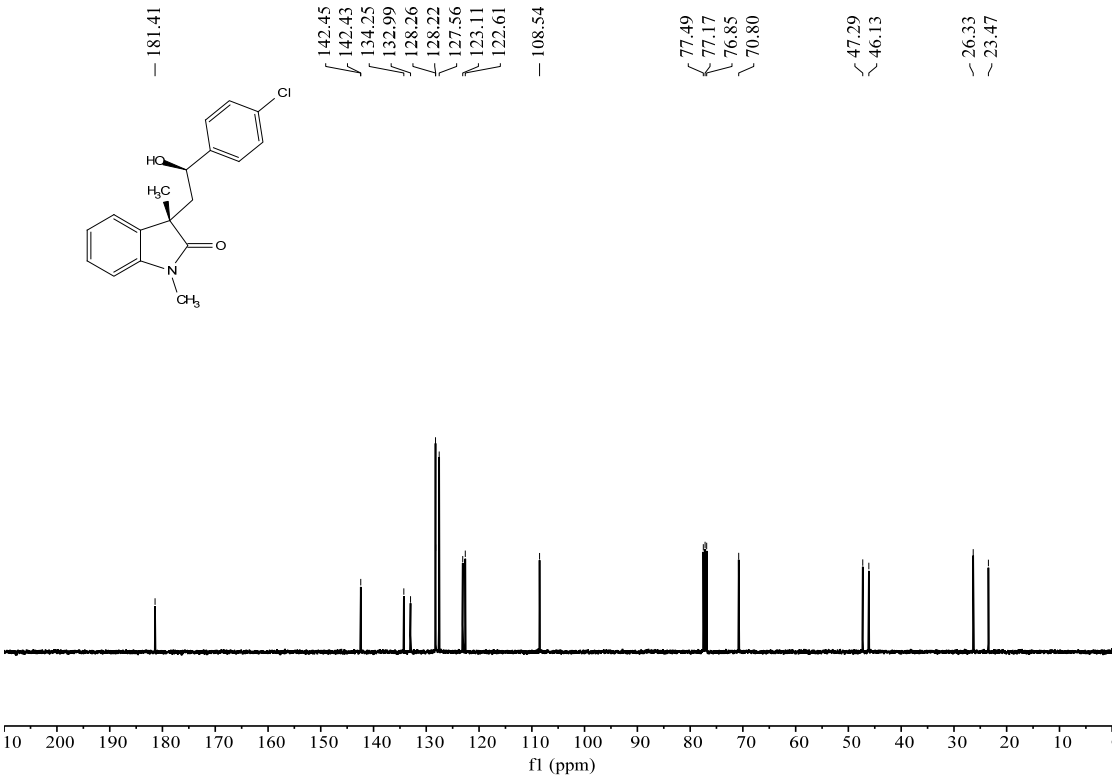
^{19}F NMR spectra of 32b (376 MHz, $CDCl_3$)



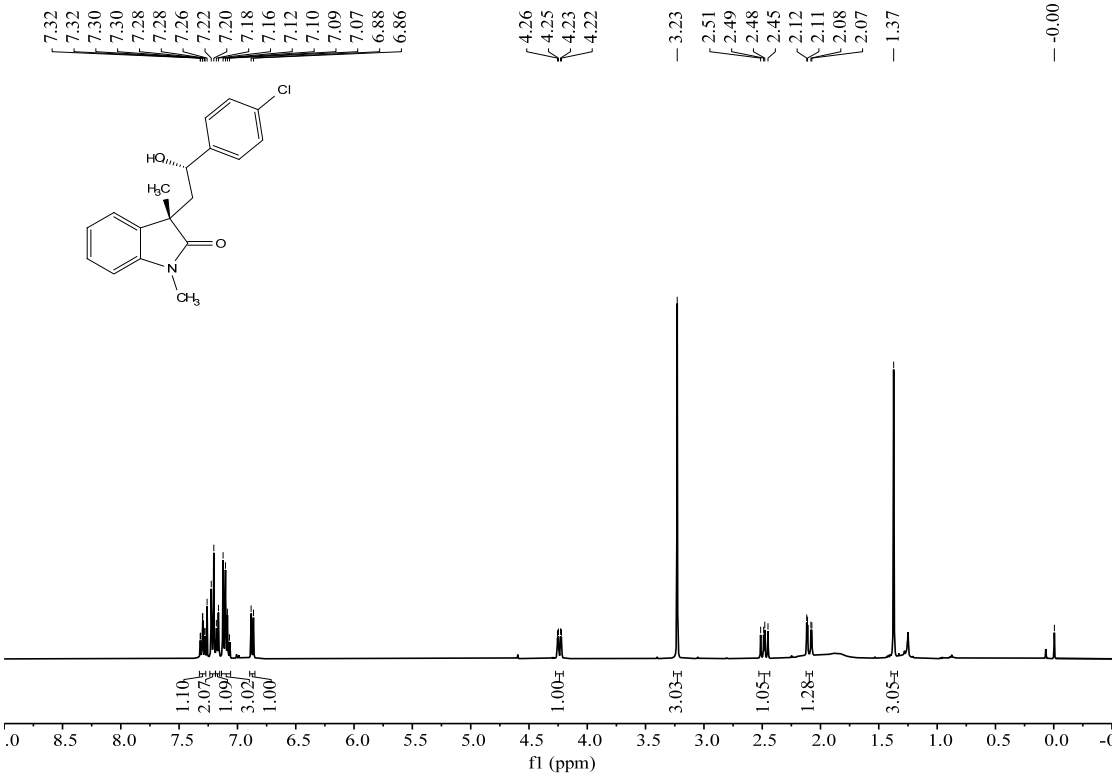
^{1}H NMR spectra of 33a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 33a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 33b (400 MHz, $CDCl_3$)



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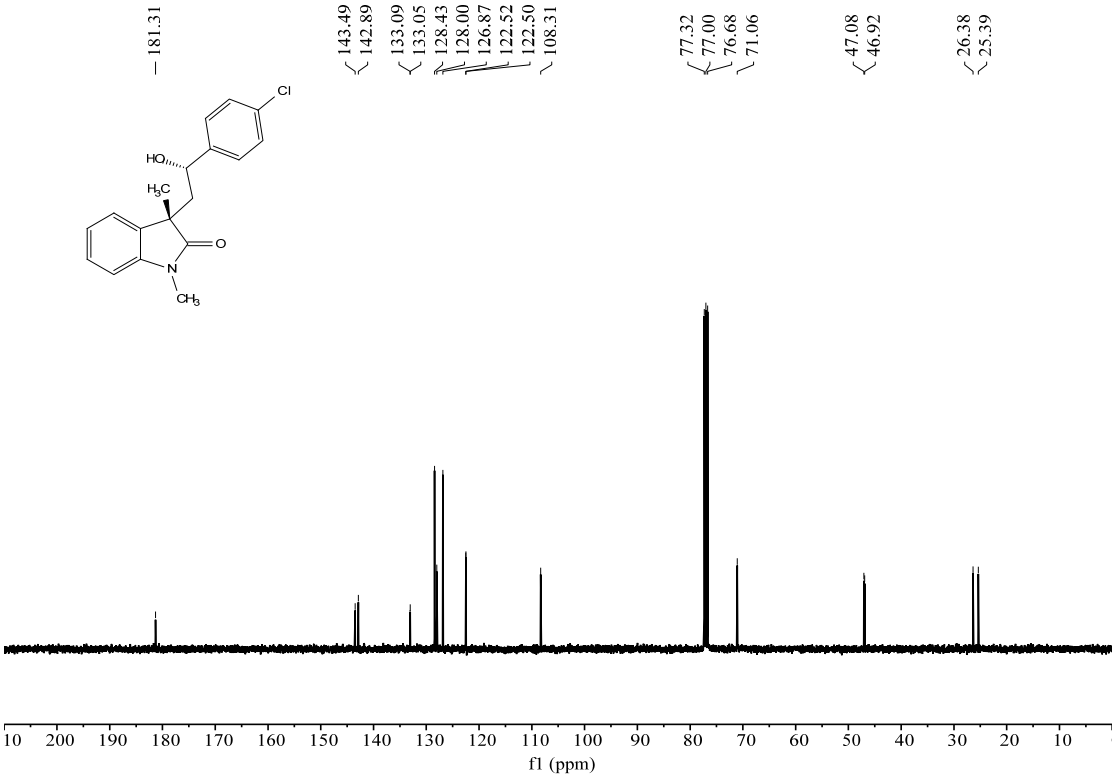

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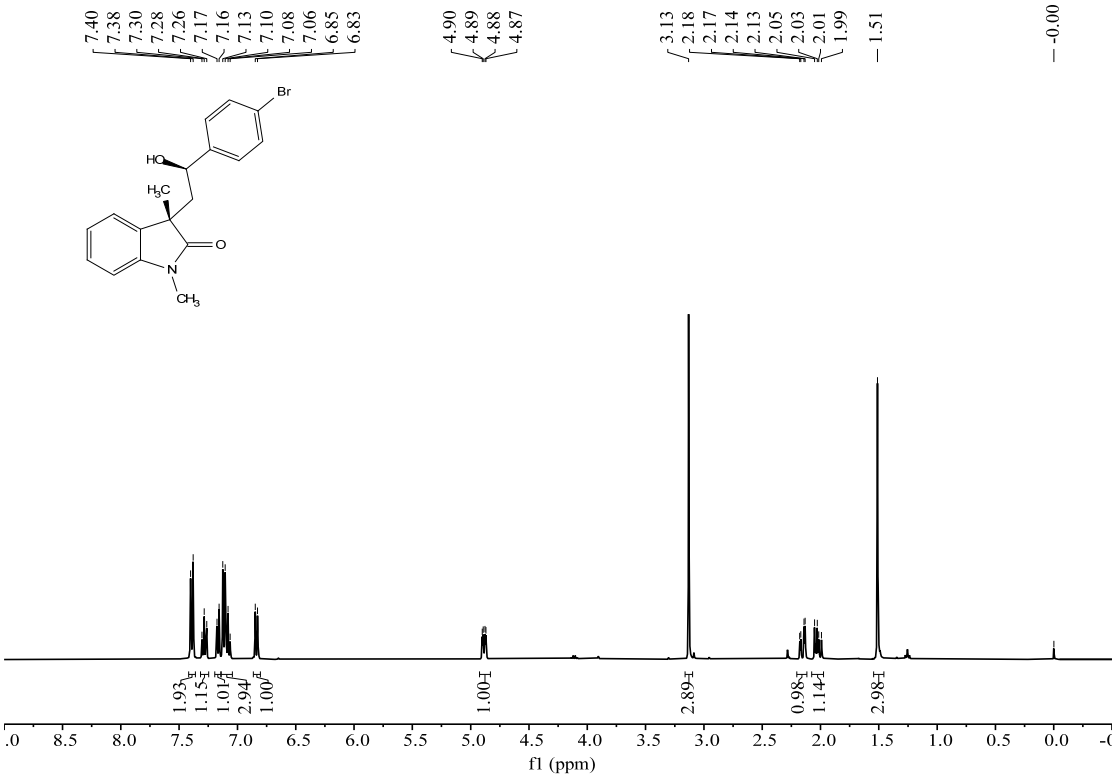
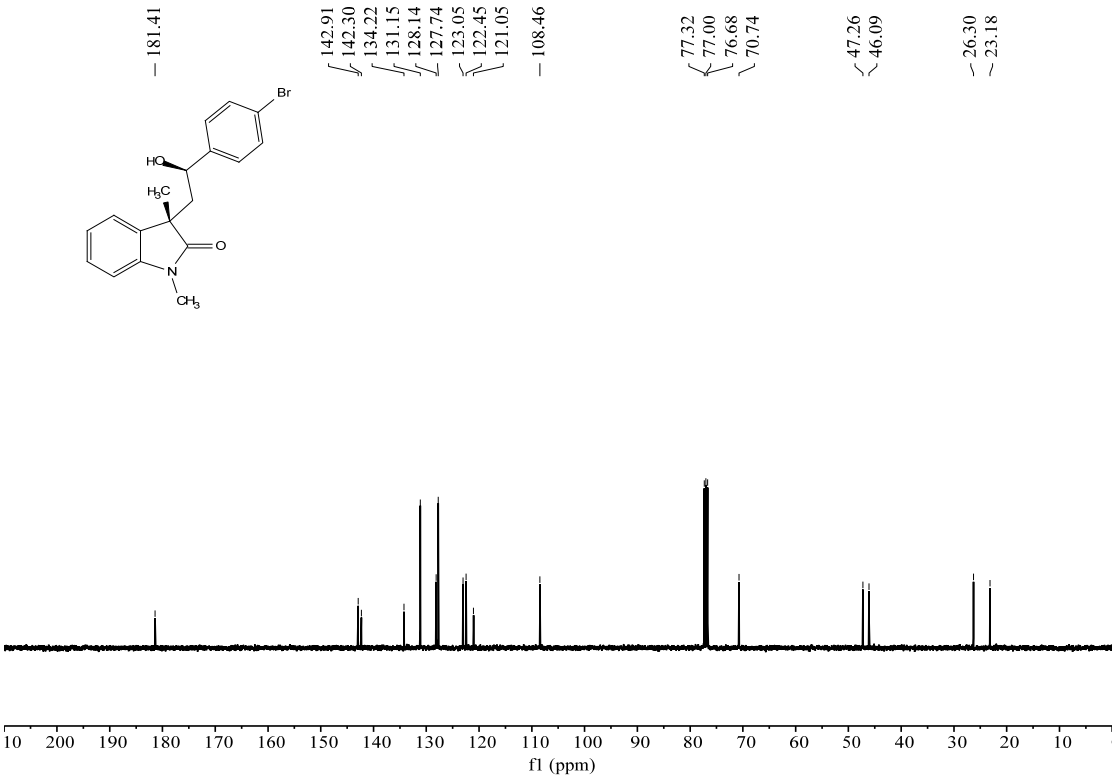
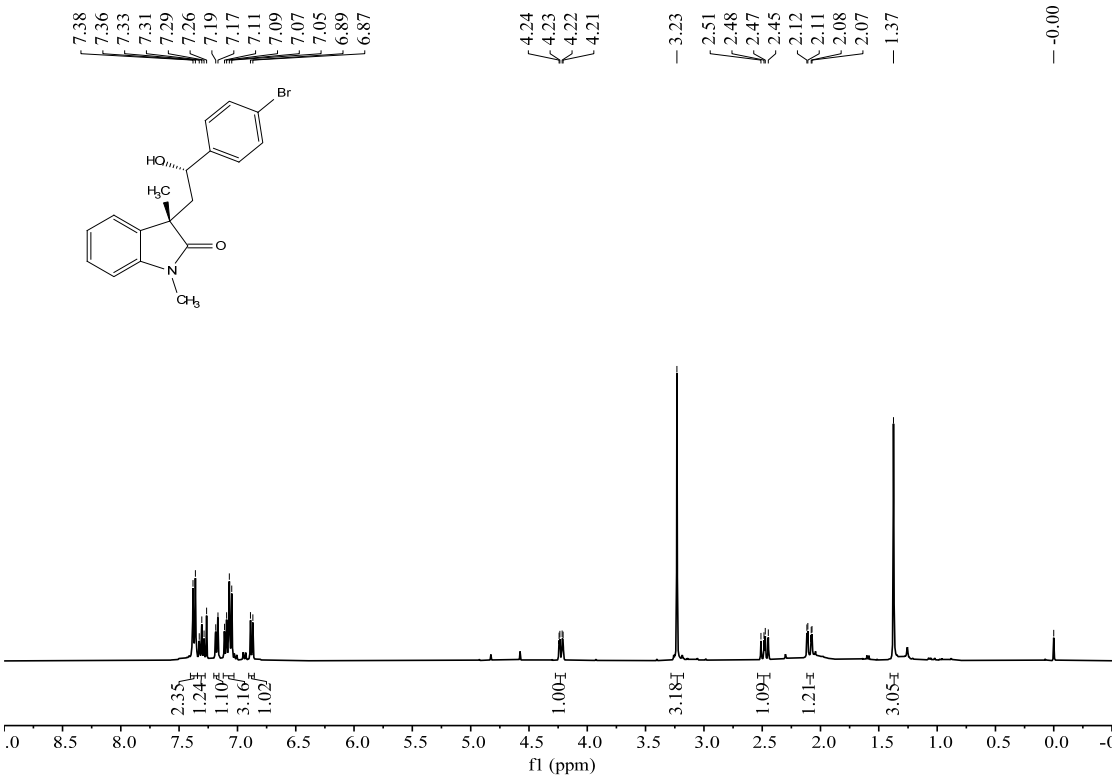


^{13}C NMR spectra of 34a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 34b (400 MHz, $CDCl_3$)



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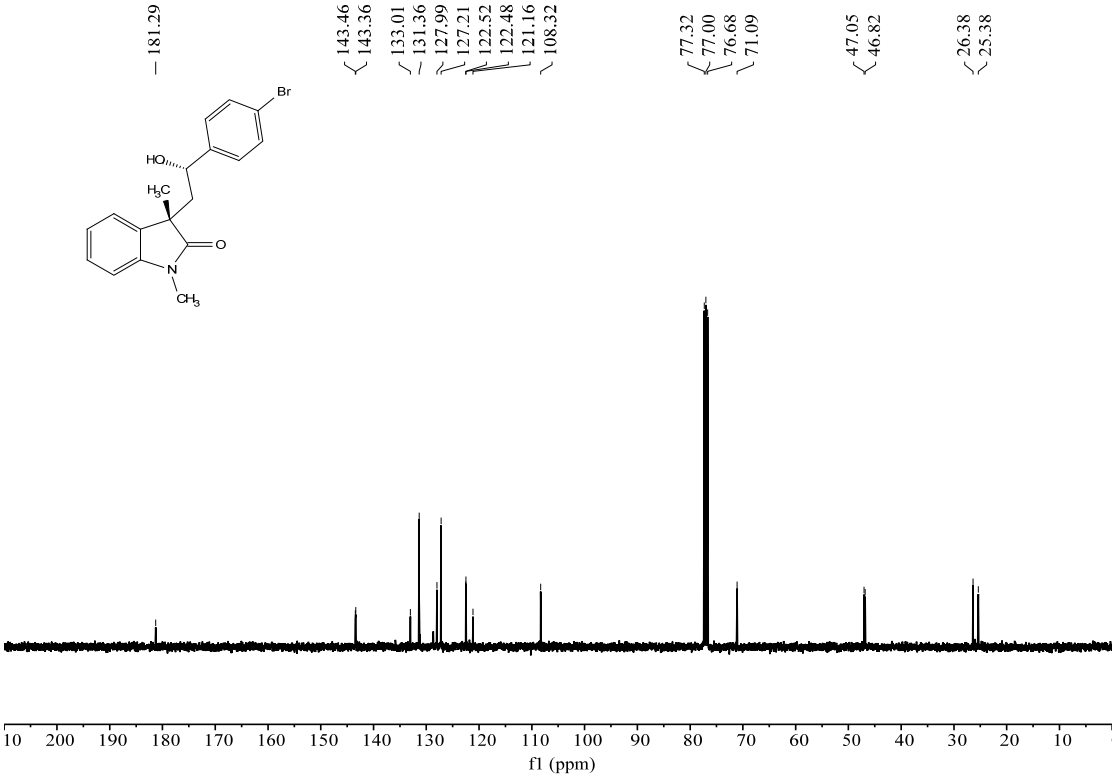
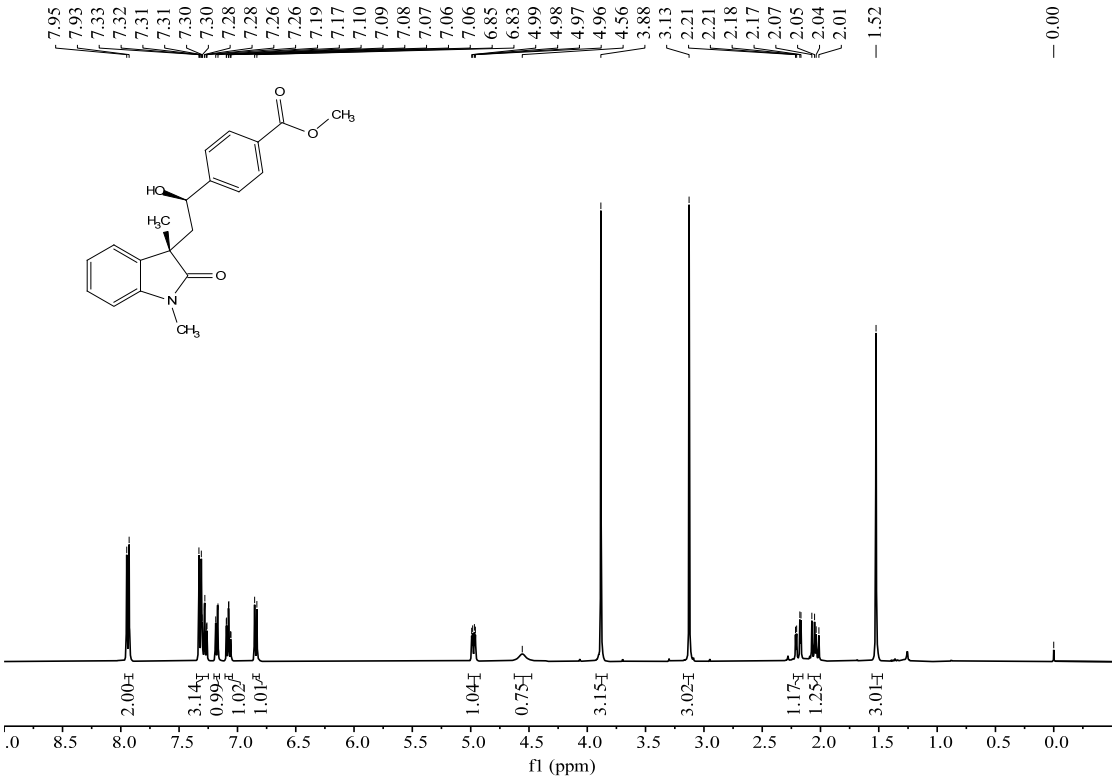
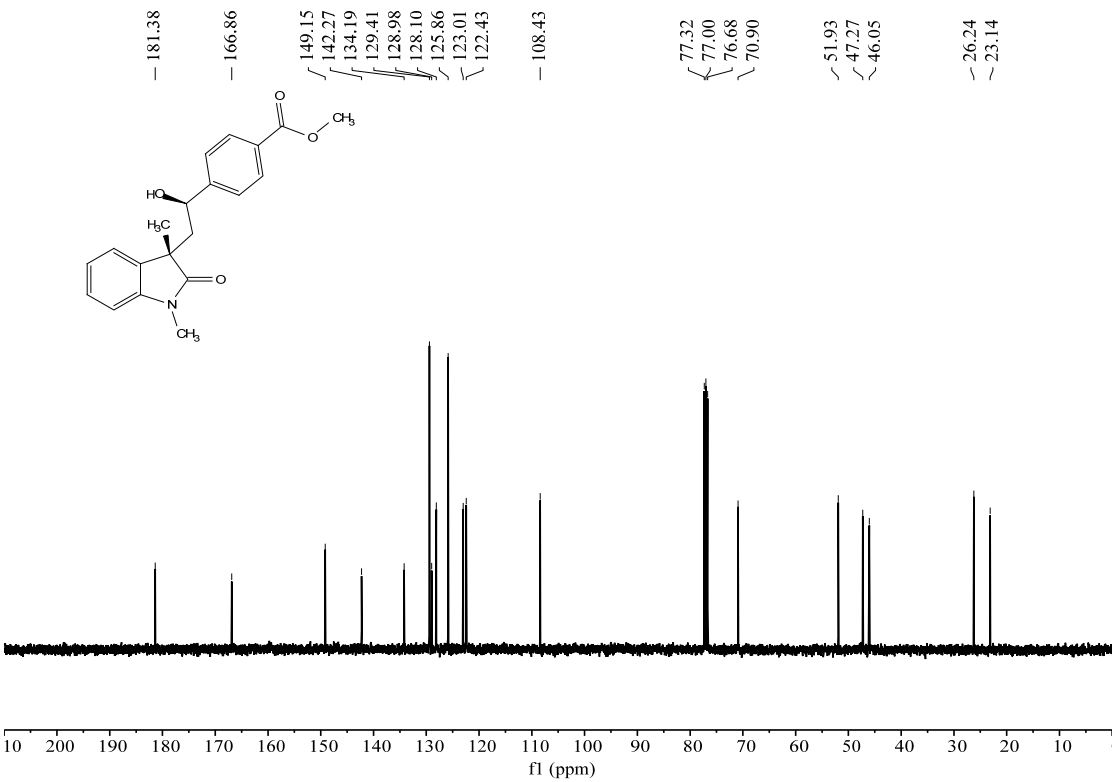


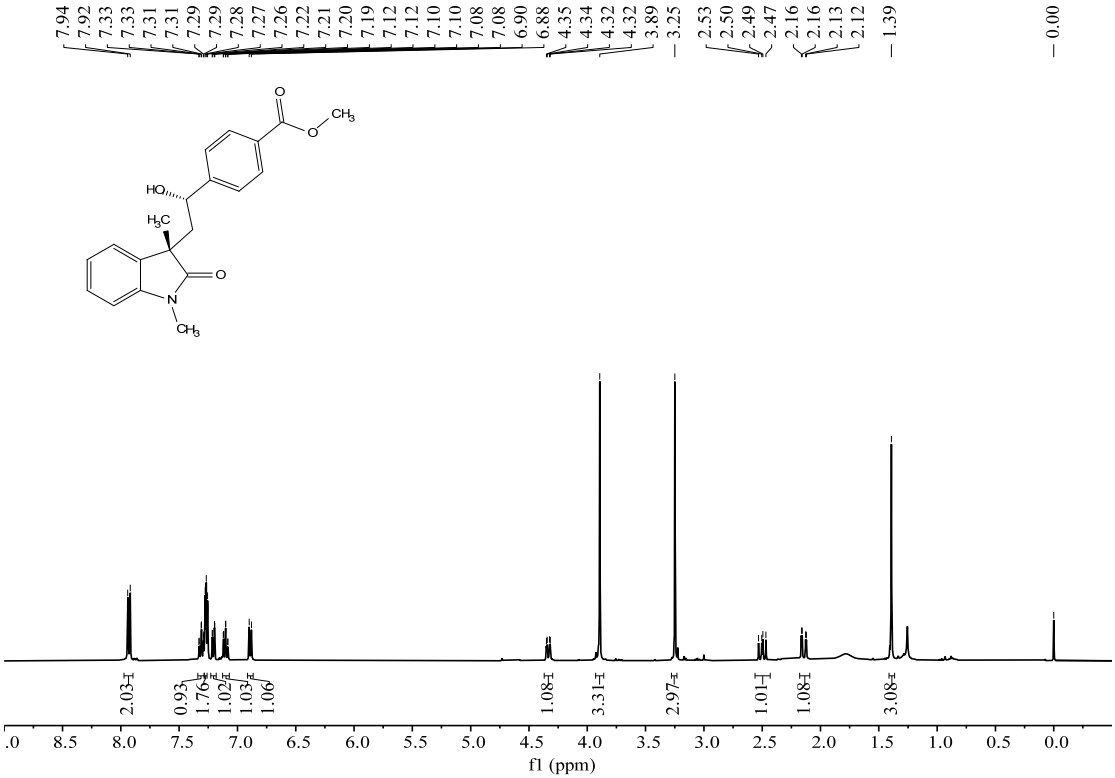
^{1}H NMR spectra of 35a (400 MHz, $CDCl_3$)



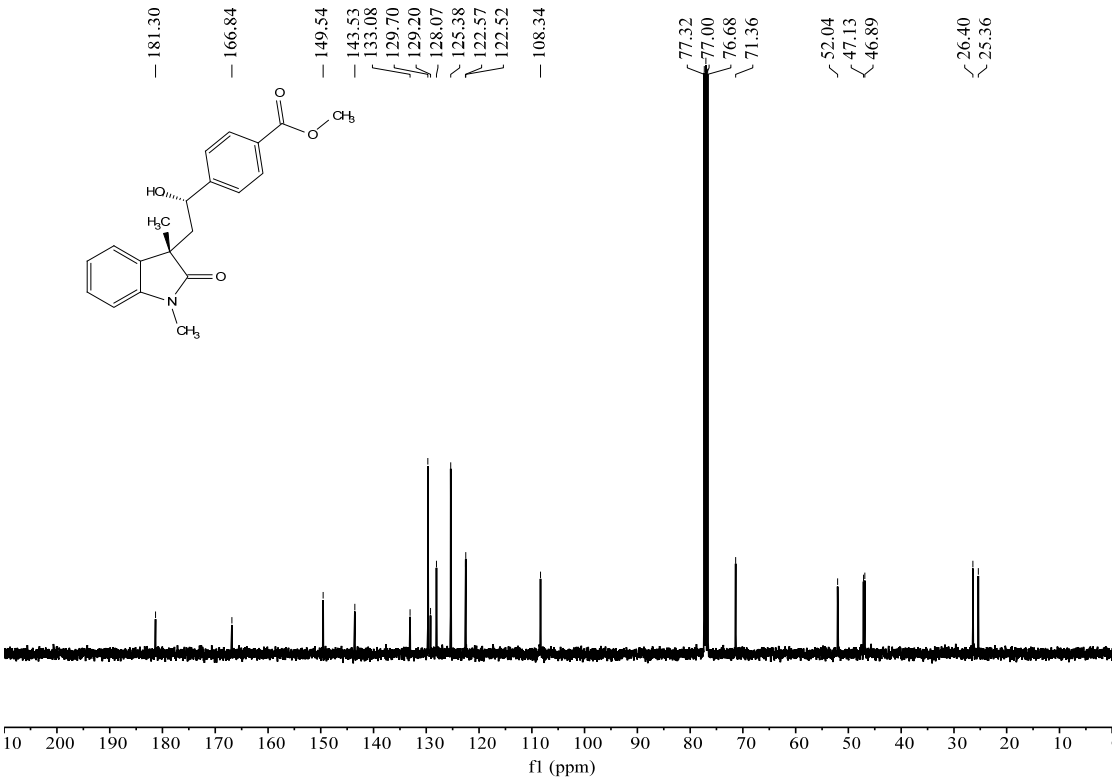
^{13}C NMR spectra of 35a (100 MHz, $CDCl_3$)



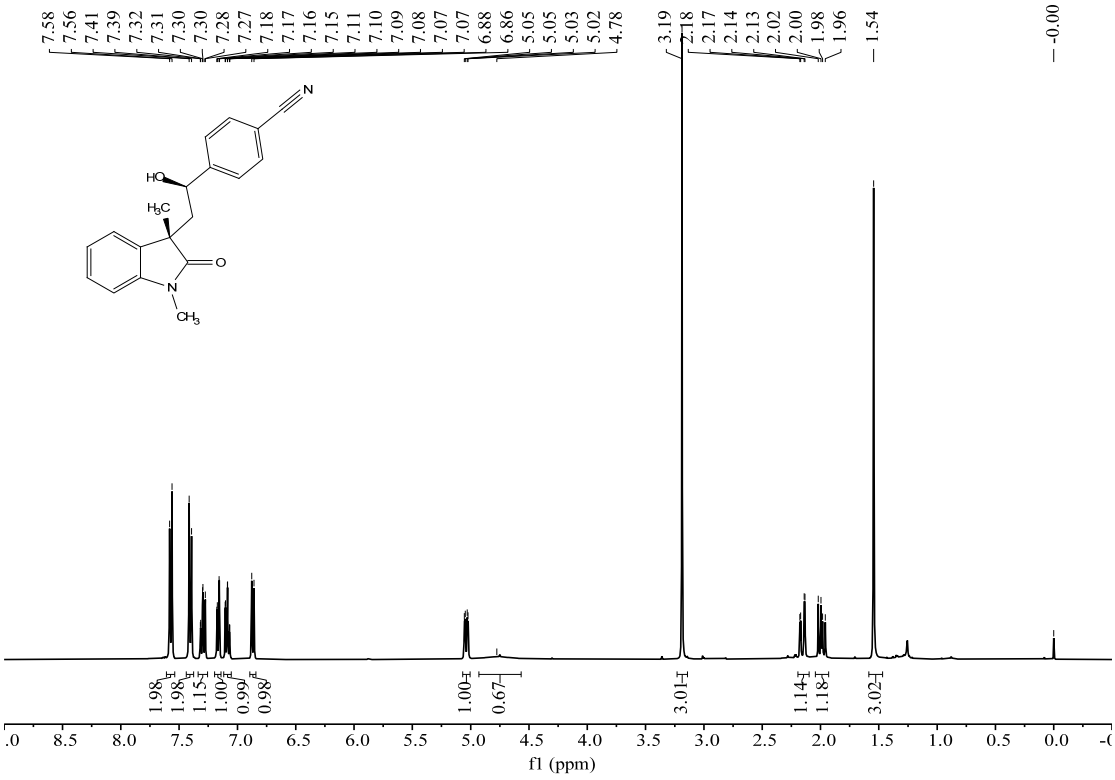
^{1}H NMR spectra of 35b (400 MHz, $CDCl_3$)



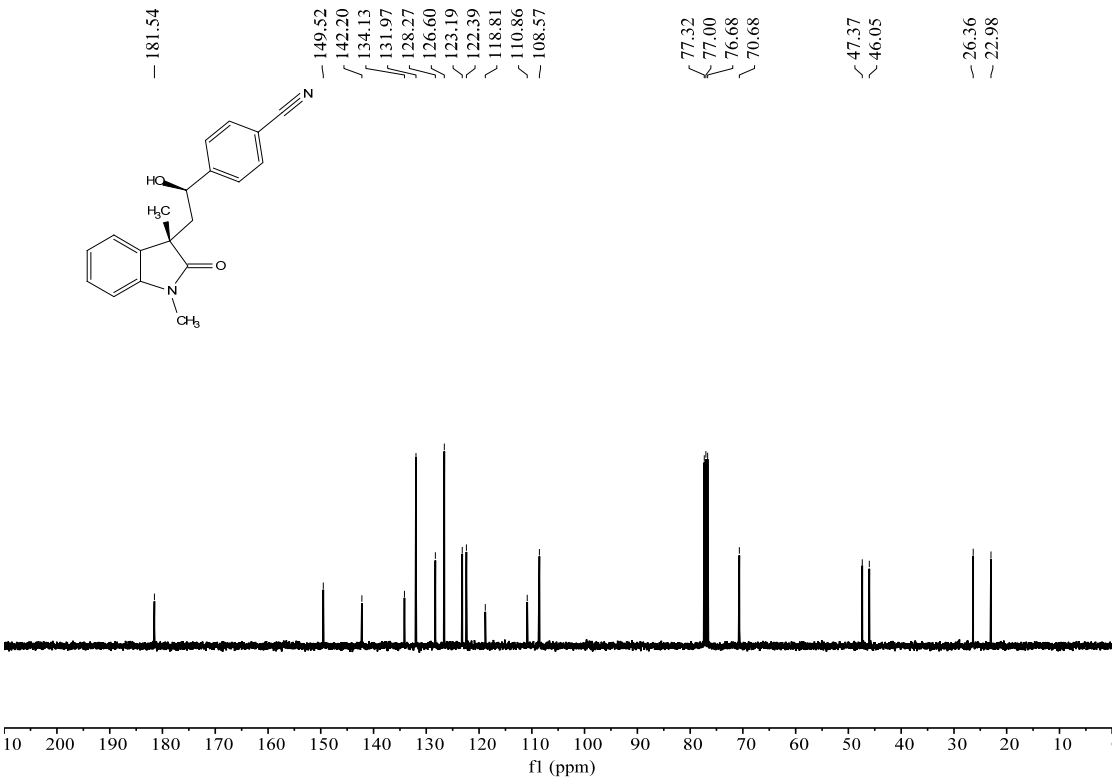
^{13}C NMR spectra of 35b (100 MHz, $CDCl_3$)



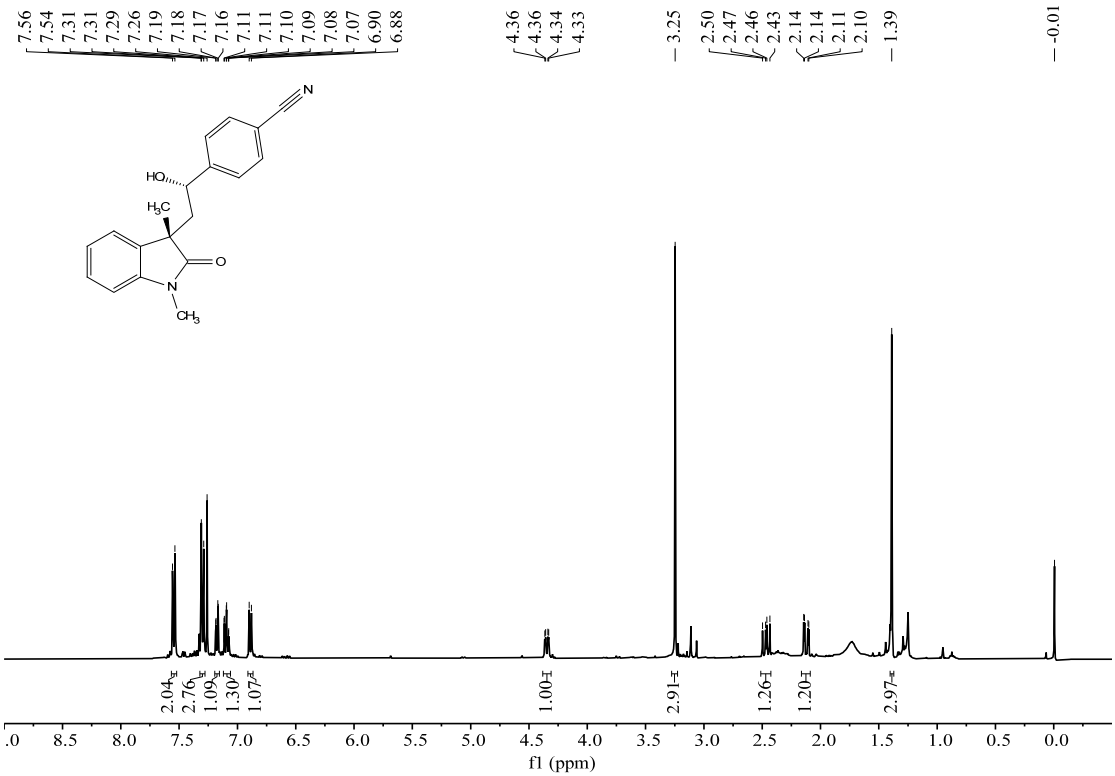
^{1}H NMR spectra of 36a (400 MHz, $CDCl_3$)



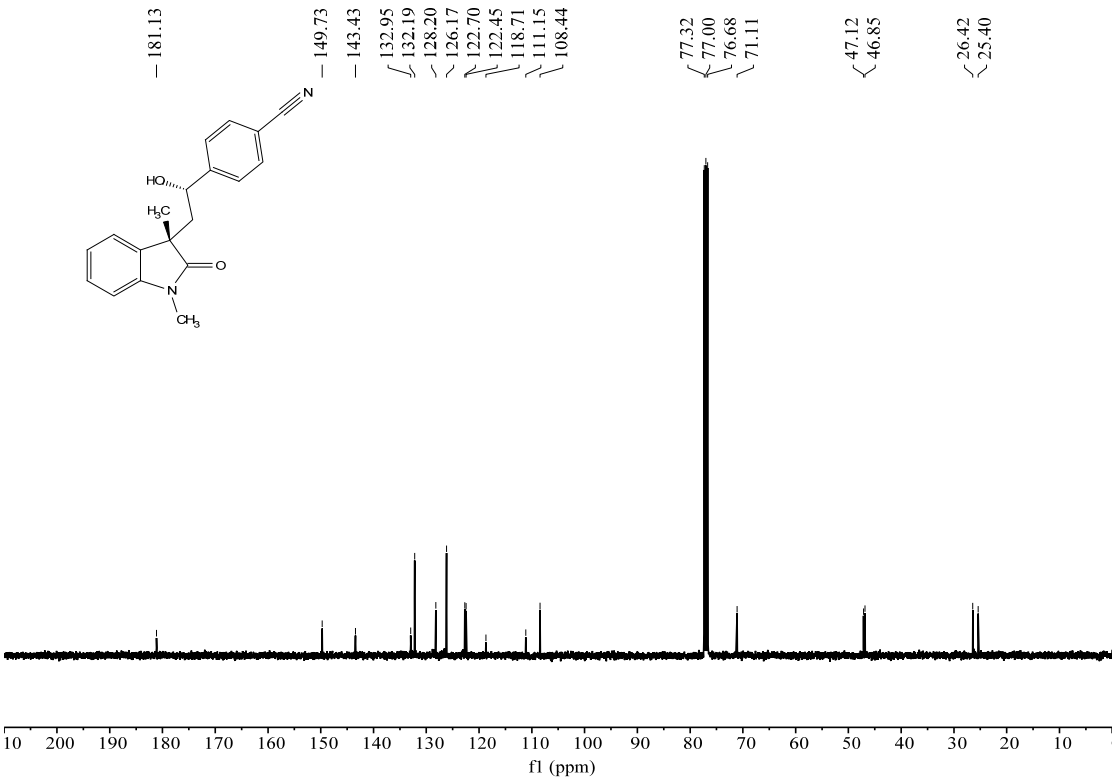
^{13}C NMR spectra of 36a (100 MHz, $CDCl_3$)



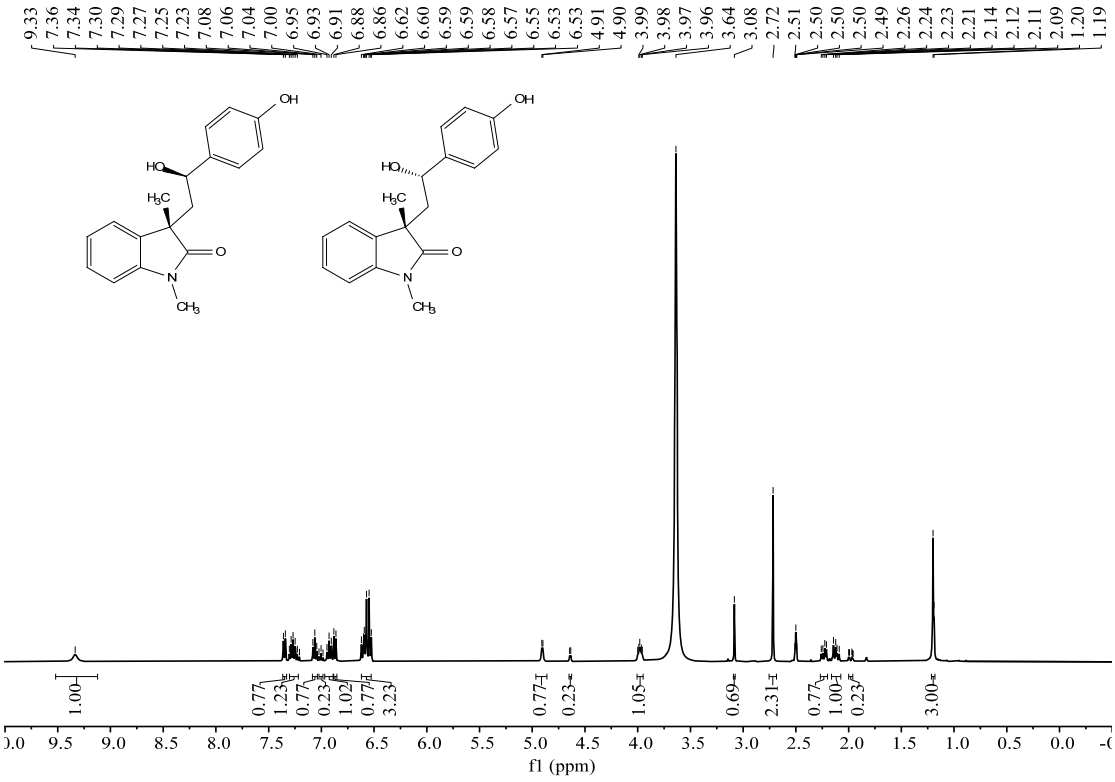
^{1}H NMR spectra of 36b (400 MHz, $CDCl_3$)



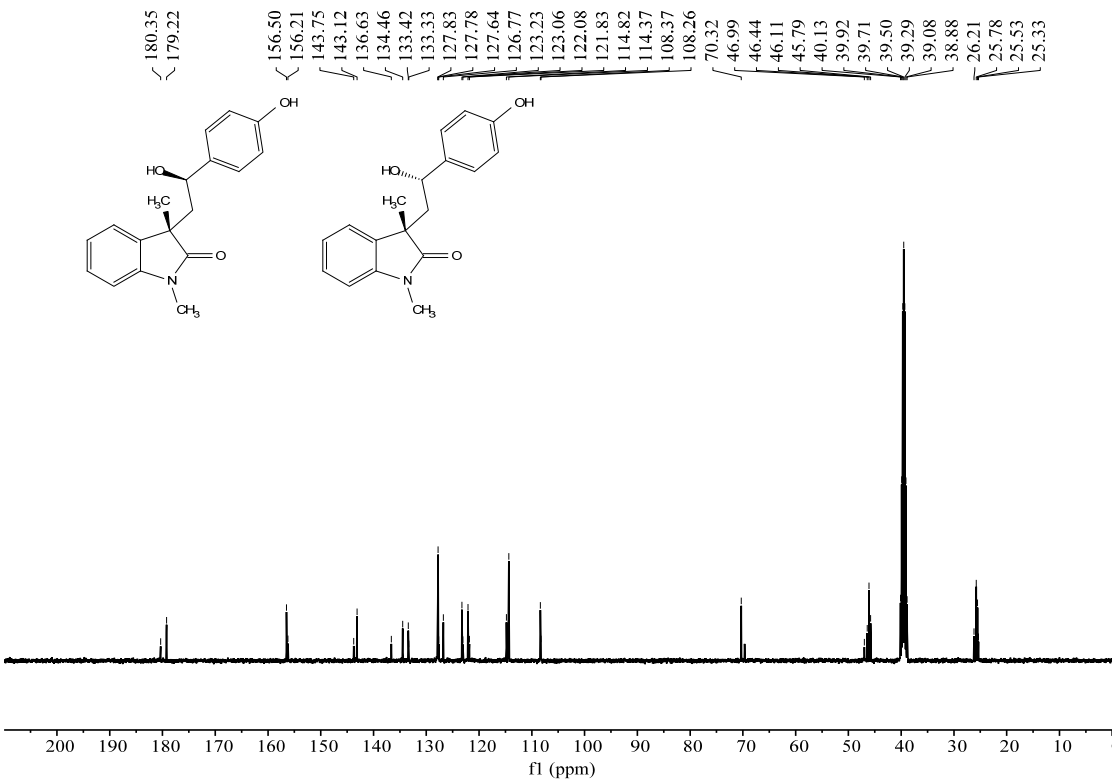
^{13}C NMR spectra of 36b (100 MHz, $CDCl_3$)



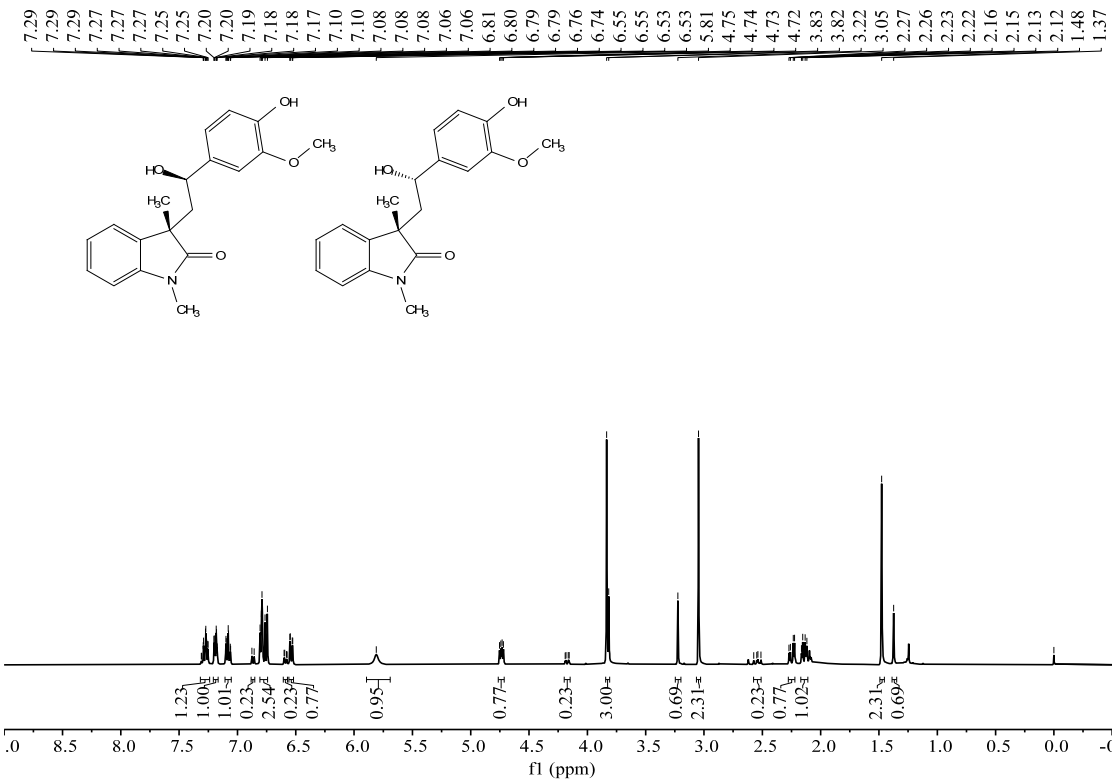
^{1}H NMR spectra of 37ab (400 MHz, DMSO-d_6)



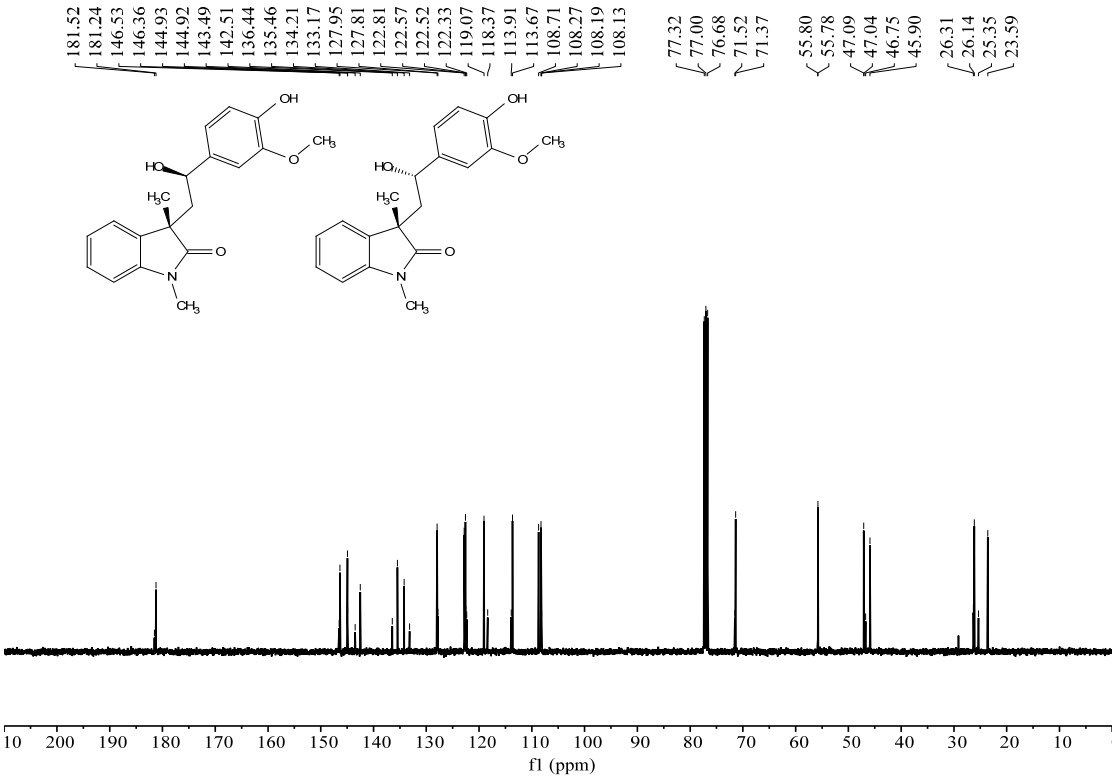
^{13}C NMR spectra of 37ab (100 MHz, DMSO-d_6)



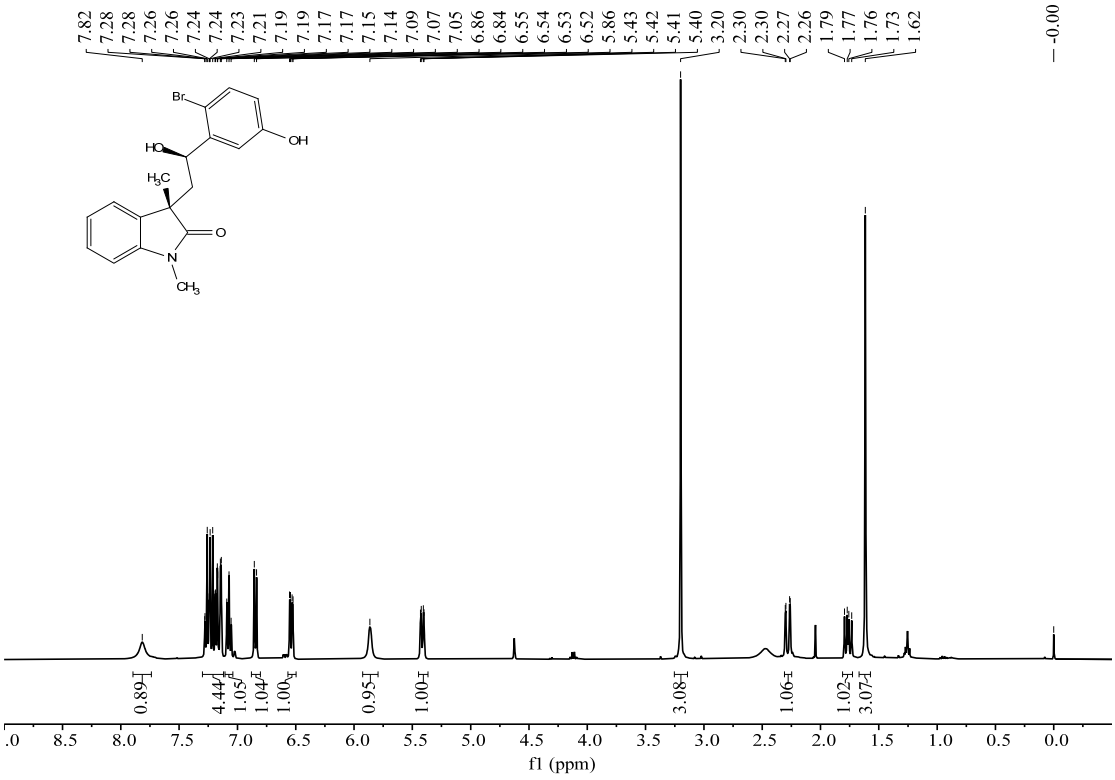
^{1}H NMR spectra of 38ab (400 MHz, $CDCl_3$)



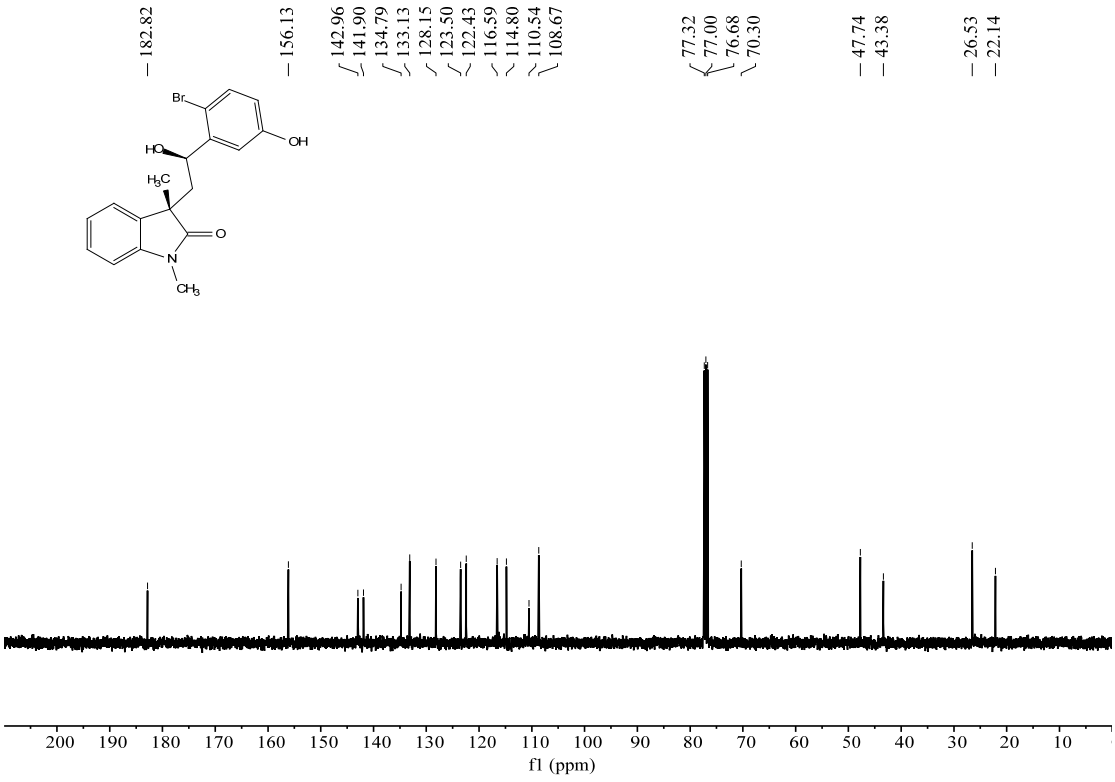
^{13}C NMR spectra of 38ab (100 MHz, $CDCl_3$)



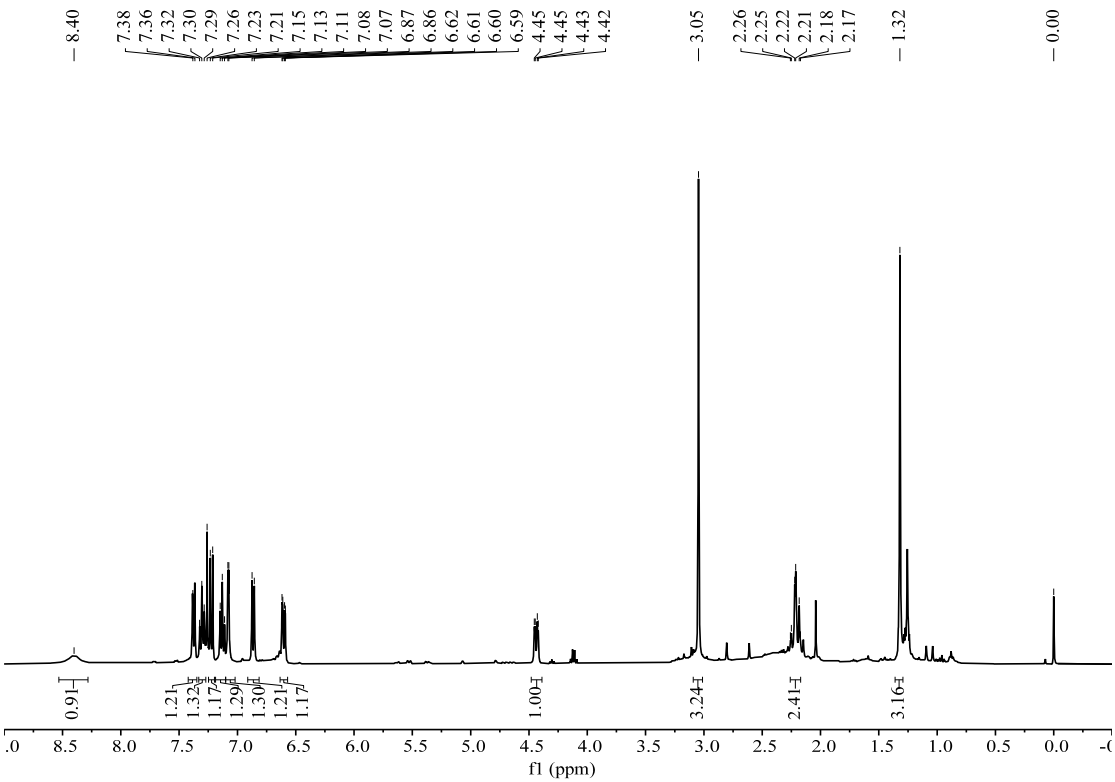
^{1}H NMR spectra of 39a (400 MHz, $CDCl_3$)



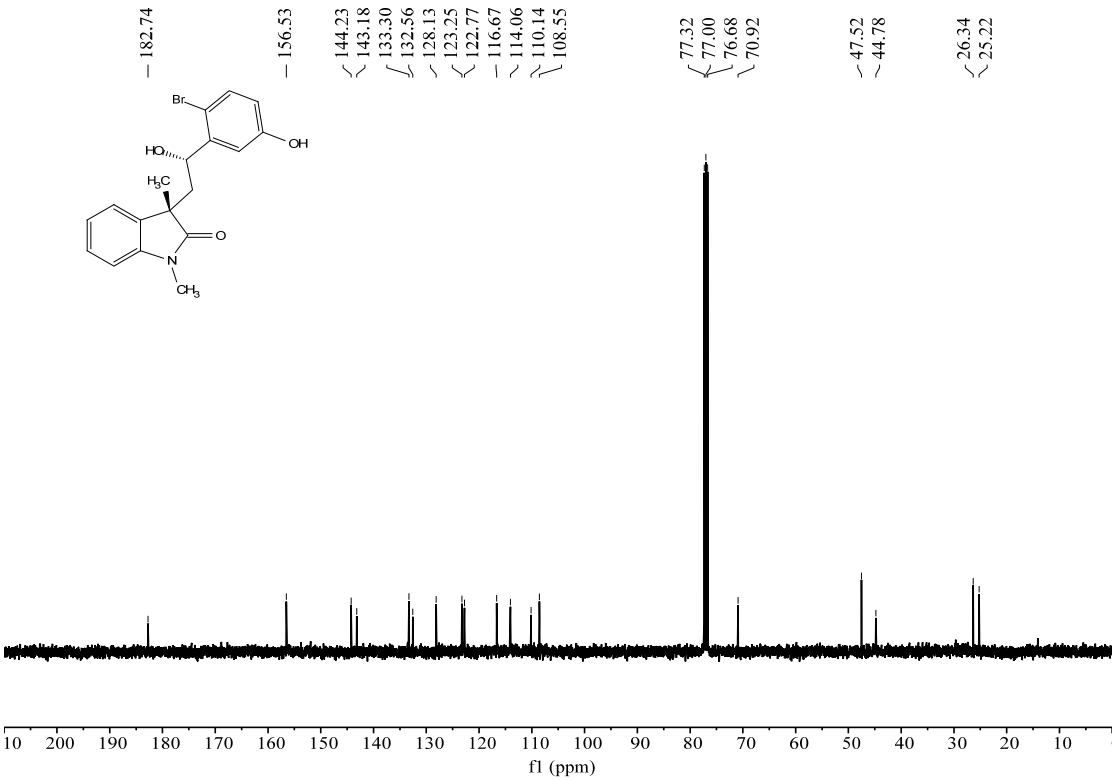
^{13}C NMR spectra of 39a (100 MHz, $CDCl_3$)



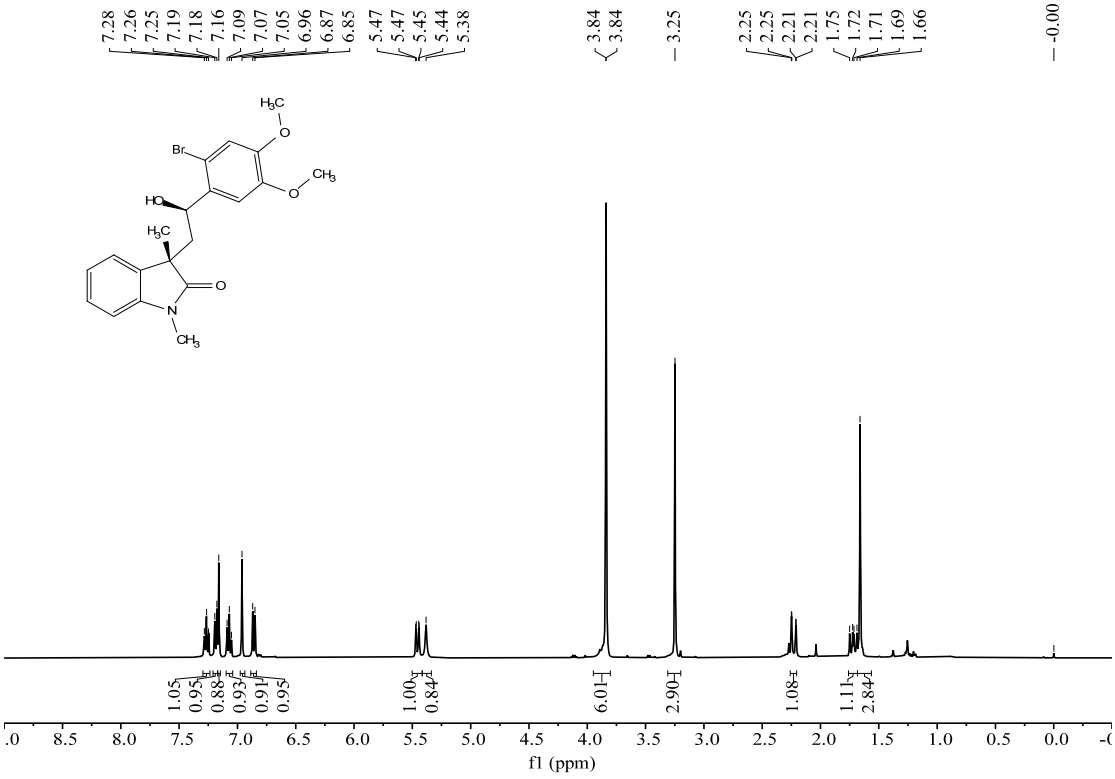
^{1}H NMR spectra of 39b (400 MHz, $CDCl_3$)



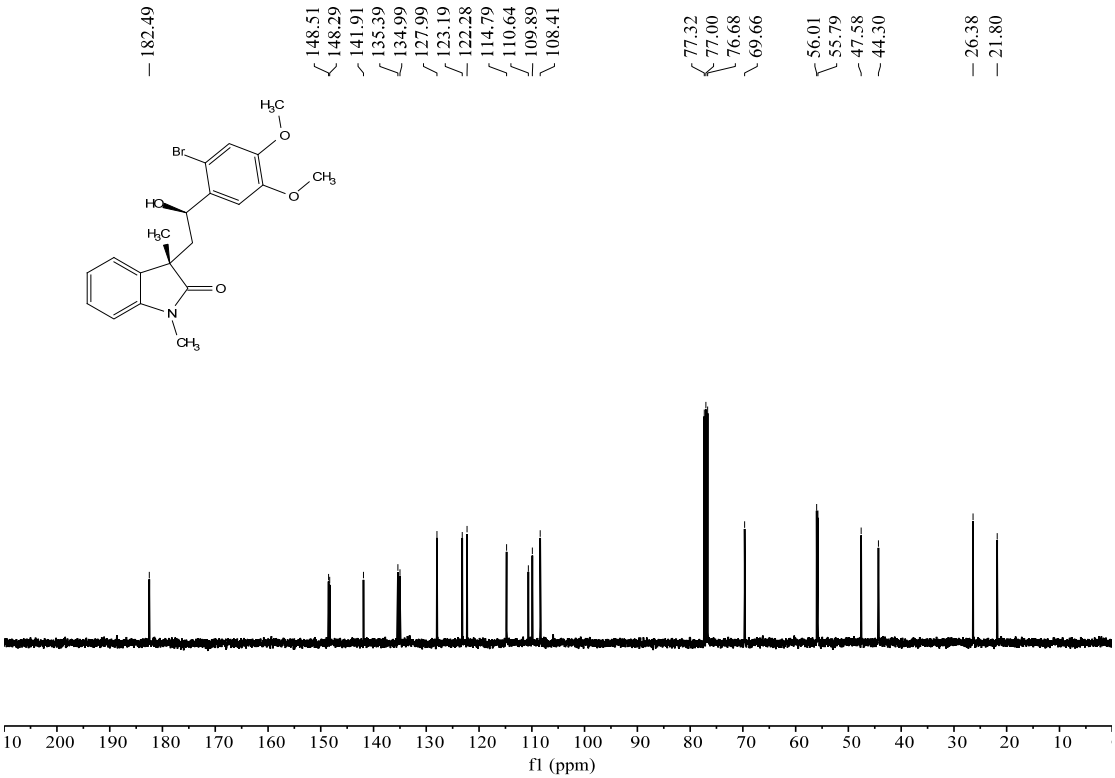
^{13}C NMR spectra of 39b (100 MHz, $CDCl_3$)



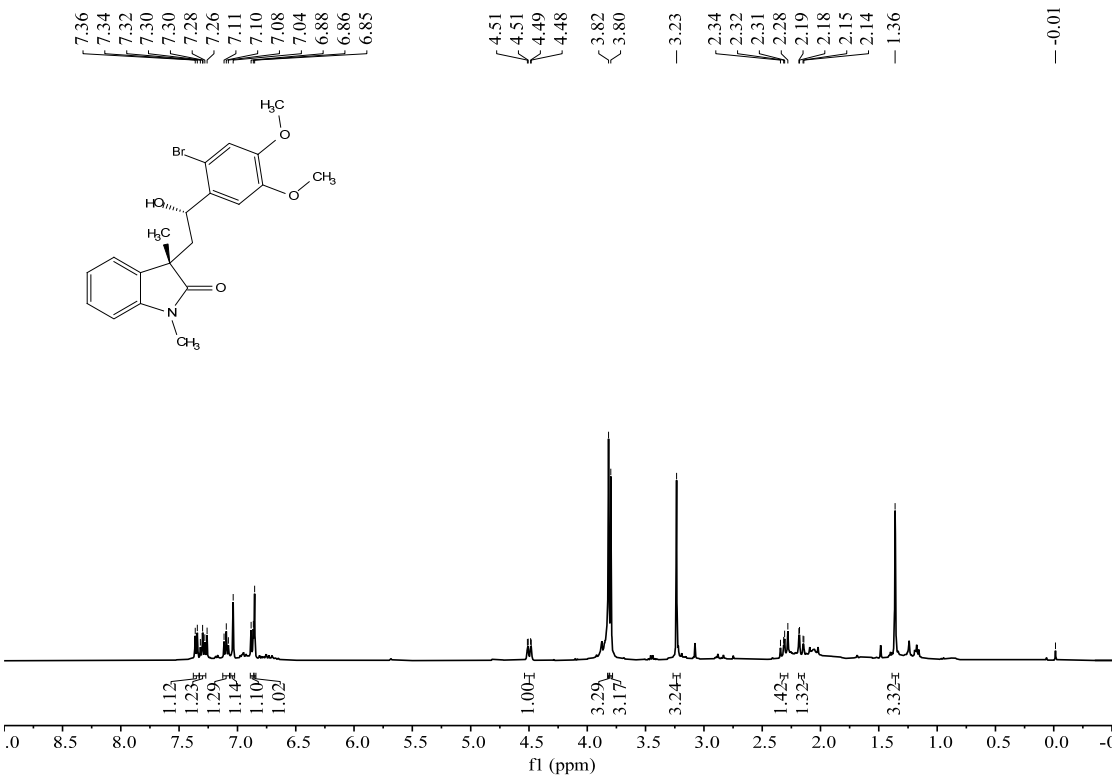
^{1}H NMR spectra of 40a (400 MHz, $CDCl_3$)



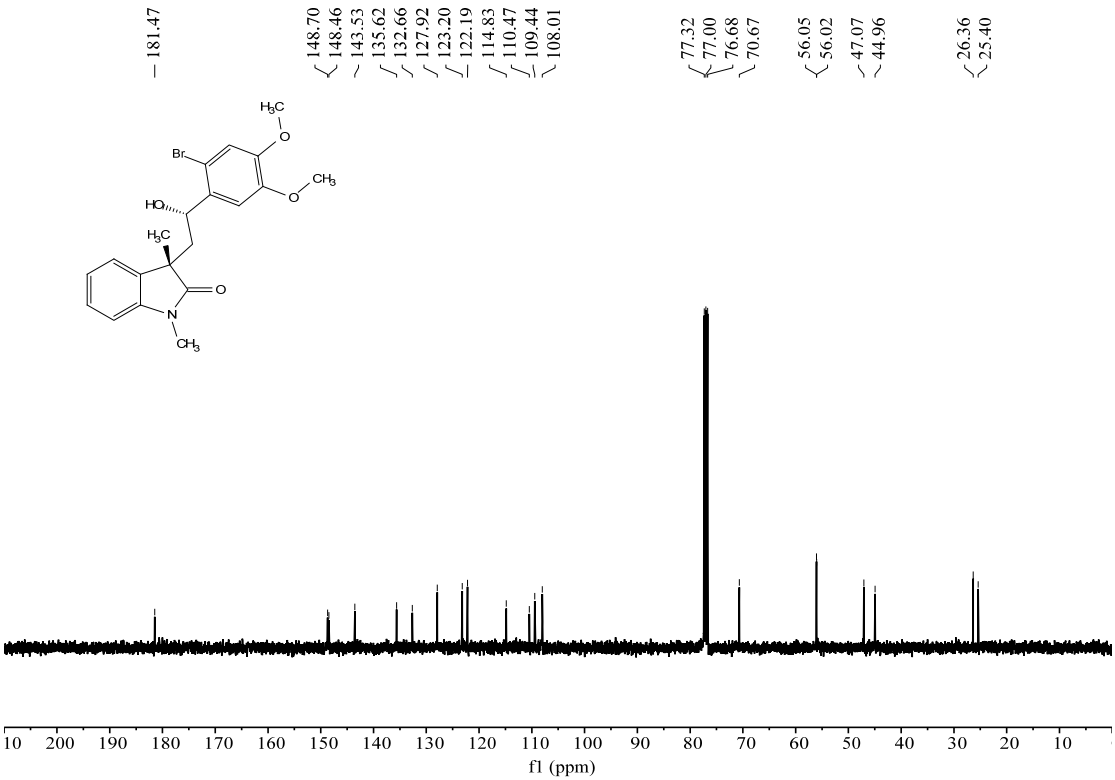
^{13}C NMR spectra of 40a (100 MHz, $CDCl_3$)



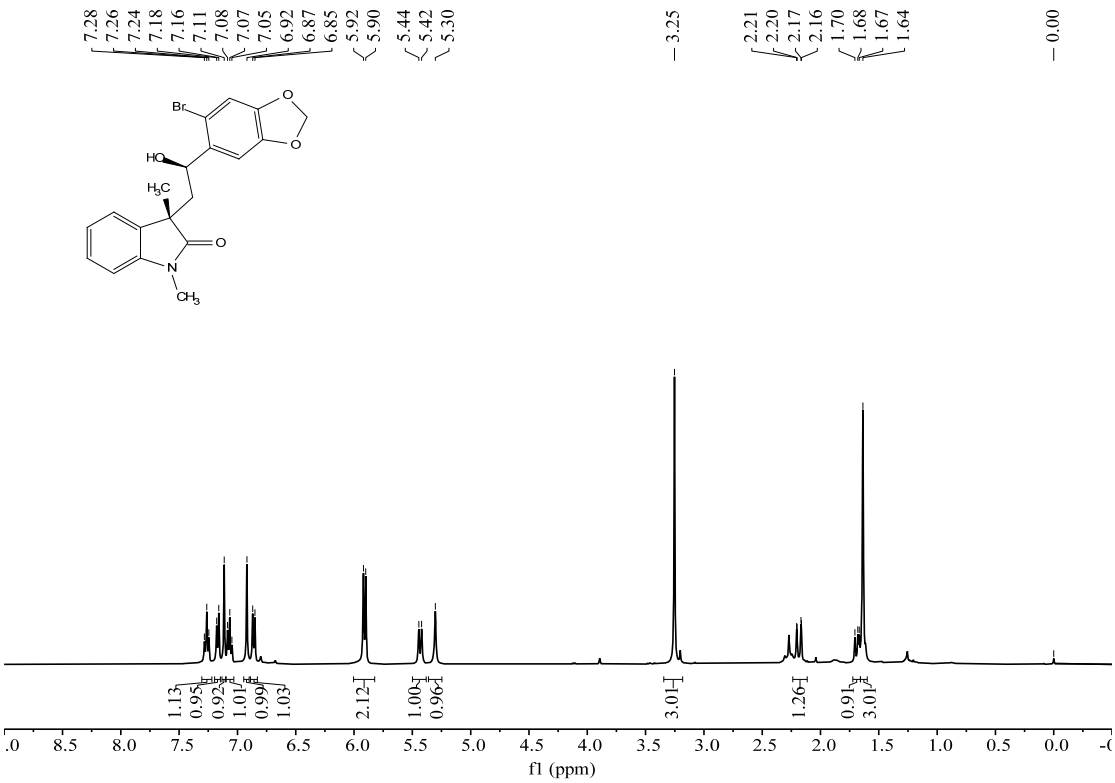
^{1}H NMR spectra of 40b (400 MHz, $CDCl_3$)



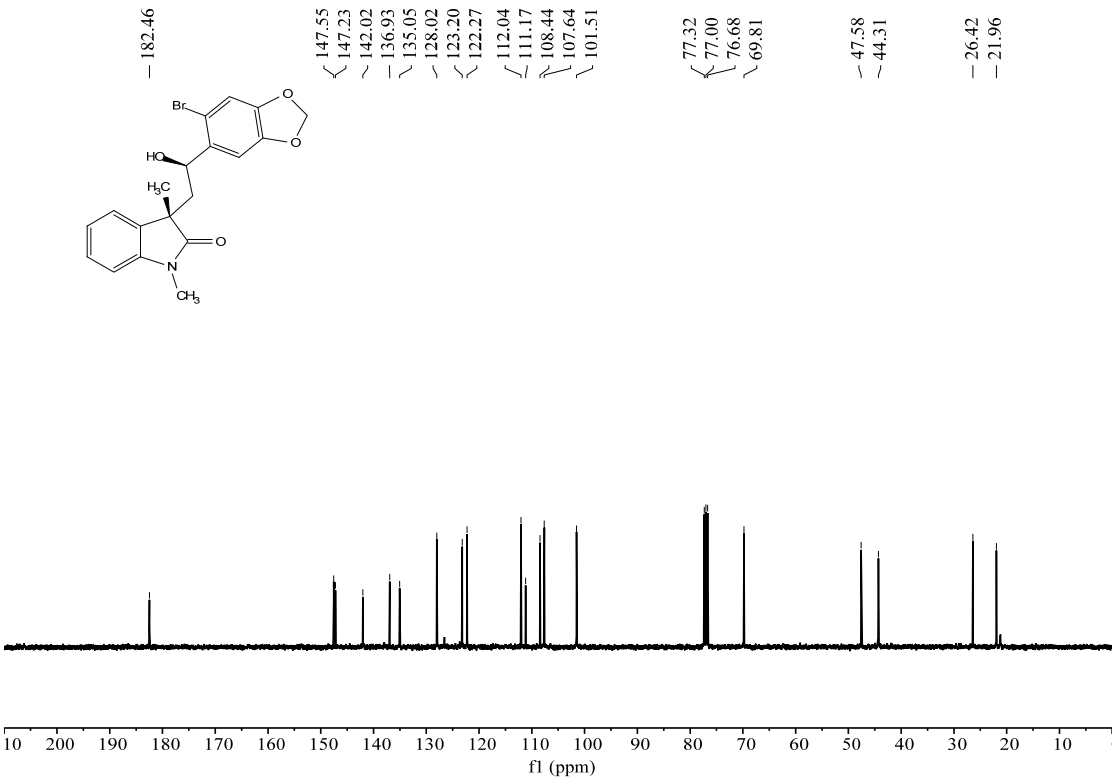
^{13}C NMR spectra of 40b (100 MHz, $CDCl_3$)



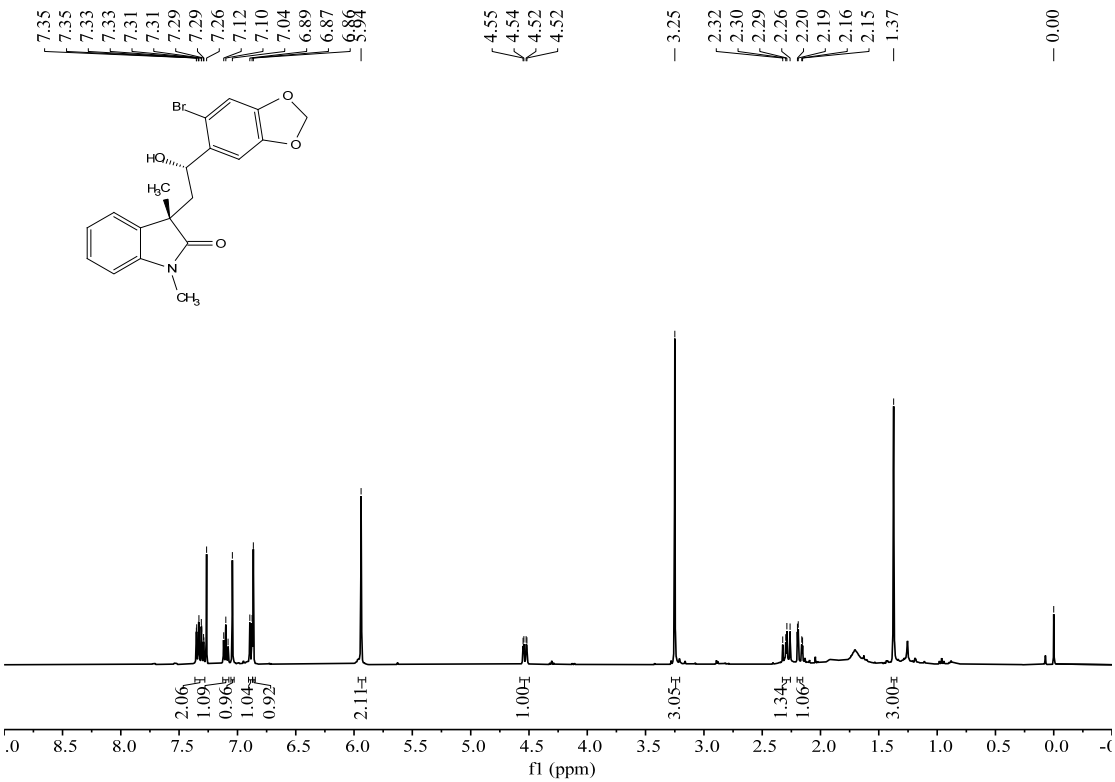
^{1}H NMR spectra of 41a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 41a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 41b (400 MHz, $CDCl_3$)



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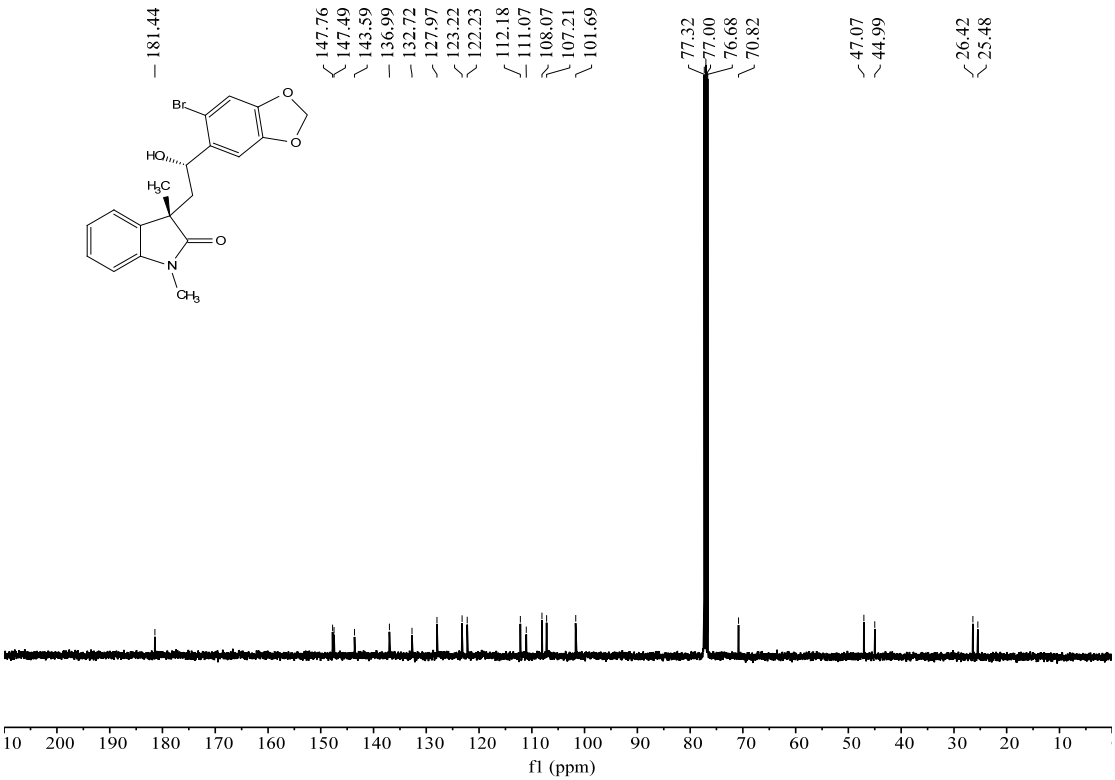
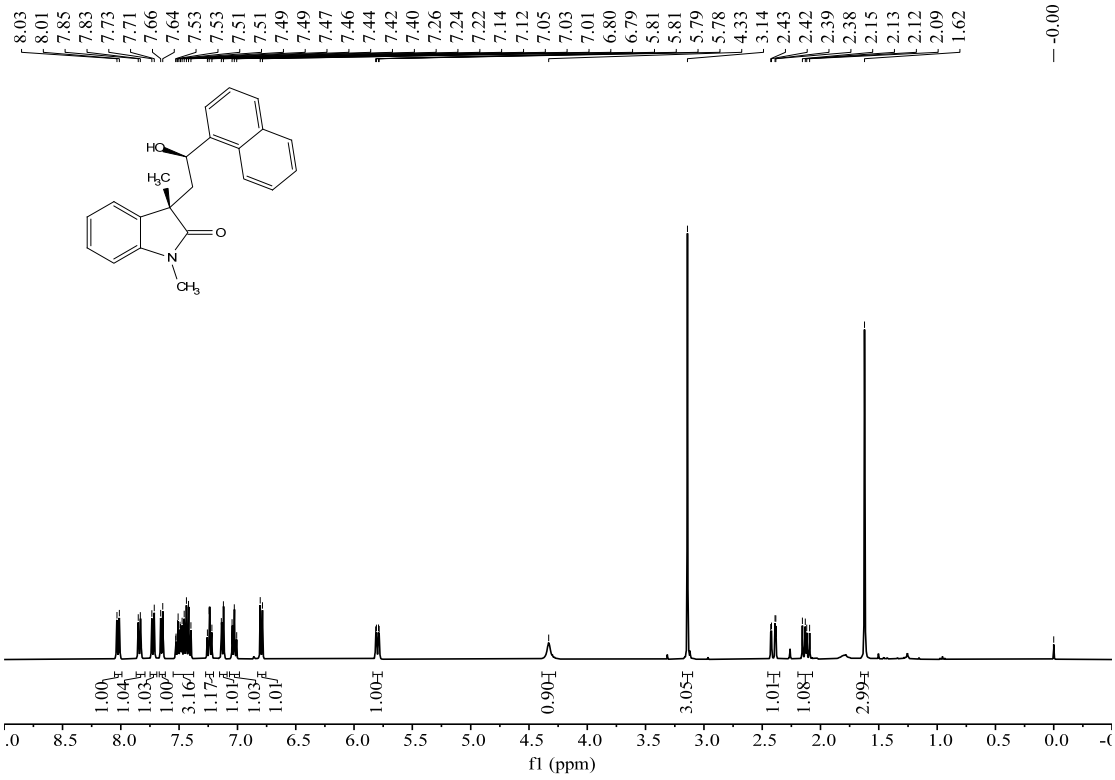
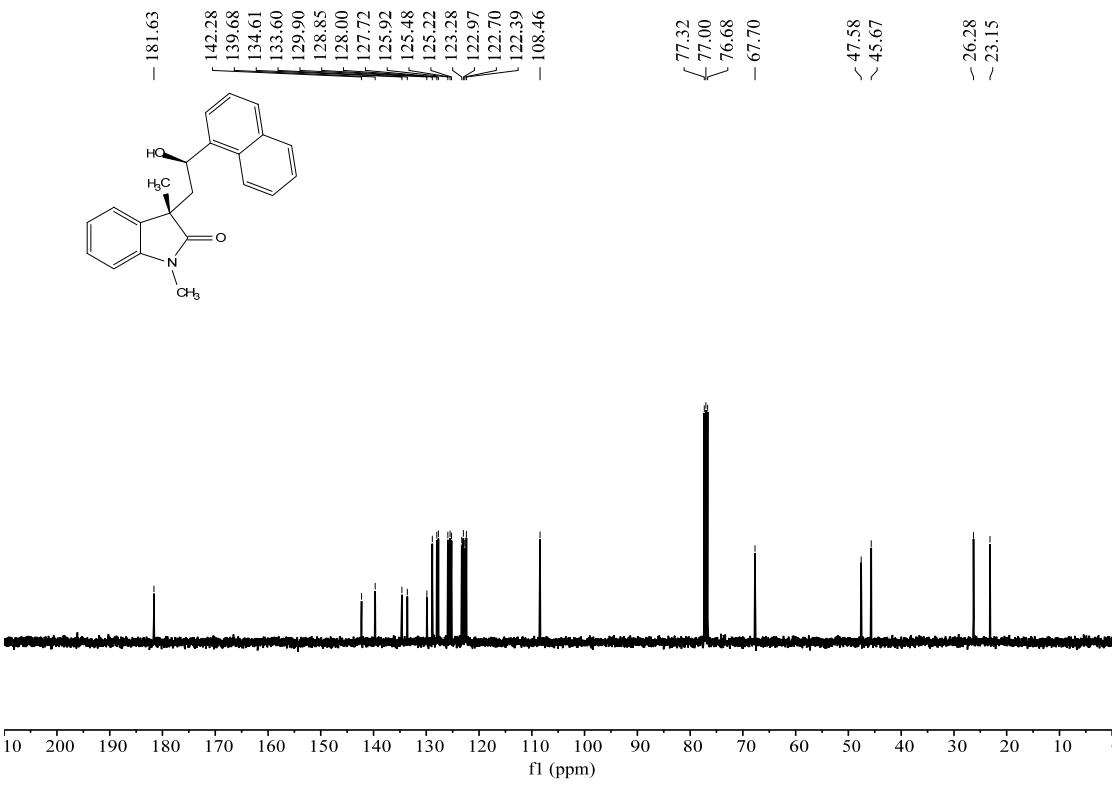


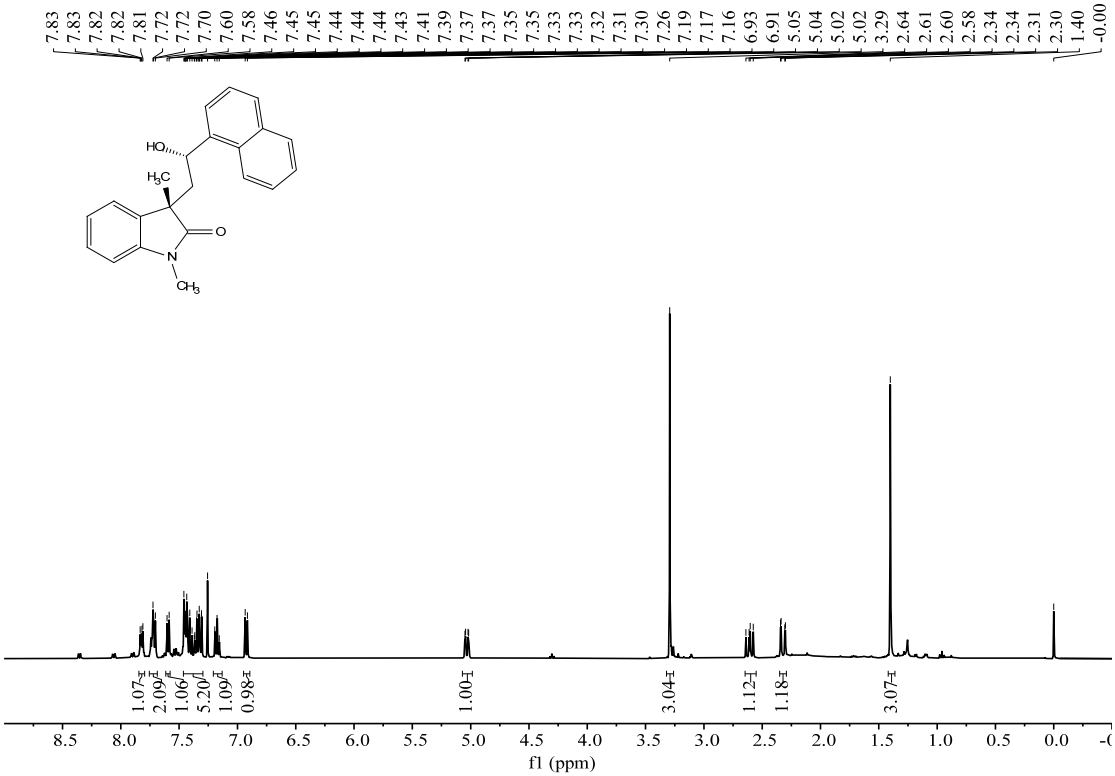
^{1}H NMR spectra of 42a (400 MHz, $CDCl_3$)



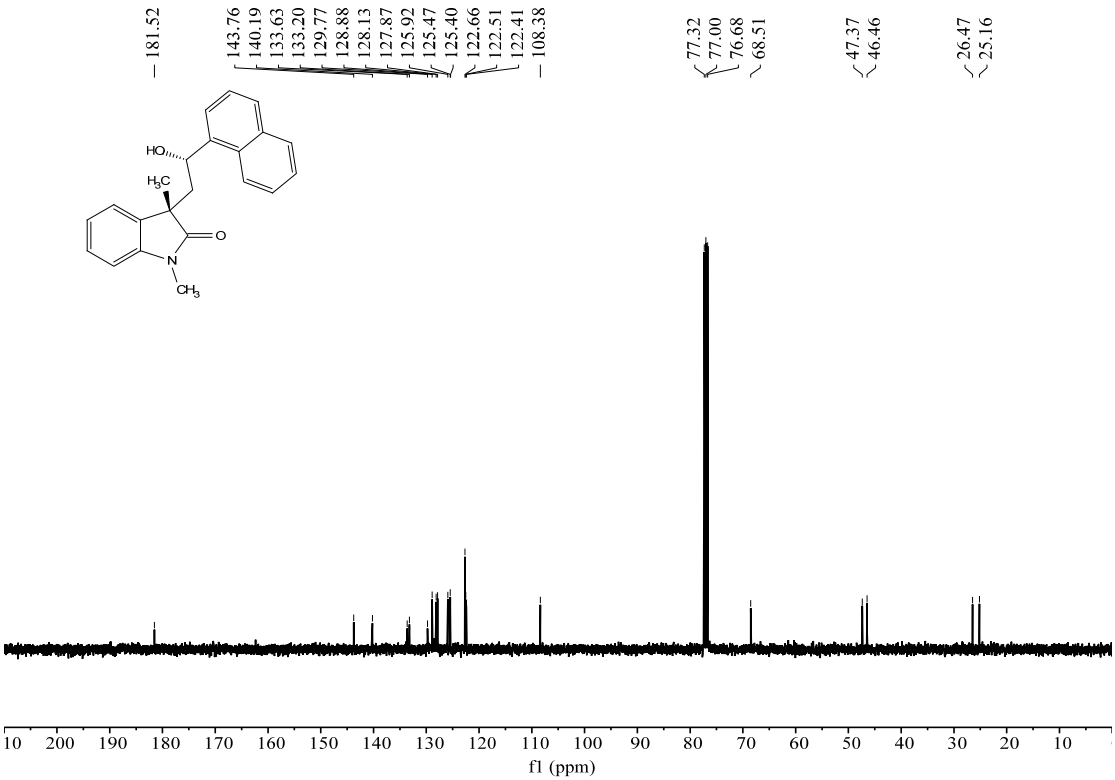
^{13}C NMR spectra of 42a (100 MHz, $CDCl_3$)



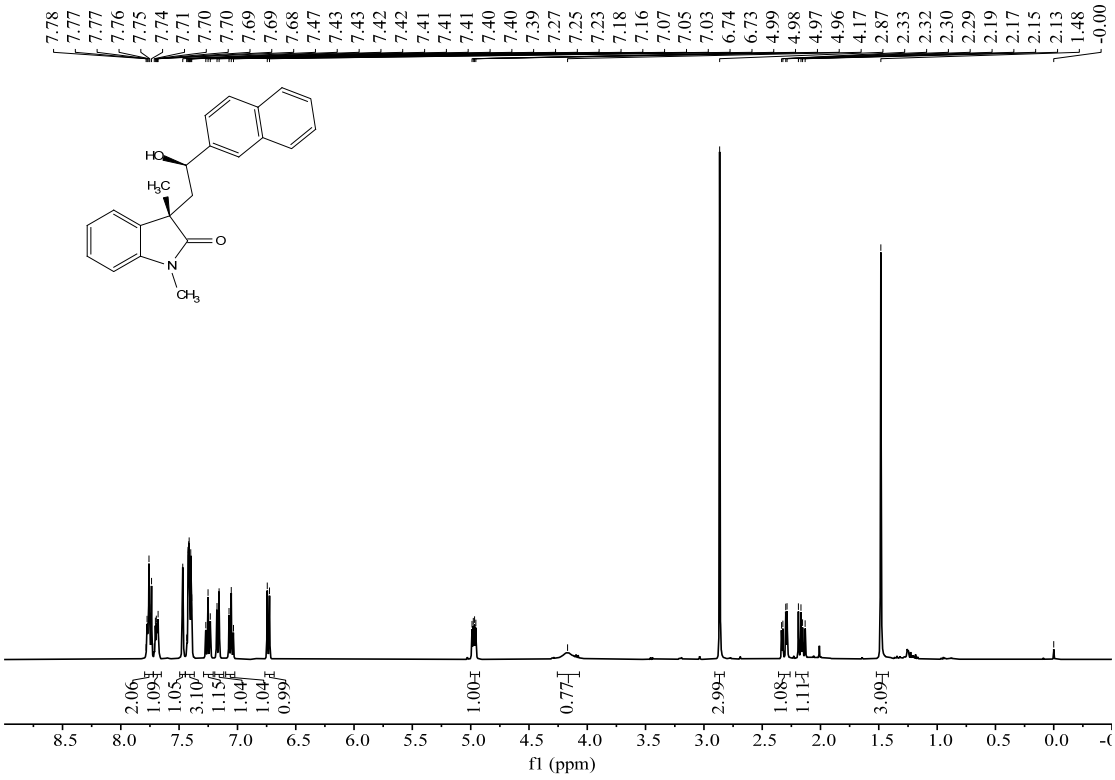
^{1}H NMR spectra of 42b (400 MHz, $CDCl_3$)



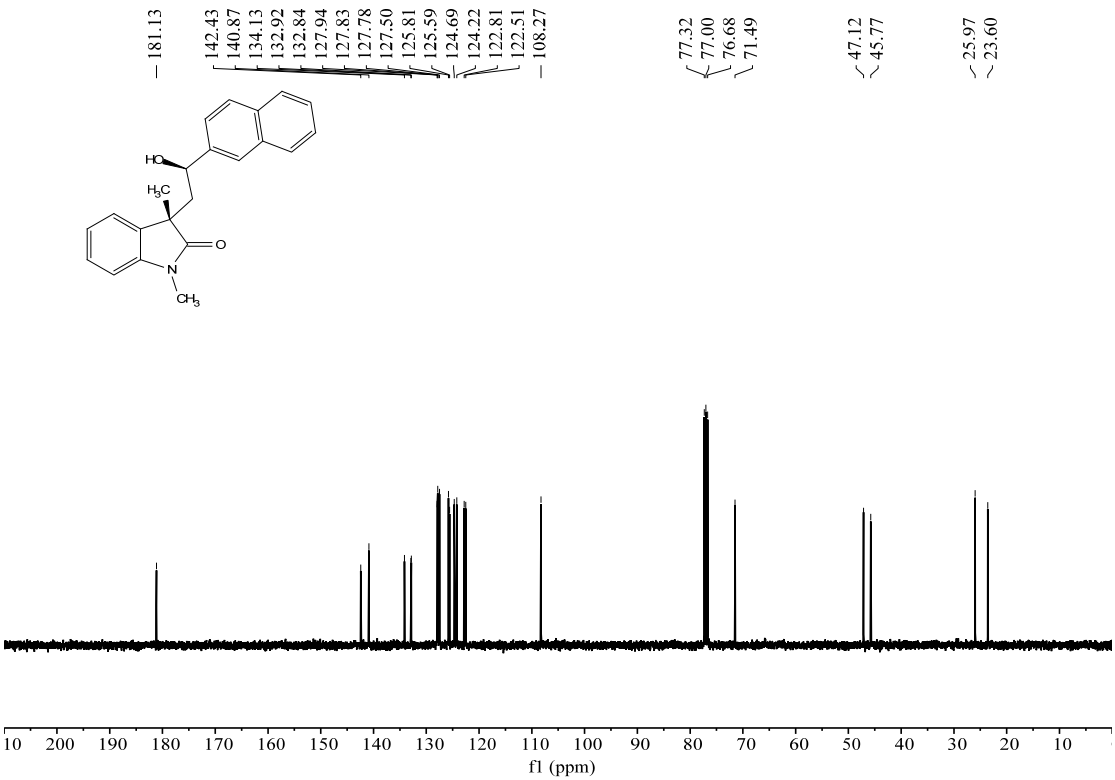
^{13}C NMR spectra of 42b (100 MHz, $CDCl_3$)



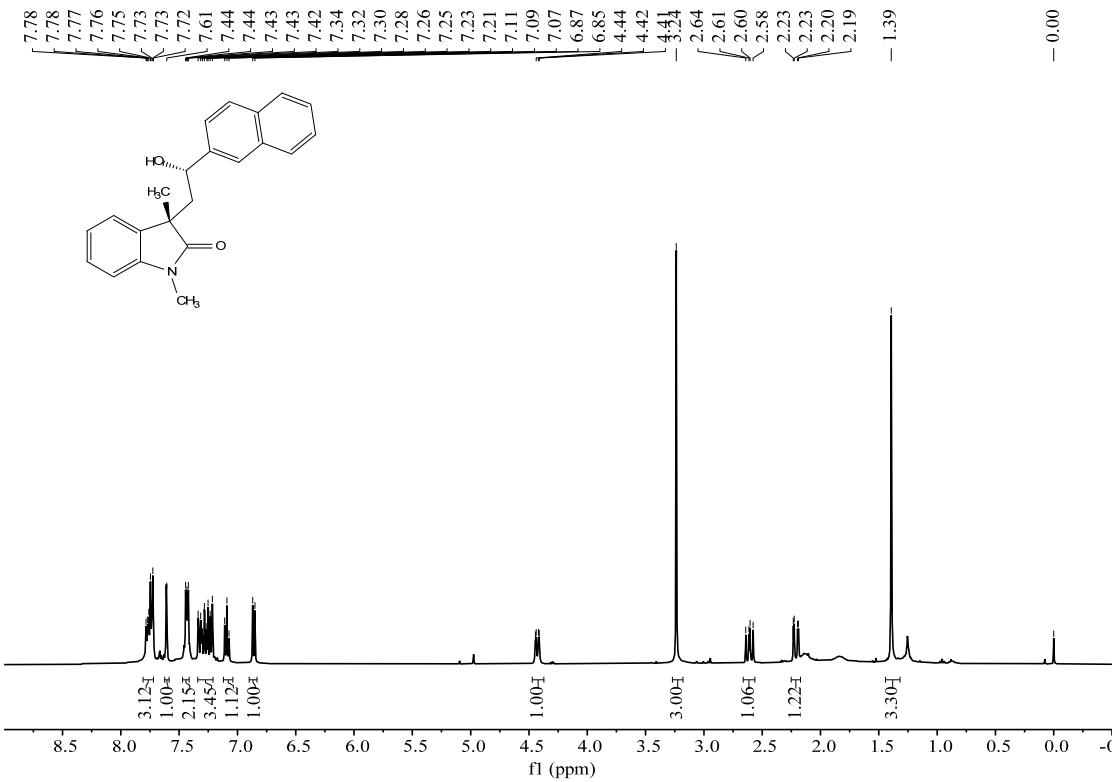
^{1}H NMR spectra of 43a (400 MHz, $CDCl_3$)



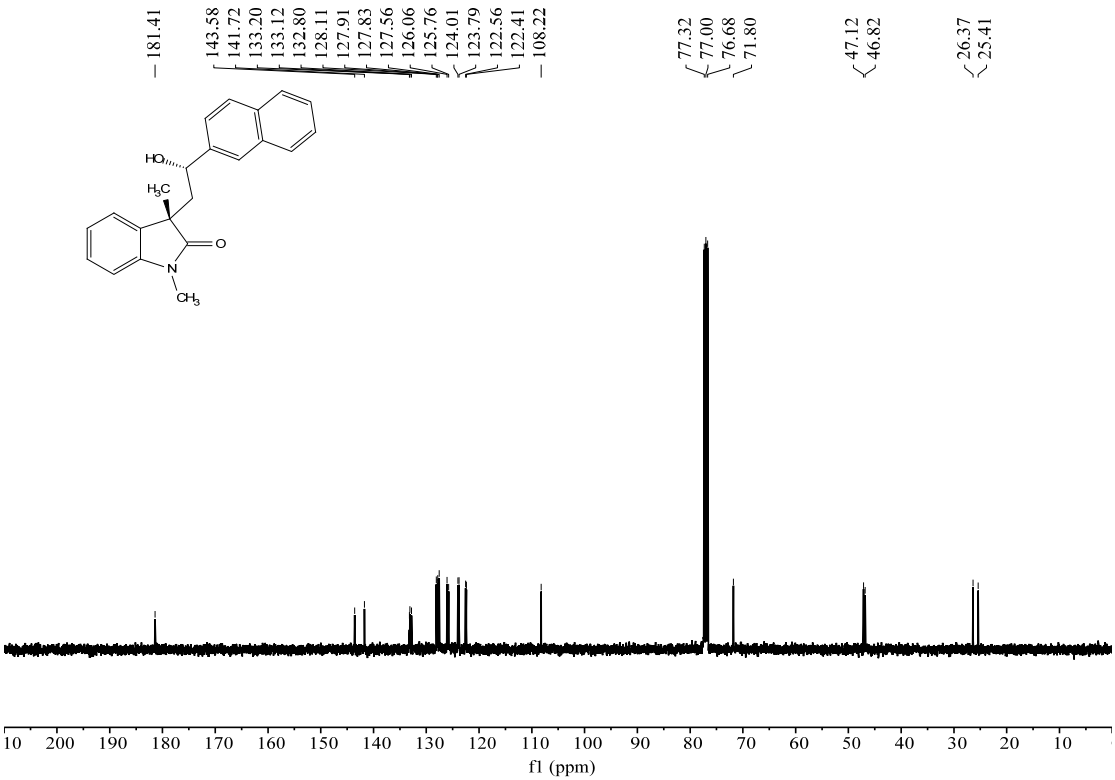
^{13}C NMR spectra of 43a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 43b (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 43b (100 MHz, $CDCl_3$)



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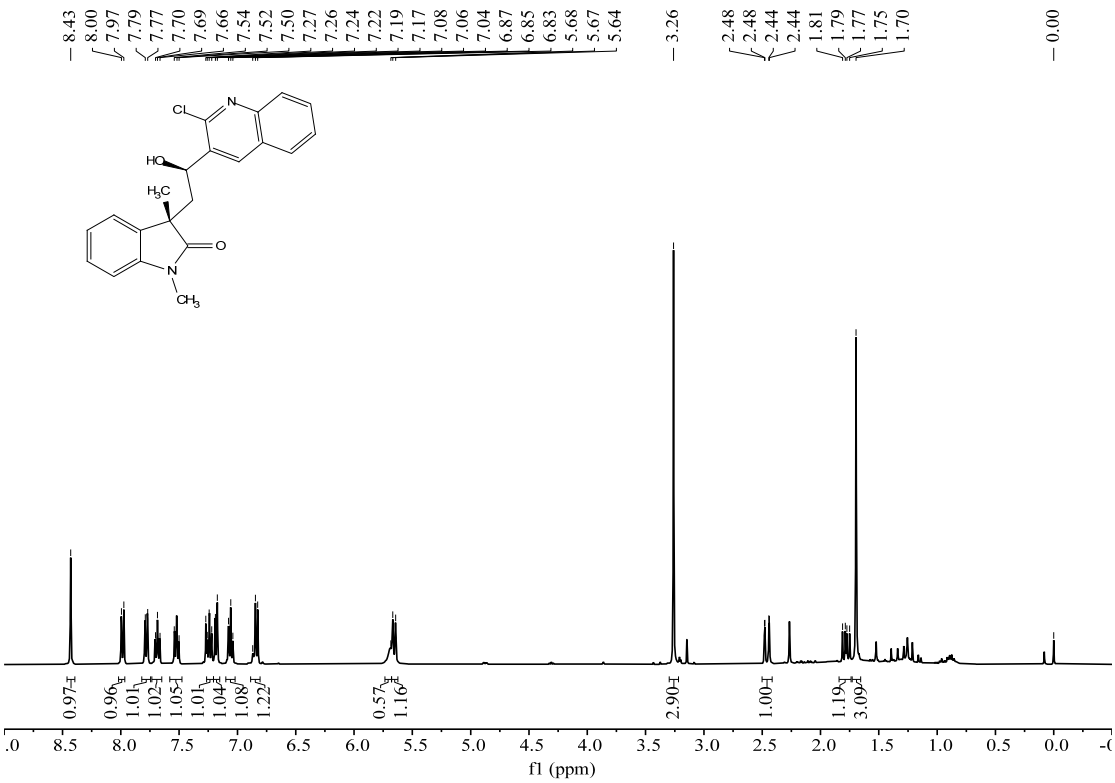
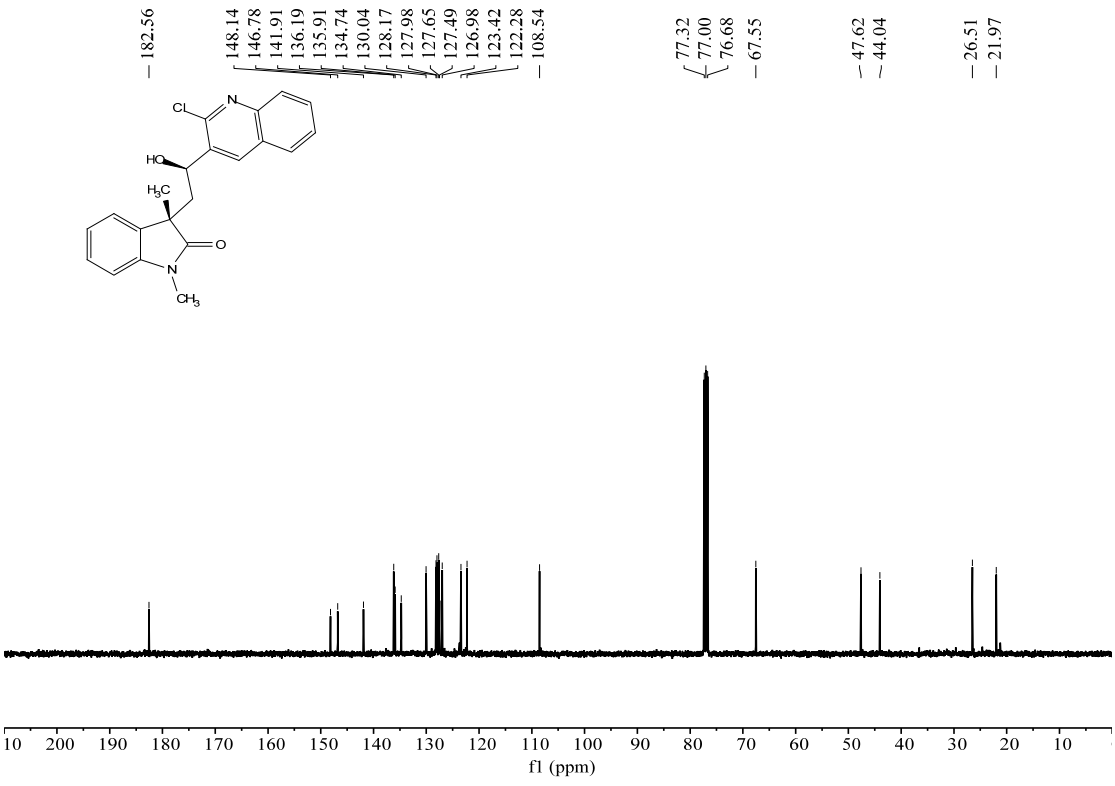
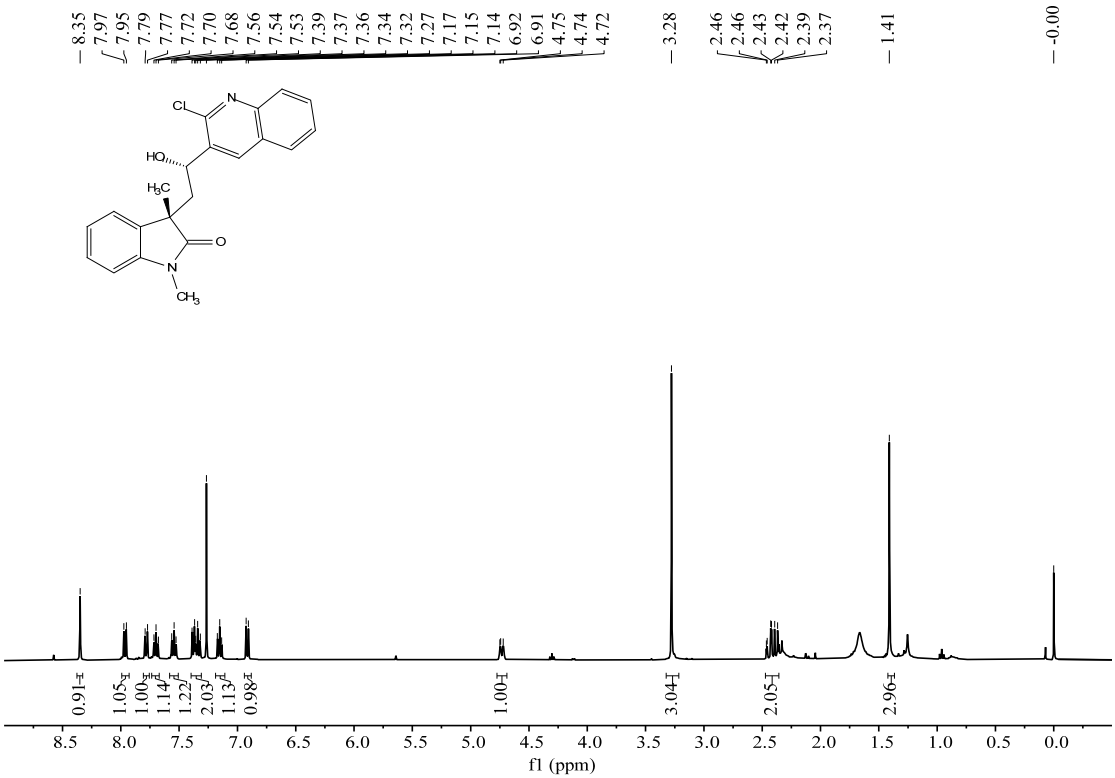


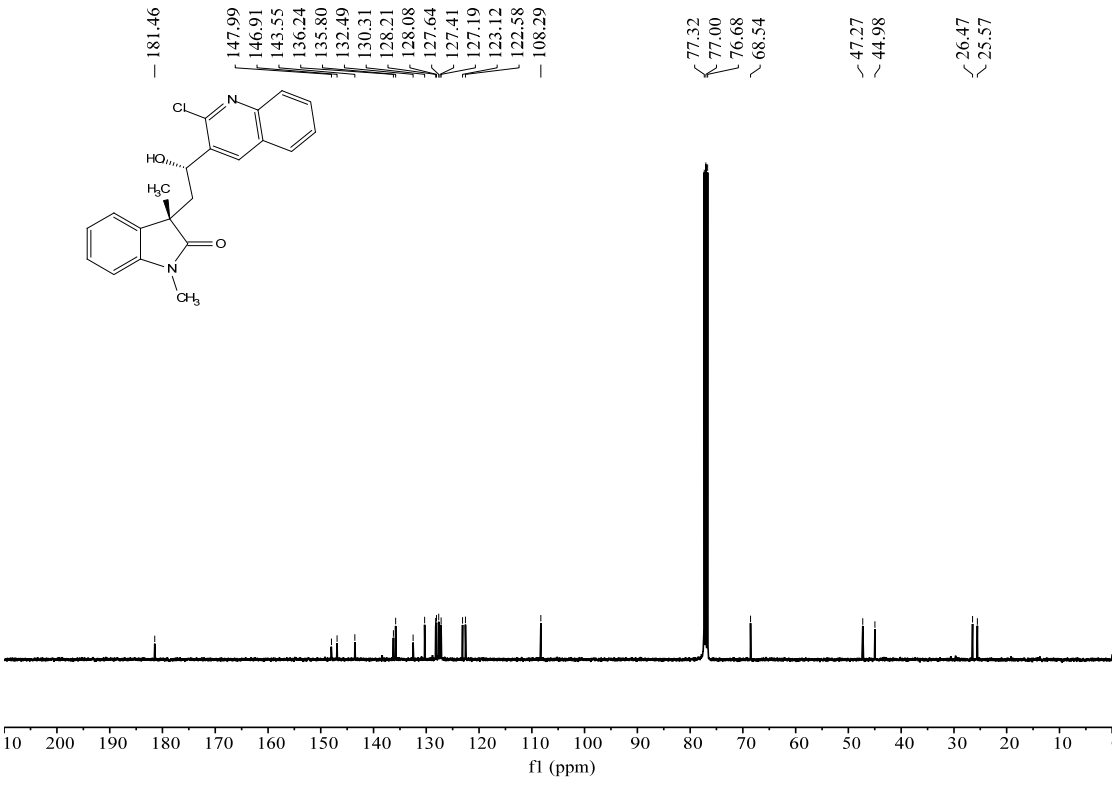
^{13}C NMR spectra of 44a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 44b (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 44b (100 MHz, $CDCl_3$)



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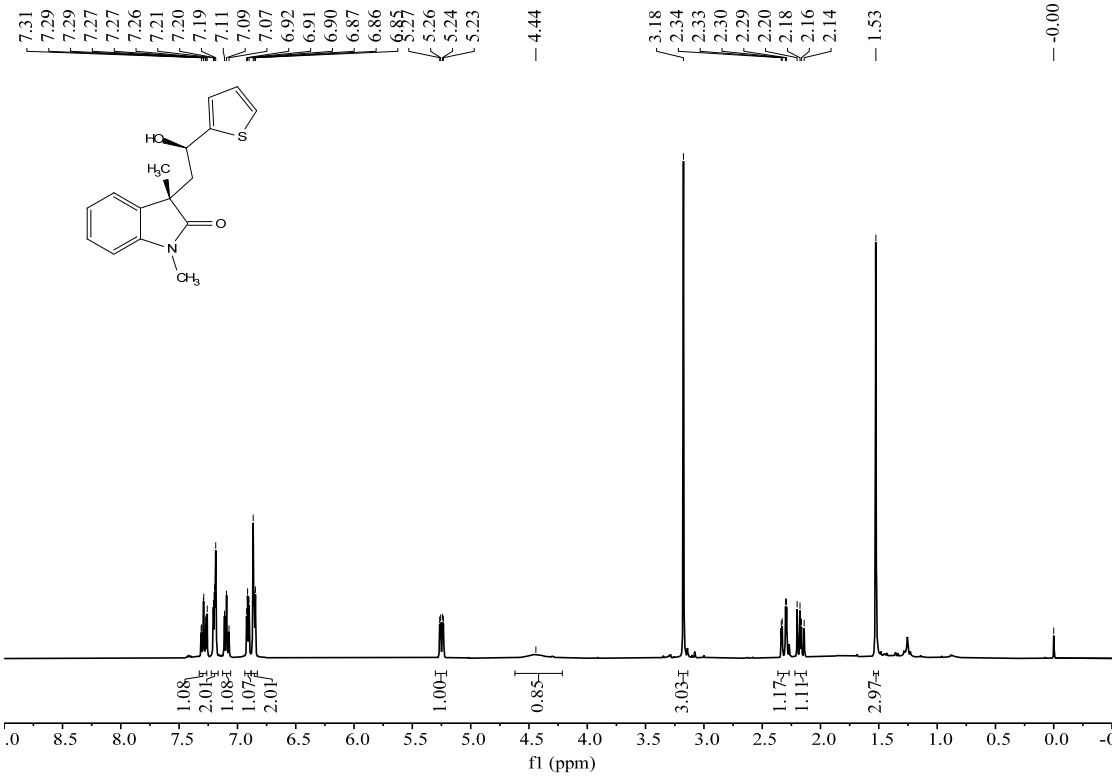
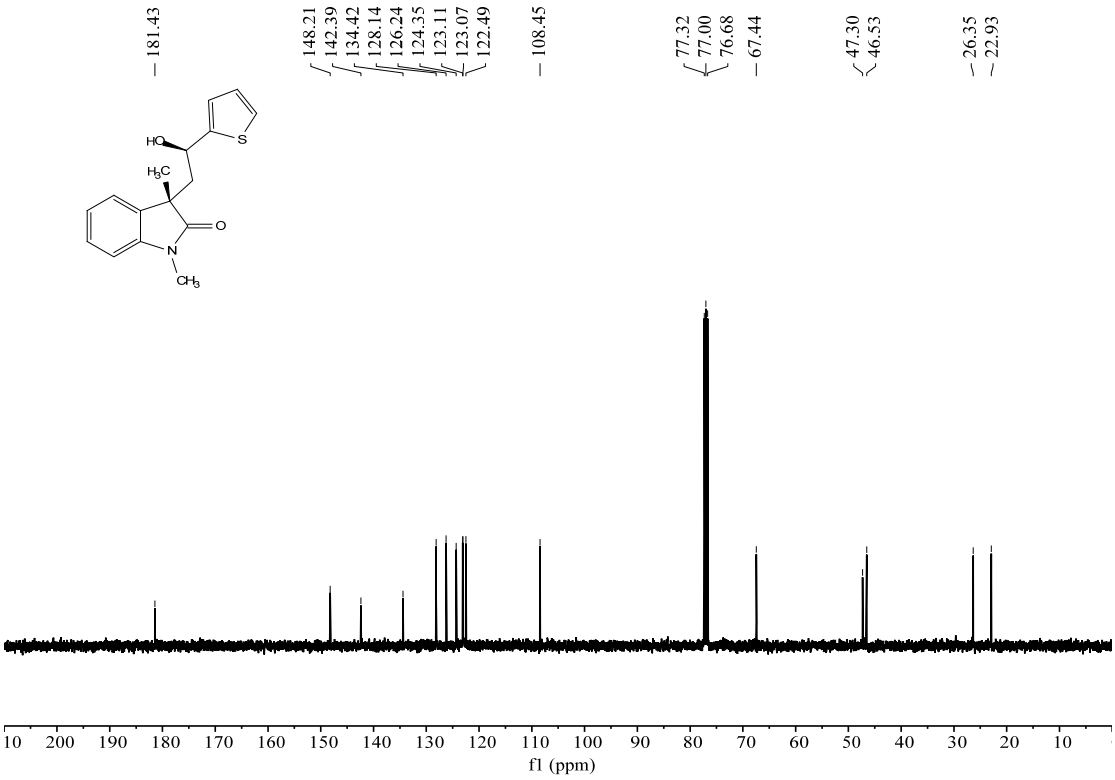
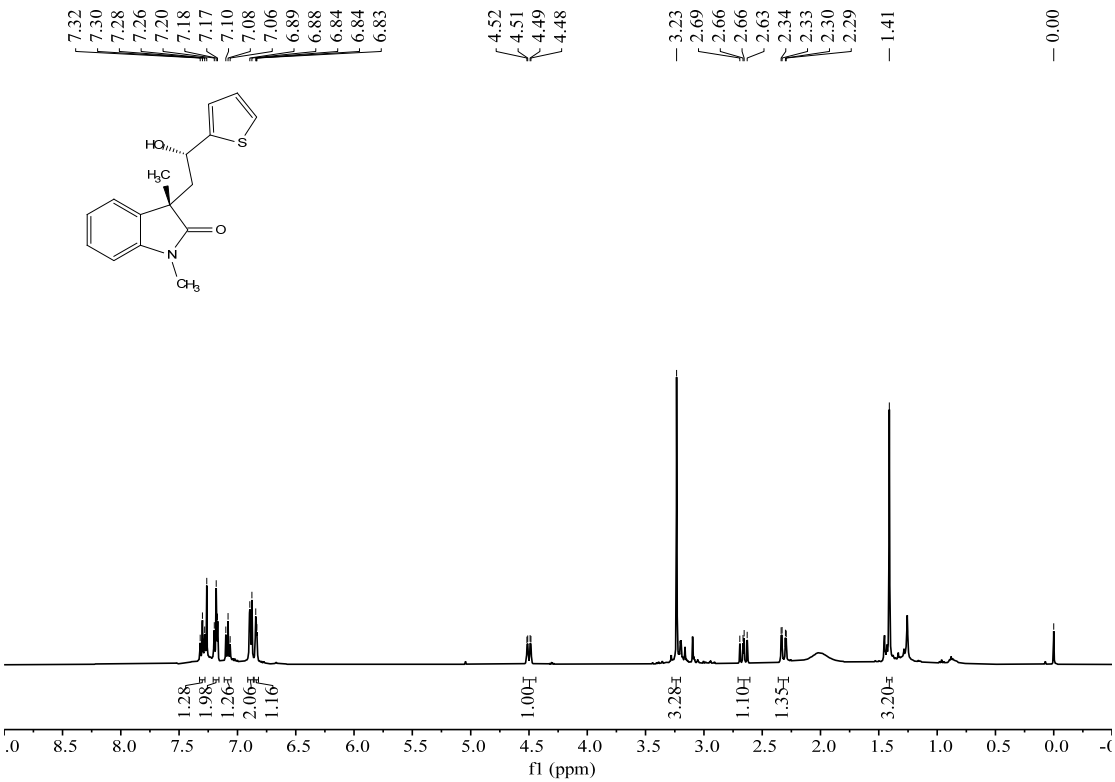


^{13}C NMR spectra of 45a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 45b (400 MHz, $CDCl_3$)



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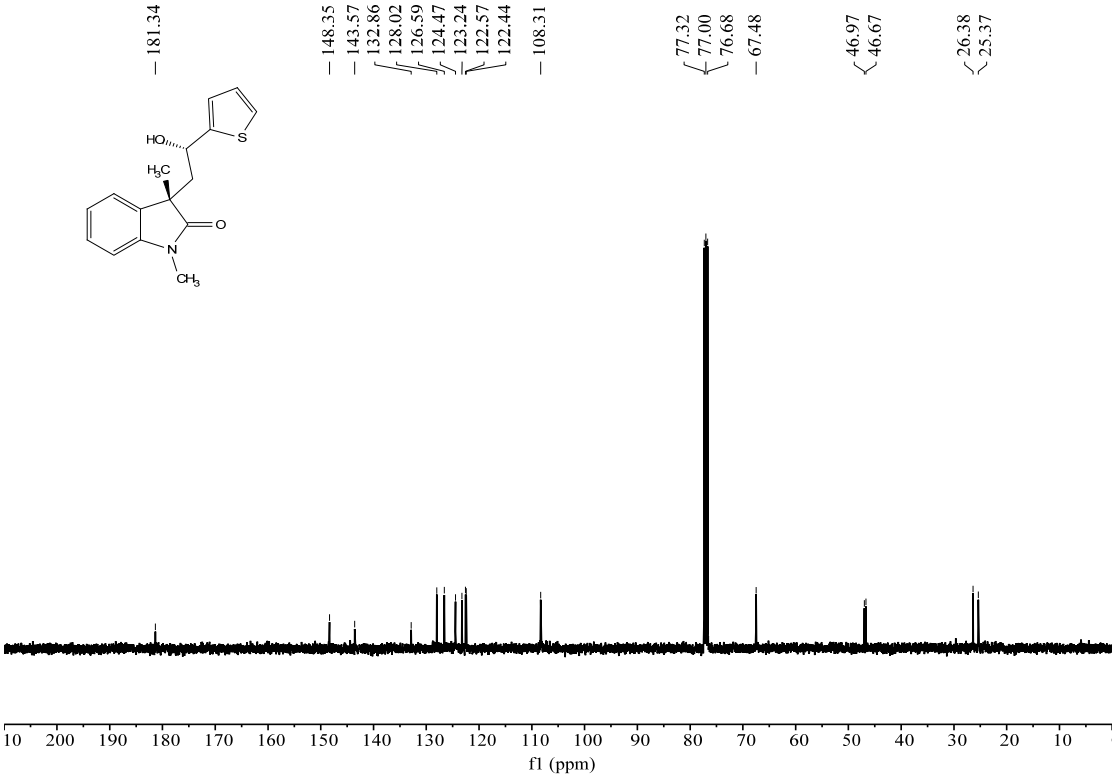
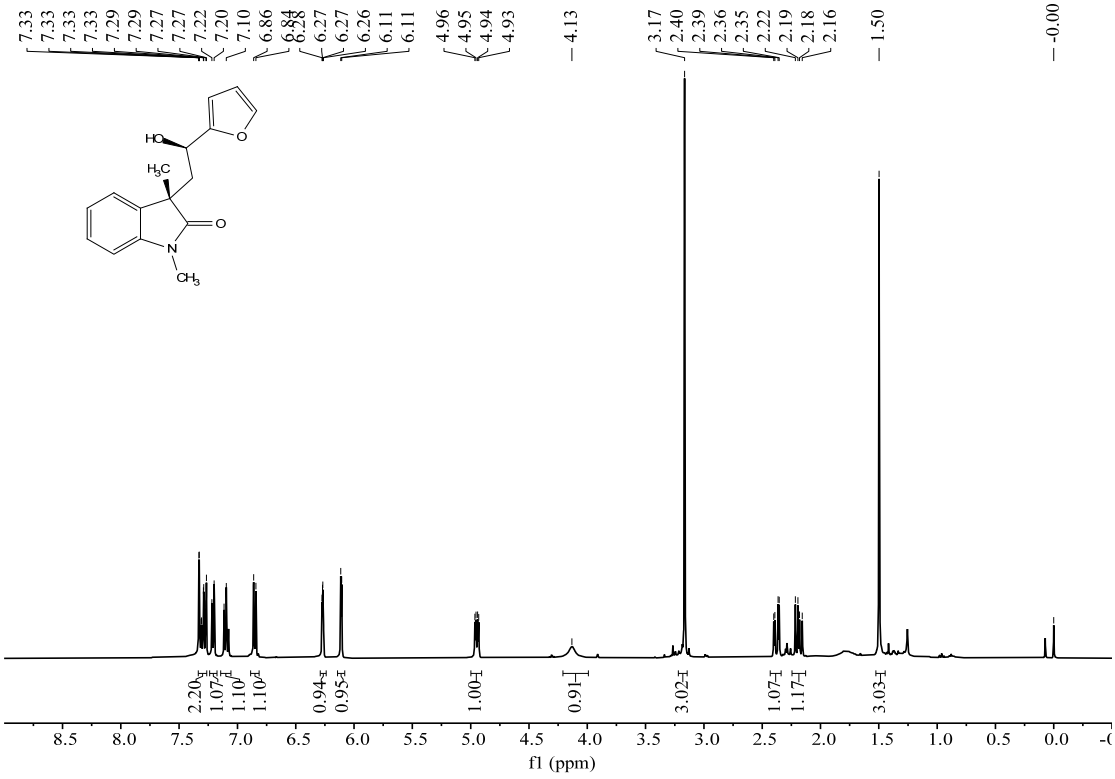
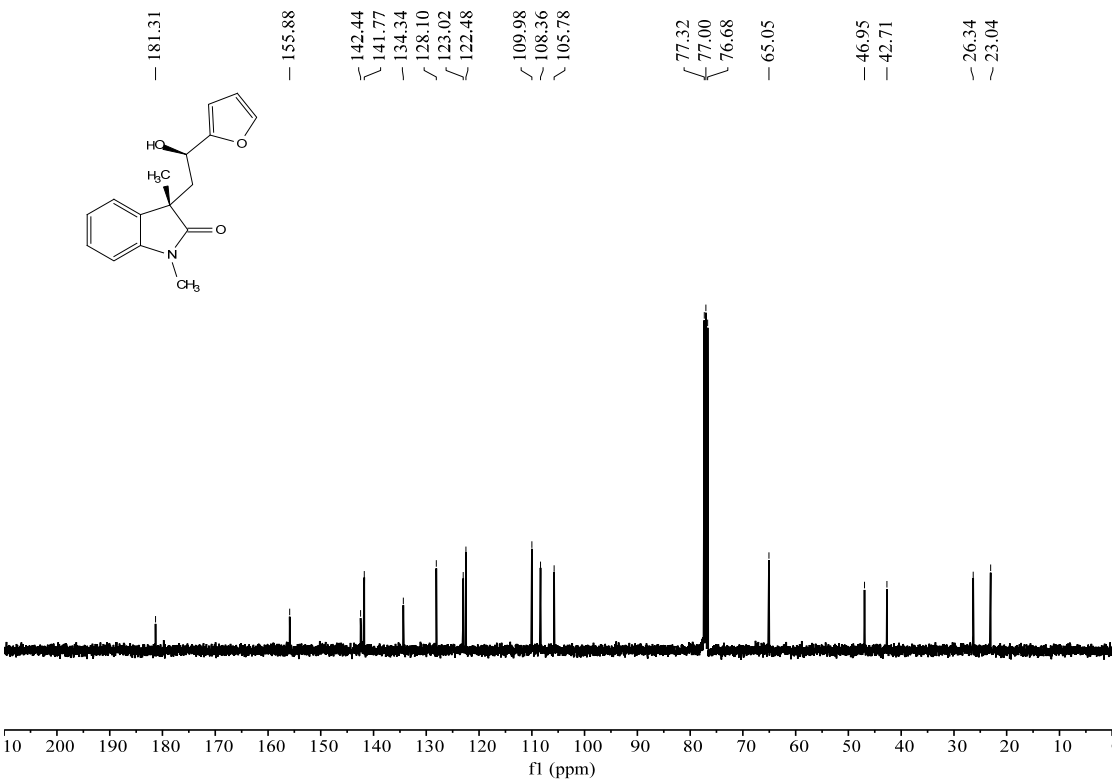


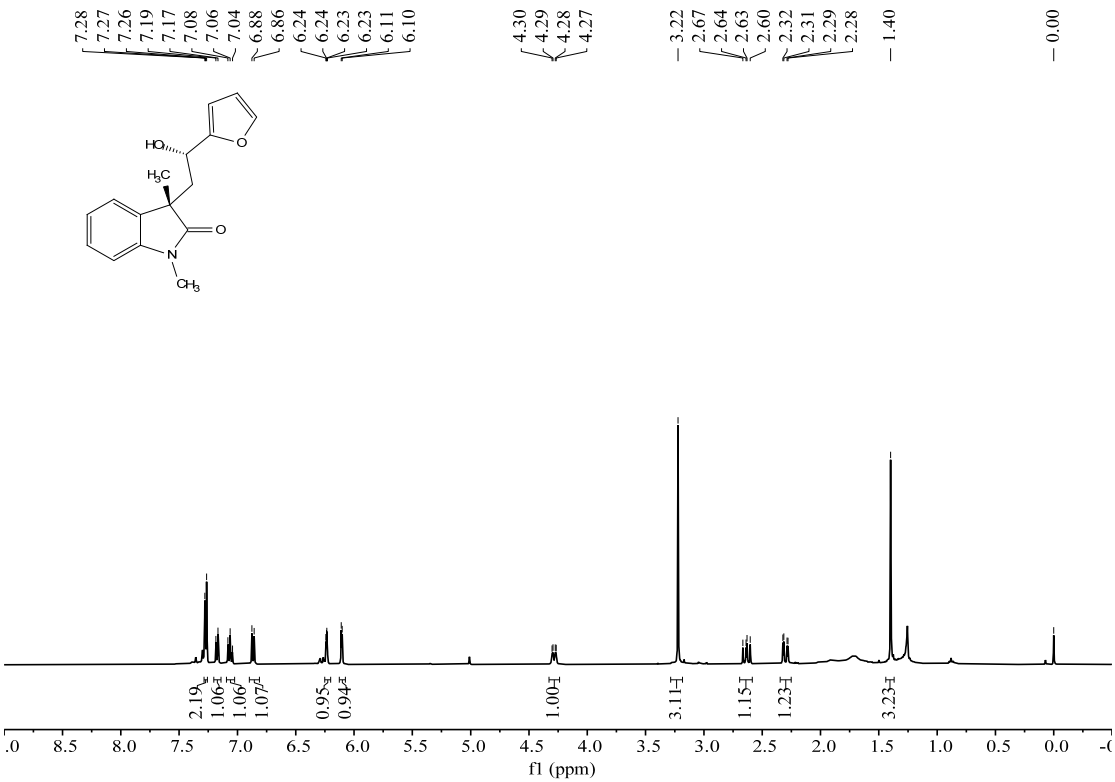
^{1}H NMR spectra of 46a (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 46a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 46b (400 MHz, $CDCl_3$)



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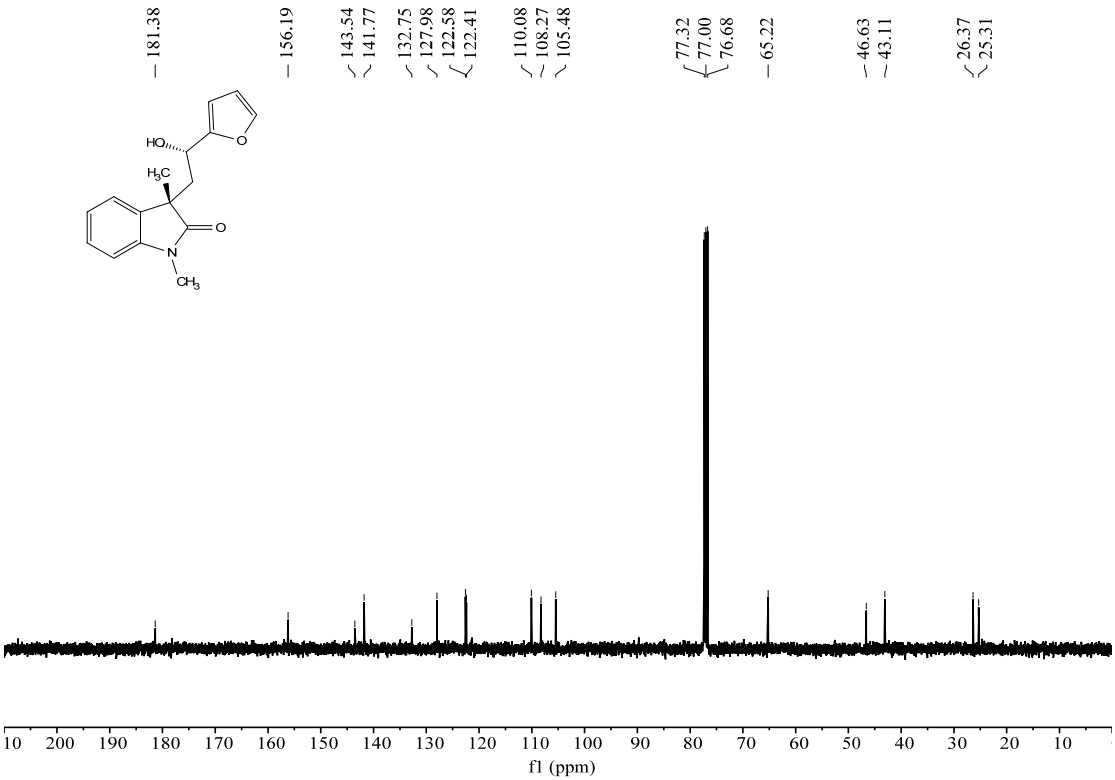

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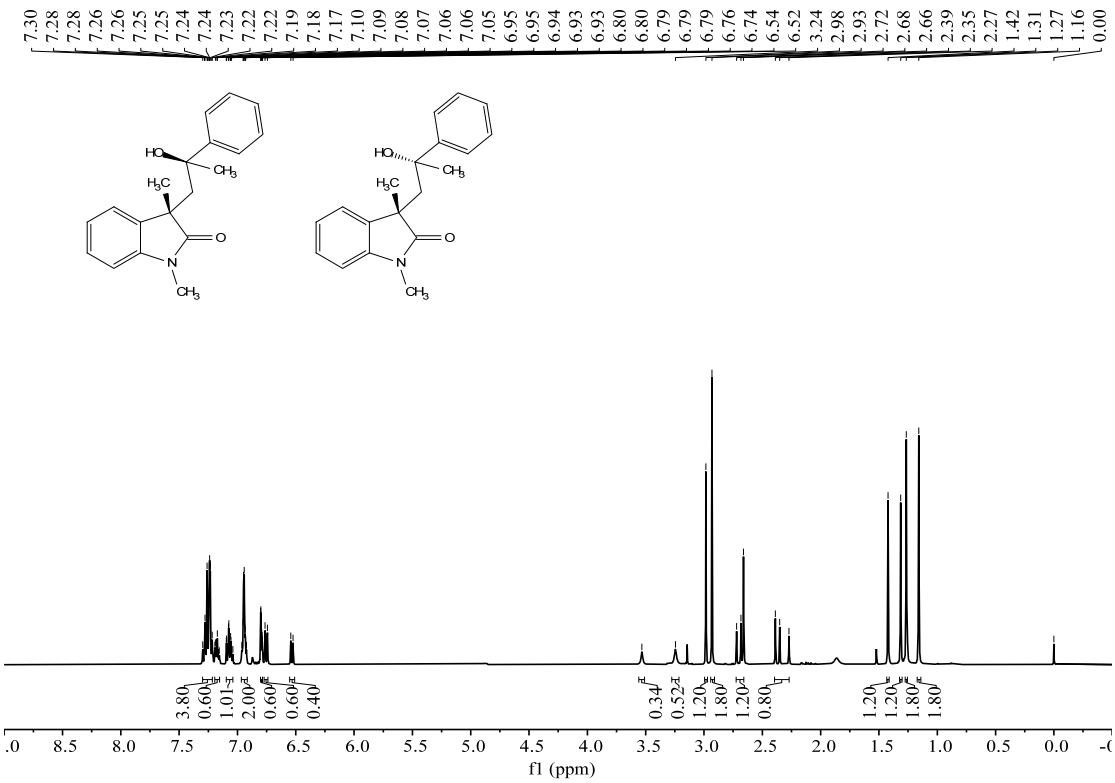

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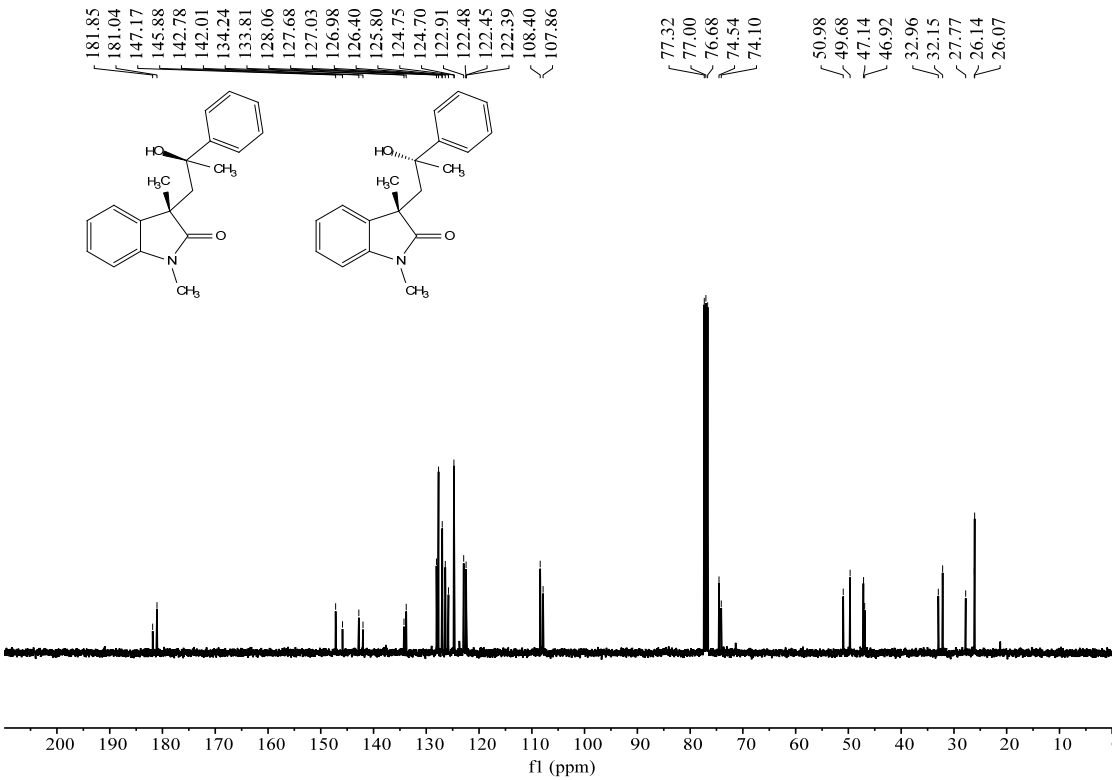
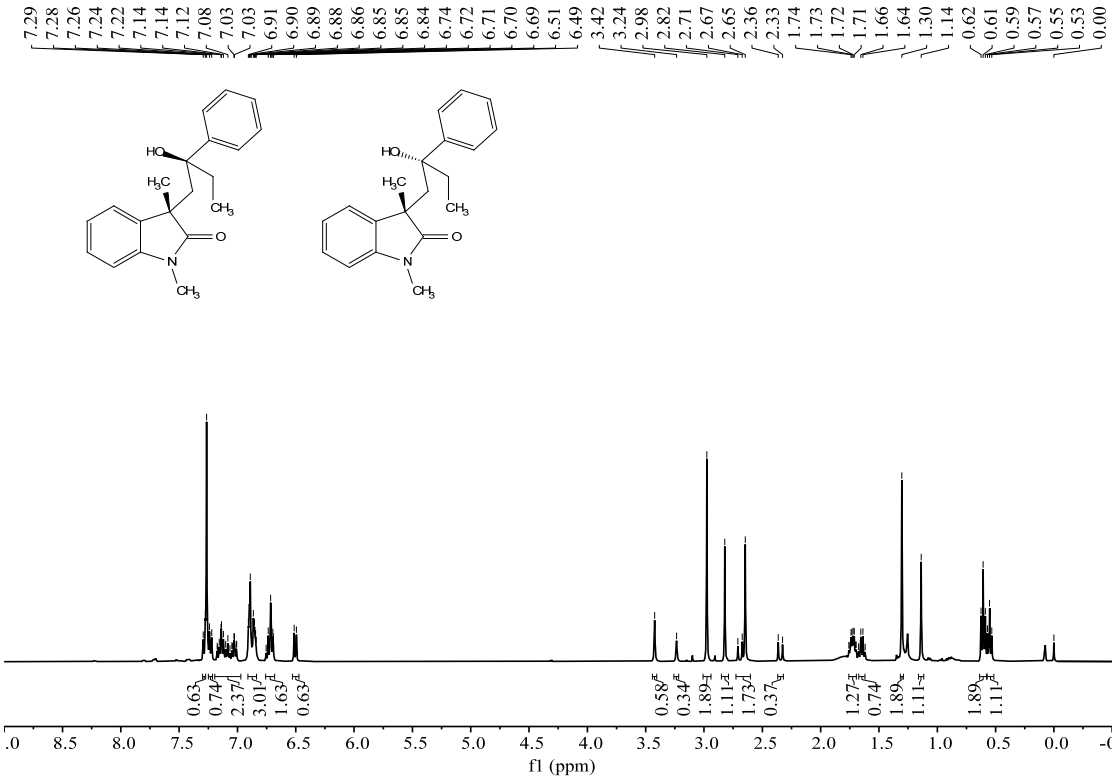
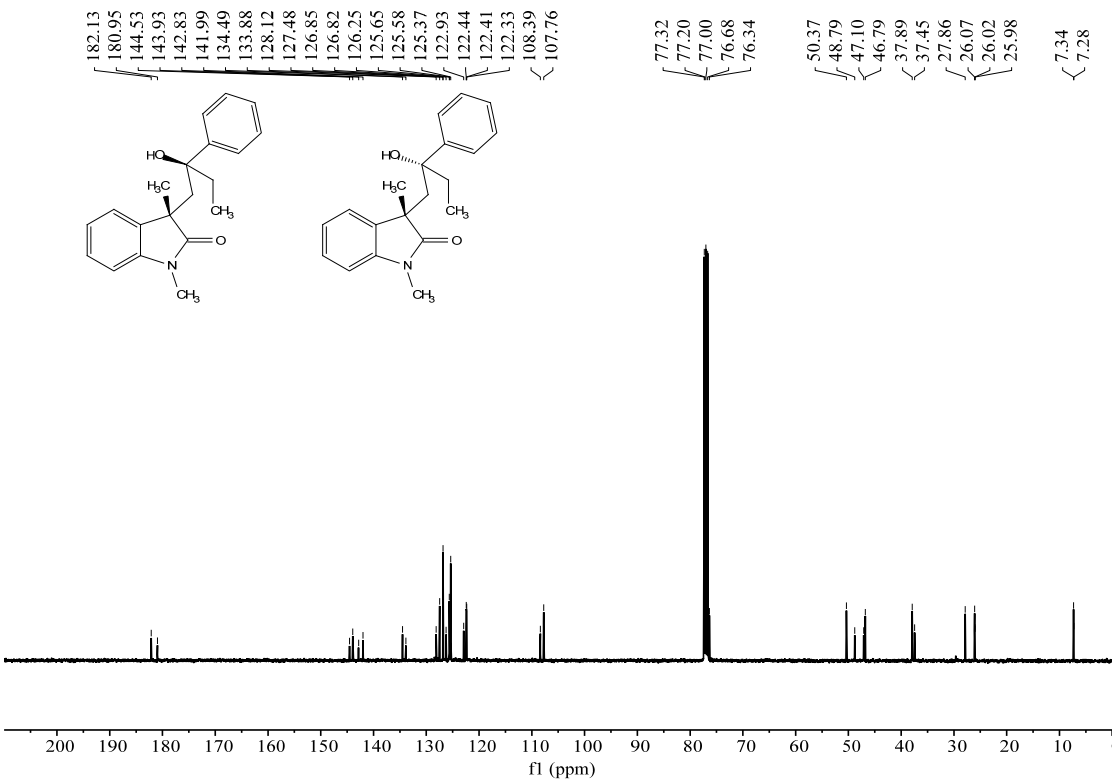


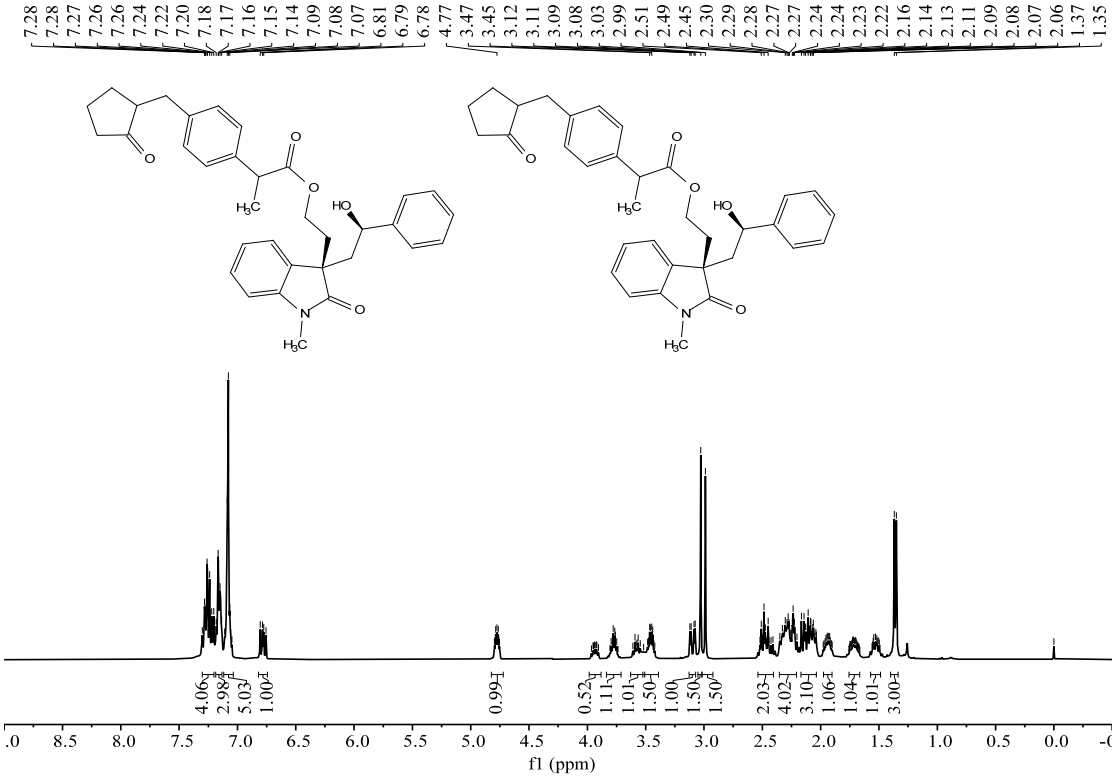
^{1}H NMR spectra of 48ab (400 MHz, $CDCl_3$)



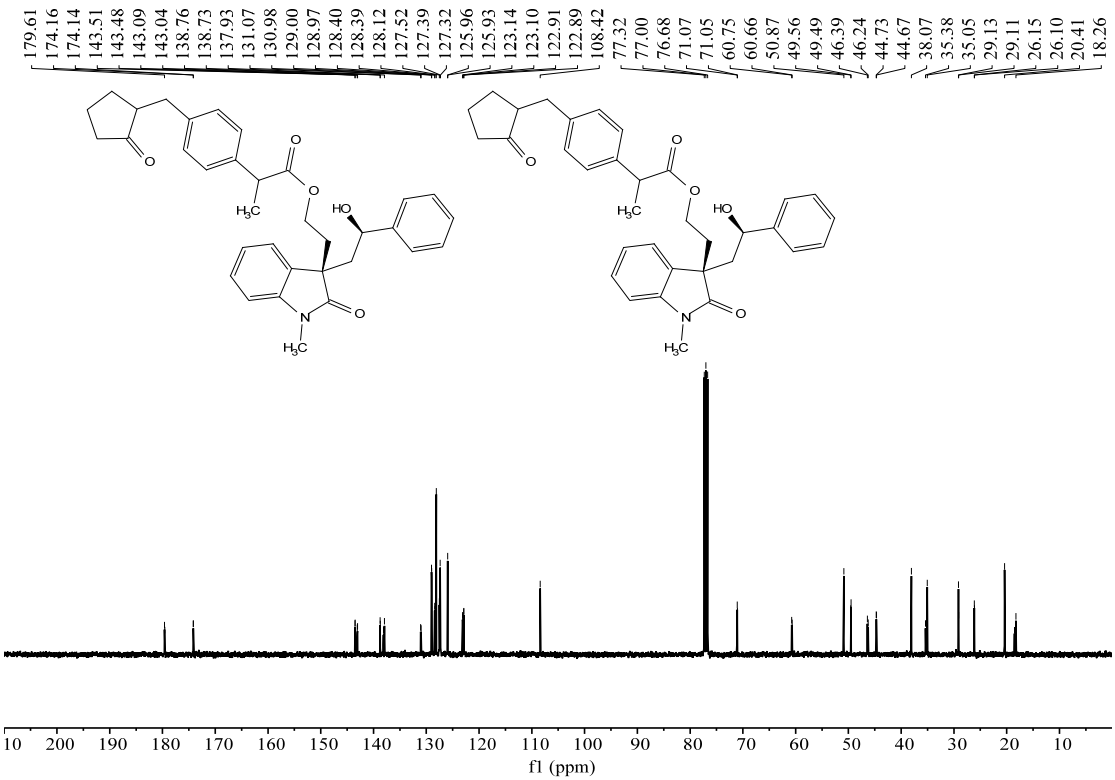
^{13}C NMR spectra of 48ab (100 MHz, $CDCl_3$)



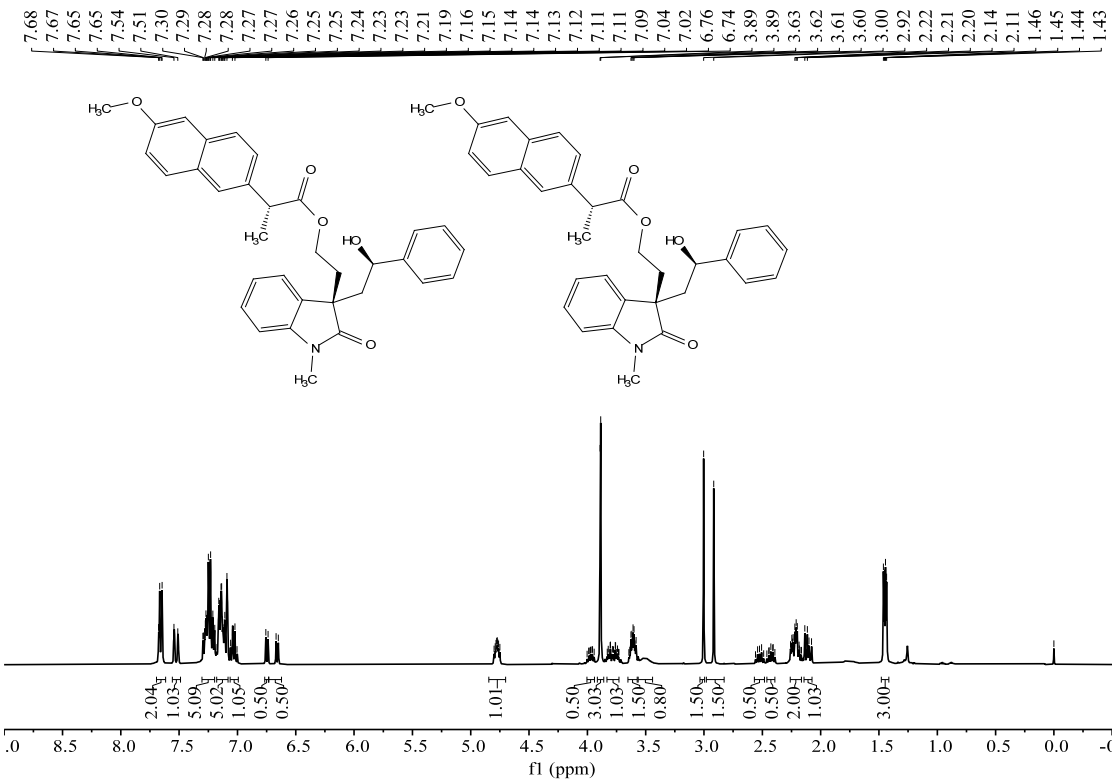
^{1}H NMR spectra of 49ab (400 MHz, $CDCl_3$)



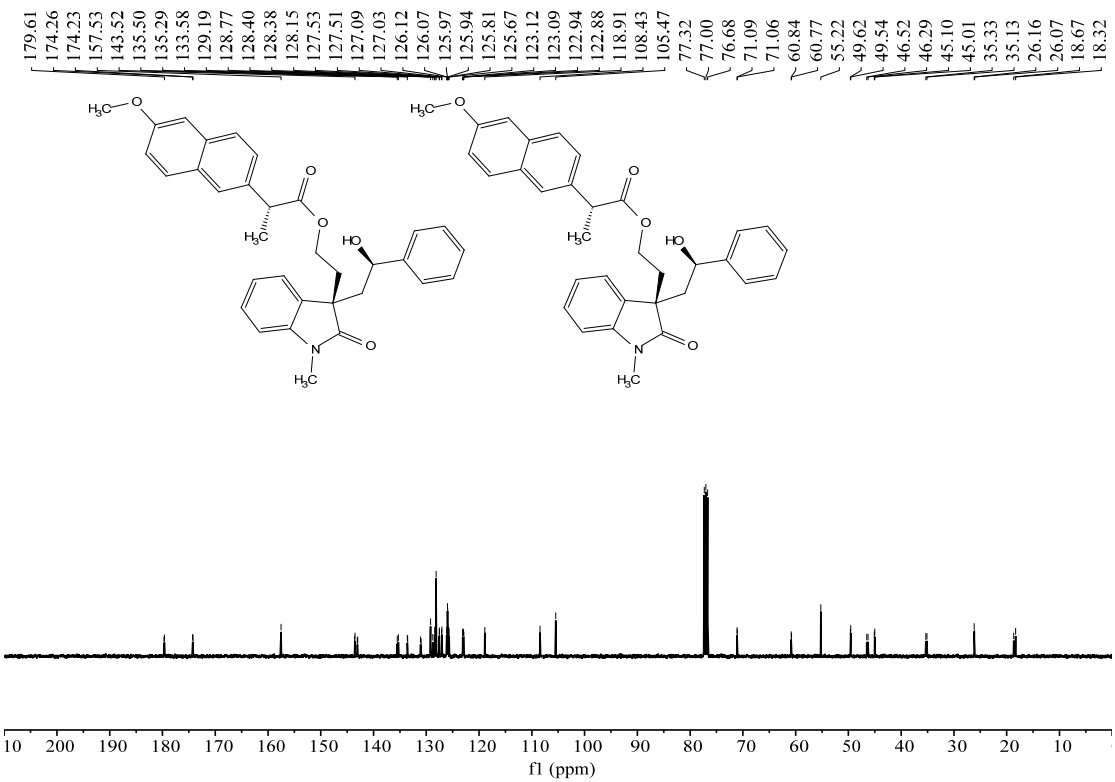
^{13}C NMR spectra of 49ab (100 MHz, $CDCl_3$)



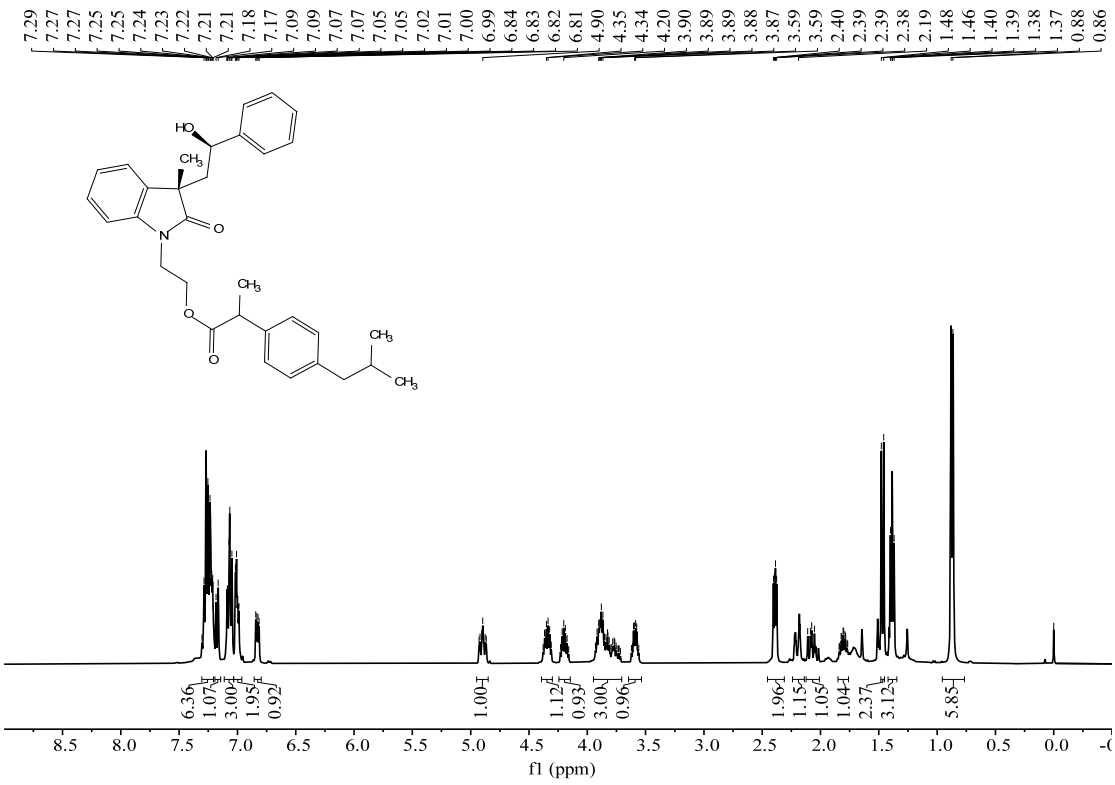
^{1}H NMR spectra of 50ab (400 MHz, $CDCl_3$)



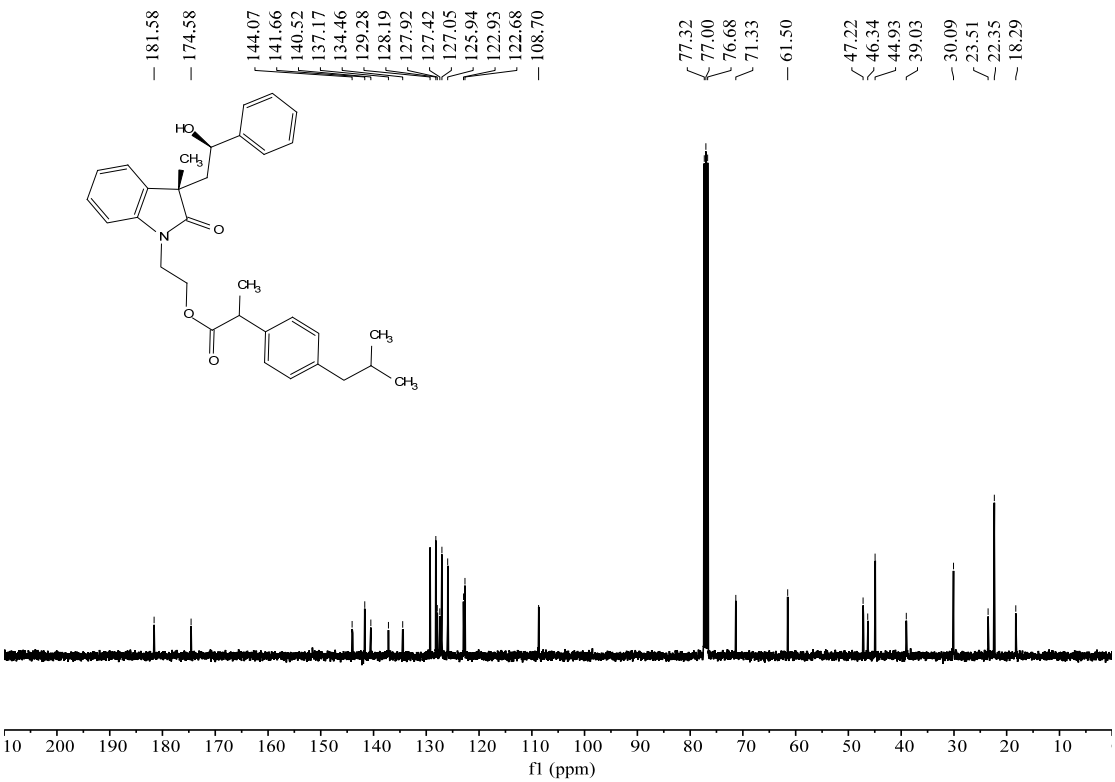
^{13}C NMR spectra of 50ab (100 MHz, $CDCl_3$)



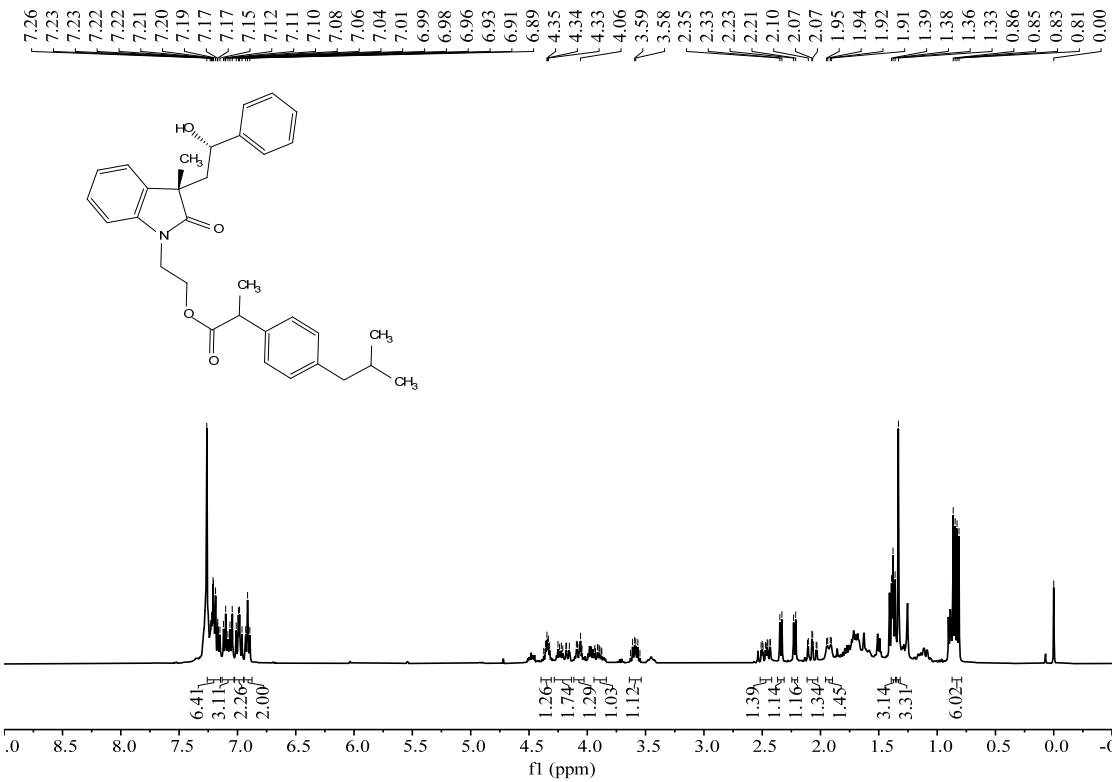
^{1}H NMR spectra of 51a (400 MHz, $CDCl_3$)



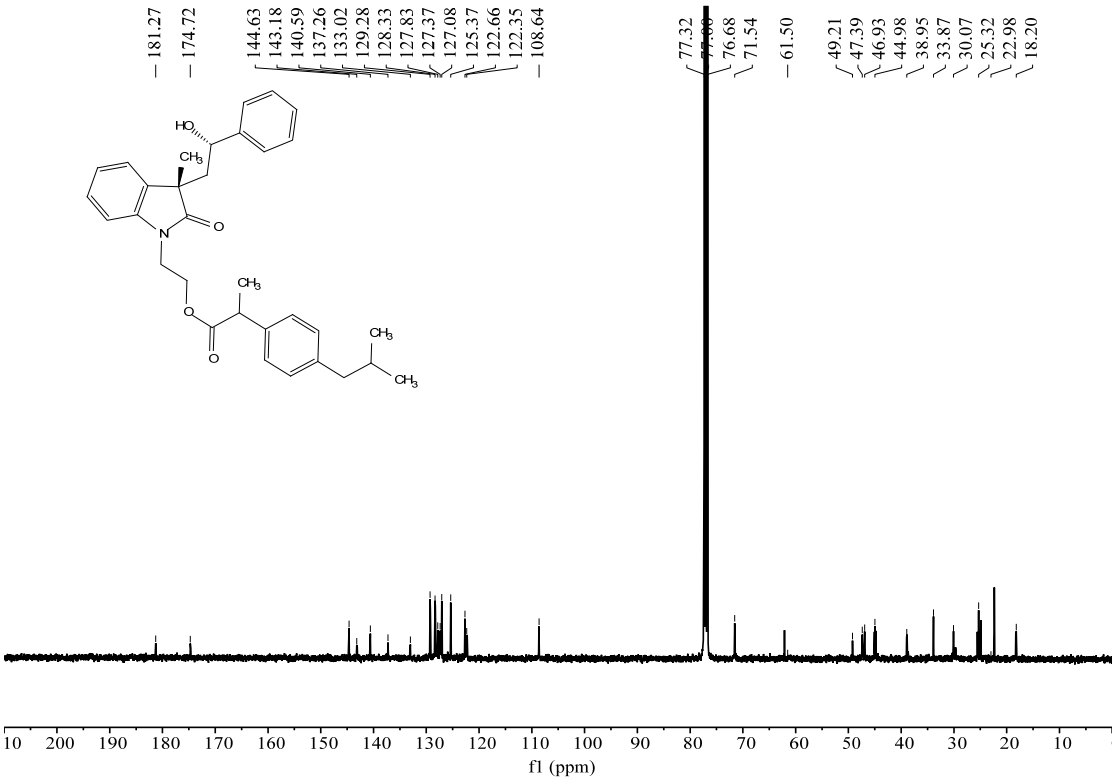
^{13}C NMR spectra of 51a (100 MHz, $CDCl_3$)



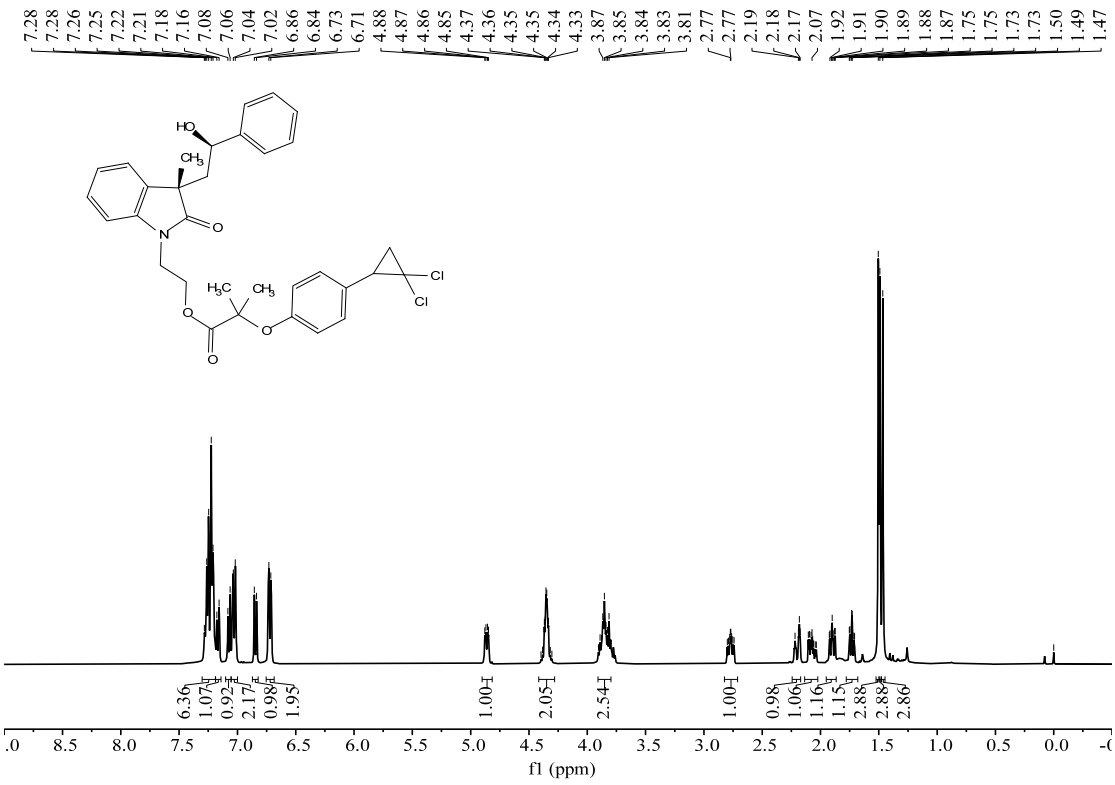
^{1}H NMR spectra of 51b (400 MHz, $CDCl_3$)



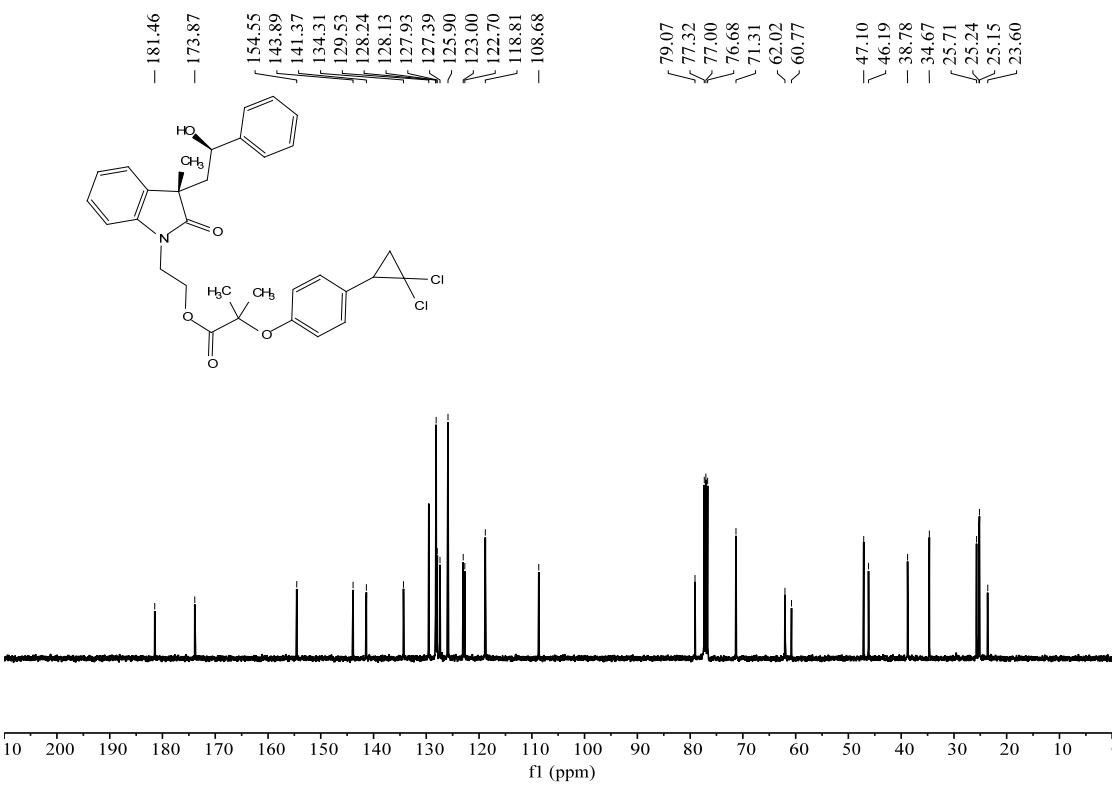
^{13}C NMR spectra of 51b (100 MHz, $CDCl_3$)



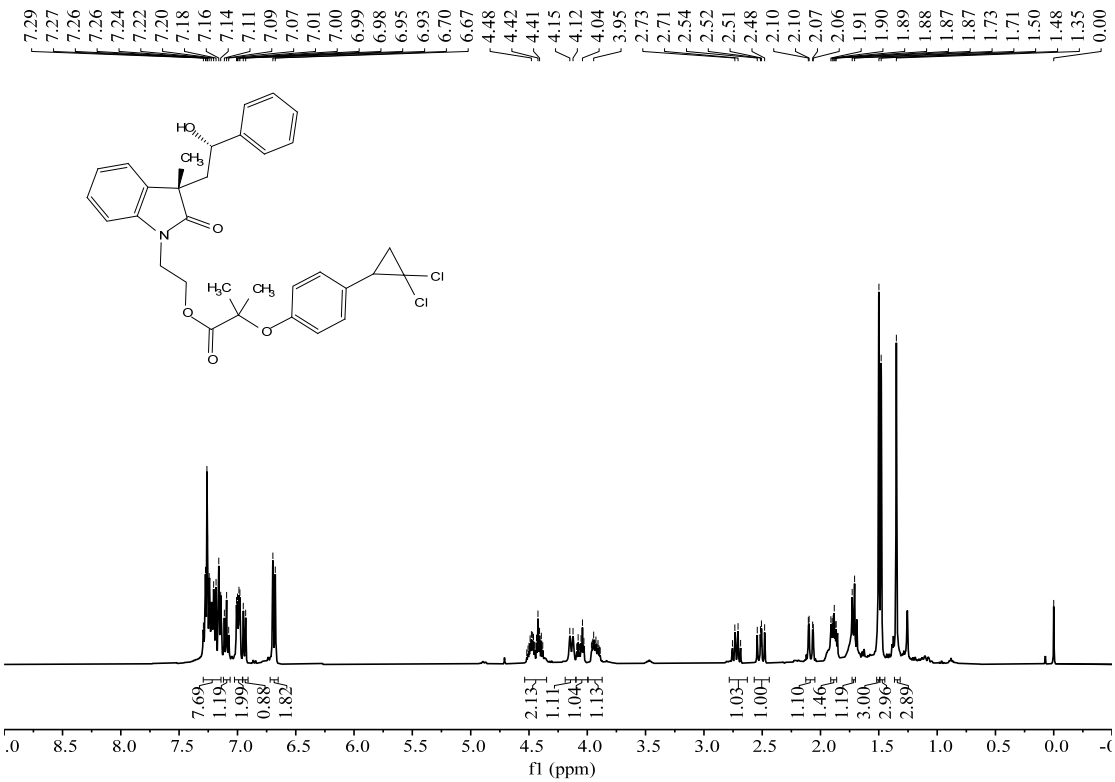
^{1}H NMR spectra of 52a (400 MHz, $CDCl_3$)



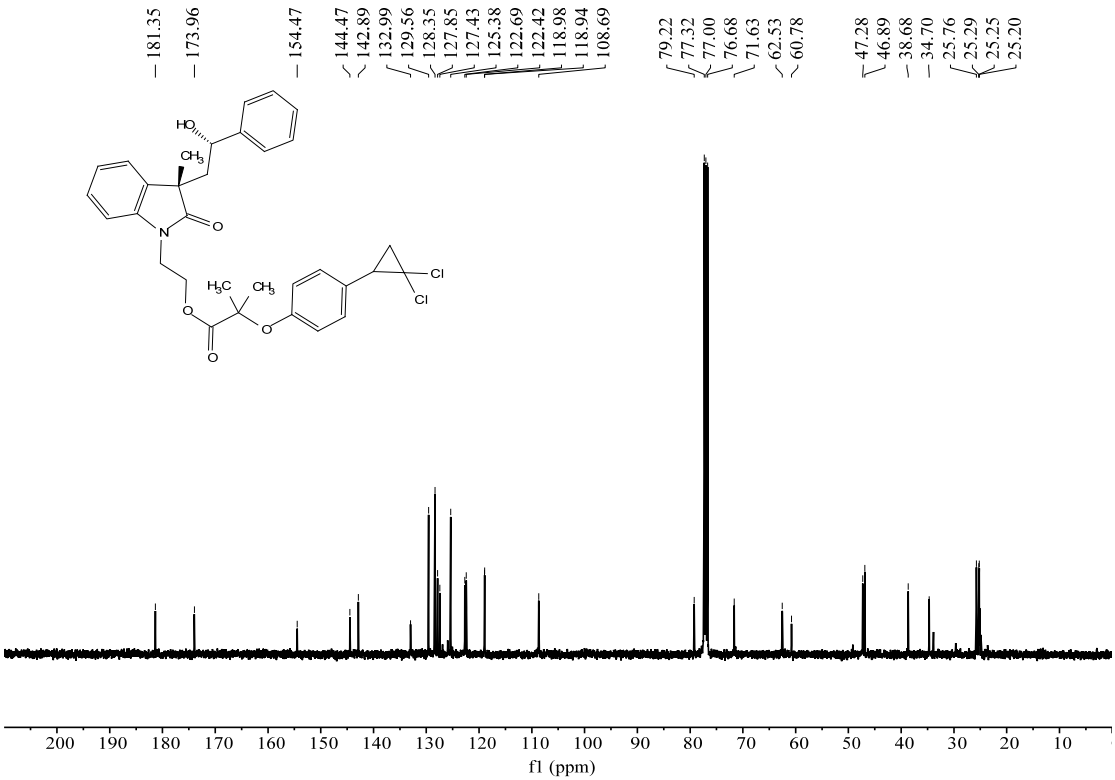
^{13}C NMR spectra of 52a (100 MHz, $CDCl_3$)



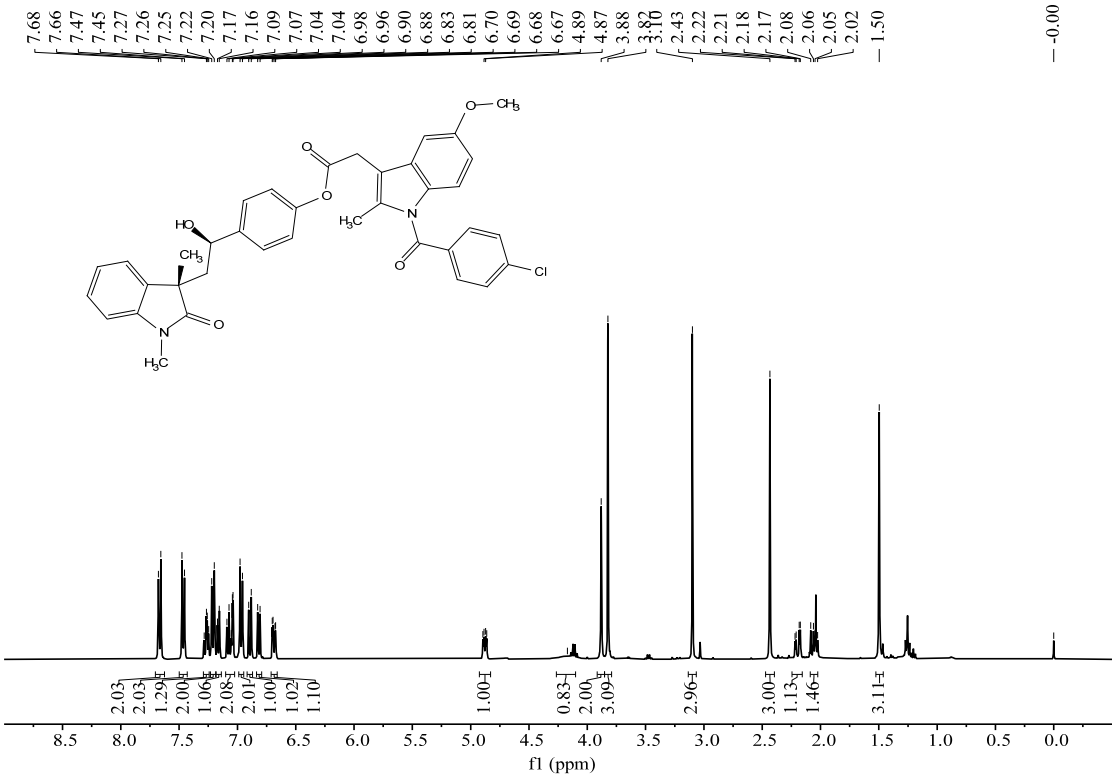
^{1}H NMR spectra of 52b (400 MHz, $CDCl_3$)



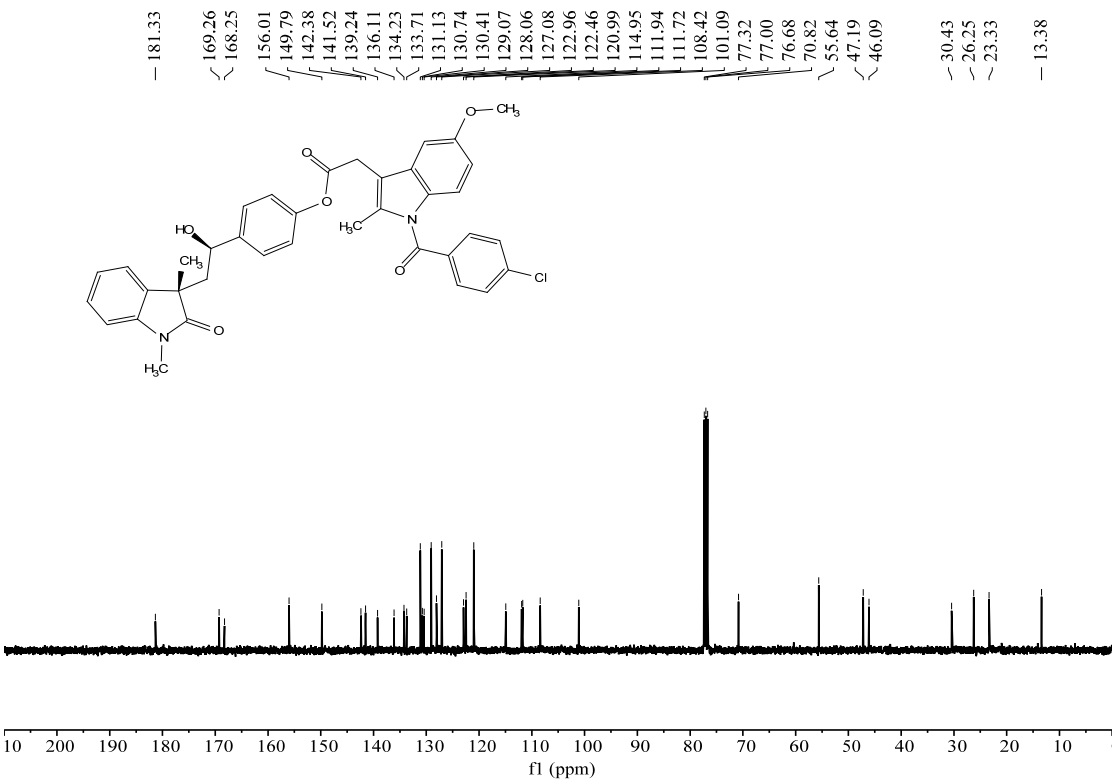
^{13}C NMR spectra of 52b (100 MHz, $CDCl_3$)



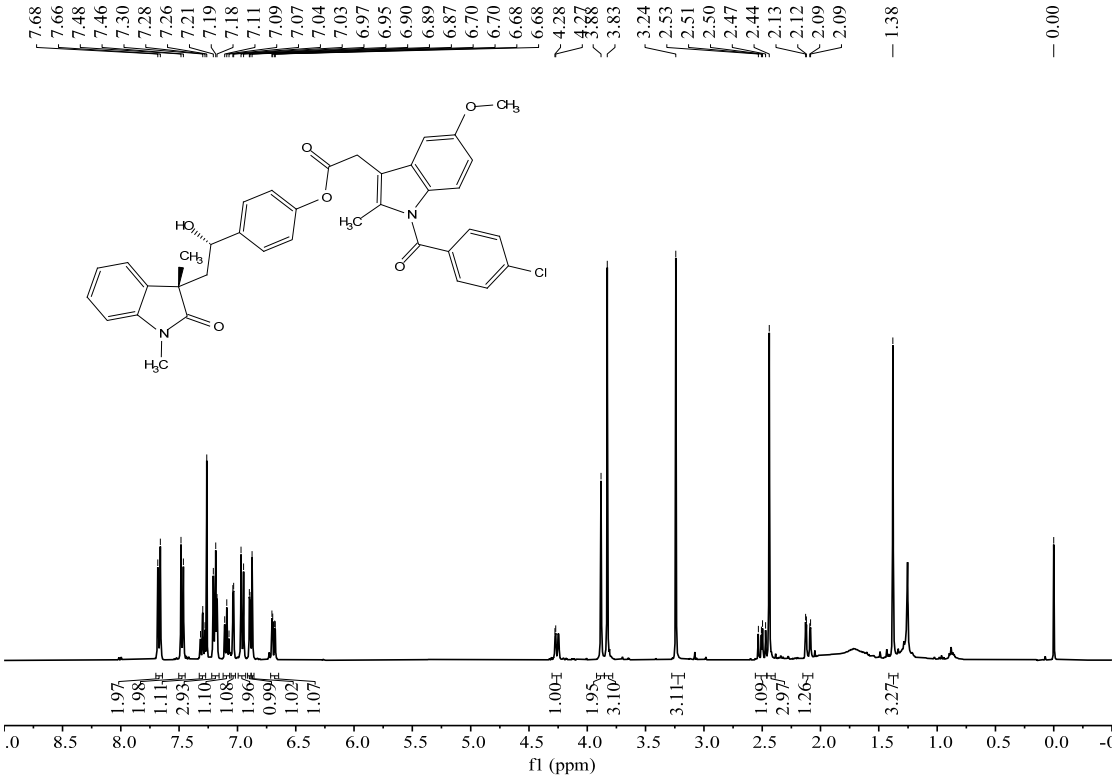
^{1}H NMR spectra of 53a (400 MHz, $CDCl_3$)



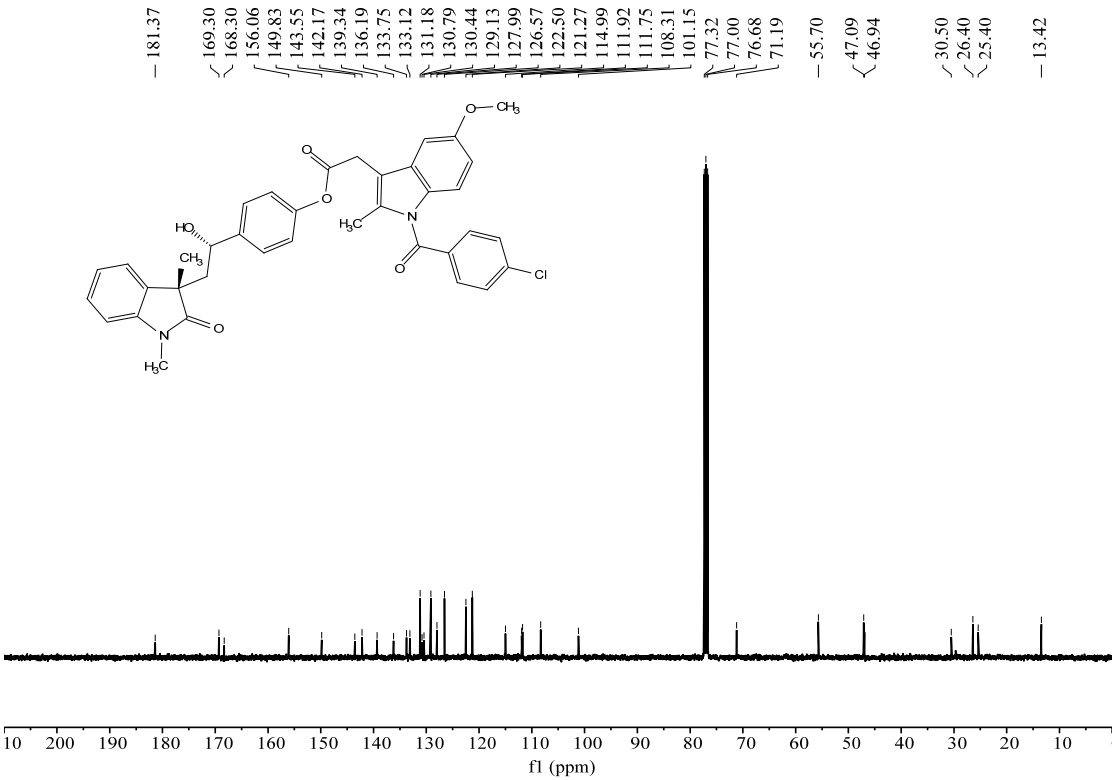
^{13}C NMR spectra of 53a (100 MHz, $CDCl_3$)



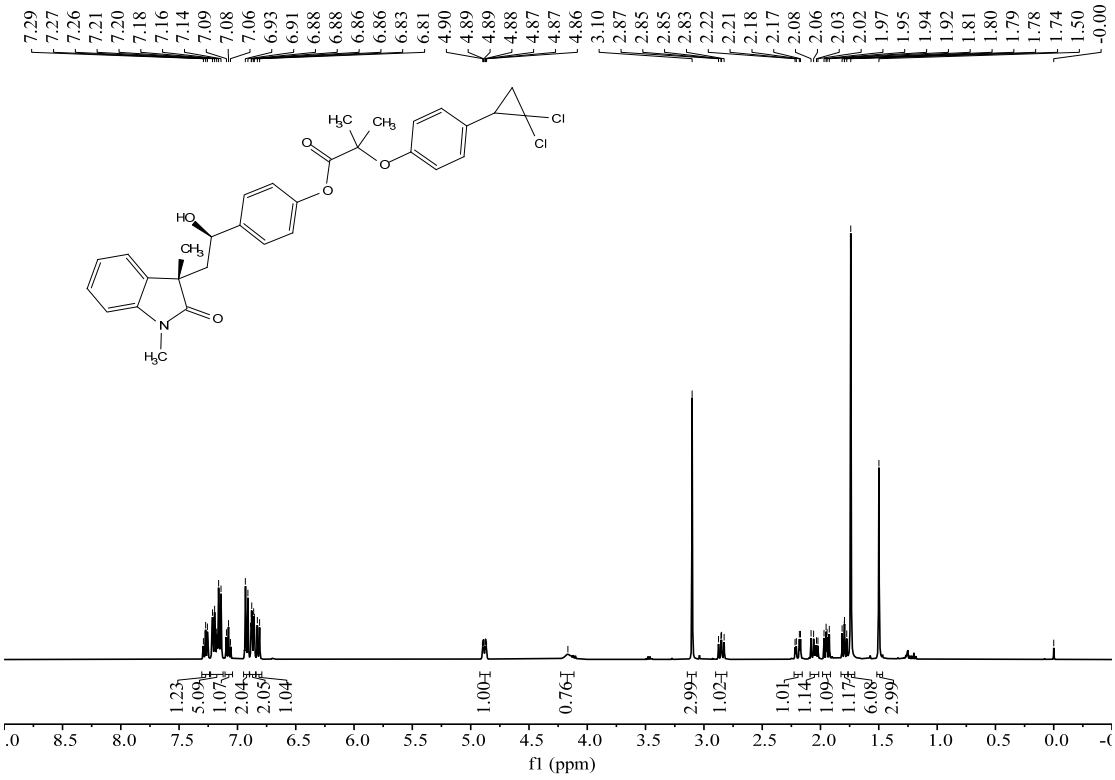
^{1}H NMR spectra of 53b (400 MHz, $CDCl_3$)



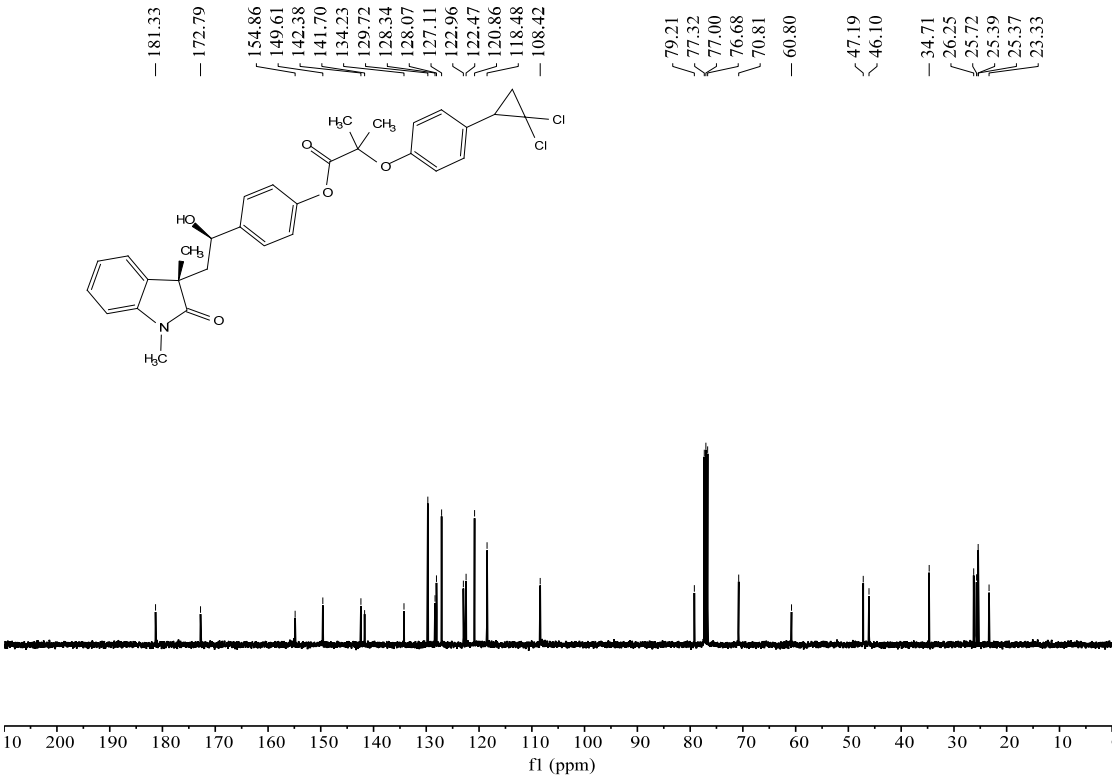
^{13}C NMR spectra of 53b (100 MHz, $CDCl_3$)



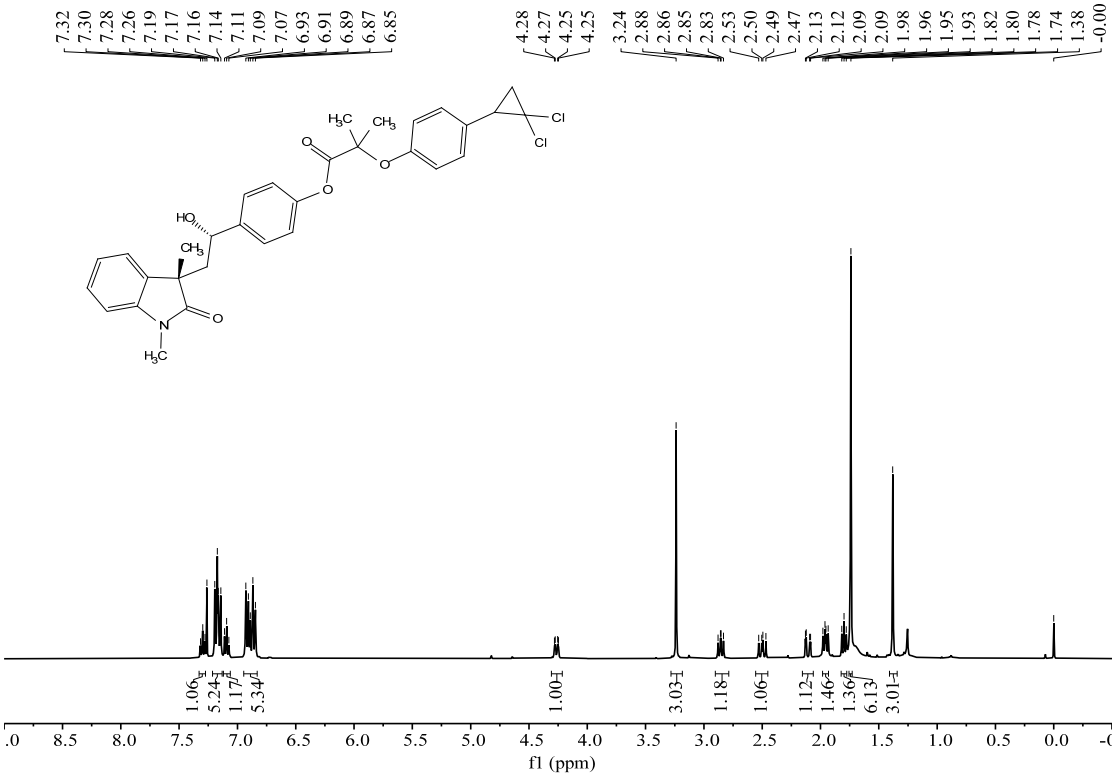
^{1}H NMR spectra of 54a (400 MHz, $CDCl_3$)



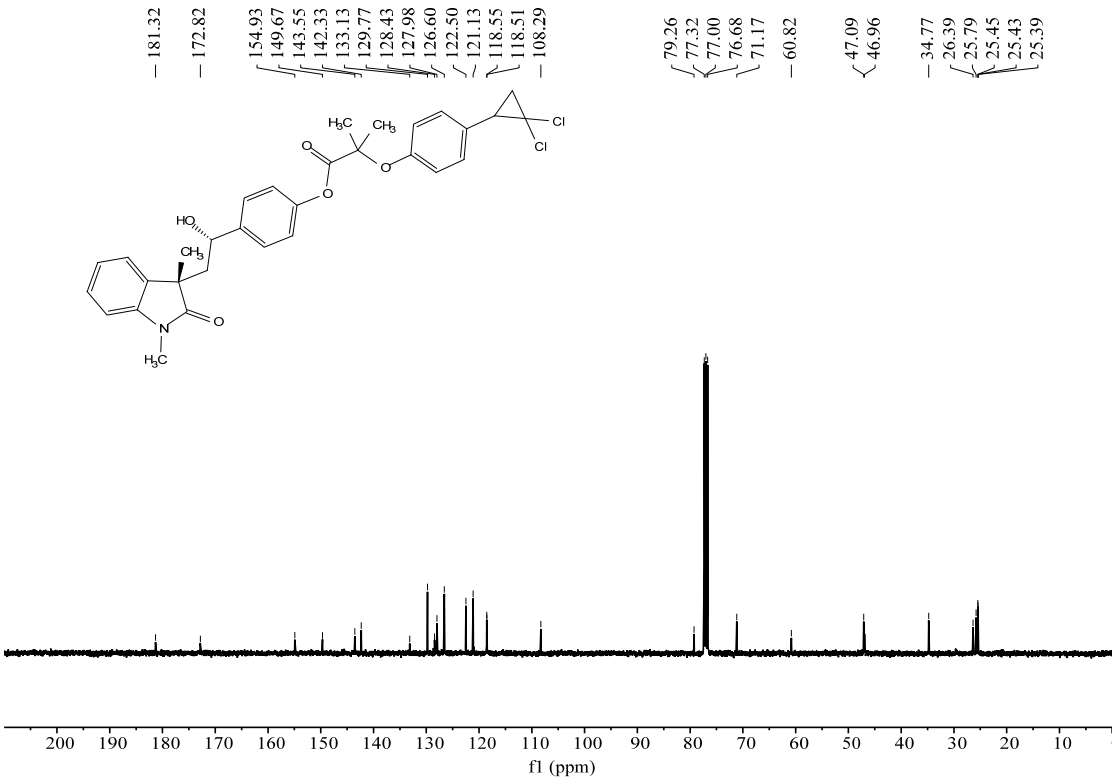
^{13}C NMR spectra of 54a (100 MHz, $CDCl_3$)



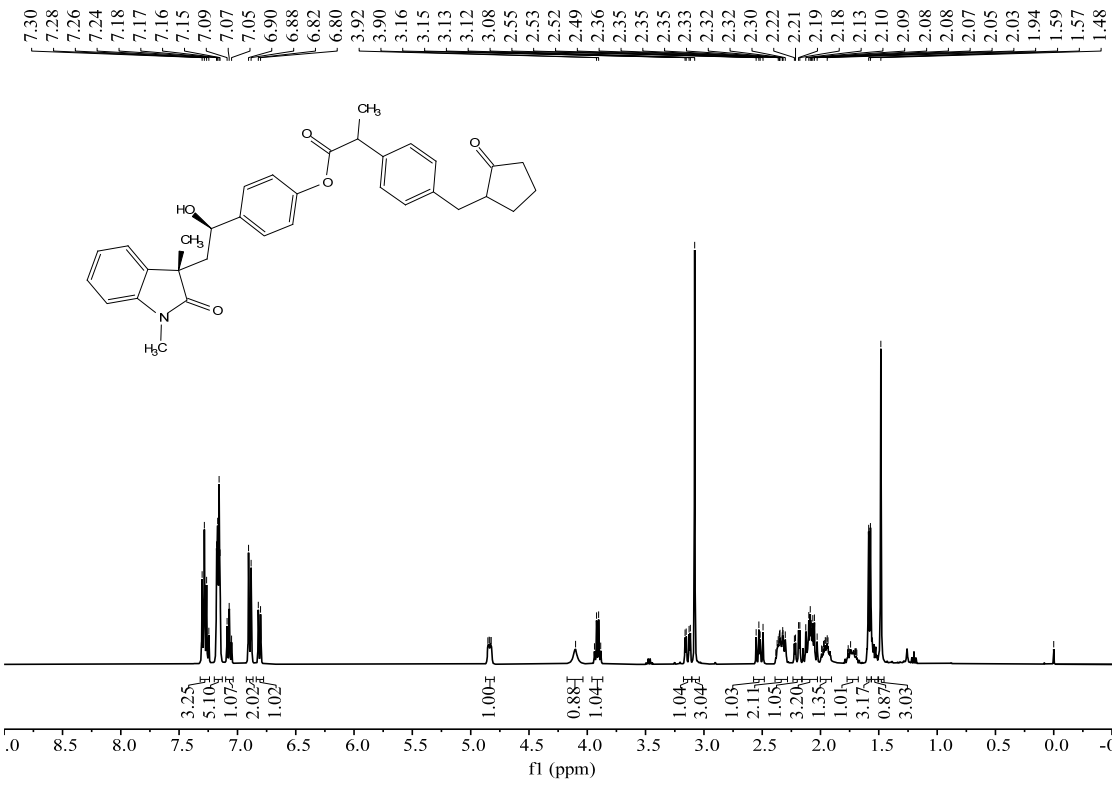
^{1}H NMR spectra of 54b (400 MHz, $CDCl_3$)



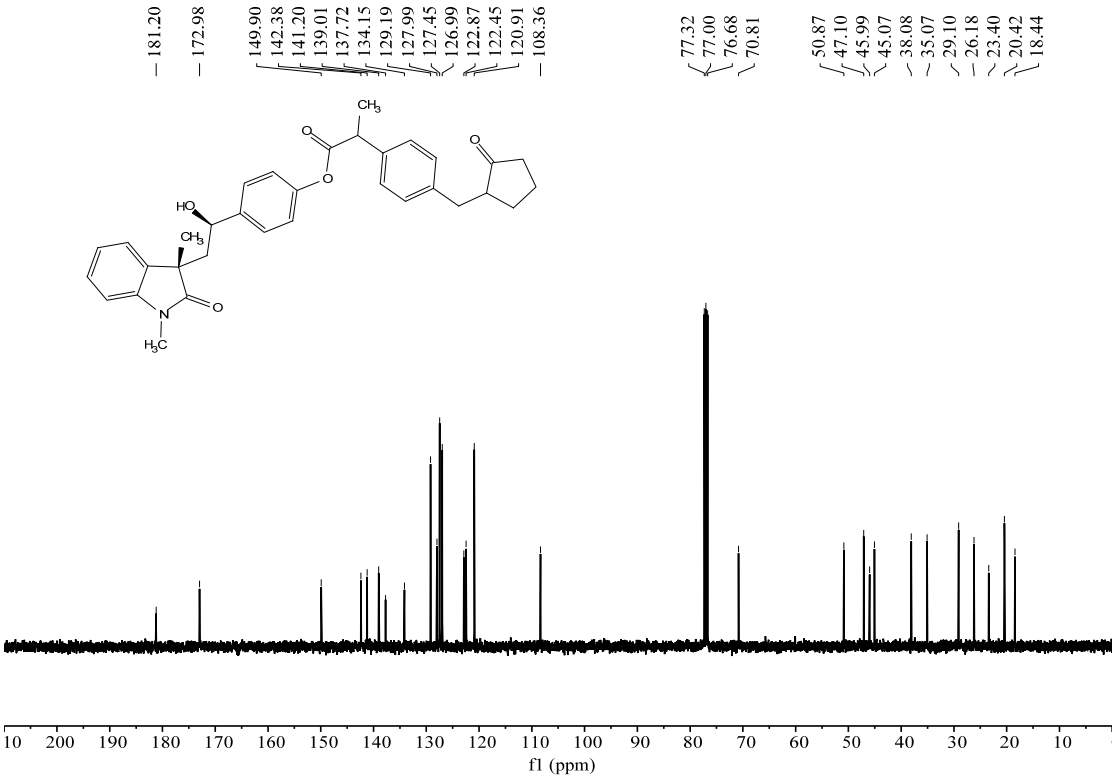
^{13}C NMR spectra of 54b (100 MHz, $CDCl_3$)



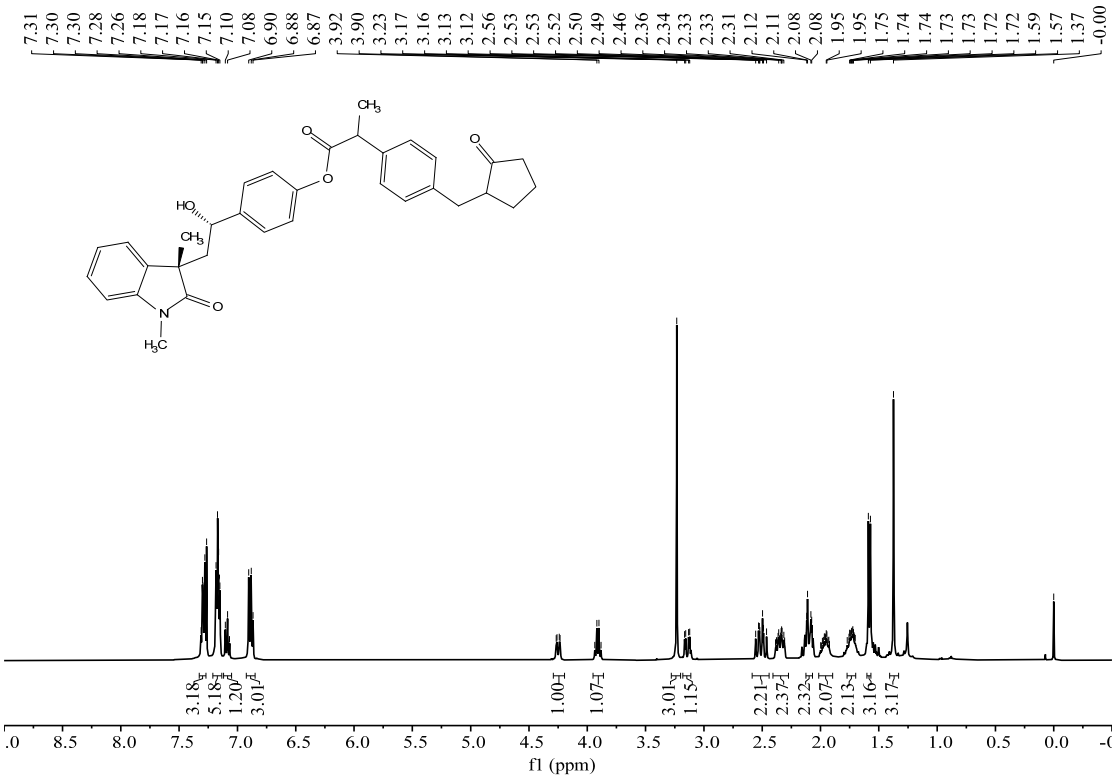
^{1}H NMR spectra of 55a (400 MHz, $CDCl_3$)



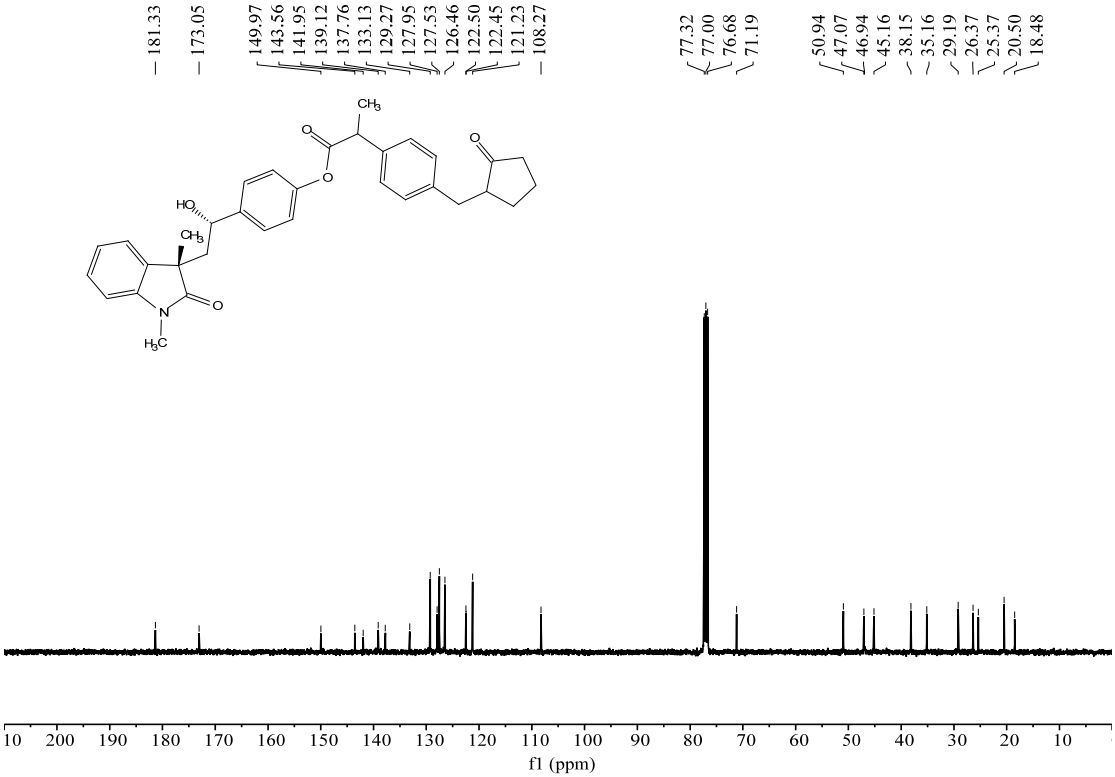
^{13}C NMR spectra of 55a (100 MHz, $CDCl_3$)



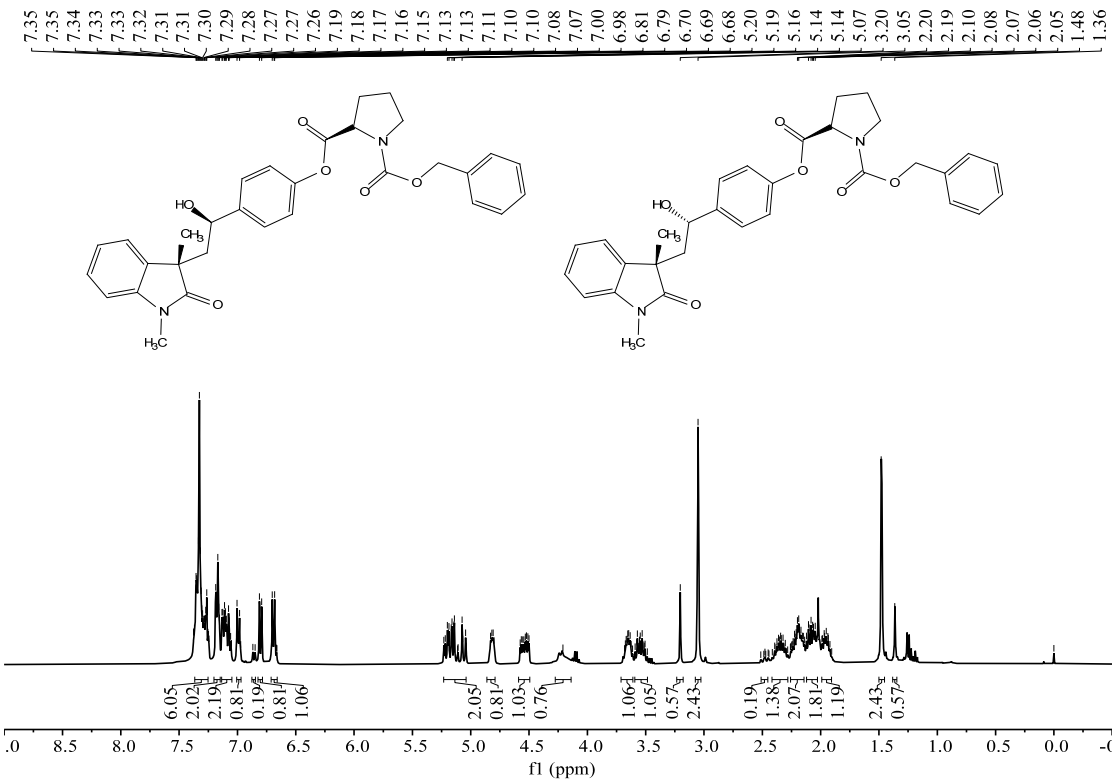
^{1}H NMR spectra of 55b (400 MHz, $CDCl_3$)



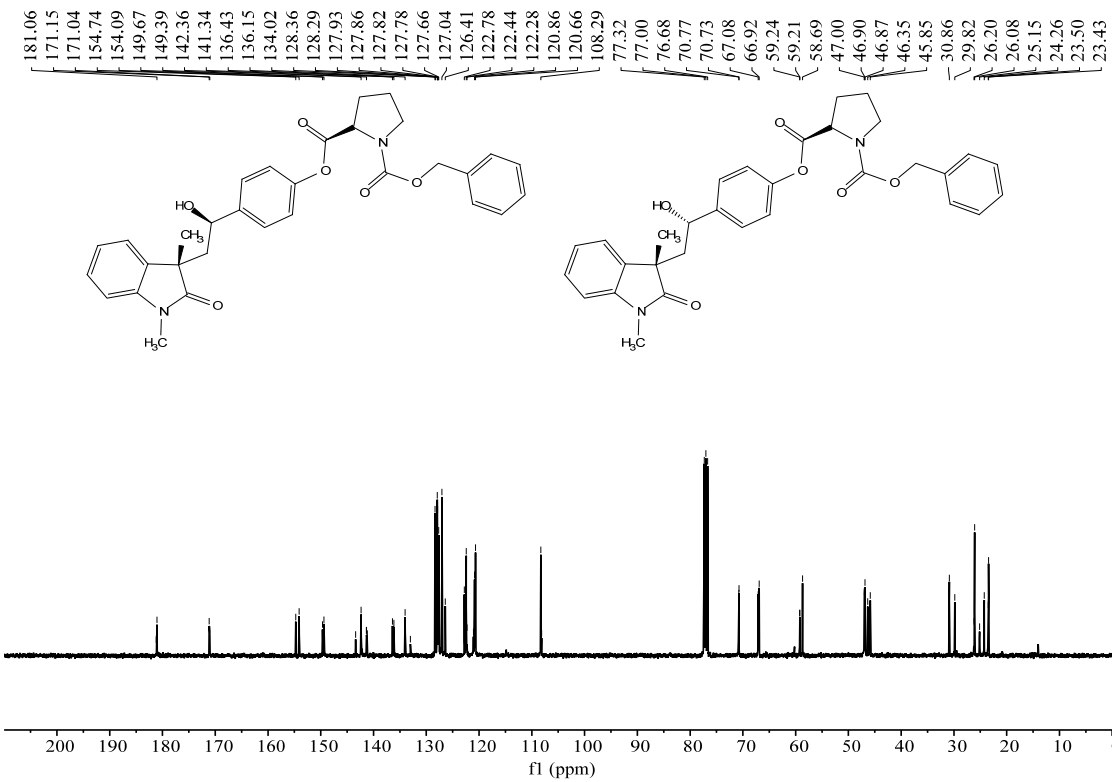
^{13}C NMR spectra of 55b (100 MHz, $CDCl_3$)



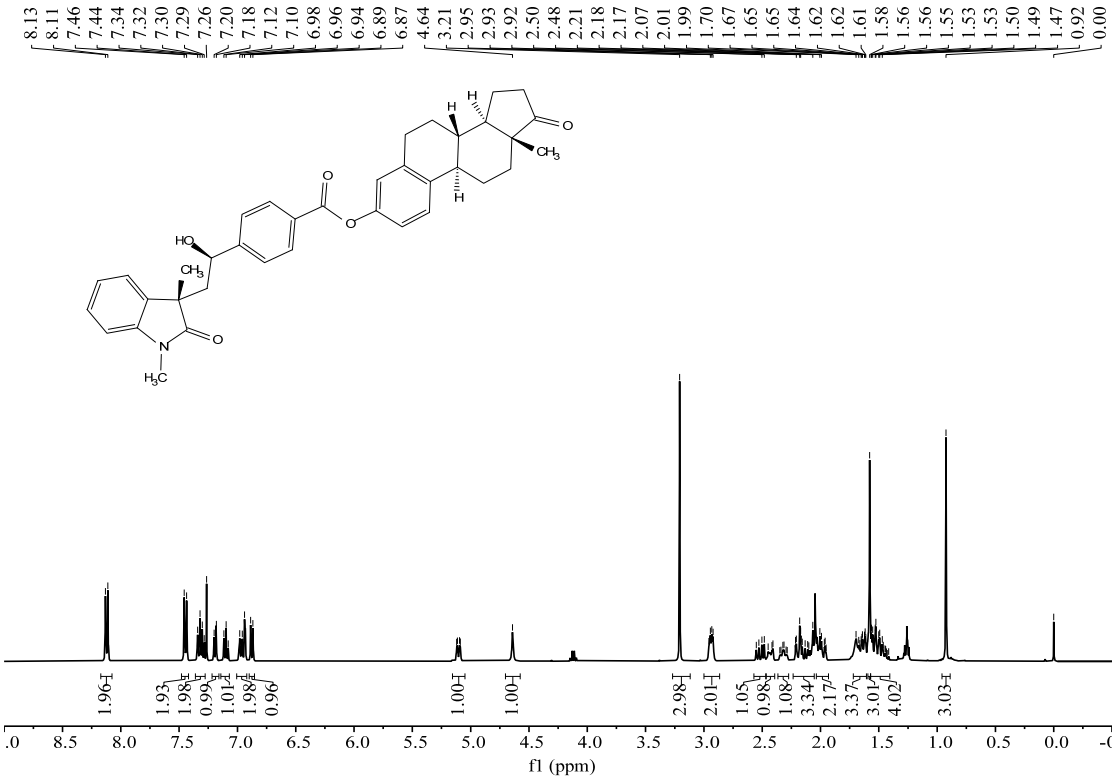
^{1}H NMR spectra of 56ab (400 MHz, $CDCl_3$)



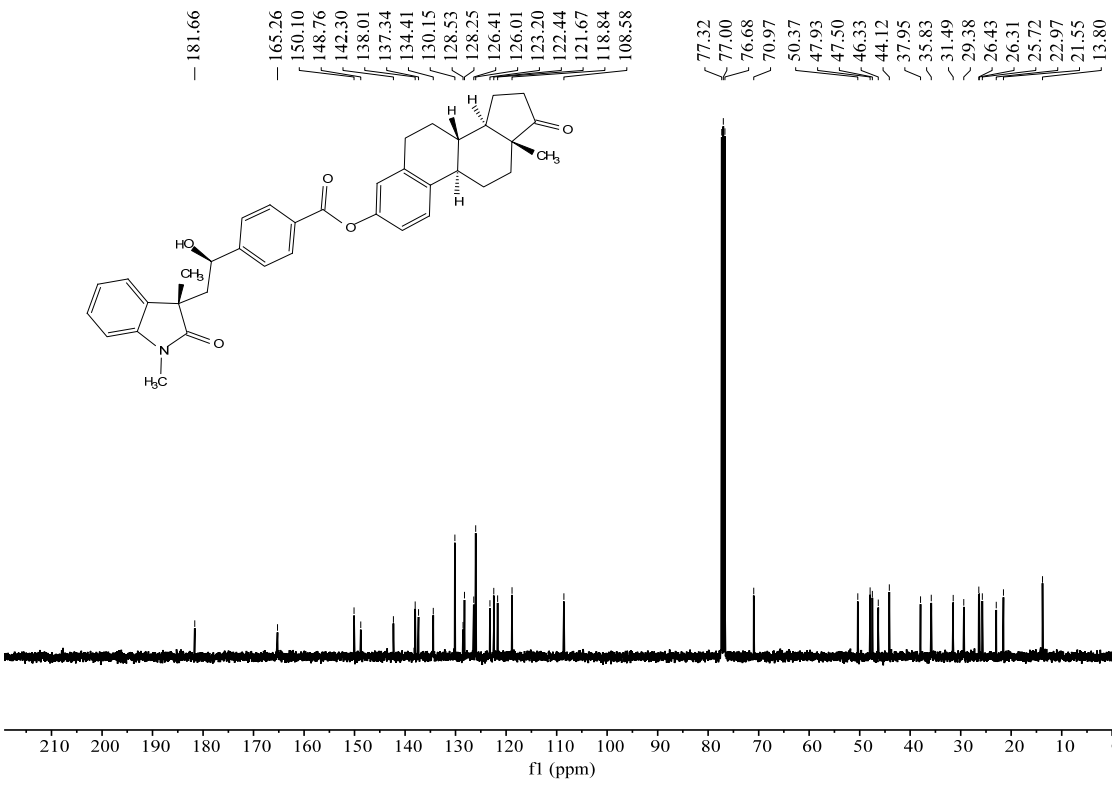
^{13}C NMR spectra of 56ab (100 MHz, $CDCl_3$)



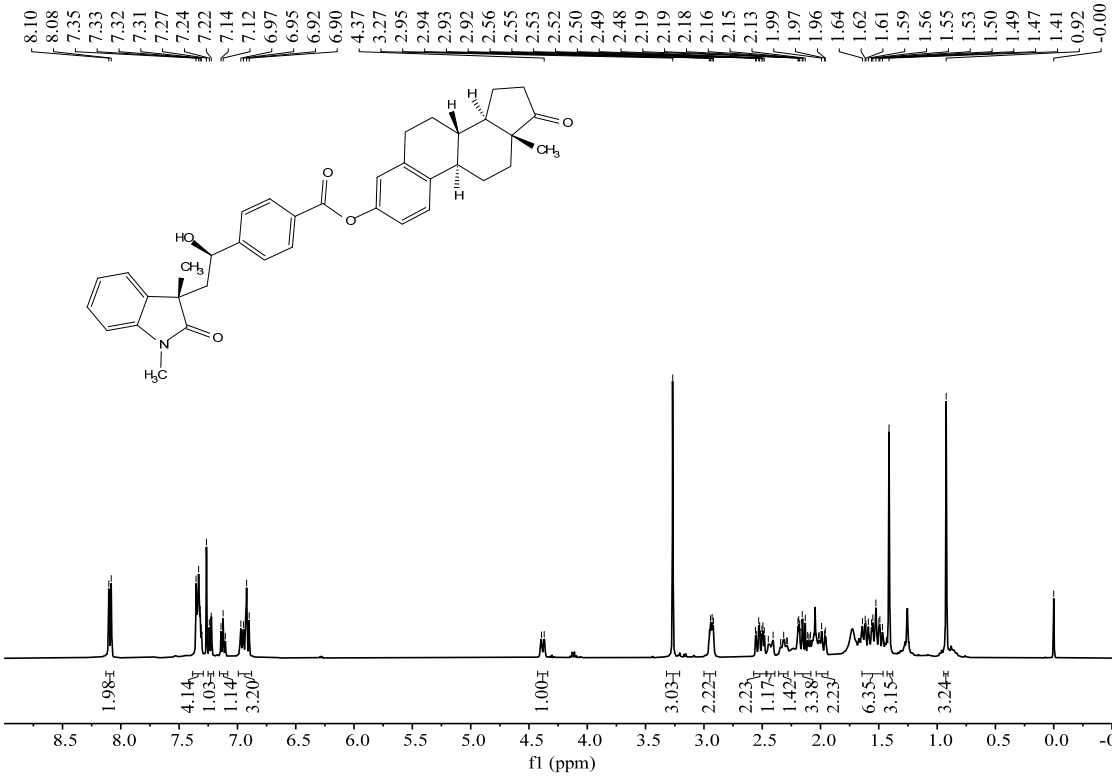
^{1}H NMR spectra of 57a (400 MHz, $CDCl_3$)



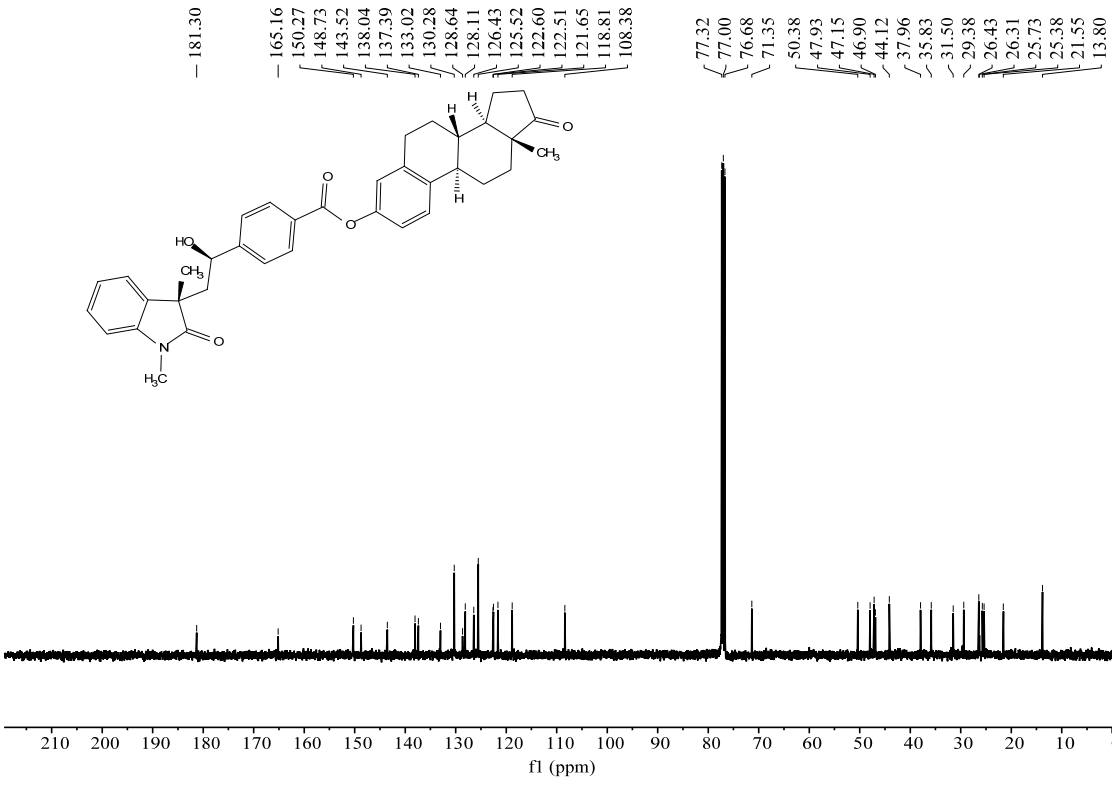
^{13}C NMR spectra of 57a (100 MHz, $CDCl_3$)



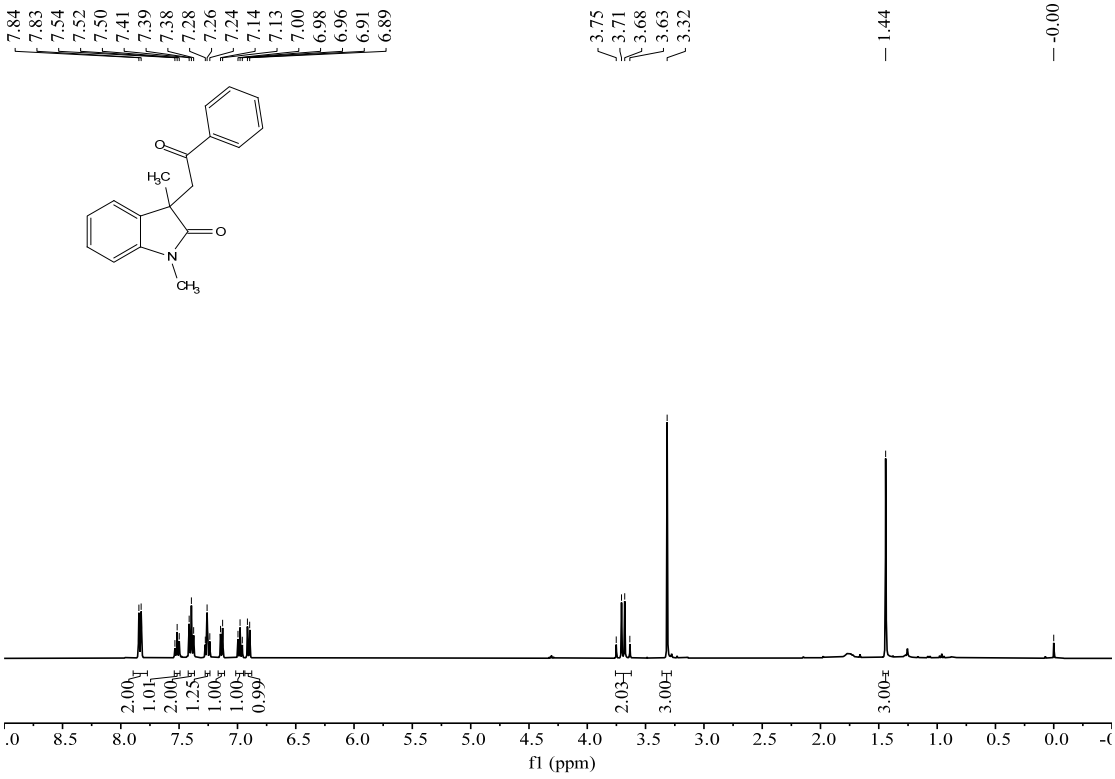
^{1}H NMR spectra of 57b (400 MHz, $CDCl_3$)



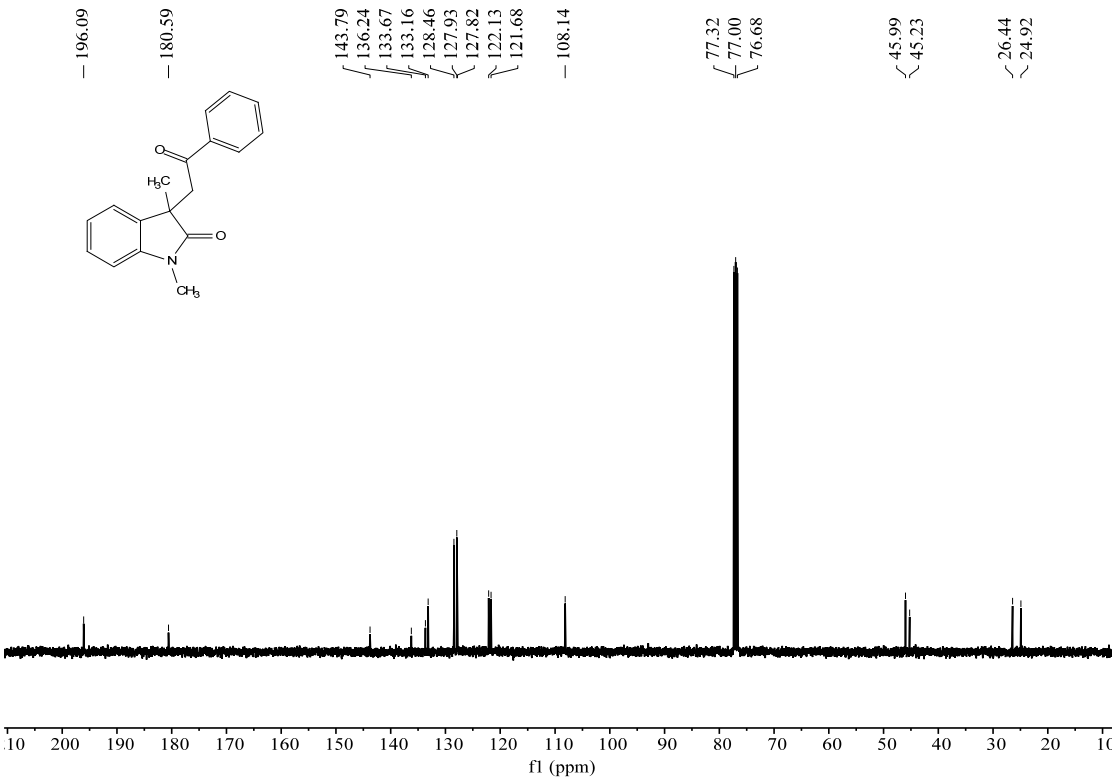
^{13}C NMR spectra of 57b (100 MHz, $CDCl_3$)



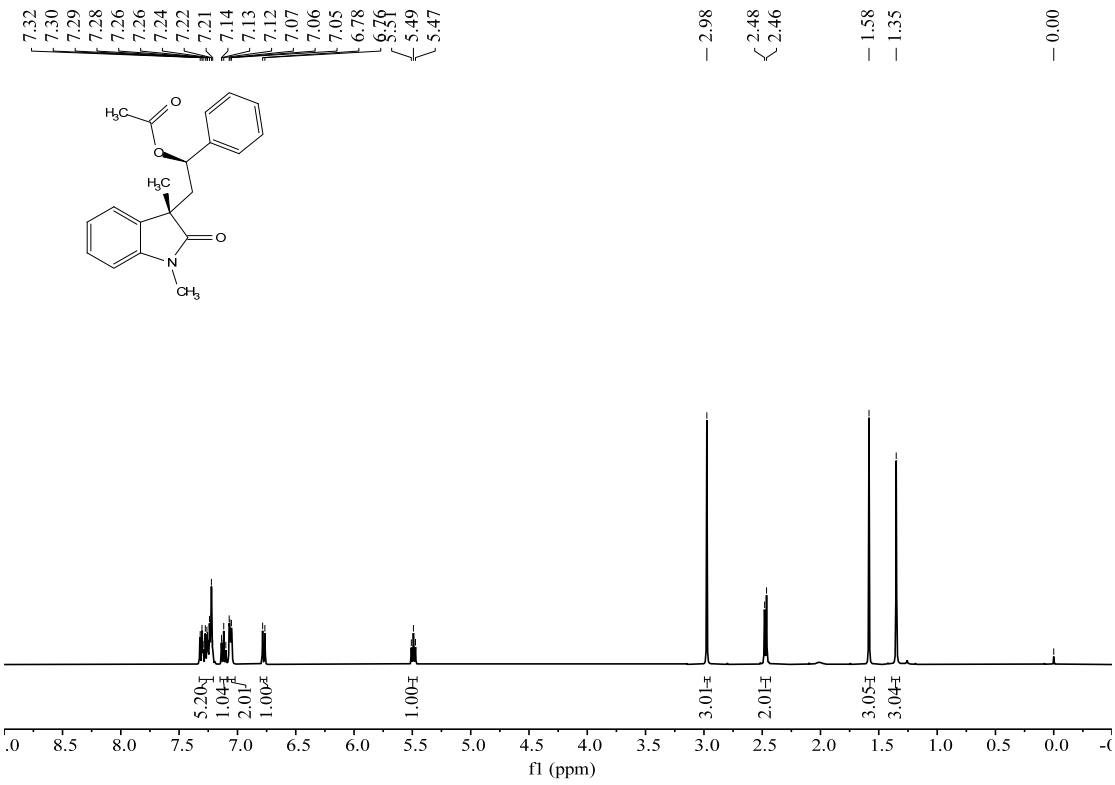
^{1}H NMR spectra of 58 (400 MHz, $CDCl_3$)



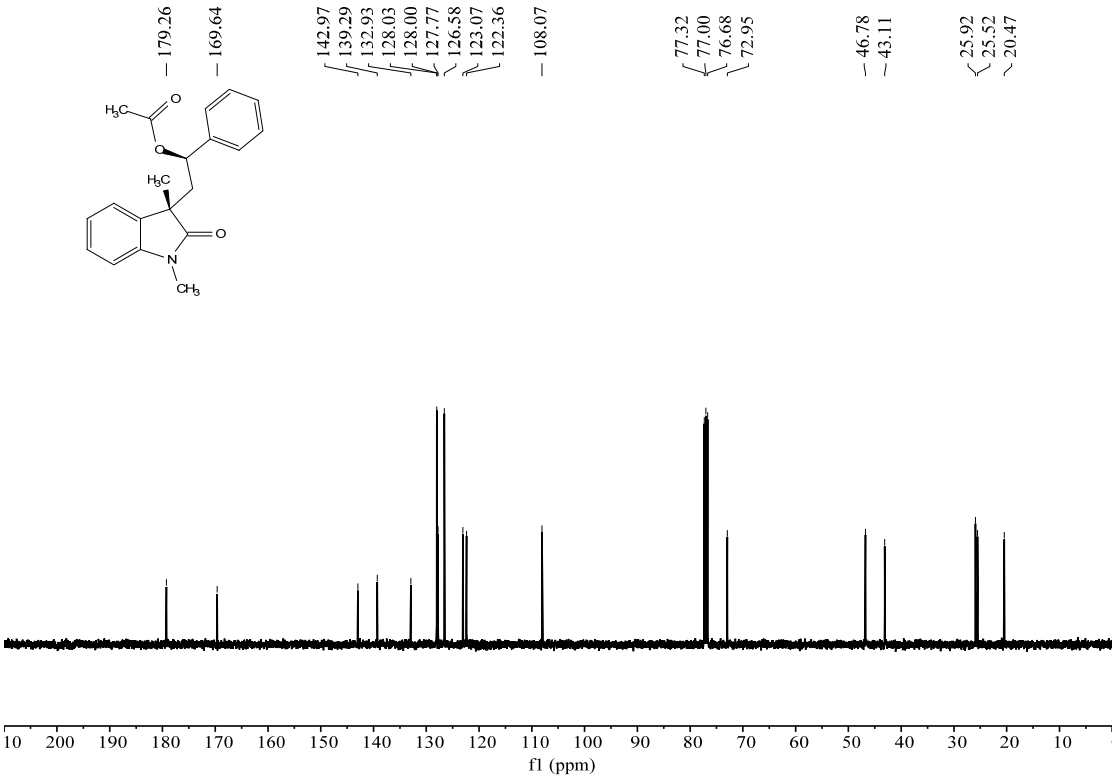
^{13}C NMR spectra of 58 (100 MHz, $CDCl_3$)



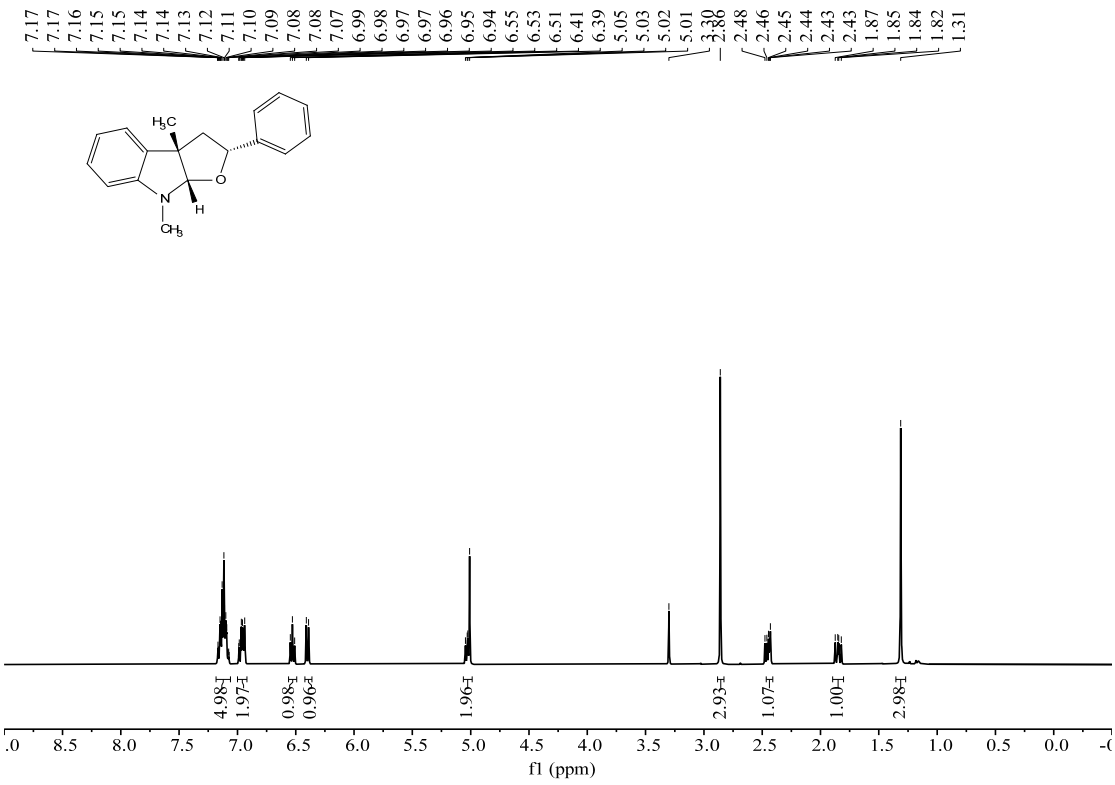
^{1}H NMR spectra of 59 (400 MHz, $CDCl_3$)



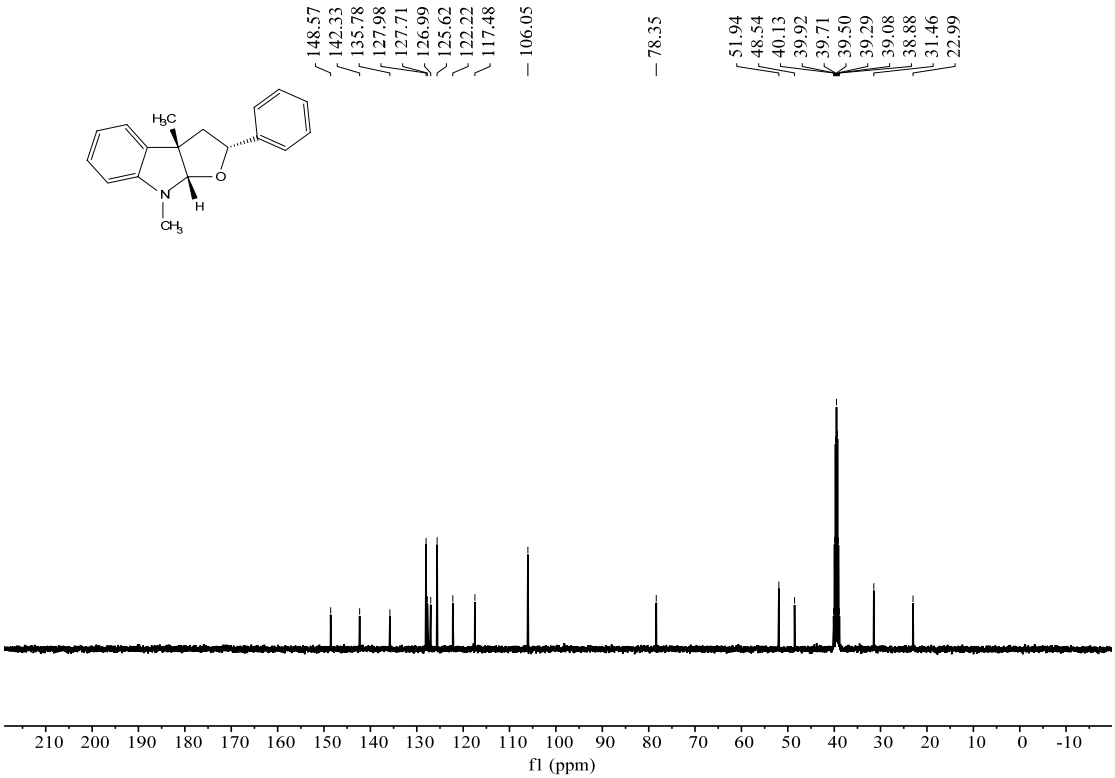
^{13}C NMR spectra of 59 (100 MHz, $CDCl_3$)



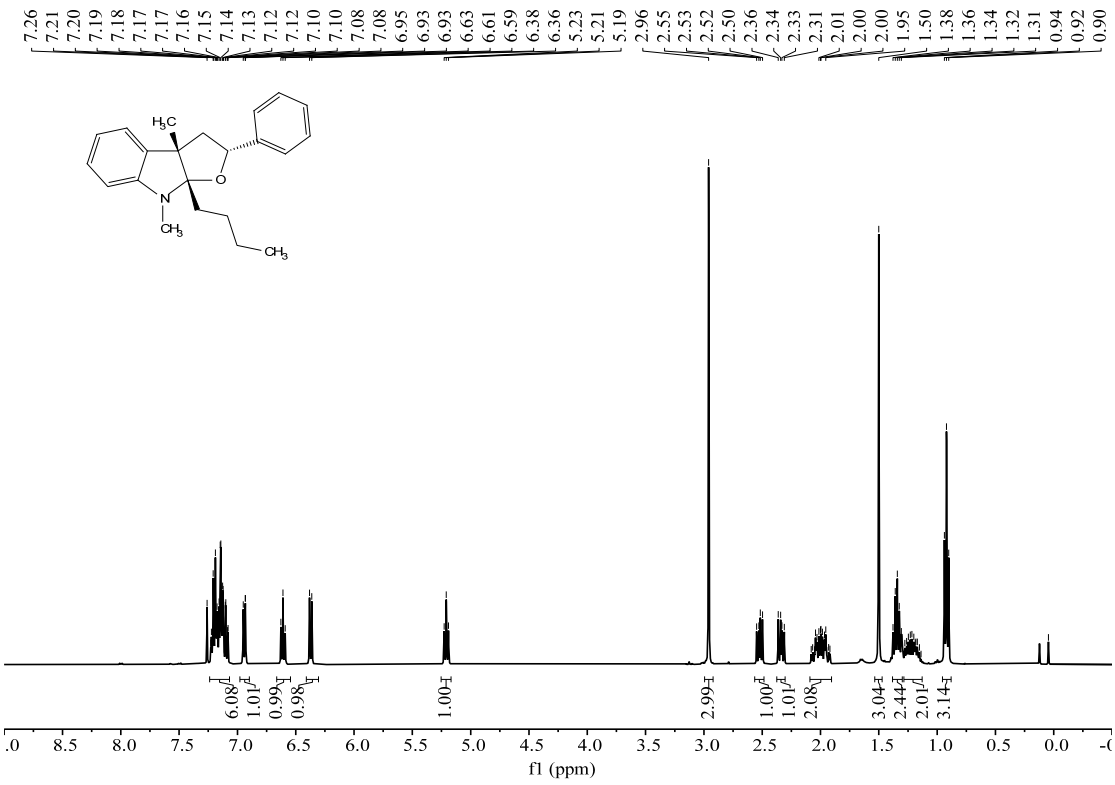
^{1}H NMR spectra of 60 (400 MHz, $CDCl_3$)



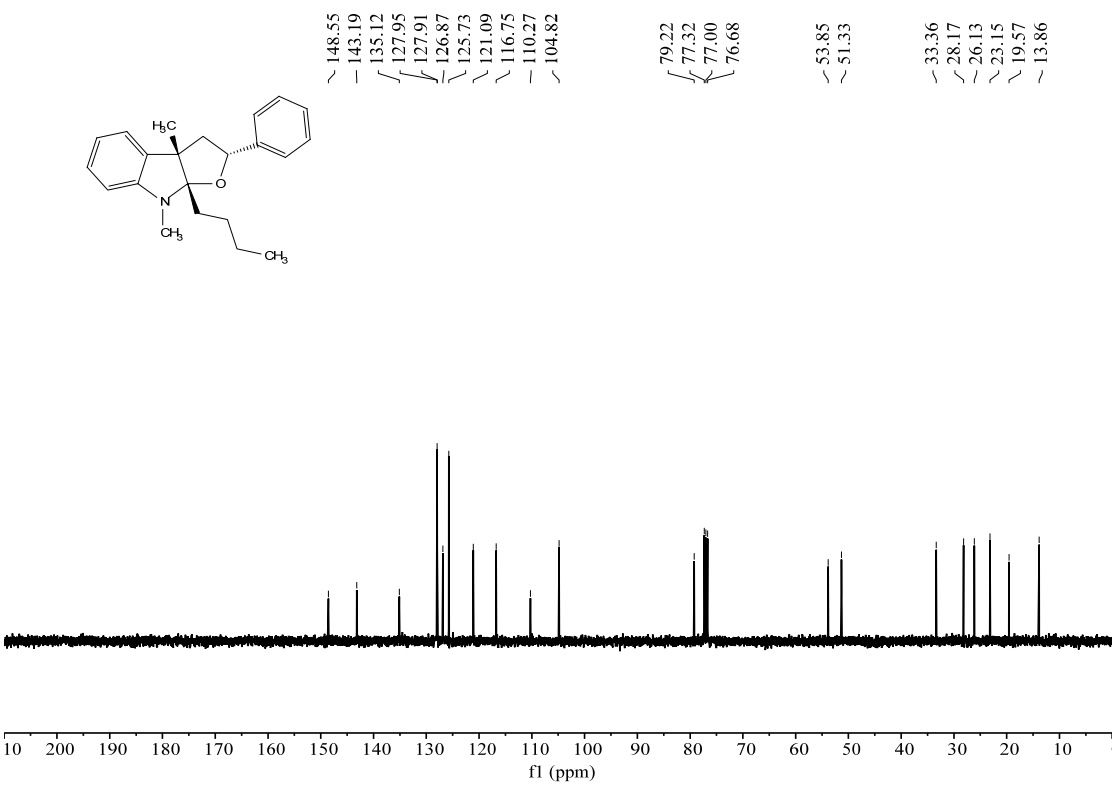
^{13}C NMR spectra of 60 (100 MHz, $CDCl_3$)



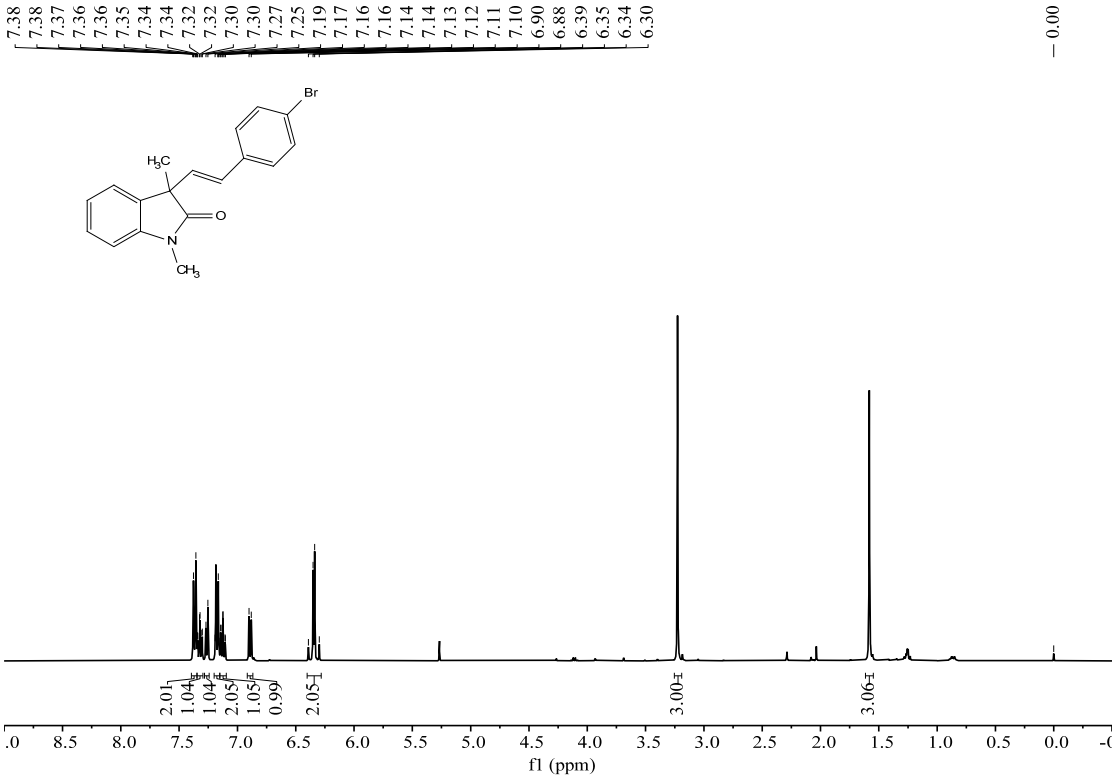
^{1}H NMR spectra of 61 (400 MHz, $CDCl_3$)



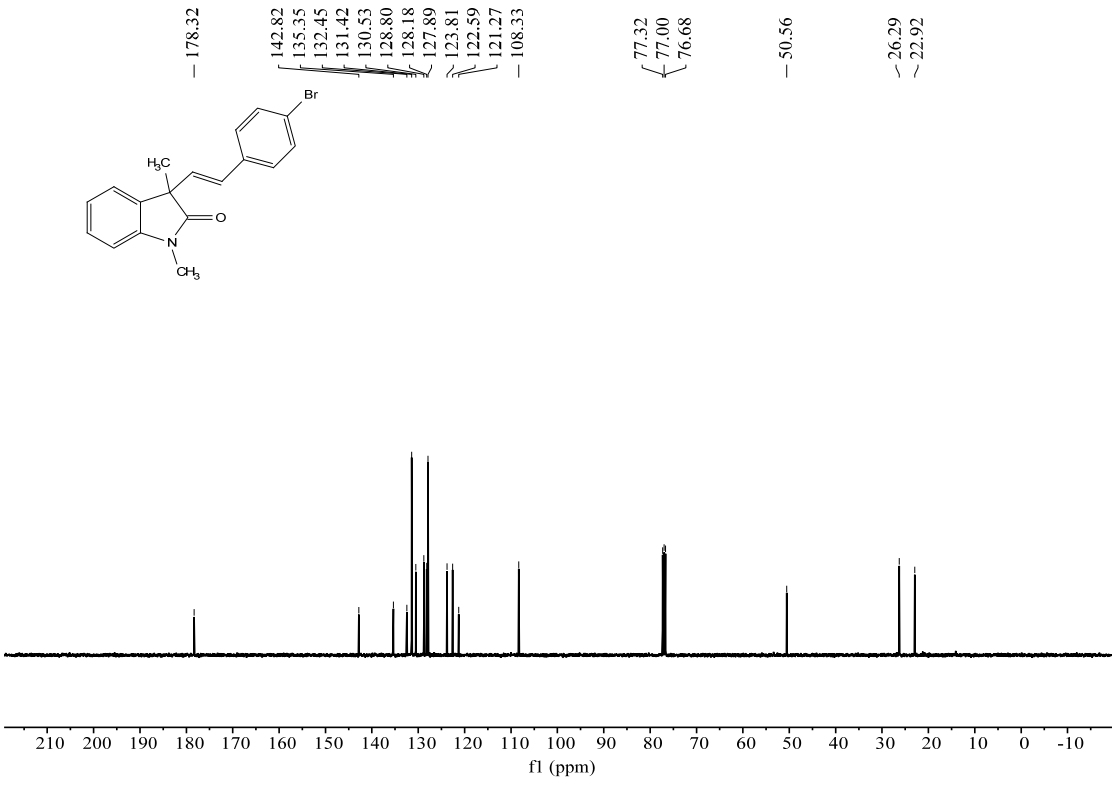
^{13}C NMR spectra of 61 (100 MHz, $CDCl_3$)



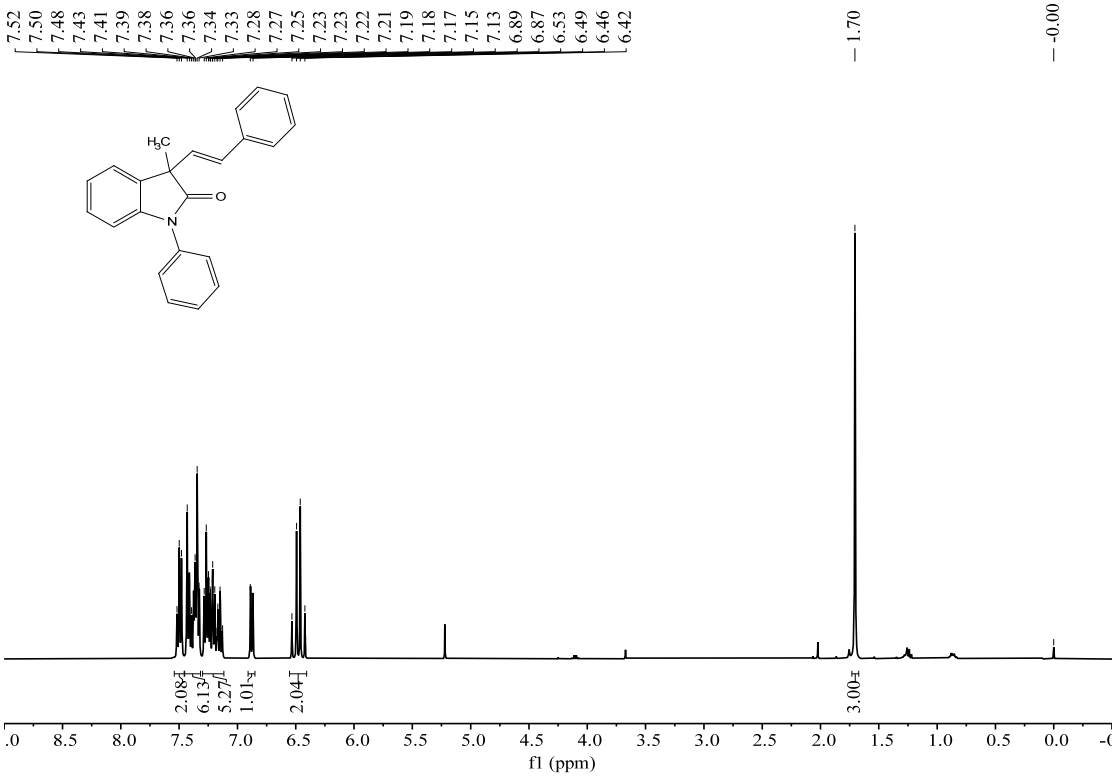
^{1}H NMR spectra of 62 (400 MHz, $CDCl_3$)



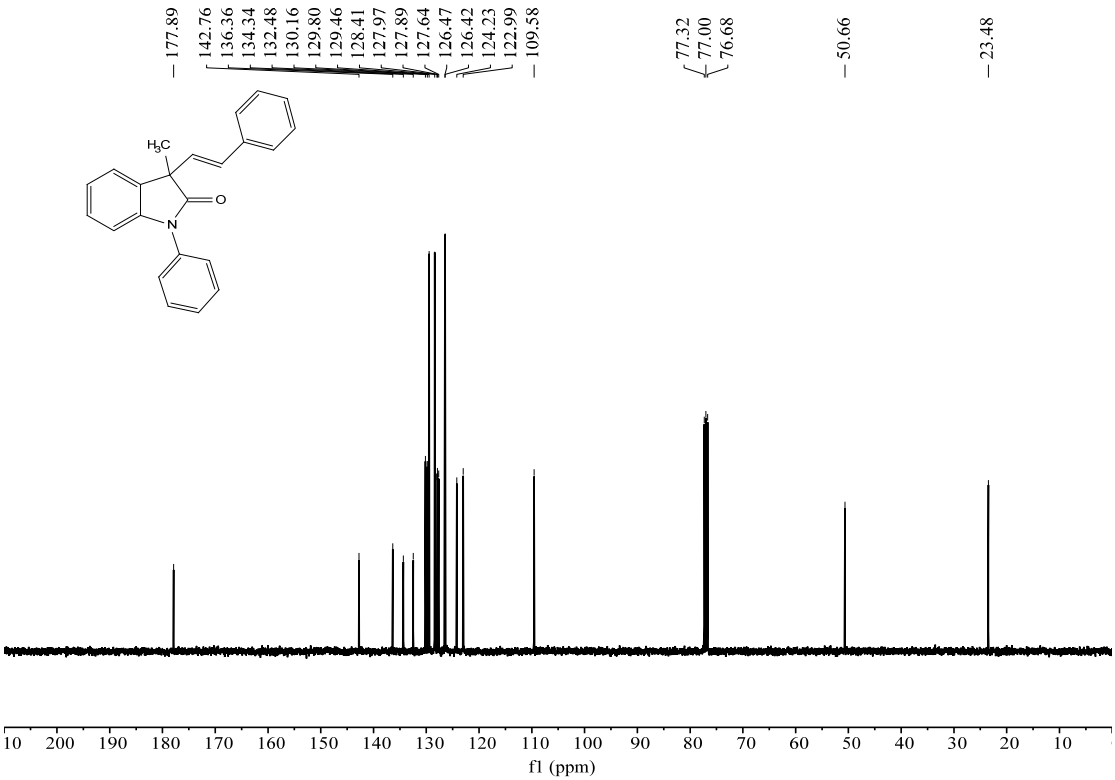
^{13}C NMR spectra of 62 (100 MHz, $CDCl_3$)



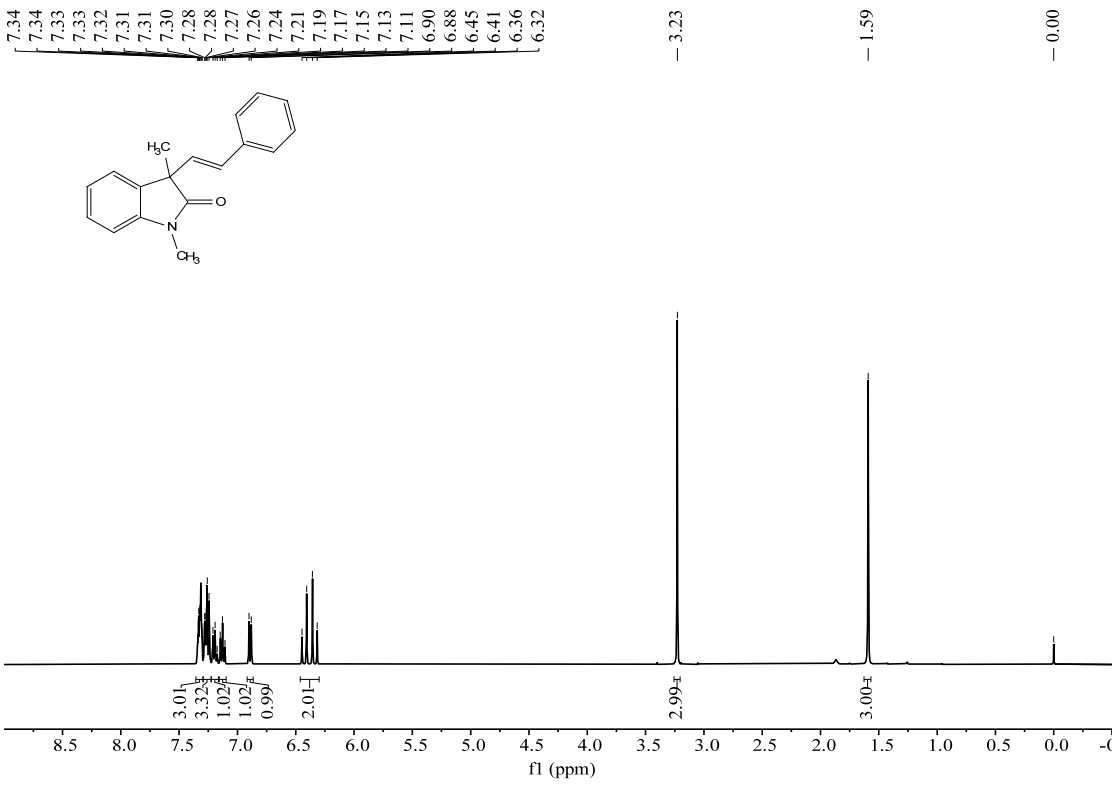
^{1}H NMR spectra of 63 (400 MHz, $CDCl_3$)



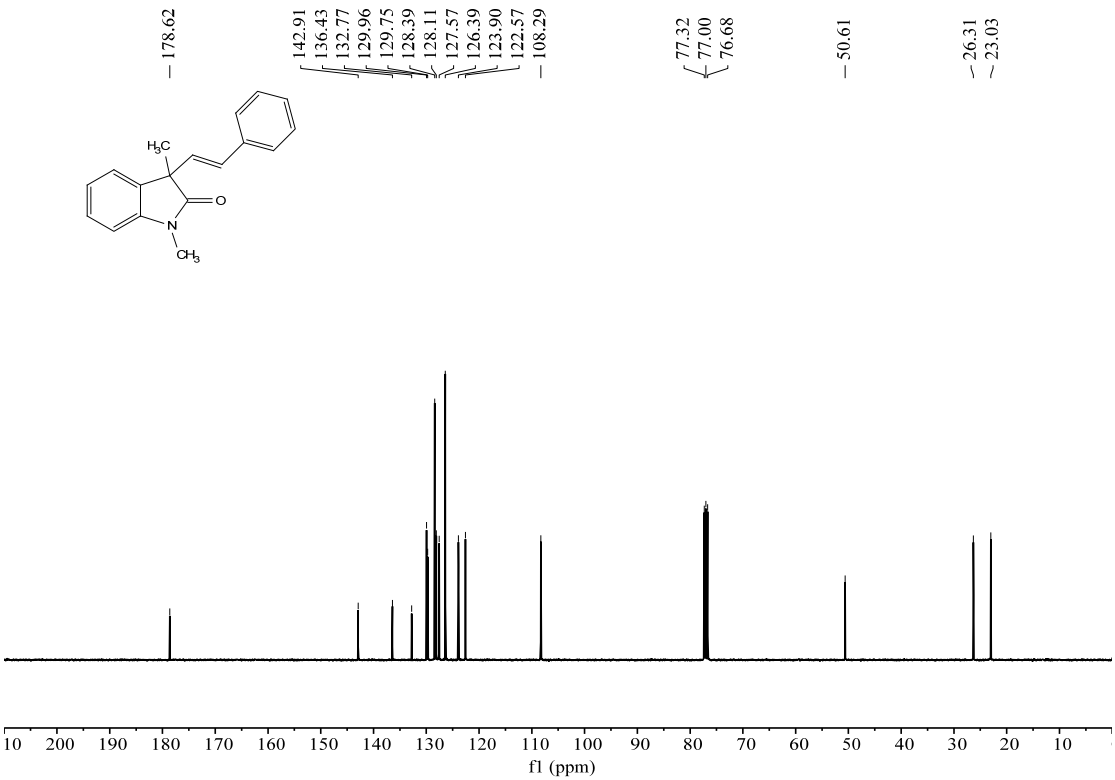
^{13}C NMR spectra of 63 (100 MHz, $CDCl_3$)



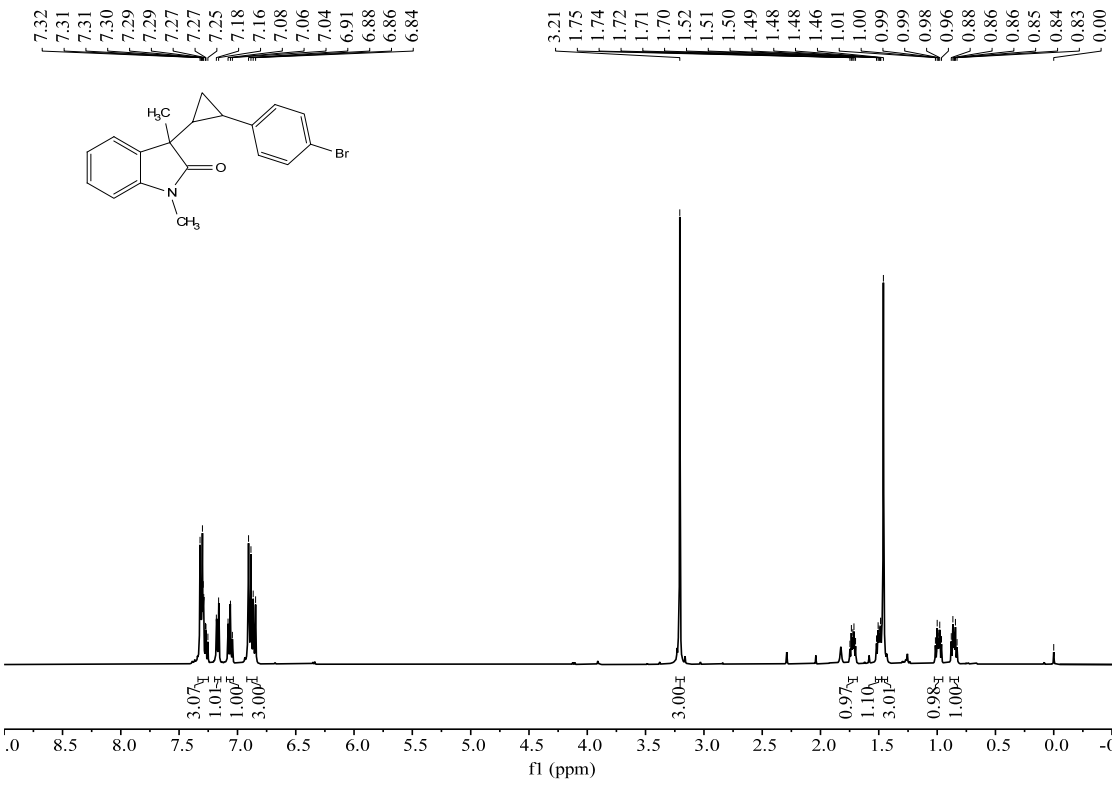
^{1}H NMR spectra of 64 (400 MHz, $CDCl_3$)



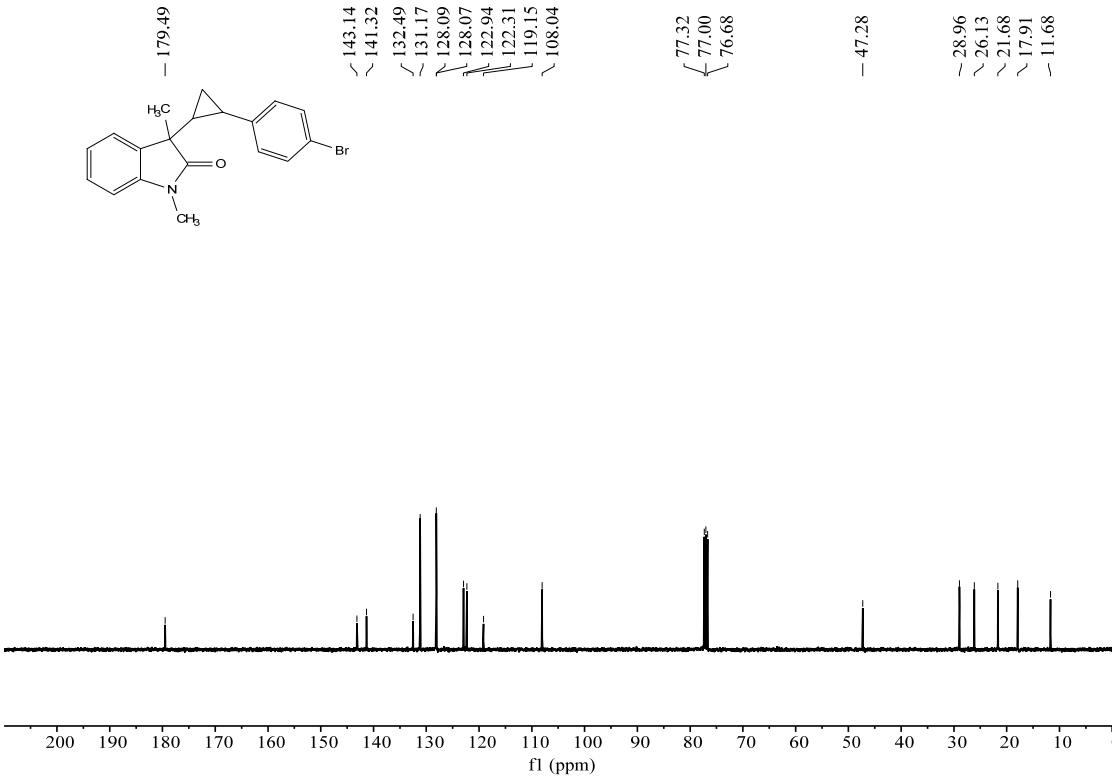
^{13}C NMR spectra of 64 (100 MHz, $CDCl_3$)



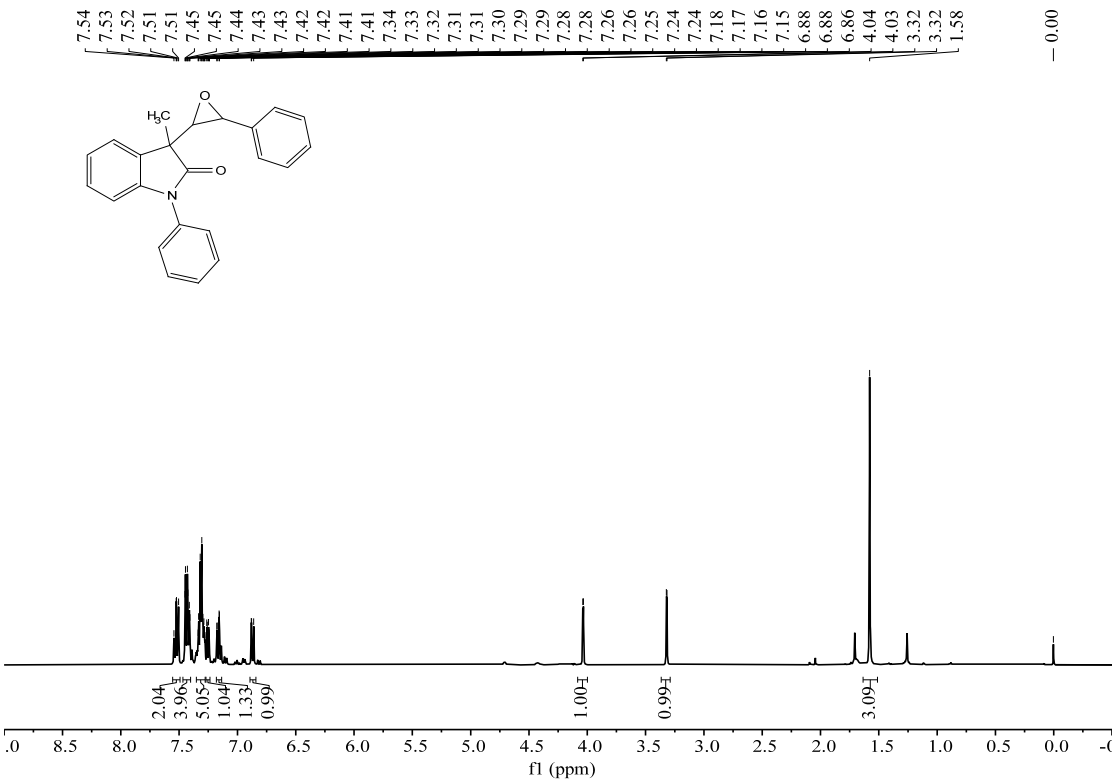
^{1}H NMR spectra of 65 (400 MHz, $CDCl_3$)



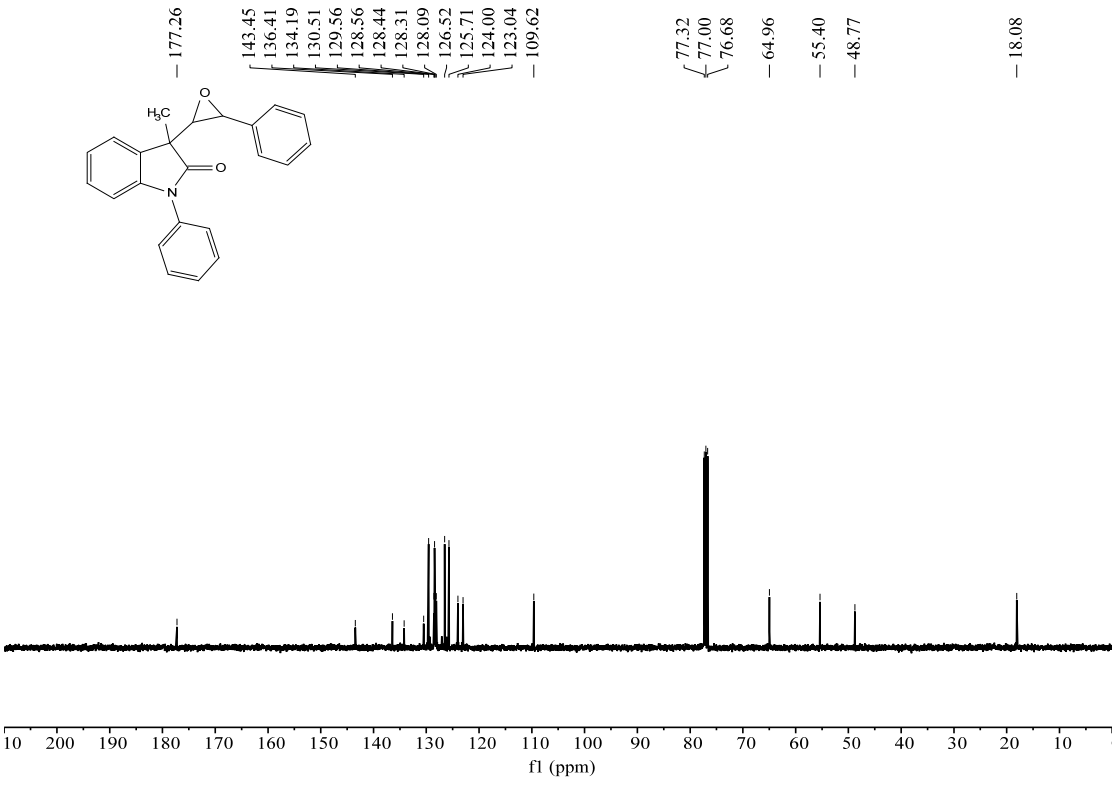
^{13}C NMR spectra of 65 (100 MHz, $CDCl_3$)



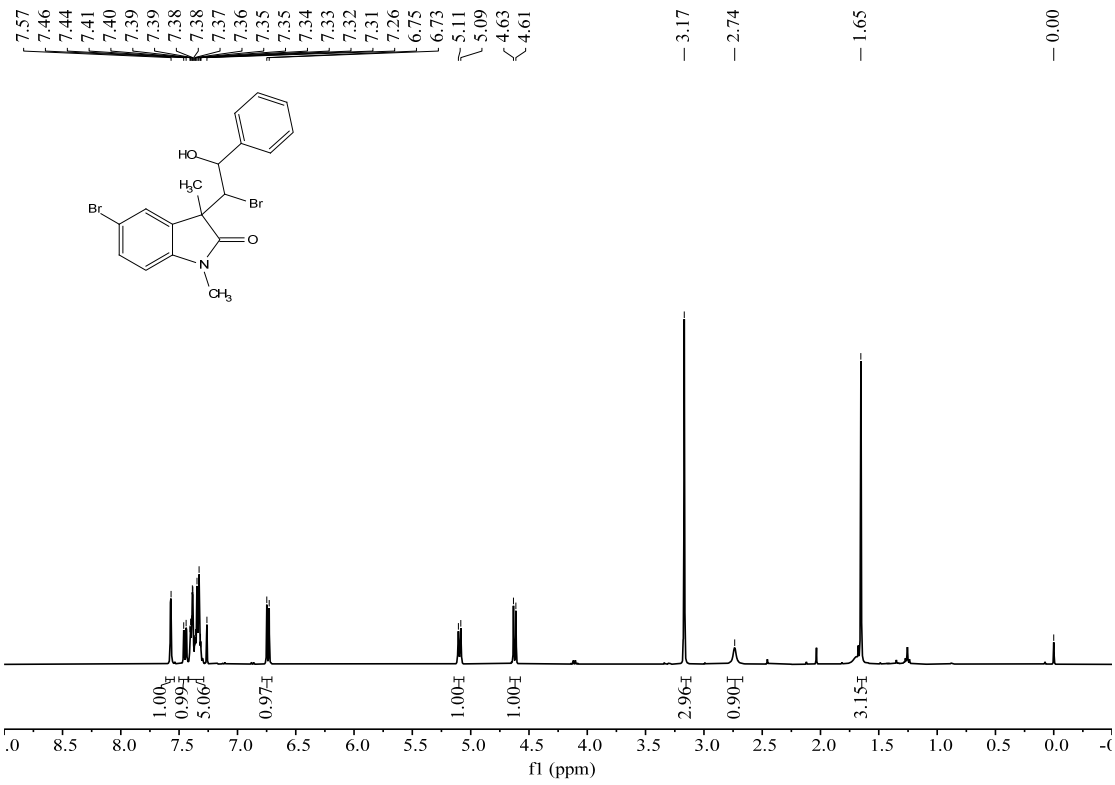
^{1}H NMR spectra of 66 (400 MHz, $CDCl_3$)



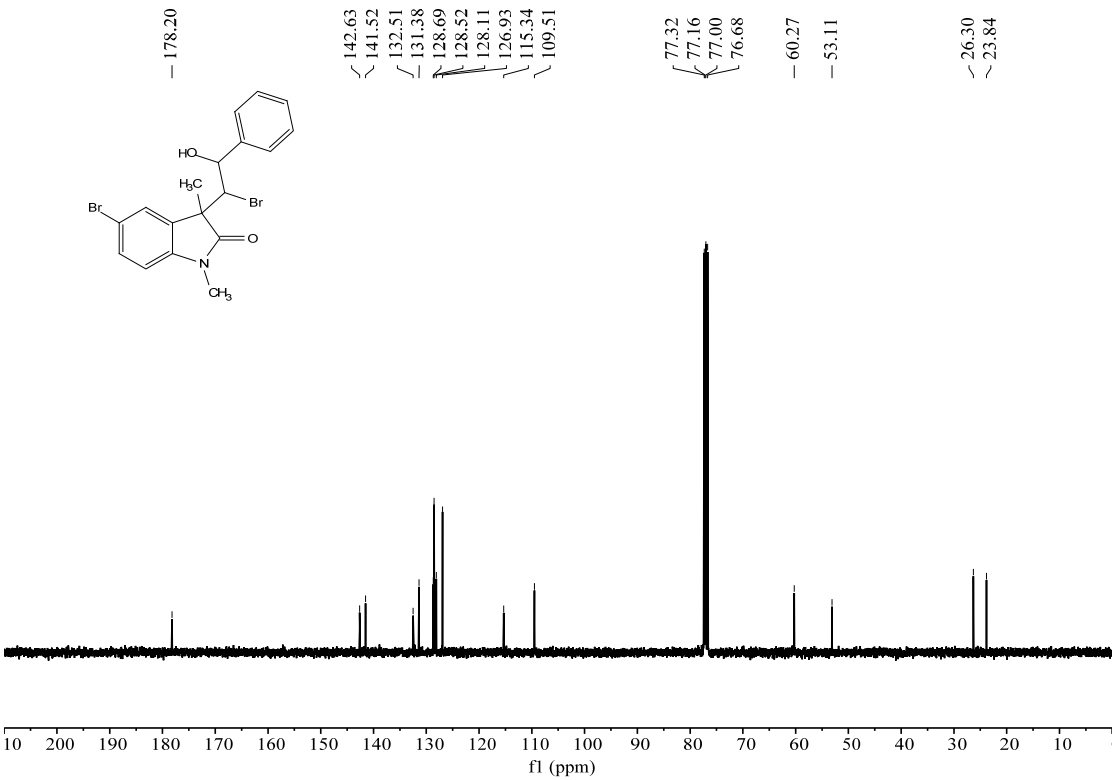
^{13}C NMR spectra of 66 (100 MHz, $CDCl_3$)



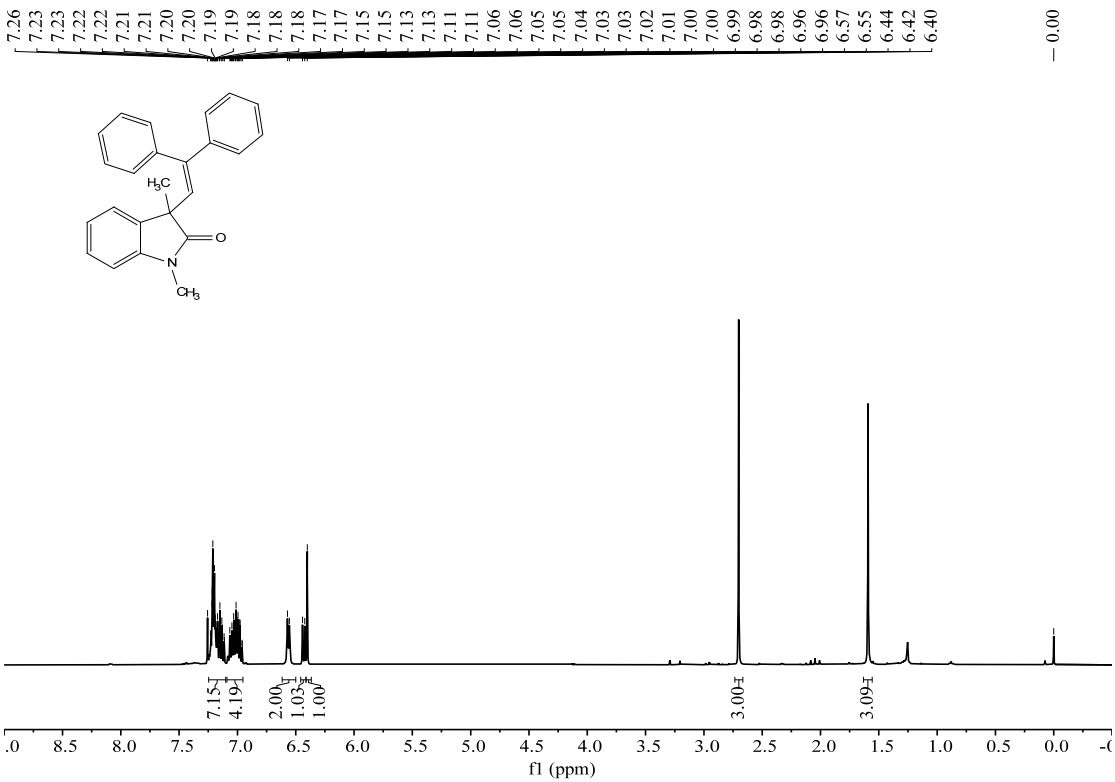
^{1}H NMR spectra of 67 (400 MHz, $CDCl_3$)



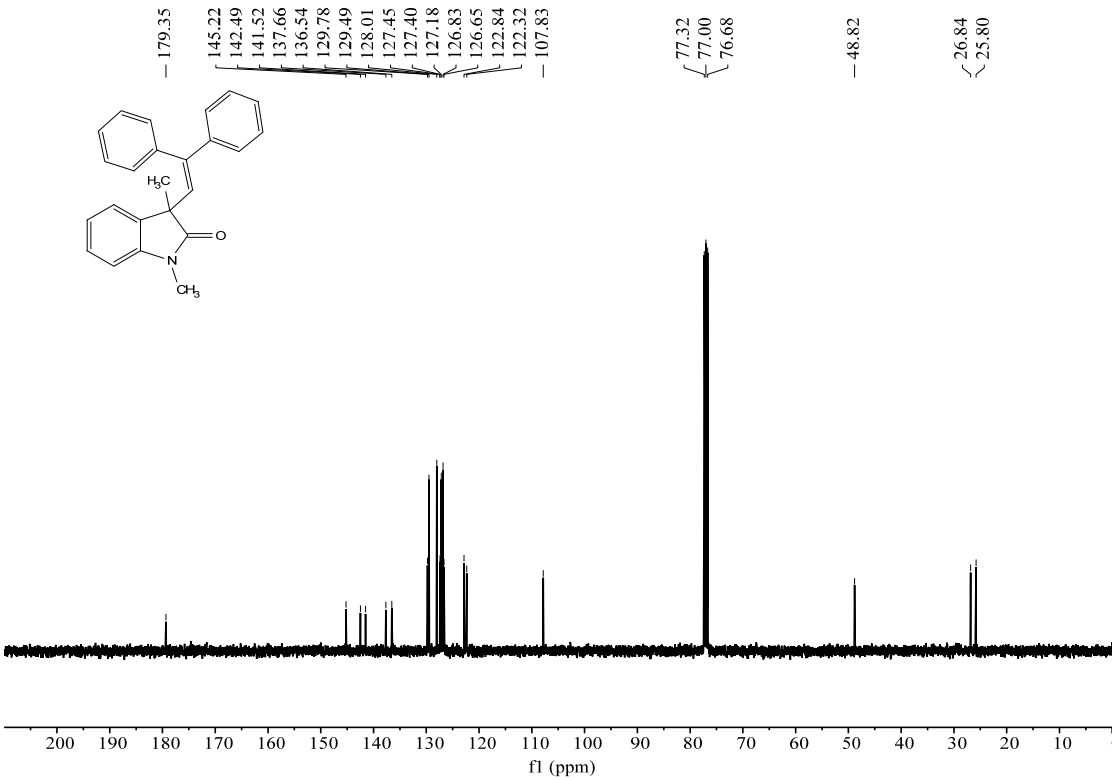
^{13}C NMR spectra of 67 (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 68 (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 68 (100 MHz, $CDCl_3$)



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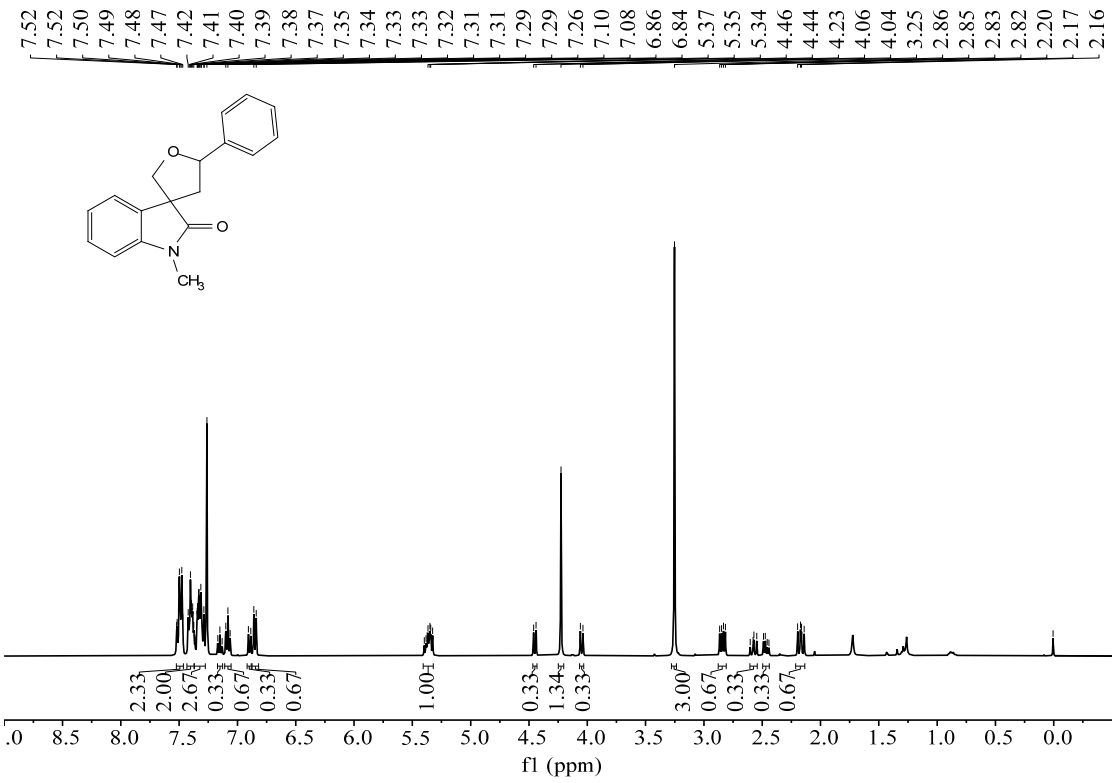

^{13}C NMR spectra of 69 (100 MHz, $CDCl_3$)