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Electronic Supplementary Information (ESI)

Photocatalytic activation of indole alkanols for intramolecular cyclization toward furoindolines

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Contents

1. General experiment

1.1 Materials and Experiments

Photocatalysis experiments were performed in an argon or oxygen atmosphere. Chemical reagents (including purified water) were obtained from commercial suppliers (*Sigma-Aldrich, Adamas,* Shanghai Titan Technology Co., LTD, Adamas et al.) and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on a 0.25 mm silica gel GF254 plate (Merck Silica gel 60-F254) using UV light as a visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate and heat as a developing agent. Silica gel (300-400 mesh) was used for normal flash column chromatography. Indole and its related derivate products were isolated by column chromatography with neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8). Ethyl acetate and petroleum ether were used as the eluent solvents. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise noted. LED lights (including every 5W 10W 20W blue LEDs with different wavenumbers) were purchased from the Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, and Changchun Changguang Chenpu Technology Co., LTD.

1.2 Characterizations and Analysis

EPR spectra were recorded at room temperature on a Bruker EMX micro A300 spectrometer operated at 9.8543 GHz.

^{1}H-NMR, and **^{13}C-NMR** were recorded with Bruker Advance (400 and 500 MHz) spectrometers. All chemical shifts were reported as δ values in parts per million (ppm) and coupling constants (J) in Hz. Tetramethylsilane (TMS) was used as the internal standard for $CDCl_3$ (7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C).

X-ray crystal structure: Single block crystals of **target molecules** were used as supplied. A suitable crystal with dimensions 0.20 × 0.15 × 0.10 mm^3 was selected and mounted on a Bruker APEX-II CCD diffractometer.

Mass spectra: **(1)** ***HR-MS (ESI)*** was taken on AB QSTAR Pulsar mass spectrometer or Agilent LC/MSD TOF mass spectrometer. HR-MS data were recorded via electron impact mass spectrometry using a time-of-flight analyzer. ***(2) GC–MS*** was performed on a Hewlett-Packard 6890 N gas chromatograph (equipped with the same HP-5MS capillary column) under identical operating conditions used in Mass Spectral Library by R. P. Adams (Adams, 2007).

Electrochemistry: cyclic voltammograms (CVs) were obtained on a Metrohm PGSTAT302N potentiostat.

UV-Visible (UV-Vis) absorption measurements were collected and analyzed using an Agilent Cary 5000 spectrophotometer.

Fluorescence (FL) emission intensities experiments were conducted on a Hitachi F-4600 luminescence Spectrophotometer.

1.3 Photocatalysis experiments device

The reaction was carried out as follows: a one, two or three-neck reaction quartz flask was fitted with a magnetic stirring bar. Septa capped the other two necks for injections and an atmosphere line. Following evacuation in a vacuum and flushing with argon or oxygen three times, the reaction vessel was charged with a solution of reactants. The reaction conditions were 25 °C and used an argon or oxygen balloon atmosphere, with water or other organic reagents as the solvent.

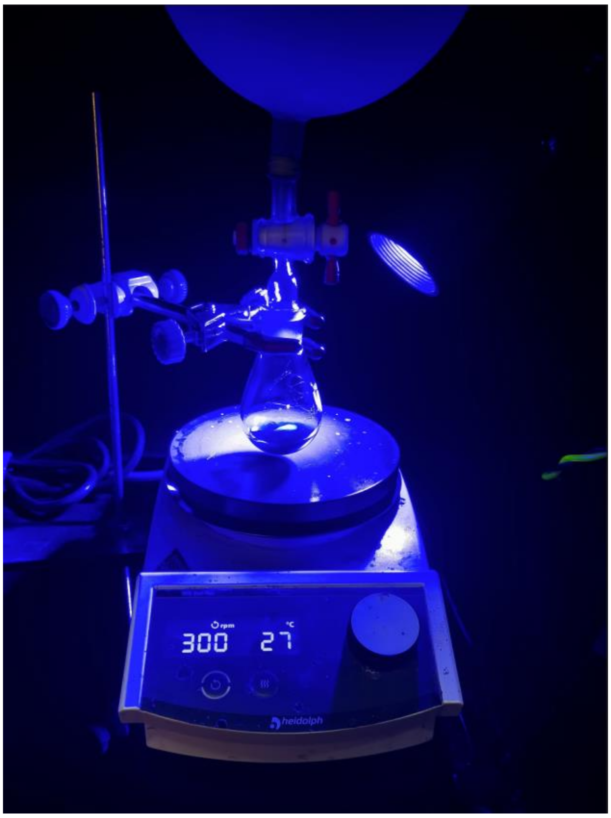


Figure S1. Photocatalysis experiment device.

2. Photocatalysis experiments

2.1 Photocatalytic synthesis of furoindoline product

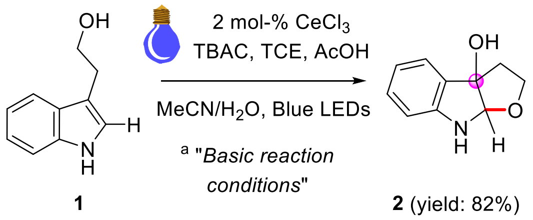
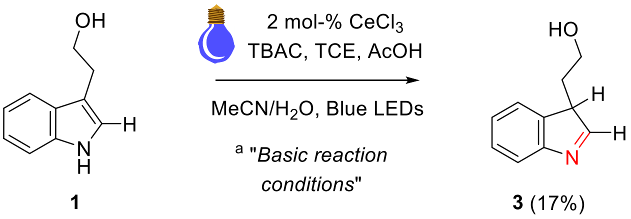


Figure S2. Photocatalytic synthesis of furoindoline product.

In an oven-dried quartz flask (50 mL) equipped with a stir bar, tryptophol (250 mg, 1.6 mmol, 1.0 equiv.), acetic acid (AcOH, 20 mol-%, 0.20 equiv.), cerium (III) chloride ($CeCl_3$, 19.11 mg, 0.08 mmol, 0.05 equiv.), tetrabutylammonium chloride (TBAC, 43.09 mg, 0.16 mmol, 0.1 equiv.), 2,2,2-trichloro-ethanol (TCE, 23.18 mg, 0.16 mmol, 0.1 equiv.), a mixture of acetonitrile and water(MeCN/H_2O, v/v=1/1, 20.0 mL) as solvents were added to a two-necked quartz flask. The reaction was carried out under the irradiation of blue LED lights (18 W, λ = 400 nm-480 nm) at room temperature in an argon (Ar) balloon atmosphere for 10 h cooling by a fan. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic acid, cerium sulfate, and heat as a developing agent. When the reactant material was no longer decreased, the solution was extracted with ethyl acetate (EtOAc, 6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a vacuum rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8, as the ideal medium) using ethyl acetate and petroleum ether (3:1, vol/vol) as the eluent solvents. The target product was obtained in a yield of 130 mg, 82%. All the products' isolated yields were calculated by column chromatography.

2.2 Photocatalytic synthesis of indole imidiation product



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3 (17%)

Figure S3. Photocatalytic synthesis of indole imidiation product.

In an oven-dried quartz flask (50 mL) equipped with a stir bar, tryptophol (250 mg, 1.6 mmol, 1.0 equiv.), acetic acid (AcOH, 20 mol-%, 0.20 equiv.), cerium (III) chloride ($CeCl_3$, 19.11 mg, 0.08 mmol, 0.05 equiv.), tetrabutylammonium chloride (TBAC, 43.09 mg, 0.16 mmol, 0.1 equiv.), 2,2,2-trichloro-ethanol (TCE, 23.18 mg, 0.16 mmol, 0.1 equiv.), acetonitrile (MeCN, 20.0 mL) as solvent was added to a two-necked quartz flask. The reaction was carried out under the irradiation of blue LED lights (18 W, λ = 400 nm-480 nm) at room temperature in an argon (Ar) balloon atmosphere for 10 h cooling by a fan. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic acid, cerium sulfate, and heat as a developing agent. When the reactant material was no longer decreased, the solution was extracted with ethyl acetate (EtOAc, 6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a vacuum rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8, as the ideal medium) using ethyl acetate and petroleum ether (3:1, vol/vol) as the eluent solvents. The product was obtained in a yield of 5 mg, 17%. All the products' isolated yields were calculated by column chromatography.

2.3 Photocatalytic synthesis of oxoindole product

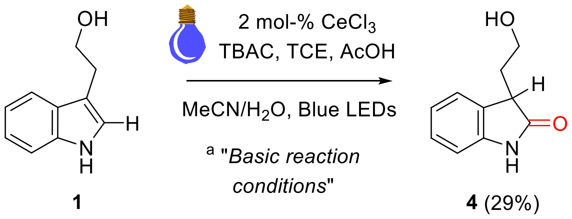


Figure S4. Photocatalytic synthesis of indole oxidation product.

In an oven-dried quartz flask (50 mL) equipped with a stir bar, tryptophol (250 mg, 1.6 mmol, 1.0 equiv.), acetic acid (AcOH, 20 mol-%, 0.20 equiv.), cerium (III) chloride ($CeCl_3$, 19.11 mg, 0.08 mmol, 0.05 equiv.), tetrabutylammonium chloride (TBAC, 43.09 mg, 0.16 mmol, 0.1 equiv.), 2,2,2-trichloro-ethanol (TCE, 23.18 mg, 0.16 mmol, 0.1 equiv.), acetonitrile (MeCN, 20.0 mL) as solvent was added to a two-necked quartz flask. The reaction was carried out under the irradiation of blue LED lights (18 W, λ = 400 nm-480 nm) at room temperature in an oxygen (O_2) balloon atmosphere for 10 h cooling by a fan. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic acid, cerium sulfate, and heat as a developing agent. When the reactant material was no longer decreased, the solution was extracted with ethyl acetate (EtOAc, 6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a vacuum rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8, as the ideal medium) using ethyl acetate and petroleum ether (3:1, vol/vol) as the eluent solvents. The target product was obtained in a yield of 35 mg, 29%. All the products' isolated yields were calculated by column chromatography.

2.4 Photocatalytic synthesis of tryptophol and chromone

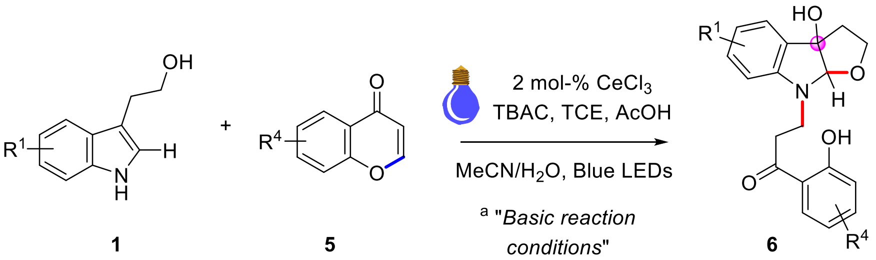


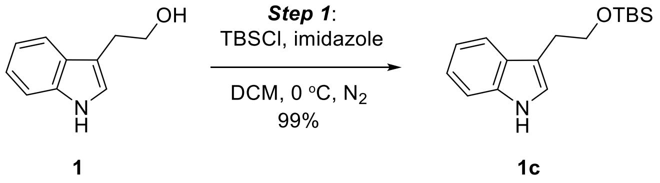
Figure S5. General photocatalysis of intermolecular 1,2-addition.

In an oven-dried quartz flask (50 mL) equipped with a stir bar, tryptophol (250 mg, 1.6 mmol, 1.0 equiv.), chromone (272.0 mg, 1.9 mmol, 1.0 equiv.), acetic acid (AcOH, 20 mol-%, 0.20 equiv.), cerium (III) chloride ($CeCl_3$, 19.11 mg, 0.08 mmol, 0.05 equiv.), tetrabutylammonium chloride (TBAC, 43.09 mg, 0.16 mmol, 0.1 equiv.), 2,2,2-trichloro-ethanol (TCE, 23.18 mg, 0.16 mmol, 0.1 equiv.), a mixture of acetonitrile and water(MeCN/H_2O, v/v=1/1, 20.0 mL) as solvents were added to a two-necked quartz flask. The reaction was carried out under the irradiation of blue LED lights (18 W, λ = 400 nm-480 nm) at room temperature in an argon (Ar) balloon atmosphere for 10 h cooling by a fan. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic acid, cerium sulfate, and heat as a developing agent. When the reactant material was no longer decreased, the solution was extracted with ethyl acetate (EtOAc, 6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a vacuum rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8, as the ideal medium) using ethyl acetate and petroleum ether (8:1, vol/vol) as the eluent solvents. The target product was obtained in a yield of 101 mg, 84%. All the products' isolated yields were calculated by column chromatography.

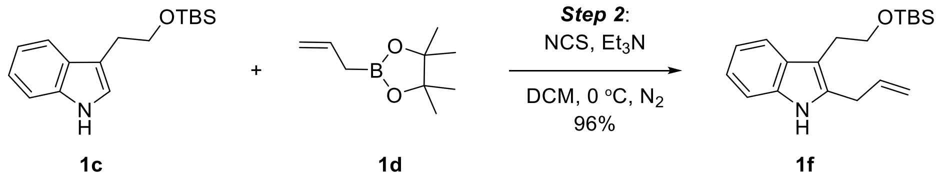
Table S1. Other reaction conditions optimization for tryptophol and chromone

Entry	**Catalysis**	**Solvent**	**Acid**	**Yield (%)**
1	$CeCl_3$	MeCN	no	0
2	$CeCl_3$	MeOH	no	2
3	$CeCl_3$	THF	no	0
4	$CeCl_3$	DMF	no	0
5	$CeCl_3$	DCM	no	1.5
6	$CeCl_3$	Acetone	no	0
7	$EuCl_3$•$6H_2O$	H_2O	AcOH	2
8	$FeCl_3$	H_2O	AcOH	41
9	$CeCl_3$	H_2O	AcOH	49
10	$Ce(NO_3)_3$•$6H_2O$	H_2O	AcOH	43
11	$Ce(H_3PO_4)_3$	H_2O	AcOH	0
12	$Ce(Ac)_3$•nH_2O	H_2O	AcOH	0
13	$Ce(AcOAc)_3$•nH_2O	H_2O	AcOH	2
14	$Ce[(CF_3$•$SO_3)_4$	H_2O	AcOH	45

2.5 Allyl indole synthesis

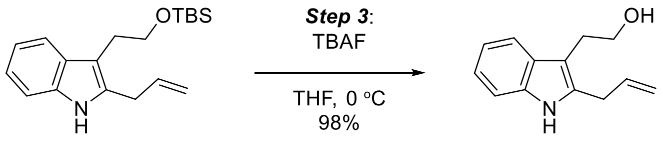


Step 1: In an oven-dried quartz flask (50 mL) equipped with a stir bar and added dichloromethane (10.0 mL) as solvent, then transfered the reaction flask to an ice bath and added tryptophol (1.0 g, 6.2 mmol, 1.0 equiv.) and imidazole (633.5 mg, 9.3 mmol, 1.5 equiv.) in turn; finally, added the diluted *tert*-butyldimethylsilyl (TBSCl, 1.0 g, 6.8 mmol, 1.1 equiv.) solution to the mixture. The reaction was conducted under an argon atmosphere using an Ar balloon. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic acid, cerium sulfate, and heat as a developing agent. When the reactant material was consumed, the solution was extracted with DCM (6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8) using ethyl acetate and petroleum ether (1:20, vol/vol) as the eluent solvents. The product was obtained in a yield of 1.1 g, 99%.



Step 2: Following the **Step 1**, in an oven-dried quartz flask (50 mL) equipped with a stir bar and added dichloromethane (10.0 mL) as solvent, then transfered the reaction flask to an ice bath and added the pure product of **step 1** 3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1H-indole (1.1 g, 4.2 mmol, 1.0 equiv.). Next, added triethylamine (633.7 mg, 6.3 mmol, 1.5 equiv.), N-chlorosuccinimide (724.5 mg, 5.4 mmol, 1.3 equiv.) and stirred for 15 minutes. added allylboronic acid pinacol ester (1052 mg, 6.3 mol, 1.5 equiv.) to the mixture. Stirring for 1 hour at room temperature, then added 0.125 M sodium hydroxide solution to quench the reaction. The reaction was conducted under an argon atmosphere using an Ar balloon. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic

acid, cerium sulfate, and heat as a developing agent. The solution was extracted with EtOAc (6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8) using ethyl acetate and petroleum ether (1:15, vol/vol) as the eluent solvents. The product was obtained in a yield of 1.4 g, 96%.



1f **7**

Step 3: In an oven-dried quartz flask (50 mL) equipped with a stir bar and added tetrahydrofuran (10.0 mL) as solvent, then transfered the reaction flask to an ice bath and added the pure product of **step 2** 2-allyl-3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1H-indole (1.4 g, 4.4 mol, 1.0 equiv.), added the 1M tetrabutylammonium fluoride (2.3 g, 8.9 mmol, 2 equiv.) solution to the mixture. The reaction was conducted under an argon atmosphere using an Ar balloon. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic acid, cerium sulfate, and heat as a developing agent. When the reactant material was consumed, the solution was extracted with EtOAc (6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8) using ethyl acetate and petroleum ether (1:10, vol/vol) as the eluent solvents. The product was obtained in a yield of 1.0 g, 98%.

2.6 Allyl indole photocatalysis reaction for mechanism investigation

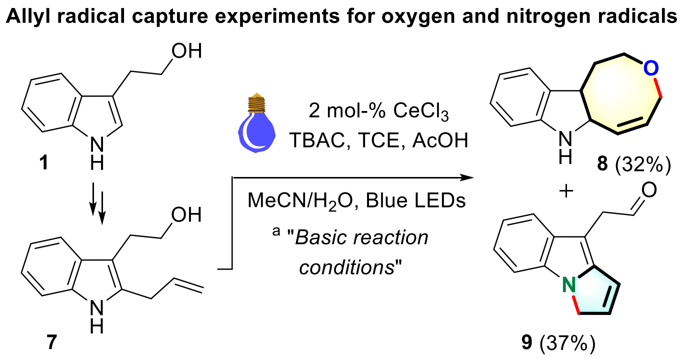


Figure S6. Photocatalytic radical capture of allyl group.

In an oven-dried quartz flask (50 mL) equipped with a stir bar, the pure substrate of **7** (180.0 mg, 1.2 mol, 1.0 equiv.), cerium (III) chloride (30.6 mg, 0.1 mmol, 0.1 equiv.), tetrabutylammonium chloride (34.5 mg, 0.1 mmol, 0.1 equiv.), 2,2,2-Trichloroethanol (92.8 mg, 0.6 mmol, 0.5 equiv.), acetic acid (14.9 mg, 0.2 mmol, 0.2 equiv.), H_2O (5.0 mL) and MeCN (5.0 mL) were combined and added. The reaction was conducted under an argon atmosphere using an Ar balloon. TLC, UV light as a visualizing agent, the reaction was monitored, and an ethanolic solution of phosphomolybdic acid, cerium sulfate, and heat as a developing agent. When the reactant material was consumed, the solution was extracted with EtOAc (6×10 mL) and H_2O (3×10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on neutral alumina (Al_2O_3, Merck KGaA, 70–230 mesh, and pH = 6.8–7.8) using ethyl acetate and petroleum ether (1:8, vol/vol) as the eluent solvents. The product **8** was obtained in a yield of 39.1 mg, 32%. The product **9** was obtained in a yield of 43.2 mg, 37%,

3. Mechanistic investigations

3.1 Light ON/OFF control experiments

Light ON/OFF control experiment was conducted, and the yield of the furoindoline **2** was measured at different reaction times using gas chromatography (GC). As shown in ***Fig. S7***, the product generation indicated that the yield was blocked immediately when the light was turned off. However, the reaction resumed when the light was turned on, indicating that constant light irradiation is essential for this transformation.

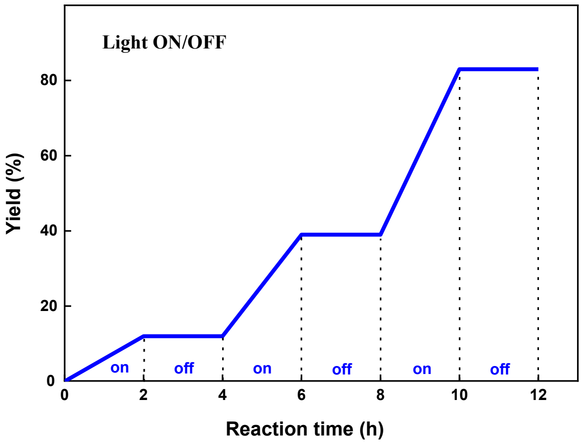


Fig. S7. Light ON/OFF experiments for radical propagation test (the yield of furoindoline **2** product was measured by GC analysis).

3.2 UV-Vis experiments

UV-Visible absorption measurements were collected and analyzed using an Agilent Cary 5000 spectrophotometer. Solutions of different indole and reaction additives were introduced to a 1 cm path length quartz cuvette equipped with a Teflon® septum under an argon atmosphere (all solutions were prepared in the dark room).

UV-Visible spectral variations observed during the photolysis of solutions containing tryptophol (5 mg, 0.05 mmol), and [Ce]-photocatalyst (0.5 mg, 0.00075 mmol), under varying reaction conditions with MeCN or H_2O as solvents, AcOH and O_2 as additives, the reaction mixtures were photo-irradiated under blue LED light about 0 h, 0.5 h, 1 h, 3 h, 5 h, 7 h, and 11 h, then reaction mixtures were separately transformed to 1 cm length quartz cuvettes, sealed with Teflon® septa, and then tested with a stream of oxygen.

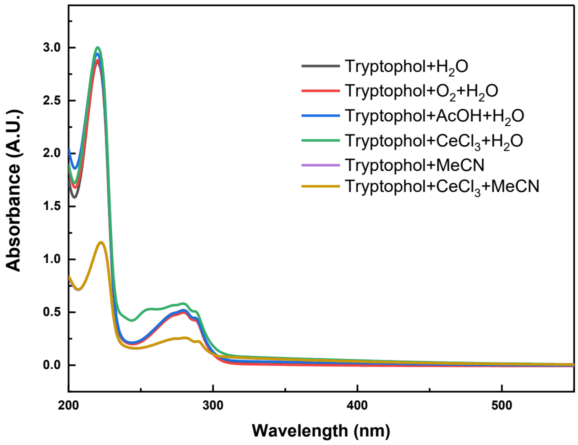


Figure S8. UV-Vis experiments for tryptophol in different solvents.

UV-Visible spectral variations observed during the photolysis of solutions containing tryptophol and its derivatives (5 mg, 0.05 mmol), and [Ce]-photocatalyst (0.5 mg, 0.00075 mmol), under varying reaction conditions with MeCN or H_2O as solvents, AcOH and O_2 as additives, the reaction mixtures were photo-irradiated under blue LED light about 0 h, 0.5 h, 1 h, 3 h, 5 h, 7 h, and 11 h, then reaction mixtures were separately transformed to 1 cm length quartz cuvettes, sealed with Teflon® septa, and then tested with a stream of oxygen.

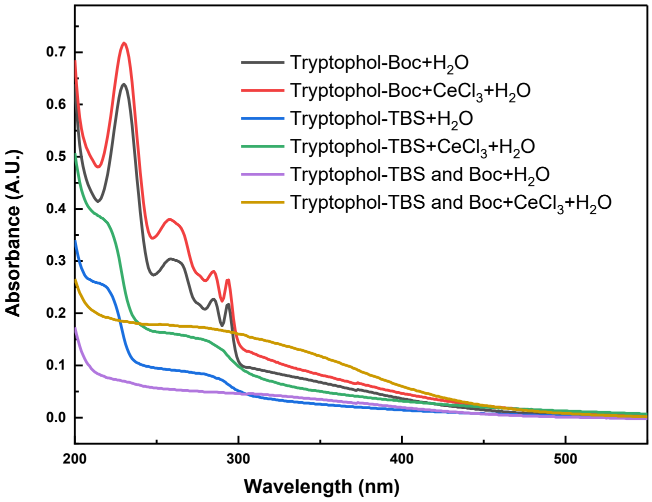


Figure S9. UV-Vis experiments for tryptophol with different protecting groups.

3.3 Fluorescence experiments

Fluorescence (FL) emission intensities experiments were conducted on a Hitachi F-4600 luminescence Spectrophotometer. All solutions of different furfuryl alcohol and *tris*-(*2*-phenylpyridine) iridium were excited at 260 nm, a pitch of 5 nm, and the emission intensity was collected at 275 nm. The scan rate was 12000 nm·min$^{-1,}$ and the photomultiplier tube voltage (PTV) was 680 V. The light source for fluorescence lifetime measurement was a 380 EPL TCSPC laser with an increment of 1.0 nm and a monochromatic band of 2.0 nm.

Fluorescence (FL) emission spectral variations observed during the photolysis of solutions containing tryptophol (5 mg, 0.05 mmol), and [Ce]-photocatalyst (0.5 mg, 0.00075 mmol), under varying reaction conditions with MeCN or H_2O as solvents, AcOH and O_2 as additives, the reaction mixtures were photo-irradiated under blue LED light about 0 h, 0.5 h, 1 h, 3 h, 5 h, 7 h, and 11 h, then reaction mixtures were separately transformed to 1 cm length quartz cuvettes, sealed with Teflon® septa, and then tested with a stream of oxygen.

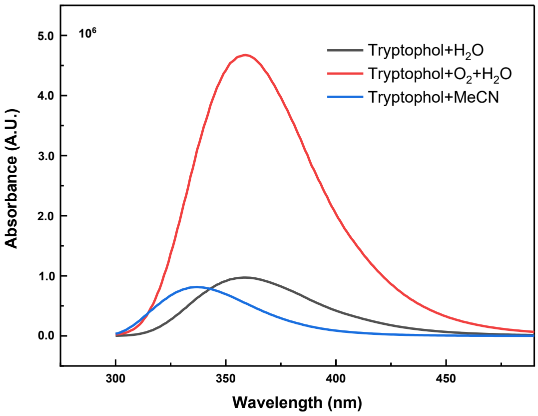


Figure S10. Fluorescence experiments of tryptophol under different reaction conditions.

Fluorescence (FL) emission spectral variations observed during the photolysis of solutions containing tryptophol and its derivatives (5 mg, 0.05 mmol), and [Ce]-photocatalyst (0.5 mg, 0.00075 mmol), under varying reaction conditions with MeCN or H_2O as solvents, AcOH and O_2 as additives, the reaction mixtures were photo-irradiated under blue LED light about 0 h, 0.5 h, 1 h, 3 h, 5 h, 7 h, and 11 h, then reaction mixtures were separately transformed to 1 cm length quartz cuvettes, sealed with Teflon® septa, and then tested with a stream of oxygen.

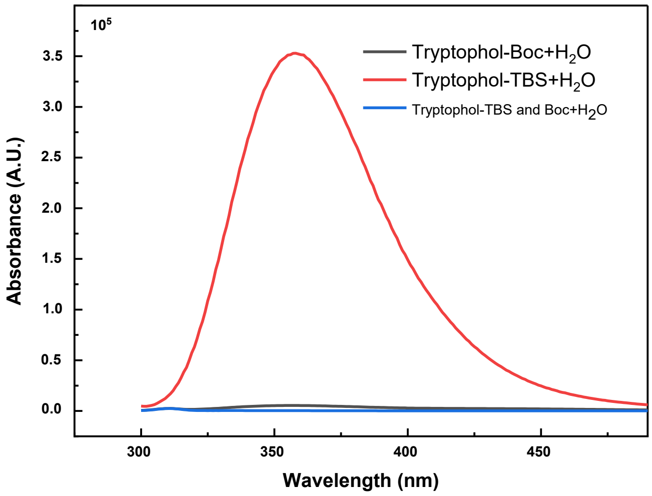


Figure S11. Fluorescence experiments of tryptophol with different protecting groups.

3.4 Cyclic voltammetry (CV) experiments

Cyclic voltammograms were conducted on a Metrohm PGSTAT302N potentiostat and performed in a three-electrode cell connected to a Schlenk line under nitrogen at room temperature. The working electrode was a carbon plate electrode. The counter electrode was a platinum wire. The reference was a Hg/Hg_2Cl_2 electrode submerged in saturated aqueous KBr solution and separated from the reaction by a salt bridge.

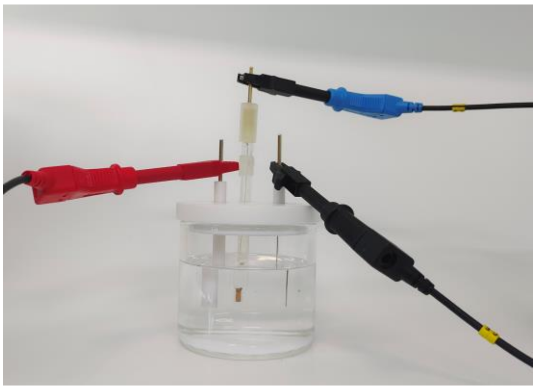


Figure S12. Cyclic voltammograms experiments device

CV Procedure for tryptophol and [Ce]. A solvent (H_2O, 40 mL) containing [Ce]-photocatalyst (10.0 mg, 3.8×10^{-4} mol·L^{-1}, 3×10^{-3} chemical equivalent), was added to the electrochemical cell in cyclic voltammetry experiments. A constant current of 0.01 mA. The scan rate was 0.10 V/s, ranging from -3.0 V to 2.0 V.

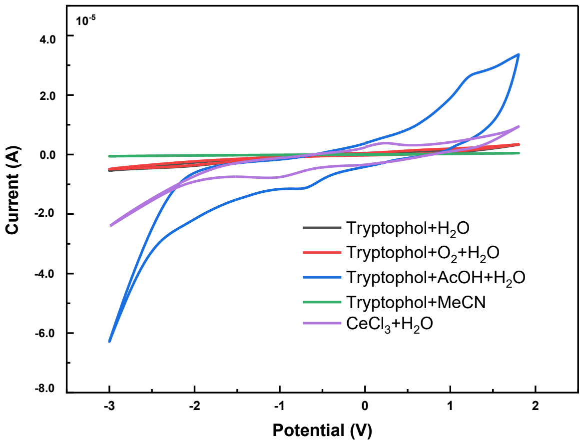
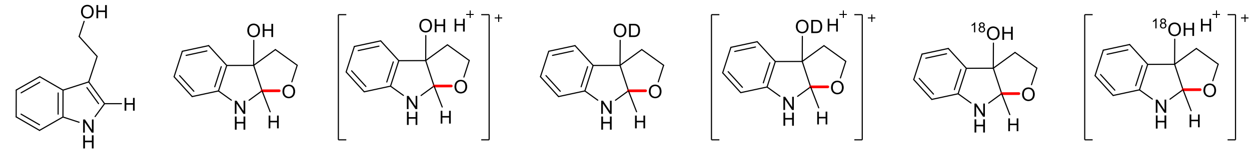


Figure S13. CV experiments of tryptophol and [Ce]-catalyst.

3.5 LC-MS spectra data for Isotopic labeling experiments with D_2O or $H_2{}^{18}O$ as solvent.

Exact Mass and Molecular Weight in isotopic labeling experiments



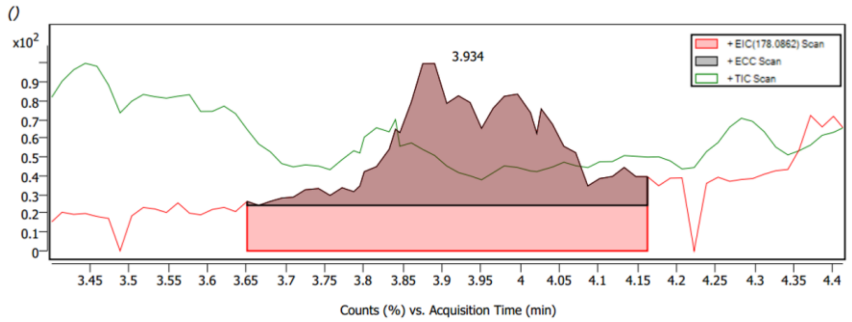
1	2a	2b	2c	2d	2e	2f
E.M.=161.0841	E.M.=177.0790	E.M.=178.0857	E.M.=178.0853	E.M.=179.0920	E.M.=179.0832	E.M.=180.0900
M.W.=161.2040	M.W.=177.2030	M.W.=178.2099	M.W.=178.2091	M.W.=179.2160	M.W.=179.2032	M.W.=180.2101

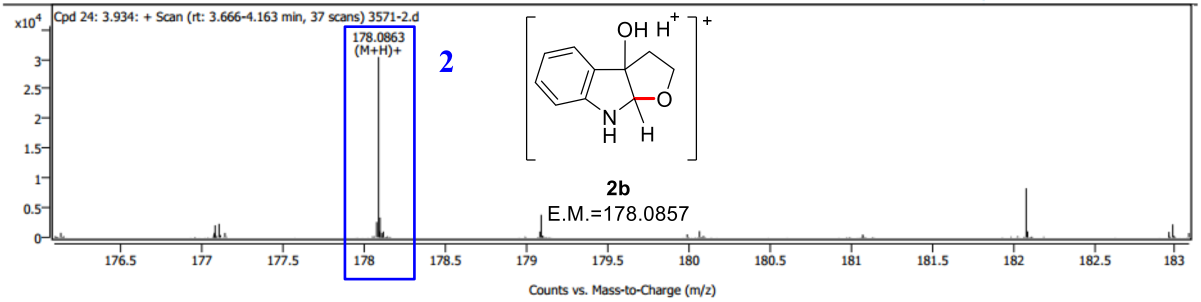
E.M.=Exact Mass, M.W.=Molecular Weight

(1) LC-MS spectra for reaction with H_2O solvent with an O_2 atmosphere. In this experiment we have found the target product **2a**.

Cpd 24: 3.934

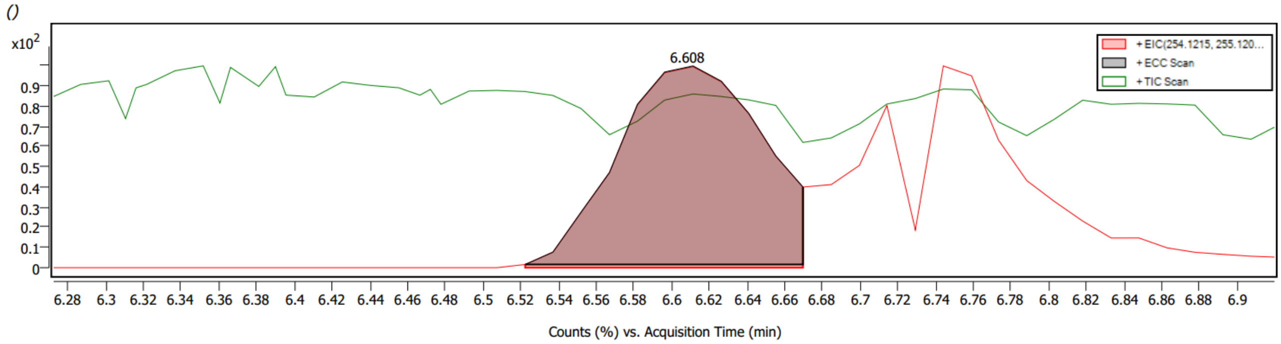
Name	Formula	RT	RI	Mass	Score	Algorithm	Lib/DB
		3.934		177.0790		MFE	

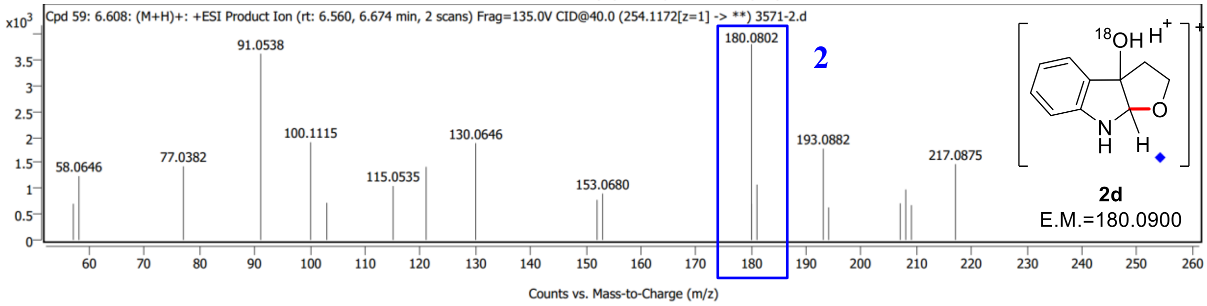




m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
178.0863			30377			(M+H)+	1
130.1591			63255				1
144.0809			52038				1
146.0601			297792				1
146.0677			28437				1
147.0636			28971				1
148.0644			44102				1
160.0758			22904				1
162.0915			57087				1
184.2061			25050				1
186.2218			766762				1
186.2300			37292				1
186.2397			28186				1
186.2527			35549				1
187.2251			100042				1
222.1026			34626				1
269.1284			91508				1
325.1547			257926				1
326.1581			59443				1
922.0098			29452				1

(2) LC-MS spectrum for Ar and $H_2{}^{18}O$ reaction

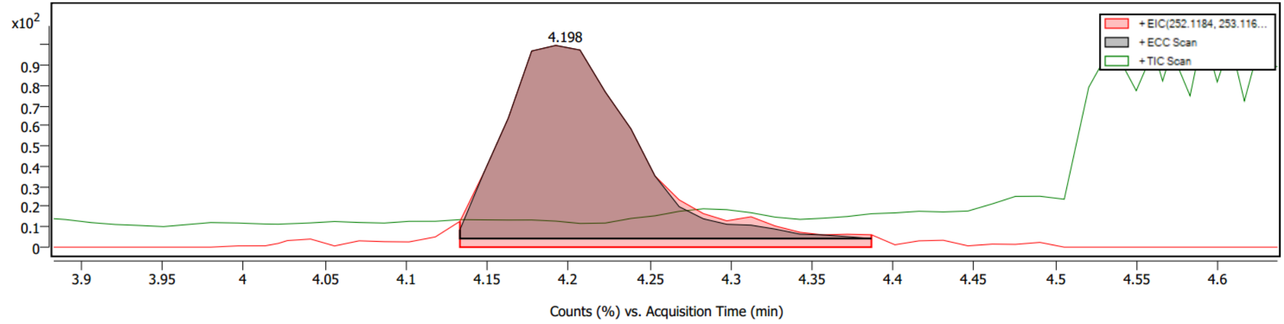


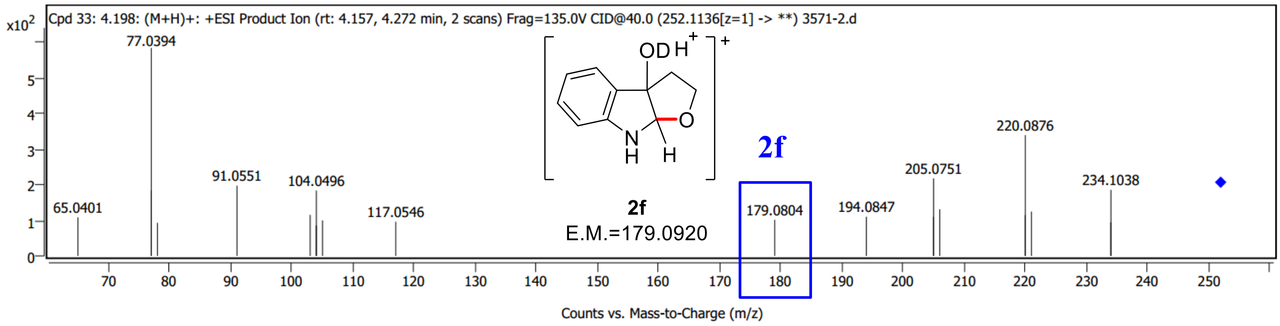


2d
E.M.=180.0900

m/z	Z	Abund	Formula	Ion Species	Loss Formula	Loss Mass	Ion Type	Diff (ppm)
57.0693	1	703						
58.0646	1	1241						
77.0382	1	1431						
91.0538	1	3623						
100.1115	1	1899						
103.0536	1	722						
115.0535	1	1048						
121.0642	1	1421						
130.0646	1	1882						
152.0619	1	779						
153.0680	1	902						
180.0802	1	3808						
180.0911	1	697						
181.0839	1	1076						
193.0882	1	1775						
194.0922	1	632						
207.0679	1	711						
208.0749	1	981						
209.0801	1	676						
217.0875	1	1474						

(3) LC-MS spectrum for Ar and D_2O reaction





m/z	Z	Abund	Formula	Ion Species	Loss Formula	Loss Mass	Ion Type	Diff (ppm)
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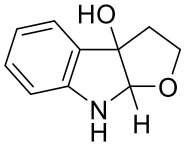
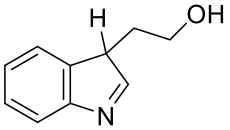
77.0376	1	184						
77.0394	1	584						
78.0423	1	93						
91.0551	1	197						
103.0416	1	115						
104.0476	1	85						
104.0496	1	184						
105.0582	1	100						
117.0546	1	96						
179.0804	1	101						
194.0847	1	110						
205.0751	1	218						
205.0800	1	110						
206.0840	1	131						
220.0841	1	115						
220.0876	1	339						
221.0919	1	125						
234.0979	1	94						
234.1038	1	186						

4. ^{1}H-NMR, ^{13}C-NMR, HRMS data and spectra



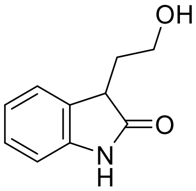
Name: 2,3,8,8a-tetrahydro-3aH-furo[2,3-b]indol-3a-ol

TLC: Petroleum ether/EtOAc = 1/2, R_f = 0.4, Yield: 82%, **^{1}H NMR (**500 MHz, CD_3OD) δ ppm: 2.88-2.91 (t, 2H, J = 14.5Hz), 3.74-3.77 (t, 2H, J = 14.25Hz), 6.35 (s, 1H), 7.03-7.06 (m, 1H), 7.14-7.17 (m, 1H), 7.17-7.20 (d, 1H, J = 12.75Hz), 7.51-7.55 (q, 2H, J = 21.65Hz). **^{13}C NMR (**125 MHz, CD_3OD) δ ppm: 28.1, 55.2, 61.9, 109.3, 112.9, 118.5, 119.1, 121.7, 125.3, 128.6, 136.3. **HRMS (ESI$^+$):** calculated for $C_{10}H_{12}NO_2$, $[M+H]^+$ 178.0857, found 178.0862.



Name: 2-(3H-indol-3-yl)ethan-1-ol

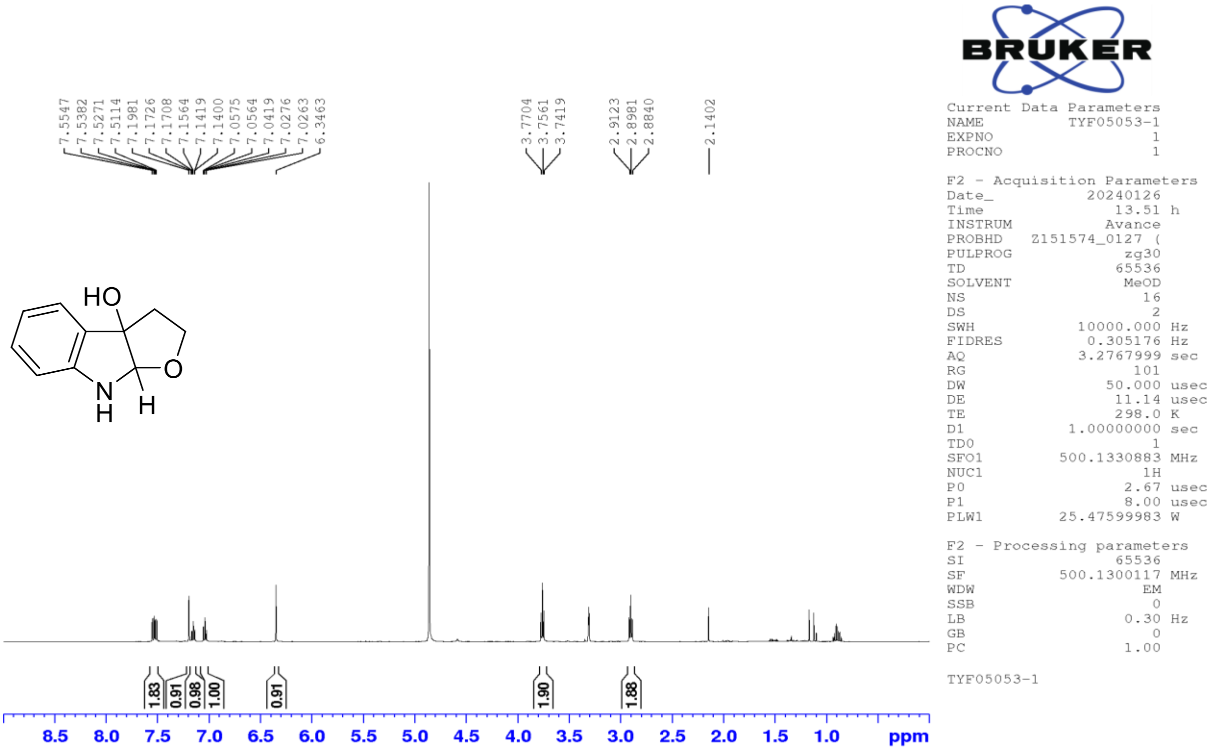
TLC: Petroleum ether/EtOAc = 15/1, R_f = 0.5, Yield: 17%, **^{1}H NMR (**500 MHz, $CDCl_3$) δ ppm: 2.80-2.85(m, 1H), 3.07-3.14(m, 1H), 3.96-4.01(m, 1H), 4.31-4.35(m, 1H), 5.78-5.80(t, 1H, J=10Hz), 7.11-7.17(m, 2H), 7.22-7.25(m, 1H), 7.37(s, 4H), 7.45(s, 1H), 7.54-7.56(d, 1H, J=10Hz). **^{13}C NMR (**125 MHz, $CDCl_3$) δ ppm: 22.3, 64.9, 76.2, 108.8, 111.0, 118.4, 119.7, 122.0, 127.0, 128.5, 128.9, 133.6, 136.1, 139.5. **HRMS (ESI$^+$):** calculated for $C_{10}H_{12}NO$, $[M+H]^+$ 162.0913, found 162.0905.



Name: 3-(2-hydroxyethyl)indolin-2-one

TLC: Petroleum ether/EtOAc = 1/2, R_f = 0.4, Yield: 29%, **^{1}H NMR (**600 MHz, $CDCl_3$) δ ppm: 2.00-2.06 (m, 1H), 2.13-2.18 (m, 1H), 3.55-3.57 (t, 1H, J = 13.14 Hz), 3.68-3.76 (m, 2H), 6.88-6.89 (d, 1H, J = 7.74 Hz), 7.00-7.02 (m, 1H), 7.18-7.21 (t, 1H, J = 15.42 Hz), 7.27-7.29 (d, 1H, J = 7.38 Hz). **^{13}C NMR (**150 MHz, $CDCl_3$) δ ppm: 33.1, 43.1, 58.6, 109.4, 121.8, 123.9, 127.6, 129.7, 142.1, 181.2. **HRMS (ESI$^+$):** calculated for $C_{10}H_{12}NO_2$, $[M+H]^+$ 178.0863, found 178.0870.

^{1}H NMR (500 MHz, $CDCl_3$)



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PROCNO                  1

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TD                65536
SOLVENT            MeOD
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DS                    2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ            3.2767999 sec
RG                  101
DW               50.000 usec
DE                11.14 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1
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NUC1                 1H
P0                 2.67 usec
P1                 8.00 usec
PLW1        25.47599983 W

F2 - Processing parameters
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PC                 1.00

TYF05053-1
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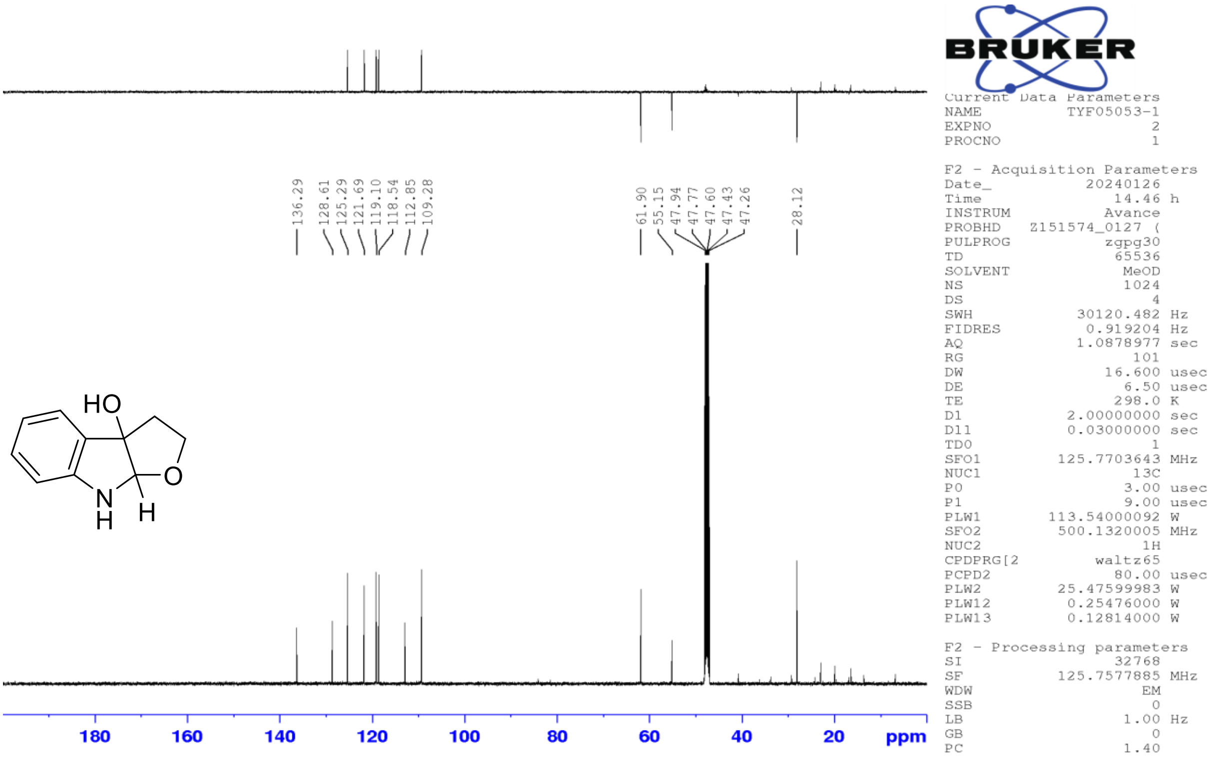
^{13}C NMR (125MHz, $CDCl_3$)



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TE                298.0 K
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P1                 9.00 usec
PLW1       113.54000092 W
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2        waltz65
PCPD2             80.00 usec
PLW2        25.47599983 W
PLW12        0.25476000 W
PLW13        0.12814000 W

F2 - Processing parameters
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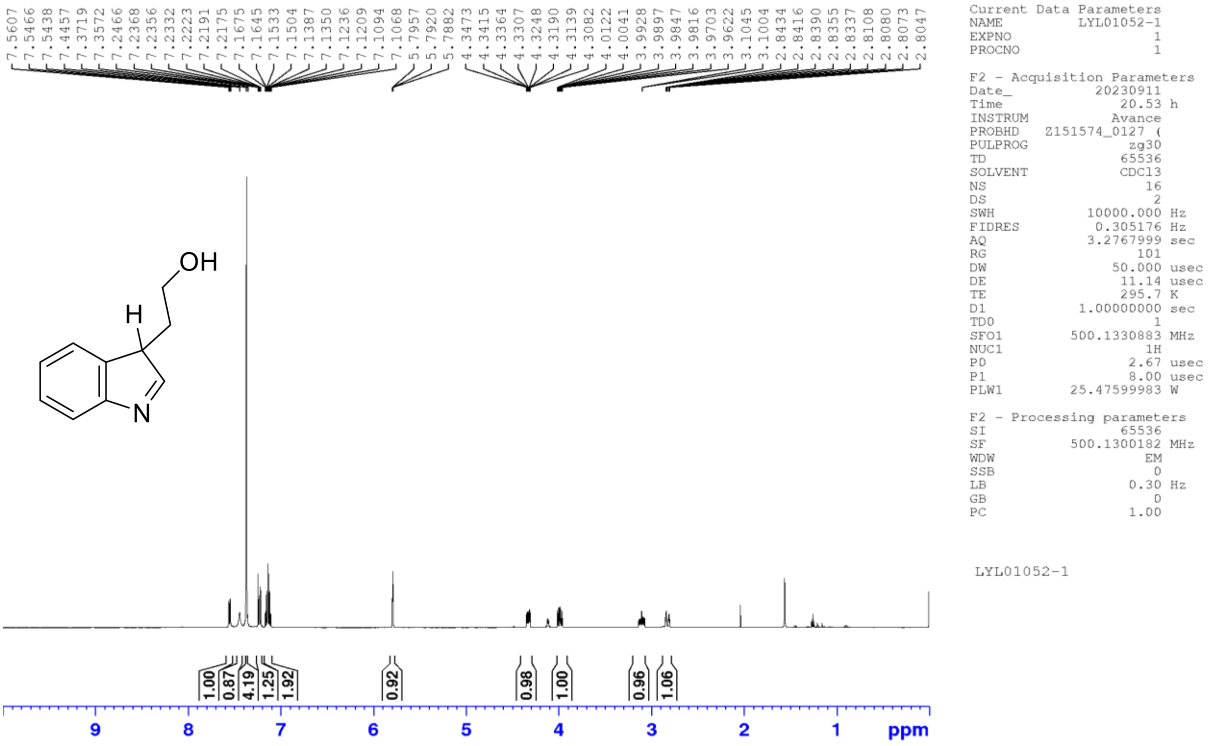
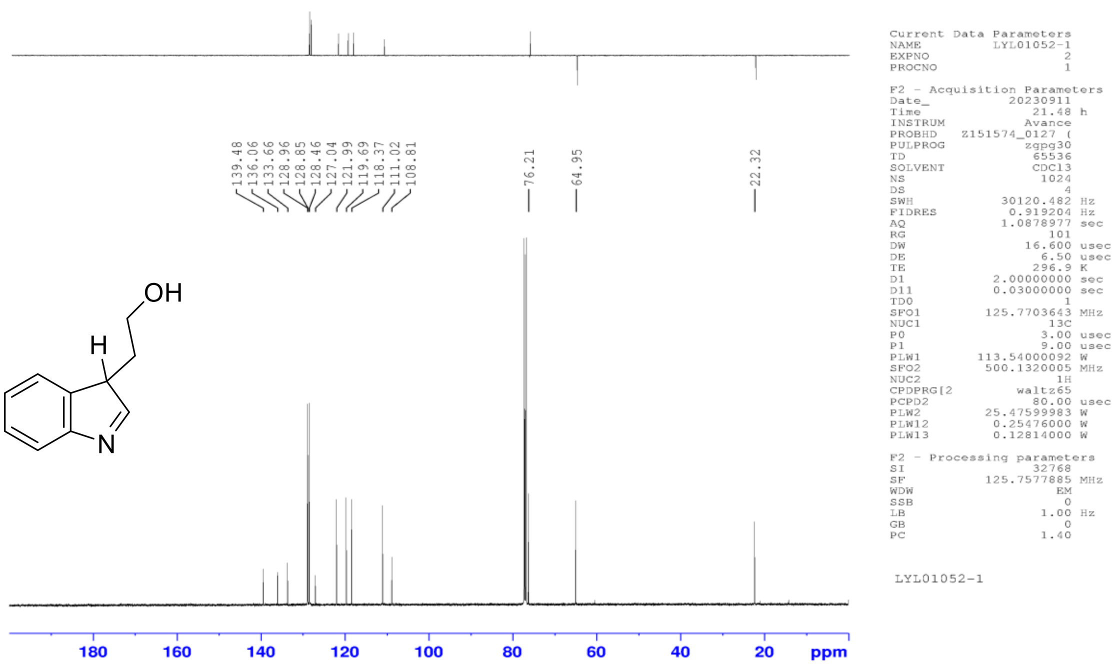
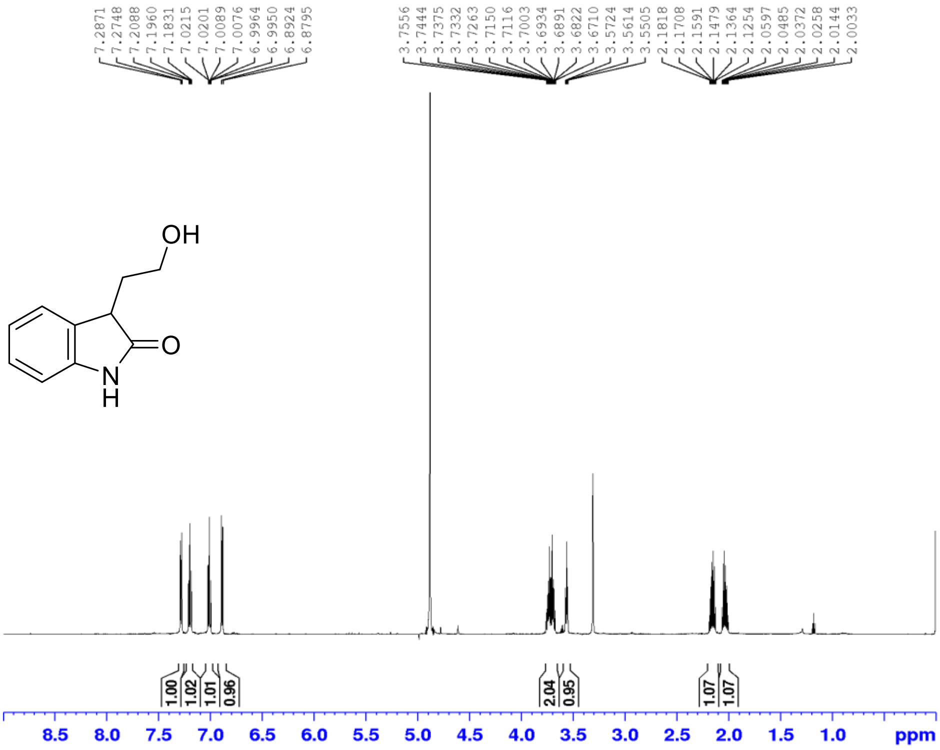
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)



^{1}H-NMR (600 MHz, MeOD)



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PLW1         26.09399986 W

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PC                   1.00

TYF03169-1
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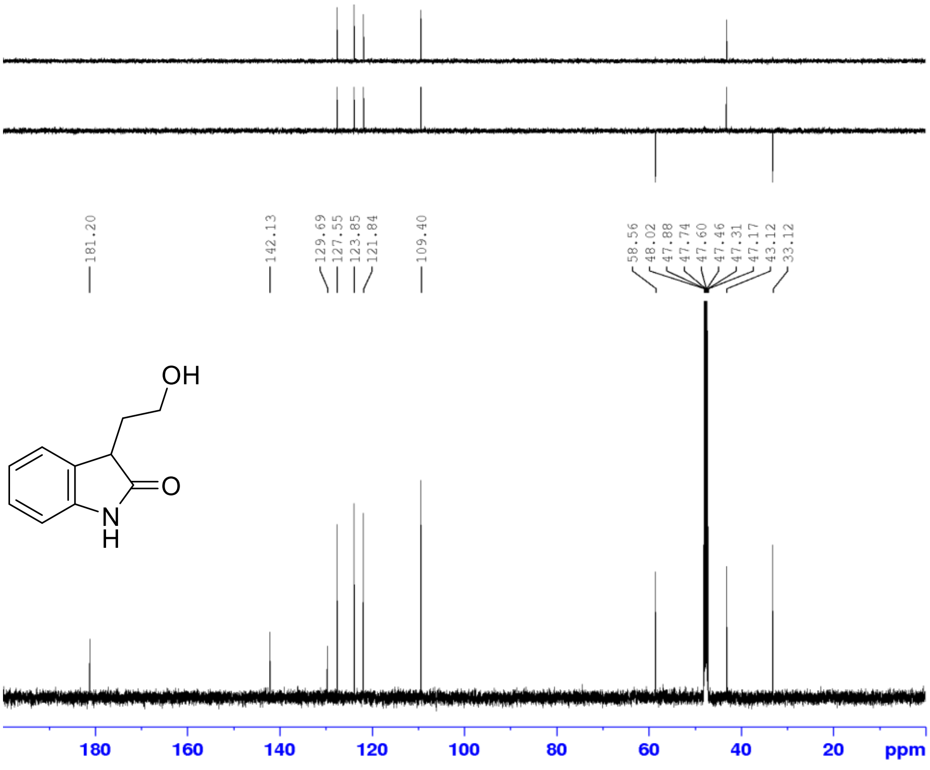
^{13}C-NMR (150 MHz, MeOD)



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PROCNO                  1

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SOLVENT              MeOD
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RG                 188.35
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D11           0.03000000 sec
DS                      4
NS                    240
TD0                     1
SFO1         150.9279578 MHz
NUC1                  13C
P1                  12.00 usec
PLW1         97.67099762 W
SFO2         600.1724007 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         26.09399986 W
PLW12         0.40399000 W
PLW13         0.20248000 W

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GB                      0
PC                   1.40

TYF03169-1
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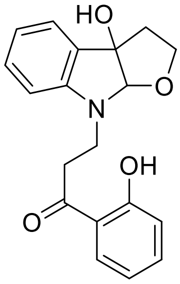
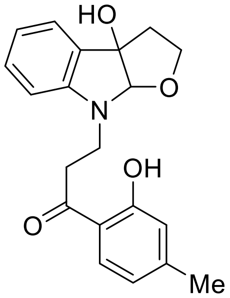


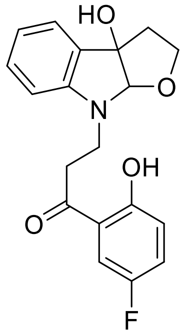
Name: 3-(3a-hydroxy-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indol-8-yl)-1-(2-hydroxyphenyl)propan-1-one

TLC: Petroleum ether/EtOAc = 12/1, R_f = 0.8, Yield: 84%, **^{1}H NMR (**500 MHz, $CDCl_3$) δ ppm: 1.05-1.07 (t, 2H, J = 13.95 Hz), 2.30-2.33 (q, 1H, J = 16.45 Hz), 2.37-2.43 (m, 1H), 4.09-4.12 (t, 1H, J = 16.3 Hz), 4.41-4.43 (t, 1H, J = 10 Hz), 5.81 (s, 1H), 6.30 (s, 1H), 6.67-6.70 (d, 1H, J = 12.8 Hz), 6.91-6.96 (q, 2H, J = 22.05 Hz), 7.14-7.16 (t, 1H, J = 14.3 Hz), 7.36-7.41 (q, 2H, J = 22.45 Hz), 7.46-7.50 (t, 2H, J = 16.9 Hz). **^{13}C NMR (**125 MHz, $CDCl_3$) δ ppm: 19.0, 56.3, 87.0, 97.6, 99.4, 109.7, 118.2, 119.2, 120.5, 124.6, 125.6, 129.9, 130.6, 134.1, 135.6, 142.2, 143.5, 162.6, 192.5. **HRMS (ESI$^+$):** calculated for $C_{19}H_{20}NO_4$, $[M+H]^+$ 326.1387, found 326.1393.



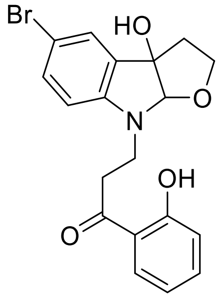
Name: 3-(3a-hydroxy-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indol-8-yl)-1-(2-hydroxy-4-methylphenyl)propan-1-one

TLC: Petroleum ether/EtOAc = 10/1, R_f = 0.8, Yield: 81%, **^{1}H NMR (**500 MHz, $CDCl_3$) δ ppm: 1.62 (s, 3H), 2.31 (s, 3H), 2.38-2.41 (m, 1H), 2.55-2.61 (m, 1H), 3.56-3.61 (m, 1H), 4.17-4.20 (t, 1H, J = 16.75 Hz), 5.71 (s, 1H), 6.50-6.53 (d, 1H, J = 12.85 Hz), 6.73-6.74 (d, 1H, J = 8.4 Hz), 7.00-7.01 (d, 1H, J = 8.15 Hz), 7.04-7.07 (t, 1H, J = 14.85 Hz), 7.14-7.16 (d, 1H, J = 9.8 Hz), 7.29-7.33 (t, 1H, J = 3.16 Hz), 7.43-7.45 (d, 1H, J = 7.4 Hz), 7.52 (s, 1H), 8.19-8.21 (d, 1H, J = 12.9 Hz), 13.3 (s, 1H). **^{13}C NMR (**125 MHz, $CDCl_3$) δ ppm: 20.6, 30.5, 41.2, 68.3, 87.9, 97.4, 99.5, 108.8, 112.2, 117.7, 117.9, 119.7, 124.1, 124.8, 127.6, 128.8, 130.9, 131.8, 136.1, 104.7, 143.7, 160.7, 192.6. **HRMS (ESI$^+$):** calculated for $C_{20}H_{22}NO_4$, $[M+H]^+$ 340.1543, found 340.1551.



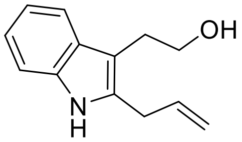
Name: 1-(5-fluoro-2-hydroxyphenyl)-3-(3a-hydroxy-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indol-8-yl)propan-1-one

TLC: Petroleum ether/EtOAc = 8/1, $R_f = 0.8$, Yield: 80%, **^{1}H NMR (**500 MHz, $CDCl_3$) δ ppm: 2.30-2.42 (m, 2H), 2.79-2.86 (m, 1H), 3.70-3.73 (q, 1H, $J = 17.4$ Hz), 4.07-4.11 (m, 1H), 5.15 (s, 1H), 5.88 (s, 1H), 6.30-6.32 (q, 1H, $J = 9$ Hz), 6.39-6.42 (m, 1H), 6.68-6.70 (d, 1H, $J = 12.75$ Hz), 6.72-6.76 (m, 1H), 6.92-6.98 (m, 2H), 7.14-7.17 (m, 1H), 7.33-7.38 (m, 2H), 7.38-7.39 (d, 1H, $J = 8$ Hz), 7.48-7.50 (t, 1H, $J = 7.55$ Hz), 7.87-7.90 (q, 1H, $J = 12.9$ Hz), 8.35-8.37 (d, 1H, $J = 12.65$ Hz). **^{13}C NMR (**125 MHz, $CDCl_3$) δ ppm: 30.9, 34.5, 41.7, 57.4, 68.1, 79.2, 86.9, 97.8, 99.2, 109.9, 111.7, 115.1, 115.3, 116.4, 119.5, 119.52, 120.7, 120.72, 122.5, 122.7, 123.9, 124.7, 125.0, 125.6, 126.8, 130.6, 134.3, 142.8, 143.5, 145.1, 154.0, 155.9, 158.7, 191.4. **HRMS (ESI$^+$):** calculated for $C_{19}H_{19}FNO_4$, $[M+H]^+$ 344.1293, found 344.1287.



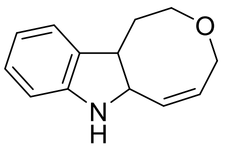
Name: 3-(5-bromo-3a-hydroxy-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indol-8-yl)-1-(2-hydroxyphenyl)propan-1-one

TLC: Petroleum ether/EtOAc = 10/1, $R_f = 0.8$, Yield: 80%, **^{1}H NMR (**500 MHz, $CDCl_3$) δ ppm: 2.36-2.39 (q, 2H, $J = 15.3$ Hz), 3.41-3.47 (m, 1H), 4.09-4.13 (m, 1H), 5.83 (s, 1H), 6.39 (s, 1H), 6.70-6.73 (d, 1H, $J = 12.85$ Hz), 6.92-6.96 (m, 2H), 7.40-7.42 (d, 1H, $J = 8.65$ Hz), 7.47-7.53 (m, 2H), 7.64-7.65 (d, 1H, $J = 2.05$ Hz), 7.99-8.00 (d, 1H, $J = 9.2$ Hz). **^{13}C NMR (**125 MHz, $CDCl_3$) δ ppm: 41.5, 68.2, 98.4, 99.5, 111.9, 115.7, 118.2, 119.3, 120.5, 128.4, 130.1, 133.2, 135.7, 136.5, 142.0, 143.0, 162.6, 192.6. **HRMS (ESI$^+$):** calculated for $C_{19}H_{19}BrNO_4$, $[M+H]^+$ 404.0492, found 404.0486.



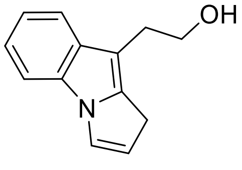
Name: 2-(2-allyl-1H-indol-3-yl)ethan-1-ol

TLC: Petroleum ether/EtOAc = 10/1, R$_f$ = 0.6, **^{1}H NMR (**500 MHz, MeOD) δ ppm: 2.86-2.89 (t, 2H, J = 15.25 Hz), 3.43-3.44 (d, 2H, J = 6.35 Hz), 3.63-3.66 (t, 2H, J = 15.15 Hz), 4.98-5.06 (m, 2H),5.90-5.95 (m, 1H), 6.89-6.92 (t, 2H, J = 14.85 Hz),6.94-6.97 (t, 2H, J = 14.05 Hz), 7.18-7.20 (t, 1H, J = 8.6 Hz), 7.39-7.41 (d, 1H, J = 7.8 Hz). **^{13}C NMR (**125 MHz, MeOD) δ ppm: 27.5, 30.2, 62.3, 107.1, 110.2, 115.0, 117.4, 118.2, 120.3, 128.6, 133.6, 135.7, 136.0. **HRMS (ESI$^+$):** calculated for $C_{13}H_{16}NO$, $[M+H]^+$ 202.1226, found 202.1220.



Name: (Z)-1,2,4,6a,7,11b-hexahydrooxocino[5,4-b]indole

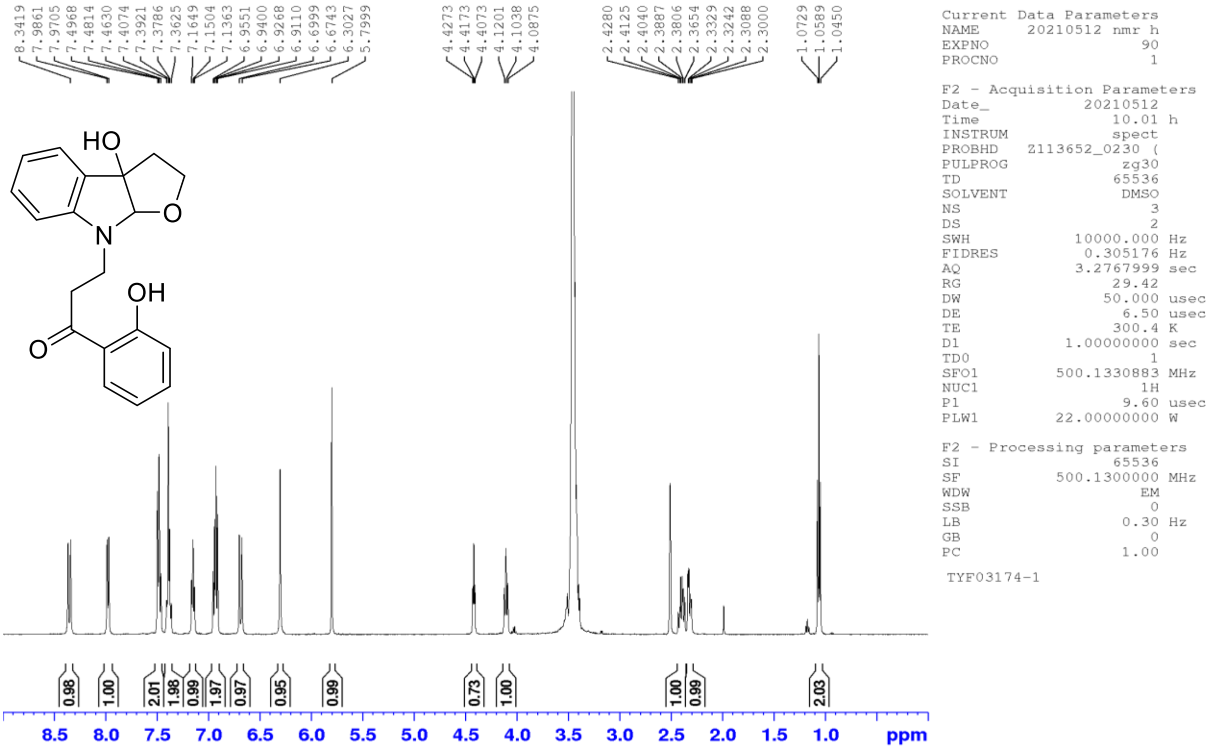
TLC: Petroleum ether/EtOAc = 8/1, R$_f$ = 0.4, Yield: 32%, **^{1}H NMR (**500 MHz, CDCl$_3$) δ ppm: 2.72-2.85 (m, 2H), 2.92-3.00 (m, 3H), 3.33-3.38 (m, 1H), 3.75-3.86 (m, 4H), 4.94-4.99(t, 1H, J = 25.15 Hz), 5.11-5.12 (d, 1H, J = 2.9 Hz), 7.08-7.12 (m, 1H), 7.17-7.20 (m, 1H), 7.30-7.32 (m, 1H), 7.52-7.53 (d, 1H, J = 8 Hz), 8.63-8.74 (d, 1H, J = 53.55 Hz). **^{13}C NMR (**125 MHz, CDCl$_3$) δ ppm: 27.0, 27.4, 44.7, 44.9, 54.3, 54.6, 62.1, 62.2, 64.4, 64.9, 109.9, 110.2, 111.3, 111.4, 118.6, 118.7, 119.5, 119.6, 122.5, 127.5, 127.52, 133.6, 135.0, 135.8. **HRMS (ESI$^+$):** calculated for $C_{13}H_{16}NO$, $[M+H]^+$ 202.1226, found 202.1232.



Name: 2-(1H-pyrrolo[1,2-a]indol-9-yl)ethan-1-ol

TLC: Petroleum ether/EtOAc = 10/1, R$_f$ = 0.6, Yield: 37%, **^{1}H NMR (**500 MHz, MeOD) δ ppm: 3.15-3.18 (t, 2H, J = 13.9 Hz), 3.77-3.79 (t, 2H, J = 13.85 Hz), 6.61-6.65 (q, 1H, J = 23.55 Hz), 7.03-7.06 (t, 1H, J = 15.7 Hz), 7.22-7.26 (t, 1H, J = 16.15 Hz), 7.34-7.35 (d, 1H, J = 8.05 Hz), 7.62-7.63 (d, 1H, J = 8.05 Hz), 7.81-7.85 (d, 1H, J = 15.6 Hz). **^{13}C NMR (**125 MHz, MeOD) δ ppm:27.5, 62.2, 111.1, 119.4, 119.6, 121.2, 124.3, 125.1, 128.1, 131.0, 138.7, 141.1, 149.5. **HRMS (ESI$^+$):** calculated for $C_{13}H_{14}NO$, $[M+H]^+$ 200.1070, found 200.1074.

^{1}H-NMR (500 MHz, DMSO)



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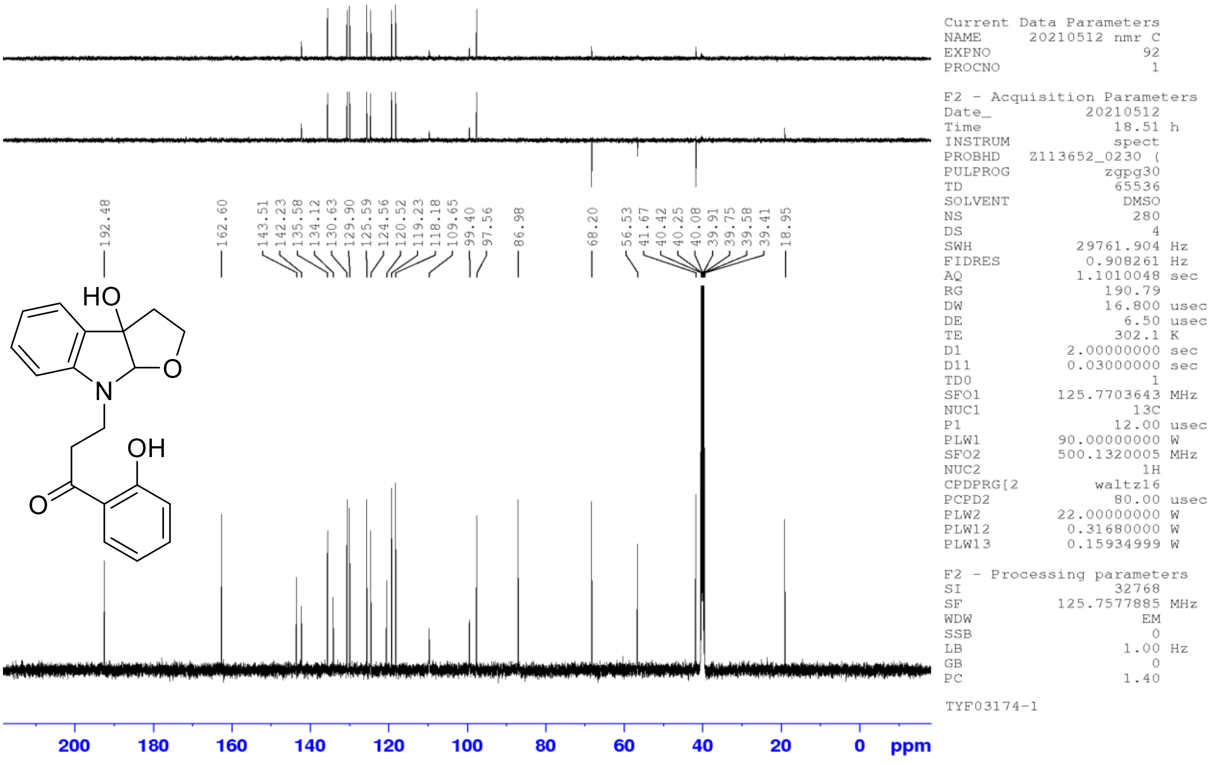
Current Data Parameters
NAME     20210512 nmr h
EXPNO                90
PROCNO                1

F2 - Acquisition Parameters
Date_          20210512
Time              10.01 h
INSTRUM           spect
PROBHD   Z113652_0230 (
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                    3
DS                    2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ            3.2767999 sec
RG                29.42
DW               50.000 usec
DE                 6.50 usec
TE                300.4 K
D1           1.00000000 sec
TD0                   1
SFO1        500.1330883 MHz
NUC1                 1H
P1                 9.60 usec
PLW1        22.00000000 W

F2 - Processing parameters
SI                65536
SF          500.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

TYF03174-1
```

^{13}C-NMR (150 MHz, DMSO)



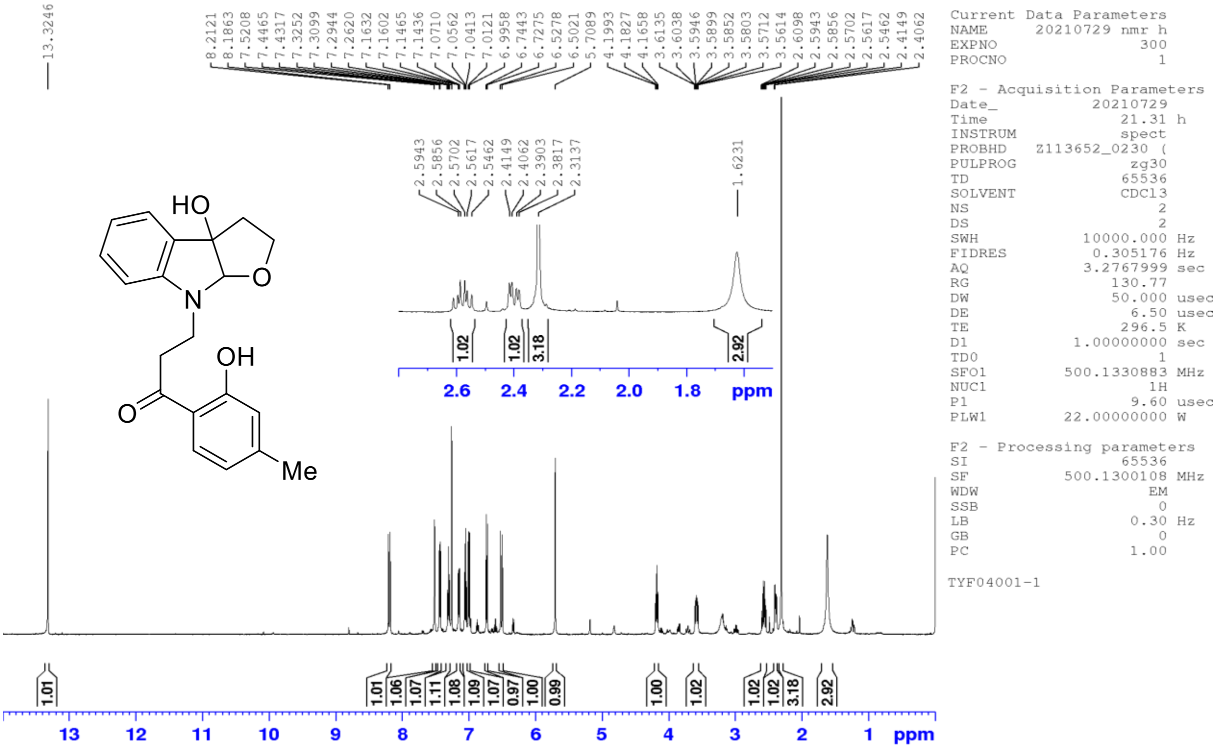
```
Current Data Parameters
NAME     20210512 nmr C
EXPNO                92
PROCNO                1

F2 - Acquisition Parameters
Date_          20210512
Time              18.51 h
INSTRUM           spect
PROBHD   Z113652_0230 (
PULPROG         zgpg30
TD                65536
SOLVENT            DMSO
NS                  280
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG               190.79
DW               16.800 usec
DE                 6.50 usec
TE                302.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7703643 MHz
NUC1                13C
P1                12.00 usec
PLW1        90.00000000 W
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        22.00000000 W
PLW12        0.31680000 W
PLW13        0.15934999 W

F2 - Processing parameters
SI                32768
SF          125.7577885 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

TYF03174-1
```

^{1}H-NMR (500 MHz, CDCl$_3$)



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Current Data Parameters
NAME      20210729 nmr h
EXPNO                300
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210729
Time               21.31 h
INSTRUM            spect
PROBHD   Z113652_0230 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     2
DS                     2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ             3.2767999 sec
RG                130.77
DW                50.000 usec
DE                  6.50 usec
TE                 296.5 K
D1            1.00000000 sec
TD0                    1
SFO1         500.1330883 MHz
NUC1                  1H
P1                  9.60 usec
PLW1         22.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300108 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

TYF04001-1
```
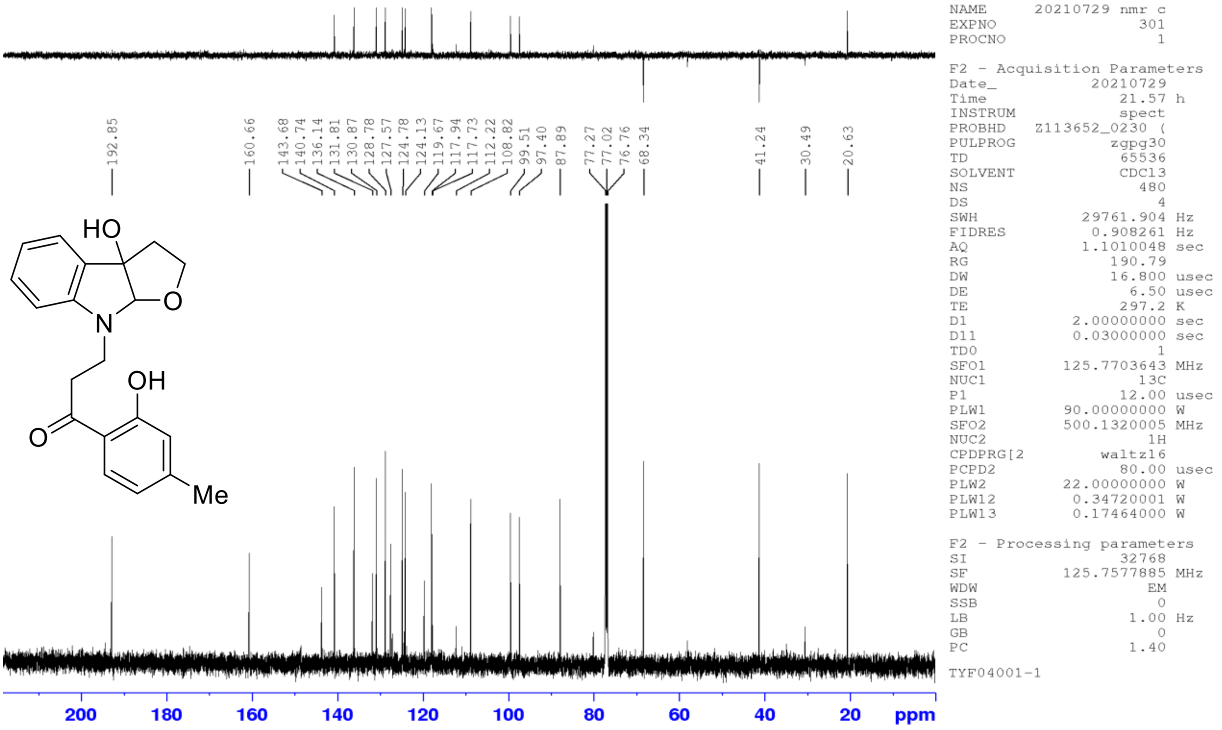
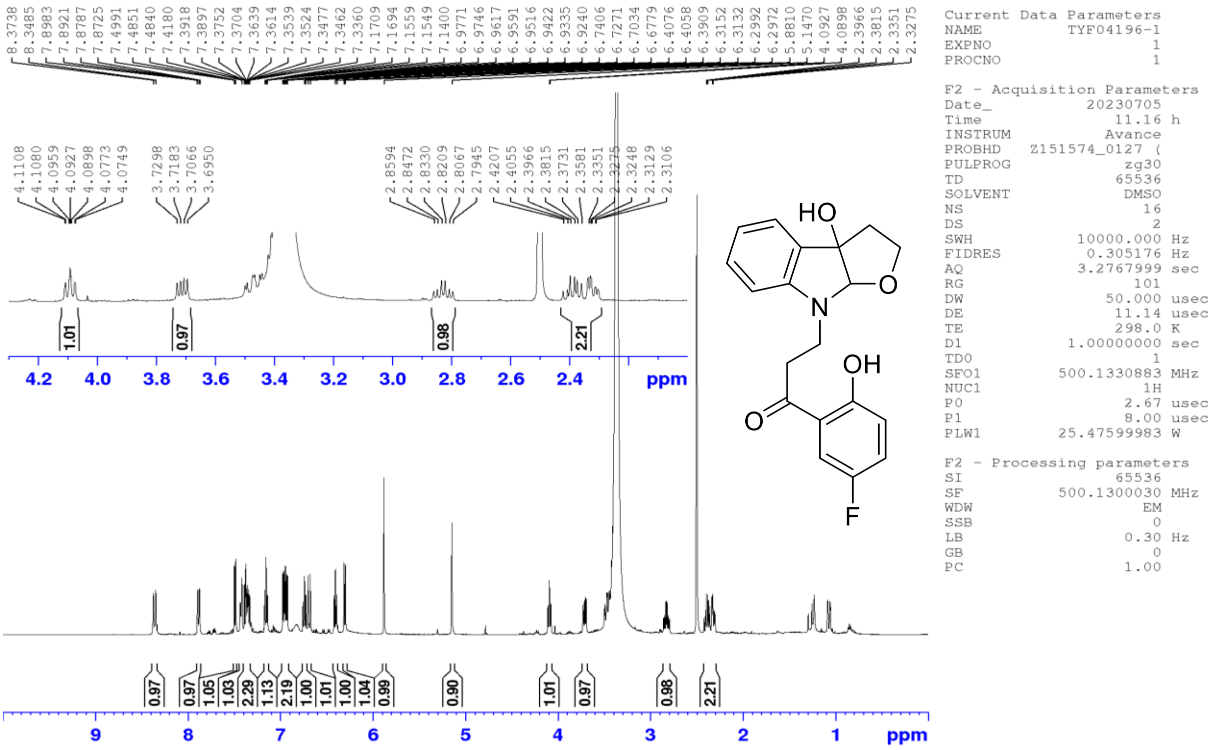

^{13}C-NMR (150 MHz, CDCl$_3$)

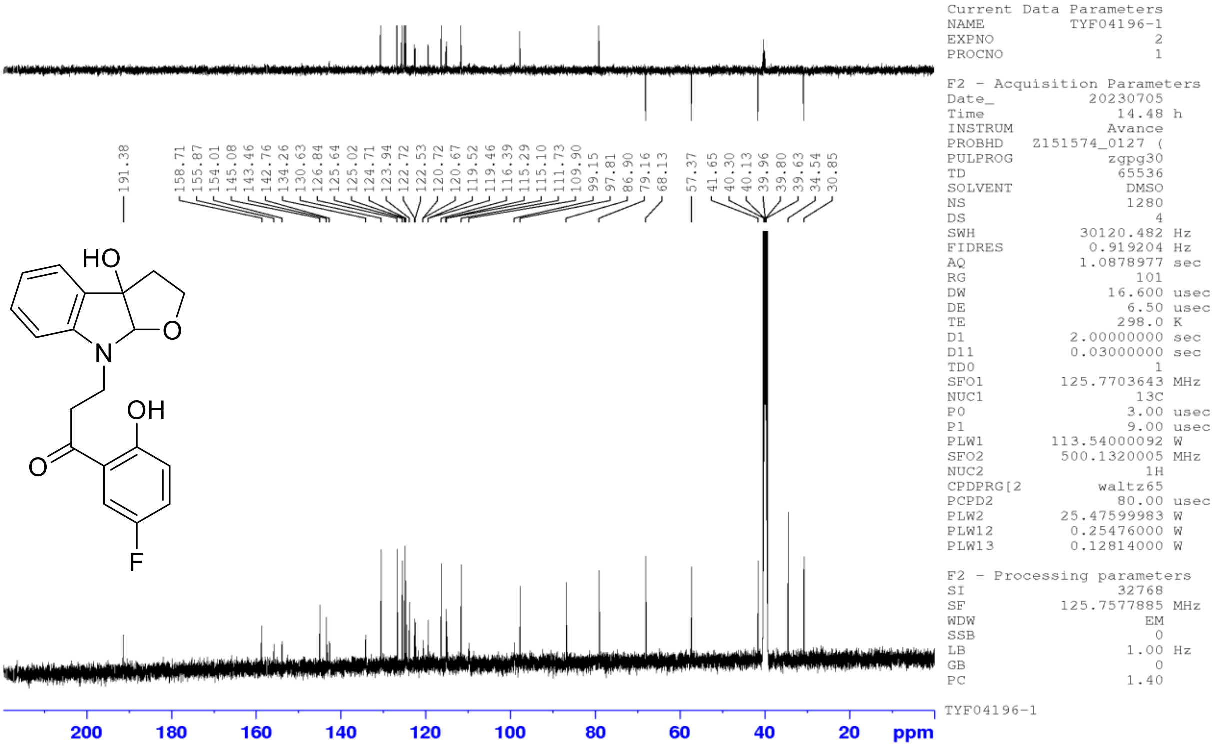


```
Current Data Parameters
NAME      20210729 nmr c
EXPNO                301
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210729
Time               21.57 h
INSTRUM            spect
PROBHD   Z113652_0230 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   480
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ             1.1010048 sec
RG                190.79
DW                16.800 usec
DE                  6.50 usec
TE                 297.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         125.7703643 MHz
NUC1                 13C
P1                 12.00 usec
PLW1         90.00000000 W
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         22.00000000 W
PLW12         0.34720001 W
PLW13         0.17464000 W

F2 - Processing parameters
SI                 32768
SF           125.7577885 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

TYF04001-1
```

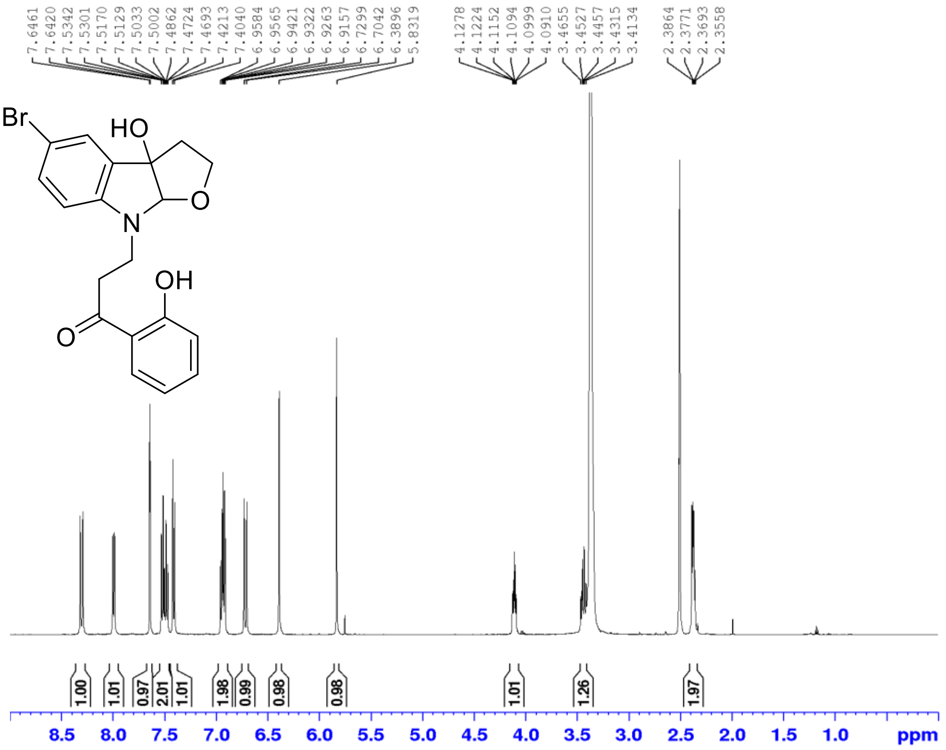
^{1}H-NMR (500 MHz, DMSO)



^{13}C-NMR (150 MHz, DMSO)

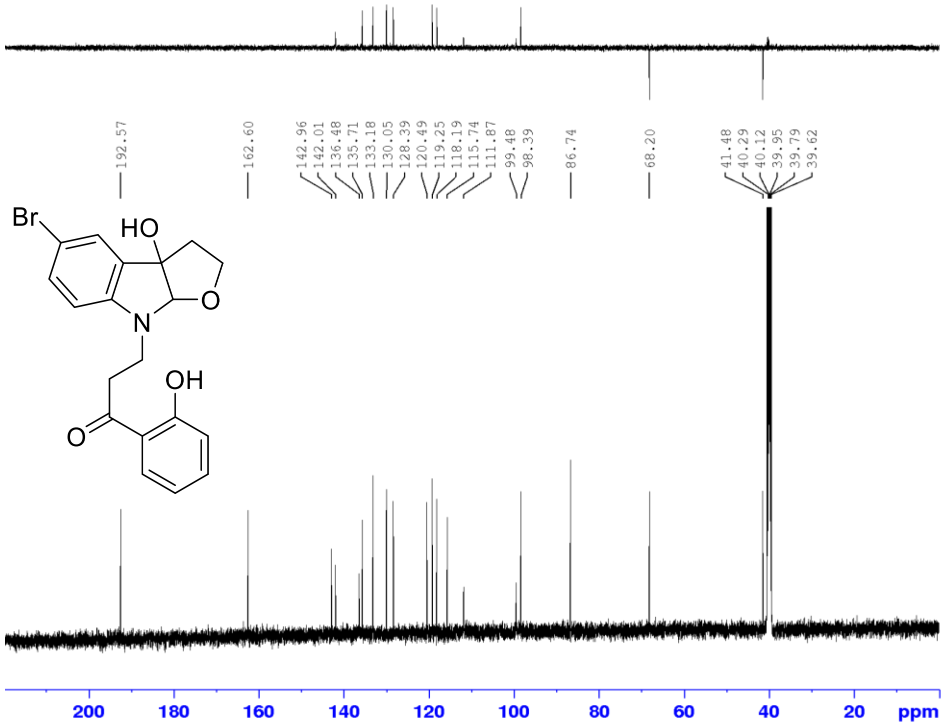


^{1}H-NMR (500 MHz, DMSO)



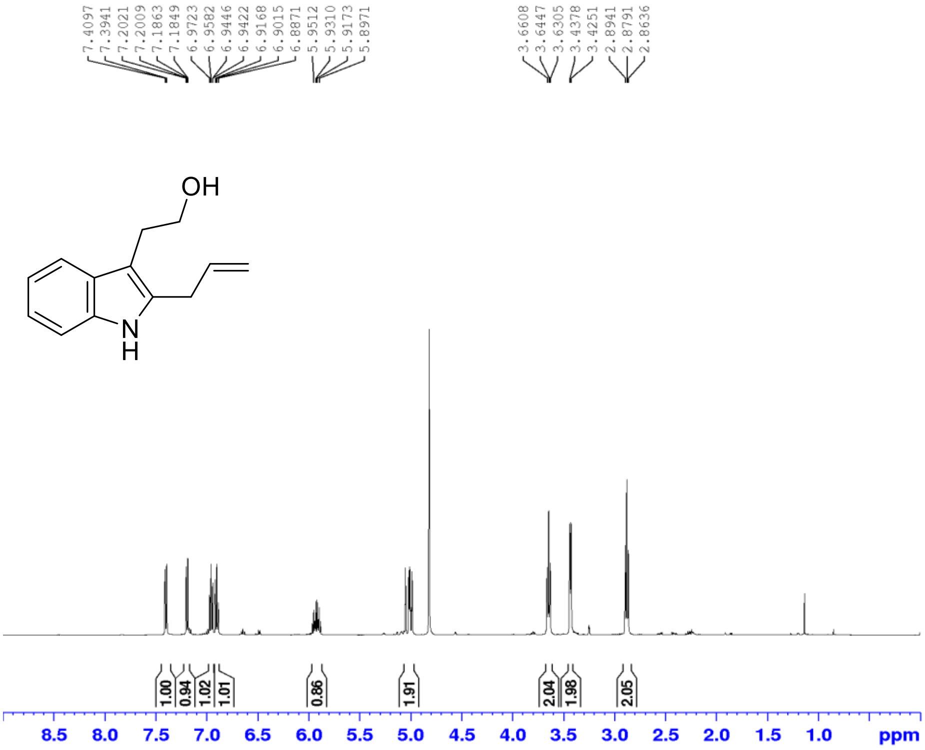
```
Current Data Parameters
NAME          TYF04199-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20230720
Time             11.48 h
INSTRUM           Avance
PROBHD   Z151574_0127 (
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ             3.2767999 sec
RG                   101
DW                50.000 usec
DE                 11.14 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         500.1330883 MHz
NUC1                  1H
P0                  2.67 usec
P1                  8.00 usec
PLW1         25.47599983 W

F2 - Processing parameters
SI                 65536
SF           500.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

TYF04199-2
```

^{13}C-NMR (150 MHz, DMSO)



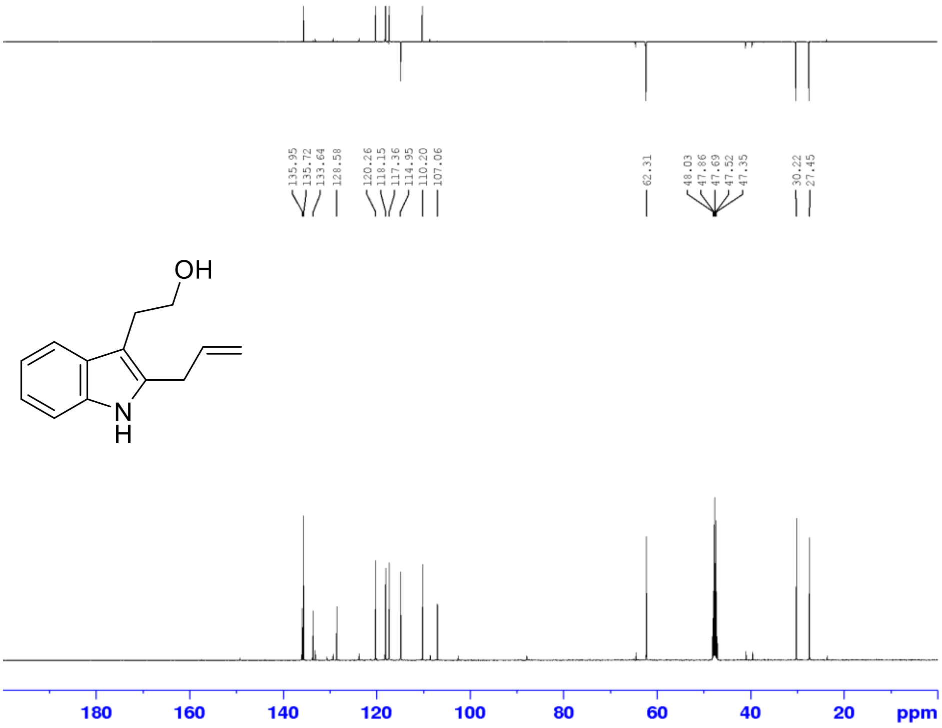
```
Current Data Parameters
NAME          TYF04199-2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20230720
Time             21.16 h
INSTRUM           Avance
PROBHD   Z151574_0127 (
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                  1024
DS                     4
SWH            30120.482 Hz
FIDRES          0.919204 Hz
AQ             1.0878977 sec
RG                   101
DW                16.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         125.7703643 MHz
NUC1                 13C
P0                  3.00 usec
P1                  9.00 usec
PLW1        113.54000092 W
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz65
PCPD2              80.00 usec
PLW2         25.47599983 W
PLW12         0.25476000 W
PLW13         0.12814000 W

F2 - Processing parameters
SI                 32768
SF           125.7577885 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

TYF04199-2
```

^{1}H-NMR (500 MHz, MeOD)



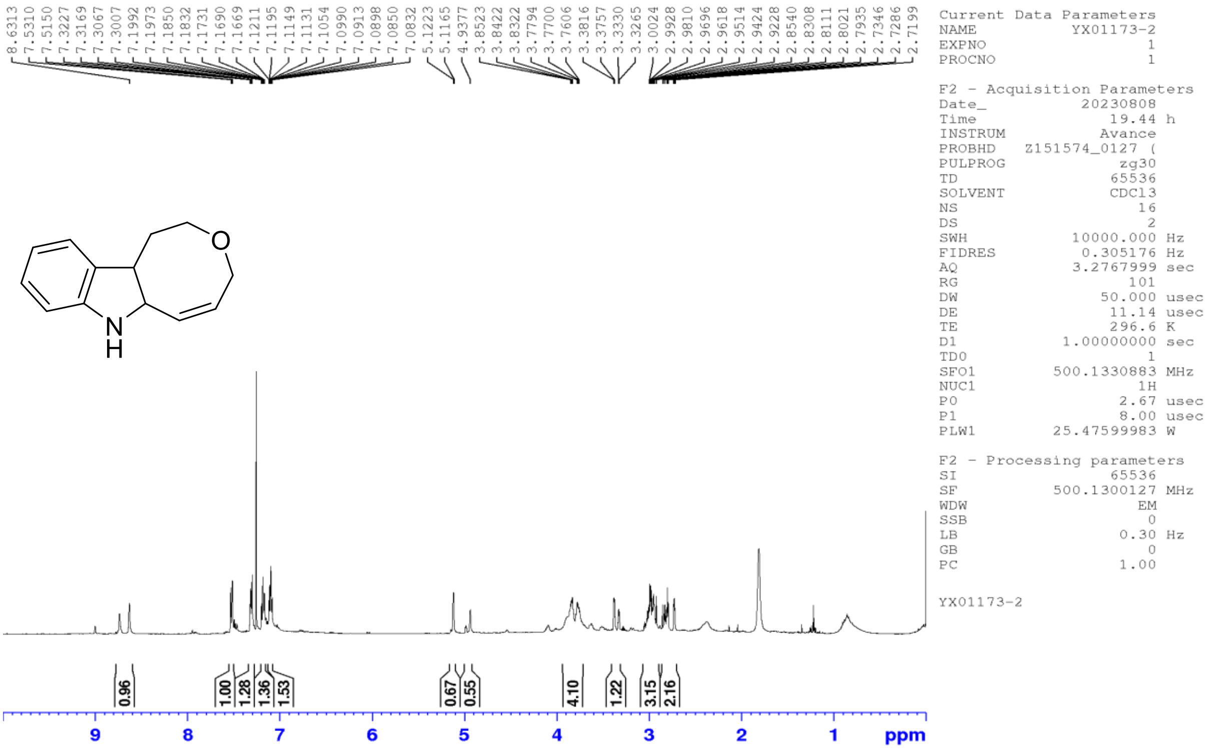
```
Current Data Parameters
NAME            YX01177-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20230814
Time                9.21 h
INSTRUM            Avance
PROBHD   Z151574_0127 (
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                     16
DS                      2
SWH             10000.000 Hz
FIDRES           0.305176 Hz
AQ              3.2767999 sec
RG                     32
DW                 50.000 usec
DE                  11.14 usec
TE                  296.6 K
D1             1.00000000 sec
TD0                     1
SFO1          500.1330883 MHz
NUC1                   1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          25.47599983 W

F2 - Processing parameters
SI                  65536
SF            500.1300402 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

YX01177-1
```

^{13}C-NMR (125 MHz, MeOD)

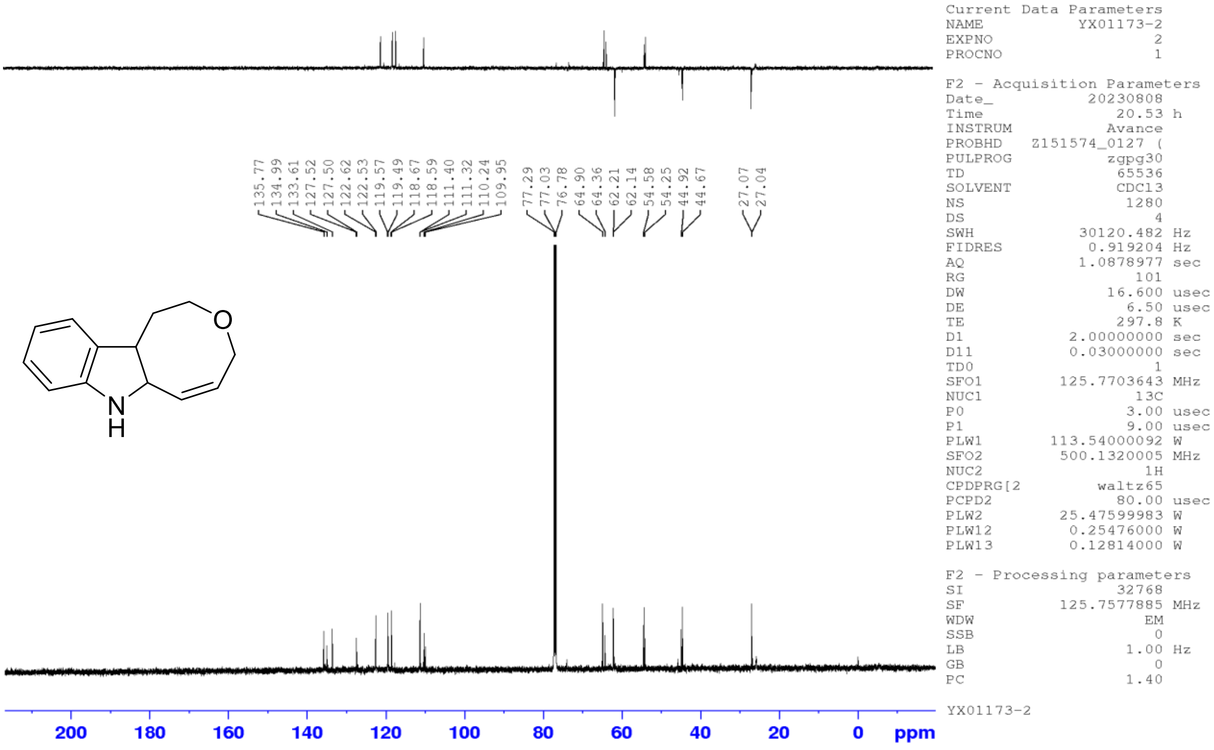


```
Current Data Parameters
NAME            YX01177-1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20230814
Time               10.16 h
INSTRUM            Avance
PROBHD   Z151574_0127 (
PULPROG           zgpg30
TD                  65536
SOLVENT              MeOD
NS                   1024
DS                      4
SWH             30120.482 Hz
FIDRES           0.919204 Hz
AQ              1.0878977 sec
RG                    101
DW                 16.600 usec
DE                   6.50 usec
TE                  297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          125.7703643 MHz
NUC1                  13C
P0                   3.00 usec
P1                   9.00 usec
PLW1         113.54000092 W
SFO2          500.1320005 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               80.00 usec
PLW2          25.47599983 W
PLW12          0.25476000 W
PLW13          0.12814000 W

F2 - Processing parameters
SI                  32768
SF            125.7577885 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

YX01177-1
```

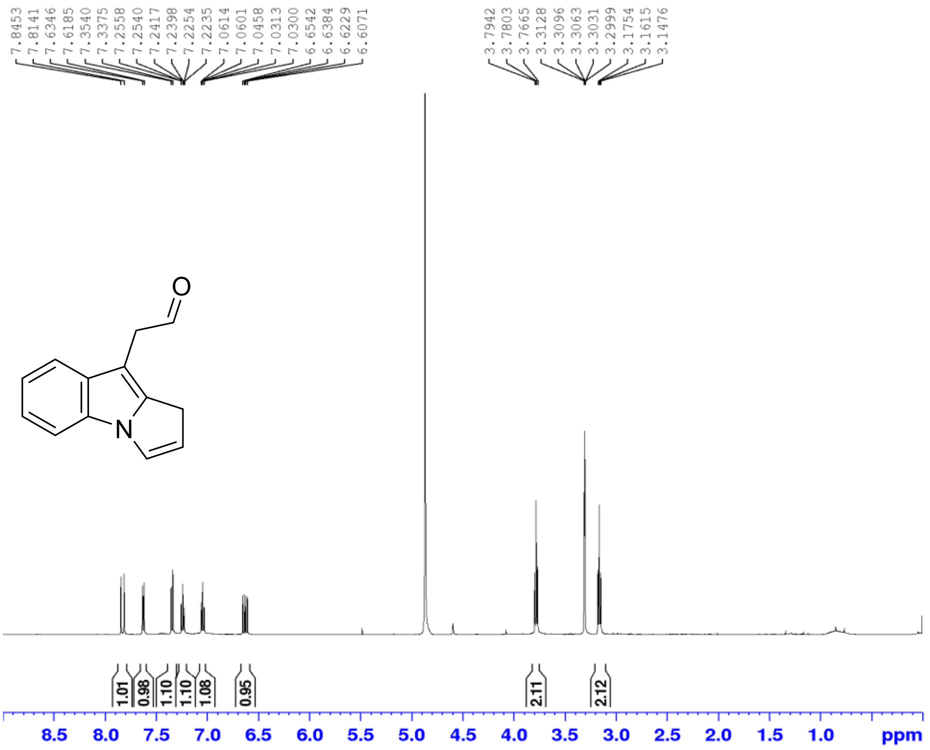
^{1}H-NMR (500 MHz, CDCl$_3$)



^{13}C-NMR (125 MHz, MeOD)

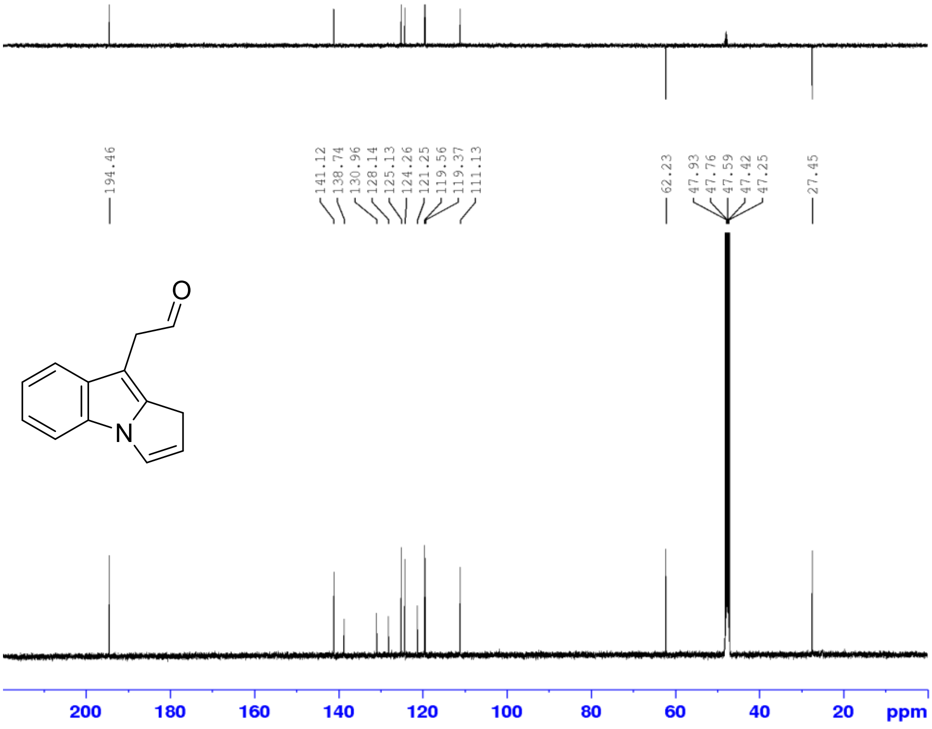


^{1}H-NMR (500 MHz, MeOD)



```
Current Data Parameters
NAME            YX01173-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20230808
Time              21.26 h
INSTRUM            Avance
PROBHD   Z151574_0127 (
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                     16
DS                      2
SWH             10000.000 Hz
FIDRES           0.305176 Hz
AQ              3.2767999 sec
RG                    101
DW                 50.000 usec
DE                  11.14 usec
TE                  296.6 K
D1             1.00000000 sec
TD0                     1
SFO1          500.1330883 MHz
NUC1                   1H
P0                   2.67 usec
P1                   8.00 usec
PLW1          25.47599983 W

F2 - Processing parameters
SI                  65536
SF            500.1300111 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

YX01173-1
```

^{13}C-NMR (125 MHz, MeOD)



```
Current Data Parameters
NAME            YX01173-1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20230808
Time              22.21 h
INSTRUM            Avance
PROBHD   Z151574_0127 (
PULPROG            zgpg30
TD                  65536
SOLVENT              MeOD
NS                   1024
DS                      4
SWH             30120.482 Hz
FIDRES           0.919204 Hz
AQ              1.0878977 sec
RG                    101
DW                 16.600 usec
DE                   6.50 usec
TE                  297.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          125.7703643 MHz
NUC1                  13C
P0                   3.00 usec
P1                   9.00 usec
PLW1         113.54000092 W
SFO2          500.1320005 MHz
NUC2                   1H
CPDPRG[2           waltz65
PCPD2               80.00 usec
PLW2          25.47599983 W
PLW12          0.25476000 W
PLW13          0.12814000 W

F2 - Processing parameters
SI                  32768
SF            125.7577885 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

YX01173-1
```

5. X-ray crystal structure data

6a **6a X-ray CCDC: 2384777**

Figure S14. X-ray crystal structure of tryptophol and chromone reaction product.

Datablock: a

Bond precision: C-C = 0.0057A Wavelength=0.71073

Cell:	a=7.110(5)		b=8.813(6)	c=12.868(9)
Temperature:	alpha=83.048(13)		beta=75.01(4)	gamma=86.742(13)
	296 K			
Volume Space	772.9(9)		772.9(9)	
group Hall group	P-1		P-1	
Moiety formula	-P1		-P1	
	C19H17N	O4	C19H17NO4	
Sum formula	C19H17N	O4	C19H17NO4	
Mr	323.34		323.33	
Dx,g cm-3	1.389		1.389	
Z	2		2	
Mu (mm-1)	0.098		0.098	
F000	340.0		340.0	
F000’	340.17			
h,k,lmax	8,10,15		8,10,15	
Nref	2730		2692	
Tmin,Tmax			0.609,0.746	
Tmin’				

Correction method= # Reported T Limits: Tmin=0.609 Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.986 Theta(max)= 24.998

R(reflections)= 0.0775(1734)

wR2(reflections)= 0.2221(2692)

S = 1.117

Npar= 220

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.