Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct Catalytic Synthesis of β-(C3)-Substituted Pyrroles: A Complementary Addition to the Paal-Knorr Reaction

Amol Prakash Pawar,[a] Jyothi Yadav,[a] Nisar Ahmad Mir,[a] Eldhose Iype,[b] Krishnan Rangan,[c] Sumati Anthal,[d] Rajni Kant,[d] Indresh Kumar*[a]

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[a]*Department of Chemistry, Birla Institute of Technology & Science, Pilani, Rajasthan, India*

E-mail: indresh.kumar@pilani.bits-pilani.ac.in, indresh.chemistry@gmail.com

[b]*Department of Chemical Engineering, BITS Pilani, Dubai Campus, Dubai, UAE*

[c]*Department of Chemistry, BITS Pilani, Hyderabad Campus, Secunderabad, India*

[d]*Post-Graduate Department of Physics & Electronics, University of Jammu, Jammu, India*

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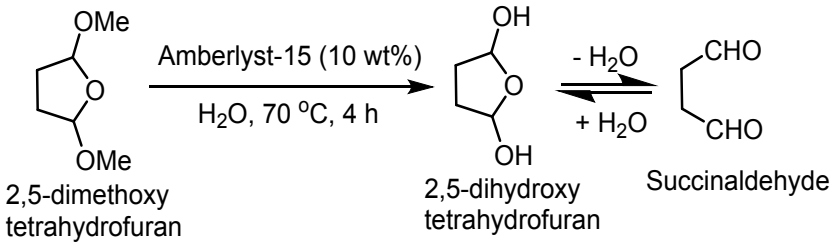
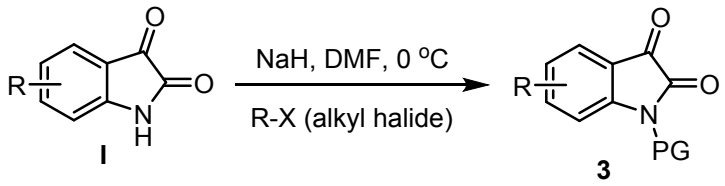
1. General Information.

Unless otherwise stated, all commercially available compounds were used as received without further purification. All solvents employed in the reactions were distilled from appropriate drying agents. Starting materials; aqueous succinaldehyde **1** (3M sol) was prepared using reported procedure, isatin was used as recurred or protected with alkyl halides following reported protocol. The reactions under the standard conditions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F254 pre-coated plates (0.25 mm). Column chromatographic purification was performed on silica gel (100–200 mesh) using a mixture of hexane/EtOAc. Chemical yields refer to pure, isolated substances. ^{1}H spectra were recorded on a BRUKER-AV400 (400 MHz) in $CDCl_3$ or DMSO-D6 solution, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as an internal standard. ^{13}C-NMR spectra were recorded on a BRUKER-AV400 (101 MHz) in $CDCl_3$ or DMSO-D6 solution with complete proton decoupling. High-resolution mass spectra were recorded on Agilent 6545 Q-TOF LC/MS. Melting points were determined by EZ–Melt Automated Melting Point Apparatus and are uncorrected.

Preparation of aqueous succinaldehyde solution:[1] To a stirred solution of 2,5-dimethoxy tetrahydrofuran (5.0 g, 37.9 mmol) in H_2O (12.5 mL) was added Amberlyst-15 (10 wt%) and further heated at 70 °C for 4 h in an open flask and allow the MeOH evaporate. The resulting solution was cooled to rt and used directly after filtration.



Preparation of *N*-Alkyl isatin 3.[2] To a stirred solution of substituted isatin **I** (3.0 mmol, 1.0 equiv.) in DMF (15.0 mL) at 0 °C, was added NaH (60% dispersion in mineral oil, 140 mg, 3.5 mmol, 1.17 equiv.) in one portion and stirred for 5 minutes. Alkyl halide (Methyl Iodide, allyl bromide, or benzyl bromide, 1.2 equiv.) was added at 0 °C, and continued to be stirred at room temperature. The progress of the reaction was monitored by TLC. The reaction mixture was then poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic portions were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated to give N-alkyl isatin (N-Methyl isatin, N-allyl isatin, N-benzyl isatin) in high yields.

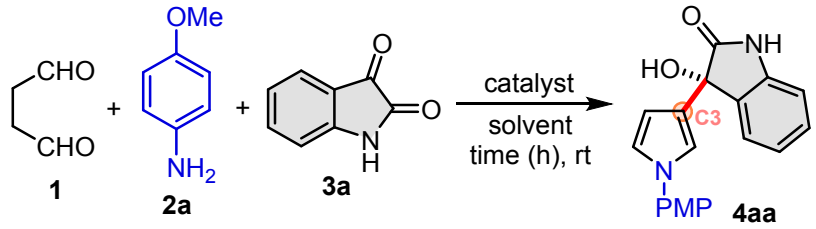


References: [1] a) Y. Hayashi, S. Umemiya, *Angew. Chem. Int. Ed*. **2013**, *52*, 3450–3452*;* b) I. Kumar, N. A. Mir, P. Ramaraju, B. P. Wakhloo, *RSC Adv.* **2012**, *2*, 8922–8925.

[2] J.-Y. Liang, H. Wang, Y.-L. Yang, S. J. Shen, J.-X. Chen, *Tetrahedron Lett*. **2017**, 58, 2636–2639.

2. Optimization of reaction conditions[a-c]

Table S1. Optimization of the solvents and catalysts



Entry	Solvent	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	DMSO	TFA (10)	10	20
2	DMSO	AcOH (10)	24	35
3	DMSO	$Yb(OTf)_3$ (10)	16	47
4	Toluene	$Yb(OTf)_3$ (10)	24	<10
5	CH_3CN	$Yb(OTf)_3$ (10)	20	35
6	THF	$Yb(OTf)_3$ (10)	14	42
7	DMF	$Yb(OTf)_3$ (10)	16	30
8	CH_2Cl_2	$Yb(OTf)_3$ (10)	16	45
9	THF	$Yb(OTf)_3$ (10)	24	38
10	**EtOH**	**$Yb(OTf)_3$ (10)**	**12**	**80**
11	EtOH	$Zn(OTf)_2$ (10)	18	48
12	EtOH	$Cu(OTf)_2$ (10)	18	42
13	EtOH	$Sc(OTf)_3$ (10)	16	62
14	EtOH	$Bi(OTf)_3$ (10)	16	45
15	EtOH	$In(OTf)_3$ (10)	16	50
16	EtOH	$Yb(OTf)_3$ (5)	18	75
17	EtOH	$Yb(OTf)_3$ (15)	8	79
18	EtOH	$YbCl_3.6H_2O$	12	64
19	EtOH	$BiCl_3$	16	49
20	EtOH	$InCl_3$	18	55
21	EtOH	$BiBr_3$	18	43
22	EtOH	No catalyst	24	trace
23	EtOH	p-TSA	24	25
24	EtOH	AcOH	24	31

[a]Unless otherwise indicated, the reaction was carried out with succinaldehyde **1** (3.0 M sol, 0.6 mmol, 2.0 equiv.), *p*-anisidine **2a** (0.3 mmol, 1.0 equiv.), Isatin **3a** (0.3 mmol, 1.0 equiv.), Catalyst (x mol%), Solvent (3.0 mL), rt. [b]Isolated yield of **4aa** refers to **3a**. [c]pyrrole **5** (≤10%) was also obtained *via* Paal-Knorr reaction.

General procedure for the reaction between succinaldehyde, aryl/alkyl amines and isatins: To a stirred solution of isatin **3** (other electrophiles) (0.3 mmol, 1.0 equiv.) and $Yb(OTf)_3$ (0.03 mmol, 0.1 equiv.) in EtOH (3.0 mL) in a round bottom-flask was added succinaldehyde **1** (3M aqueous sol., 0.6 mmol, 2.0 equiv.), aryl/alkyl amine **2** (0.3 mmol, 1.0 equiv.) at room temperature. The combined reaction mixture was stirred for 2-12 h at the same temperature and progress of the reaction was monitored by TLC. Upon completion solvent was removed under reduced pressure. The reaction mass was stirred between $NaHCO_3$ (3.0 mL, 10% aqueous sol.) and ethyl acetate (4.0 mL) for five minutes, and the organic layer was separated. The aqueous layer was again extracted with ethyl acetate (1 × 4 mL) and combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mass was passed through a small pad of silica gel column by eluting with petroleum ether/EtOAc to get corresponding pyrrole **4** (up to 91% yields).

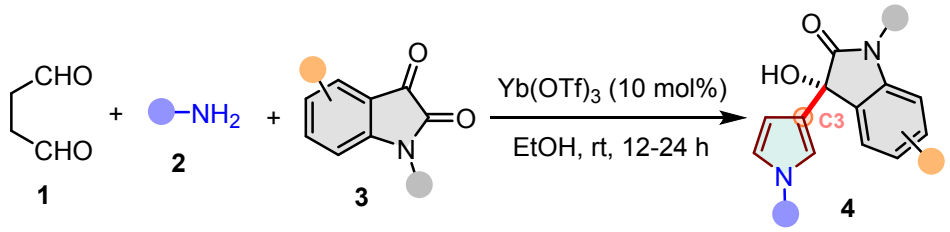
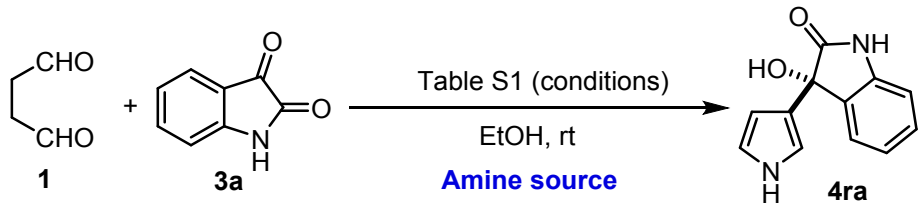


Table S2: Study for reaction between succinaldehyde, and isatin with amine source



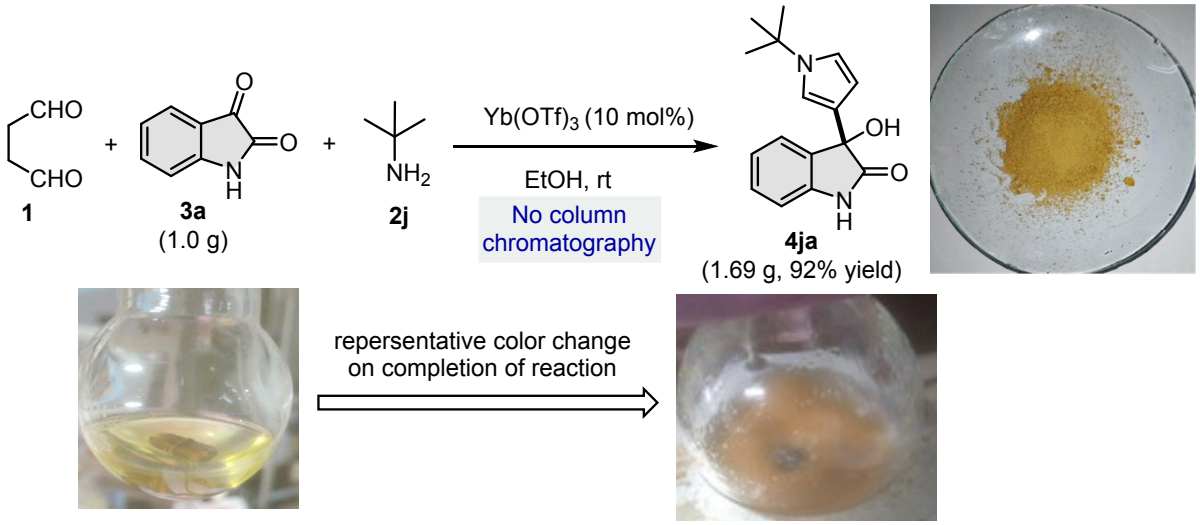
Entry	Amine source	Catalyst (10 mol%)	Time (h)	Yield **4aa** (%)
1	NH_4OAc (1.0 equiv.)	$Yb(OTf)_3$	18	55
2	**NH_4OAc (2.0 equiv.)**	**$Yb(OTf)_3$**	**12**	**71**
3	NH_4OAc (3.0 equiv.)	$Yb(OTf)_3$	10	71
4	NH_4OAc (2.0 equiv.)	No catalyst	24	35
5	Aqueous NH_3 (3.0 equiv.)	$Yb(OTf)_3$	24	30
6	Aqueous NH_3 (3.0 equiv.)	No catalyst	24	-
6	NH_4Cl (2.0)	$Yb(OTf)_3$	12	-

Procedure for the reaction between succinaldehyde, NH_4OAc and isatins:

To a stirred solution of isatin **3** (0.3 mmol, 1.0 equiv.) and $Yb(OTf)_3$ (0.03 mmol, 0.1 equiv.) in EtOH (3.0 mL) in a round bottom-flask was added succinaldehyde **1** (3M aqueous sol., 0.6 mmol, 2.0 equiv.) and NH_4OAc **2r** (43 mg, 0.6 mmol, 2.0 equiv.) at room temperature The combined reaction mixture was stirred for 12 h at the same temperature and progress of the reaction was monitored by TLC. Upon completion solvent was removed under reduced pressure. The reaction was stirred between brine (3.0 mL) and ethyl acetate (4.0 mL) for five minutes, and the organic layer was separated. The aqueous layer was again extracted with ethyl acetate (1 × 4 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mass was passed through a small pad of silica gel column by eluting with petroleum ether/EtOAc (1:1) to get corresponding pyrrole **4** (up to 75% yields).

Procedure for the gram-scale synthesis of 4ja:

To a stirred solution of isatin **3a** (1.0 g, 6.8 mmol, 1.0 equiv.) and $Yb(OTf)_3$ (421 mg, 0.68 mmol, 0.1 equiv.) in EtOH (45.0 mL) in a round bottom-flask was added succinaldehyde **1** (3 M aqueous sol., 4.5 mL, 13.6 mmol, 2.0 equiv.) and *tert*-butyl amine **2j** (0.5 g, 6.8 mmol, 1.0 equiv.) at room temperature, and further stirred for 4 h. The progress of the reaction was monitored by TLC and observed through the formation of solid material, which was initially transparent. The reaction mixture was cooled in ice-water bath, filtered, and washed with cold EtOH to obtain the brownish-yellow solid compounds **4ja** (1.69 g, 92 % yield) with >95% purity. The purity of the compound was checked with the HPLC using C-18 column (CH_3CN: H_2O (90:10), flow rate 1.0 ml/min) and the chart of the same is attached.

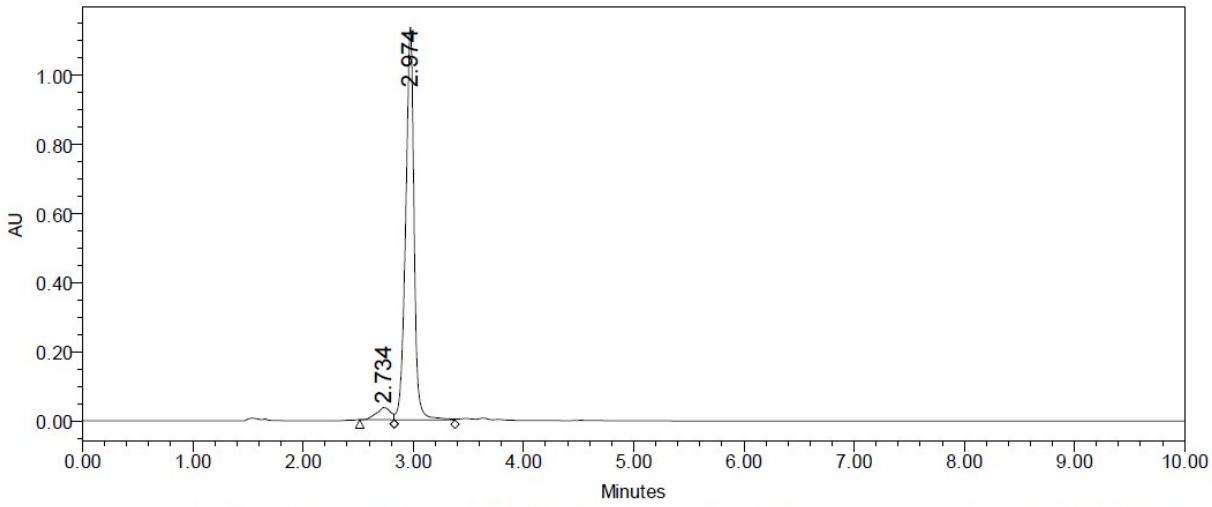


Empower 2 software

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	AP tBu-1	Acquired By:	System
Sample Type:	Unknow n	Sample Set Name:	
Vial:	1	Acq. Method Set:	amol
Injection #:	2	Processing Method:	AP ISA tBu 1
Injection Volume:	20.00 ul	Channel Name:	252.0nm
Run Time:	10.0 Minutes	Proc. Chnl. Descr.:	PDA 252.0 nm
Date Acquired:	6/15/2020 11:28:59 PM IST		
Date Processed:	6/15/2020 11:59:34 PM IST		



Channel: 2998; Processed Channel: PDA 252.0 nm; Result Id: 8778; Processing Method: AP ISA tBu 1

Processed Channel Descr.: PDA 252.0 nm

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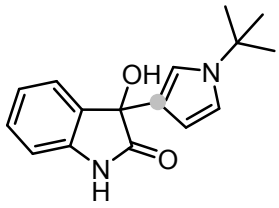
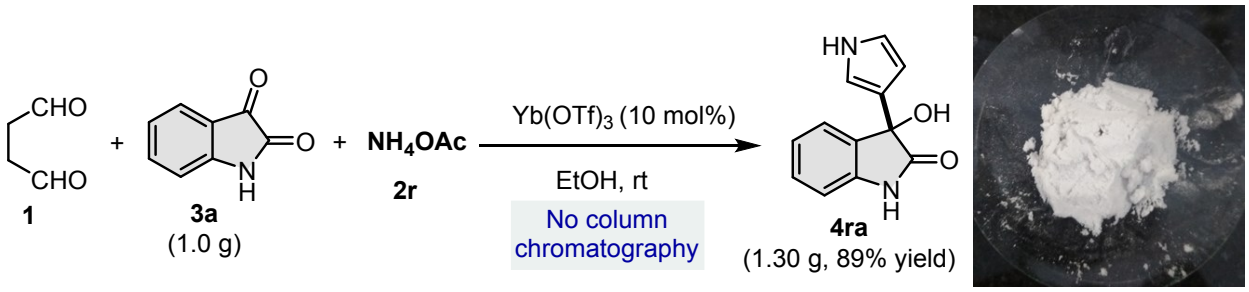


4ja

HPLC chart at the gram scale after filteration and washing with cold EtOH

Procedure for the gram-scale synthesis of 4ra:

To a stirred solution of isatin **3a** (1.0 g, 6.8 mmol, 1.0 equiv.) and $Yb(OTf)_3$ (421 mg, 0.68 mmol, 0.1 equiv.) in EtOH (45.0 mL) was added succinaldehyde **1** (3 M aqueous sol., 4.5 mL, 13.6 mmol, 2.0 equiv.) and ammonium acetate (NH_4OAc) **2r** (0.967 g, 13.6 mmol, 2.0 equiv.), and further stirred for 8 h. The progress of the reaction was monitored by TLC. The complete reaction mass was poured into the crushed ice to get solid precipitate which was filtered and washed with cold EtOH to obtain the gray-solid compounds **4ra** (1.30 g, 89% yield) with >95% purity. The purity of the compound was checked with the HPLC using C-18 column (CH_3CN: H_2O (90:10), flow rate 1.0 ml/min) and the chart of the same is attached.



Empower 2 software

Injection Summary Report

SAMPLE INFORMATION

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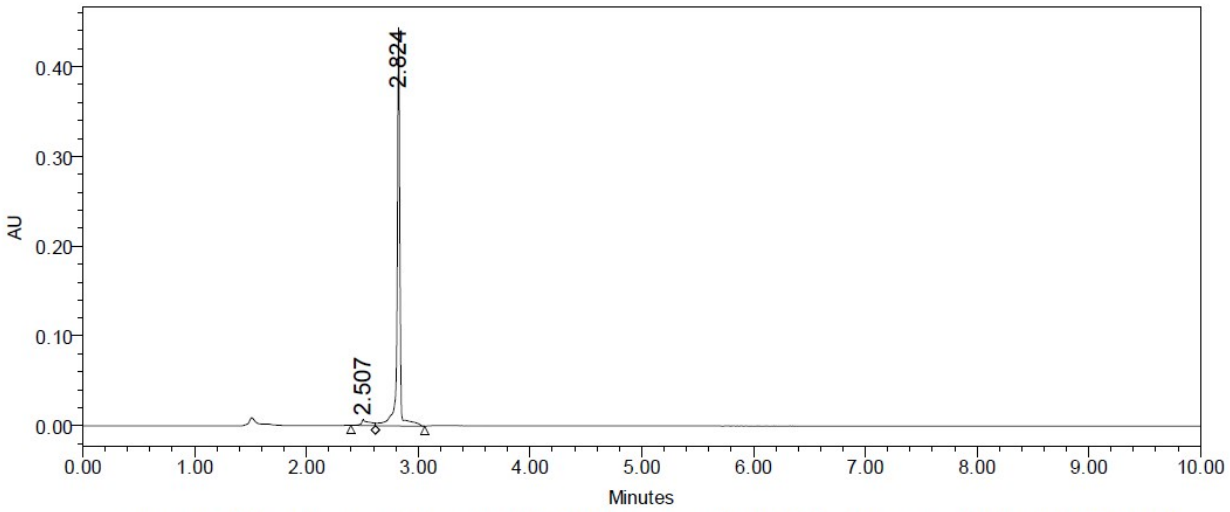
Injection Volume:	20.00 ul	Channel Name:	359.0nm
Run Time:	10.0 Minutes	Proc. Chnl. Descr.:	PDA 359.0 nm
Date Acquired:	6/16/2020 12:13:00 AM IST		
Date Processed:	6/16/2020 12:15:02 AM IST		



Channel: 2998; Processed Channel: PDA 359.0 nm; Result Id: 8797; Processing Method: AP Fr NH 02

Processed Channel Descr.: PDA 359.0 nm

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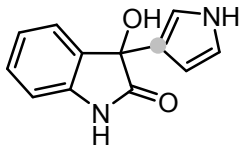
2	PDA 359.0 nm	2.824	773827	95.96	444204



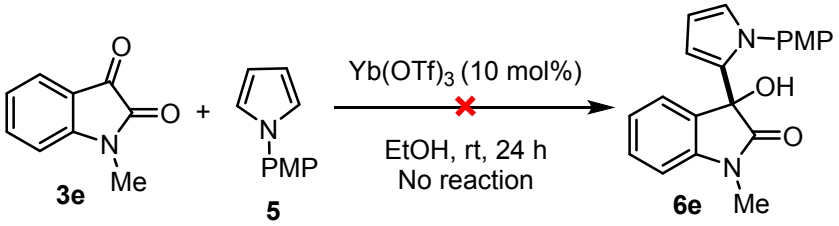
4ra

HPLC chart at the gram scale after filteration and washing with cold EtOH

Controlled experiments:

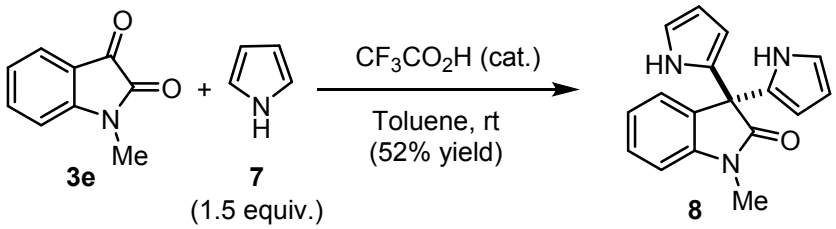
Model reaction between isatin 3e and preformed pyrrole 5:

To a stirred solution of N-methylisatin **3e** (48 mg, 0.3 mmol, 1.0 equiv.) and *N*-PMP-pyrrole **5** (78 mg, 0.45 mmol, 1.5 equiv.) in EtOH (3.0 mL) was added $Yb(OTf)_3$ (0.03 mmol, 10 mol%) at room temperature. We did not observe any reaction between them even after 24 h.

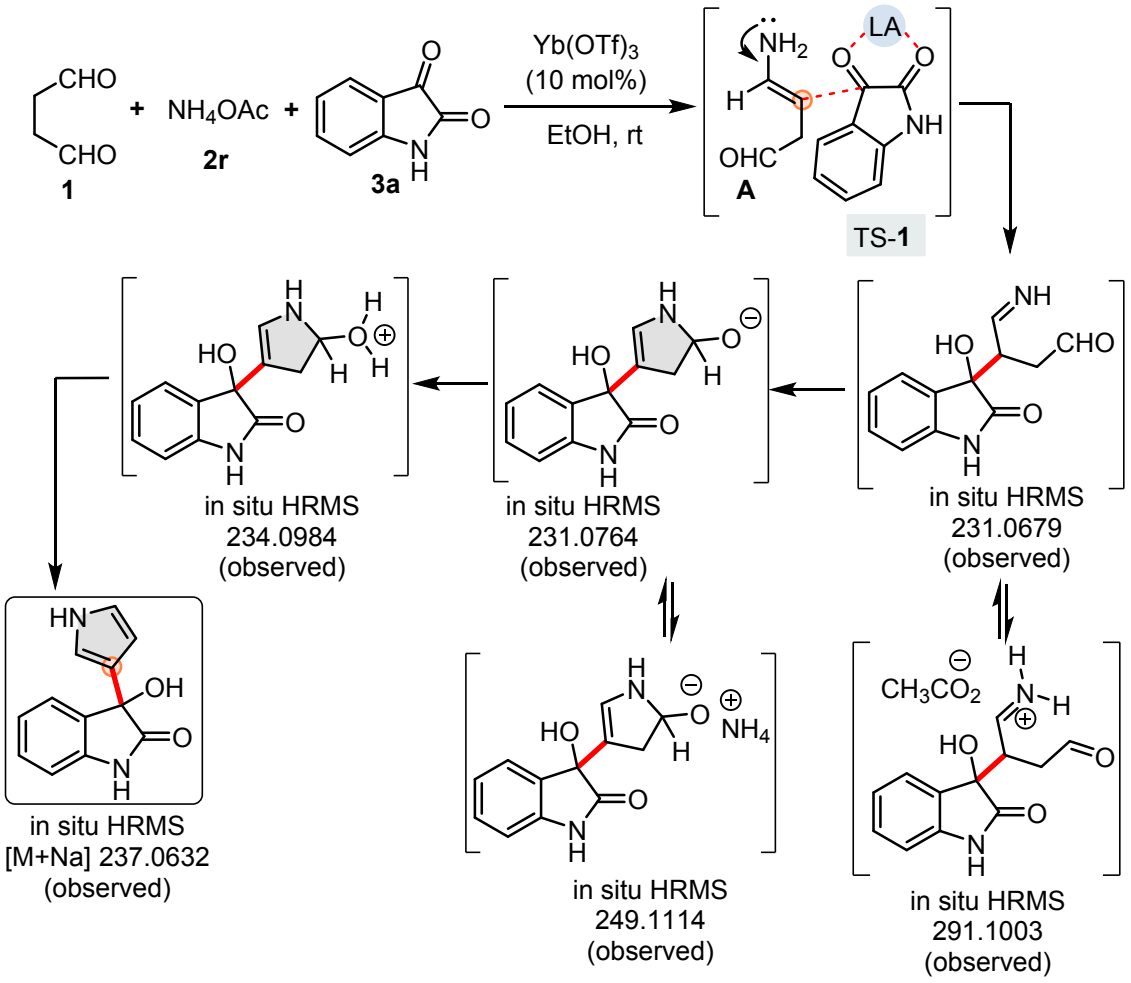


Model reaction between isatin 3e and pyrrole 7:

To a stirred solution of N-methyl isatin **3e** (48 mg, 0.3 mmol, 1.0 equiv.) and pyrrole **7** (30 mg, 0.45 mmol, 1.5 equiv.) in Toluene (1.5 mL) was added CF_3CO_2H (10 mol %) at 0 °C and further stirred at room temperature. The progress of the reaction was monitored by TLC and quenched by stirring with saturated $NaHCO_3$ (2.0 mL, 10% aqueous sol.) and ethyl acetate (3.0 mL) for five minutes, and the organic layer was separated. The aqueous layer was then extracted with ethyl acetate (1 × 3.0 mL) and the combined organic layers were washed with brine once and dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified through a silica gel column by eluting with hexane: ethyl acetate (3:2) to give bis-pyrrole **8** as white solid product (43 mg, 52% yields).



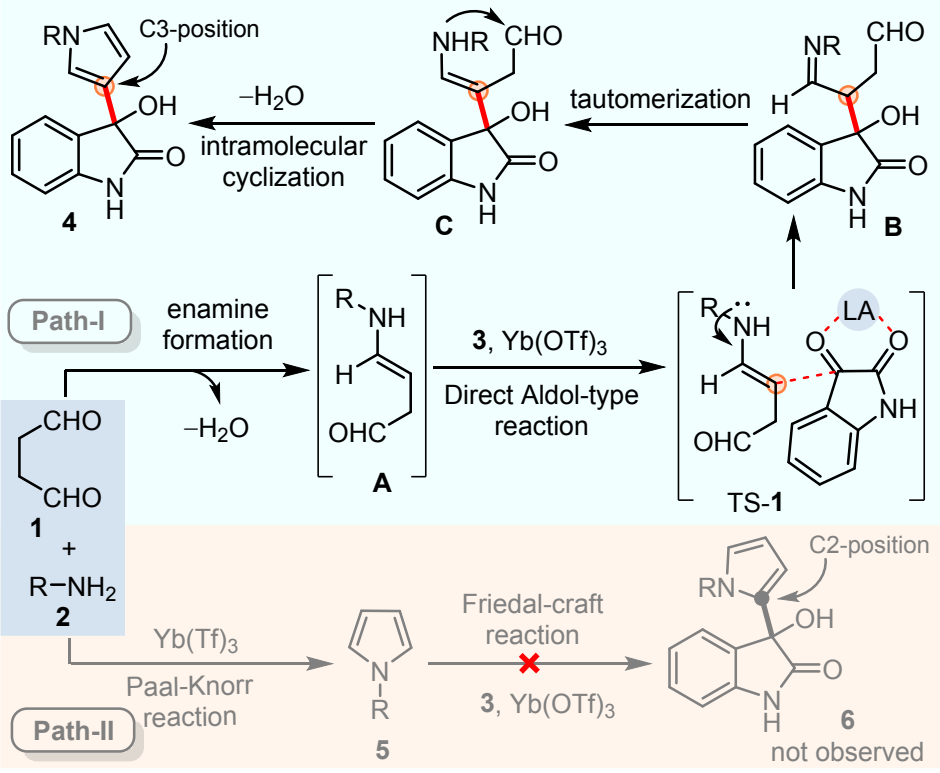
In-situ HRMS study of a model reaction



Scheme S1. *In situ* HRMS study of the reaction between succinaldehyde **1**, ammonium acetate **2r**, and isatin **3a**.

Detailed reaction mechanism for the developed protocol:

Based on theoretical study and in situ HRMS study (Scheme S1), we proposed a plausible mechanism (Scheme S2. We predicted that the reaction could take place in two-different possible pathways. In **Path-I**, a direct aldol-type response between enamine-A and Lewis acid activated isatin **3** via TS-1 resulted in intermediate-**B**. Following a tautomerization-cyclization sequence as Paal-Knorr reaction, intermediate-**B** furnished the experimentally observed C3-substituted pyrrole **4**, in a complete regiospecific manner. Whereas, in **Path-II** pyrrole **5**, in situ generated through Paal-Knorr reaction succinaldehyde **1** and amine **2**, could undergo a Friedel-Craft reaction with activated isatin **3**, led to α-(C2)-pyrrole **6**, which was not observed in this reaction. In all the cases, we observed the formation of Paal-Knorr reaction N-PMP-pyrrole **5** (≤10%). Thus, the trapping of enamine-**A** with suitable electrophile prior to the Paal-Knorr reaction is the key to success.



Scheme S2. The plausible reaction mechanism with expected path-I and path-II.

Synthesis applications of the developed methodology:

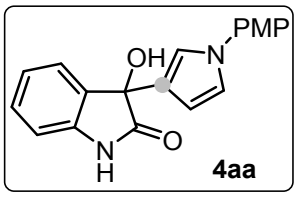
Preparation of quaternary oxindole tethered pyrrole 10:

To a stirred solution of **4ae** (100 mg, 0.3 mmol, 1.0 equiv.) and *p*-cresol **9** (97 mg, 0.9 mmol, 3.0 equiv.) in dry CH_2Cl_2 (3.0 mL) was added trifluoroacetic acid (20 mol%) at room temperature and further stirred for 12 h. The progress of the reaction was monitored by TLC. Once completed, reaction was stirred with $NaHCO_3$ (3.0 mL, 10% aqueous sol.) and CH_2Cl_2 (3.0 mL) for five minutes, and the organic layer was separated. The organic layer was washed with brine once and dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by passing through a small pad of silica gel column by eluting with hexane: ethyl acetate (3:2) to give quaternary oxindole **10** as white solid product (108 mg, 85% yields).

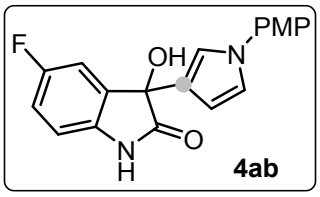
Preparation of quaternary oxindole tethered pyrrole 12:

To a stirred solution of **4ae** (200 mg, 0.75 mmol, 1.0 equiv.) and phenol **9** (208 mg, 2.25 mmol, 3.0 equiv.) in dry CH_2Cl_2 (7.0 mL) was added trifluoroacetic acid (20 mol%) at room temperature and further stirred for 12 h. The progress of the reaction was monitored by TLC. Once completed, reaction was stirred with $NaHCO_3$ (10% aqueous solution, 6.0 mL) and CH_2Cl_2 (5.0 mL) for five minutes, and the organic layer was separated. The organic layer was washed with brine once and dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by passing through a small pad of silica gel column by eluting with hexane: ethyl acetate (3:2) to give quaternary oxindole-tethered pyrrole **12** as while solid product (236 mg, 92% yields).

Spectral data of synthesized compounds:

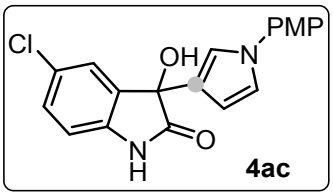


3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4aa). Purification with petroleum ether/EtOAc (3/2) as eluent; Yellow solid (77 mg, 80% yield, mp = 122-124 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.25 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 3H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.16 (s, 1H), 6.98 (q, *J* = 8.5 Hz, 4H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.24 (d, *J* = 9.0 Hz, 2H), 3.76 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 179.1, 157.5, 141.9, 133.9, 133.8, 129.3, 126.5, 125.1, 122.1, 121.4 (2C), 120.0, 117.6, 115.2 (2C), 110.0, 109.6, 74.1, 55.8. **IR (KBr)/cm^{-1}** 3232, 2932, 1713, 1612, 1520, 1466, 1396,1342, 1242, 1196. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_3$ 321.1239; Found 321.1244.

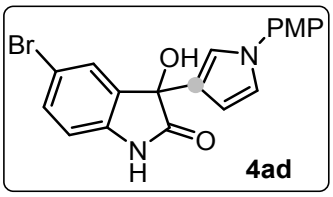


5-fluoro-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ab). Purification with petroleum ether/EtOAc (3/2) as eluent; Brown solid (84 mg, 83% yield, mp = 128-130 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.27 (s, 1H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.24 (dd, *J* = 8.2, 2.7 Hz, 1H), 7.19 – 7.16 (m, 1H), 7.06 (ddd, *J* = 9.6, 8.6, 2.7 Hz, 1H), 7.01 – 6.96 (m, 3H), 6.83 (dd, *J* = 8.5, 4.3 Hz, 1H), 6.37 (s, 1H), 6.25 (dd, *J* = 2.9, 1.7 Hz, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 178.5, 158.1 (d, *J* = 237.1 Hz), 157.1, 137.5, 135.1 (d, *J* = 7.4 Hz), 133.3, 125.4, 121.0 (2C), 119.6, 117.2, 115.0 (d, *J* = 23.2 Hz), 114.7 (2C), 112.3 (d, *J* = 24.2 Hz), 110.3

(d, J = 7.7 Hz), 109.0, 73.9, 55.3. **IR (KBr)/cm^{-1}** 3425, 2924, 1713, 1636, 1589, 1474, 1358, 1257, 1196. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}FN_2O_3$ 339.1145; Found 339.1148.

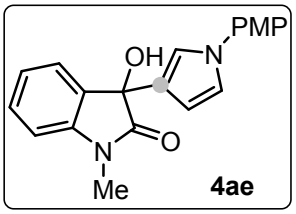


5-chloro-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ac). Purification with petroleum ether/EtOAc (3/2) as eluent; White solid (82 mg, 78% yield, mp = 120-122 ^{o}C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.40 (s, 1H), 7.42 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 2.2 Hz, 1H), 7.28 (dd, J = 8.3, 2.3 Hz, 1H), 7.18 (t, J = 2.6 Hz, 1H), 7.02 – 6.97 (m, 3H), 6.86 (d, J = 8.3 Hz, 1H), 6.40 (s, 1H), 6.23 (dd, J = 3.0, 1.7 Hz, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 178.7, 157.6, 140.8, 136.0, 133.7, 129.1, 126.2, 125.8, 125.1, 121.5 (2C), 120.2, 117.7, 115.2 (2C), 111.6, 109.4, 74.2, 55.8. **IR (KBr)/cm^{-1}** 3348, 2924, 1720, 1666, 1520, 1466, 1342, 1242, 1180. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}ClN_2O_3$ 355.0849; Found 355.0855.



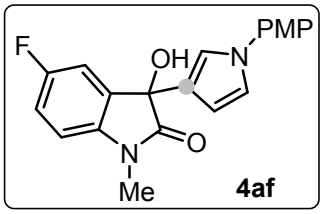
5-bromo-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ad). Purification with petroleum ether/EtOAc (3/2) as eluent; Brown solid (92 mg, 77% yield, mp = 115-117 ^{o}C**).** **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.41 (s, 1H), 7.48 (d, J = 1.9 Hz, 1H), 7.41 (td, J = 5.8, 5.2, 2.9 Hz, 3H), 7.18 (t, J = 2.6 Hz, 1H), 7.00 (d, J = 9.0 Hz, 3H), 6.81 (d, J = 8.2 Hz, 1H), 6.40 (s, 1H), 6.23 – 6.20 (m, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 178.1, 157.1, 140.7, 135.9, 133.3, 131.5, 127.3, 125.3, 121.0 (2C), 119.7, 117.1, 114.7 (2C), 113.4, 111.7, 108.9,

73.8, 55.4. **IR (KBr)/cm^{-1}** 3430, 2947, 1720, 1612, 1512, 1466, 1319, 1242, 1196. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{15}BrN_2O_3$ 399.0344; Found 399.0350.



4ae

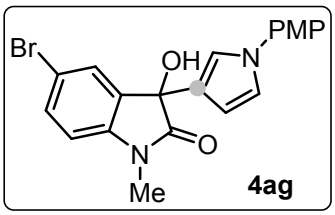
3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)-1-methylindolin-2-one (4ae). Purification with petroleum ether/EtOAc (4/1) as eluent; White solid (80 mg, 80% yield, mp = 138-140 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.36 (td, *J* = 7.7, 1.3 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.16 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 (t, *J* = 2.1 Hz, 1H), 6.95 (t, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.52 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.83 (s, 3H), 3.39 (s, 1H), 3.23 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.6, 157.7, 143.0, 133.8, 131.1, 129.4, 124.5, 124.3, 123.1, 122.1 (2C), 120.6, 118.6, 114.5 (2C), 108.6, 108.5, 74.0, 55.4, 26.3. **IR (KBr)/cm^{-1}** 3394, 2924, 1713, 1597, 1514, 1350, 1265, 1203, 1080. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_3$ 335.1395; Found 335.1401.



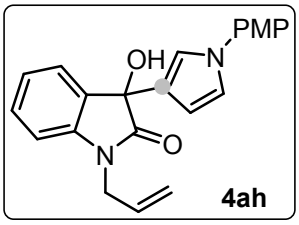
4af

5-fluoro-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)-1-methylindolin-2-one (4af). Purification with petroleum ether/EtOAc (4/1 as eluent; Red solid (86 mg, 81% yield, mp = 166-168 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (dd, *J* = 7.7, 2.6 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.06 (ddd, *J* = 9.2, 8.5, 2.6 Hz, 1H), 6.99 (t, *J* = 2.0 Hz, 1H), 6.96 (dd, *J* = 3.0, 2.3 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.80 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.49 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.84 (s, 3H), 3.23 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.3, 159.8 (d, *J* = 241.6 Hz), 158.0, 139.1,

133.8, 132.6 (d, J = 7.6 Hz), 123.9, 122.3 (2C), 121.0, 118.7, 115.7 (d, J = 23.5 Hz), 114.6 (2C), 112.8 (d, J = 24.9 Hz), 109.1 (d, J = 8.0 Hz), 108.4, 74.1, 55.5, 26.5. **IR (KBr)/cm^{-1}** 3417, 2926, 1713, 1628, 1566, 1512, 1360, 1257, 1103, 1049. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}FN_2O_3$ 353.1301; Found 353.1305.

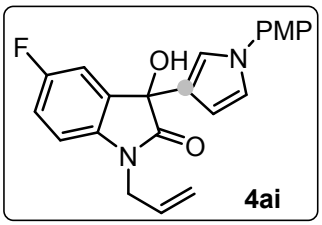


5-bromo-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)-1-methylindolin-2-one (4ag). Purification with petroleum ether/EtOAc (4/1) as eluent; Light brown solid (96 mg, 78% yield, mp = 191-194 ^{o}C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, J = 1.7 Hz, 1H), 7.46 (dd, J = 8.3, 1.8 Hz, 1H), 7.24 (d, J = 8.9 Hz, 2H), 6.98 – 6.95 (m, 1H), 6.95 – 6.93 (m, 1H), 6.91 (d, J = 8.9 Hz, 2H), 6.73 (d, J = 8.3 Hz, 1H), 6.46 (dd, J = 2.9, 1.9 Hz, 1H), 3.81 (s, 3H), 3.20 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.0, 158.0, 142.3, 133.8, 133.0, 132.3, 127.8, 123.8, 122.4 (2C), 121.0, 118.7, 115.8, 114.6 (2C), 110.0, 108.4, 74.0, 55.5, 26.5. **IR (KBr)/cm^{-1}** 3387, 2916, 1713, 1651, 1605, 1512, 1350, 1250, 1188, 1049. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}BrN_2O_3$ 413.0501; Found 413.0506.

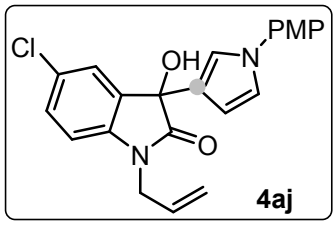


1-allyl-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ah). Purification with petroleum ether/EtOAc (4/1) as eluent; Colorless semi-solid (78 mg, 72% yield). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.45 (dd, J = 7.3, 1.3 Hz, 1H), 7.39 (d, J = 9.0 Hz, 2H), 7.30 (td, J = 7.7, 1.3 Hz, 1H), 7.17 (t, J = 2.6 Hz, 1H), 7.07 (tt, J = 7.5, 1.2 Hz, 1H), 7.02 – 6.94 (m, 4H), 6.39 (s,

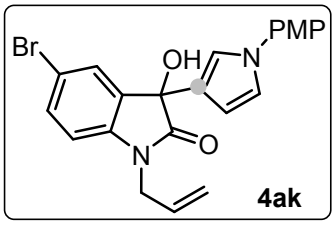
1H), 6.21 (dd, *J* = 3.0, 1.7 Hz, 1H), 5.86 (ddt, *J* = 17.1, 10.2, 4.9 Hz, 1H), 4.38 – 4.22 (m, 2H), 3.77 (s, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 177.2, 157.8, 142.3, 133.9, 131.1 (2C), 129.4, 124.6, 124.5, 123.0, 122.2 (2C), 120.8, 118.6, 117.5 , 114.5 (2C), 109.4, 108.5, 74.0, 55.5, 42.4. **IR (KBr)/cm^{-1}** 3414, 2924, 1733, 1625, 1532, 1358, 1188, 1049. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{21}N_2O_3$ 361.1552; Found 361.1558.



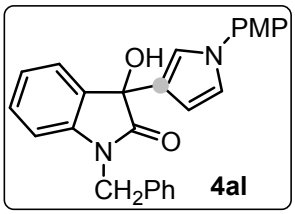
1-allyl-5-fluoro-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ai). Purification with petroleum ether/EtOAc (4/1) as eluent; Yellow semi-solid (86 mg, 76% yield). **^1H NMR (400 MHz, $CDCl_3$)** δ 7.33 (dd, *J* = 7.7, 2.6 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.01 (dp, *J* = 6.4, 3.9, 3.2 Hz, 2H), 6.97 – 6.87 (m, 3H), 6.79 (dd, *J* = 8.6, 4.1 Hz, 1H), 6.51 – 6.41 (m, 1H), 5.83 (ddd, *J* = 15.9, 10.6, 5.2 Hz, 1H), 5.32 – 5.13 (m, 2H), 4.41 (dd, *J* = 16.5, 5.2 Hz, 1H), 4.27 (dd, *J* = 16.5, 5.3 Hz, 1H), 3.83 (s, 3H), 3.64 (s, 1H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 177.1, 159.4 (d, *J* = 241.6 Hz), 157.9, 138.2, 133.8, 132.8 (d, *J* = 7.9 Hz), 131.0, 124.1, 122.3 (2C), 120.9, 118.5, 117.7, 115.5 (d, *J* = 23.5 Hz), 114.6 (2C), 112.8 (d, *J* = 24.8 Hz), 110.1 (d, *J* = 7.9 Hz), 108.4, 74.2, 55.5, 42.5. **IR (KBr)/cm^{-1}** 3425, 2932, 1723, 1635, 1504, 1360, 1257, 1180. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{19}FN_2O_3$ 379.1458; Found 379.1463.



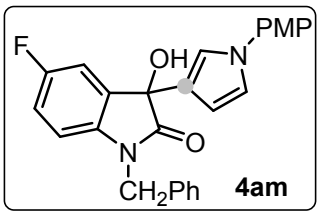
1-allyl-5-chloro-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4aj). Purification with petroleum ether/EtOAc (4/1) as eluent; Brown semi-solid (85 mg, 72% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 2.2 Hz, 1H), 7.28 (td, *J* = 8.8, 8.3, 2.2 Hz, 3H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.97 (t, *J* = 2.7 Hz, 1H), 6.95 (d, *J* = 6.9 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.48 (t, *J* = 2.4 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.3, 5.2 Hz, 1H), 5.26 (s, 1H), 5.23 (d, *J* = 5.6 Hz, 1H), 4.43 (dd, *J* = 16.4, 5.3 Hz, 1H), 4.29 (dd, *J* = 16.4, 5.1 Hz, 1H), 3.85 (s, 3H), 3.32 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 176.8, 158.0, 140.9, 133.9, 132.8, 130.9, 129.3, 128.5, 125.2, 124.0, 122.4 (2C), 121.1, 118.6, 117.8, 114.7 (2C), 110.5, 108.3, 74.1, 55.6, 42.5. **IR (KBr)/cm^{-1}** 3435, 2924, 1713, 1615, 1514, 1435, 1348, 1250, 1180. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{20}ClN_2O_3$ 395.1162; Found 395.1157.



1-allyl-5-bromo-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ak). Purification with petroleum ether/EtOAc (4/1) as eluent; Brown solid (92 mg, 70% yield, mp = 188-191 ^{o}C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.49 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.19 (t, *J* = 2.6 Hz, 1H), 7.04 (t, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.56 (s, 1H), 6.22 (dd, *J* = 2.9, 1.8 Hz, 1H), 5.90 – 5.79 (m, 1H), 5.18 (t, *J* = 1.7 Hz, 1H), 5.15 (dq, *J* = 7.1, 1.6 Hz, 1H), 4.38 – 4.22 (m, 2H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 176.5, 157.6, 141.6, 135.7, 133.7, 132.1, 132.0, 127.6, 125.6, 121.5 (2C), 120.3, 117.7, 117.3, 115.2, 114.7 (2C), 111.7, 109.3, 74.0, 55.8, 41.9. **IR (KBr)/cm^{-1}** 3410, 2924, 1713, 1605, 1522, 1350, 1265, 1180, 1057. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{20}BrN_2O_3$ 439.0657; Found 439.0662.

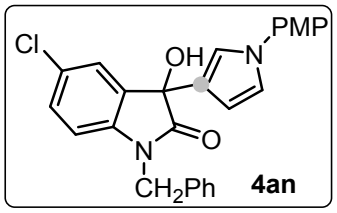


1-benzyl-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4al). Purification with petroleum ether/EtOAc (4/1) as eluent; Brown solid (98 mg, 80% yield, mp = 114-116 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.54 (m, 1H), 7.34 – 7.27 (m, 5H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.09 (td, *J* = 7.6, 0.9 Hz, 1H), 7.00 (t, *J* = 2.0 Hz, 1H), 6.98 – 6.95 (m, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.51 (dd, *J* = 2.9, 1.8 Hz, 1H), 4.99 (d, *J* = 15.8 Hz, 1H), 4.87 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 3.20 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.5, 157.7, 142.3, 135.5, 133.9, 131.1, 129.5, 128.8 (2C), 127.6, 127.1 (2C), 124.6, 124.5, 123.2, 122.3 (2C), 120.9, 118.6, 114.6 (2C), 109.6, 108.5, 74.1, 55.5, 43.8. **IR (KBr)/cm^{-1}** 3425, 2932, 1713, 1605, 1512, 1358, 1296, 1050. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O_3$ 411.1708; Found 411.1714.

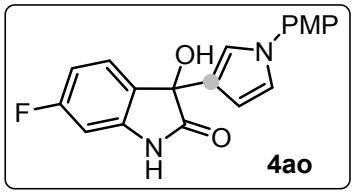


1-benzyl-5-fluoro-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4am). Purification with petroleum ether/EtOAc (4/1) as eluent; Dark brown solid (104 mg, 81% yield, mp = 128-130 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.28 (m, 8H), 7.05 (t, *J* = 2.1 Hz, 1H), 7.01 (dd, *J* = 3.0, 2.3 Hz, 1H), 6.98 – 6.91 (m, 3H), 6.67 (dd, *J* = 8.6, 4.0 Hz, 1H), 6.52 (dd, *J* = 3.0, 1.8 Hz, 1H), 5.02 (d, *J* = 15.8 Hz, 1H), 4.89 (d, *J* = 15.8 Hz, 1H), 3.86 (s, 4H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.4, 159.4 (d, *J* = 241.9 Hz), 158.0, 138.1, 135.2, 133.8, 128.8 (2C), 128.7 (d, *J* = 17.7 Hz), 127.7, 127.1 (2C), 124.1, 122.3 (2C), 121.1, 118.5, 115.6 (d, *J* = 23.5 Hz), 114.6

(2C), 112.7 (d, J = 24.7 Hz), 110.3 (d, J = 8.0 Hz), 108.3, 74.3, 55.5, 44.0. **HRMS (ESI)** *m*/*z*: [M + H]$^+$ Calcd for $C_{26}H_{22}FN_2O_3$ 429.1614; Found 429.1618.

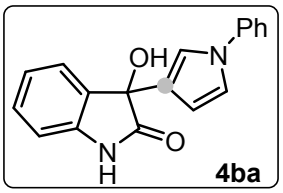


1-benzyl-5-chloro-3-hydroxy-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4an). Purification with petroleum ether/EtOAc (4/1) as eluent; Red solid (102 mg, 77% yield, mp = 148-150 ^{o}C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.48 (d, J = 2.3 Hz, 1H), 7.42 (d, J = 8.9 Hz, 2H), 7.35 – 7.28 (m, 5H), 7.21 (t, J = 2.6 Hz, 1H), 7.06 (t, J = 2.1 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 8.3 Hz, 1H), 6.65 (s, 1H), 6.28 – 6.22 (m, 1H), 4.91 (s, 2H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 176.1, 157.6, 141.1, 136.6, 135.4, 133.7, 129.1 (3C), 127.9, 127.6 (2C), 127.2, 125.6, 125.0, 121.5 (2C), 120.4, 117.7, 115.2 (2C), 111.2, 109.3, 74.1, 55.9, 43.1. **IR (KBr)/cm^{-1}** 3425, 2924, 1713, 1605, 1504, 1342, 1250, 1180. **HRMS (ESI)** *m*/*z*: [M + H]$^+$ Calcd for $C_{26}H_{21}ClN_2O_3$ 445.1319; Found 445.1325.

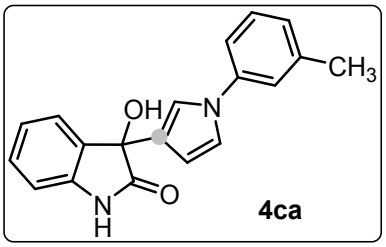


6-fluoro-3-hydroxy-3-(1-(4-methoxyphenyl)-1H-pyrrol-3-yl)indolin-2-one (4ao). Purification with petroleum ether/EtOAc (4/1) as eluent; brown solid (80 mg, 79% yield, mp = 200-202 ^{o}C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.27 (s, 1H), 7.46 – 7.36 (m, 2H), 7.23 (dd, J = 8.2, 2.7 Hz, 1H), 7.17 (t, J = 2.6 Hz, 1H), 7.05 (td, J = 9.1, 2.8 Hz, 1H), 7.01 – 6.95 (m, 3H), 6.82 (dd, J = 8.4, 4.3 Hz, 1H), 6.36 (s, 1H), 6.28 – 6.20 (m, 1H), 3.76 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 179.0, 158.5 (d, J = 236.9 Hz), 157.6, 138.0, 135.6 (d, J = 7.3 Hz), 133.8, 125.9, 121.5 (2C),

120.1, 117.7, 115.5 (d, J = 23.4 Hz), 115.2 (2C), 112.8 (d, J = 24.2 Hz), 110.8 (d, J = 7.8 Hz), 109.5, 74.4, 55.8. **IR (KBr)/cm^{-1}** 3425, 2924, 1720, 1504, 1350, 1250, 1180. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{16}FN_2O_3$ 339.1139; Found 339.1143.

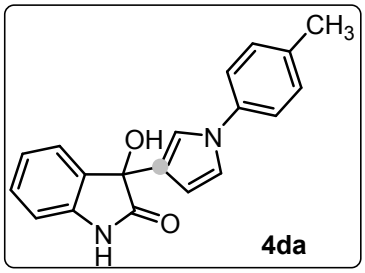


3-hydroxy-3-(1-phenyl-1*H*-pyrrol-3-yl)indolin-2-one (4ba). Purification with petroleum ether/EtOAc (3/2) as eluent; Yellow solid (59 mg, 68% yield, mp = 121-123 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (s, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.11 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 7.6 Hz, 1H), 6.51 (s, 1H), 3.32 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 179.3, 140.3, 140.2, 131.5, 129.6, 129.5 (2C), 126.0, 125.0, 124.8, 123.2, 120.6 (2C), 120.5, 118.3, 110.3, 109.0, 74.4; **IR (KBr)/cm^{-1}** 3433, 2932, 1713, 1605, 1497, 1350. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O_2$ 291.1133; Found 291.1139.

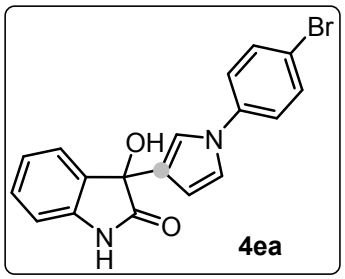


3-hydroxy-3-(1-(m-tolyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ca). Purification with petroleum ether/EtOAc (3/2) as eluent; Brown solid (64 mg, 70% yield, mp = 183-186 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.56 (d, J = 6.5 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.13 (d, J = 7.9 Hz, 3H), 7.05 (d, J = 6.9 Hz, 3H), 6.92 (d, J = 6.8 Hz, 1H), 6.52 (s, 1H), 3.27 (s, 1H), 2.39 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 179.1, 140.2, 140.1, 139.6, 131.5, 129.6, 129.3, 126.8, 125.1, 124.6, 123.2, 121.4, 120.6, 118.3, 117.8, 110.2, 108.8, 74.3, 21.4. **IR (KBr)/cm^{-1}** 3435, 2930,

1717, 1607, 1495, 1352. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_2$ 305.1290; Found 305.1288.

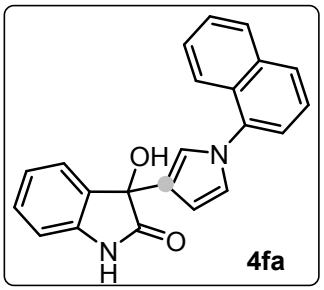


3-hydroxy-3-(1-(p-tolyl)-1*H*-pyrrol-3-yl)indolin-2-one (4da). Purification with petroleum ether/EtOAc (3/2) as eluent; Brown solid (65 mg, 72% yield, mp = 189-192 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (s, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.17 (d, *J* = 2.3 Hz, 4H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.00 (dt, *J* = 13.2, 2.3 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.53 – 6.44 (m, 1H), 3.36 (s, 1H), 2.34 (s, 3H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 179.3, 140.2, 138.0, 135.8, 131.5, 130.0 (2C), 129.6, 125.0, 124.5, 123.1, 120.6 (3C), 118.4, 110.3, 108.7, 72.9, 20.8. **IR (KBr)/cm^{-1}** 3433, 2932, 1713, 1605, 1497, 1350, 1255, 1140. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_2$ 305.1290; Found 305.1294.

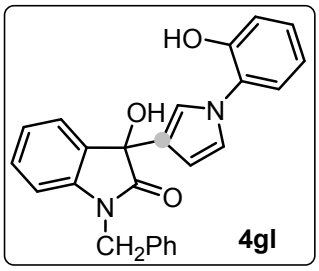


3-(1-(4-bromophenyl)-1*H*-pyrrol-3-yl)-3-hydroxyindolin-2-one (4ea). Purification with petroleum ether/EtOAc (3/2) as eluent; Yellow solid (70 mg, 63% yield, mp = 132-136 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.26 (s, 1H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.36 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.22 (td, *J* = 7.7, 1.3 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.99 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 – 6.79 (m, 1H), 6.28 (s, 1H), 6.26 (dd, *J* = 3.0, 1.7 Hz,

1H). **^{13}C{1H} NMR (101 MHz, $CDCl_3$)** δ 183.6, 146.7, 144.1, 138.4, 137.7 (2C), 134.1, 132.3, 129.9, 126.9, 126.4 (2C), 124.6, 122.7, 122.0, 115.2, 114.8, 78.8. **IR (KBr)/cm^{-1}** 3410, 2924, 1720, 1605, 1481, 1342, 1196, 1057. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{14}BrN_2O_2$ 369.0238; Found 369.0242.

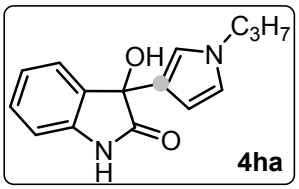


3-hydroxy-3-(1-(naphthalen-2-yl)-1*H*-pyrrol-3-yl)indolin-2-one (4fa). Purification with petroleum ether/EtOAc (3/2) as eluent; Brown solid (66 mg, 65% yield, mp = 144-146 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.26 (s, 1H), 8.02 (dd, *J* = 21.9, 7.9 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.58 (qd, *J* = 7.8, 6.4, 2.2 Hz, 3H), 7.45 (dd, *J* = 13.7, 7.5 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.05 (q, *J* = 2.2 Hz, 1H), 7.00 (t, *J* = 7.7 Hz, 1H), 6.84 (dd, *J* = 11.7, 4.8 Hz, 2H), 6.40–6.34 (m, 1H), 6.30 (d, *J* = 1.8 Hz, 1H). **^{13}C{1H} NMR (101 MHz, DMSO-d_6)** δ 179.1, 141.9, 137.6, 134.3, 133.9, 129.3, 129.1, 128.8, 128.3, 127.7, 127.1, 126.1, 125.7, 125.2, 123.9, 123.6, 122.8, 122.1, 121.6, 110.1, 109.0 74.0. **IR (KBr)/cm^{-1}** 3410, 2924, 1720, 1605, 1481, 1342, 1196, 1057. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{17}N_2O_2$ 341.1290; Found 341.1294.

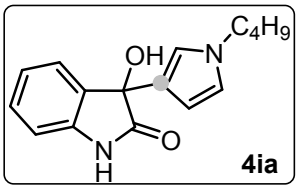


1-Benzyl-3-hydroxy-3-(1-(2-hydroxyphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (4gl). Purification with petroleum ether/EtOAc (7/3) as eluent; Brown solid (81 mg, 68% yield, mp =179-182 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.28 (m, 5H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 1.8 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 2.5 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.52 – 6.48 (m, 1H), 5.01 – 4.81 (m, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.9, 150.3, 142.1, 135.4, 131.2, 129.4, 128.8 (3C), 127.9, 127.6, 127.1 (2C), 126.4, 124.7, 124.5, 123.3, 123.0, 120.8, 120.6, 117.2, 109.7, 108.6, 74.3, 43.9. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_3$ 397.1551; Found 397.1557.

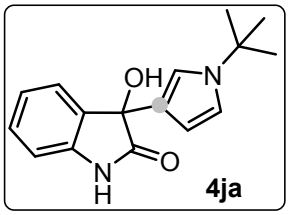


3-hydroxy-3-(1-propyl-1*H*-pyrrol-3-yl)indolin-2-one (4ha). Purification with petroleum ether/EtOAc (7/3) as eluent; Brown solid (68 mg, 88% yield, mp = 153-156 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.14 (s, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.64 (t, *J* = 2.4 Hz, 1H), 6.50 (t, *J* = 1.9 Hz, 1H), 6.05 (s, 1H), 6.04–6.01 (m, 1H), 3.72 (t, *J* = 7.1 Hz, 2H), 1.62 (h, *J* = 7.3 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 179.4, 141.8, 134.3, 129.0, 125.0, 123.7, 121.9, 121.1, 119.5, 109.9, 107.4, 74.1, 50.8, 24.8, 11.5. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}N_2O_2$ 257.1290; Found: 557.1279.

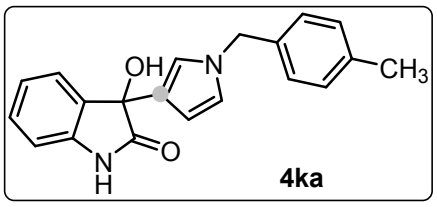


3-(1-butyl-1*H*-pyrrol-3-yl)-3-hydroxyindolin-2-one (4ia). Purification with petroleum ether/EtOAc (7/3) as eluent; Brown solid (73 mg, 90% yield, mp = 162-165 °C). **^{1}H NMR (400**

MHz, DMSO-d_6) δ 10.13 (s, 1H), 7.31 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.19 (td, *J* = 7.7, 1.3 Hz, 1H), 6.97 (td, *J* = 7.5, 1.1 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.64 (t, *J* = 2.5 Hz, 1H), 6.50 (t, *J* = 2.0 Hz, 1H), 6.03 (s, 1H), 6.02 (dd, *J* = 2.7, 1.8 Hz, 1H), 3.76 (t, *J* = 7.2 Hz, 2H), 1.63–1.55 (m, 2H), 1.24 – 1.17 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 178.9, 141.3, 133.8, 128.5, 124.5, 123.2, 121.4, 120.6, 119.0, 109.4, 106.9, 73.6, 48.4, 33.1, 19.3, 13.5. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{19}N_2O_2$ 271.1446; Found: 271.1442.

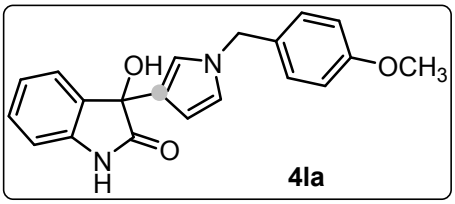


3-(1-(tert-butyl)-1*H*-pyrrol-3-yl)-3-hydroxyindolin-2-one (4ja). Purification with petroleum ether/EtOAc (7/3) as eluent; Brownish solid (73 mg, 90% yield, mp = 178–181 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.31 (s, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.18 (td, *J* = 8.7, 7.7, 1.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.74 (t, *J* = 2.7 Hz, 1H), 6.28 (dd, *J* = 2.8, 1.9 Hz, 1H), 4.15 (s, 1H), 1.41 (s, 9H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 180.8, 140.4, 132.1, 129.0, 124.6, 122.7, 121.5 118.3, 116.7, 110.6, 106.4, 74.8, 54.9, 30.5 (3C). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{19}N_2O_2$ 271.1446; Found: 271.1449.



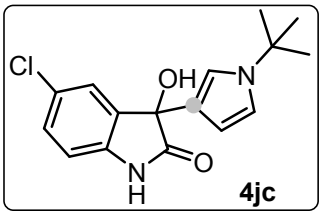
3-hydroxy-3-(1-(4-methylbenzyl)-1*H*-pyrrol-3-yl)indolin-2-one (4ka). Purification with petroleum ether/EtOAc (7/3) as eluent; Pale yellow solid (82 mg, 86% yield, mp = 157-160 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.16 (s, 1H), 7.30 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.18 (td, *J* = 7.7,

1.3 Hz, 1H), 7.14 – 7.08 (m, 4H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 2.5 Hz, 1H), 6.57 (t, *J* = 2.0 Hz, 1H), 6.08 (s, 1H), 6.04 (dd, *J* = 2.8, 1.7 Hz, 1H), 4.94 (s, 2H), 2.26 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ 178.9, 141.4, 136.7, 135.6, 133.8, 129.0 (2C), 128.6, 127.6 (2C), 124.5, 123.7, 121.5, 121.0, 119.2, 109.4, 107.3, 73.6, 52.0, 20.7. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_2$ 319.1446; Found: 319.1453.



4la

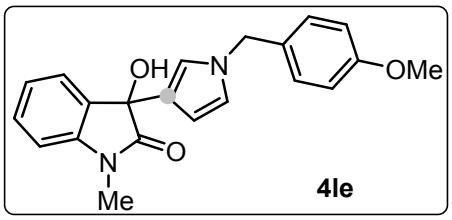
3-hydroxy-3-(1-(4-methoxybenzyl)-1*H*-pyrrol-3-yl)indolin-2-one (4la). Purification with petroleum ether/EtOAc (7/3) as eluent; Pale yellow solid (88 mg, 88% yield, mp =157-160 °C). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.12 (s, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.21–7.14 (m, 3H), 6.98 – 6.93 (m, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.70 (t, *J* = 2.5 Hz, 1H), 6.57 (t, *J* = 1.9 Hz, 1H), 6.05 (s, 1H), 6.03 (dd, *J* = 2.6, 1.8 Hz, 1H), 4.91 (s, 2H), 3.72 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$)** δ 178.8, 158.7, 141.3, 133.8, 130.5, 129.0 (2C), 128.5, 124.5, 123.7, 121.5, 120.8, 119.1, 113.9 (2C), 109.4, 107.3, 73.6, 55.1, 51.7. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_3$ 335.1395; Found: 335.1387.



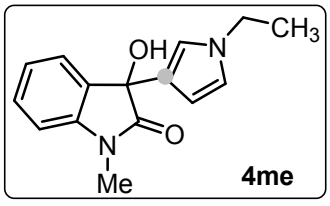
4jc

3-(1-(tert-butyl)-1*H*-pyrrol-3-yl)-5-chloro-3-hydroxyindolin-2-one (4jc). Purification with petroleum ether/EtOAc (7/3) as eluent; Brown solid (77 mg, 85% yield, mp = 191–194 °C). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.21 (s, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.1 Hz, 1H),

6.85 (t, *J* = 2.1 Hz, 1H), 6.82 – 6.77 (m, 2H), 6.26 (dd, *J* = 2.9, 1.9 Hz, 1H), 3.27 (s, 1H), 1.47 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 179.2, 138.6, 133.5, 129.2, 128.3, 125.5, 121.0, 118.9, 116.7, 111.2, 106.2, 74.6, 55.3, 30.7 (3C). **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{18}ClN_2O_2$ 305.1057; Found: 305.1065.

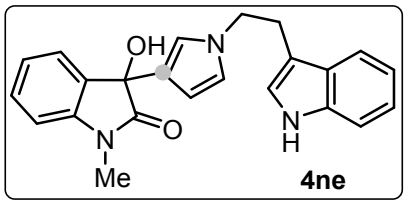


3-hydroxy-3-(1-(4-methoxybenzyl)-1*H*-pyrrol-3-yl)-1-methylindolin-2-one (4le). Purification with petroleum ether/EtOAc (4/1) as eluent; Brown solid (83 mg, 80% yield, mp = 136-139 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.50 (m, 1H), 7.31 (td, *J* = 7.7, 1.2 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.85 – 6.80 (m, 3H), 6.71 (t, *J* = 2.0 Hz, 1H), 6.57 (t, *J* = 2.5 Hz, 1H), 6.32 (dd, *J* = 2.8, 1.8 Hz, 1H), 4.87 (s, 2H), 3.77 (s, 3H), 3.16 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 177.6, 159.1, 143.1, 131.3, 129.3, 129.2, 128.7 (2C), 124.4, 122.8 (2C), 121.6, 120.1, 114.0 (2C), 108.3, 107.3, 73.9, 55.2, 52.9, 26.2. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_3$ 349.1552; Found: 349.1558.



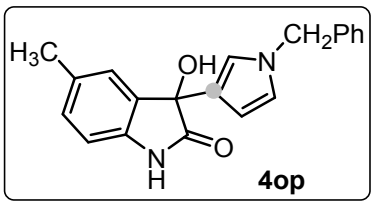
3-(1-ethyl-1*H*-pyrrol-3-yl)-3-hydroxy-1-methylindolin-2-one (4me). Purification with petroleum ether/EtOAc (4/1) as eluent; White solid (67 mg, 87% yield, mp = 123-126 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (ddd, *J* = 7.3, 1.3, 0.6 Hz, 1H), 7.32 (td, *J* = 7.8, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.83 (dt, *J* = 7.7, 0.8 Hz, 1H), 6.68 (t, *J* = 2.0 Hz, 1H), 6.60 (t, *J* = 2.5 Hz, 1H), 6.31 (dd, *J* = 2.8, 1.8 Hz, 1H), 3.83 (q, *J* = 7.3 Hz, 2H), 3.23 (s, 1H), 3.18 (s, 3H),

1.36 (t, *J* = 7.3 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 177.7, 143.2, 131.3, 129.3, 124.4, 122.9, 122.3, 120.8, 119.2, 108.3, 106.9, 74.0, 44.3, 26.3, 16.3. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}N_2O_2$ 257.1290; Found: 257.1287.



4ne

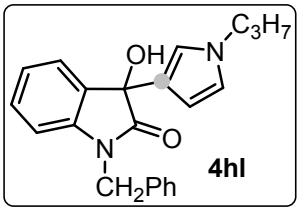
3-(1-(2-(1H-indol-3-yl)ethyl)-1*H*-pyrrol-3-yl)-3-hydroxy-1-methylindolin-2-one (4ne). Purification with petroleum ether/EtOAc (3/2) as eluent; White solid (78 mg, 70% yield, mp = 144-147°C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.3 Hz, 2H), 7.12 (td, *J* = 7.3, 2.9 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.74 (m, 1H), 6.59 (d, *J* = 2.2 Hz, 2H), 6.32 (t, *J* = 2.2 Hz, 1H), 4.06 (t, *J* = 7.0 Hz, 2H), 3.31 (s, 1H), 3.20 (s, 3H), 3.16 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.7, 143.1, 136.1, 131.4, 129.3, 127.1, 124.5, 122.9, 122.4, 122.3, 121.9, 121.5, 119.9, 119.3, 118.2, 112.0, 111.3, 108.4, 106.9, 74.1, 50.4, 27.6, 26.3. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_2$ 372.1712; Found: 372.1717.



4op

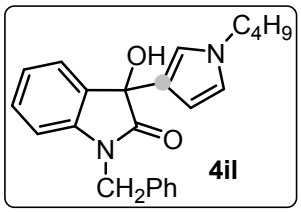
3-(1-benzyl-1H-pyrrol-3-yl)-3-hydroxy-5-methylindolin-2-one (4op) Purification with petroleum ether/EtOAc (3/2) as eluent; White solid (62 mg, 65% yield, mp = 197-200 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.02 (s, 1H), 7.32 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.22 – 7.16 (m, 2H), 7.11 (d, *J* = 1.8 Hz, 1H), 6.98 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.71 (t, *J* = 2.6 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 2.1 Hz, 1H), 6.02 (t, *J* = 2.3 Hz, 1H), 6.00 (s, 1H), 5.01 (s, 2H), 2.25 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6)** δ 179.8, 139.7, 139.6, 134.8, 131.1,

129.6, 129.4 (2C), 128.3 (3C), 126.1, 124.8, 121.9, 120.2, 110.0, 108.2, 74.6, 53.1, 21.6. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_2$ 319.1441; Found: 319.1447.



4hl

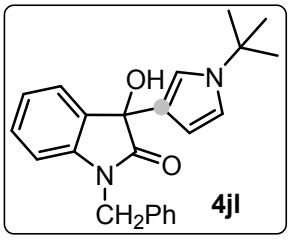
1-benzyl-3-hydroxy-3-(1-propyl-1*H*-pyrrol-3-yl)indolin-2-one (4hl). Purification with petroleum ether/EtOAc (7/3) as eluent; White solid (89 mg, 86% yield, mp = 231–235 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.42 (d, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 4.2 Hz, 4H), 7.25 (dt, *J* = 9.1, 4.5 Hz, 1H), 7.19 (td, *J* = 7.7, 1.1 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.68 (t, *J* = 2.4 Hz, 1H), 6.56 (t, *J* = 1.9 Hz, 1H), 6.31 (s, 1H), 6.11 – 6.06 (m, 1H), 4.87 (q, *J* = 15.8 Hz, 2H), 3.74 (t, *J* = 7.1 Hz, 2H), 1.63 (h, *J* = 7.3 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 177.8, 142.2, 136.9, 133.8, 129.0 (3C), 127.8, 127.6 (2C), 124.8, 123.5, 122.8, 121.3, 119.6, 109.4, 107.3, 74.0, 50.8, 42.9, 24.8, 11.5. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_2$ 347.1759; Found: 347.1767.



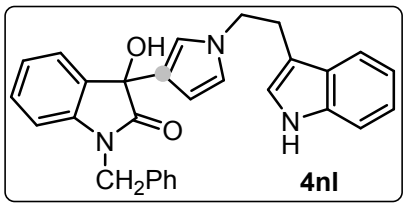
4il

1-benzyl-3-(1-butyl-1*H*-pyrrol-3-yl)-3-hydroxyindolin-2-one (4il). Purification with petroleum ether/EtOAc (4/1) as eluent; Pale yellow solid, 95 mg, 88% yield, mp = 242-246 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.46 – 7.41 (m, 1H), 7.31 (d, *J* = 4.4 Hz, 3H), 7.28 – 7.22 (m, 1H), 7.20 (td, *J* = 7.7, 1.2 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.68 (t, *J* = 2.5 Hz, 1H), 6.58 (t, *J* = 2.0 Hz, 1H), 6.32 (s, 1H), 6.10 (dd, *J* = 2.6, 1.8 Hz, 1H), 4.99 – 4.76 (m, 2H), 3.78 (t, *J* = 7.1 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.21 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 177.3, 141.7, 136.5, 133.3, 128.5 (3C), 127.3, 127.1 (2C), 124.3, 123.0, 122.3, 120.8, 119.1, 108.9, 106.9, 73.5, 48.4, 42.4, 33.1, 19.3, 13.5. **HRMS (ESI**) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2O_2$ 361.1916; Found: 361.1924.

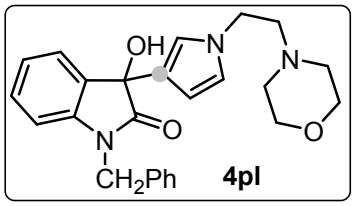


1-benzyl-3-(1-(*tert*-butyl)-1*H*-pyrrol-3-yl)-3-hydroxyindolin-2-one (4jl). Purification with petroleum ether/EtOAc (4/1) as eluent; White solid (98 mg, 91% yield, mp =174-176 °C). **^1H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.29 (q, *J* = 2.9 Hz, 5H), 7.21 (td, *J* = 7.7, 1.1 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 2.1 Hz, 1H), 6.83 (t, *J* = 2.7 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.39 – 6.34 (m, 1H), 5.01 (d, *J* = 15.8 Hz, 1H), 4.86 (d, *J* = 15.8 Hz, 1H), 3.26 (s, 1H), 1.51 (s, 9H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 177.8, 142.1, 135.6, 131.5, 129.1, 128.6 (2C), 127.4, 127.1 (2C), 124.5, 122.9, 122.0, 118.6, 116.7, 109.3, 106.4, 74.3, 55.0, 43.6, 30.6 (3C). **HRMS (ESI**) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2O_2$ 361.1916; Found: 361.1913.



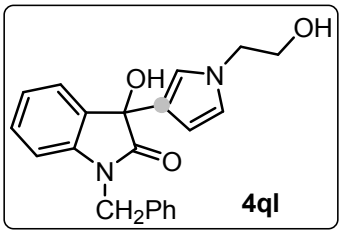
3-(1-(2-(1*H*-indol-3-yl) ethyl)-1*H*-pyrrol-3-yl)-1-benzyl-3-hydroxyindolin-2-one (4nl). Purification with petroleum ether/EtOAc (3/2) as eluent; White solid (98 mg, 73% yield, mp =173-176 °C). **^1H NMR (400 MHz, $CDCl_3$)** δ 8.11 (s, 1H), 7.52 – 7.45 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 5H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.10 (dt, *J* = 17.7, 7.5 Hz, 3H), 6.78 – 6.68 (m, 2H), 6.61 (d, *J* = 2.2 Hz, 1H), 6.33 (t, *J* = 2.2 Hz, 1H), 5.00 (d, *J* = 15.8 Hz, 1H), 4.84 (d, *J* =

15.8 Hz, 1H), 4.09 (t, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 3.03 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.8, 142.2, 136.1, 135.7, 131.5, 129.2, 128.8 (2C), 127.6, 127.1 (3C), 124.6, 123.1, 122.6, 122.4, 122.0, 121.6, 119.8, 119.4, 118.3, 112.1, 111.3, 109.4, 106.8, 74.2, 50.5, 43.8, 27.7. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{29}H_{26}N_3O_2$ 448.2025; Found: 448.2029.



4pl

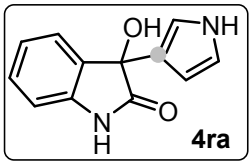
1-Benzyl-3-hydroxy-3-(1-(2-morpholinoethyl)-1*H*-pyrrol-3-yl) indolin-2-one (4pl). Purification with petroleum ether/EtOAc (4/1) as eluent; White solid (90 mg, 72% yield, mp =165-168 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.30 – 7.25 (m, 5H), 7.22 – 7.16 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.74 (t, *J* = 2.1 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.66 (t, *J* = 2.6 Hz, 1H), 6.32 (t, *J* = 2.3 Hz, 1H), 5.03 – 4.79 (m, 2H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.66 (t, *J* = 4.6 Hz, 4H), 2.68 (t, *J* = 6.9 Hz, 2H), 2.45 (t, *J* = 4.7 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.1, 142.2, 135.6, 131.3, 129.3 (2C), 128.7, 127.6, 127.1 (2C), 124.5, 123.0 (2C), 121.9, 119.9, 109.5, 107.1, 74.1, 66.7 (2C), 59.3, 53.7 (2C), 47.1, 43.8. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{28}N_3O_3$ 418.2130; Found: 418.2128.



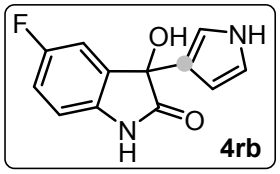
4ql

1-Benzyl-3-hydroxy-3-(1-(2-hydroxyethyl)-1*H*-pyrrol-3-yl) indolin-2-one (4ql). Purification with petroleum ether/EtOAc (3/2) as eluent; Light-yellow solid (85 mg, 81% yield, mp =167-170 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.31 – 7.22 (m, 5H), 7.18 (td,

J = 7.7, 1.3 Hz, 1H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 6.80 (t, *J* = 2.1 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.63 (t, *J* = 2.5 Hz, 1H), 6.27 (dd, *J* = 2.8, 1.8 Hz, 1H), 4.95 (d, *J* = 15.8 Hz, 1H), 4.80 (d, *J* = 15.8 Hz, 1H), 4.06 (s, 1H), 3.91 – 3.85 (m, 2H), 3.74 (t, *J* = 5.2 Hz, 2H), 2.85 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 178.1, 142.0, 135.5, 131.6, 129.2, 128.7 (2C), 127.6, 127.1 (2C), 124.6, 123.2, 123.0, 122.0, 120.0, 109.5, 107.2, 74.3, 62.4, 52.2, 43.7. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_3$ 349.1552; Found: 349.1546.

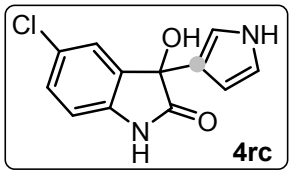


3-Hydroxy-3-(1*H*-pyrrol-3-yl) indolin-2-one (4ra). Purification with petroleum ether/EtOAc (1/1) as eluent; Brown solid (48 mg, 74% yield, mp =167-169 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.30 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.19 (td, *J* = 7.7, 1.3 Hz, 1H), 6.97 (td, *J* = 7.5, 1.1 Hz, 1H), 6.82 (dd, *J* = 7.7, 0.8 Hz, 1H), 6.64 (dd, *J* = 2.8, 2.0 Hz, 1H), 6.48 (t, *J* = 1.8 Hz, 1H), 6.04 (dd, *J* = 2.8, 1.6 Hz, 1H), 3.74 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 179.6, 141.3, 134.0, 129.2, 125.0, 123.3, 122.2, 118.2, 116.5, 110.0, 107.1. **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_{12}H_{10}N_2O_2Na$ 237.0640; Found: 237.0632.

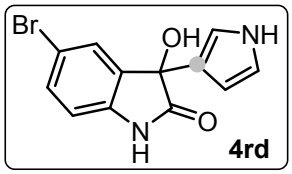


5-Fluoro-3-hydroxy-3-(1H-pyrrol-3-yl) indolin-2-one (4rb). Purification with petroleum ether/EtOAc (1/1) as eluent; Brown Solid (52 mg, 75% yield, mp =153-157 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.12 (dd, *J* = 8.2, 2.7 Hz, 1H), 7.02 (ddd, *J* = 9.5, 8.4, 2.7 Hz, 1H), 6.82 (dd, *J* = 8.5, 4.4 Hz, 1H), 6.65 (t, *J* = 2.3 Hz, 1H), 6.51 (t, *J* = 1.8 Hz, 1H), 6.06 (dd, *J* = 2.8, 1.7 Hz,

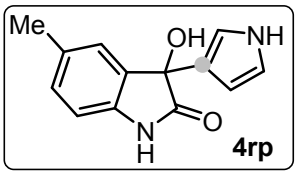
1H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6)** δ 179.4, 158.5 (d, *J* = 237.2 Hz), 137.5, 136.9 (d, *J* = 7.4 Hz), 122.8, 118.4, 116.5, 115.3 (d, *J* = 23.4 Hz), 112.5 (d, *J* = 24.3 Hz), 110.9 (d, *J* = 7.8 Hz), 107.0, 74.5. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{12}H_{10}FN_2O_2$ 233.0726; Found: 233.0723.



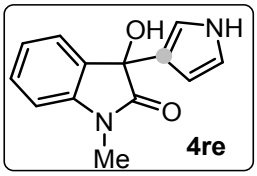
5-Chloro-3-hydroxy-3-(1*H*-pyrrol-3-yl) indolin-2-one (4rc). Purification with petroleum ether/EtOAc (1/1) as eluent; Brown Solid (54 mg, 73% yield, mp = 140-142^{o}C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.40 (d, *J* = 1.9 Hz, 1H), 7.37 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.53 (s, 1H), 6.07 – 6.00 (m, 1H), 3.16 (s, 1H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6)** δ 179.1, 140.3, 136.3, 128.9, 126.1, 124.9, 122.8, 118.5, 116.5, 111.6, 106.9, 74.3. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{12}H_{10}ClN_2O_2$ 249.0431; Found: 249.0437.



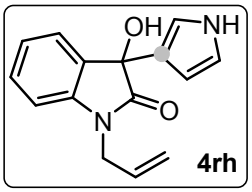
5-Bromo-3-hydroxy-3-(1*H*-pyrrol-3-yl)indolin-2-one (4rd). Purification with petroleum ether/EtOAc (1/1) as eluent; Reddish solid (61 mg, 71% yield, mp = 156-158 ^{o}C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.40 (d, *J* = 1.9 Hz, 1H), 7.37 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.68 – 6.65 (m, 1H), 6.53 (s, 1H), 6.04 (dd, *J* = 2.5, 1.5 Hz, 1H), 3.16 (s, 1H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6)** δ 179.00, 140.8, 136.7, 131.8, 127.6, 122.8, 118.5, 116.5, 113.8, 112.2, 106.9, 74.3. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{12}H_{10}BrN_2O_2$ 292.9925; Found: 292.9929.



3-Hydroxy-5-methyl-3-(1*H*-pyrrol-3-yl)indolin-2-one (4rp). Purification with petroleum ether/EtOAc (3/2) as eluent; White solid (48 mg, 70% yield, mp = 161-164 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.11 (s, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.65 – 6.62 (m, 1H), 6.50 (t, *J* = 1.7 Hz, 1H), 6.04 (dd, *J* = 2.7, 1.6 Hz, 1H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 179.5, 138.9, 134.2, 131.0, 129.3, 125.6, 123.5, 118.1, 116.4, 109.7, 107.1, 74.3, 21.1. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{13}H_{13}N_2O_2$ 229.0977; Found: 229.0983.

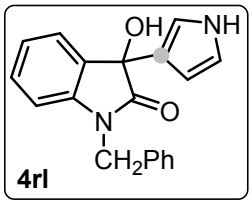


3-hydroxy-1-methyl-3-(1*H*-pyrrol-3-yl)indolin-2-one (4ee). Purification with petroleum ether/EtOAc (3/2) as eluent; White solid (48 mg, 72% yield, mp = 181-184 °C). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.66 (s, 1H), 7.39 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.31 (td, *J* = 7.7, 1.3 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.66 (q, *J* = 2.4 Hz, 1H), 6.50 (q, *J* = 2.1 Hz, 1H), 6.12 (s, 1H), 6.10 (dt, *J* = 4.1, 2.0 Hz, 1H), 3.10 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 177.2, 142.8, 133.2, 128.6, 124.1, 122.9, 122.1, 117.8, 116.3, 108.2, 106.8, 73.4, 25.8. **HRMS (ESI)** *m*/*z*: $[M + Na]^+$ Calcd for $C_{13}H_{13}N_2O_2$ 251.0791; Found: 251.0782.



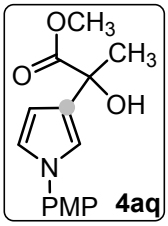
1-Allyl-3-hydroxy-3-(1*H*-pyrrol-3-yl) indolin-2-one (4rh). Purification with petroleum ether/EtOAc (3/2) as eluent; White solid (56 mg, 73% yield, mp = 170-174 °C). **^{1}H NMR (400**

MHz, DMSO-d_6) δ 10.68 (s, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.67 (p, *J* = 2.4 Hz, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 6.09 (t, *J* = 2.3 Hz, 1H), 5.89 – 5.78 (m, 1H), 5.19 – 5.08 (m, 2H), 4.38 – 4.18 (m, 2H). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)** δ 177.5, 142.3, 133.8, 132.5, 129.0, 124.7, 123.6, 122.6, 118.4, 117.0, 116.6, 109.3, 107.1, 74.0, 41.7. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{14}N_5O_2$ 255.1133; Found: 255.1129.



4rl

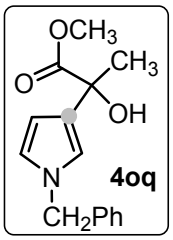
1-Benzyl-3-hydroxy-3-(1*H*-pyrrol-3-yl) indolin-2-one (4rl). Purification with petroleum ether/EtOAc (3/2) as eluent; Purple solid (65 mg, 71% yield, mp = 169-171 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.60 – 4.75 (m, 1H), 4.83 (dt, *J* = 16.2, 5.1 Hz, 1H), 6.22 (dd, *J* = 6.6, 3.4 Hz, 1H), 6.50 – 6.69 (m, 3H), 6.94 (td, *J* = 7.5, 2.8 Hz, 1H), 7.06 (td, *J* = 7.7, 2.6 Hz, 1H), 7.11 – 7.24 (m, 5H), 7.40 (dt, *J* = 9.9, 4.9 Hz, 1H), 9.50 (s, 1H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.8, 141.7, 135.4, 128.5, 128.3 (2C), 127.1, 126.7 (2C), 124.3, 122.5, 118.3, 118.1, 116.6, 116.4, 108.8, 106.4, 73.8, 43.2. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O_2$ 305.1290; Found: 305.1296.



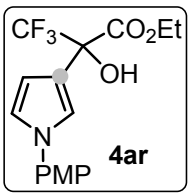
4aq

Methyl 2-hydroxy-2-(1-(4-methoxyphenyl)-1H-pyrrol-3-yl)propanoate (4aq). Purification with petroleum ether/EtOAc (9/1) as eluent; Reddish oil (52 mg, 62% yield). **^{1}H NMR (400 MHz,**

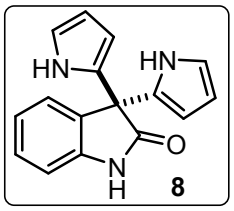
$CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 2H), 7.02 (dd, *J* = 2.3, 1.8 Hz, 1H), 6.95 – 6.90 (m, 3H), 6.31 (dd, *J* = 2.9, 1.8 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.77 (s, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 176.6, 157.8, 134.2, 128.6, 122.1 (2C), 120.0, 116.8, 114.6 (2C), 107.9, 72.8, 55.5, 53.0, 26.7. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{18}NO_4$ 276.1230; Found: 276.1236.



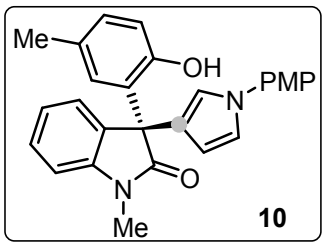
Methyl 2-(1-benzyl-1H-pyrrol-3-yl)-2-hydroxypropanoate (4oq). Purification with petroleum ether/EtOAc (9/1) as eluent; Brown oil (53 mg, 68% yield). **^1H NMR (400 MHz, $CDCl_3$)** δ 7.37–7.26 (m, 3H), 7.17–7.11 (m, 2H), 6.74 (t, *J* = 2.1 Hz, 1H), 6.61 (t, *J* = 2.6 Hz, 1H), 6.21 (dd, *J* = 2.8, 1.8 Hz, 1H), 5.00 (s, 2H), 3.77 (s, 3H), 3.64 (s, 1H), 1.76 (s, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 179.5, 137.5, 128.5 (2C), 127.6, 127.2, 127.0 (2C), 121.2, 118.1, 106.4, 72.7, 53.3, 52.7, 26.5. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{18}NO_3$ 260.1281; Found: 260.1276.



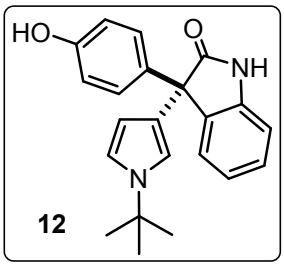
Ethyl 3,3,3-trifluoro-2-hydroxy-2-(1-(4-methoxyphenyl)-1H-pyrrol-3-yl)propanoate (4ar). Purification with petroleum ether/EtOAc (9/1) as eluent; Slight yellow oil (74 mg, 72% yield). **^1H NMR (400 MHz, $CDCl_3$)** δ 7.31 (d, *J* = 8.9 Hz, 2H), 7.23 (t, *J* = 2.1 Hz, 1H), 6.99 – 6.94 (m, 3H), 6.51 (ddt, *J* = 2.6, 1.7, 0.9 Hz, 1H), 4.50 – 4.37 (m, 2H), 4.34 – 4.21 (m, 1H), 3.85 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 169.4, 158.0, 133.9, 123.1 (q, *J* = 285.4 Hz), 122.3 (2C), 120.2, 119.3, 118.1, 114.7 (2C), 109.1, 75.8 (q, *J* = 31.5 Hz), 64.0, 55.5, 13.9. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{17}F_3NO_4$ 344.1104; Found: 260.1094.



3,3-di(1*H*-pyrrol-2-yl)indolin-2-one (8). Purification with petroleum ether/EtOAc (3/1) as eluent; White solid (41 mg, 52% yield, mp =126-129 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.74 (s, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.68 (m, 2H), 6.11 (q, *J* = 3.0 Hz, 2H), 5.98 (d, *J* = 3.3 Hz, 2H), 3.25 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 176.2, 142.9, 131.0, 128.8, 128.7, 125.2, 123.2, 118.4 (2C), 108.8, 108.4 (2C), 106.9 (2C), 52.1, 26.6. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{14}N_3O$ 264.1137; Found 264.1145.

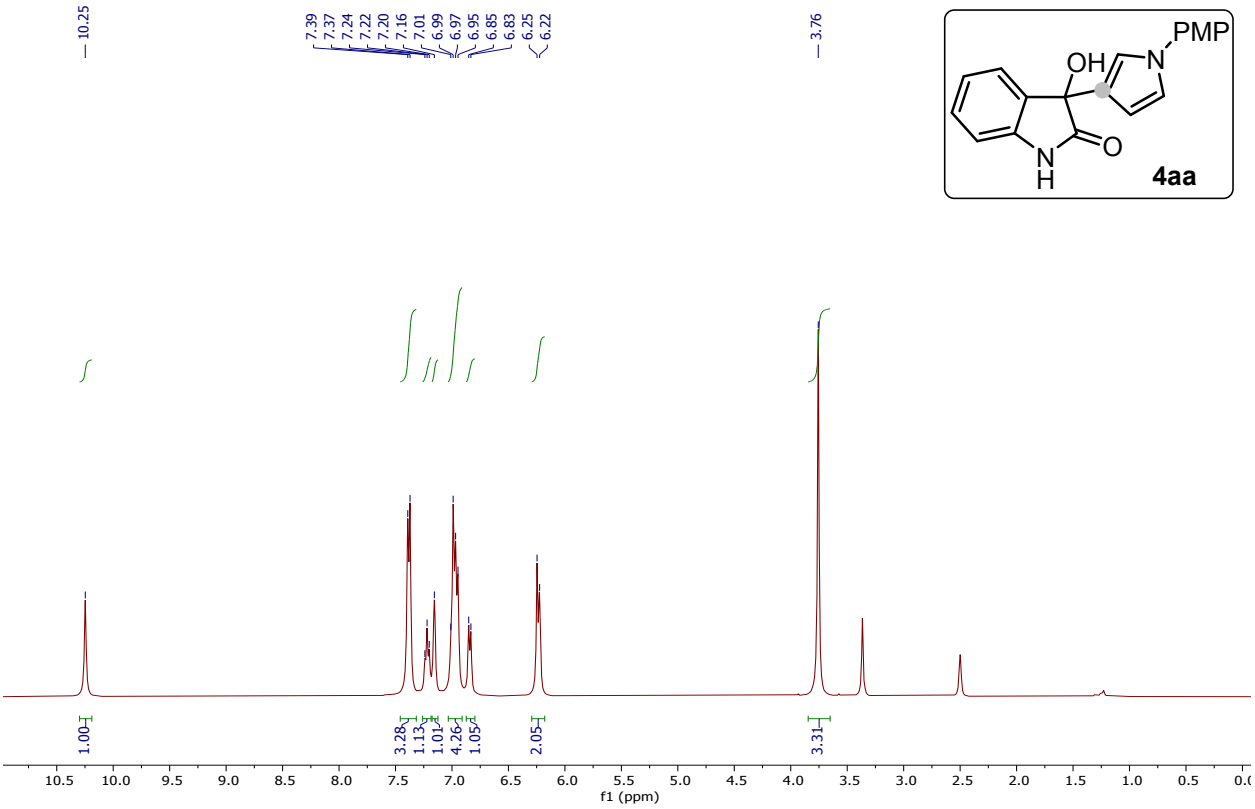


3-(2-hydroxy-5-methylphenyl)-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)-1-methylindolin-2-one (10). Purification with petroleum ether/EtOAc (4/1) as eluent; White solid (108 mg, 85% yield, mp = 208–211 °C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.34 (q, *J* = 5.8, 3.6 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 2H), 7.12 (dt, *J* = 14.2, 7.0 Hz, 3H), 6.97 – 6.94 (m, 1H), 6.94 – 6.91 (m, 1H), 6.87 (dd, *J* = 13.9, 8.4 Hz, 3H), 6.52 – 6.46 (m, 1H), 3.80 (s, 3H), 3.20 (s, 3H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 177.6, 157.8, 143.1, 140.1, 133.9, 132.0, 131.0, 129.7, 129.5, 128.4, 127.6, 124.5, 124.3, 123.1, 122.2 (3C), 120.7, 118.7, 114.5 (2C), 108.6, 108.5, 74.0, 55.5, 26.3, 21.1. **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{27}H_{25}N_2O_3$ 425.1865; Found 425.1871.

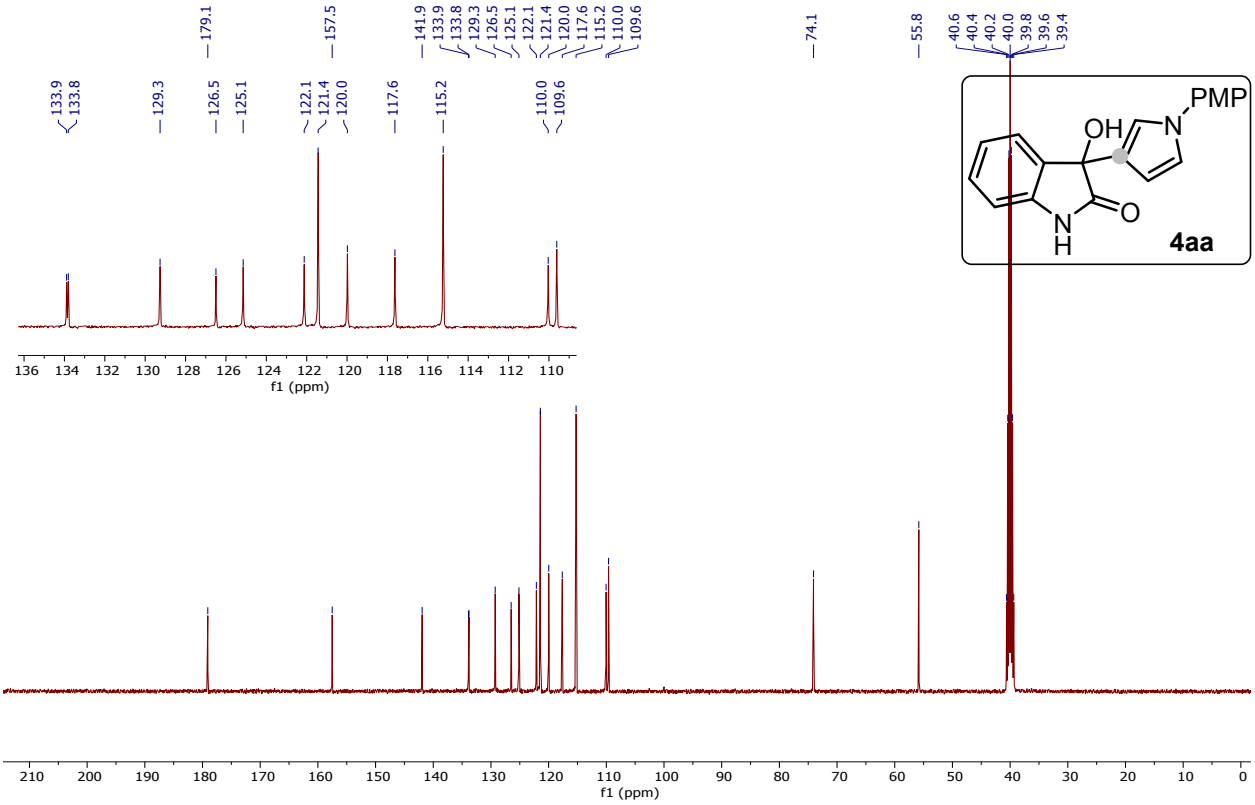


3-(1-(*tert*-butyl)-1H-pyrrol-3-yl)-3-(4-hydroxyphenyl)indolin-2-one (12). Purification with petroleum ether/EtOAc (3/2) as eluent; White sloid (236 mg, 92% yield, mp = 203–206 ^{o}C). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (s, 1H), 7.25 (s, 1H), 7.20 (td, *J* = 7.7, 1.3 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.04 (td, *J* = 7.6, 1.1 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.74 (m, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.12 (dd, *J* = 2.9, 1.9 Hz, 1H), 5.04 (s, 1H), 1.48 (s, 9H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, few drops of DMSO-d_6 was added)** δ 180.1, 155.5, 135.4, 133.0, 128.4 (2C), 127.0, 124.9, 121.8, 121.5, 117.3, 116.5, 114.7, 114.6 (2C), 109.4, 107.2, 56.5, 54.2, 30.3 (3C). **HRMS (ESI)** *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_2$ 347.1754; Found 347.1745.

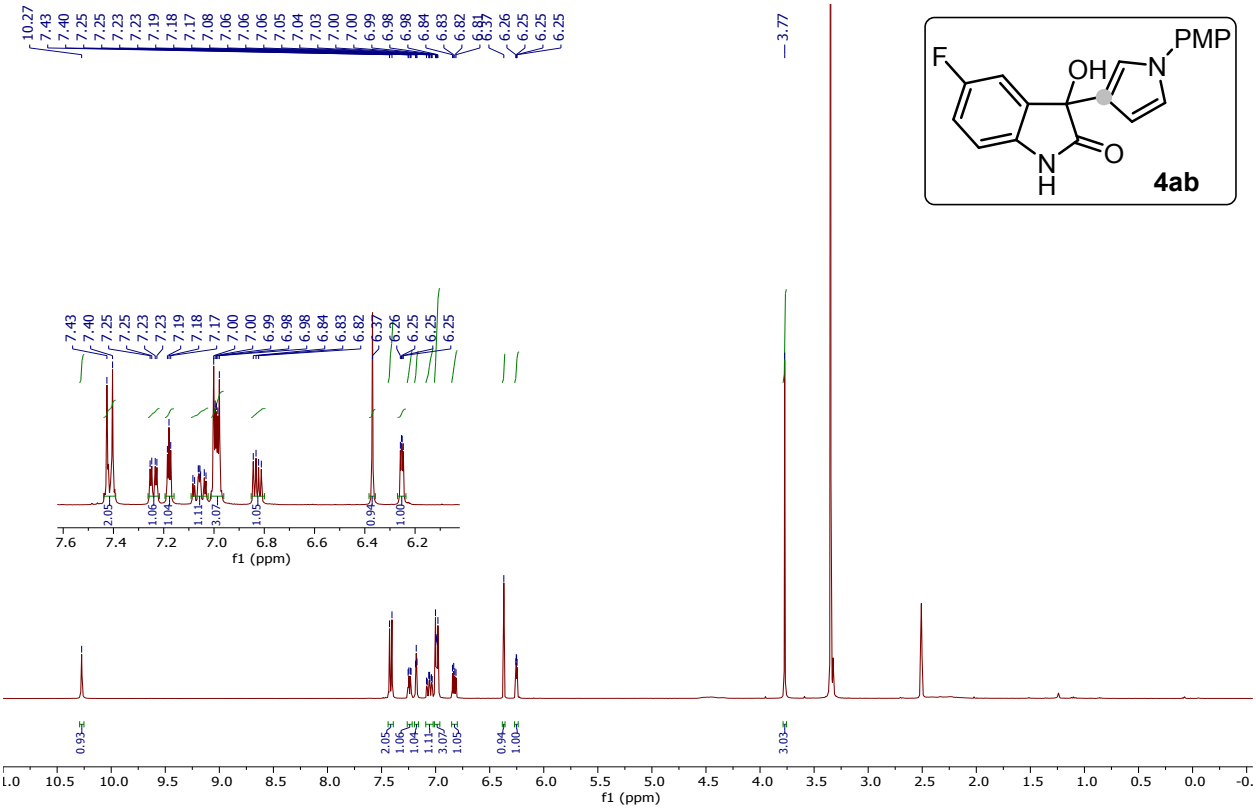
^{1}H NMR (400 MHz, DMSO-d_6)



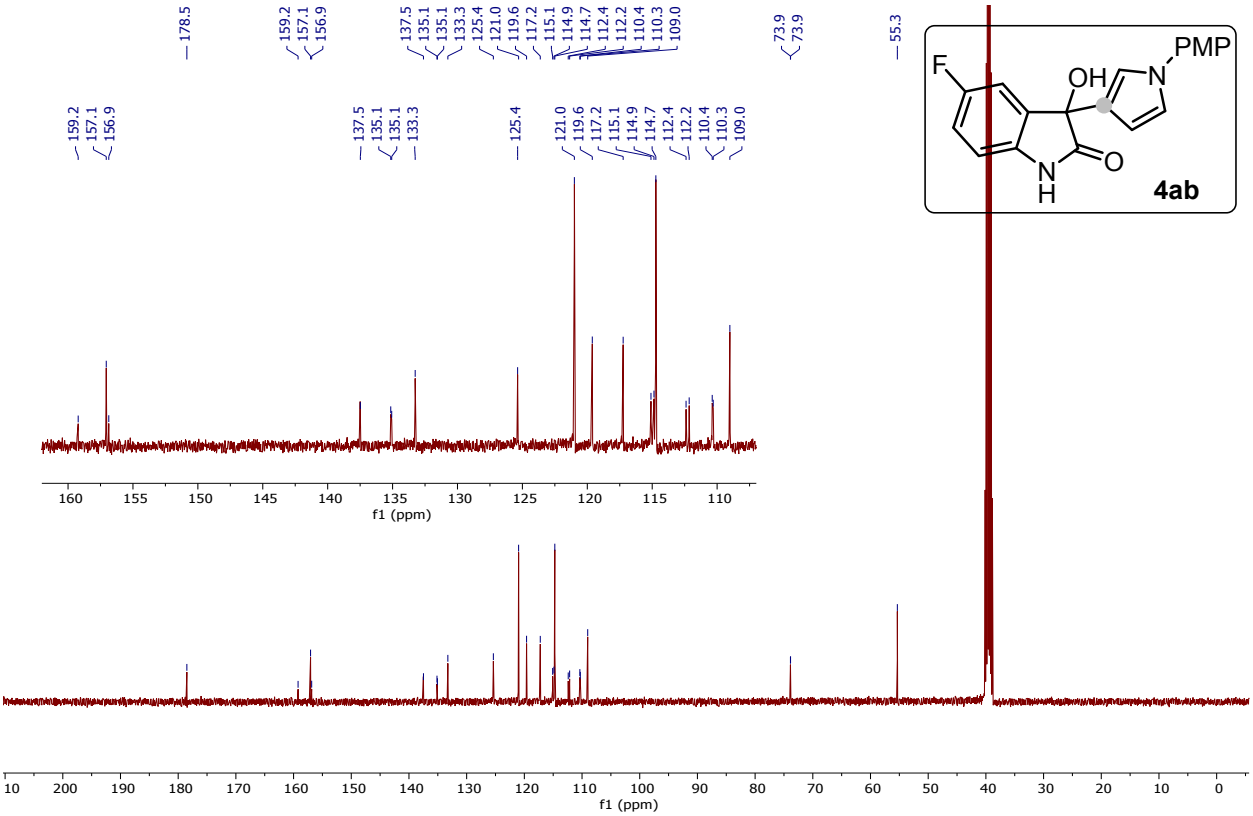
^{13}C NMR (101 MHz, DMSO-d_6)



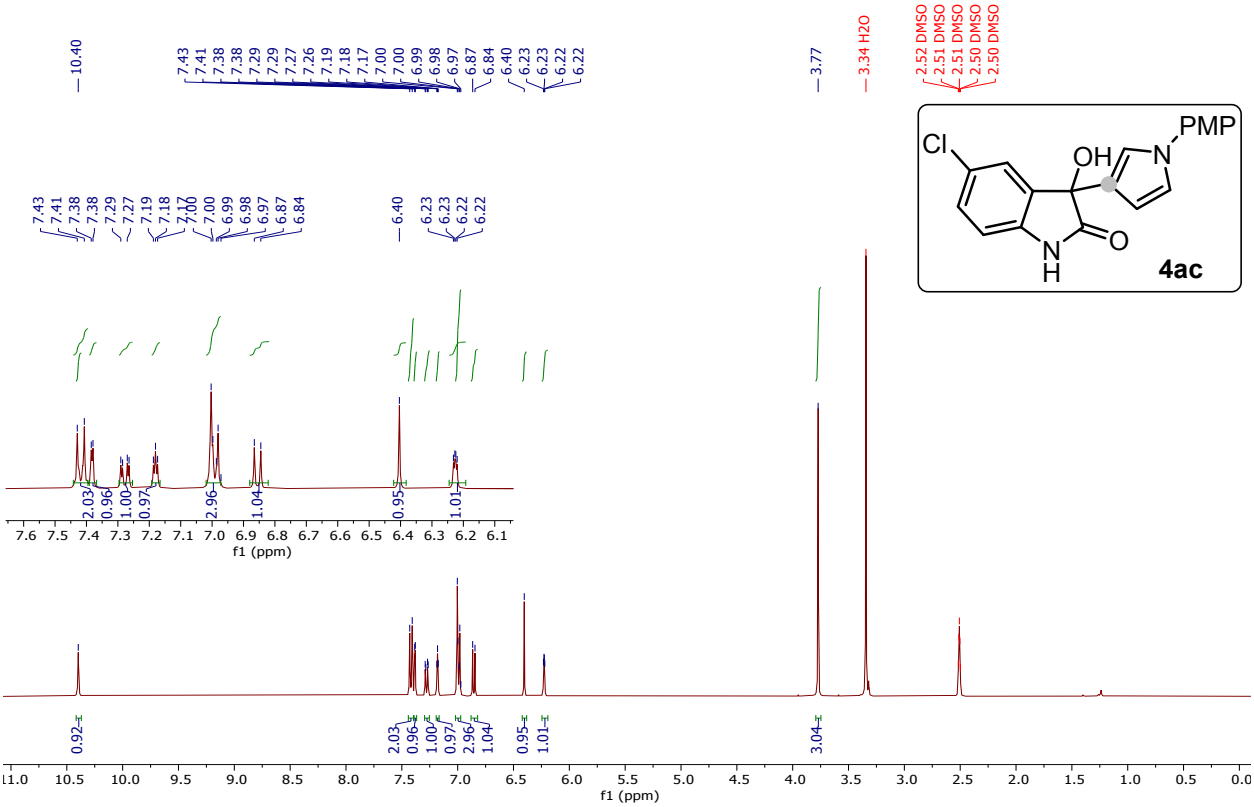
^{1}H NMR (400 MHz, DMSO-d_6)



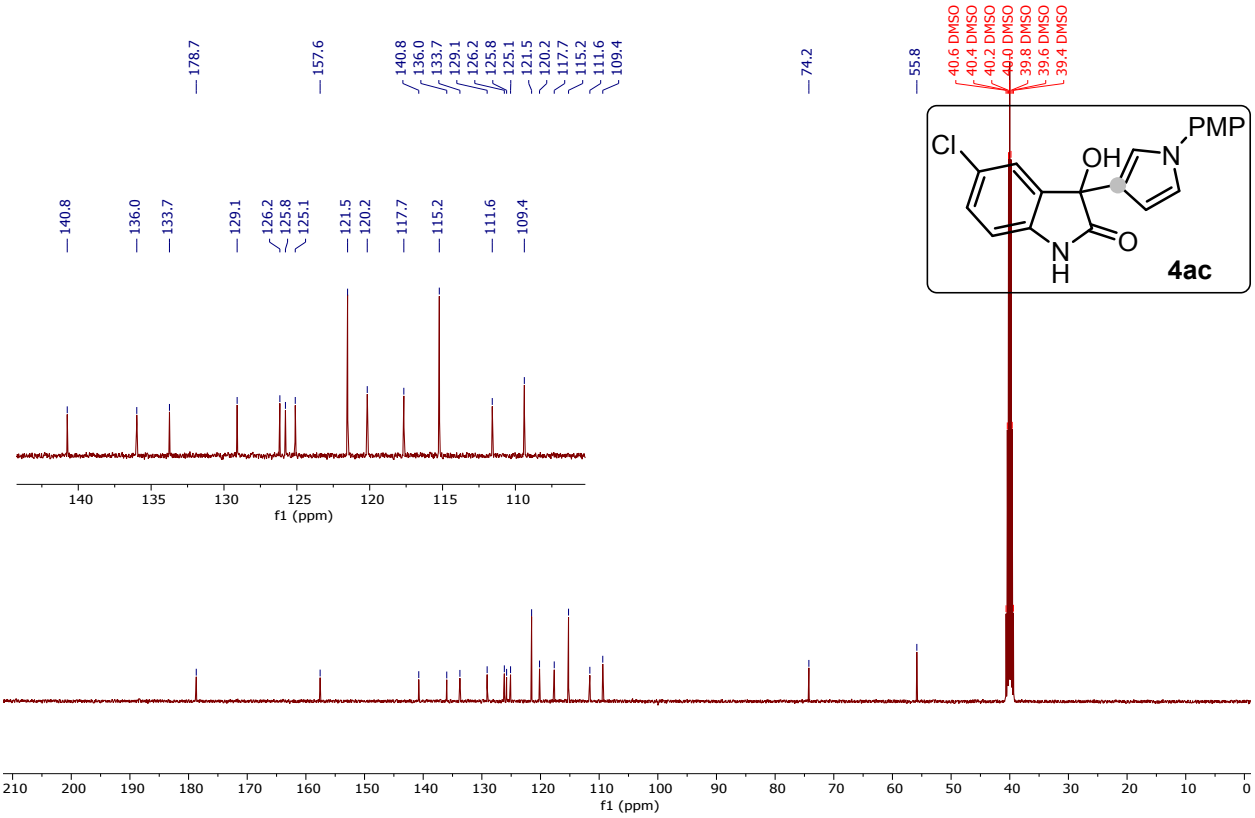
^{13}C NMR (101 MHz, DMSO-d_6)



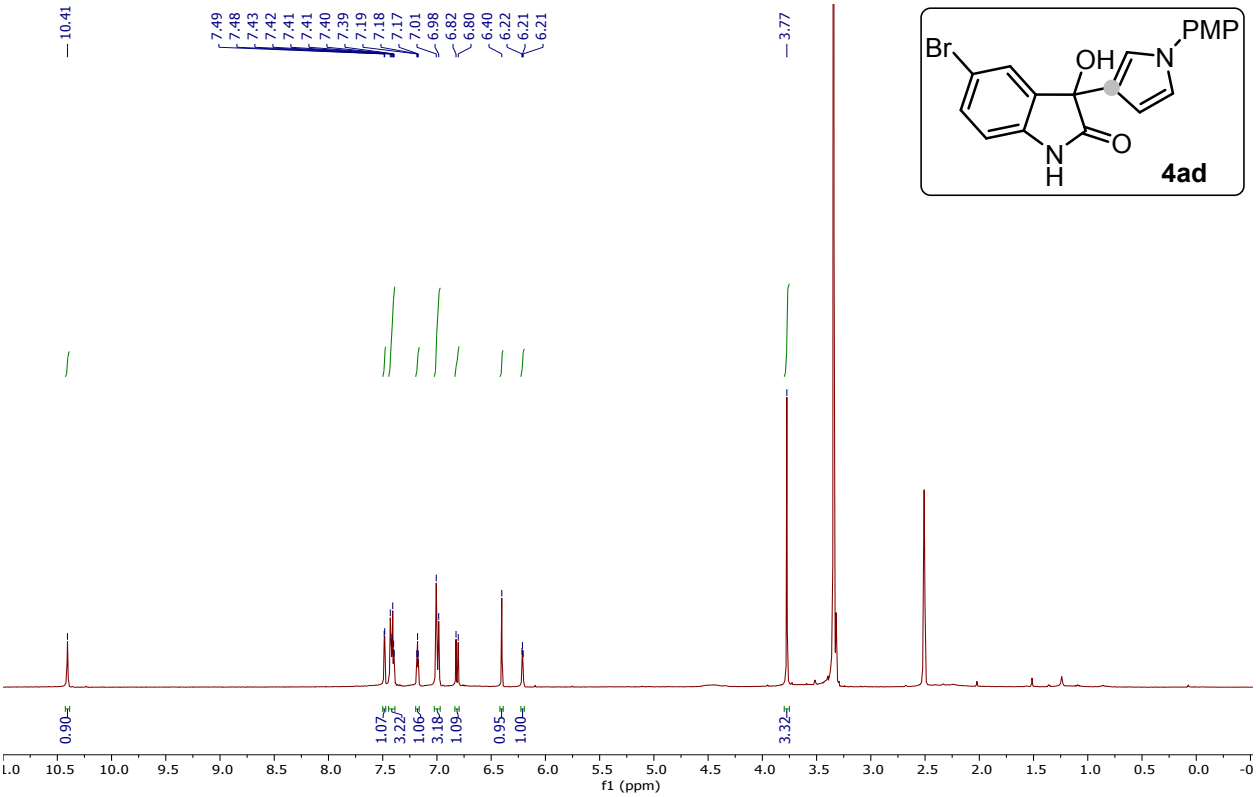
^{1}H NMR (400 MHz, DMSO-d_6)



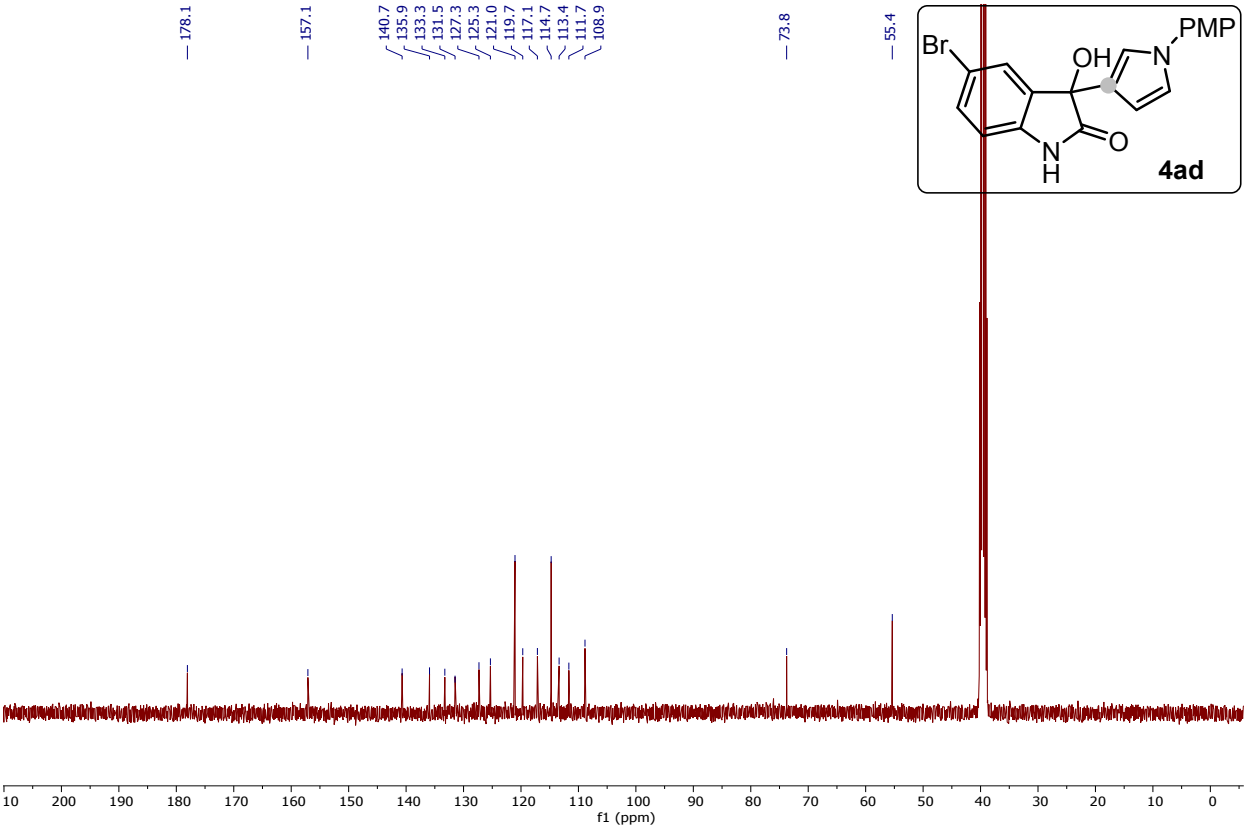
^{13}C NMR (101 MHz, DMSO-d_6)



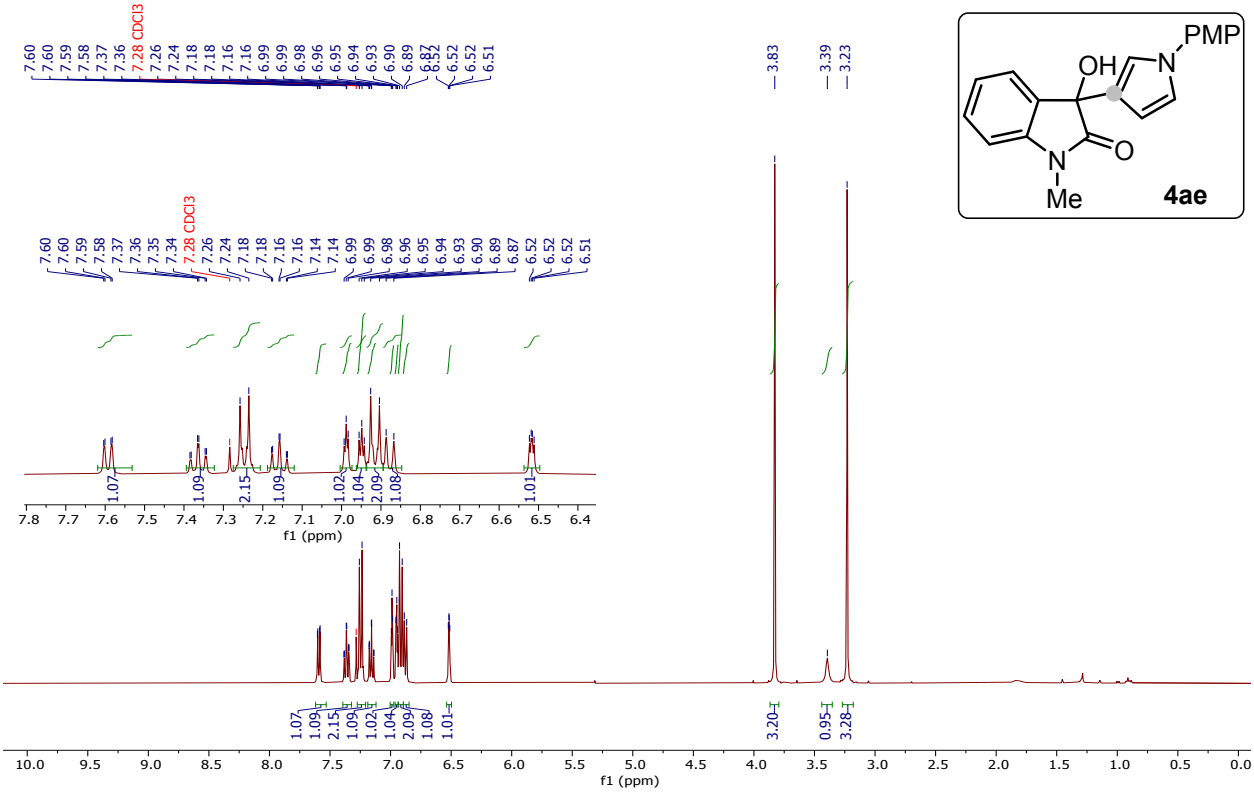
^{1}H NMR (400 MHz, DMSO-d_6)



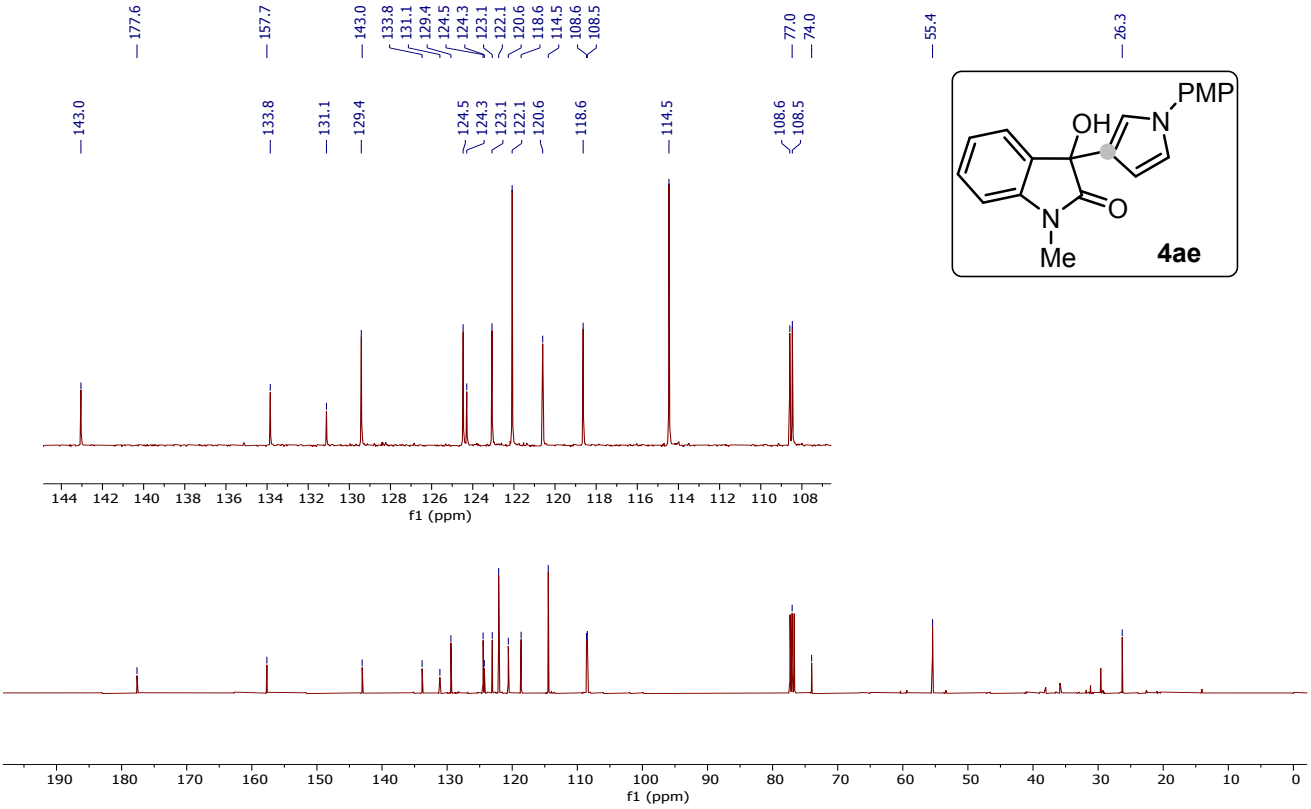
^{13}C NMR (101 MHz, DMSO-d_6)



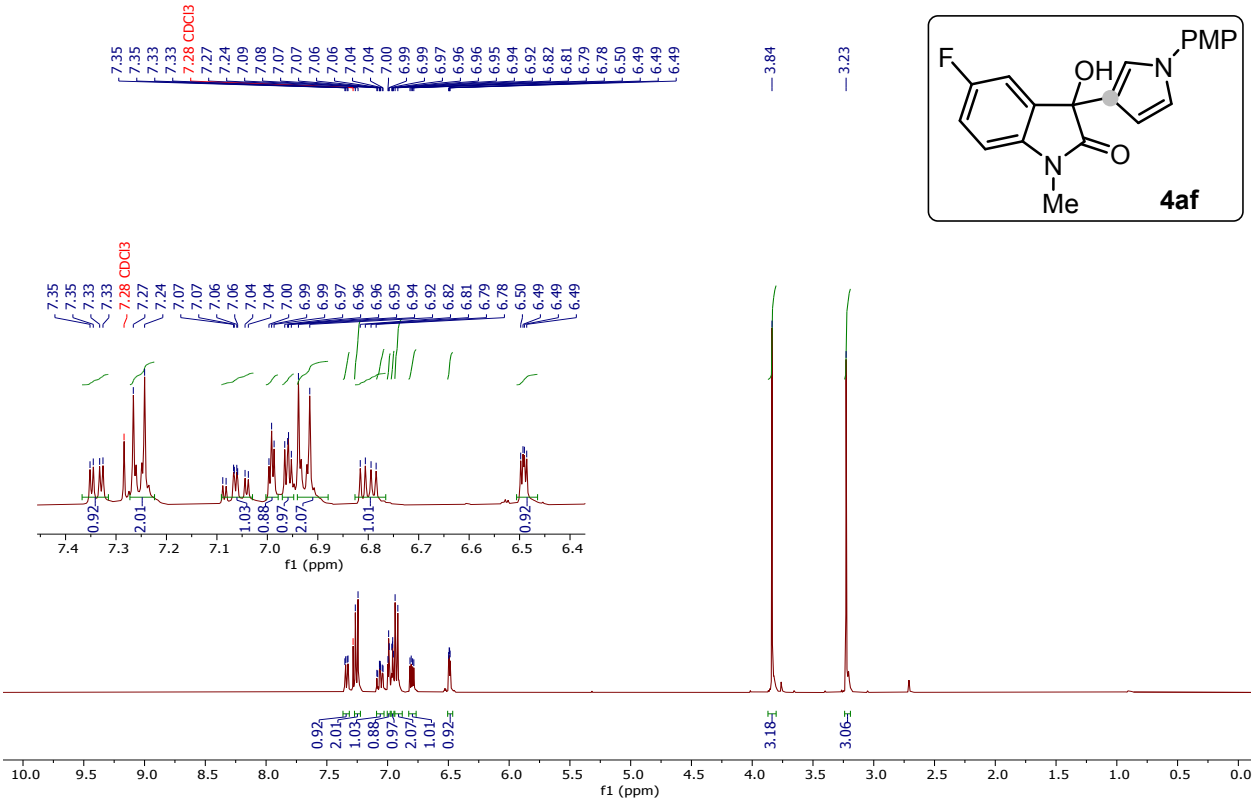
^{1}H NMR (400 MHz, $CDCl_3$)



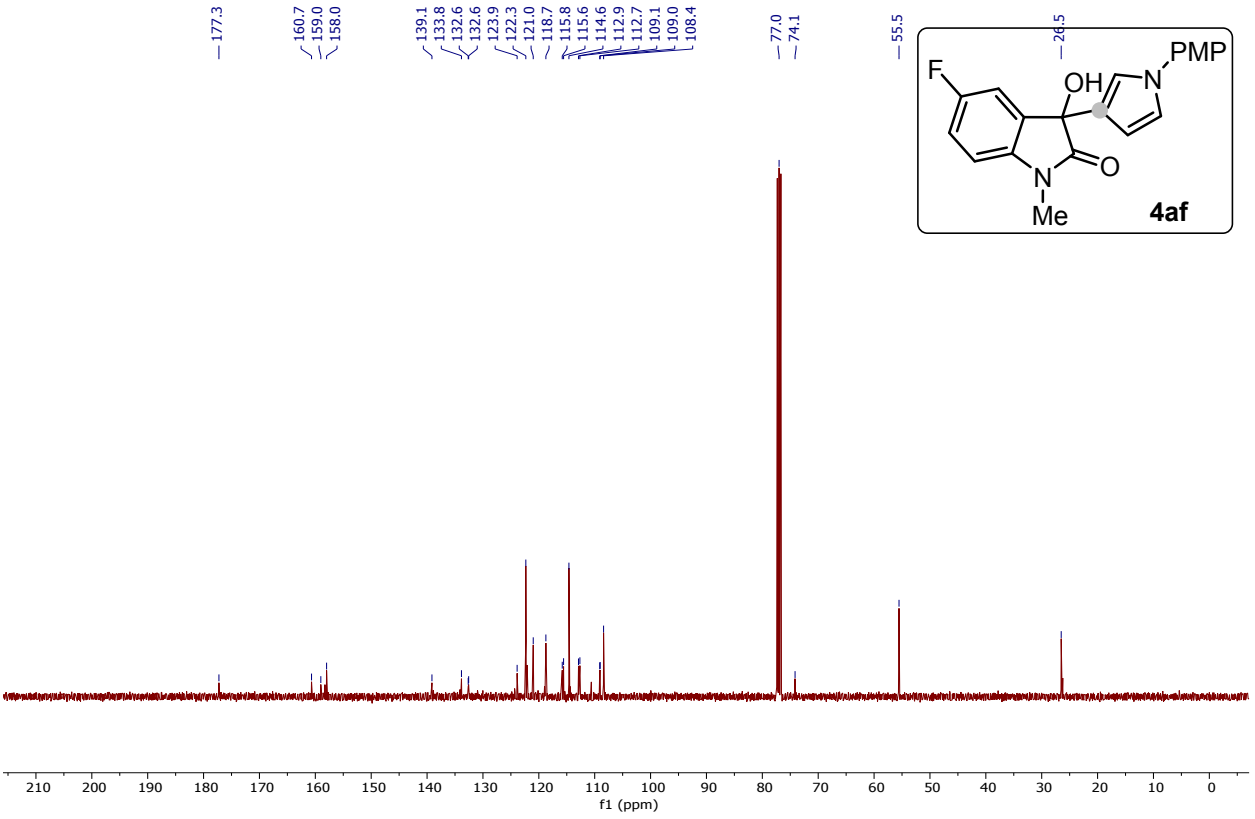
^{13}C NMR (101 MHz, $CDCl_3$)



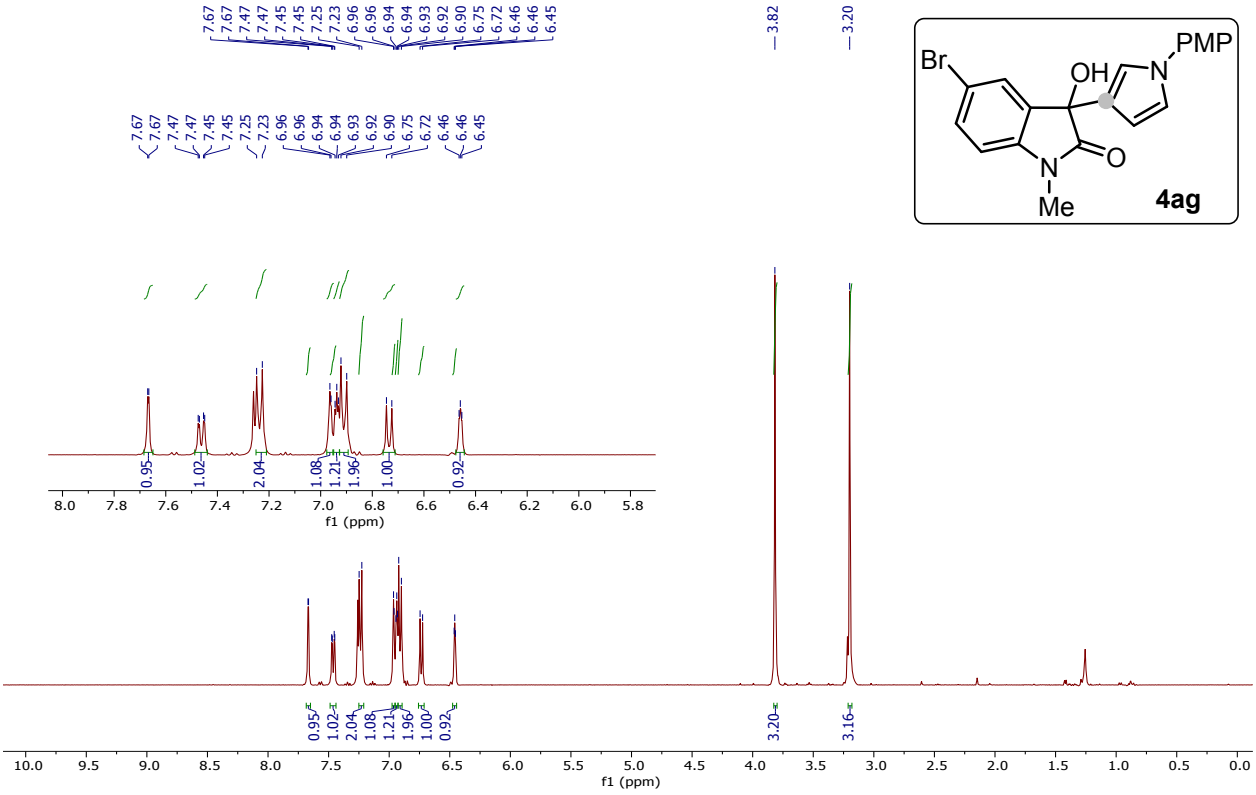
^{1}H NMR (400 MHz, $CDCl_3$)



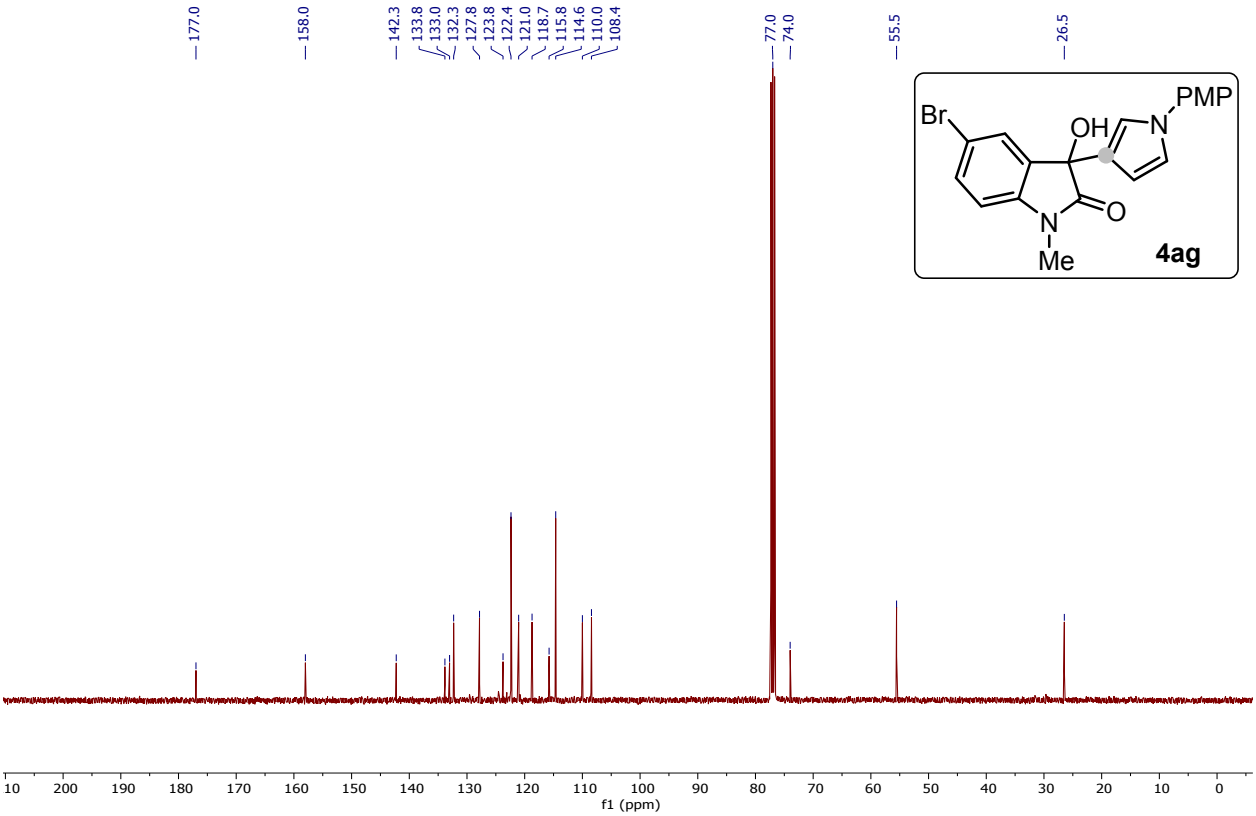
^{13}C NMR (101 MHz, $CDCl_3$)



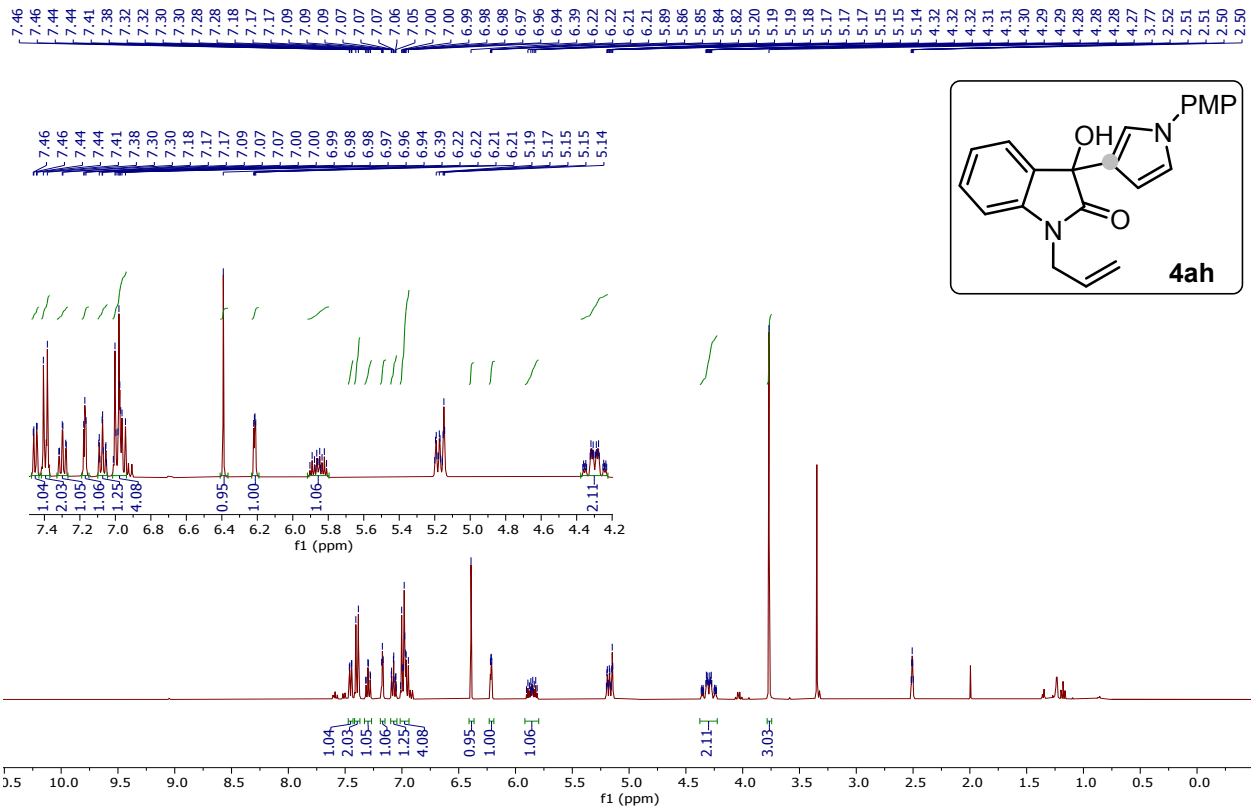
^{1}H NMR (400 MHz, $CDCl_3$)



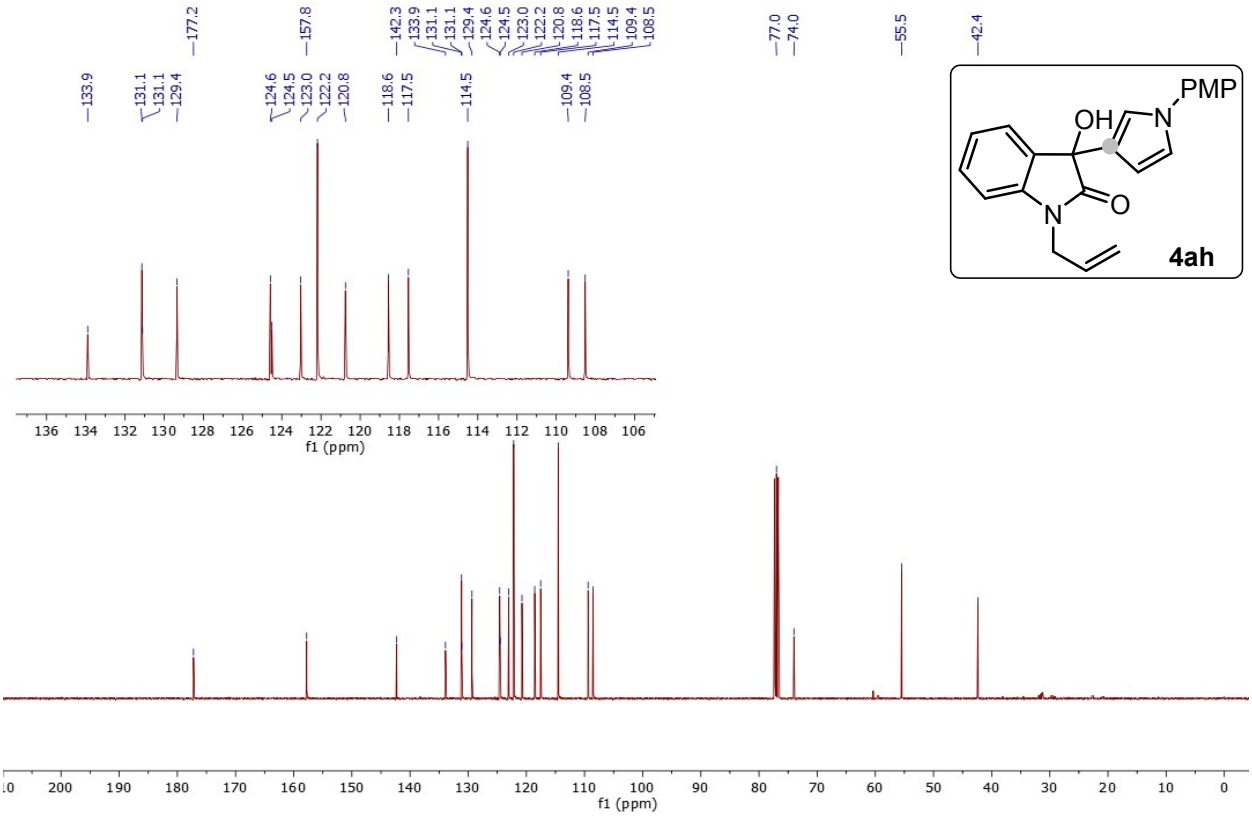
^{13}C NMR (101 MHz, $CDCl_3$)



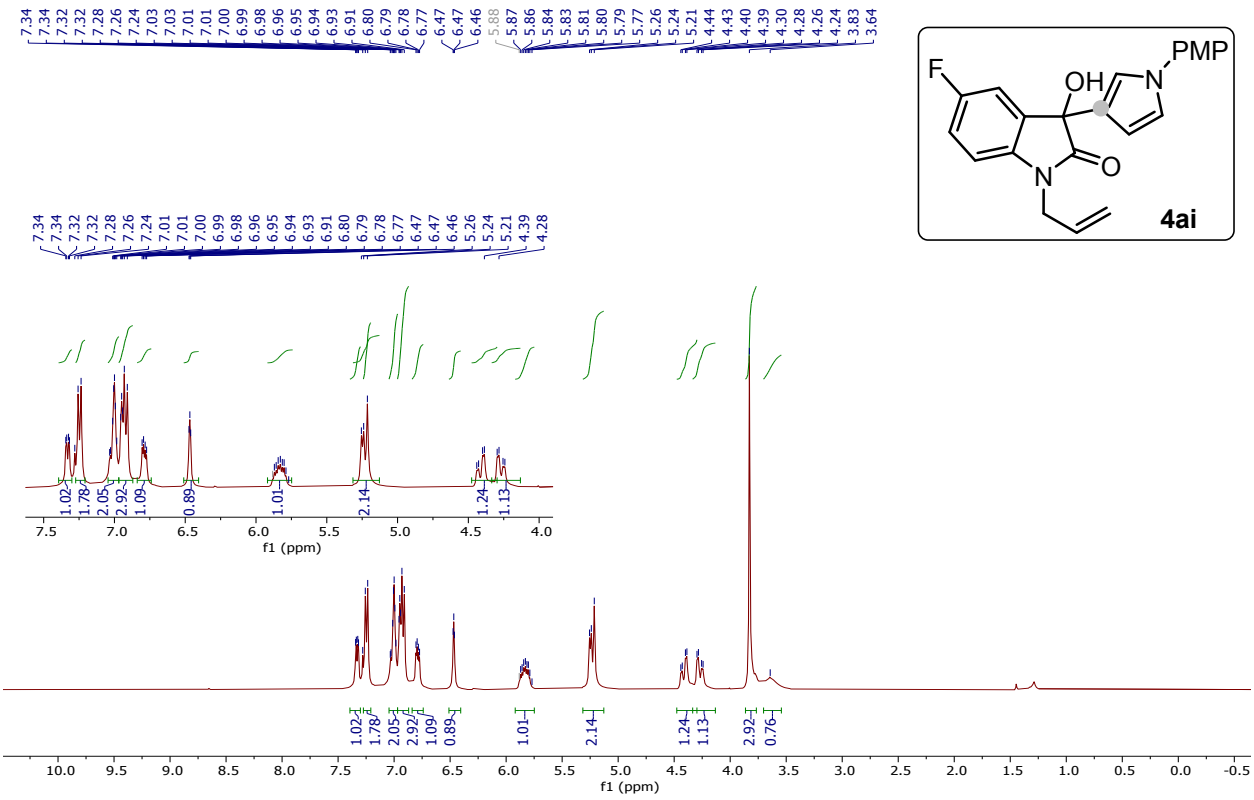
^{1}H NMR (400 MHz, DMSO-d_6)



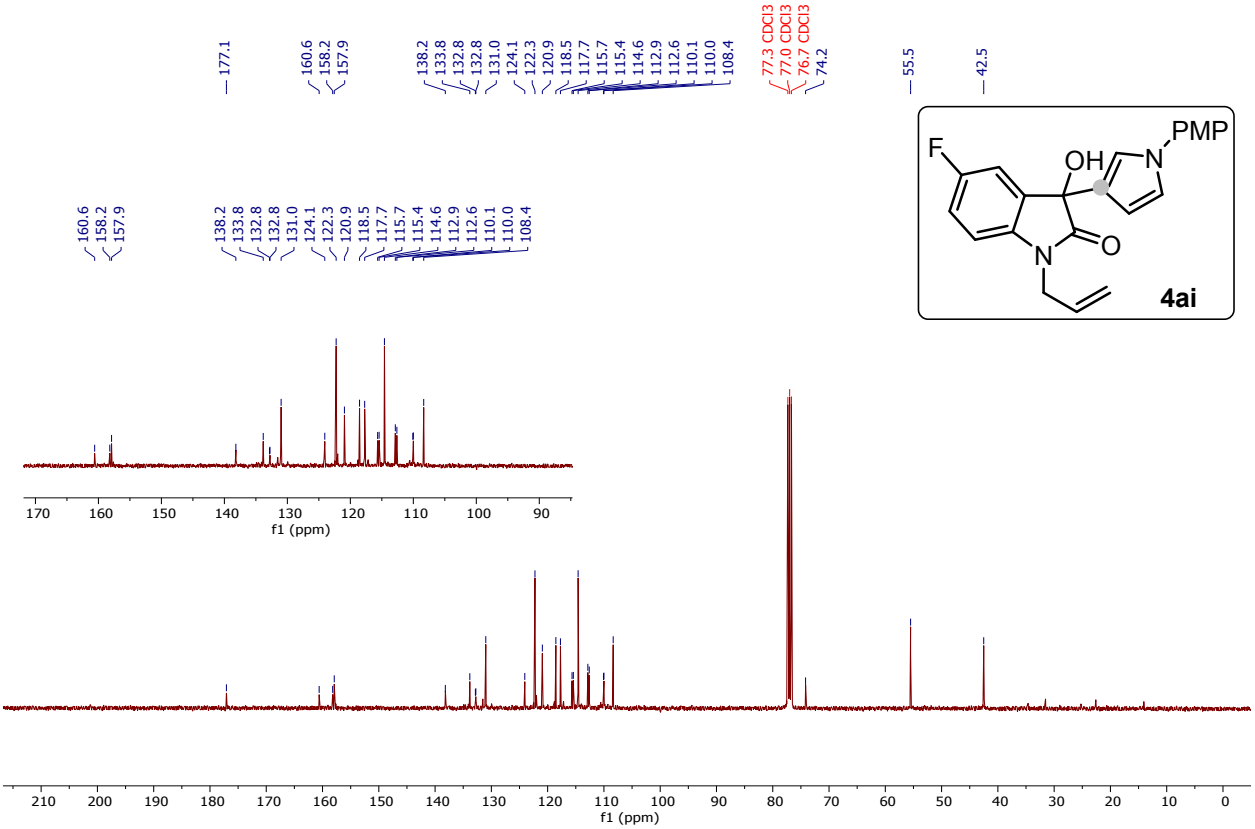
^{13}C NMR (101 MHz, $CDCl_3$)



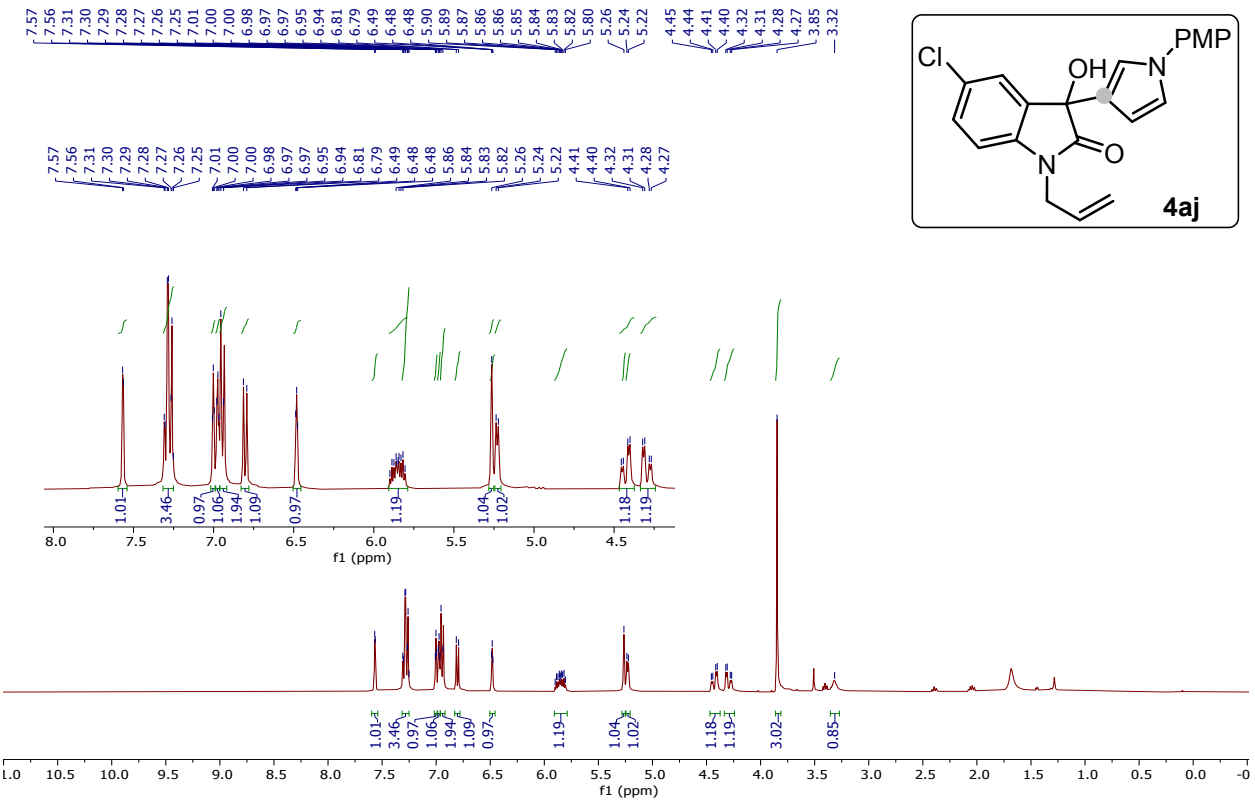
^{1}H NMR (400 MHz, $CDCl_3$)

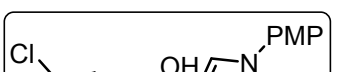


^{13}C NMR (101 MHz, $CDCl_3$)

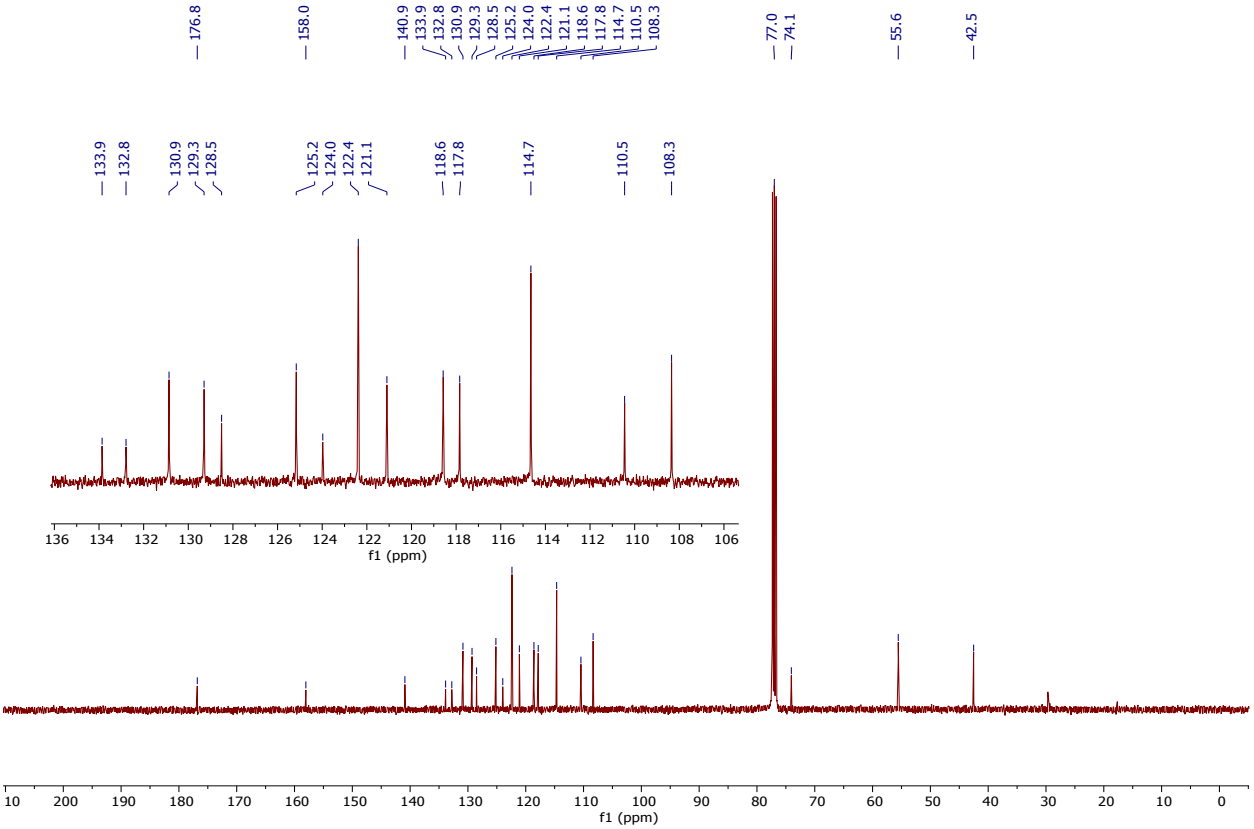


^{1}H NMR (400 MHz, $CDCl_3$)

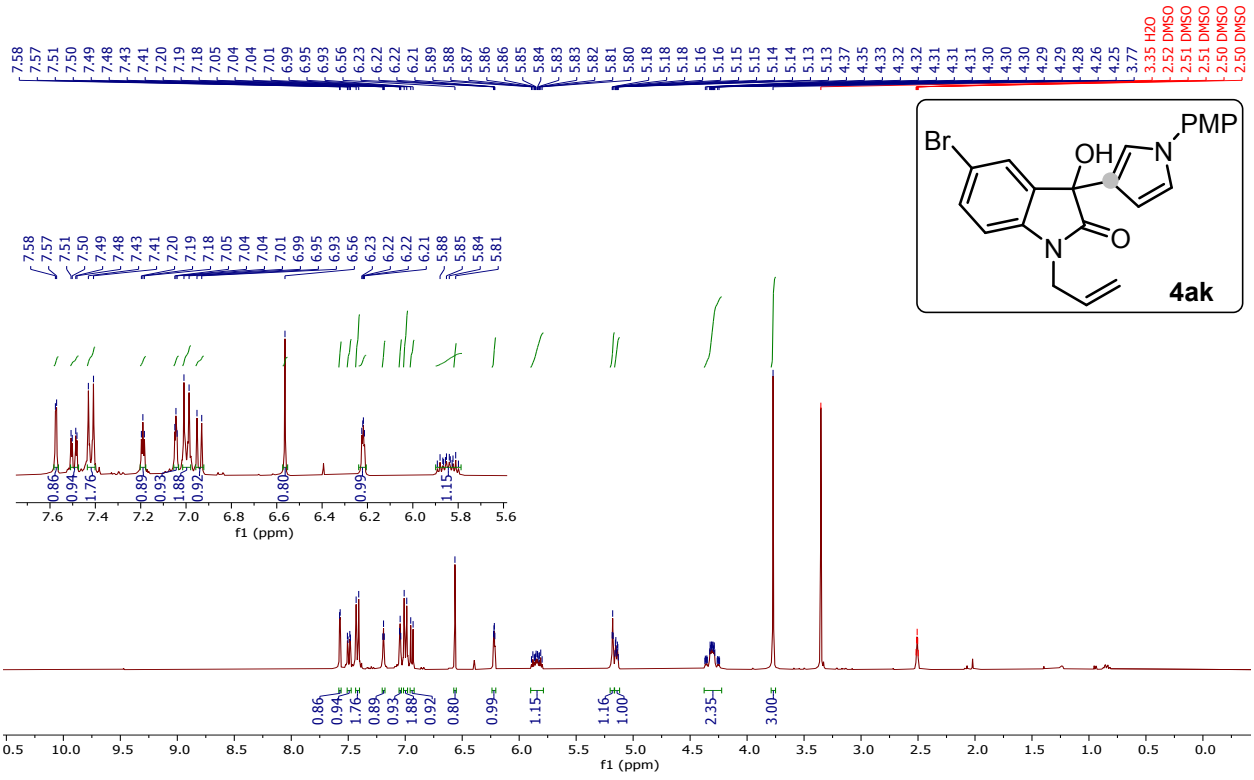




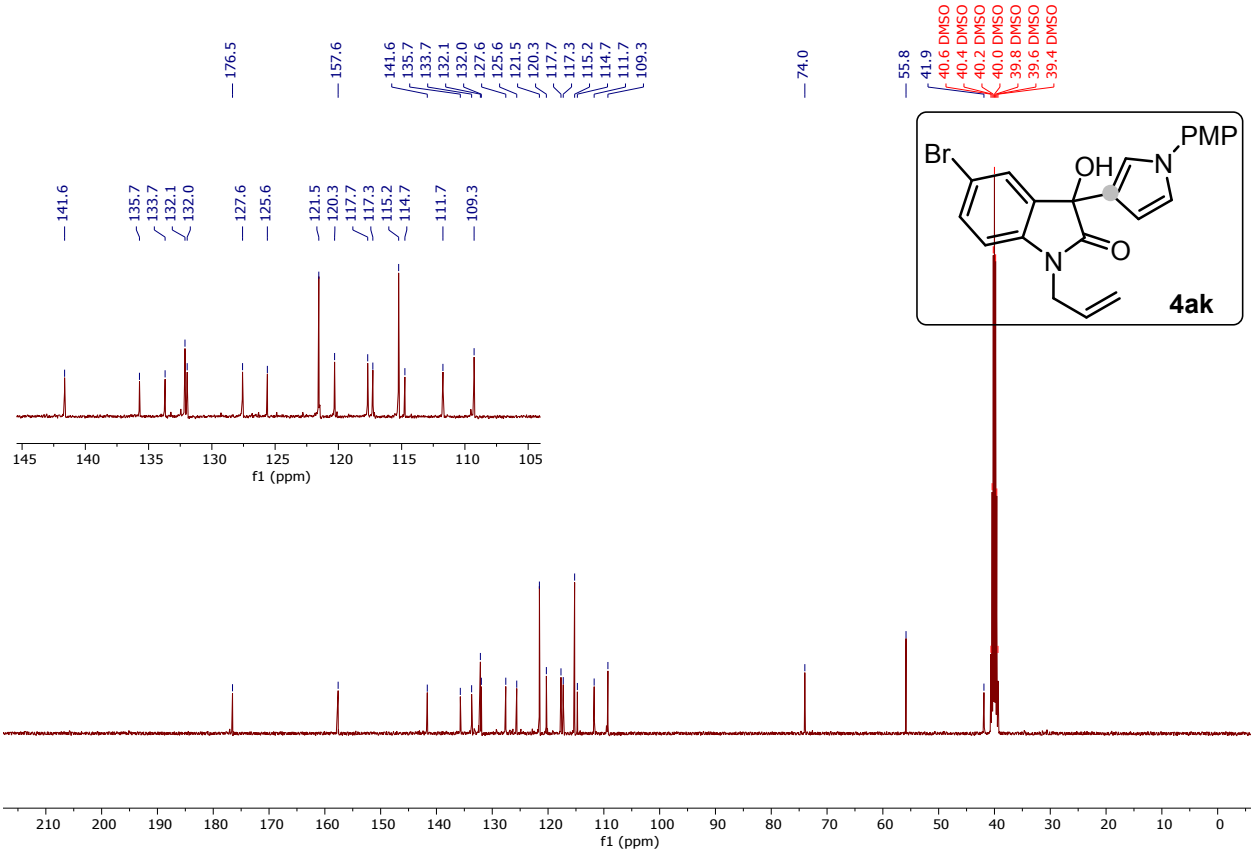
^{13}C NMR (101 MHz, $CDCl_3$)



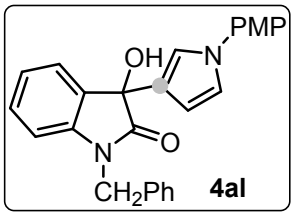
^{1}H NMR (400 MHz, DMSO-d_6)

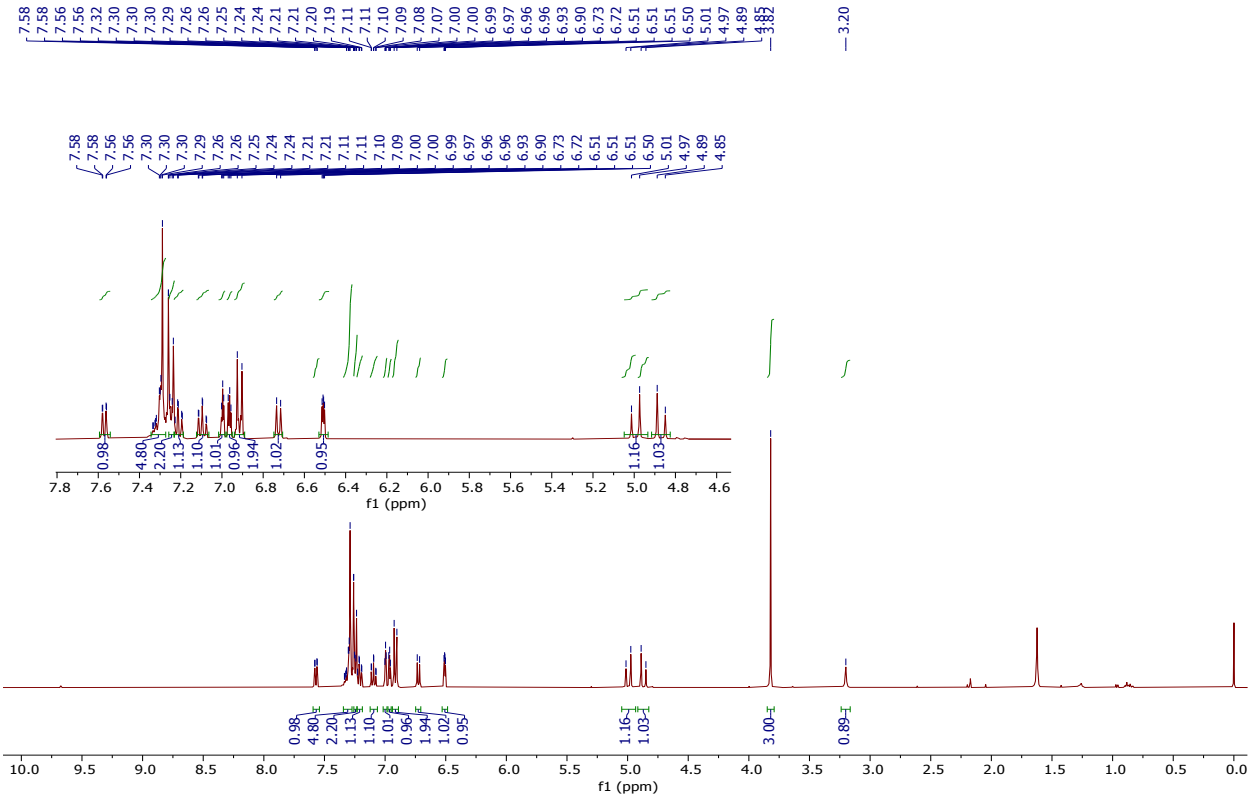


^{13}C NMR (101 MHz, DMSO-d_6)

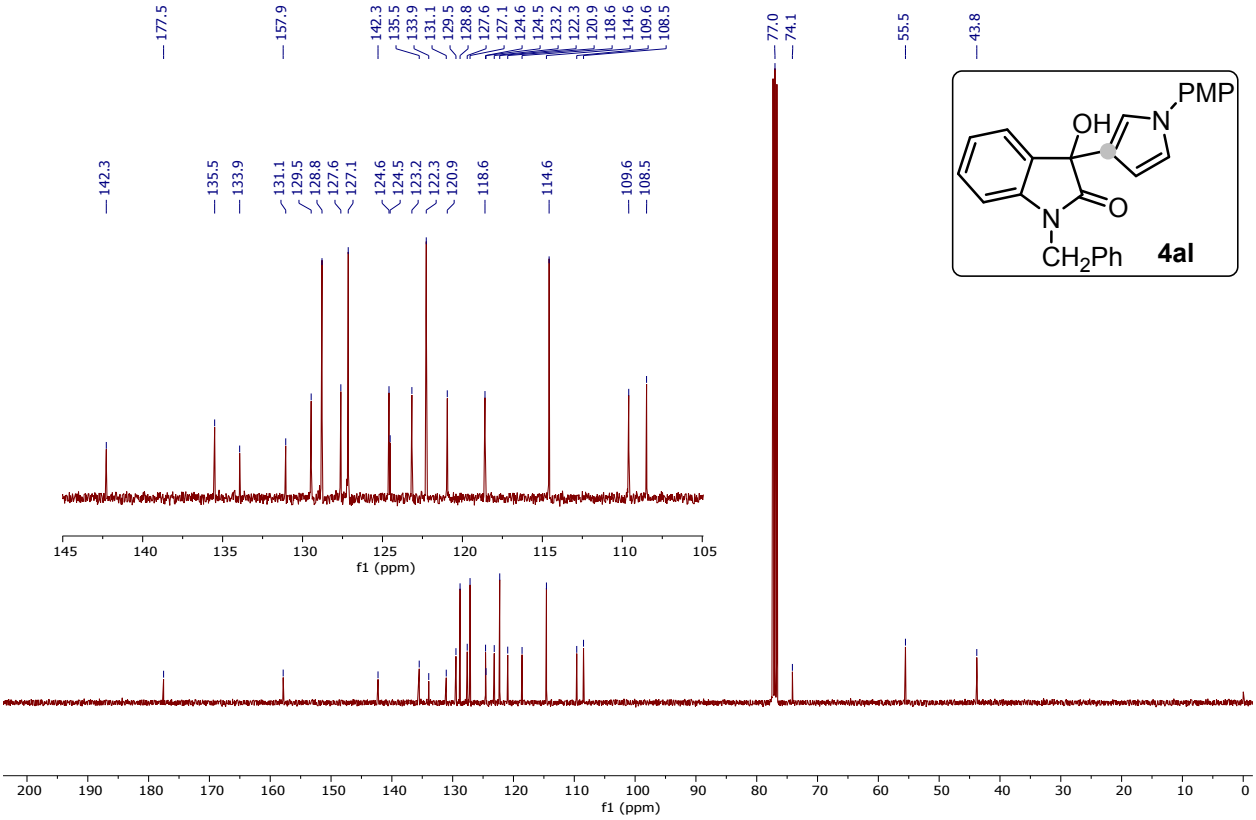


^{1}H NMR (400 MHz, $CDCl_3$)

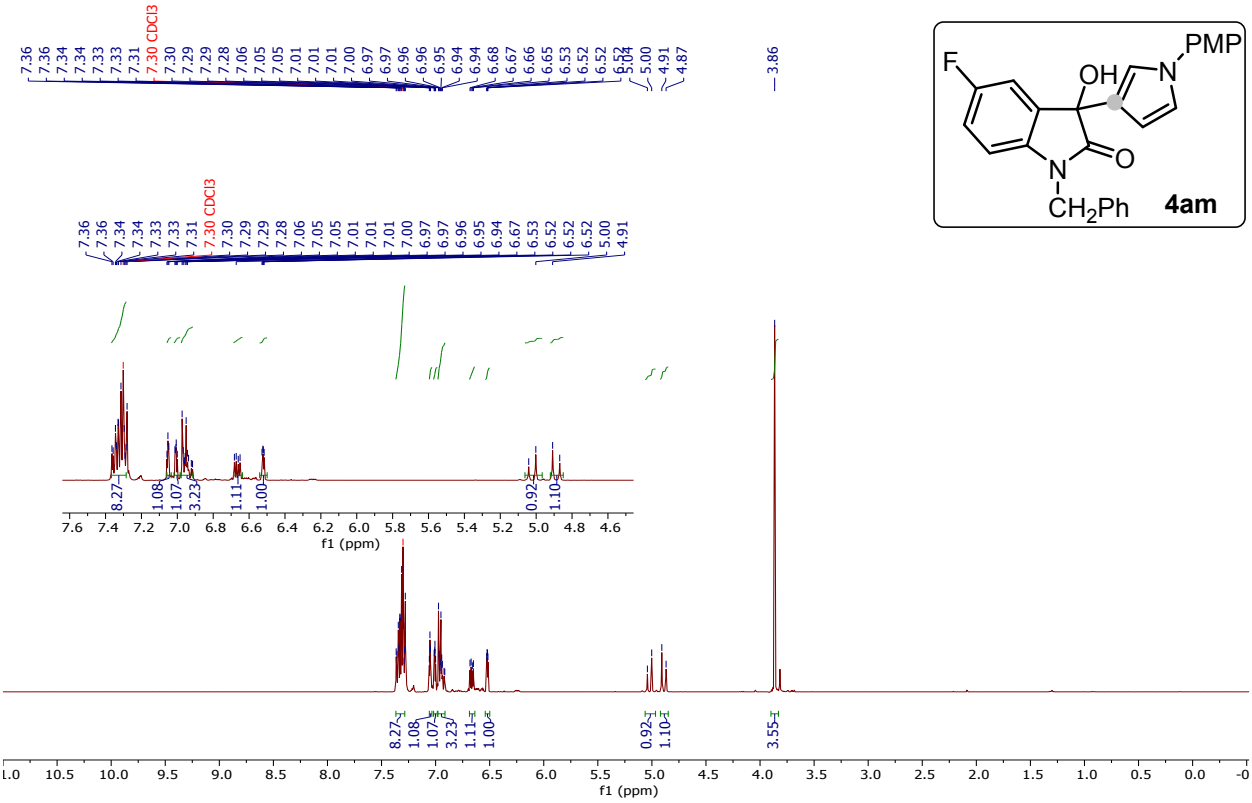




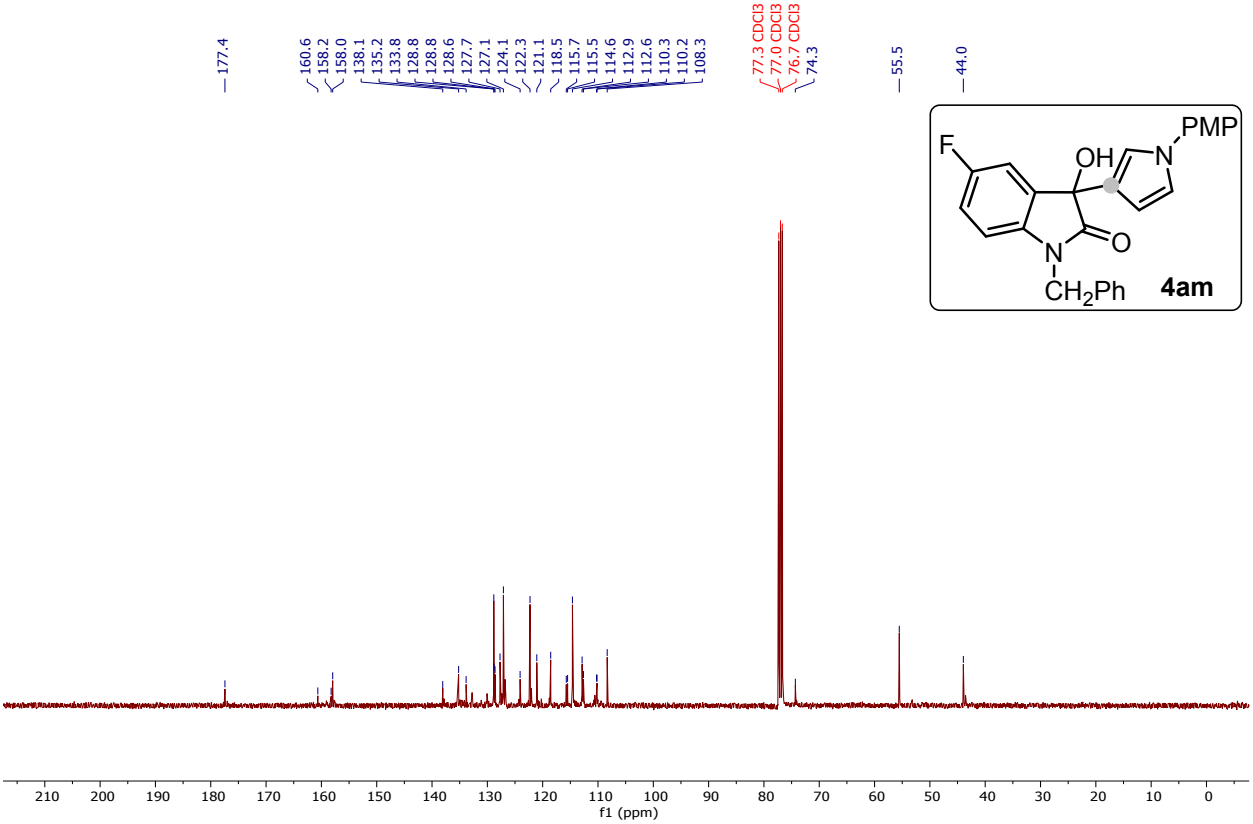
^{13}C NMR (101 MHz, $CDCl_3$)



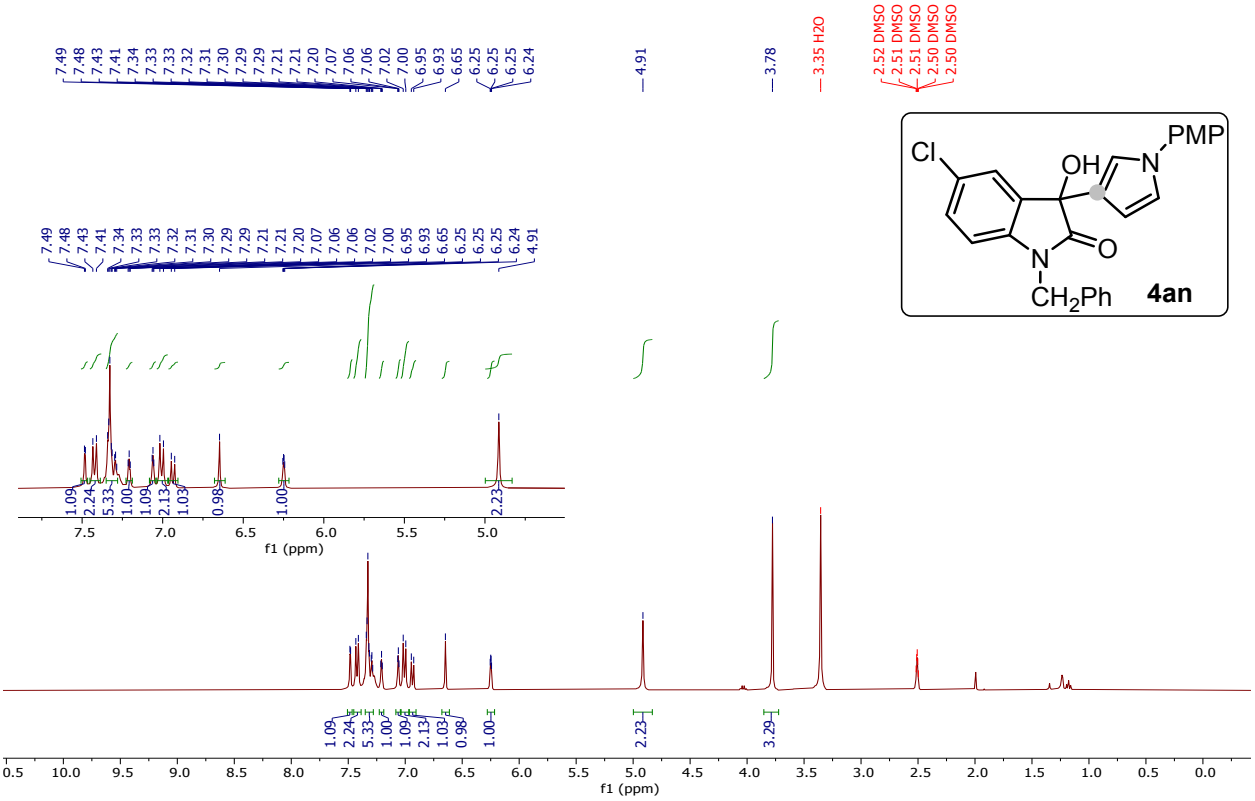
^{1}H NMR (400 MHz, $CDCl_3$)



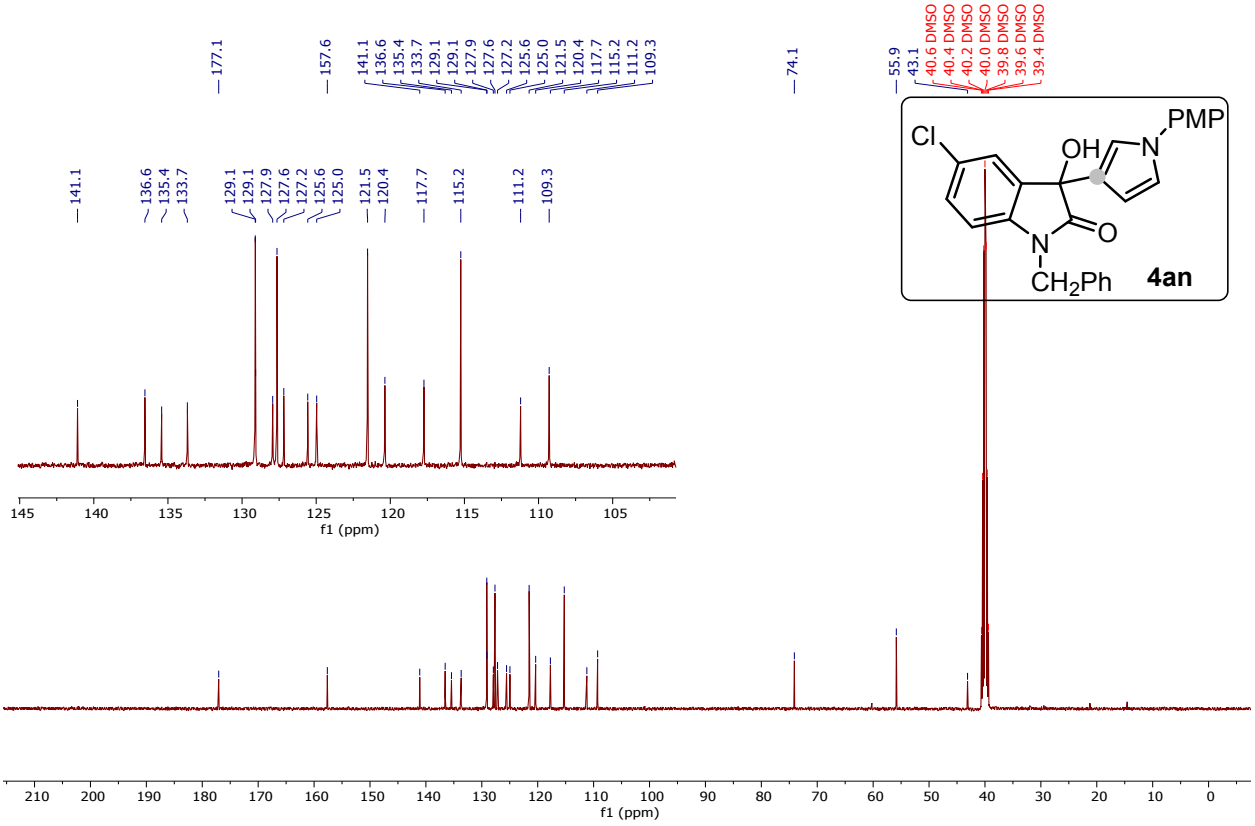
^{13}C NMR (101 MHz, $CDCl_3$)



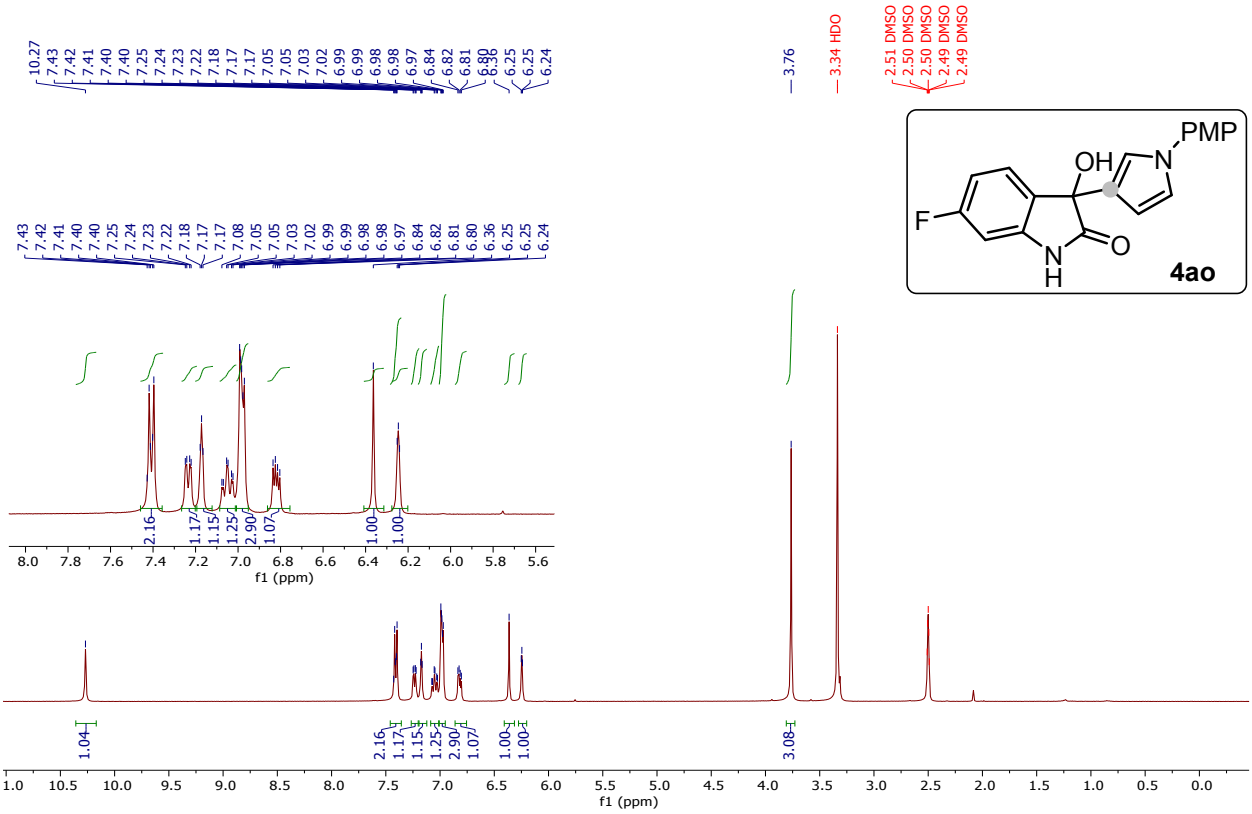
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, DMSO-d_6)



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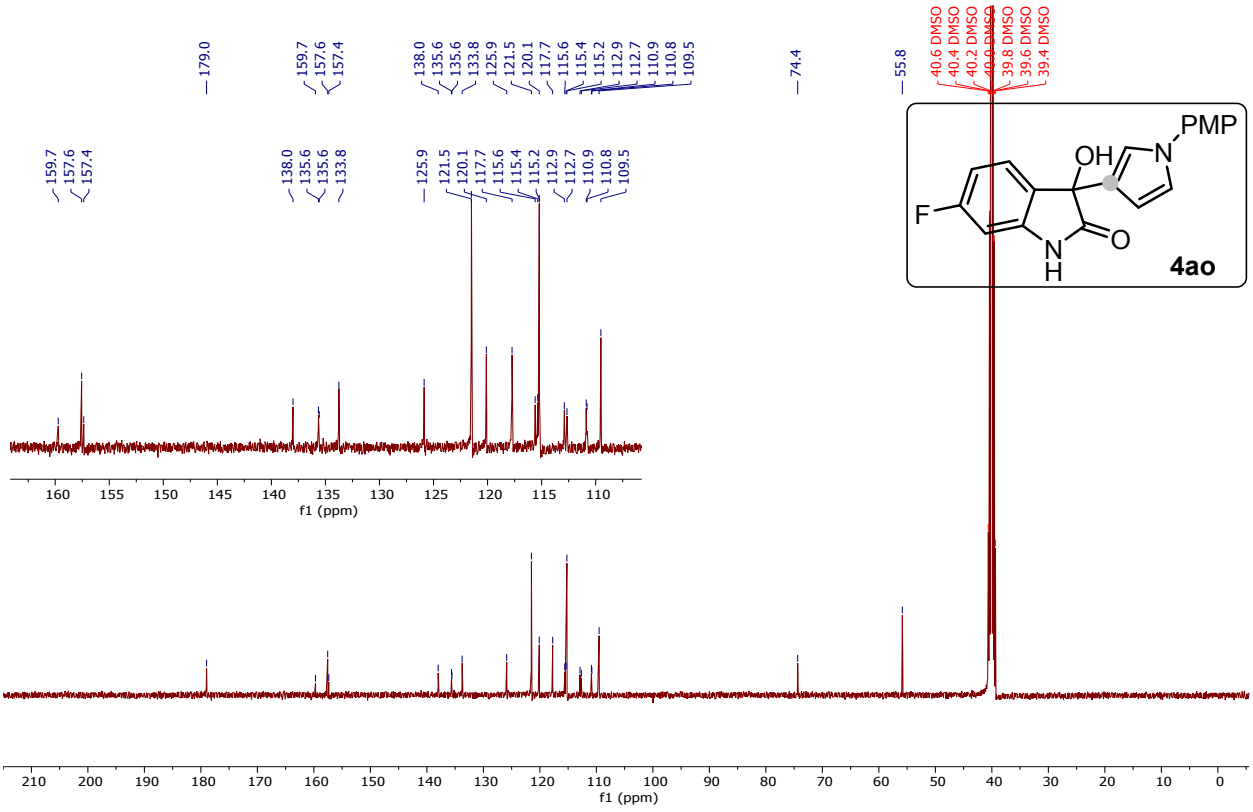

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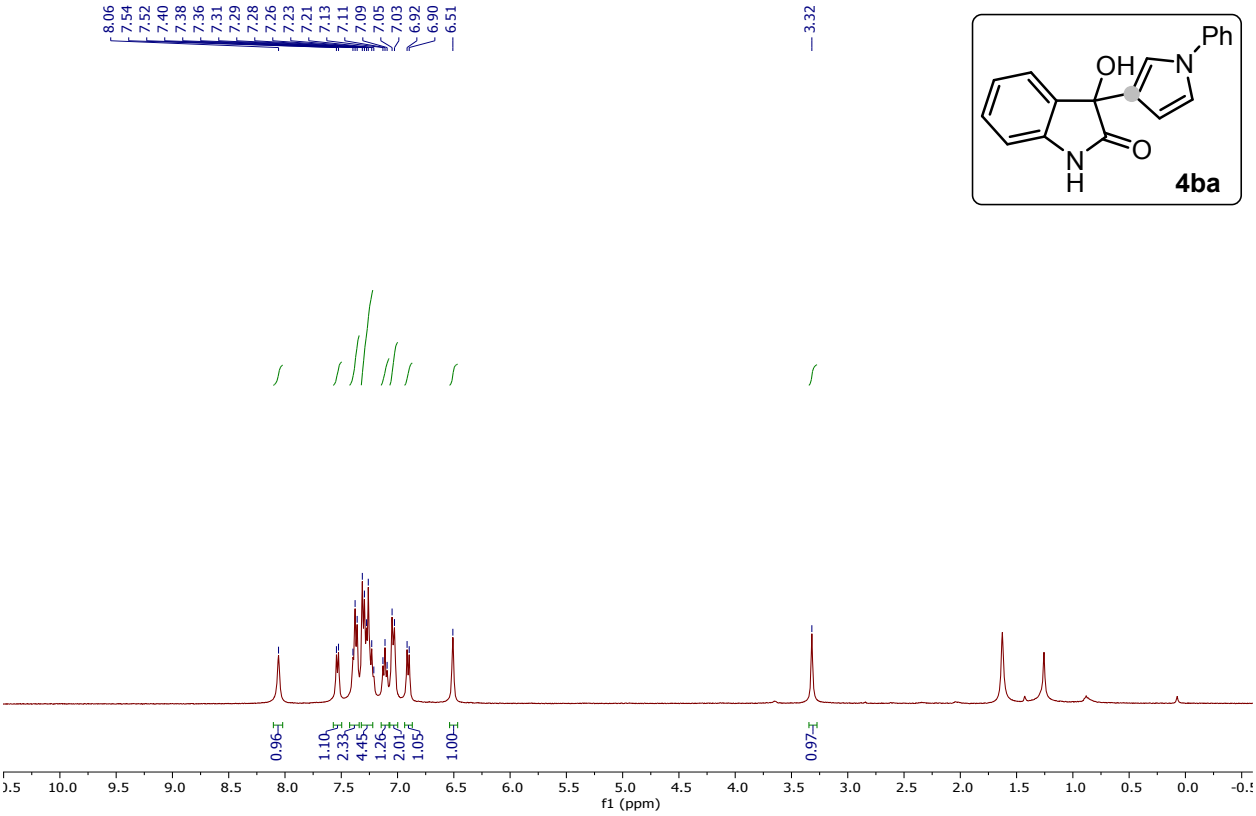

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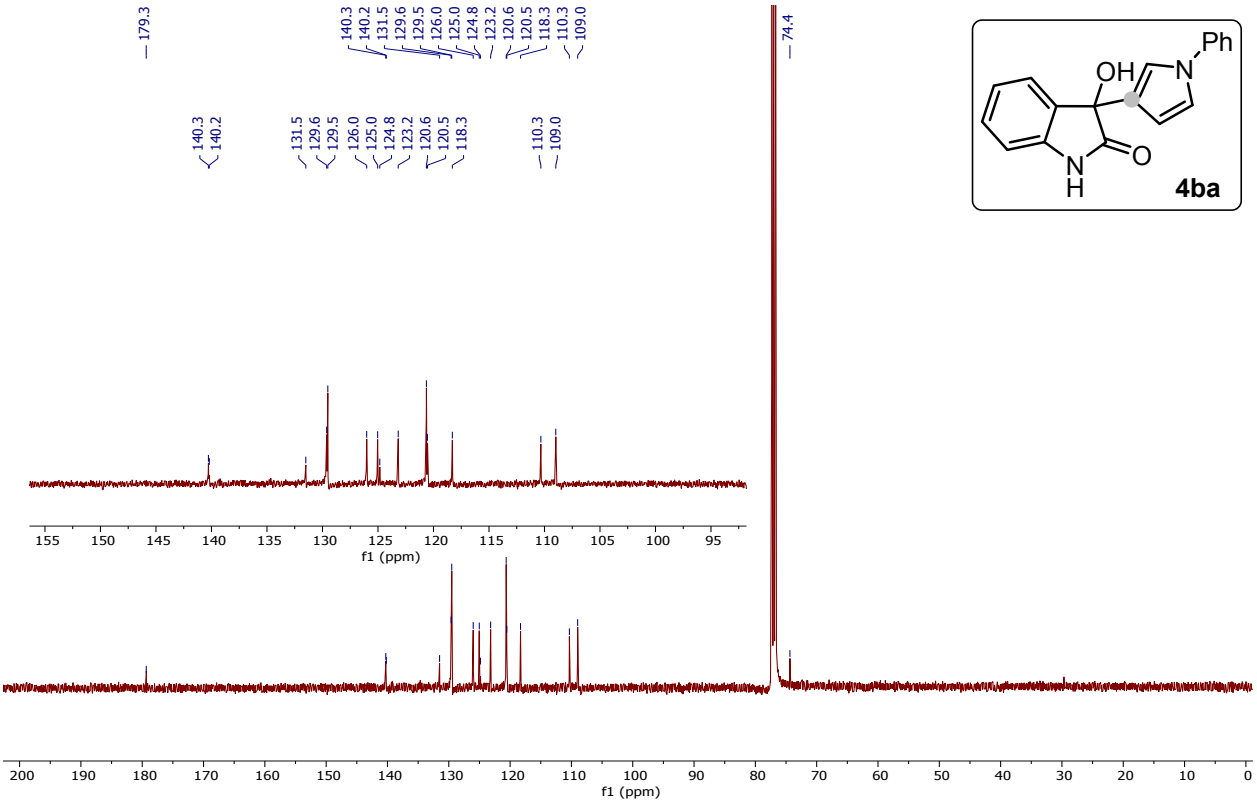

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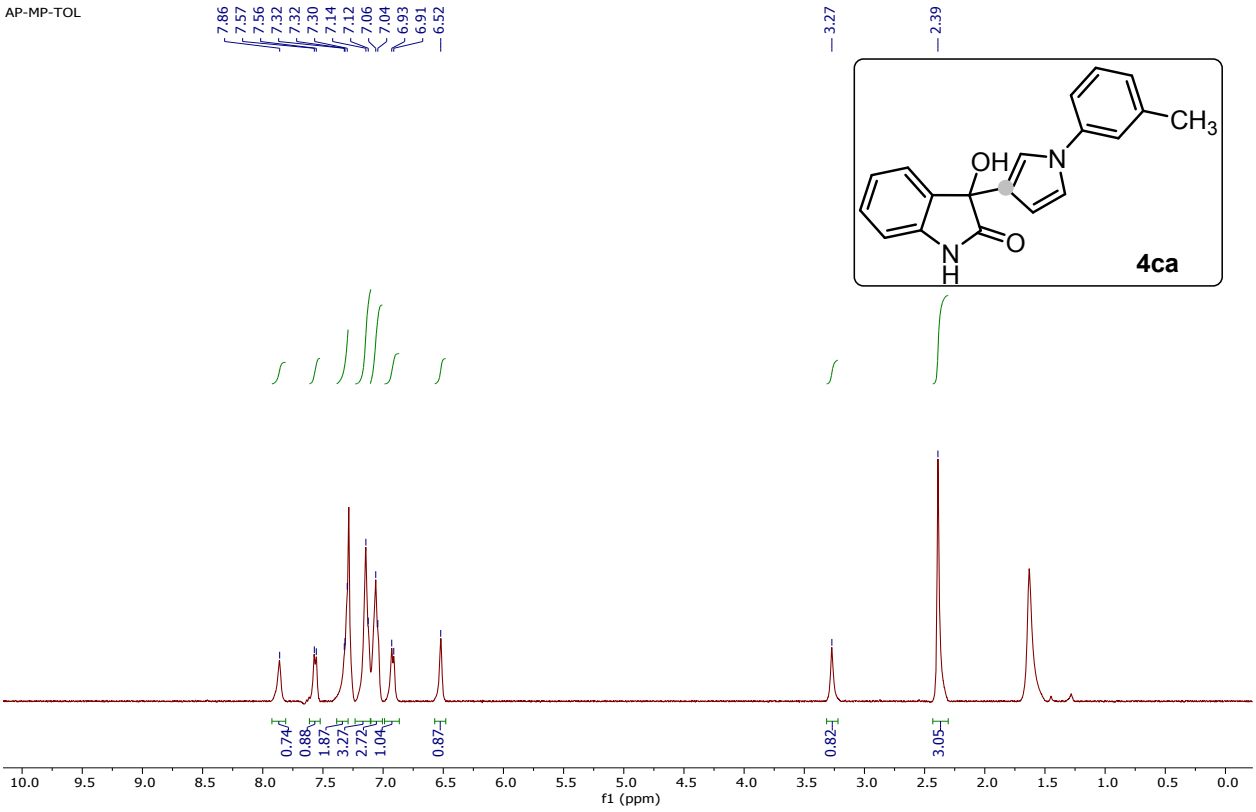

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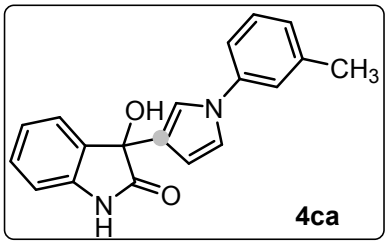

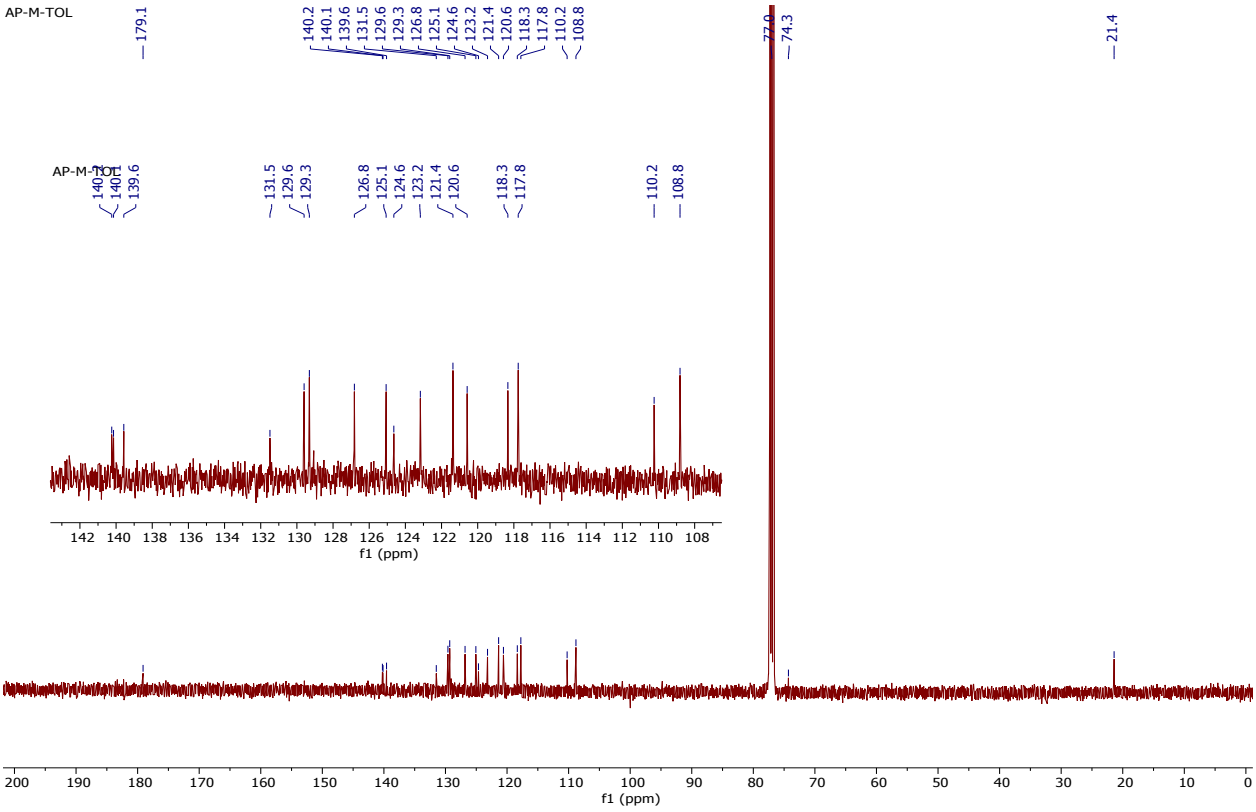

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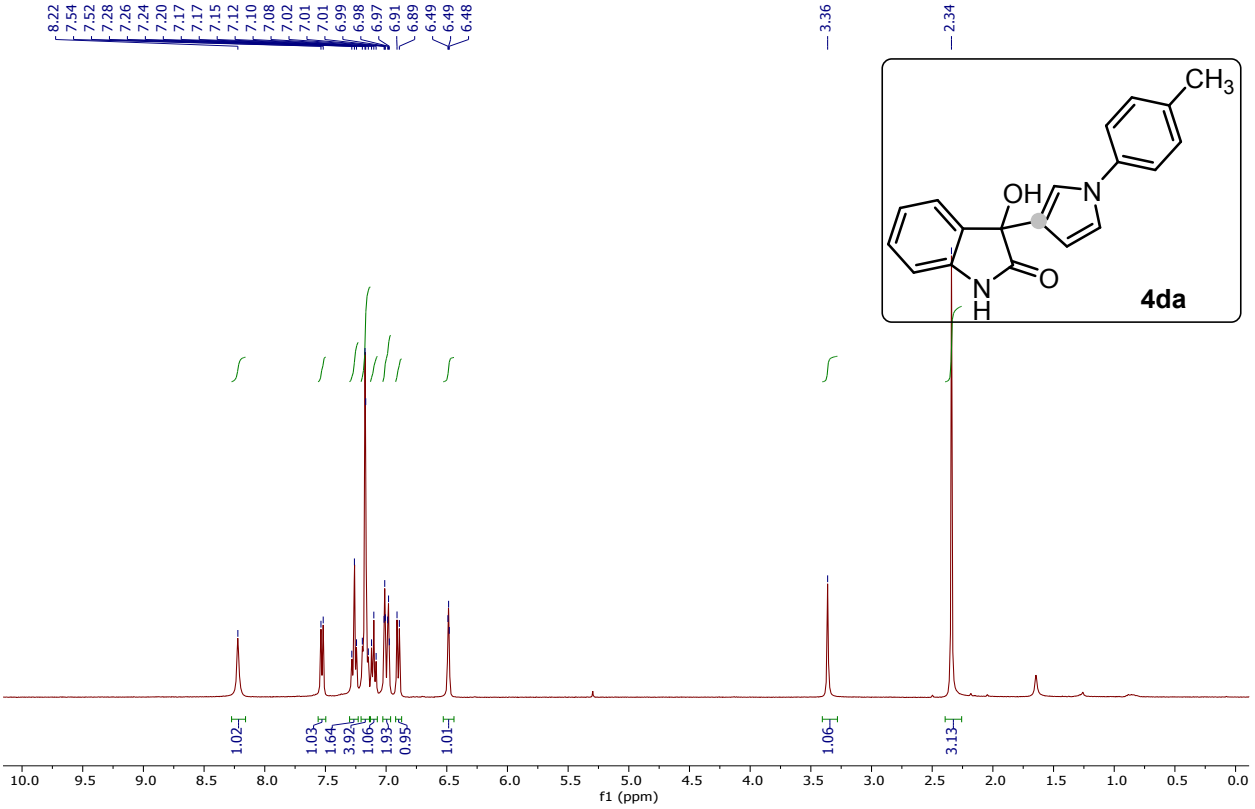
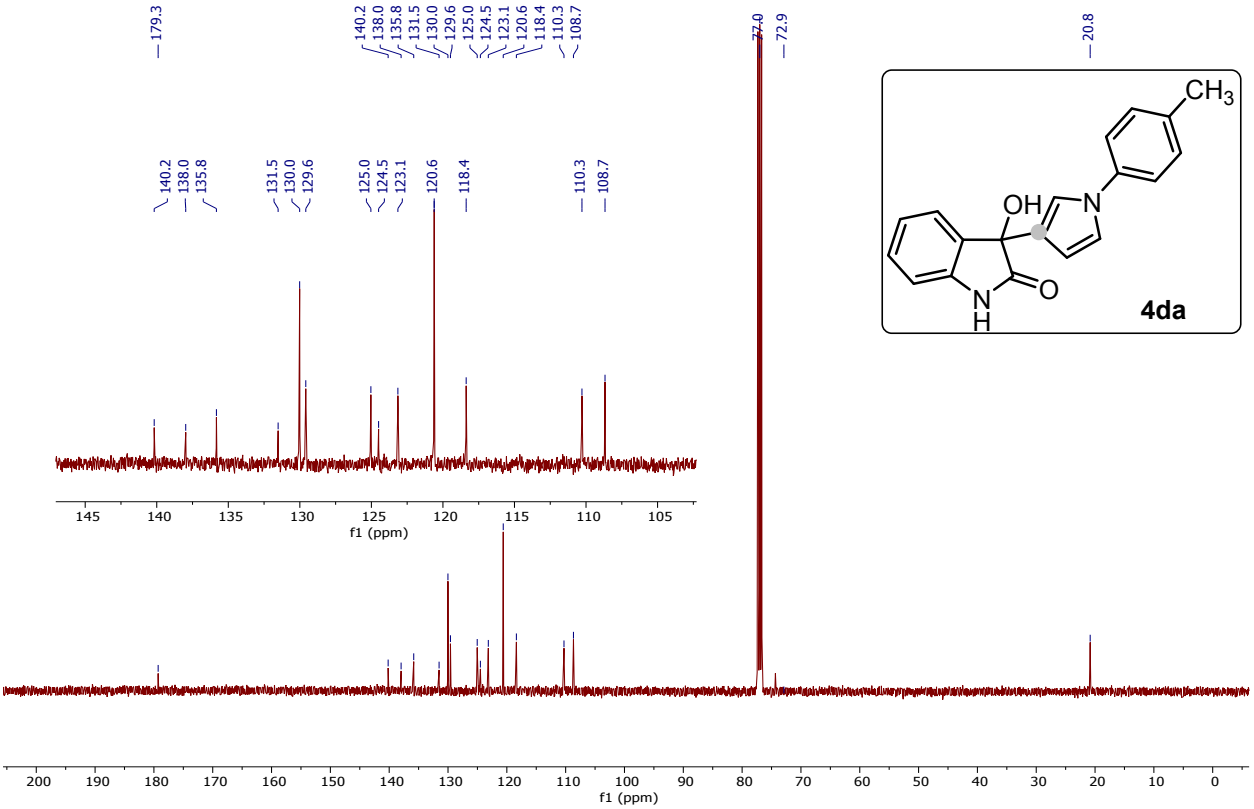
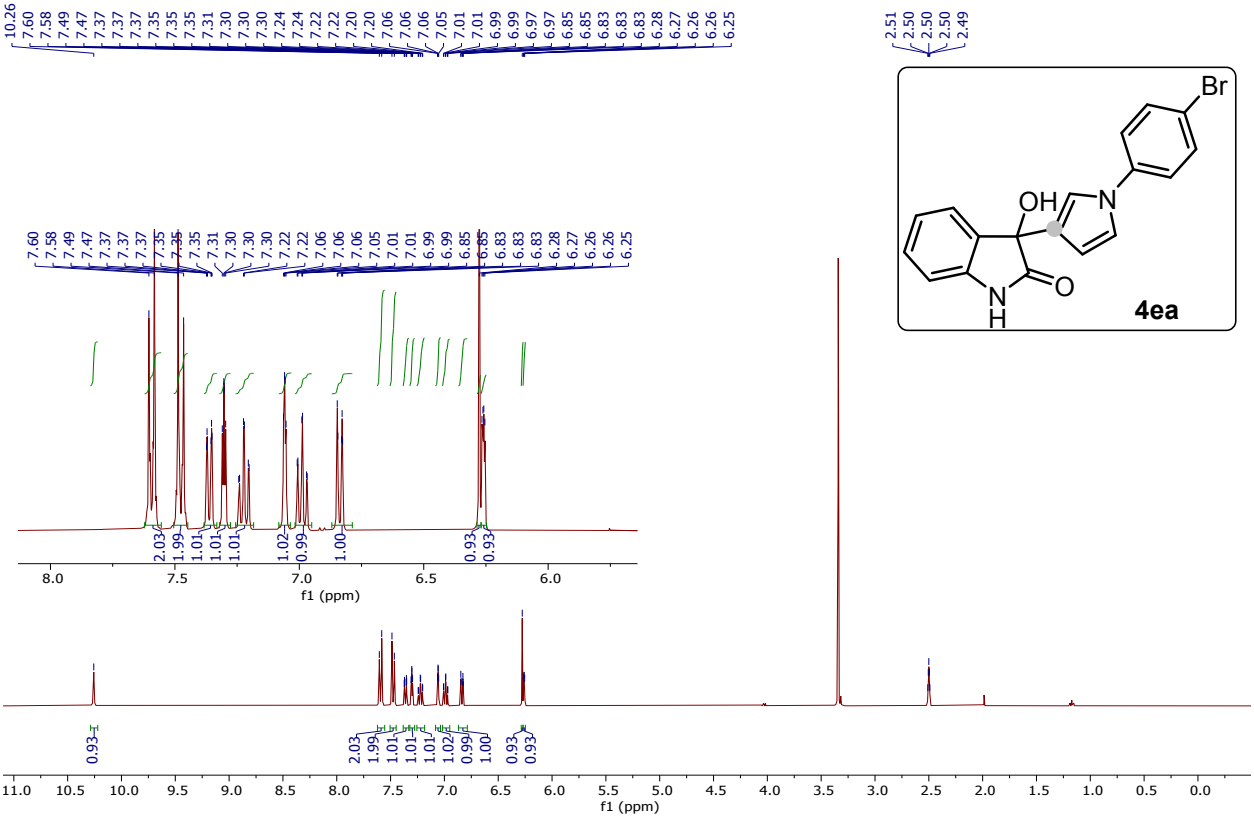


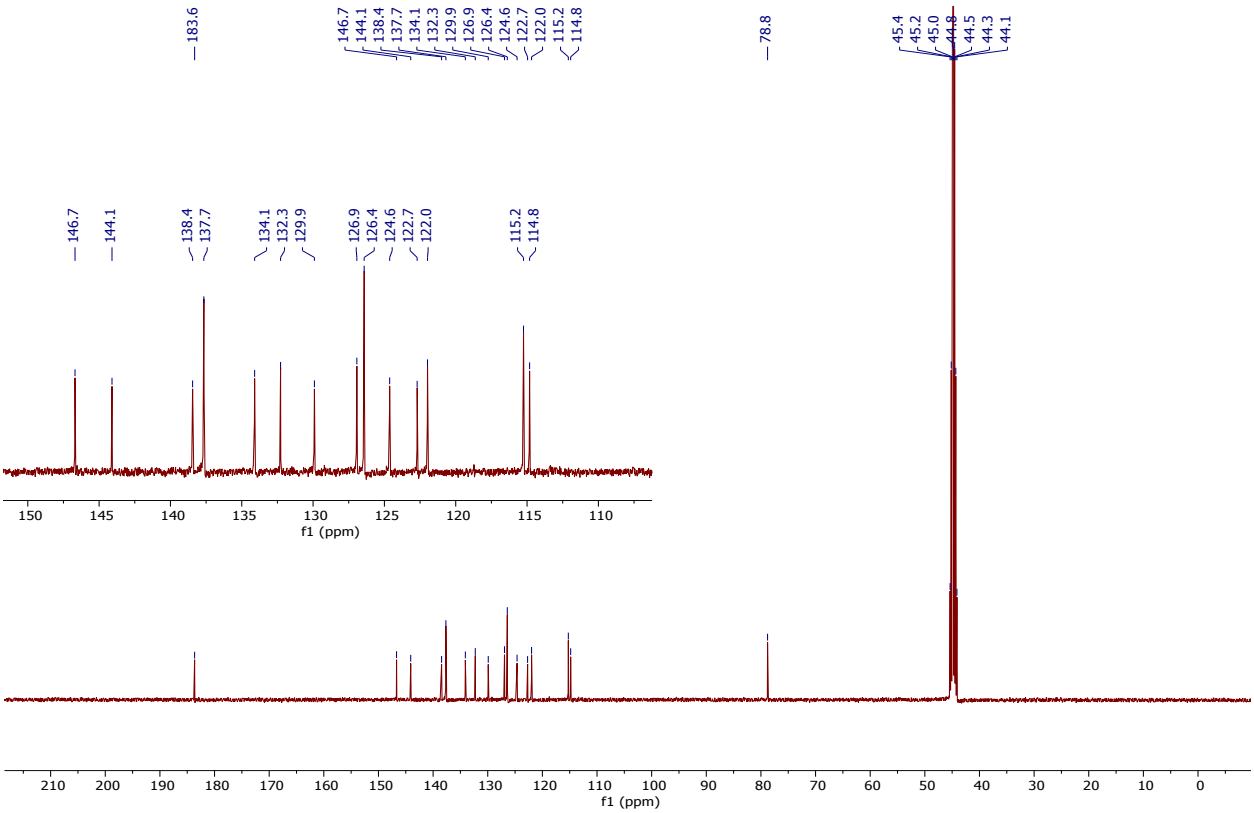
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)



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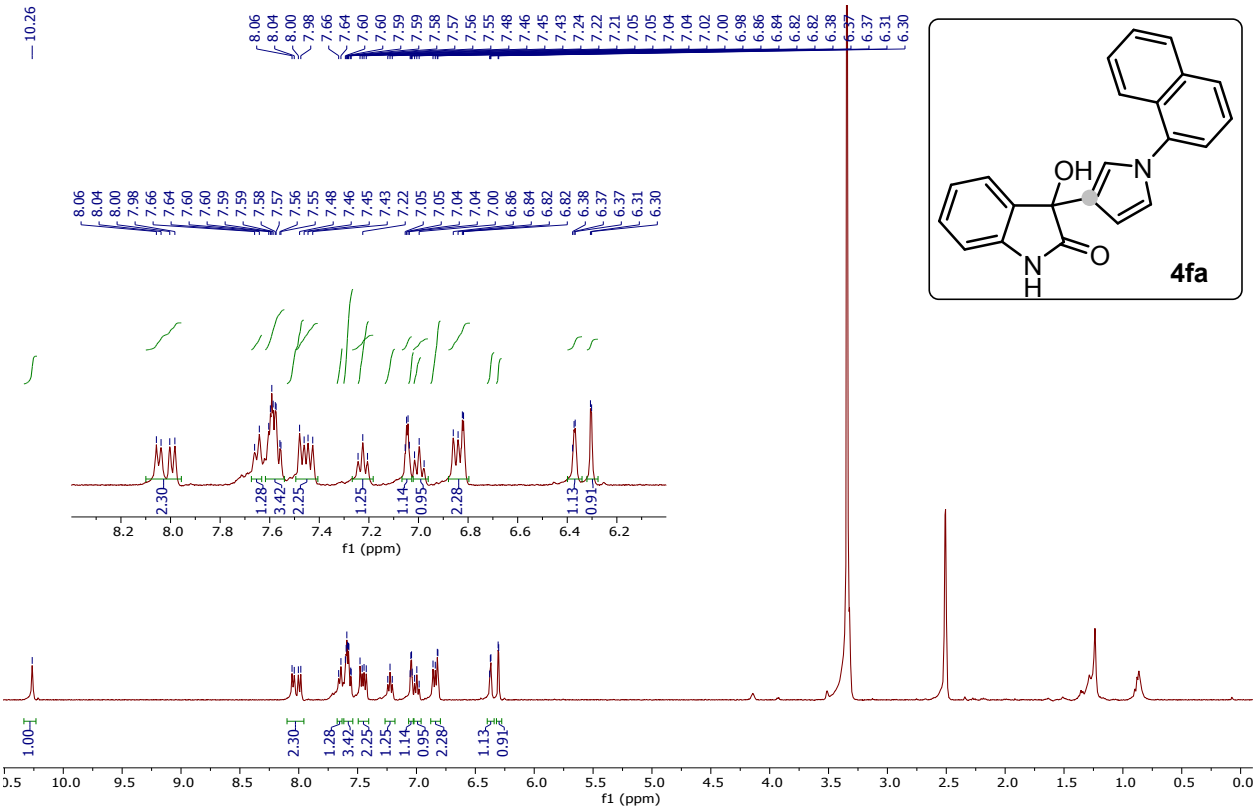

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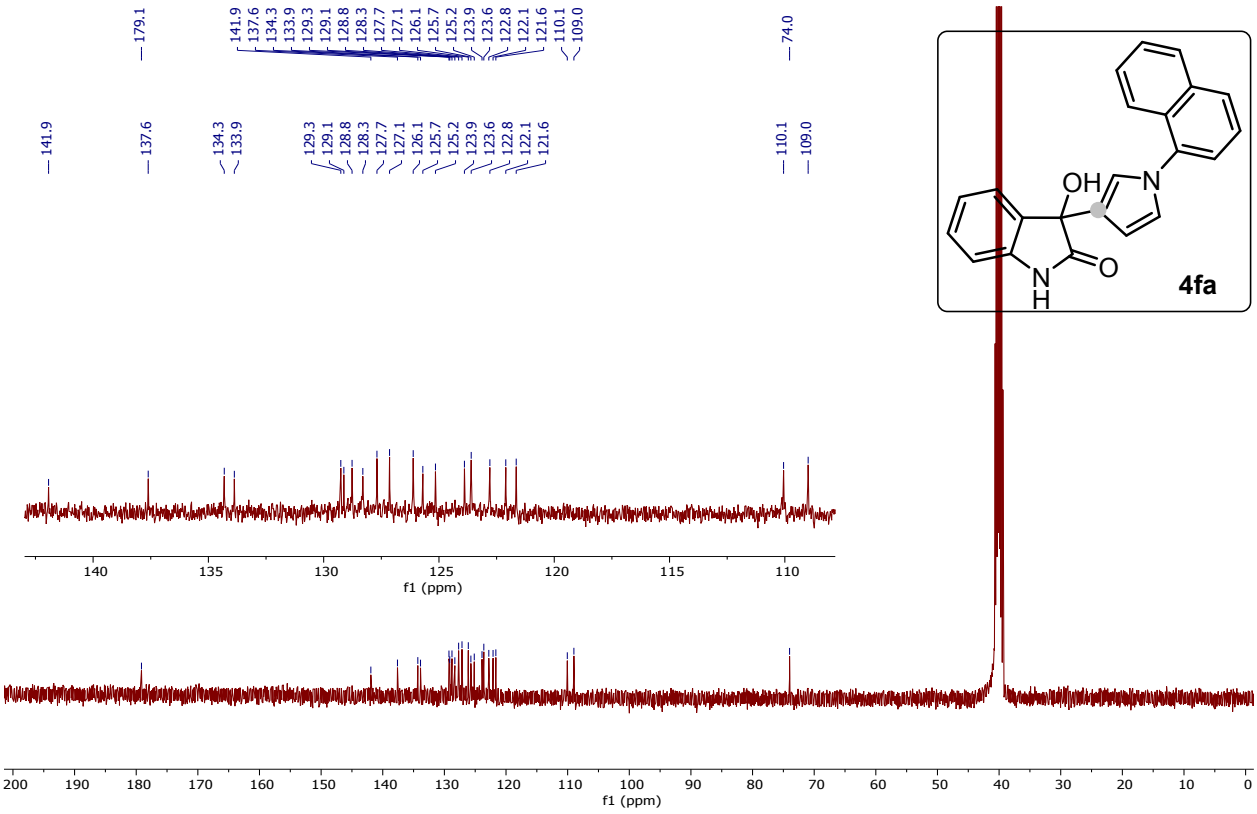
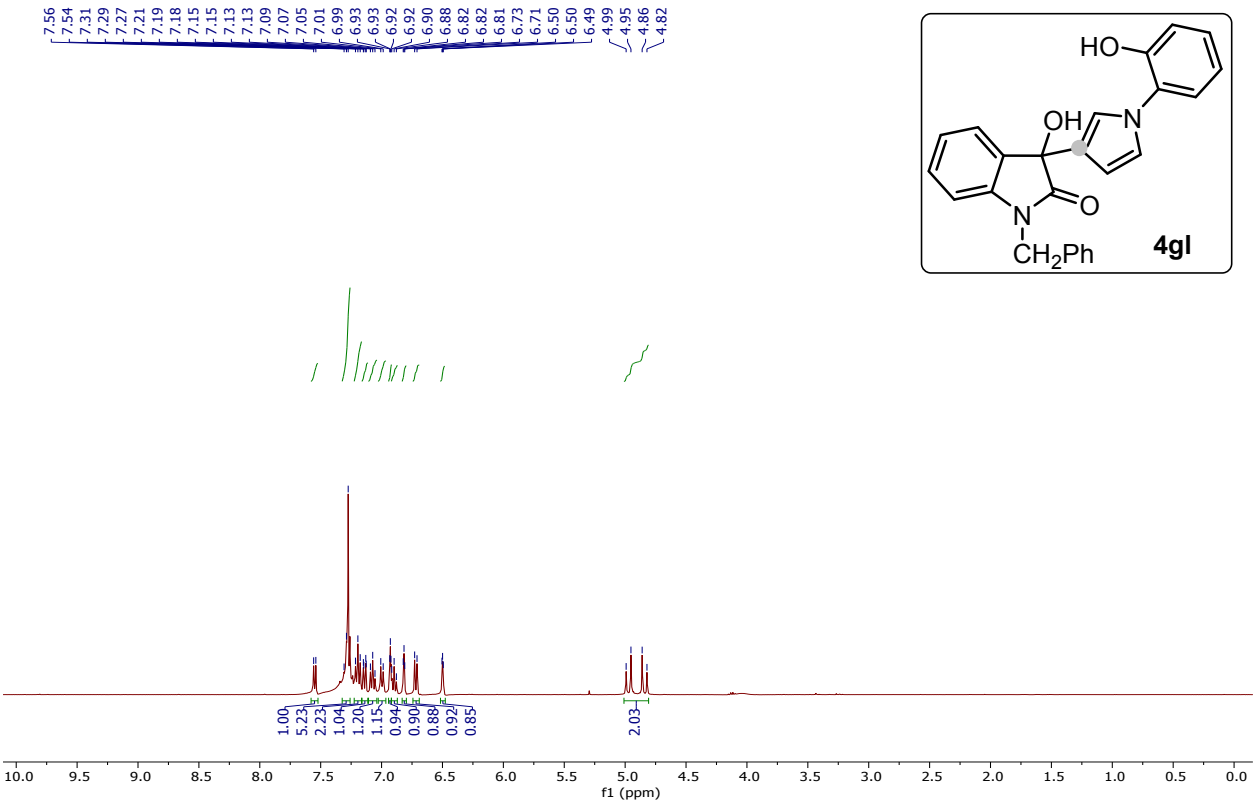


^{1}H NMR (400 MHz, $CDCl_3$)



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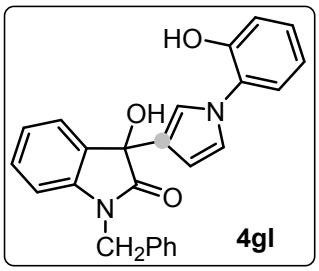

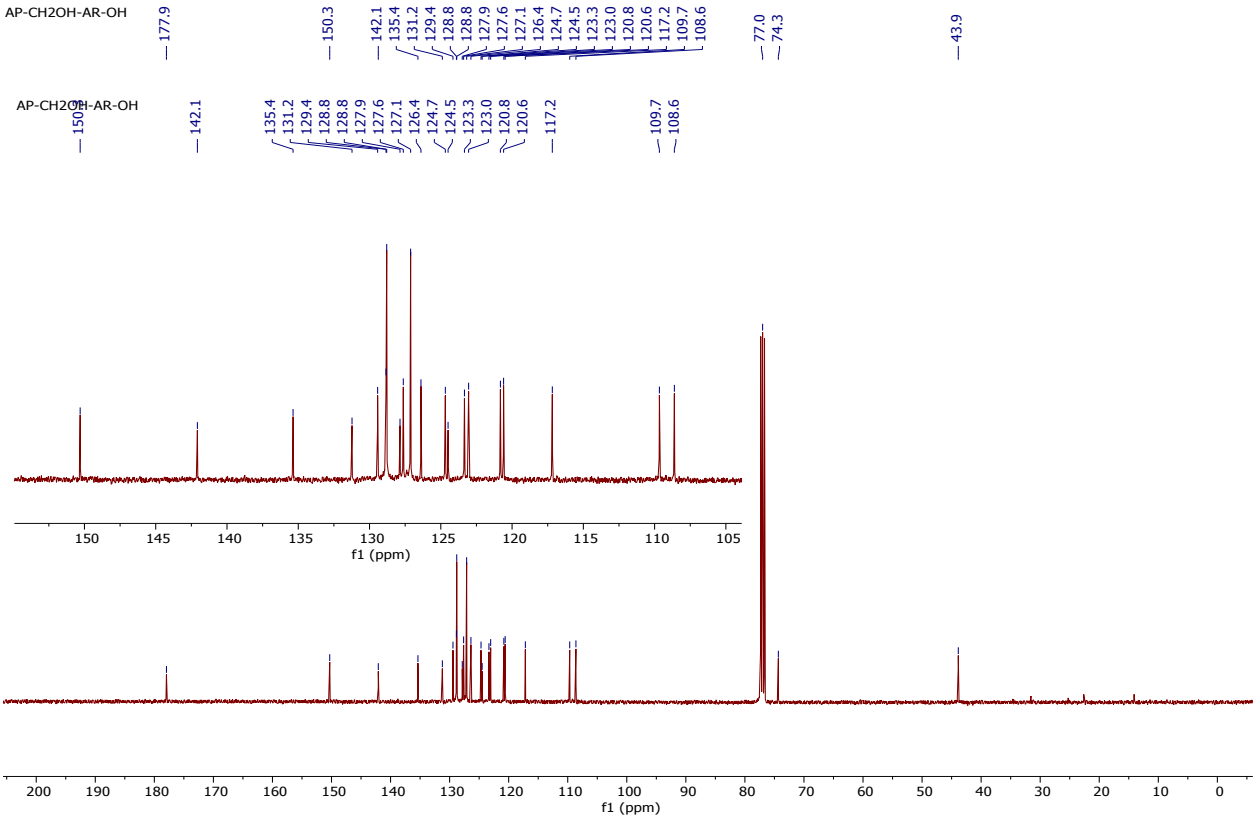

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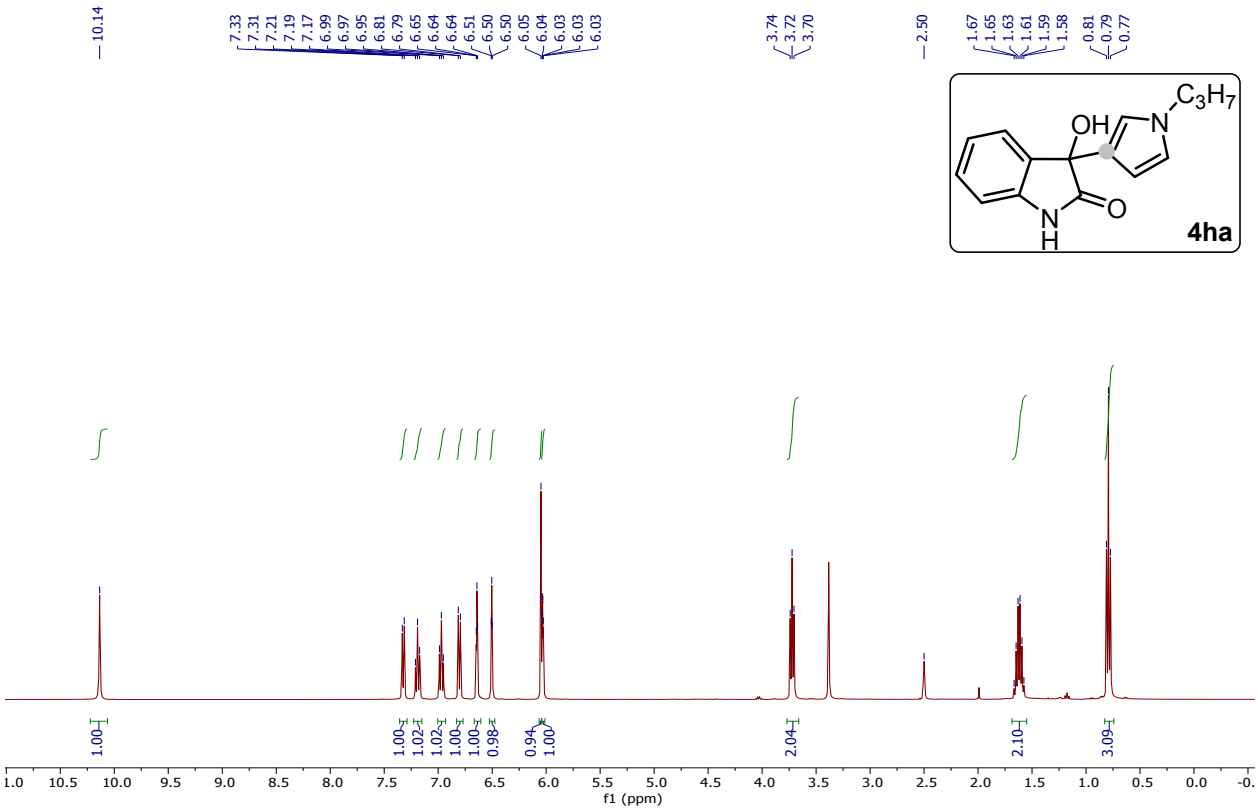
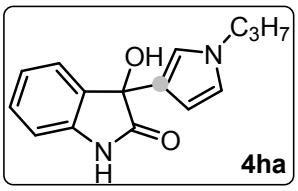
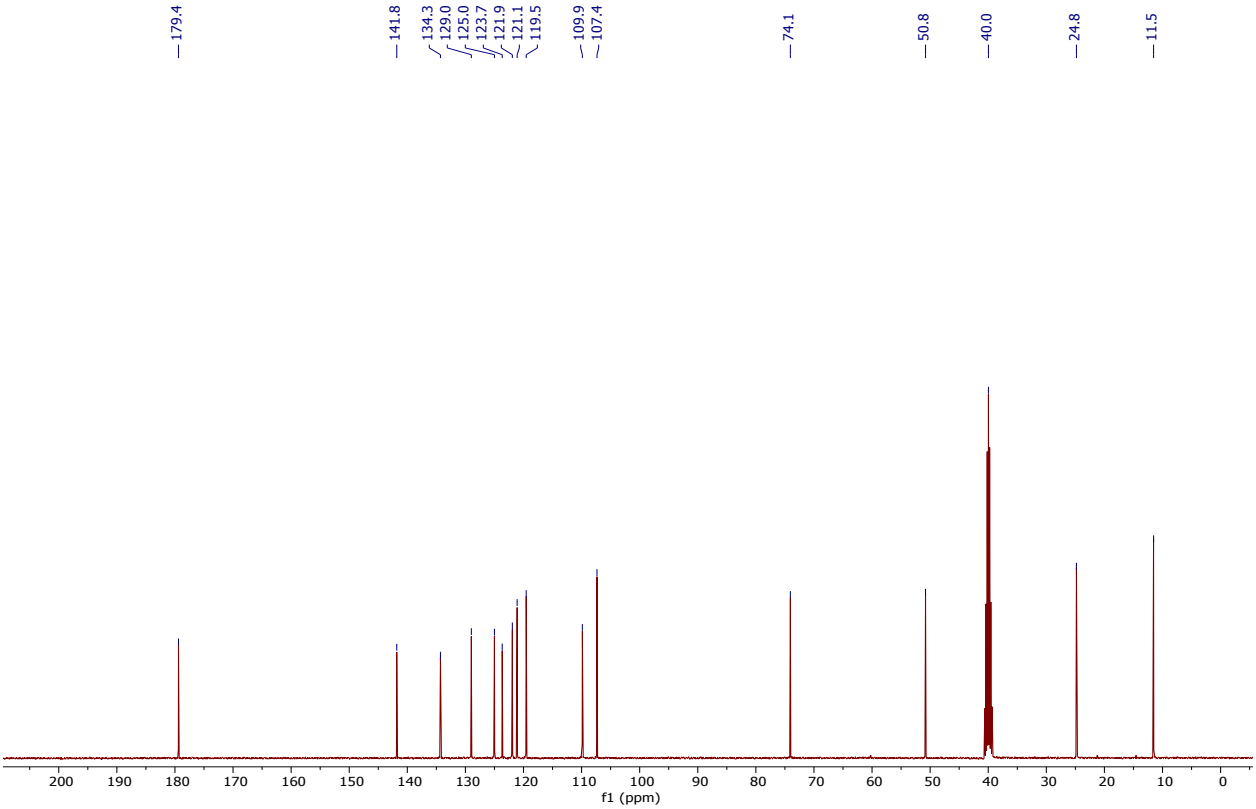

10.14
7.33
7.31
7.21
7.19
7.17
6.99
6.97
6.95
6.81
6.79
6.65
6.64
6.64
6.51
6.50
6.50
6.05
6.04
6.03
6.03
6.03
3.74
3.72
3.70
2.50
1.67
1.65
1.63
1.61
1.59
1.58
0.81
0.79
0.77
OH
N
C3H7
O
N
H
4ha
1.00
1.00
1.02
1.02
1.00
1.00
0.98
0.94
1.00
2.04
2.10
3.09
f1 (ppm)


OH
N
C3H7
O
N
H
4ha

^{13}C NMR (101 MHz, DMSO-d_6)



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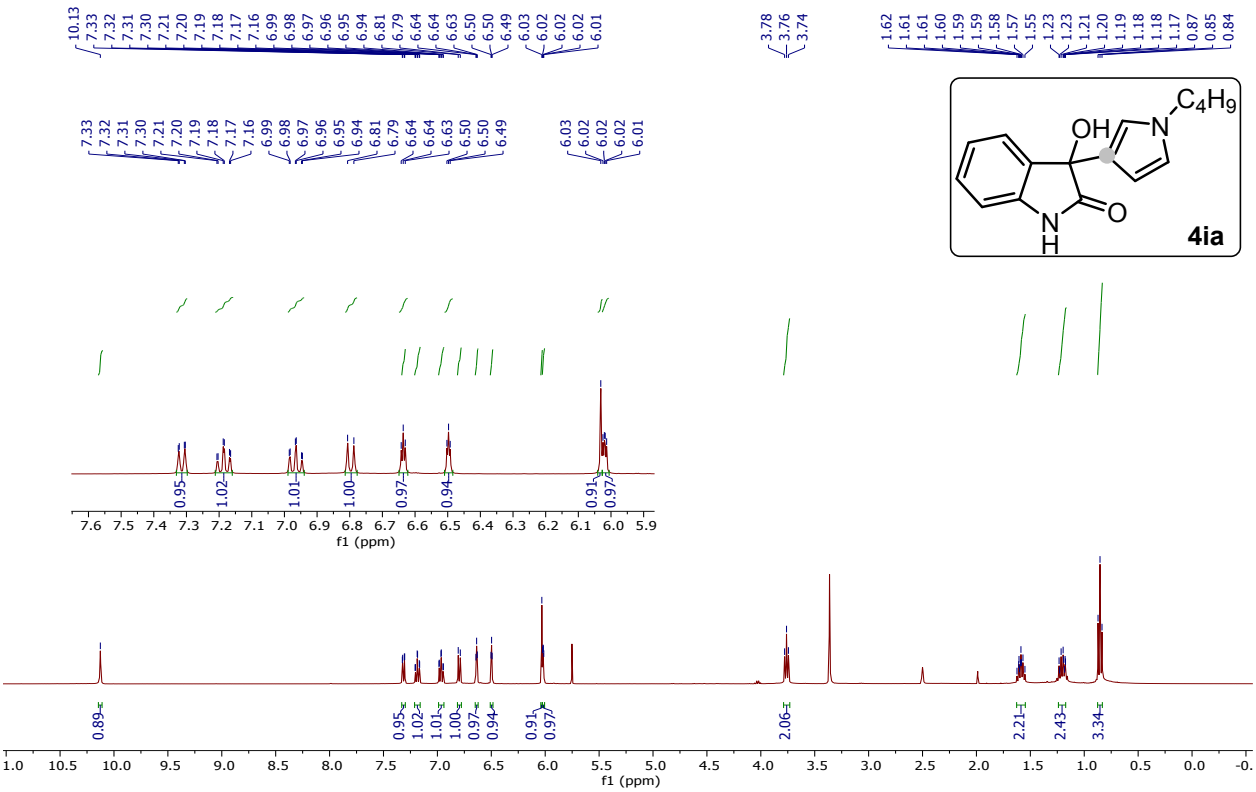

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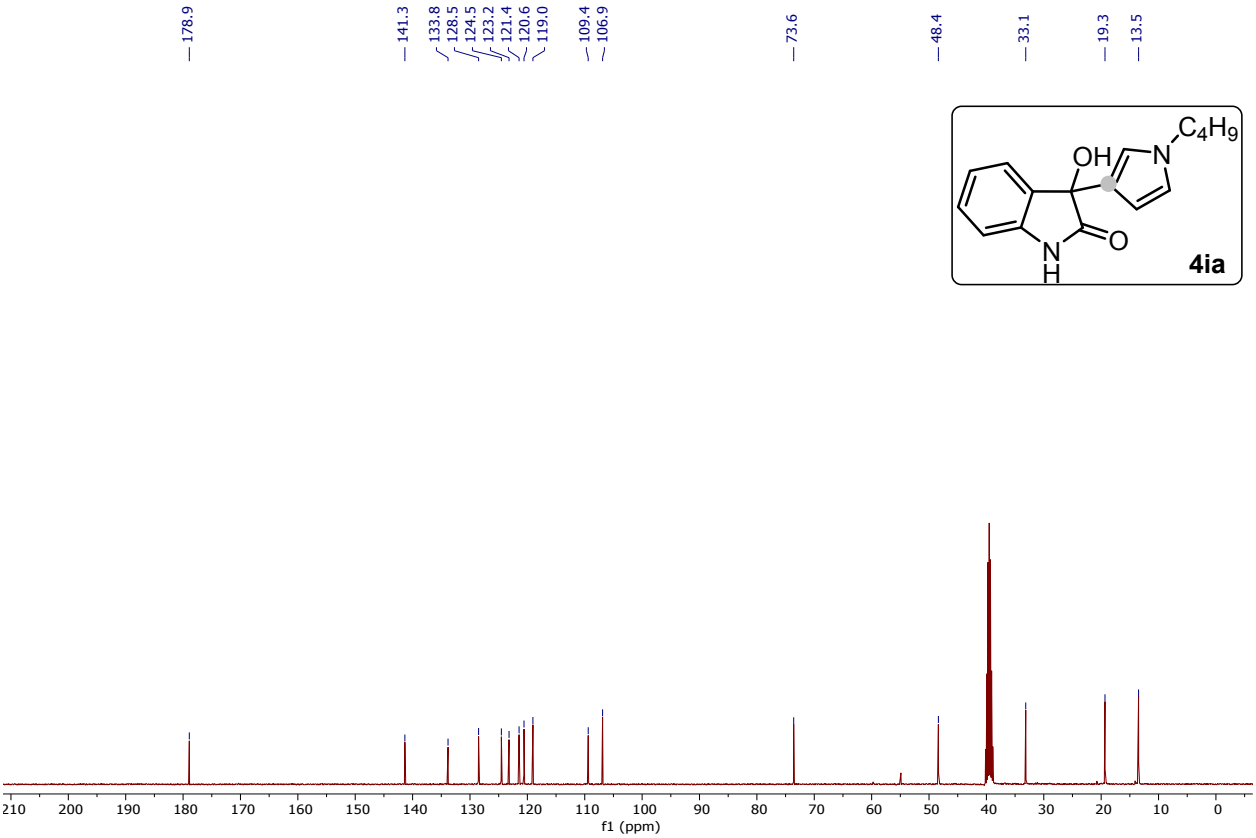

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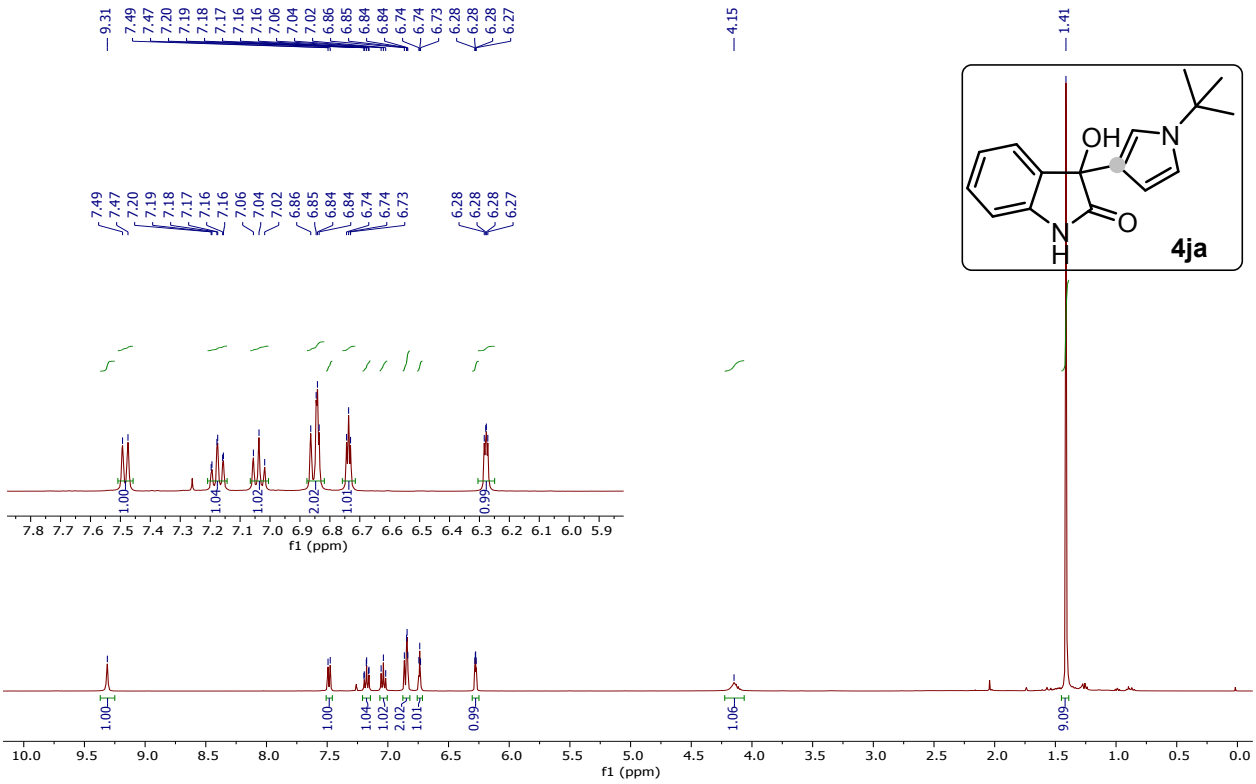
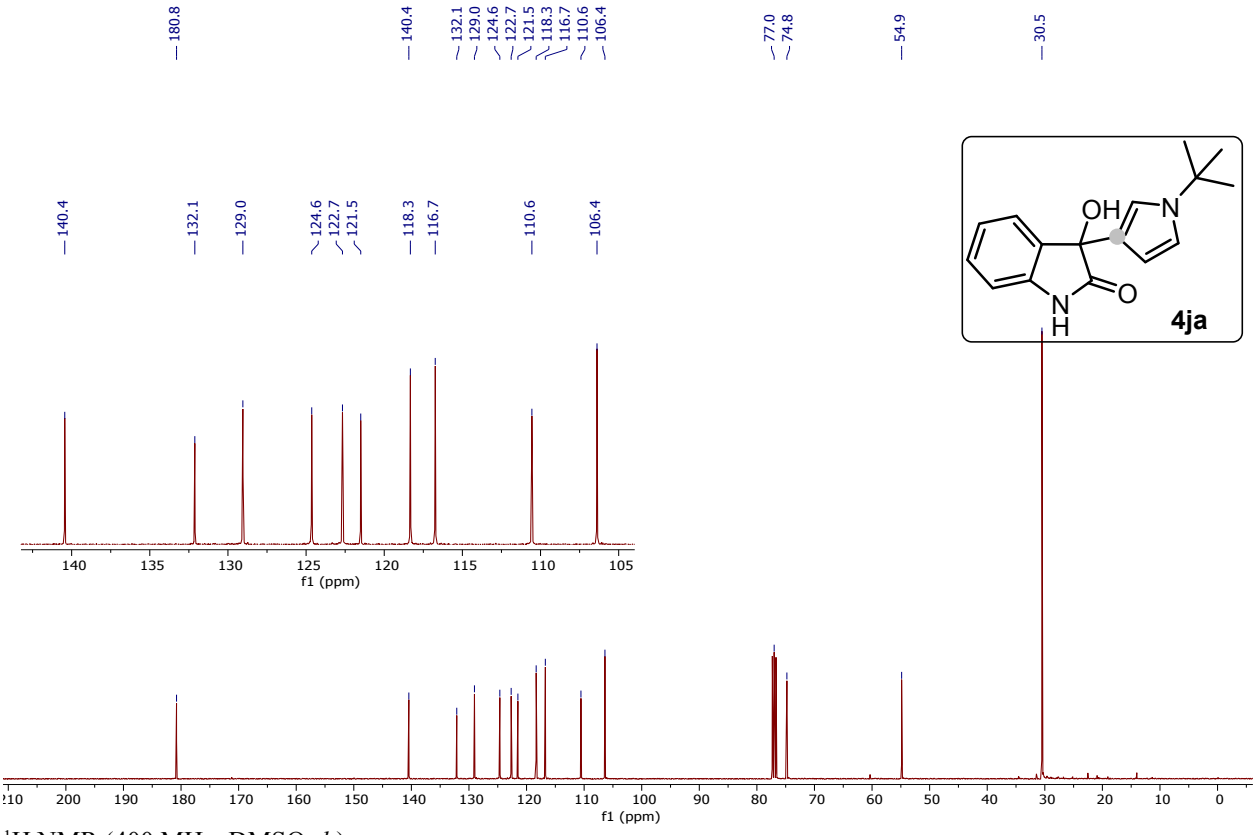


^{13}C NMR (101 MHz, $CDCl_3$)



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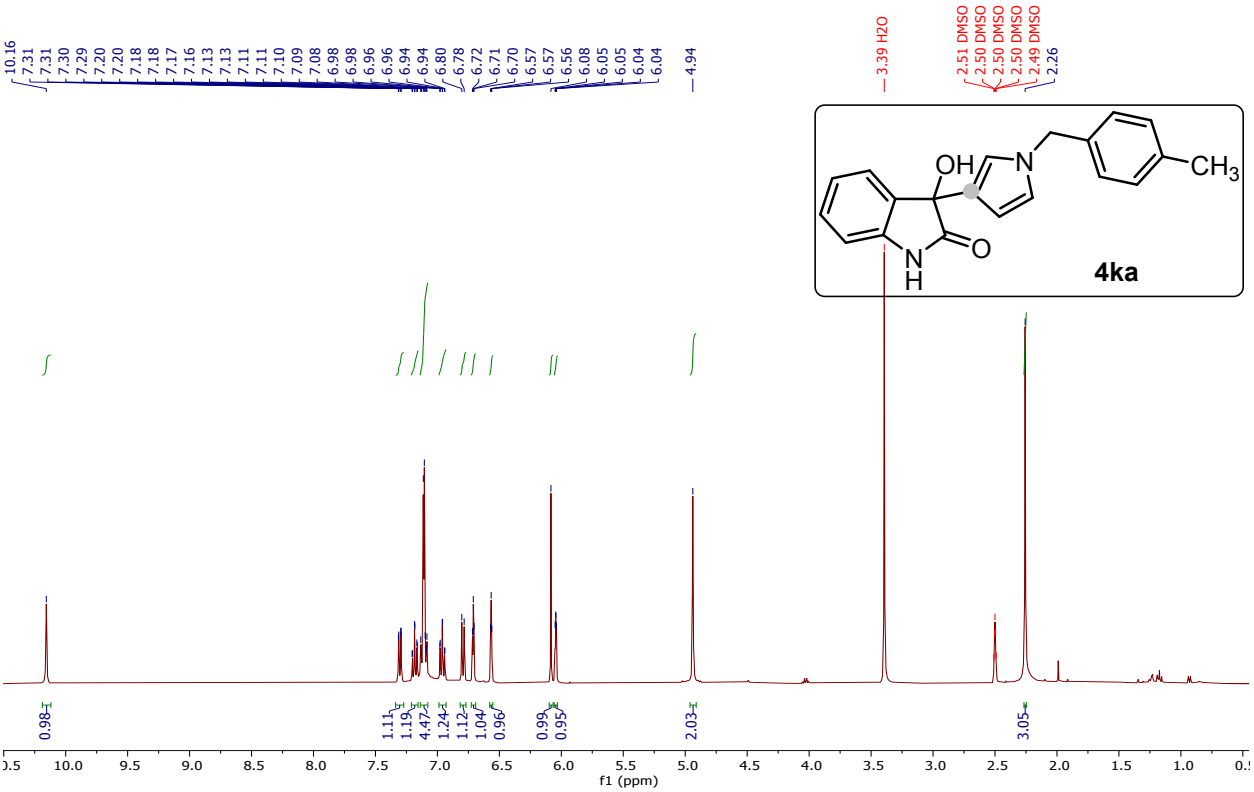

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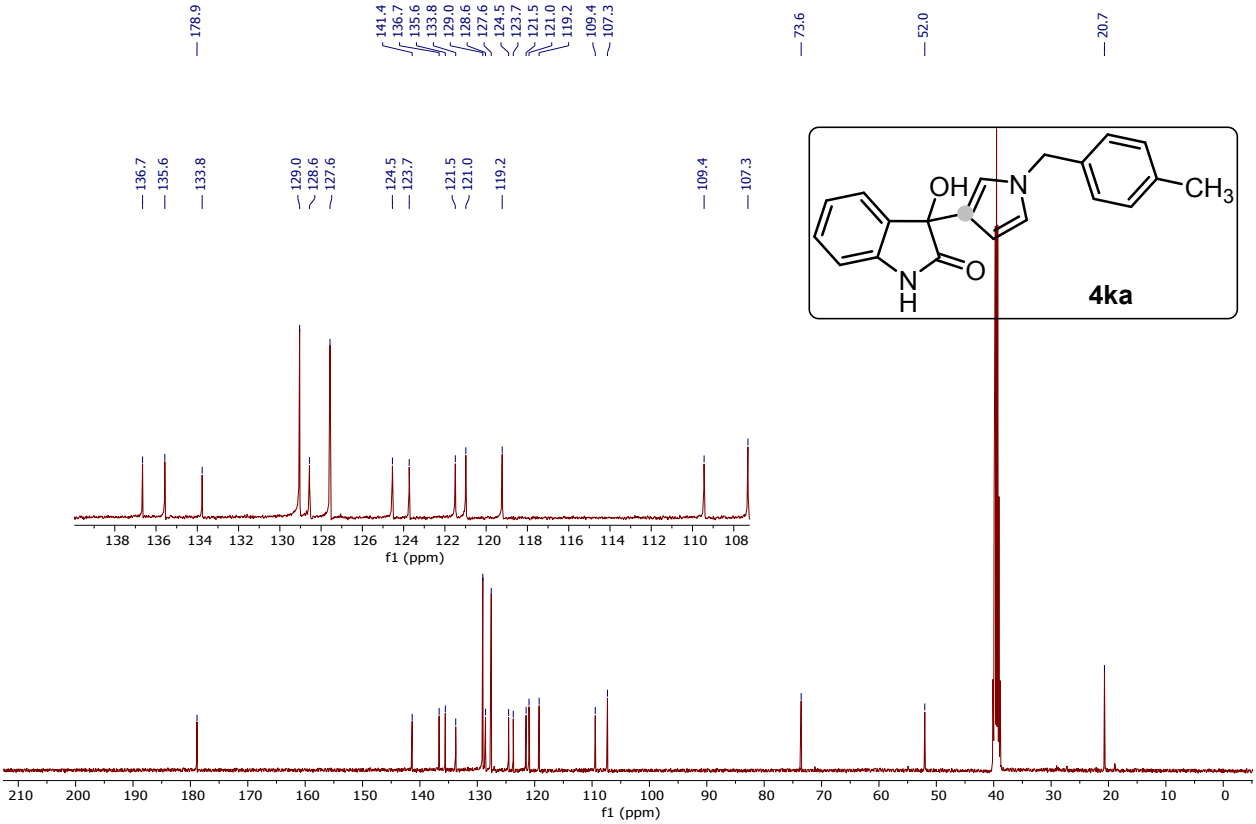

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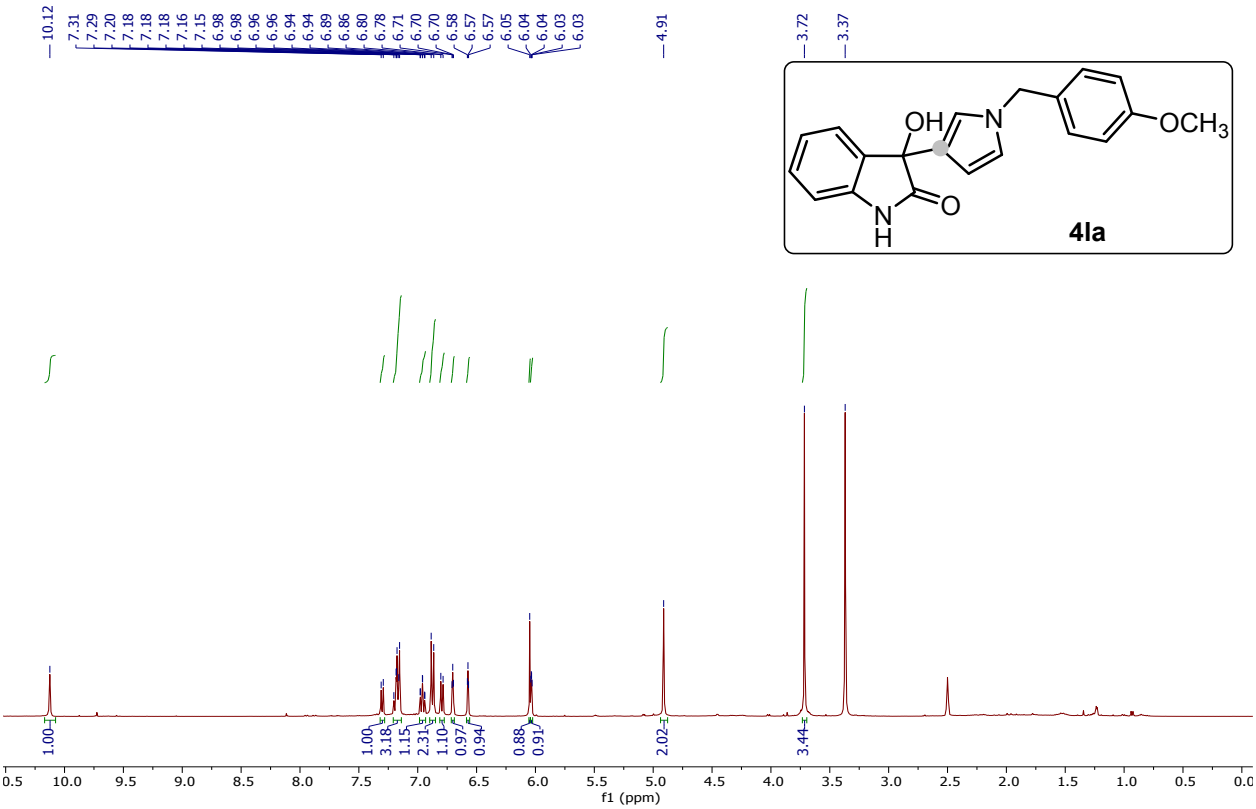

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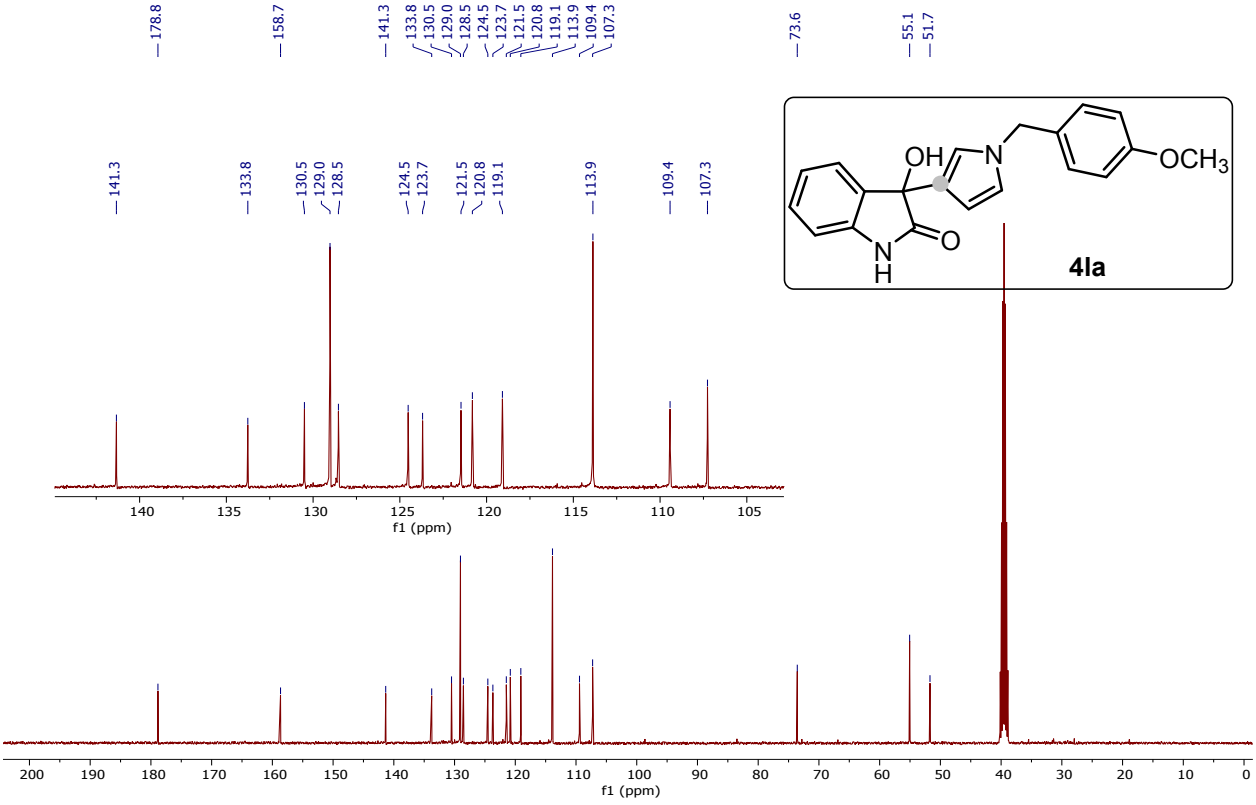
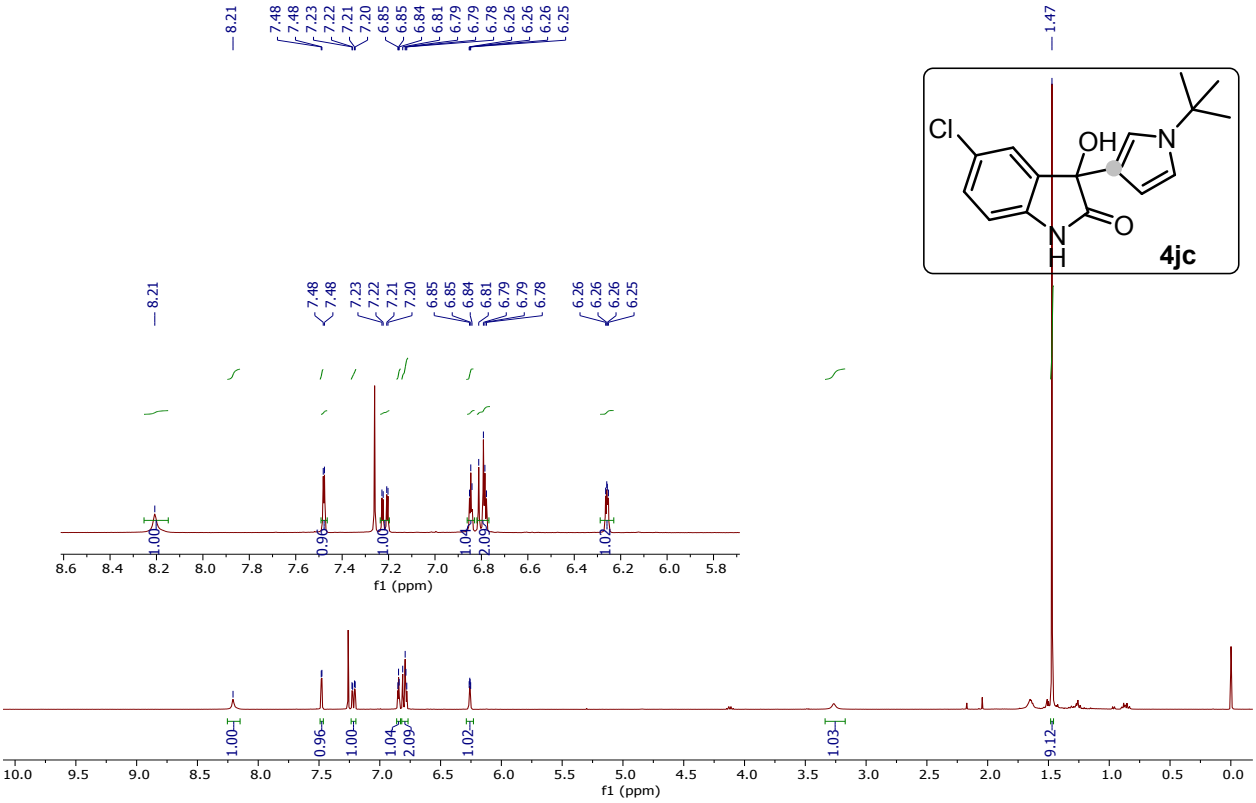
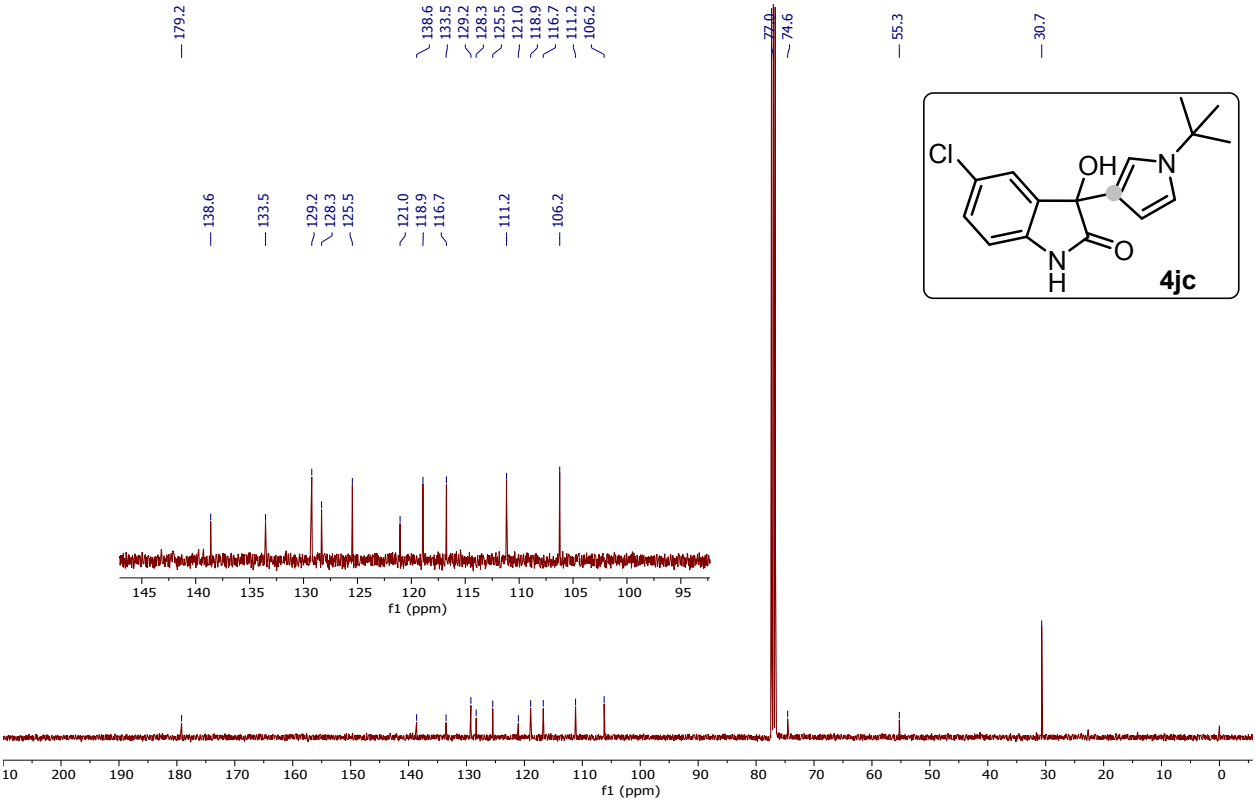


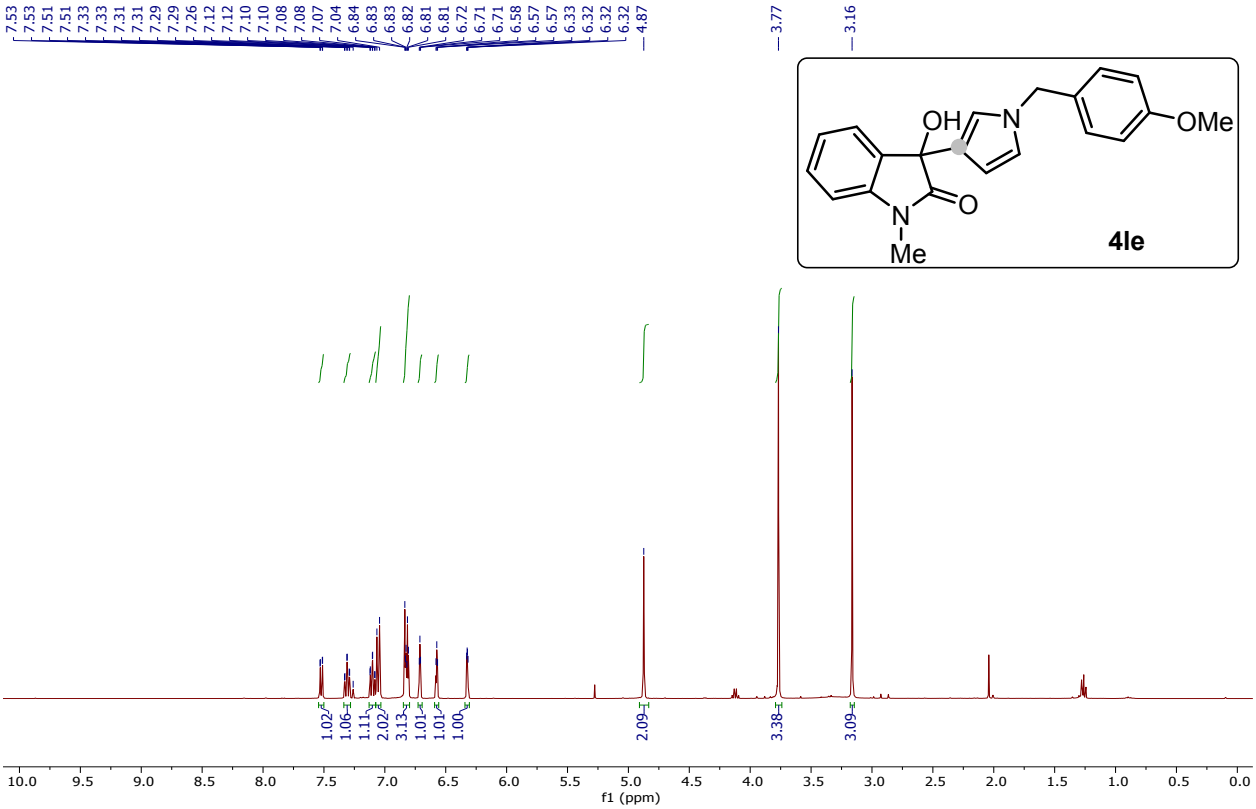
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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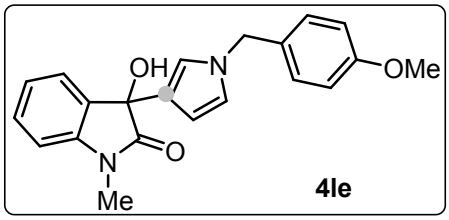
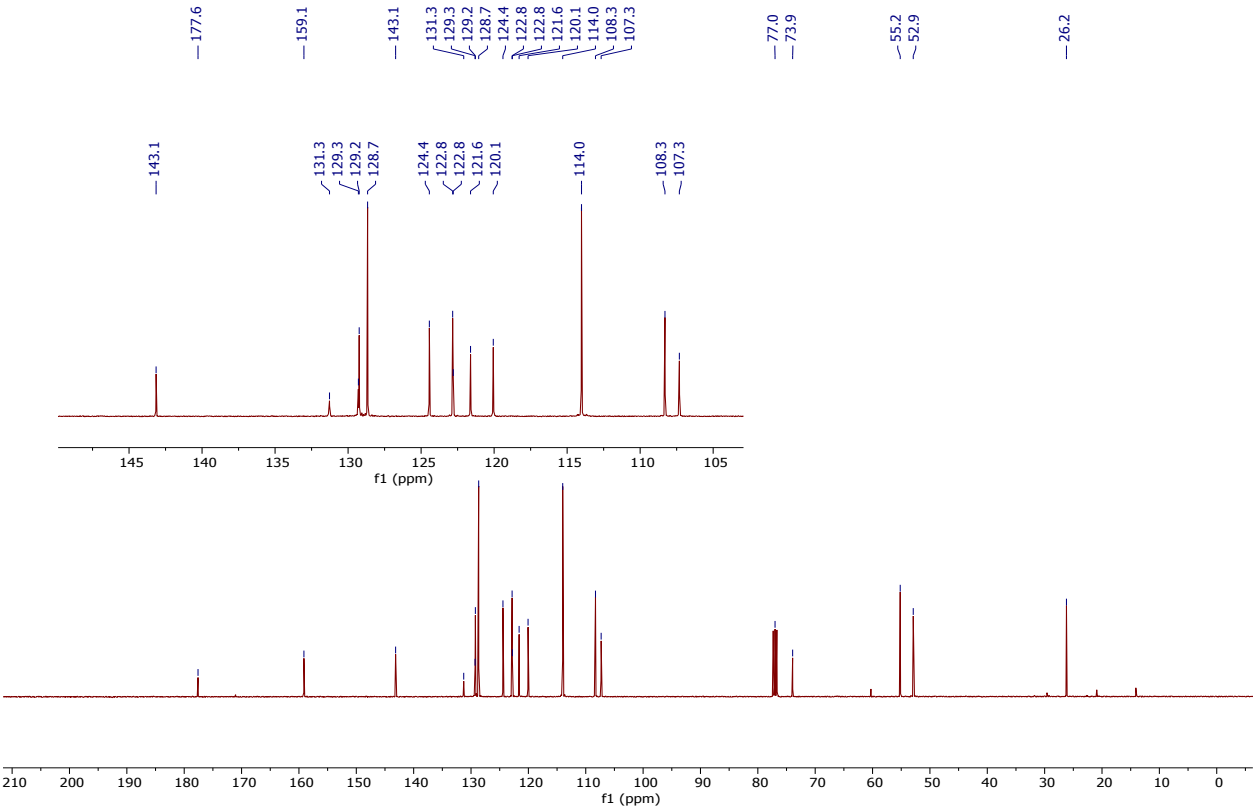
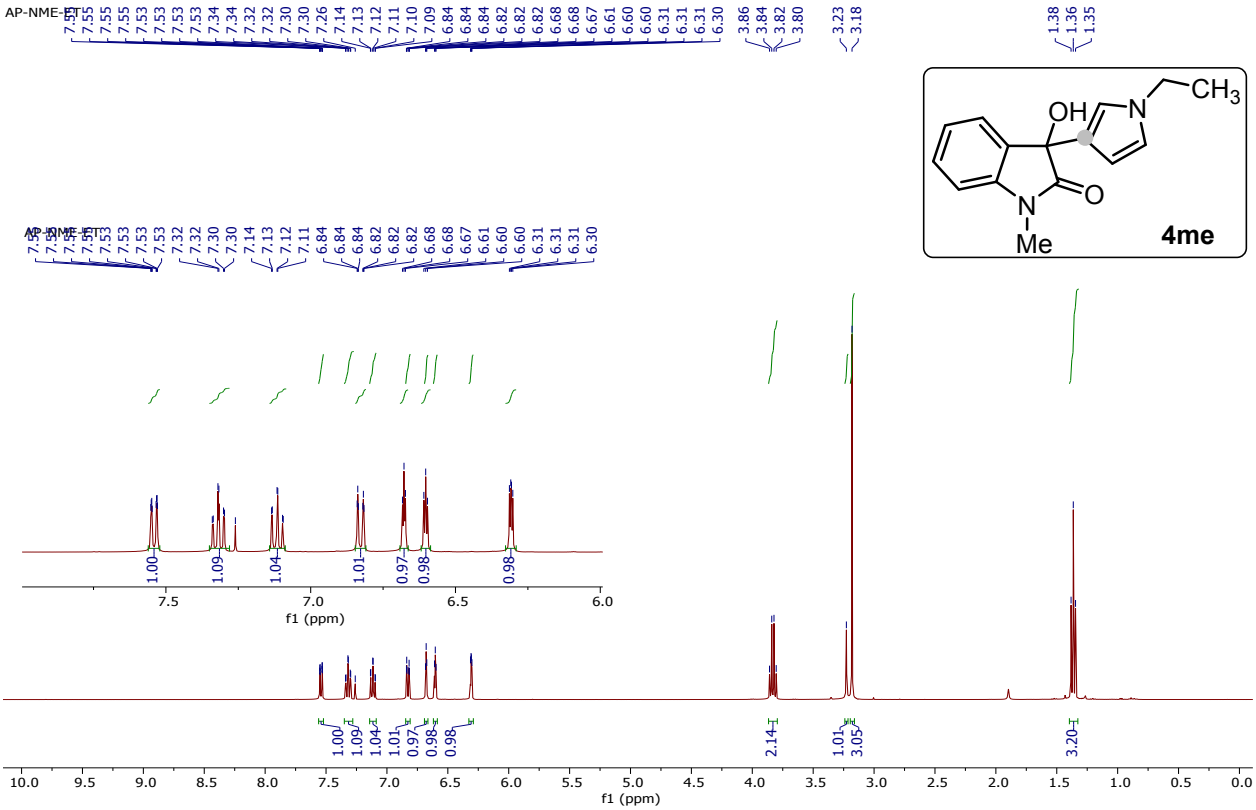
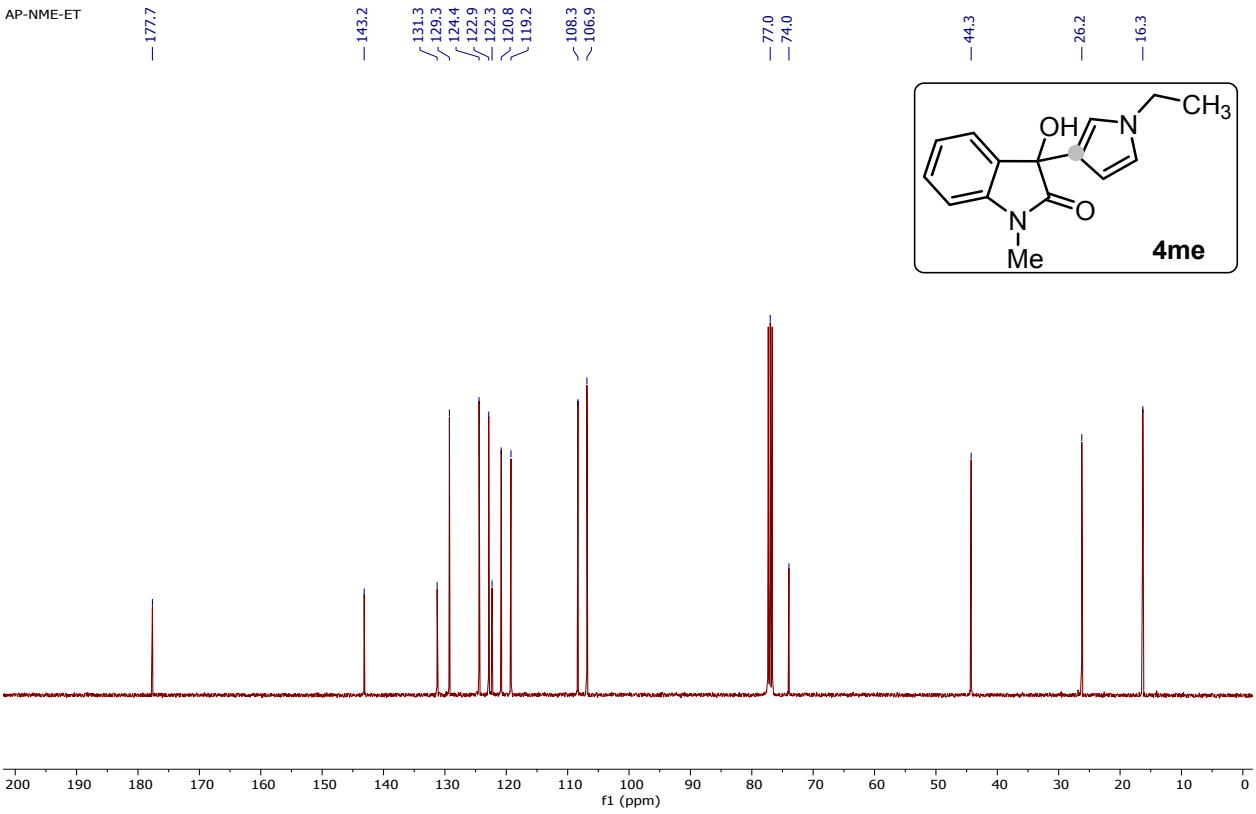




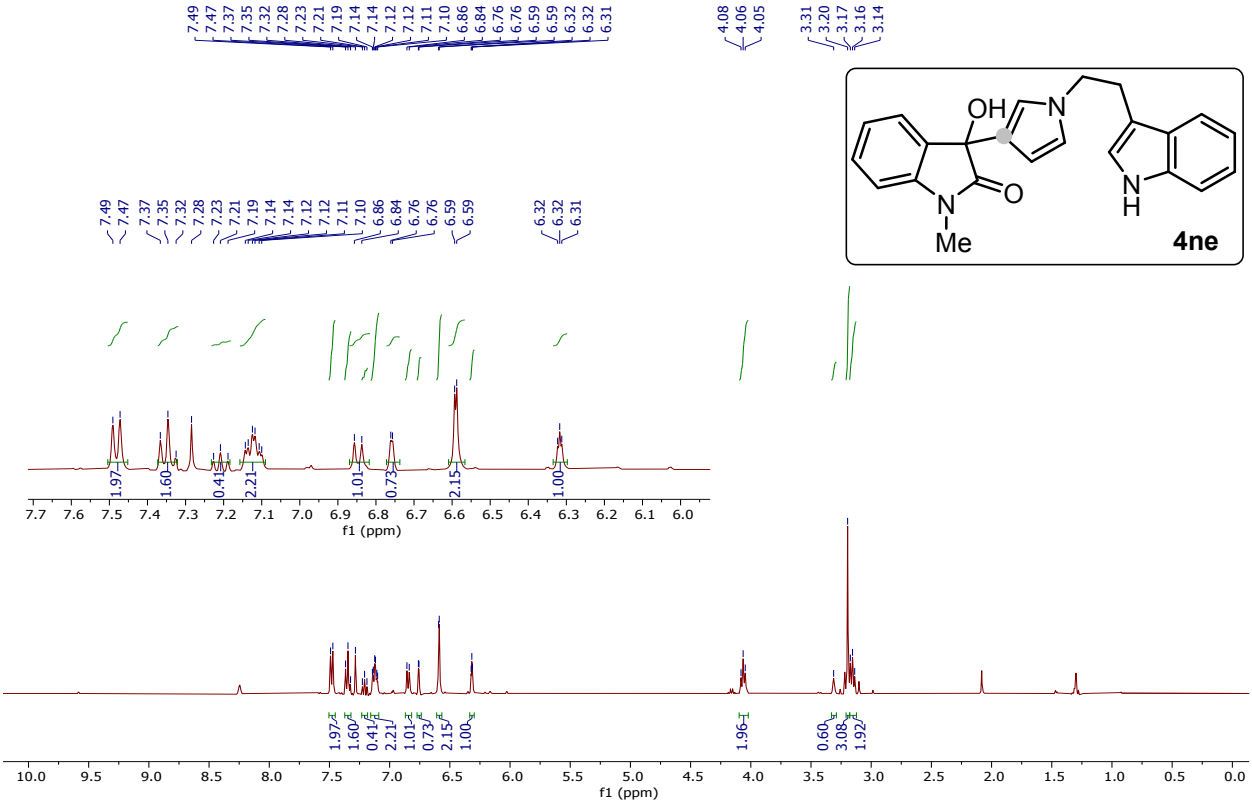
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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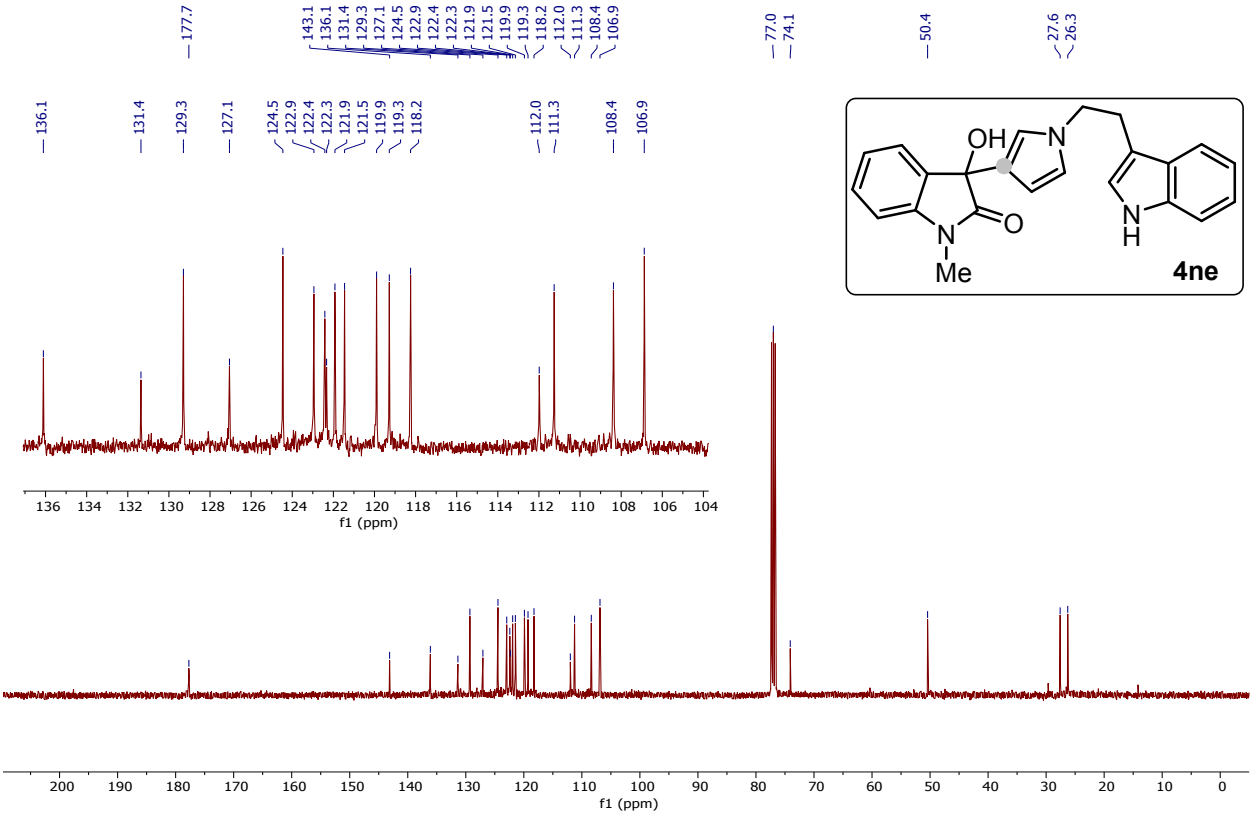

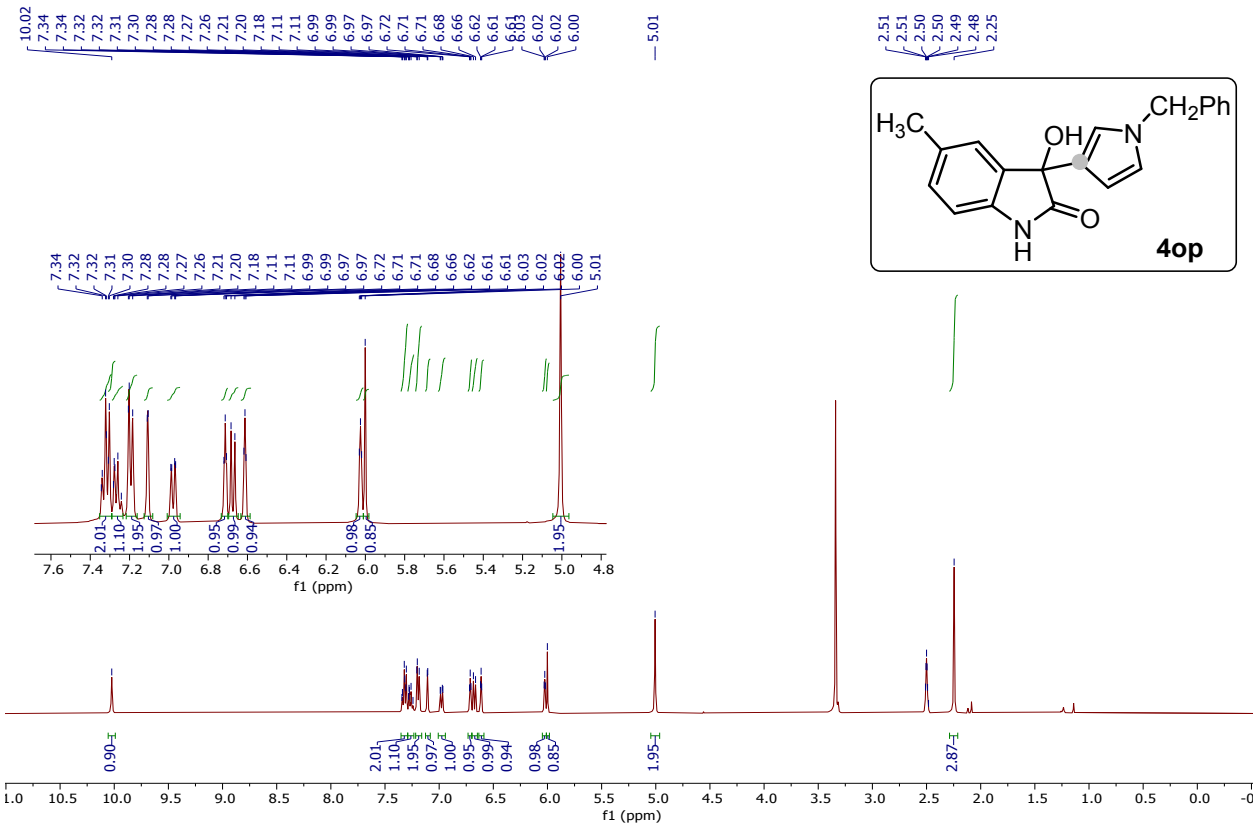
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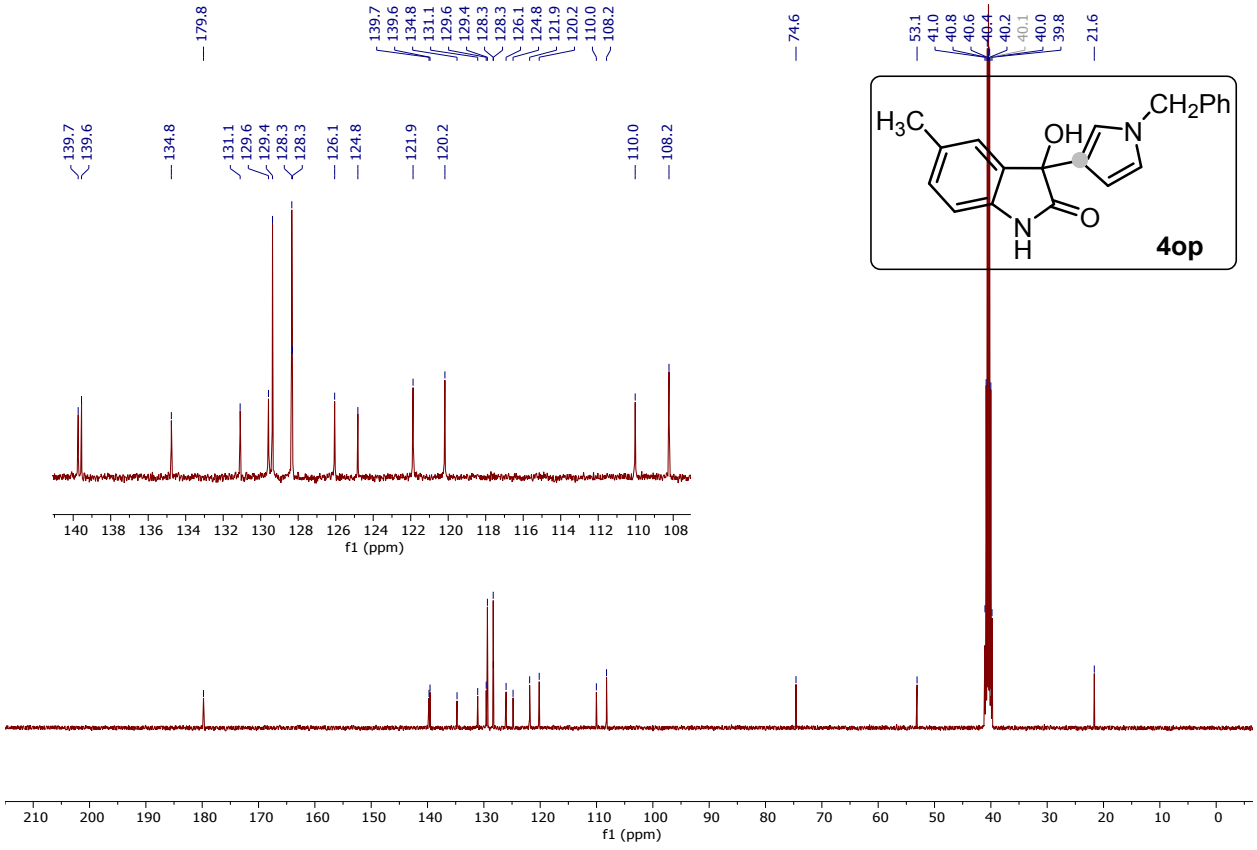
f1 (ppm)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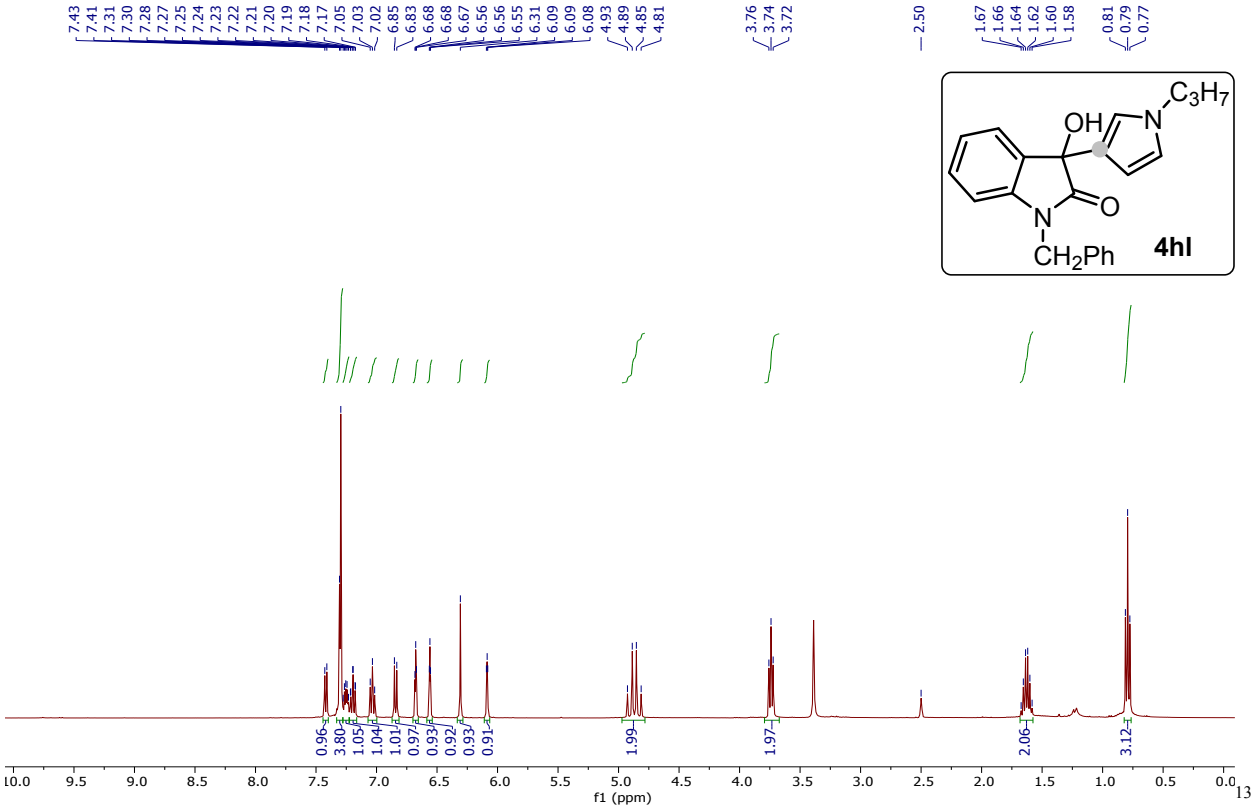
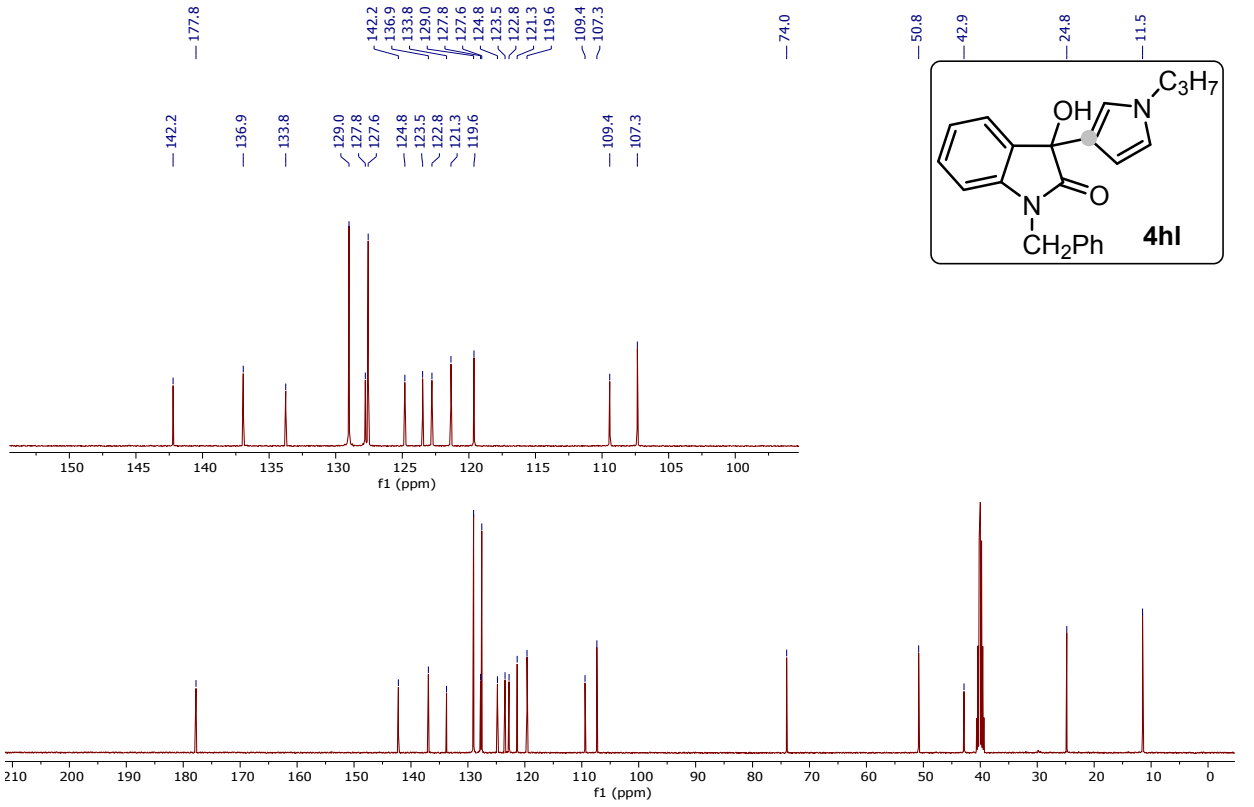
f1 (ppm)

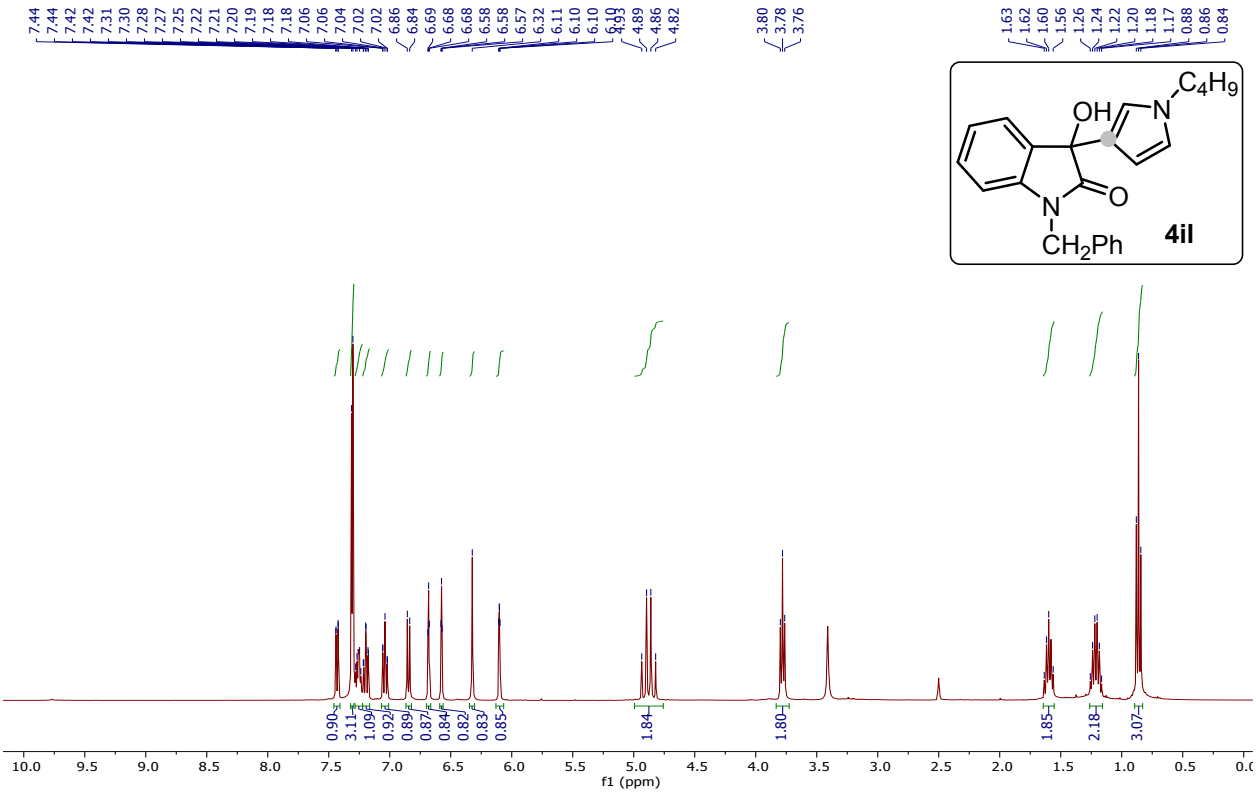
^{1}H NMR (400 MHz, DMSO-d_6)



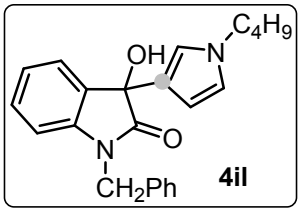
C NMR (101 MHz, DMSO-d_6)

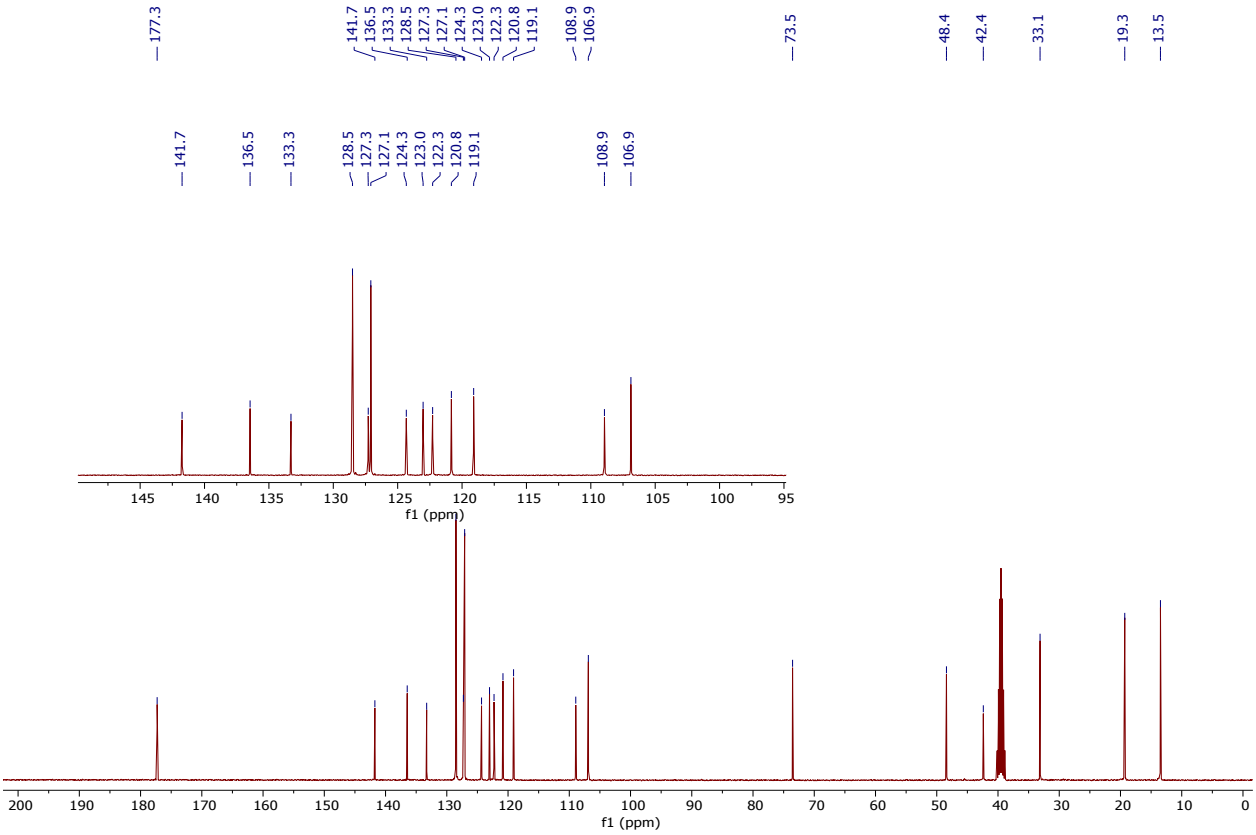


^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (101 MHz, DMSO-d_6)





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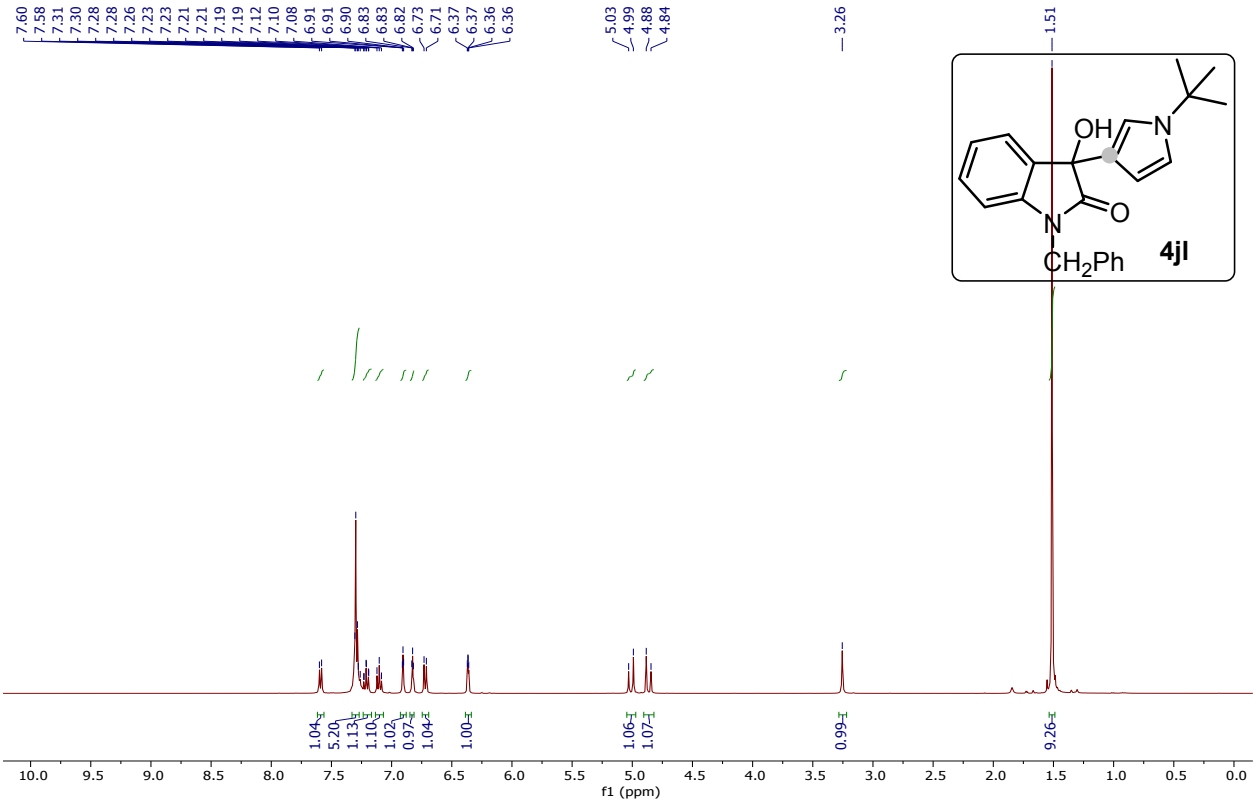
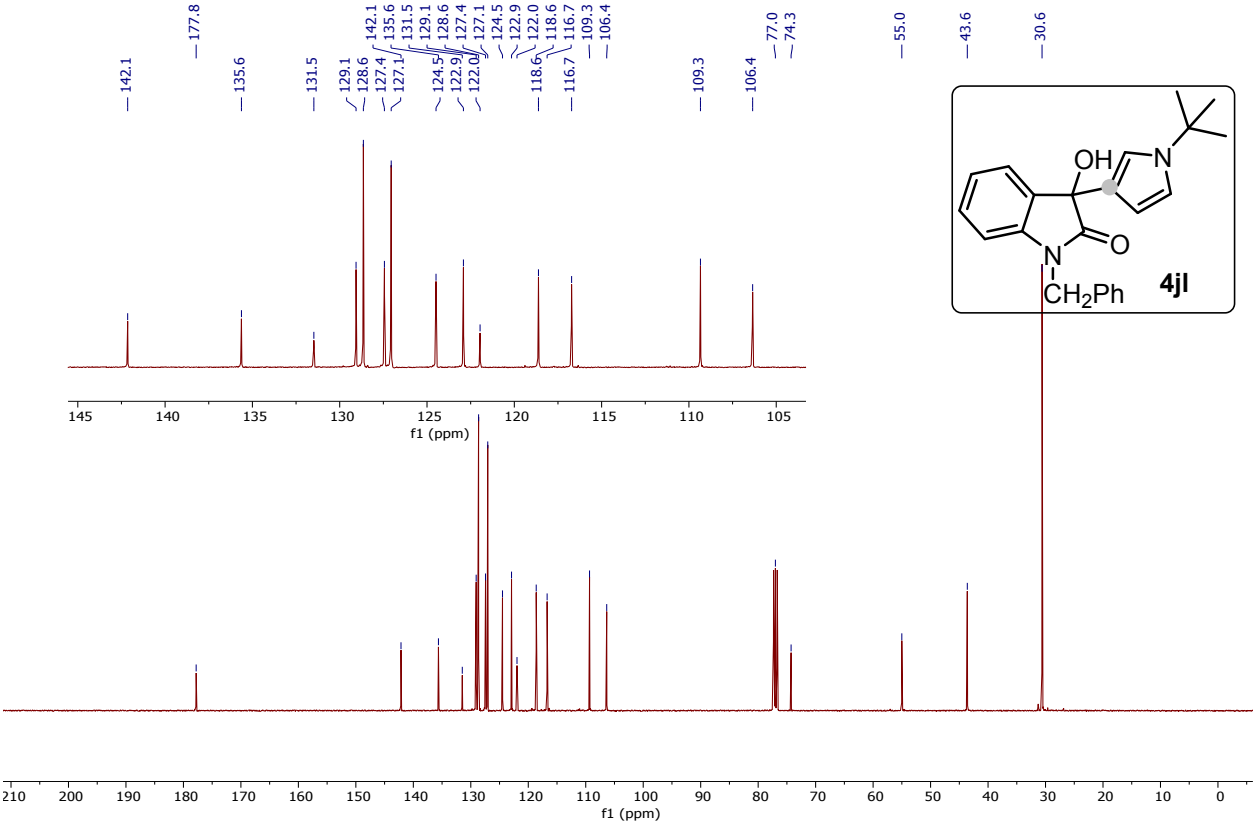
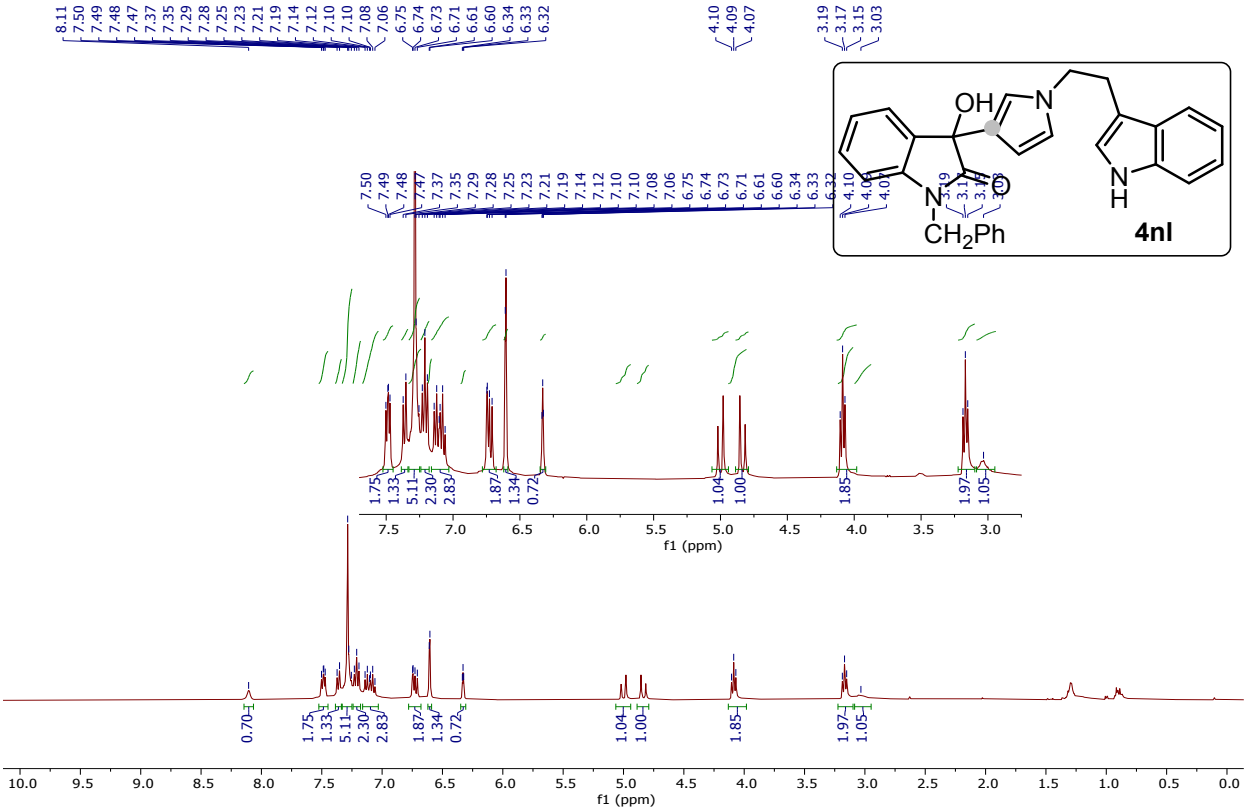


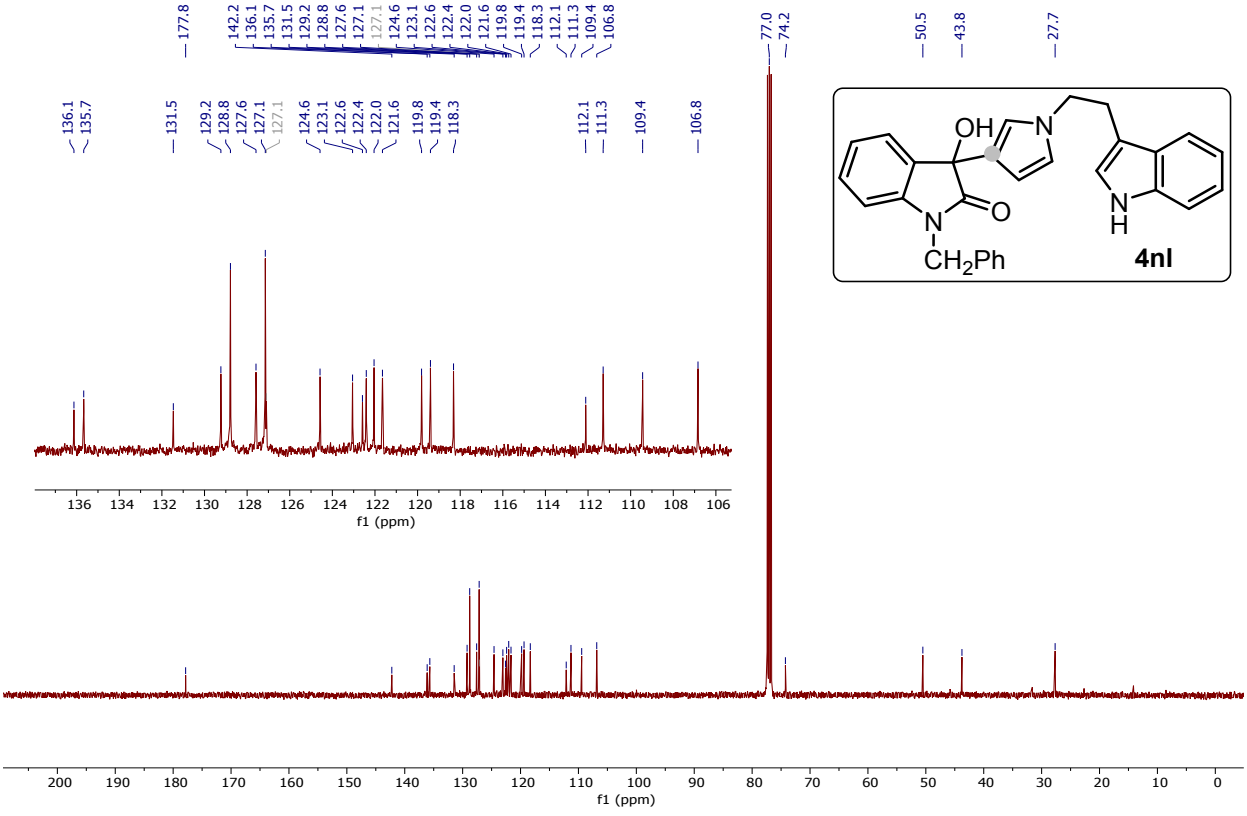
^{13}C NMR (101 MHz, $CDCl_3$)



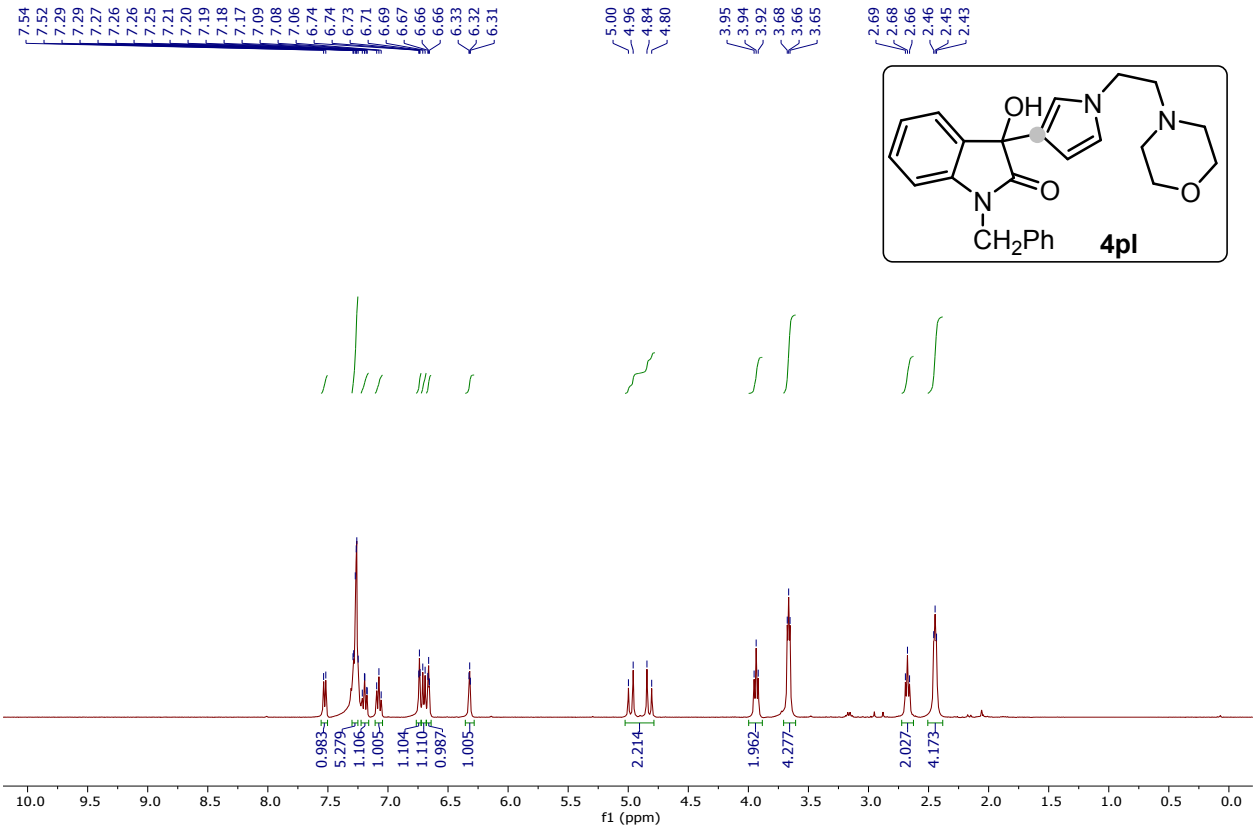
^{1}H NMR (400 MHz, $CDCl_3$)



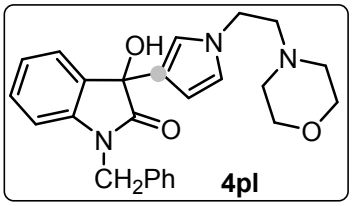
^{13}C NMR (101 MHz, $CDCl_3$)

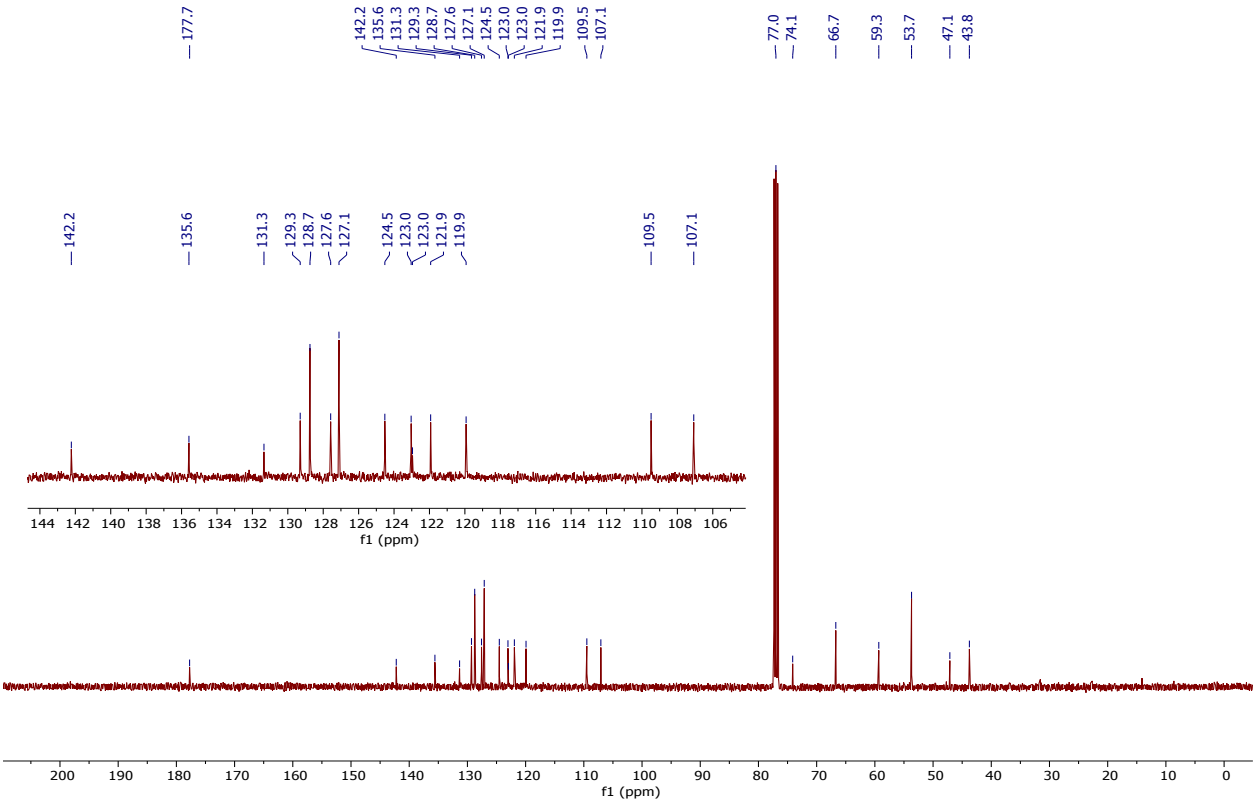


^{1}H NMR (400 MHz, $CDCl_3$)

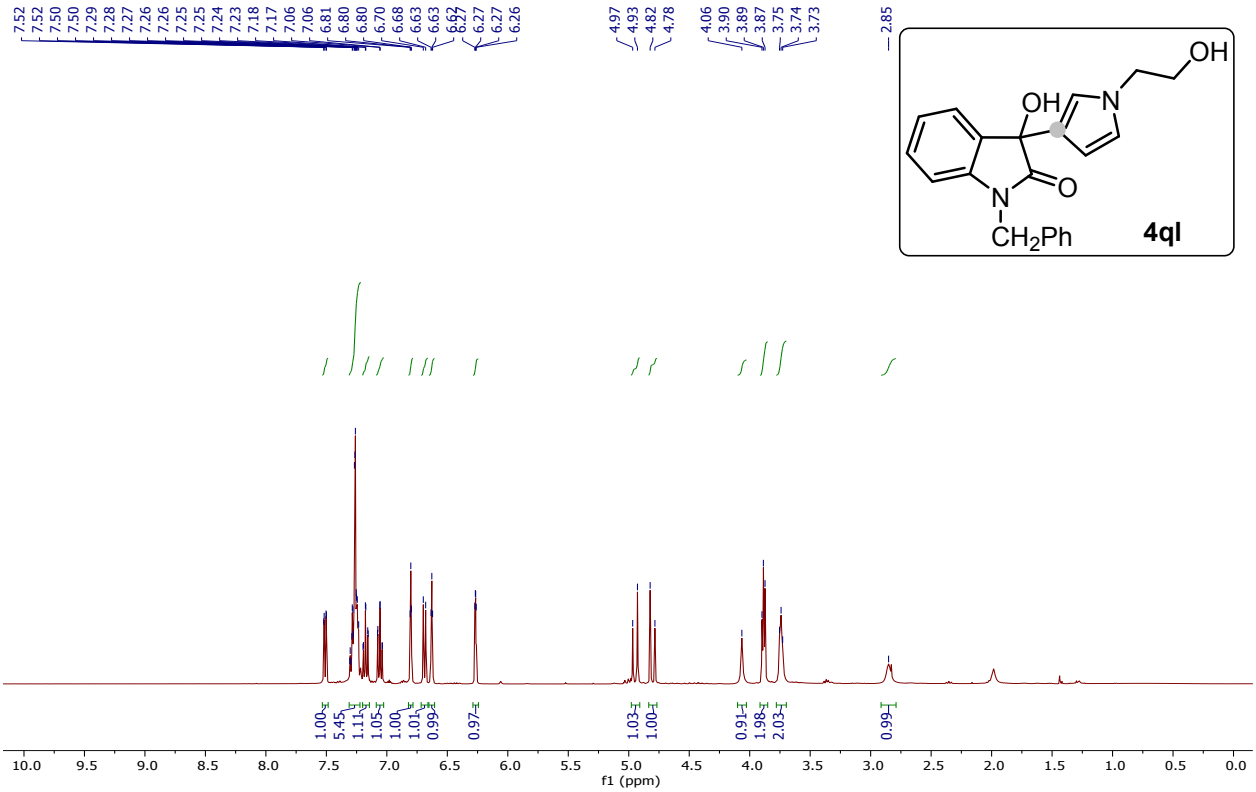


^{13}C NMR (101 MHz, $CDCl_3$)

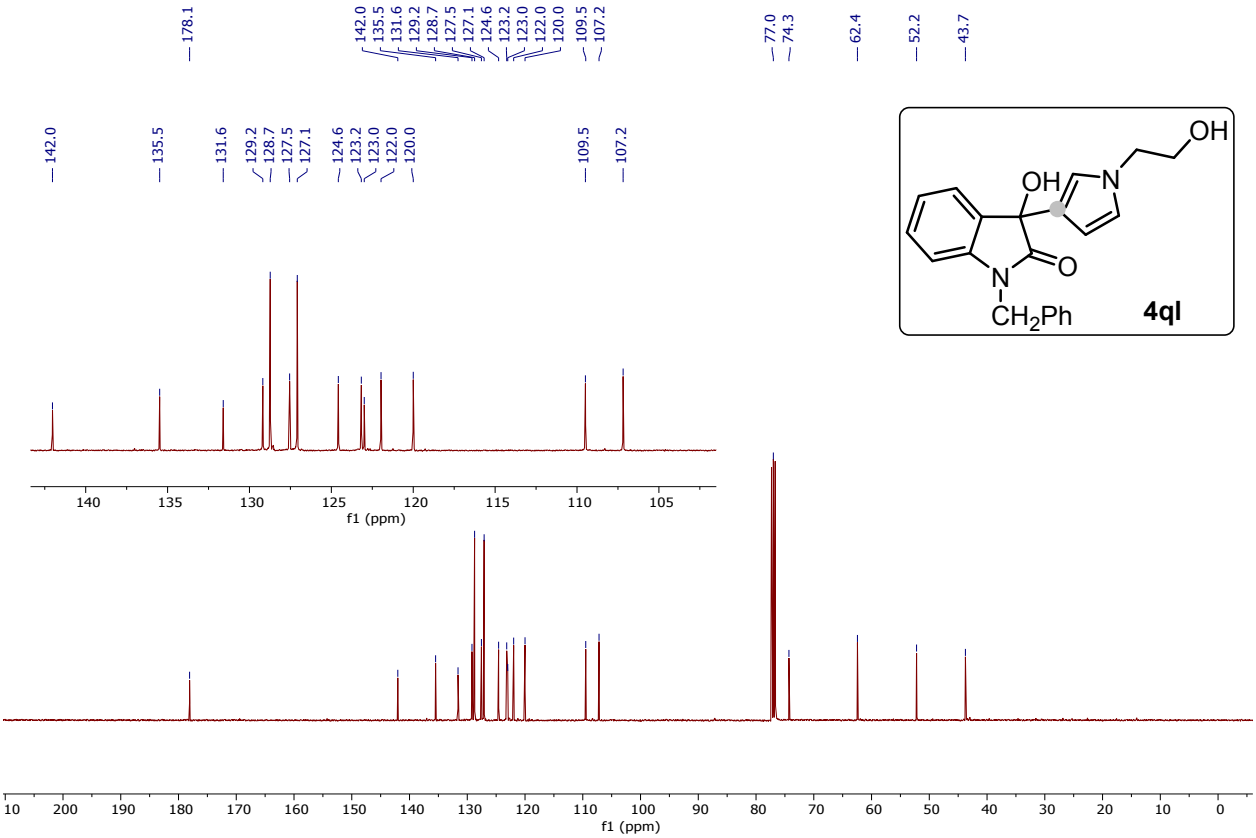




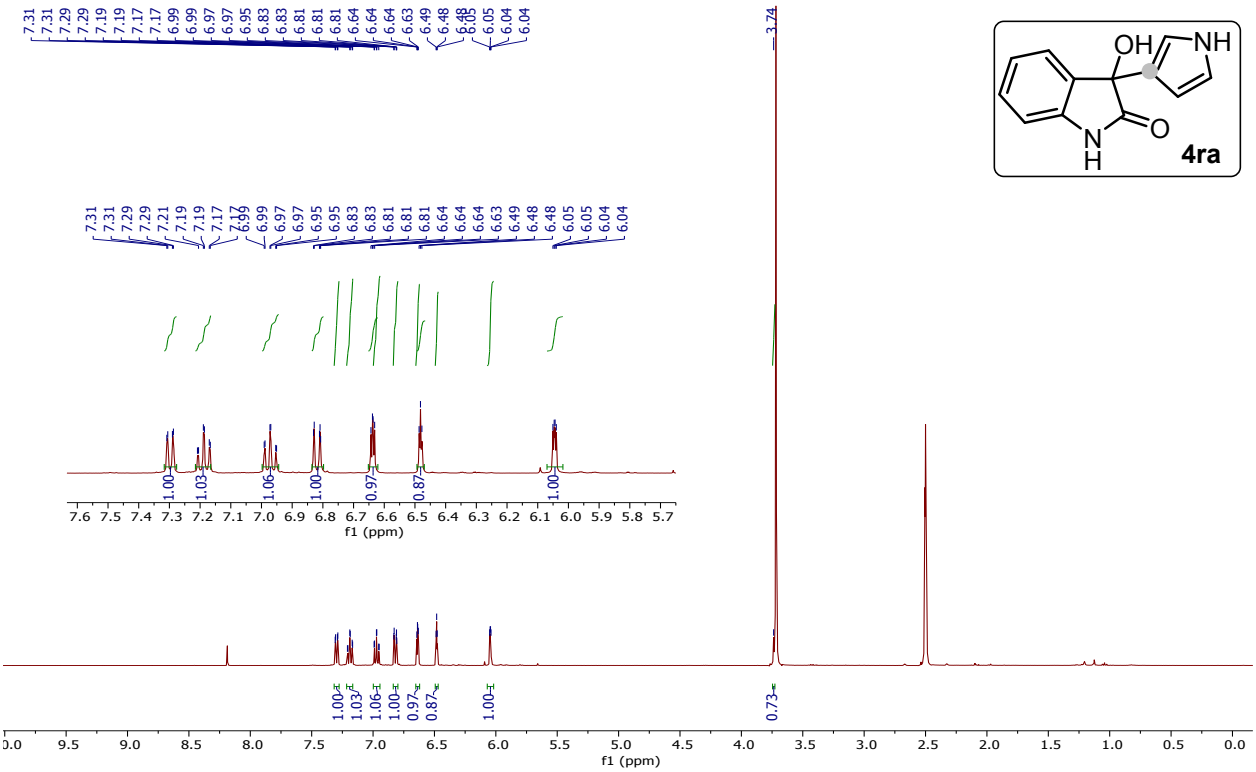
^{1}H NMR (400 MHz, $CDCl_3$)



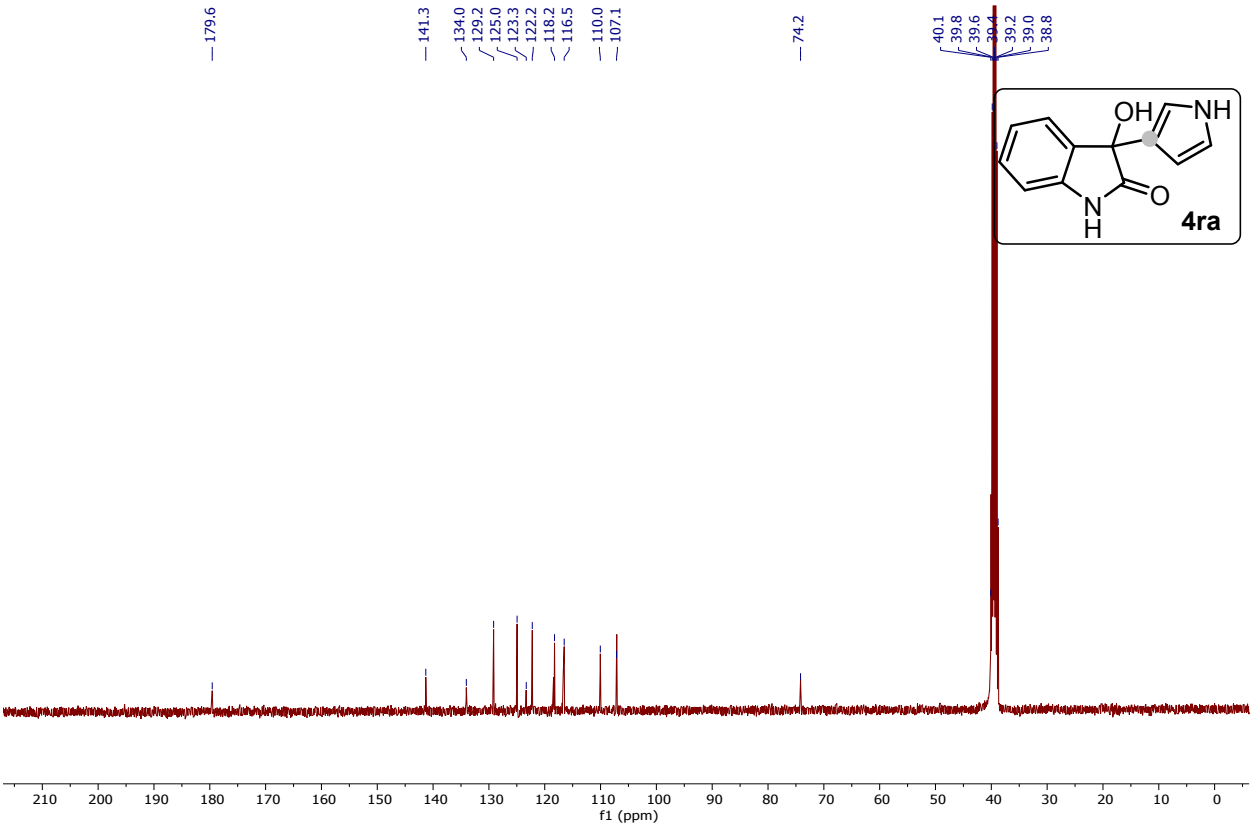
^{13}C NMR (101 MHz, $CDCl_3$)

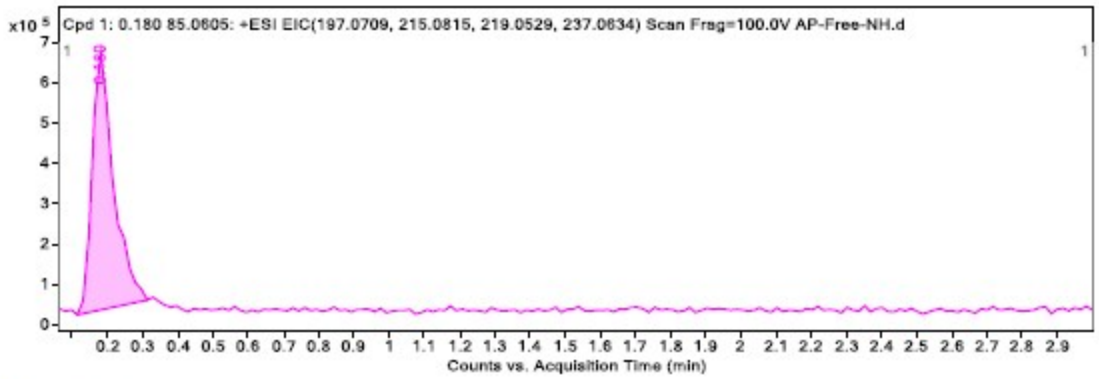


^{1}H NMR (400 MHz, DMSO-d_6)

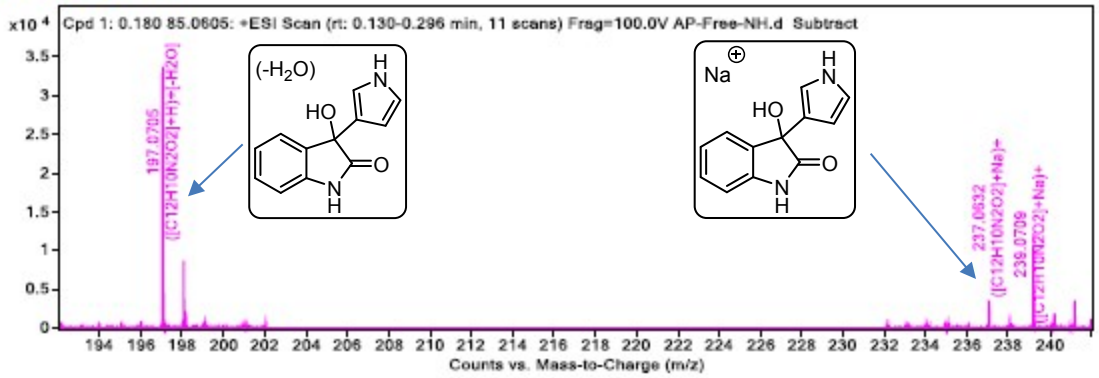


^{13}C NMR (101 MHz, DMSO-d_6)





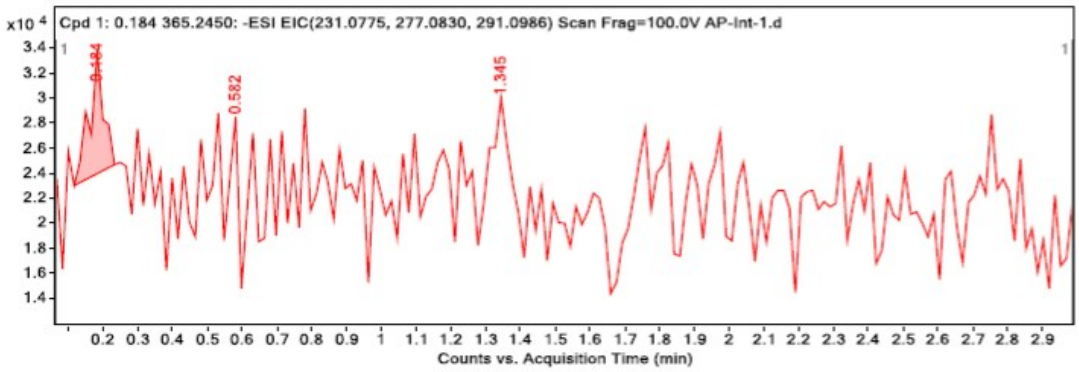
MS Zoomed Spectrum



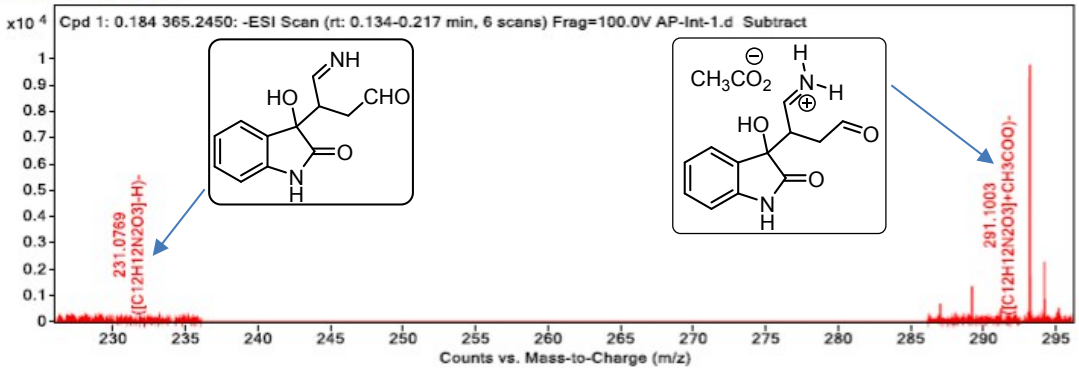
MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
197.0705	197.0709	2.23	1	34149.23	C12H10N2O2	(M+H)+[-H2O]
237.0632	237.0634	0.84	1	3659.85	C12H10N2O2	(M+Na)+
238.068	238.0665	-6.34	1	1073.82	C12H10N2O2	(M+Na)+
239.0709	239.0689	-8.19	1	230.72	C12H10N2O2	(M+Na)+

Chemical Formula: $C_{12}H_{11}N_2O_3$ Exact Mass: 231.0775
In Negative mode ESI With CH_3COO^-



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
231.0769	231.0775	2.85	1	164.29	C12H12N2O3	(M-H)-
291.1003	291.0986	-5.69	1	158.21	C12H12N2O3	(M+CH3COO)-

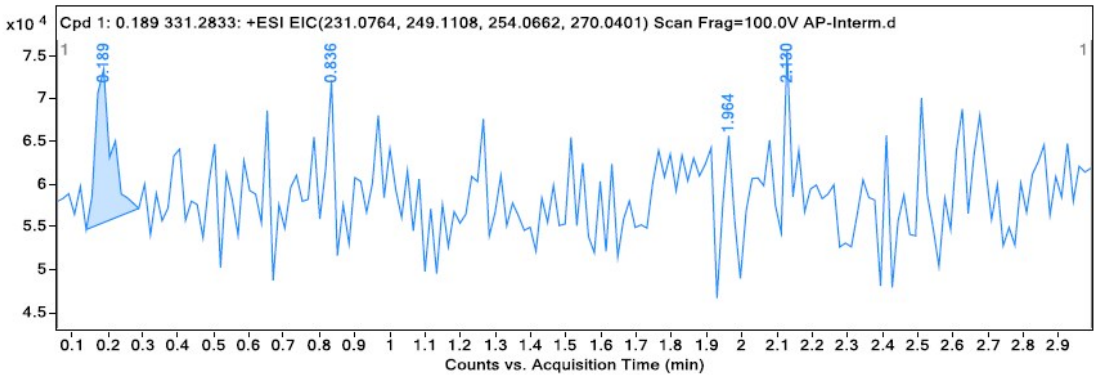
Instrument Info : Agilent Technologies 6545 Q-TOF LC/MS

Chemical Formula: $C_{12}H_{11}N_2O_3$Exact Mass: 231.0775
In Positive Mode ESI NH_4^+

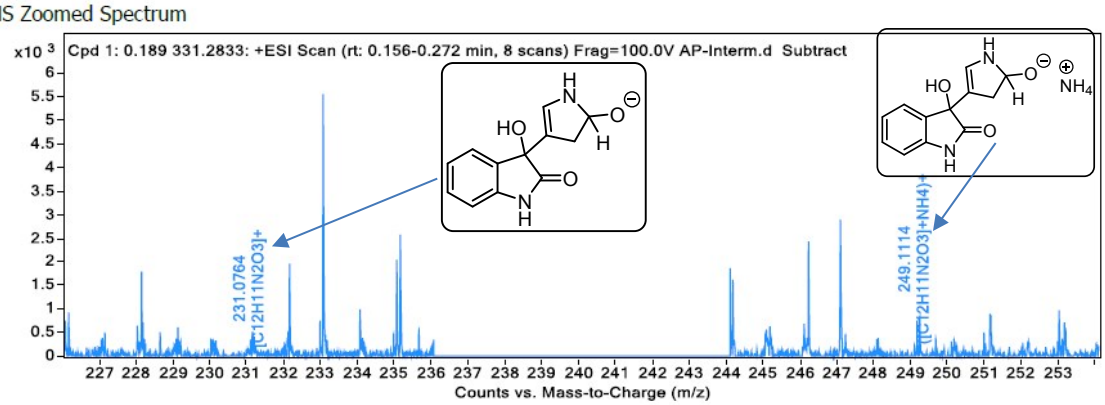
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 0.189 331.2833	0.189	231.0774	119	C12 H11 N2 O3	231.077	1.71

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: 0.189 331.2833	231.0764	0.189	Find By Formula	231.0774



MS Zoomed Spectrum

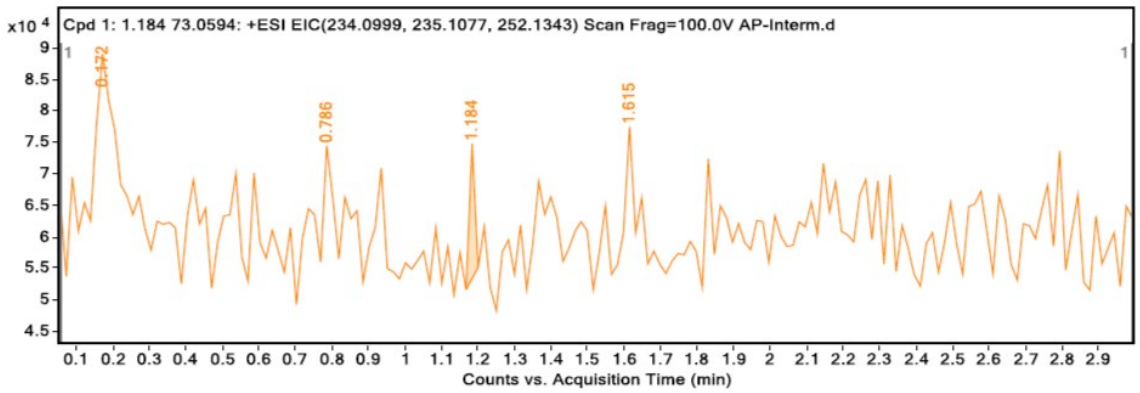


MS Spectrum Peak List

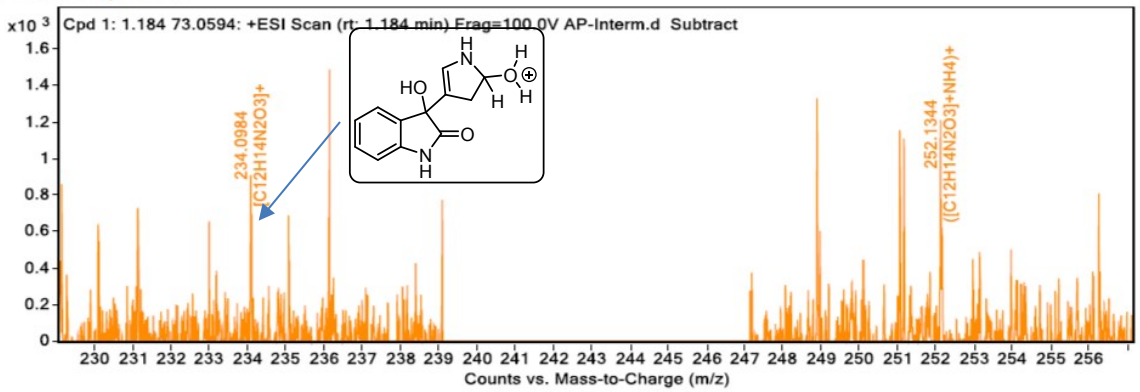
m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
231.0764	231.0764	-0.08	1	119.08	C12H11N2O3	M+
249.1114	249.1108	-2.52	1	191.85	C12H11N2O3	(M+NH4)+

Exact Mass: 234.0993 Chemical Formula: $C_{12}H_{14}N_2O_3^{2+}$

In Positive Mode ESI NH_4^+



MS Zoomed Spectrum

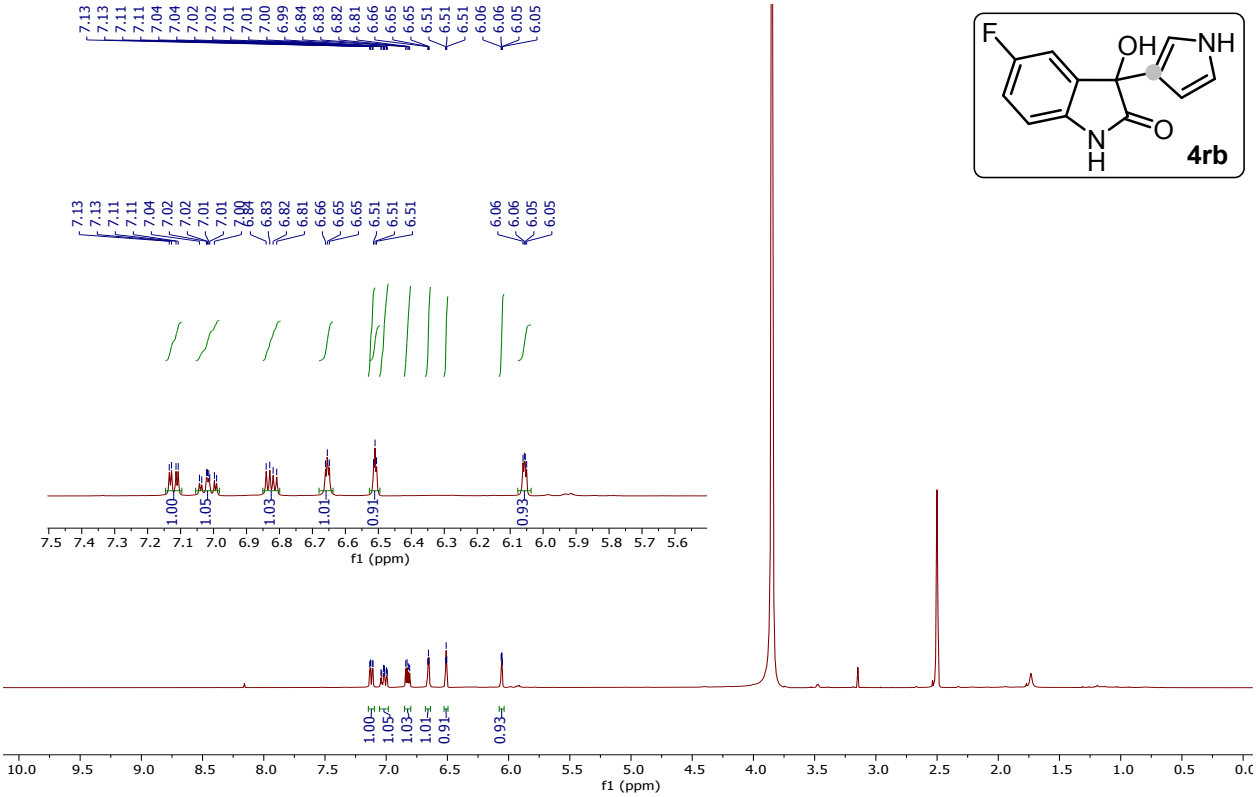


MS Spectrum Peak List

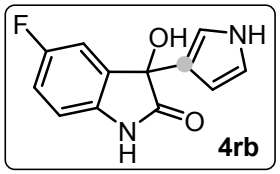
m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
234.0984	234.0999	6.43	1	721.2	C12H14N2O3	M+
252.1344	252.1343	-0.4	1	778.63	C12H14N2O3	(M+NH4)+

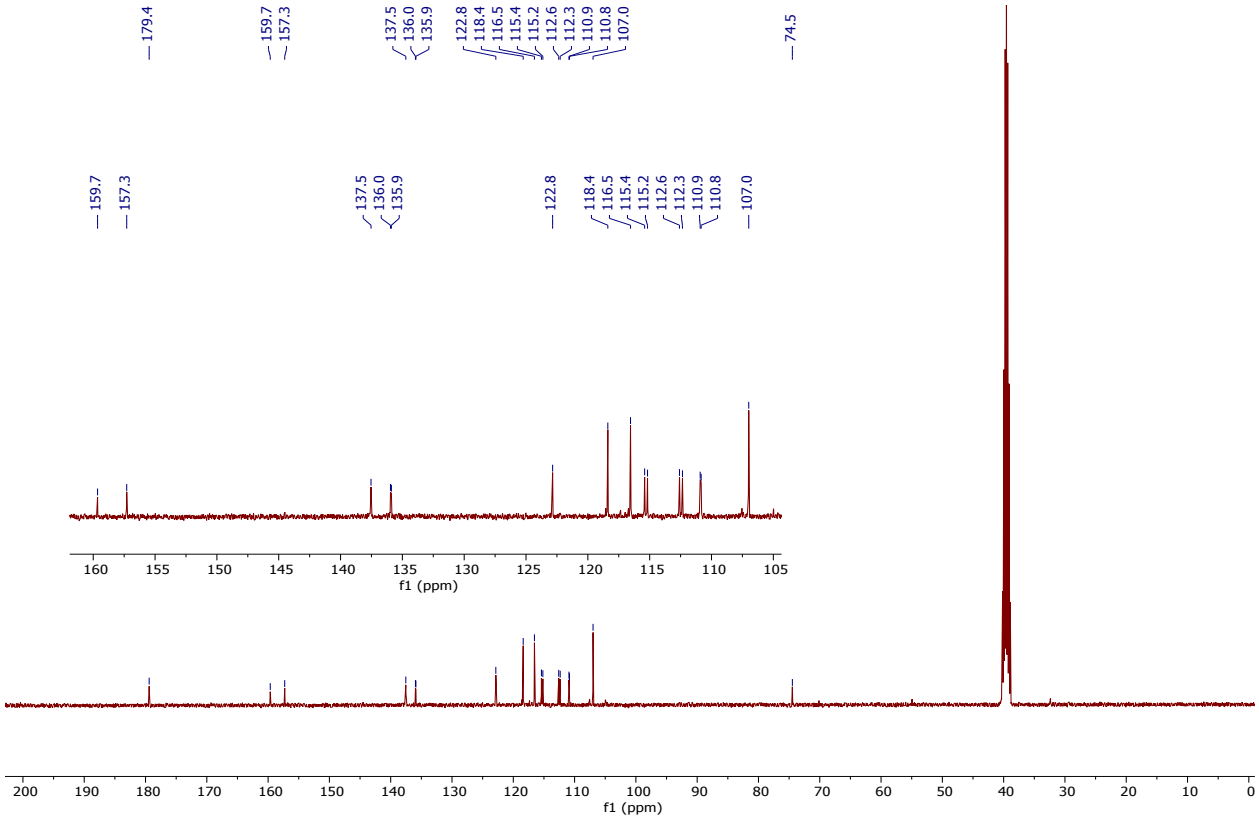
Instrument Info : Agilent Technologies 6545 Q-TOF LC/MS

^{1}H NMR (400 MHz, DMSO-d_6)

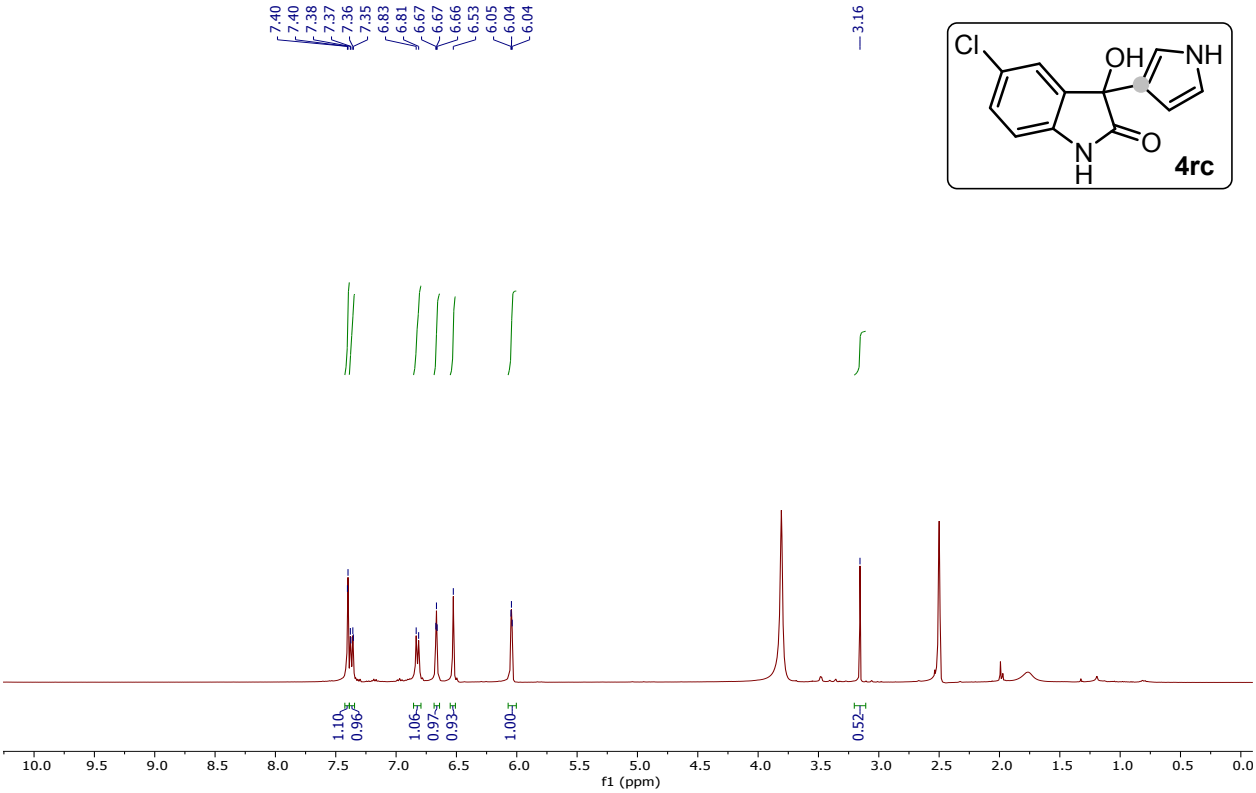


^{13}C NMR (101 MHz, DMSO-d_6)

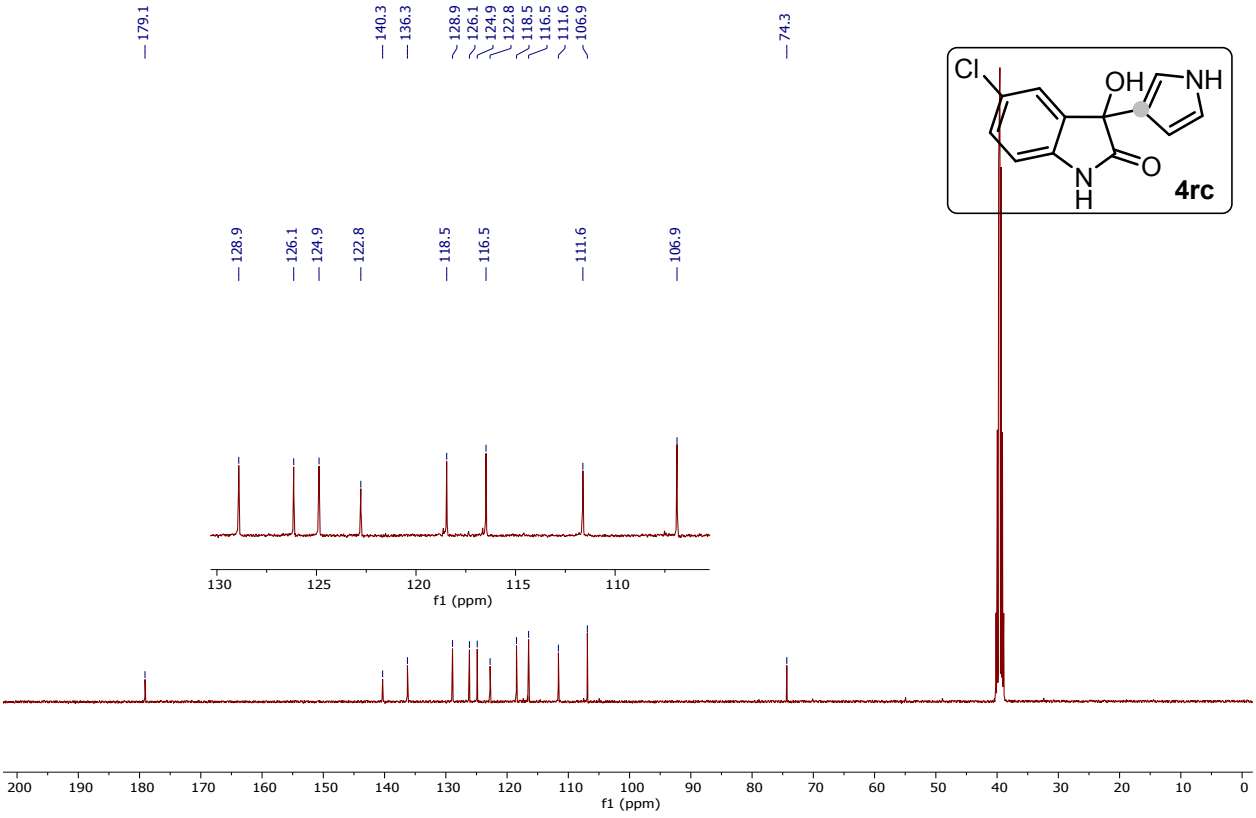



179.4
159.7
157.3
137.5
136.0
135.9
122.8
118.4
116.5
115.4
115.2
112.6
112.3
110.9
110.8
107.0
74.5
f1 (ppm)

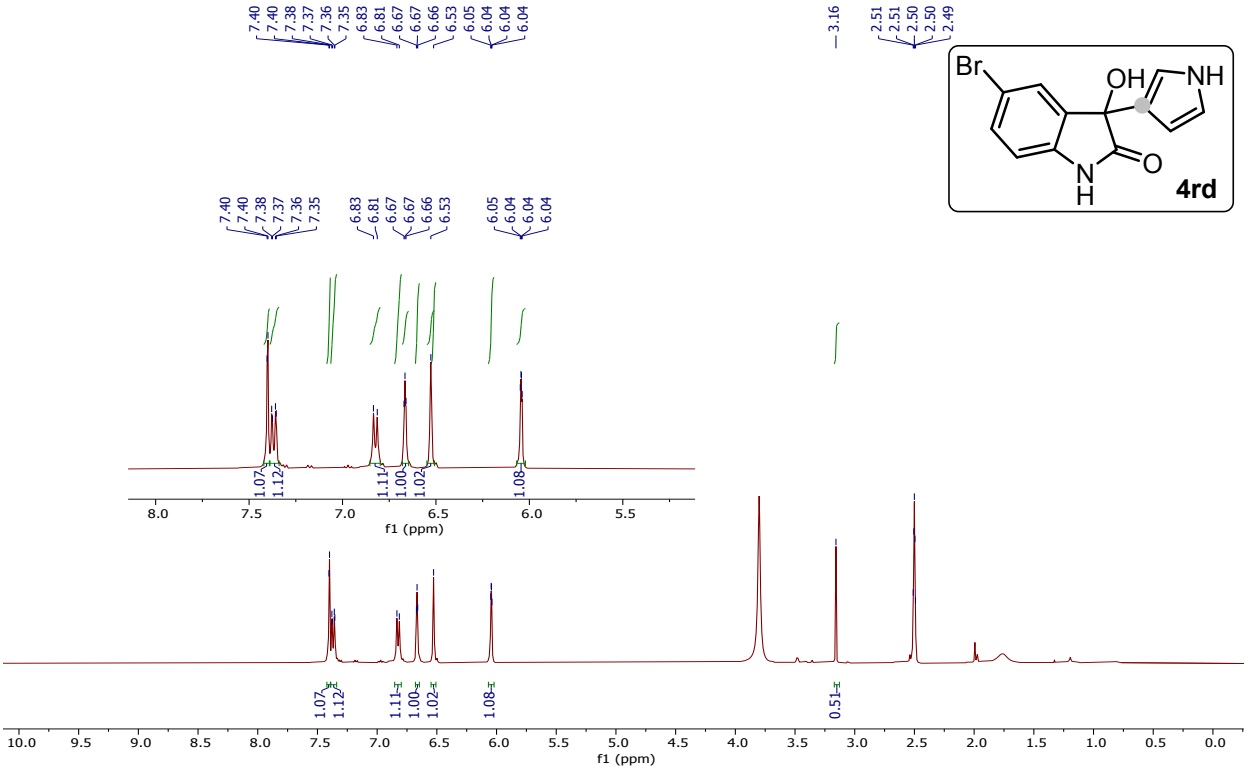
^{1}H NMR (400 MHz, DMSO-d_6)



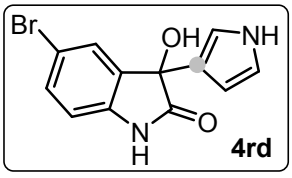
^{13}C NMR (101 MHz, DMSO-d_6)

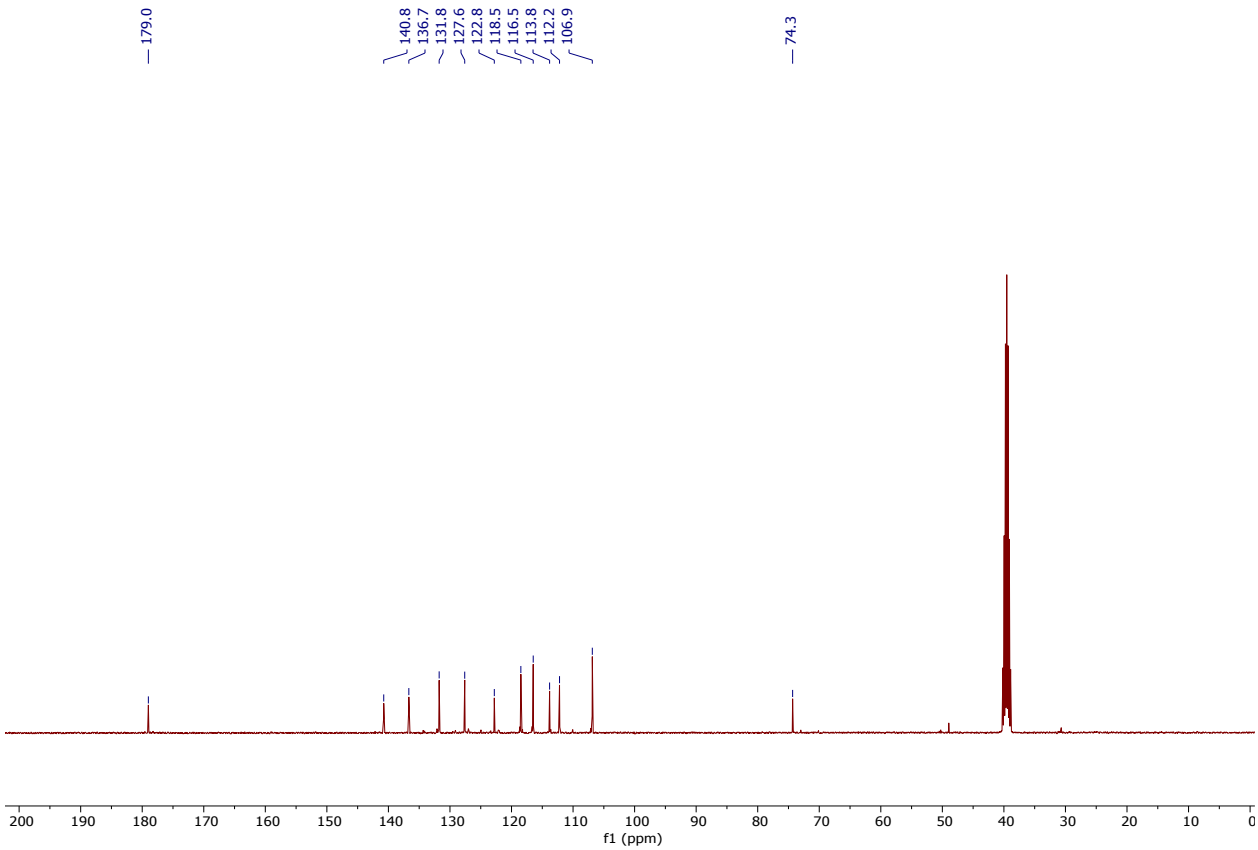


^{1}H NMR (400 MHz, DMSO-d_6)

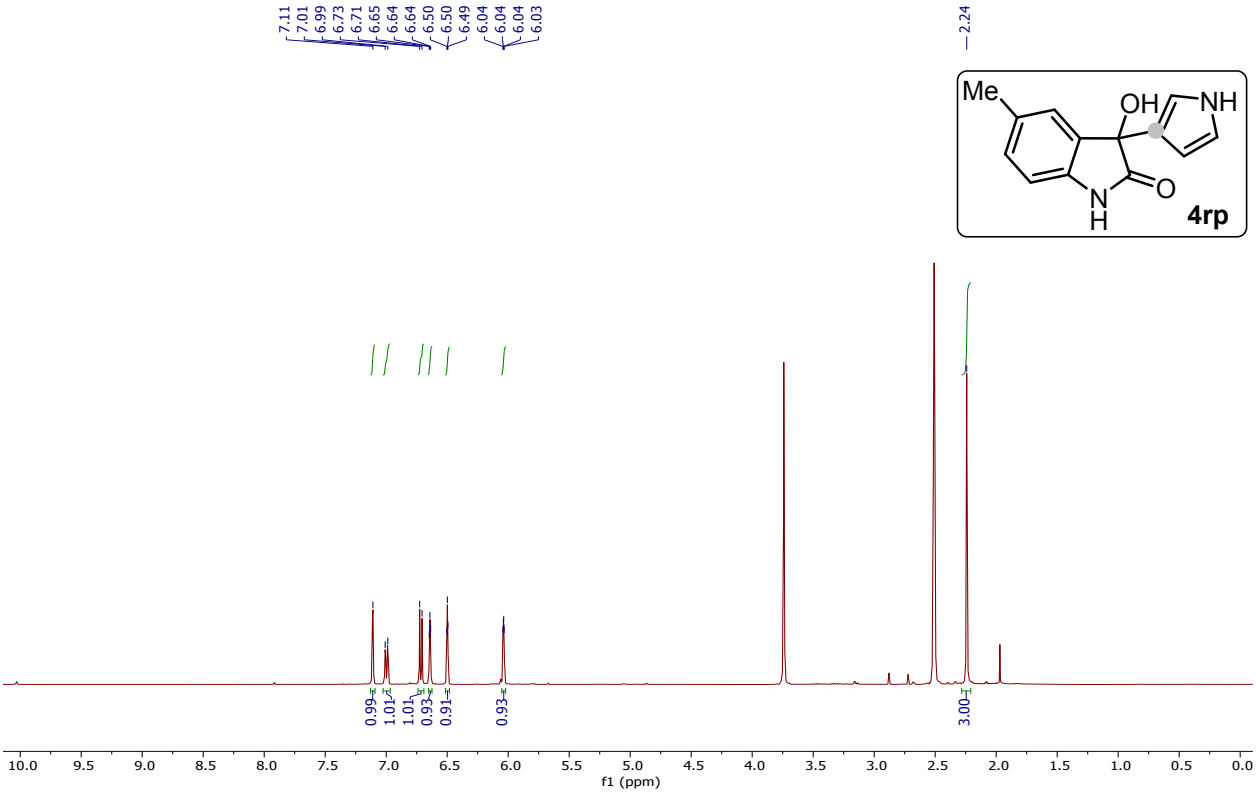


^{13}C NMR (101 MHz, DMSO-d_6)

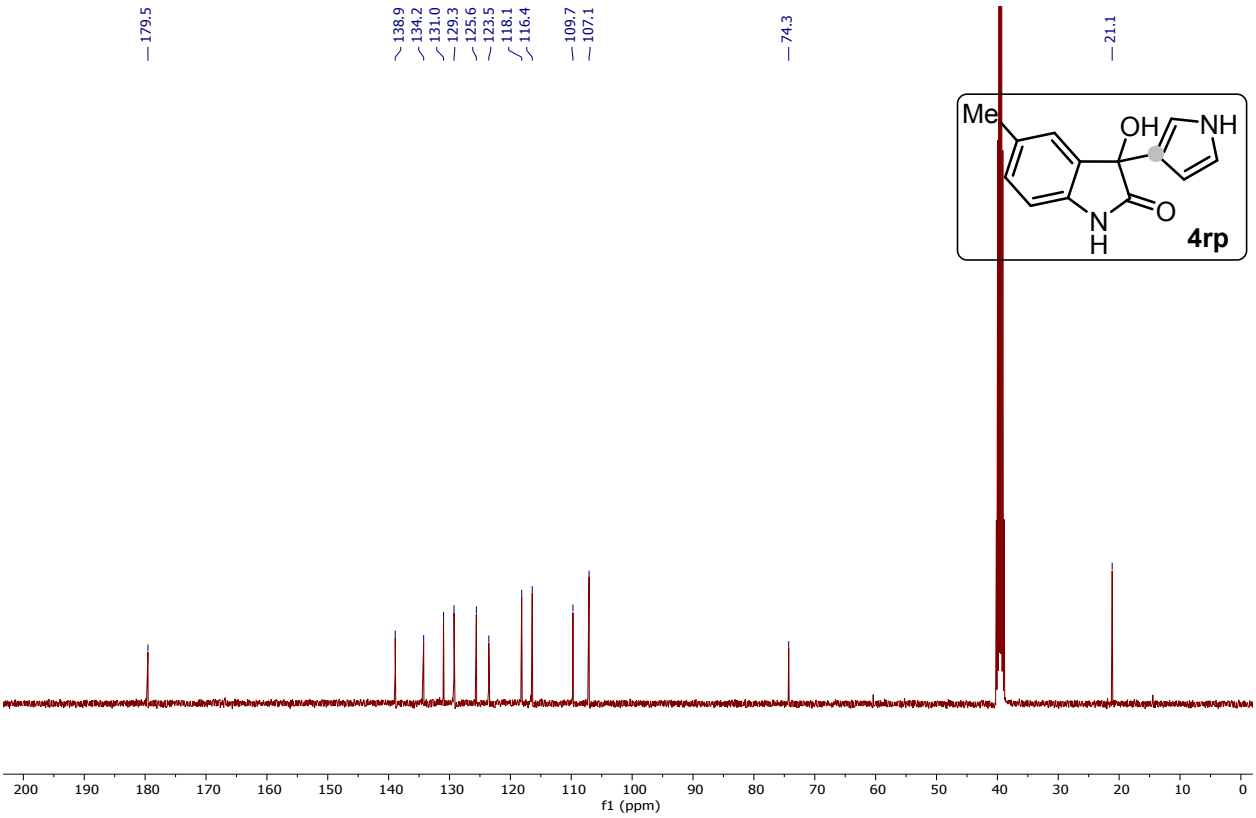



179.0
140.8
136.7
131.8
127.6
122.8
118.5
116.5
113.8
112.2
106.9
74.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

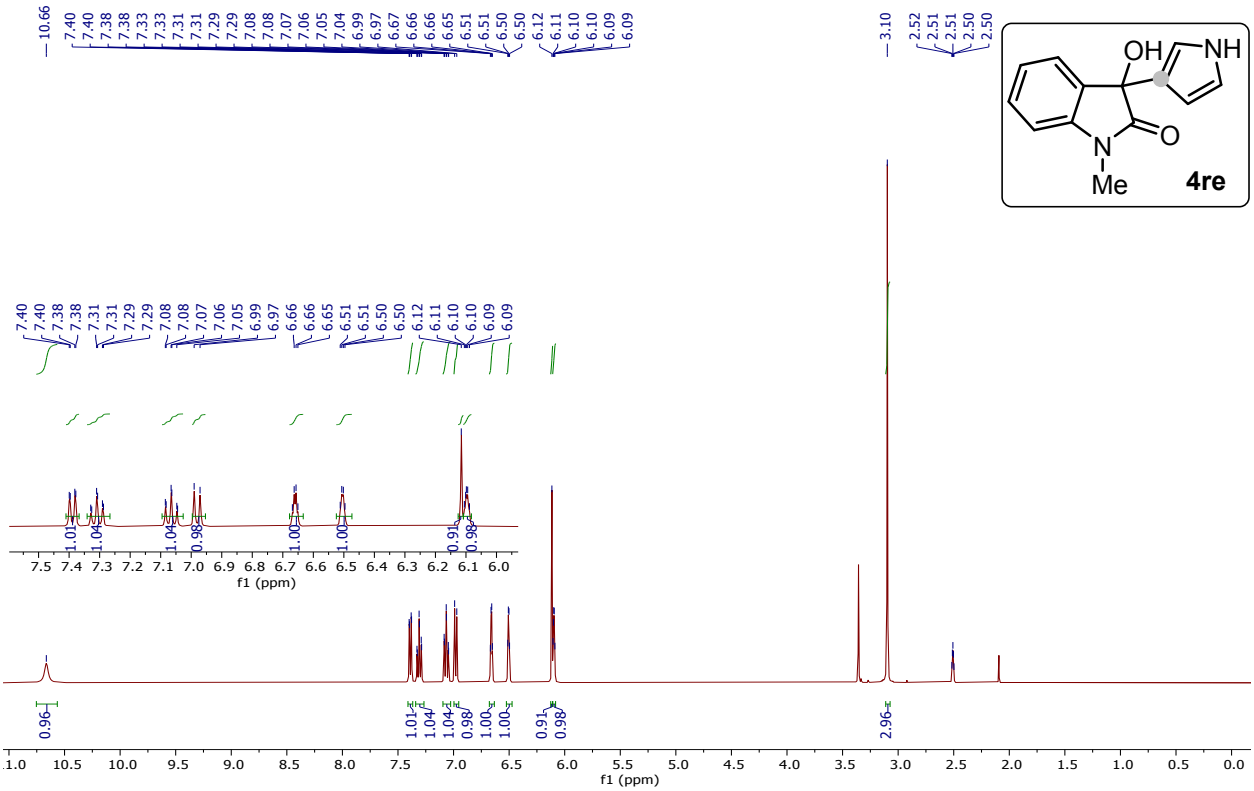
^{1}H NMR (400 MHz, DMSO-d_6)



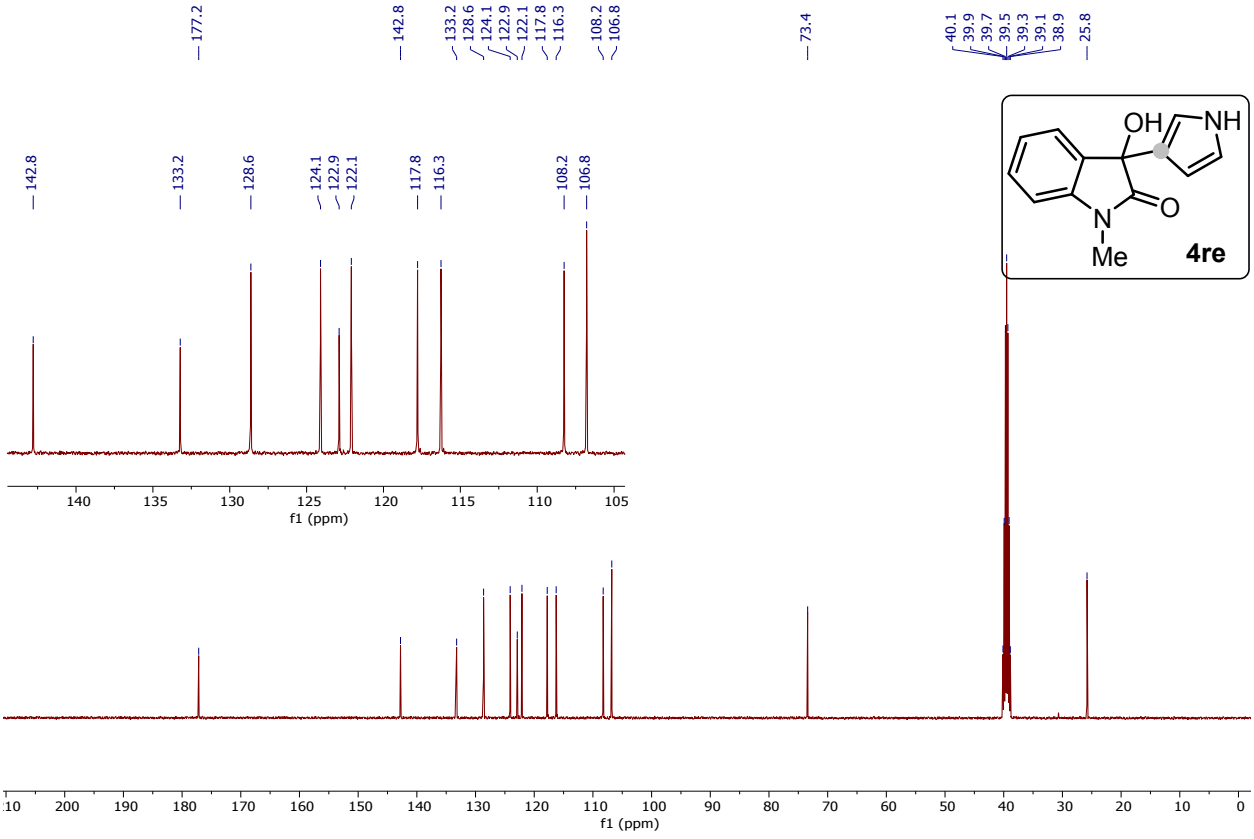
^{13}C NMR (101 MHz, DMSO-d_6)

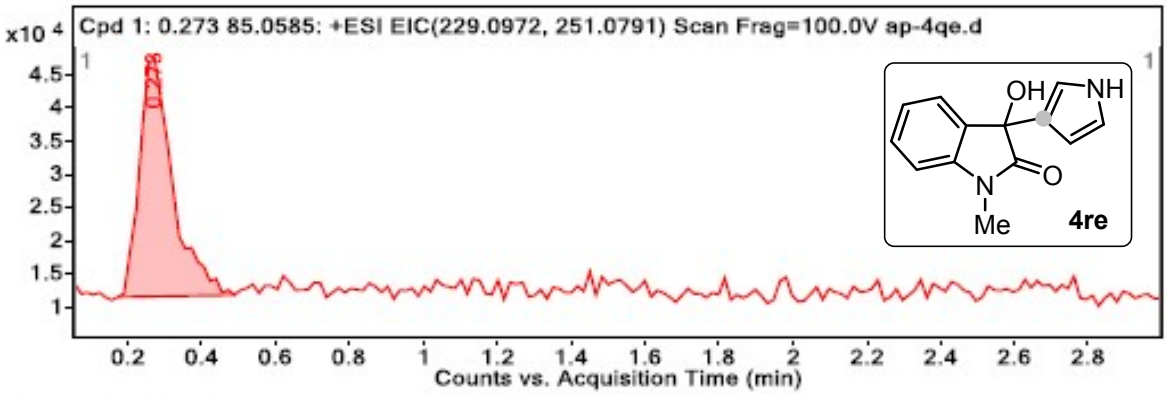


^{1}H NMR (400 MHz, DMSO-d_6)

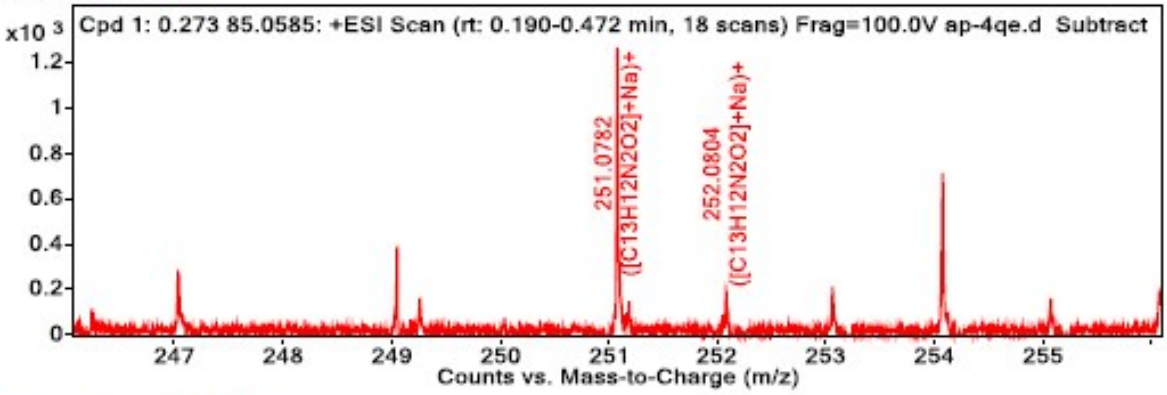


^{13}C NMR (101 MHz, DMSO-d_6)





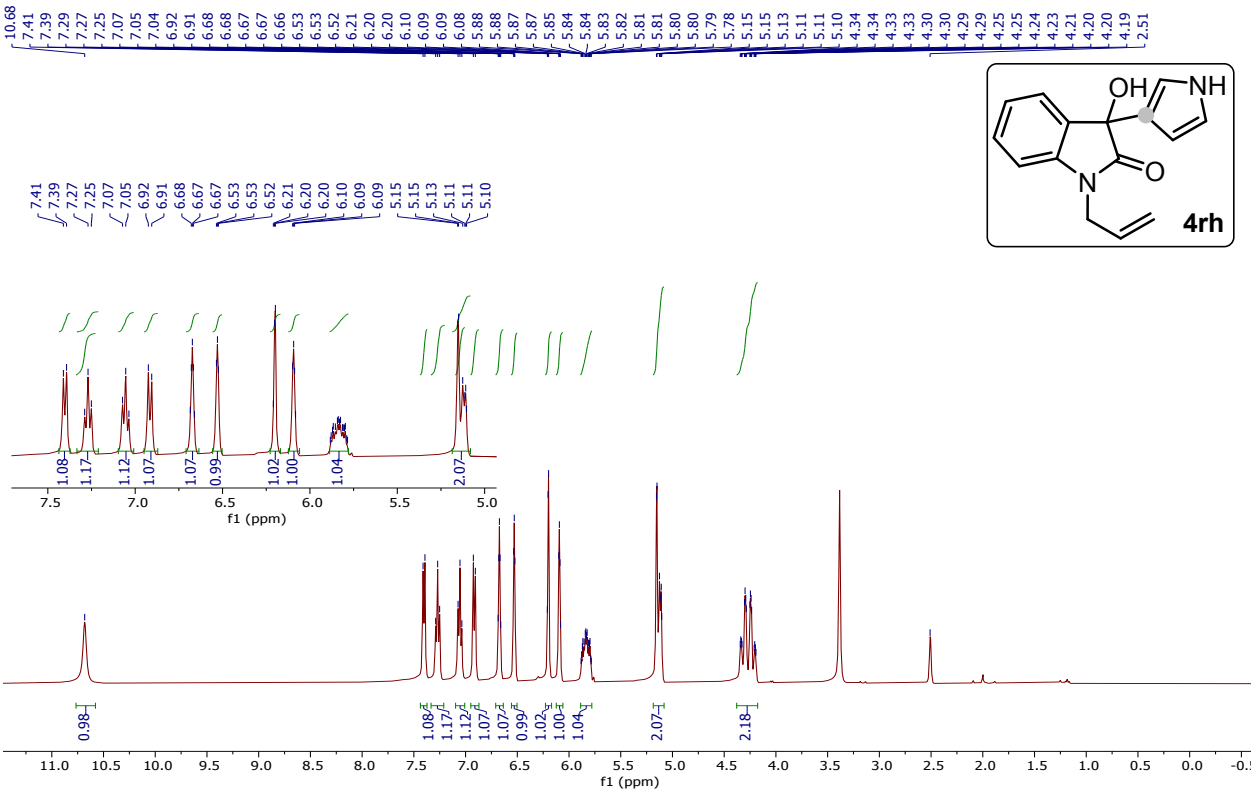
MS Zoomed Spectrum



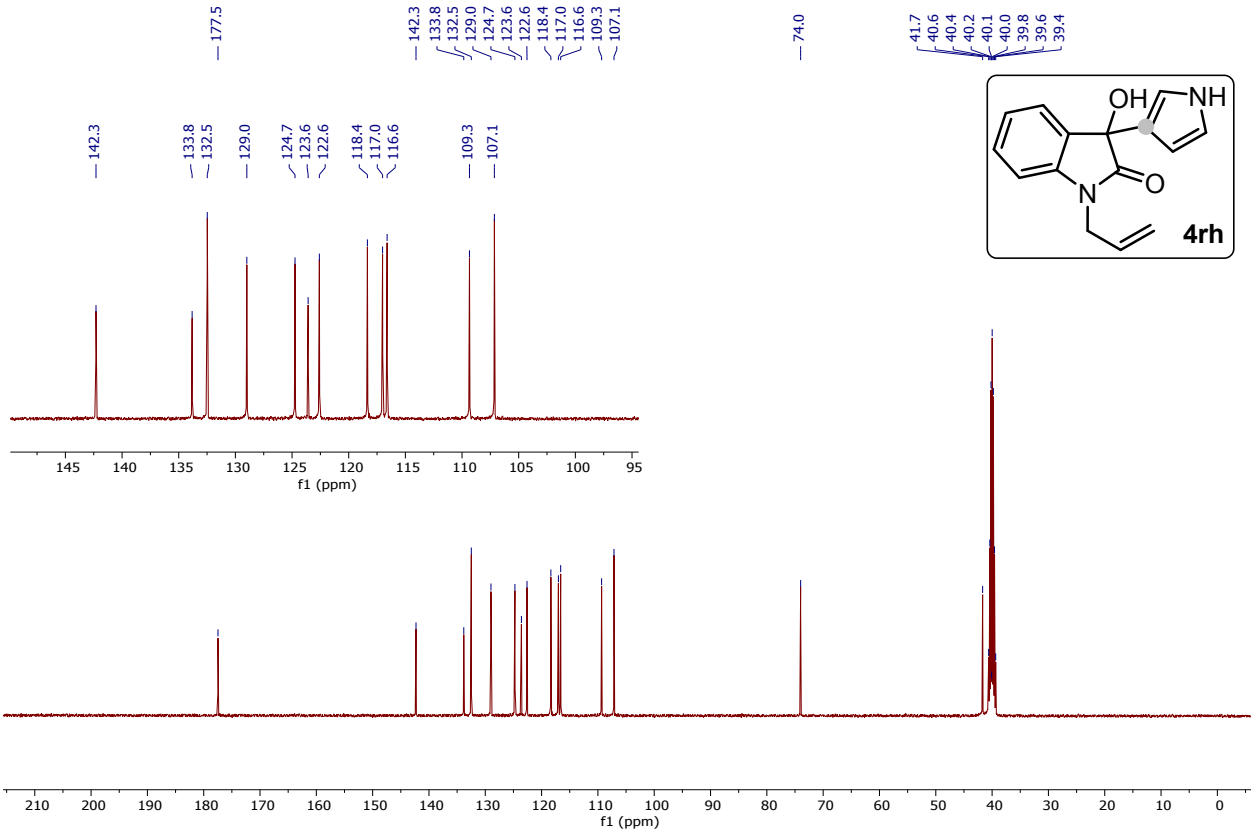
MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
251.0782	251.0791	3.66	1	1286.41	C13H12N2O2	(M+Na)+
252.0804	252.0822	7.18	1	196.22	C13H12N2O2	(M+Na)+

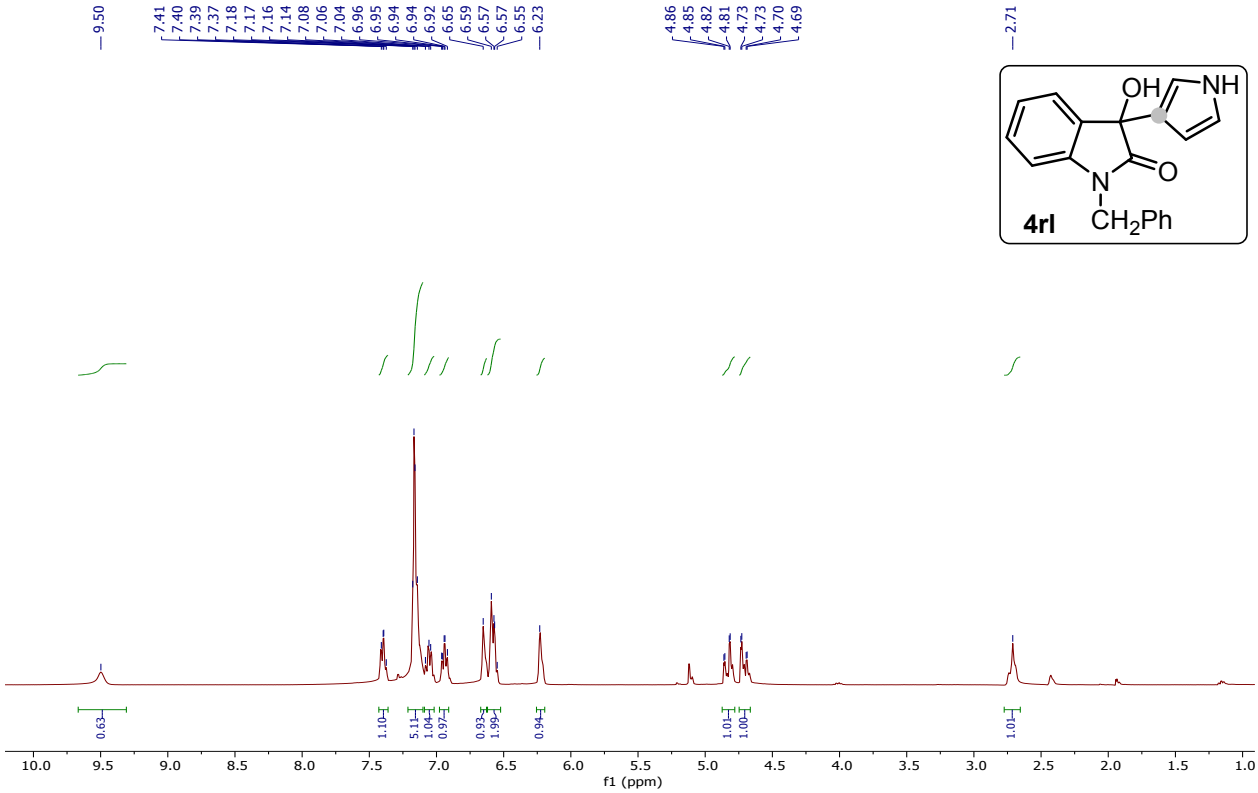
^{1}H NMR (400 MHz, DMSO-d_6)



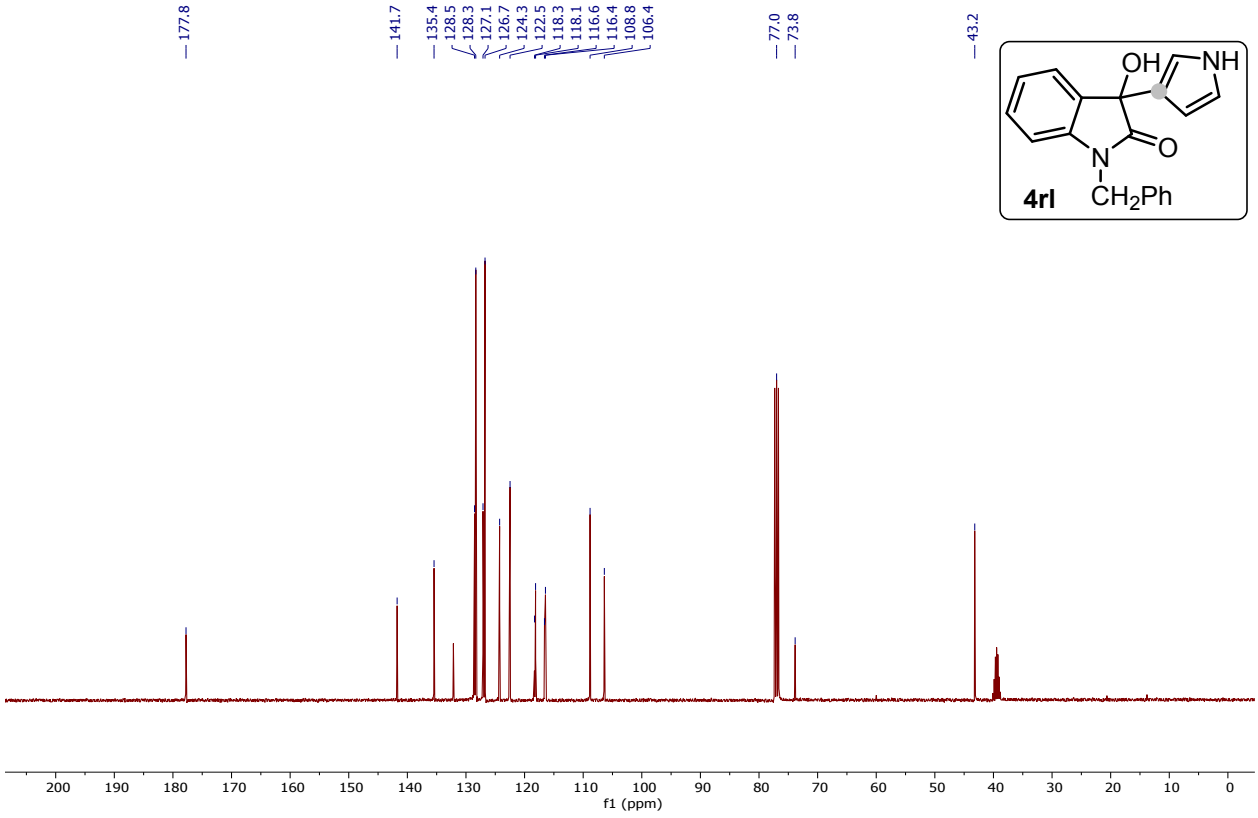
^{13}C NMR (101 MHz, DMSO-d_6)



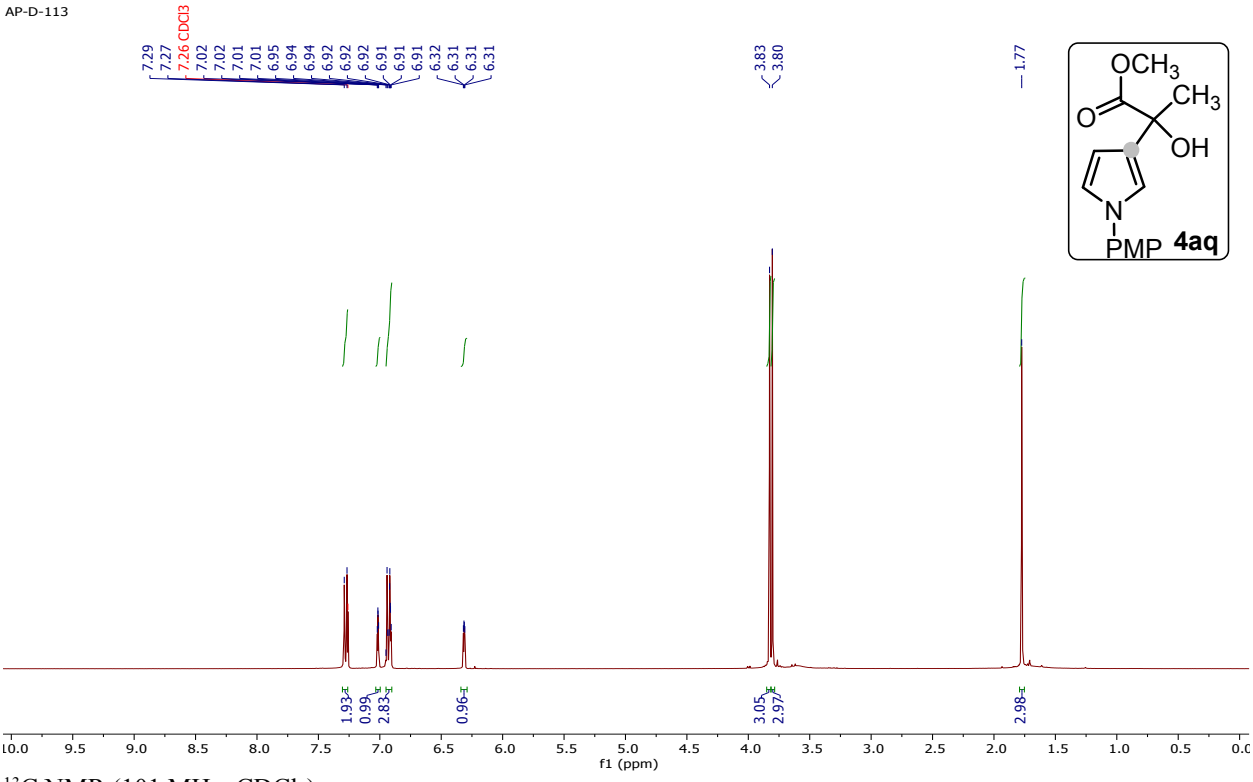
^{1}H NMR (400 MHz, $CDCl_3$)



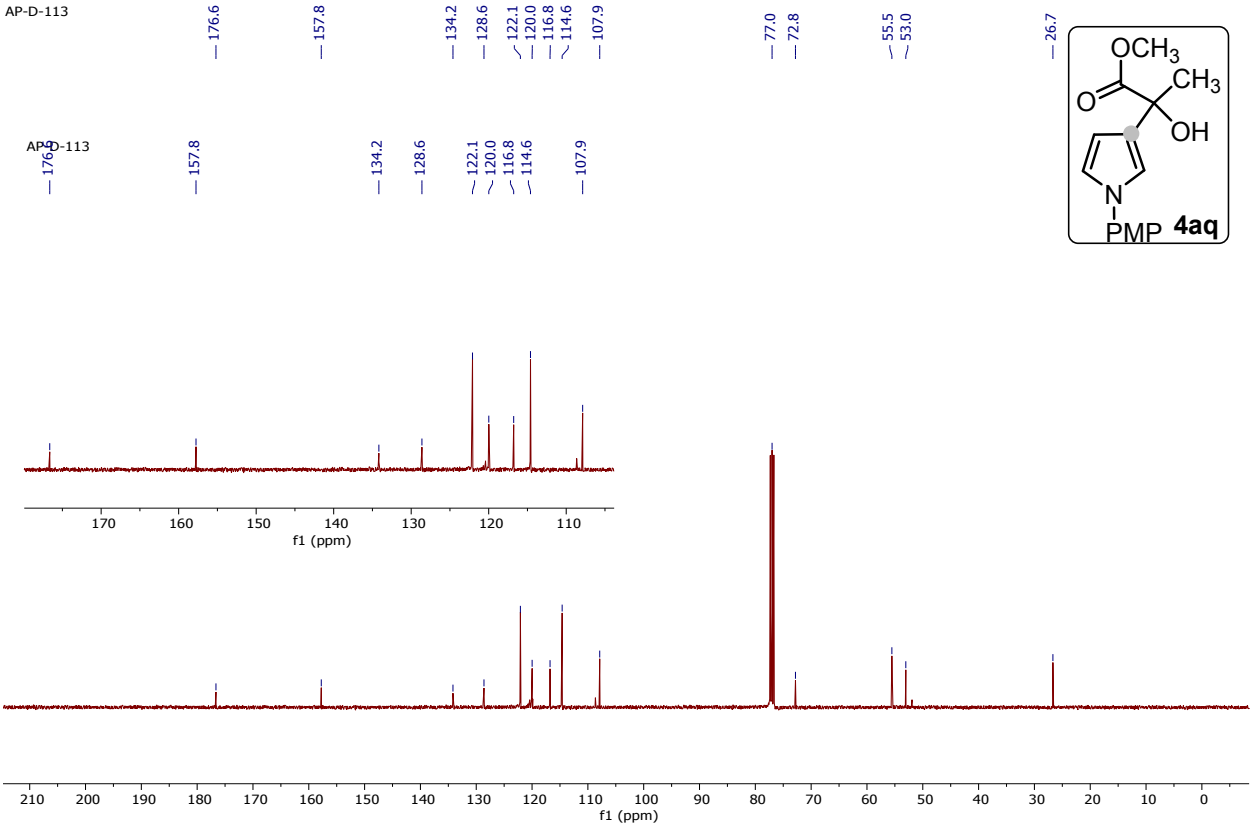
^{13}C NMR (101 MHz, $CDCl_3$ with a few drops of DMSO-d_6)



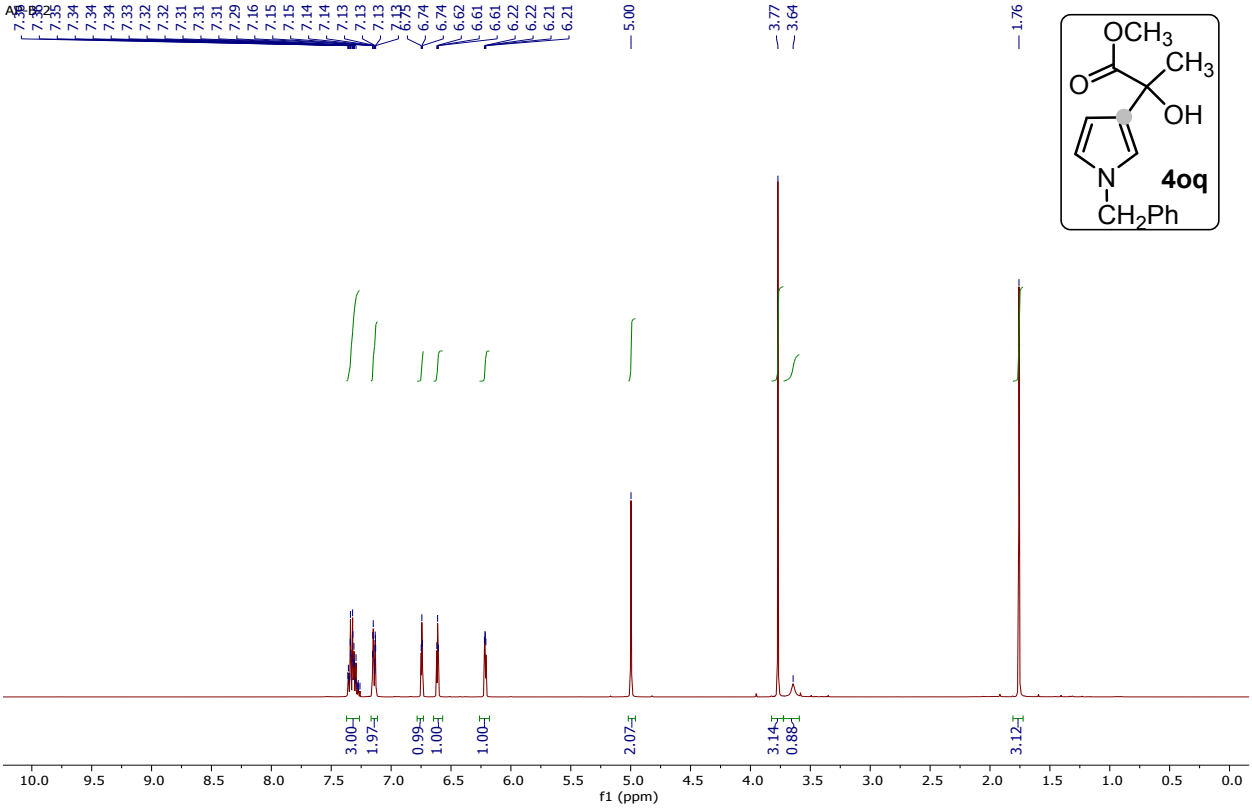
^{1}H NMR (400 MHz, $CDCl_3$)



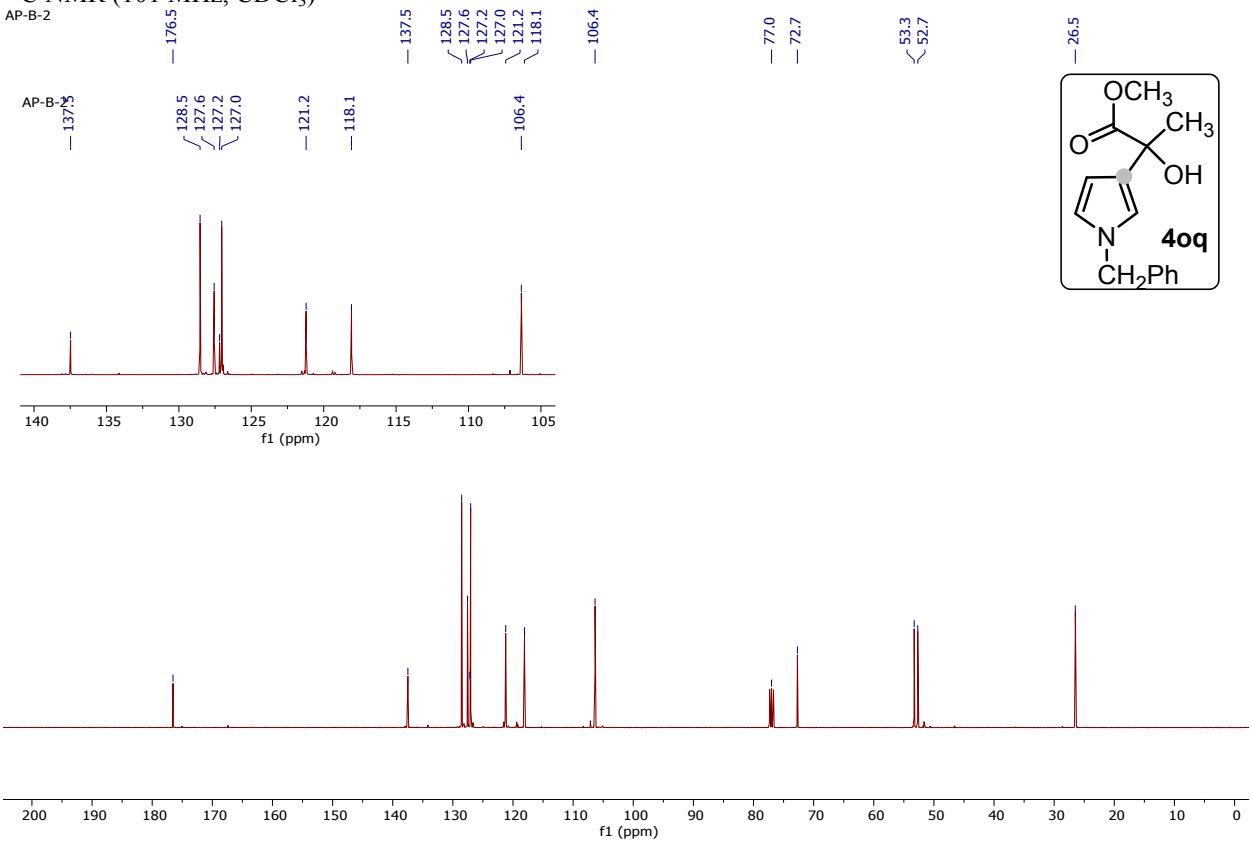
^{13}C NMR (101 MHz, $CDCl_3$)



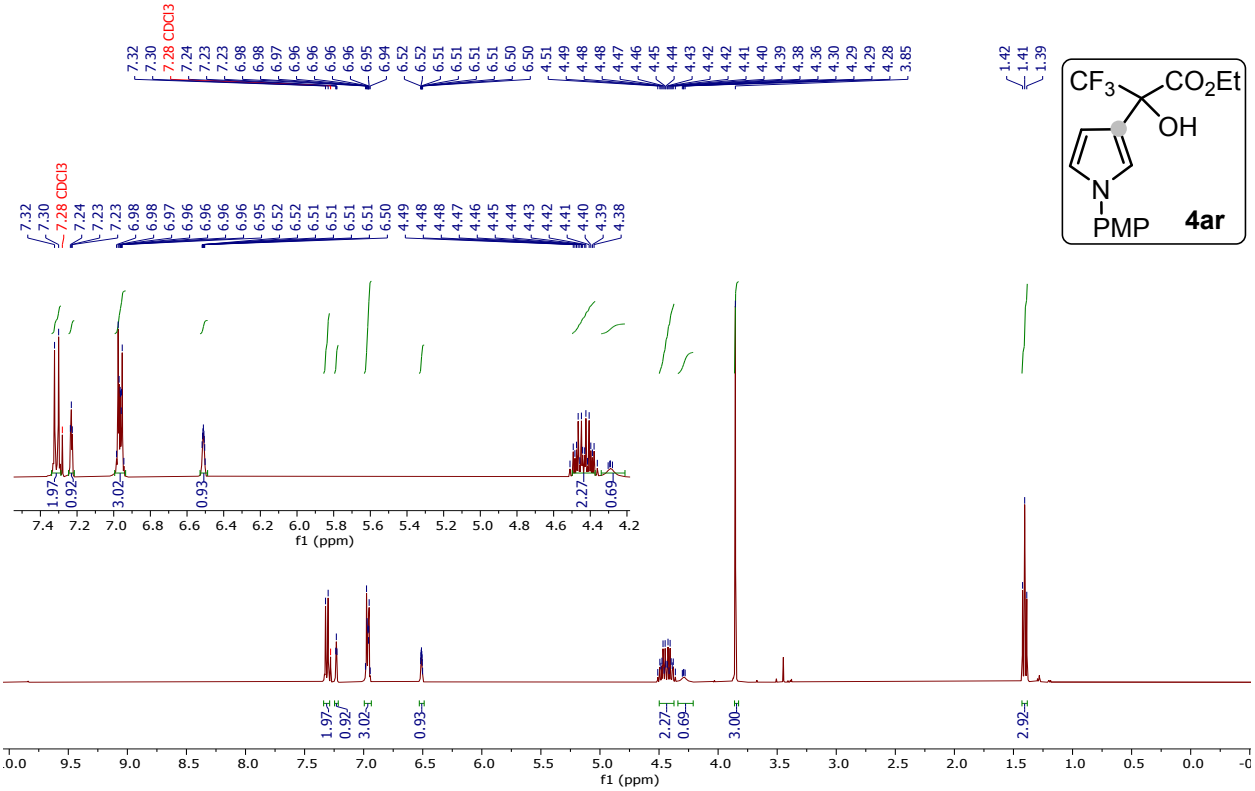
^{1}H NMR (400 MHz, $CDCl_3$)



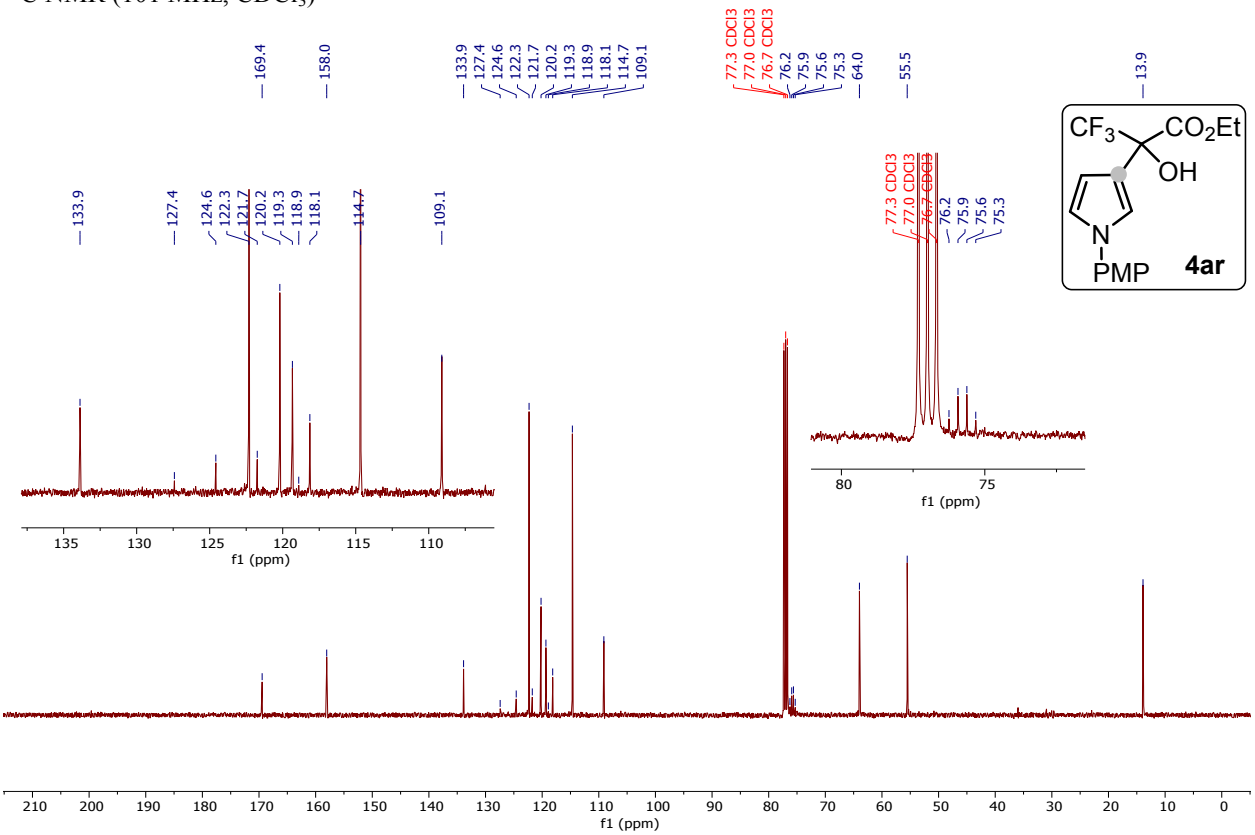
^{13}C NMR (101 MHz, $CDCl_3$)



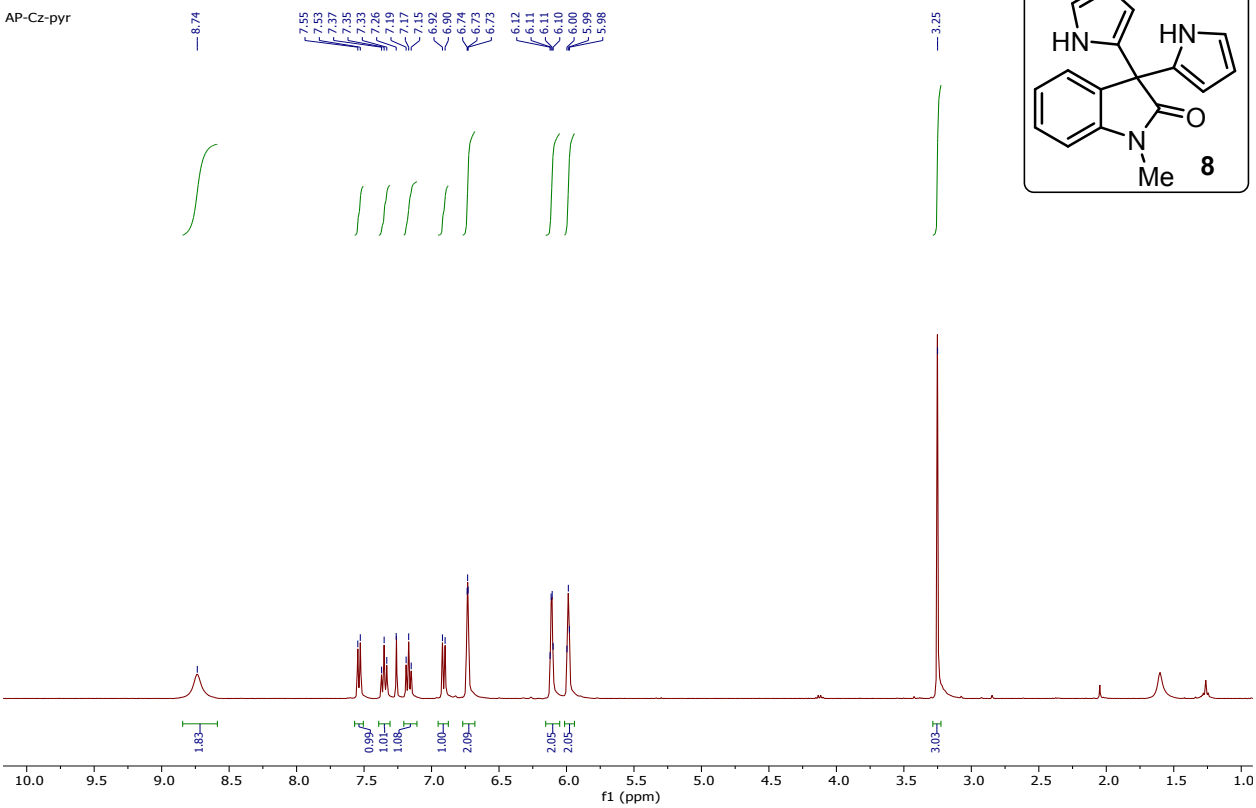
^{1}H NMR (400 MHz, $CDCl_3$)



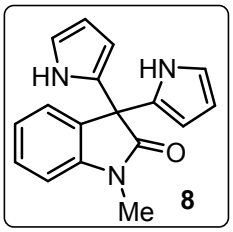
^{13}C NMR (101 MHz, $CDCl_3$)

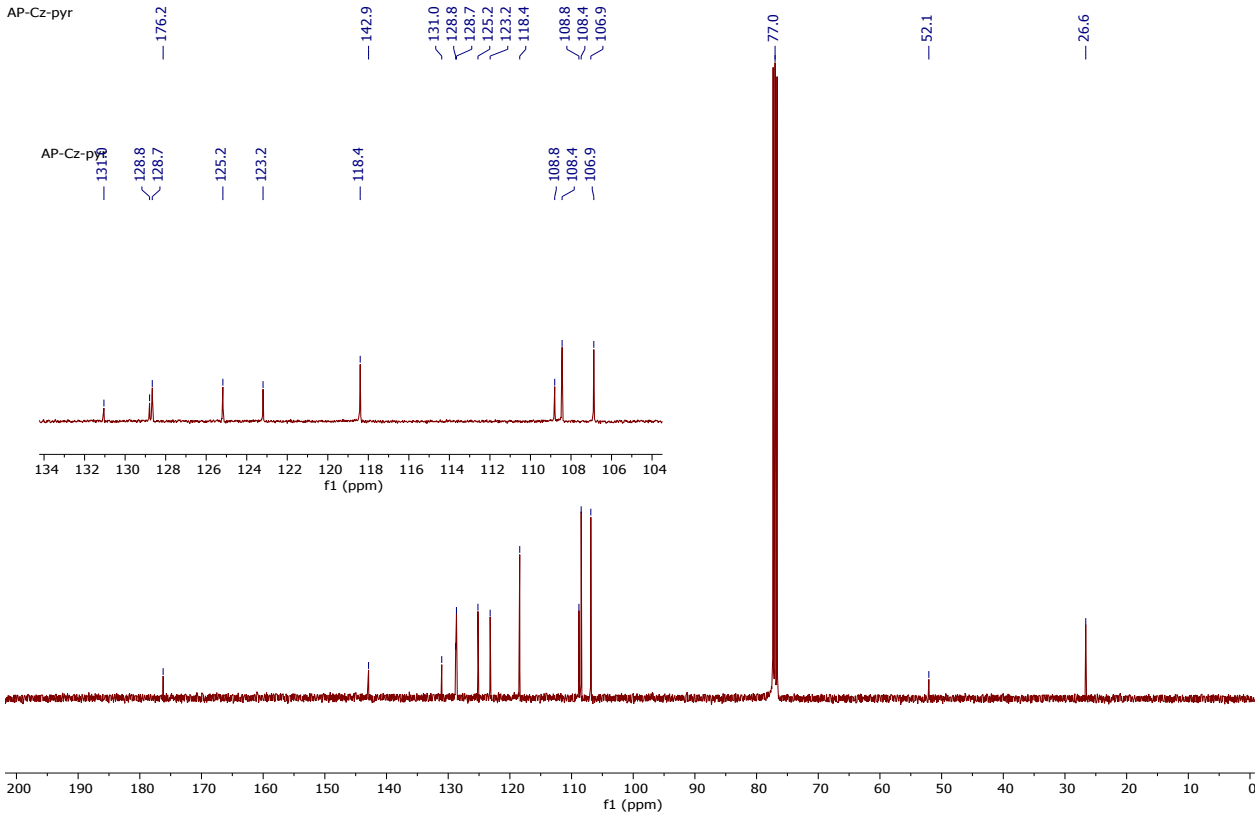


^{1}H NMR (400 MHz, $CDCl_3$)

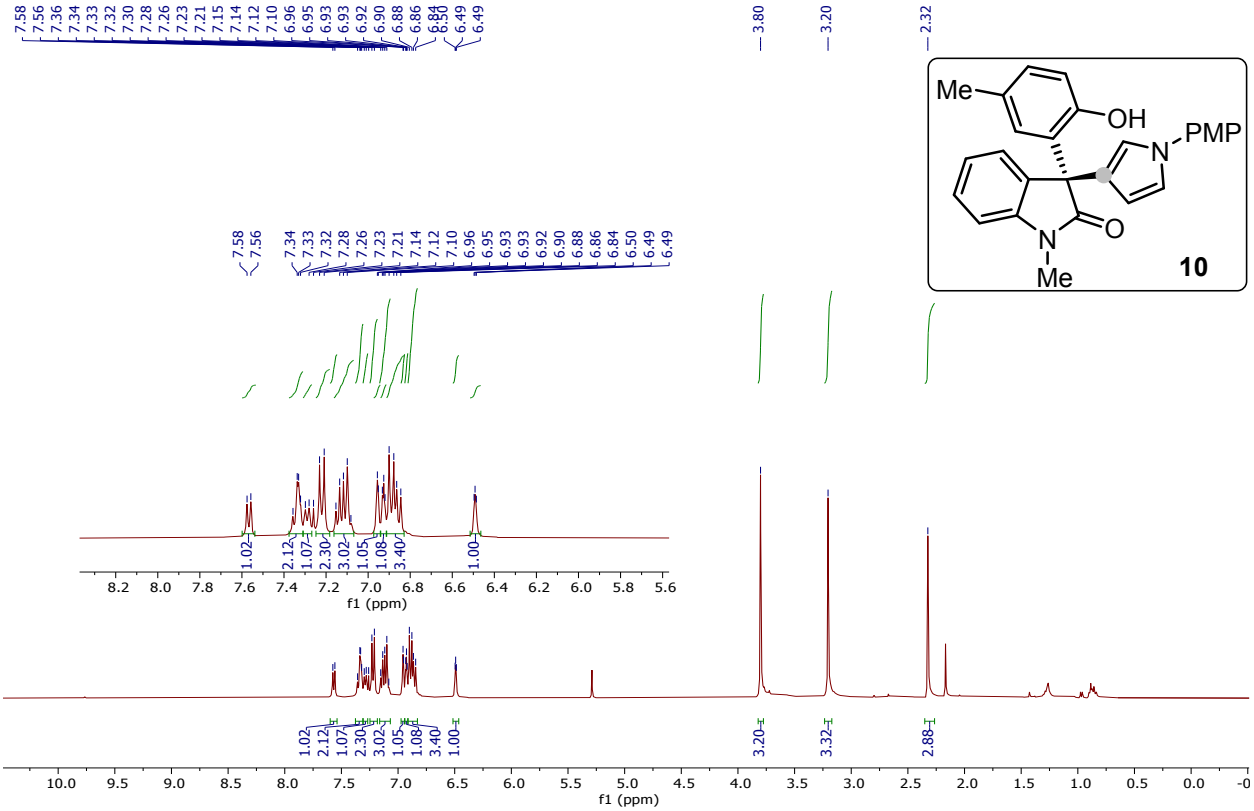


^{13}C NMR (101 MHz, $CDCl_3$)

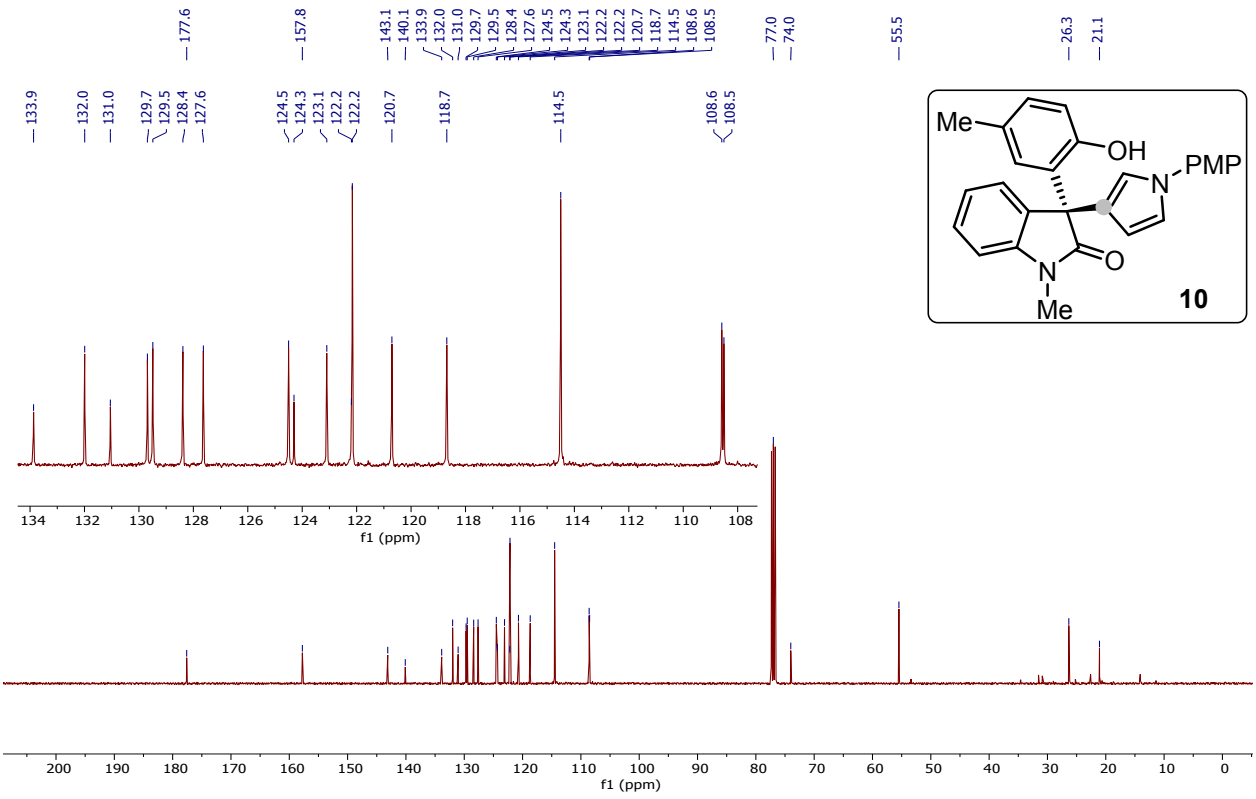



AP-Cz-pyr
176.2
142.9
131.0
128.8
128.7
125.2
123.2
118.4
108.8
108.4
106.9
77.0
52.1
26.6
AP-Cz-pyr
131.0
128.8
128.7
125.2
123.2
118.4
108.8
108.4
106.9
134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

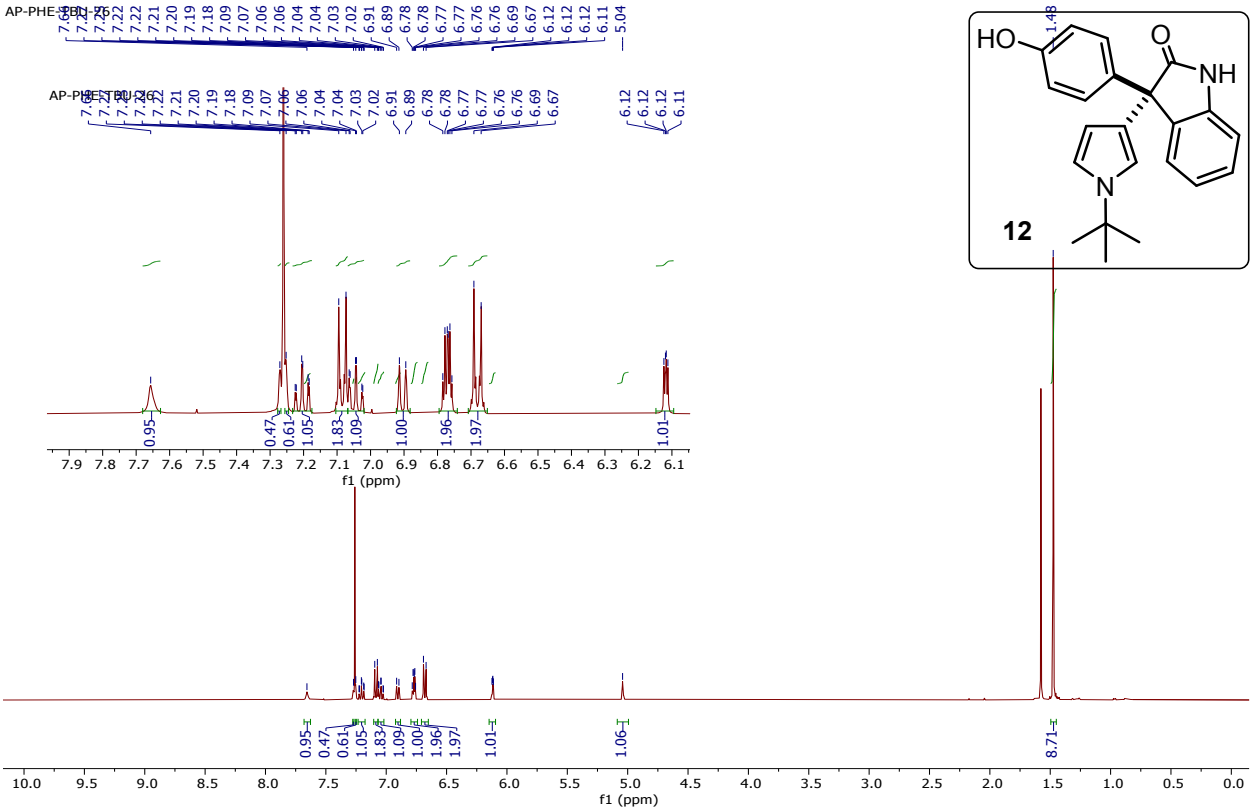
^{1}H NMR (400 MHz, $CDCl_3$)



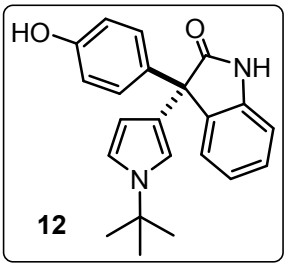
^{13}C NMR (101 MHz, $CDCl_3$)

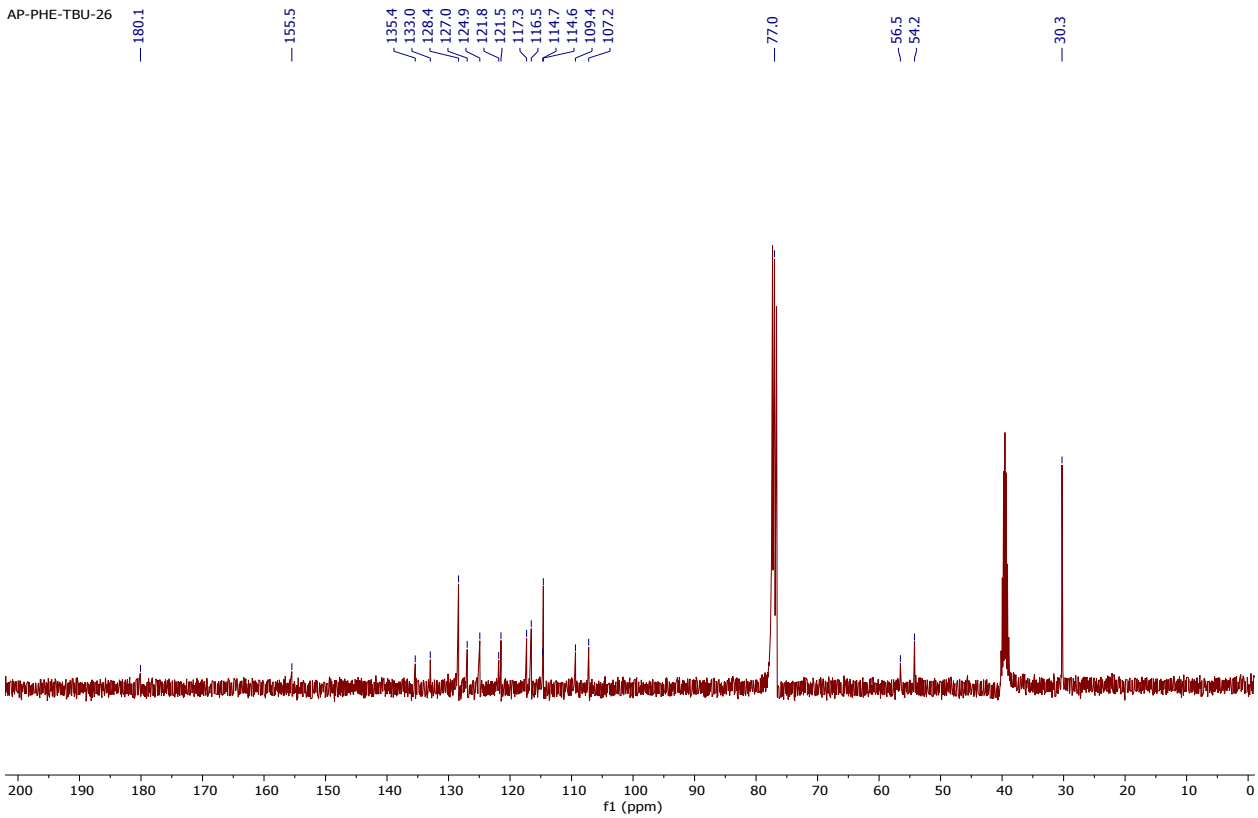


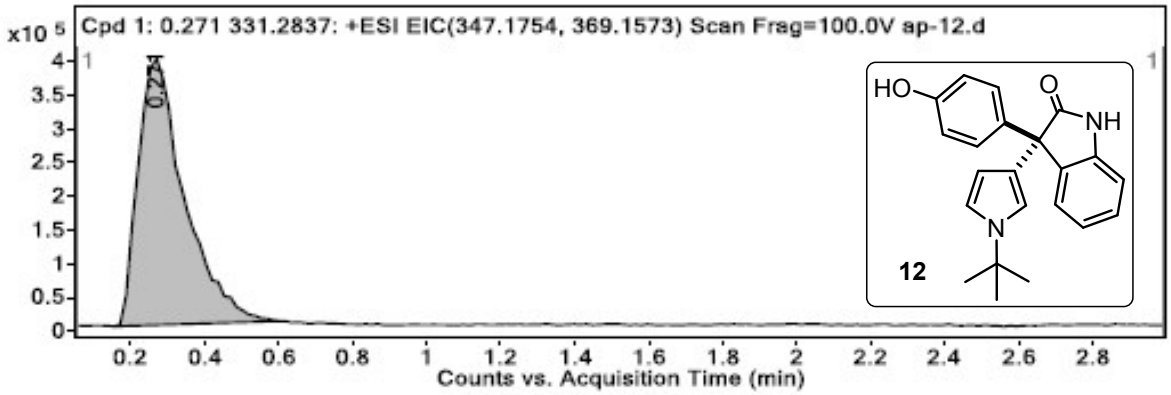
^{1}H NMR (400 MHz, $CDCl_3$)



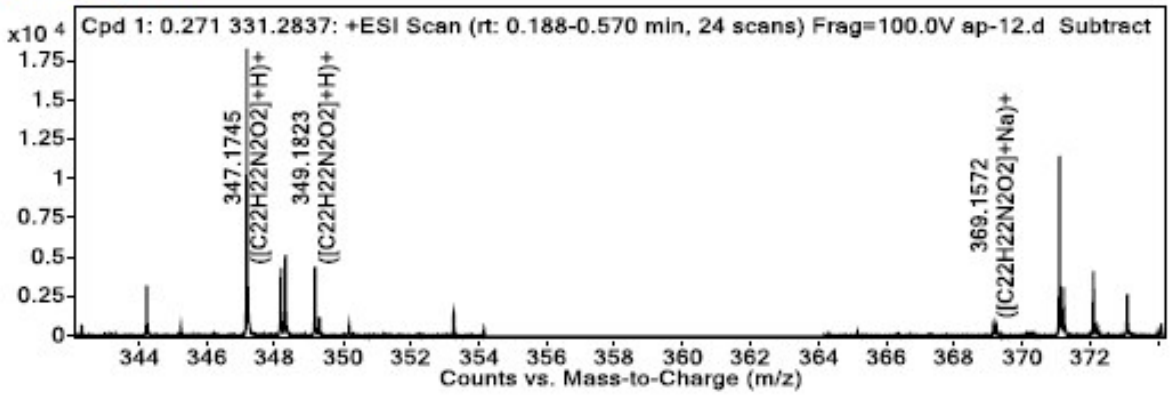
^{13}C NMR (101 MHz, $CDCl_3$)




AP-PHE-TBU-26
180.1
155.5
135.4
133.0
128.4
127.0
124.9
121.8
121.5
117.3
116.5
114.7
114.6
109.4
107.2
77.0
56.5
54.2
30.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
347.1745	347.1754	2.54	1	18417.85	C22H22N2O2	(M+H)+
348.1778	348.1786	2.29	1	4348.87	C22H22N2O2	(M+H)+
349.1823	349.1815	-2.11	1	4481.9	C22H22N2O2	(M+H)+
369.1572	369.1573	0.5	1	898.09	C22H22N2O2	(M+Na)+
370.1607	370.1606	-0.34	1	203.51	C22H22N2O2	(M+Na)+

Crystal Structure Data Tables for compound (4ae)

The structure of the compound 3-hydroxy-3-(1-(4-methoxyphenyl)-1H-pyrrol-3-yl)-1-methylindolin-2-one ($C_{20}H_{18}N_2O_3$) (**CCDC-1825913)** has been established by X-ray diffraction studies. The compound crystallizes in the triclinic space group P-1 with unit cell parameters: a = 8.5340(5), b = 10.2010(5), c = 11.6720 (5) Å, α=90.880(5), β=110.076(5), ɤ=114.477(5)^o and Z= 2. The crystal structure was solved by direct methods using single-crystal X-ray diffraction data and refined to R = 0.1463 for 1852 observed reflections.

Crystal Structure Determination and Refinement (4ae)

X-ray intensity data of 5442 reflections (of which 2981 unique) were collected at 293(2) K *X'calibur system – Oxford diffraction make, U.K.* equipped with graphite monochromated Mo*Kα* radiation (λ=0.71073 Å). The crystal used for data collection was of dimensions 0.3 x 0.2 x 0.1 mm. The intensities were measured by ω scan mode for θ ranges 3.68 to 25.00^o. 1852 reflections were treated as observed (I > 2σ(I)). Data were corrected for absorption, Extinction and Lorentz and polarization factors. The structure was solved by direct methods using SHELXS97.[1] All non-hydrogen atoms of the molecule were in the best E-map. Full-matrix least-squares refinement was carried out using SHELXL97.[1] All the hydrogen atoms were geometrically fixed and allowed to ride on their parent carbon atoms with C-H= 0.84-0.96 Å. The final refinement cycles converged to an R = 0.1463 and wR(F^2) = 0.4146 for the observed data. Residual electron densities ranged from -0.509 to 0.461 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography. The crystallographic data of **4ae** are summarized in Table S2. The geometry of the molecule was calculated using the PLATON[3] and PARST[4] software's. An ORTEP view

of the title compound with atomic labeling and packing view of the molecules in the unit cell viewed down the a-axis is shown in Figure S1.

Table S2: Crystal and experimental data of compound (**4ae**)

CCDC No.	**1825913**
Crystal description	block
Crystal colour	transparent
Crystal size	0.30 x 0.20 x 0.10 mm
Empirical formula	$C_{20}H_{18}N_2O_3$
Formula weight	334.36
Radiation, Wavelength	Mo *K*α, 0.71073 Å
Unit cell dimensions	a=8.5340(5), b=10.2010(5), c=11.6720(5) Å
	α=90.880(5)°, β=110.076(5)°, ɤ=114.477(5)°
Crystal system	Triclinic
Space group	P-1
Unit cell volume	853.71(4)
No. of molecules per unit cell, Z	2
Temperature	293(2)
Absorption coefficient	0.089 mm^{-1}
F(000)	352
Scan mode	ω scan

θ range for entire data collection	$3.76 < \theta < 25.00$ º
Range of indices	h= -9 to 10, k= -12 to 12, l= -11 to 13
Reflections collected / unique	5442 / 2981
Absorption correction	Multi-scan Crys Alis RED
Reflections observed ($I > 2\sigma(I)$)	1852
R_{int}	0.0602
R_{sigma}	0.0924
Structure determination	direct methods
Refinement	Full-matrix least-squares on F^2
No. of parameters refined	241
No. of Restraints	1.425
Final R	0.1463
$wR(F^2)$	0.4146
Weight	$1/[\sigma^2(F_o^2)+(0.2000\ P)^2+0.0000P]$
	Where $P = [F_o^2 + 2F_c^2] / 3$
Goodness-of-fit	1.425
$(\Delta/\sigma)_{max}$	0.000
Final residual electron density	$-0.509 < \Delta\rho < 0.461$ eÅ^{-3}
Measurement	*X'calibur system - Oxford diffraction make, U.K.*
Software for structure solution:	SHELXS97 (Sheldrick, 2008)
Software for refinement:	SHELXL97 (Sheldrick, 2008)
Software for molecular plotting:	ORTEP-3 (Farrugia, 2012) PLATON (Spek, 2009)

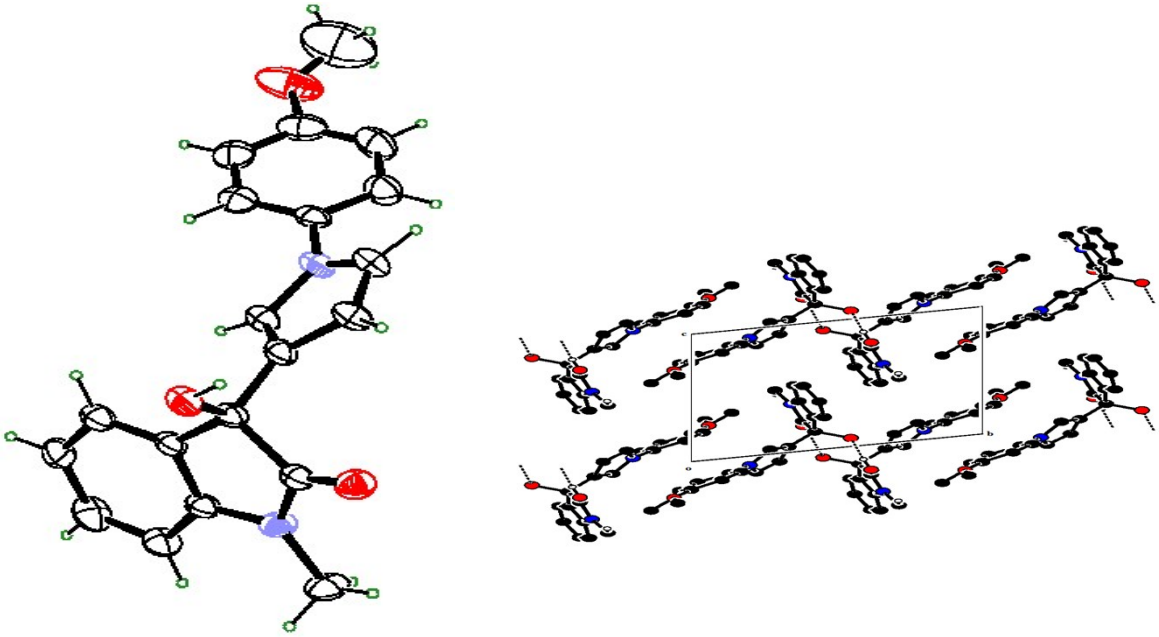


Figure S1: The ORTEP view of (**4ae**) and Packing view of the molecule viewed down the a-axis. (The thermal ellipsoids are drawn to the 40% probability level.)

Crystal Structure Data Tables for compound (4ja)

Single Crystal XRD Experiments for 4ja:

The single crystal XRD data collection and data reduction were performed using CrysAlis PRO on a single crystal Rigaku Oxford XtaLab Pro diffractometer. The crystals were kept at 93(2) K during data collection using CuKα (λ = 1.54184 Å) radiation. Using Olex2[5], the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimisation.

Single Crystal structure data of compound (4ja)

Single Crystal structure, Cell parameters and structure data of compound (4ja):

The single crystals suitable for XRD data collection were obtained from Ethyl acetate–hexane solvent mixture as light red blocks. The compound **4ja** ($C_{16}H_{18}N_2O_2$) crystallized in monoclinic, P21/c crystal group and crystallized as racemic mixture with total of four molecules (Z=4), two each of enantiomers, found per unit cell. The crystal structure of the compound **4ja** (**CCDC 1973218**) is shown in Figure S2, whereas crystal packing is shown in Figure S3. The detailed crystallographic data of **4ja** are summarized in Table S3.

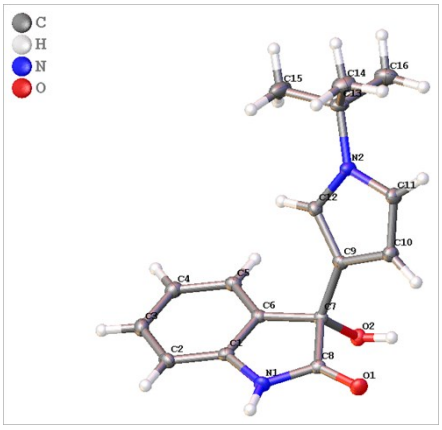


Figure S2. Crystal structure of compound **4ja** (**CCDC 1973218**). (The thermal ellipsoids are drawn to the 50% probability level.)

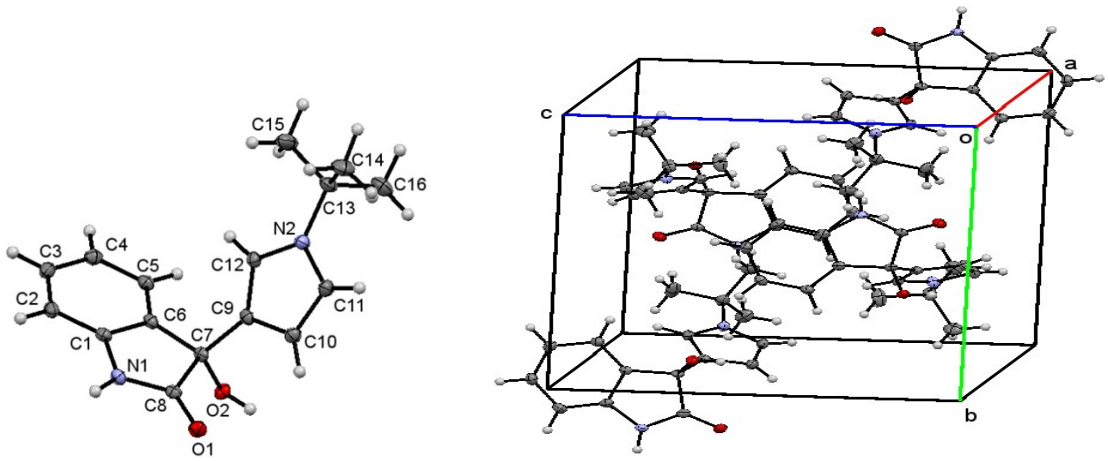


Figure S3. Crystal packing in a unit cell. Four molecule per unit cell (Z=4), consisting of 1:1 enantiomeric racemic mixture.

The Crystal Data for $C_{16}H_{18}N_2O_2$ (**4ja**) (M =270.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 10.8918(2) Å, b = 10.9673(2) Å, c = 11.9061(3) Å, β = 102.324(2)°, V = 1389.45(5) Å^3, Z = 4, T = 93(2) K, μ(CuKα) = 0.692 mm^{-1}, *Dcalc* = 1.292 g/cm^3, 7404 reflections measured (8.31° ≤ 2Θ ≤ 159.908°), 2934 unique (R_{int} = 0.0264, R_{sigma} = 0.0317) which were used in all calculations. The final R_1 was 0.0400 (I > 2σ(I)) and wR_2 was 0.1088 (all data).

Table S3: Crystal data and structure refinement for Compound (4ja).

Identification code	exp_518_INDRESH-01
Empirical formula	$C_{16}H_{18}N_2O_2$
Formula weight	270.32
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8918(2)
b/Å	10.9673(2)
c/Å	11.9061(3)
α/°	90
β/°	102.324(2)

γ/°	90
Volume/Å^3	1389.45(5)
Z	4
ρ_{calc}g/cm^3	1.292
μ/mm^{-1}	0.692
F(000)	576.0
Crystal size/mm^3	0.1 × 0.08 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.31 to 159.908
Index ranges	-13 ≤ h ≤ 13, -8 ≤ k ≤ 13, -15 ≤ l ≤ 14
Reflections collected	7404
Independent reflections	2934 [R_{int} = 0.0264, R_{sigma} = 0.0317]
Data/restraints/parameters	2934/0/185
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.1058
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.1088
Largest diff. peak/hole / e Å^{-3}	0.23/-0.28

Crystal Structure Data Tables for compound (4rl)

Single Crystal XRD Experiments for 4rl:

The single crystal XRD data collection and data reduction were performed using CrysAlis PRO on a single crystal Rigaku Oxford XtaLab Pro diffractometer. The crystals were kept at 93(2) K during data collection using CuKα (λ = 1.54184 Å) radiation. Using Olex2[5], the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimisation.

Single Crystal structure data of compound (4rl)

The single crystals suitable for XRD data collection were obtained from Ethyl acetate – hexane solvent mixture as colorless blocks. The compound (**4rl**), $C_{19}H_{16}N_2O_2$, crystallized in monoclinic, $P2_1/n$ crystal group and crystallized as racemic mixture with total of four molecules (Z=4), two each of enantiomers, found per unit cell. The crystal structure of the compound (**4rl**) **(CCDC 1973219)** is shown in Figure S4, whereas crystal packing is shown in Figure S5. The detailed crystallographic data of **4rl** are summarized in Table S4.

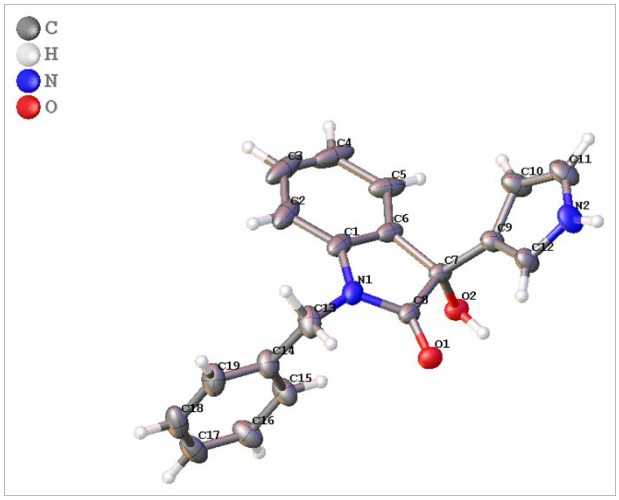


Figure S4. Crystal structure of compound (**4rl**) **(CCDC 1973219)**. (The thermal ellipsoids are drawn to the 50% probability level.)

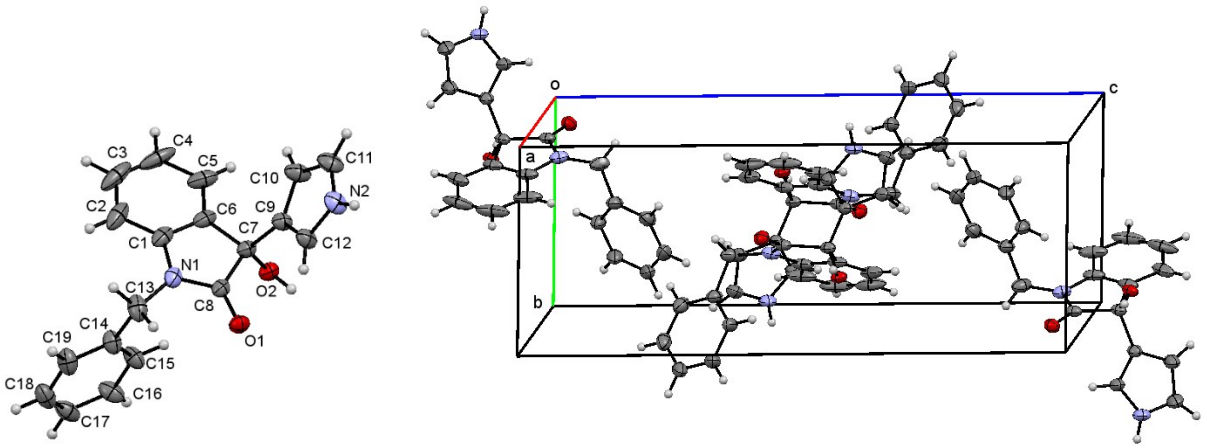


Figure S5. Crystal packing in a unit cell. Four molecule per unit cell (Z=4), consisting of 1:1 enantiomeric racemic mixture.

The Crystal Data for $C_{19}H_{16}N_2O_2$ (**4rl**) (M =304.34 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 11.2879(2) Å, b = 7.27320(10) Å, c = 19.0032(3) Å, β = 103.460(2)°, V = 1517.29(4) Å^3, Z = 4, T = 93(2) K, μ(CuKα) = 0.705 mm^{-1}, *Dcalc* = 1.332 g/cm^3, 7899 reflections measured (8.356° ≤ 2Θ ≤ 160.764°), 3183 unique (R_{int} = 0.0296, R_{sigma} = 0.0339) which were used in all calculations. The final R_1 was 0.0442 (I > 2σ(I)) and wR_2 was 0.1213 (all data).

Table S4: Crystal data and structure refinement for compound (4rl).

Identification code	exp_534_INDRESH-AP-CH2Ph-Fr-NH
Empirical formula	$C_{19}H_{16}N_2O_2$
Formula weight	304.34
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.2879(2)
b/Å	7.27320(10)
c/Å	19.0032(3)
α/°	90

β/°	103.460(2)
γ/°	90
Volume/Å^3	1517.29(4)
Z	4
ρ_{calc}g/cm^3	1.332
μ/mm^{-1}	0.705
F(000)	640.0
Crystal size/mm^3	0.15 × 0.13 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.356 to 160.764
Index ranges	-14 ≤ h ≤ 13, -8 ≤ k ≤ 8, -24 ≤ l ≤ 24
Reflections collected	7899
Independent reflections	3183 [R_{int} = 0.0296, R_{sigma} = 0.0339]
Data/restraints/parameters	3183/0/209
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1187
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.1213
Largest diff. peak/hole / e Å^{-3}	0.18/-0.28

References:

[1]. G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112.

[2]. L. J. Farrugia, *J. Appl. Cryst.*, **2012**, *45*, 849-854.

[3]. A. L. Spek, *Acta Cryst.*, **2009**, *D65*, 148–155.

[4]. M. Nardelli, *J Appl. Cryst.*, **1995**, *28*, 659.

[5]. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K., Puschmann, H. (2009), *J. Appl. Cryst*. 42, 339-341.

[6]. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

[7]. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Supporting information for the Theoretical Calculations at the DFT-Level

The computational part was first done using TiCl4 catalyst using B3LYP functional[1] with def2-TZVP basis set[2] with RIJCOSX approximation. A correction for dispersion interaction is added using Grimme D3 with Becke-Johnson damping.[3] All the calculations, including geometry optimization and frequencies, were performed using ORCA 4.2 program in the gas phase, with RIJCOSX approximation for Coulomb and exchange integrals.[4]

In order to reproduce the results using $Yb(OTF)_3$ catalyst, the calculations (unrestricted) were repeated using PW91 functional with def2-SVP basis sets for geometry optimization and transition state optimization. For relativistic correction, ZORA with SARC/J auxiliary basis sets were used without any dispersion correction. Final single point calculations were done at PW91/def2-TZVP level. The energy-trends appear to be identical in both the cases, i.e., $TiCl_4$ and $Yb(OTf)_3$.

References:

[1] K. Kim, K. D. Jordan, *J. Phys. Chem.* **1994**, *98*, 10089–10094.

[2] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[3] B. R. Brooks, C. L. Brooks III,; A. D. Mackerell Jr, L. Nilsson, R. J. Petrella, B. Roux, Y. Won, G. Archontis, C. Bartels, S. Boresch, A. Caflisch, L. Caves, Q. Cui, A. R. Dinner, M. Feig, S. Fischer, J. Gao, M. Hodoscek, W. Im, K. Kuczera, T. Lazaridis, J. Ma, V. Ovchinnikov, E. Paci, R. W. Pastor, C. B. Post, J. Z. Pu, M. Schaefer, B. Tidor, R. M. Venable, H. L. Woodcock, X. Wu, W. Yang, D. M. York, M. Karplus, B. *J. Comput. Chem.* **2009**, *30*, 1545–1614.

[4] a) F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73–78; b) F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, 1–6.

DFT-Calculation results for $TiCl_4$ catalyst using B3LYP functional

Table S5: The optimized structures of the molecules.

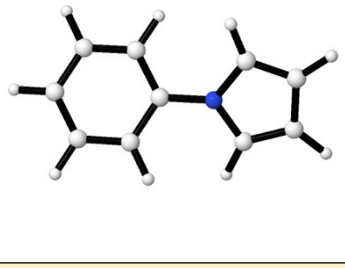
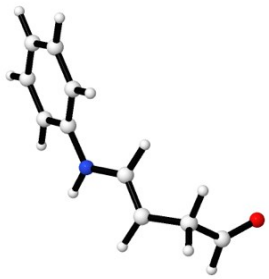
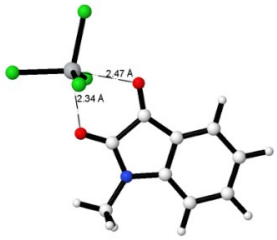
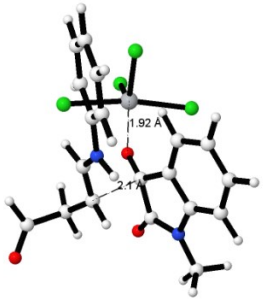
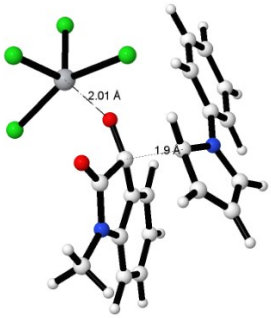
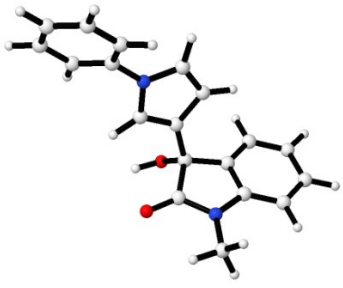
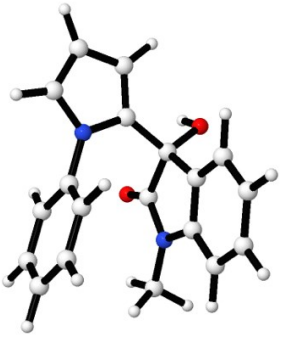
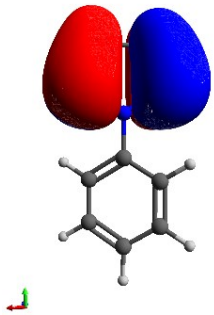
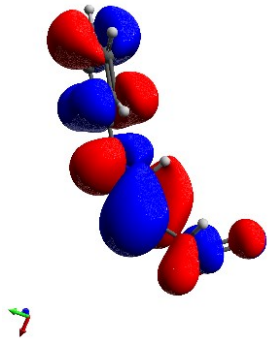
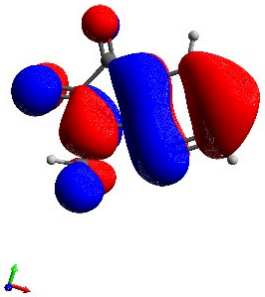
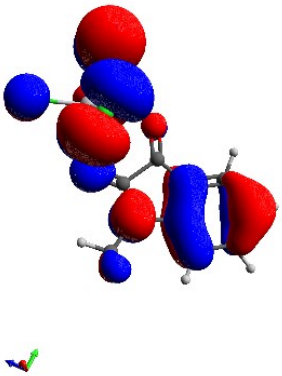
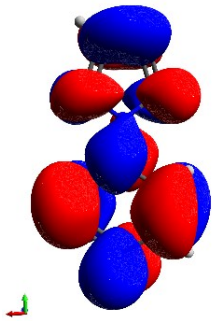
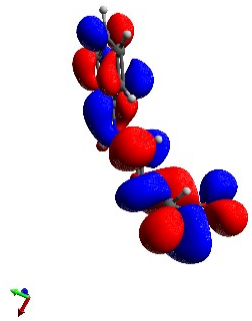
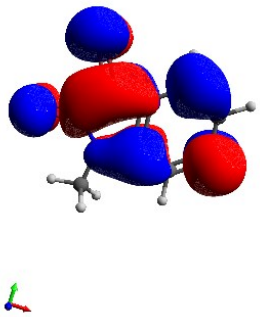
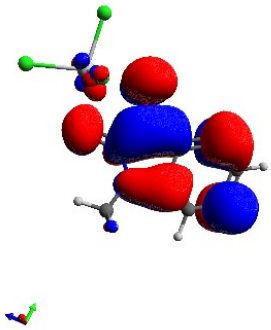
Pyrrole **5**	Enamine **A**
	
N-Methyl Isatin **3**	N-Methyl Isatin **3** with $TiCl_4$ complex **B**
	
TS-**1** C-3 substituted pyrrole	TS-2 C-2 substituted pyrrole
	
Compound **4** C-3 substituted Pyrrole	Compound **6** C-2 substituted Pyrrole
	

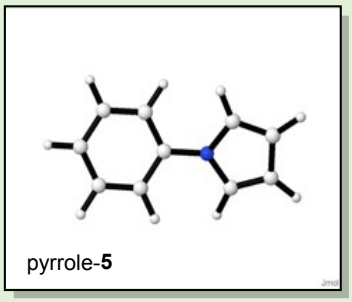
Figure S6: The pictures of the frontier orbitals are given below

			
a) HOMO of preformed Pyrrole **5** (-5.9 eV)	b) HOMO of in situ enamine-**A** (-5.5 eV)	c) HOMO of Isatin **3** (-6.6 eV)	d) HOMO of the activated Isatin 3 (with LA= $TiCl_4$), complex **B** (-7.4 eV)
			
e) LUMO of preformed pyrrole **5** (-0.72 eV)	f) LUMO of in situ enamine-**A** (-0.87eV)	g) LUMO Isatin **3** (-2.8 eV)	h) LUMO of the Activated Isatin 3 (with LA= $TiCl_4$), complex **B** (-4.02 eV).

XYZ coordinates, energies and frequencies

Note: All thermochemistry calculations are done at 298.15K and 1.00 atm

Pyrrole **5**



GIBBS FREE ENERGY

The Gibbs free energy is G = H - T*S

Total enthalpy = -440.97125487 Eh

Total entropy correction = -0.04233938 Eh -26.57 kcal/mol

Final Gibbs free energy = -441.01359425 Eh

Number of imaginary frequencies = 0

H	1.47946820095924	-0.49850223719398	0.16868885816511
C	-0.52992697598587	-1.49208451292852	0.17797938984646
C	-0.86132089303445	-2.81118661546090	0.01394828549244
N	0.30309788701507	-3.53314119899713	-0.16310484945374
C	1.37234049089367	-2.65960266022526	-0.11172472873611
C	0.88716797007578	-1.39499823164331	0.09432216719188
H	-1.22403316013681	-0.68730141614299	0.35338746459419
H	-1.81702762941733	-3.30150873900663	0.04881727195731
H	2.37695275516425	-3.00590070240143	-0.27334796847902
C	0.38584774285264	-4.92335830151177	-0.39510283160284
C	-0.67300302854997	-5.59792457020739	-1.00359327817955
C	-0.58745510338388	-6.96371495314648	-1.23574732690582
C	0.55714338235512	-7.66974468044149	-0.88420897656456
C	1.61218134895298	-6.99661049015833	-0.27952670403633
C	1.52938871441754	-5.63375899450858	-0.02775092211886
H	-1.54978946839855	-5.05044724163701	-1.31809194136426
H	-1.41500378589500	-7.47403161047208	-1.71140559029127
H	0.62755573521775	-8.73143567906115	-1.08096173600467
H	2.50434442358497	-7.53630913004776	0.01138854447563

H 2.34028565331282 -5.12430038480770 0.47294284201403

Enamine-**A**

GIBBS FREE ENERGY

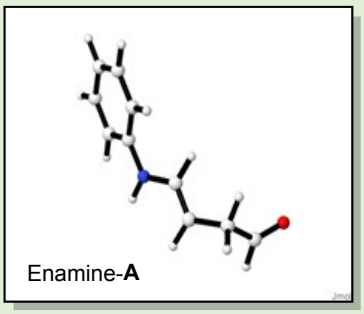
The Gibbs free energy is G = H - T*S

Total enthalpy = -517.35736582 Eh

Total entropy correction = -0.04975416 Eh -31.22 kcal/mol

Final Gibbs free energy = -517.40711998 Eh

Number of imaginary frequencies = 0



C	1.95453701199794	-7.21285698048699	-2.36901290223140
C	1.96867653255497	-6.14370533315804	-1.31160389135980
H	-1.83702554463039	-2.69824236236114	3.36270214396042
N	0.77063026120758	-4.69235628442266	0.20940916722717
H	1.56134057651459	-4.62630535304568	0.82884421665854
H	0.20053029871156	-3.89109352621572	2.65320670507855
H	3.11771017392766	-8.66371324349632	-1.15011182524696
H	2.75064487959084	-7.03562769621148	-3.10307218131070
H	2.92905356848235	-5.85624543510925	-0.89385823654814
C	0.84816548123118	-5.58932640110523	-0.83457289201905
H	-0.11267133781937	-5.85681406847249	-1.26039065004483
O	1.44908551164714	-9.51854408661373	-1.87522206782183
C	2.19073570027072	-8.57853651647723	-1.75838576127236
C	-0.38326369941609	-4.00655245523423	0.58718135016450
C	-1.37280735567494	-3.67581560510465	-0.34415423639378
C	-2.52975198338151	-3.02966443962333	0.06972559885023
C	-2.70979128343401	-2.67460027166882	1.40090352380308
C	-1.71206070370546	-2.97348556090959	2.32292881889956
C	-0.56045176063006	-3.63499254573573	1.92500339497938
H	-1.22800905132331	-3.90430333413852	-1.39101208786903

H	-3.28944481730982	-2.78616057150925	-0.66223686064490
H	-3.61126332179213	-2.16769574177904	1.71731569312250
H	1.00253010298054	-7.24182327712018	-2.90143750998116

Isatin **3**

GIBBS FREE ENERGY

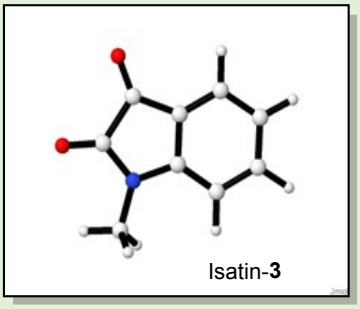
The Gibbs free energy is G = H - T*S

Total enthalpy = -552.16511084 Eh

Total entropy correction = -0.04528602 Eh -28.42 kcal/mol

Final Gibbs free energy = -552.21039686 Eh

Number of imaginary frequencies = 0



C	-0.14001291940419	-0.24880945010895	0.20030757709301
C	-4.08060779503211	1.17535960013596	-0.07851097387804
C	-4.77394092933771	-0.23334235413370	-0.07969735902058
N	-3.74237770905305	-1.15115058795606	-0.02230605903637
C	-0.27189127101342	1.13783520126318	0.16168525666044
C	-1.53701304219803	1.71416598439031	0.07033147653575
C	-2.64394367600530	0.88333438414006	0.01719116942849
C	-2.49828165956996	-0.51391072628500	0.05183622434616
C	-1.24802063883482	-1.09842613092939	0.14873642398962
O	-5.95209330390244	-0.47699330814046	-0.12535324317832
H	-1.66783776604803	2.78826517866954	0.04068524892424
H	0.84761985895815	-0.68631069081521	0.27426295165245
O	-4.66593807211769	2.22269201571902	-0.15242002472684
H	0.60944524571710	1.76285912174824	0.20407621377164
H	-1.12292610993269	-2.17171838285175	0.18517119370731
C	-3.93569830613578	-2.58224772397750	-0.04882845806900
H	-3.64772788025220	-3.03579900351039	0.90278412173670
H	-4.99146120984975	-2.77093279583512	-0.23115742957727

H -3.34349994598807 -3.03205838152282 -0.84774363035941

Isatin **3** complex with $TiCl_4$

GIBBS FREE ENERGY

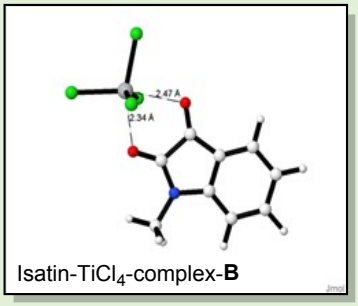
The Gibbs free energy is G = H - T*S

Total enthalpy = -3242.50937552 Eh

Total entropy correction = -0.06518356 Eh -40.90 kcal/mol

Final Gibbs free energy ... -3242.57455908 Eh

Number of imaginary frequencies = 0



Isatin-$TiCl_4$-complex-**B**

C	-4.86700306338698	0.32952821522034	-1.69381290930089
C	-3.14305052683768	1.70848871983387	1.84163164931585
C	-2.96608981629945	0.32721901951960	2.49719649466798
N	-3.42531389588452	-0.59403347369404	1.62183673504323
C	-4.73829519130331	1.71343891643666	-1.60147947491115
C	-4.17625786907291	2.28854643361024	-0.46543297317359
C	-3.76638752690039	1.44988537453385	0.55891875840391
C	-3.90630122519486	0.05134660487797	0.45542274759914
C	-4.45256250356855	-0.52879995425991	-0.66853645895663
O	-2.48746229059318	0.17199199200381	3.60711391934557
H	-4.05487380975316	3.35935583842259	-0.36937886728957
H	-5.30233711772776	-0.10242843955499	-2.58547998969612
O	-2.76251404248224	2.71143544881799	2.40246122939267
H	-5.07352878560169	2.33899436208862	-2.41666625874577
H	-4.56368591789558	-1.59953671486384	-0.76608440248637
C	-3.35518572760233	-2.02949030595136	1.80756232634776
H	-2.72227422257997	-2.47629643342282	1.03962747106393
H	-2.92014221305998	-2.22070812838681	2.78540495356270
H	-4.35117603918553	-2.47016273049715	1.75828270627565
Ti	-1.59534551535546	2.13943739118629	4.50392733087725

Cl	-3.74975596232574	2.30456532794274	5.22186273986274
Cl	-1.01881409343368	4.25518818599039	4.71171879218433
Cl	-0.00758267159031	1.56392336888403	2.95370746701292
Cl	-0.68187997236442	1.18035098126183	6.25863601360429

Compound **4** (C3-substituted pyrrole)

GIBBS FREE ENERGY

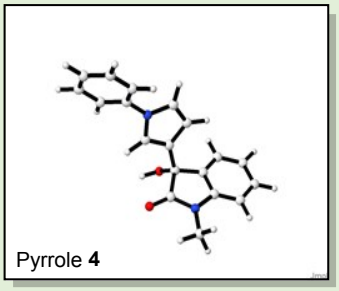
The Gibbs free energy is G = H - T*S

Total enthalpy = -993.15287474 Eh

Total entropy correction = -0.06321065 Eh -39.67 kcal/mol

Final Gibbs free energy = -993.21608539 Eh

Number of imaginary frequencies = 0



C	0.41925481891260	-1.48317067586155	-3.98105863896245
C	-2.46364539915859	-0.44821800251427	-1.03385920419258
C	-3.24858932728473	-1.78229248961270	-1.16946246719736
N	-2.51611849092202	-2.61599242716997	-1.97760672090969
C	0.45879420521630	-0.17059250429753	-3.52852628825255
C	-0.45374007769971	0.27012473295037	-2.56292553118199
C	-1.39523490526353	-0.61368449907604	-2.08322153616187
C	-1.44144986090707	-1.92607461799763	-2.56327426920605
C	-0.53648551120848	-2.38547078714760	-3.50434699146943
O	-4.31938735067908	-2.02695630780261	-0.65485453358565
H	-0.42630838208628	1.28897788000885	-2.19900200602175
H	1.13443428262081	-1.81690418699783	-4.72177099005170
O	-3.32414481762229	0.64110980045636	-1.34463457566509
H	1.19797627159873	0.51431521409162	-3.92202602783737
H	-0.56934709923140	-3.40174956175460	-3.87285235712255
C	-2.89362882057036	-3.97934753453439	-2.26642449898519
H	-2.09544598536884	-4.66552187039669	-1.97511141119743

H	-3.78895747216240	-4.20085100909846	-1.69030190213827
H	-3.10859145030627	-4.11239030009243	-3.32974501188756
C	-1.43529038974204	-1.26638328883216	4.84962678170669
C	-1.82220780245624	-1.32486297908115	6.18200257368050
C	-2.94160720509244	-0.62742810155093	6.62193322384379
C	-3.66750394735167	0.14581461668445	5.72277085503706
C	-3.28081199031343	0.22037964992363	4.39149890692960
H	-0.58637880567662	-1.83581577221616	4.49690487798606
H	-1.25593103067970	-1.93383403754162	6.87477399013606
H	-3.24950064977430	-0.68912336572572	7.65764626185436
H	-4.53344101009352	0.70155391162787	6.05864085910383
H	-3.82633442146213	0.84070605130722	3.69371212485786
H	-4.14091597227014	0.50873020778783	-0.84440756186956
C	-1.89655607894537	-0.38890015671715	0.36468510024207
C	-0.52467077505391	-0.34666282516084	0.75446203576427
C	-0.48264155065937	-0.37834179342337	2.12425330638469
N	-1.77969982678158	-0.42901945778839	2.59296188939642
C	-2.64148924471534	-0.44238790716128	1.52235297664177
H	-3.70034961610150	-0.56512522451824	1.66526007104100
H	0.32455991115880	-0.29450265035947	0.09565609415803
H	0.34650691362675	-0.32632696059853	2.80722381489276
C	-2.16530979549341	-0.48980304980880	3.95228536023917

Compound **6** (C2-substituted pyrrole)

GIBBS FREE ENERGY

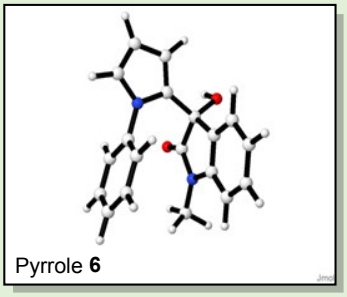
The Gibbs free energy is G = H - T*S

Total enthalpy = -993.16293265 Eh

Total entropy correction = -0.06439435 Eh -40.41 kcal/mol

Final Gibbs free energy = -993.22732700 Eh

Number of imaginary frequencies = 0



Pyrrole **6**

C	-1.68830580044920	2.29924599808032	-2.25193865517594
C	-3.86661010965246	-0.83944911063424	-0.38835921107455
C	-3.02269516740236	-1.97154600090659	-1.04877458574394
N	-2.08046532748787	-1.38418704750594	-1.85080343074843
C	-2.72407866136181	2.69079991051862	-1.41018735262474
C	-3.50315514764316	1.72990319737413	-0.75918256181715
C	-3.23062624640173	0.39832433644379	-0.97757922593237
C	-2.18383151687706	0.01456444317326	-1.81886382393977
C	-1.39564951721939	0.94947646531294	-2.46710424301686
O	-3.22389757445395	-3.15835228483784	-0.91582793755337
H	-4.30349535821755	2.01963196299226	-0.09074494432735
H	-1.09083215179892	3.05236292112532	-2.74984876399400
O	-5.19875364055357	-0.98382787343851	-0.86721344549900
H	-2.93086886486323	3.74193137267103	-1.25744918736450
H	-0.57984085473608	0.65485157710378	-3.11265097874609
C	-1.13072345293581	-2.13152109175339	-2.63824878298877
H	-0.11103642570657	-1.84391200238053	-2.37542223486015
H	-1.27753613678628	-3.18530265642735	-2.41338840686589
H	-1.29387677579062	-1.96145473477021	-3.70531075759356
H	-1.03632172086239	1.05900169178524	1.31653053206270
H	1.30391066993536	0.83444893986636	0.51275857772686
H	2.26629355282534	-1.41615645927540	0.13909796485748
H	0.89547786081910	-3.43300587800819	0.56259787530055
H	-4.96886199689981	-0.74025713351518	4.21550413545914
C	-0.59620832188318	0.08400066884626	1.15862483151338
C	0.71039652098320	-0.04949909260473	0.70578359652628
C	1.24828263148538	-1.31444479720695	0.49355629082284
C	0.47905159991457	-2.44841278235235	0.73164726496397
C	-0.82661645547175	-2.32015836111564	1.18708092577873
H	-5.45879588044204	-1.89868550798851	-0.68496154512149
C	-3.85188738484792	-0.87351503441955	1.11292428531946

N	-2.69779174991741	-0.92330130858382	1.87191919086836
C	-3.03597244444461	-0.87463806173226	3.20719703318176
C	-4.40163399399676	-0.79098267003841	3.30152760003853
C	-4.91794154876173	-0.78581736890987	1.97826406715886
H	-5.94897061072201	-0.71252989424145	1.67849512606863
H	-1.44650602264580	-3.18804499082487	1.36323121097414
H	-2.26714466028417	-0.91804266296422	3.95929603265257
C	-1.35913925444574	-1.05261714885734	1.39751491371364

TS-**1**

GIBBS FREE ENERGY

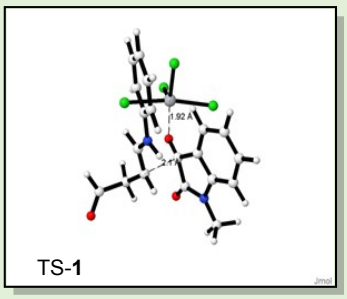
The Gibbs free energy is G = H - T*S

Total enthalpy = -3759.87888765 Eh

Total entropy correction = -0.08524180 Eh -53.49 kcal/mol

Final Gibbs free energy = -3759.96412945 Eh

Number of imaginary frequencies = 1



C	-0.41978192439938	2.73302081623602	0.56188011270195
C	-1.35751451736134	0.66822075270586	4.12566667725049
C	-1.98795894778858	-0.56717447019271	3.44261661084944
N	-1.76849915895489	-0.40145393849205	2.08180598379858
C	-0.22032336179477	3.45268856876367	1.74416824084723
C	-0.51248253910654	2.87225143004173	2.98692183924804
C	-0.99390038387878	1.56628520373080	3.01551295656391
C	-1.21728563698835	0.85599124052344	1.81229763008590
C	-0.93003155322338	1.42349689138538	0.57543099494688
O	-2.55473446602424	-1.48951282498468	3.97377416284885
H	-0.38938587502861	3.44570174885351	3.90651042148200
H	-0.18773324765664	3.20340006987057	-0.39701635250431
O	-1.80258264002550	1.02223299098593	5.27611432957387

H	0.15715019650059	4.47609423494153	1.70204639622082
H	-1.11482303094300	0.88281481182705	-0.35380692596686
C	-2.27312084183258	-1.31952021714868	1.08540003884775
H	-1.45602039213985	-1.73432288572481	0.47315008887061
H	-2.77969134695732	-2.13645745780746	1.61614189372351
H	-2.99486380698043	-0.81343186630594	0.42324079145436
Ti	-2.23600508077395	2.55296397939058	6.34259223675989
Cl	-3.58356539808539	3.16062792772940	4.62681795677434
Cl	-1.19880793623630	4.53772443302713	6.33654410093720
Cl	-0.51772925642139	1.67441076881700	7.72979938847894
Cl	-3.78628636146621	2.40257806614774	7.87858870060151
C	0.11812343290492	-1.37954347328909	5.49273122459326
C	0.47091503659114	-0.29793762825567	4.49088352569388
H	4.70502189929899	5.19841304681723	3.58263670704495
N	1.87419100783085	1.66732911239491	4.23380143064671
H	1.99483626271826	1.44685176120478	3.24725000132252
H	3.69305882508832	3.03148703653919	2.90171137933255
H	2.07073105861594	-1.44313835468448	6.56883134891486
H	-0.56528998661145	-2.11791027699402	5.05698488389122
H	0.72051143788425	-0.63834556742695	3.47772158227922
C	1.18612867717717	0.81330468955785	4.97716618019308
H	1.07039492362379	1.07474695687588	6.03383349382165
O	1.67581834706978	-3.21843290866444	5.67646797494396
C	1.38128068508015	-2.08542751688813	5.95327016350217
C	2.43365435153948	2.89979499397394	4.65959313419552
C	2.03138187665888	3.50666545785771	5.85659833774788
C	2.60221834119147	4.72363021637744	6.22620974433872
C	3.56898379203035	5.33362289631464	5.42120835820439
C	3.95773786309219	4.72505684605592	4.22328282687823
C	3.38943319744968	3.51084443710404	3.83649198972591
H	1.25776712878579	3.06816334401313	6.48734084769924

H	2.26027983401652	5.20319698632538	7.14591879819566
H	4.01234175132569	6.28525942730648	5.72311932003874
H	-0.36900223579614	-0.90530175684330	6.36323847238436

VIBRATIONAL FREQUENCIES

Number of imaginary frequencies = 1

Scaling factor for frequencies = 1.000000000 (already applied!)

0:	0.00 cm**-1	21:	144.04 cm**-1	43:	436.43 cm**-1
1:	0.00 cm**-1	22:	153.27 cm**-1	44:	444.50 cm**-1
2:	0.00 cm**-1	23:	158.03 cm**-1	45:	455.38 cm**-1
3:	0.00 cm**-1	24:	160.84 cm**-1	46:	477.92 cm**-1
4:	0.00 cm**-1	25:	173.03 cm**-1	47:	495.93 cm**-1
5:	0.00 cm**-1	26:	183.13 cm**-1	48:	512.03 cm**-1
6:	-177.02 cm**-1	27:	184.84 cm**-1	49:	523.17 cm**-1
imaginary mode		28:	203.26 cm**-1	50:	537.59 cm**-1
7:	31.16 cm**-1	29:	224.78 cm**-1	51:	546.90 cm**-1
8:	36.67 cm**-1	30:	260.83 cm**-1	52:	560.05 cm**-1
9:	49.05 cm**-1	31:	267.93 cm**-1	53:	593.34 cm**-1
10:	53.19 cm**-1	32:	273.81 cm**-1	54:	629.82 cm**-1
11:	61.30 cm**-1	33:	292.18 cm**-1	55:	635.78 cm**-1
12:	61.93 cm**-1	34:	304.24 cm**-1	56:	667.68 cm**-1
13:	77.54 cm**-1	35:	322.55 cm**-1	57:	704.25 cm**-1
14:	83.33 cm**-1	36:	331.66 cm**-1	58:	721.48 cm**-1
15:	90.51 cm**-1	37:	336.78 cm**-1	59:	732.85 cm**-1
16:	97.67 cm**-1	38:	345.31 cm**-1	60:	754.64 cm**-1
17:	105.79 cm**-1	39:	364.04 cm**-1	61:	760.58 cm**-1
18:	115.93 cm**-1	40:	370.80 cm**-1	62:	794.65 cm**-1
19:	128.84 cm**-1	41:	393.67 cm**-1	63:	810.24 cm**-1
20:	138.39 cm**-1	42:	406.81 cm**-1	64:	816.13 cm**-1

65: 842.66 cm**-1
66: 875.63 cm**-1
67: 883.90 cm**-1
68: 889.78 cm**-1
69: 910.88 cm**-1
70: 955.92 cm**-1
71: 965.09 cm**-1
72: 967.53 cm**-1
73: 981.43 cm**-1
74: 995.93 cm**-1
75: 1001.10 cm**-1
76: 1012.50 cm**-1
77: 1021.70 cm**-1
78: 1030.99 cm**-1
79: 1044.07 cm**-1
80: 1044.99 cm**-1
81: 1051.94 cm**-1
82: 1059.84 cm**-1
83: 1070.79 cm**-1
84: 1101.50 cm**-1
85: 1105.95 cm**-1
86: 1117.64 cm**-1
87: 1147.52 cm**-1
88: 1174.93 cm**-1
89: 1184.06 cm**-1
90: 1190.91 cm**-1
91: 1193.46 cm**-1
92: 1209.42 cm**-1
93: 1222.63 cm**-1
94: 1248.86 cm**-1
95: 1254.61 cm**-1
96: 1271.33 cm**-1
97: 1312.21 cm**-1
98: 1326.58 cm**-1
99: 1337.93 cm**-1
100: 1361.98 cm**-1
101: 1371.89 cm**-1
102: 1376.89 cm**-1
103: 1386.76 cm**-1
104: 1392.58 cm**-1
105: 1426.31 cm**-1
106: 1453.91 cm**-1
107: 1463.77 cm**-1
108: 1470.48 cm**-1
109: 1486.47 cm**-1
110: 1499.21 cm**-1
111: 1503.58 cm**-1
112: 1505.43 cm**-1
113: 1514.92 cm**-1
114: 1525.74 cm**-1
115: 1532.87 cm**-1
116: 1607.19 cm**-1
117: 1608.94 cm**-1
118: 1619.99 cm**-1
119: 1626.74 cm**-1
120: 1653.09 cm**-1
121: 1791.52 cm**-1
122: 1797.88 cm**-1
123: 2742.21 cm**-1
124: 2942.99 cm**-1
125: 2953.00 cm**-1
126: 2989.85 cm**-1
127: 3017.36 cm**-1
128: 3049.38 cm**-1
129: 3055.32 cm**-1
130: 3065.05 cm**-1
131: 3075.80 cm**-1
132: 3084.35 cm**-1
133: 3088.26 cm**-1
134: 3099.84 cm**-1
135: 3102.06 cm**-1
136: 3107.74 cm**-1
137: 3111.83 cm**-1
138: 3114.67 cm**-1
139: 3115.24 cm**-1
140: 3479.86 cm**-1

TS-**2**

GIBBS FREE ENERGY

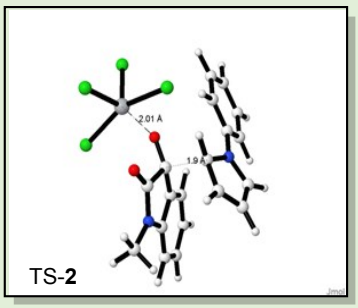
The Gibbs free energy is G = H - T*S

Total enthalpy = -3683.47906999 Eh

Total entropy correction = -0.07986442 Eh -50.12 kcal/mol

Final Gibbs free energy = -3683.55893441 Eh

Number of imaginary frequencies = 1



C	-1.68911733757335	-1.09999433581710	0.30456468177946
C	1.06406587579917	1.86788373270555	1.56672487259436
C	-0.00311944139931	2.96824617177060	1.76960371321274
N	-1.23235965814081	2.37454859897994	1.60686837435230
C	-0.33912064207989	-1.43624866169785	0.16548325505088
C	0.66105221682017	-0.52601399767061	0.54400619638202
C	0.28120800840242	0.70586912339300	1.06209521653622
C	-1.08445839233085	1.05018969967225	1.15853754118241
C	-2.08451239706126	0.15400399180881	0.79778694508576
O	0.24679951065167	4.12664641029410	2.01687080332849
H	1.71735185498646	-0.76773898213071	0.41808176959528
H	-2.45683644928905	-1.81756522382123	0.00573207292547
O	2.18851614396509	2.25036447257807	1.06544347470203
H	-0.05997336960369	-2.40511598003401	-0.25435490846498
H	-3.13997489574058	0.42093636588472	0.87506002187383
C	-2.49106834772739	3.07469122049287	1.73275243507033
H	-3.13727028722364	2.58583183725990	2.48007972067992
H	-2.27296733547285	4.10230409555401	2.05283766346224
H	-3.02222297017240	3.10441872967093	0.76751140355729
Ti	2.83645914871950	4.11953168073453	0.73842146737451
Cl	1.40960108680040	4.02185966570060	-1.03116688031520
Cl	4.78767670232666	3.63792166309595	-0.13957121491418

Cl	3.41797742607749	4.11029732938436	3.02320590398948
Cl	2.79022444162331	6.33873945001546	0.76838988938675
H	-0.91695872732901	-0.35029821601400	4.95870809797538
C	0.19436890852826	1.39630559660527	4.14310076216769
C	1.41576980385375	1.47387550551898	3.39184455495799
N	1.95258995175799	0.15063889218713	3.41229153699497
C	1.05123038906345	-0.66926438930327	3.97548840640014
C	-0.05641302953118	0.07045002640210	4.44250391393923
H	-0.41952821678039	2.26060489293621	4.38671224186628
H	2.10979753111611	2.31753709983038	3.51529225709126
H	1.22637735540845	-1.73960210605975	4.04835100846331
C	3.17931665165721	-0.24339000310045	2.80163682566491
C	4.17024718003229	0.71296009793899	2.55394752980374
C	5.35400963522252	0.32942449945992	1.92123358860259
C	5.56760454838160	-1.00099222368203	1.55728357054636
C	4.57917066960301	-1.95621184134054	1.81943900613903
C	3.38164911502031	-1.58243621060324	2.42694609404187
H	4.02969601753214	1.75542724787042	2.83471458146037
H	6.10213204676372	1.09360732786482	1.70332338683552
H	6.49332368074944	-1.29689739341581	1.05880336299211
H	4.73204056641646	-2.99715224015522	1.52458857953320
H	2.60205503017122	-2.33011362076715	2.57575627608878

VIBRATIONAL FREQUENCIES

Number of imaginary frequencies = 1

Scaling factor for frequencies = 1.000000000 (already applied!

0:	0.00 cm**-1	3:	0.00 cm**-1	6:	-274.89 cm**-1
1:	0.00 cm**-1	4:	0.00 cm**-1		***imaginary mode***
2:	0.00 cm**-1	5:	0.00 cm**-1	7:	20.26 cm**-1

8:	36.80 cm**-1	39:	439.89 cm**-1	70:	987.41 cm**-1
9:	51.79 cm**-1	40:	444.85 cm**-1	71:	1007.15 cm**-1
10:	55.32 cm**-1	41:	458.86 cm**-1	72:	1010.33 cm**-1
11:	69.02 cm**-1	42:	460.47 cm**-1	73:	1013.42 cm**-1
12:	78.00 cm**-1	43:	497.11 cm**-1	74:	1032.63 cm**-1
13:	91.81 cm**-1	44:	507.38 cm**-1	75:	1040.29 cm**-1
14:	99.61 cm**-1	45:	536.13 cm**-1	76:	1043.46 cm**-1
15:	109.20 cm**-1	46:	547.44 cm**-1	77:	1053.62 cm**-1
16:	118.49 cm**-1	47:	586.23 cm**-1	78:	1063.56 cm**-1
17:	121.05 cm**-1	48:	605.22 cm**-1	79:	1087.19 cm**-1
18:	135.82 cm**-1	49:	612.00 cm**-1	80:	1089.08 cm**-1
19:	146.80 cm**-1	50:	634.25 cm**-1	81:	1112.71 cm**-1
20:	151.64 cm**-1	51:	666.03 cm**-1	82:	1117.67 cm**-1
21:	163.93 cm**-1	52:	696.88 cm**-1	83:	1123.12 cm**-1
22:	170.64 cm**-1	53:	709.61 cm**-1	84:	1144.76 cm**-1
23:	180.13 cm**-1	54:	724.48 cm**-1	85:	1155.79 cm**-1
24:	186.39 cm**-1	55:	731.14 cm**-1	86:	1173.13 cm**-1
25:	199.98 cm**-1	56:	750.69 cm**-1	87:	1187.97 cm**-1
26:	213.54 cm**-1	57:	790.26 cm**-1	88:	1191.03 cm**-1
27:	223.46 cm**-1	58:	811.64 cm**-1	89:	1195.90 cm**-1
28:	264.92 cm**-1	59:	812.60 cm**-1	90:	1229.79 cm**-1
29:	284.33 cm**-1	60:	836.36 cm**-1	91:	1273.89 cm**-1
30:	304.97 cm**-1	61:	876.85 cm**-1	92:	1275.80 cm**-1
31:	320.51 cm**-1	62:	883.80 cm**-1	93:	1295.81 cm**-1
32:	332.18 cm**-1	63:	888.14 cm**-1	94:	1327.75 cm**-1
33:	337.74 cm**-1	64:	906.40 cm**-1	95:	1331.68 cm**-1
34:	354.30 cm**-1	65:	926.93 cm**-1	96:	1343.99 cm**-1
35:	372.34 cm**-1	66:	939.97 cm**-1	97:	1360.86 cm**-1
36:	386.33 cm**-1	67:	970.63 cm**-1	98:	1392.17 cm**-1
37:	401.26 cm**-1	68:	976.96 cm**-1	99:	1395.72 cm**-1
38:	424.55 cm**-1	69:	981.31 cm**-1	100:	1418.45 cm**-1

101:	1455.79 cm**-1	112:	1611.01 cm**-1	123:	3098.07 cm**-1
102:	1458.84 cm**-1	113:	1619.20 cm**-1	124:	3108.19 cm**-1
103:	1471.02 cm**-1	114:	1629.50 cm**-1	125:	3110.23 cm**-1
104:	1497.62 cm**-1	115:	1783.89 cm**-1	126:	3114.09 cm**-1
105:	1500.20 cm**-1	116:	2943.61 cm**-1	127:	3117.71 cm**-1
106:	1501.52 cm**-1	117:	2960.37 cm**-1	128:	3124.58 cm**-1
107:	1504.78 cm**-1	118:	2990.82 cm**-1	129:	3144.76 cm**-1
108:	1526.73 cm**-1	119:	3048.35 cm**-1	130:	3159.30 cm**-1
109:	1532.47 cm**-1	120:	3083.87 cm**-1	131:	3169.73 cm**-1
110:	1549.38 cm**-1	121:	3083.97 cm**-1		
111:	1610.54 cm**-1	122:	3097.47 cm**-1		

DFT-Calculation results for $Yb(OTf)_3$ catalyst using PW91/ZORA-def2-SVP level

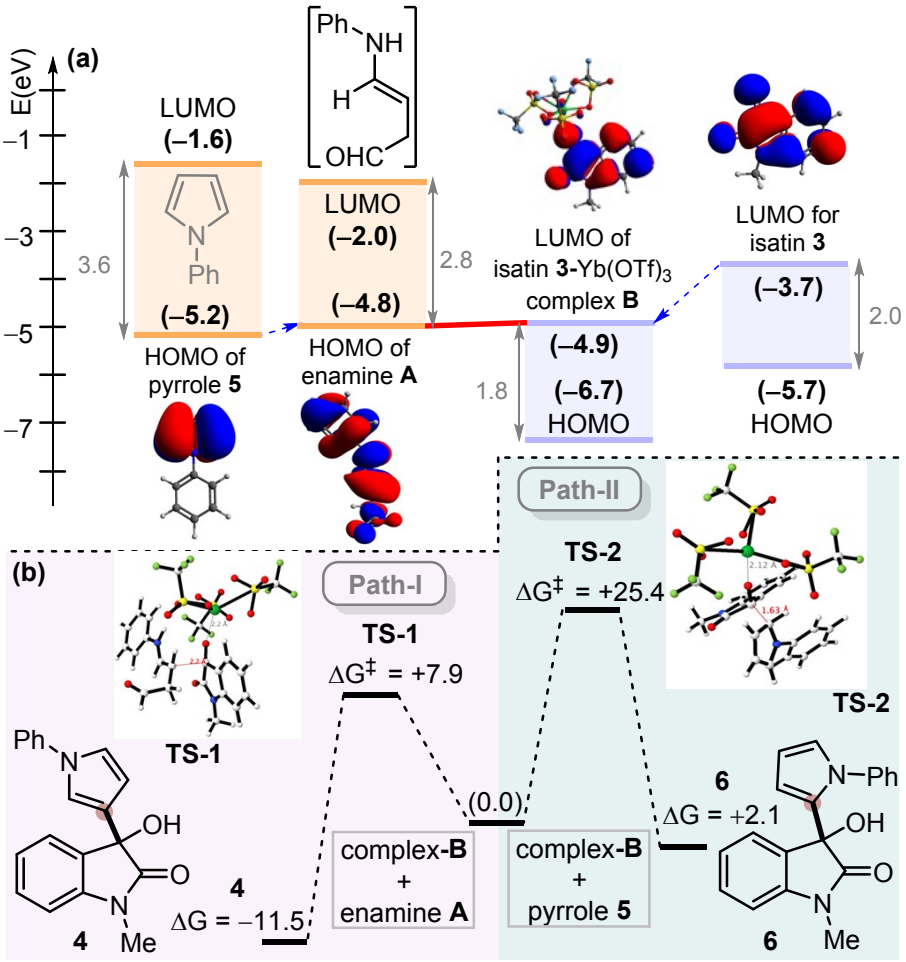
Settings:

Geometry optimization and transition state search:

PW91 OPT ZORA ZORA-def2-SVP SARC/J
NewGTO Yb "SARC-ZORA-TZVP"

Final single point run:

PW91 SP ZORA ZORA-def2-TZVP SARC/J Grid5
NewGTO Yb "SARC-ZORA-TZVP"



Scheme-S3: The HOMO & LUMO of pyrrole **5**, enamine **A**, isatin **3** and isatin-$Yb(OTf)_3$ complex **B**. (b) Transition State Geometries and Relative Activation Energies for the two possible ways of reacting partners. Path-I: access to C-3 substituted pyrrole via reaction of enamine-**A** with complex-**B** (**TS-1**), Path-II: access to C2-substituted pyrrole via Friedel-Craft reaction of pyrrole **5** with complex-**B** (**TS-2**). Gibbs activation energies ($\Delta G^{\ddagger}$, kcal/mol) and Gibbs reaction energies (ΔG, kcal/mol) are shown.

Figure S7: The pictures of the frontier orbitals are given below

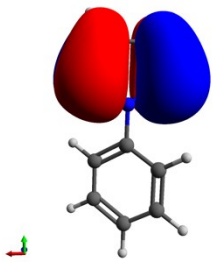
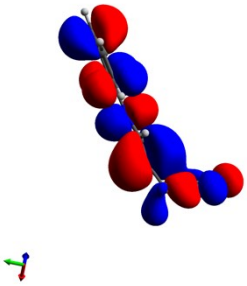
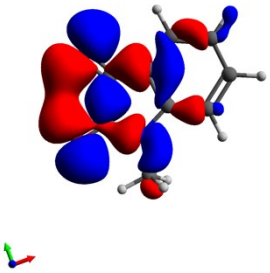
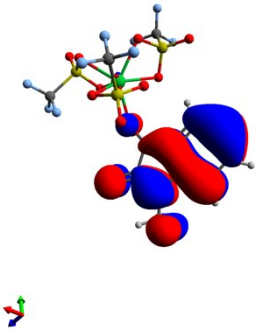
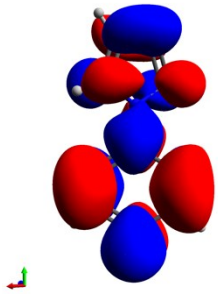
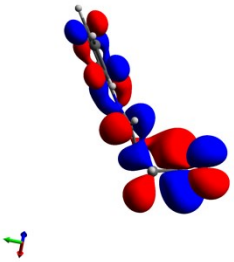
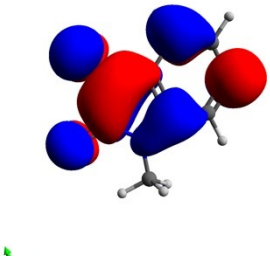
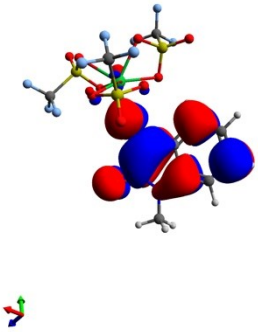
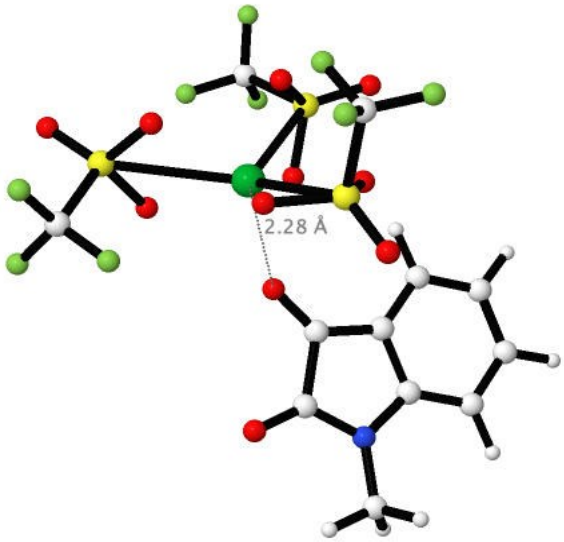
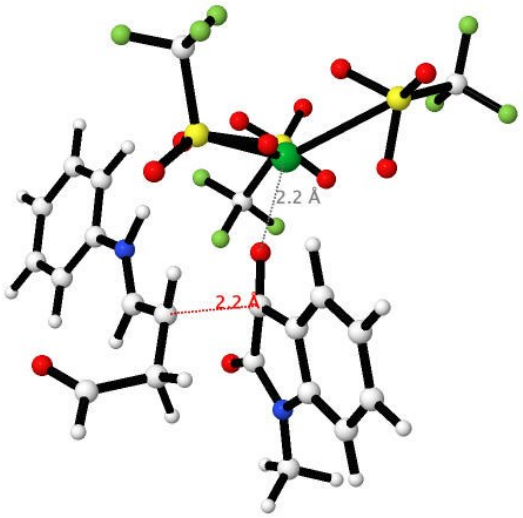
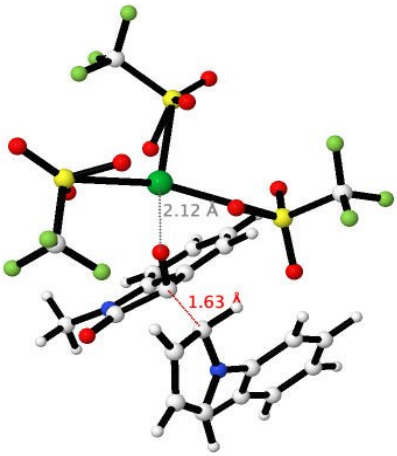
			
e) HOMO of preformed Pyrrole **5** (-5.2 eV)	f) HOMO of in situ enamine-**A** (-4.8 eV)	g) HOMO of Isatin **3** (-5.7 eV)	h) HOMO of the activated Isatin 3 (with LA= $Yb(OTf)_3$), complex **B** (-6.7 eV)
			
e) LUMO of preformed pyrrole **5** (-1.6 eV)	f) LUMO of in situ enamine-**A** (-2.0 eV)	g) LUMO Isatin **3** (-3.7 eV)	h) LUMO of the Activated Isatin 3 (with LA= $Yb(OTf)_3$), complex **B** (-4.9 eV).

Table S8: The optimized structures of Isatine-**3**, TS-**1**, and TS-**2** with $Yb(OTf)_3$

Isatin **3** with $Yb(OTf)_3$ complex **B**	
	
TS-**1** with $Yb(OTf)_3$	TS-2 with $Yb(OTf)_3$
	

Isatine-**3**

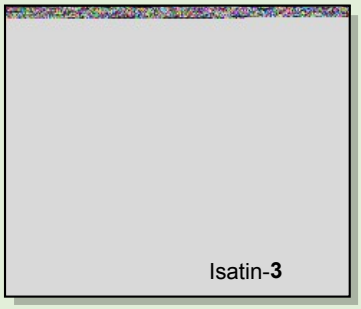
GIBBS FREE ENERGY

Single point energy (Uel) = -552.8628985Eh

Thermal correction = 0.10562902 Eh

Final Gibbs free energy = -552.7572695 Eh

Number of imaginary frequencies = 0



C	-0.11392989556882	-0.24217666651395	0.20497921423982
C	-4.08619201719259	1.17696140015383	-0.08821599632589
C	-4.77772803573991	-0.23432584427579	-0.11852748865789
N	-3.73956426530080	-1.16487189257156	-0.03670778724907
C	-0.25406185511528	1.15752203071509	0.17689629794657
C	-1.53344474240543	1.73058408048650	0.08085500883433
C	-2.64481076403870	0.88541259859418	0.01477490091548
C	-2.49409888281323	-0.52609685636543	0.04285436461057
C	-1.22496727456393	-1.10668827291806	0.13887554693862
O	-5.96377486872447	-0.48648893910388	-0.19745612420385
H	-1.67956180267558	2.81663419187969	0.05673607812735
H	0.88827668037102	-0.67857641230180	0.28096085674312
O	-4.67865057388928	2.23659009597280	-0.14157207627953
H	0.63421291519932	1.79438765643780	0.23014867252040
H	-1.09133159489085	-2.19284705568471	0.16255354779342
C	-3.95716274212456	-2.59361086720361	-0.03379885692162
H	-3.59015227233094	-3.05542192985192	0.90054941026706
H	-5.04365974156027	-2.75485209659975	-0.11301882542278
H	-3.45560539663567	-3.07932327084945	-0.88983606387611

Isatine **3** – $Yb(OTf)_3$

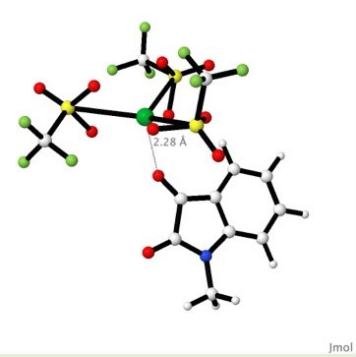
GIBBS FREE ENERGY

Single point energy (Uel) = -17883.36652 Eh

Thermal correction = 0.15642893 Eh

Final Gibbs free energy = -17883.21009 Eh

Number of imaginary frequencies = 0



S	-0.43038957089967	4.02910620801403	1.69331644623251
C	0.39047249838508	2.90918459466572	2.96654655045335
F	1.68945927399665	3.17140056412264	3.00286257689708
F	0.18869950304028	1.64295195004762	2.59300869737643
F	-0.16325282304390	3.12704378756864	4.15214323382421
O	-0.26361003653459	5.41852189205213	2.12251864192236
O	0.19849105063948	3.60047280963744	0.36382763104964
O	-1.86804235915146	3.47597229449734	1.62462672884671
S	-3.21309065335851	4.00865082368769	-2.15089318328360
C	-3.49096164947215	5.76263160744414	-1.52130764352669
F	-2.88069809549677	5.89393087778672	-0.34561120646030
F	-4.79644184299377	5.96075808720822	-1.38432690436297
F	-2.98102495840655	6.61386702989298	-2.40120172319659
O	-1.68974129155114	3.83889919296518	-2.10719991045572
O	-3.73276778914975	3.11274941610349	-1.01254267419860
O	-3.88388318637879	3.87848400402276	-3.44822733246156
Yb	-1.63058512960832	2.33281854980966	-0.35244462731664
S	-0.52369290613058	-0.02401701087945	-1.70558345077128
C	0.76539276260282	0.45352519672526	-2.99238278955767
F	1.91457095311531	-0.13313465420090	-2.68609438419422
F	0.90384669535507	1.77875969940864	-2.96965706937886
F	0.34349839944675	0.05768603659122	-4.18607621872196
O	-0.64250685087673	-1.48587077260837	-1.68330036883079
O	-0.02839637945577	0.66311090841264	-0.42455029180816
O	-1.76728212926957	0.77375669929520	-2.11765144583212
C	-6.62308868129089	-1.67368113388145	-2.12553684740540
C	-3.74618197439569	-0.18058672109880	0.52882742426390
C	-3.86614031499995	-1.30692008735053	1.60746093722092
N	-4.83217698068177	-2.18032286491915	1.12188749212662
C	-6.01766222637139	-0.46378559678484	-2.51917723798495
C	-5.04648174170876	0.13343924572863	-1.70677341098954
C	-4.70109066897531	-0.50784303764842	-0.50195166108226
C	-5.32615818435624	-1.73132253812755	-0.10883053169111
C	-6.29293830319660	-2.32680353032710	-0.92036008112404
O	-3.23999866948139	-1.40142582806284	2.64216588739290
H	-4.56967454127842	1.07859708851481	-1.97992174624601
H	-7.37942763953354	-2.12701062036089	-2.77596070759996
O	-2.93391750166905	0.74294794600807	0.63654571733926

H	-6.30629516000647	0.00833307233229	-3.46230769408881
H	-6.77851032884716	-3.26546042749933	-0.64044049176819
C	-5.22807111534046	-3.39218160696636	1.80852231878070
H	-5.01113297556207	-4.28427470121418	1.19565909424809
H	-4.64474894068587	-3.44416323047252	2.73952908910372
H	-6.30327753642041	-3.37629522014110	2.05639316725985

Pyrrole **5**

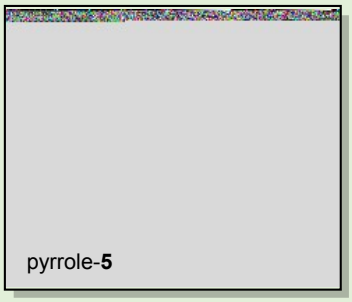
GIBBS FREE ENERGY

Single point energy (Uel) = -441.5165959 Eh

Thermal correction = 0.12638898 Eh

Final Gibbs free energy = -441.390207 Eh

Number of imaginary frequencies = 0



H	1.48421127654596	-0.45532797018456	0.12421806120211
C	-0.52991273719164	-1.47721981241430	0.23725448356354
C	-0.86149547511368	-2.81163539672026	0.06625920974636
N	0.30362084540500	-3.52195516241006	-0.18722640089200
C	1.37349670268059	-2.63812357556055	-0.18063427025542
C	0.88639056910186	-1.36612675493988	0.07435147915991
H	-1.22950314714689	-0.67326306902875	0.46855726210941
H	-1.81748549338180	-3.32490884673002	0.16226564213675
H	2.37993928059473	-2.98056716997452	-0.41654252773170
C	0.38697441878334	-4.91742794817676	-0.41502777838188
C	-0.66293568712156	-5.59586142223892	-1.06656789903576
C	-0.57881064557490	-6.97737548354554	-1.28297041532926
C	0.55452279601345	-7.69637488600163	-0.87262552384090
C	1.60328891269779	-7.01884494650680	-0.23144028324320
C	1.52123491090352	-5.64068508672767	0.00614380604984
H	-1.52971010671762	-5.03276451805790	-1.42569360687490
H	-1.40159830344626	-7.49123488569453	-1.79216574350365
H	0.62069746644608	-8.77426514035533	-1.05301061117210
H	2.48994219033376	-7.56846788355957	0.10277501273766
H	2.32534648618823	-5.12343239117232	0.53898807355520

Enamine **A**

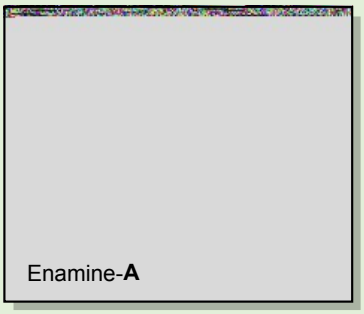
GIBBS FREE ENERGY

Single point energy (Uel) = -518.0265712 Eh

Thermal correction = 0.14558654 Eh

Final Gibbs free energy = -517.8809847 Eh

Number of imaginary frequencies = 0



C	2.16996522869975	-7.12689975021523	-2.38046794216133
C	2.03923517018910	-6.21688524691621	-1.18738497437383
H	-1.62015726939090	-2.25041381239996	3.27105258649691
N	0.67524552534376	-4.83161116805278	0.27566284305969
H	1.44693913910049	-4.78365730128169	0.93817212321333
H	0.35328490197853	-3.58182832690567	2.56992936383945
H	2.85495245887598	-8.87202888355174	-1.16325598974630
H	3.14389762763807	-6.96720136952955	-2.88667342492772
H	2.92252780981633	-6.08802708320730	-0.54586240218478
C	0.87187363749732	-5.61328688168466	-0.84271588824734
H	-0.01284536545328	-5.74001375217529	-1.47743644155451
O	1.29410437089755	-9.39346529800767	-2.36827162368079
C	2.09841767229980	-8.58765001164062	-1.95130688131651
C	-0.45687449603274	-4.09272533107110	0.61806537859848
C	-1.56584214750306	-3.93654903935799	-0.24711562867789
C	-2.67861315850842	-3.19062597841619	0.16294802643681
C	-2.71743233561680	-2.57742630278309	1.42461331379251
C	-1.61399355230775	-2.72087149137721	2.28207503254075
C	-0.49937420218548	-3.46814477890025	1.88842931793348
H	-1.56097723731656	-4.38174841192132	-1.24600453312054
H	-3.52552659123393	-3.08207449200593	-0.52392889805737
H	-3.59113283396955	-1.99517008695040	1.73345996269022
H	1.36942488718178	-6.96015629164736	-3.12183381055274

$Yb(OTf)_3$

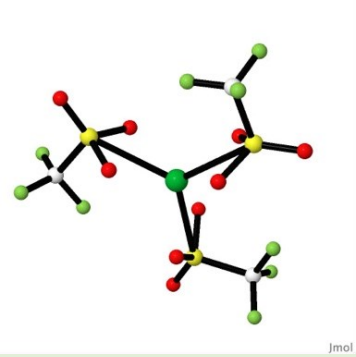
GIBBS FREE ENERGY

Single point energy (Uel) = -17330.46718 Eh

Thermal correction = 0.02619771 Eh

Final Gibbs free energy = -17330.44099 Eh

Number of imaginary frequencies = 0



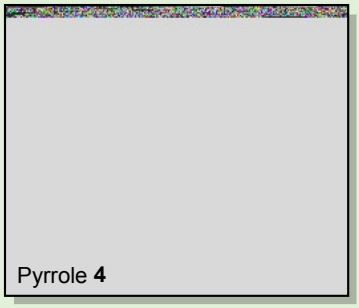
S	-2.20072383285541	3.37542330971281	1.87809397179470
C	-2.92267893266216	1.71766604702555	2.41604867889298
F	-2.17062178960616	1.19863376544514	3.37003235379258
F	-2.89999259718275	0.92383497326916	1.32998886391628
F	-4.16655150591935	1.88552389404247	2.82679541566200
O	-2.21095644180256	4.31249202569434	2.99714287896682
O	-0.83754429711813	2.96253506909118	1.28446312030767
O	-3.04496414940294	3.71751967707180	0.63136886735242
S	-0.16510191064717	4.95532663714189	-2.38153890595287
C	0.01771277463355	6.44608081910660	-1.23839075163960
F	-0.57217682233229	6.13451446136759	-0.07941678111342
F	-0.58226651241295	7.48667292958878	-1.79170304823857
F	1.30383070961029	6.68630913132327	-1.04713379388971
O	0.44640889840371	3.79984991103949	-1.56641118683309
O	-1.67881704748122	4.65848157076041	-2.33300831824041
O	0.42764035631637	5.26551992600088	-3.68068801378973
Yb	-1.54809234783092	2.90204442628794	-0.88819303982624
S	-2.08221263165620	0.43284591603538	-2.29887110645413
C	-1.40365406646177	0.53833356862175	-4.05810578128081
F	-0.50647391000714	-0.41858323370989	-4.22505001013243
F	-0.83551595747386	1.73779992268320	-4.19648976279025
F	-2.40683833027750	0.40282413307942	-4.90910500931912
O	-2.70679252837533	-0.87249065523661	-2.09086817747496
O	-0.86417725047728	0.79100260571768	-1.42153080831627
O	-2.98077095698070	1.68246062883956	-2.18616590539374

Compound **4**

GIBBS FREE ENERGY

Single point energy (Uel) = -994.3939076 Eh
Thermal correction = 0.25752651 Eh

Final Gibbs free energy = -994.1363811 Eh
Number of imaginary frequencies = 0



C	0.46625122138264	-1.93544812021108	-3.92796613753601
C	-2.30162676356605	-0.32642959261886	-1.07409962209769
C	-3.28199404073200	-1.53415998423890	-1.18061502439437
N	-2.70530682299233	-2.48614559745007	-2.00564410532162
C	0.73265703275545	-0.63318332336555	-3.47990090771808
C	-0.12075868097258	-0.01371680961170	-2.54319040210010
C	-1.22434765337094	-0.71597856336500	-2.06495687976401
C	-1.50060545503262	-2.01332552332501	-2.55168401141434
C	-0.66196498033942	-2.64670471883213	-3.47484705997059
O	-4.38169680626474	-1.61892082386794	-0.64874399482048
H	0.06758384903706	1.01190105757858	-2.21055963193392
H	1.13851636743826	-2.40769372714605	-4.65277459792605
O	-2.95739104642767	0.86120705687381	-1.51220897714071
H	1.60419023643375	-0.09323639684164	-3.86360611164089
H	-0.87794414877656	-3.65305718659245	-3.84558046802958
C	-3.35168059208919	-3.73424080083221	-2.33895458711824
H	-2.74026492330290	-4.59842301634467	-2.02454217724001
H	-4.31230105346326	-3.75302328427905	-1.80246155420005
H	-3.54079112546920	-3.80900033060683	-3.42475403902396
C	-1.17971990030229	-0.78656923699835	4.93114645893416
C	-1.56062348671396	-1.01611162425185	6.25988916524047
C	-2.91506489871892	-0.99301396602598	6.62681398037310
C	-3.88838779786024	-0.72885216929974	5.65105032907015
C	-3.51736490800632	-0.47951801592489	4.32333252457561
H	-0.12623527171592	-0.84765139649134	4.64127915791703
H	-0.79144726005096	-1.23135758695955	7.00925449539988
H	-3.21005056762925	-1.18220059593347	7.66396548196684
H	-4.94841889066163	-0.70060362696449	5.92576236037810
H	-4.27704317088445	-0.23836769909679	3.57376060555731
H	-3.70676307042993	0.98329699068866	-0.90189294158686

C	-1.80675001282593	-0.21583103963043	0.35689062972429
C	-0.58133127510569	0.37347144634142	0.81726630699548
C	-0.58917052879050	0.32461795873355	2.19889445167997
N	-1.77597255479083	-0.26771415843128	2.61065929107933
C	-2.51953732550265	-0.59691551253185	1.49197733820697
H	-3.47620266007065	-1.11087055881863	1.56710007187924
H	0.21702146103011	0.78877186656375	0.20291395593042
H	0.12982804594877	0.69994749675868	2.92576941439330
C	-2.15747920116618	-0.51097116665055	3.95449579167581

Compound **6**

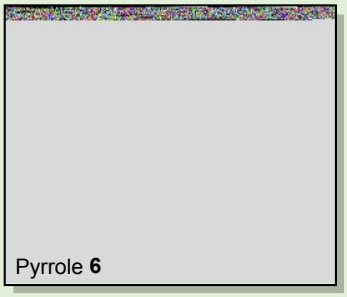
GIBBS FREE ENERGY

Single point energy (Uel) = -994.4020106 Eh

Thermal correction = 0.25799963 Eh

Final Gibbs free energy = -994.144011 Eh

Number of imaginary frequencies = 0



Pyrrole **6**

C	-1.87999827177131	2.48086398200386	-2.44343743207809
C	-3.79996876406648	-0.75031841880942	-0.38243927683677
C	-2.91962431036196	-1.85650882191289	-1.05986738130276
N	-2.06950998658079	-1.23327217190887	-1.95849933185714
C	-2.87905514002691	2.84277437716017	-1.52617619745399
C	-3.56633305849183	1.85066360392833	-0.79607705224789
C	-3.23916949166334	0.51468008443617	-1.00572934953522
C	-2.23337228656055	0.15998566051094	-1.93107073269392
C	-1.53802757889095	1.13075958062613	-2.66001792540538
O	-3.03779165112332	-3.06037505756309	-0.89251112903014
H	-4.34402912494720	2.11786612025293	-0.07218641035627
H	-1.35144317799042	3.25982297213130	-3.00316782834583
O	-5.12889814822213	-0.94804417218281	-0.86071594037042
H	-3.12649443383012	3.89913691712856	-1.37860517596454
H	-0.75515617050276	0.85690782088273	-3.37525099336513
C	-1.14800902655247	-1.95667085766063	-2.80281342415386
H	-0.10116013389622	-1.68968868291724	-2.56890887483448
H	-1.29977629106918	-3.03001796116745	-2.60580114740184
H	-1.34060724956177	-1.75119061437869	-3.87157561448959

H	-1.08197304210178	0.85008666610229	0.87063212121125
H	1.29330406578786	0.53554321110438	0.14725370132293
H	2.39343437919524	-1.70053927128253	0.40217502135174
H	1.10545768632988	-3.61846567480310	1.36437219098404
H	-5.03848769444829	-0.83836331434627	4.21827543505723
C	-0.59765951156989	-0.12730515394484	0.96174492394783
C	0.73410908867185	-0.30999019808870	0.56153376157969
C	1.35095373066548	-1.56266024878890	0.70780086166753
C	0.62969894808852	-2.63832937792700	1.25114901854370
C	-0.70543546952653	-2.46743268338339	1.64058444564255
H	-5.35933694095385	-1.86004642684097	-0.59909868175442
C	-3.79066016034492	-0.80823762814470	1.12731391110346
N	-2.67238543999669	-1.03528601535494	1.92274913459571
C	-3.06697396344873	-1.08000453550940	3.25079860056179
C	-4.43570182542423	-0.86883505810429	3.30997980405269
C	-4.89396332821727	-0.69992593233964	1.97058370679556
H	-5.91480447172245	-0.52847225081405	1.63021000339414
H	-1.29119924412038	-3.30193197534253	2.03774224810883
H	-2.32622921718951	-1.23782878413850	4.03476386946155
C	-1.32038123356448	-1.21046817861295	1.49397852009543

TS-**1** with $Yb(OTf)_3$

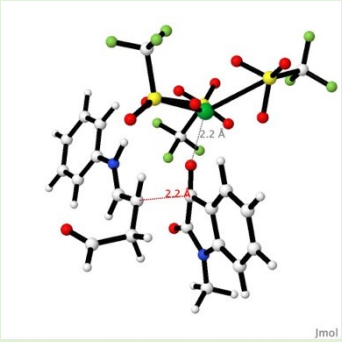
GIBBS FREE ENERGY

Single point energy (Uel) = -18401.41019 Eh

Thermal correction = 0.33181216 Eh

Final Gibbs free energy = -18401.07838 Eh

Number of imaginary frequencies = 1



S	0.27817985629093	3.75553749267330	2.49074987601439
C	0.55158853487918	2.87323781836839	4.13675348371250
F	1.79414671134250	3.11377983998640	4.55562613611054
F	0.37566285380292	1.56002273675600	3.96799124075499
F	-0.32766293743115	3.33580979618781	5.02212322966793
O	0.48532378028798	5.18826739382408	2.73455564388026
O	1.24322429669729	3.05243954268864	1.51959042048802
O	-1.12056474791220	3.29988484162483	2.05335181906495
S	-1.97840146022462	3.59106706172552	-1.66506936714789

C	-2.73241183138022	5.21659568568114	-1.06347334086155
F	-2.39677114557049	5.42640249690115	0.20610956659762
F	-4.05741877201335	5.13180734608790	-1.17732789219396
F	-2.26835167404603	6.20302533740852	-1.82832829562591
O	-0.48046047880862	3.72288593092327	-1.33165047565381
O	-2.50825084320013	2.52913561292975	-0.68832975732819
O	-2.34636690471200	3.45416736072279	-3.08084116676181
Yb	-0.42160591302504	2.00851345705375	0.23410669634462
S	1.05586723947932	0.09141648994523	-1.58966062106607
C	2.17404327174909	0.96653033210802	-2.83927555060485
F	3.42141992949279	0.53722599633965	-2.66166464973772
F	2.10533170801260	2.27796980961660	-2.62634512702024
F	1.75200339195754	0.67270910849134	-4.06397055215365
O	1.22490290975012	-1.36299444088155	-1.78018118346327
O	1.53293373939480	0.63933987376211	-0.22497271195440
O	-0.33058370888400	0.67388668926205	-1.80835373494236
C	-5.07419645734252	-2.55920144954480	-0.62902834719641
C	-1.74532260366309	-0.90550344642190	1.41493689714729
C	-2.15964296230112	-1.37511916504549	2.83931612721850
N	-3.33030573191971	-2.11900277475467	2.66804961822604
C	-4.17152636748206	-1.82697582212782	-1.42693150164399
C	-3.02799158004846	-1.23802049804018	-0.85402307373938
C	-2.80995270748705	-1.40755381536884	0.52037385091512
C	-3.73426730920949	-2.13351178514291	1.32108267174008
C	-4.87279975670881	-2.72325276839592	0.75875215369120
O	-1.60548740891504	-1.15182631867416	3.90410662624288
H	-2.32028978813345	-0.65504946517541	-1.45711034905345
H	-5.96393028643704	-3.00406595061966	-1.09168751912125
O	-1.06511520047844	0.15553976558004	1.23520555667694
H	-4.36590150002106	-1.70600580815128	-2.49897990778557
H	-5.59650994436413	-3.27508023563303	1.36983837914005
C	-4.07020275806558	-2.69245931114555	3.77705583418264
H	-4.17199035655046	-3.78851303263089	3.67231096094171
H	-3.50869658201777	-2.46366480856486	4.69783468227122
H	-5.07895868486630	-2.24646781380852	3.85086336454180
C	-0.89699722075097	-3.86529548299449	1.15385308755135
C	-0.25871565017655	-2.50040782198068	1.12120240246399
H	4.68998494314290	1.84804437680584	3.42122018369493
N	1.56516370009058	-1.17682877153224	2.00669784973791
H	1.56787333900812	-0.62479687645000	1.12338119077948
H	2.96994159861305	1.03405249394497	1.81257222199546
H	-0.33536287621852	-6.02203895495445	0.93164296683744
H	-1.57378025898374	-4.01344000165892	0.29186764530859
H	-0.04922600209272	-2.10557469239521	0.11696362380657

C	0.68105887270446	-2.17286769564881	2.12166706249519
H	0.65835337846738	-2.69041086548128	3.08686104254340
O	1.26804304459451	-4.91692690045724	1.52916152313581
C	0.10414174445385	-5.02057391274984	1.20058355659891
C	2.52171032631409	-0.76379183048687	2.95798045139950
C	2.81814232162279	-1.51807740551909	4.11697022270249
C	3.78278478142063	-1.04880594243301	5.01724409735524
C	4.46142500340233	0.16118464742501	4.77696540699284
C	4.17197572869231	0.90216966081950	3.61758422195653
C	3.21114706972710	0.44643284802437	2.70629043697561
H	2.32473816361987	-2.47667865662522	4.30888419810070
H	4.01289321697166	-1.63974192486321	5.91209016375631
H	5.21460226144795	0.51930056587786	5.48918589071182
H	-1.54010730598829	-4.01082596318793	2.05180084258305

VIBRATIONAL FREQUENCIES

Number of imaginary frequencies = 1

0:	0.00 cm**-1	20:	53.39 cm**-1	41:	178.93 cm**-1
1:	0.00 cm**-1	21:	59.13 cm**-1	42:	182.44 cm**-1
2:	0.00 cm**-1	22:	61.82 cm**-1	43:	202.18 cm**-1
3:	0.00 cm**-1	23:	66.36 cm**-1	44:	205.28 cm**-1
4:	0.00 cm**-1	24:	69.39 cm**-1	45:	206.09 cm**-1
5:	0.00 cm**-1	25:	73.37 cm**-1	46:	210.24 cm**-1
6:	-188.57 cm**-1	26:	75.68 cm**-1	47:	215.41 cm**-1
imaginary mode		27:	79.68 cm**-1	48:	228.81 cm**-1
7:	13.85 cm**-1	28:	85.24 cm**-1	49:	233.61 cm**-1
8:	22.93 cm**-1	29:	98.67 cm**-1	50:	241.31 cm**-1
9:	24.93 cm**-1	30:	103.08 cm**-1	51:	244.70 cm**-1
10:	28.04 cm**-1	31:	116.83 cm**-1	52:	256.66 cm**-1
11:	30.05 cm**-1	32:	120.94 cm**-1	53:	279.96 cm**-1
12:	34.98 cm**-1	33:	135.02 cm**-1	54:	286.31 cm**-1
13:	36.18 cm**-1	34:	143.52 cm**-1	55:	290.25 cm**-1
14:	38.51 cm**-1	35:	146.02 cm**-1	56:	291.62 cm**-1
15:	41.74 cm**-1	36:	151.38 cm**-1	57:	302.17 cm**-1
16:	46.56 cm**-1	37:	157.22 cm**-1	58:	308.71 cm**-1
17:	47.91 cm**-1	38:	161.12 cm**-1	59:	309.57 cm**-1
18:	49.96 cm**-1	39:	164.89 cm**-1	60:	314.62 cm**-1
19:	52.73 cm**-1	40:	177.01 cm**-1	61:	316.09 cm**-1

62: 324.32 cm**-1
63: 336.60 cm**-1
64: 342.66 cm**-1
65: 349.83 cm**-1
66: 351.42 cm**-1
67: 352.75 cm**-1
68: 359.27 cm**-1
69: 392.80 cm**-1
70: 403.86 cm**-1
71: 467.59 cm**-1
72: 468.83 cm**-1
73: 469.97 cm**-1
74: 472.28 cm**-1
75: 475.40 cm**-1
76: 496.69 cm**-1
77: 509.01 cm**-1
78: 514.90 cm**-1
79: 515.37 cm**-1
80: 519.99 cm**-1
81: 525.39 cm**-1
82: 547.21 cm**-1
83: 550.92 cm**-1
84: 551.56 cm**-1
85: 552.80 cm**-1
86: 557.28 cm**-1
87: 558.20 cm**-1
88: 558.89 cm**-1
89: 584.90 cm**-1
90: 590.68 cm**-1
91: 593.45 cm**-1
92: 595.72 cm**-1
93: 603.85 cm**-1
94: 607.62 cm**-1
95: 652.84 cm**-1
96: 675.20 cm**-1
97: 678.45 cm**-1
98: 694.77 cm**-1
99: 710.83 cm**-1
100: 748.31 cm**-1
101: 749.77 cm**-1
102: 750.57 cm**-1
103: 751.04 cm**-1
104: 752.17 cm**-1
105: 756.13 cm**-1
106: 781.77 cm**-1
107: 803.87 cm**-1
108: 834.91 cm**-1
109: 852.01 cm**-1
110: 853.08 cm**-1
111: 855.38 cm**-1
112: 871.30 cm**-1
113: 894.36 cm**-1
114: 910.71 cm**-1
115: 912.70 cm**-1
116: 917.17 cm**-1
117: 925.45 cm**-1
118: 941.85 cm**-1
119: 951.16 cm**-1
120: 953.29 cm**-1
121: 975.15 cm**-1
122: 975.48 cm**-1
123: 976.15 cm**-1
124: 977.84 cm**-1
125: 987.33 cm**-1
126: 1001.18 cm**-1
127: 1012.83 cm**-1
128: 1019.91 cm**-1
129: 1025.85 cm**-1
130: 1028.59 cm**-1
131: 1036.00 cm**-1
132: 1066.84 cm**-1
133: 1077.96 cm**-1
134: 1088.81 cm**-1
135: 1111.62 cm**-1
136: 1111.92 cm**-1
137: 1139.28 cm**-1
138: 1139.63 cm**-1
139: 1142.45 cm**-1
140: 1144.73 cm**-1
141: 1150.58 cm**-1
142: 1166.07 cm**-1
143: 1170.39 cm**-1
144: 1177.20 cm**-1
145: 1216.78 cm**-1
146: 1220.00 cm**-1
147: 1224.16 cm**-1
148: 1233.72 cm**-1
149: 1234.46 cm**-1
150: 1240.31 cm**-1
151: 1242.19 cm**-1
152: 1247.92 cm**-1
153: 1249.16 cm**-1
154: 1252.85 cm**-1
155: 1265.93 cm**-1
156: 1268.97 cm**-1
157: 1271.42 cm**-1
158: 1297.72 cm**-1
159: 1301.15 cm**-1
160: 1315.55 cm**-1
161: 1342.66 cm**-1
162: 1349.80 cm**-1
163: 1362.19 cm**-1
164: 1373.55 cm**-1
165: 1383.90 cm**-1
166: 1393.16 cm**-1
167: 1399.93 cm**-1
168: 1438.83 cm**-1
169: 1445.99 cm**-1
170: 1452.78 cm**-1
171: 1464.68 cm**-1
172: 1472.50 cm**-1
173: 1482.62 cm**-1
174: 1491.42 cm**-1
175: 1523.17 cm**-1
176: 1580.14 cm**-1
177: 1593.47 cm**-1
178: 1602.10 cm**-1
179: 1611.42 cm**-1
180: 1636.61 cm**-1
181: 1763.34 cm**-1
182: 1775.61 cm**-1
183: 2815.21 cm**-1
184: 2933.37 cm**-1
185: 2973.67 cm**-1
186: 3033.23 cm**-1
187: 3049.61 cm**-1
188: 3094.76 cm**-1
189: 3097.25 cm**-1
190: 3121.63 cm**-1
191: 3122.54 cm**-1
192: 3128.02 cm**-1
193: 3132.83 cm**-1

194:	3136.21 cm**-1	197:	3145.12 cm**-1	200:	3176.78 cm**-1
195:	3138.21 cm**-1	198:	3148.05 cm**-1		
196:	3144.54 cm**-1	199:	3151.62 cm**-1		

TS-**2** with $Yb(OTf)_3$

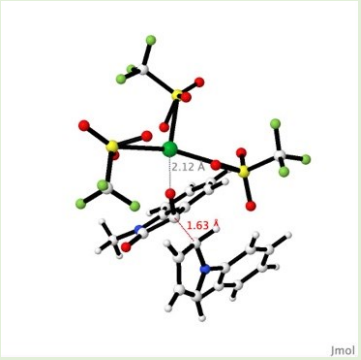
GIBBS FREE ENERGY

Single point energy (Uel) = -1832487184 Eh

Thermal correction = 0.31208115 Eh

Final Gibbs free energy = 18324.55976 Eh

Number of imaginary frequencies = 1



S	-1.058383	4.676783	1.918189
C	0.013692	4.351495	3.446514
F	0.990889	5.259221	3.528408
F	0.572394	3.121945	3.333247
F	-0.727040	4.388245	4.557855
O	-1.459651	6.083789	1.973375
O	-0.158505	4.217531	0.770167
O	-2.147793	3.607311	2.025779
S	-3.133240	2.229146	-1.847459
C	-4.214187	3.783621	-1.832235
F	-3.858284	4.571855	-0.805566
F	-5.498338	3.431878	-1.695779
F	-4.055740	4.450913	-2.981194
O	-1.704877	2.781039	-1.800837
O	-3.359886	1.616237	-0.460467
O	-3.540245	1.452012	-3.020830
Yb	-1.246363	2.156933	0.404463
S	0.778028	-0.160308	-0.713324
C	2.155750	-0.052556	-2.007120
F	3.321315	0.220588	-1.406451
F	1.874614	0.904805	-2.894584
F	2.248992	-1.232653	-2.638281
O	1.259086	-1.214929	0.238356
O	0.777510	1.247368	-0.108249
O	-0.486512	-0.447347	-1.445812
C	-4.942876	-2.860755	0.759822
C	-1.713451	-0.576975	2.441736
C	-2.472152	-0.325232	3.813805

N	-3.704986	-0.947043	3.736276
C	-3.820701	-2.669543	-0.068342
C	-2.697185	-1.954140	0.394697
C	-2.709338	-1.468854	1.704450
C	-3.863560	-1.624105	2.511404
C	-4.987703	-2.330779	2.064411
O	-2.034657	0.298969	4.768731
H	-1.842786	-1.754894	-0.270669
H	-5.814760	-3.412499	0.376174
O	-1.438971	0.565712	1.792905
H	-3.824487	-3.067512	-1.093576
H	-5.883732	-2.444042	2.691663
C	-4.700395	-0.873272	4.789204
H	-4.946957	-1.882559	5.178927
H	-4.278969	-0.256180	5.604320
H	-5.630715	-0.398701	4.414091
H	1.363425	-0.868671	5.792517
C	0.434456	-0.403801	3.821552
C	-0.275520	-1.239342	2.833894
N	-0.257645	-2.570221	3.443250
C	0.375075	-2.504962	4.626911
C	0.824475	-1.184770	4.892245
H	0.594503	0.671212	3.681118
H	0.263565	-1.257350	1.841510
H	0.526996	-3.414035	5.225366
C	-0.678900	-3.784669	2.809021
C	-0.328297	-4.028366	1.465829
C	-0.699642	-5.247324	0.878383
C	-1.407018	-6.212237	1.615997
C	-1.753983	-5.956634	2.953611
C	-1.396688	-4.740621	3.554907
H	0.245118	-3.281323	0.893185
H	-0.423421	-5.443744	-0.168144
H	-1.693051	-7.165407	1.146590
H	-2.318202	-6.703549	3.532581
H	-1.693001	-4.521782	4.591758

VIBRATIONAL FREQUENCIES

Number of imaginary frequencies = 1

0:	0.00 cm**-1	43:	216.21 cm**-1	87:	595.76 cm**-1
1:	0.00 cm**-1	44:	222.19 cm**-1	88:	607.97 cm**-1
2:	0.00 cm**-1	45:	234.29 cm**-1	89:	639.53 cm**-1
3:	0.00 cm**-1	46:	238.75 cm**-1	90:	660.22 cm**-1
4:	0.00 cm**-1	47:	264.61 cm**-1	91:	677.02 cm**-1
5:	0.00 cm**-1	48:	278.50 cm**-1	92:	694.22 cm**-1
6:	-35.14 cm**-1	49:	282.91 cm**-1	93:	701.16 cm**-1
imaginary mode		50:	287.07 cm**-1	94:	739.47 cm**-1
7:	20.35 cm**-1	51:	288.83 cm**-1	95:	740.57 cm**-1
8:	23.77 cm**-1	52:	293.88 cm**-1	96:	743.97 cm**-1
9:	28.24 cm**-1	53:	300.99 cm**-1	97:	744.93 cm**-1
10:	34.57 cm**-1	54:	306.83 cm**-1	98:	754.28 cm**-1
11:	35.52 cm**-1	55:	308.97 cm**-1	99:	765.66 cm**-1
12:	38.73 cm**-1	56:	319.13 cm**-1	100:	771.56 cm**-1
13:	42.33 cm**-1	57:	329.59 cm**-1	101:	792.60 cm**-1
14:	47.06 cm**-1	58:	340.25 cm**-1	102:	819.84 cm**-1
15:	49.58 cm**-1	59:	348.21 cm**-1	103:	847.35 cm**-1
16:	54.12 cm**-1	60:	352.25 cm**-1	104:	849.12 cm**-1
17:	57.45 cm**-1	61:	354.27 cm**-1	105:	863.98 cm**-1
18:	62.35 cm**-1	62:	358.73 cm**-1	106:	889.55 cm**-1
19:	64.79 cm**-1	63:	386.88 cm**-1	107:	911.02 cm**-1
20:	65.87 cm**-1	64:	412.79 cm**-1	108:	914.16 cm**-1
21:	66.62 cm**-1	65:	440.15 cm**-1	109:	920.71 cm**-1
22:	68.18 cm**-1	66:	447.20 cm**-1	110:	922.71 cm**-1
23:	69.92 cm**-1	67:	467.46 cm**-1	111:	924.03 cm**-1
24:	77.46 cm**-1	68:	468.23 cm**-1	112:	931.83 cm**-1
25:	78.66 cm**-1	69:	471.59 cm**-1	113:	934.66 cm**-1
26:	84.36 cm**-1	70:	474.23 cm**-1	114:	953.14 cm**-1
27:	94.15 cm**-1	71:	481.50 cm**-1	115:	957.42 cm**-1
28:	110.73 cm**-1	72:	498.25 cm**-1	116:	975.97 cm**-1
29:	123.84 cm**-1	73:	517.15 cm**-1	117:	979.72 cm**-1
30:	131.85 cm**-1	74:	521.32 cm**-1	118:	986.91 cm**-1
31:	145.04 cm**-1	75:	526.66 cm**-1	119:	993.54 cm**-1
32:	154.61 cm**-1	76:	533.97 cm**-1	120:	1004.65 cm**-1
33:	158.75 cm**-1	77:	545.23 cm**-1	121:	1013.93 cm**-1
34:	161.58 cm**-1	78:	548.34 cm**-1	122:	1021.64 cm**-1
35:	163.21 cm**-1	79:	551.72 cm**-1	123:	1029.81 cm**-1
36:	174.87 cm**-1	80:	555.02 cm**-1	124:	1030.28 cm**-1
37:	185.70 cm**-1	81:	556.50 cm**-1	125:	1039.40 cm**-1
38:	188.77 cm**-1	82:	557.47 cm**-1	126:	1050.79 cm**-1
39:	194.22 cm**-1	83:	558.07 cm**-1	127:	1064.35 cm**-1
40:	200.73 cm**-1	84:	586.63 cm**-1	128:	1076.54 cm**-1
41:	209.27 cm**-1	85:	587.63 cm**-1	129:	1085.16 cm**-1
42:	213.55 cm**-1	86:	590.65 cm**-1	130:	1087.76 cm**-1

131: 1103.86 cm**-1
132: 1119.73 cm**-1
133: 1122.20 cm**-1
134: 1125.26 cm**-1
135: 1138.15 cm**-1
136: 1139.87 cm**-1
137: 1146.94 cm**-1
138: 1157.54 cm**-1
139: 1163.17 cm**-1
140: 1176.89 cm**-1
141: 1177.47 cm**-1
142: 1181.12 cm**-1
143: 1188.30 cm**-1
144: 1197.73 cm**-1
145: 1210.60 cm**-1
146: 1215.58 cm**-1
147: 1222.15 cm**-1
148: 1225.44 cm**-1
149: 1234.04 cm**-1
150: 1248.07 cm**-1
151: 1255.24 cm**-1
152: 1277.44 cm**-1
153: 1279.48 cm**-1
154: 1288.16 cm**-1
155: 1291.60 cm**-1
156: 1302.96 cm**-1
157: 1316.74 cm**-1
158: 1345.10 cm**-1
159: 1369.75 cm**-1
160: 1389.95 cm**-1
161: 1404.88 cm**-1
162: 1408.86 cm**-1
163: 1448.26 cm**-1
164: 1454.57 cm**-1
165: 1455.75 cm**-1
166: 1463.00 cm**-1
167: 1464.73 cm**-1
168: 1483.62 cm**-1
169: 1487.87 cm**-1
170: 1542.55 cm**-1
171: 1596.31 cm**-1
172: 1599.33 cm**-1
173: 1608.33 cm**-1
174: 1609.40 cm**-1
175: 1757.96 cm**-1
176: 2714.83 cm**-1
177: 2940.34 cm**-1
178: 3013.32 cm**-1
179: 3066.92 cm**-1
180: 3075.24 cm**-1
181: 3086.35 cm**-1
182: 3087.31 cm**-1
183: 3090.58 cm**-1
184: 3096.25 cm**-1
185: 3103.41 cm**-1
186: 3103.98 cm**-1
187: 3110.44 cm**-1
188: 3112.12 cm**-1
189: 3137.52 cm**-1
190: 3162.30 cm**-1
191: 3179.43 cm**-1