Supporting Information for

Red-Light Mediated Formylation of Indoles Using Helical Carbenium Ion as Photoredox Catalyst

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1. General Information

Unless otherwise specified, all reactions were carried out in oven-dried vials or reaction vessels with magnetic stirring under an argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringes cooled to ambient temperature in a desiccator. All experiments were monitored by analytical thin-layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, the plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ and charring on a hot air gun. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in hexane and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

NMR spectroscopy. NMR spectra were recorded on JEOL 400 spectrometers in deuterated solvents using TMS as internal standard, or the solvent residue signals as secondary standards, and the chemical shifts are shown in δ scales. Deuterated solvents were degassed by three freeze-pump-thaw cycles and then dried by storing over molecular sieves (3 or 4 Å) for at least one day before use. Multiplicities of the 1H NMR signals are denoted by s(singlet), d (doublet), dd (doublet of doublet), dt (doublet of the triplet), t (triplet), quin (quintet), m (multiplet), br.s (broad singlet)… etc. Compounds were drawn using ChemDraw and the assignments of NMR spectra were done on MestReNova.

UV-Visible Studies: Absorption spectra were recorded in a JASCO V-670 spectrophotometer at room temperature in analytical-grade solvents.

Mass spectrometry. HRMS (ESI) was performed via Waters YEA955 mass spectrometer. GCMS was performed on Agilent 7890B Gas Chromatograph & 5977A Mass Selective.

Cyclic Voltammetry. Cyclic voltammetry analysis was carried out in CH instrument electrochemical analyzer (CHI1210C).

Photochemical Setup: Two parallel Red LED lamps (Kessil PR160L-640-C Red LED 640nm Photoredox Light customized wavelength, Kessil LED Lights) are placed perpendicular to the sidewall of Schlenk tubes, so that the two tubes can be equally exposed to the LEDs. The stir plate/water bath/LEDs are surrounded by an open-top cardboard box covered with aluminum foil to increase the light reflections. A small fan over the water bath is always turned on when the reaction is running.

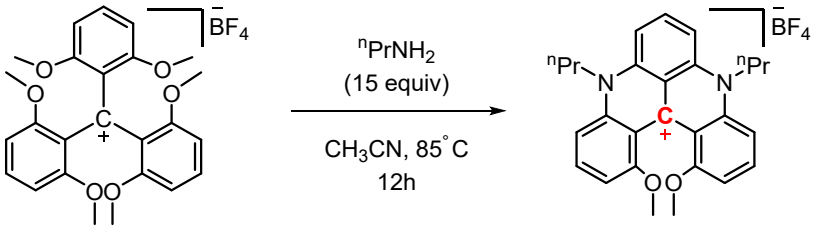
Note: The combination of an overhead fan and a water bath is to offset the heat generated from the LED lights and stabilize the reaction temperature for reproducible results. The water bath needs to be refilled with room temperature deionized water every 12-18 hours. With the above

setup, the reaction temperature can be maintained at 21-23 °C within the water bath during the reaction for us.

Figure S1 : Red light photochemical setup

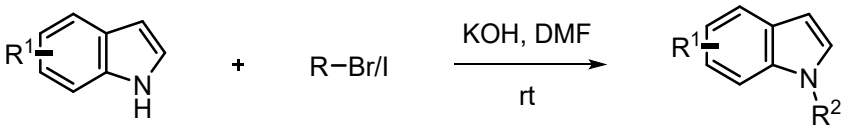
2. General Procedures

The photocatalyst nPr-DMQA-BF_4 was synthesized according to previously reported literature.[1] The spectroscopic data for PC has been compared and matched with the reported literature data.



[1] A. C. Shaikh, J. Moutet, J. M. Veleta, Md M. Hossain, J. Bloch, A. V. Astashkin and T. L. Gianetti, *Chem. Sci.*, 2020, **11**, 11060-11067.

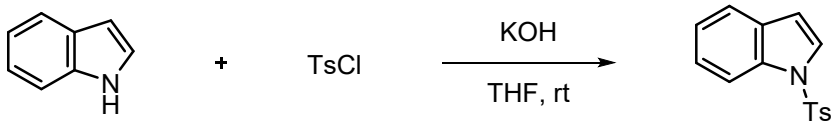
2.1 General procedure for the synthesis of N-protected indoles with alkyl bromides (GP1):



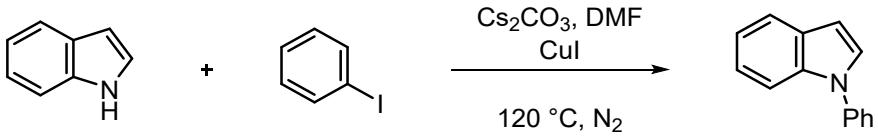
According to the previous literature,[2] in a 50 mL flask, halogenoalkane (2 equiv. in DMF) was added in dropped-wised at 0 ℃ to a stirred solution of the corresponding indoles (8.5 mmol, 1 equiv.) and KOH (3 equiv.) in DMF (20 mL). After stirring at 0 ℃ for 30 min, the reaction system was moved to room temperature to react for 6 h. After the completion (as indicated by TLC), the mixture was then extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (n-hexane/EtOAc) to give the desired product.

The spectroscopic data for all the indoles (**S1**) has been compared and matched with the reported literature data.

The *N*-Tosyl indole synthesized according to the literature method[3]



The *N*-phenyl indole synthesized according to the literature method[4]



The *N*-Boc indole synthesized according to the literature method[5]

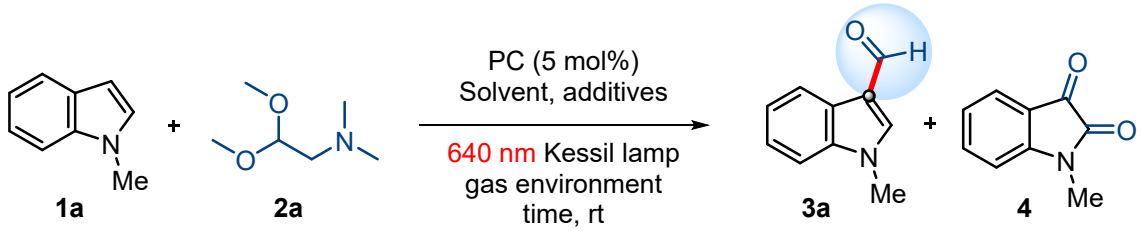
[2] Letian Zhang, Yibin Wang, Jiabin Shen, Hao Xu and Chao Shen, ***Org. Chem. Front.***, 2024, **11**, 2727

[3] Changqing Rao, Shaoyu Mai and Qiuling Song, ***Chem. Commun.***, 2018, **54**, 5964

[4] Ouyang JY, Shen FF, Zhao HQ, Chen JJ, Wen ZD, Jiang HM, Qin JH, Sun Q, Li JH and Ouyang XH, Org Lett. 2023, 25(35), 6549-6554.

[5] Changqing Rao, Shaoyu Mai and Qiuling Song, ***Chem. Commun.***, 2018, **54**, 5964

2.2 Optimization studies for formylation of Indole.



a. Screening of Solvents

Entry	Solvent	3a Yield (%) [a]	4 Yield (%) [a]
1	ACN	52[b]	45[b]
2	DMSO	28	0
3	MeOH	32	0
4	THF	trace	0
5	DCE	15	0
6	DMF	<1	0
7	ACN+H_2O	29	0
8	ACN+THF	15	0

Reaction conditions: 1a (15 mg, 0.11 mmol, 1 equiv.), **2a** (239.4 mg, 1.8 mmol, 3 equiv.), solvent (1 mL), photocatalyst (5 mol%), 24 h, under 640 nm Kessil lamp, at room temperature. a, NMR yield with internal standard. b, isolated yield.

b. Screening of additives and reaction environment

Entry	Additive	Gas environment	Solvent	3a yield[a]	4a yield
1	K_2CO_3	N_2	ACN	-	-
2	K_2CO_3	O_2 balloon	ACN	<5	-
3	Cs_2CO_3	N_2	ACN	-	-
4	Cs_2CO_3	O_2 balloon	ACN	6	-
5	KI	Ambient air	ACN	75	<1
6	KI	O_2 balloon	ACN	70	<10

Reaction conditions: 1a (15 mg, 0.11 mmol, 1 equiv.), **2a** (239.4 mg, 1.8 mmol, 3 equiv.), ACN (1 mL), additives, photocatalyst (5 mol%), 24 h, under 640 nm Kessil lamp, at room temperature. a, NMR yield with internal standard.

c. Screening of equivalents of 2a and time

Entry	**2a** equivalents	Time	Solvent	**3a** yield[a]

1	3 equiv.	16 h	ACN	<35
2	3 equiv.	18 h	ACN	<50
3	3 equiv.	24 h	ACN	73
4	1.5 equiv.	24 h	ACN	35

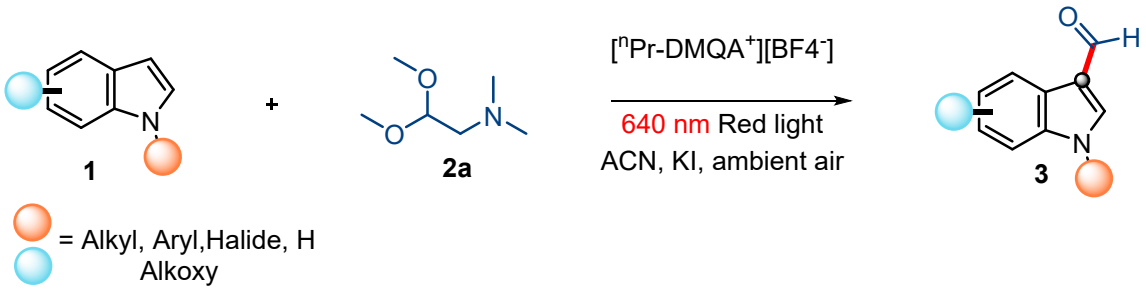
Reaction conditions: 1a (15 mg, 0.11 mmol, 1 equiv.), **2a**, ACN (1 mL), KI (4 equiv), photocatalyst (5 mol%), under 640 nm Kessil lamp, at room temperature under ambient air. a, NMR yield with internal standard.

d. Screening of other amines

Entry	Amines	Time	Solvent	3a yield[a]
1	TEMDA	24 h	ACN	<40
2	TEA	24 h	ACN	0
3	DIPEA	24h	ACN	40

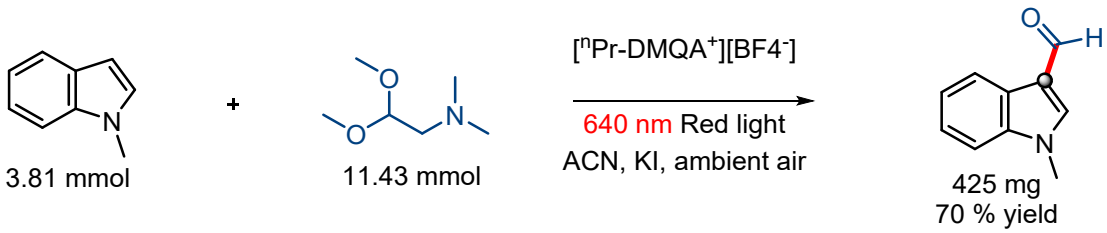
Reaction conditions: 1a (15 mg, 0.11 mmol, 1 equiv.), Amine, ACN (1 mL), KI (4equiv), photocatalyst (5 mol%), under 640 nm Kessil lamp, at room temperature under ambient air. a, NMR yield with internal standard. (diisopropyl ethyl amine (DIPEA), triethyl amine (TEA), and tetramethyl ethylamine (TEMDA))

2.3 General procedure for the C-3 formylation of indoles (GP2):



A 20 mL Schlenk tube was charged with indole 1 (0.6 mmol), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (3.2 mg, 5 mol %), KI (398.4 mg, 2.4 mmol), and MeCN (3 mL) under ambient air. To avoid the heating, the Schlenck tube was placed in a clear water bath at room temperature under a cooling fan. A 640 nm Kessil lamp was placed at a distance of about 5 cm from the reaction vessel. Upon completion, monitored by TLC, the solvent was removed from the reaction mixture using a rotary evaporator. The product was then purified by silica gel chromatography using hexane/EtOAc.

Gram scale reaction:



This reaction is done according to procedure GP2 by adding indole 1a (3.81 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (11.43 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (15.24 mmol, 4 equiv), and MeCN (10-15 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (425 mg, 70% yield).

2.4 Control experiments

a. Stern-Volmer Fluorescence Quenching Studies:

Stern-Volmer experiments were carried out monitoring the emission intensity of nitrogen-degassed solutions of ^{n}Pr-DMQA-BF_4 (1 x 10^{-5} M) containing variable amounts of the quencher in acetonitrile.

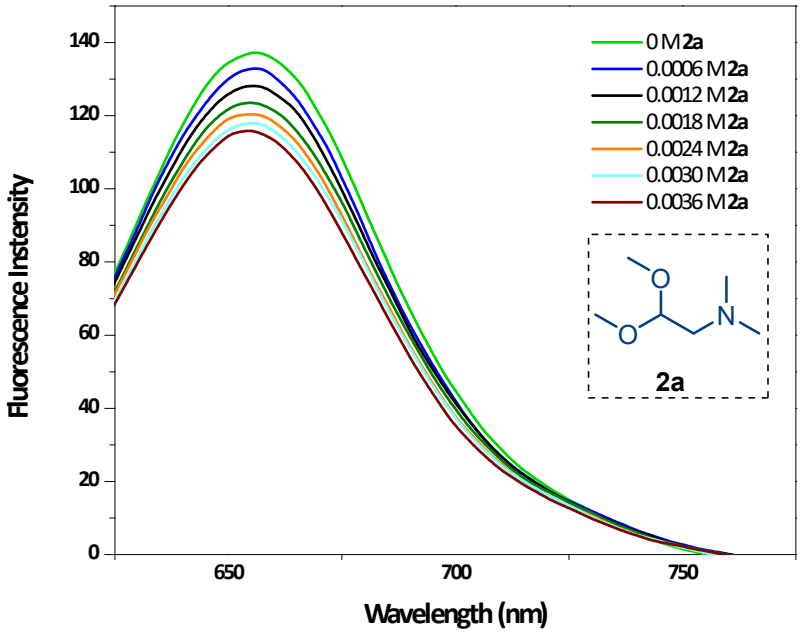


Figure S2: Stern-Volmer plot of ^{n}Pr-DMQA-BF_4 with **2a** in MeCN.

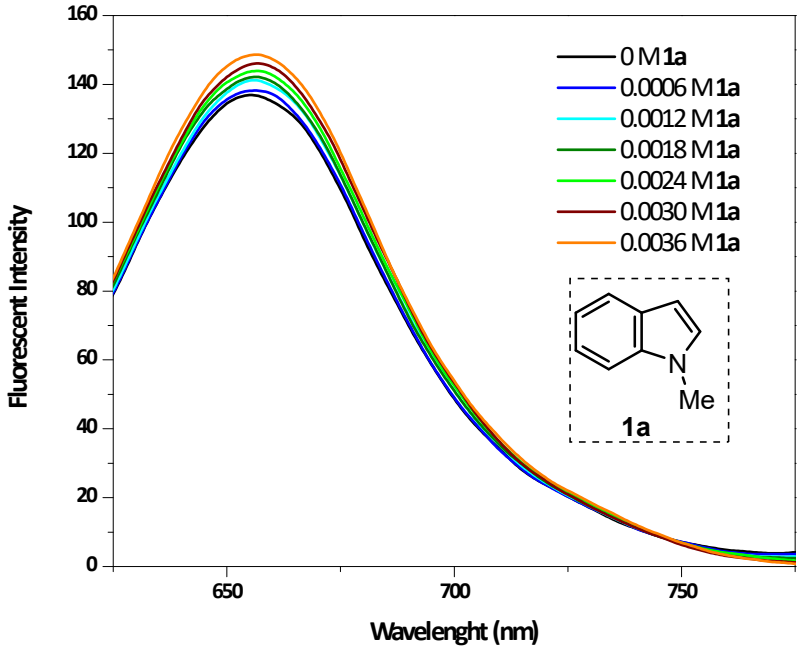


Figure S3: Stern-Volmer plot of ^{n}Pr-DMQA-BF_4 with **1a** in MeCN.

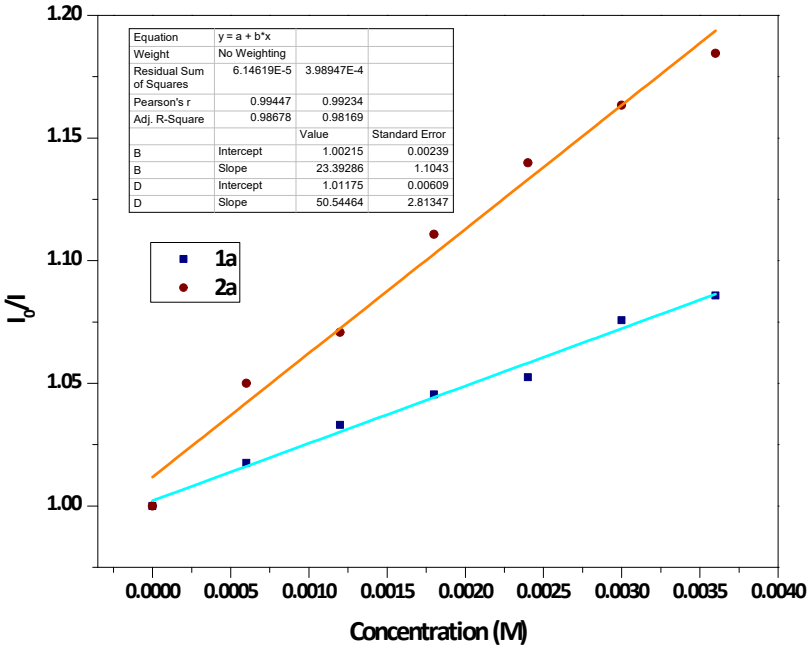


Figure S4: Stern-Volmer plot of ^{n}Pr-DMQA-BF_4 in MeCN with **1a** and **2a**.

b. Cyclic Voltammetry experiment:

Cyclic voltammetry analysis was carried out in CH instrument electrochemical analyzer (CHI1210C). Samples were prepared in 5 ml vial with 0.01 M of substrate (**2a**) and 0.1 M of Bu_4NBF_4 in Acetonitrile (4ml). Measurements employed glassy carbon working electrode (Disk electrode), platinum wire counter electrode and a silver-silver chloride(non-aqueous) reference electrode. The sweep rate applied was 50 mV/s ranging from 0 to 3V. The oxidation potential of **2a** was observed to be 1.15 V (vs Fc/Fc*). The CV experiments was carried out in argon atmosphere in positive or oxidative direction.

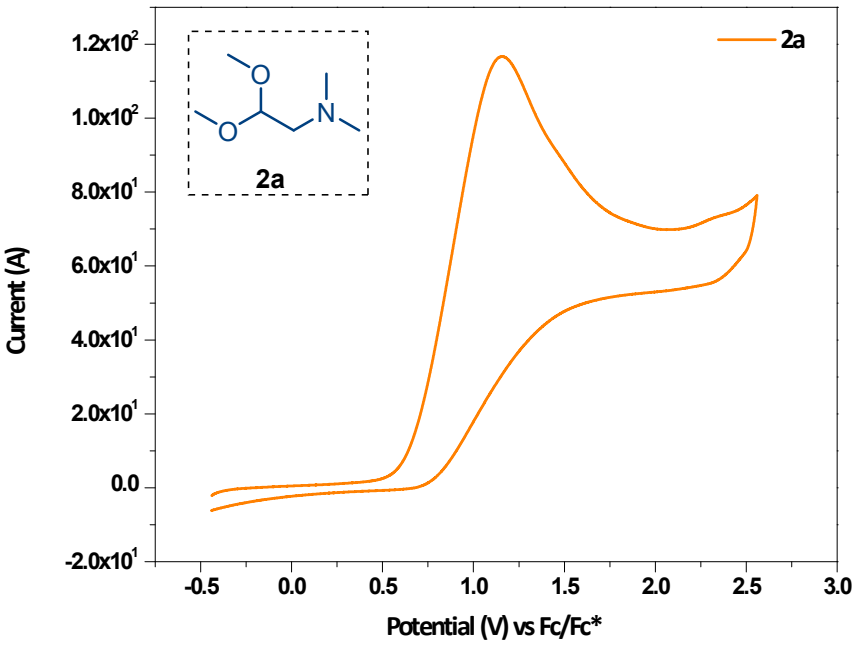


Figure S5: Cyclic Voltammetry experiment of amine **2a** (1.15V vs Fc/Fc*).

c. Light on/off experiment:

N-Methylindole (**1a**) (10 mg, 0.076 mmol, 1.0 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine (**2a**) (30 mg, 0.228 mmol, 3.0 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (50 mg, 0.304 mmol), and MeCN (0.8-1 mL) were added in a pre-dried 15 mL Schlenk tube under ambient air. The reaction mixture was exposed to a Kessil Red LED lamp emitting light at 640 nm. Following each 4-hour period, the reaction alternated between being placed in light and darkness. The progress of the reaction was

checked using TLC and correspondingly NMR yield was determined using 1,3,5 trimethoxy benzene as internal standard.

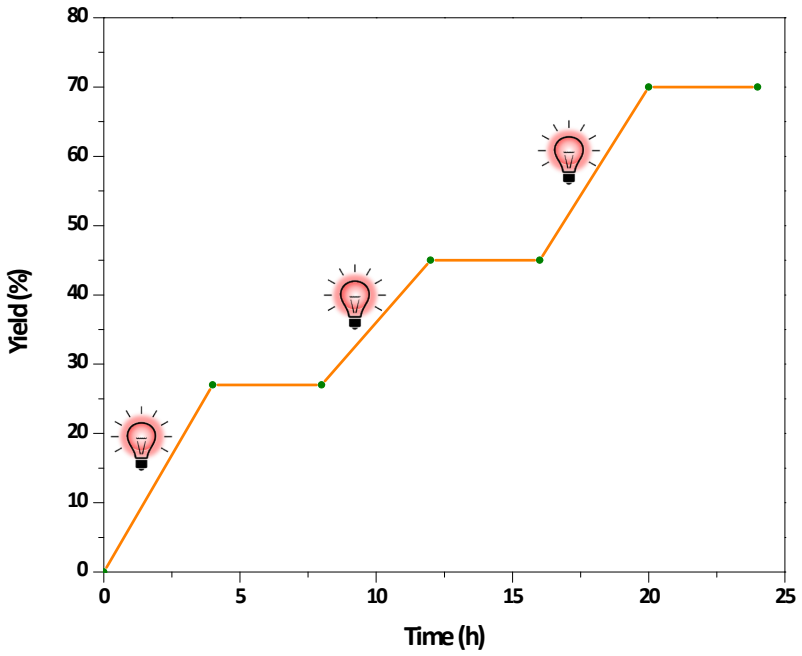


Figure S6: Light on/off experiment for optimized reaction

d. UV-Visible Absorption:

The UV-Vis absorption profile of the ^{n}Pr-DMQA^{+} (PC) (10^{-5} M), the mixture of PC (10^{-5} M) with 1a (0.0006 M), and a mixture of PC with **1a** (0.0006 M) and **2a** (0.0006 M) were recorded in JASCO V-670 spectrophotometer.

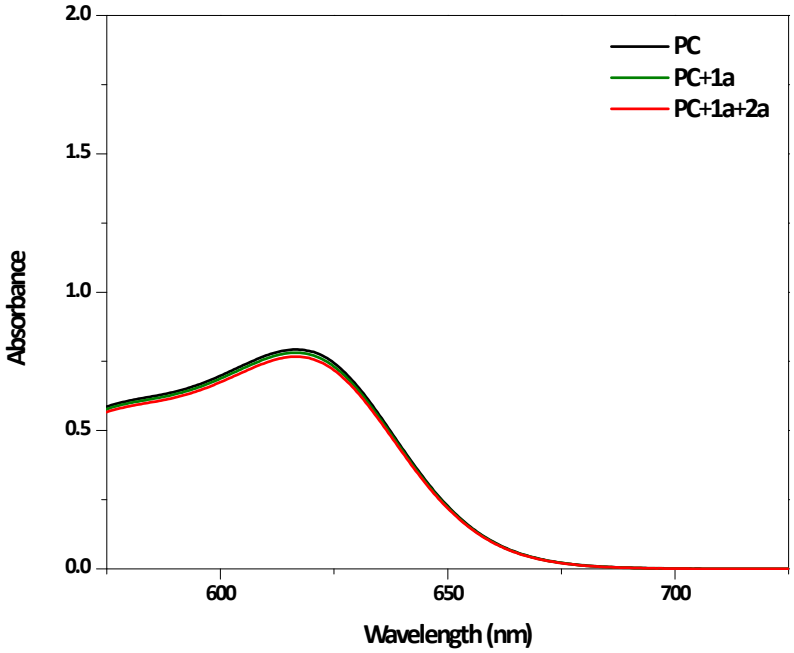
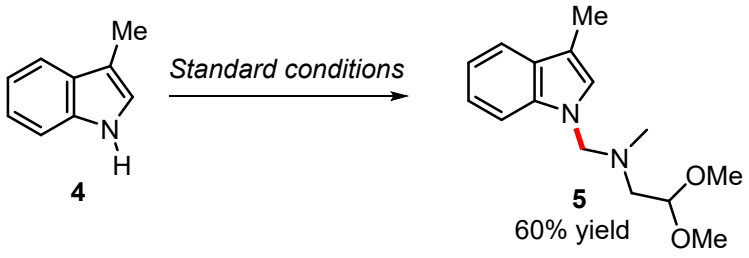


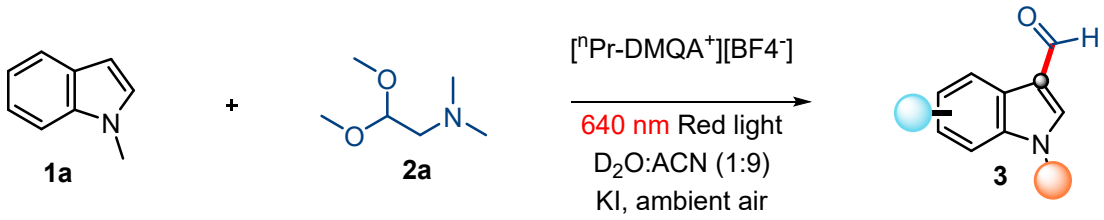
Figure S7: UV-visible absorption profile of PC with **1a** and **2a**

e. Reaction with C-3 substituted indoles:

This reaction is done according to procedure GP2 by adding indole **4** (0.6 mmol), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398.4 mg, 2.4 mmol), and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (60% yield).



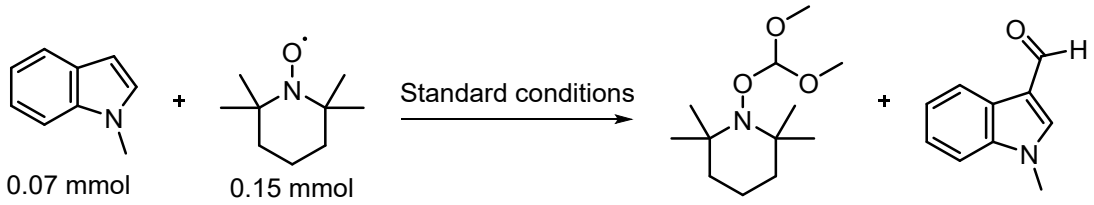
f. Reaction using D_2O:



The reaction is done according to procedure GP2 by adding indole **1a** (0.6 mmol), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398.4 mg, 2.4 mmol), D_2O (0.3 mL)/MeCN (2.7 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound.

However, we haven't observed any deuterium exchange. The final product does not contain any deuterated formylation product.

g. Reaction with radical scavenger:



Radical trapping experiment is done according to procedure GP2 by adding indole **1a** (0.07 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (0.22 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (2.4 mmol, 4 equiv), and MeCN (1 mL) and TEMPO (0.15 mmol, 2 equiv).

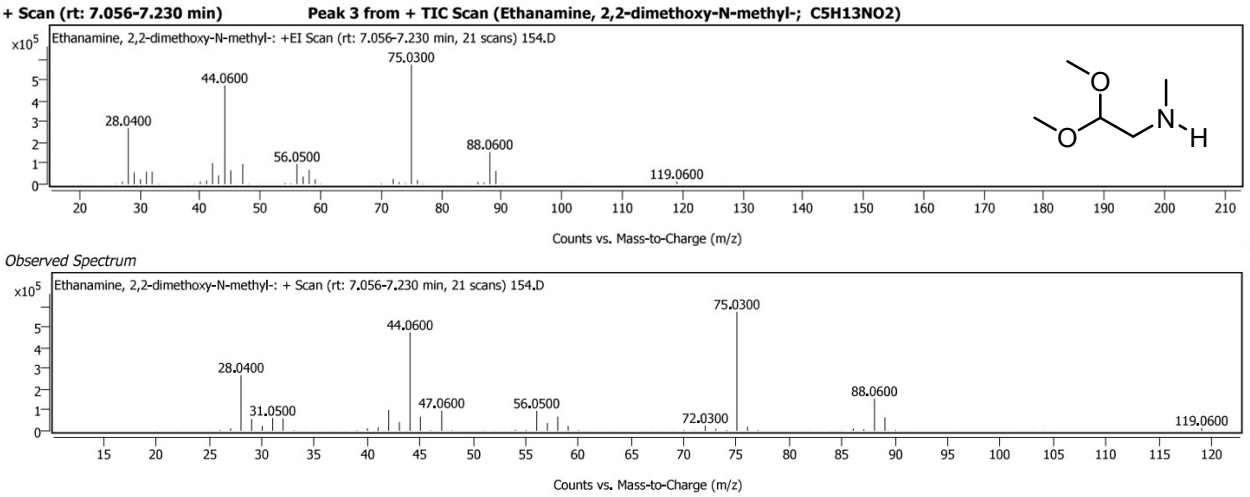
Crude NMR analysis with internal standard trimethoxy benzene shows the formation of a 30 % yield for the formylated product.

Also, we have detected some adduct in LCMS analysis as given below in Figure S12.

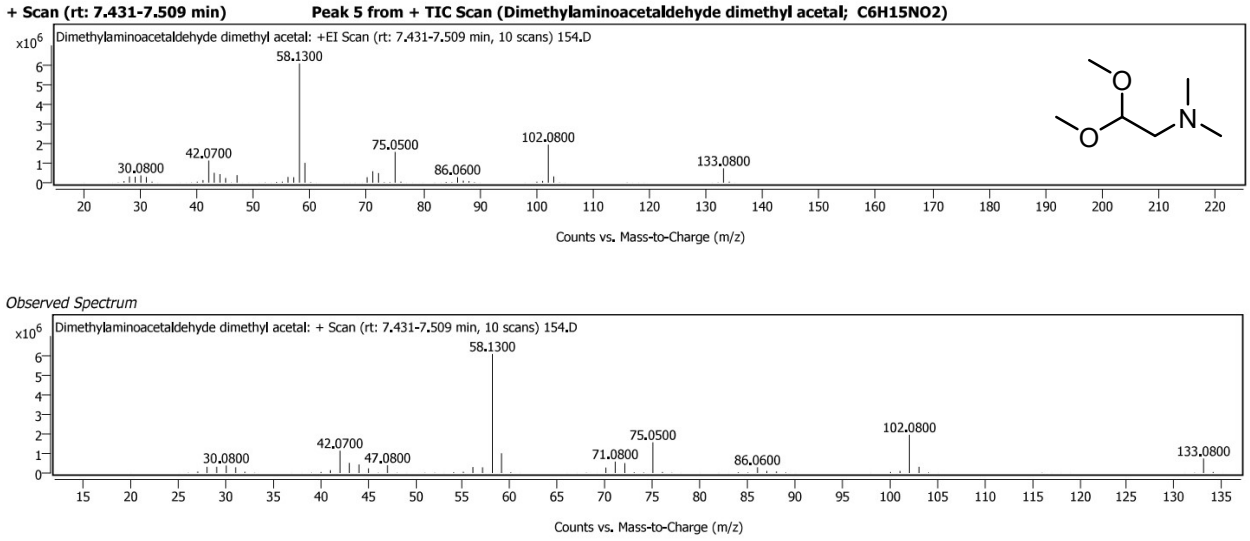
h. GC-MS analysis of reaction mixture:

We have analyzed the crude reaction mixture of standard reaction and reaction with TEMPO radical with GCMS and HRMS to identify possible intermediate forming during the reaction.

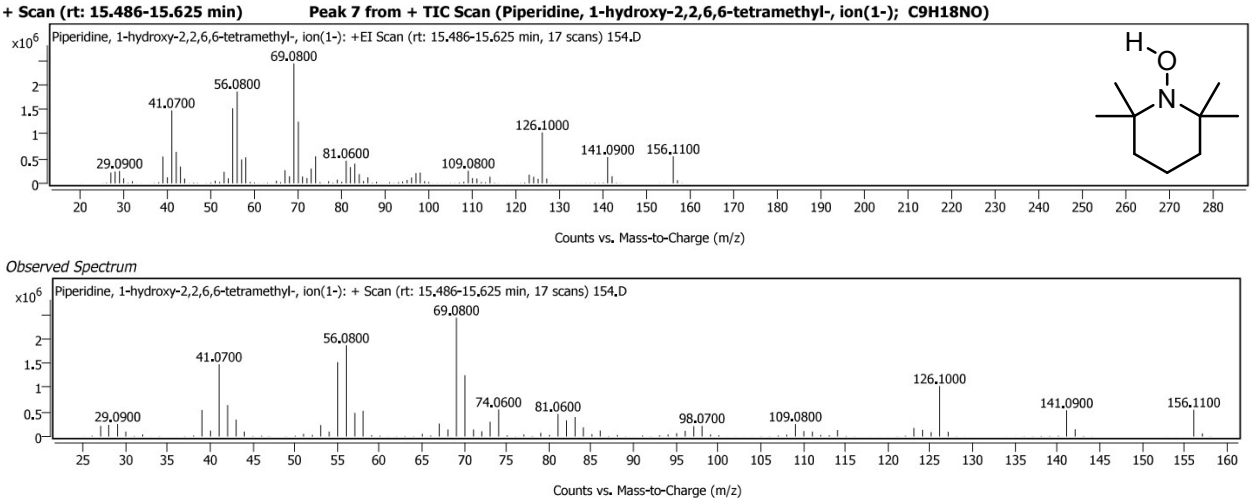
2,2-Dimethoxy-N-methylethanamine (Exact mass: 119.0946)



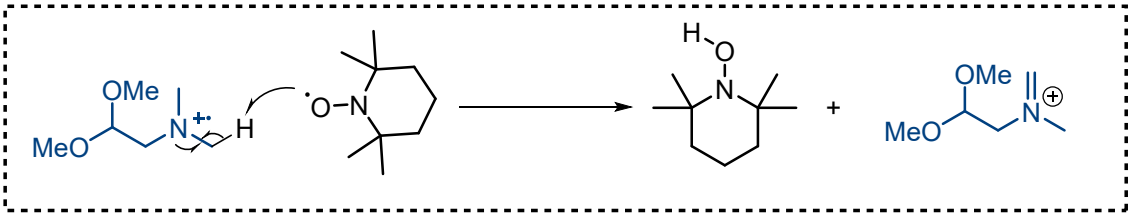
Dimethylaminoacetaldehyde dimethyl acetal (Exact mass: 133.1103)



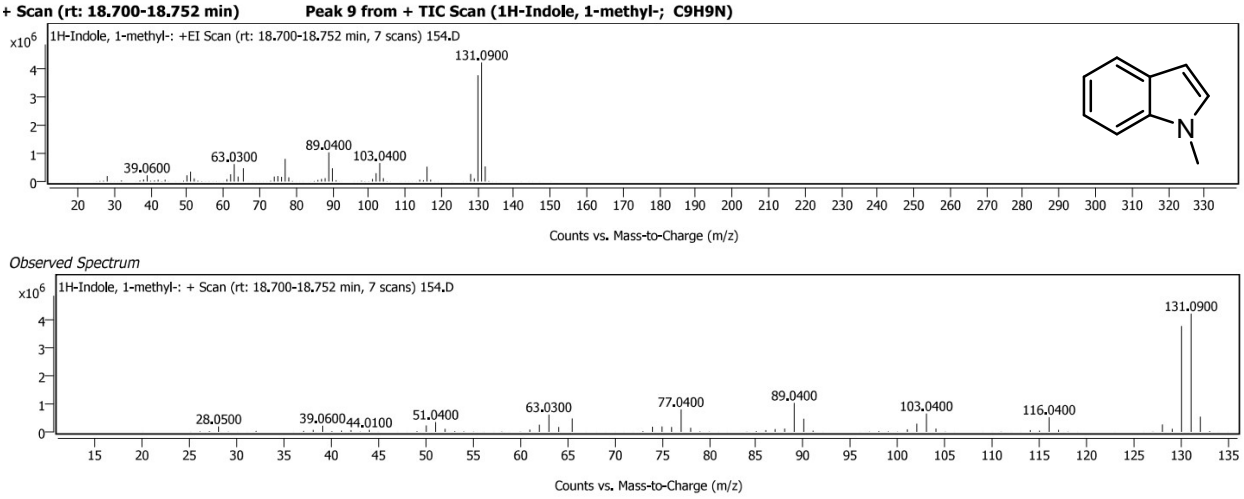
2,2,6,6-Tetramethyl-1-hydroxypiperidine (Exact mass: 157.1467)



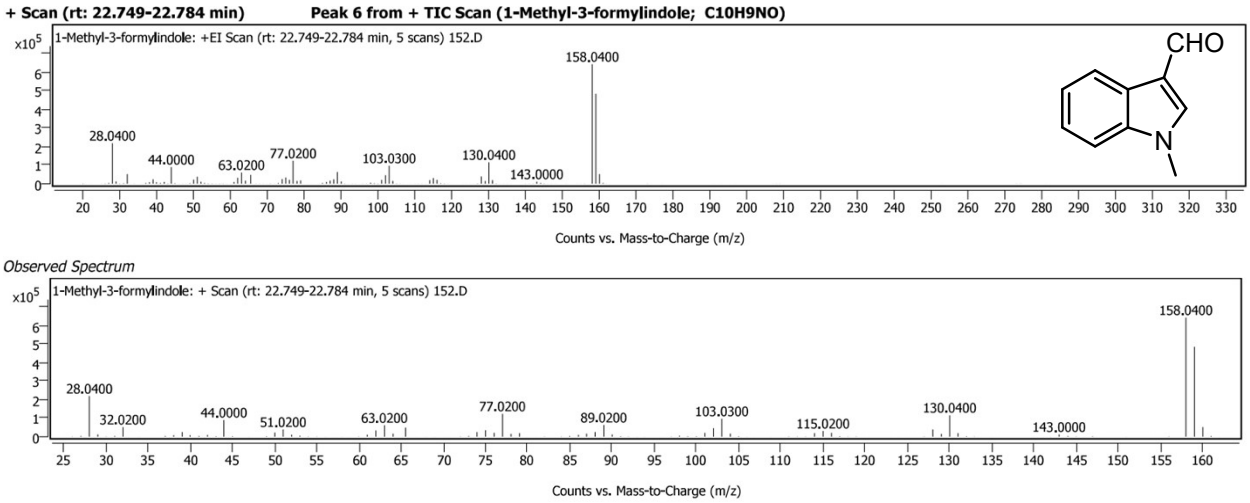
The intermediate is formed after the coupling of the H-radical with TEMPO, as shown in mechanism path B. This suggests that Path B may also be available.



1-methylindole (Exact Mass: 131.0735)



1-Methylindole-3-carboxaldehyde (Exact Mass: 159.0684)



HRMS analysis of crude reaction mixture:

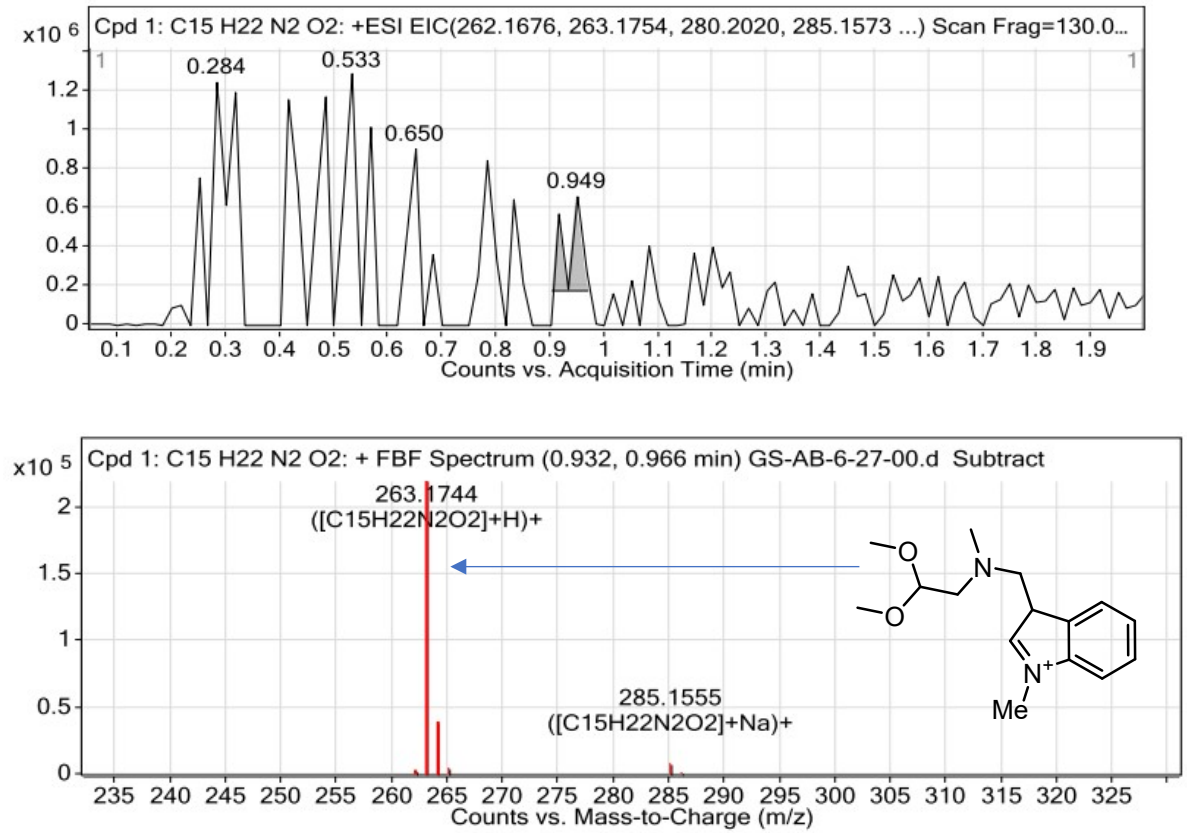


Figure S8: Observed HRMS for species **VI**

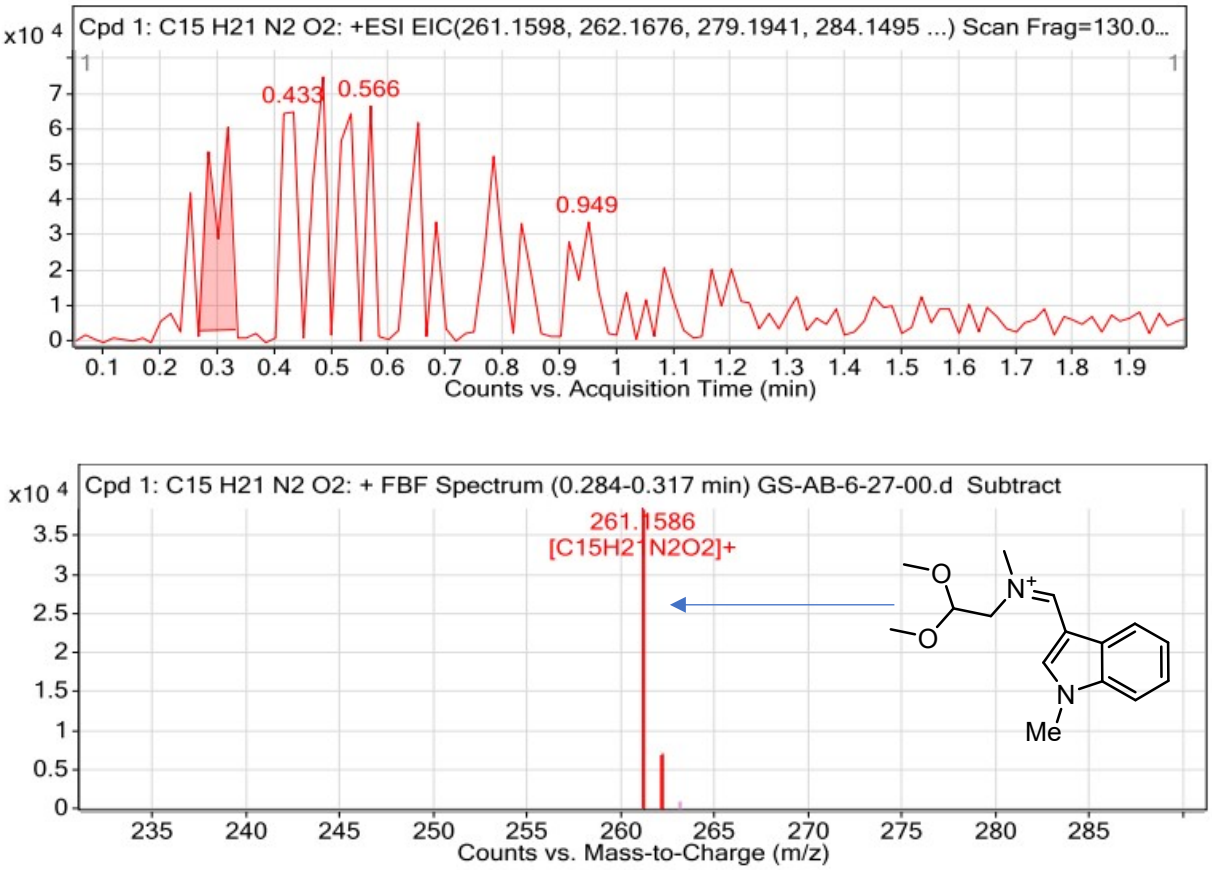
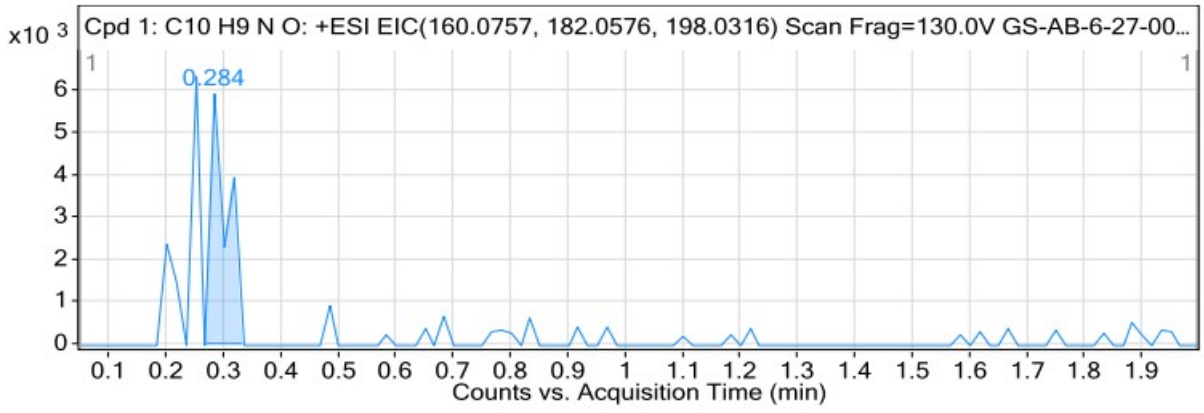


Figure S9: Observed HRMS for species **VIII**



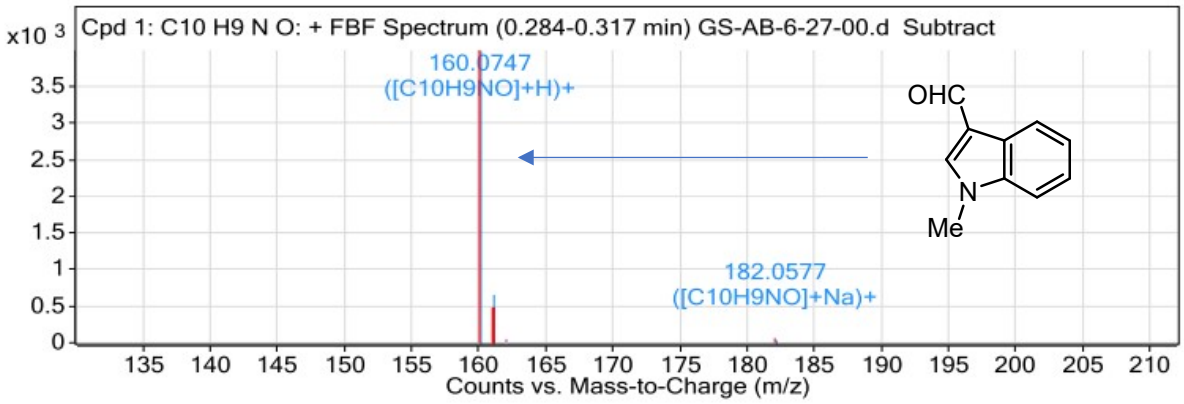


Figure S10: Observed HRMS for species **3a**

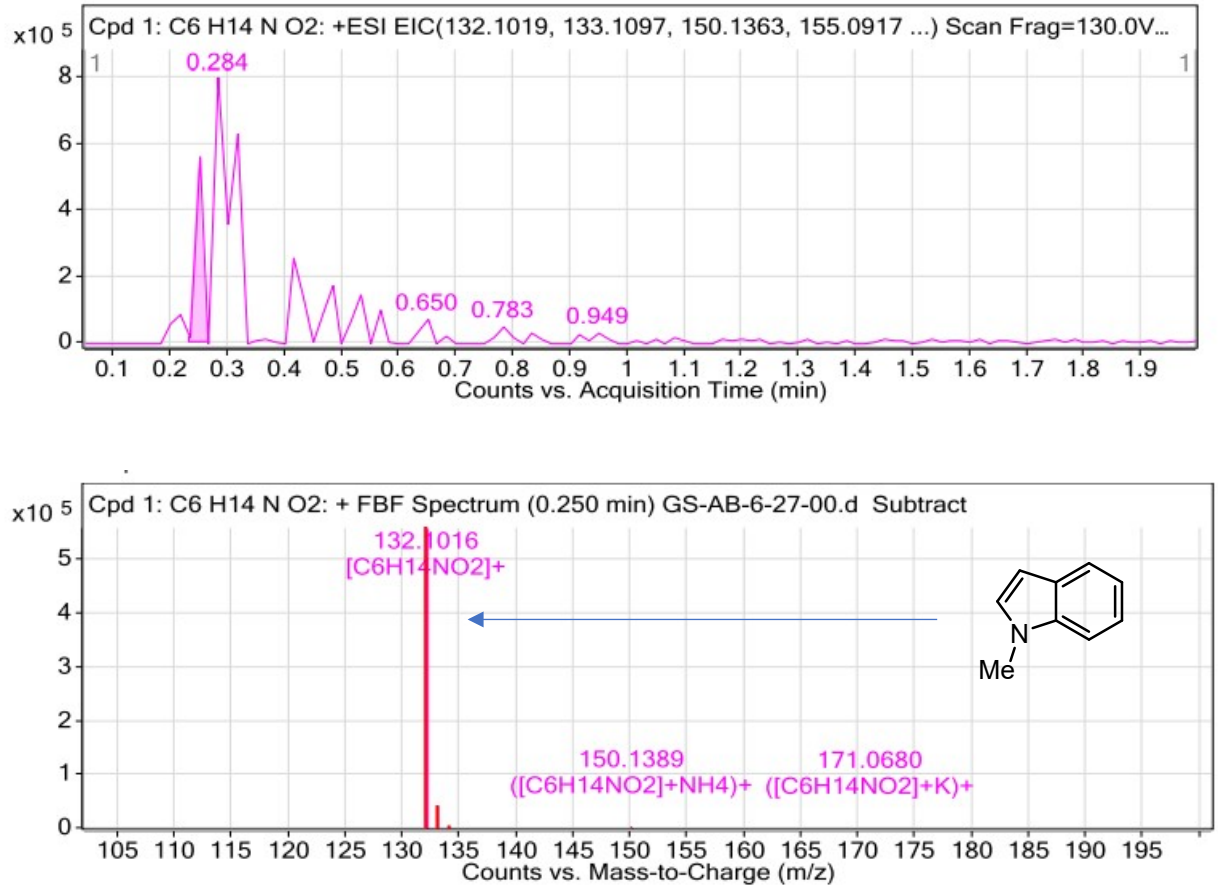


Figure S11: Observed HRMS for species **1a**

LC-MS analysis of crude reaction mixture:

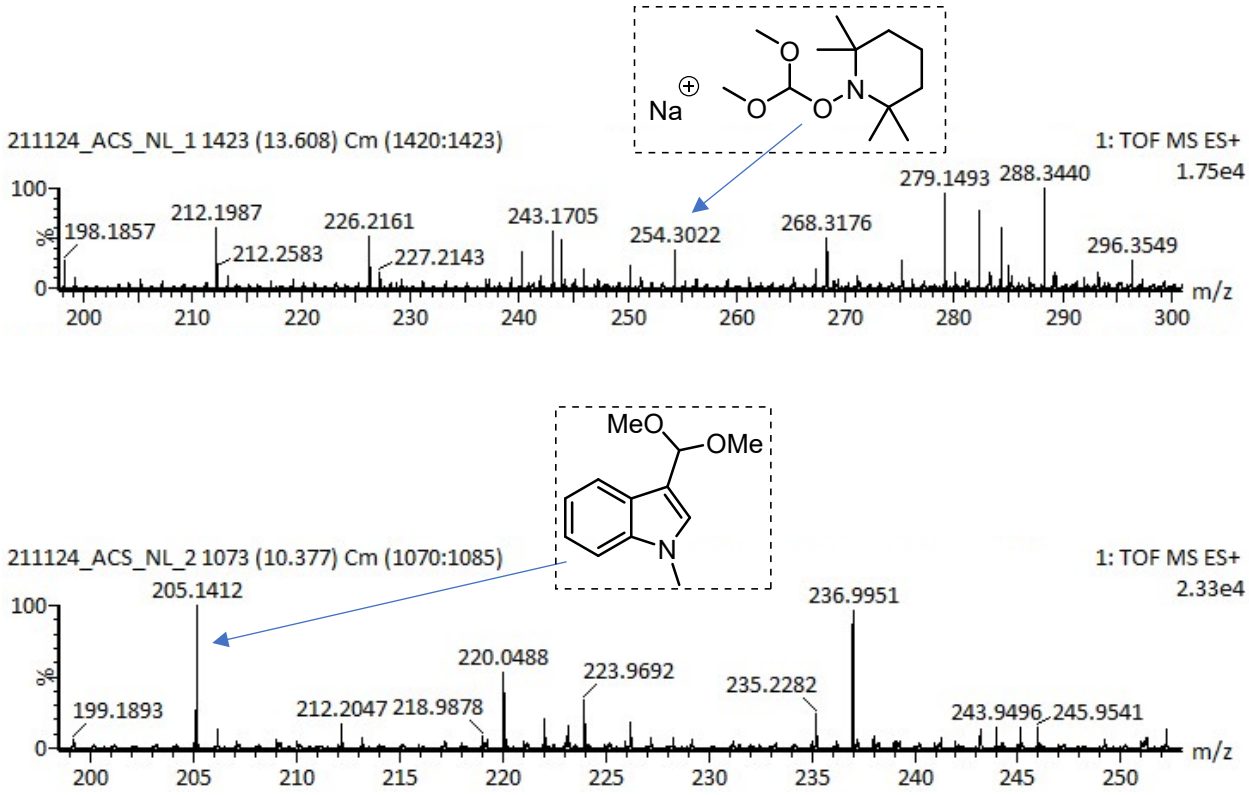


Figure S12: Observed LCMS for probable TEMPO adduct and species **IV**

i. Plausible reaction mechanism:

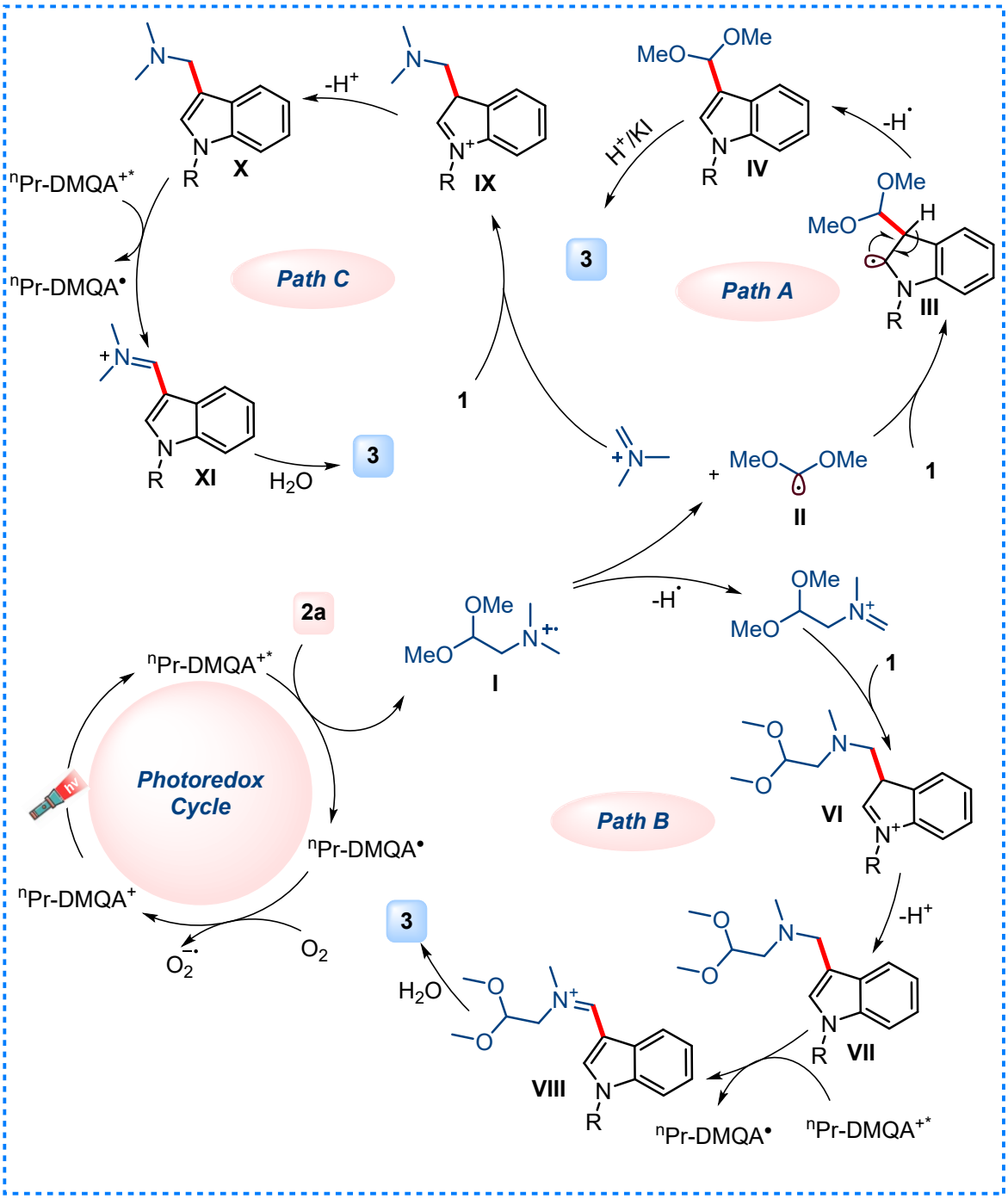
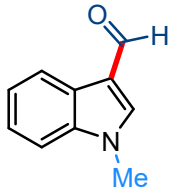


Figure S13: Plausible reaction mechanism.

3. Spectral Data for C-3 formylate indoles 3a-3y



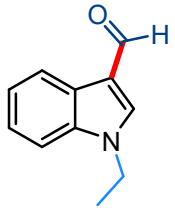
3a

1-Methyl-1H-indole-3-carboxaldehyde (3a): Prepared according to GP-2 using 1-Methyl-1H-indole (78.70 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (73% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.96 (s, 1H), 8.29 (dd, *J* = 6.0, 1.4 Hz, 1H), 7.64 (s, 1H), 7.44 – 7.27 (m, 3H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.57, 184.55, 139.38, 137.95, 125.33, 124.12, 123.03, 122.12, 118.12, 109.95, 33.81.



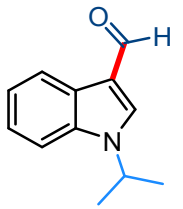
3b

1-Ethyl-1H-indole-3-carbaldehyde (3b): Prepared according to GP-2 using 1-Ethyl-1H-indole (87.12 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (72% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.98 (s, 1H), 8.31 (dd, *J* = 6.3, 2.4 Hz, 1H), 7.74 (s, 1H), 7.41 – 7.29 (m, 3H), 4.22 (q, *J* = 7.3 Hz, 2H), 1.54 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.54, 137.62, 137.09, 125.58, 123.98, 122.96, 122.21, 118.22, 110.06, 41.96, 15.12.



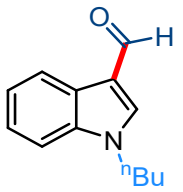
3c

1-isopropyl-1H-indole-3-carbaldehyde (3c): Prepared according to GP-2 using 1-isopropyl-1H-indole (95.53 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (54% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.00 (s, 1H), 8.32 (dd, *J* = 6.4, 2.5 Hz, 1H), 7.85 (s, 1H), 7.49 – 7.27 (m, 3H), 4.71 (hept, *J* = 6.7 Hz, 1H), 1.60 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.64, 136.98, 134.71, 125.62, 123.88, 123.01, 122.17, 118.29, 110.26, 48.17, 22.69, 22.69.



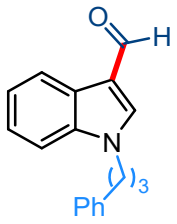
3d

1-butyl-1H-indole-3-carbaldehyde (3d): Prepared according to GP-2 using 1-butyl-1H-indole (103.95mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (64 % yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.00 (s, 1H), 8.31 (dd, *J* = 6.1, 2.4 Hz, 1H), 7.72 (s, 1H), 7.61 – 7.15 (m, 3H), 4.18 (t, *J* = 7.1 Hz, 2H), 1.89 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.38 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.58, 138.46, 137.30, 125.54, 124.00, 122.99, 122.23, 118.03, 110.19, 47.14, 31.85, 20.15, 13.70.



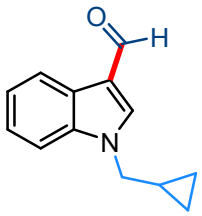
3e

1-(3-Phenylpropyl)-1H-indole-3-carbaldehyde (3e): Prepared according to GP-2 using 1-benzyl-1H-indole (141.198 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (55% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.00 (s, 1H), 8.39 – 8.23 (m, 1H), 7.73 – 7.63 (s, 1H), 7.32 (ddd, *J* = 7.8, 5.2, 1.8 Hz, 5H), 7.21 (dd, *J* = 31.2, 7.2 Hz, 3H), 4.18 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.32 – 2.21 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.64, 140.20, 138.35, 137.23, 128.77, 128.44, 126.54, 125.56, 124.06, 123.04, 122.27, 118.21, 110.16, 46.54, 32.83, 30.99.



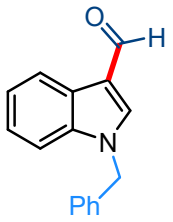
3f

1-(cyclopropylmethyl)-1H-indole-3-carbaldehyde (3f): Prepared according to GP-2 using 1-(cyclopropylmethyl)-1H-indole (102.74 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (60% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.03 (s, 1H), 8.39 – 8.22 (m, 1H), 7.90 (s, 1H), 7.51 – 7.29 (m, 3H), 4.03 (d, *J* = 7.0 Hz, 2H), 1.40 – 1.28 (m, 1H), 0.78 – 0.72 (m, 2H), 0.44 (q, *J* = 5.0 Hz, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.53, 137.88, 137.33, 125.30, 123.80, 122.81, 121.95, 117.94, 109.98, 51.34, 10.53, 4.35, 4.30.



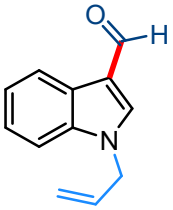
3g

1-benzyl-1H-indole-3-carbaldehyde (3g): Prepared according to GP-2 using 1-benzyl-1H-indole (124.36 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (70% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.00 (s, 1H), 8.38 – 8.27 (m, 1H), 7.72 (s, 1H), 7.37 – 7.29 (m, 6H), 7.19 (dd, *J* = 7.1, 1.5 Hz, 2H), 5.37 (s, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.75, 138.61, 137.55, 135.38, 129.22, 128.50, 127.31, 125.58, 124.26, 123.18, 122.27, 118.58, 110.46, 51.02.



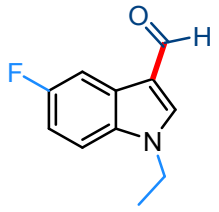
3h

1-allyl-1H-indole-3-carbaldehyde (3h): Prepared according to GP-2 using 1-Allyl-1H-indole (94.326 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (85% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.01 (s, 1H), 8.45 – 8.22 (m, 1H), 7.74 (s, 1H), 7.39 – 7.30 (m, 3H), 6.09 – 5.97 (m, 1H), 5.33 (d, *J* = 10.3 Hz, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 4.79 (dt, *J* = 5.5, 1.6 Hz, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.69, 138.35, 137.35, 131.79, 125.50, 124.13, 123.10, 122.24, 119.16, 118.46, 110.34, 49.62.



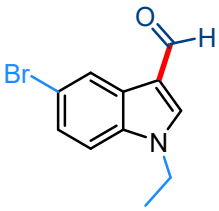
3i

1-ethyl-5-fluoro-1H-indole-3-carbaldehyde (3i): Prepared according to GP-2 using 1-ethyl-5-fluoro-1H-indole (97.92 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (60% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.96 (s, 1H), 7.98 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.77 (s, 1H), 7.31 (dd, *J* = 9.0, 4.2 Hz, 1H), 7.08 (td, *J* = 9.0, 2.6 Hz, 1H), 4.23 (q, *J* = 7.3 Hz, 2H), 1.56 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.31 δ 159.88 (d, $J_{C\text{-}F}$ = 238.9 Hz), 138.37, 133.55, 126.14, 118.11, 112.41 (d, $J_{C\text{-}F}$ = 26.4 Hz), 110.87 (d, $J_{C\text{-}F}$ = 9.7 Hz), 107.69 (d, $J_{C\text{-}F}$ = 24.7 Hz) , 42.26, 15.11.



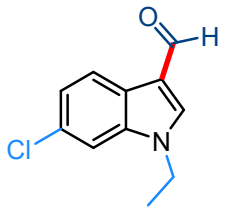
3j

5-bromo-1-ethyl-1H-indole-3-carbaldehyde (3j): Prepared according to GP-2 using 5-bromo-1-ethyl-1H-indole (134.46 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (69% yield).

NMR Spectroscopy:

1H NMR (400 MHz, CHLOROFORM-D) δ 9.82 (s, 1H), 8.35 (d, J = 1.9 Hz, 1H), 7.63 (s, 1H), 7.30 (dd, J = 8.7, 1.9 Hz, 1H), 7.14 (d, J = 8.7 Hz, 1H), 4.12 (q, J = 7.3 Hz, 2H), 1.48 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, CHLOROFORM-D) δ 184.15, 138.31, 135.50, 126.61, 126.56, 124.35, 117.15, 116.19, 111.47, 41.97, 14.83..



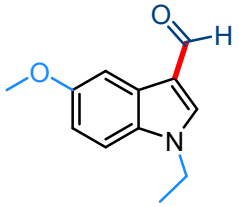
3k

6-chloro-1-ethyl-1H-indole-3-carbaldehyde (3k): Prepared according to GP-2 using 6-chloro-1-ethyl-1H-indole (107.78 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (70% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.97 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.28 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.20 (q, *J* = 7.3 Hz, 2H), 1.55 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.44, 138.00, 137.52, 129.98, 123.98, 123.63, 123.22, 118.21, 110.21, 42.13, 15.12.



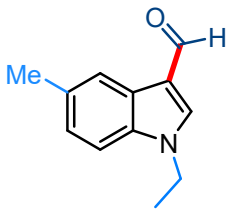
3l

1-Ethyl-5-methoxy-1H-indole-3-carbaldehyde (3l): Prepared according to GP-2 using 1-Ethyl-5-methoxy-1H-indole (105.138 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (90% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.92 (s, 1H), 7.79 (d, *J* = 2.5 Hz, 1H), 7.67 (s, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 6.96 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.17 (q, *J* = 7.3 Hz, 2H), 3.89 (s, 3H), 1.52 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.54, 156.69, 137.74, 131.98, 126.27, 117.93, 114.47, 110.91, 103.42, 55.91, 42.12, 15.16.



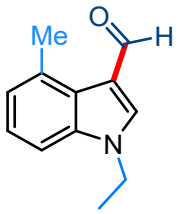
3m

1-ethyl-5-methyl-1H-indole-3-carbaldehyde (3m): Prepared according to GP-2 using 2-phenyl-1H-indole (95.53 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (68% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.01 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.72 (s, 1H), 7.25 (t, *J* = 4.2 Hz, 2H), 4.23 (q, *J* = 7.3 Hz, 2H), 2.61 (s, 3H), 1.60 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.23, 137.64, 137.23, 133.66, 124.26, 122.89, 121.40, 117.76, 109.90, 41.48, 21.72, 14.77.



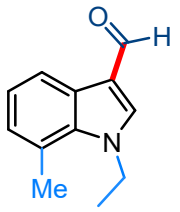
3n

1-ethyl-4-Methyl-1H-indole-3-carbaldehyde (3n): Prepared according to GP-2 using 1-ethyl-4-Methyl-1H-indole (95.53 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (65% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.03 (d, *J* = 1.1 Hz, 1H), 7.77 (s, 1H), 7.20 – 7.13 (m, 2H), 7.06 – 7.02 (m, 1H), 4.07 (dd, *J* = 7.3, 1.5 Hz, 2H), 2.81 (s, 3H), 1.44 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.02, 137.11, 137.11 131.94, 124.71, 123.85, 123.14, 119.12, 107.58, 41.45, 22.27, 14.47.



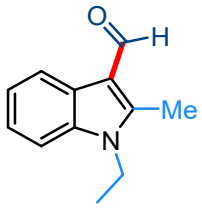
3o

1-ethyl-7-methyl-1H-indole-3-carbaldehyde (3o): Prepared according to GP-2 using 1-ethyl-7-methyl-1H-indole (95.53 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (67% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.95 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.64 (s, 1H), 7.22 – 7.14 (m, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.71 (s, 3H), 1.51 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.54, 139.27, 135.89, 127.09, 126.62, 123.06, 121.48, 120.09, 118.01, 44.57, 19.70, 17.40.



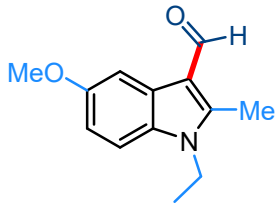
3p

1-ethyl-2-methyl-1H-indole-3-carbaldehyde (3p): Prepared according to GP-2 using 1-ethyl-2-methyl-1H-indole (95.53 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (50% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.11 (s, 1H), 8.25 (dd, *J* = 5.7, 3.2 Hz, 1H), 7.45 – 7.15 (m, 3H), 4.18 (q, *J* = 7.3 Hz, 2H), 2.70 (s, 3H), 1.40 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.28, 146.83, 135.96, 126.08, 123.14, 122.80, 121.04, 114.37, 109.34, 38.17, 14.86, 10.44.



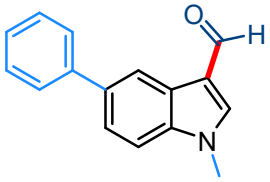
3q

1-ethyl-5-methoxy-2-methyl-1H-indole-3-carbaldehyde (3q): Prepared according to GP-2 using 1-ethyl-5-methoxy-2-methyl-1H-indole (113.55 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (65% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.12 (s, 1H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.20 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.6 Hz, 1H), 4.13 (q, *J* = 7.3 Hz, 2H), 3.90 (s, 3H), 2.66 (s, 3H), 1.39 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.11, 156.62, 146.96, 130.78, 126.69, 114.36, 113.11, 110.11, 103.01, 55.93, 38.30, 14.92, 10.35.



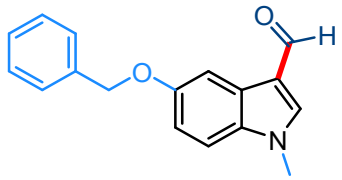
3r

1-methyl-5-phenyl-1H-indole-3-carbaldehyde (3r): Prepared according to GP-2 using 1-methyl-5-phenyl-1H-indole (124.362 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (69% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.98 (s, 1H), 8.55 (d, *J* = 1.7 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.67 – 7.57 (m, 2H), 7.49 – 7.43 (m, 2H), 7.37 (dd, *J* = 13.6, 8.0 Hz, 2H), 3.94 – 3.79 (m, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.49, 141.60, 139.93, 137.42, 136.55, 128.81, 127.60, 126.99, 125.85, 123.78, 120.54, 118.34, 110.24, 33.87.



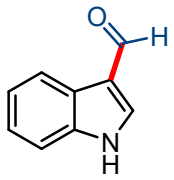
3s

1-Methyl-5-(phenylmethoxy)-1*H*-indole-3-carboxaldehyde (3s): Prepared according to GP-2 using 1-Methyl-5-(phenylmethoxy)-1*H*-indole-3-carboxaldehyde (159.18 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (64% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.94 (s, 1H), 7.91 (d, *J* = 2.5 Hz, 1H), 7.62 (s, 1H), 7.52 – 7.48 (m, 2H), 7.43 – 7.32 (m, 3H), 7.27 – 7.24 (m, 1H), 7.07 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.15 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.54, 155.97, 139.51, 137.28, 133.07, 128.67, 128.04, 127.84, 126.10, 117.93, 115.18, 110.87, 104.76, 70.69, 34.01.



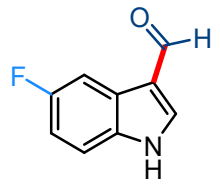
3t

1H-indole-3-carbaldehyde (3t): Prepared according to GP-2 using 1H-indole (70.29 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (74% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-D6) δ 12.10 (s, 1H), 9.89 (s, 1H), 8.25 (s, 1H), 8.05 (d, *J* = 7.1 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.20 (dtd, *J* = 18.1, 7.2, 1.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-D6) δ 185.55, 139.06, 137.55, 124.60, 124.00, 122.67, 121.33, 118.66, 112.95.



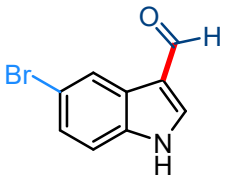
3u

5-fluoro-1H-indole-3-carbaldehyde (3u): Prepared according to GP-2 using 5-fluoro-1H-indole (81.08 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (61% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-D6) δ 12.25 (s, 1H), 9.92 (s, 1H), 8.35 (d, *J* = 3.0 Hz, 1H), 7.76 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.53 (dd, *J* = 8.8, 4.6 Hz, 1H), 7.23 – 7.06 (m, 1H).

^{13}C NMR (101 MHz, DMSO-D6) δ 185.20, 158.81 (d, *J* = 235.3 Hz), 139.78, 133.69, 124.77 (d, *J* = 11.0 Hz), 118.19 (d, *J* = 4.2 Hz), 113.89 (d, *J* = 9.8 Hz), 111.74 (d, *J* = 26.0 Hz), 105.79 (d, *J* = 24.3 Hz).



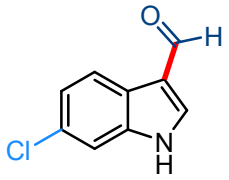
3v

5-bromo-1H-indole-3-carbaldehyde (3v): Prepared according to GP-2 using 5-bromo-1H-indole (117.62mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (67% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-D6) δ 12.31 (s, 1H), 9.92 (s, 1H), 8.35 (s, 1H), 8.22 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.39 (dd, *J* = 8.6, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D6) δ 185.31, 139.40, 135.84, 126.17, 125.96, 123.02, 117.51, 114.94, 114.67.



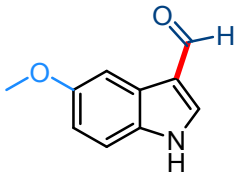
3w

6-chloro-1H-indole-3-carbaldehyde (3w): Prepared according to GP-2 using 6-chloro-1H-indole (90.95 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (63% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-D6) δ 12.23 (s, 1H), 9.93 (s, 1H), 8.34 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.25 (dd, *J* = 8.4, 2.0 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D6) δ 185.50, 139.55, 137.68, 128.15, 123.01, 122.70, 122.29, 118.13, 112.43.



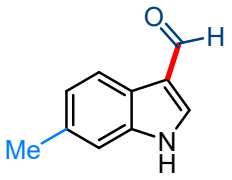
3x

5-Methoxy-1H-indole-3-carbaldehyde (3x): Prepared according to GP-2 using 5-Methoxy-1H-indole (88.3 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (66% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-D6) δ 12.02 (s, 1H), 9.89 (s, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, DMSO-D6) δ 184.87, 155.66, 138.48, 131.82, 124.92, 118.06, 113.33, 113.23, 102.49, 55.30.



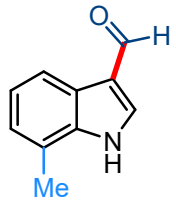
3y

6-Methyl-1H-indole-3-carbaldehyde (3y): Prepared according to GP-2 using 2-Methyl-1H-indole (78.7 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (72% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-D6) δ 12.00 (s, 1H), 9.88 (s, 1H), 8.20 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.04 (dd, *J* = 8.1, 1.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, DMSO-D6) δ 184.85, 138.15, 137.53, 132.84, 123.78, 121.94, 120.54, 118.20, 112.19, 21.36.



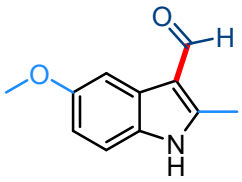
3z

7-Methyl-1H-indole-3-carbaldehyde (3z): Prepared according to GP-2 using 7-Methyl-1H-indole (78.7 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (95% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, DMSO-D6) δ 12.17 (s, 1H), 9.94 (s, 1H), 8.29 (d, *J* = 3.1 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.20 – 6.99 (m, 2H), 2.51 – 2.49 (s 3H).

^{13}C NMR (101 MHz, DMSO-D6) δ 185.13, 138.28, 136.61, 124.10, 123.96, 122.41, 121.83, 118.61, 118.45, 16.74.



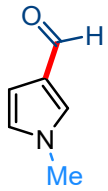
3aa

5-methoxy-2methyl-1H-indole-3-carbaldehyde (3aa): Prepared according to GP-2 using 5-methoxy-2methyl-1H-indole (96.72 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (62% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 10.14 (s, 1H), 7.76 (d, *J* = 2.5 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.88 (s, 3H), 2.72 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 184.62, 156.61, 146.99, 129.68, 126.87, 115.05, 113.59, 111.54, 102.93, 55.93, 12.36.



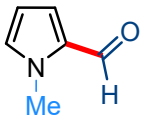
3ab

3-Formyl-1-methylpyrrole (3ab) Major: Prepared according to GP-2 using 1-methylpyrrole (48.67 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (60% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.69 (s, 1H), 7.23 (t, *J* = 1.9 Hz, 1H), 6.60 (dt, *J* = 4.6, 2.8 Hz, 2H), 3.70 (s, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 185.34, 130.04, 126.69, 124.47, 108.44, 36.80.

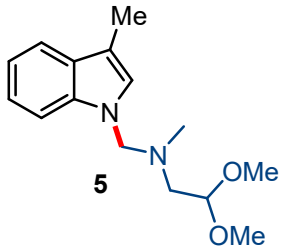


3ab'

2-Formyl-1-methylpyrrole (3ab') Minor:

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.54 (d, *J* = 1.1 Hz, 1H), 6.92 – 6.89 (m, 1H), 6.88 (s, 1H), 6.22 – 6.19 (m, 1H), 3.95 (d, *J* = 1.4 Hz, 3H).



5

2,2-dimethoxy-N-methyl-N-((3-methyl-1H-indol-1-yl)methyl)ethan-1-amine (5): Prepared according to GP-2 using 3-methyl-1H-indole (78.70 mg, 0.6 mmol, 1 equiv), 2,2-Dimethoxy-N,N-dimethylethanamine **2a** (257 µL, 1.8 mmol, 3 equiv), N,N'-di-n-propyl-1,13-dimethoxyquinacridinium (^{n}Pr-DMQA^{+}) tetrafluoroborate photocatalyst (5 mol %), KI (398 mg, 2.3 mmol, 4 equiv) and MeCN (3 mL). Purification by flash column chromatography (EtOAc/Hexanes) afforded the title compound (60% yield).

NMR Spectroscopy:

^{1}H NMR (400 MHz, CHLOROFORM-D) δ ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.21 – 7.15 (m, 1H), 6.99 (d, *J* = 0.8 Hz, 1H), 4.87 (s, 2H), 4.49 (t, *J* = 5.3 Hz, 1H), 3.39 (s, 6H), 2.72 (d, *J* = 5.3 Hz, 2H), 2.41 (s, 3H), 2.39 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.26, 128.84, 126.21, 121.69, 118.90, 118.86, 110.74, 109.88, 102.97, 67.52, 55.91, 53.60, 40.97, 9.65.

HRMS (ESI) m/z: [M+H]+ calculated for ($C_{15}H_{23}N_2O_2$+) 263.1760; found 263.1770;

5. NMR Spectral Data

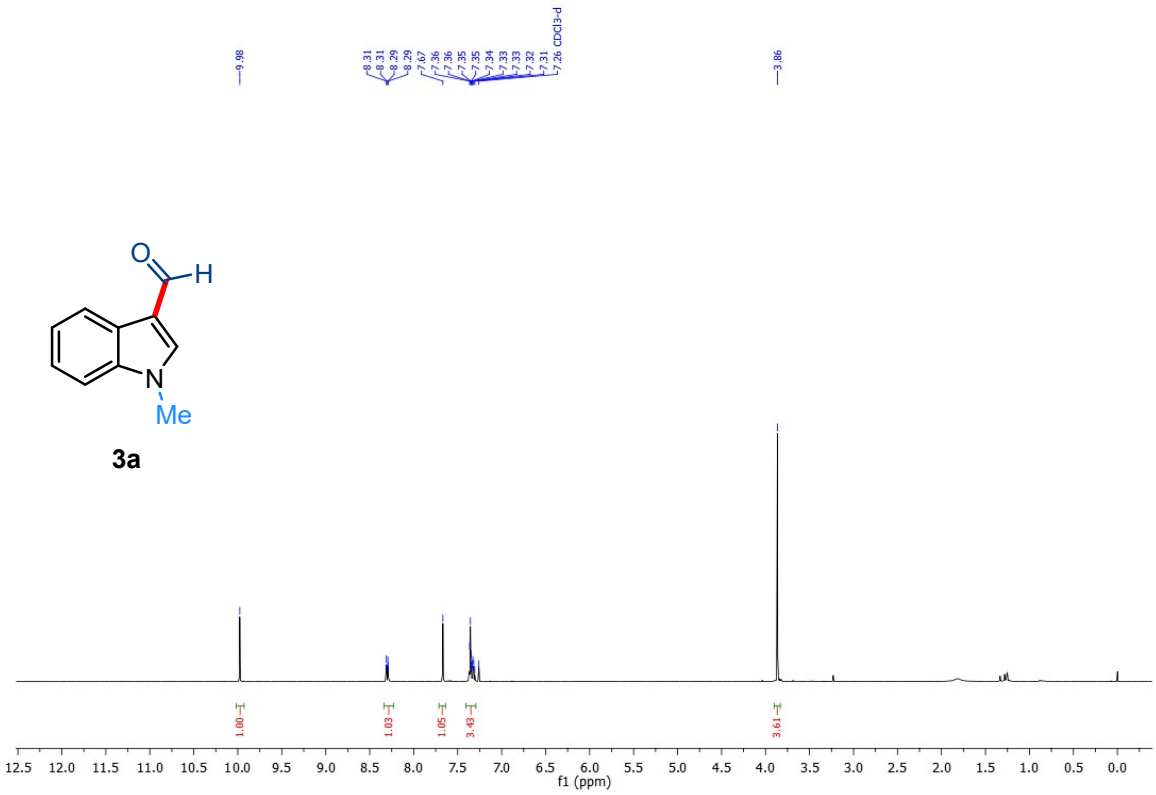


Figure S14: ^{1}H NMR of product **3a** in $CDCl_3$-d (400 MHz)

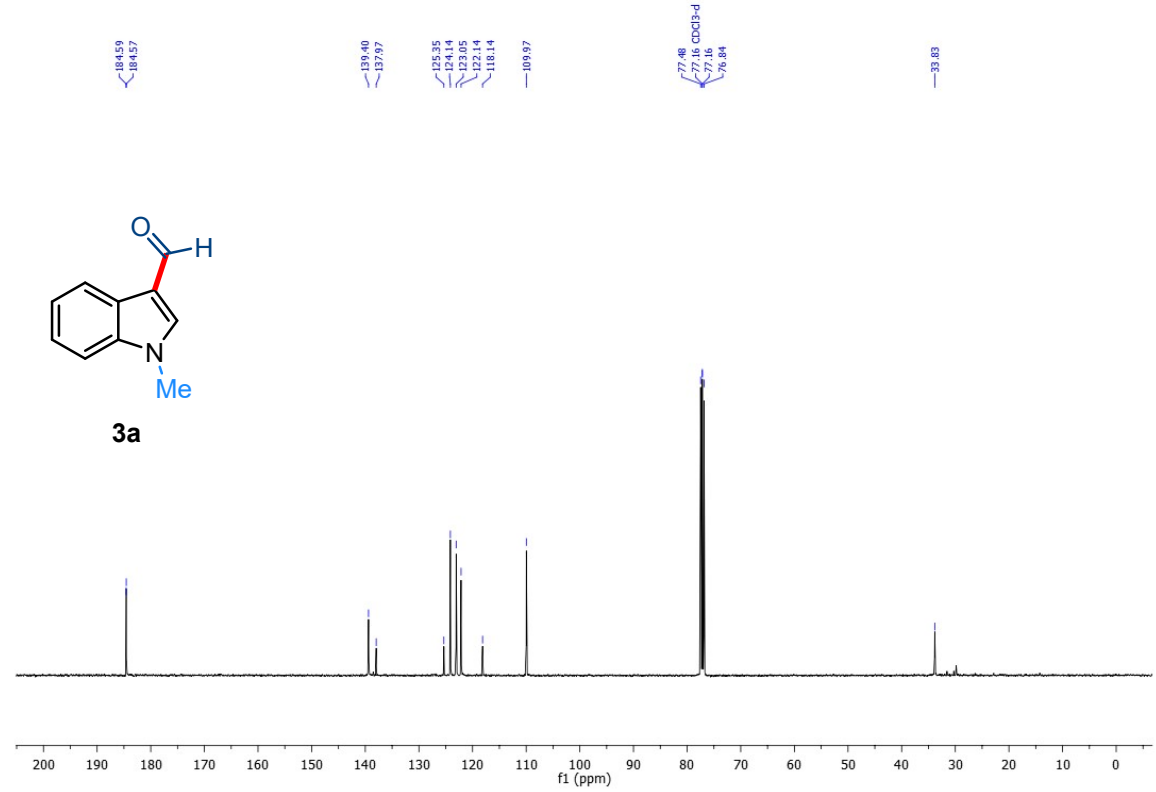


Figure S15: ^{13}C NMR of product **3a** in $CDCl_3$-d (101 MHz)

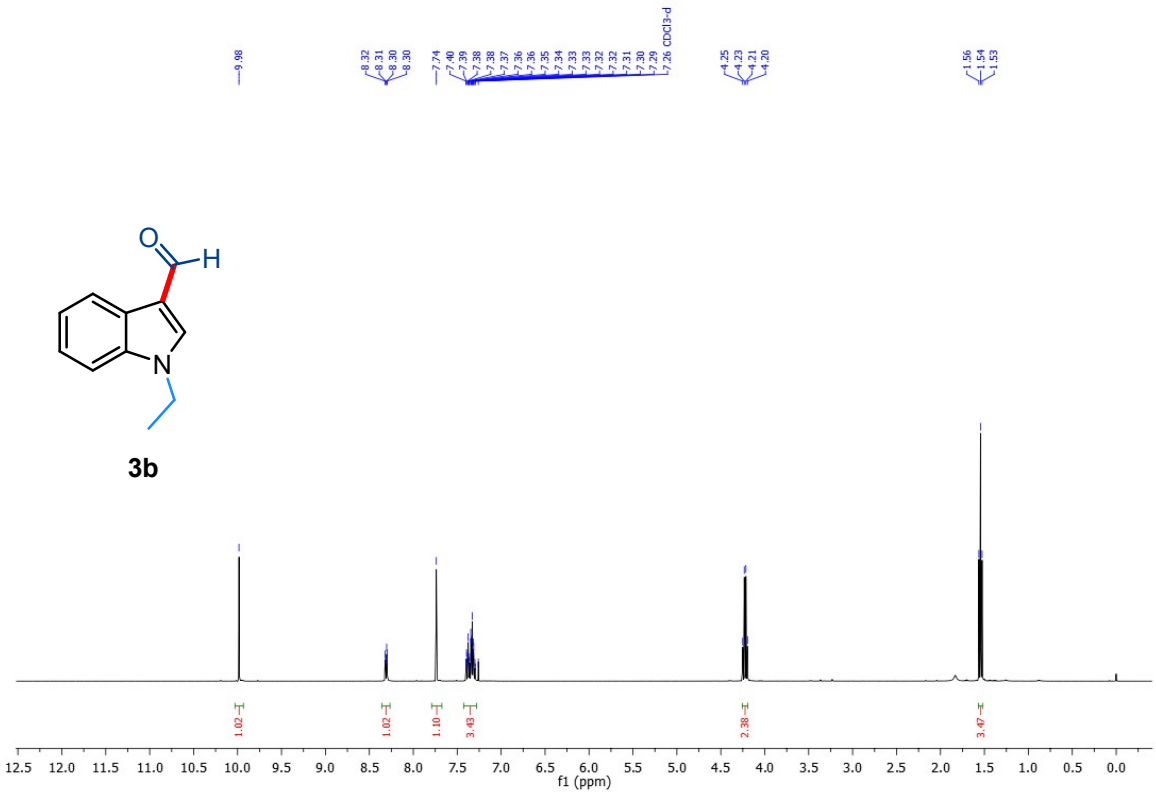


Figure S16: ^{1}H NMR of product **3b** in $CDCl_3$-d (400 MHz)

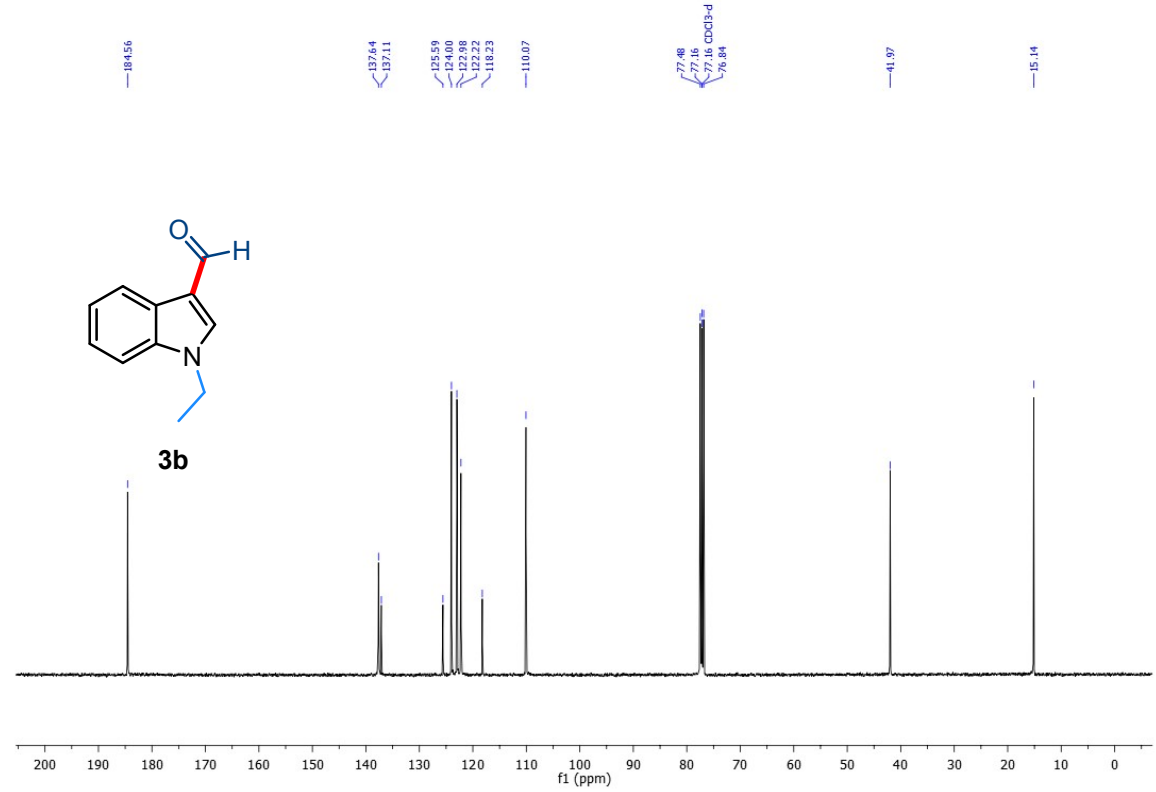


Figure S17: ^{13}C NMR of product **3b** in $CDCl_3$-d (101 MHz)

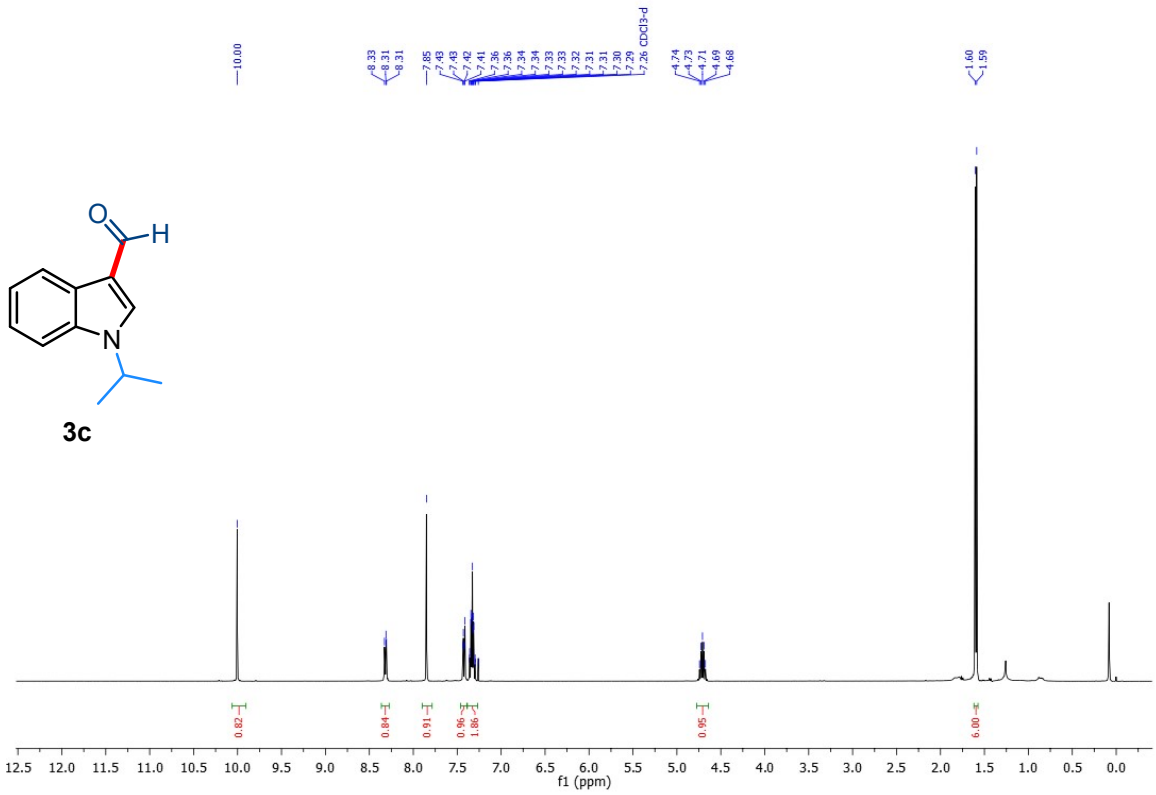


Figure S18: ^{1}H NMR of product **3c** in $CDCl_3$-d (400 MHz)

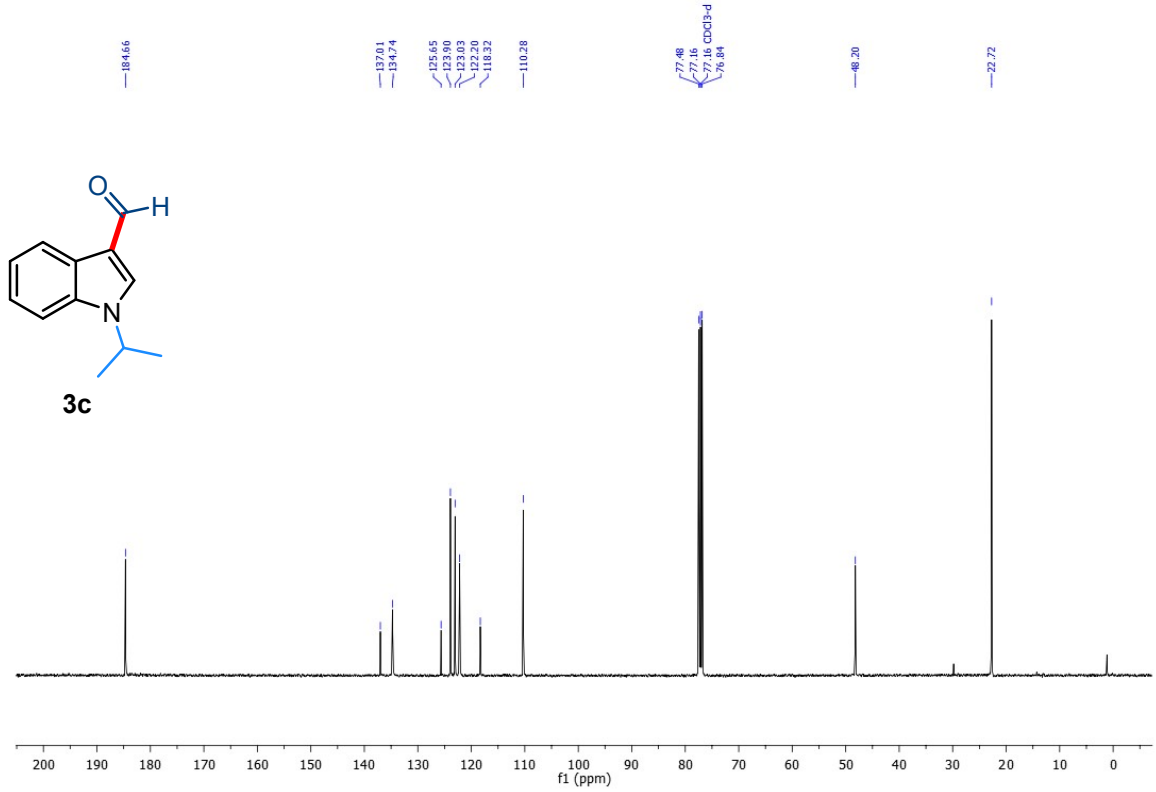
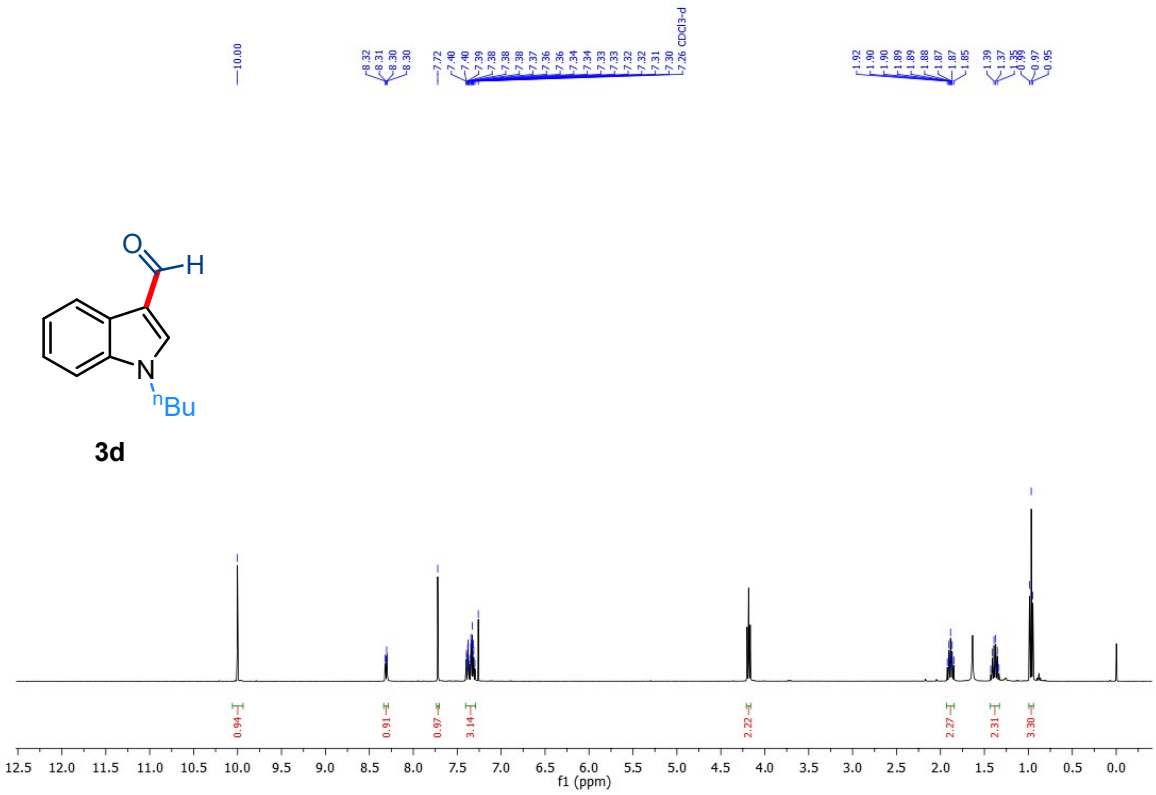
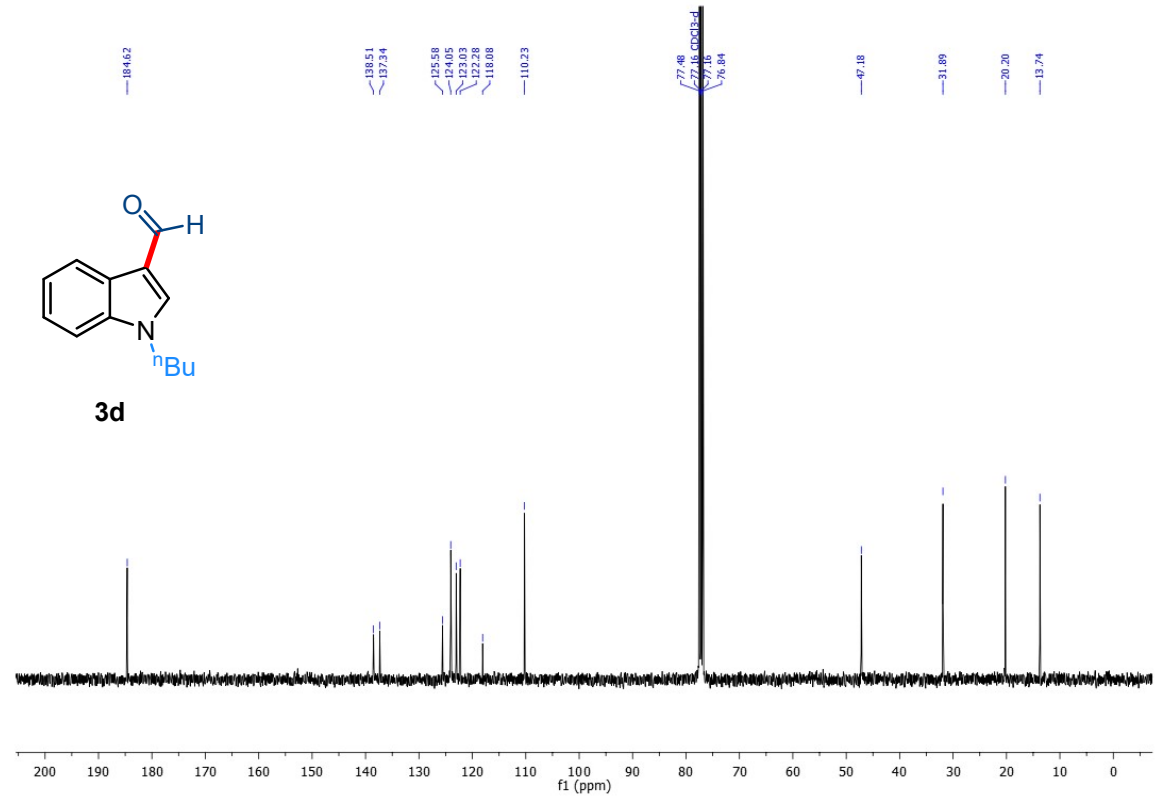


Figure S19: ^{13}C NMR of product **3c** in $CDCl_3$-d (101 MHz)



3d

Figure S20: ^{1}H NMR of product **3d** in $CDCl_3$-d (400 MHz)



3d

Figure S21: ^{13}C NMR of product **3d** in $CDCl_3$-d (101 MHz)

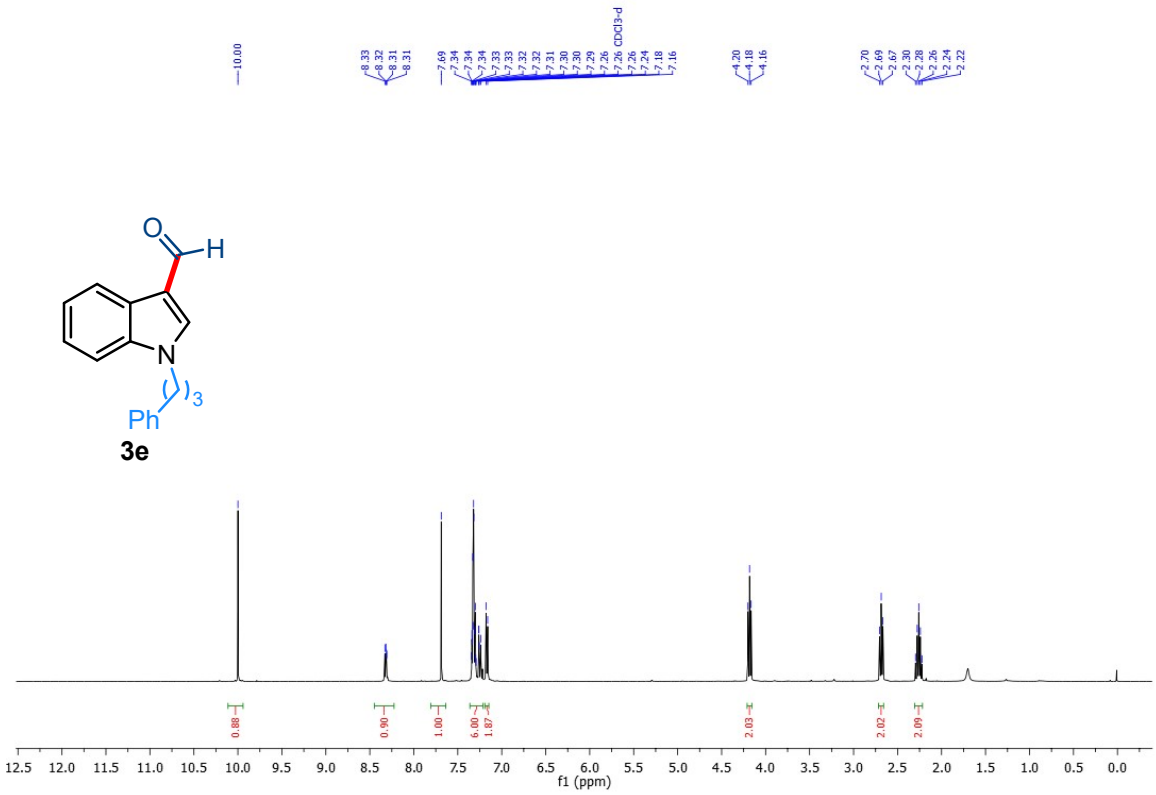


Figure S22: ^{1}H NMR of product **3e** in $CDCl_3$-d (400 MHz)

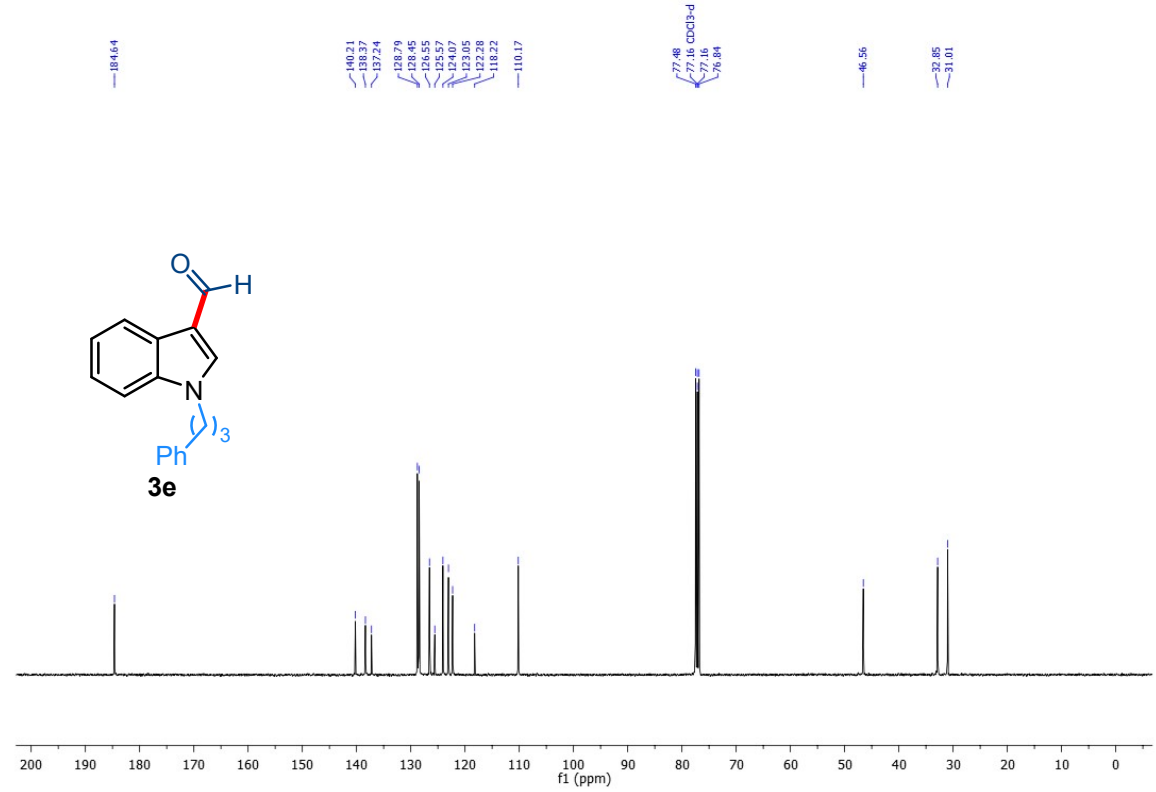


Figure S23: ^{13}C NMR of product **3e** in $CDCl_3$-d (101 MHz)

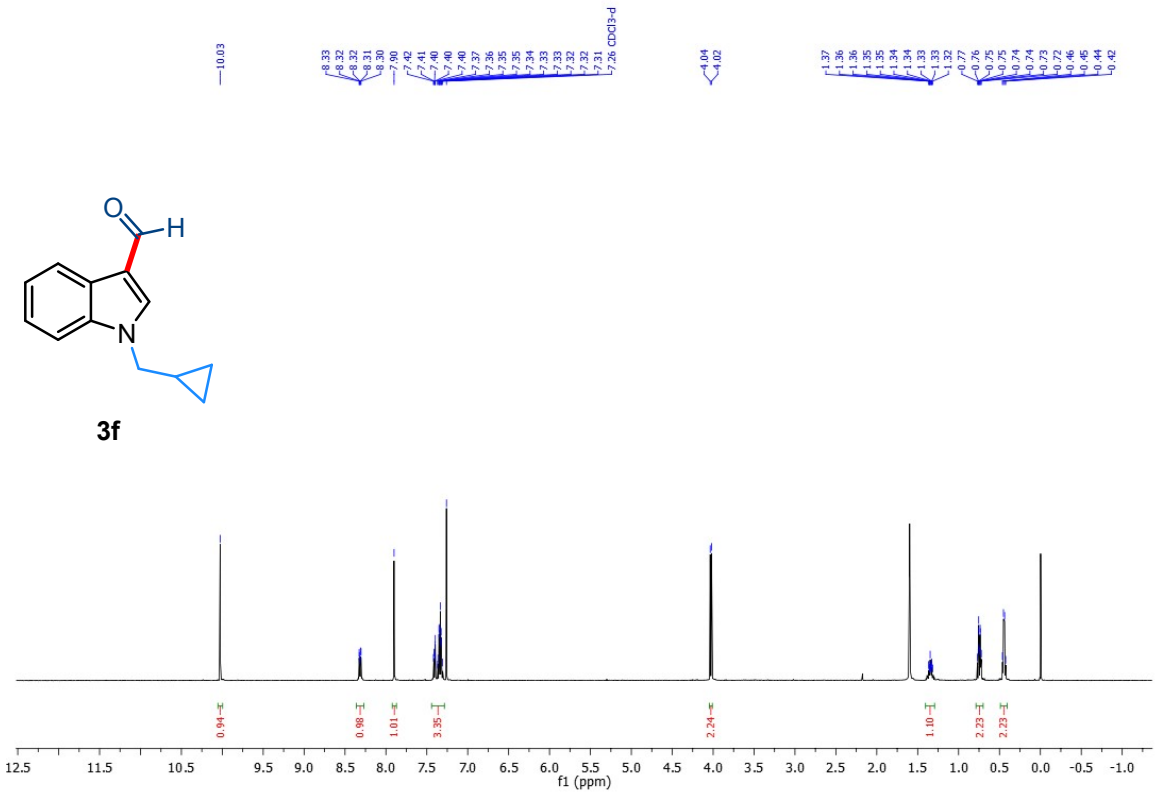


Figure S24: ^{1}H NMR of product **3f** in $CDCl_3$-d (400 MHz)

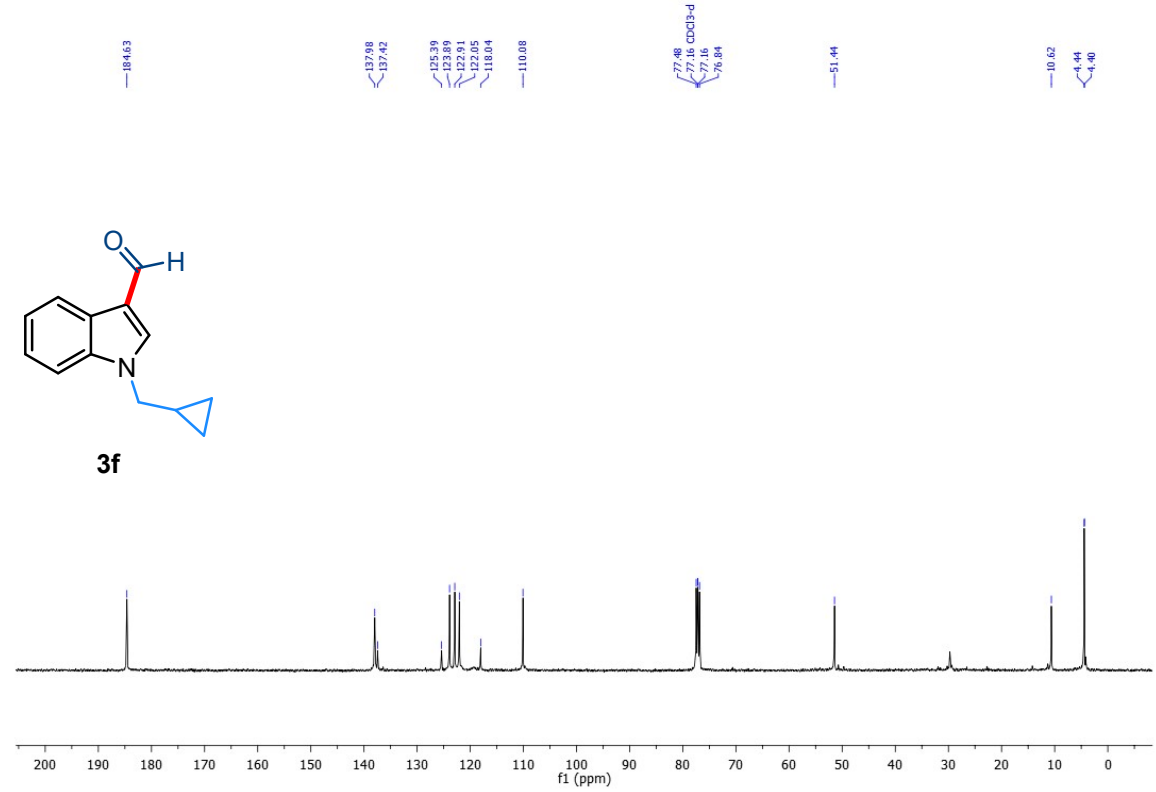


Figure S25: ^{13}C NMR of product **3f** in $CDCl_3$-d (101 MHz)

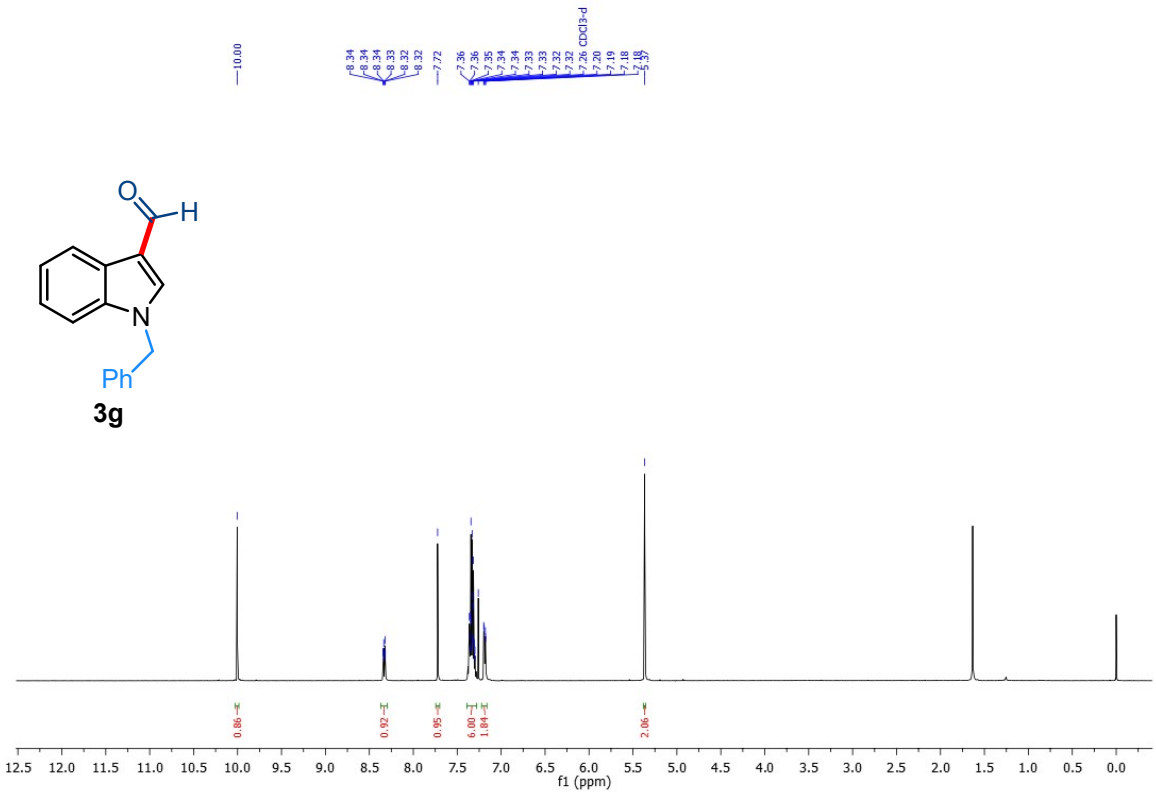


Figure S26: ^{1}H NMR of product **3g** in $CDCl_3$-d (400 MHz)

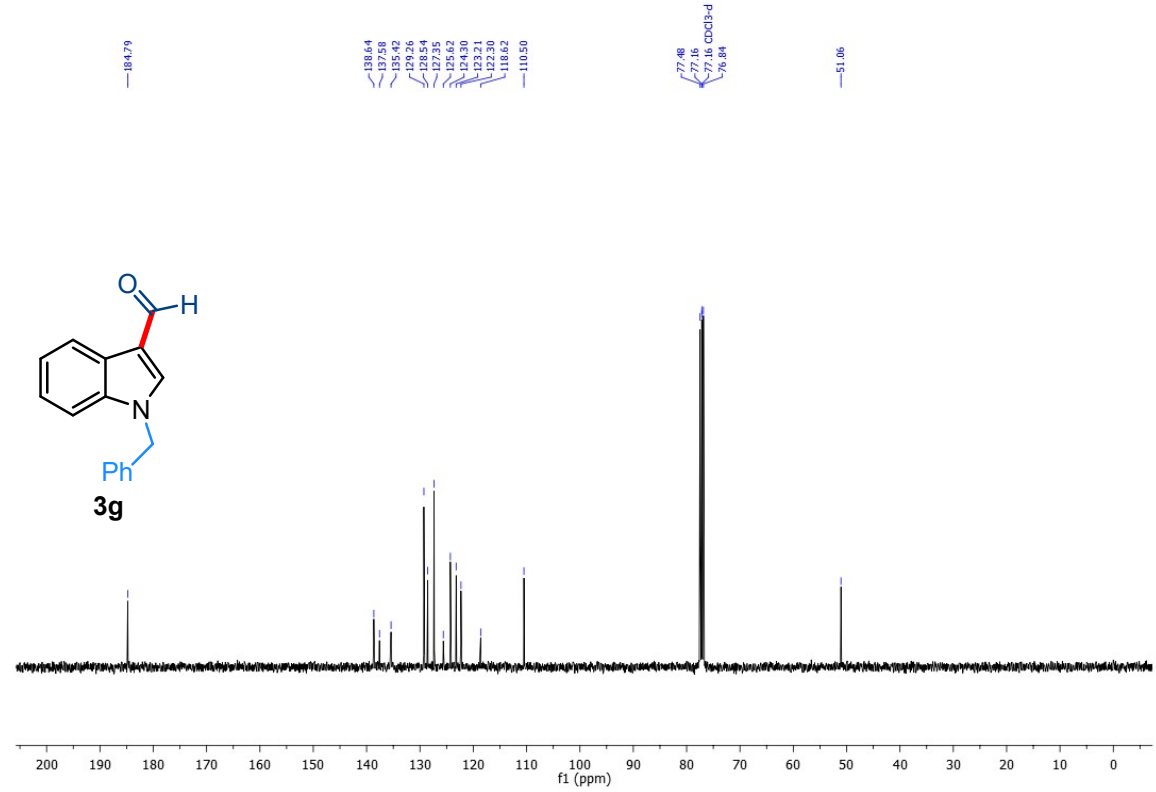


Figure S27: ^{13}C NMR of product **3g** in $CDCl_3$-d (101 MHz)

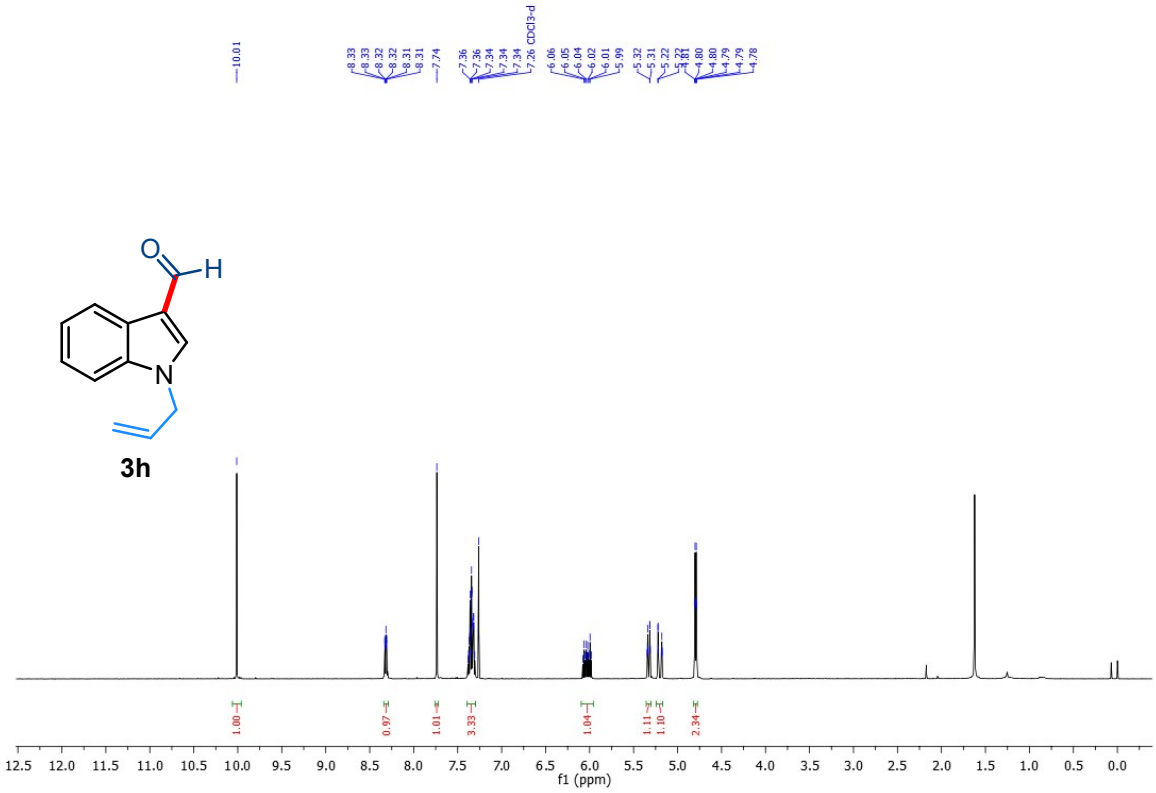


Figure S28: ^{1}H NMR of product **3h** in $CDCl_3$-d (400 MHz)

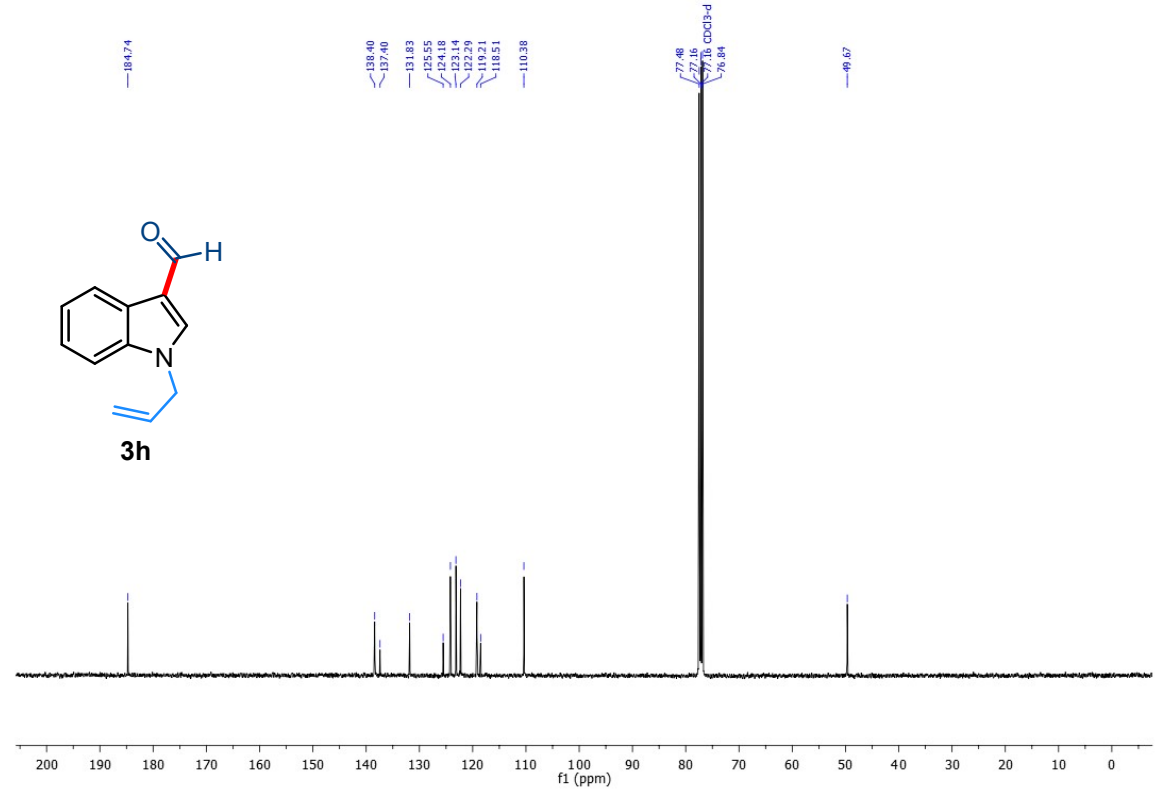


Figure S29: ^{13}C NMR of product **3h** in $CDCl_3$-d (101 MHz)

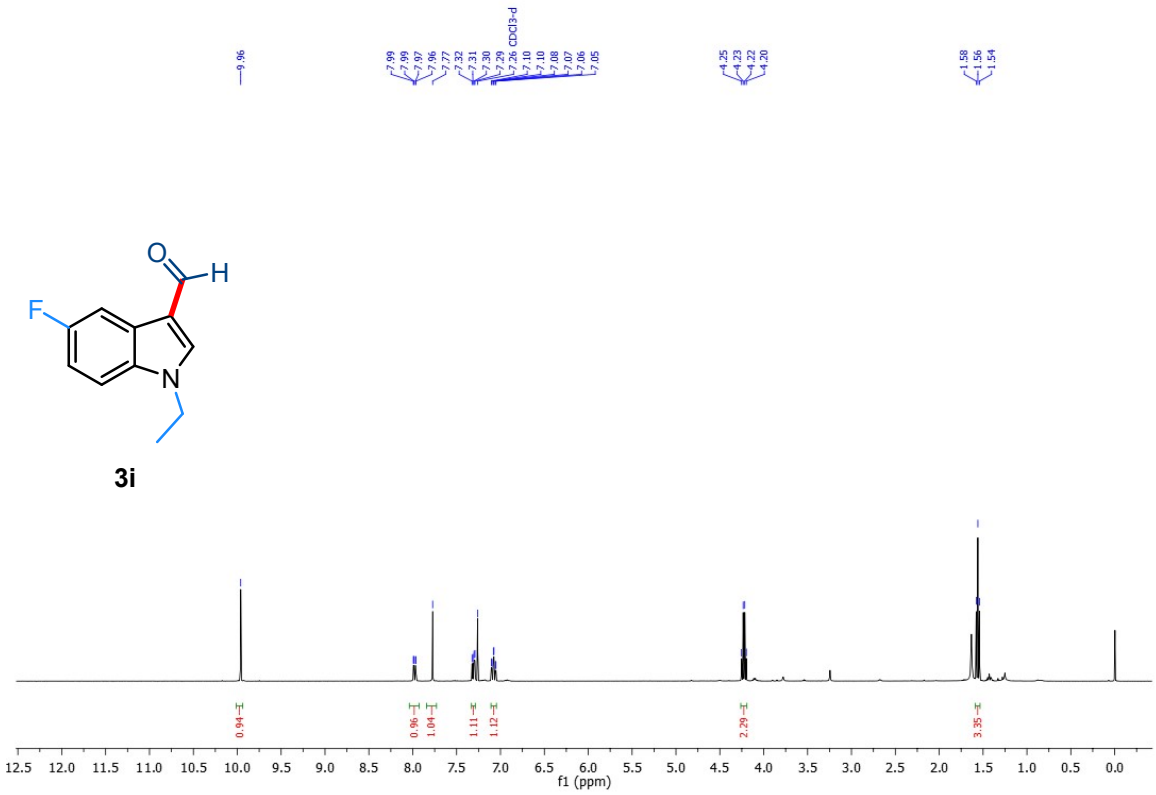


Figure S30: ^{1}H NMR of product **3i** in $CDCl_3$-d (400 MHz)

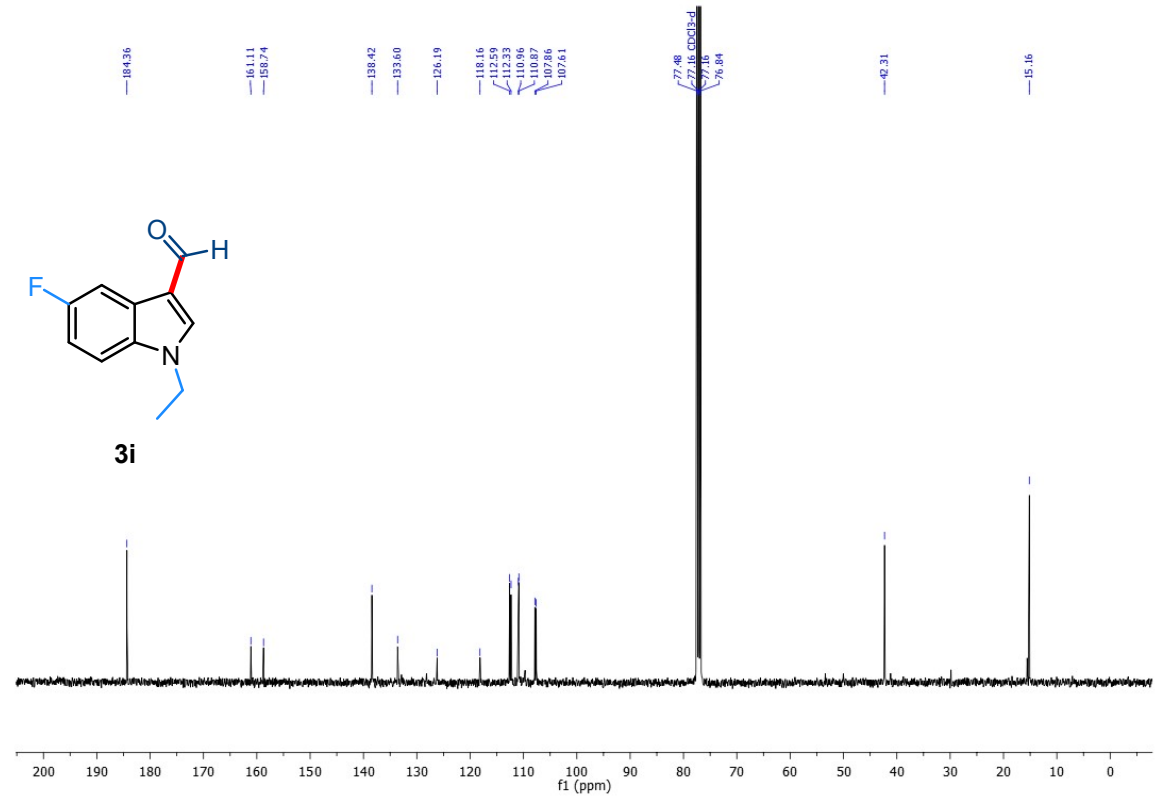


Figure S31: ^{13}C NMR of product **3i** in $CDCl_3$-d (101 MHz)

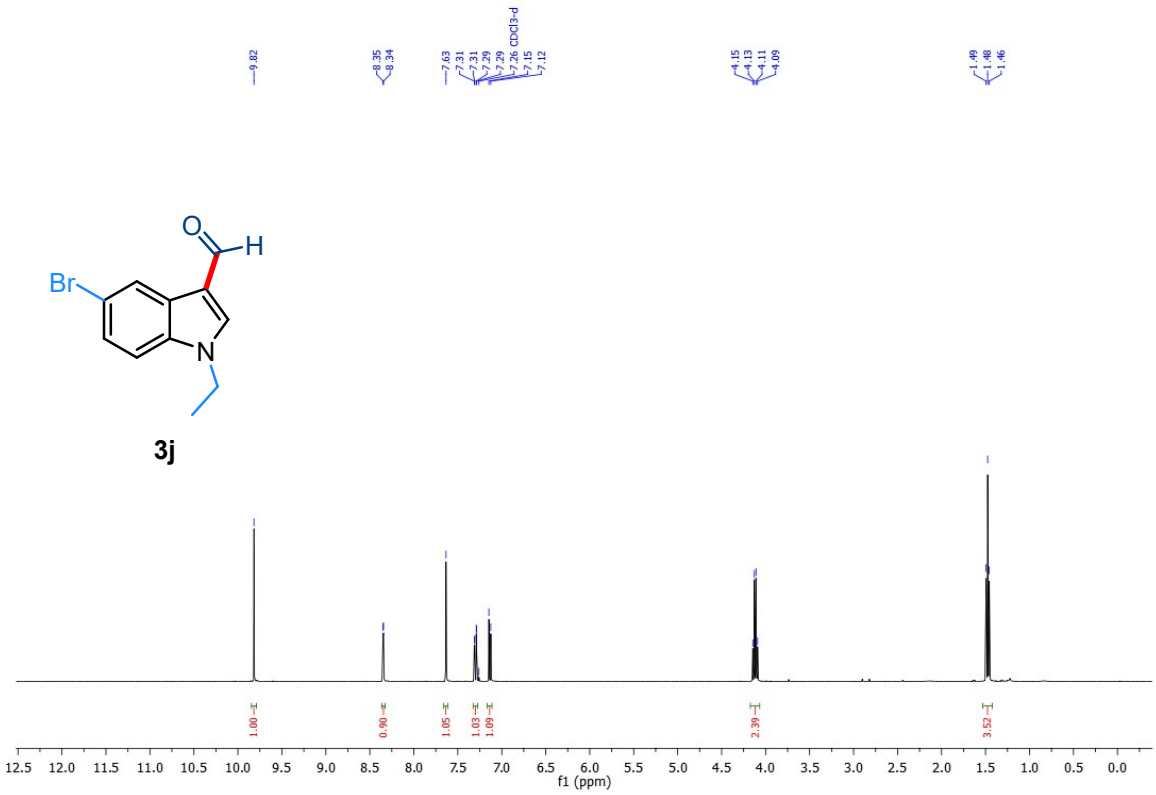


Figure S32: ^{13}C NMR of product **3j** in $CDCl_3$-d (101 MHz)

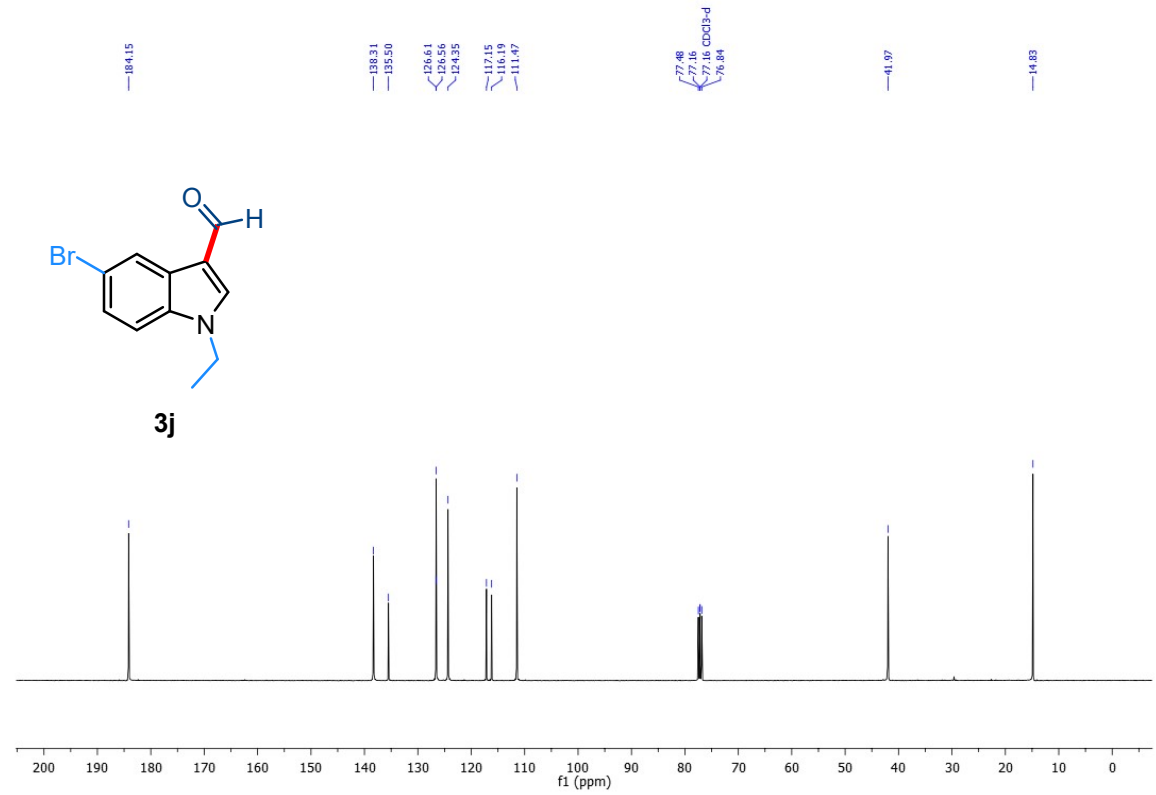


Figure S33: ^{13}C NMR of product **3j** in $CDCl_3$-d (101 MHz)

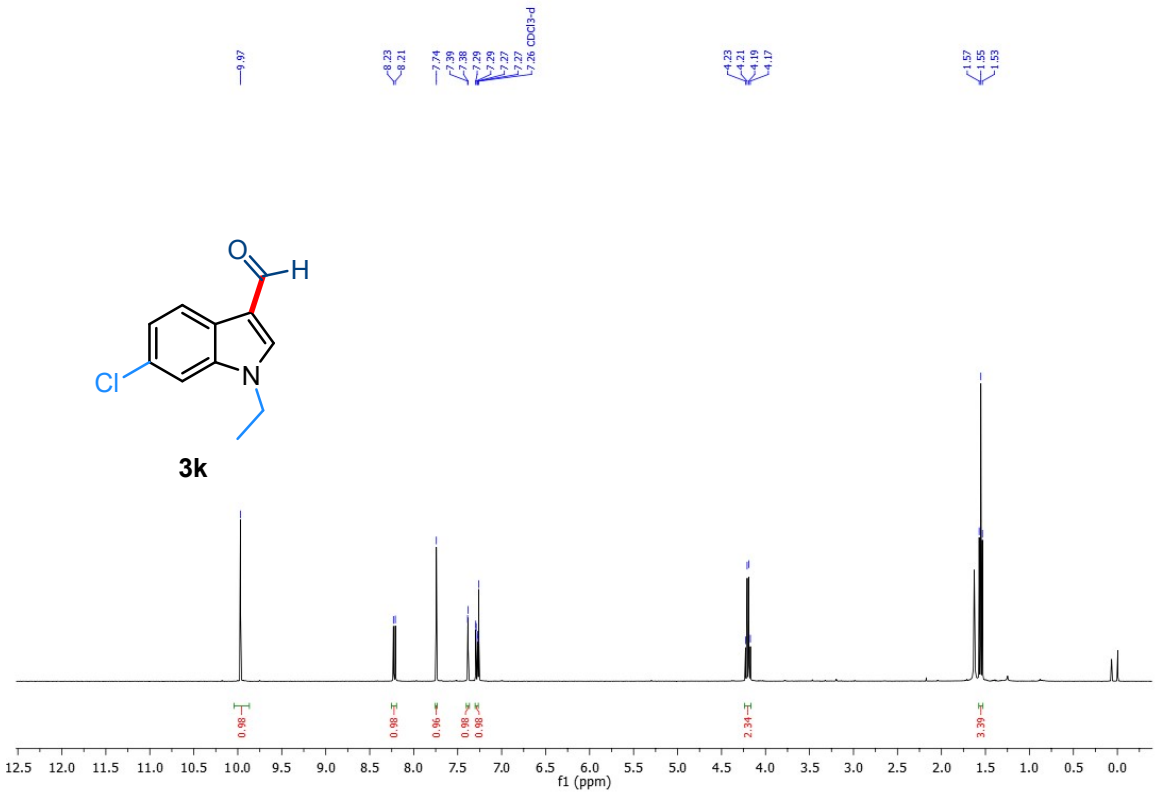


Figure S34: ^{1}H NMR of product **3k** in $CDCl_3$-d (400 MHz)

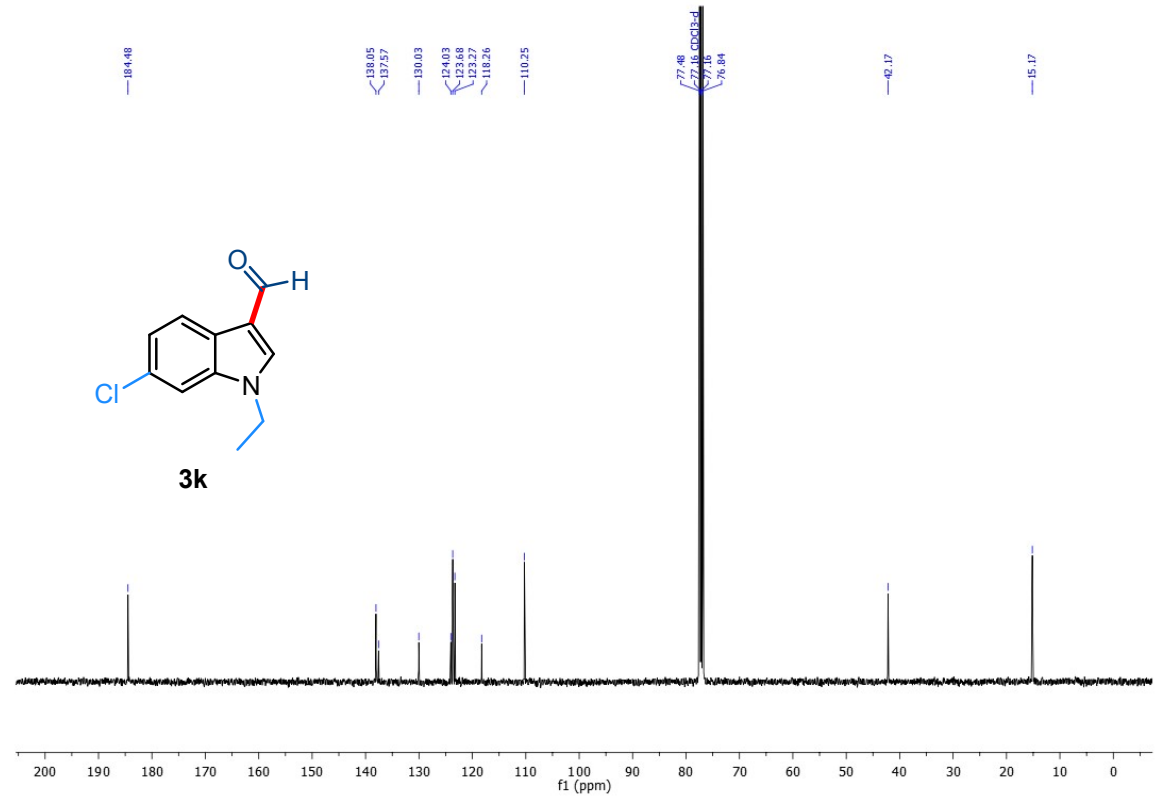


Figure S35: ^{13}C NMR of product **3k** in $CDCl_3$-d (101 MHz)

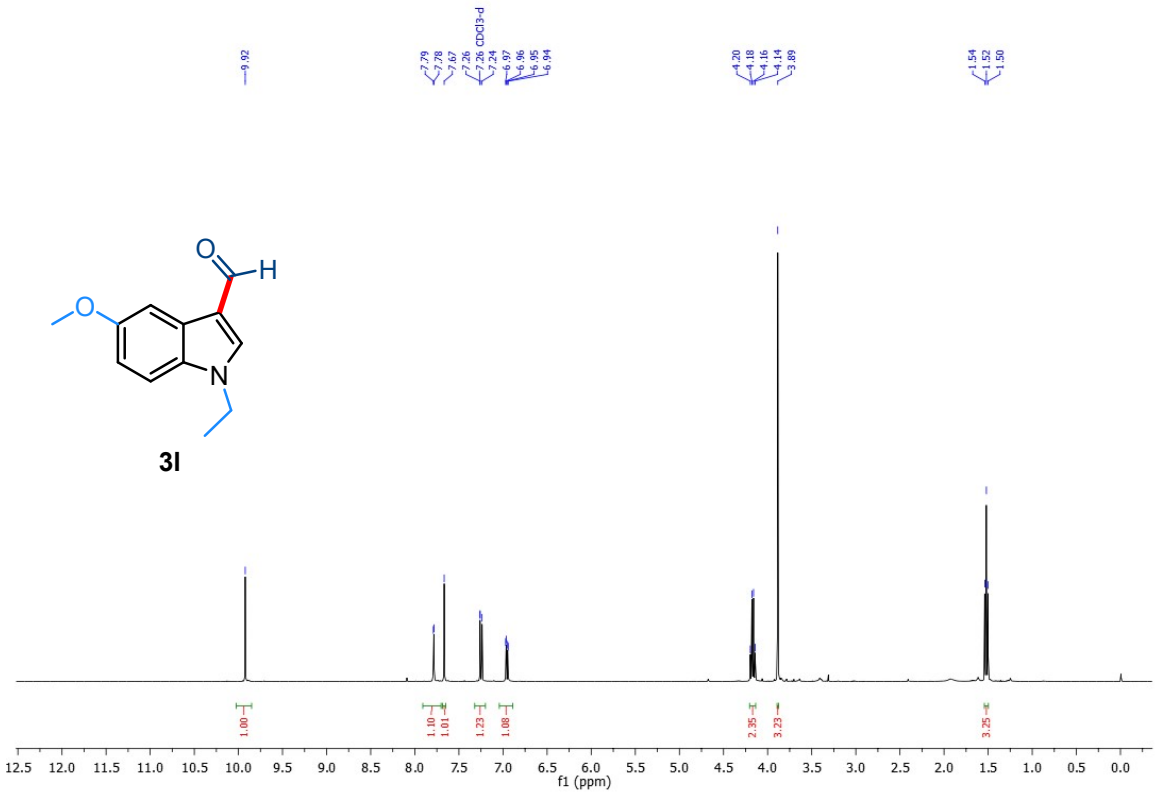


Figure S36: ^{1}H NMR of product **3l** in $CDCl_3$-d (400 MHz)

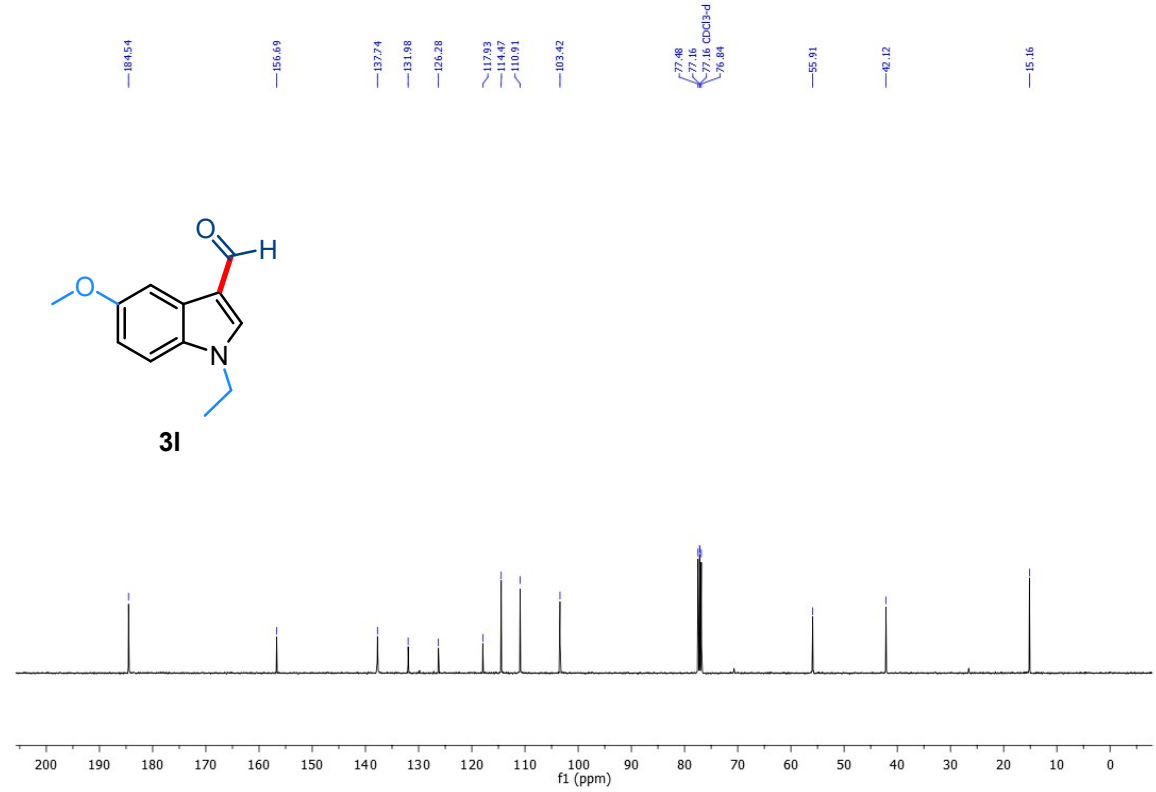


Figure S37: ^{13}C NMR of product **3l** in $CDCl_3$-d (101 MHz)

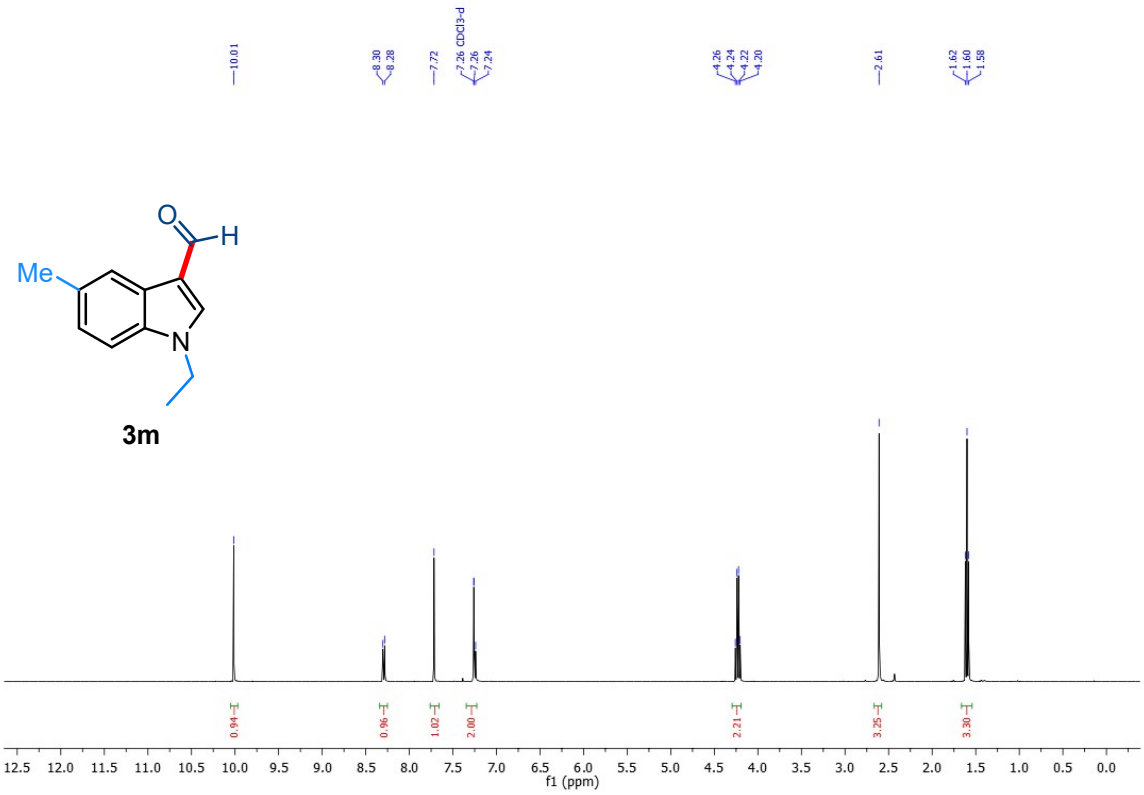


Figure S38: ^{1}H NMR of product **3m** in $CDCl_3$-d (400 MHz)

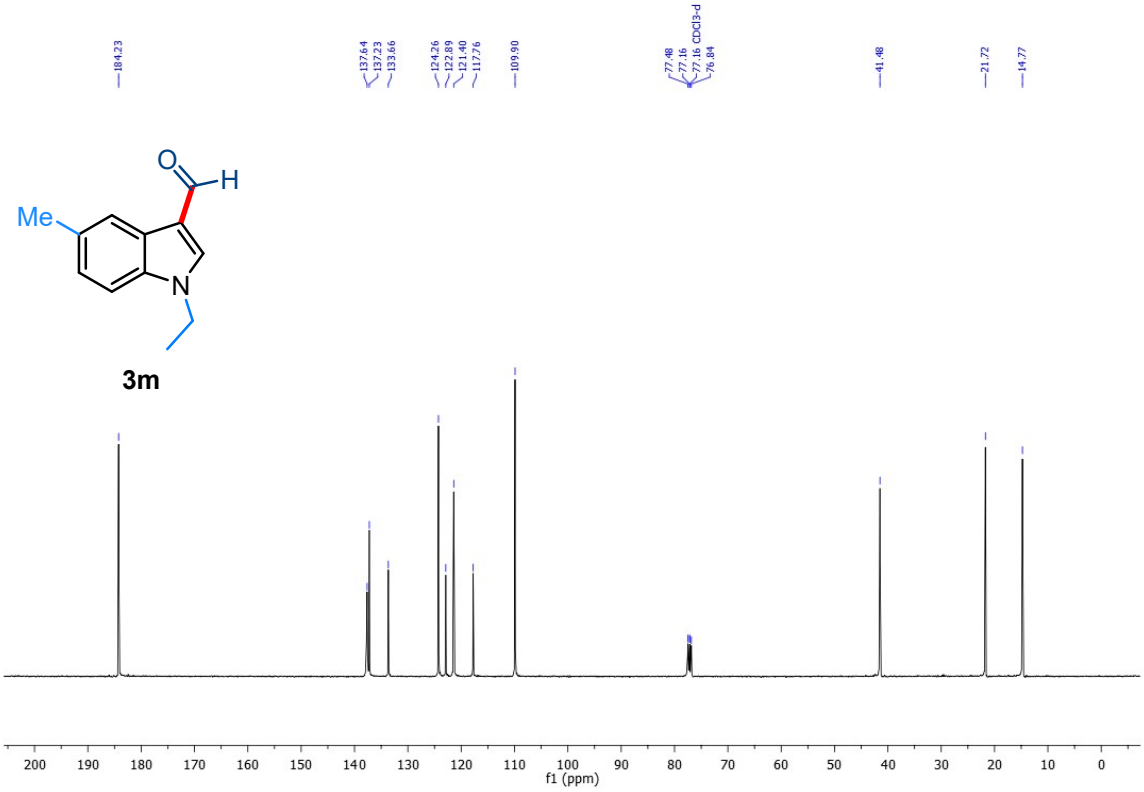


Figure S39: ^{13}C NMR of product **3m** in $CDCl_3$-d (101 MHz)

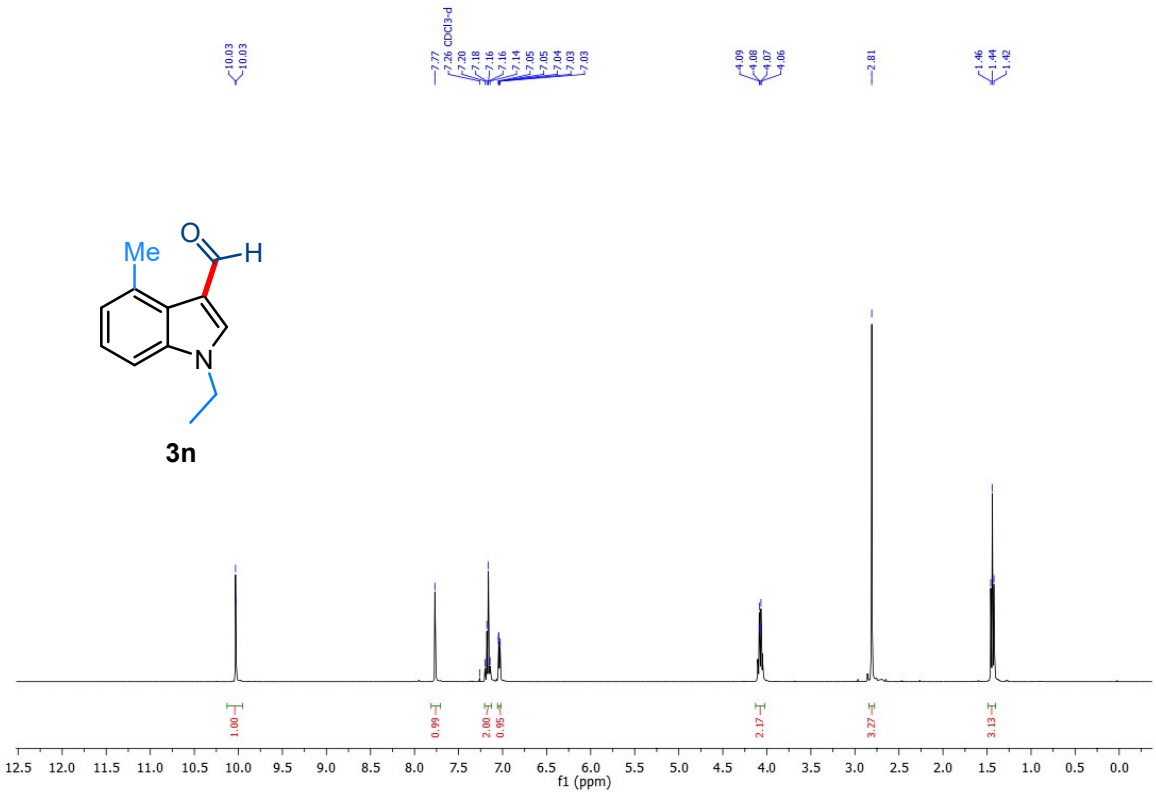


Figure S40: ^{1}H NMR of product **3n** in $CDCl_3$-d (400 MHz)

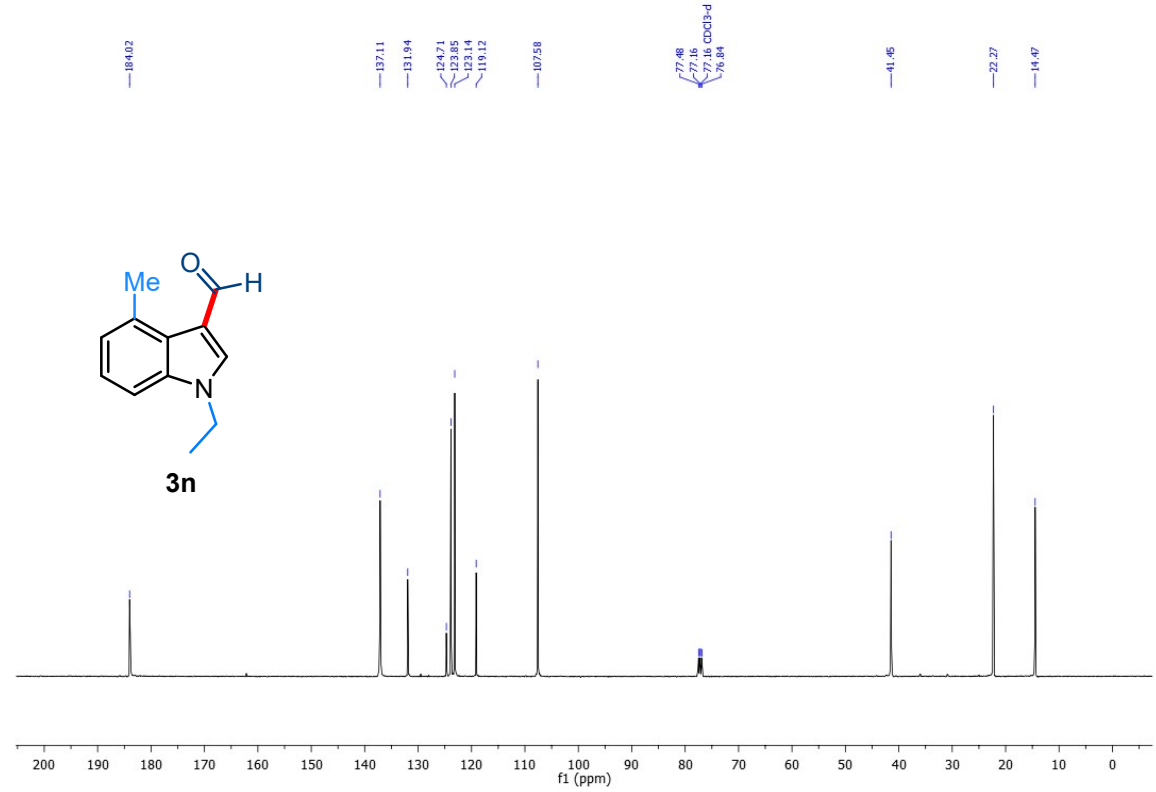


Figure S41: ^{13}C NMR of product **3n** in $CDCl_3$-d (101 MHz)

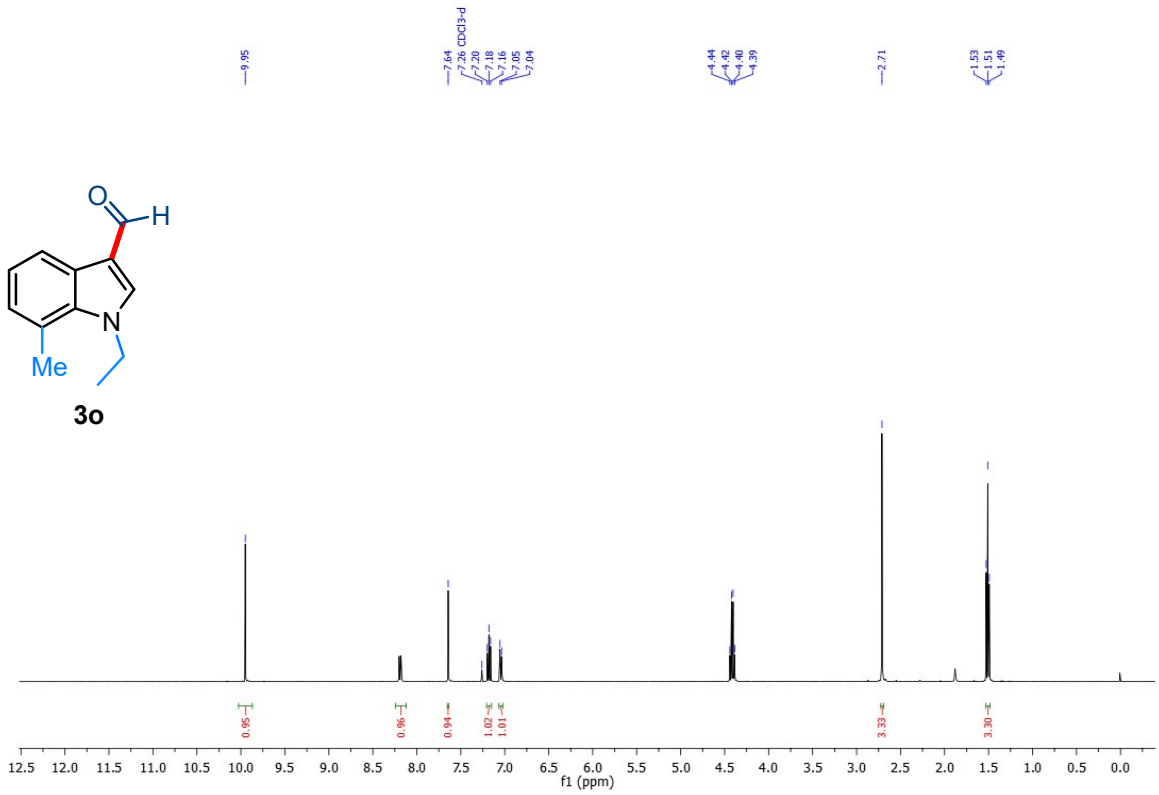


Figure S42: ^{1}H NMR of product **3o** in $CDCl_3$-d (400 MHz)

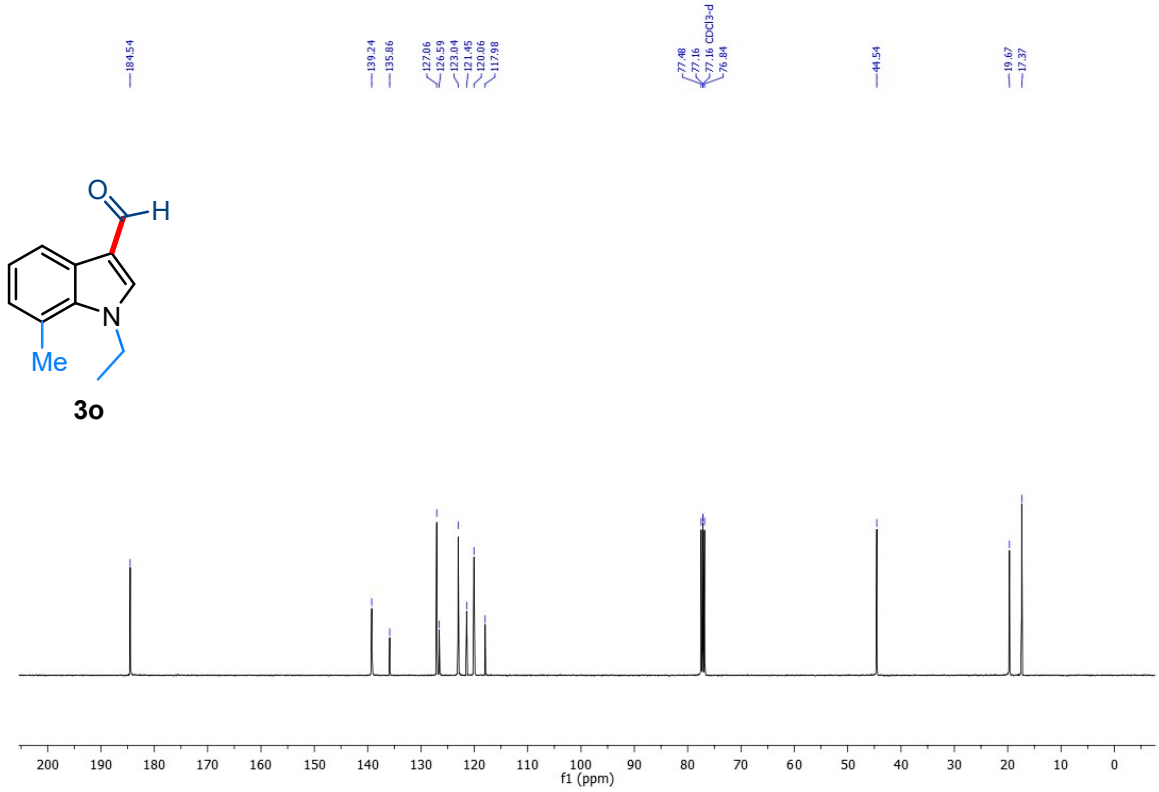


Figure S43: ^{13}C NMR of product **3o** in $CDCl_3$-d (101 MHz)

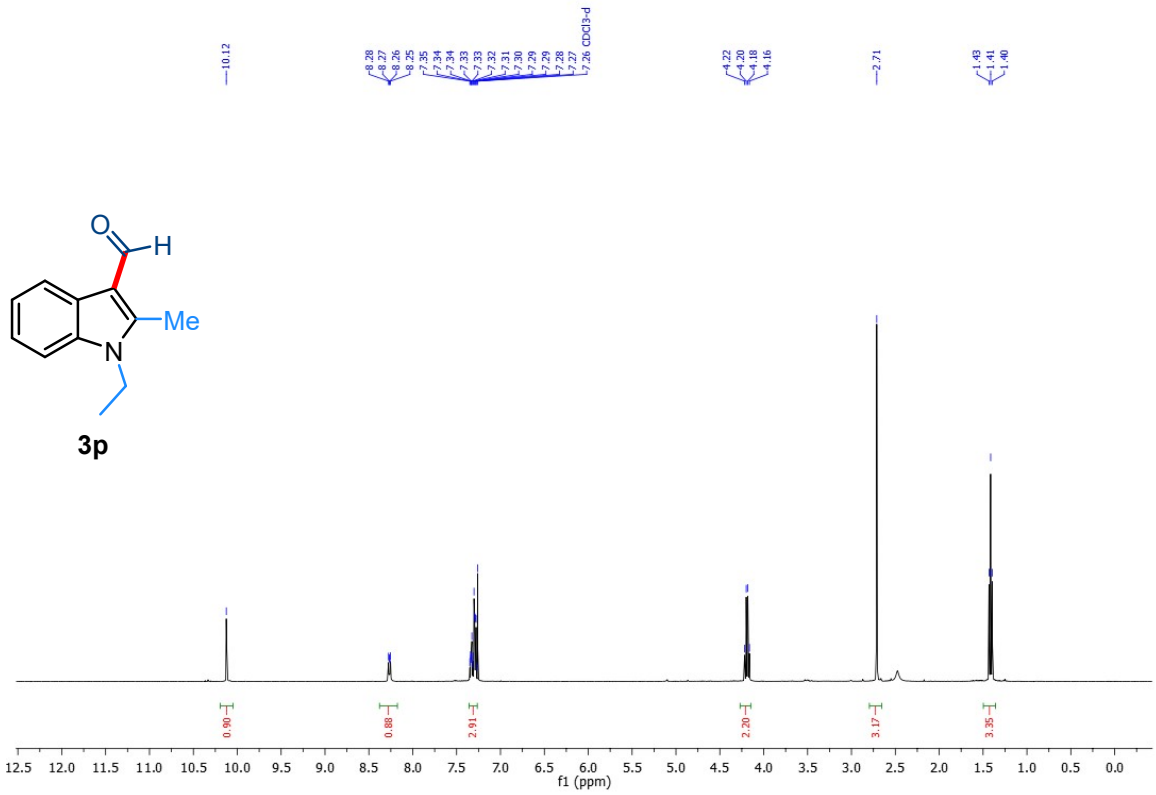


Figure S44: ^{1}H NMR of product **3p** in $CDCl_3$-d (400 MHz)

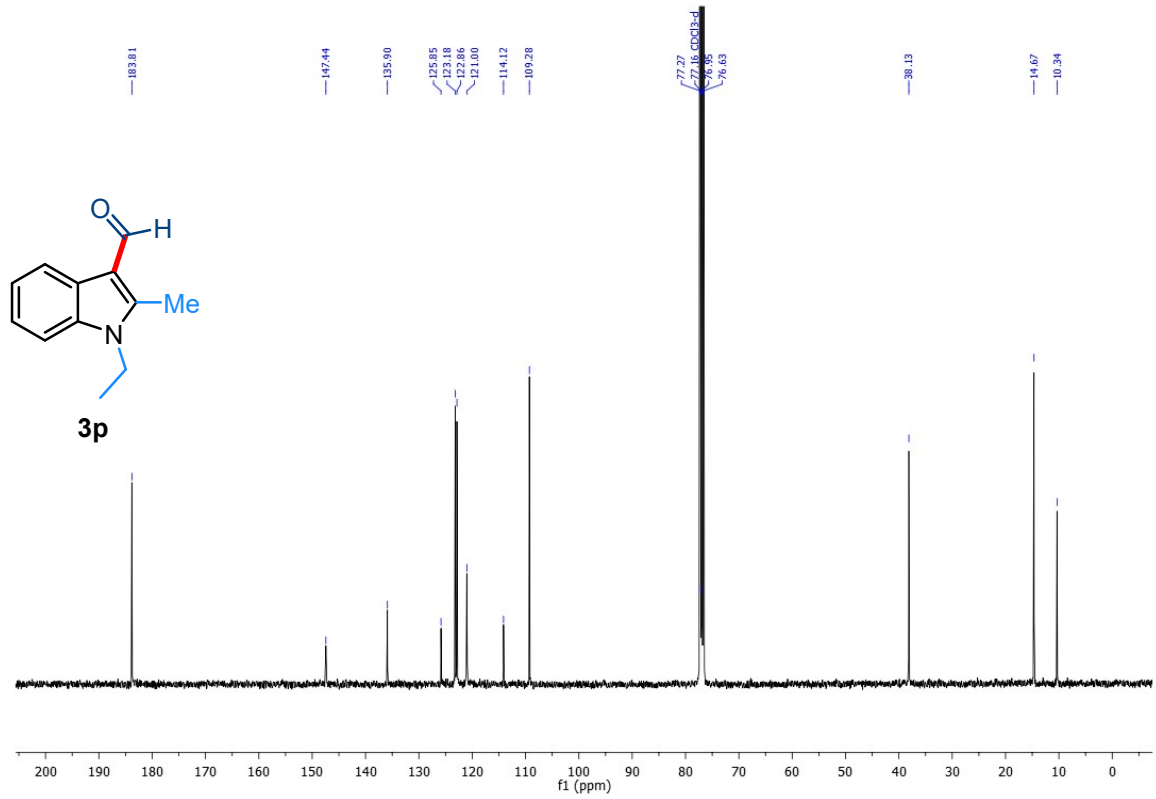


Figure S45: ^{1}H NMR of product **3p** in $CDCl_3$-d (400 MHz)

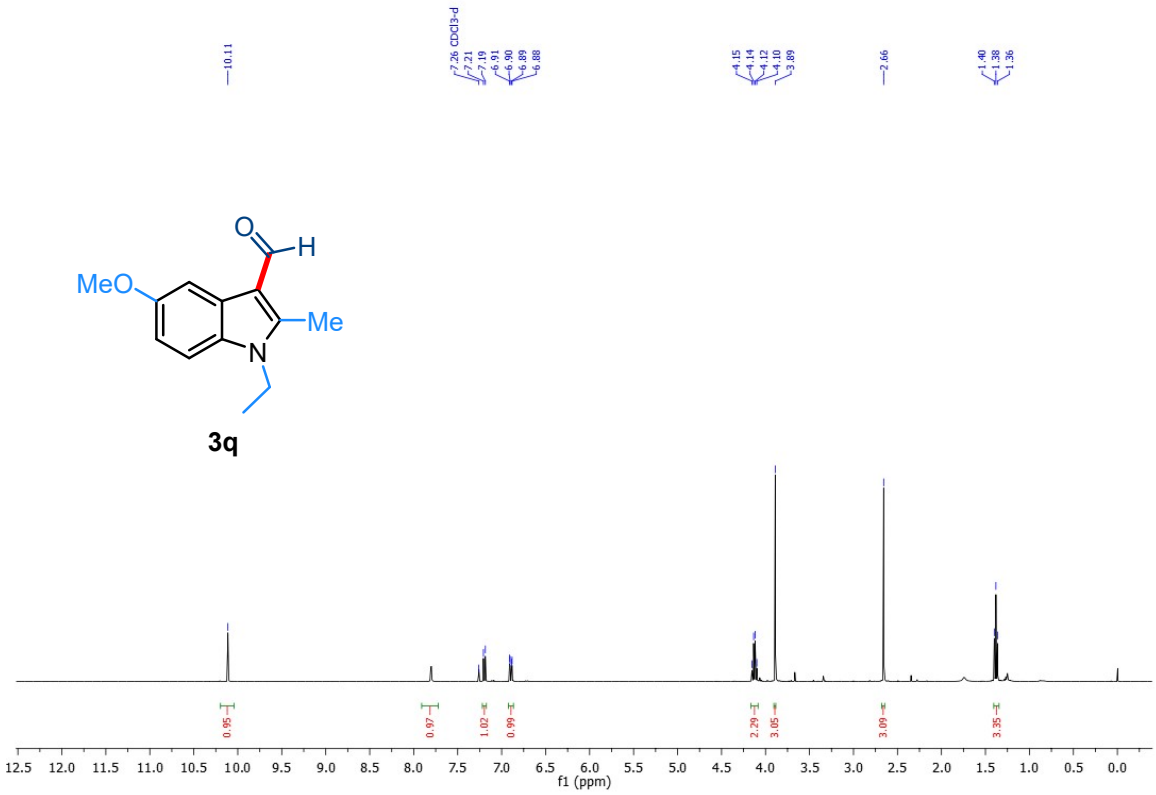


Figure S46: ^{1}H NMR of product **3q** in $CDCl_3$-d (400 MHz)

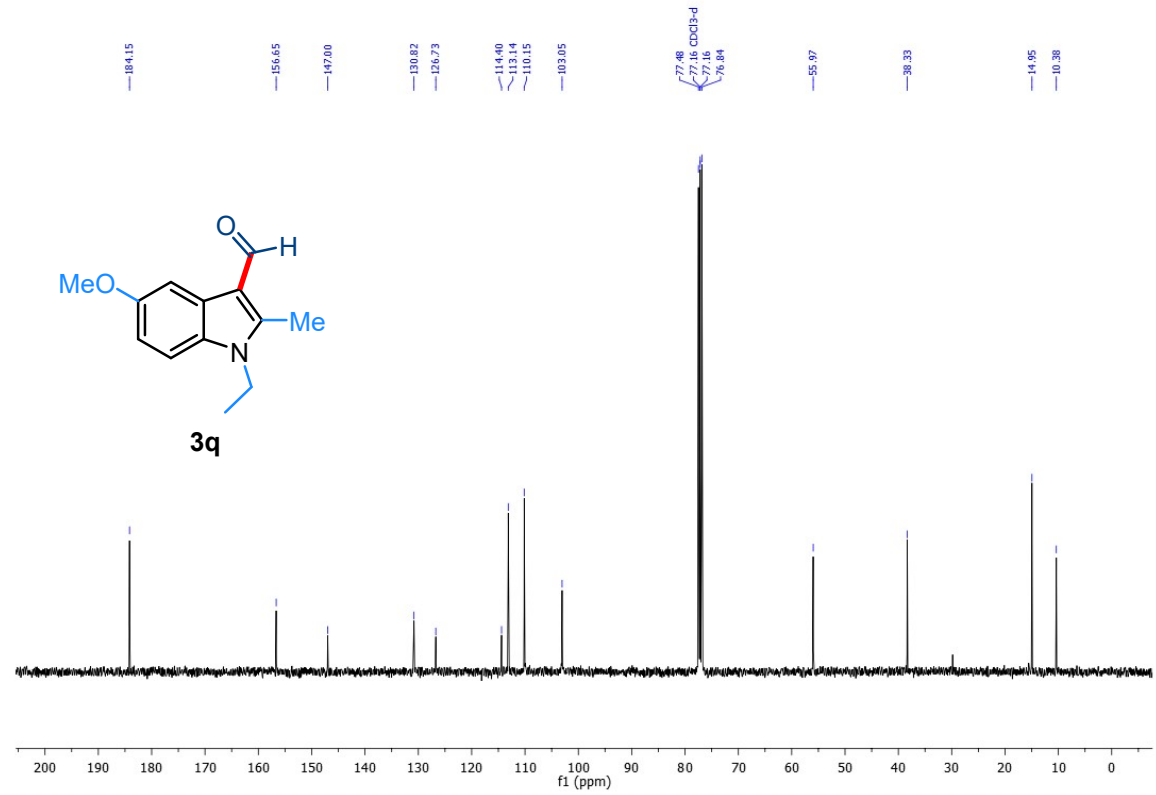


Figure S47: ^{13}C NMR of product **3q** in $CDCl_3$-d (101 MHz)

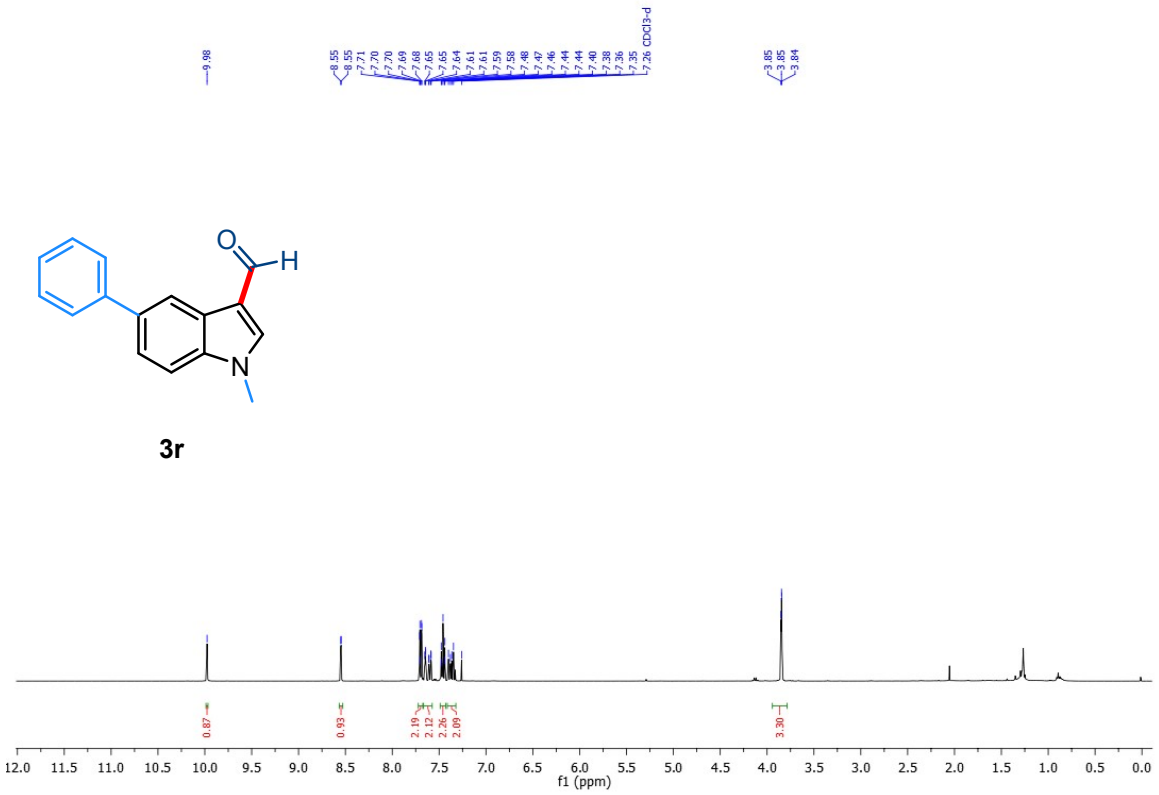


Figure S48: ^{1}H NMR of product **3r** in $CDCl_3$-d (400 MHz)

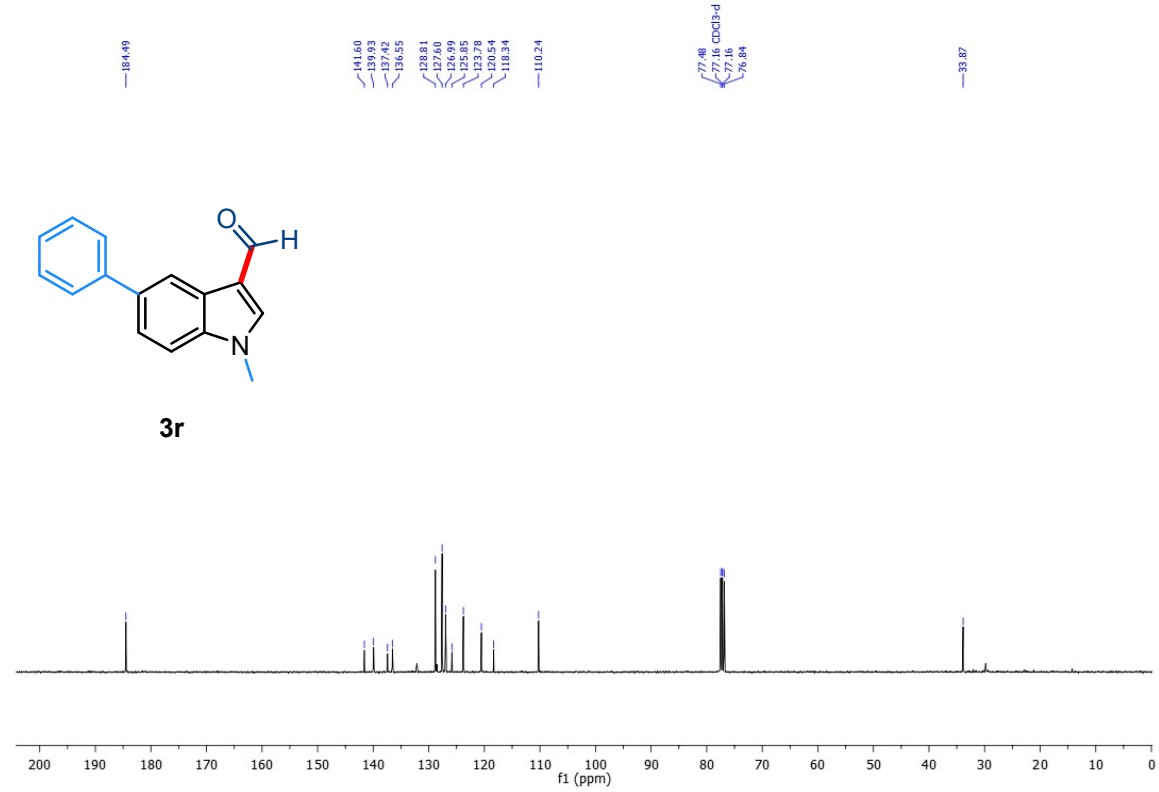


Figure S49: ^{13}C NMR of product **3r** in $CDCl_3$-d (101 MHz)

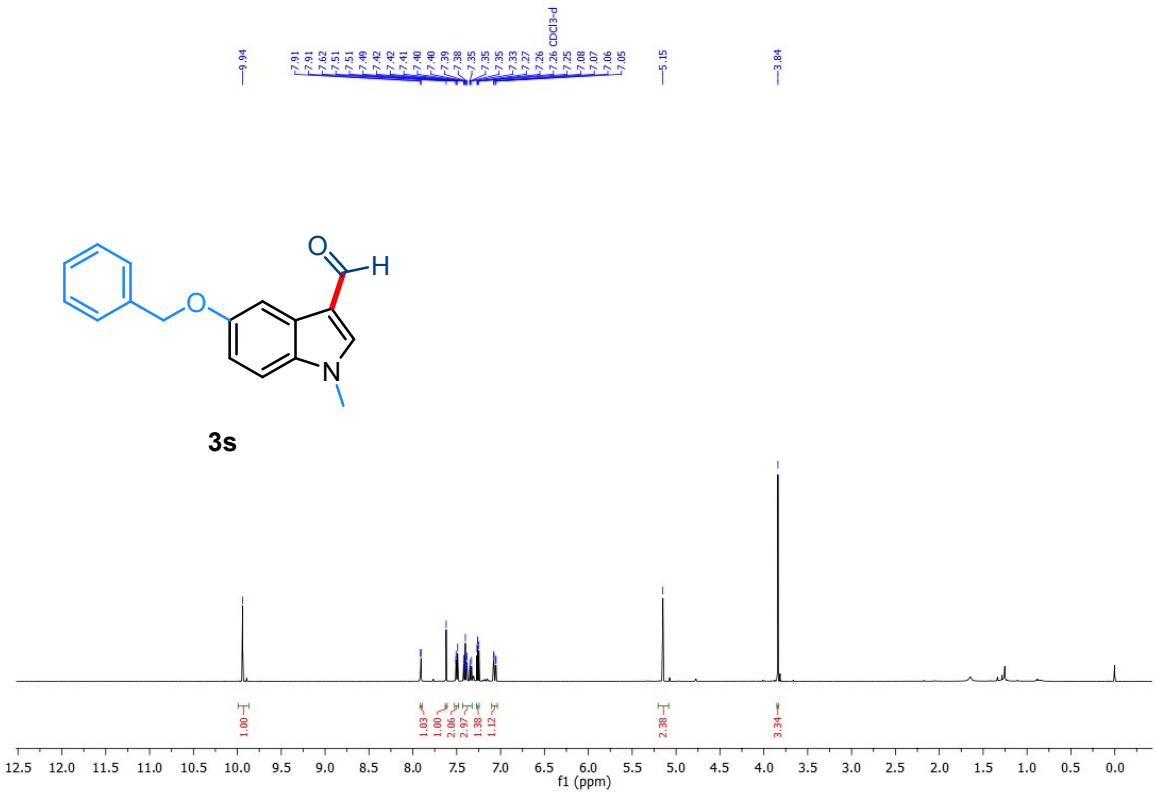


Figure S50: ^{1}H NMR of product **3s** in $CDCl_3$-d (400 MHz)

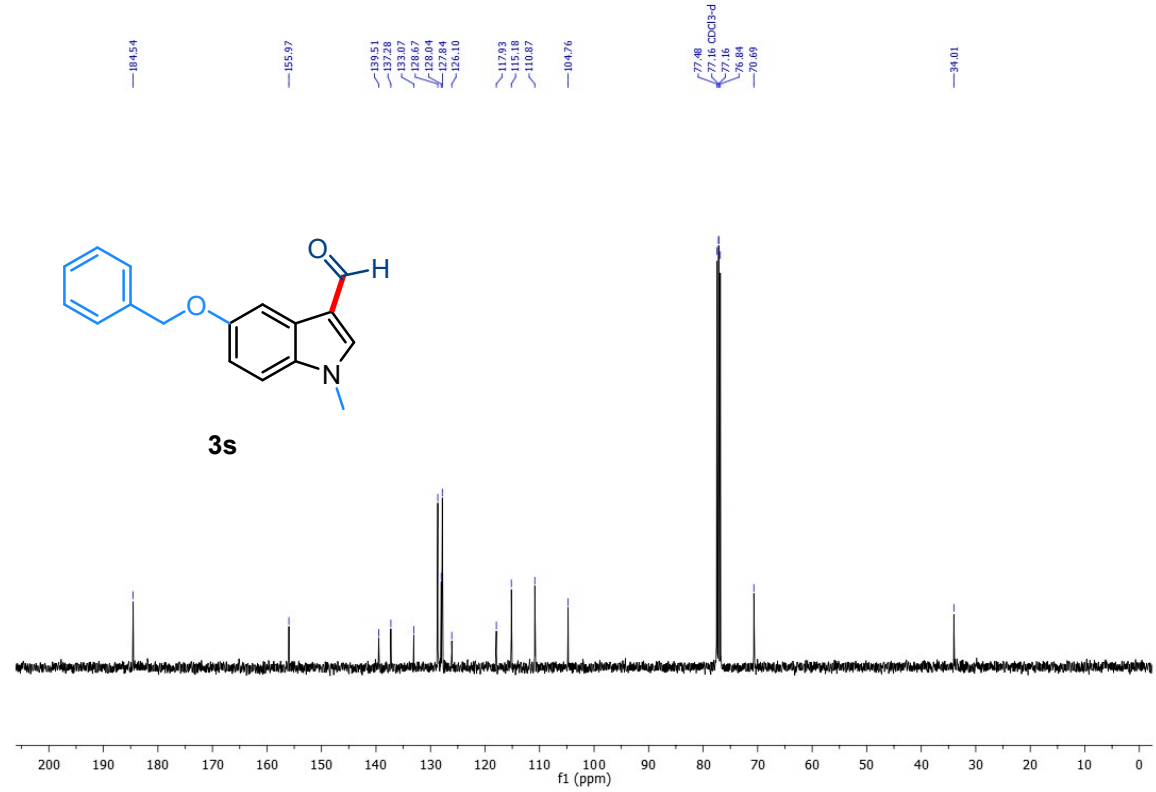


Figure S51: ^{13}C NMR of product **3s** in $CDCl_3$-d (101 MHz)

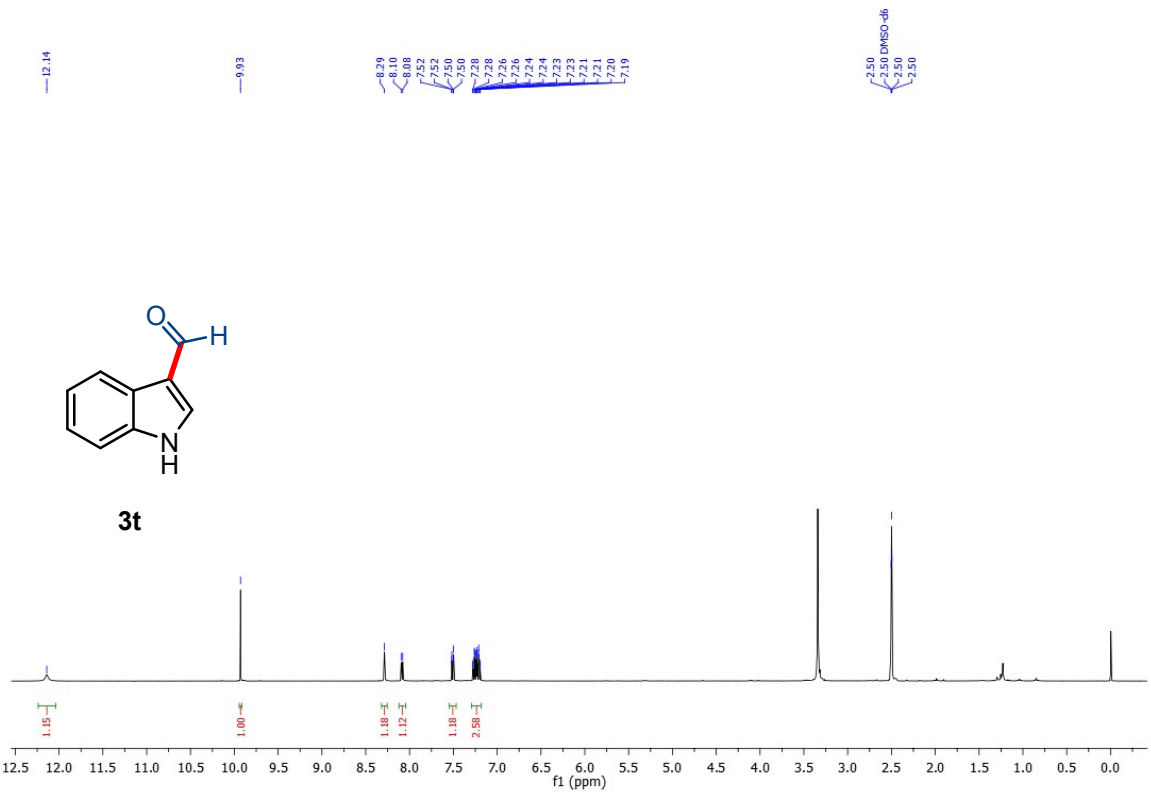


Figure S52: ^{1}H NMR of product **3t** in DMSO-d_6 (400 MHz)

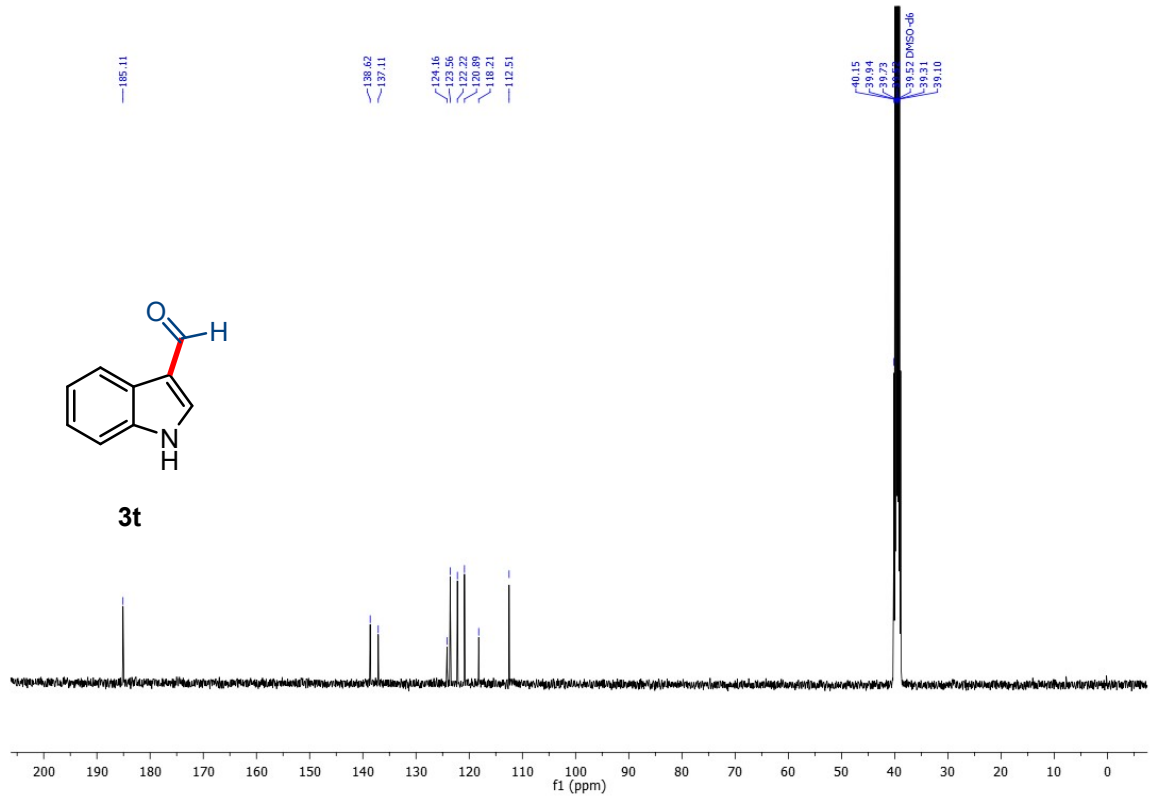


Figure S53: ^{13}C NMR of product **3t** in DMSO-d6 (101 MHz)

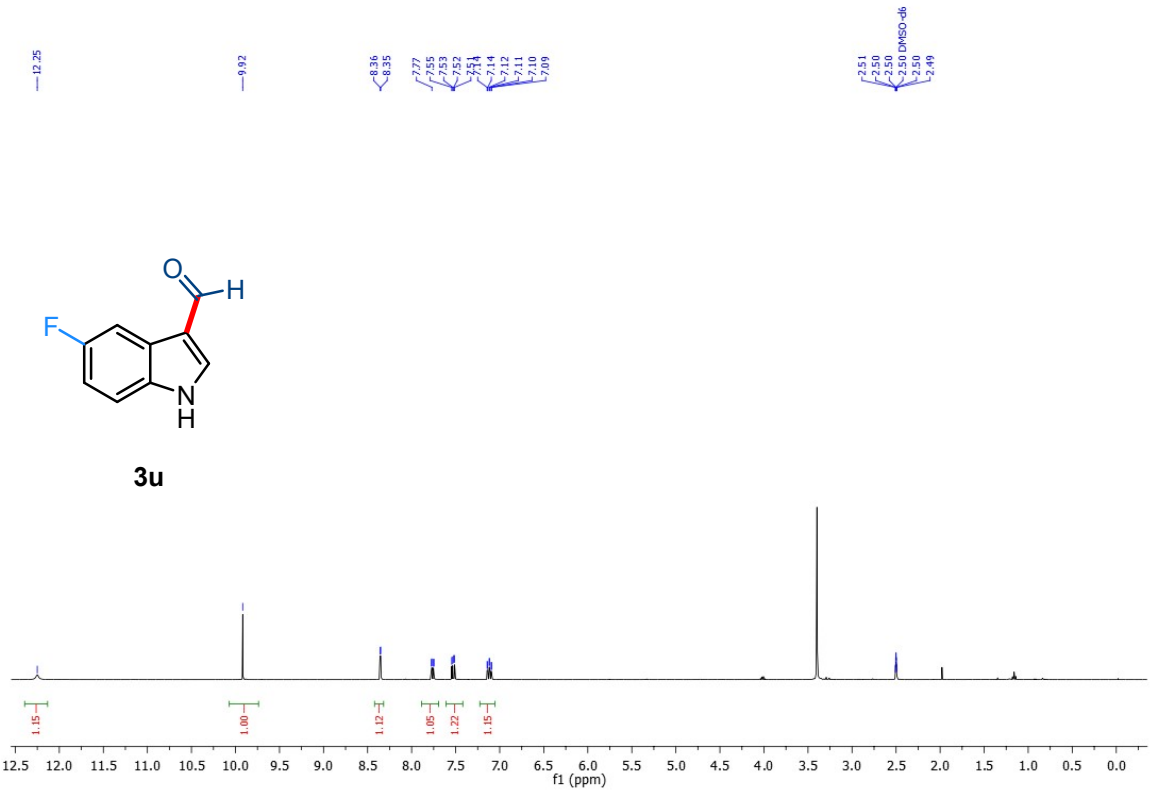


Figure S54: ^{1}H NMR of product **3u** in DMSO-d_6 (400 MHz)

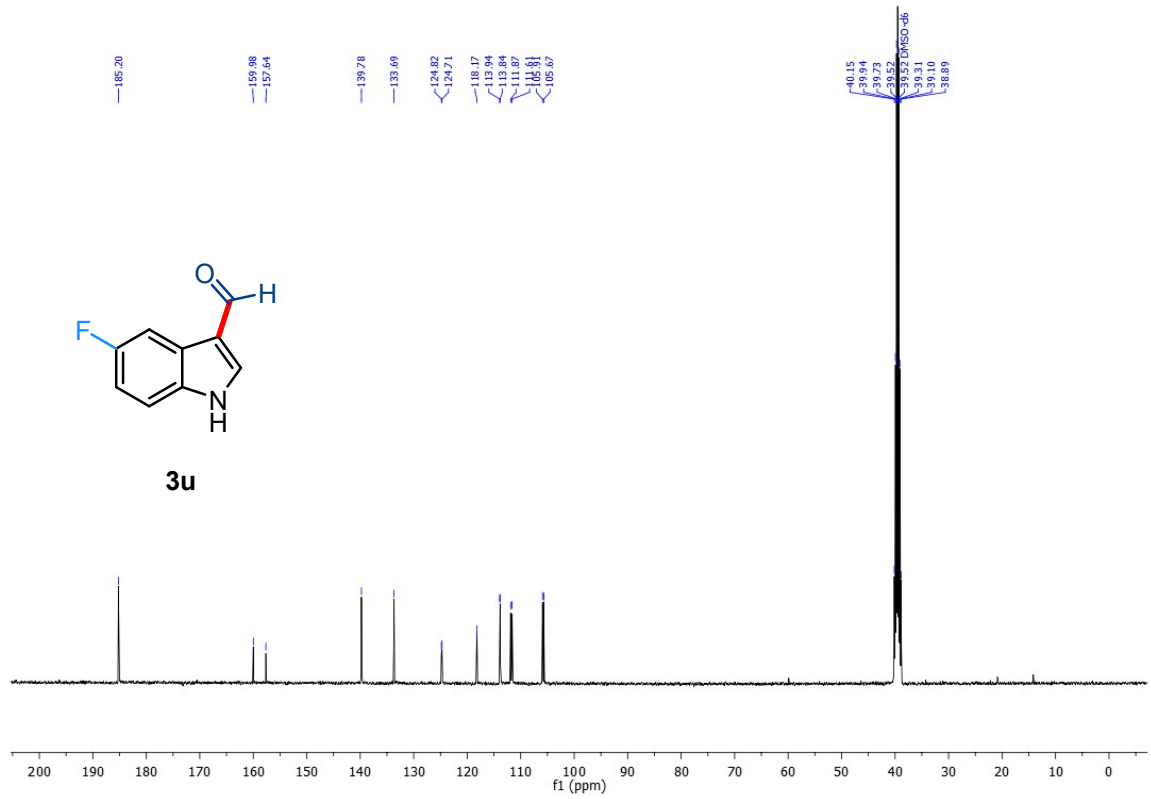


Figure S55: ^{13}C NMR of product **3u** in DMSO-d6 (101 MHz)

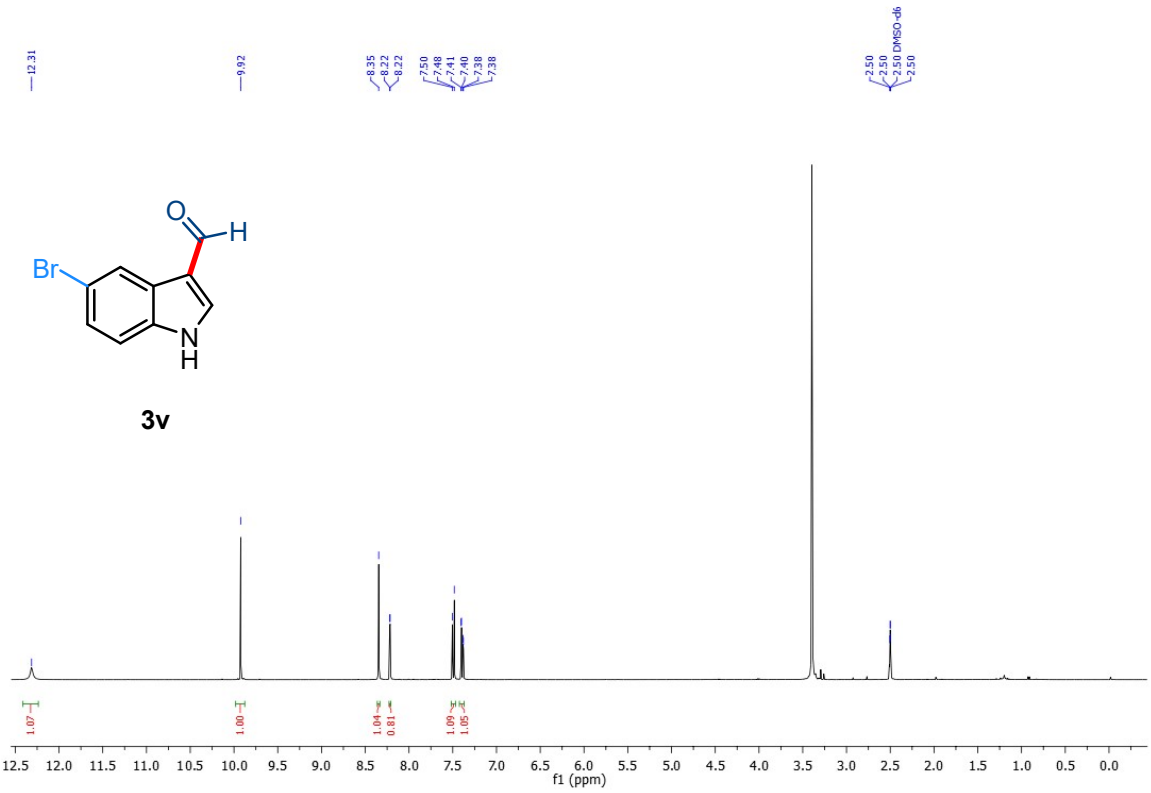


Figure S56: ^{1}H NMR of product **3v** in DMSO-d_6 (400 MHz)

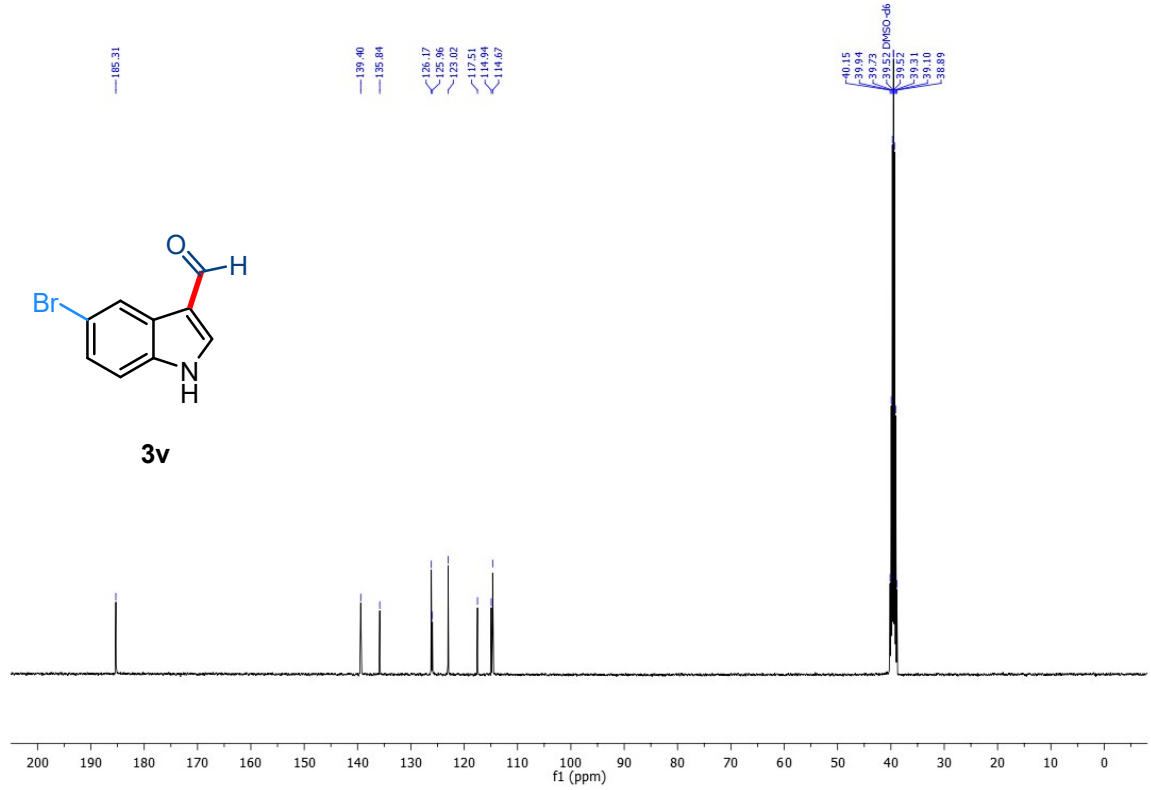


Figure S57: ^{13}C NMR of product **3v** in DMSO-d6 (101 MHz)

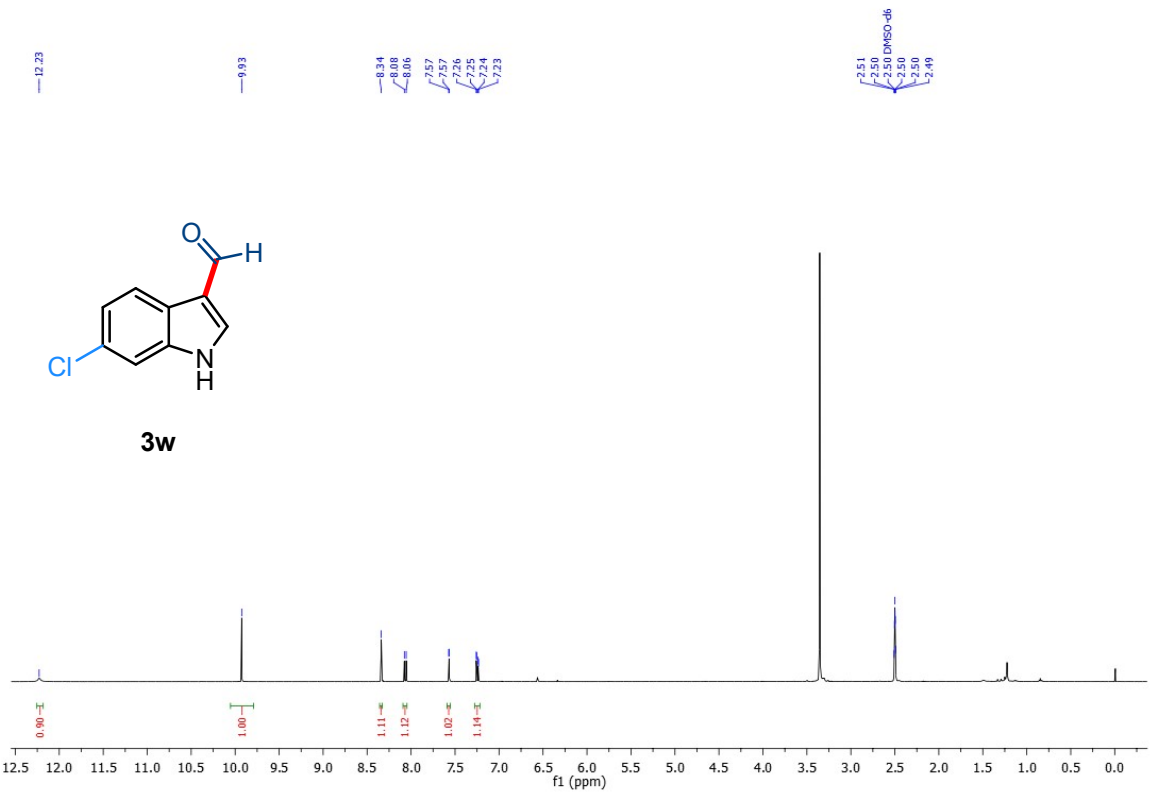


Figure S58: ^{1}H NMR of product **3w** in DMSO-d_6 (400 MHz)

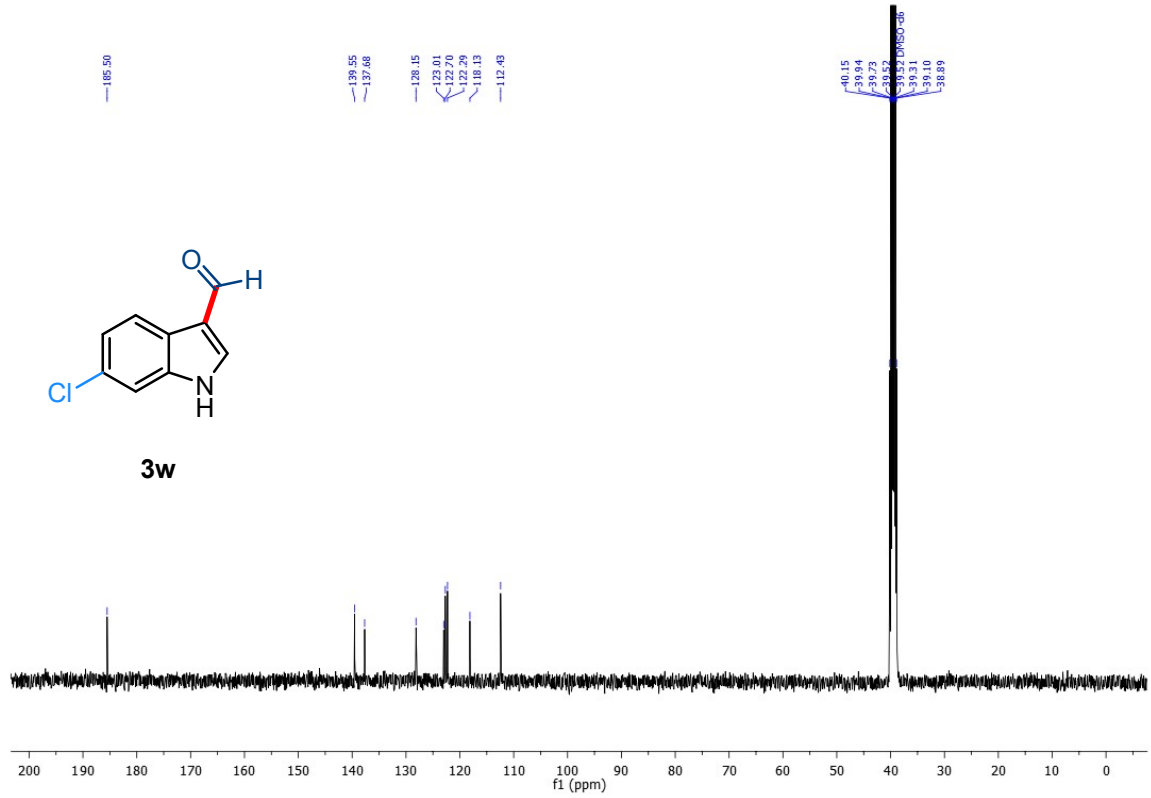


Figure S59: ^{13}C NMR of product **3w** in DMSO-d6 (101 MHz)

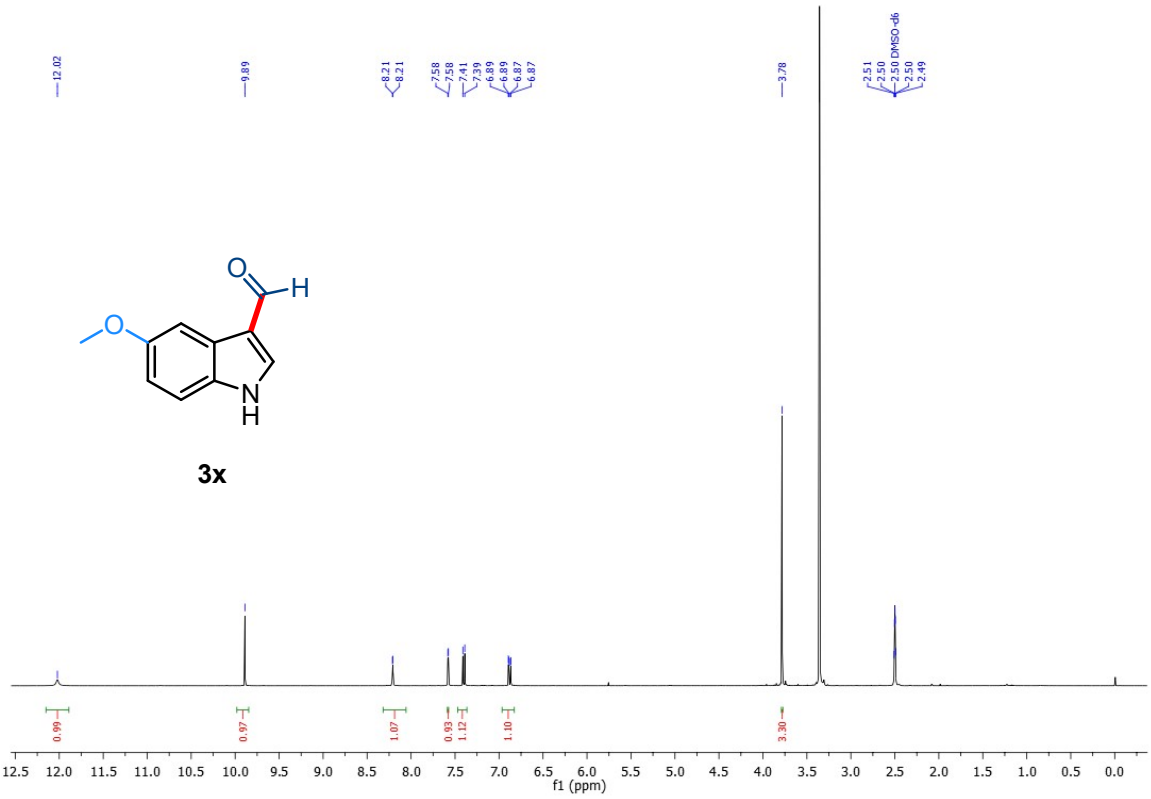


Figure S60: ^{1}H NMR of product **3x** in DMSO-d_6 (400 MHz)

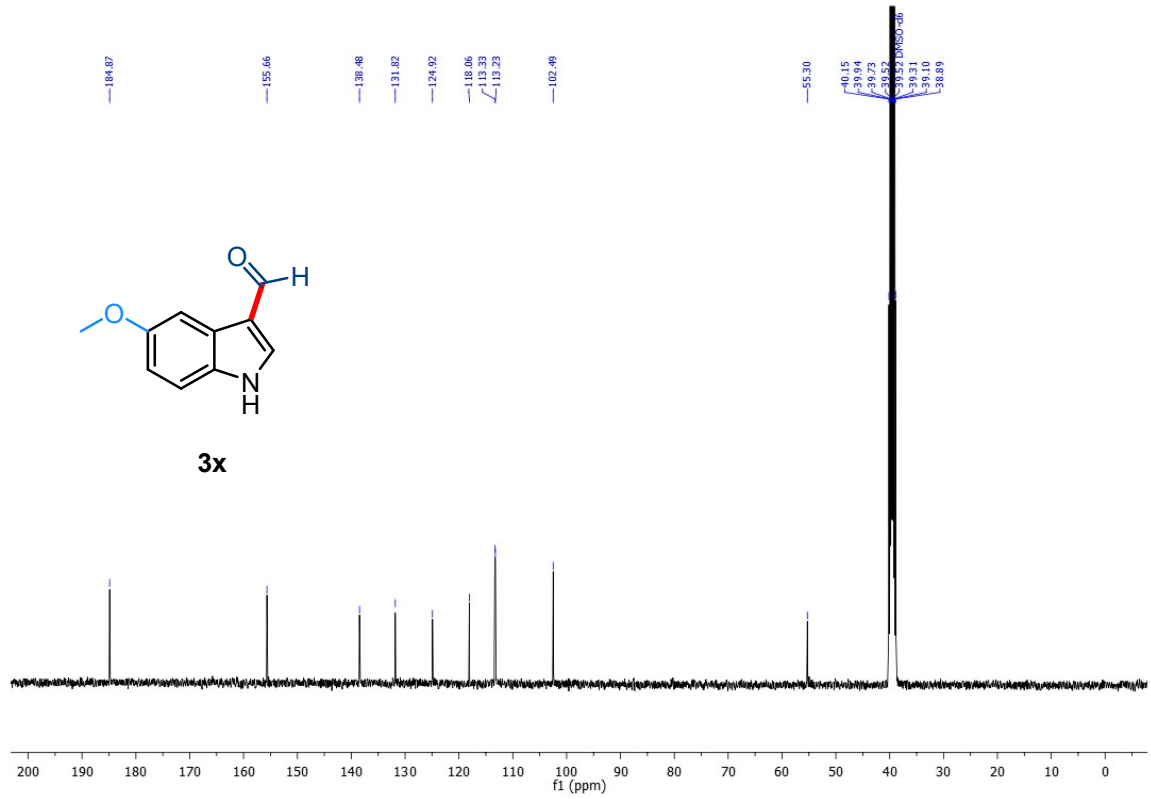


Figure S61: ^{13}C NMR of product **3x** in DMSO-d6 (101 MHz)

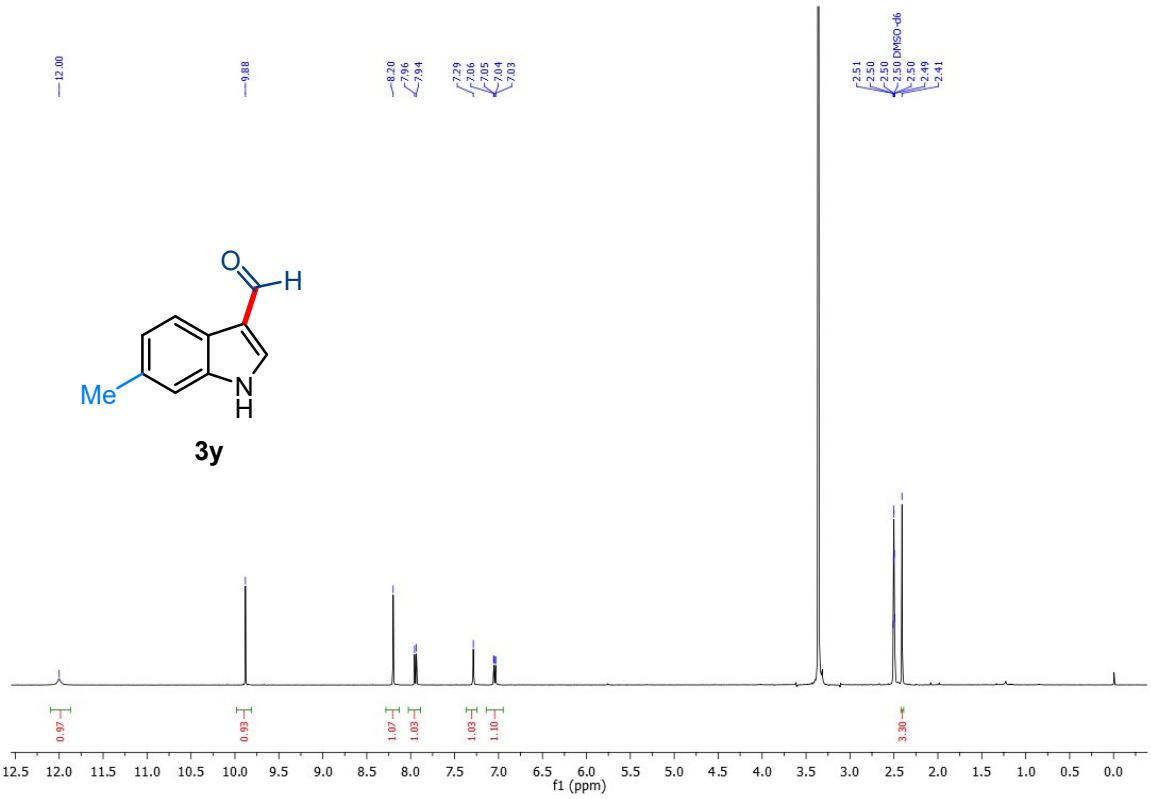


Figure S62: ^{1}H NMR of product **3y** in DMSO-d_6 (400 MHz)

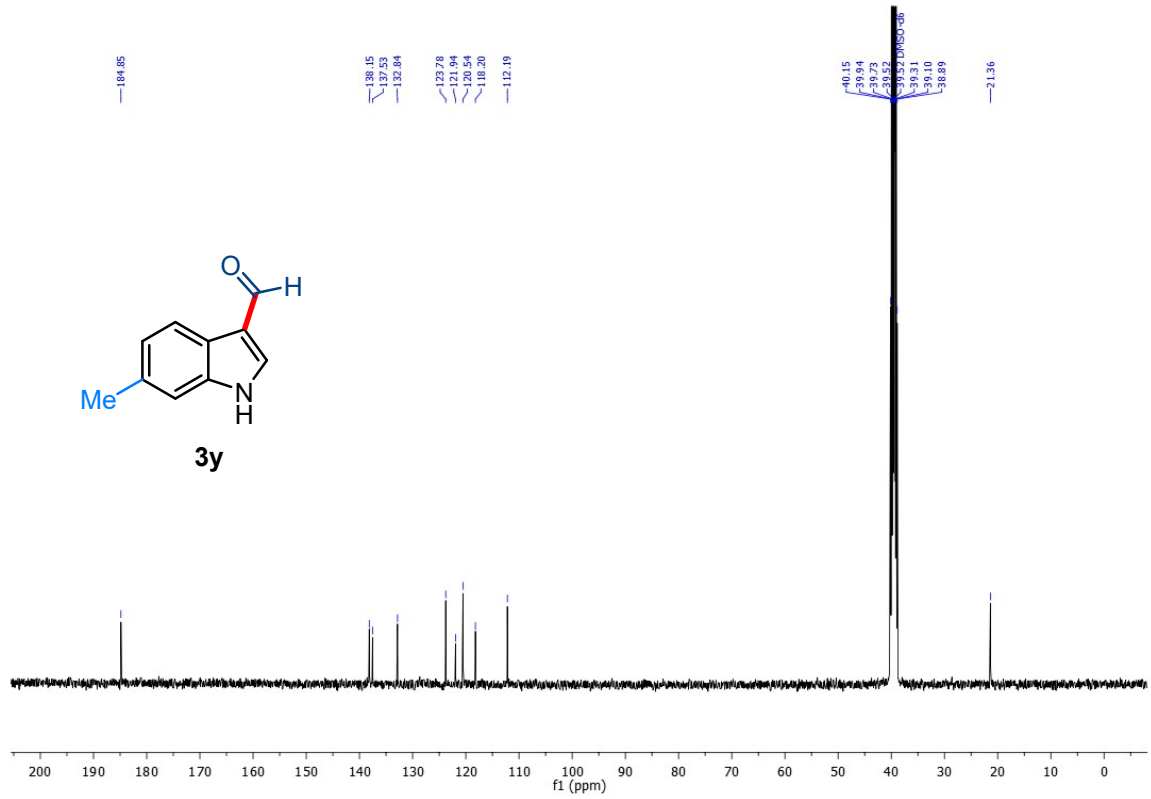


Figure S63: ^{13}C NMR of product **3y** in DMSO-d6 (101 MHz)

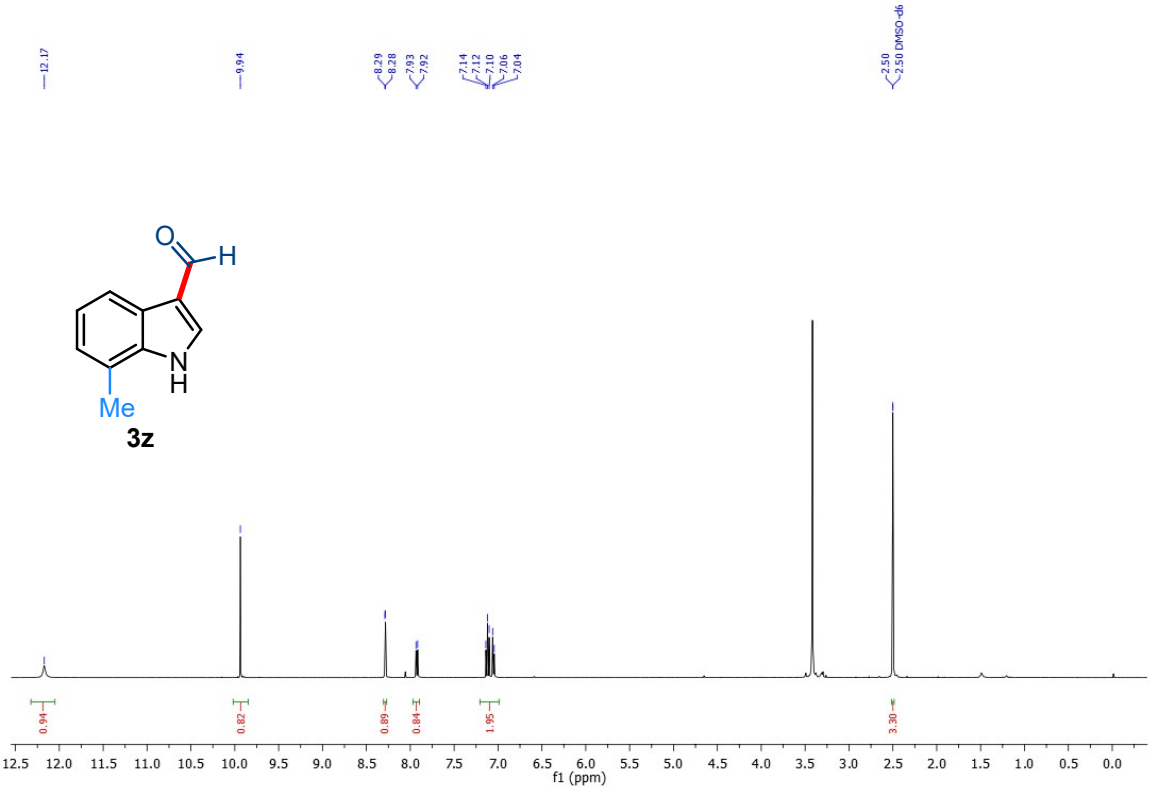


Figure S64: ^{1}H NMR of product **3z** in DMSO-d_6 (400 MHz)

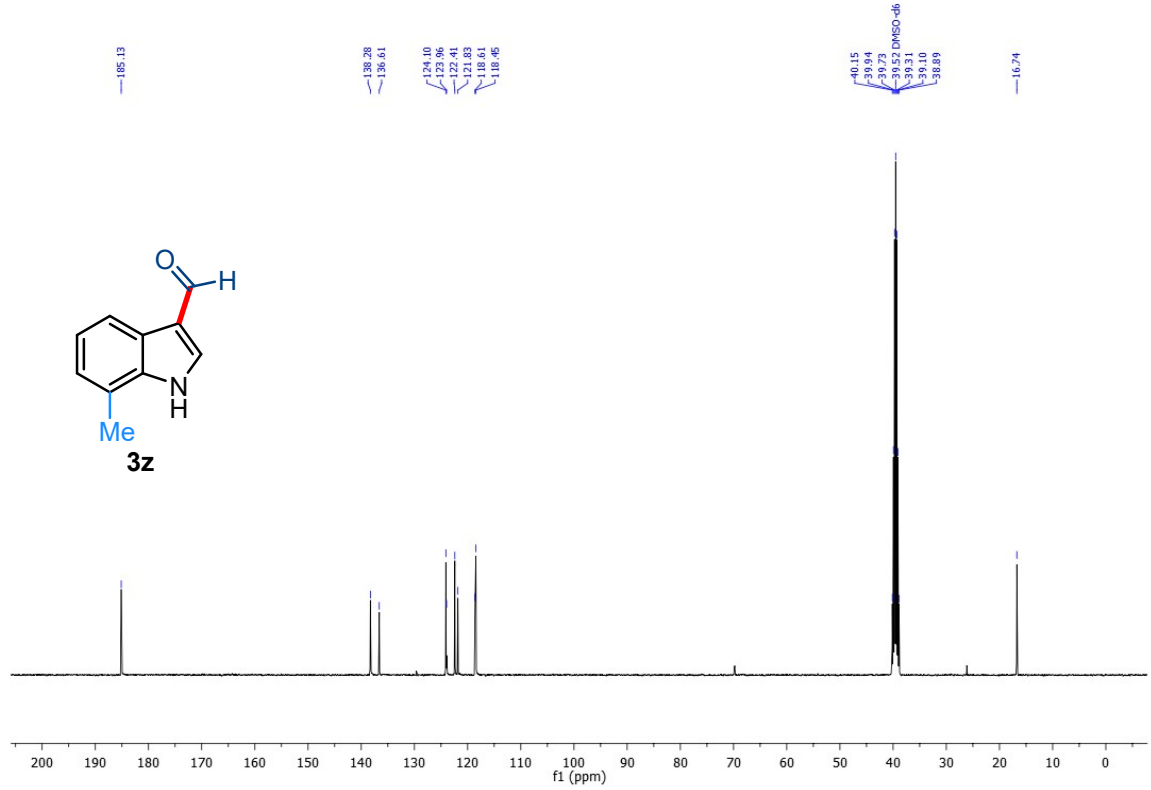


Figure S65: ^{13}C NMR of product **3z** in DMSO-d6 (101 MHz)

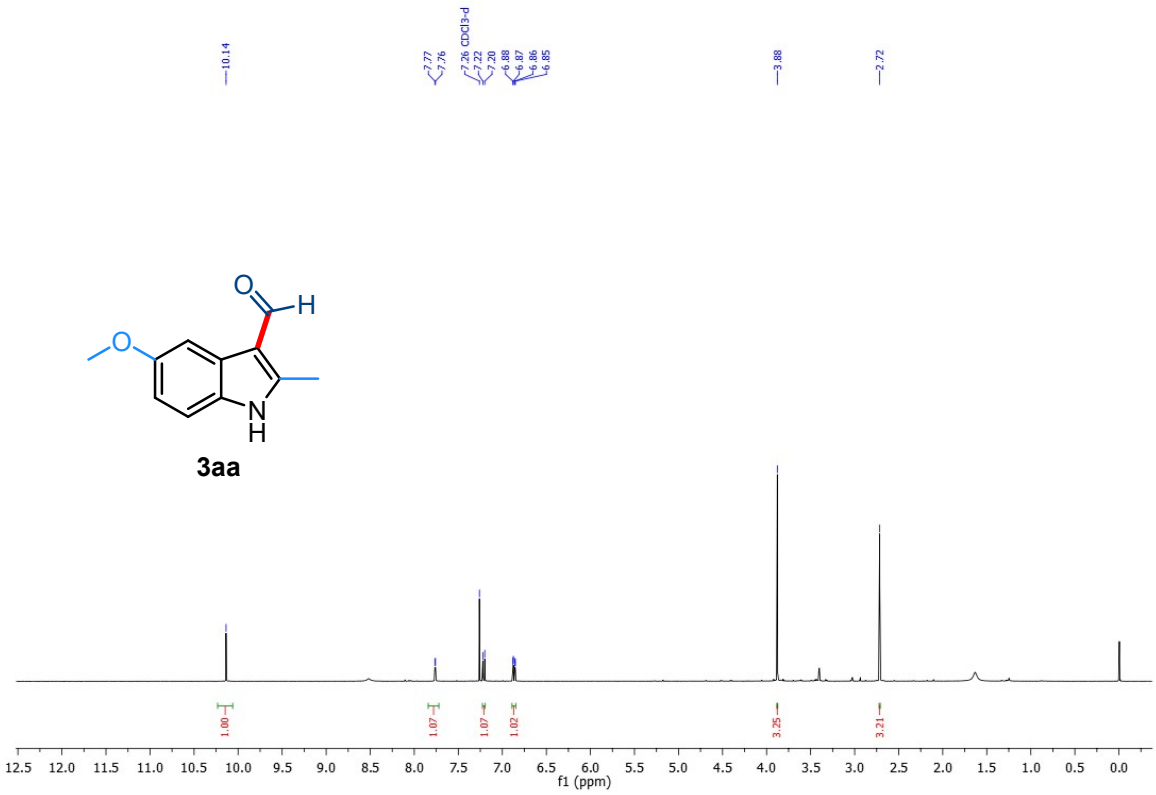


Figure S66: ^{1}H NMR of product **3aa** in $CDCl_3$-d (400 MHz)

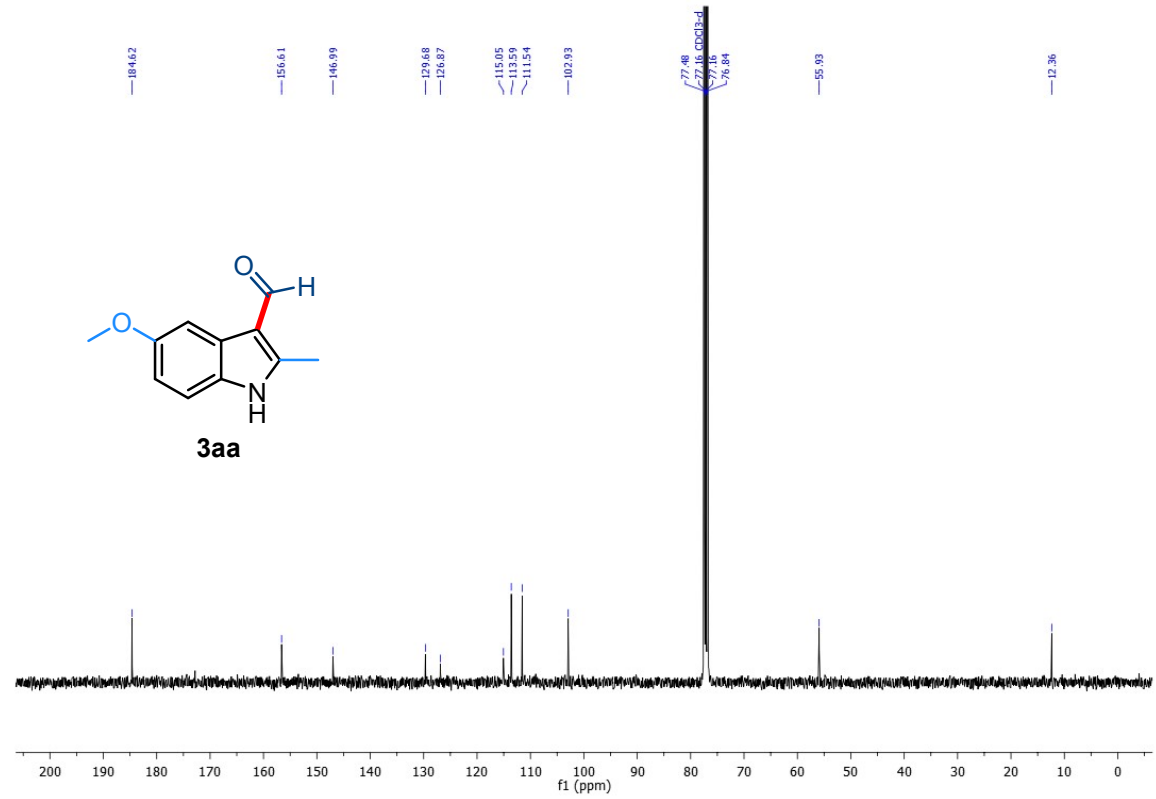


Figure S67: ^{13}C NMR of product **3aa** in $CDCl_3$-d (101 MHz)

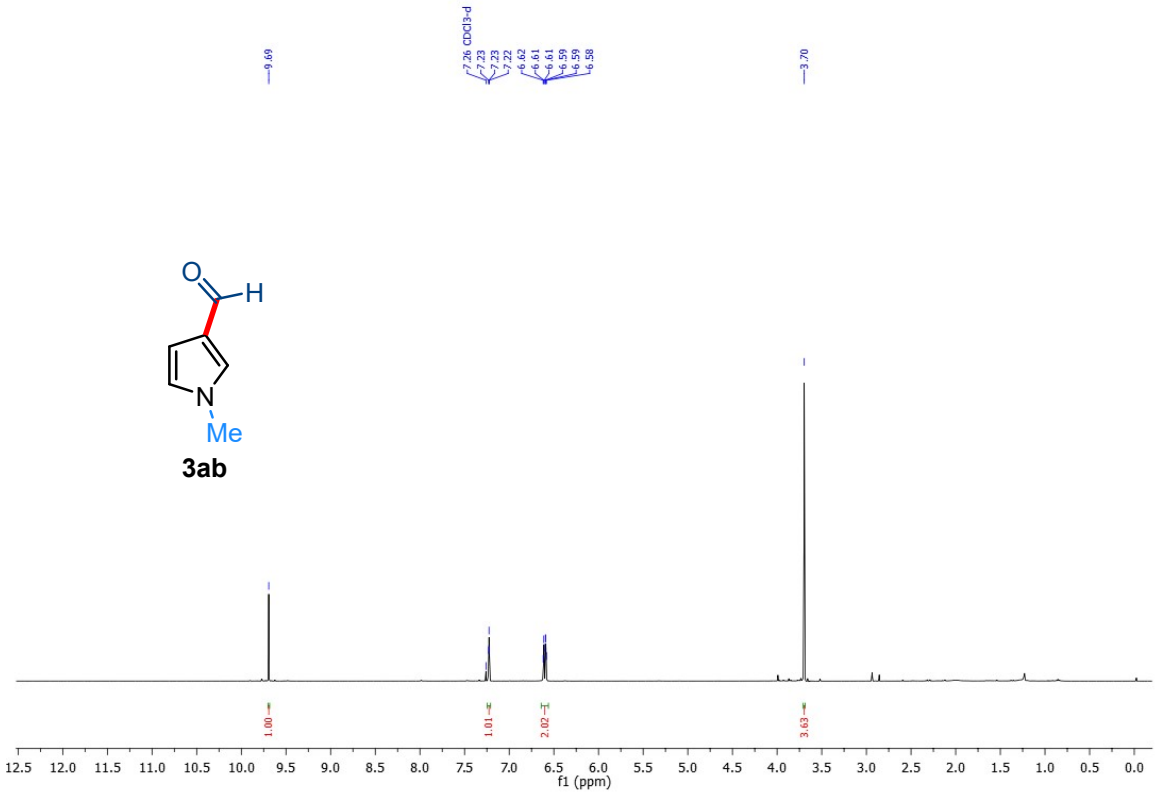


Figure S68: ^{1}H NMR of product **3ab** in $CDCl_3$-d (400 MHz)

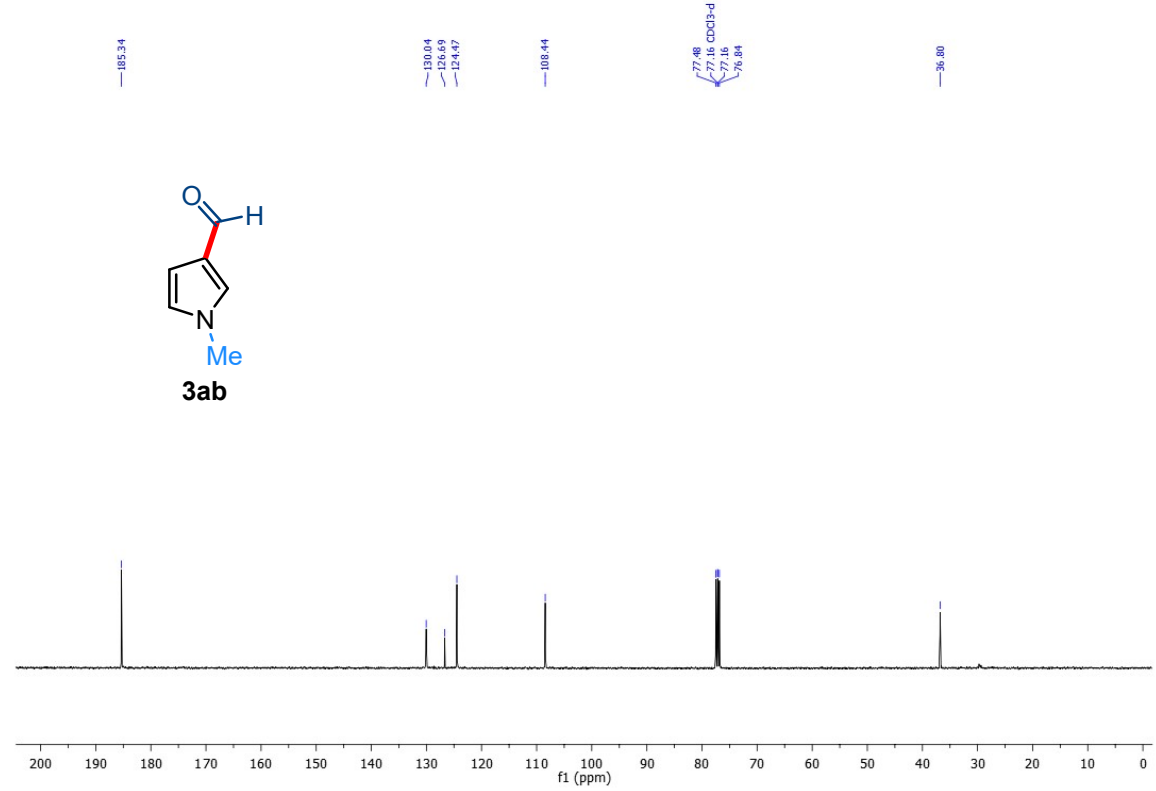


Figure S69: ^{13}C NMR of product **3ab** in $CDCl_3$-d (101 MHz)

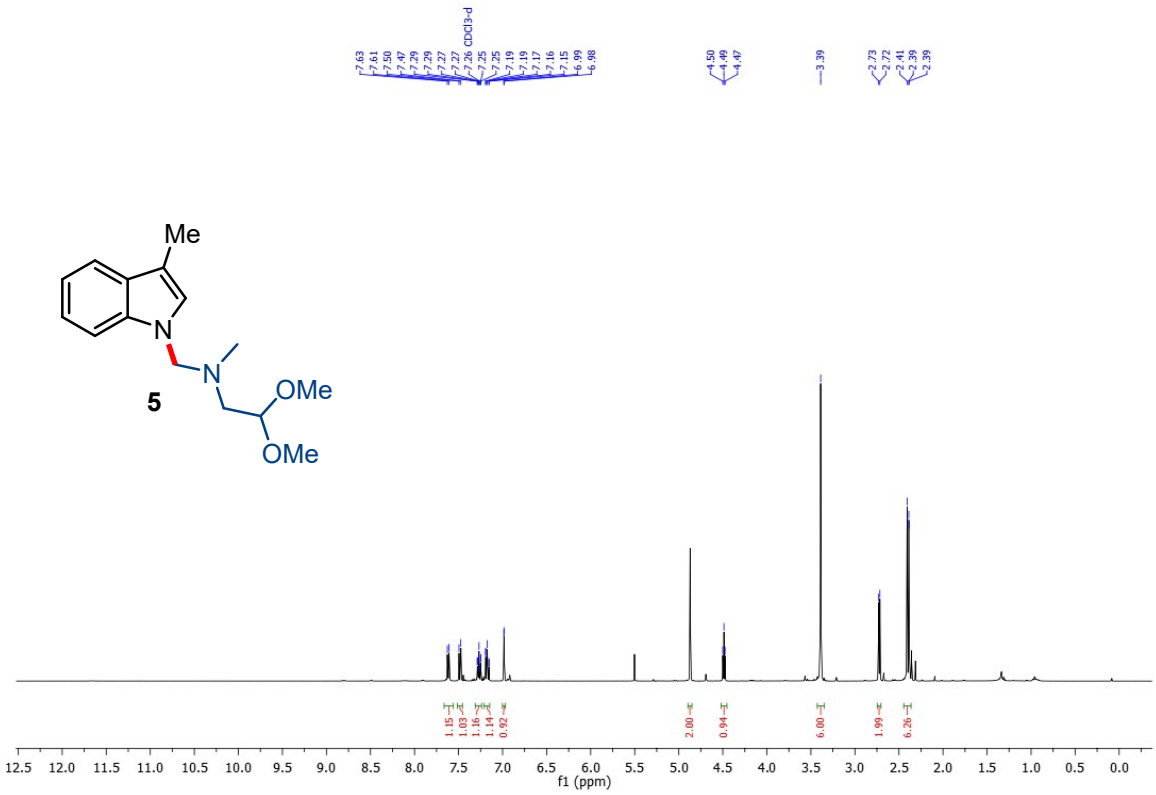


Figure S70: ^{1}H NMR of product **5** in $CDCl_3$-d (400 MHz)

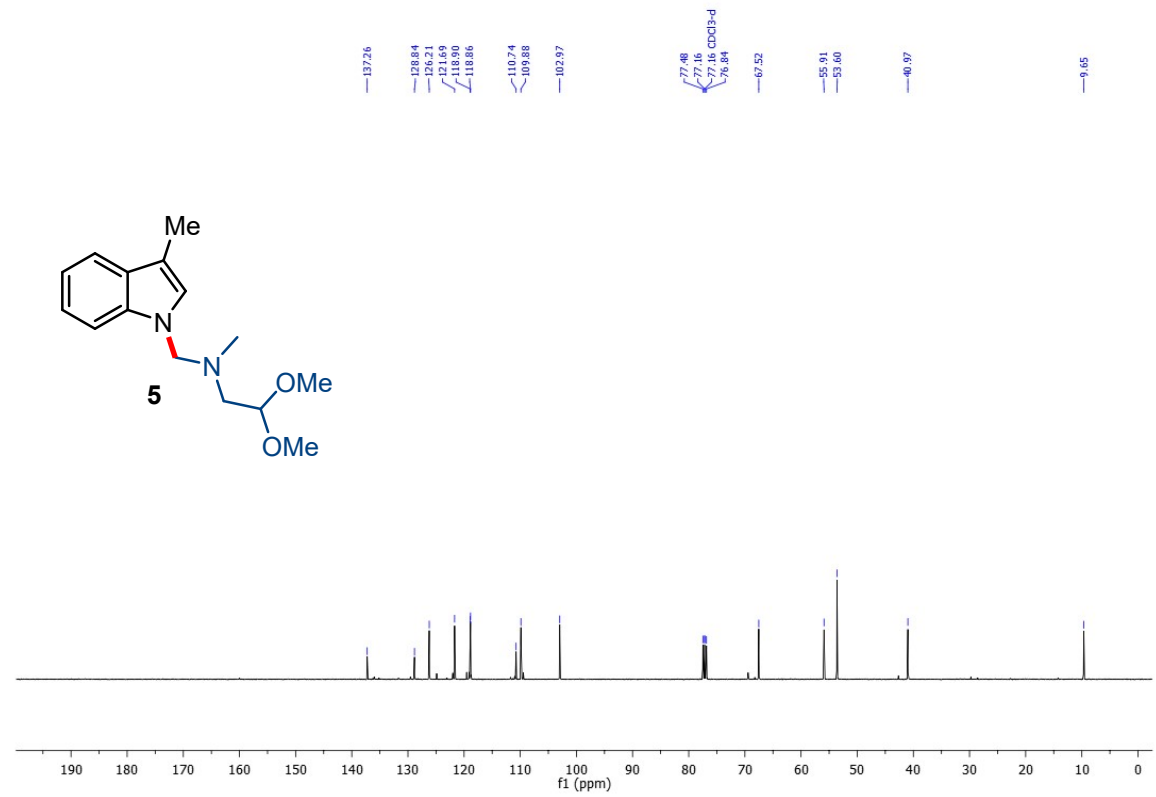


Figure S71: ^{13}C NMR of product **5** in $CDCl_3$-d (101 MHz)