Supporting Information

Stable and recyclable Z-scheme g-C_3N_4/rGO/$BiVO_4$ heterojunction photocatalyst for site-selective C-3 formylation of indoles with methanol as a formyl source under visible light

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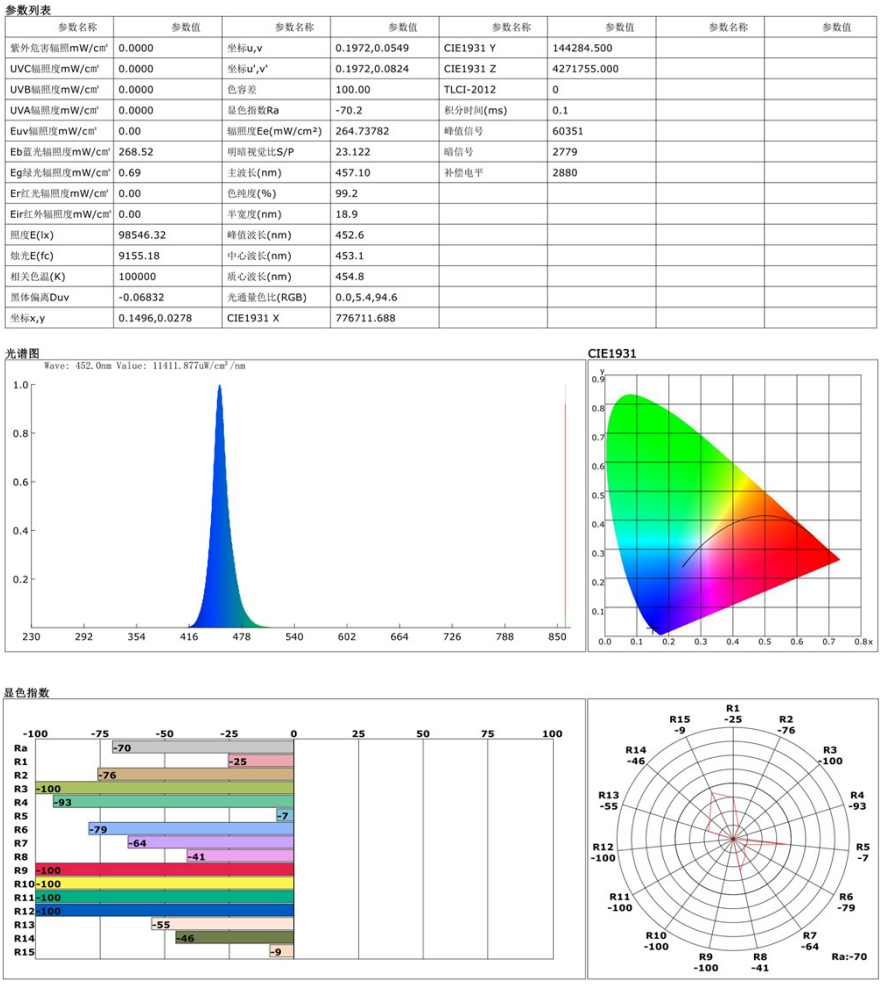
1. The spectrum of our lamp and the visible light irradiation instrument

Photocatalytic reaction was implemented under visible light irradiation by a blue LED at room temperature. In this reaction system, RLH-18 8-position Photo Reaction System manufactured by Beijing RogerTech Ltd. was used. In this photo reactor, eight 10 W blue LEDs were equipped. The blue LED's energy peak wavelength is 452.6 nm, peak width at half-height is 18.9 nm, irradiance/10 W is 264.7 mW/cm^2. The reaction vessel is glass reaction tube and the distance between it and the lamp is 15 mm, no filter applied.



参数列表

参数名称	参数值	参数名称	参数值	参数名称	参数值	参数名称	参数值
紫外危害辐照mW/cm²	0.0000	坐标u,v	0.1972,0.0549	CIE1931 Y	144284.500		
UVC辐照度mW/cm²	0.0000	坐标u',v'	0.1972,0.0824	CIE1931 Z	4271755.000		
UVB辐照度mW/cm²	0.0000	色容差	100.00	TLCI-2012	0		
UVA辐照度mW/cm²	0.0000	显色指数Ra	-70.2	积分时间(ms)	0.1		
Euv辐照度mW/cm²	0.00	辐照度Ee(mW/cm²)	264.73782	峰值信号	60351		
Eb蓝光辐照度mW/cm²	268.52	明暗视觉比S/P	23.122	暗信号	2779		
Eg绿光辐照度mW/cm²	0.69	主波长(nm)	457.10	补偿电平	2880		
Er红光辐照度mW/cm²	0.00	色纯度(%)	99.2				
Eir红外辐照度mW/cm²	0.00	半宽度(nm)	18.9				
照度E(lx)	98546.32	峰值波长(nm)	452.6				
烛光E(fc)	9155.18	中心波长(nm)	453.1				
相关色温(K)	100000	质心波长(nm)	454.8				
黑体偏离Duv	-0.06832	光通量色比(RGB)	0.0,5.4,94.6				
坐标x,y	0.1496,0.0278	CIE1931 X	776711.688				

Fig. S1 The spectrum of light source (blue LED).

Fig. S2 The visible light irradiation instrument.

2. Experimental procedures

2.1. Materials

Substituted indoles are all known compounds and synthesized according to the reported method. The other chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

2.2. Preparation of CN nanosheets, BVO, rGO, and rGO/CN binary composite

The CN sample was prepared according to the reported literature.[1] The CN was synthesized by thermal treatment of 10 g urea in a crucible with a cover under ambient pressure in air. After drying at 80 °C for 24 h, the precursor was heated to 550 °C at a heating rate of 2.3 °C min^{-1} in a tube furnace for 4 h in air. The resulting final light yellow powder was washed with nitric acid (0.1 M) and distilled water to remove any residual alkaline species (e.g. ammonia) adsorbed on the sample surface. The CN power was obtained by vacuum drying at 80 °C for 24 h.

The BVO was synthesized according to a previous work.[2] Specifically, 1.08 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ and 1.08 mmol of NH_4VO_3 were dissolved into 20 mL of HNO_3 solution (2 M) and 20 mL of $NH_3 \cdot H_2O$ solution (2 M), separately. Then, 0.2 g

of sodium dodecyl sulfonate (SDS) dissolved in water was added to the $Bi(NO_3)_3$ solution. Subsequently, the $Bi(NO_3)_3$ solution was added to the NH_4VO_3 solution drop by drop with constant stirring for 30 min. And then, using the $NH_3 \cdot H_2O$ solution adjusted the pH of the mixed solution to 7, and the mixture was persisted in stirring for 2 h. Nextly, the obtained solution was transferred into a 100 mL Teflonlined stainless steel autoclave and maintained at 180 °C for 24 h. After that, the stainless autoclave was cooled to room temperature naturally. The obtained product was collected and washed three times with deionized water and absolute ethanol to remove the adsorbed surfactant on BVO surfaces. Finally, the BVO power was obtained by vacuum drying at 80 °C for 8 h.

The GO was prepared according to a improved Hummers' method.[3] A mixture of concentrated H_2SO_4/H_3PO_4 (43.2 mL/4.8 mL) was added to graphite powder (2.0 g) with magnetic stirring below 5 °C for 30 min. Then, $KMnO_4$ (6.0 g) was added extremely slowly to above mixture with magnetic stirring below 5 °C for 2 h. The reaction was warmed to 39 °C and maintained for 2.5 h with magnetic stirring. Nextly, the reaction was warmed to 60 °C, and deionized water (98 mL) was added slowly. The reaction was warmed to 98 °C, and maintained for 2.5 h with magnetic stirring. Subsequently, 30% H_2O_2 (120 mL) was added to the mixture, the heating was removed and the reaction was cooled to room temperature naturally. After that, the reaction mixture was centrifuged (4000 rpm, 20min) and washed three times with HCl (0.5 M). The crude product was washed with deionized water until the sulfate was completely removed. Finally, the GO samlpe was obtained by vacuum drying at 60 °C for 12 h.

The rGO was obtained from GO (0.5 g) and $NaBH_4$ (5.0 g) in deionized water by refluxing for 8 h. The crude product was washed three times with deionized water. Finally, the rGO sample was obtained by vacuum drying at 60 °C for 12 h.

The CN/rGO binary composite was fabricated by a hydrothermal method.[4] In a typical process, 5.0 mg of rGO and 100.0 mg of CN powder were dispersed in 100 mL of water, and the mixture was sonicated for 1 h. The as-obtained dispersion was transferred into a 100 mL Teflonlined stainless steel autoclave and kept at 180 °C for 24 h. The stainless autoclave was cooled to room temperature naturally. The as-

obtained crude product was collected, and washed three times with deionized water and absolute ethanol to remove the adsorbed surfactant on CN/rGO surfaces. Finally, the CN/rGO binary composite was obtained by vacuum drying at 60 °C for 12 h.

2.3. Preparation of rGO/BVO, CN/BVO binary composites, and x wt% CN/rGO/BVO ternary composites

The 30% CN/rGO/BVO ternary composite was prepared by a hydrothermal method.[4] Specifically, 1.08 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ and 1.08 mmol of NH_4VO_3 were dissolved into 20 mL of HNO_3 solution (2 M) and 20 mL of $NH_3 \cdot H_2O$ solution (2 M), separately. Then, 0.2 g of sodium dodecyl sulfonate (SDS) dissolved in water was added to the $Bi(NO_3)_3$ solution. Subsequently, the $Bi(NO_3)_3$ solution was added to the NH_4VO_3 solution drop by drop with constant stirring for 30 min. And then, using the $NH_3 \cdot H_2O$ solution adjusted the pH of the mixed solution to 7, and the mixture was persisted in stirring for 2 h. Nextly, 5.0 mg of rGO and 100.0 mg of CN powder were added to the above mixture with the help of ultrasonic dispersion for 1 h. The as-obtained dispersion was transferred into a 100 mL Teflonlined stainless steel autoclave and kept at 180 °C for 24 h. After that, the stainless autoclave was cooled to room temperature naturally. The as-obtained product was collected and washed three times with deionized water and absolute ethanol to remove the adsorbed surfactant on CN/rGO/BVO surfaces. Finally, the 30% CN/rGO/BVO ternary composite was obtained by vacuum drying at 60 °C for 12 h. In addition, rGO/BVO or CN/BVO binary composite was fabricated according to similar procedure of 30% CN/rGO/BVO composite without the addition of CN or rGO. According to the analogous procedure of 30% CN/rGO/BVO composite, 10 wt% of CN/rGO in BVO and 50 wt% of CN/rGO in BVO with different weight of CN/rGO (33.4 mg/1.7 mg and 166.6 mg/8.3 mg) were obtained and denoted as 10% CN/rGO/BVO and 50% CN/rGO/BVO, respectively.

2.4. Characterization

X-ray diffraction (XRD) was performed on a Bruker D8 X-ray diffractometer with

a Cu-Kα radiation in the 2θ range of 5-80°. The morphology, sizes of the obtained photocatalysts and elemental mapping images were measured using a Hitachi Regulus SU8010 scanning electron microscopy (SEM) at 15 kV. The high-resolution transmission electron microscopy (HRTEM) images of the as-synthesized materials were recorded on a JEOL JEM-2100 transmission electron microscope at 200 kV. The X-ray photoelectron spectroscopy (XPS) was measured on a Thermo Fisher Scientific ESCALAB 250Xi photoelectron spectrometer. All of the binding energies of all elements were calibrated by the C 1s peak at 284.8 eV. UV–vis diffuse reflectance spectra (DRS) of the as-obtained photocatalysts were measured using a Shimadzu UV-3600 spectrophotometer during 200-800 nm at room temperature. CHI 660E electrochemical instrument was used to perform the photocurrent with a three-electrode quartz cells (Counter electrode: Pt wire; Reference electrode: Ag/AgCl; Working electrode: photocatalysts coated ITO glass) and 300 W Xe lamp. The photoluminescence spectra (PL) were obtained on a Hitachi F-4500 fluorescence spectrophotometer (excitation wavelength: 325 nm). The H_2 of was detected by a gas chromatograph (SHIMADZU GC-2014 C) and analyzed by a thermal conductivity detector (TCD, 5A molecular sieve column) with column diameter (2 m × 4 mm) and argon as the carrier gas. The raman spectra (Fig. S3) was observed on Horiba LabRAM HR Evolution raman spectrometer with a 532 nm laser.

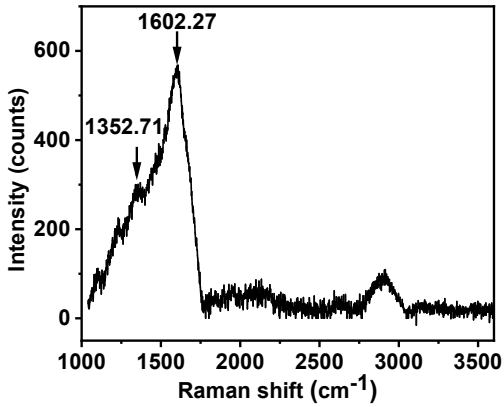


Fig. S3 The Raman spectrum of 30% CN/rGO/BVO ternary composite.

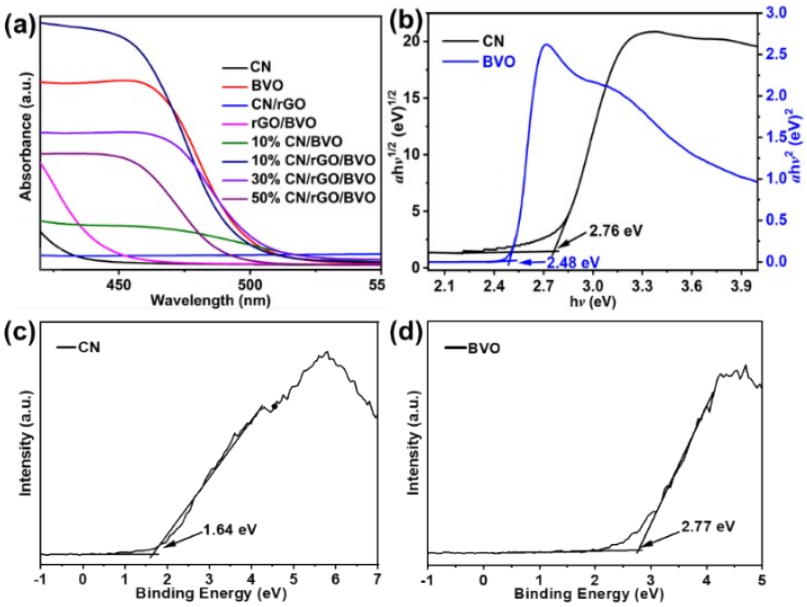


Fig. S4 (a) UV-vis DRS of the as-synthesized different specimens, (b) the band gap of CN and BVO, (c) and (d) the valence band XPS plots of CN and BVO.

^{1}H and ^{13}C NMR spectra of the obtained organic compounds were recorded on a Varian Inova-400 or Bruker-400 (400 MHz and 100 MHz, respectively) spectrometer. ^{1}H and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, $CDCl_3$(δ(^{1}H), 7.26 ppm; δ(^{13}C), 77.16 ppm) or DMSO-d_6(δ(^{1}H), 2.50 ppm; δ(^{13}C), 39.52 ppm). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The HRMS analysis was obtained on Thermo Scientific Q-Exactive Focus mass spectrometer. The melting point was recorded on BÜCHI (M-560) and uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel.

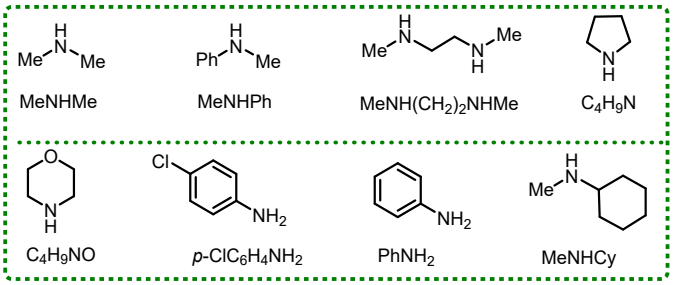
2.5. Optimization of the photocatalytic reaction conditions

Table S1 Different photocatalysts and dosage of photocatalyst screening.[a]

Entry	Photocatalyst	Yield (%)[b]
1	CN (5 mg)	46
2	BVO (5 mg)	25
3	CN/rGO (5 mg)	36
4	rGO/BVO (5 mg)	48
5	10 % CN/BVO (5 mg)	55
6	10 % CN/rGO/BVO (5 mg)	65
7	30 % CN/rGO/BVO (5 mg)	72
8	50 % CN/rGO/BVO (5 mg)	59
9	30 % CN/rGO/BVO (8 mg)	82
10	30 % CN/rGO/BVO (10 mg)	75
11	30 % CN/rGO/BVO (12 mg)	51
12	30 % CN/rGO/BVO (14 mg)	56
13	30 % CN/rGO/BVO (16 mg)	48

[a]Reaction conditions: **1a** (0.4 mmol), MeNHCy (0.4 mmol), AcOH (0.8 mmol), photoatalyst, CH_3OH (3 mL), 10 W blue LED, room temperature, 58 h. [b]Isolated yields.

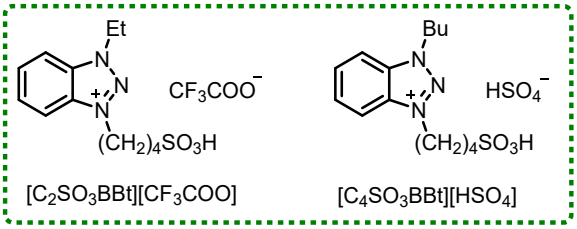
Table S2 Different amines and the dosage of amine screening.[a]



Entry	Amine	Yield (%)[b]
1	MeNHMe (1.0 equiv.)	63/48[c]
2[d]	MeNHPh (1.0 equiv.)	n.r.
3	$MeNH(CH_2)_2NHMe$ (1.0 equiv.)	9
4	C_4H_9N (1.0 equiv.)	25
5	C_4H_9NO (1.0 equiv.)	25
6	*p*-$ClC_6H_4NH_2$ (1.0 equiv.)	trace
7	$PhNH_2$ (1.0 equiv.)	trace
8	MeNHCy (0.05 equiv.)	23
9	MeNHCy (0.1 equiv.)	26
10	MeNHCy (0.2 equiv.)	41
11	MeNHCy (0.5 equiv.)	54
12	MeNHCy (0.8 equiv.)	57
13	MeNHCy (1.2 equiv.)	63
14	MeNHCy (2.0 equiv.)	36

[a]Reaction conditions: **1a** (0.4 mmol), amine, AcOH (0.8 mmol), 30 % CN/rGO/BVO (5 mg), CH_3OH (3 mL), 10 W blue LED, room temperature, 58 h. [b]Isolated yields. [c]48 h. [d]n.r. = no reaction.

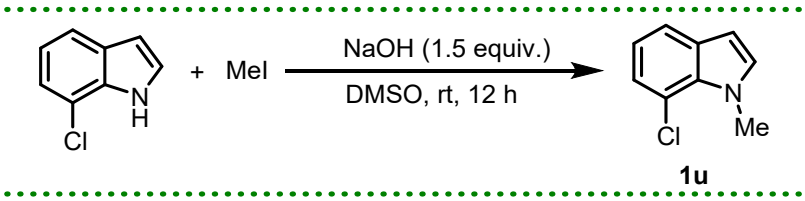
Table S3 Different acids and the dosage of acid screening.[a]



Entry	Acid	Yield (%)[b]
1	$[C_2SO_3BBt][CF_3COO]$ (2 equiv.)	trace
2	$[C_4SO_3BBt][HSO_4]$ (2.0 equiv.)	45
3	H_3PO_4 (2.0 equiv.)	15
4[c]	HCl (2.0 equiv.)	n.d.
5[c]	H_2SO_4 (2.0 equiv.)	n.d.
6	HCOOH (2.0 equiv.)	27
7	PhCOOH (2.0 equiv.)	41
8	AcOH (1.0 equiv.)	41
9	AcOH (1.2 equiv.)	34
10	AcOH (1.4 equiv.)	45
11	AcOH (1.6 equiv.)	51

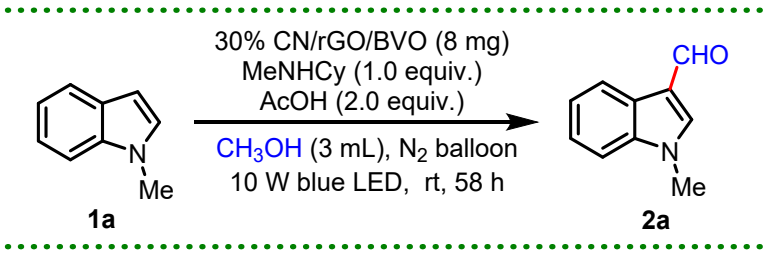
[a]Reaction conditions: **1a** (0.4 mmol), MeNHCy (0.4 mmol), acid, 30 % CN/rGO/BVO (5 mg), CH_3OH (3 mL), 10 W blue LED, room temperature, 58 h. [b]Isolated yields. [c]n.d. = not detected.

2.6. General procedure for synthesis of substrates (taking 1u as an example)



According to a literature procedure,[5] 7-Chloroindole (758 mg, 5 mmol) and NaOH (300 mg, 7.5 mmol) were dissolved in DMSO (10 mL), and iodomethane (374 μL, 6 mmol) was slowly added to the mixed solution with magnetic stirring at room temperature for 12 h. After the reaction finished, the resulting mixture was extracted with dichloromethane (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 40:1, v/v) to afford the desired product **1u** in 90% yield.

2.7. General procedure for synthesis of products (taking 2a as an example)

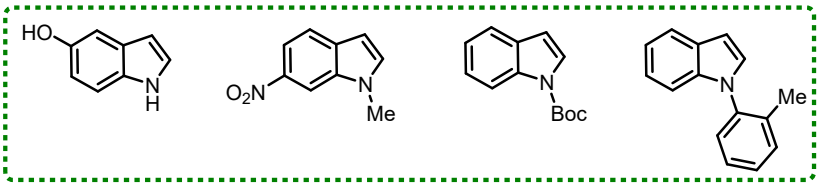


A mixture of 1-methyl-1*H*-indole **1a** (50 μL, 0.4 mmol), 30% CN/rGO/BVO (8 mg), MeNHCy (53 μL, 0.4 mmol), AcOH (48 μL, 0.8 mmol) and CH_3OH (3 mL) was added to a 10 mL reaction tube. The reaction tube was purged with nitrogen for 5 min to exclude air inside the tube. Then, the mixture was stirred at room temperature for 58 h under 10 W blue LED irradiation with N_2 atmosphere. After the reaction finished, the photocatalyst was separated by centrifugation (4,000 rpm, 3 min) and washed with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5:1, v/v) to

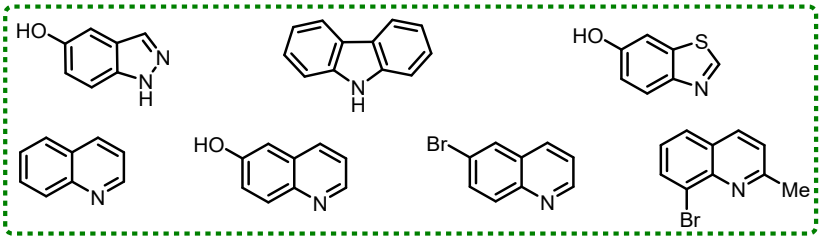
afford the desired product **2a** in 82% yield.

2.8. Unreacted substrates

Unreacted indole compounds

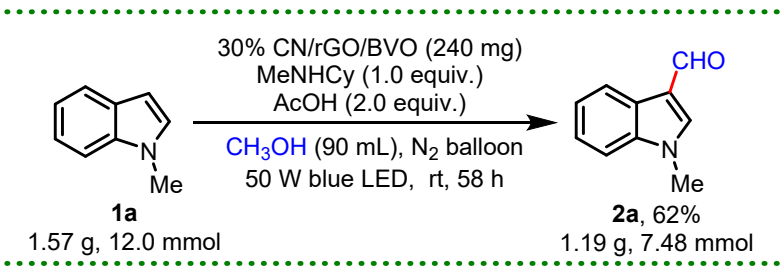


Unreacted heterocyclic compounds



3. Gram-scale reaction and application of present work

3.1. Gram-scale reaction

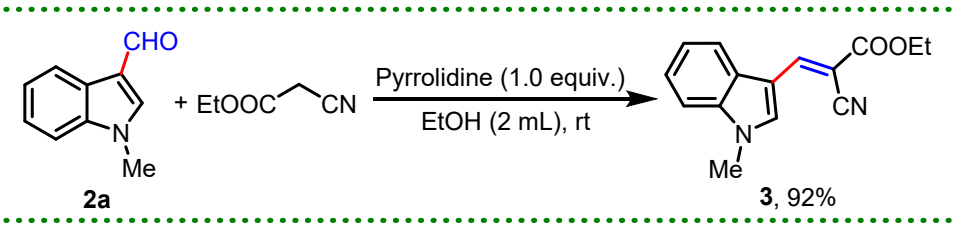


A mixture of 1-methyl-1*H*-indole **1a** (1500 μL, 12.0 mmol), 30% CN/rGO/BVO (240 mg), MeNHCy (1590 μL, 12.0 mmol), AcOH (1440 μL, 24.0 mmol) and CH_3OH (90 mL) was added to a 250 mL round bottom flask. The reaction tube was purged with nitrogen for 8 min to exclude air inside the tube. Then, the mixture was stirred at room temperature for 58 h under 50 W blue LED irradiation with N_2 atmosphere. After the reaction finished, most of the reaction solution was evaporated under reduced pressure. Nextly, the photocatalyst was separated by centrifugation (4,000 rpm, 3 min) and washed with EtOAc (5×10 mL). The combined organic phase was extracted with brine

(3×20 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5:1, v/v) to afford the desired product **2a** in 62% yield.

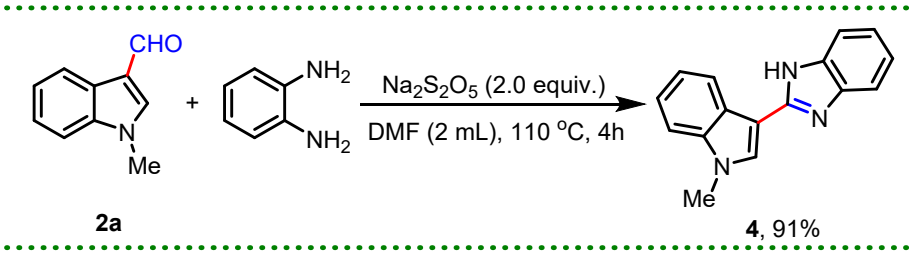
3.2. Application of present work

3.2.1. Procedure for synthesis of product **3** through Knoevenagel condensation reaction



A mixture of 1-methyl-1*H*-indole-3-carbaldehyde **2a** (31.9 mg, 0.2 mmol), ethyl 2-cyanoacetate (32 μL, 0.3 mmol), pyrrolidine (17 μL, 0.2 mmol) and EtOH (2 mL) was added to a 10 mL reaction tube. Then, the mixture was stirred at room temperature for 4 h. After the reaction finished, a large amount of yellow solid was precipitated in the reaction tube, and filtered. After vacuum drying at 60 °C for 12 h, the desired product **3** was gave in 92% yield.

3.2.2. Procedure for synthesis of 2-(1-methyl-1*H*-indol-3-yl)-1*H*-benzo[*d*]imidazole (**4**)

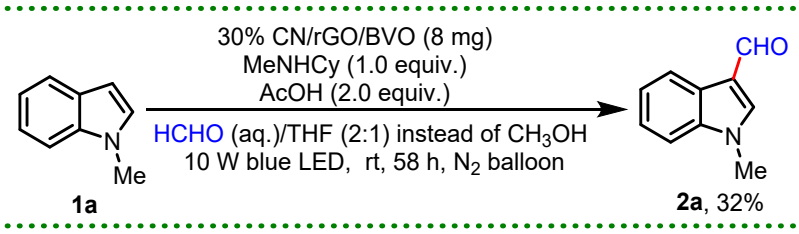


A mixture of 1-methyl-1*H*-indole-3-carbaldehyde 2a (63.8 mg, 0.4 mmol), *o*-phenylenediamine (43.3 mg, 0.4 mmol), $Na_2S_2O_5$ (152.1 mg, 0.8 mmol) and DMF (2 mL) was added to a 10 mL reaction tube. The mixture was stirred at 110 °C for 4 h. After the reaction finished, crushed ice was added to the mixture. Then, a yellow solid precipitated in reaction tube. The resulting mixture was filtered and washed with water

to obtain yellow solid. After vacuum drying at 80 °C for 12 h, the desired product **4** was gave in 91% yield.

4. Mechanistic studies

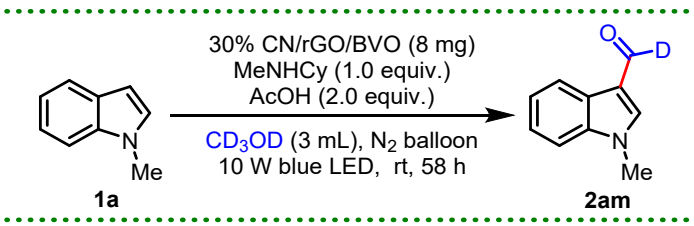
4.1. HCHO (aq.) as a formyl source



A mixture of 1-methyl-1*H*-indole **1a** (50 μL, 0.4 mmol), 30% CN/rGO/BVO (8 mg), MeNHCy (53 μL, 0.4 mmol), AcOH (48 μL, 0.8 mmol), and 37% HCHO (aq.)/THF (v/v = 2:1, 3 mL) was added to a 10 mL reaction tube. The reaction tube was purged with nitrogen for 5 min to exclude air inside the tube. Then, the mixture was stirred at room temperature for 58 h under 10 W blue LED irradiation with N_2 atmosphere. After the reaction finished, the resulting mixture was evaporated under reduced pressure. Nextly, the photocatalyst was separated by centrifugation (4,000 rpm, 3 min) and washed with EtOAc (3×10 mL). The combined organic phase was extracted with brine (3×10 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5:1, v/v).

4.2. Isotope labeling experiments

4.2.1. Isotope labeling experiment with CD_3OD



A mixture of 1-methyl-1*H*-indole **1a** (50 μL, 0.4 mmol), 30% CN/rGO/BVO (8 mg), MeNHCy (53 μL, 0.4 mmol), AcOH (48 μL, 0.8 mmol), and CD_3OD (3 mL) was added to a 10 mL reaction tube. The reaction tube was purged with nitrogen for 5 min

to exclude air inside the tube. Then, the mixture was stirred at room temperature for 58 h under 10 W blue LED irradiation with N_2 atmosphere. After the reaction finished, the photocatalyst was separated by centrifugation (4,000 rpm, 3 min) and washed with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5:1, v/v) to afford the desired product **2am** in 83% yield. Then the products were analyzed by ^{1}H NMR (Fig. S5) and HRMS (Fig. S6). Deuterated ratio of formyl group in **2a** was 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 0.33H), 8.30 (d, J = 6.7 Hz, 1H), 7.65 (s, 1H), 7.36-7.31 (m, 3H), 3.85 (s, 3H). HRMS *m/z* of **2am**: Calcd for $C_{10}H_8DNO$ $[M+H]^+$: 161.0820; Found: 161.0818.

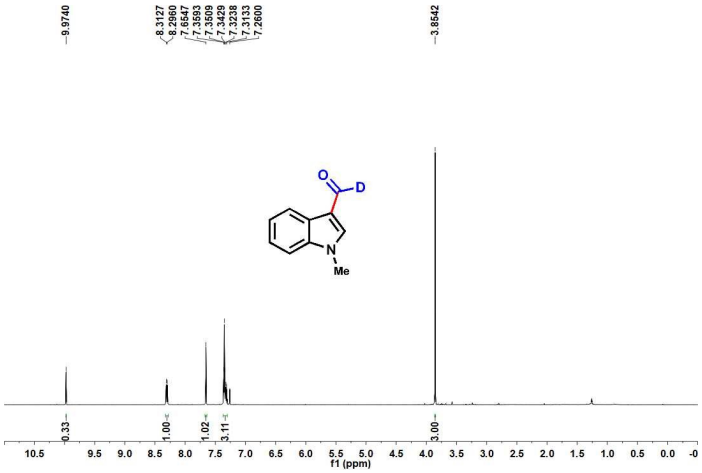


Fig. S5 ^{1}H NMR spectrum of the isotope labeling experiment with CD_3OD.

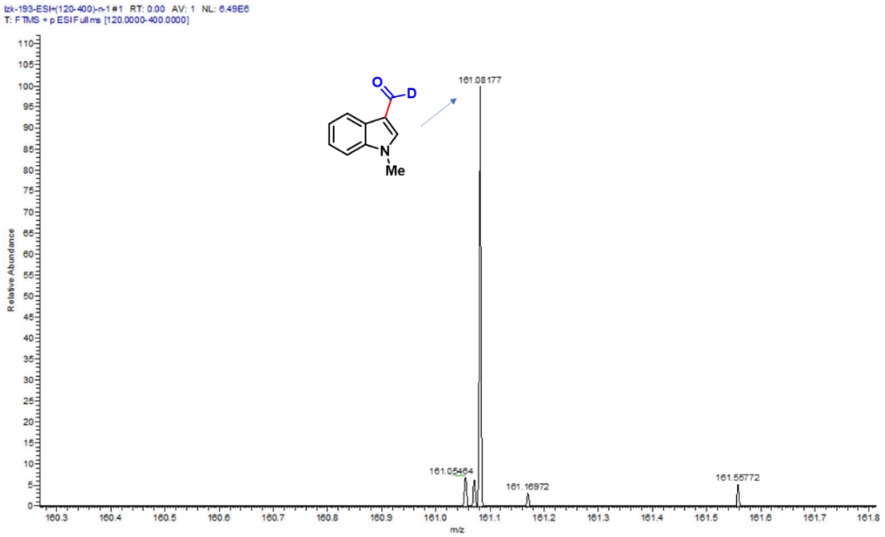


Fig. S6 HRMS spectrum of the isotope labeling experiment with CD_3OD.

4.2.2. Detection of intermediates

The reaction intermediate was proved with by HRMS. Under the optimal conditions, using the model reaction of **1a** reacted with CD_3OD, the intermediate **IV'** was obtained (Fig. S7). HRMS *m/z*: Calcd for $C_{17}H_{22}DN_2^+$ $[M]^+$: 256.1919; Found: 256.1911. As a comparison, when **1a** reacted with CH_3OH, the intermediate **IV** was obtained (Fig. S8). HRMS *m/z*: Calcd for $C_{17}H_{23}N_2^+$ $[M]^+$: 255.1856; Found: 255.1850.

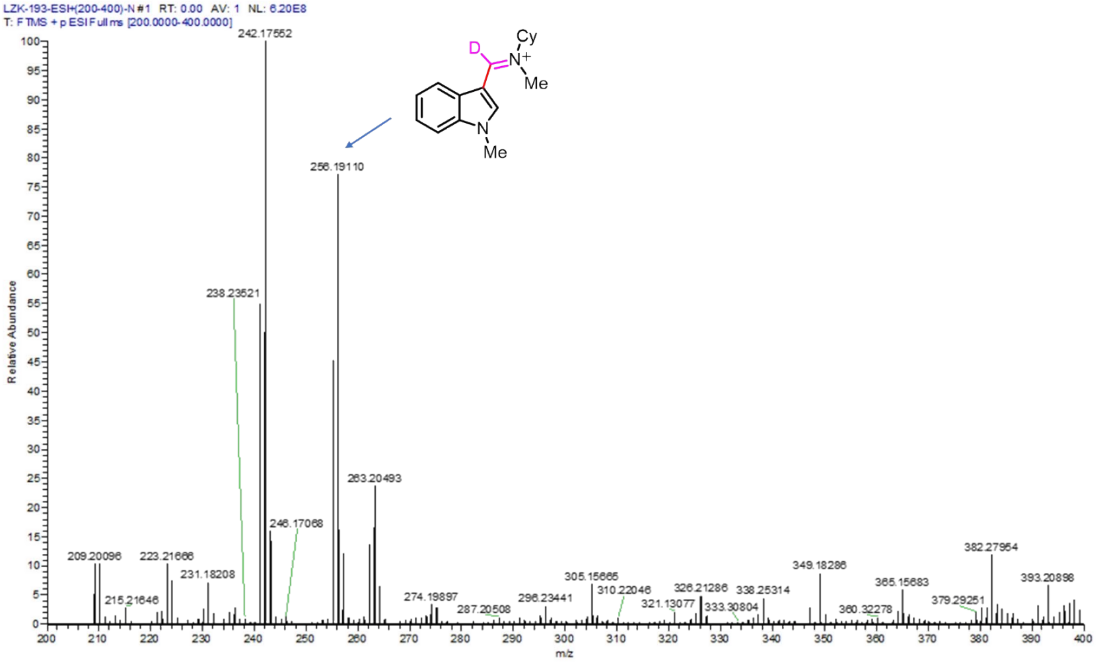


Fig. S7 HRMS spectrum of the intermediate **IV'**.

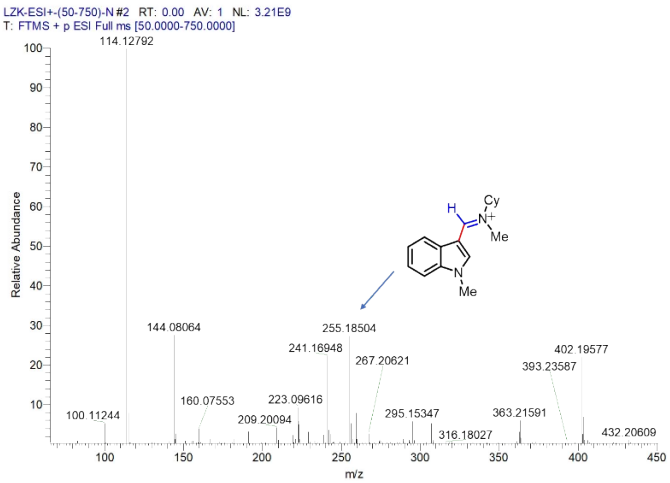
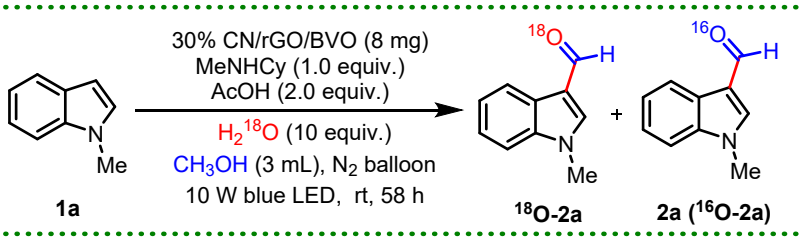


Fig. S8 HRMS spectrum of the intermediate **IV**.

4.2.3. Isotope labeling experiment with $H_2{}^{18}O$



A mixture of 1-methyl-1*H*-indole **1a** (50 μL, 0.4 mmol), 30% CN/rGO/BVO (8 mg), MeNHCy (53 μL, 0.4 mmol), AcOH (48 μL, 0.8 mmol, purity of 99.7%), dry CH_3OH (3 mL, purity of 99.9%) and $H_2{}^{18}O$ (73 μL, 4.0 mmol) were added to a 10 mL reaction tube. The reaction tube was purged with nitrogen for 5 min to exclude air inside the tube. Then, the mixture was stirred at room temperature for 58 h under 10 W blue LED irradiation with N_2 atmosphere. After the reaction finished, the photocatalyst was separated by centrifugation (4,000 rpm, 3 min) and washed with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5:1, v/v) to afford the products. The products were analyzed by HRMS (Fig. S9). HRMS *m/z* of **^{18}O-2a**: Calcd for $C_{10}H_{10}N^{18}O$ $[M+H]^+$: 162.0799; Found: 162.0796. HRMS *m/z* of **^{16}O-2a**: Calcd for $C_{10}H_{10}N^{16}O$ $[M+H]^+$: 160.0757; Found: 160.0754. The ratio of **^{18}O-2a** and **^{16}O-2a** in HRMS is 1.8:1.

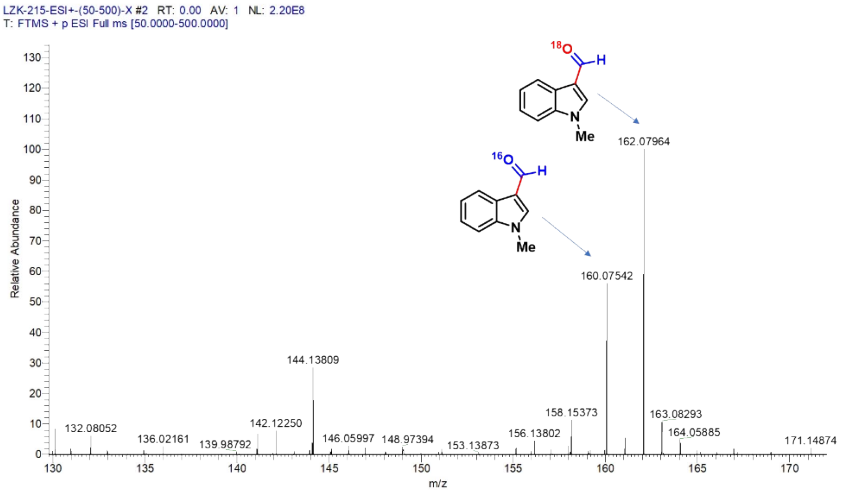
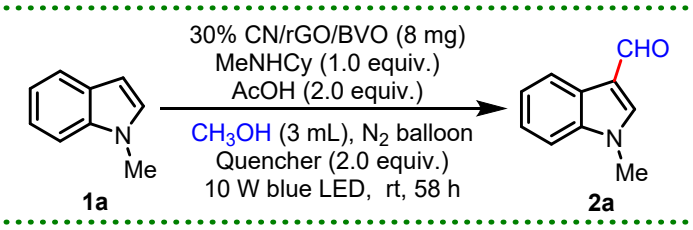


Fig. S9 HRMS spectrum of the **^{18}O-2a** and **^{16}O-2a**.

4.3. Quenching experiments



A mixture of 1-methyl-1*H*-indole **1a** (50 μL, 0.4 mmol), 30% CN/rGO/BVO (8 mg), MeNHCy (53 μL, 0.4 mmol), AcOH (48 μL, 0.8 mmol), quencher (e.g. $CuCl_2$, $AgNO_3$, KI, $(NH_4)_2C_2O_4$, TEOA, TEMPO, or BHT) (0.8 mmol) and CH_3OH (3 mL) were added to a 10 mL reaction tube. The reaction tube was purged with nitrogen for 5 min to exclude air inside the tube. Then, the mixture was stirred at room temperature for 58 h under 10 W blue LED irradiation with N_2 atmosphere. After the reaction finished, the photocatalyst was separated by centrifugation (4,000 rpm, 3 min) and washed with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5:1, v/v).The BHT-trapped product was detected by HRMS analysis (Fig. S10). HRMS *m/z*: Calcd for $C_{16}H_{24}O_2K$ $[M+K]^+$: 287.1408; Found: 287.1421.

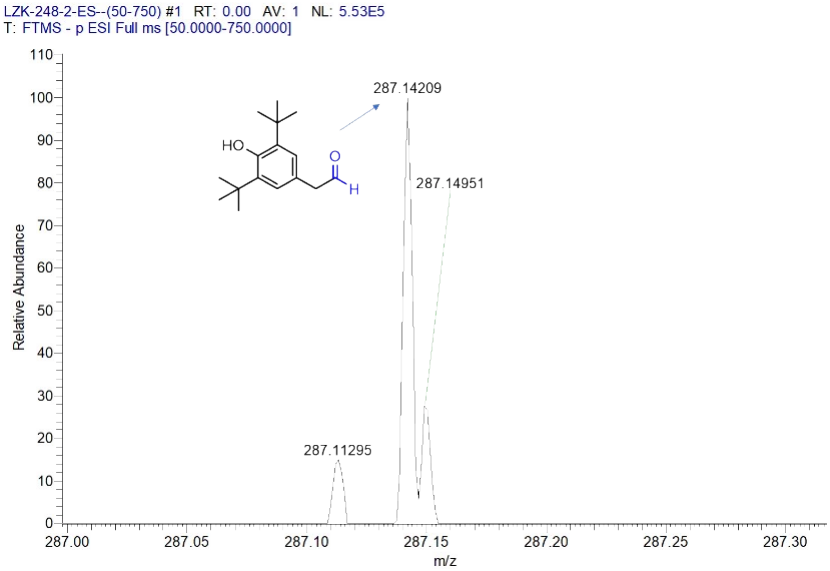


Fig. S10 HRMS spectrum of the BHT trapping experiment.

4.4. H_2 detection experiment

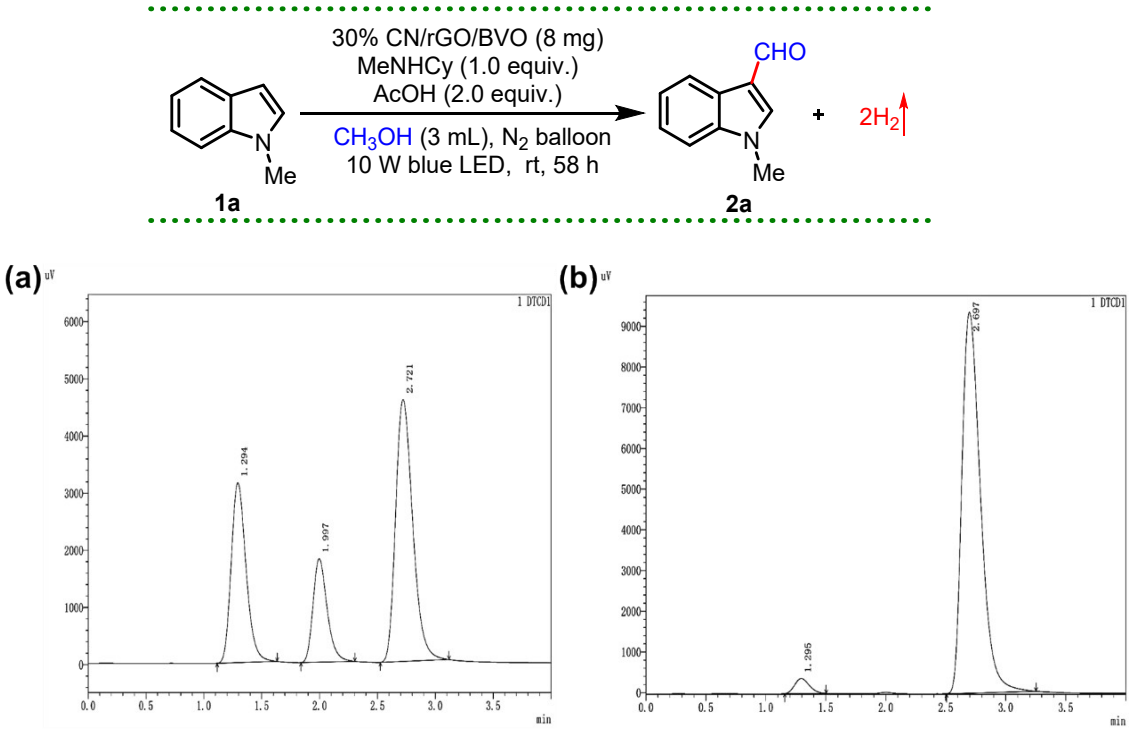
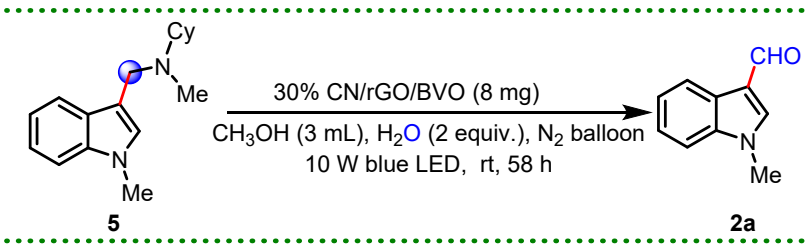


Fig. S11 H_2 detection experiment by GC.

In order to demonstrate the H_2 evolution during this photochemical formylation procedure, the model reaction of 1-methyl-1*H*-indole (**1a**) with methanol was detected by GC under standard conditions. As a standard, we first tested the retention time of a mixture of hydrogen, oxygen, and nitrogen at 1.294, 1.997, and 2,721 min, respectively (Fig. S11a). Then, we tested the gas in the reaction tube, and the retention time of H_2 at 1.295 min was observed (Fig. S11b).

*4.5. Convention of **5** to **2a***



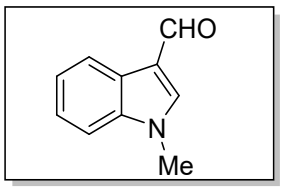
A mixture of **5** (102.6 mg, 0.4 mmol), 30% CN/rGO/BVO (8 mg), CH_3OH (3 mL) and H_2O (15 uL, 2 equiv.) was added to a 10 mL reaction tube. The reaction tube was purged with nitrogen for 5 min to exclude air inside the tube. Then, the mixture was

stirred at room temperature for 58 h under 10 W blue LED irradiation with N_2 atmosphere. After the reaction finished, the photocatalyst was separated by centrifugation (4,000 rpm, 3 min) and washed with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5:1, v/v) to afford the product **2a** in 89% yield.

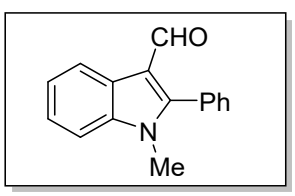
5. Reusability of photocatalyst

Reusability of 30% CN/rGO/BVO was investigated using the model reaction under the optimal conditions. After each cycle, 30% CN/rGO/BVO photocatalyst was separated from the reaction mixture by centrifugation (4000 rpm, 3 min) and washed with EtOAc (3×10 mL). The photocatalyst was obtained by vacuum drying at 60 °C for 12 h and used for next cycle. The photocatalyst after the fifth cycle was characterized by XRD.

6. Spectral Data

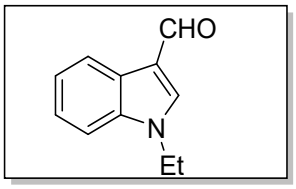


1-Methyl-1*H*-indole-3-carbaldehyde (2a)[6]**:** Known compound. 52.2 mg, 82% yield. Beige solid. m.p.: 68.2-69.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 8.30-8.28 (m, 1H), 7.61 (s, 1H), 7.34-7.29 (3H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.5, 139.5, 137.9, 125.2, 124.1, 123.0, 122.0, 118.0, 110.0, 33.7. **HRMS** (ESI) *m/z* Calcd for $C_{10}H_9ON$ $[M+H]^+$: 160.0757; Found: 160.0756.

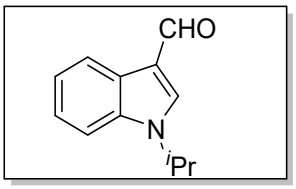


1-Methyl-2-phenyl-1*H*-indole-3-carbaldehyde (2b)[7]**:** Known compound. 64.0 mg,

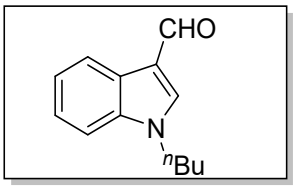
68% yield. Yellow solid. m.p.: 124.6-126.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.45-8.42 (m, 1H), 7.57-7.55 (m, 3H), 7.50-7.48 (m, 2H), 7.43-7.35 (m, 3H), 3.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 151.6, 137.5, 131.0, 130.0, 128.8, 128.7, 125.3, 124.2, 123.4, 122.3, 115.8, 109.9, 31.1.



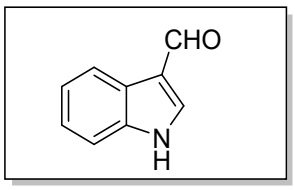
1-Ethyl-1*H*-indole-3-carbaldehyde (2c)[7]**:** Known compound. 45.0 mg, 65% yield. Beige solid. m.p.: 103.6-105.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.34-8.28 (m, 1H), 7.74 (s, 1H), 7.40-7.31 (m, 3H), 4.23 (q, *J* = 7.3 Hz, 2H), 1.55 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.6, 137.6, 137.1, 125.6, 124.0, 123.0, 122.3, 118.3, 110.1, 42.0, 15.2.



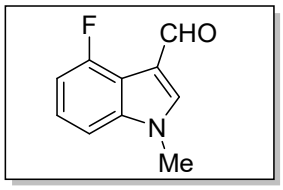
1-Isopropyl-1*H*-indole-3-carbaldehyde (2d)[7]**:** Known compound. 53.9 mg, 72% yield. Beige solid. m.p.: 90.6-93.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.32 (d, *J* = 6.5 Hz, 1H), 7.84 (s, 1H), 7.43-7.32 (m, 3H), 4.70 (sept, *J* = 6.5 Hz,1H), 1.59 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.6, 137.0, 134.8, 125.6, 123.9, 123.0, 122.2, 118.3, 110.3, 48.2, 22.7.



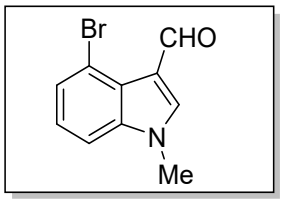
1-Butyl-1*H*-indole-3-carbaldehyde (2e)[8]**:** Known compound. 45.9 mg, 57% yield. Beige solid. m.p.: 102.6-104.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.32-8.30 (m, 1H), 7.72 (s, 1H), 7.40-7.29 (m, 3H), 4.18 (t, *J* = 7.1 Hz, 2H), 1.90-1.87 (m, 2H), 1.43-1.33 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.6, 138.4, 137.4, 125.6, 124.0, 123.0, 122.3, 118.2, 110.2, 47.2, 31.9, 20.2, 13.7.



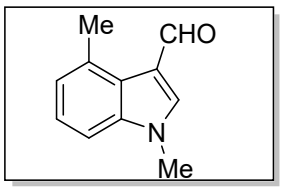
1*H*-Indole-3-carbaldehyde (2f)[8]**:** Known compound. 31.9 mg, 55% yield. Yellow solid. m.p.: 196.5-197.8 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.12 (s, 1H), 9.93 (s, 1H), 8.28 (d, J = 3.1 Hz, 1H), 8.09 (d, J = 7.0 Hz, 1H), 7.52-7.50 (m, 1H), 7.28-7.19 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.0, 138.5, 137.1, 124.1, 123.5, 122.1, 120.8, 118.2, 112.4.



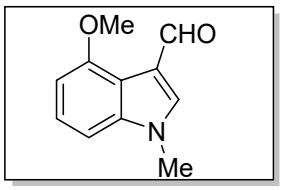
4-Fluoro-1-methyl-1*H*-indole-3-carbaldehyde (2h)[9]**:** Known compound. 36.9 mg, 52% yield. Yellow solid, m.p.: 67.2-69.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.80 (s, 1H), 7.27-7.22 (m, 1H), 7.17 (d, J = 8.1 Hz, 1H), 6.99 (dd, J = 10.2, 8.3 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 157.0 (d, $J_{C\text{-}F}$ = 248.0 Hz), 140.1 (d, $J_{C\text{-}F}$ = 11.0 Hz), 134.9, 124.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 116.7 (d, $J_{C\text{-}F}$ = 5.0 Hz), 115.2 (d, $J_{C\text{-}F}$ = 22.0 Hz), 108.1 (d, $J_{C\text{-}F}$ = 20.0 Hz), 106.6 (d, $J_{C\text{-}F}$ = 4.0 Hz), 34.2.



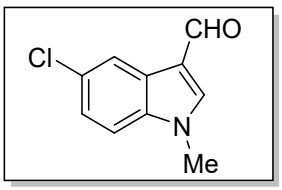
4-Bromo-1-methyl-1*H*-indole-3-carbaldehyde (2i)[10]**:** Known compound. 45.7 mg, 48% yield. Yellow solid, m.p.: 135.8-138.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.96 (s, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.1, 138.8, 135.3, 126.9, 126.2, 123.8, 118.2, 113.9, 109.7, 34.1.



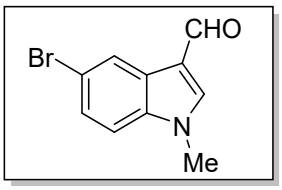
1,4-Dimethyl-1*H*-indole-3-carbaldehyde (2j)[11]**:** Known compound. 31.9 mg, 46% yield. Beige solid, m.p.: 75.2-77.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.77 (s, 1H), 7.25-7.18 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 1H), 3.82 (s, 3H), 2.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.6, 138.6, 138.4, 132.4, 125.1, 124.3, 123.6, 119.6, 107.8, 33.9, 22.6.



4-Methoxy-1-methyl-1*H*-indole-3-carbaldehyde (2k)[12]**:** Known compound. 47.7 mg, 63% yield. White solid, m.p.: 119.4-120.7°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.78 (s, 1H), 7.24 (t, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.2, 0.6 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 4.00 (s, 3H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.9, 154.7, 138.9, 132.2, 123.9, 118.2, 116.9, 103.5, 102.5, 55.5, 34.0.

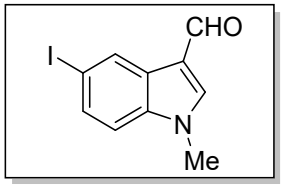


5-Chloro-1-methyl-1*H*-indole-3-carbaldehyde (2l)[11]**:** Known compound. 44.1 mg, 57% yield. Beige solid, m.p.: 177.3-178.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.29 (d, *J* = 1.8 Hz, 1H), 7.67 (s, 1H), 7.29 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.26-7.24 (m, 1H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.3, 140.1, 136.3, 129.0, 126.2, 124.5, 121.7, 117.5, 111.0, 34.0.

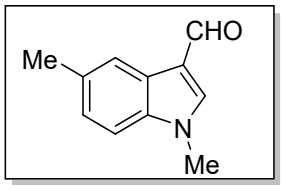


5-Bromo-1-methyl-1*H*-indole-3-carbaldehyde (2m)[7]**:** Known compound. 55.2 mg,

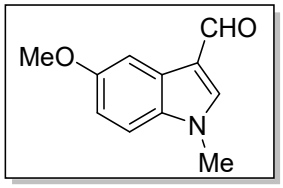
58% yield. Orange solid, m.p.: 123.8-126.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.44 (d, *J* = 1.9 Hz, 1H), 7.64 (s, 1H), 7.42 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.3, 139.9, 136.6, 127.1, 126.7, 124.7, 117.4, 116.7, 111.4, 34.0.



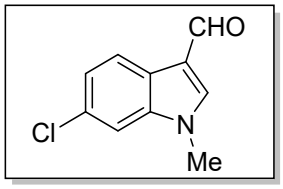
5-Iodo-1-methyl-1*H*-indole-3-carbaldehyde (2n)[13]**:** Known compound. 84.4 mg, 74% yield. Beige solid, m.p.: 128.8-130.7 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.87 (s, 1H), 8.43 (s, 1H), 8.24 (s, 1H), 7.58-7.42 (m, 2H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 184.6, 141.9, 136.9, 131.5, 129.2, 126.9, 115.9, 113.5, 87.1, 33.5.



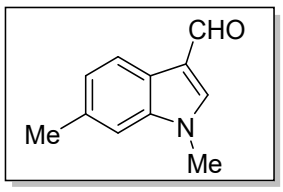
5-Methyl-1-methyl-1*H*-indole-3-carbaldehyde (2o)[7]**:** Known compound. 43.0 mg, 62% yield. Brown solid, m.p.: 119.0-121.3℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.11 (s, 1H), 7.61 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 1.4 Hz, 1H), 3.83 (s, 3H), 2.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.6, 139.5, 136.4, 132.8, 125.6, 125.5, 121.9, 117.7, 109.6, 33.8, 21.5.



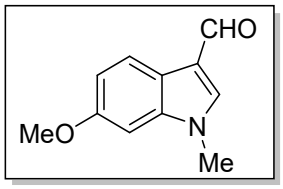
5-Methoxy-1-methyl-1*H*-indole-3-carbaldehyde (2p)[12]**:** Known compound. 65.8 mg, 87% yield. White solid, m.p.: 106.7-108.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.79 (d, *J* = 2.5 Hz, 1H), 7.62 (s, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 6.98 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.5, 156.8, 139.4, 132.9, 126.1, 117.9, 114.6, 110.8, 103.4, 55.9, 34.0.



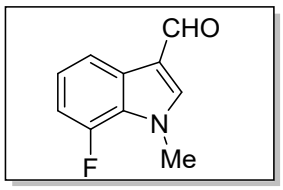
6-Chloro-1-methyl-1*H*-indole-3-carbaldehyde (2q)[12]**:** Known compound. 50.3 mg, 65% yield. Yellow solid, m.p.: 104.7-107.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.59 (s, 1H), 7.26 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 4.19 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.2, 141.6, 133.1, 128.2, 125.5, 123.7, 120.7, 117.5, 37.9.



6-Methyl-1-methyl-1*H*-indole-3-carbaldehyde (2r)[12]**:** Known compound. 44.3 mg, 64% yield. Beige solid, m.p.: 106.3-108.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.55 (s, 1H), 7.16-7.12 (m, 2H), 3.79 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.4, 139.1, 138.4, 134.2, 124.6, 123.0, 121.7, 118.1, 109.9, 33.6, 22.0.

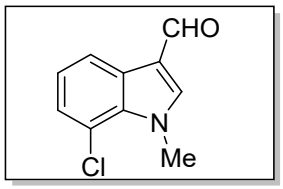


6-Methoxy-1-methyl-1H-indole-3-carbaldehyde (2s)[12]**:** Known compound. 62.8 mg, 83% yield. Beige solid, m.p.: 123.0-124.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.51 (s, 1H), 6.94 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.4, 157.8, 138.9, 138.9, 122.8, 119.2, 118.2, 112.2, 93.7, 55.8, 33.7.

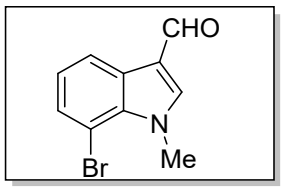


7-Fluoro-1-methyl-1*H*-indole-3-carbaldehyde (2t)[14]**:** Known compound. 54.6 mg,

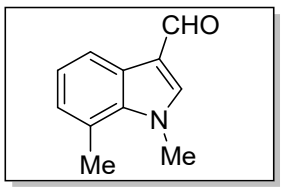
77% yield. Beige solid, m.p.: 89.8-92.2℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.90 (s, 1H), 8.26 (s, 1H), 7.91 (d, J = 7.4 Hz, 1H), 7.20-7.08 (m, 2H), 4.03 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 184.6, 149.6 (d, $J_{C\text{-}F}$ = 243.0 Hz), 142.8, 128.6 (d, $J_{C\text{-}F}$ = 5.0 Hz), 125.1(d, $J_{C\text{-}F}$ = 10.0 Hz), 123.3(d, $J_{C\text{-}F}$ = 6.0 Hz), 117.3, 117.2 (d, $J_{C\text{-}F}$ = 4.0 Hz), 109.3 (d, $J_{C\text{-}F}$ = 17.0 Hz), 36.3 (d, $J_{C\text{-}F}$ = 5.0 Hz).



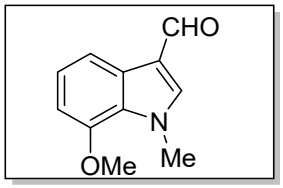
7-Chloro-1-methyl-1*H*-indole-3-carbaldehyde (2u)[15]**:** Known compound. 57.3 mg, 74% yield. Beige solid, m.p.: 149.3-151.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.57 (s, 1H), 7.26-7.22 (m, 2H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.3, 139.8, 138.3, 130.0, 123.7, 123.5, 122.9, 118.0, 110.1, 33.8.



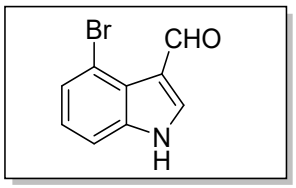
7-Bromo-1-methyl-1*H*-indole-3-carbaldehyde (2v)[16]**:** Known compound. 63.8 mg, 67% yield. Beige solid, m.p.: 105.7-108.1℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.27 (d, J = 7.7 Hz, 1H), 7.60 (s, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 4.19 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.3, 141.8, 134.5, 129.2, 128.4, 124.2, 121.5, 117.4, 104.4, 38.2.



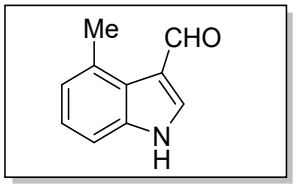
1,7-Dimethyl-1*H*-indole-3-carbaldehyde (2w)[12]**:** Known compound. 54.7 mg, 79% yield. Beige solid, m.p.: 112.4-114.3 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.55 (s, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.05-7.03 (m, 1H), 4.11 (s, 3H), 2.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.4, 141.0, 136.6, 126.8, 126.4, 123.1, 121.9, 120.0, 117.5, 37.9, 19.5.



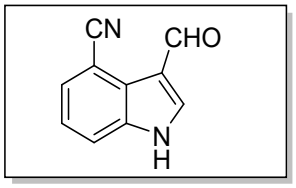
7-Methoxy-1-methyl-1*H*-indole-3-carbaldehyde (2x)[8]**:** Known compound. 67.4 mg, 89% yield. Beige solid, m.p.: 130.1-131.4℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.87 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.53 (s, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 4.11 (s, 3H), 3.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.5, 147.8, 139.9, 127.8, 127.5, 123.8, 117.9, 114.4, 104.8, 55.5, 37.9.



4-Bromo-1*H*-indole-3-carbaldehyde (2y)[17]**:** Known compound. 44.4 mg, 50% yield. Yellow solid, m.p.: 170.8-172.9℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.56 (s, 1H), 10.69 (s, 1H), 8.30 (s, 1H), 7.56 (s, 1H), 7.43 (s, 1H), 7.14 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 184.6, 138.3, 133.7, 125.9, 124.7, 123.7, 117.9, 112.4, 112.3.

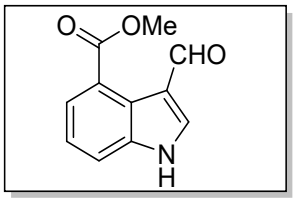


4-Methyl-1*H*-indole-3-carbaldehyde (2z)[18]**:** Known compound. 28.0 mg, 44% yield. Beige solid, m.p.: 183.2-185.1℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 9.91 (s, 1H), 8.23 (s, 1H), 7.30 (s, 1H), 7.13 (s, 1H), 6.97 (s, 1H), 2.77 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 184.2, 139.0, 137.9, 131.2, 123.5, 123.4, 123.3,119.8, 110.0, 22.2.

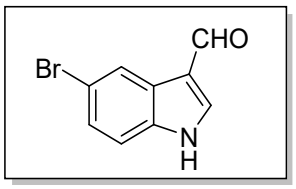


4-Cyano-1*H*-indole-3-carbaldehyde (2aa)[19]**:** Known compound. 32.0 mg, 47% yield. Yellow solid, m.p.: 215.4-218.0 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.74 (s,

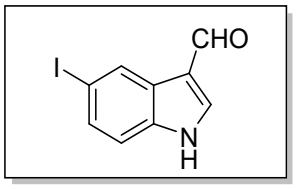
1H), 10.19 (s, 1H), 8.50 (s, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 7.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 183.7, 138.4, 137.5, 129.0, 123.8, 123.3, 119.1, 118.2, 117.2, 102.1.



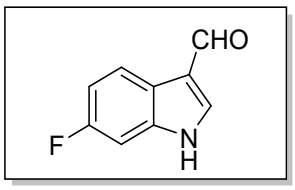
4-carboxylic acid methyl ester-1*H*-indole-3-carbaldehyde (2ab)[20]**:** Known compound. 55.3 mg, 68% yield. Yellow solid, m.p.: 133.6-135.0 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 10.19 (s, 1H), 8.34 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 186.2, 168.7, 137.9, 136.7, 124.7, 123.2, 122.4, 121.4, 118.2, 116.4, 51.9.



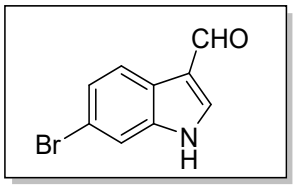
5-Bromo-1*H*-indole-3-carbaldehyde (2ac)[8]**:** Known compound. 48.4 mg, 54% yield. Beige solid, m.p.: 174.4-175.3 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.30 (s, 1H), 9.93 (s, 1H), 8.35 (s, 1H), 8.22 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.40 (dd, J = 8.6, 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.3, 139.4, 135.8, 126.2, 126.0, 123.0, 117.5, 114.9, 114.7.



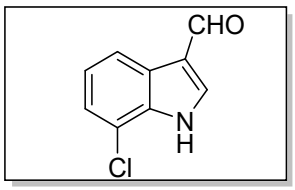
5-Iodo-1H-indole-3-carbaldehyde (2ad)[20]**:** Known compound. 73.7 mg, 68% yield. Beige solid, m.p.: 223.6-225.2 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 9.92 (s, 1H), 8.44 (d, J = 1.4 Hz, 1H), 8.29 (s, 1H), 7.53 (dd, J = 8.5, 1.7 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.1, 138.9, 136.2, 131.5, 129.2, 126.6, 117.2, 114.9, 86.6.



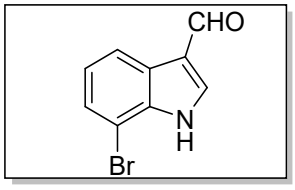
6-Fluoro-1*H*-indole-3-carbaldehyde (2ae)[17]**:** Known compound. 36.5 mg, 56% yield. Beige solid, m.p.: 203.2-204.4 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.16 (s, 1H), 9.92 (s, 1H), 8.30 (d, J = 3.0 Hz, 1H), 8.07 (dd, J = 8.7, 5.6 Hz, 1H), 7.33-7.29 (m, 1H), 7.08 (ddd, J = 9.8, 8.7, 2.4 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.1, 159.6 (d, $J_{C\text{-}F}$ = 236.0 Hz), 139.2, 137.2 (d, $J_{C\text{-}F}$ = 13.0 Hz), 122.0 (d, $J_{C\text{-}F}$ = 10.0 Hz), 120.8, 118.1, 110.5 (d, $J_{C\text{-}F}$ = 23.0 Hz), 98.9 (d, $J_{C\text{-}F}$ = 25.0 Hz).



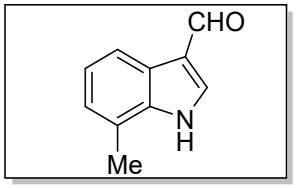
6-Bromo-1*H*-indole-3-carbaldehyde (2af)[21]**:** Known compound. 49.3 mg, 55% yield. Beige solid, m.p.: 198.2-199.7 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.21 (s, 1H), 9.94 (s, 1H), 8.32 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 1.4 Hz, 1H), 7.36 (dd, J = 8.4, 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.1, 139.2, 137.9, 125.1, 123.2, 122.5, 118.0, 115.9, 115.2.



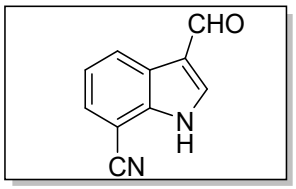
7-Chloro-1*H*-indole-3-carbaldehyde (2ag)[22]**:** Known compound. 51.7 mg, 72% yield. Beige solid, m.p.: 180.0-181.2 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.54 (s, 1H), 9.97 (s, 1H), 8.38 (s, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.35 (dd, J = 7.7, 0.7 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.4, 139.2, 133.9, 126.0, 123.3, 123.1, 119.8, 118.9, 116.7.



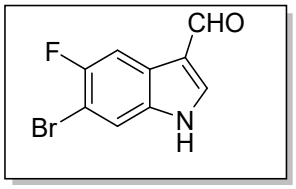
7-Bromo-1*H*-indole-3-carbaldehyde (2ah)[21]**:** Known compound. 35.8 mg, 64% yield. Beige solid, m.p.: 165.2-167.2 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.39 (s, 1H), 9.97 (s, 1H), 8.37 (s, 1H), 8.10 (dd, J = 7.8, 0.6 Hz, 1H), 7.49 (dd, J = 7.6, 0.6 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.4, 139.2, 135.5, 126.2, 125.8, 123.7, 120.3, 118.9, 104.8.



7-Methyl-1*H*-indole-3-carbaldehyde (2ai)[23]**:** Known compound. 41.4 mg, 65% yield. Yellow solid, m.p.: 201.7-203.8 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.15 (s, 1H), 9.94 (s, 1H), 8.29 (d, J = 3.2 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.12 (t, J = 7.3 Hz,1H), 7.07-7.05 (m, 1H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.2, 138.3, 136.6, 124.1, 124.0, 122.5, 121.9, 118.6, 118.5, 16.8.

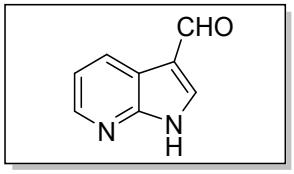


7-Cyano-1*H*-indole-3-carbaldehyde (2aj)[24]**:** Known compound. 33.4 mg, 49% yield. Beige solid, m.p.: 206.0-208.1 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.87 (s, 1H), 10.00 (s, 1H), 8.46 (s, 1H), 8.41 (dd, J = 8.0, 1.0 Hz, 1H), 7.77 (dd, J = 7.5, 1.0 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.5, 139.9, 136.6, 128.6, 126.4, 125.1, 122.4, 118.6, 116.6, 95.1.

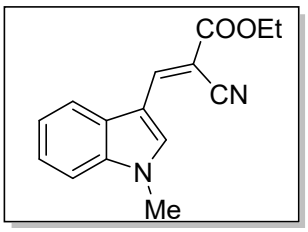


6-Bromo-5-Fluoro-1*H*-indole-3-carbaldehyde (2ak)[25]**:** Known compound. 66.8 mg, 69% yield. Yellow solid, m.p.: 251.6-253.5 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.26 (s, 1H), 9.92 (s, 1H), 8.36 (s, 1H), 7.88 (d, J = 9.1 Hz, 1H), 7.80 (d, J = 5.4 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.0 (s), 155.4 (d, $J_{C\text{-}F}$ =236.0 Hz), 140.0, 133.9, 124.0 (d, $J_{C\text{-}F}$ = 10.0 Hz), 118.0 (d, $J_{C\text{-}F}$ = 5.0 Hz), 116.6, 106.8 (d, $J_{C\text{-}F}$ = 25.0

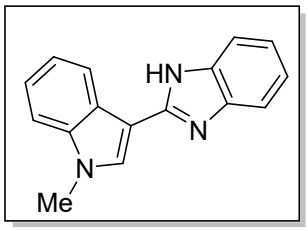
Hz), 103.5 (d, $J_{C\text{-}F}$ = 24.0 Hz).



1*H*-Pyrrolo[2,3-b]pyridine-3-carbaldehyde (2al)[8]**:** Known compound. 25.1 mg, 43% yield. Beige solid, m.p.: 207.8-210.1 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.67 (s, 1H), 9.91 (s, 1H), 8.44 (s, 1H), 8.38 (d, J = 7.8 Hz, 1H), 8.34 (d, J = 4.5 Hz, 1H), 7.24 (dd, J = 7.8, 4.8 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 185.4, 149.4, 144.8, 138.7, 129.2, 118.4, 116.6, 116.5.



Ethyl (*E*)-2-cyano-3-(1-methyl-1*H*-indol-3-yl)acrylate (3)[26]**:** Known compound. 36.8 mg, 92% yield. Yellow solid, m.p.: 145.6-148.3 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.51 (s, 1H), 7.85-7.82 (m, 1H), 7.43-7.32 (m, 3H), 4.37 (q, J = 7.2 Hz, 2H), 3.93 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 146.0, 137.0, 134.8, 128.4, 124.0, 122.8, 118.6, 118.5, 110.5, 110.0, 93.8, 62.0, 34.1, 14.4. **HRMS** (ESI) *m/z* Calcd for $C_{15}H_{15}N_2O_2$ $[M+H]^+$: 255.1134; Found: 255.1126.



2-(1-Methyl-1H-indol-3-yl)-1H-benzo[d]imidazole (4)[27]**:** Known compound. 98.9 mg, 91% yield. Yellow solid, m.p.: 230.5-233.1℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 8.52 (d, J = 7.2 Hz, 1H), 8.09 (s, 1H), 7.56-7.53 (m, 3H), 7.31-7.22 (m, 2H), 7.16-7.12 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 149.1, 137.0, 129.9, 125.5, 122.3, 121.5, 121.2, 120.4, 110.2, 105.7, 33.0.

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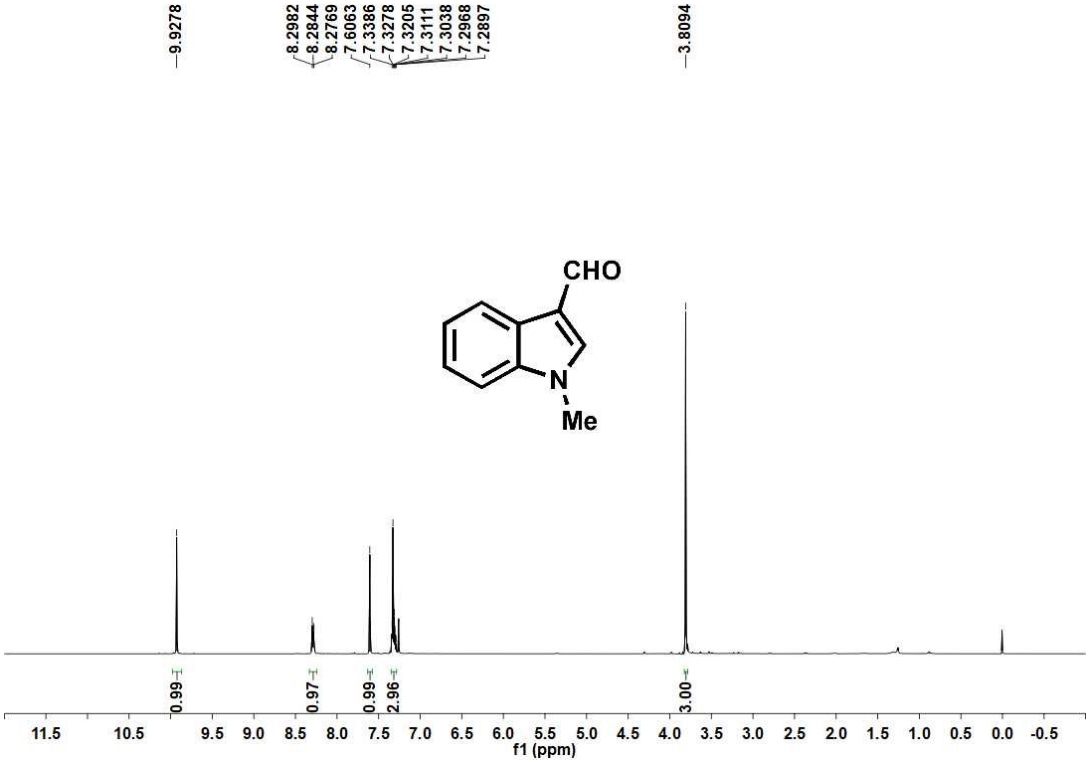
8. Copies of NMR spectra

^{1}H NMR of product 2a in $CDCl_3$ (400 MHz)



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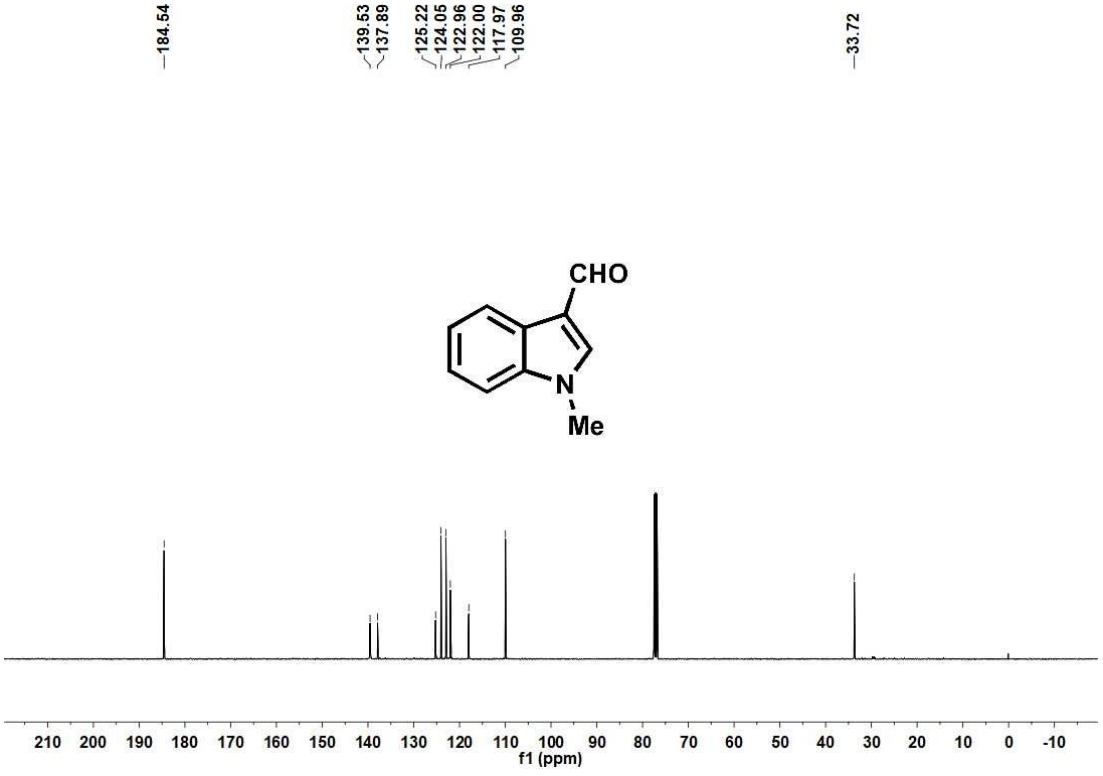
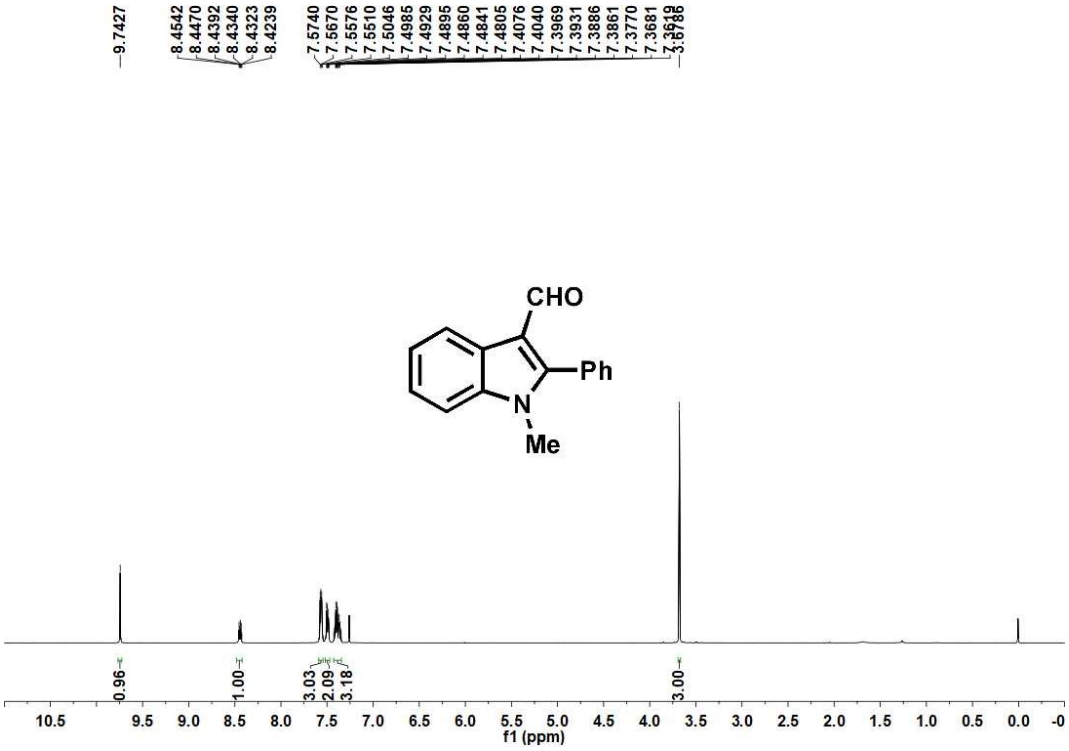


^{1}H NMR of product 2b in $CDCl_3$ (400 MHz)



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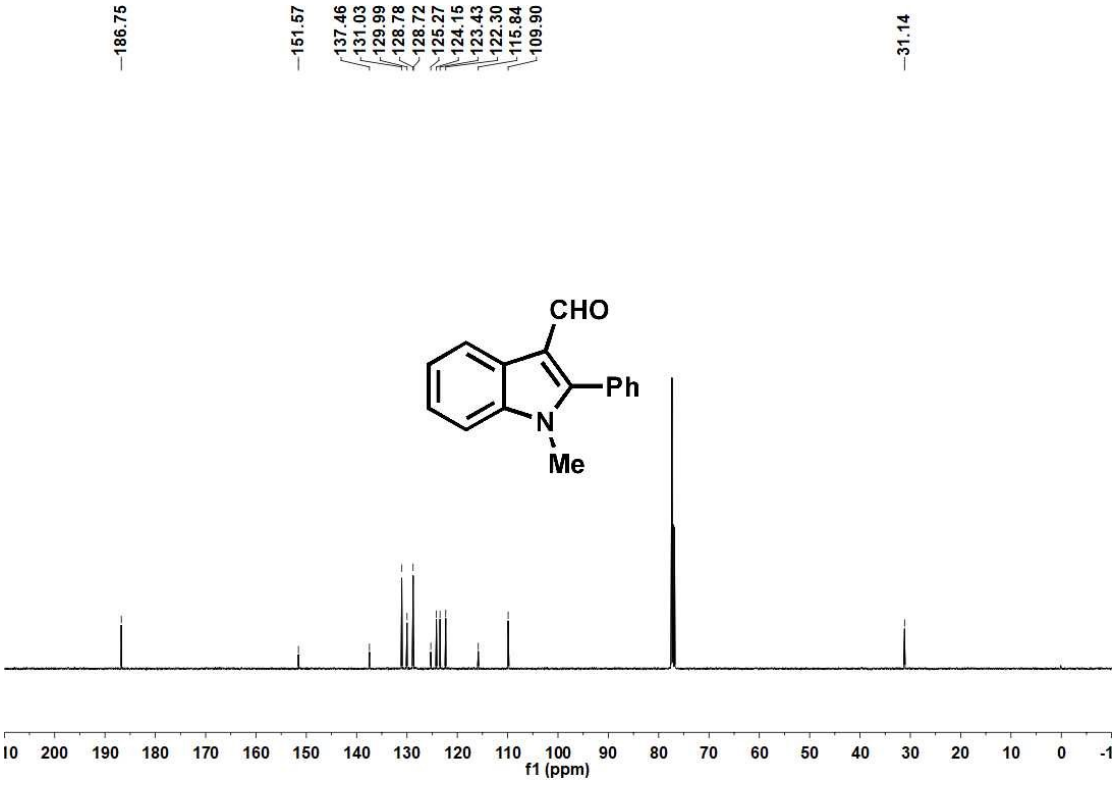

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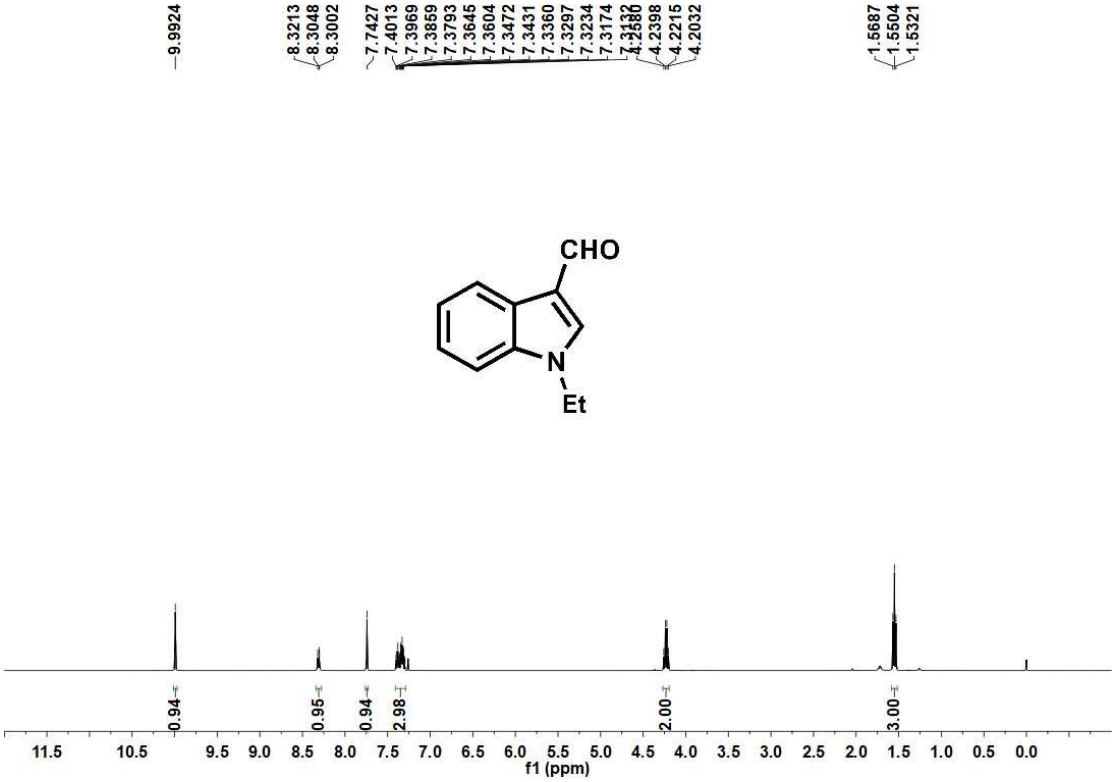

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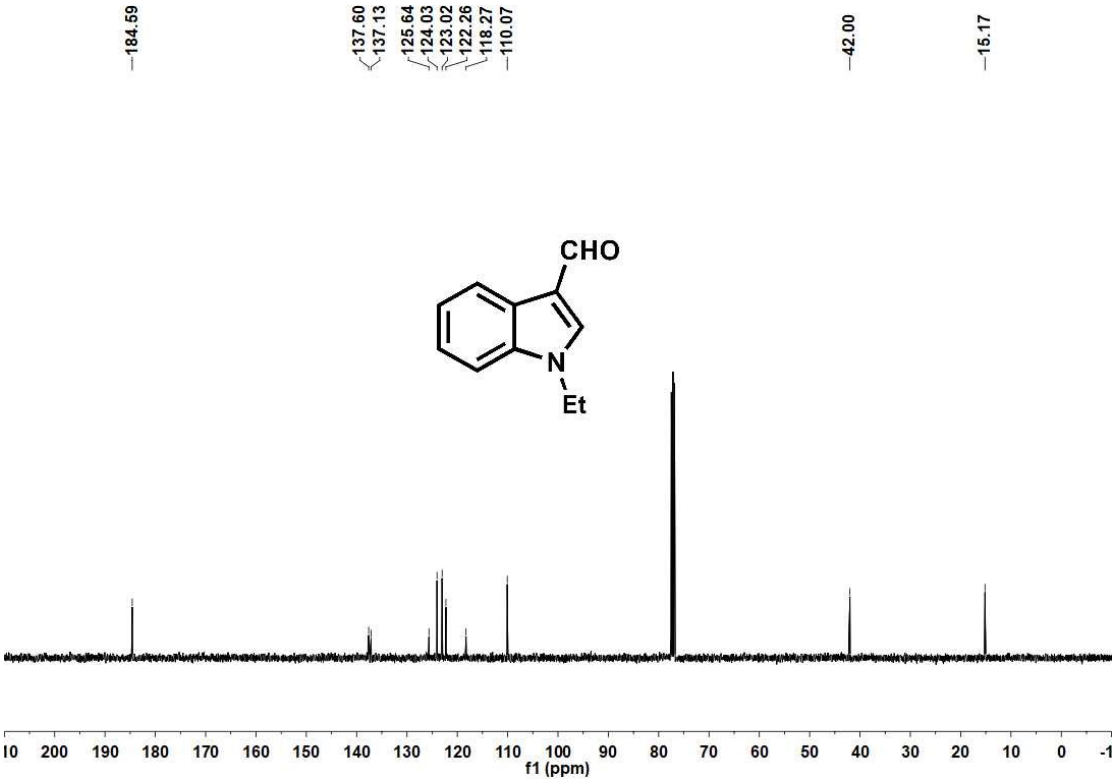

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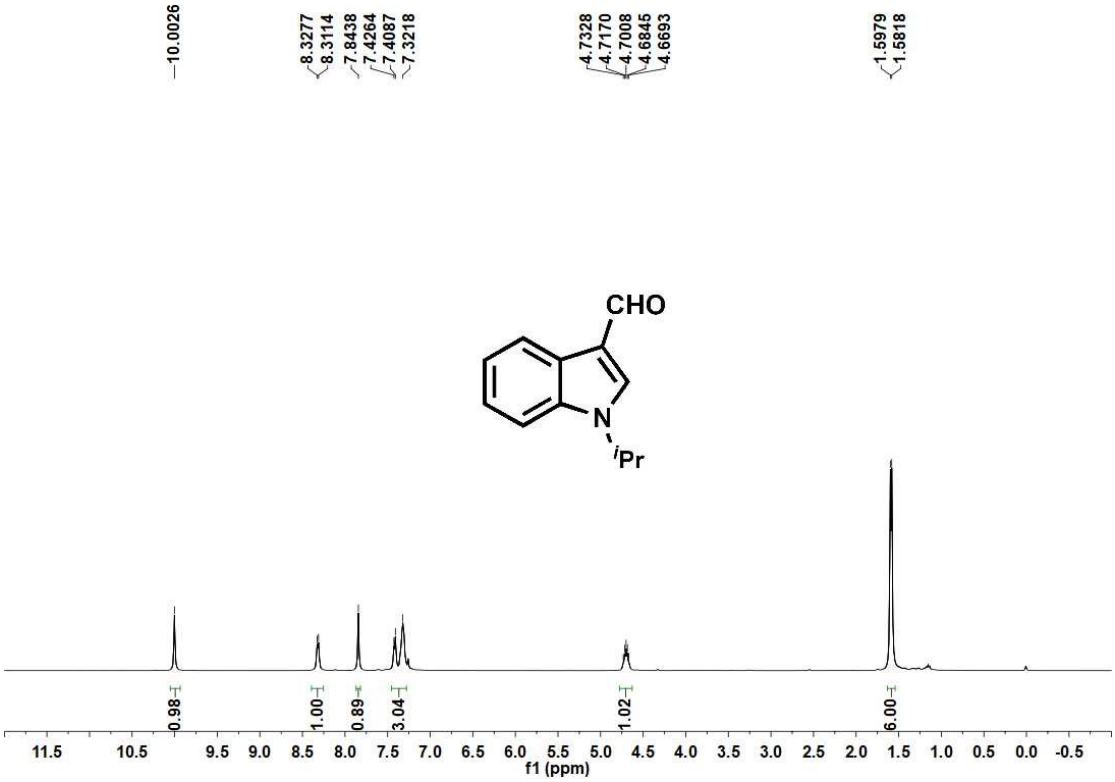

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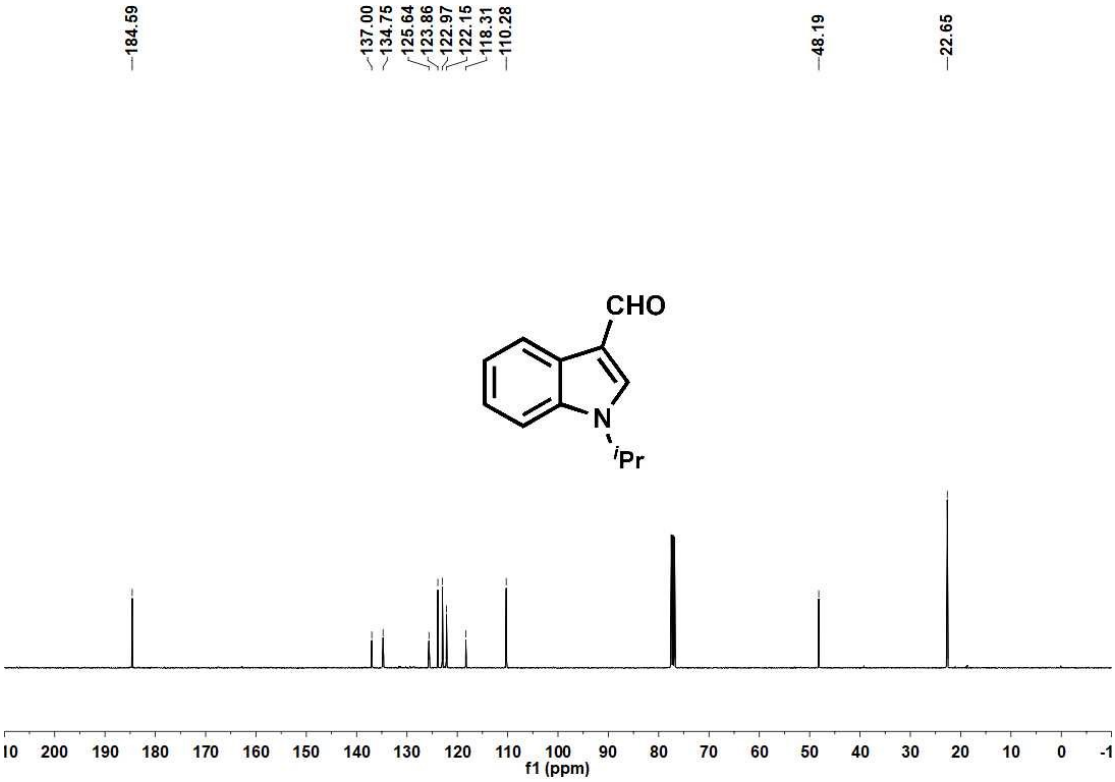

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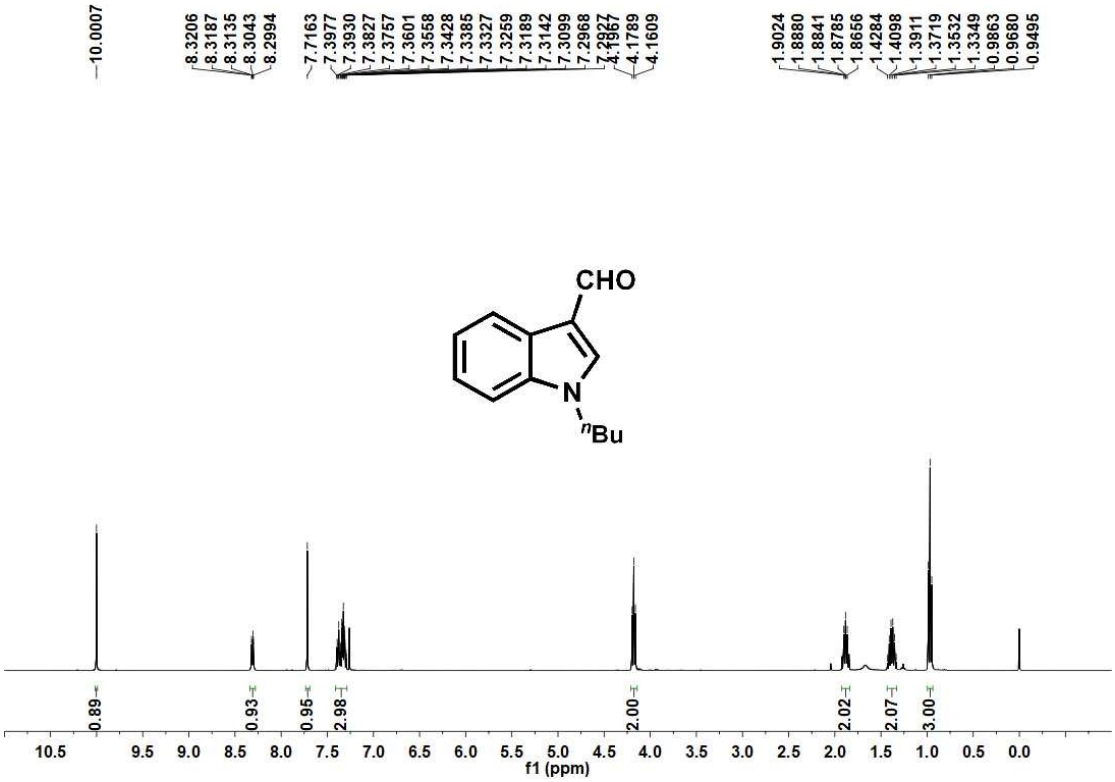

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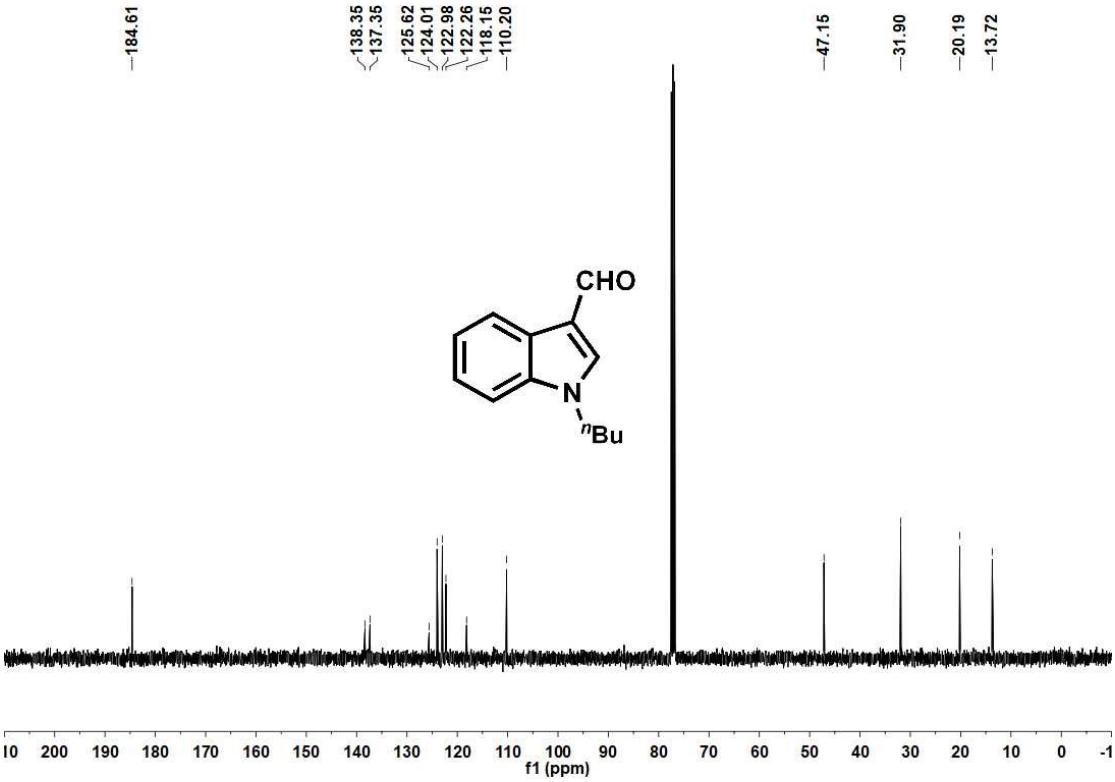
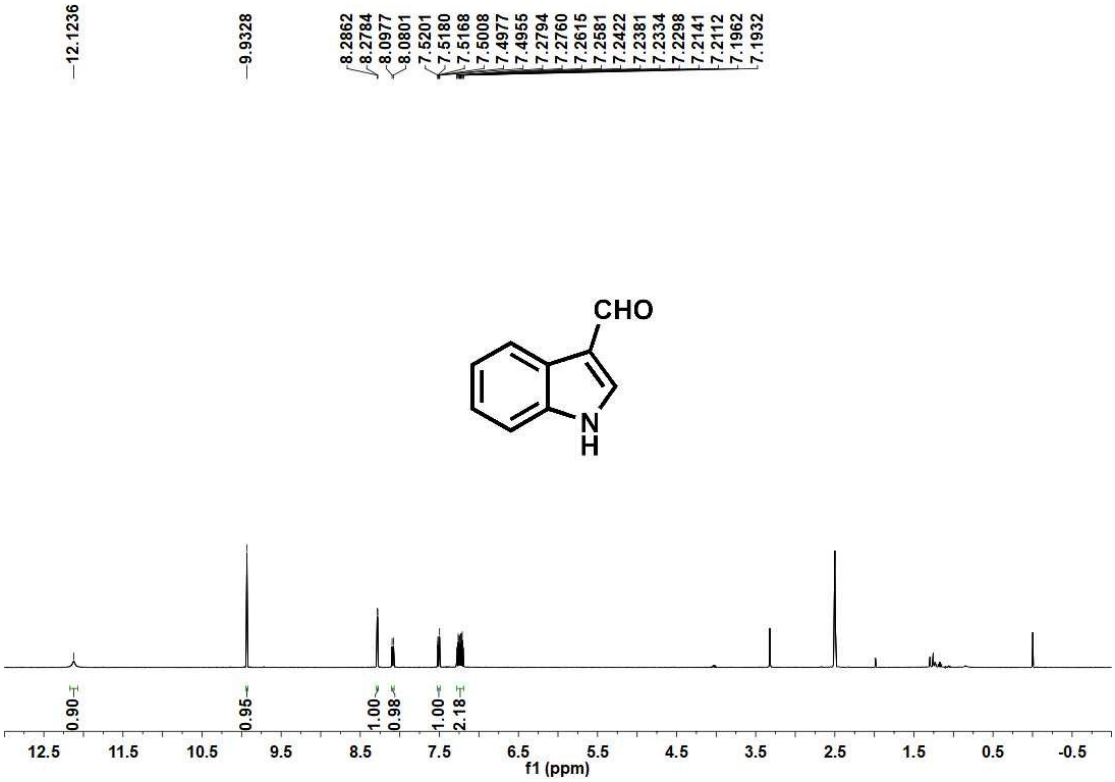
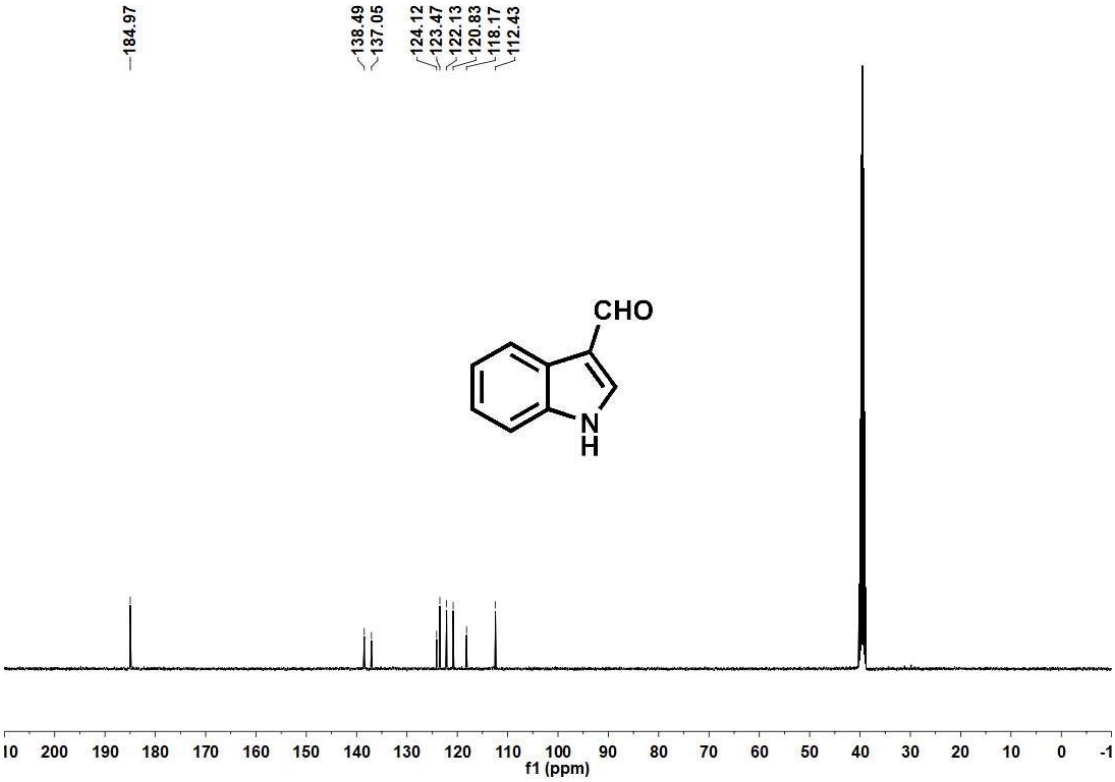


^{1}H NMR of product 2f in DMSO-d_6 (400 MHz)



^{13}C NMR of product 2f in DMSO-d_6 (100 MHz)



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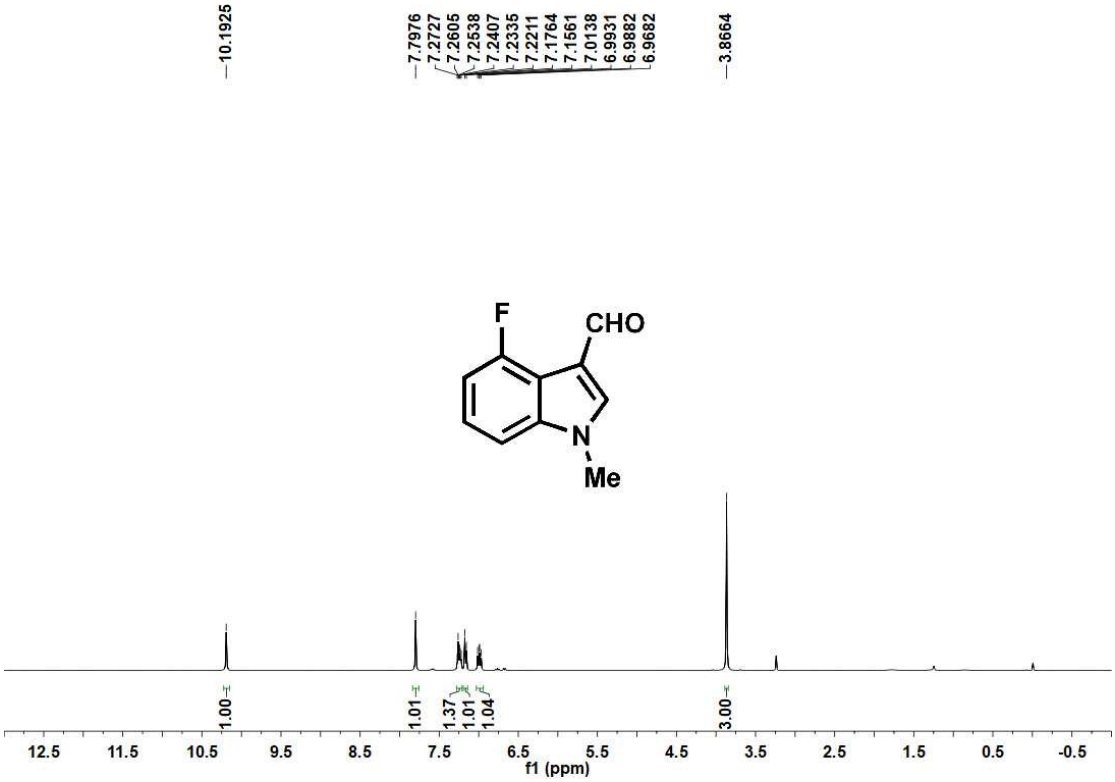
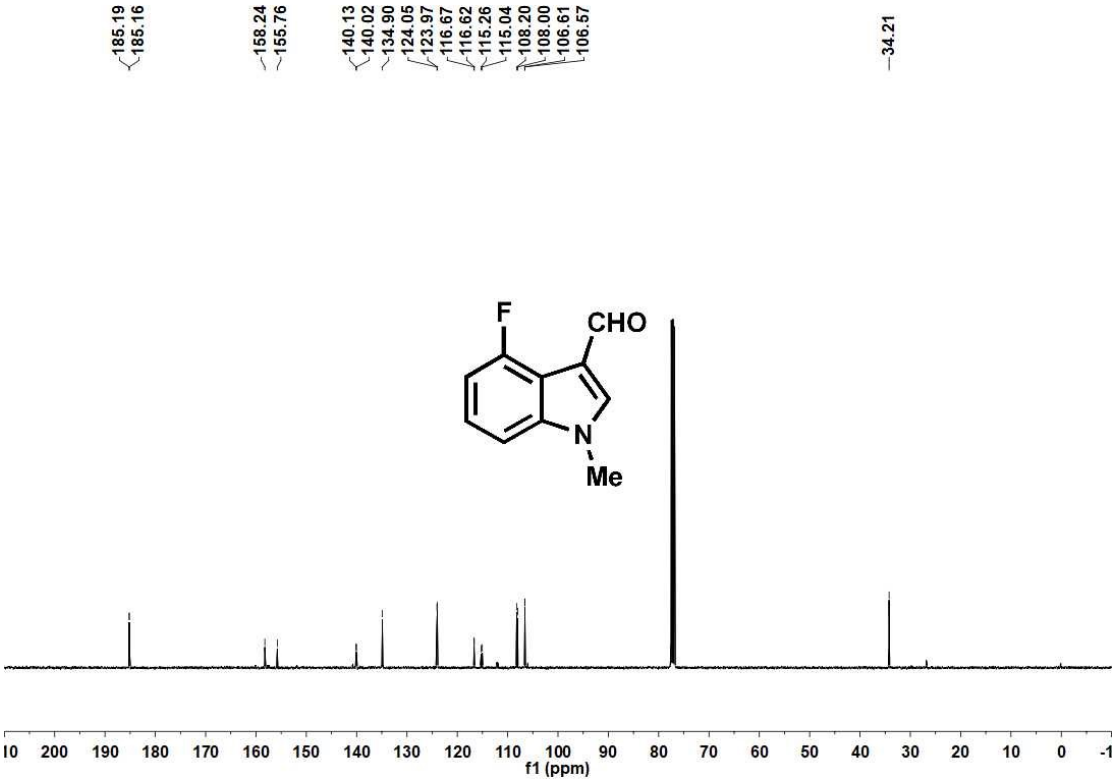
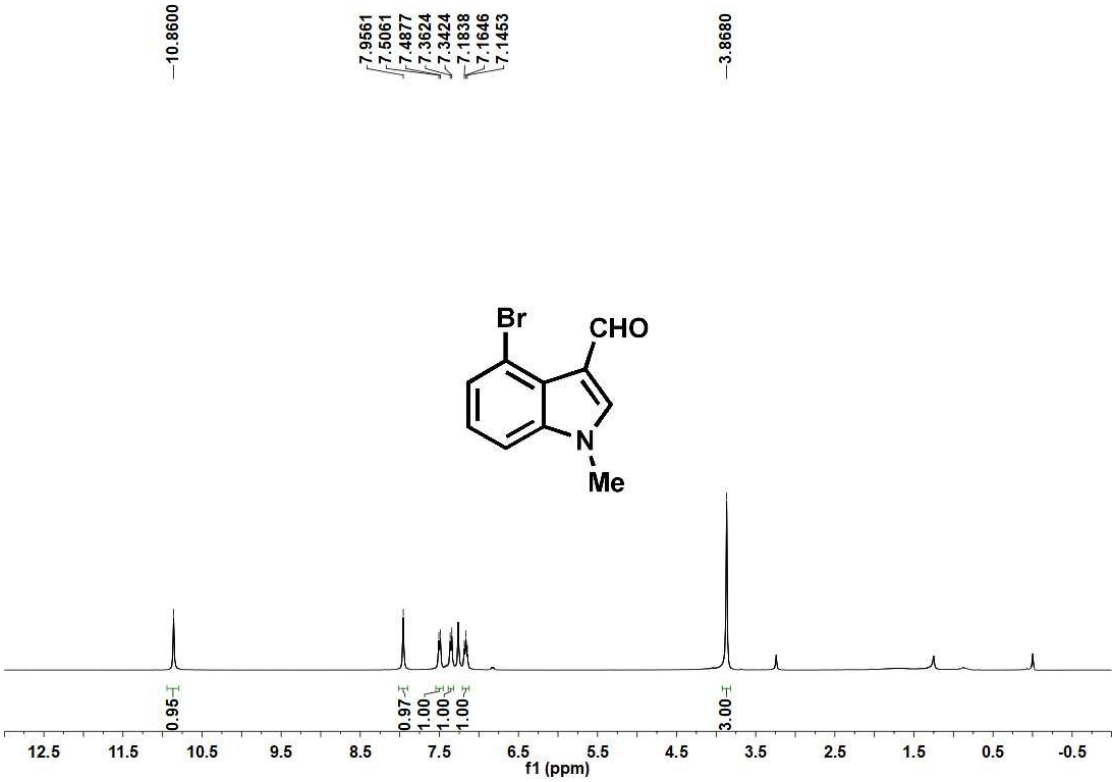


^{13}C NMR of product 2h in $CDCl_3$ (100 MHz)



^{1}H NMR of product 2i in $CDCl_3$ (400 MHz)



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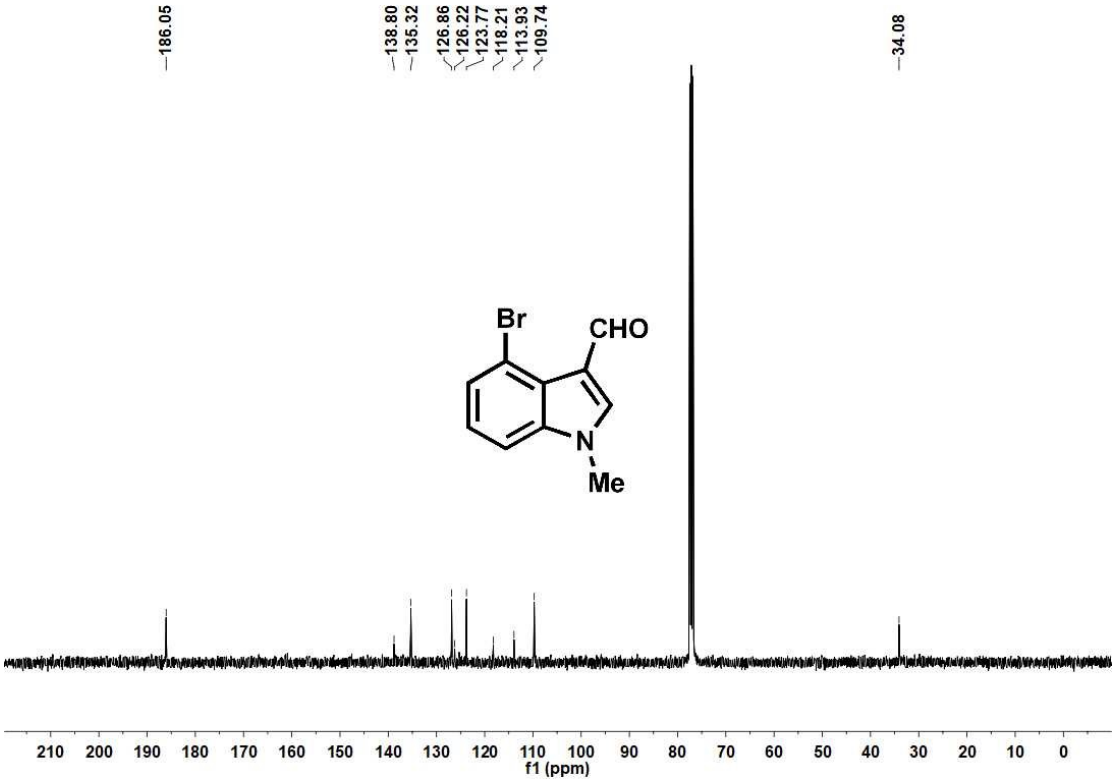

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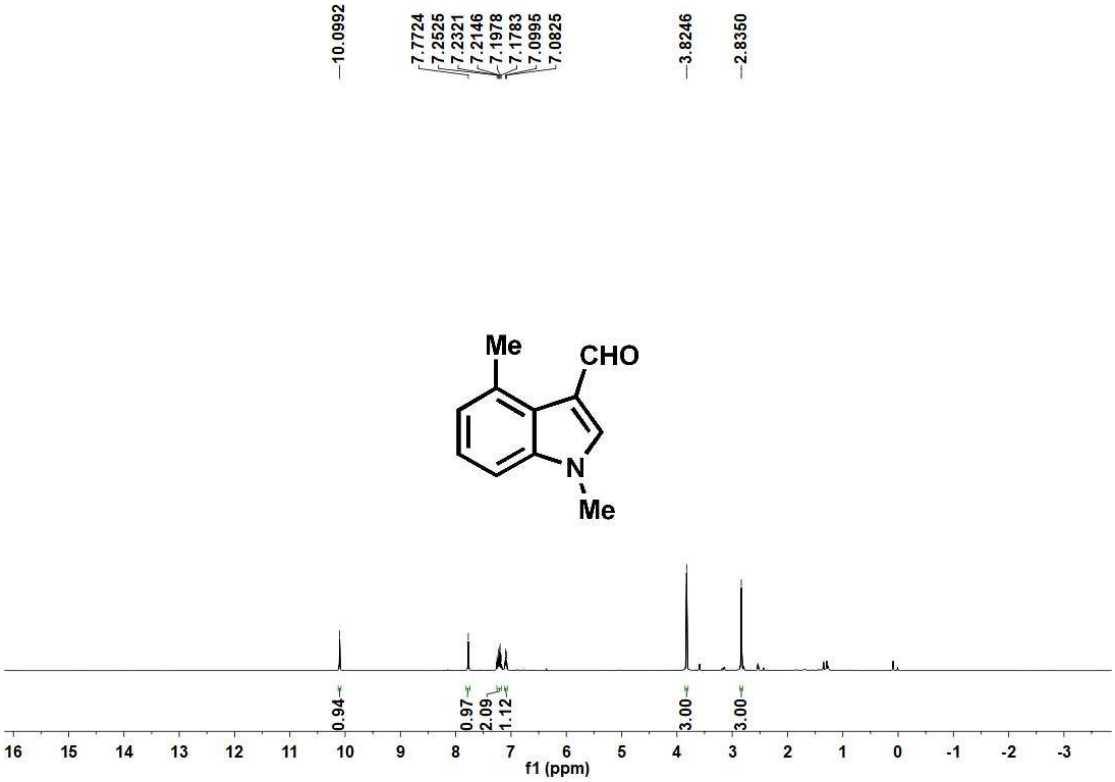

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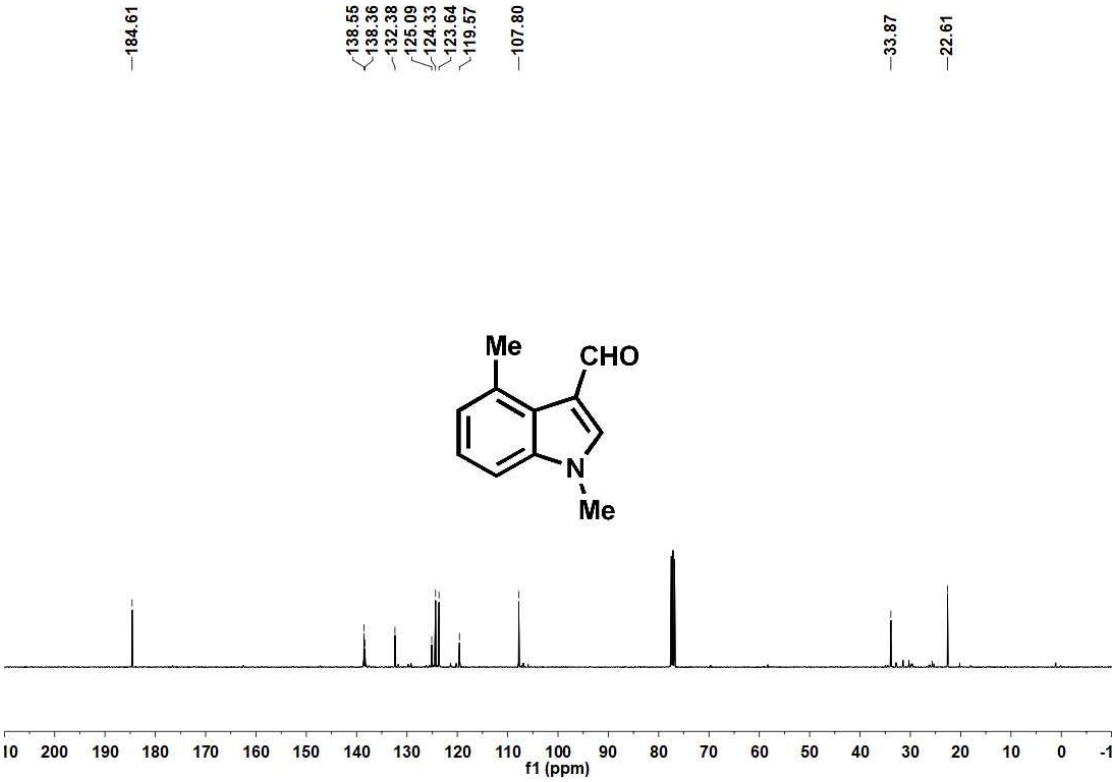
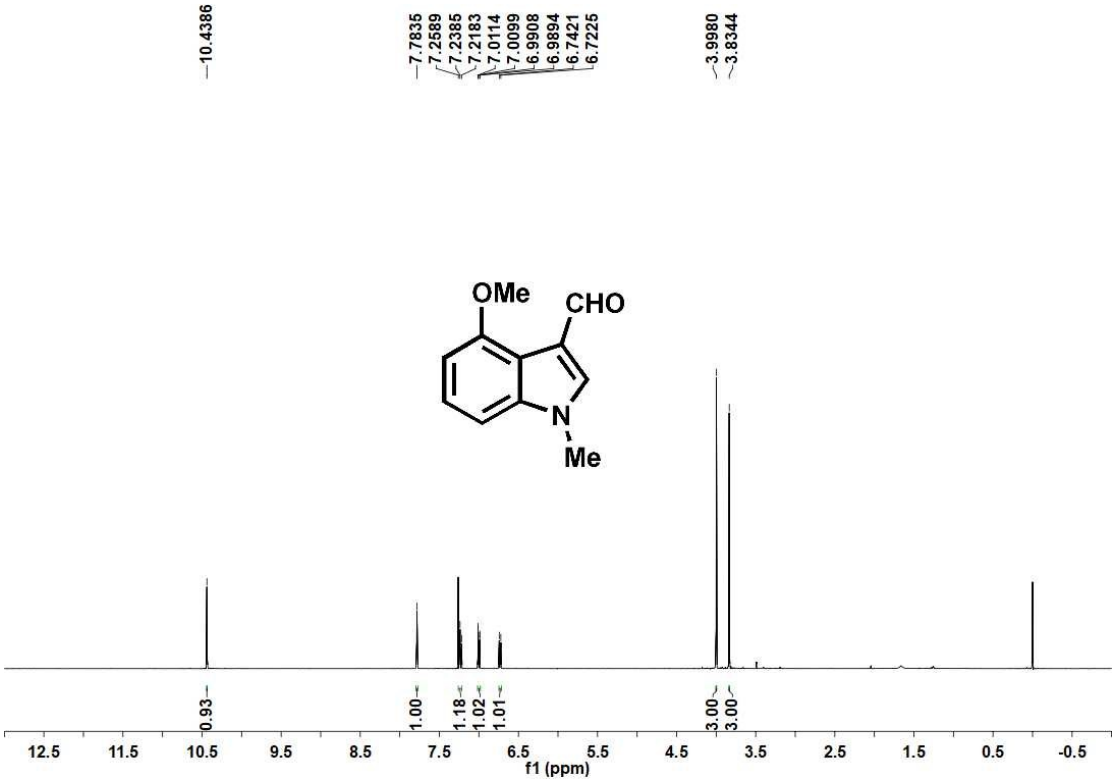


^{1}H NMR of product 2k in $CDCl_3$ (400 MHz)



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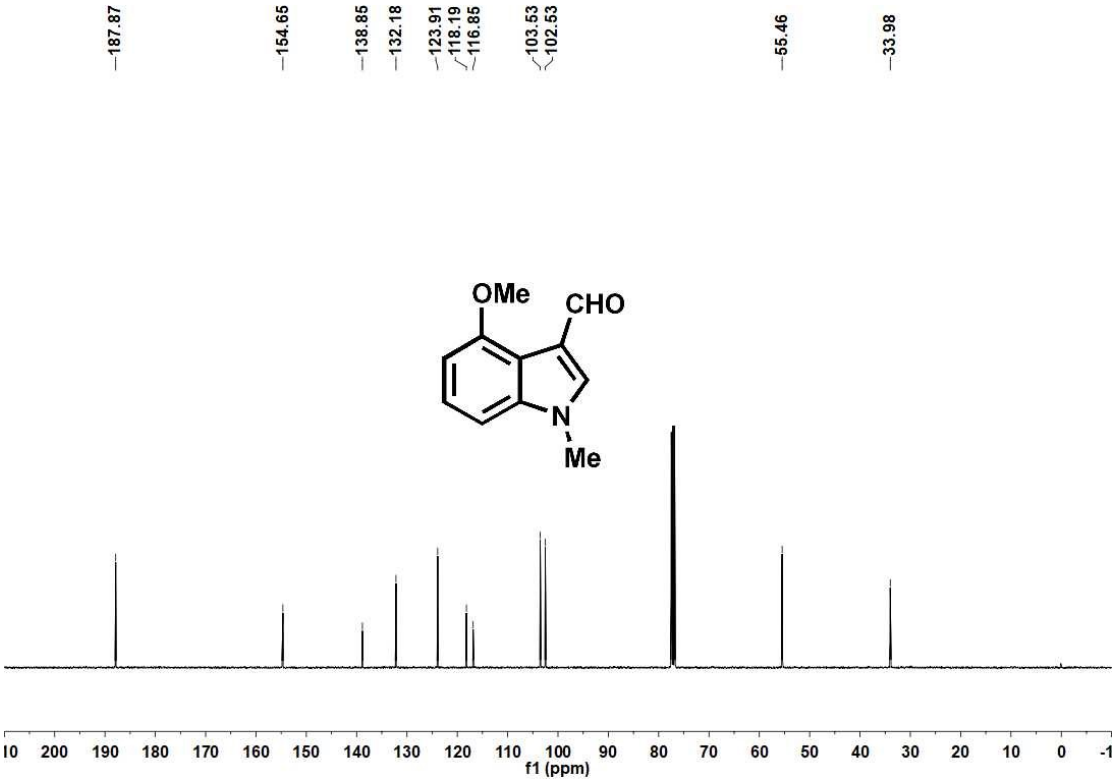

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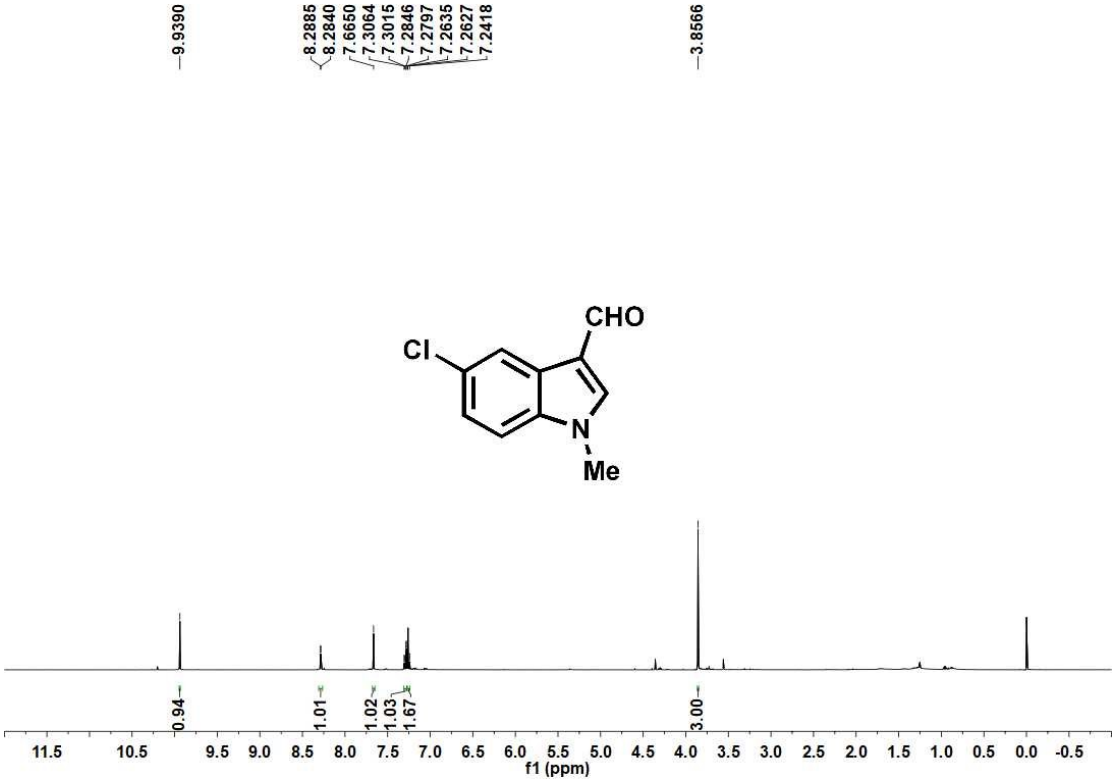

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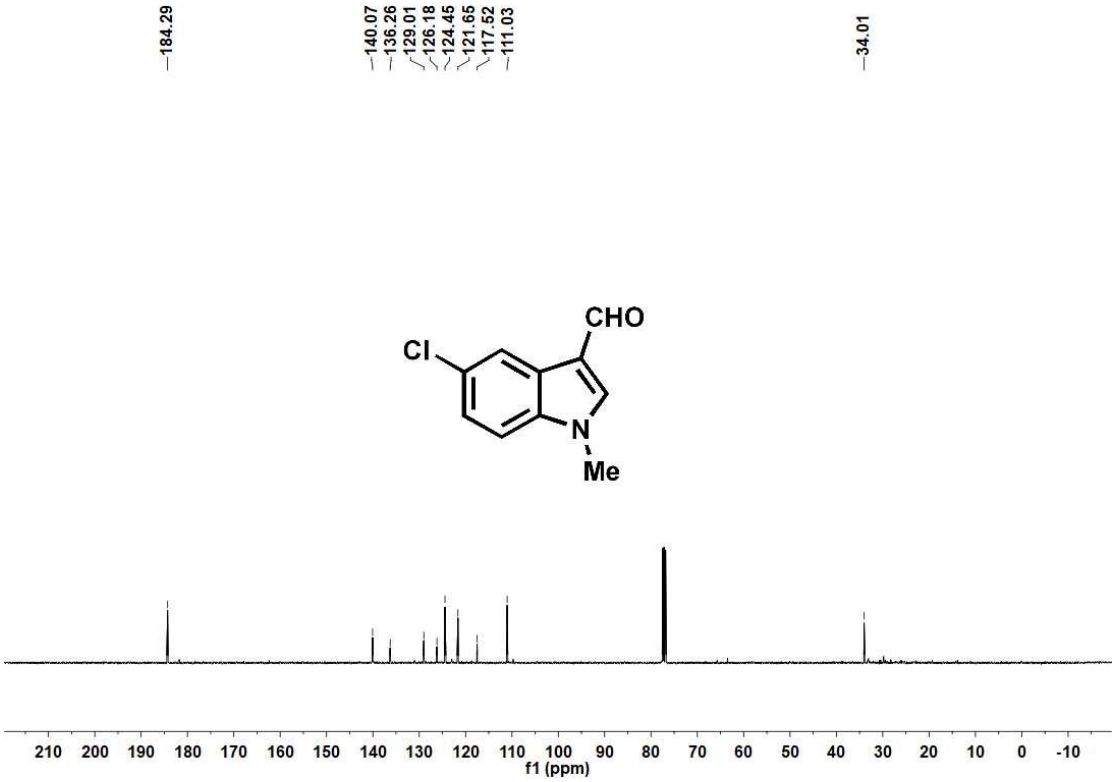

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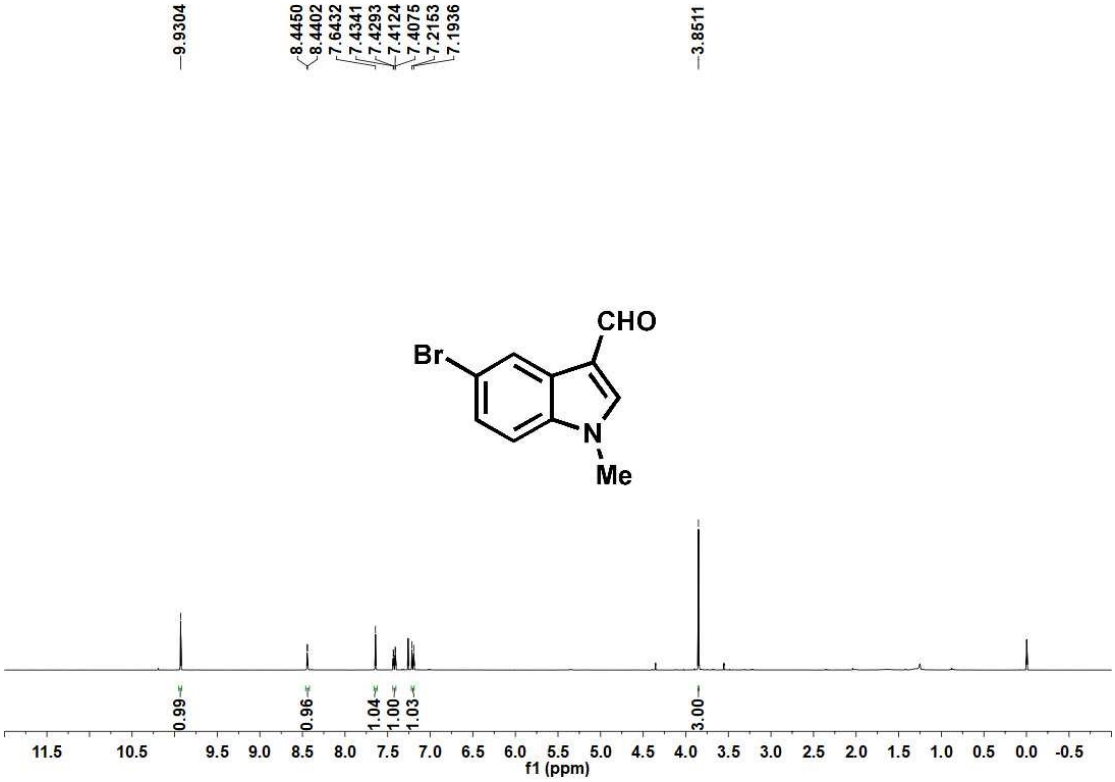
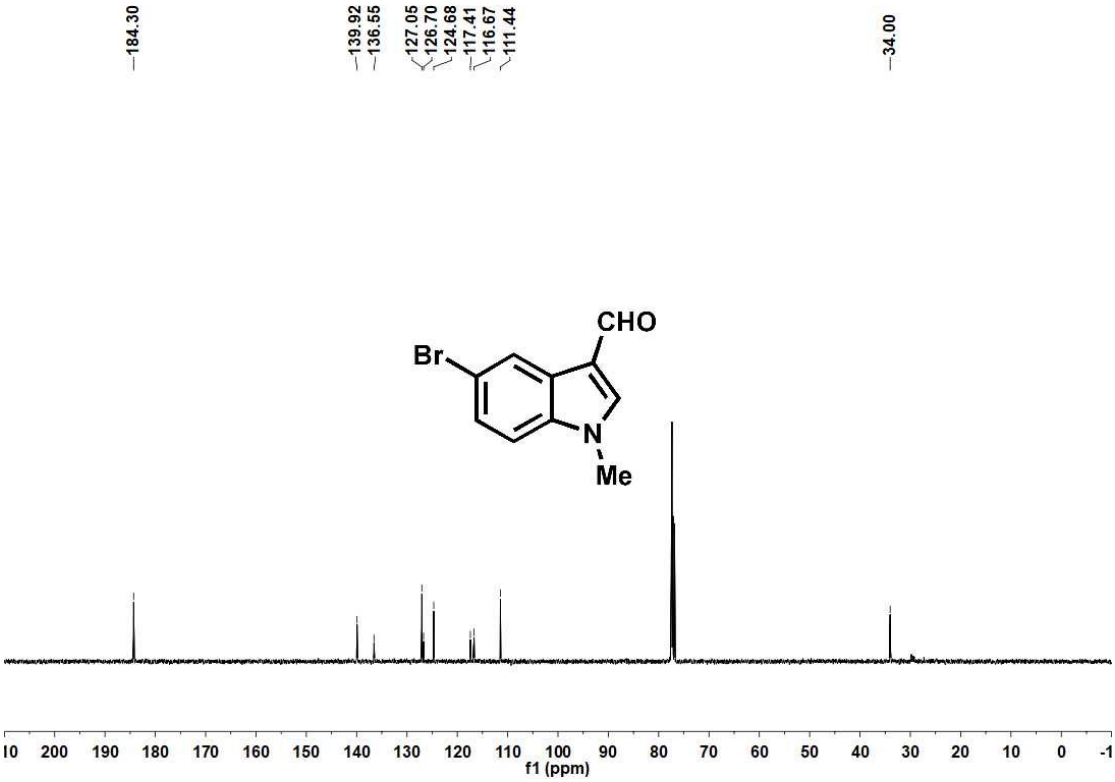


^{13}C NMR of product 2m in $CDCl_3$ (100 MHz)



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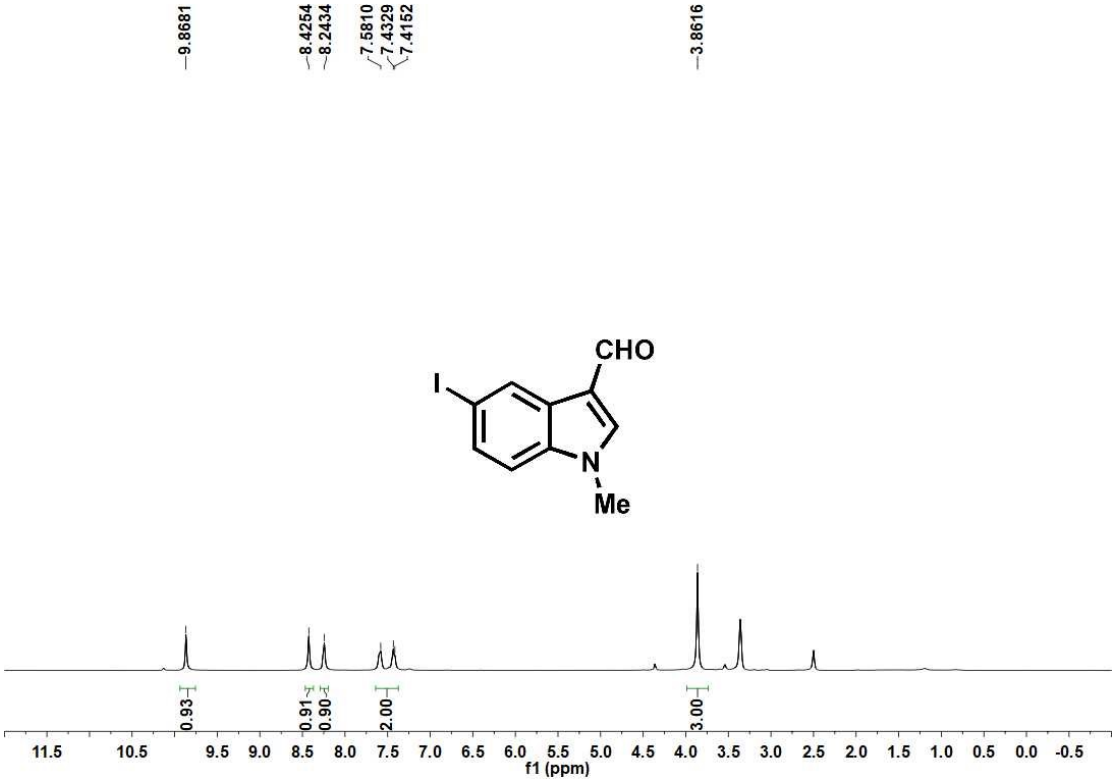

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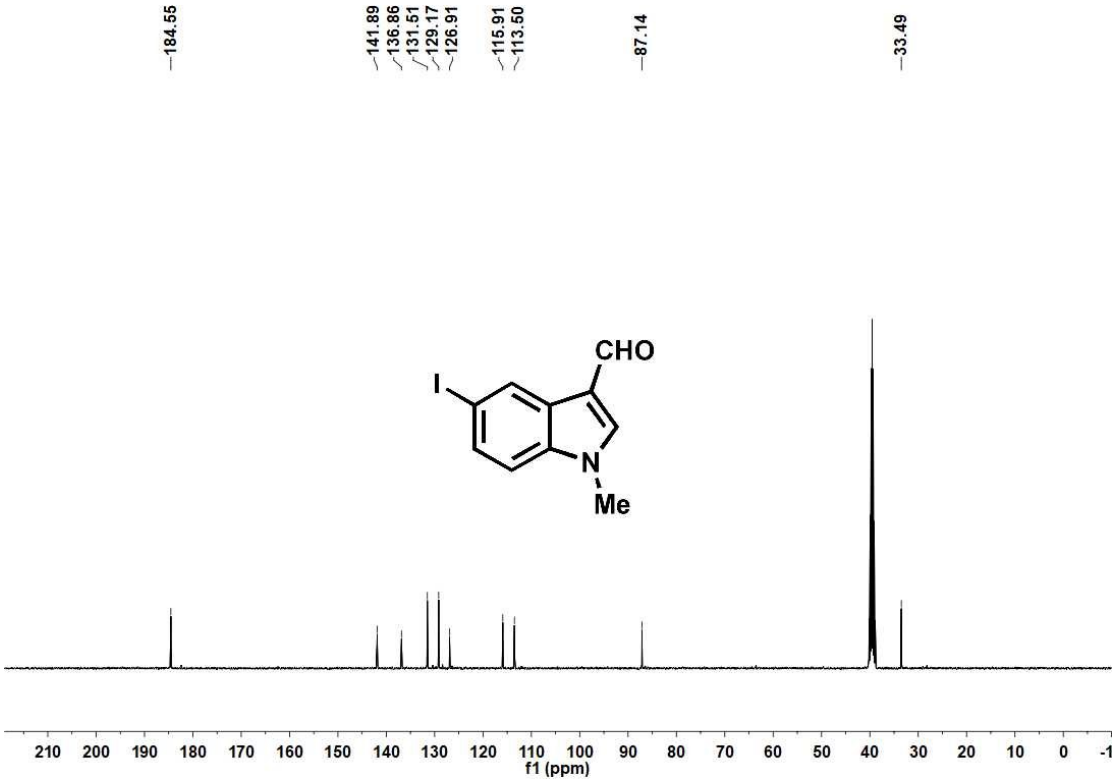

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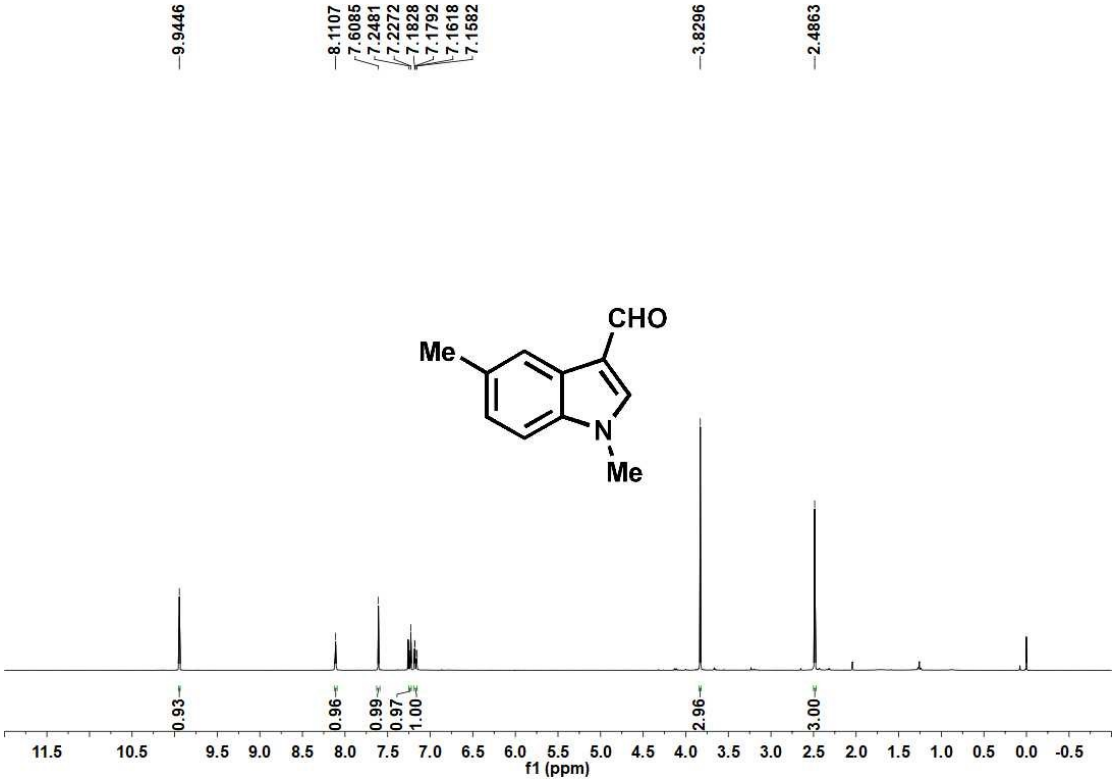

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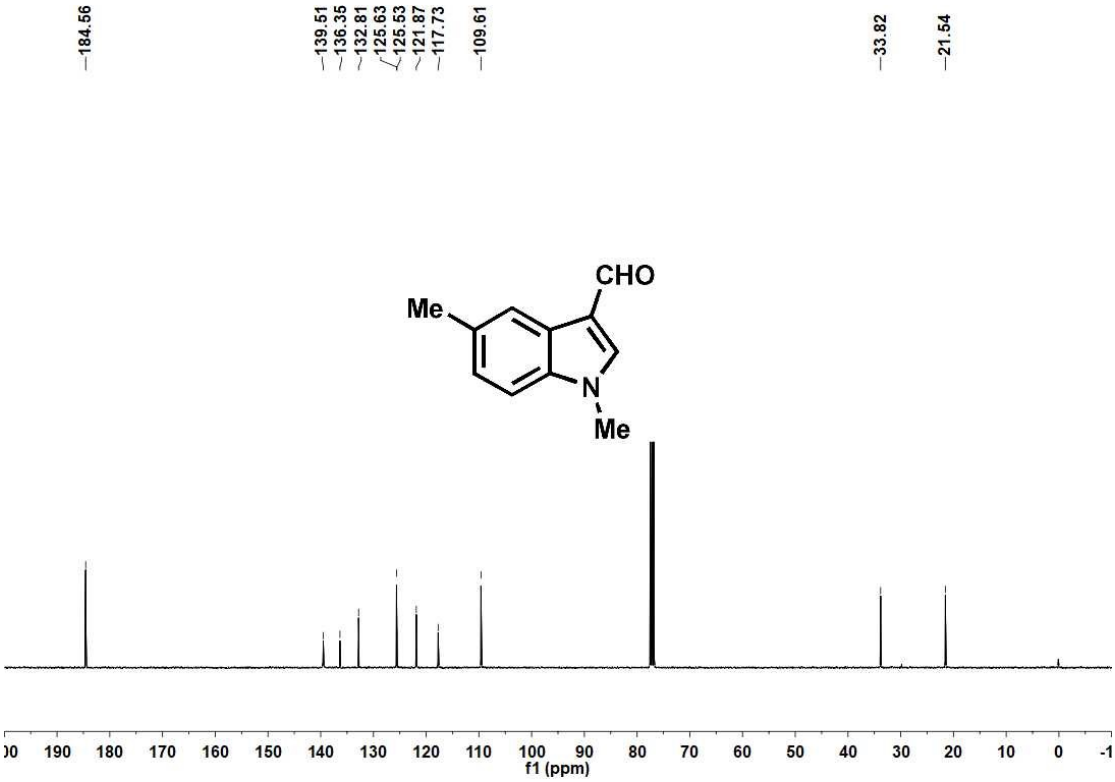

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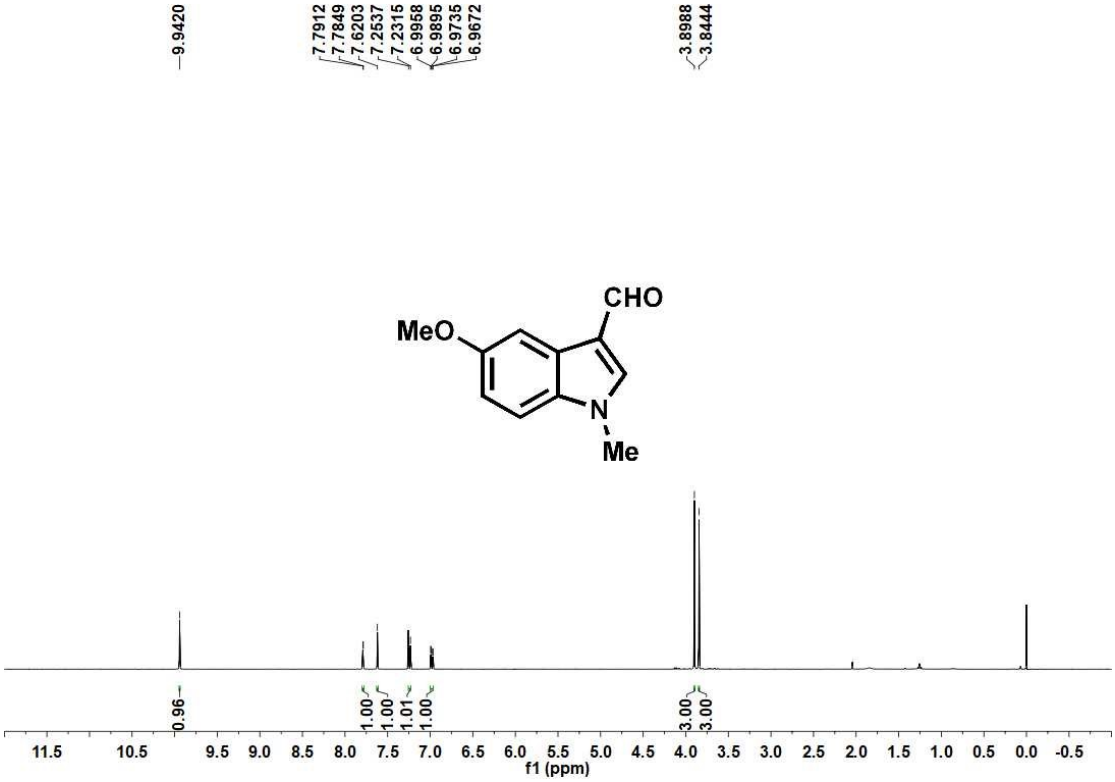

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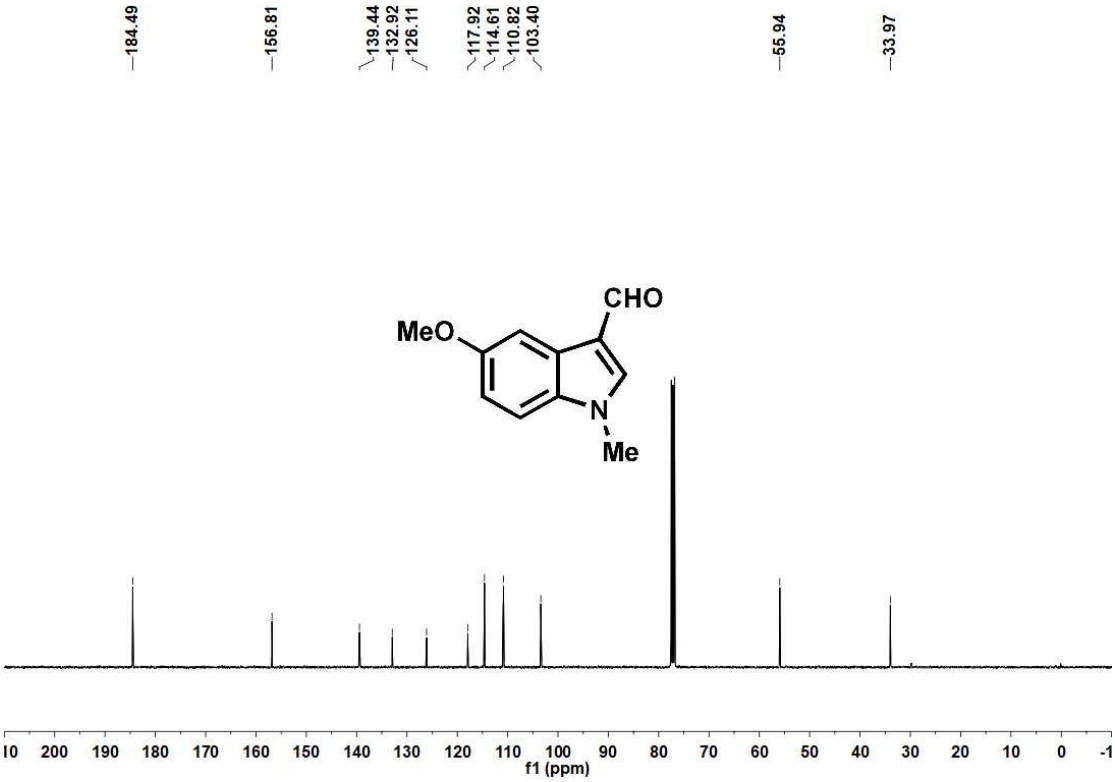

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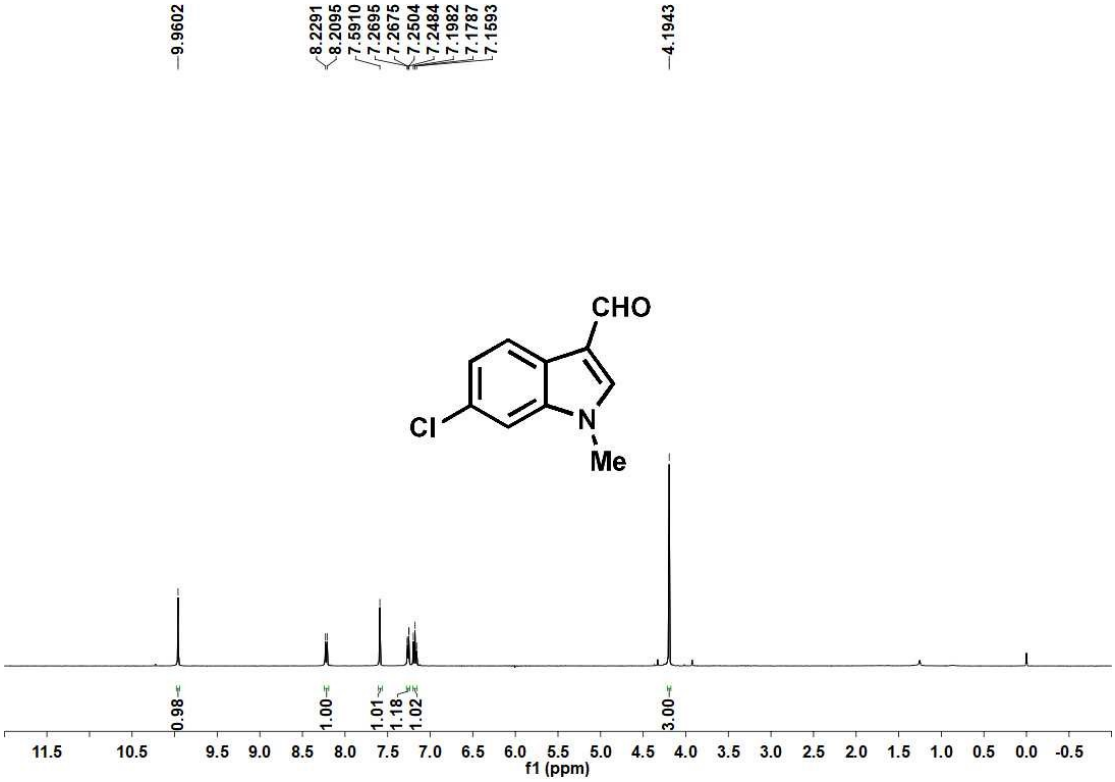
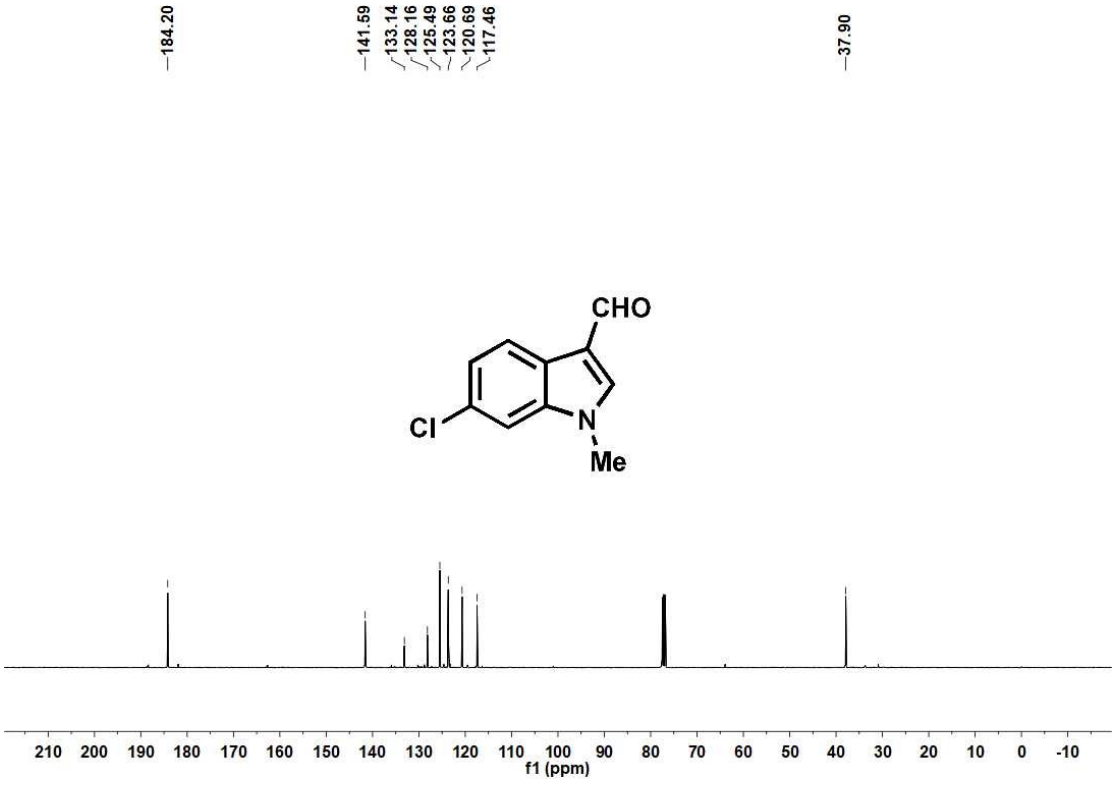


^{13}C NMR of product 2q in $CDCl_3$ (100 MHz)



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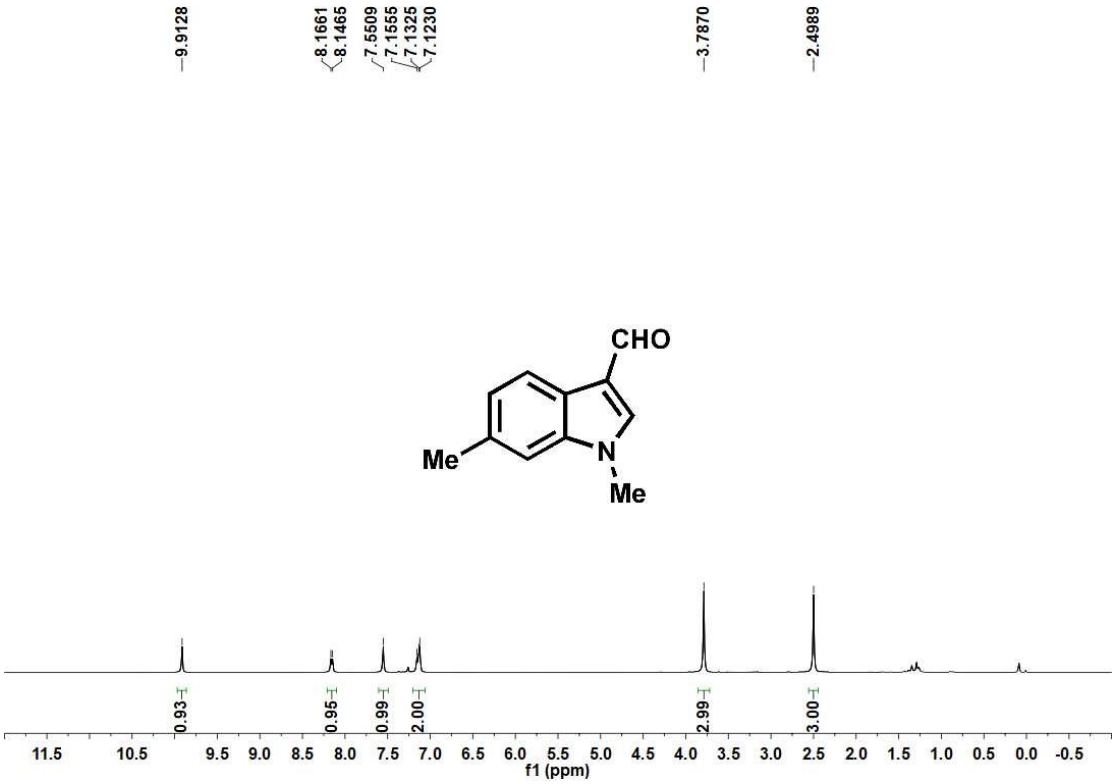

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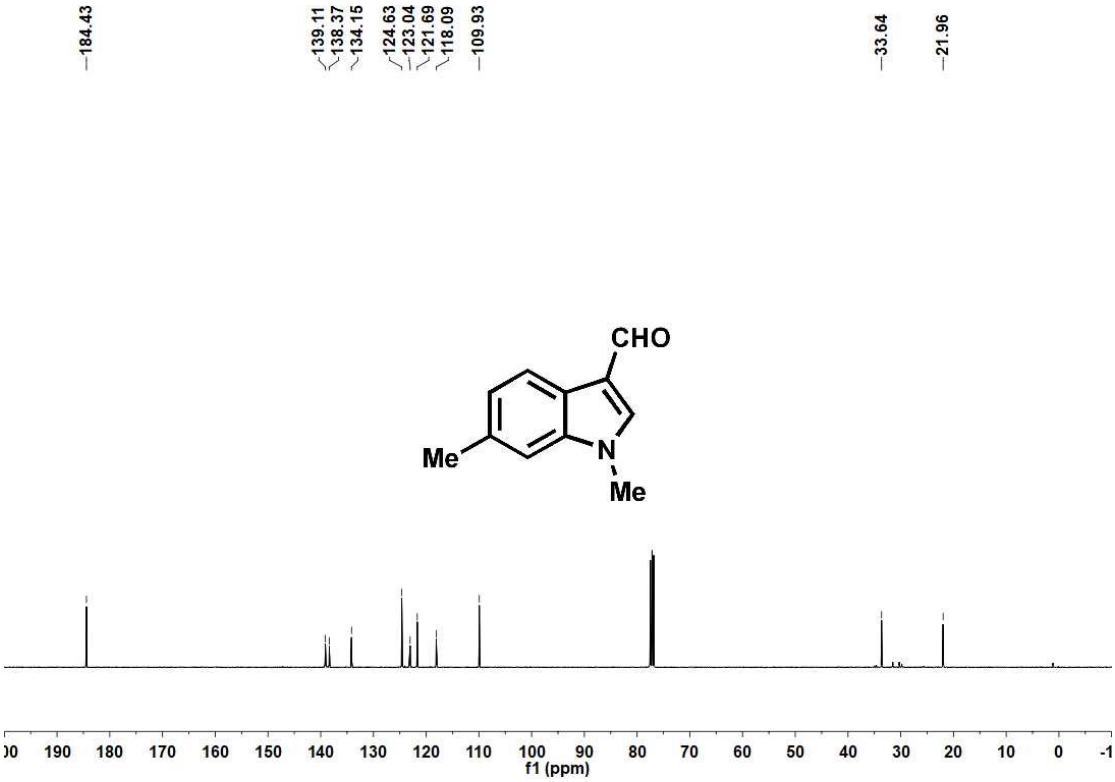
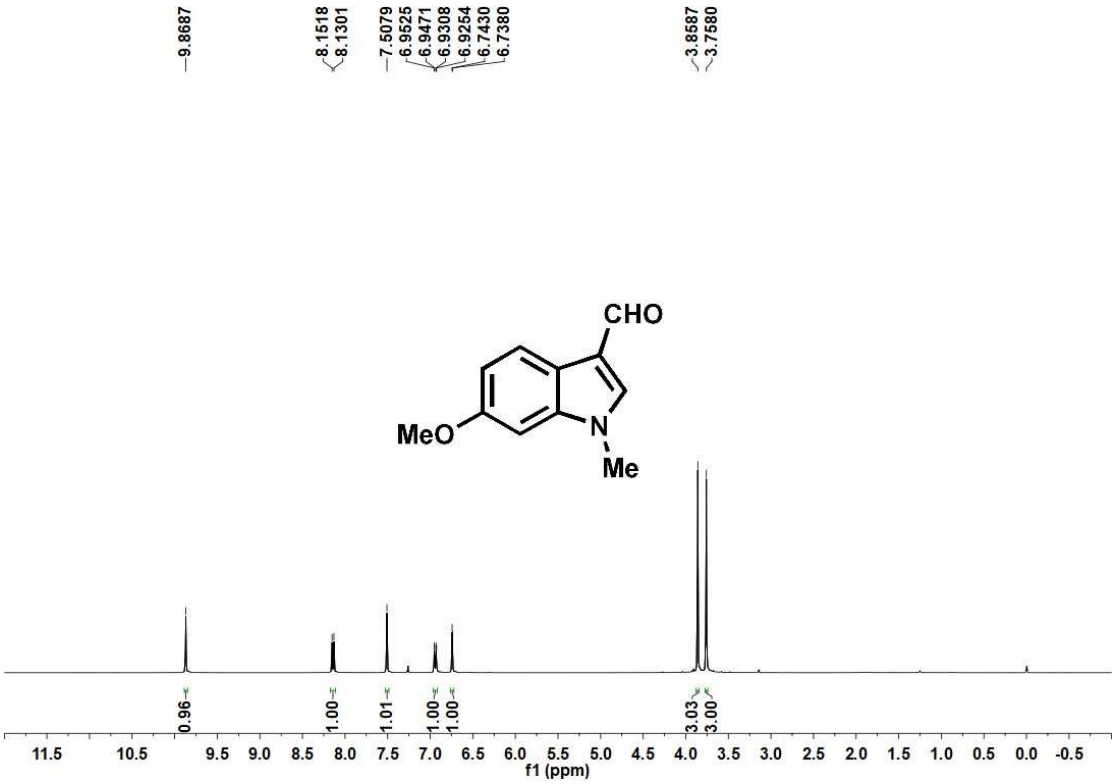
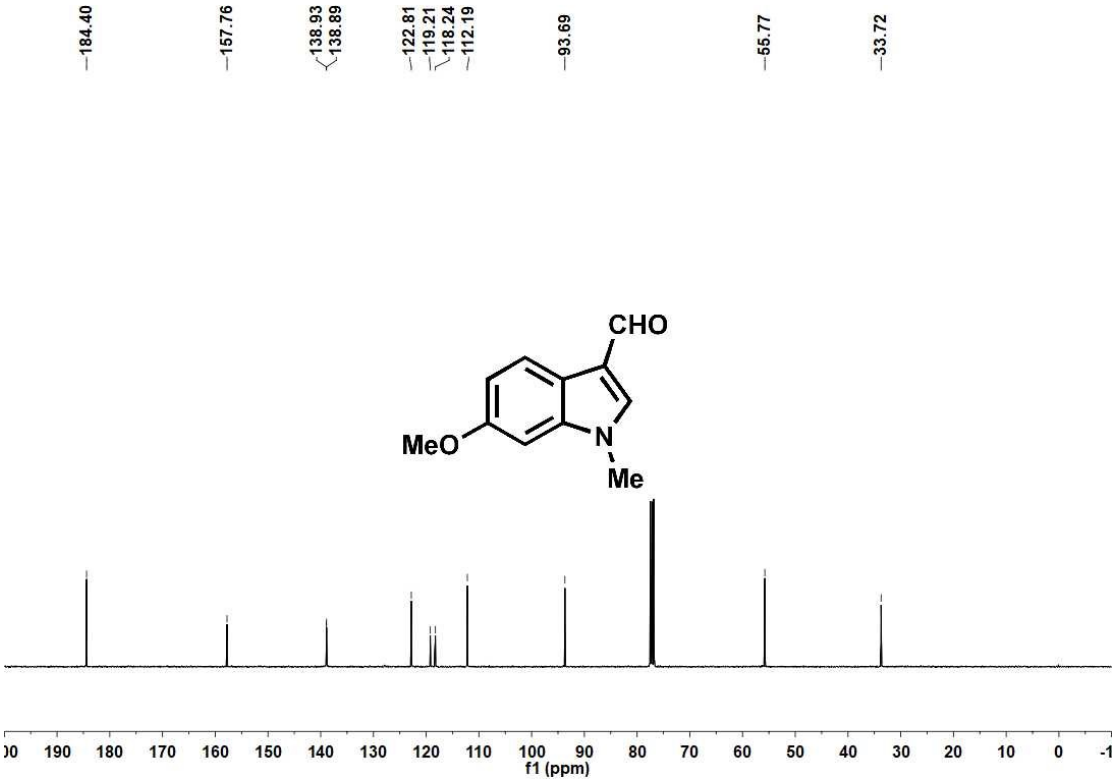


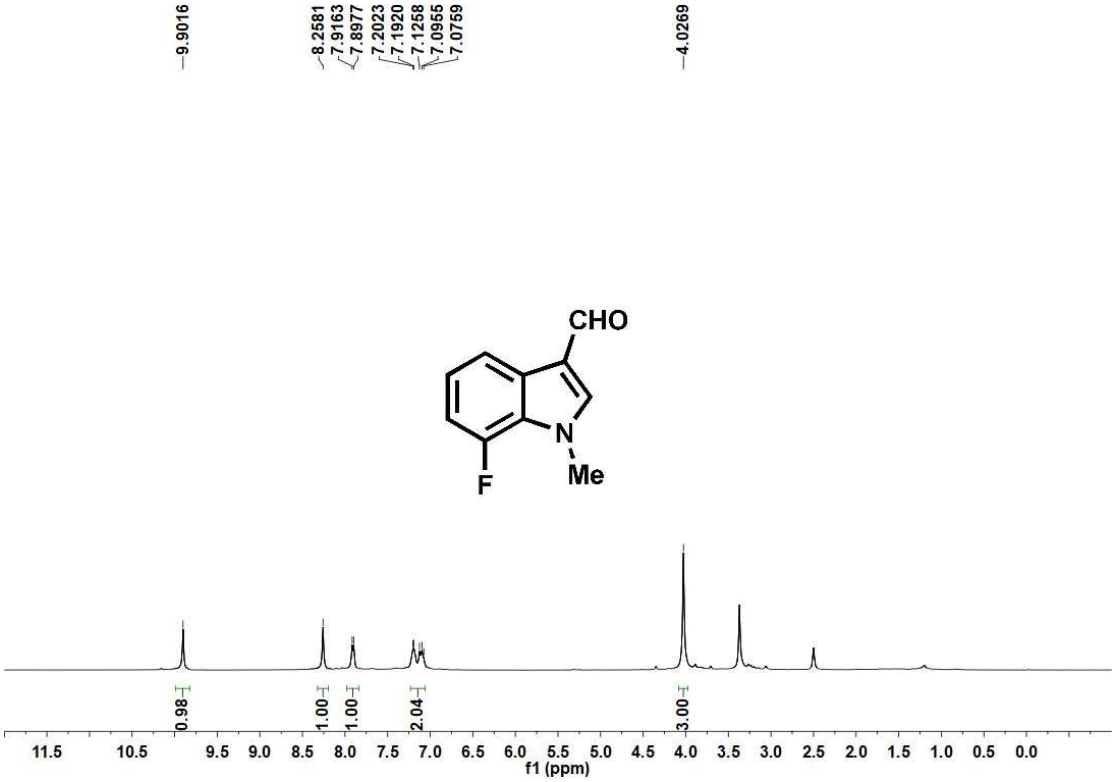
^{1}H NMR of product 2s in $CDCl_3$ (400 MHz)



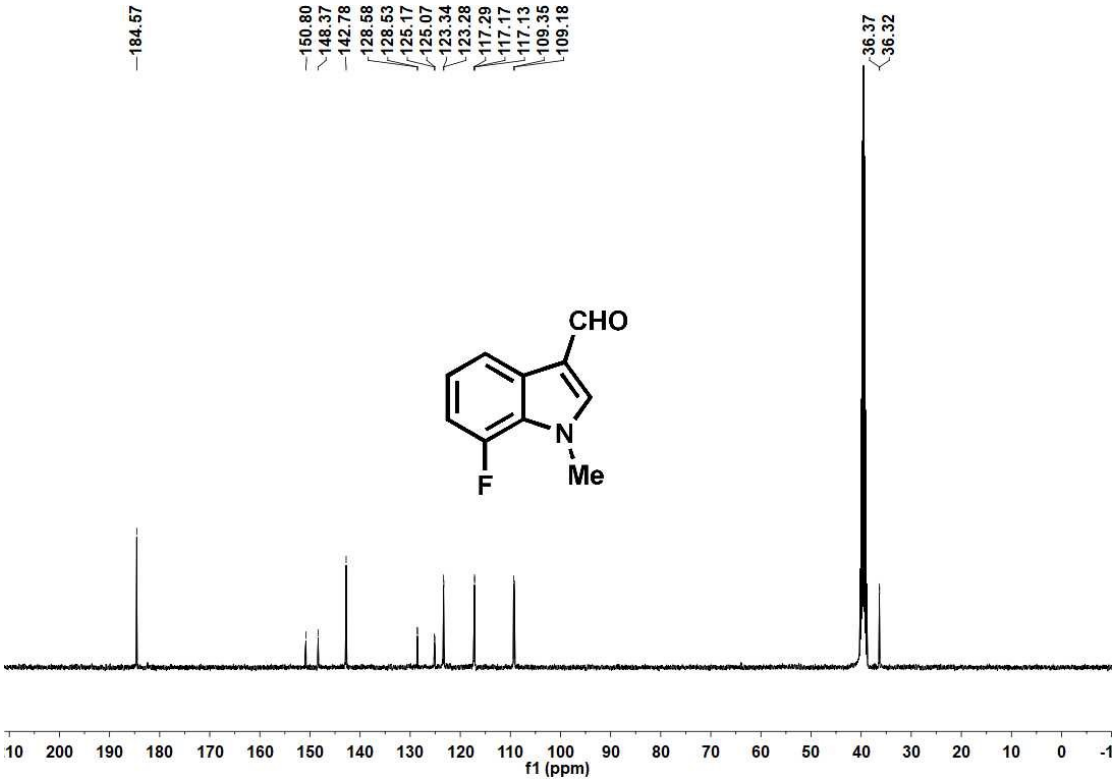
^{13}C NMR of product 2s in $CDCl_3$ (100 MHz)



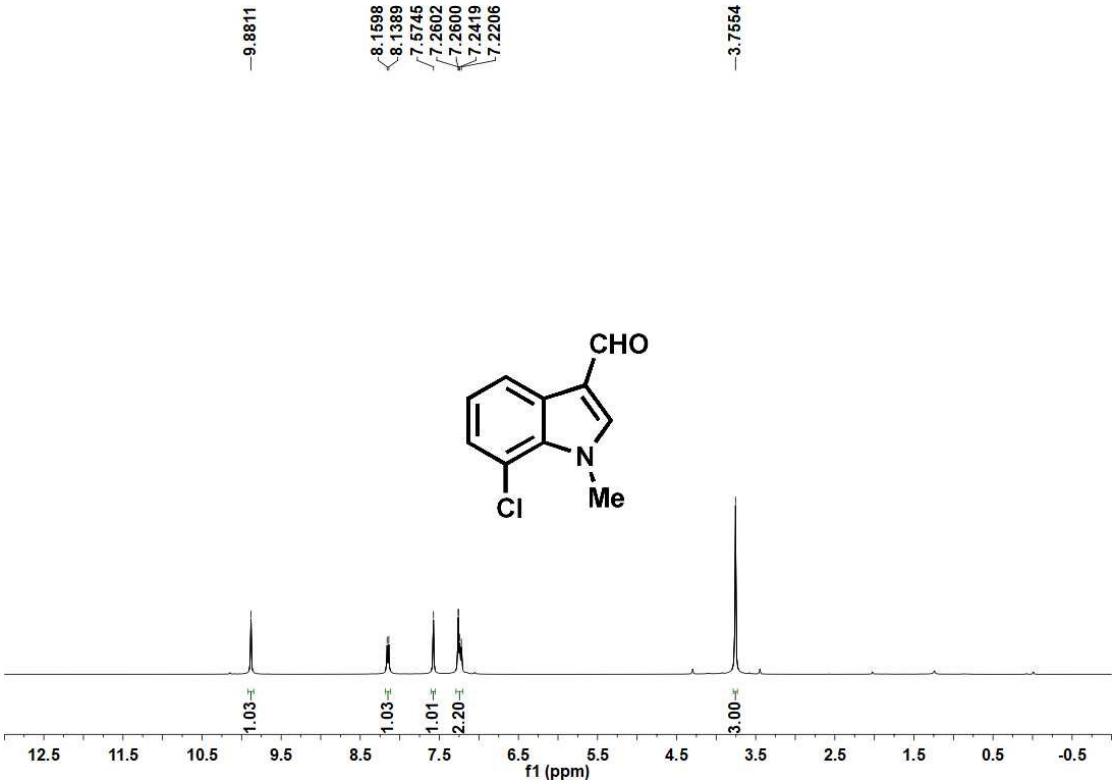
^{1}H NMR of product 2t in DMSO-d_6 (400 MHz)



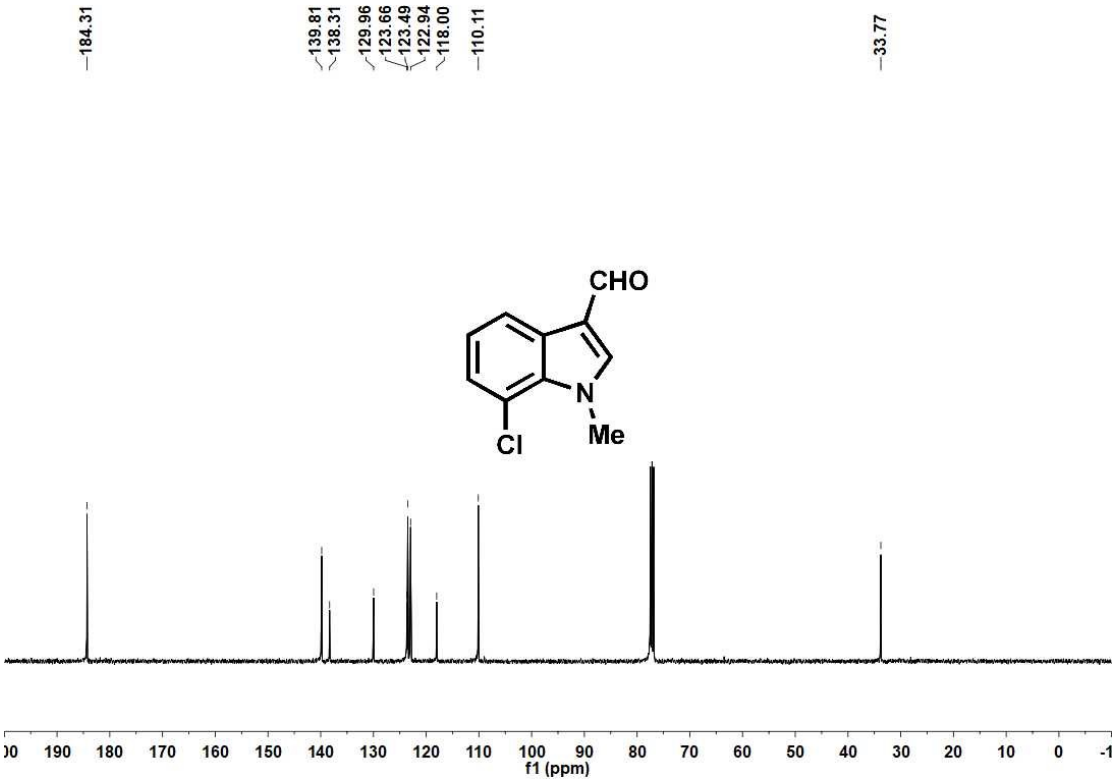
^{13}C NMR of product 2t in DMSO-d_6 (100 MHz)



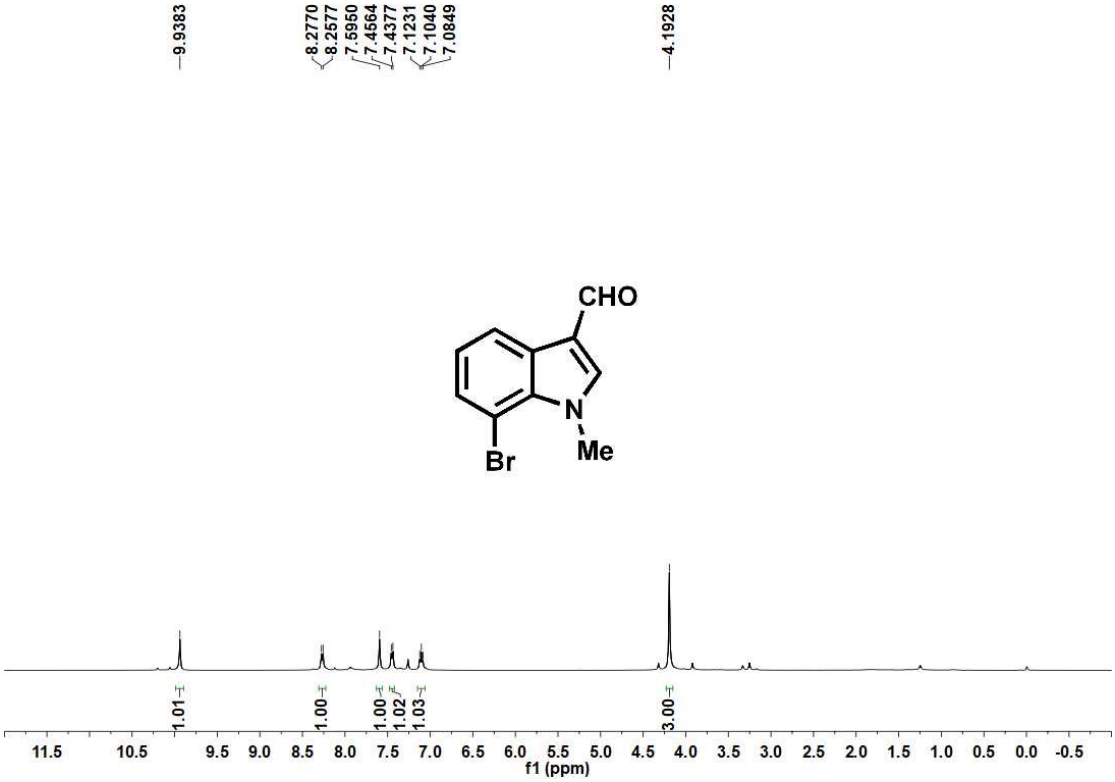
^{1}H NMR of product 2u in $CDCl_3$ (400 MHz)



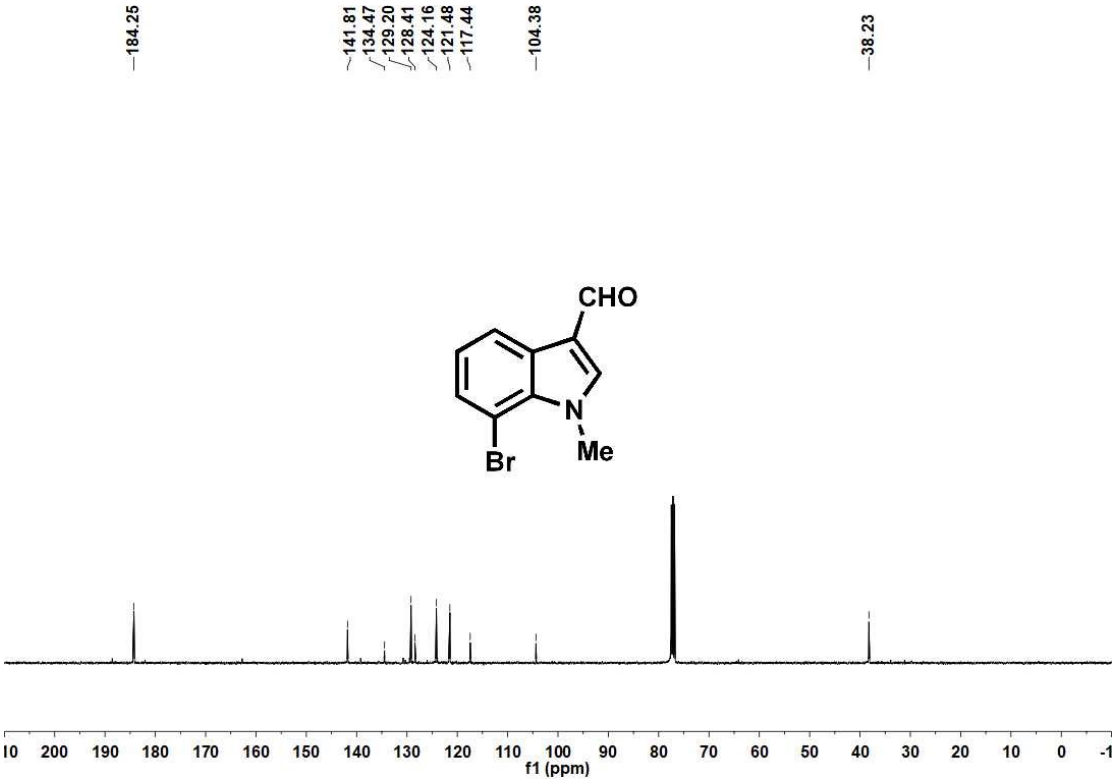
^{13}C NMR of product 2u in $CDCl_3$ (100 MHz)



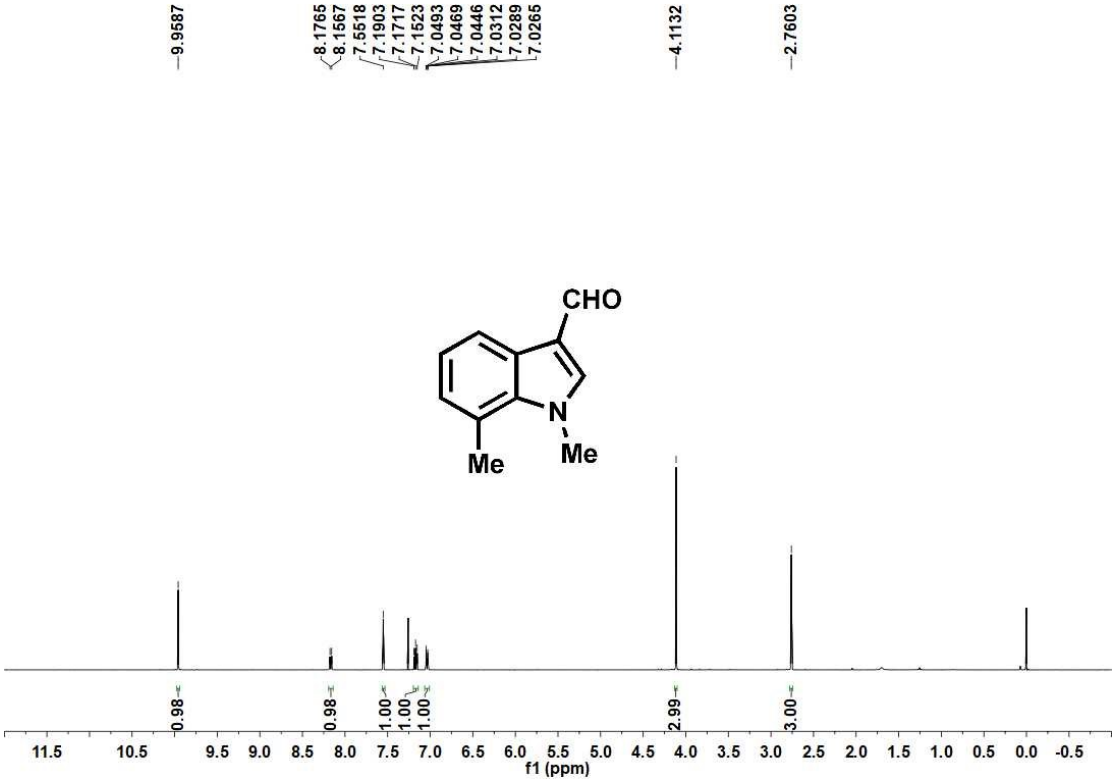
^{1}H NMR of product 2v in $CDCl_3$ (400 MHz)



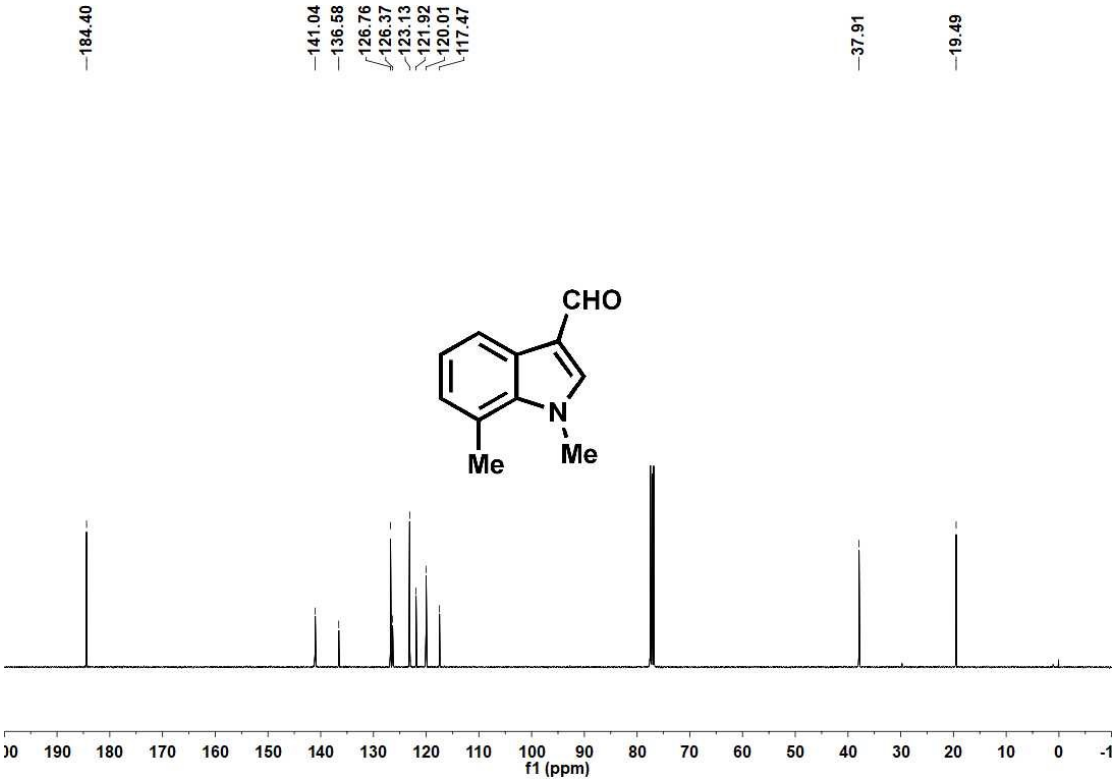
^{13}C NMR of product 2v in $CDCl_3$ (100 MHz)



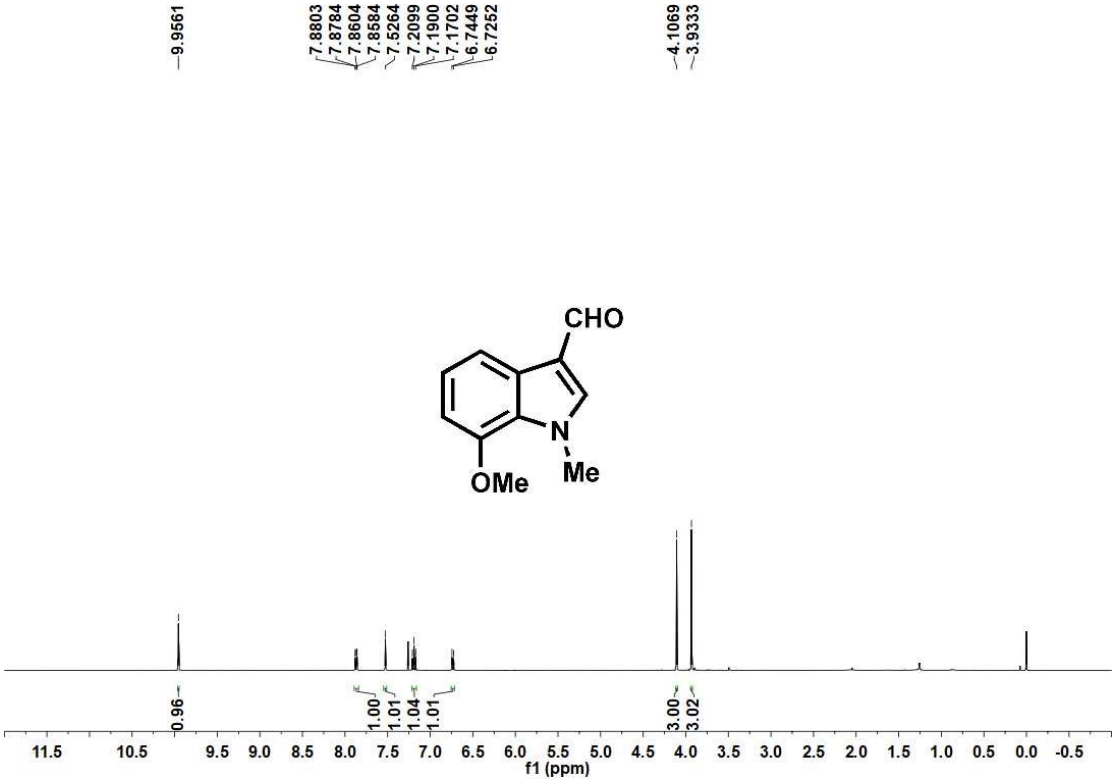
^{1}H NMR of product 2w in $CDCl_3$ (400 MHz)



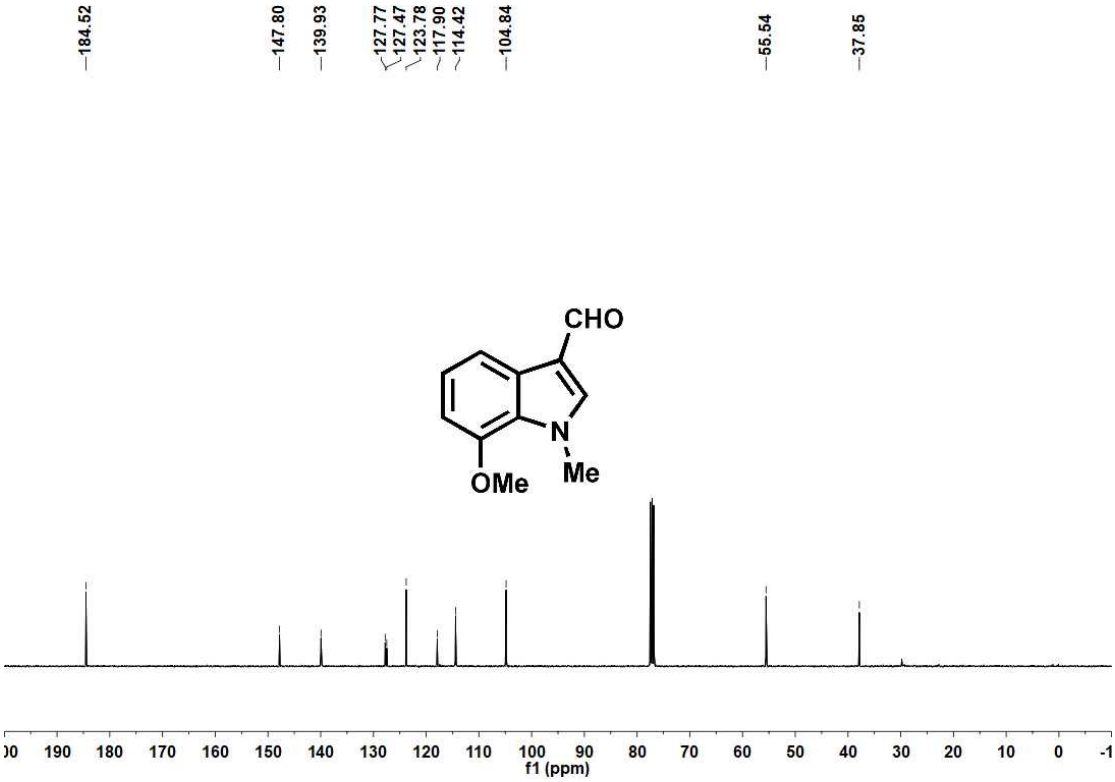
^{13}C NMR of product 2w in $CDCl_3$ (100 MHz)



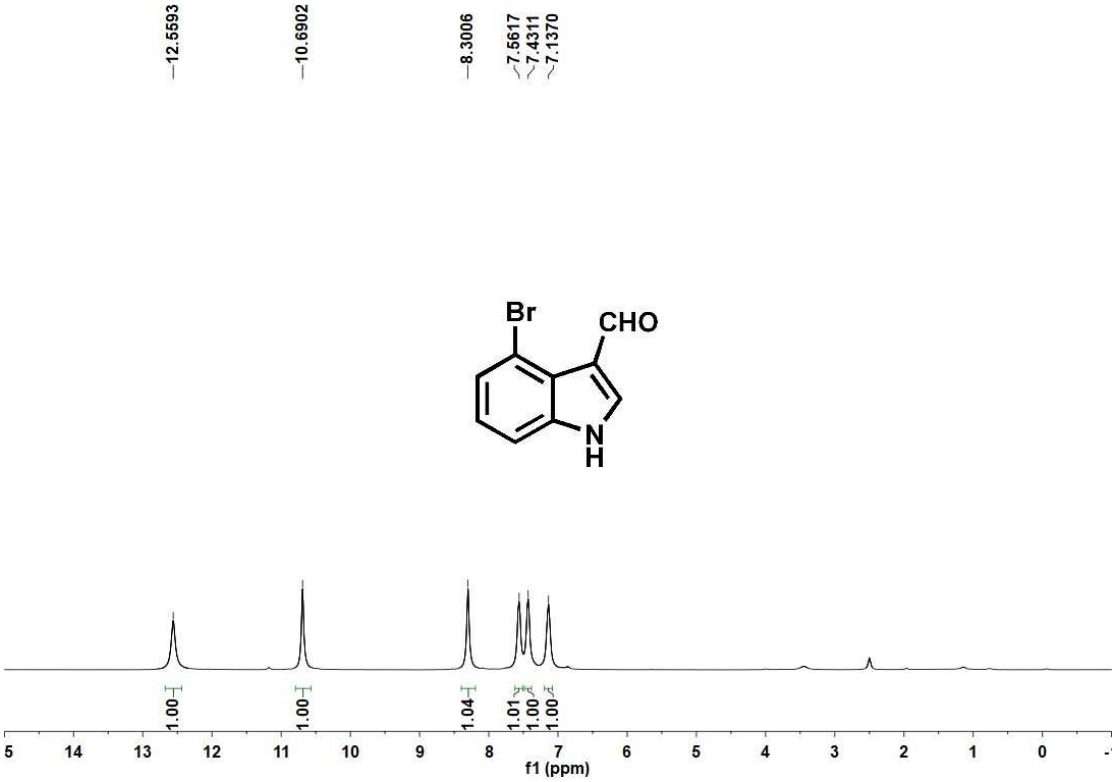
^{1}H NMR of product 2x in $CDCl_3$ (400 MHz)



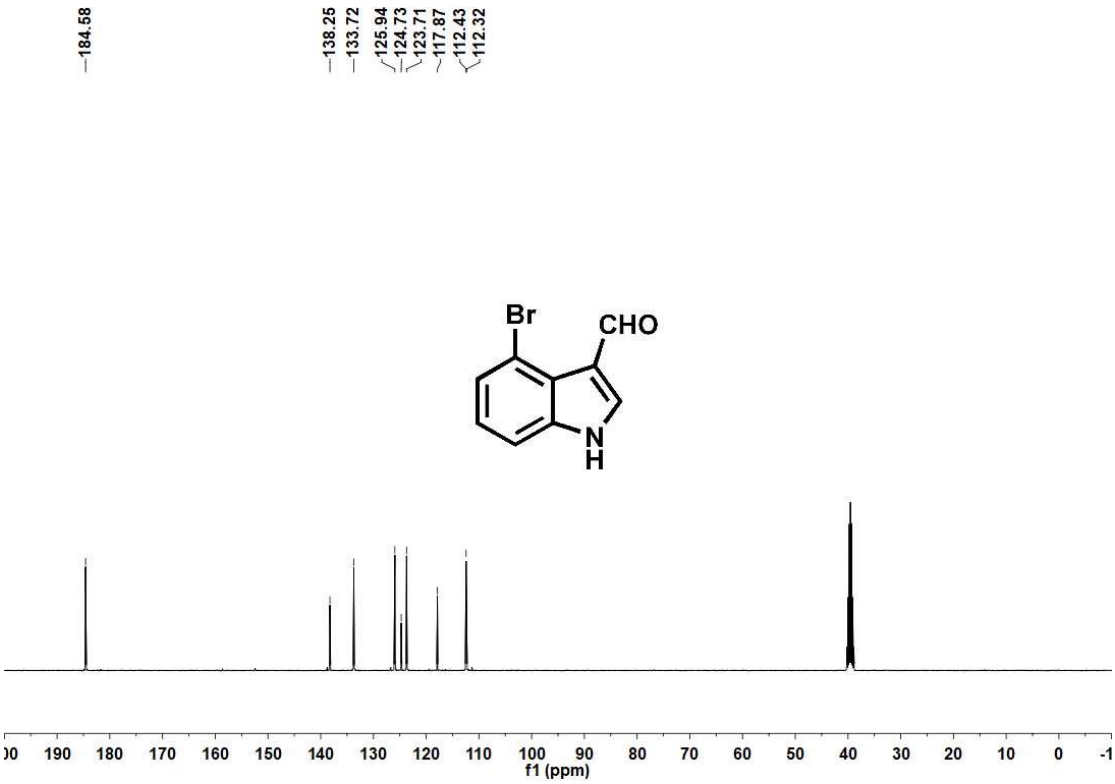
^{13}C NMR of product 2x in $CDCl_3$ (100 MHz)



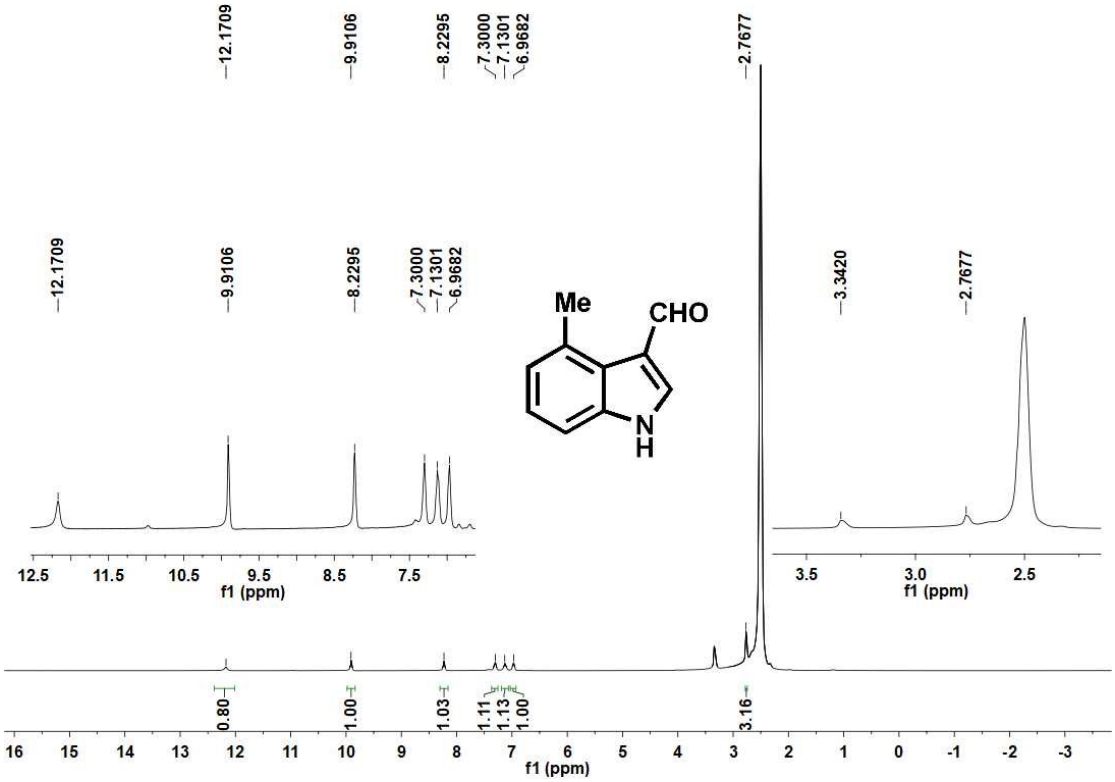
^{1}H NMR of product 2y in DMSO-d_6 (400 MHz)



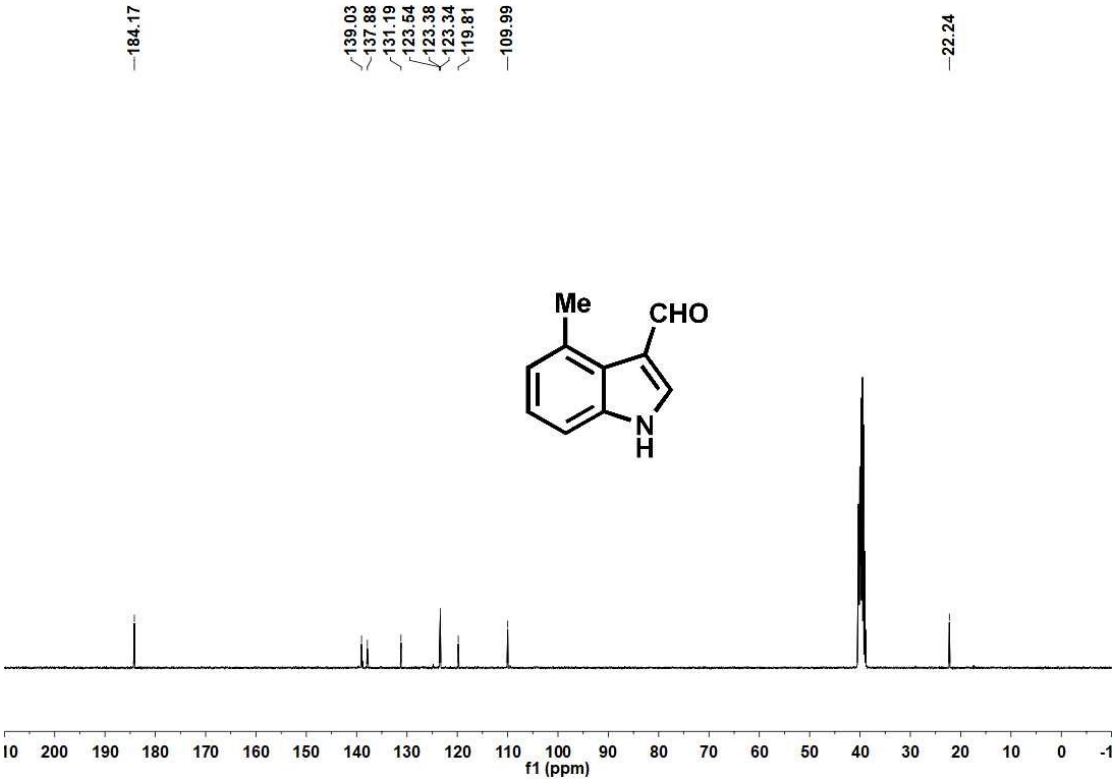
^{13}C NMR of product 2y in DMSO-d_6 (100 MHz)



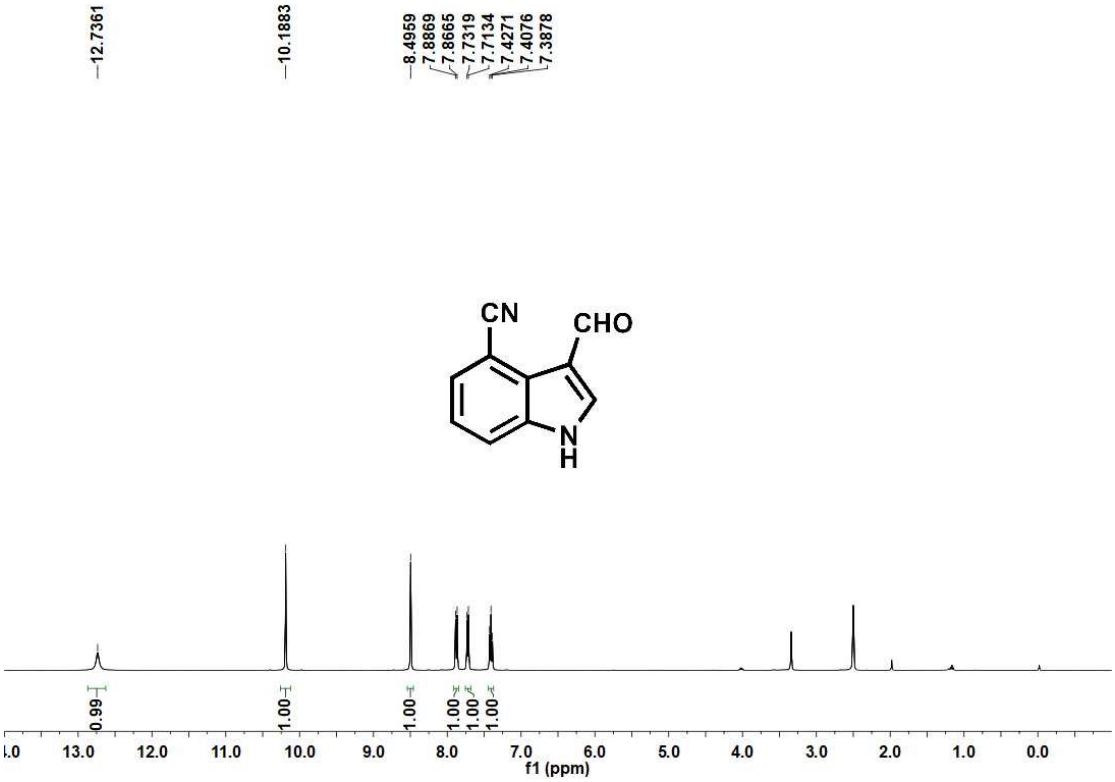
^{1}H NMR of product 2z in DMSO-d_6 (400 MHz)



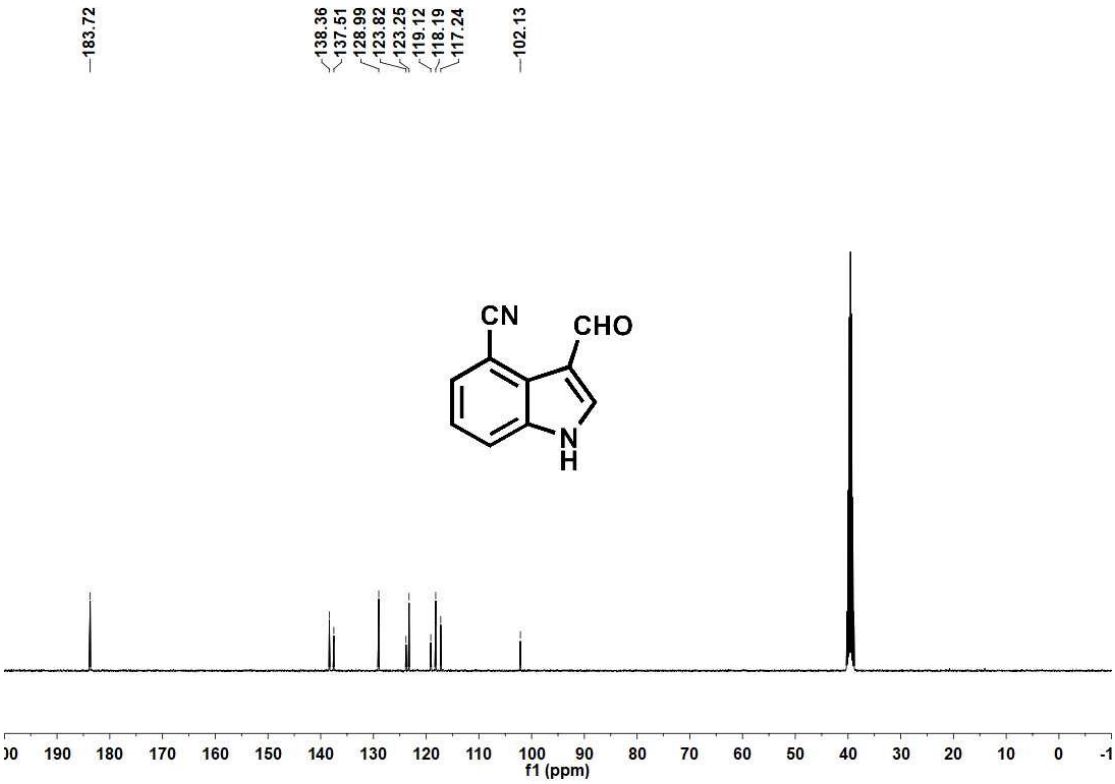
^{13}C NMR of product 2z in DMSO-d_6 (100 MHz)



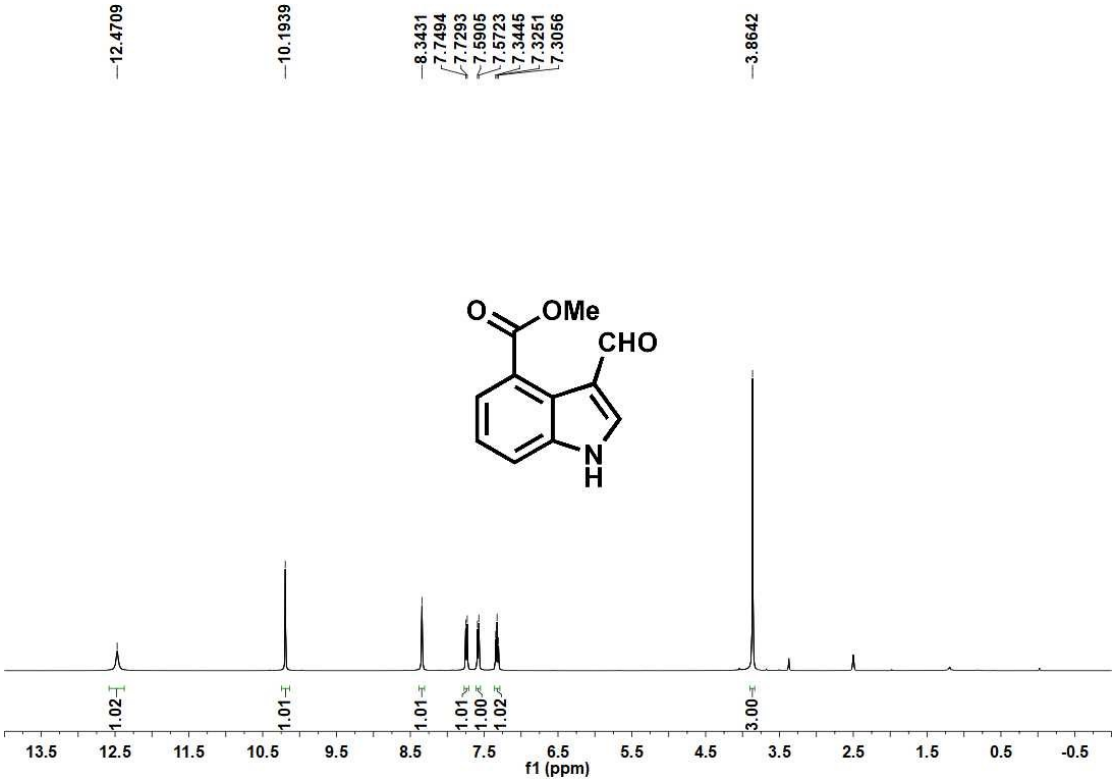
^{1}H NMR of product 2aa in DMSO-d_6 (400 MHz)



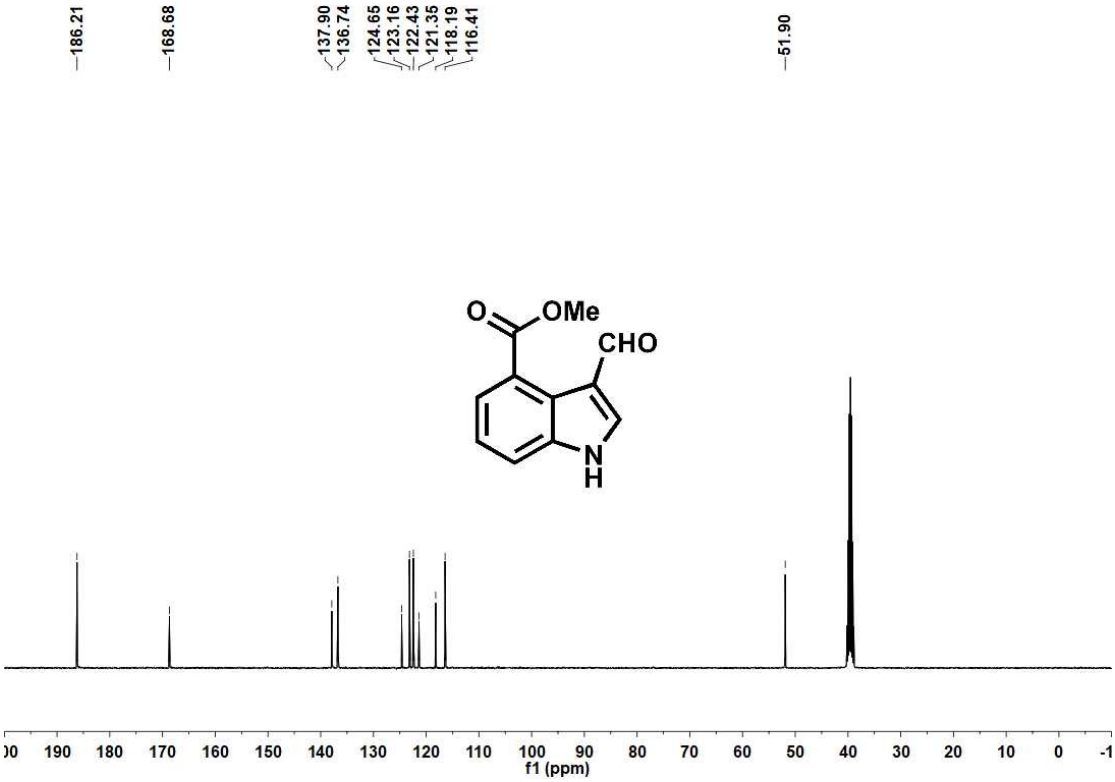
^{13}C NMR of product 2aa in DMSO-d_6 (100 MHz)



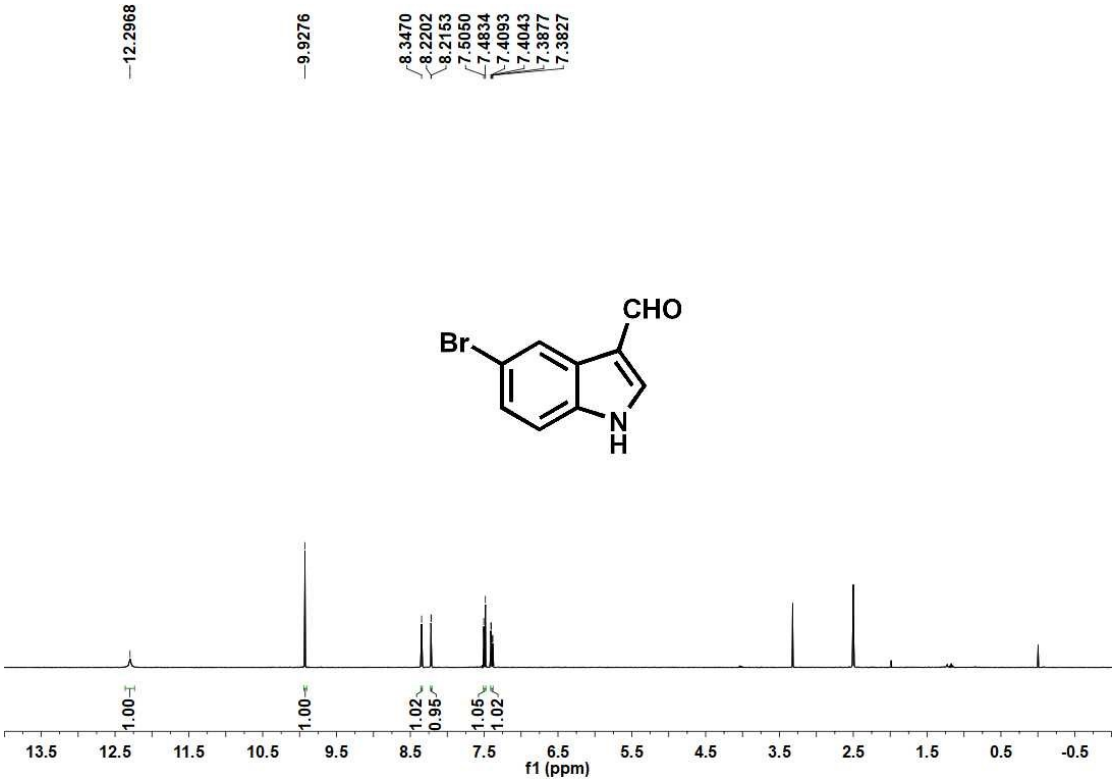
^{1}H NMR of product 2ab in DMSO-d_6 (400 MHz)



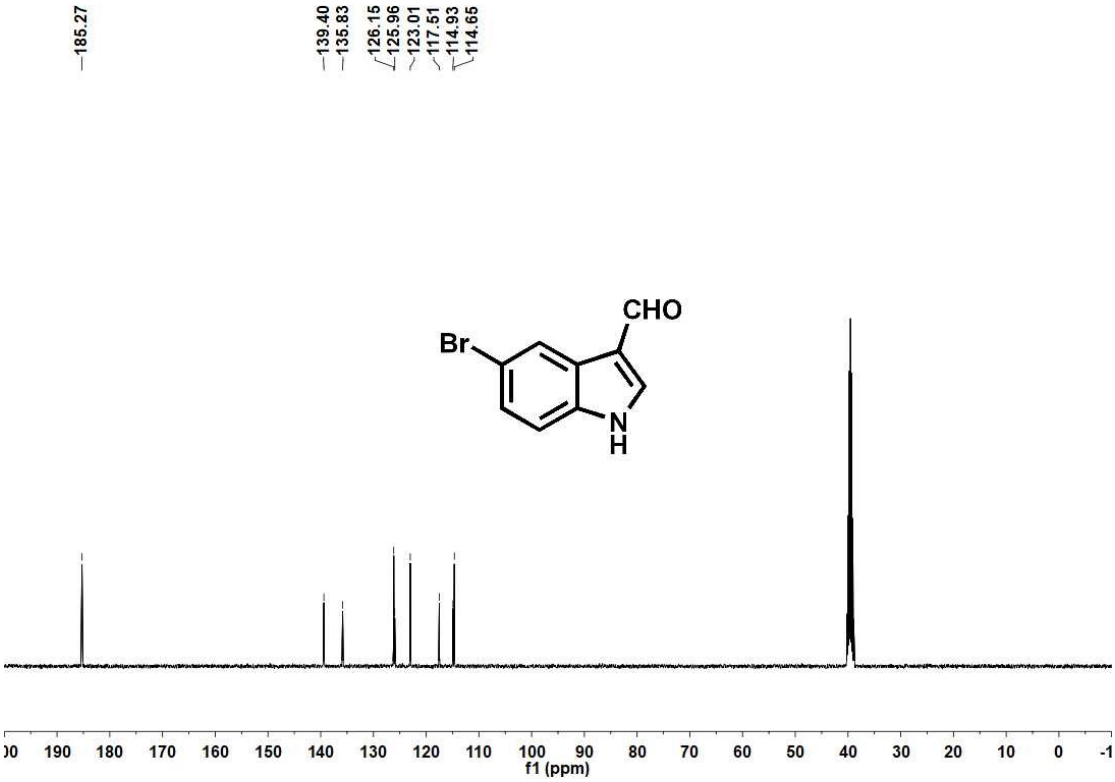
^{13}C NMR of product 2ab in DMSO-d_6 (100 MHz)



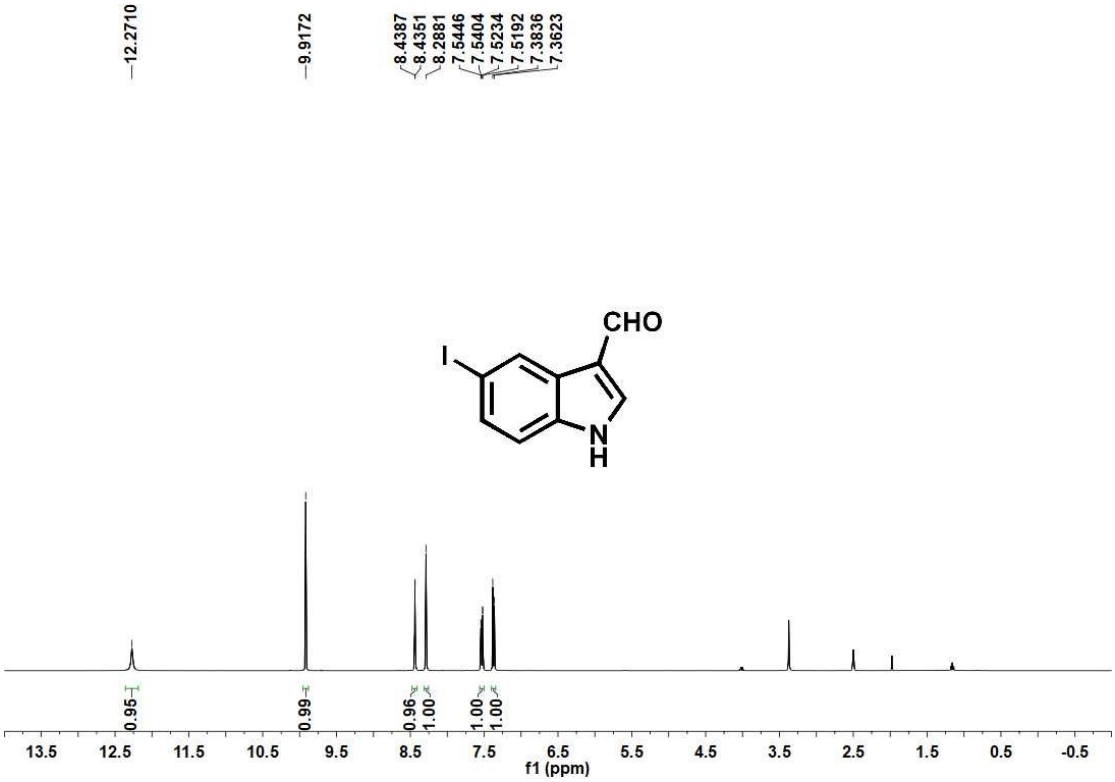
^{1}H NMR of product 2ac in DMSO-d_6 (400 MHz)



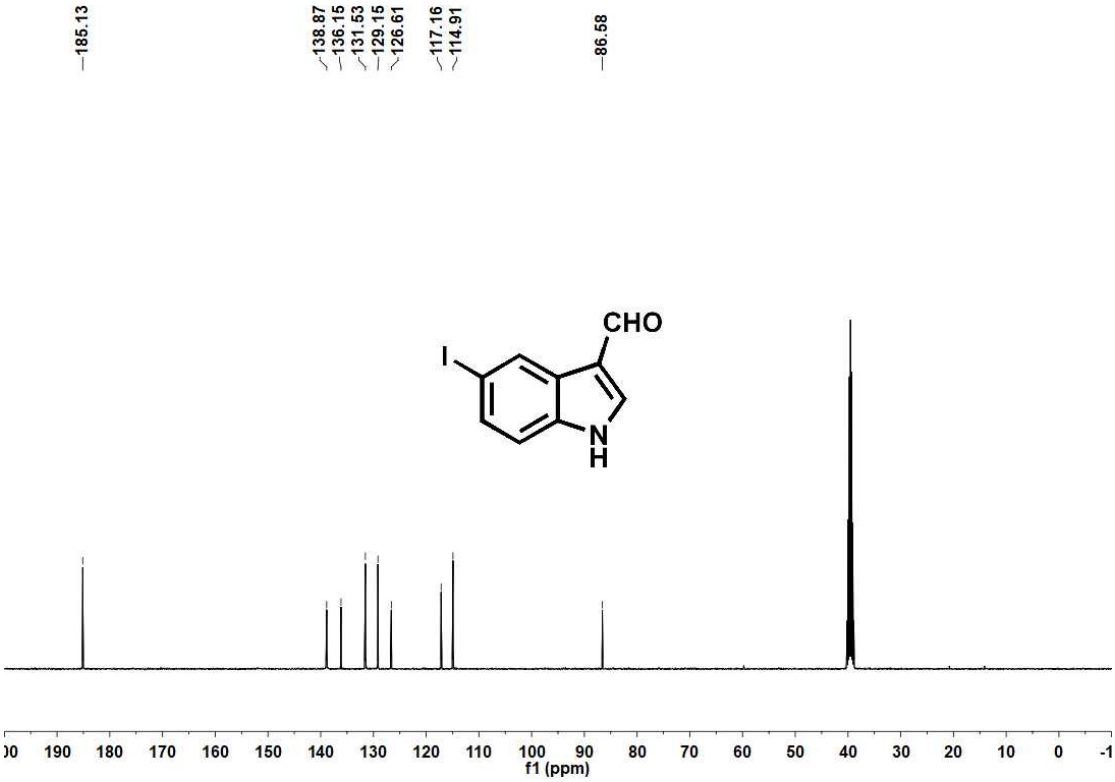
^{13}C NMR of product 2ac in DMSO-d_6 (100 MHz)



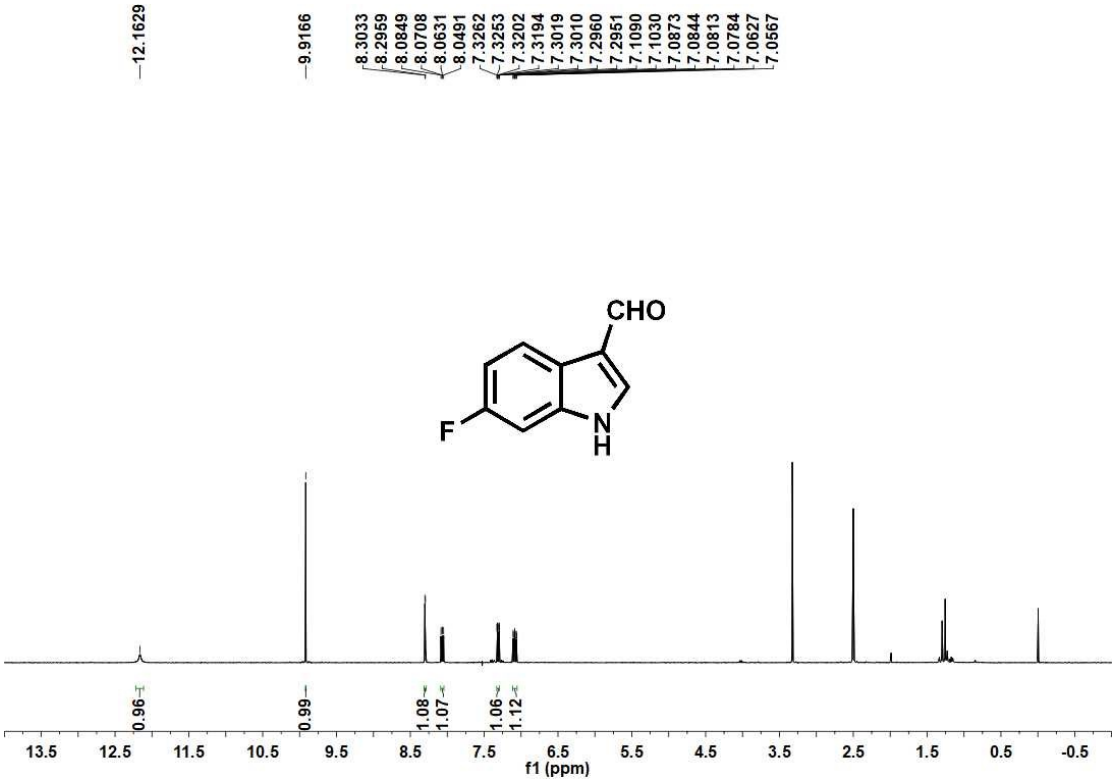
^{1}H NMR of product 2ad in DMSO-d_6 (400 MHz)



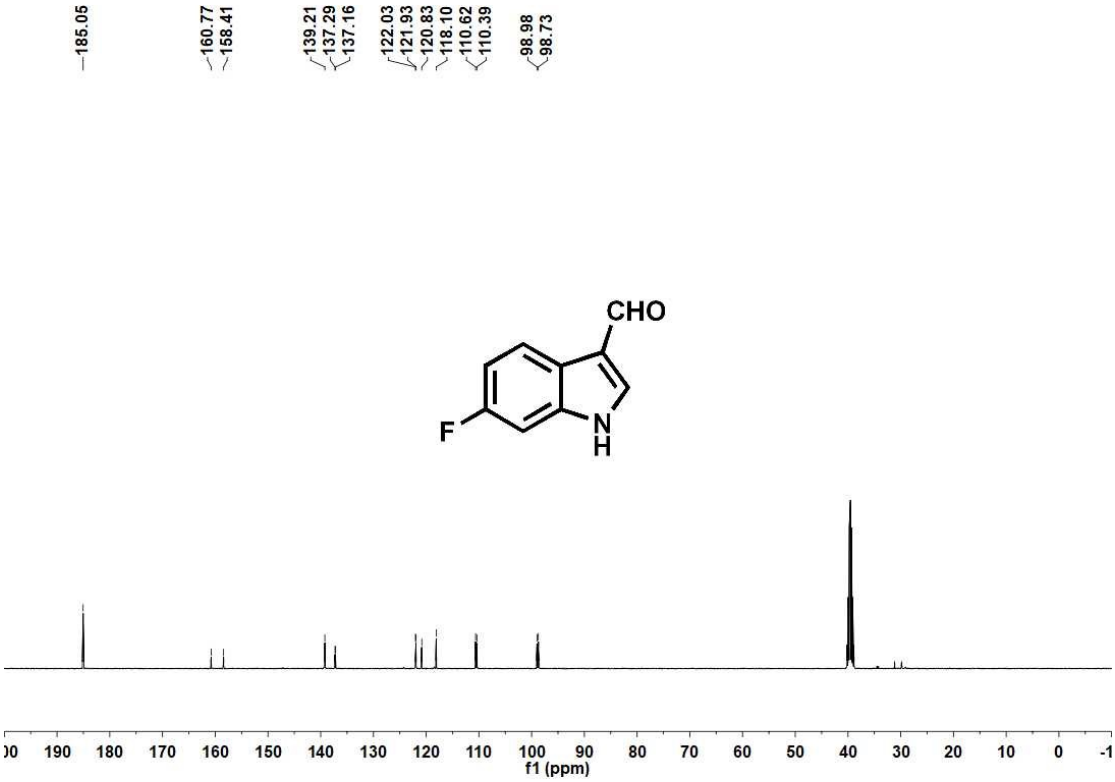
^{13}C NMR of product 2ad in DMSO-d_6 (100 MHz)



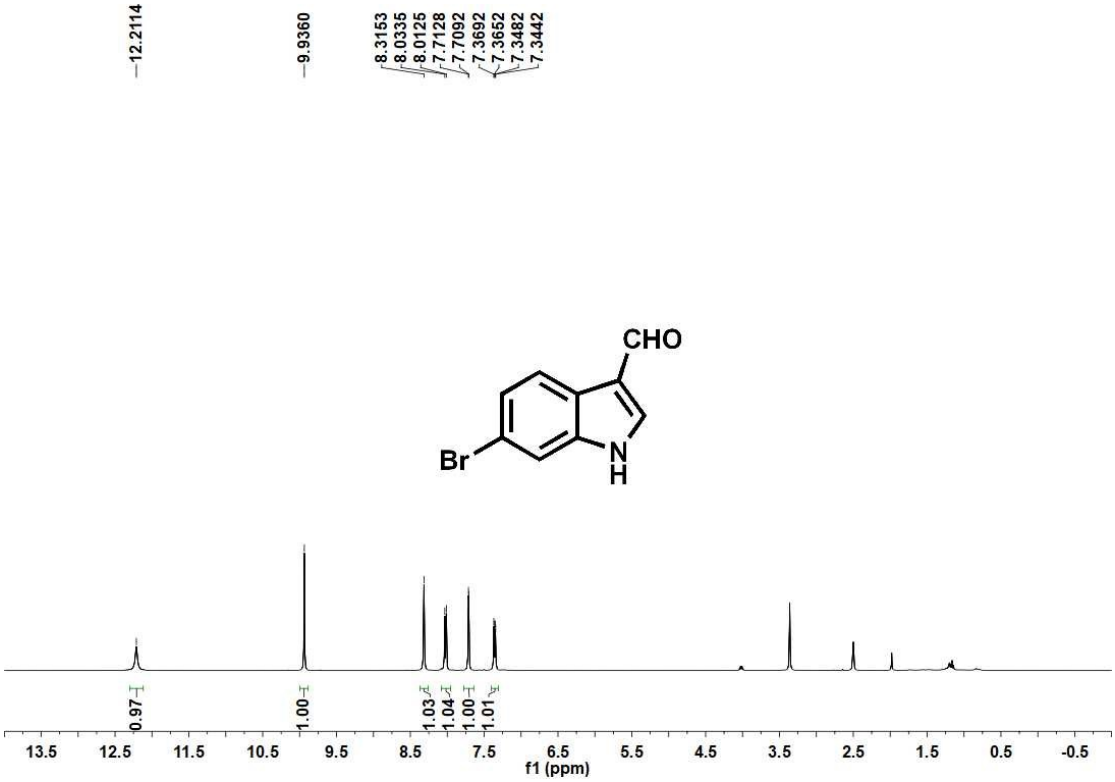
^{1}H NMR of product 2ae in DMSO-d_6 (400 MHz)



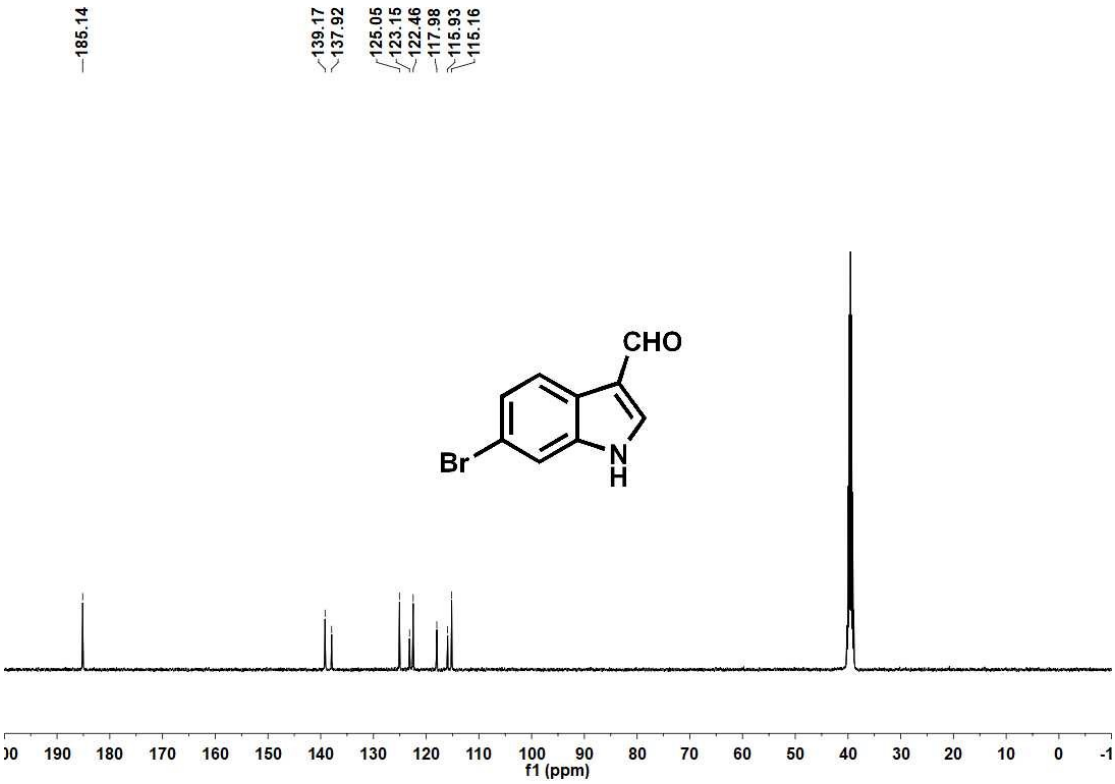
^{13}C NMR of product 2ae in DMSO-d_6 (100 MHz)



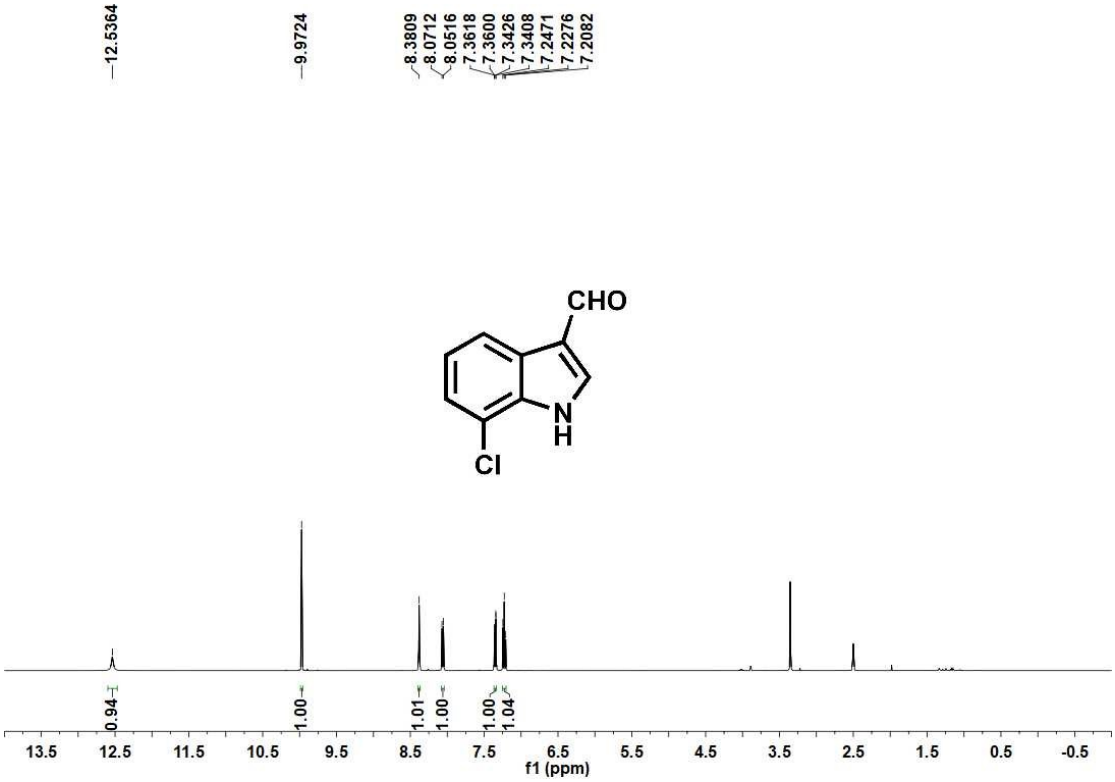
^{1}H NMR of product 2af in DMSO-d_6 (400 MHz)



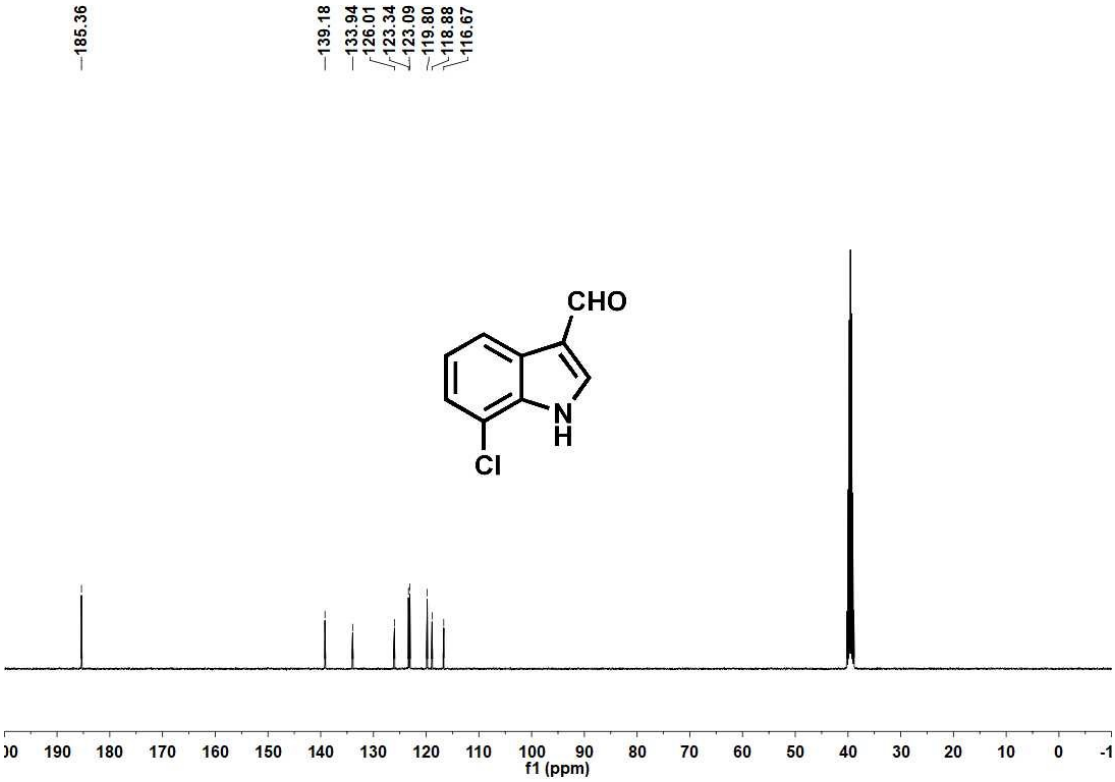
^{13}C NMR of product 2af in DMSO-d_6 (100 MHz)



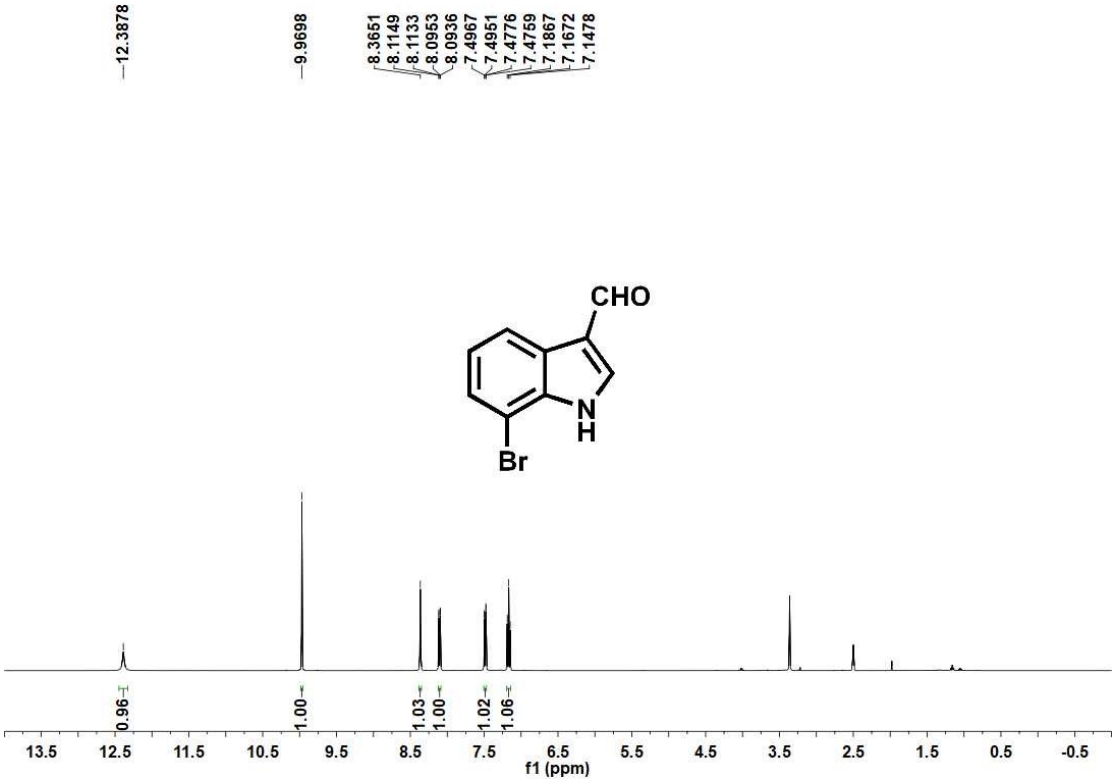
^{1}H NMR of product 2ag in DMSO-d_6 (400 MHz)



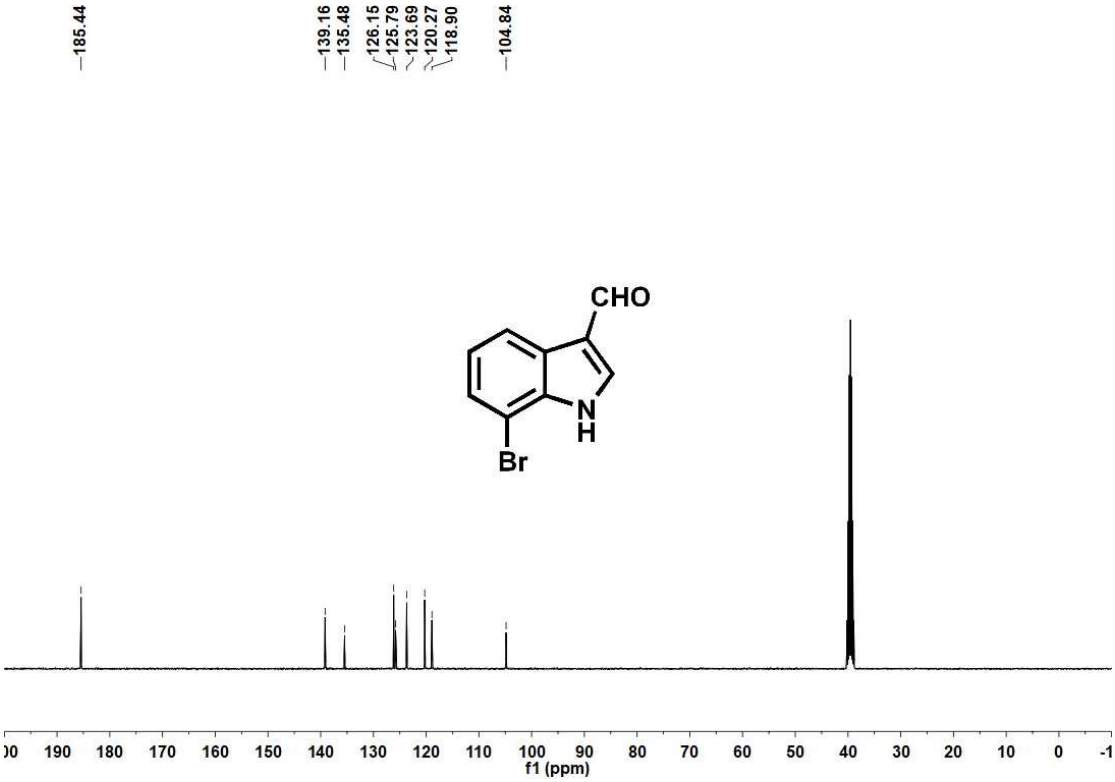
^{13}C NMR of product 2ag in DMSO-d_6 (100 MHz)



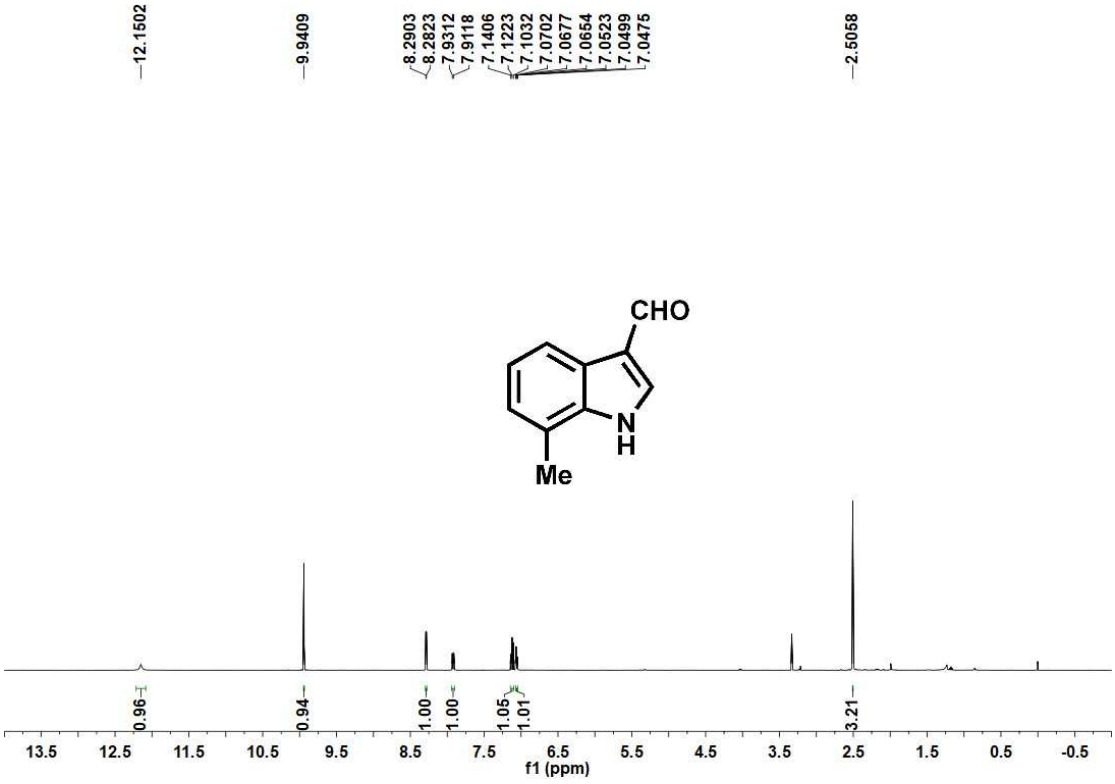
^{1}H NMR of product 2ah in DMSO-d_6 (400 MHz)



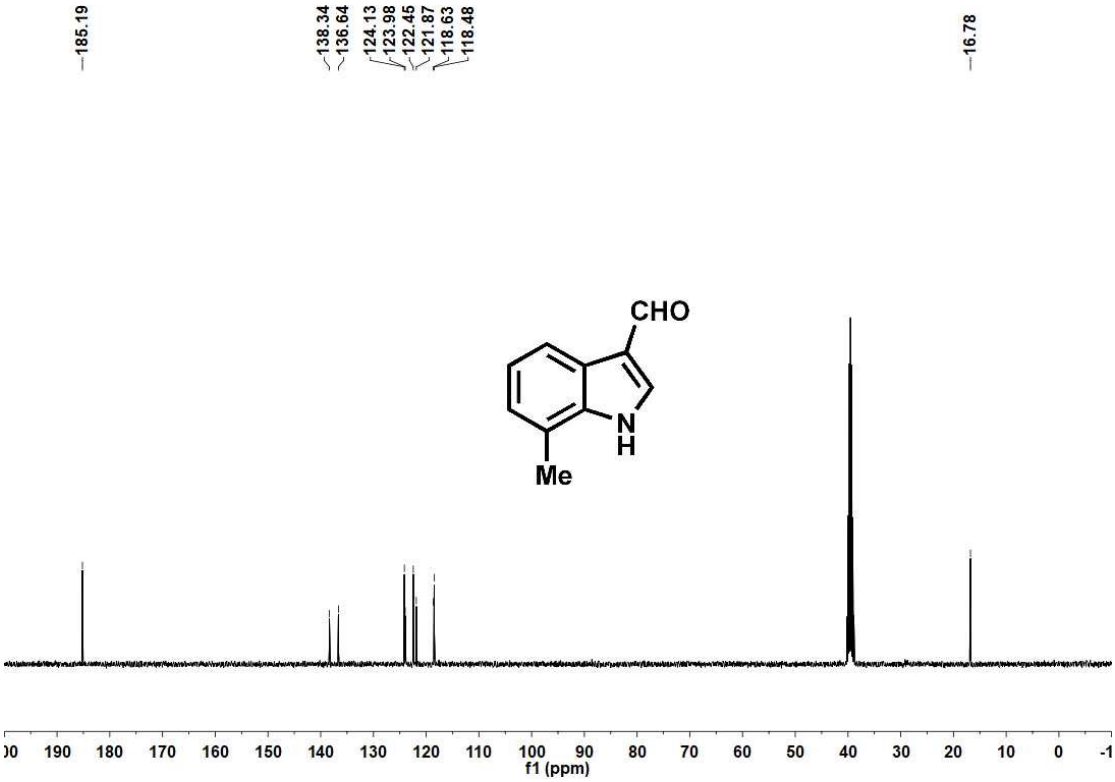
^{13}C NMR of product 2ah in DMSO-d_6 (100 MHz)



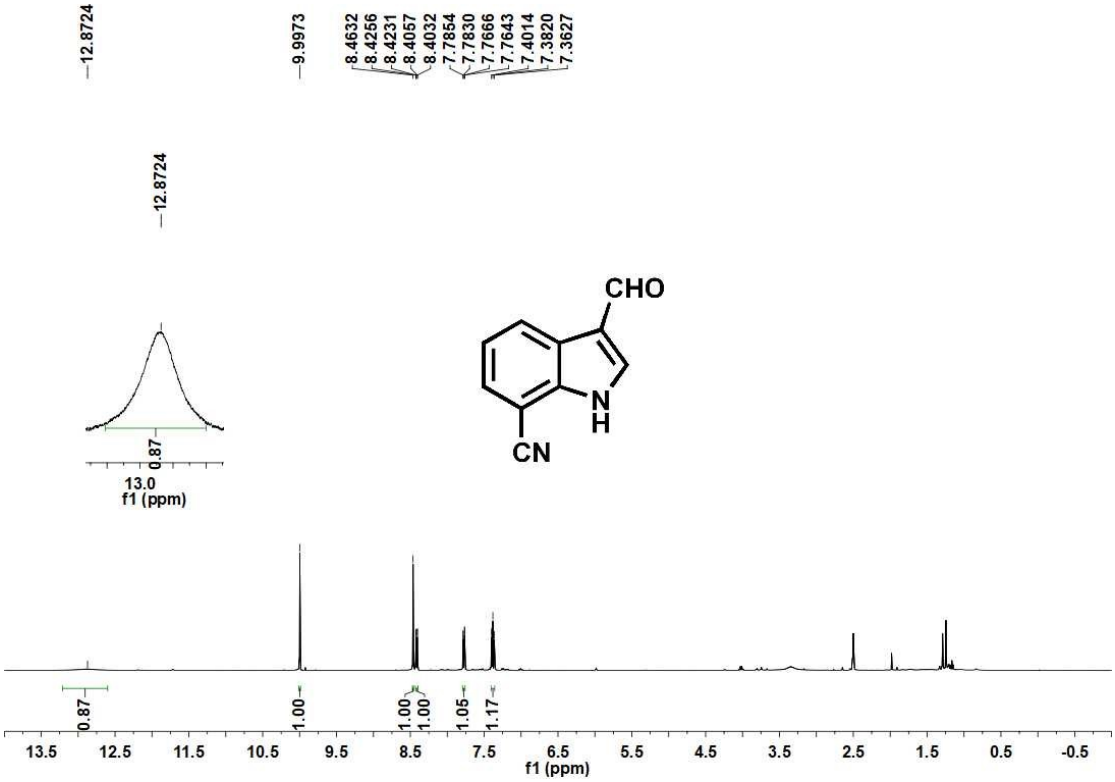
^{1}H NMR of product 2ai in DMSO-d_6 (400 MHz)



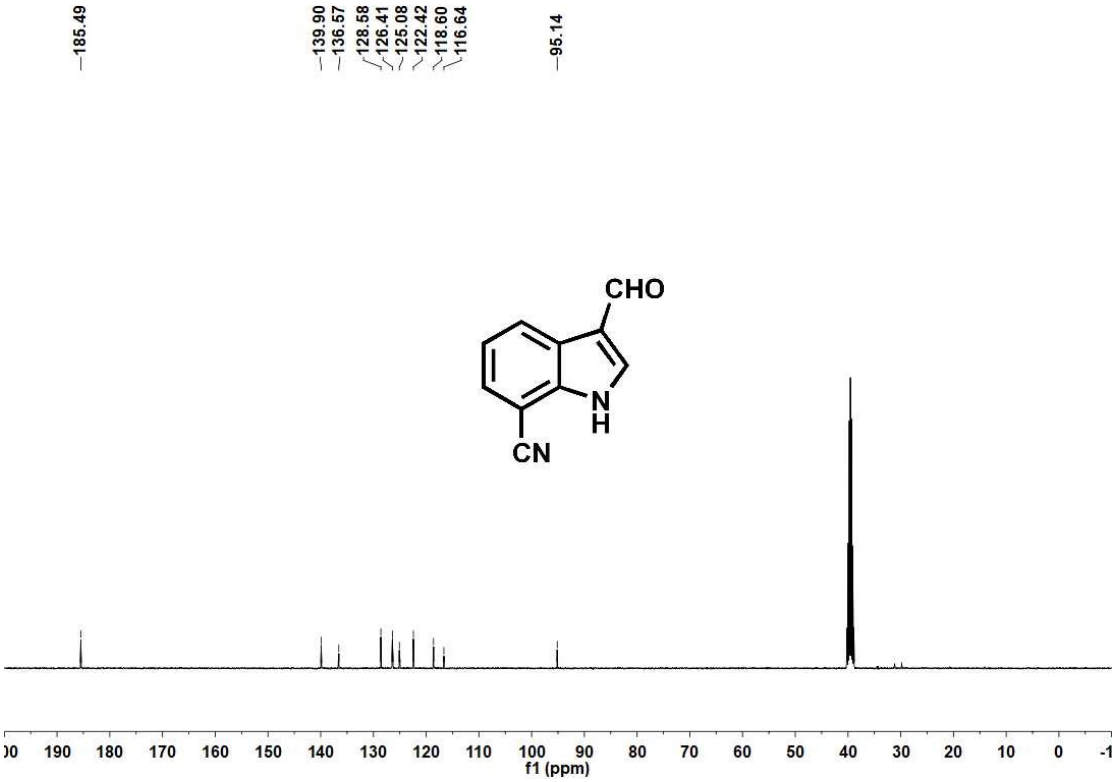
^{13}C NMR of product 2ai in DMSO-d_6 (100 MHz)



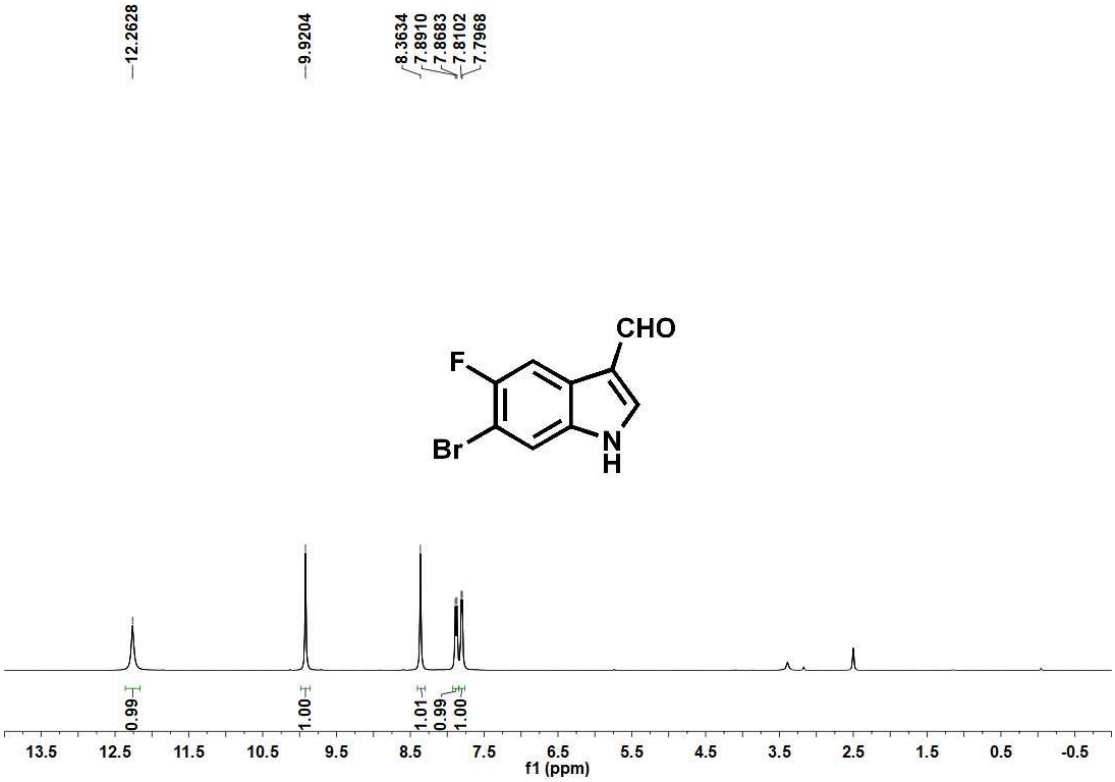
^{1}H NMR of product 2aj in DMSO-d_6 (400 MHz)



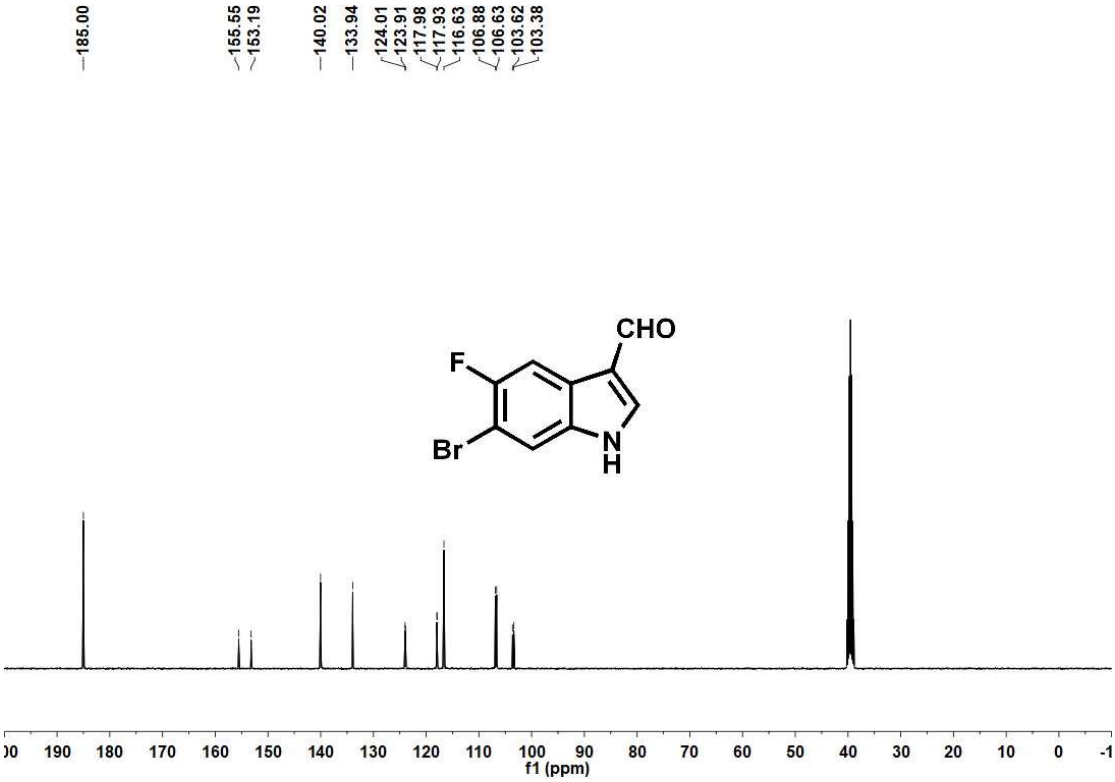
^{13}C NMR of product 2aj in DMSO-d_6 (100 MHz)



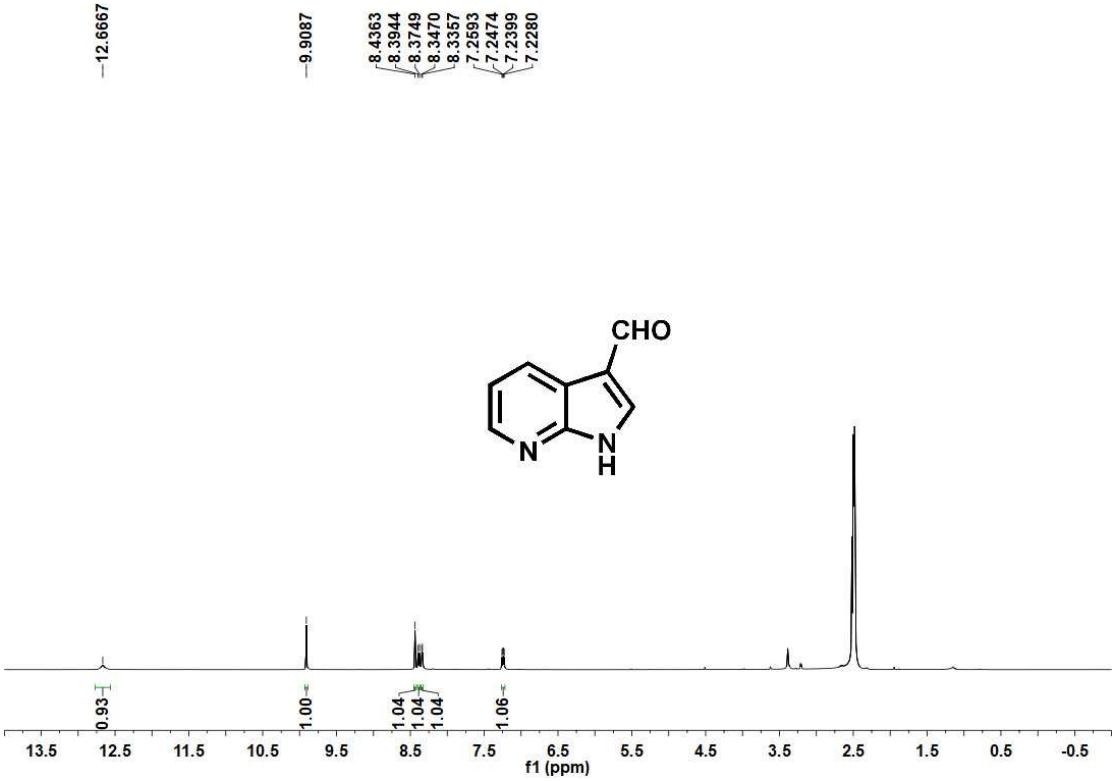
^{1}H NMR of product 2ak in DMSO-d_6 (400 MHz)



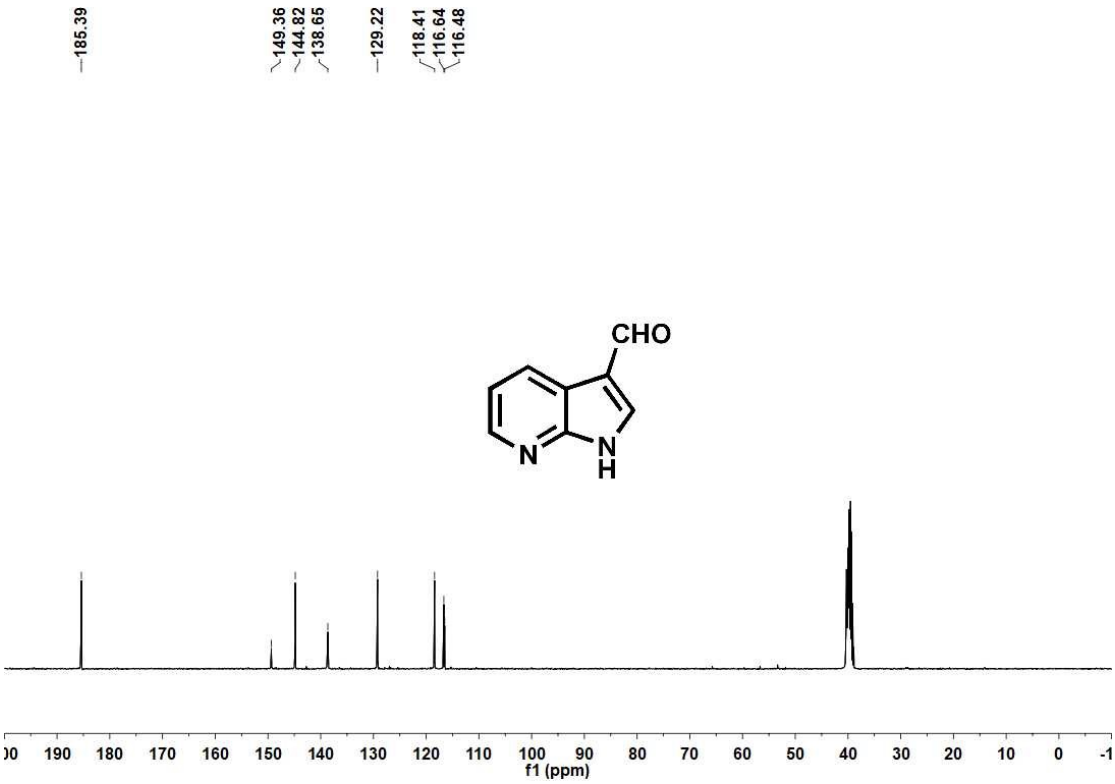
^{13}C NMR of product 2ak in DMSO-d_6 (100 MHz)



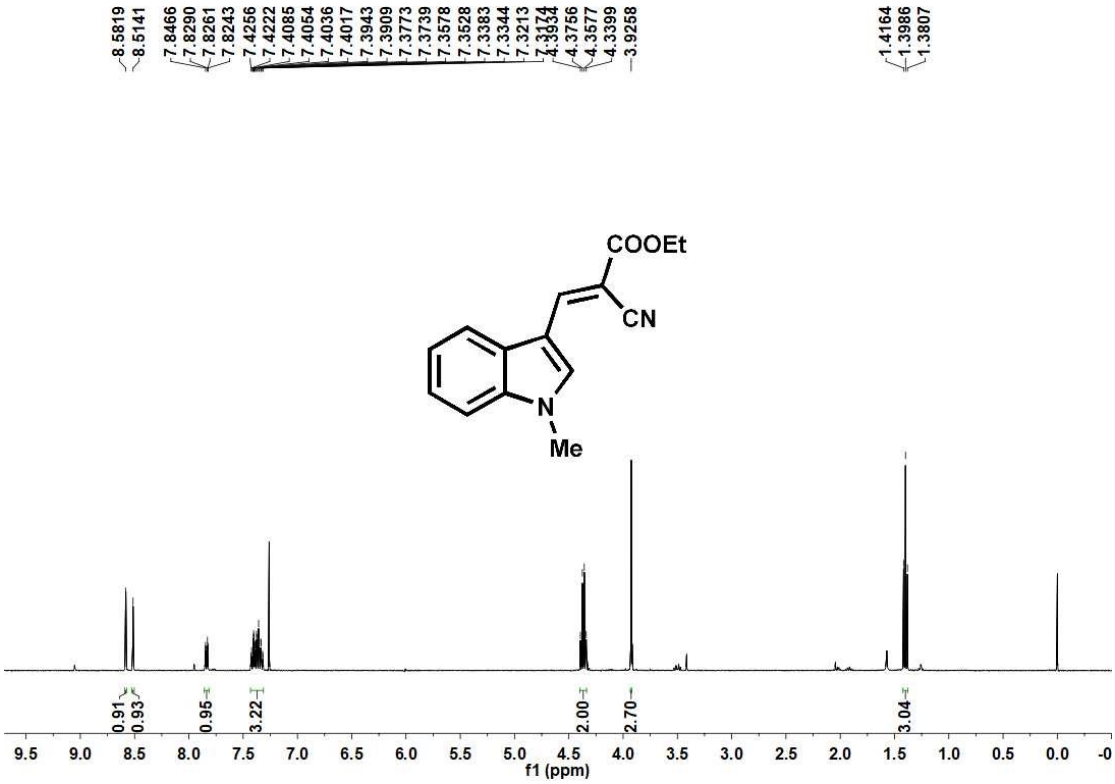
^{1}H NMR of product 2al in DMSO-d_6 (400 MHz)



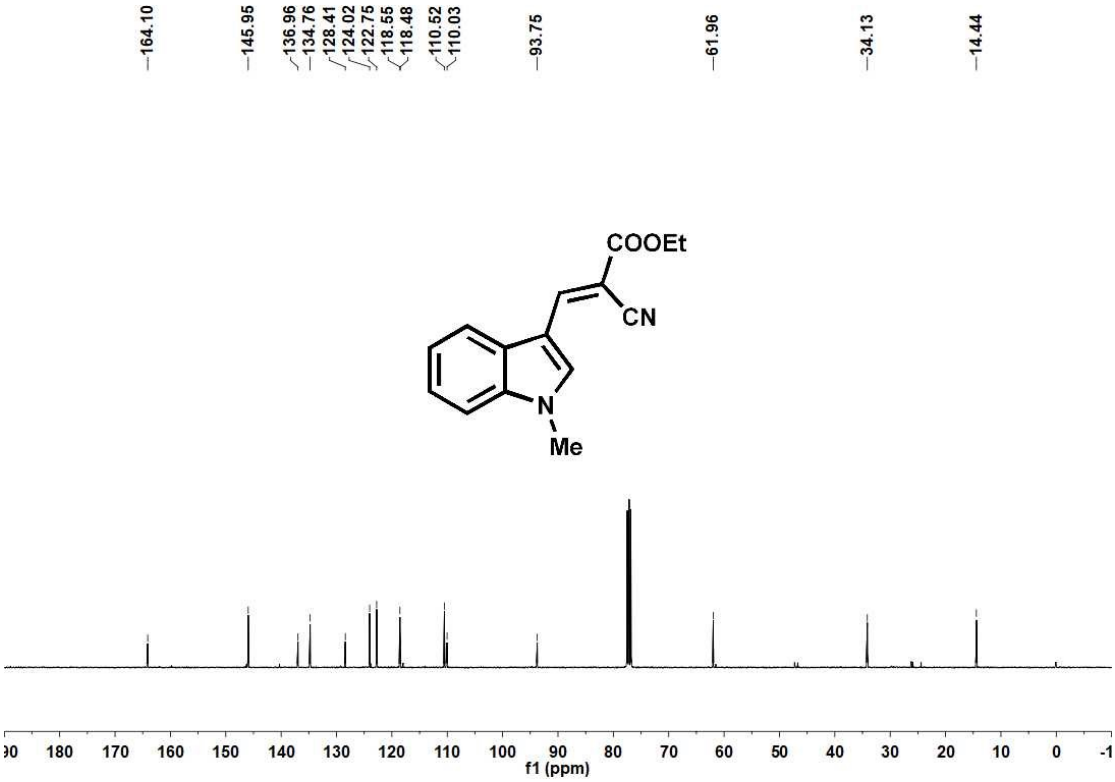
^{13}C NMR of product 2al in DMSO-d_6 (100 MHz)



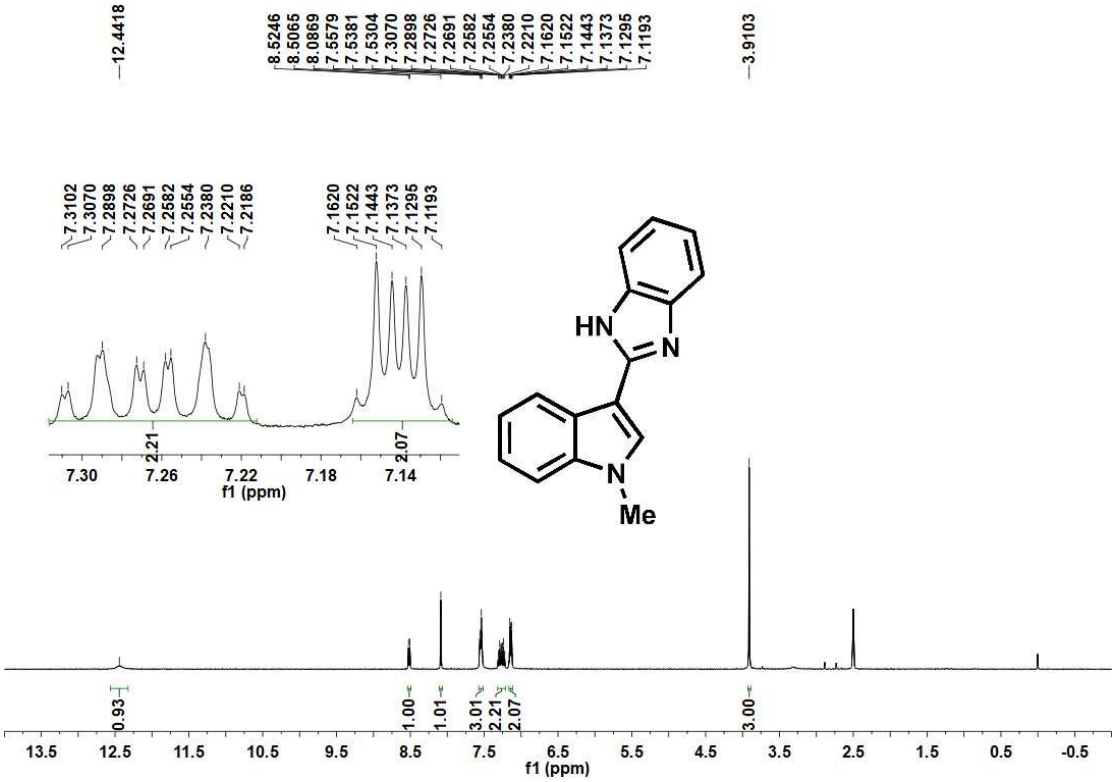
^{1}H NMR of product 3 in $CDCl_3$ (400 MHz)



^{13}C NMR of product 3 in $CDCl_3$ (400 MHz)



^{1}H NMR of product 4 in DMSO-d_6 (400 MHz)



^{13}C NMR of product 4 in DMSO-d_6 (100 MHz)