Supporting Information

Recyclable and Reusable *n*-Bu_4NBF_4/PEG-400/H_2O System for Electrochemical C-3 Formylation of Indoles with Me_3N as a Carbonyl Source

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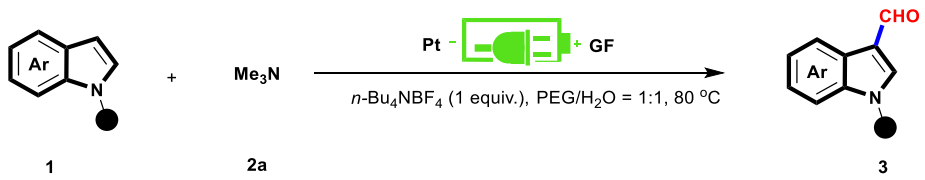
1. General information

NMR spectra were recorded with tetramethylsilane (TMS) as the internal standard. ^{1}H NMR spectra were recorded at 500 MHz or 400 MHz, and ^{13}C NMR spectra were recorded at 125 MHz or 100 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. All the solvents were used directly without any purification. Cyclic voltammetry experiments were carried out in an equipment of CHI761E. CV curves were recorded using a three-electrode scheme. The working electrode was a glassy carbon electrode, A platinum electrode served as counter electrode. Ag/AgCl (KCl sat'd) was used as the reference electrode. The working electrode was polished before recording each CV curve.

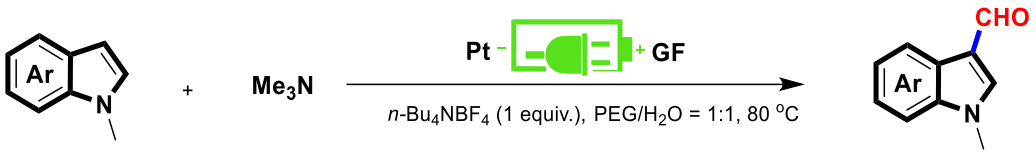
2. General procedure of the synthesis of the products



1 2a 3

General procedure A for the preparation of products 3: A tube was charged with the indole derivative **1** (0.5 mmol), Me_3N (**2a**, 1.5 mmol), and *n*-Bu_4NBF_4 (0.5 mmol). The flask was equipped with a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a platinum plate (1 cm x 1 cm) cathode, and flushed with argon. PEG-400 (2 mL) and H_2O (2 mL) were added. The constant current (5 mA) electrolysis was carried out at 80 °C (oil bath temperature) under argon. After complete consumption of the starting material, the reaction mixture was cooled to ambient temperature, extracted with toluene (3 x 20 mL). The combined organic solution was washed with brine, dried over $MgSO_4$ and

concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with ethyl acetate/hexanes to give the desired product **3**.



1a, 1.32 g **2a** **3a**, 1.32 g, 83%

Gram scale preparation of 3a: A tube was charged with the indole derivative **1a** (10 mmol), Me_3N (**2a**, 30 mmol), and *n*-Bu_4NBF_4 (10 mmol). The flask was equipped with a graphite felt anode (4 cm x 5 cm x 0.5 cm) and a platinum plate (4 cm x 5 cm) cathode, and flushed with argon. PEG-400 (20 mL) and H_2O (20 mL) were added. The constant current (5 mA) electrolysis was carried out at 80 °C (oil bath temperature) under argon. After 28h, the reaction mixture was cooled to ambient temperature, extracted with toluene (3 x 50 mL). The combined organic solution was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with ethyl acetate/hexanes to give the desired product **3a**.

Notes: 1. Toluene can be recovered by rotary evaporation for repeated use. 2. The PEG-400 and water can recovered by extracted from the reaction system. 3. Moreover, *n*-Bu_4NBF_4 is dissolved in water and PEG-400 access to the recovery and application of electrolyte.

Figure S1. Electrolysis setup

3. Cyclic voltammetry studies.

The cyclic voltammograms were recorded in an electrolyte of *n*-Bu_4NBF_4 (0.1 M) in MeCN (10.0 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and anAg/AgCl (KCl sat'd) reference electrode. The scan rate is 100 mV/s.

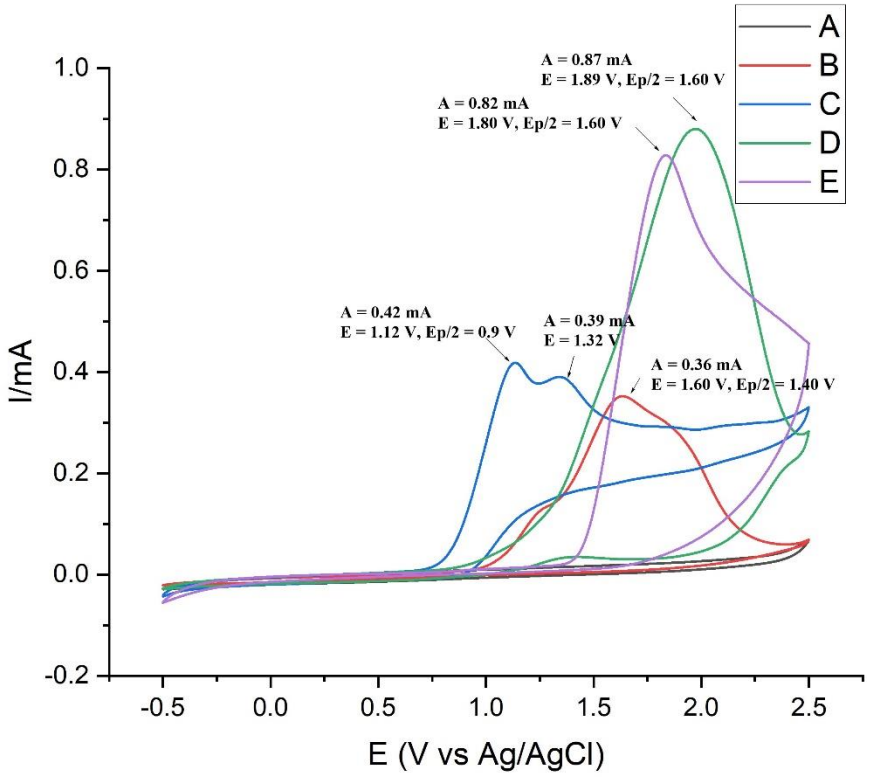
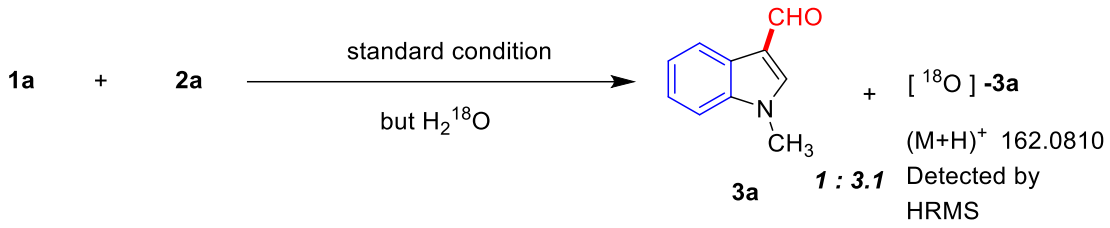


Figure S2. Cyclic voltammograms. A: Blank; B: **1a** (30 mM); C: **2a** (30 mM); D: **1a** (30 mM) + **2a** (30 mM); E: **3a** (30 mM).

The data was summarized of cyclic voltammograms in Figure S2. The results showed that Me_3N was preferentially oxidized to iminium ion since it has lower oxidation potential (1.12 V vs Ag/AgCl) than indole **1a** (1.60 V vs Ag/AgCl). Moreover, the cyclic voltammogram of **1a** + **2a** gave an Ep/2 of 1.6V, which was coincident with that of product **3a** (Ep/2 =1.6V), indicating that the oxidation peak of **1a** + **2a** might owes to the product generation.

4. Mechanism studies

(1) An isotopic labeling reaction.



An isotopic labeling reaction was carried out by treatment of **1a** and **2a** in the presence of $H_2{}^{18}O$ under standard conditions, leading to a mixture of **3a** and [^{18}O]-**3a** (1:3.1) in 75% yield. The HMRS spectra of the mixture of **3a** and [^{18}O]-**3a** was listed as bellow (Figure S3).

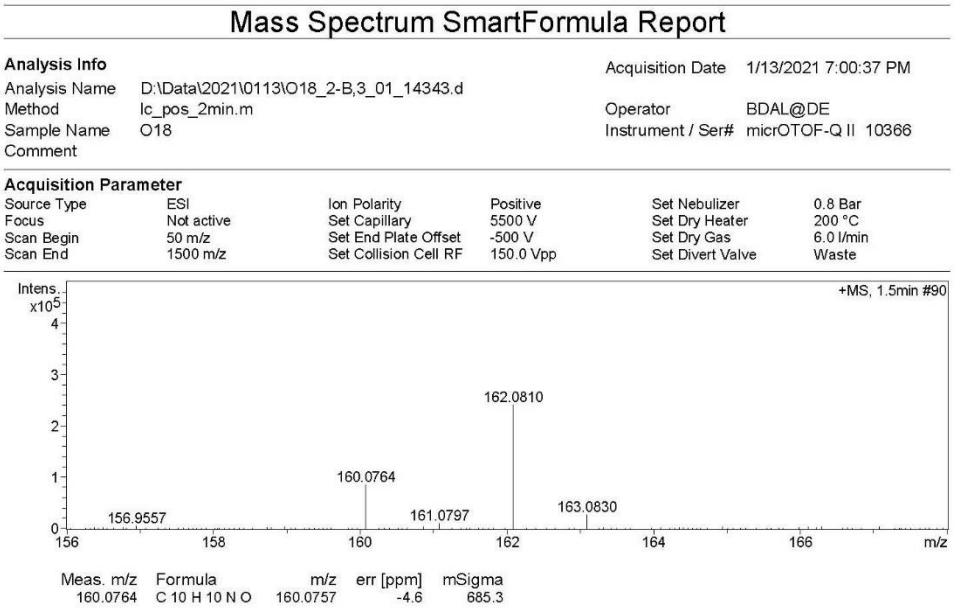
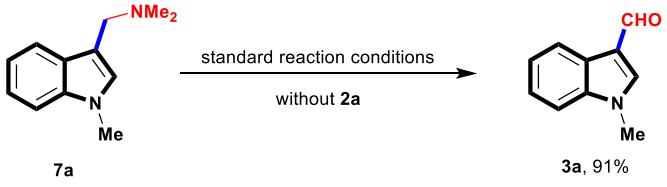


Figure S3. The HMRS spectra of the mixture of **3aa** and [^{18}O]-**3aa**.

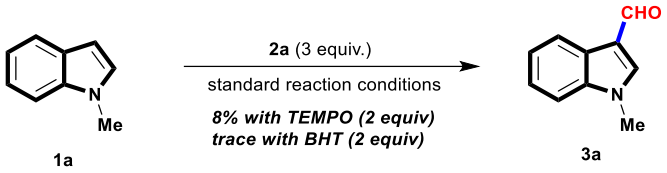
(2) Convention of 7a to 3a under current conditions.



A tube was charged with the indole derivative **7a** (0.5 mmol), and *n*-Bu_4NBF_4 (0.5 mmol). The flask was equipped with a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a platinum plate (1 cm x

1 cm) cathode, and flushed with argon. PEG-400 (2 mL) and H_2O (2 mL) were added. The constant current (5 mA) electrolysis was carried out at 80 °C (oil bath temperature) under argon. After complete consumption of the starting material, the reaction mixture was cooled to ambient temperature, extracted with toluene (3 x 20 mL). The combined organic solution was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with ethyl acetate/hexanes to give the desired product **3a**.

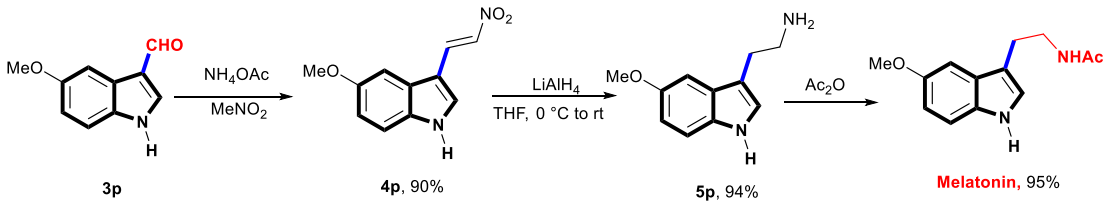
(3) Radical capture experiments.



A tube was charged with the indole derivative **1a** (0.5 mmol), Me_3N (**2a**, 1.5 mmol), and *n*-Bu_4NBF_4 (0.5 mmol), **2,2,6,6-tetramethyl-1-piperidinyloxy** (TEMPO, 1.0 mmol). The flask was equipped with a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a platinum plate (1 cm x 1 cm) cathode, and flushed with argon. PEG-400 (2 mL) and H_2O (2 mL) were added. The constant current (5 mA) electrolysis was carried out at 80 °C (oil bath temperature) under argon. After 24h, the reaction mixture was cooled to ambient temperature, extracted with toluene (3 x 20 mL). The combined organic solution was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with ethyl acetate/hexanes to give the desired product **3a** (only 8%).

A tube was charged with the indole derivative **1a** (0.5 mmol), Me_3N (**2a**, 1.5 mmol), and *n*-Bu_4NBF_4 (0.5 mmol), **2,6-ditert-butyl-4-methylphenol** (BHT, 1.0 mmol). The flask was equipped with a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a platinum plate (1 cm x 1 cm) cathode, and flushed with argon. PEG-400 (2 mL) and H_2O (2 mL) were added. The constant current (5 mA) electrolysis was carried out at 80 °C (oil bath temperature) under argon. After 24h, only trace of **3a** was observed.

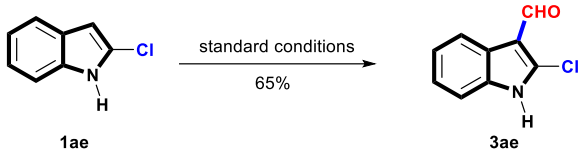
5. General procedure for the synthesis of Melatonin from 3p



To an oven-dried 25mL round bottom flask were added the aldehyde **3p**, nitromethane (2 mL), and ammonium acetate (169 mg, 2.19 mmol). The reaction was then heated to reflux for 90 min with vigorous stirring. Then, the reaction mixture was concentrated by rotary evaporation and the residue was dissolved in EtOAc (30 mL). The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the nitro alkene **4p**, which was used for the next step without further purification.

Under an inert nitrogen atmosphere, a THF solution (5 mL) of nitro olefin **4p** was added to a stirred slurry of $LiAlH_4$ powder (228 mg, 6.6 mmol) in THF (5 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 36 h. The reaction was quenched by dropwise addition of water until effervescence ceased. The mixture was then diluted with diethyl ether before addition of a saturated aqueous solution of Rochelle's salt. The subsequent biphasic mixture was stirred for 24h. The layers were separated and the organic layer was extracted with aqueous 1 N HCl. The aqueous phase was basified with 3 N KOH aqueous, and extracted with diethyl ether, dried over Na_2SO_4, filtered and concentrated in vacuo to provide the desired tryptamine derivative **5p**, which was used for the next step without further purification. The tryptamine derivative **5p** was dissolved in CH_2Cl_2 (10 mL) and 10% aqueous Na_2CO_3 (1 mL), and then to the reaction mixture was added Ac_2O (1.0 mmol). After vigorous stirring for 2h, the reaction mixture was diluted with water. The organic layer was collected and the aqueous phase was extracted with EtOAc (3x10 mL). The combined extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give the desired tryptamine derivative Melatonin. [1]

6. General procedure for the synthesis of 3ae



1ae 3ae

A tube was charged with the indole derivative **1ae** (0.5 mmol), Me_3N (**2a**, 1.5 mmol), and *n*-Bu_4NBF_4 (0.5 mmol). The flask was equipped with a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a platinum plate (1 cm x 1 cm) cathode, and flushed with argon. PEG-400 (2 mL) and H_2O (2 mL) were added. The constant current (5 mA) electrolysis was carried out at 80 °C (oil bath temperature) under argon. After 28h, the reaction mixture was cooled to ambient temperature, extracted with toluene (3 x 20 mL). The combined organic solution was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel eluting with ethyl acetate/hexanes to give the desired product **3ae** (65%).

7. Reference

(1) J. Xu and R.-B. Tong, An Environment-Friendly Protocol for Oxidative Halocyclization of Tryptamine and Tryptophol Derivatives. *Green Chem.*, 2017, **19**, 2952-2956.

8. Spectra data of products

Methyl-1H-indole-3-carbaldehyde (***3a***): Compound **3a** was prepared following the general procedure, starting from Methyl-1*H*-indole (65.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3a** was obtained as a light yellow solid (68 mg, 85% isolated yield). m.p. 69-70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.32 (d, J = 6.2 Hz, 1H), 7.64 (s, 1H), 7.37 – 7.32 (m, 3H), 3.85 (s, 3H). **^{13}C {1H} NMR** (100 MHz, $CDCl_3$) δ 184.3, 139.2, 138.0, 125.3, 124.0, 122.9, 122.0, 118.1, 109.9, 33.6. HRMS (ESI-TOF): m/z calcd for $C_{10}H_{10}NO^+$ ($[M+H]^+$) 160.0757, found 160.0765.

1,2-Dimethyl-1H-indole-3-carbaldehyde (***3b***): Compound **3b** was prepared following the general procedure, starting from 1,2-Dimethyl -1*H*-indole (72.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3b** was obtained as yellow solid (67.4 mg, 78% isolated yield). m.p. 127-129 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.25 – 8.20 (m, 1H), 7.25 – 7.19 (m, 3H), 3.56 (s, 3H), 2.54 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.0, 147.7, 137.0, 125.7, 123.0, 122.7, 120.8, 114.2, 109.2, 29.6, 10.5. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO^+$ ($[M+H]^+$) 174.0913, found 174.0910.

Methyl-2-phenyl-1H-indole-3-carbaldehyde (***3c***): Compound **3c** was prepared following the general procedure, starting from 1-Methyl-2-phenyl-1*H*-indole (103.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3c** was obtained as yellow solid (96 mg, 82% isolated yield). m.p. 128-130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.47 (dd, *J* = 5.5, 2.8 Hz, 1H), 7.61 – 7.57 (m, 3H), 7.54 – 7.49 (m, 2H), 7.44 – 7.37 (m, 3H), 3.70 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 186.6, 151.5, 137.4, 131.0, 130.0, 128.7, 128.6, 125.2, 124.1, 123.3, 122.2, 115.7, 109.8, 31.1. **HRMS** (ESI-TOF): m/z calcd for $C_{16}H_{14}NO^+$ ($[M+H]^+$) 236.1070, found 236.1076.

1,4-Dimethyl-1H-indole-3-carbaldehyde (***3d***): Compound **3d** was prepared following the general procedure, starting from 1,4-Dimethyl-1*H*-indole (72.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). The purification by column chromatography (hexane/ethyl acetate = 3:1), **3d** was obtained as yellow solid (60.5 mg, 70% isolated yield). m.p. 82-83 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.70 (s, 1H), 7.23 – 7.12 (m, 2H), 7.06 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 2.81 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.4, 138.6, 138.4, 132.3, 125.0, 124.2, 123.6, 119.5, 107.7, 33.7, 22.5. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO^+$ ($[M+H]^+$) 174.0913, found 174.0915.

4-Methoxy-1-methyl-1H-indole-3-carbaldehyde (***3e***): Compound **3e** was prepared following the general procedure, starting from 4-Methoxy-1-methyl-1*H*-indole (80.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3e** was obtained as

white solid (67 mg, 71% isolated yield). m.p. 120-121 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.70 (s, 1H), 7.17 (t, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 3.72 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 187.5, 154.5, 138.7, 132.1, 123.8, 118.1, 116.7, 103.5, 102.4, 55.3, 33.7. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO_2^+$ ($[M+H]^+$) 190.0863, found 190.0862.

5-Methoxy-1-methyl-1H-indole-3-carbaldehyde (***3f***): Compound **3f** was prepared following the general procedure, starting from 5-Methoxy-1-methyl-1*H*-indole (80.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3f** was obtained as yellow solid (73 mg, 78% isolated yield). m.p. 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.60 (s, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 6.98 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.4, 156.7, 139.3, 132.8, 126.0, 117.8, 114.5, 110.7, 103.3, 55.9, 33.9. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO_2^+$ ($[M+H]^+$) 190.0863, found 190.0866.

5-Ethoxy-1-methyl-1H-indole-3-carbaldehyde (***3g***): Compound **3g** was prepared following the general procedure, starting from 5-Ethoxy-1-methyl-1*H*-indole (87.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3g** was obtained as yellow solid (77 mg, 76% isolated yield). m.p. 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.77 (s, 1H), 7.54 (s, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.4, 156.0, 139.5, 132.8, 126.0, 117.7, 114.8, 110.8, 104.2, 64.0, 33.8, 15.0. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO^+$ ($[M+H]^+$) 190.0863, found 190.0866.

5-Bromo-1-methyl-1H-indole-3-carbaldehyde (***3h***): Compound **3h** was prepared following the general procedure, starting from 5-Bromo-1-methyl-1*H*-indole (104 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3h** was obtained as yellow solid (83 mg, 70% isolated yield). m.p. 128-130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.40 (d, J = 1.4 Hz, 1H), 7.60 (s, 1H), 7.38 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 3.82 (s,

3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.4, 139.6, 136.5, 127.0, 126.7, 124.6, 117.5, 116.6, 111.3, 33.8. **HRMS** (ESI-TOF): m/z calcd for $C_{10}H_9BrNO^+$ ($[M+H]^+$) 237.9862, found 237.9863.

5-Cyano-1-methyl-1H-indole-3-carbaldehyde (***3i***): Compound **3i** was prepared following the general procedure, starting from 5-*Cyano-1-methy*l-1*H*-indole (78 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 1:1), **3i** was obtained as yellow Oil (57 mg, 62% isolated yield). **^{1}H NMR** (400 MHz, DMSO) δ 9.92 (s, 1H), 8.44 – 8.38 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 8.6, 1.5 Hz, 1H), 3.91 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, DMSO) δ 185.3, 143.7, 139.7, 126.8, 126.1, 124.6, 120.3, 117.2, 112.9, 105.1, 34. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_9N_2O^+$ ($[M+H]^+$) 185.0709, found 185.0708.

Methyl 3-formyl-1-methyl-1H-indole-5-carboxylate (***3j***): Compound **3j** was prepared following the general procedure, starting from *methyl* 3-formyl-1-methyl-1*H*-indole (94.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 1:1), **3j** was obtained as yellow Oil (65 mg, 60% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.95 (d, *J* = 1.3 Hz, 1H), 8.01 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.71 (s, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.3, 167.6, 140.5, 140.2, 125.4, 124.8, 124.7, 124.4, 118.6, 109.8, 52.1, 33.9. **HRMS** (ESI-TOF): m/z calcd for $C_{12}H_{12}NO_3^+$ ($[M+H]^+$) 218.0812, found 185.0813.

1,6-Dimethyl-1H-indole-3-carbaldehyde (***3k***): Compound **3k** was prepared following the general procedure, starting from 1,6-Dimethyl-1*H*-indole (72.5 mg, 0.5 mmol) and Me_3 N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3k** was obtained as white solid (71 mg, 82% isolated yield). m.p. 113-114 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.19 – 7.14 (m, 2H), 3.81 (s, 3H), 2.52 (s, 3H).**^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.2, 157.7, 138.9, 138.8, 122.6, 119.1, 118.1, 112.1, 93.6, 55.7, 33.5. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO^+$ ($[M+H]^+$) 174.0913, found 174.0915.

6-Methoxy-1-methyl-1H-indole-3-carbaldehyde (***3l***): Compound **3l** was prepared following the general procedure, starting from 6-Methoxy-1-methyl-1*H*-indole (80.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3l** was obtained as white solid (71 mg, 76% isolated yield). m.p. 130-131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.17 (d, *J* = 7.9 Hz, 1H), 7.46 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 4.04 (s, 3H), 2.72 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.4, 156.7, 139.3, 132.8, 126.0, 117.8, 114.5, 110.7, 103.3, 55.9, 33.9. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO_2^+$ ($[M+H]^+$) 190.0863, found 190.0872.

6-Clomo-1-methyl-1H-indole-3-carbaldehyde (***3m***): Compound **3m** was prepared following the general procedure, starting from 6-Clomo-1-methyl-1*H*-indole (82.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3m** was obtained as white solid (72 mg, 75% isolated yield). m.p. 152-154 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.30 – 7.21 (m, 2H), 3.77 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.2, 139.6, 138.3, 130.0, 123.7, 123.4, 122.9, 118.0, 110.0, 33.7. **HRMS** (ESI-TOF): m/z calcd for $C_{10}H_{10}ClNO^+$ ($[M+H]^+$) 194.0369, found 194.0367.

1,7-Dimethyl-1H-indole-3-carbaldehyde (***3n***): Compound **3n** was prepared following the general procedure, starting from 1,7-Dimethyl-1*H*-indole (72.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3n** was obtained as white solid (62 mg, 72% isolated yield). m.p. 113-115 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.19 – 7.14 (m, 2H), 3.81 (s, 3H), 2.52 (s, 3H).**^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.2, 140.7, 136.6, 126.7, 126.4, 123.1, 121.8, 120.0, 117.6, 37.8, 19.4. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO^+$ ($[M+H]^+$) 174.0913, found 174.0919.

1H-indole-3-carbaldehyde (***3o***): Compound **3o** was prepared following the general procedure, starting from 1*H*-indole (58.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 1:1), **3o** was obtained as yellow solid (49 mg, 68% isolated yield). m.p. 196-198 °C. **^{1}H NMR** (400 MHz, DMSO) δ 12.18 (s, 1H), 9.98 (s, 1H), 8.29 (s, 1H), 8.16

(d, J = 7.2 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.30 – 7.20 (m, 2H). **^{13}C {^{1}H} NMR** (100 MHz, DMSO) δ 185.4, 138.8, 137.6, 124.6, 124.0, 122.6, 121.3, 118.7, 112.9. **HRMS** (ESI-TOF): m/z calcd for $C_9H_8NO^+$ ($[M+H]^+$) 146.0600, found 146.0602.

5-Methoxy-1H-indole-3-carbaldehyde (***3p***): Compound **3p** was prepared following the general procedure, starting from 5-Methoxy-1*H*-indole (73.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 1:1), **3p** was obtained as yellow solid (63 mg, 72% isolated yield). m.p. 178-179 °C. **^{1}H NMR** (400 MHz, DMSO) δ 12.07 (s, 1H), 9.91 (s, 1H), 8.23 (s, 1H), 7.61 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 3.80 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, DMSO) δ 185.3, 156.0, 132.2, 125.3, 118.5, 113.8, 113.7, 102.9, 55.7. **HRMS** (ESI-TOF): m/z calcd for $C_{10}H_{10}NO_2^+$ ($[M+H]^+$) 176.0706, found 190.0708.

1-Ethyl-1H-indole-3-carbaldehyde (***3q***): Compound **3q** was prepared following the general procedure, starting from 1-Ethyl-1*H*-indole (72.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3q** was obtained as yellow solid (73 mg, 84% isolated yield). m.p. 98-100 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.33 (dd, *J* = 6.2, 2.7 Hz, 1H), 7.72 (s, 1H), 7.40 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 4.21 (q, *J* = 7.3 Hz, 2H), 1.54 (t, *J* = 7.3 Hz, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.4, 137.5, 137.1, 125.5, 123.9, 122.8, 122.1, 118.2, 110.0, 41.8, 15.0. **HRMS** (ESI-TOF): m/z calcd for $C_{11}H_{12}NO^+$ ($[M+H]^+$) 174.0913, found 174.0915.

Isopropyl-1H-indole-3-carbaldehyde (***3r***): Compound **3r** was prepared following the general procedure, starting from 1-Isopropyl-1*H*-indole (80 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3r** was obtained as white solid (67 mg, 72% isolated yield). m.p. 69-70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.37 – 8.33 (m, 1H), 7.86 (s, 1H), 7.43 (dd, *J* = 6.6, 2.1 Hz, 1H), 7.37 – 7.30 (m, 2H), 4.68 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.58 (dd, *J* = 6.7, 1.1 Hz, 7H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.6, 136.9, 135.1, 125.5, 123.8, 123.0, 122.1, 118.2, 110.3, 48.2, 22.6. **HRMS** (ESI-TOF): m/z calcd for $C_{12}H_{14}NO^+$ ($[M+H]^+$) 173.0841, found 173.0843.

benzyl-1H-indole-3-carbaldehyde (***3s***): Compound **3s** was prepared following the general procedure, starting from 1-benzyl-1*H*-indole (103.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3s** was obtained as yellow solid (85 mg, 73% isolated yield). m.p. 106-108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.36 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.73 (s, 1H), 7.41 – 7.32 (m, 6H), 7.23 – 7.18 (m, 2H), 5.37 (s, 2H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.7, 138.6, 137.5, 135.3, 129.1, 128.4, 127.3, 125.5, 124.2, 123.1, 122.2, 118.5, 110.4, 51.0. **HRMS** (ESI-TOF): m/z calcd for $C_{16}H_{14}NO^+$ ($[M+H]^+$) 236.1070, found 236.1072.

1-Allyl-1H-indole-3-carbaldehyde (***3t***): Compound **3t** was prepared following the general procedure, starting from 1-Allyl-1*H*-indole (78.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 3:1), **3t** was obtained as yellow solid (75 mg, 81% isolated yield). m.p. 73-74 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.34 (dd, *J* = 5.9, 2.7 Hz, 1H), 7.73 (s, 1H), 7.40 – 7.31 (m, 3H), 6.08 – 5.99 (m, 1H), 5.34 (d, *J* = 10.3 Hz, 1H), 5.21 (d, *J* = 17.1 Hz, 1H), 4.79 (dd, *J* = 5.5, 1.4 Hz, 2H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 184.6, 138.4, 137.3, 131.7, 125.4, 124.0, 123.0, 122.1, 119.0, 118.4, 110.3, 49.5. **HRMS** (ESI-TOF): m/z calcd for $C_{12}H_{12}NO^+$ ($[M+H]^+$) 186.0913, found 186.0916.

N-Acetyl-1H-indole-3-carboxaldehyde (***3u***) Compound **3u** was prepared following the general procedure, starting from N-Acetyl-1*H*-indole (80 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 1:1), **3u** was obtained as white solid (60 mg, 65% isolated yield). m.p. 159-161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.41 (d, *J* = 7.7 Hz, 1H), 8.28 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.08 (s, 1H), 7.44 (m, 2H), 2.76 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.7, 168.6, 136.3, 135.3, 126.9, 126.0, 125.5, 122.6, 122.0, 116.4, 24.0. **HRMS** (ESI-TOF): m/z calcd for $C_{10}H_{10}NO_2^+$ ($[M+H]^+$) 188.0706, found 188.0708.

N-Boc-1H-indole-3-carboxaldehyde (***3v***): Compound **3v** was prepared following the general procedure, starting from N-Boc-1*H*-indole (108 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification

by column chromatography (hexane/ethyl acetate = 1:1), **3v** was obtained as white solid (77 mg, 63% isolated yield). m.p. 125-126 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.30 – 8.26 (m, 1H), 8.22 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.43 - 7.35 (m, 2H), 1.71 (s, 9H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.7, 148.8, 136.6, 136.0, 126.1, 124.6, 122.2, 121.6, 115.2, 85.7, 28.1. **HRMS** (ESI-TOF): m/z calcd for $C_{14}H_{16}NO_3^+$ ($[M+H]^+$) 246.1125, found 246.1126.

N-Benzyl-1H-indole-3-carbaldehyde (***3w***) Compound **3w** was prepared following the general procedure, starting from N-Benzyl-1*H*-indole (110 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 1:1), **3w** was obtained as white solid (77mg, 62% isolated yield). m.p. 84-85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.34 – 8.29 (m, 2H), 7.94 (s, 1H), 7.80 – 7.75 (m, 2H), 7.73 – 7.66 (m, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.50 – 7.42 (m, 2H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.8, 168.6, 137.7, 133.0, 129.5, 129.1, 126.7, 126.3, 125.7, 122.2, 122.1, 116.2. **HRMS** (ESI-TOF): m/z calcd for $C_{16}H_{12}NO_2^+$ ($[M+H]^+$) 250.0863, found 188.0865.

1-Tosyl-1H-indole-3-carbaldehyde (***3x***) Compound **3x** was prepared following the general procedure, starting from 1-tosyl-1*H*-indole (149 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 5:1), **3x** was obtained as yellow solid (68mg, 46% isolated yield). m.p. 144-146 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.25 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.43 - 7 34 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.5, 146.2, 136.3, 135.2, 134.2, 130.4, 127.3, 126.3, 125.1, 122.6, 122.3, 113.3, 21.7. **HRMS** (ESI-TOF): m/z calcd for $C_{16}H_{13}NO_3S^+$ ($[M+H]^+$) 300.0616, found 300.0619.

2-(3-Formyl-1H-indole-1-carbonyl)phenyl acetate (***3y***) Compound **3y** was prepared following the general procedure, starting from 2-(1H-indole-1-carbonyl)phenyl acetate (139 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 5:1), **3y** was obtained as yellow solid (70 mg, 46% isolated yield). m.p. 109-110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.34 (dd, *J* = 6.9, 1.6 Hz, 1H), 8.29 (dd, *J* = 6.6, 2.1 Hz, 1H), 7.81 (s, 1H), 7.64 (td, *J* = 8.2,

1.6 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 2.07 (s, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.8, 169.0, 165.7, 148.4, 137.7, 136.4, 133.2, 129.5, 126.9, 126.7, 126.3, 126.2, 125.7, 123.7, 122.4, 122.2, 116.1, 20.6. **HRMS** (ESI-TOF): m/z calcd for $C_{18}H_{13}NO_4^+$ ($[M+H]^+$) 308.0845, found 308.0843.

*(R)-1-(2-(4-isoButylphenyl)-1H-indole-3-carbaldehyde) (**3z**)* Compound **3z** was prepared following the general procedure, starting from (R)-1-(1*H*-indole-1-yl-1-*H*-indole-1-yl)-2-(4-isobutylphenyl)propan-1-one) (152 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 5:1), **3z** was obtained as yellow oil (88 mg, 53% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.03 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 5.2 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.45 (q, *J* = 6.7 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.81 (td, *J* = 13.5, 6.7 Hz, 1H), 1.66 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.6, 172.7, 141.5, 137.2, 136.9, 135.1, 130.3, 126.9, 126.7, 125.8, 125.4, 122.5, 121.8, 116.8, 46.2, 45.0, 30.1, 22.4, 22.3, 20.3. **HRMS** (ESI-TOF): m/z calcd for $C_{22}H_{23}NO_2^+$ ($[M+H]^+$) 334.1729, found 334.1734

*(R)-1-(2-(6-Methoxynaphthalen-2-yl)propanoyl)-1H-indole-3-carbaldehyde (3**aa**)* Compound **3aa** was prepared following the general procedure, starting from *(R)-1-(1H-indol-1-yl)-2-(6-methoxynaphthalen-2-yl)propan)-1-one* (164 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 5:1), **3aa** was obtained as yellow oil (99 mg, 56% isolated yield). **^{1}H NMR** (400 MHz, DMSO) δ 10.06 (s, 1H), 9.09 (s, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.10 (dd, *J* = 13.5, 8.3 Hz, 2H), 8.05 (d, *J* = 0.8 Hz, 1H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.75 (dd, *J* = 8.9, 1.5 Hz, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 5.17 (q, *J* = 6.7 Hz, 1H), 3.98 (s, 3H), 1.68 (d, *J* = 6.7 Hz, 3H). **^{13}C {^{1}H} NMR** (100 MHz, DMSO) δ 187.2, 174.0, 153.0, 138.9, 136.6, 130.6, 129.5, 128.9, 127.9, 127.0, 126.9, 126.0, 125.7, 124.1, 121.9, 121.7, 116.8, 115.3, 115.2, 57.2, 44.5, 20.0. **HRMS** (ESI-TOF): m/z calcd for $C_{23}H_{19}NO_3^+$ ($[M+H]^+$) 358.1365, found 358.1369.

*(E)-1-(2-(But-2-enoyl)-1-H-indole-3-carbaldehyde (3**ab**)* Compound **3ab** was prepared following the general procedure, starting from (E)-1-(2-(but-2-enoyl)-1-*H*-indole (105 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 5:1), **3ab** was obtained as yellow oil (65 mg, 61% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.41 (d, *J* = 7.7 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.16 (s, 1H), 7.47 – 7.33 (m, 3H), 6.70 (d, *J* = 15.0 Hz, 1H), 2.09 (d, *J* = 7.0 Hz, 3H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.6, 163.9, 149.4, 136.6, 134.9, 126.6, 126.2, 122.4, 121.9, 121.3, 116.5, 18.8. **HRMS** (ESI-TOF): m/z calcd for $C_{13}H_{11}NO_2^+$ ($[M+H]^+$) 214.0790, found 214.0793.

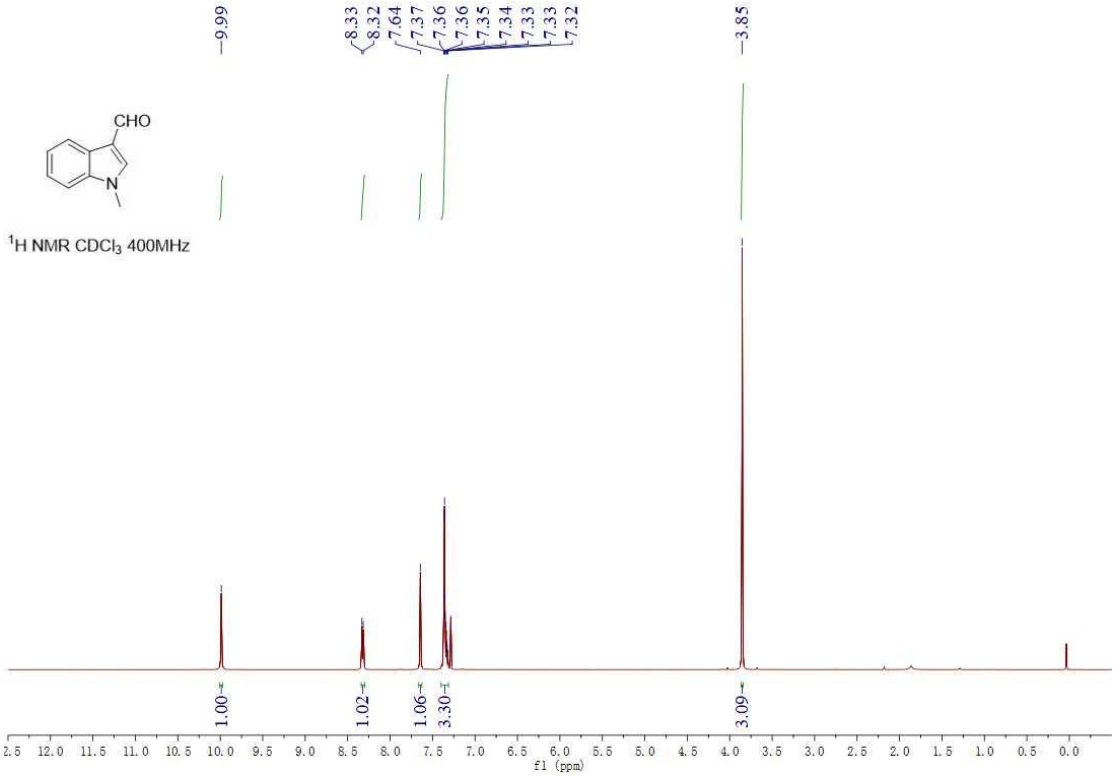
*1-Dodecanoyl-1H-indole-3-carbaldehyde (3**ac**)* **3ac** was prepared following the general procedure, starting from 1-(1*H*-indole)dodecan-1-one (150 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 5:1), **3ac** was obtained as yellow oil (79 mg, 53% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.28 (d, *J* = 7.4 Hz, 1H), 8.10 (s, 1H), 7.53 – 7.36 (m, 2H), 2.99 (t, *J* = 7.1 Hz, 2H), 1.87 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.47 (d, *J* = 7.0 Hz, 2H), 1.34 (d, *J* = 39.9 Hz, 14H), 0.91 (t, *J* = 6.4 Hz, 3H).**^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.7, 171.6, 136.4, 134.8, 126.8, 126.0, 125.3, 122.5, 121.9, 116.5, 35.8, 32.0, 29.6, 29.5, 29.4, 29.4, 29.1, 24.4, 22.7, 14.2. **HRMS** (ESI-TOF): m/z calcd for $C_{21}H_{19}NO_2^+$ ($[M+H]^+$) 328.2198, found 328.2199.

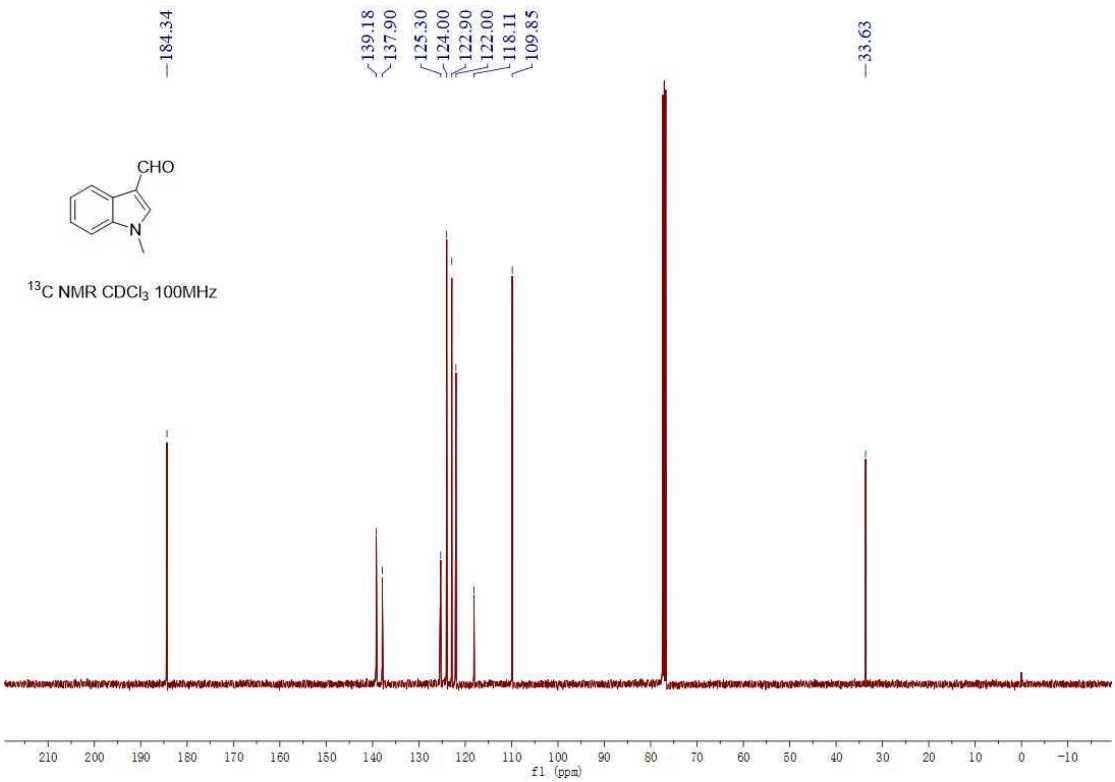
*(E)-1-(Octadic-9-enoyl)-1H-indole-3-carbaldehyde (3**ad**)* **3ad** was prepared following the general procedure, starting from (E)-1-(1*H*-indole-1-yl)octadec-9-en-one (190 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 5:1), **3ad** was obtained as yellow oil (83 mg, 44% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 7.4 Hz, 1H), 8.09 (s, 1H), 7.47 – 7.37 (m, 2H), 5.36 (dd, *J* = 13.1, 5.9 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.06 – 1.97 (m, 4H), 1.90 – 1.82 (m, 2H), 1.46 (s, 2H), 1.36 – 1.26 (m, 18H), 0.87 (t, *J* = 6.6 Hz, 4H). **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$) δ 185.5, 171.5, 136.5, 134.6, 130.1, 129.6, 126.8, 126.0, 125.3, 122.5, 121.8, 116.5, 35.8, 32.6, 32.0, 29.8, 29.5, 29.3, 29.1, 27.2, 24.4, 22.7, 14.1. **HRMS** (ESI-TOF): m/z calcd for $C_{27}H_{39}NO_2^+$ ($[M+H]^+$) 410.2981, found 410.2991.

2-Chloro-1*H*-indole-3-carbaldehyde (3***ae***): Compound **3ae** was prepared following the general procedure, starting from 2-chloro-1*H*-indole (75.5 mg, 0.5 mmol) and Me_3N (268 mg, 1.5 mmol). After purification by column chromatography (hexane/ethyl acetate = 1:1), **3ae** was obtained as yellow solid (58 mg, 65% isolated yield). m.p. 196-198 ^oC. **^{1}H NMR** (400 MHz, DMSO) δ 13.12 (s, 1H), 10.01 (s, 1H), 8.08 (d, *J* = 7.1 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.23 (m, 2H). **^{13}C {^{1}H} NMR** (100 MHz, DMSO) δ 183.8, 135.2, 135.1, 124.8, 124.3, 123.3, 120.4, 112.5, 112.2. **HRMS** (ESI-TOF): m/z calcd for C_9H_6ClNO+ ($[M+H]^+$) 180.0138, found 180.0145.

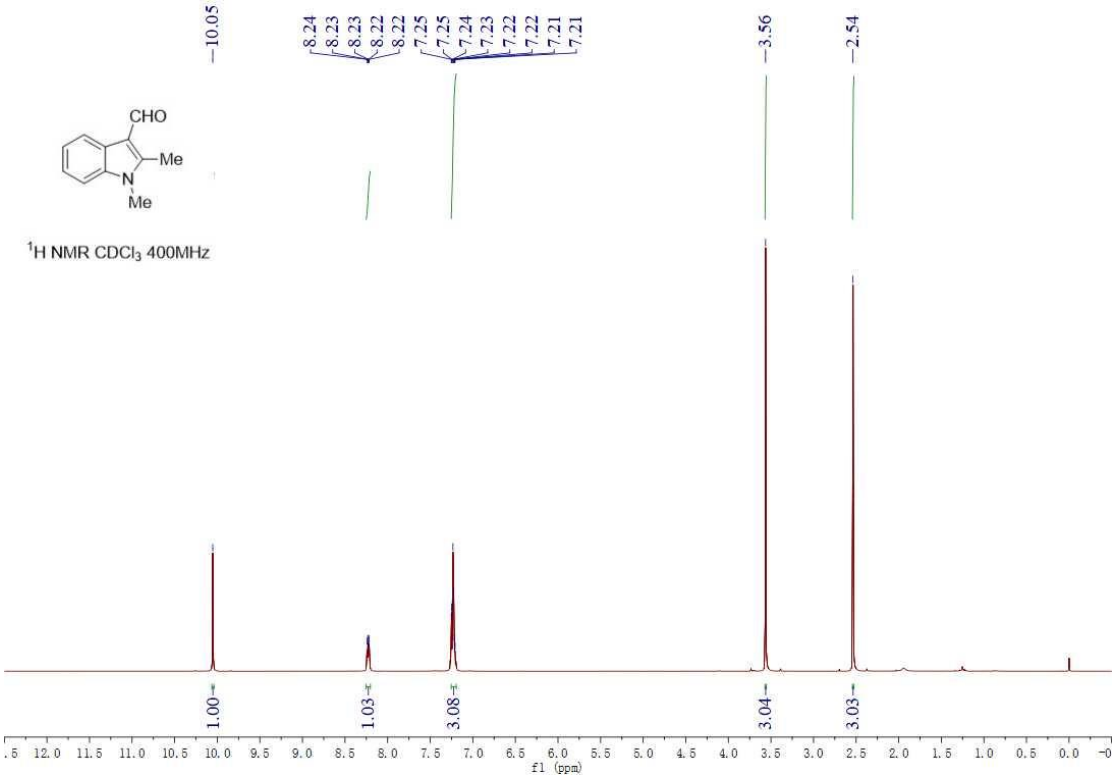
9. NMR spectra

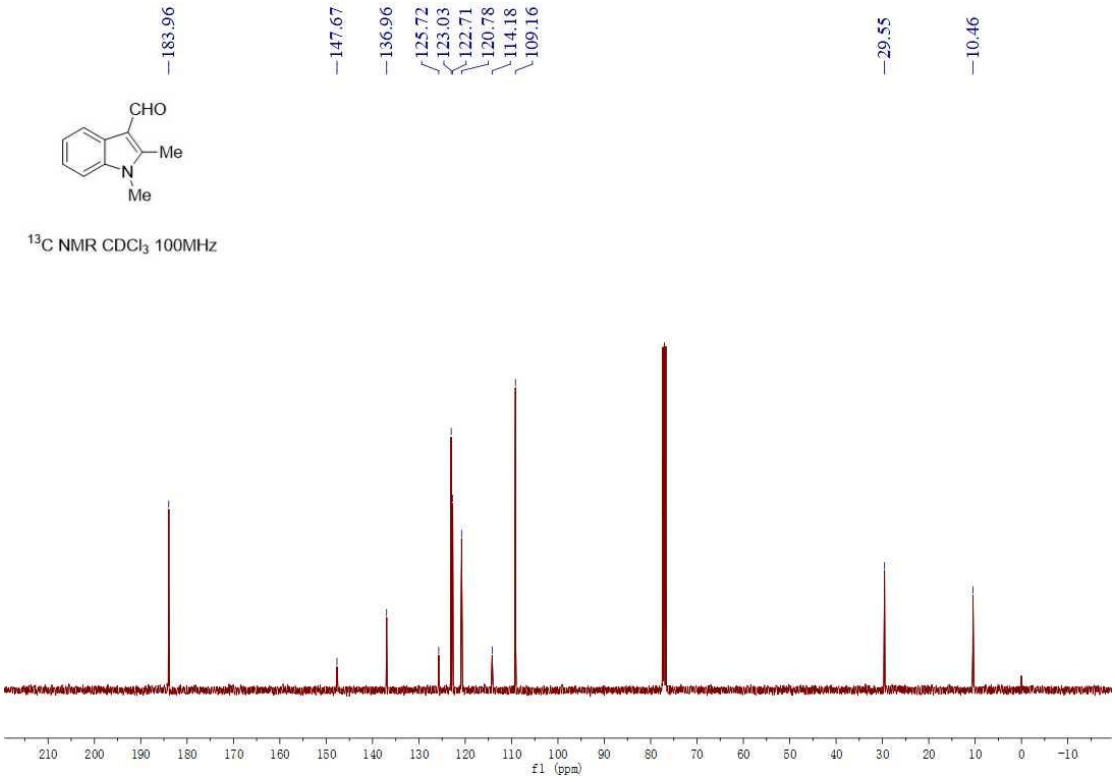
Methyl-1H-indole-3-carbaldehyde(***3a***)



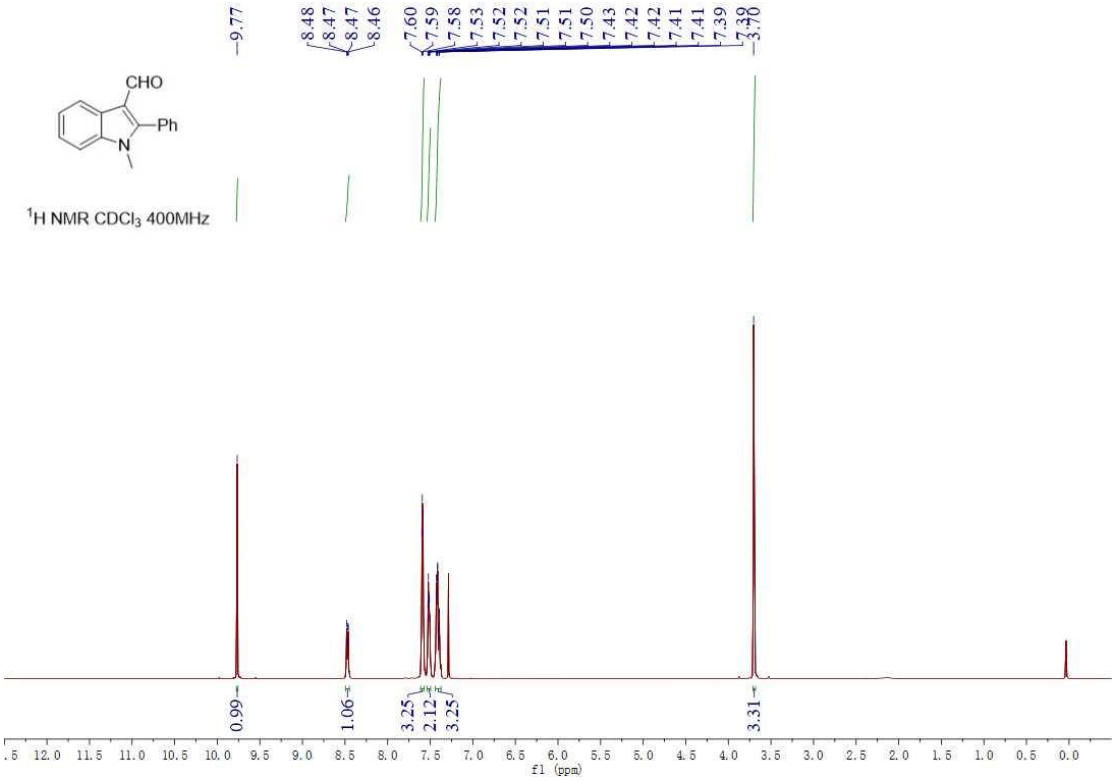


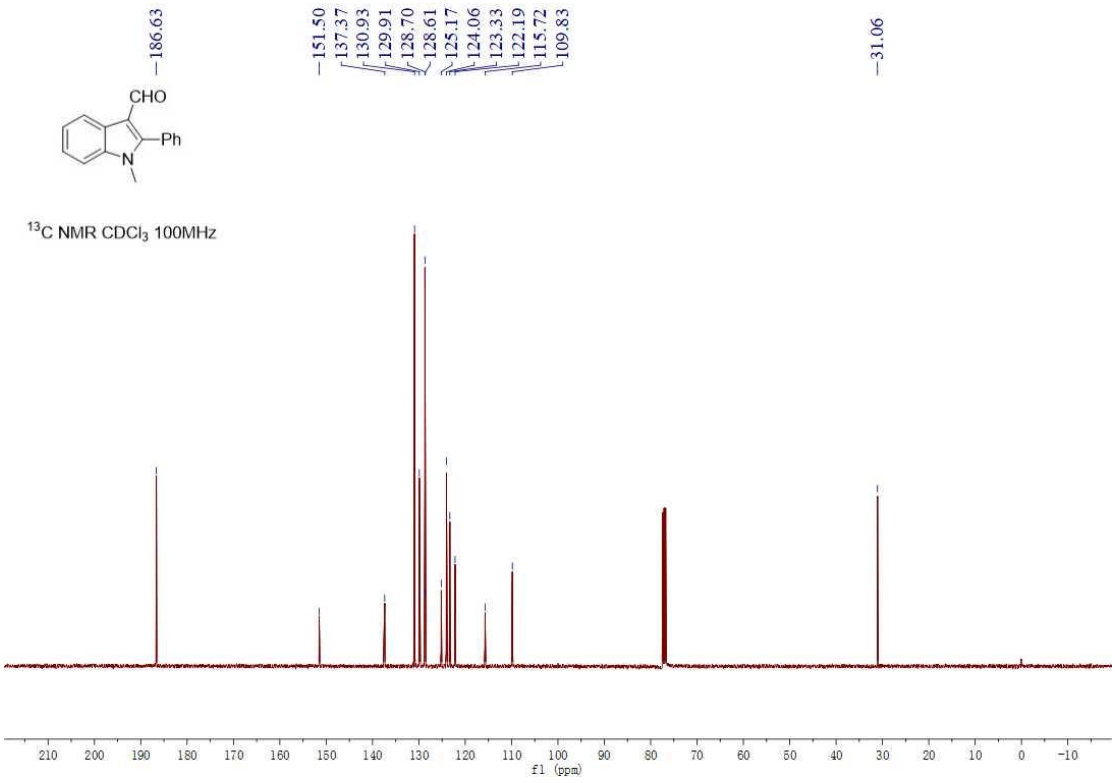
1,2-Dimethyl-1H-indole-3-carbaldehyde (***3b***)



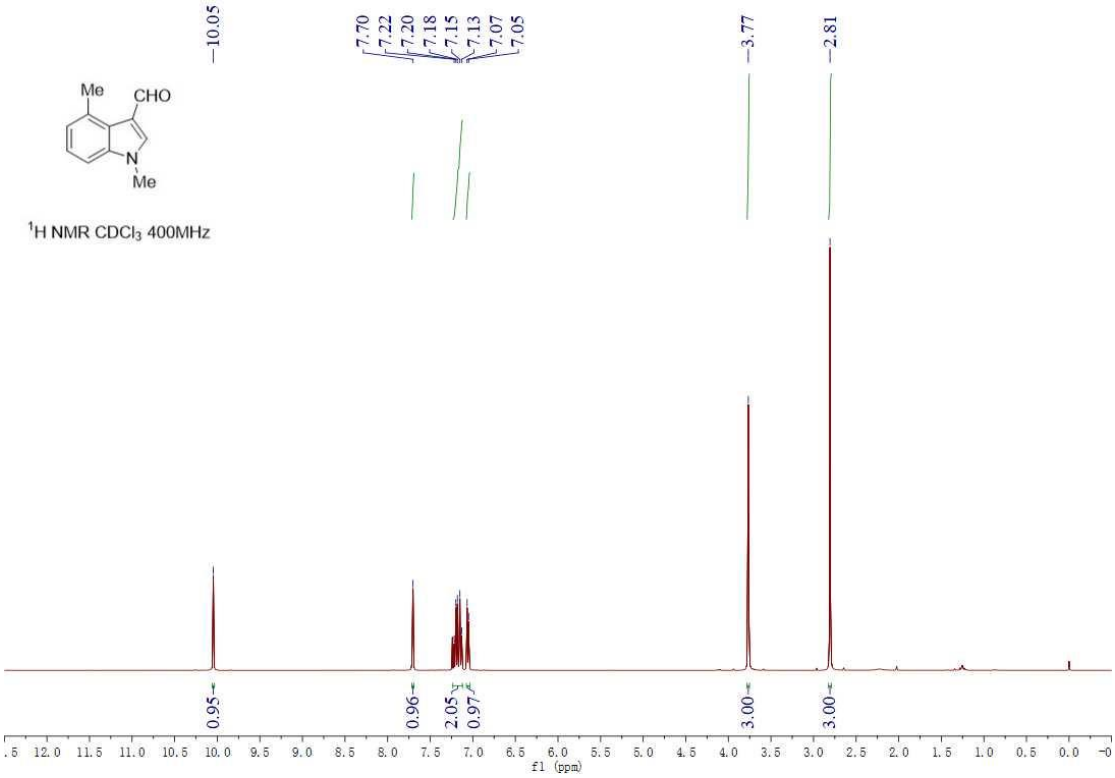


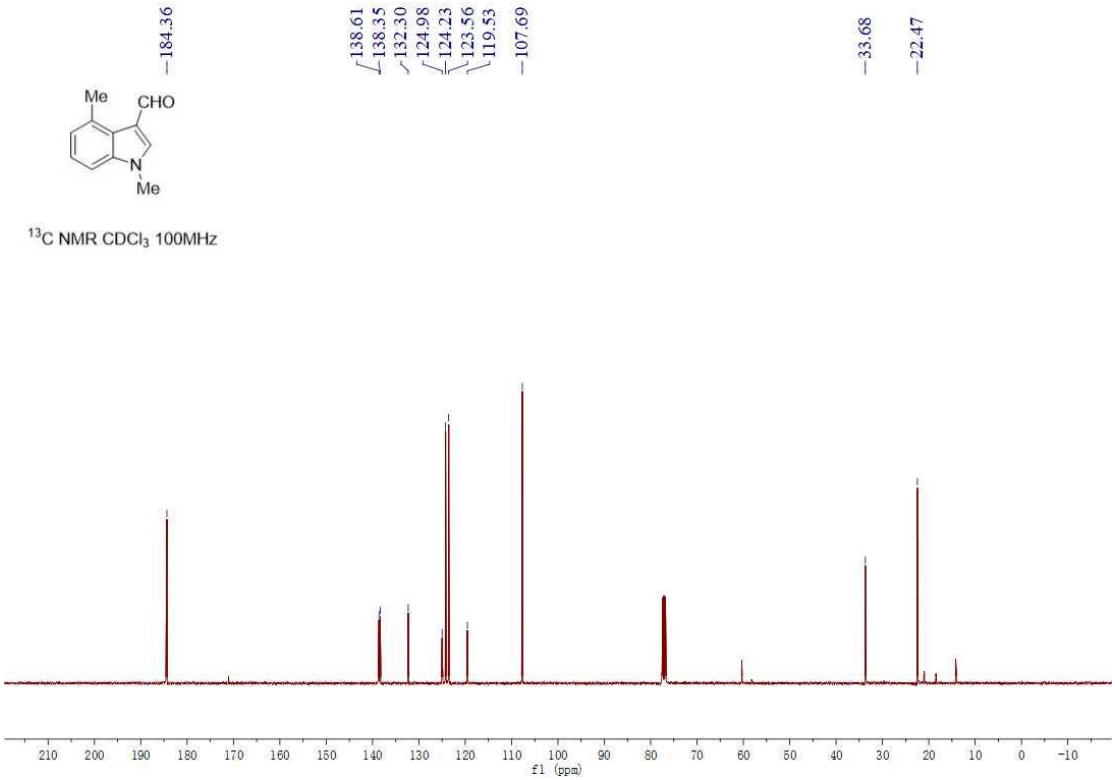
Methyl-2-phenyl-1H-indole-3-carbaldehyde (***3c***)



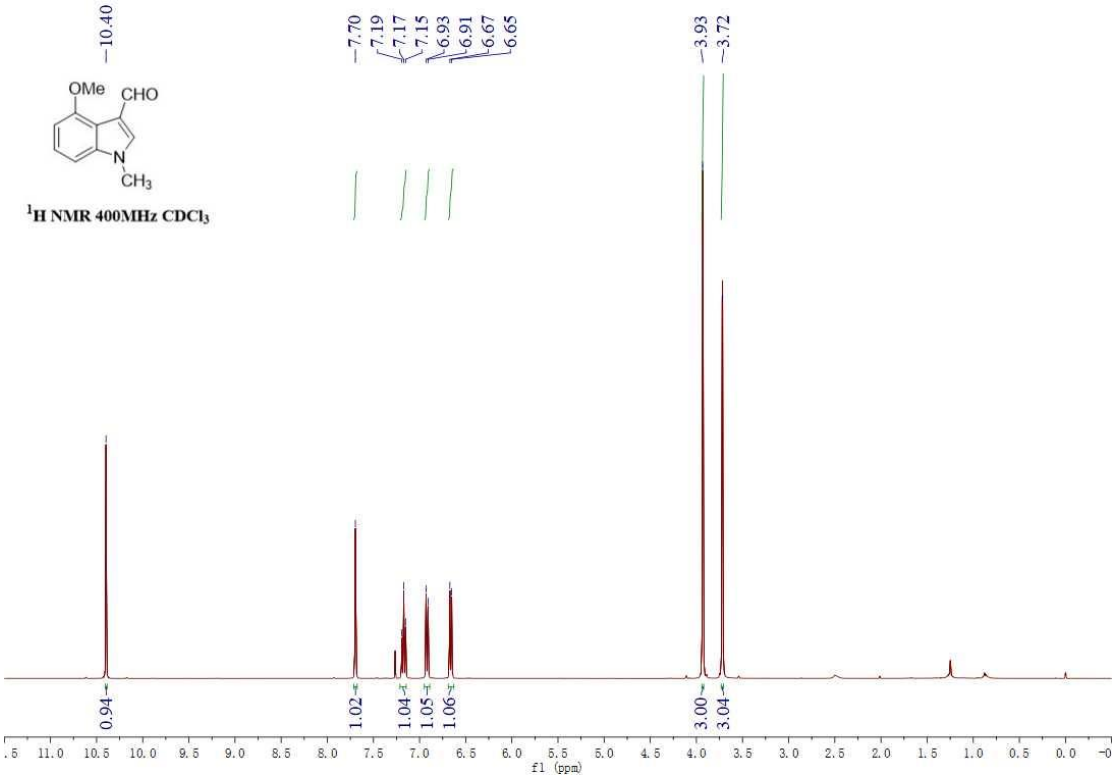


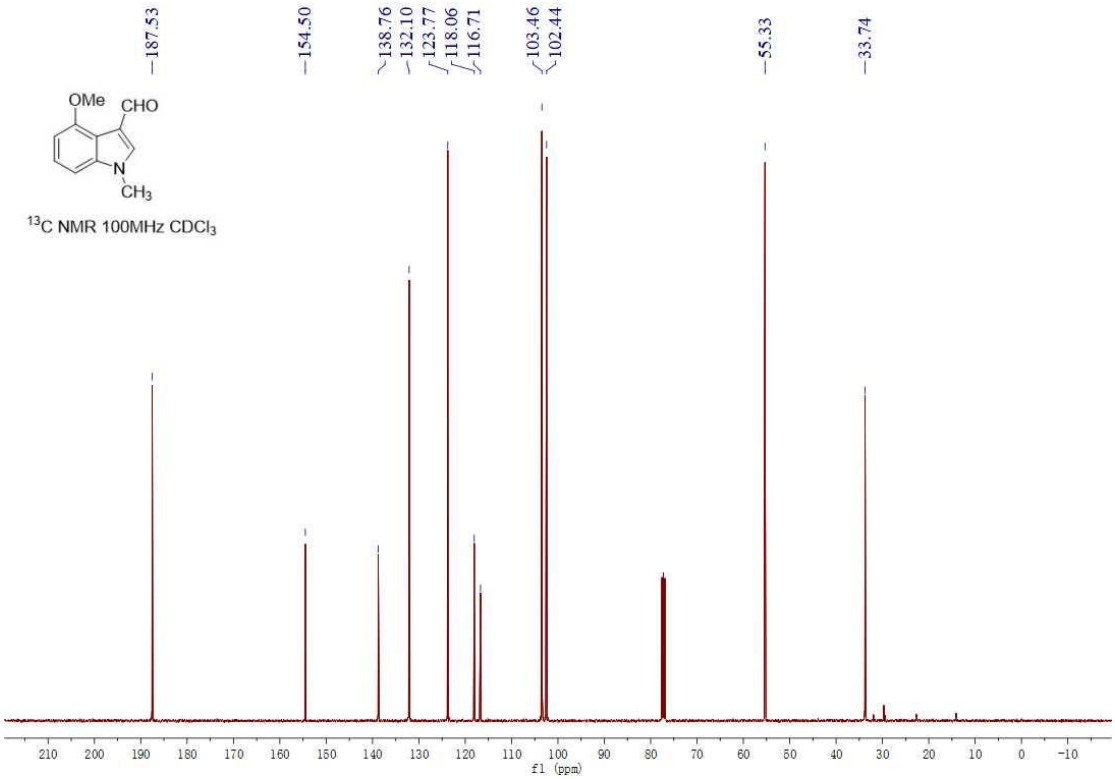
1,4-Dimethyl-1H-indole-3-carbaldehyde (***3d***)



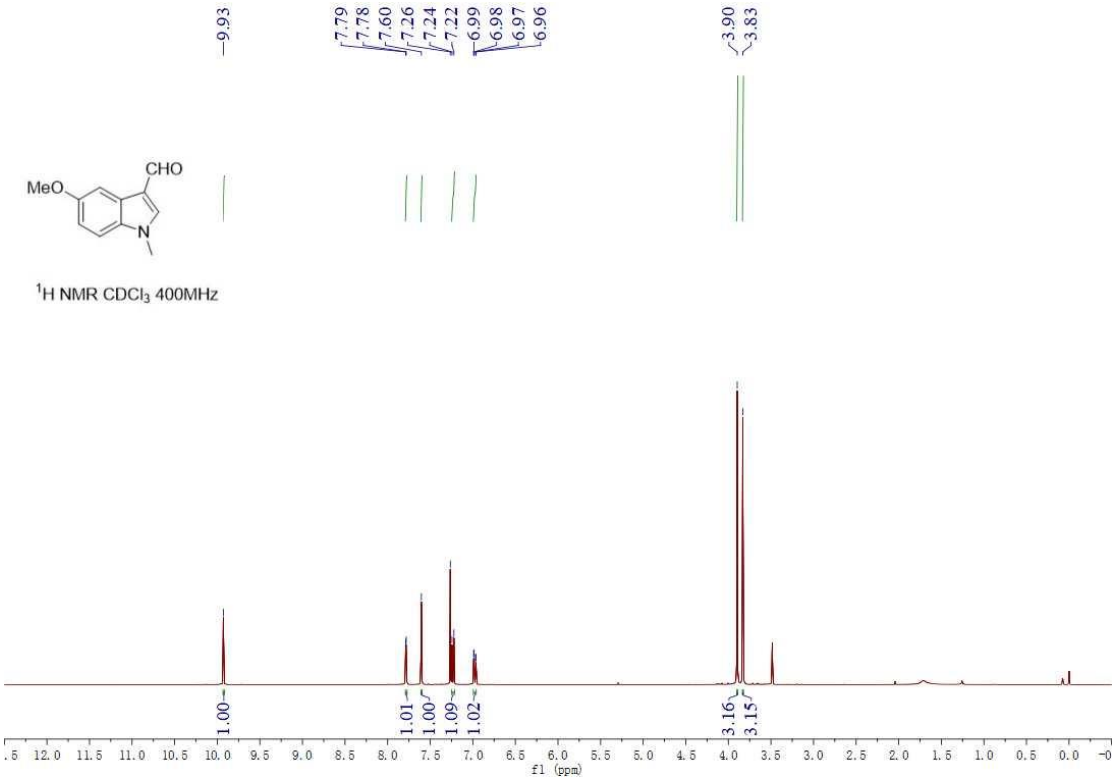


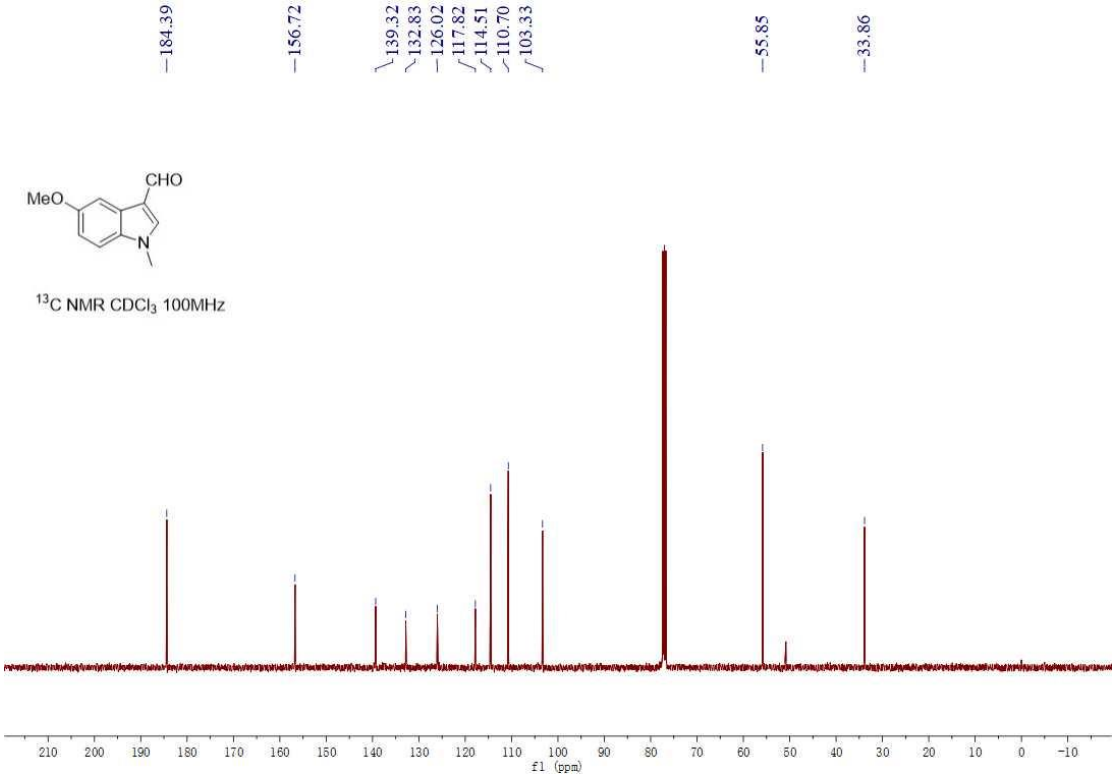
4-Methoxy-1-methyl-1H-indole-3-carbaldehyde (***3e***)



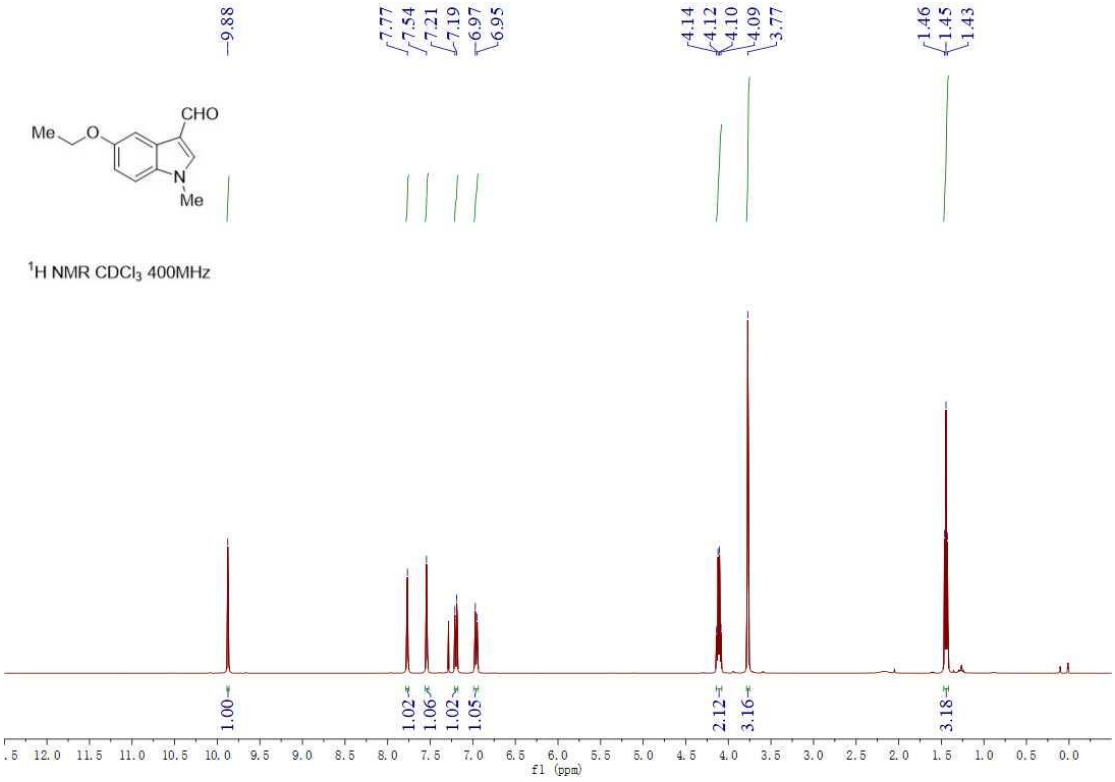


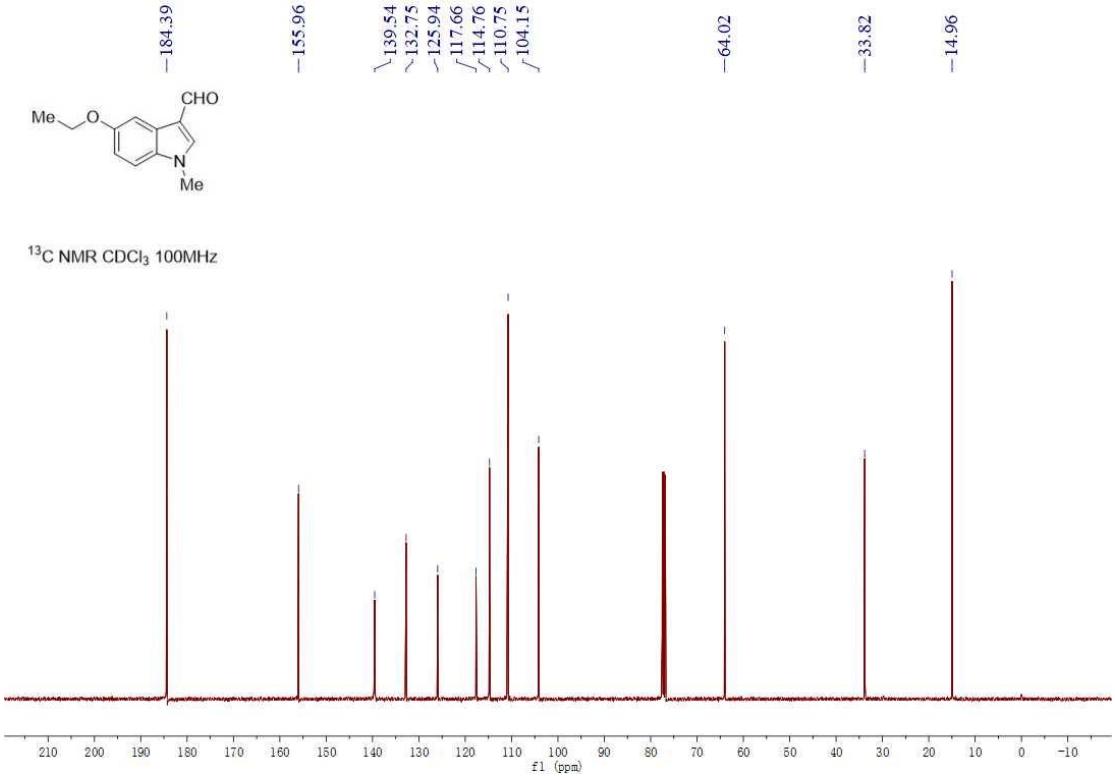
5-Methoxy-1-methyl-1H-indole-3-carbaldehyde (***3f***)



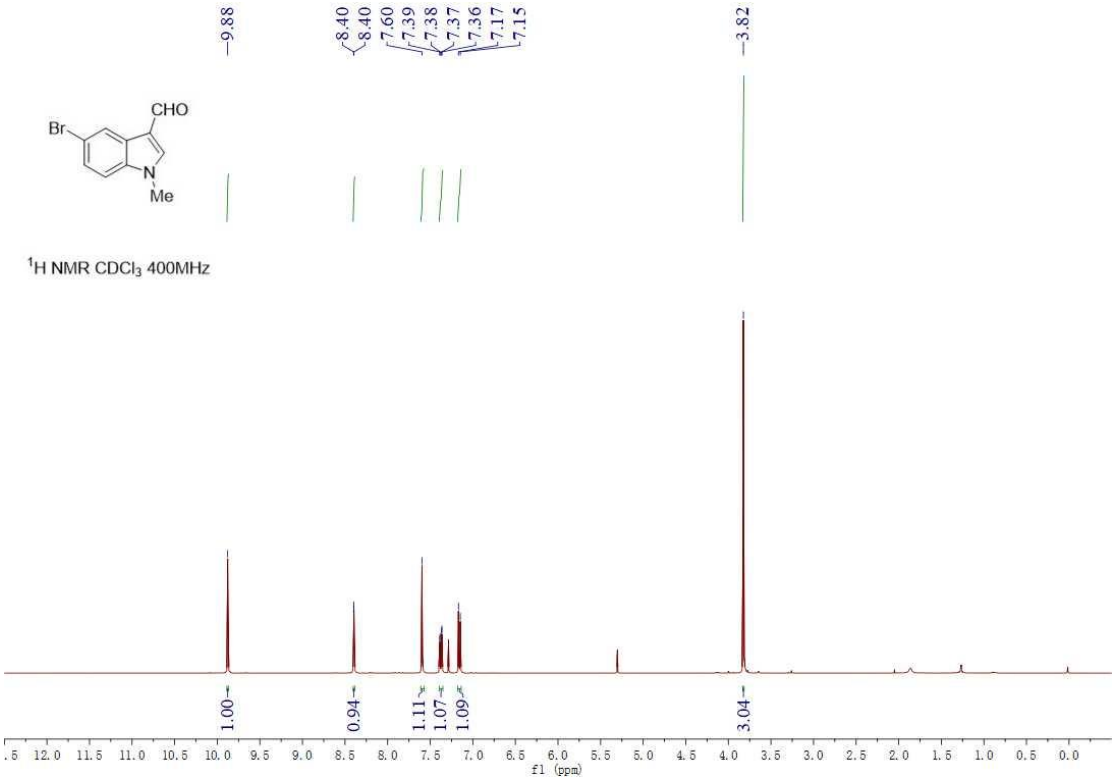


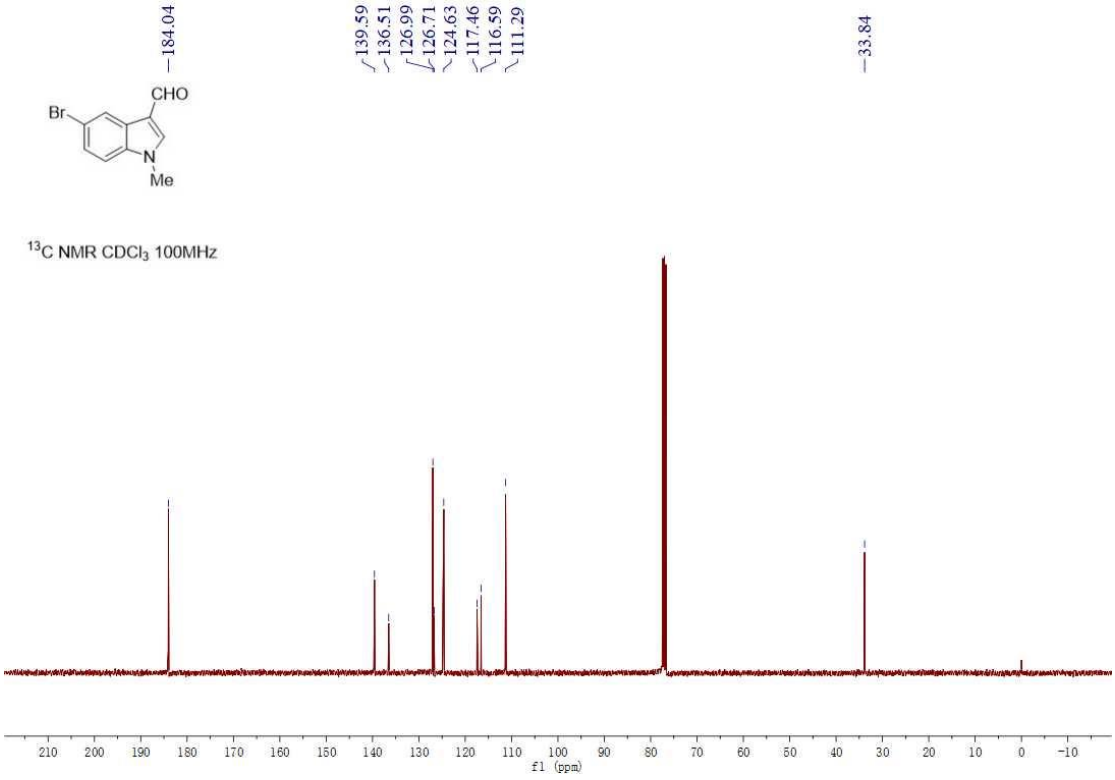
5-Ethoxy-1-methyl-1H-indole-3-carbaldehyde (***3g***):



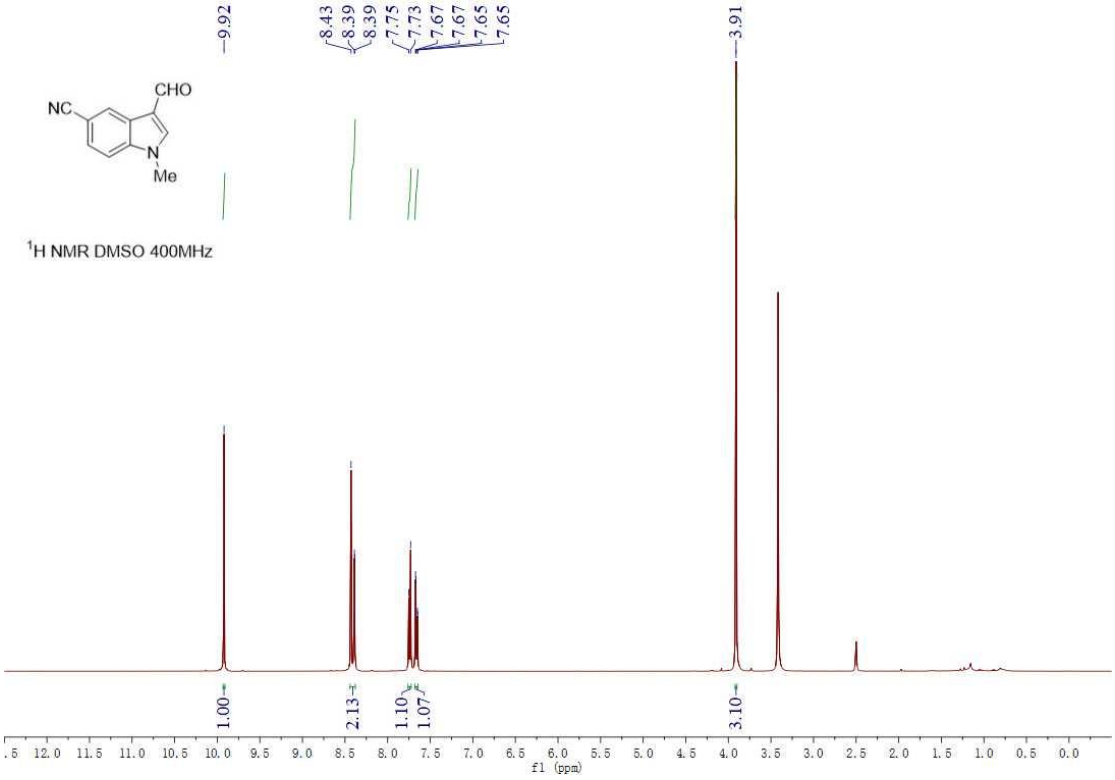


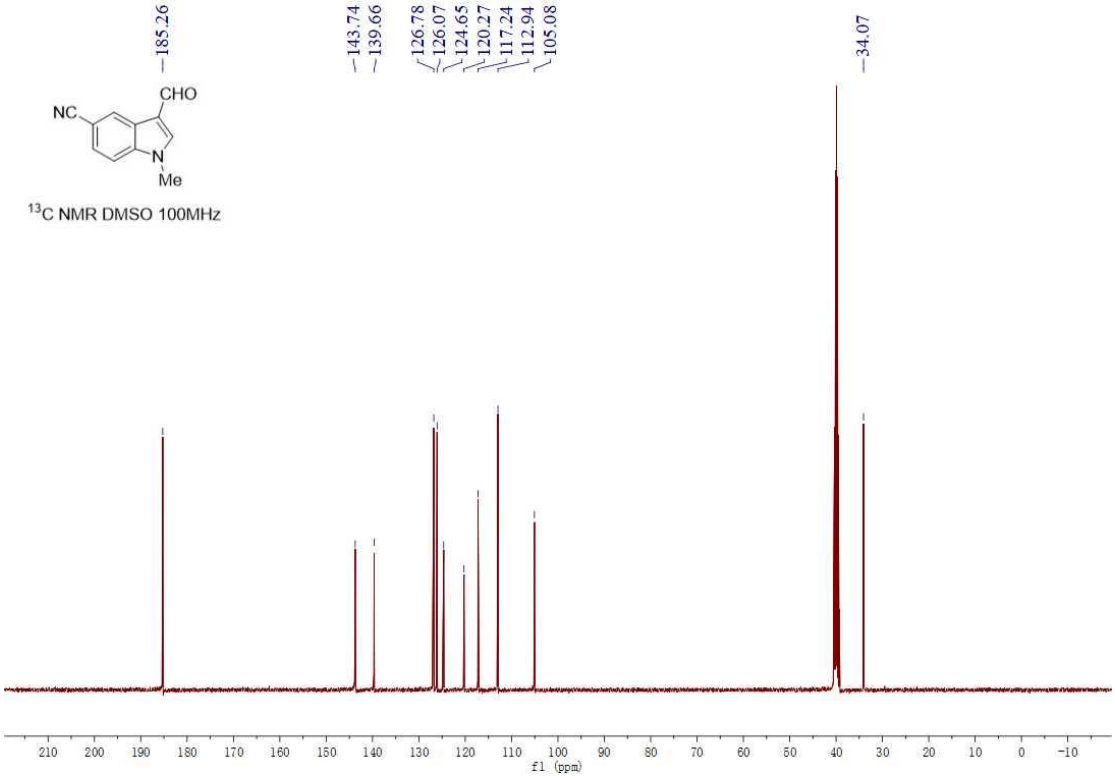
5-Bromo-1-methyl-1H-indole-3-carbaldehyde (***3h***):



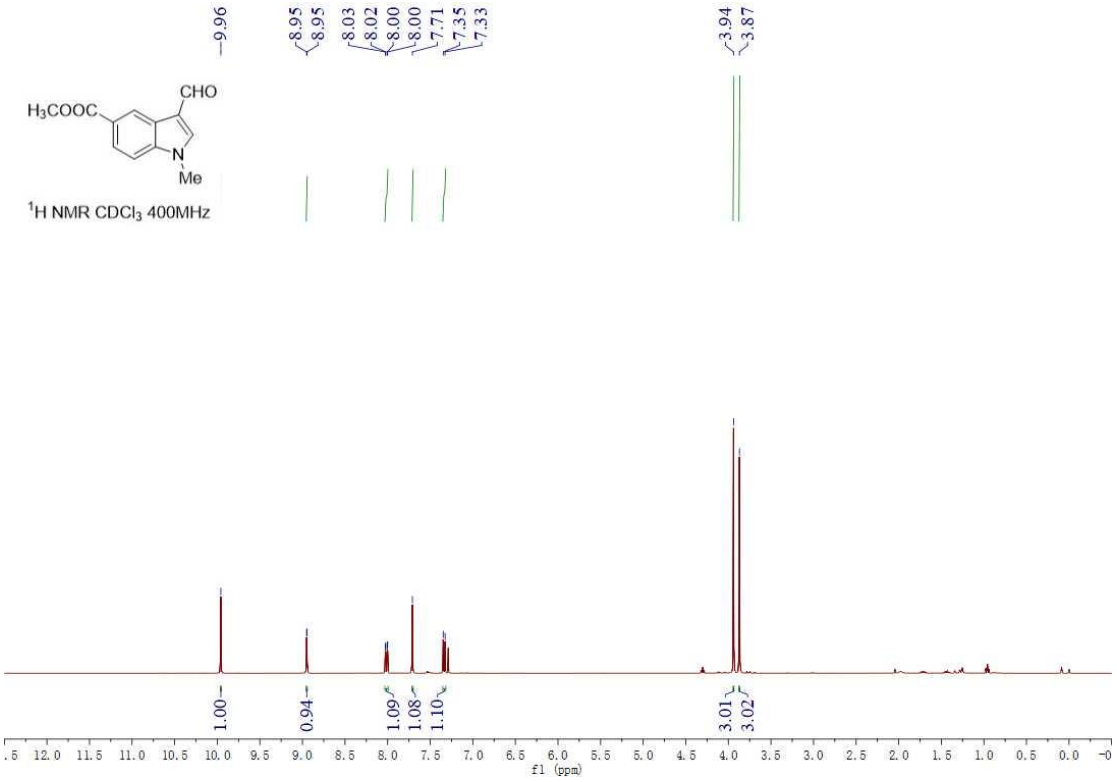


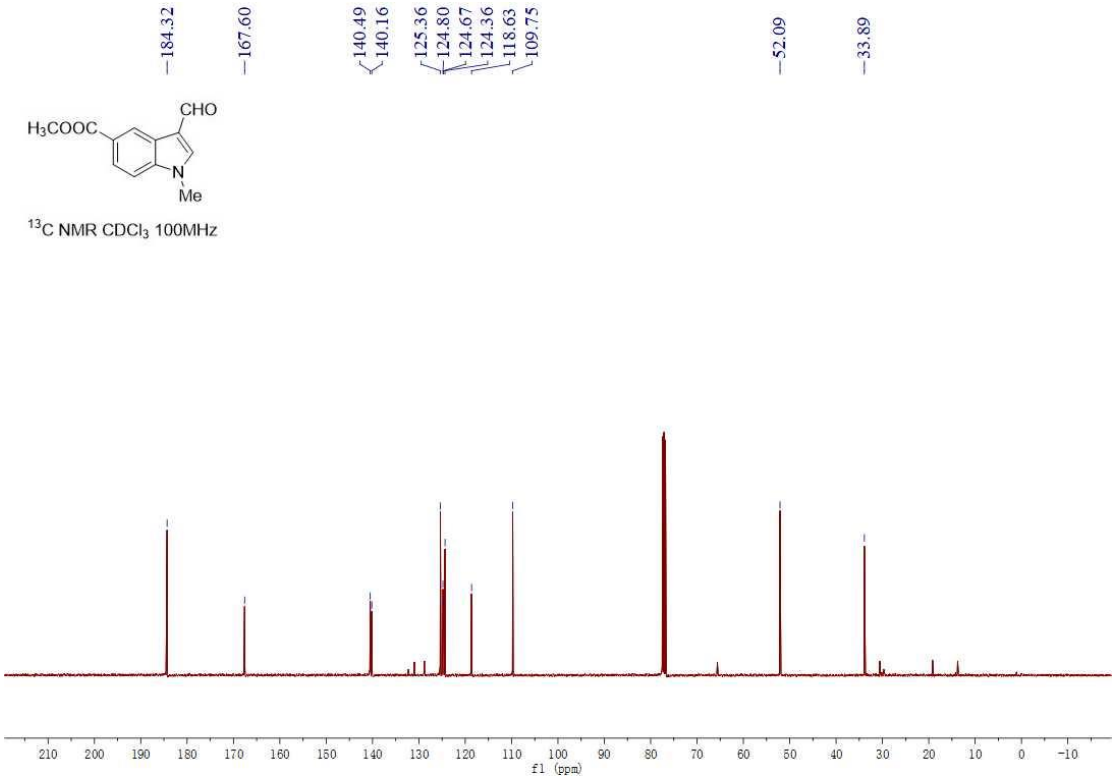
5-Cyano-1H-indole-3-carbaldehyde (***3i***):



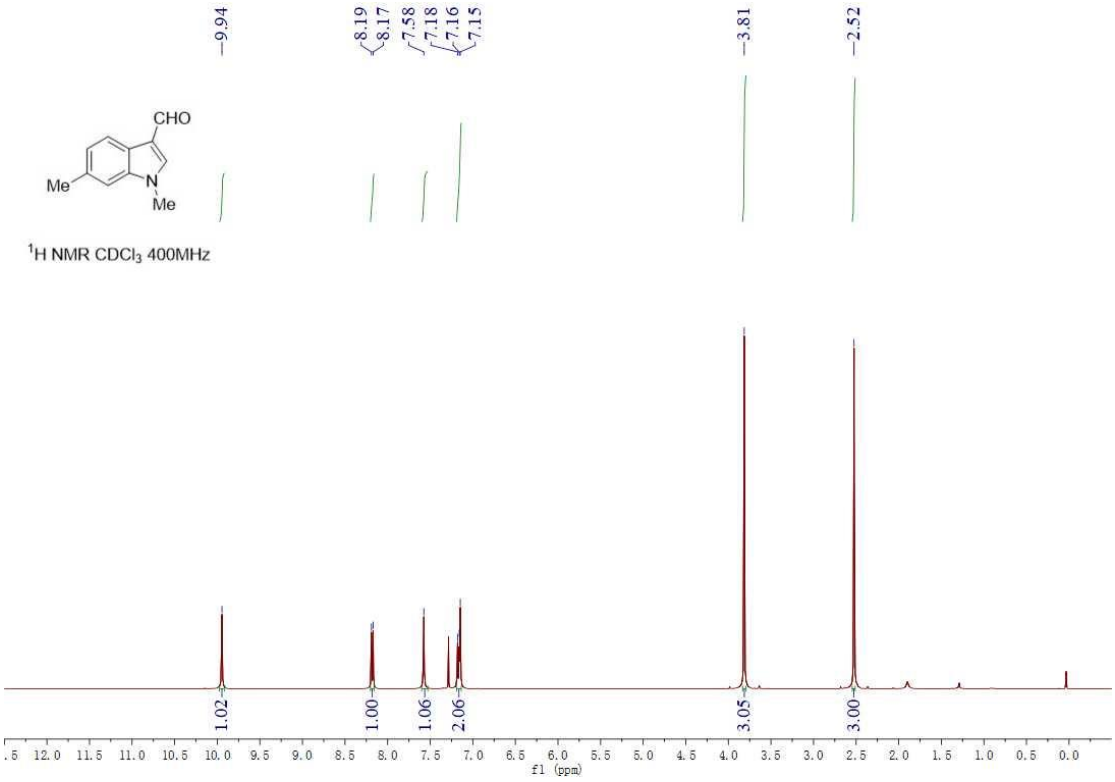


Methyl 3-formyl-1-methyl-1H-indole-5-carboxylate (***3j***):

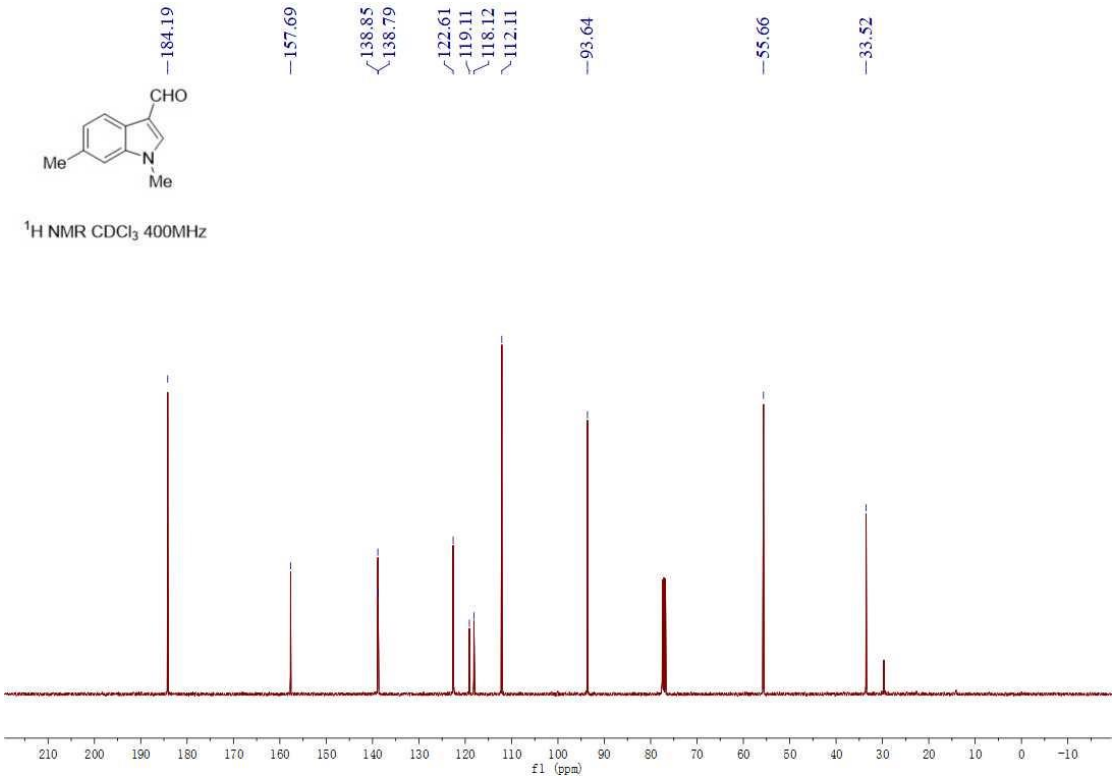




1,6-Dimethyl-1H-indole-3-carbaldehyde (***3k***)

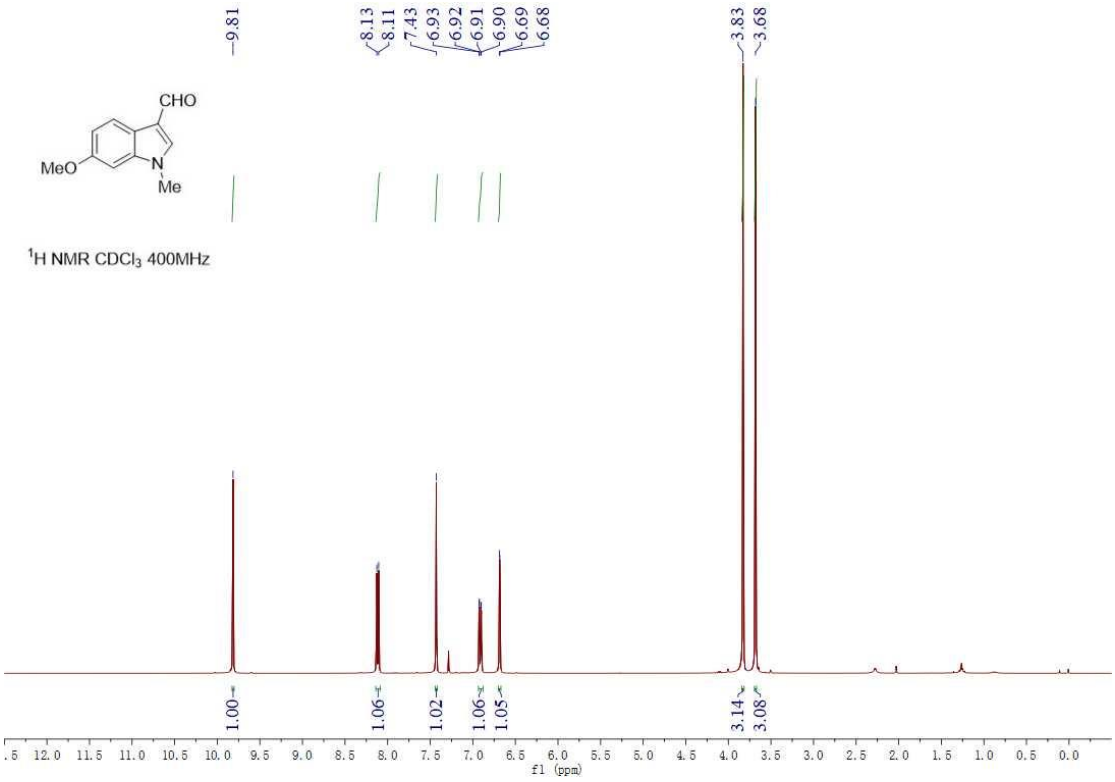


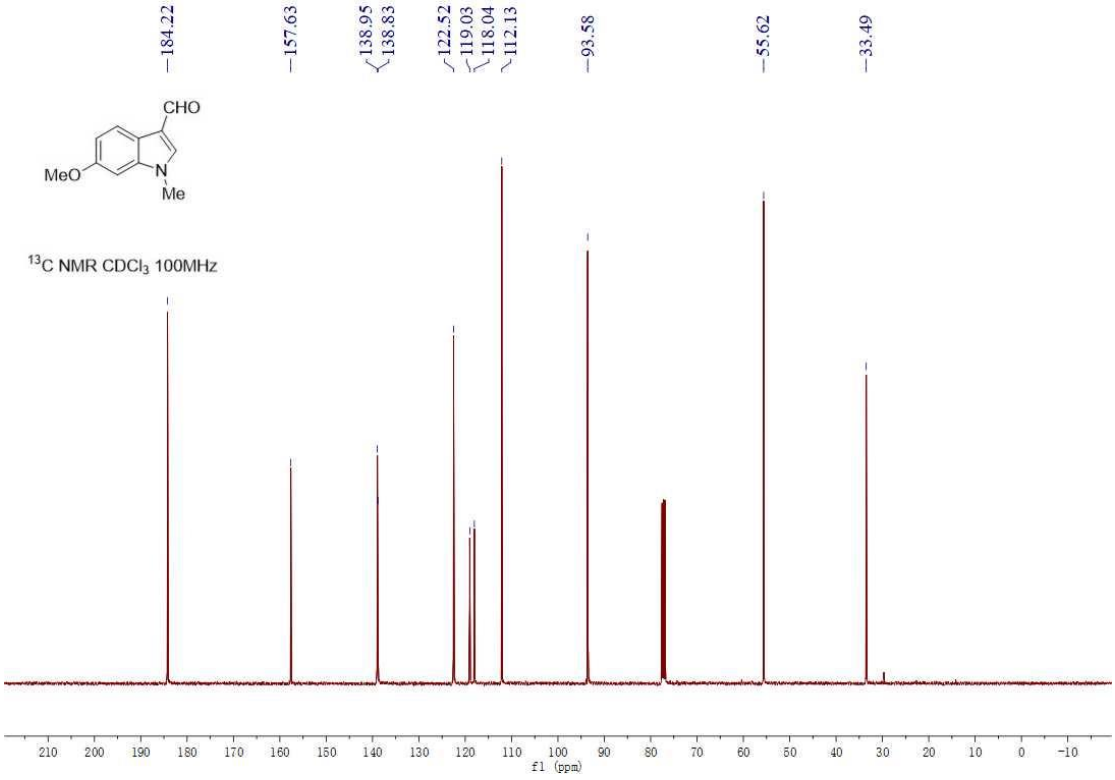
^{1}H NMR $CDCl_3$ 400MHz



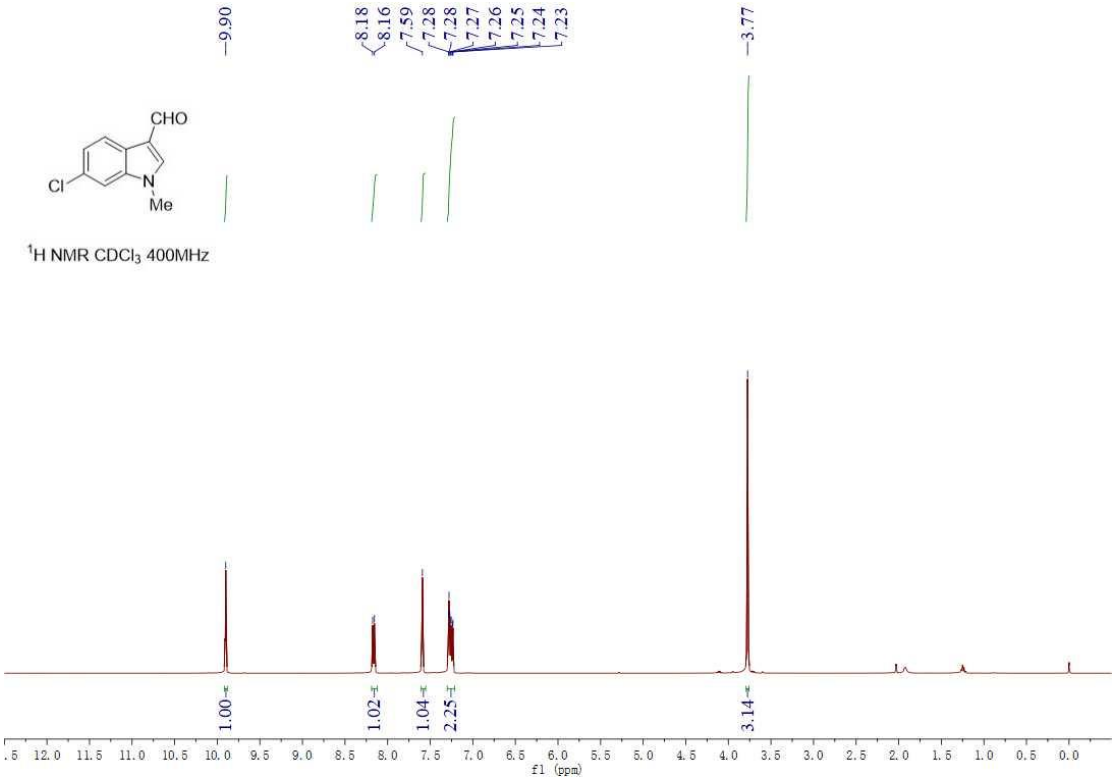
^{1}H NMR $CDCl_3$ 400MHz

6-Methoxy-1-methyl-1H-indole-3-carbaldehyde (***3l***)

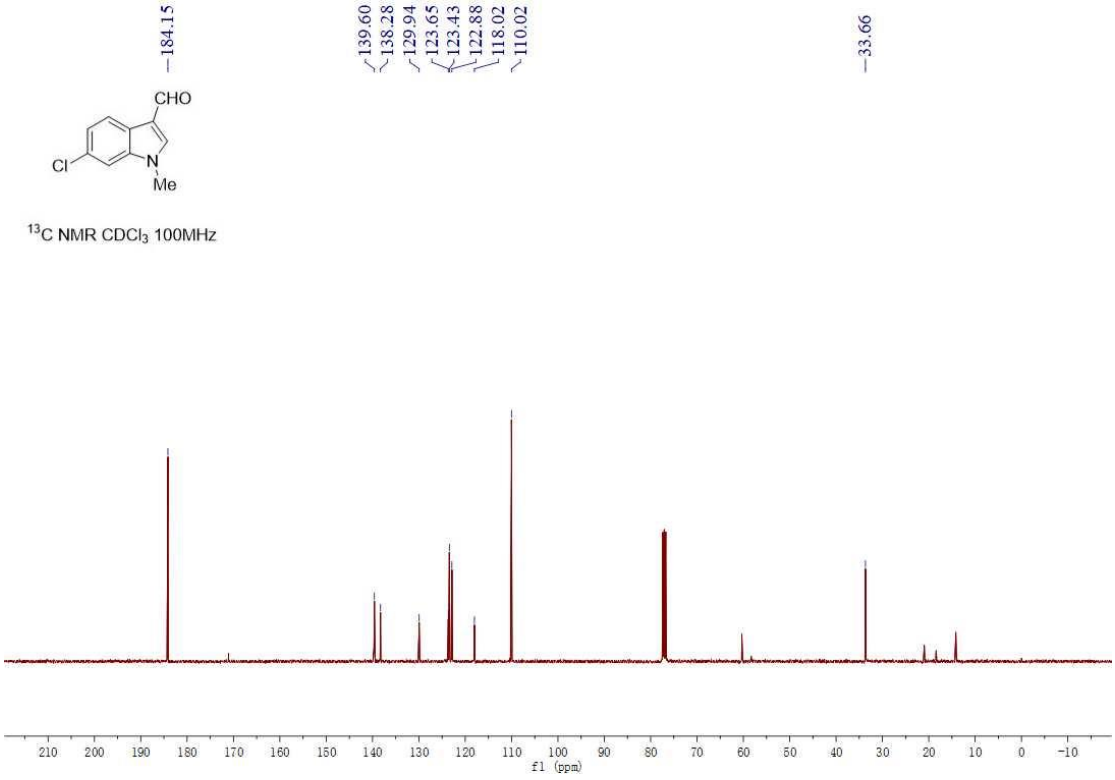




6-Clomo-1-methyl-1H-indole-3-carbaldehyde (***3m***):

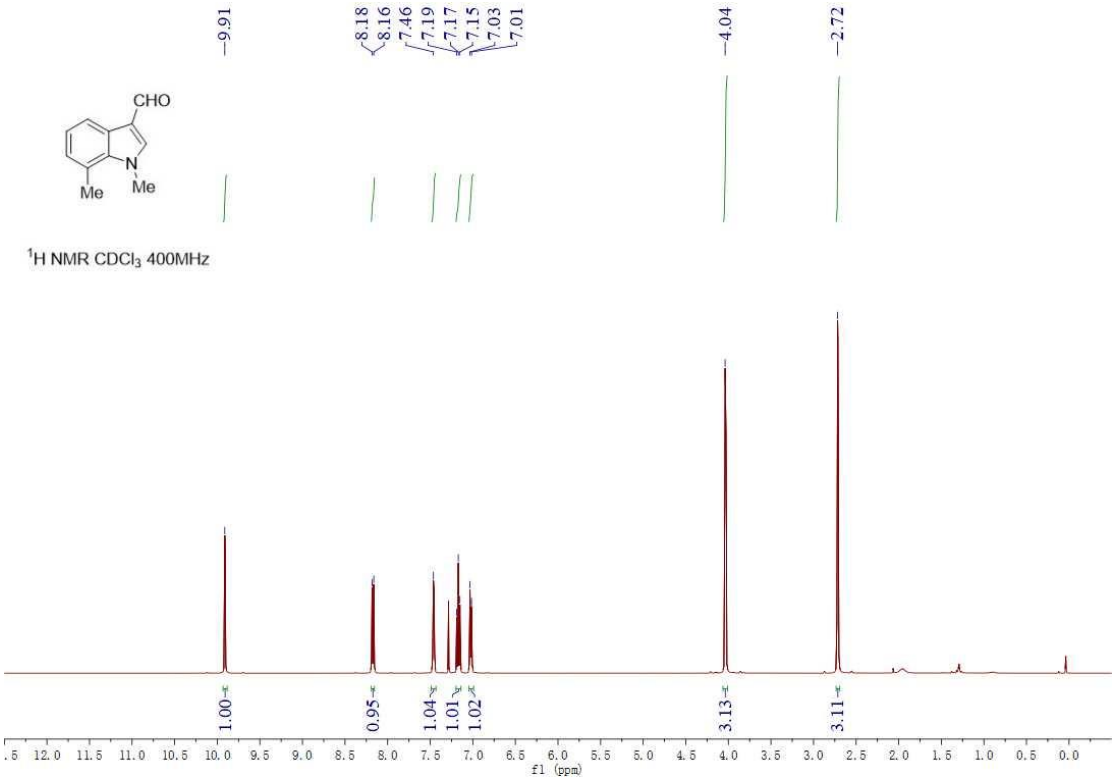


^{1}H NMR $CDCl_3$ 400MHz

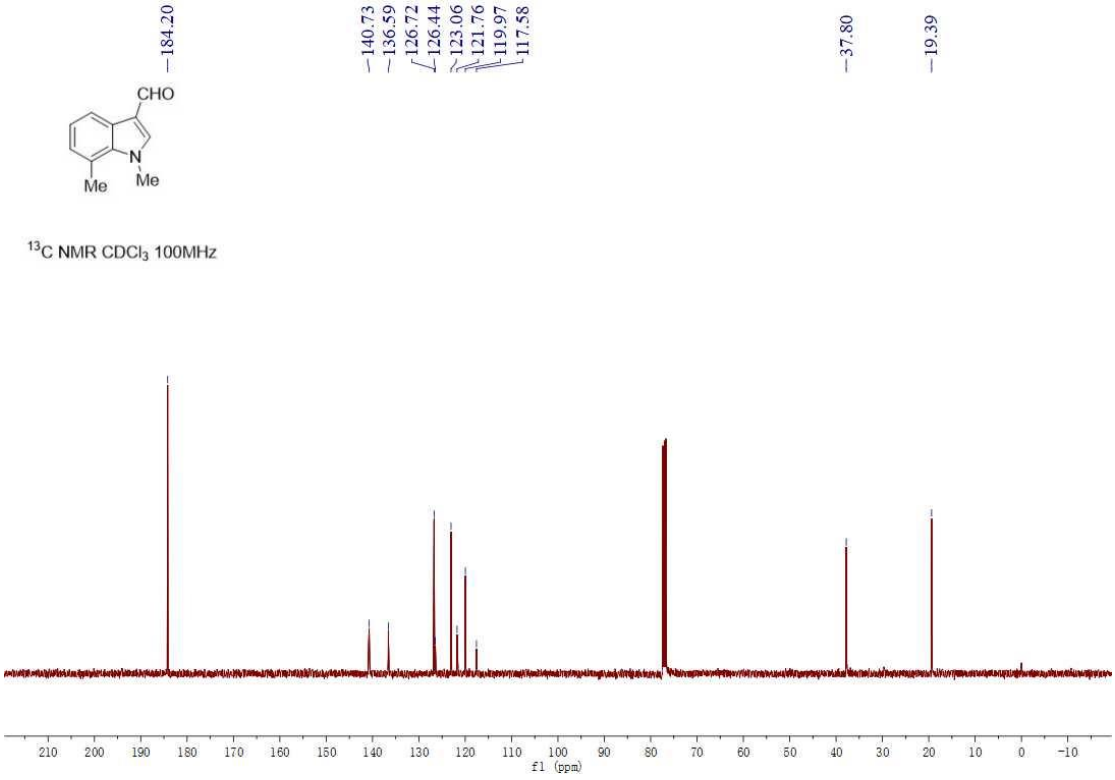


^{13}C NMR $CDCl_3$ 100MHz

1,7-Dimethyl-1H-indole-3-carbaldehyd (***3n***)

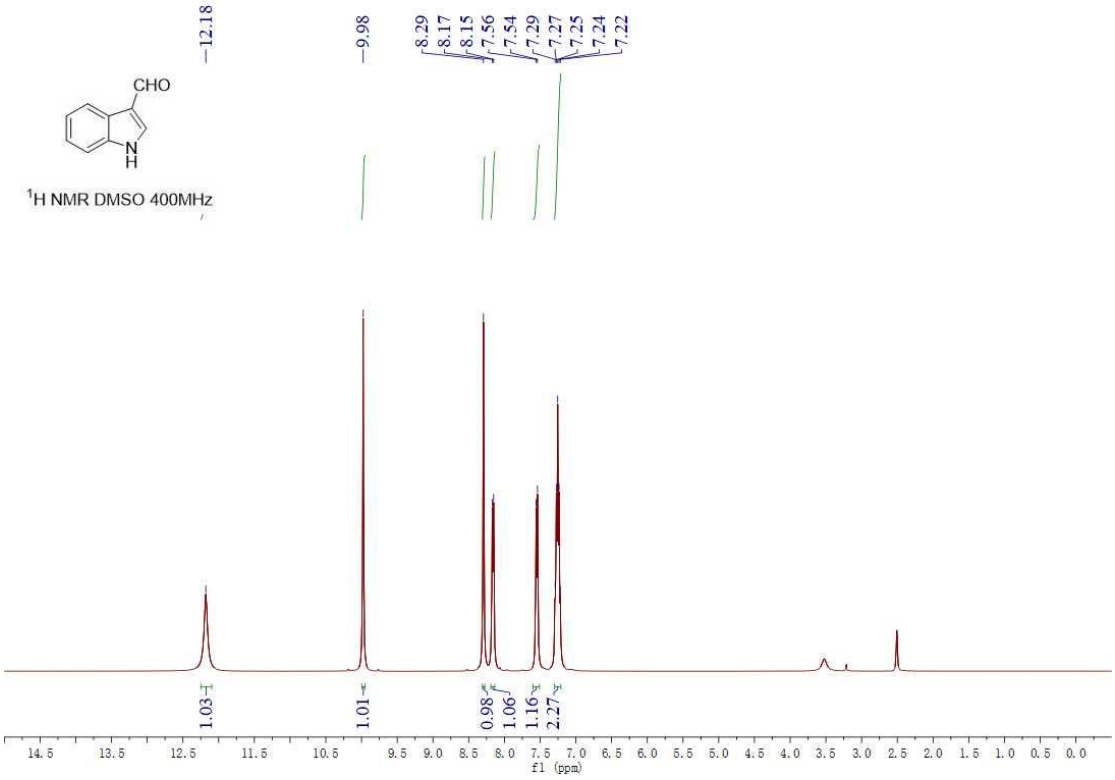


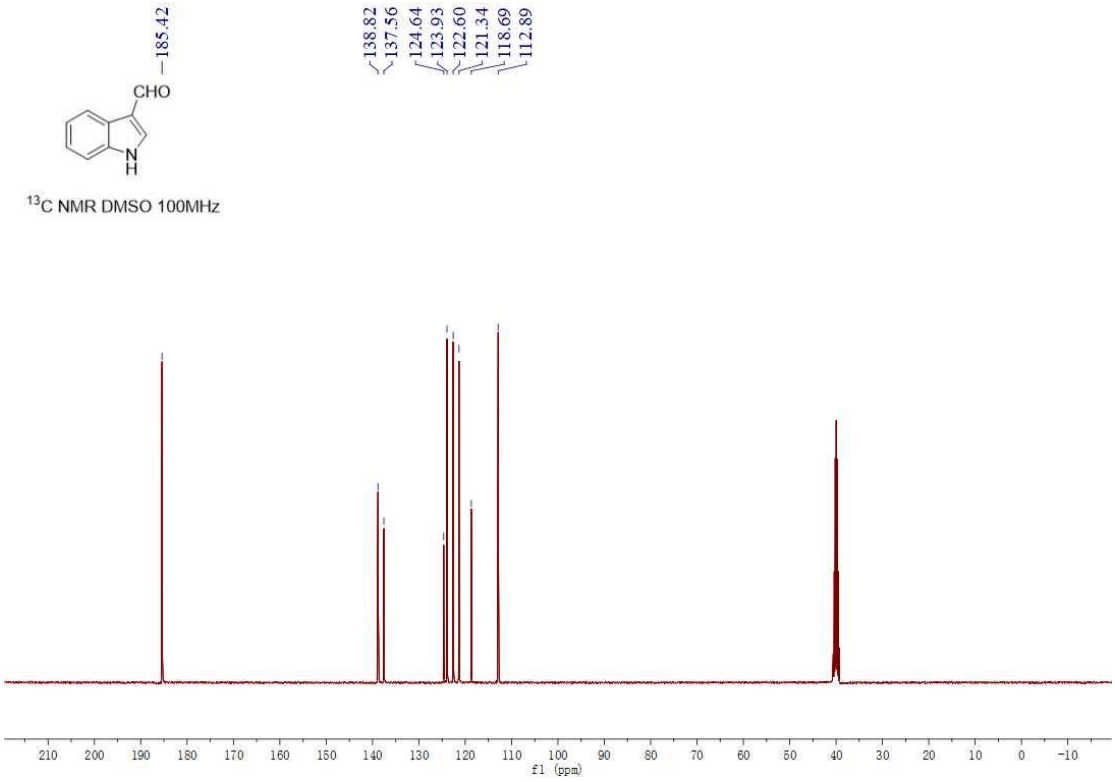
^{1}H NMR $CDCl_3$ 400MHz



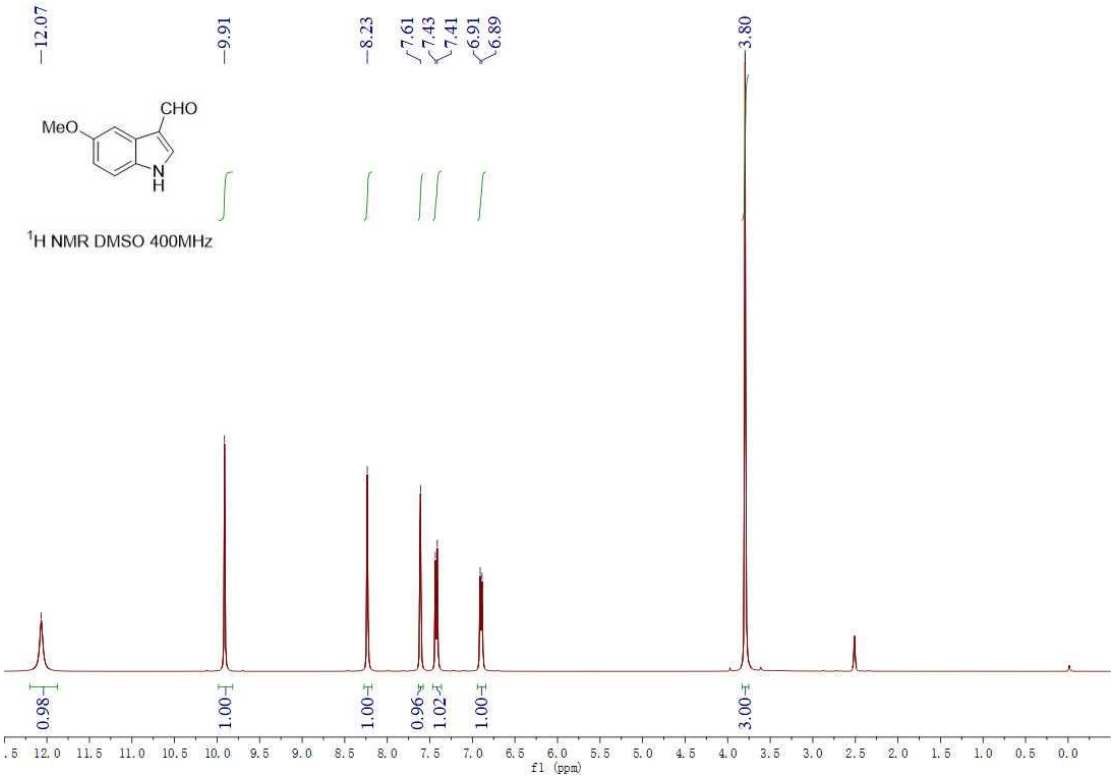
^{13}C NMR $CDCl_3$ 100MHz

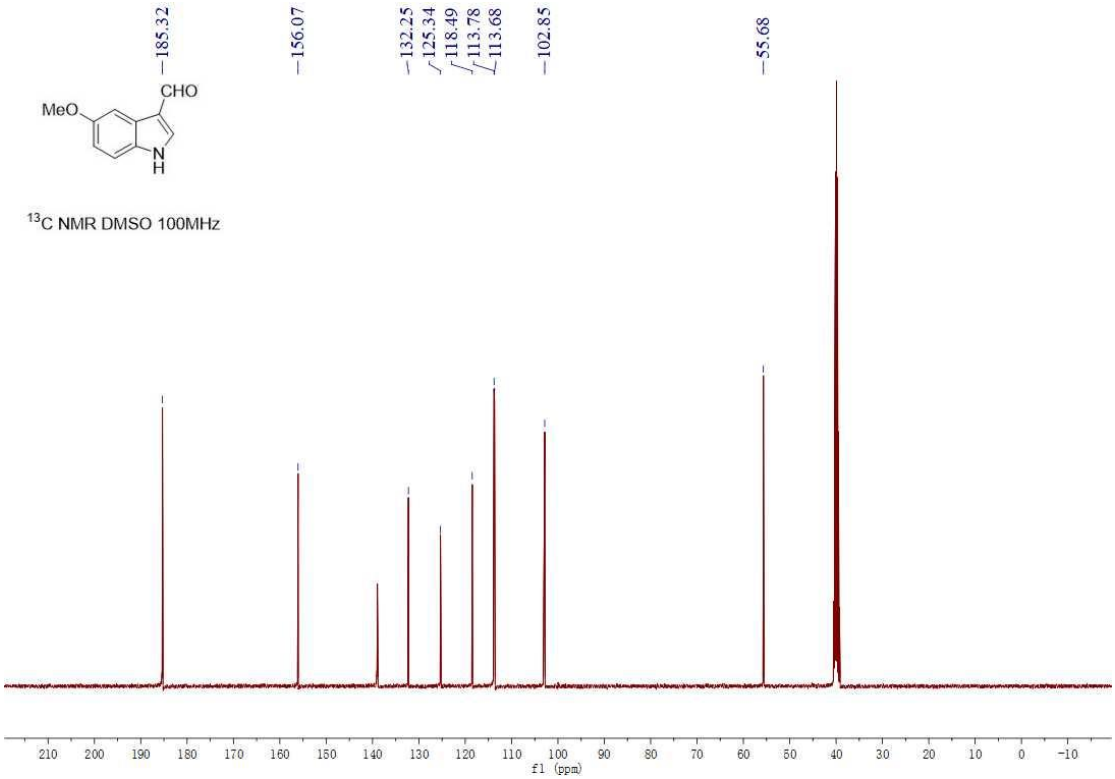
1H-Indole-3-carbaldehyde (***3o***):



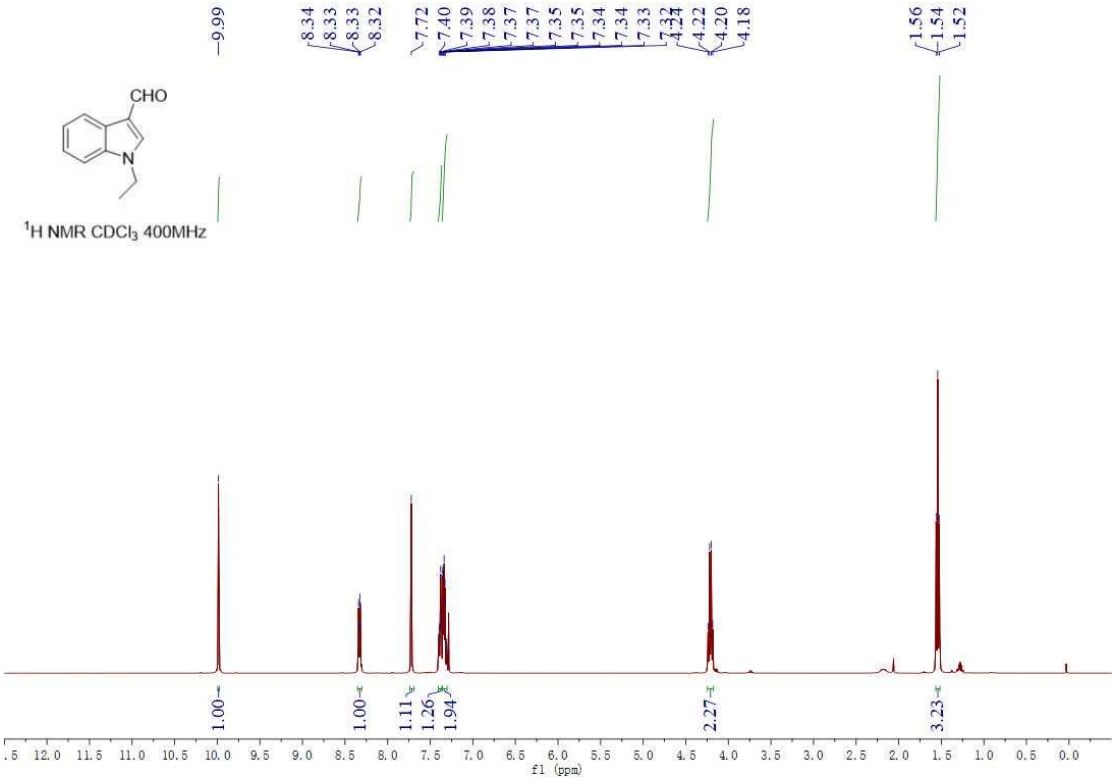


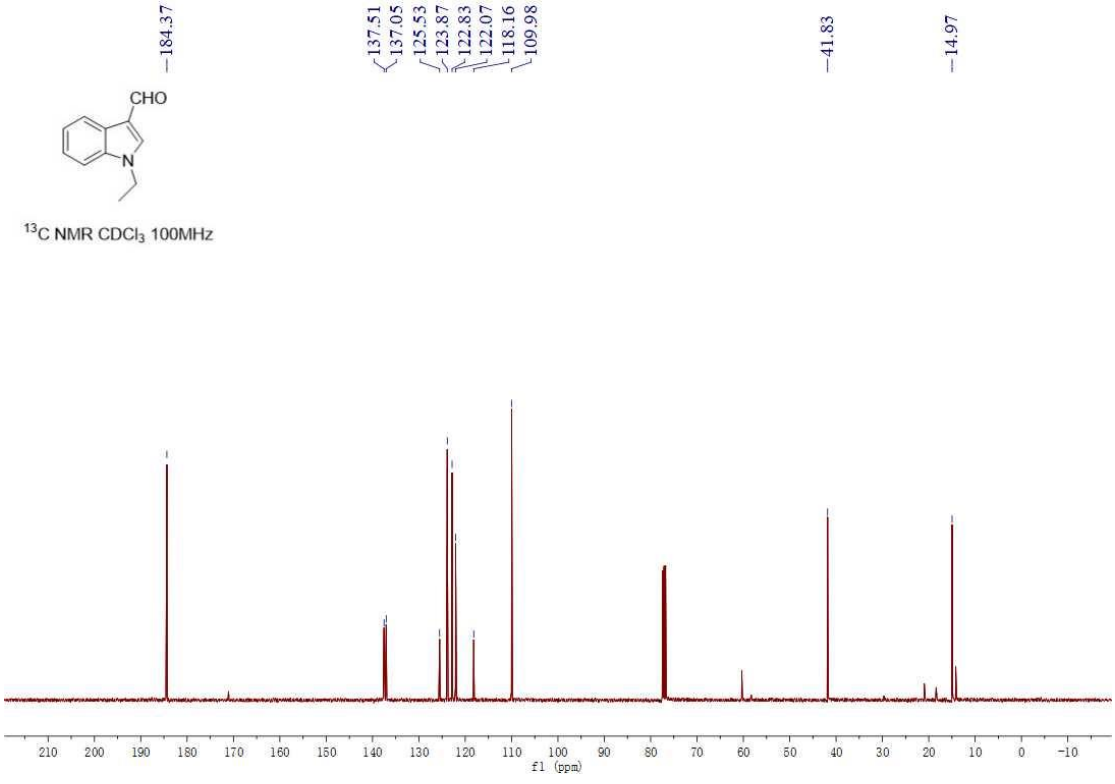
5-Methoxy-1H-indole-3-carbaldehyde (***3p***):



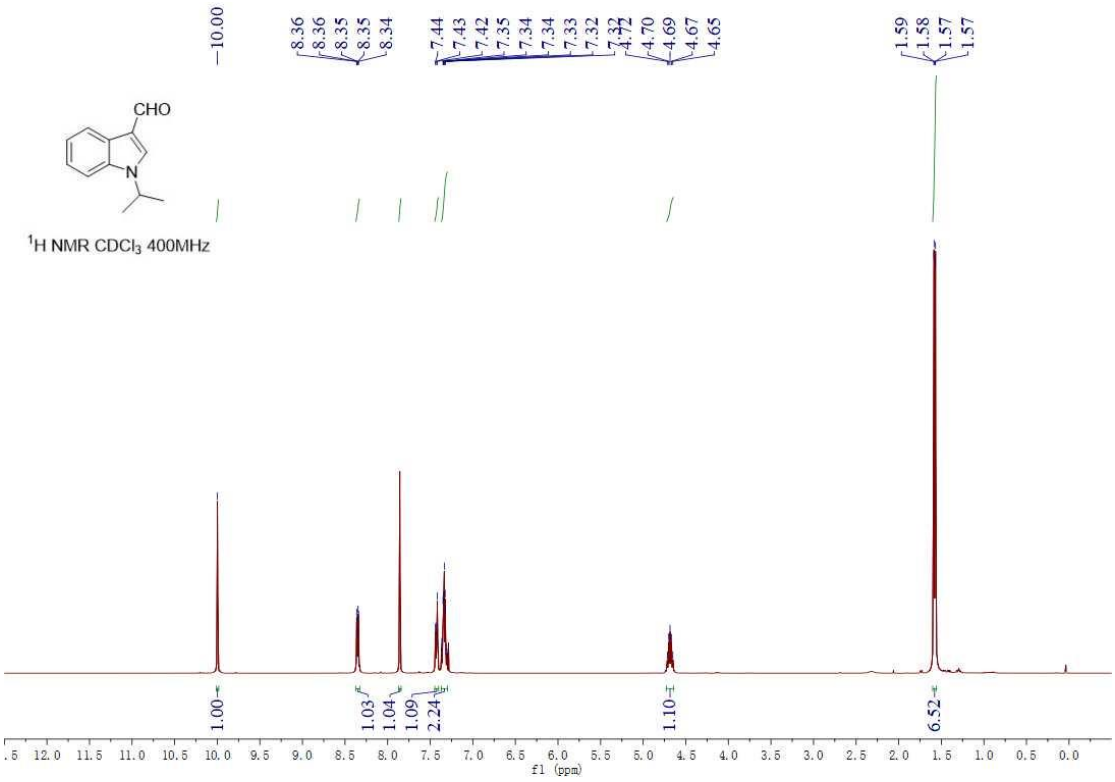


1-Ethyl-1H-indole-3-carbaldehyde (***3q***)

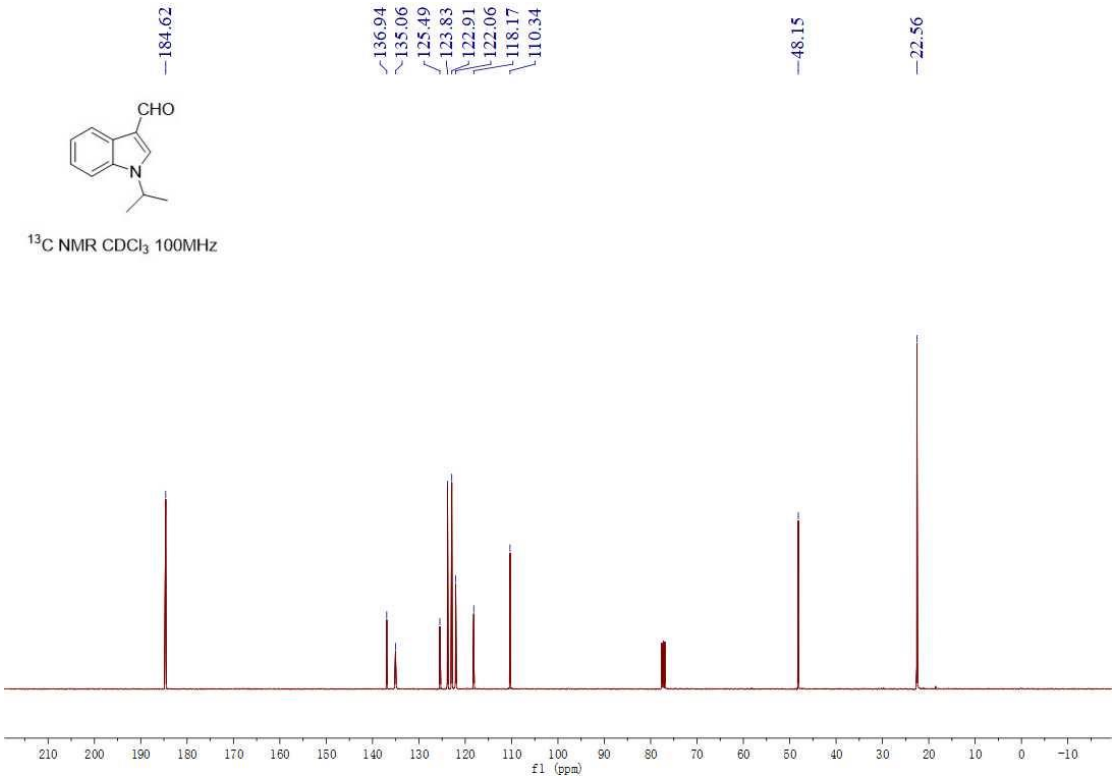




iso-Propyl-1H-indole-3-carbaldehyde (***3r***)

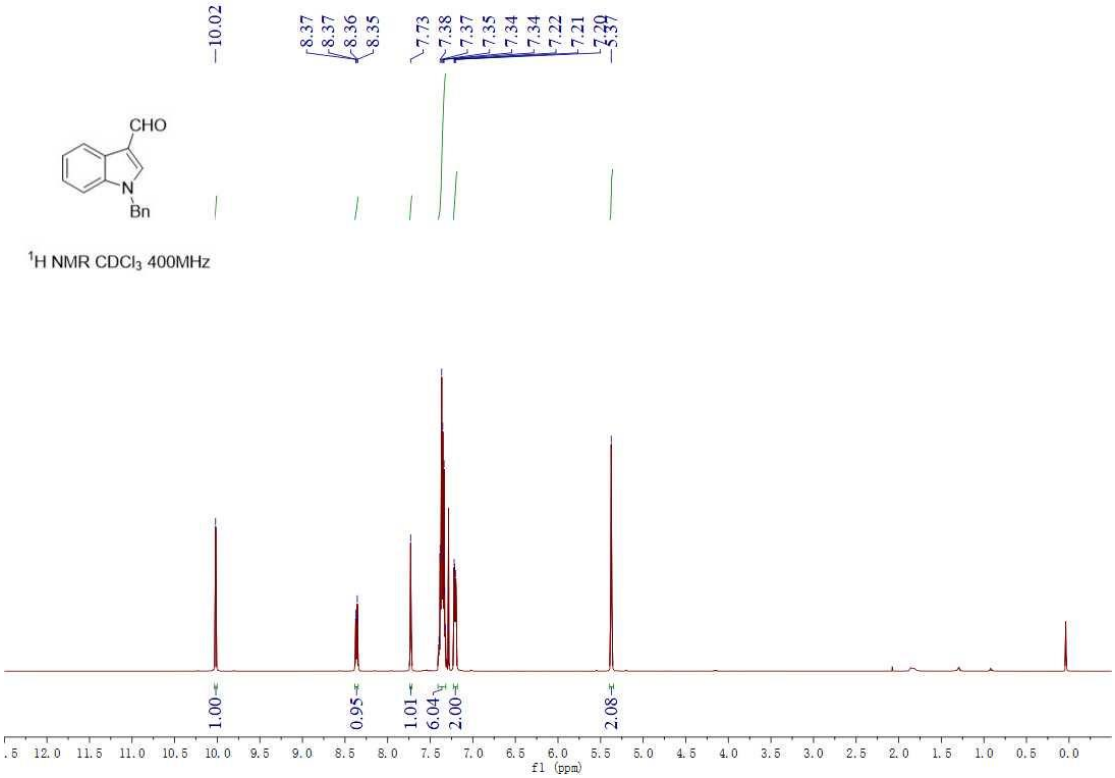


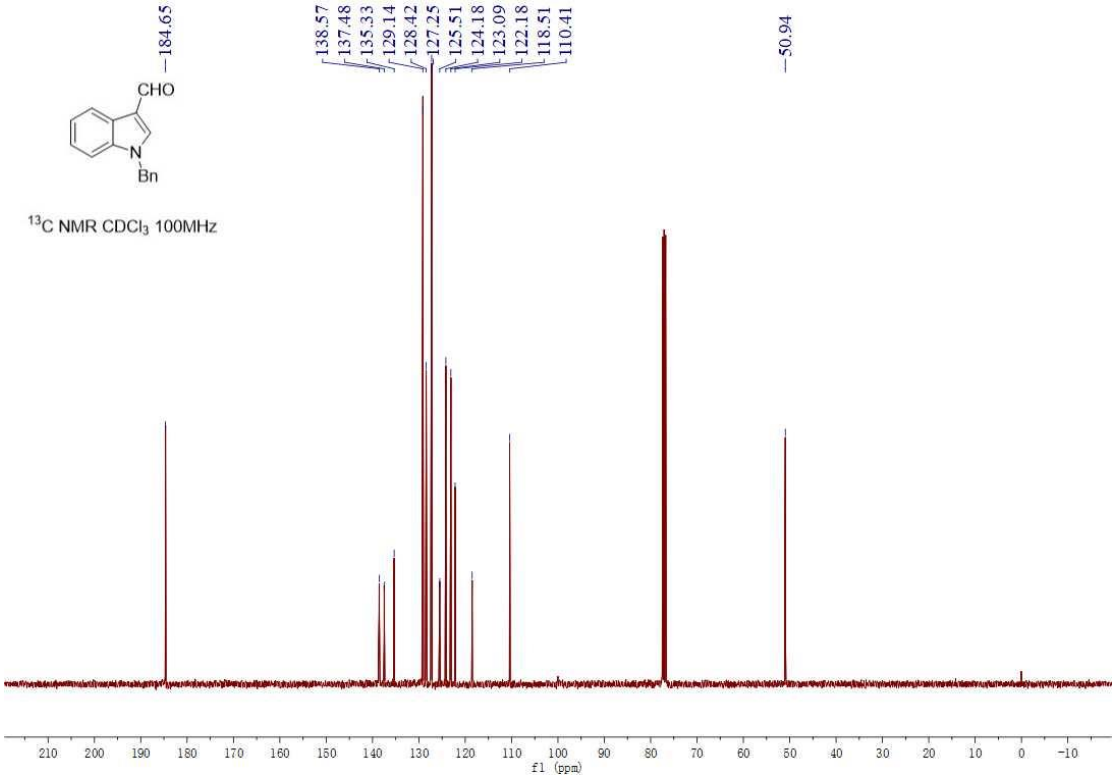
^{1}H NMR $CDCl_3$ 400MHz



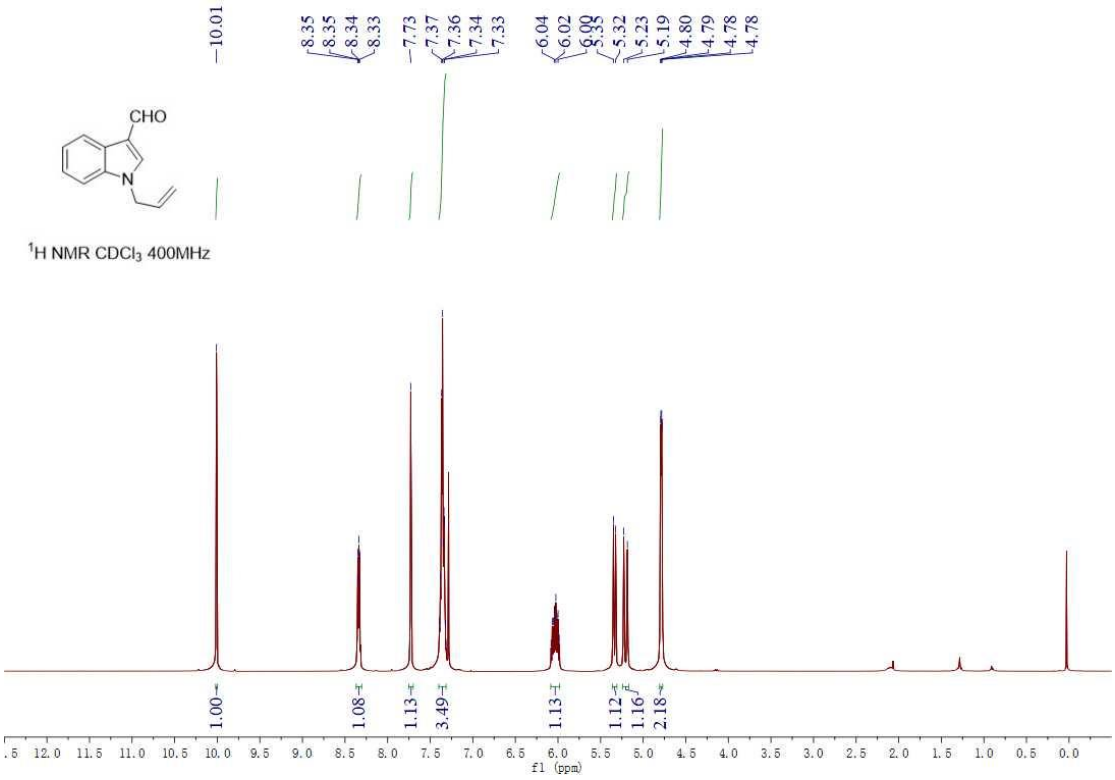
^{13}C NMR $CDCl_3$ 100MHz

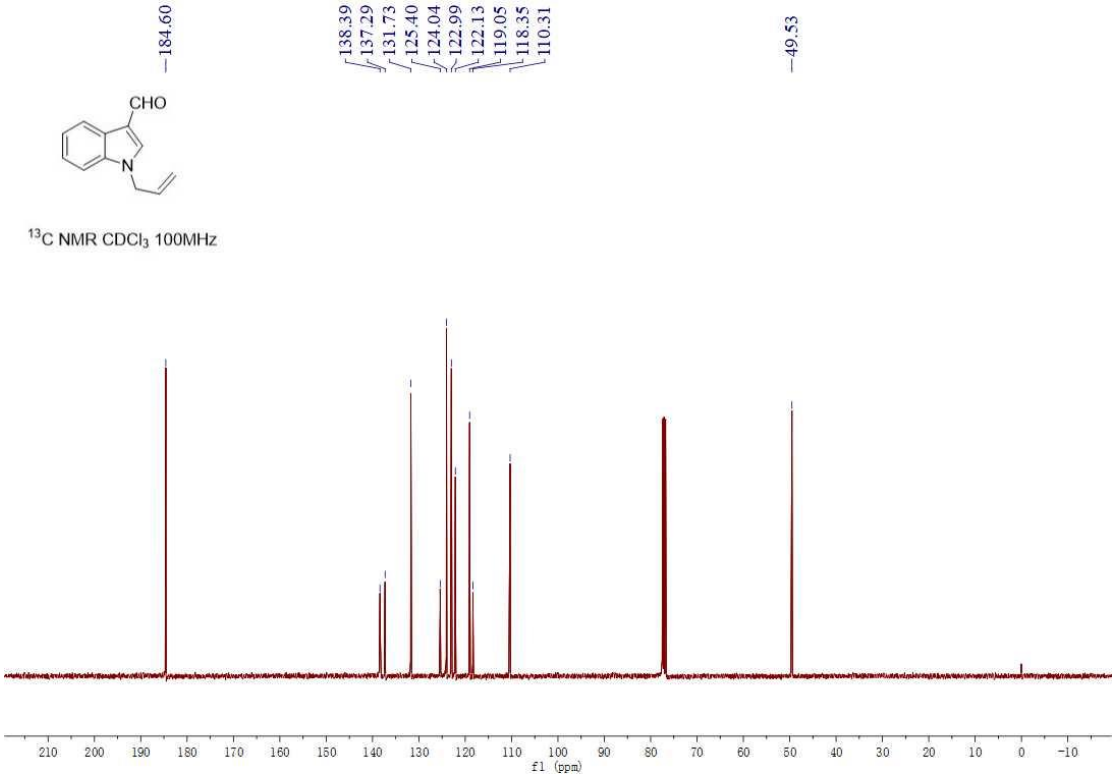
Benzyl-1H-indole-3-carbaldehyde (***3s***)



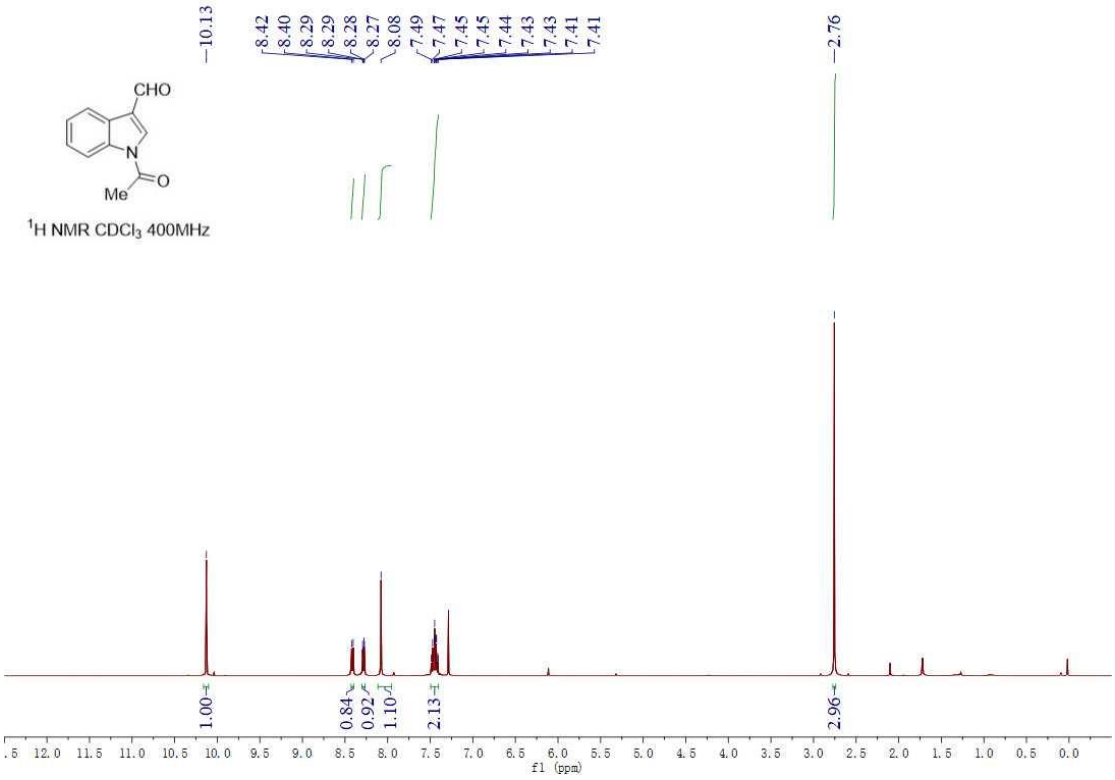


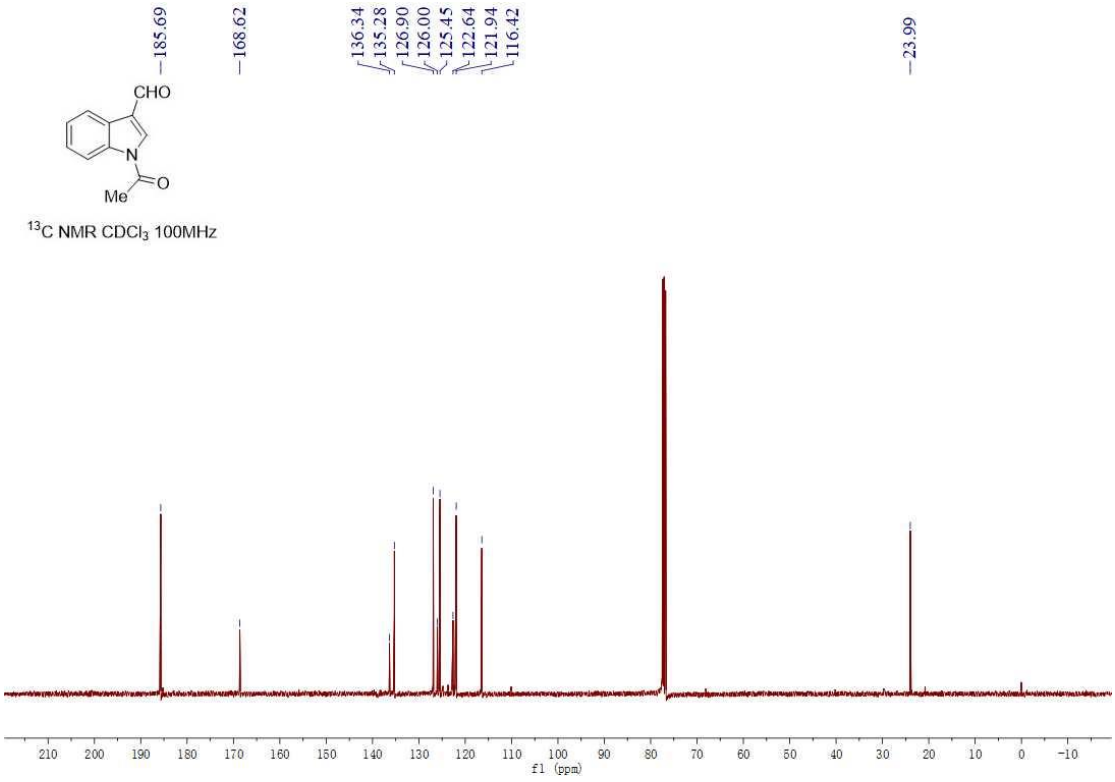
1-Allyl-1H-indole-3-carbaldehyde (***3t***)



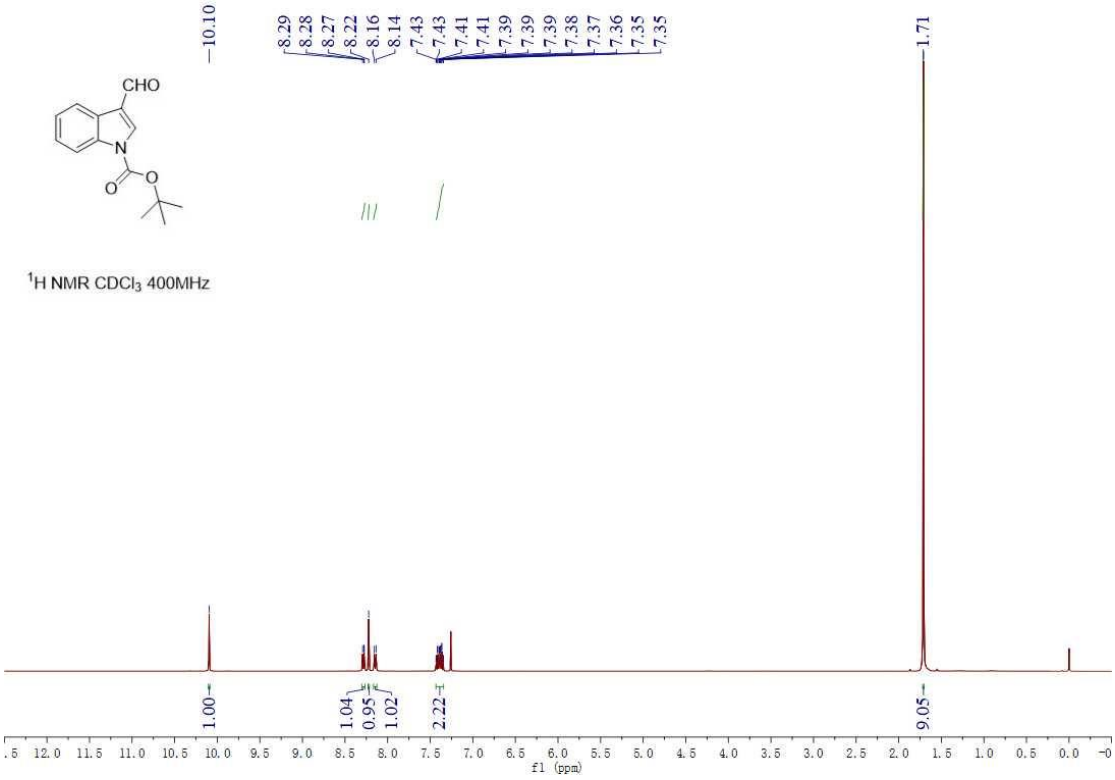


1-Acetyl-1H-indole-3-carbaldehyde (***3u***)

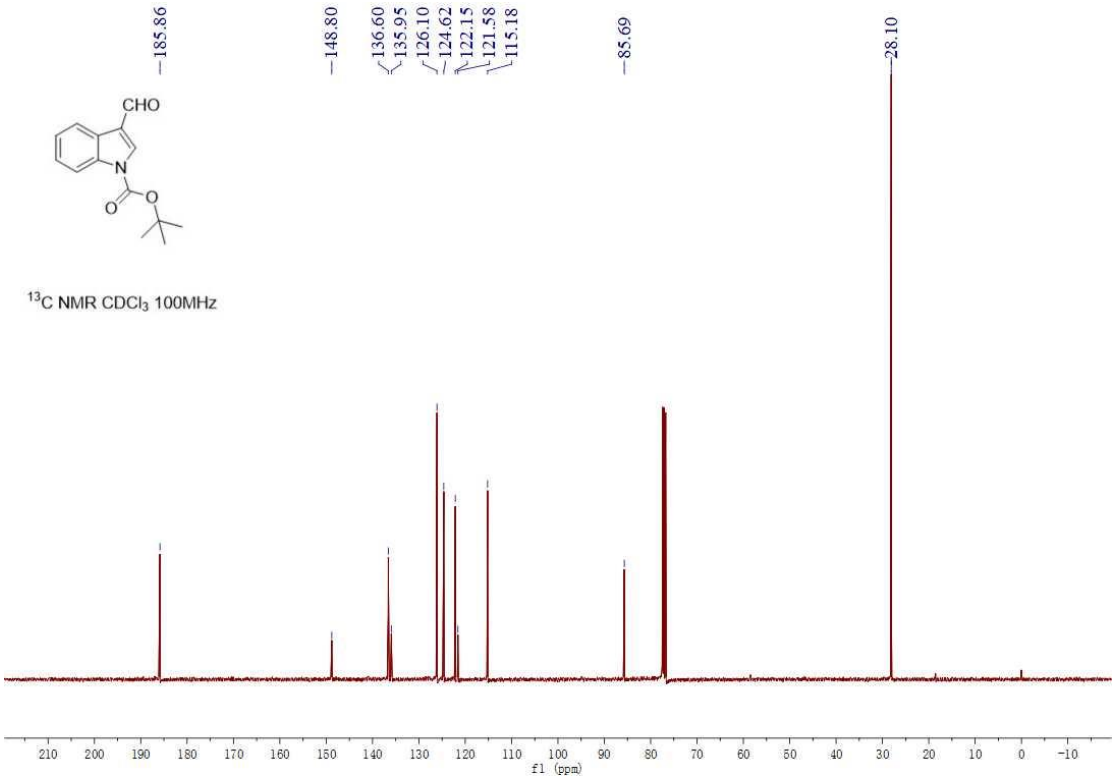




tert-Butyl-3-formyl-1H-indole-1-carboxylate (***3v***)

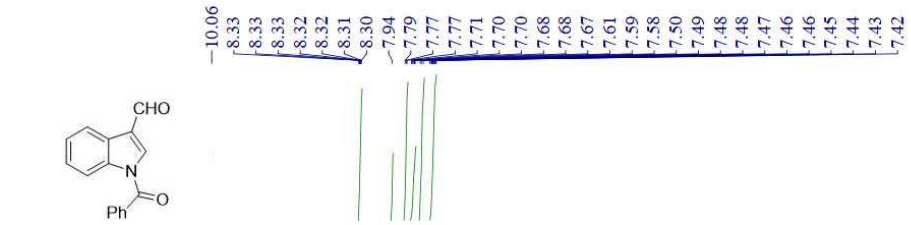


^{1}H NMR $CDCl_3$ 400MHz

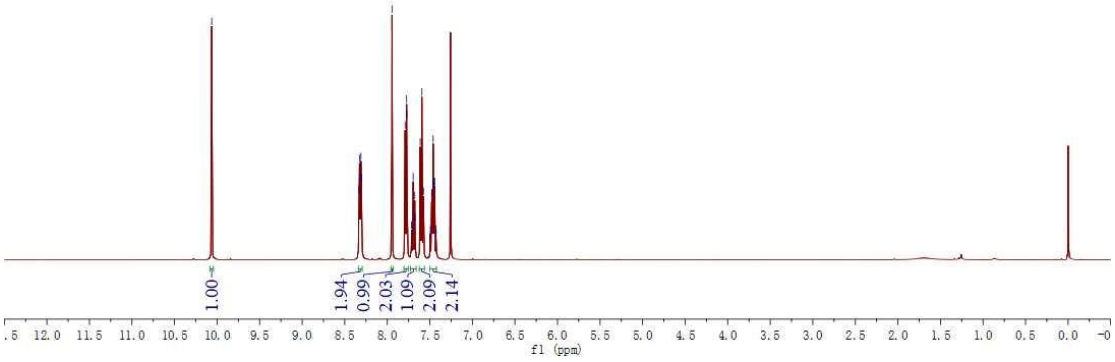


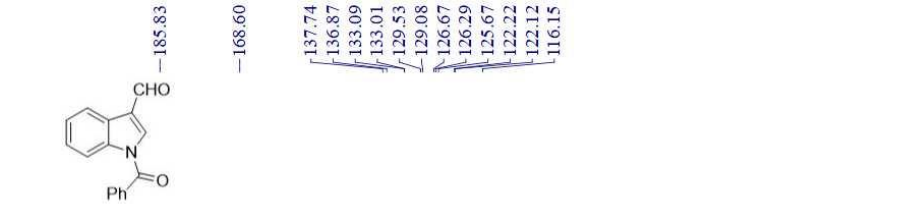
^{13}C NMR $CDCl_3$ 100MHz

1-Benzoyl-1H-indole-3-carbaldehyde (***3w***)

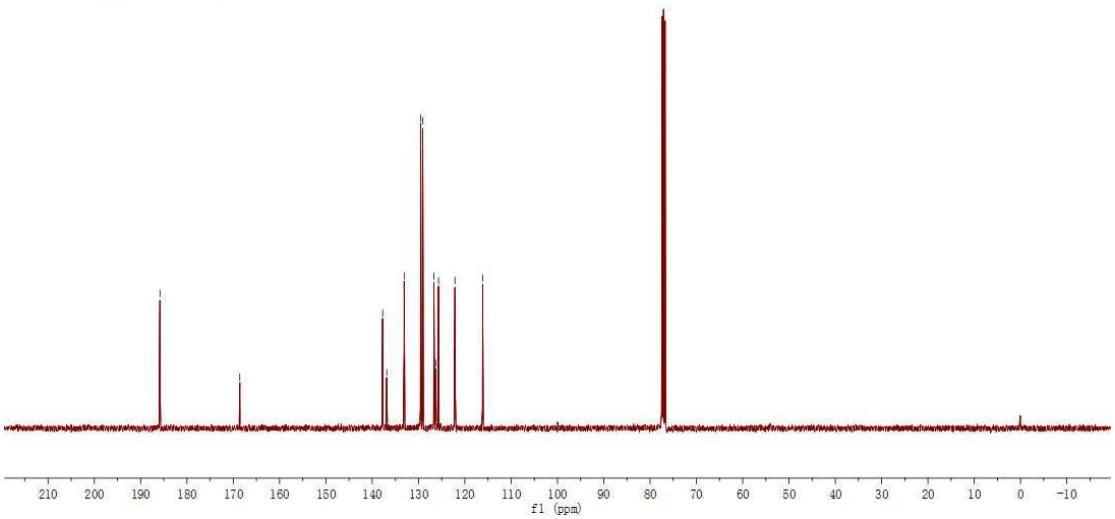


^{1}H NMR $CDCl_3$ 400MHz

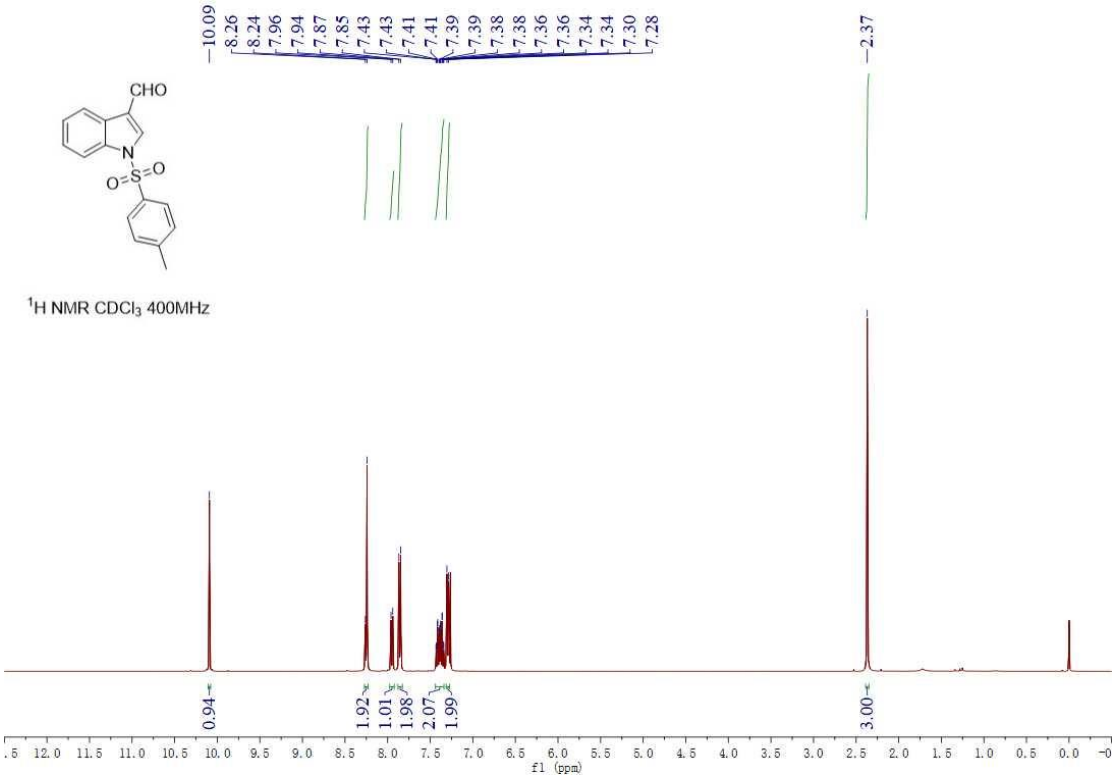


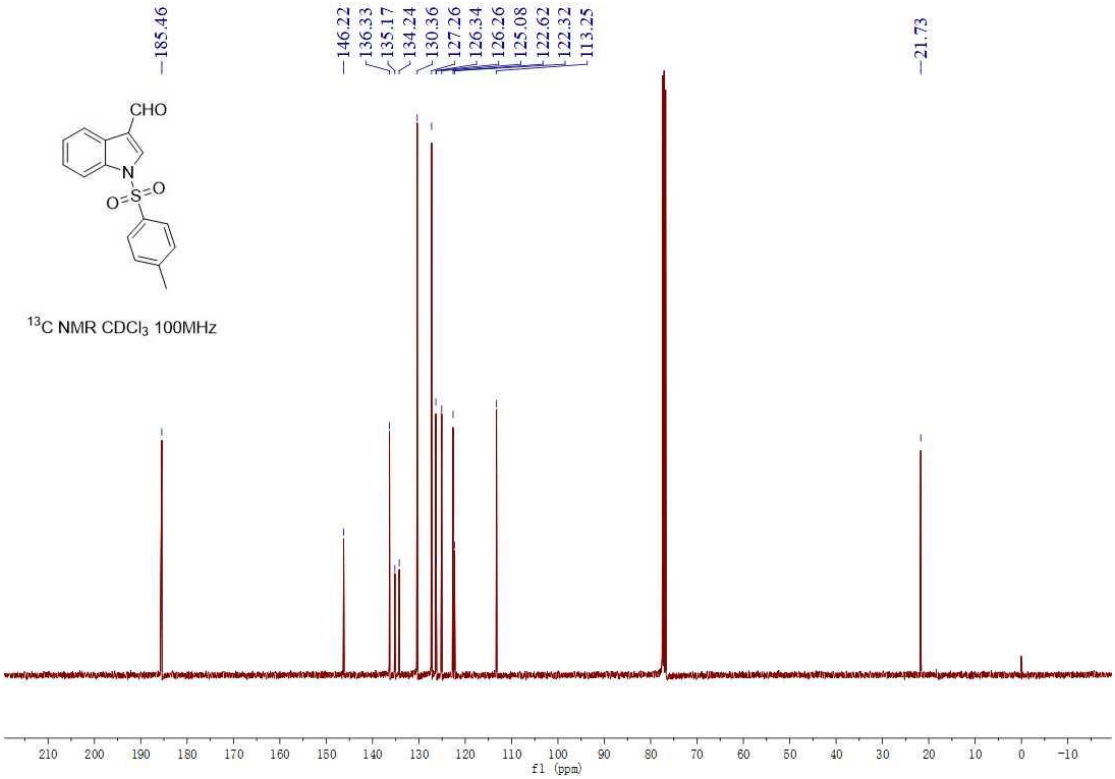


^{13}C NMR $CDCl_3$ 100MHz

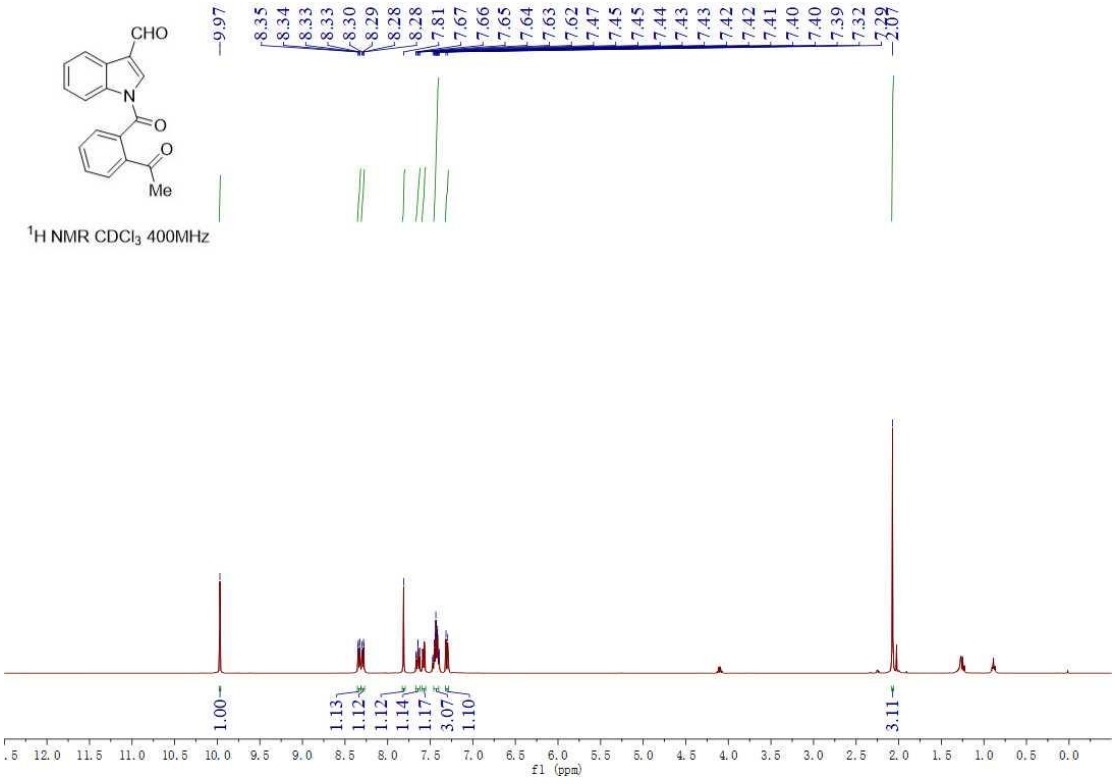


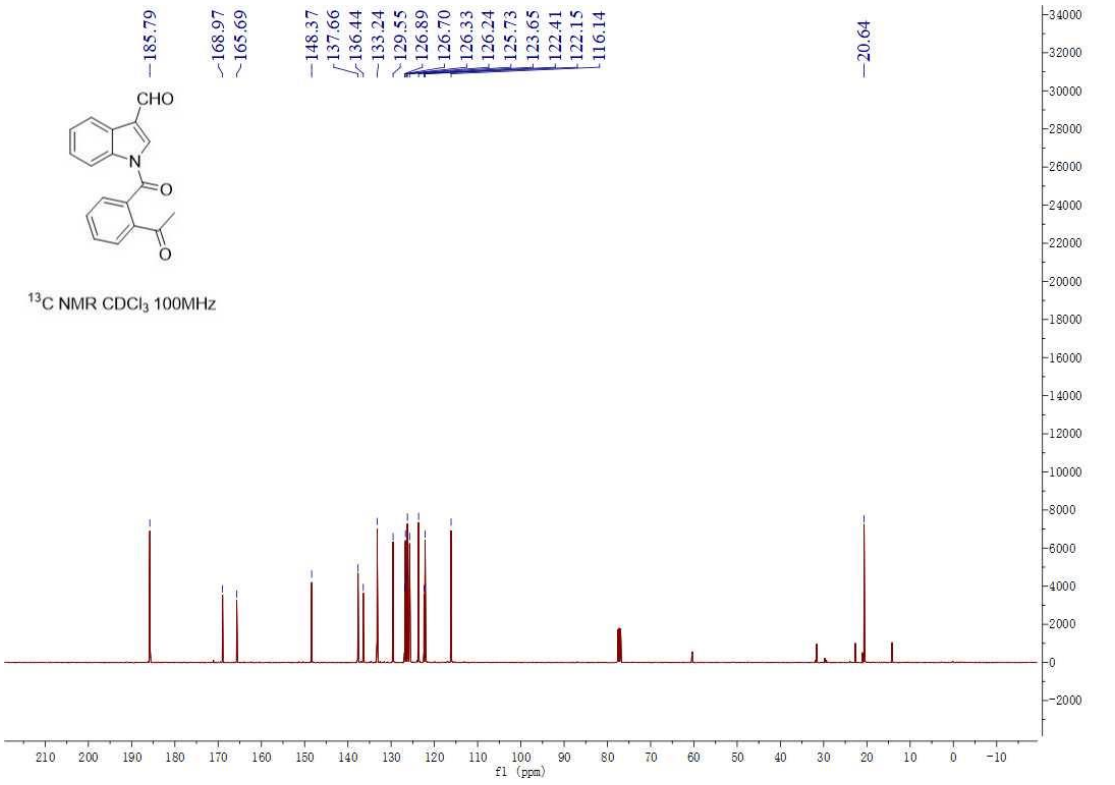
1-Tosyl-1H-indole-3-carbaldehyde (***3x***)



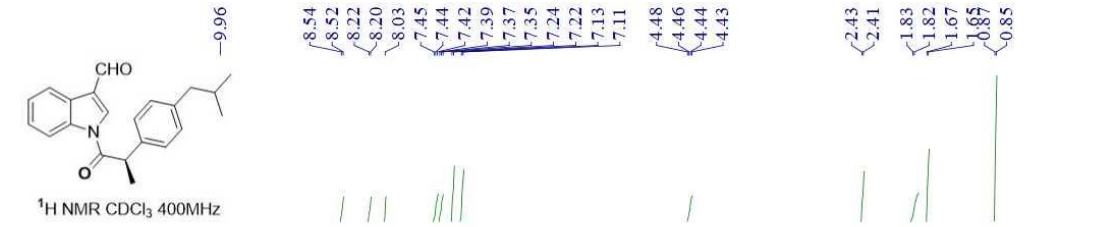


2-(3-Formyl-1H-indole-1-carbonyl)phenyl acetate (***3y***)

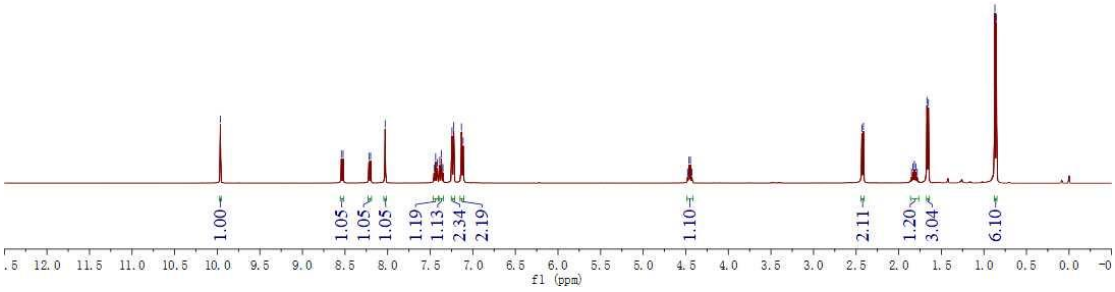




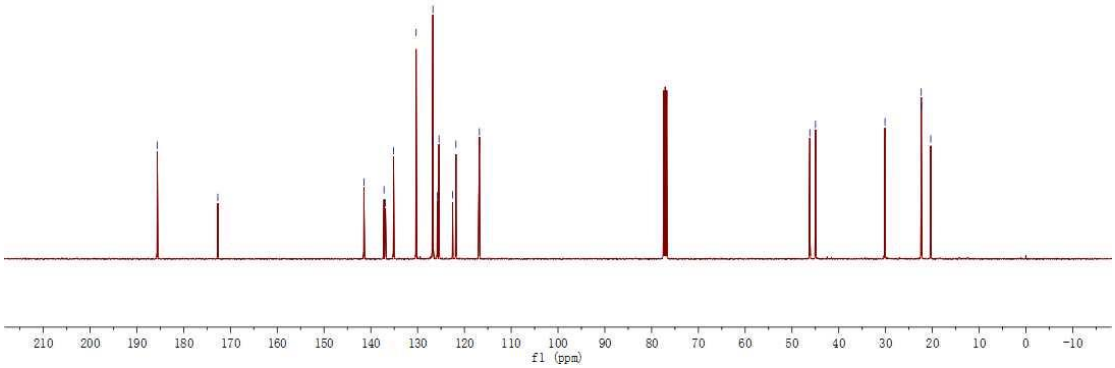
(R)-1-(2-(4-isoButylphenyl)propanoyl)-1-H-indole-3-carbaldehyde (3z)



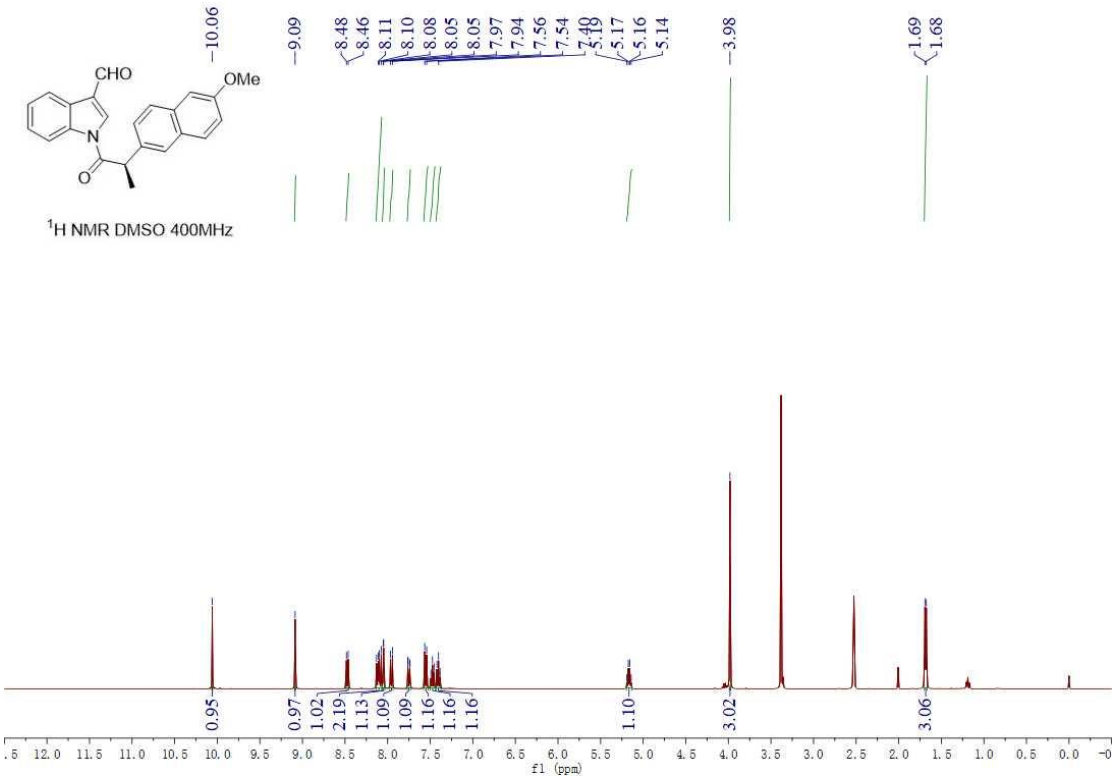
^{1}H NMR $CDCl_3$ 400MHz

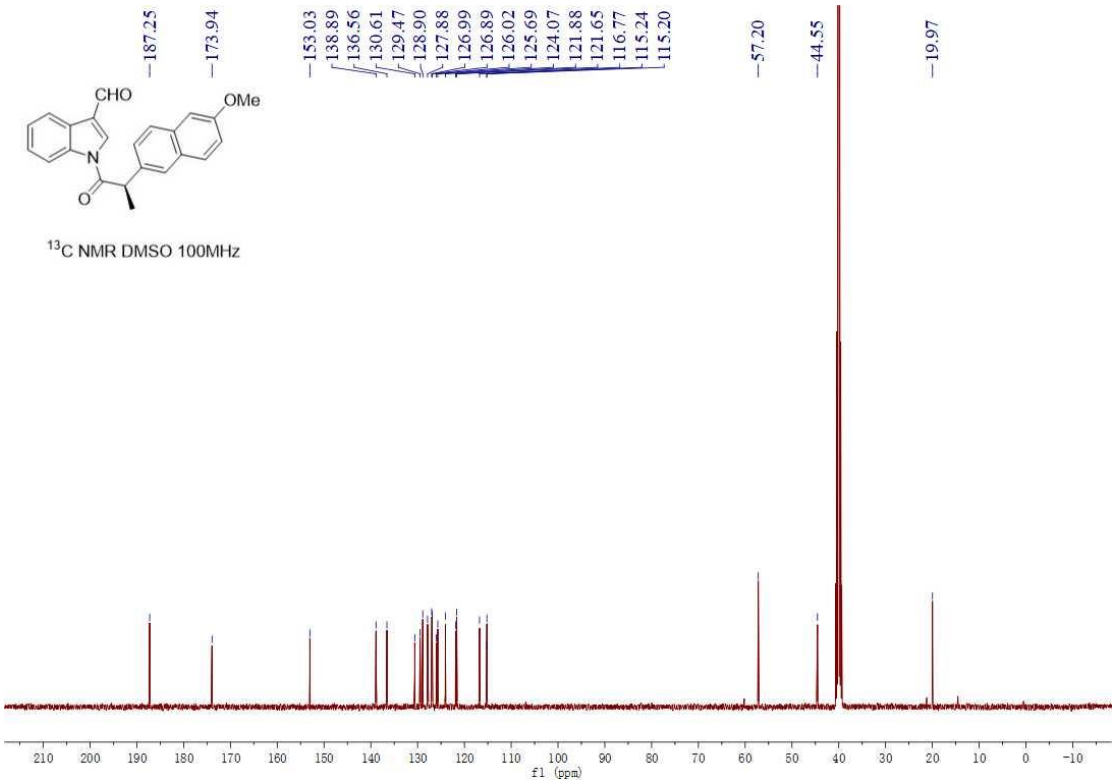


^{13}C NMR $CDCl_3$ 100MHz

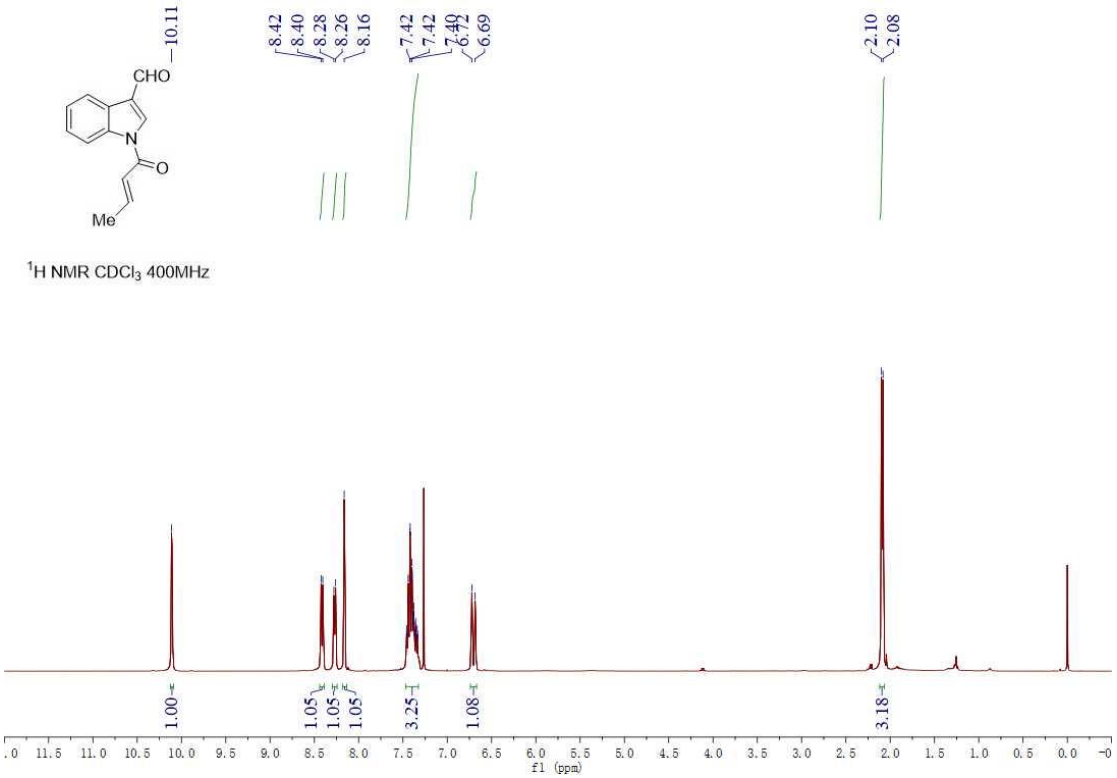


*(R)-1-(2-(6-Methoxynaphthalen-2-yl)propanoyl)-1H-indole-3-carbaldehyde (3**aa**)*

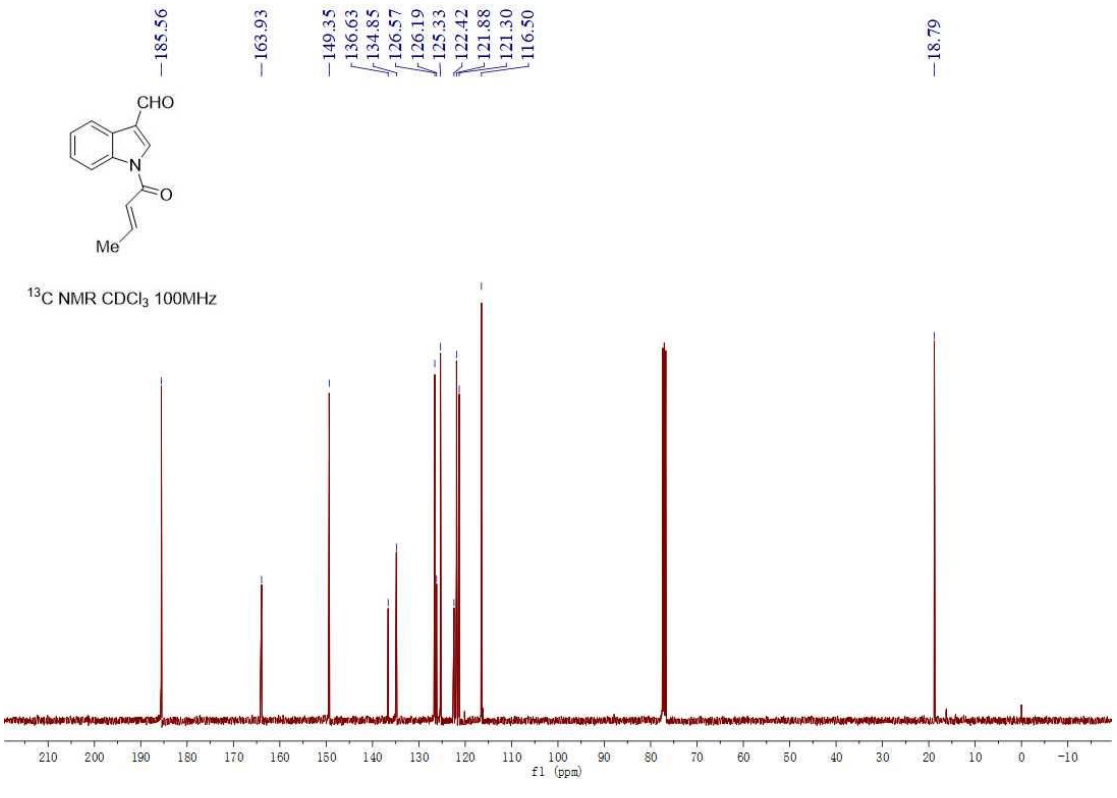




*(E)-1-(2-(But-2-enoyl)-1-H-indole-3-carbaldehyde (**3ab**)*

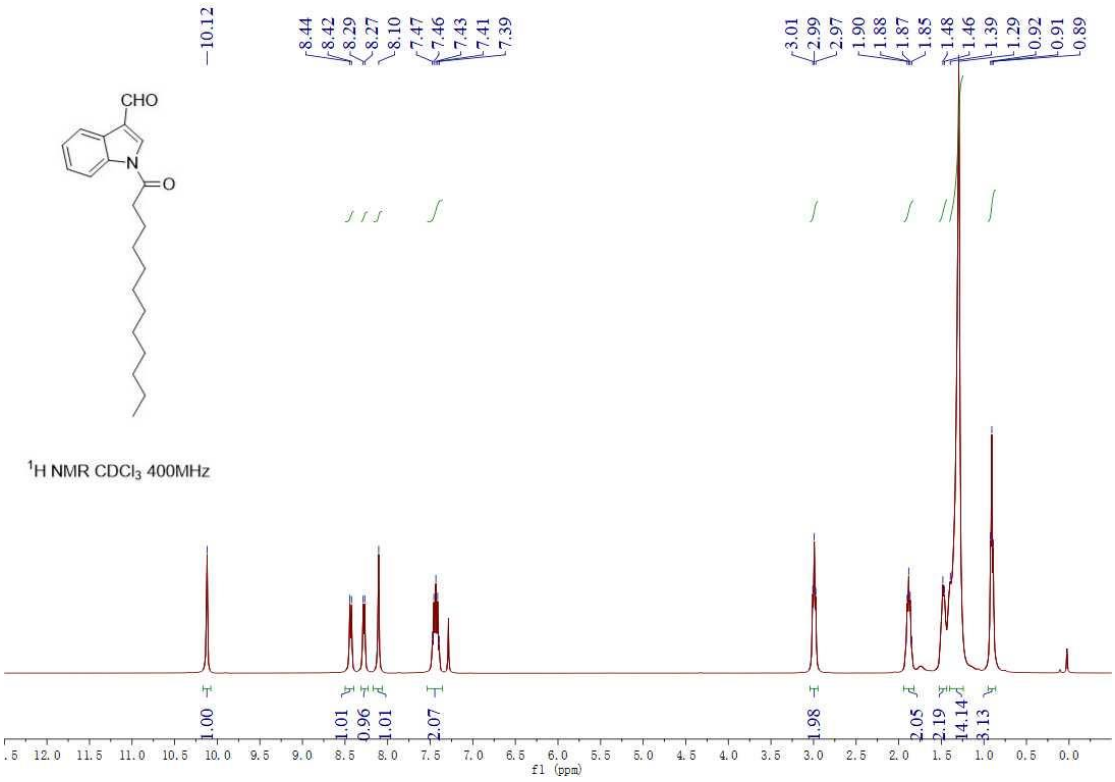


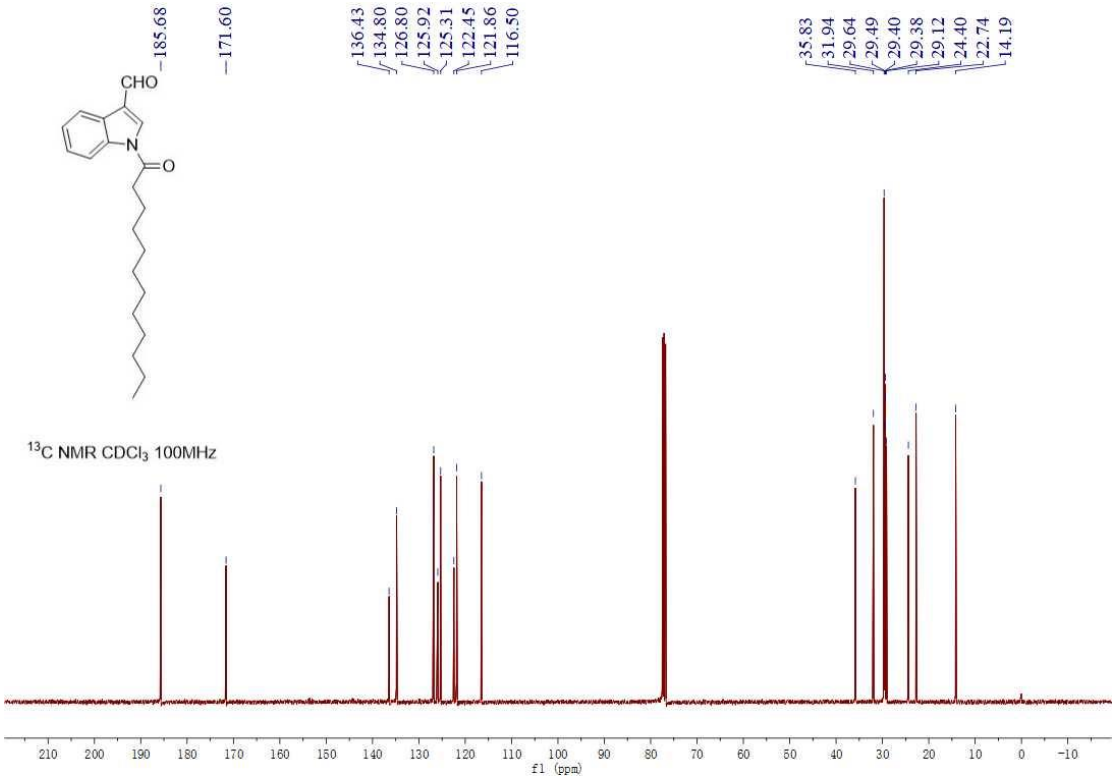
^{1}H NMR $CDCl_3$ 400MHz



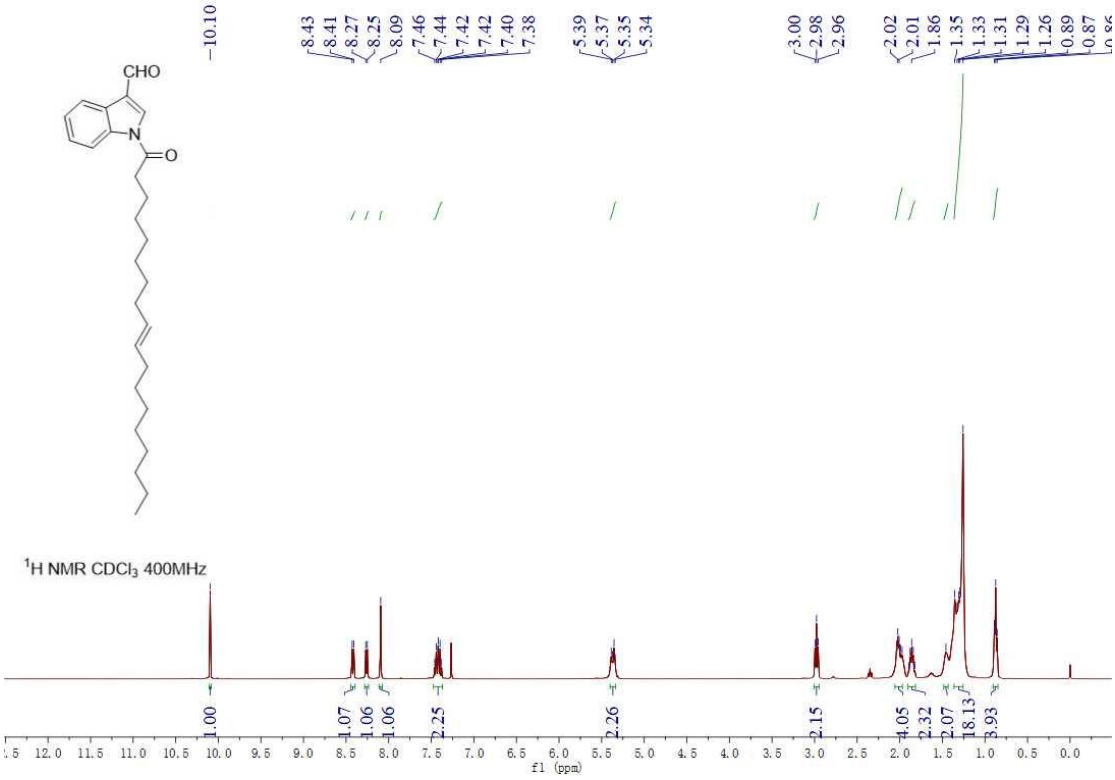
^{13}C NMR $CDCl_3$ 100MHz

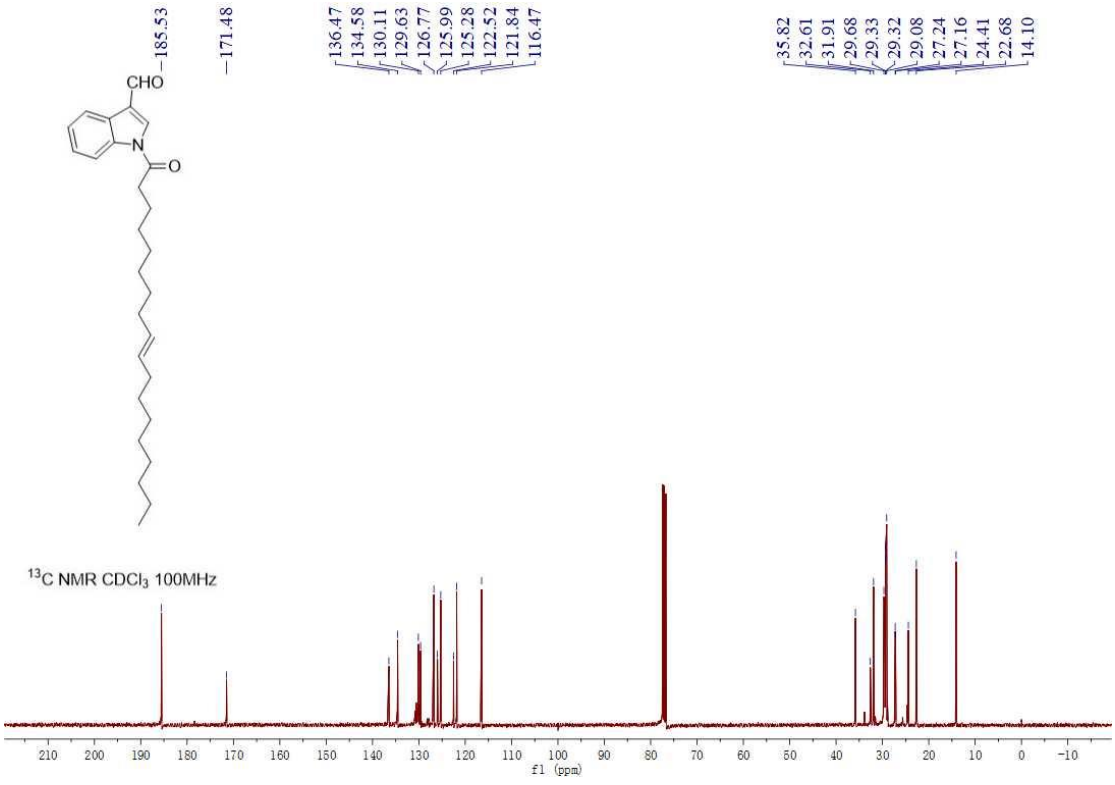
*1-Dodecanoyl-1H-indole-3-carbaldehyde (**3ac**)*



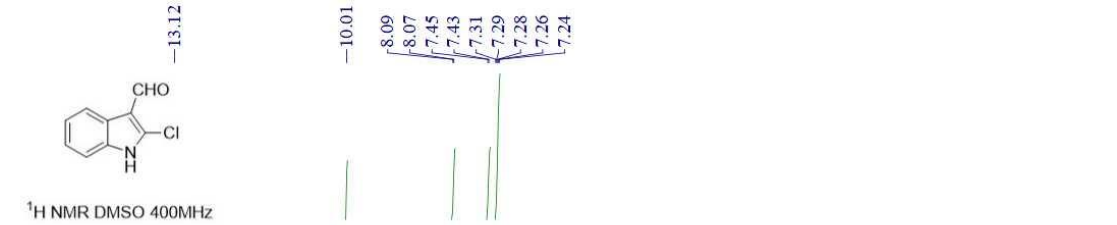


*(E)-1-(Octadic-9-enoyl)-1H-indole-3-carbaldehyde (**3ad**)*

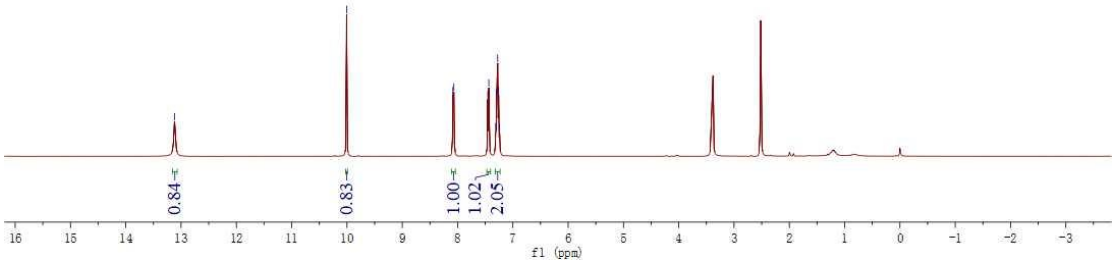


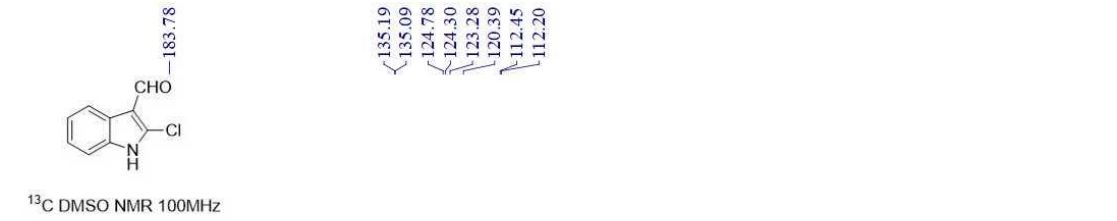


2-Chloro-1*H*-indole-3-carbaldehyde (***3ae***):

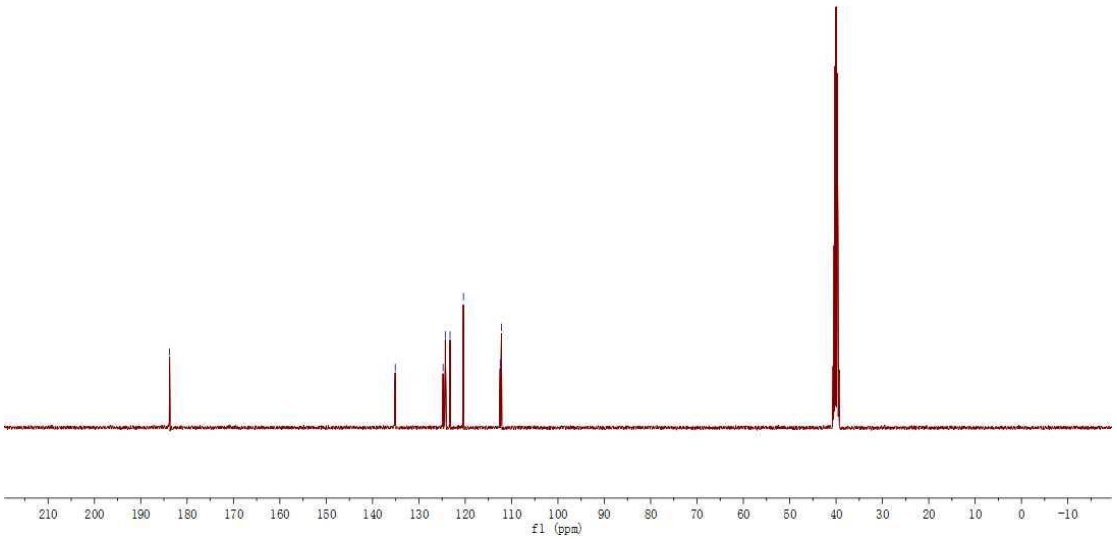


^{1}H NMR DMSO 400MHz

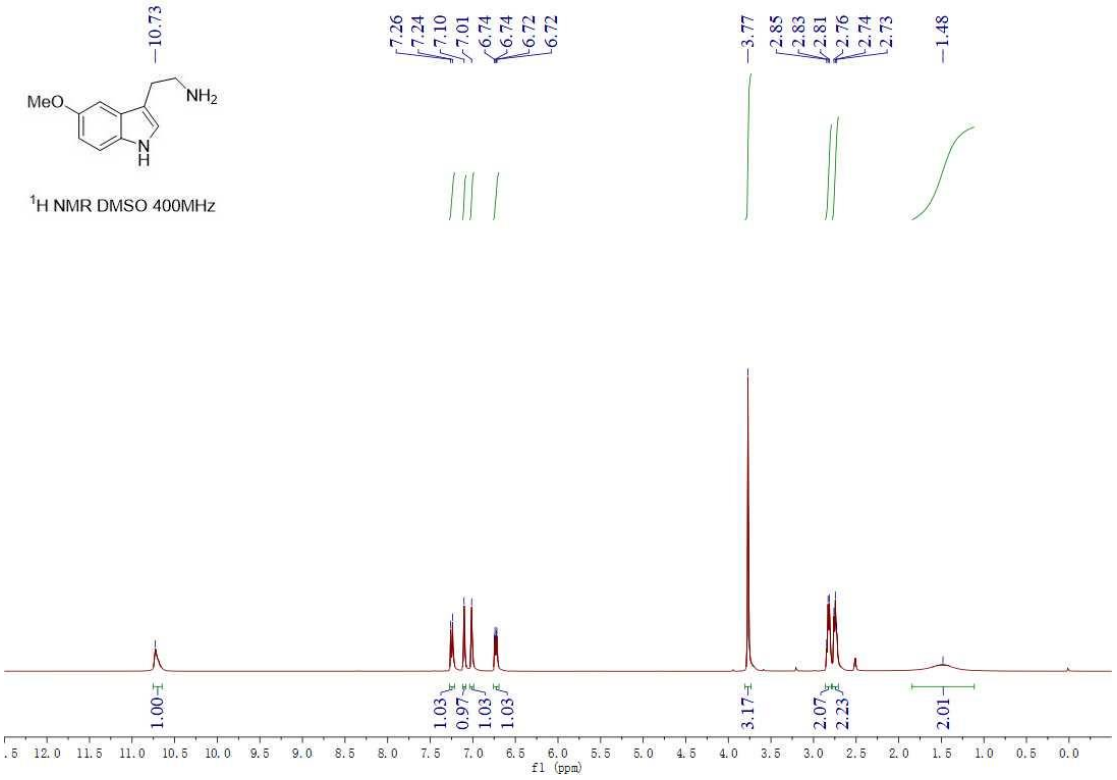


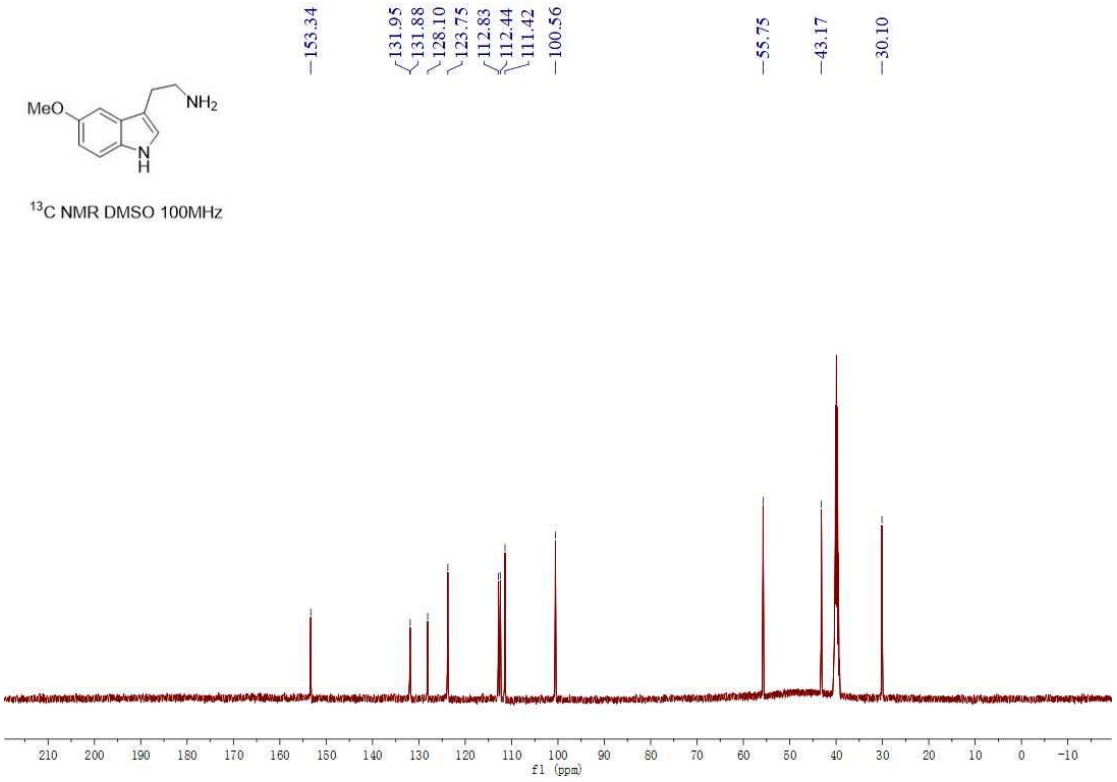


^{13}C DMSO NMR 100MHz

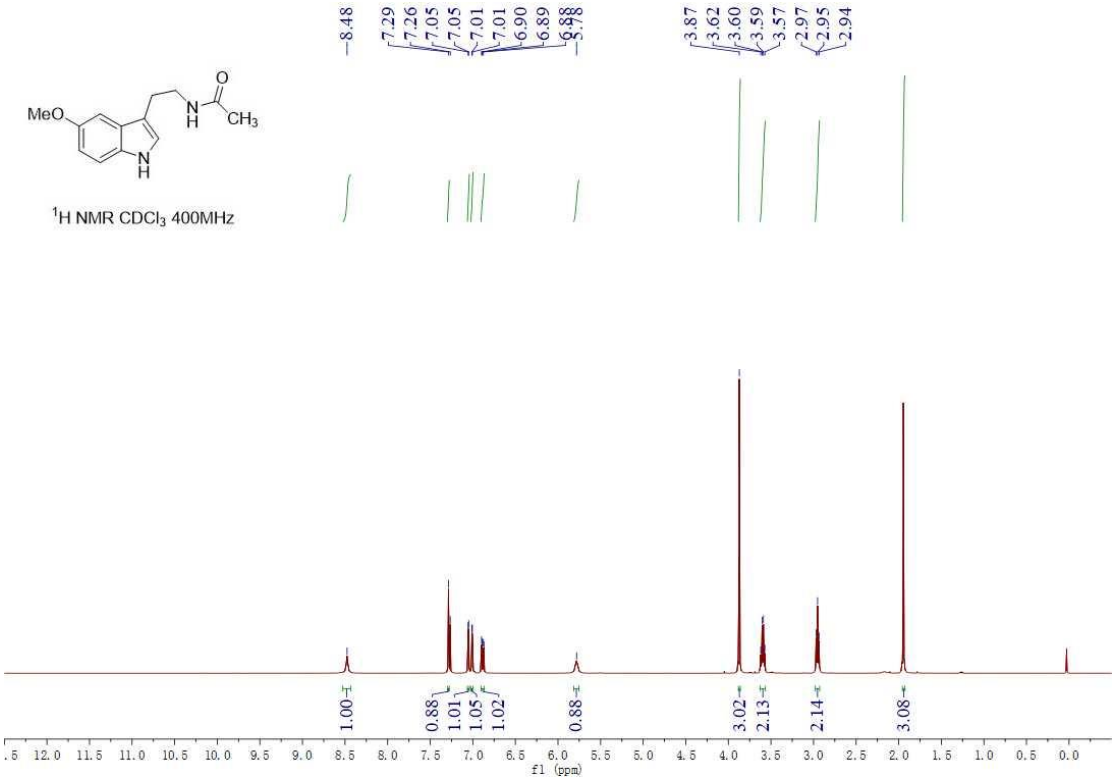


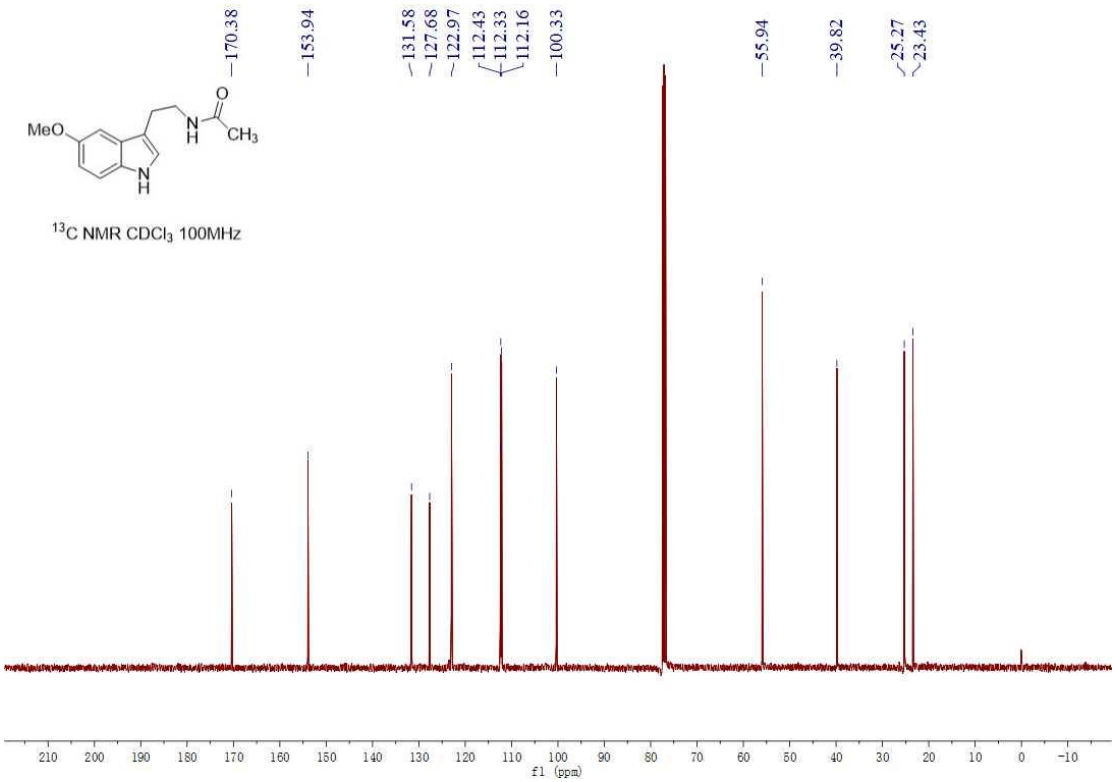
*Compound **5p**:*


10.73
7.26
7.24
7.10
7.01
6.74
6.74
6.72
6.72
3.77
2.85
2.83
2.81
2.76
2.74
2.73
1.48
MeO
NH2
N
H
1H NMR DMSO 400MHz
1.00
1.03
0.97
1.03
1.03
3.17
2.07
2.23
2.01
f1 (ppm)


153.34
131.95
131.88
128.10
123.75
112.83
112.44
111.42
100.56
55.75
43.17
30.10
MeO
NH2
N
H
13C NMR DMSO 100MHz
f1 (ppm)

Melatonin:


MeO
N
H
O
CH3
N
H
1H NMR CDCl3 400MHz
8.48
7.29
7.26
7.05
7.05
7.01
7.01
6.90
6.89
6.88
6.88
5.78
3.87
3.62
3.60
3.59
3.57
2.97
2.95
2.94
1.00
0.88
1.01
1.05
1.02
0.88
3.02
2.13
2.14
3.08
f1 (ppm)


MeO
N
H
O
CH3
N
H
13C NMR CDCl3 100MHz
170.38
153.94
131.58
127.68
122.97
112.43
112.33
112.16
100.33
55.94
39.82
25.27
23.43
f1 (ppm)