[Supporting Information]

Screening metal-free photocatalysts from isomorphic covalent organic frameworks for C-3 functionalization of indoles

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Section 1. Material and Characterization

Materials. The pyrene and sodium borohydride was obtained from J&K Scientific. The bromine was obtained from Sinopharm Chemical Reagent. 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline was obtained from Bide Pharmatech Ltd. Tetrakis(triphenylphosphine)palladium(0) and Iodomethane was obtained from Energy Chemical. The thionyl chloride was obtained from Macklin Chemical Reagent. The selenium dioxide was obtained from Aladdin Chemical Reagent. 3,4-Pyridinediamine was obtained from Chembee Chemical Reagent. The 4,7-dibromo-2,1,3-benzothiadiazole was obtained from Puyang Huicheng Electronic Material Co Ltd. 4-formylphenylboronic acid was obtained from Boka Chemical. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aladdin.

Instrumentations. The Fourier Transform Infrared (FT-IR) spectroscopy were recorded on an Avatar FT-IR 360 spectrometer by using KBr pellets within the wavenumber range 400 to 4000 cm^{-1}. The Nuclear Magnetic Resonance (NMR) spectroscopy were measured by an Avance III-400 NMR spectrometer, and the chemical shift (δ, ppm) is measured with the residual protons of the solvent as the standard. The solid-state ^{13}C CP/MAS NMR spectra was recorded on a Bruker AVANCE III 400 WB spectrometer with a CP contact time of 2 ms and a MAS rate of 5 kHz. The elemental analysis measurement were carried out on an Elementar model vario EL cube analyzer. The UV-vis absorption spectrum was recorded from 200–800 nm on a Shimadzu Corporation U-4100 Spectrophotometer. The field-

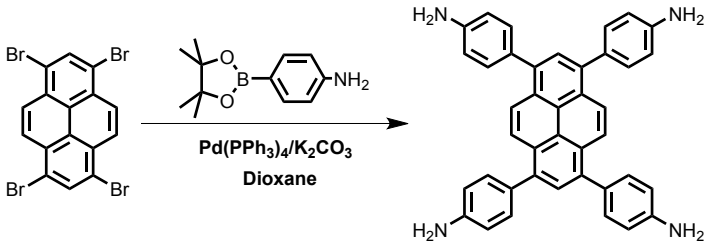
emission scanning electron microscopy (FE-SEM) was carried out on a SU8020 model HITACHI microscope. The powder X-ray diffraction (PXRD) data were carried out on a PANalytical BV Empyrean diffractometer, the powder was deposited on glass substrate with 2θ range of 1.5° to 45° at 298 K. The thermogravimetric analysis (TGA) spectrum was recorded from 20 to 800 °C on a TA Q500 thermogravimeter at a rate of 10 °C min^{-1} under nitrogen. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume on a JW-BK 132F analyzer at 77 K, the polymer was dried in vacuum at 80 °C for more than 6 hours before measurement. Pore size distribution was estimated by Barrett-Joyner-Halenda (BJH) method. Fluorescence emission spectrum was recorded on FLUOROMAX-4 spectrometer and Cary Eclipse Fluorescence Spectrophotometer. The photocatalytic process is carried out under the irradiation of 30W blue LED lamp (460 nm, 36.2 ± 0.1 mW cm^{-2}, distance app. 3 cm; 28.1 ± 0.1 mW cm^{-2}, distance app. 5 cm). The electron paramagnetic resonance (EPR) spectra were measured by a JEOL JES-FA200 EPR spectrometer. The date of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethylpiperiding (TMP) solution with the concentration of 0.1 M were collected on the measurement parameters, scanning frequency: 9050 MHz; scanning power, 5 mW; central field, 323 mT; scanning width, 100 G; scanning temperature: 25 °C.

Electrochemical measurements. The photocurrent of the polymer was performed on a VersaSTAT 3 electrochemical workstation under irradiation of 300 W Xe lamp. Glassy carbon electrode, platinum wire electrode and saturated calomel electrode

(SCE) are used as working electrode, assistant electrode and reference electrode respectively. The working electrode was prepared from the polymer and 5 wt% Nafion, the experiment was carried out in 0.1 M Na_2SO_4 aqueous solution. The Mott-Schottky analysis and electrochemical impedance spectra (EIS) was performed on a CHI760E electrochemical workstation at room temperature in the dark. Glassy carbon electrode, platinum wire electrode and saturated calomel electrode (SCE) are used as working electrode, assistant electrode and reference electrode respectively. The Mott-Schottky measurement was carried out in 0.1 M Na_2SO_4 aqueous solution at frequency of 1000 Hz. The electrochemical impedance spectra was obtained by immersing in a 0.1 M Na_2SO_4 aqueous solution.

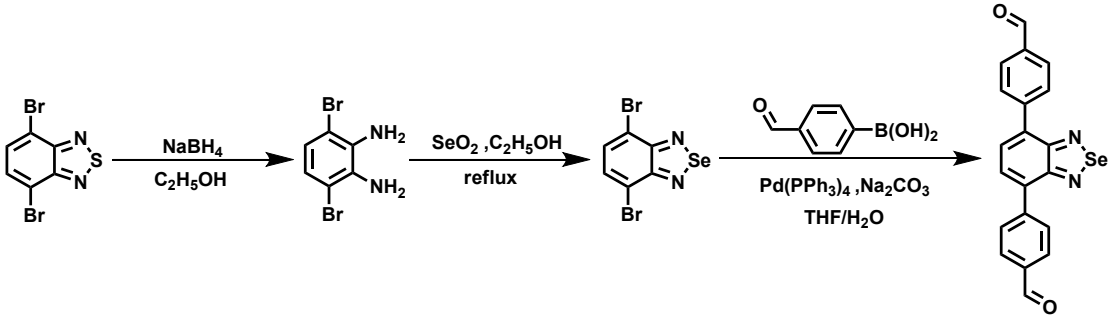
Section 2. Synthesis and Photocatalysis

Synthesis of 1,3,6,8-tetrakis(4-aminophenyl)pyrene (TTA-Py)



The 1,3,6,8-tetrabromopyrene was synthesized as reported[1]. A mixture of 1,3,6,8-tetrabromopyrene (500 mg, 0.96 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (1.3 g, 5.94 mmol), potassium carbonate (1.07 g, 7.74 mmol) and palladium tetrakis(triphenylphosphine) (0.08 g, 0.07 mmol) in dioxane (16 mL) was degassed for three times. After reflux in N_2 for 72 h, it was poured into 100 mL H_2O and stirred for 1h. The resulting precipitate was collected via filtration and washed with H_2O and MeOH for three times. The crude product was chromatographed on silica gel with acetone/dichloromethane (1/4) eluent. A yellow green solid recrystallized from chloroform/acetone with 58% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.13 (s, 4H), 7.79 (s, 2H), 7.35 (d, J = 8.0 Hz, 8H), 6.77 (d, J = 8.0 Hz, 8H), 5.32 (s, 8H) ppm. FT-IR (KBr, cm^{-1}): 3033, 2924, 2855, 1619, 1592, 1551, 1489, 1407, 1305, 1271, 12.3, 1169, 1114, 1011, 888, 827, 731.

Synthesis of 4,4'-(Benzoselenadiazole-4,7-diyl)dibenzaldehyde



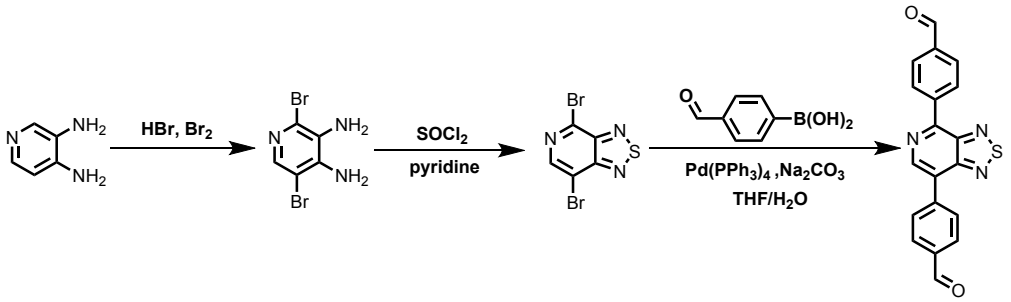
Synthesis of 4,7-dibromo-2,1,3-benzoselenadiazole. To a 250 mL flask of 4,7-

dibromo-2,1,3-benzothiadiazole (1.0 g, 3.4 mmol) in ethanol (50 mL) was added slowly $NaBH_4$ (2.45 g, 64.8 mmol) at 0 °C. Then the mixture was stirred overnight at room temperature. After evaporation of the ethanol, 30 mL water was added. The mixture was extracted with ethyl acetate and solvents were evaporated under reduced pressure, we can got 3,6-dibromo-1,2-benzenediamine (0.85 g) as a near white solid in 94% yield.

Obtained product was immediately used for the next step. A solution of the diamine (0.74 g, 2.78 mmol) in ethanol (15 mL) was heated at 80 °C in N_2, a solution of SeO_2 (0.34 g, 3.06 mmol) in hot water (4 mL) added slowly over 10 minutes. Then the mixture was refluxed for 4 h. After cooling down to room temperature, the mixture was filtered and recrystallization from ethyl acetate obtain a yellow solid (0.74 g, 78%). ^{1}H NMR (400 MHz, $CHCl_3$): δ 7.62 (s, 2H) ppm.

Synthesis of 4,4'-(Benzoselenadiazole-4,7-diyl)dibenzaldehyde. To a 25 mL flask was added 4,7-dibromo-2,1,3-benzoselenadiazole (220 mg, 0.64 mmol), 4-formylphenylboronic acid (291 mg, 1.94 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), Na_2CO_3 (480 mg, 4.53 mmol), H_2O (2 mL) and THF (10 mL), then the flask was degassed with N_2 for 1 h. The mixture was refluxed in N_2 over 48h, it was poured into water and extracted by dichloromethane for three times. After the solvent was evaporated, the crude product was chromatographed on silica gel using dichloromethane as an eluent to afford a yellow solid (154 mg, 61 %). ^{1}H NMR (400 MHz, $CHCl_3$): δ 10.12 (s, 2H), 8.10-8.05 (q, J = 20.8 Hz, 8H), 7.75 (s, 2H) ppm.

Synthesis of 4,4'-([1,2,5]Thiadiazolo[3,4-*c*]pyridine-4,7-diyl)dibenzaldehyde



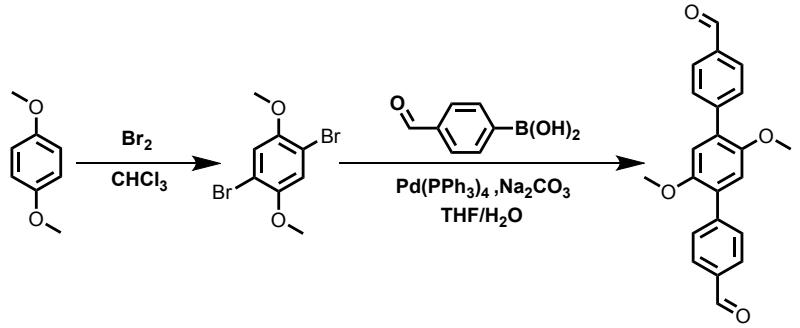
Synthesis of 2,5-dibromopyridine-3,4-diamine. 3,4-diaminopyridine (0.5 g, 4.6 mmol) and 5 mL 48% aqueous hydrobromic acid was placed in a two-neck bottom, bromine (0.76 mL, 14.8 mmol) was added slowly over 20 minutes, then the mixture was refluxed overnight. After cooling down to room temperature, aqueous Na_2SO_3 solution was added to the mixture. The resultant precipitation was filtered, refluxed in a 20% solution of Na_2CO_3 for 4 h and filtrated to get the product with 68% yield. Obtained pale yellow powder was used for next step without further purification.

Synthesis of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine. 3,4-diamino-2,5-dibromopyridine (1 g, 3.75 mmol) and pyridine (12 mL) was placed in a round bottom, $SOCl_2$ (0.4 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 5 h and then was poured into ice water. The crude product was filtrated and washed with water to obtain a pink solid (0.62 g, 56%). The product was used for next step without further purification.

Synthesis of 4,4'-([1,2,5]Thiadiazolo[3,4-*c*]pyridine-4,7-diyl)dibenzaldehyde. To a 25 mL flask was added 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine (189 mg, 0.64 mmol), 4-formylphenylboronic acid (291 mg, 1.94 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), Na_2CO_3 (480 mg, 4.53 mmol), H_2O (2 mL) and THF (10 mL), then the flask was degassed with N_2 for 1 h. The mixture was refluxed in N_2 over 48h, it was poured

into water and extracted by dichloromethane for three times. After the solvent was evaporated, the crude product was chromatographed on silica gel using dichloromethane as an eluent to afford a yellow solid (93 mg, 42 %). ^{1}H NMR (400 MHz, $CHCl_3$): δ 10.16 (d, J = 10 Hz, 2H), 8.97 (s, 1H), 8.88 (d, J = 8 Hz, 2H), 8.24 (d, J = 8 Hz, 2H), 8.13-8.10 (m, 4H) ppm.

Synthesis of 4-[4-(4-Formylmethyl)-2,5-dimethoxyphenyl]benzaldehyde



Synthesis of 1,4-dibromo-2,5-dimethoxybenzene. 1,4-dimethoxybenzene (1 g, 7.24 mmol) and $CHCl_3$ (20 mL) was placed in a 25 mL flask, bromine (0.94 mL, 18.4 mmol) was added slowly over 20 minutes. The mixture was stirred overnight, aqueous Na_2SO_3 solution was added, then the mixture was extracted with DCM and solvents were evaporated under reduced pressure. Finally, the crude product was washed with water and methanol to obtain a white solid (2 g, 94%).

Synthesis of 4-[4-(4-Formylmethyl)-2,5-dimethoxyphenyl]benzaldehyde. To a 25 mL flask was added 1,4-dibromo-2,5-dimethoxybenzene (190 mg, 0.64 mmol), 4-formylphenylboronic acid (291 mg, 1.94 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), Na_2CO_3 (480 mg, 4.53 mmol), H_2O (2 mL) and THF (10 mL), then the flask was degassed with N_2 for 1 h. The mixture was refluxed in N_2 over 48h, it was poured into

water and extracted by dichloromethane for three times. After the solvent was evaporated, the crude product was chromatographed on silica gel using dichloromethane as an eluent to afford a green solid (160 mg, 72 %). ^{1}H NMR (400 MHz, $CHCl_3$): δ 10.07 (s, 2H), 7.96 (d, *J* = 8 Hz, 4H), 7.77 (d, *J* = 8 Hz, 4H), 7.01 (s, 2H), 3.83 (s, 6H) ppm.

Synthesis of COF-JLUs. To a mixture of 1,3,6,8-tetrakis(4-aminophenyl)pyrene (0.04 mmol, 22.6 mg) and 4,4'-(benzoselenadiazole-4,7-diyl)dibenzaldehyde (0.08 mmol, 31.3 mg) was added *o*-dichlorobenzene (*o*-DCB)/1-butanol (*n*-BuOH) (1 mL/1 mL) and 6M HOAc (0.2 mL), which was degassed three times. After flame-sealing, the mixture was heated at 120 °C for 72h. A dark-red powder was collected by centrifugation, washed with tetrahydrofuran (THF, 3 × 3 mL) and acetone (3 × 3 mL). The solid was gathered and dried at 100 °C in vacuum to produce COF-JLU23 with 89% isolated yield. According to the similar procedure, the COF-JLU24 and COF-JLU25 were obtained with 87% and 85% isolated yield, respectively.

Synthesis of g-C_3N_4. The g-C_3N_4 powder was synthesized according to a procedure described in a previous literature [2]. In a typical synthesis, the dicyandiamide powder was placed in an alumina crucible, covered with cap and heated at 550 °C for 4 h in a muffle furnace with a ramp rate of 2.3 °C/min. The sample was then allowed to cool to room temperature before removal from the furnace. The obtained light yellow solid were ground to fine powders in a quartz mortar for further use.

A general procedure for C-3 Formylation of indoles. An acetonitrile (CH_3CN)/H_2O

(5:1 by vol.; 1.8 mL) mixture of the COF (5.0 mg), indoles (0.2 mmol), tetramethyl ethylenediamine (TMEDA, 61 μL, 0.4 mmol), KI (132.8 mg, 0.8 mmol) were stirred in O_2 atmosphere (~1 atm) under irradiation on a 30W blue LED lamp (460 nm, distance app. 3 cm). Upon completion monitored by thin layer chromatography (TLC), the mixture was filtered and washed with CH_3CN, the filtrate was concentrated in vacuum. The concentrate was purified by column chromatography using petroleum ether/ethyl acetate (2:1) to obtain the corresponding products.

A general procedure for C-3 thiocyanation of indoles. A 10-mL Pyrex tube was charged with the COF (3.0 mg), indoles (0.3 mmol), ammonium thiocyanate (NH_4SCN, 45.7 mg, 0.6 mmol) and anhydrous THF (2.0 mL). The tube was stirred in O_2 atmosphere (~1 atm) under irradiation with a 30W blue LED lamp (460 nm, distance app. 5 cm). Upon completion monitored by TLC, the mixture was filtered and washed with THF, the filtrate was concentrated in vacuum. The concentrate was purified by column chromatography using petroleum ether/dichloromethane (1:5) to obtain the corresponding products.

Recycle experiment. After the first run catalysis was completed, the photocatalyst COF-JLU24 was recycled by centrifugation, then washed with water and THF repeatedly to remove products and unreacted substrates. The recovered COF-JLU24 was dried under vacuum and reused in next cycle in identical conditions.

Section 3. Elemental Analysis

Photocatalyst	Anal. Calcd.			Found		
	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
COF-JLU23	75.23	3.63	8.77	73.87	4.17	8.24
COF-JLU24	79.03	3.74	11.82	76.96	4.23	11.11
COF-JLU25	84.97	4.92	4.72	82.72	5.18	4.33

Figure S1. Elemental analysis of COF-JLUs

Section 4. Thermogravimetric Analysis

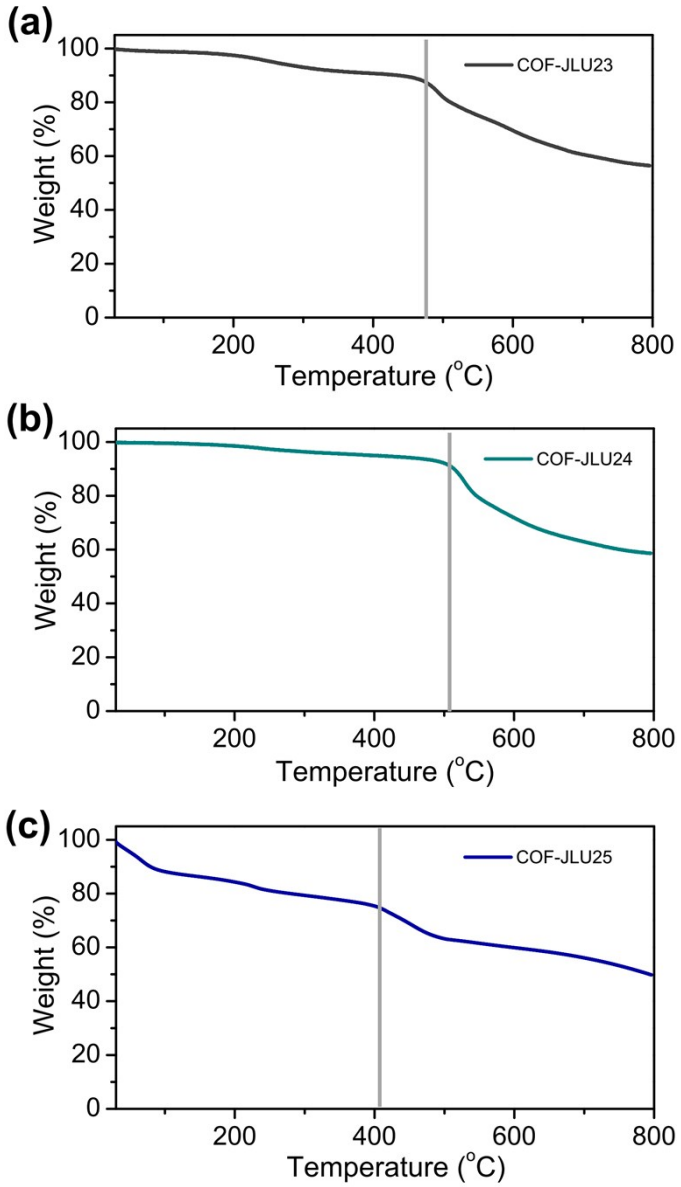


Figure S2. TGA curves of COF-JLU23 (a), COF-JLU24 (b) and COF-JLU25 (c) under a nitrogen atmosphere. TGA analysis indicates that these frameworks are thermally stable up to ~465 °C for COF-JLU23, ~508 °C for COF-JLU24, and ~404 °C for COF-JLU25, respectively. The weight loss at low temperature for COF-JLU25 may be due to adsorbed water, air and other matter in the pore of framework.

Section 5. IR and PXRD Spectra

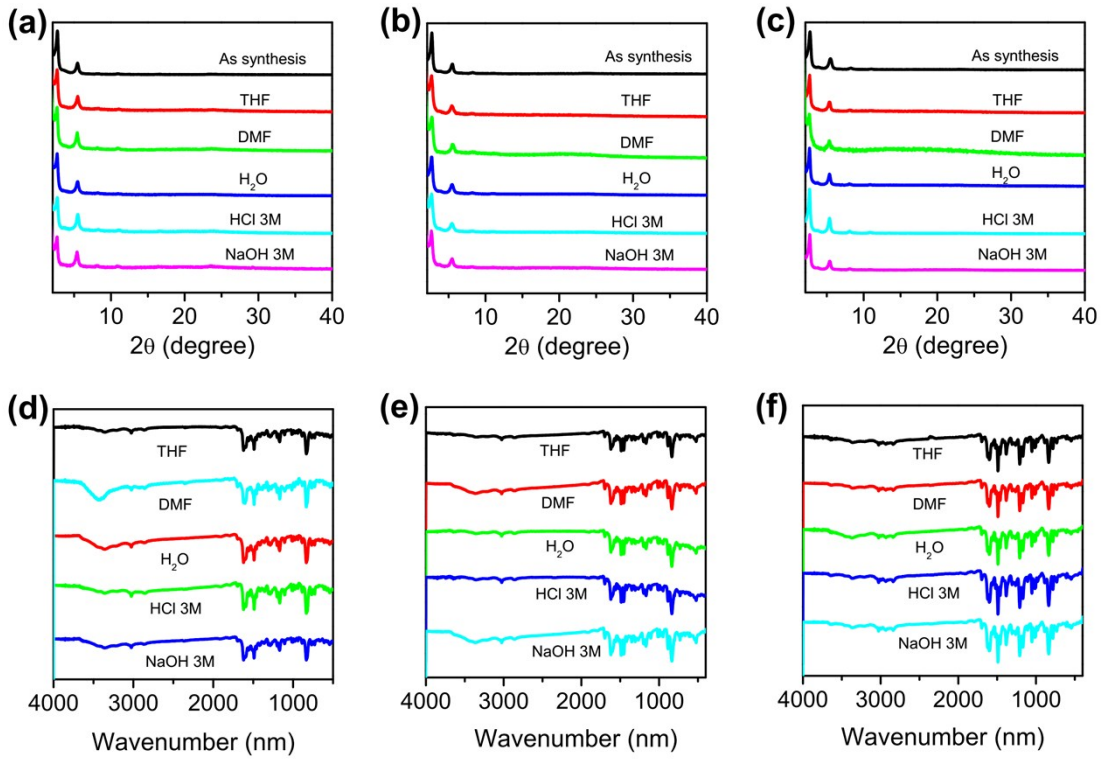


Figure S3. PXRD curves of COF-JLU23 (a), COF-JLU24 (b) and COF-JLU25 (c) after treatment in different solvents. IR spectra of COF-JLU23 (d), COF-JLU24 (e) and COF-JLU25 (f) after treatment in different solvents.

Section 6. Fluorescence Quenching Experiments

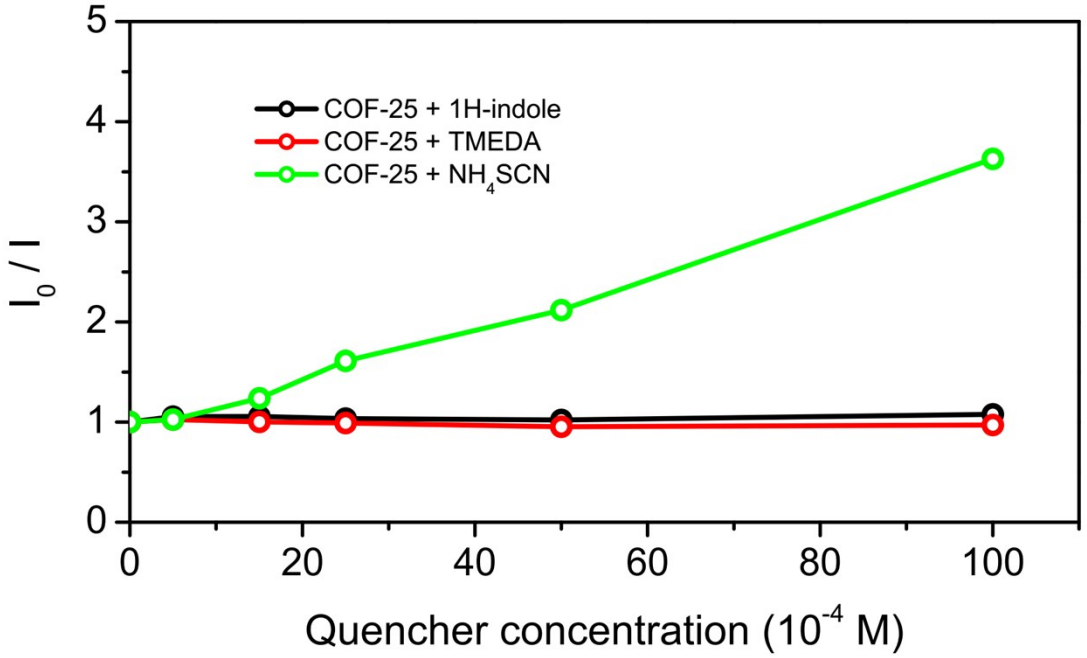
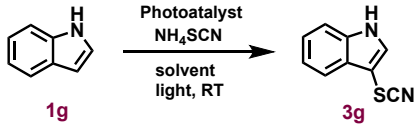


Figure S4. Plot of fluorescence intensity of COF-JLU25 (0.1 mg/mL in CH_3CN) vs concentration of 1*H*-indole, NH_4SCN, TMEDA (λ_{ex} = 470 nm, λ_{em} = 535 nm).

Section 7. Catalytic Data

Table S1. Photocatalytic C-3 thiocyanation of 1*H*-lindole by COF-JLUs[a]



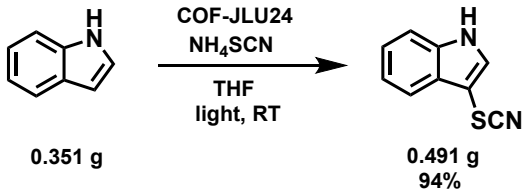
1g 3g

Entry	Catalyst	Solvent (mL)	Yield (%)[b]
1	COF-JLU24	CH_3CN	53
2	COF-JLU24	THF	95
3	COF-JLU24	CH_3OH	34
4	COF-JLU24	DMF	24
5[c]	COF-JLU24	THF	58
6[d]	COF-JLU24	THF	50
7[e]	COF-JLU24	THF	97
8[f]	COF-JLU24	THF	57
9[g]	COF-JLU24	THF	27
10[h]	COF-JLU24	THF	49
11[i]	COF-JLU24	THF	0
12	~	THF	33
13[j]	COF-JLU24	THF	20
14	g-C_3N_4	THF	79
15	COF-JLU23	THF	93
16	COF-JLU25	THF	86
17[k]	COF-JLU25	THF	59
18[m]	COF-JLU25	THF	40
19[n]	COF-JLU25	THF	26
20[o]	COF-JLU25	THF	35

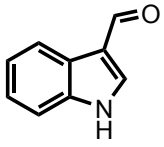
[a]Reaction conditions: photocatalyst (3.0 mg), 1*H*-indole (35.2 mg, 0.3 mmol), NH_4SCN (45.7 mg, 0.6 mmol), solvent (2.0 mL), O_2 balloon (~0.1 MPa), 30 W blue LED lamp with 460 nm, 25 °C, 7 h. [b]Isolated yield. [c]2.0 equiv of KSCN was used.

[d]2.0 equiv of NaSCN was used. [e]3.0 equiv of NH_4SCN was used. [f]1.0 equiv of NH_4SCN was used. [g]8 W white LED lamp. [h]30 W green LED lamp with 520 nm. [i]Dark. [j]In N_2. [k]2,6-di-tert-butyl-4-methylphenol as the radical scavenger. [m]DIPEA as the hole scavenger. [n]BQ as the superoxide scavenger. [o]NaN_3 as the single oxygen scavenger.

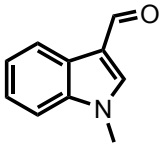
Scheme S1. Large-scale photocatalytic reaction using COF-JLU24 as a heterogeneous photocatalyst.



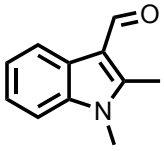
Section 8. Characterization Data of Catalytic Products



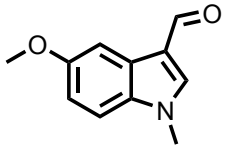
1*H*-Indole-3-carbaldehyde: ^{1}H NMR (DMSO, 400 MHz): δ 12.14 (s, 1H), 9.93 (s, 1H), 8.29 (d, J = 2.8 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8 Hz, 1H), 7.27-7.19 (m, 2H) ppm.



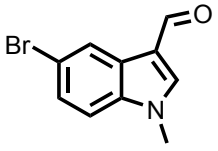
1-Methyl-1*H*-indole-3-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.98 (s, 1H), 8.30 (d, J = 6.8 Hz, 1H), 7.66 (s, 1H), 7.36-7.30 (m, 3H), 3.86 (s, 3H) ppm.



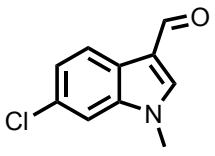
1, 2-Dimethyl-1*H*-indole-3-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.11 (s, 1H), 8.26 (s, 1H), 7.28-7.27 (m, 3H), 3.65 (s, 3H), 2.62 (s, 3H) ppm.



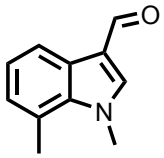
5-Methoxy-1-methyl-1*H*-indole-3-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.92 (s, 1H), 7.78 (d, J = 2.4 Hz, 1H), 7.59 (s, 1H), 7.22 (d, J = 9.2 Hz, 1H), 6.98-6.95 (m, 1H), 3.89 (s, 3H), 3.82 (s, 3H) ppm.



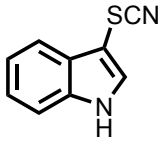
5-Bromo-1-methyl-1*H*-indole-3-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.94 (s, 1H), 8.45 (d, J = 1.6 Hz, 1H), 7.65 (s, 1H), 7.44-7.41 (m, 1H), 7.21 (d, J = 8.8 Hz, 1H), 3.86 (s, 3H) ppm.



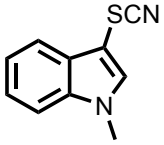
6-Chloro-1-methyl-1*H*-indole-3-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.95 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.66 (s, 1H), 7.35 (s, 1H), 7.30-7.27 (m, 1H), 3.84 (s, 3H) ppm.



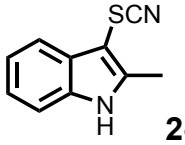
1, 7-Dimethyl-1*H*-indole−3-carbaldehyde: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.93 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.52 (s, 1H), 7.18-7.15 (m, 1H), 7.03 (d, J = 7.2 Hz, 1H), 4.09 (s, 3H), 2.74 (s, 3H) ppm.



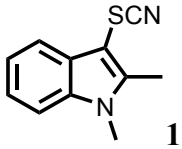
3-Thiocyanato-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (s, 1H), 7.83-7.80 (m, 1H), 7.53 (d, J = 2.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.34-7.32 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.3, 131.4, 127.9, 124.1, 122.1, 118.9, 112.5, 92.1 ppm.



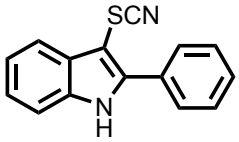
1-Methyl-3-thiocyanato-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 7.2 Hz, 1H), 7.37-7.31 (m, 4H), 3.74 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.3, 135.3, 128.6, 123.6, 121.8, 119.1, 112.2, 110.5, 89.8, 33.6 ppm.



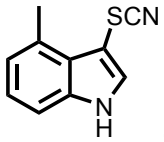
2-Methyl-3-thiocyanato-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (s, 1H), 7.70-7.68 (m, 1H), 7.34-7.32 (m, 1H), 7.28-7.22 (m, 2H), 2.58 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.4, 135.4, 128.9, 123.2, 121.8, 118.3, 112.5, 111.6, 88.9, 12.3 ppm.



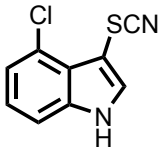
1, 2-Dimethyl-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.71 (m, 1H), 7.32-7.27 (m, 3H), 3.66 (s, 3H), 2.57 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ143.7, 137.1, 128.5, 122.9, 121.7, 118.4, 112.2, 109.8, 88.1, 30.7, 11.3 ppm.



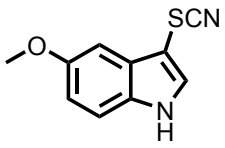
2-Phenyl-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.78 (s, 1H), 7.85-7.83 (m, 1H), 7.73-7.72 (m, 2H), 7.56-7.43 (m, 4H), 7.34-7.32 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 135.7, 130.3, 130.0, 129.9, 129.4, 128.9, 124.4, 122.4, 119.4, 112.3, 112.0, 89.4 ppm.



4-Methyl-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (s, 1H), 7.48 (d, J = 2.8 Hz, 1H), 7.24 (s, 1H), 7.19-7.15 (m, 1H), 7.01 (d, J = 6.8 Hz, 1H), 2.94 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.8, 132.4, 131.3, 125.9, 124.3, 123.8, 113.7, 110.4, 92.4, 19.5 ppm.

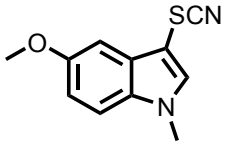


4-Chloro-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.81 (s, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.23-7.16 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 132.7, 126.7, 124.9, 124.1, 123.3, 113.1, 111.2, 93.5 ppm.

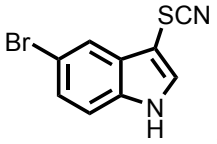


5-Methoxy-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.72 (s, 1H), 7.44 (d, J = 2.8 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 2.4 Hz,

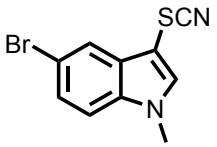
1H), 6.96-6.93 (m, 1H), 3.91 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.0, 131.7, 131.2, 128.8, 114.8, 113.4, 112.4, 100.1, 91.7, 56.2 ppm.



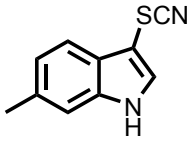
5-Methoxy-1-Methyl-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (s, 1H), 7.24 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.00-6.97 (m, 1H), 3.92 (s, 3H), 3.74 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.9, 135.5, 132.4, 129.5, 114.3, 112.3, 111.5, 100.2, 89.0, 56.2, 33.8 ppm.



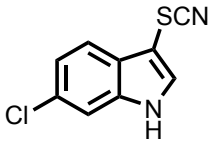
5-Bromo-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (s, 1H), 7.92 (d, J = 1.6 Hz, 1H), 7.53 (d, J = 2.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.30 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.0, 132.4, 129.7, 127.4, 121.8, 115.7, 113.9, 111.8, 92.5 ppm.



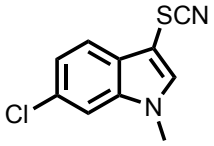
5-Bromo-1-Methyl-3-thiocyanato-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, J = 1.6 Hz, 1H), 7.42-7.40 (m, 2H), 7.23 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.4, 136.2, 130.4, 126.8, 121.9, 115.6, 112.1, 111.7, 90.1, 34.0 ppm.



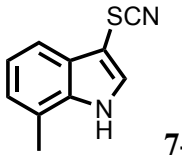
6-Methyl-3-thiocyanato-1*H*-indole：^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 1H), 7.67 (d, J = 8 Hz, 1H), 7.36 (d, J = 2.8 Hz, 1H), 7.20 (s, 1H), 7.14 (d, J = 8 Hz, 1H), 2.48 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.8, 134.2, 130.8, 125.8, 123.9, 118.5, 112.6, 112.3, 91.8, 22.0 ppm.



6-Chloro-3-thiocyanato-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.76 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 2.8 Hz, 1H), 7.42 (d, J = 1.6 Hz, 1H), 7.29-7.26 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.7, 131.9, 130.4, 126.6, 123.1, 120.0, 112.4, 111.9, 93.2 ppm.

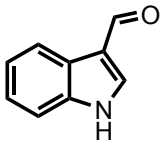


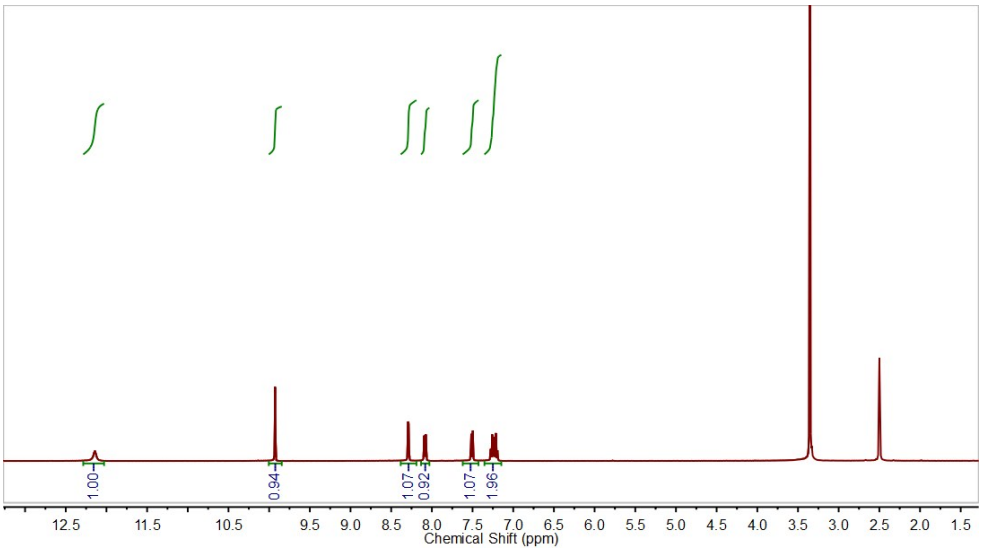
6-Chloro-1-Methyl-3-thiocyanato-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, J = 8.4 Hz, 1H), 7.40-7.38 (m, 2H), 7.29-7.27 (m, 1H), 3.80 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 136.0, 130.1, 127.3, 122.8, 120.3, 111.8, 110.7, 91.1, 33.9 ppm.



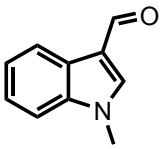
7-Methyl-3-thiocyanato-1*H*-indole: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.75 (s, 1H), 7.65 (d, J = 8 Hz, 1H), 7.46 (d, J = 2.4 Hz, 1H), 7.25-7.21 (m, 1H), 7.12-7.11 (m, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.9, 131.0, 127.6, 124.7, 122.4, 121.7, 116.6, 112.4, 92.7, 16.7 ppm.

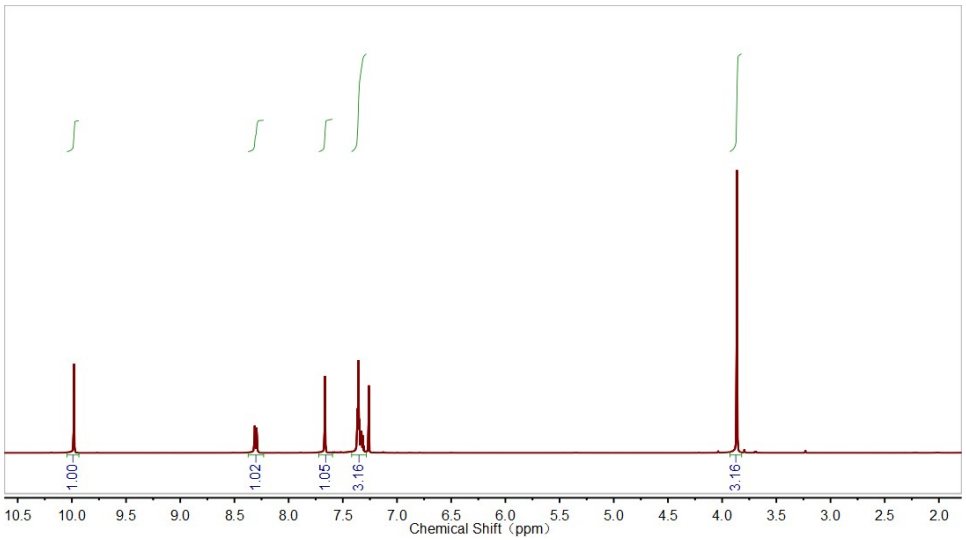
Section 9. NMR Spectra of Catalytic Products



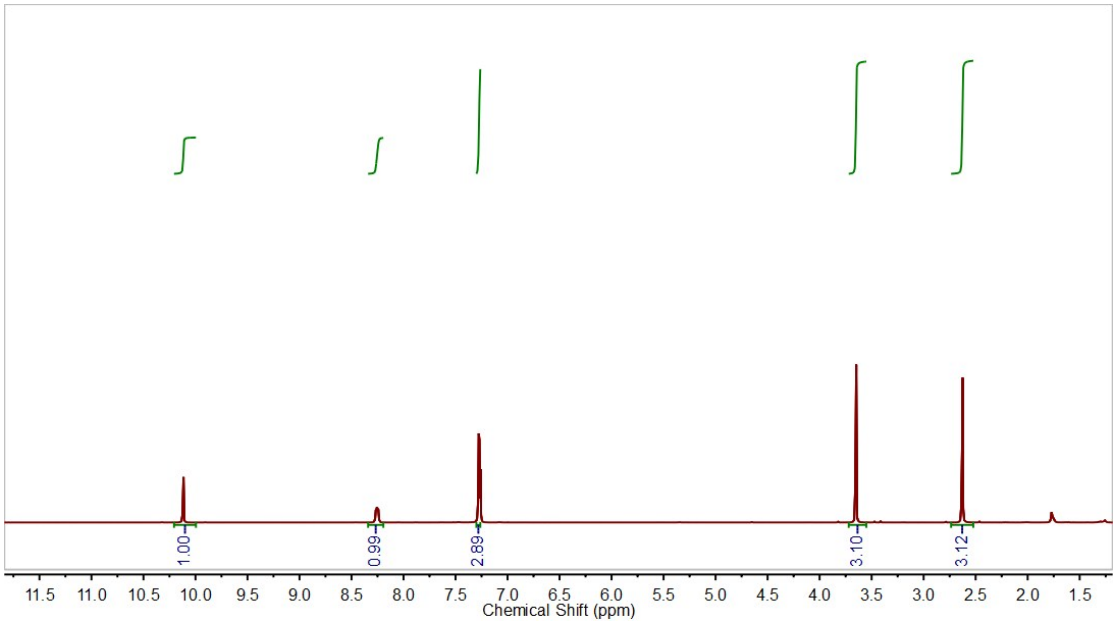


The ^{1}H-NMR spectra of 1*H*-Indole-3-carbaldehyde

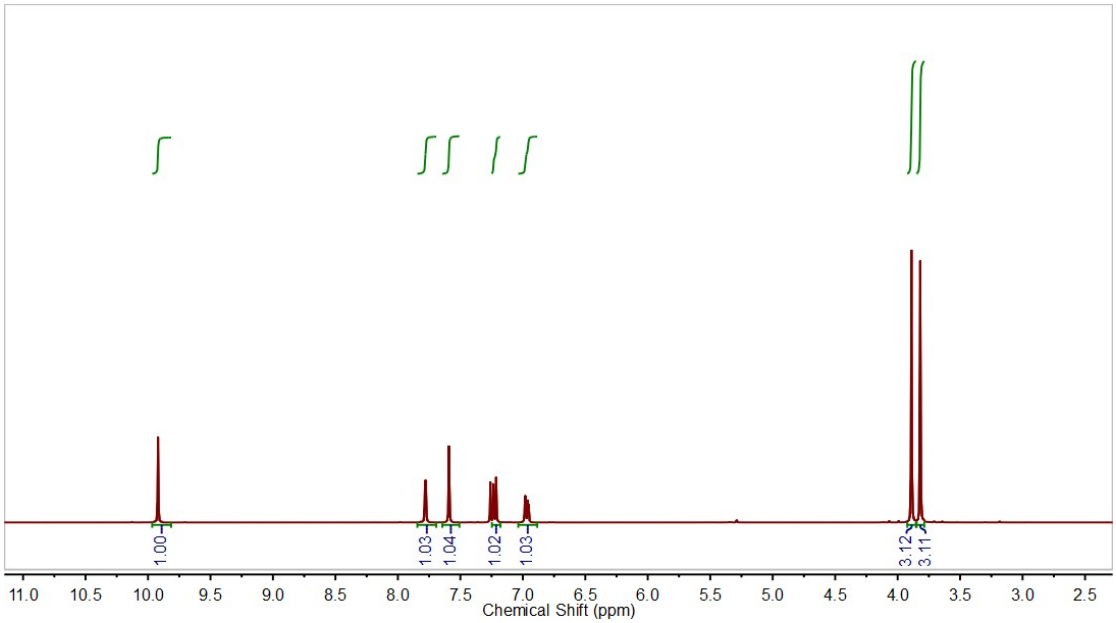




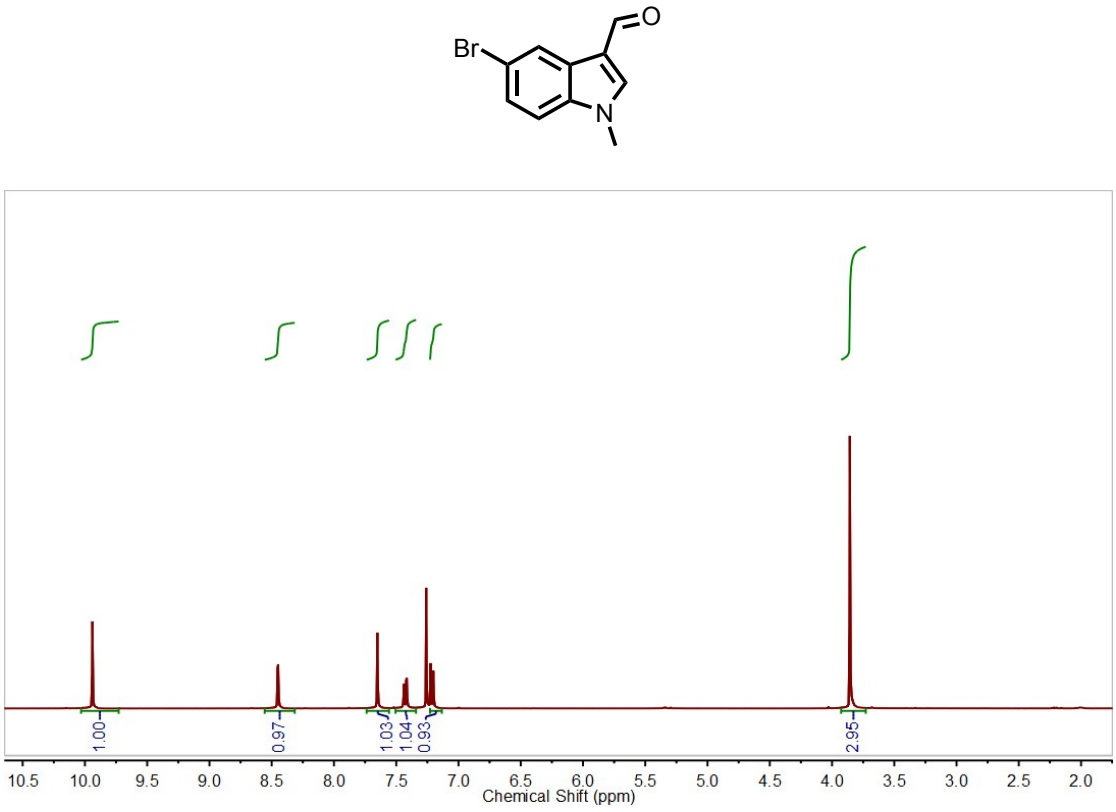
The ^{1}H-NMR spectra of 1-Methyl-1*H*-indole-3-carbaldehyde



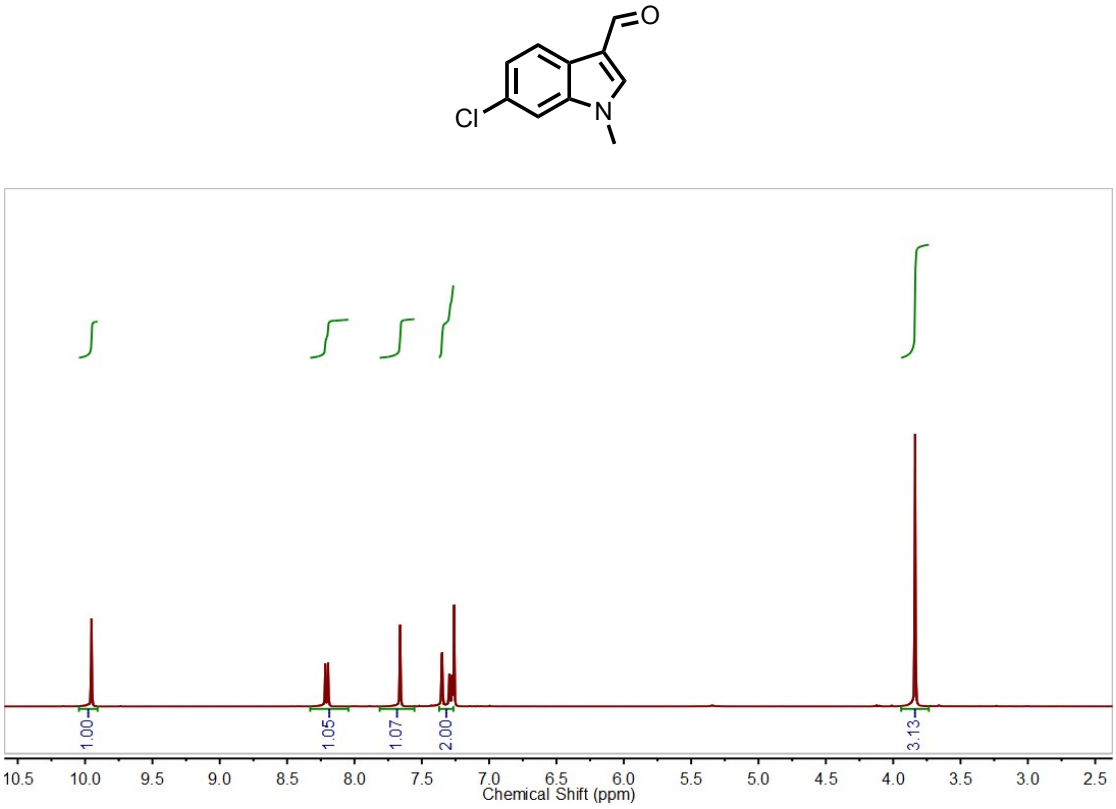
The ^{1}H-NMR spectra of 1, 2-Dimethyl-1*H*-indole-3-carbaldehyde



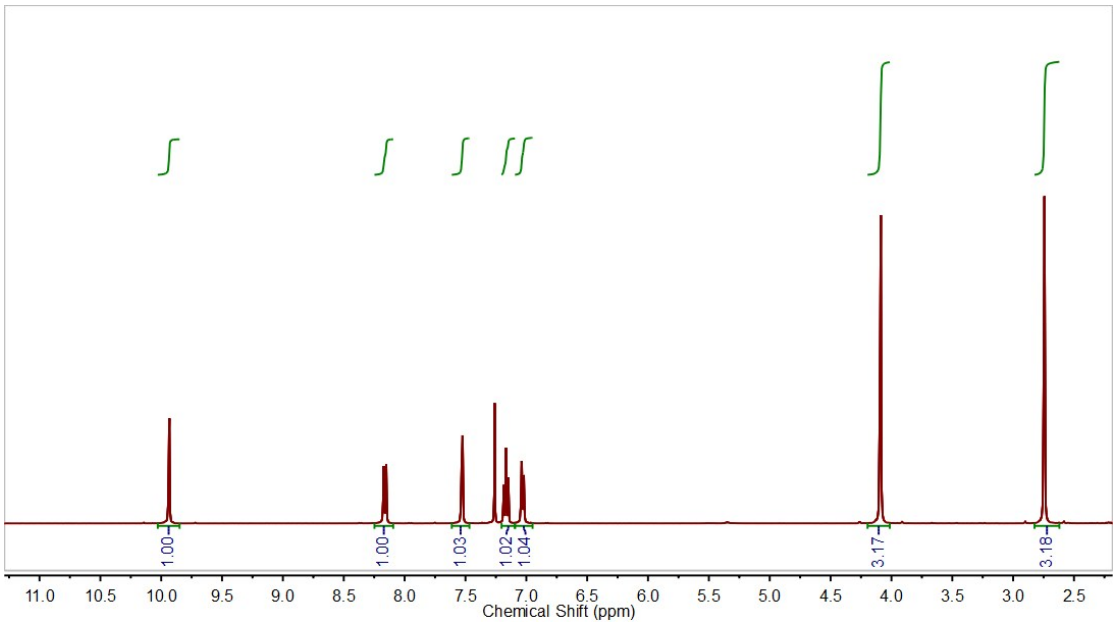
The ^{1}H-NMR spectra of 5-Methoxy-1-methyl-1*H*-indole-3-carbaldehyde



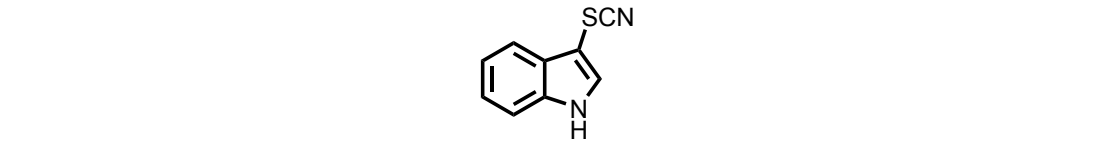
The ^{1}H-NMR spectra of 5-Bromo-1-methyl-1*H*-indole-3-carbaldehyde

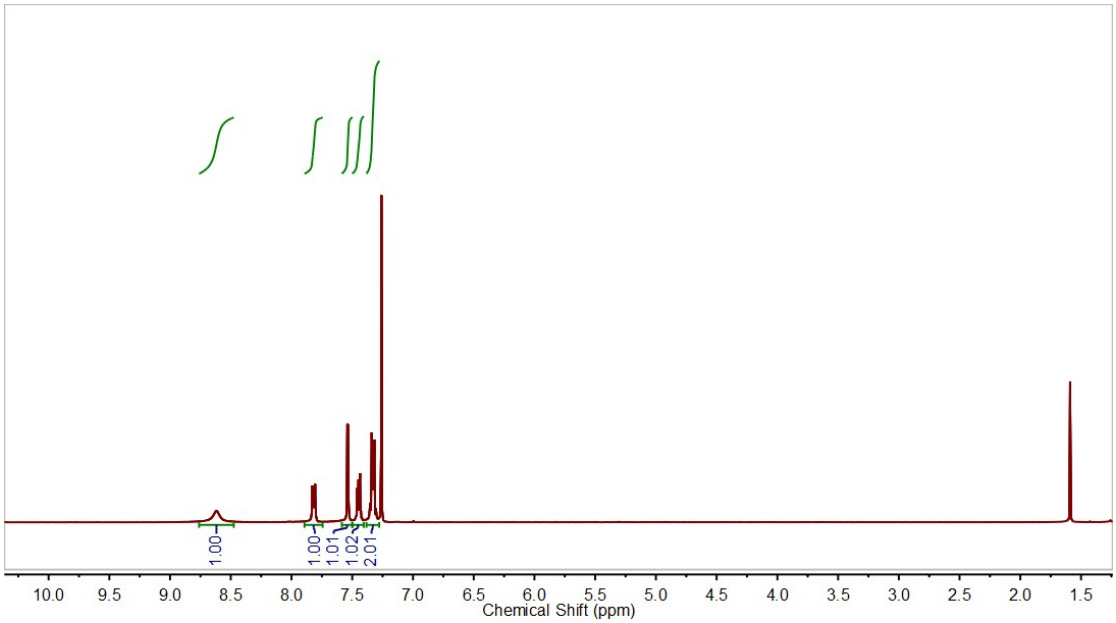


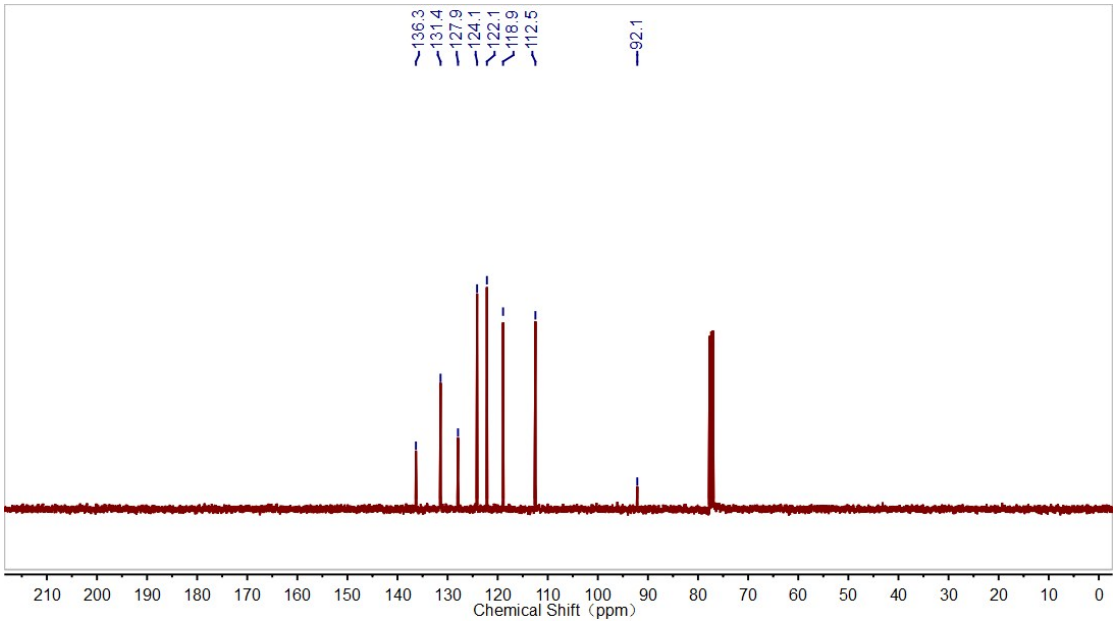
The ^{1}H-NMR spectra of 6-Chloro-1-methyl-1*H*-indole-3-carbaldehyde



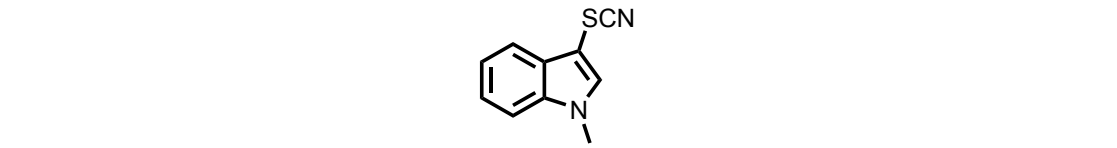
The ^{1}H-NMR spectra of 1, 7-Dimethyl-1*H*-indole-3-carbaldehyde

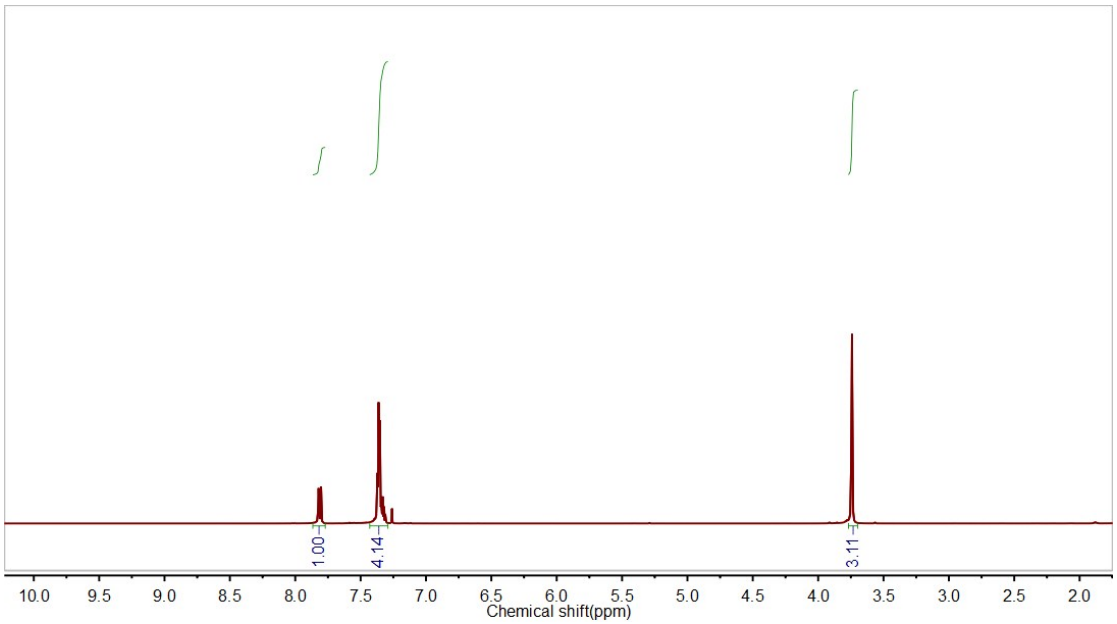


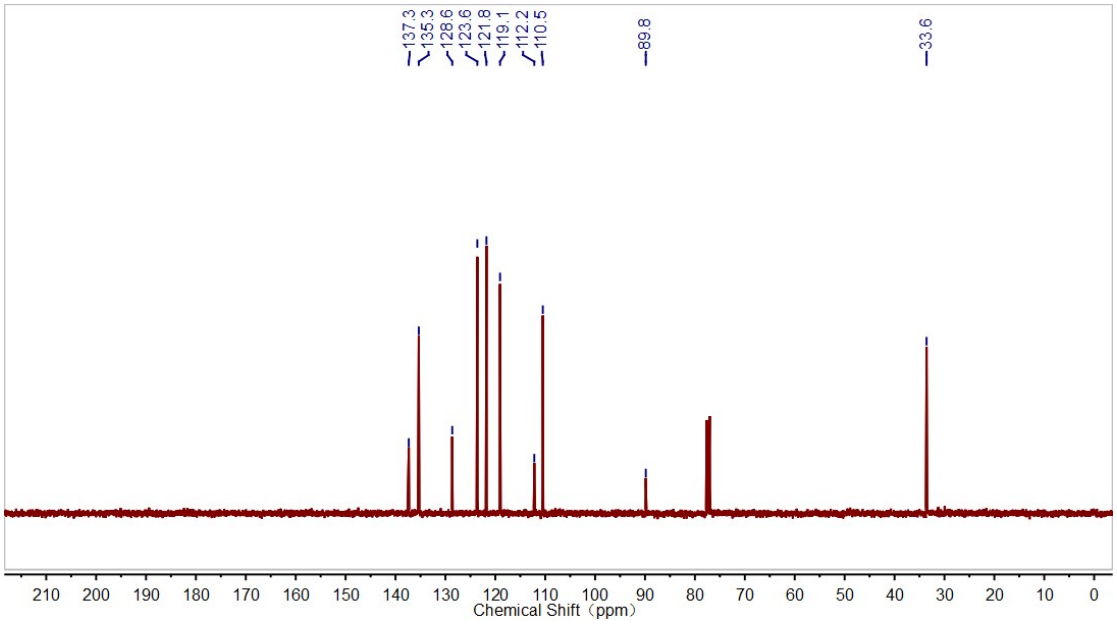




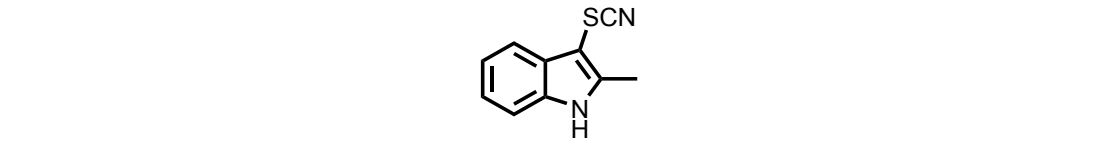
The ^{1}H-NMR and ^{13}C-NMR spectra of 3-Thiocyanato-1*H*-indole

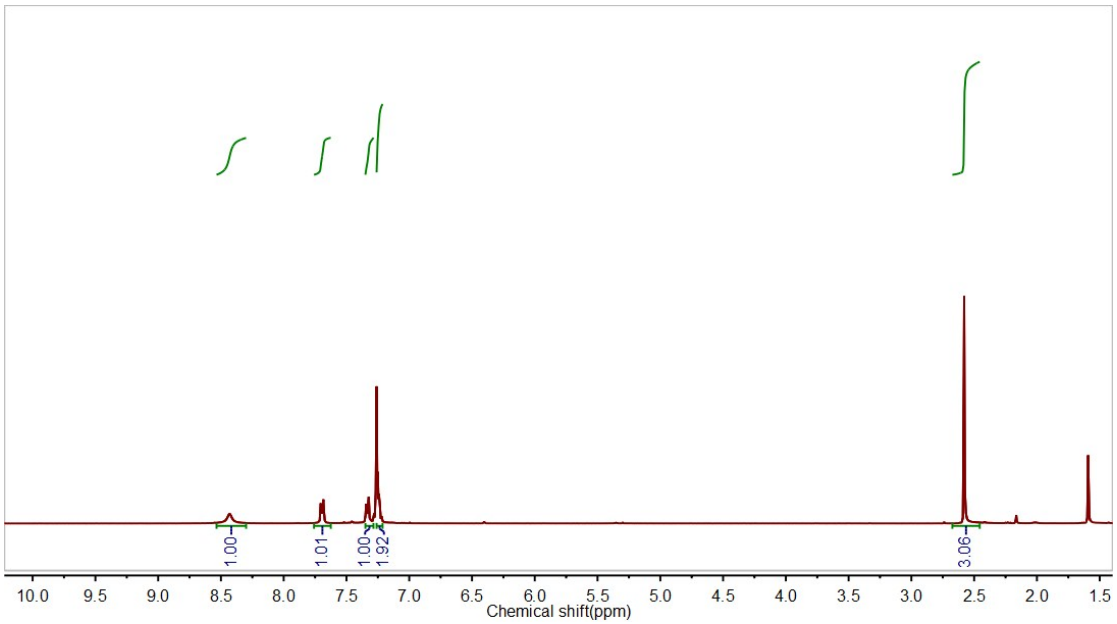


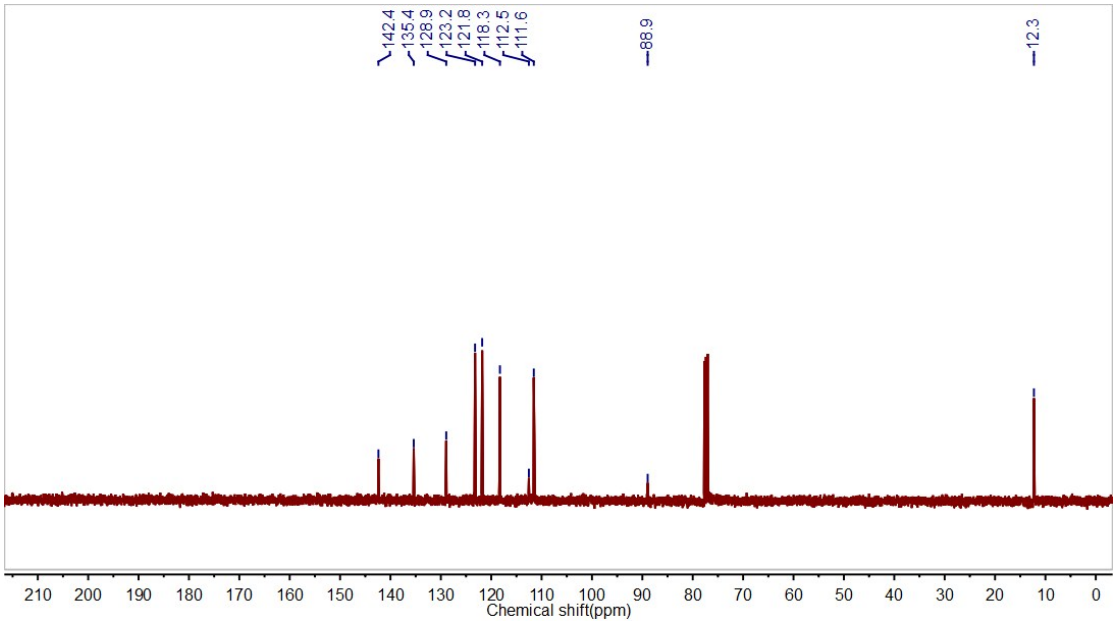




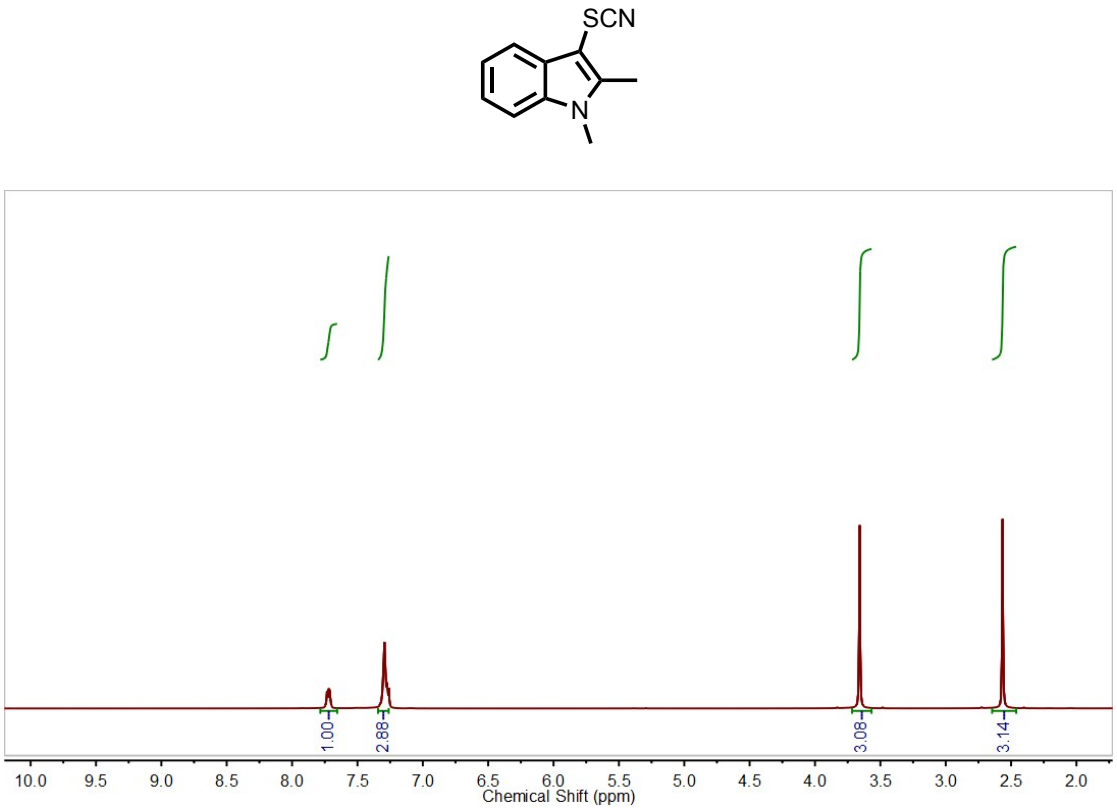
The ^{1}H-NMR and ^{13}C-NMR spectra of 1-Methyl-3-thiocyanato-1*H*-indole

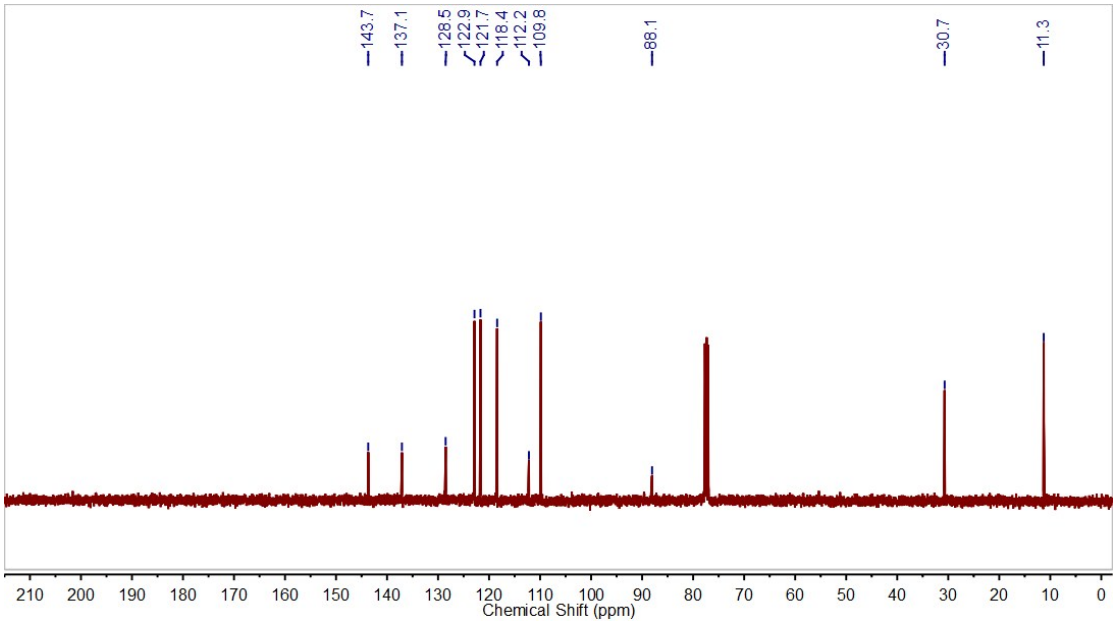




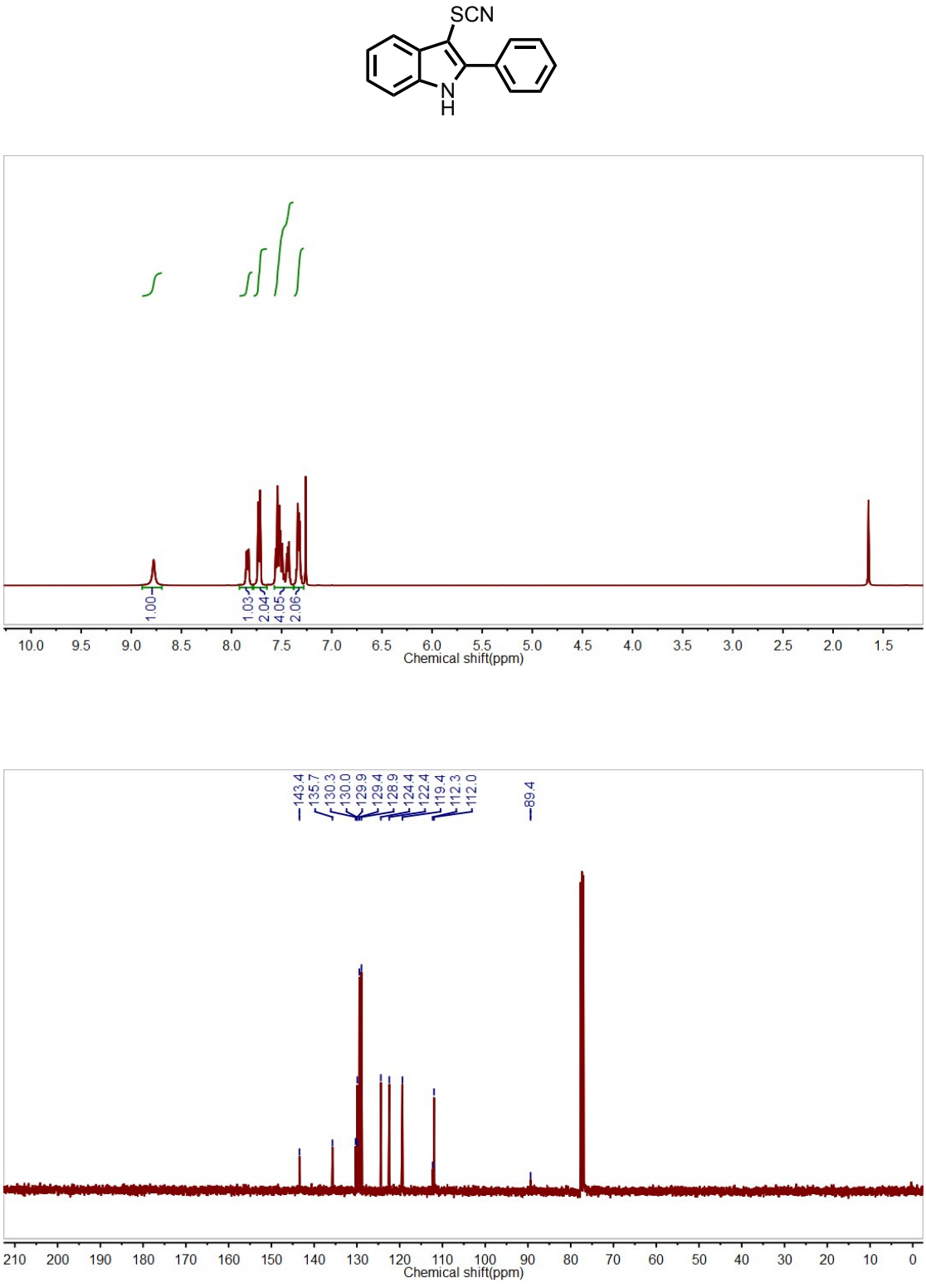


The ^{1}H-NMR and ^{13}C-NMR spectra of 2-Methyl-3-thiocyanato-1*H*-indole

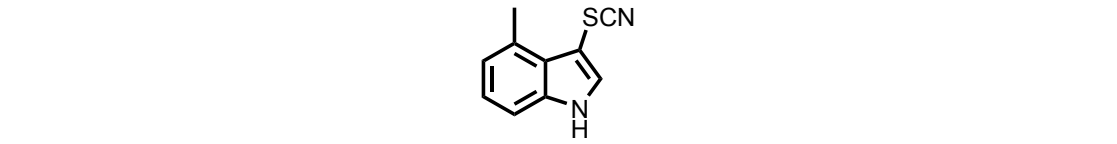


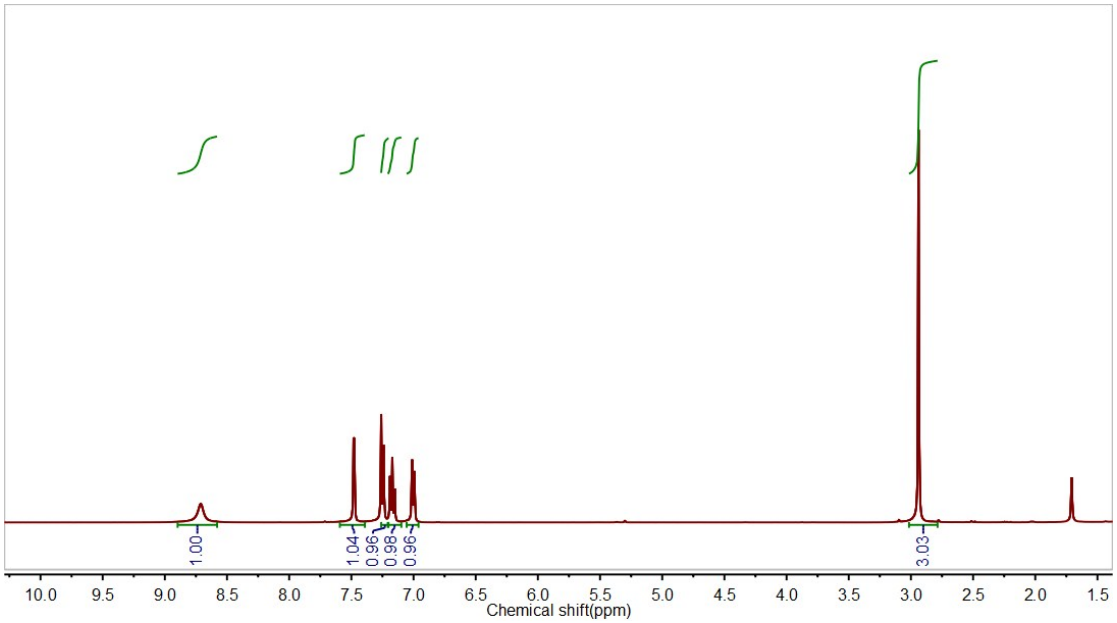


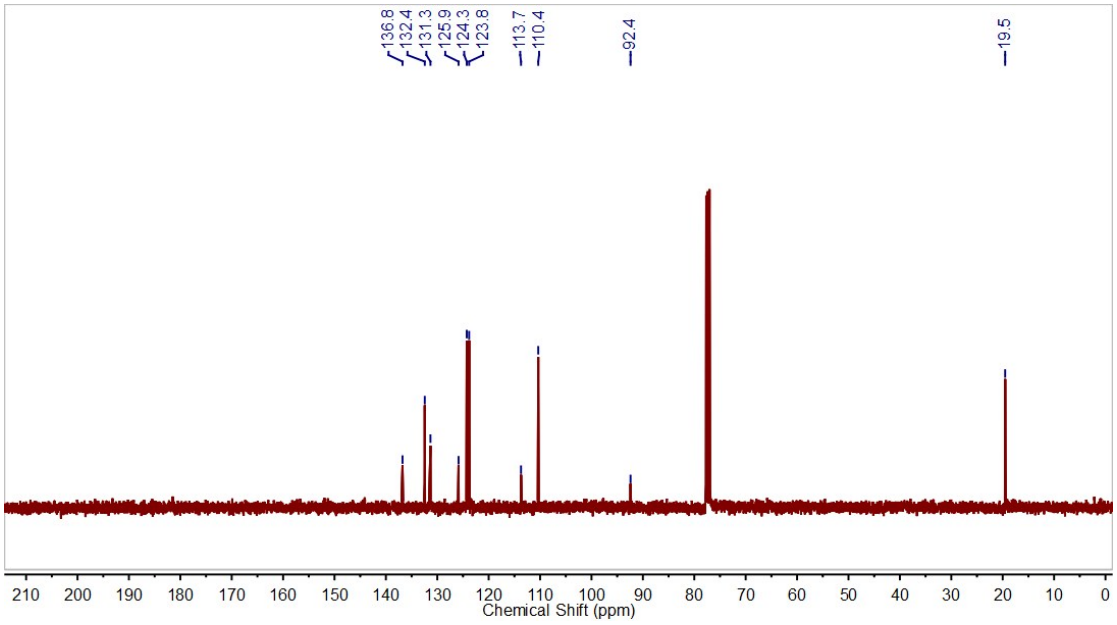
The ^{1}H-NMR and ^{13}C-NMR spectra of 1, 2-Dimethyl-3-thiocyanato-1*H*-indole



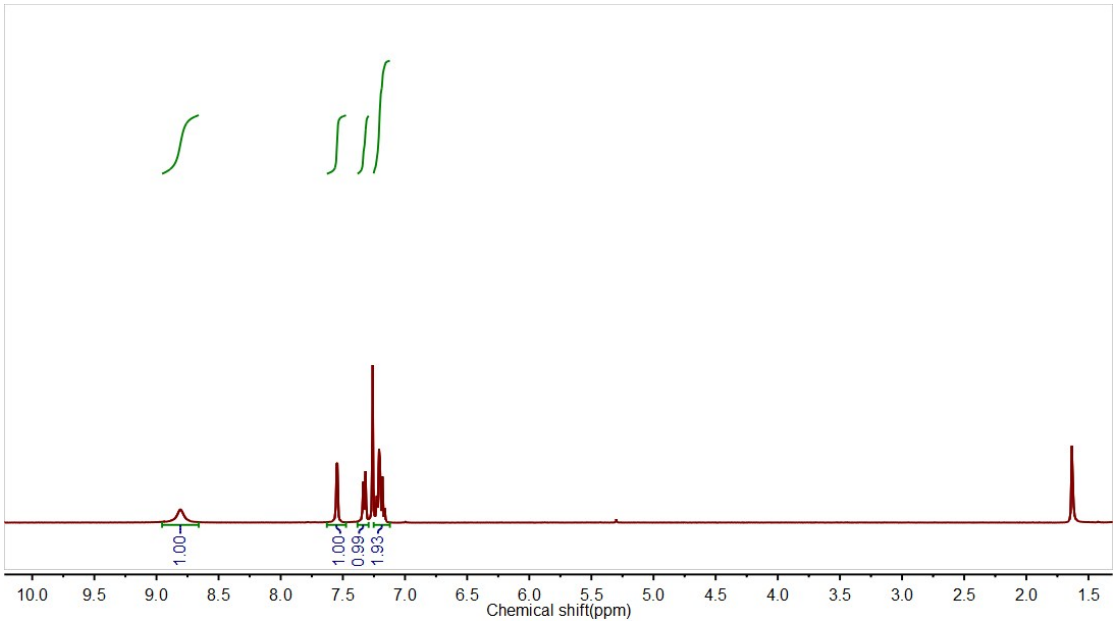
The ^{1}H-NMR and ^{13}C-NMR spectra of 2-Phenyl-3-thiocyanato-1*H*-indole

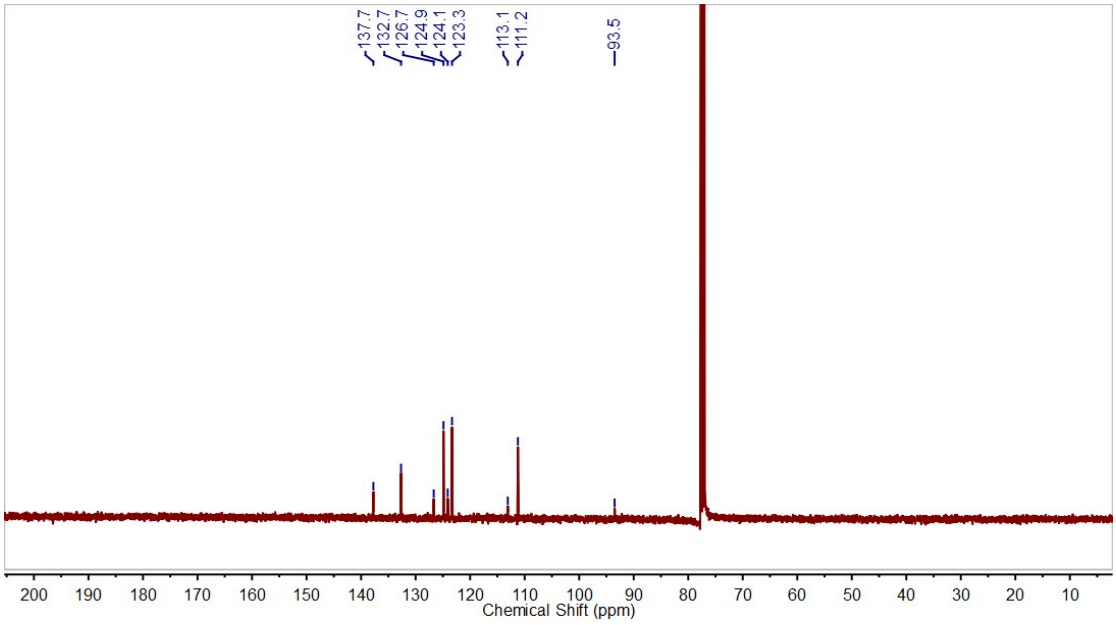






The ^{1}H-NMR and ^{13}C-NMR spectra of 4-Methyl-3-thiocyanato-1*H*-indole





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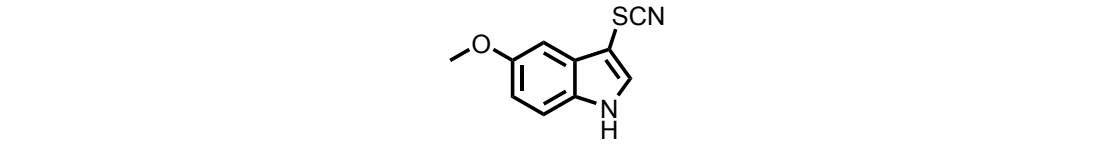
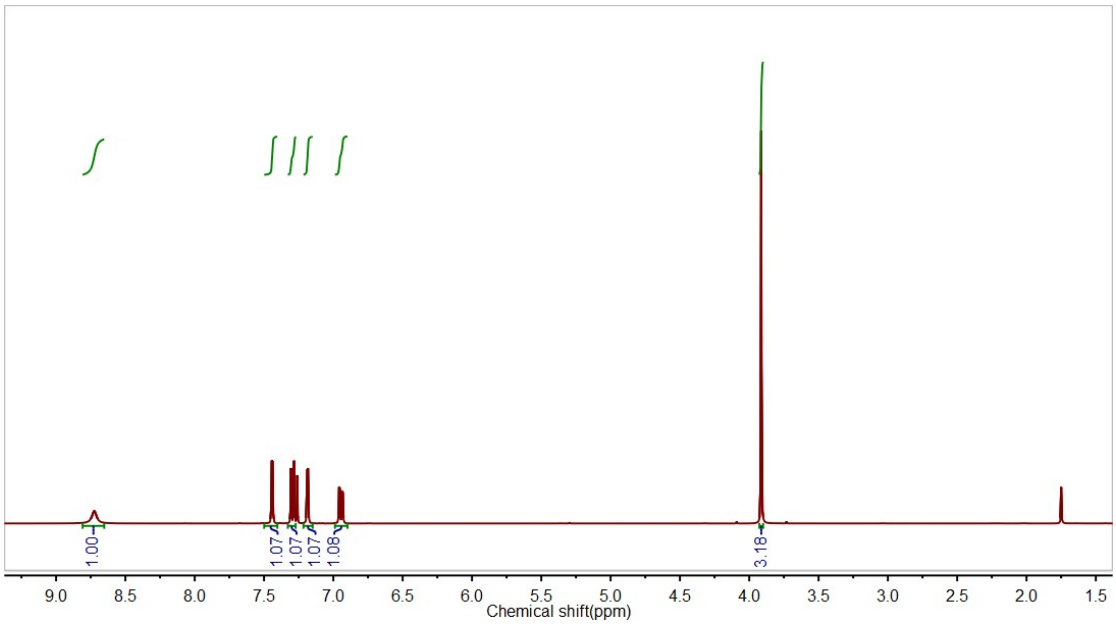
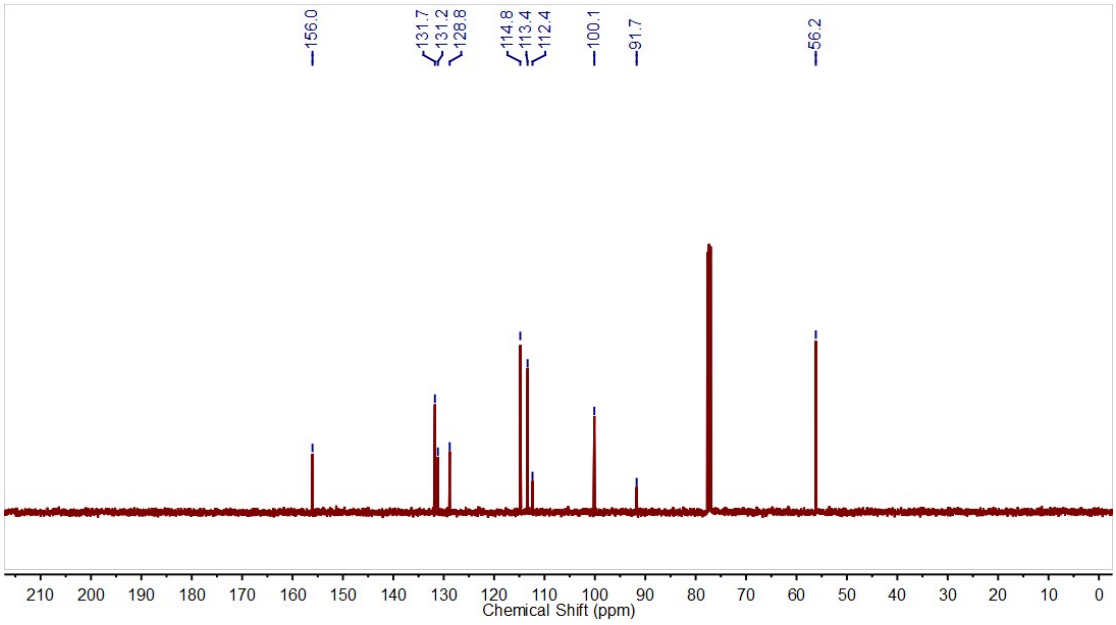
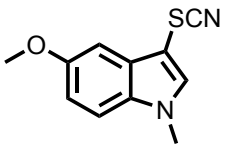
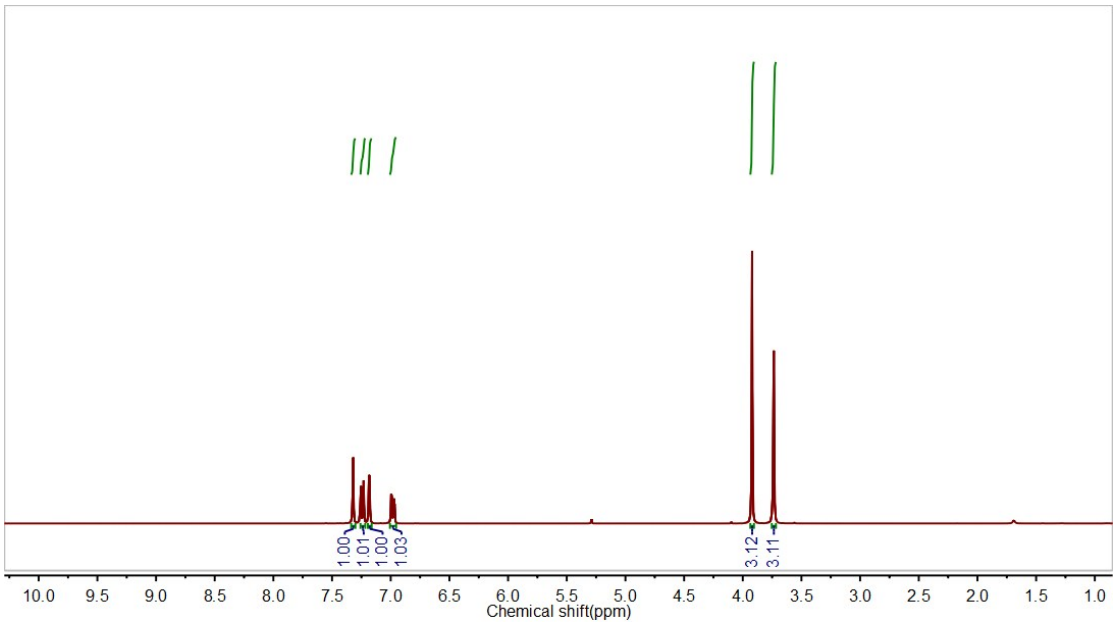


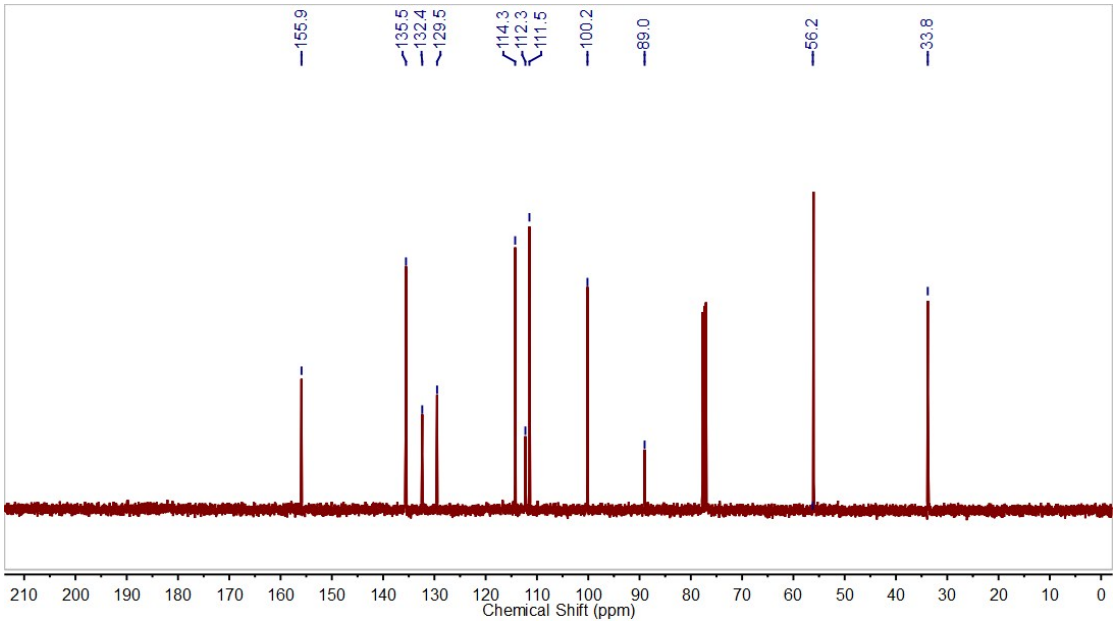




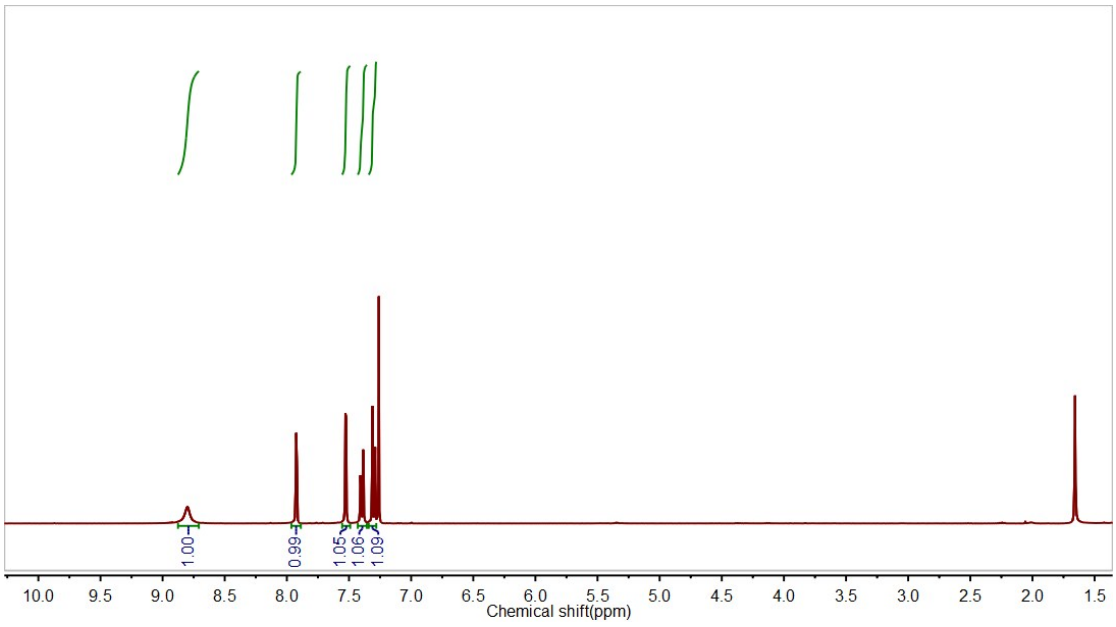
The ^{1}H-NMR and ^{13}C-NMR spectra of 5-Methoxy-3-thiocyanato-1*H*-indole

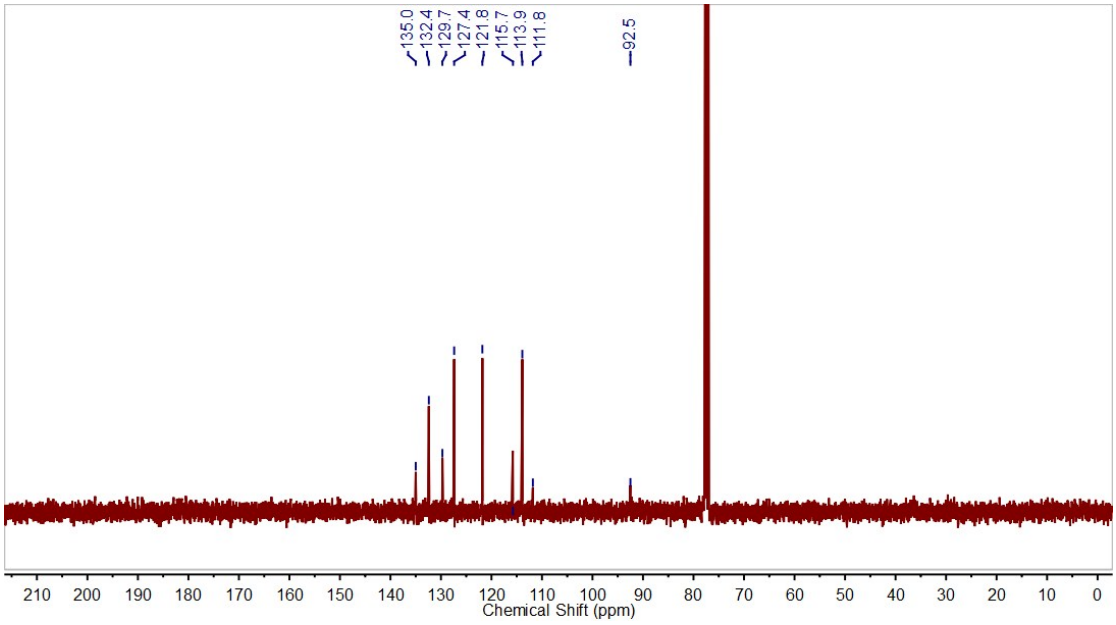




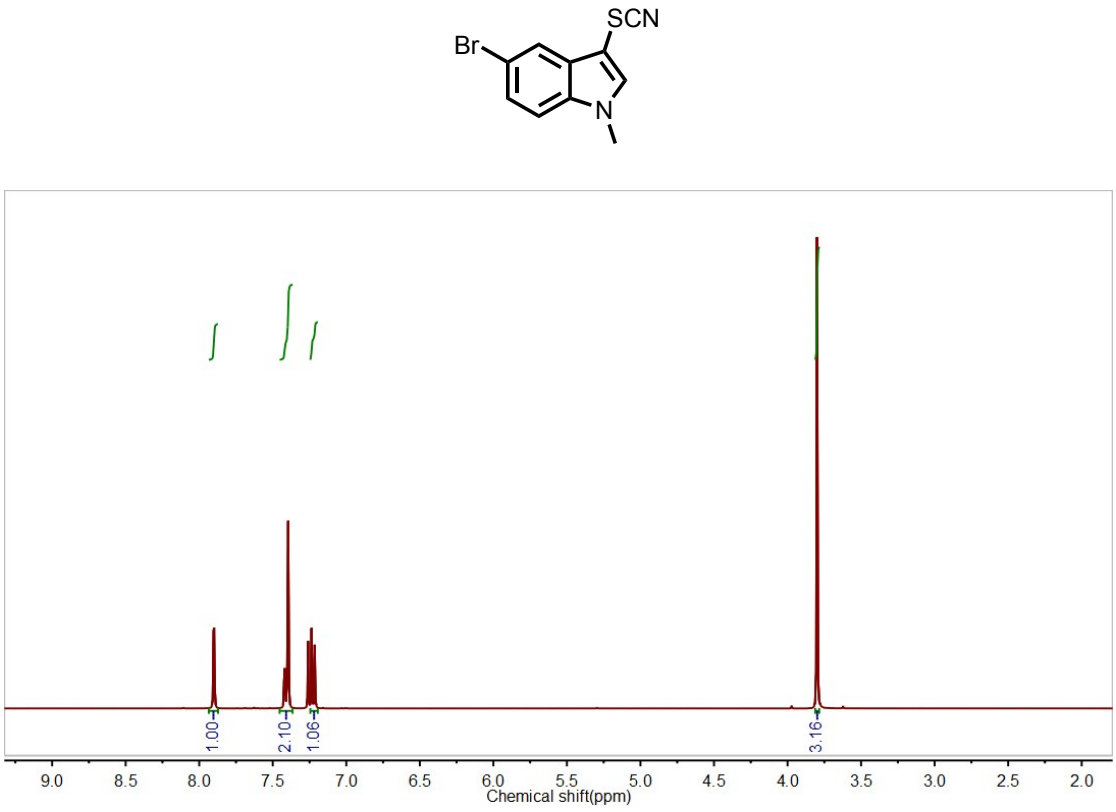


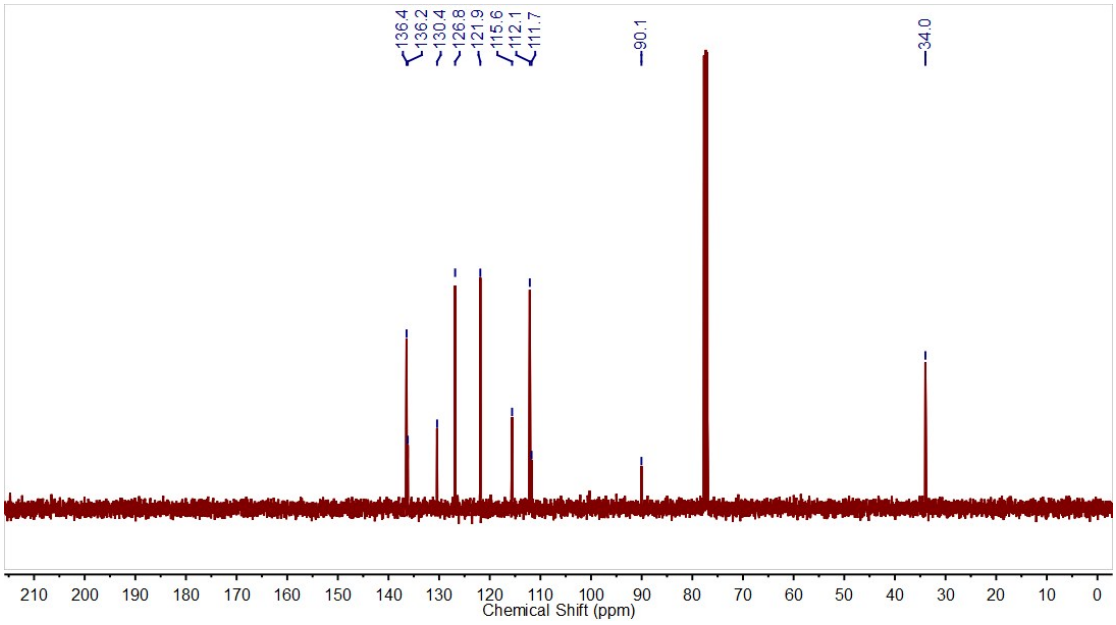
The ^{1}H-NMR and ^{13}C-NMR spectra of 5-Methoxy-1-Methyl-3-thiocyanato-1*H*-indole



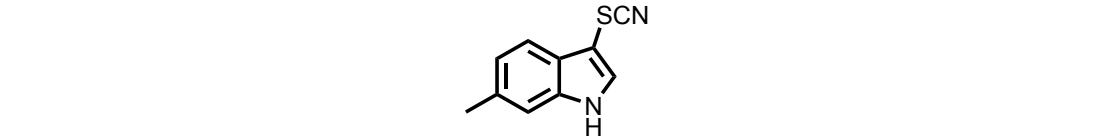


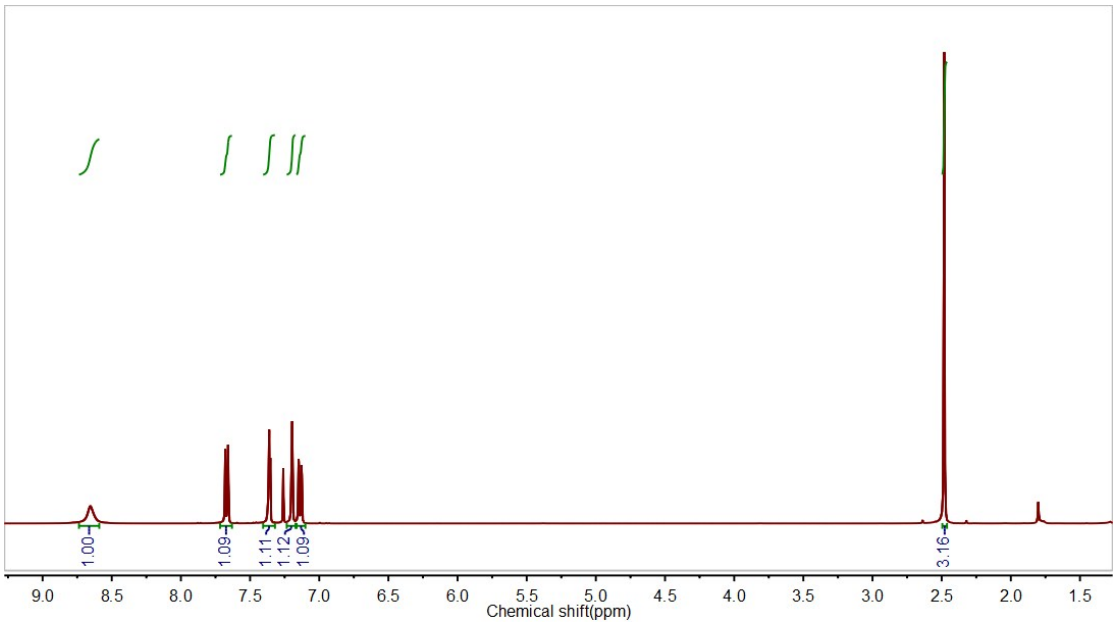
The ^{1}H-NMR and ^{13}C-NMR spectra of 5-Bromo-3-thiocyanato-1*H*-indole

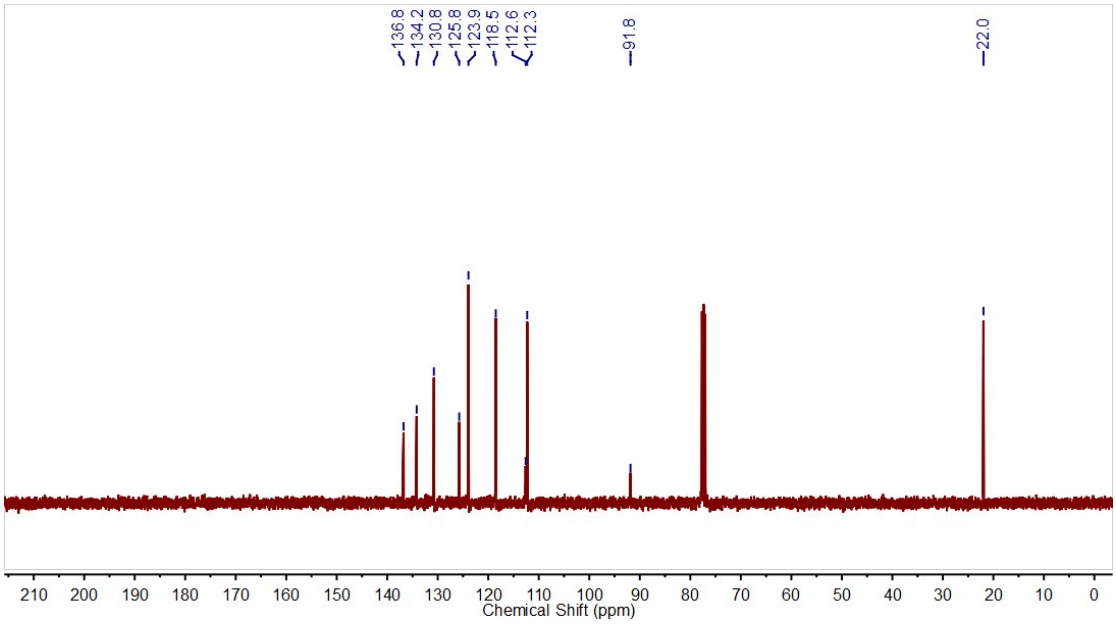




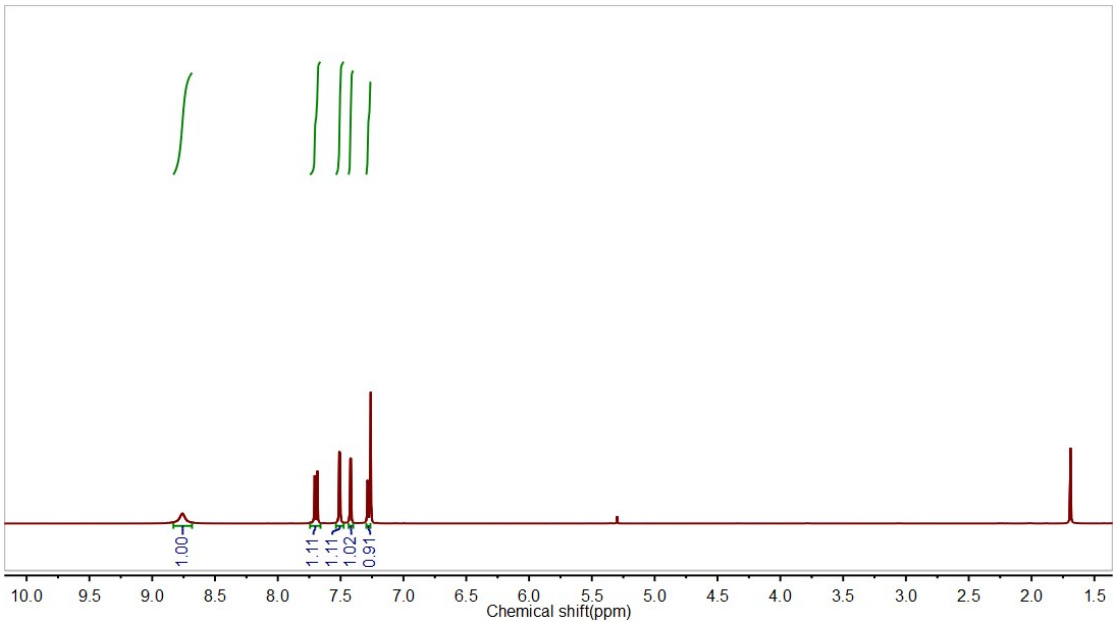
The ^{1}H-NMR and ^{13}C-NMR spectra of 5-Bromo-1-Methyl-3-thiocyanato-1*H*-indole

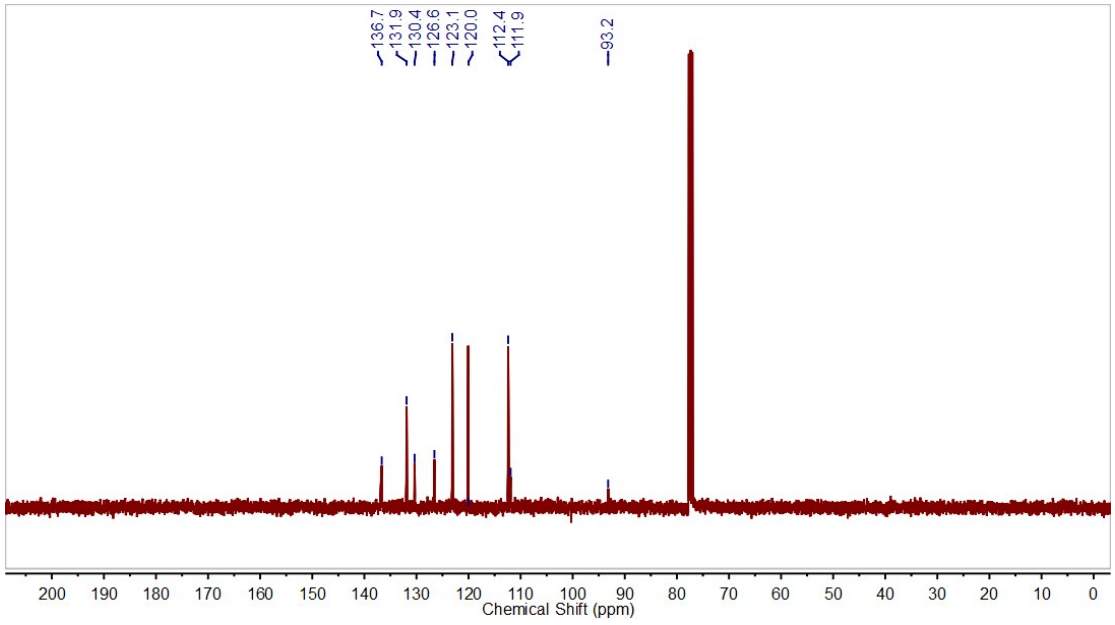




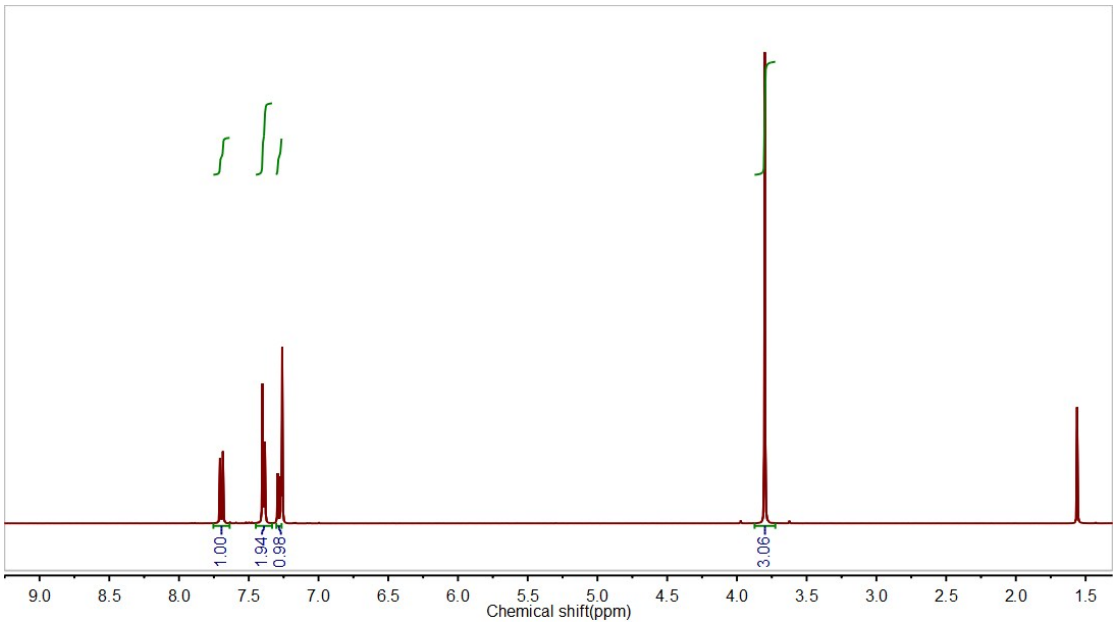


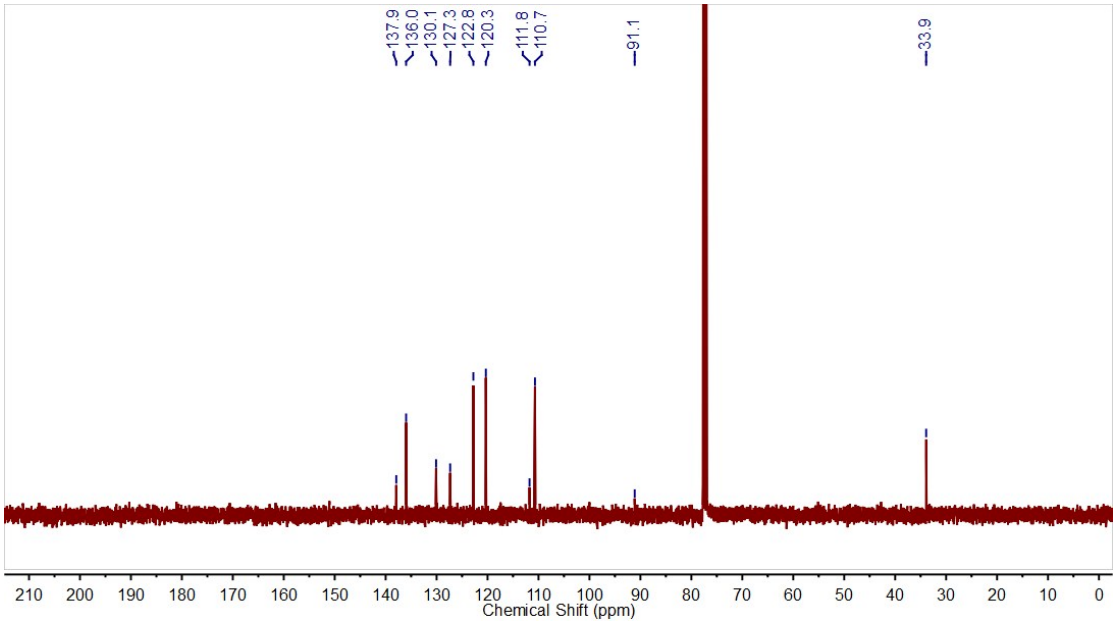
The ^{1}H-NMR and ^{13}C-NMR spectra of 6-Methyl-3-thiocyanato-1*H*-indole





The ^{1}H-NMR and ^{13}C-NMR spectra of 6-Chloro-3-thiocyanato-1*H*-indole





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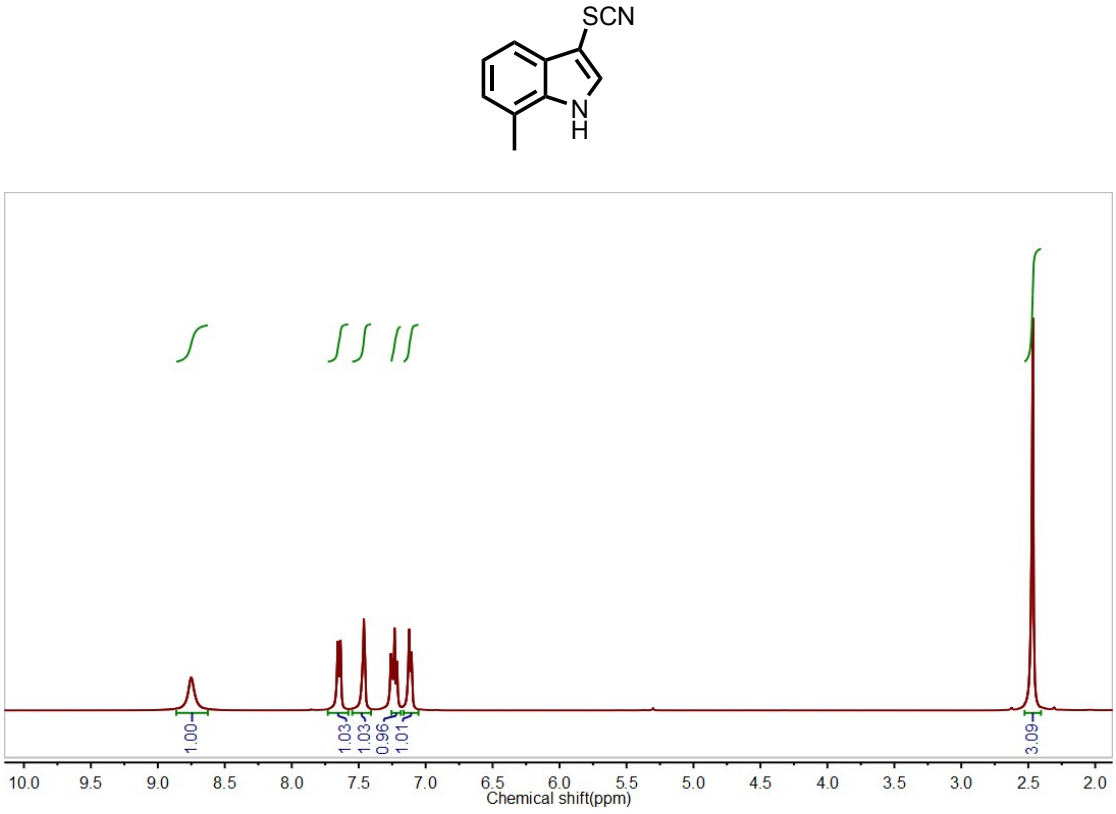

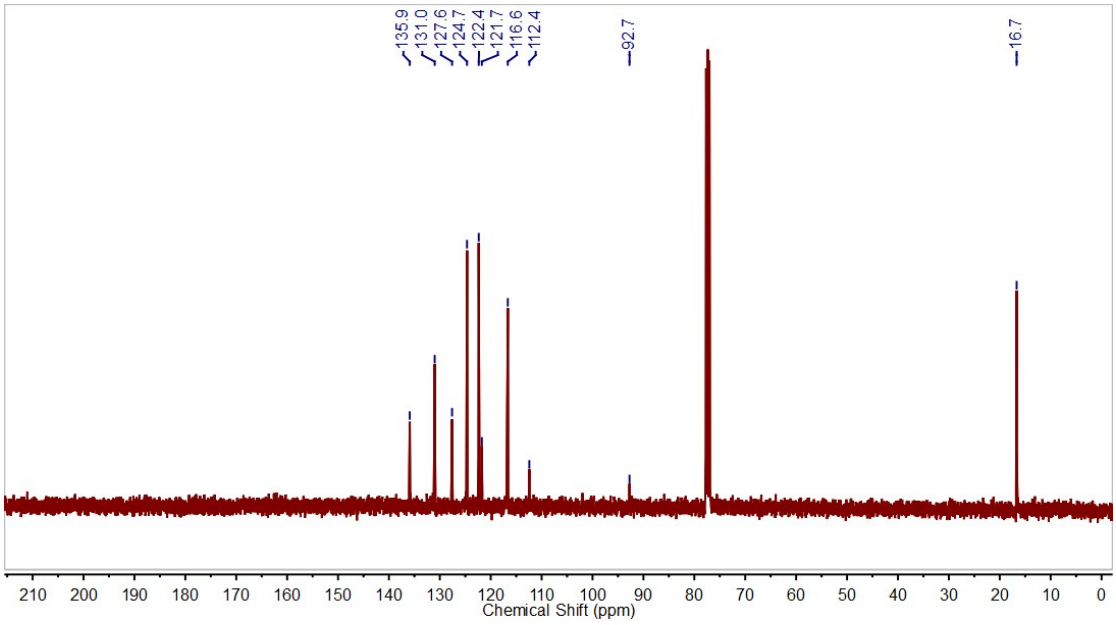

The ^{1}H-NMR and ^{13}C-NMR spectra of 7-Methyl-3-thiocyanato-1*H*-indole

Section 10. References

[1] Li, Z.; Zhi, Y.; Shao, P.; Xia, H.; Li, G.; Feng, X.; Chen, X.; Shi, Z.; Liu, X. Covalent Organic Framework as An Efficient, Metal-Free, Heterogeneous Photocatalyst for Organic Transformations under Visible Light. *Appl. Catal. B: Environ.* **2019**, 245, 334-342.

[2] Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light, *Nat. Mater.* **2009**, 8, 76−80.