

# Supporting Information For

## Visible Light-Promoted Thiocyanation of $sp^2$ C-H bonds over Heterogeneous Graphitic Carbon Nitrides

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## 1. General information

All reagents and solvents were purchased from commercial suppliers (Aldrich, U.S.A. and Aladdin Industrial, Inc., China) and used without further purification. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 500 or 600 MHz spectrometer at 298K. The chemical shifts ( $\delta$ ) are reported in ppm relative to tetramethylsilane (TMS) as the internal standard. Peaks are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, with coupling constants ( $J$ ) in Hz. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates (GF254), and the analytical was performed on pre-coated TLC-sheets. Products were purified by column chromatography by using 200-300 mesh silica gel as the stationary phase. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer using KBr pellets. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder diffractometer. Diffuse reflectance UV-vis spectra (DRS) were recorded on a Shimadzu U-3010 spectrophotometer and referenced to  $\text{BaSO}_4$ . Electron paramagnetic resonance (EPR) spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. The BET surface area and pore size distribution were estimated from the isotherms of nitrogen adsorption–desorption measurements (Quantachrome Instruments, Autosorb-iQ).

## 2. Experimental Procedures

### 2.1 Preparation of Carbon Nitride (CN)

Graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ )<sup>1</sup>, mesoporous graphitic carbon nitride ( $\text{mpg-C}_3\text{N}_4$ )<sup>1</sup>, carbon nitride derivative prepared through co-condensation of urea and oxamide followed by post-calcination in amolten salt ( $\text{CN-OA-m}$ )<sup>2</sup>, cyanamide-modified carbon nitride ( $^{\text{N}}\text{CN}^{\text{CN}}$ )<sup>3</sup> and potassium poly(heptazine imide) (K-PHI)<sup>4</sup> were synthesized according to the previously described procedure. All analytical data (FTIR, XRD, UV/Vis, SEM, etc., see Figure S1-S4) are in full agreement with those published in the literature.<sup>1-4</sup>

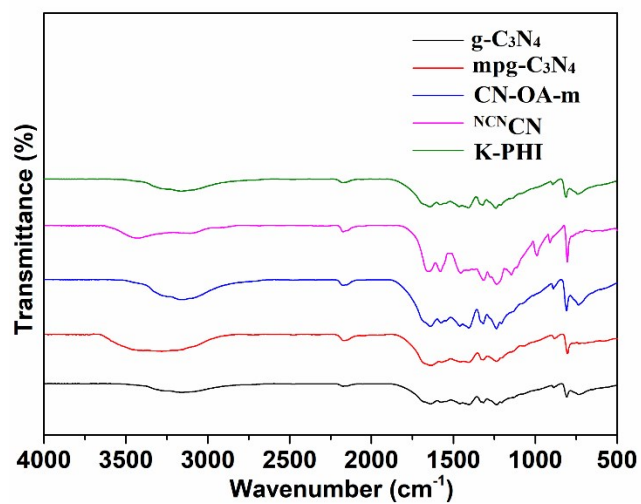


Figure S1. FTIR spectra of PCN samples

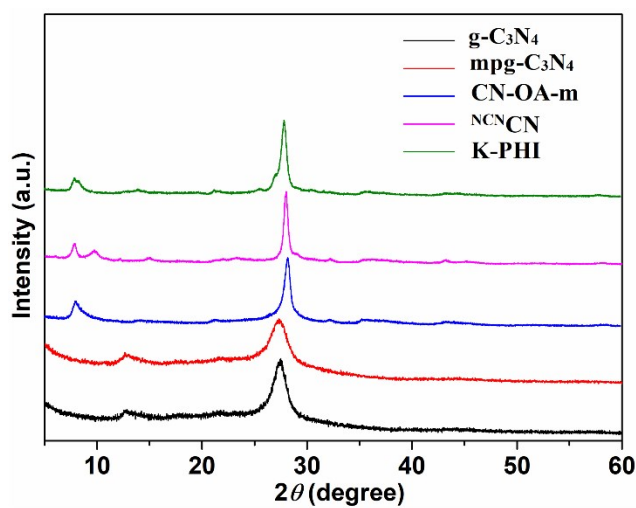


Figure S2. XRD patterns of PCN samples

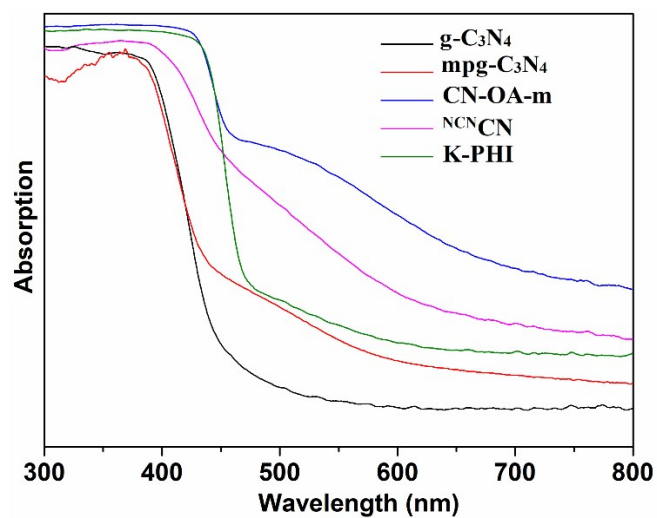


Figure S3. UV/Vis spectra of PCN samples

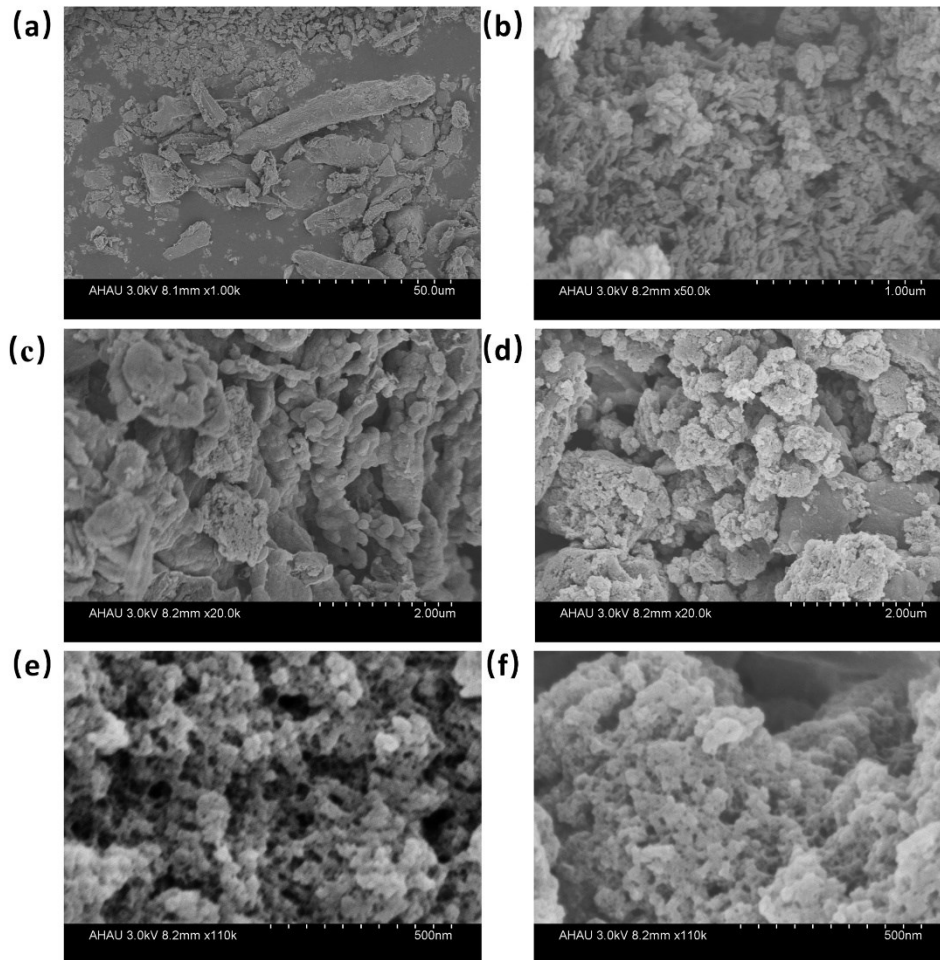


Figure S4. SEM images of g-C<sub>3</sub>N<sub>4</sub> (a), CN-OA-m (b), <sup>NCN</sup>CN (c), K-PHI (d), fresh mpg-C<sub>3</sub>N<sub>4</sub> (e) and recovered mpg-C<sub>3</sub>N<sub>4</sub> (f)

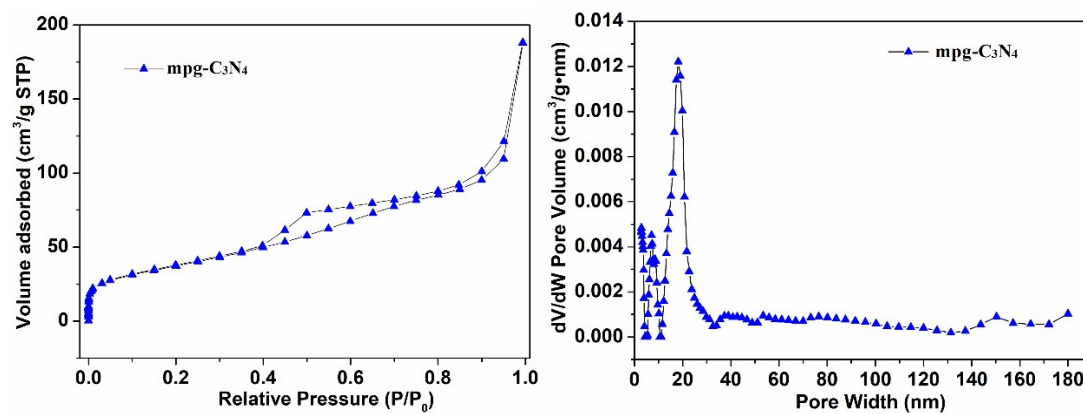


Figure S5. N<sub>2</sub> adsorption-desorption isothermal and BJH pore-size distribution curve of mpg-C<sub>3</sub>N<sub>4</sub>. The calculated BET specific surface area is 106.3 m<sup>2</sup>/g

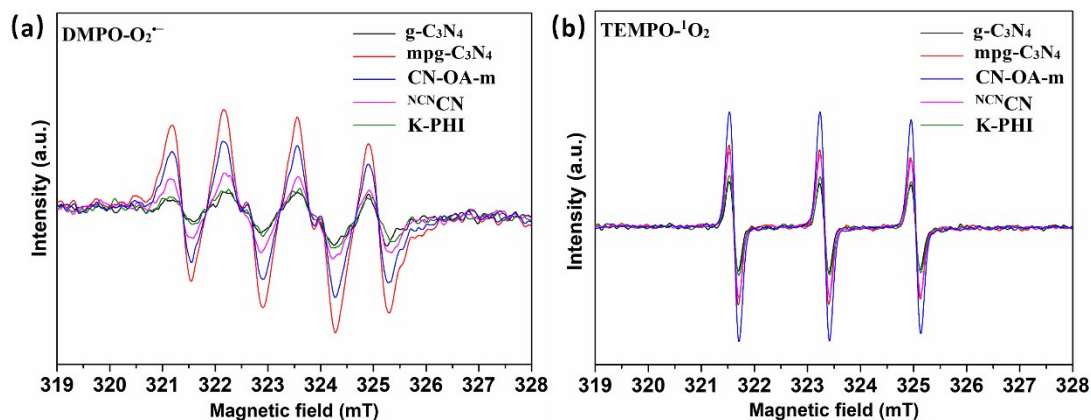


Figure S6. EPR spectra of DMPO- $\text{O}_2^{\bullet-}$  (a) and TEMPO- $^1\text{O}_2$  (b) adducts using PCN samples as photocatalyst under visible-light irradiation. Reaction condition: a solution of PCN samples (2 mg/mL) and trapping reagents ( $5.0 \times 10^{-2}$  M) in  $\text{CH}_3\text{CN}$  (1.0 mL) upon irradiation for 5 min.

## 2.2 General Procedure for the Synthesis of Products 3

The mixture of alkene **1** (0.2 mmol), ammonium thiocyanate **2** (0.4 mmol), mpg- $\text{C}_3\text{N}_4$  (10 mg) and  $\text{CH}_3\text{CN}$  (3 mL) were sequentially added to an oven-dried reaction tube equipped with a stir bar, and the tube was sealed with a Rubber-Lined Cap. The reaction mixture was sonicated for 10 min. Then the reaction tube equipped with an air balloon. After that, the reaction mixture was stirred under the irradiation of an 18 W blue LED strip at room temperature for 10 h. Upon the completion of reaction as monitored by TLC, the catalyst was filtered. Then filtrate was quenched with brine (10 mL) and extracted three times with ethyl acetate (15 mL). The combined organic extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) afforded the desired products.

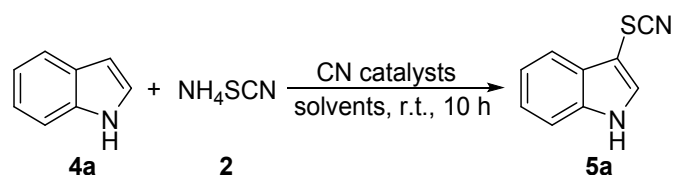
## 2.3 General Procedure for the Synthesis of Products 5

The mixture of indole **4** (0.2 mmol), ammonium thiocyanate **2** (0.4 mmol), mpg- $\text{C}_3\text{N}_4$  (10 mg) and THF (3 mL) were sequentially added to an oven-dried reaction tube equipped with a stir bar, and the tube was sealed with a Rubber-Lined Cap. The reaction mixture was sonicated for 10 min. Then the reaction tube equipped with an air balloon. After that, the reaction mixture was stirred under the irradiation of an 18 W blue LED strip at room temperature for 10 h. Upon the completion of reaction as monitored by TLC, the catalyst was filtered. Then filtrate was quenched with brine (10 mL) and

extracted three times with ethyl acetate (15 mL). The combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) afforded the desired 3-thiocyano indole products.

## 2.4 Optimization of Reaction Conditions

Table S1. Optimization of Reaction Conditions<sup>a</sup>



Entry	CN catalyst	Solvent	yield (%) <sup>b</sup>
1	g-C <sub>3</sub> N <sub>4</sub>	CH <sub>3</sub> CN	78
2	mpg-C <sub>3</sub> N <sub>4</sub>	CH <sub>3</sub> CN	88
3	CN-OA-m	CH <sub>3</sub> CN	83
4	<sup>N</sup> C <sup>N</sup> C <sup>N</sup>	CH <sub>3</sub> CN	80
5	K-PHI	CH <sub>3</sub> CN	70
6	mpg-C <sub>3</sub> N <sub>4</sub>	THF	92
7	mpg-C <sub>3</sub> N <sub>4</sub>	1,4-Dioxane	86
8	mpg-C <sub>3</sub> N <sub>4</sub>	DMF	58
9	mpg-C <sub>3</sub> N <sub>4</sub>	DCE	30
10	mpg-C <sub>3</sub> N <sub>4</sub>	H <sub>2</sub> O	trace
11	mpg-C <sub>3</sub> N <sub>4</sub>	THF/H <sub>2</sub> O (9:1)	36
12 <sup>c</sup>	mpg-C <sub>3</sub> N <sub>4</sub>	THF	41
13 <sup>d</sup>	-	THF	21
14 <sup>e</sup>	mpg-C <sub>3</sub> N <sub>4</sub>	THF	NR
15 <sup>f</sup>	mpg-C <sub>3</sub> N <sub>4</sub>	THF	NR
16 <sup>g</sup>	mpg-C <sub>3</sub> N <sub>4</sub>	THF	93

<sup>a</sup> Reaction conditions: **4a** (0.2 mmol), **2** (0.4 mmol), CN catalysts (5.0 mg), solvent (2.0 mL) in a capped reaction tube with air balloon irradiated under an 18 W blue LED strip at room temperature for 10 h. <sup>b</sup> Yields were determined by crude <sup>1</sup>H-NMR spectra using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup> KSCN was used instead of NH<sub>4</sub>SCN. <sup>d</sup> Without photocatalyst. <sup>e</sup> Without light. <sup>f</sup> Under N<sub>2</sub> atmosphere. <sup>g</sup> Under O<sub>2</sub> atmosphere. NR = No Reaction.

## 2.5 Procedure for gram-scale synthesis of **3a**

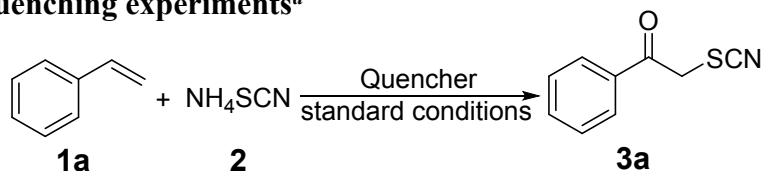
For large-scale performance: styrene **1a** (10.0 mmol), ammonium thiocyanate **2** (20.0 mmol), mpg-C<sub>3</sub>N<sub>4</sub> (150 mg) and CH<sub>3</sub>CN (50 mL) were sequentially added to an oven-dried reaction tube equipped with a stir bar, and the tube was sealed with a Rubber-Lined Cap. The reaction mixture was sonicated for 20 min. Then the reaction tube equipped with an air balloon. After that, the reaction mixture was stirred under the irradiation of an 18 W blue LED strip at room temperature for 14 h. Upon the



### 3. Active species trapping experiments

To get insight into the contribution of different active species to the reaction, radical trapping and active species trapping experiments were performed. The commonly used scavengers 2,2,6,6-tetramethylpiperidinoxy (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT), *p*-benzoquinone (BQ), carotene, ammonium oxalate (AO) and *tert*-butanol were used in the model reaction, respectively. In a typical experiment: styrene **1a** (0.2 mmol), ammonium thiocyanate **2** (0.4 mmol), mpg-C<sub>3</sub>N<sub>4</sub> (5.0 mg), quencher and CH<sub>3</sub>CN (2.0 mL) were sequentially added to an oven-dried reaction tube equipped with a stir bar, and the tube was sealed with a Rubber-Lined Cap. The reaction mixture was sonicated for 10 min. Then the reaction tube equipped with an air balloon. After that, the reaction mixture was stirred under the irradiation of an 18 W blue LED strip at room temperature for 10 h. When each round of the reactions was completed, one equivalent of 1,3,5-trimethoxybenzene was added and the mixture was stirred for 10 min. The catalyst was separated by centrifugation and the supernatant liquid phase was analyzed by <sup>1</sup>H-NMR. The results were presented in Table S3.

**Table S3. Quenching experiments<sup>a</sup>**



quencher	equivalent	Yield [%] <sup>b</sup>	notes
TEMPO	2.0	0	radical scav.
BHT	2.0	0	radical scav.
benzoquinone	1.0	4	superoxide radical anion scav.
carotene	1.0	38	singlet oxygen scav.
ammonium oxalate	1.0	56	hole scav.
<i>tert</i> -butanol	1.0	83	hydroxide radical scav.

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), mpg-C<sub>3</sub>N<sub>4</sub> (5.0 mg), quencher, CH<sub>3</sub>CN (2.0 mL) in a capped reaction tube with air balloon at room temperature for 10 h. <sup>b</sup> Yields were determined by crude <sup>1</sup>H-NMR spectra using 1,3,5-trimethoxybenzene as an internal standard.

### 4. Emission Quenching Experiments

Fluorescence quenching studies (Stern–Volmer Studies) of Emission intensities were recorded using a FluoroMax-4 spectrofluorometer (Horiba Jobin Yvon Inc.) with a 150 W xenon lamp at room temperature. The quenching follows the Stern-Volmer plots:  $I_0/I = 1 + K_{sv}[C]$ , where  $I_0$  and  $I$  ascertain the fluorescence intensity in the absence and



presence of quencher,  $[C]$  is the quencher concentration. All mpg- $C_3N_4$  solutions were measured at 350 nm and the emission intensity was collected at 450-460 nm. These wavelengths were used for further measurements. Initially, fluorescence quenching studies were carried out in air-saturated  $CH_3CN$  and oxygen-saturated  $CH_3CN$ , respectively, shows no obvious difference between the collected intensities under the above-mentioned two conditions. Thus, the blank sample was performed under air atmosphere without substrate and the received intensity was set as  $I_0$ . In a typical experiment, to a solution of mpg- $C_3N_4$  in  $CH_3CN$  (0.5 g/L) was added the appropriate amount of quencher in a quartz cuvette. The emission intensity was collected, and the results were presented in Figure S7-S8.

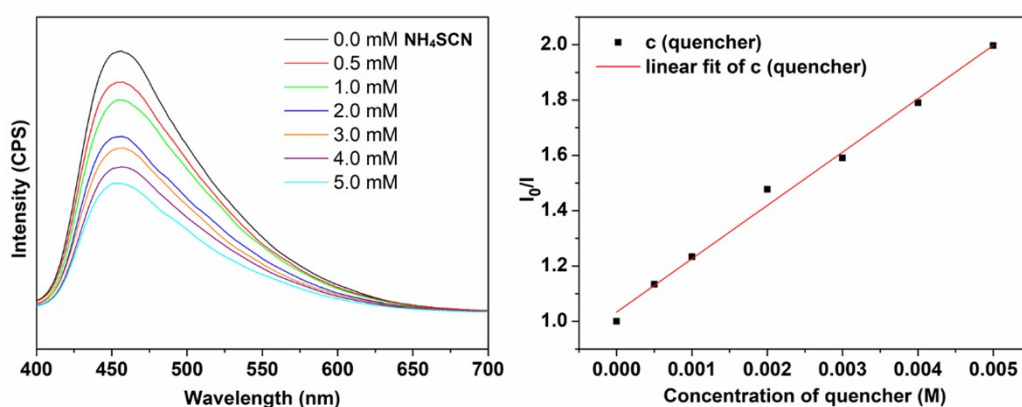


Figure S7. Fluorescence quenching of mpg- $C_3N_4$  by increasing concentration of substrate **2**. Fluorescence emission quenching of mpg- $C_3N_4$  (0.5 g/L) in acetonitrile solvent with addition of 0, 10, 20, 40, 60, 80, 100  $\mu L$  of  $NH_4SCN$  ( $10^{-1}M$ ), respectively. The mpg- $C_3N_4$  was excited at 350 nm and emission intensity monitored at 450-460 nm.

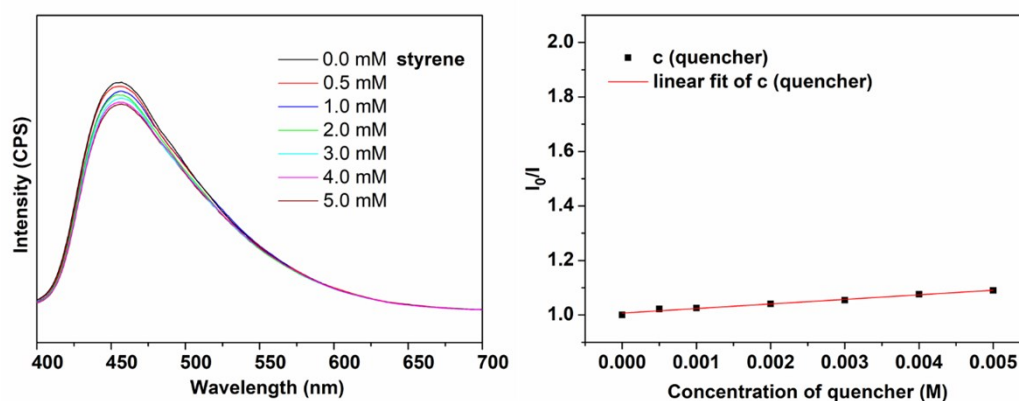
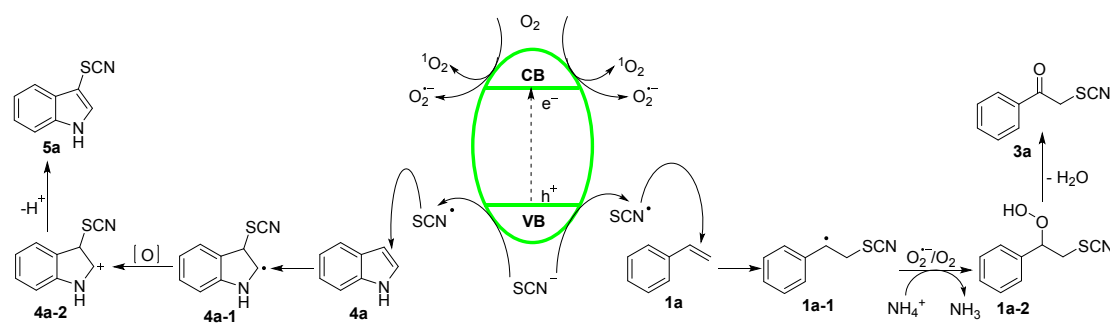


Figure S8. Fluorescence quenching of mpg- $C_3N_4$  by increasing concentration of substrate **1a**. Fluorescence emission quenching of mpg- $C_3N_4$  (0.5 g/L) in acetonitrile solvent with addition of 0, 10, 20, 40, 60, 80, 100  $\mu L$  of styrene ( $10^{-1}M$ ), respectively. The mpg- $C_3N_4$  was excited at 350 nm and emission intensity monitored at 450-460 nm.

## 5. Plausible Mechanism

We depict a working hypothesis in the Scheme S1 based on the experimental results and previously published reports<sup>5,6</sup>. Light absorption by the heterogeneous semiconductor photocatalyst mpg-C<sub>3</sub>N<sub>4</sub> results in charge separation yielding electron-hole pairs. The photoelectrons can activate O<sub>2</sub> to superoxide radical anion (O<sub>2</sub><sup>•-</sup>) or singlet oxygen (<sup>1</sup>O<sub>2</sub>). The photogenerated hole of mpg-C<sub>3</sub>N<sub>4</sub> further undergoes single electron transfer (SET) with the substrate ammonium thiocyanate (**2**) to afford the SCN radical. Adding SCN radical to alkene **1a** generates the corresponding benzyl radical **1a-1**, which is oxidized by O<sub>2</sub><sup>•-</sup> or O<sub>2</sub> and NH<sub>4</sub><sup>+</sup> to give hydroperoxide intermediate **1a-2**. Finally, the elimination of water to form the corresponding product **3a**. For C-3 thiocyanation of indoles, the reaction mechanism was similar to the aforementioned reaction of the  $\alpha$ -thiocyanato ketones.



Scheme S1. Plausible Mechanism

## 6. Measurements

### 6.1 XRD Spectroscopy

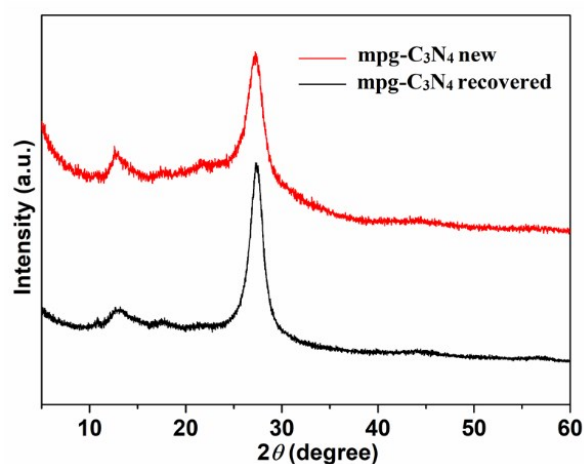


Figure S9. XRD patterns of mpg-C<sub>3</sub>N<sub>4</sub> before and after the photocatalytic reaction. The two obvious diffraction peaks at 13.2° and 27.6°, corresponds to the (100) and (002) plane, respectively.

## 6.2 FT-IR Spectroscopy

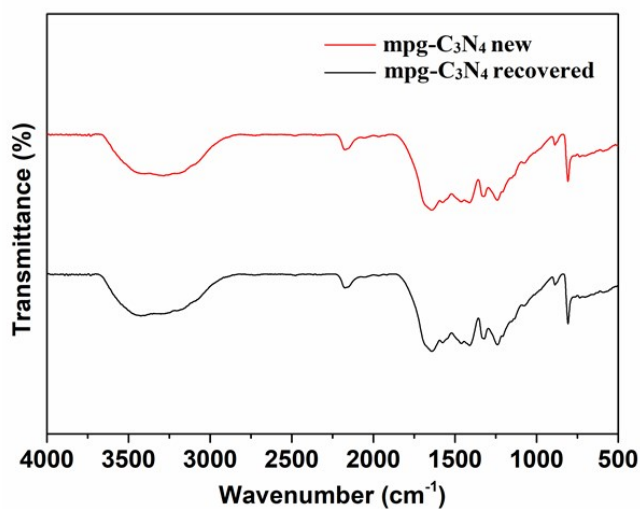


Figure S10. FTIR spectra of mpg-C<sub>3</sub>N<sub>4</sub> before and after the photocatalytic reaction. A sharp peak at 810 cm<sup>-1</sup> is attributed to the breathing vibration of triazine units, while the fingerprint peaks in the region from 900 cm<sup>-1</sup> to 1700 cm<sup>-1</sup> corresponded to the typical stretching vibration of CN heterocycles. The weak peak at around 2170 cm<sup>-1</sup> associated with tri-bond cyano groups C≡N in the synthesized material is usually attributed to incomplete polymerization of the precursor. The broad peak around 3000-3500 cm<sup>-1</sup>, which is assigned to the terminal amino groups.

## 6.3 UV-Vis Absorption Spectroscopy

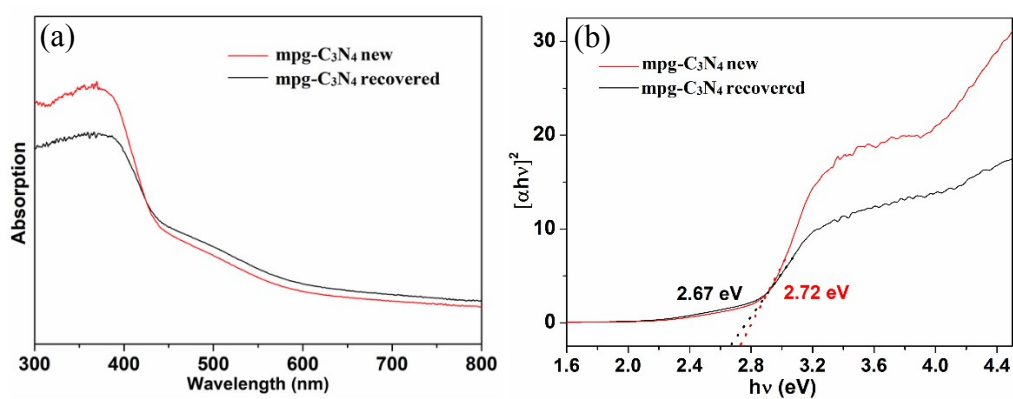
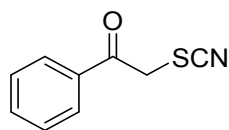


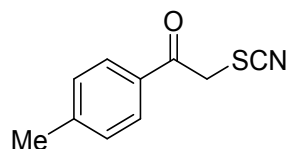
Figure S11. UV-vis absorption spectra (a) and the Tauc Plot (b) of mpg-C<sub>3</sub>N<sub>4</sub> before and after the photocatalytic reaction. Selected data were fit linearly (red and black lines) to yield a band gap of 2.72 eV and 2.67 eV for fresh mpg-C<sub>3</sub>N<sub>4</sub> and recovered mpg-C<sub>3</sub>N<sub>4</sub>, respectively.

## 7. Characterization Data of the Products



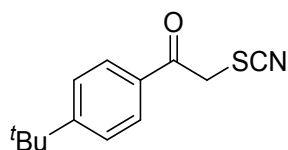
### 1-Phenyl-2-thiocyanatoethan-1-one (3a)<sup>5</sup>

Yellow liquid (Yield 86%, 30.5 mg), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.94 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 4.74 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 190.8, 134.8, 134.0, 129.2, 128.4, 111.8, 43.0.



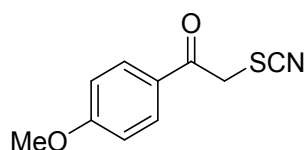
### 2-Thiocyanato-1-(*p*-tolyl)ethan-1-one (3b)<sup>5</sup>

Yellow liquid (Yield 85%, 23.5 mg), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.84 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 4.72 (s, 2H), 2.45 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 190.4, 146.1, 131.5, 129.8, 128.6, 111.9, 43.0, 21.8.



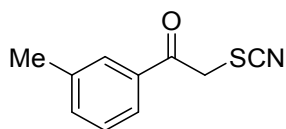
### 1-(4-(*tert*-Butyl)phenyl)-2-thiocyanatoethan-1-one (3c)<sup>5</sup>

White solid (Yield 80%, 37.3 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.87 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 4.72 (s, 2H), 1.35 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 190.4, 159.0, 131.5, 128.5, 126.1, 111.9, 42.9, 35.4, 31.0.



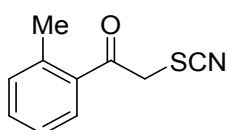
### 1-(4-Methoxyphenyl)-2-thiocyanatoethan-1-one (3d)<sup>5</sup>

White solid (Yield 75%, 31.1 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.91 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.70 (s, 2H), 3.90 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 189.1, 164.8, 130.9, 127.0, 114.4, 112.0, 55.6, 42.8.



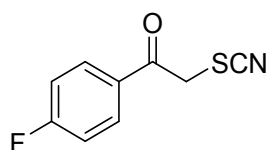
**2-Thiocyanato-1-(m-tolyl)ethan-1-one (3e)<sup>5</sup>**

Yellow liquid (Yield 77%, 29.5 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.74 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 4.72 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 190.9, 139.1, 135.5, 134.0, 128.9, 128.9, 125.6, 111.8, 42.9, 21.2.



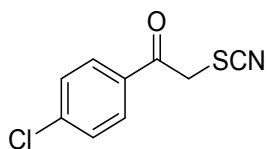
**2-Thiocyanato-1-(o-tolyl)ethan-1-one (3f)<sup>5</sup>**

Yellow liquid (Yield 69%, 26.4 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.69 (d, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.35–7.32 (m, 2H), 4.70 (s, 2H), 2.56 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 193.1, 140.3, 133.5, 133.4, 132.8, 129.5, 126.2, 111.8, 44.8, 21.8.



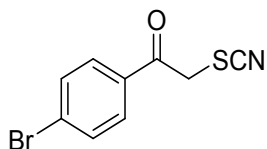
**1-(4-Fluorophenyl)-2-thiocyanatoethan-1-one (3g)<sup>5</sup>**

White solid (Yield 81%, 31.6 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.00–7.97 (m, 2H), 7.23–7.19 (m, 2H), 4.71 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 189.3, 166.6 (d, *J* = 256.5 Hz), 131.28 (d, *J* = 10.5 Hz), 130.4 (d, *J* = 3.0 Hz), 116.5 (d, *J* = 22.5 Hz), 111.6, 42.7.



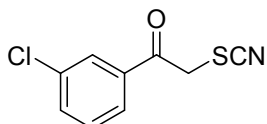
**1-(4-Chlorophenyl)-2-thiocyanatoethan-1-one (3h)<sup>5</sup>**

White solid (Yield 77%, 32.6 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.88 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 4.69 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 189.7, 141.5, 132.3, 129.8, 129.6, 111.4, 42.5.



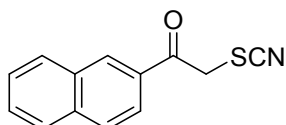
**1-(4-Bromophenyl)-2-thiocyanatoethan-1-one (3i)<sup>5</sup>**

White solid (Yield 79%, 40.5 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.80 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 4.68 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 189.9, 132.7, 132.6, 130.3, 129.8, 111.4, 42.5.



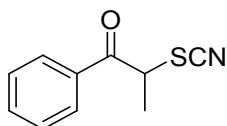
**1-(3-Chlorophenyl)-2-thiocyanatoethan-1-one (3j)<sup>5</sup>**

Yellow liquid (Yield 72%, 30.5 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 9.92 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 4.69 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 189.7, 135.6, 135.5, 134.7, 130.5, 128.5, 126.5, 111.3, 42.5.



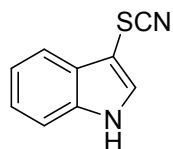
**1-(Naphthalen-1-yl)-2-thiocyanatoethan-1-one (3k)<sup>5</sup>**

White solid (Yield 74%, 33.6 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.45 (s, 1H), 8.0-7.94 (m, 3H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 4.88 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 190.7, 136.2, 132.3, 131.3, 130.8, 129.7, 129.5, 129.2, 128.0, 127.4, 123.3, 111.8, 43.0.



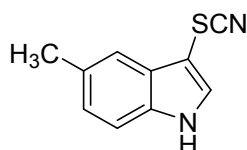
**1-Phenyl-2-thiocyanatopropan-1-one (3l)<sup>5</sup>**

Yellow liquid (Yield 68%, 26.0 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.93 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 5.08 (q, *J* = 7.2 Hz, 1H), 1.86(d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 194.7, 134.5, 133.3, 129.2, 128.8, 111.3, 49.8, 19.8.



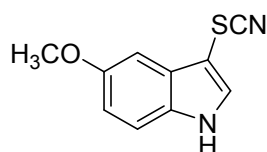
### 3-Thiocyanato-1H-indole (5a)<sup>6</sup>

White solid (Yield 92%, 32.1 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.84 (s, 1H), 7.81–7.80 (m, 1H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.41–7.39 (m, 1H), 7.33–7.30 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 136.0, 131.1, 127.6, 123.7, 121.8, 118.5, 112.2, 112.1, 91.7.



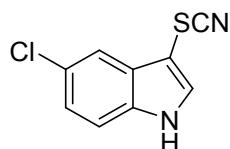
### 5-Methyl-3-thiocyanato-1H-indole (5b)<sup>6</sup>

White solid (Yield 91%, 34.3 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.70 (s, 1H), 7.58 (s, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 134.3, 131.4, 131.0, 127.8, 125.4, 118.2, 112.2, 111.8, 91.1, 21.5.



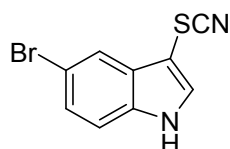
### 5-Methoxy-3-thiocyanato-1H-indole (5c)<sup>6</sup>

Yellow solid (Yield 93%, 38.0 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.71 (s, 1H), 7.45 (d, *J* = 3.0 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.95 (dd, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H), 3.91 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 155.7, 131.4, 130.8, 128.5, 114.5, 113.0, 112.0, 99.8, 91.5, 55.8.



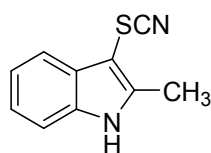
### 5-Chloro-3-thiocyanato-1H-indole (5d)<sup>6</sup>

White solid (Yield 89%, 37.1 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.76 (s, 1H), 7.76 (s, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.26 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 134.4, 132.2, 128.8, 128.0, 124.5, 118.4, 113.2, 111.4, 92.4.



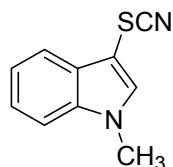
**5-Bromo-3-thiocyanato-1H-indole (5e)<sup>6</sup>**

White solid (Yield 87%, 44.0 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.81 (s, 1H), 7.92 (s, 1H), 7.52 (d, *J* = 3.0 Hz, 1H), 7.39 (dd, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 1.8 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 134.7, 132.1, 129.4, 127.0, 121.4, 115.4, 113.6, 111.5, 92.1.



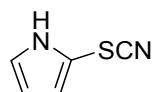
**2-Methyl-3-thiocyanato-1H-indole (5f)<sup>6</sup>**

White solid (Yield 88%, 33.1 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.60 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.26-7.21 (m, 2H), 2.49 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 142.0, 135.1, 128.6, 122.9, 121.5, 118.0, 112.1, 111.2, 88.8, 12.0.



**1-Methyl-3-thiocyanato-1H-indole (5g)<sup>6</sup>**

White solid (Yield 90%, 33.9 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.81 (d, *J* = 7.2 Hz, 1H), 7.38-7.35 (m, 3H), 7.34-7.32 (m, 1H), 3.80 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 137.1, 135.0, 128.4, 123.4, 121.5, 118.9, 111.8, 110.2, 89.8, 33.3.



**2-Thiocyanato-1H-pyrrole (5h)<sup>7</sup>**

Colorless liquid (Yield 85%, 21.1 mg), <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.75 (s, 1H), 7.01-7.00 (m, 1H), 6.66-6.65 (m, 1H), 6.30-6.28 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 124.3, 120.2, 111.3, 110.5, 103.2.



## 8. References

1. X. Wang, K. Maeda, X. Chen, K. Takanahe, K. Domen, Y. Hou, X. Fu and M. Antonietti, *J. Am. Chem. Soc.*, 2009, **131**, 1680–1681.
2. G. Zhang, G. Li, Z. Lan, L. Lin, A. Savateev, T. Heil, S. Zafeiratos, X. Wang and M. Antonietti, *Angew. Chem., Int. Ed.*, 2017, **56**, 13445–13449.
3. V. W. H. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum and B. V. Lotsch, *Nat. Commun.*, 2016, **7**, 12165.
4. D. Dontsova, S. Pronkin, M. Wehle, Z. Chen, C. Fettkenhauer, G. Clavel and M. Antonietti, *Chem. Mater.*, 2015, **27**, 5170–5179.
5. G. Nan and H. Yue, *Synlett*, 2018, **29**, 1340–1345.
6. W. Zhang, J. Tang, W. Yu, Q. Huang, Y. Fu, G. Kuang, C. Pan and G. Yu, *ACS Catal.*, 2018, **8**, 8084–8091.
7. M. Koohgard, Z. Hosseinpour, A. M. Sarvestani and M. Hosseini-Sarvari, *Catal. Sci. Technol.*, 2020, **10**, 1401–1407.

## 9. Copies of products NMR Spectra

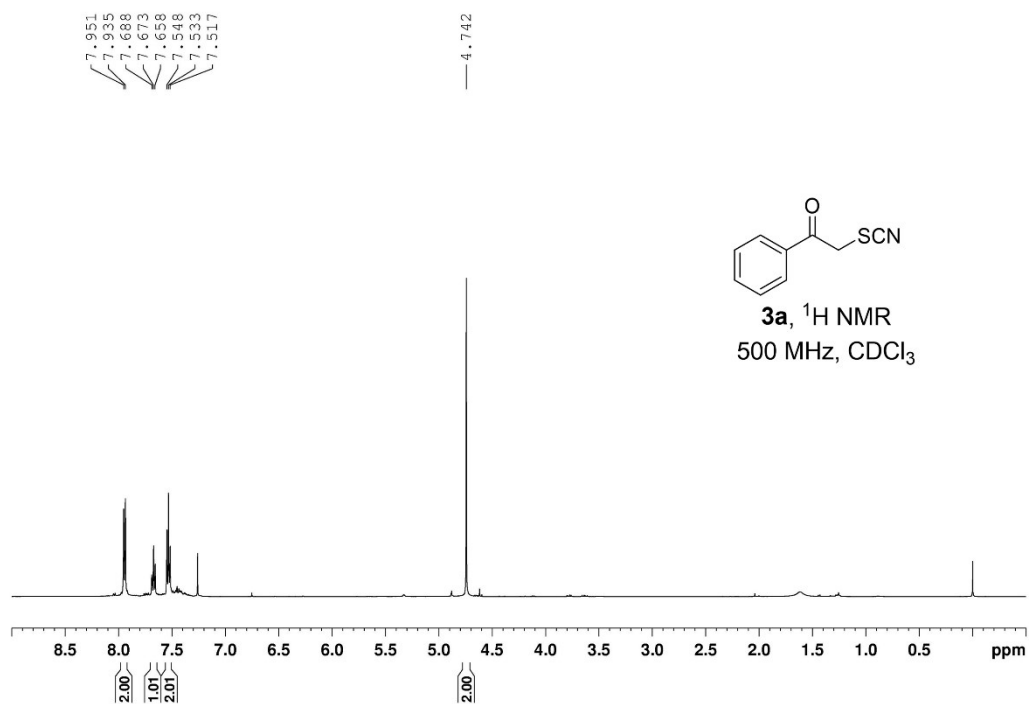


Figure S12. The <sup>1</sup>H NMR spectrum of **3a**

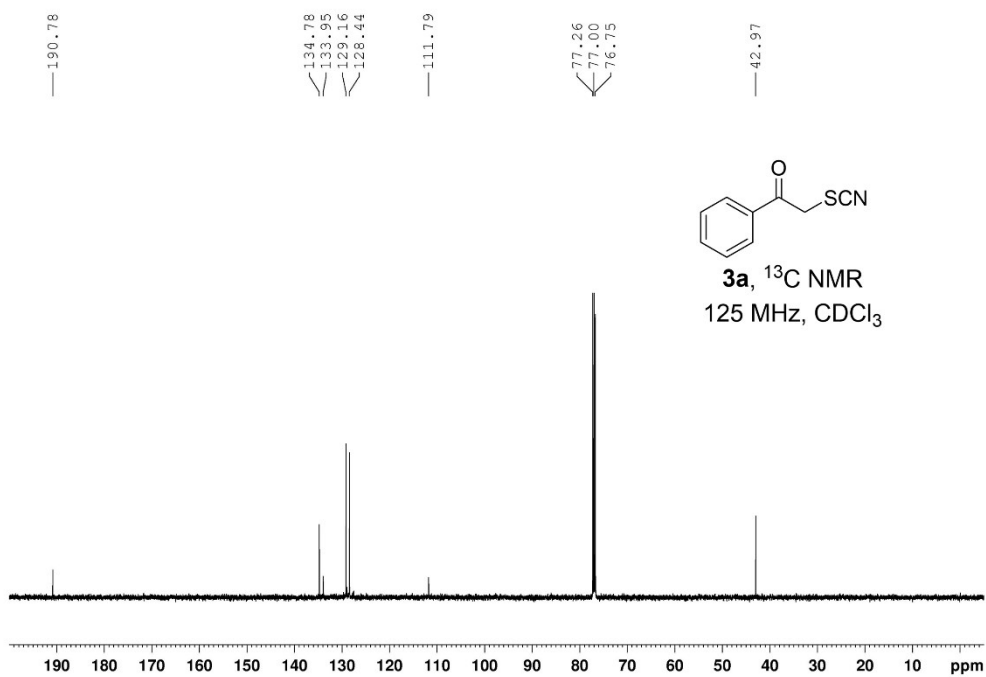


Figure S13. The <sup>13</sup>C NMR spectrum of **3a**

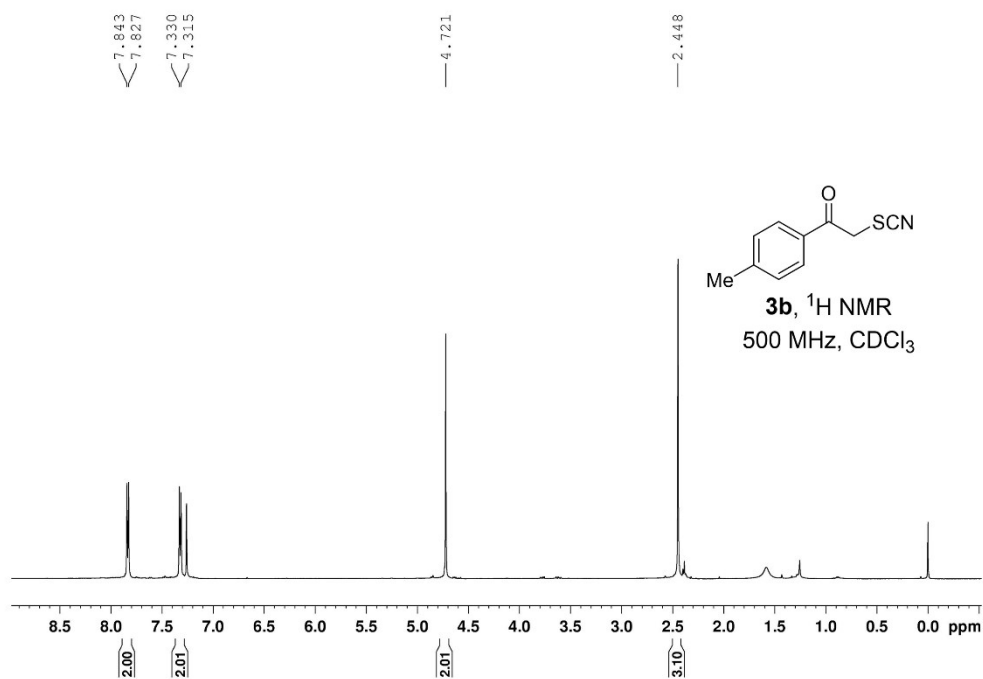


Figure S14. The  $^1\text{H NMR}$  spectrum of **3b**

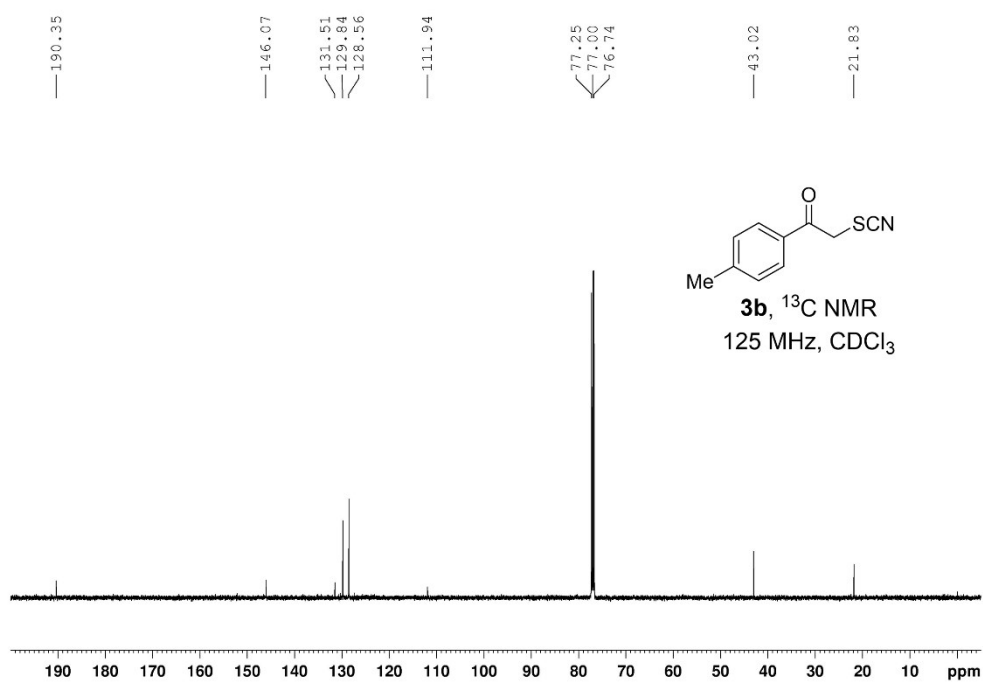


Figure S15. The  $^{13}\text{C NMR}$  spectrum of **3b**

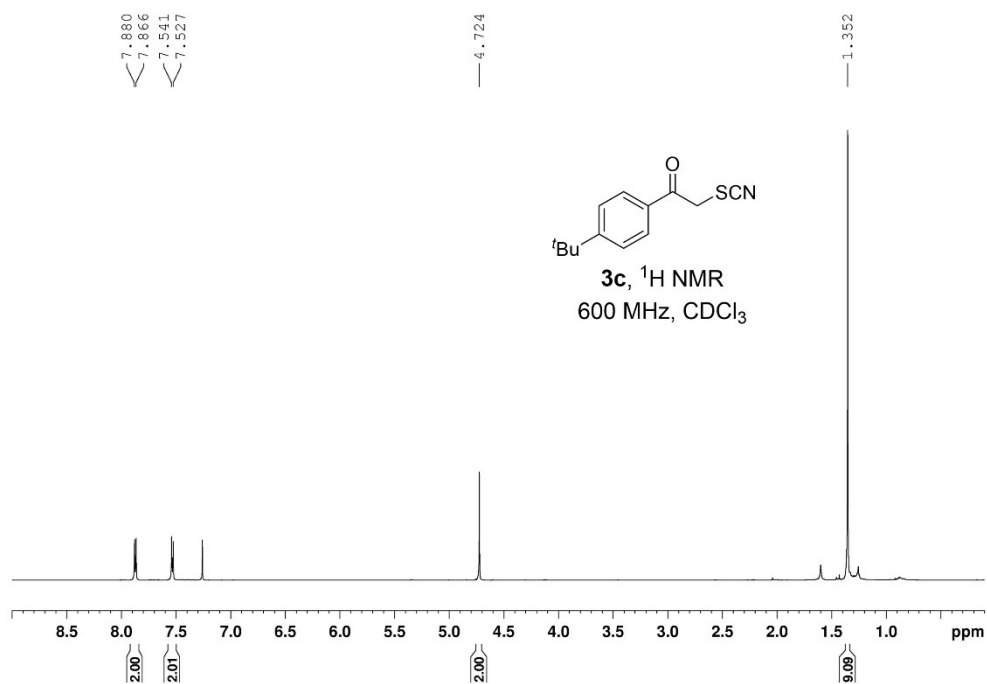


Figure S16. The  $^1\text{H NMR}$  spectrum of **3c**

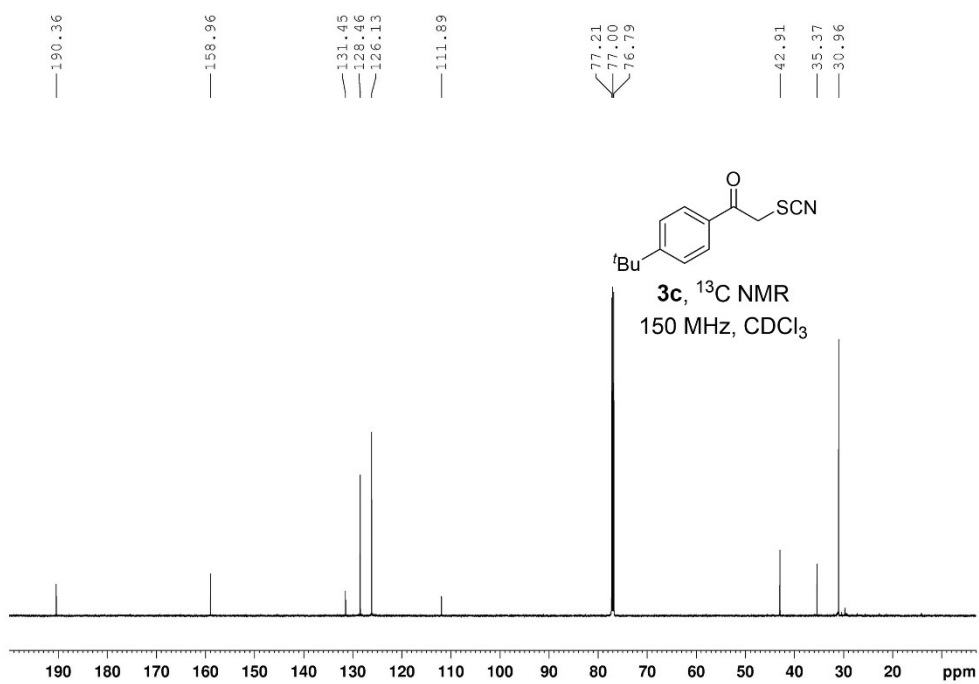


Figure S17. The  $^{13}\text{C NMR}$  spectrum of **3c**

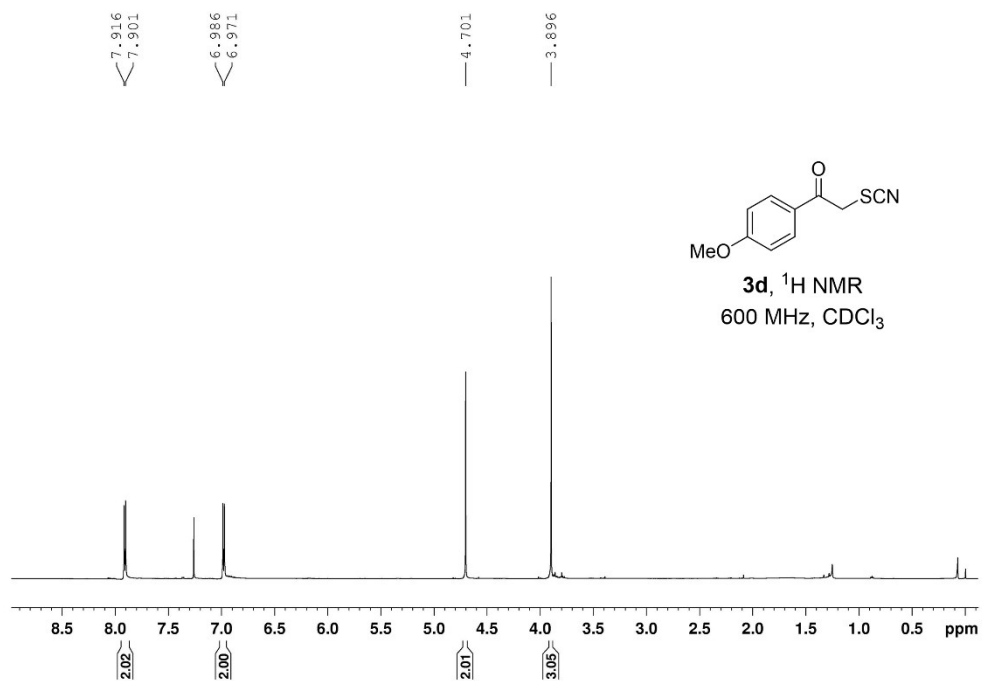


Figure S18. The  $^1\text{H}$  NMR spectrum of **3d**

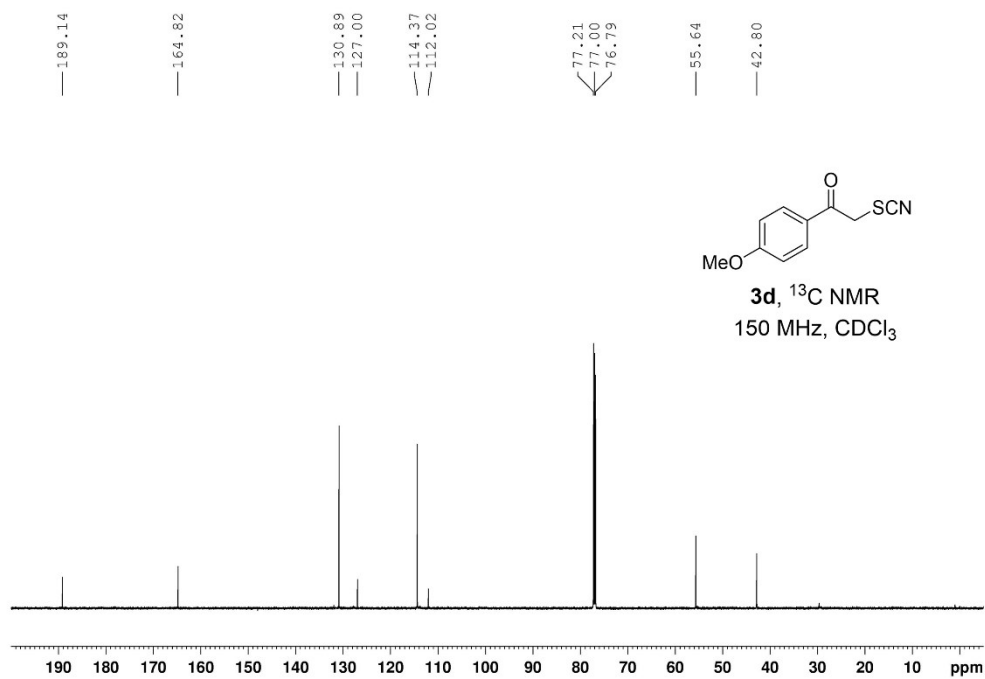


Figure S19. The  $^{13}\text{C}$  NMR spectrum of **3d**

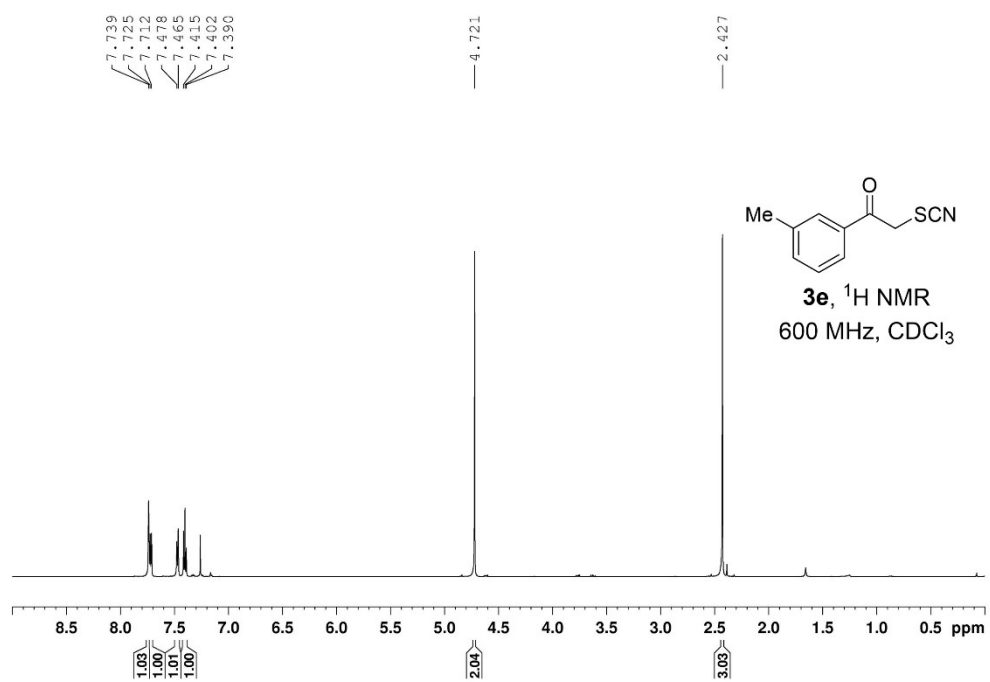


Figure S20. The  $^1\text{H}$  NMR spectrum of **3e**

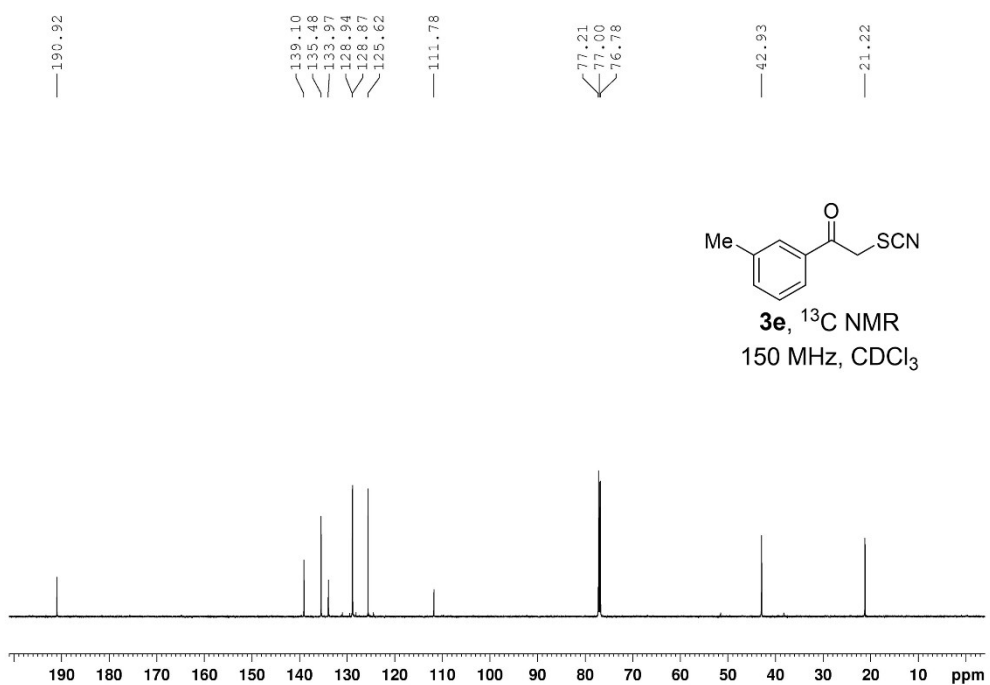


Figure S21. The  $^{13}\text{C}$  NMR spectrum of **3e**

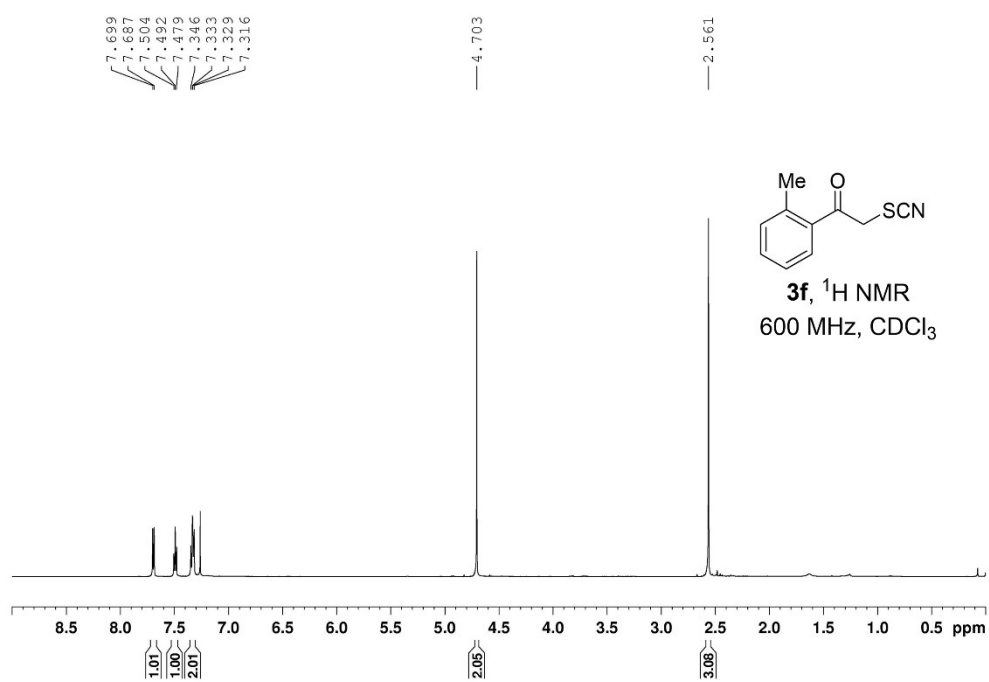


Figure S22. The  $^1\text{H}$  NMR spectrum of **3f**

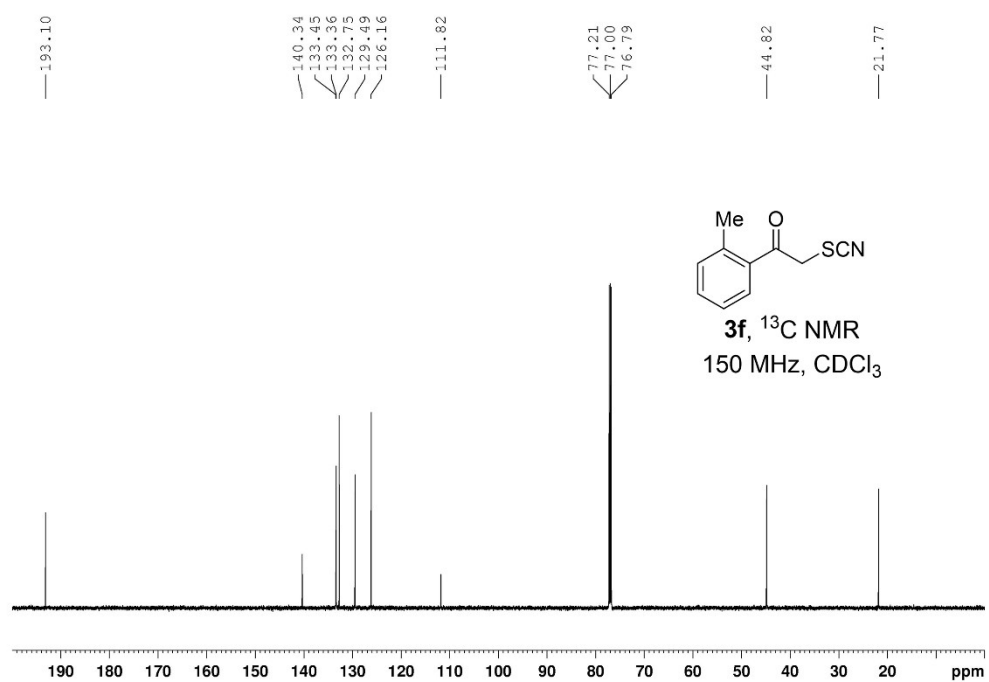


Figure S23. The  $^{13}\text{C}$  NMR spectrum of **3f**

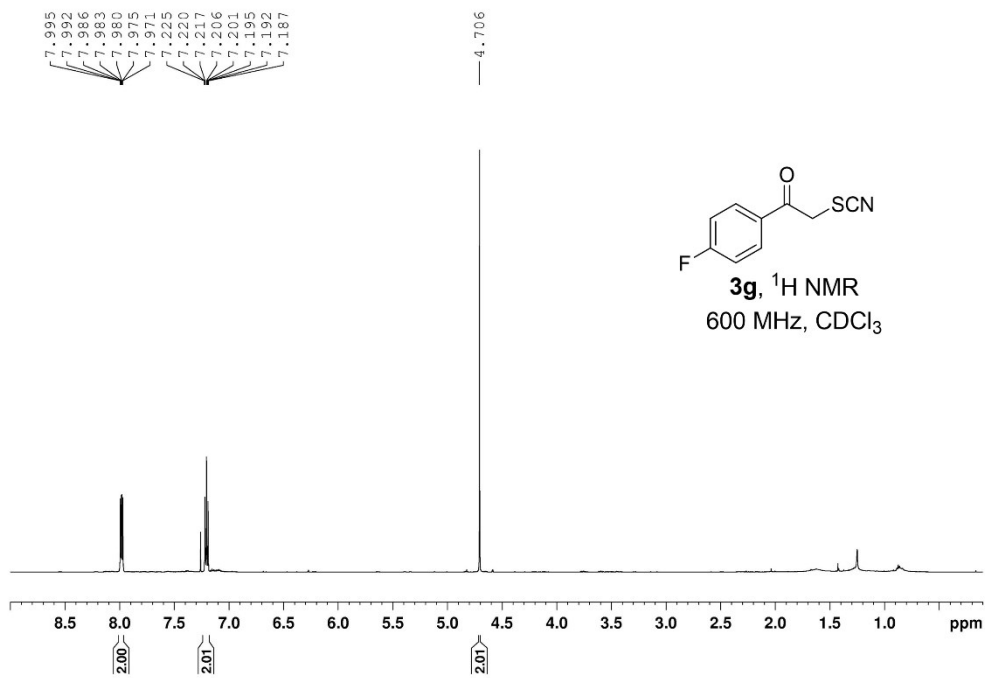


Figure S24. The  $^1\text{H}$  NMR spectrum of **3g**

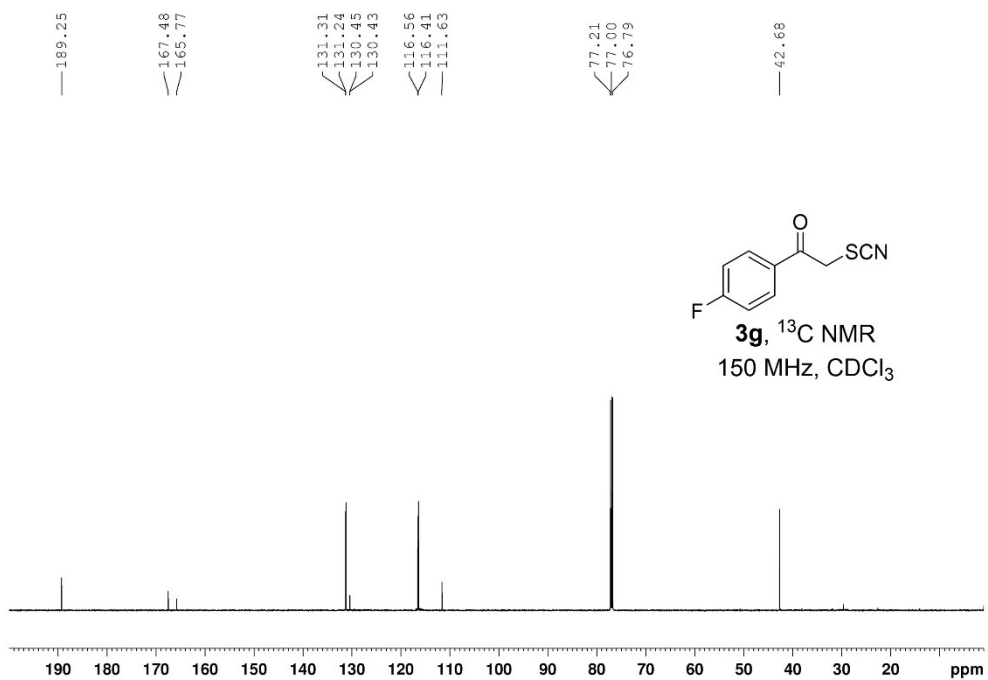


Figure S25. The  $^{13}\text{C}$  NMR spectrum of **3g**



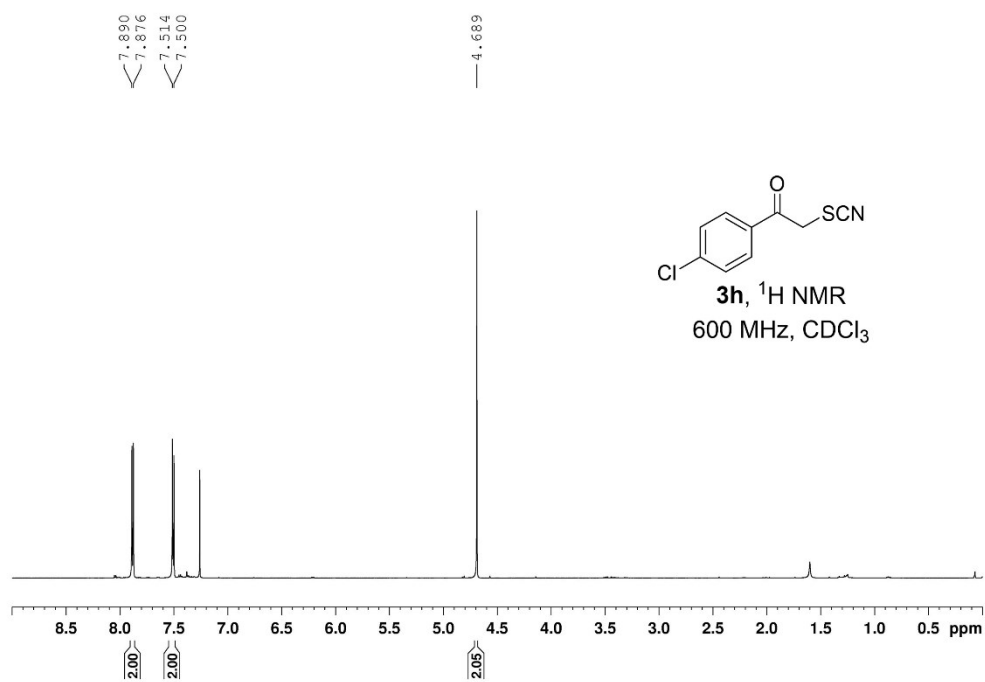


Figure S26. The  $^1\text{H NMR}$  spectrum of **3h**

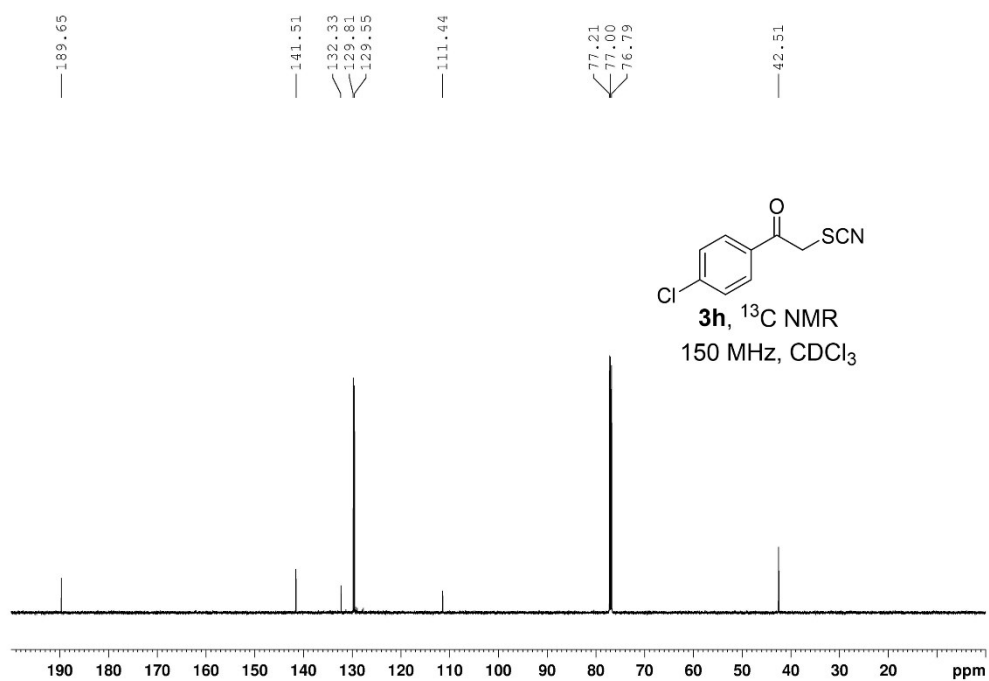


Figure S27. The  $^{13}\text{C NMR}$  spectrum of **3h**

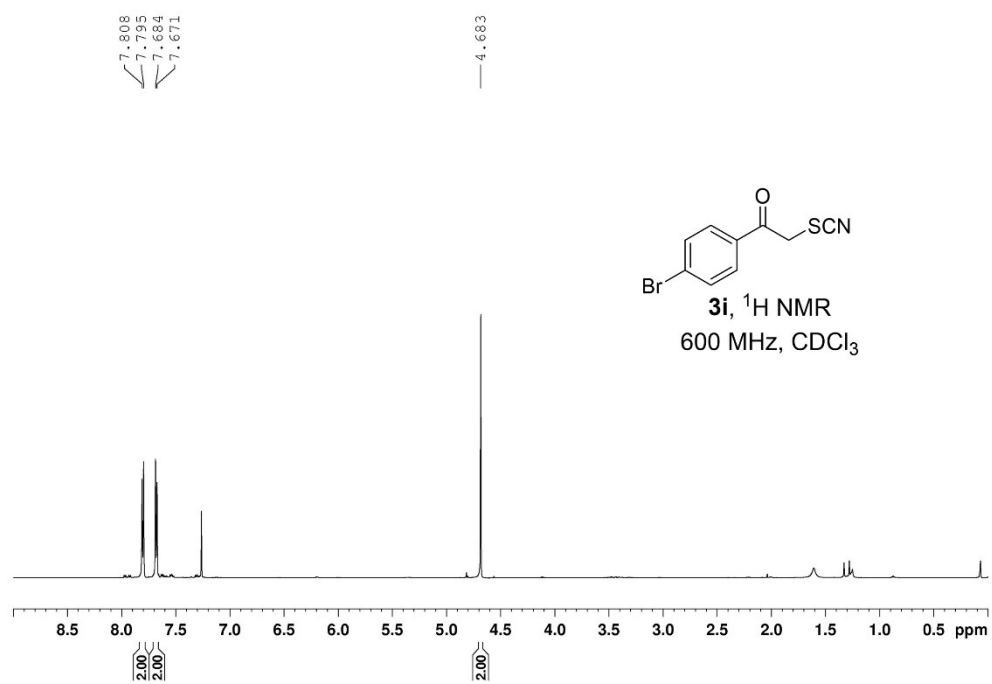


Figure S28. The  $^1\text{H}$  NMR spectrum of **3i**

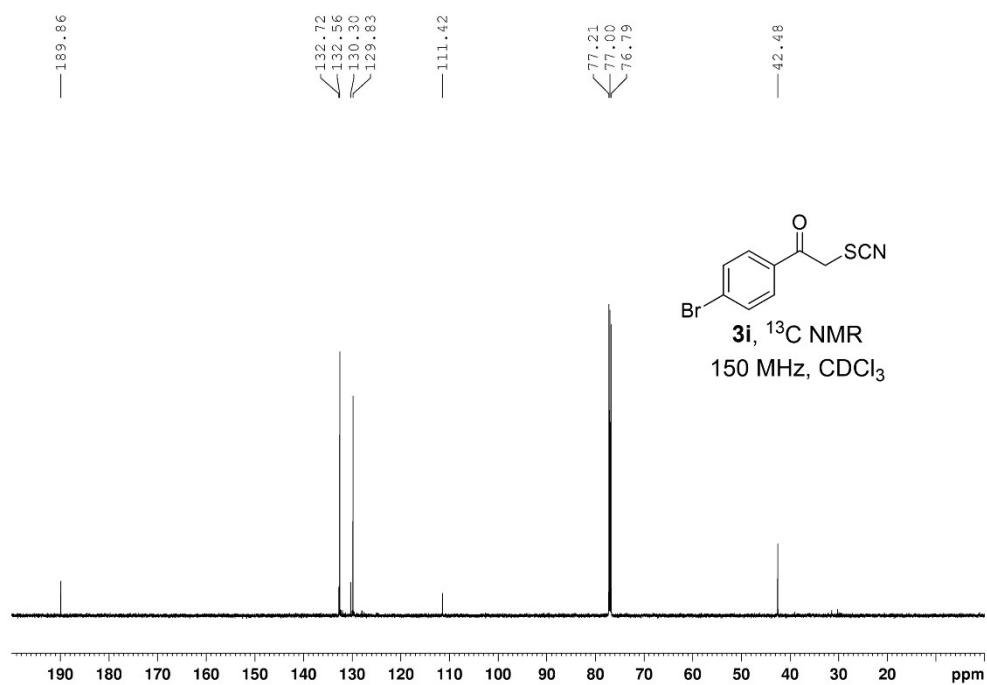


Figure S29. The  $^{13}\text{C}$  NMR spectrum of **3i**

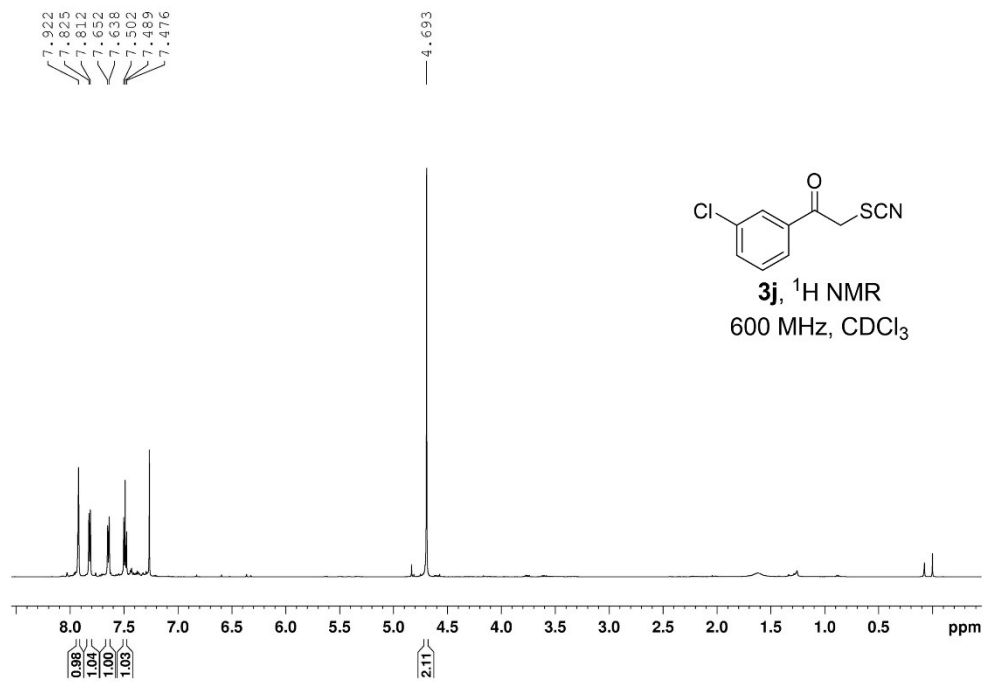


Figure S30. The  $^1\text{H}$  NMR spectrum of **3j**

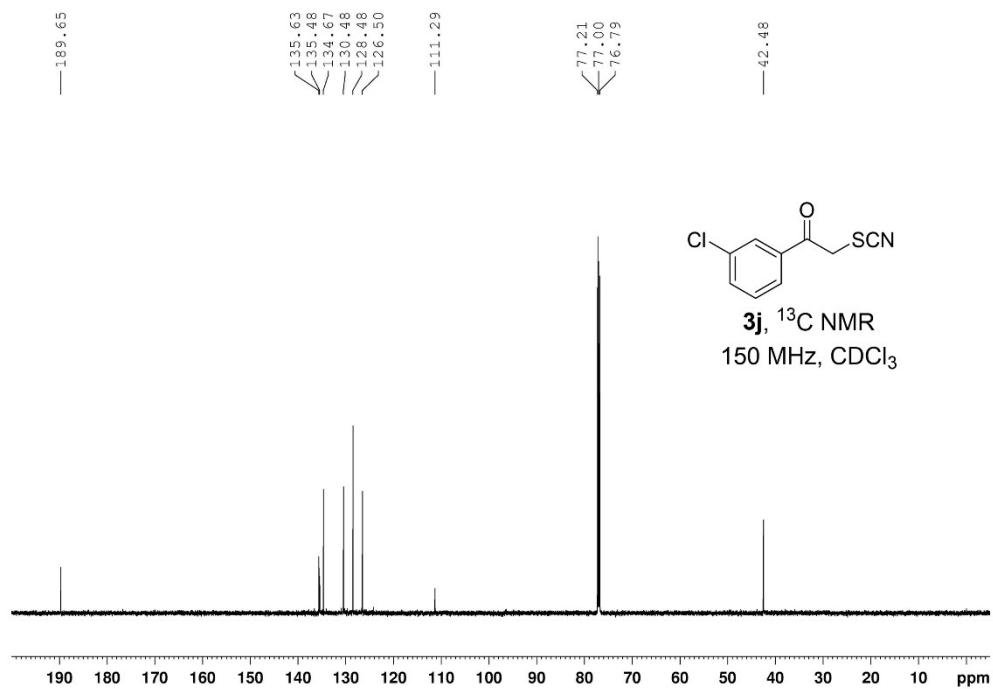


Figure S31. The  $^{13}\text{C}$  NMR spectrum of **3j**

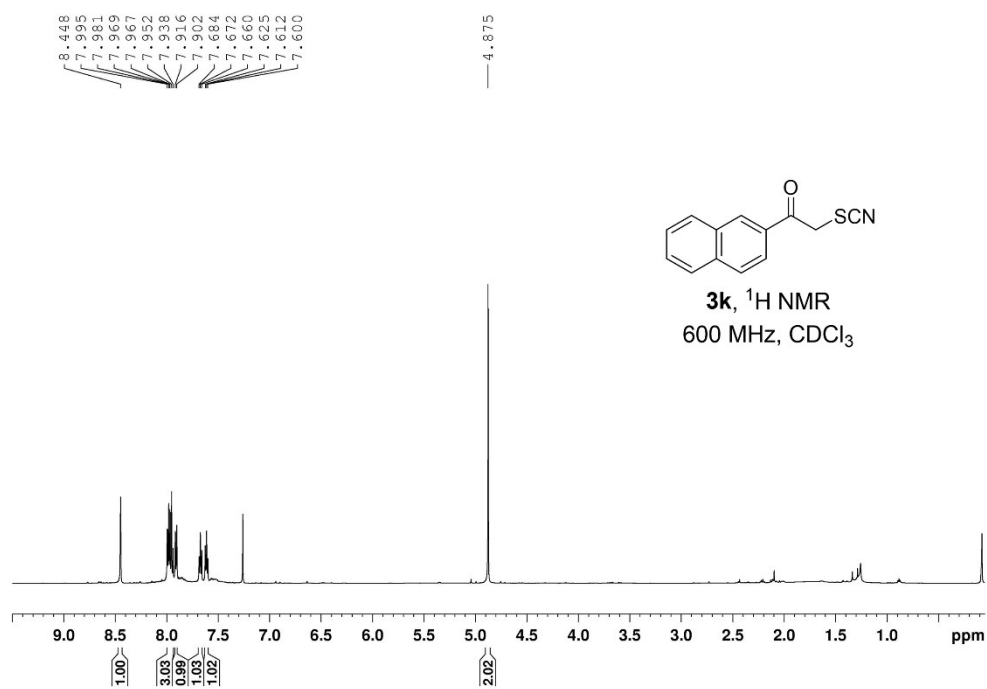


Figure S32. The  $^1\text{H}$  NMR spectrum of **3k**

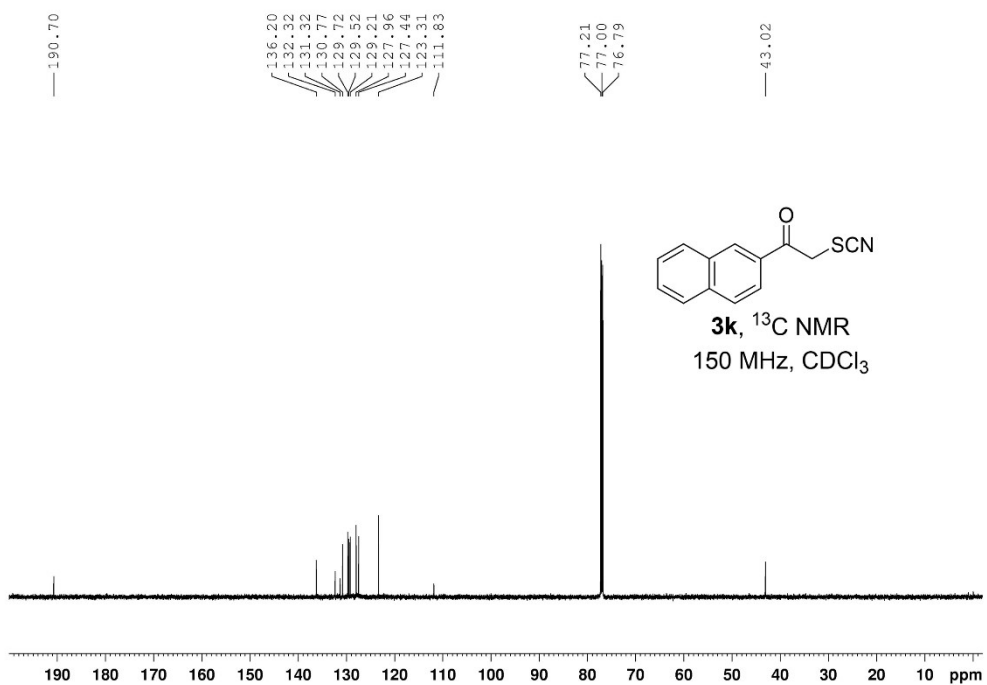


Figure S33. The  $^{13}\text{C}$  NMR spectrum of **3k**

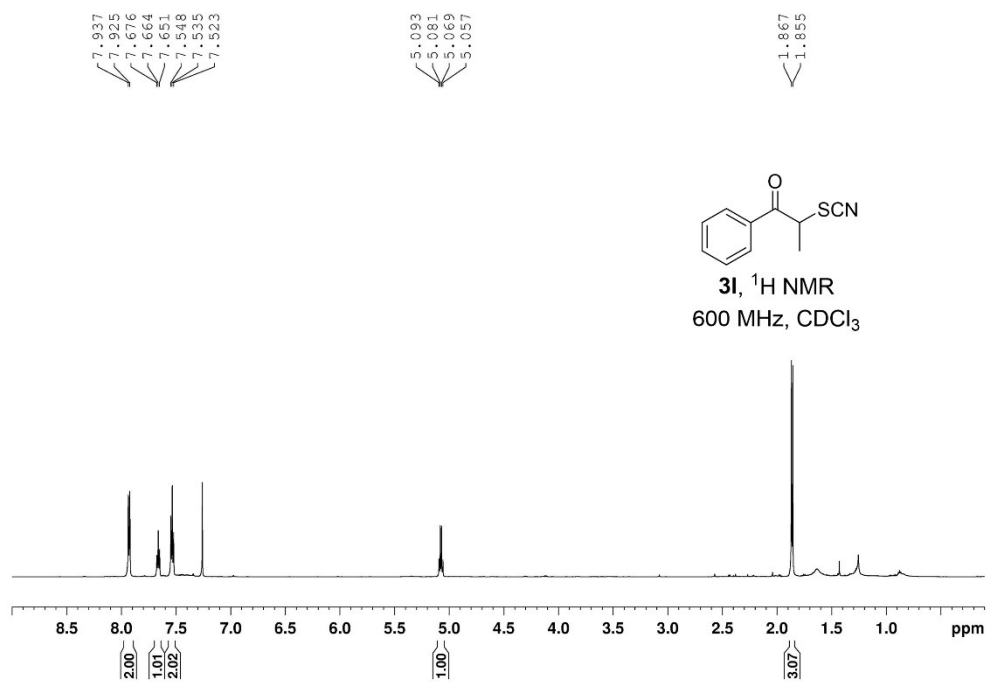


Figure S34. The  $^1\text{H}$  NMR spectrum of **3I**

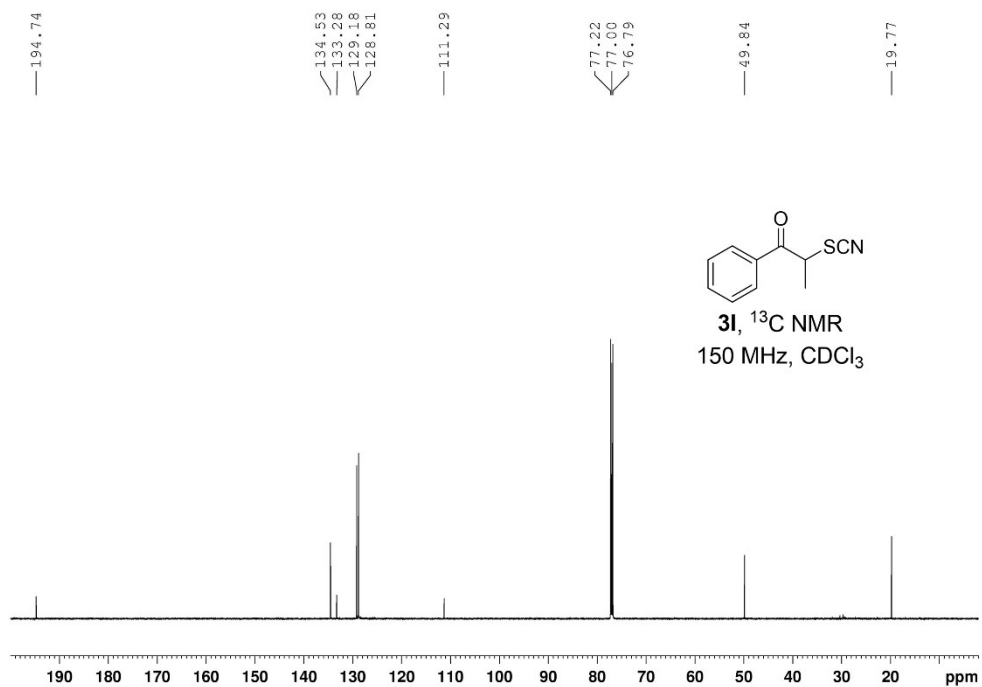


Figure S35. The  $^{13}\text{C}$  NMR spectrum of **3I**

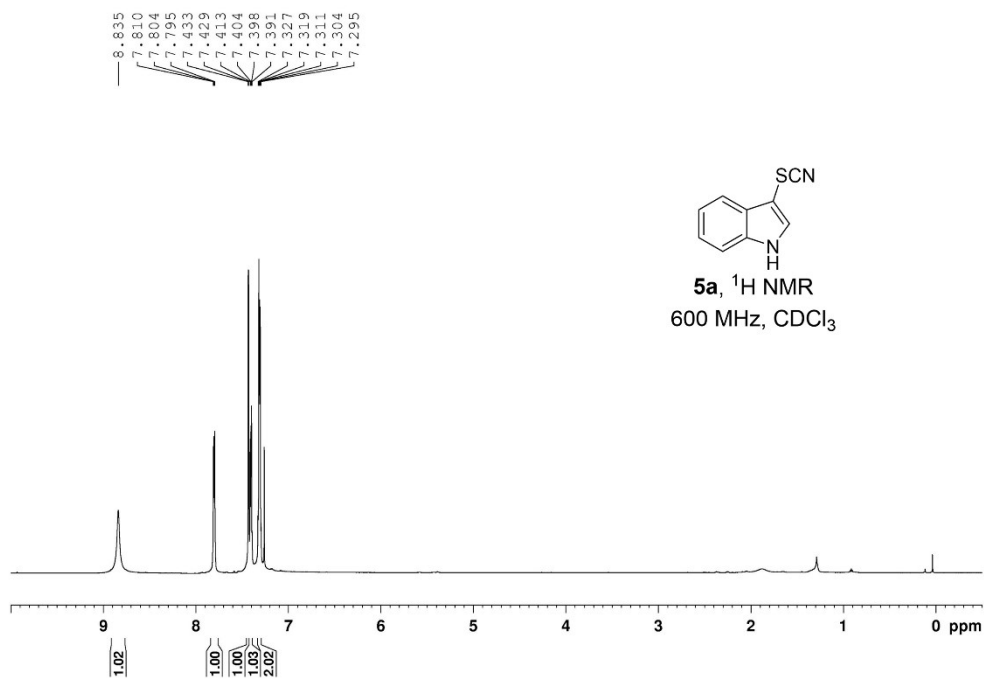


Figure S36. The  $^1\text{H}$  NMR spectrum of **5a**

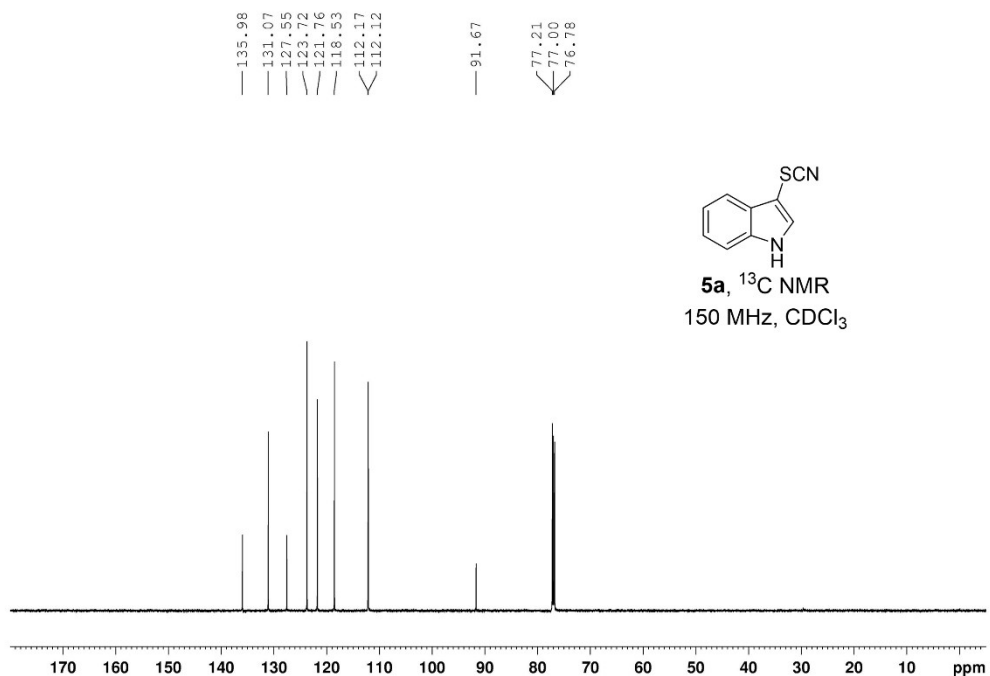


Figure S37. The  $^{13}\text{C}$  NMR spectrum of **5a**

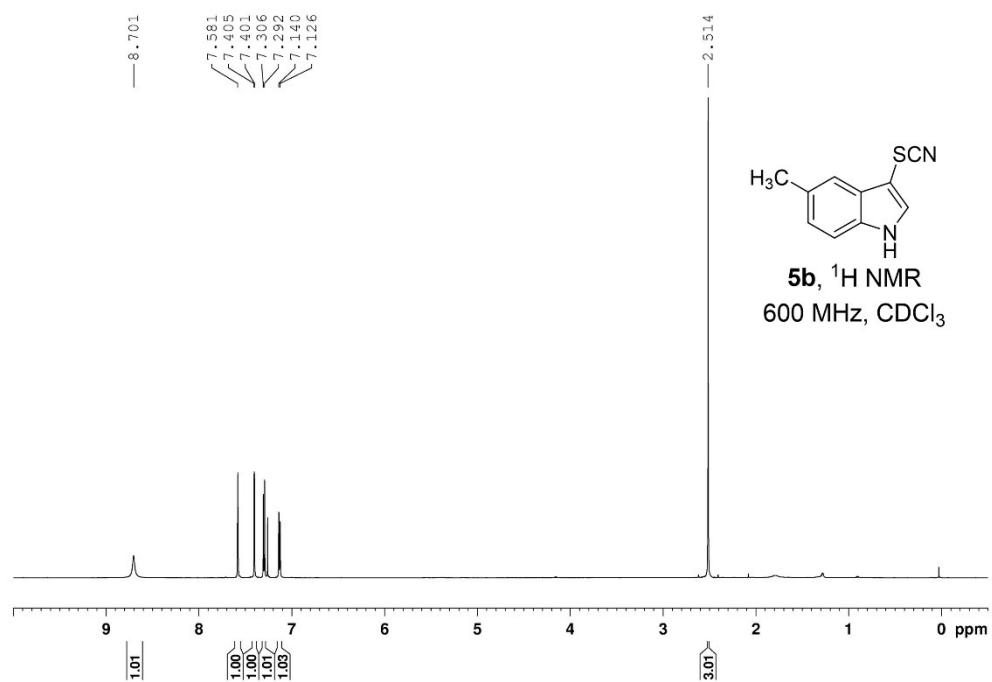


Figure S38. The  $^1\text{H}$  NMR spectrum of **5b**

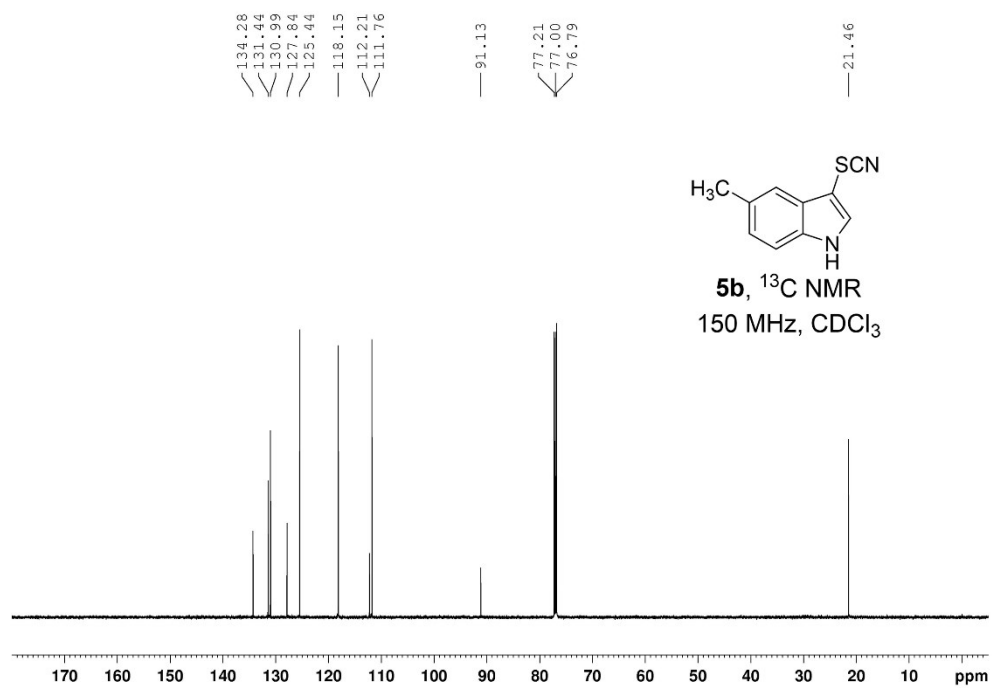


Figure S39. The  $^{13}\text{C}$  NMR spectrum of **5b**

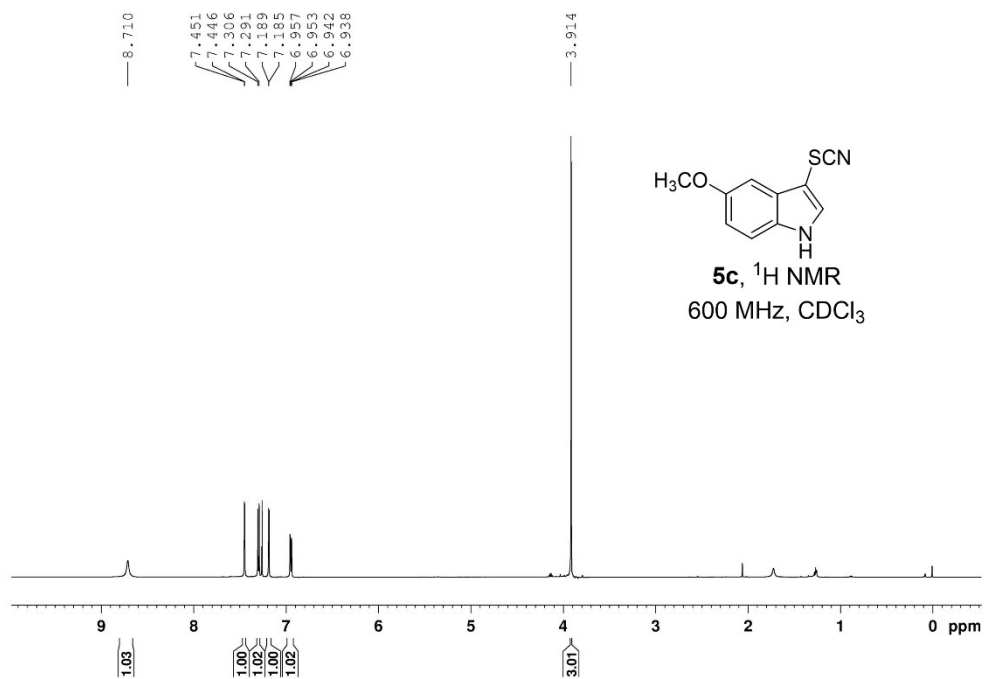


Figure S40. The  $^1\text{H}$  NMR spectrum of **5c**

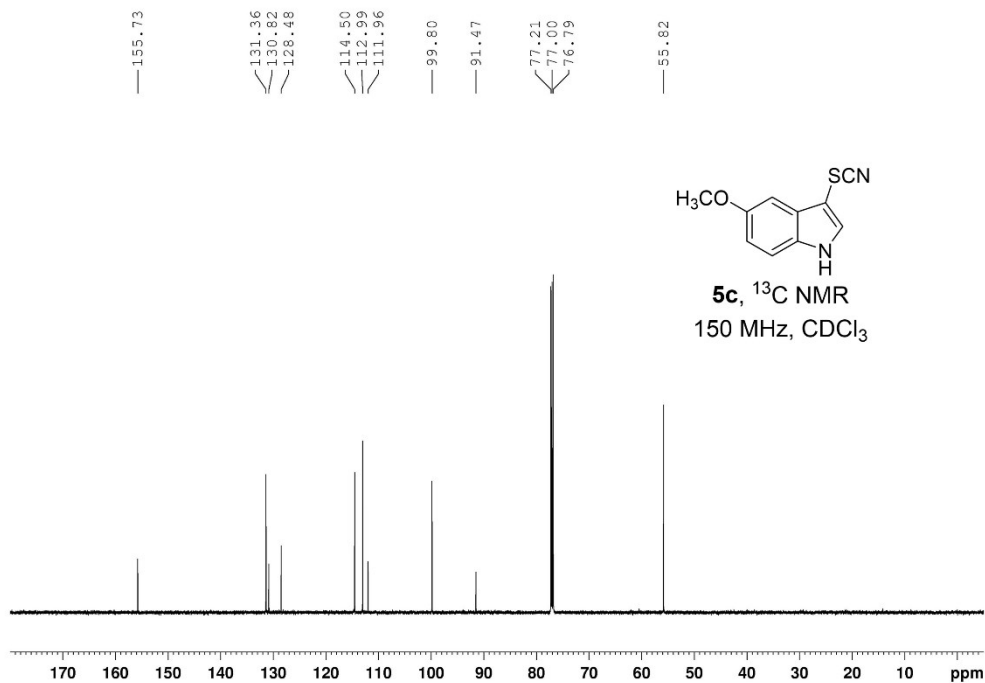


Figure S41. The  $^{13}\text{C}$  NMR spectrum of **5c**



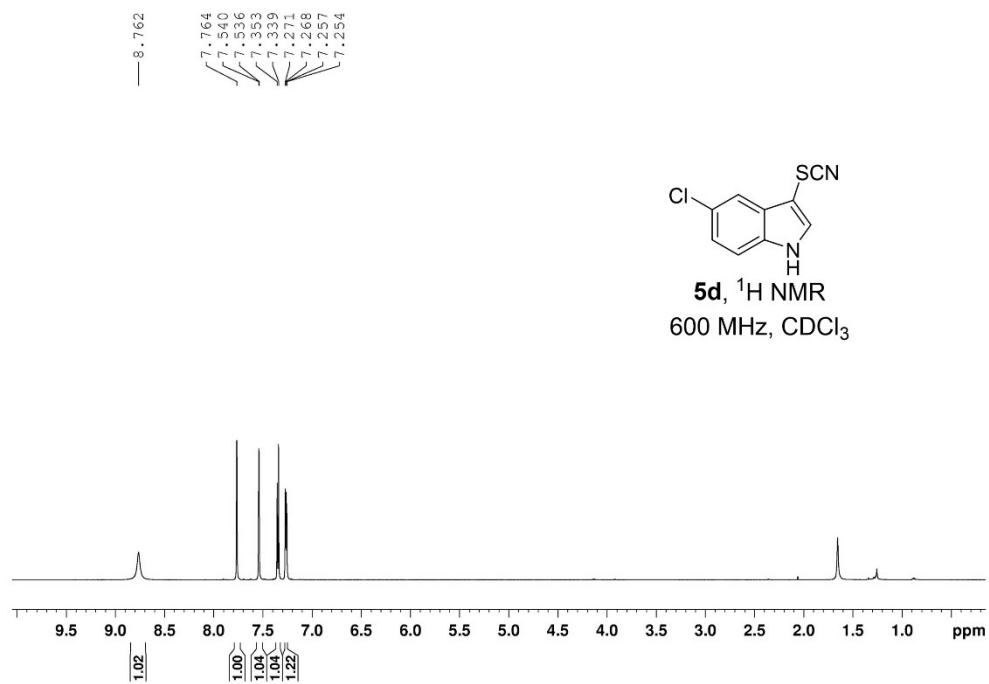


Figure S42. The  $^1\text{H}$  NMR spectrum of **5d**

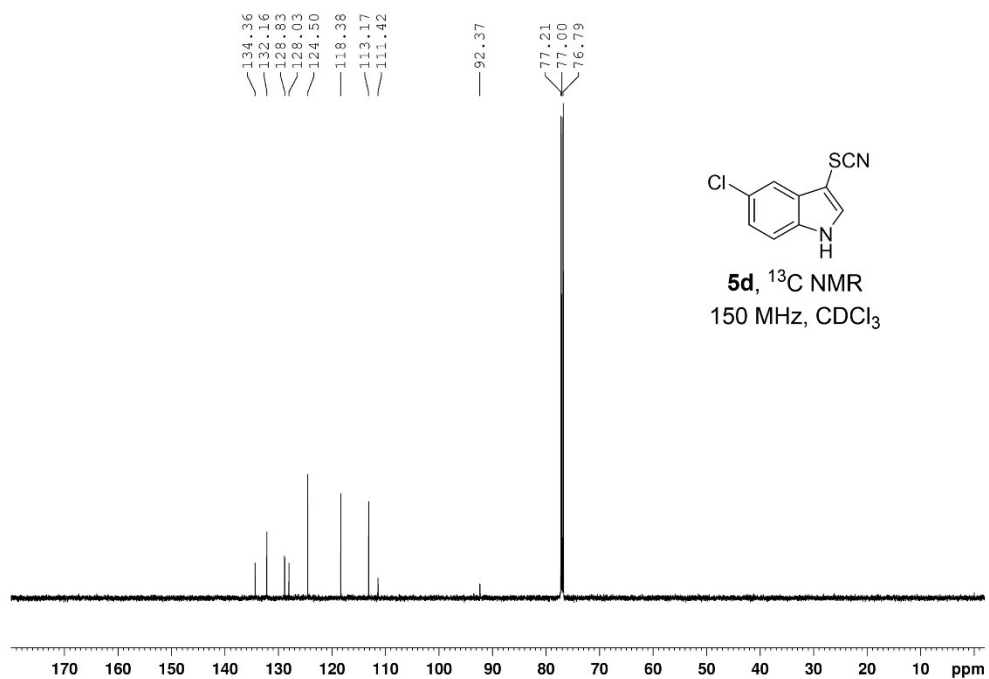


Figure S43. The  $^{13}\text{C}$  NMR spectrum of **5d**

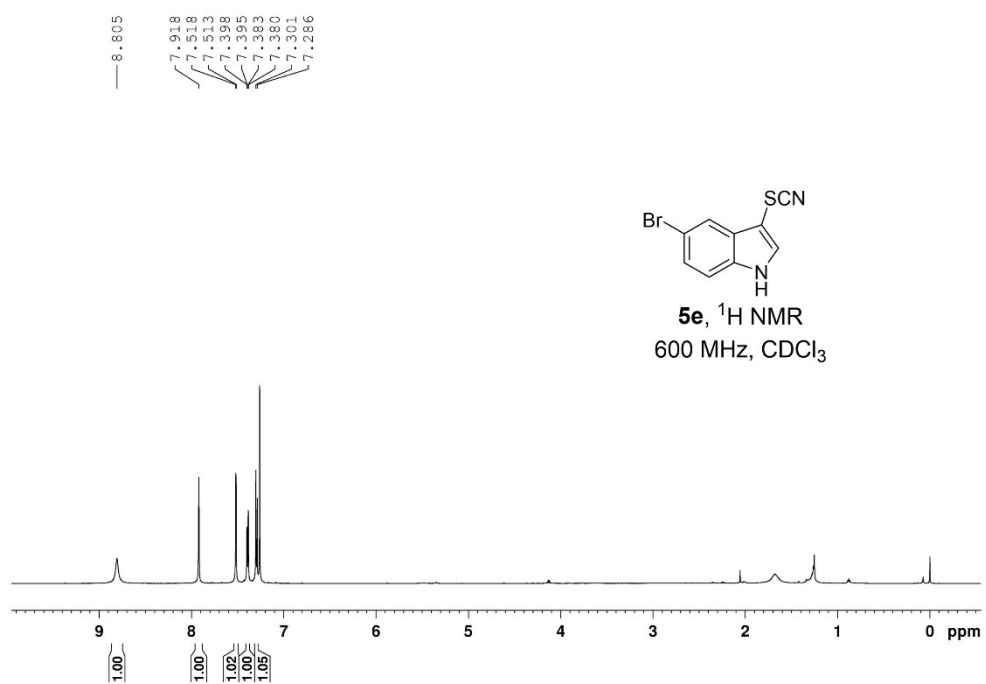


Figure S44. The  $^1\text{H}$  NMR spectrum of **5e**

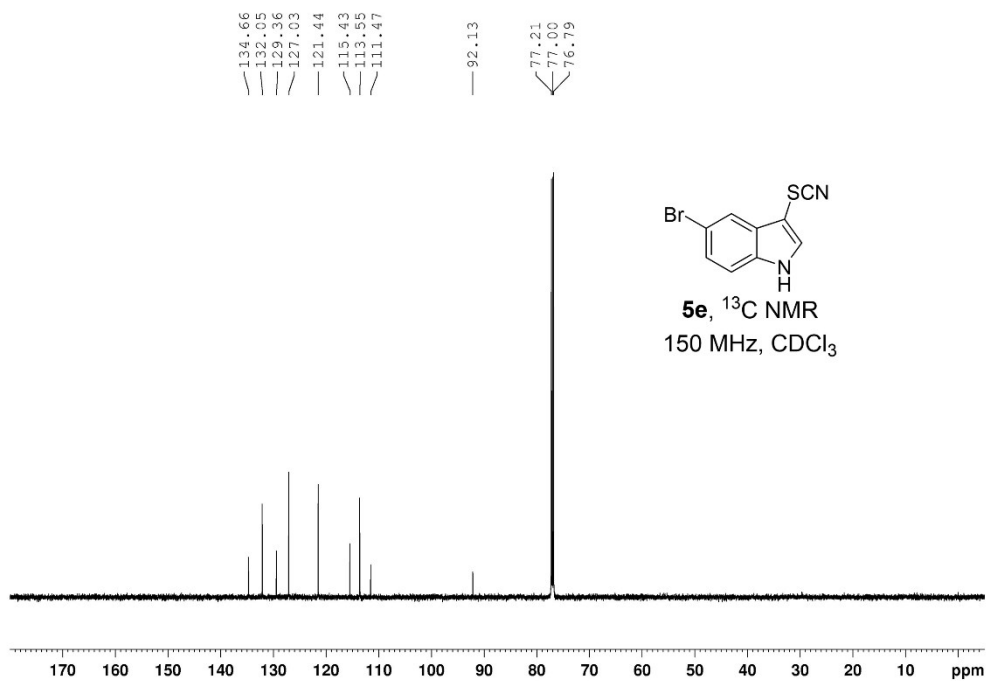


Figure S45. The  $^{13}\text{C}$  NMR spectrum of **5e**

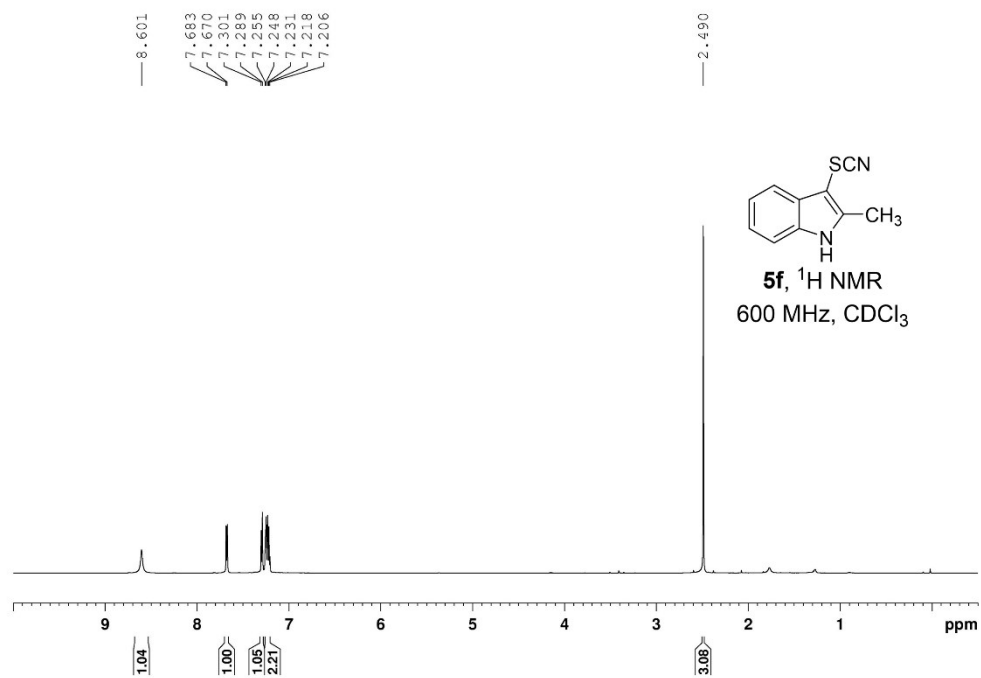


Figure S46. The  $^1\text{H}$  NMR spectrum of **5f**

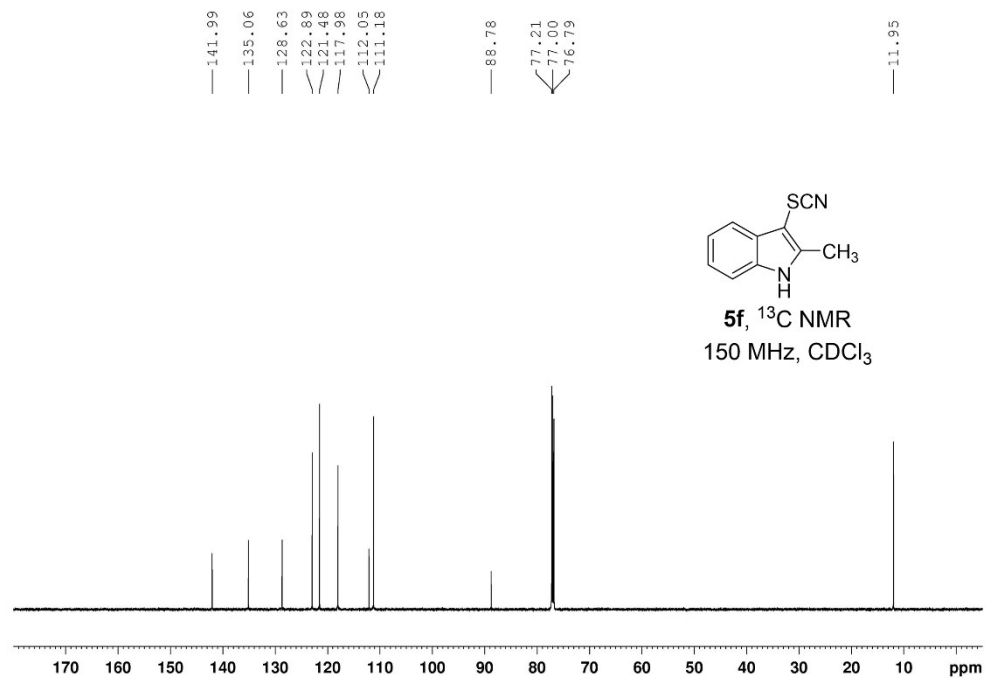


Figure S47. The  $^{13}\text{C}$  NMR spectrum of **5f**

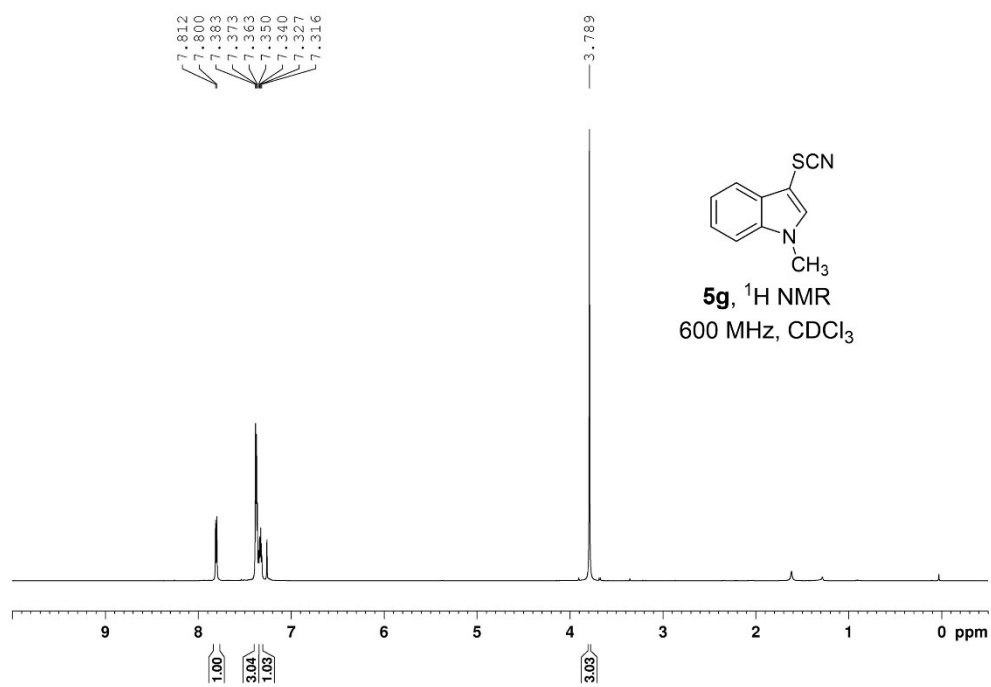


Figure S48. The  $^1\text{H}$  NMR spectrum of **5g**

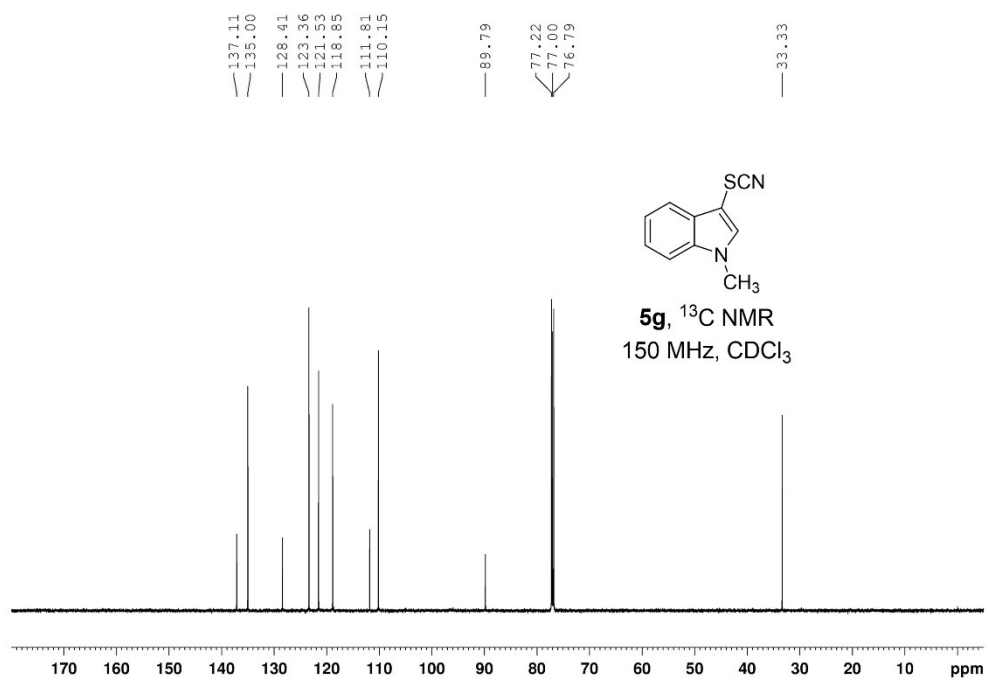


Figure S49. The  $^{13}\text{C}$  NMR spectrum of **5g**

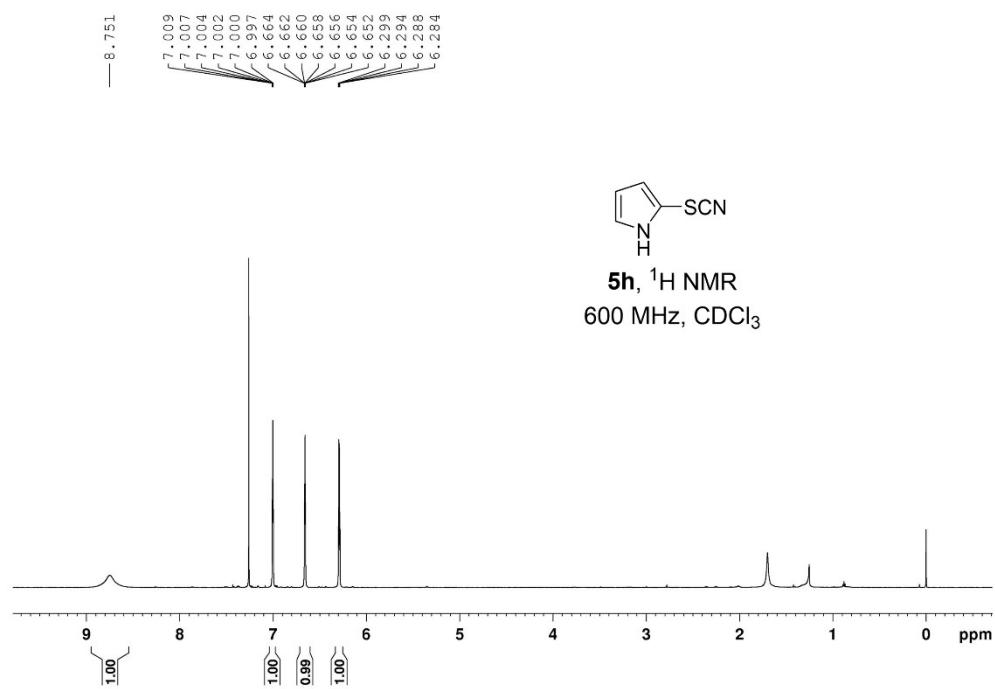


Figure S50. The  $^1\text{H}$  NMR spectrum of **5h**

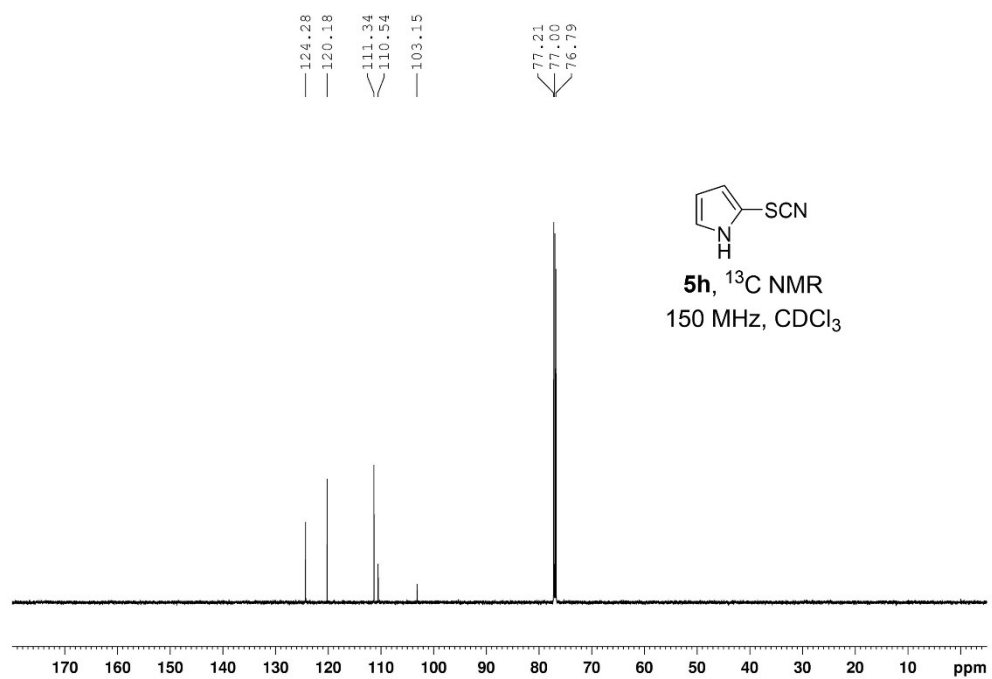


Figure S51. The  $^{13}\text{C}$  NMR spectrum of **5h**