Supporting Information

Visible Light-Induced Recyclable g-C_3N_4 Catalyzed Thiocyanation of C(sp^2)-H Bonds in Sustainable Solvents

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1. General Information

1.1 Materials and instruments

All commercially available reagents were used directly without further purification. All reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Products were purified by column chromatography using 200-300 mesh silica gel as the stationary phase. All the ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 400 or 600 spectrometers. All NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at room temperature (20 ± 2 °C). Proton chemical shifts δ were given in ppm using TMS as the internal standard. High-resolution mass spectra (HRMS) were obtained with a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique. Cyclic voltammetry was performed on the CHI-660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China).

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

Photochemical reaction was carried out under visible light irradiation by a blue LED at 25 ºC. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. Eight 10 W blue LEDs were equipped in this Photo reactor. The blue LED'S energy peak wavelength is 458 nm, peak width at half-height is 23.4 nm, lirradiance@10 W is 188.65 mW/cm^2. The reaction vessel is a borosilicate glass tube with 1.5 cm from the lamp, and no filter is applied.

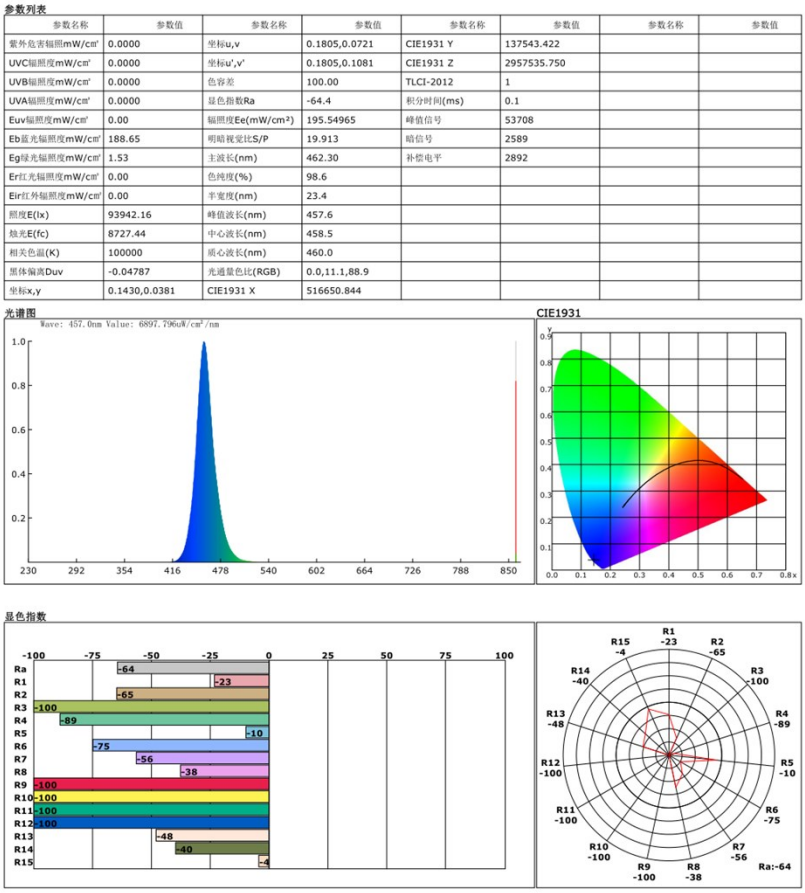


Figure S1a. The spectrum of our lamp (blue LED)

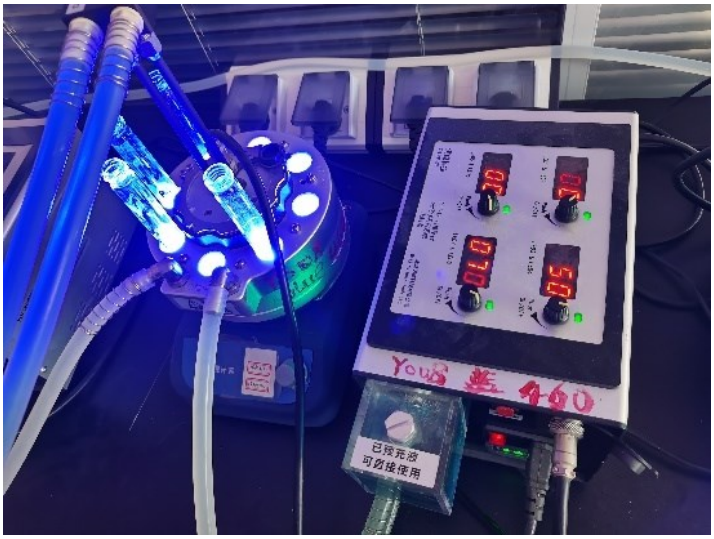


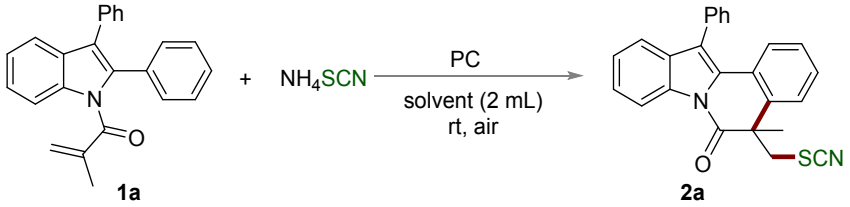
Figure S1b. The visible-light irradiation instrument

2. Experimental procedures

2.1 Optimization of reaction conditions

We started with establishing a suitable reaction condition for accessing **2a** using the model reaction of **1a** with commercially available thiocyanates (NH_4SCN) in the presence of different conditions under irradiation of blue LED at room temperature in open air, as summarized in Table S1. First, we investigated different catalysts. What was gratifying that g-C_3N_4 (10 mg) used as a catalyst to obtain the target product at 76% yield (entry 2), which was better than the corresponding yield of homogeneous catalyst 4CzIPN (entry 1). Then influence of a variety of solvents on the model reaction was examined by g-C_3N_4 (10 mg) as catalyst (entries 3-10). Among them, the target product **3a** was obtained in the highest yield of (82%) in DMC (entry 8). Encouraged by this satisfied result, light sources of different wavelengths, light intensities, and the amount of catalyst were further examined (entries 11-15). However, in sharp contrast, much less yields were observed with them. Among them, the highest yield was produced by using g-C_3N_4 (13 mg) and up to 79% (entry 15). At last, the model reaction was carried out in dark and no g-C_3N_4, as predicted, no any product of **2a** was obtained (entry 16-17). After a wide exploration, the optimal conditions were finally established as follows: **1a** (0.2 mmol), NH_4SCN (0.4 mmol), g-C_3N_4 (10 mg), DMC (2 mL) in air atmosphere under the irradiation of 10 W blue LED at room temperature for 12 h.

Table S1. Optimization of reaction conditions of **2a**

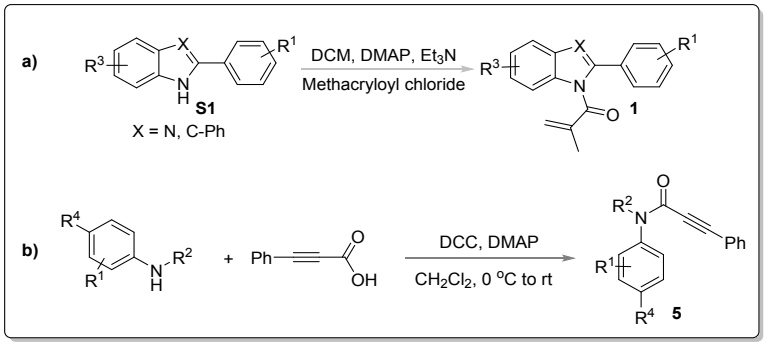


Entry	Solvent	Photocatalyst	Light Source	Yield (%)
1	MeCN	4CzIPN (5 mol%)	460 nm	70
2	MeCN	g-C_3N_4 (10 mg)	460 nm	76
3	DEC	g-C_3N_4 (10 mg)	460 nm	54
4	H_2O	g-C_3N_4 (10 mg)	460 nm	trace
5	2-MeTHF	g-C_3N_4 (10 mg)	460 nm	45
6	TBME	g-C_3N_4 (10 mg)	460 nm	42
7	DME	g-C_3N_4 (10 mg)	460 nm	62
8	**DMC**	**g-C_3N_4 (10 mg)**	**460 nm**	**82**
9	EG	g-C_3N_4 (10 mg)	460 nm	16
10	DCE	g-C_3N_4 (10 mg)	460 nm	68
11[b]	DMC	g-C_3N_4 (10 mg)	430 nm	77
12[c]	DMC	g-C_3N_4 (10 mg)	460 nm	61
13[d]	DMC	g-C_3N_4 (10 mg)	460 nm	57
14	DMC	g-C_3N_4 (7 mg)	460 nm	75
15	DMC	g-C_3N_4 (13 mg)	460 nm	79
16	DMC	---	460 nm	N.D.
17[e]	DMC	g-C_3N_4 (10 mg)	---	N.D.

[a] Reaction conditions: 1**a** (0.2 mmol), **2a** (0.4 mmol), PC = photocatalyst (10 mg), solvent (2 mL) under air for 12 h, rt, 460 nm blue LED (10 W), N.D. = not detected, DEC = diethyl carbonate, TBME = tert-butyl methyl ether, DME = 1,2-ethanediol dimethyl ether, EG = ethylene glycol, DCE = 1,2-dichloroethane, 4CzIPN = 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile. Isolated yields were given.

[b] 430 nm blue LED (10 W). [c] 460 nm blue LED (7 W). [d] 460 nm blue LED (5 W). [e] In dark.

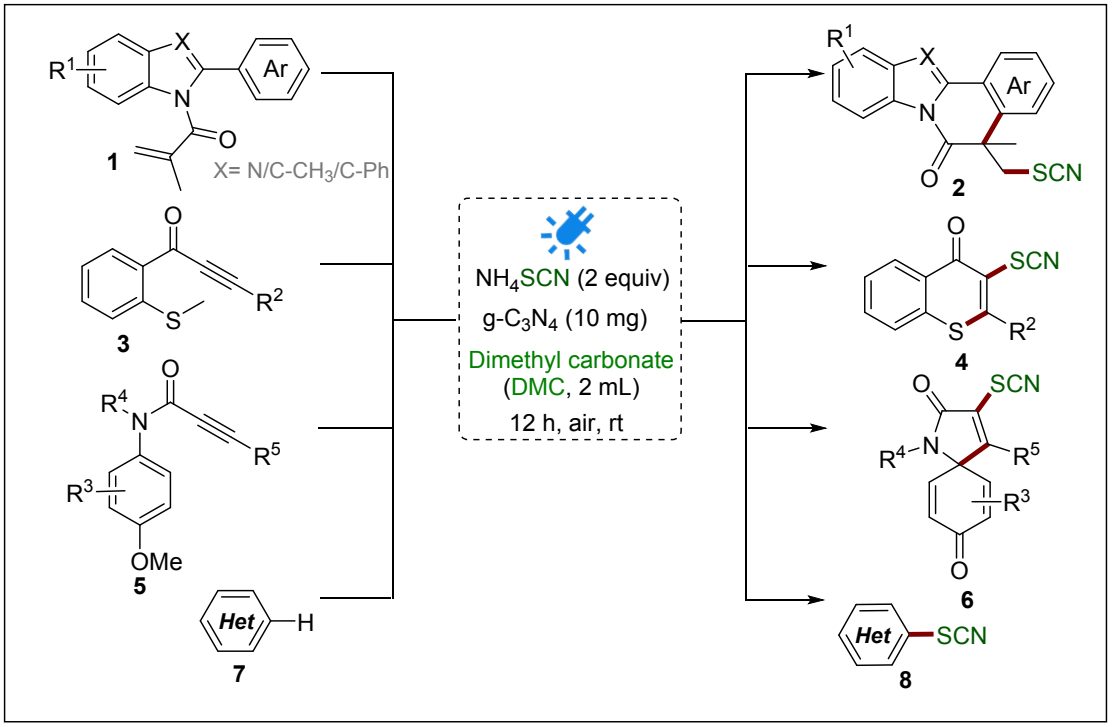
2.2 Preparation of starting materials and target products.



Scheme S1. General experimental procedures for substrates **1** and **5**

General procedure a): According to a modified literature procedure, to the solution of benzimidazole S1 (5 mmol, 1.0 equiv.) and DMAP (1.0 mmol, 0.2 equiv.) in DCM (0.5 M) was added Et_3N (10 mmol, 2.0 equiv.) and methacryloyl chloride (10 mmol, 2.0 equiv.) at 0 °C. The solution was warmed up to room temperature and stirred for 12–24 h. Reaction progress was checked by thin layer chromatography (TLC). The mixture was diluted with DCM (20 mL) and saturated $NaHCO_3$ solution (20 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with DCM (20 mL × 2). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give a residue, which was purified by flash chromatography and then recrystallized from petroleum ether (PE)/ ethyl acetate (EA) to afford the product **1**.[1]

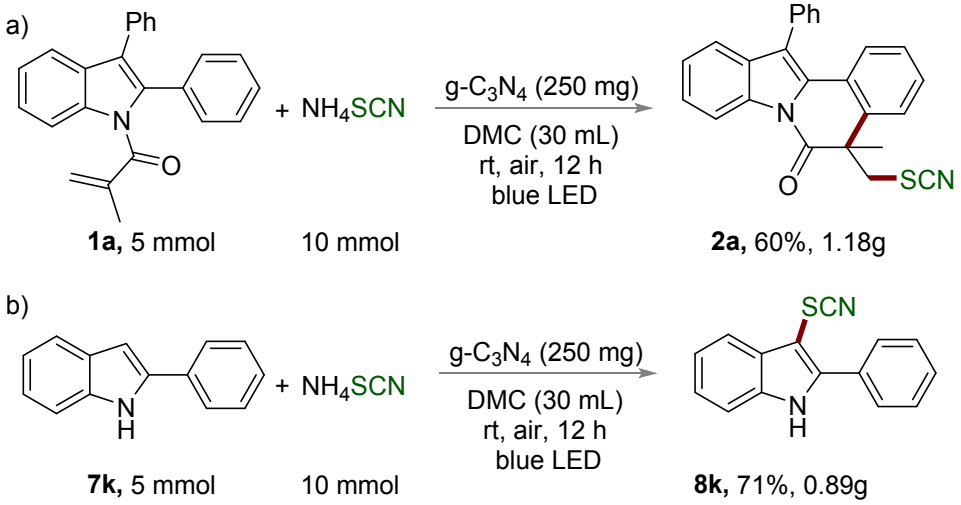
General procedure b): The mixture of *N*-methylaniline (or the relative aniline) (2.5 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added the corresponding propynoic acid (2.75 mmol, 1.1 equiv) at 0 ℃, then a mixture of dicyclohexylcarbodiimide (DCC) (3.75 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP) (0.25 mmol, 0.1 equiv) in CH_2Cl_2 (10 mL) was added dropwise, stirred at room temperature for 12 h. Then, the mixture was filtered and washed with CH_2Cl_2 (3 × 50 mL) and concentrated. The residue was purified by a silica gel column chromatography (PE/EA (v/v = 5/1)) to give the products **5**.[2]

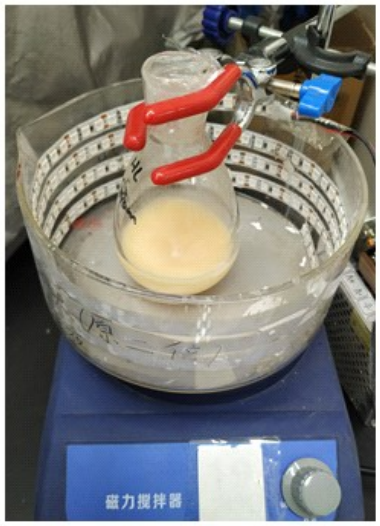


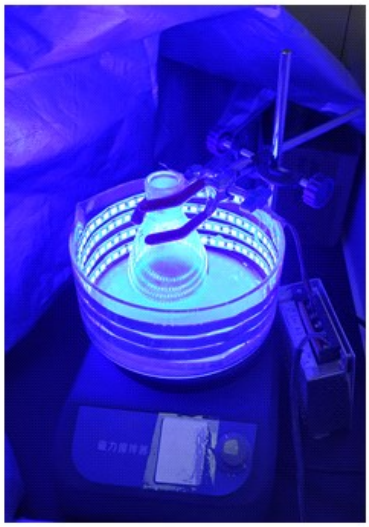
Scheme S2. General experimental procedures for the thiocyanato heterocycles (**2**, **4**, **6** and **8**)

General procedure: The mixture of substrates **1** or **3** or **5** or **7** (0.2 mmol), NH_4SCN (0.4 mmol), g-C_3N_4 (10 mg) and DMC (2 mL) were sequentially added in a 25 mL reaction tube. Then the reaction vessel was exposed to the irradiation of 10 W blue LED at room temperature for 12 h or 76 h under open-air (the reaction time of **2**, **4**, **6**, **8a-l** was 12 h; the reaction time of **8m** was 76 h). After the reaction, the solvent was evaporated under vacuum, all the crude products were purified by thin-layer chromatography using PE and EA as eluting solvent to give the desired products **2** or **4** or **6** or **8** (PE:EA, **2**: v/v = 20:1, **4**: v/v = 10:1, **6**: v/v = 3:1, **8a-l**: v/v = 50:1- 10:1. **8m** = DCM:EA, 5:1).

2.3 The gram-scale synthesis







Scheme S3. The gram-scale synthesis of **2a** and **8k**

The reactor for gram-scale synthesis: gram-scale synthesis of **2a** or **8k** with blue LEDs light irradiation in air atmosphere: **1a** or **7k** (5 mmol), NH_4SCN (10 mmol), g-C_3N_4 (250 mg) in 30 mL DMC at room temperature for 12 h with the assistance of specially designed reactor. The isolated yield of **2a** (60%, 1.18 g), or **8k** (71%, 0.89 g) were given.

2.4 HRMS data analysis

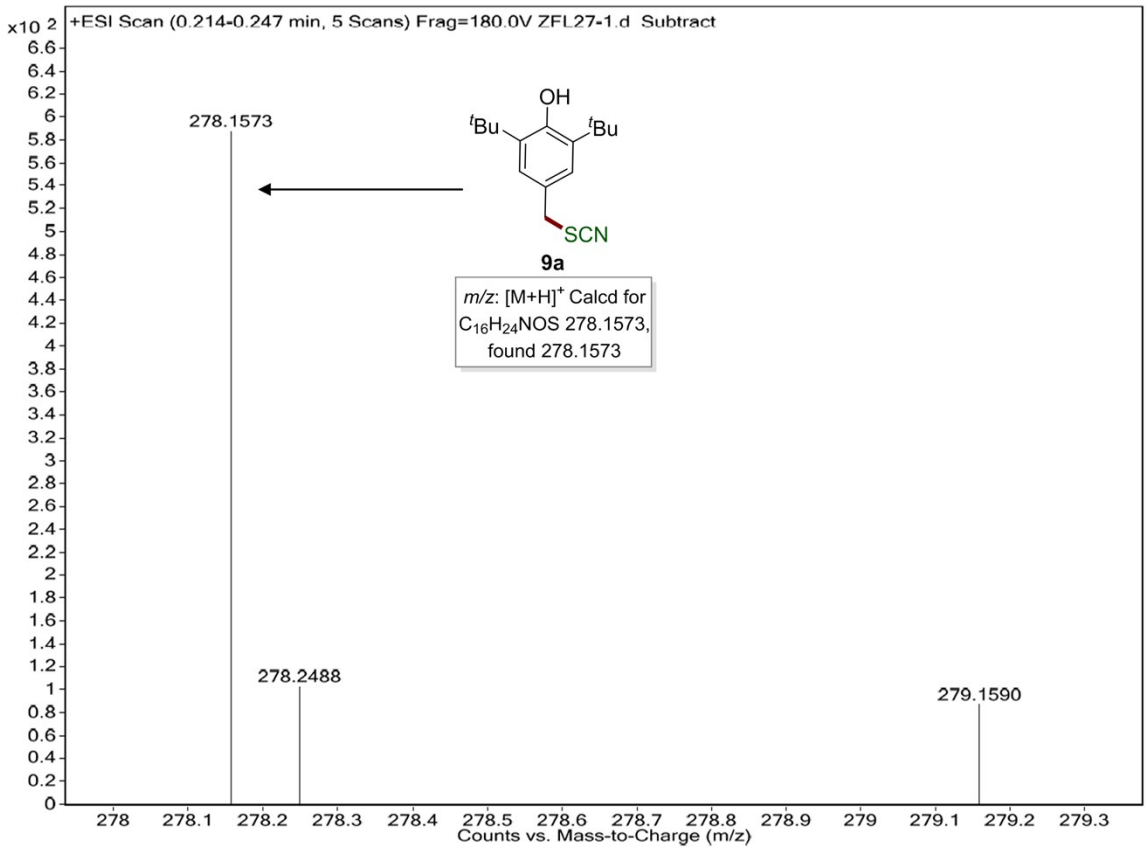


Figure S2. HRMS data analysis of **9a**.

2.5 Cyclic voltammograms of NH_4SCN

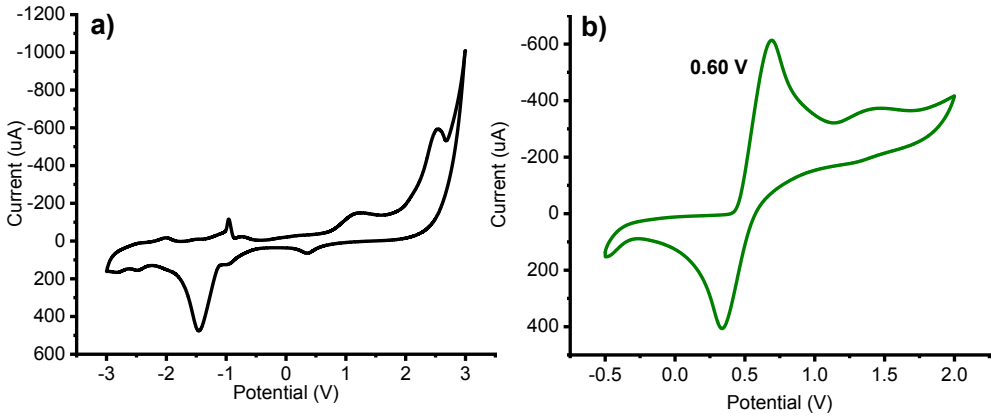
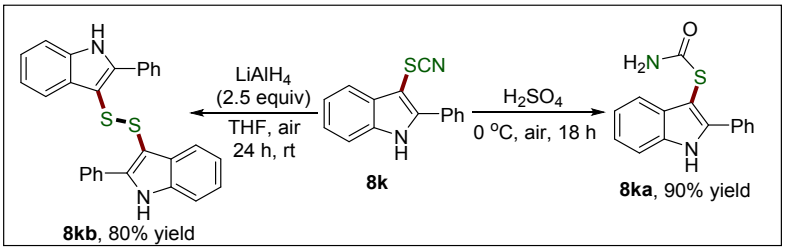


Figure S3. Cyclic voltammograms of 0.1 M $LiClO_4$ and related compounds in CH_3CN using Pt working electrode, Pt wire, and saturated calomel electrode (SCE) as counter and reference electrode at 100 mV/s scan rate: a) Blank. b) NH_4SCN (0.02 M).

2.6 Synthetic transformations of 8k.



Synthesis of product **8ka**: **8k** (0.2 mmol) was added slowly to a solution of 95% sulfuric acid (1 mL) and the mixture was stirred at 0 °C for 18 h. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed under vacuo. The product **8ka** was isolated in 90% yield (PE:EA, v/v = 3:1).

Synthesis of product **8kb**: A mixture of **8k** (0.2 mmol) and $LiAlH_4$ (0.5 mmol) in dry THF (2 mL) was stirred in air at room temperature for 24 h. Upon completion of the reaction. The solvent was then removed under vacuo. The product **8kb** was isolated in 80% yield (PE:EA, v/v = 5:1).

2.7 EPR spectrum.

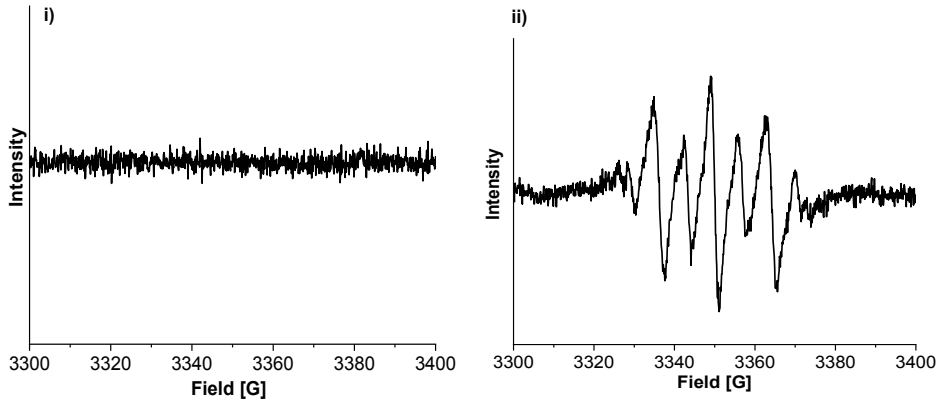
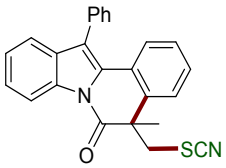


Figure S4. EPR spectra obtained at room temperature and open air in the presence of DMPO (1 mmol) in MeCN (2 mL) under the irradiation of blue LED for 30 min: i) No NH_4SCN; ii) NH_4SCN (0.2 mmol).

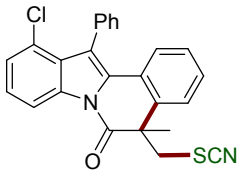
3. Characterization Data for Products

5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2a)



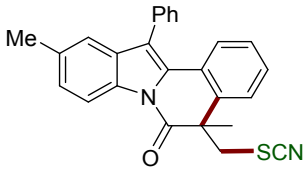
White solid (65 mg, 82% yield), mp 133 – 135 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.31 (m, 11H), 7.18 – 7.14 (m, 1H), 4.02 (d, *J* = 13.1 Hz, 1H), 3.71 (d, *J* = 13.1 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.37, 134.56, 134.22, 133.56, 132.35, 130.12, 129.41, 128.99, 128.84, 128.40, 128.12, 126.46, 126.21, 125.98, 125.92, 125.12, 121.63, 119.81, 116.66, 111.39, 49.80, 43.58, 28.78. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{19}N_2OS$, 395.1213; Found: 395.1212.

11-chloro-5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2b)



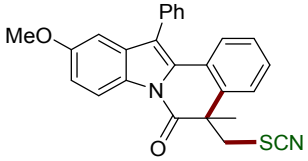
White solid (74 mg, 86% yield), mp 124 – 126 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 – 8.59 (m, 1H), 7.57 – 7.47 (m, 4H), 7.46 – 7.39 (m, 1H), 7.38 – 7.29 (m, 3H), 7.27 – 7.24 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.08 – 7.04 (m, 1H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.66 (d, *J* = 13.2 Hz, 1H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.48, 135.42, 134.63, 134.22, 130.97, 130.48, 130.27, 129.22, 128.99, 128.90, 128.44, 128.22, 128.06, 126.92, 126.71, 126.63, 126.22, 126.09, 125.61, 121.02, 115.34, 111.17, 49.83, 43.58, 29.00. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{18}ClN_2OS$, 429.0823; Found: 429.0828.

5,10-dimethyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2c)



White solid (70 mg, 86% yield), mp 157 – 159 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.48 (m, 5H), 7.47 – 7.41 (m, 1H), 7.40 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 7.14 – 7.07 (m, 2H), 3.97 (d, *J* = 12.1 Hz, 1H), 3.66 (d, *J* = 13.1 Hz, 1H), 2.41 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.10, 134.94, 134.54, 133.70, 132.54, 132.36, 130.11, 129.38, 128.88, 128.83, 128.31, 128.06, 127.70, 126.17, 126.06, 125.82, 121.46, 119.66, 116.30, 111.39, 49.65, 43.68, 28.71, 21.49. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{21}N_2OS$, 409.1369; Found: 409.1371.

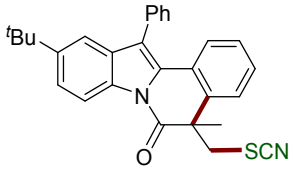
10-methoxy-5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2d)



Colorless oil (70 mg, 82% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 8.9 Hz, 1H),

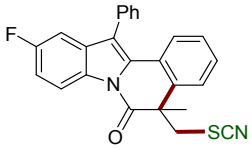
7.65 – 7.52 (m, 5H), 7.49 – 7.44 (m, 1H), 7.42 – 7.33 (m, 2H), 7.17 – 7.10 (m, 1H), 7.07 – 7.04 (m, 1H), 6.79 (d, J = 2.5 Hz, 1H), 4.00 (d, J = 13.1 Hz, 1H), 3.82 (s, 3H), 3.69 (d, J = 13.1 Hz, 1H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.88, 157.71, 134.67, 133.59, 133.49, 130.07, 129.50, 129.45, 128.89, 128.77, 128.38, 128.06, 126.20, 125.95, 125.80, 121.43, 117.53, 114.53, 111.33, 102.63, 55.75, 49.53, 43.73, 28.74. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{21}N_2O_2S$, 425.1318; Found: 425.1317.

10-(tert-butyl)-5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2e)



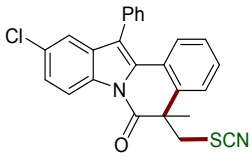
Colorless oil (75 mg, 83% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, J = 8.7 Hz, 1H), 7.62 – 7.49 (m, 6H), 7.42 (d, J = 8.0 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.14 – 7.06 (m, 1H), 3.97 (d, J = 13.1 Hz, 1H), 3.67 (d, J = 13.1 Hz, 1H), 1.81 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.09, 148.50, 134.50, 133.67, 132.26, 132.13, 130.13, 129.40, 128.91, 128.79, 128.32, 128.04, 126.17, 126.09, 125.82, 124.38, 121.93, 116.15, 115.79, 111.40, 49.67, 43.57, 34.91, 31.64, 28.80. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{27}N_2OS$, 451.1839; Found: 451.1834.

10-fluoro-5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2f)



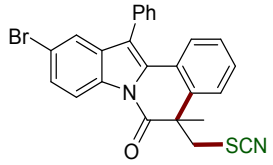
White solid (73 mg, 89% yield), mp 135 – 137 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 – 8.54 (m, 1H), 7.61 – 7.44 (m, 6H), 7.40 – 7.33 (m, 2H), 7.17 – 7.09 (m, 2H), 6.98 – 6.96 (m, 1H), 3.96 (d, J = 13.2 Hz, 1H), 3.66 (d, J = 13.2 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.20, 161.92 (C-F, $^1J_{C\text{-}F}$ = 242.4 Hz), 159.51 (C-F, $^1J_{C\text{-}F}$ = 242.4 Hz), 134.77, 133.78, 133.69, 133.05, 130.46, 130.33, 129.99, 129.54, 129.32, 128.62, 128.20, 126.27, 125.99, 125.64, 121.10 (d, J = 4.1 Hz), 114.05 (C-F, $^2J_{C\text{-}F}$ = 24.9 Hz), 113.82 (C-F, $^2J_{C\text{-}F}$ = 24.9 Hz), 111.20, 105.71 (C-F, $^3J_{C\text{-}F}$ = 24.6 Hz), 105.47 (C-F, $^3J_{C\text{-}F}$ = 24.6 Hz), 49.69, 43.65, 28.79. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.71. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{18}FN_2OS$, 413.1118; Found: 413.1123.

10-chloro-5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2g)



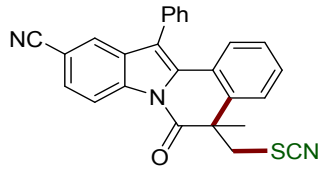
Colorless oil (68 mg, 80% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.44 (m, 6H), 7.41 – 7.35 (m, 3H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.15 – 7.11 (m, 1H), 3.96 (d, *J* = 13.2 Hz, 1H), 3.67 (d, *J* = 13.2 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.30, 134.72, 133.72, 132.88, 132.48, 130.89, 130.05, 130.00, 129.54, 129.35, 128.63, 128.22, 126.45, 126.22, 126.03, 125.57, 120.69, 119.41, 117.71, 111.08, 49.75, 43.68, 28.72. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{18}ClN_2OS$, 429.0823; Found: 429.0821.

10-bromo-5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2h)



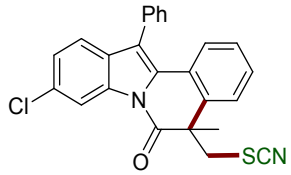
Colorless oil (86 mg, 91% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.41 (m, 8H), 7.40 – 7.32 (m, 2H), 7.14 – 7.10 (m, 1H), 3.95 (d, *J* = 13.2 Hz, 1H), 3.65 (d, *J* = 13.2 Hz, 1H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.36, 134.75, 134.15, 132.85, 130.03, 129.97, 129.59, 129.42, 129.16, 128.68, 128.25, 126.27, 126.05, 125.52, 122.45, 120.55, 118.64, 118.09, 111.14, 49.80, 43.65, 28.75. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{18}BrN_2OS$, 473.0318; Found: 473.0319.

5-methyl-6-oxo-12-phenyl-5-(thiocyanatomethyl)-5,6-dihydroindolo[2,1-a]isoquinoline-10-carbonitrile (2i)



Yellow solid (70 mg, 84% yield), mp 211.3 – 212.8 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 8.5 Hz, 1H), 7.69 – 7.48 (m, 8H), 7.41 (d, *J* = 3.9 Hz, 2H), 7.19 – 7.13 (m, 1H), 3.97 (d, *J* = 13.3 Hz, 1H), 3.67 (d, *J* = 13.3 Hz, 1H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.75, 135.96, 134.71, 132.58, 132.20, 130.94, 129.93, 129.89, 129.72, 129.37, 128.98, 128.42, 126.30, 126.26, 125.14, 124.39, 120.56, 119.24, 117.46, 110.88, 108.57, 50.04, 43.58, 28.75. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{18}N_3OS$, 420.1165; Found: 420.1163.

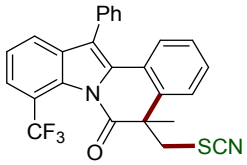
9-chloro-5-methyl-12-phenyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2j)



Colorless oil (78 mg, 91% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 4.2 Hz,1H), 7.51 (m, 6H), 7.39 – 7.33 (m, 2H), 7.30 – 7.21 (m, 2H), 7.15 – 7.09 (m, 1H), 3.96 (d, *J* = 13.2 Hz,

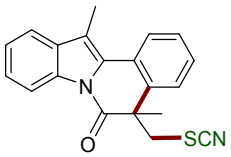
1H), 3.67 (d, J = 13.2 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.46, 134.45, 134.39, 133.03, 132.21, 130.85, 130.02, 129.49, 129.32, 129.24, 128.59, 128.22, 126.25, 125.87, 125.67, 125.63, 121.13, 120.50, 116.88, 111.16, 49.87, 43.51, 28.81. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{18}ClN_2OS$, 429.0823; Found: 429.0821.

5-methyl-12-phenyl-5-(thiocyanatomethyl)-8-(trifluoromethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2k)



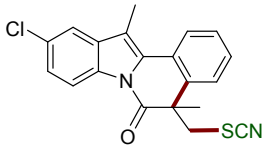
Colorless oil (65 mg, 70% yield), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 7.6 Hz, 1H), 7.61 – 7.46 (m, 6H), 7.43 – 7.37 (m, 4H), 7.17 – 7.10 (m, 1H), 3.98 (d, J = 13.3 Hz, 1H), 3.65 (d, J = 13.3 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.79, 135.39, 135.20, 132.69, 132.53, 130.24, 130.17, 129.56 (d, J = 2.0 Hz), 128.68, 128.28, 126.41, 126.21, 126.19, 124.95 (q, C-F, $^3J_{C\text{-}F}$ = 5.0 Hz), 124.81, 123.98 (q, C-F, $^1J_{C\text{-}F}$ = 271.8 Hz), 123.77, 121.28, 120.90, 119.94 (q, C-F, $^2J_{C\text{-}F}$ = 33.8 Hz), 111.44, 50.80, 42.77, 28.53. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.48. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{18}F_3N_2OS$, 463.1086; Found: 463.1086.

5,12-dimethyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2l)



Yellow solid (58 mg, 88% yield), mp 78 – 79 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dd, J = 7.1, 1.4 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.56 – 7.50 (m, 1H), 7.50 – 7.37 (m, 4H), 3.98 (d, J = 13.1 Hz, 1H), 3.67 (d, J = 13.1 Hz, 1H), 2.70 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.92, 134.31, 134.15, 132.51, 129.02, 128.53, 128.41, 127.01, 126.49, 126.24, 125.60, 124.76, 118.69, 116.67, 115.83, 111.42, 49.67, 43.58, 28.86, 11.52. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{17}N_2OS$, 333.1056; Found: 333.1060.

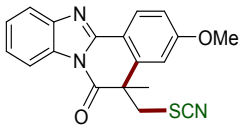
10-chloro-5,12-dimethyl-5-(thiocyanatomethyl)indolo[2,1-a]isoquinolin-6(5H)-one (2m)



White solid (66 mg, 90% yield), mp 124 – 126 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, J = 8.7 Hz, 1H), 8.04 (d, J = 7.7 Hz, 1H), 7.56 – 7.40 (m, 4H), 7.35 – 7.32 (m, 1H), 3.92 (d, J = 13.2 Hz, 1H), 3.62 (d, J = 13.2 Hz, 1H), 2.62 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.89, 134.52, 133.94, 132.41, 130.49, 130.32, 128.84, 128.64, 126.58, 126.55, 126.16, 125.74,

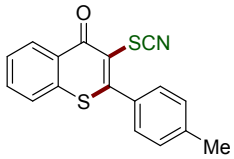
118.50, 117.69, 114.87, 111.18, 49.64, 43.64, 28.81, 11.49. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{16}N_2OS$, 367.0666; Found: 367.0669.

3-methoxy-5-methyl-5-(thiocyanatomethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (2n)



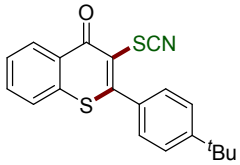
White solid (57 mg, 81% yield), mp 145 – 146 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 8.8 Hz, 1H), 8.35 – 8.27 (m, 1H), 7.84 – 7.75 (m, 1H), 7.47 – 7.39 (m, 2H), 7.14 – 7.12 (m, 1H), 6.93 (d, *J* = 2.3 Hz, 1H), 3.98 (s, 1H), 3.94 (s, 3H), 3.65 (d, *J* = 13.4 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.39, 162.92, 149.26, 144.19, 139.28, 131.06, 128.64, 126.28, 125.55, 119.69, 116.20, 115.56, 114.76, 112.12, 110.52, 55.77, 50.49, 43.40, 29.21. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{16}N_3O_2S$, 350.0958; Found: 350.0962.

3-thiocyanato-2-(p-tolyl)-4H-thiochromen-4-one (4a)



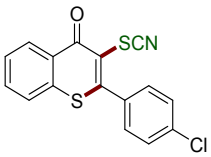
White solid (57 mg, 93% yield), mp 172 – 174 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.74 – 7.59 (m, 3H), 7.39 (dd, *J* = 7.4, 5.1 Hz, 4H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.60, 159.94, 141.67, 136.10, 132.53, 132.47, 129.87, 129.81, 129.79, 128.87, 128.37, 125.74, 118.72, 109.74, 21.56. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{12}NOS_2$, 310.0355; Found: 310.0352.

2-(4-(tert-butyl)phenyl)-3-thiocyanato-4H-thiochromen-4-one (4b)



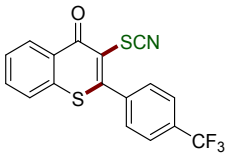
White solid (50 mg, 71% yield), mp 170 – 172 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 – 8.38 (m, 1H), 7.72 – 7.68 (m, 1H), 7.66 – 7.53 (m, 4H), 7.43 (d, *J* = 8.4 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.53, 160.12, 154.70, 136.11, 132.52, 132.45, 129.84, 129.79, 128.85, 128.27, 126.08, 125.76, 118.64, 109.80, 35.07, 31.20. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{18}NOS_2$, 352.0824; Found: 352.0820.

2-(4-chlorophenyl)-3-thiocyanato-4H-thiochromen-4-one (4c)



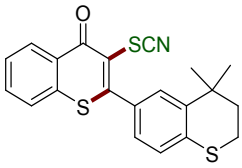
Pale yellow solid (52 mg, 79% yield), mp 170 – 172 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 – 8.59 (m, 1H), 7.80 – 7.60 (m, 3H), 7.58 – 7.41 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.45, 158.34, 137.54, 135.77, 133.52, 132.74, 129.92, 129.82, 129.74, 129.56, 129.12, 125.80, 119.27, 109.38. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_9ClNOS_2$, 329.9809; Found: 329.9805.

3-thiocyanato-2-(4-(trifluoromethyl)phenyl)-4H-thiochromen-4-one (4d)



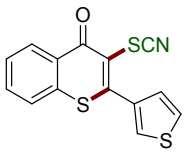
White solid (54 mg, 74% yield), mp 178 – 180 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 – 8.61 (m, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.77 – 7.73 (m, 1H), 7.71 – 7.62 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.28, 157.99, 138.45, 135.58, 132.98 (q, C-F, $^{2}J_{C\text{-}F}$ = 36.3 Hz), 132.86, 129.99, 129.76, 129.28, 129.01, 126.27 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 125.87, 123.47 (q, C-F, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 119.57, 109.16. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.99. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_9F_3NOS_2$, 364.0072; Found: 364.0070.

4',4'-dimethyl-3-thiocyanato-3',4'-dihydro-2'H,4H-[2,6'-bithiochromen]-4-one (4e)



Pale yellow solid (55 mg, 70% yield), mp 192 – 194 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 – 8.56 (m, 1H), 7.73 – 7.69 (m, 1H), 7.67 – 7.59 (m, 2H), 7.49 (d, J = 1.9 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.17 – 7.14 (m, 1H), 3.27 – 2.98 (m, 2H), 2.10 – 1.94 (m, 2H), 1.39 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.71, 159.96, 142.76, 137.21, 136.05, 132.50, 130.79, 129.87, 129.84, 128.83, 127.07, 126.85, 125.71, 125.67, 118.29, 109.86, 36.92, 33.27, 30.01, 23.25. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{18}NOS_3$, 396.0545; Found: 396.0545.

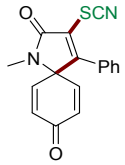
3-thiocyanato-2-(thiophen-3-yl)-4H-thiochromen-4-one (4f)



Yellow solid (54 mg, 90% yield), mp 148 – 150 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 – 8.57 (m, 1H), 7.76 – 7.68 (m, 2H), 7.67 – 7.59 (m, 2H), 7.56 – 7.54 (m, 1H), 7.40 – 7.38 (m, 1H).

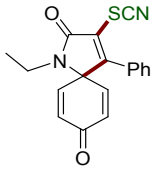
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.80, 154.01, 135.95, 135.21, 132.59, 129.83, 129.73, 128.93, 128.38, 127.61, 127.54, 125.67, 118.45, 109.59. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_8NOS_3$, 301.9763; Found: 301.9765.

1-methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6a)[2]



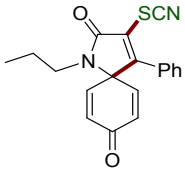
White solid (52 mg, 84% yield), mp 147 – 148 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.37 (m, 3H), 7.34 – 7.16 (m, 2H), 6.70 – 6.40 (m, 4H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.33, 164.94, 157.07, 143.13, 133.94, 131.08, 129.07, 128.91, 127.81, 122.28, 106.33, 68.37, 26.59.

1-ethyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6b)[2]



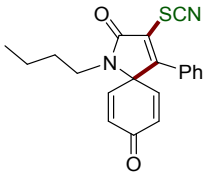
White solid (48 mg, 75% yield), mp 143 – 145 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.38 (m, 3H), 7.26 – 7.22 (m, 2H), 6.61 – 6.54 (m, 2H), 6.53 – 6.44 (m, 2H), 3.41 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.50, 164.86, 156.66, 143.43, 133.44, 130.99, 129.03, 128.86, 127.81, 122.68, 106.24, 68.81, 36.77, 15.06.

4-phenyl-1-propyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6c)[2]



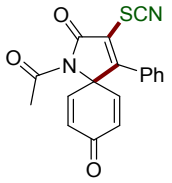
White solid (53 mg, 78% yield), mp 155 – 156 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.39 (m, 3H), 7.26 – 7.20 (m, 2H), 6.61 – 6.53 (m, 2H), 6.51 – 6.44 (m, 2H), 3.34 – 3.25 (m, 2H), 1.71 – 1.60 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.49, 165.15, 156.57, 143.51, 133.43, 130.99, 129.03, 128.84, 127.81, 122.72, 106.20, 68.86, 43.73, 22.91, 11.39.

1-butyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6d)[2]



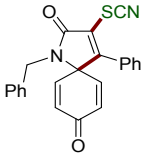
Light yellow solid (57 mg, 80% yield), mp 172 – 173 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.39 (m, 3H), 7.26 – 7.20 (m, 2H), 6.60 – 6.53 (m, 2H), 6.51 – 6.45 (m, 2H), 3.36 – 3.29 (m, 2H), 1.64 – 1.57 (m, 2H), 1.38 – 1.28 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.50, 165.10, 156.55, 143.54, 133.43, 130.98, 129.02, 128.86, 127.82, 122.70, 106.21, 68.86, 41.91, 31.66, 20.16, 13.63.

1-acetyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6e)[2]



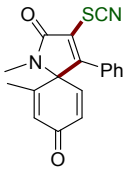
Light yellow solid (40 mg, 60% yield), mp 202 – 204 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 1H), 7.43 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.19 – 7.10 (m, 2H), 6.59 – 6.52 (m, 2H), 6.48 – 6.39 (m, 2H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.37, 168.44, 163.76, 161.54, 141.92, 133.00, 131.47, 128.98, 128.00, 127.56, 122.29, 105.64, 68.53, 25.67.

1-benzyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6f)[2]



White solid (58 mg, 75% yield), mp 137 – 139 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.36 (m, 3H), 7.30 – 7.23 (m, 5H), 7.20 – 7.14 (m, 2H), 6.31 (q, *J* = 10.3 Hz, 4H), 4.59 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.49, 165.15, 157.26, 143.24, 136.55, 133.09, 131.03, 129.00, 128.99, 128.72, 128.66, 128.23, 127.82, 122.37, 106.22, 68.84, 45.47.

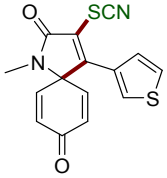
1,6-dimethyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6g)[2]



Light yellow solid (50 mg, 78% yield), mp 144 – 146 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.40 (m, 3H), 7.30 – 7.27 (m, 2H), 6.58 – 6.45 (m, 2H), 6.43 – 6.34 (m, 1H), 2.87 (s, 3H),

1.77 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.04, 165.40, 157.37, 151.55, 143.24, 133.46, 132.58, 131.33, 129.26, 128.74, 127.56, 122.36, 106.31, 70.50, 26.14, 17.71.

1-methyl-3-thiocyanato-4-(thiophen-3-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (6h)[2]

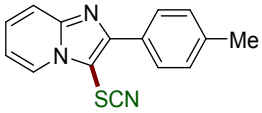


Light yellow solid (52 mg, 82% yield), mp 143 – 145 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.45 (dd, *J* = 5.2, 2.9 Hz, 1H), 7.41 (dd, *J* = 5.1, 1.4 Hz, 1H), 6.63 – 6.59 (m, 2H), 6.57 – 6.52 (m, 2H), 2.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.46, 165.22, 151.68, 144.08, 133.65, 129.45, 128.84, 127.54, 126.35, 118.90, 106.47, 67.26, 26.20.

2-phenyl-3-thiocyanatoimidazo[1,2-a]pyridine (8a)[3]

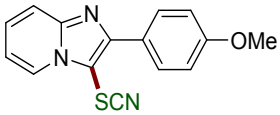
Red solid (46 mg, 89% yield), mp 141 – 142 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 6.7 Hz, 1H), 8.06 (d, *J* = 7.4 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.14 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.09, 147.95, 131.92, 129.46, 128.82, 128.76, 128.02, 124.40, 118.29, 114.43, 108.12, 94.69.

3-thiocyanato-2-(p-tolyl)imidazo[1,2-a]pyridine (8b)[3]



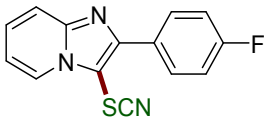
Yellow solid (46 mg, 86% yield), mp 135 – 136 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.08 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.24, 147.96, 139.62, 129.49, 129.08, 128.69, 127.93, 124.36, 118.20, 114.30, 108.16, 94.29, 21.44.

2-(4-methoxyphenyl)-3-thiocyanatoimidazo[1,2-a]pyridine (8c)[3]



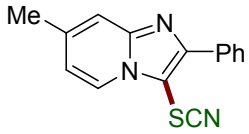
White solid (49 mg, 88% yield), mp 139 – 141 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 6.8 Hz, 1H), 8.09 – 7.98 (m, 2H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.16 – 7.02 (m, 3H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.65, 152.99, 147.95, 130.15, 127.90, 124.47, 124.33, 118.05, 114.21, 114.19, 108.23, 93.70, 55.40.

2-(4-fluorophenyl)-3-thiocyanatoimidazo[1,2-a]pyridine (8d)[3]



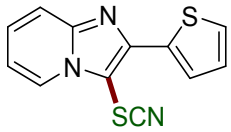
White solid (47 mg, 87% yield), mp 115 – 116 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 6.8 Hz, 1H), 8.14 – 8.01 (m, 2H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.25 (t, *J* = 4.2 Hz, 1H), 7.23 – 7.11 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.38 (C-F, $^1J_{C\text{-}F}$ = 249.9 Hz), 162.72 (C-F, $^1J_{C\text{-}F}$ = 249.9 Hz), 152.19, 147.97, 130.73 (C-F, $^3J_{C\text{-}F}$ = 8.3 Hz), 130.67 (C-F, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.17, 128.14, 124.41, 118.27, 115.94 (C-F, $^2J_{C\text{-}F}$ = 21.6 Hz), 115.80 (C-F, $^2J_{C\text{-}F}$ = 21.6 Hz), 114.51, 107.90, 94.52. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.32.

7-methyl-2-phenyl-3-thiocyanatoimidazo[1,2-a]pyridine (8e)[3]



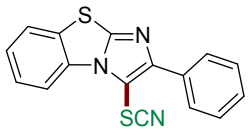
Pale yellow solid (44 mg, 83% yield), mp 131 – 133 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 6.9 Hz, 1H), 8.12 – 7.97 (m, 2H), 7.62 – 7.40 (m, 4H), 6.97 – 6.95 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.12, 148.35, 139.49, 132.12, 129.35, 128.76, 128.70, 123.52, 116.96, 116.82, 108.32, 93.72, 21.49.

3-thiocyanato-2-(thiophen-2-yl)imidazo[1,2-a]pyridine (8f)



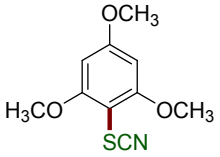
White solid (49 mg, 96% yield), mp 140 – 142 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 – 8.39 (m, 1H), 7.96 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.54 – 7.42 (m, 2H), 7.21 (dd, *J* = 5.1, 3.7 Hz, 1H), 7.13 – 7.09 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.96, 147.89, 134.72, 128.26, 128.16, 128.09, 127.71, 124.25, 117.97, 114.46, 107.54, 93.17. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_8N_3S_2$, 258.0154; Found: 258.0149.

2-phenyl-3-thiocyanatobenzo[d]imidazo[2,1-b]thiazole (8g)



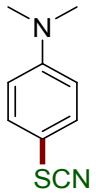
Pale yellow solid (49 mg, 80% yield), mp 187 – 189 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 8.3 Hz, 1H), 7.98 (t, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.40 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.56, 152.74, 132.87, 131.72, 130.21, 129.29, 128.73, 128.42, 126.95, 125.78, 124.52, 113.88, 108.83, 98.02. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{10}N_3S_2$, 308.0311; Found: 308.0307.

1,3,5-trimethoxy-2-thiocyanatobenzene (8h)[4]



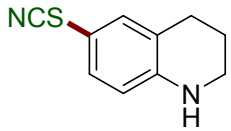
Light yellow solid (27 mg, 60% yield), mp 158 – 160 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.16 (s, 2H), 3.92 (s, 6H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.25, 161.39, 111.83, 89.79, 56.36, 55.59.

N,N-dimethyl-4-thiocyanatoaniline (8i)[5]



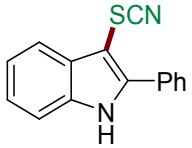
Light yellow solid (20 mg, 56% yield), mp 72 – 74 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.38 (m, 1H), 6.73 – 6.63 (m, 1H), 3.00 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.69, 134.45, 113.15, 112.56, 106.62, 40.14.

6-thiocyanato-1,2,3,4-tetrahydroquinoline (8j)



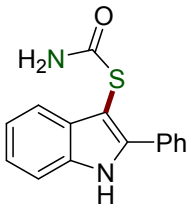
Colorless oil (20 mg, 53% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.10 (m, 2H), 6.47 – 6.38 (m, 1H), 4.17 (s, 1H), 3.39 – 3.28 (m, 2H), 2.74 (t, *J* = 6.3 Hz, 2H), 1.96 – 1.84 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.82, 134.58, 132.27, 122.72, 114.82, 112.83, 106.58, 41.61, 26.88, 21.17. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{11}N_2S$, 191.0637; Found: 191.0638.

2-phenyl-3-thiocyanato-1H-indole (8k)



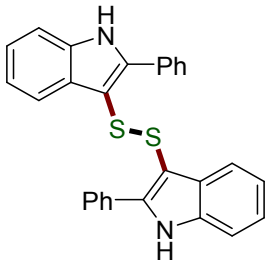
Yellow solid (40 mg, 80% yield), mp 159 – 161 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (s, 1H), 7.87 (t, *J* = 8.2 Hz, 2H), 7.73 (t, *J* = 8.1 Hz,1H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.36 – 7.24 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.61, 136.29, 130.43, 129.77, 129.62, 129.37, 129.28, 123.85, 121.88, 118.49, 112.93, 112.80, 87.57. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{11}N_2S$, 251.0637; Found: 251.0640.

2-phenyl-1H-indol-3-yl carbamothioate (8ka)



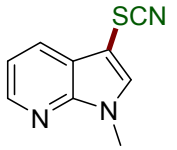
Yellow solid (48 mg, 90% yield), mp 160 – 161 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.94 (s, 1H), 7.93 – 7.77 (m, 2H), 7.64 – 7.40 (m, 7H), 7.23 – 7.10 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.33, 142.59, 136.33, 131.93, 131.73, 128.90, 128.86, 128.83, 122.83, 120.66, 119.17, 112.18, 96.26. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}N_2OS$, 269.0743; Found: 269.0742.

1,2-bis(2-phenyl-1H-indol-3-yl)disulfane (8kb)



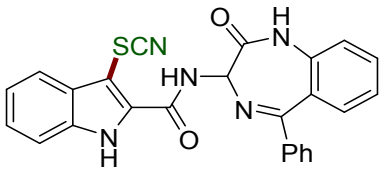
Yellow solid (72 mg, 80% yield), mp 146 – 148 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 2H), 7.62 – 7.54 (m, 2H), 7.29 – 7.20 (m, 8H), 7.17 – 7.10 (m, 4H), 7.02 (dd, *J* = 8.4, 7.0 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.29, 135.41, 131.03, 130.79, 128.09, 127.97, 127.89, 123.15, 120.99, 120.09, 110.80, 104.17. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{21}N_2S_2$, 449.1141; Found: 449.1142.

1-methyl-3-thiocyanato-1H-pyrrolo[2,3-b]pyridine (8l)



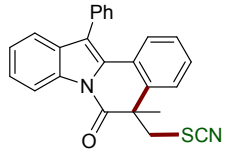
White solid (25 mg, 66% yield), mp 121 – 123 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56 (s, 1H), 7.25 (dd, *J* = 7.9, 4.7 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.88, 144.78, 135.36, 127.31, 120.86, 117.55, 111.34, 89.07, 31.78. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_9H_8N_3S$, 190.0433; Found: 190.0434.

N-(2-oxo-5-phenyl-2,3-dihydro-1H-benzo[e][1,4]diazepin-3-yl)-3-thiocyanato-1H-indole-2-carboxamide (8m)

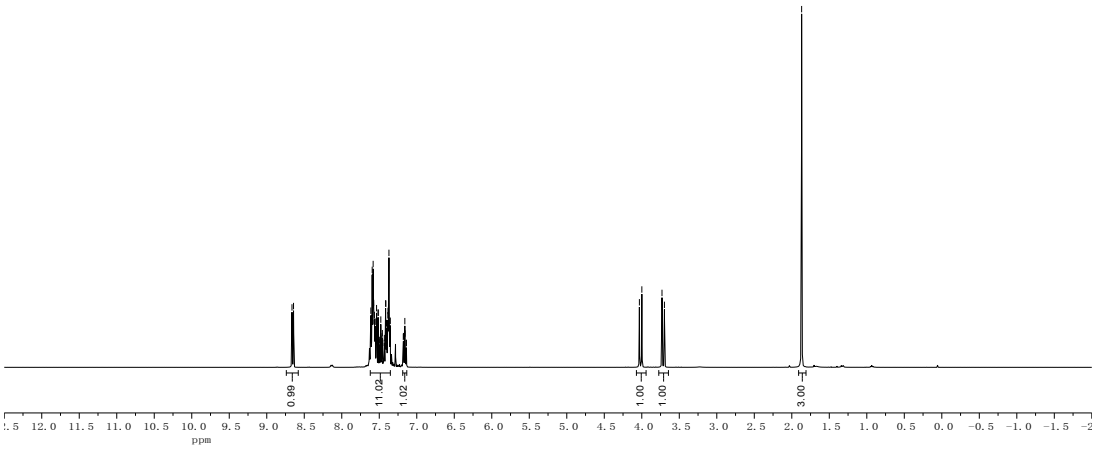


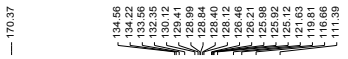
White solid (63 mg, 70% yield), mp 280 – 282 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.66 (s, 1H), 10.97 (s, 1H), 9.54 (d, J = 7.9 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.56 – 7. 45 (m, 6H), 7.40 – 7.33 (m, 3H), 7.28 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 5.54 (d, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.57, 167.60, 161.37, 139.31, 138.64, 137.11, 132.71, 131.38, 131.08, 129.99, 128.79, 127.52, 126.79, 124.10, 123.74, 122.21, 121.93, 120.27, 112.82, 104.92, 69.04. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{17}N_5NaO_2S$, 474.0995; Found: 474.1000.

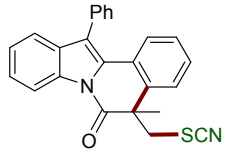
4. NMR Copies of Products



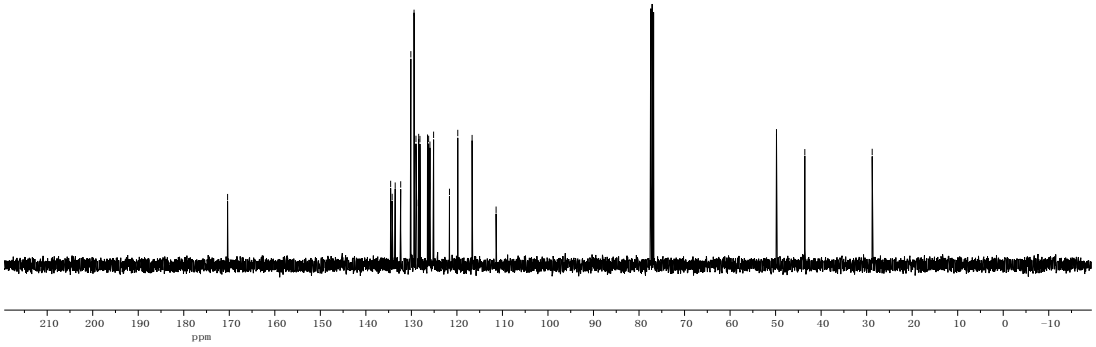
2a, ^{1}H NMR, 400 MHz, $CDCl_3$

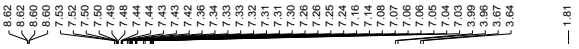


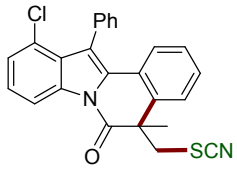




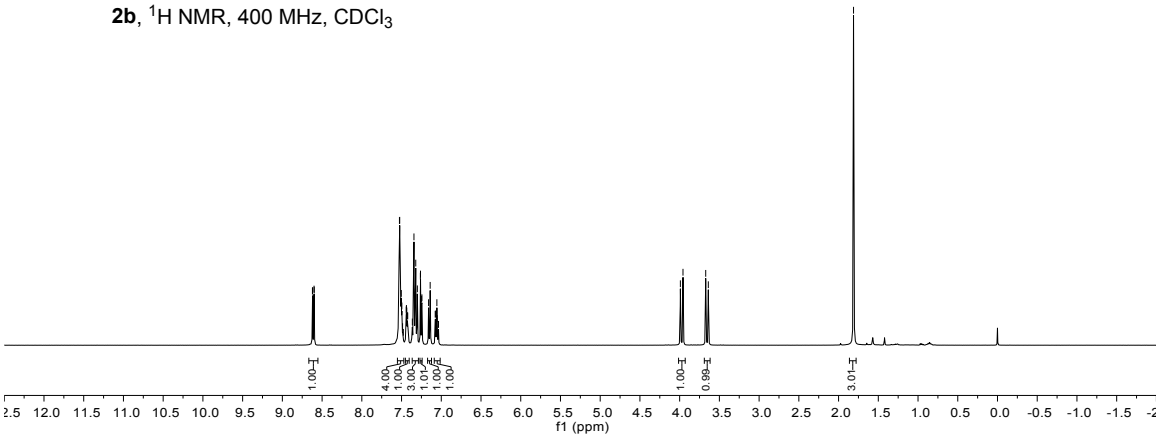
2a, ^{13}C NMR, 101 MHz, $CDCl_3$

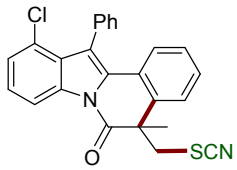




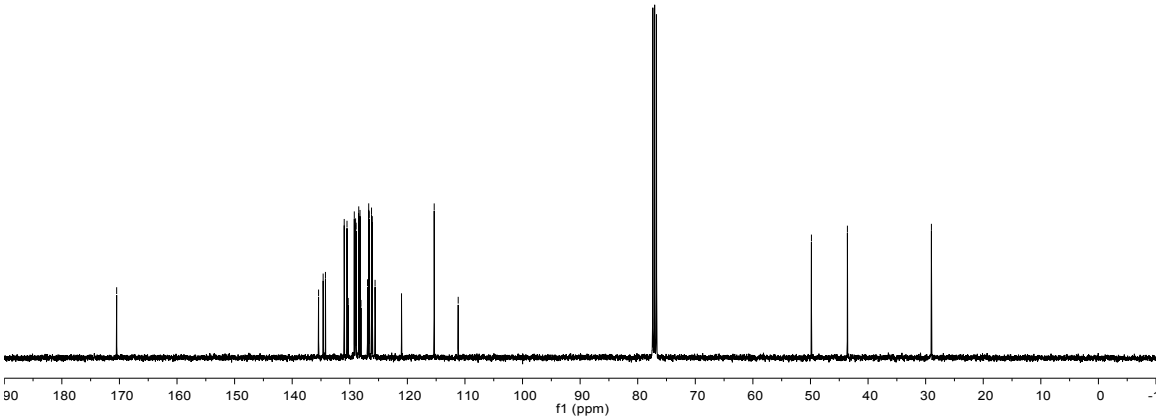


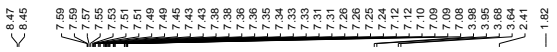
2b, ^{1}H NMR, 400 MHz, $CDCl_3$

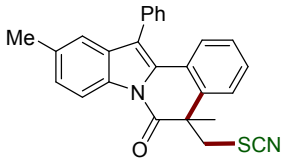




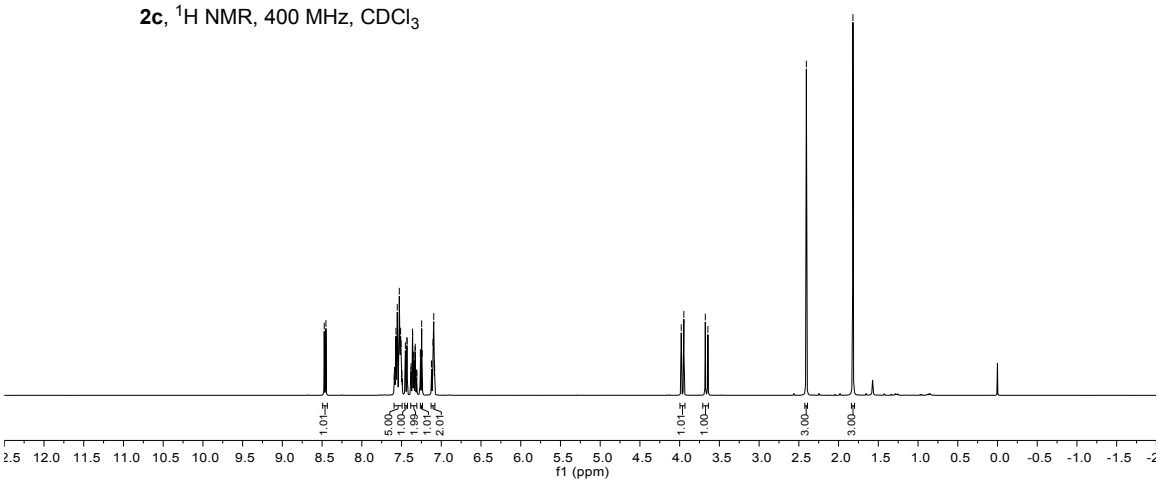
2b, ^{13}C NMR, 101 MHz, $CDCl_3$

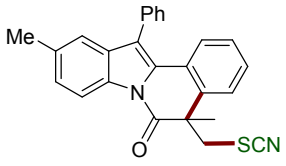




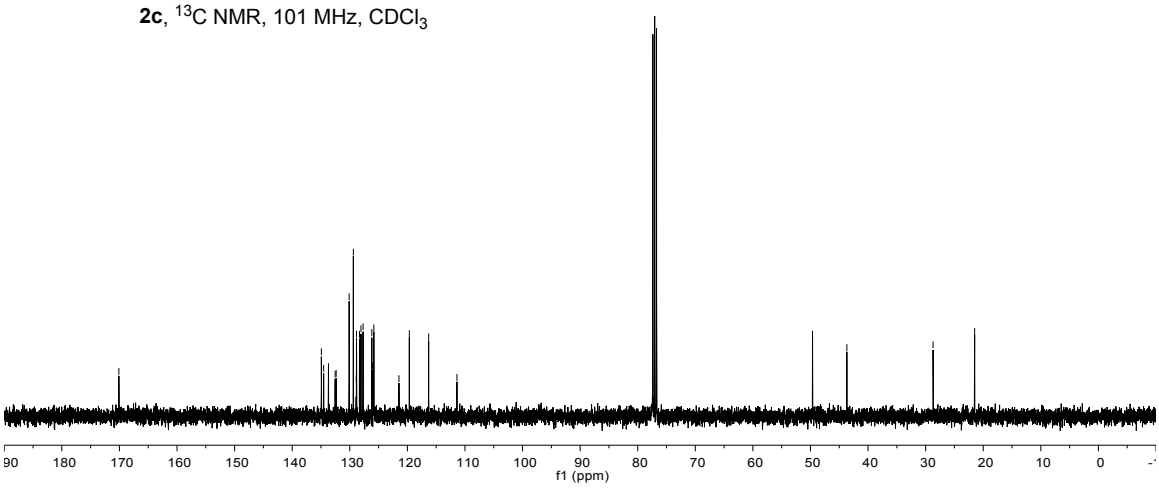


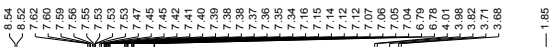
2c, ^{1}H NMR, 400 MHz, $CDCl_3$

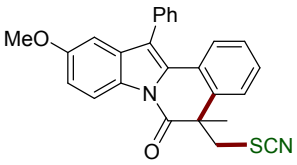




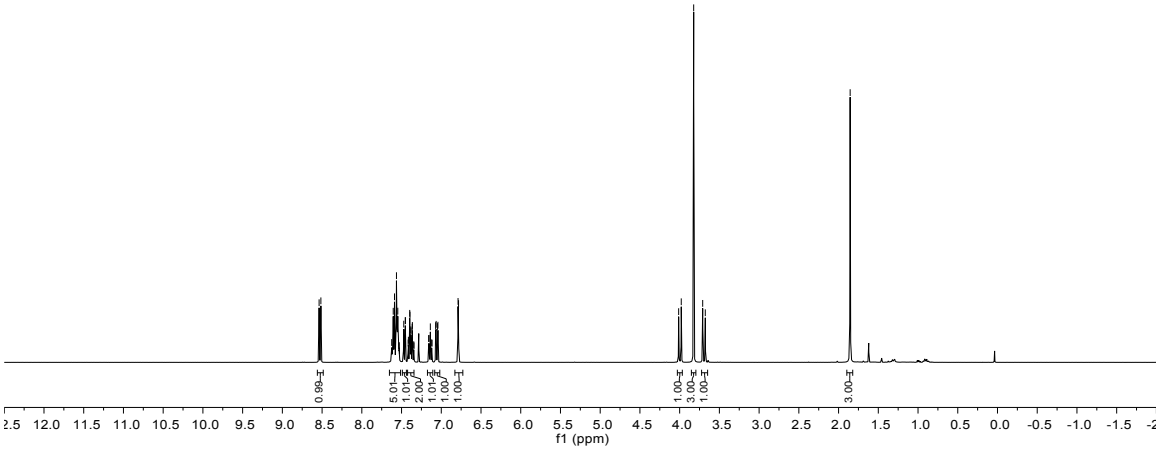
2c, ^{13}C NMR, 101 MHz, $CDCl_3$

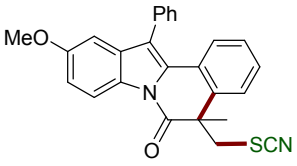




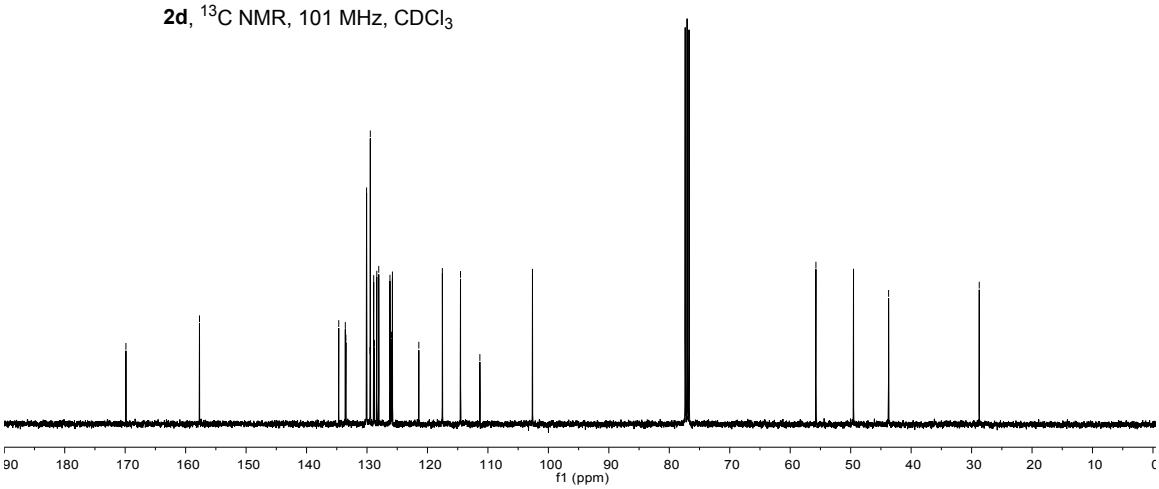


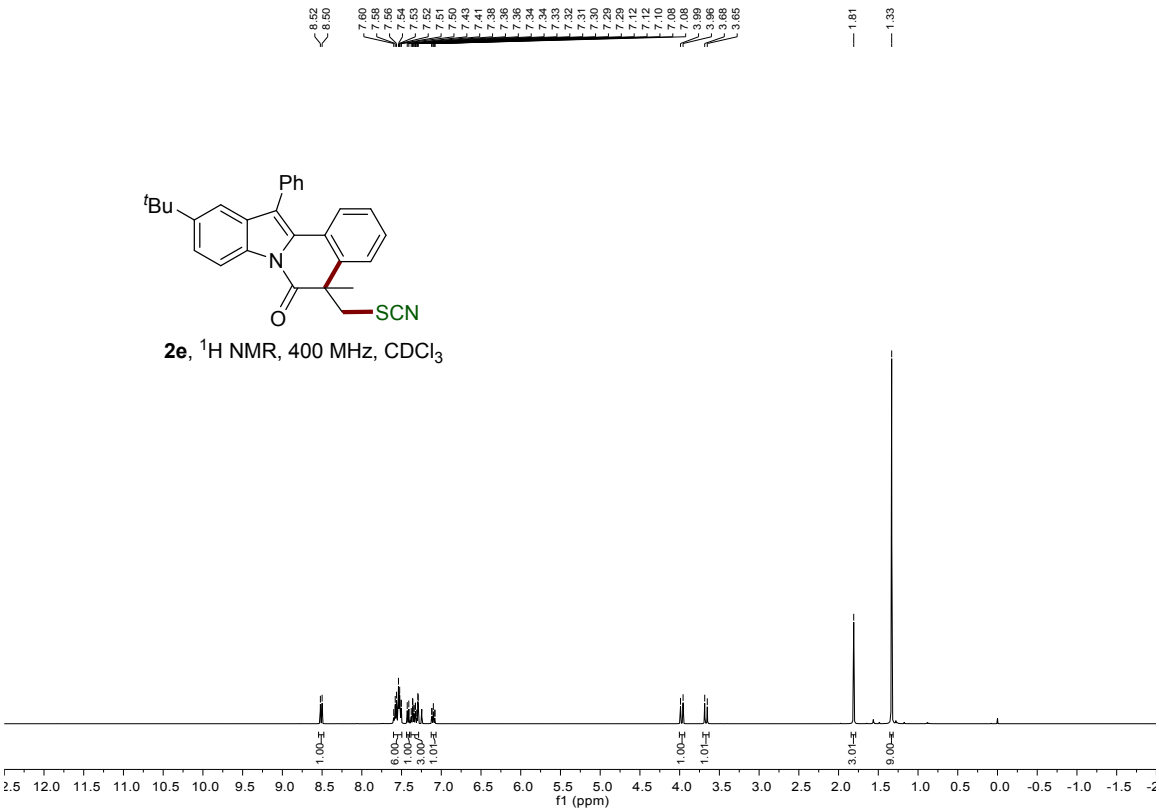
2d, ^{1}H NMR, 400 MHz, $CDCl_3$



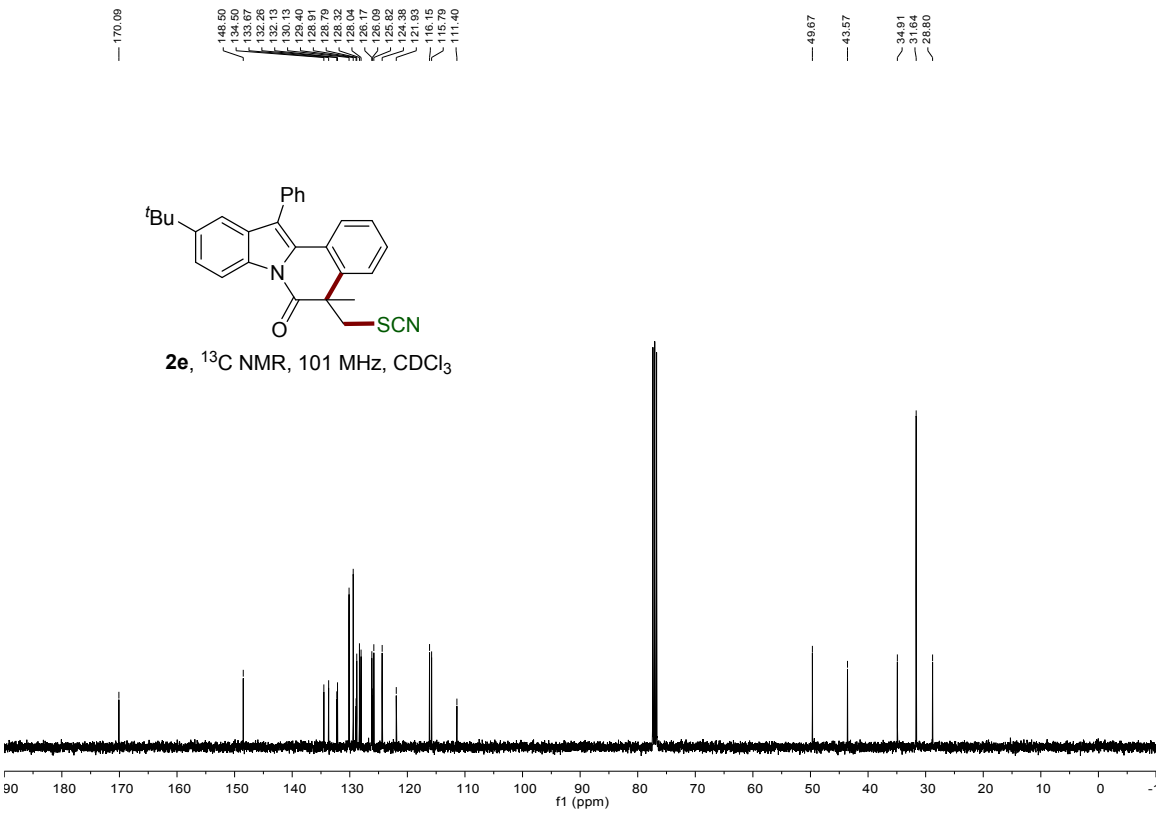


2d, ^{13}C NMR, 101 MHz, $CDCl_3$

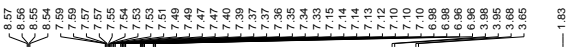


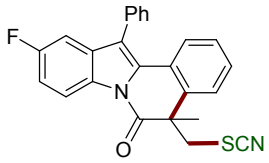


2e, ^{1}H NMR, 400 MHz, $CDCl_3$

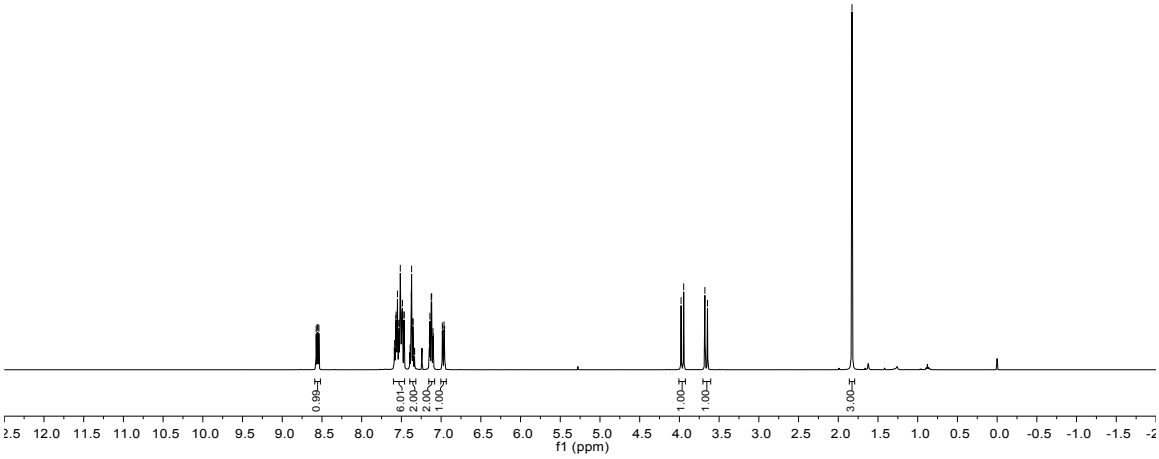


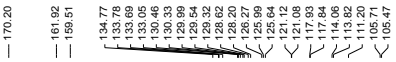
2e, ^{13}C NMR, 101 MHz, $CDCl_3$

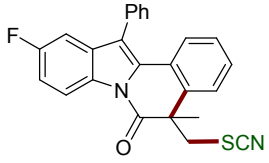




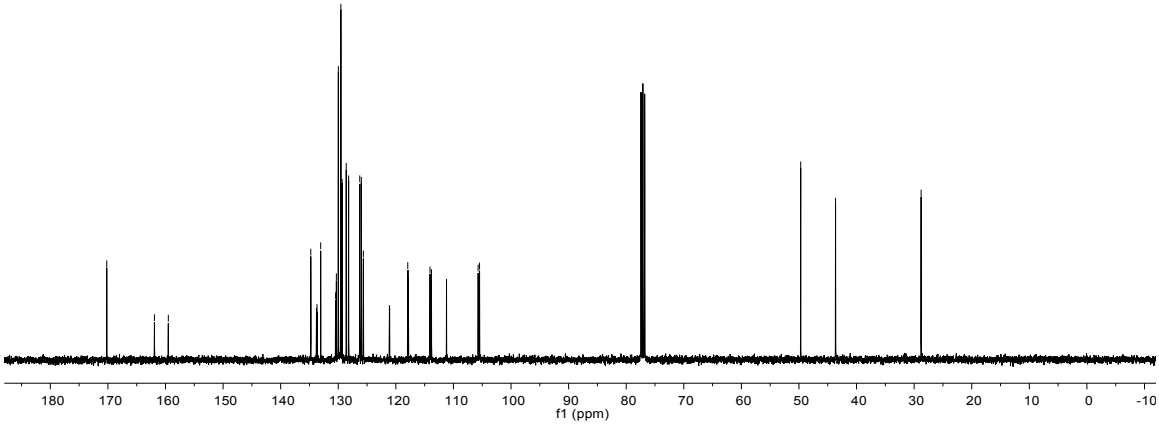
2f, ^{1}H NMR, 400 MHz, $CDCl_3$

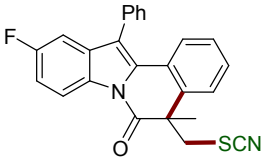




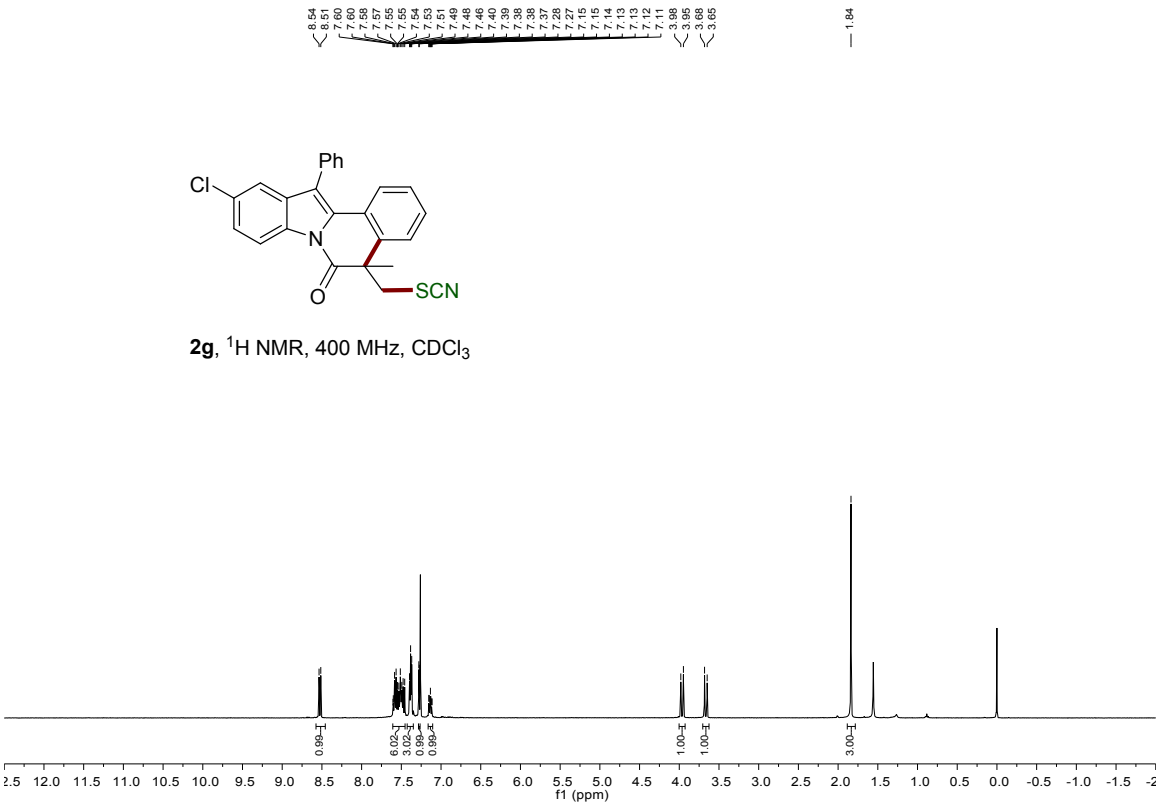


2f, ^{13}C NMR, 101 MHz, $CDCl_3$

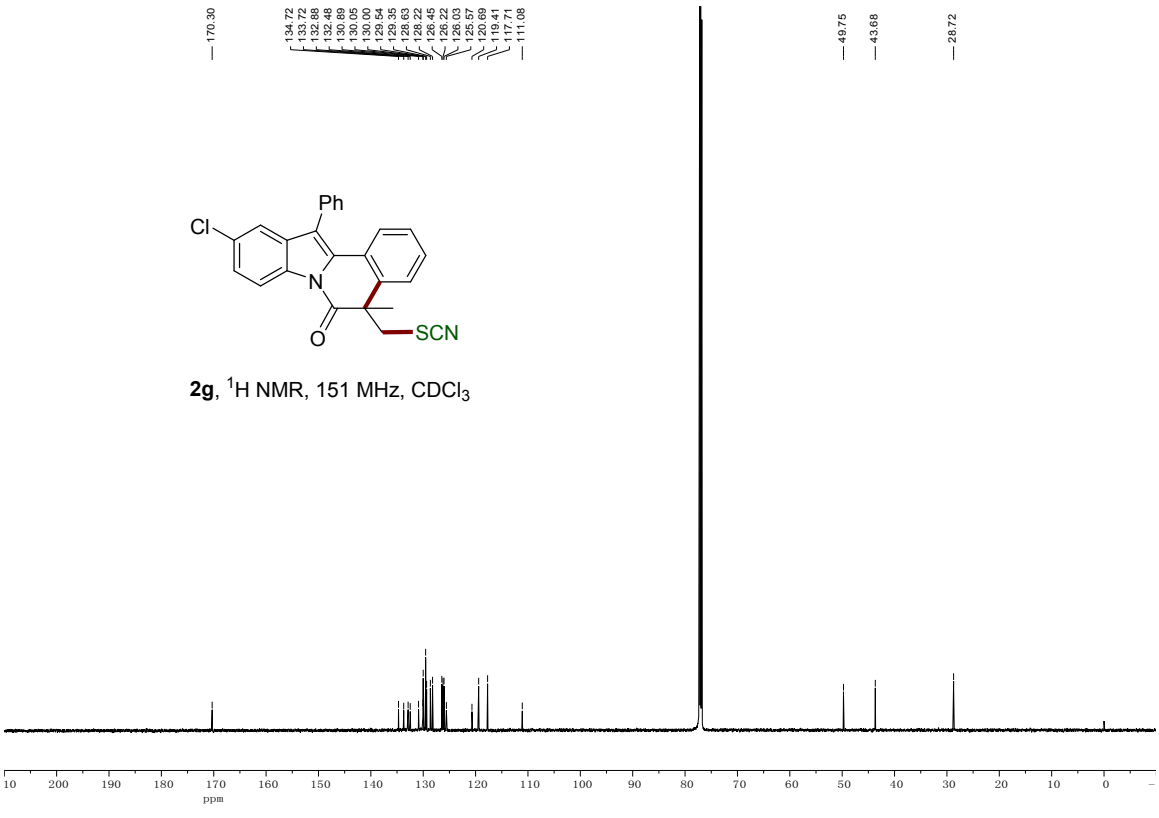




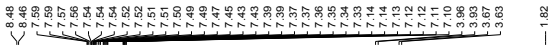
2f, ^{19}F NMR, 376 MHz, $CDCl_3$

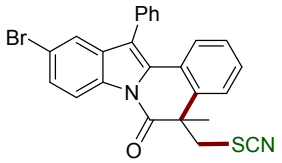


2g, ^{1}H NMR, 400 MHz, $CDCl_3$

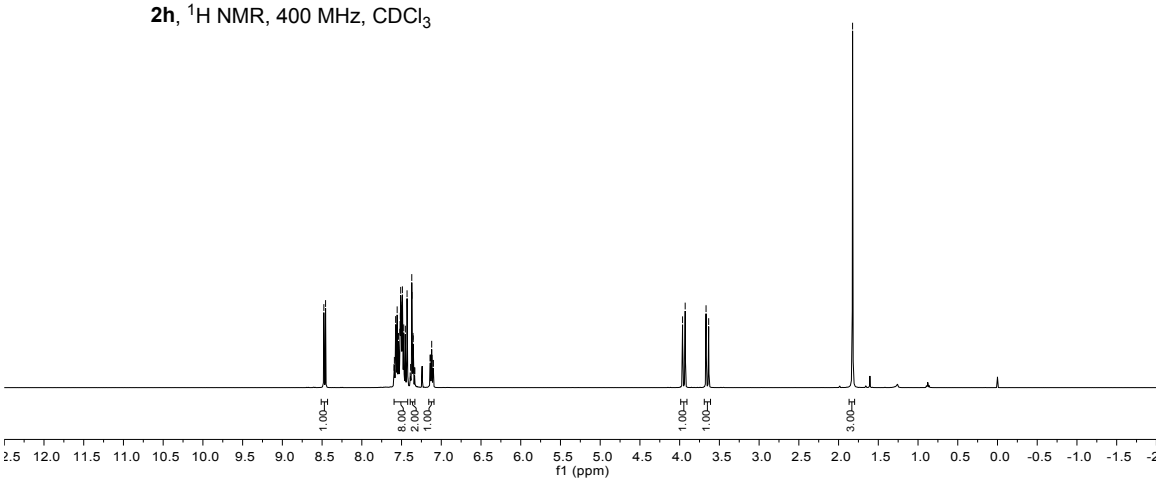


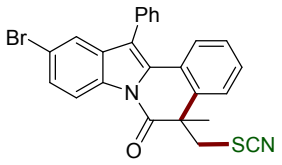
2g, ^{1}H NMR, 151 MHz, $CDCl_3$



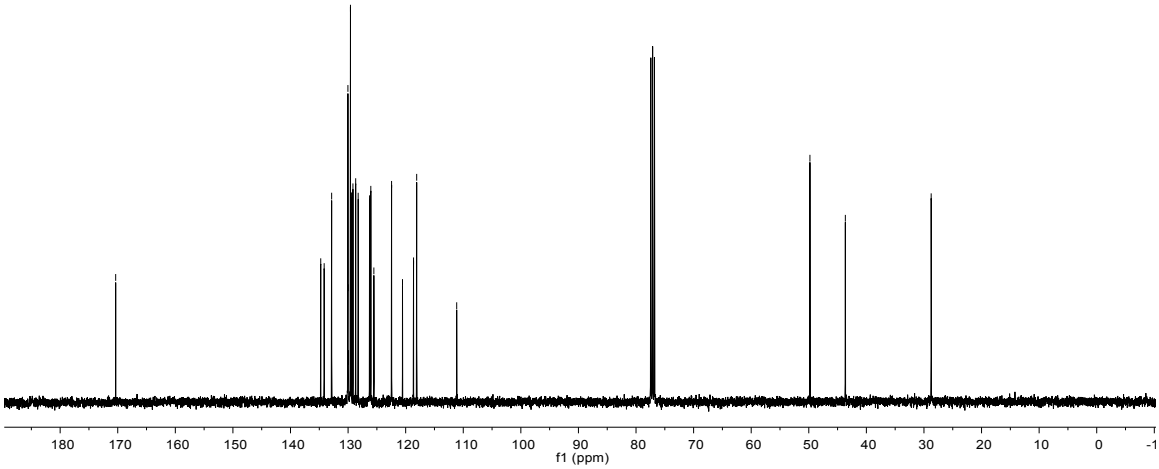


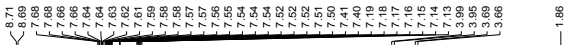
2h, ^{1}H NMR, 400 MHz, $CDCl_3$

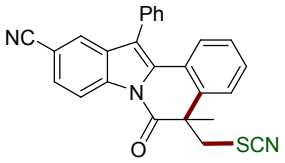




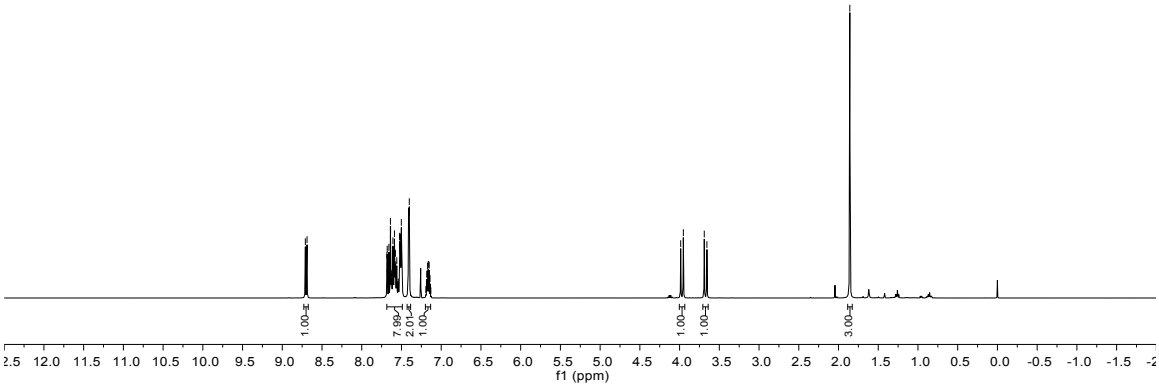
2h, ^{13}C NMR, 101 MHz, $CDCl_3$

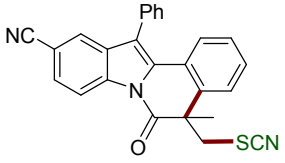




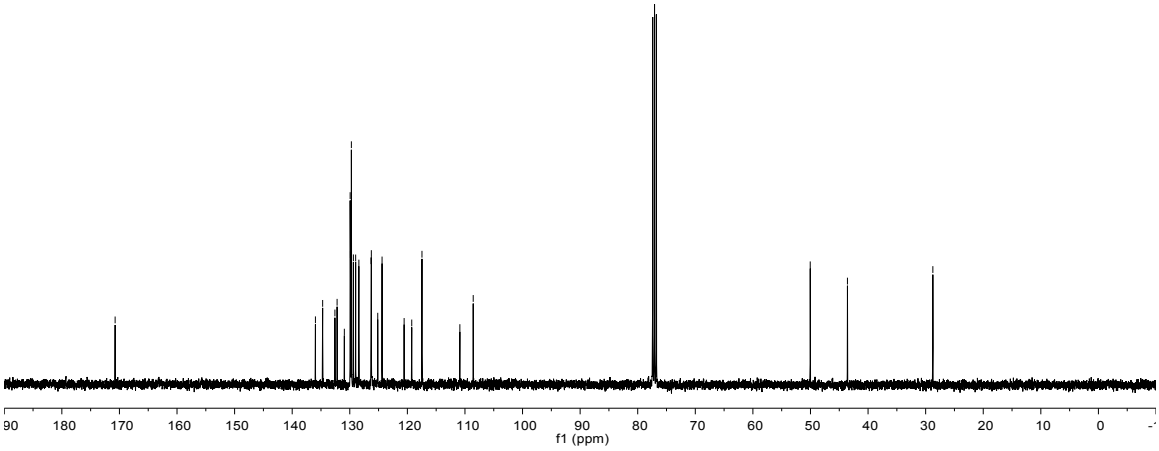


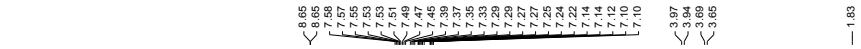
2i, ^{1}H NMR, 400 MHz, $CDCl_3$

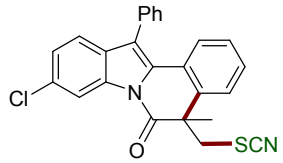




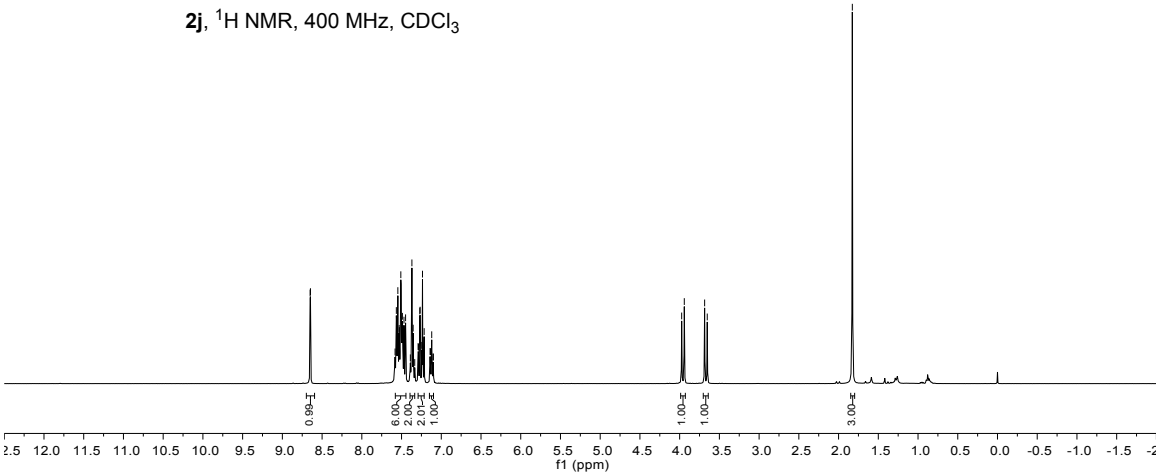
2i, ^{13}C NMR, 101 MHz, $CDCl_3$

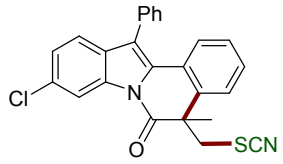




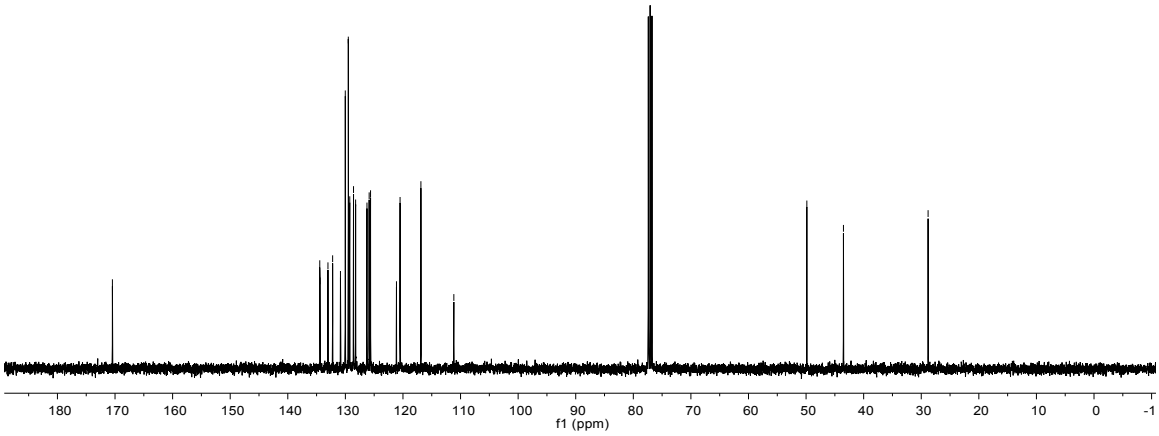


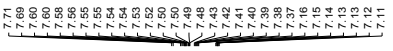
2j, ^{1}H NMR, 400 MHz, $CDCl_3$

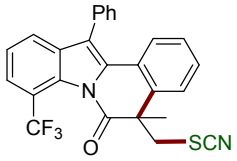




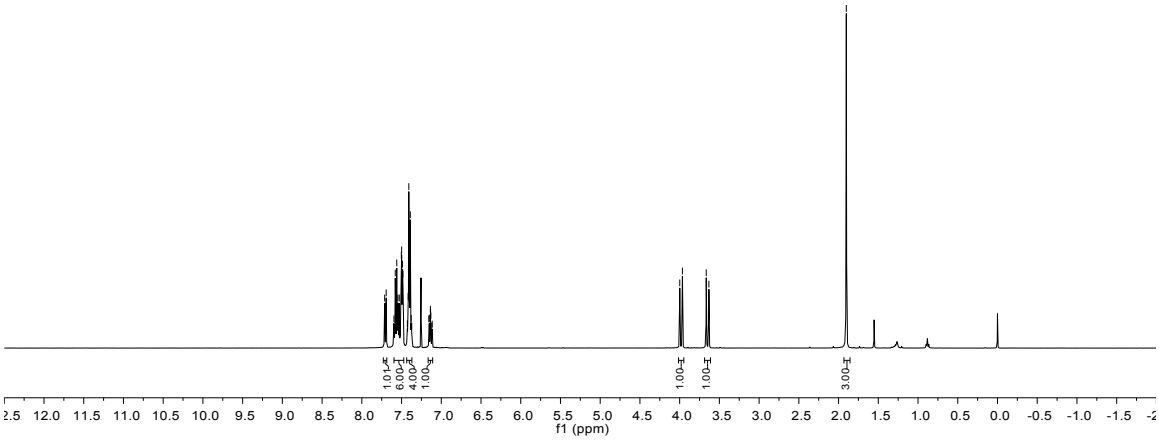
2j, ^{13}C NMR, 101 MHz, $CDCl_3$

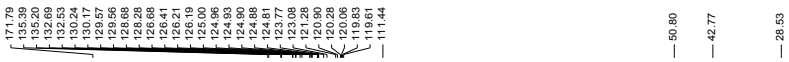


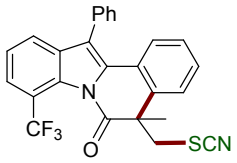




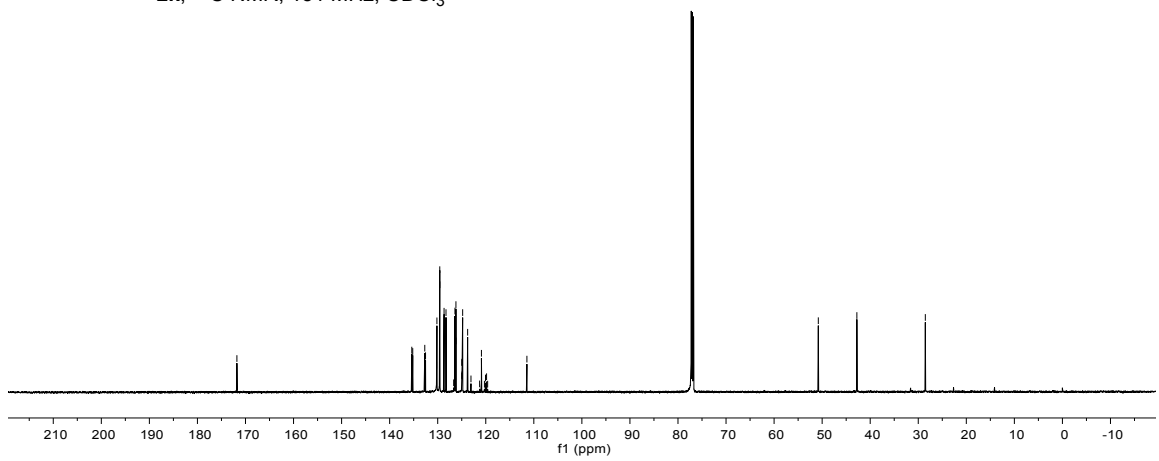
2k, ^{1}H NMR, 400 MHz, $CDCl_3$

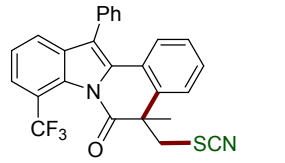




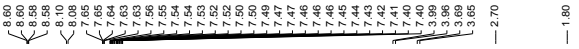


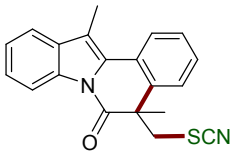
2k, ^{13}C NMR, 151 MHz, $CDCl_3$



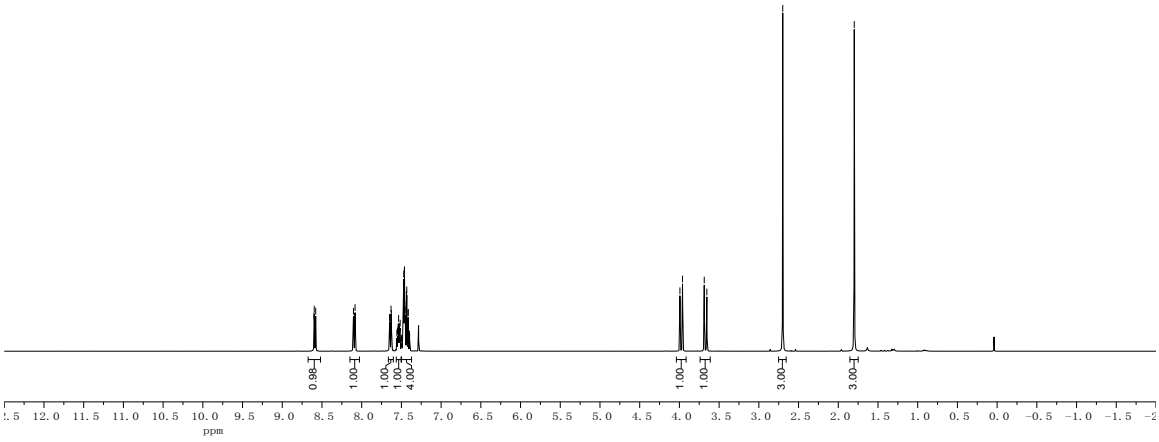


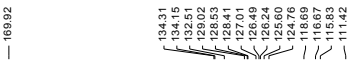
2k, ^{19}F NMR, 376 MHz, $CDCl_3$

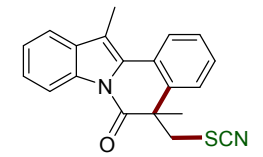




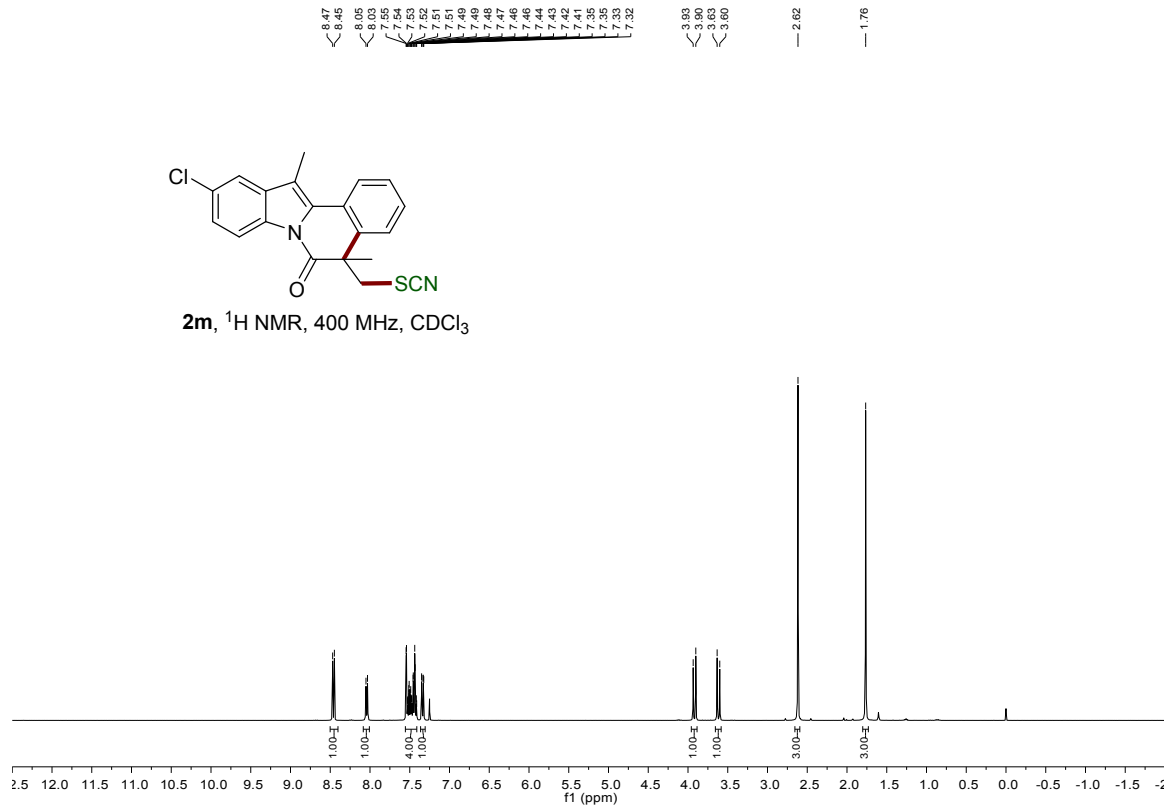
2l, ^{1}H NMR, 400 MHz, $CDCl_3$



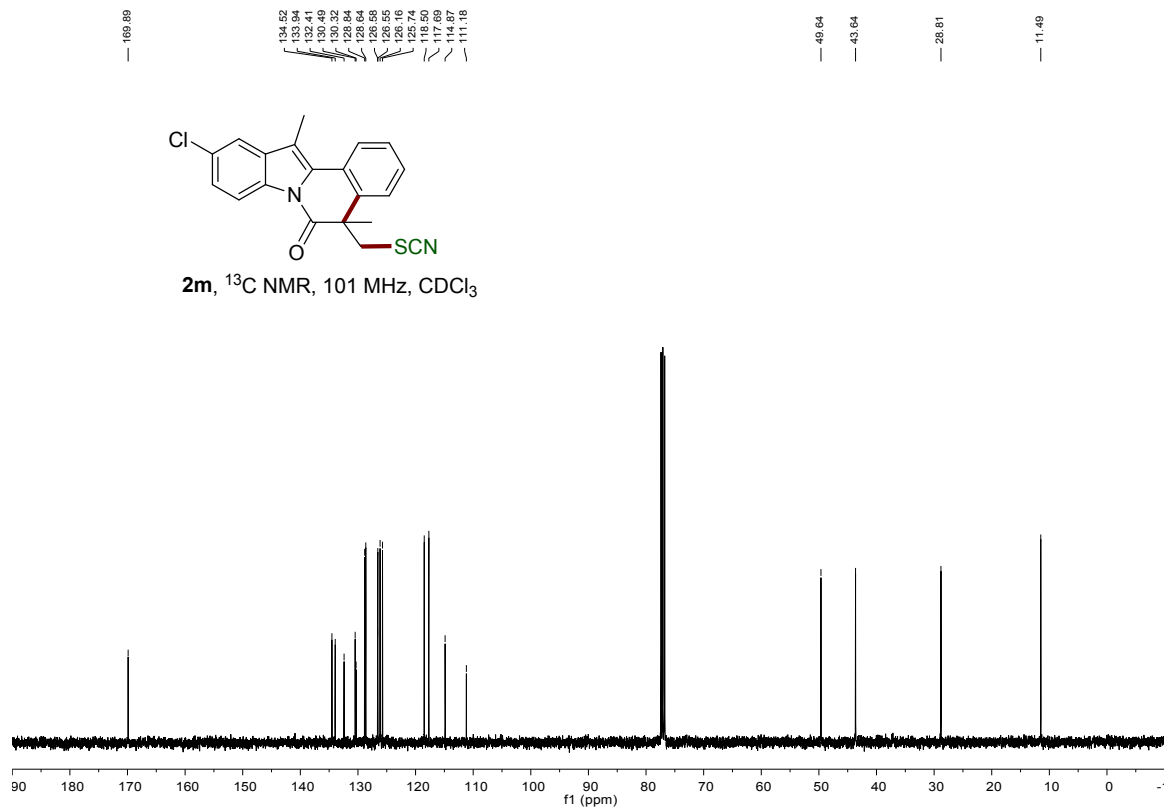




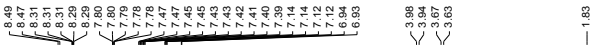
2l, ^{13}C NMR, 101 MHz, $CDCl_3$

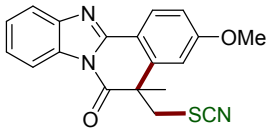


2m, ^{1}H NMR, 400 MHz, $CDCl_3$

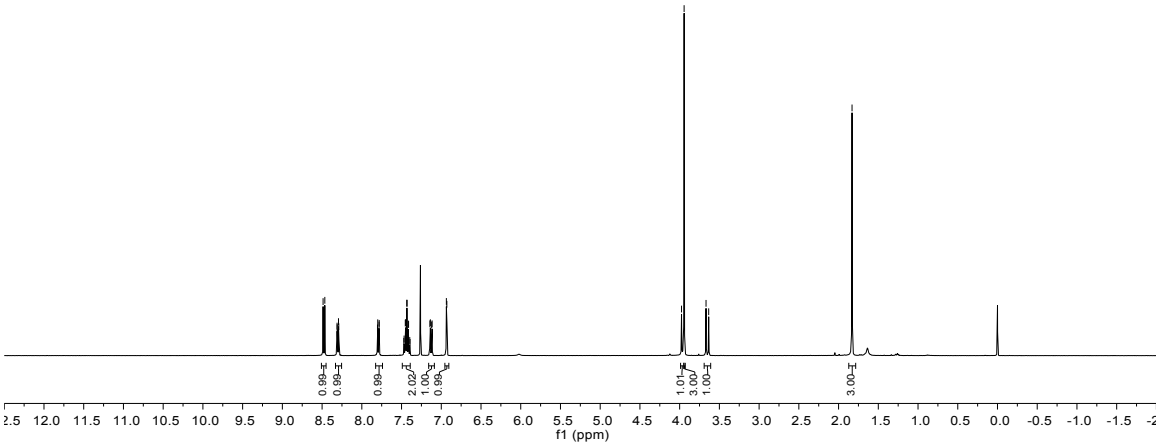


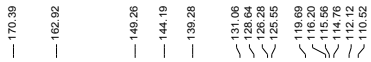
2m, ^{13}C NMR, 101 MHz, $CDCl_3$

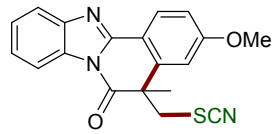




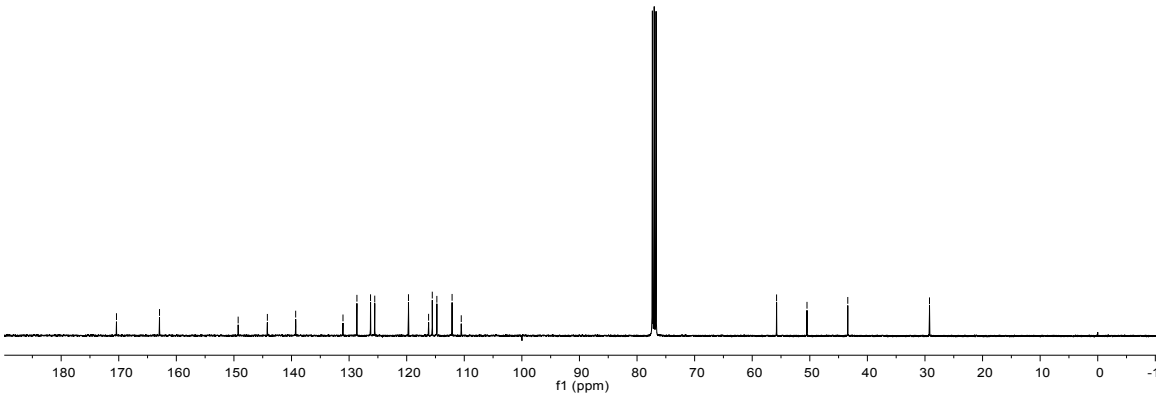
2n, ^{1}H NMR, 400 MHz, $CDCl_3$

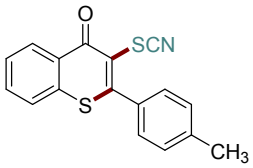




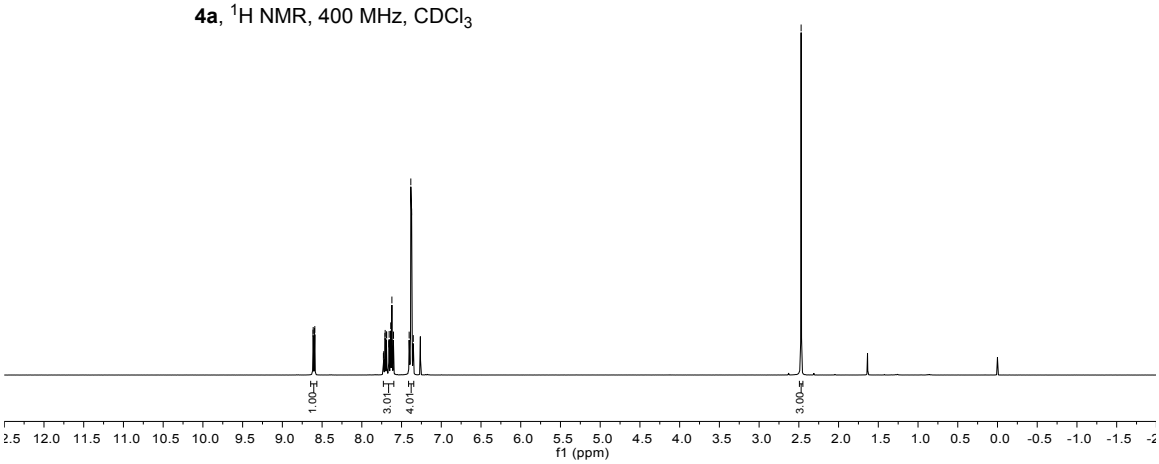


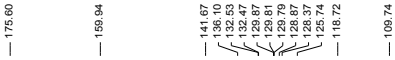
2n, ^{13}C NMR, 101 MHz, $CDCl_3$

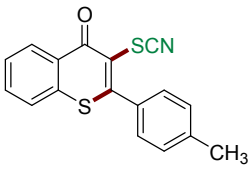




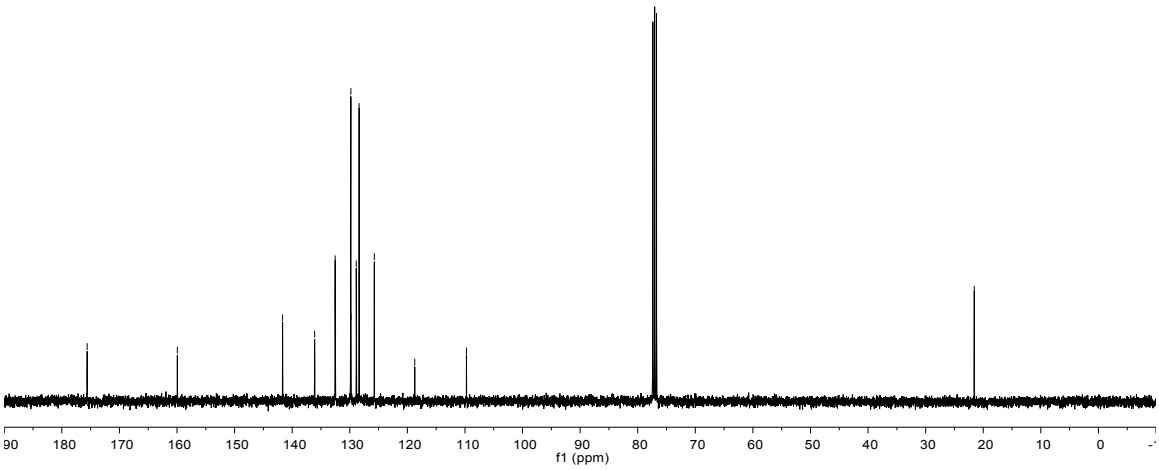
4a, ^{1}H NMR, 400 MHz, $CDCl_3$

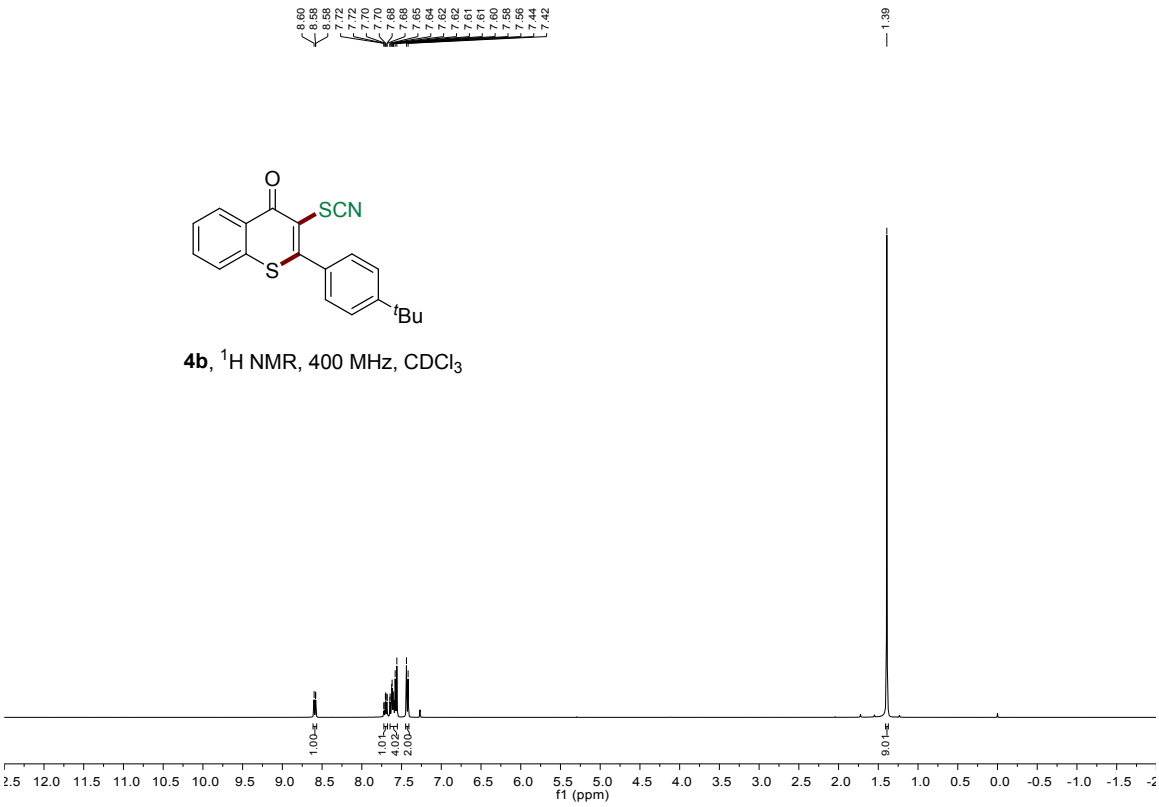




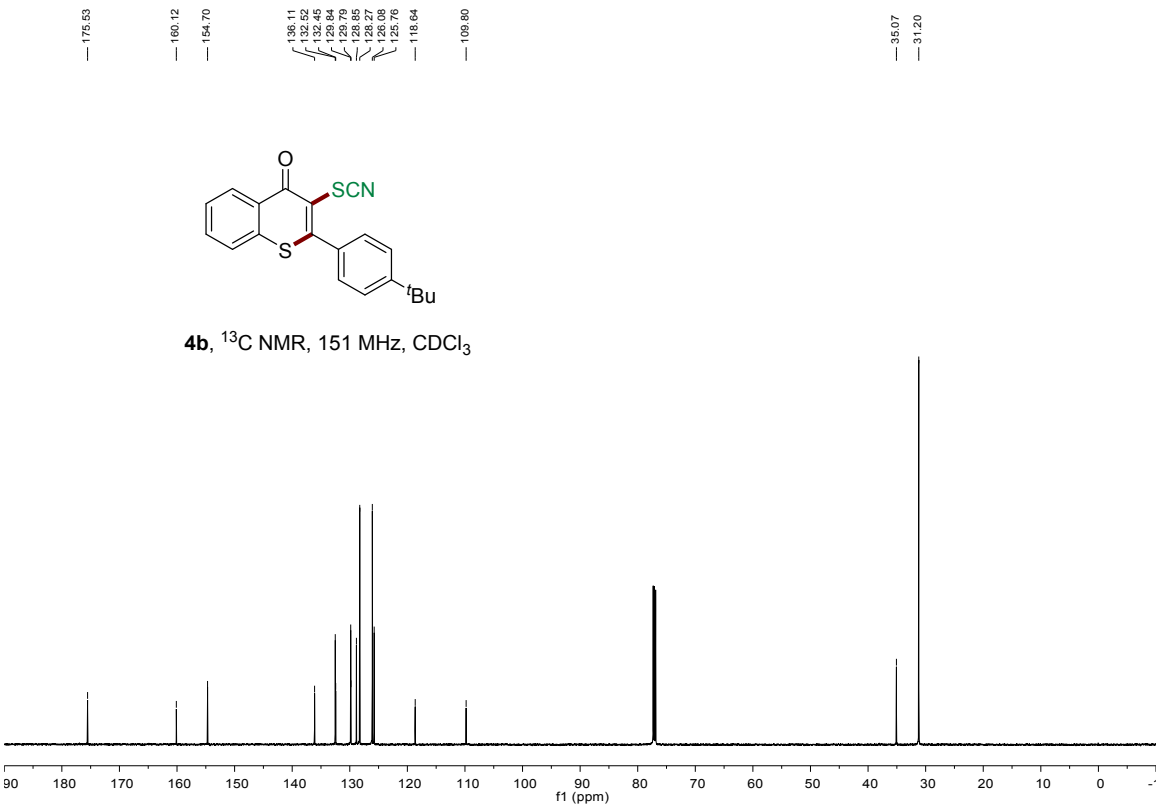


4a, ^{13}C NMR, 101 MHz, $CDCl_3$

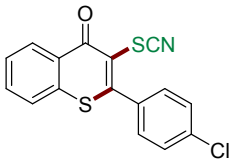




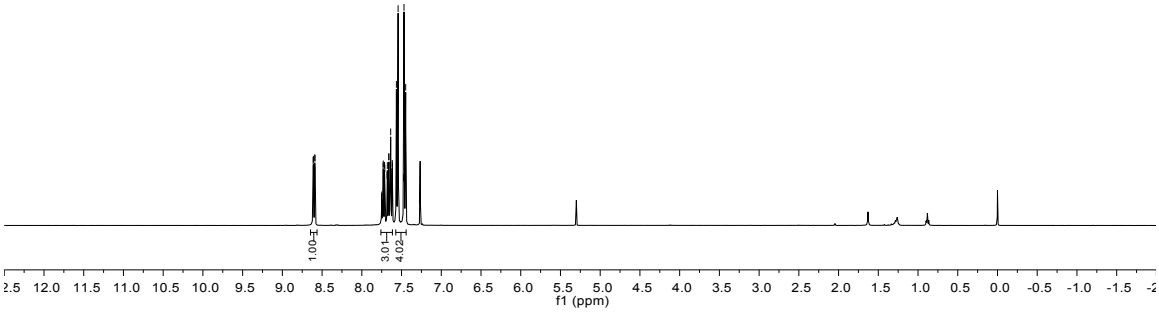
4b, ^{1}H NMR, 400 MHz, $CDCl_3$

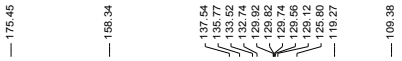


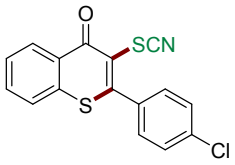
4b, ^{13}C NMR, 151 MHz, $CDCl_3$



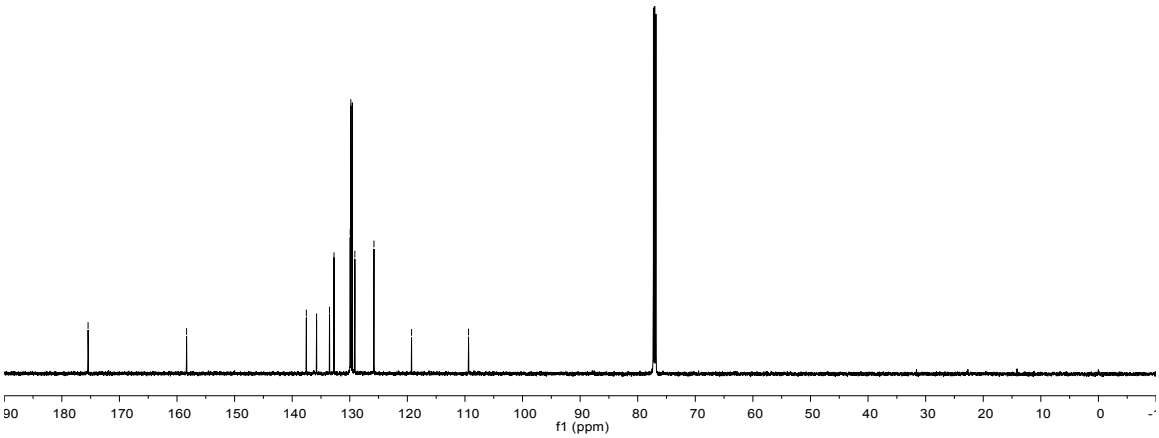
4c, ^{1}H NMR, 400 MHz, $CDCl_3$

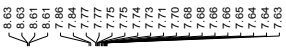


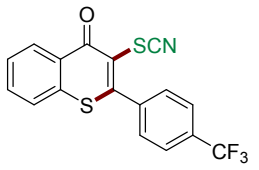




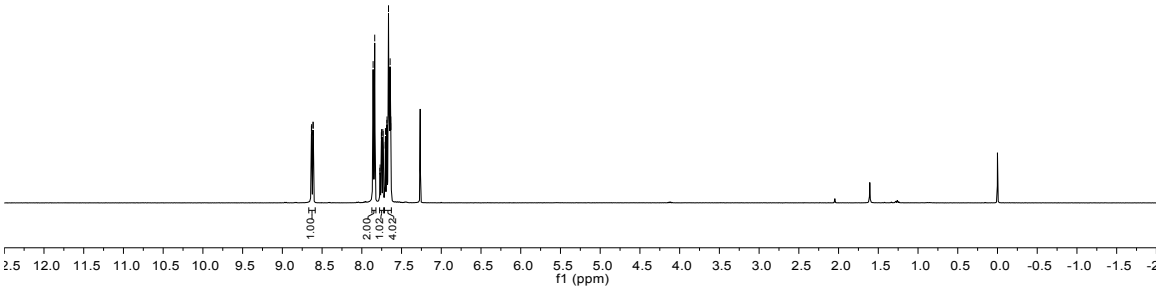
4c, ^{13}C NMR, 151 MHz, $CDCl_3$

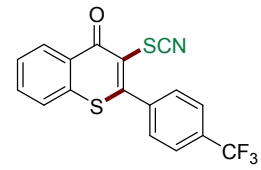




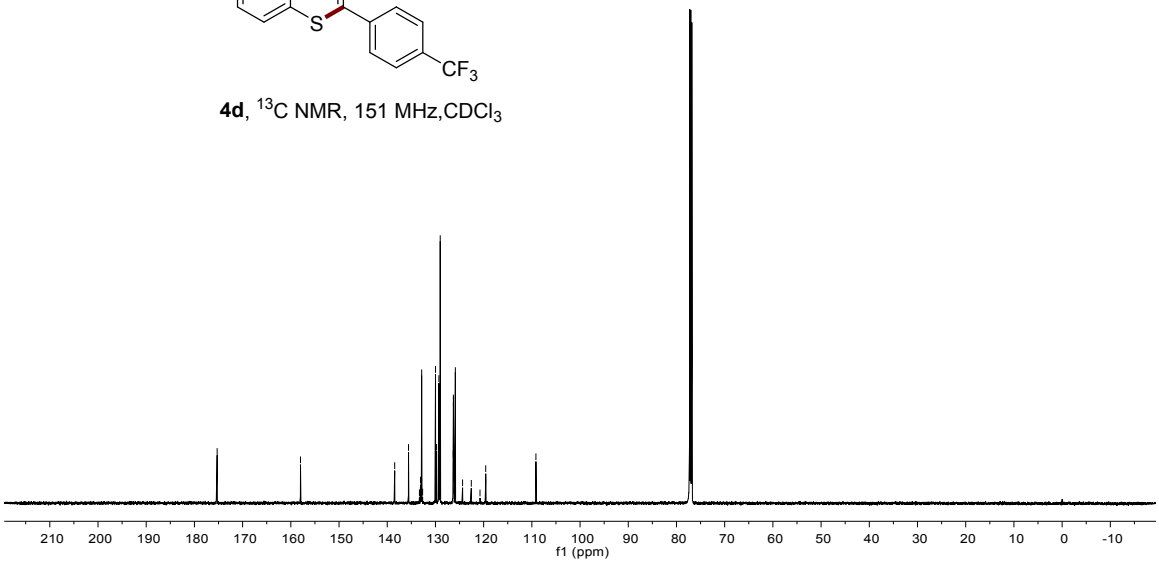


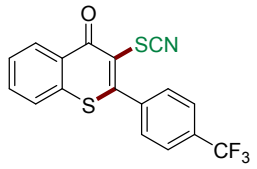
4d, ^{1}H NMR, 400 MHz, $CDCl_3$



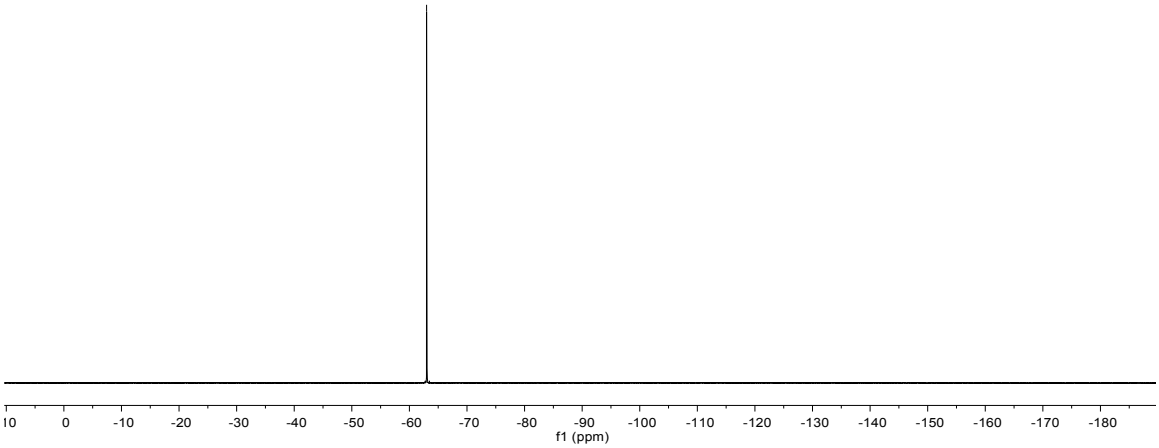


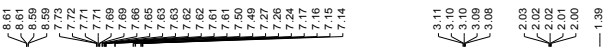
4d, ^{13}C NMR, 151 MHz,$CDCl_3$

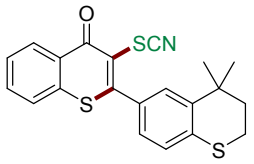




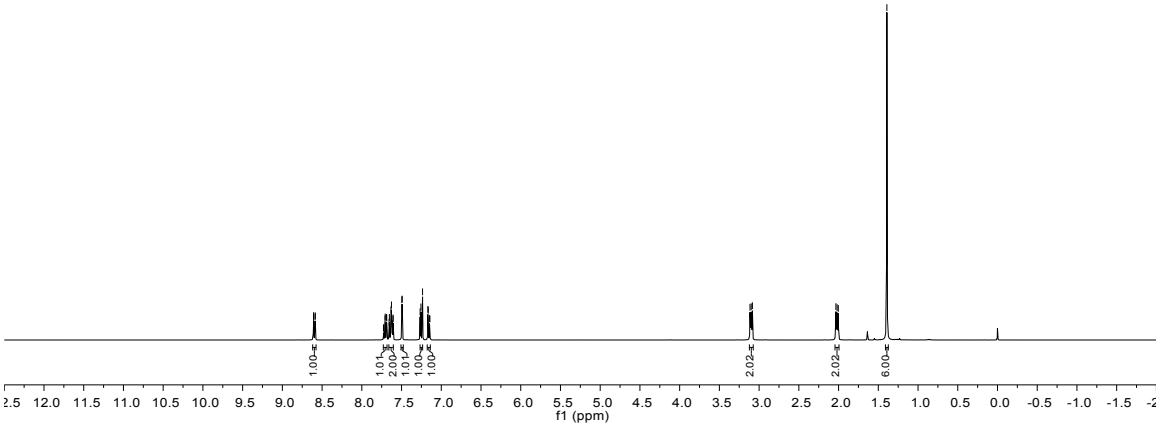
4d, ^{19}F NMR, 376 MHz, $CDCl_3$

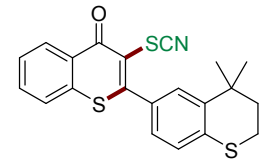




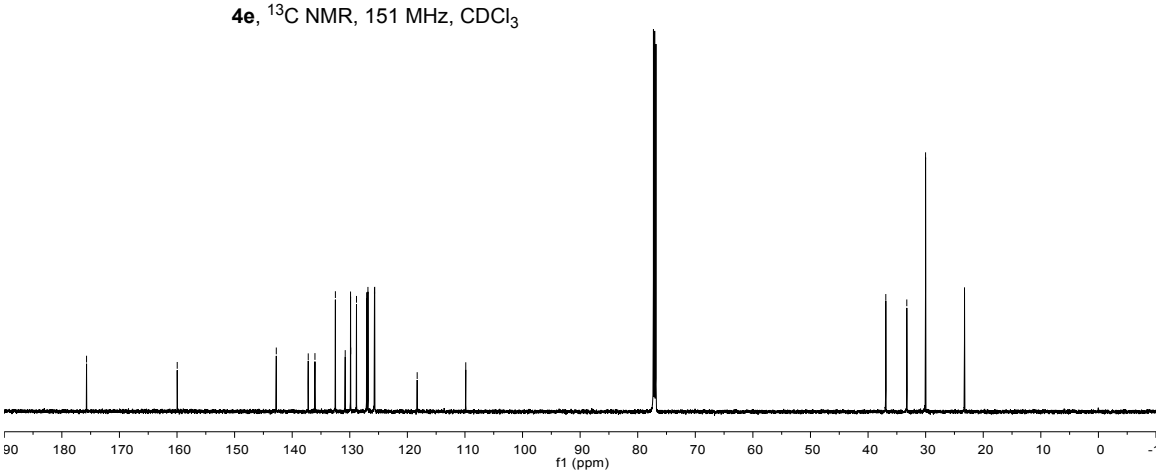


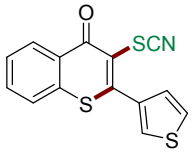
4e, ^{1}H NMR, 400 MHz, $CDCl_3$



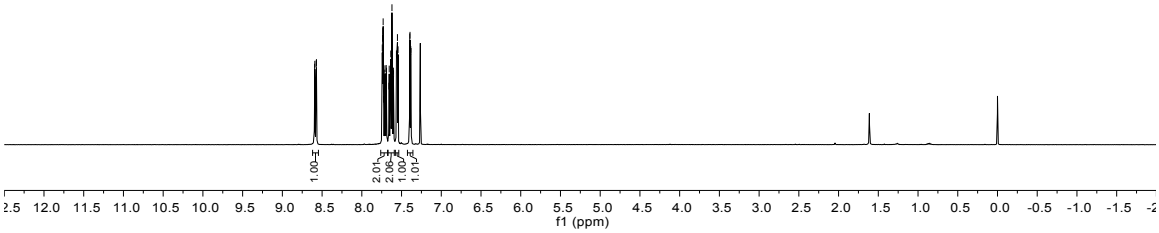


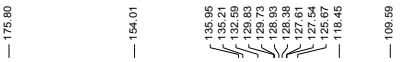
4e, ^{13}C NMR, 151 MHz, $CDCl_3$

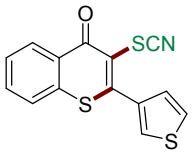




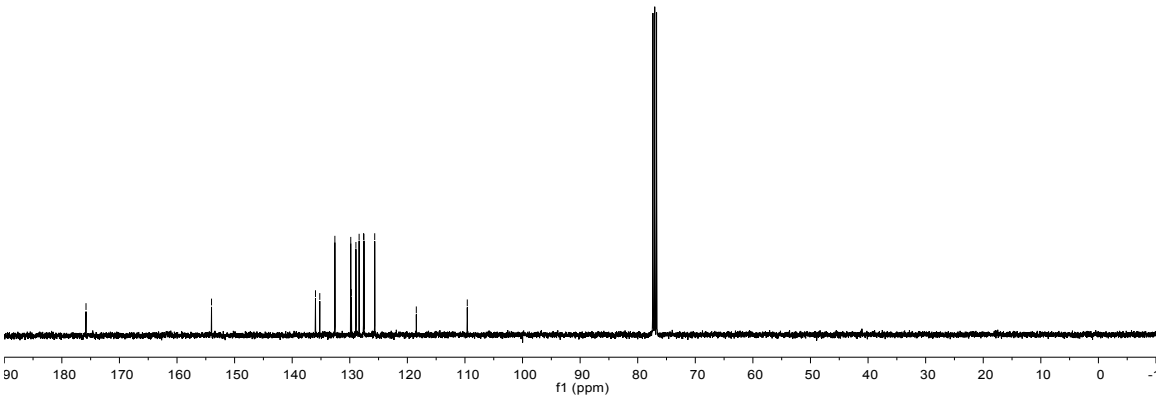
4f, ^{1}H NMR, 400 MHz, $CDCl_3$

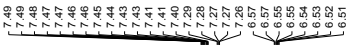


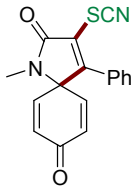




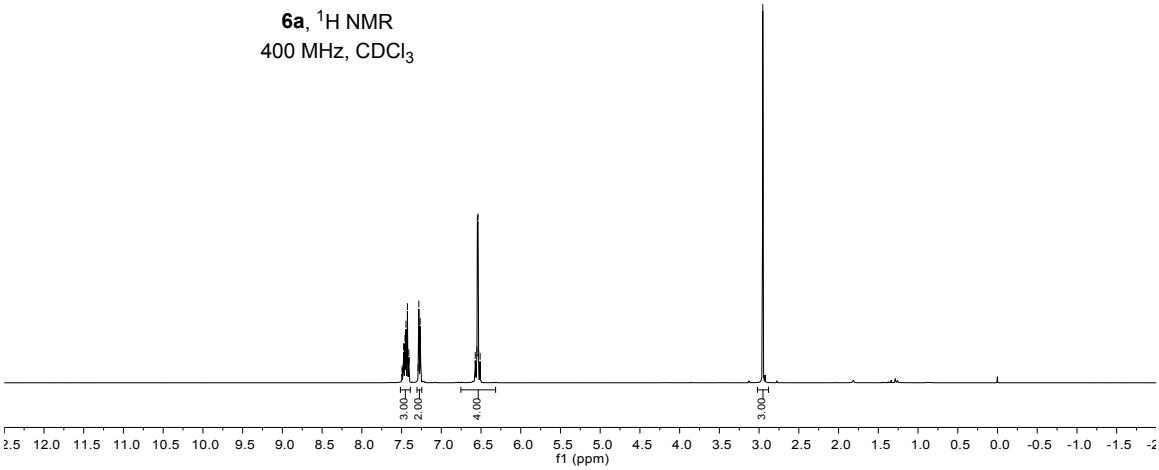
4f, ^{13}C NMR, 101 MHz, $CDCl_3$



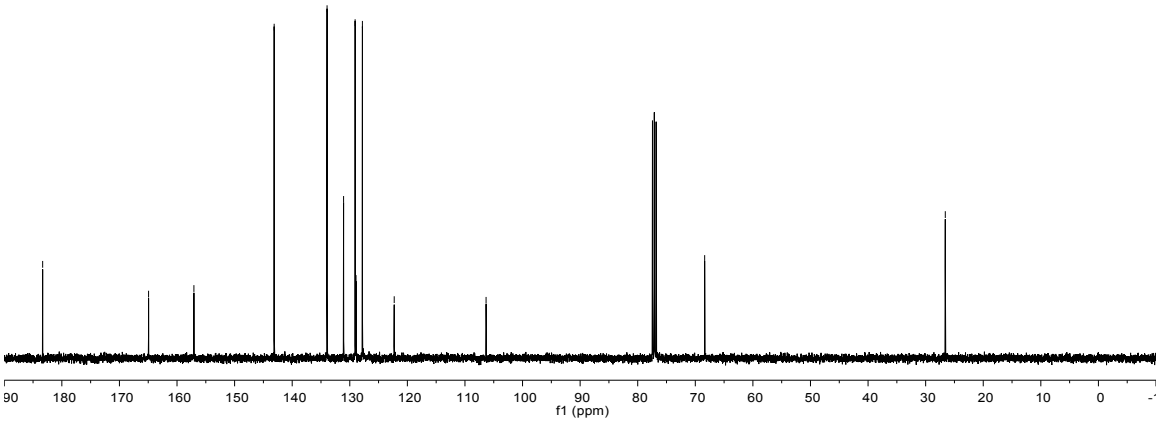


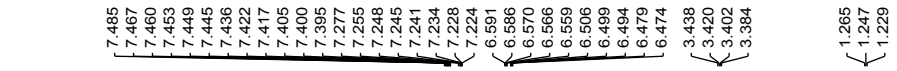


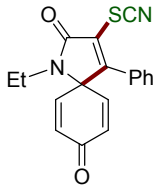
6a, ^{1}H NMR
400 MHz, $CDCl_3$



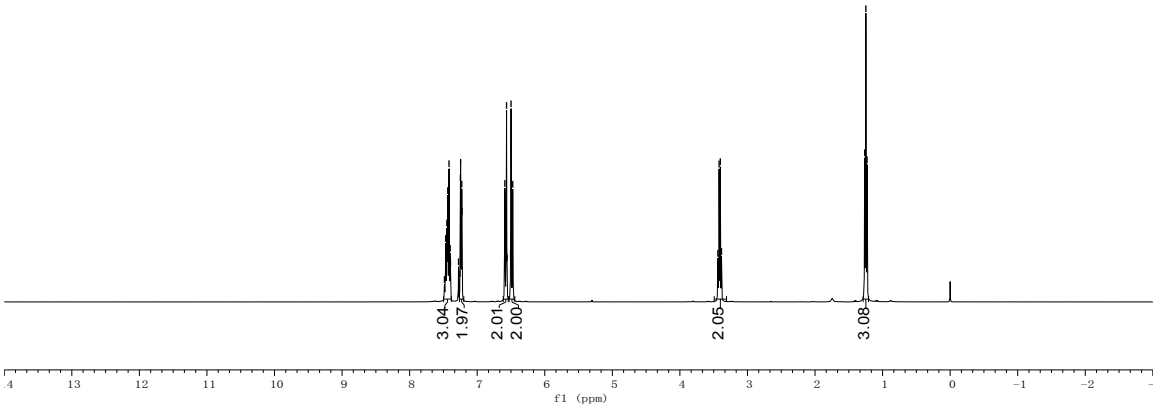
6a, ^{13}C NMR
101 MHz, $CDCl_3$

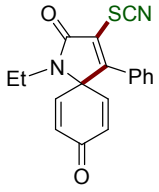




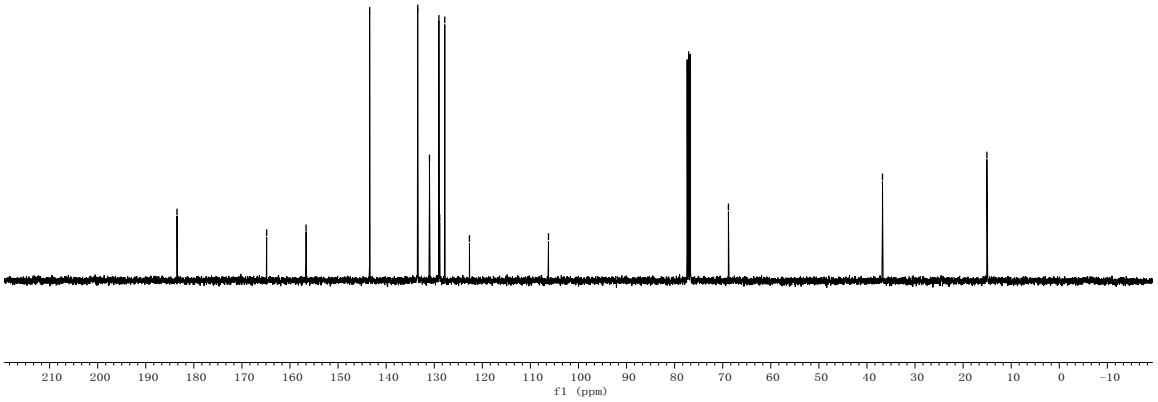


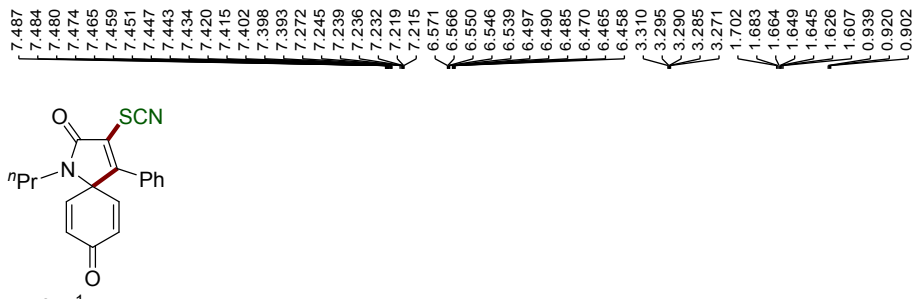
6b, ^{1}H NMR
400 MHz, $CDCl_3$



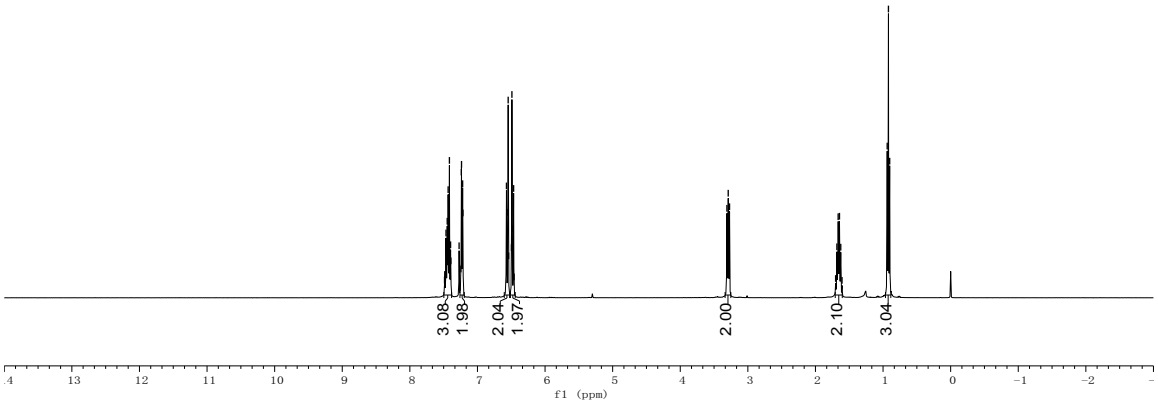


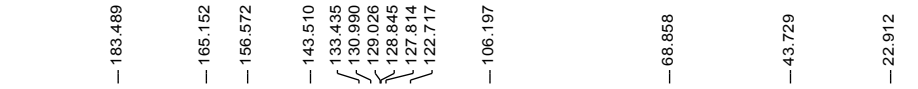
6b, ^{13}C NMR
101 MHz, $CDCl_3$

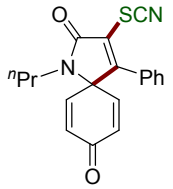




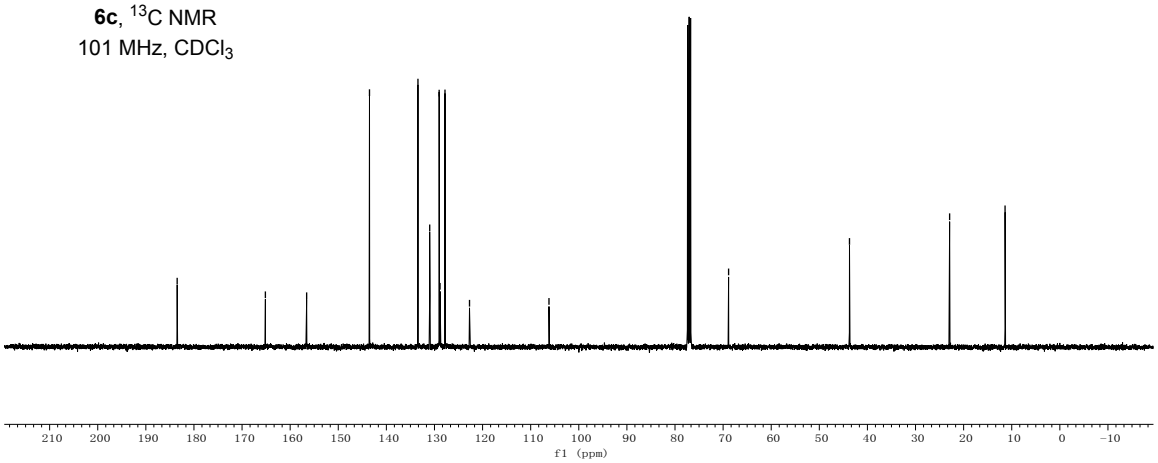
6c, ^{1}H NMR
400 MHz, $CDCl_3$

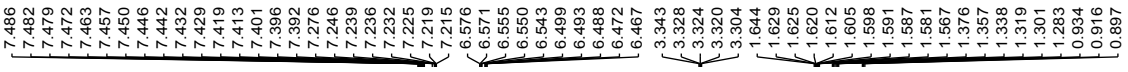


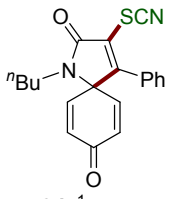




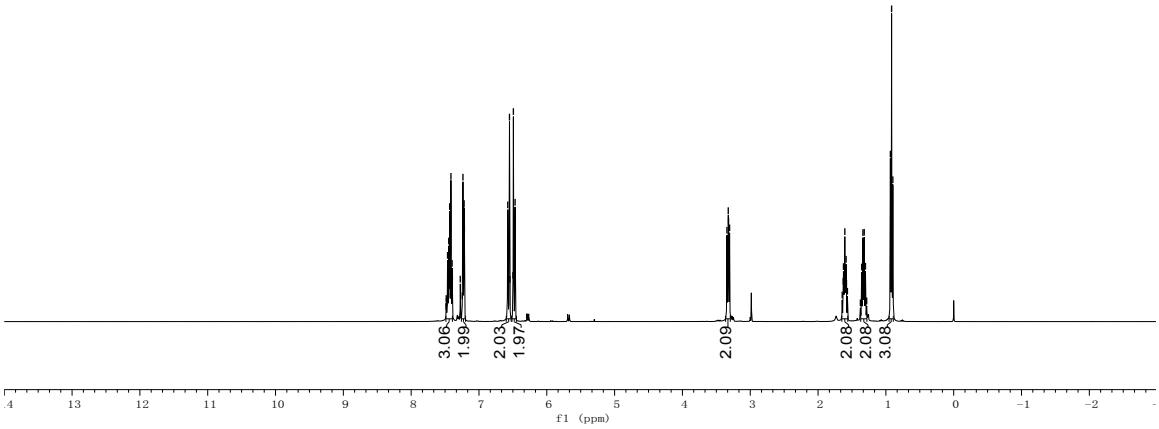
6c, ^{13}C NMR
101 MHz, $CDCl_3$

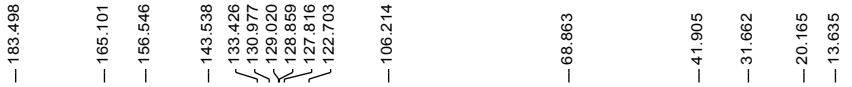


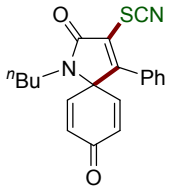




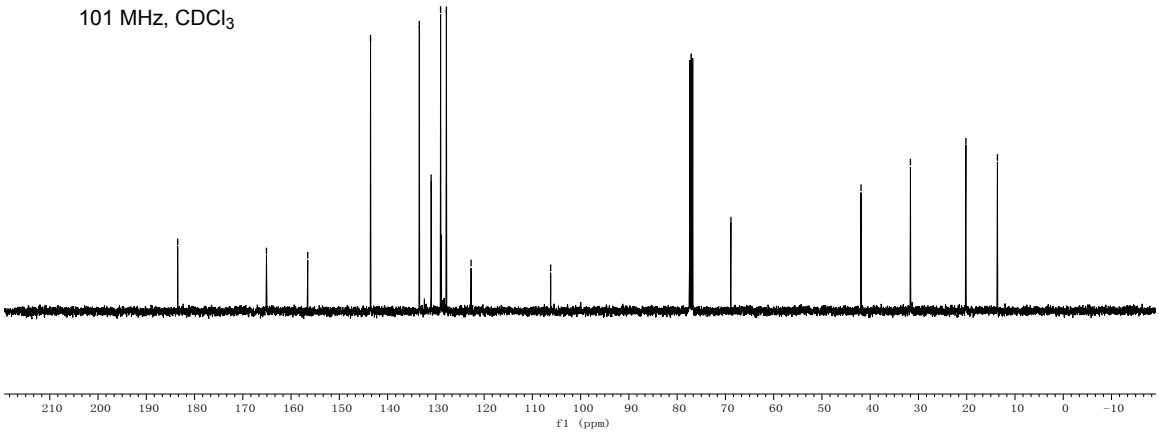
6d, ^{1}H NMR
400 MHz, $CDCl_3$

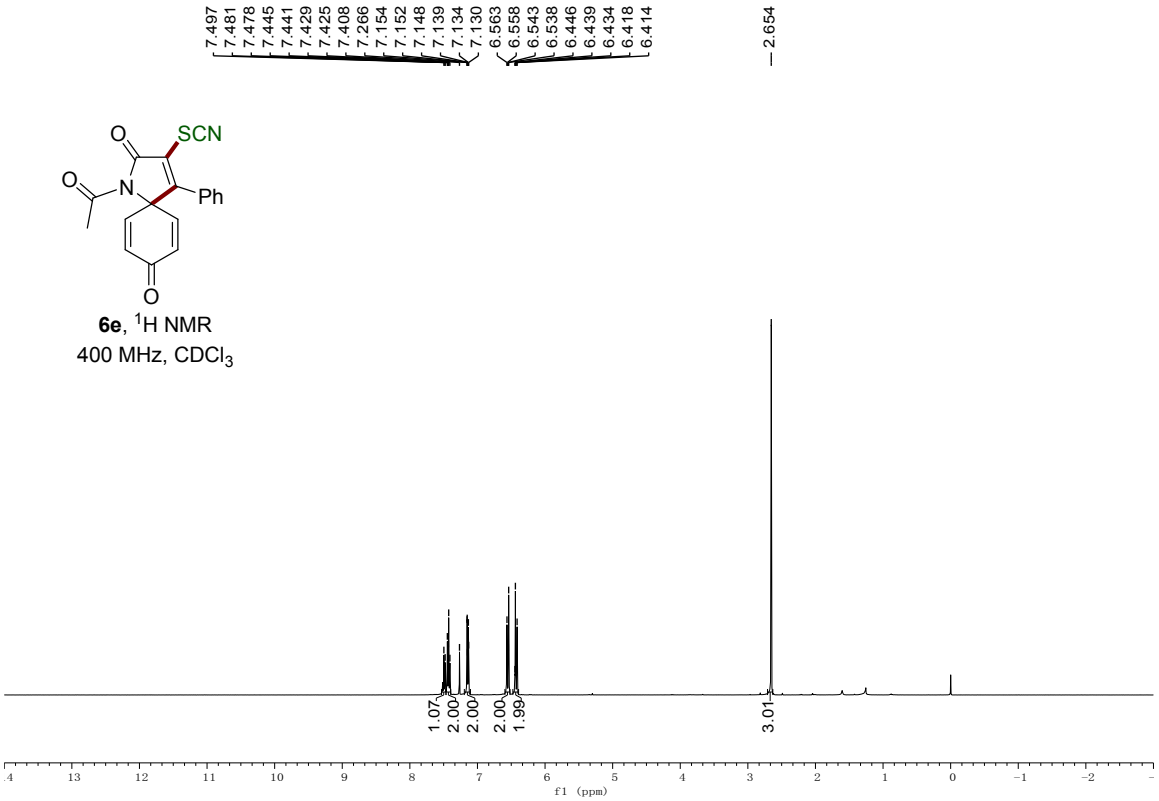




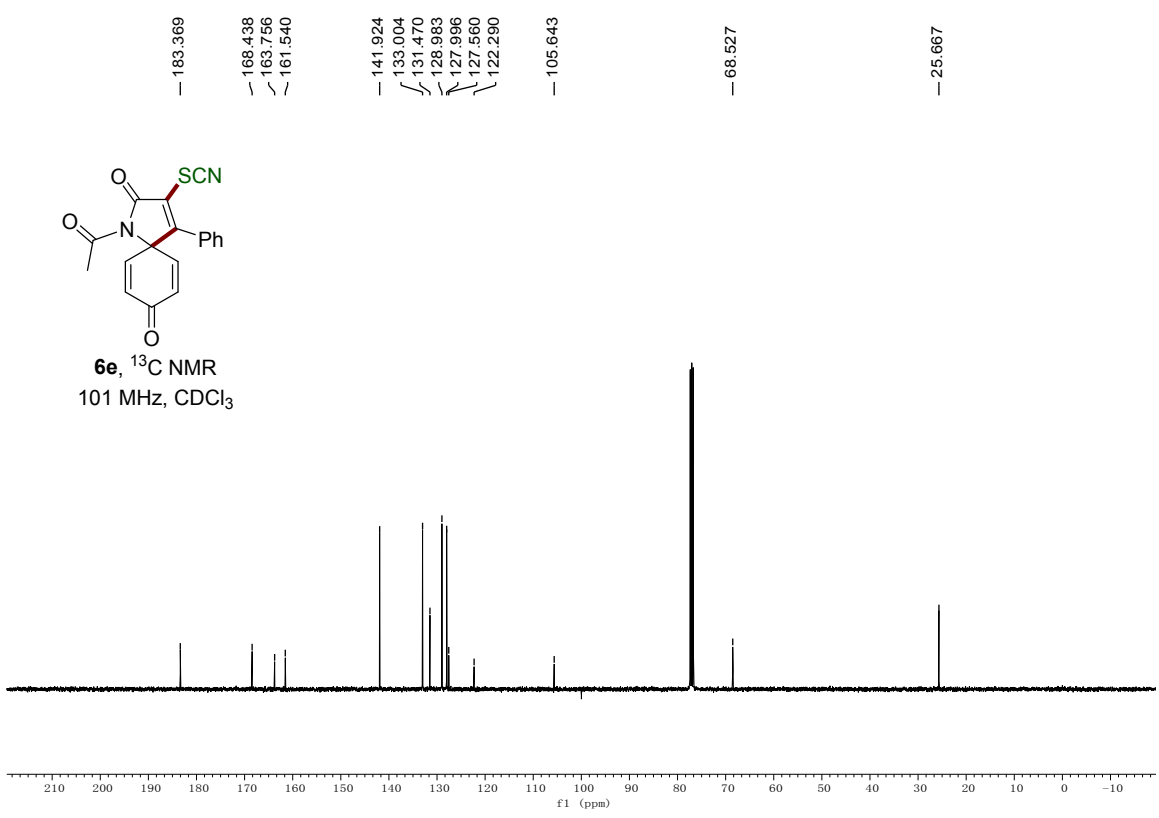


6d, ^{13}C NMR
101 MHz, $CDCl_3$

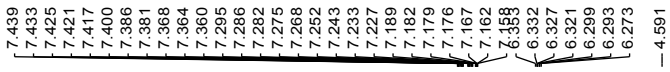


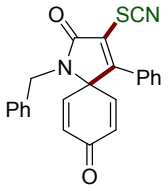


6e, ^{1}H NMR
400 MHz, $CDCl_3$

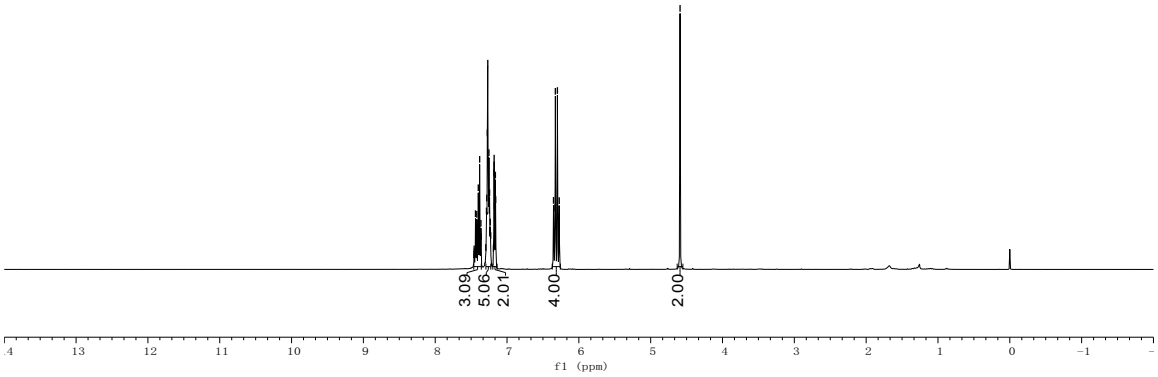


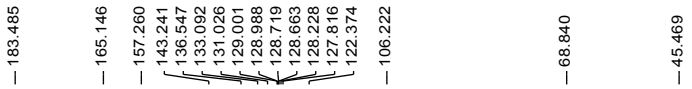
6e, ^{13}C NMR
101 MHz, $CDCl_3$

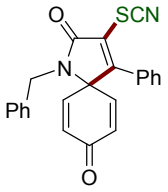




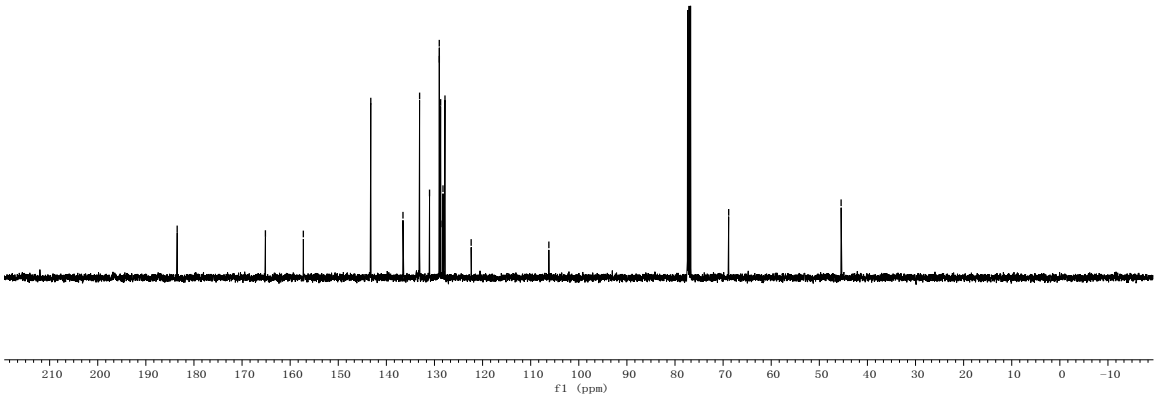
6f, ^{1}H NMR
400 MHz, $CDCl_3$

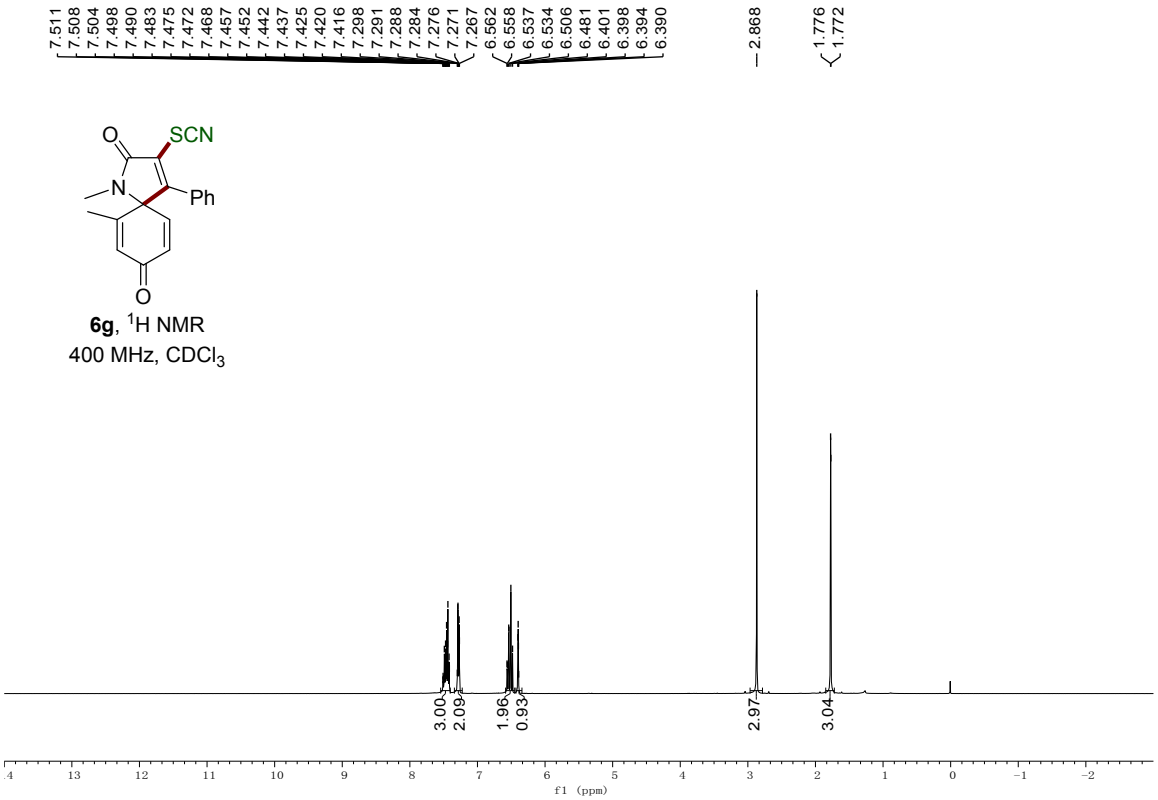




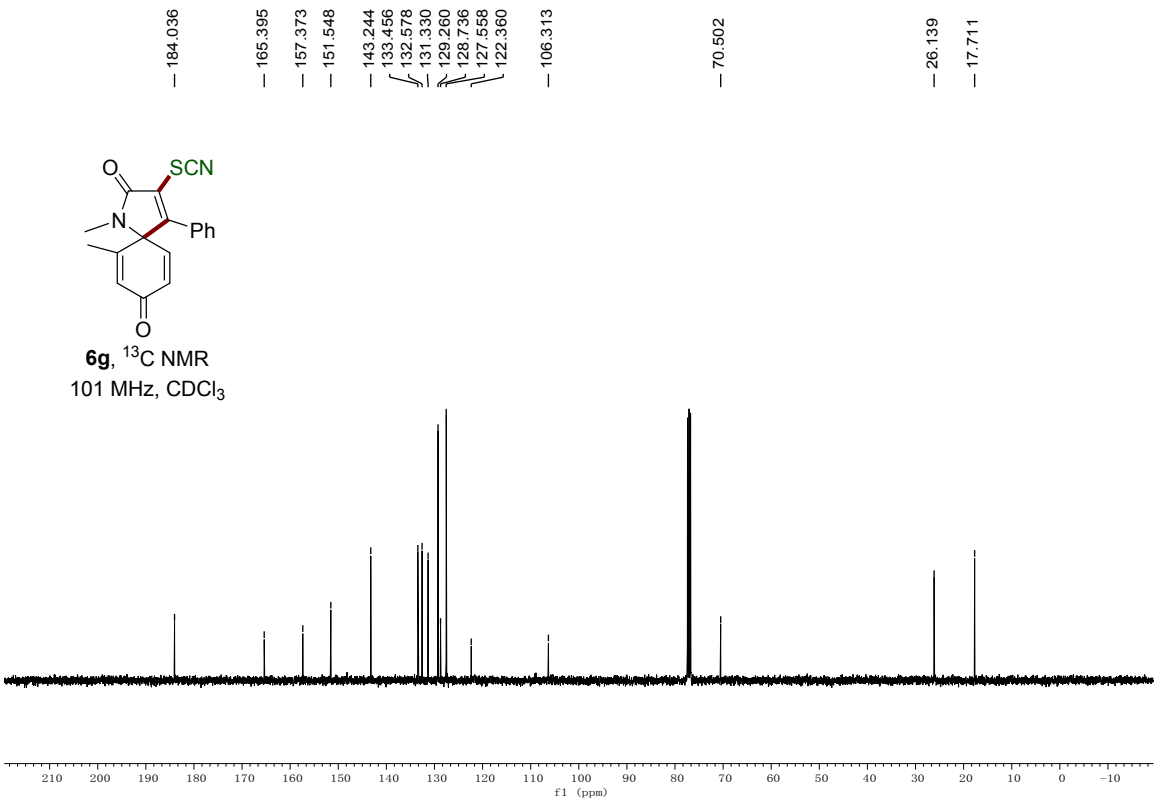


6f, ^{13}C NMR
101 MHz, $CDCl_3$

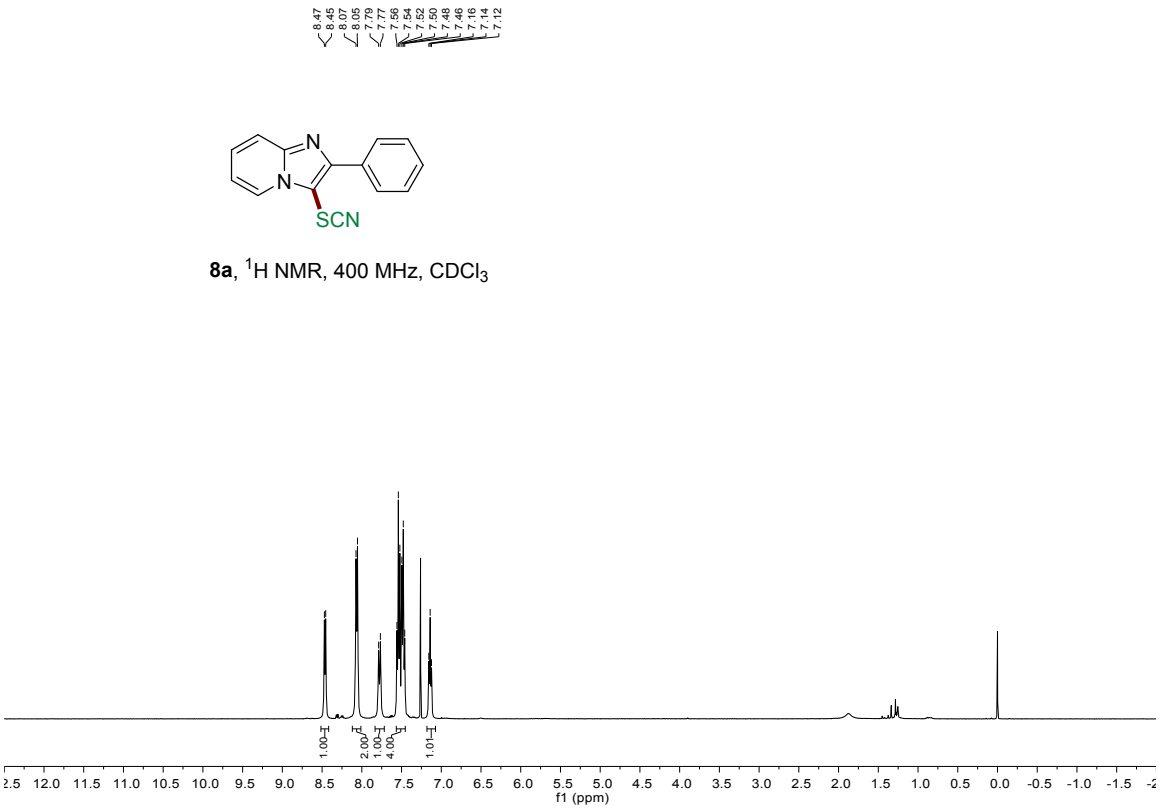




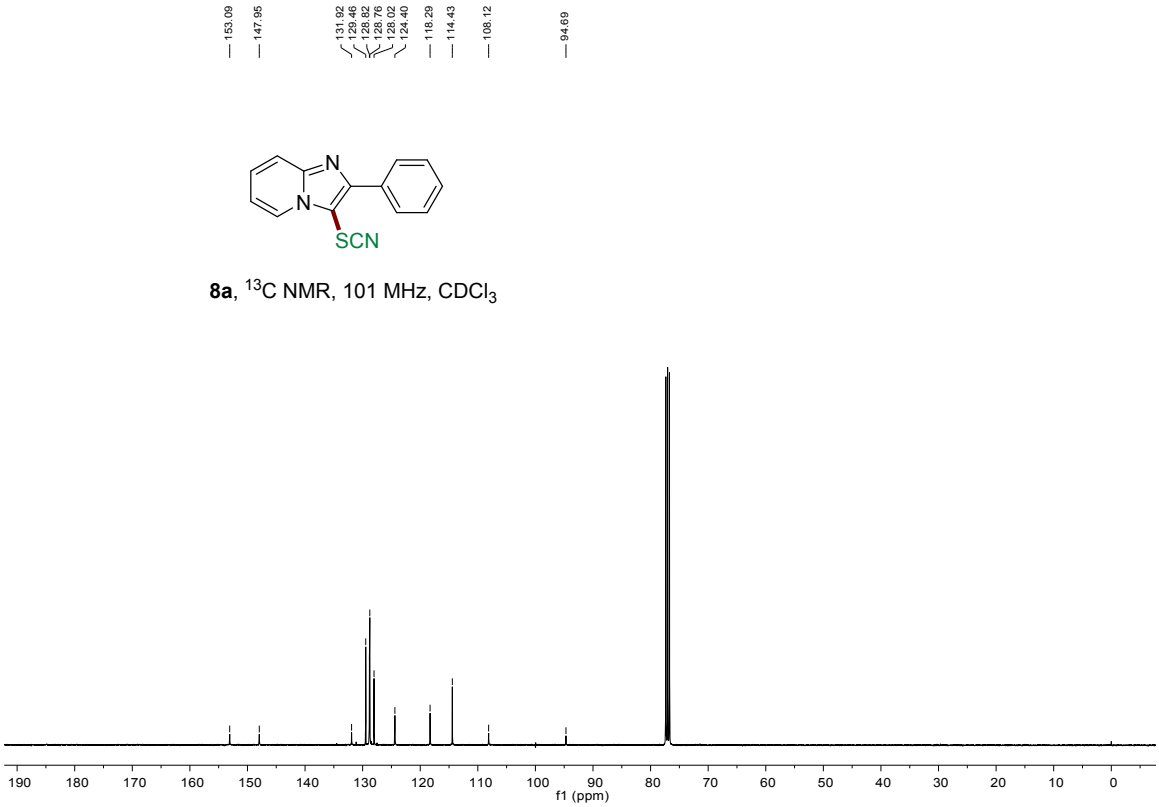
6g, ^{1}H NMR
400 MHz, $CDCl_3$



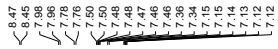
6g, ^{13}C NMR
101 MHz, $CDCl_3$



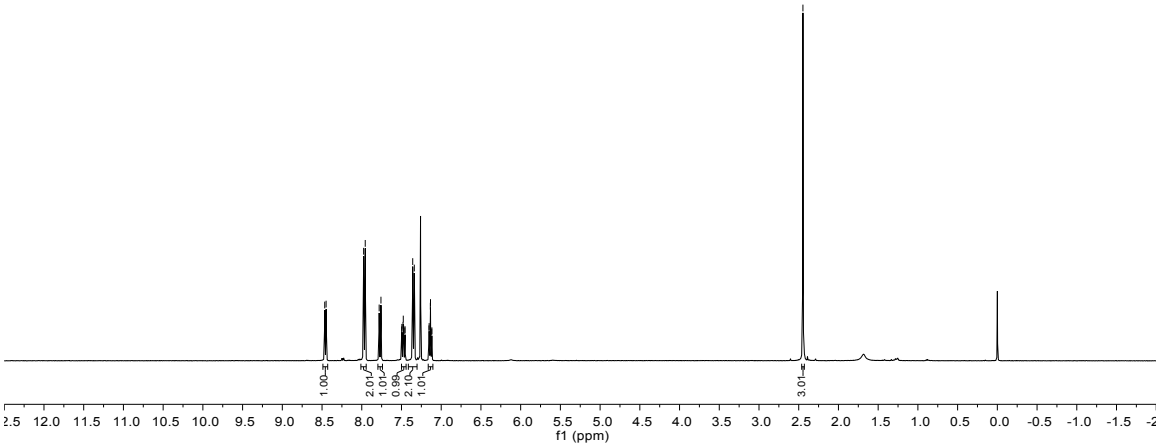
8a, ^{1}H NMR, 400 MHz, $CDCl_3$



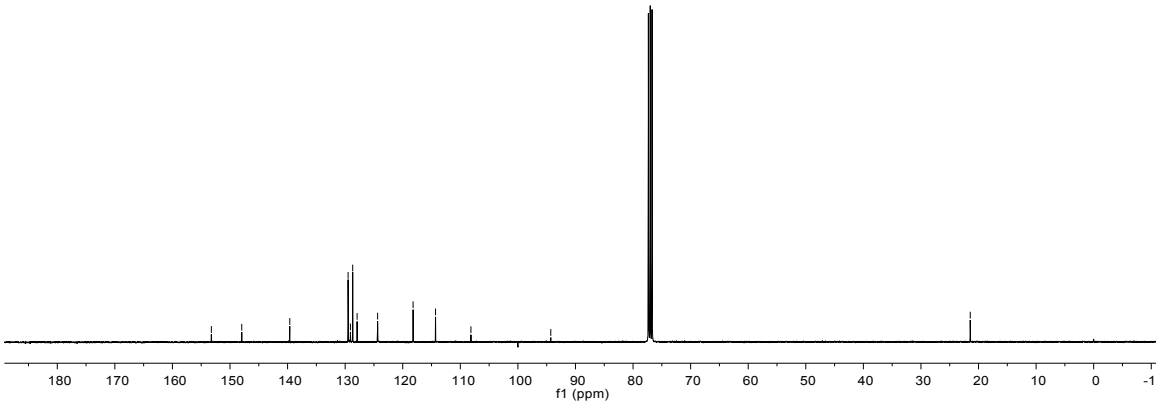
8a, ^{13}C NMR, 101 MHz, $CDCl_3$

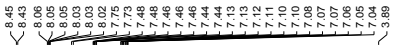


8b, ^{1}H NMR, 400 MHz, $CDCl_3$

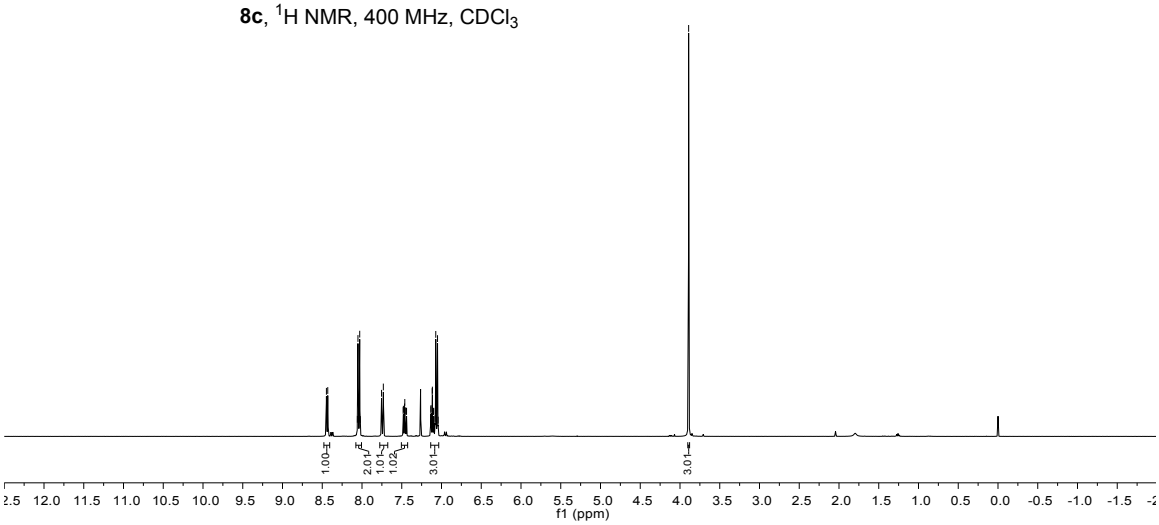


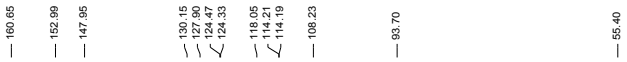
8b, ^{13}C NMR, 101 MHz, $CDCl_3$



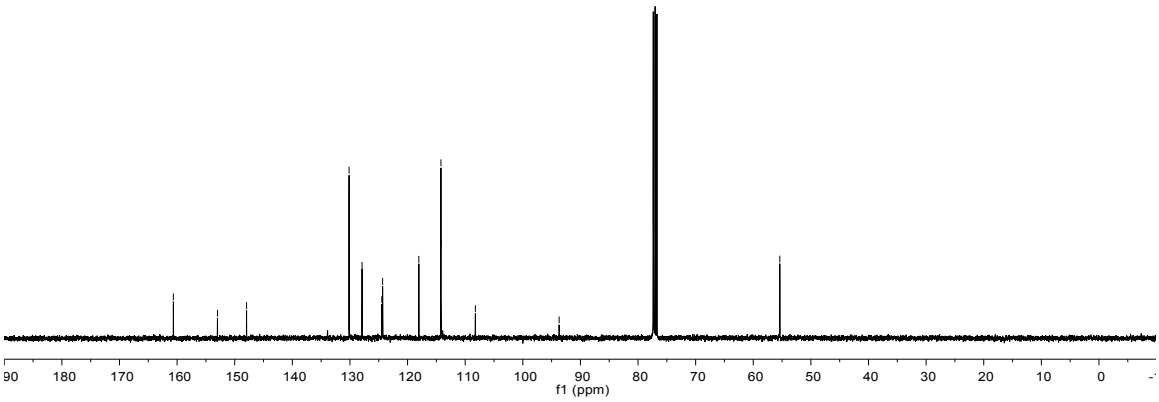


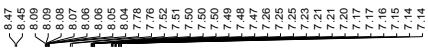
8c, ^{1}H NMR, 400 MHz, $CDCl_3$



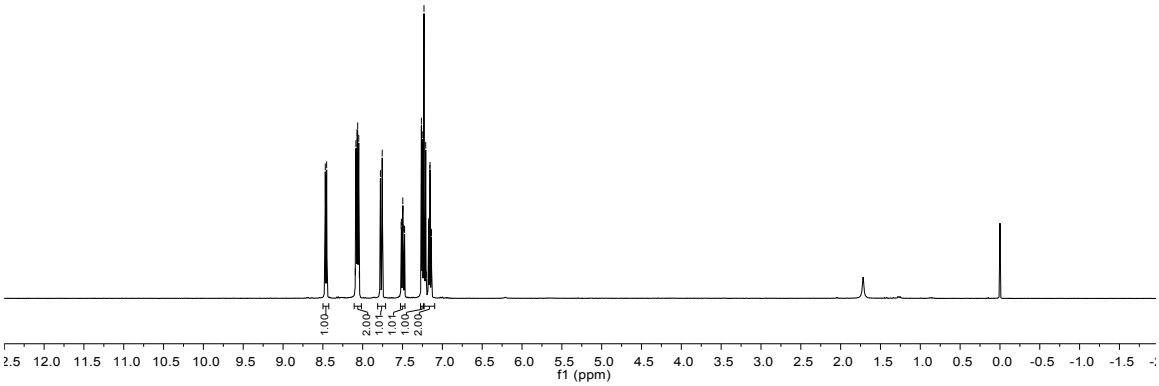


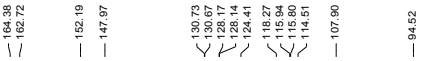
8c, ^{13}C NMR, 101 MHz, $CDCl_3$

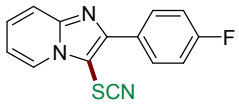




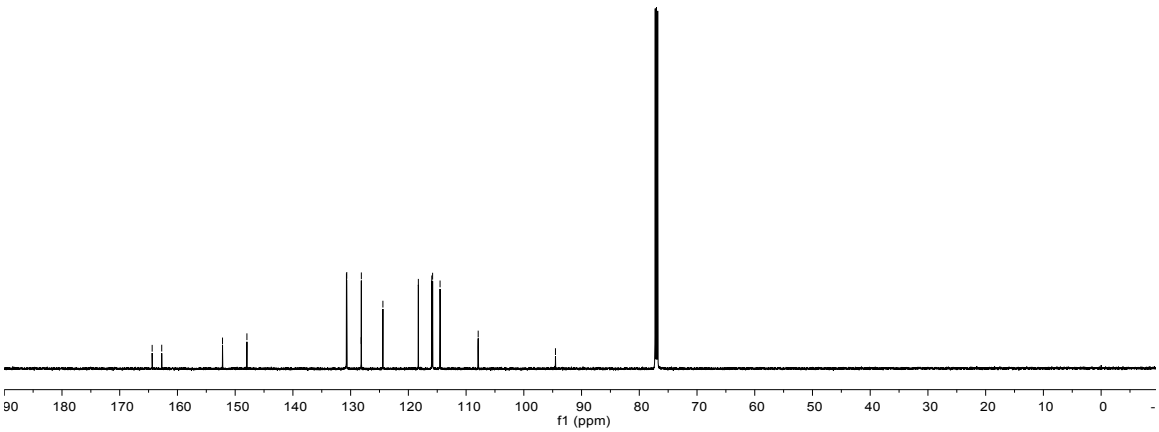
8d, ^{1}H NMR, 400 MHz, $CDCl_3$

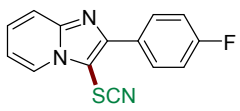




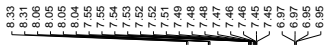


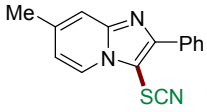
8d, ^{13}C NMR, 151 MHz, $CDCl_3$



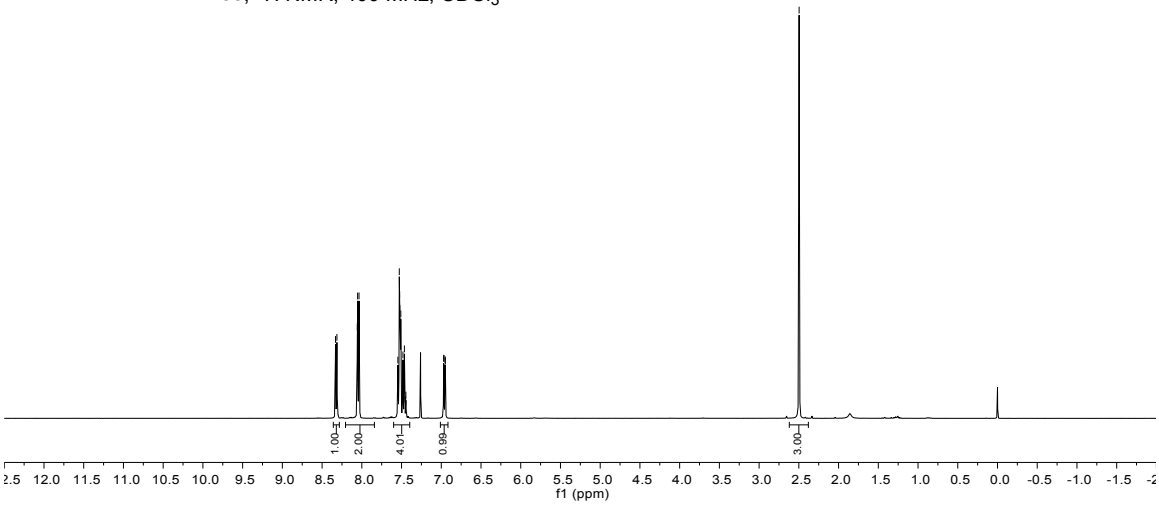


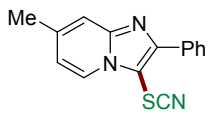
8d, ^{19}F NMR, 376 MHz, $CDCl_3$



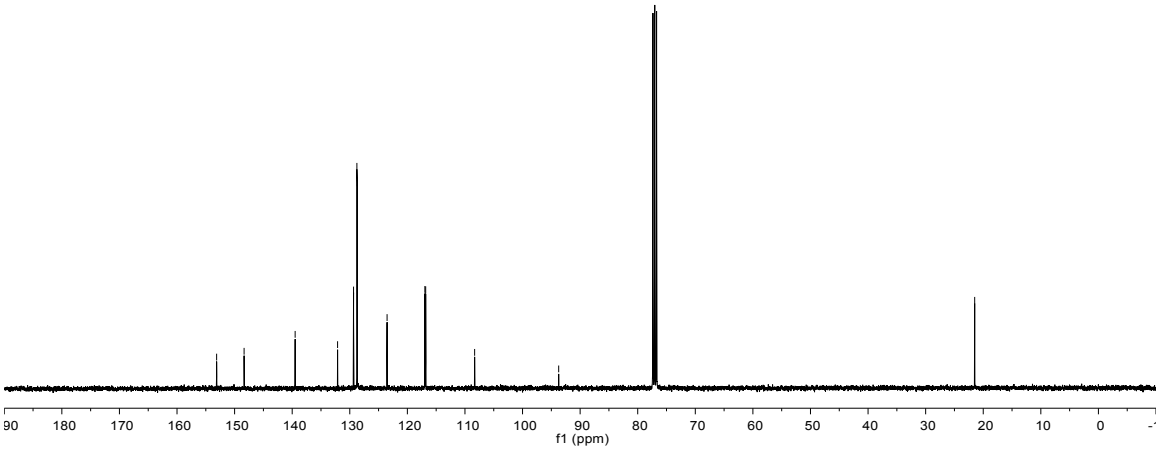


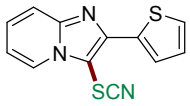
8e, ^{1}H NMR, 400 MHz, $CDCl_3$



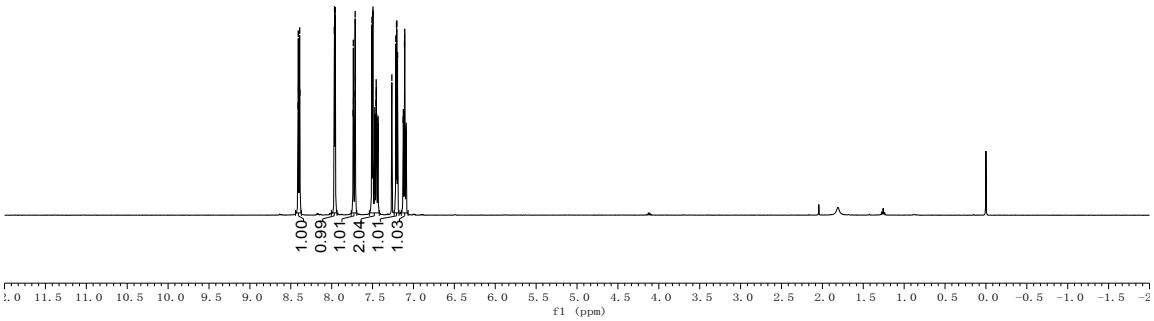


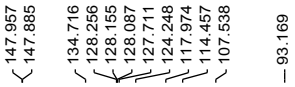
8e, ^{13}C NMR, 101 MHz, $CDCl_3$



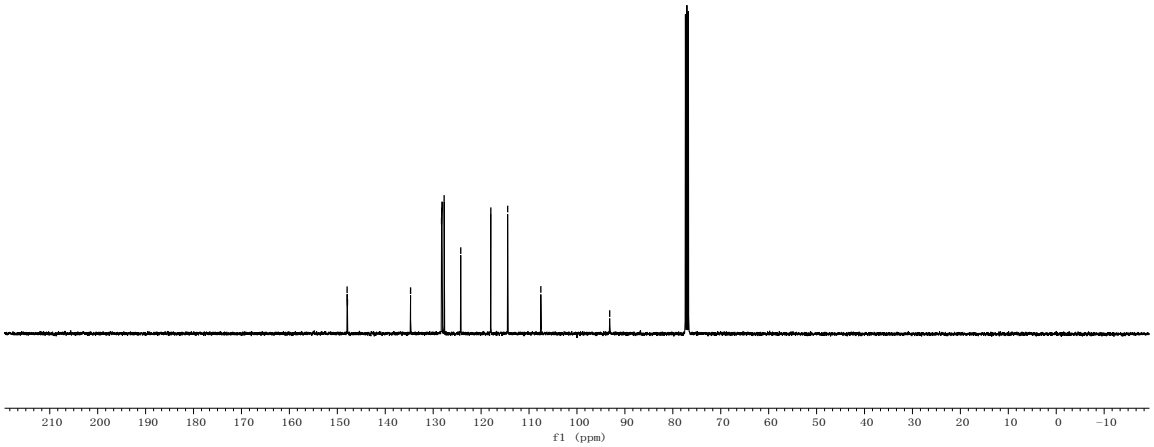


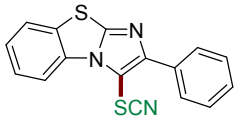
8f, ^{1}H NMR, 400 MHz, $CDCl_3$



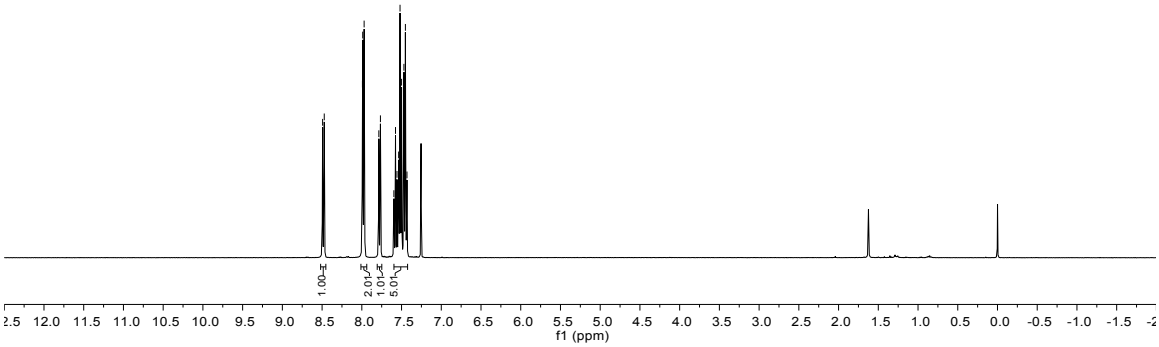


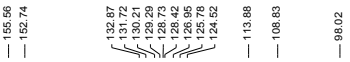
8f, ^{13}C NMR, 101 MHz, $CDCl_3$

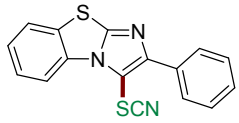




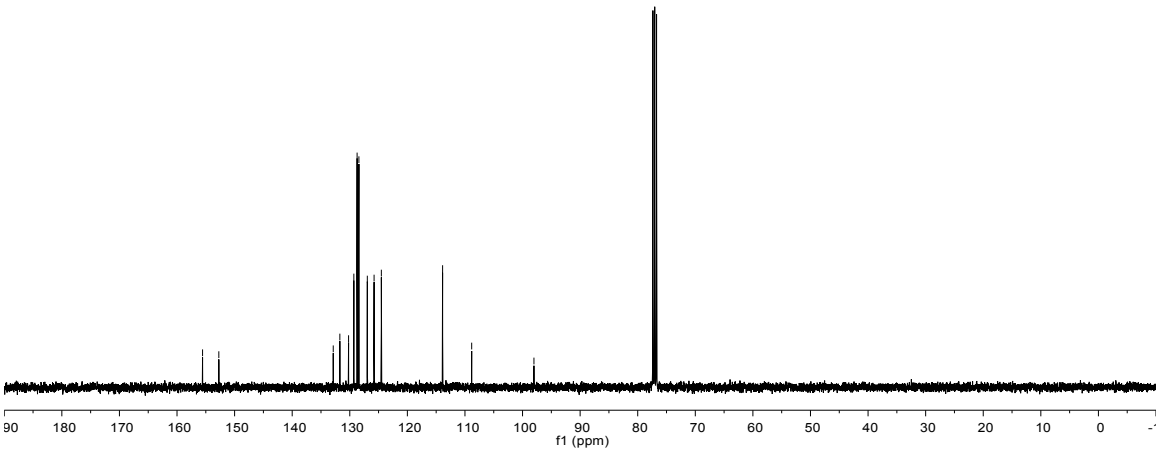
8g, ^{1}H NMR, 400 MHz, $CDCl_3$

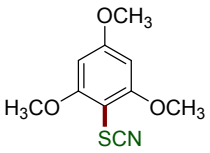




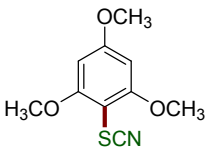


8g, ^{13}C NMR, 101 MHz, $CDCl_3$

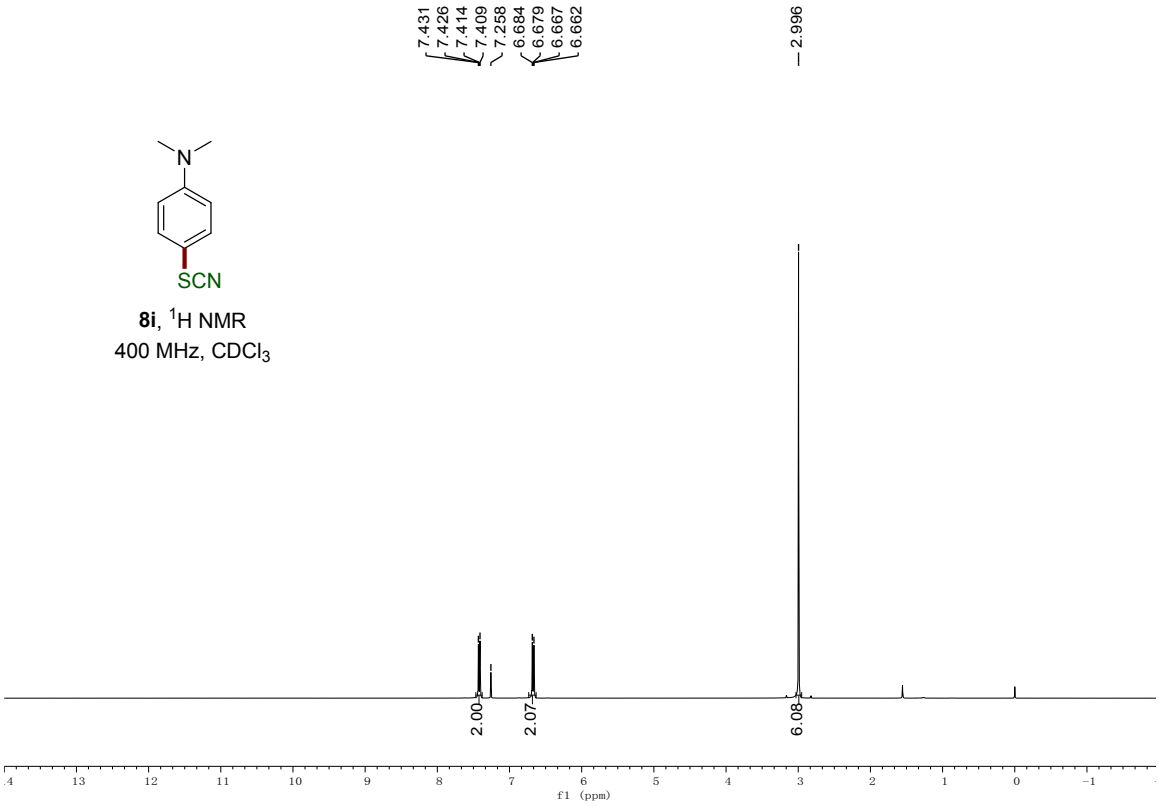




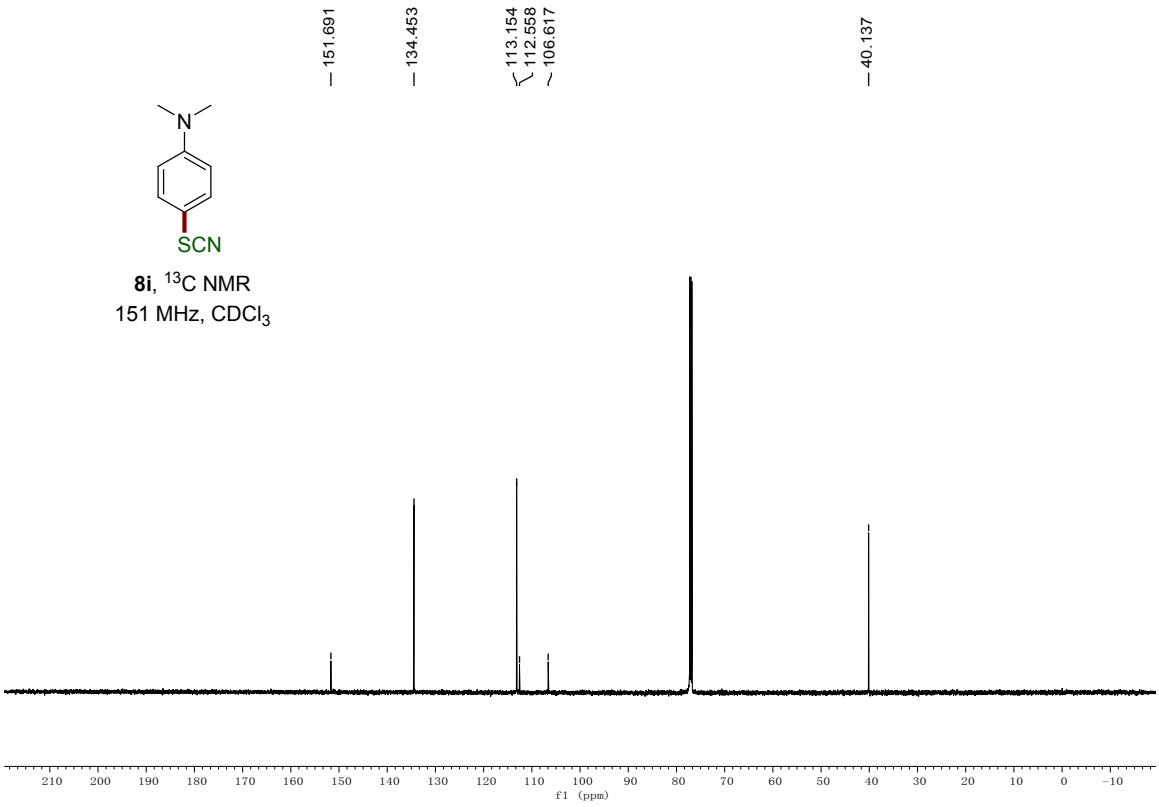
8h, ^{1}H NMR
400 MHz, $CDCl_3$



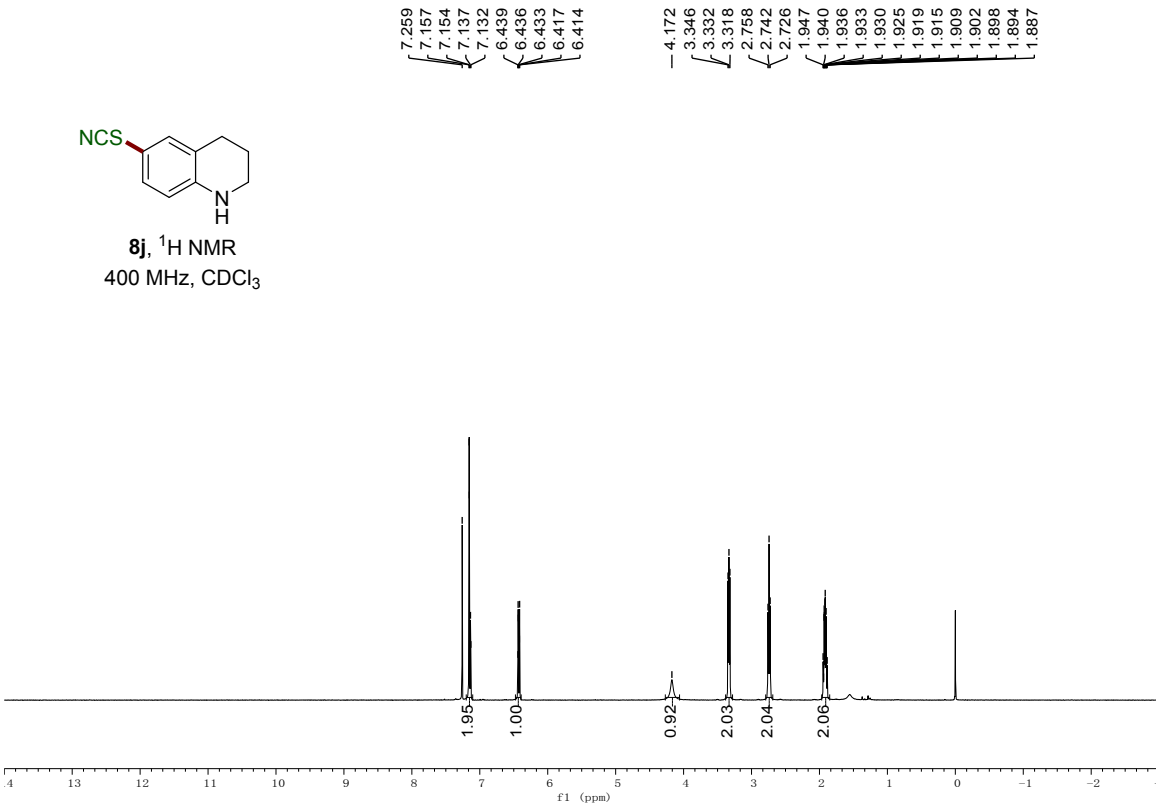
8h, ^{13}C NMR
101 MHz, $CDCl_3$



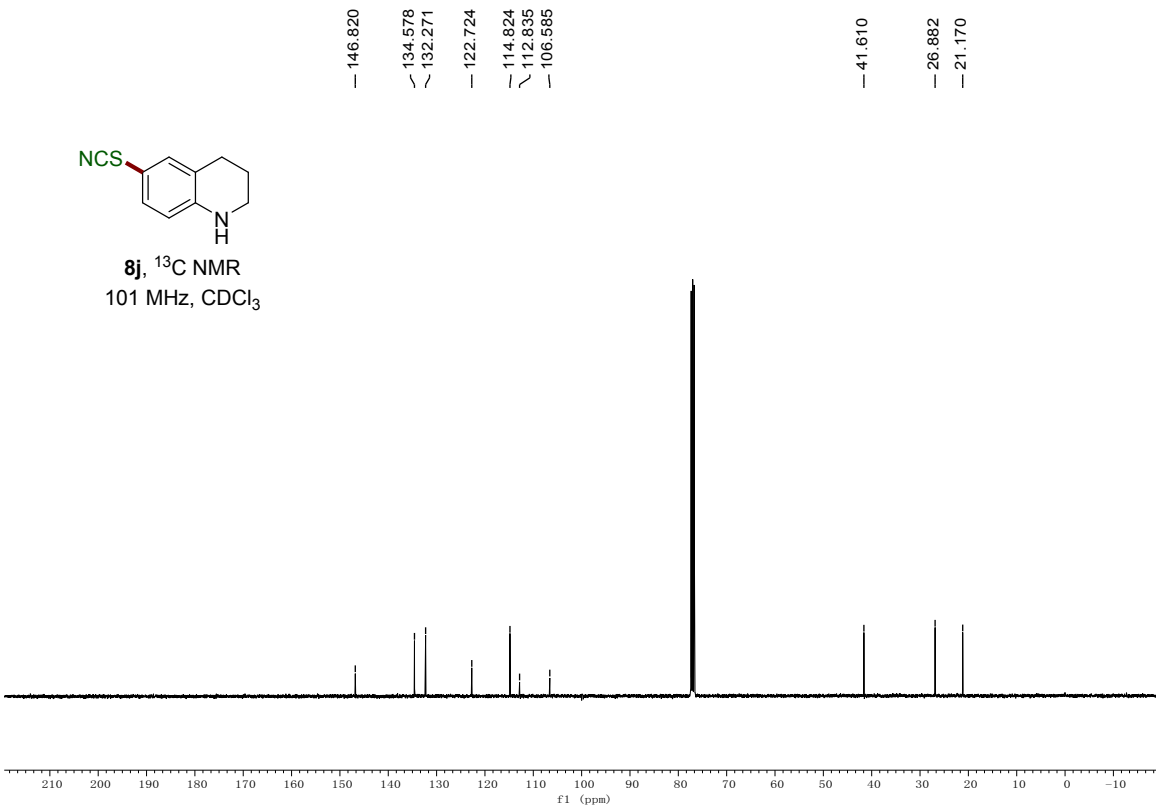
8i, ^{1}H NMR
400 MHz, $CDCl_3$



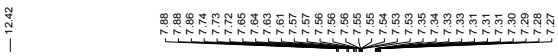
8i, ^{13}C NMR
151 MHz, $CDCl_3$

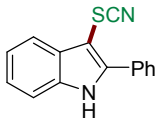


8j, ^{1}H NMR
400 MHz, $CDCl_3$

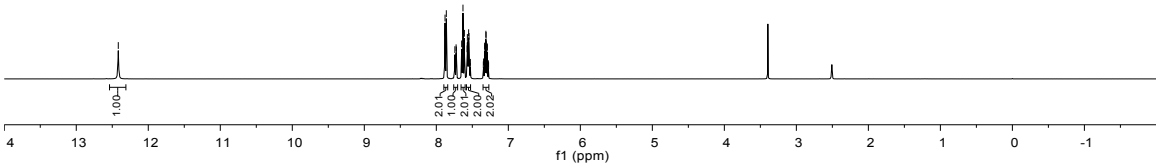


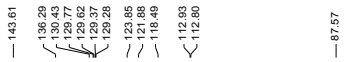
8j, ^{13}C NMR
101 MHz, $CDCl_3$

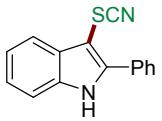




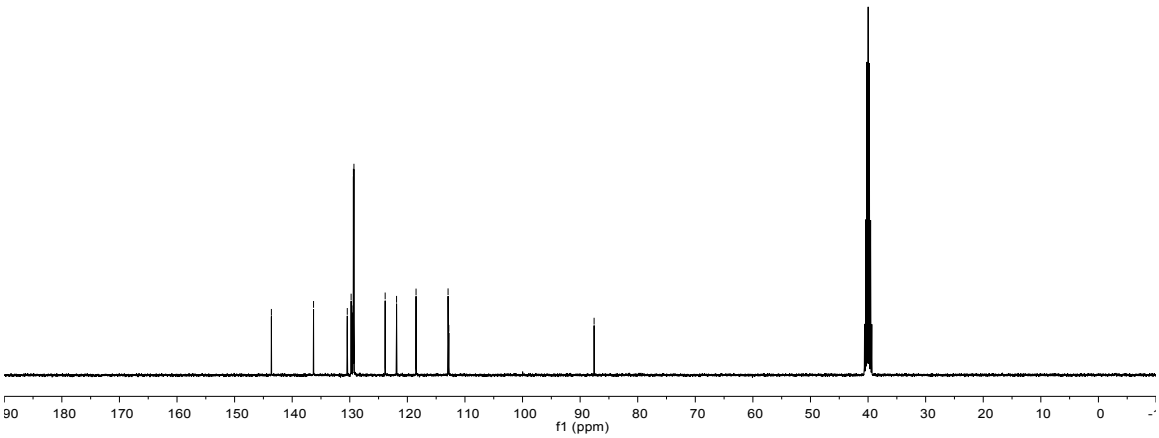
8k, ^{1}H NMR, 400 MHz, DMSO-d_6

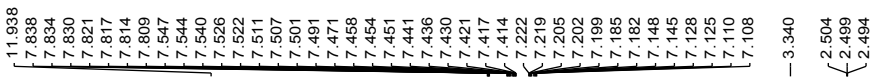


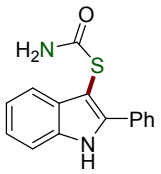




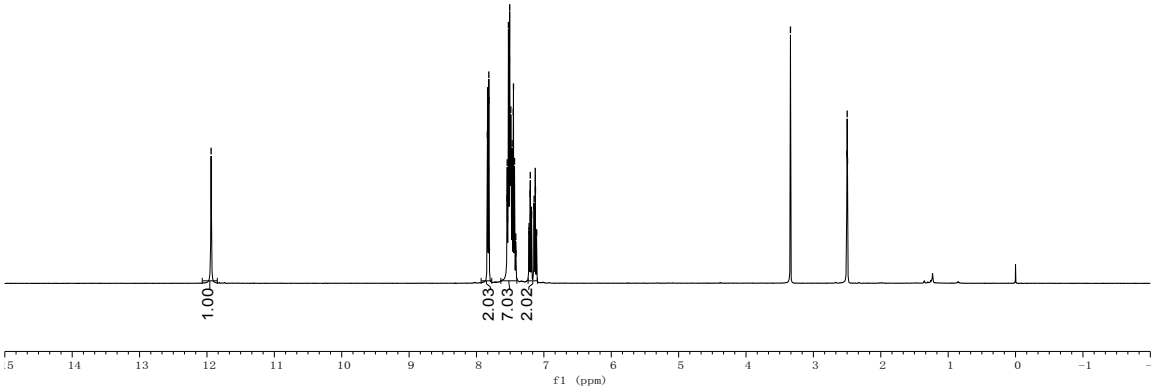
8k, ^{13}C NMR, 101 MHz, DMSO-d_6

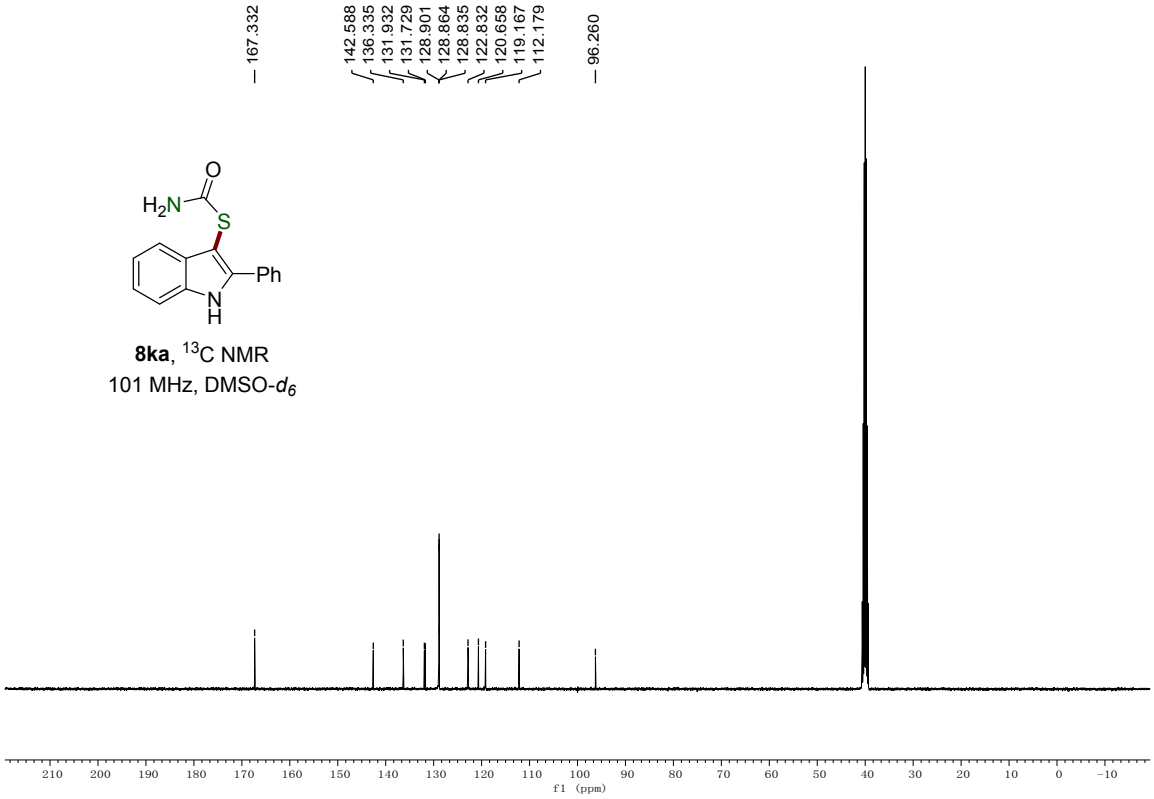




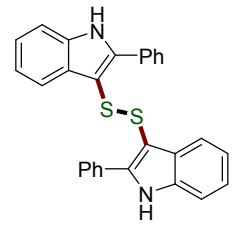


8ka, ^{1}H NMR
400 MHz, DMSO-d_6

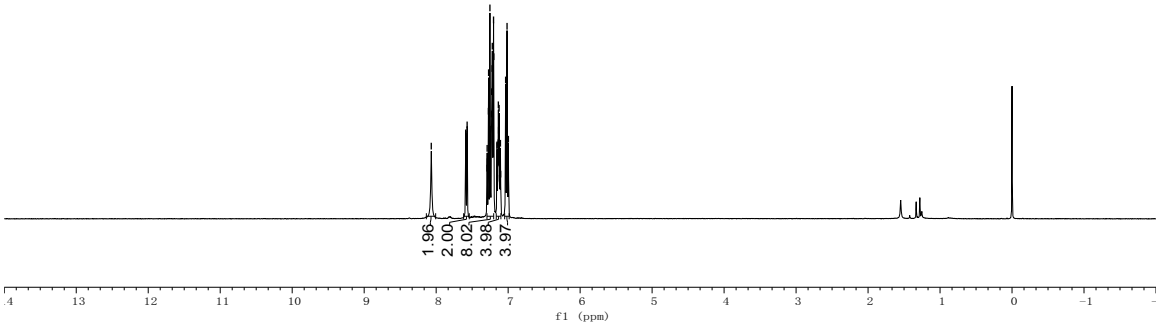


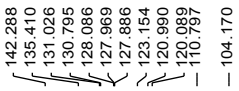


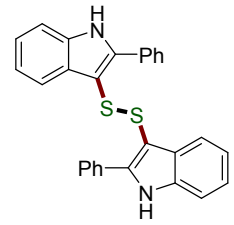
8ka, ^{13}C NMR
101 MHz, DMSO-d_6



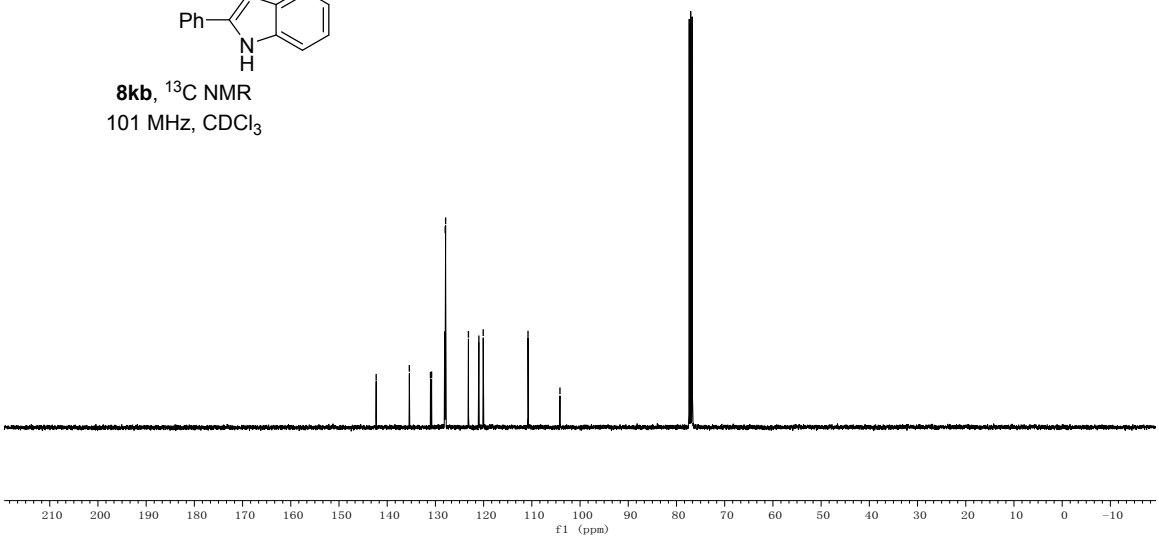
8kb, ^{1}H NMR
400 MHz, $CDCl_3$

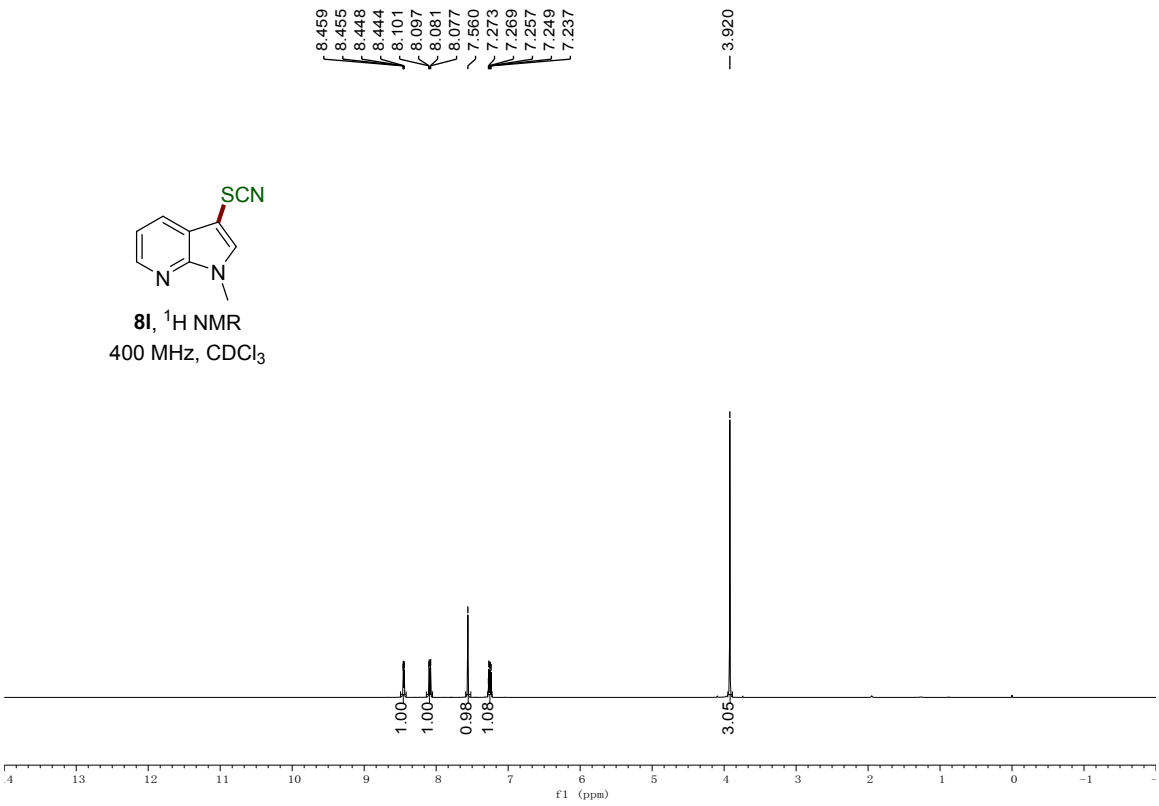




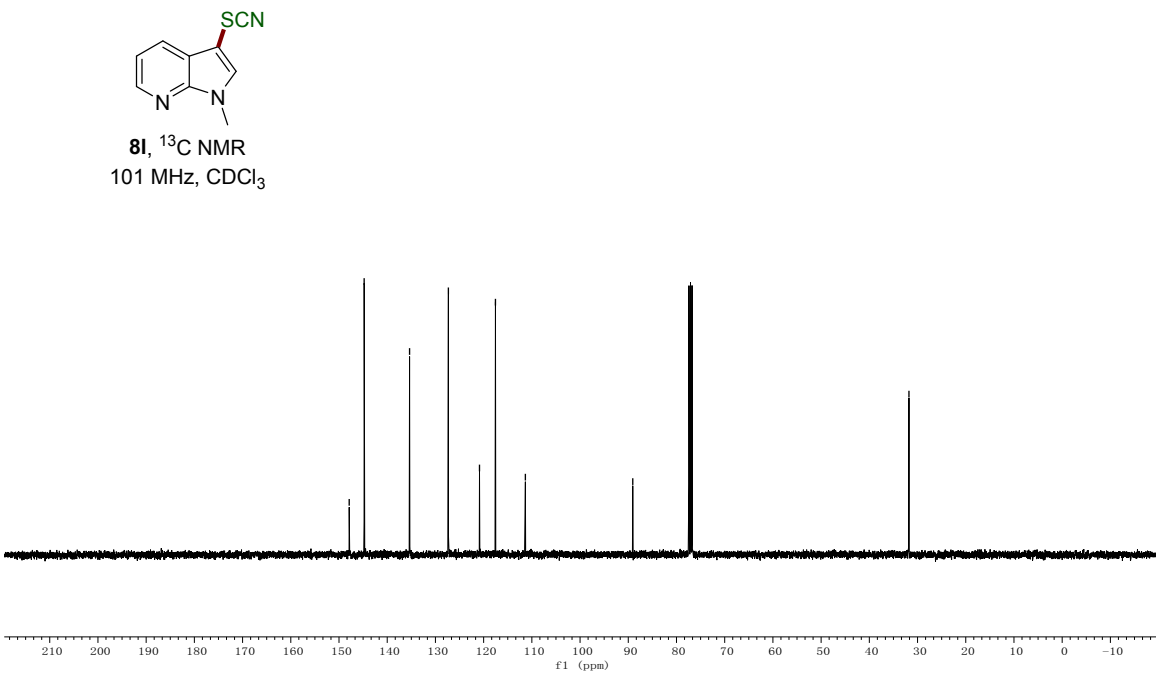


8kb, ^{13}C NMR
101 MHz, $CDCl_3$

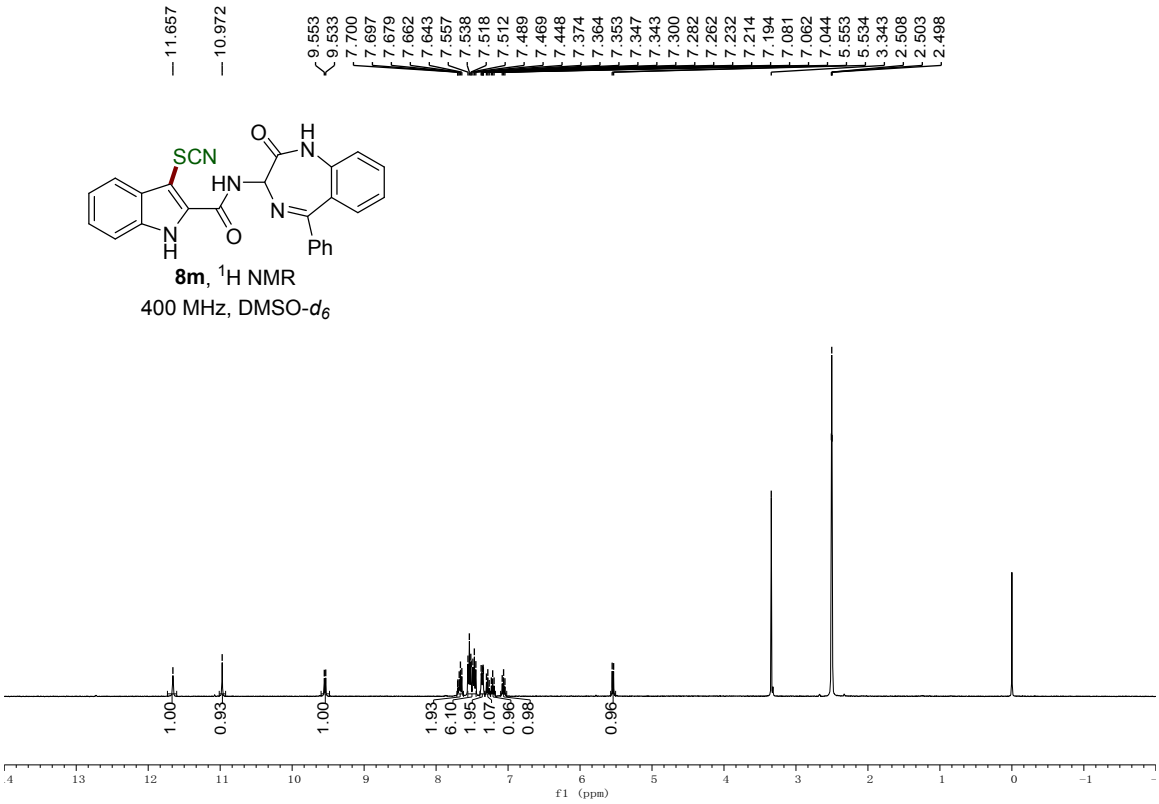




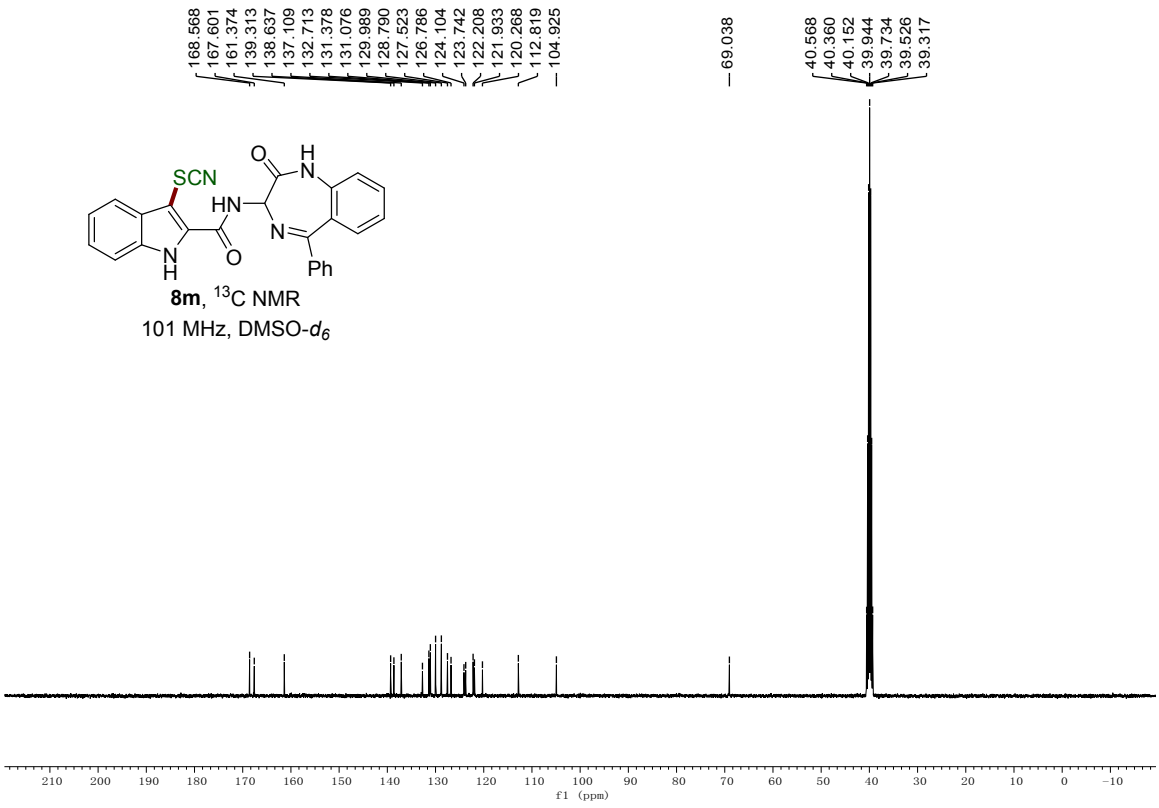
8l, ^{1}H NMR
400 MHz, $CDCl_3$



8l, ^{13}C NMR
101 MHz, $CDCl_3$



8m, ^{1}H NMR
400 MHz, DMSO-d_6



8m, ^{13}C NMR
101 MHz, DMSO-d_6

5. Reference

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