# Thiocyanate promoted difunctionalization and cyclization of unsaturated C-C bonds to construct 1-sulfur-2-nitrogen-functionalized alkenes and 2-thiocyanate indolines

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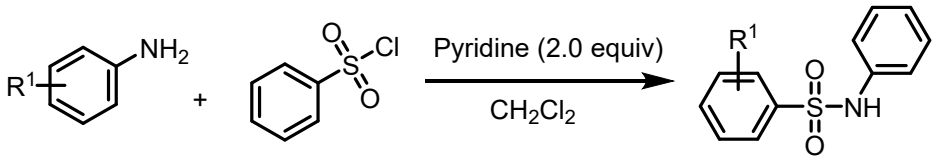
# 1. General Information

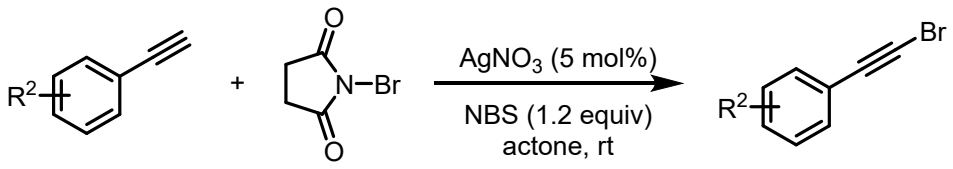
Unless otherwise indicated, all commercially available chemicals were used without purification. $^{1}H$ NMR (400 MHz), $^{13}C$ NMR (100 MHz) and $^{19}F$ NMR (376 MHz) were measured on 400 M spectrometer. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. $^{1}H$ NMR chemical shifts were determined relative to internal TMS at δ 0.0 ppm. $^{13}C$ NMR chemical shifts were determined relative to $CDCl_3$ at δ 77.00 ppm. The following abbreviations were used to explain multiplicities: s =singlet, d =doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on 0.2 mm coated silica gel plates and visualized the course of the reactions using a UV light 254 nm. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

# 2. Experimental section

## 2.1 General Procedure for the synthesis of starting materials[1-4]

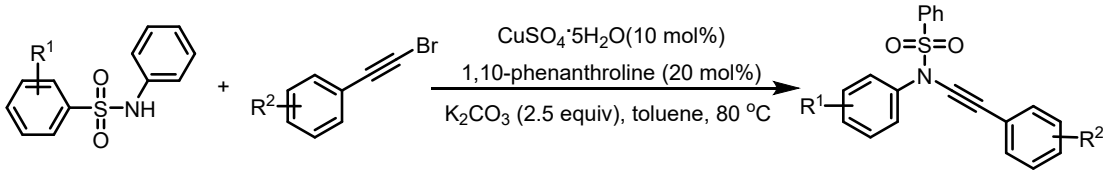



In an oven-dried flash (100 mL), the solution of aniline (465.7 mg, 5 mmol) in DCM (6 mL) were added pyridine (791mg, 10 mmol) and TsC1 (1.91 g, 10 mmol). The resulting solution was stirred for 2 h. Then themixture was quenched with saturated NH4CI solution, extracted with DCM. The combinedorganic layers were washed with water, dried over anhydrous $NaSO_4$ and filtered. Theorganic solvent was evaporated under the reduced pressure and the residue was purified bycolumn chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to affordthe desired product in quantitive yield (1.237 g) as a white solid.

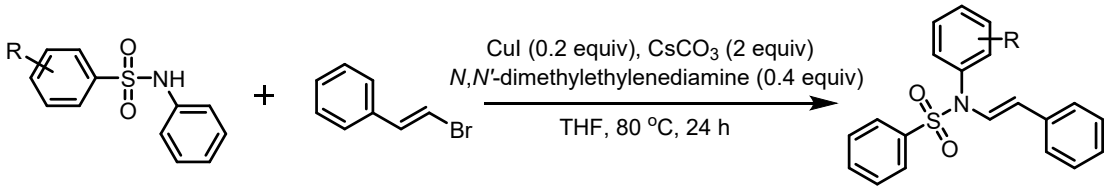



In an oven-dried flash (100 mL), to a solution of terminal aklynes (3.0 mmol) in acetone (10 mL) were added NBS (3.6 mmol) and $AgNO_3$ (0.15 mmol), the resulting mixture was stirred under $N_2$ at room temperature for 3 hours. After removing excess acetone, the reacton

was quenched with saturated $NH_4Cl$ solution, and the organic layer was extracted with petroleum ether (10 mL×2), dried over anhydrous $NaSO_4$, filtered and concertrated under reduced pressure to give bromoalkynes.

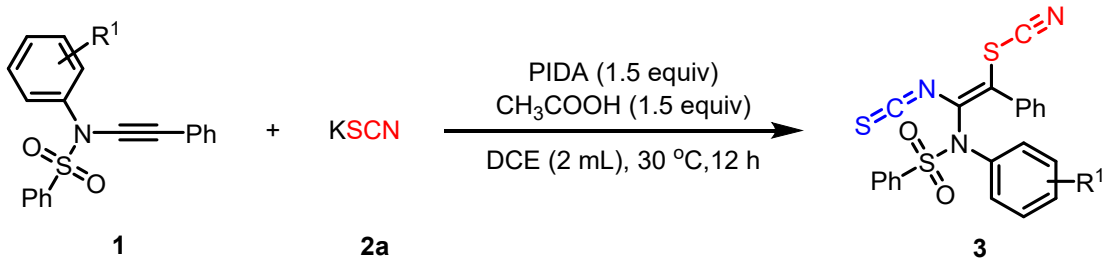



To a dried flask were added sulfonamides (12.0 mmol), $CuSO_4$•$5H_2O$ (1.0 mmol), 1,10-phenanthroline (2.0 mmol) and $K_2CO_3$ (25.0 mmol). The rsulting mixture was subsequently treated with anhydrous toluene (50 mL) and bromoalkynes (10.0 mmol), and stirred at 80 ℃ overnight under $N_2$. When the reaction mixture was cooled to room temperature, to the reaction mixture was added $H_2O$ (50 mL), with subsequent extraction with $CH_2Cl_2$ (50 mL×3). The organic layer was dried over $Na_2SO_4$. After the filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel using *n*-hexane as eluent.



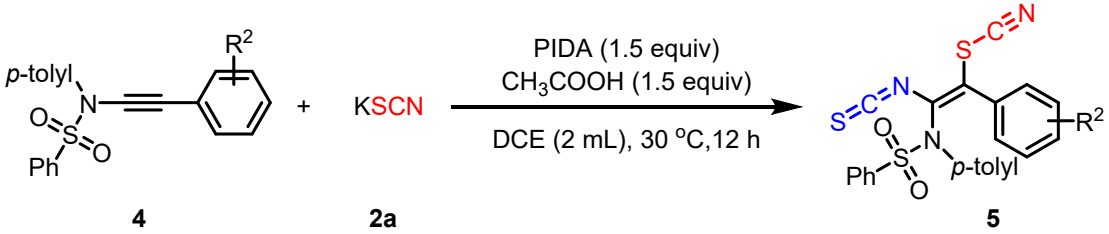

Copper iodide (1.0 mmol, 0.2 equiv), cesium carbonate (10.0 mmol, 2.0 equiv), and aniline analogs (5.0 mmol, 1.0 equiv) were first added sequentially to a 100 mL flask, and then displaced by three successive vacuum-argon cycles. The solvent THF (50 mL) was then added, followed by *N*,*N'*-dimethylethylenediamine (2.0 mmol, 0.4 equiv) and *β*-bromostyrene (11 mmol, 1.1 equiv). The mixture was then heated to reflux for 3 h at 80 °C (monitored by TLC). After cooling to room temperature, water (20 mL) was added to the reaction mixture, which was subsequently extracted with ethyl acetate (50 mL × 3), and the organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude product was separated by silica gel column chromatography using *n*-hexane/ EtOAc (25:1) as eluent to finally obtain the target compound.

## 2.2 General Procedure for the synthesis of product 3 and product 5




**1** **2a** **3**

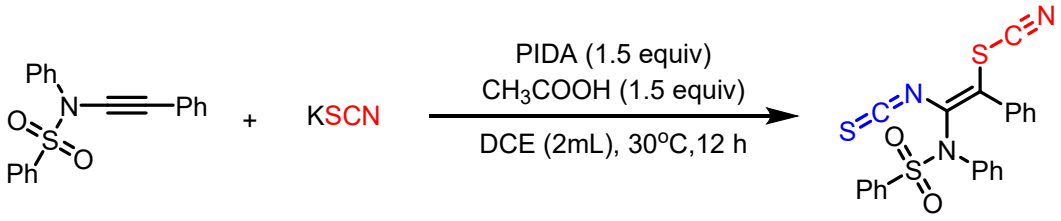
A 20 mL vial was charged with substrate **1** (0.1 mmol, 1.0 equiv), **2a** (2.0 equiv), PIDA (1.5 equiv), $CH_3COOH$ (1.5 equiv), 1,1-Dichloroethane (DCE, 2 mL) and a magnetic stir bar. The reaction mixture was reacted at 30 ℃ for 12 hours. After completing reaction, it was monitored with TLC. Then the reaction mixture was diluted with EtOAc (10 mL) and filtered through a pad of silica gel. The vial and silica gel were washed with an additional of EtOAc (20 mL). The filtrate was concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using EtOAc /*n*-hexane as the eluent to afford the product.




**4** **2a** **5**

A 20 mL vial was charged with substrate **1b** (0.1 mmol, 1.0 equiv), **2a** (2.0 equiv), PIDA (1.5 equiv), $CH_3COOH$ (1.5 equiv), 1,1-Dichloroethane (DCE, 2 mL) and a magnetic stir bar. The reaction mixture was reacted at 30 ℃ for 12 hours. After completing reaction, it was monitored with TLC. Then the reaction mixture was diluted with EtOAc (10 mL) and filtered through a pad of silica gel. The vial and silica gel were washed with an additional of EtOAc (20 mL). The filtrate was concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using EtOAc/*n*-hexane as the eluent to afford the product.

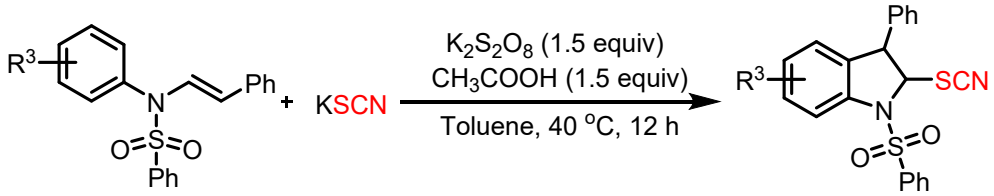
## 2.3 Gram-scale synthesis of 3a




**1a** (3 mmol,1 g) **2a** (2.0 equiv) **3a** ( 0.81g 60%)

In an oven-dried undivided three-necked bottle (250 mL) equipped with a stir bar, *N*-(phenylethynyl)-*N*-(p-tolyl) benzenesulfonamide **1a** (3 mmol, 1.005g), potassium thiocyanate **2a** (6 mmol), PIDA (4.5 mmol), acetic acid (4.5 mmol) and DCE (60 mL) were combined and added. The reaction mixture was reacted at 30 ℃ for 12 hours. When the reaction was finished, the reaction mixture was washed with water and extracted with $CH_2Cl_2$ (100 mL x 3). The organic layers were combined, dried over $Na_2SO_4$, and concentrated. The crude product was purified by column chromatography on silica gel using EtOAc/*n*-hexane (1:20) as eluent to afford the product **3a** in 60% yield.

## 2.4 General Procedure for the synthesis of product 7




**6** **2a** **7**

A 15 mL tube was charged with substrate **6** (0.1 mmol, 1.0 equiv), **2a** (2.0 equiv), $K_2S_2O_8$ (1.5 equiv), $CH_3COOH$ (1.5 equiv), Toluene (2 mL). The reaction mixture was reacted at 40 ℃ for 12 hours. After completing reaction, it was monitored with TLC. Then the reaction mixture was diluted with EtOAc (5 mL) and filtered through a pad of silica gel. The vial and silica gel were washed with an additional of EtOAc (5 mL). The filtrate was concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using EtOAc/*n*-hexane as the eluent to afford the product.

## 2.5 Characterization data

Table S1. Crystal data and structure refinement for **3d**.

| | |
|---|---|
| Identification code | 2104011479_0m |
| Empirical formula | C26 H23 N3 O2 S3 |
| Formula weight | 505.65 |

| | | |
|---|---|---|
| Temperature | 173.0 K | |
| Wavelength | 1.34139 Å | |
| Crystal system | Monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 20.0220(3) Å | a= 90°. |
| | b = 11.6268(2) Å | b= 107.0630(10)°. |
| | c = 22.3898(3) Å | g = 90°. |
| Volume | 4982.74(13) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.348 $Mg/m^3$ | |
| Absorption coefficient | 1.920 $mm^{-1}$ | |
| F(000) | 2112 | |
| Crystal size | 0.07 x 0.06 x 0.05 $mm^3$ | |
| Theta range for data collection | 3.870 to 54.954°. | |
| Index ranges | -24<=h<=24, -12<=k<=14, -27<=l<=26 | |
| Reflections collected | 20255 | |
| Independent reflections | 4675 [R(int) = 0.0314] | |
| Completeness to theta = 53.594° | 98.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7508 and 0.6144 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4675 / 0 / 310 | |
| Goodness-of-fit on $F^2$ | 1.031 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0334, wR2 = 0.0809 | |
| R indices (all data) | R1 = 0.0386, wR2 = 0.0845 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.475 and -0.396 $e.Å^{-3}$ | |

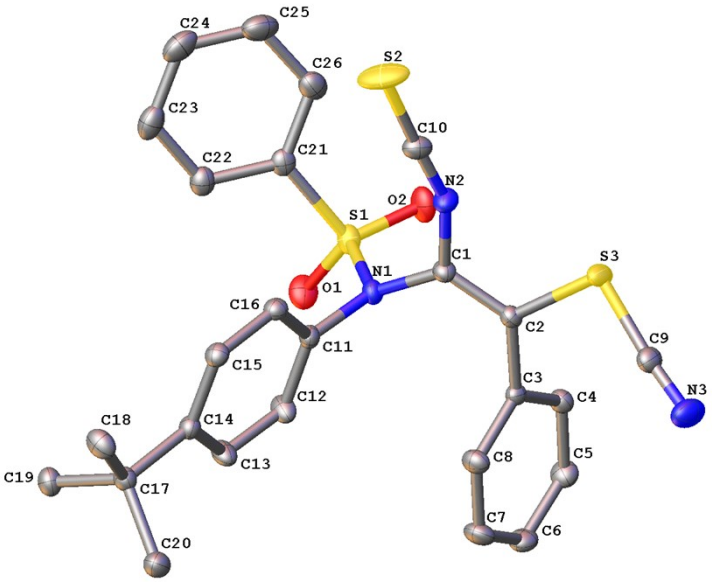



Figure 2-1 *X*-ray structure of **3d**

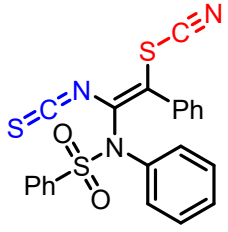
## 2.6 optimization of solvents

Table S2 Optimization of the reaction conditions[a]

| Entry | Variation from standard conditions | Yield (%, **3a**)[b] |
|---|---|---|
| 1 | DCM instead of DCE | trace |
| 2 | EtOAc instead of DCE | 9 |
| 3 | acetone instead of DCE | trace |
| 4 | $H_2O_2$ instead of PIDA | 14 |
| 5 | $O_2$ instead of PIDA | 0 |

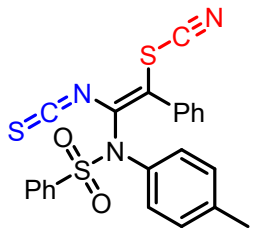
[a]Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (0.2 mmol), oxidant (0.15 mmol) and additive (0.15 mmol) in solvent (2 mL) at 30 °C for 12 h. [b]Isolated yield. [c]Measured by $^1$H NMR of the crude products. NR = no reaction.

**(*E*)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)-*N*-phenylbenzenesulfonamide (3a)**




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.56 – 7.52 (m, 2H), 7.48 – 7.41 (m, 5H), 7.38 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.28 (t, *J* = 1.2 Hz, 0.5H), 7.24

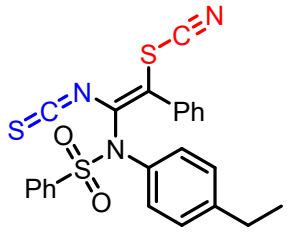
(t, $J$ = 1.2 Hz, 0.5H), 7.19 – 7.14 (m, 2H), 6.68 – 6.63 (m, 2H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.56, 138.07, 137.74, 133.74, 131.87, 130.45, 129.65, 129.33, 129.15, 128.89, 128.79, 128.18, 127.99, 127.77, 124.73, 107.31. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{15}N_3O_2S_3$ $[M+H]^+$: 450.0405, found: 450.0412.



**(*E*)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)-*N*-(*p*-tolyl) benzenesulfonamide (3b)**

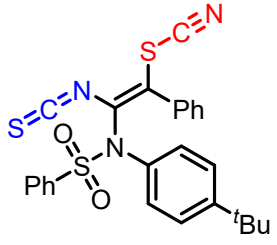
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.55 – 7.52 (m, 2H), 7.48 – 7.40 (m, 7H), 6.96 (d, $J$ = 8.2 Hz, 2H), 6.51 (d, $J$ = 8.4 Hz, 2H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.45, 139.26, 137.75, 135.29, 133.68, 131.91, 130.44, 129.97, 129.72, 129.13, 128.77, 128.23, 127.84, 127.78, 124.74, 107.42, 21.16. HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{17}N_3O_2S_3$ $[M+H]^+$:464.0561, found: 464.0540.

**(*E*)-*N*-(4-ethylphenyl)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl) benzenesulfonamide (3c)**



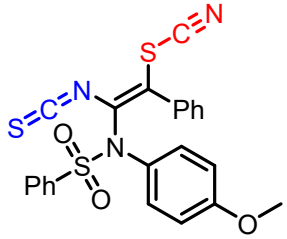
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (td, $J$ = 7.2, 1.3 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.48 – 7.39 (m, 7H), 6.99 (d, $J$ = 8.4 Hz, 2H), 6.54 (d, $J$ = 8.4 Hz, 2H), 2.59 (q, $J$ = 7.6 Hz, 2H), 1.19 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 145.44, 140.48, 137.83, 135.43, 133.66, 131.93, 130.41, 129.73, 129.12, 128.74, 128.73, 128.24, 127.95, 127.77, 124.74, 107.40, 28.39, 15.17. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{19}N_3O_2S_3$ $[M+H]^+$: 478.0718, found: 478.0705.

**(*E*)-*N*-(4-(*tert*-butyl)phenyl)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)benzenesulfonamide (3d)**



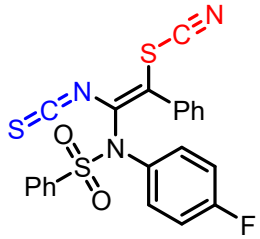
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.44 (dt, $J$ = 13.9, 6.8 Hz, 7H), 7.18 (d, $J$ = 8.9 Hz, 2H), 6.57 (d, $J$ = 8.6 Hz, 2H), 1.26 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.34, 140.50, 137.85, 135.12, 133.63, 131.86, 130.37, 129.70, 129.11, 128.69, 128.20, 127.73, 127.59, 126.26, 124.57, 107.41, 34.67, 31.16. HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{23}N_3O_2S_3$ $[M+H]^+$: 506.1031, found: 506.1022.

**(*E*)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)-*N*-(4-methoxyphenyl) benzenesulfonamide (3e)**



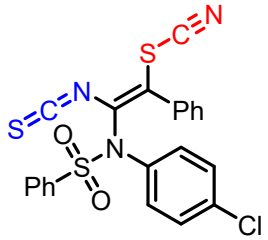
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.55 – 7.52 (m, 2H), 7.49 – 7.42 (m, 7H), 6.68 – 6.63 (m, 2H), 6.53 – 6.49 (m, 2H), 3.75 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.88, 140.47, 137.67, 133.67, 131.98, 130.44, 130.29, 129.76, 129.66, 129.11, 128.79, 128.27, 127.50, 124.93, 114.41, 107.40, 55.45. HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{17}N_3O_3S_3$ $[M+H]^+$: 480.0510, found: 480.0503.

**(*E*)-*N*-(4-fluorophenyl)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)benzenesulfonamide (3f)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 1H), 7.55 – 7.52 (m, 2H), 7.49 – 7.43 (m, 5H), 7.41 – 7.37 (m, 2H), 6.88 – 6.82 (m, 2H), 6.61 – 6.55 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.43 (d, *J*=251.49 Hz), 140.70, 137.47, 133.92, 133.82 (d, *J*= 3.03 Hz), 131.84, 130.58, 130.9 (d, *J*= 9.09 Hz), 129.64, 129.26, 128.90, 128.19, 128.07, 124.66, 116.33 (d, *J*= 22.22 Hz), 107.23. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -110.58 (s, 1F). HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{14}FN_3O_2S_3$ $[M+H]^+$: 468.0310, found: 468.0301.

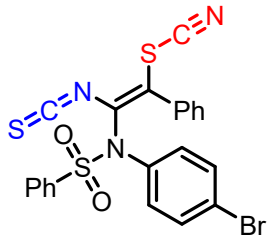
**(*E*)-*N*-(4-chlorophenyl)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)benzenesulfonamide (3g)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.46 (dt, *J* = 6.3, 3.4 Hz, 5H), 7.37 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.76, 137.49, 136.49, 134.94, 133.93, 131.74, 130.57, 129.56, 129.53, 129.28, 128.98, 128.88, 128.27, 128.12, 124.48, 107.13. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{14}ClN_3O_2S_3$ $[M+H]^+$: 484.0015, found: 484.0024.

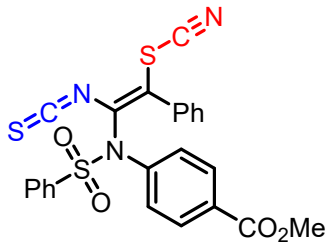
**(*E*)-*N*-(4-bromophenyl)-*N*-(1-isothiocyanato-2-phenyl-2-**

**thiocyanatovinyl)benzenesulfonamide (3h)**



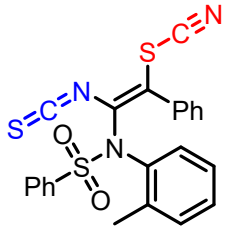
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 1H), 7.57 – 7.54 (m, 2H), 7.48 – 7.43 (m, 5H), 7.37 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.31 – 7.27 (m, 2H), 6.54 – 6.49 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.79, 137.50, 137.06, 133.94, 132.54, 131.74, 130.57, 129.55, 129.29, 129.19, 128.88, 128.31, 128.11, 124.43, 123.03, 107.11. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{14}BrN_3O_2S_3$ $[M+H]^+$: 527.9510, found: 527.9499.

**methyl(*E*)-4-(*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)phenylsulfonamido)benzoate (3i)**



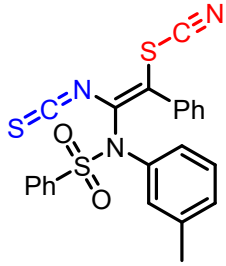
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2H), 7.65 – 7.54 (m, 3H), 7.42 (dt, *J* = 9.5, 7.1 Hz, 5H), 7.31 (d, *J* = 6.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.89 , 142.20 , 137.56 , 134.00 , 131.62 , 130.65 , 130.54 , 129.75 , 129.40 , 129.30 , 128.86 , 127.99 , 126.21 , 124.38 , 107.06 , 52.39 . HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{17}N_3O_4S_3$ $[M+H]^+$: 508.0459, found: 508.0449.

**(*E*)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)-*N*-(*o*-tolyl) benzenesulfonamide (3j)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 3H), 7.49 – 7.38 (m, 5H), 7.33 – 7.29 (m, 2H), 7.11 (td, *J* = 7.5, 1.3 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.80 (td, *J* = 7.7, 1.8 Hz, 1H), 6.36 (dd, *J* = 8.1, 1.3 Hz, 1H), 1.56 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.76, 137.81, 137.44, 136.74, 133.86, 132.15, 131.70, 130.52, 130.12, 129.92, 129.35, 129.14, 129.02, 128.28, 126.92, 126.11, 125.44, 107.49, 17.99. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{17}N_3O_4S_3$ $[M+H]^+$: 464.0561, found: 464.0557.

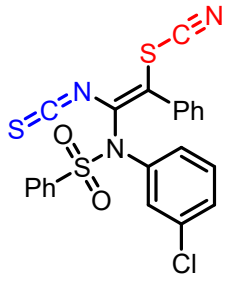
**(*E*)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl)-*N*-(*m*-tolyl) benzenesulfonamide (3k)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 3H), 7.48 – 7.42 (m, 5H), 7.37 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.05 (d, *J* = 6.7 Hz, 2H), 6.46 – 6.35 (m, 2H), 2.16 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.59, 139.40, 137.85, 138.84, 133.66, 131.92, 130.36, 129.69, 129.64, 129.07, 128.96, 128.80, 128.71,

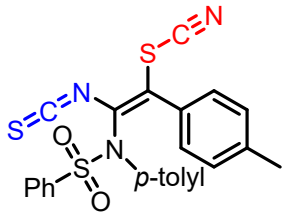
128.20, 127.63, 124.83, 124.61, 107.34, 21.18. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{17}N_3O_4S_3$ $[M+H]^+$: 464.0561, found: 464.0569.

**(*E*)-*N*-(3-chlorophenyl)-*N*-(1-isothiocyanato-2-phenyl-2-thiocyanatovinyl) benzenesulfonamide (3l)**



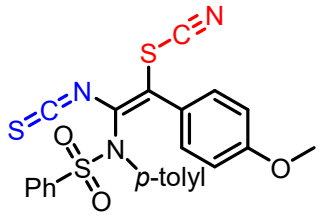
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.47 (dq, *J* = 8.0, 3.4 Hz, 5H), 7.34 (d, *J* = 6.1 Hz, 2H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.11 (t, *J* = 8.4 Hz, 1H), 6.60 – 6.56 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.04, 139.06, 137.55, 134.72, 134.02, 131.66, 130.65, 130.15, 129.51, 129.32, 129.03, 128.90, 128.36, 128.12, 128.03, 125.51, 124.38, 107.13. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{14}ClN_3O_2S_3$ $[M+H]^+$: 484.0015, found: 484.0009.

**(*E*)-*N*-(1-isothiocyanato-2-thiocyanato-2-(*p*-tolyl) vinyl)-*N*-(*p*-tolyl) benzenesulfonamide (5a)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 3.0 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.54 (d, *J* = 8.3 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.74, 140.23, 139.22, 137.85, 135.35, 133.61, 129.96, 129.61, 129.45, 129.10, 128.91, 128.41, 128.24, 127.89, 124.11, 107.55, 21.59, 21.14. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{19}N_3O_2S_3$ $[M+H]^+$: 478.0718, found: 478.0713.

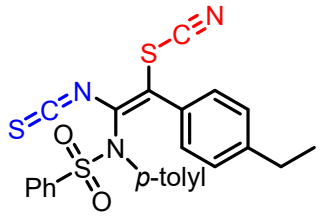
**(*E*)-*N*-(1-isothiocyanato-2-(4-methoxyphenyl)-2-thiocyanatovinyl)-*N*-(*p*-tolyl) benzenesulfonamide (5b)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 3H), 7.47 – 7.42 (m, 2H), 7.40 – 7.35 (m, 2H), 7.00 – 6.95 (m, 4H), 6.57 – 6.52 (m, 2H), 3.88 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.15, 140.12, 139.21, 137.86, 135.39, 133.63, 131.33, 129.98, 129.13, 128.29, 128.23, 127.82, 123.92, 123.89, 114.18, 107.65, 55.42, 21.14. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{19}N_3O_3S_3$ $[M+H]^+$: 494.0667, found: 494.0655.

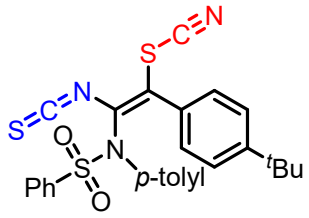
**(*E*)-*N*-(2-(4-ethylphenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl)**

**benzenesulfonamide (5c)**



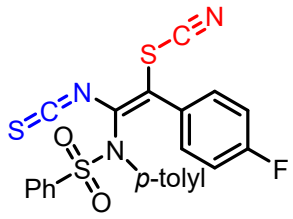
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.26 (m, 4H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.62 – 6.45 (m, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.97, 140.22, 139.16, 137.86, 135.33, 133.59, 130.45, 129.90, 129.68, 129.13, 129.07, 128.21, 128.14, 127.86, 124.32, 107.54, 28.80, 21.12, 15.31. HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{21}N_3O_2S_3$ $[M+H]^+$: 492.0874, found: 492.0866.

**(*E*)-*N*-(2-(4-(*tert*-butyl)phenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl) benzenesulfonamide (5d)**



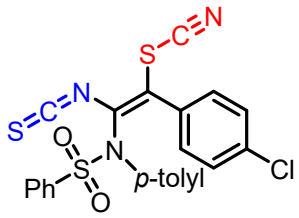
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.46 – 7.40 (m, 4H), 7.35 – 7.31 (m, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.51 – 6.47 (m, 2H), 2.28 (s, 3H), 1.37 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.90, 140.26, 139.12, 137.90, 135.34, 133.60, 129.84, 129.44, 129.08, 128.97, 128.21, 127.85, 127.66, 125.63, 124.71, 107.59, 34.97, 31.26, 21.13. HRMS (ESI-TOF) m/z Calcd for $C_{27}H_{25}N_3O_2S_3$ $[M+H]^+$: 520.1187, found: 520.1168.

**(*E*)-*N*-(2-(4-fluorophenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl) benzenesulfonamide (5e)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.15 (t, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 8.3 Hz, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.70 (d, *J*= 252.50 Hz), 140.61, 139.35, 137.69, 135.29, 133.76, 131.94 (d, *J*= 8.08 Hz), 130.06, 129.17, 128.20, 127.92 (d, *J*= 2.02 Hz), 127.62, 126.69, 125.21, 116.09 (d, *J*= 23.23 Hz), 107.27, 21.13. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -108.78 (s, 1F). HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{16}FN_3O_2S_3$ $[M+H]^+$: 482.0467, fund: 482.0474.

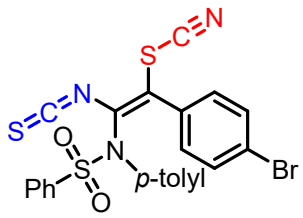
**(*E*)-*N*-(2-(4-chlorophenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl) benzenesulfonamide (5f)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.1

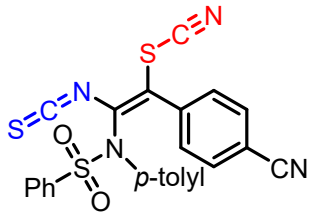
Hz, 2H), 7.47 – 7.42 (m, 4H), 7.36 (d, $J$ = 8.5 Hz, 2H), 7.00 (d, $J$ = 8.1 Hz, 2H), 6.55 (d, $J$ = 8.3 Hz, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.66, 139.41, 137.63, 136.65, 135.25, 133.79, 131.12, 130.40, 130.11, 129.18, 129.16, 128.20, 127.62, 126.39, 125.44, 107.20, 21.14. HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{16}ClN_3O_2S_3$ $[M+H]^+$: 498.0171, found: 498.0169.

**(*E*)-*N*-(2-(4-bromophenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl) benzenesulfonamide (5g)**



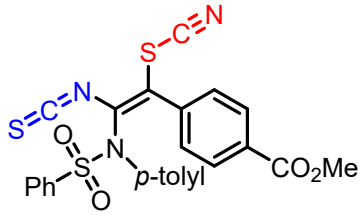
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 3H), 7.56 – 7.52 (m, 2H), 7.48 – 7.42 (m, 2H), 7.31 – 7.27 (m, 2H), 7.00 (d, $J$ = 8.3 Hz, 2H), 6.58 – 6.53 (m, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.67, 139.42, 137.62, 135.23, 133.79, 132.11, 131.30, 130.91, 130.12, 129.18, 128.20, 127.62, 126.38, 125.43, 125.00, 107.19, 21.14. HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{16}BrN_3O_2S_3$ $[M+H]^+$: 541.9666, found: 541.9659.

**(*E*)-*N*-(2-(4-cyanophenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl) benzenesulfonamide (5h)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, $J$ = 8.9 Hz, 2H), 7.64 – 7.58 (m, 1H), 7.58 – 7.55 (m, 2H), 7.51 – 7.40 (m, 4H), 6.94 (d, $J$ = 8.1 Hz, 2H), 6.57 (d, $J$ = 8.4 Hz, 2H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.86 , 145.42 , 139.49 , 138.96 , 136.74 , 134.96 , 134.23 , 130.29 , 130.15 , 129.12 , 128.26 , 126.95 , 126.28 , 124.15 , 106.89 , 105.87 , 21.05. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{16}N_4O_2S_3$ $[M+H]^+$: 489.0514, found: 489.0511.

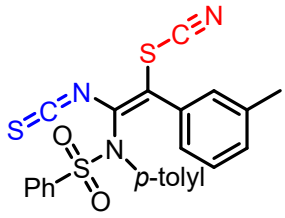
**methyl(*E*)-4-(2-isothiocyanato-1-thiocyanato-2-(*N*-(*p*-tolyl) phenylsulfonamido)vinyl)benzoaye (5i)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, $J$ = 8.6, 2.0 Hz, 2H), 7.60 (t, $J$ = 7.4 Hz, 1H), 7.55 (d, $J$ = 7.1 Hz, 2H), 7.50 (d, $J$ = 8.5 Hz, 2H), 7.47 – 7.41 (m, 2H), 6.97 (d, $J$ = 8.0 Hz, 2H), 6.52 (d, $J$ = 8.4 Hz, 2H), 3.97 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.26, 140.78, 139.41, 137.57, 136.42, 135.25, 133.80, 131.66, 130.10, 129.96, 129.88, 129.17, 128.21, 127.56, 126.21, 125.94, 107.04, 52.45, 21.13. HRMS (ESI-TOF) m/z Calcd for

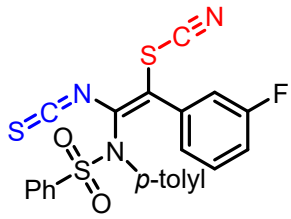
$C_{25}H_{19}N_3O_4S_3$ [M+H]$^+$: 522.0616, found: 522.0609.

**(*E*)-*N*-(1-isothiocyanato-2-thiocyanato-2-(*m*-tolyl)vinyl)-*N*-(*p*-tolyl)benzenesulfonamide (5j)**



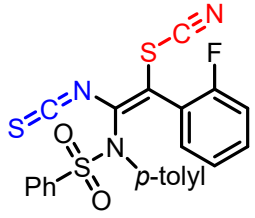
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 3H), 7.45 – 7.40 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.28 (s, 1H), 7.20 – 7.17 (m, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.54 – 6.50 (m, 2H), 2.38 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.41, 139.18, 138.48, 137.85, 135.42, 133.61, 131.75, 131.15, 130.20, 129.89, 129.07, 128.62, 128.21, 128.01, 127.88, 126.73, 124.52, 107.47, 21.37, 21.13. HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{19}N_3O_2S_3$ [M+H]$^+$: 478.0718, found: 478.0722.

**(*E*)-*N*-(2-(3-fluorophenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl)benzenesulfonamide (5k)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 7.44 (ddt, *J* = 9.9, 4.5, 3.0 Hz, 3H), 7.24 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 7.17 (tdd, *J* = 8.5, 2.6, 1.0 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.60 – 6.51 (m, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.41 (d, *J*= 249.47 Hz), 140.85, 139.44, 137.63, 136.17, 135.27, 133.90, 133.80, 130.52 (d, *J*= 9.09 Hz), 130.09, 129.17, 128.21, 127.65, 125.81 (d, *J*= 4.04 Hz), 125.70 (d, *J*= 3.03 Hz), 117.48 (d, *J*= 20.2 Hz), 116.84 (d, *J*= 23.23 Hz), 107.10, 21.14. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.02 (s, 1F). HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{16}FN_3O_2S_3$ [M+H]$^+$: 482.0467, found: 482.0459.

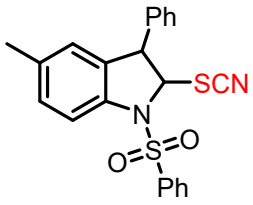
**(*E*)-*N*-(2-(2-fluorophenyl)-1-isothiocyanato-2-thiocyanatovinyl)-*N*-(*p*-tolyl)benzenesulfonamide (5l)**



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 3H), 7.53 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.32 – 7.27 (m, 1H), 7.08 (t, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.62 (d, *J*= 252.50 Hz), 141.05, 139.31, 137.75, 135.04, 133.72, 132.75 (d, *J*= 8.08 Hz), 131.95, 129.98, 129.13, 128.18, 127.72, 126.72, 124.64 (d, *J*= 3.03 Hz), 121.97, 119.81 (d, *J*= 14.14 Hz), 115.98 (d, *J*= 20.2 Hz), 107.13, 21.16. $^{19}$F NMR (376 MHz,

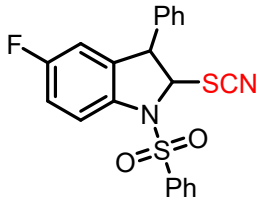
$CDCl_3$) δ -110.23 (s, 1F). HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{16}FN_3O_2S_3$ $[M+H]^+$: 482.0467, found: 482.0471.

**5-methyl-3-phenyl-1-(phenylsulfonyl)-2-thiocyanatoindoline (7a)**



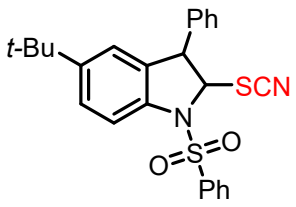

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.47 – 7.42 (m, 5H), 7.25 (d, *J* = 2.8 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 10.5 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 2H), 4.03 (d, *J* = 10.5 Hz, 1H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.55，140.41, 137.57, 133.68, 133.08, 130.85, 130.45, 130.02, 129.92, 129.42, 129.14, 128.36, 128.20, 109.51, 72.35, 56.08, 21.29. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{18}O_2S_2N_2$ $[M+H]^+$: 406.0810, found: 406.0812.

**5-fluoro-3-phenyl-1-(phenylsulfonyl)-2-thiocyanatoindoline (7b)**



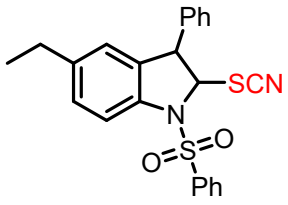

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, *J* = 7.0 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.52 – 7.45 (m, 6H), 6.97 – 6.90 (m, 2H), 6.84 (d, *J* = 10.5 Hz, 1H), 6.62 (s, 1H), 3.99 (d, *J* = 10.5 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.14 (d, *J*=252.5 Hz), 142.45, 137.22, 133.88, 133.06 (d, *J*=9.09 Hz), 131.51 (d, *J*=269.67 Hz), 129.66, 129.52, 129.24, 128.76, 128.32, 128.26, 128.18, 116.30 (d, *J*=23.23 Hz), 109.27, 72.35, 56.14. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -109.21 (s, 1F). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{15}O_2S_2N_2F$ $[M+H]^+$: 411.0632, found: 411.0629.

**5-(tert-butyl)-3-phenyl-1-(phenylsulfonyl)-2-thiocyanatoindoline (7c)**



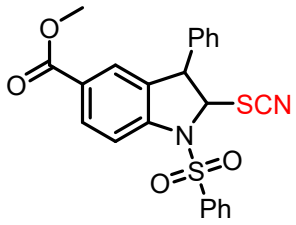

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.47 (dd, *J* = 6.6, 2.4 Hz, 5H), 7.27 – 7.24 (m, 3H), 6.82 (d, *J* = 10.5 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.06 (d, *J* = 10.5 Hz, 1H), 1.30 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.45, 141.29, 137.71, 133.63, 133.08, 130.56, 130.39, 130.01, 129.41, 129.14, 128.37, 128.18, 126.20, 109.54, 72.42, 56.02, 34.85, 31.24. HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{24}O_2S_2N_2$ $[M+H]^+$: 448.1279, found: 448.1277.

**5-ethyl-3-phenyl-1-(phenylsulfonyl)-2-thiocyanatoindoline (7d)**



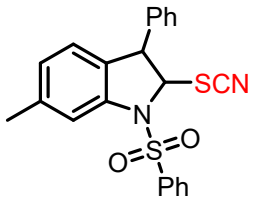

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.43 (m, 5H), 7.26 (d, *J* = 2.8 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 10.5 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 2H), 4.05 (d, *J* = 10.5 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 146.50, 141.51, 137.66, 133.62, 133.08, 130.92, 130.63, 130.01, 129.40, 129.11, 128.64, 128.36, 128.20, 109.46, 72.41, 56.10, 28.49, 15.10. HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{20}O_2S_2N_2$ $[M+H]^+$: 420.0966, found: 420.0965.

**methyl 3-phenyl-1-(phenylsulfonyl)-2-thiocyanatoindoline-5-carboxylate (7e)**



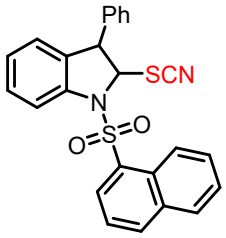

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.50 – 7.45 (m, 4H), 7.20 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.85 (d, *J* = 10.6 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.00 (d, *J* = 10.6 Hz, 1H), 3.93 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.89, 142.80, 137.78, 137.24, 133.97, 132.72, 131.42, 130.86, 130.38, 130.19, 129.51, 129.30, 128.21, 128.11, 109.22, 72.38, 56.16, 52.56. HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{18}O_4S_2N_2$ $[M+H]^+$: 450.0708, found: 450.0778.

**6-methyl-3-phenyl-1-(phenylsulfonyl)-2-thiocyanatoindoline (7f)**




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.46 (p, *J* = 4.8, 4.1 Hz, 5H), 7.25 – 7.23 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 10.5 Hz, 1H), 6.40 (d, *J* = 37.0 Hz, 2H), 4.02 (d, *J* = 10.5 Hz, 1H), 2.20 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.59, 139.31, 137.58, 133.68, 133.10, 132.20, 130.79, 130.02, 129.34, 129.08, 128.88, 128.36, 128.22, 127.54, 109.45, 72.35, 56.12, 21.21. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{18}O_2S_2N_2$ $[M+H]^+$: 406.0810, found: 406.0812.

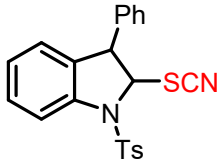
**1-(naphthalen-1-ylsulfonyl)-3-phenyl-2-thiocyanatoindoline (7g)**




$^1$H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.93 – 7.85 (m, 3H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.43 (m, 4H), 7.36 (t, *J* = 7.4 Hz,

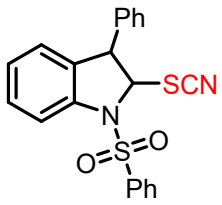
1H), 7.26 (dd, *J* = 5.7, 2.3 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 10.5 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.04 (d, *J* = 10.5 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.14 , 135.11 , 134.31 , 133.33 , 132.94 , 131.95 , 131.07 , 129.97 , 129.89 , 129.46 , 129.34 , 129.29 , 129.19 , 129.15 , 128.25 , 127.85 , 127.62 , 109.36 , 72.38 , 56.00. HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{18}O_2S_2N_2$ $[M+H]^+$: 442.0810, found: 442.0811.

**3-phenyl-2-thiocyanato-1-tosylindoline (7h)**




$^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 3H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.21 (m, 6H), 6.84 (d, *J* = 10.5 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 2H), 4.03 (d, *J* = 10.5 Hz, 1H), 2.42 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 144.78 , 131.10 , 130.01 , 129.98 , 129.75 , 129.40 , 129.20 , 128.33 , 128.21 , 109.46 , 72.36 , 56.15 , 21.71 . HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{19}O_2S_2N_2$ $[M+H]^+$: 407.0882, found: 407.0881.

**3-phenyl-1-(phenylsulfonyl)-2-thiocyanatoindoline (7i)**

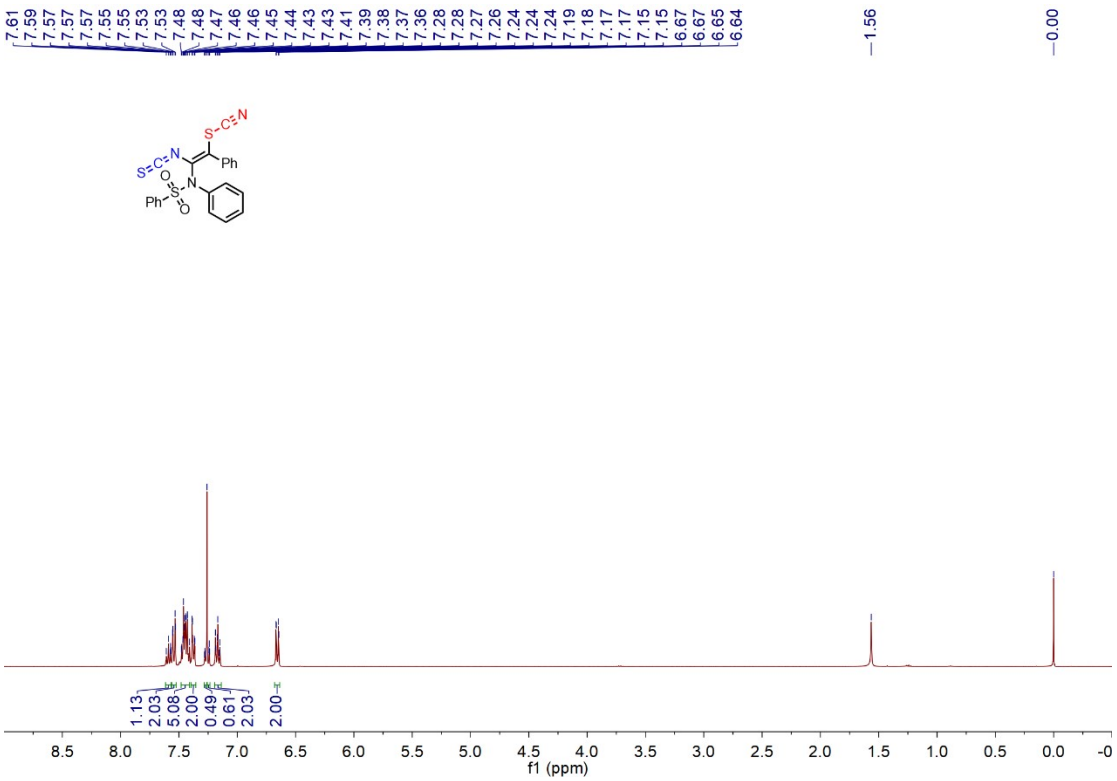



$^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.48 – 7.42 (m, 5H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.21 (m, 3H), 6.85 (d, *J* = 10.5 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 2H), 4.03 (d, *J* = 10.5 Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 137.48 , 133.74 , 133.39 , 133.00 , 131.08 , 130.08 , 130.07 , 129.43 , 129.25 , 129.16 , 128.32 , 128.19 , 72.36 , 56.10 . HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{17}O_2S_2N_2$ $[M+H]^+$: 393.0726, found: 393.0723.

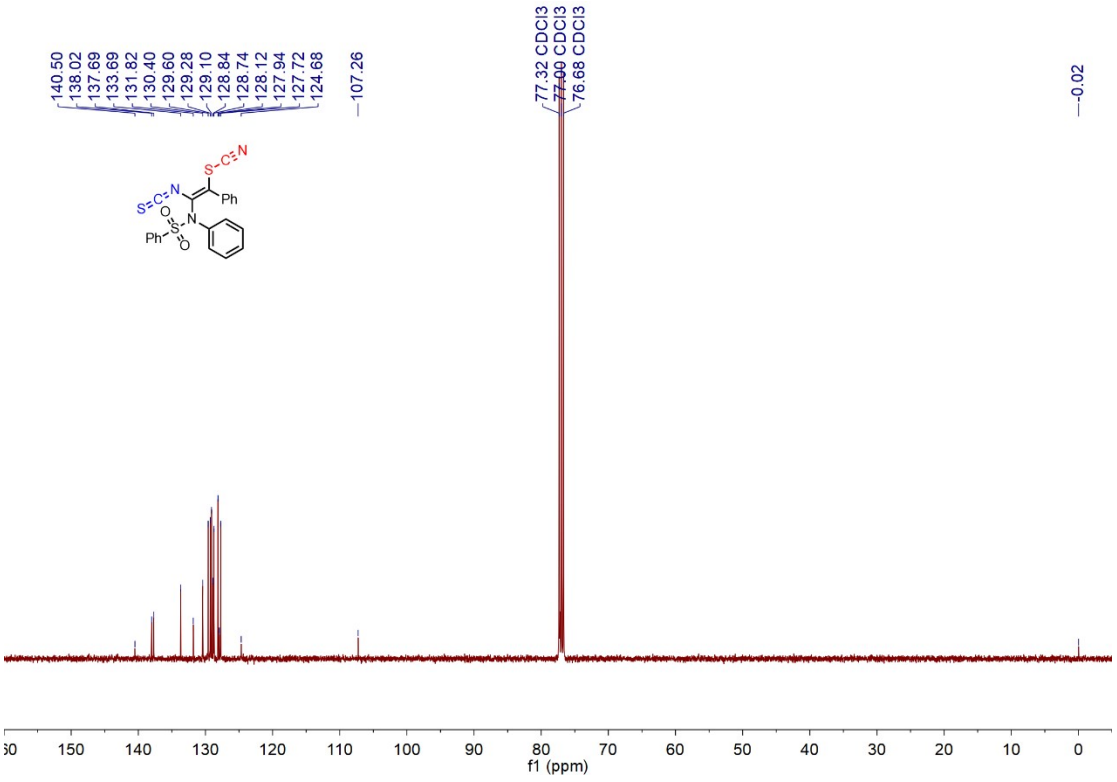
## 3. References


1. F. Pan, X.-L. Li, X.-M. Chen, C. Shu, P.-P. Ruan, C.-H. Shen, X. Lu and L.-W. Ye, *ACS Catalysis*, 2016, **6**, 6055-6062.
2. Z. Zeng, H. Jin, J. Xie, B. Tian, M. Rudolph, F. Rominger and A. S. Hashmi, *Org Lett*, 2017, **19**, 1020-1023.
3. L. Zhu, Y. Yu, Z. Mao and X. Huang, *Org Lett*, 2015, **17**, 30-33.
4. L. Liao, H. Zhang and X. Zhao, *ACS Catalysis*, 2018, **8**, 6745-6750.

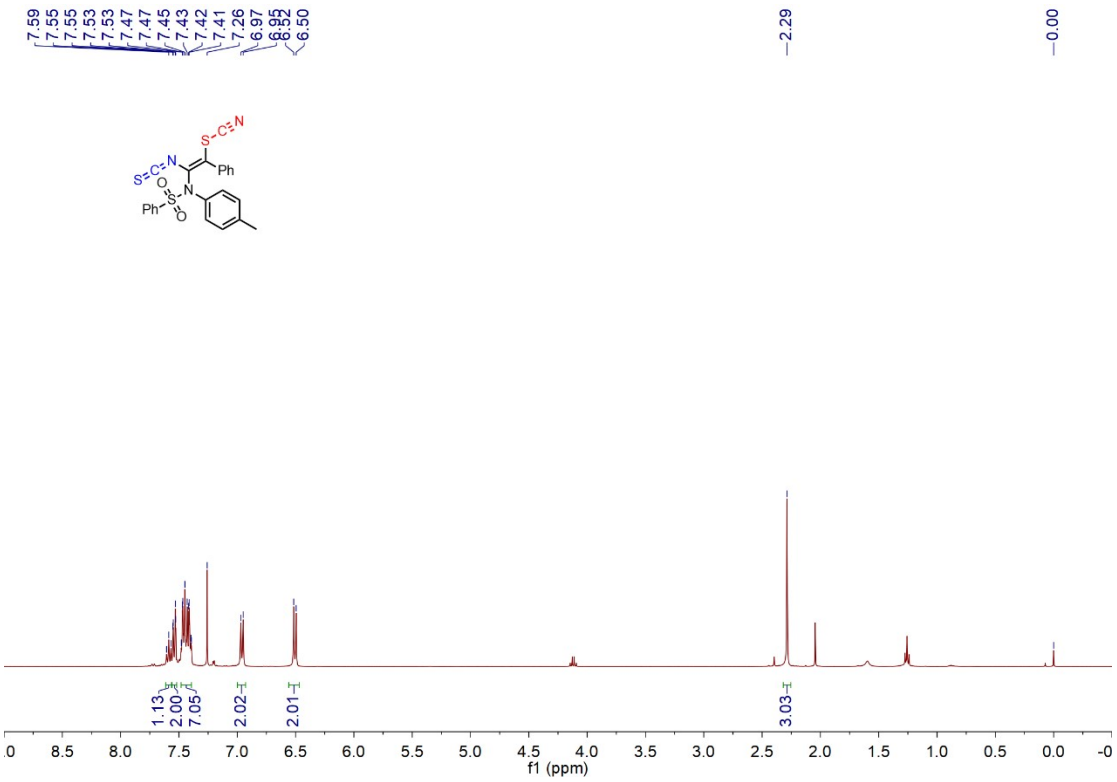

## 4. $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra



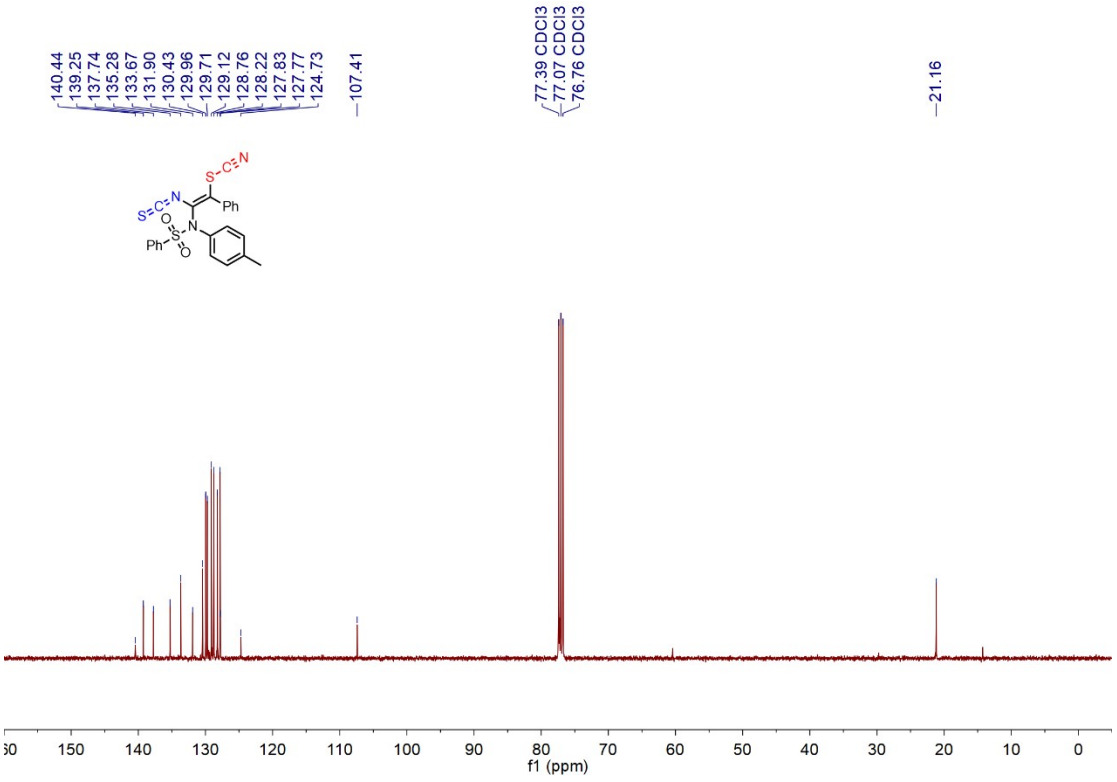

$^{1}$H NMR Spectrum of Compound **3a** (400 MHz, $CDCl_3$)



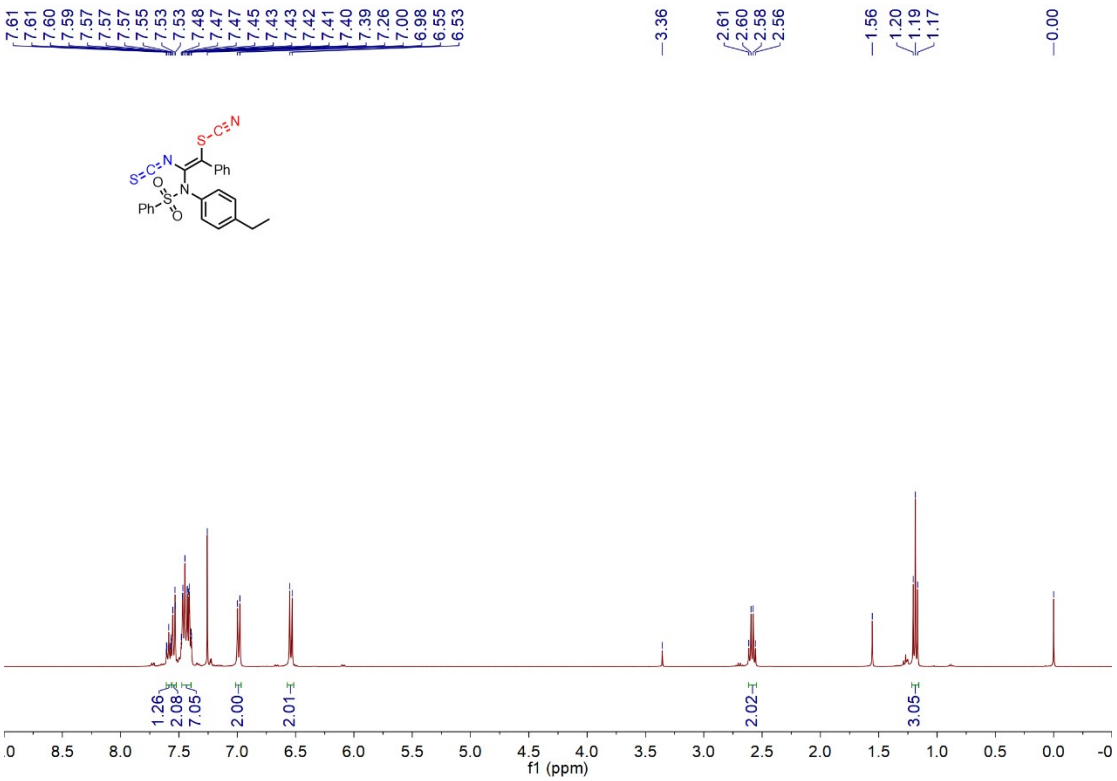

$^{13}$C NMR Spectrum of Compound **3a** (100 MHz, $CDCl_3$)



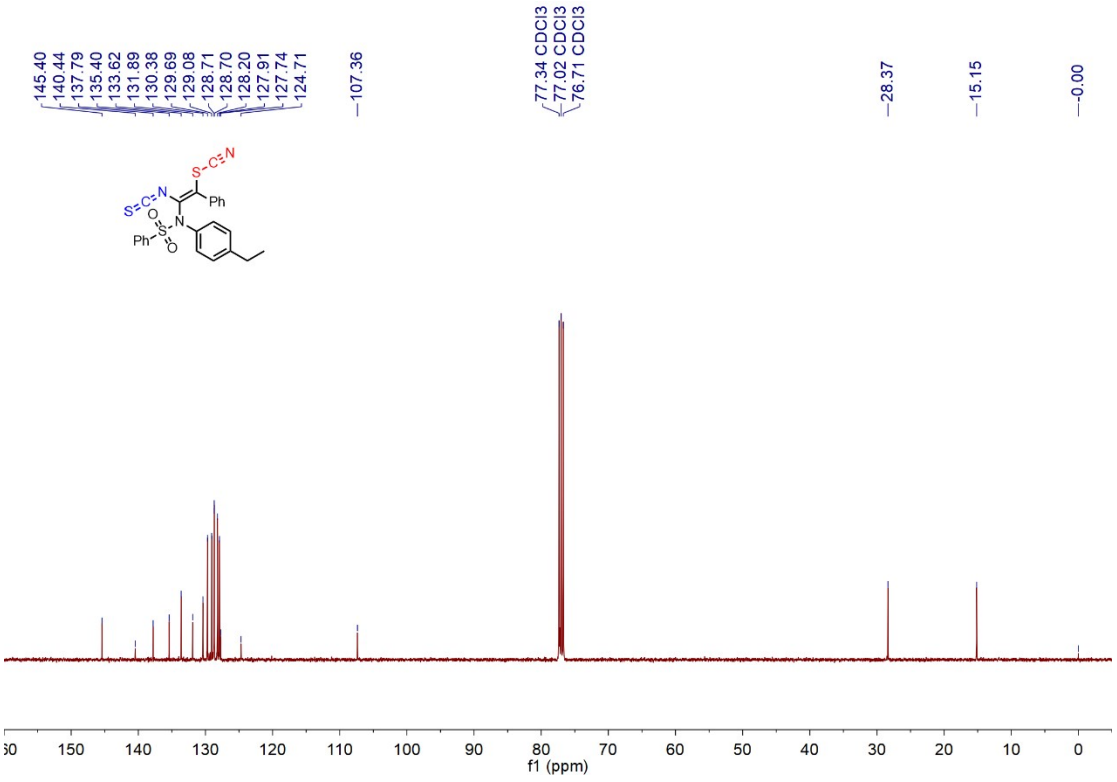

$^{1}$H NMR Spectrum of Compound **3b** (400 MHz, $CDCl_3$)



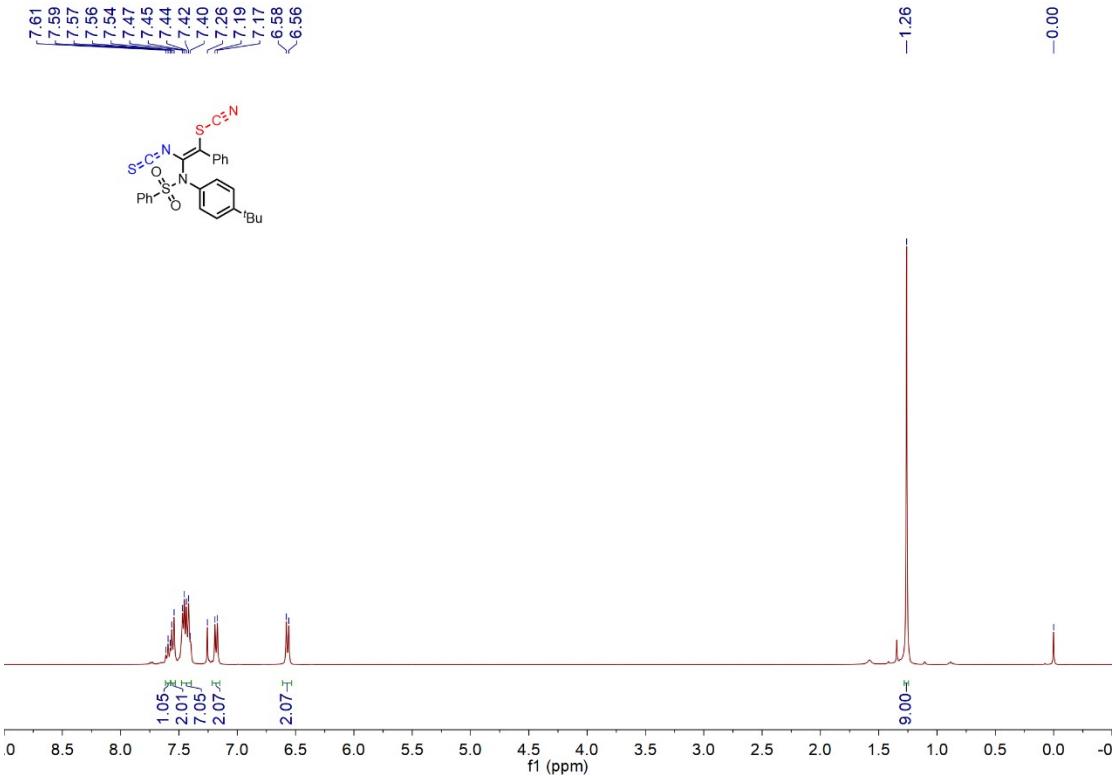

$^{13}$C NMR Spectrum of Compound **3b** (100 MHz, $CDCl_3$)



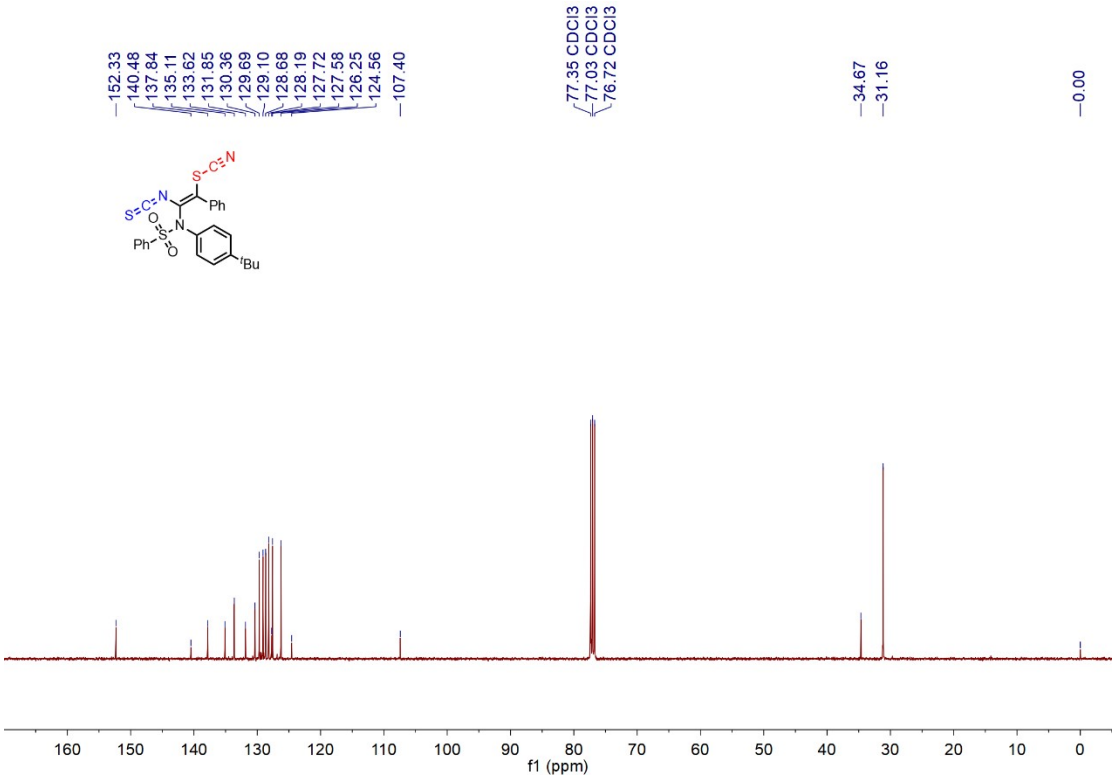

$^{1}$H NMR Spectrum of Compound **3c** (400 MHz, $CDCl_3$)



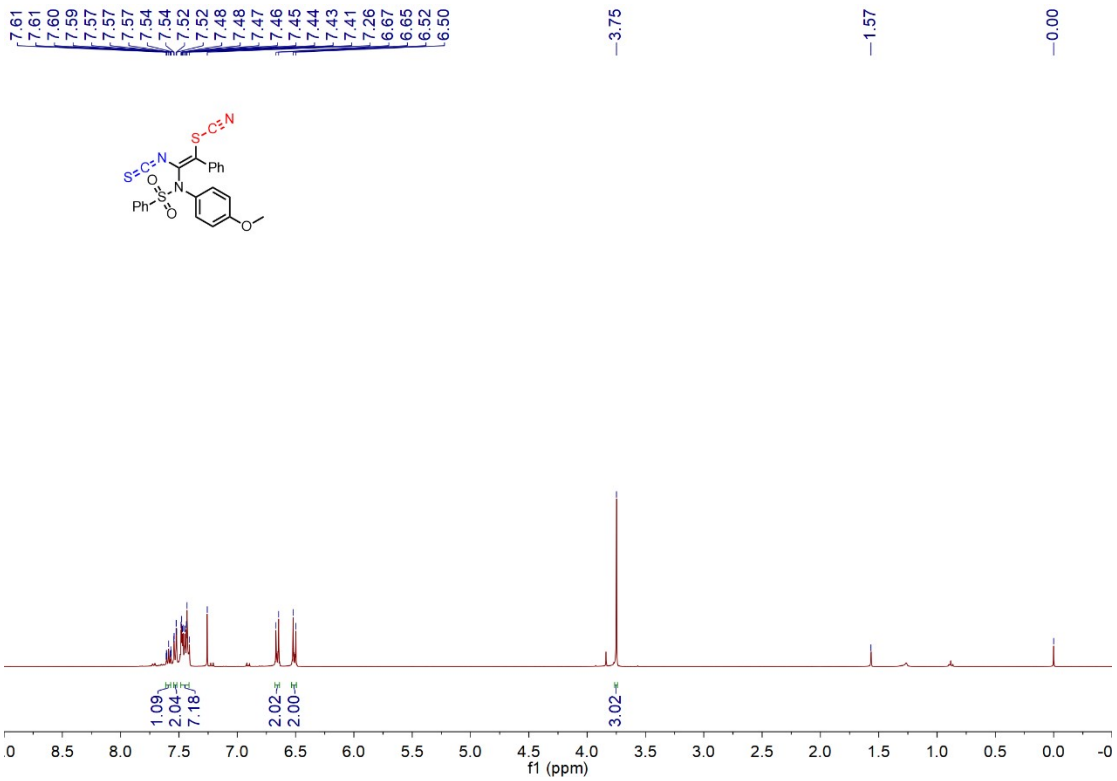

$^{13}$C NMR Spectrum of Compound **3c** (100 MHz, $CDCl_3$)



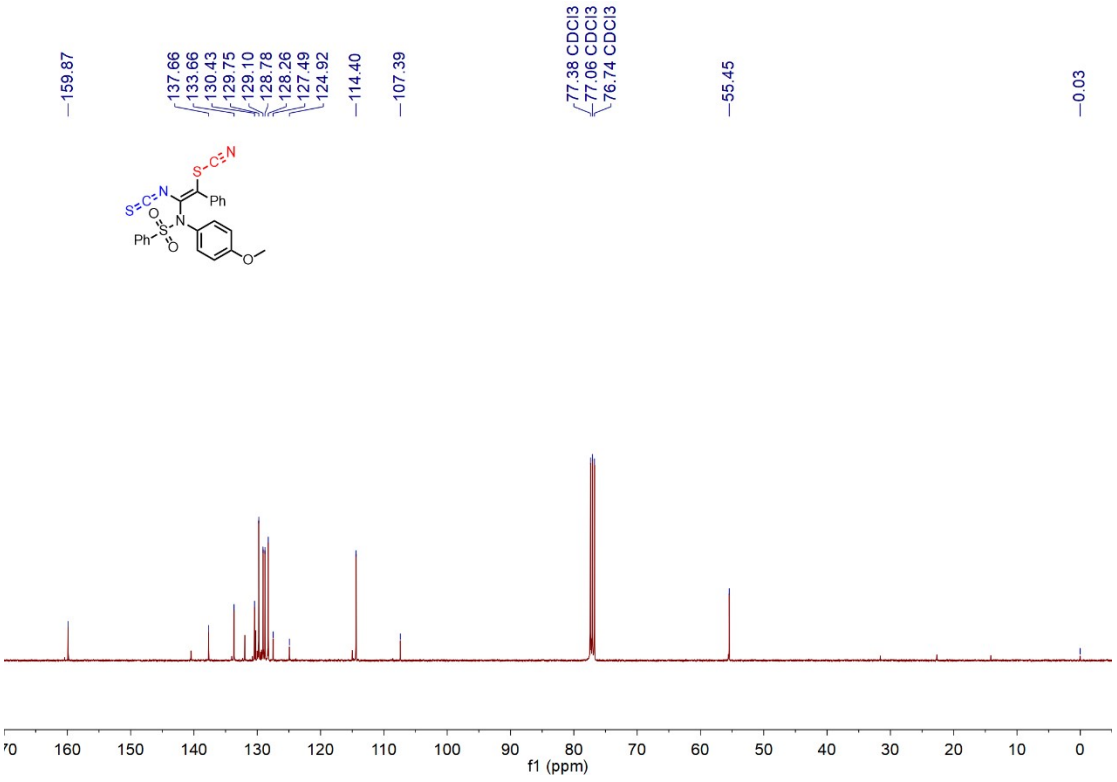

$^{1}$H NMR Spectrum of Compound **3d** (400 MHz, $CDCl_3$)



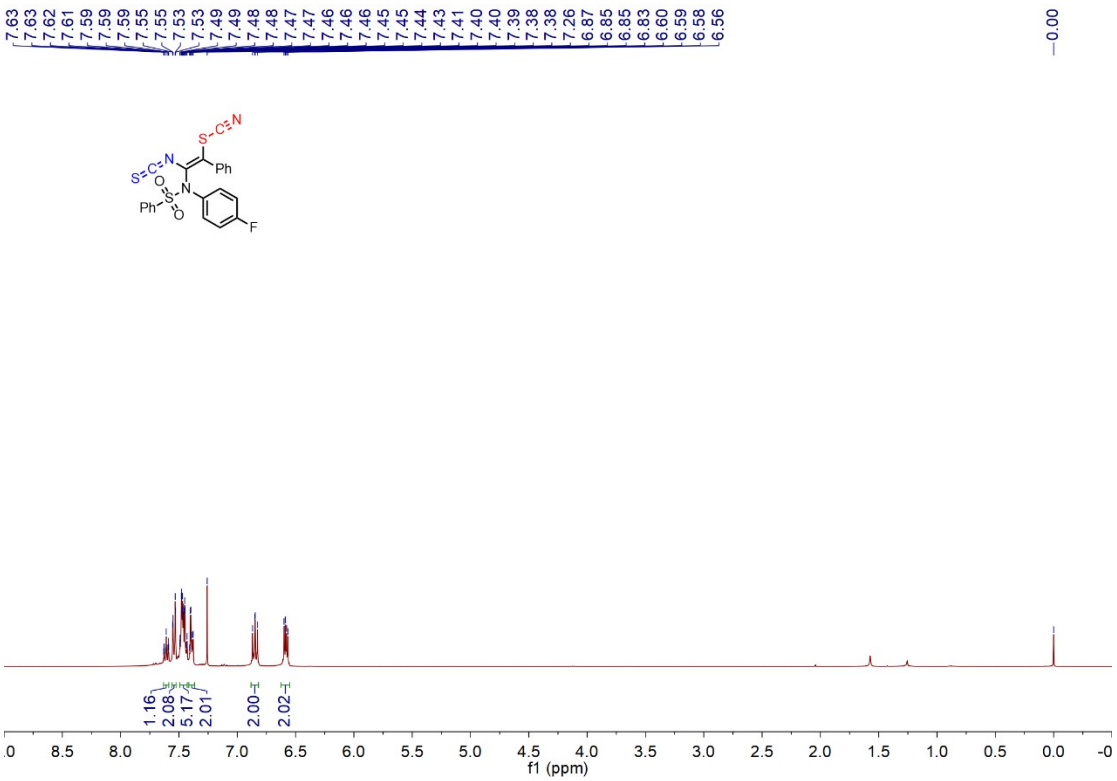

$^{13}$C NMR Spectrum of Compound **3d** (100 MHz, $CDCl_3$)



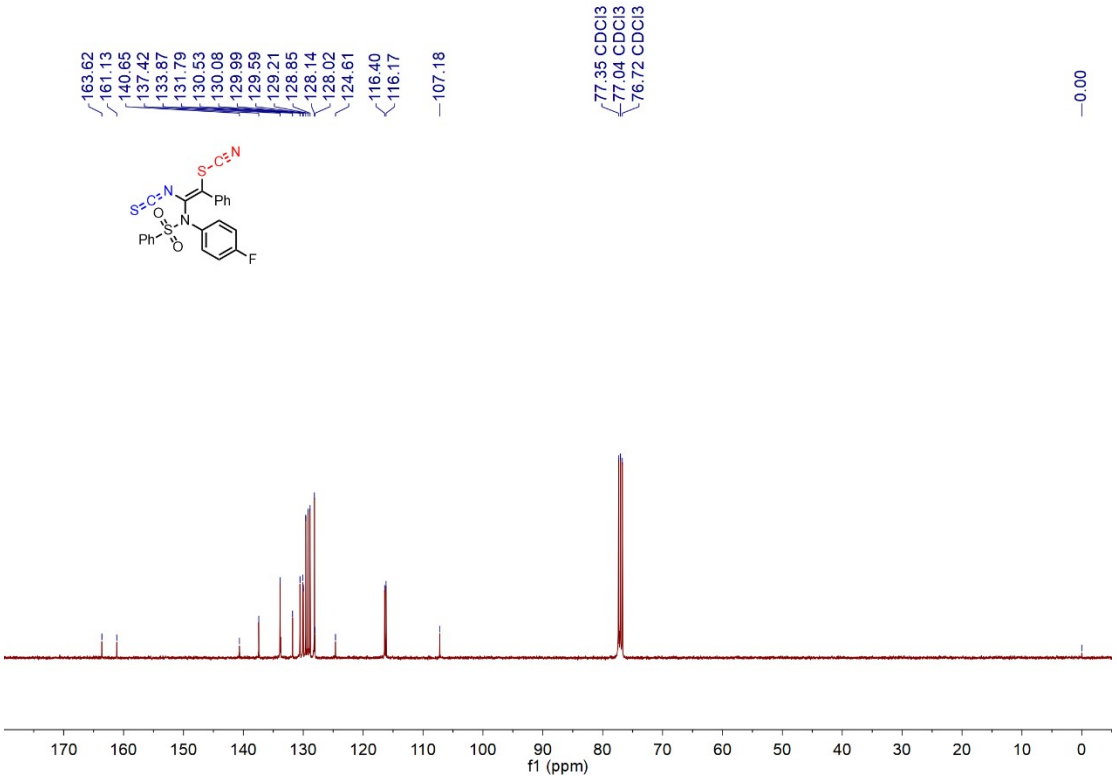

$^{1}$H NMR Spectrum of Compound **3e** (400 MHz, $CDCl_3$)



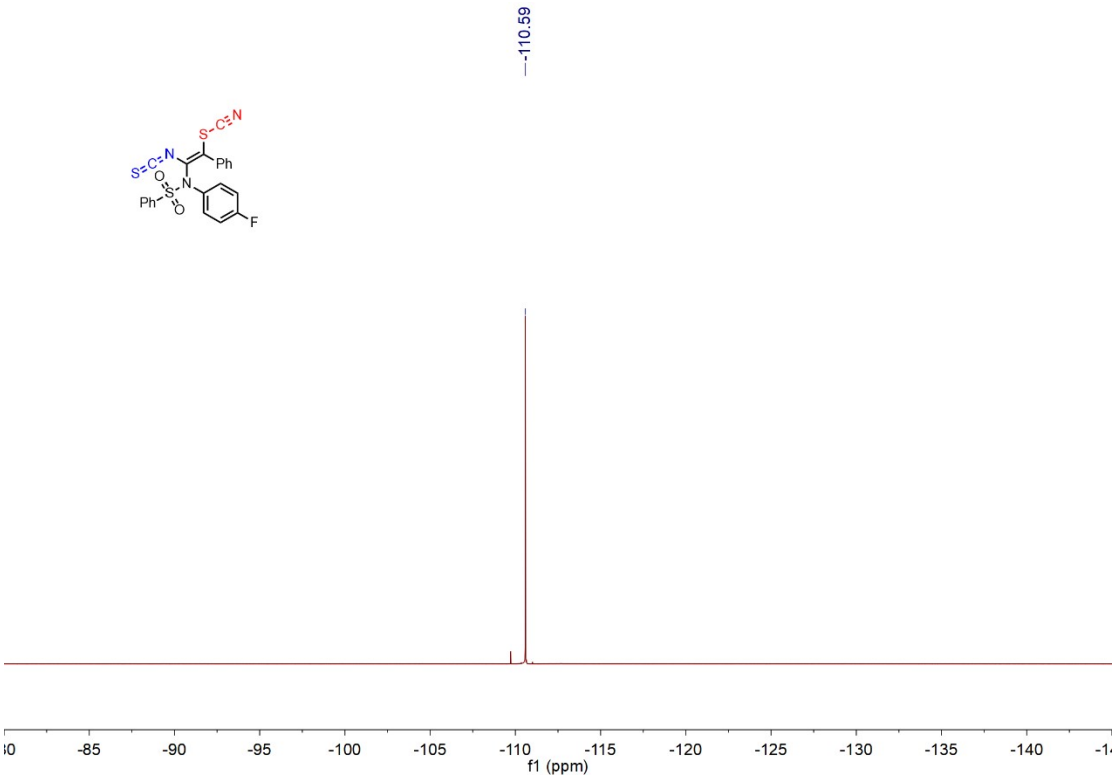

$^{13}$C NMR Spectrum of Compound **3e** (100 MHz, $CDCl_3$)



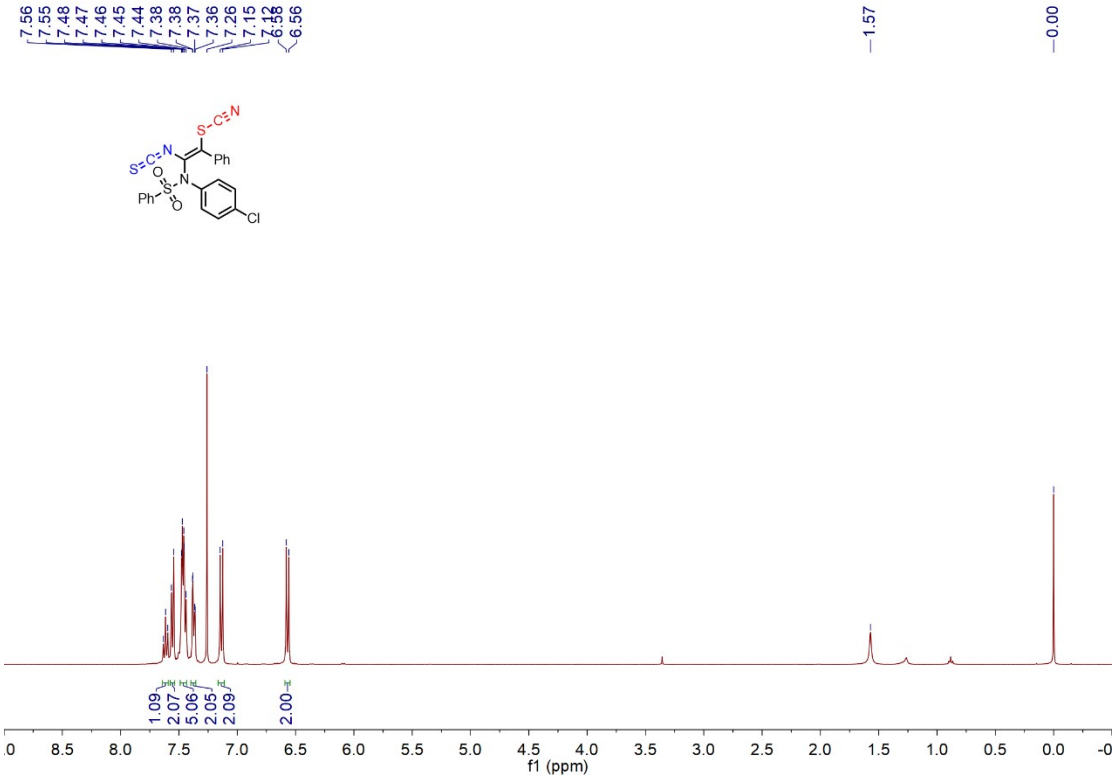

$^{1}$H NMR Spectrum of Compound **3f** (400 MHz, $CDCl_3$)



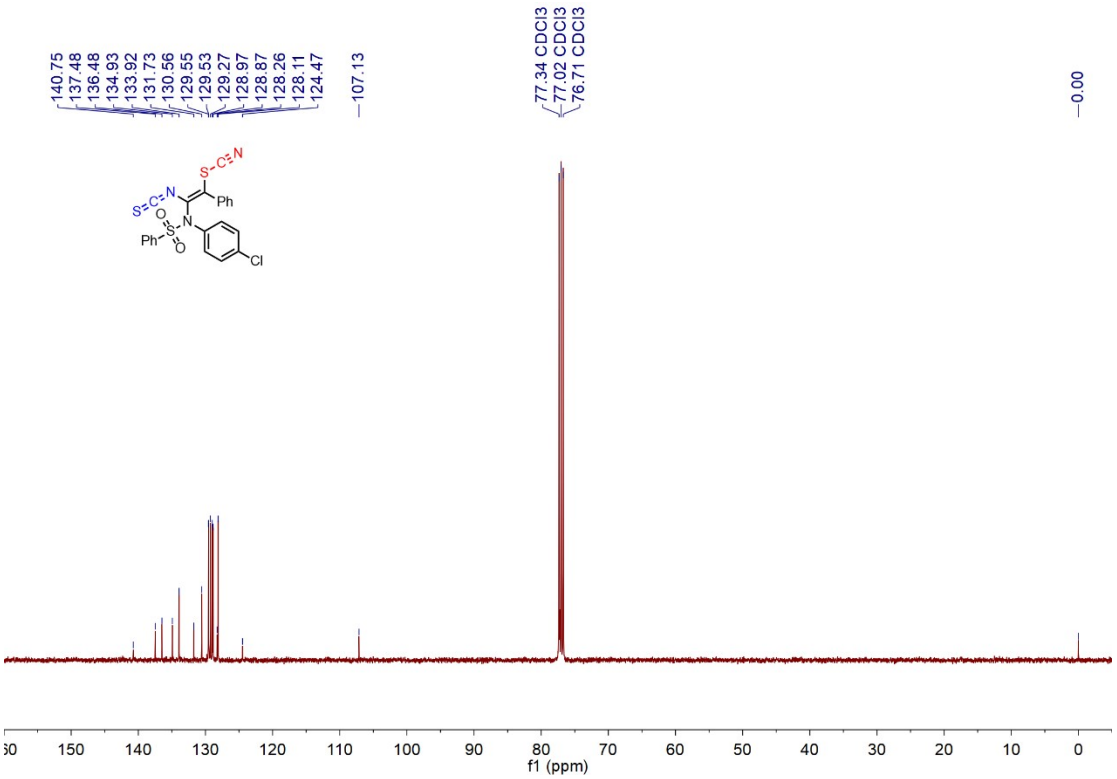

$^{13}$C NMR Spectrum of Compound **3f** (100 MHz, $CDCl_3$)



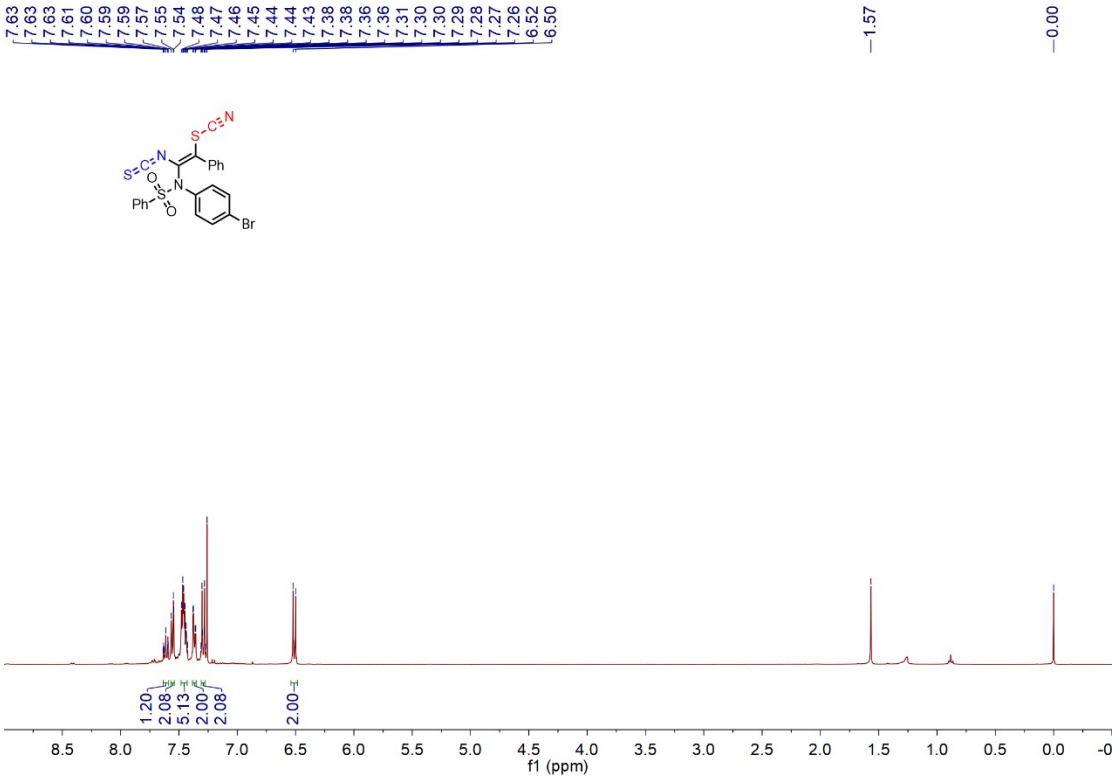

$^{19}$F NMR Spectrum of Compound **3f** (376 MHz, $CDCl_3$)



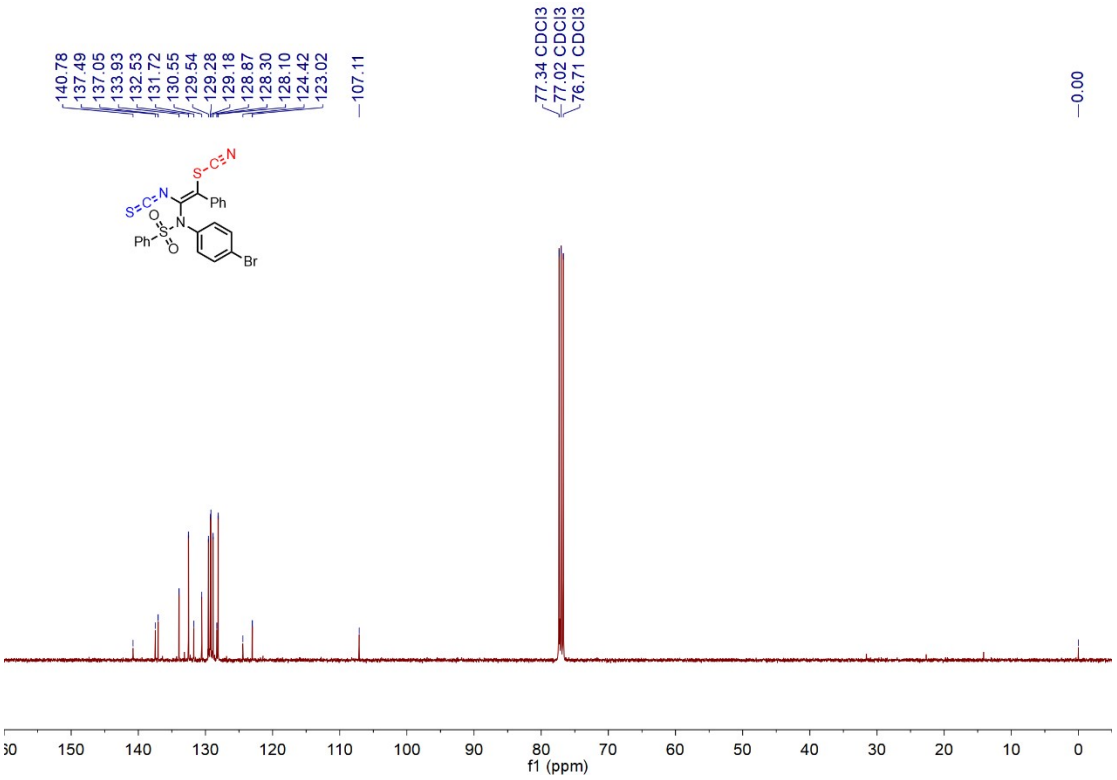

$^{1}$H NMR Spectrum of Compound **3g** (400 MHz, $CDCl_3$)



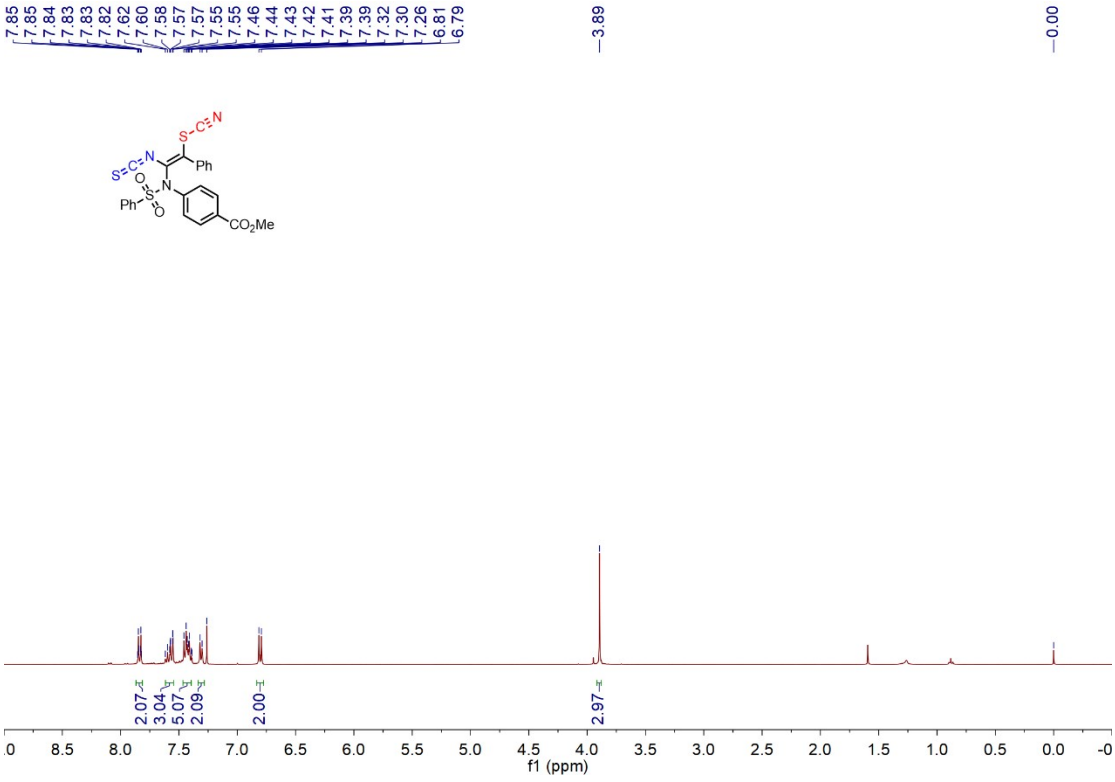

$^{13}$C NMR Spectrum of Compound **3g** (100 MHz, $CDCl_3$)



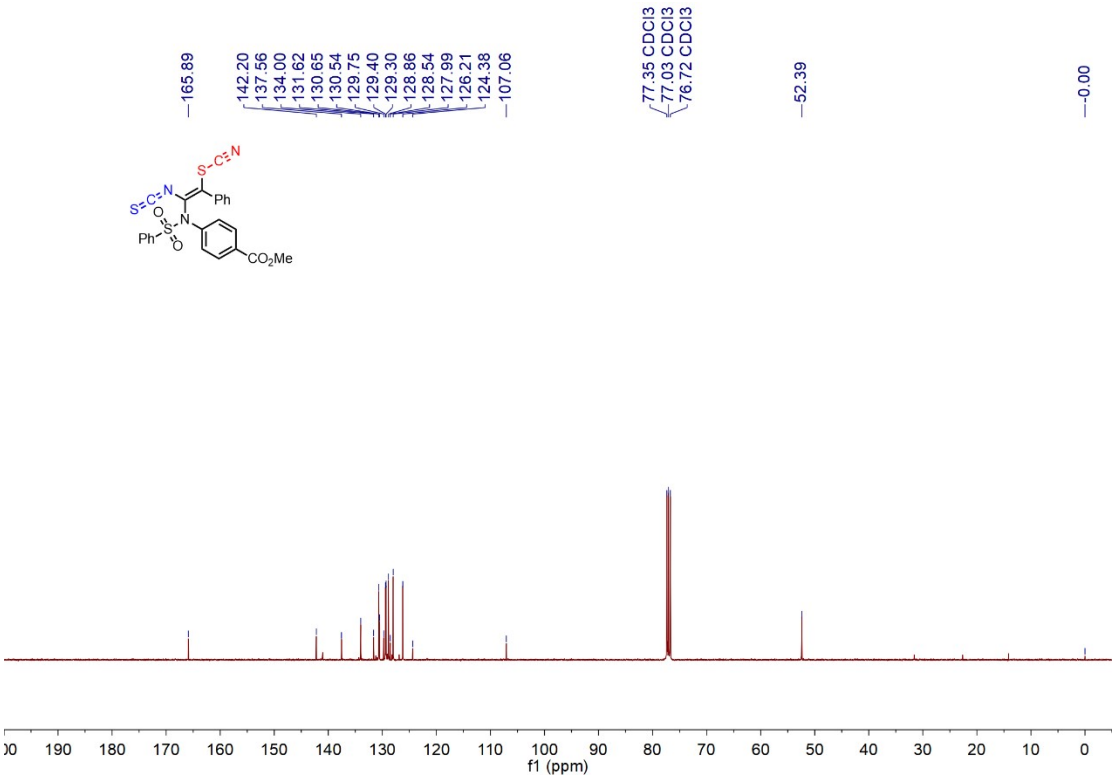

$^{1}$H NMR Spectrum of Compound **3h** (400 MHz, $CDCl_3$)



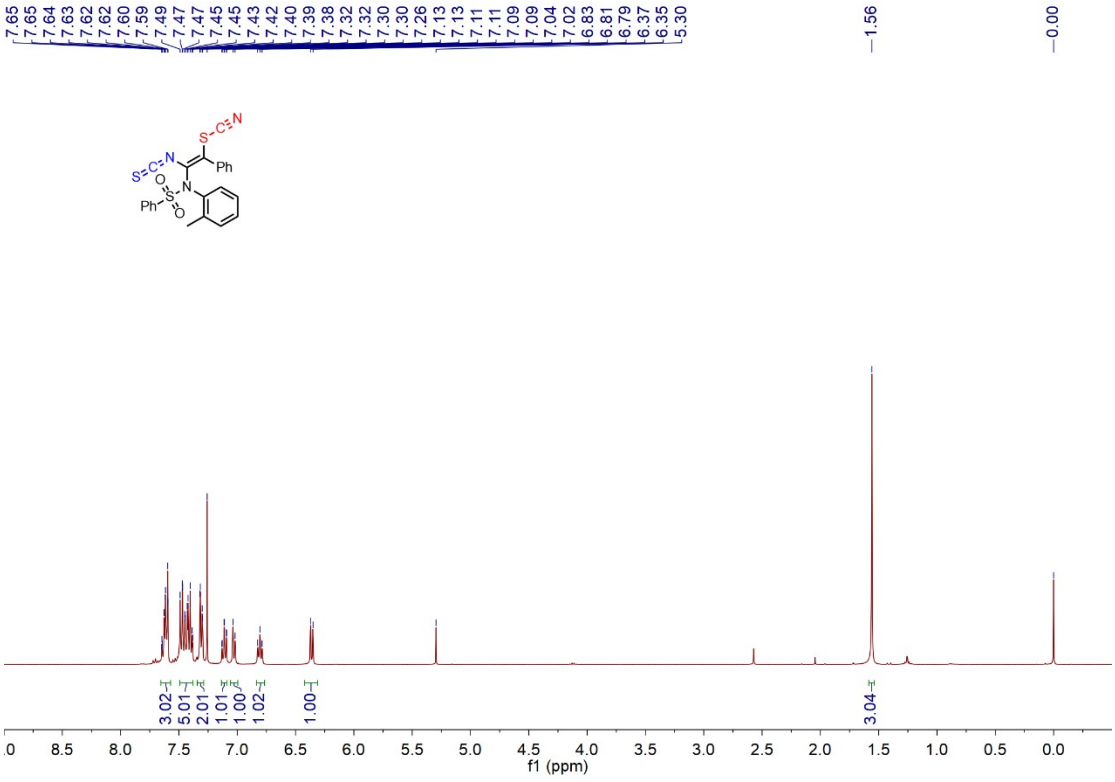

$^{13}$C NMR Spectrum of Compound **3h** (100 MHz, $CDCl_3$)



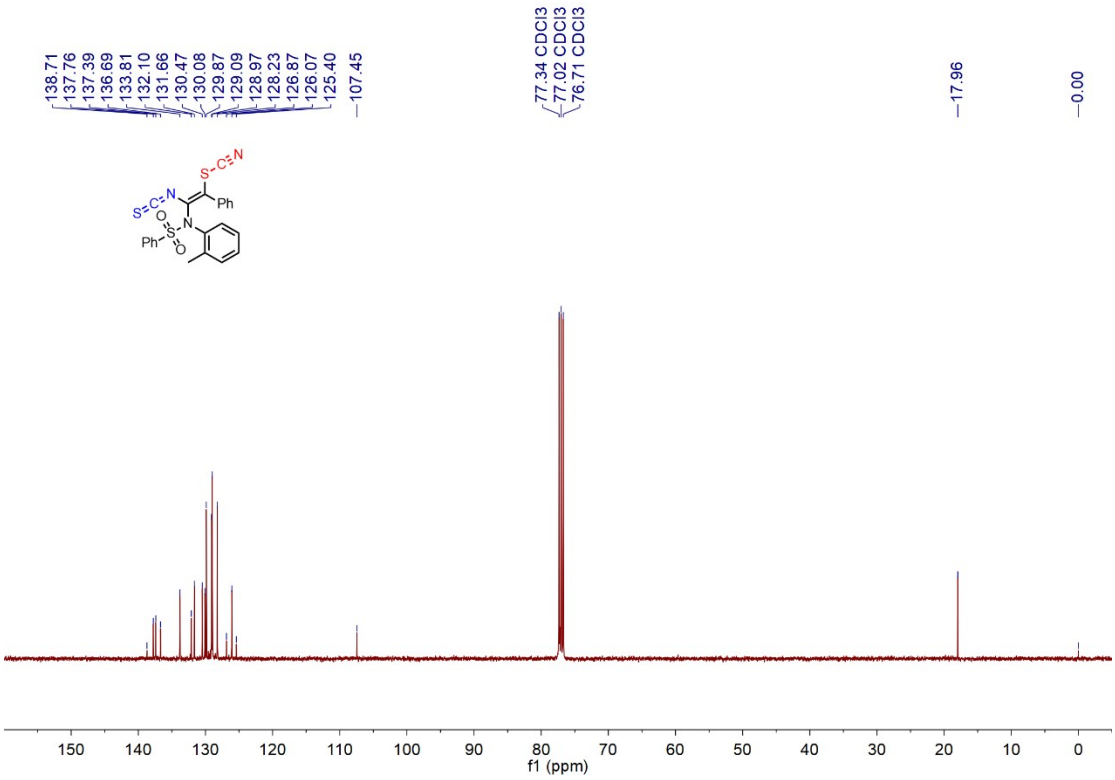

$^{1}$H NMR Spectrum of Compound **3i** (400 MHz, $CDCl_3$)



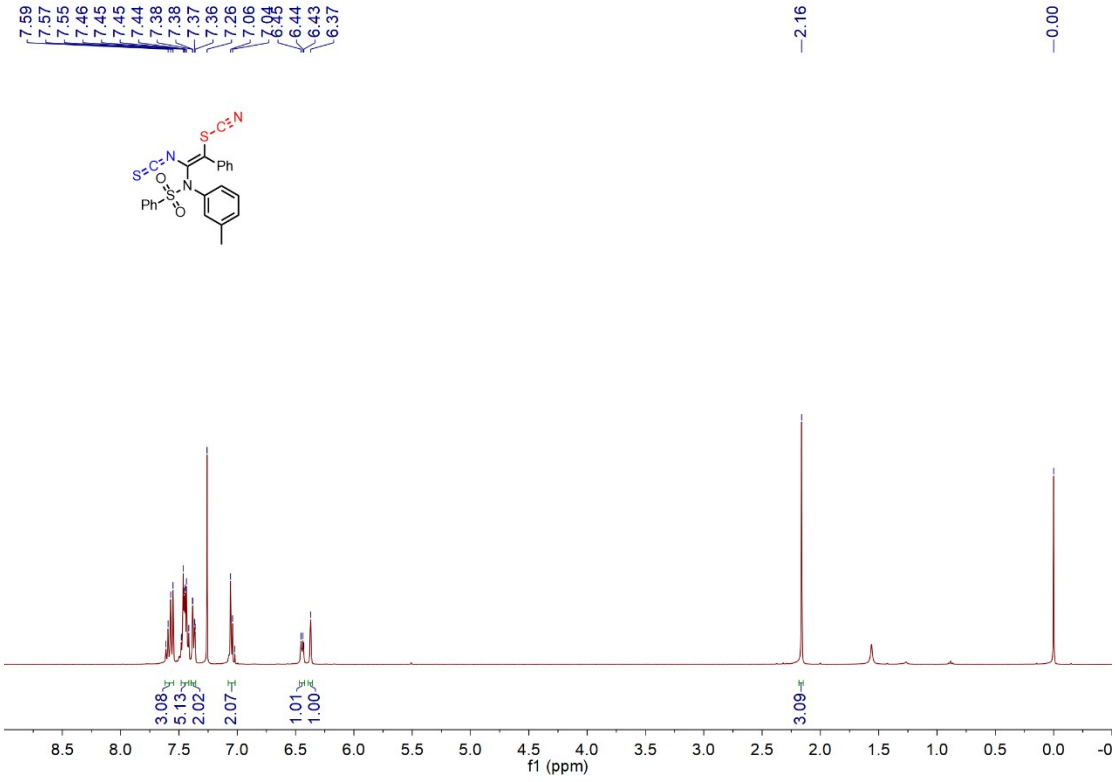

$^{13}$C NMR Spectrum of Compound **3i** (100 MHz, $CDCl_3$)



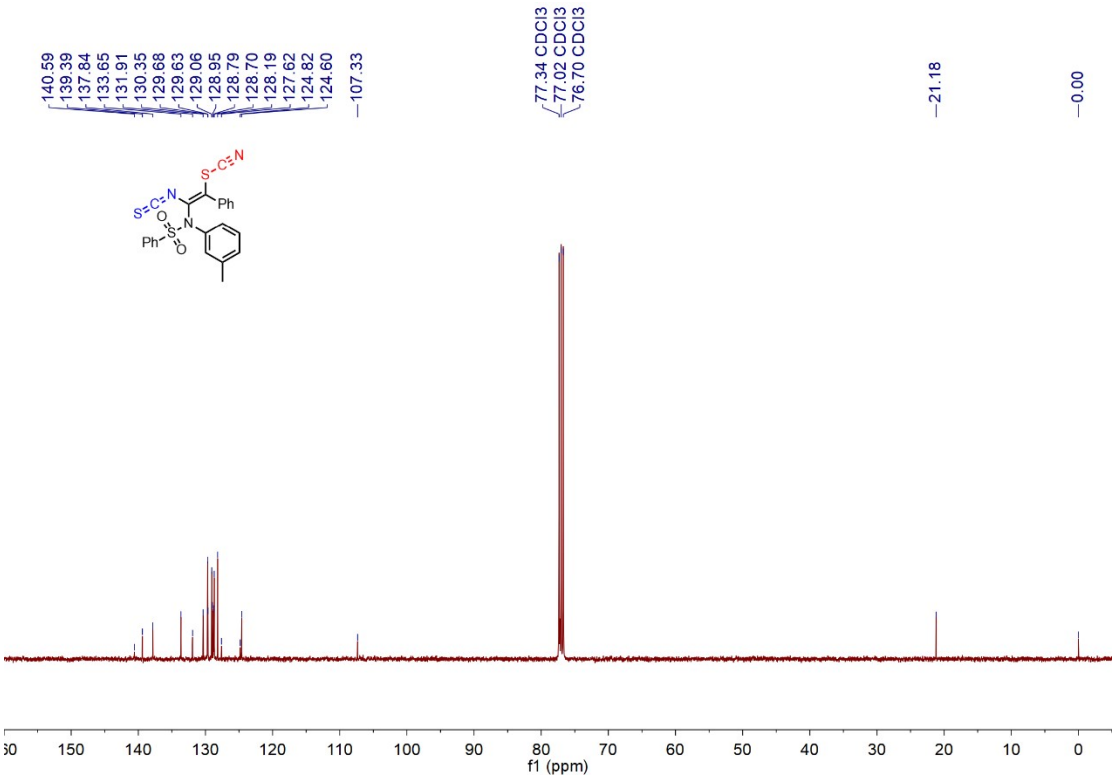

$^{1}$H NMR Spectrum of Compound **3j** (400 MHz, $CDCl_3$)



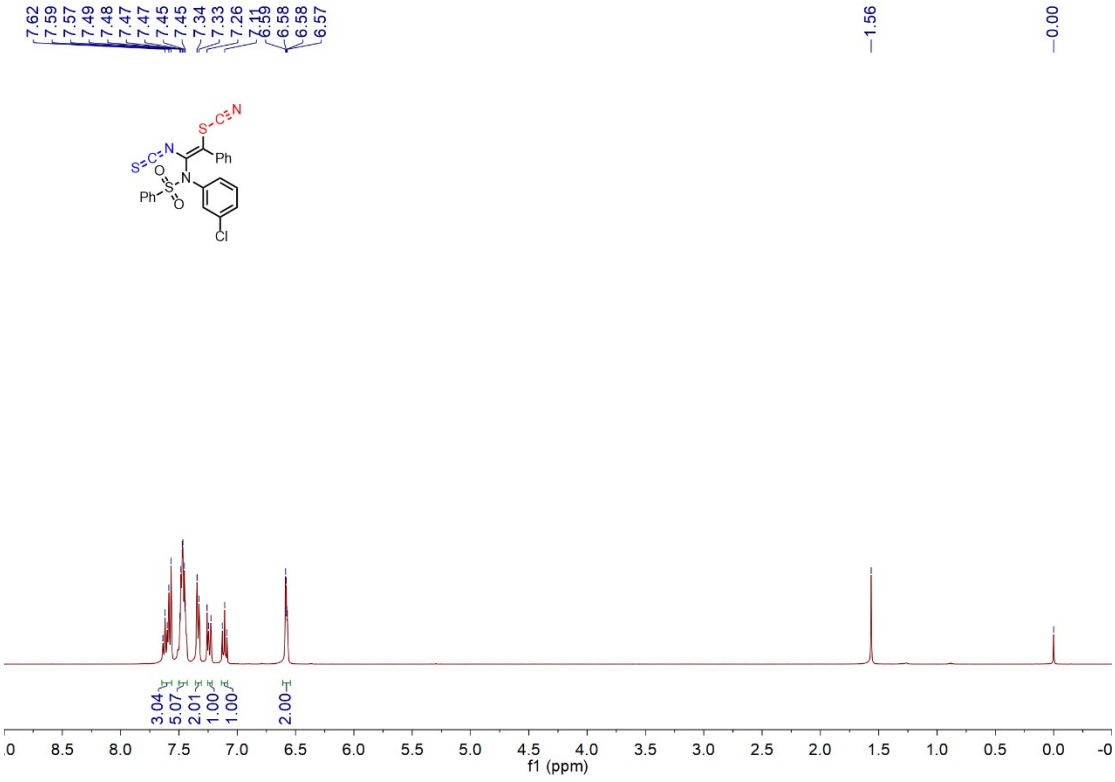

$^{13}$C NMR Spectrum of Compound **3j** (100 MHz, $CDCl_3$)



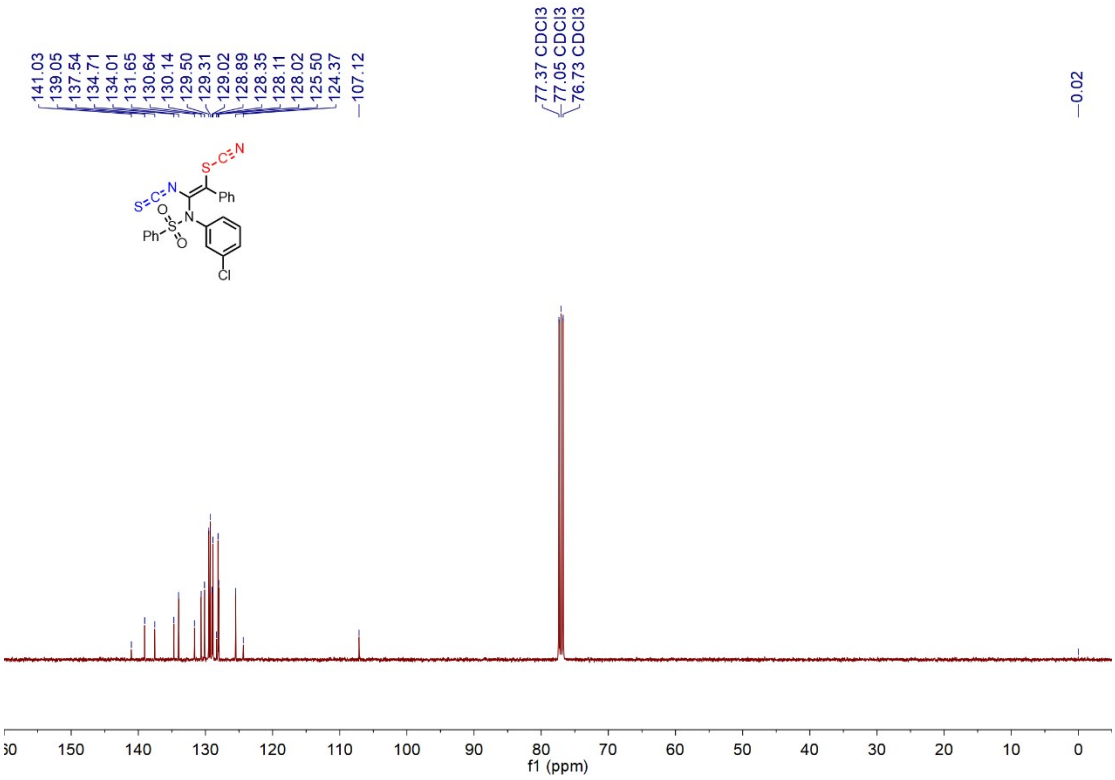

$^{1}$H NMR Spectrum of Compound **3k** (400 MHz, $CDCl_3$)



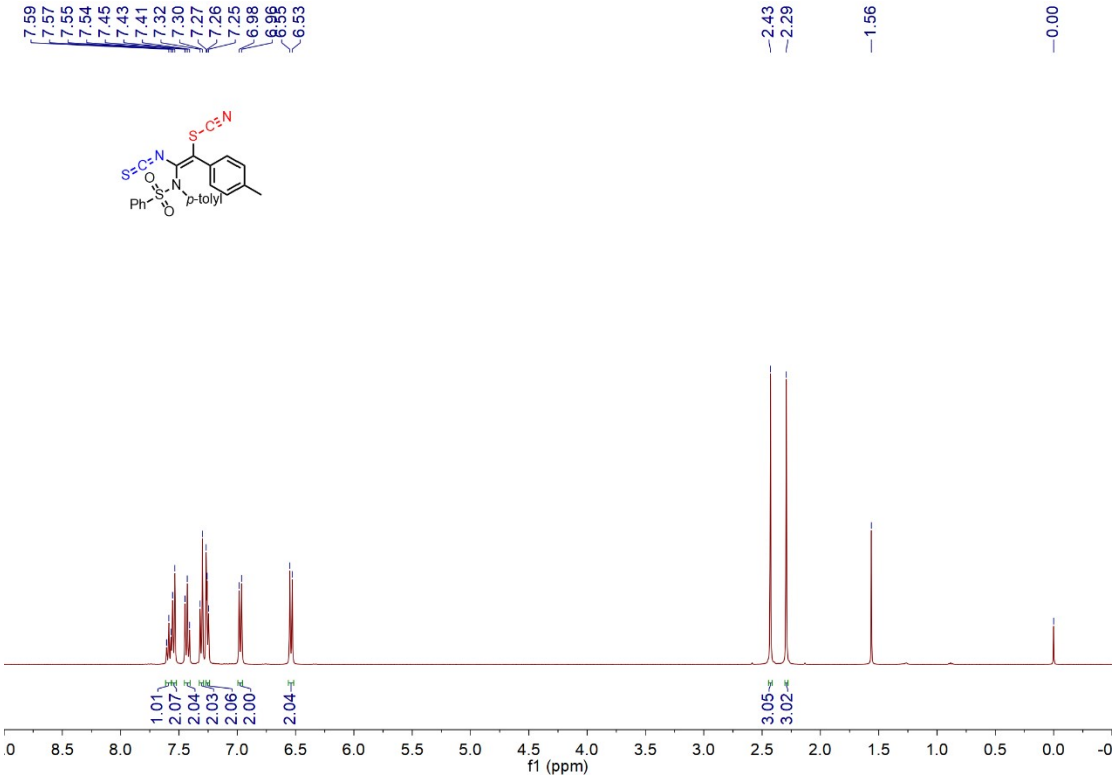

$^{13}$C NMR Spectrum of Compound **3k** (100 MHz, $CDCl_3$)



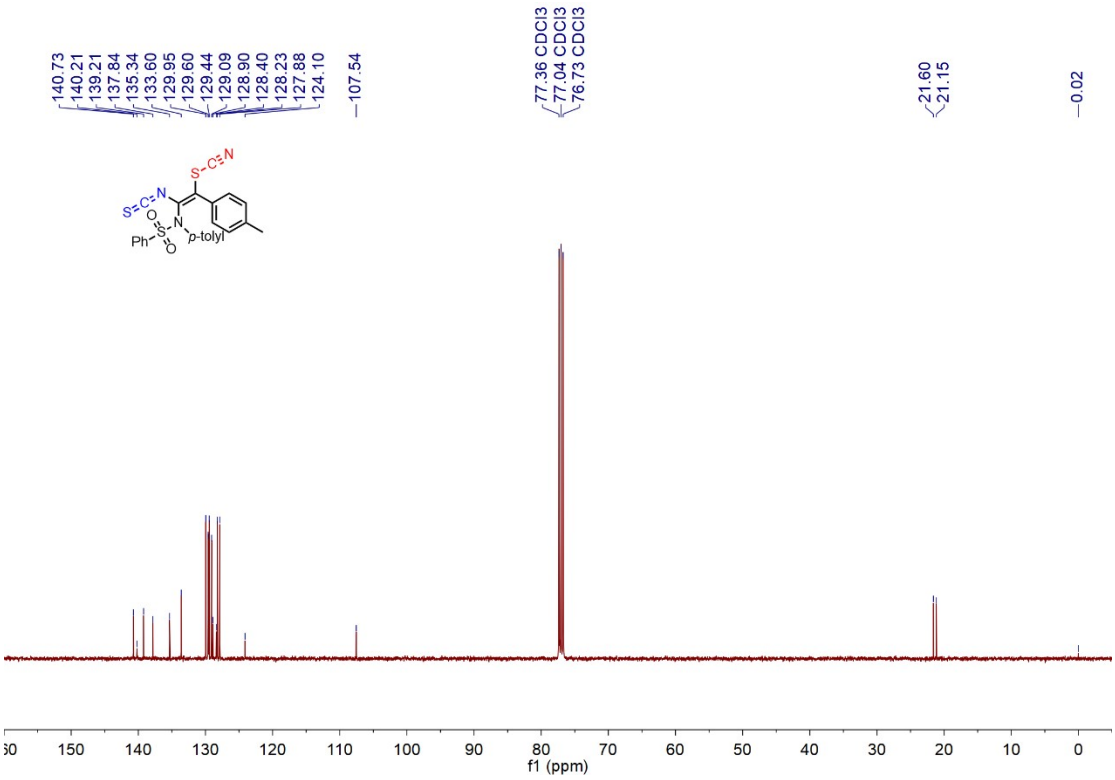

$^{1}$H NMR Spectrum of Compound **3l** (400 MHz, $CDCl_3$)



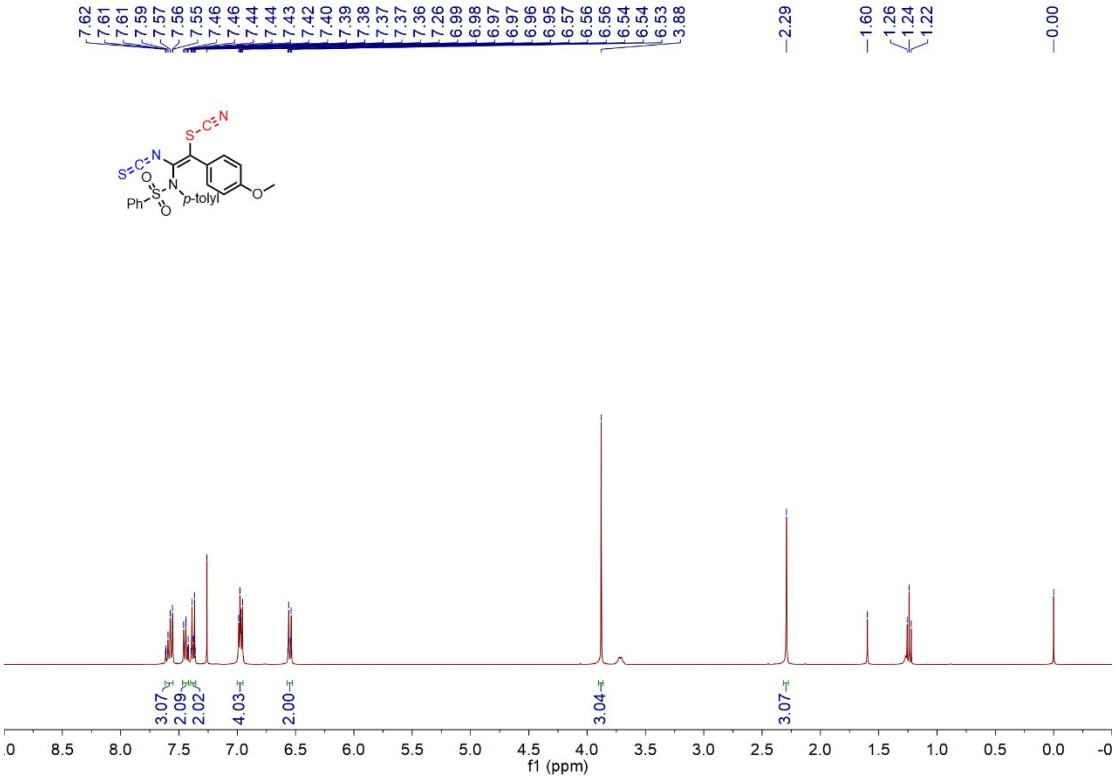

$^{13}$C NMR Spectrum of Compound **3l** (100 MHz, $CDCl_3$)



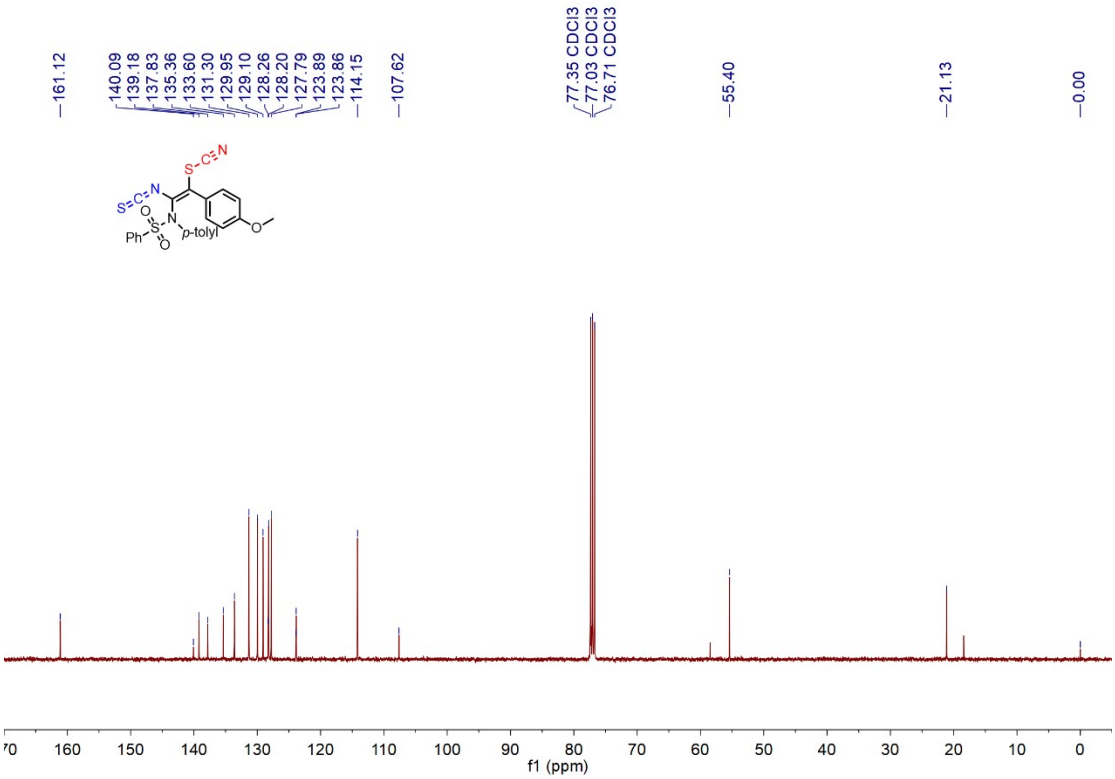

$^{1}$H NMR Spectrum of Compound **5a** (400 MHz, $CDCl_3$)



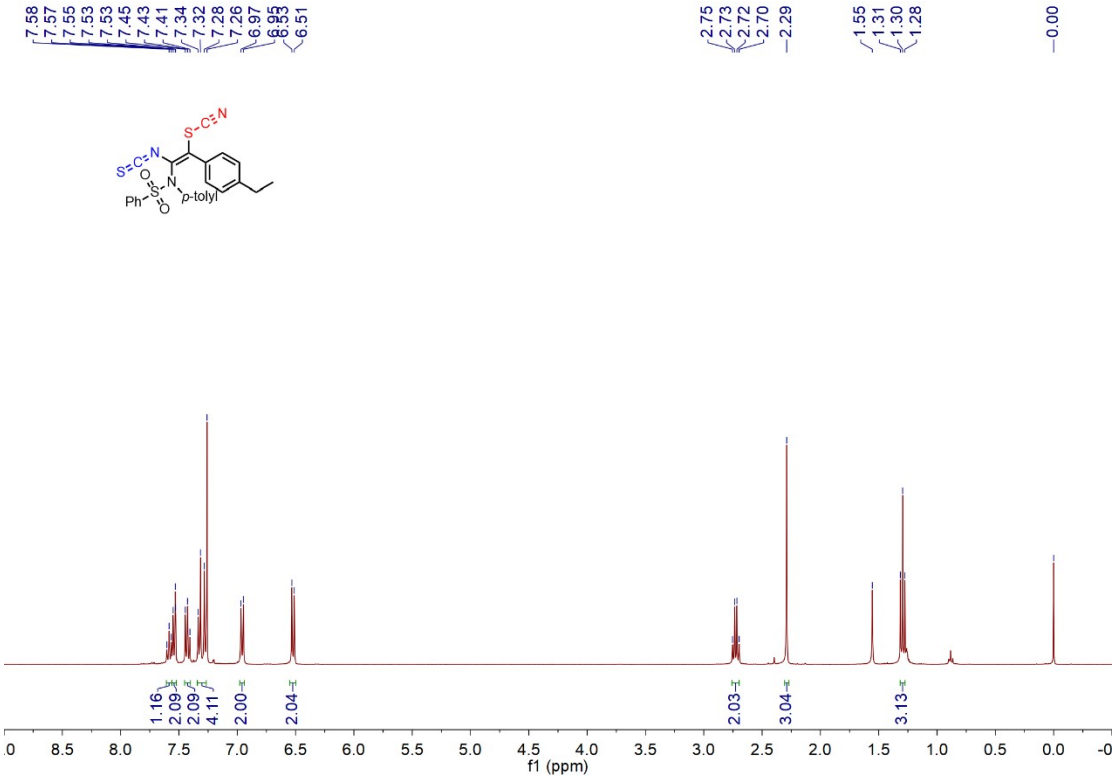

$^{13}$C NMR Spectrum of Compound **5a** (100 MHz, $CDCl_3$)



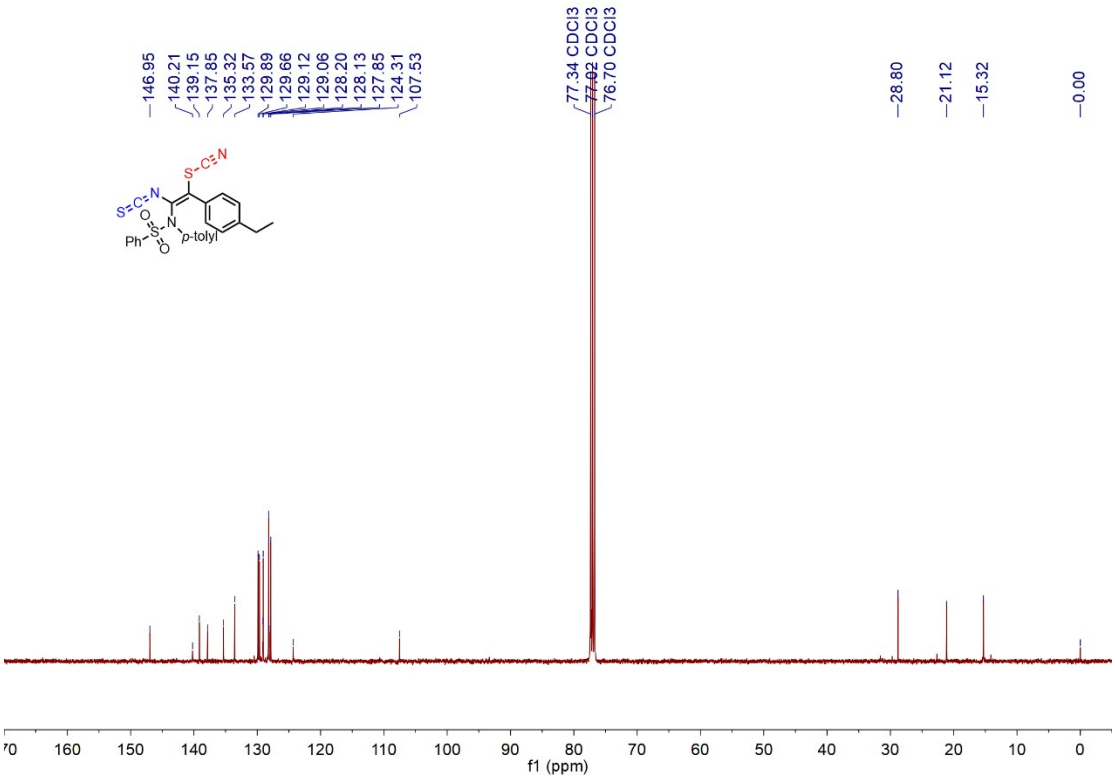

$^{1}$H NMR Spectrum of Compound **5b** (400 MHz, $CDCl_3$)



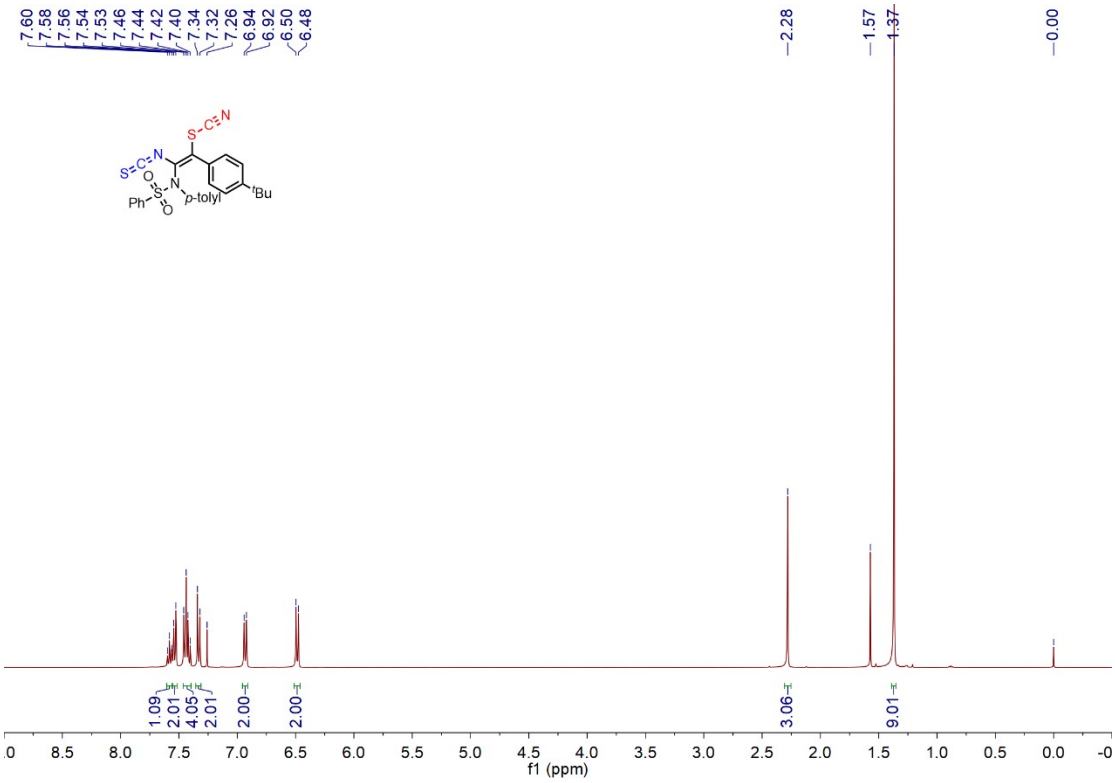

$^{13}$C NMR Spectrum of Compound **5b** (100 MHz, $CDCl_3$)



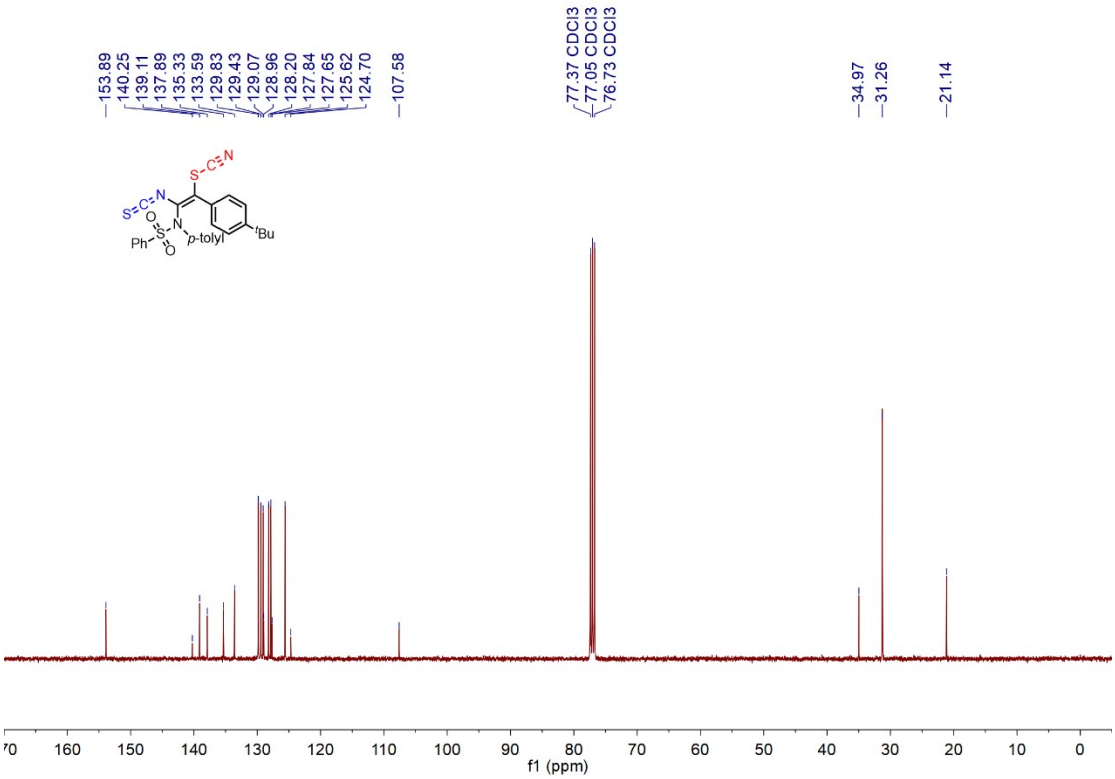

$^{1}$H NMR Spectrum of Compound **5c** (400 MHz, $CDCl_3$)



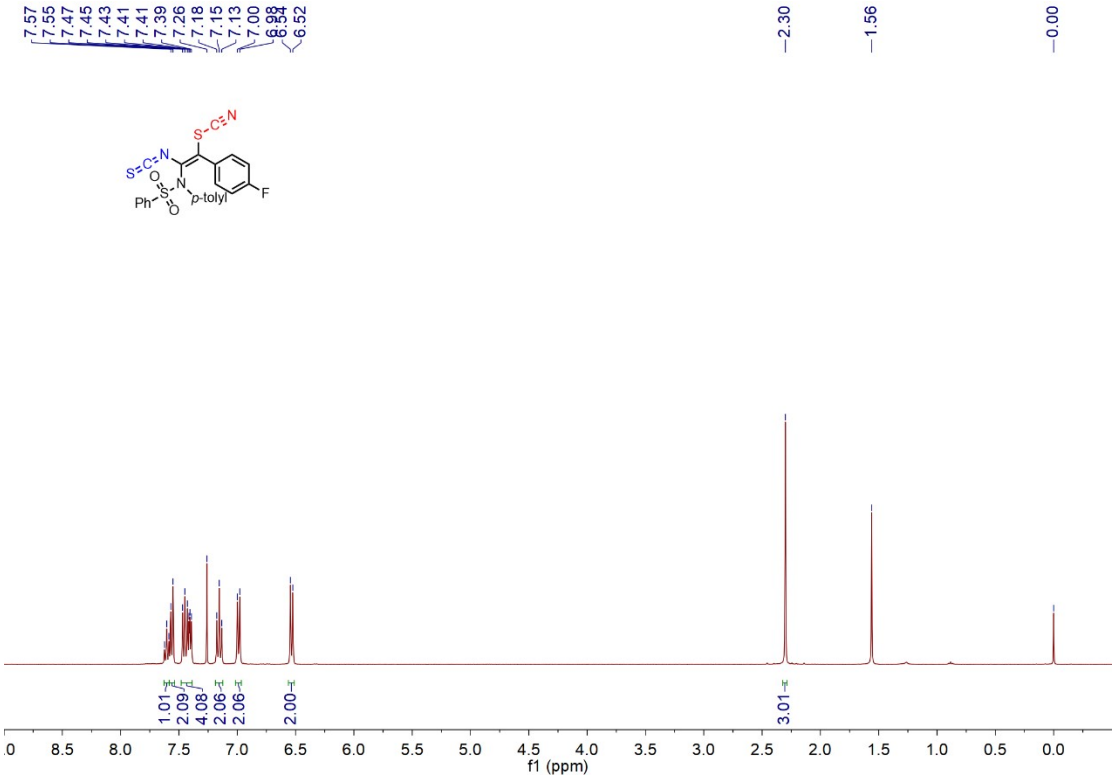

$^{13}$C NMR Spectrum of Compound **5c** (100 MHz, $CDCl_3$)



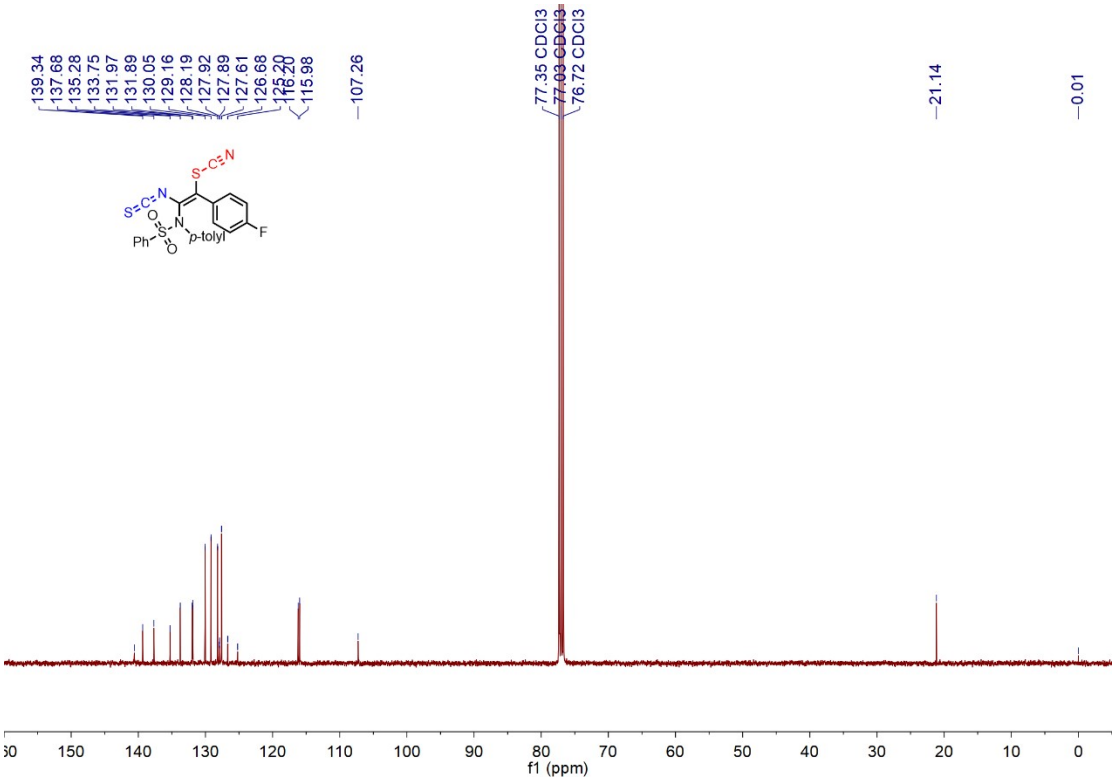

$^{1}$H NMR Spectrum of Compound **5d** (400 MHz, $CDCl_3$)



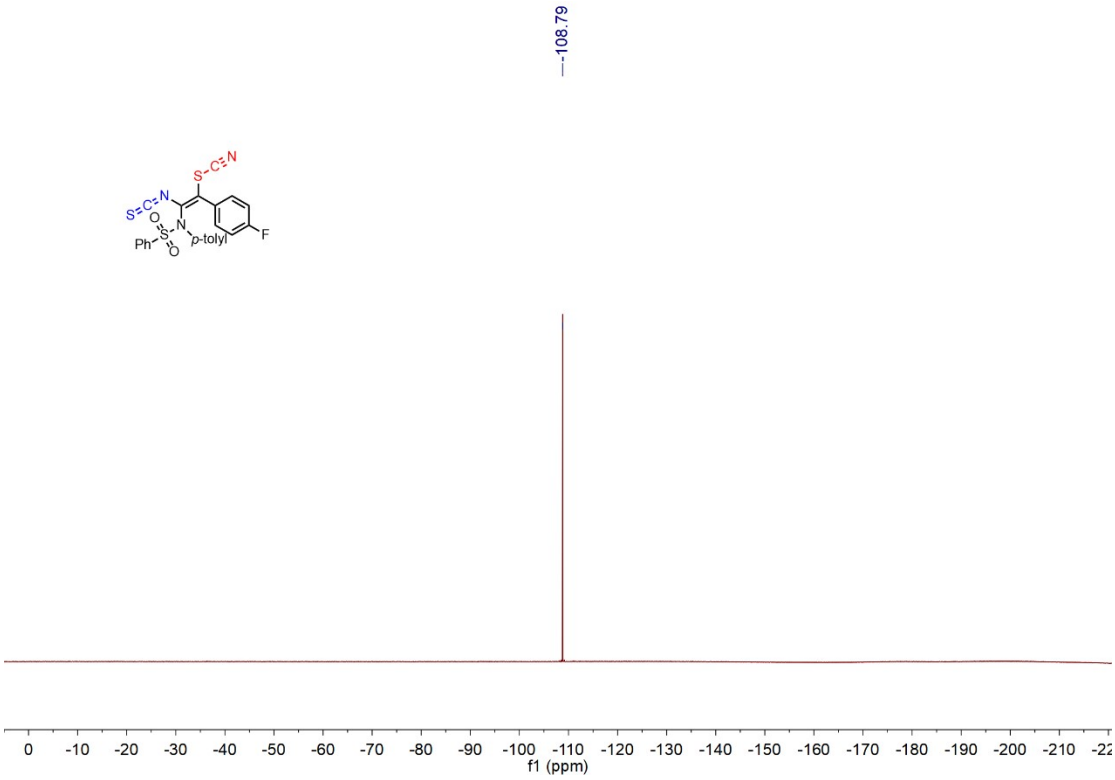

$^{13}$C NMR Spectrum of Compound **5d** (100 MHz, $CDCl_3$)



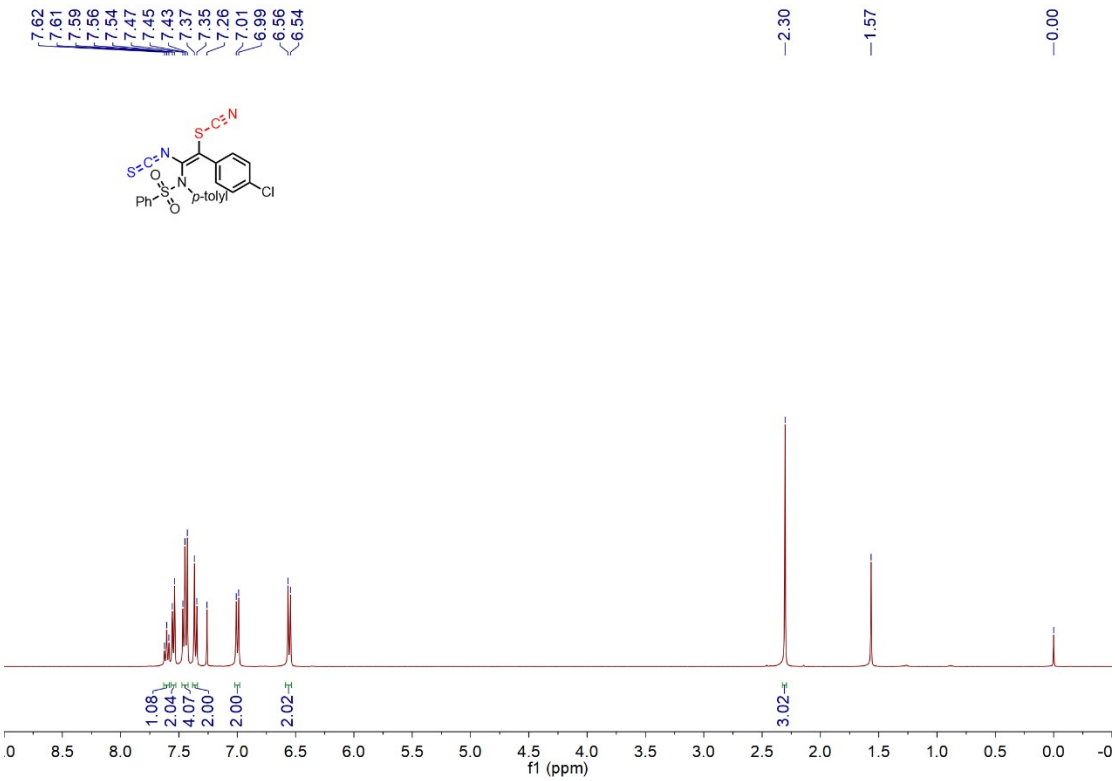

$^{1}$H NMR Spectrum of Compound **5e** (400 MHz, $CDCl_3$)



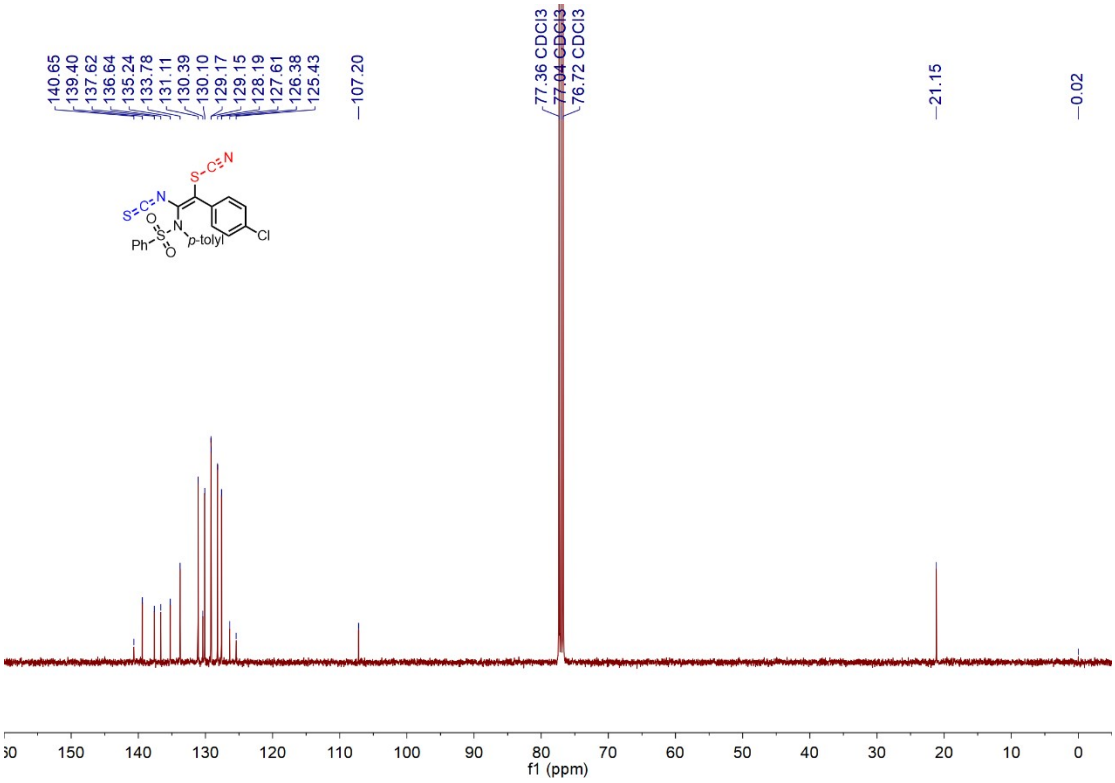

$^{13}$C NMR Spectrum of Compound **5e** (100 MHz, $CDCl_3$)



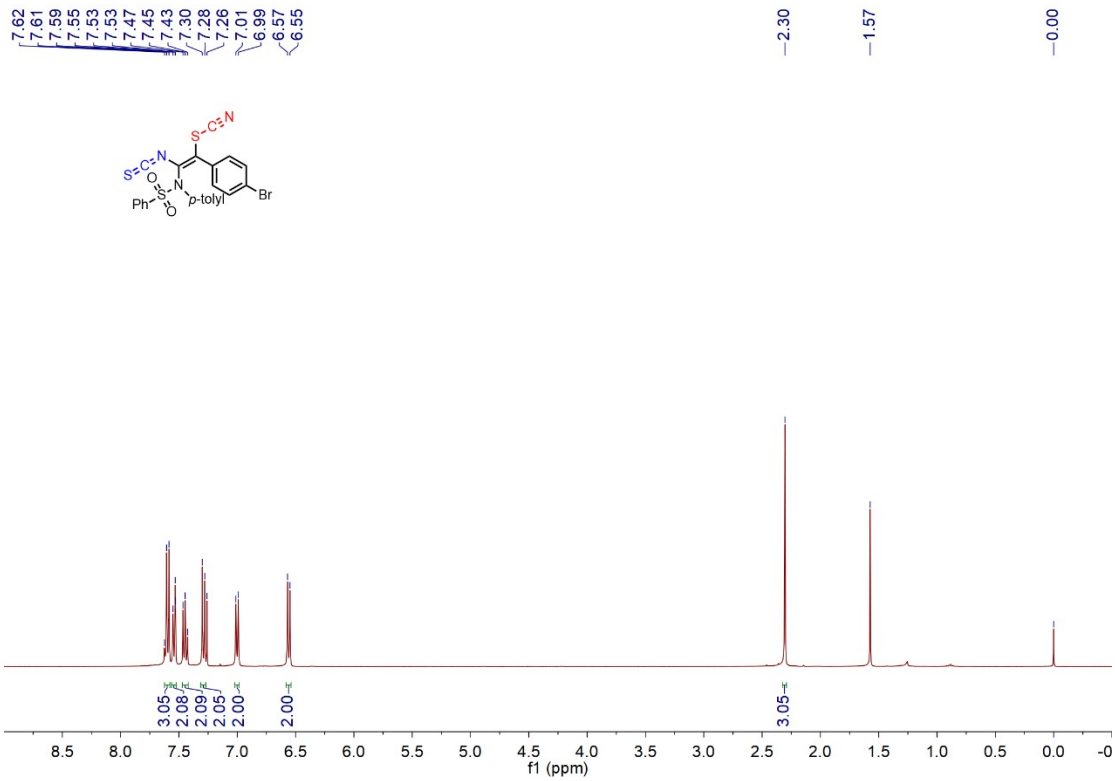

$^{19}$F NMR Spectrum of Compound **5e** (376 MHz, $CDCl_3$)



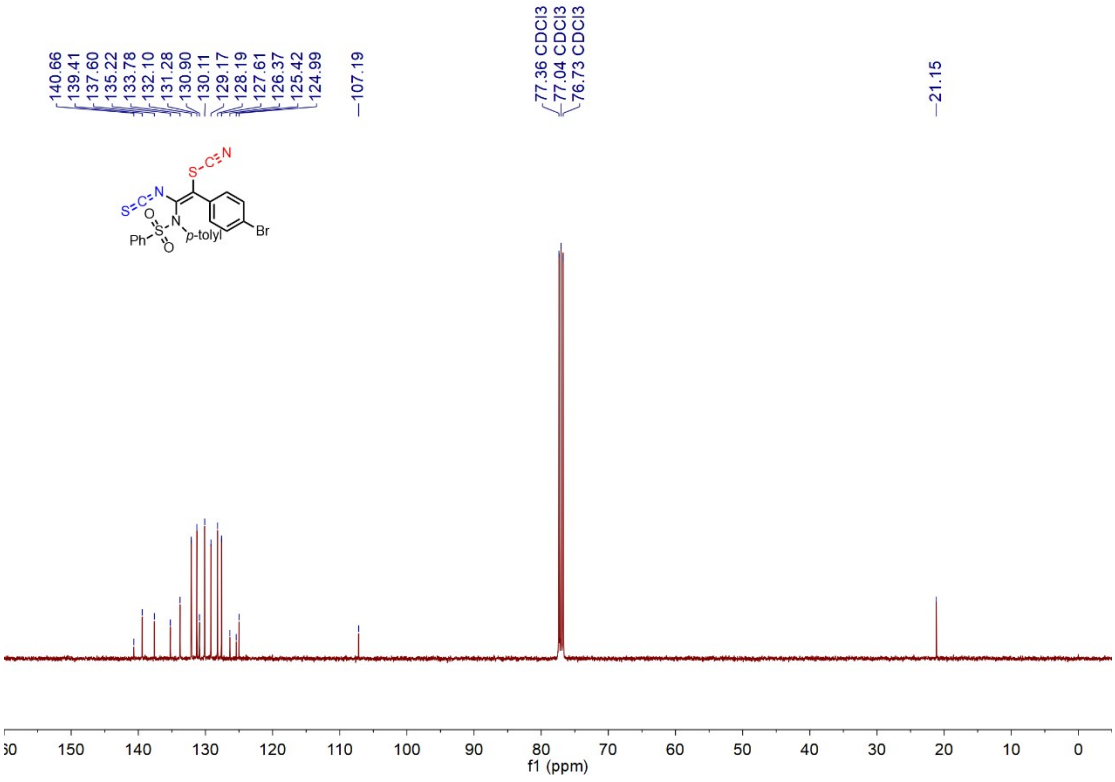

$^{1}$H NMR Spectrum of Compound **5f** (400 MHz, $CDCl_3$)



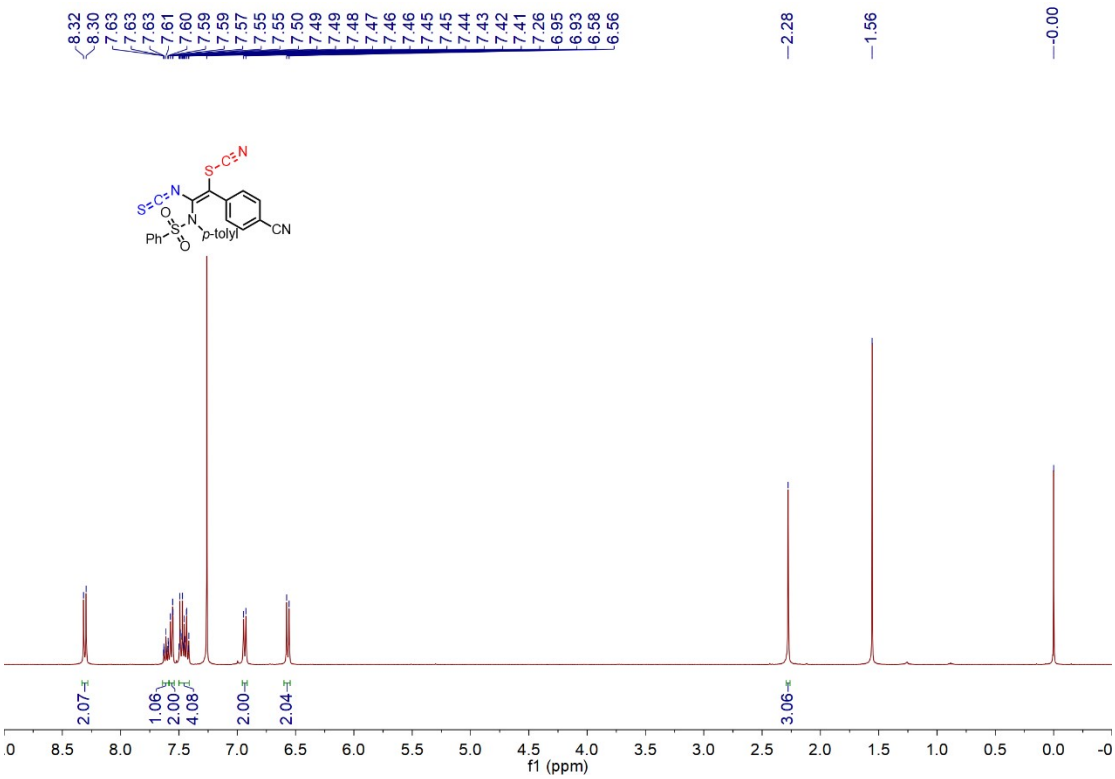

$^{13}$C NMR Spectrum of Compound **5f** (100 MHz, $CDCl_3$)



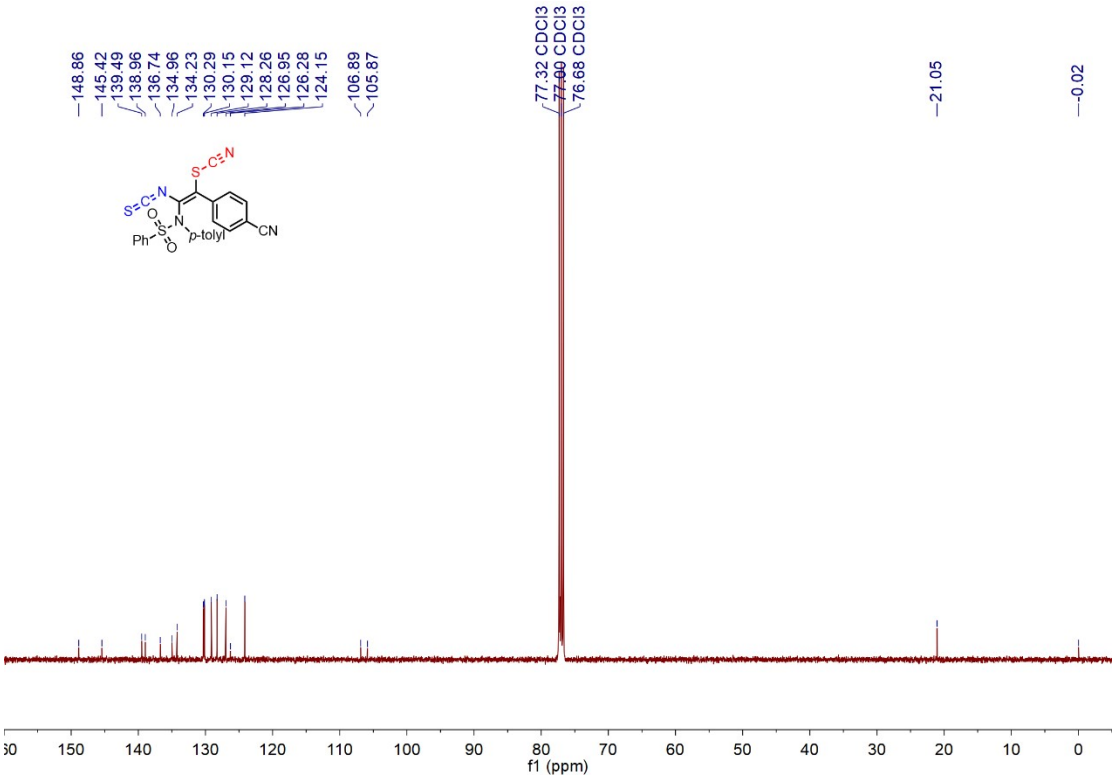

$^{1}$H NMR Spectrum of Compound **5g** (400 MHz, $CDCl_3$)



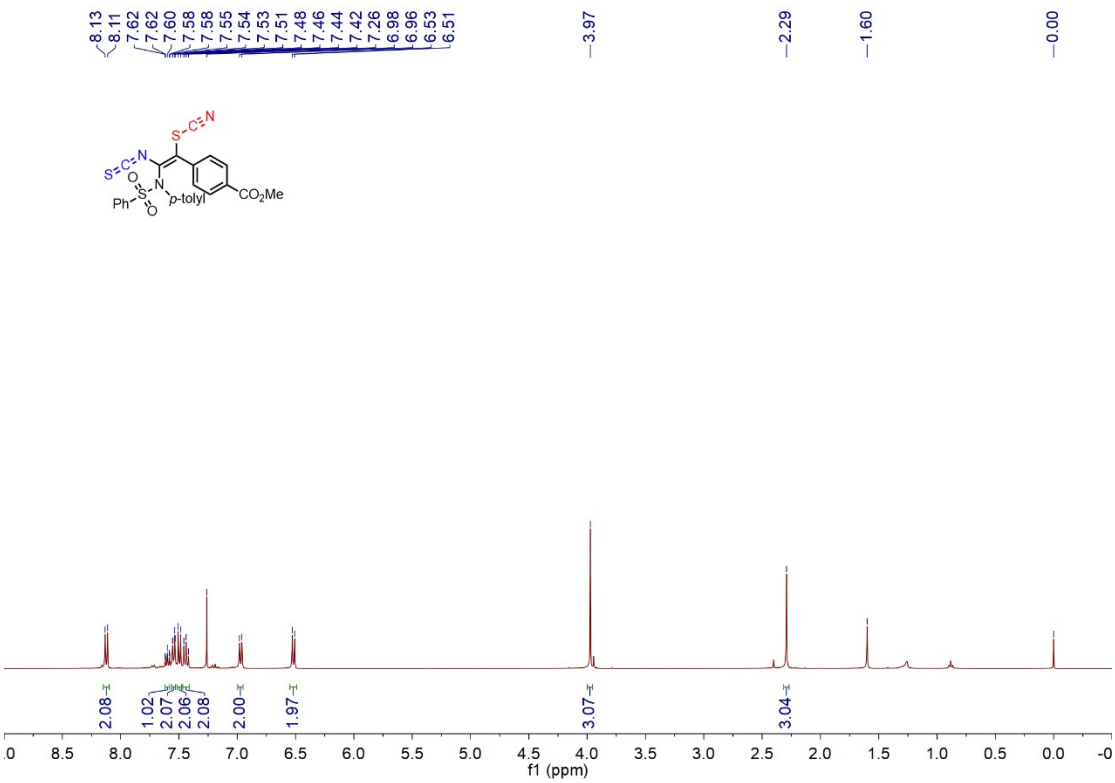

$^{13}$C NMR Spectrum of Compound **5g** (100 MHz, $CDCl_3$)



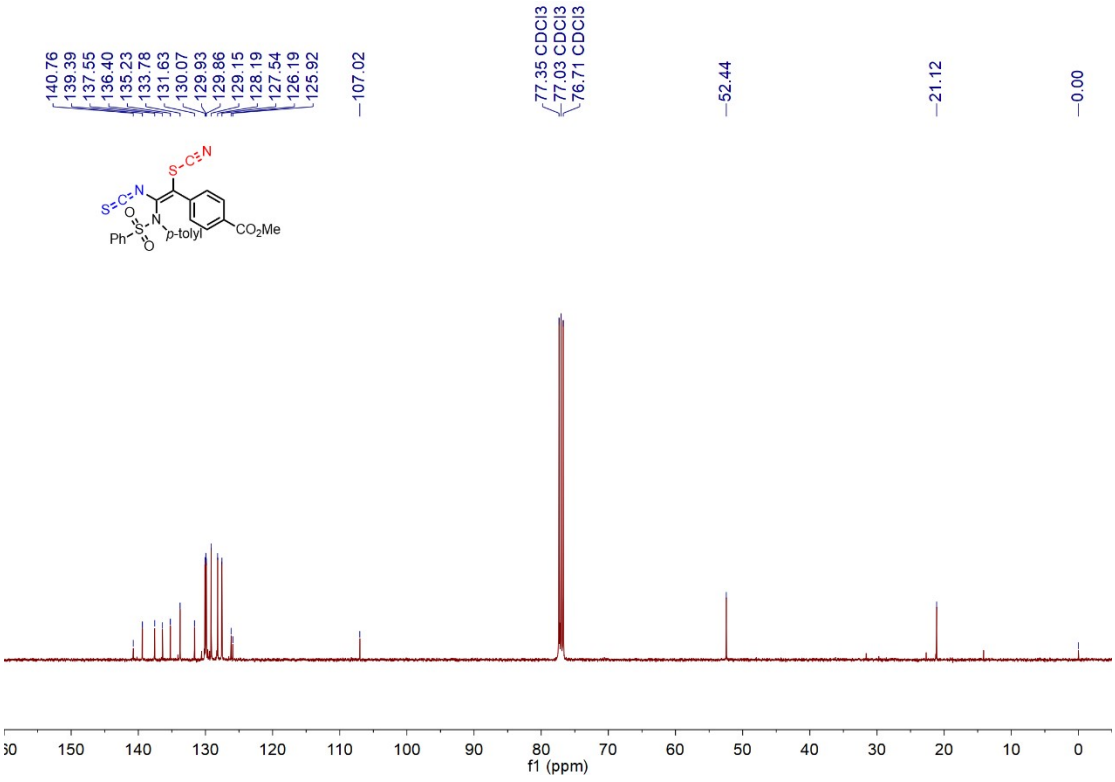

$^{1}$H NMR Spectrum of Compound **5h** (400 MHz, $CDCl_3$)



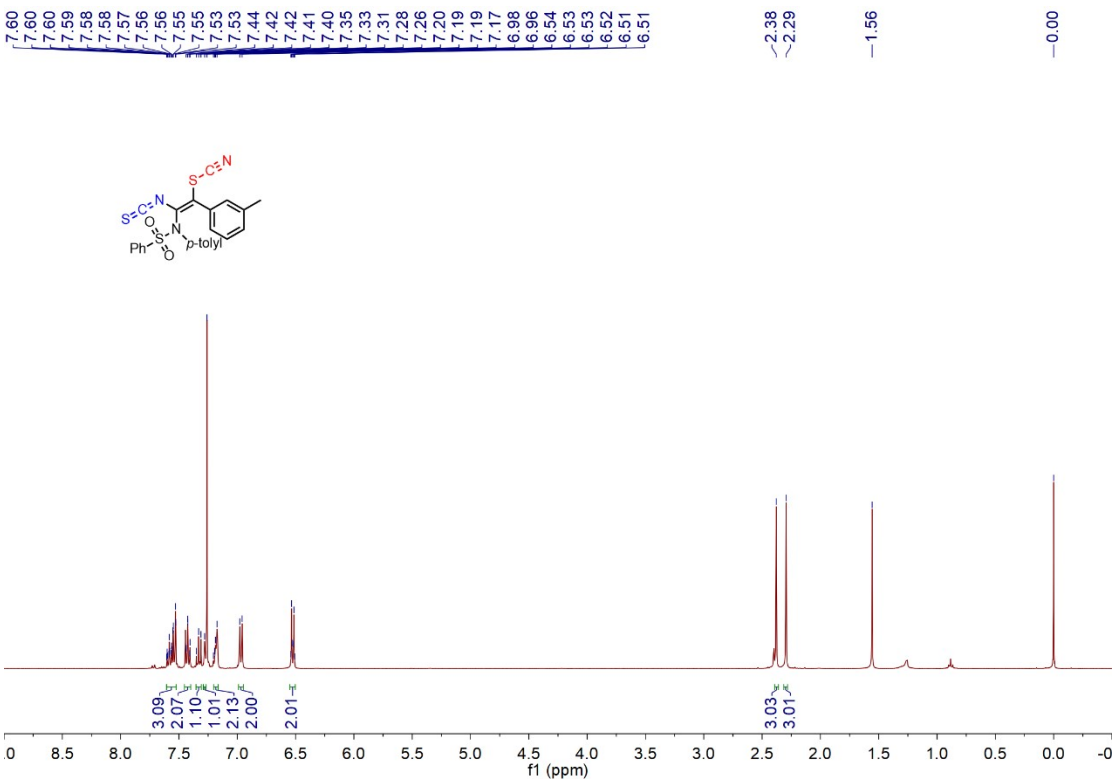

$^{13}$C NMR Spectrum of Compound **5h** (100 MHz, $CDCl_3$)



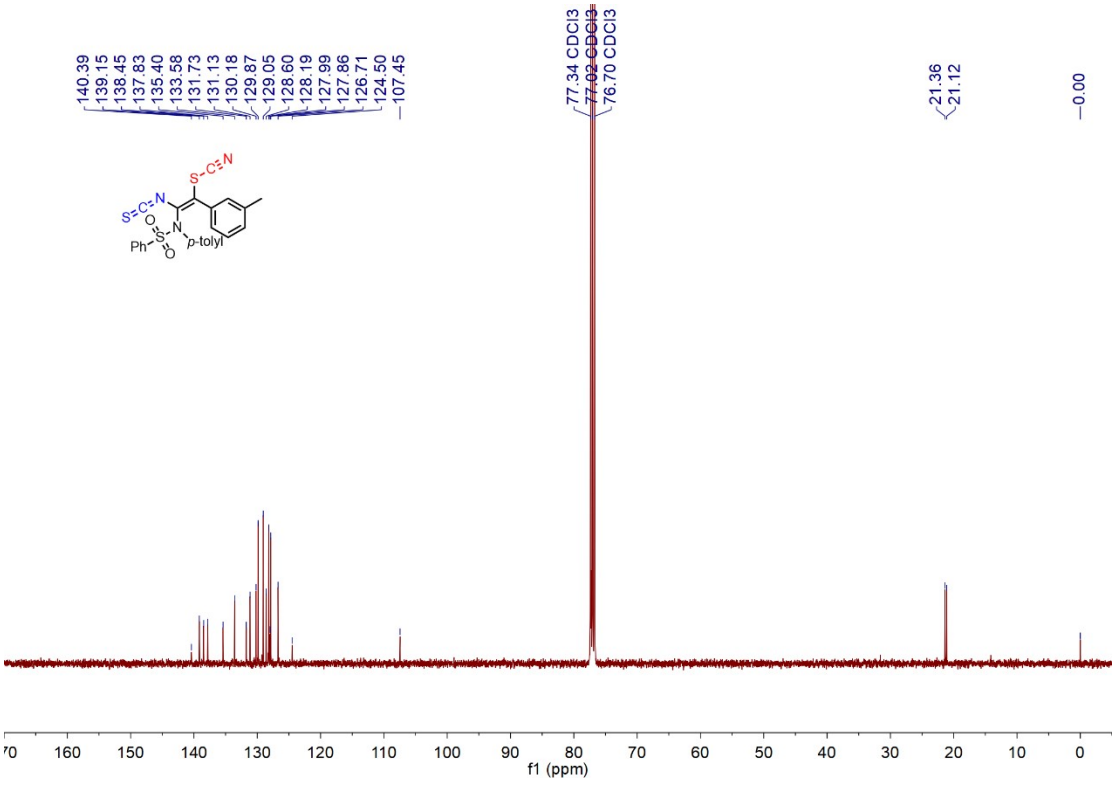

$^{1}$H NMR Spectrum of Compound **5i** (400 MHz, $CDCl_3$)



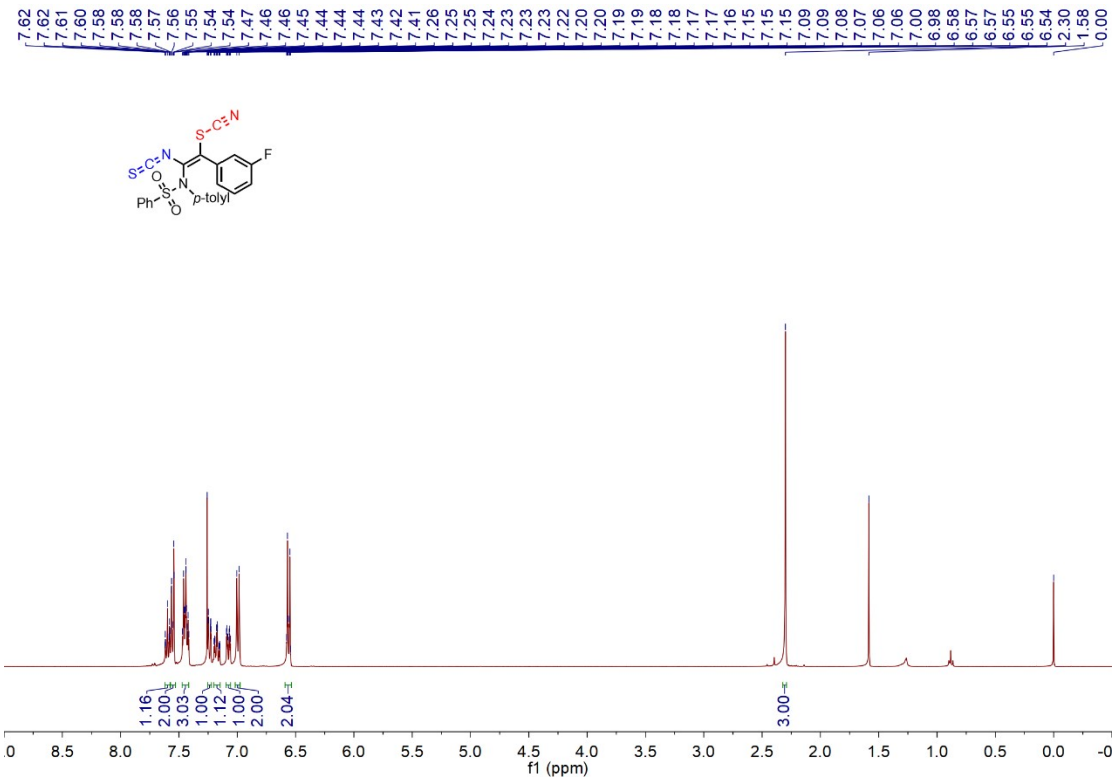

$^{13}$C NMR Spectrum of Compound **5i** (100 MHz, $CDCl_3$)



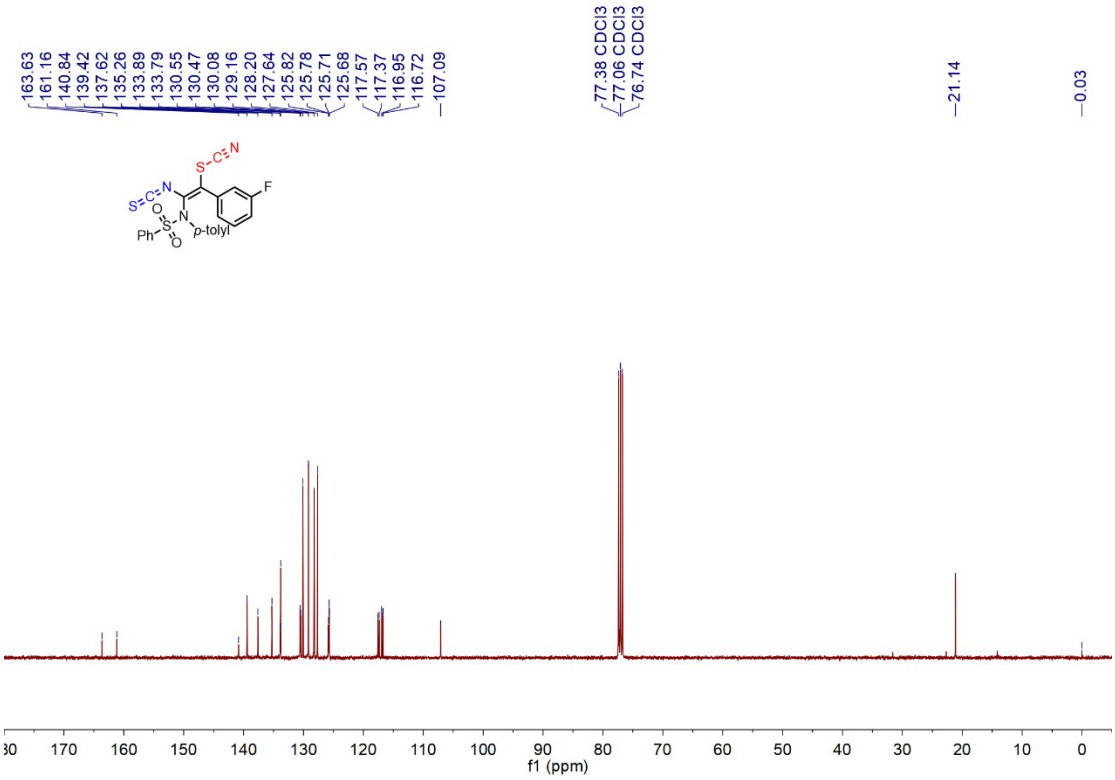

$^{1}$H NMR Spectrum of Compound **5j** (400 MHz, $CDCl_3$)



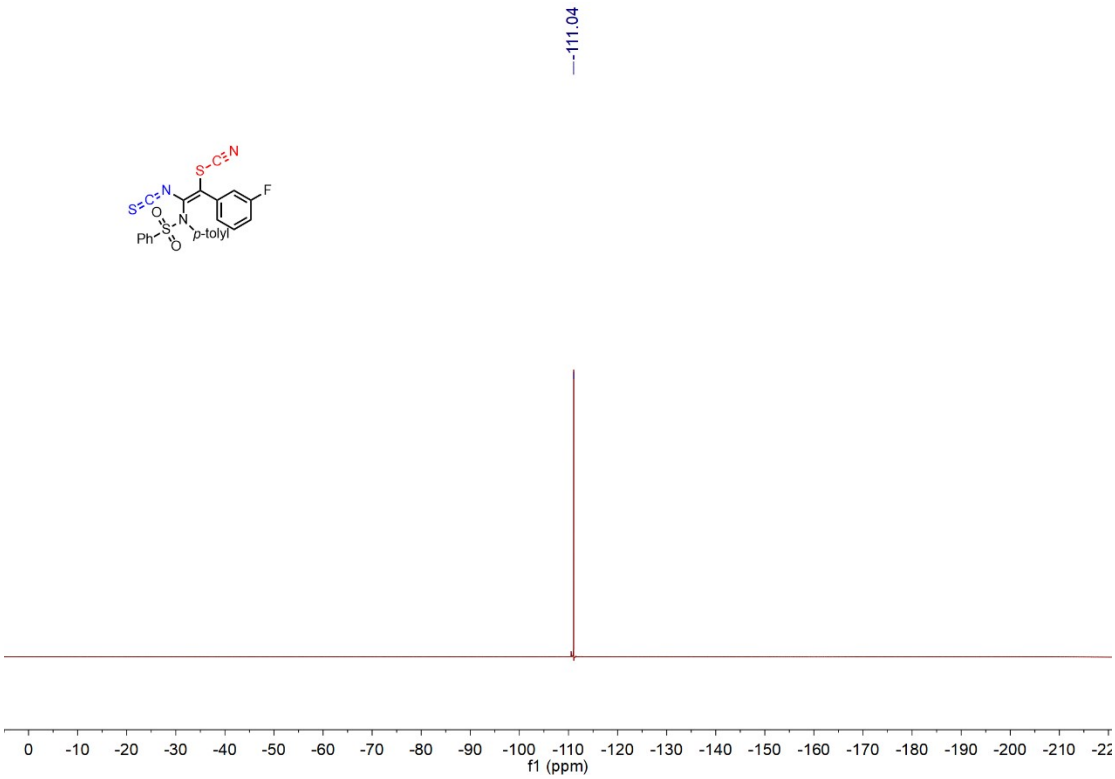

$^{13}$C NMR Spectrum of Compound **5j** (100 MHz, $CDCl_3$)



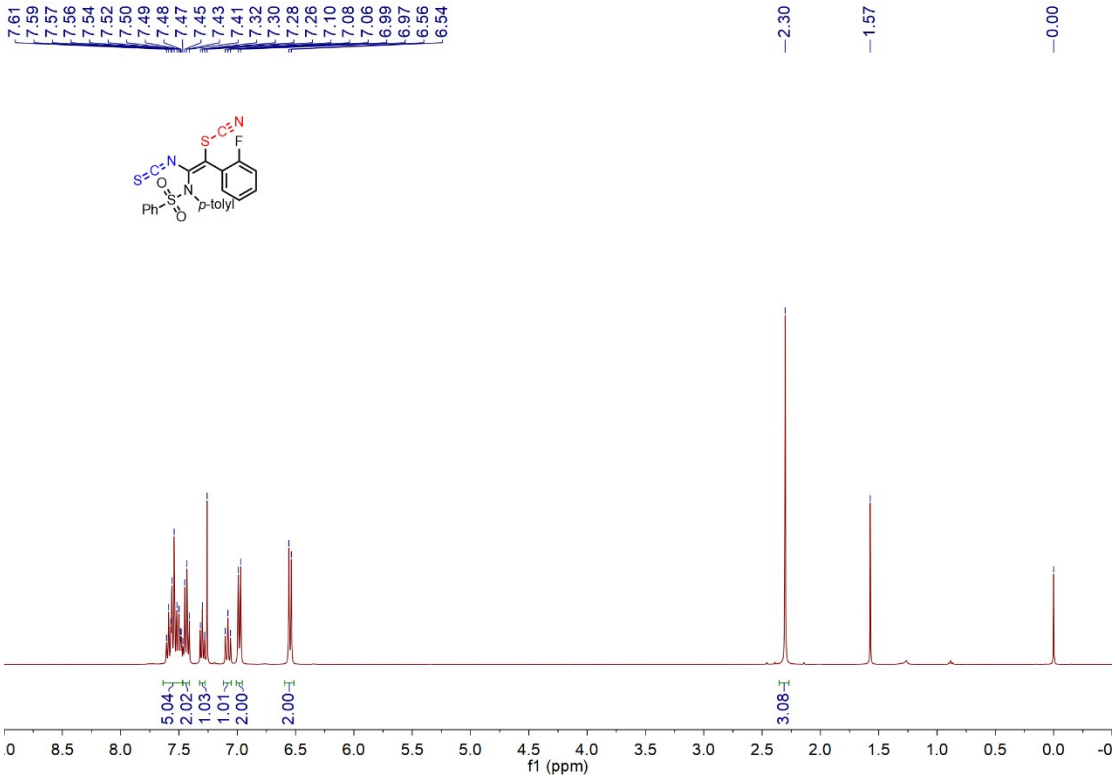

$^{1}$H NMR Spectrum of Compound **5k** (400 MHz, $CDCl_3$)



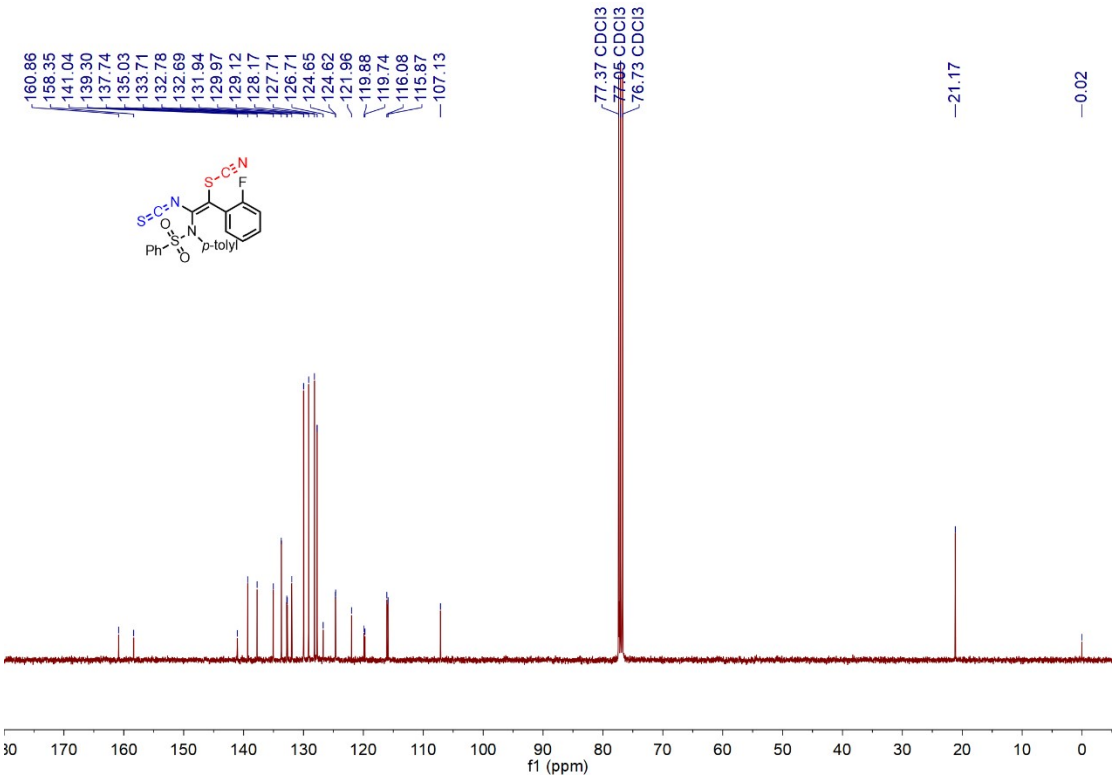

$^{13}$C NMR Spectrum of Compound **5k** (100 MHz, $CDCl_3$)



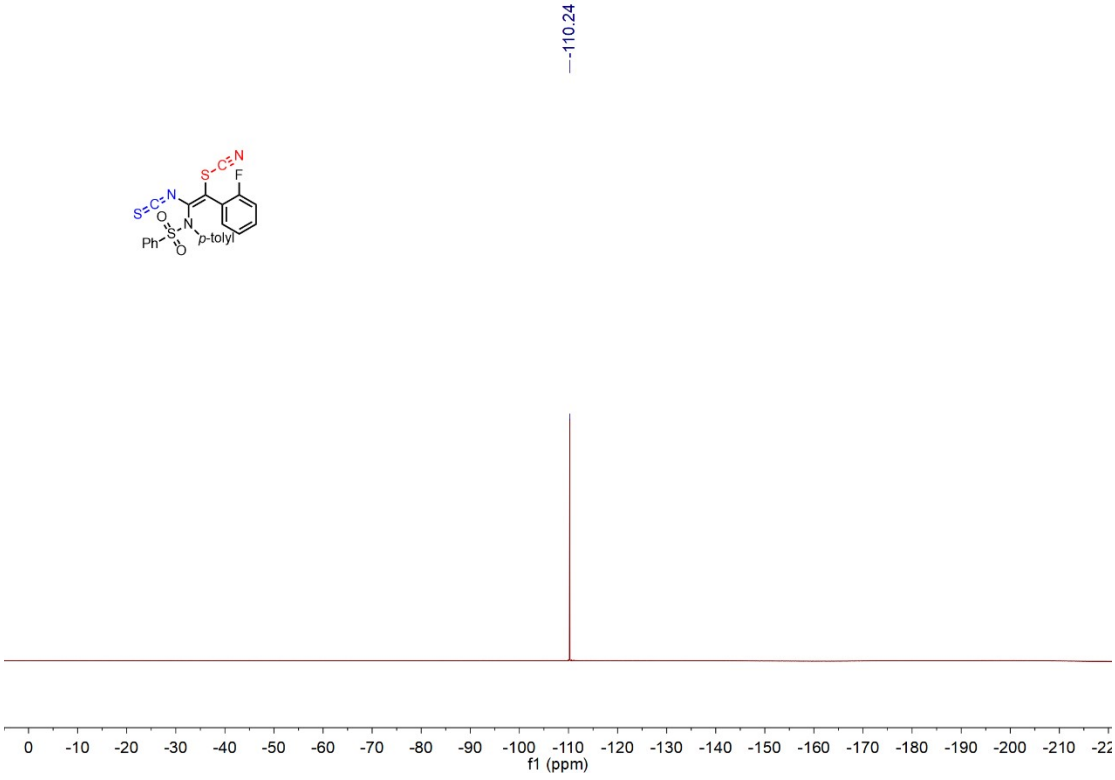

$^{19}$F NMR Spectrum of Compound **5k** (376 MHz, $CDCl_3$)



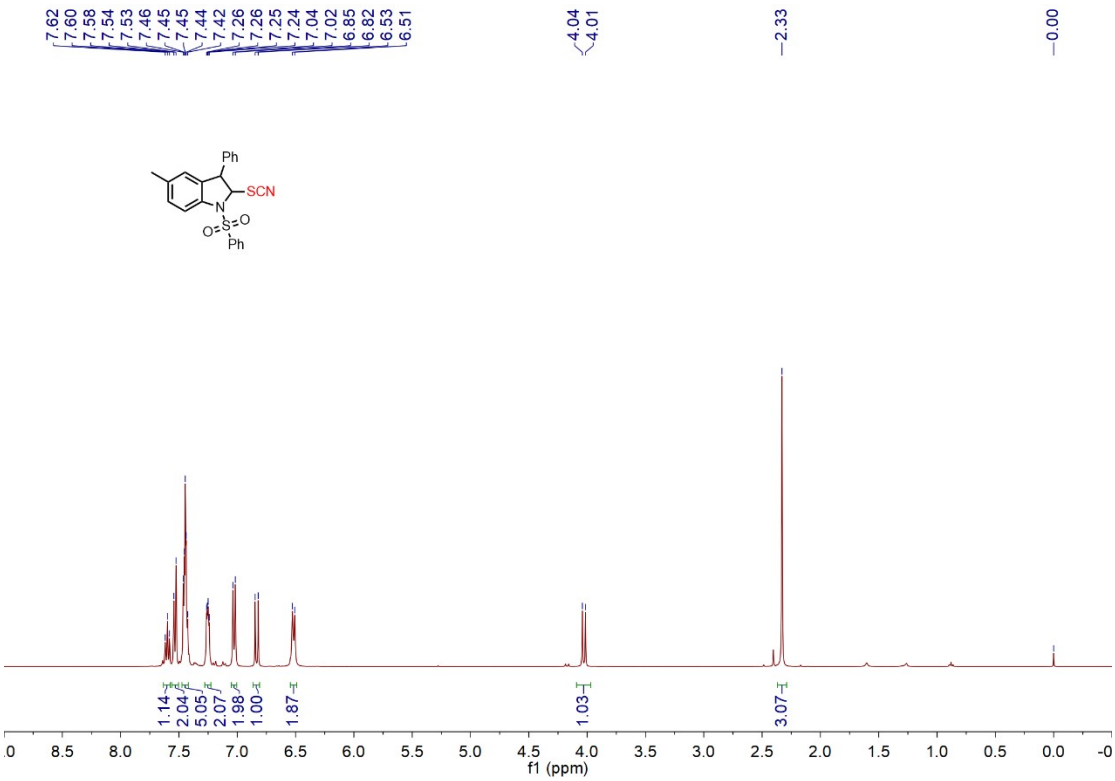

$^{1}$H NMR Spectrum of Compound **5l** (400 MHz, $CDCl_3$)



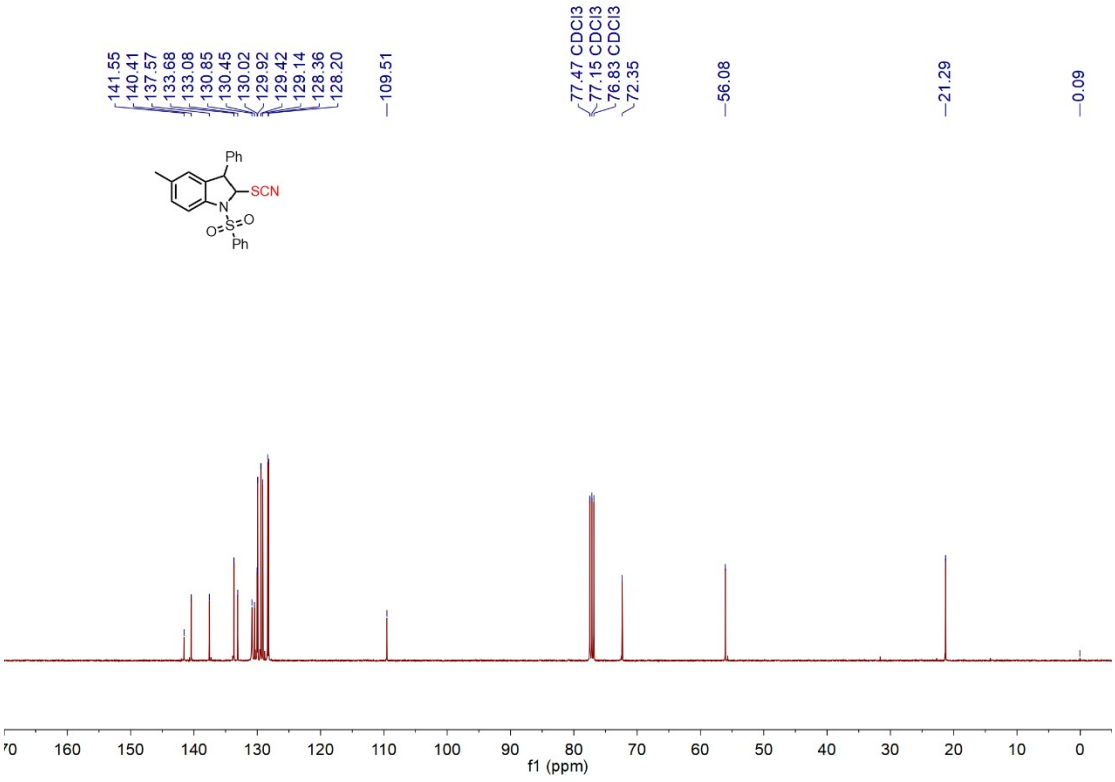

$^{13}$C NMR Spectrum of Compound **5l** (100 MHz, $CDCl_3$)



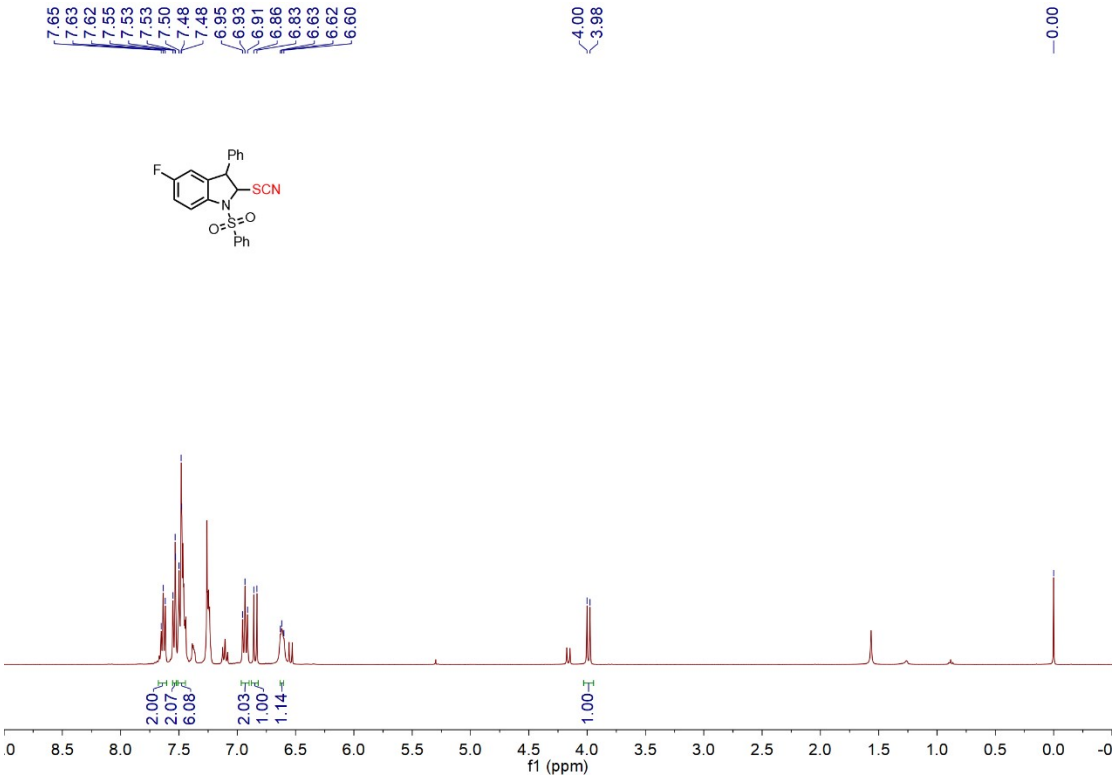

$^{19}$F NMR Spectrum of Compound **5l** (376 MHz, $CDCl_3$)



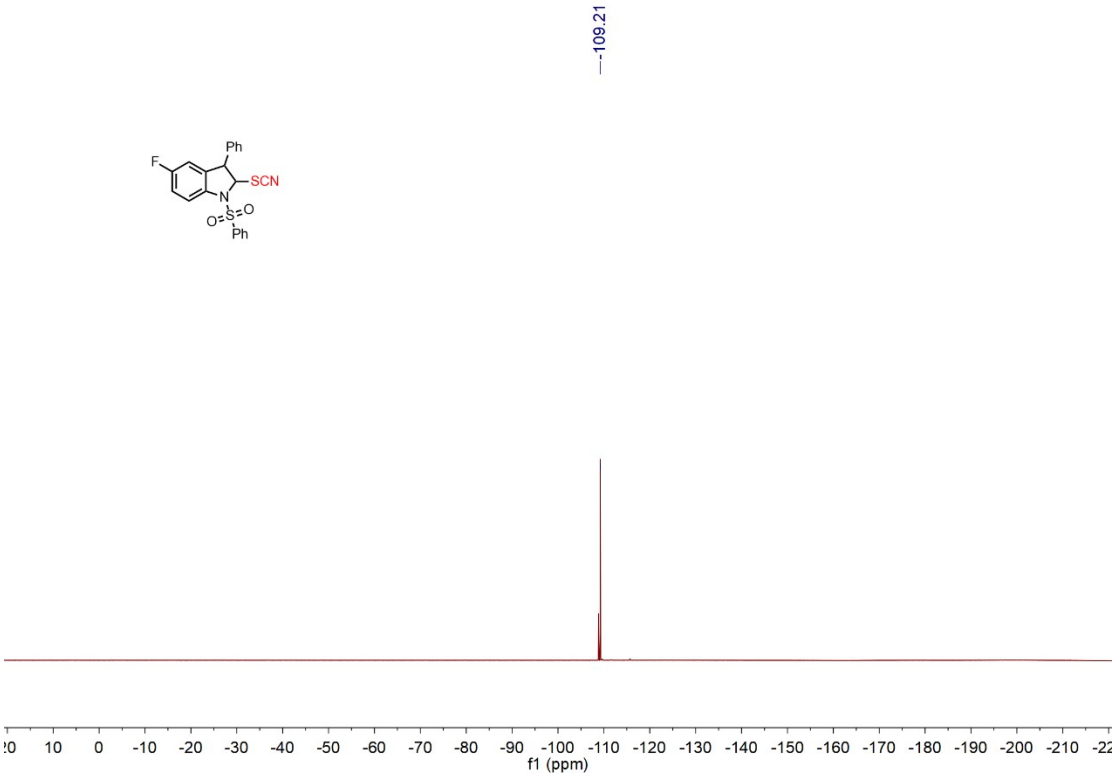

$^{1}$H NMR Spectrum of Compound **7a** (400 MHz, $CDCl_3$)



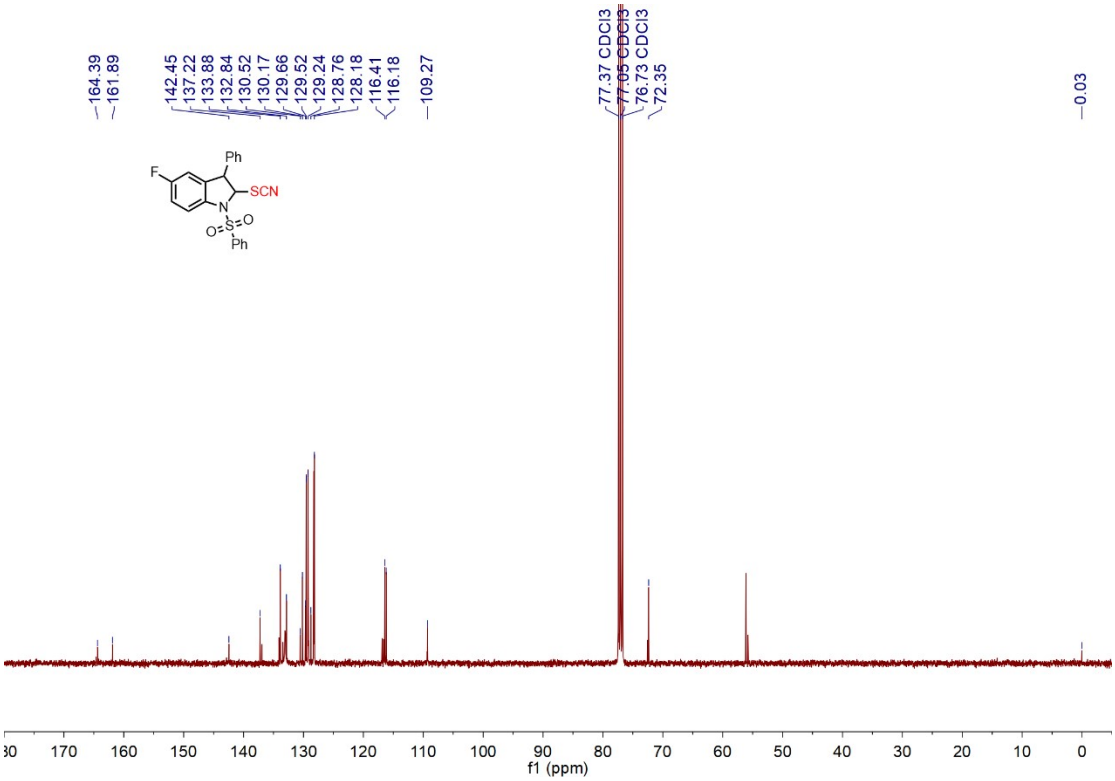

$^{13}$C NMR Spectrum of Compound **7a** (100 MHz, $CDCl_3$)



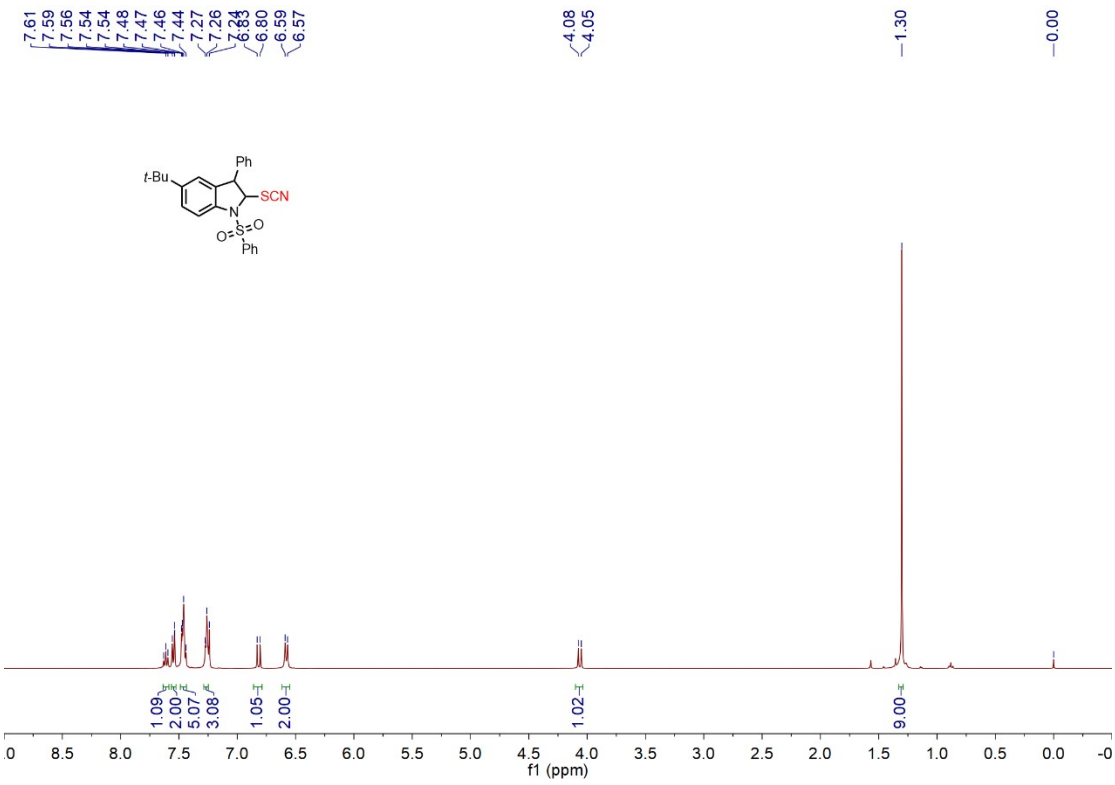

$^{1}$H NMR Spectrum of Compound **7b** (400 MHz, $CDCl_3$)



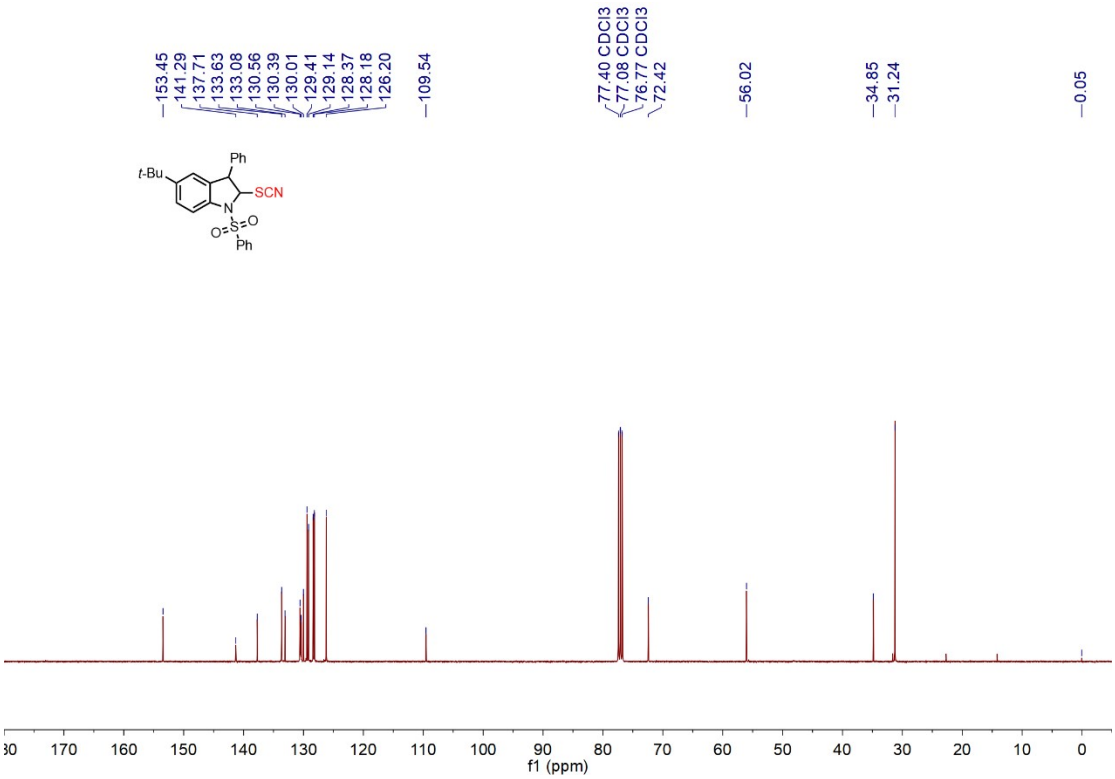

$^{19}$F NMR Spectrum of Compound **7b** (376 MHz, $CDCl_3$)



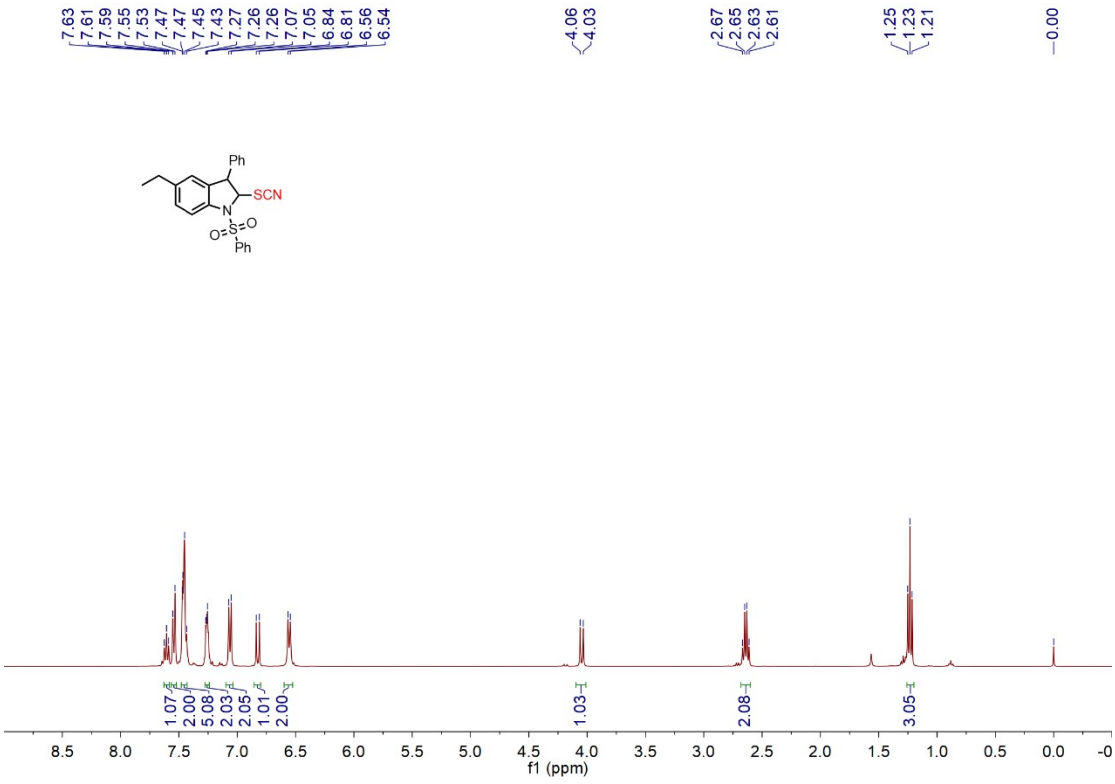

$^{13}$C NMR Spectrum of Compound **7b** (100 MHz, $CDCl_3$)



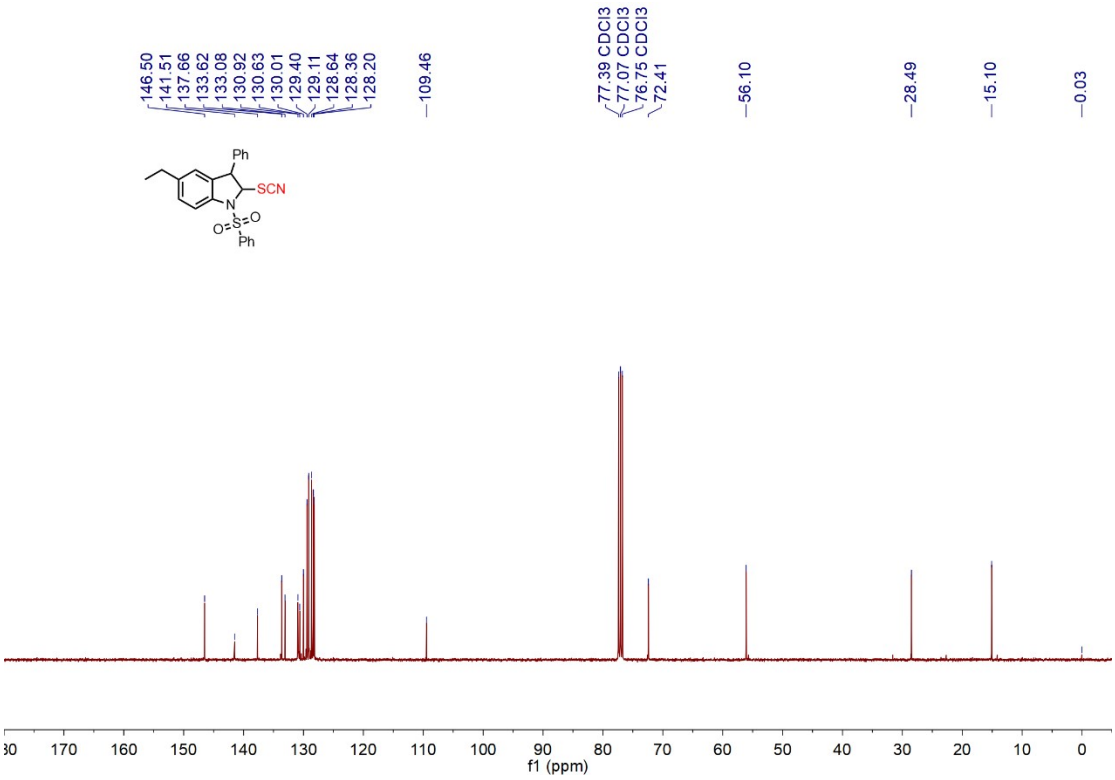

$^{1}$H NMR Spectrum of Compound **7c** (400 MHz, $CDCl_3$)



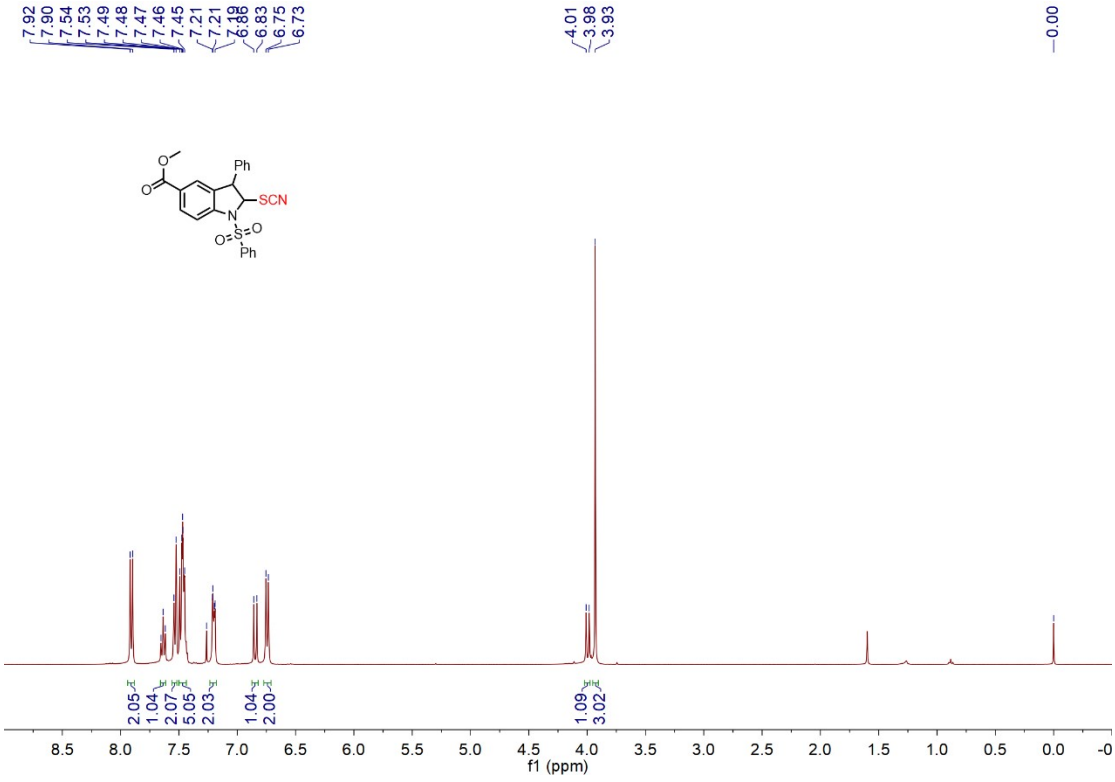

$^{13}$C NMR Spectrum of Compound **7c** (100 MHz, $CDCl_3$)



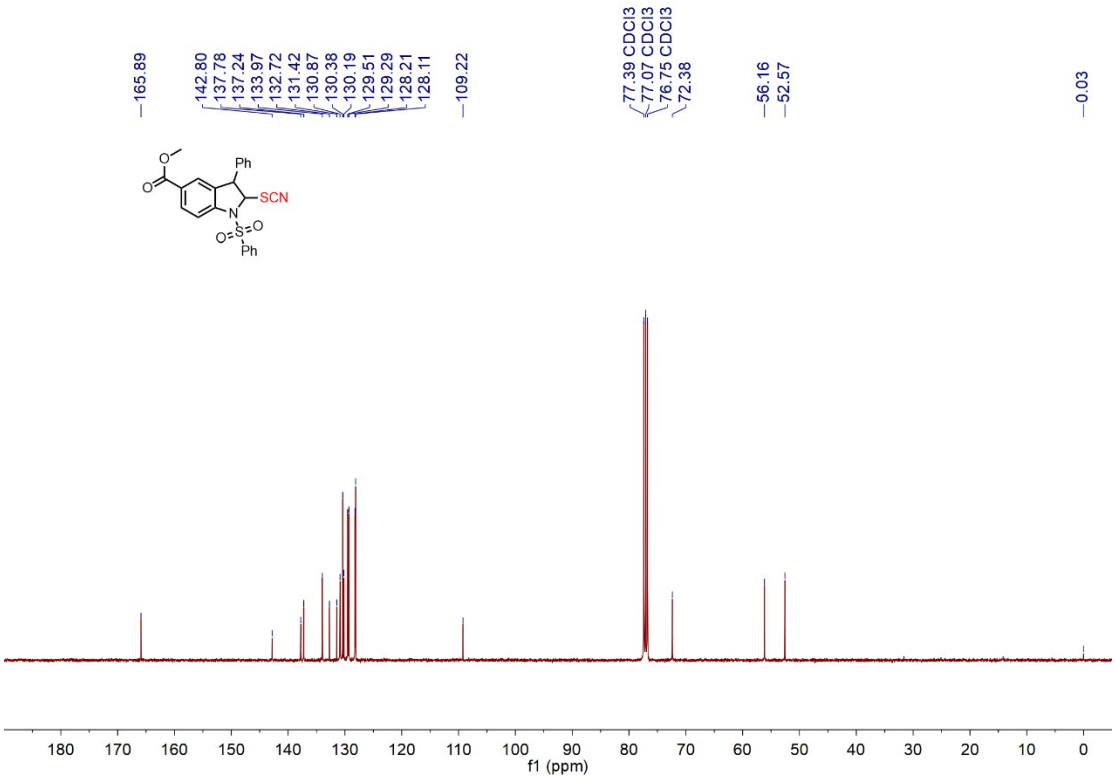

$^{1}$H NMR Spectrum of Compound **7d** (400 MHz, $CDCl_3$)



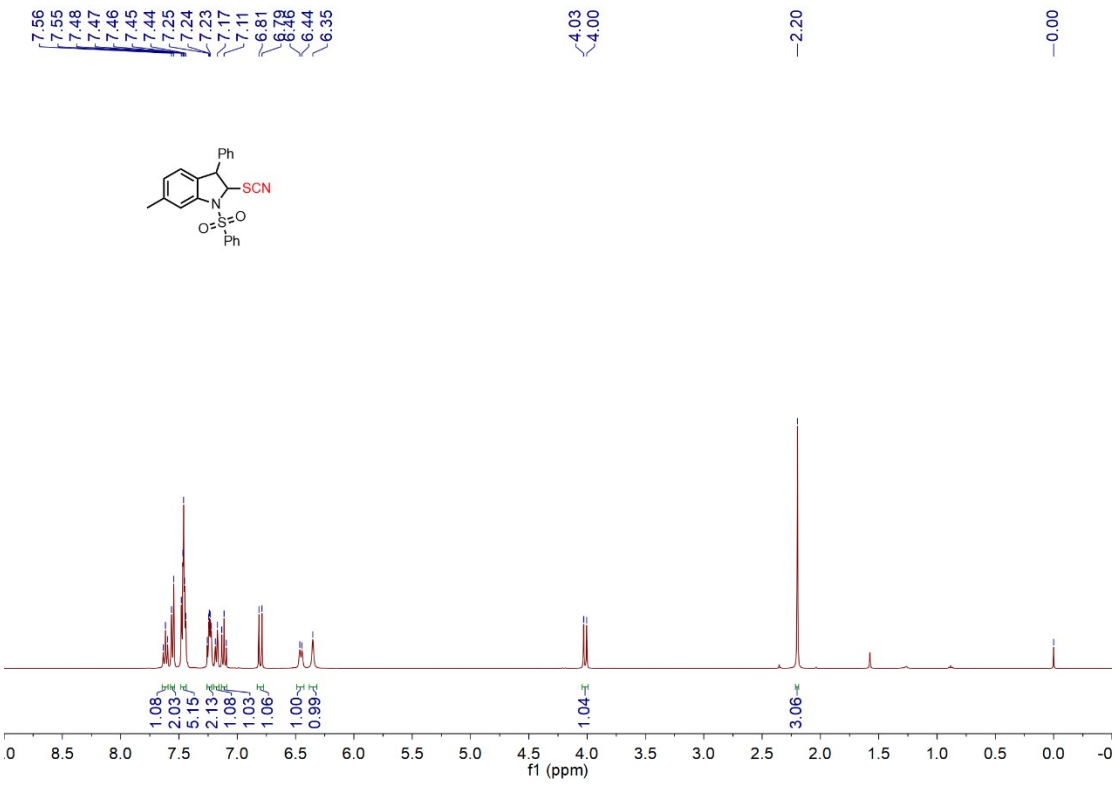

$^{13}$C NMR Spectrum of Compound **7d** (100 MHz, $CDCl_3$)



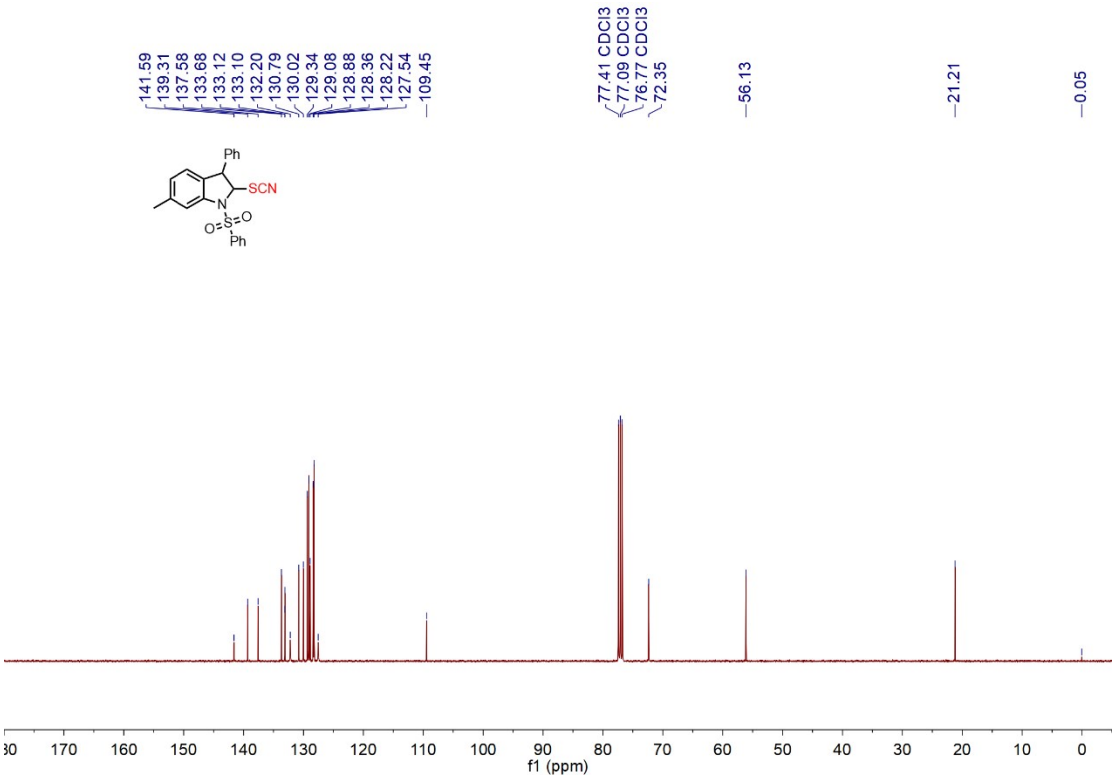

$^{1}$H NMR Spectrum of Compound **7e** (400 MHz, $CDCl_3$)



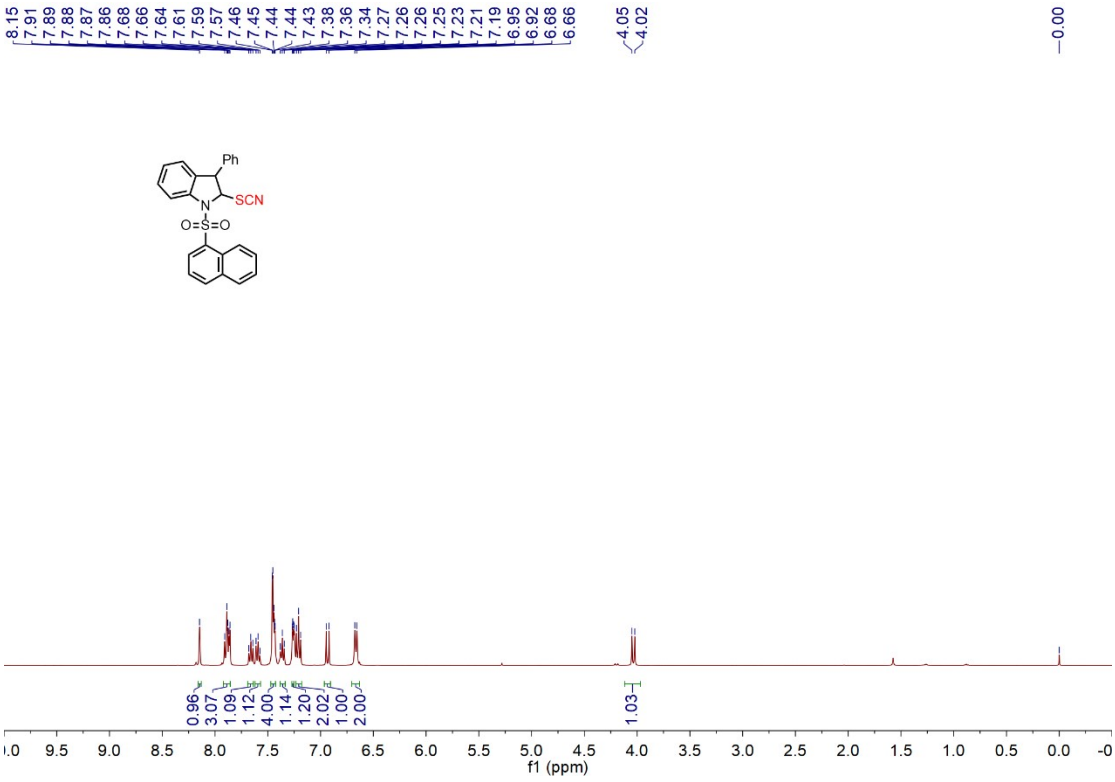

$^{13}$C NMR Spectrum of Compound **7e** (100 MHz, $CDCl_3$)



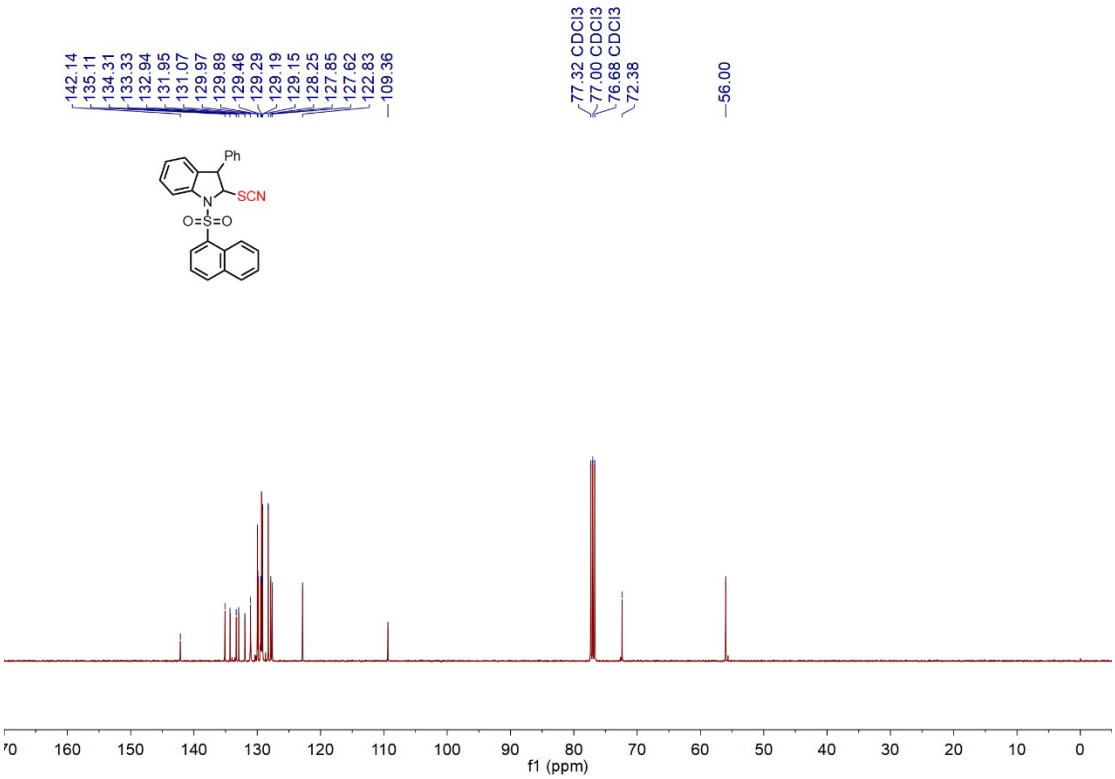

$^{1}$H NMR Spectrum of Compound **7f** (400 MHz, $CDCl_3$)



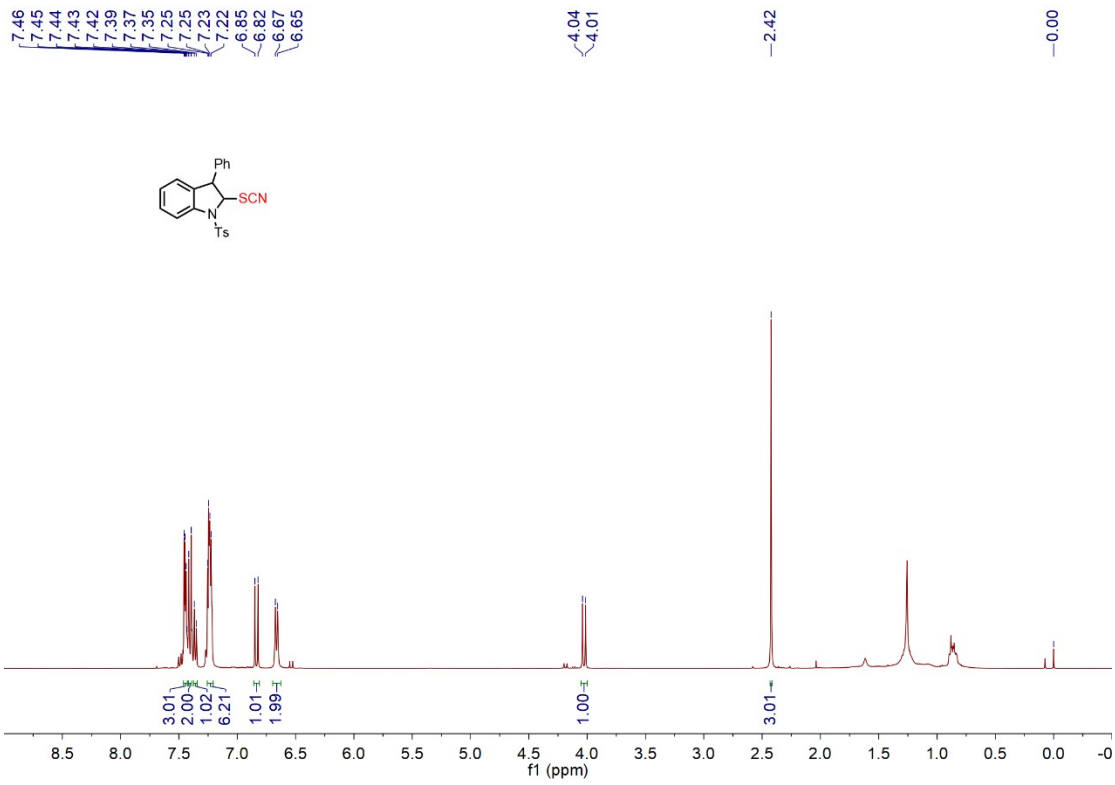

$^{13}$C NMR Spectrum of Compound **7f** (100 MHz, $CDCl_3$)



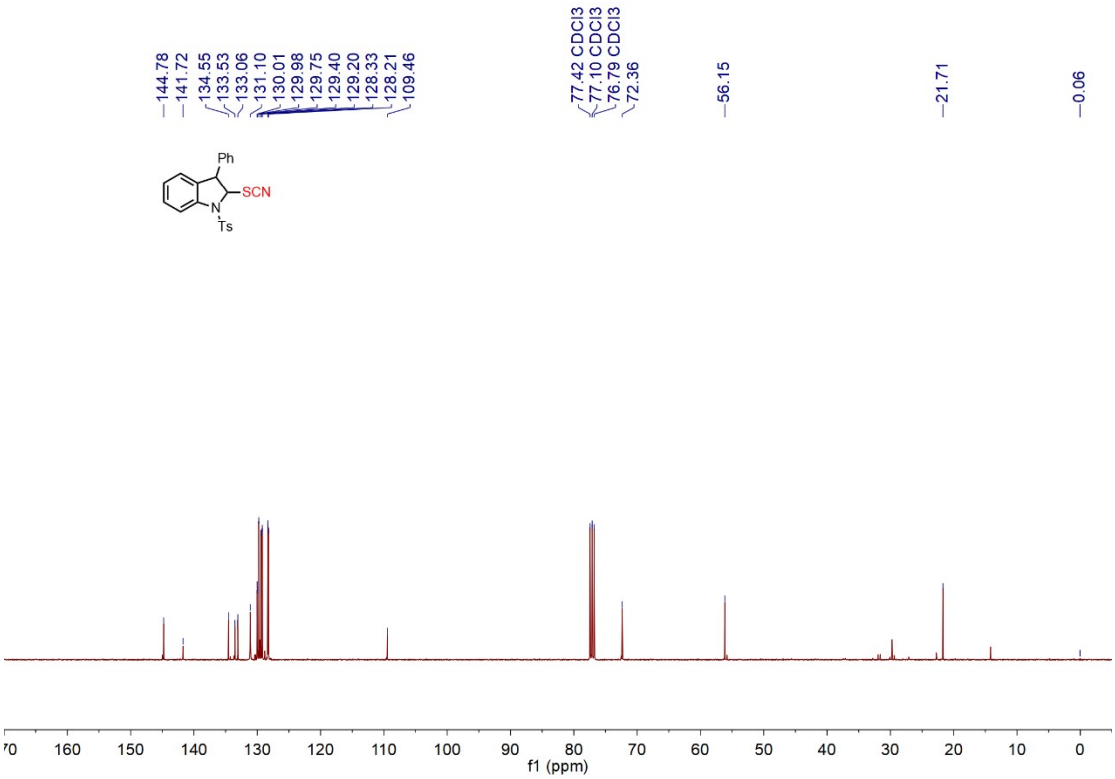

$^{1}$H NMR Spectrum of Compound **7g** (400 MHz, $CDCl_3$)



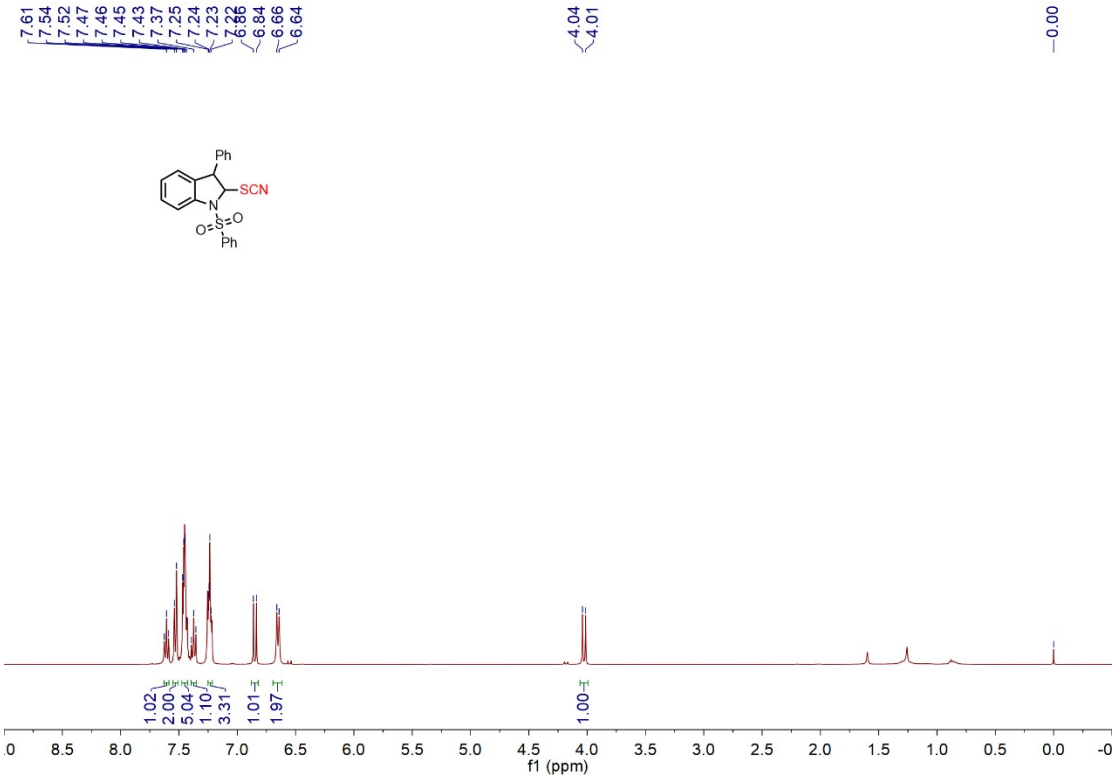

$^{13}$C NMR Spectrum of Compound **7g** (100 MHz, $CDCl_3$)



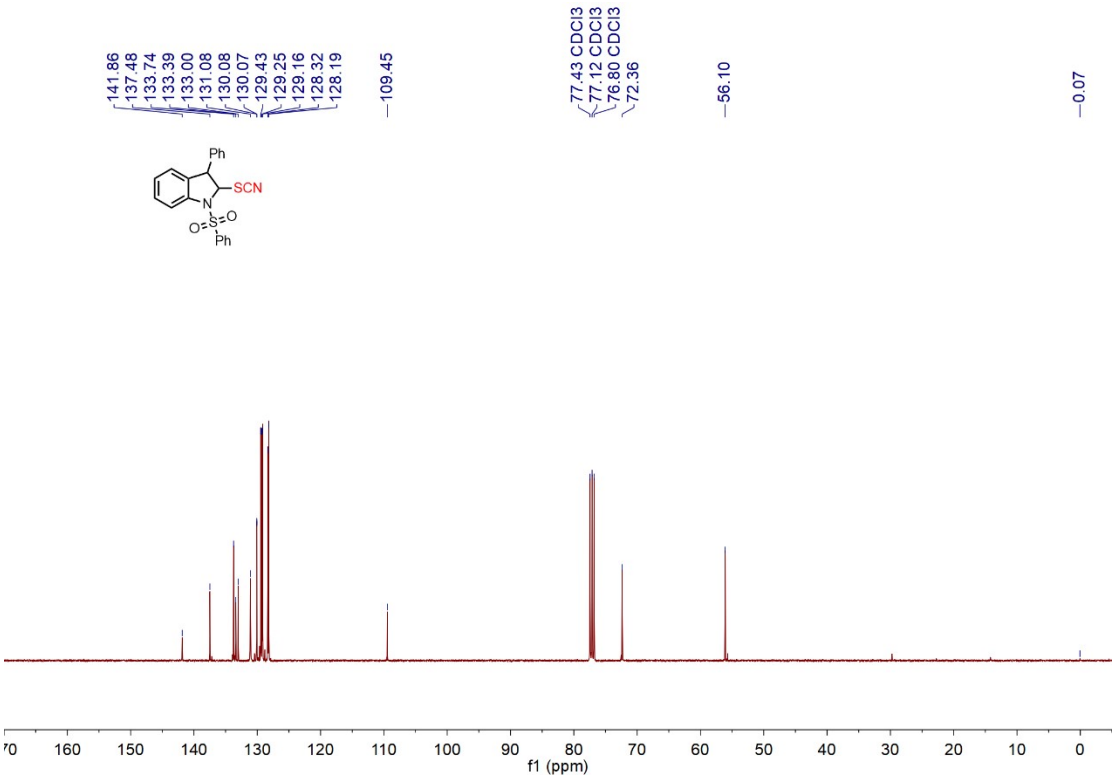

$^{1}$H NMR Spectrum of Compound **7h** (400 MHz, $CDCl_3$)




$^{13}$C NMR Spectrum of Compound **7h** (100 MHz, $CDCl_3$)




$^{1}$H NMR Spectrum of Compound **7i** (400 MHz, $CDCl_3$)




$^{13}$C NMR Spectrum of Compound **7i** (100 MHz, $CDCl_3$)