# Supporting Information

# Dual *ipso*-Hydroxylation and *para*-C-H Chalcogenation of Arylboronic Acids Using NDI Photocatalyst in Visible Light

Anirban Datta and Nidhi Jain*

Department of Chemistry, Indian Institute of Technology Delhi, India-110016

email: njain@chemistry.iitd.ac.in

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## 1. General Information:

The commercially available analytical grade reagents were used directly without additional purification. Dry solvents were used for the reaction and column chromatography. The progress of the reactions was monitored using thin-layer chromatography carried out on 0.25 mm Merck silica plates (60F-254). UV light ($\lambda_{max}$ = 254 nm) was used as a visualizing agent, and iodine vapor as a staining agent. Merck silica gel with particle sizes 60-120, 100-200 and 230-400 mesh was used as the stationary phase, while an appropriate amount of hexane and ethyl acetate was used as eluent (mobile phase) in column chromatography. $^{1}$H NMR spectra were recorded at 500 and 400 MHz, $^{13}$C {$^{1}$H} NMR at 125 and 100 MHz, $^{19}$F NMR at 376 MHz and $^{11}$B {$^{1}$H} NMR at 128 MHz using DMSO-$d_6$ and $CDCl_3$ as solvents. The splitting pattern of the peaks in $^{1}$H NMR is mentioned as singlet (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), quintet (quin), septet (sep), doublet of doublet (dd), triplet of triplet (tt), doublet of doublet of triplet (ddt) and multiplet (m). The chemical shifts and coupling constants are reported as parts per million (ppm) and hertz (Hz), respectively, in $^{1}$H NMR. High-resolution mass spectra were recorded on a mass spectrometer using electrospray ionization time-of-flight (ESI-TOF) reflection experiments. Melting points were recorded on an electrothermal digital melting point apparatus. Gas chromatography-mass spectrometry with an Agilent 8860 was used to detect GC-MS spectra. Melting points were recorded on an electrothermal digital melting point apparatus. Mixing a small amount of the sample with spectrophotometer KBr powder and compressing the combination under 12 tons of pressure yielded IR disks. A Perkin-Elmer FT-IR / FIR Spectrometer Frontier was used to capture FT-IR spectra. For reactions that require heating, a silicon oil bath was used. Starting materials naphthalenediamide, **1a** – **1an**, **BE1** – **BE3**, reagents dibromohydantoin, *n*-hexylamine, $NH_4SCN$, KSeCN, PhSSPh, and PhSeSePh were purchased from Alfa Aesar, Lancaster, Combi Blocks, ACROS, Frontier Scientific, Aldrich, Boron Molecular, Fluorochem, BLD Pharma, and TCI and used without further purification. All solvents used in the study, unless otherwise specified, were obtained from Merck (India). TLC plates (Merck, grade 60 $F_{254}$) and UVA and UVB lamps were used to investigate chemical reactions.

**UV-Vis, Emission, and *in situ* FT-IR Spectroscopy:** UV-Vis spectra were recorded on a SHIMADZU-UV-2450 and emission spectra were recorded on Horiba-Jobin-Yvon Fluorescence Spectrophotometer using HPLC grade acetonitrile as solvent. All UV-Vis and emission spectroscopic experiments were performed in a quartz cuvette with 10.0 mm optical pathlength. UV grade solvents were used for the spectroscopic experiments. Wavelength

reported in nanometres (nm). The *in situ* FT-IR experiment was conducted using a Mettler-Toledo React IR 700 (SN: C049640472) equipped with a TEMCT detector, DiComp (Dimond) probe, with a 9.5 mm × 2 m AgX fiber interface. Data was collected using the 2500 to 650 $cm^{-1}$ spectral window with 8 $cm^{-1}$ resolution and sampled in 60 second intervals.

**ESR Spectroscopy:** ESR spectra were obtained by taking samples in Wilmad quartz (CFQ) ESR tubes (length 250 mm; outer diameter 4 mm) using a Bruker A300-9.5/12/S/W instrument using microwave strength 9.8 GHz, sweep time 60 seconds, and one scan.

## 2. LED emission spectra and reaction setup:

The measurement was recorded using open spectrophotometer Ava Light-DH-S-BAL Avantes. The light source used for illuminating the reaction vessel is 50 W blue LEDs ($\lambda_{max}$ = 445 nm). Light source: DEEPSUN, Model No HC2436A1. The material of the irradiation vessel is borosilicate glass. The distance from the light source to the irradiation vessel is 2.5 cm and no filters were used.

**(a)** **(b)** **(c)**

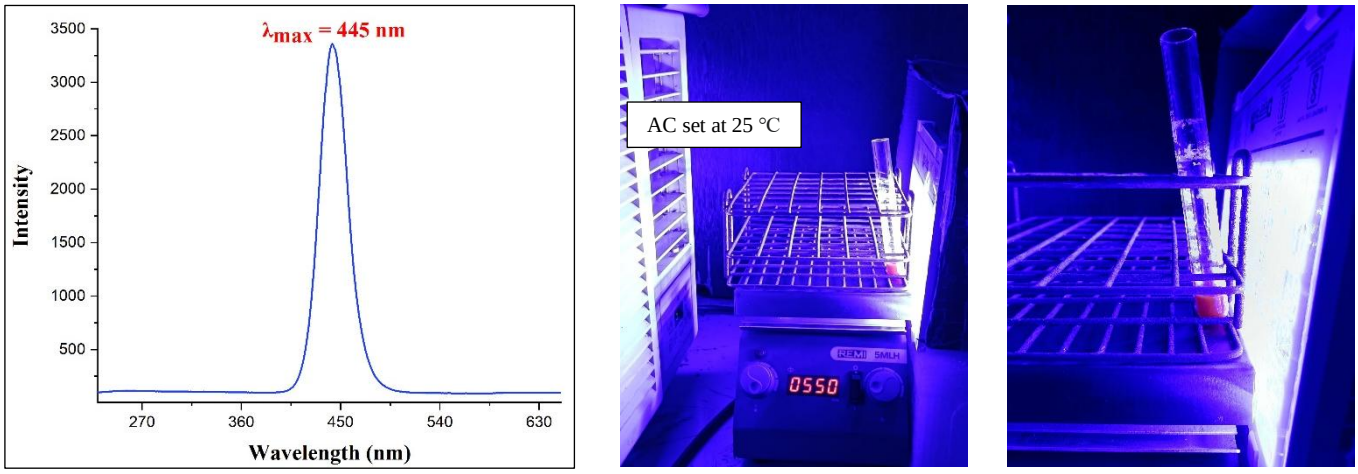
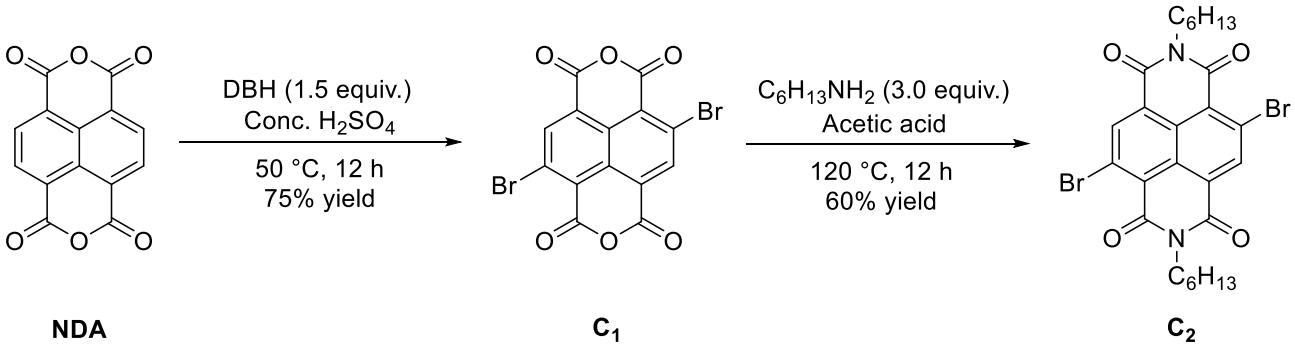



**Figure S1. (a)** The emission spectrum of 50 W blue LED; **(b)** and **(c)** Reaction setup.

### 3. Experimental procedure for synthesis of NDI-PC:

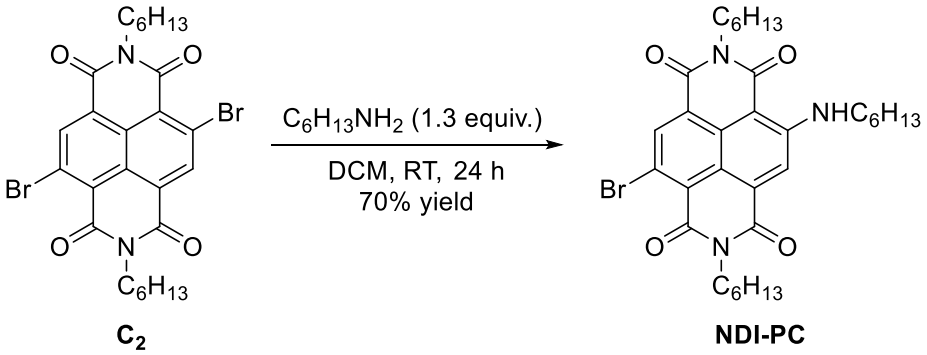
**NDI-PC** was synthesized according to the literature procedure reported by Datta *et al.*[1]




**Scheme S1.** Synthesis of 2, 6-dibromo NDI ($C_2$)

**Step 1.** In a single neck RB flask, 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA) (2.7 g, 1.0 equiv., 10.0 mmol) was stirred in concentrated sulfuric acid (about 25.0 mL) at 0 ℃ to room temperature for about 5 min to achieve dissolution. Dibromohydantoin (DBH) (3.6 g, 1.5 equiv., 15.0 mmol) was added in four portions over a period of 1 hour at about 0 ℃ to rt. The resulting brown solution was stirred at 50 ℃ for about 12 h. After that, the mixture was poured into crushed ice to precipitate the solid. The precipitated solid was filtered, washed with water then with methanol, and finally dried under vacuo to afford a crude product 2,6-dibromo-NDA or **$C_1$**, which was further purified by recrystallization in DMF (Yield = 75%). **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** $\delta$ 8.79 (s, 2H) ppm. **$^{13}$C {$^1$H} NMR (125 MHz, DMSO-*d*$_6$)** $\delta$ 158.4, 156.9, 138.0, 129.9, 127.9, 124.7, 123.9 ppm.

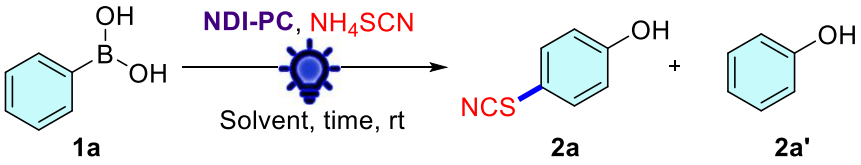
**Step 2.** A mixture of **$C_1$** (1.1 g, 1.0 equiv., 2.5 mmol), n-hexylamine (1 mL, 3.0 equiv., 7.5 mmol), and acetic acid (25.0 mL) was stirred at 120 ℃ for about 12 h. The mixture was cooled to about 0 ℃, the precipitate formed was collected by filtration, washed with methanol and dried under vacuum to obtain **$C_2$** as a pale yellow solid (Yield = 60 %). **$^1$H NMR (500 MHz, CDCl$_3$)** $\delta$ 8.99 (s, 2H), 4.18 (t, *J* = 7.5 Hz, 4H), 1.73 (p, *J* = 7.5 Hz, 4H), 1.46-1.40 (m, 4H), 1.38-1.31 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 6H) ppm. **$^{13}$C {$^1$H} NMR (125 MHz, CDCl$_3$)** $\delta$ 161.0, 160.9, 139.3, 128.5, 127.9, 125.6, 124.3, 41.8, 31.7, 28.1, 26.9, 22.7, 14.2 ppm. HRMS (ESI, Q-TOF) m/z: calcd for $C_{26}H_{28}Br_2N_2O_4$ $[M]^-$ 590.0416; found 590.0414.




**Scheme S2.** Synthesis of 6-bromo-*N*-hexyl-2-amine NDI (NDI-PC)

A mixture of **C2** (592.0 mg, 1.0 equiv., 1.0 mmol) and n-hexylamine (0.17 mL, 1.3 equiv., 1.3 mmol) in DCM (20.0 mL) was stirred for 24 h. After completion of the reaction, DCM was removed on a rotary evaporator and the product was purified by column chromatography on silica gel (100-200 mesh) column eluted with 25% DCM in hexane. The NDI photocatalyst, NDI-PC was obtained as red solid (Yield = 70%). **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 9.89 (t, $J$ = 5.0 Hz, 1H), 8.51 (s, 1H), 7.98 (s, 1H), 4.03 (q, $J$ = 7.5 Hz, 4H), 3.48 (q, $J$ = 7.0 Hz, 2H), 1.81 (p, $J$ = 7.5 Hz, 2H), 1.69 – 1.60 (m, 4H), 1.52 (p, $J$ = 7.0 Hz, 2H), 1.38 – 1.37 (m, 8H), 1.33 – 1.31 (m, 8H), 0.92 (t, $J$ = 7.0 Hz, 3H), 0.89 – 0.86 (m, 6H) ppm. **$^{13}$C {$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 165.6, 161.5, 161.3, 160.9, 151.5, 137.8, 128.1, 126.9, 123.0, 122.8, 120.9, 120.2, 120.1, 99.4, 43.5, 41.5, 40.6, 31.6, 31.6, 31.6, 29.4, 28.0, 27.9, 27.0, 26.9, 26.9, 22.7, 14.2, 14.1 ppm. HRMS (ESI, Q-TOF) m/z: calcd for $C_{32}H_{41}BrN_3O_4$ $[M - H]^-$ 610.2281; found 610.2304.

## 4. Optimization of reaction conditions for the synthesis of 2a:




| Entry | Solvent | Yield (%)[b] | |
|---|---|---|---|
| | | 2a | 2a' |
| **1[a]** | **MeCN** | **82** | **10** |
| 2 | DCM | Trace | 25 |
| 3 | DMF | 0 | Trace |
| 4 | THF | 30 | 16 |

| | | | |
|---|---|---|---|
| 5 | MeCN | 25[c]/48[d]/82[e] | 30[c]/20[d]/Trace[e] |
| 6[f] | MeCN | Trace | 35 |
| 7 | MeCN | Trace[g]/51[h]/75[i] | 72[g]/25[h]/Trace[i] |
| 8 | MeCN | N.R.[j]/ 83[k] | N.R.[j]/ 12[k] |
| 9[l] | MeCN | 78 | 14 |

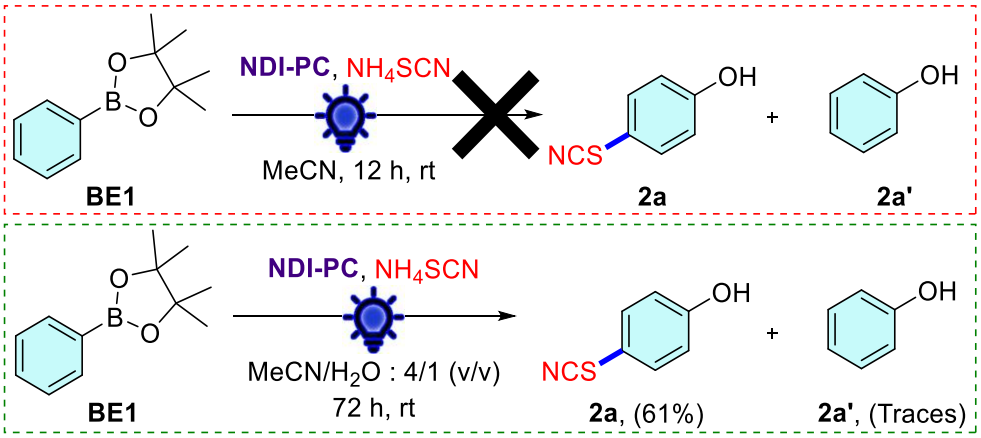
**Table S1.** [a]Reaction conditions: **1a** (12.0 mg, 1.0 equiv., 0.1 mmol), $NH_4SCN$ (15.0 mg, 2.0 equiv., 0.2 mmol), NDI-PC (1.8 mg, 3.0 mol%, 0.003 mmol), MeCN (2.0 mL), blue LED, RT, 12 h; [b]Isolated yield; [c,d,e] Product yield at 4 h, 8 h, and 24 h respectively; [f]Reaction in green light; [g,h,i]$NH_4SCN$ in 0.5, 1.0, 3.0 equiv. respectively; [j,k]Under $N_2$ atmosphere and $O_2$ atmosphere respectively; [l]1.0 equiv. $NEt_3$ was added as an additive.

Additional optimization studies (other than those discussed in MS) were carried out which involved screening of solvents, optimization of reaction time, light source, stoichiometry, reaction atmosphere etc. Changing to other nonpolar and polar solvents like DCM, DMF, and THF gave either no reaction or poor yields of **2a** (Table S1, entries 2-4) in all cases. When the reaction time was reduced to 4 h and 8 h, the yield of **2a** dropped to 25% and 48%, respectively. On increasing the reaction time to 24 h, no change in the yield of **2a** was noticed and traces of **2a'** were seen (Table S1, entry 5). Next, when the light source was changed to green light, **2a** formed in traces, and **2a'** formed with a 35% yield (Table S1, entry 6). Decreasing or increasing the stoichiometry of $NH_4SCN$ to 0.5, 1.0, or 3.0 equiv. did not help and gave a lower yield of **2a** in all the cases (Table S1, entry 7). In the absence of oxygen, i.e., under a nitrogen atmosphere, both **2a** and **2a'** did not form, while under an oxygen atmosphere, the yields of **2a** and **2a'** did not change much (Table S1, entry 8). When 1.0 equiv. $NEt_3$ was added as an additive, no improvement in yield was noticed. **2a** formed in 78% and **2a'** in 14% yield since both $SCN^-$ anion and $NEt_3$ could participate in the redox cycle enabling conversion of **NDI-PC*** to **NDI-PC**$^{\bullet-}$ (Table S1, entry 9).

## 5. Experimental procedure for the synthesis of 2a – 2am:

In a reaction tube, 12.0 mg of **1a** (1.0 equiv., 0.1 mmol) was taken and dissolved in 2.0 ml MeCN. Then, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol) was added to it, followed by the addition of 1.8 mg of photocatalyst NDI-PC (3.0 mol%, 0.003 mmol). After this, the reaction tube was irradiated in the blue LED light setup for 12 hours at room temperature. After completion of the reaction, monitored by TLC, the reaction was diluted with ethyl acetate and washed with water. The combined organic phases were dried over $Na_2SO_4$, and the solvent was evaporated under reduced pressure to obtain the crude. The crude residue was purified by column chromatography silica gel of mesh size 100-200 or 230-400 with hexane/ethyl acetate (80/20) as the eluent and afforded the resulting 4-thiocyanatophenol as the product.

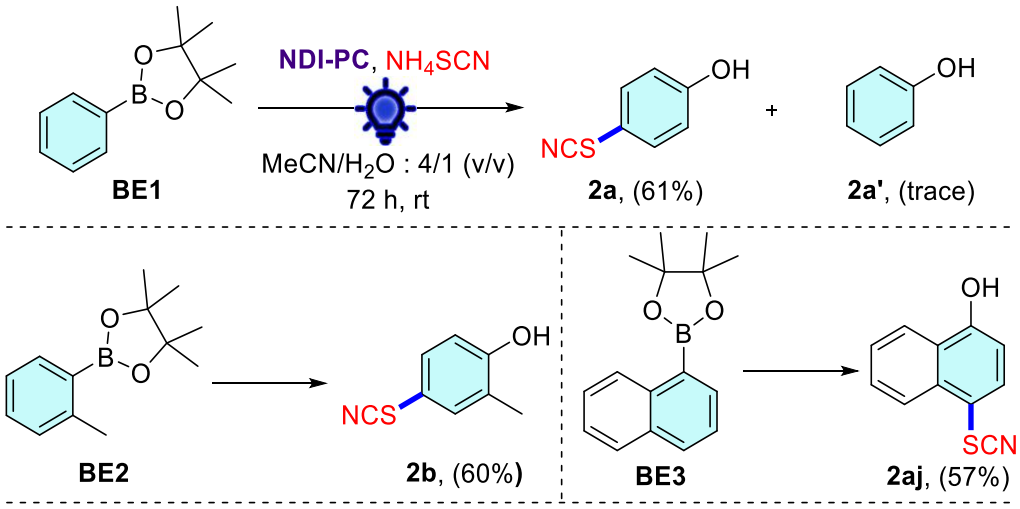
- **Synthesis of 2a, 2b and 2aj from pinacol boronate esters**




| Entry | Deviation from standard conditions | Observation |
|---|---|---|
| 1 | none | N. R. |
| 2 | After 72 h instead of 12 h | Traces of phenylboronic acid formed |
| 3 | $MeCN/H_2O$ : 4/1 (v/v) instead of MeCN | N. R. |
| 4[a] | $MeCN/H_2O$ : 4/1 (v/v) instead of MeCN and after 72 h instead of 12 h | **2a** formed with 61% yield |

**Table S2.** [a]Reaction conditions: **BE1** (12.0 mg, 1.0 equiv., 0.1 mmol), $NH_4SCN$ (15.0 mg, 2.0 equiv., 0.2 mmol), NDI-PC (1.8 mg, 3.0 mol%, 0.003 mmol), $MeCN/H_2O$ : 4/1 (v/v) (2.4 mL MeCN + 0.6 mL $H_2O$), blue LED, RT, 72 h. N. R. = No reaction.

When **BE1** was reacted under the standard condition {**BE1** (12.0 mg, 1.0 equiv., 0.1 mmol), $NH_4SCN$ (15.0 mg, 2.0 equiv., 0.2 mmol), NDI-PC (1.8 mg, 3.0 mol%, 0.003 mmol), MeCN (2.0 mL), blue LED, RT, 12 h.}, no reaction took place (Table S2, entry 1). On increasing the reaction time to 72 h, traces of phenylboronic acid were seen (Table S2, entry 2). The conversion of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (**BE1**) to phenylboronic acid (**1a**) in solvent DMSO-$d_6$/$D_2O$ : 10/1 (v/v) with $t_{1/2}$ = 78 h, has been reported previously– H. Ihara, M. Koyanagi, and M. Suginome, *Org. Lett*., 2011, **13**, 2662. Guided by this, we changed the solvent to MeCN/$H_2O$ : 4/1 (v/v) but no product formation was seen (Table S2, entry 3). Subsequently, on increasing the reaction time to 72 h, we got the desired product **2a** in 61% yield along with traces of phenol (Table S2, entry 4). The results indicated that the boronate ester starting material **BE1**, first gets hydrolyzed to boronic acid **1a**, which then reacts in the usual manner to give the product **2a**.

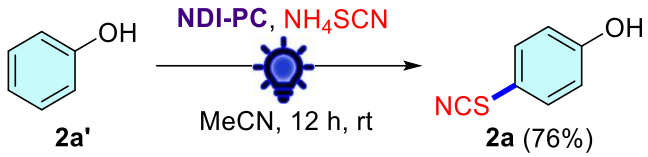



**Scheme S3.** Synthesis of **2a**, **2b** and **2aj** from pinacol boronate esters.

In a reaction tube, 20.0 mg of **BE1** (1.0 equiv., 0.1 mmol) was taken and dissolved in 3.0 ml MeCN/$H_2O$ : 4/1 (v/v) (2.4 mL MeCN + 0.6 mL $H_2O$). Then, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol) was added to it, followed by the addition of 1.8 mg of photocatalyst NDI-PC (3.0 mol%, 0.003 mmol). After this, the reaction tube was irradiated in the blue LED light setup for 72 hours at room temperature. After this, the reaction was diluted with ethyl acetate and washed with water. The combined organic phases were dried over $Na_2SO_4$, and the solvent was evaporated under reduced pressure to obtain the crude. The crude residue was purified by column chromatography silica gel of mesh size 100-200 with hexane/ethyl acetate (80/20) as the eluent and afforded **2a** in 61% yield with a trace of **2a'**. Similarly, **2b** and **2aj** were synthesized from **BE2** and **BE3** with 60% and 57% yields, respectively.

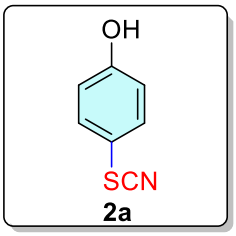
- **Synthesis of 2a from phenol (2a') as the starting material:**

In a reaction tube, 9.0 mg of **2a'** (1.0 equiv., 0.1 mmol) was taken and dissolved in 2.0 ml MeCN. 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol) was added to it, followed by the addition of 1.8 mg of NDI-PC (3.0 mol%, 0.003 mmol). After this, the reaction tube was irradiated in the blue LED for 12 hours at room temperature. After completion of the reaction, monitored by TLC, the reaction was diluted with ethyl acetate and washed with water. The combined organic phases were dried over $Na_2SO_4$, and the solvent was evaporated under reduced pressure to obtain the crude product. The crude residue was purified by column chromatography on silica gel of mesh size 100-200 with hexane/ethyl acetate (80/20) as the eluent and afforded 4-thiocyanatophenol (**2a**) in 76% yield along with traces of unreacted **2a'**.

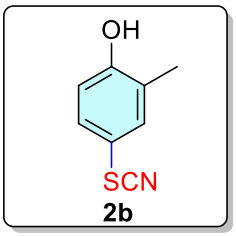



**Scheme S4.** Direct synthesis of **2a** from **2a'**.

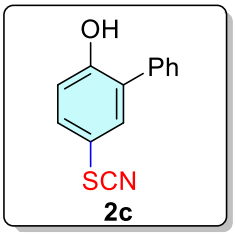
**4-thiocyanatophenol (2a):**[2] Orange solid, yield 203.0 mg (82%); hexane/EtOAc (80/20); **$^1$H NMR (500 MHz, DMSO-$d_6$)** $\delta$ 10.21 (s, 1H), 7.51 (d, $J$ = 9.0 Hz, 2H), 6.90 (d, $J$ = 9.0 Hz, 2H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, DMSO-$d_6$)** $\delta$ 160.1, 134.9, 117.9, 113.1, 111.7 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_7H_4NOS$ 150.0014; Found 150.0011.



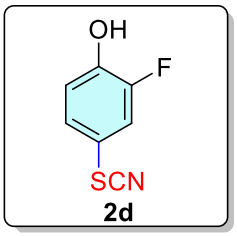

**2-methyl-4-thiocyanatophenol (2b):**[2] Orange solid, yield 194 mg (80%); hexane/EtOAc (80/20); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.36 (d, $J$ = 2.0 Hz, 1H), 7.28 (dd, $J$ = 8.5, 2.0 Hz, 1H), 6.83 (d, $J$ = 8.5 Hz, 1H), 5.53 (brs, 1H), 2.26 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 156.6, 135.2, 131.7, 127.1, 116.8, 112.9, 112.4, 15.9 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_8H_6NOS$ 164.0170; Found 164.0173.



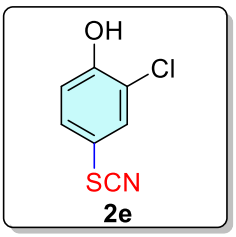
**5-thiocyanato-[1,1'-biphenyl]-2-ol (2c):** Brown liquid, yield 178 mg (78%); hexane/EtOAc (80/20); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.53 – 7.50 (m, 2H), 7.47 – 7.43 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.74 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 154.8, 135.3, 134.3, 133.3, 130.6, 129.7, 129.1, 128.9, 118.1, 114.1, 111.8 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_8NOS$ 226.0327; Found 226.0319.



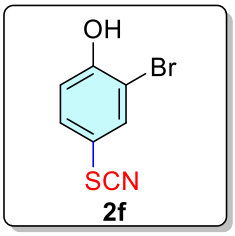

**2-fluoro-4-thiocyanatophenol (2d):**[3] Yellow solid, yield 150 mg (62%); hexane/EtOAc (75/25); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.35 (dd, *J* = 9.6, 2.0 Hz, 1 H), 7.29 – 7.25 (m, 1H), 7.07 (t, *J* = 8.4 Hz, 1H), 5.86 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR (100MHz, $CDCl_3$)** $\delta$ 151.3 (d, *J* = 242.5 Hz), 146.1 (d, *J* = 14.0 Hz), 129.3 (d, *J* = 3.6 Hz), 119.7 (d, *J* = 20.7 Hz), 119.2 (d, *J* = 2.5 Hz), 114.3 (d, *J* = 6.9 Hz), 111.0 ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -135.83 (ddd, *J* = 9.8, 8.6, 1.1 Hz) ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_3NOS$ 167.9920; Found 167.9922.



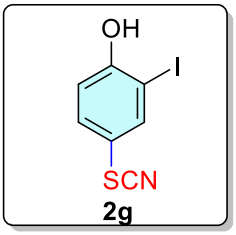

**2-chloro-4-thiocyanatophenol (2e):**[2] Yellow solid, yield 154 mg (65%); hexane/EtOAc (80/20); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.59 (d, *J* = 2.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 5.90 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 153.6, 132.7, 132.6, 121.7, 118.2, 115.1, 110.9 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_3ClNOS$ 183.9624; Found 183.9619.



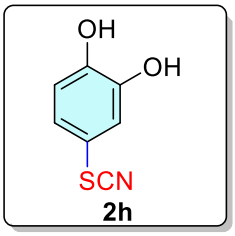

**2-bromo-4-thiocyanatophenol (2f):**[4] Yellow solid, yield 162 mg (70%); hexane/EtOAc (75/25); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.72 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.00 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 154.6, 135.7, 133.3, 117.9, 115.3, 111.6, 111.0 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_3BrNOS$ 227.9119; Found 227.9121.



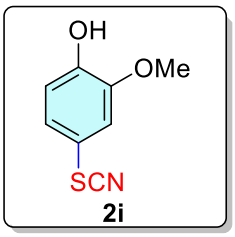
**2-iodo-4-thiocyanatophenol (2g):**[4] Brown solid, yield 147 mg (66%); hexane/EtOAc (75/25); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.88 (s, 1H), 7.46 (d, $J$ = 8.5 Hz, 1H), 7.02 (d, $J$ = 8.5 Hz, 1H), 5.91 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 157.2, 141.8, 134.3, 116.7, 115.5, 111.2, 86.6 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_3INOS$ 275.8980; Found 275.8974.



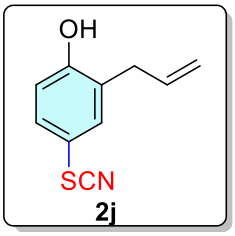

**4-thiocyanatobenzene-1,2-diol (2h):**[4] Brown solid, yield 191 mg (79%); hexane/EtOAc (65/35); **$^1$H NMR (400 MHz, DMSO-$d_6$)** $\delta$ 9.66 (s, 2H), 7.02 (d, $J$ = 2.4 Hz, 1H), 6.95 (dd, $J$ = 8.4, 2.4 Hz, 1H), 6.85 (d, $J$ = 8.4 Hz) ppm. **$^{13}$C{$^1$H} NMR (100MHz, DMSO-$d_6$)** $\delta$ 148.4, 147.3, 124.5, 119.5, 117.5, 113.0, 111.5 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_4NO_2S$ 165.9963; Found 165.9967.



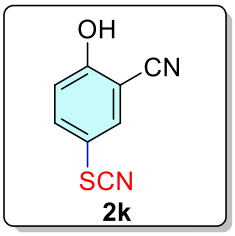

**2-methoxy-4-thiocyanatophenol (2i):**[5] Light yellow solid, yield 202 mg (85%); hexane/EtOAc (70/30); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.11 (dd, $J$ = 8.4, 2.0 Hz, 1H), 7.06 (d, $J$ = 2.0 Hz, 1H), 6.95 (d, $J$ = 8.4 Hz, 1H), 5.86 (brs, 1H), 3.94 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 148.0, 147.7, 126.5, 116.0, 114.6, 113.2, 111.8, 56.5 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_8H_6NO_2S$ 180.0119; Found 180.0111.



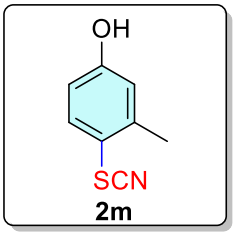

**2-allyl-4-thiocyanatophenol (2j):**[2] Orange semi-solid, yield 151 mg (64%); hexane/EtOAc (85/15); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ δ 7.36 – 7.33 (m, 2H), 6.85 (d, $J$ = 8.8 Hz, 1H), 5.98 (ddt, $J$ = 16.8, 10.0, 6.4 Hz, 1H), 5.55 (brs, 1H), 5.23 – 5.15 (m, 2H), 3.41 (d, $J$ = 6.4 Hz, 2H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 156.4, 135.2, 134.6, 132.3, 128.4, 117.7, 117.6, 113.7, 112.1, 34.8 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{10}H_8NOS$ 190.0327; Found 190.0321.



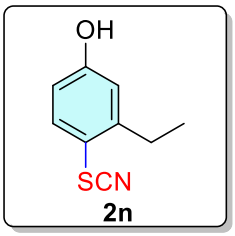
**2-hydroxy-5-thiocyanatobenzonitrile (2k):**[6] Red solid, yield 110 mg (46%); hexane/EtOAc (75/25); **$^1$H NMR (500 MHz, DMSO-*d*$_6$)** $\delta$ 11.93 (s, 1H), 8.06 (brs, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, DMSO-*d*$_6$)** $\delta$ 162.4, 139.3, 138.0, 118.7, 115.9, 113.8, 112.5, 101.2 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_8H_2N_2OS$ 174.9966; Found 174.9961.



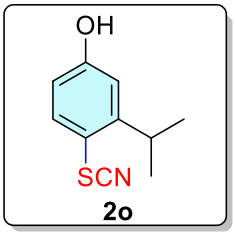

**3-methyl-4-thiocyanatophenol (2m):**[4] Orange solid, yield 193 mg (79%); hexane/EtOAc (80/20); **$^1$H NMR (500 MHz, CDCl$_3$)** $\delta$ 7.44 (d, *J* = 8.5 Hz, 1H), 6.79 (d, *J* = 1.5 Hz, 1H), 6.70 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.46 (brs, 1H), 2.46 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$)** $\delta$ 158.7, 143.5, 136.2, 118.8, 115.1, 112.5, 112.2, 21.1 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_8H_6NOS$ 164.0170; Found 164.0162.



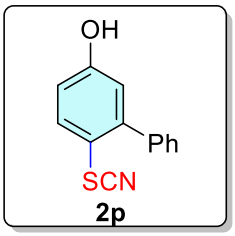

**3-ethyl-4-thiocyanatophenol (2n):**[7] yellow oil, yield 200 mg (84%); hexane/EtOAc (80/20); **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta$ 7.48 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 2.8 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.07 (brs, 1H), 2.82 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** $\delta$ 158.8, 149.0, 136.5, 117.2, 115.2, 112.5, 112.3, 27.7, 14.7 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_9H_8NOS$ 178.0327; Found 178.0323.



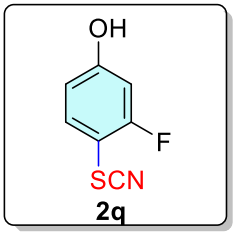

**3-isopropyl-4-thiocyanatophenol (2o):** yellow oil, yield 183 mg (78%); hexane/EtOAc (80/20); **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta$ 7.49 (d, *J* = 8.8 Hz, 1H), 6.85 (d, *J* = 2.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.43 (hept, *J* = 6.8 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 6H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** $\delta$ 158.9, 153.4, 136.4, 115.1, 114.6, 112.5, 112.3, 31.8, 23.5 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{10}H_{10}NOS$ 192.0483; Found 192.0490.



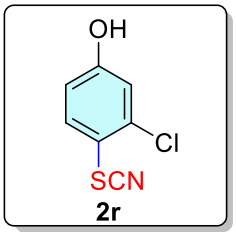
**6-thiocyanato-[1,1'-biphenyl]-3-ol (2p):** Brown liquid, yield 183 mg (80%); hexane/EtOAc (80/20); **$^{1}$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.61 (d, $J$ = 8.5 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.31 (d, $J$ = 5.0 Hz, 2H), 6.91 – 6.89 (m, 2H), 6.56 (brs, 1H) ppm. **$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 157.9, 146.4, 138.9, 134.5, 129.1, 128.7, 128.6, 118.7, 116.7, 112.6, 112.5 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_8NOS$ 226.0327; Found 226.0324.



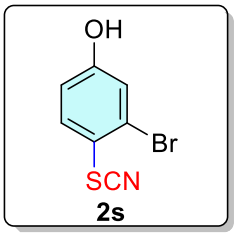

**3-fluoro-4-thiocyanatophenol (2q):**[3] Brown solid, yield 154 mg (64%); hexane/EtOAc (75/25); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.46 – 7.41 (m, 1H), 6.73 – 6.69 (m, 2H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 162.6 (d, $J$ = 250.1 Hz), 160.9 (d, $J$ = 11.1 Hz), 135.8 (d, $J$ = 1.0 Hz), 113.6 (d, $J$ = 3.0 Hz), 111.00, 105.0 (d, $J$ = 24.3 Hz), 100.2 (d, $J$ = 18.7 Hz). **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -103.44 – -103.49 (m) ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_3FNOS$ 167.9920; Found 167.9914.



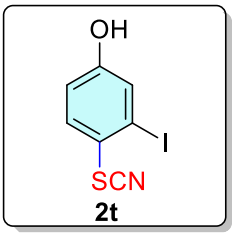

**3-chloro-4-thiocyanatophenol (2r):**[3] Yellow solid, yield 124 mg (62%); hexane/EtOAc (75/25); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.55 (d, $J$ = 8.8 Hz, 1H), 7.02 (d, $J$ = 2.4 Hz, 1H), 6.83 (dd, $J$ = 8.8, 2.4 Hz, 1H), 6.15 (brs, 1H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 158.8, 136.9, 134.4, 118.2, 116.3, 113.4, 110.8 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_3ClNOS$ 183.9624; Found 183.9633.



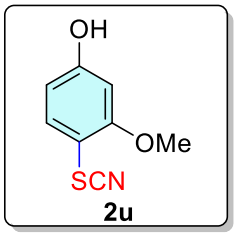

**3-bromo-4-thiocyanatophenol (2s):**[8] Yellow solid, yield 175 mg (76%); hexane/EtOAc (75/25); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.55 (d, $J$ = 8.8 Hz, 1H), 7.18 (d, $J$ = 2.8 Hz, 1H), 6.87 (dd, $J$ = 8.8, 2.8 Hz, 1H), 6.39 (brs, 1H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 158.5, 134.1, 126.4, 121.4, 116.9, 115.6, 111.1 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_3BrNOS$ 227.9119; Found 227.9114.



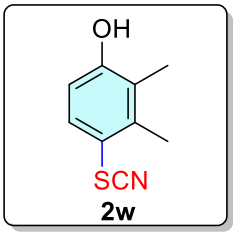
**3-iodo-4-thiocyanatophenol (2t):**[9] Brown solid, yield 134 mg (60%); hexane/EtOAc (75/25); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.58 (d, $J$ = 8.5 Hz, 1H), 7.42 (s, 1H), 6.92 (d, $J$ = 8.5 Hz, 1H), 6.40 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 157.9, 133.5, 127.8, 119.8, 117.7, 111.6, 101.8 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_7H_3INOS$ 275.8980; Found 275.8986.



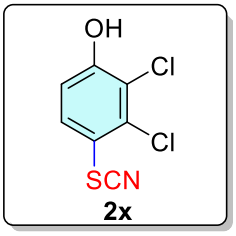

**3-methoxy-4-thiocyanatophenol (2u):**[5] Light yellow solid, yield 162 mg (81%); hexane/EtOAc (70/25); **$^1$H NMR (400 MHz, DMSO-$d_6$)** $\delta$ 10.24 (s, 1H), 7.41 (d, $J$ = 8.8 Hz, 1H), 6.58 (d, $J$ = 2.4 Hz, 1H), 6.50 (dd, $J$ = 8.8, 2.4 Hz, 1H), 3.87 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$)** $\delta$ 162.3, 159.9, 135.5, 112.4, 109.5, 100.9, 99.0, 56.6 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_8H_6NO_2S$ 180.0119; Found 180.0114.



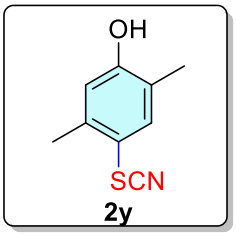

**2,3-dimethyl-4-thiocyanatophenol (2w):**[4] Brown solid, yield 176 mg (74%); hexane/EtOAc (80/20); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.35 (d, $J$ = 8.5 Hz, 1H), 6.68 (d, $J$ = 8.5 Hz, 1H), 5.79 (brs, 1H), 2.48 (s, 3H), 2.20 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 156.4, 141.6, 132.9, 125.7, 114.3, 113.6, 112.3, 18.2, 12.7 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for 178.0327; Found 178.0321.



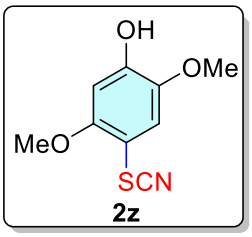

**2,3-dichloro-4-thiocyanatophenol (2x):**[9] Brown solid, yield 155 mg (67%); hexane/EtOAc (75/25); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ $^1$H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, $J$ = 9.0 Hz, 1H), 7.06 (d, $J$ = 9.0 Hz, 1H), 6.03 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 154.2, 133.9, 131.2, 121.3, 116.0, 115.9, 109.7 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_7H_2Cl_2NOS$ 217.9234; Found 217.9232.



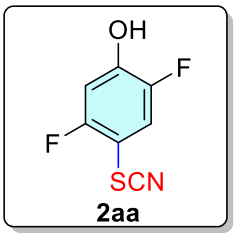
**2,5-dimethyl-4-thiocyanatophenol (2y):**[10] Light yellow solid, yield 171 mg (72%); hexane/EtOAc (80/20); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.36 (s, 1H), 6.71 (s, 1H), 5.43 (brs, 1H), 2.43 (s, 3H), 2.20 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 156.6, 140.6, 137.0, 124.1, 118.0, 112.6, 112.0, 20.6, 15.3 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_9H_8NOS$ 178.0327; Found 178.0320.



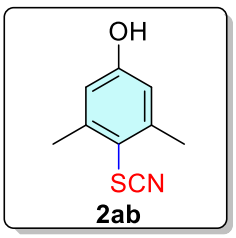

**2,5-dimethoxy-4-thiocyanatophenol (2z):** White solid, yield 174 mg (75%); hexane/EtOAc (65/35); mp: 77 - 81 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.03 (s, 1H), 6.62 (s, 1H), 5.91 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 153.6, 149.1, 141.4, 115.1, 111.6, 100.4, 100.0, 56.9, 56.9 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_9H_8NO_3S$ 210.0225; Found 201.0215.



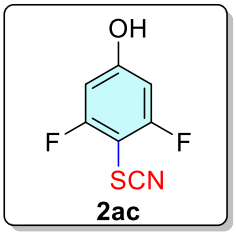

**2,5-difluoro-4-thiocyanatophenol (2aa):** Yellow solid, yield 144 mg (61%); hexane/EtOAc (75/25); mp: 92 - 96 °C; **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.37 (dd, $J$ = 9.0, 6.5 Hz, 1H), 6.89 (dd, $J$ = 9.0, 6.5 Hz, 1H), 6.26 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 158.3 (dd, $J$ = 246.6, 2.4 Hz), 147.9 (dd, $J$ = 16.0, 12.0 Hz), 147.7 (dd, $J$ = 238.6, 3.0 Hz), 120.3 (dd, $J$ = 22.2, 1.4 Hz), 109.7, 106.5 (dd, $J$ = 26.8, 2.1 Hz), 100.6 (dd, $J$ = 21.0, 7.2 Hz) ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -109.94 (ddd, $J$ = 13.5, 9.8, 6.8 Hz), -138.35 (ddd, $J$ = 13.5, 9.8, 7.1 Hz) ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_7H_2F_2NOS$ 185.9825; Found 185.9828.



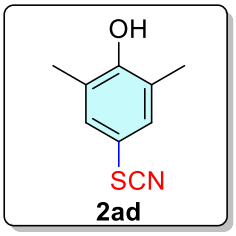

**3,5-dimethyl-4-thiocyanatophenol (2ab):**[4] White solid, yield 174 mg (73%); hexane/EtOAc (80/20); **$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 6.65 (s, 2H), 5.95 (brs, 1H), 2.52 (s, 6H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 158.3, 145.2, 116.4, 112.7, 111.8, 22.2 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_9H_8NOS$ 178.0327; Found 178.0320.



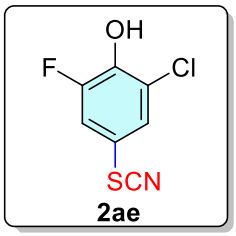
**3,5-difluoro-4-thiocyanatophenol (2ac):** Brown solid, yield 142 mg (60%); hexane/EtOAc (80/20); mp: 115 - 119 °C; **$^{1}$H NMR (500 MHz, $CDCl_3$)** $\delta$ 6.55 (d, $J$ = 8.5 Hz, 2H) ppm. **$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 163.3 (dd, $J$ = 250.8, 6.1 Hz), 162.1 (t, $J$ = 14.3 Hz), 110.6, 101.2 (dd, $J$ = 24.9, 3.0 Hz), 88.9 (t, $J$ = 22.5 Hz) ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -102.12 (d, $J$ = 8.3 Hz) ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7H_2F_2NOS$ 185.9825; Found 185.9828.



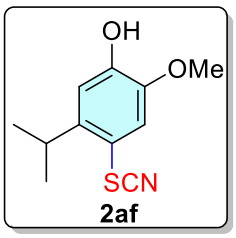

**2,6-dimethyl-4-thiocyanatophenol (2ad):**[2] Yellow solid, yield 176 mg (74%); hexane/EtOAc (80/20); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.20 (s, 2H), 5.04 (s, 1H), 2.25 (s, 6H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 154.4, 132.6, 125.7, 112.9, 112.2, 16.0 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_9H_8NOS$ 178.0327; Found 178.0319.



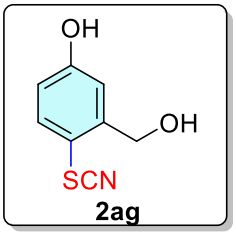

**2-chloro-6-fluoro-4-thiocyanatophenol (2ae):** Brown solid, yield 128 mg (55%); hexane/EtOAc (75/25); mp: 76 - 79 °C; **$^{1}$H NMR (500 MHz, DMSO-$d_6$)** $\delta$ 11.28 (s, 1H), 7.66 – 7.63 (m, 2H) ppm. **$^{13}$C{$^{1}$H} NMR (125 MHz, DMSO-$d_6$)** $\delta$ 152.2 (d, $J$ = 245 Hz), 144.3 (d, $J$ = 16.0 Hz), 129.5 (d, $J$ = 3.1 Hz), 123.6 (d, $J$ = 4.9 Hz), 119.4 (d, $J$ = 21.8 Hz), 113.7 (d, $J$ = 8.9 Hz), 112.3 ppm. **19F NMR (376 MHz, DMSO-$d_6$)** $\delta$ 129.79 (dd, $J$ = 9.4, 1.9 Hz))ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{15}H_{20}NOS$ 201.9530; Found 201.9522.



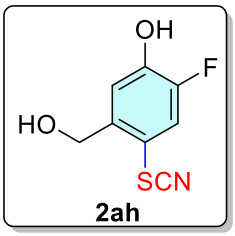

**5-isopropyl-2-methoxy-4-thiocyanatophenol (2af):** Light orange solid, yield 193 mg (84%); hexane/EtOAc (70/30); mp: 85 - 89 °C; **$^{1}$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.09 (s, 1H), 6.93 (s, 1H), 5.83 (s, 1H), 3.92 (s, 3H), 3.34 (sep, $J$ = 7.0 Hz, 1H), 1.24 (d, $J$ = 7.0 Hz, 6H). **$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$)** $\delta$ 148.6, 145.6, 145.4, 116.1, 113.3, 112.2, 110.9, 56.5, 31.4, 23.7 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{11}H_{12}NO_2S$ 222.0589; Found 222.0578.



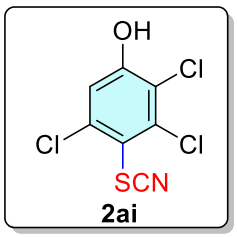
**3-(hydroxymethyl)-4-thiocyanatophenol (2ag):** Brown liquid, yield 190 mg (80%); hexane/EtOAc (75/25); **$^{1}$H NMR (400 MHz, DMSO-*d*$_6$)** $\delta$ 10.13 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.61 (s, 2H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-*d*$_6$)** $\delta$ 160.3, 146.5, 135.9, 116.1, 116.1, 112.8, 109.8, 61.6 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_8H_6NO_2S$ 180.0119; Found 180.0112.



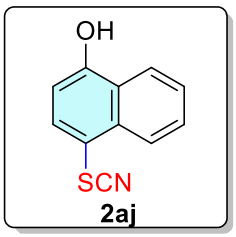

**5-fluoro-2-(hydroxymethyl)-4-thiocyanatophenol (2ah):** Brown liquid, yield 168 mg (72%); hexane/EtOAc (75/25); **$^{1}$H NMR (400 MHz, DMSO-*d*$_6$)** $\delta$ 10.67 (brs, 1H), 7.56 (d, *J* = 10.8 Hz, 1H), 7.20 (d, *J* = 9.2 Hz, 1H), 4.58 (s, 2H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-*d*$_6$)** $\delta$ 150.2 (d, *J* = 243.3 Hz), 147.8 (d, *J* = 11.5 Hz), 141.9 (d, *J* = 3.1 Hz), 121.8 (d, *J* = 20.5 Hz), 118.0 (d, *J* = 3.2 Hz), 112.6, 110.1 (d, *J* = 7.2 Hz), 61.2 ppm. **$^{19}$F NMR (376 MHz, DMSO-*d*$_6$)** $\delta$ -136.15 (dd, *J* = 10.2, 9.0 Hz) ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_8H_5FNO_2S$ 198.0025; Found 198.0016.



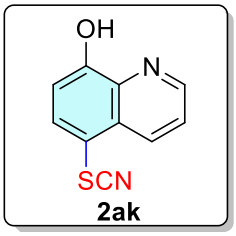

**2,3,5-trichloro-4-thiocyanatophenol (2ai):** Red solid, yield 113 mg (50%); hexane/EtOAc (70/30); mp: 201 - 205 °C; **$^{1}$H NMR (400 MHz, DMSO-*d*$_6$)** $\delta$ 12.09 (brs, 1H), 7.24 (s, 1H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-*d*$_6$)** $\delta$ 158.0, 139.3, 138.4, 120.7, 116.7, 113.6, 111.1 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_7HCl_3NOS$ 251.8845; Found 251.8843.



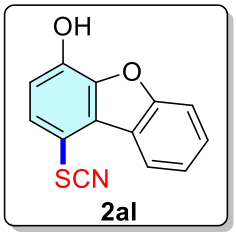

**4-thiocyanatonaphthalen-1-ol (2aj):**[2] Yellow solid, yield 177 mg (76%); hexane/EtOAc (80/20); **$^{1}$H NMR (500 MHz, DMSO-*d*$_6$)** $\delta$ 11.12 (s, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-*d*$_6$)** $\delta$ 158.3, 137.8, 135.0, 130.1, 127.4, 127.1, 125.6, 124.6, 114.1, 110.0, 108.9 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{11}H_6NOS$ 200.0170; Found 200.0170.



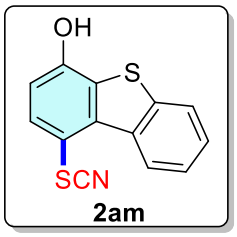
**5-thiocyanatoquinolin-8-ol (2ak):**[11] Light yellow solid, yield 159 mg (68%); hexane/EtOAc (80/20); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 8.90 (dd, $J$ = 4.0, 1.2 Hz, 1H), 8.67 (dd, $J$ = 8.4, 1.2 Hz, 1H), 7.93 (d, $J$ = 8.0 Hz, 1H), 7.69 (dd, $J$ = 8.4, 4.0 Hz, 1H), 7.20 (d, $J$ = 8.0 Hz, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 156.1, 148.9, 139.2, 137.5, 133.9, 129.3, 123.9, 111.1, 110.7, 108.1 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{10}H_5N_2OS$ 201.0123; Found 201.0130.



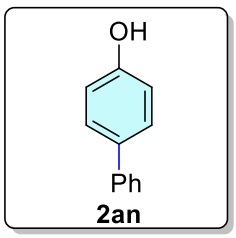

**1-thiocyanatodibenzo[b,d]furan-4-ol (2al):** White solid, yield 170 mg (75%); hexane/EtOAc (70/30); mp: 192 - 197 °C; **$^1$H NMR (400 MHz, DMSO-$d_6$)** $\delta$ 11.14 (s, 1H), 8.41 (d, $J$ = 7.6 Hz, 1H), 7.83 (d, $J$ = 8.0 Hz, 1H), 7.66 (dd, $J$ = 8.4, 7.6 Hz, 1H), 7.58 (dd, $J$ = 8.4, 0.4 Hz, 1H), 7.54 (t, $J$ = 7.6 Hz, 1H), 7.10 (d, $J$ = 8.4 Hz, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$)** $\delta$ 156.1, 146.6, 144.9, 132.3, 129.1, 127.1, 124.1, 123.1, 122.9, 115.3, 112.6, 112.3, 104.7 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_6NO_2S$ 240.0119; Found 240.0108.



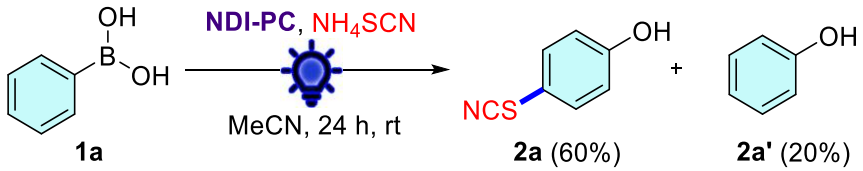

**1-thiocyanatodibenzo[b,d]thiophen-4-ol (2am):** Yellow solid, yield 138 mg (61%); hexane/EtOAc (70/30); mp: 228 - 232 °C; **$^1$H NMR (400 MHz, DMSO-$d_6$)** $\delta$ 11.44 (s, 1H), 9.03-9.0 (m, 1H), 8.17-8.15 (m, 1H), 7.77 (d, $J$ = 8.0 Hz, 1H), 7.65 (dd, $J$ = 6.4, 3.2 Hz, 2H), 7.05 (d, $J$ = 8.4 Hz, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, DMSO-$d_6$)** $\delta$ 155.7, 140.2, 136.7, 136.6, 134.8, 129.3, 128.1, 125.5, 125.4, 124.1, 112.8, 112.2, 107.2 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_6NOS_2$ 255.9891; Found 255.9895.




**[1,1'-biphenyl]-4-ol (2an):**[12] Light orange solid, yield 137 mg (80%); hexane/EtOAc (80/20); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.55 (dd, $J$ = 8.4, 1.2 Hz, 2H), 7.49 (d, $J$ = 8.8 Hz, 2H), 7.42 (t, $J$ = 7.6 Hz, 2H), 7.31 (tt, $J$ = 7.6, 1.2 Hz, 1H), 6.92 (d, $J$ = 8.4 Hz, 2H), 5.01 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 155.3, 140.9, 134.2, 128.9, 128.6, 126.9, 126.9, 115.8 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_{11}O$ 169.0654; Found 169.0650.



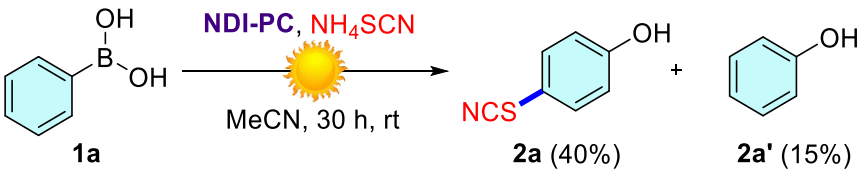
**6. Gram-scale synthesis and reaction in the sunlight of 2a:**




**Scheme S5.** Gram-scale synthesis of **2a.**

In a 100 mL round bottom flask, **1a** (1.0 g, 1.0 equiv., 8.2 mmol) was taken and dissolved in 200.0 ml of MeCN. Then, 1.3 g of $NH_4SCN$ (2.0 equiv., 16.4 mmol) was added to it, followed by the addition of 150.0 mg of photocatalyst NDI-PC (3.0 mol%, 0.246 mmol). After this, the reaction was irradiated in the blue LED light for 24 h at room temperature (reaction setup shown in Figure S1). After completion of the reaction, monitored by TLC, the reaction was diluted with ethyl acetate and washed with water. The combined organic phases were dried over $Na_2SO_4$, and the solvent was evaporated under reduced pressure to obtain the crude. The crude residue was purified by column chromatography using silica gel of mesh size 100-200 with hexane and ethyl acetate solvent mixtures (80/20) as the eluent and afforded **2a** in 60% yield (745.0 mg). **2a'** was also obtained as the minor product in 20% yield (153.0 mg).

**Figure S2.** Reaction setup for gram scale synthesis of **1a**.




**Scheme S6.** Synthesis of **2a** in sunlight.

To an oven-dried 100 ml conical flask, 250.0 mg of **1a** (1.0 equiv., 2.1 mmol) was taken and dissolved in 60.0 ml of MeCN. Then, 320.0 mg of $NH_4SCN$ (2.0 equiv., 4.2 mmol) was added to it, followed by the addition of 38.5 mg of photocatalyst **NDI-PC** (3.0 mol%, 0.06 mmol). After this, the reaction setup was kept in an open atmosphere and placed in sunlight ($28^{th}$, $29^{th}$, and $30^{th}$ November, at IIT Delhi, $8^{th}$-floor rooftop, clear sky with maximum temperature of 26 °C), without magnetic stirring from 8 a.m. to 6 p.m. (total 30 h) (reaction setup shown in Figure S3). The contents were concentrated under reduced pressure and subjected to column chromatography using silica gel of mesh size 100-200 with hexane/ethyl acetate (80/20) as the eluent to obtain the pure product **2a** in 40% yield (126.0 mg) and the minor product **2a'** in 15% (28.0 mg) yield.

(a) (b)

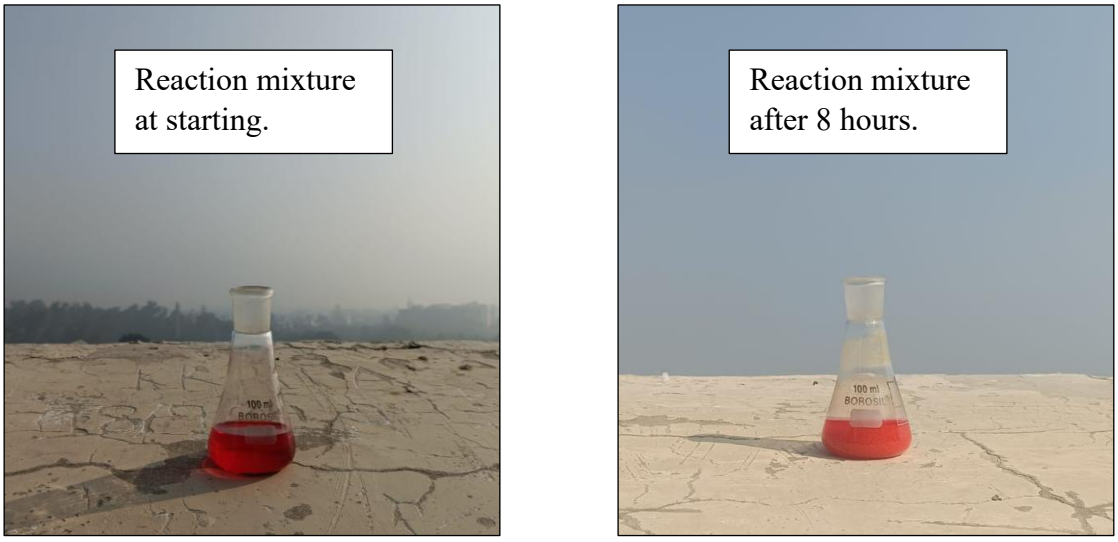



**Figure S3.** Reaction setup in sunlight on the rooftop without any magnetic stirring – (a) reaction mixture at the start of the reaction; (b) reaction mixture after 8 h.

## 7. Mechanistic studies:

### 7a) Quantum yield calculation:

Quantum yield was calculated by Yoon's Method[13] and modified appropriately.

**Step 1: Preparation of 0.15 M Ferrioxalate solution:**

2.21 g of potassium ferrioxalate hexahydrate was dissolved in 30.0 mL of 0.05 M sulphuric acid solution, and stored in dark.

**Step 2: Preparation of buffer solution of phenanthroline:**

50.0 mg of phenanthroline and 11.25 g of sodium acetate were dissolved in 50.0 mL of 0.5 M sulphuric acid solution, and stored in dark.

**Step 3: Determination of molar absorptivity of ferrioxalate solution at 270 nm:**

$7.5 \times 10^{-5}$ M solution of ferrioxalate in 0.5 M sulphuric acid was added to a quartz cuvette and its absorbance was observed at 270 nm. According to Beer's Lambert law,

$$\text{Absorbance} = \varepsilon \times c \times l \quad \text{.....(S1)}$$

where ε is molar absorptivity of ferrioxalate solution at 270 nm, $l$ is path length (1.0 cm), c is the concentration of solution ($7.5 \times 10^{-5}$ M).

From equation S1,
$$\varepsilon = \frac{\text{Absorbance}}{c \times l} \quad \text{.....(S2)}$$

$$\varepsilon = \frac{0.258}{7.5\times10^{-5}\ \text{M} \times 1.0\ \text{cm}} = 3440\ \text{L mol}^{-1}\ \text{cm}^{-1}$$

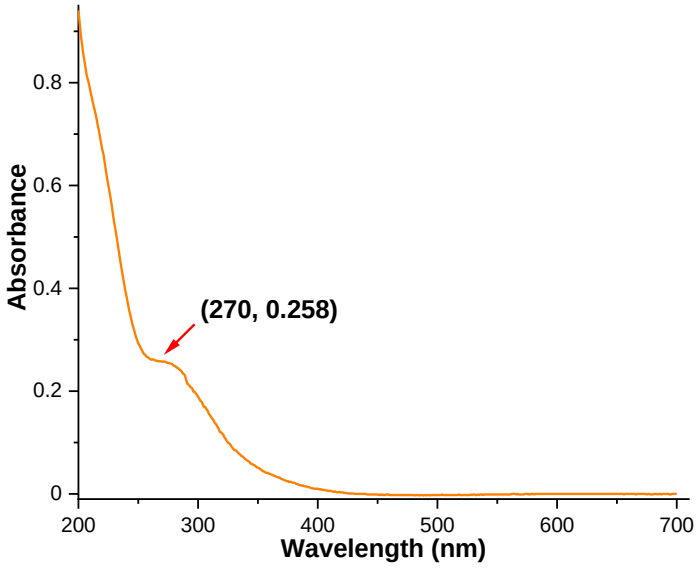



**Figure S4.** UV-Visible spectrum of ferrioxalate solution.

**Step 4: Determination of mol $Fe^{2+}$:**

1.0 mL of ferrioxalate solution (0.15 M) was placed into a reaction tube and irradiated under 10 W Blue LED ($\lambda_{max}$ = 440 nm) for 70 sec. After irradiation, 0.175 mL of phenanthroline solution was added immediately, and the mixture was stirred for 1 h in the dark to allow the complete coordination of $Fe^{2+}$ ions with phenanthroline. A non-irradiated sample solution of 1.0 mL of ferrioxalate and 0.175 mL phenanthroline was also prepared and stirred in the dark for 1 h.

The absorbance of both the solution was measured at 270 nm. The absorbance values were used in the following equation to get the mol $Fe^{2+}$ ion.

$$\text{mol } Fe^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} \quad \text{.....(S3)}$$

where V (0.001175 L) is the total volume of the solution. ε is the molar absorptivity of ferrioxalate solution at 270 nm (3440 L $mol^{-1}$ $cm^{-1}$ ), *l* is path length (1.0 cm), ΔA (0.033) is the difference of absorbance between irradiated and non-irradiated solution at 270 nm.

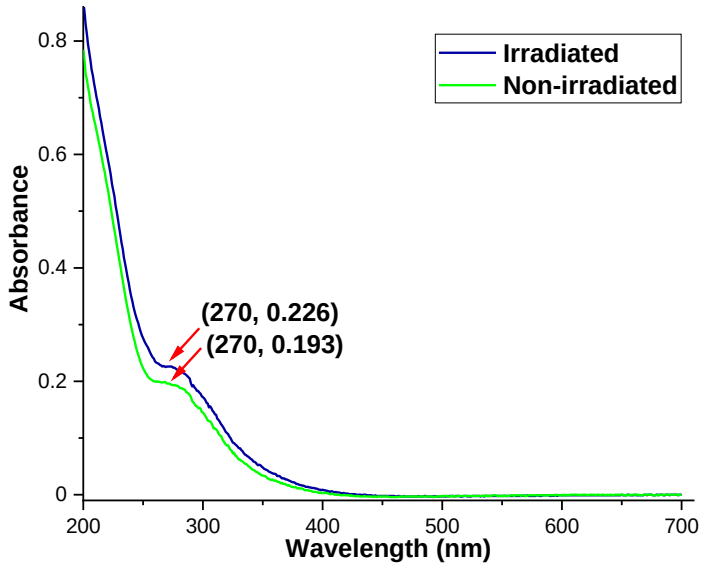



**Figure S5.** UV-visible spectra of the irradiated and non-irradiated ferrioxalate solution after interacting with the buffered phenanthroline solution.

$$\text{mol } Fe^{2+} = \frac{0.001175 \text{ L} \times 0.033}{1.0 \text{ cm} \times 3440 \text{ L mol}^{-1}\text{cm}^{-1}}$$

$$= 1.1272 \times 10^{-8} \text{ mol}$$

**Step 5: Determination of photon flux:**

The photon flux can be calculated using the following equation:

$$\text{Photon flux} = \frac{\text{mol } Fe^{2+}}{\phi \times t \times f} \quad \text{.....(S4)}$$

Where ϕ is the quantum yield for 0.15 M solution of ferrioxalate actinometer (0.92 at $\lambda_{max}$ = 468 nm)[14], t is the irradiation time (70 s), and f is the fraction of light absorbed by 0.15 M ferrioxalate actinometer at λ = 468 nm (0.850)[3].

Photon flux = $\frac{1.1272 \times 10^{-8}\ \text{mol}}{0.92 \times 70\ \text{s} \times 0.850}$ $1.1272 \times 10^{-8}$ mol / 0.92 × 70 s × 0.850 = $2.059 \times 10^{-10}$ einstein $s^{-1}$

**Step 6: Calculation of f:**

The fraction of incident light absorbed by the photocatalyst was calculated using the following equation

$f = 1 - 10^{-A}$ ……..(S5)

where A is the absorbance of $1.9 \times 10^{-3}$ M NDI-PC in MeCN.

$f = 1 - 10^{-0.910}$

f = 0.8770

**Determination of quantum yield of reaction:**

In an oven-dried reaction tube, **1a** (12.0 mg, 1.0 equiv., 0.1 mmol), NH4SCN (0.2 mmol), and NDI-PC (1.8 mg, 3.0 mol%, 0.003 mmol) were mixed in MeCN (3.0 mL) and irradiated under 10 W Blue LED at room temperature for 4 h. After irradiation, the reaction mixture was quenched with water (20.0 mL) and extracted with ethyl acetate (2 × 30.0 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, concentrated, and purified through column chromatography to afford the desired product. To obtain the quantum yield, the reaction proceeded in three different sets, and the yields obtained were 25%, 24%, and 20%. The average value of all three yields (23.33%, 3.5 mg, $2.3 \times 10^{-5}$ mol) was used to calculate the quantum yield as below.

$$\phi = \frac{\text{Moles of product formed}}{\text{Photon Flux} \times t \times f} \quad \text{……(S6)}$$

where the mol product of the reaction is $2.3 \times 10^{-5}$ mol, Photon flux is $2.059 \times 10^{-10}$ einstein $s^{-1}$, t is the time (14400 sec), and f is the fraction of incident light absorbed by photocatalyst (0.8770).

$$\phi = \frac{2.3 \times 10^{-5}\ \text{mol}}{2.059 \times 10^{-10}\ \text{s}^{-1} \times 14400\ \text{s} \times 0.8770}$$

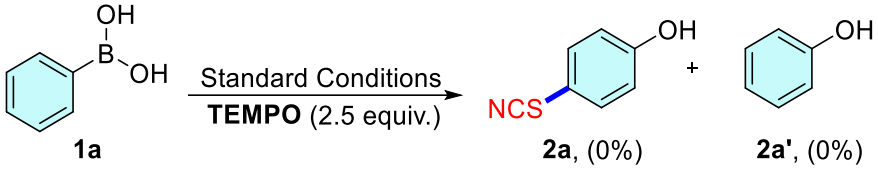
= **8.84**

The quantum yield of the photoredox reaction was found to be greater than 1.0, showing that the reaction involved radical chain processes.

**7b) Control experiments:**

**A. (i) Radical trapping with TEMPO:**

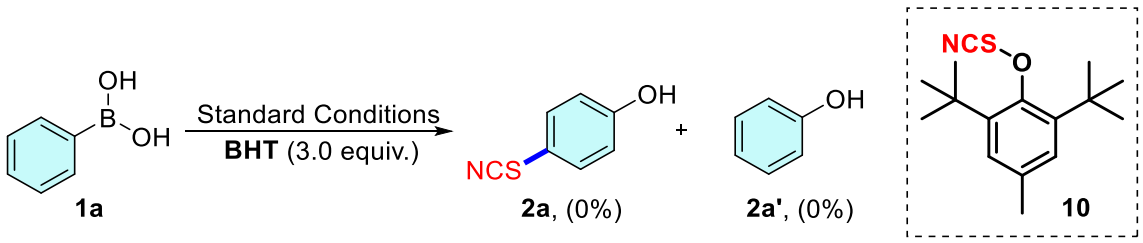
To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), 1.8 mg (3.0 mol%, 0.003 mmol) of **NDI-PC** and 39.0 mg (2.5 equiv., 0.25 mmol) of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) were added, the reaction mixture was irradiated by blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 12 h. After the completion of the reaction, no formation of either the minor product **2a'** or the major product **2a** was seen. This proves the radical pathway mechanism of the reaction.




**Scheme S7.** Reaction in presence of TEMPO.

**A. (ii) Radical trapping with BHT:**

To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), 1.8 mg (3.0 mol%, 0.003 mmol) of **NDI-PC**, and 66.0 mg (3.0 equiv., 0.3 mmol) of butylated hydroxytoluene (BHT) were added, the reaction mixture was irradiated by blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 12 h. After the completion of the reaction, no formation of either the minor product **2a'** or the major product **2a** was seen. This proves the radical pathway mechanism of the reaction. The BHT-SCN adduct **10** was identified by HRMS of the reaction mixture (Figure S6).

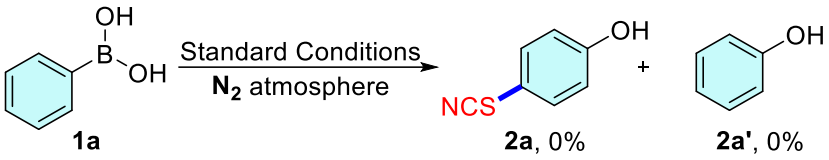



**Calcd. $[M+H]^+$ = 278.1573**
**Found $[M+H]^+$ = 278.1573**

**Scheme S8.** Reaction in presence of BHT.

**B. Reaction under $N_2$ atmosphere:**

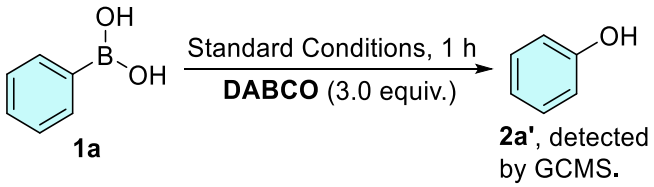
To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), and 1.8 mg (3.0 mol%, 0.003 mmol) of **NDI-PC** were added, and the reaction mixture was irradiated by a blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature, sealed with a teflon cap and purged with $N_2$, with constant stirring for 12 h. After the completion of the reaction, no formation of either the minor product **2a'** or the major product **2a** was seen. This clearly proves the presence of oxygen is essential for the reaction to proceed.




**Scheme S9.** Controlled experiment under $N_2$ atmosphere.

**C. (i) Singlet oxygen ($^1O_2$) quenching experiment:**

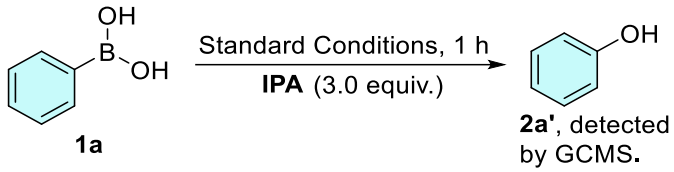
To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), 1.8 mg (3.0 mol%, 0.003 mmol) of **NDI-PC** and 34.0 mg (3.0 equiv., 0.3 mmol) of 1,4-diazabicyclo[2.2.2]octane (DABCO) were added, the reaction mixture was irradiated by blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 1 h. After 1 h, the reaction mixture was monitored by TLC, which showed the formation of phenol (**2a'**). Then, the reaction mixture was filtered through a short silica column, followed by washing with 1 ml of ethyl acetate 3 times. After that, the reaction mixture was injected for a GC-MS analysis, which confirmed the formation of **2a'** with a mass of 94.0 (Figure S7). The conversion of **1a** to **2a'** in the presence of DABCO proves that the reaction is not going via singlet oxygen ($^1O_2$).




**Scheme S10.** Controlled experiment with 1,4-diazabicyclo[2.2.2]octane (DABCO).

**C. (ii) Hydroxyl radical ($HO^{\bullet}$) quenching experiment:**

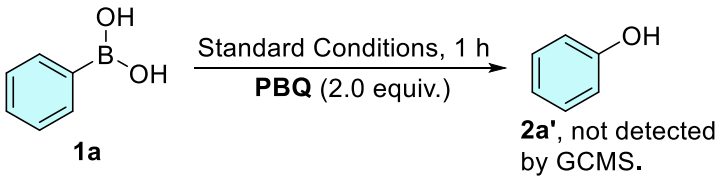
To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 24.0 mg (1.0 equiv., 0.2 mmol) of **1a** and 3.0 ml of MeCN were added. After that, 30 mg of $NH_4SCN$ (2.0 equiv., 0.4 mmol), 3.6 mg (3.0 mol%, 0.003 mmol) of **NDI-PC** and ~50.0 µL (3.0 equiv., 0.6 mmol) of *iso*-propyl alcohol (IPA) were added, the reaction mixture was irradiated by a blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 1 h. After 1 h, the reaction mixture was monitored by TLC, which showed the formation of phenol (**2a'**). Then, the reaction mixture was filtered through a short silica column, followed by washing with 1 ml of ethyl acetate 3 times. After that, the reaction mixture was injected for a GC-MS analysis, which confirmed the formation of **2a'** with a mass of 94.0 (Figure S8). The conversion of **1a** to **2a'** in the presence of IPA proves that the reaction is not going via hydroxyl radical ($HO^{\bullet}$).




**Scheme S11.** Controlled experiment with *iso*-propyl alcohol (IPA).

**D. Superoxide anion radical ($O_2^{\bullet-}$) quenching experiment:**

To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), 1.8 mg (3.0 mol%, 0.003 mmol) of **NDI-PC**, and 32.0 mg (3.0 equiv., 0.3 mmol) *para*-benzoquinone (PBQ) were added. The reaction mixture was irradiated by a blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 2 h. After 2 h, the reaction mixture was monitored by TLC, which showed no formation of phenol (**2a'**). Then, the reaction mixture was filtered through a short silica column, followed by washing with 1 ml of ethyl acetate 3 times. After that, the reaction mixture was injected for a GC-MS analysis, where no formation of **2a'** was seen. No formation of **2a'** in the presence of PBQ proves that the reaction is going via superoxide anion radical ($O_2^{\bullet-}$).




**Scheme S12.** Controlled experiment with *para*-benzoquinone (PBQ).

**7c) HRMS and GCMS data:**

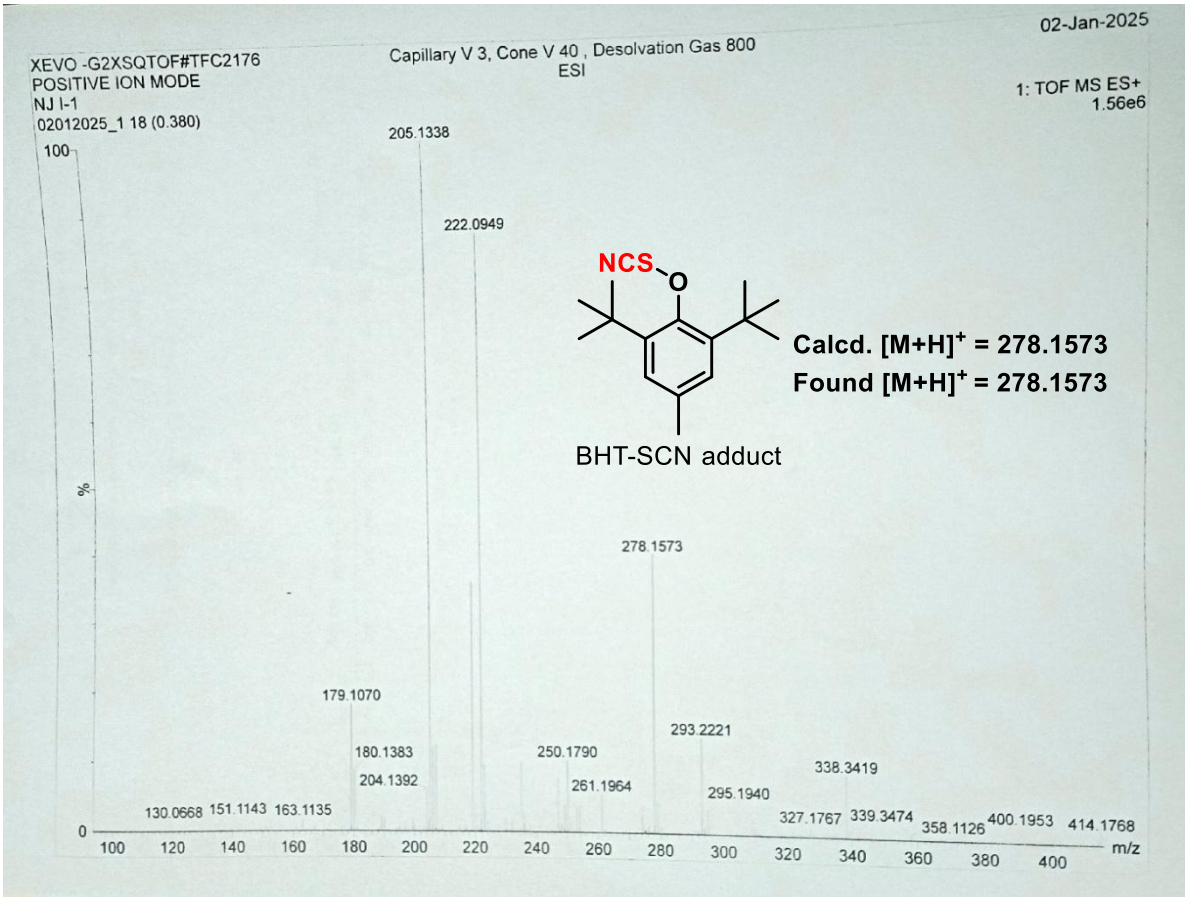



**Figure S6.** HRMS of the reaction mixture of the control experiment with BHT taken after 2 hours.

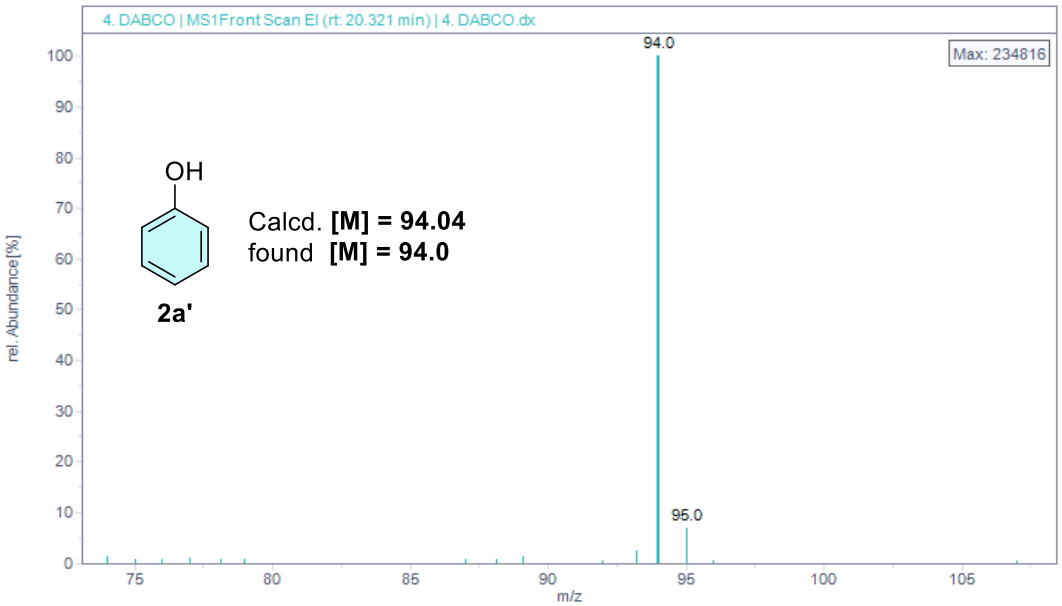



**Figure S7.** GCMS of the reaction mixture of the control experiment with DABCO taken after 1 hour.

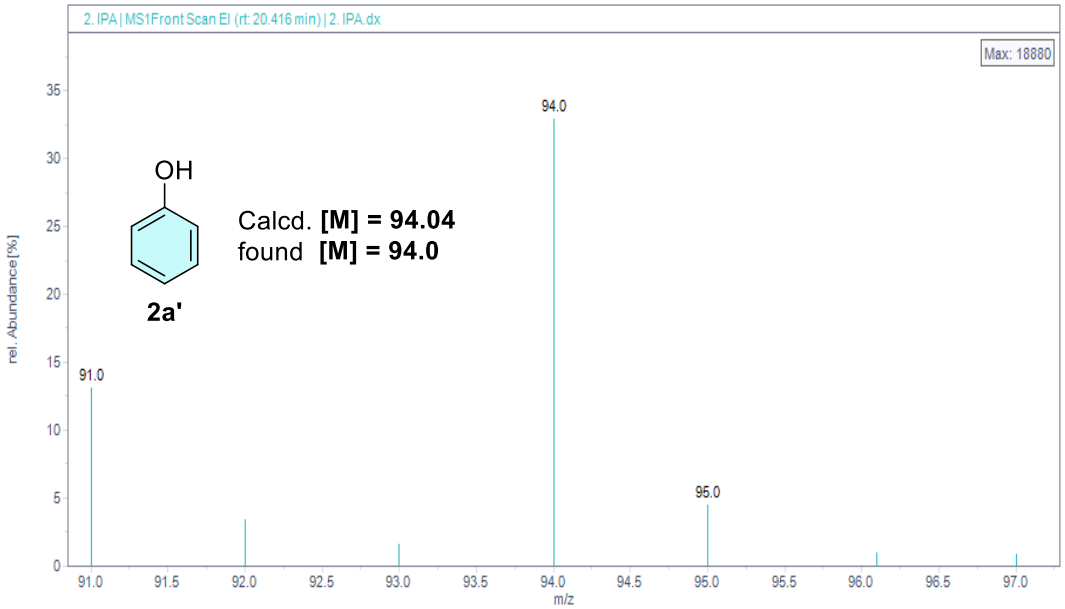



**Figure S8.** GCMS of the reaction mixture of the control experiment with IPA taken after 1 hour.

### 7d) ESR studies:

Reaction Conditions: **1a** (12.0 mg, 1.0 equiv., 0.1 mmol), $NH_4SCN$ (15.0 mg, 2.0 equiv., 0.2 mmol, ), NDI-PC (1.8 mg, 3 mol%, 0.003 mmol), MeCN (2.0 mL), rt. After 10 min of stirring under 50 W blue LED, DMPO (2.0 equiv.) was added, and the ESR spectrum was recorded.

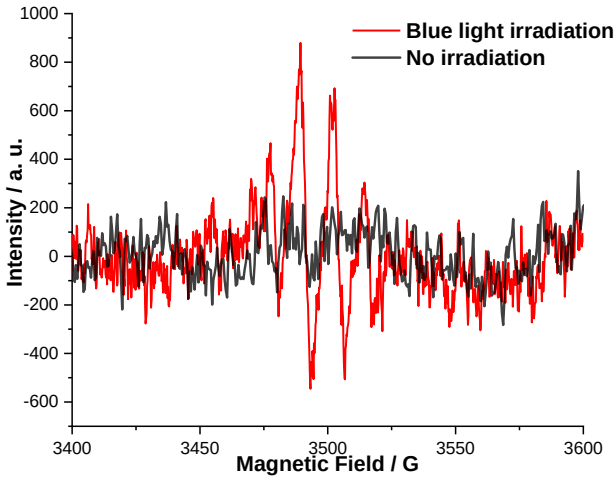



**Figure S9.** ESR experiment of the reaction mixture **1a** (0.1 mmol), $NH_4SCN$ (0.2 mmol), NDI-PC (3.0 mol%), and DMPO (2.0 equiv.) in 2.0 mL MeCN solvent without any visible light irradiation (black line) and with blue light irradiation (red line).

**7e) Stern-Volmer Study: Fluorescence Quenching Experiments:**

Fluorescence quenching studies were performed using Horiba-Jobin-Yvon Fluorescence Spectrophotometer. A ($0.5 \times 10^{-5}$) M solution of NDI-PC in MeCN was prepared, and $10^{-3}$ M of quencher **1a**, $NH_4SCN$, and $O_2$ were added successively to the measured solution in quartz cuvette and emission spectrum was observed. All the solutions were excited at 500 nm and emission intensity was collected at 573 nm. Plots were derived in between quencher concentration and $I_0/I$ (intensities of the emission in the absence and presence of the quencher at 573 nm) to calculate Ksv.

From Stern-Volmer Equation,

$$I_0/I = 1 + Ksv\,[Q]$$

Q = concentration of added quencher

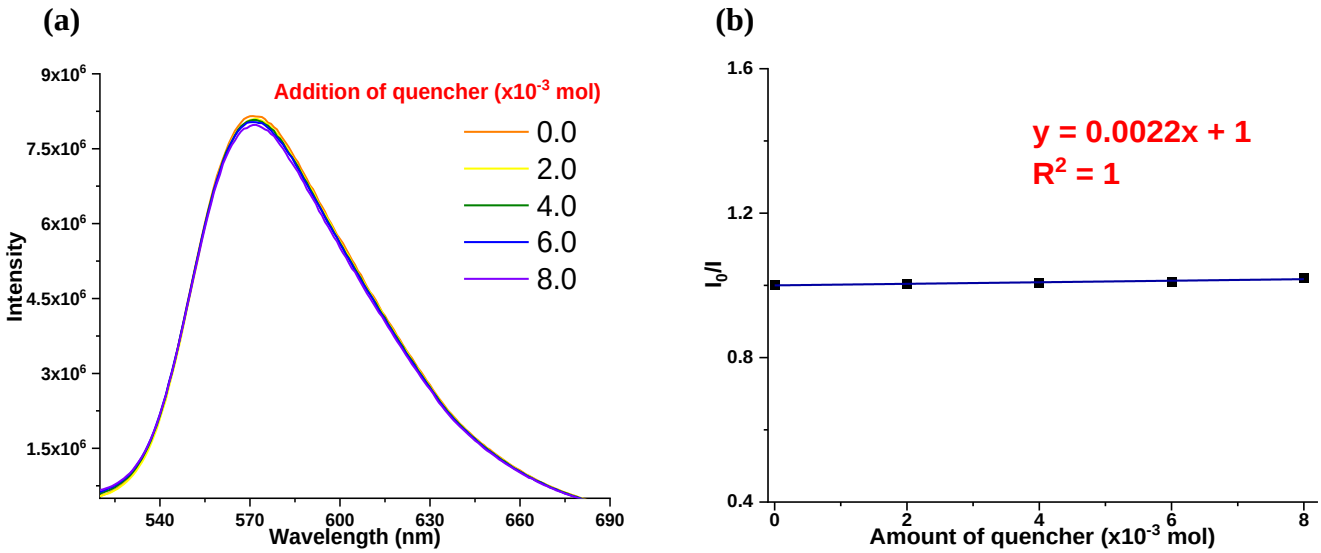



**Figure S10.** Fluorescence quenching of NDI-PC with **1a: (a)** Emission spectrum of NDI-PC with varying concentrations of **1a**; **(b)** Stern-Volmer plot.

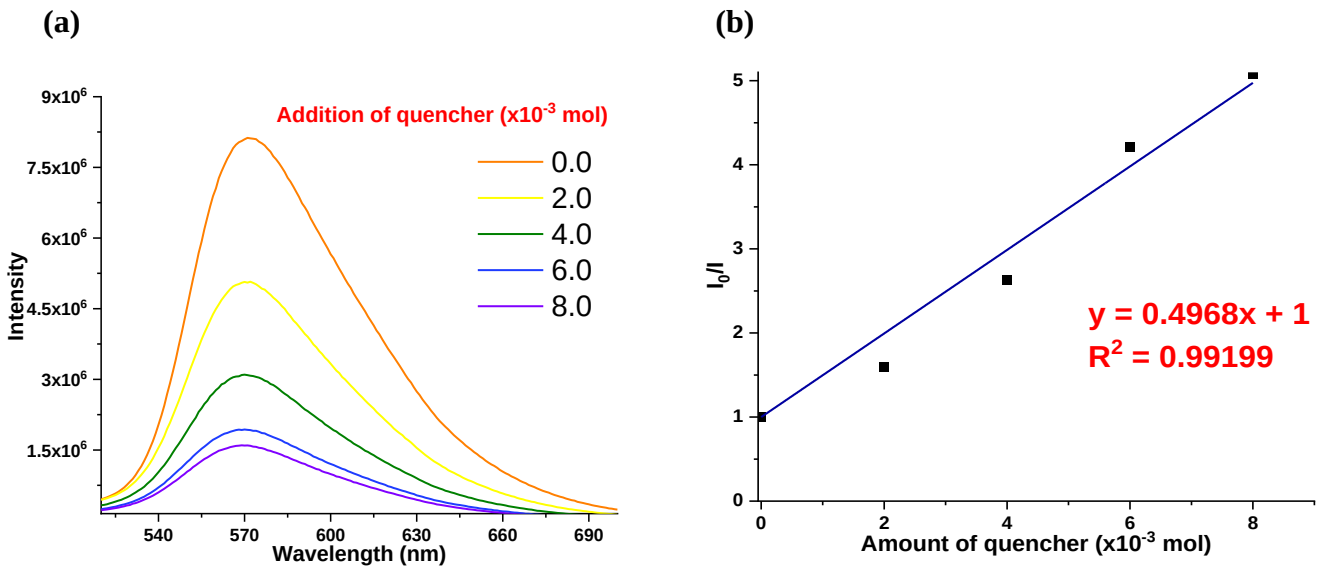



**Figure S11.** Fluorescence quenching of NDI-PC with $NH_4SCN$**: (a)** Emission spectrum of NDI-PC with varying concentrations of $NH_4SCN$; **(b)** Stern-Volmer plot.

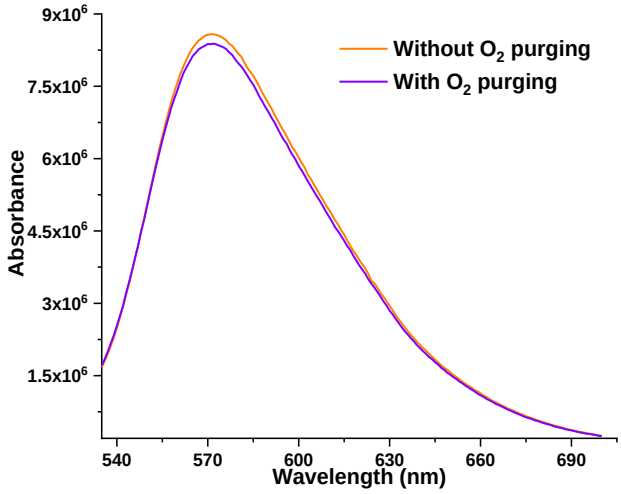



**Figure S12.** Fluorescence quenching of NDI-PC with $O_2$: Emission spectrum of NDI-PC without and with purging of $O_2$.

**7f) FT-IR and *In-situ* FT-IR studies:**

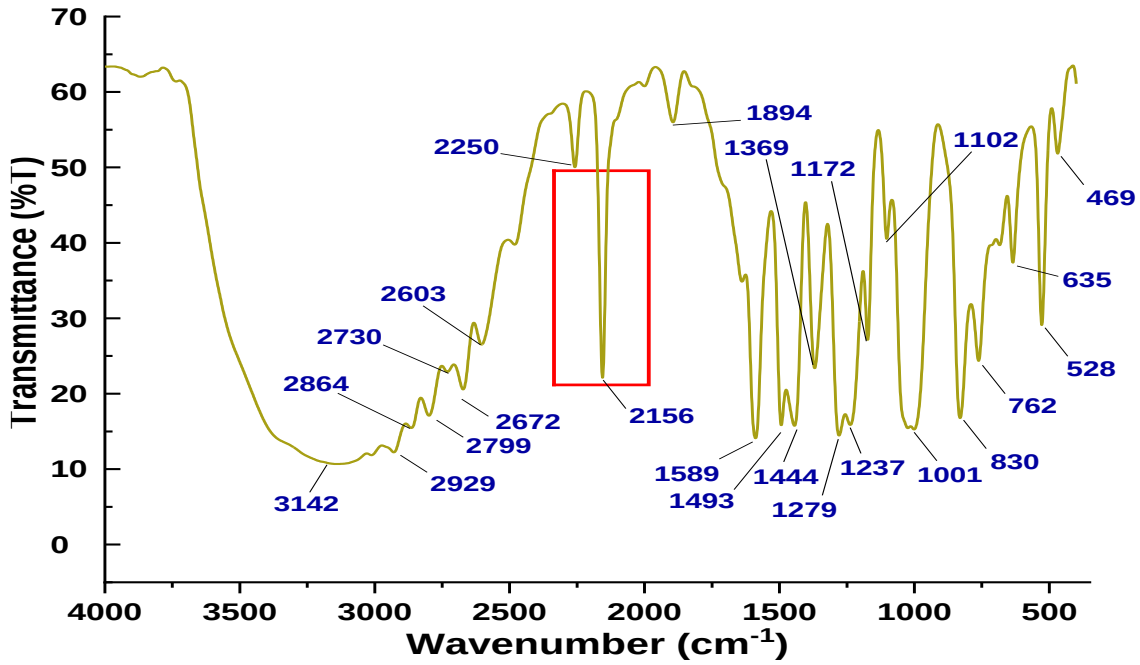



**Figure S13.** FT-IR spectrum of 4-thiocyanatophenol (**2a**).

The FT-IR data shows a sharp peak at 2156 $cm^{-1}$, which corresponds to the thiocyanate IR stretching frequency, and no formation of isothiocyanate was observed. Also, the broad peak at 3142 $cm^{-1}$ corresponds to phenolic OH stretching frequency.

For detecting the formation of intermediates or the starting of product formation in the reaction, an *in-situ* FT-IR experiment was conducted. To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), and 1.8 mg (3 mol%, 0.003 mmol) of NDI-PC were added, and the reaction mixture was irradiated by a blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature. Then, the diamond probe of the instrument was inserted into the solution contained in the reaction tube, and *in-situ* FT-IR spectra were recorded for 24 h at intervals of 60 seconds. As shown in Figure S14, the intensity of the band at 1104 $cm^{-1}$ (corresponding to C-O stretching of **2a**) increased steadily as the reaction progressed and became constant after around 12h, which justified the reaction time. Also, as this peak increased steadily and never decreased, so this peak must correspond to product **2a,** and not the intermediate or minor product **2a'**.

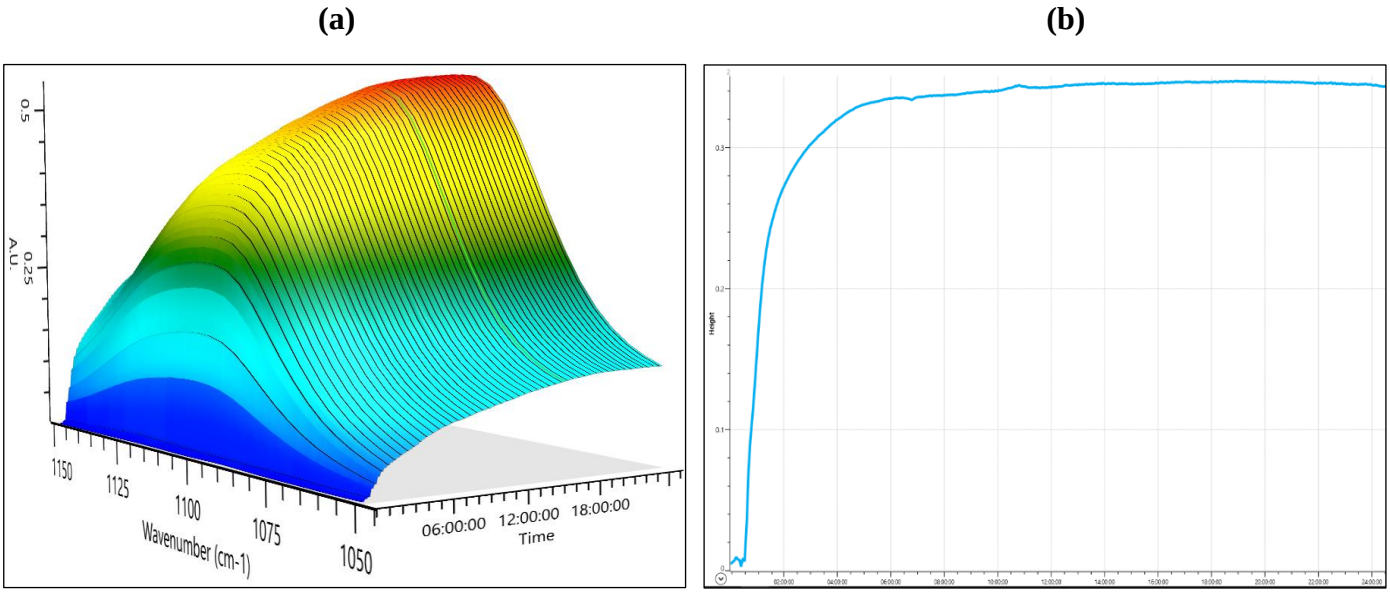
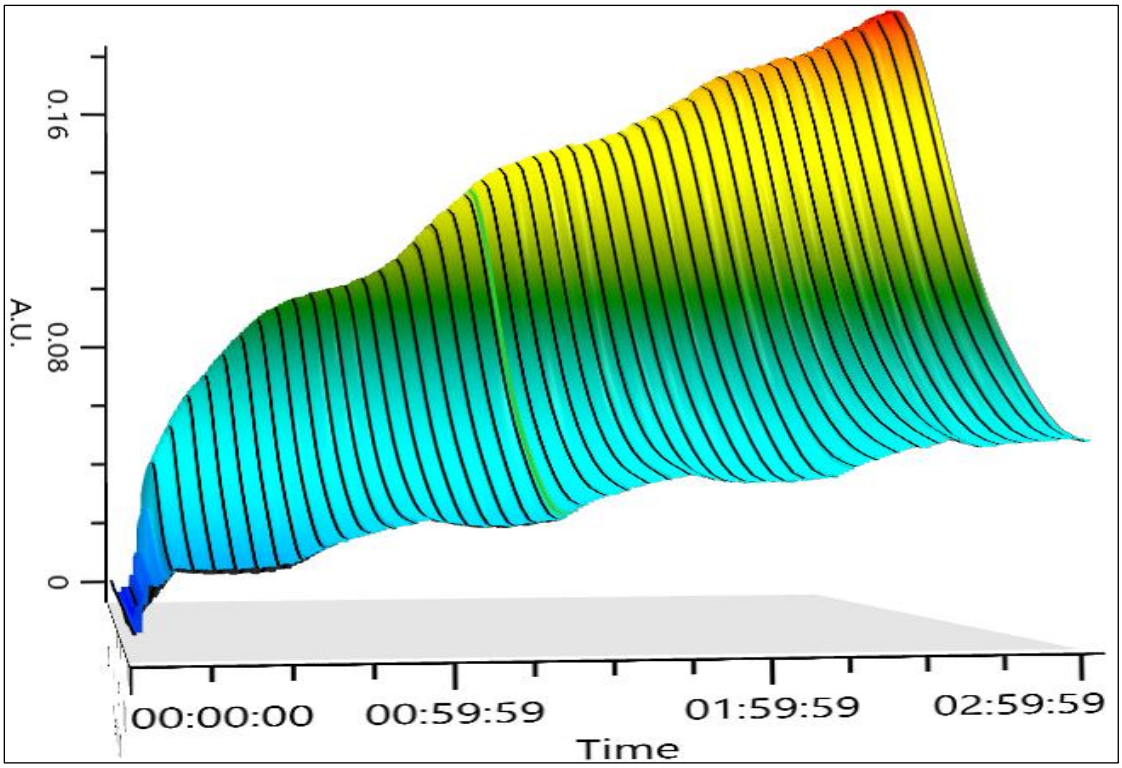



**Figure S14.** *in-situ* FT-IR spectrum of thiocyanation reaction of **2a** - **(a)** 3D representation and **(b)** 2D representation of reaction progress with increasing intensity of 1104 $cm^{-1}$ of C-O stretching frequency of **2a**.

**7g) Light-On-Off Experiment:**

The C-O stretching band of **2a** at 1104 $cm^{-1}$, which was found in the *in-situ* FT-IR experiment, can be utilized to conduct a light-on-off experiment. To perform this experiment, a 15 ml high borosilicate glass reaction tube was taken and then equipped with a magnetic stirring bar. To it, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), and 1.8 mg (3 mol%, 0.003 mmol) of NDI-PC were added, and the reaction mixture was kept in front of a blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature. Then, the diamond probe of the instrument was inserted into the solution contained in the reaction tube, and *in-situ* FT-IR spectra were recorded for 3 h at intervals of 30 seconds. After irradiating for 25 minutes, the reaction mixture was stirred for 25 minutes without any light. Similarly, these processes were repeated several times. During all these processes, the FT-IR value was recorded, which showed the peak intensity at 1104 $cm^{-1}$ only increased when the light was kept on, and it remained constant when the light was kept off (Figure S15).

**(a)**




**(b)**

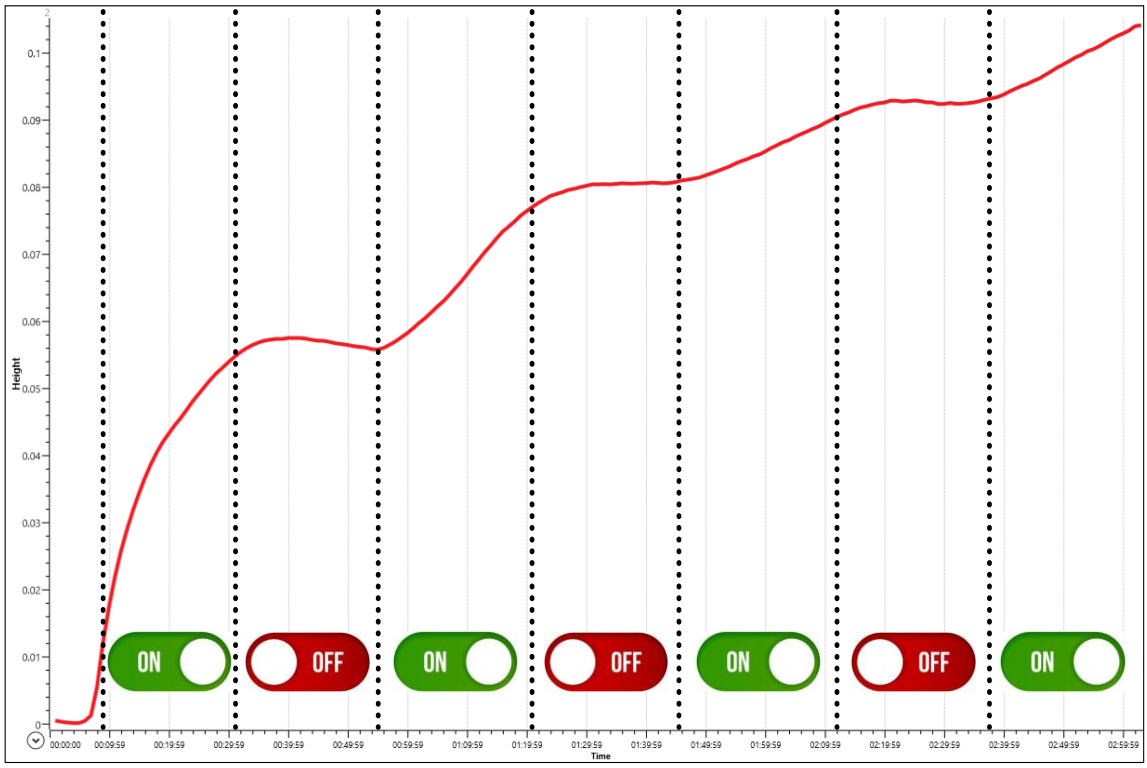



**Figure S15.** Light-on-off experiment via *in-situ* FT-IR experiment - **(a)** 3D representation and **(b)** 2D representation of light-on-off experiment.

### 7h) Real-time Reaction Monitoring via $^{11}B$ {$^{1}H$} NMR:

To verify the reaction mechanism, we explored further by $^{11}B$ {$^{1}H$} NMR spectroscopy in real-time, monitoring the reaction progress in standard conditions. After 30 minutes, it showed that the peak of **1a** at $\delta$ 28.45 was decreased than that of starting (at t = 0 minutes), which means that **1a** started consuming, and a new signal peak at $\delta$ −7.32 ppm appeared. After 1 h, **1a** was consumed significantly, and the new peak intensity increased further. This new signal may correspond to intermediate I or II or III (MS, Scheme 4).

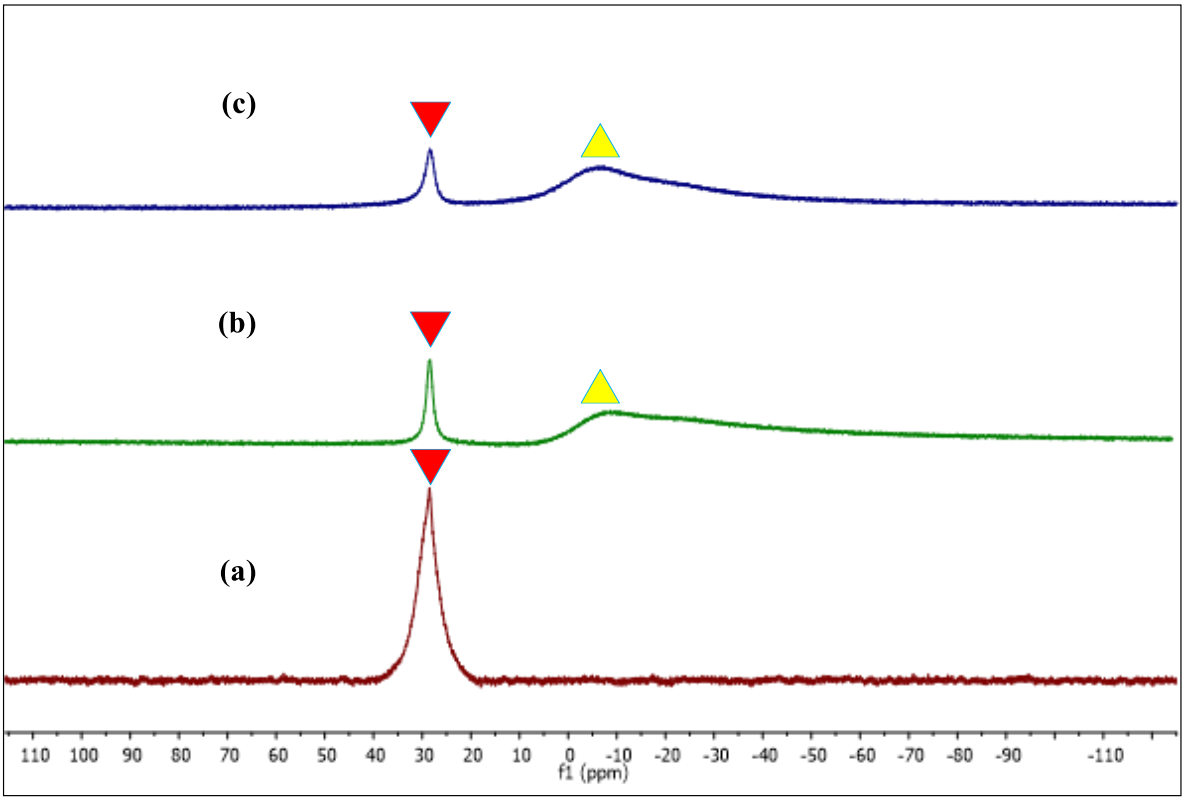



**Figure S16.** Intermediate trapping experiment via $^{11}B$ {$^{1}H$} NMR spectroscopy (128 MHz, CDCl3) spectra - (a) reaction under standard conditions after t = 0 min; (b) after 30 min; (c) after 1 h.▼1a;△ I or II or III.

### 7i) $H_2O_2$ detection test:

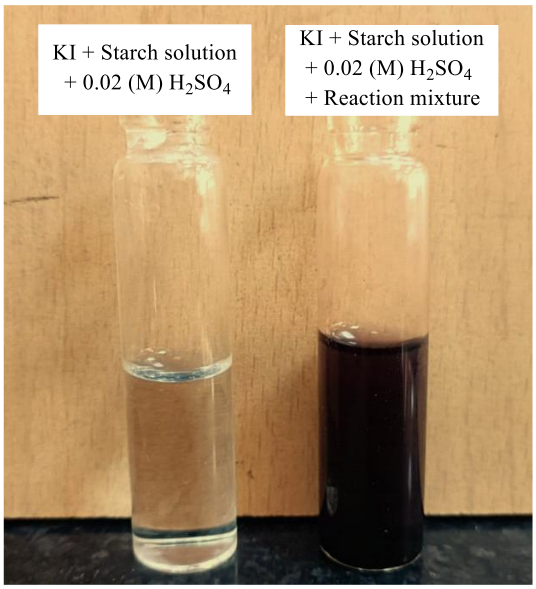
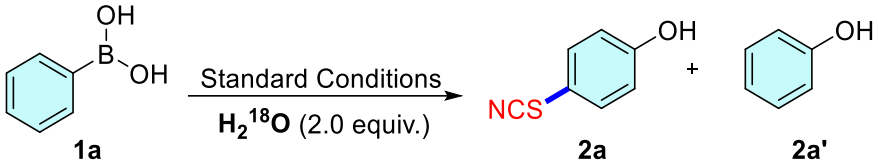



**Figure S17.** Detection of $H_2O_2$ by KI and starch solution.

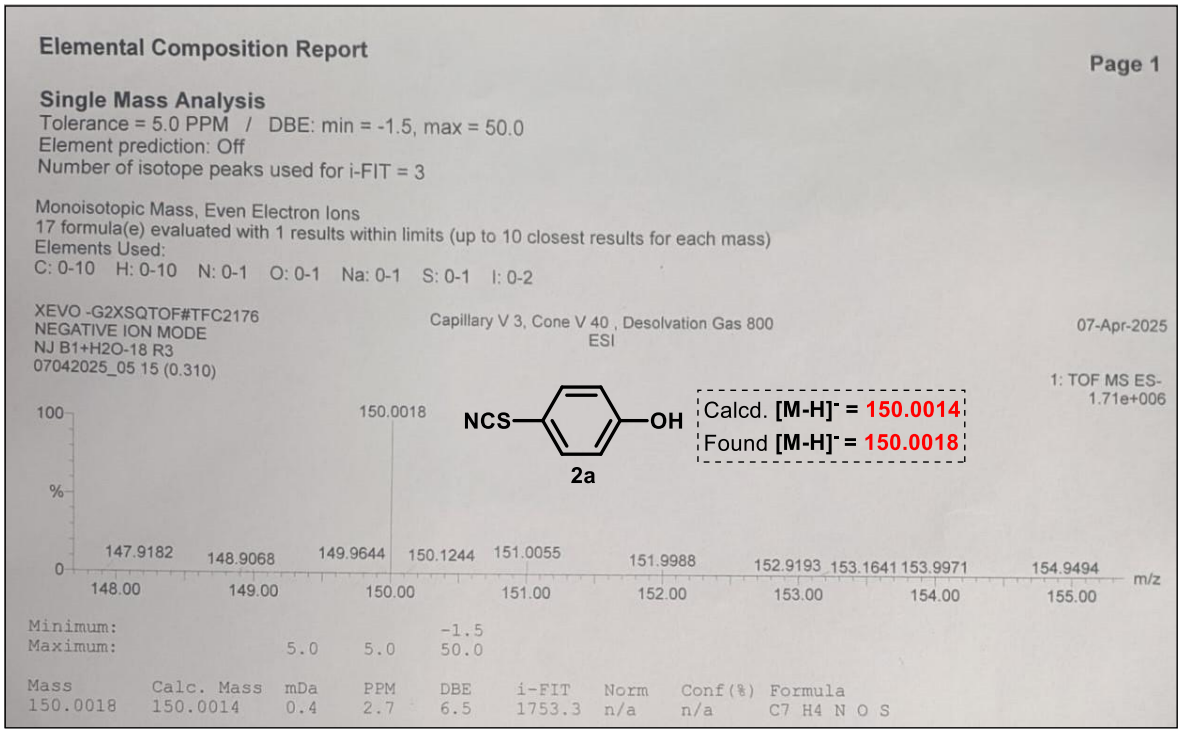
### 7j) $^{18}O$ Labelling Experiments:




**Scheme S13.** $^{18}O$ labelling experiments using $H_2{}^{18}O$.

To a 15 ml high borosilicate glass tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 15.0 mg of $NH_4SCN$ (2.0 equiv., 0.2 mmol), 1.8 mg (3.0 mol%, 0.003 mmol) of **NDI-PC**, and 4.0 µL (2.0 equiv., 0.2 mmol) of $H_2{}^{18}O$ were added, the reaction mixture was irradiated by a blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 12 h. After the completion of the reaction, monitored by TLC, the reaction mixture was filtered and subjected to HRMS and GCMS analysis. The HRMS and GCMS of the reaction mixture showed no incorporation of labeled oxygen in **2a** and **2a'**. This confirmed that the source of oxygen atom in **2a** and **2a'** is oxygen (air) and not water (moisture).

(a)




(b)

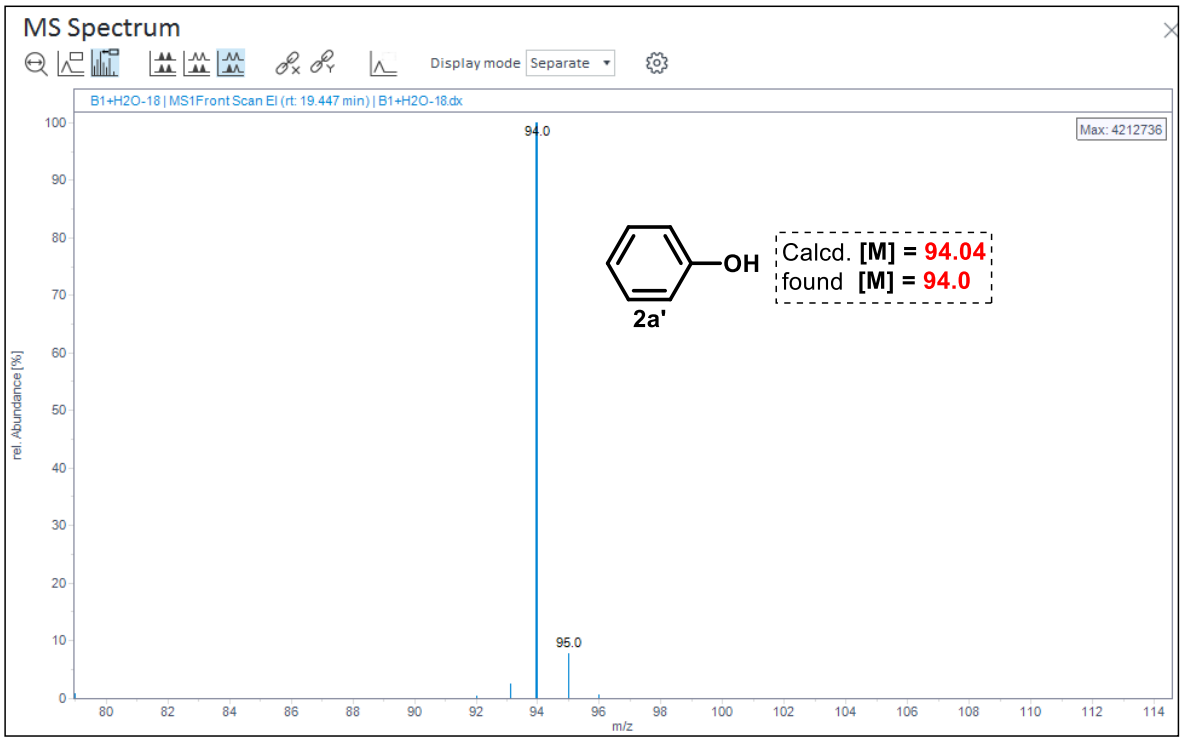
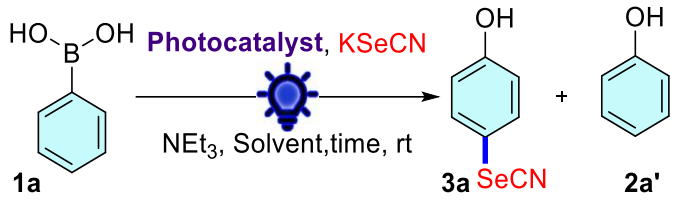



**Figure S18. (a)** HRMS and **(b)** GCMS data of the reaction mixture in presence of $H_2{}^{18}O$.

## 8. Optimization of reaction conditions for the synthesis of 3a:




| S. No. | Photocatalyst | Solvent | Yield (%)[b] | |
|---|---|---|---|---|
| | | | 3a | 2a' |
| **1[a]** | **NDI-PC** | **MeCN** | **60** | **25** |
| 2 | Mes-Acr-$ClO_4$ | MeCN | 40 | 33 |
| 3 | Ir[dF($CF_3$)ppy]$_2$(dtbpy))$PF_6$ | MeCN | Trace | 39 |
| 4 | Ru(bpy)3Cl2 | MeCN | Trace | 33 |
| 5 | Eosin Y | MeCN | Trace | 44 |
| 6 | Rose Bengal | MeCN | 20 | 41 |
| 7 | NDI-PC | DCM | 0 | 22 |
| 8 | NDI-PC | THF | 29 | 18 |
| 9 | NDI-PC | DMF | 0 | Trace |
| 10 | NDI-PC | MeCN | 35[c]/42[d]/56[e] | 37[c]/31[d]/15[e] |
| 11 | - | MeCN | 0 | 0 |
| 12[f] | NDI-PC | MeCN | 0 | 0 |
| 13[g] | NDI-PC | MeCN | 0 | 0 |
| 14 | NDI-PC | MeCN | 19[h]/36[i]/60[j] | 38[h]/29[i]/Trace[j] |
| 15[k] | NDI-PC | MeCN | Trace | 42 |
| 16 | NDI-PC | MeCN | Trace[l]/32[m]/57[n] | 53[l]/37[m]/Trace[n] |
| 17 | NDI-PC | MeCN | N.R.[o]/61[p] | N.R.[o]/ 25[p] |
| 18 | NDI-PC | MeCN | 0 [q] | 0 [q] |
| 19 | NDI-PC | MeCN | 31[r]/43[s]/60[t] | 15[r]/22[s]/27[t] |

**Table S3.** [a]**1a** (12.0 mg, 1.0 equiv., 0.1 mmol), KSeCN (29.0 mg, 2.0 equiv., 0.2 mmol), NDI-PC (1.8 mg, 3.0 mol%, 0.003 mmol), $NEt_3$ (30.0 µL, 2.0 equiv., 0.2 mmol), MeCN (2.0 mL), rt, 12 h. [b]Isolated yield. [c,d e]With 1, 2, and 5 mol% NDI-PC respectively. [f]Reaction in the dark. [g]Reaction at 70 °C without light. [h,i,j]Yields at 4 h, 8 h, and 24 h, respectively. [k]Reaction in green

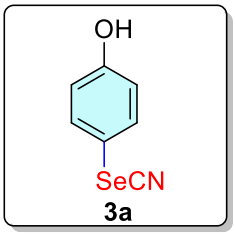
light; [l,m,n]KSeCN in 0.5, 1.0, 3.0 equiv. respectively. [o,p]Under $N_2$ atmosphere and $O_2$ atmosphere respectively. [q,r,s,t]With 0, 1.0, 1.5, 2.5 equiv. of $NEt_3$ respectively.

At the outset of our investigation, we selected phenylboronic acid (**1a**) and potassium selenocyanate as the model substrates. Different photocatalysts, solvents, and conditions were explored to optimize the reaction conditions. Upon irradiation of **1a** with a 10 W blue LED using KSeCN (2.0 equiv.) and NDI-PC photocatalyst (3.0 mol %) in MeCN as a solvent, the desired product 4-selenocyanatophenol (**3a**) was isolated in 60% yield with a 25% phenol (**2a'**) as the minor product (Table S3, entry 1). The screening of photocatalysts was done thoroughly with the known photocatalysts. Significantly lower yield of **3a** was obtained with Mes-Acr-$ClO_4$ (Table S3, entry 2). **3a** was obtained in traces in cases of $Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$, $Ru(bpy)_3Cl_2$ and Eosin Y while **2a'** was obtained in 33-44% respectively (Table S3, entries 3-5). **3a** was formed in 20% with Rose Bengal and **2a'** was found to be formed in 41% (Table S3, entry 6). Changing the solvent from MeCN to other polar and non-polar solvents did not increase the yield of **3a** while gave either lower yields or no formation of **3a** (Table S3, entries 7 – 9). Decreasing or increasing the catalyst loading did not help but gave lower yields in all cases (Table S3, entry 10). Control reactions in the absence of a photocatalyst (Table S3, entry 11), in dark conditions at room temperature, or on heating at 70 °C(Table S3, entries 12, 13) did not give any product, confirming it to be a photocatalyst-assisted and visible light-driven reaction. When the reaction time decreased to 4 h and 8 h, the yield of **3a** decreased to 19% and 36%, respectively; while when the time was increased to 24 h, no change in the yield of **3a** was noticed, but **2a'** was almost consumed (Table S3, entry 14). Next, when the light source was changed to green light, **3a** was formed in traces, and **2a'** was formed with a 42% yield (Table S3, entry 15). Decreasing or increasing the stoichiometry of KSeCN to 0.5, 1.0, or 3.0 equiv. did not help and gave a lower yield of **3a** in all the cases (Table S3, entry 16). In the absence of oxygen, *i.e.*, under a nitrogen atmosphere, both **3a** and **2a'** were not formed, while under an oxygen atmosphere, there was no significant increase in the yields of both **3a** and **2a**' (Table S3, entry 17). In absence of $NEt_3$, the reaction did not give any product (Table S3, entry 18). When the stoichiometry of additive $NEt_3$ was decreased to 1.0 and 1.5 equiv., the yield of **3a** decreased to 31% and 43% respectively; while when it was increased to 2.5 equiv., no change in the yield of **3a** was observed (Table S3, entry 19).

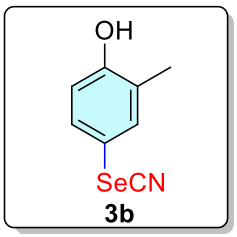
**9. Experimental procedure for the synthesis of 3, 4, and 5:**

In a reaction tube, 12 mg of **1a** (1.0 equiv., 0.1 mmol) was taken and dissolved in 2.0 ml MeCN. Then, 29.0 mg of KSeCN (2.0 equiv., 0.2 mmol) / 22.0 mg of PhSSPh (1.0 equiv., 1.0 mmol) / 31.0 mg of PhSeSePh (1.0 equiv., 1.0 mmol) was added to it, followed by the addition of 1.8 mg of photocatalyst NDI-PC (3 mol%, 0.003 mmol). After this, the reaction tube was irradiated in the blue LED light setup for 12 hours at room temperature. After completion of the reaction, monitored by TLC, the reaction was diluted with ethyl acetate and washed with water. The combined organic phases were dried over $Na_2SO_4$ and the solvent was evaporated under reduced pressure to obtain the crude. The crude residue was purified by silica gel column chromatography of mesh size 100-200 or 230-400 with hexane and ethyl acetate solvent mixtures as the eluent and afforded the resulting 4-selenocyanatophenol as described below.

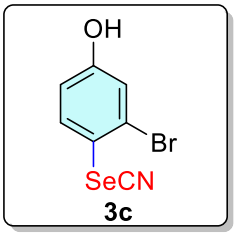
**4-selenocyanatophenol (3a):**[15] Brown semisolid, yield 196.0 mg (60%); hexane/EtOAc (80/20); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.52 (dd, $J$ = 8.8, 1.2 Hz, 2H), 6.85 (dd, $J$ = 8.8, 0.8 Hz, 2H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 158.3, 136.5, 117.8, 110.6, 102.9 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_7H_4NOSe$ 197.9458; Found 197.9453.



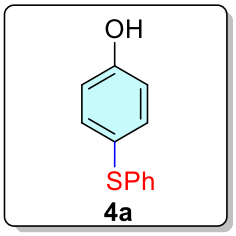

**2-methyl-4-selenocyanatophenol (3b):**[16] Brown oil, yield 194.0 mg (62%); hexane/EtOAc (80/20); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.44 (dd, $J$ = 2.0, 0.8 Hz, 1H), 7.37 (dd, $J$ = 8.0, 2.0 Hz, 1H), 6.77 (d, $J$ = 8.0 Hz, 1H), 5.48 (brs, 1H), 2.25 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 156.2, 137.4, 133.8, 127.0, 116.9, 110.8, 102.6, 15.9 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_8H_6NOSe$ 211.9615; Found 211.9613.



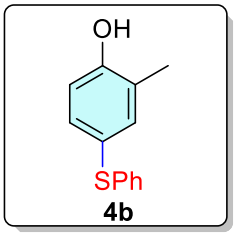

**3-bromo-4-selenocyanatophenol (3c):** Brown oil, yield 153.0 mg (55%); hexane/EtOAc (75/25); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.61 (d, $J$ = 8.8 Hz, 1H), 7.14 (d, $J$ = 2.4 Hz, 1H), 6.86 (dd, $J$ = 8.8, 2.4 Hz) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 157.7, 133.7, 124.6, 120.9, 117.2, 115.6, 102.2 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_7H_3BrNOSe$ 275.8563; Found 275.8573.



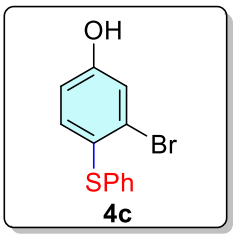
**4-(phenylthio)phenol (4a):**[17] Brown oil, yield 215.0 mg (65%); hexane/EtOAc (90/10); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.37 (d, $J$ = 8.4 Hz, 2H), 7.24 – 7.12 (m, 5H), 6.83 (d, $J$ = 8.4 Hz, 2H), 5.83 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 156.1, 138.6, 135.7, 129.1, 128.5, 126.0, 124.8, 116.7 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_9NOS$ 201.0374; Found 201.0376.



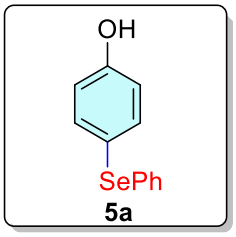

**2-methyl-4-(phenylthio)phenol (4b):**[18] Brown oil, yield 200.0 mg (63%); hexane/EtOAc (90/10); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.29 (s, 1H), 7.24 – 7.12 (m, 6H), 6.77 (d, $J$ = 8.4 Hz, 1H), 5.08 (brs, 1H), 2.24 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 154.4, 138.9, 136.9, 133.3, 129.1, 128.2, 125.8, 125.4, 124.2, 116.1, 15.8 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_{11}OS$ 215.0531; Found 215.0523.



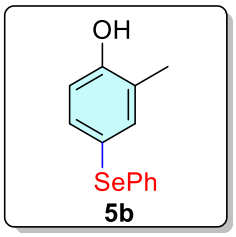

**3-bromo-4-(phenylthio)phenol (4c):**[18] Brown oil, yield 159.0 mg (57%); hexane/EtOAc (85/15); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.31 – 7.27 (m, 2H), 7.25 – 7.22 (m, 4H), 7.18 (d, $J$ = 2.4 Hz, 1H), 6.75 (dd, $J$ = 8.8, 2.4 Hz, 1H), 5.35 (brs, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 156.2, 136.2, 135.6, 129.8, 129.4, 128.3, 127.0, 126.9, 120.7, 115.9 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_8BrOS$ 278.9479; Found 278.9469.



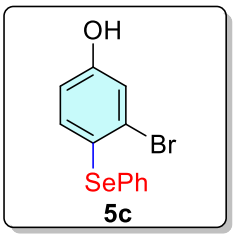

**4-(phenylselanyl)phenol (5a):**[19] Brown oil, yield 241.0 mg (59%); hexane/EtOAc (90/10); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.46 (d, $J$ = 8.8 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.24 – 7.20 (m, 3H), 6.79 (d, $J$ = 8.8 Hz, 2H), 5.18 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 155.9, 136.9, 133.2, 131.2, 129.3, 126.7, 120.3, 116.8 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_9NOSe$ 248.9819; Found 248.9816.



**2-methyl-4-(phenylselanyl)phenol (5b):**[19] Brown oil, yield 213.0 mg (55%); hexane/EtOAc (90/10); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.38 (dd, $J$ = 2.0, 0.8 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.24 – 7.18 (m, 3H), 6.73 (d, $J$ = 8.0 Hz, 1H), 4.93 (s, 1H), 2.23 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 154.3, 138.1, 134.5, 133.5, 130.9, 129.3, 126.5, 125.5, 119.9, 116.2, 15.8 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{13}H_{11}OSe$ 262.9975; Found 262.9967.




**3-bromo-4-(phenylselanyl)phenol (5c):**[19] Brown oil, yield 165.0 mg (50%); hexane/EtOAc (85/15); **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.48 (d, $J$ = 8.4 Hz, 1H), 7.24 (d, $J$ = 2.0 Hz, 1H), 7.22 (s, 5H), 7.04 (dd, $J$ = 8.4, 2.0 Hz, 1H), 6.45 (s, 1H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 157.6, 138.9, 132.9, 129.9, 129.8, 127.3, 125.9, 124.7, 118.7, 114.2 ppm. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_8BrOSe$ 326.8924; Found 326.8920.

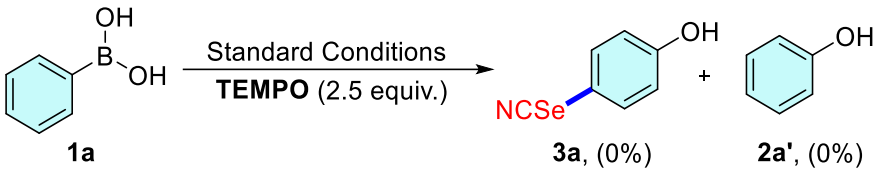



## 10. Mechanistic studies:

### 10a) Control experiments:

### A. Radical trapping with TEMPO:

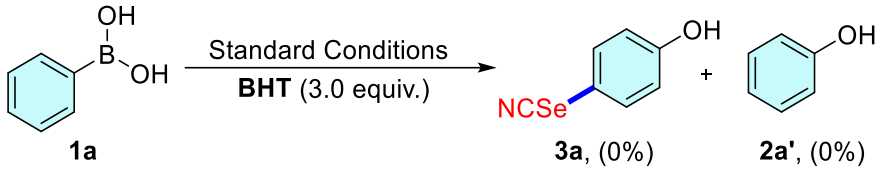
To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 29.0 mg of KSeCN (2.0 equiv., 0.2 mmol), 1.8 mg (3 mol%, 0.003 mmol) of **NDI-PC** and 39.0 mg (2.5 equiv., 0.25 mmol) of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) were added, the reaction mixture was irradiated by blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 12 h. After the completion of the reaction, no formation of either the minor product **3a'** or the major product **3a** was seen. This proves the radical pathway mechanism of the reaction.




**Scheme S14.** Controlled experiment with TEMPO.

**B. Radical trapping with BHT:**

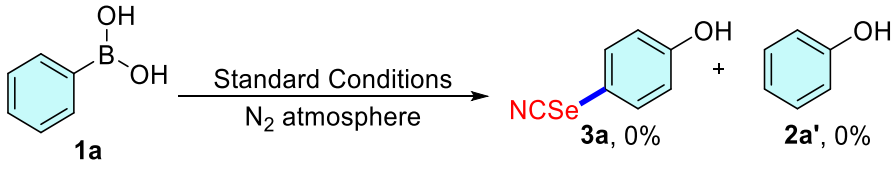
To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 29.0 mg of KSeCN (2.0 equiv., 0.2 mmol), 1.8 mg (3 mol%, 0.003 mmol) of **NDI-PC** and 66.0 mg (3.0 equiv., 0.3 mmol) of Butylated hydroxytoluene (BHT) were added, the reaction mixture was irradiated by blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature with constant stirring for 12 h. After the completion of the reaction, no formation of either the minor product **3a'** or the major product **3a** was seen. This proves the radical pathway mechanism of the reaction.




**Scheme S15.** Controlled experiment with BHT.

**C. Reaction under $N_2$ atmosphere:**

To a 15 ml high borosilicate glass reaction tube equipped with a magnetic stirring bar, 12.0 mg (1.0 equiv., 0.1 mmol) of **1a** and 2.0 ml of MeCN were added. After that, 29.0 mg of KSeCN (2.0 equiv., 0.2 mmol), and 1.8 mg (3 mol%, 0.003 mmol) of **NDI-PC** were added, and the reaction mixture was irradiated by a blue LED light source ($\lambda_{max}$ = 445 nm) at room temperature, sealed with a teflon cap and purged with $N_2$, with constant stirring for 12 h. After the completion of the reaction, no formation of either the minor product **3a'** or the major product **3a** was seen. This clearly proves the presence of oxygen is essential for the reaction to proceed.




**Scheme S16.** Controlled experiment under $N_2$ atmosphere.

**10b) Stern-Volmer Study: Fluorescence Quenching Experiments:**

Fluorescence quenching studies were performed using Horiba-Jobin-Yvon Fluorescence Spectrophotometer. A ($0.5 \times 10^{-5}$) M solution of **NDI-PC** in MeCN was prepared, and $10^{-3}$ M of quencher $NEt_3$, and KSeCN were added successively to the measured solution in quartz cuvette and emission spectrum was observed. All the solutions were excited at 500 nm and emission intensity was collected at 573 nm. Plots were derived in between quencher concentration and $I_0/I$ (intensities of the emission in the absence and presence of the quencher at 573 nm) to calculate Ksv.

From Stern-Volmer Equation,

$$I_0/I = 1 + Ksv\,[Q]$$

Q = concentration of added quencher

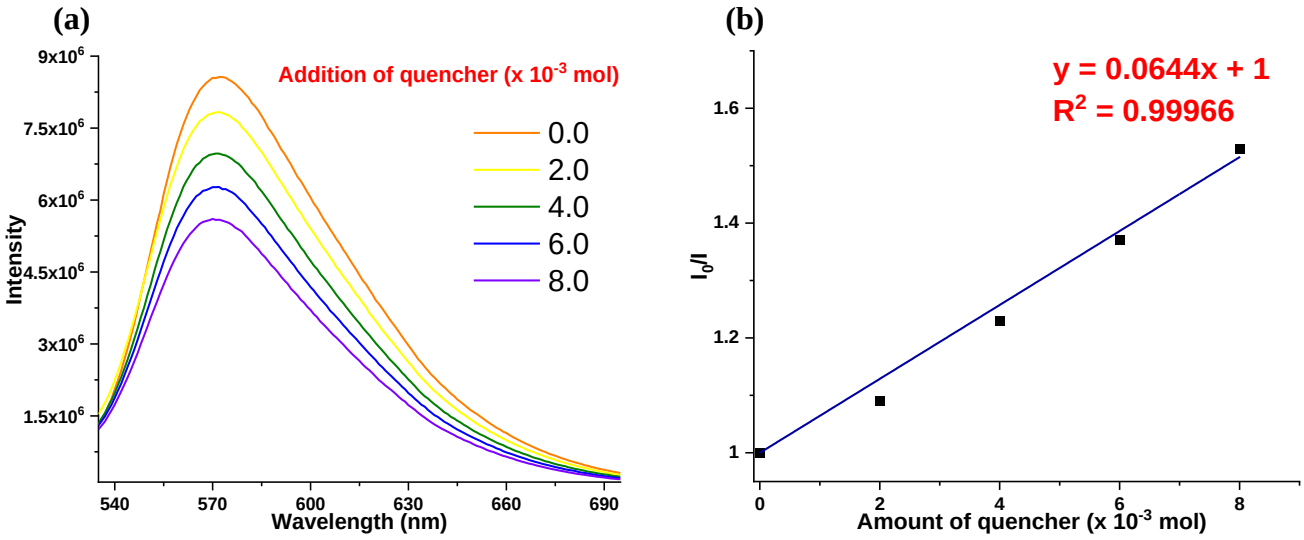



**Figure S19.** Fluorescence quenching of **NDI-PC** with $NEt_3$**: (a)** Emission spectrum of NDI-PC with varying concentrations of $NEt_3$; **(b)** Stern-Volmer plot.

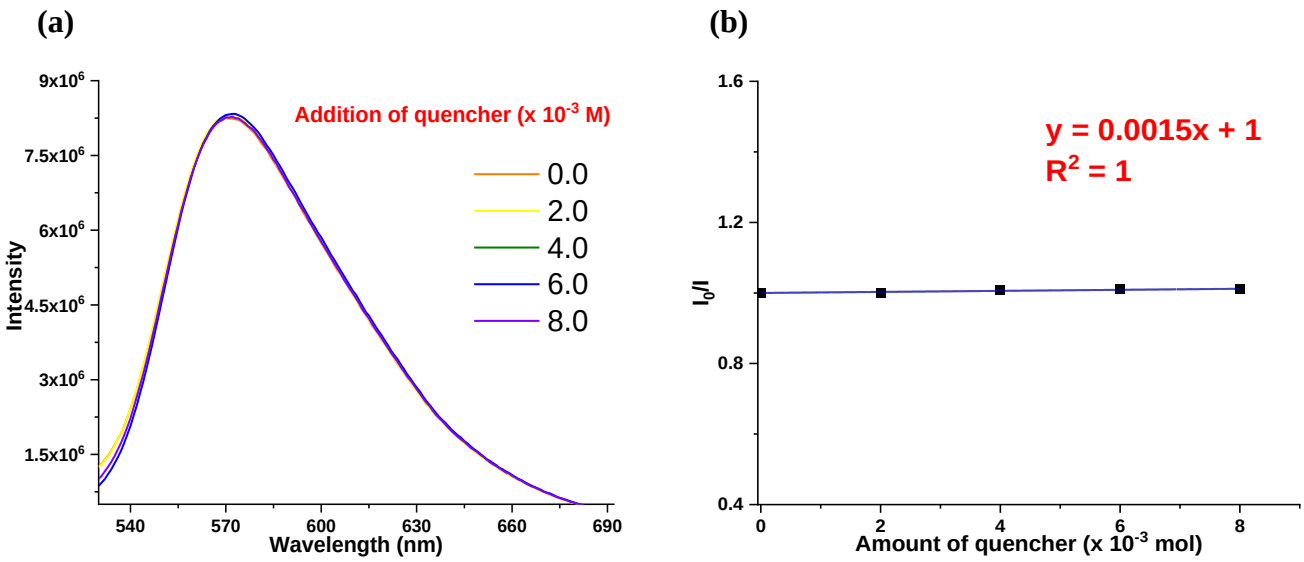
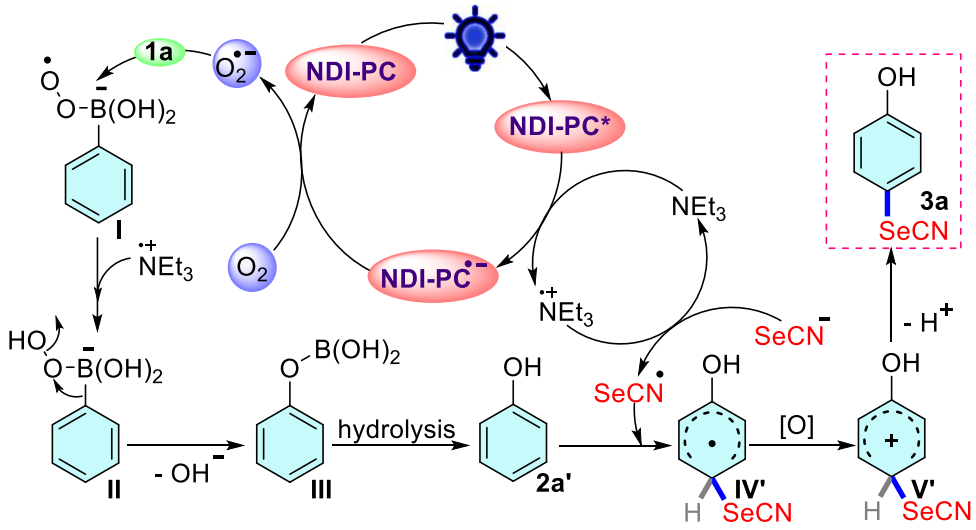



**Figure S20.** Fluorescence quenching of **NDI-PC** with KSeCN**: (a)** Emission spectrum of NDI-PC with varying concentrations of KSeCN; **(b)** Stern-Volmer plot.

## 11. Plausible mechanistic pathway:

Based on the control experiments and previous literature reports,[20] we propose a plausible mechanism for the reaction (Scheme S14). NDI-PC gets photoexcited in the presence of blue LED and goes into its excited state NDI-PC*. A single-electron transfer oxidises the $NEt_3$ to the $NEt_3^{+\bullet}$ radical cation and NDI-PC* gets converted to NDI-$PC^{\bullet-}$. Then, $SeCN^-$ anion gives an electron to $NEt_3^{+\bullet}$ and it was again converted to $NEt_3$ and the $SeCN^-$ anion is transformed to $SeCN^\bullet$. Next, molecular oxygen completes the photocatalytic cycle by oxidizing NDI-$PC^{\bullet-}$ to its ground state (which subsequently enters the next photocatalytic cycle) and itself gets converted to superoxide radical anion ($O_2^{\bullet-}$). $O_2^{\bullet-}$ attacks the electron-deficient boron atom to give an intermediate **I**, which may abstract a hydrogen atom from $NEt_3^{+\bullet}$ to give intermediate **II.** The formation of **2a'** occurs by rearrangement of **II** into **III** with subsequent hydrolysis. **2a'** is attacked by the $SeCN^\bullet$ radical, resulting in the formation of radical intermediate **IV'**, which was oxidized quickly to form a cationic intermediate **V'**. On deprotonation, **V'** yields the target product **3a** along with **2a'** which is isolated in minor amount.

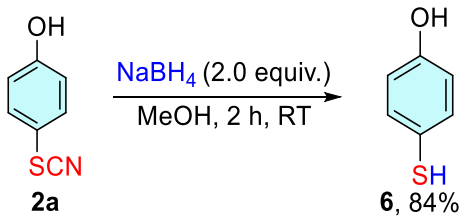



**Scheme S17.** Plausible Mechanism.

## 12. Experimental procedure for the synthesis of 6, 7, 8, and 9:

- **Synthesis of 4-mercaptophenol (6):**

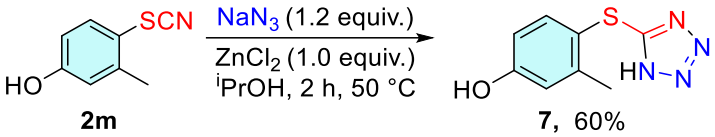
To a 25 mL round bottomed flask, 200.0 mg (1.0 equiv., 1.6 mmol) of **2a** was taken in 5.0 mL MeOH. To this solution, 100.0 mg of $NaBH_4$ (2.0 equiv., 2.6 mmol) was added portion wise at room temperature, and the mixture was stirred for 2 h. After completion of the reaction, as observed by TLC, the reaction was quenched with $H_2O$, and the resulting mixture was extracted with 10.0 mL EtOAc three times. The combined organic layers were dried over $Na_2SO_4$, the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel of mesh size 100-200 with hexane/EtOAc (90/10) as the eluent to obtain the reduced product **6** in 84% yield (140.0 mg).




**Scheme S18.** Procedure for the synthesis of **6**.

- **Synthesis of 4-((1H-tetrazol-5-yl)thio)-3-methylphenol (7):**

In a 25 mL round bottomed flask, 200.0 mg (1.0 equiv., 1.2 mmol) of **2m** was taken in 10.0 mL *iso*-propanol. To this solution, 94.0 mg (1.2 equiv., 1.4 mmol) of $NaN_3$ and 158.0 mg (1.0 equiv., 1.2 mmol) of $ZnCl_2$ were added. The reaction mixture was stirred vigorously at 50 °C for 2 h. When the starting material had been consumed (monitored by TLC), the solvent was evaporated under reduced pressure. Then the resulting mixture was extracted with 10 mL EtOAc three times. The organic layer was dried over $Na_2SO_4$, the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel of mesh size 60-120 with hexane/EtOAc (70/30) as the eluent obtain the tetrazole **7** in 60% yield (151.0 mg).

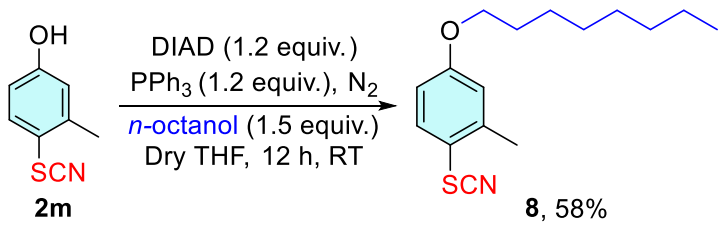



**2m** **7**, 60%

**Scheme S19.** Procedure for the synthesis of **7**.

- **Synthesis of 2-methyl-4-(octyloxy)-1-thiocyanatobenzene (8):**

In a 25 mL round bottom flask, 200.0 mg (1.0 equiv., 1.2 mmol) of **2m**, 377.0 mg (1.2 equiv., 1.4 mmol) of triphenylphosphine, and 234.0 mg (1.5 equiv., 1.8 mmol) of *n*-octanol were dissolved in completely dry THF (10.0 mL). To it, 291.0 mg (1.2 equiv., 1.4 mmol) of diisopropyl azodicarboxylate (DIAD) was added at 0 °C under a nitrogen atmosphere. After the reaction mixture was brought to room temperature, stirring was continued for 12 h. After the completion, the reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water and dried over anhydrous sodium sulfate. After removing the toluene, ether was added to the residue and diisopropyl hydrazodicarboxylate separated out was filtered off. After removing the solvent, the residue was purified by column chromatography on silica gel of mesh size 100-200 with hexane/EtOAc (95/5) as the eluent, giving 195.0 mg of **8** as a light-yellow coloured oil with a 58% yield.

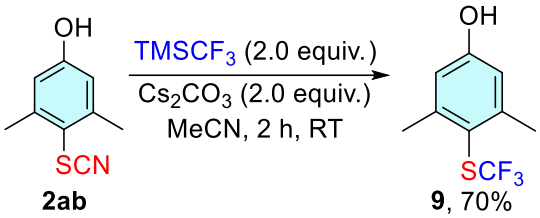



**2m** **8**, 58%

**Scheme S20.** Procedure for the synthesis of **8**.

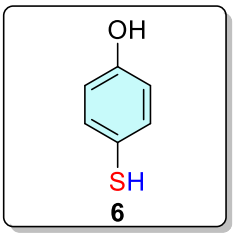
- **Synthesis of 3,5-dimethyl-4-((trifluoromethyl)thio)phenol (9):**

To a 25 mL round bottomed flask, 200.0 mg (1.0 equiv., 1.12 mmol) of **2ab**, 730.0 mg (2.0 equiv., 2.2 mmol) of $Cs_2CO_3$ and 330.0 µL (2.0 equiv., 2.2 mmol) of $TMSCF_3$ were added. The round bottomed flask was covered with a teflon pressure cap and reacted at room temperature for 12 hours. After the reaction was completed, it was cooled to room temperature, filtered through celite, washed with ethyl acetate, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel of mesh size 100-200 with hexane/EtOAc (90/10) as the eluent to afford 174.0 mg of the desired product **9** with 70% yield.

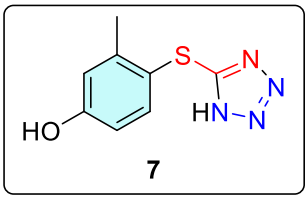



**Scheme S21.** Procedure for the synthesis of **9**.

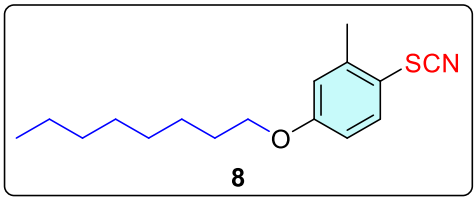
**4-mercaptophenol (6):**[21] Light pink oil, yield 140 mg (84%); hexane/EtOAc (90/10); **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** $\delta$ 9.83 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, DMSO-*d*$_6$)** $\delta$ 158.7, 133.5, 125.6, 116.8 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_6H_5OS$ 125.0061; Found 125.0058.




**4-((1H-tetrazol-5-yl)thio)-3-methylphenol (7):** White solid, yield 151 mg (60%); hexane/EtOAc (70/30); mp: 170 - 175 °C; **$^1$H NMR (400 MHz, DMSO-*d*$_6$)** $\delta$ 9.90 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 2.8 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.8 Hz, 1H), 2.28 (s, 3H) ppm. **$^{13}$C{$^1$H} NMR (100 MHz, DMSO-*d*$_6$)**δ 159.9, 155.1, 143.9, 137.8, 118.5, 115.6, 114.9, 21.1 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_8H_7N_4OS$ 207.0341; Found 207.0332.

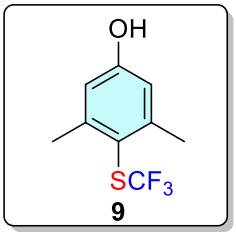


**2-methyl-4-(octyloxy)-1-thiocyanatobenzene (8):**[22] Light yellow oil, yield 195 mg (58%); hexane/EtOAc (95/5); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ 7.51 (d, $J$ = 8.4 Hz, 1H), 6.84 (d, $J$ = 2.8 Hz, 1H), 6.76 (dd, $J$ = 8.4, 2.8 Hz, 1H), 3.95 (t, $J$ = 6.4 Hz, 2H), 2.51 (s, 3H), 1.81 – 1.74 (m, 2H), 1.48 – 1.41 (m, 2H), 1.35 – 1.28 (m, 8H), 0.89 (t, $J$ = 6.8 Hz, 3H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 161.5, 143.0, 135.9, 117.9, 113.8, 113.0, 111.5, 68.4, 31.9, 29.5, 29.4, 29.2, 26.1, 22.8, 21.3, 14.3 ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{16}H_{22}NOS$ 276.1422; Found 276.1430.



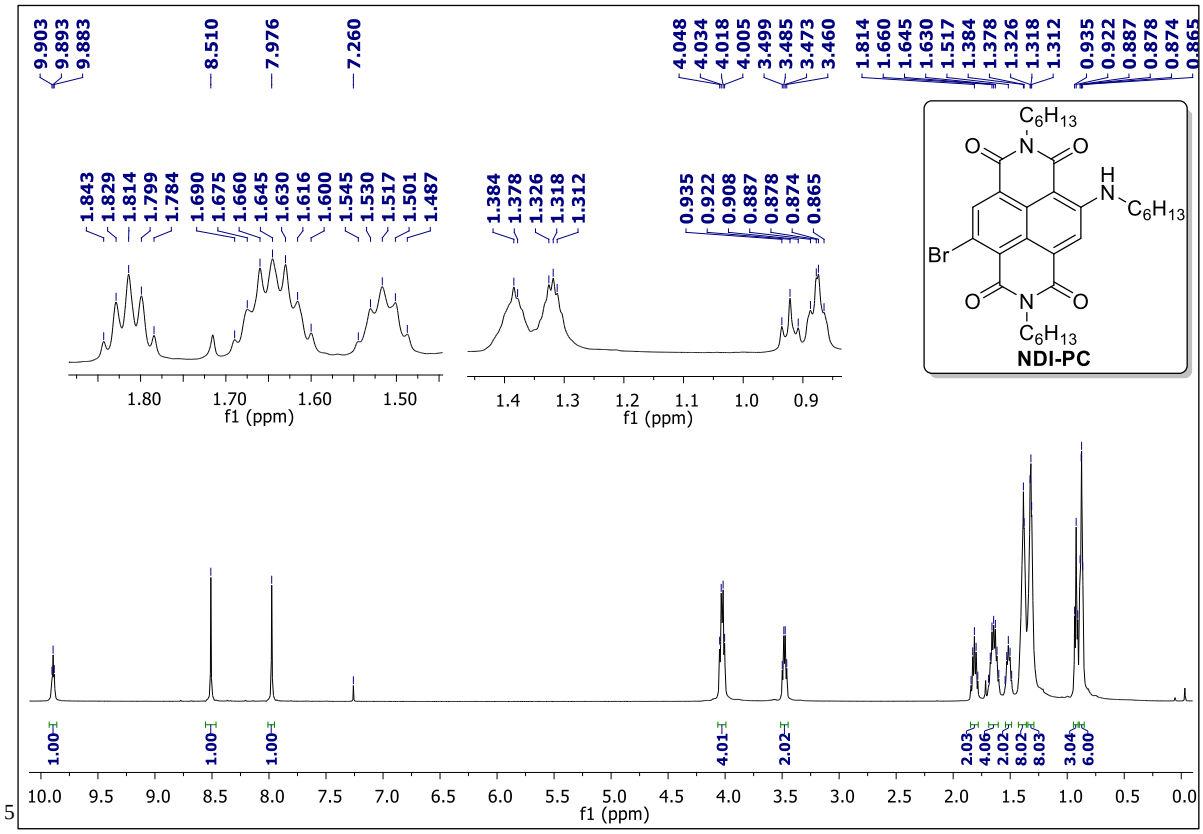
**8**

**3,5-dimethyl-4-((trifluoromethyl)thio)phenol (9):**[23] White solid, yield 174 mg (70%); hexane/EtOAc (90/10); **$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$ 6.66 (s, 2H), 5.20 (brs, 1H), 2.51 (s, 6H) ppm. **$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$)** $\delta$ 157.7, 147.8, 130.2 (q, $J$ = 308 Hz), 115.8, 114.8 (d, $J$ = 1.6 Hz), 22.4 ppm. **$^{19}$F NMR (376 MHz, $CDCl_3$)** $\delta$ -42.45 (s) ppm. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_9H_8F_3OS$ 221.0248; Found 221.0238.

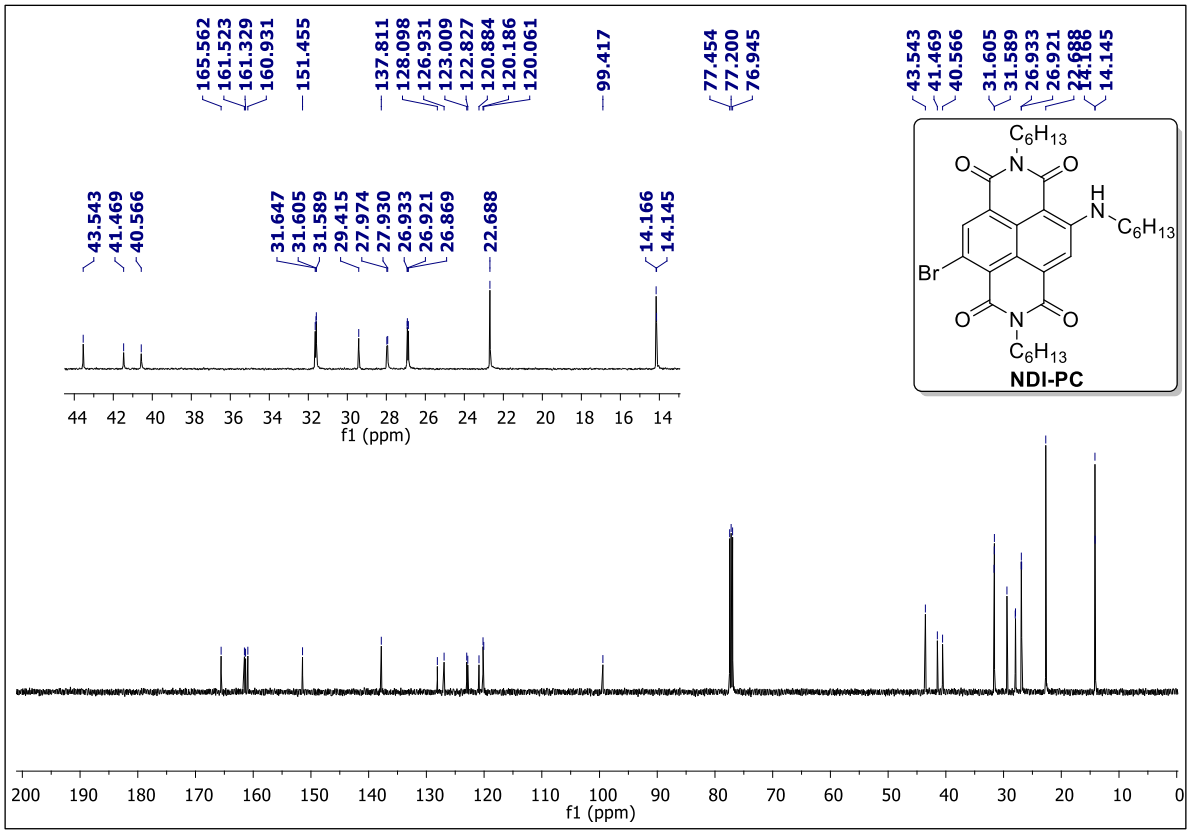


**9**

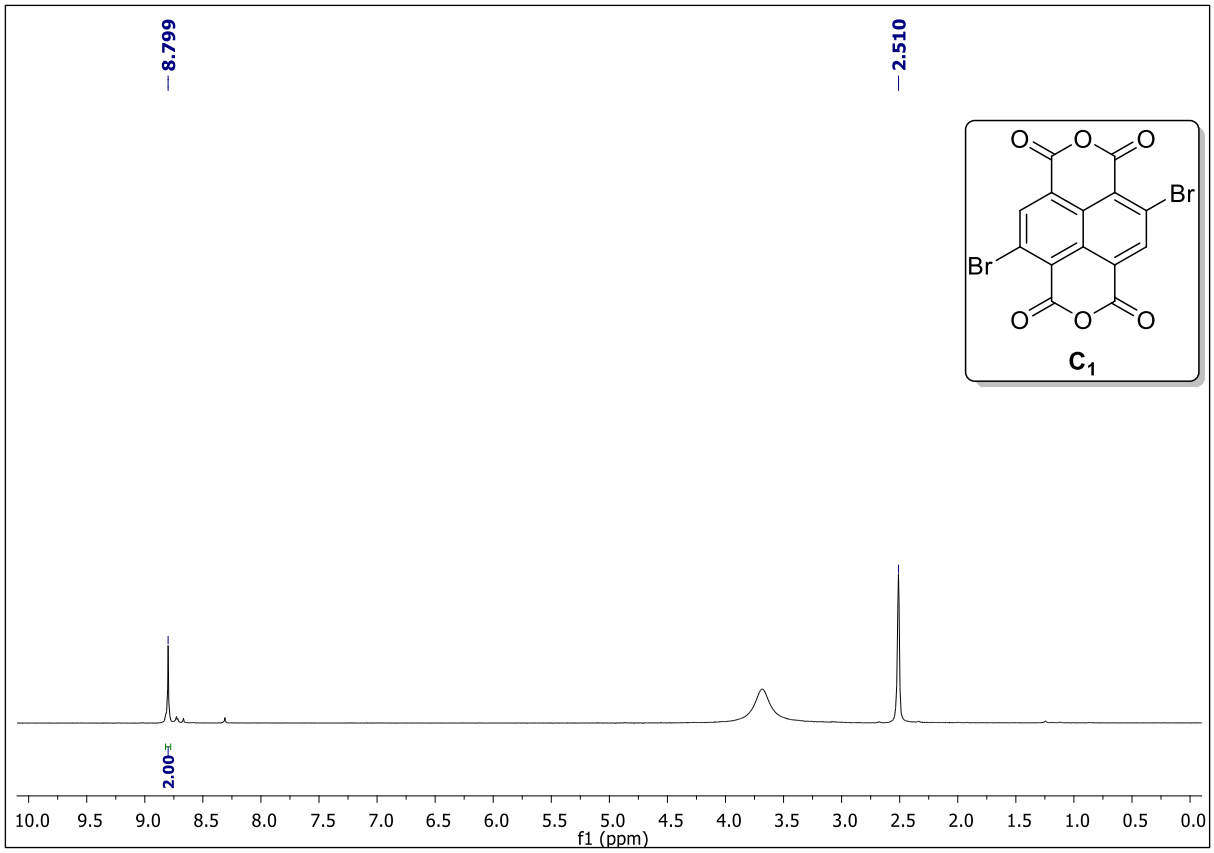
## 13. Copies of $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of synthesized compounds:



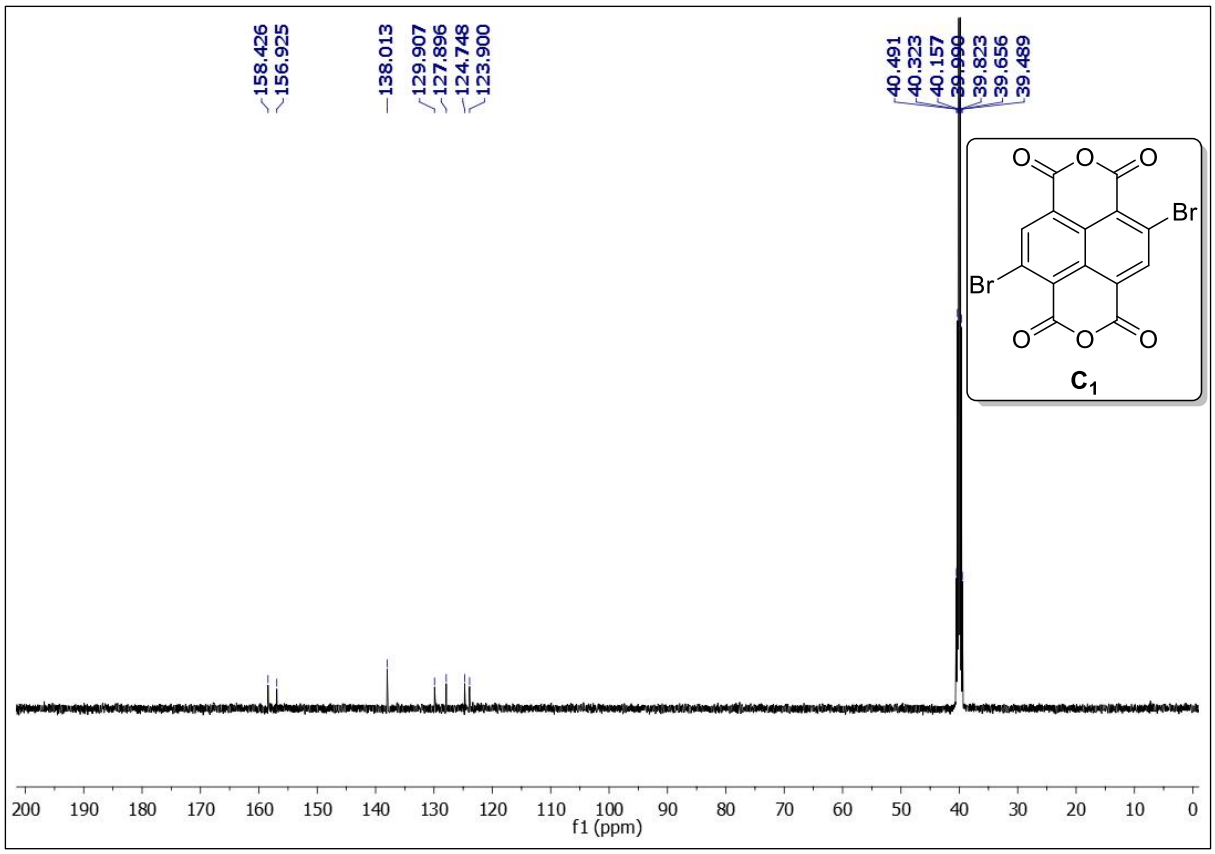

$^{1}H$ NMR of NDI-PC (500 MHz, $CDCl_3$)



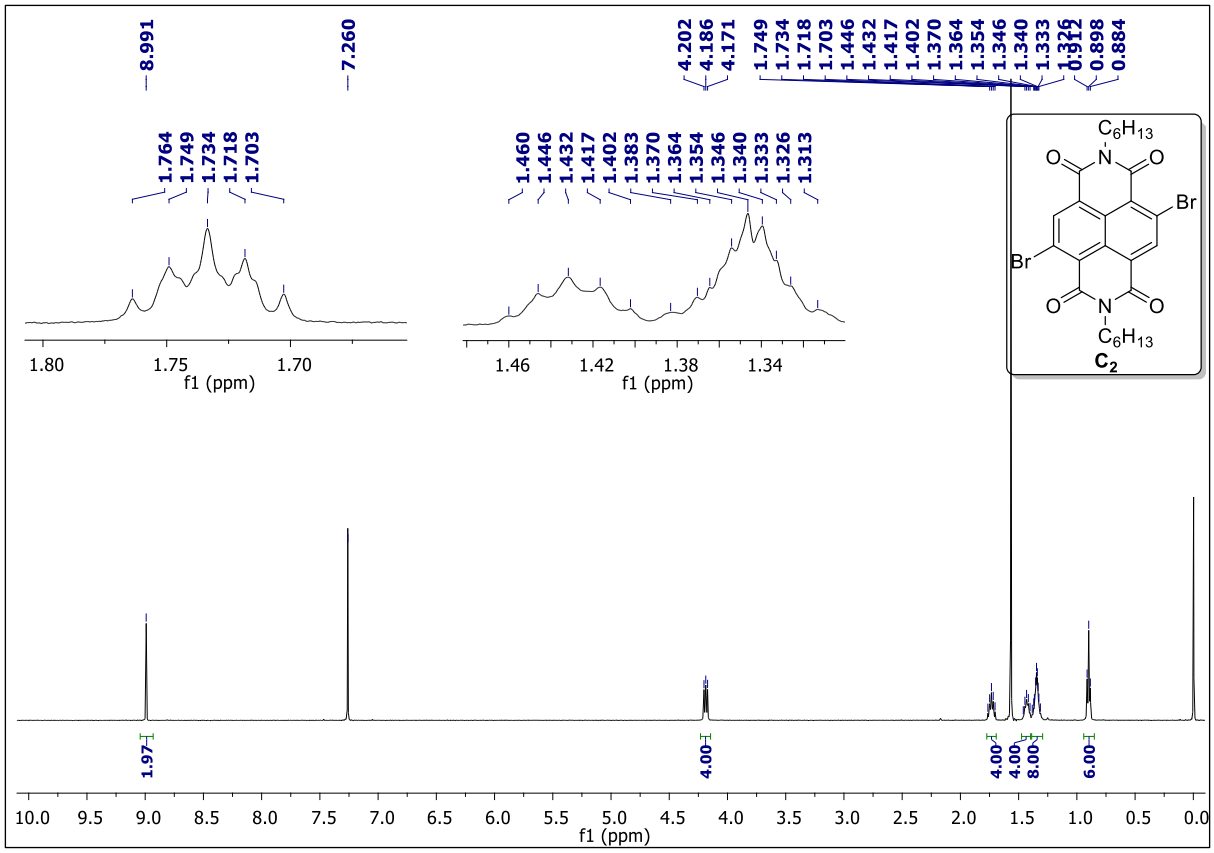

$^{13}C\{^{1}H\}$ NMR of NDI-PC (125 MHz, $CDCl_3$)



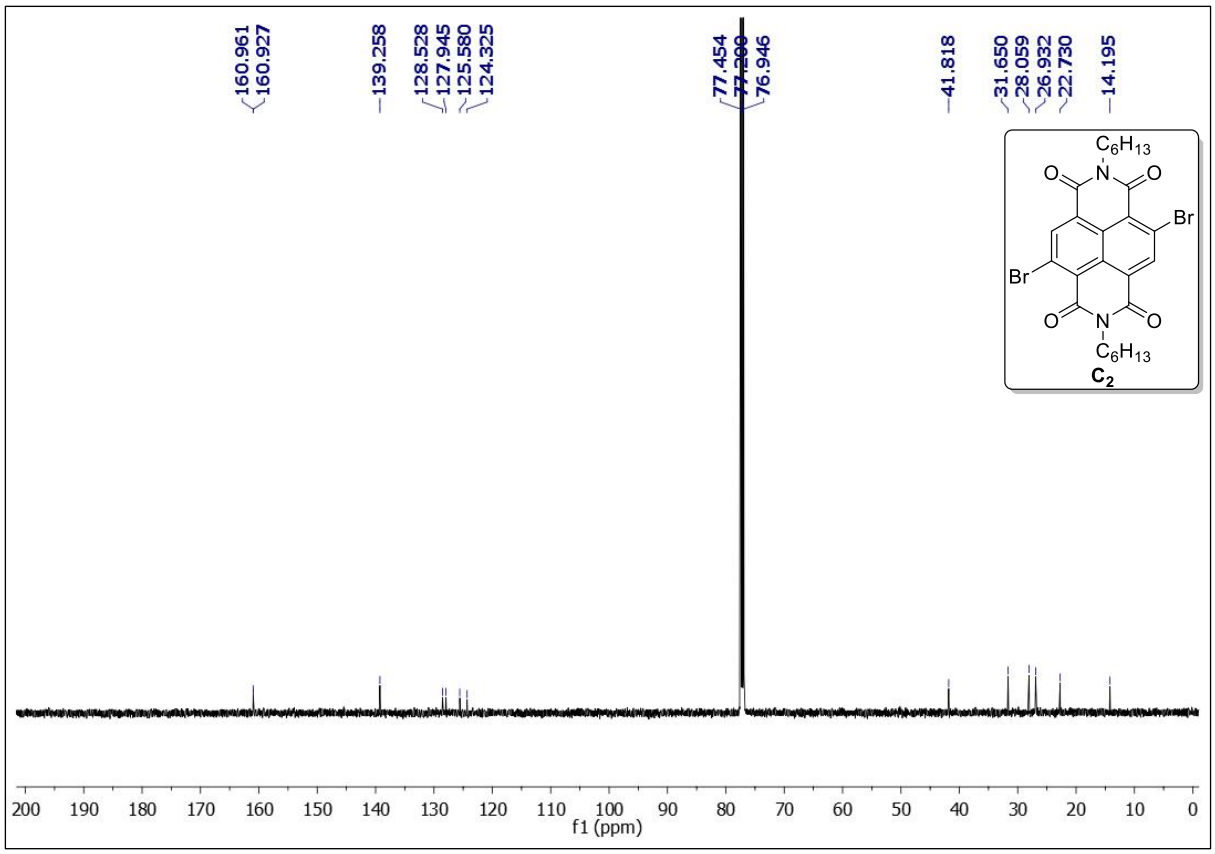

$^{1}$H NMR of **C₁** (500 MHz, DMSO-*d*$_6$)



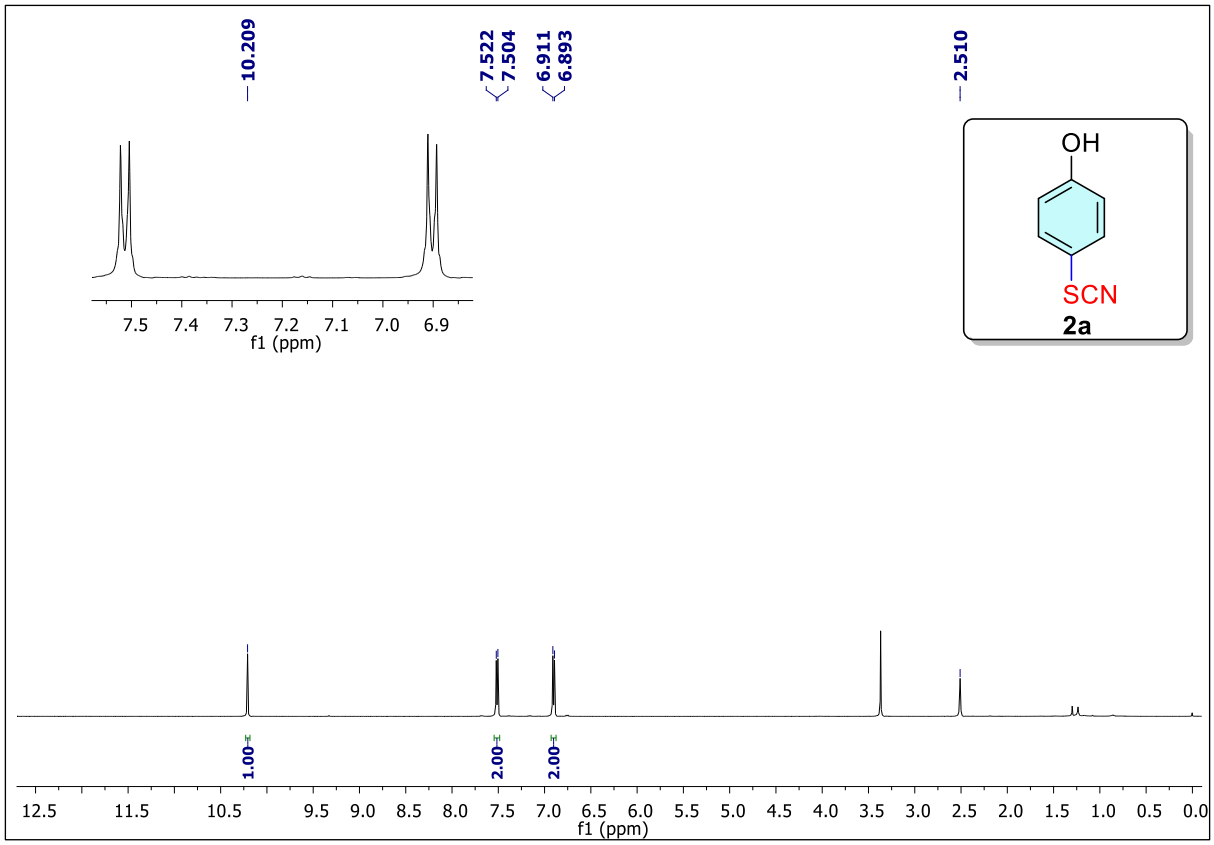

$^{13}$C{$^{1}$H} NMR of **C₁** (125 MHz, DMSO-*d*$_6$)



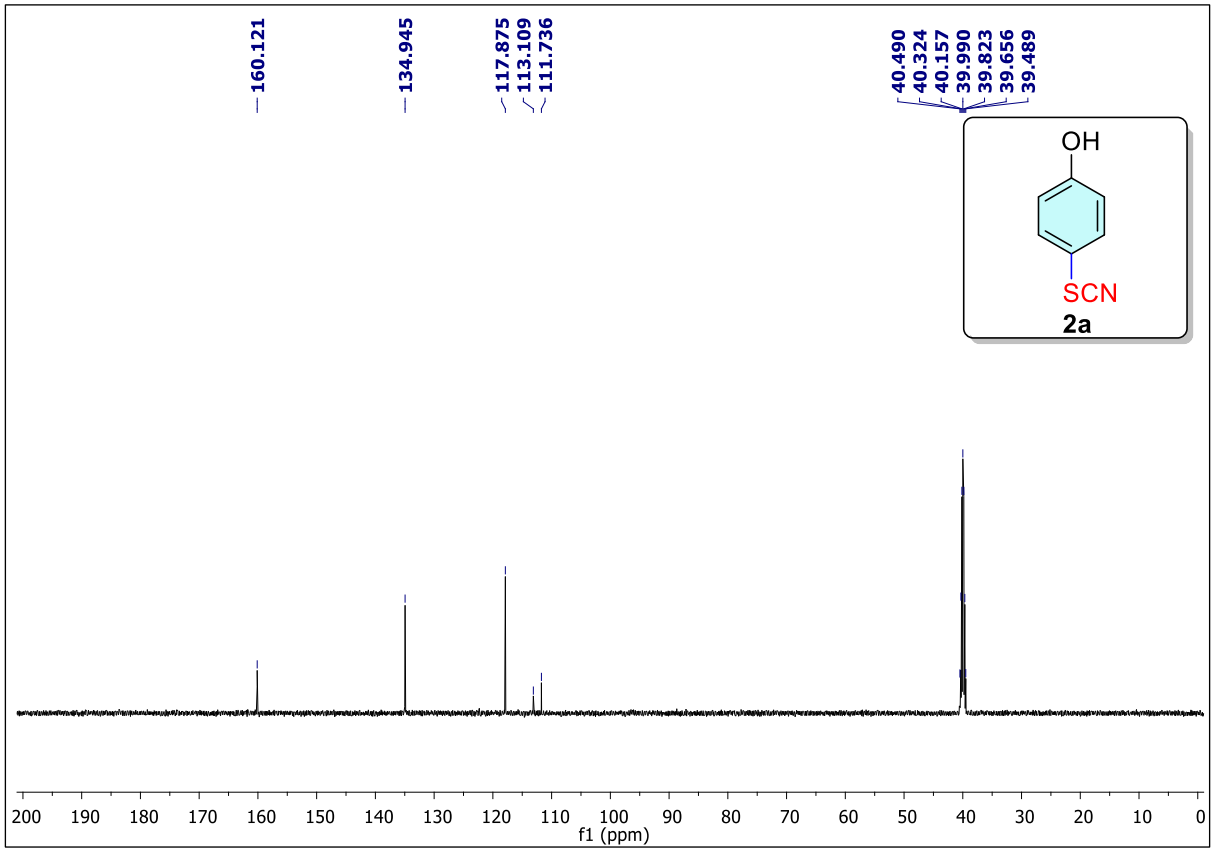

$^{1}$H NMR of **C2** (500 MHz, $CDCl_3$)



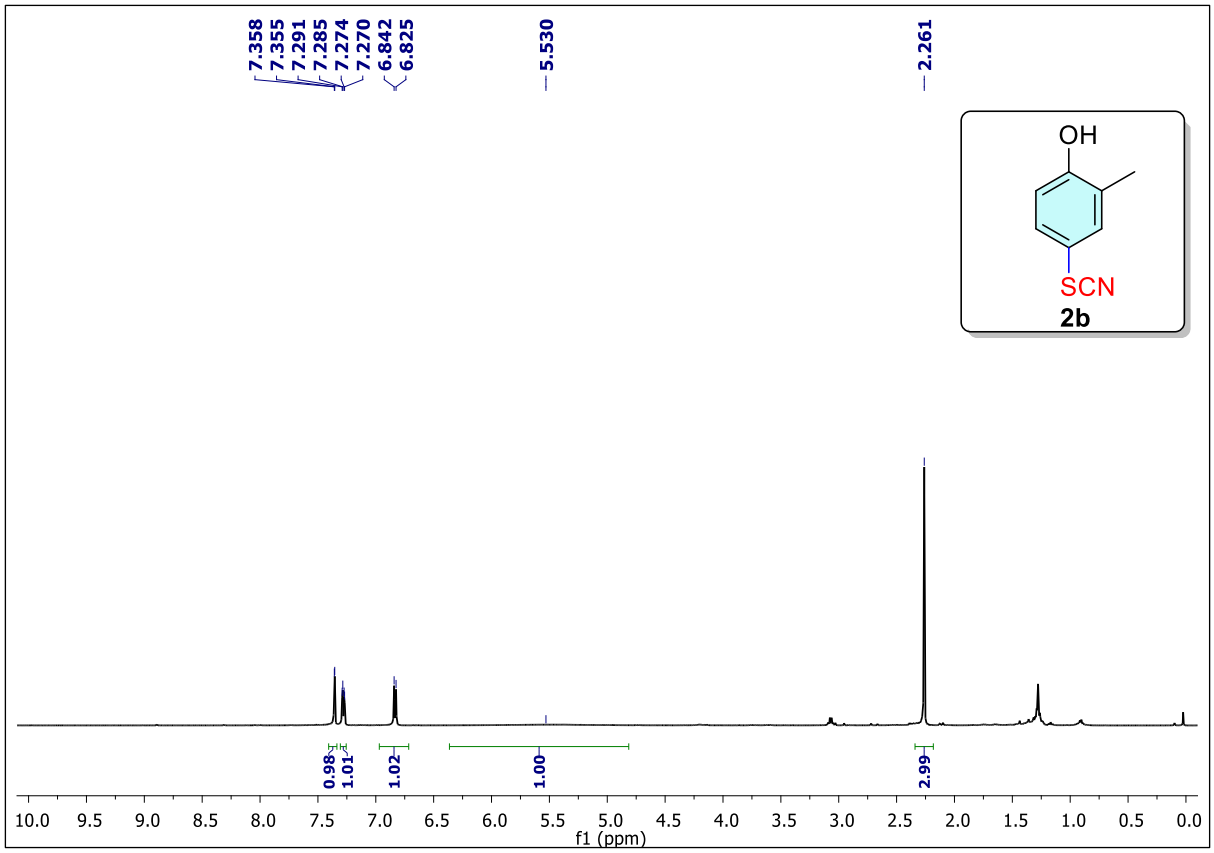

$^{13}$C{$^{1}$H} NMR of **C2** (125 MHz, $CDCl_3$)



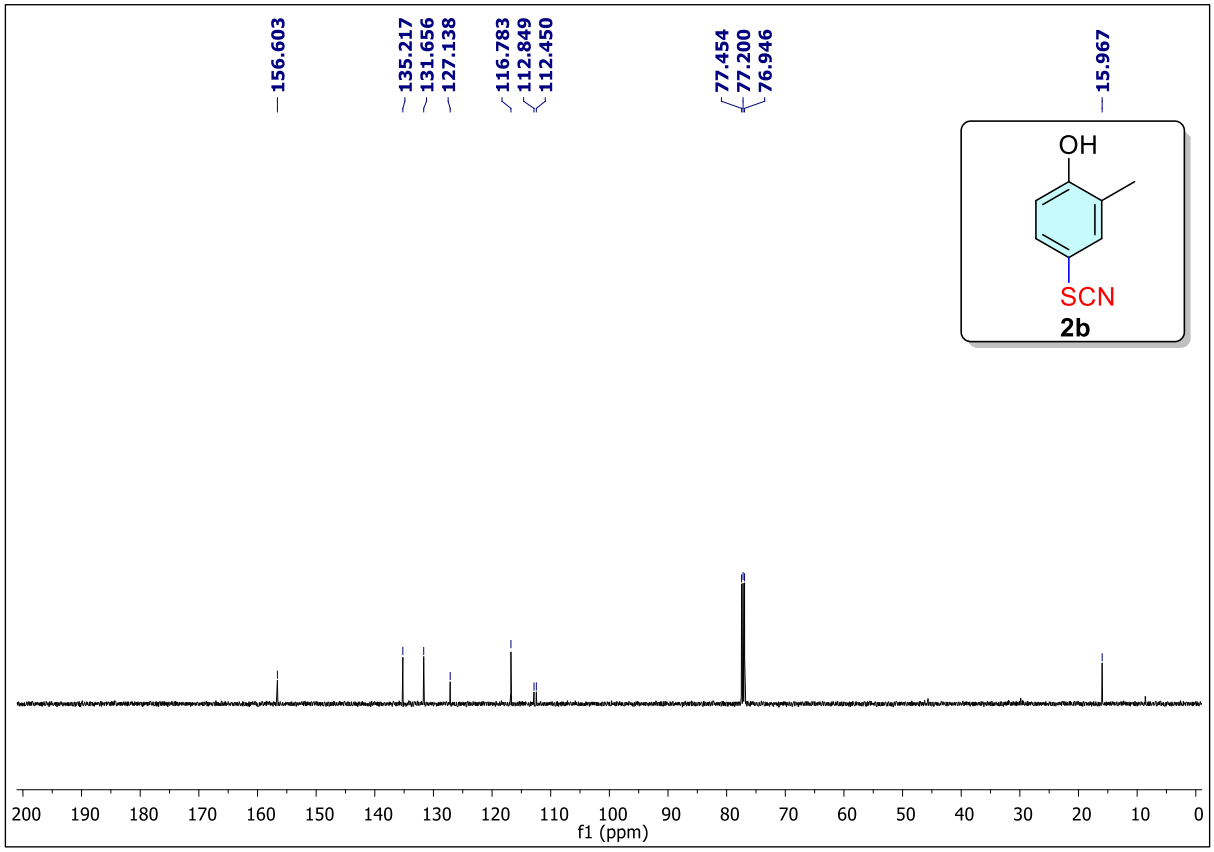

$^{1}$H NMR of **2a** (500 MHz, DMSO-$d_6$)



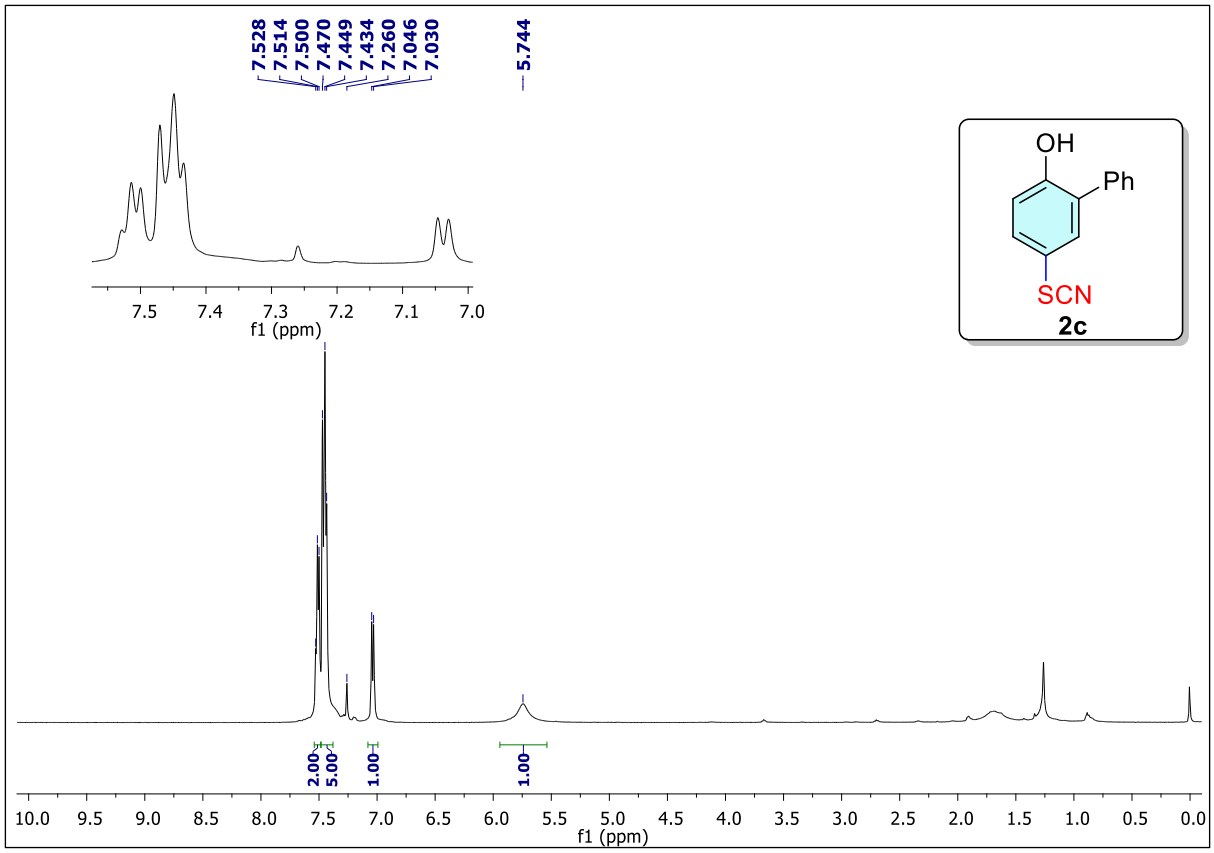

$^{13}$C{$^{1}$H} NMR of **2a** (125 MHz, DMSO-$d_6$)



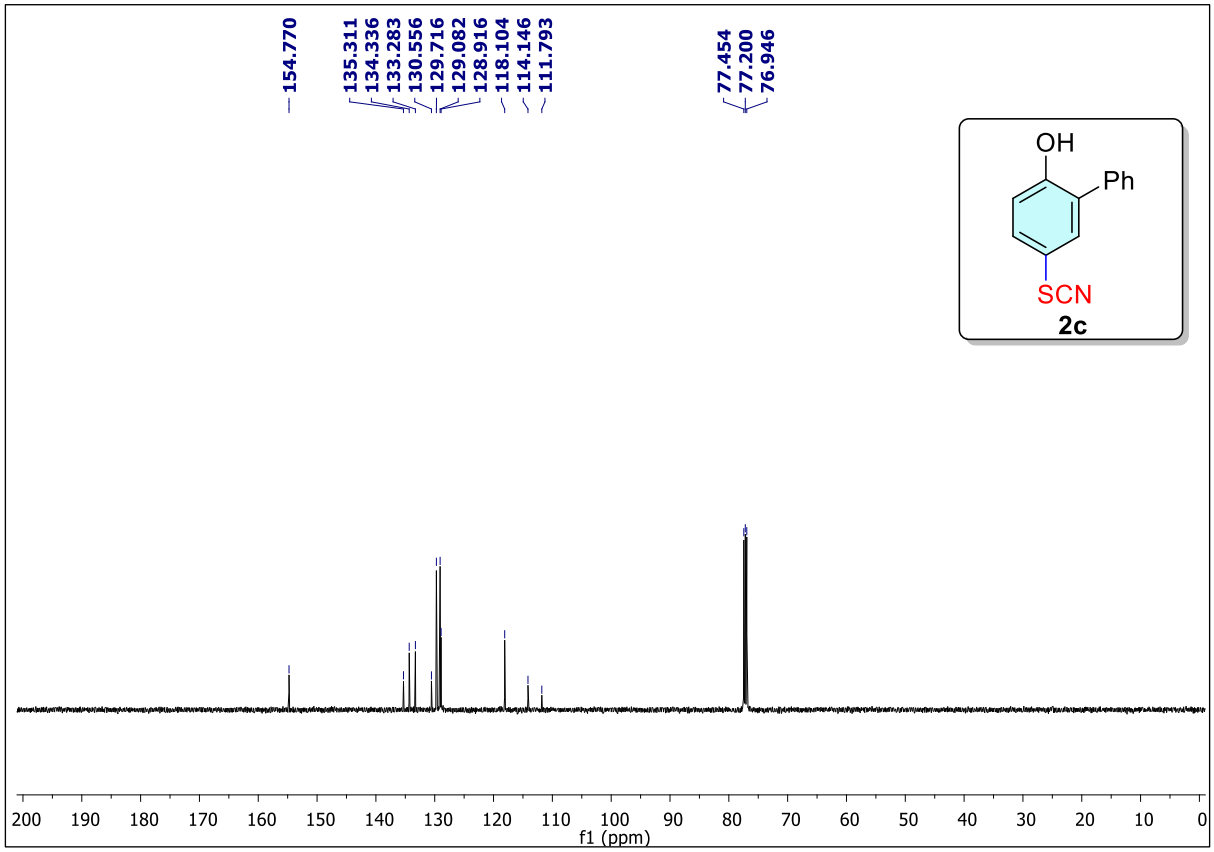

$^{1}$H NMR of **2b** (500 MHz, $CDCl_3$)



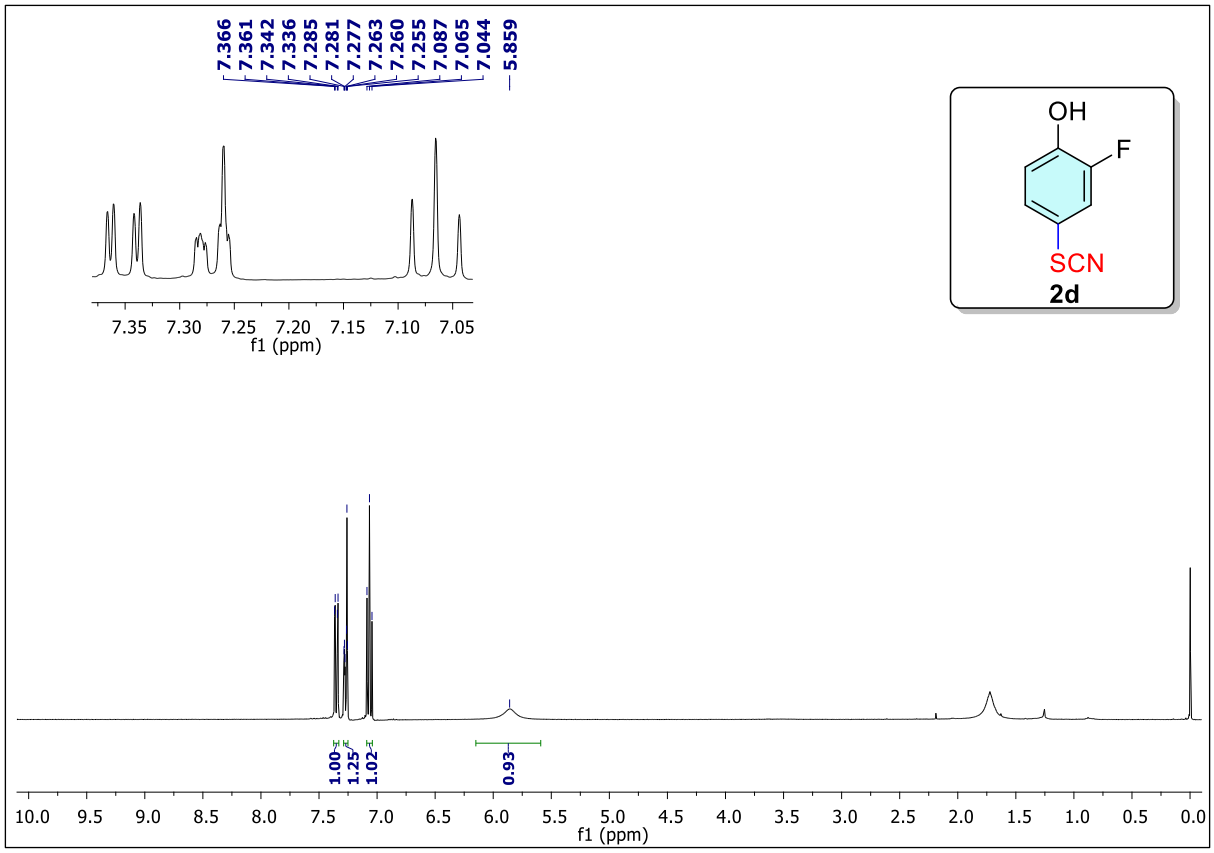

$^{13}$C{$^{1}$H} NMR of **2b** (125 MHz, $CDCl_3$)



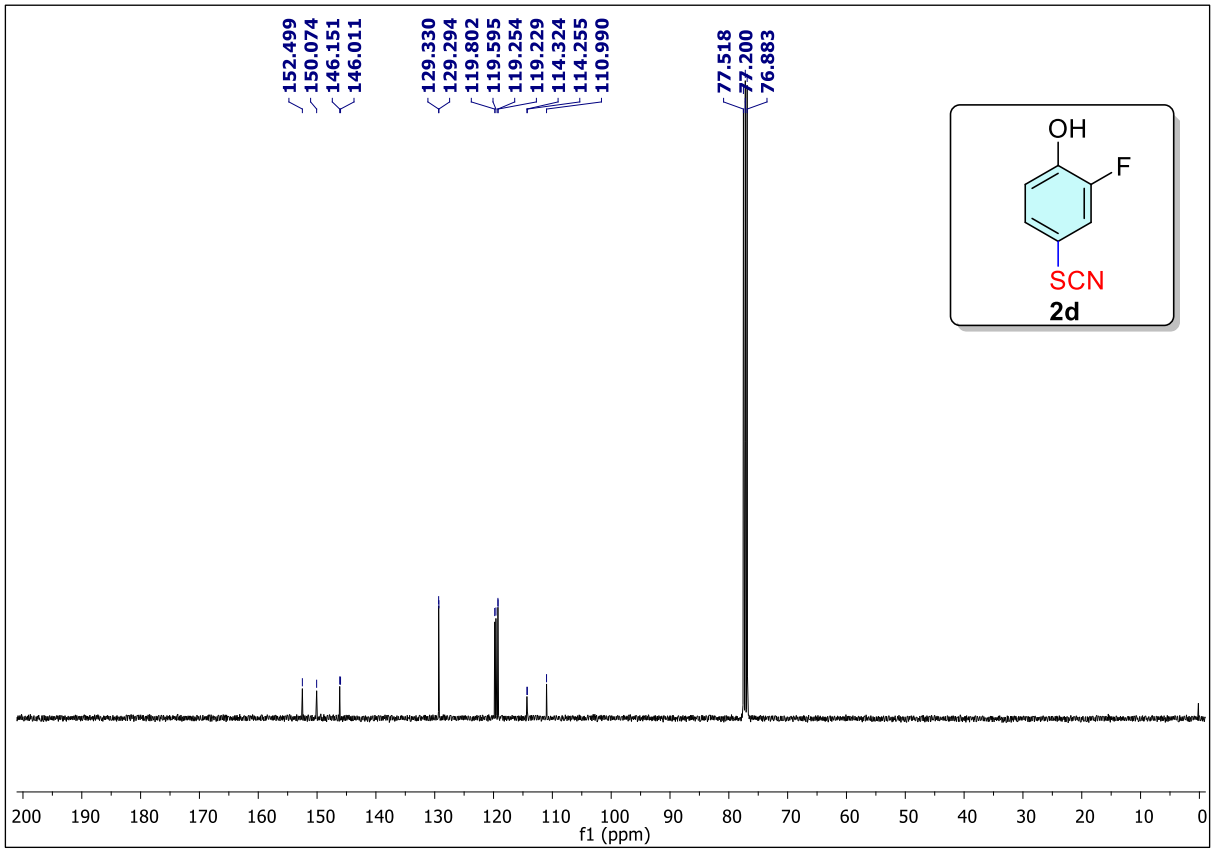

$^{1}$H NMR of **2c** (500 MHz, $CDCl_3$)



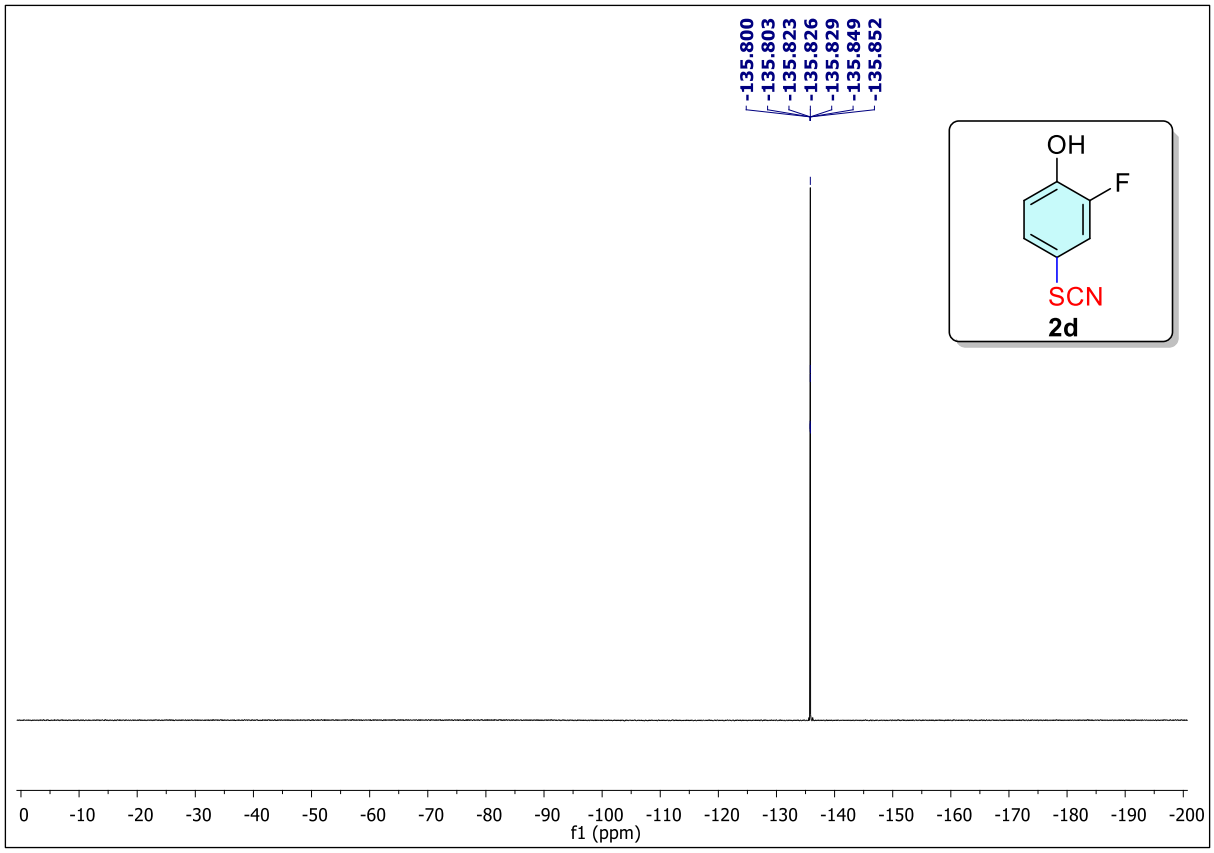

$^{13}$C{$^{1}$H} NMR of **2c** (125 MHz, $CDCl_3$)



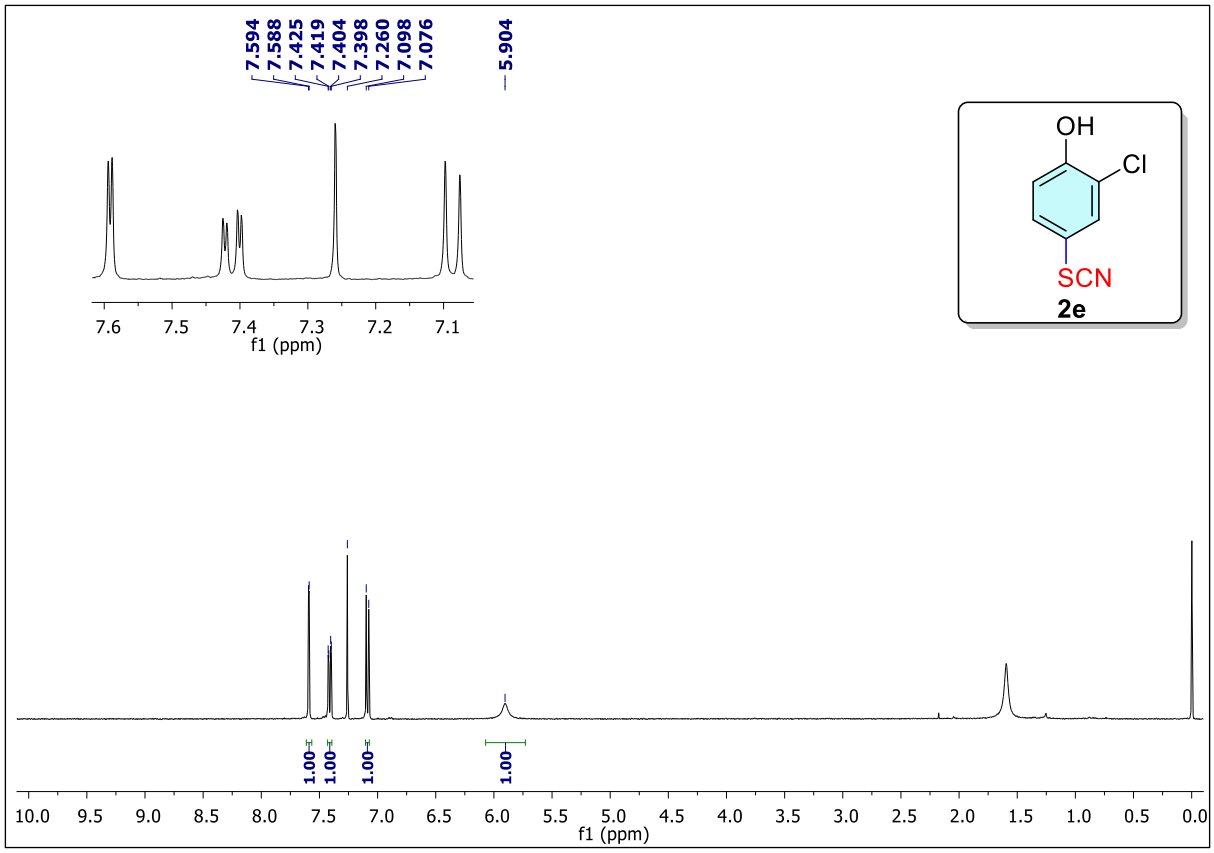

$^{1}$H NMR of **2d** (400 MHz, $CDCl_3$)



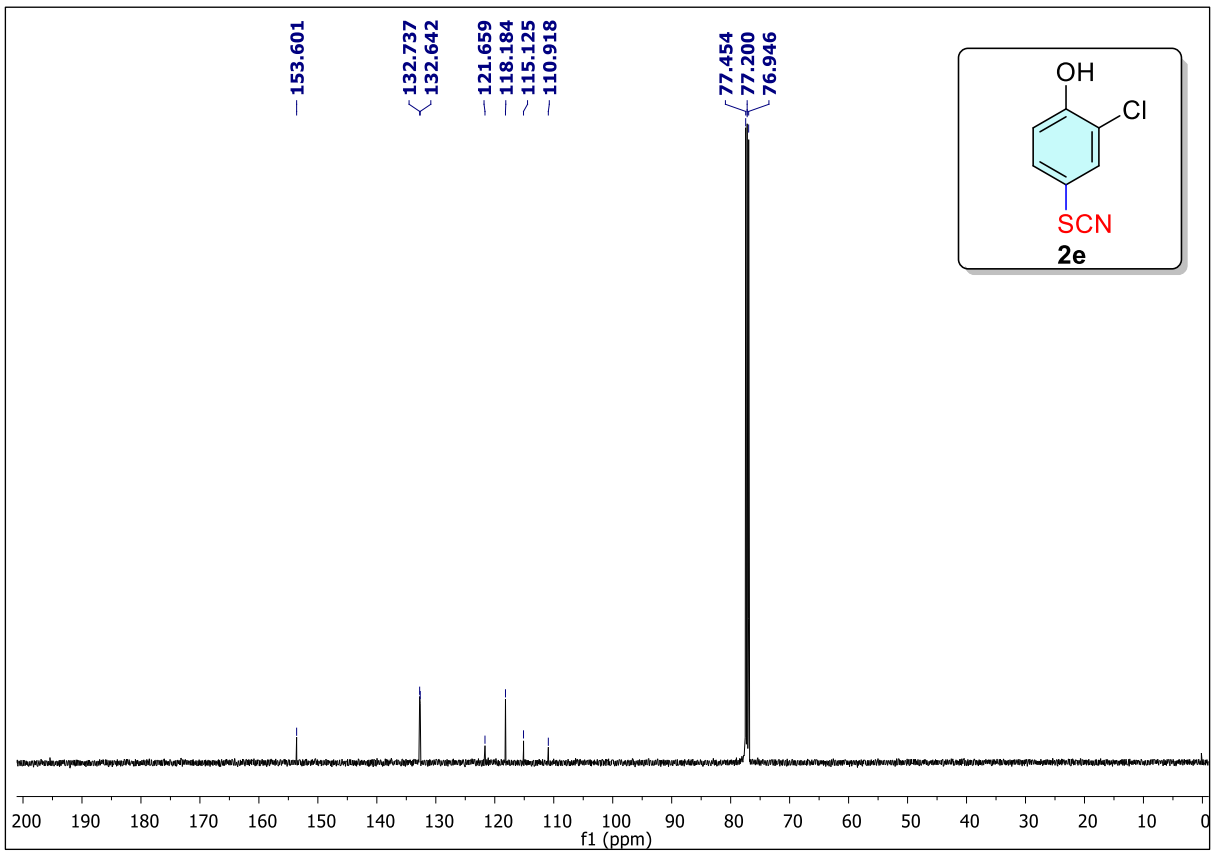

$^{13}$C{$^{1}$H} NMR of **2d** (100 MHz, $CDCl_3$)



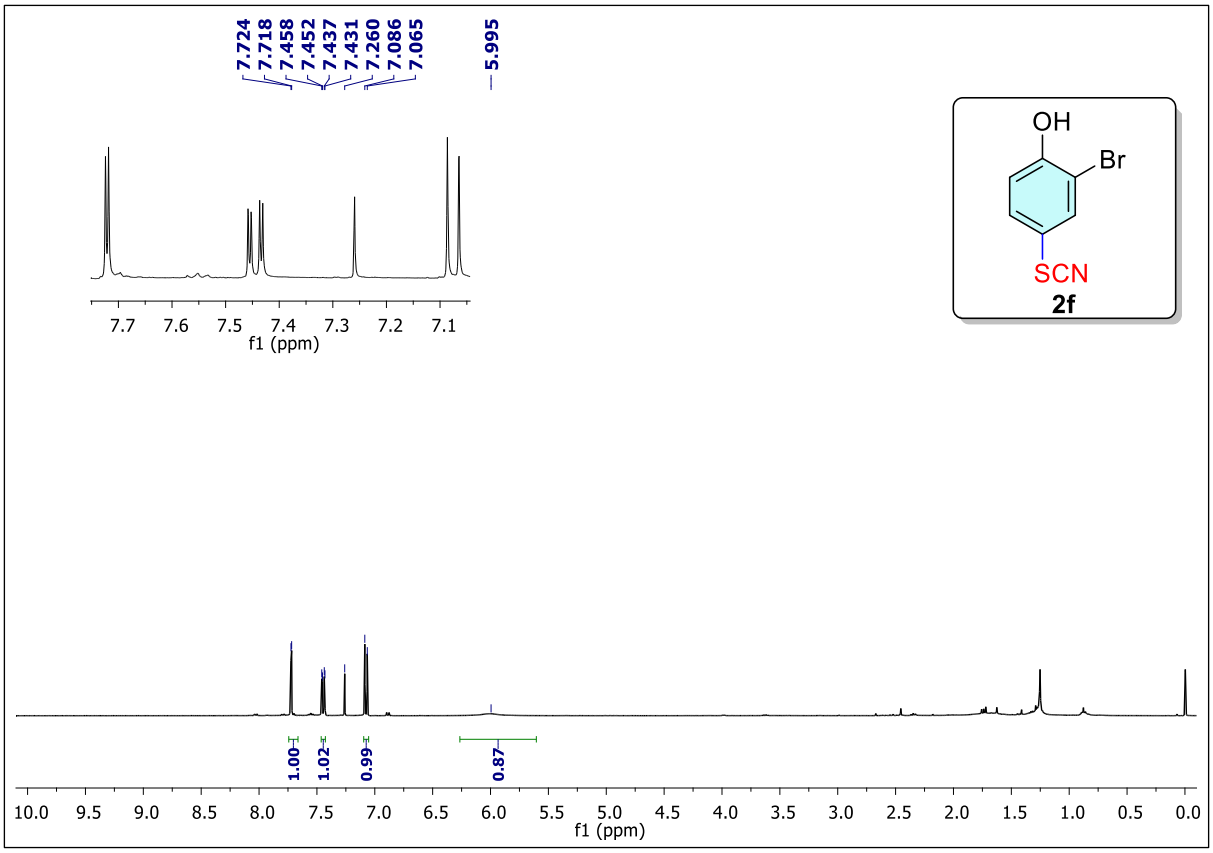

$^{19}$F NMR of **2d** (376 MHz, $CDCl_3$)



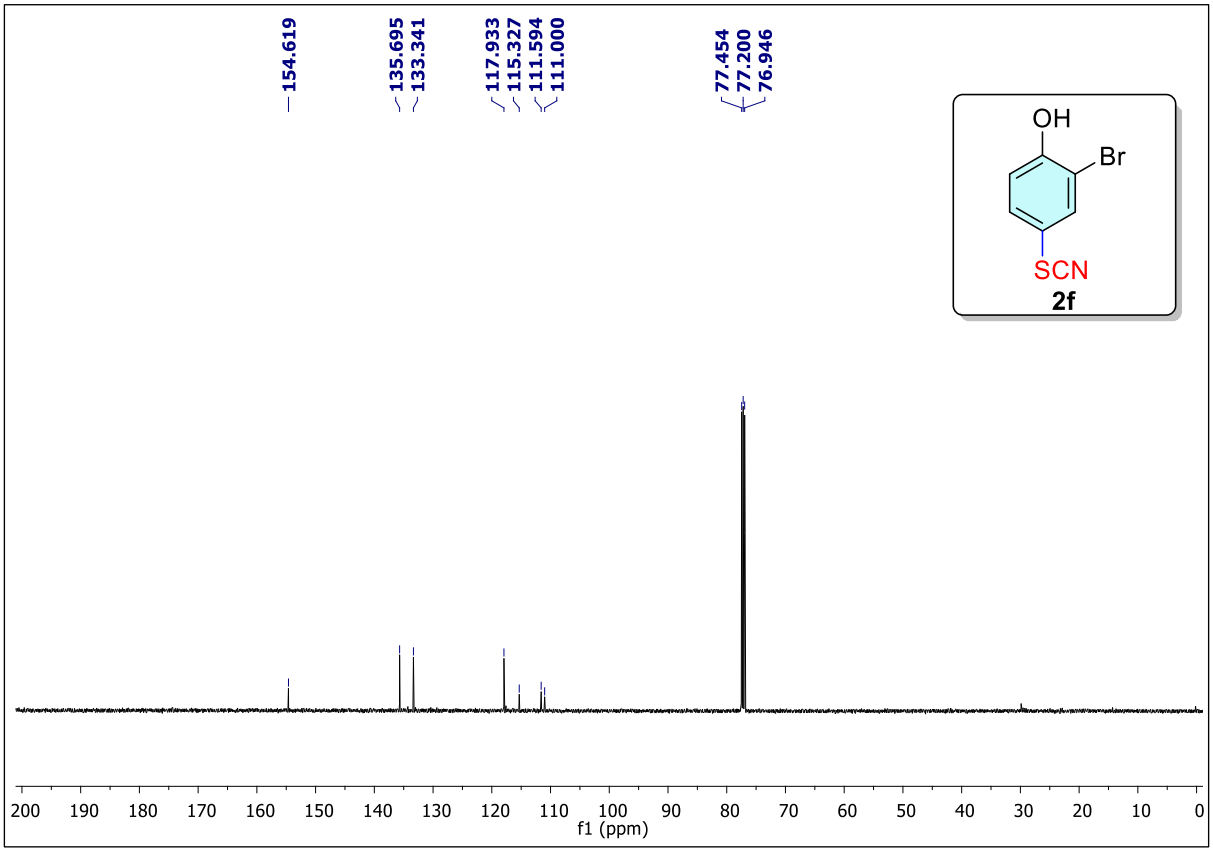

$^{1}$H NMR of **2e** (400 MHz, $CDCl_3$)



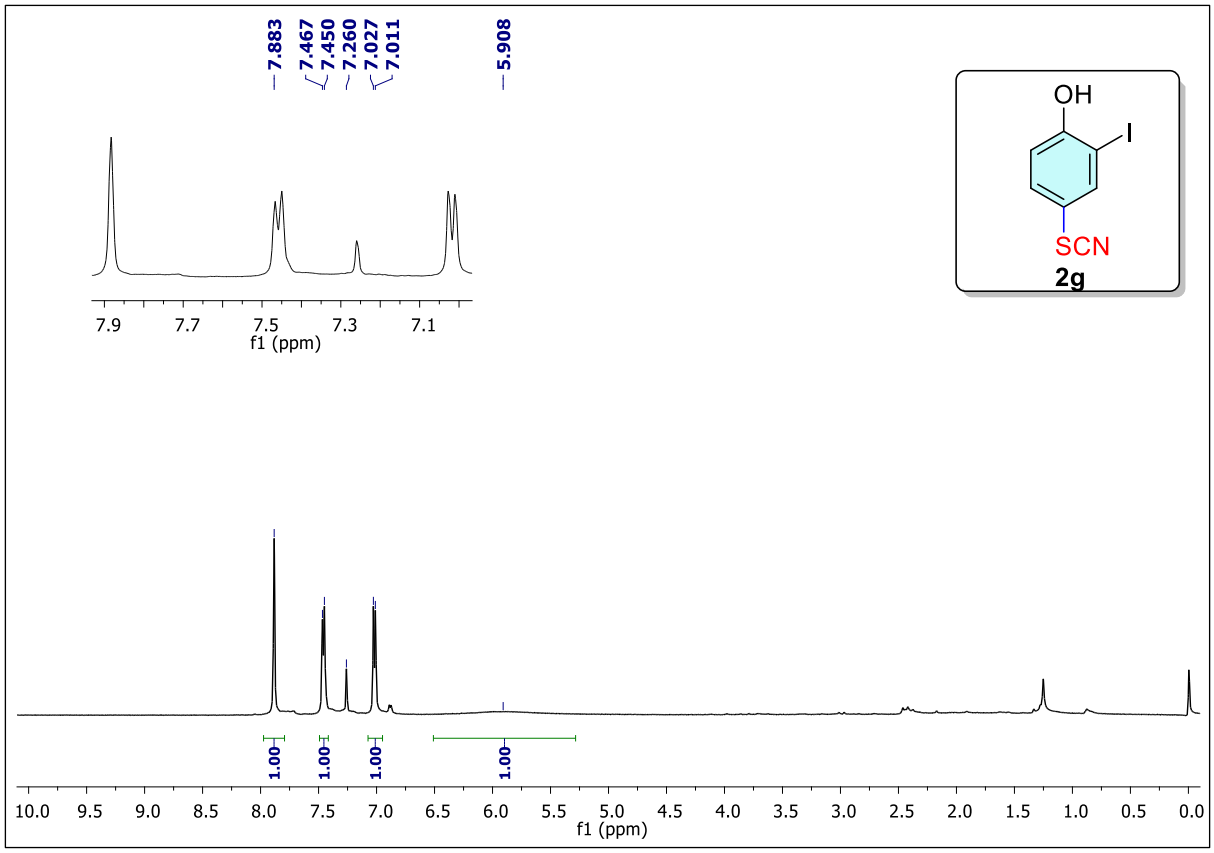

$^{13}$C{$^{1}$H} NMR of **2e** (125 MHz, $CDCl_3$)



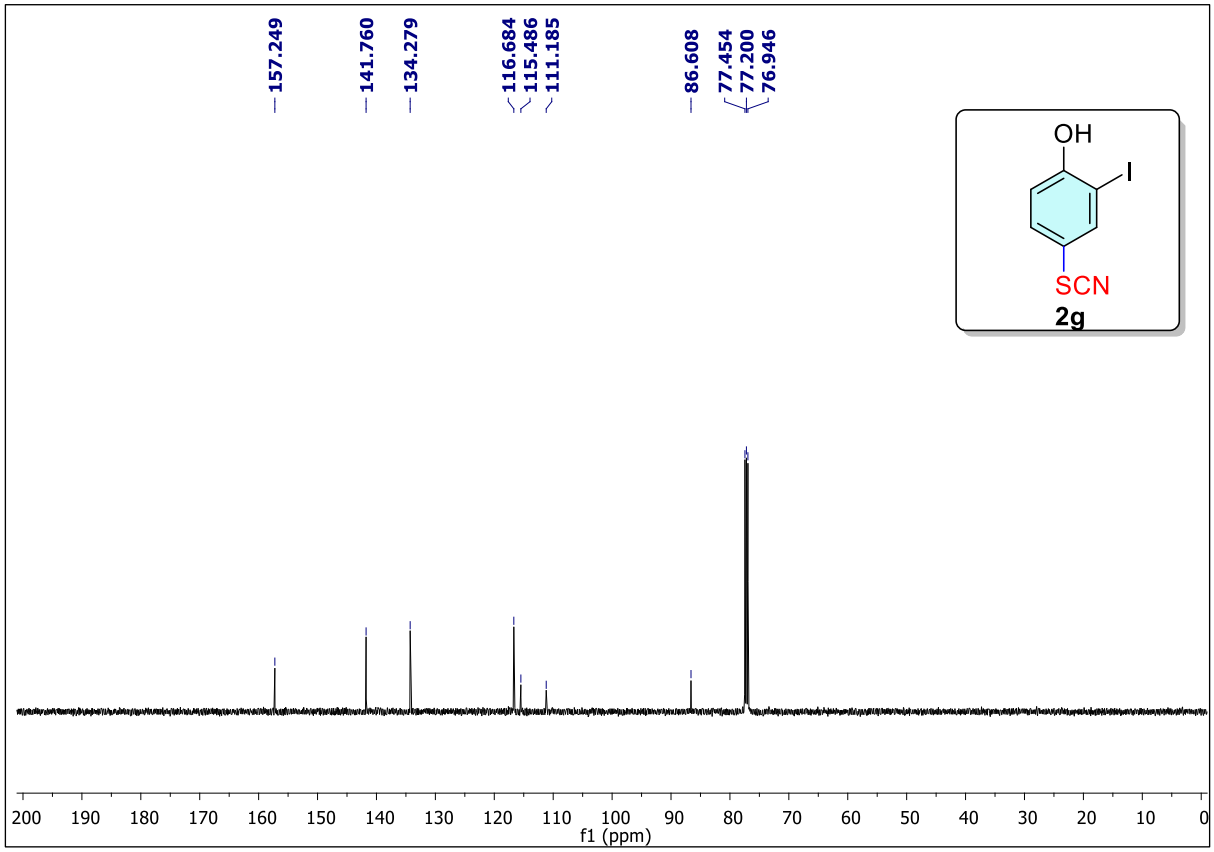

$^{1}$H NMR of **2f** (400 MHz, $CDCl_3$)



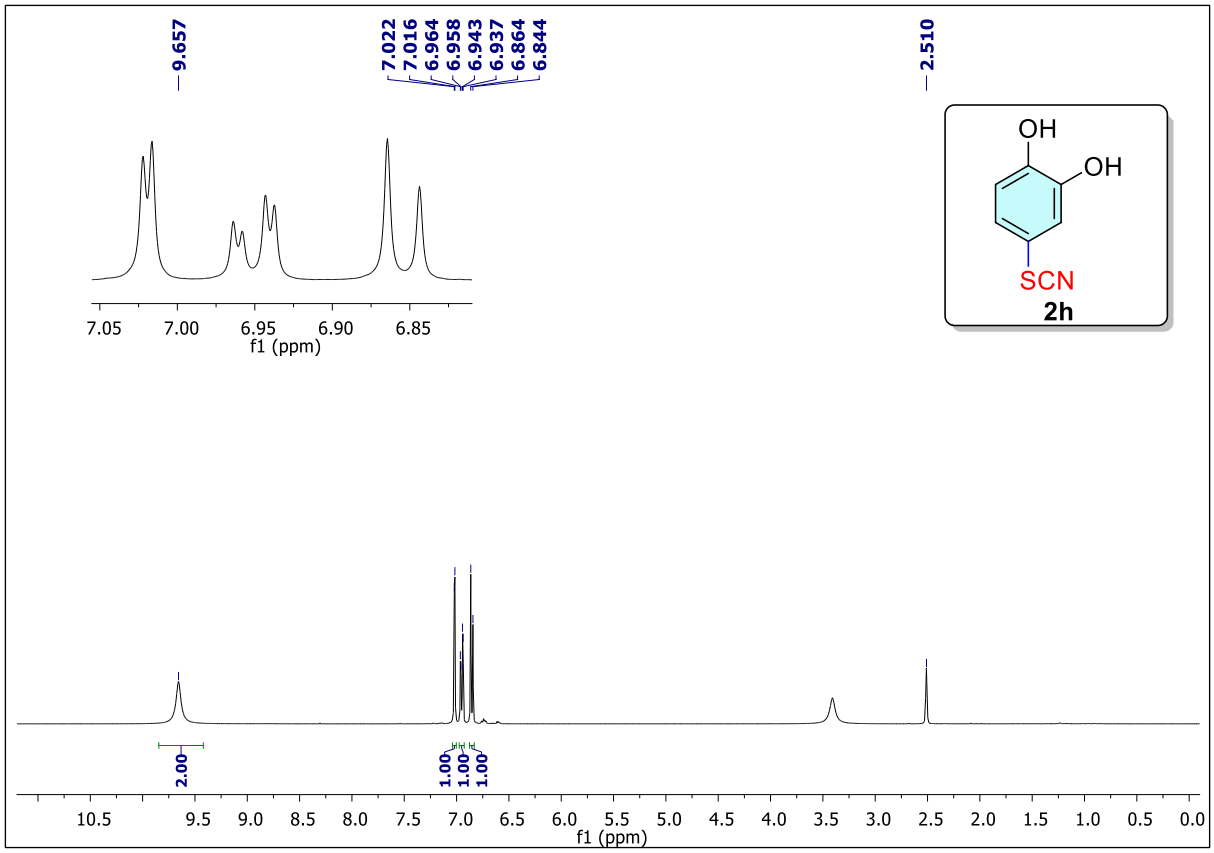

$^{13}$C{$^{1}$H} NMR of **2f** (125 MHz, $CDCl_3$)



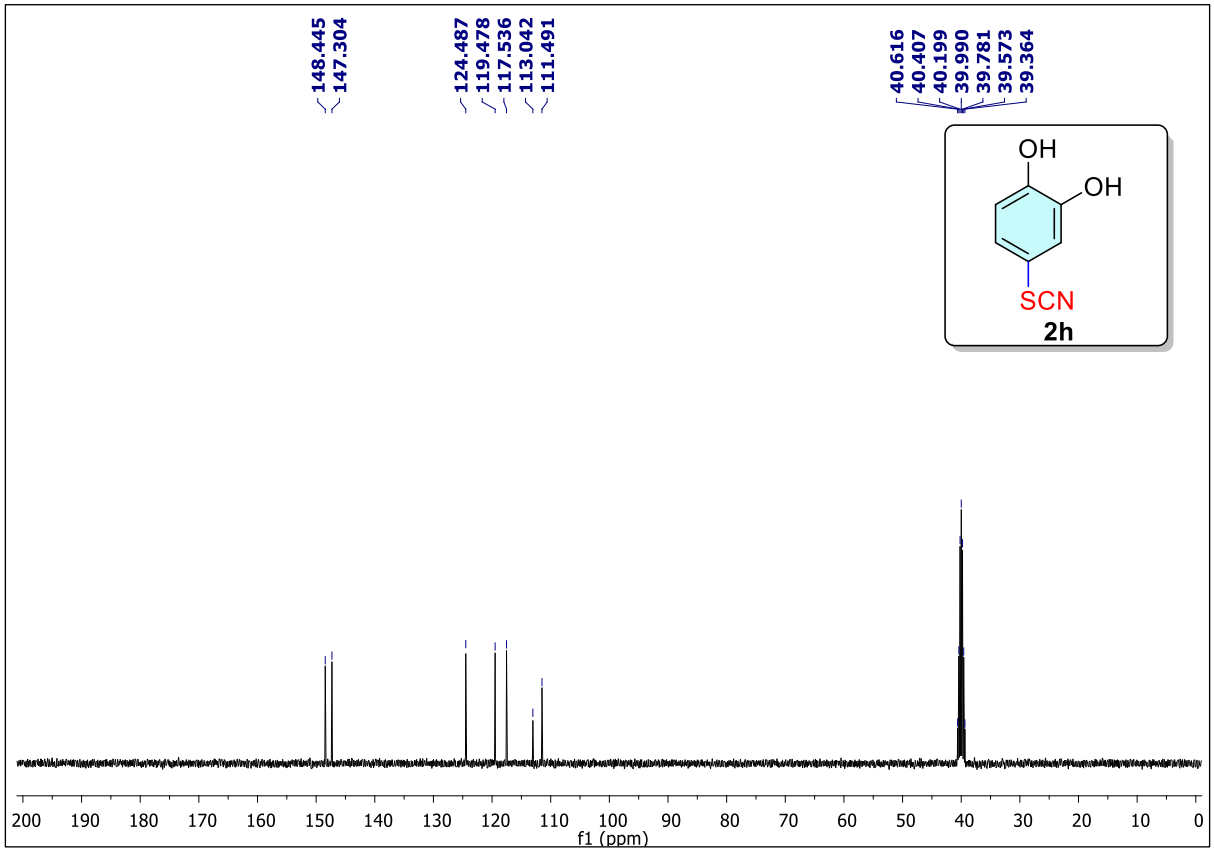

$^{1}$H NMR of **2g** (500 MHz, $CDCl_3$)



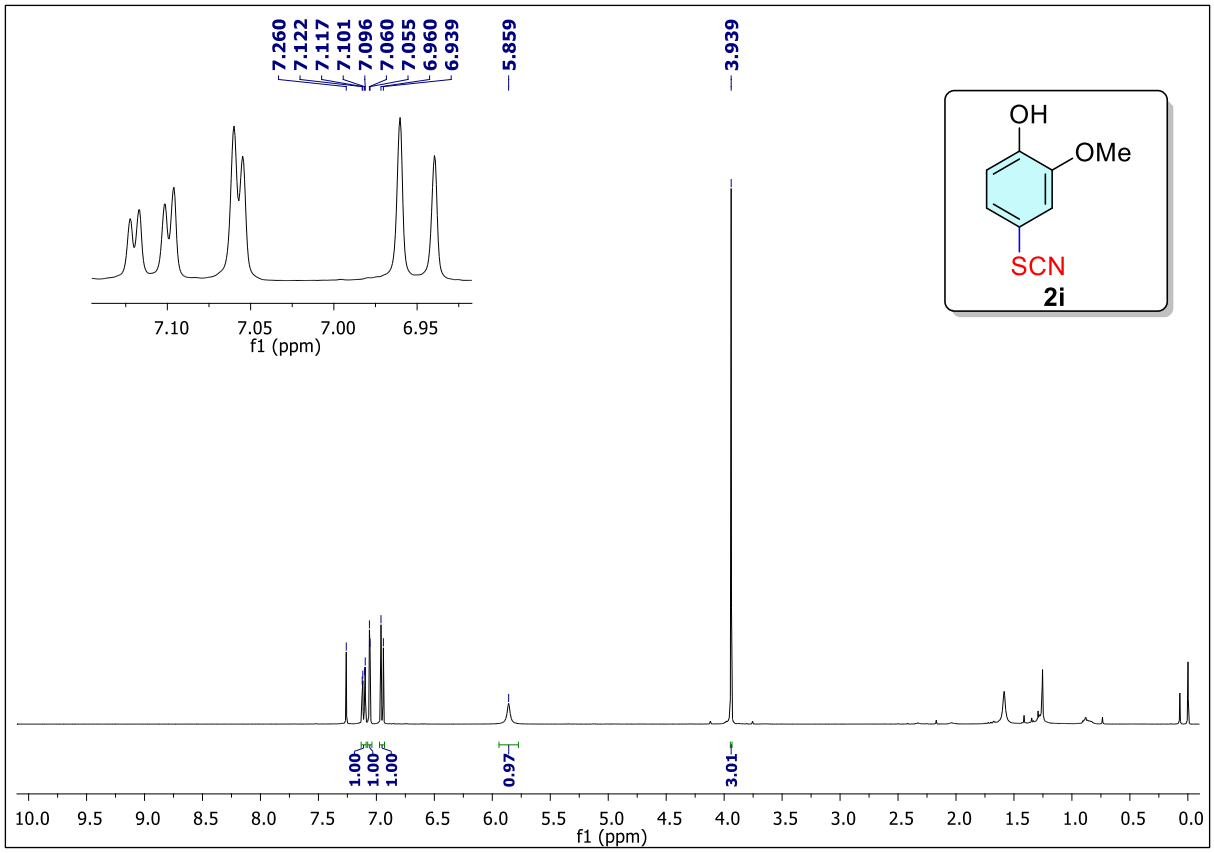

$^{13}$C{$^{1}$H} NMR of **2g** (125 MHz, $CDCl_3$)



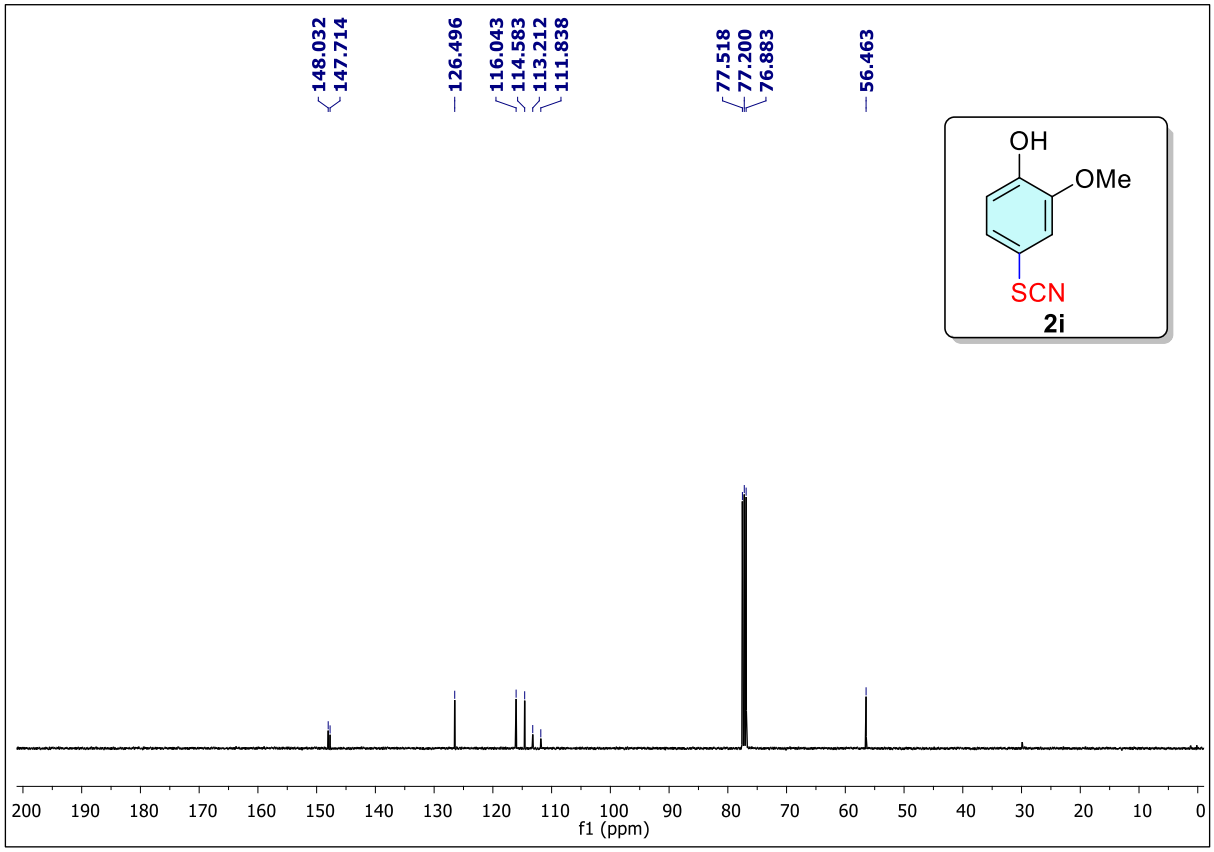

$^{1}$H NMR of **2h** (400 MHz, DMSO-$d_6$)



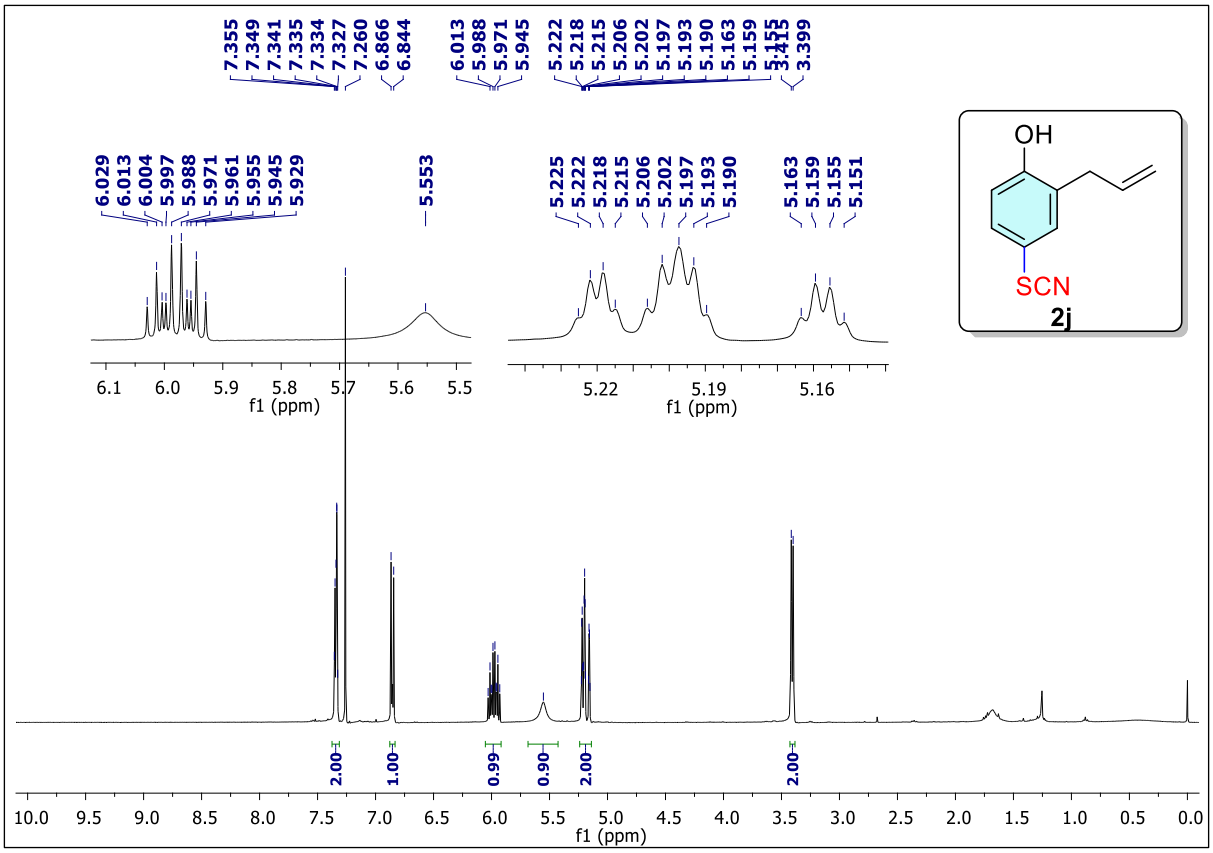

$^{13}$C{$^{1}$H} NMR of **2h** (100 MHz, DMSO-$d_6$)



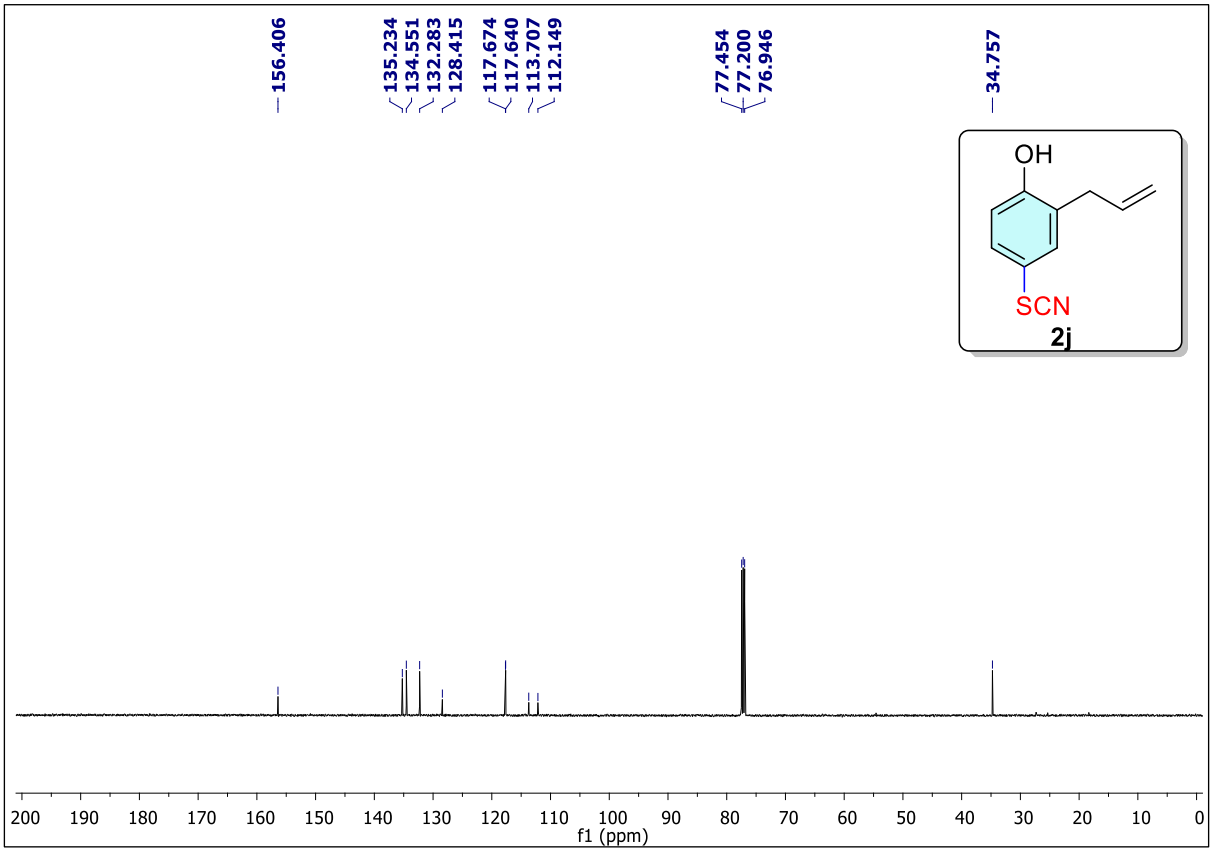

$^{1}$H NMR of **2i** (400 MHz, $CDCl_3$)



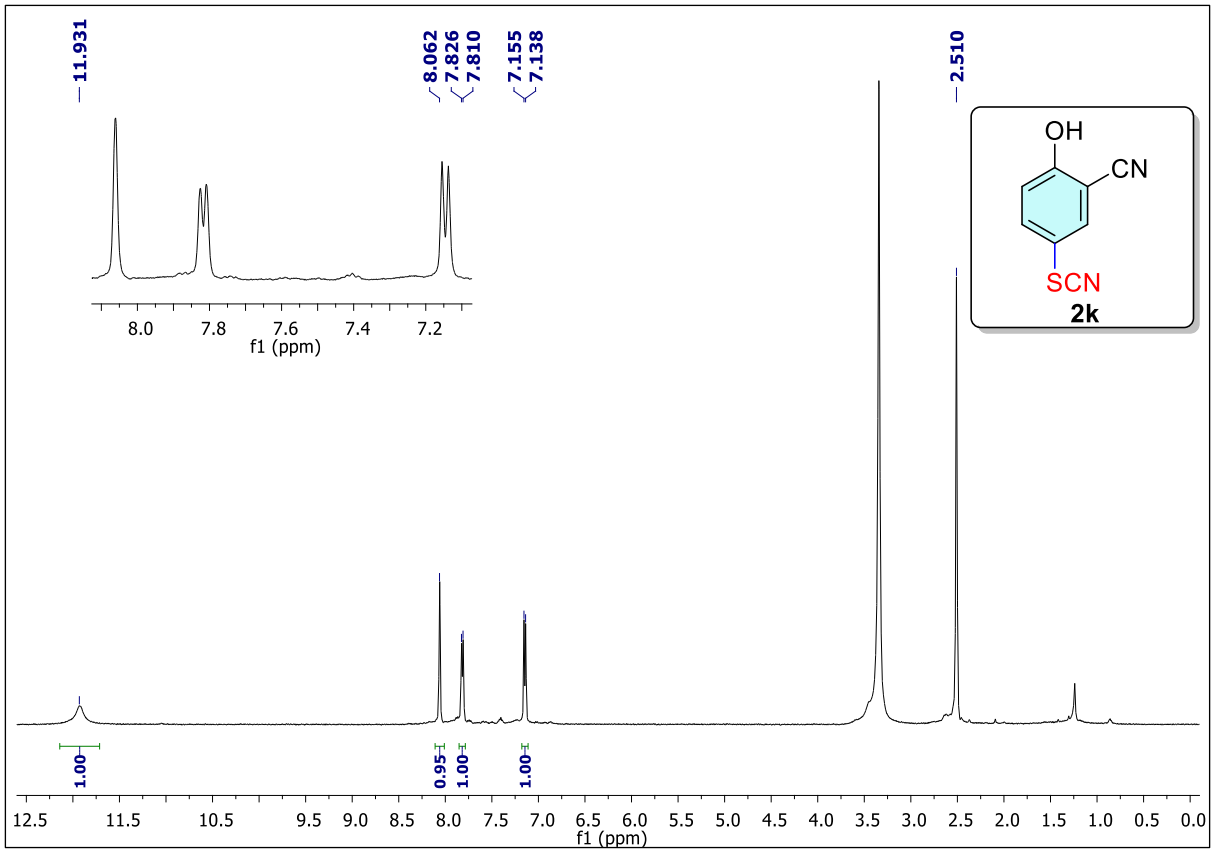

$^{13}$C{$^{1}$H} NMR of **2i** (100 MHz, $CDCl_3$)



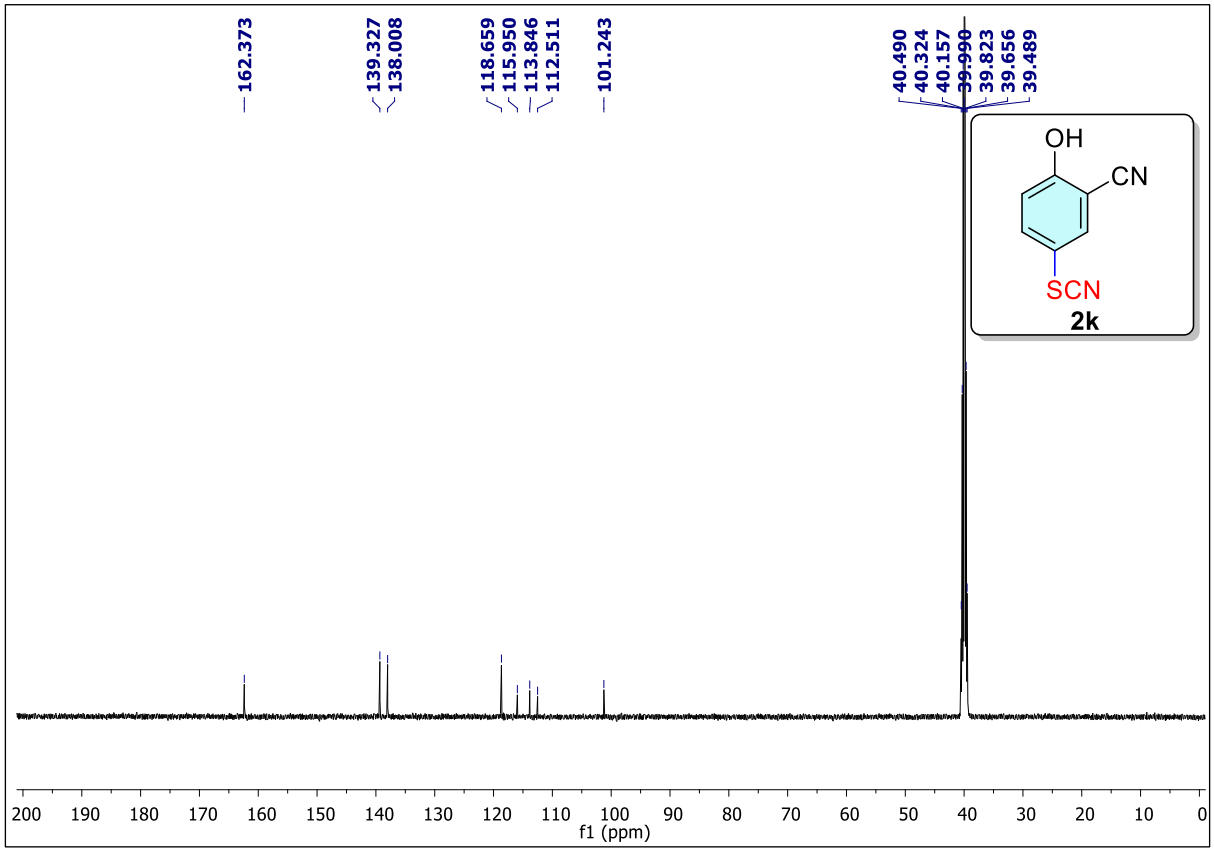

$^{1}$H NMR of **2j** (400 MHz, $CDCl_3$)



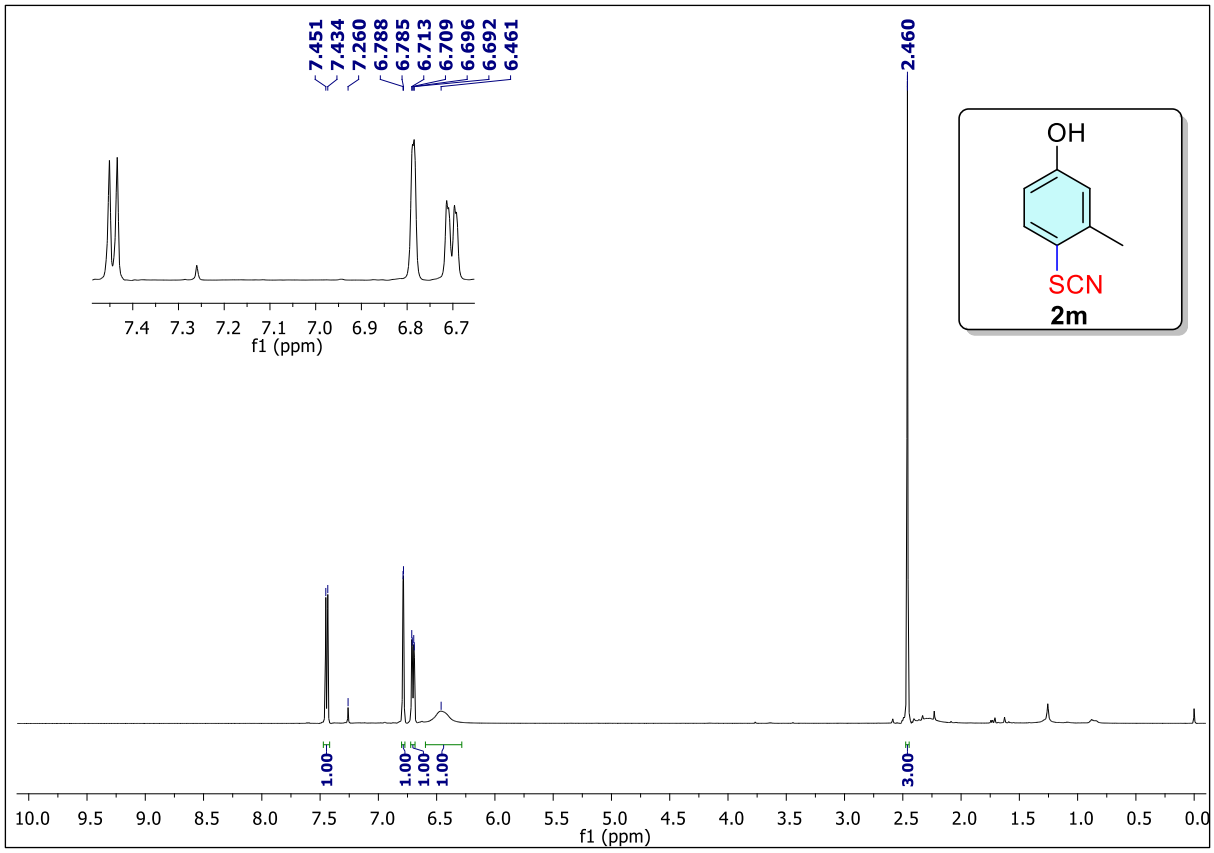

$^{13}$C{$^{1}$H} NMR of **2j** (125 MHz, $CDCl_3$)



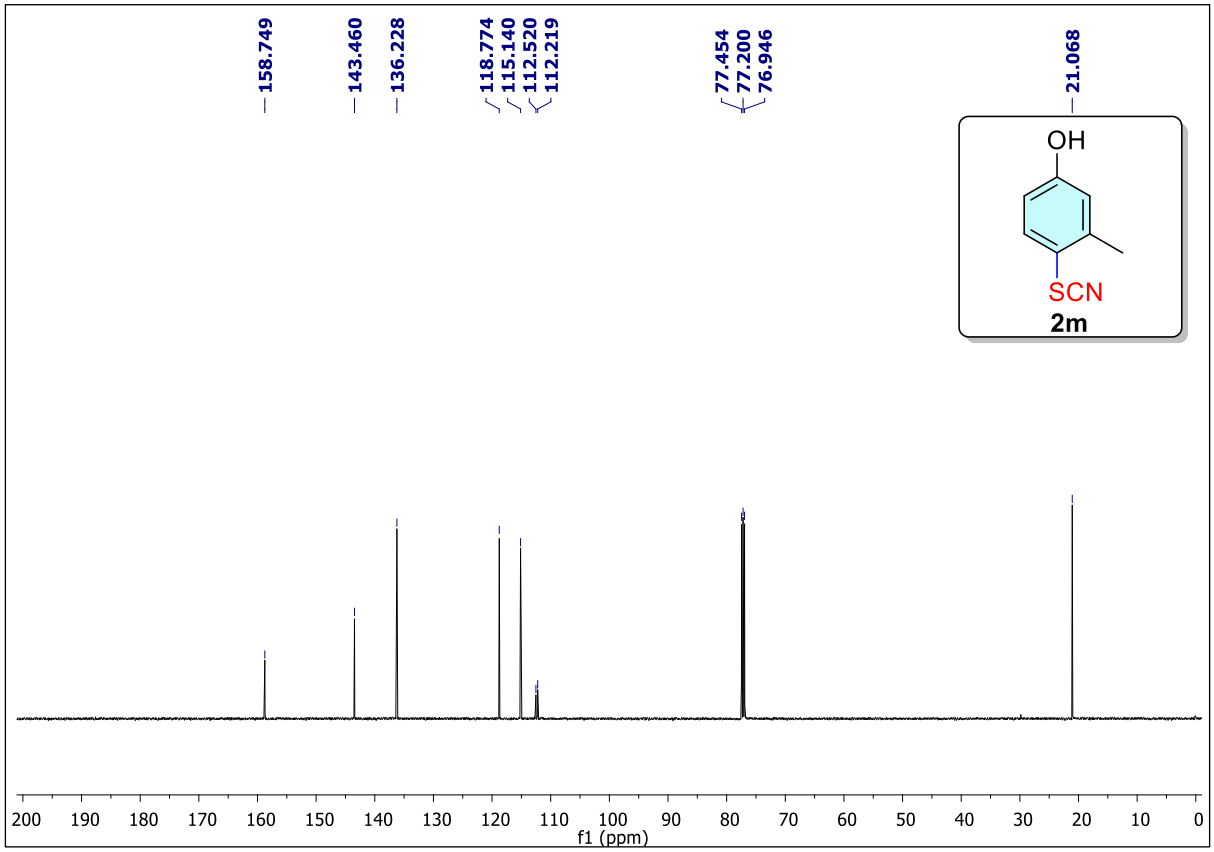

$^{1}$H NMR of **2k** (500 MHz, DMSO-$d_6$)



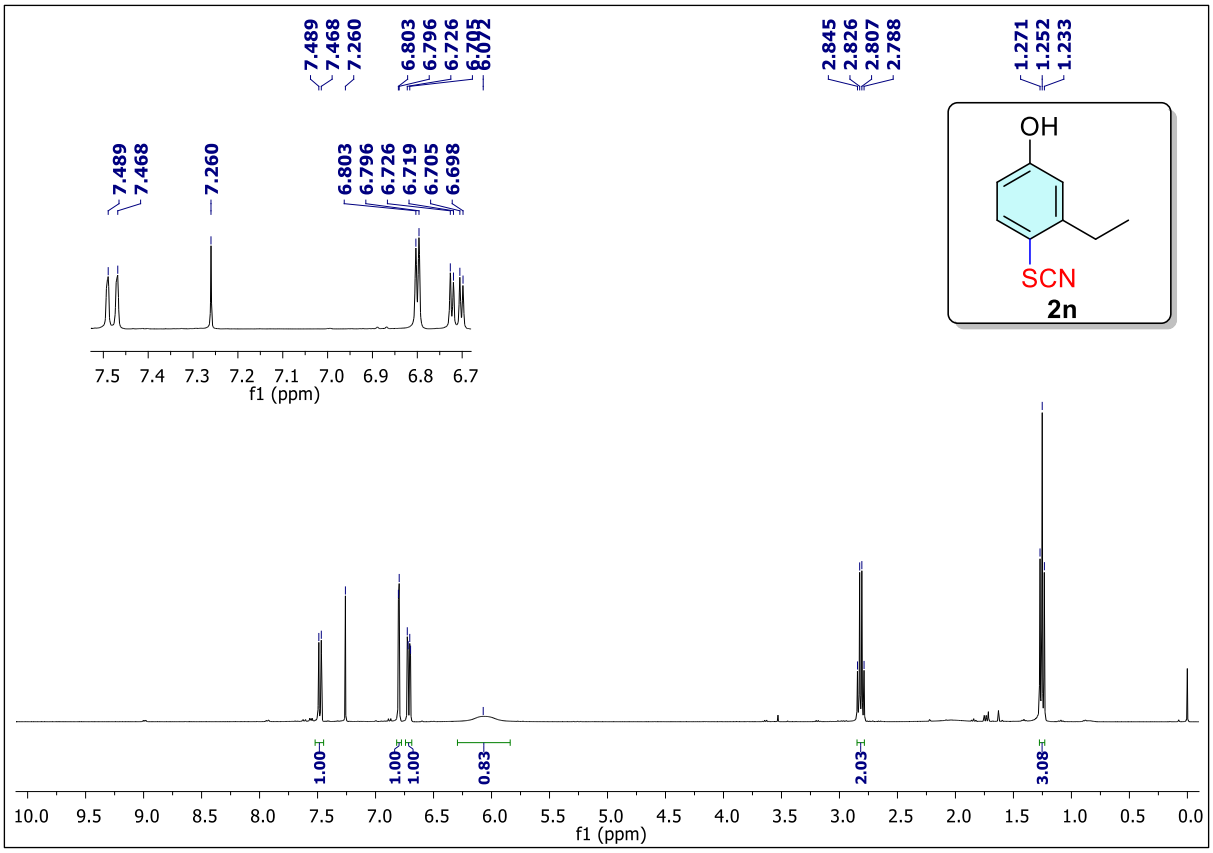

$^{13}$C{$^{1}$H} NMR of **2k** (125 MHz, DMSO-$d_6$)



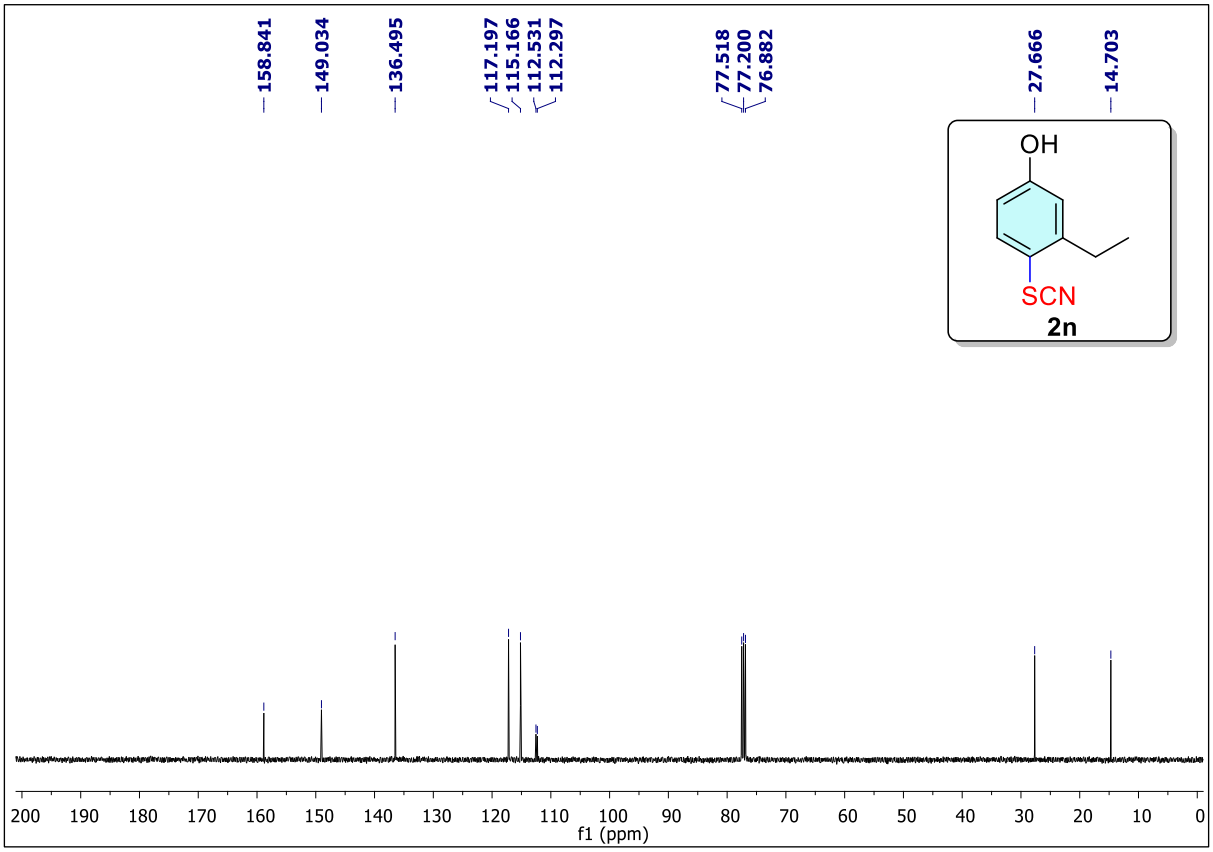

$^{1}$H NMR of **2m** (500 MHz, $CDCl_3$)



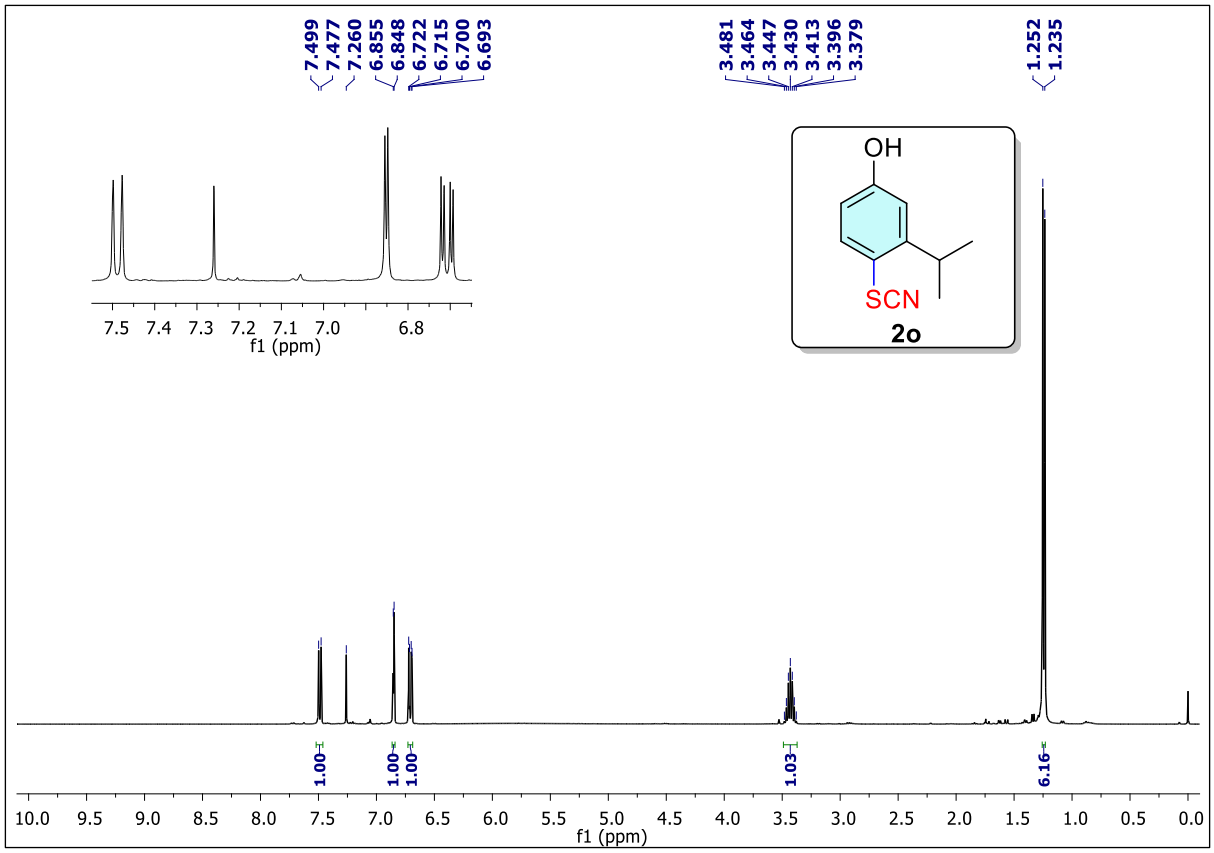

$^{13}$C{$^{1}$H} NMR of **2m** (125 MHz, $CDCl_3$)



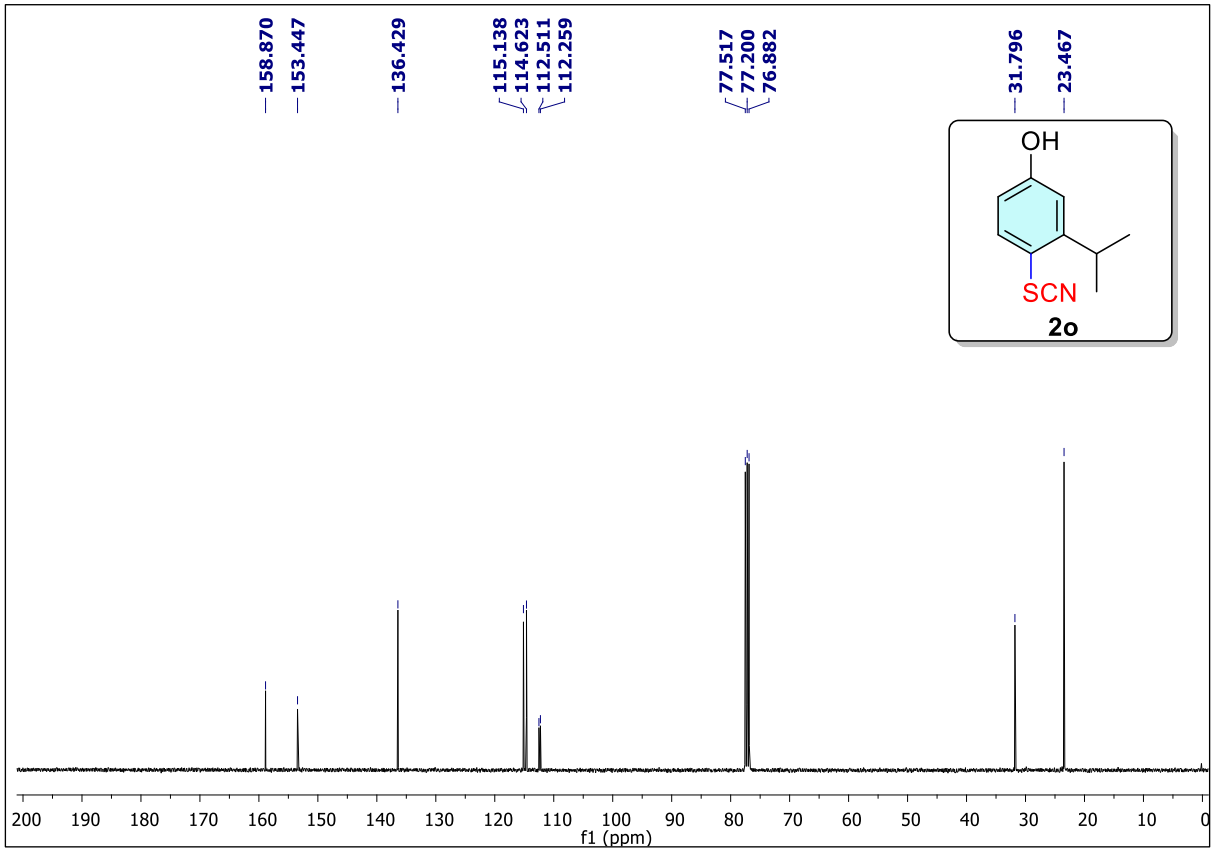

$^{1}$H NMR of **2n** (400 MHz, $CDCl_3$)



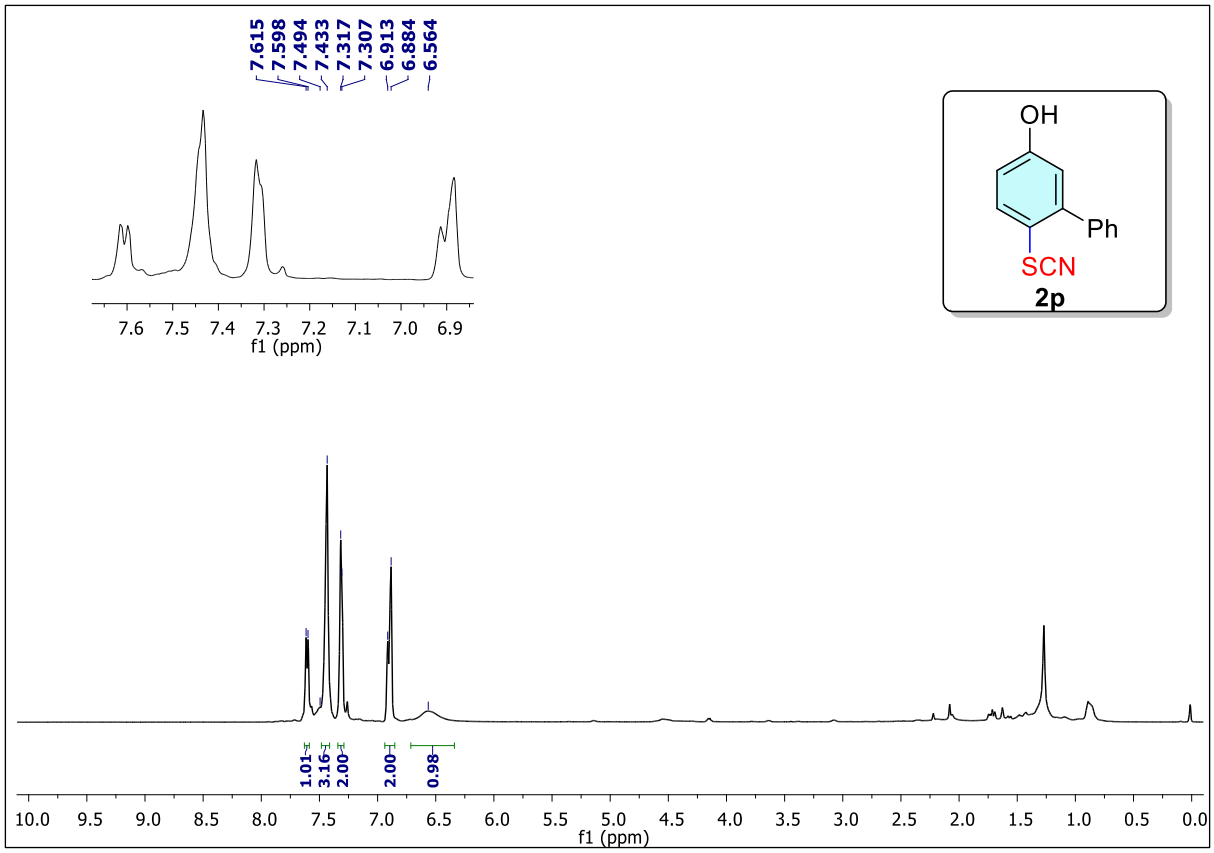

$^{13}$C{$^{1}$H} NMR of **2n** (100 MHz, $CDCl_3$)



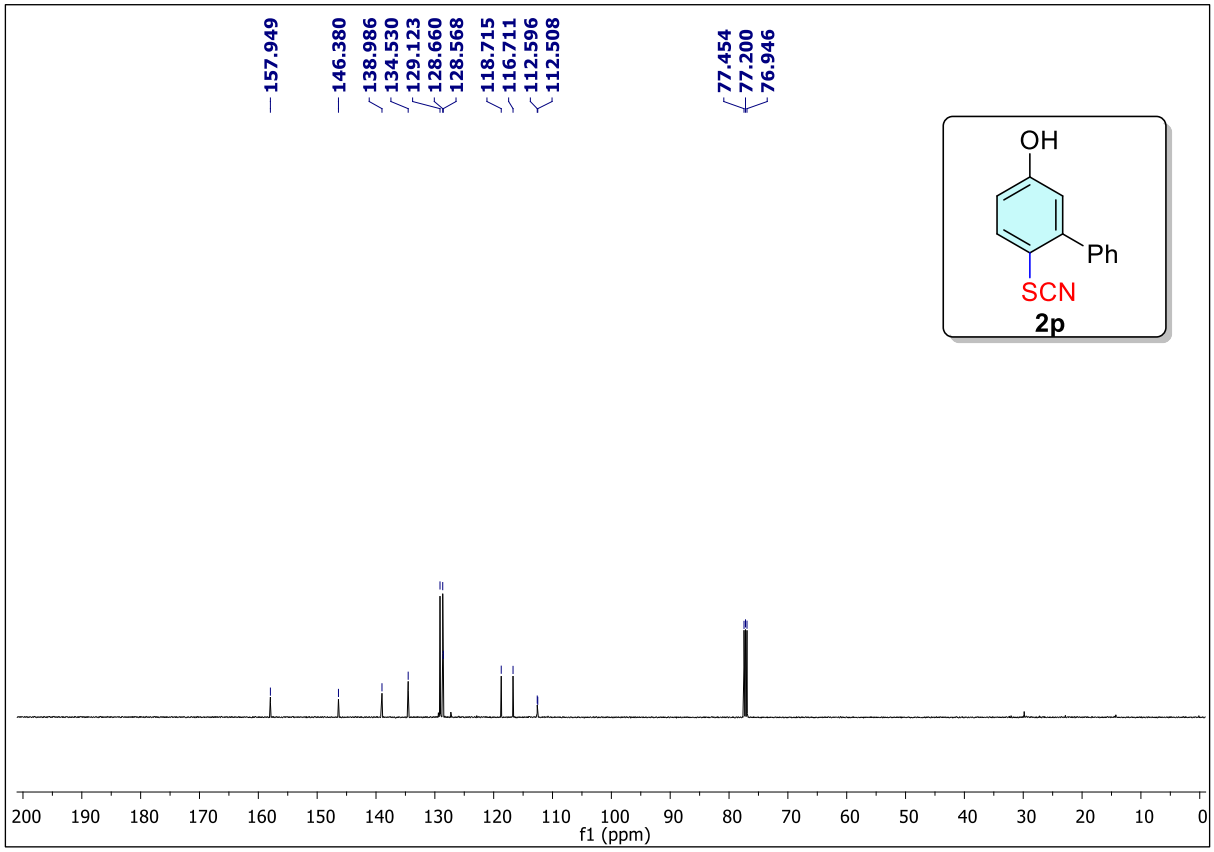

$^{1}$H NMR of **2o** (400 MHz, $CDCl_3$)



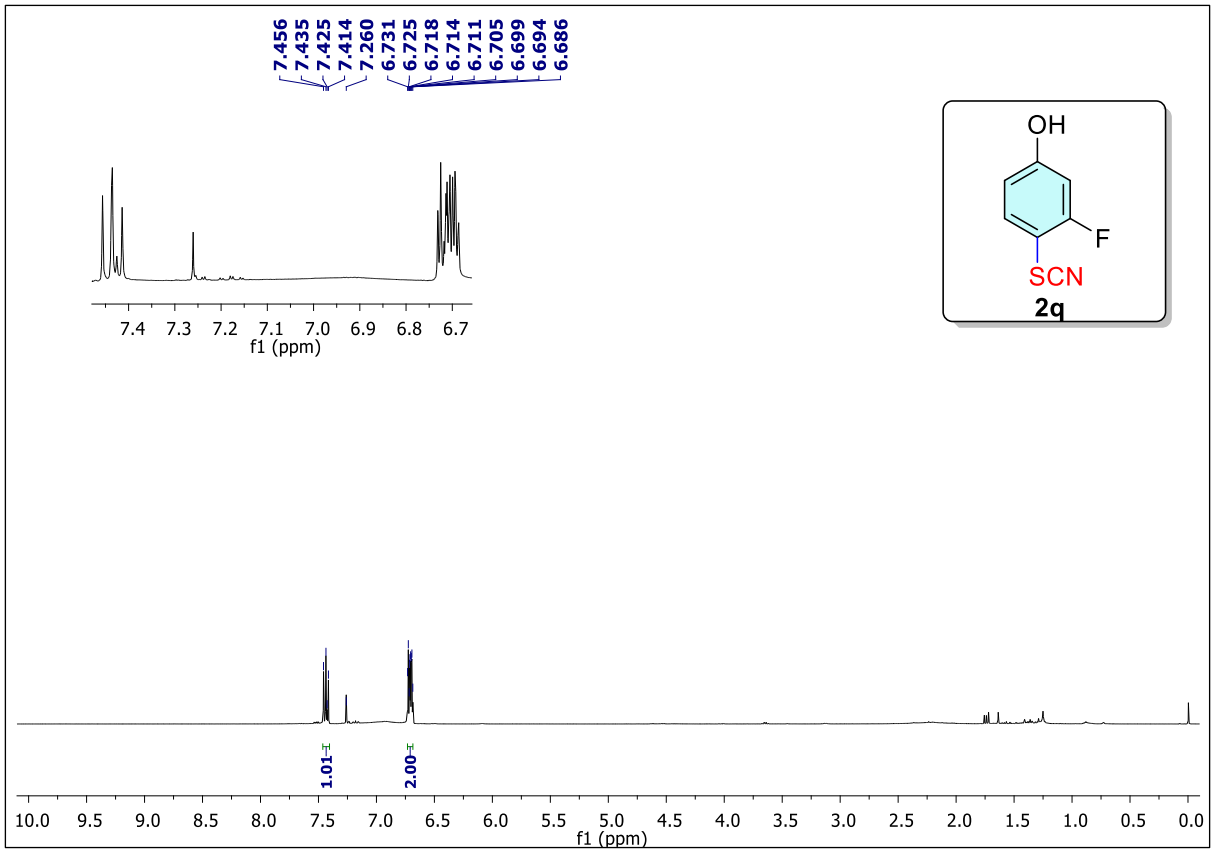

$^{13}$C{$^{1}$H} NMR of **2o** (100 MHz, $CDCl_3$)



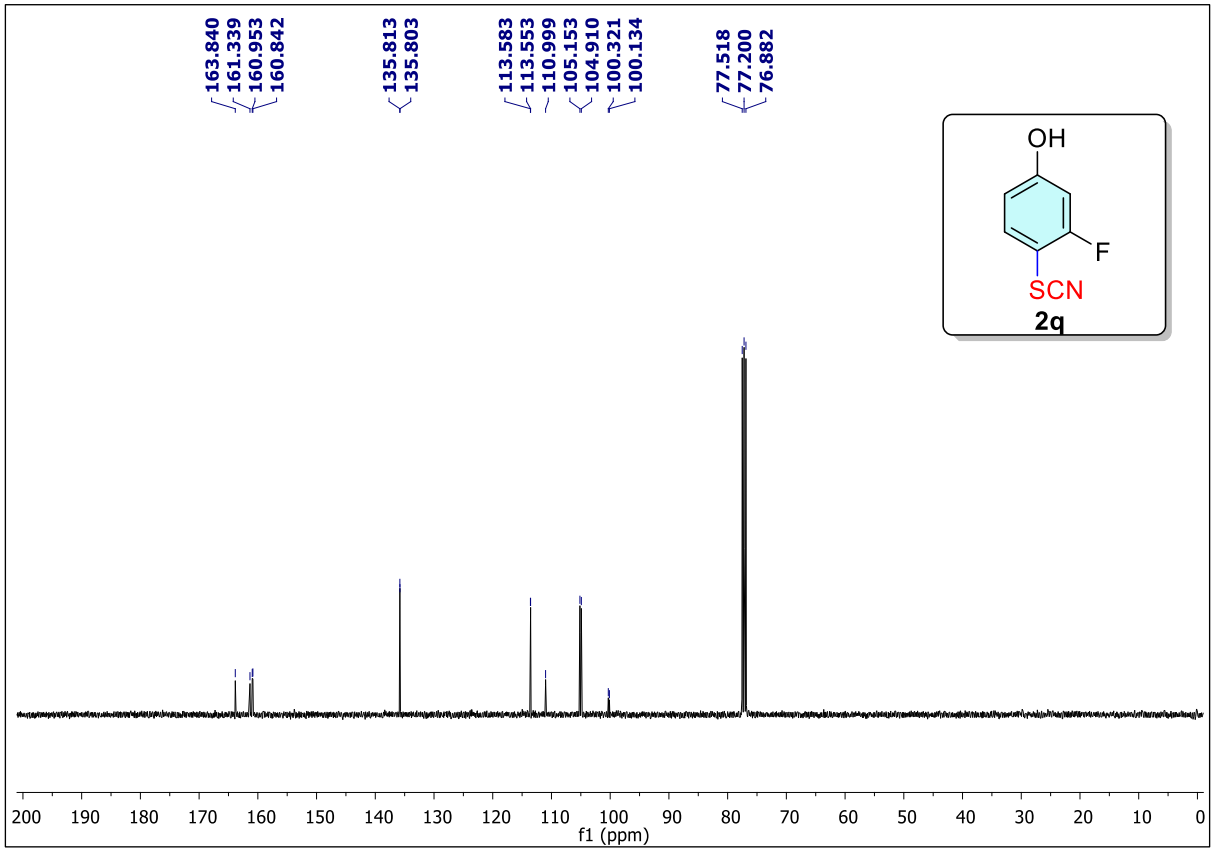

$^{1}$H NMR of **2p** (500 MHz, $CDCl_3$)



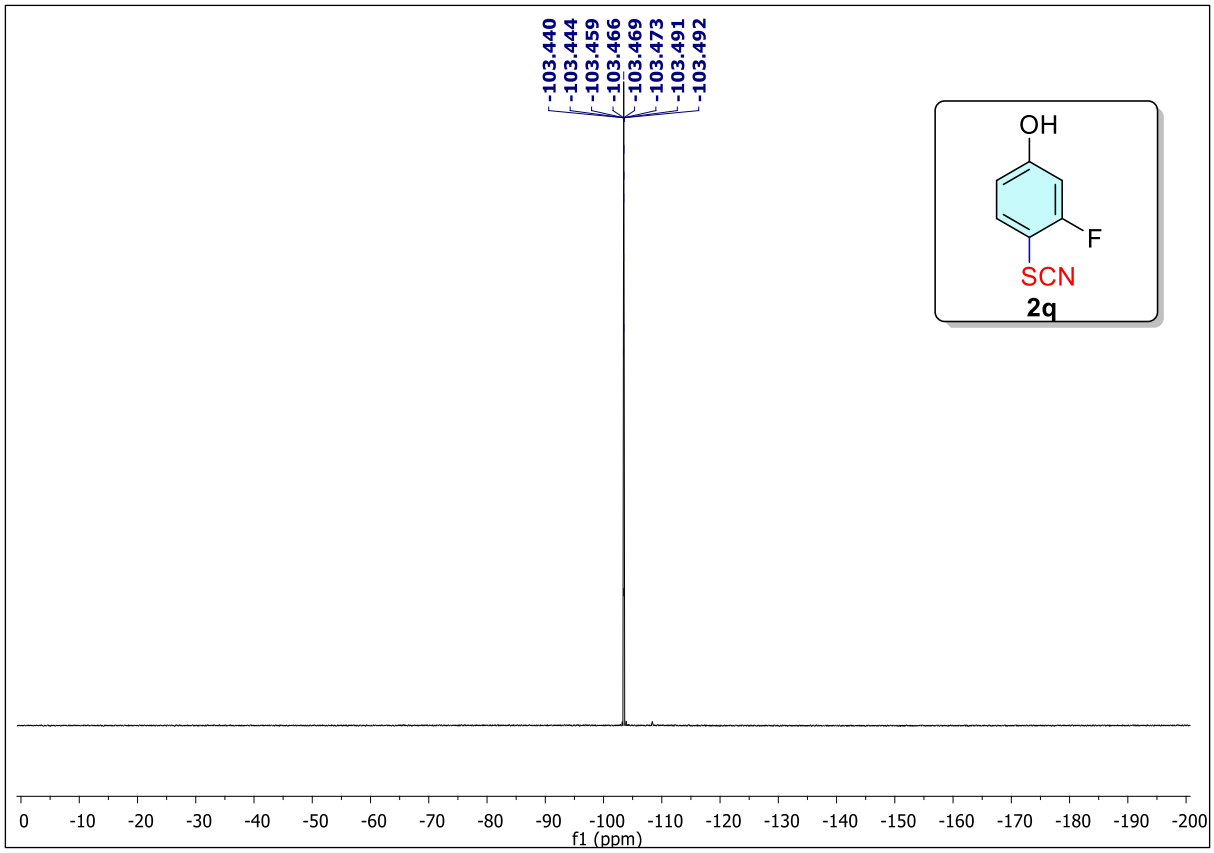

$^{13}$C{$^{1}$H} NMR of **2p** (125 MHz, $CDCl_3$)



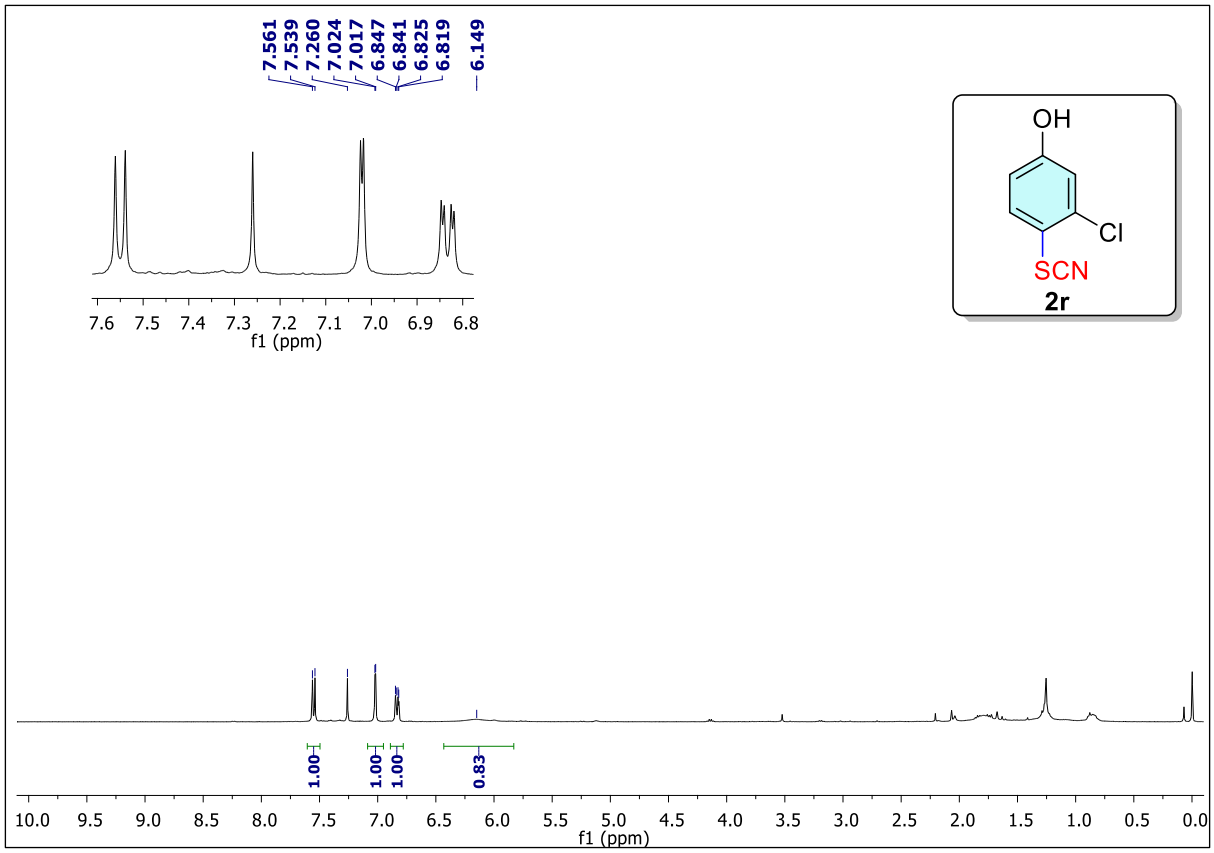

$^{1}$H NMR of **2q** (400 MHz, $CDCl_3$)



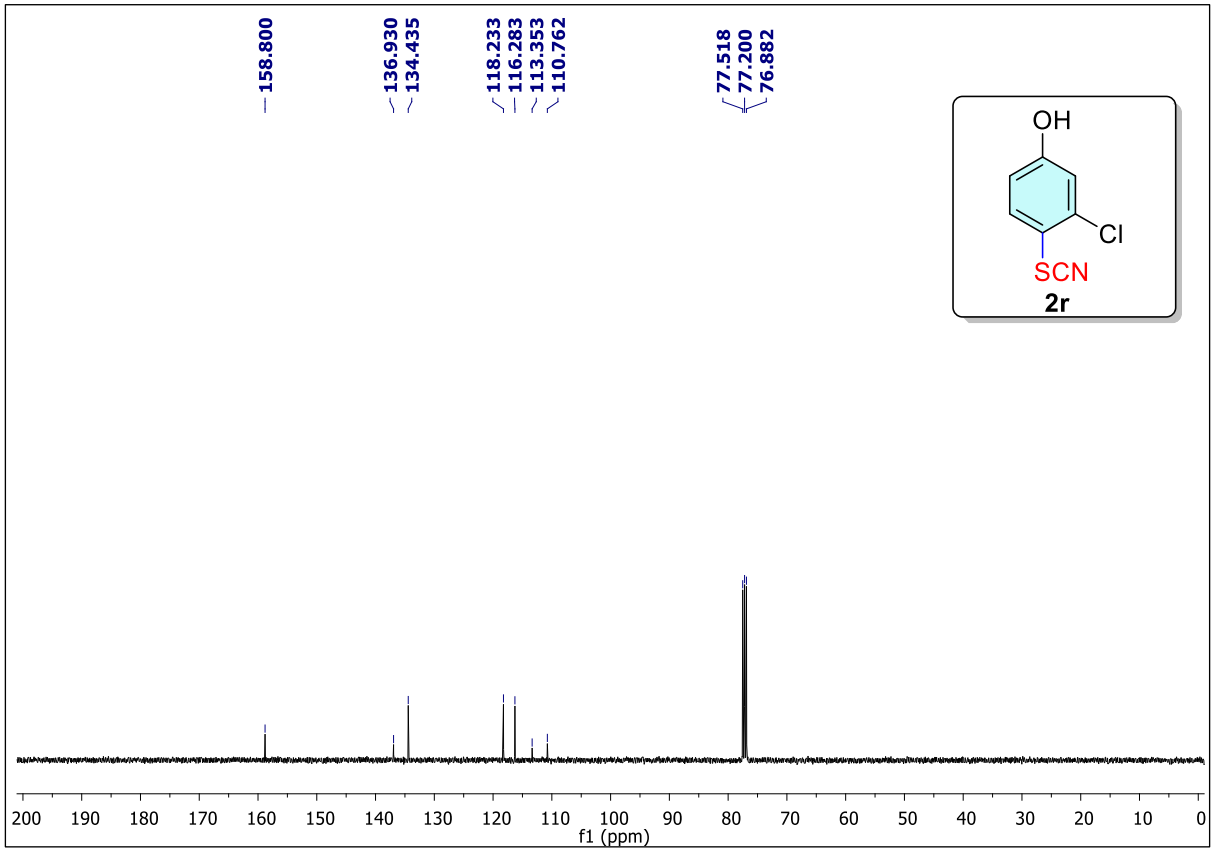

$^{13}$C{$^{1}$H} NMR of **2q** (100 MHz, $CDCl_3$)



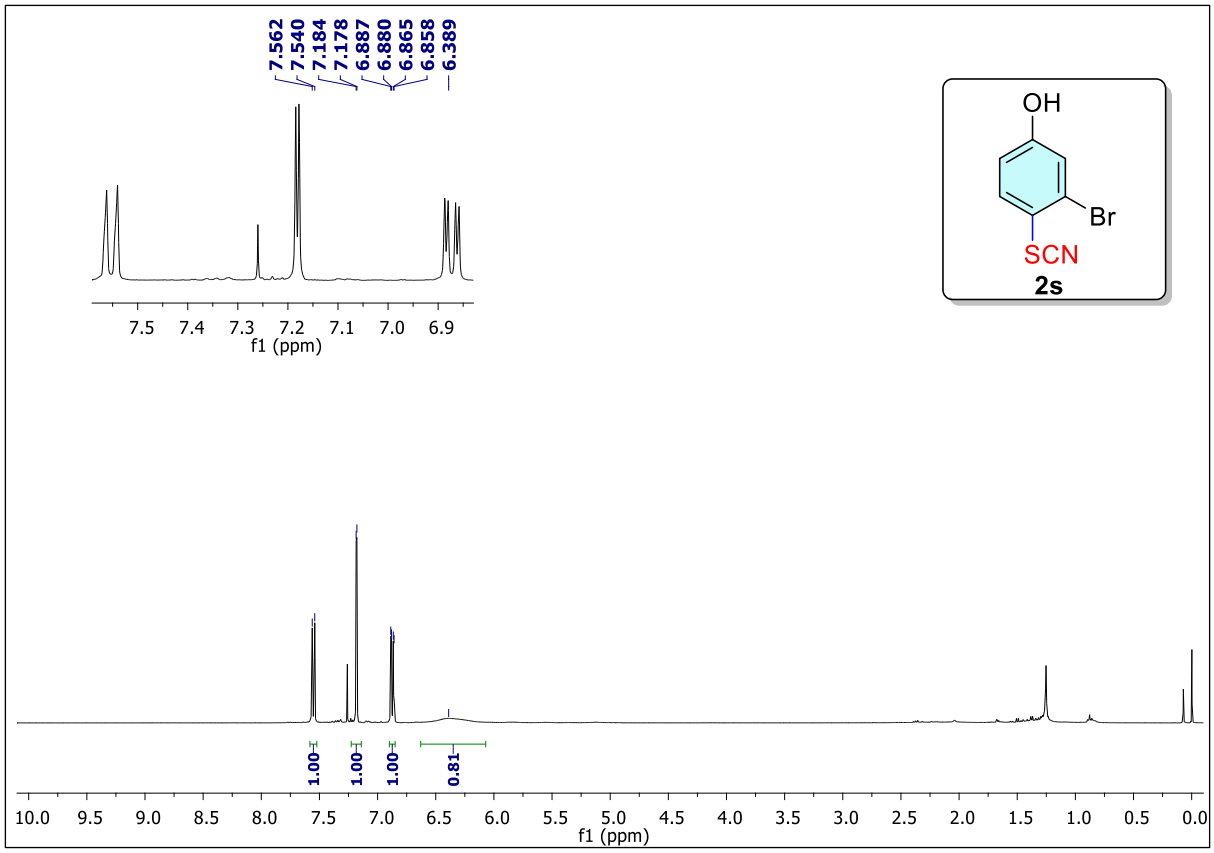

$^{19}$F NMR of **2q** (376 MHz, $CDCl_3$)



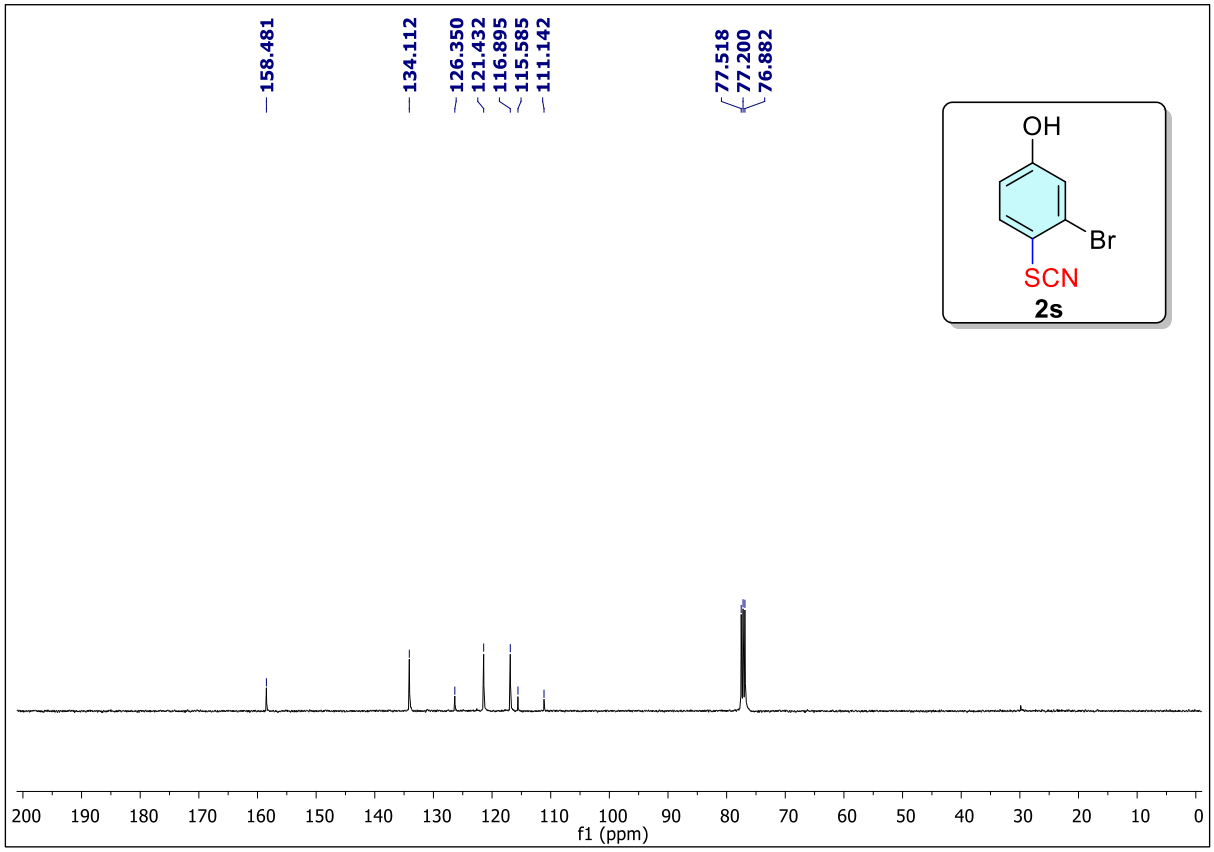

$^{1}$H NMR of **2r** (400 MHz, $CDCl_3$)



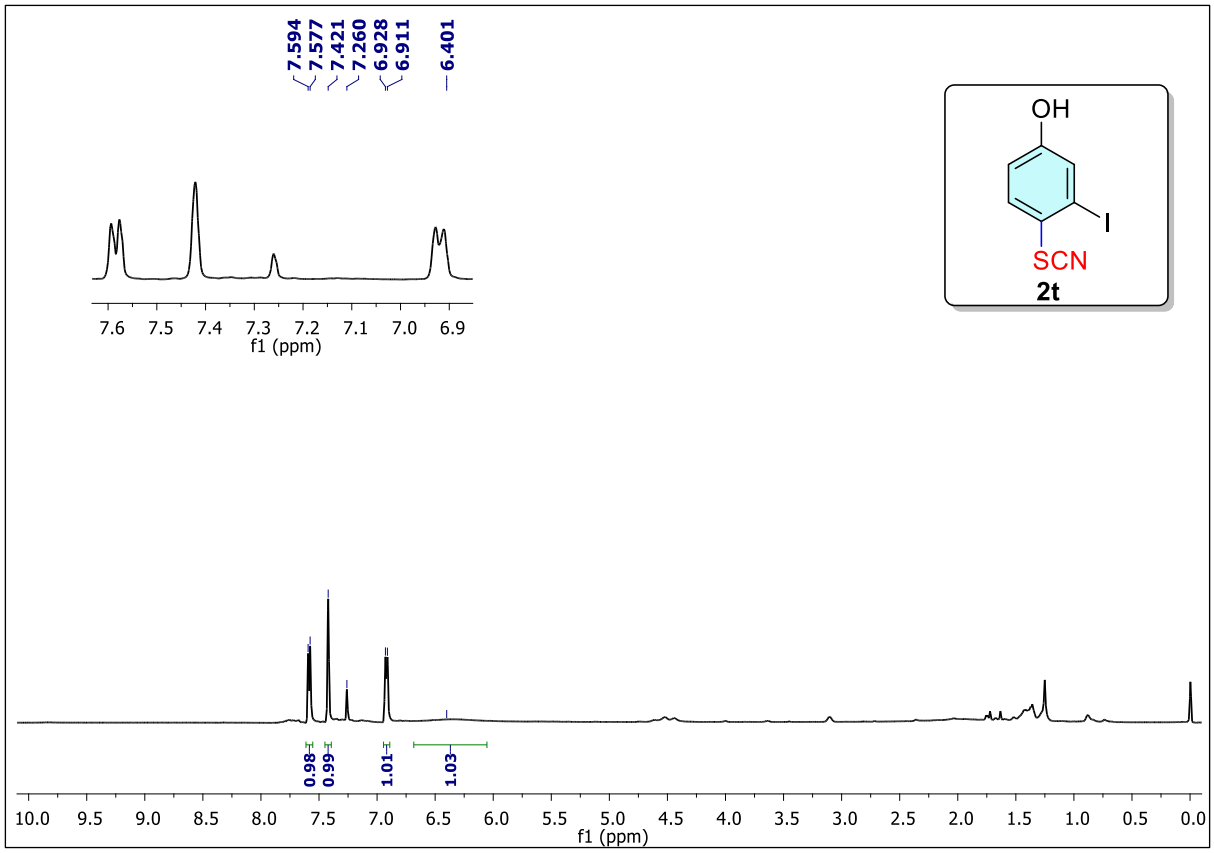

$^{13}$C{$^{1}$H} NMR of **2r** (100 MHz, $CDCl_3$)



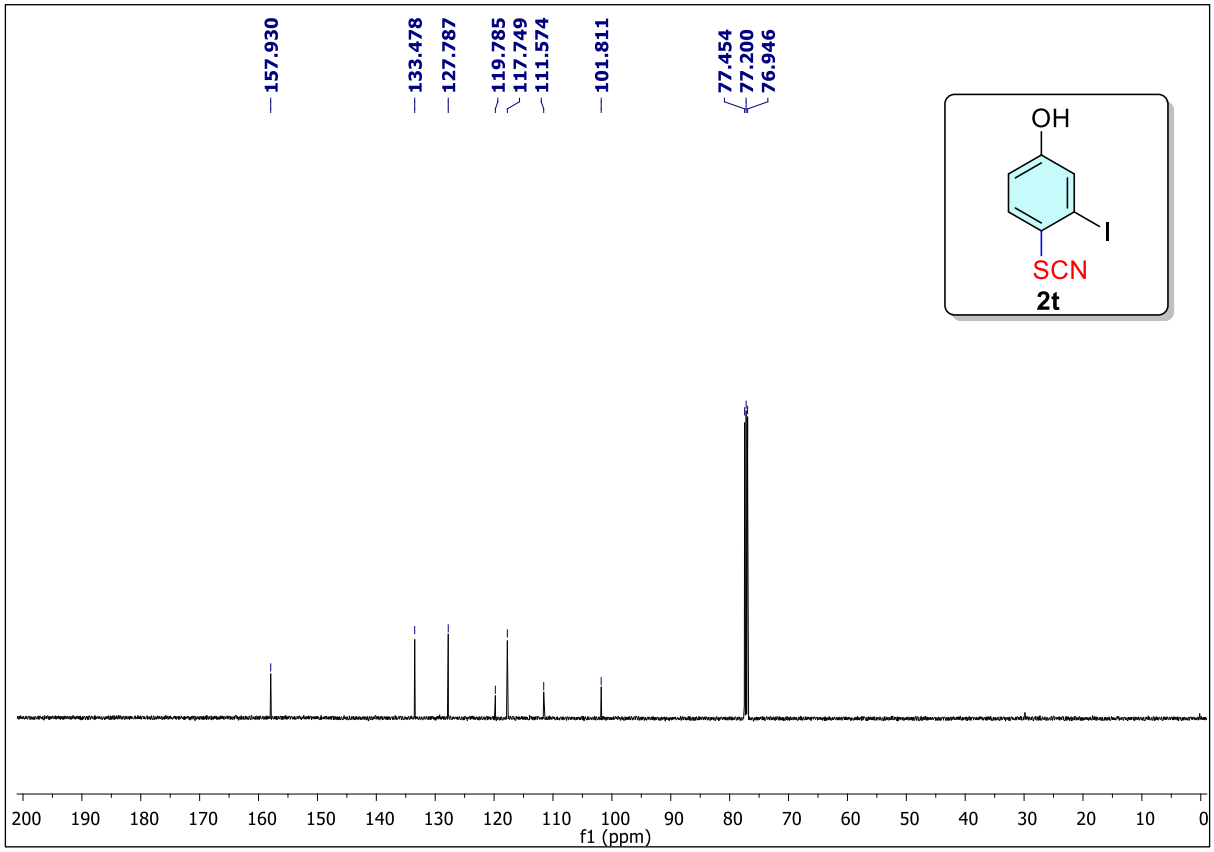

$^{1}$H NMR of **2s** (400 MHz, $CDCl_3$)



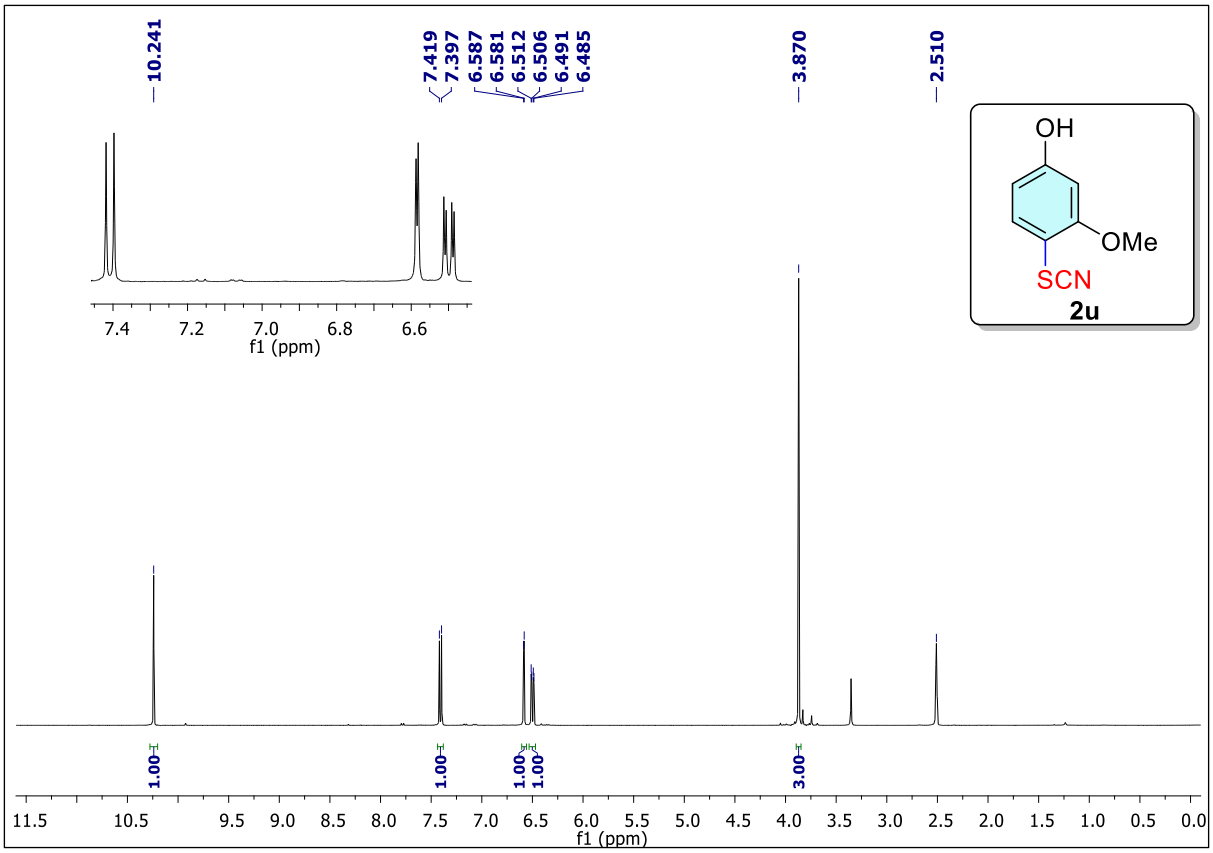

$^{13}$C{$^{1}$H} NMR of **2s** (100 MHz, $CDCl_3$)



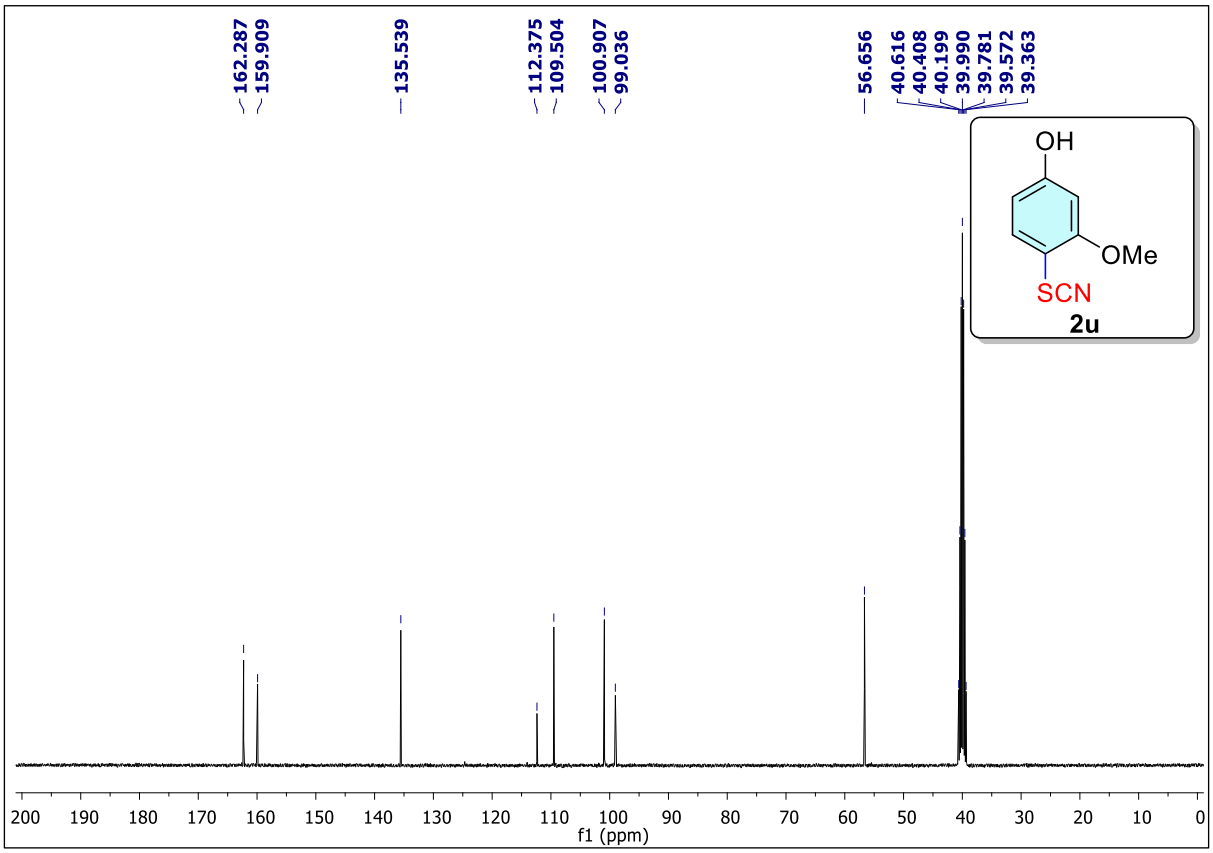

$^{1}$H NMR of **2t** (500 MHz, $CDCl_3$)



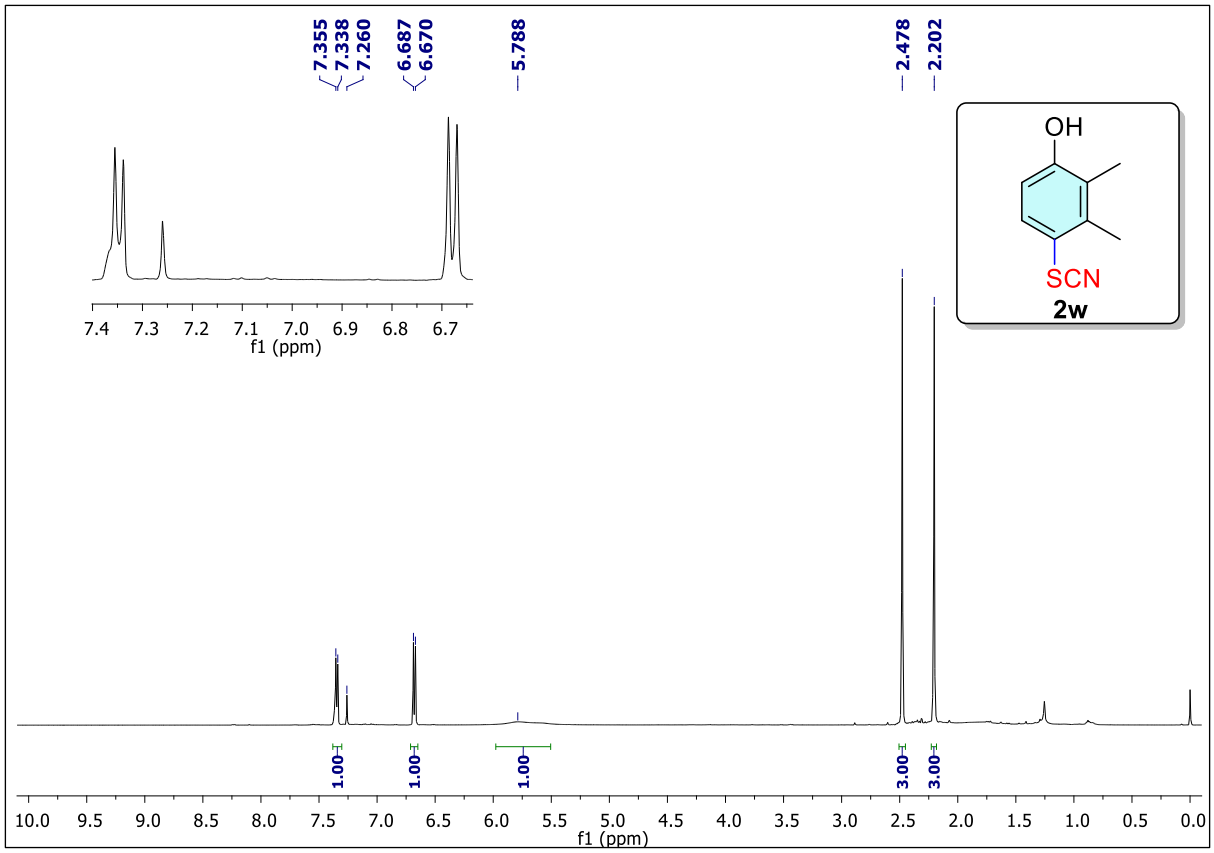

$^{13}$C{$^{1}$H} NMR of **2t** (125 MHz, $CDCl_3$)



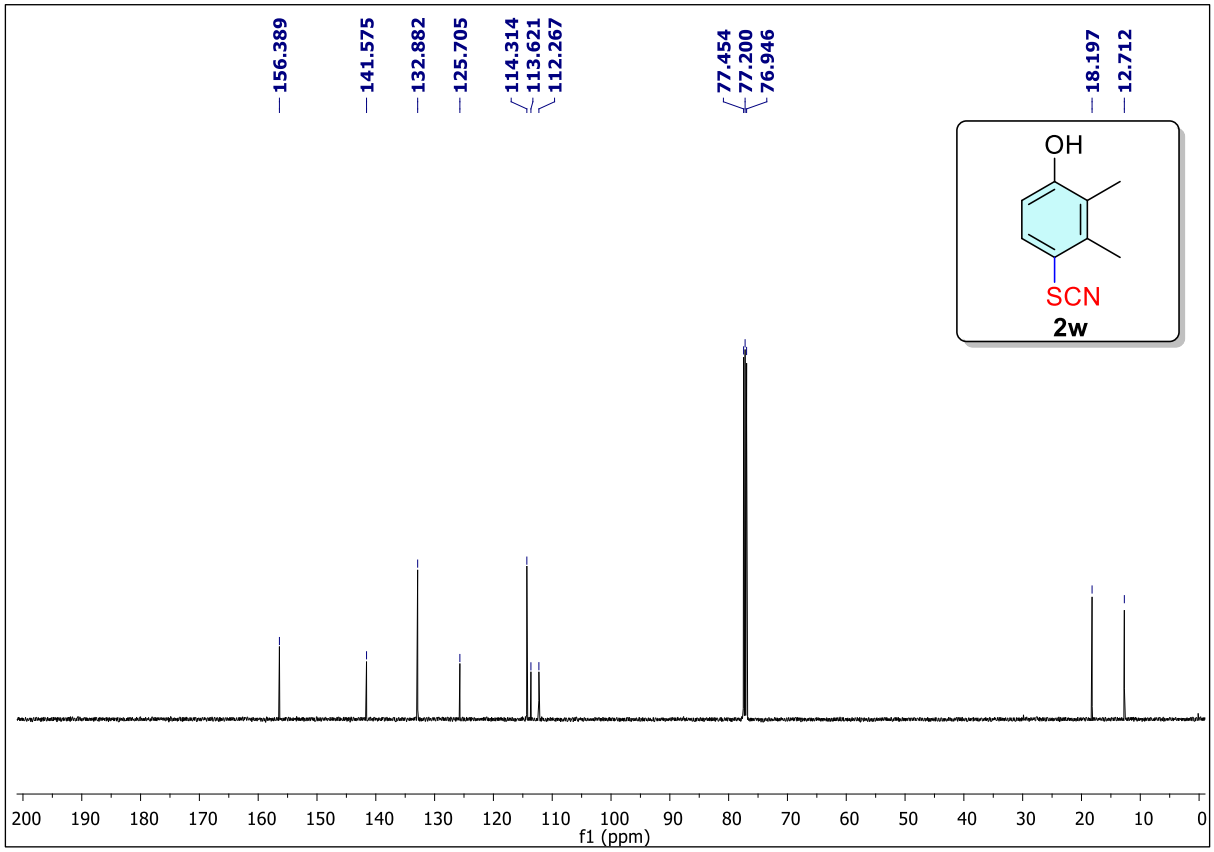

$^{1}$H NMR of **2u** (400 MHz, DMSO-$d_6$)



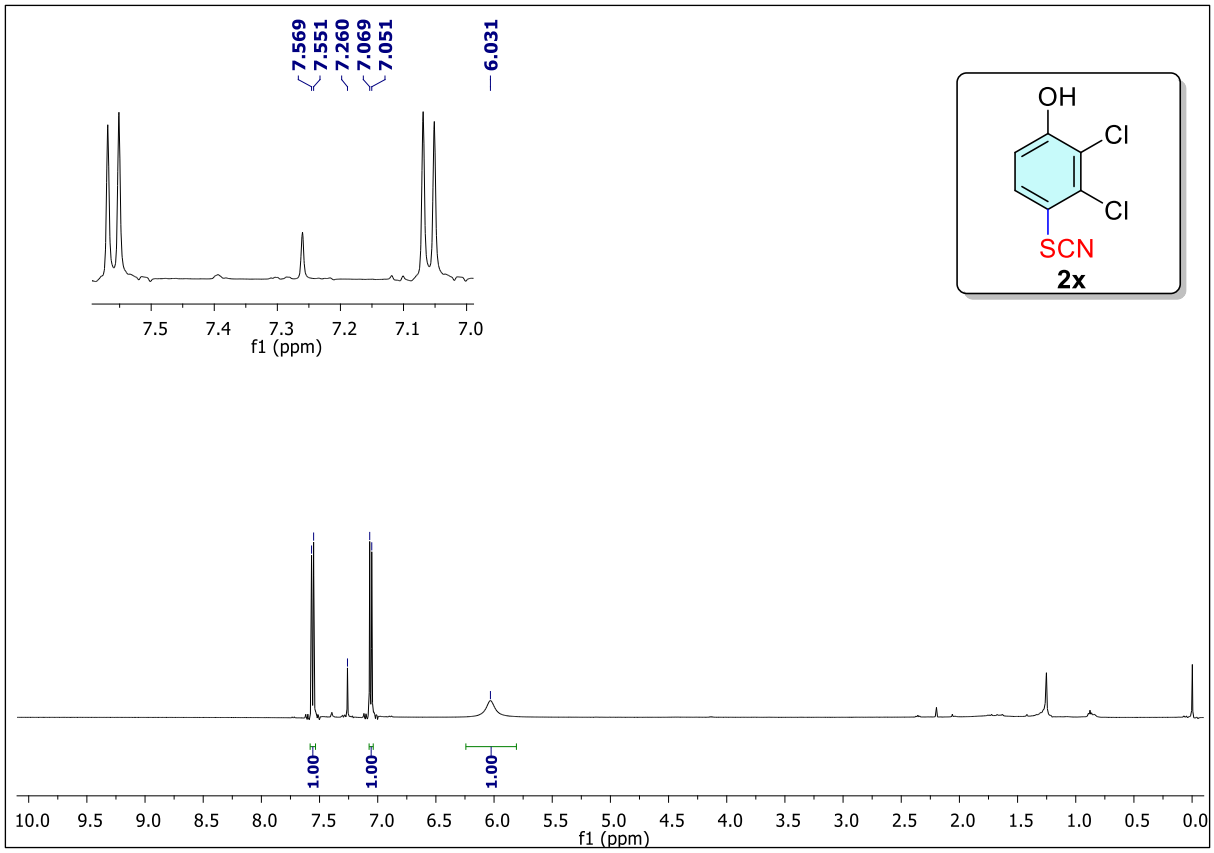

$^{13}$C{$^{1}$H} NMR of **2u** (100 MHz, DMSO-$d_6$)



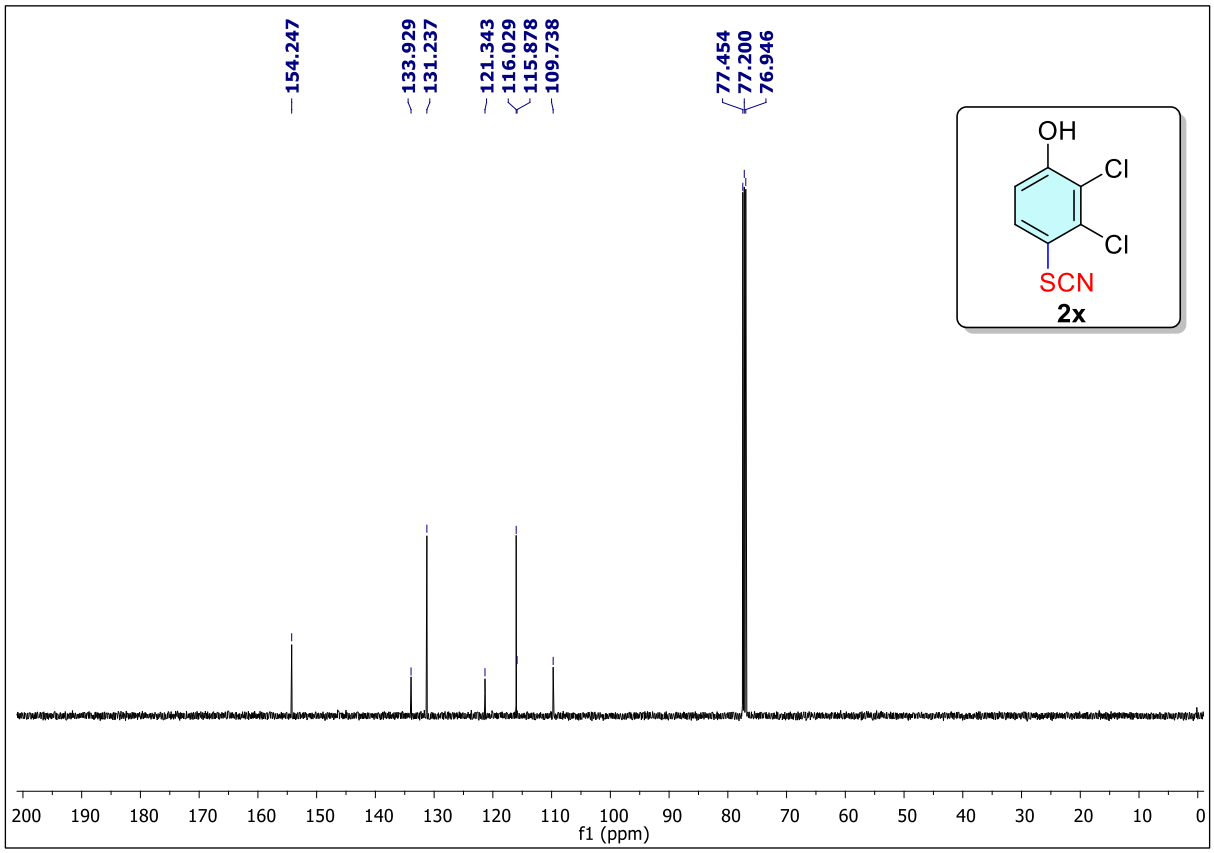

$^{1}$H NMR of **2w** (500 MHz, $CDCl_3$)



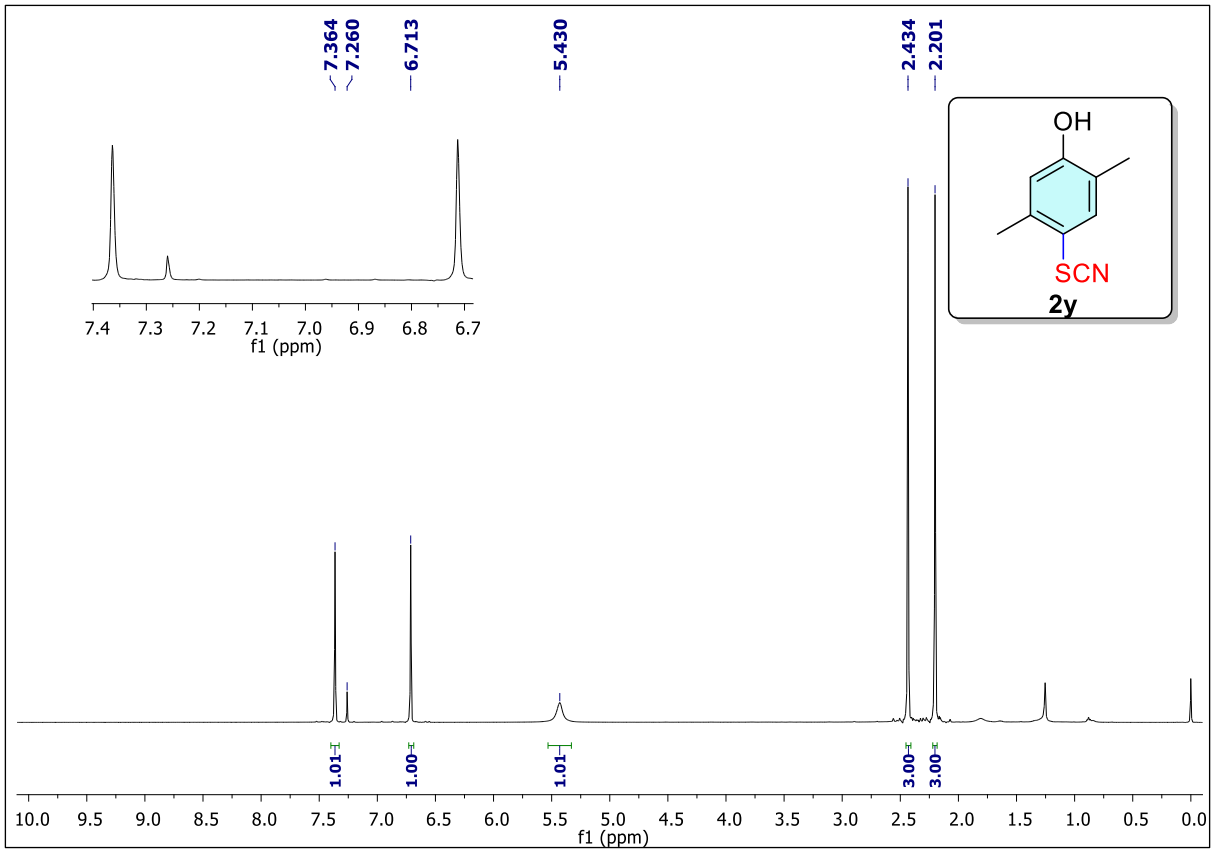

$^{13}$C{$^{1}$H} NMR of **2w** (125 MHz, $CDCl_3$)



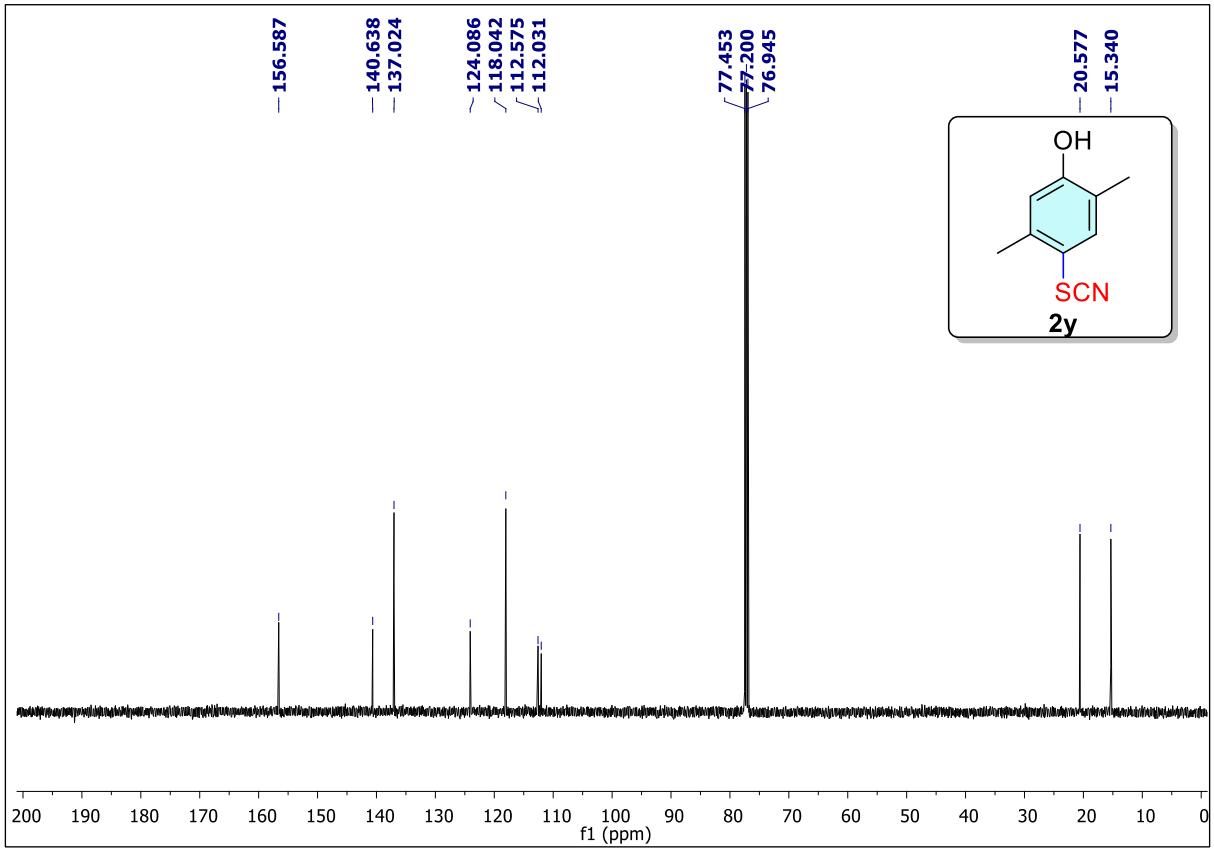

$^{1}$H NMR of **2x** (500 MHz, $CDCl_3$)



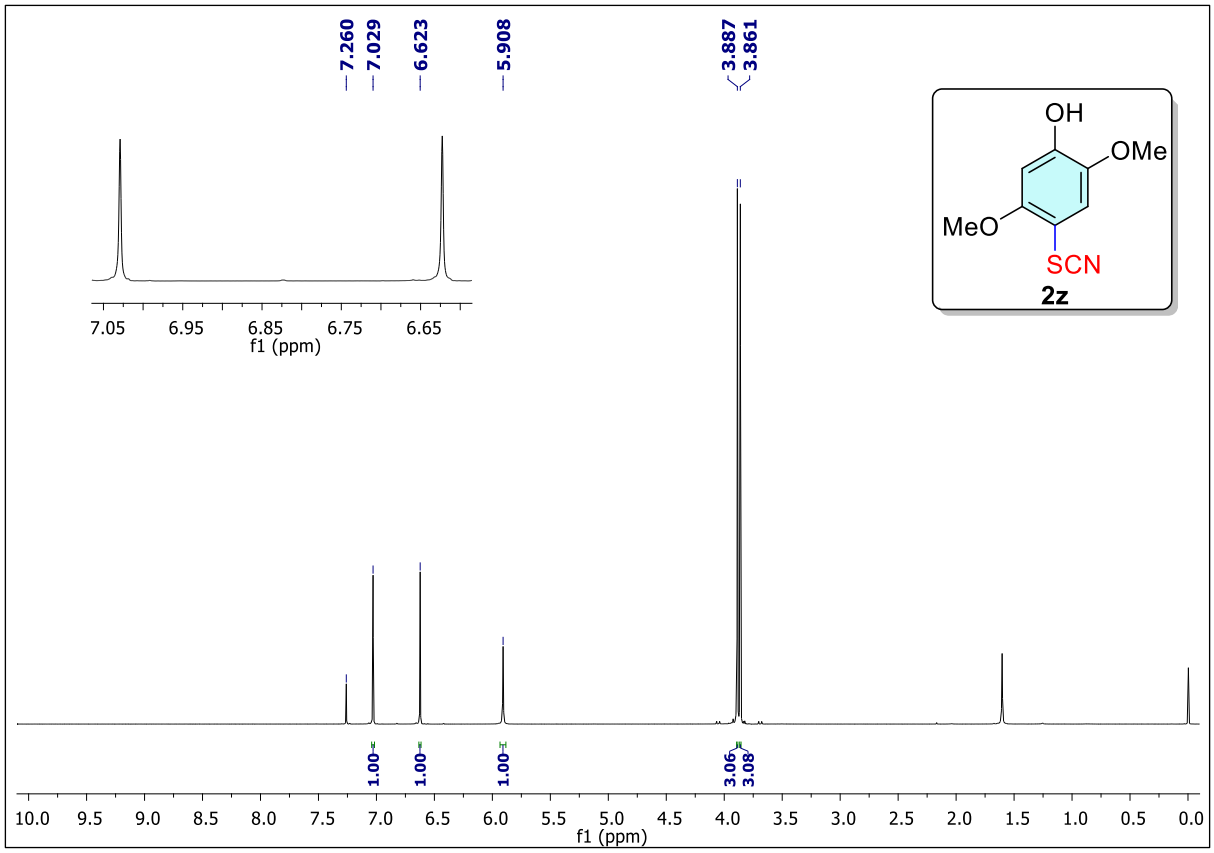

$^{13}$C{$^{1}$H} NMR of **2x** (125 MHz, $CDCl_3$)



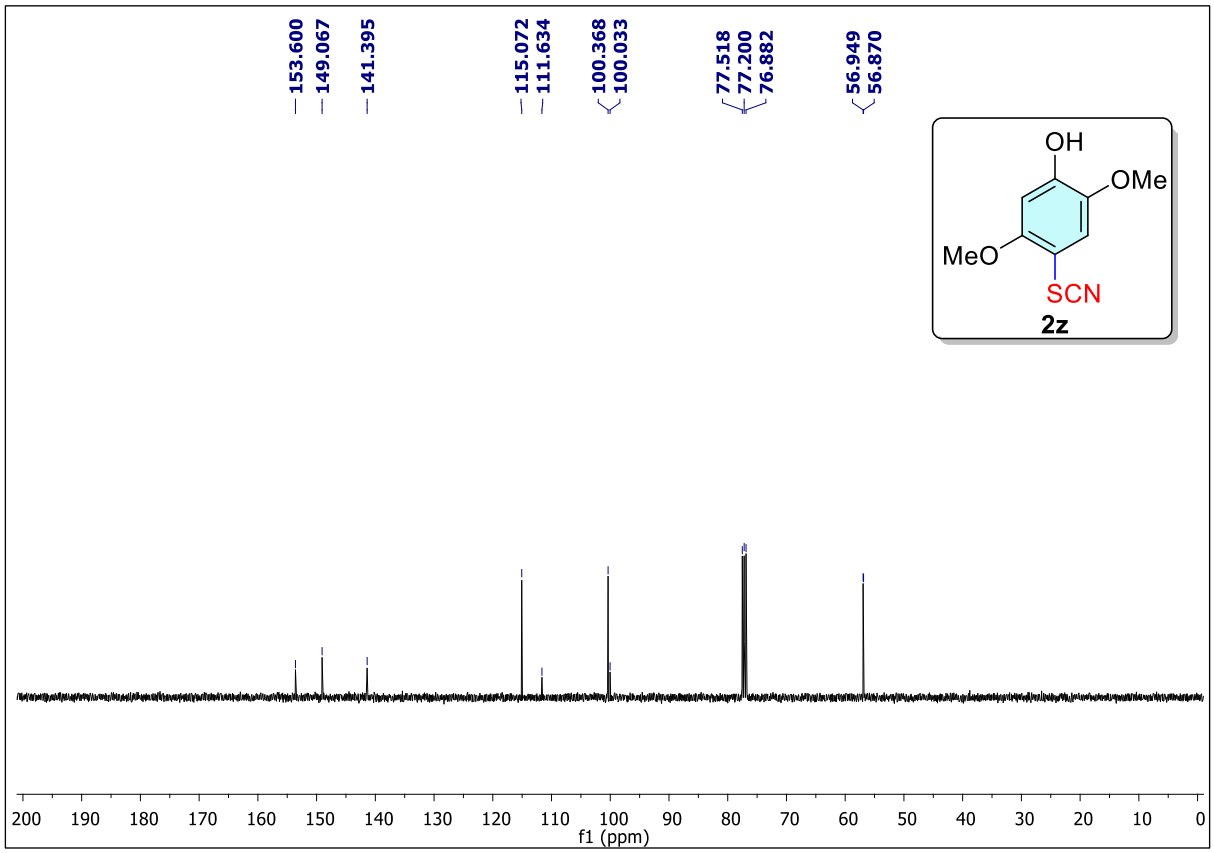

$^{1}$H NMR of **2y** (500 MHz, $CDCl_3$)



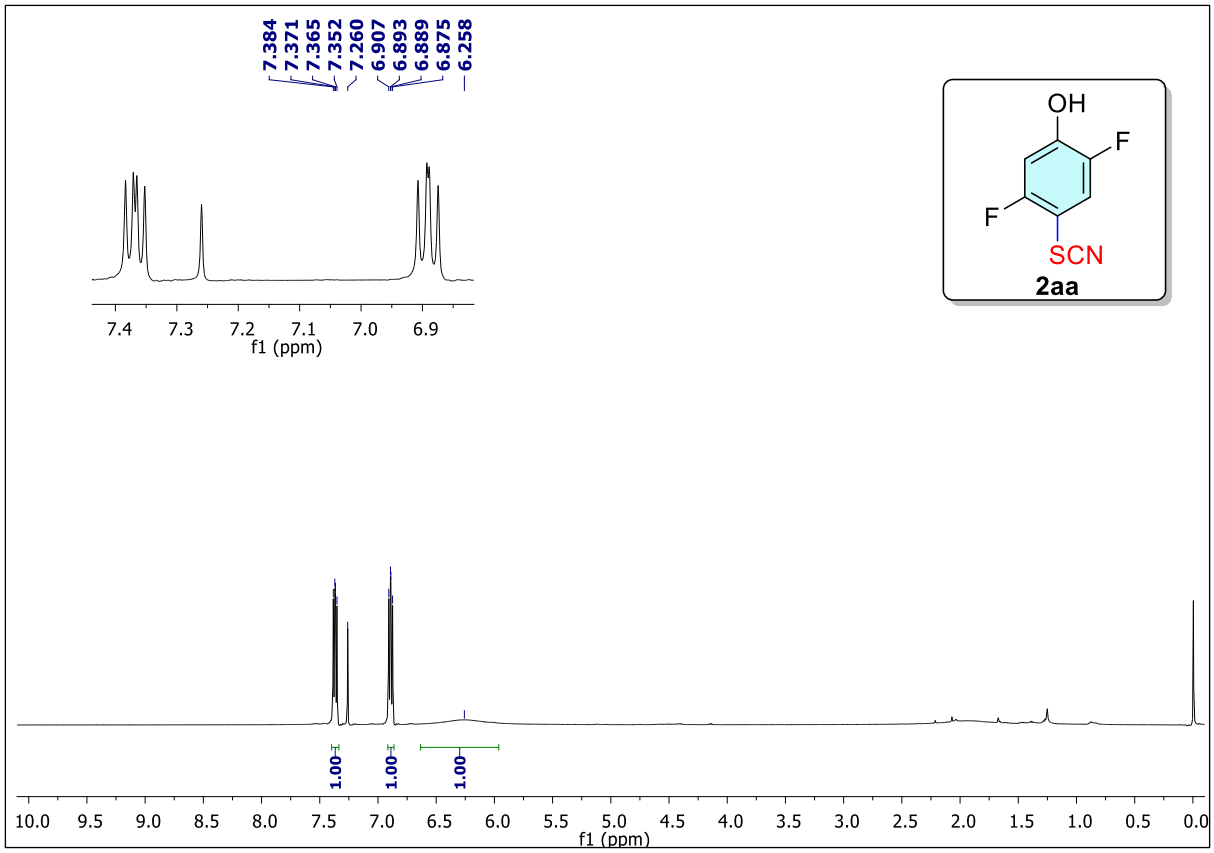

$^{13}$C{$^{1}$H} NMR of **2y** (125 MHz, $CDCl_3$)



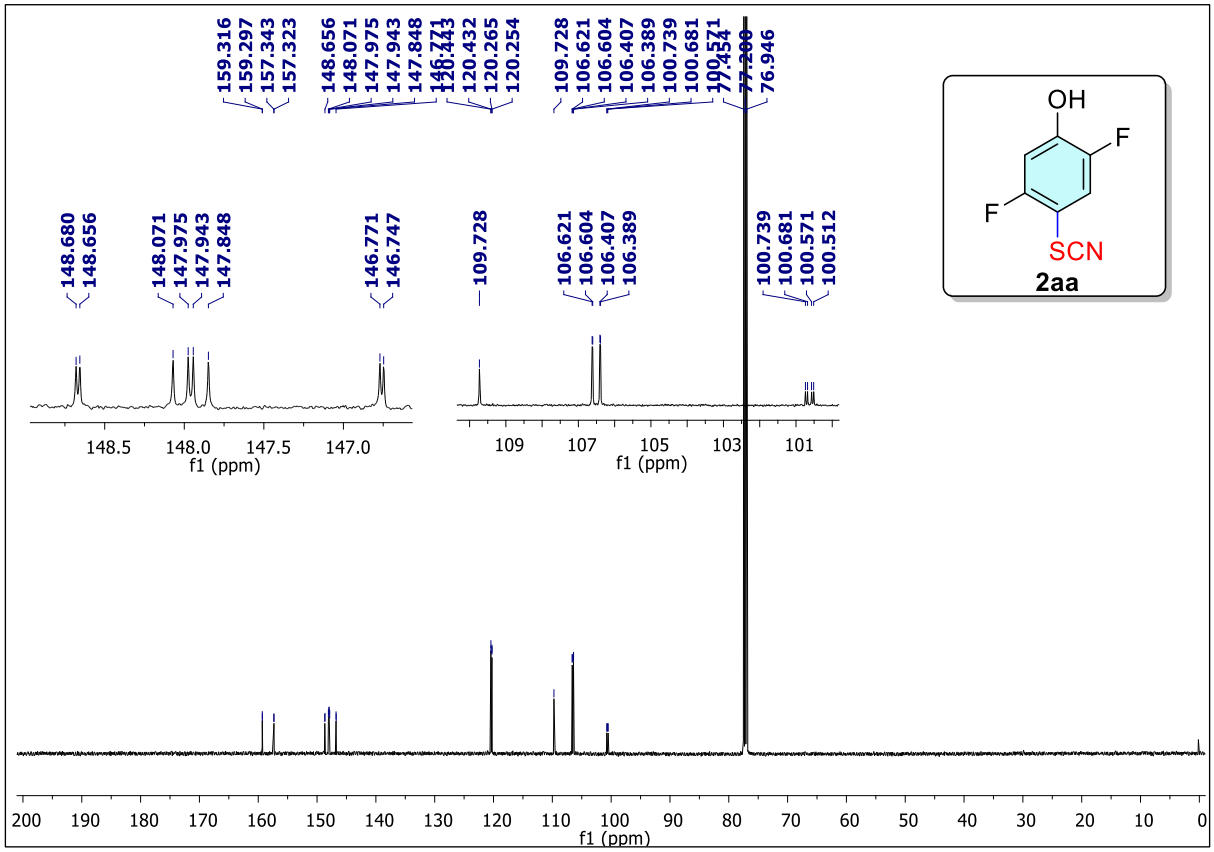

$^{1}$H NMR of **2z** (400 MHz, $CDCl_3$)



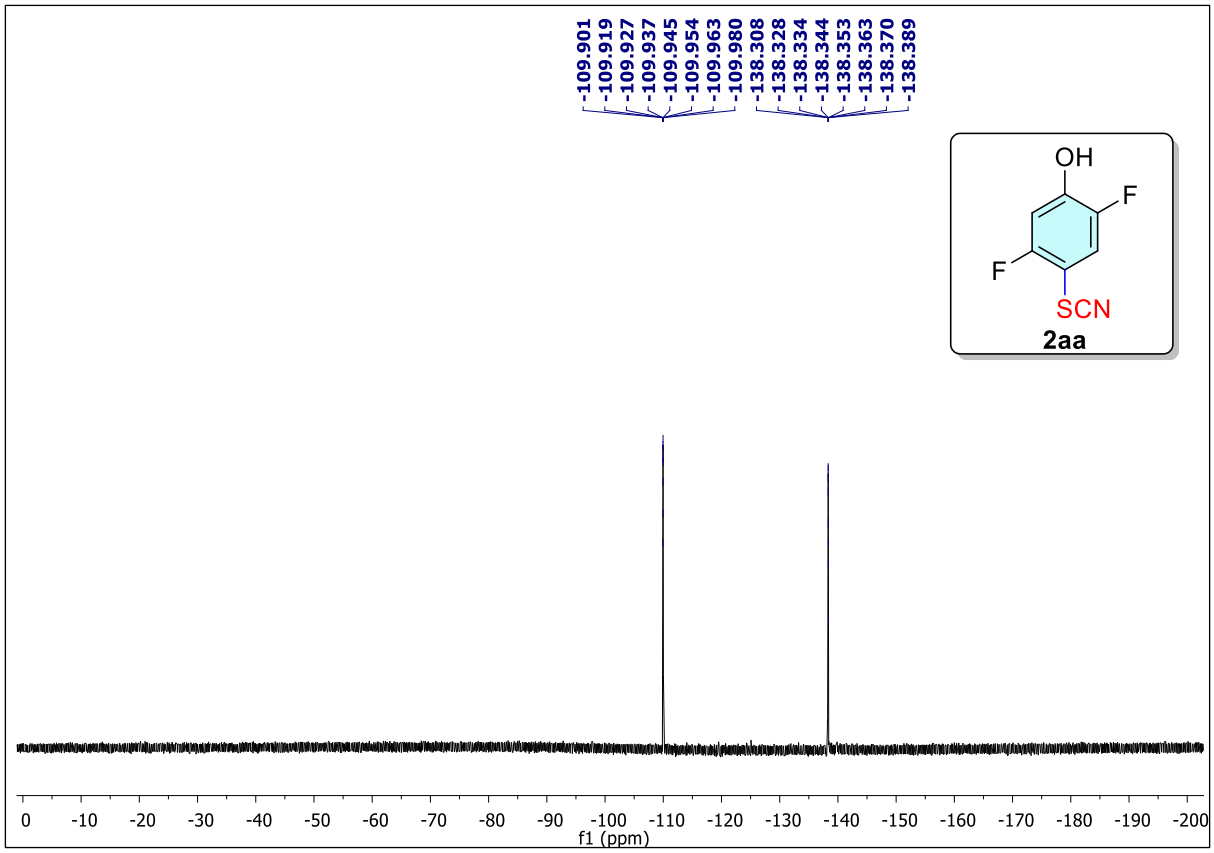

$^{13}$C{$^{1}$H} NMR of **2z** (100 MHz, $CDCl_3$)



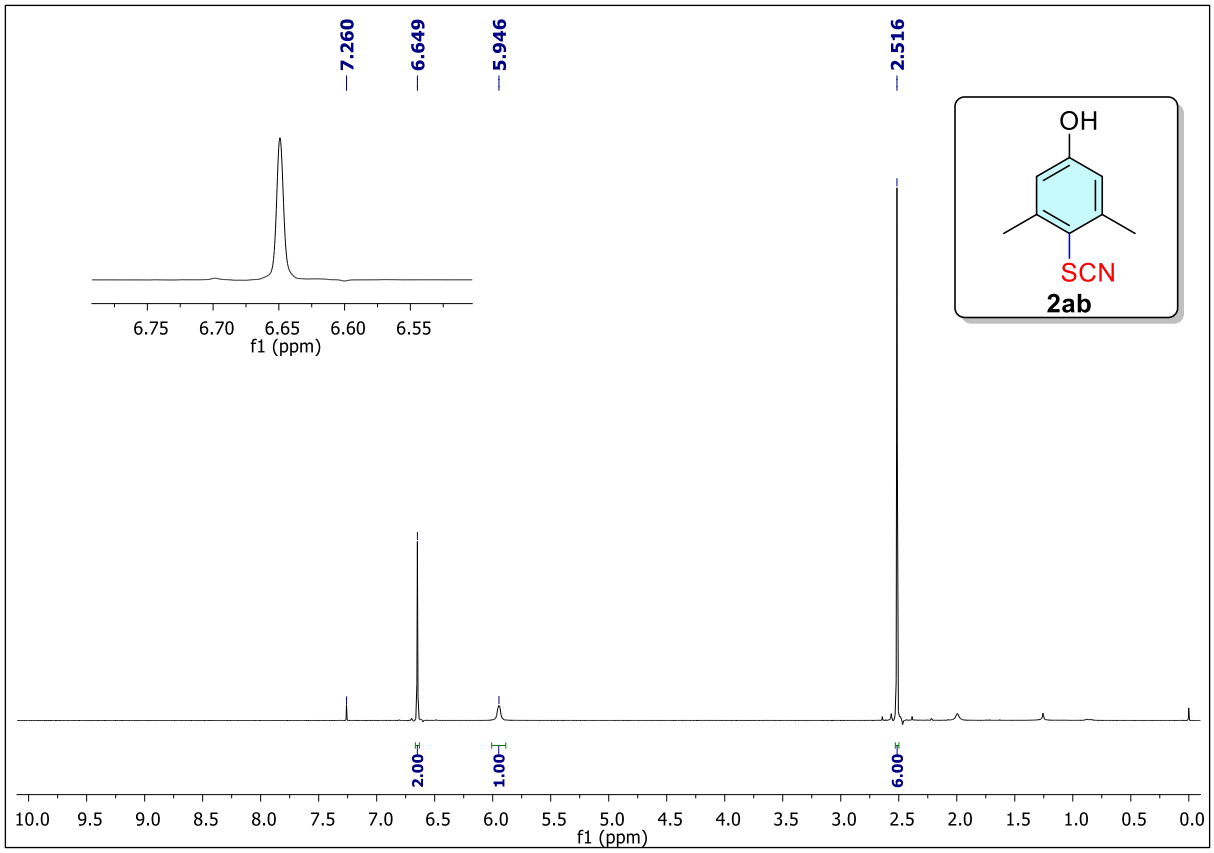

$^{1}$H NMR Spectra of **2aa**(500 MHz, $CDCl_3$)



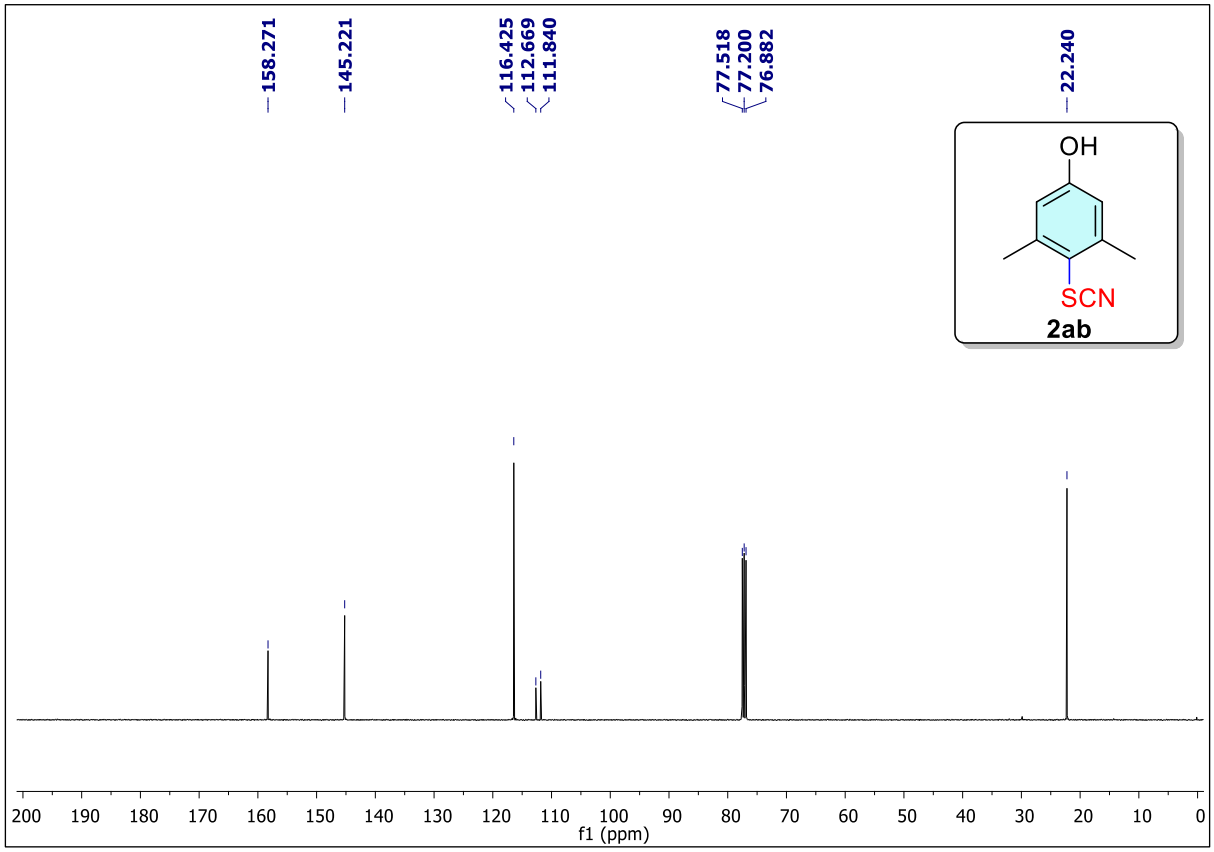

$^{13}$C{$^{1}$H} NMR of **2aa** (125 MHz, $CDCl_3$)



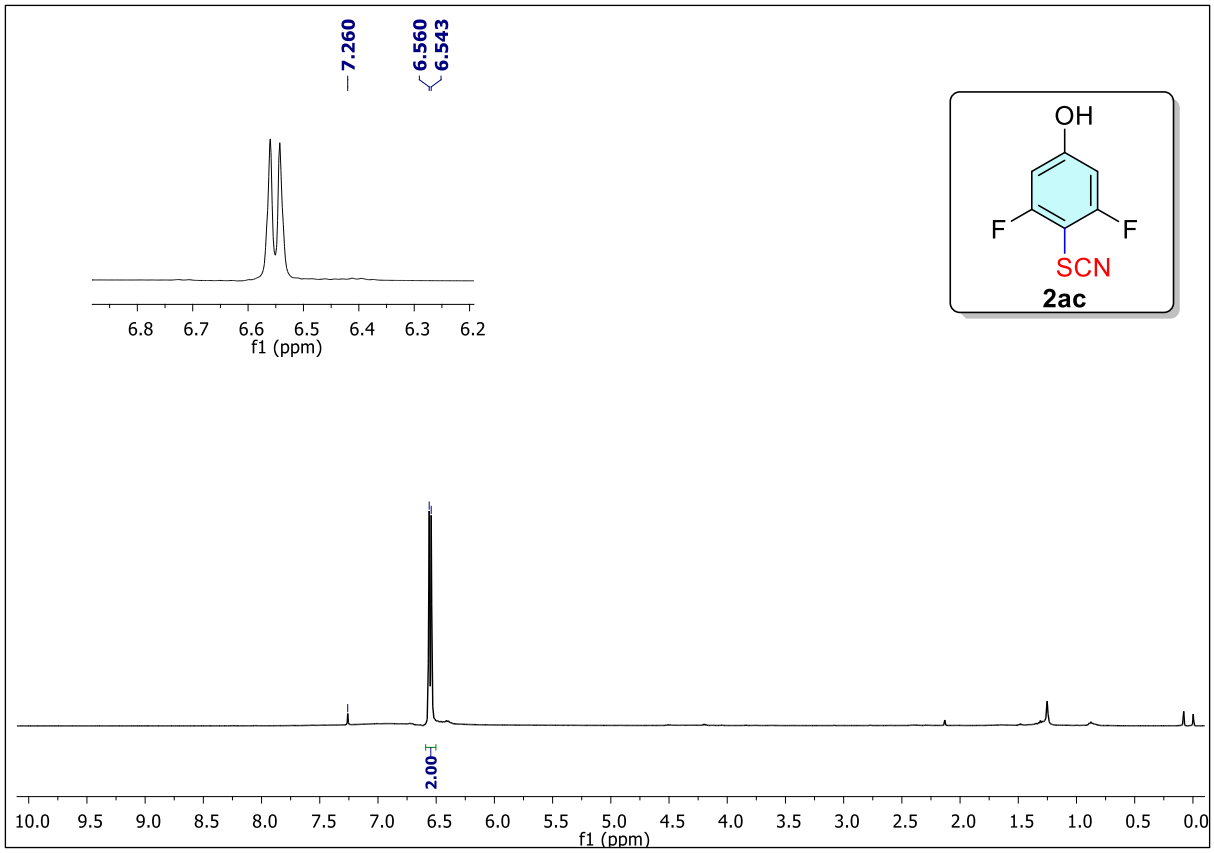

$^{19}$F NMR of **2aa** (376 MHz, $CDCl_3$)



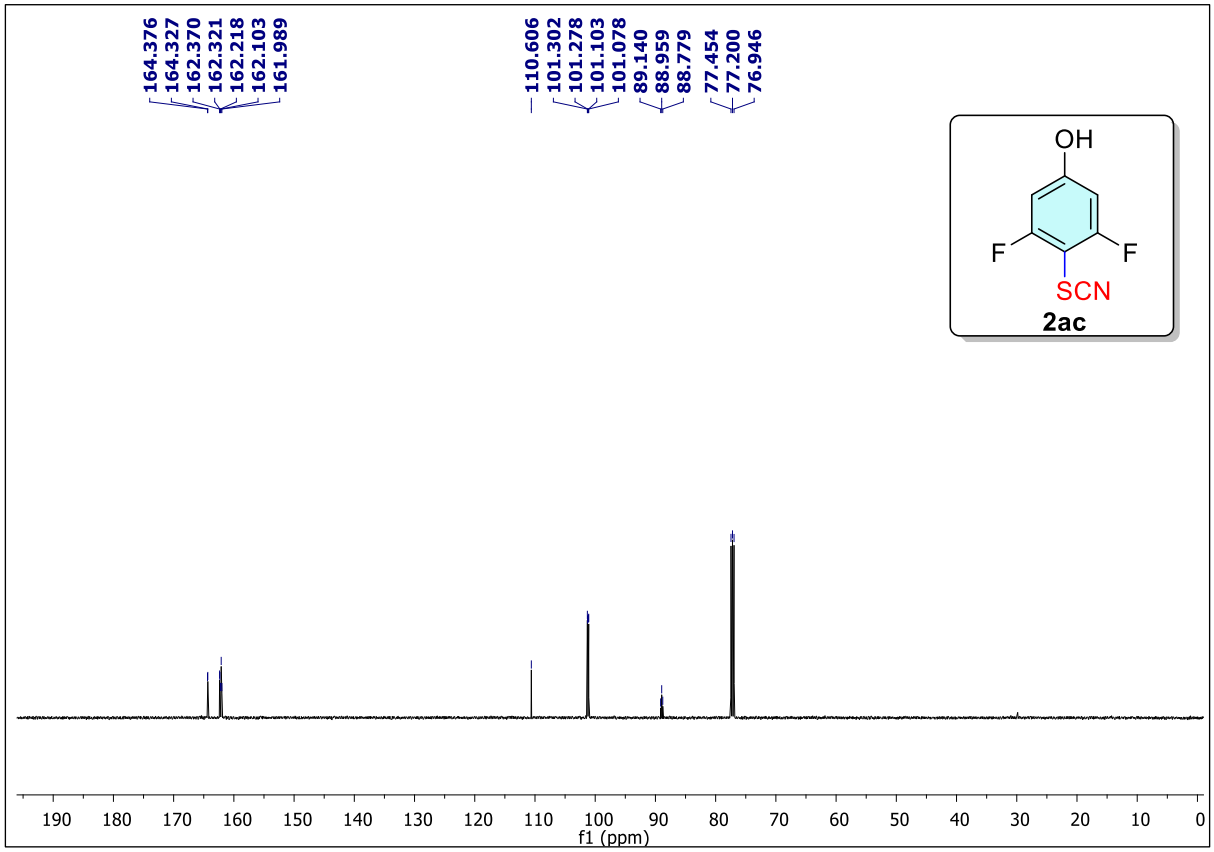

$^{1}$H NMR of **2ab** (500 MHz, $CDCl_3$)



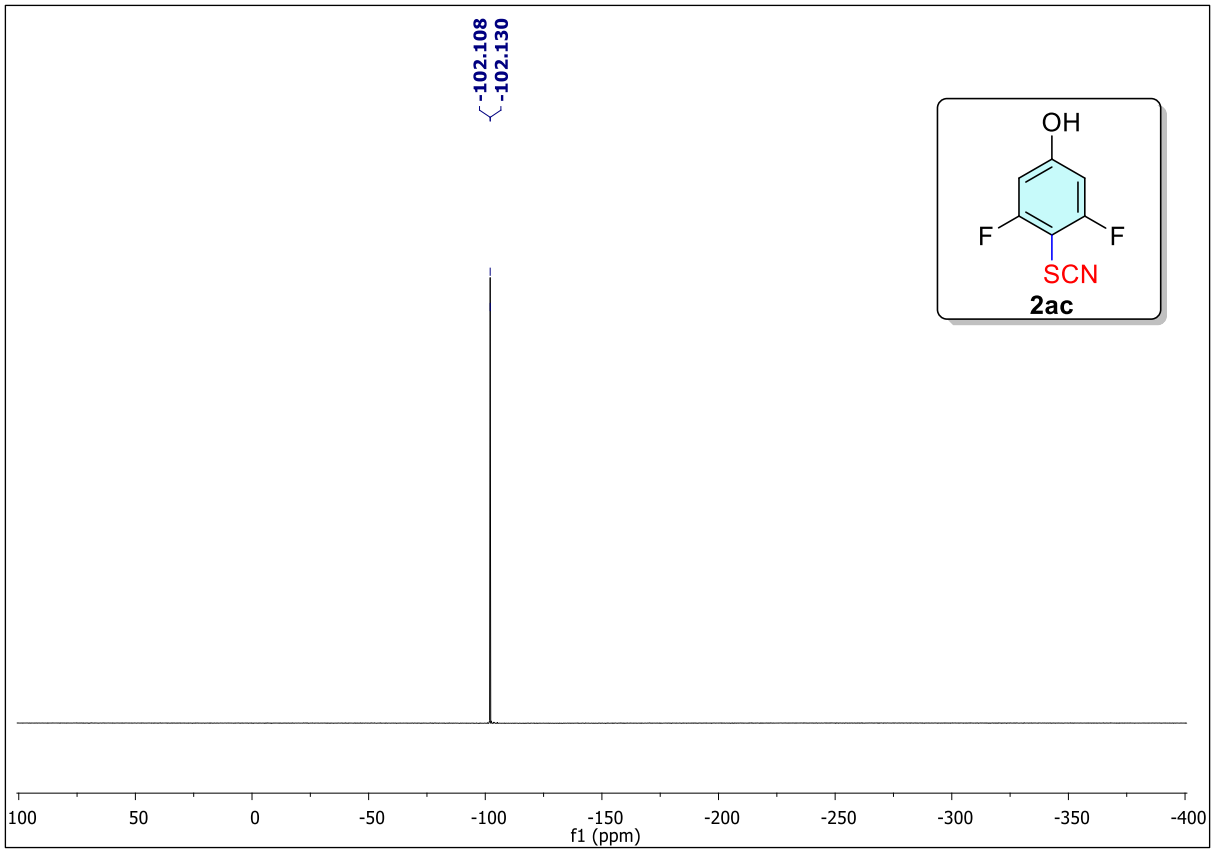

$^{13}$C{$^{1}$H} NMR of **2ab** (100 MHz, $CDCl_3$)



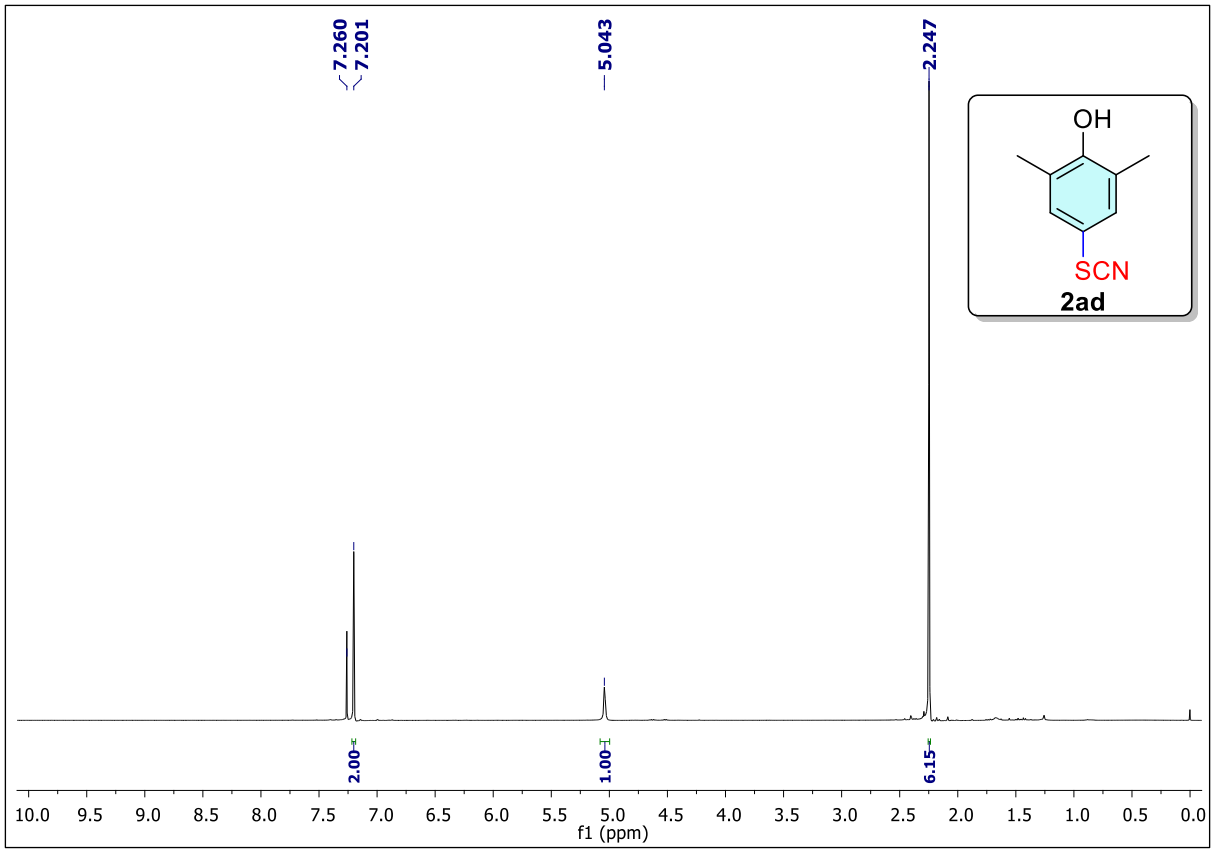

$^{1}$H NMR of **2ac** (500 MHz, $CDCl_3$)



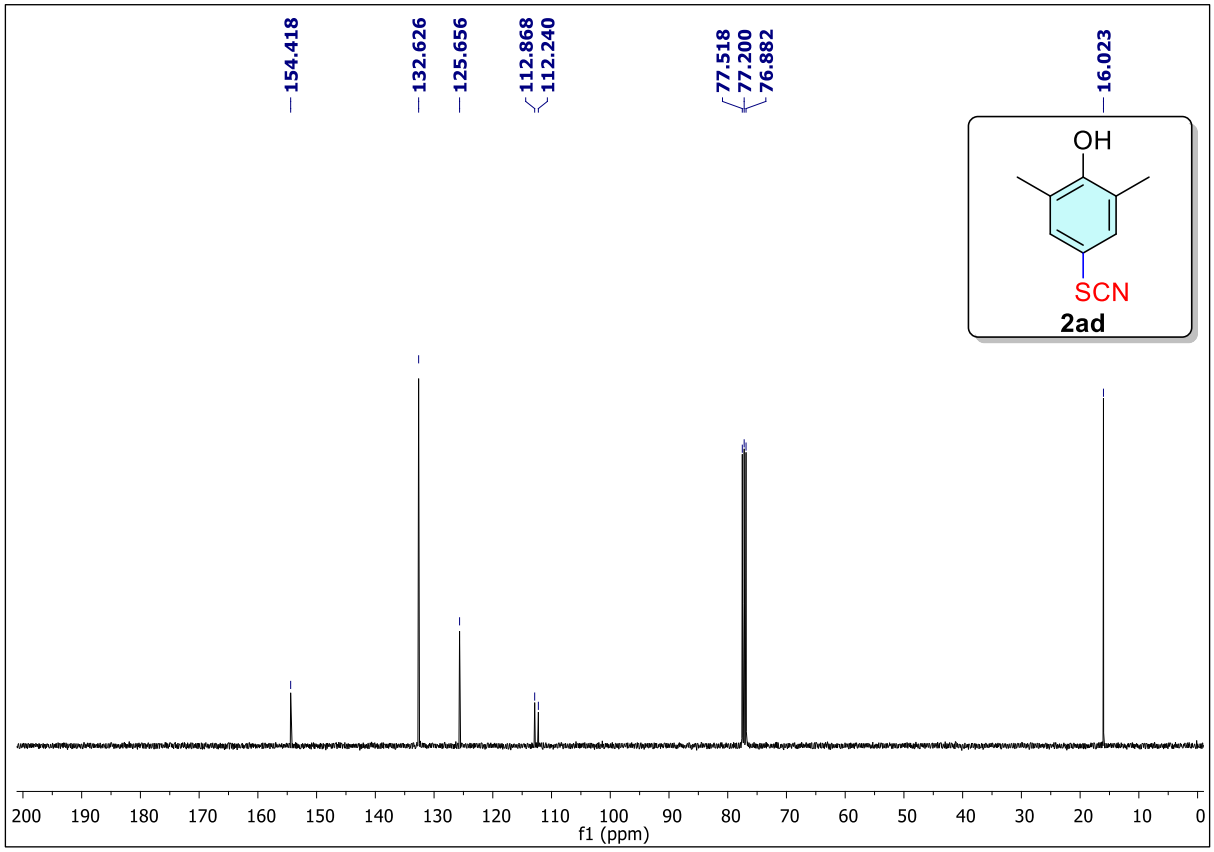

$^{13}$C{$^{1}$H} NMR of **2ac** (125 MHz, $CDCl_3$)



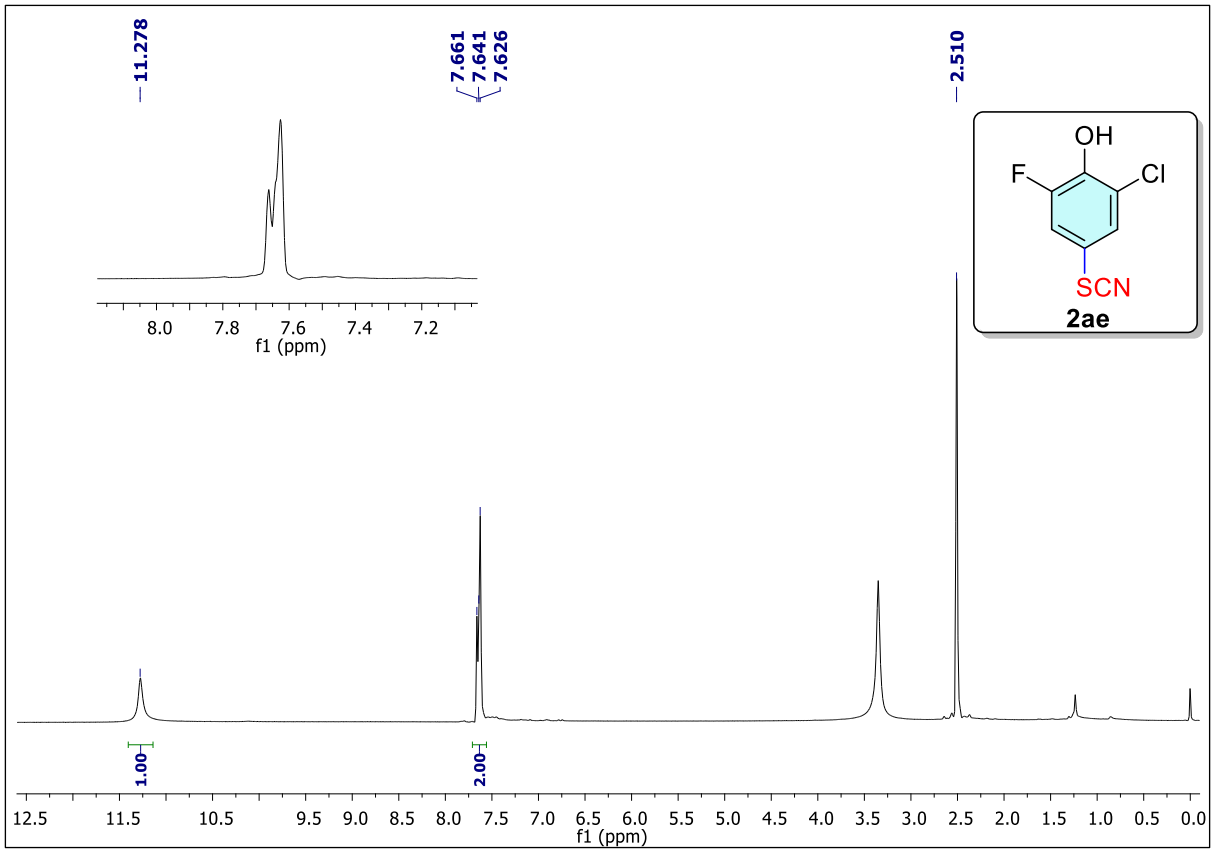

$^{19}$F NMR of **2ac** (376 MHz, $CDCl_3$)



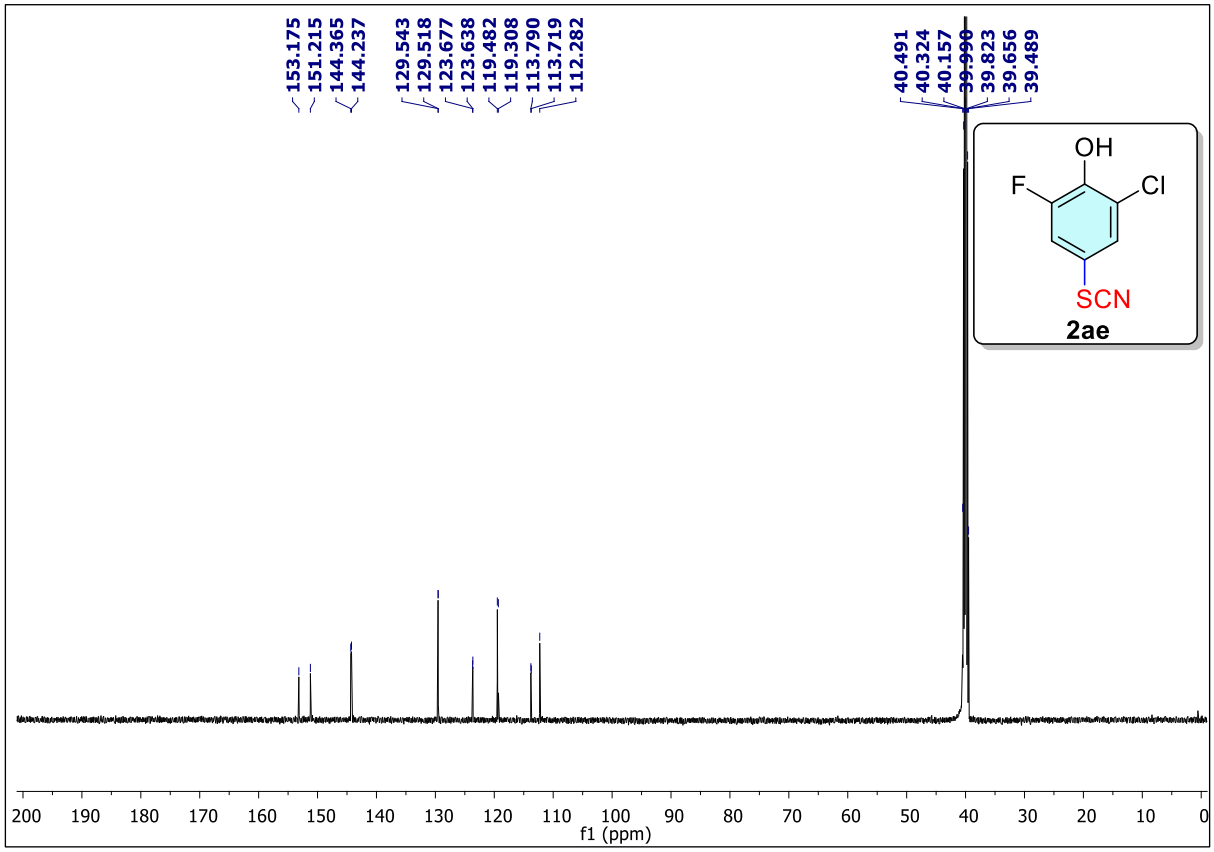

$^{1}$H NMR of **2ad** (400 MHz, $CDCl_3$)



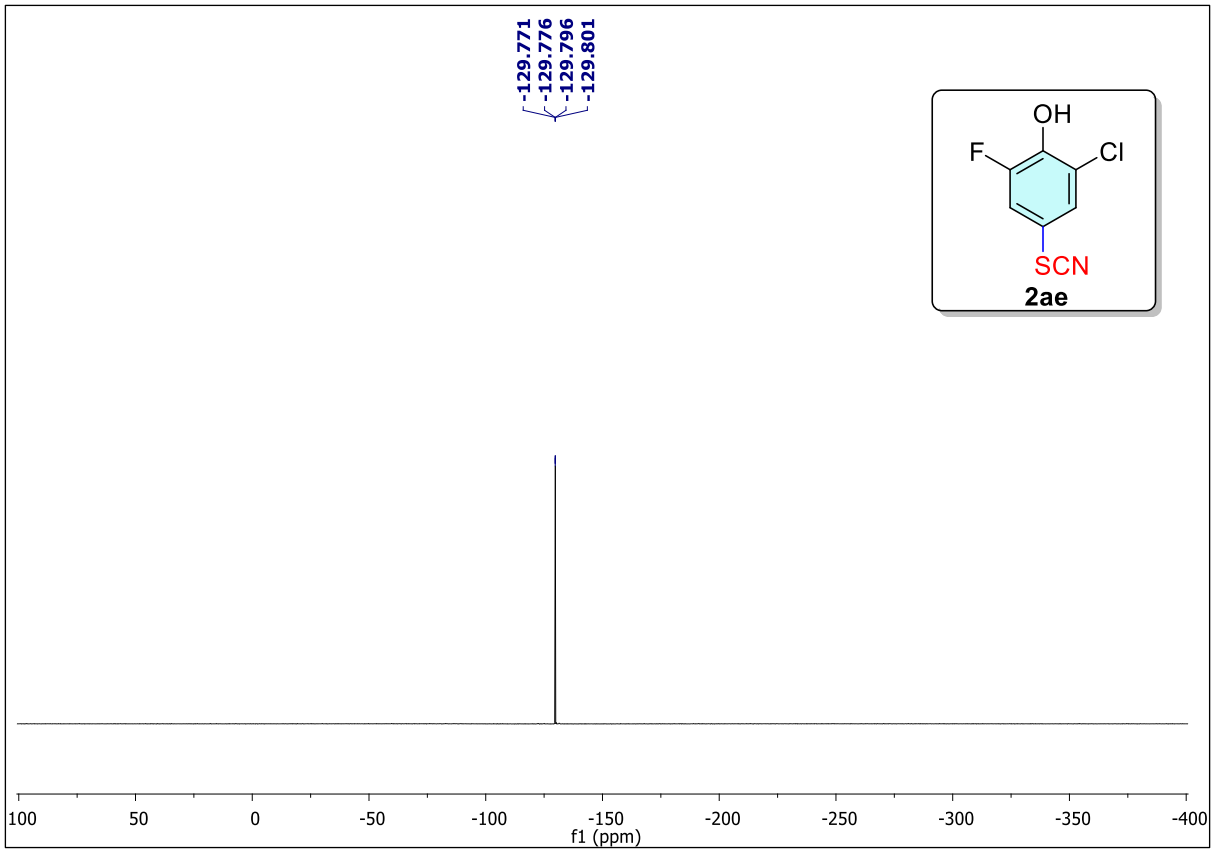

$^{13}$C{$^{1}$H} NMR of **2ad** (100 MHz, $CDCl_3$)



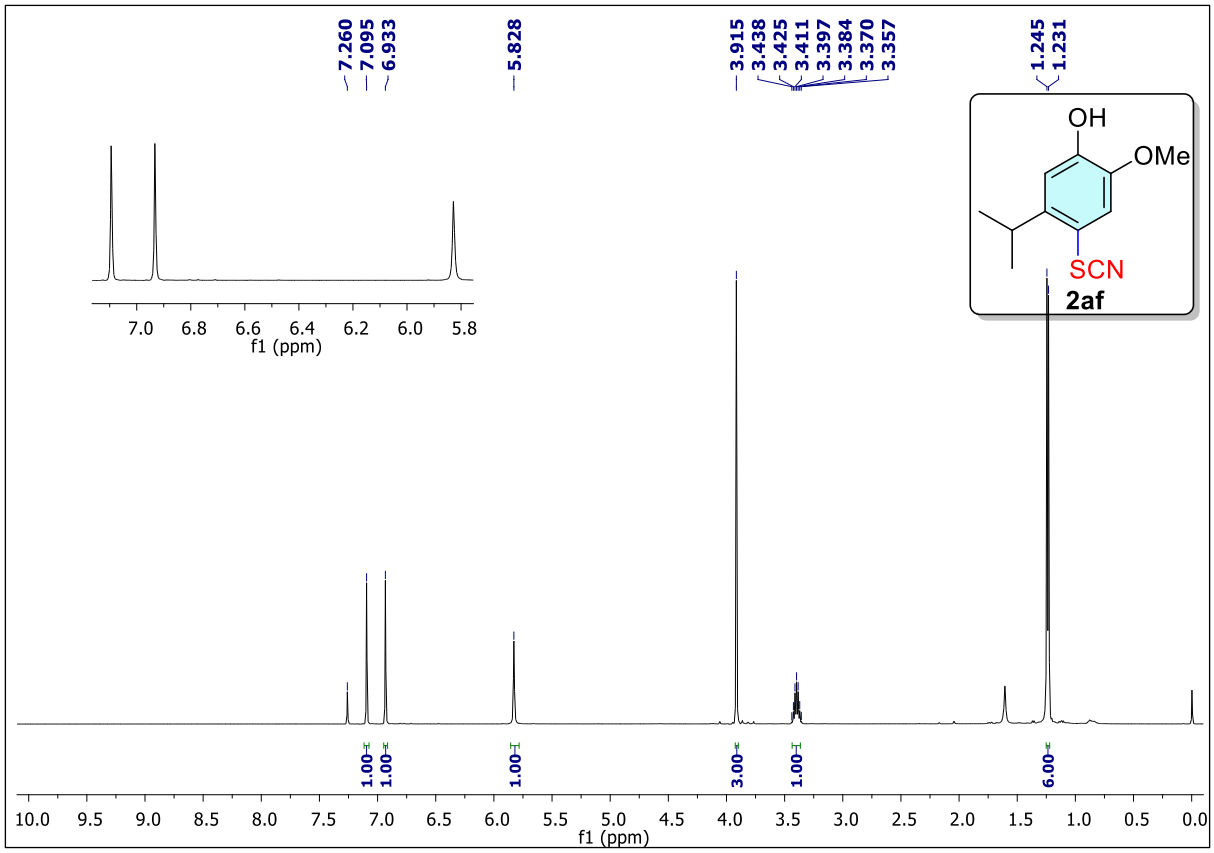

$^{1}$H NMR of **2ae** (500 MHz, DMSO-$d_6$)



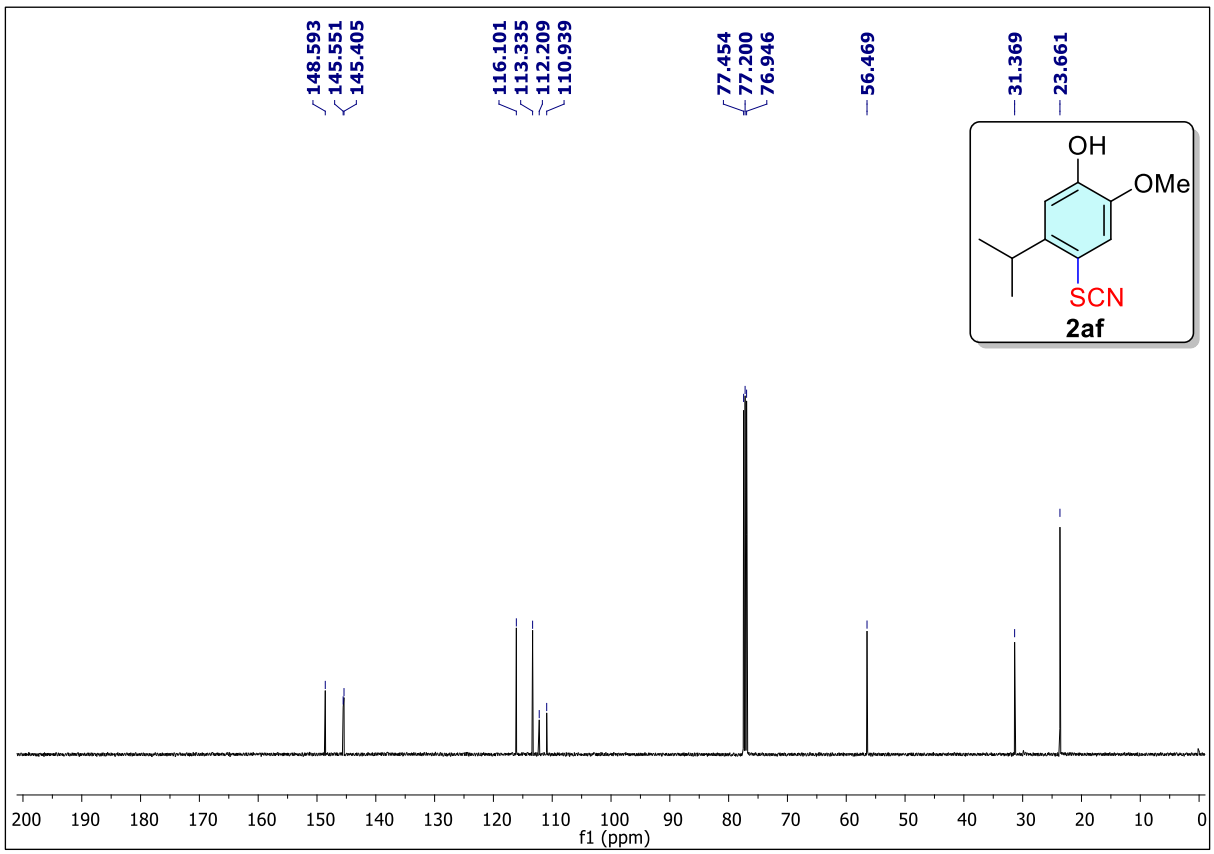

$^{13}$C{$^{1}$H} NMR of **2ae** (125 MHz, DMSO-$d_6$)



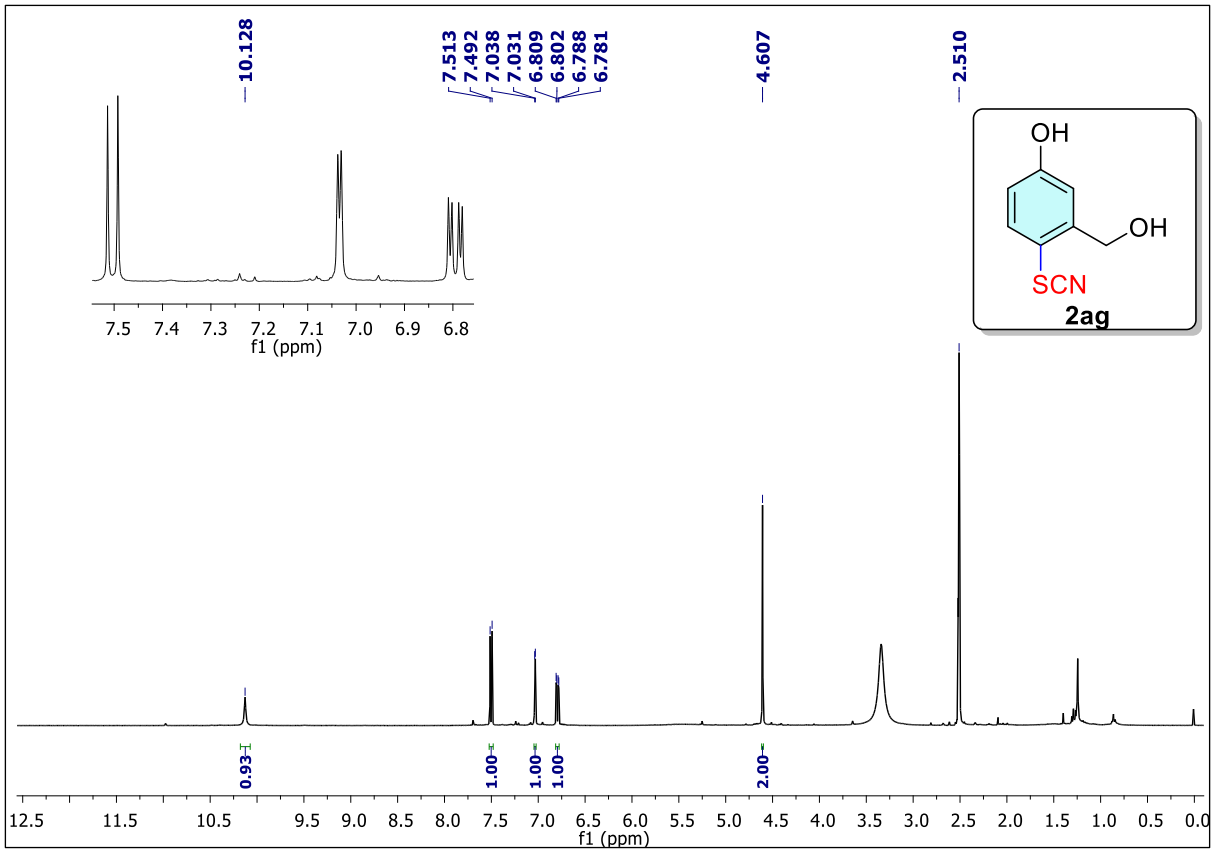

$^{19}$F NMR of **2ae** (376 MHz, DMSO-$d_6$)



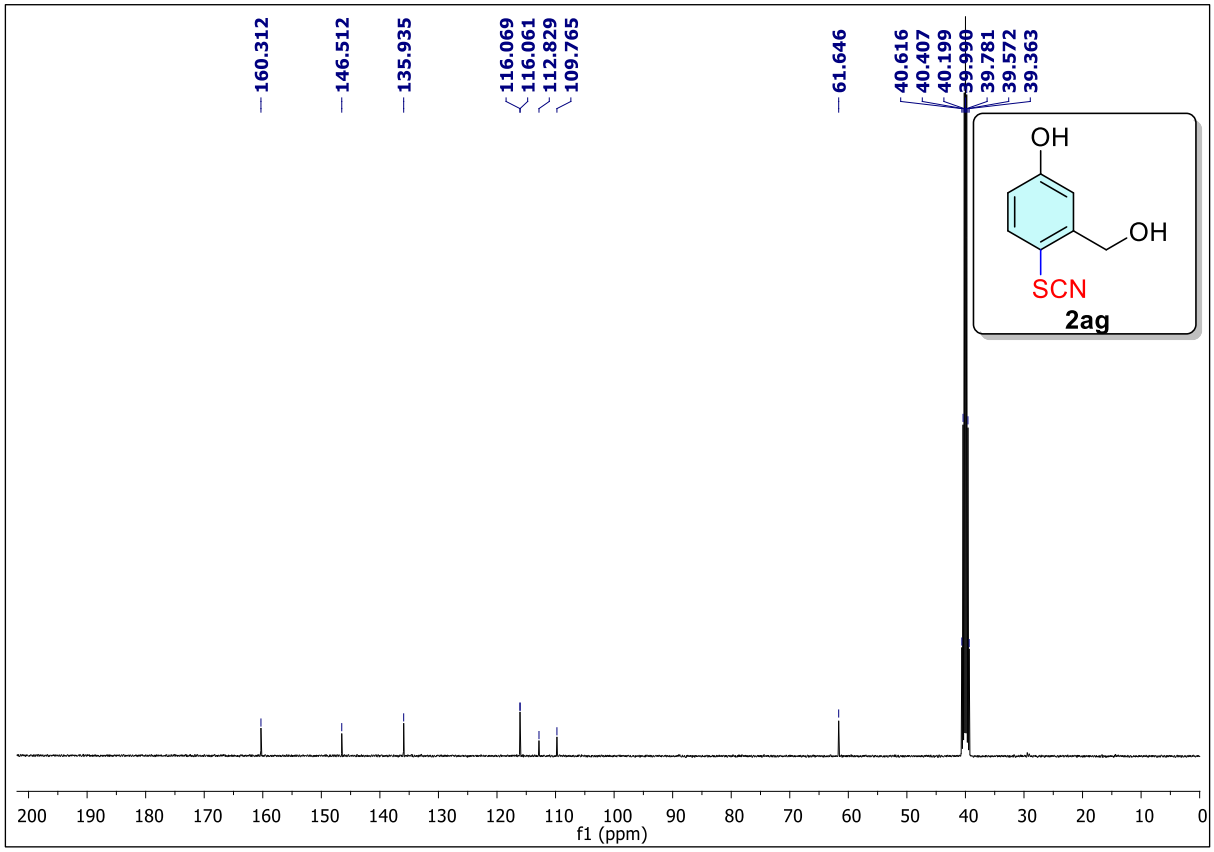

$^{1}$H NMR of **2af** (500 MHz, $CDCl_3$)



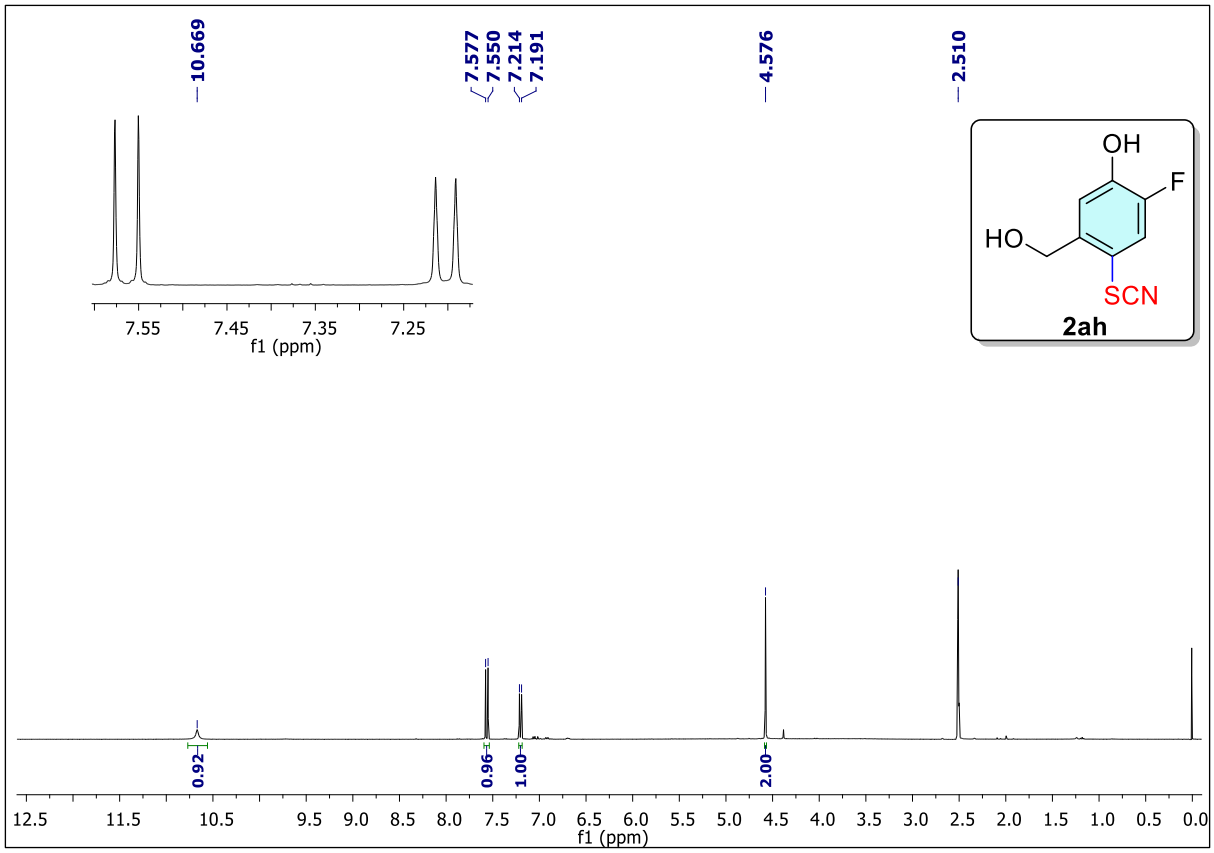

$^{13}$C{$^{1}$H} NMR of **2af** (125 MHz, $CDCl_3$)



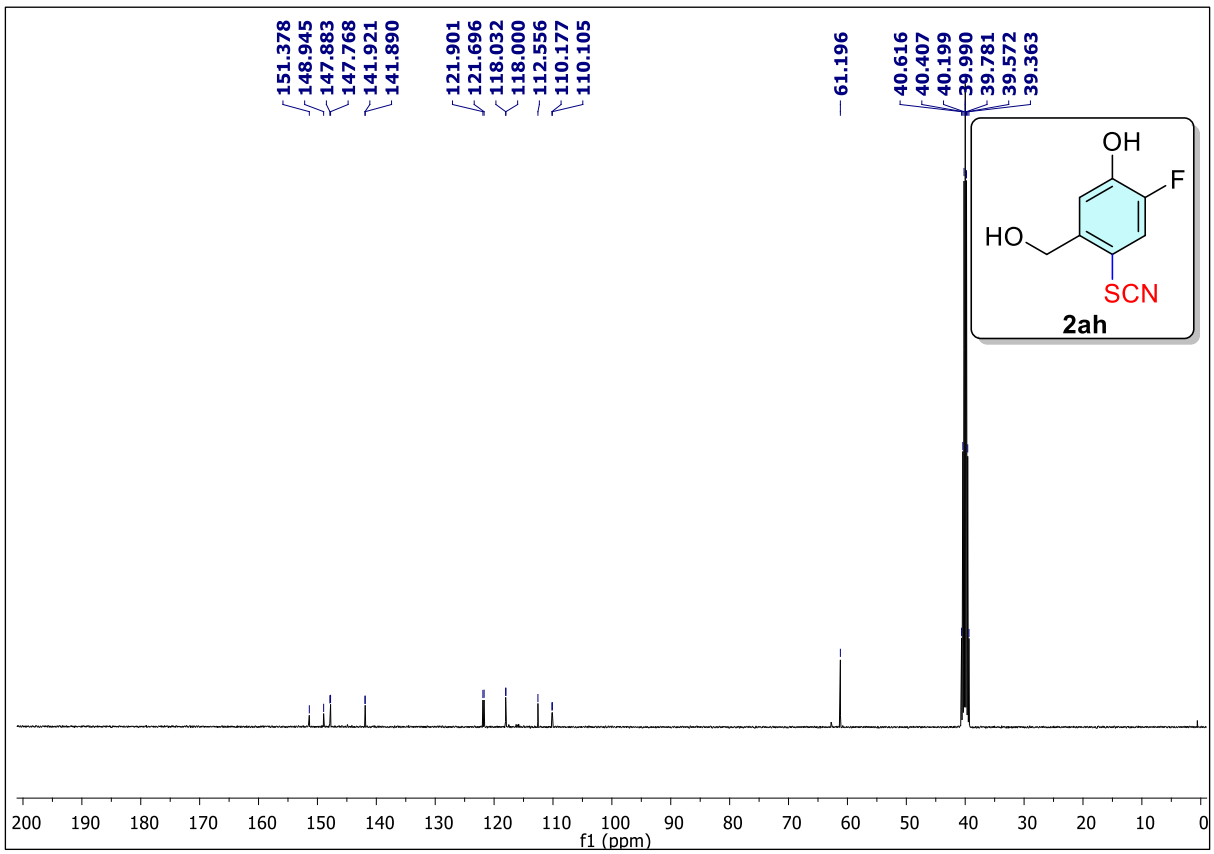

$^{1}$H NMR of **2ag** (400 MHz, DMSO-$d_6$)



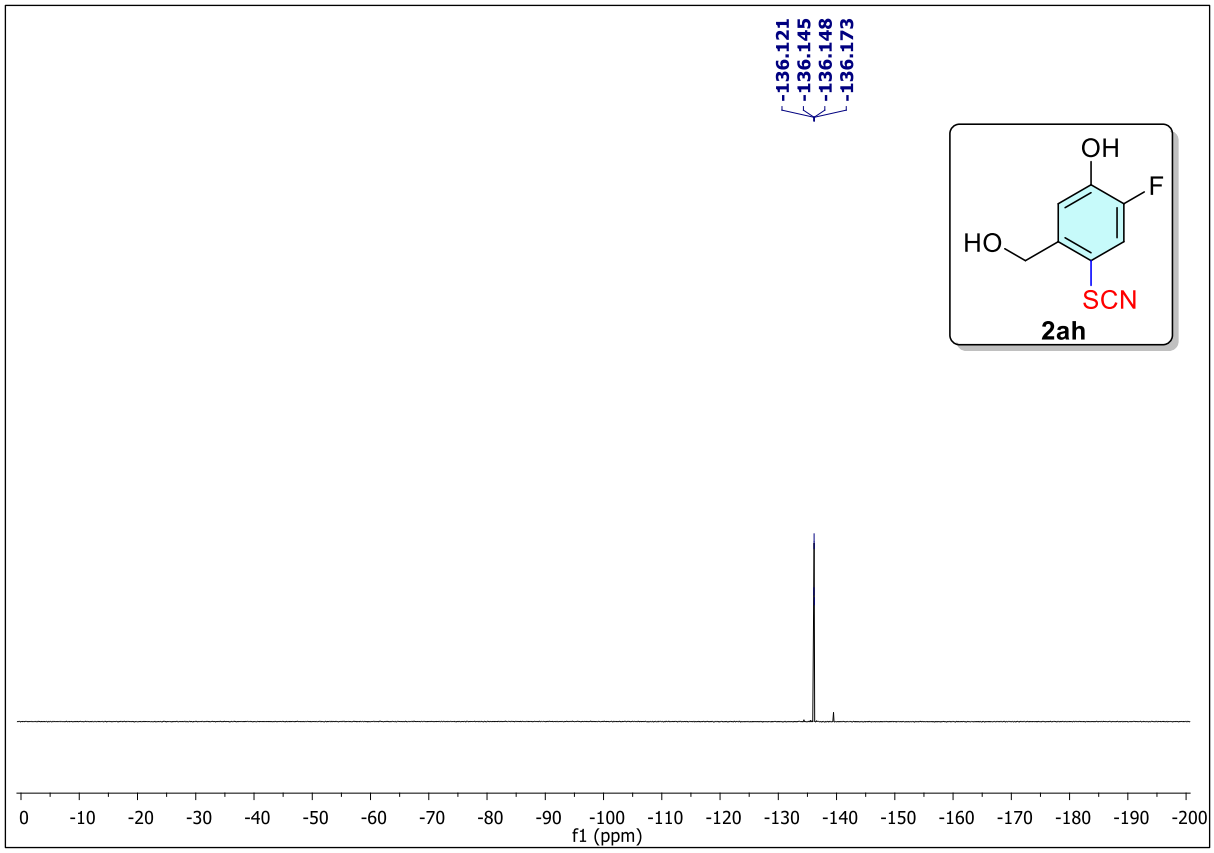

$^{13}$C{$^{1}$H} NMR of **2ag** (100 MHz, DMSO-$d_6$)



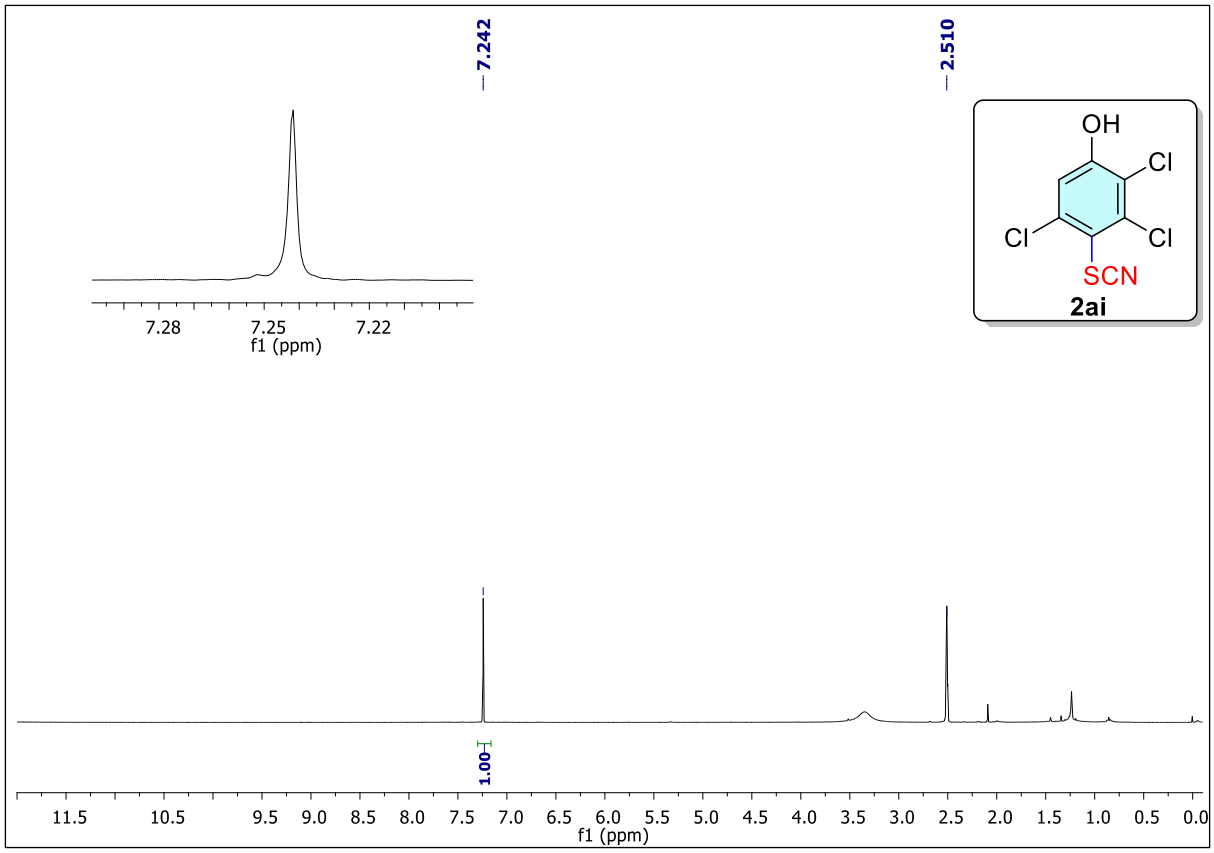

$^{1}$H NMR of **2ah** (400 MHz, DMSO-$d_6$)



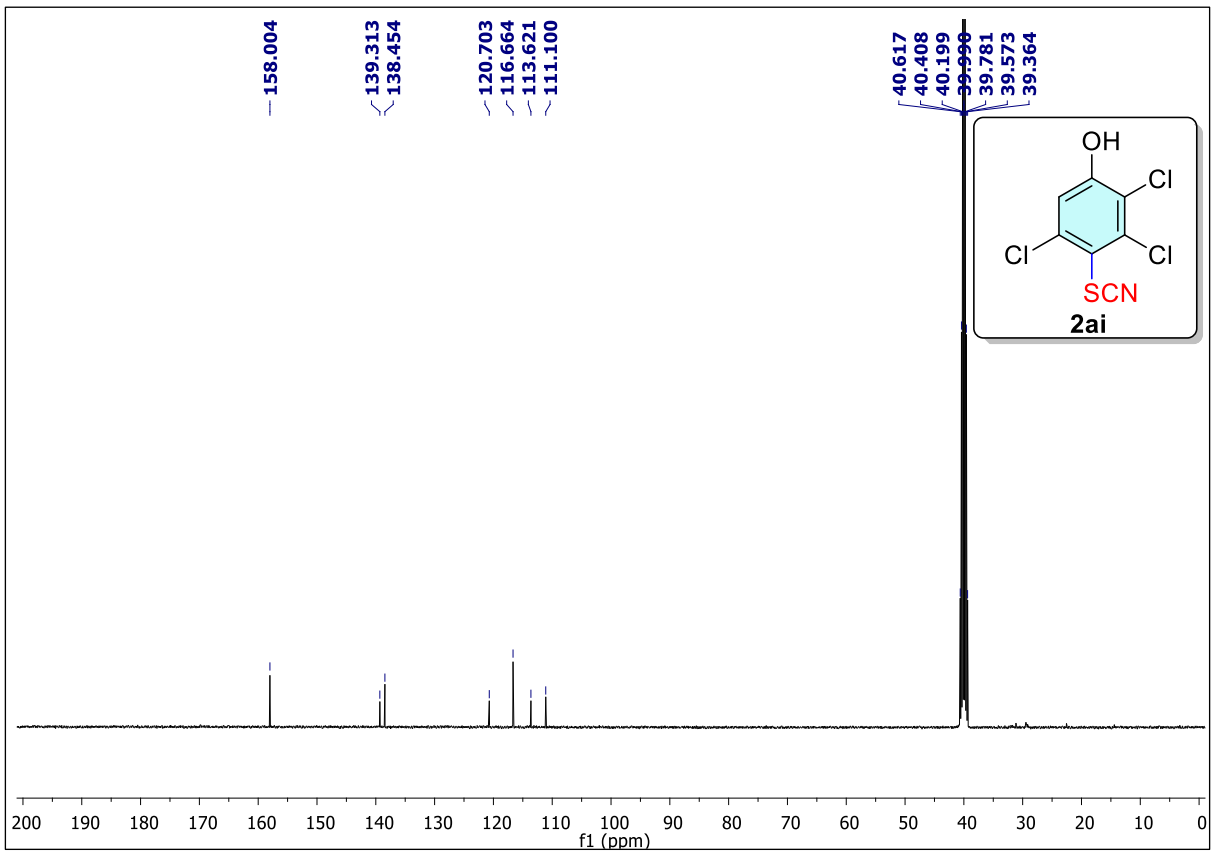

$^{13}$C{$^{1}$H} NMR of **2ah** (100 MHz, DMSO-$d_6$)



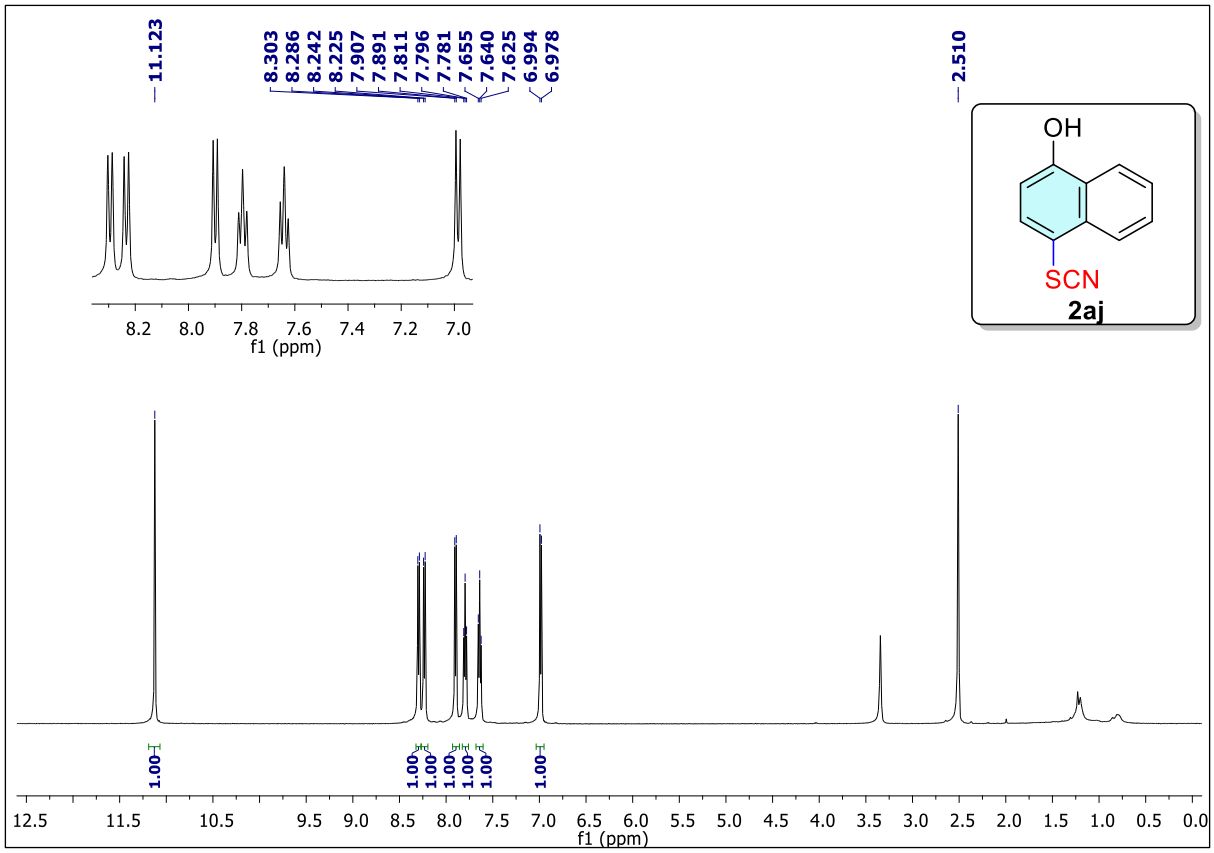

$^{19}$F NMR of **2ah** (376 MHz, DMSO-$d_6$)



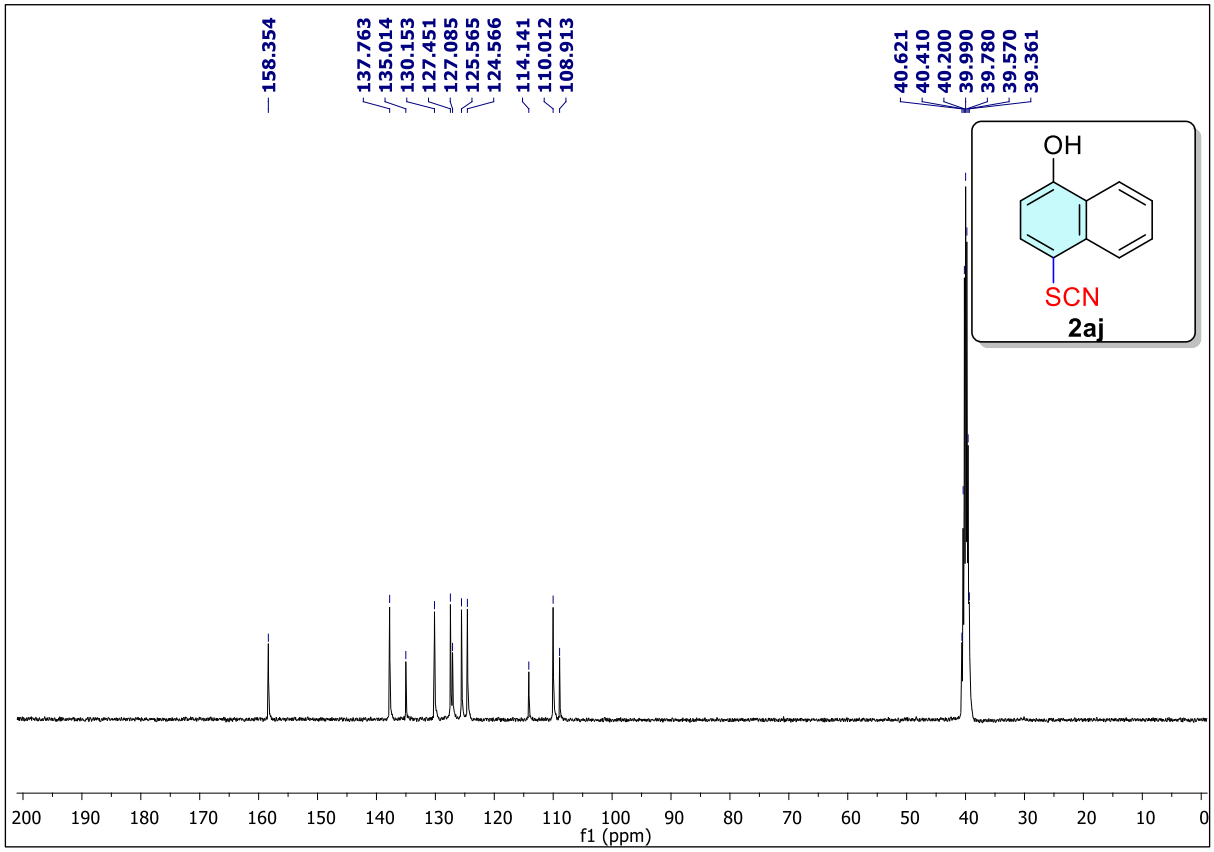

$^{1}$H NMR of **2ai** (400 MHz, DMSO-$d_6$)



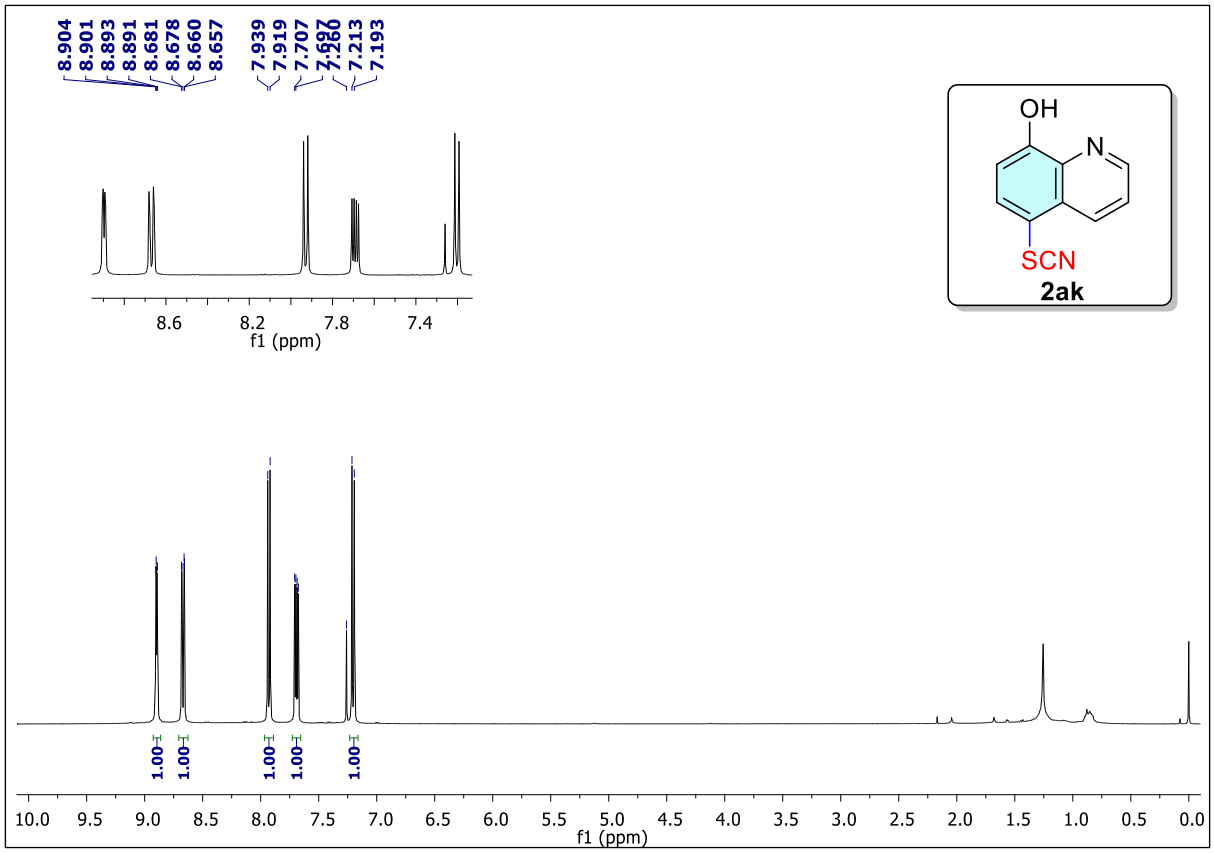

$^{13}$C{$^{1}$H} NMR of **2ai** (100 MHz, DMSO-$d_6$)



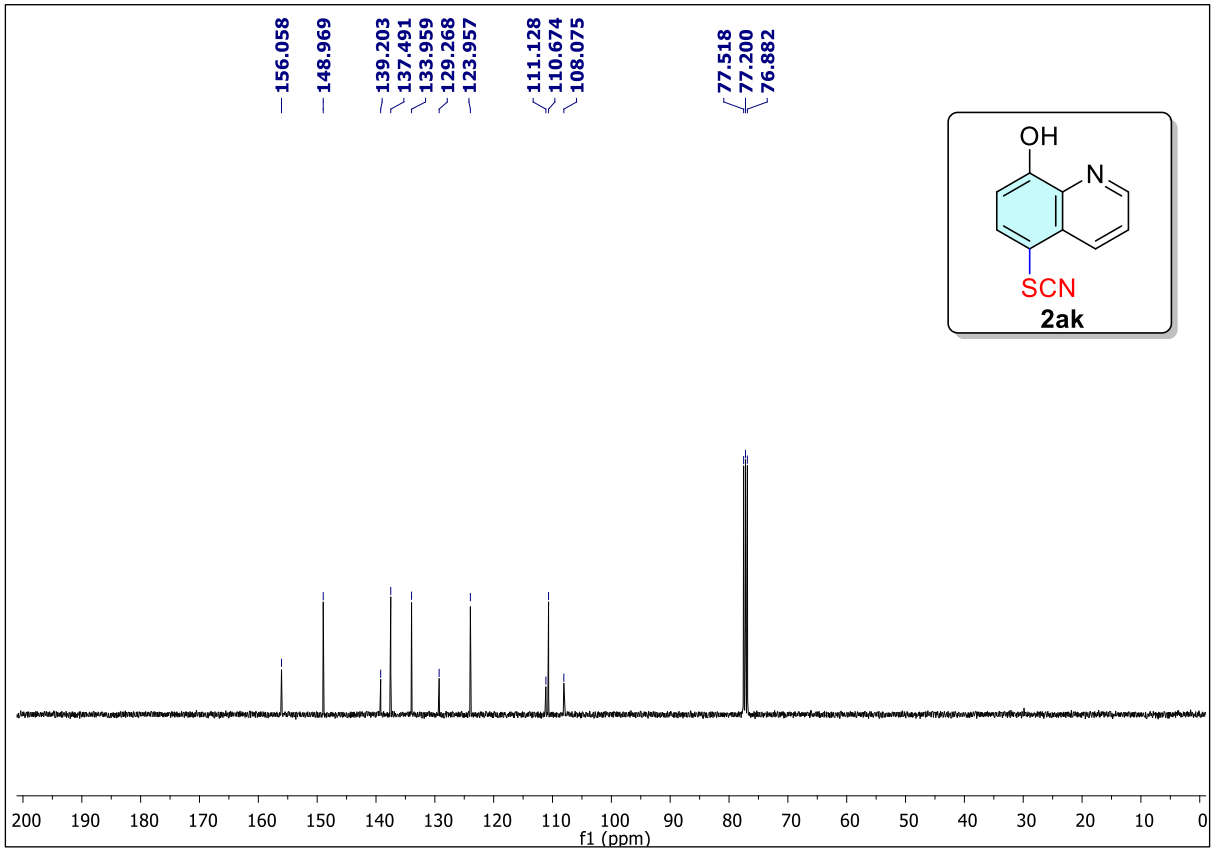

$^{1}$H NMR of **2aj** (500 MHz, DMSO-$d_6$)



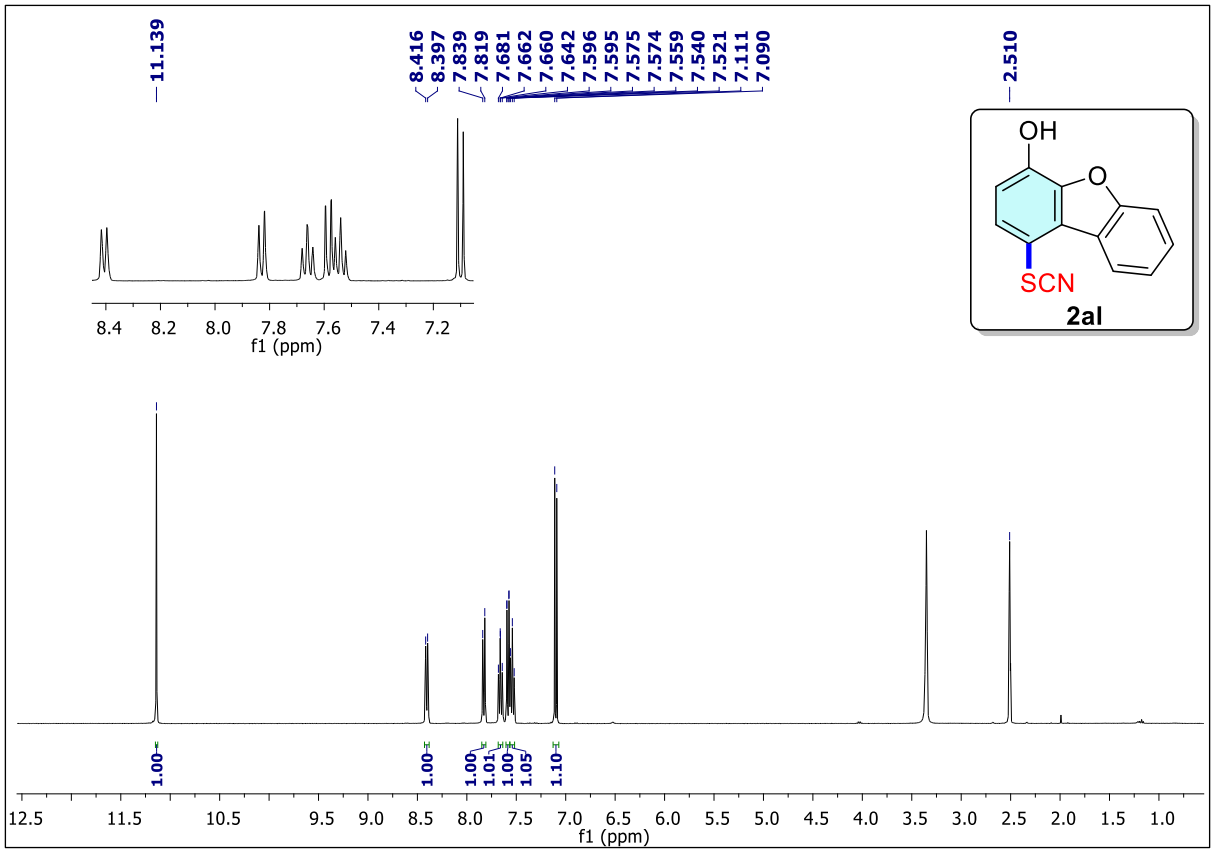

$^{13}$C{$^{1}$H} NMR of **2aj** (100 MHz, DMSO-$d_6$)



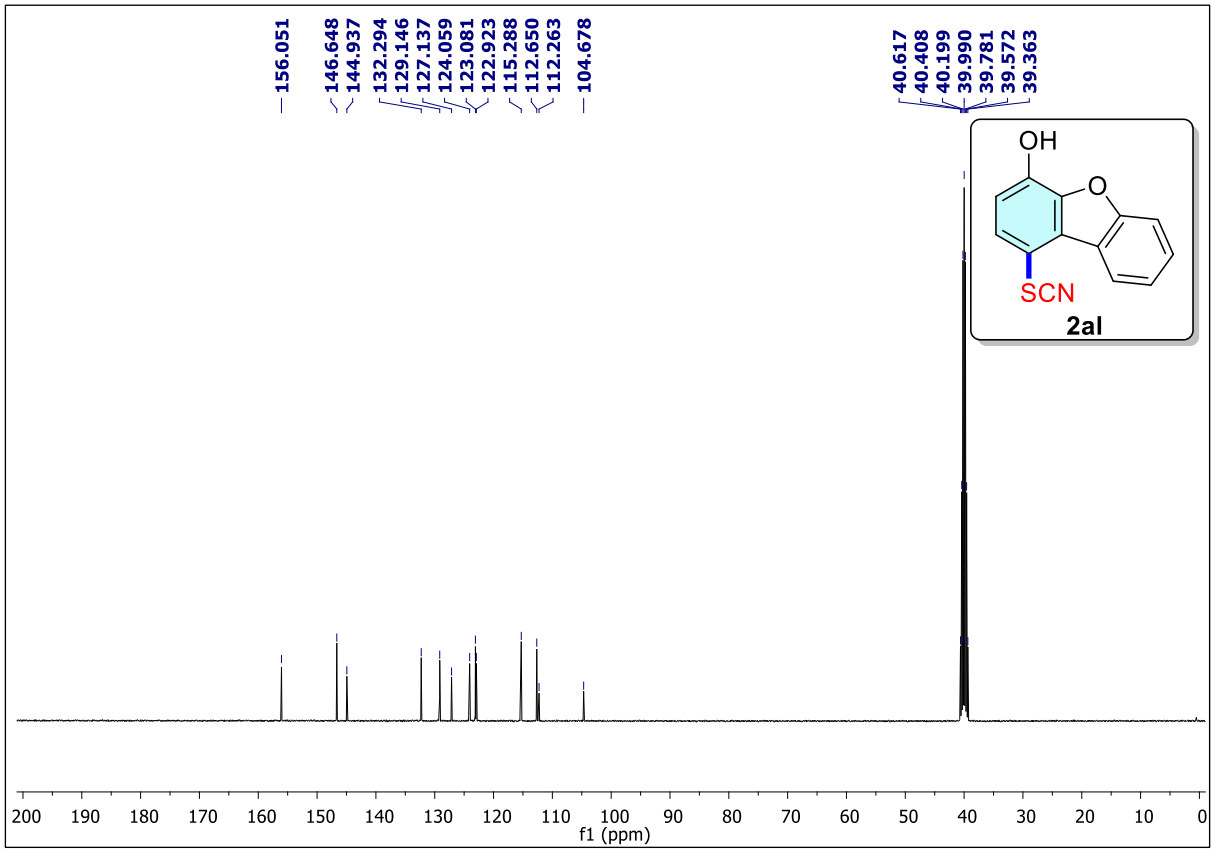

$^{1}$H NMR of **2ak** (400 MHz, $CDCl_3$)



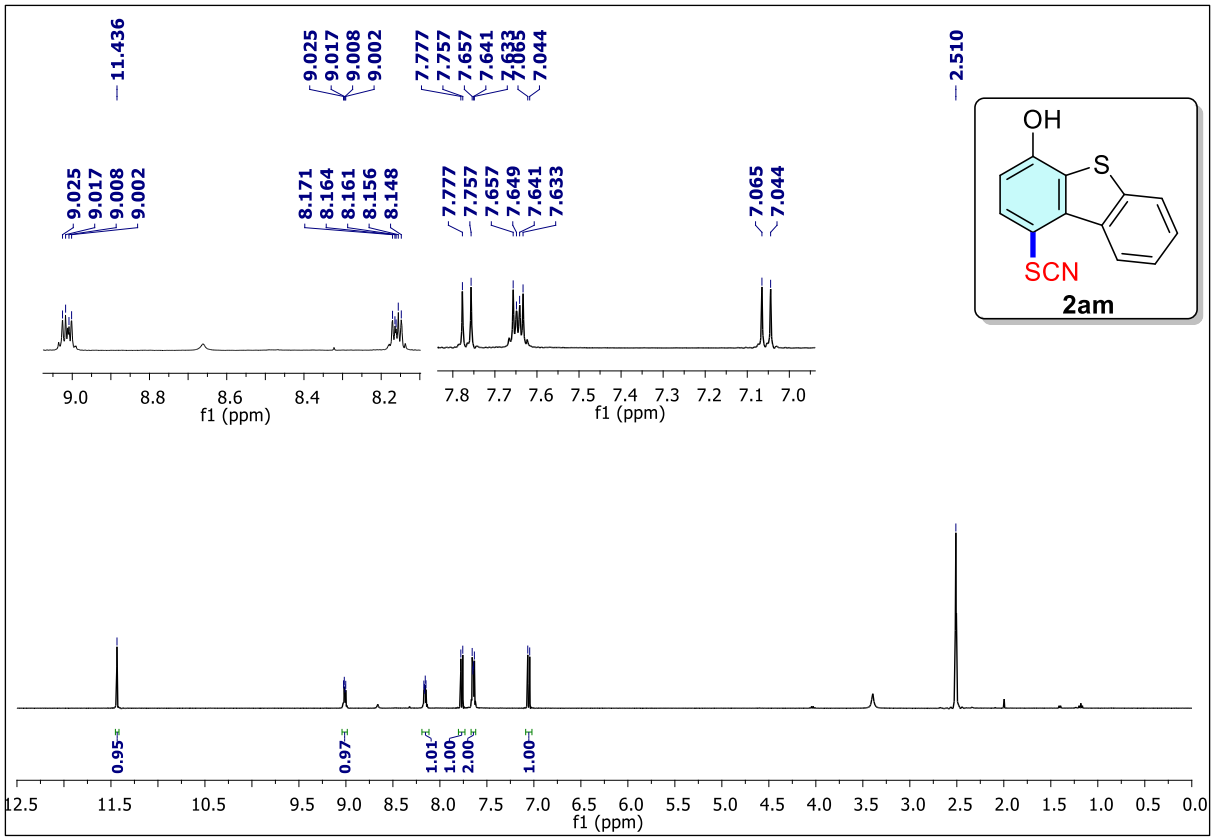

$^{13}$C{$^{1}$H} NMR of **2ak** (100 MHz, $CDCl_3$)



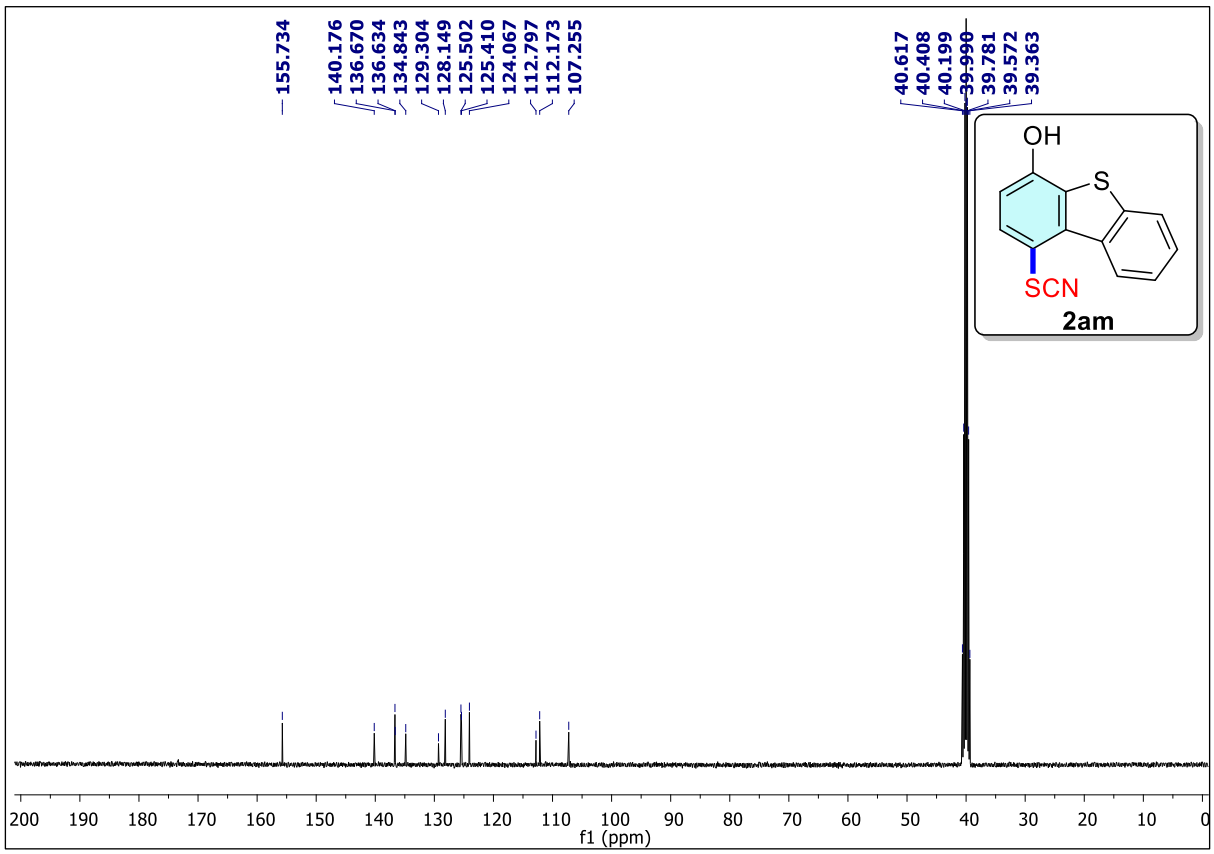

$^{1}$H NMR of **2al** (400 MHz, DMSO-$d_6$)



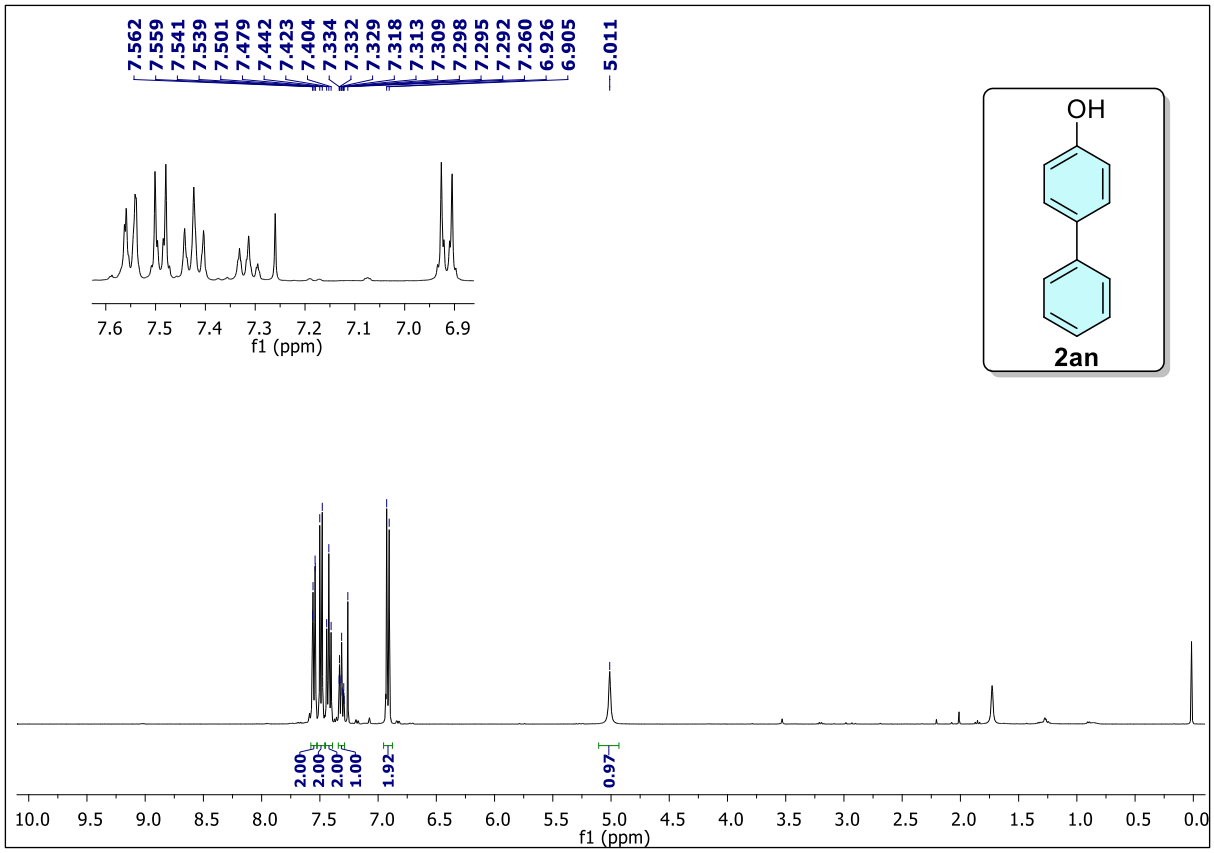

$^{13}$C{$^{1}$H} NMR of **2al** (100 MHz, DMSO-$d_6$)



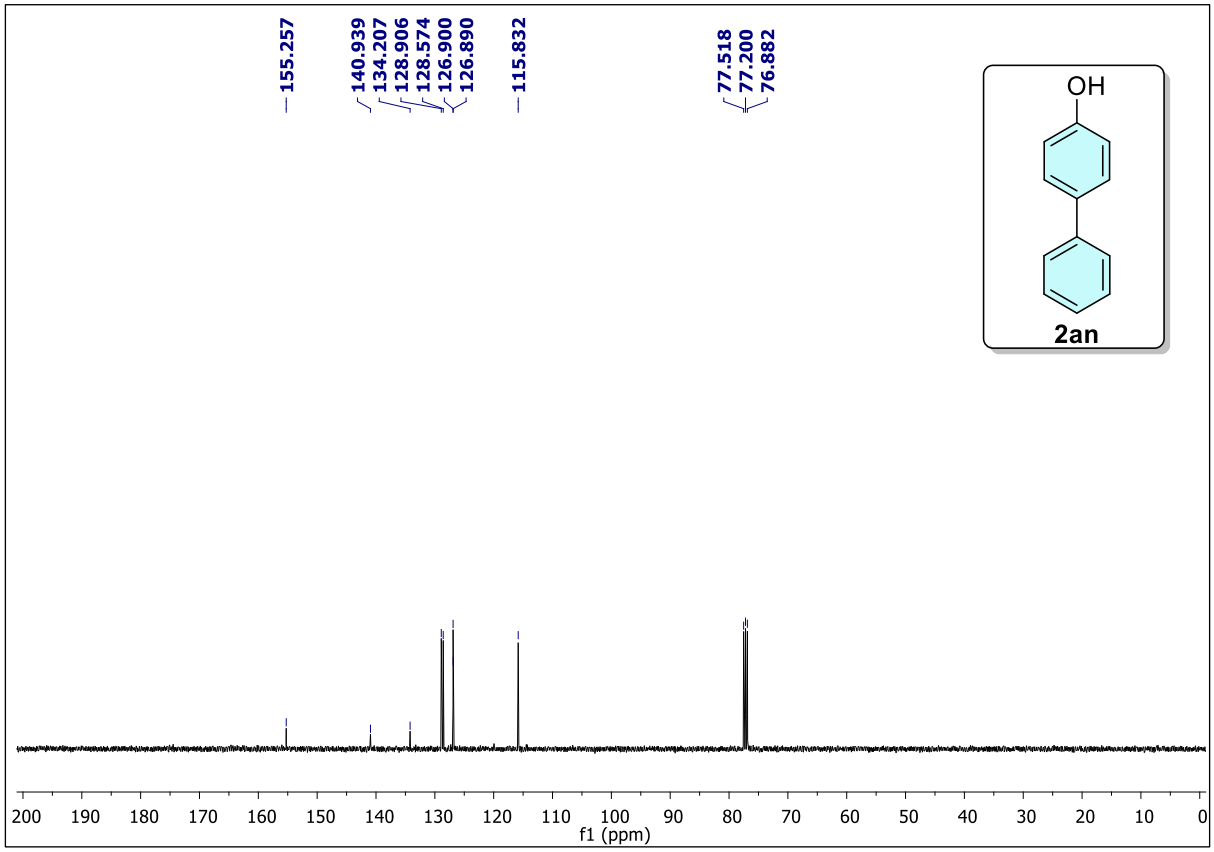

$^{1}$H NMR of **2am** (400 MHz, DMSO-$d_6$)



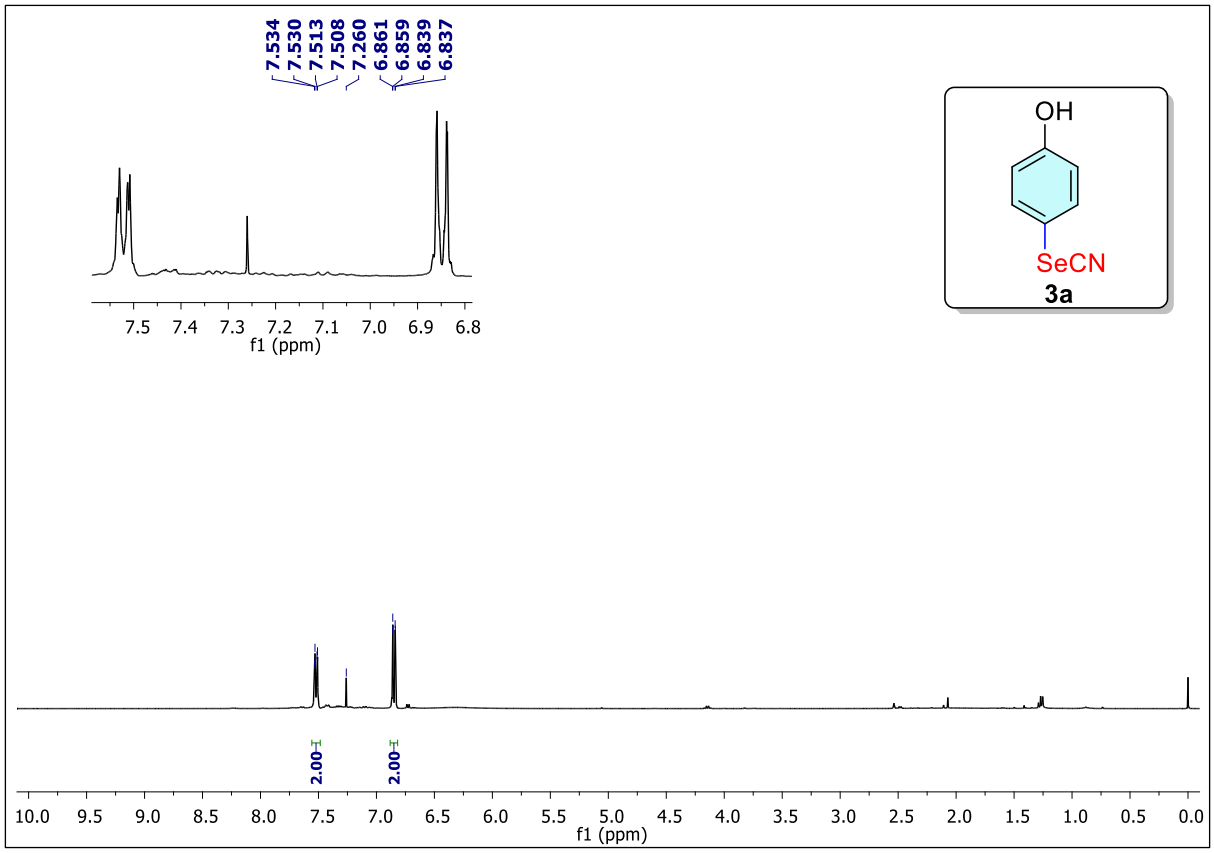

$^{13}$C{$^{1}$H} NMR of **2am** (100 MHz, DMSO-$d_6$)



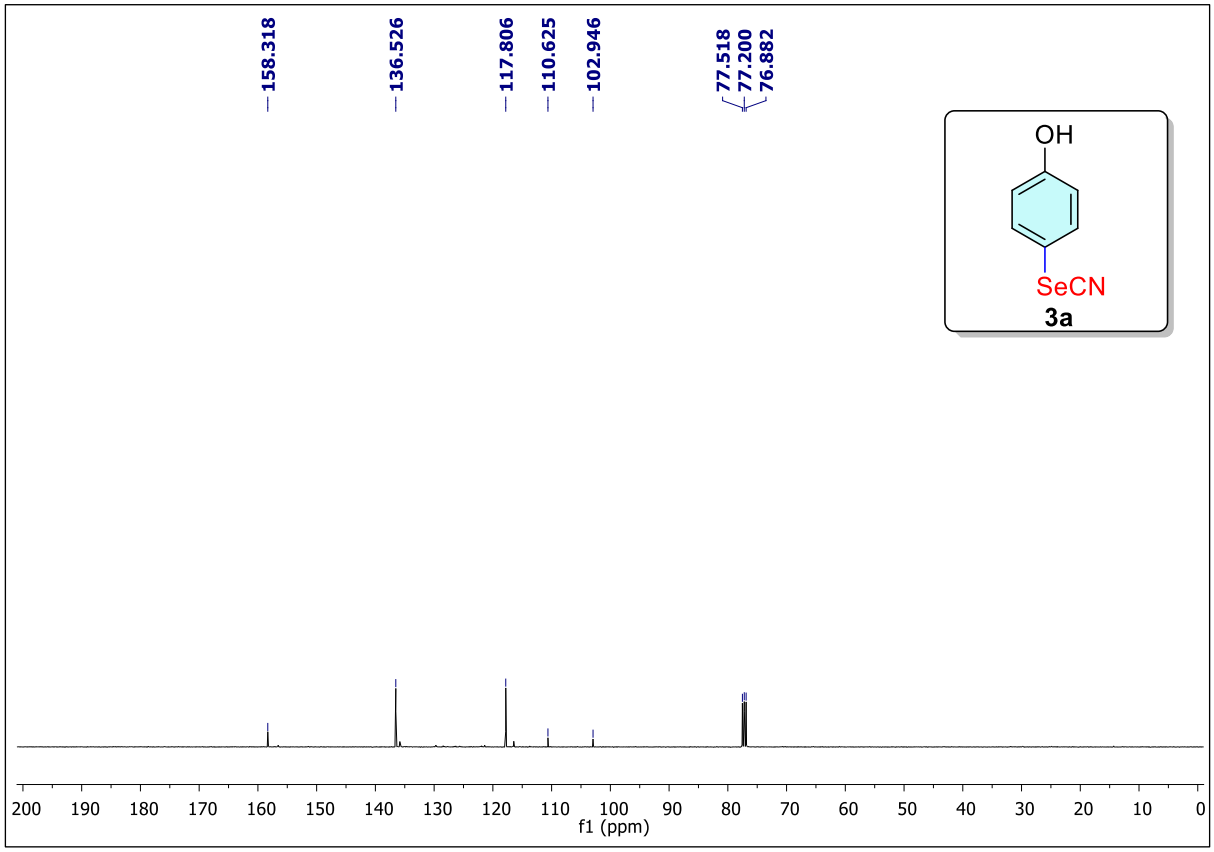

$^{1}$H NMR of **2an** (400 MHz, $CDCl_3$)



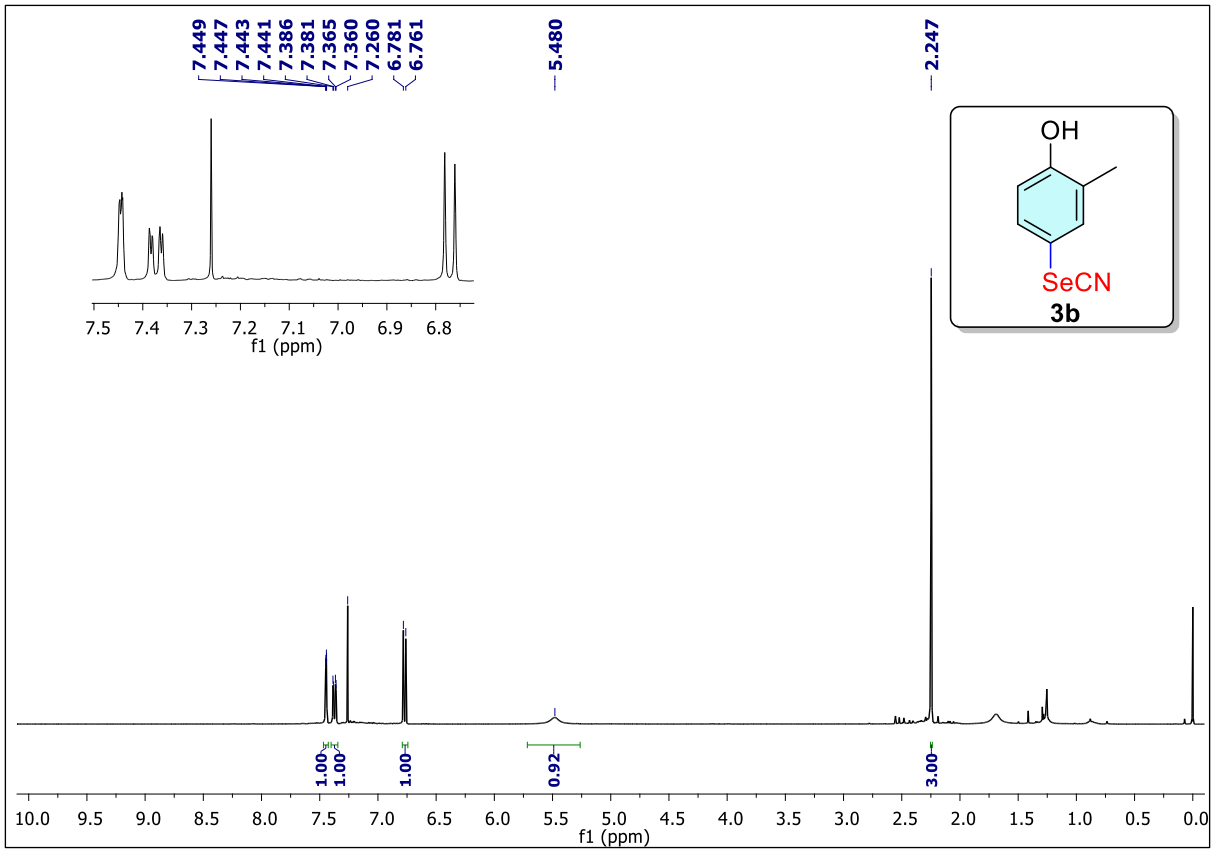

$^{13}$C{$^{1}$H} NMR of **2an** (100 MHz, $CDCl_3$)



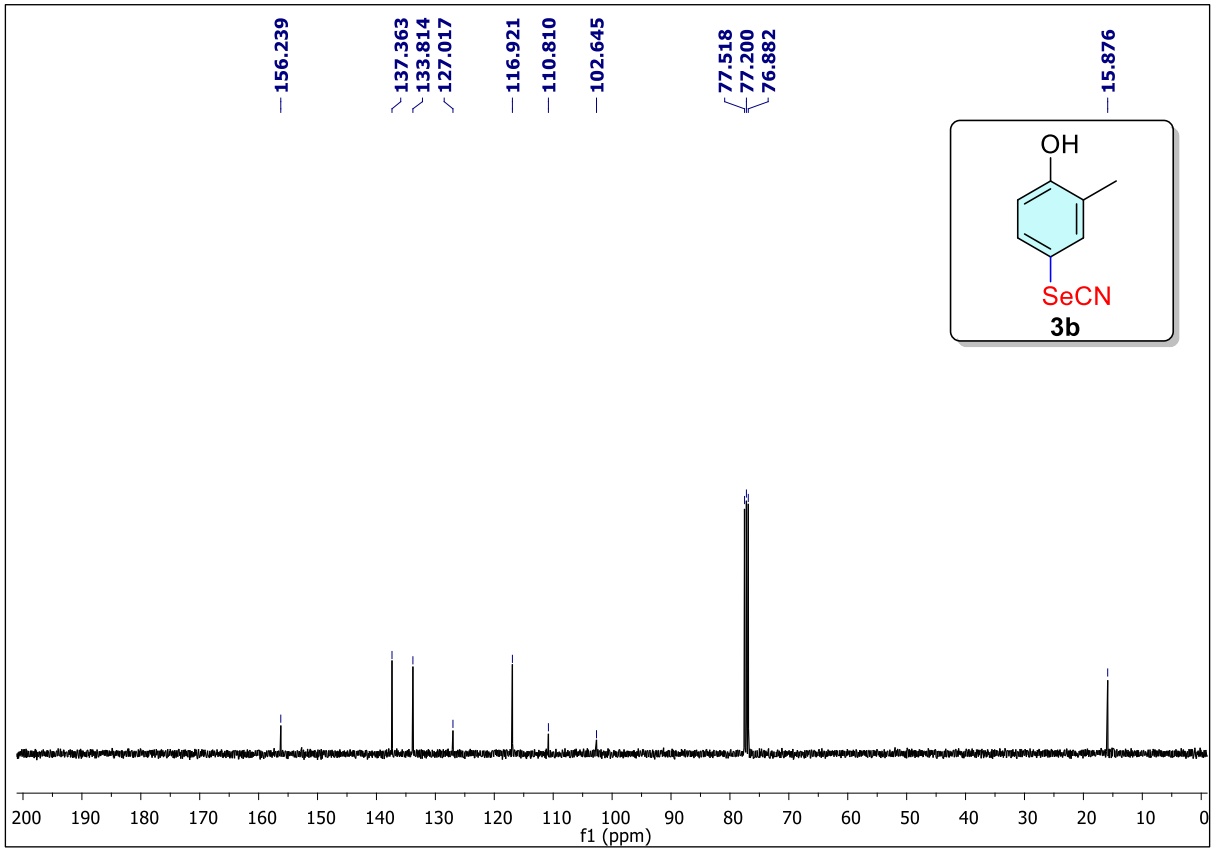

$^{1}$H NMR of **3a** (400 MHz, $CDCl_3$)



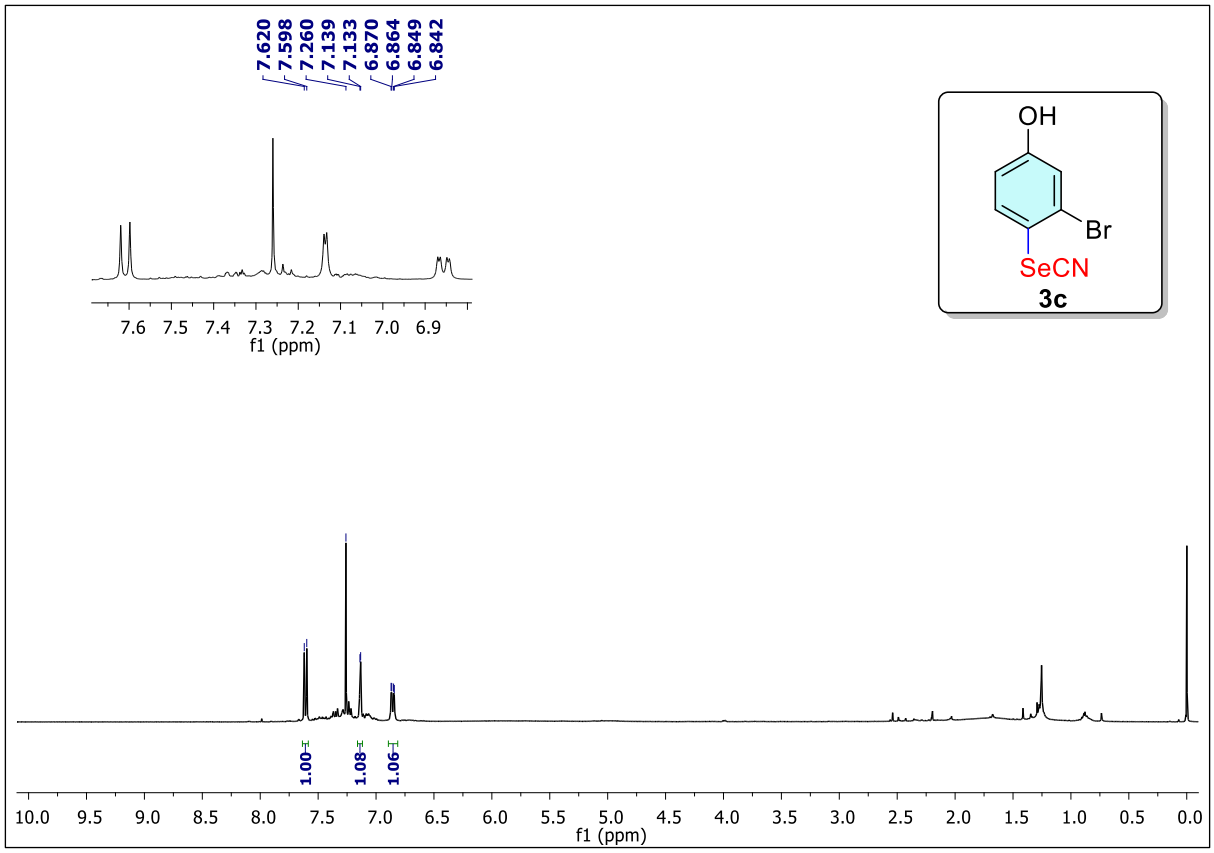

$^{13}$C{$^{1}$H} NMR of **3a** (100 MHz, $CDCl_3$)



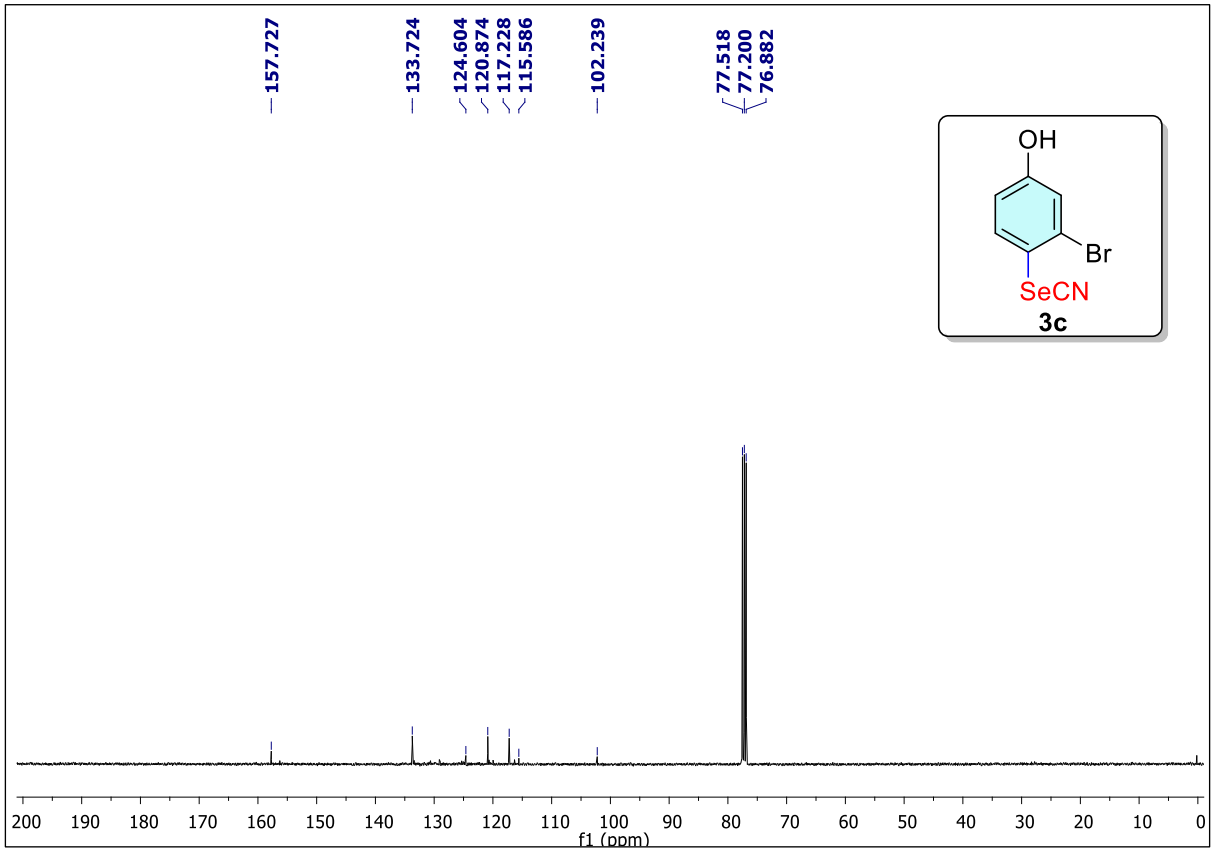

$^{1}$H NMR of **3b** (400 MHz, $CDCl_3$)



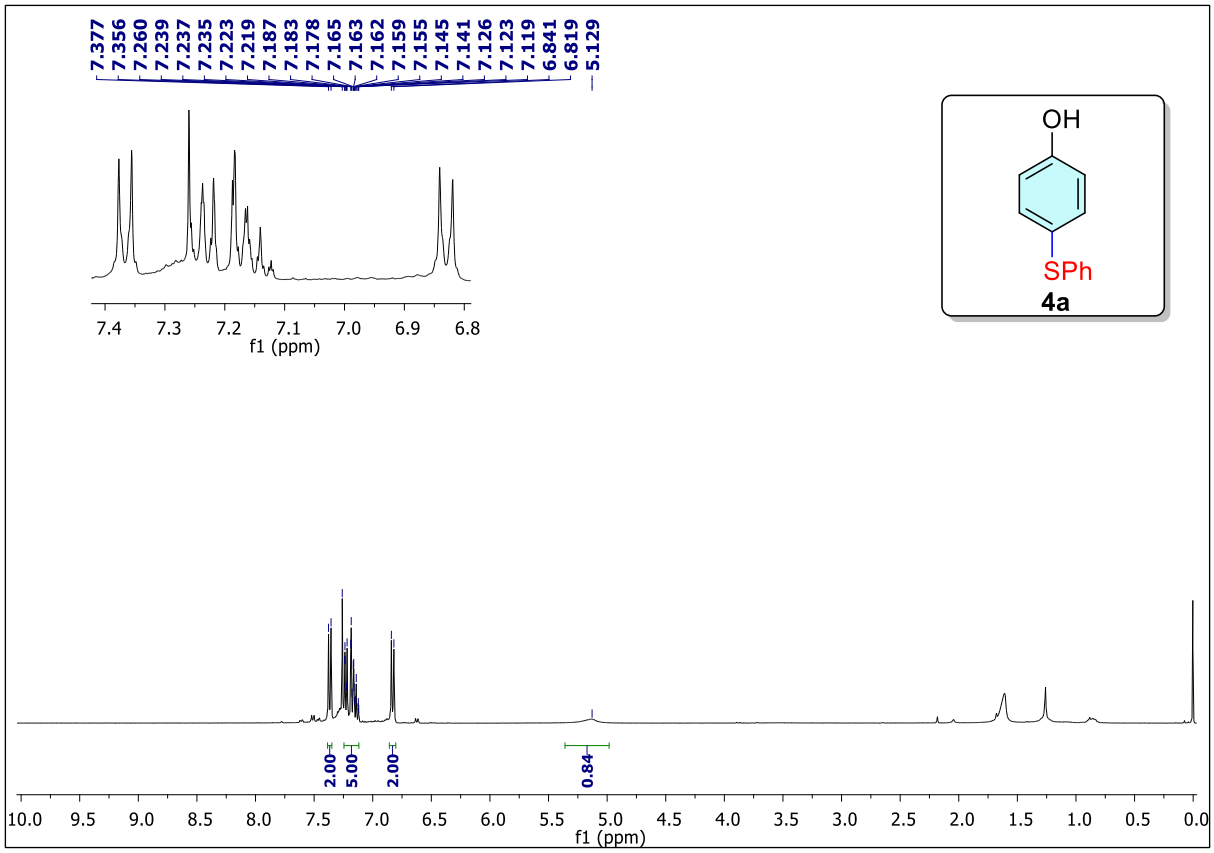

$^{13}$C{$^{1}$H} NMR of **3b** (100 MHz, $CDCl_3$)



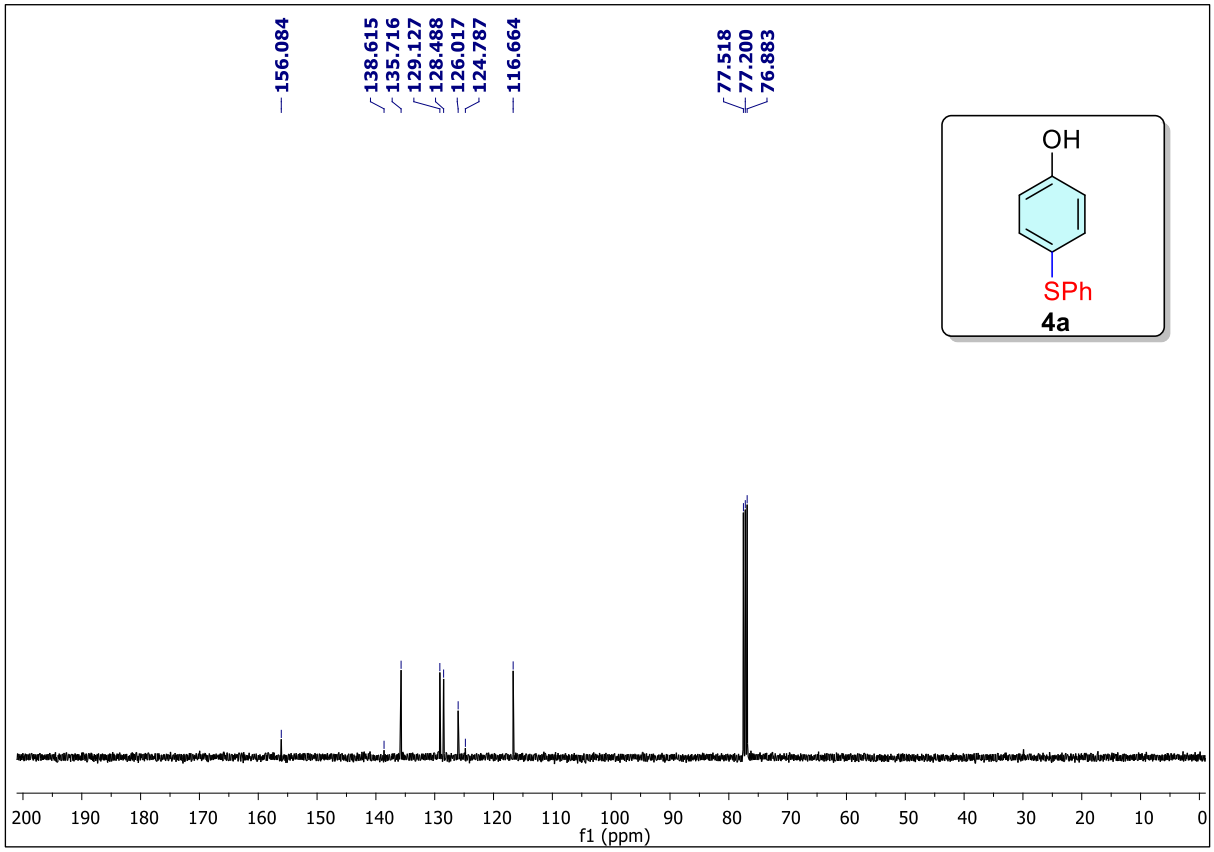

$^{1}$H NMR of **3c** (400 MHz, $CDCl_3$)



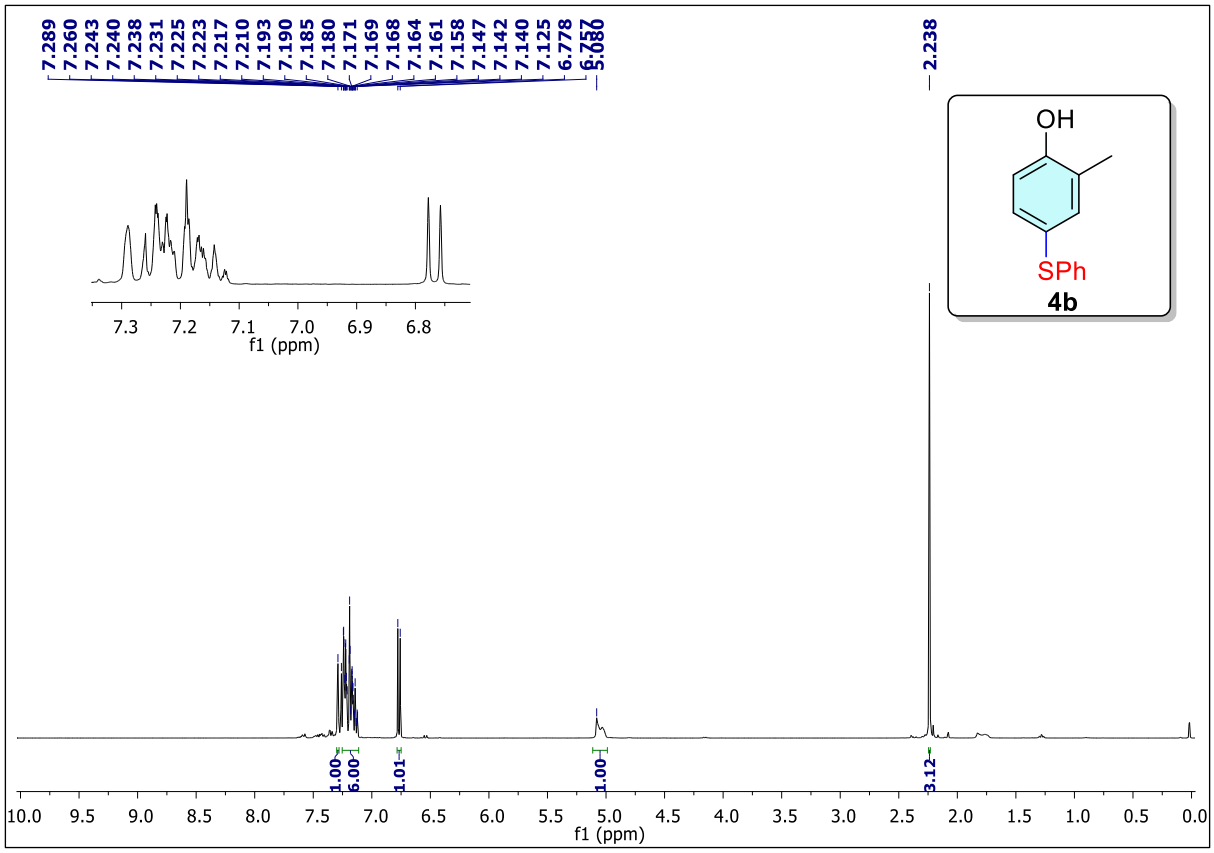

$^{13}$C{$^{1}$H} NMR of **3c** (100 MHz, $CDCl_3$)




$^{1}$H NMR of **4a** (400 MHz, $CDCl_3$)




$^{13}$C{$^{1}$H} NMR of **4a** (100 MHz, $CDCl_3$)

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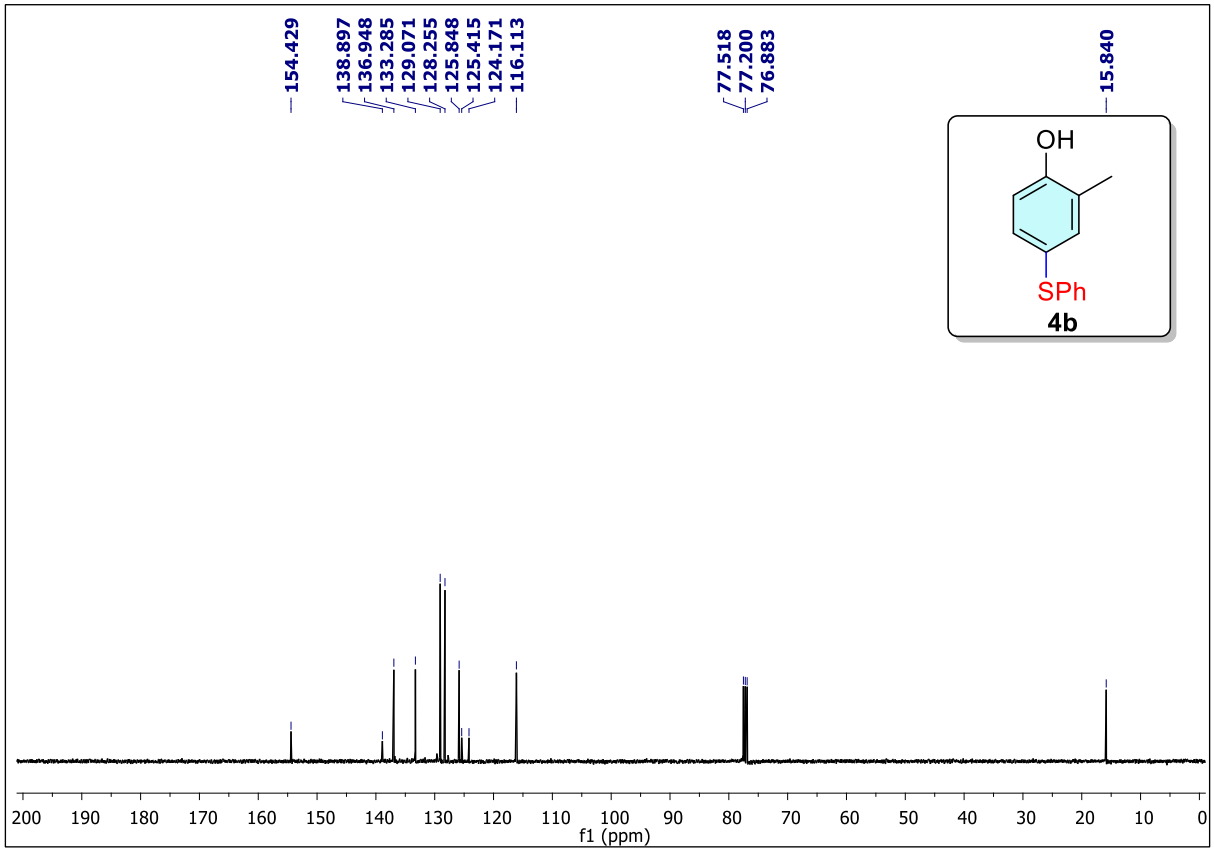
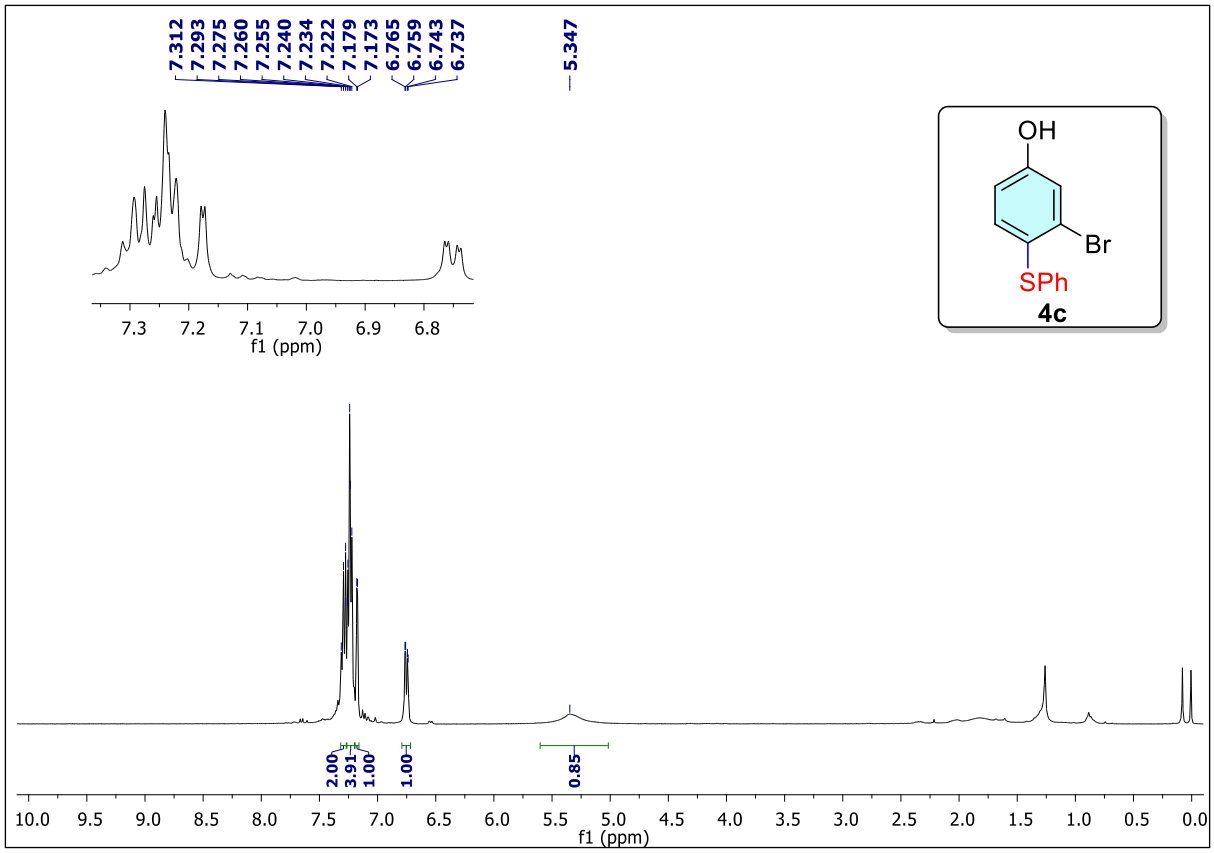
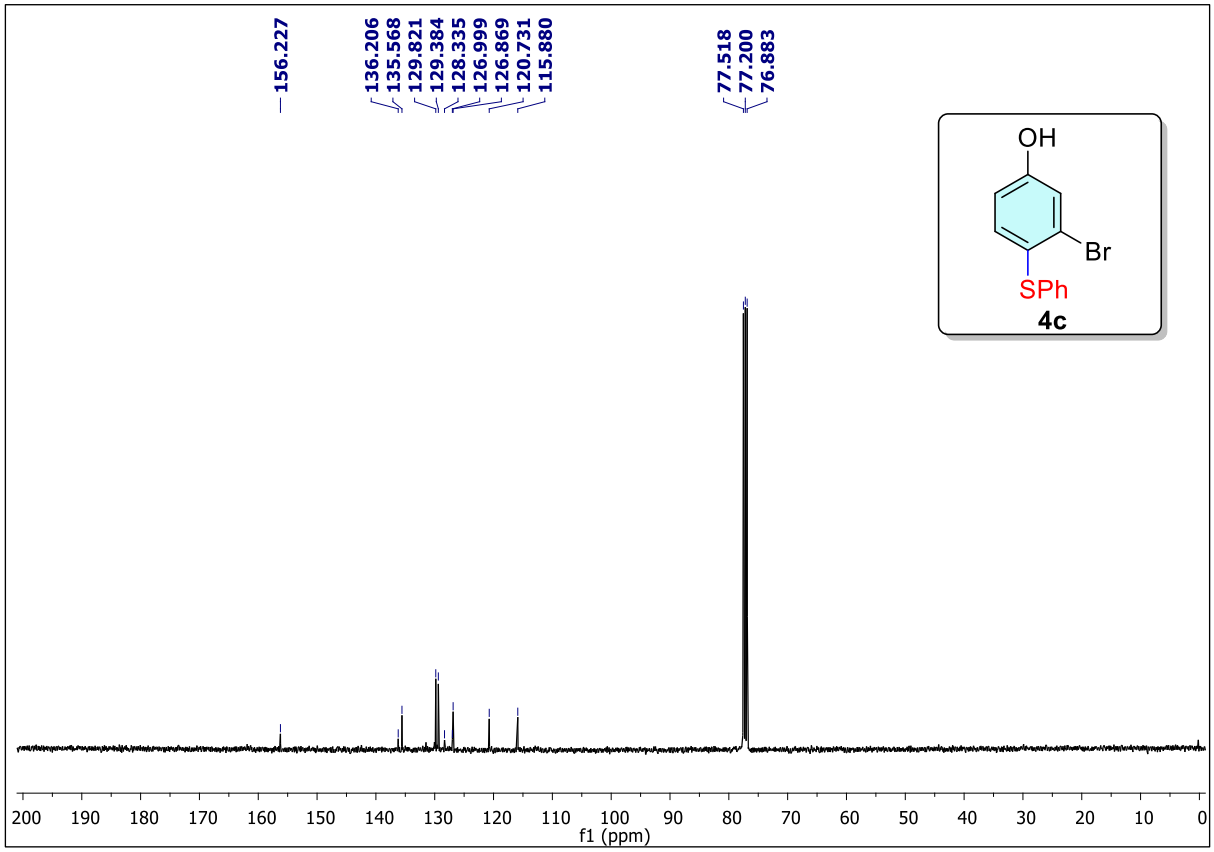



$^{13}$C{$^{1}$H} NMR of **4b** (100 MHz, $CDCl_3$)




$^{1}$H NMR of **4c** (400 MHz, $CDCl_3$)

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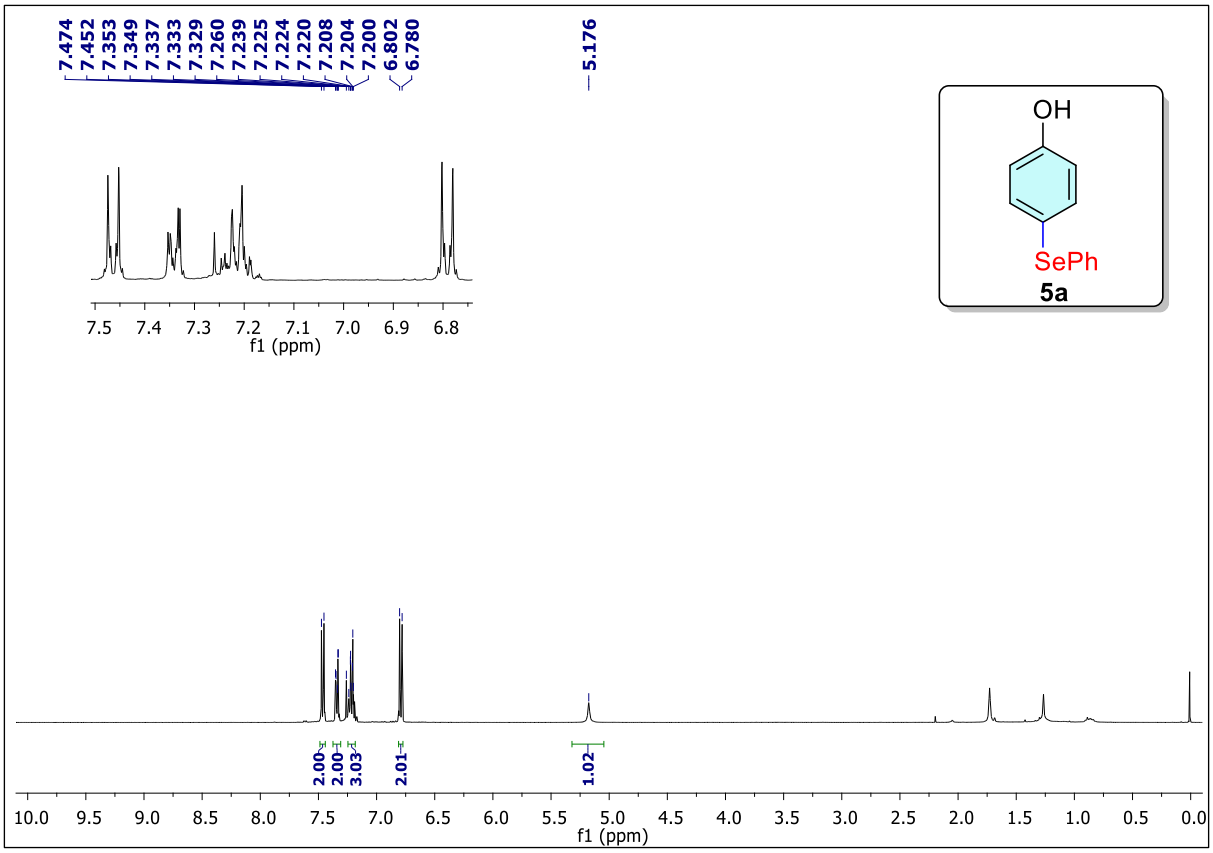
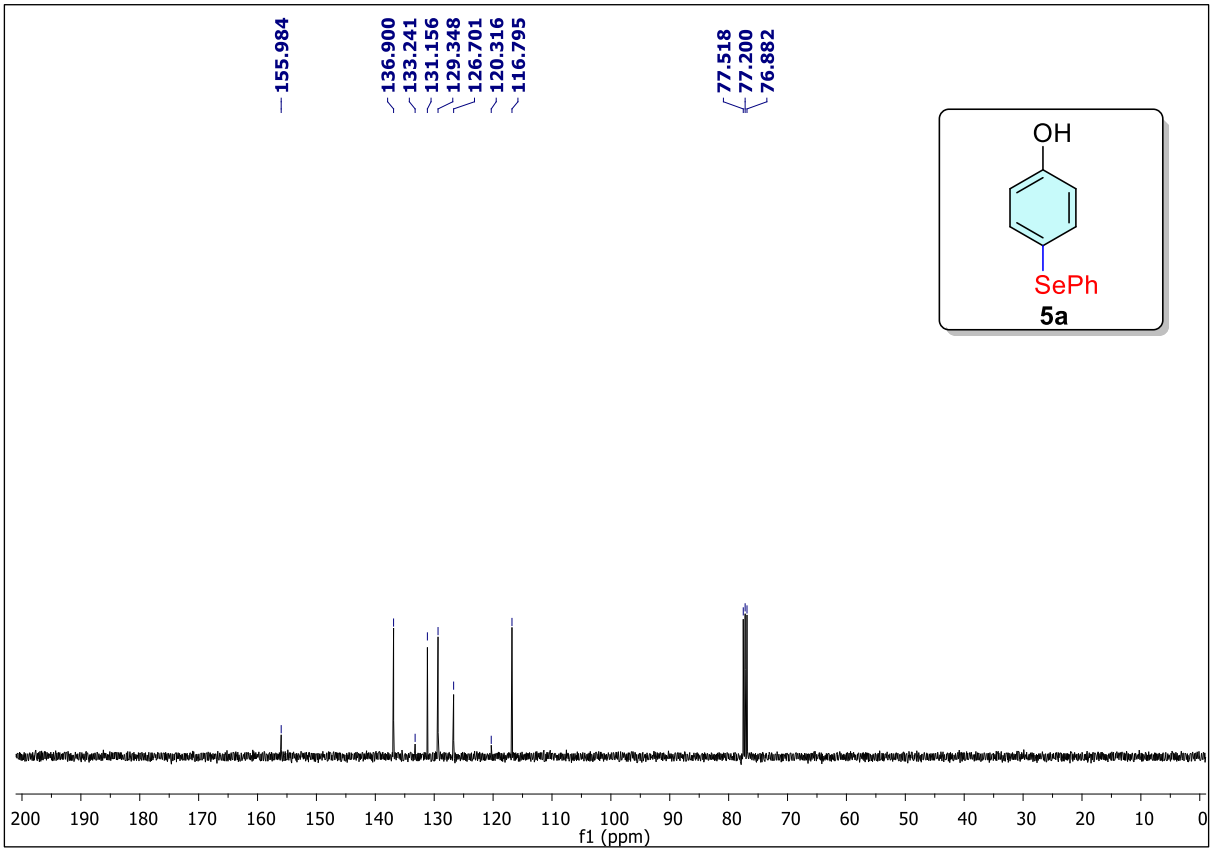
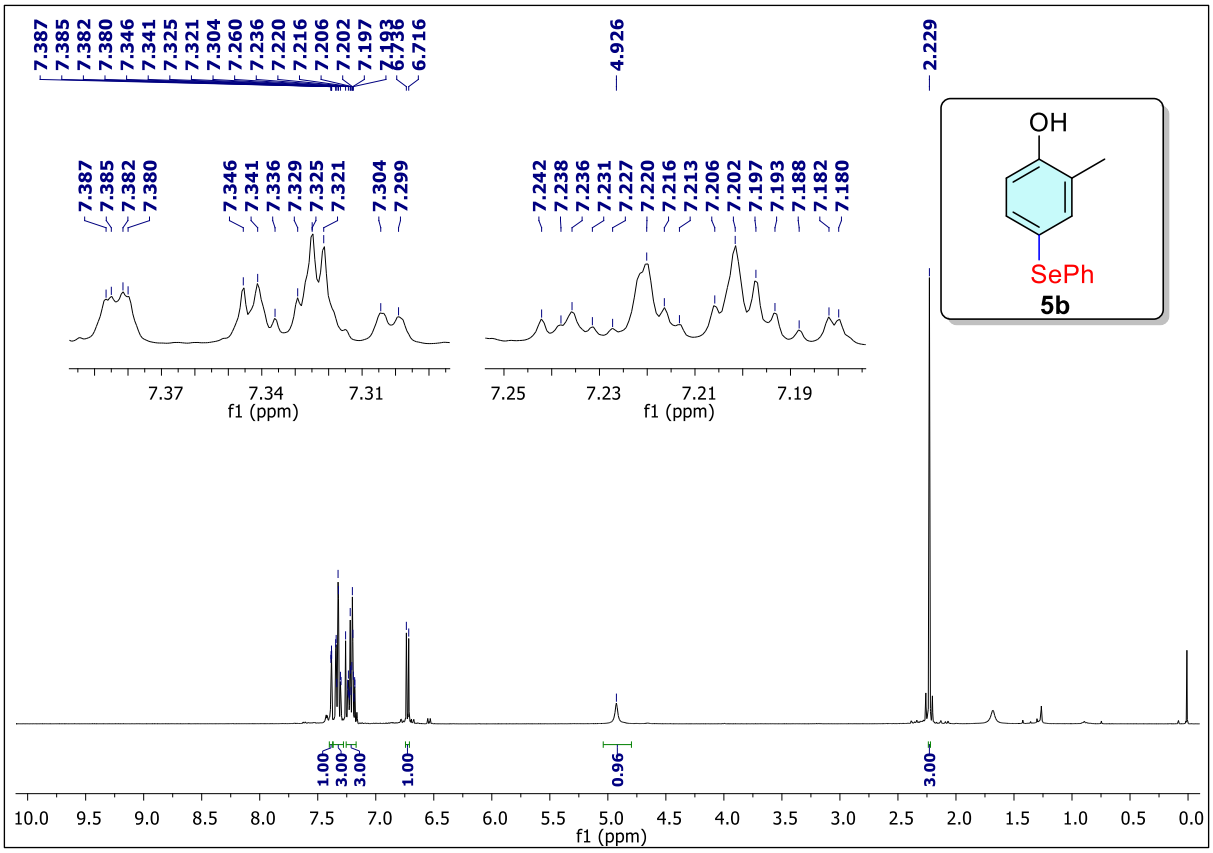


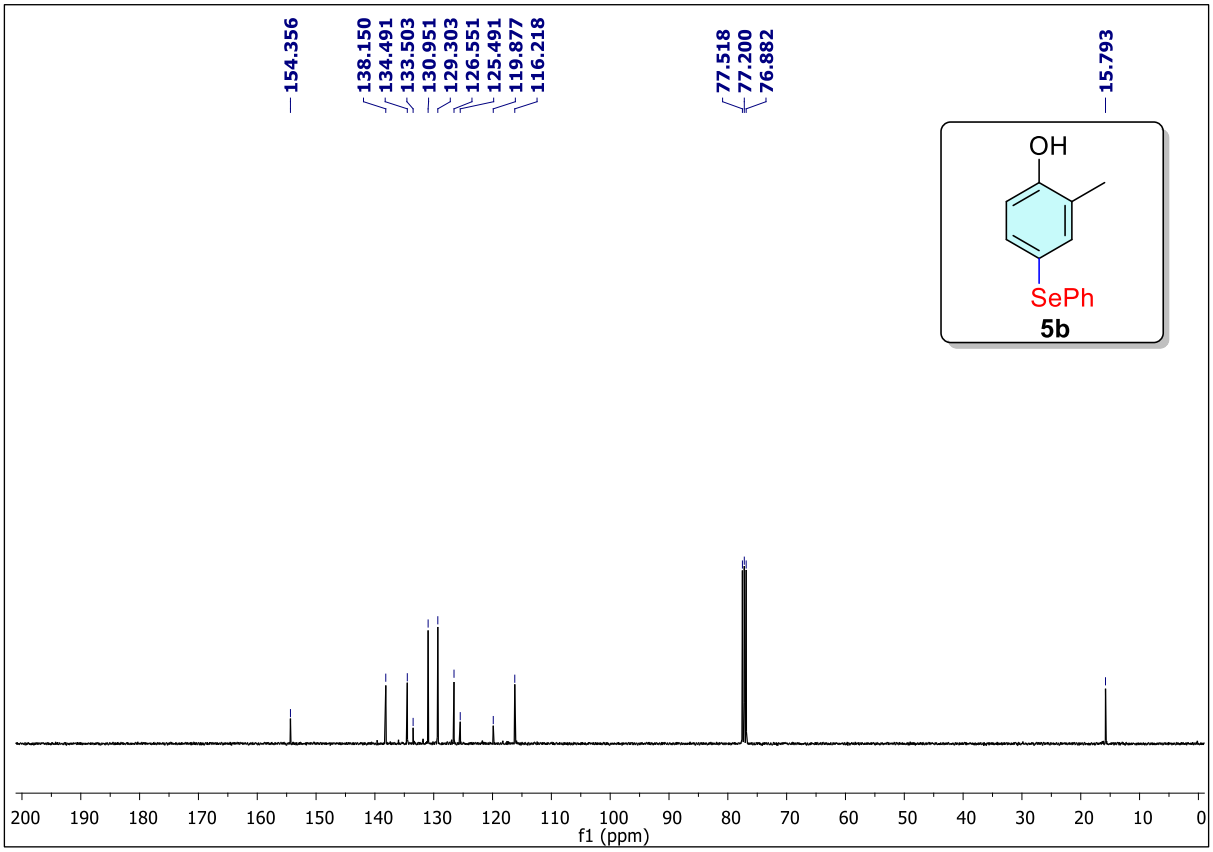

$^{1}$H NMR of **5a** (400 MHz, $CDCl_3$)




$^{13}$C{$^{1}$H} NMR of **5a** (100 MHz, $CDCl_3$)




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

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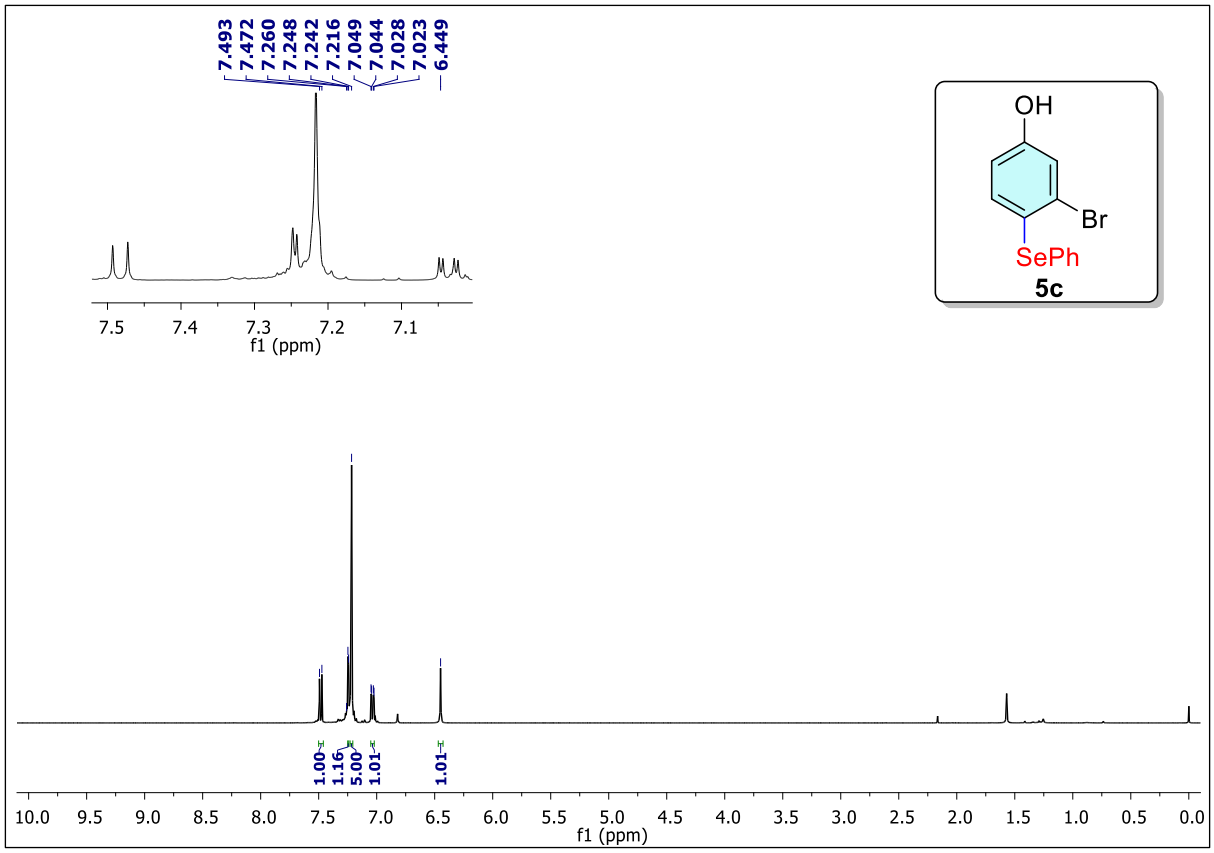
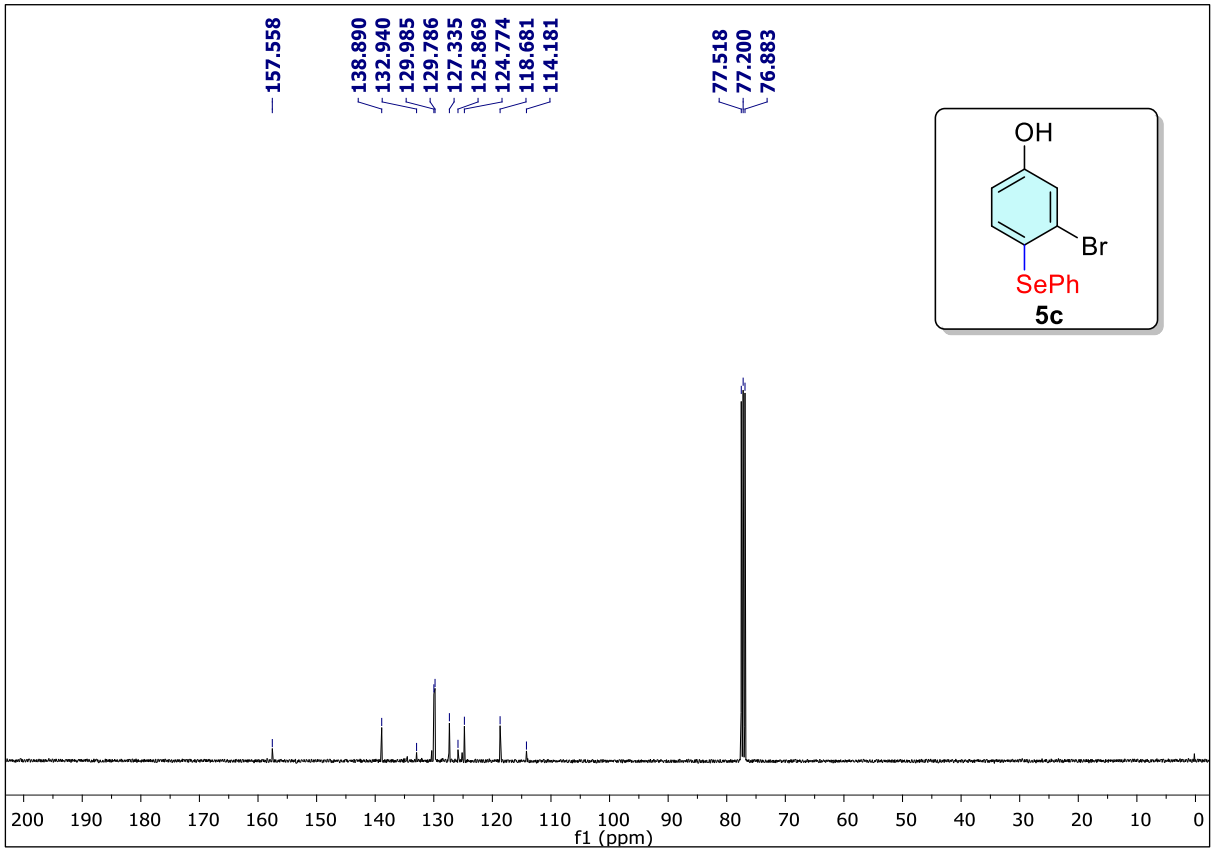
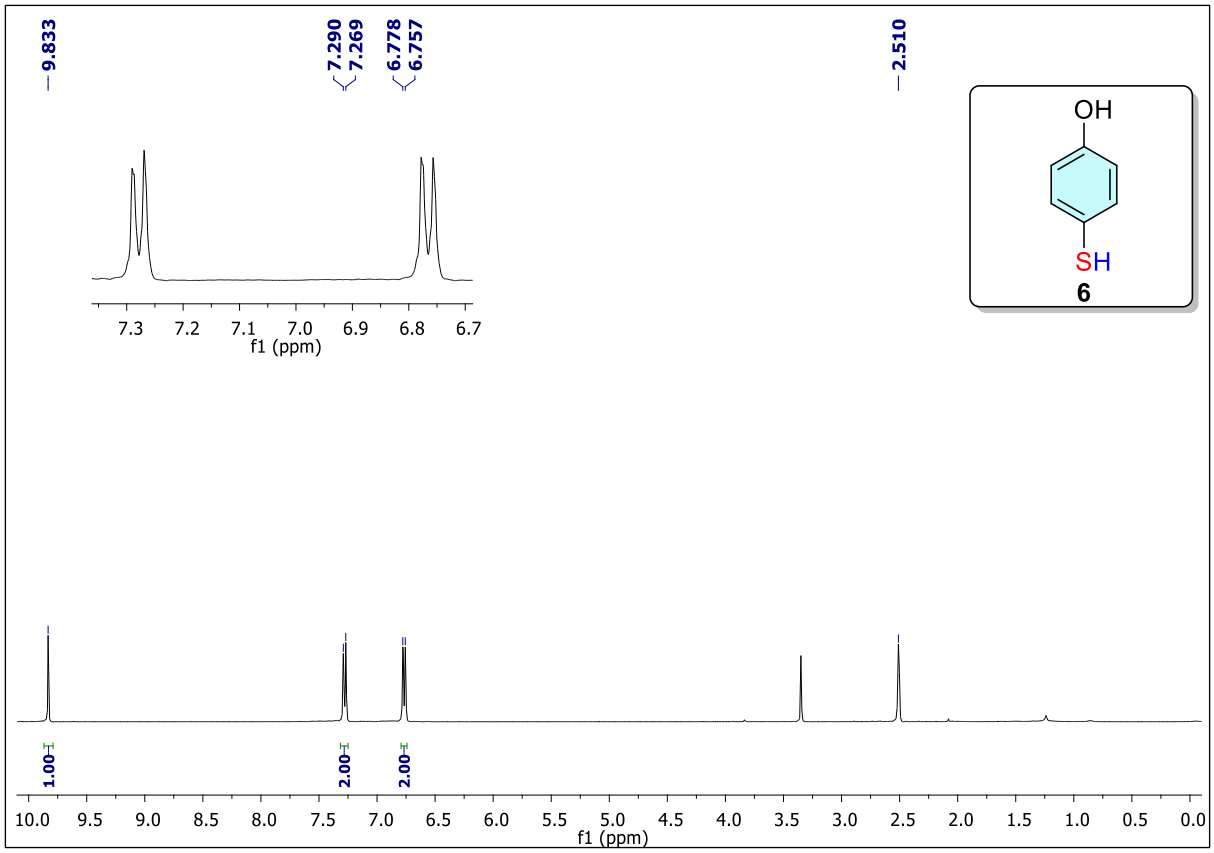


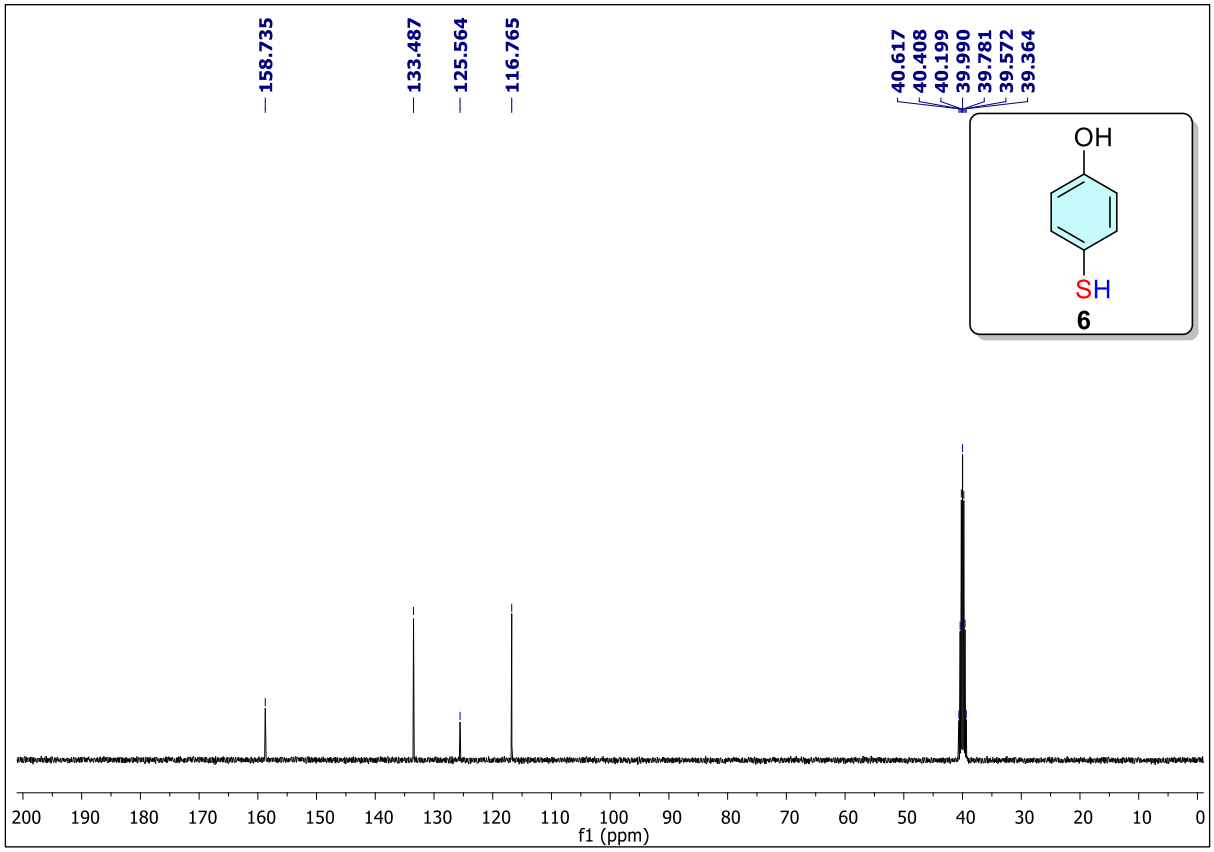

$^{1}$H NMR of **5c** (400 MHz, $CDCl_3$)



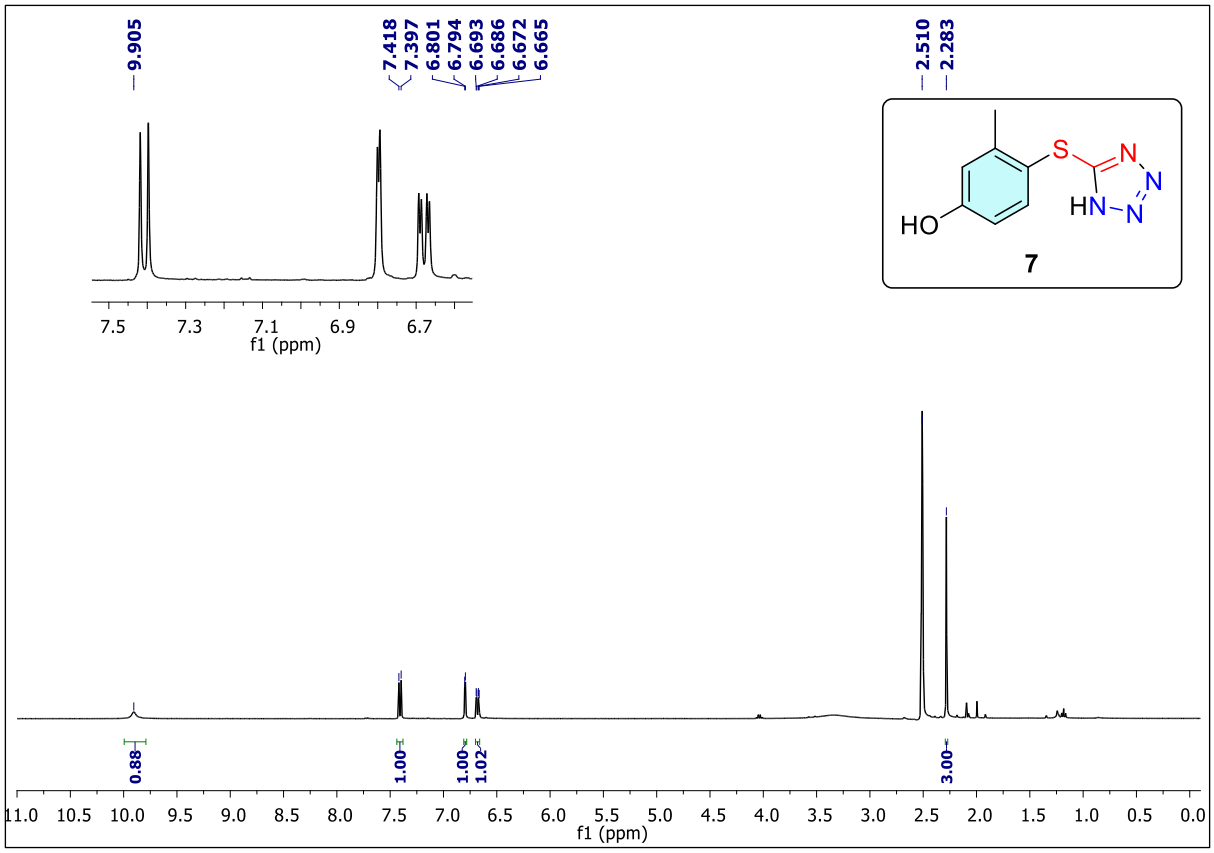

$^{13}$C{$^{1}$H} NMR of **5c** (100 MHz, $CDCl_3$)



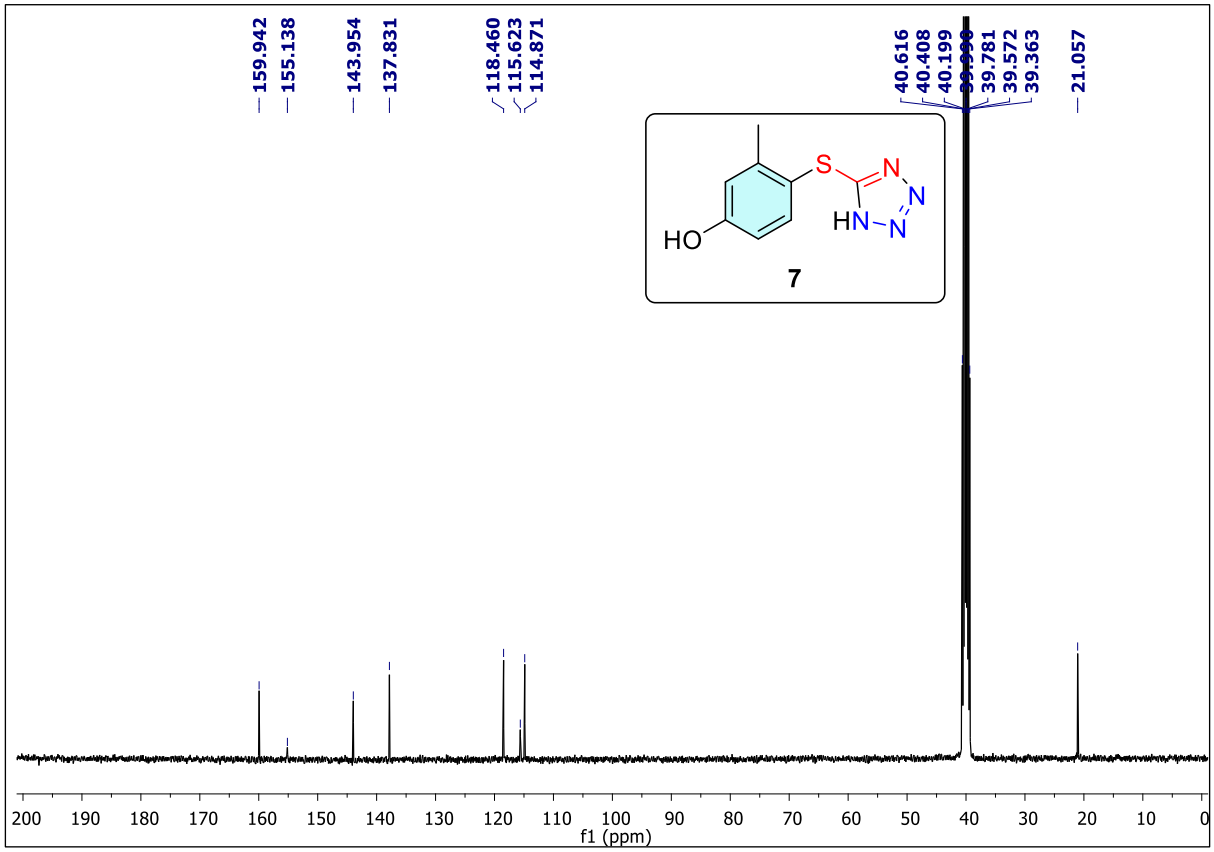

$^{1}$H NMR of **6** (400 MHz, DMSO-$d_6$)



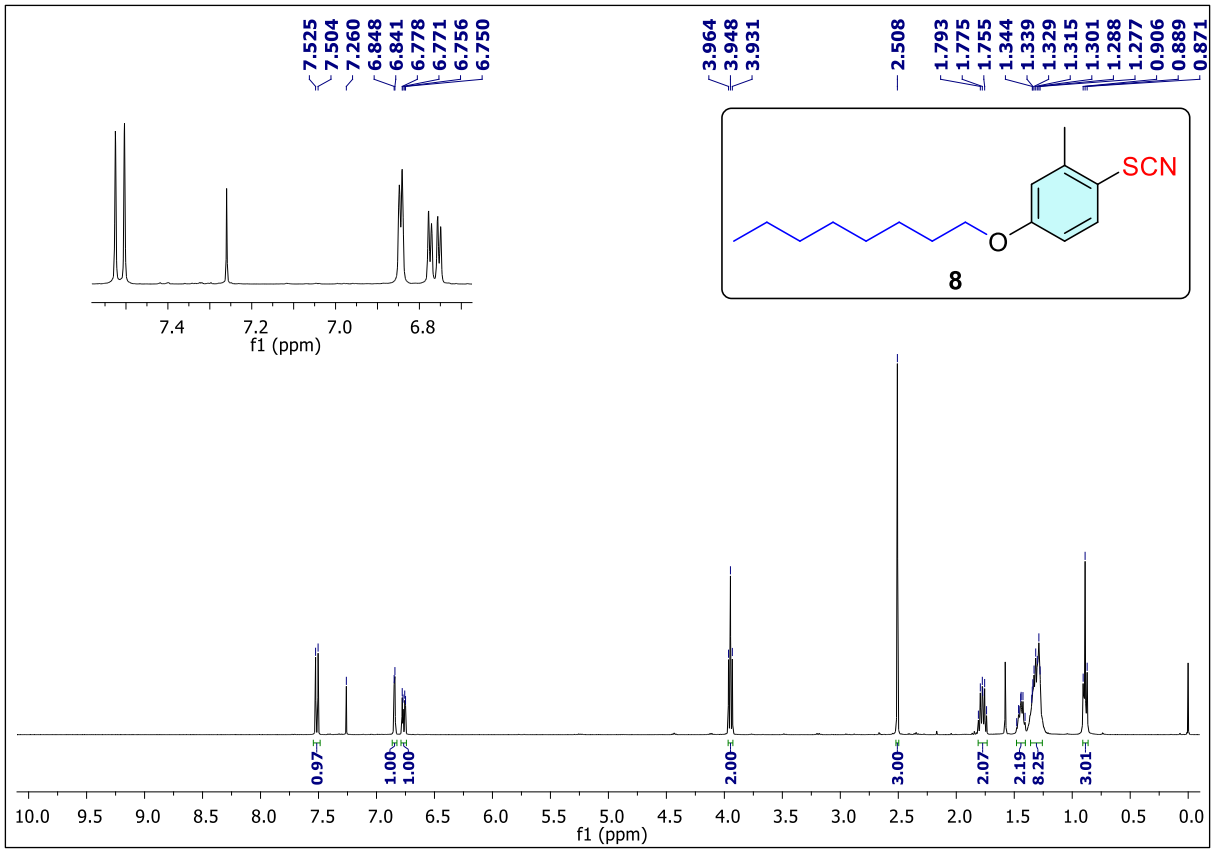

$^{13}$C{$^{1}$H} NMR of **6** (100 MHz, DMSO-$d_6$)



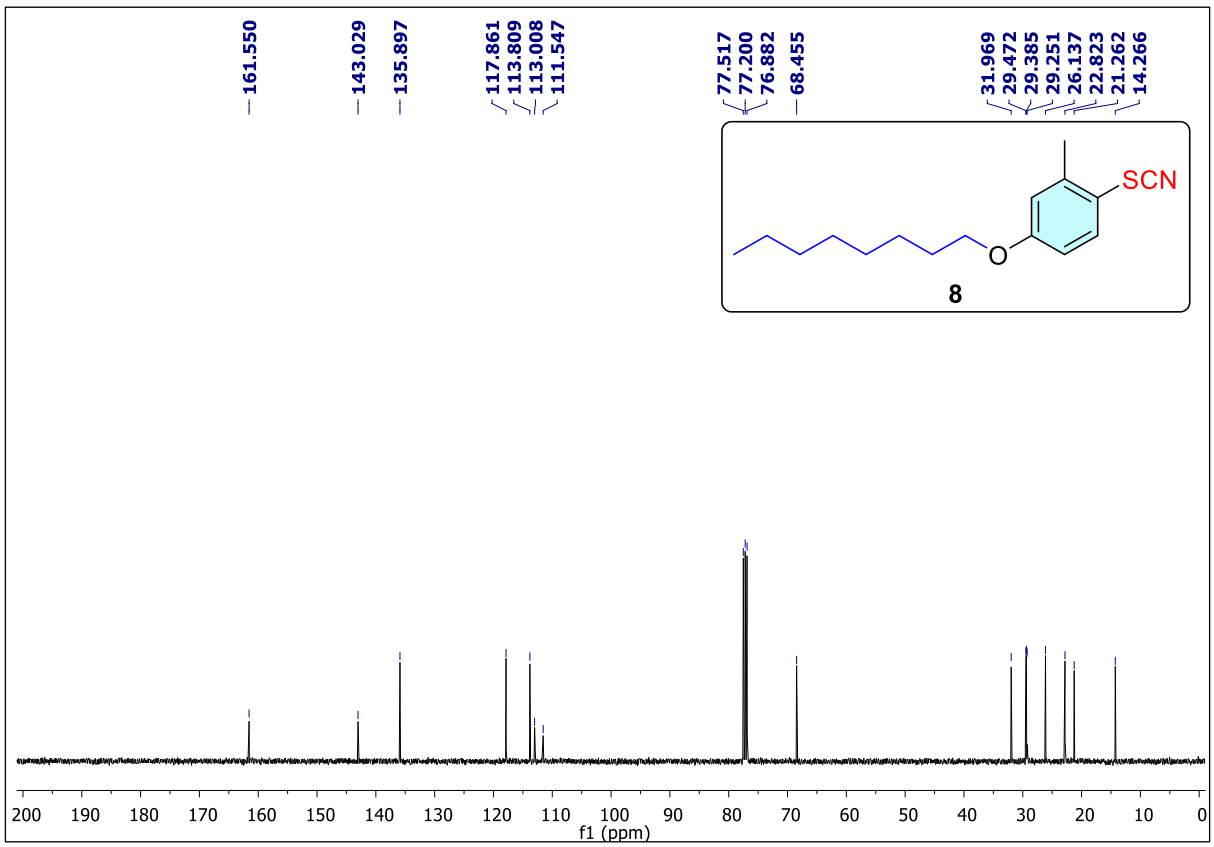

$^{1}$H NMR of **7** (400 MHz, DMSO-$d_6$)



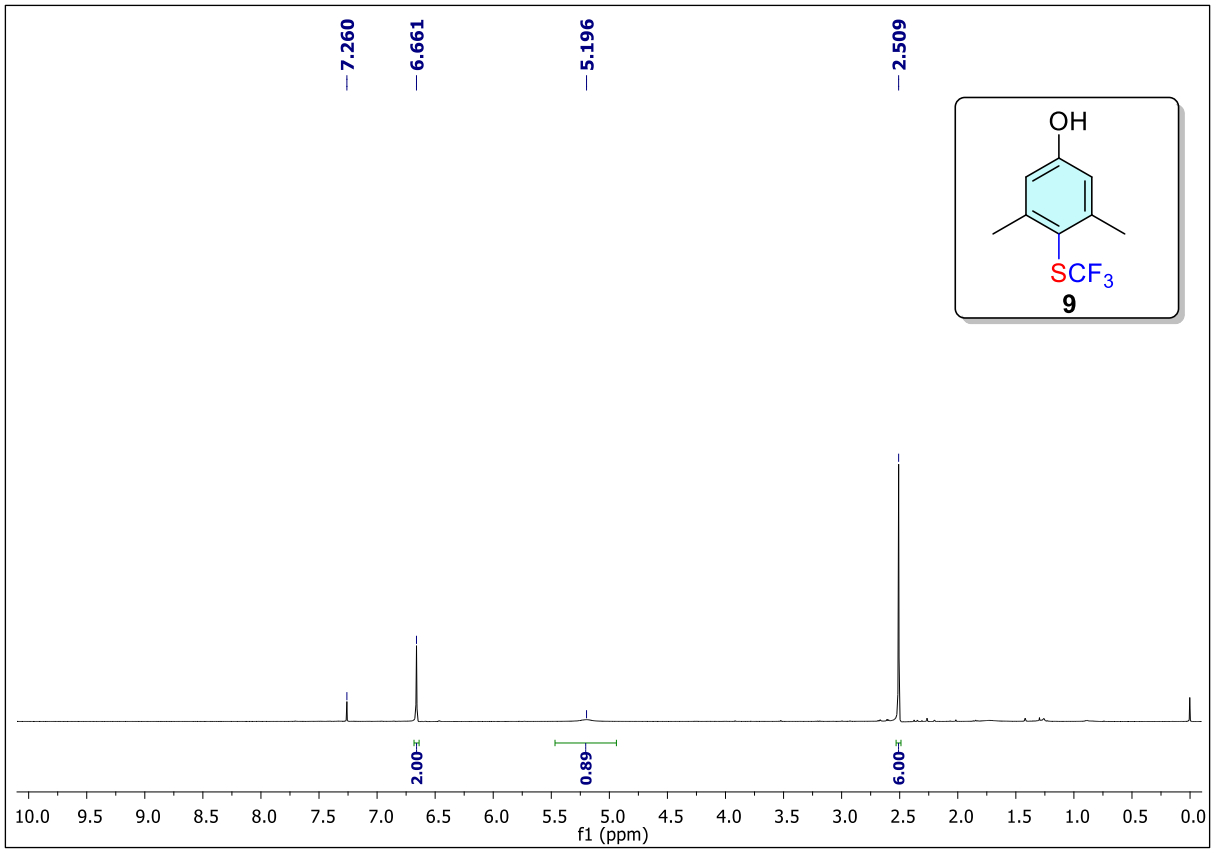

$^{13}$C{$^{1}$H} NMR of **7** (100 MHz, DMSO-$d_6$)



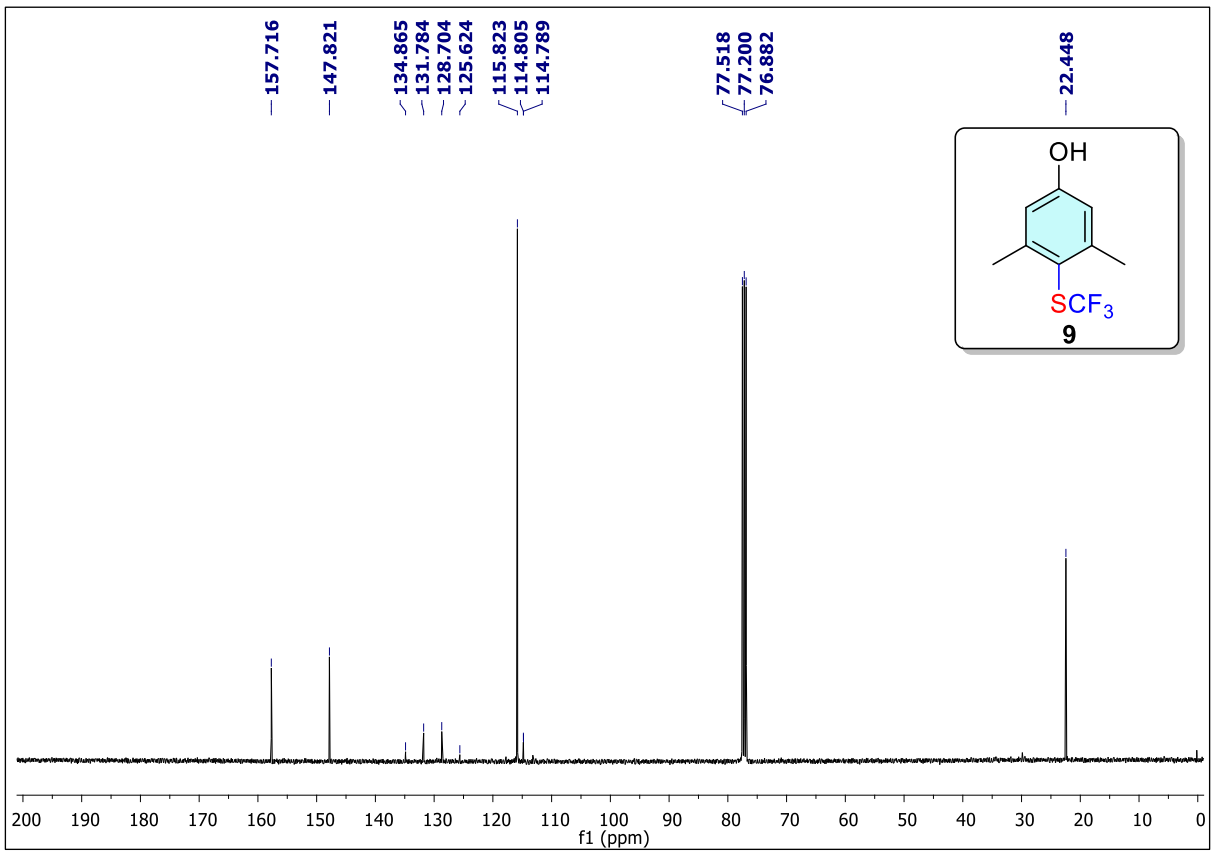

$^{1}$H NMR of **8** (400 MHz, $CDCl_3$)



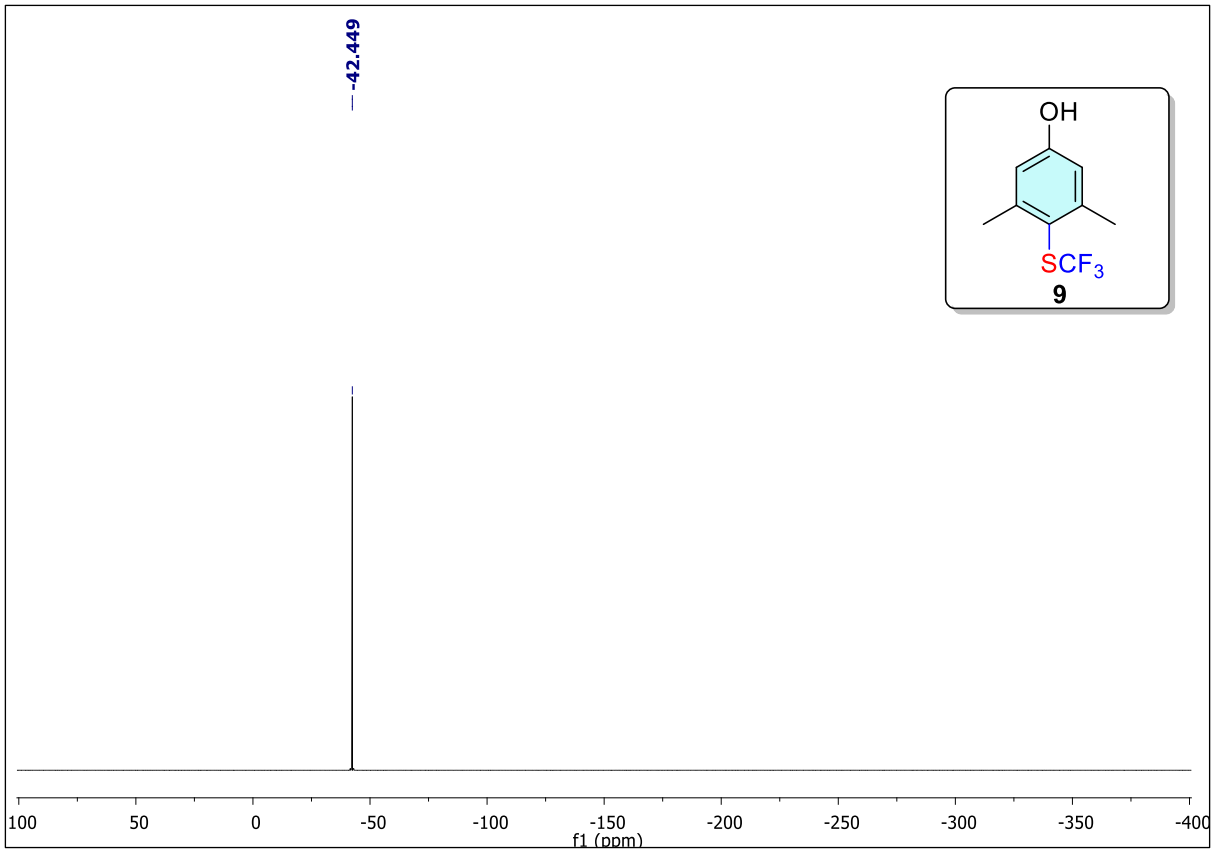

$^{13}$C{$^{1}$H} NMR of **8** (100 MHz, $CDCl_3$)




$^{1}$H NMR of **9** (400 MHz, $CDCl_3$)




$^{13}$C{$^{1}$H} NMR of **9** (100 MHz, $CDCl_3$)




$^{19}$F NMR of **9** (376 MHz, $CDCl_3$)

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