

## *Supporting Information*

### **Linker Engineering in UiO-68-Type Metal–Organic Frameworks for the Photocatalytic Thioamide Cyclization**

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## 1. Materials and Methods

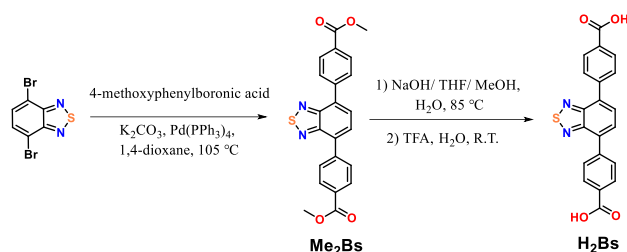
All chemicals were purchased from Innochem or Aladdin and used directly unless otherwise indicated. All solvents and starting materials for synthesis were purchased commercially and used without further purification. Powder X-ray diffraction (PXRD) measurements were carried out at room temperature on a BRUKER D8 Advance diffractometer 45 kV, 40 mA for Cu K $\alpha$  ( $\lambda = 1.5418$  Å). Mass spectra (MS) were carried out on a Bruker microTOF-Q II Spectroscopy. UV-visible diffuse reflection spectra were conducted with BaSO<sub>4</sub> pellets on a UV-3600PLUS spectrometer. Fluorescence spectra were recorded on Hitach F-4600 fluorescence spectrometer equipped with a xenon discharge lamp. The electrochemical measurements were performed in a conventional three-electrode cell on a CHI-760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd, China). The photocatalytic measurements were conducted on a WP-TEC-1020HSL of WATTCAS photoreactor instrument (White LED, 10 W, 2059 mW/cm<sup>2</sup>). Electron paramagnetic resonance (EPR) signals were recorded on a Bruker E500-9.5/12 at room temperature under visible-light irradiation. <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments were performed with a JEOL ECZ400S spectrometer.



**Figure S1.** Schematic view of WP-TEC-1020HSL of WATTCAS photoreactor instrument for the photocatalytic measurements.

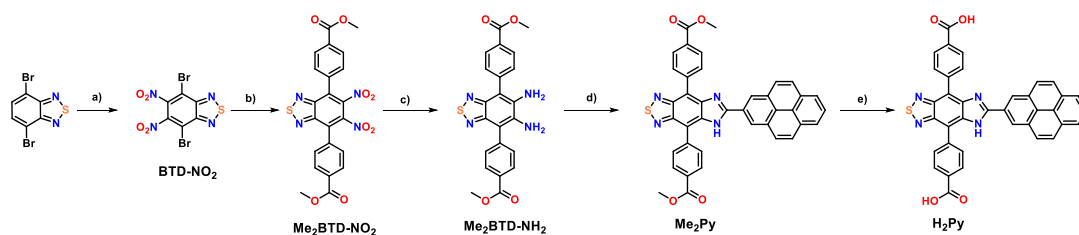
## 2. Synthesis and Characterization of organic linker

### 2.1 the synthesis of H<sub>2</sub>Bs



**The synthesis of Me<sub>2</sub>Bs:** 4,7-dibromo-2,1,3-benzothiadiazole (1.0 g, 3.4 mmol), methyl 4-boronobenzoate (1.5 g, 8.5 mmol), potassium carbonate (2.6 g, 20.4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (78.6 mg, 0.068 mmol) were added into one 250 mL round-bottle flask containing 80 mL dioxane. The reaction solution was degassed four times. Then the mixture was heated to reflux at 110 °C for 72 h under argon atmosphere. After cooling down to room temperature, the mixture was extracted five times with ethyl acetate, then the organic layers were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product (yield 83%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 7.9 Hz, 4H), 8.10 (d, *J* = 7.7 Hz, 4H), 7.90 (s, 2H), 4.01(s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 166.8, 153.8, 141.5, 132.9, 129.9, 129.2, 128.5, 52.3. HRMS calcd (ESI) *m/z* for C<sub>22</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>S: [M+H]<sup>+</sup> 405.0909, found 405.0849.

**The synthesis of H<sub>2</sub>Bs:** 2.5 mmol compound Me<sub>2</sub>Bs was added to a solution containing 30 mL CH<sub>3</sub>OH, 30 mL THF and 30 mL water with 1.0 g NaOH. The mixture was heated to reflux at 80 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure and the resulted aqueous was filtered. Then the filtrate was neutralized using 2M HCl to obtain the precipitate, which was filtered to offer the final product H<sub>2</sub>Bs (yield 91%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 13.16 (s, 2H), 8.22 (d, *J* = 8.0 Hz, 4H), 8.17 (d, *J* = 8.3 Hz, 4H), 8.14 (s, 2H). HRMS (ESI) *m/z* for C<sub>20</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>S: [M-H]<sup>-</sup> 375.0445, found 375.0486.



Reagents and conditions: a) fuming trifluoromethane sulfonic acid, fuming nitric acid; b) 4-methoxyphenylboronic acid,  $K_2CO_3$ ,  $Pd(PPh_3)_4$ , 1,4-dioxane, 105 °C; c) Fe, HAc; d) 2-pyrenecarboxaldehyde,  $CF_3COOH$ , DMSO, 100 °C for 8 h; e) NaOH, THF, MeOH,  $H_2O$ , 85 °C for 6 h; TFA,  $H_2O$ , 1 h, room temperature.

**The synthesis of BTD- $NO_2$ .** Fuming nitric acid (2.5 g, 40.8 mmol) was added dropwise to fuming trifluoromethane sulfonic acid (24.5 g, 163.2 mmol) in a two-necked flask at 0 °C. And then an insoluble complex  $CF_3SO_3H/HNO_3$  was produced immediately. To the mixed acid, 4,7-dibromo-2,1,3-benzothiadiazole (4.0 g, 13.6 mmol) was added in portions over 20 min. After stirring at 50 °C overnight, the mixture was poured into ice water slowly, and then sodium hydroxide solution was carefully added to neutralize the excess acid. The precipitate was filtered and washed with water. Purification by recrystallization from ethanol yielded BTD- $NO_2$  as a light-yellow powder (yield 91%).

**The synthesis of  $Me_2BTD-NO_2$ .** BTD- $NO_2$  (1.3 g, 3.4 mmol), methyl 4-boronobenzoate (1.5 g, 8.5 mmol), potassium carbonate (2.6 g, 20.4 mmol) and  $Pd(PPh_3)_4$  (78.6 mg, 0.068 mmol) were added into one 250 mL round-bottle flask containing 80 mL dioxane. The reaction solution was degassed four times. Then the mixture was heated to reflux at 110 °C for 72 h under argon atmosphere. After cooling down to room temperature, the mixture was extracted five times with ethyl acetate, then the organic layers were combined and dried over anhydrous  $Na_2SO_4$  and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product (yield 85%).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.13 (d,  $J = 8.2$  Hz, 4H), 7.70 (d,  $J = 8.2$  Hz, 4H), 3.95 (s, 6H).  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  167.1, 153.7, 144.1, 136.6, 132.1, 130.3, 129.4, 128.8, 54.8.

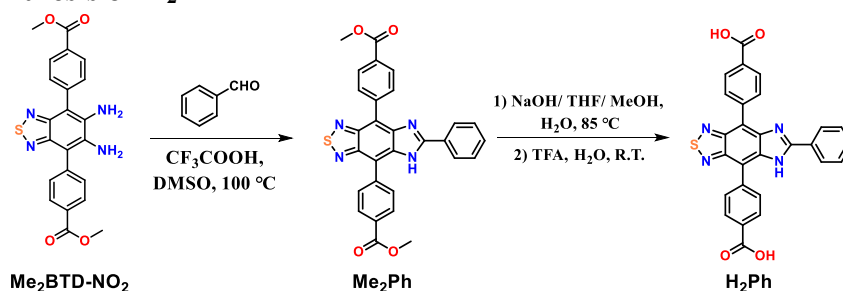
**The synthesis of  $Me_2BTD-NH_2$ .** A 100 mL round bottom flask was charged with  $Me_2BTD-NO_2$  (1.0 g, 2.0 mmol), iron powder (1.36 g, 24.2 mmol), and acetic acid (60 mL). The reaction was heated to 100 °C for 2 h, then cooled to room temperature and diluted with water (100 mL). The product was extracted with  $CH_3COOC_2H_5$  ( $3 \times 80$  mL). The combined organic layers were washed with water and dried over anhydrous  $Na_2SO_4$ , filtered, and solvent removed under reduced pressure to give the crude product, which was further purified using column chromatograph to give orange

solid (yield: 72%).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.11 (d,  $J = 8.3$  Hz, 4H), 7.67 (d,  $J = 8.3$  Hz, 4H), 5.62 (s, 4H), 3.91 (s, 6H). HRMS calcd (ESI)  $m/z$  for  $\text{C}_{22}\text{H}_{19}\text{N}_4\text{O}_4$ :  $[\text{M}+\text{H}]^+$  435.1127, found 435.1127.

**The synthesis of Me<sub>2</sub>Py.** 2-pyrenecarboxaldehyde, and Me<sub>2</sub>BTD-NH<sub>2</sub> (0.087 g, 0.2 mmol) were dissolved in DMSO (5 mL). Then, trifluoroacetic acid (100  $\mu\text{L}$ ) was added dropwise into the mixture with rapid stirring. Then the mixture was heated to reflux at 110  $^\circ\text{C}$  for 12 h under nitrogen atmosphere. After cooling down to room temperature, the mixture was diluted with distilled water (100 mL), the mixture was extracted five times with ethyl acetate, then the organic layers were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product (yield 81%).  $^1\text{H NMR}$  (400 MHz,  $\text{CF}_3\text{COOD}$ )  $\delta$  8.43 (d,  $J = 8.3$  Hz, 6H), 8.40 (s, 1H), 8.38 (s, 1H), 8.36 (d,  $J = 3.5$  Hz, 3H), 8.18 (d,  $J = 8.4$  Hz, 2H), 8.10 (d,  $J = 8.4$  Hz, 4H), 4.15 (s, 6H). HRMS calcd (ESI)  $m/z$  for  $\text{C}_{39}\text{H}_{23}\text{N}_4\text{O}_4\text{S}$ :  $[\text{M}-\text{H}]^-$  643.1445, found 643.1460.

**The synthesis of H<sub>2</sub>Py.** 2.5 mmol compound Me<sub>2</sub>Py was added to a solution containing 30 mL  $\text{CH}_3\text{OH}$ , 30 mL THF and 30 mL water with 1.0 g NaOH. The mixture was heated to reflux at 80  $^\circ\text{C}$  overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure and the resulted aqueous was filtered. Then the filtrate was neutralized using 2M HCl to obtain the precipitate, which was filtered to offer the final product H<sub>2</sub>Py (yield 90%).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  13.22 (s, 1H), 13.01 (s, 2H), 9.29 (d,  $J = 9.2$  Hz, 1H), 8.65 (d,  $J = 8.3$  Hz, 1H), 8.52 (d,  $J = 7.5$  Hz, 2H), 8.46 – 8.23 (m, 7H), 8.20 – 8.04 (m, 6H). HRMS calcd (ESI)  $m/z$  for  $\text{C}_{37}\text{H}_{19}\text{N}_4\text{O}_4\text{S}$ :  $[\text{M}-\text{H}]^-$  615.1132, found 615.1152.

## 2.2 the synthesis of H<sub>2</sub>Ph



**The synthesis of Me<sub>2</sub>Ph.** Benzaldehyde (0.0244 g, 0.23 mmol), and Me<sub>2</sub>BTD-NH<sub>2</sub> (0.087 g, 0.2 mmol) were dissolved in DMSO (5 mL). Then, trifluoroacetic acid (100  $\mu\text{L}$ ) was added dropwise into the mixture with rapid stirring. Then the mixture was heated to reflux at 110  $^\circ\text{C}$  for 12 h under nitrogen atmosphere. After cooling down to room temperature, the mixture was diluted with distilled

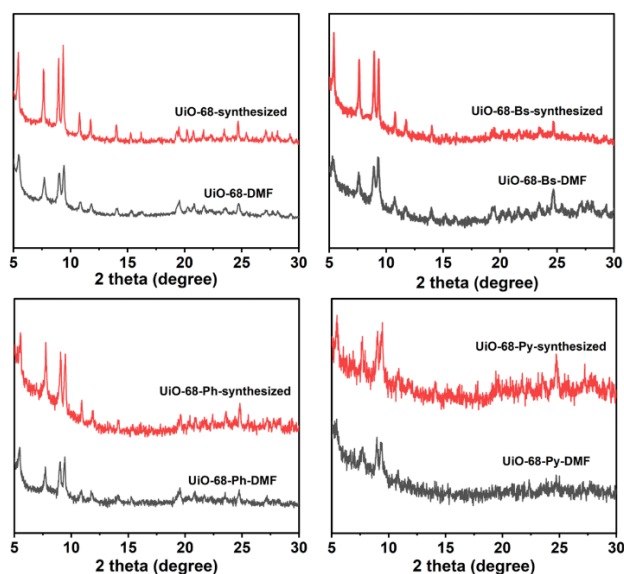
water (100 mL), the mixture was extracted five times with ethyl acetate, then the organic layers were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product (yield 83%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  12.85 (s, 1H), 8.48 (d,  $J = 8.1$  Hz, 2H), 8.35 (d,  $J = 8.0$  Hz, 2H), 8.22 – 8.15 (m, 4H), 8.06 (d,  $J = 8.0$  Hz, 2H), 7.57 (q,  $J = 7.1, 6.3$  Hz, 3H), 3.95 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  169.8, 158.6, 151.1, 136.6, 136.1, 132.1, 130.8, 130.7, 130.4, 130.0, 128.8, 119.9, 118.5, 117.6, 115.7, 112.90, 110.1, 52.9. HRMS calcd (ESI)  $m/z$  for  $\text{C}_{29}\text{H}_{19}\text{N}_2\text{O}_4\text{SN}_2$ :  $[\text{M-H}]^-$  519.1122, found 519.1088.

**The synthesis of  $\text{H}_2\text{Ph}$ .** 1.25 mmol compound  $\text{Me}_2\text{Ph}$  was added to a solution containing 15 mL  $\text{CH}_3\text{OH}$ , 15 mL THF and 15 mL water with 0.5 g NaOH. The mixture was heated to reflux at 90 °C overnight. After cooling down to room temperature, the organic solvent was removed under reduced pressure and the resulted aqueous was filtered. Then the filtrate was neutralized using 2M HCl to obtain the precipitate, which was filtered to offer the final product  $\text{H}_2\text{Ph}$  (yield 88%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  13.07 (s, 2H), 12.88 (s, 1H), 8.45 (d,  $J = 8.1$  Hz, 2H), 8.38 (dd,  $J = 7.5, 2.0$  Hz, 2H), 8.23 – 8.14 (m, 4H), 8.05 (d,  $J = 7.9$  Hz, 2H), 7.59 (d,  $J = 7.1$  Hz, 3H). HRMS calcd (ESI)  $m/z$  for  $\text{C}_{27}\text{H}_{15}\text{N}_4\text{O}_4\text{S}$ :  $[\text{M+H}]^+$  491.0819, found 491.0808.

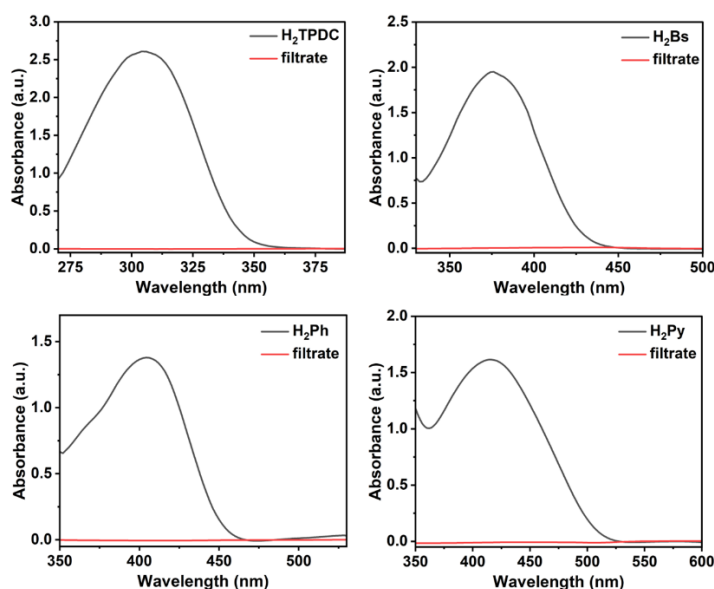
### 3. Synthesis and Characterization of MOFs

#### The synthesis of UiO-68s

$\text{ZrCl}_4$  (25 mg, 0.1 mmol), organic linker (0.1 mmol) and trifluoroacetic acid (0.49 mL) were added into a 10 mL vial containing 3 mL DMF. After sonicated for 5 minutes, the vial was put into a preheated oven at 120 °C for 48 hours. After cooling down to room temperature, the product was separated by centrifugal to afford the target solid which was washed with DMF ( $3 \times 5$  mL) and acetone ( $3 \times 5$  mL), respectively. The sample was dried in vacuum. The powder X-ray diffraction (PXRD) pattern generated from single crystal data of MOF UiO-68, confirming their UiO-68 topological framework and the phase purity.



**Figure S2.** PXRD patterns of the UiO-68s samples which was immersed in DMF for three days.

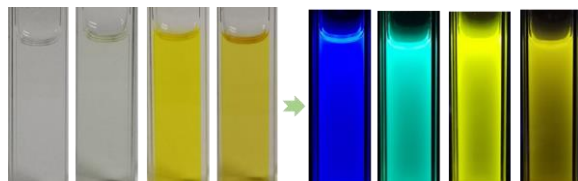


**Figure S3.** UV-vis absorption spectra of filtrate for UiO-68s being immersed in DMF for three days.

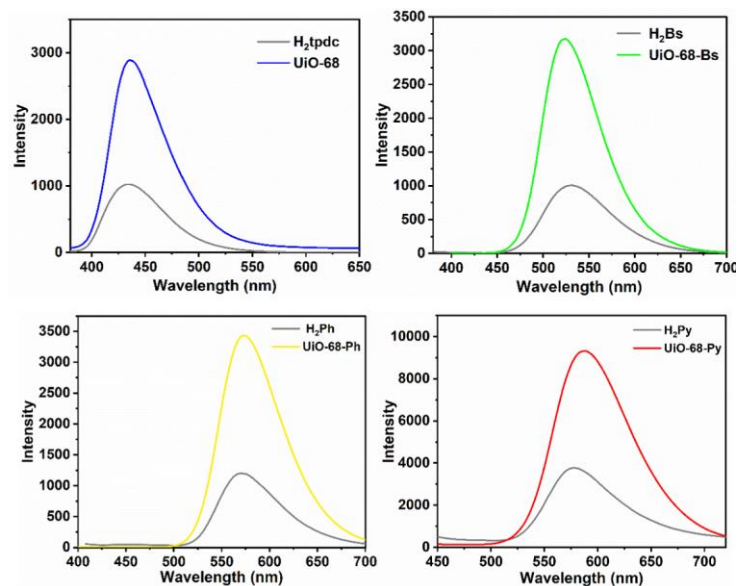
#### 4. Optical and Electrochemical Measurements of MOFs

MOF powder (5 mg) was ultrasonically dispersed in 2 mL of acetone. The resultant slurry was then drop-casted onto indium tin oxide (ITO) glass with an area of  $0.5 \times 0.5 \text{ cm}^2$ . A Pt wire (counter electrode), a Ag/AgCl electrode (reference electrode), and a coated ITO conductive glass (working electrode) were assembled into a three-electrode system with 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution used as the electrolyte. The Mott–Schottky plots were collected in dark at 500 Hz, 750 Hz, 1000 Hz. The photocurrent measurements were conducted under the irradiation of a 300 W xenon lamp ( $100 \text{ mW cm}^{-2}$ ) with a 420 nm cut-off filter. For electrochemical impedance spectroscopy (EIS) measurements, the amplitude of the sinusoidal wave was 5 mV, and the frequency range from 100 kHz to 0.01 Hz

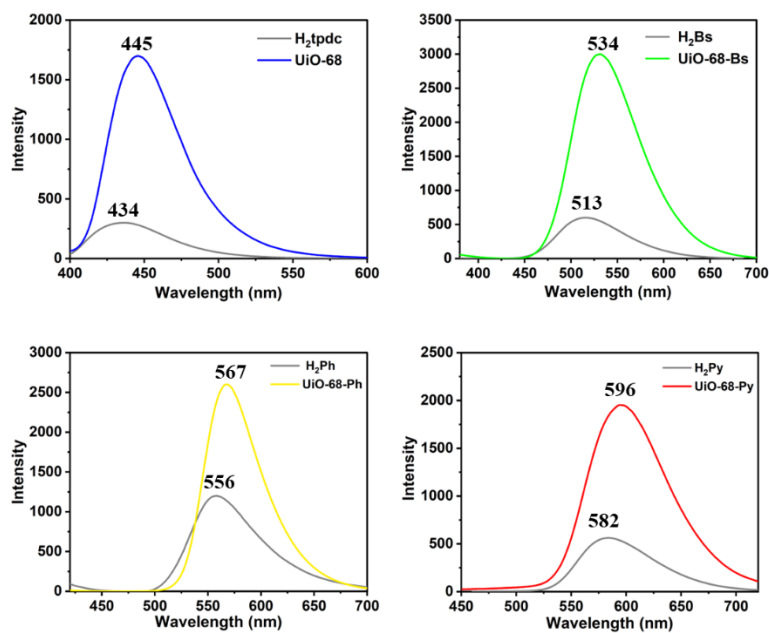
under the irradiation of a 300 W xenon lamp ( $100 \text{ mW cm}^{-2}$ ).



**Figure S4.** Photographs of the samples in DMF under daylight and 365 nm excitation of  $\text{H}_2\text{TPDC}$ ,  $\text{H}_2\text{Bs}$ ,  $\text{H}_2\text{Ph}$ ,  $\text{H}_2\text{Py}$ .

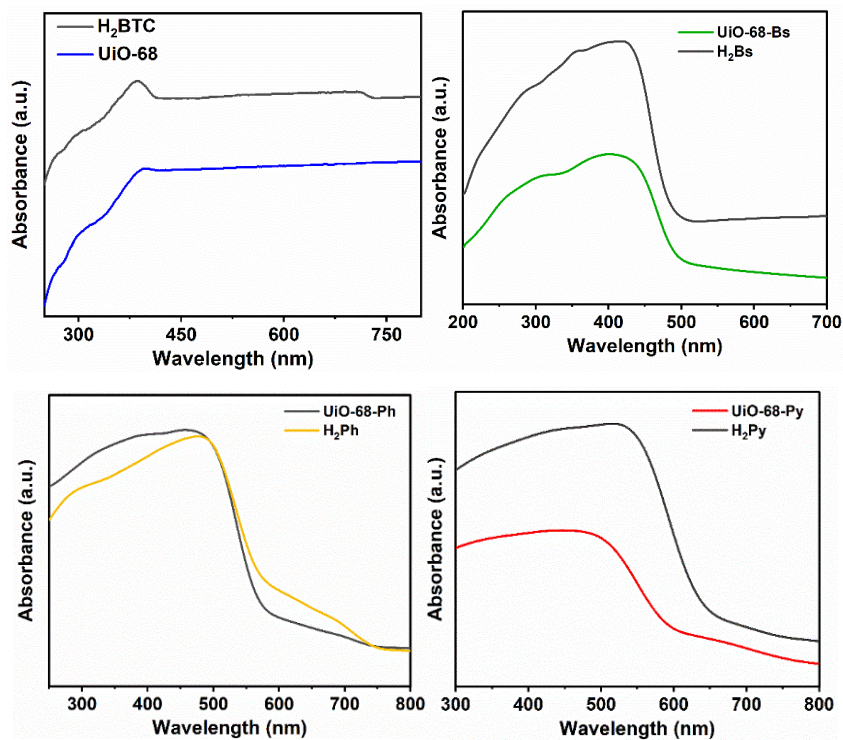


**Figure S5.** Fluorescence spectra of UiO-68s and the relevant linkers in DMF.

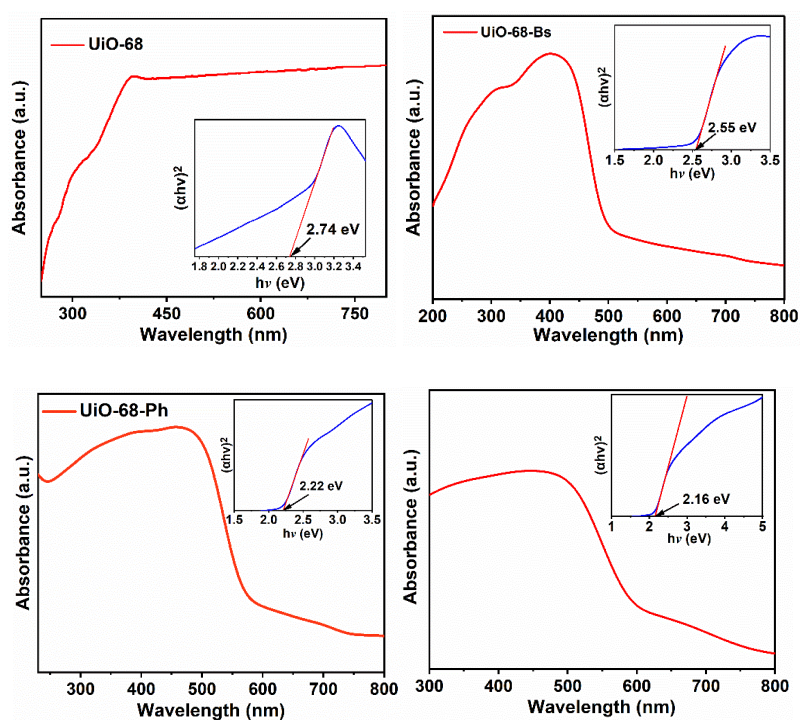


**Figure S6.** Fluorescence spectra of UiO-68s and the relevant linkers in solid.





**Figure S7.** UV-visible diffuse reflectance spectrum of UiO-68s and relevant linkers.



**Figure S8.** UV-visible diffuse reflectance spectrum of UiO-68s. Inset is a Tauc plot for UiO-68s.

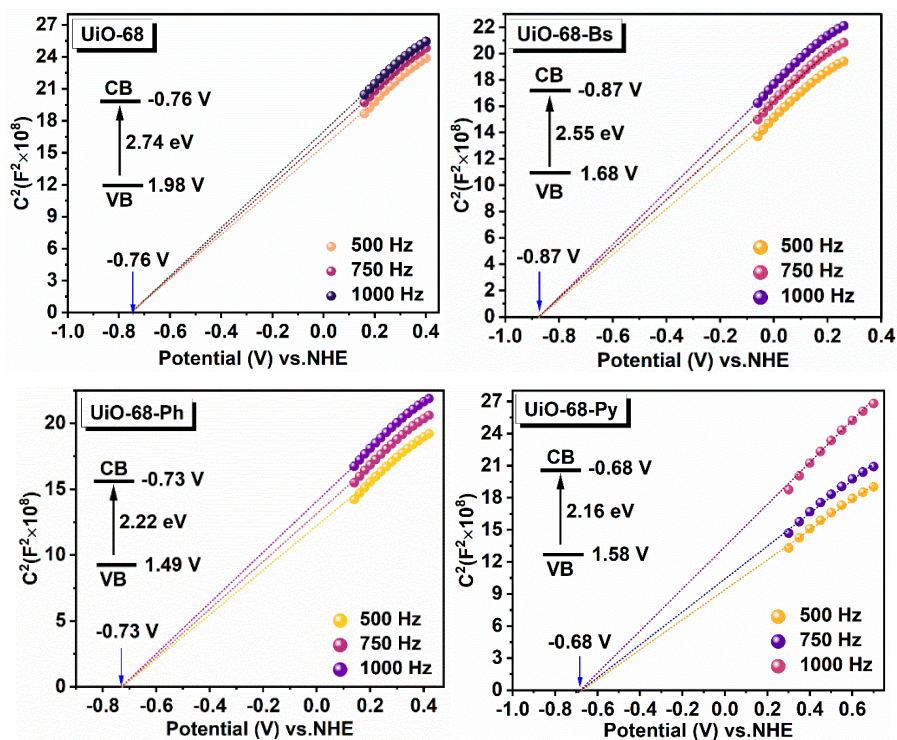


Figure S9. Mott-Schottky plots of the UiO-68s.

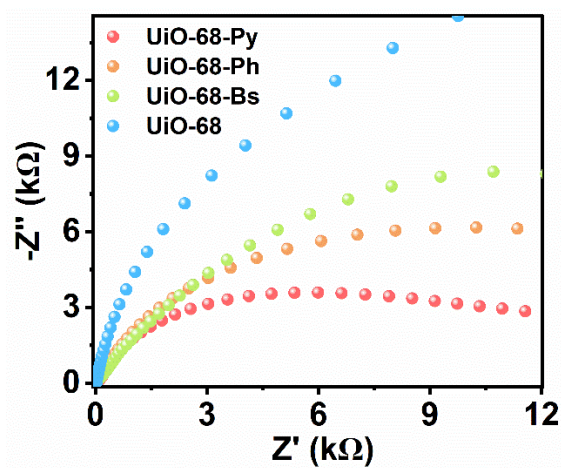



Figure S10. Mott-Schottky plots of the UiO-68s.

## 5. Photocatalytic Reactions


In a flat quartz glass jar with a magnetic stirrer, thiobenzamide (0.1 mmol), N,N-dimethylformamide (2 mL) and UiO-68-Py (1.0 mol%) were added. The open-air reaction container was placed under a 10 W white LED lamp and stirred until the end of the reaction was observed using thin-layer chromatography (TLC) analysis. The mixture was extracted with dichloromethane, then the organic layers were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product.

**Table S1.** Optimization of the reaction conditions <sup>a</sup>

The reaction scheme shows thiobenzamide (a benzene ring attached to a C=S-NH<sub>2</sub> group) reacting under various conditions to form a 1,2,4-thiazole derivative (two benzene rings attached to a 1,2,4-thiazole ring).

Entry	Amount (mol%)	Solvent	Yield <sup>b</sup> (%)
1	1.0	DMF	83
2	1.0	MeOH	47
3	1.0	THF	42
4	1.0	MeCN	35
5	1.0	DMSO	71
6	0.5	DMF	75
7	2.0	DMF	82
8	3.0	DMF	74

<sup>a</sup> Reaction conditions: thiobenzamide, (0.1 mmol), UiO-68-Py (1.0 mmol%), room temperature, air, 6 h, 10 W white LED; <sup>b</sup> Isolated yield;

**Table S2.** Optimization of the reaction conditions <sup>a</sup>

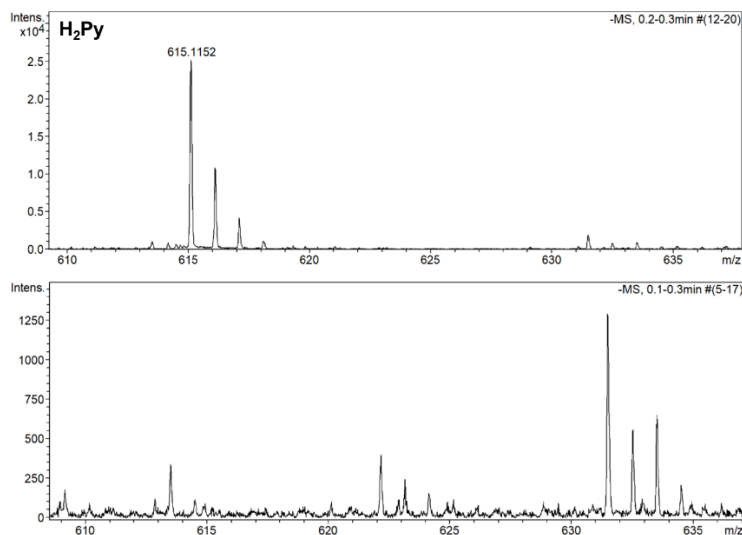
The reaction scheme shows thiobenzamide reacting under various conditions with different photocatalysts to form a 1,2,4-thiazole derivative.

Entry	Photocatalyst	Yield <sup>b</sup> (%)
1	H <sub>2</sub> TPDC	trace
2	H <sub>2</sub> Bs	11
3	H <sub>2</sub> Ph	17
4	H <sub>2</sub> Py	36
5	ZrCl <sub>4</sub>	trace

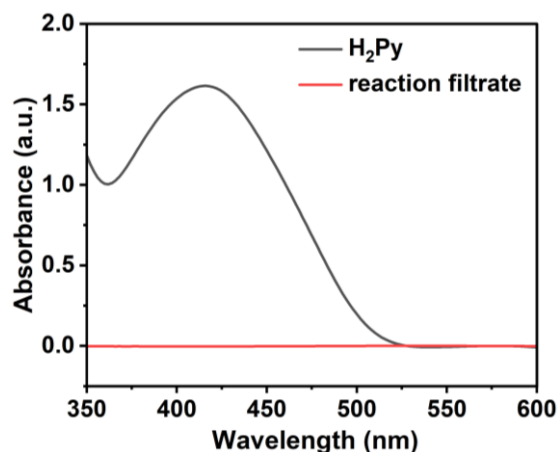
<sup>a</sup> Reaction conditions: thiobenzamide, (0.1 mmol), DMF, room temperature, air, 6 h, 10 W white LED; <sup>b</sup> Isolated yield;

### 3.5 leaching test

Thiobenzamide (0.1 mmol), N,N-dimethylformamide (2 mL) and UiO-68-Py (1.0 mol%) were added. The open-air reaction container was placed under a 10 W white LED lamp and stirred for 12 h. After the reaction completed, the catalyst was removed through gravity filtration. Then the filtrate was detected by ICP-MS, HRMS or UV-vis spectra.



**Figure S11.** The HRMS of H<sub>2</sub>Py and the reaction filtrate.



**Figure S12.** UV-Vis absorption spectra were tested by taking H<sub>2</sub>Py (10  $\mu$ M), and the reaction filtrate after 12 h of reaction.

## 7. Recycle Test

In a flat quartz glass jar with a magnetic stirrer, thiobenzamide (0.1 mmol), N,N-dimethylformamide (2 mL) and UiO-68-Py (1.0 mol%) were added. The open-air reaction container was placed under a 10 W white LED lamp and stirred until the end of the reaction which was observed using TLC analysis. The mixture was extracted five times with dichloromethane, then the organic layers were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the target product. After reaction, the MOF catalyst was recovered *via* centrifugation, washed with dichloromethane, and then used for the subsequent cycles of reactions. The aforementioned procedure was repeated three times.

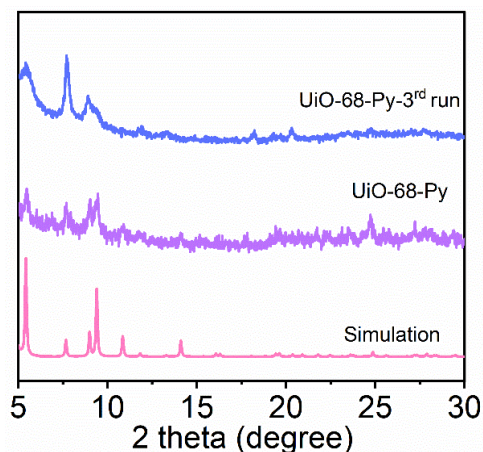
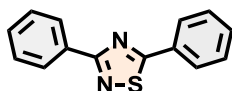
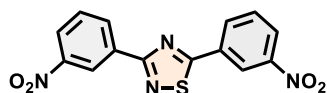


Figure S13. PXRD patterns of UiO-68-Py after three runs of the photocatalytic reaction.

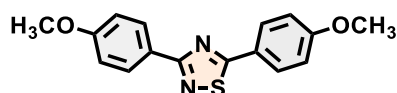
## 7. Characterizations of 1,2,4-thiadiazoles



**3,5-diphenyl-1,2,4-thiadiazole (2a):** white solid, yield 83%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.40 (dd,  $J = 7.8, 1.8$  Hz, 2H), 8.06 (dd,  $J = 7.2, 2.1$  Hz, 2H), 7.58 – 7.47 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  188.2, 173.9, 133.0, 132.0, 130.8, 130.5, 129.4, 128.8, 128.4, 127.6. HRMS (ESI)  $m/z$  for  $\text{C}_{13}\text{H}_9\text{ClN}_2^+$   $[\text{M}+\text{H}]^+$ : 239.0637, found 239.0638. Characterization data matched that reported in the literature.<sup>1</sup>



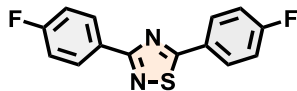
**3,5-bis(3-nitrophenyl)-1,2,4-thiadiazole (2b):** Milky yellow solid, yield 78%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.25 (s, 1H), 8.91 (s, 1H), 8.74 (d,  $J = 9.1$  Hz, 1H), 8.46 – 8.35 (m, 3H), 7.76 (dt,  $J = 24.4, 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  186.5, 171.8, 148.9, 148.7, 134.1, 133.9, 133.2, 131.8, 130.8, 130.1, 126.6, 125.3, 123.5, 122.4. HRMS (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_9\text{N}_4\text{O}_4\text{S}^-$   $[\text{M}-\text{H}]^-$ : 329.0345, found 329.0337.



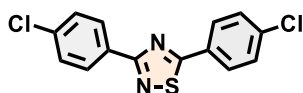
**3,5-bis(4-methoxyphenyl)-1,2,4-thiadiazole (2c):** white solid, yield 85%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.32 (d,  $J = 8.5$  Hz, 2H), 7.99 (d,  $J = 8.5$  Hz, 2H), 7.01 (dd,  $J = 8.8, 2.6$  Hz, 4H),



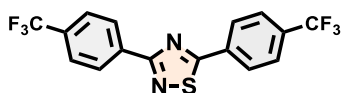
3.89 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  187.5, 173.4, 162.5, 161.3, 130.0, 129.2, 126.1, 123.8, 114.6, 114.0, 55.6, 55.5. HRMS (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_2\text{S}^+$   $[\text{M}+\text{H}]^+$ : 299.0849, found 299.0800. Characterization data matched that reported in the literature.<sup>1</sup>



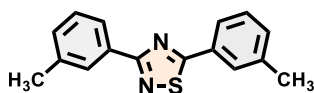
**3,5-bis(4-fluorophenyl)-1,2,4-thiadiazole (2d)**: white solid, yield 80%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.41 – 8.34 (m, 2H), 8.08 – 8.02 (m, 2H), 7.25 – 7.15 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  187.0, 172.7, 166.3, 165.5, 163.7, 130.5, 129.8, 129.2, 127.1, 122.9, 116.7, 116.5, 115.9, 115.7. HRMS (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_9\text{F}_2\text{N}_2\text{S}^+$   $[\text{M}+\text{H}]^+$ : 275.0455, found 275.0432. Characterization data matched that reported in the literature.<sup>2</sup>



**3,5-bis(4-chlorophenyl)-1,2,4-thiadiazole (2e)**: white solid, yield 86%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.31 (d,  $J = 8.4$  Hz, 2H), 7.98 (d,  $J = 8.4$  Hz, 2H), 7.49 (dd,  $J = 13.1, 8.4$  Hz, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  187.1, 172.9, 138.3, 136.7, 131.2, 129.73, 129.70, 129.1, 128.8. HRMS (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_9\text{Cl}_2\text{N}_2\text{S}^+$   $[\text{M}+\text{H}]^+$ : 306.9858, found 306.9837. Characterization data matched that reported in the literature.<sup>2</sup>

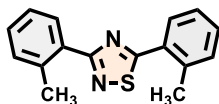


**3,5-bis(4-(trifluoromethyl)phenyl)-1,2,4-thiadiazole (2f)**: white solid, yield 77%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.50 (d,  $J = 8.2$  Hz, 2H), 8.17 (d,  $J = 8.2$  Hz, 2H), 7.78 (dd,  $J = 13.6, 8.3$  Hz, 4H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  187.0, 172.7, 135.6, 133.9, 133.5, 132.4, 132.1, 128.7, 127.9, 126.5, 125.8, 125.4, 125.0, 122.7, 122.3. HRMS (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_9\text{F}_6\text{N}_2\text{S}^+$   $[\text{M}+\text{H}]^+$ : 375.0391, found 375.0323. Characterization data matched that reported in the literature.<sup>1</sup>

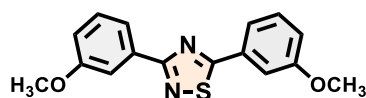


**3,5-di-m-tolyl-1,2,4-thiadiazole (2g)**: white solid, yield 81%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.24-8.18 (m, 2H), 7.92-7.82 (m, 2H), 7.40 (td,  $J = 7.6, 3.8$  Hz, 2H), 7.35 (d,  $J = 7.7$  Hz, 1H), 7.30

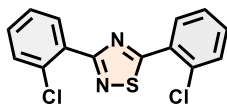
(d,  $J = 7.4$  Hz, 1H), 2.47 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  188.3, 174.0, 139.2, 138.5, 132.9, 132.8, 131.2, 130.7, 129.2, 129.0, 128.7, 128.0, 125.6, 124.8, 21.6, 21.5. HRMS (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{N}_2^+\text{S}$   $[\text{M}+\text{H}]^+$ : 267.0950, found 267.0964. Characterization data matched that reported in the literature.<sup>3</sup>



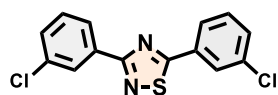
**3,5-di-o-tolyl-1,2,4-thiadiazole (2h):** white solid, yield 76%.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.19 – 8.15 (m, 1H), 8.06 (d,  $J = 7.6$  Hz, 1H), 7.46 – 7.41 (m, 1H), 7.41 – 7.30 (m, 5H), 2.74 (s, 3H), 2.70 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  186.6, 173.9, 138.1, 137.2, 132.5, 131.9, 131.6, 131.14, 131.10, 130.3, 130.0, 129.8, 126.6, 126.0, 22.3, 22.2. HRMS (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{N}_2^+\text{S}$   $[\text{M}+\text{H}]^+$ : 267.0950, found 267.0971. Characterization data matched that reported in the literature.<sup>3</sup>



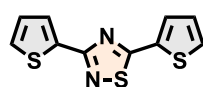
**3,5-bis(3-methoxyphenyl)-1,2,4-thiadiazole (2i):** White solid, yield 82%.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.99 (dt,  $J = 7.8, 1.1$  Hz, 1H), 7.92 (dd,  $J = 2.5, 1.5$  Hz, 1H), 7.62 – 7.57 (m, 2H), 7.42 (dd,  $J = 7.9, 2.8$  Hz, 2H), 7.08 (dd,  $J = 8.7, 3.0$  Hz, 2H), 3.91 (d,  $J = 1.3$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  188.1, 173.6, 160.2, 159.9, 134.2, 131.9, 130.4, 129.8, 121.0, 120.2, 118.1, 116.9, 113.1, 112.2, 55.6, 55.5. HRMS (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_2\text{S}^+$   $[\text{M}+\text{H}]^+$ : 299.0849, found 299.0819. Characterization data matched that reported in the literature.<sup>4</sup>



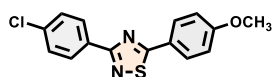
**3,5-di-p-tolyl-1,2,4-thiadiazole (2j):** White solid, yield 78%.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.27 (d,  $J = 8.0$  Hz, 2H), 7.94 (d,  $J = 8.0$  Hz, 2H), 7.31 (t,  $J = 7.1$  Hz, 4H), 2.43 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  188.1, 173.9, 142.6, 140.6, 130.4, 130.0, 129.5, 128.4, 128.2, 127.5, 21.8, 21.6. HRMS (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{N}_2^+\text{S}$   $[\text{M}+\text{H}]^+$ : 267.0950, found 267.0936. Characterization data matched that reported in the literature.<sup>3</sup>



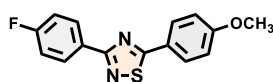
**3,5-bis(3-chlorophenyl)-1,2,4-thiadiazole (2k):** White solid, yield 82%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.38 (d,  $J = 1.9$  Hz, 1H), 8.26 (dt,  $J = 6.7, 1.7$  Hz, 1H), 8.07 (t,  $J = 1.8$  Hz, 1H), 7.91 – 7.87 (m, 1H), 7.55 – 7.50 (m, 1H), 7.49 – 7.42 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  186.9, 172.5, 135.5, 134.9, 134.2, 132.0, 130.7, 130.6, 130.1, 128.5, 127.4, 126.5, 125.7. HRMS (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_9\text{Cl}_2\text{N}_2\text{S}^+$   $[\text{M}+\text{H}]^+$ : 306.9858, found 306.9820. Characterization data matched that reported in the literature.<sup>5</sup>



**3,5-di(thiophen-2-yl)-1,2,4-thiadiazole (2l):** white solid, yield 75%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (dd,  $J = 3.7, 1.2$  Hz, 1H), 7.70 (dd,  $J = 3.8, 1.1$  Hz, 1H), 7.59 (dd,  $J = 5.1, 1.1$  Hz, 1H), 7.46 (dd,  $J = 5.0, 1.2$  Hz, 1H), 7.16 (ddd,  $J = 10.6, 5.1, 3.7$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  180.8, 168.5, 136.3, 133.2, 130.7, 130.0, 129.3, 129.0, 128.6, 128.0. HRMS (ESI)  $m/z$  for  $\text{C}_{10}\text{H}_7\text{N}_2\text{S}_3^+$   $[\text{M}+\text{H}]^+$ : 250.9771, found 250.9774. Characterization data matched that reported in the literature.<sup>1</sup>



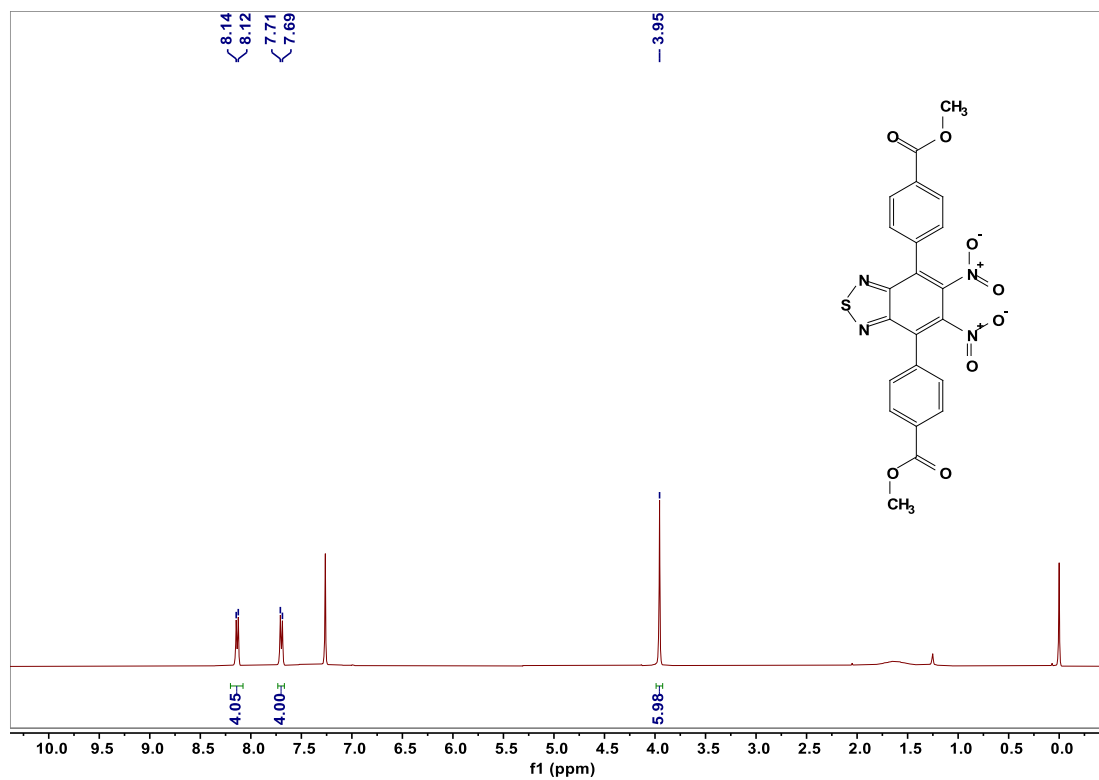
**3-(4-chlorophenyl)-5-(4-methoxyphenyl)-1,2,4-thiadiazole (2m):** white solid, yield 36%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.32 (d,  $J = 9.0$  Hz, 2H), 7.99 (dd,  $J = 8.6, 1.9$  Hz, 2H), 7.48 (dd,  $J = 12.8, 8.6$  Hz, 2H), 7.02 (dd,  $J = 8.9, 2.7$  Hz, 2H), 3.90 (s, 3H). HRMS (ESI)  $m/z$  for  $\text{C}_{15}\text{H}_{12}\text{ClN}_2\text{OS}^+$   $[\text{M}+\text{H}]^+$ : 303.0359, found 303.0355.



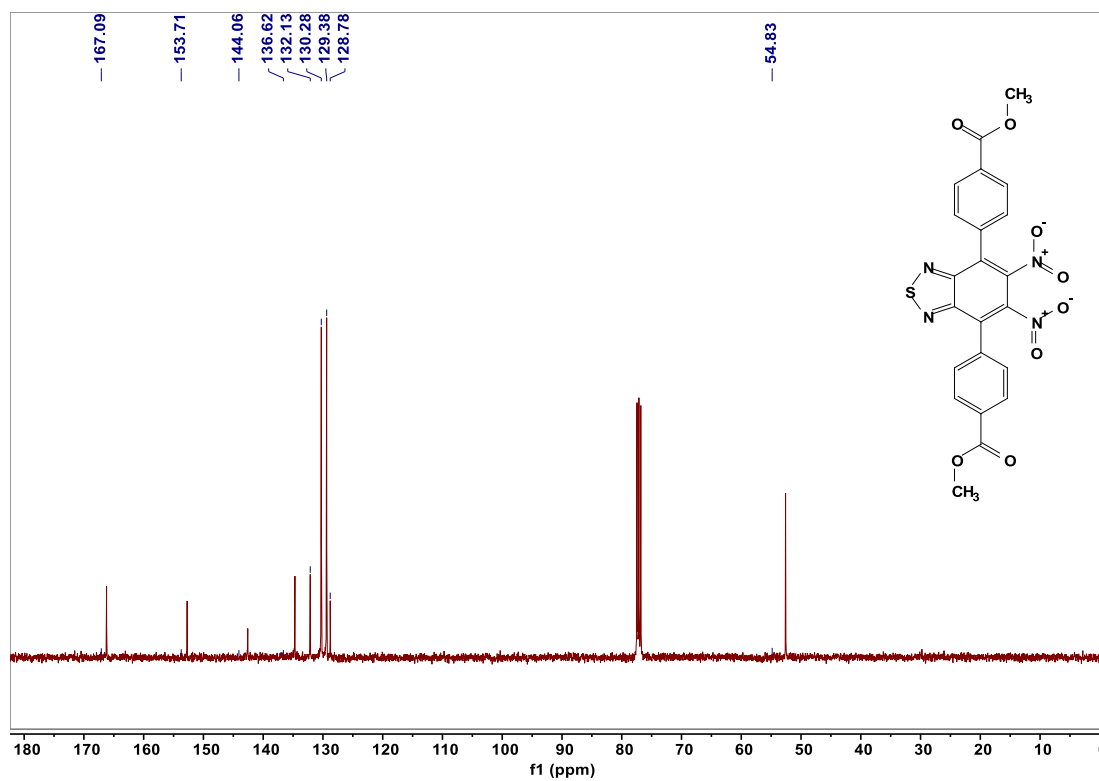
**3-(4-fluorophenyl)-5-(4-methoxyphenyl)-1,2,4-thiadiazole:** white solid, yield 40%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.41 – 8.27 (m, 2H), 8.09 – 7.94 (m, 2H), 7.18 (dt,  $J = 14.9, 8.6$  Hz, 2H), 7.00 (dd,  $J = 8.9, 2.9$  Hz, 2H), 3.89 (s, 3H). HRMS (ESI)  $m/z$  for  $\text{C}_{15}\text{H}_{12}\text{FN}_2\text{OS}^+$   $[\text{M}+\text{H}]^+$ : 287.0654, found 287.0653.



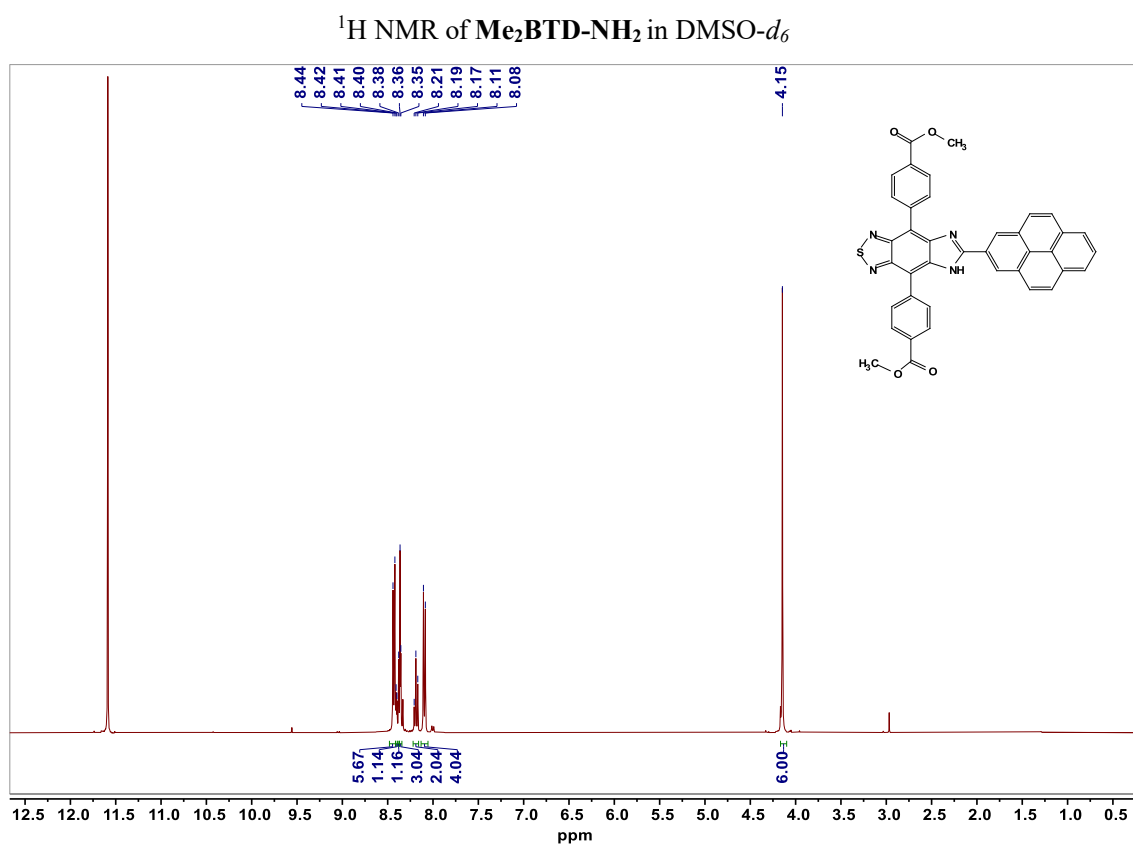
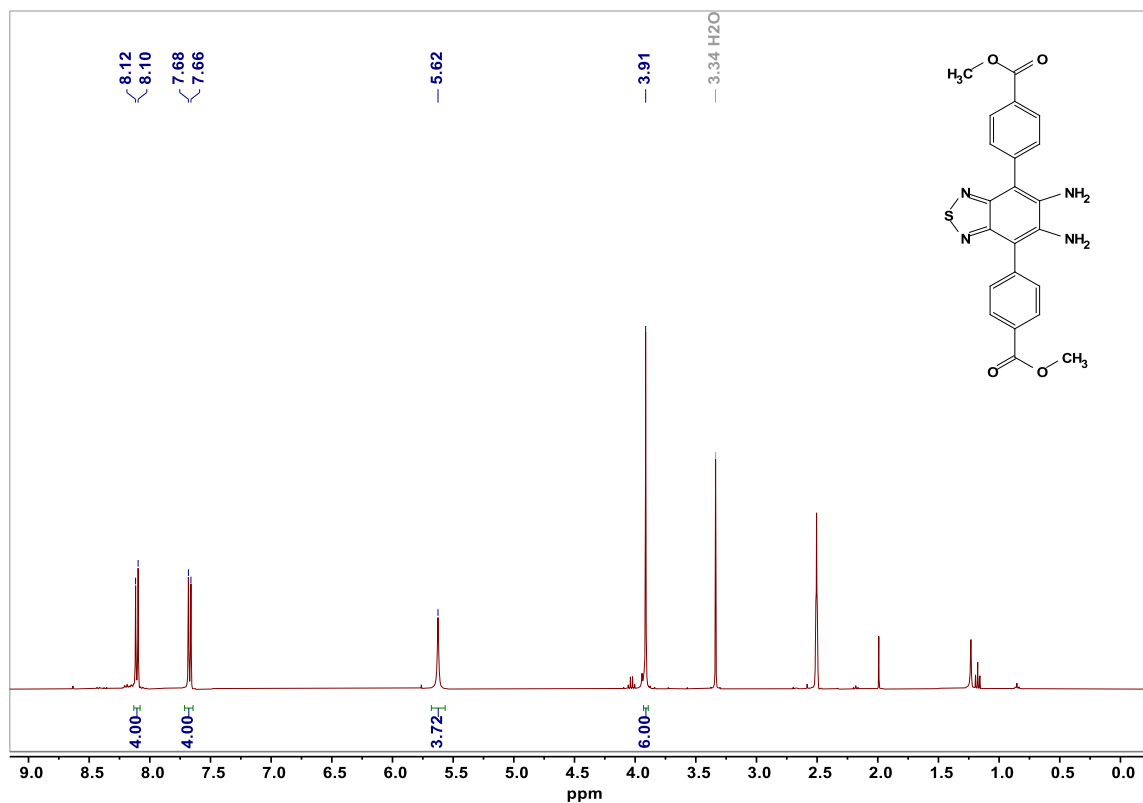
## NMR and HRMS analysis

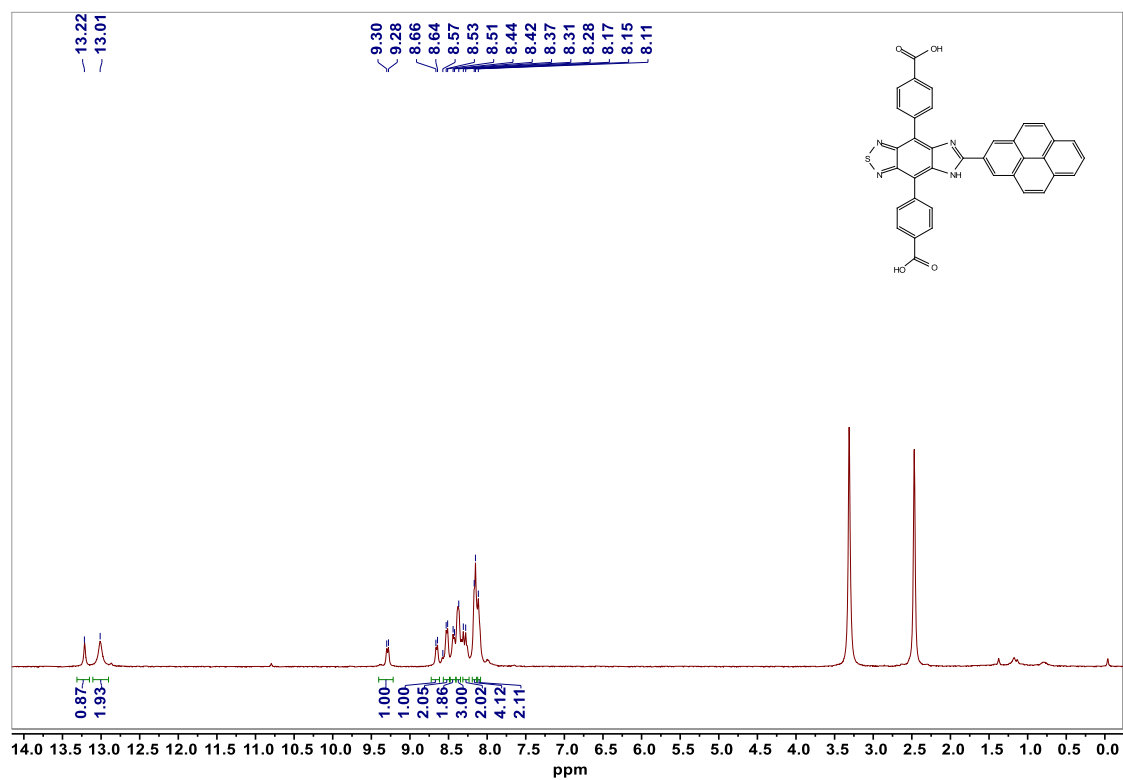


<sup>1</sup>H NMR of Me<sub>2</sub>BTD-NO<sub>2</sub> in Chloroform-*d*

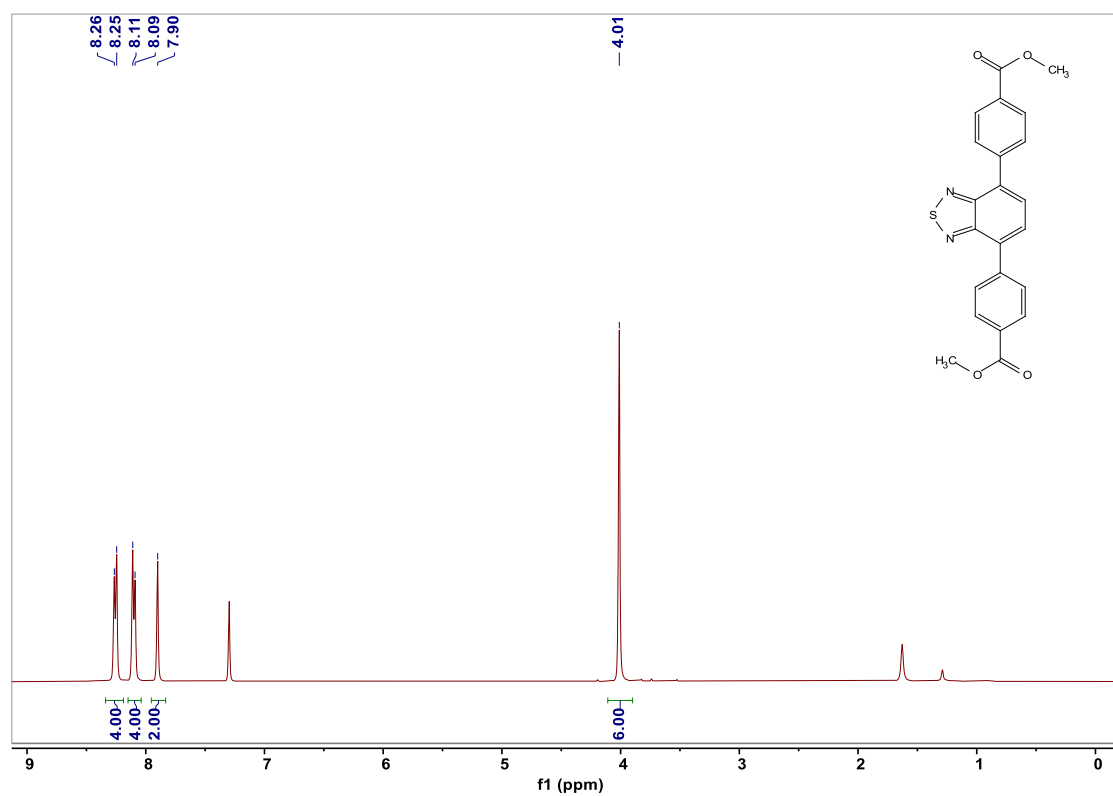


<sup>13</sup>C NMR of Me<sub>2</sub>BTD-NO<sub>2</sub> in Chloroform-*d*

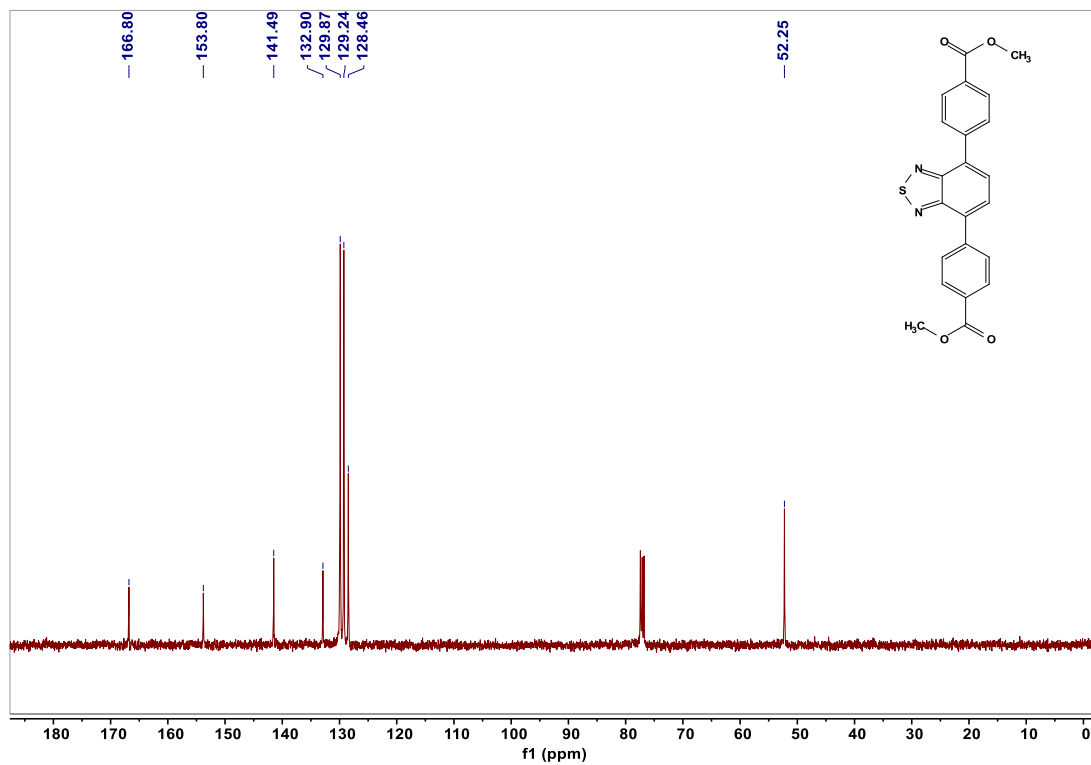




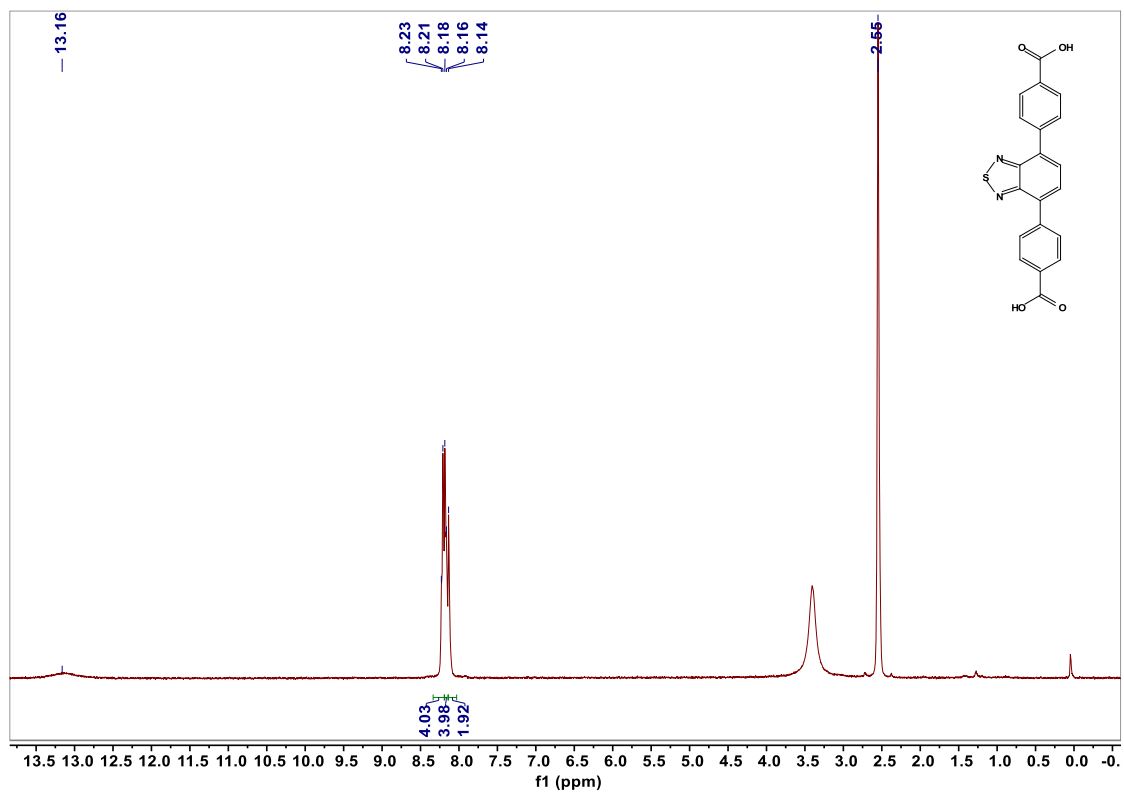
$^1\text{H}$  NMR of  $\text{H}_2\text{Py}$  in  $\text{DMSO-}d_6$



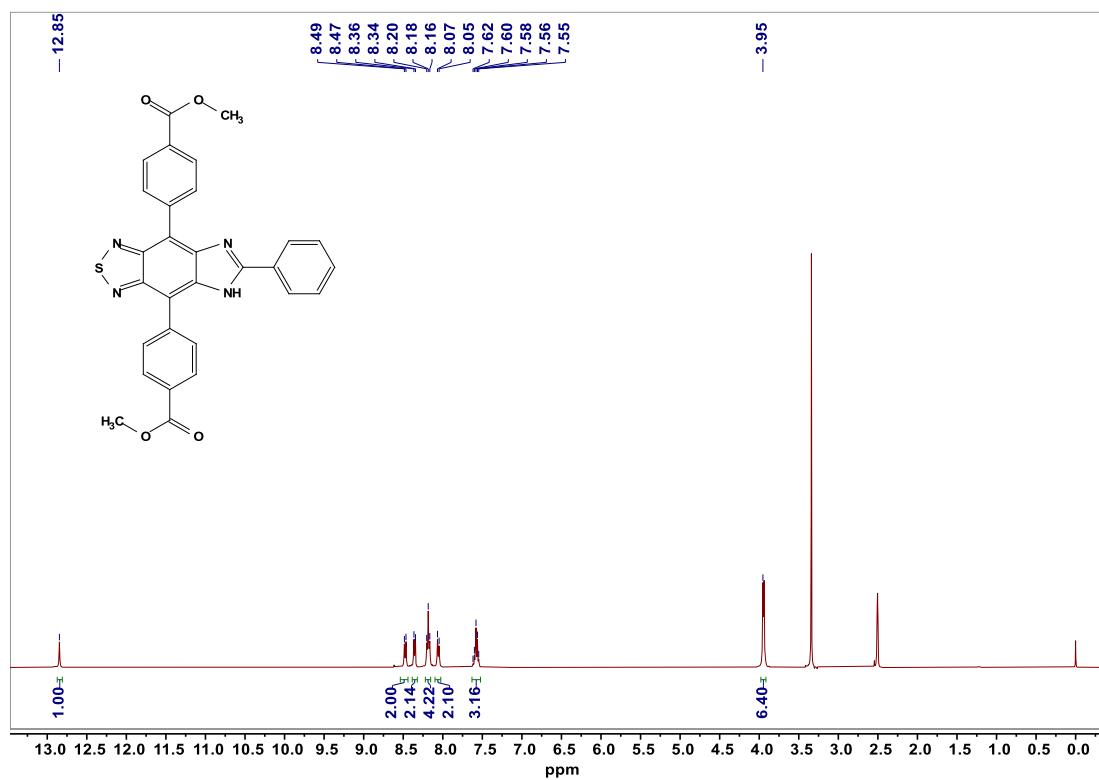
$^1\text{H}$  NMR of  $\text{Me}_2\text{Bs}$  in  $\text{Chloroform-}d$



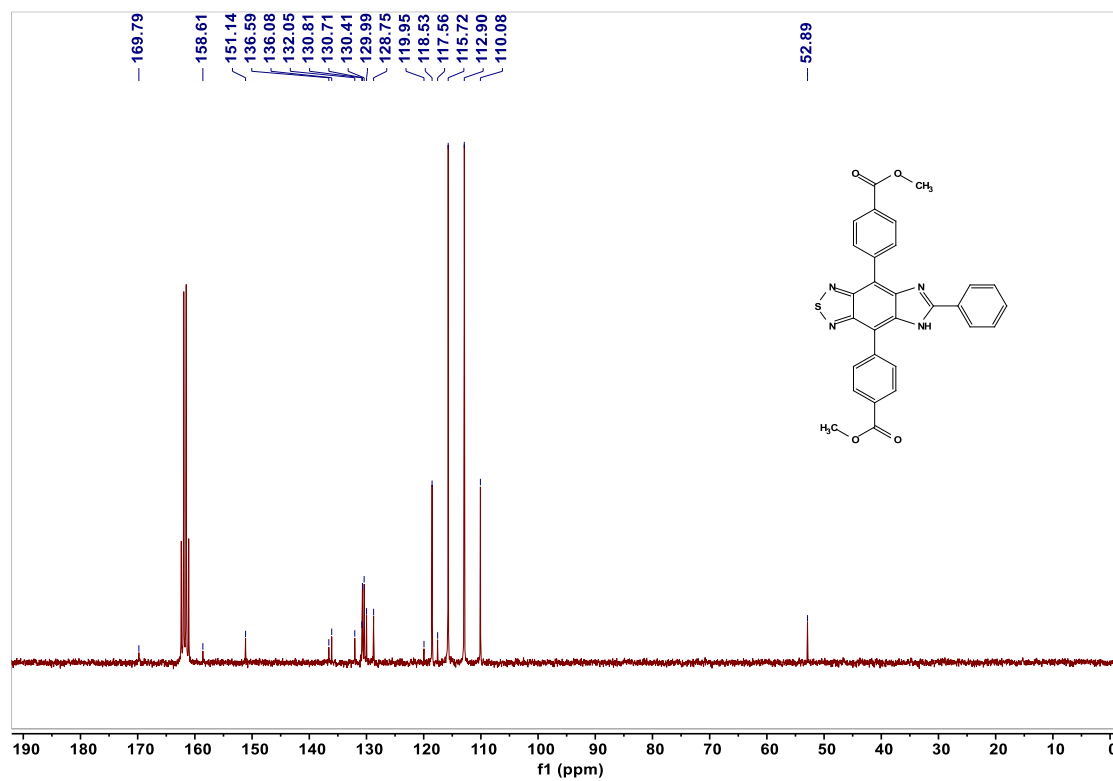
<sup>13</sup>C NMR of Me<sub>2</sub>Bs in Chloroform-*d*



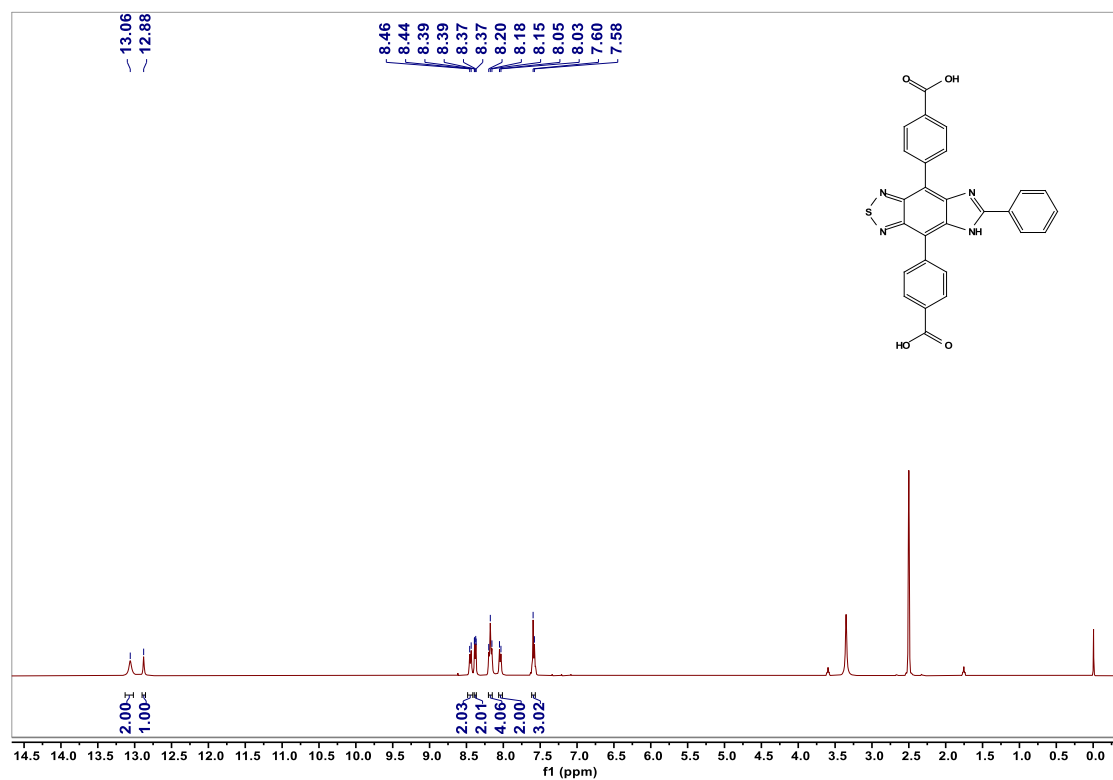
<sup>1</sup>H NMR of H<sub>2</sub>Bs in DMSO-*d*<sub>6</sub>



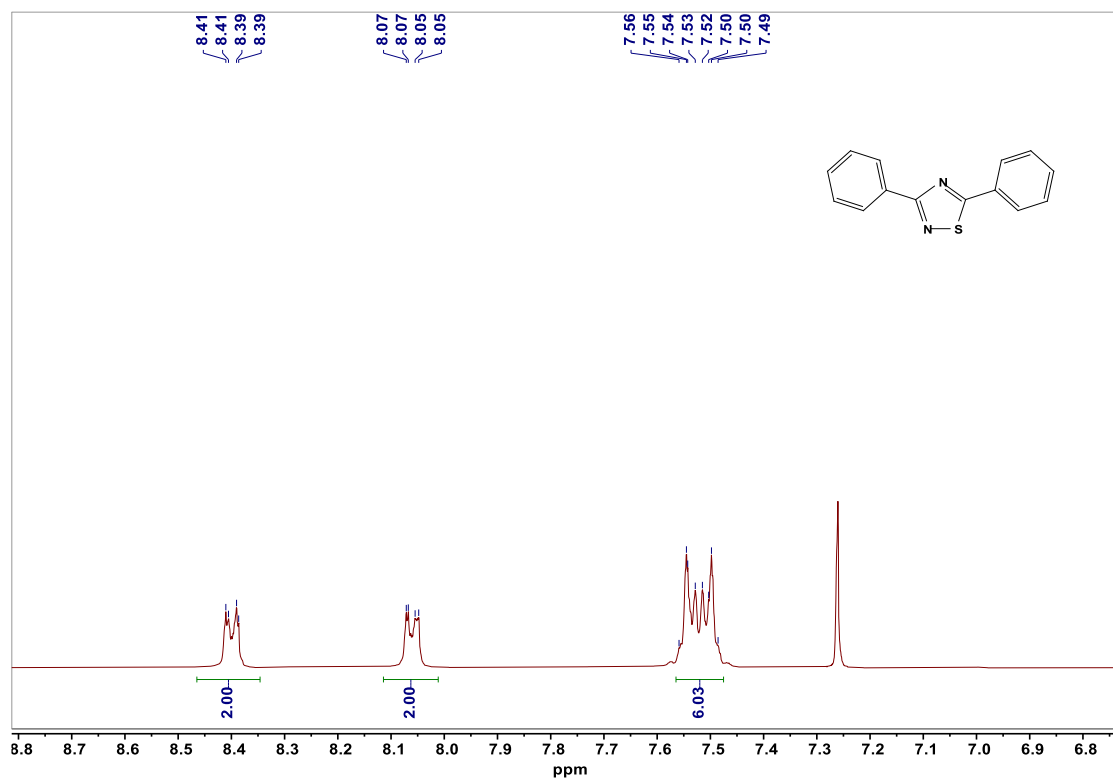
<sup>1</sup>H NMR of **Me<sub>2</sub>Ph** in DMSO-*d*<sub>6</sub>



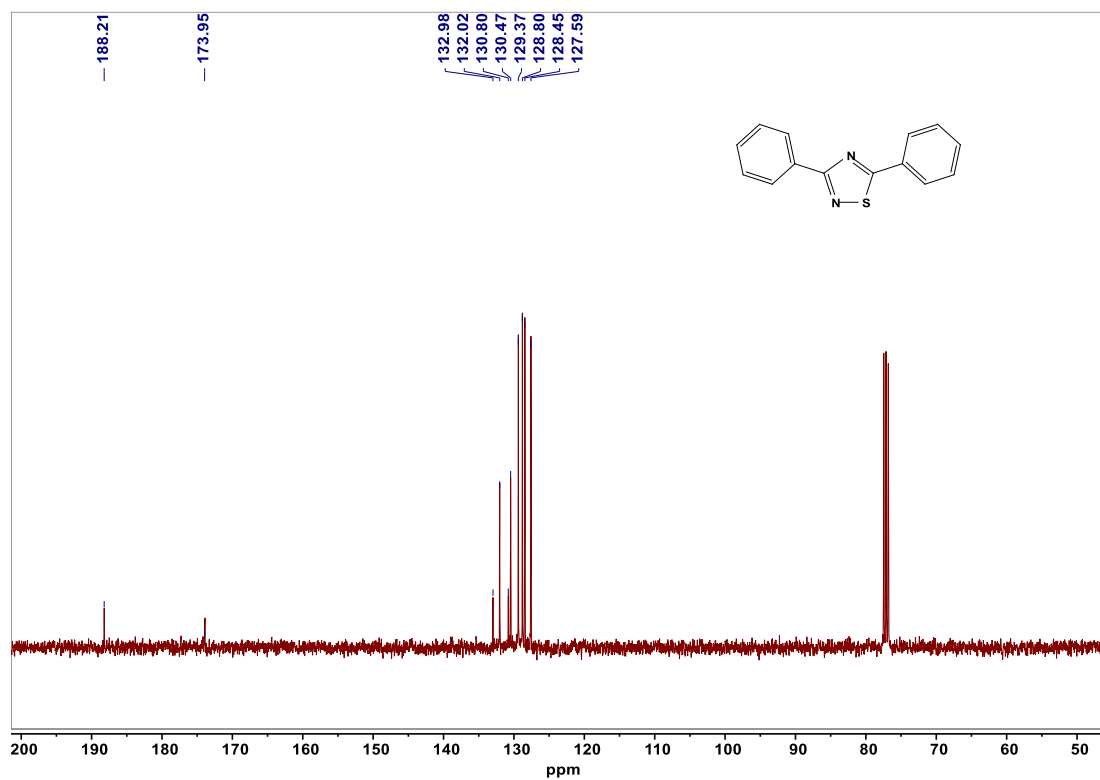
<sup>13</sup>C NMR of **Me<sub>2</sub>Ph** in CF<sub>3</sub>COOD



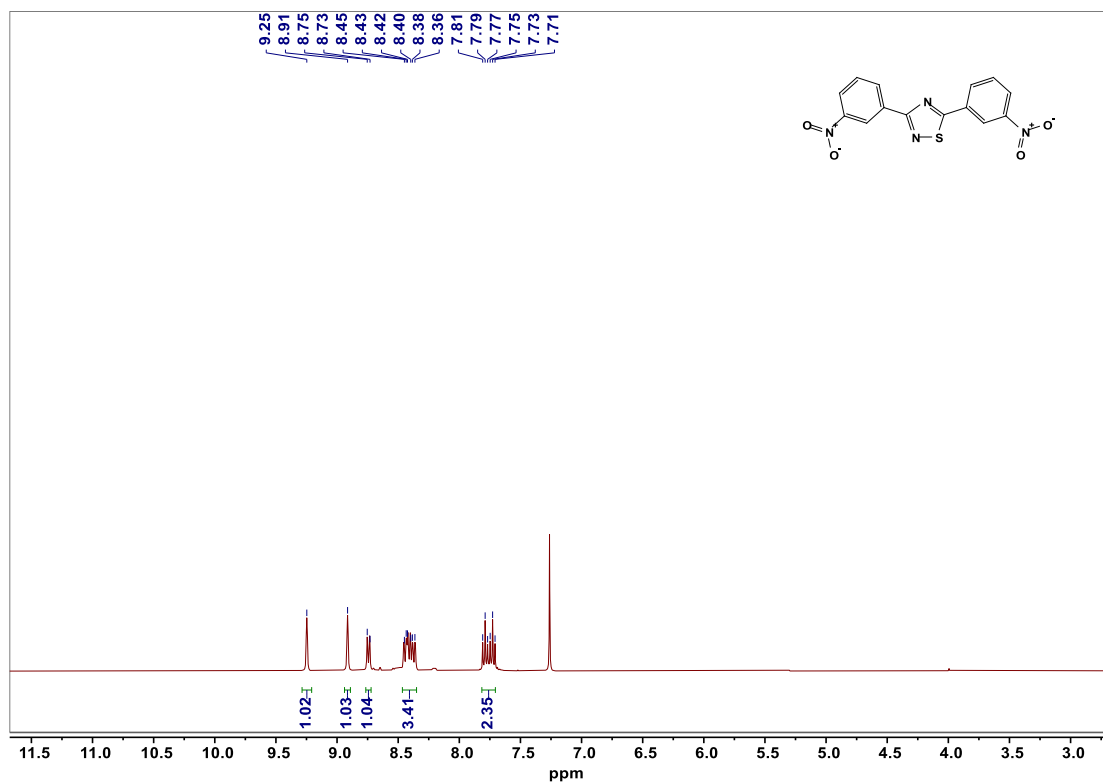
<sup>1</sup>H NMR of H<sub>2</sub>Ph in DMSO-*d*<sub>6</sub>



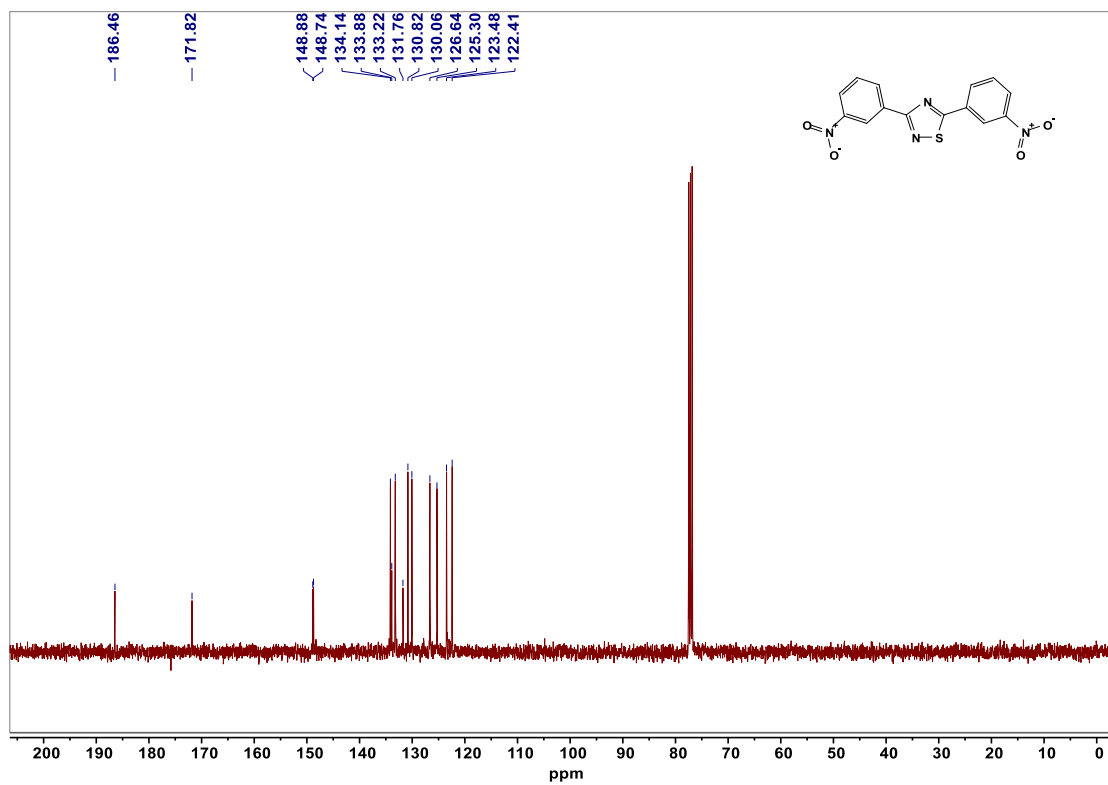
<sup>1</sup>H NMR of 2a in Chloroform-*d*



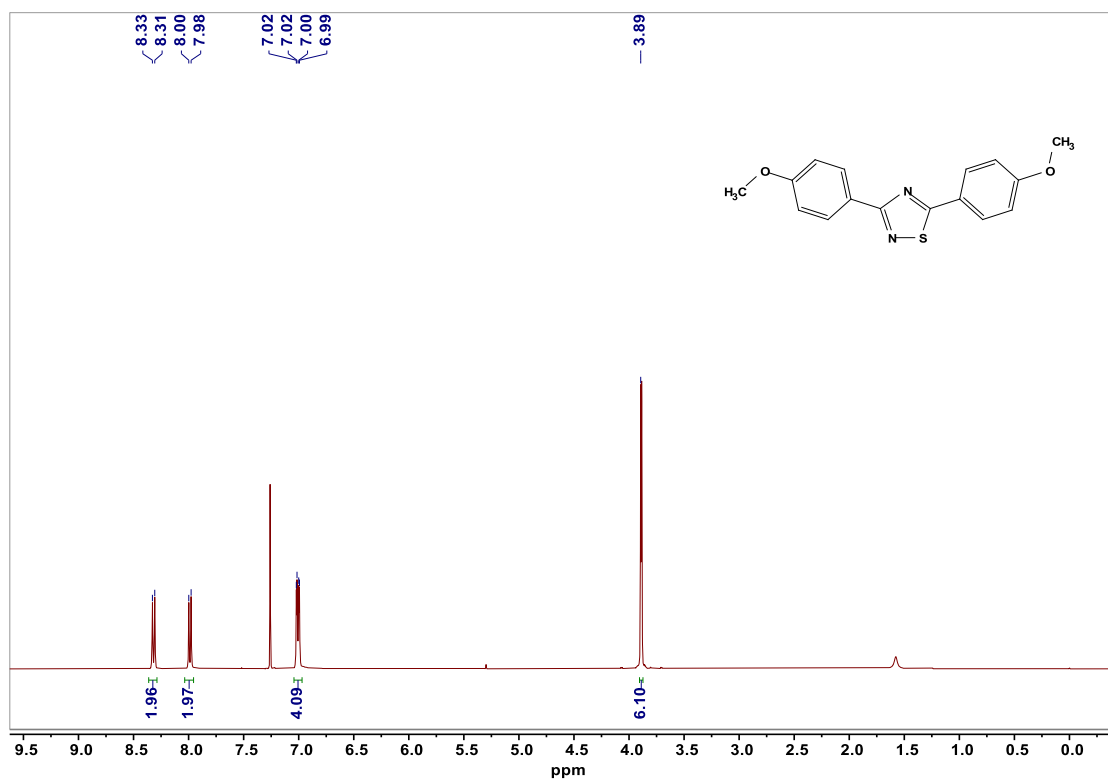
$^{13}\text{C}$  NMR of **2a** in Chloroform-*d*



$^1\text{H}$  NMR of **2b** in Chloroform-*d*

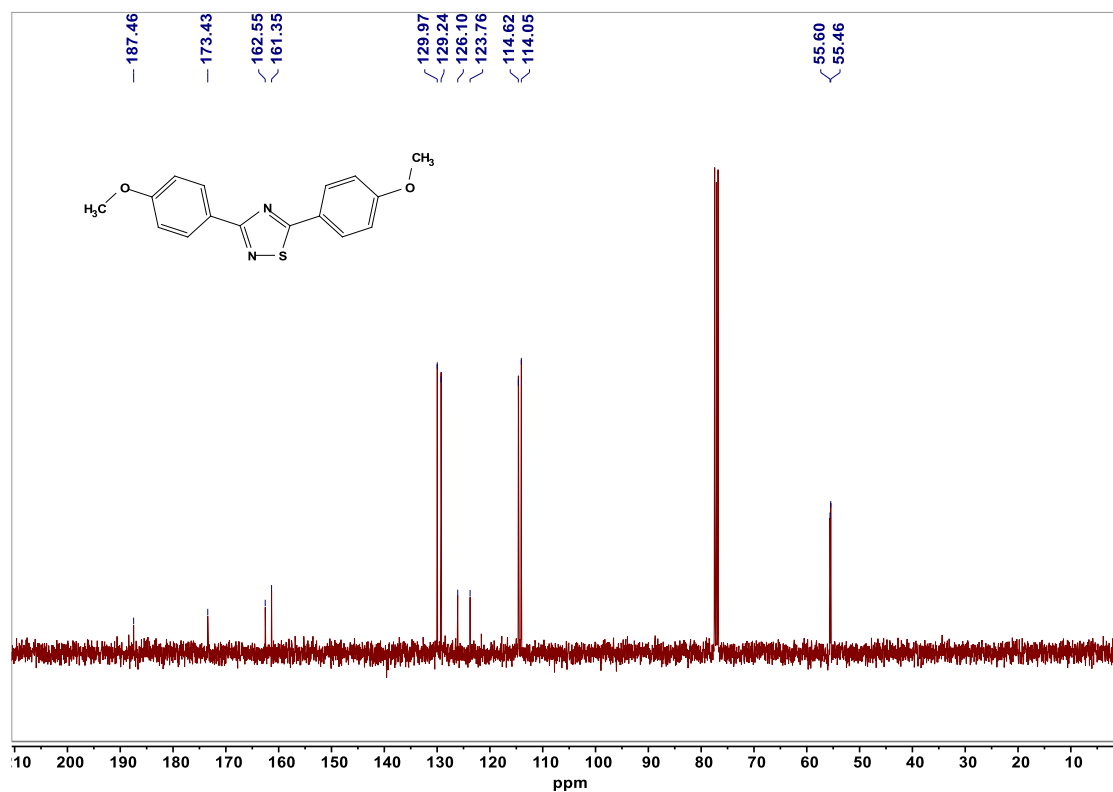


<sup>13</sup>C NMR of **2b** in Chloroform-*d*

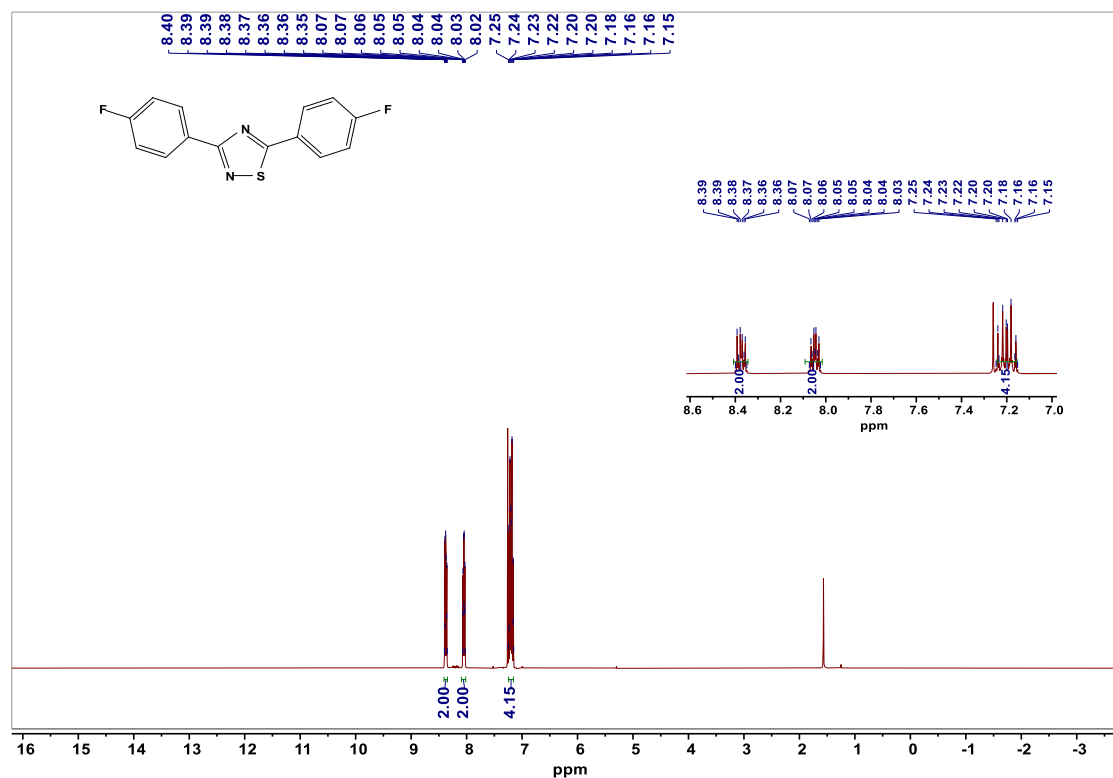


<sup>1</sup>H NMR of **2c** in Chloroform-*d*

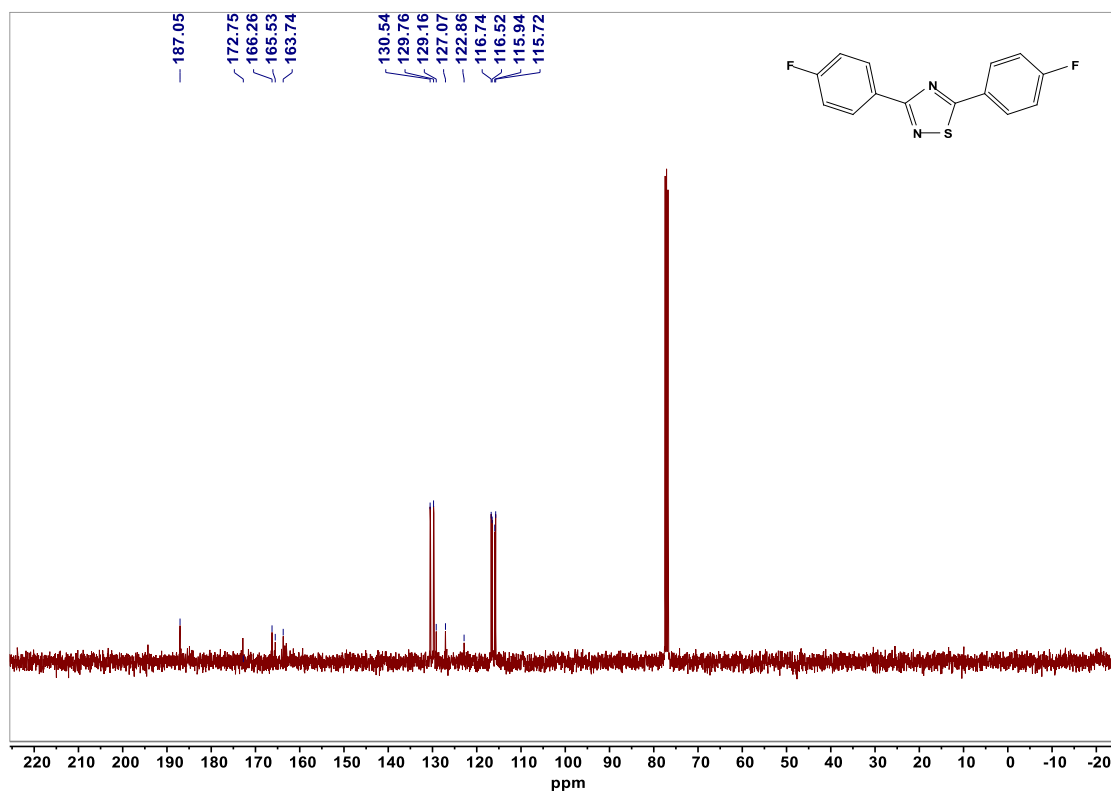




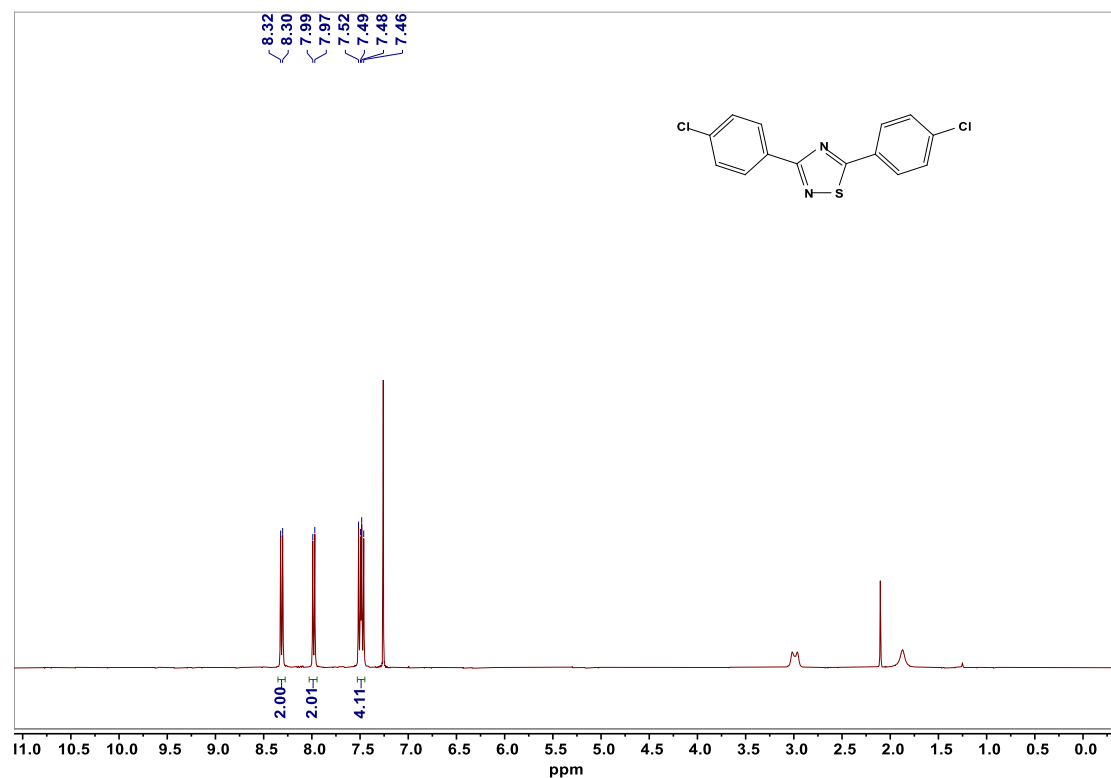
<sup>13</sup>C NMR of 2c in Chloroform-*d*



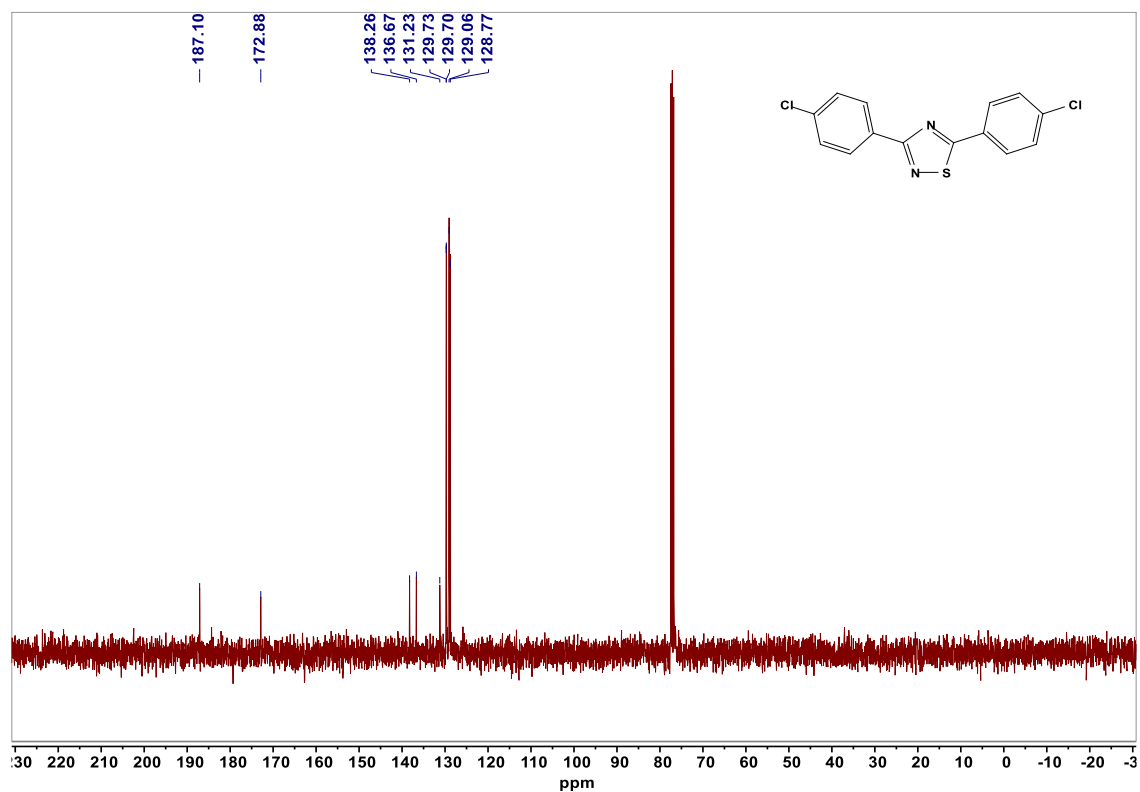
<sup>1</sup>H NMR of 2d in Chloroform-*d*



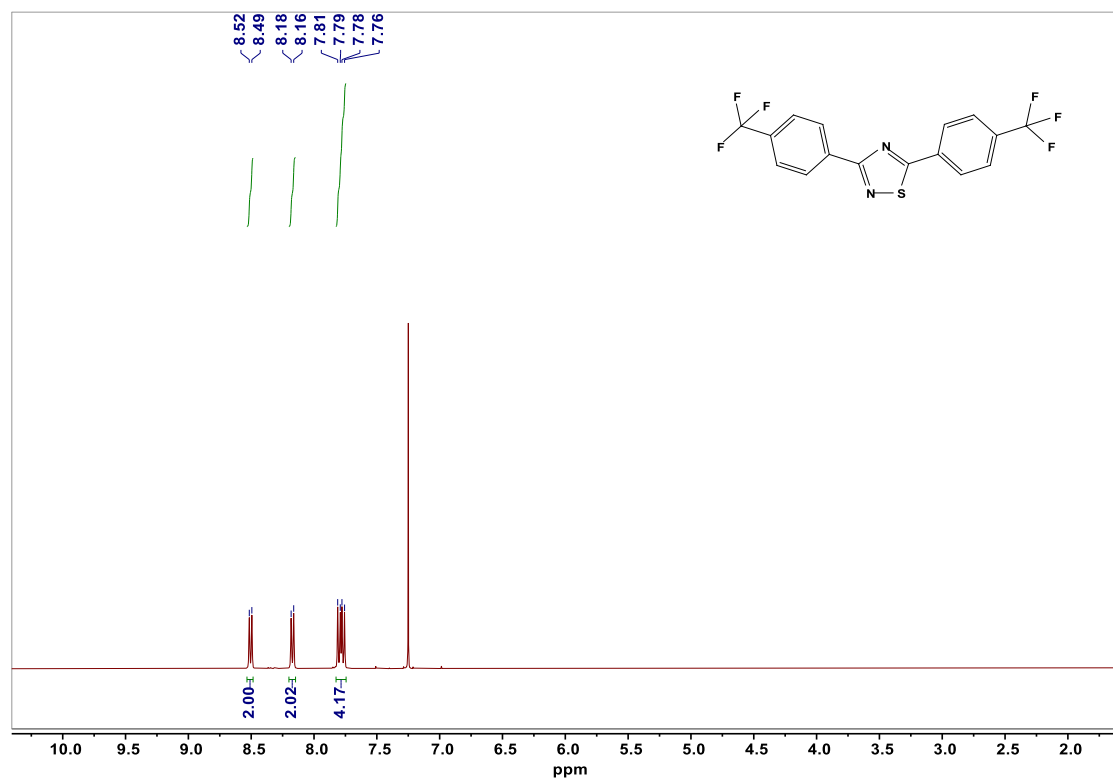
<sup>13</sup>C NMR of **2d** in Chloroform-*d*



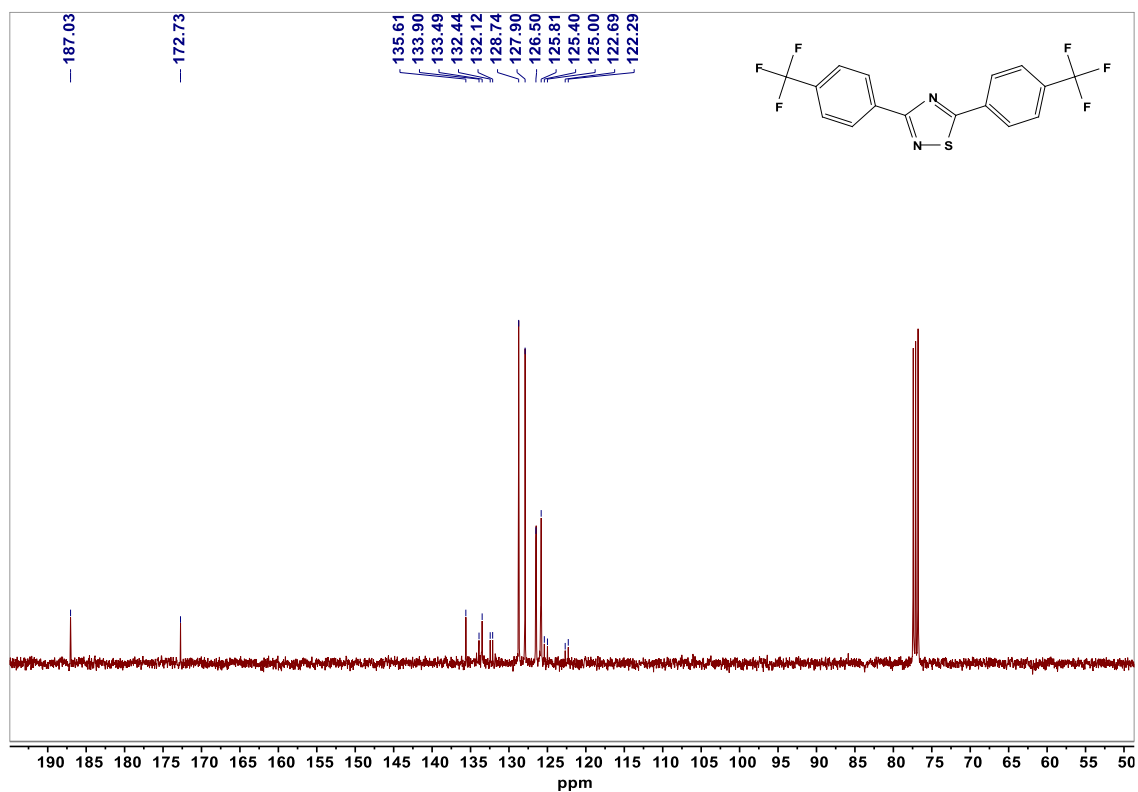
<sup>1</sup>H NMR of **2e** in Chloroform-*d*



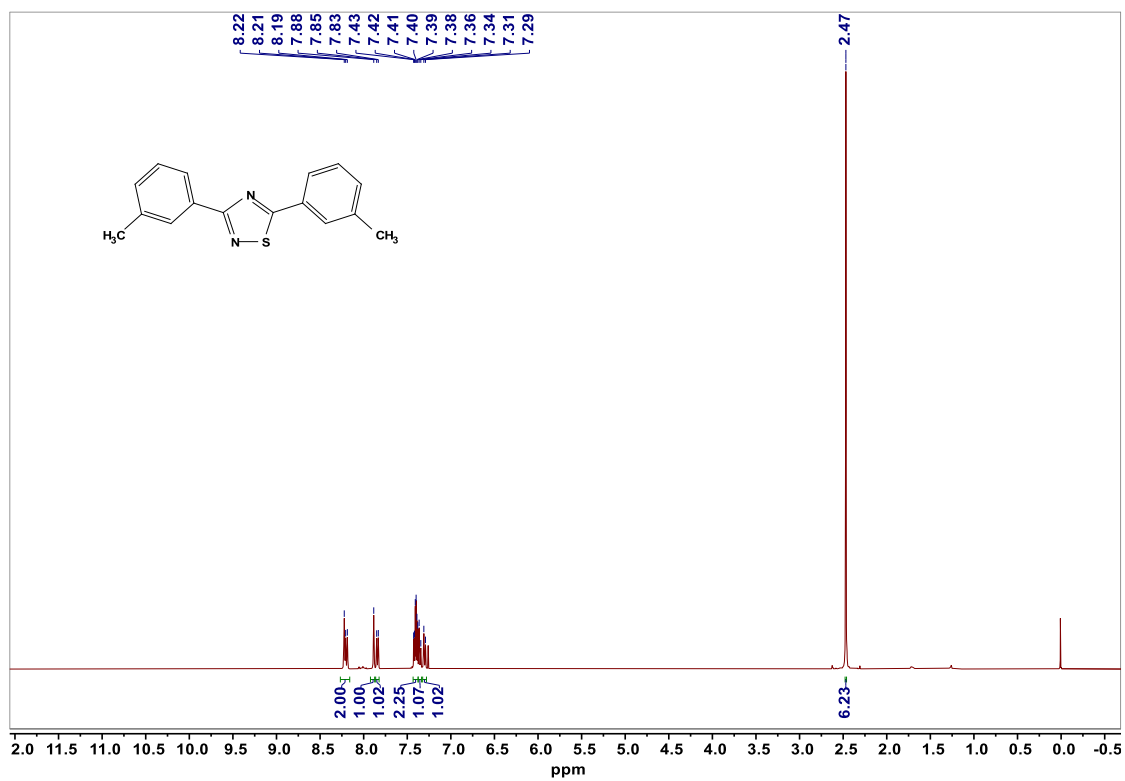
<sup>13</sup>C NMR of **2e** in Chloroform-*d*



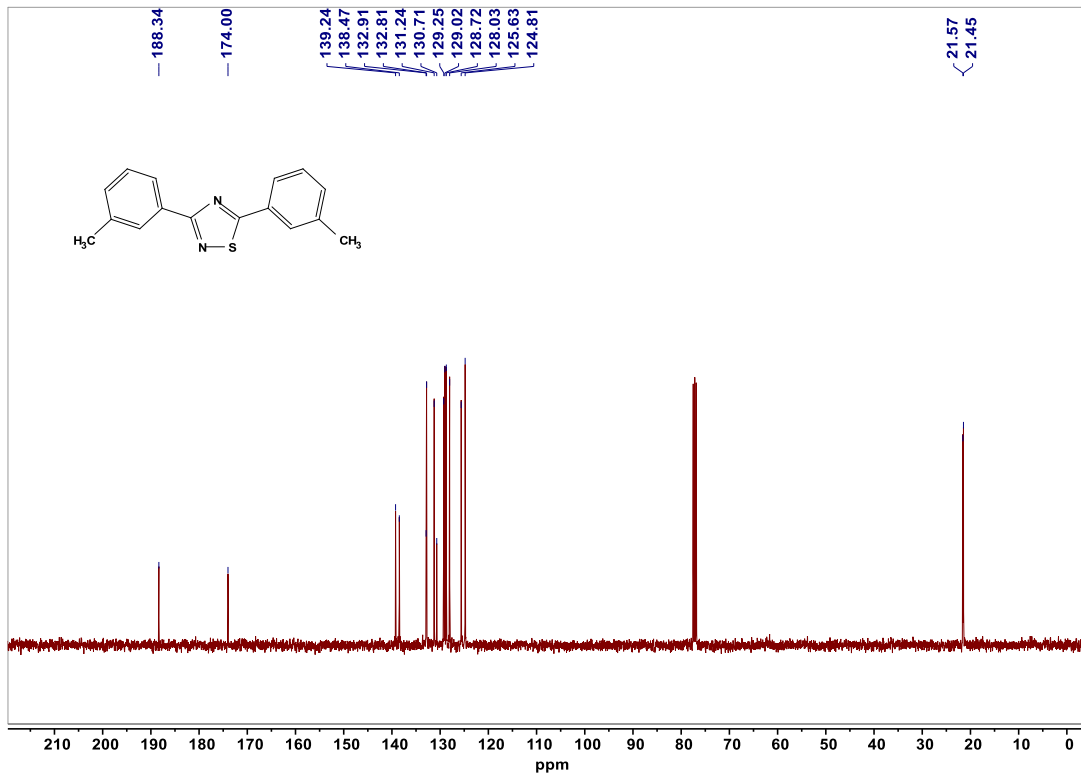
<sup>1</sup>H NMR of **2f** in Chloroform-*d*



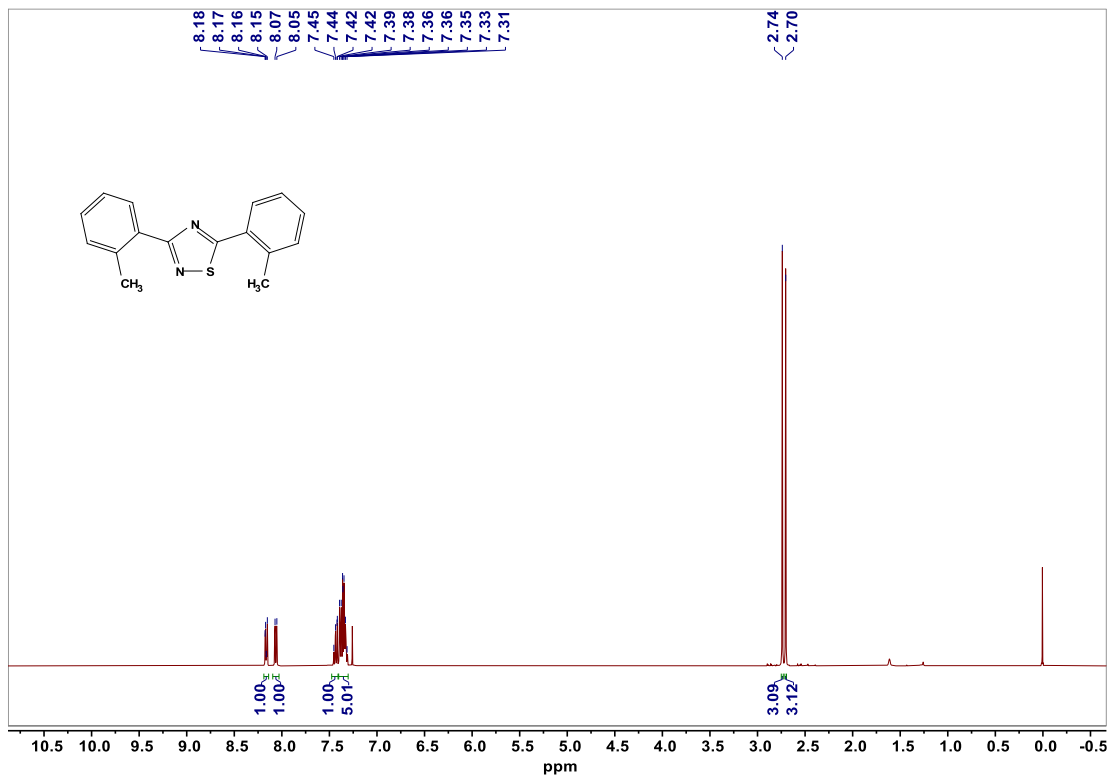
$^{13}\text{C}$  NMR of **2f** in Chloroform-*d*



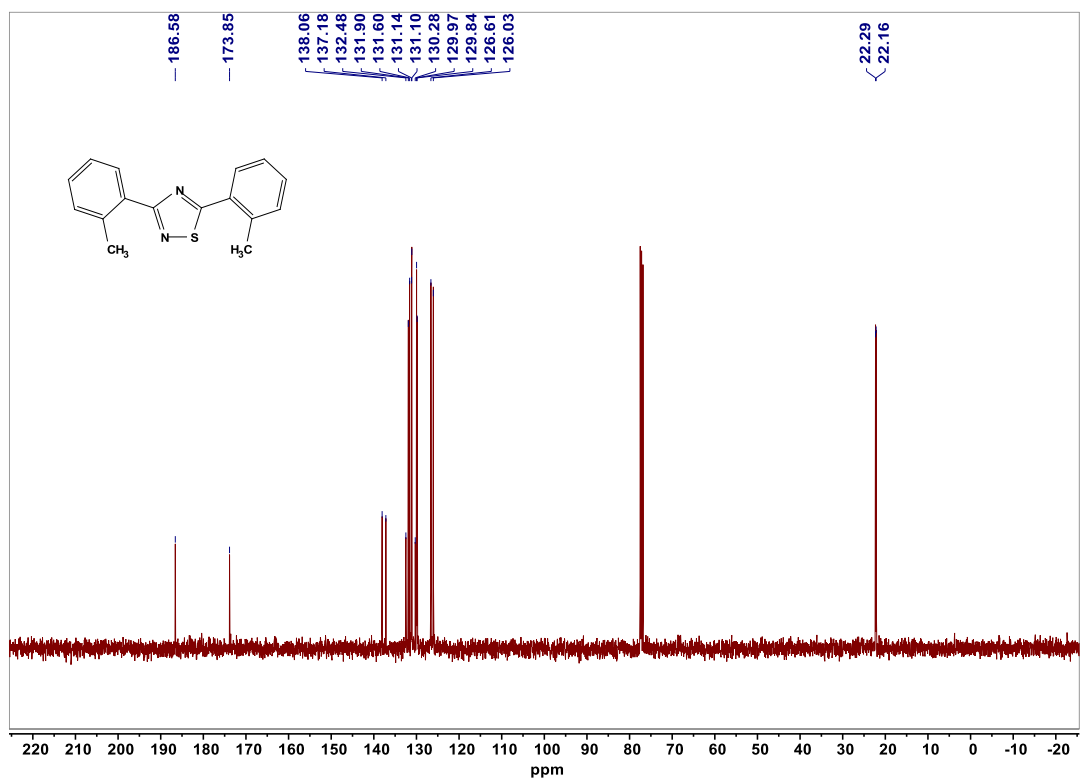
$^1\text{H}$  NMR of **2g** in Chloroform-*d*



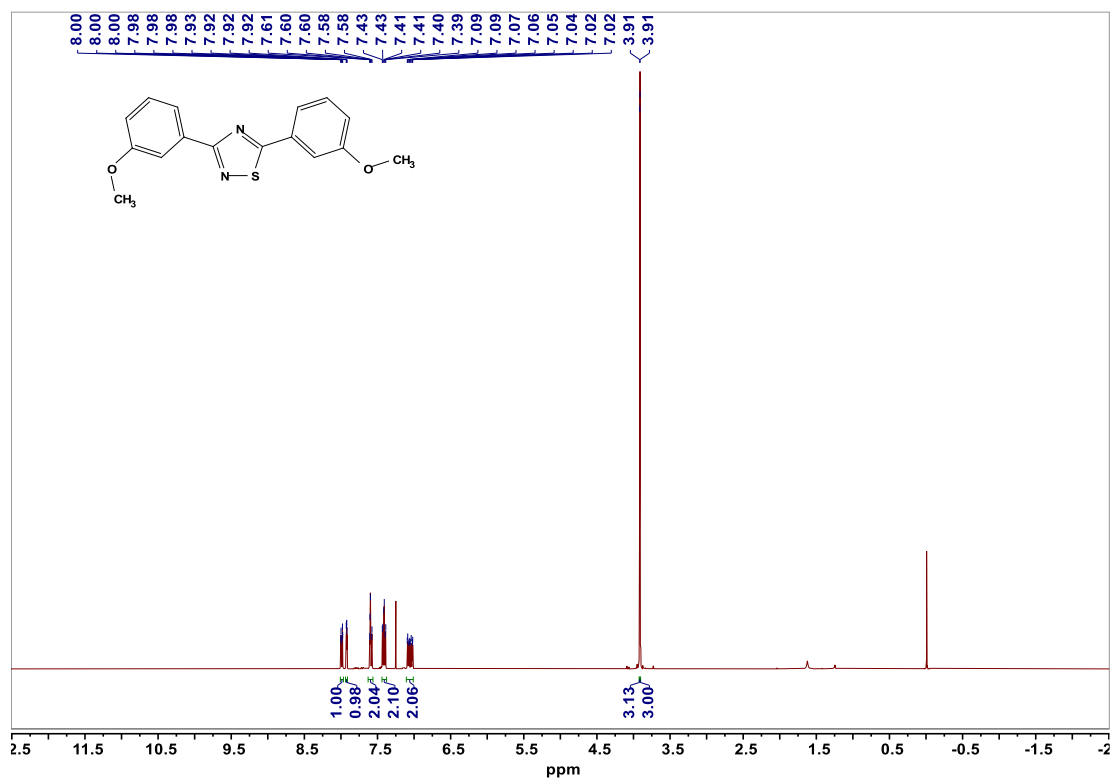
$^{13}\text{C}$  NMR of **2g** in Chloroform-*d*



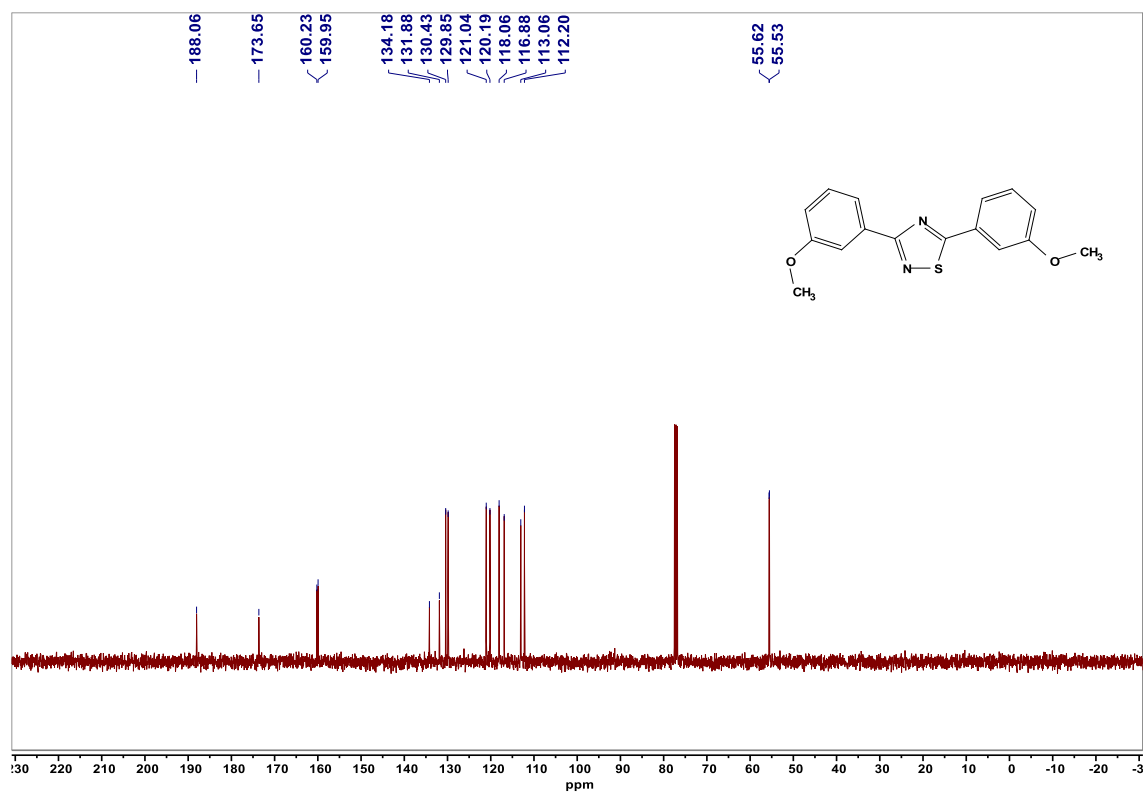
$^1\text{H}$  NMR of **2h** in Chloroform-*d*



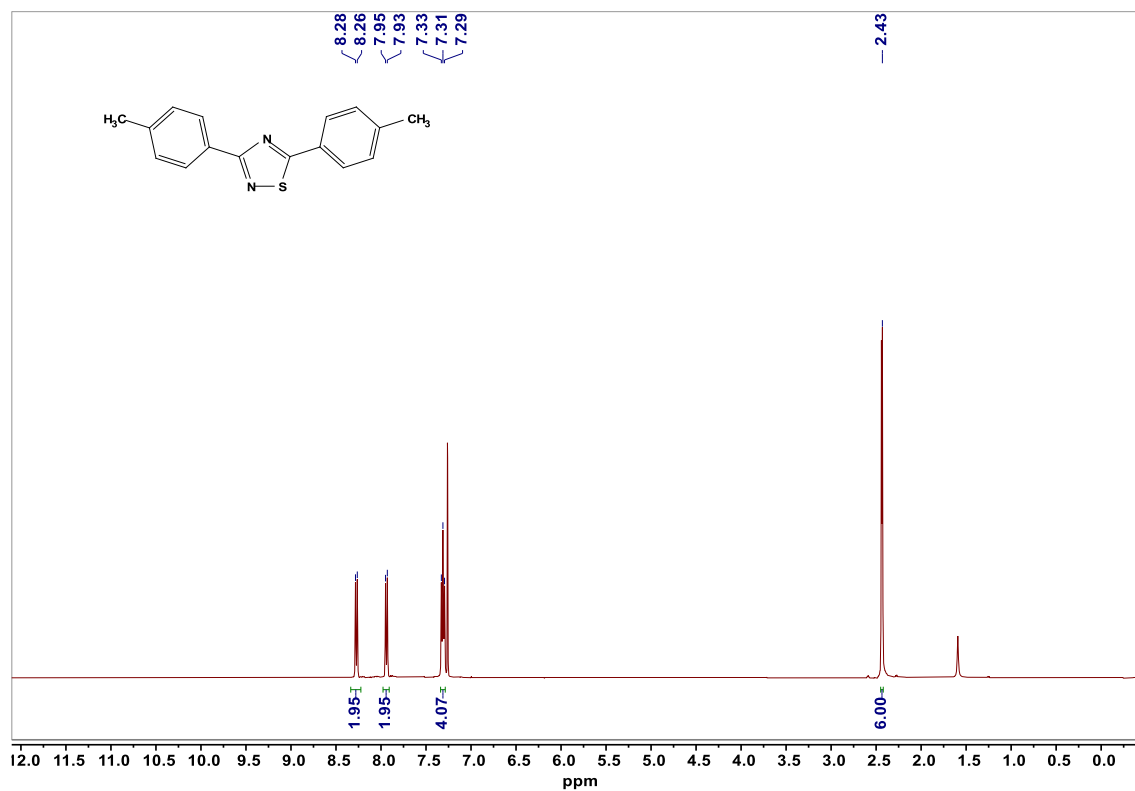
<sup>13</sup>C NMR of **2h** in Chloroform-*d*



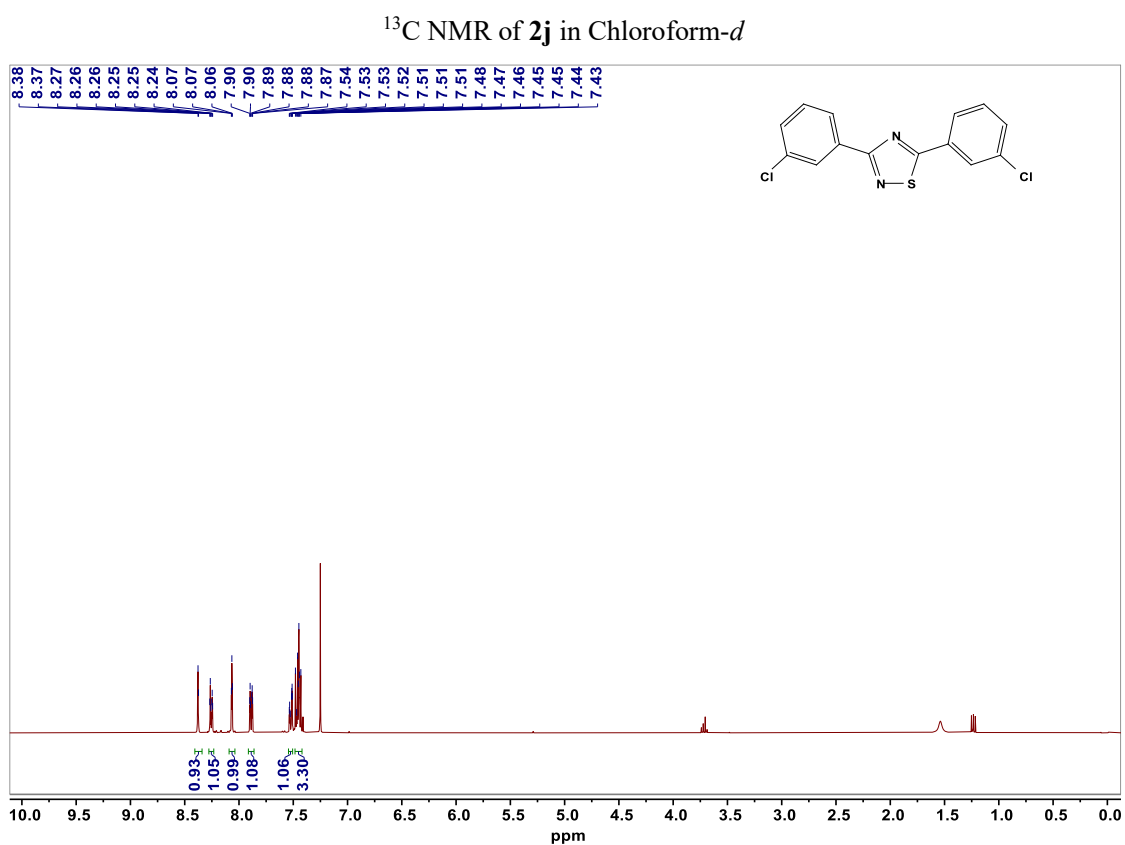
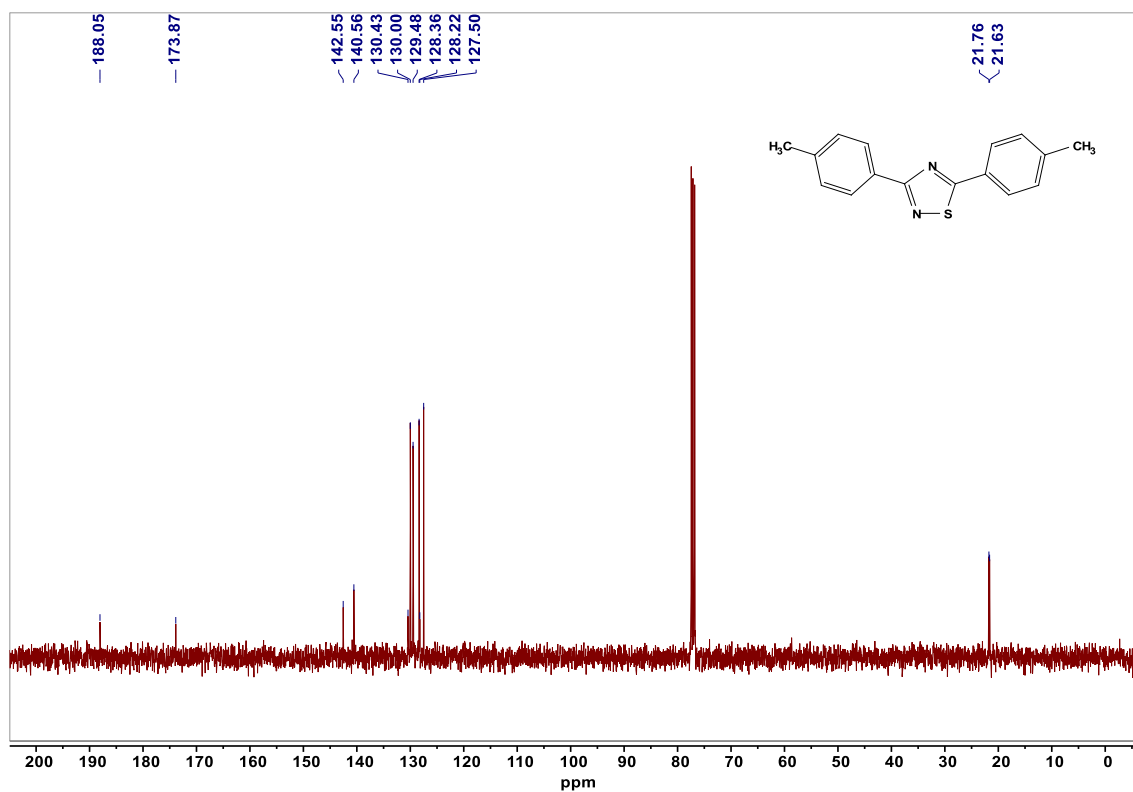
<sup>1</sup>H NMR of **2i** in Chloroform-*d*



$^{13}\text{C}$  NMR of **2i** in Chloroform-*d*

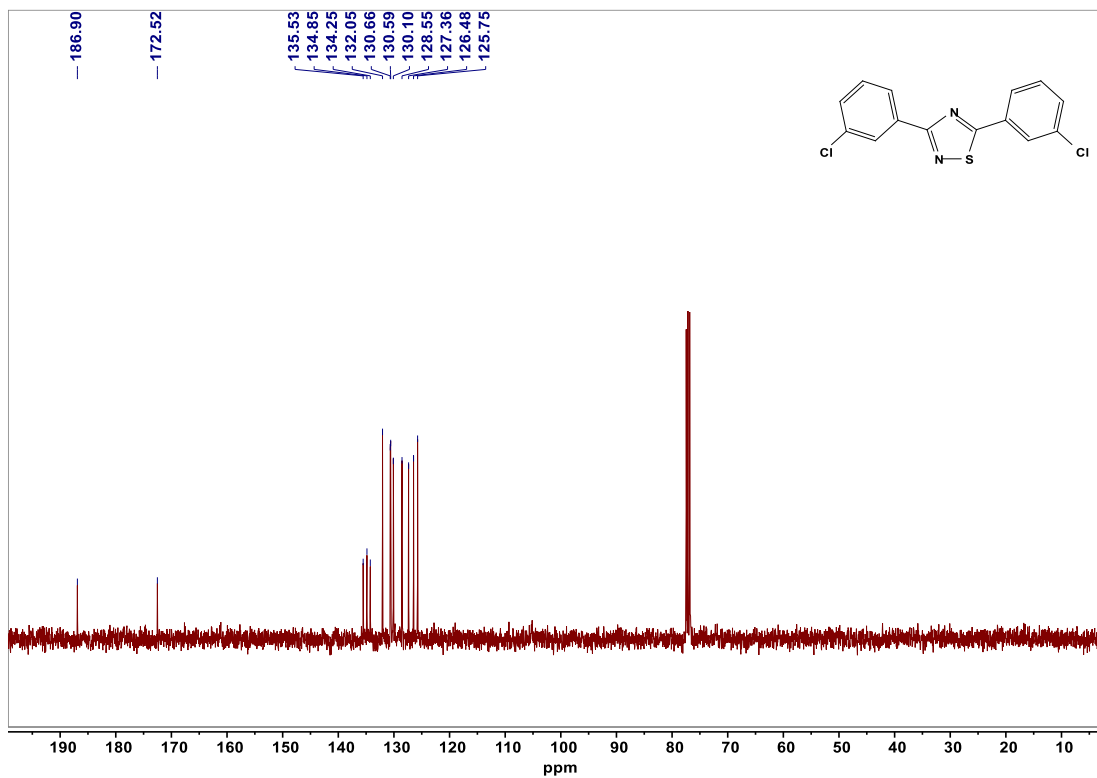


$^1\text{H}$  NMR of **2j** in Chloroform-*d*

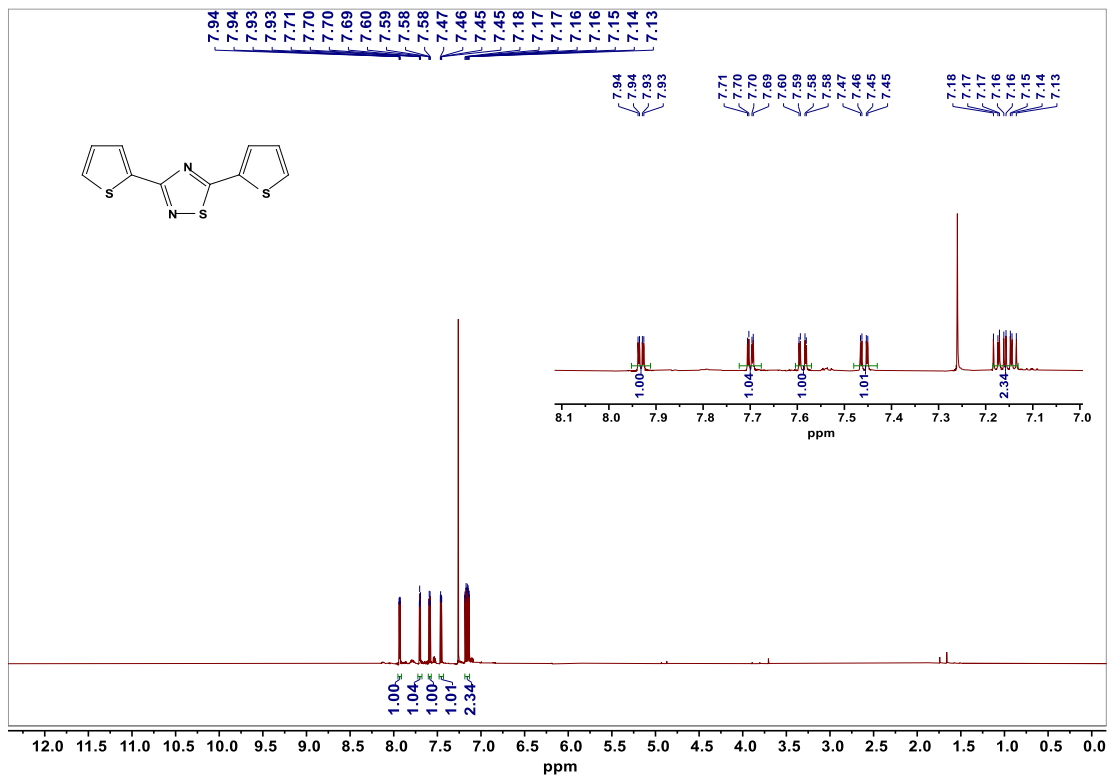


**<sup>1</sup>H NMR of 2k in Chloroform-*d***

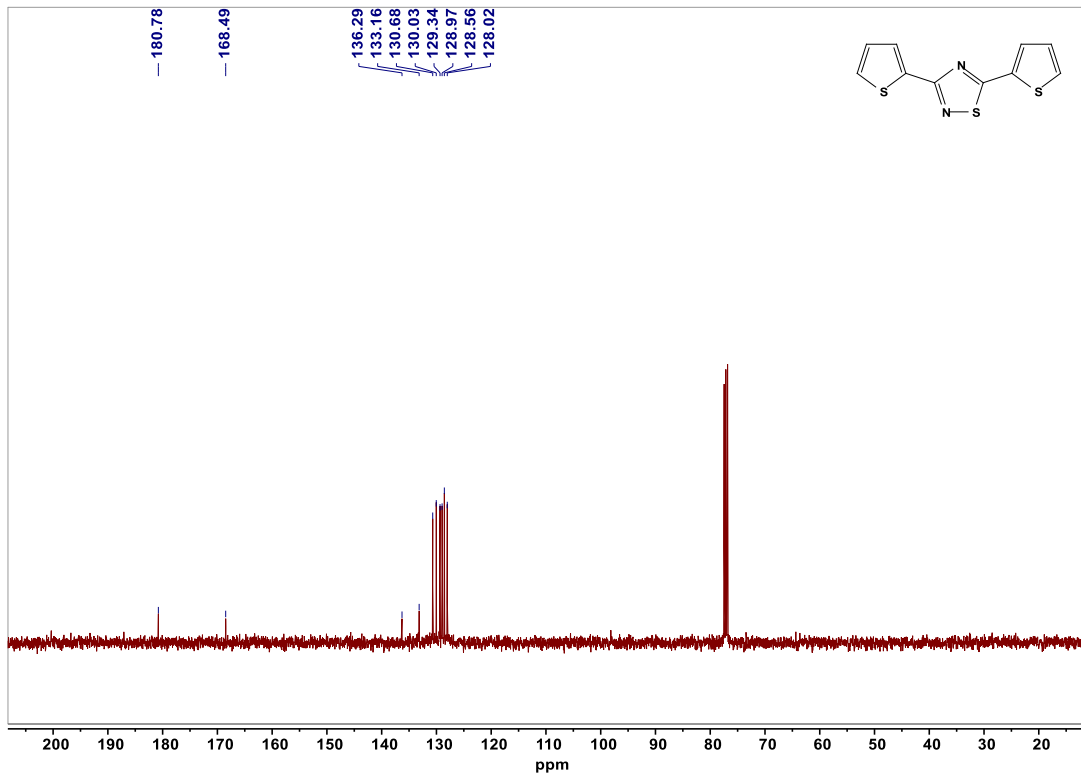




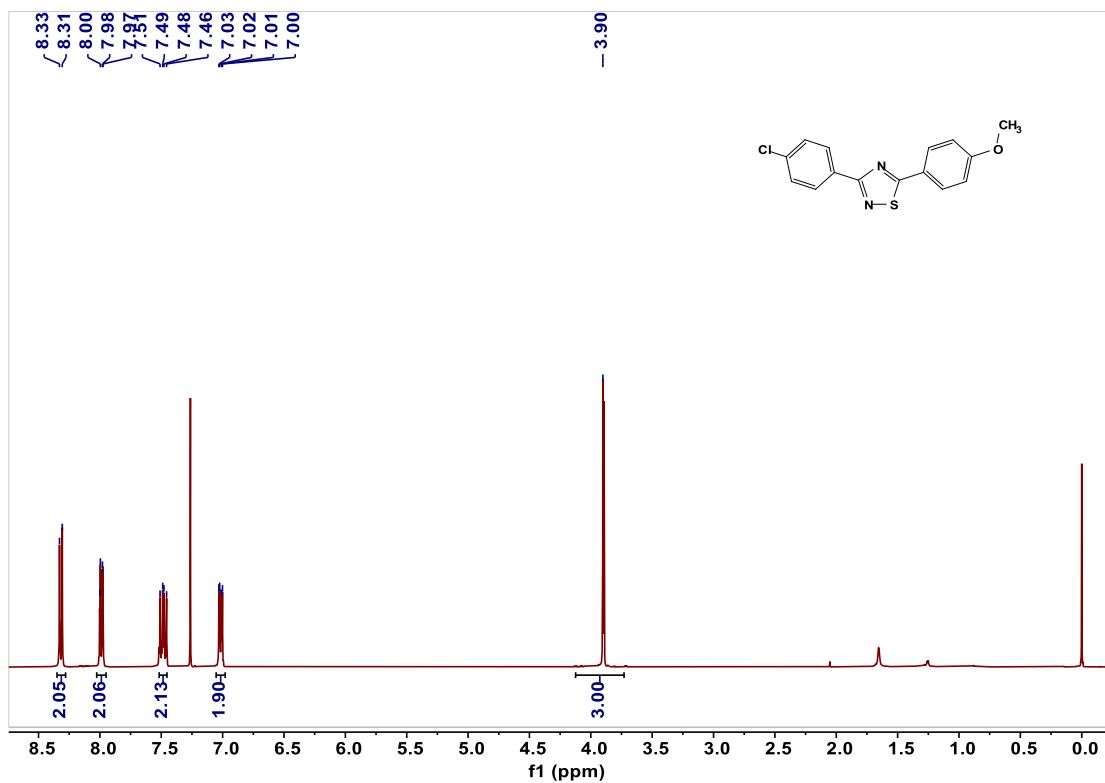
$^{13}\text{C}$  NMR of **2k** in Chloroform-*d*



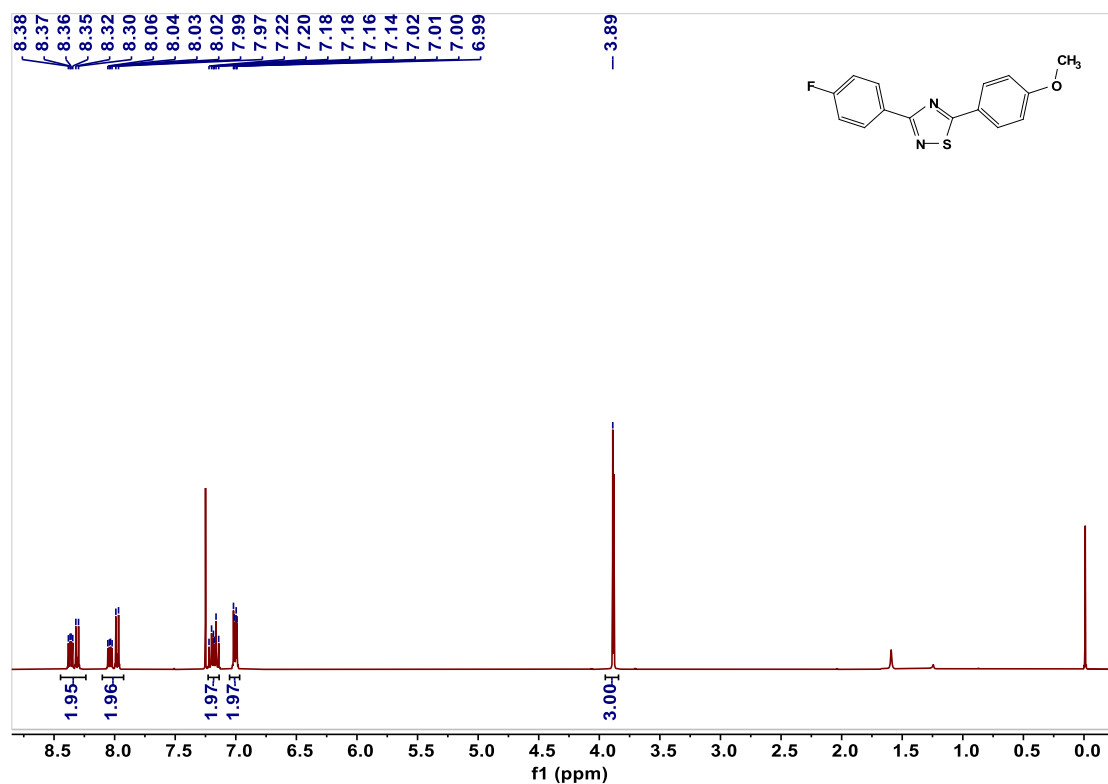
$^1\text{H}$  NMR of **2l** in Chloroform-*d*



$^{13}\text{C}$  NMR of **2i** in Chloroform-*d*



$^1\text{H}$  NMR of **2m** in Chloroform-*d*



<sup>1</sup>H NMR of **2n** in Chloroform-*d*

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