Supplementary Information (SI) for RSC Advances.

# Supplementary Information

## Sulfhydryl-Functionalized Diarylethenes: Synthesis, Photoswitching, and Fluorescent Properties

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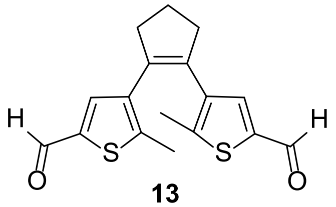
## I. Synthesis and characterization of compounds 13-16 and S1

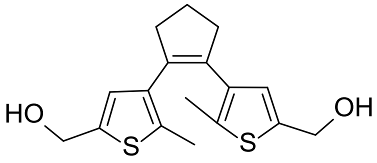
### 1. Synthesis of compound **13**



**13**

Compound **7** (500 mg, 1.581 mmol, 1 equiv) was dissolved in anhydrous diethyl ether (10 mL) in a dried and argon-flushed round-bottomed flask. n-Butyl Lithium (1.52 mL, 3.79 mmol, 2.5 equiv) was added dropwise at -78 °C and the reaction was stirred for 1 hour. The reaction mixture turned into purple color immediately after the addition and stirred for half an hour. Anhydrous DMF (0.3 mL, 3.79 mmol, 2.5 equiv) was added to the reaction mixture dropwise at -20 °C and the reaction continued to stir for 1 hour. The reaction mixture was then dropped into a stirring 2 M HCl solution (10 mL). THF was removed under reduced pressure. The aqueous solution was then extracted with DCM (15 mL x 3). The organic layers were combined, dried over $Na_2SO_4$, and filtered, and the solvent was removed under reduced pressure. The crude product was purified via column chromatography ($SiO_2$) using 0-10% EtOAc/hexanes to obtain white solid 324 mg (68%) as a desired product. $R_f$ = 0.2 in 10% EtOAc/Hexane. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 2H), 7.41 (s, 4H), 2.83 (t, *J* = 7.5 Hz, 4H), 2.16-2.07 (m, 2H), 2.05 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 182.3, 146.3, 140.2, 137.3, 137.0, 135.0, 38.4, 22.8, 15.3.

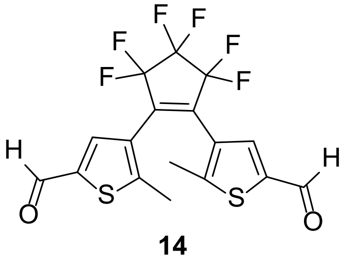
2. Synthesis of compound **15**



**15**

Compound **18** (200 mg, 0.63 mmol, 1 equiv) was dissolved in anhydrous MeOH (5 mL) in a dried 50 mL round-bottomed flask. The temperature was reduced to 0 °C via an ice bath and $NaBH_4$ (48 mg, 1.26 mmol, 2 equiv) was added at 0 °C and stirred for 4 hours, at which point it was quenched with saturated $NH_4Cl$ solution (3 mL). Methanol was then removed under reduced pressure, and the remaining aqueous layer was extracted with DCM (10 mL x 3). The organic layers were combined, dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure. The crude was purified via column chromatography ($SiO_2$) using 0-20% acetone/hexanes to afford light yellow viscous sticky solid, 163 mg (81%). $R_f = 0.3$ in 30% acetone/hexane. $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 2H), 4.65 (s, 4H), 2.75 (t, $J = 7.4$ Hz, 4H), 2.08-1.98 (m, 2H), 1.94 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.4, 135.4, 135.0, 134.6, 126.9, 60.1, 38.3, 22.9, 14.3.

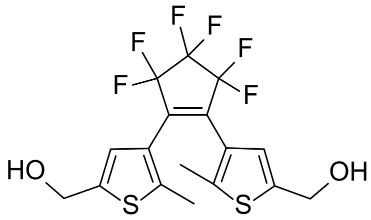
3. Synthesis of compound **14**



**14**

Compound **10** (482 mg, 1.10 mmol, 1 equiv) was dissolved in anhydrous diethyl ether (6 mL) in a dried and argon-flushed round-bottomed flask. Then n-Butyl Lithium (1.31 mL, 2.75 mmol, 2.5 equiv) was added dropwise at 0 °C and the reaction was stirred for 1 hour. Anhydrous DMF (0.2 mL, 2.75 mmol, 2.5 equiv) was added to the reaction mixture dropwise and the reaction continued to stir for 2 hours. The reaction mixture was then dropped into a stirring 2 M HCl solution (10 mL). Brown precipitate was formed after the addition of HCl. Precipitate was filtered to get 339 mg solid and aqueous layer (filtrate) was then extracted with ethyl acetate (15 mL x 3). The organic layers were combined, dried over $Na_2SO_4$, and filtered, and the solvent was removed under reduced pressure. The crude product was purified via column chromatography ($SiO_2$) using 0-10% EtOAc/hexanes to afford 384 mg white solid with 82% yield. $R_f = 0.5$ in 25% EtOAc/hexanes. $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.17 (s, 4H), 2.71 (t, $J = 7.4$ Hz, 4H), 2.34 (s, 6H), 2.04-1.95 (m, 2H), 1.86 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 181.2, 151.5, 142.2, 135.5, 125.8, 15.39.

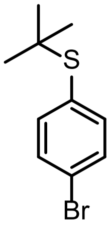
4. Synthesis of compound **16**



**16**

Compound **22** (200 mg, 0.47 mmol, 1 equiv) was dissolved in anhydrous MeOH (5 mL) in a dried 50 mL round-bottomed flask. The temperature was reduced to 0 °C via an ice bath and $NaBH_4$ (36 mg, 0.94 mmol, 2 equiv) was added. The reaction mixture remained at 0 °C and stirred for 4 hours, at which point it was quenched with saturated $NH_4Cl$ solution (3 mL). Methanol was then removed under reduced pressure and the remaining aqueous layer was extracted with DCM (10 mL x 3). The organic layers were combined, dried over $Na_2SO_4$, and filtered and the solvent was removed under reduced pressure. The crude product was purified via column chromatography ($SiO_2$) using 0-25% EtOAc/Hexanes to afford white solid 183 mg (91%) as a desired product. $R_f = 0.4$ in 40% EtOAc/Hexane. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 6.94 (s, 2H), 4.75 (s, 4H), 1.89 (s, 6H); $^{13}C$ NMR (400 MHz, $CDCl_3$) $\delta$ 142.2, 142.1, 125.0, 124.5, 60.0, 14.5.

5. Synthesis of compound **S1**

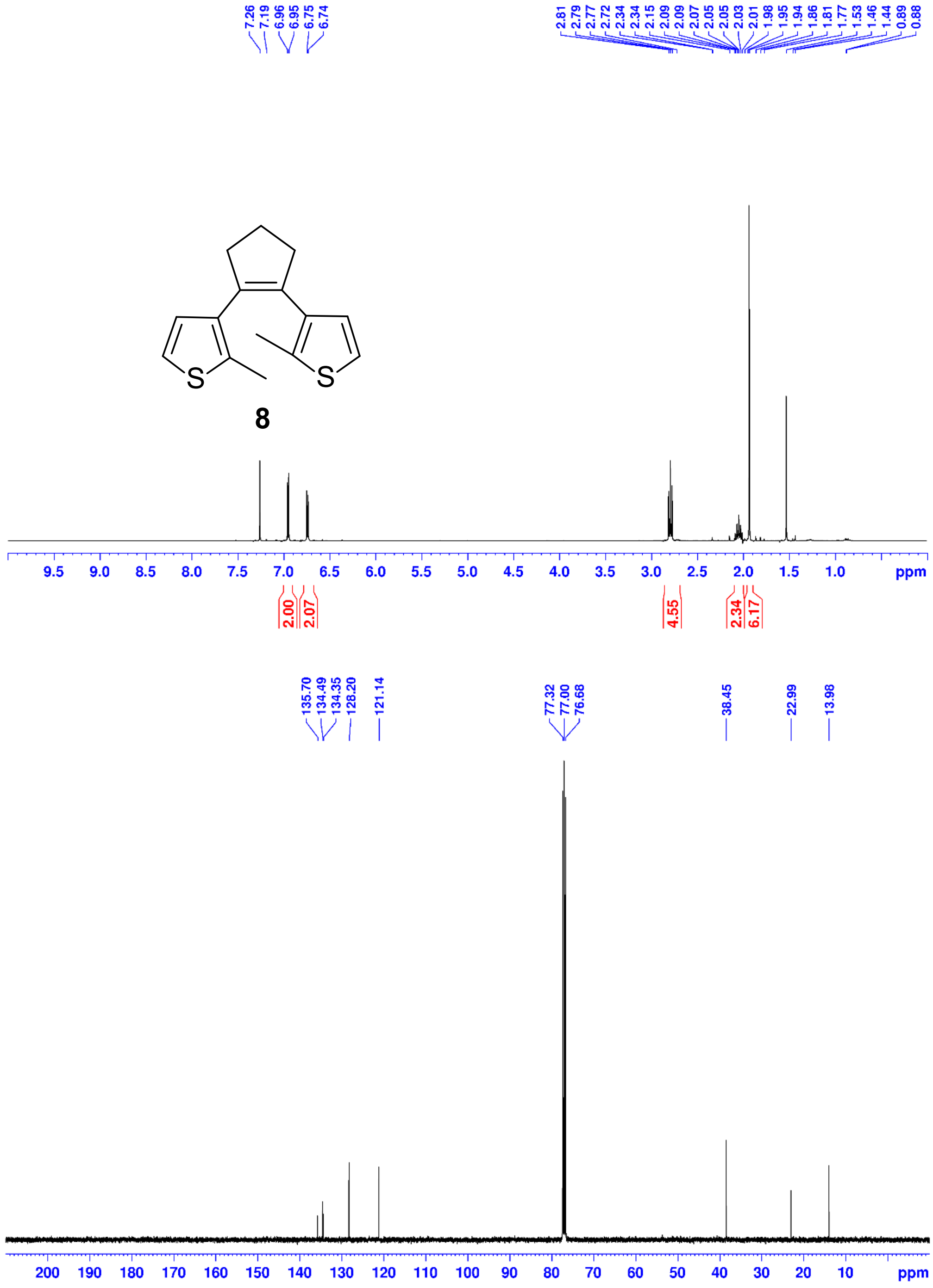


**S1**

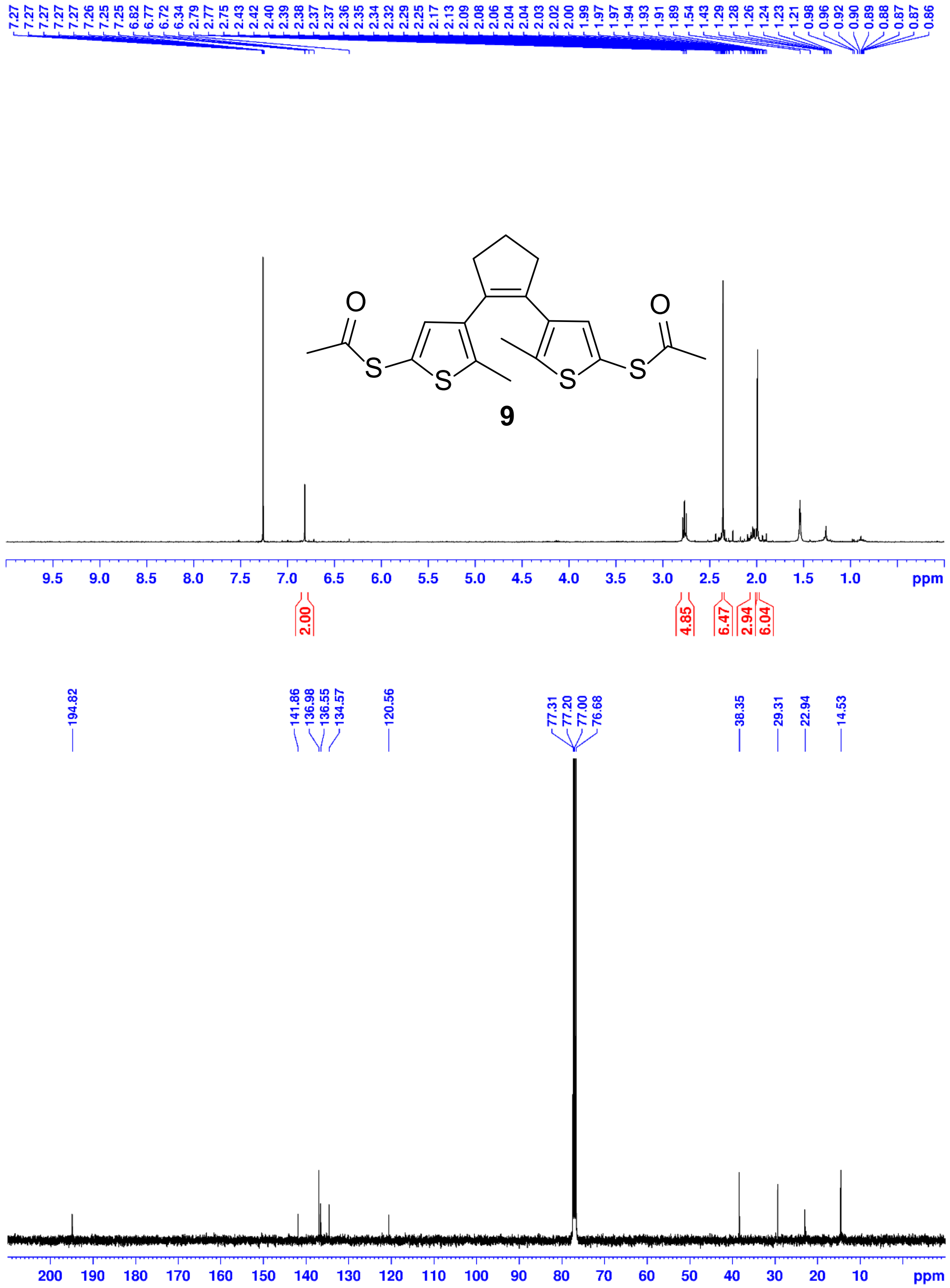
To a solution of 4-bromothiophenol (2.0 g 10.58 mmol, 1 equiv) and tertiary butyl chloride (700 mg, 5.29 mmol, 0.5 equiv) in DCM, $AlCl_3$ was added portion wise at 0°C over 5 mins. The reaction mixture was stirred at rt for 2 hours. Then the reaction mixture was quenched with water and extracted with DCM, dried using anhydrous sodium sulphate and removed under reduced pressure to obtain desired product compound **S1,** 2.18 g (84%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 4H), 7.38 (d, *J* = 8.5 Hz, 4H), 1.27 (s, 9H).

## II. NMR spectra for compounds

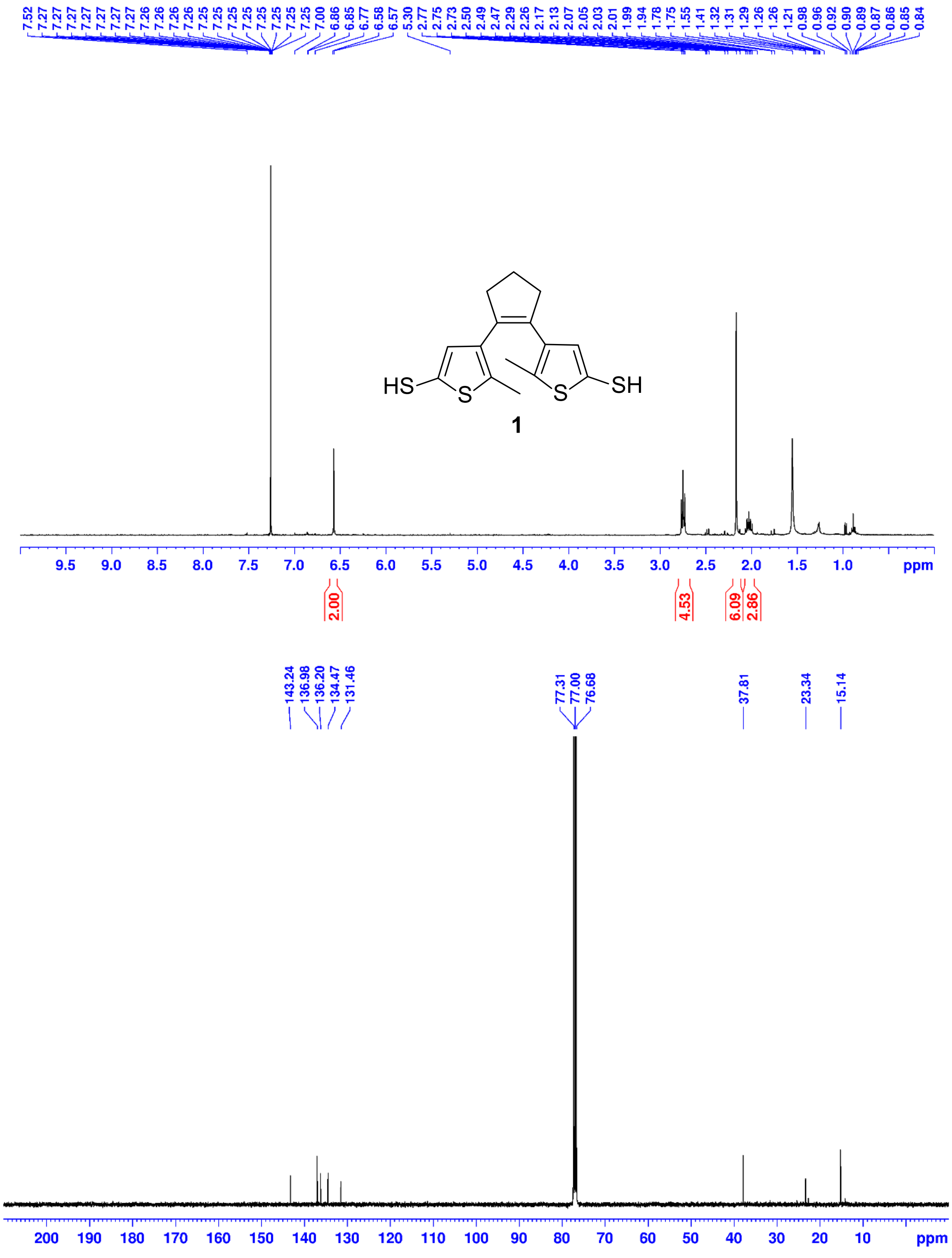
### 1. $^1H$ and $^{13}C$ NMR spectra of compounds **1-24**



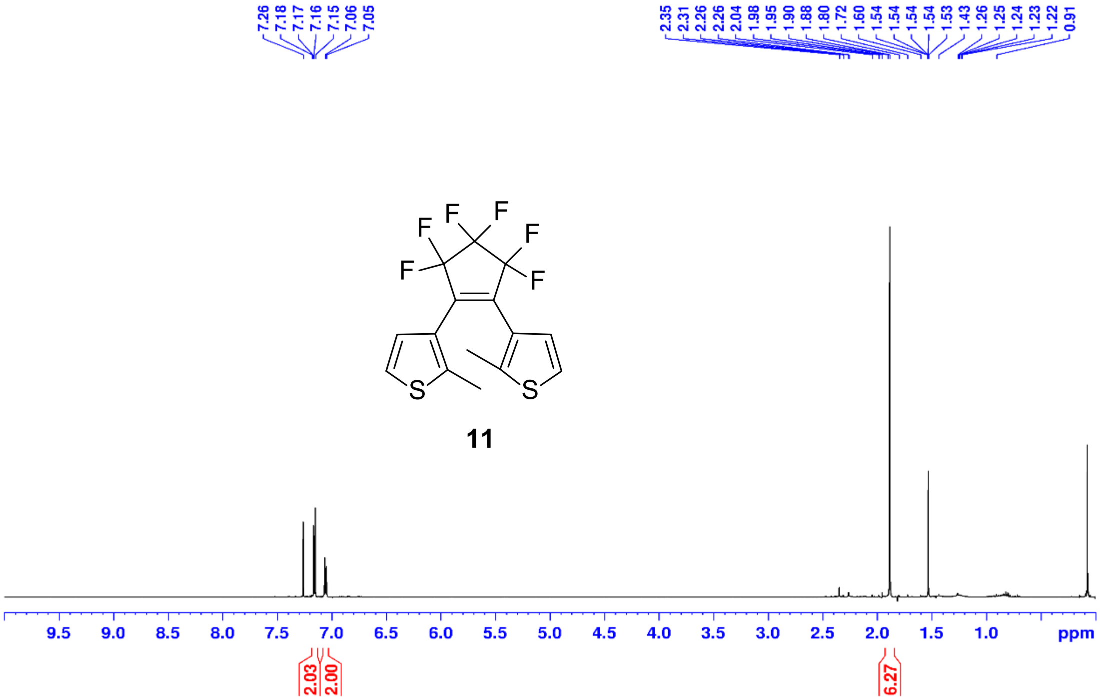
$^1H$ and $^{13}C$ NMR spectra of compound **8** in $CDCl_3$



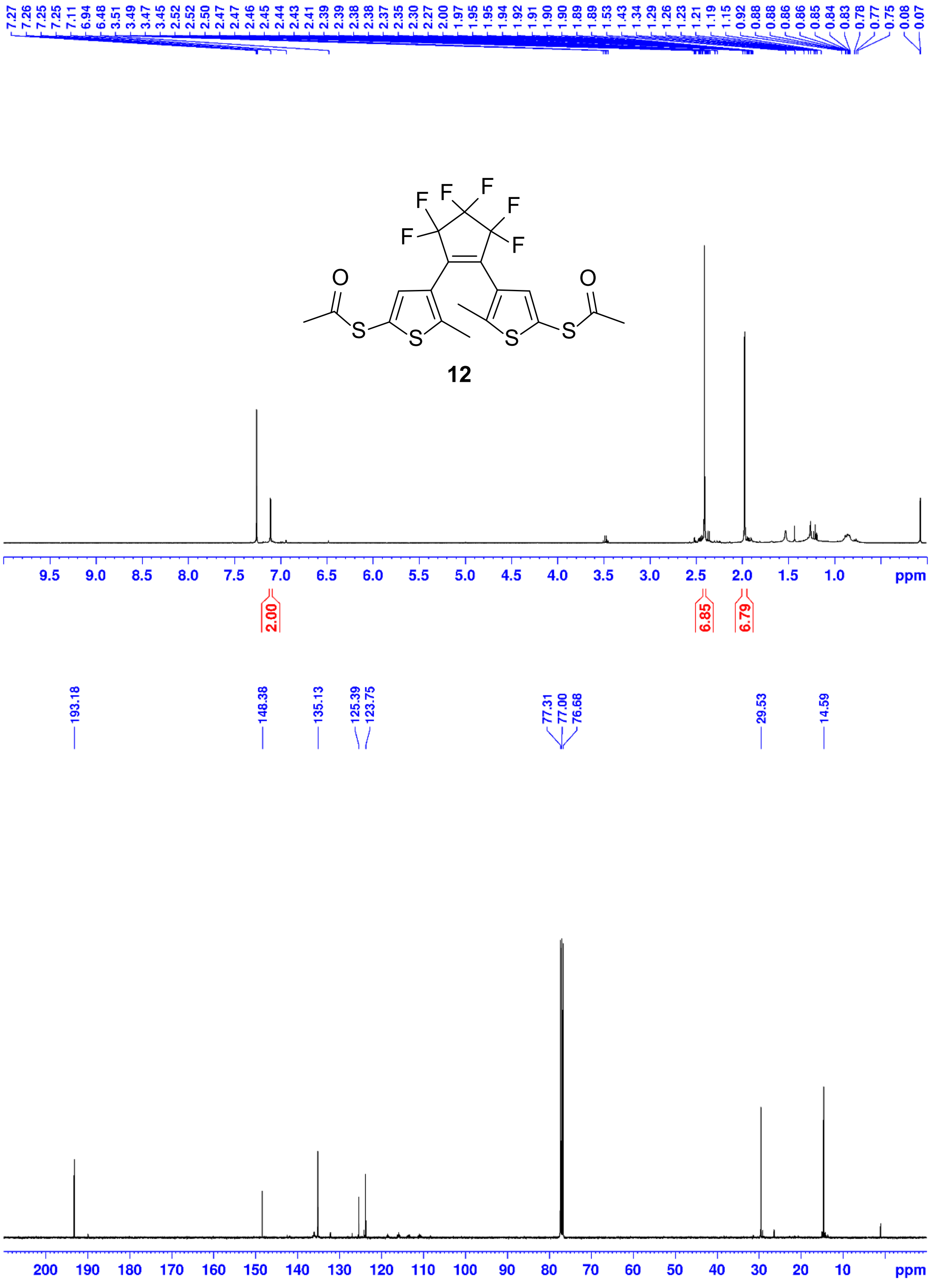
$^{1}$H and $^{13}$C NMR spectra of compound **9** in $CDCl_3$



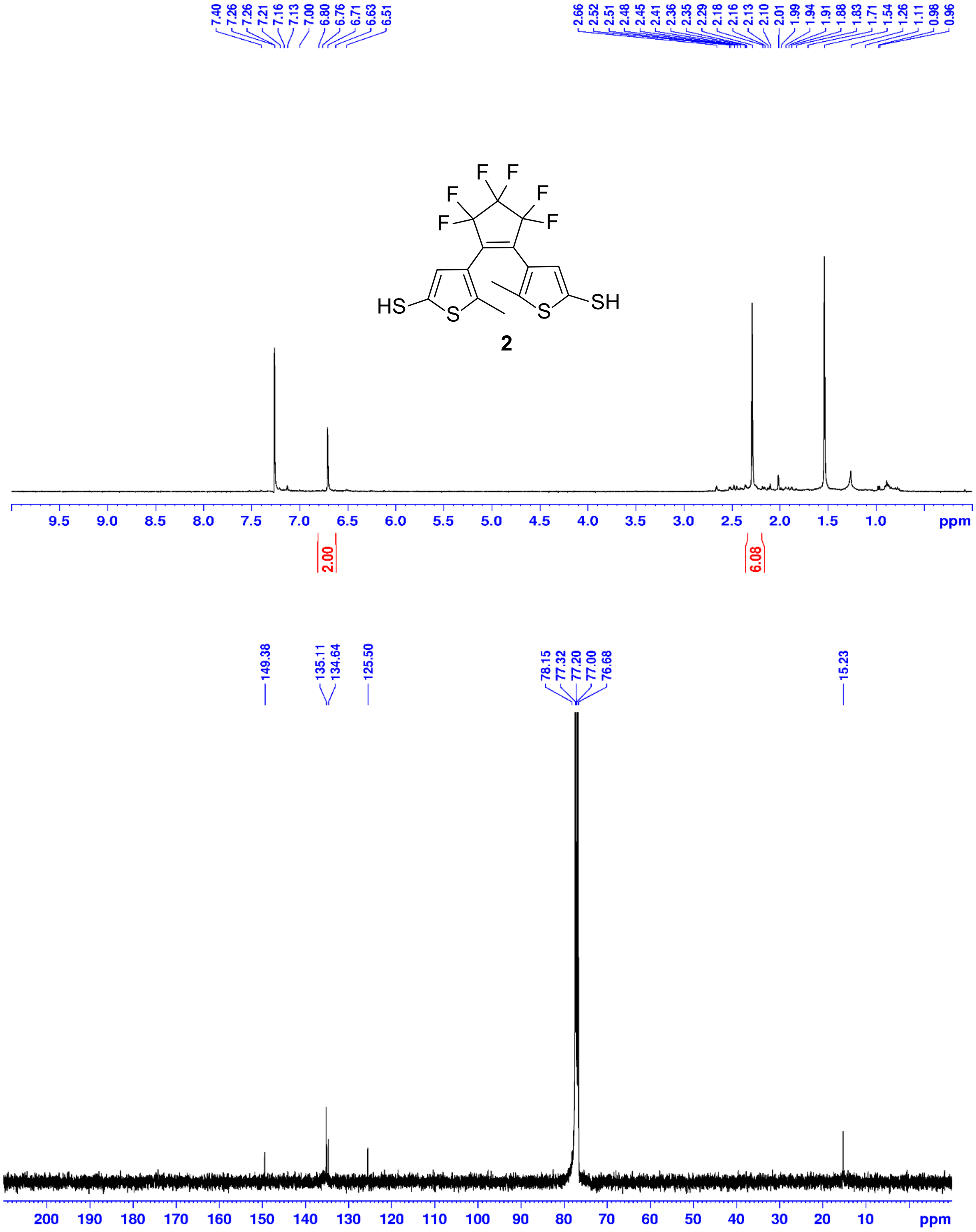
$^1$H and $^{13}$C NMR spectra of compound **1** in $CDCl_3$



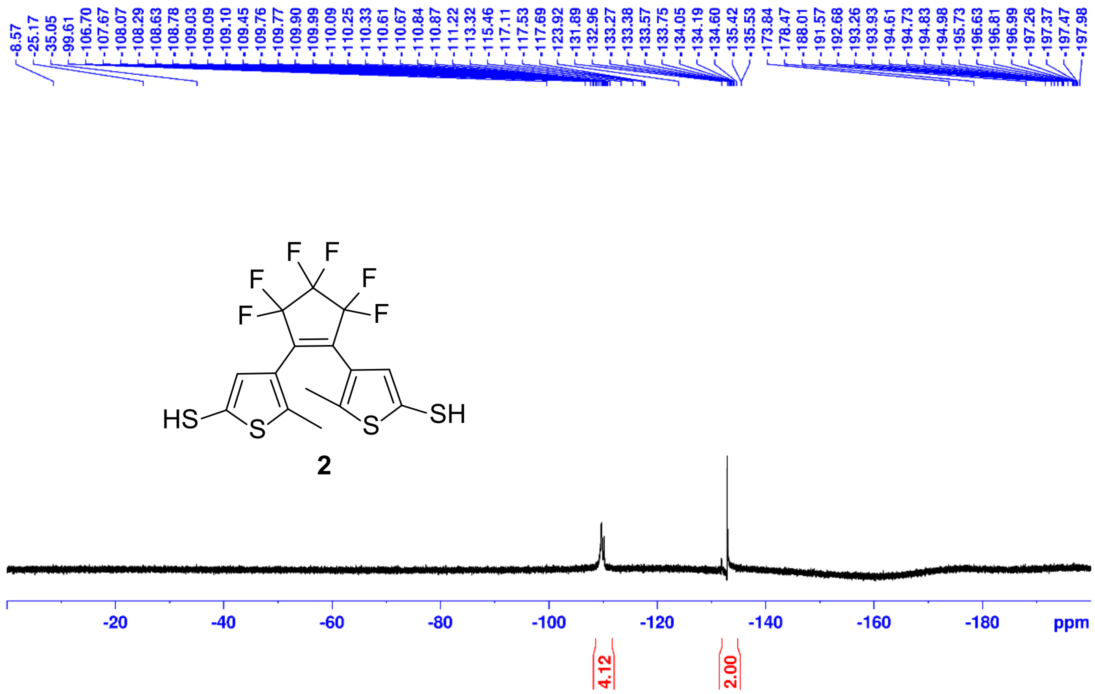
$^1$H spectra of compound **11** in $CDCl_3$



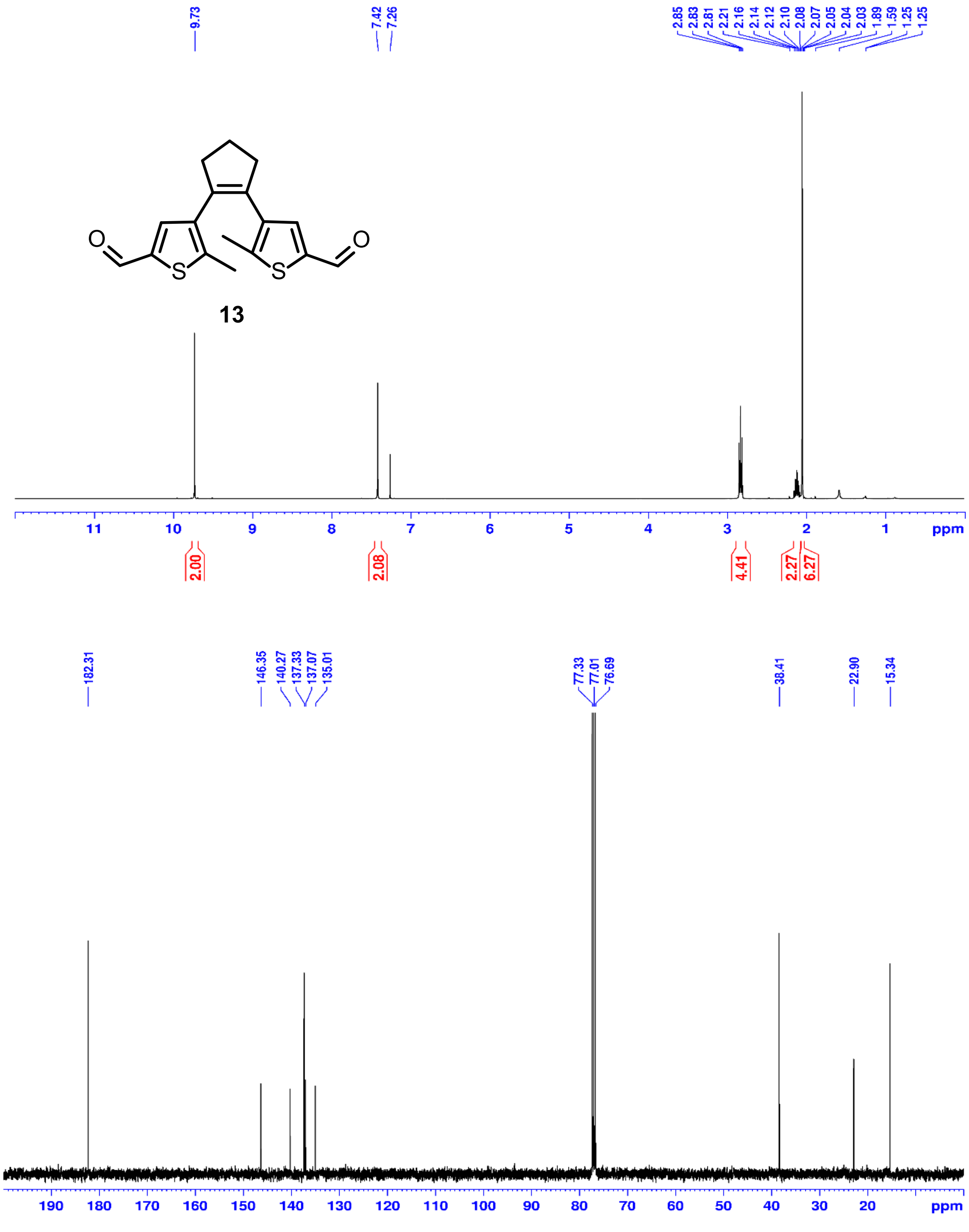
$^{1}$H and $^{13}$C NMR spectra of compound **12** in $CDCl_3$



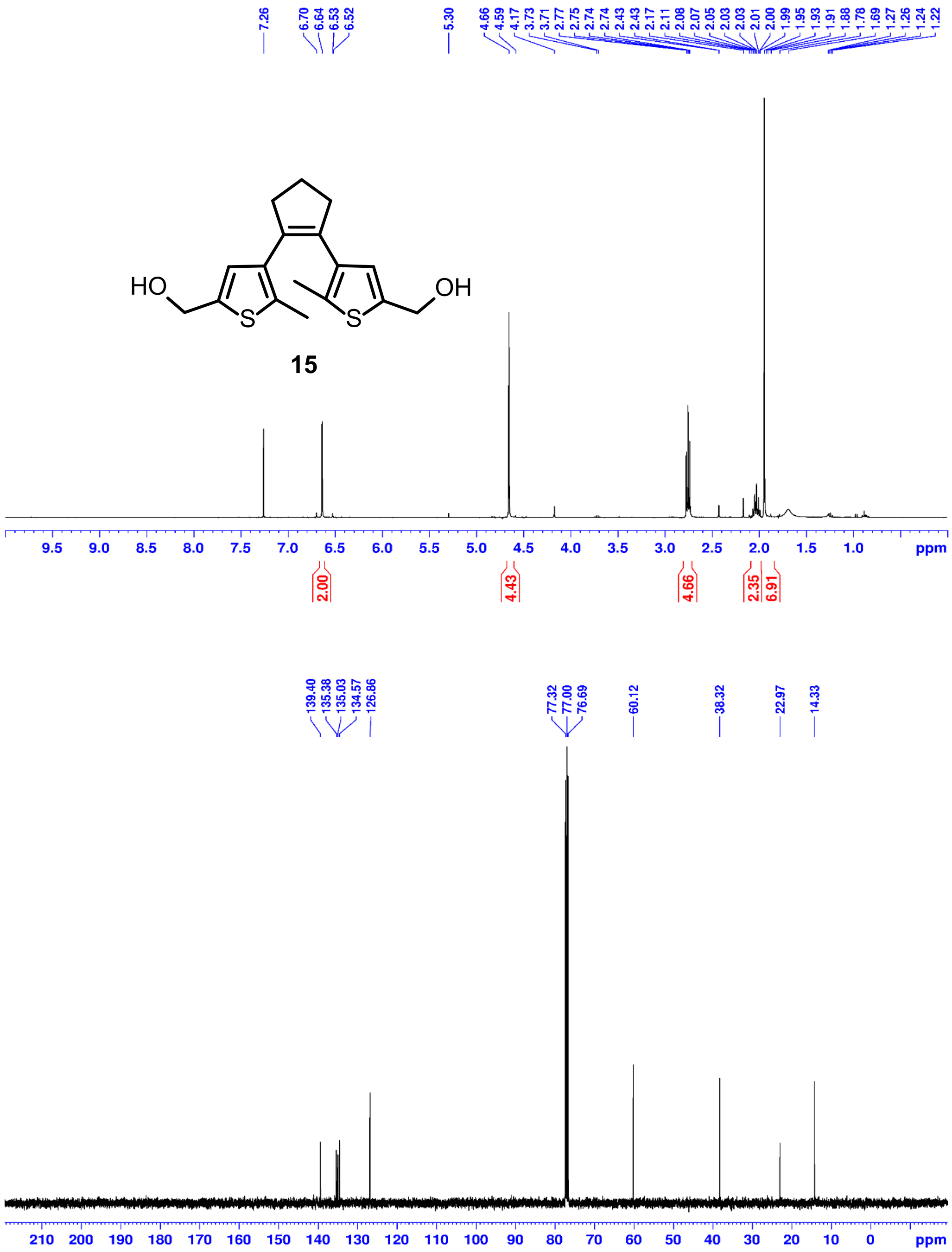
$^{1}$H and $^{13}$C NMR spectra of compound **2** in $CDCl_3$



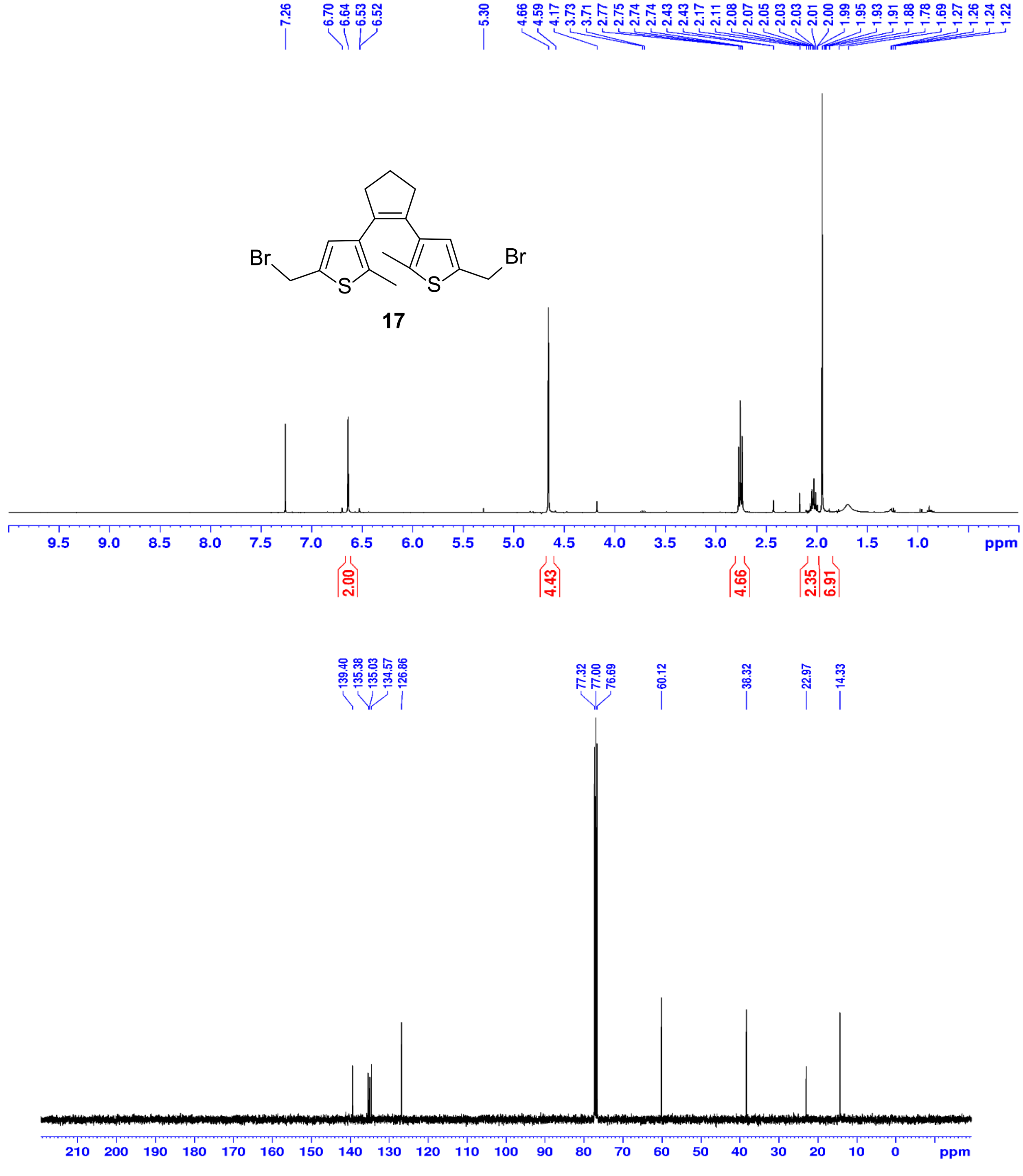
$^{19}$F NMR spectra (CDCl$_3$, 400MHz) compound **2**



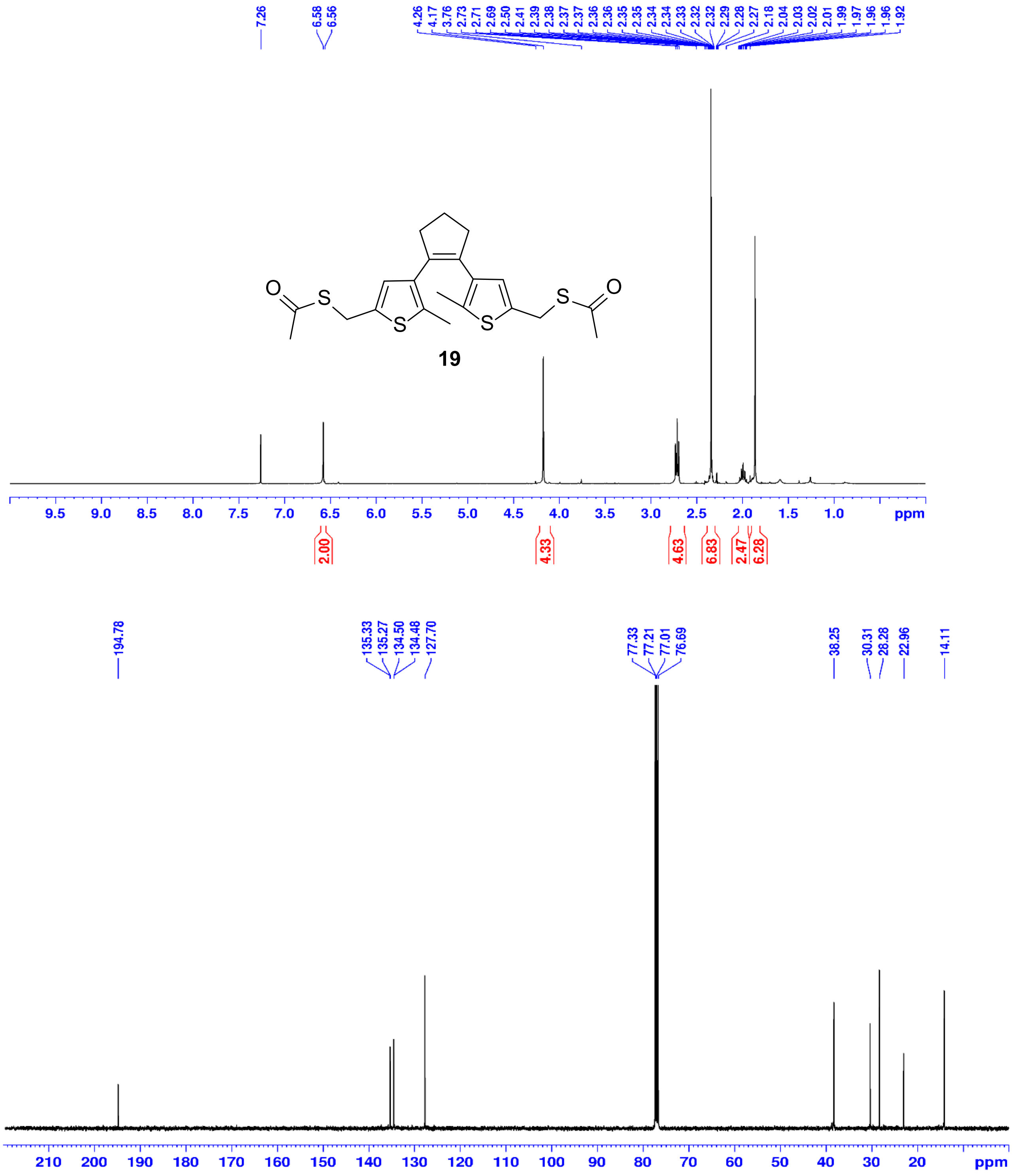
$^{1}$H and $^{13}$C NMR spectra of compound **13** in $CDCl_3$



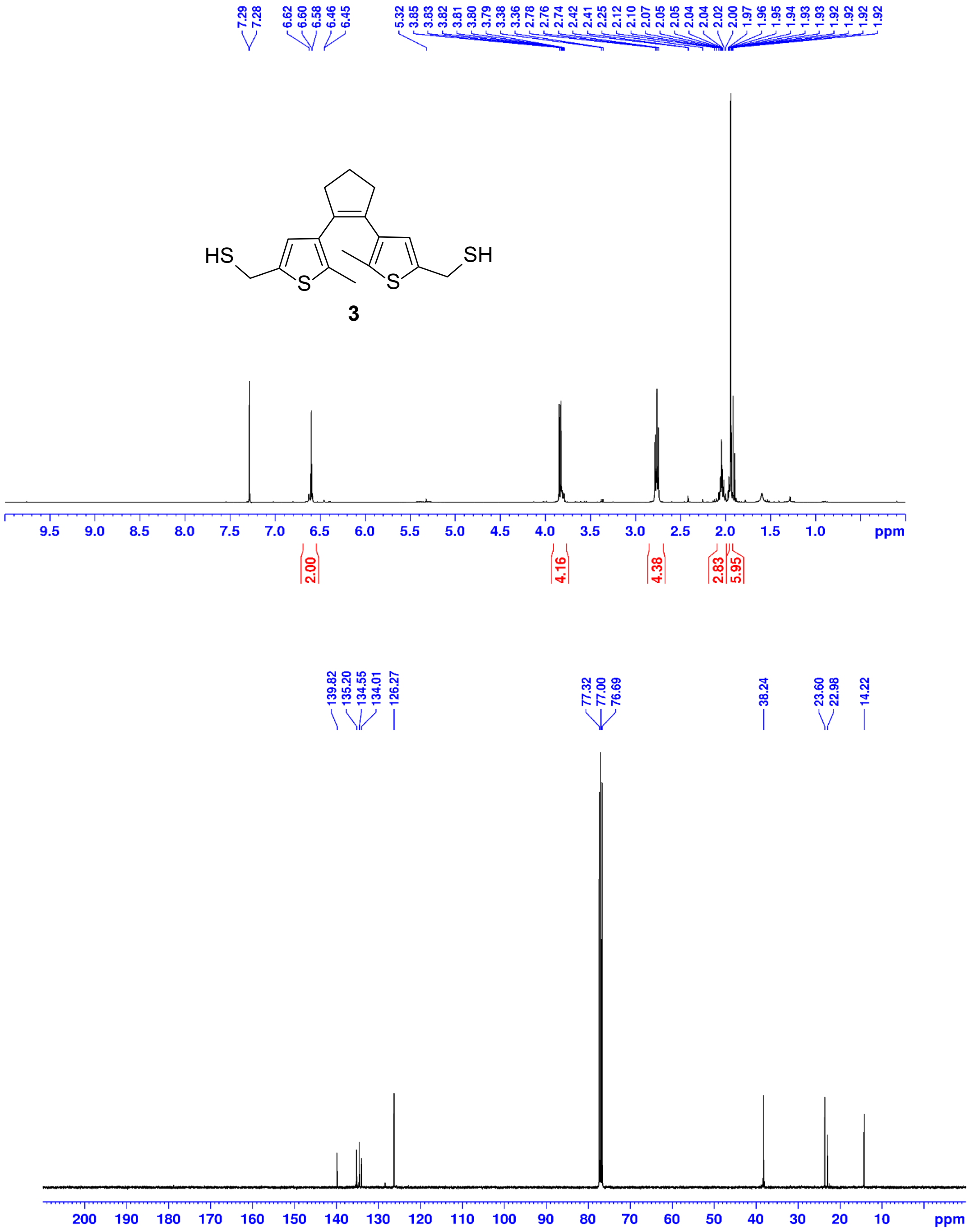
$^1$H and $^{13}$C NMR spectra of compound **15** in CDCl$_3$



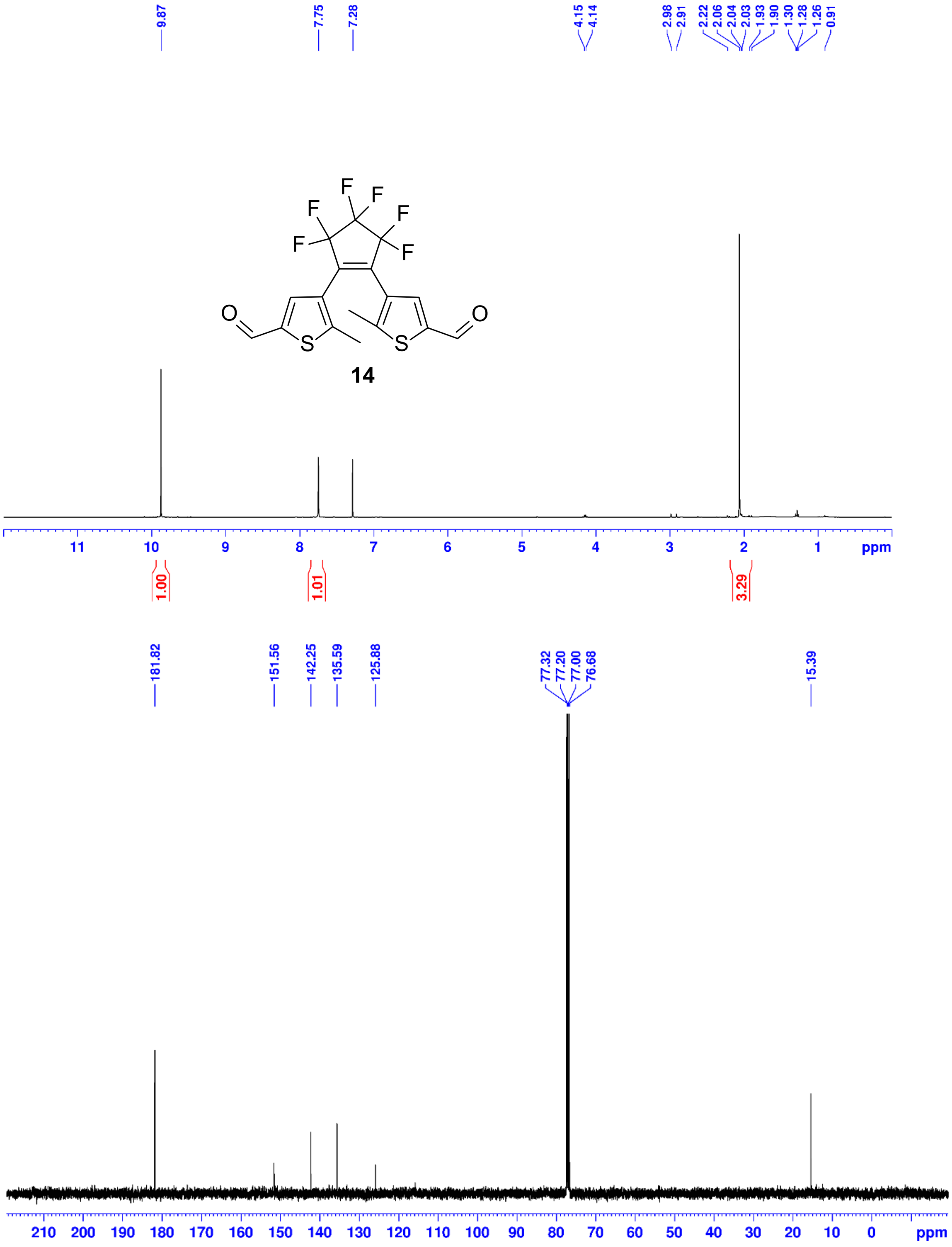
$^1$H and $^{13}$C NMR spectra of compound **17** in $CDCl_3$



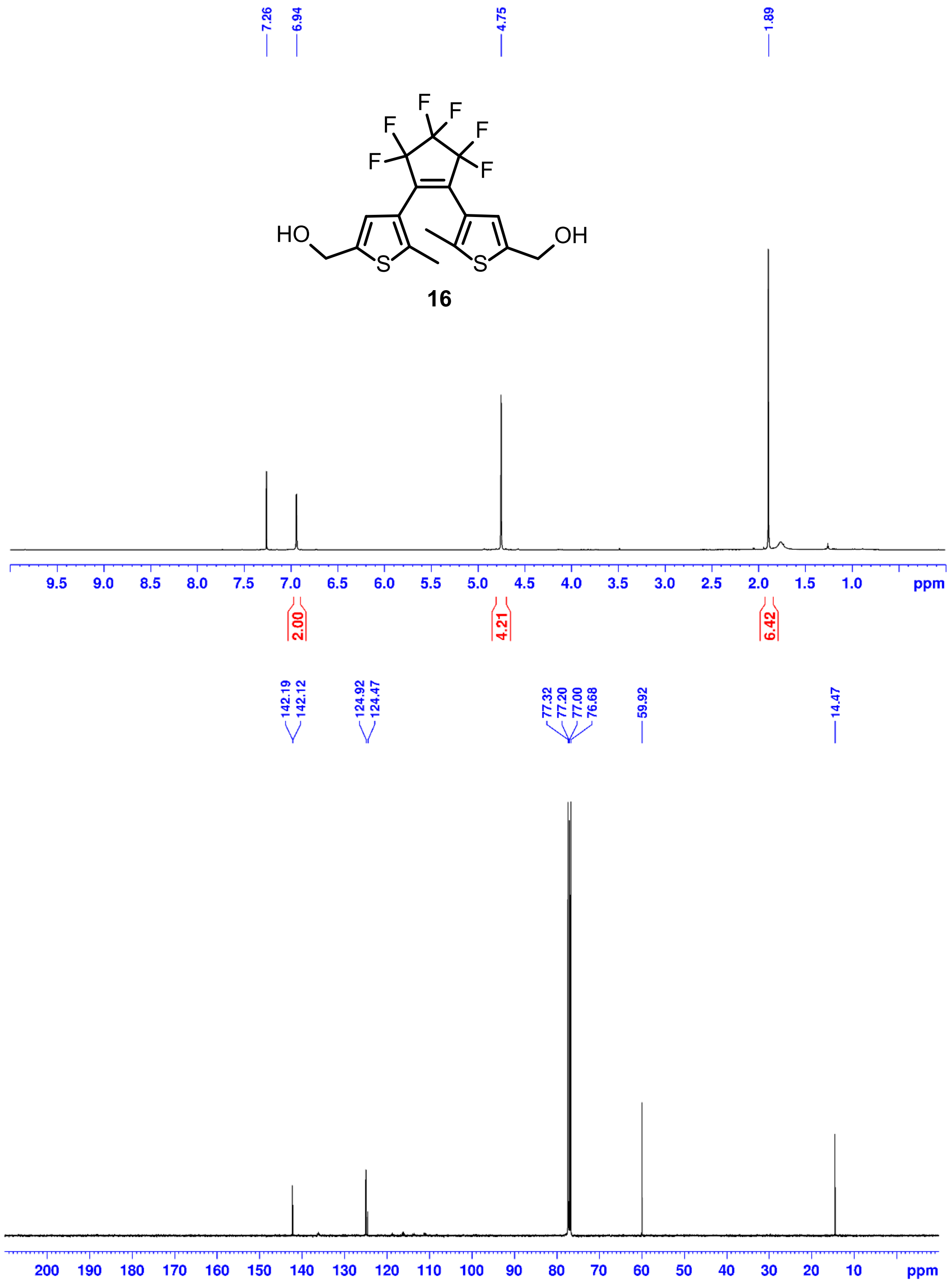
$^{1}H$ and $^{13}C$ NMR spectra of compound **19** in $CDCl_3$



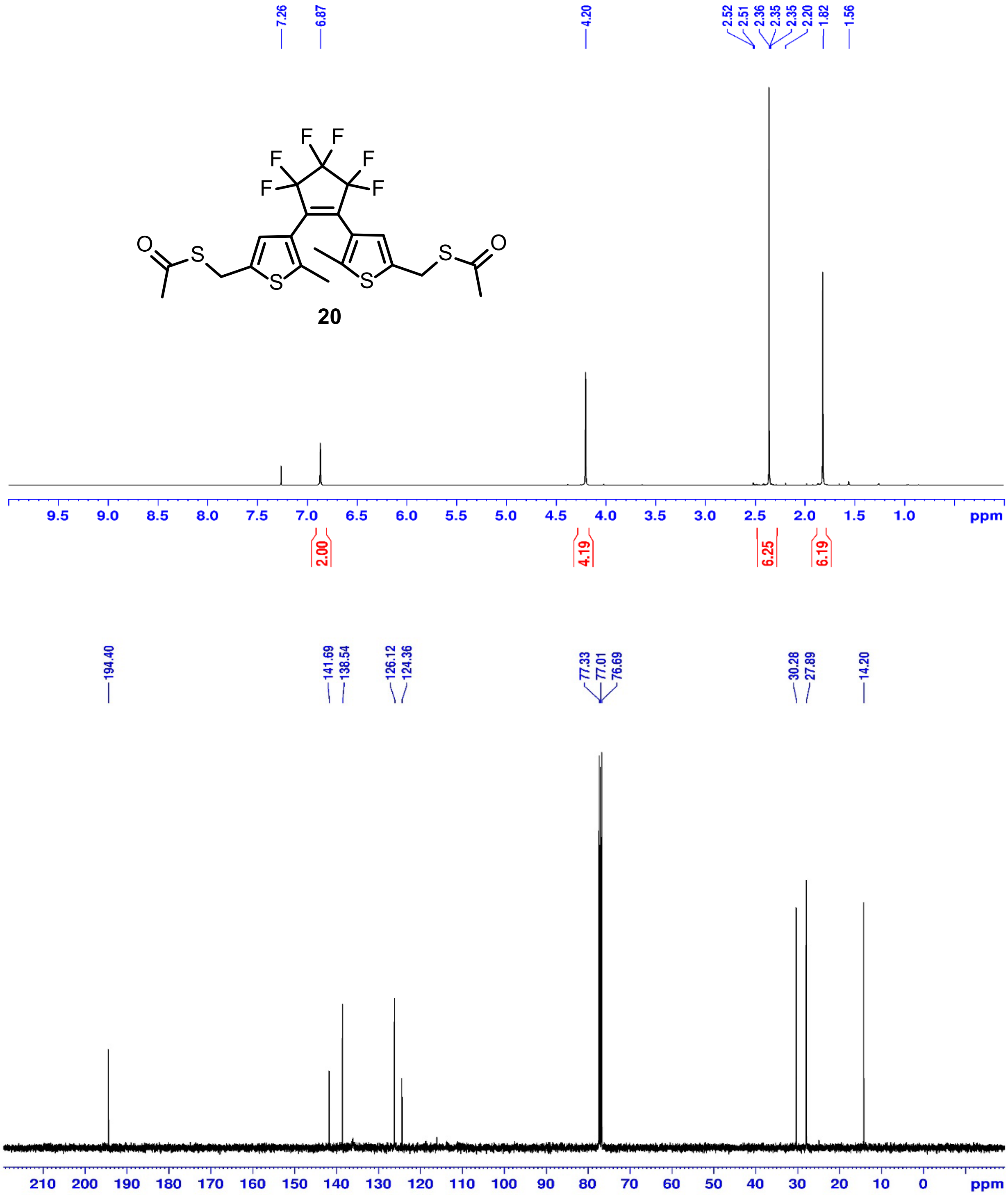
$^1$H and $^{13}$C NMR spectra of compound **3** in $CDCl_3$



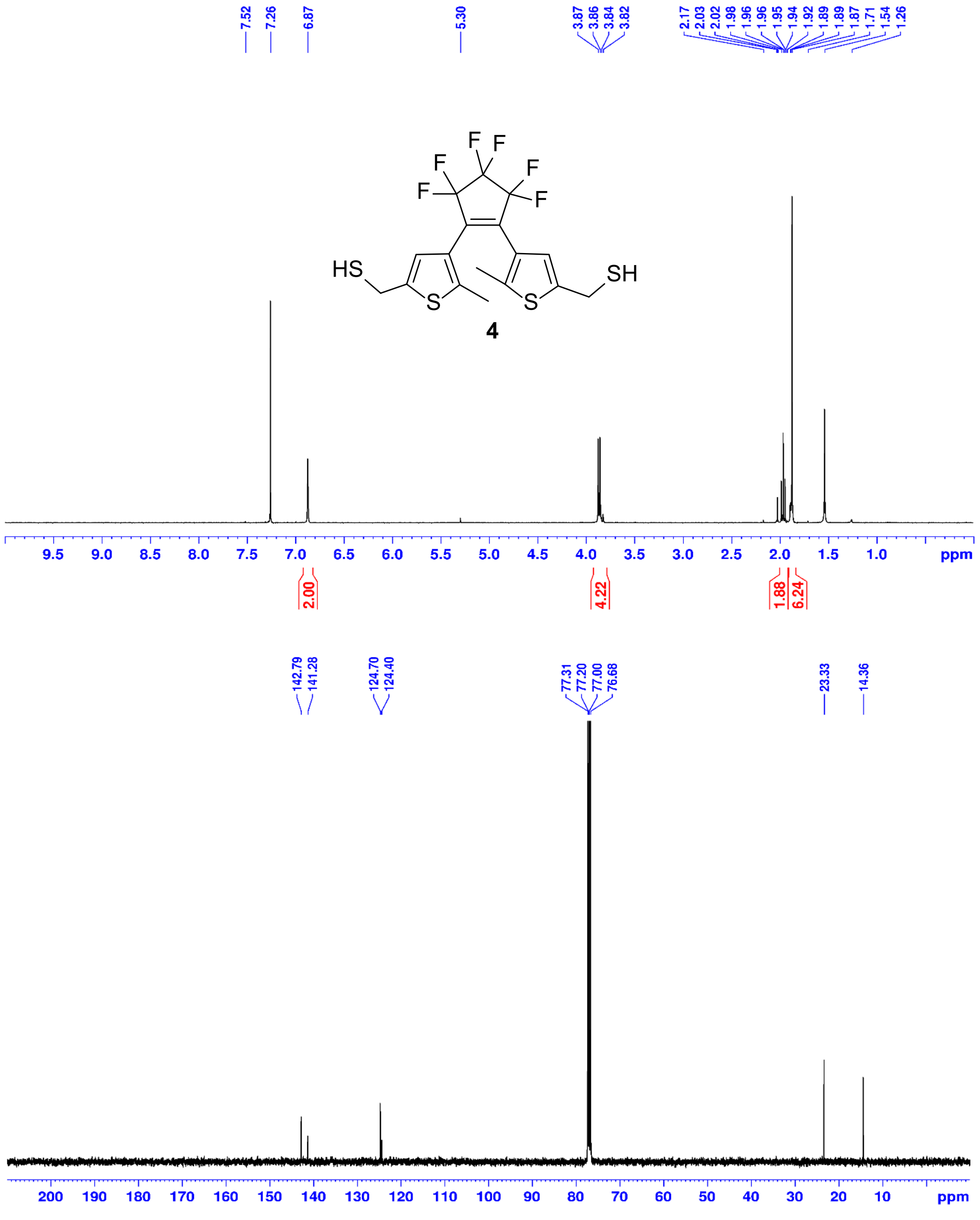
$^{1}$H and $^{13}$C NMR spectra of compound **14** in $CDCl_3$



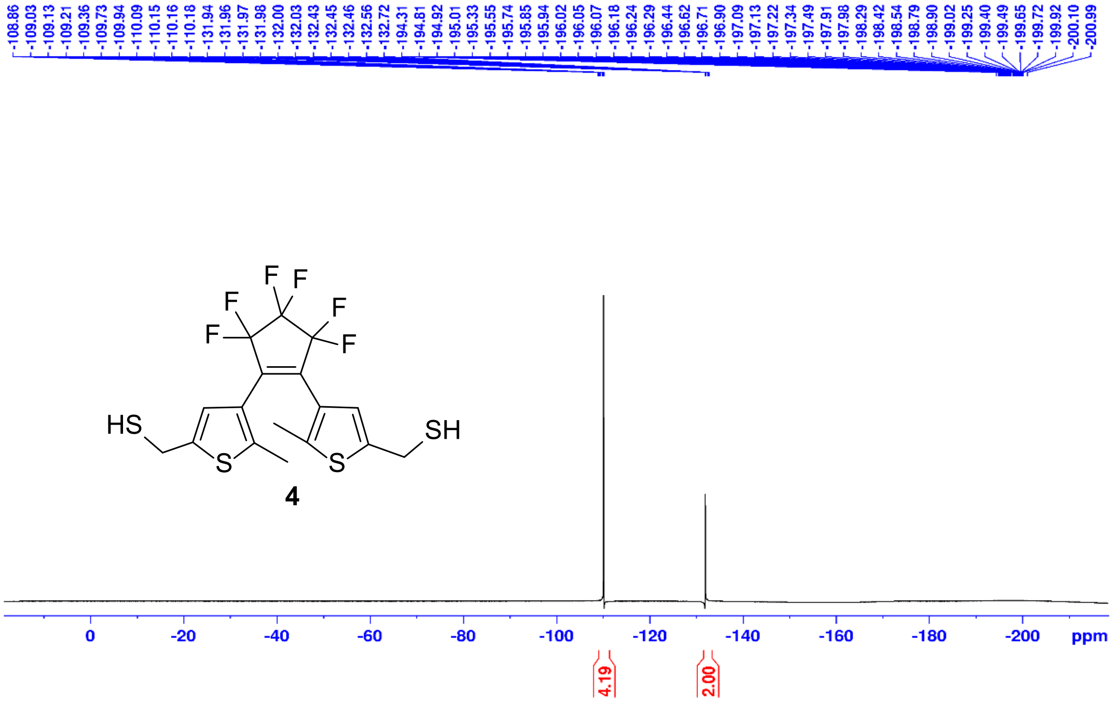
$^1$H and $^{13}$C NMR spectra of compound **16** in $CDCl_3$



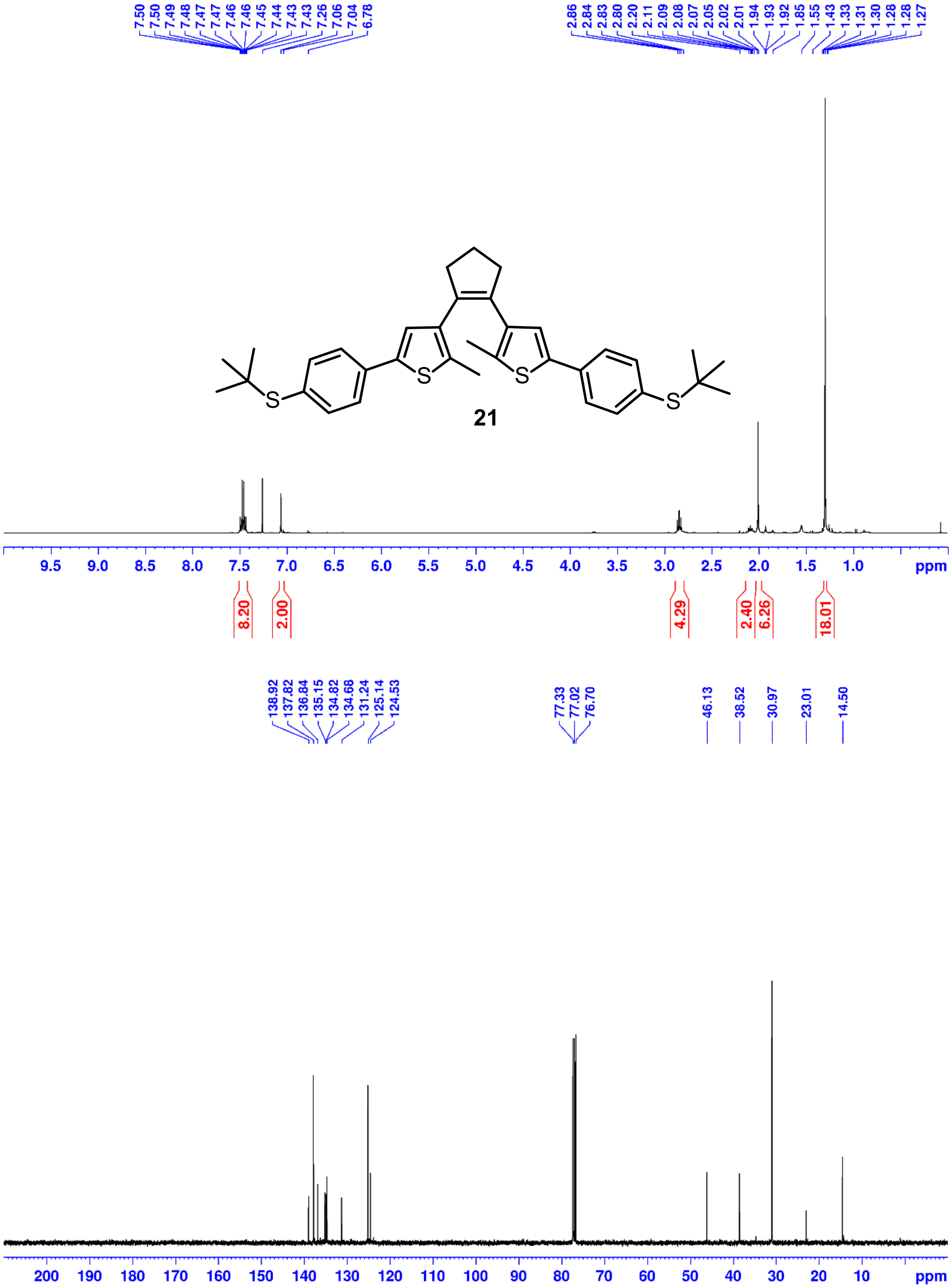
$^1$H and $^{13}$C NMR spectra of compound **20** in $CDCl_3$



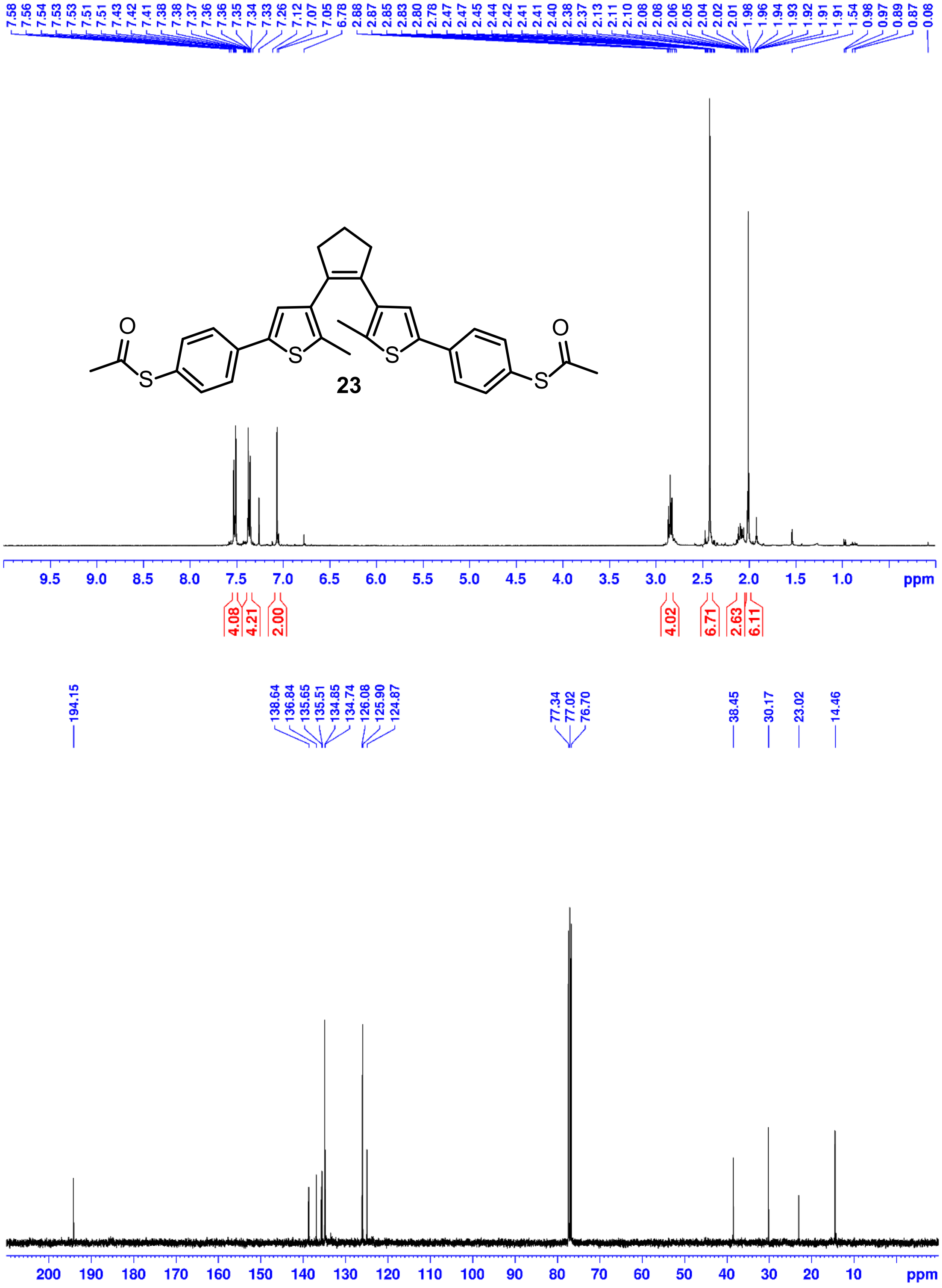
$^1$H and $^{13}$C NMR spectra of compound **4** in $CDCl_3$



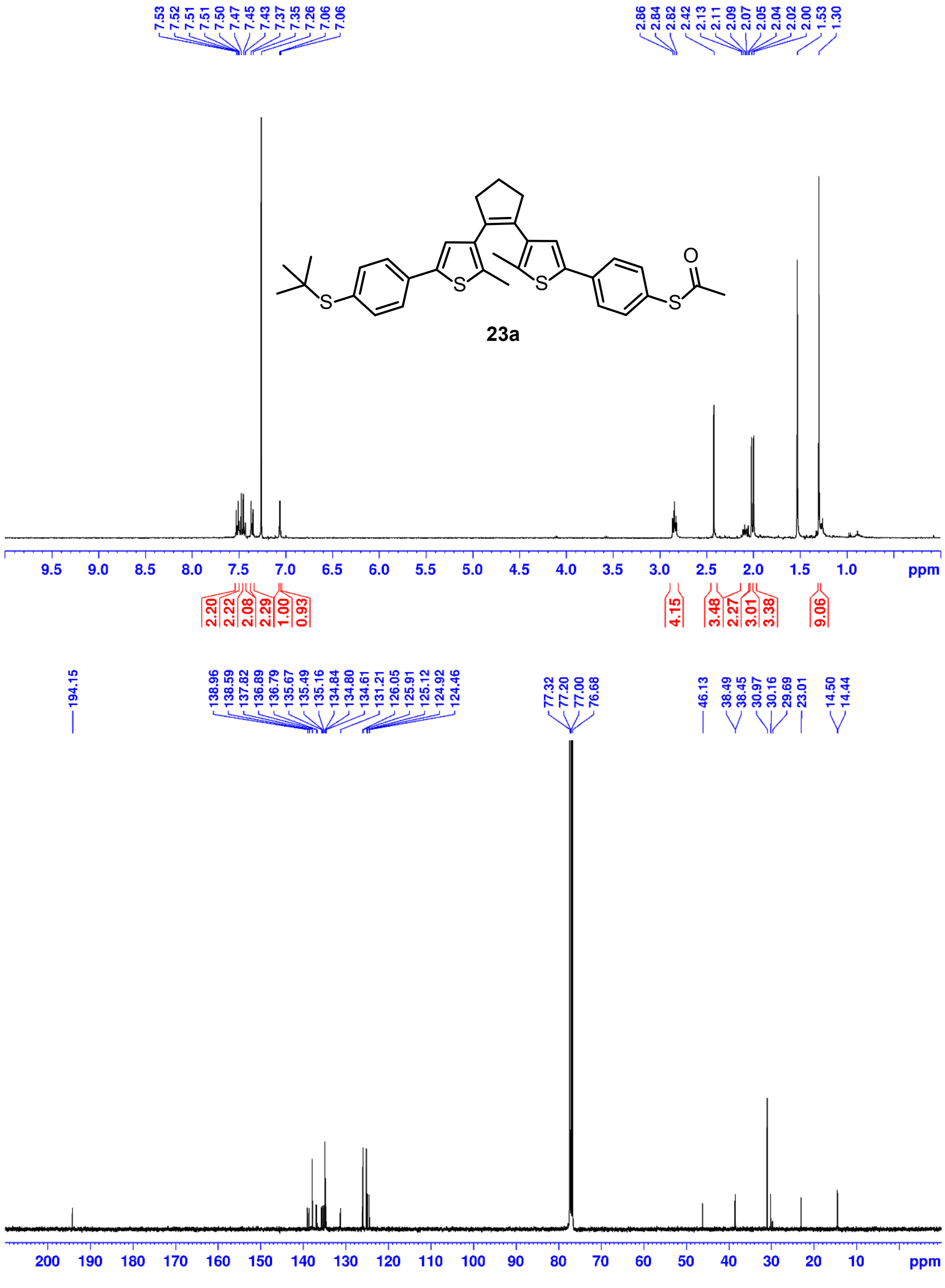
$^{19}$F NMR spectra (CDCl3, 400MHz) compound **4**



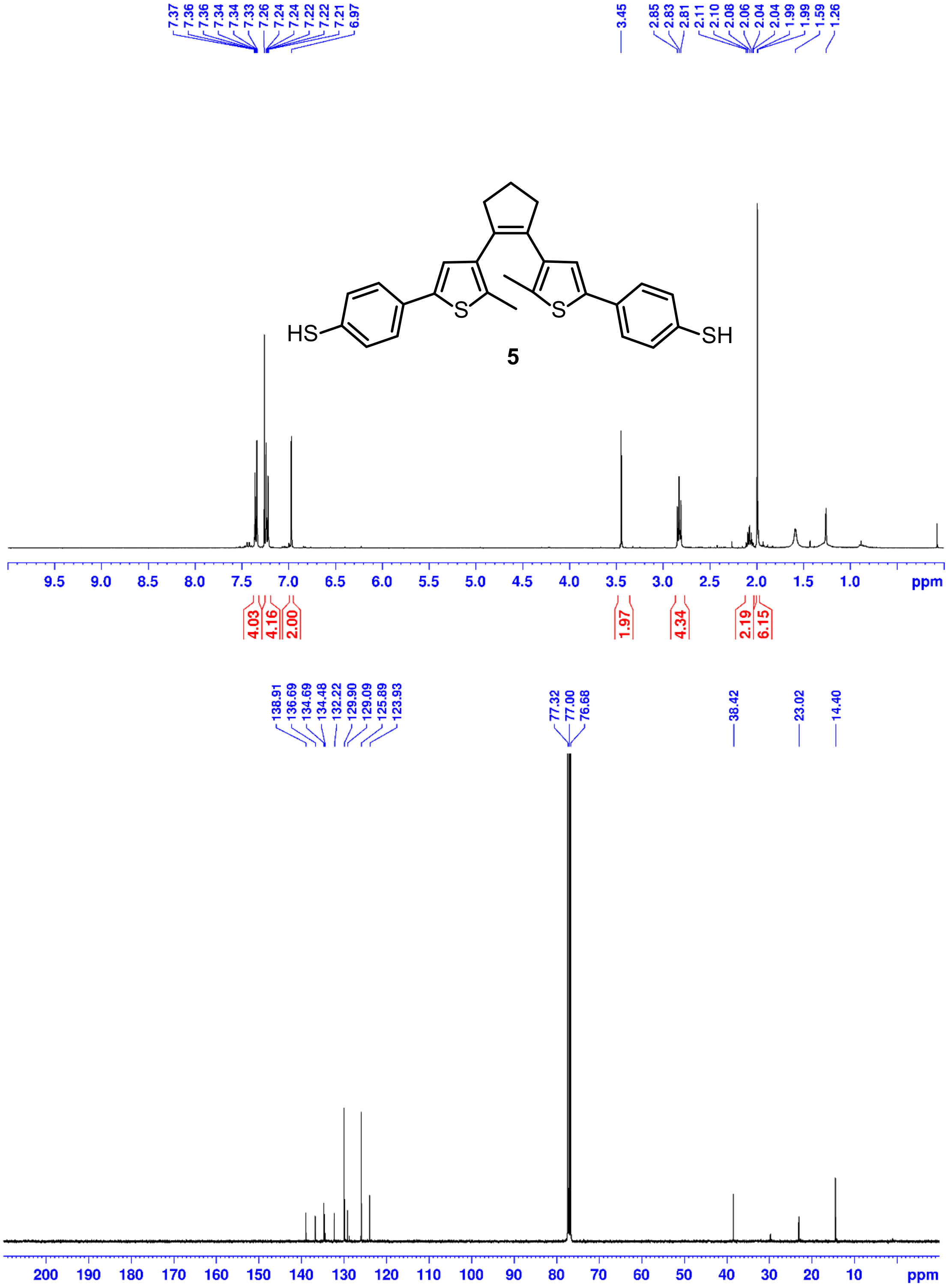
$^1H$ and $^{13}C$ NMR spectra of compound **21** in $CDCl_3$



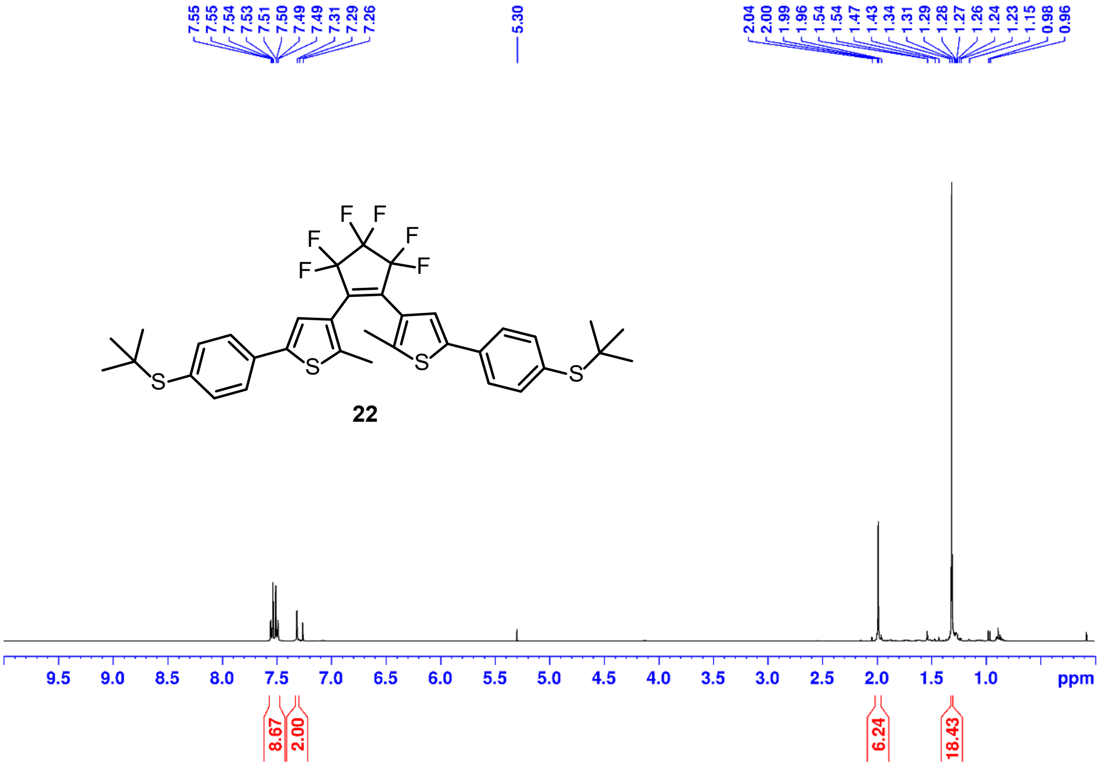
$^{1}$H and $^{13}$C NMR spectra of compound **23** in $CDCl_3$



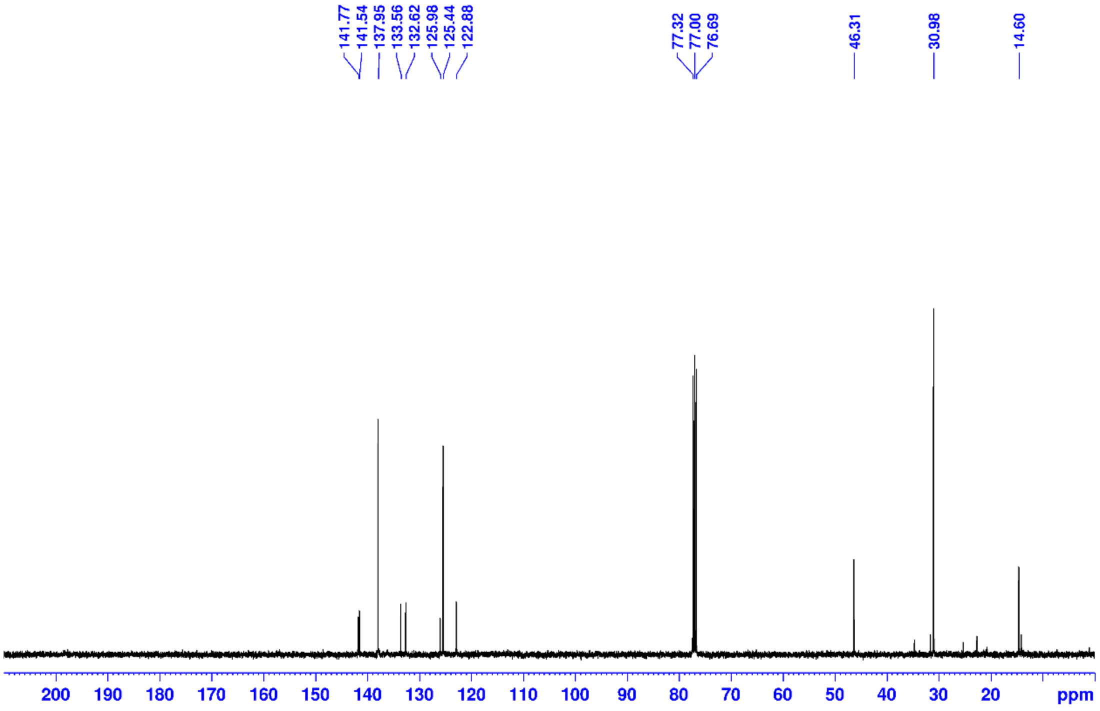
$^{1}$H and $^{13}$C NMR spectra of compound **23a** (mono acetate) in $CDCl_3$



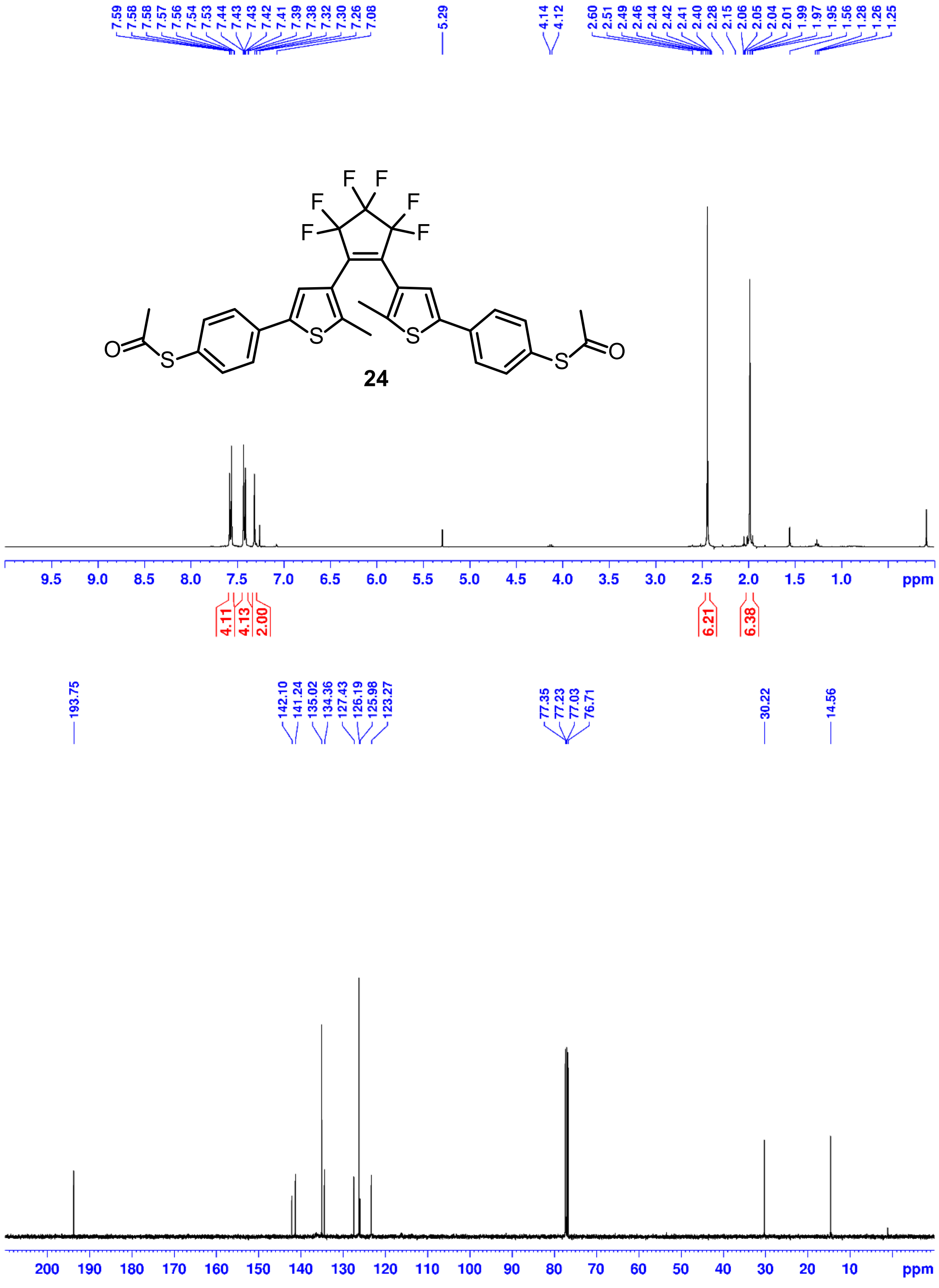
$^{1}$H and $^{13}$C NMR spectra of compound **5** in $CDCl_3$



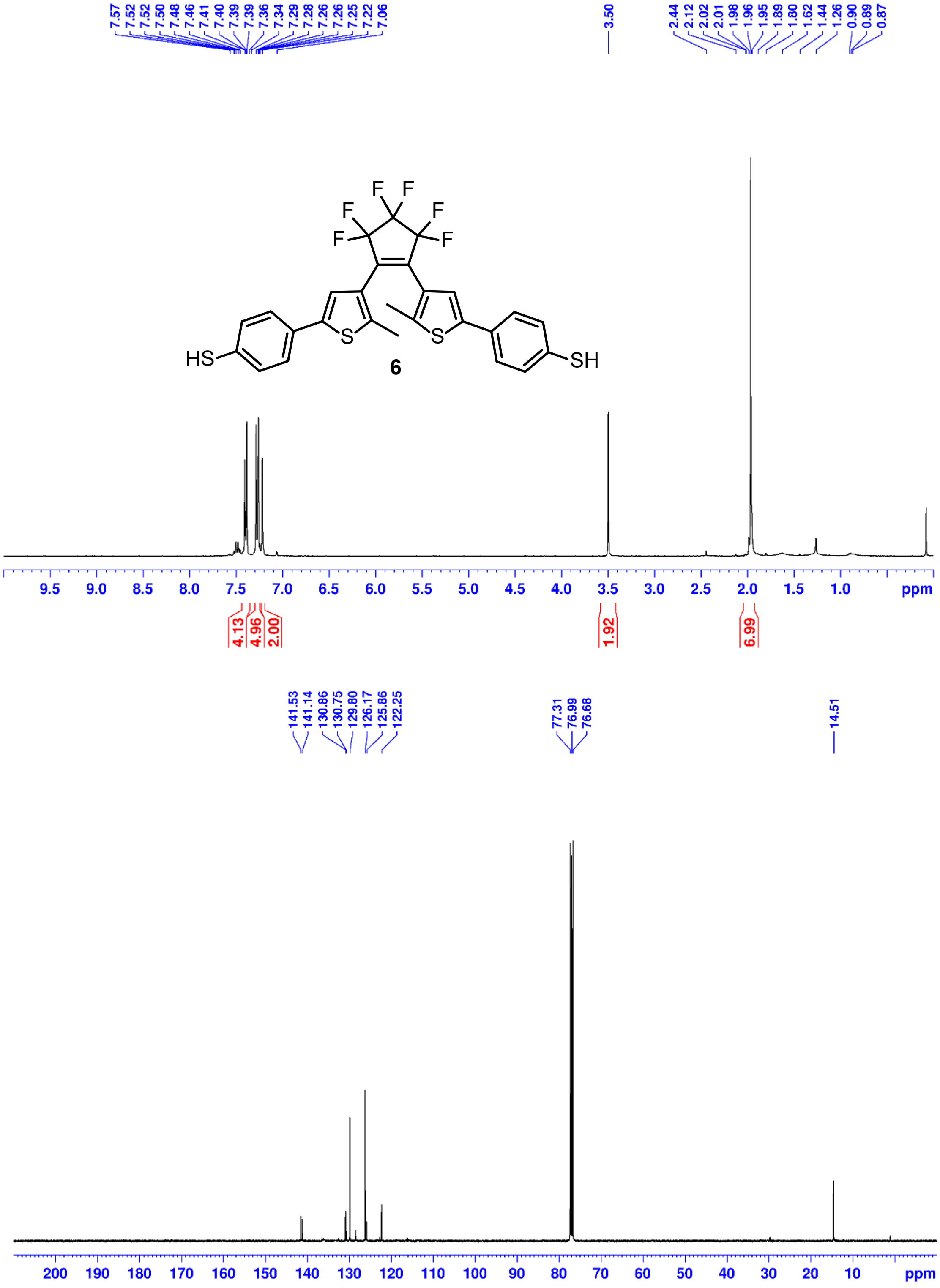
**22**



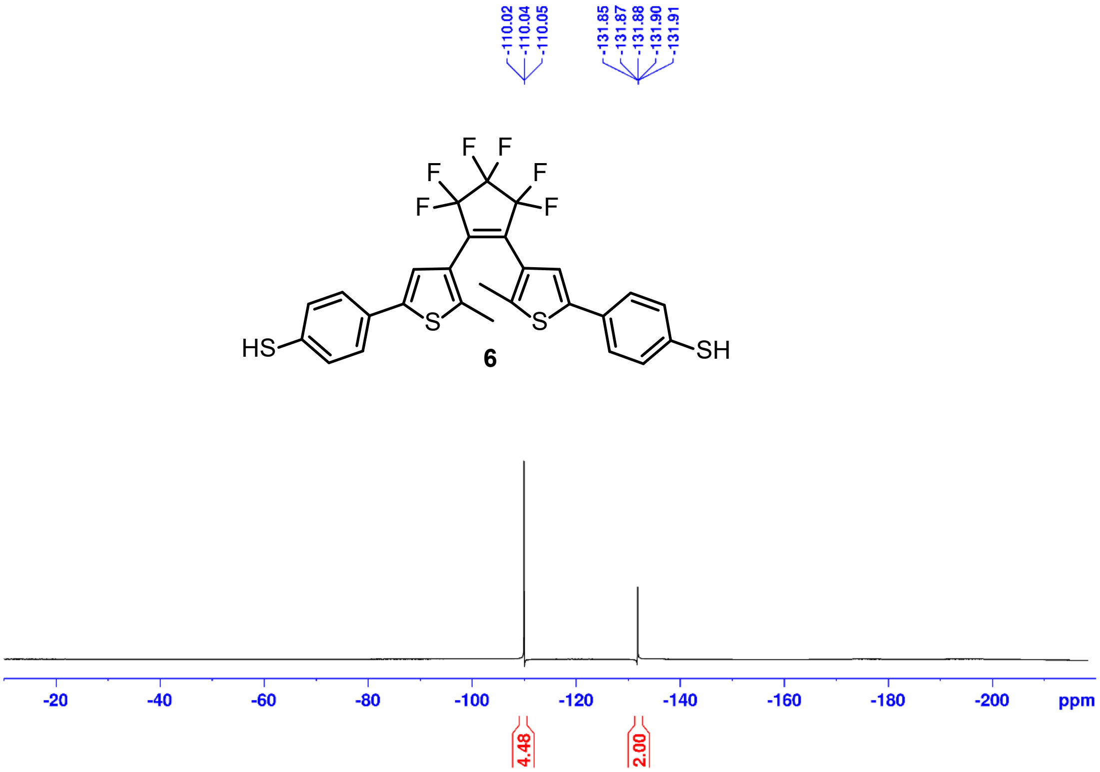
$^1$H and $^{13}$C NMR spectra of compound **22** in $CDCl_3$



$^1$H and $^{13}$C NMR spectra of compound **24** in $CDCl_3$

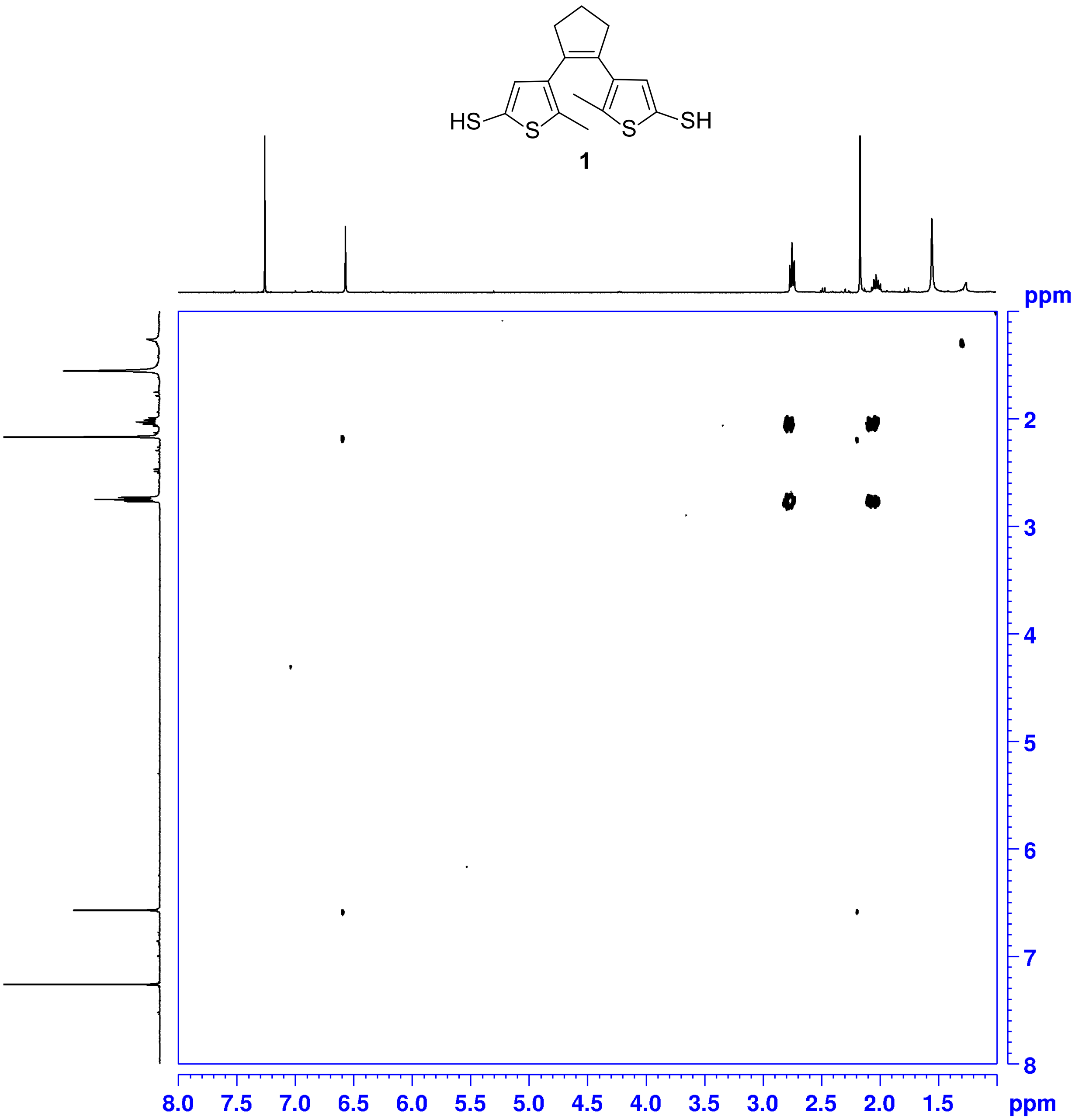


$^1$H and $^{13}$C NMR spectra of compound **6** in $CDCl_3$

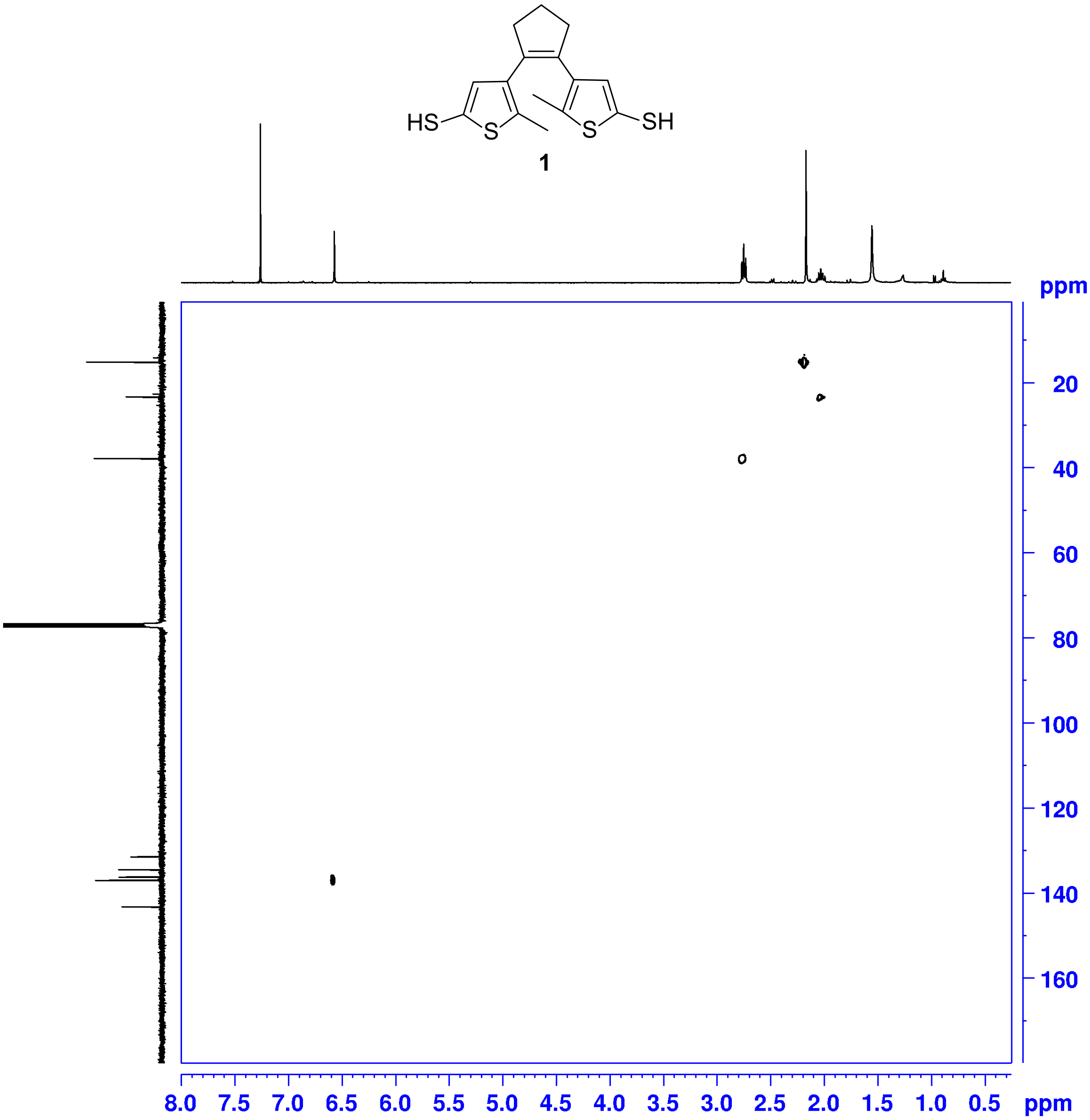


$^{19}$F NMR spectra of compound **6** in $CDCl_3$

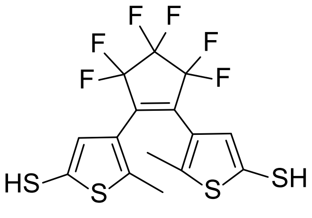
## 2. 2D NMR spectra of compounds **1-3, 19**



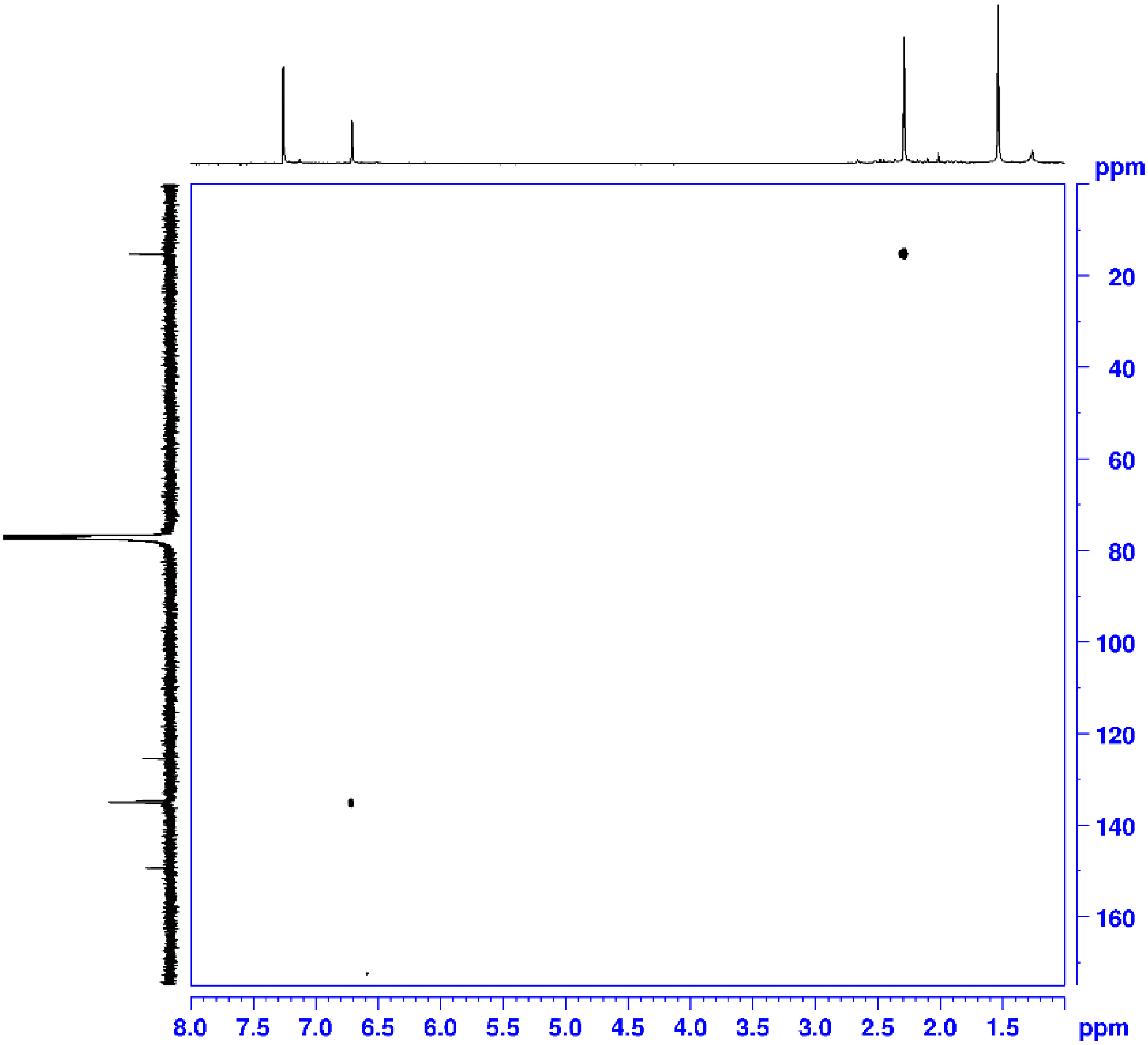
2D COSY NMR spectra ($CDCl_3$, 400MHz) compound **1**



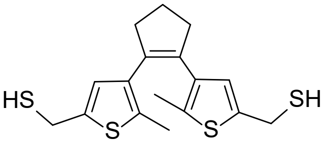
2D HSQC NMR spectra (CDCl$_3$, 400MHz) compound **1**



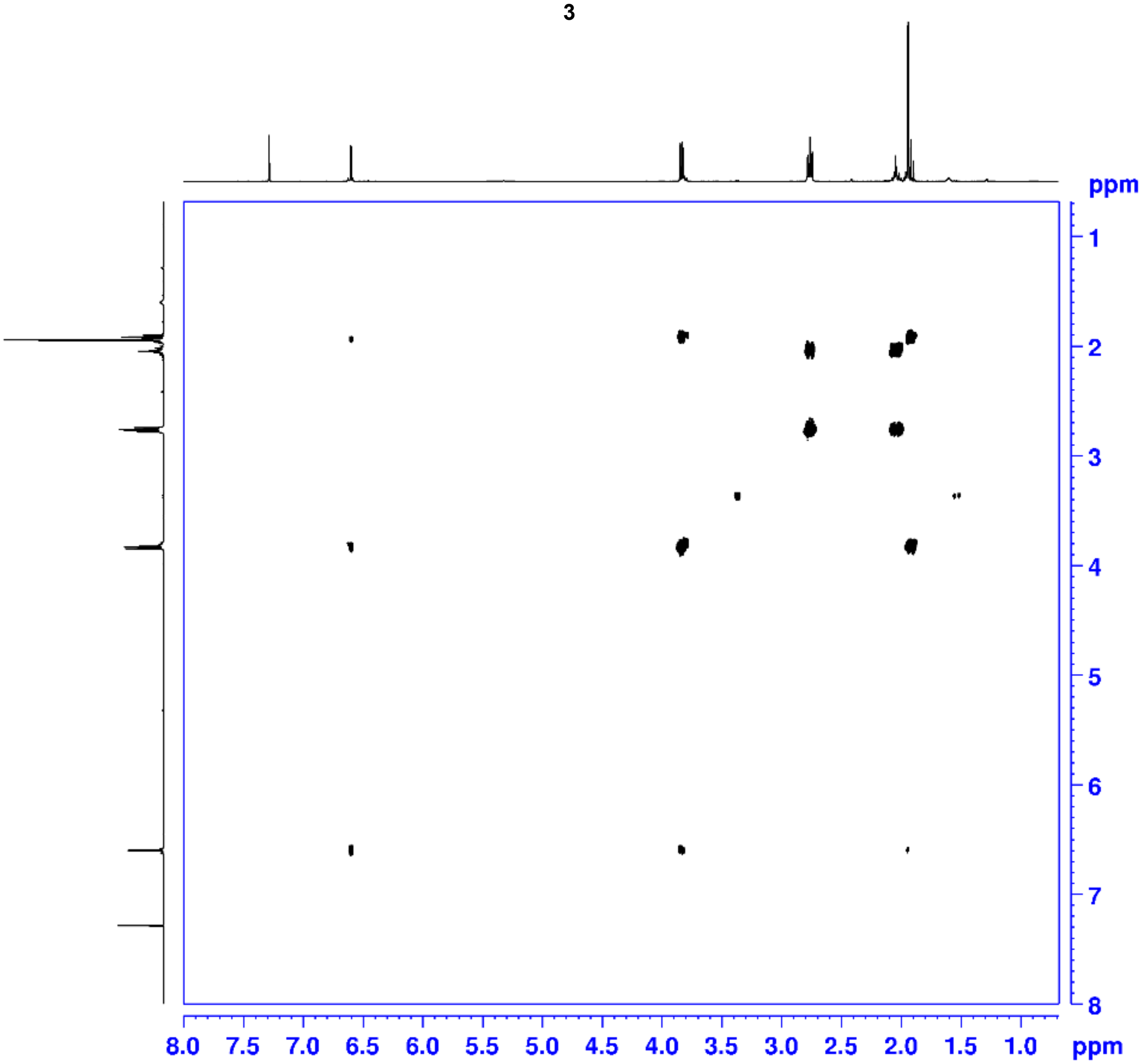
**2**



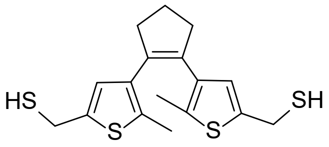
2D HSQC NMR spectra (CDCl$_3$, 400MHz) compound **2**



**3**



2D COSY NMR spectra ($CDCl_3$, 400MHz) compound **3**



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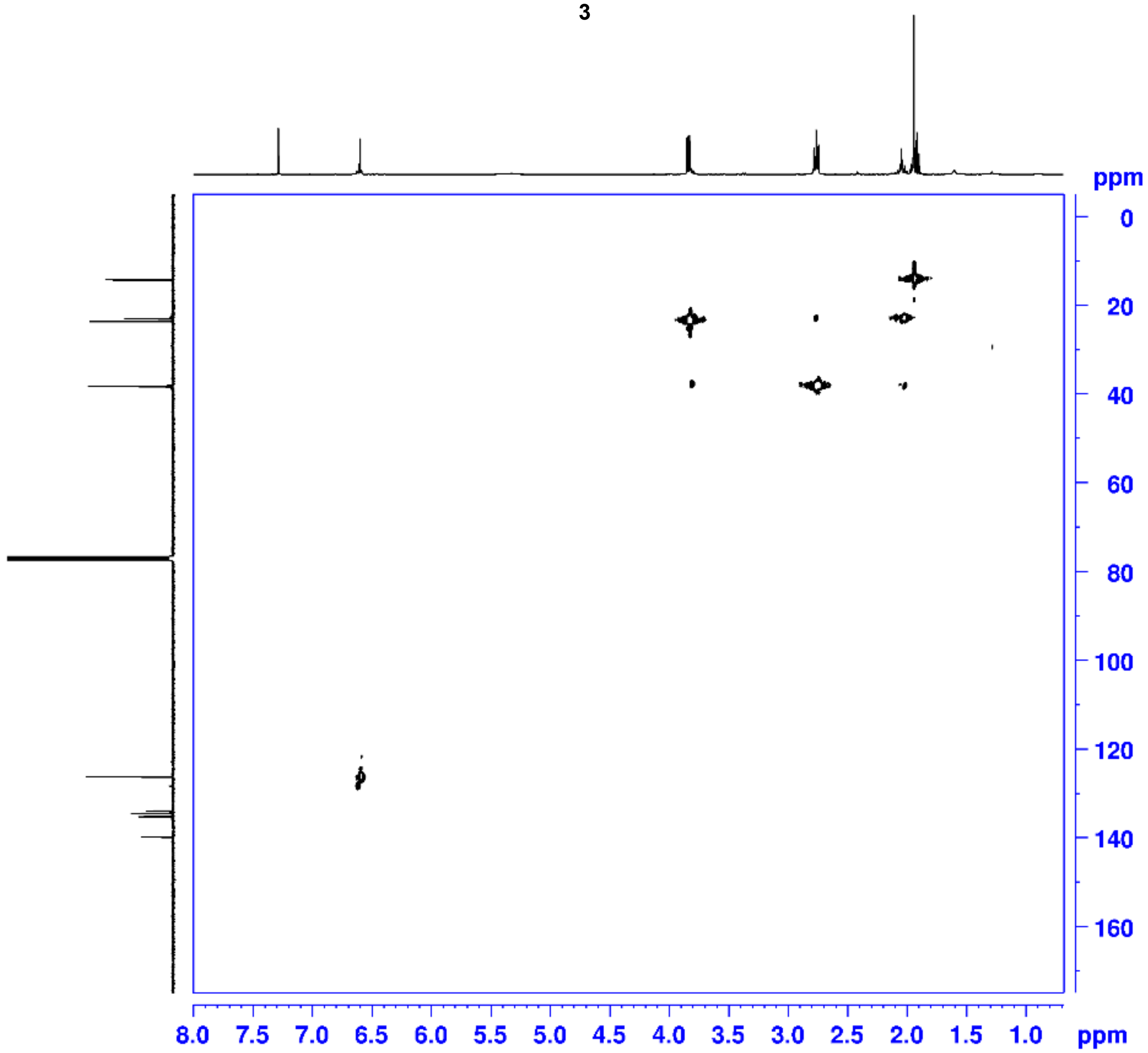
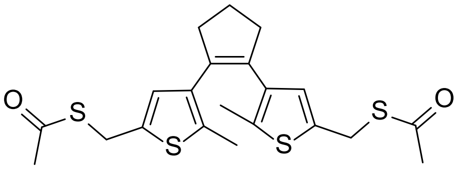
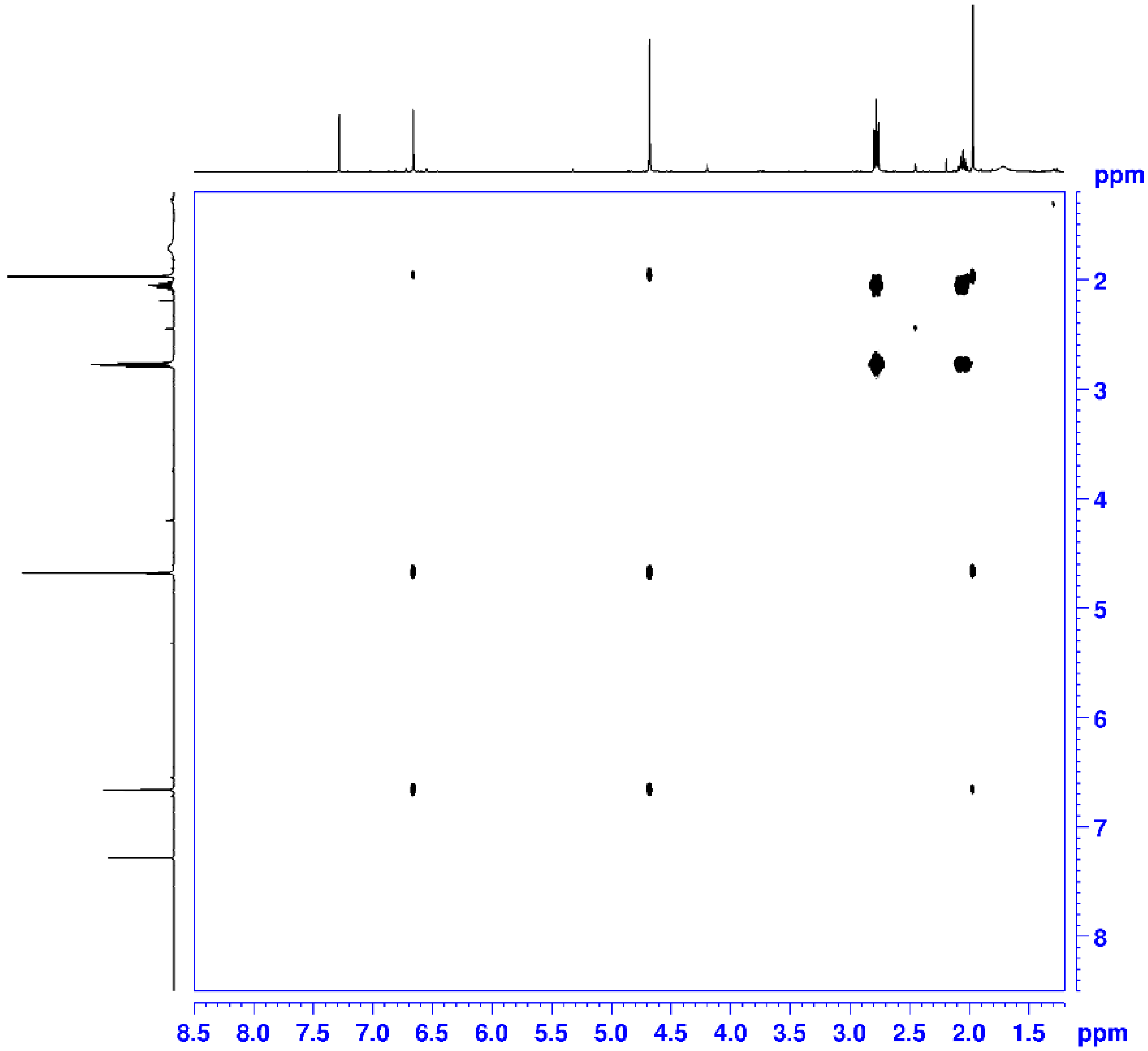


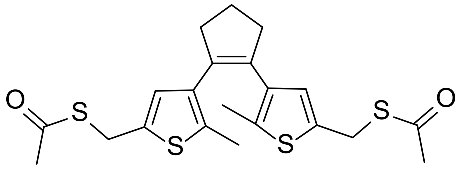
2D HSQC NMR spectra ($CDCl_3$, 400MHz) compound **3**



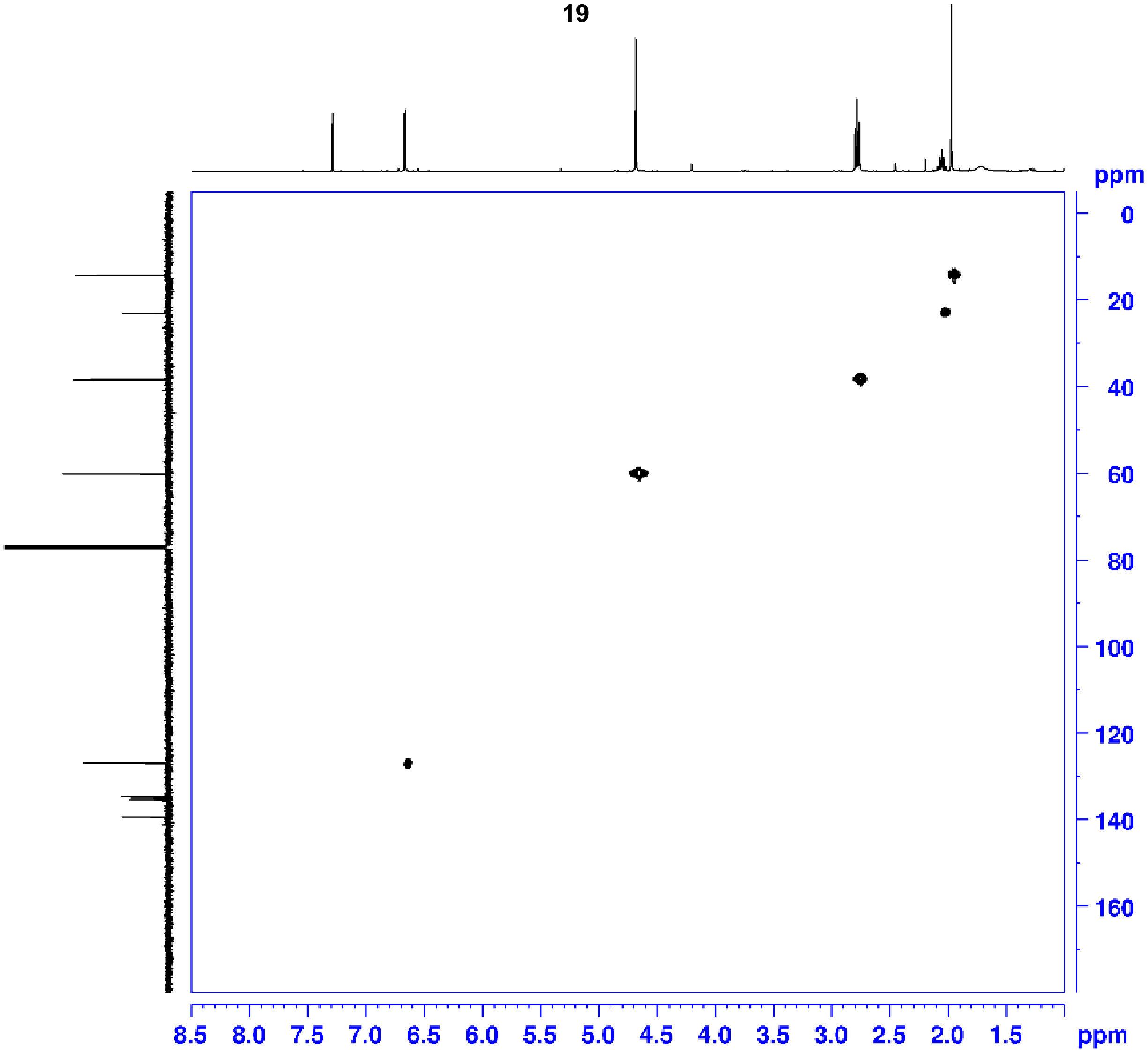
**19**



2D COSY NMR spectra ($CDCl_3$, 400MHz) compound **19**



**19**



2D HSQC NMR spectra ($CDCl_3$, 400MHz) compound **19**

## III. Photocyclization studies of compounds 9, 19, 23, 23a and 24

### 1. UV spectra for compound **9** in acetonitrile

Compound **9** (4 mg) was dissolved in 2 mL acetonitrile to prepare a 4.89 mM solution. Then the solution was diluted to prepare a 0.1 mM solution, 2 mL. UV absorbance was recorded after exposing the solution to 302 nm at different times.

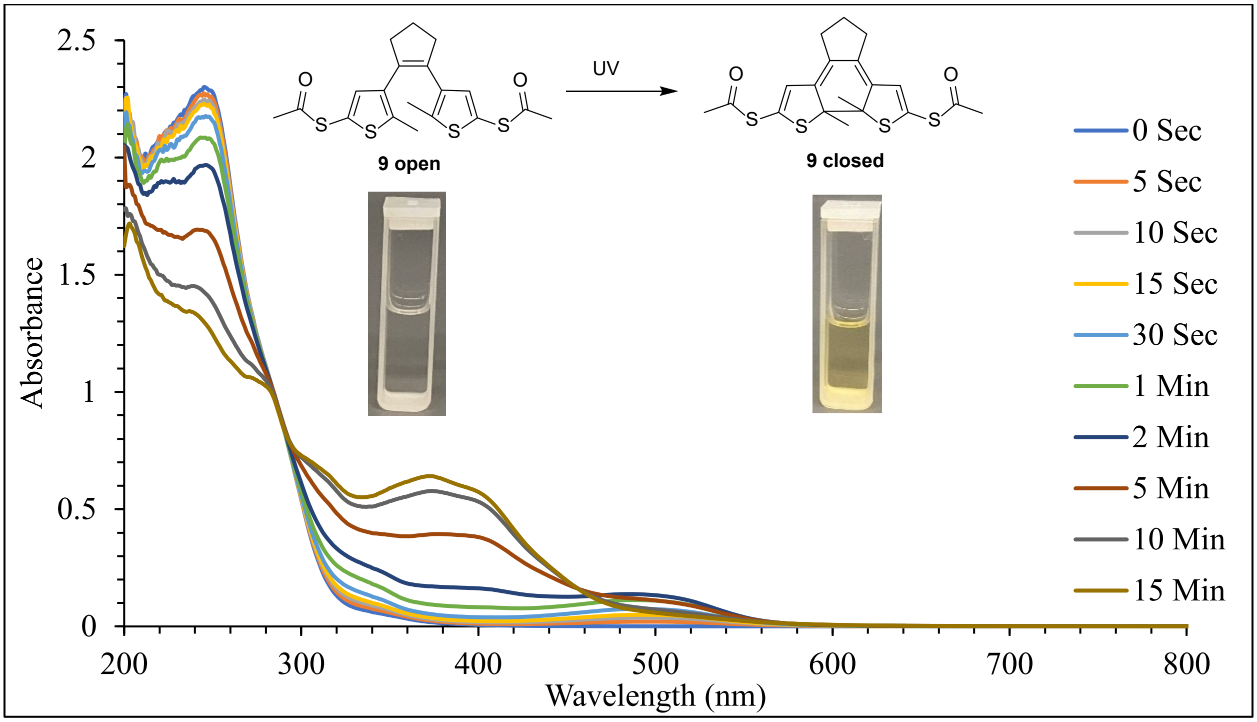


Figure S1. UV absorption spectra of compound **9** at 0.1 mM in acetonitrile.

2. UV-Vis spectra for compound **19** in acetonitrile upon irradiation at 302 nm

Compound **19** (1.3 mg) was dissolved in 2 mL acetonitrile to make 1.0 mM solution. Then the solution was diluted to make a 2 mL 0.05 mM solution. UV absorbance was recorded after exposing the solution to 302 nm at different times.

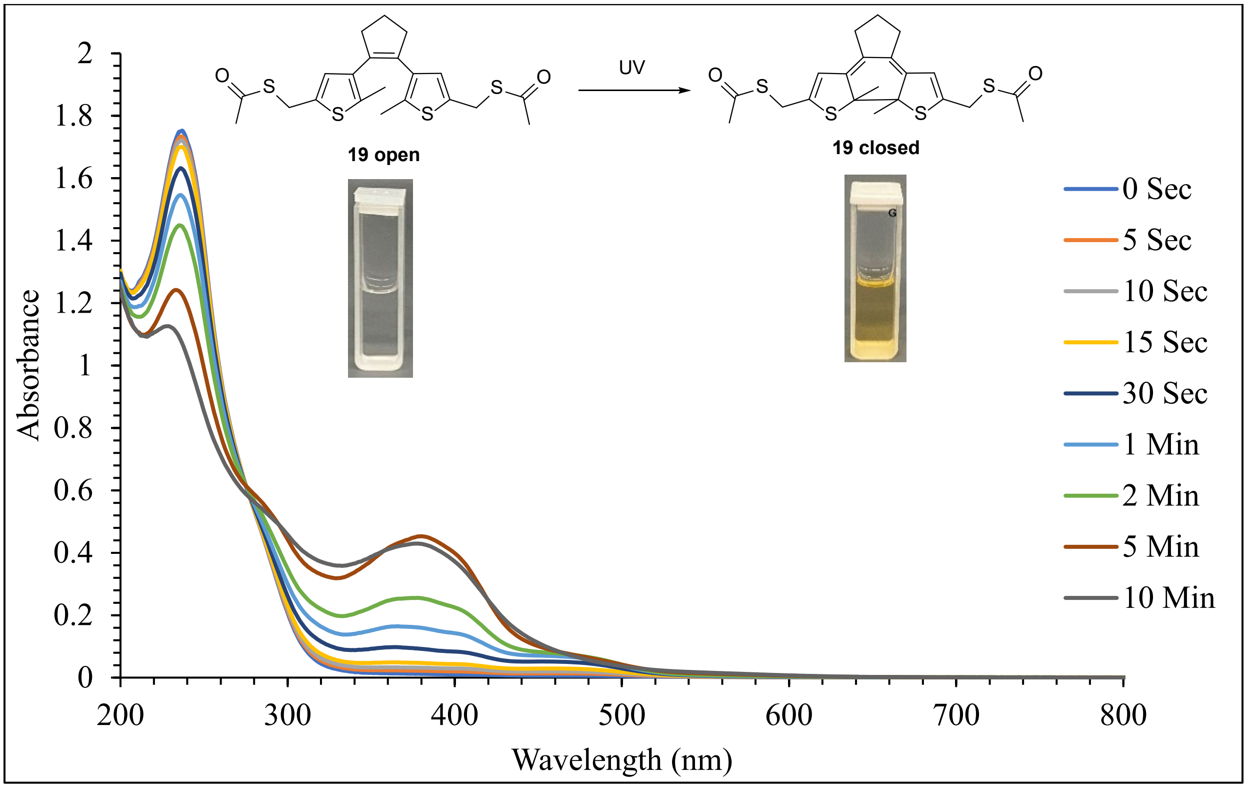


Figure S2. UV absorption spectra of compound **19** at 0.05 mM in acetonitrile.

3. UV spectra of compound **23** and **23a** in acetonitrile upon irradiation at 302 nm

Compound **23** (4.0 mg) was added to a 2 mL volumetric flask and then acetonitrile was added to make the solution at 3.57 mM concentration. Then the solution was diluted to make a 2.0 mL solution at 0.10 mM concentration and UV absorbance was taken at different times of UV irradiations.

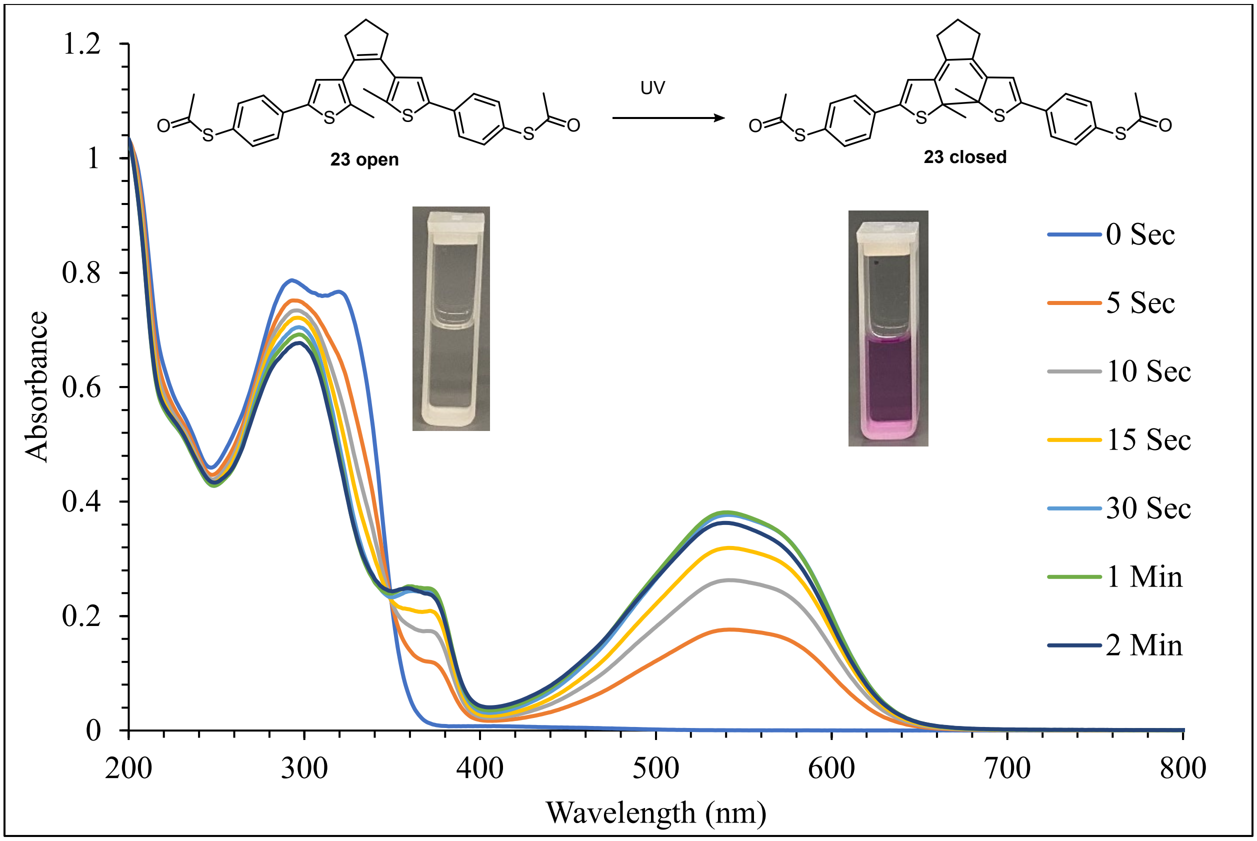


Figure S3. UV absorption spectra of compound **23** at 0.10 mM in acetonitrile after exposure at 302 nm at different times.

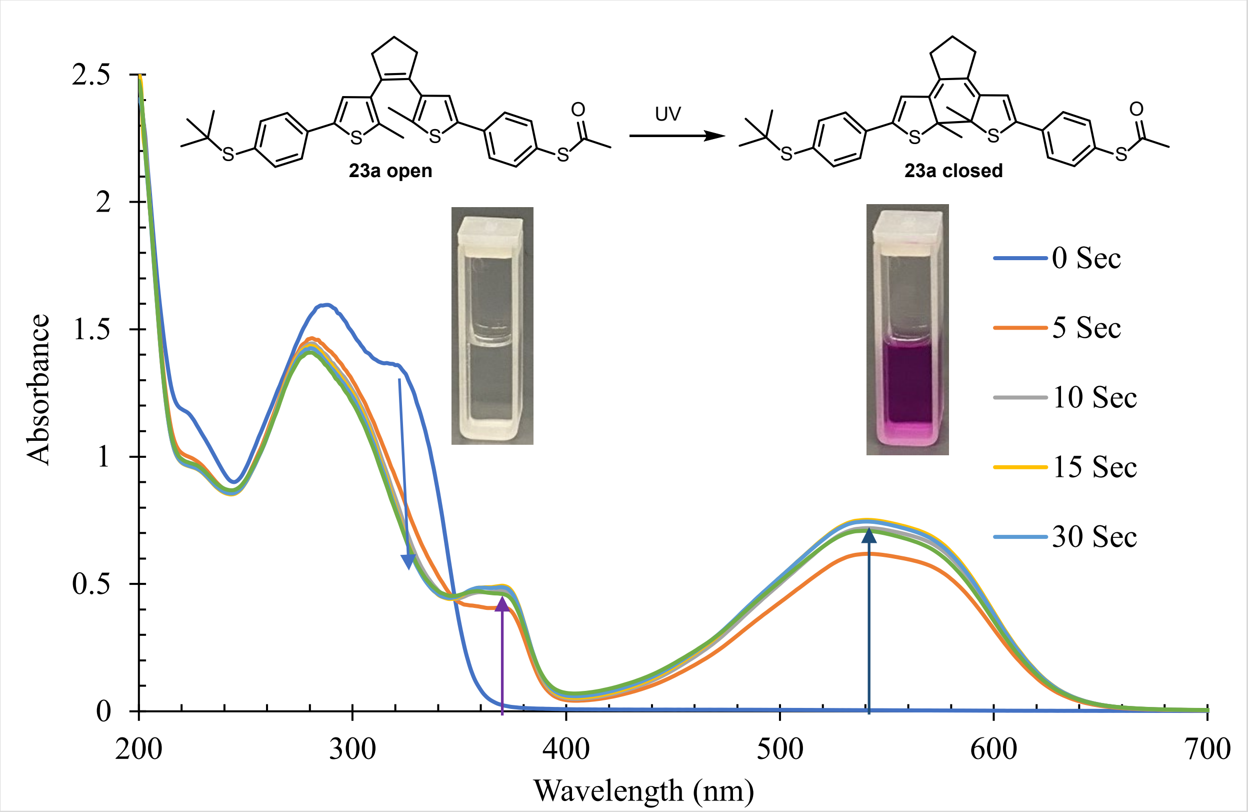


Figure S4. UV absorption spectra of compound **23a**, at 0.07 mM in acetonitrile after exposure at 302 nm at different times.

4. UV absorption spectra of compound **24** in acetonitrile upon irradiation at 302 nm

Compound **24** (1.3 mg) was added to a 2 mL volumetric flask and then acetonitrile was added to make a solution at 0.97 mM concentration. Then the solution was diluted to prepare two 2 mL solutions at 0.10 mM and 0.05 mM concentrations. The solutions were treated with 302 UV light and the UV-Vis absorbance of the solutions were taken at different times.

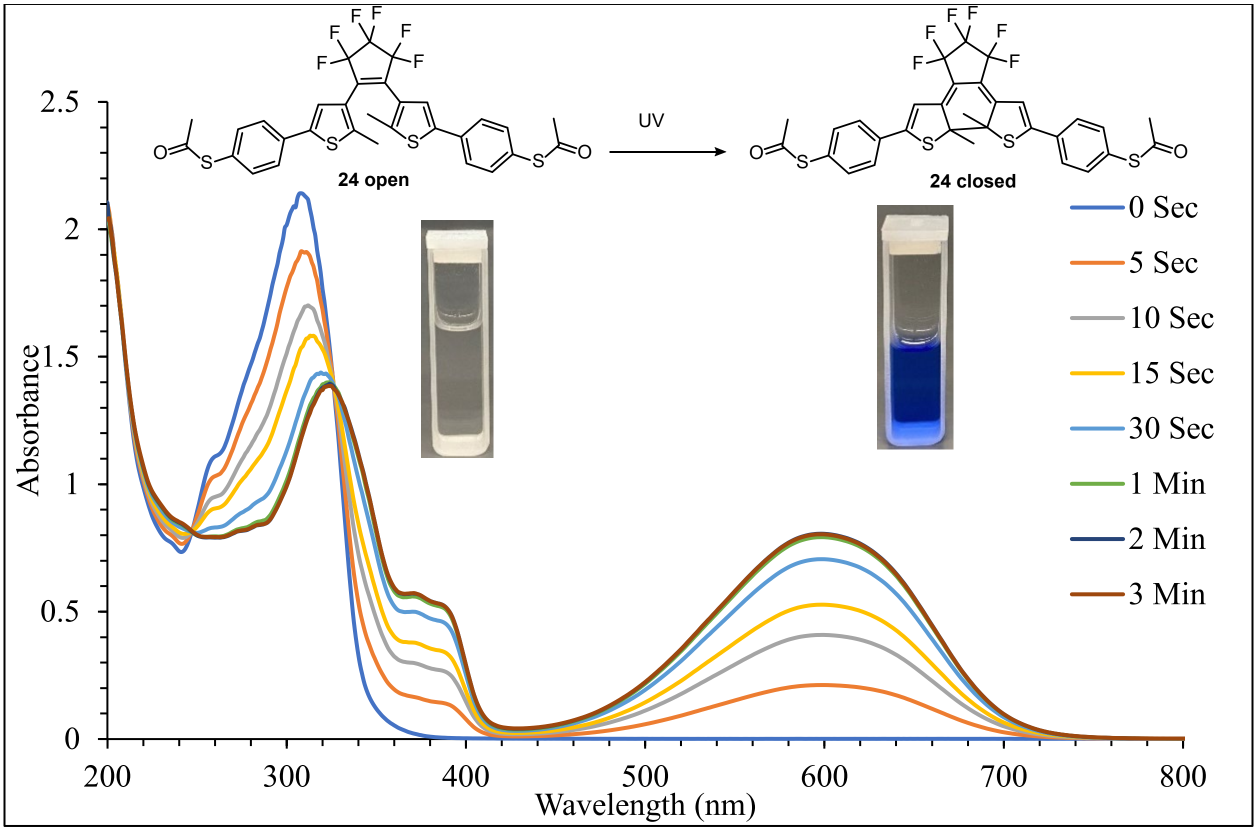


Figure S5. UV absorption spectra of compound **24** at 0.05 mM in acetonitrile after exposure at 302 nm at different times.

## 5. Relative rate of cyclization for compounds **12**, **20**, **23**, **23a**, and **24**

The rates of the cyclization reaction for compounds **12**, **20**, **23**, **23a**, and **24** were estimated using the UV-Vis absorption of the cyclized compounds. The absorbance intensity ratio to the maximum absorbance at different time points, this ratio was plotted versus time of irradiation. These corresponds are shown in Figures S6a-6e.

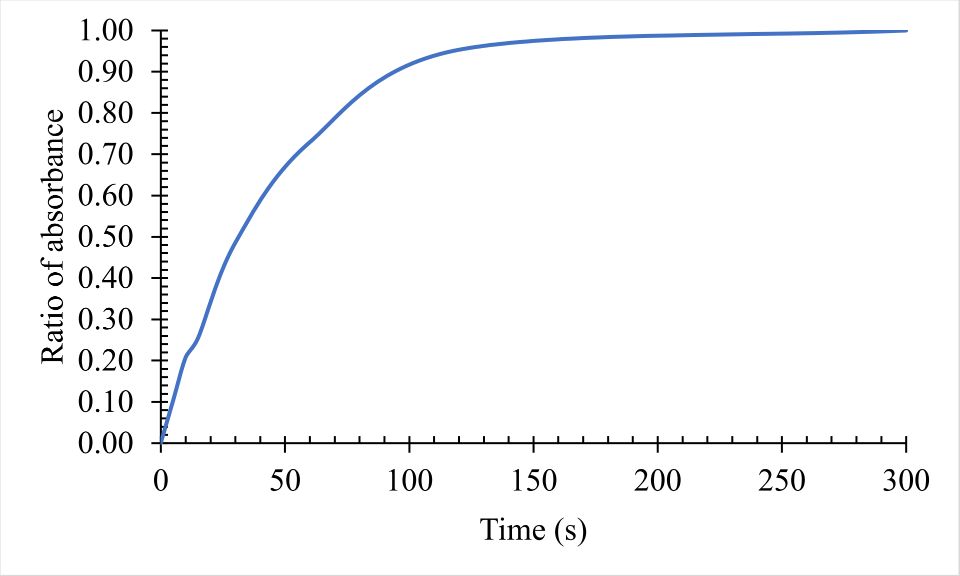


Figure S6a. Rate of cyclization of compound **12** in acetonitrile (0.1 mM).

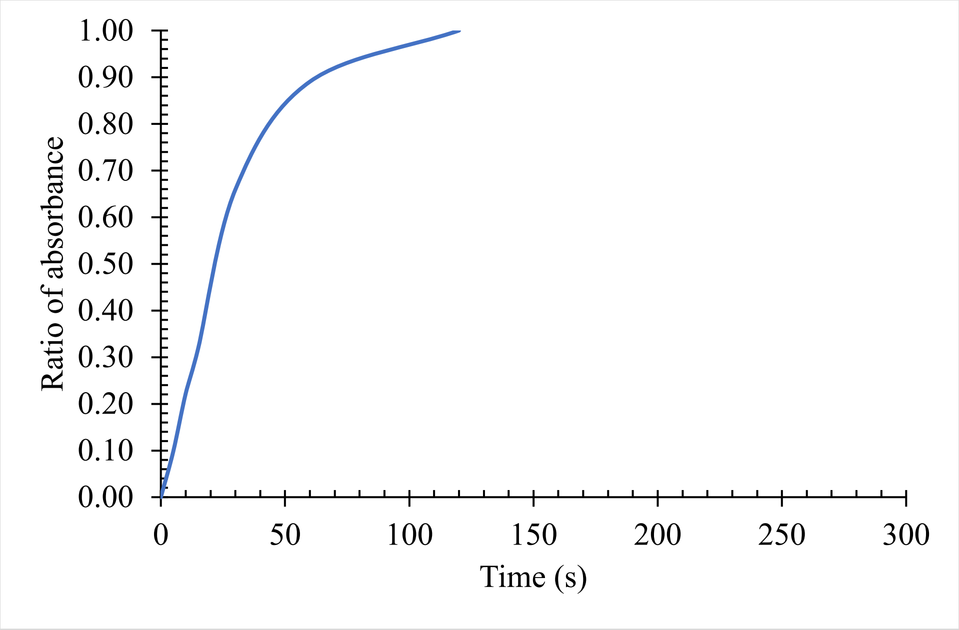


Figure S6b. Rate of cyclization of compound **20** in acetonitrile (0.1 mM).

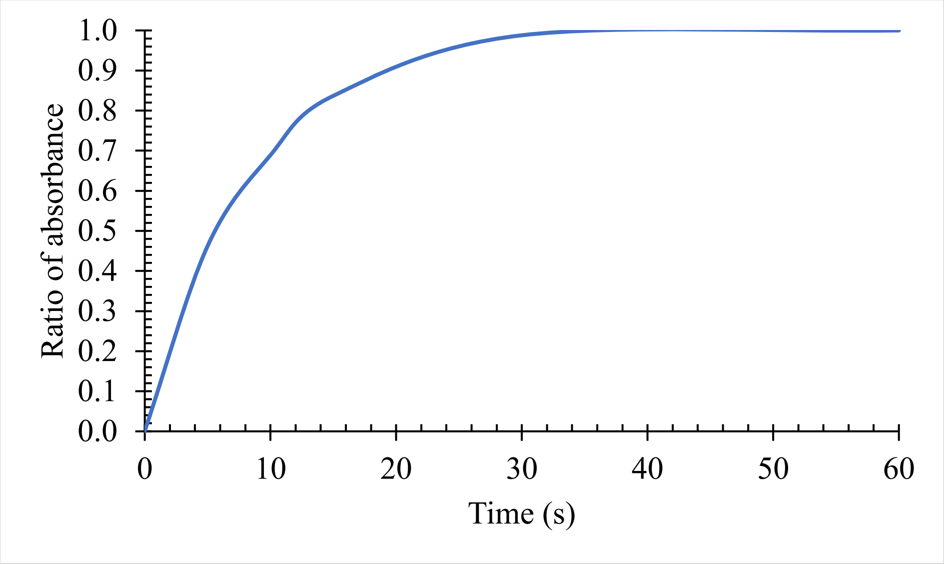


Figure S6c. Rate of cyclization of compound **23** in acetonitrile (0.1 mM).

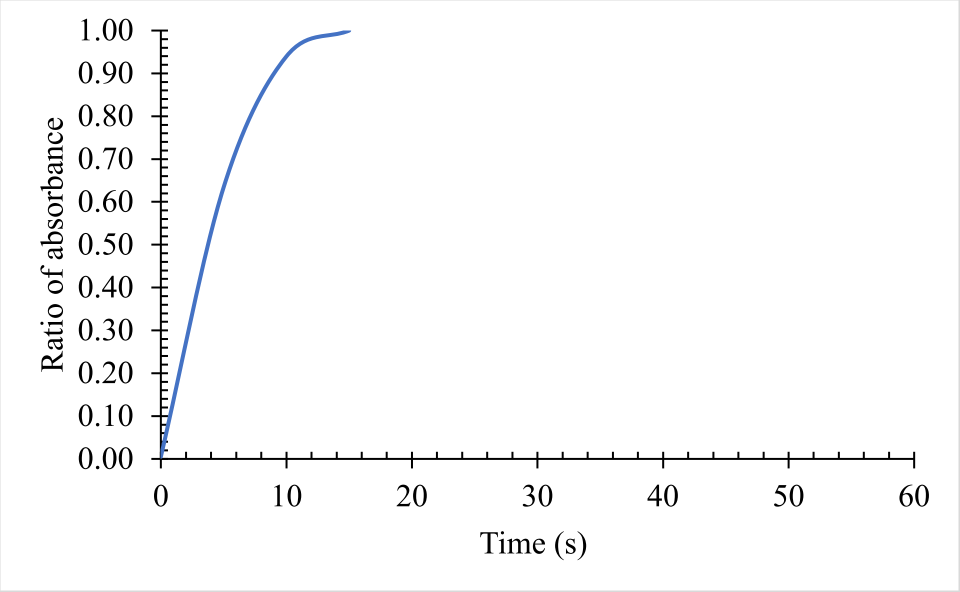


Figure S6d. Rate of cyclization of compound **23a** in acetonitrile (0.1 mM).

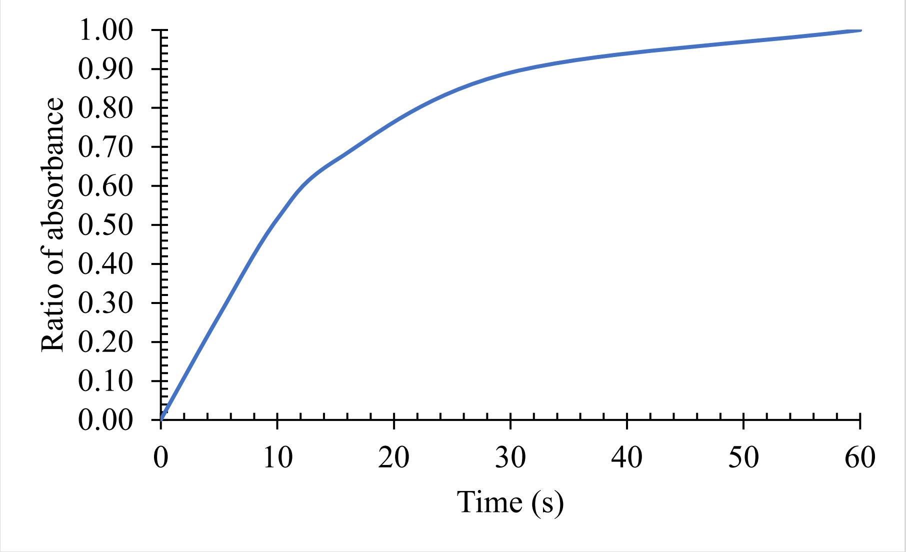


Figure 6e. Rate of cyclization of compound **24** in acetonitrile (0.05 mM).

## 6. Ring closing study using $^1$H NMR

The $^1$H NMR spectrum of compound **20** was obtained, (1.5 mg dissolved in 0.5 mL DMSO-$d_6$), then the sample from the NMR tube was exposed under UV (6W, 302 nm) for 25 minutes and the $^1$H NMR was recorded again. The compound had mostly cyclized to form the closed form and NMR spectrum exhibited two sets of signals, corresponding to the open and the closed forms.

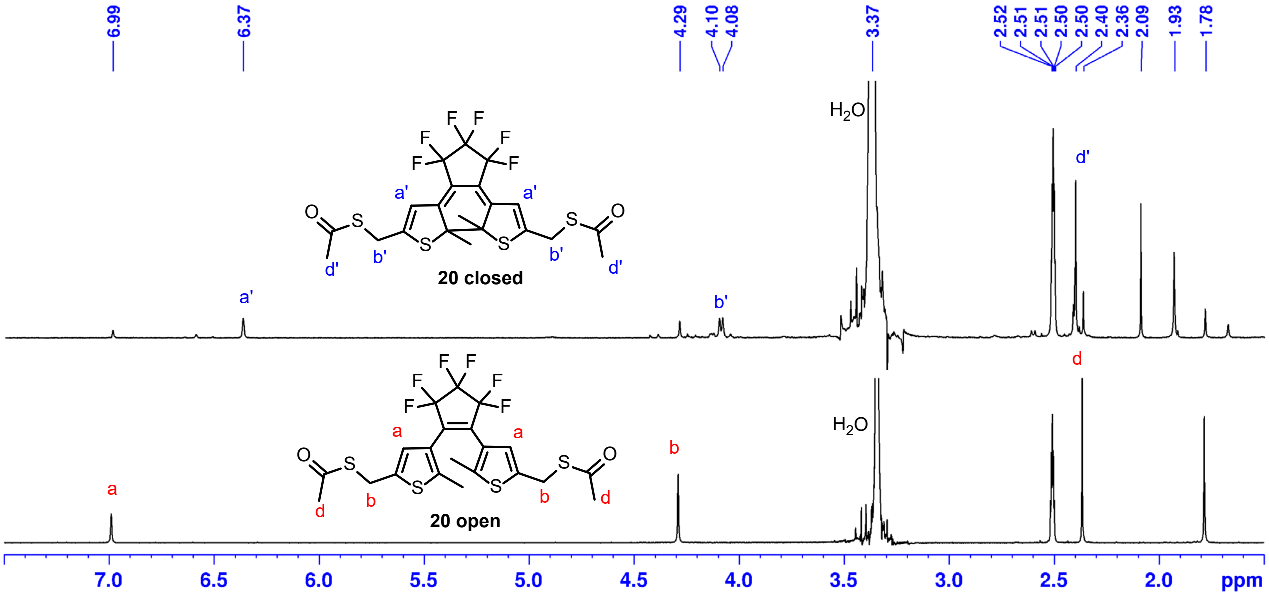
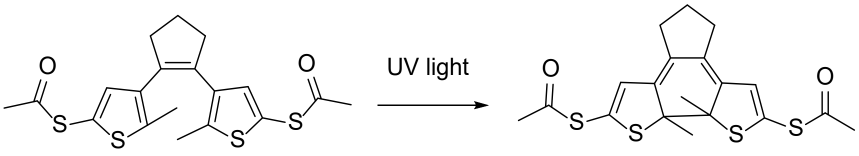


Figure S7. $^1$H NMR spectra of the open form (bottom) and closed form (top) of compound **20** in DMSO-$d_6$, 400 MHz.

## IV. Fluorescence properties of compounds **9**, **12**, **20**, **23**, and **24**

### 1. Fluorescence spectra of compound **9**

A 0.2 mM solution of compound **9** was prepared and exposed to 302 nm light to obtain the closed form. The fluorescent excitation spectra were obtained first, and the fluorescent emission spectra at different time points were recorded at a 375 nm excitation wavelength. The UV-Vis spectra are shown in Figure S8 and fluorescence emission spectra with λex = 375 nm are included in Figure S9.



**9 open** **9 closed**

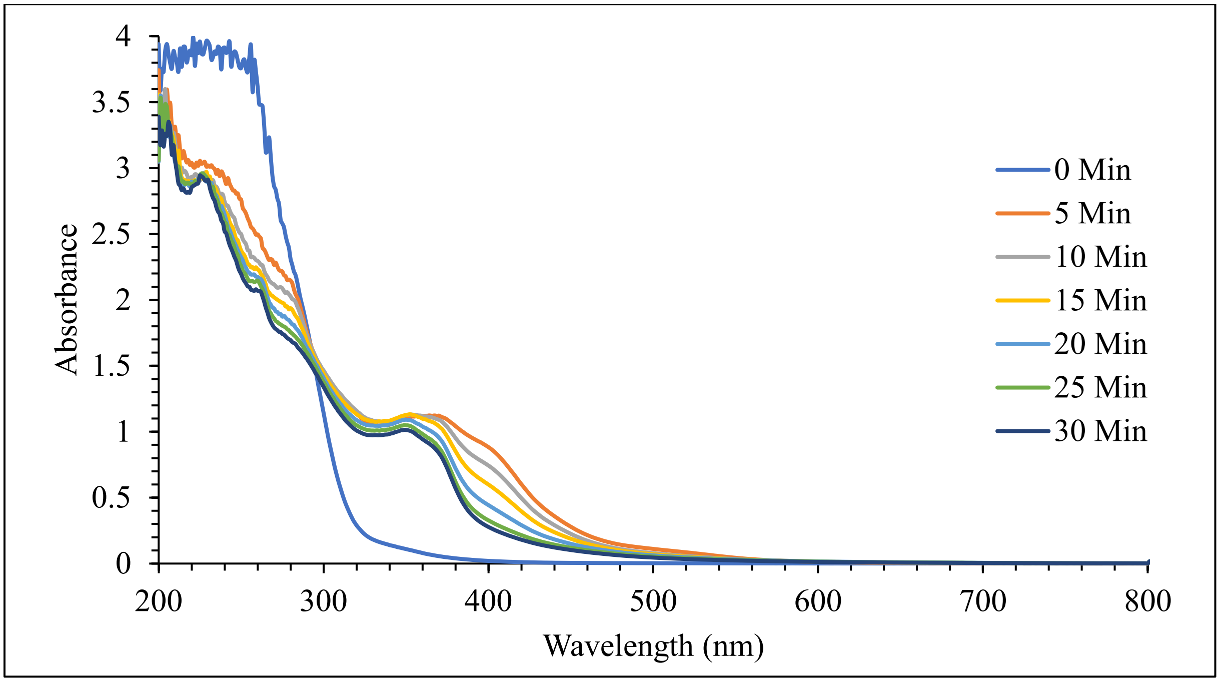


Figure S8. UV absorption spectra of compound **9** at 0.2 mM in acetonitrile after exposure at 302 nm at different times.

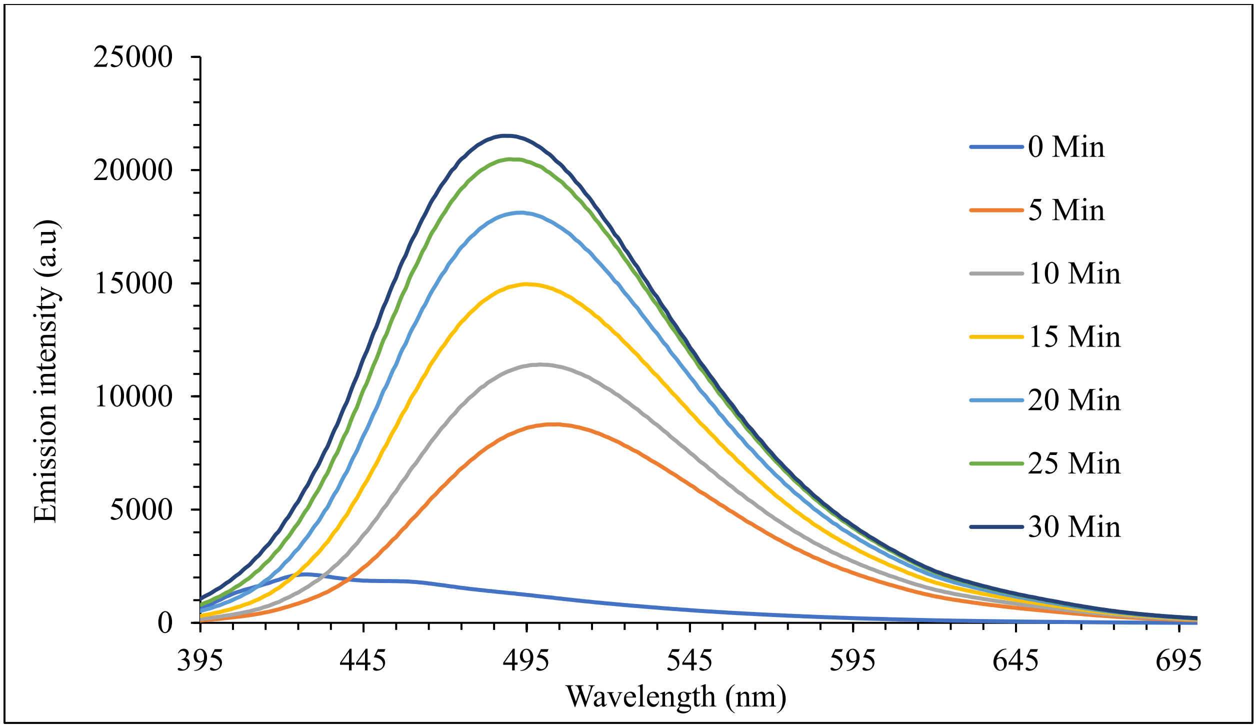
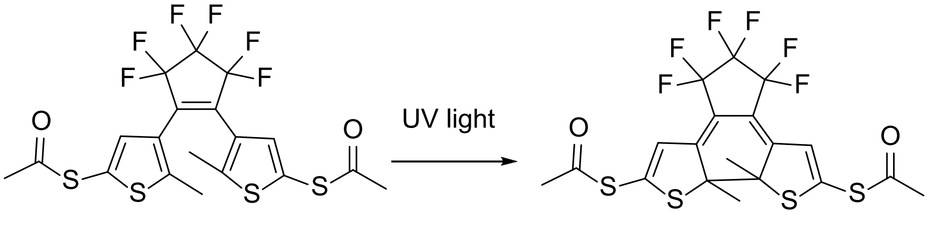


Figure S9. Fluorescence emission spectra of compound **9** at different time points of UV irradiation (302 nm), the concentration was 0.2 mM in acetonitrile, excitation wavelength was 375 nm for all.

## 2. Fluorescence emission spectra of compound **12**

A 0.1 mM solution of compound **12** was prepared and the sample was exposed to 302 nm light for 10 mins to obtain the closed form, the UV-Vis spectra are shown in Figure S10 and fluorescence emission spectra with λex = 364 nm are included in Figure S11.



**12 open**

**12 closed**

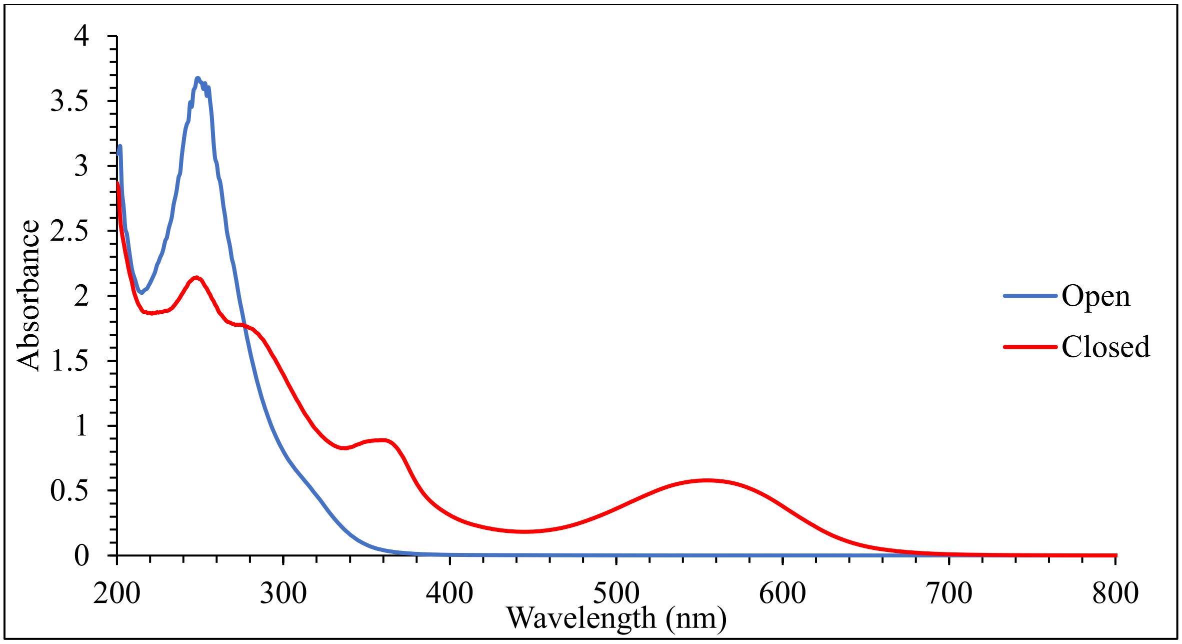


Figure S10. UV absorption spectra of compound **12** at 0.1 mM in acetonitrile after exposure at 302 nm light.

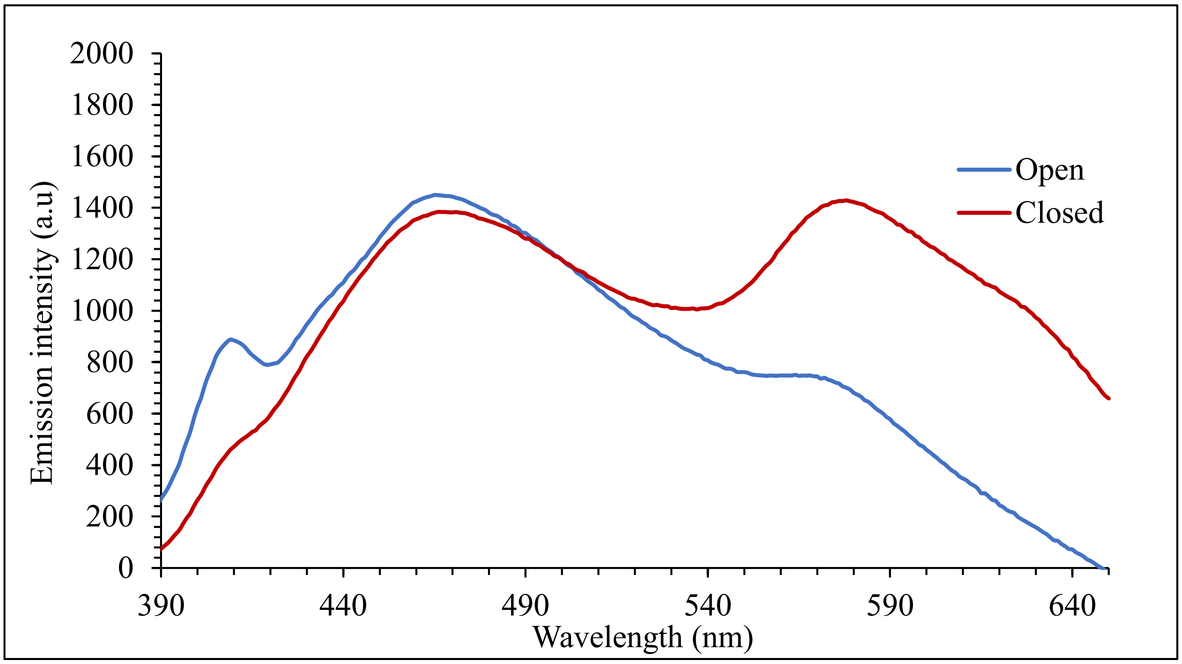
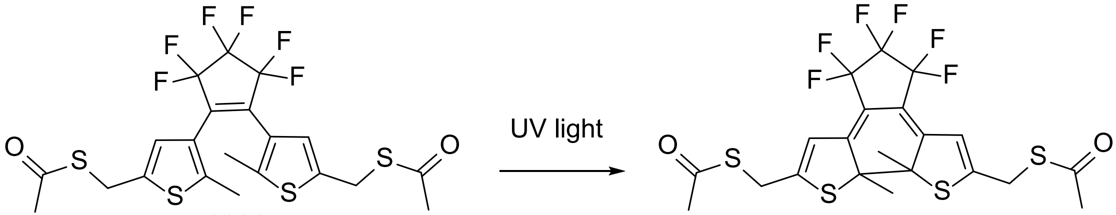


Figure S11. Fluorescence emission spectra of compound **12** in acetonitrile at 0.1 mM with excitation wavelength 364 nm.

## 3. Fluorescence emission spectra of compound **20**

In a 10 mL volumetric flask, 2.2 mg of compound **20** was dissolved in acetonitrile to make a 10 mL 0.403 mM solution. Then the solution was diluted to 0.10 mM and exposed to 302 nm light to obtain the closed form, and fluorescence emission spectra at different time points were recorded at a 348 nm excitation wavelength. The UV-Vis spectra are shown in Figure S12 and fluorescence spectra are shown in Figure S13.



**20** open

**20** closed

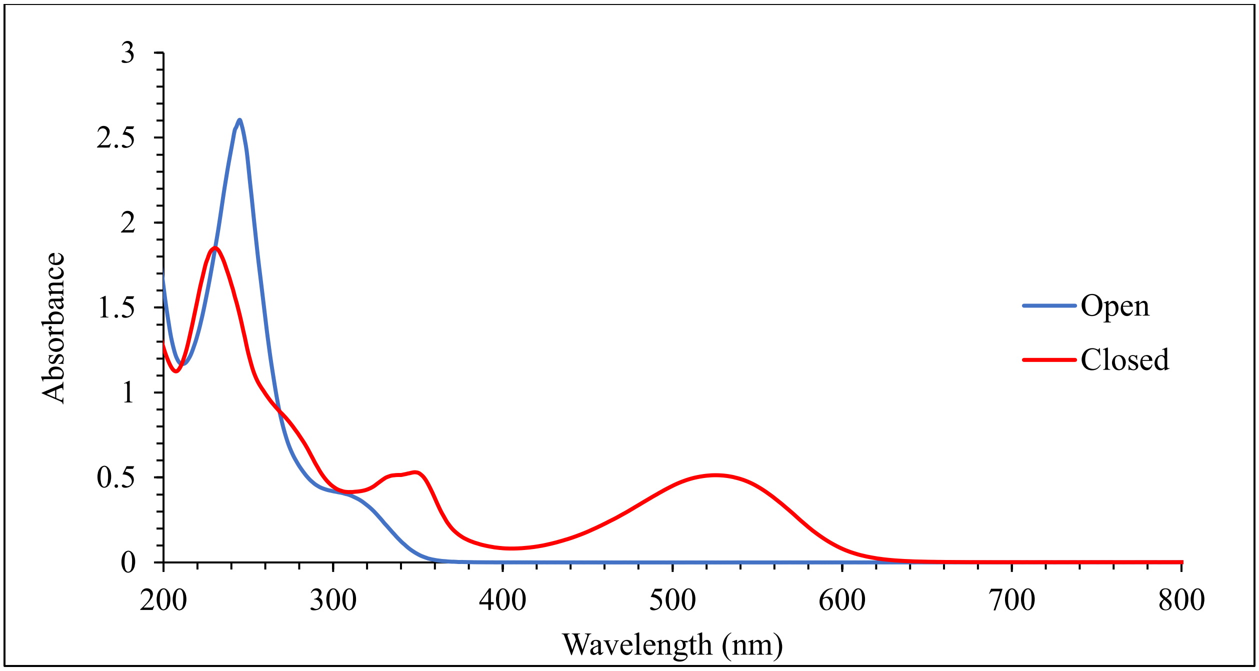


Figure S12. UV absorption spectra of compound **20** at 0.1 mM in acetonitrile after exposure at 302 nm light for 5 min.

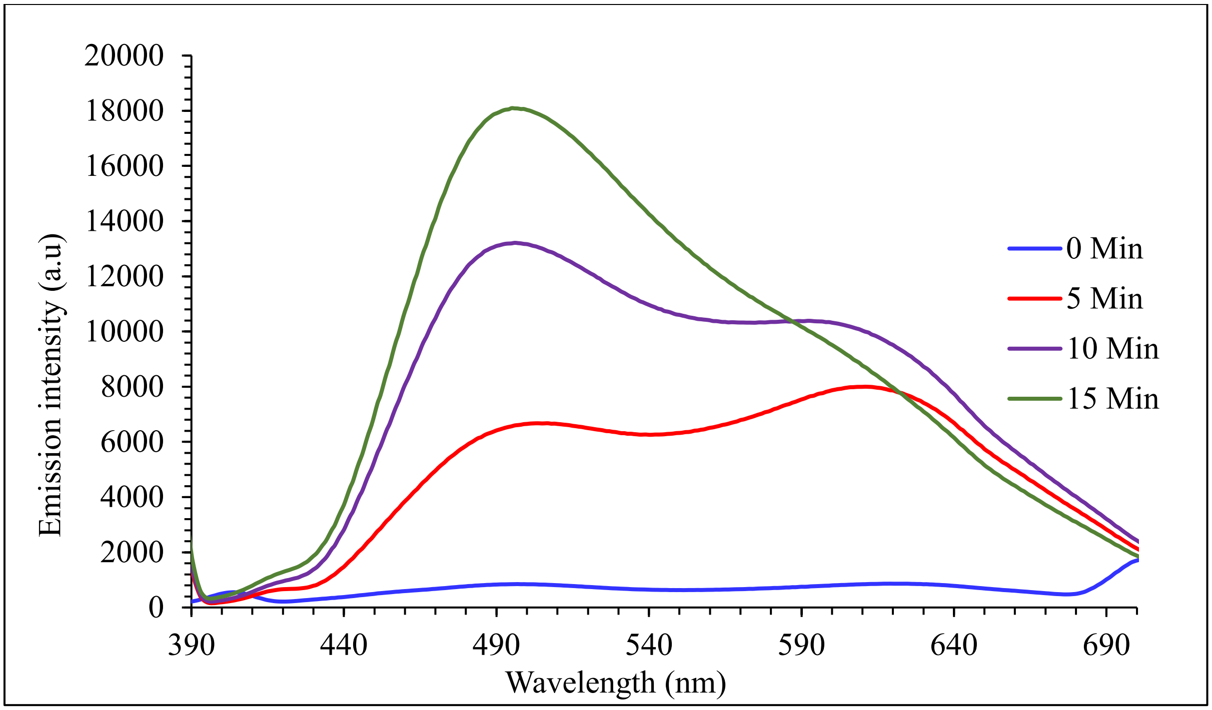
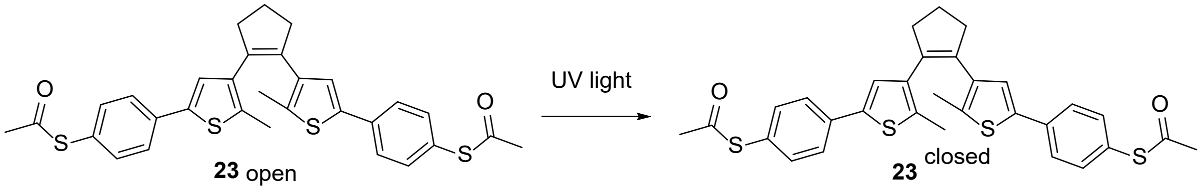


Figure S13. Fluorescence emission spectra of compound **20-C** in acetonitrile at 0.1 mM with excitation wavelength 348 nm.

## 4. Fluorescence spectra of compound **23**

In a volumetric flask, 1.0 mg compound **23** was added to prepare a 0.178 mM acetonitrile solution. This solution was diluted to 0.1 mM solution. This solution (open form) was irradiated under 302 nm UV light for 10 minutes to make a closed form, the UV-Vis spectra are shown in Figure S14 and the fluorescence spectra at two different excitation wavelengths are shown in Figure S15-16.



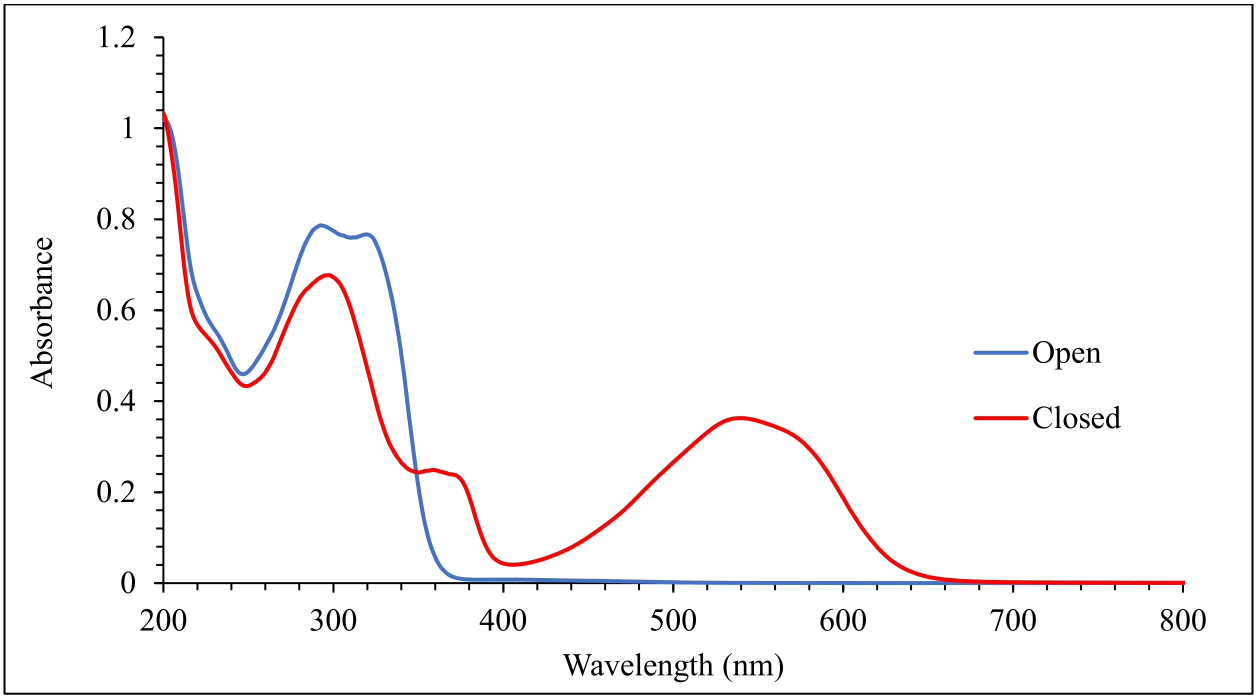


Figure S14. UV absorption spectra of compound **23** at 0.1 mM in acetonitrile after exposure at 302 nm light.

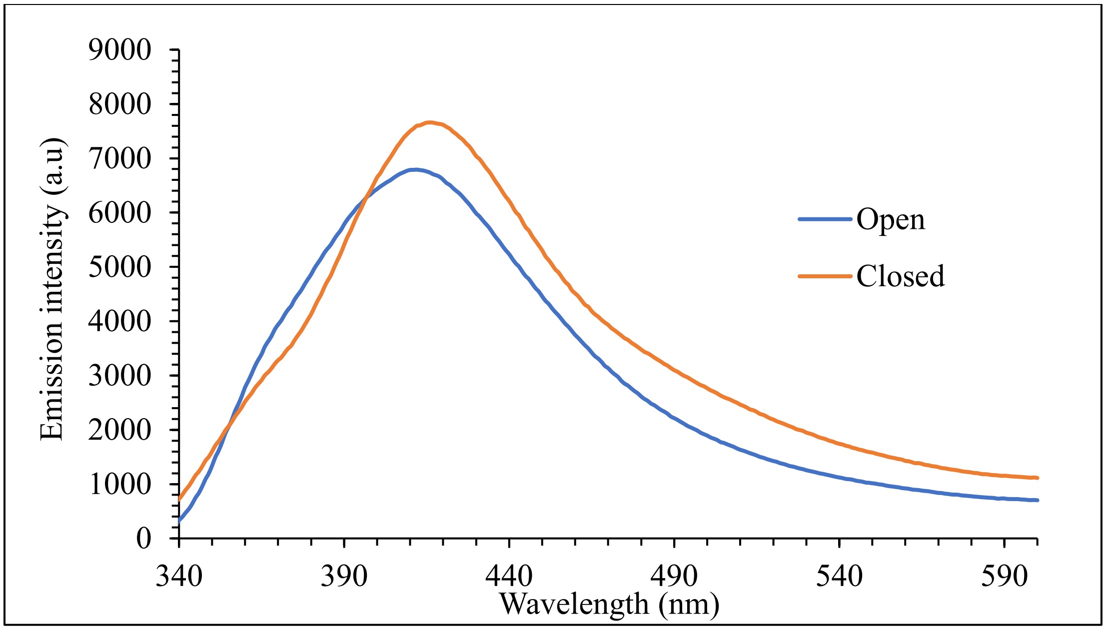


Figure S15. Fluorescence emission spectra of compound **23** in acetonitrile at 0.1 mM with excitation wavelength 320 nm.

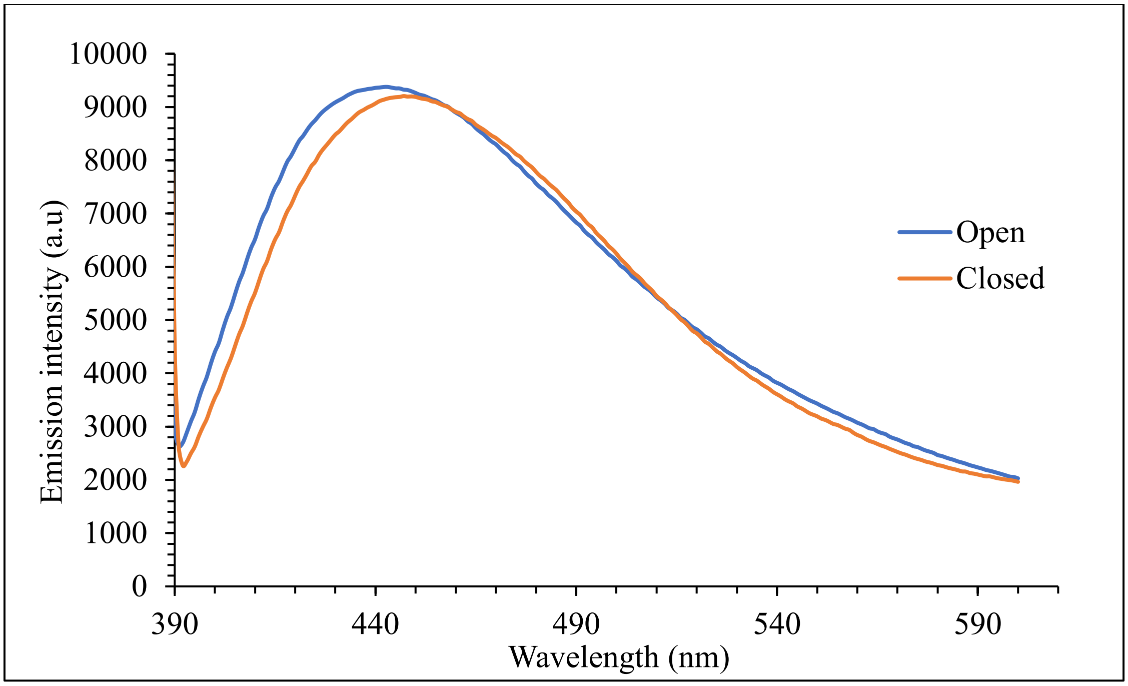
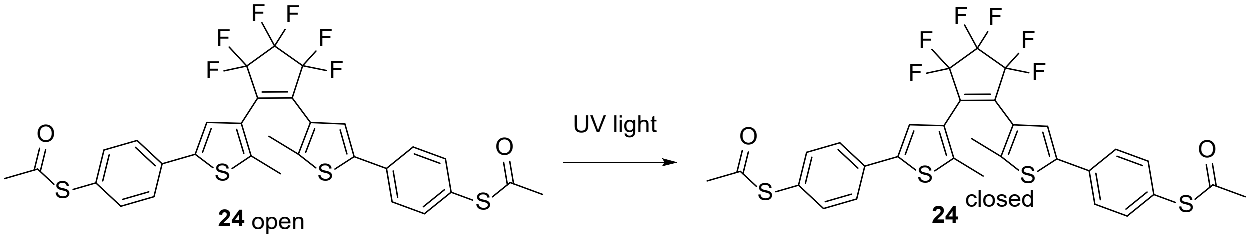


Figure S16. Fluorescence emission spectra of compound **23** in acetonitrile at 0.1 mM with excitation wavelength 373 nm.

## 5. Fluorescence emission spectra of compound **24**

In a volumetric flask, 1.7 mg compound **24** was added to prepare a 0.254 mM acetonitrile solution. Then the solution was diluted to 0.1 mM, and the solution was irradiated under 302 nm UV light for 10 minutes to prepare the closed form. The UV-vis spectra are shown in Figure S17 and the fluorescence spectra are shown in Figure S18.



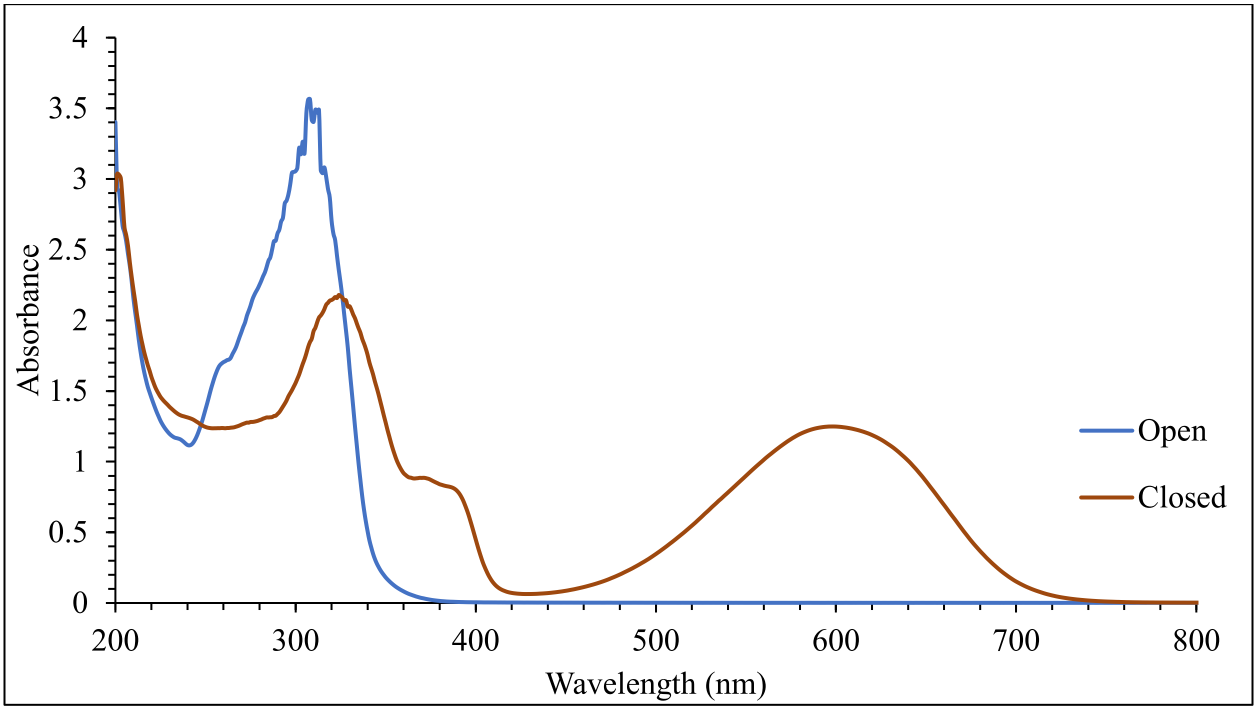


Figure S17. UV absorption spectra of compound **24** at 0.1 mM in acetonitrile after exposure at 302 nm light.

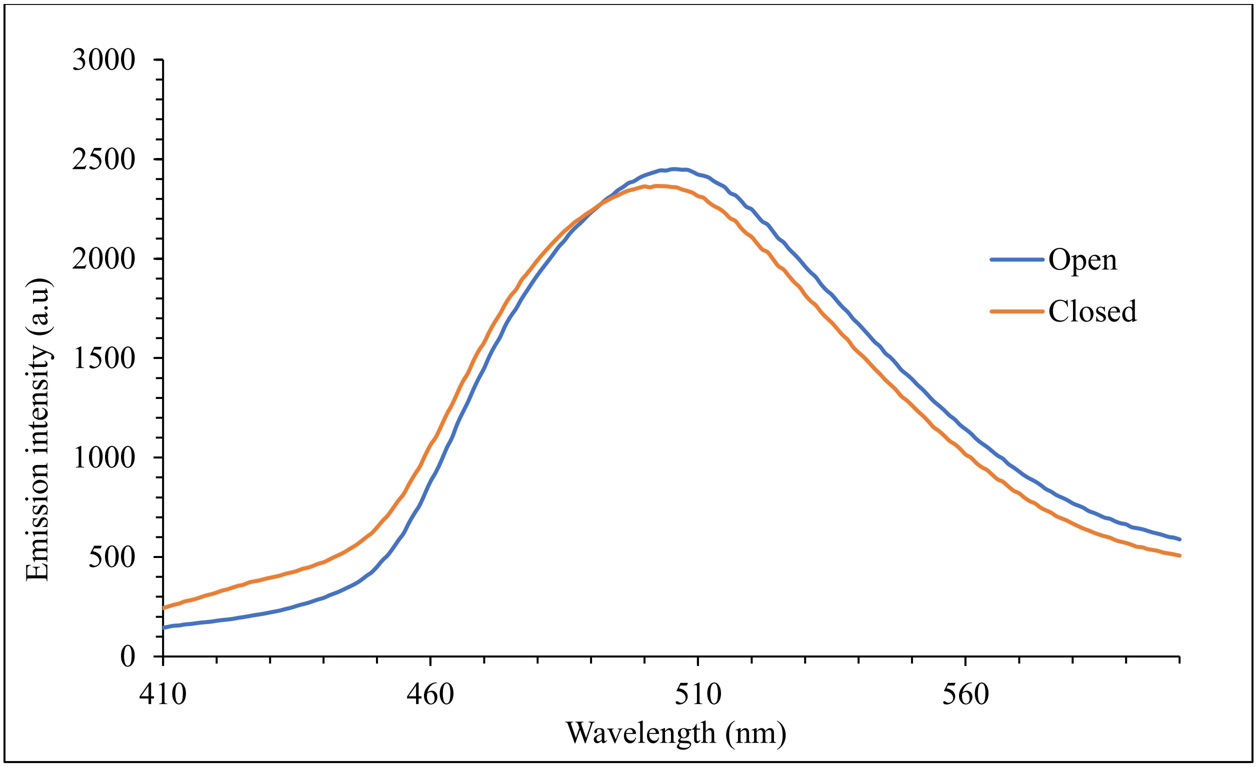


Figure S18. Fluorescence emission spectra of compound **24** in acetonitrile at 0.1 mM with excitation wavelength 390 nm.

6. The fluorescence spectra of compound **9-C** at different concentrations

Different concentrations of the solution were prepared, and the closed form of the compound was obtained after irradiation of the compound with 302 nm light. Then fluorescence was measured.

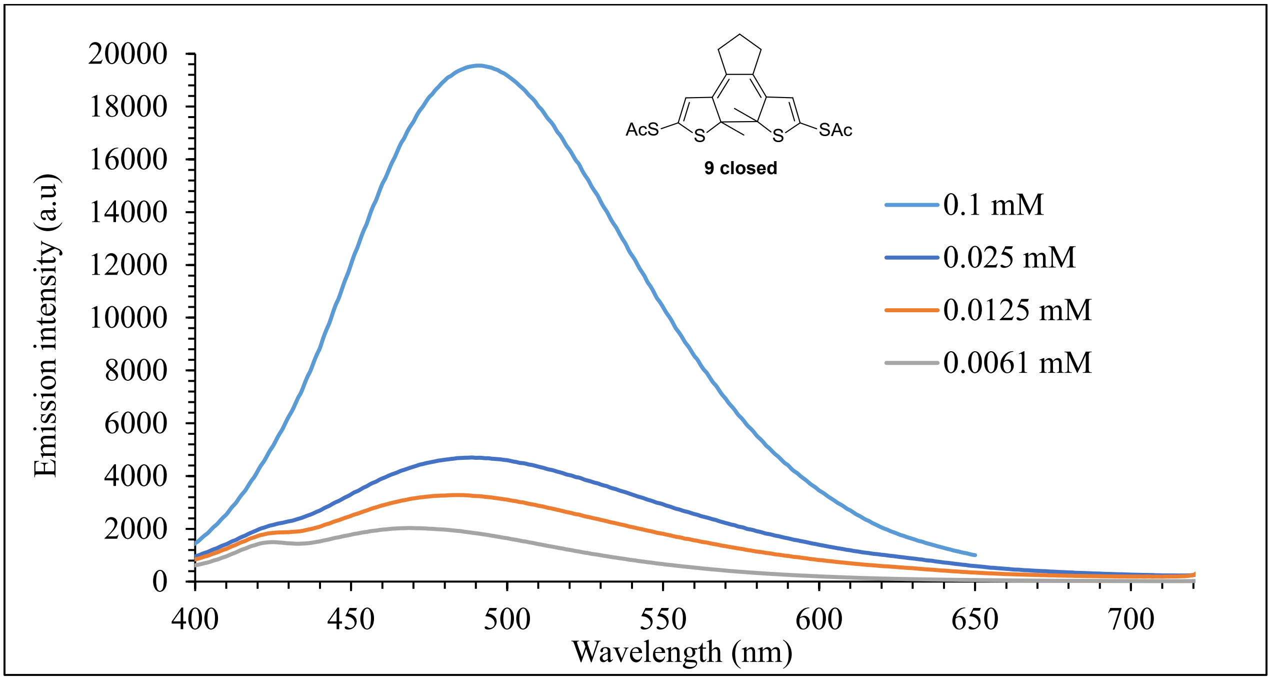


Figure S19. Fluorescence emission spectra of compound **9-C** (in closed form) in acetonitrile at different concentrations, $\lambda_{ex} = 375$ nm.