

# When dithiafulvenyl functionalized $\pi$ -conjugated oligomers meet fullerenes and single-walled carbon nanotubes

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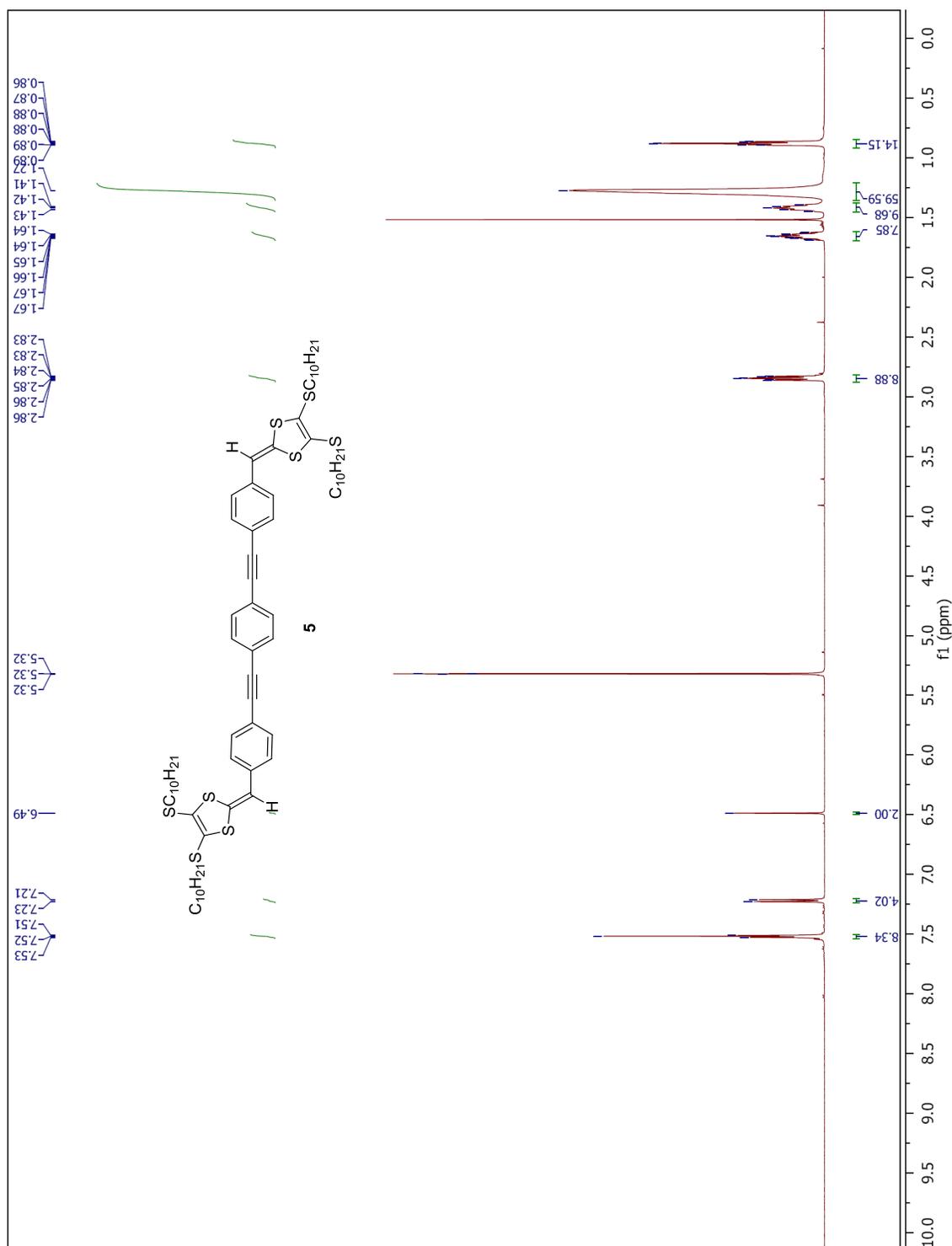
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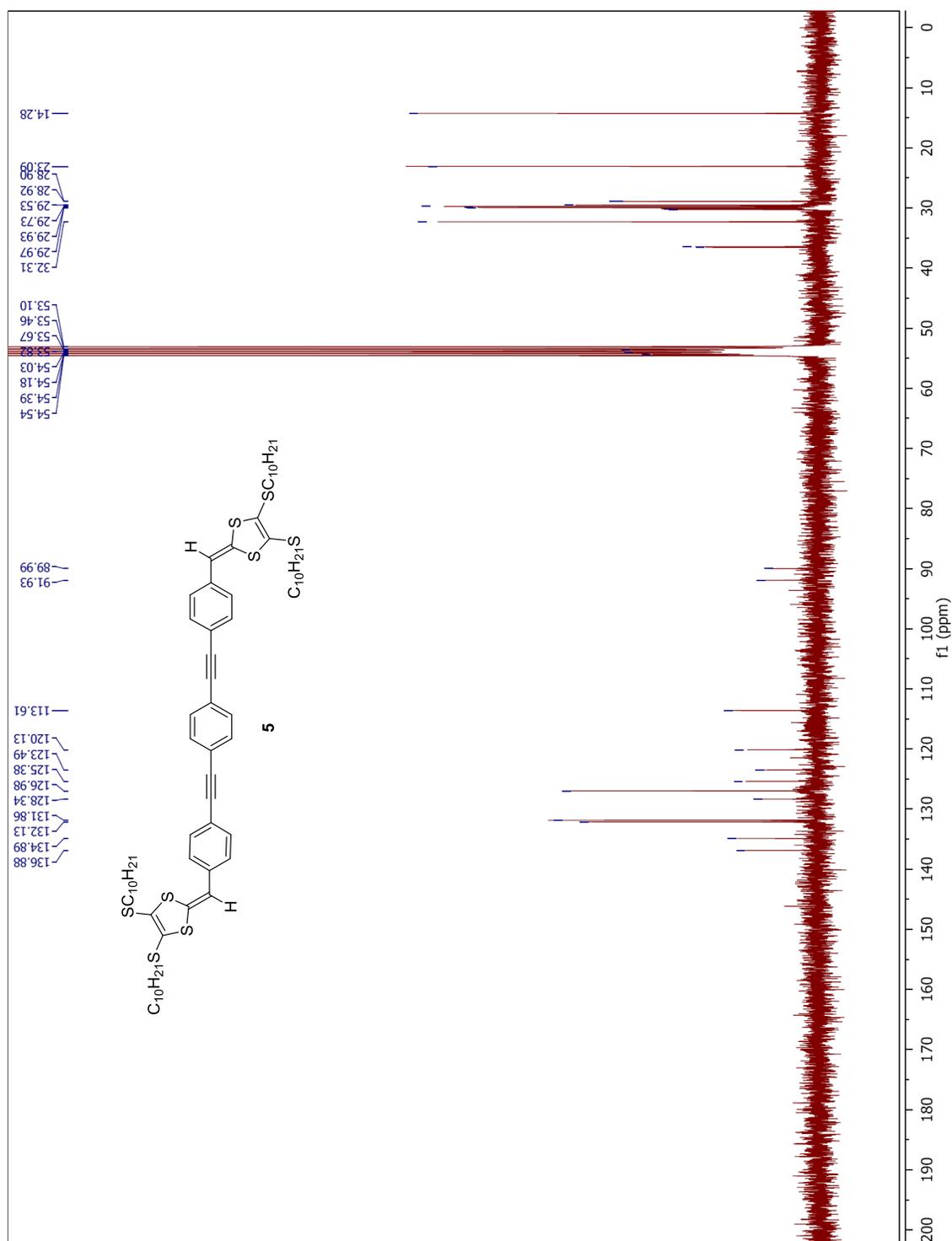
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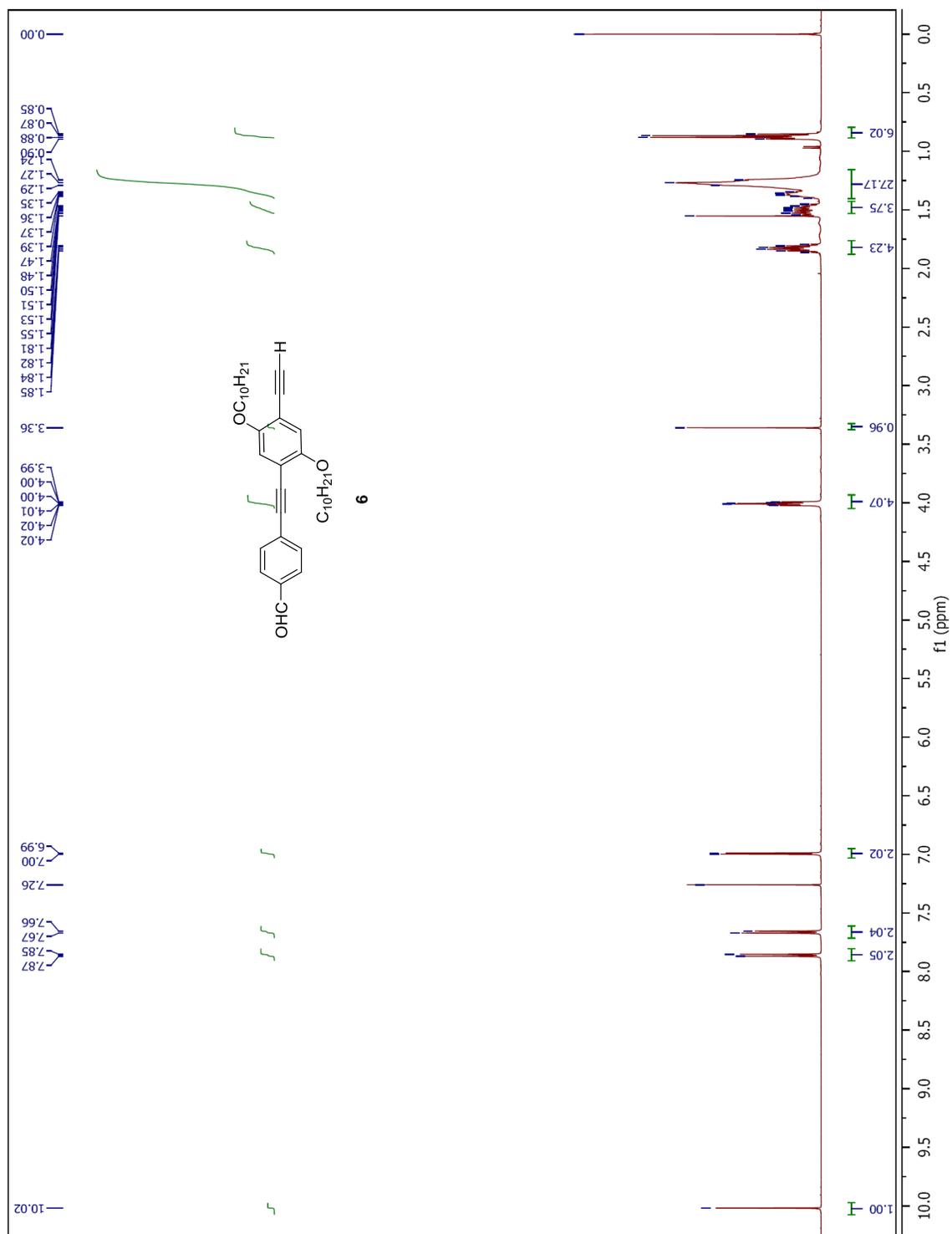
## 1. NMR Spectra for New Compounds



**Fig. S-1.** <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of compound **5**.



**Fig. S-2.** <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of compound **5**.



**Fig. S-3.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **6**.

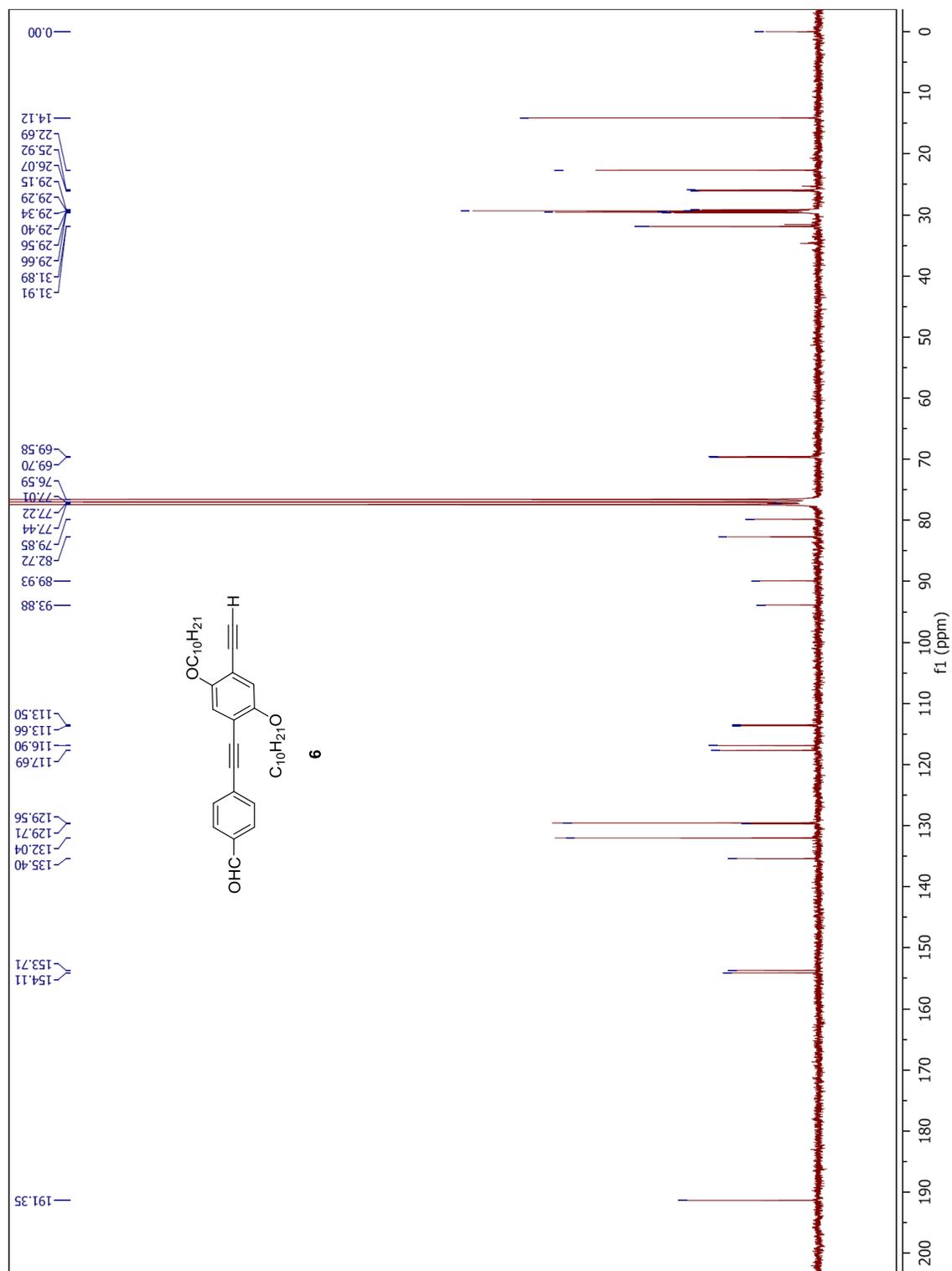


Fig. S-4.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ) spectrum of compound **6**.

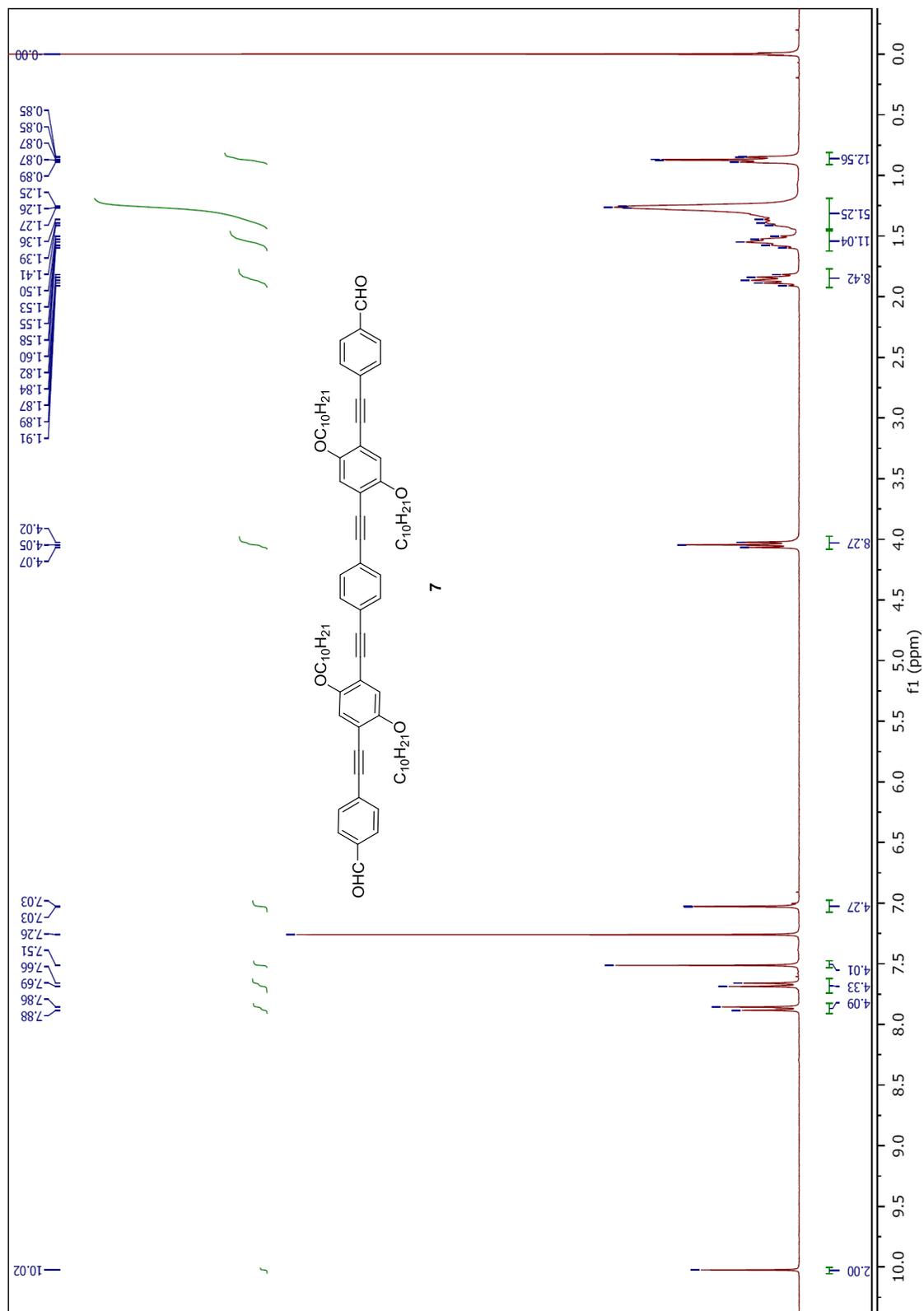


Fig. S-5.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) spectrum of compound 7.

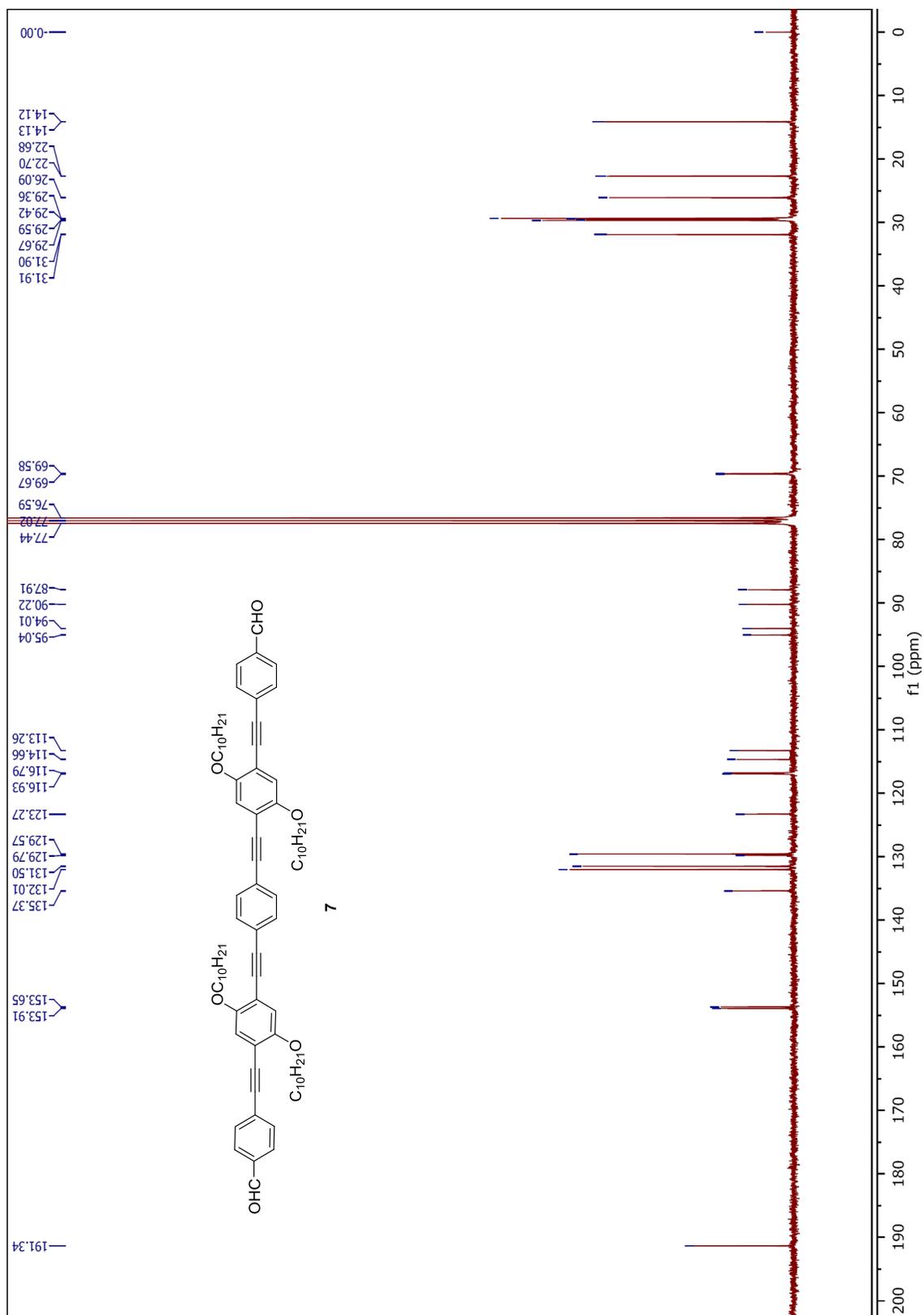
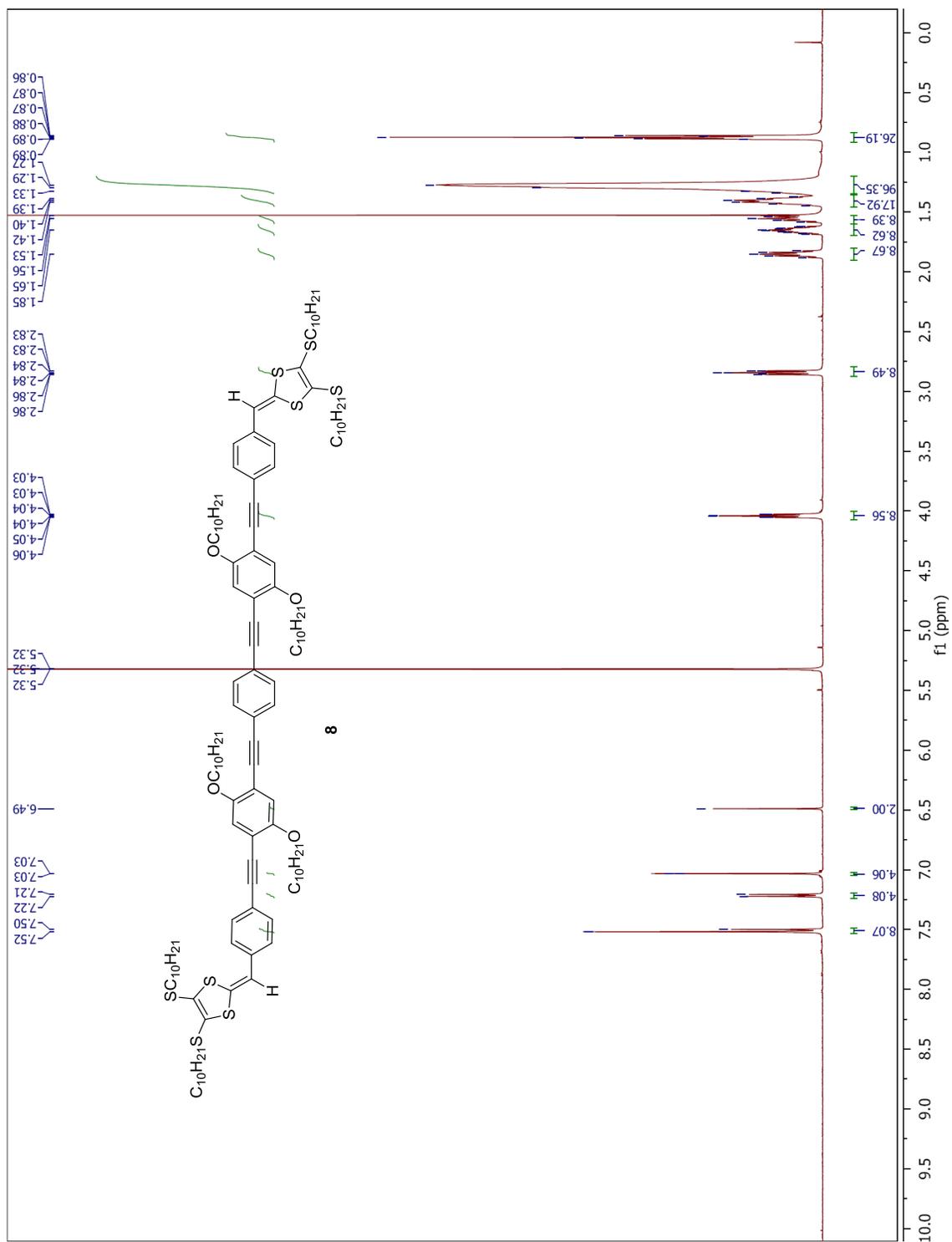
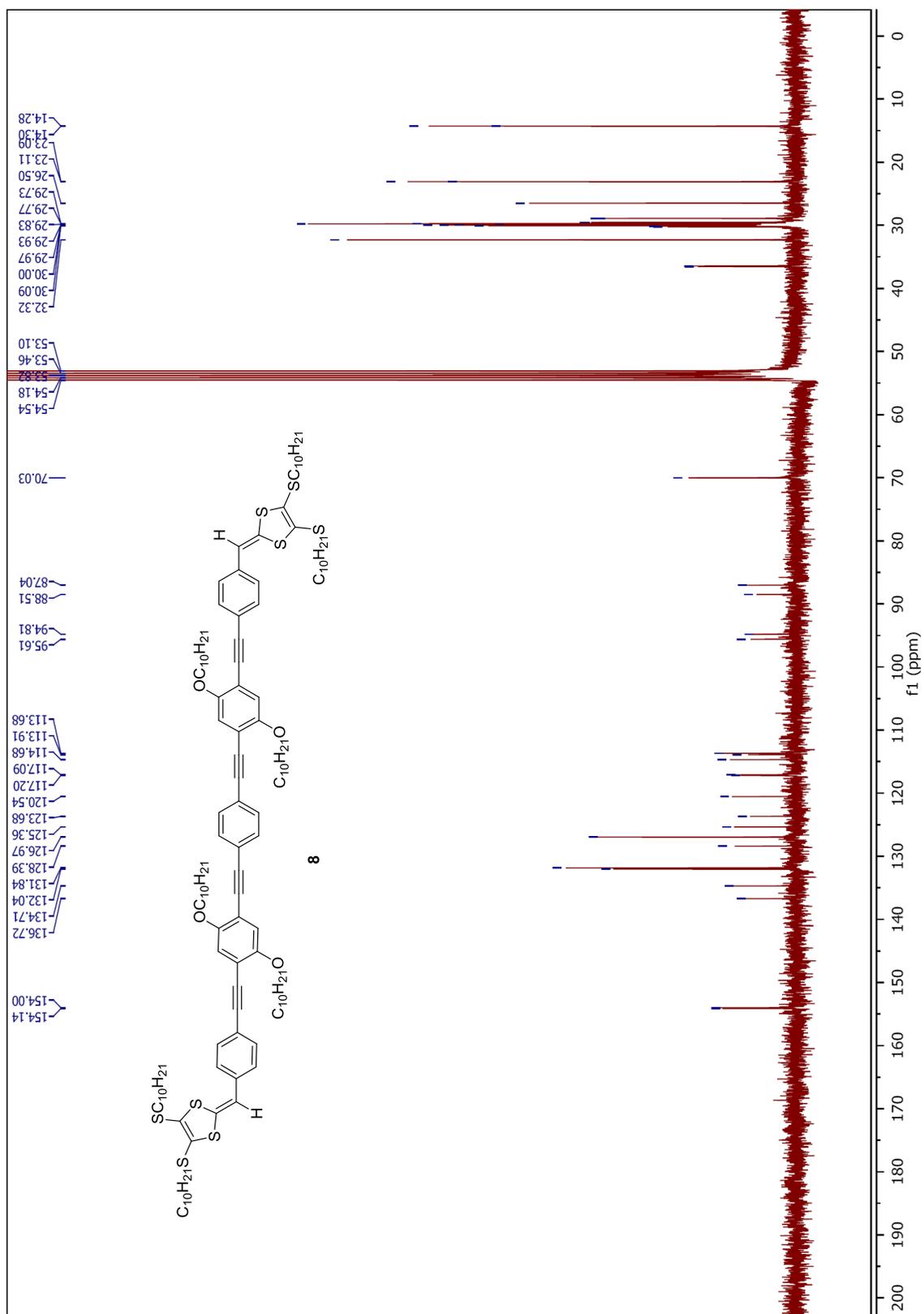


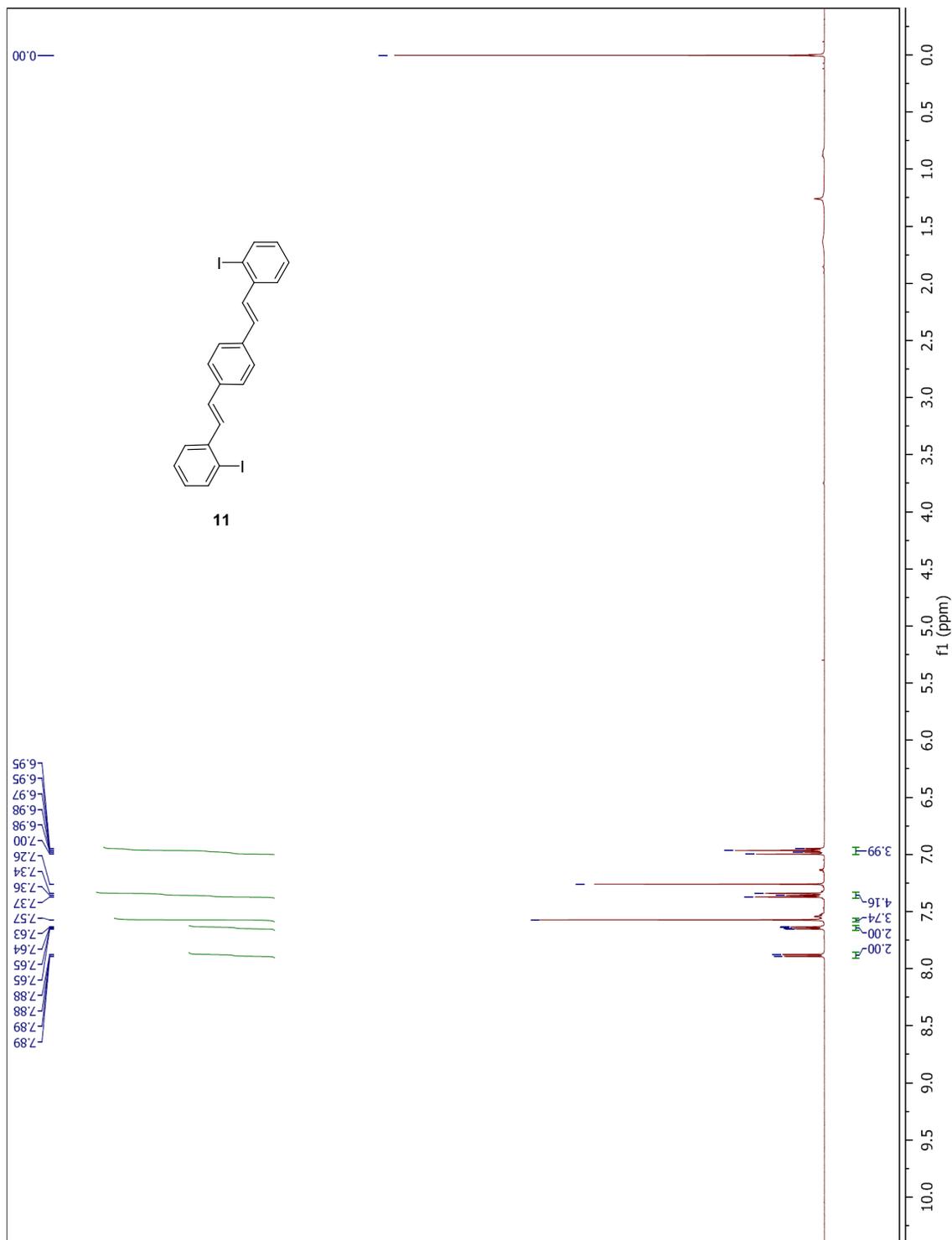
Fig. S-6. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of compound 7.



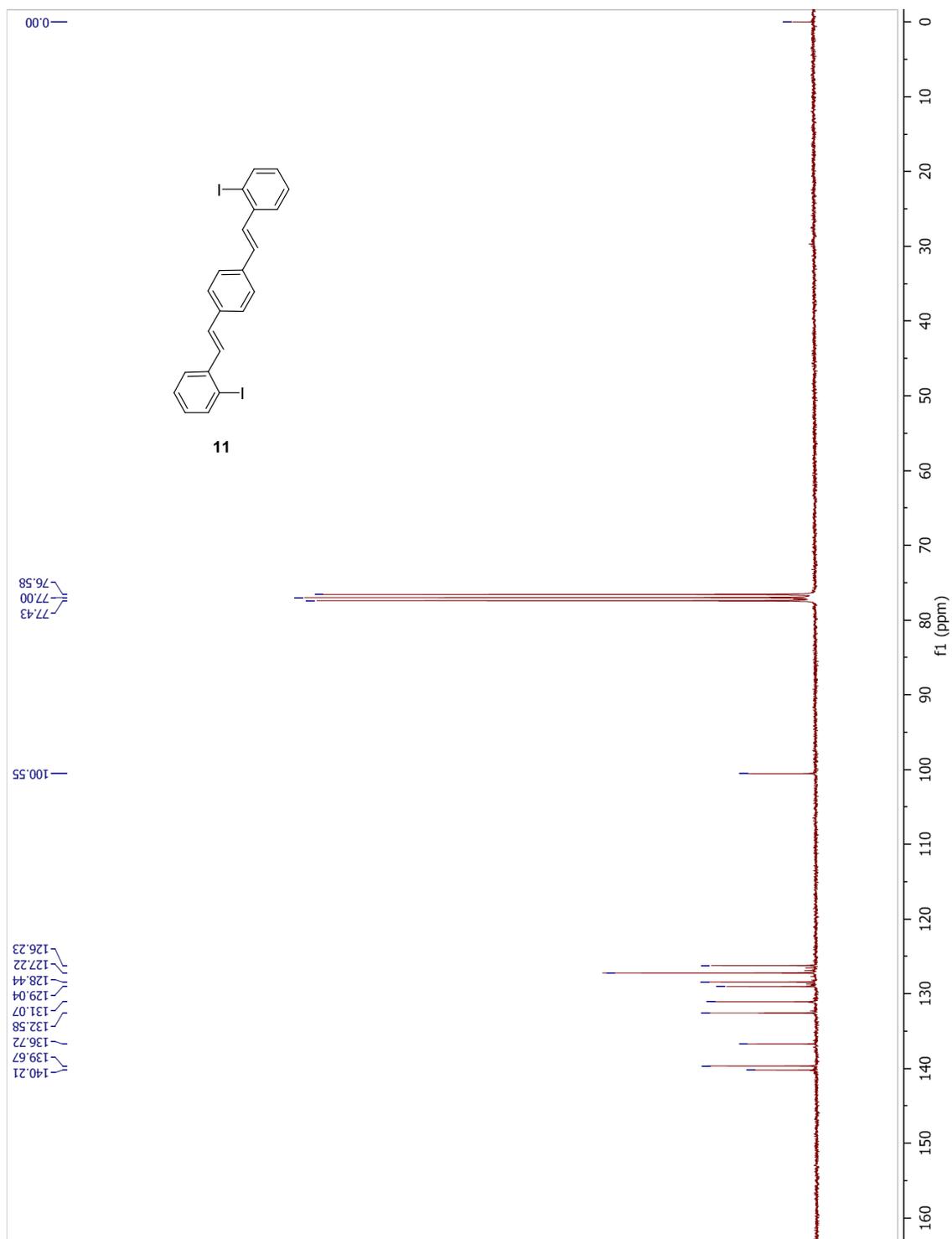
**Fig. S-7.**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum of compound **8**.



**Fig. S-8.**  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum of compound **8**.



**Fig. S-9.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **11**.



**Fig. S-10.** <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of compound 11.

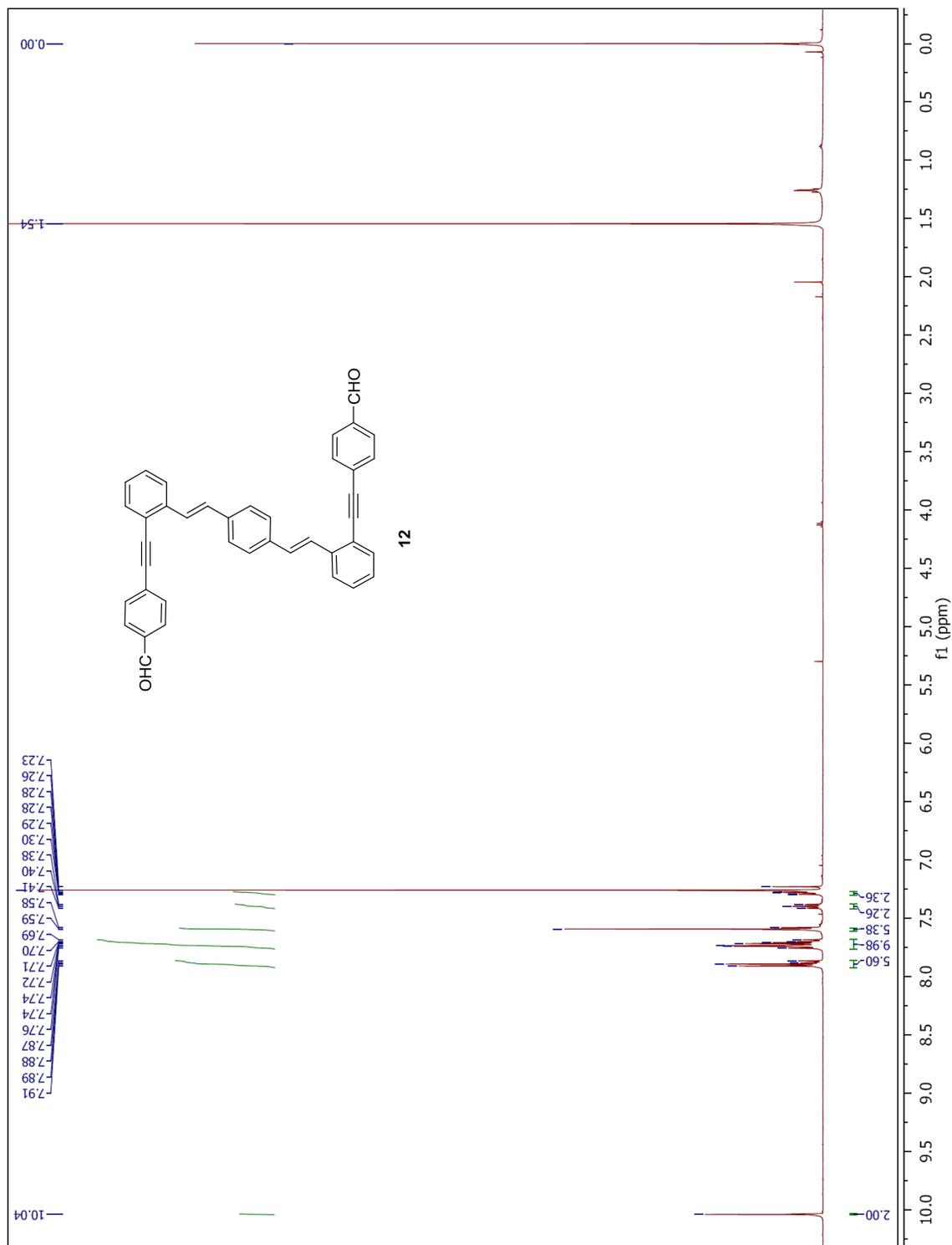


Fig. S-11.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **12**.

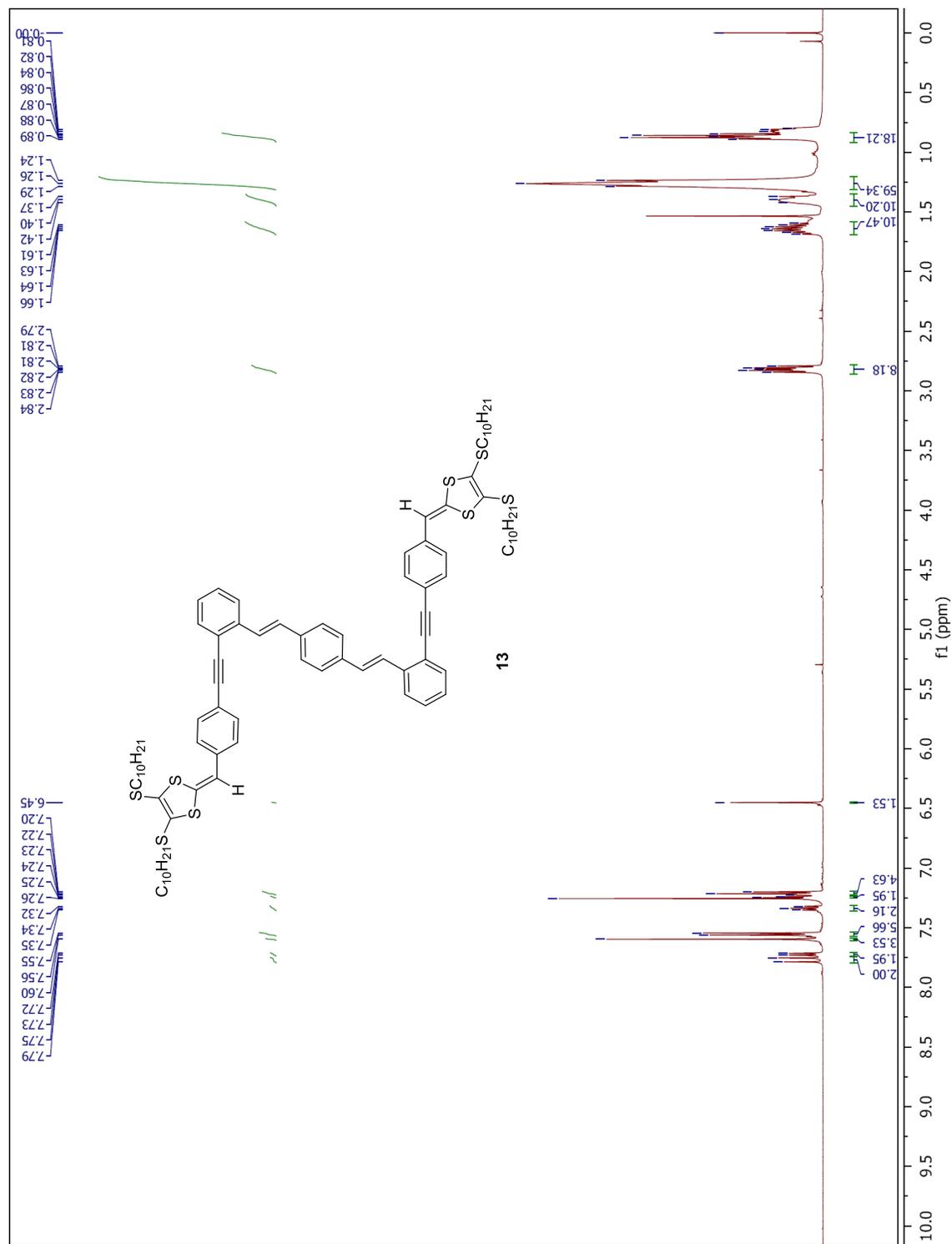
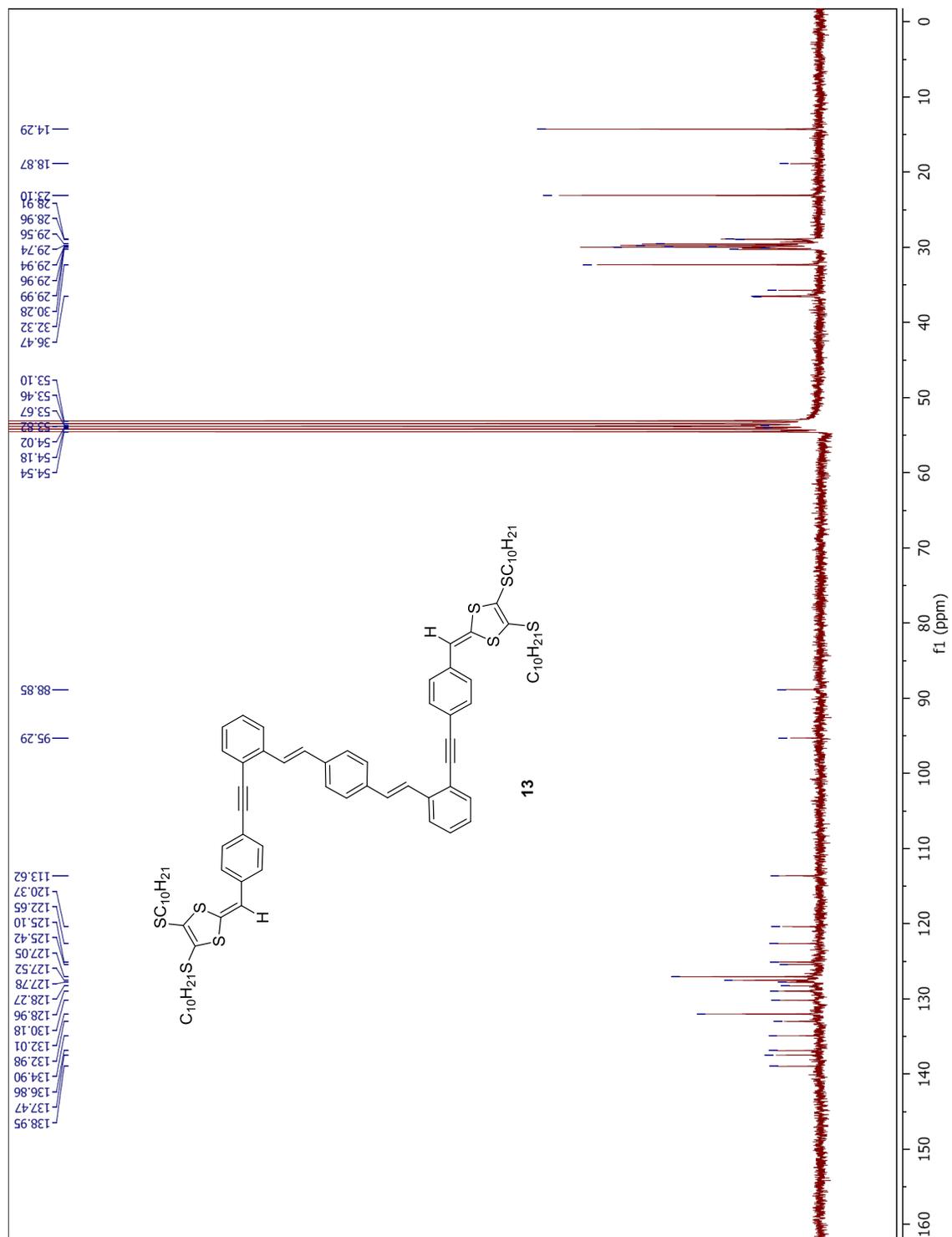


Fig. S-12.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **13**.





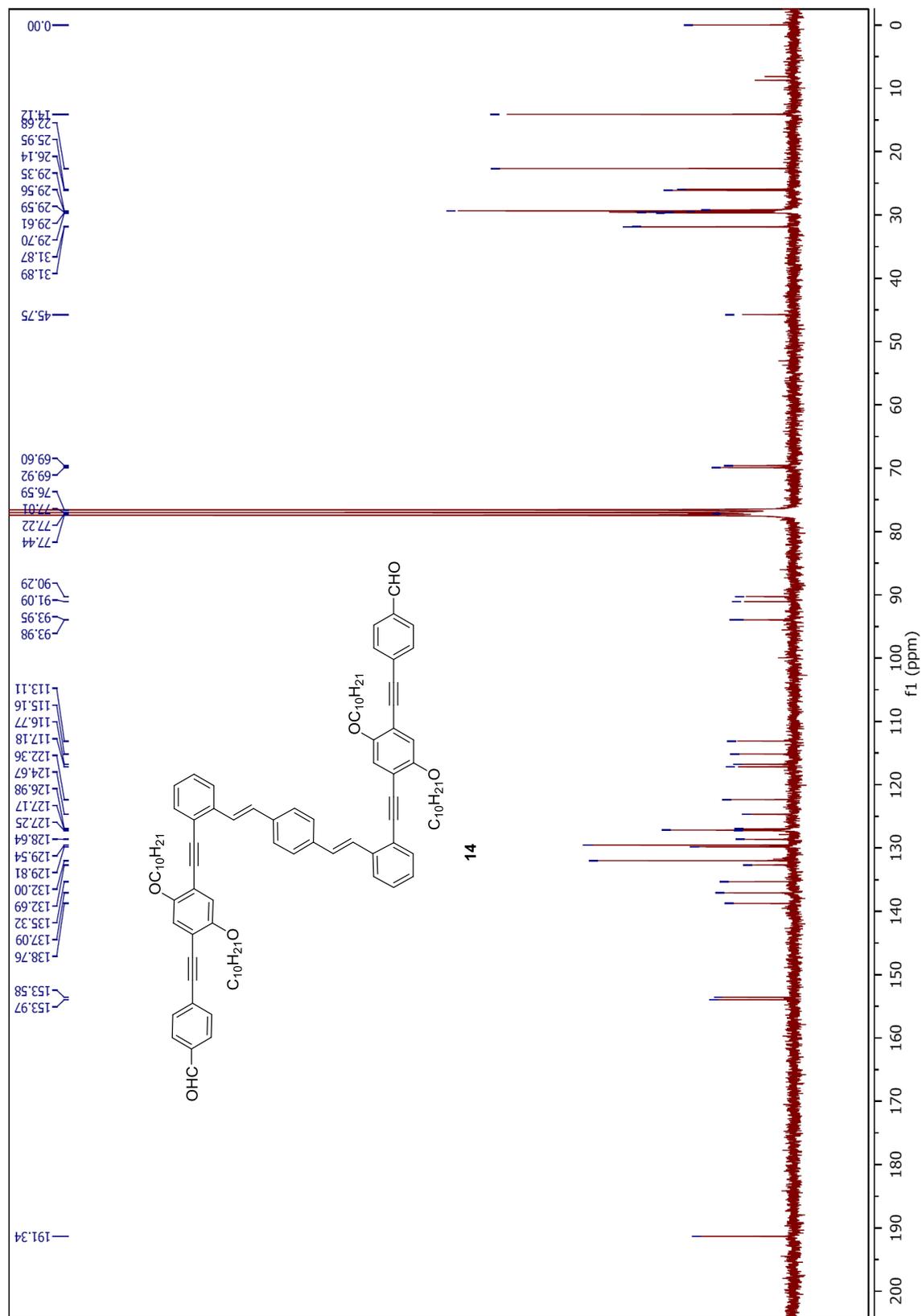


Fig. S-15.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ) spectrum of compound 14.



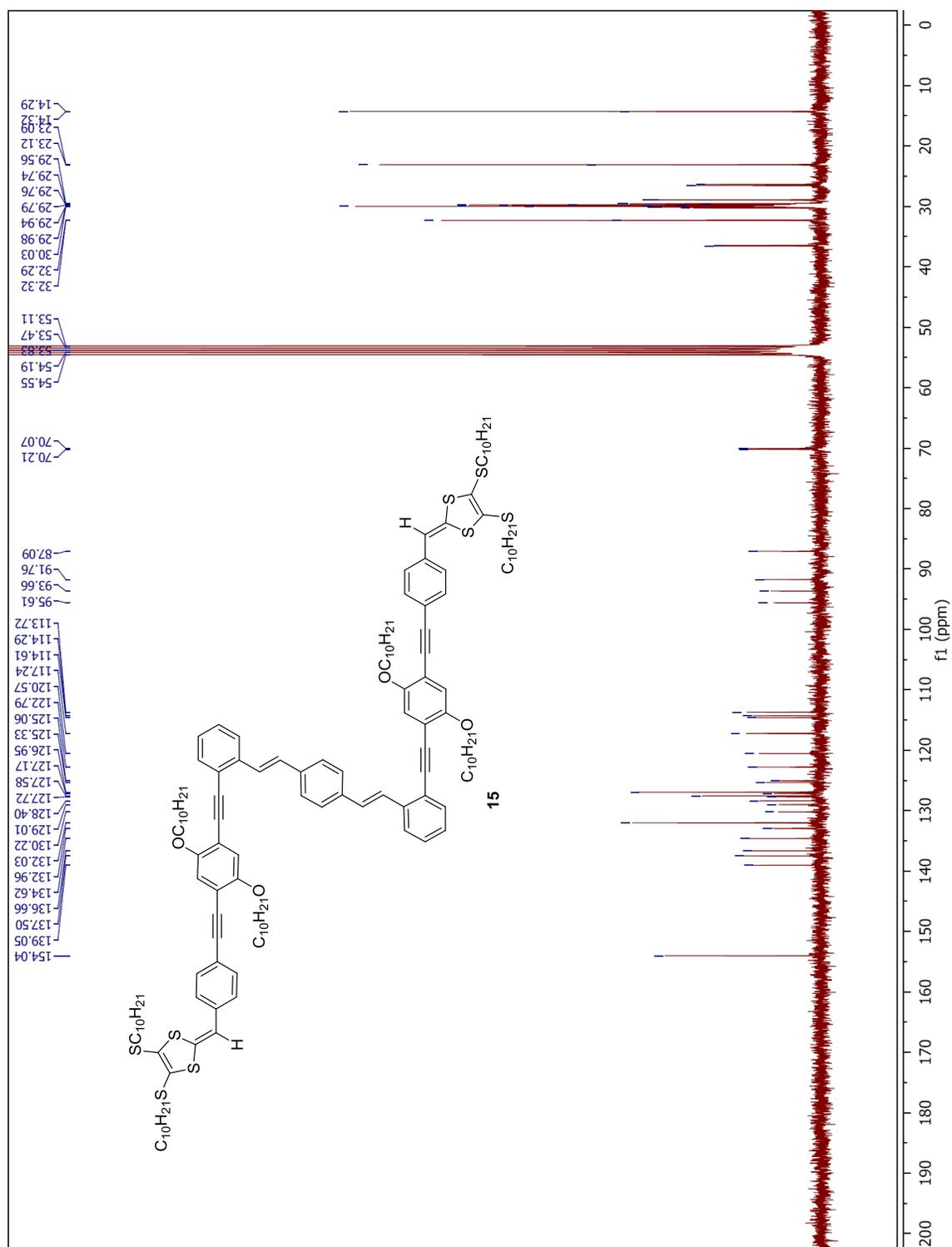
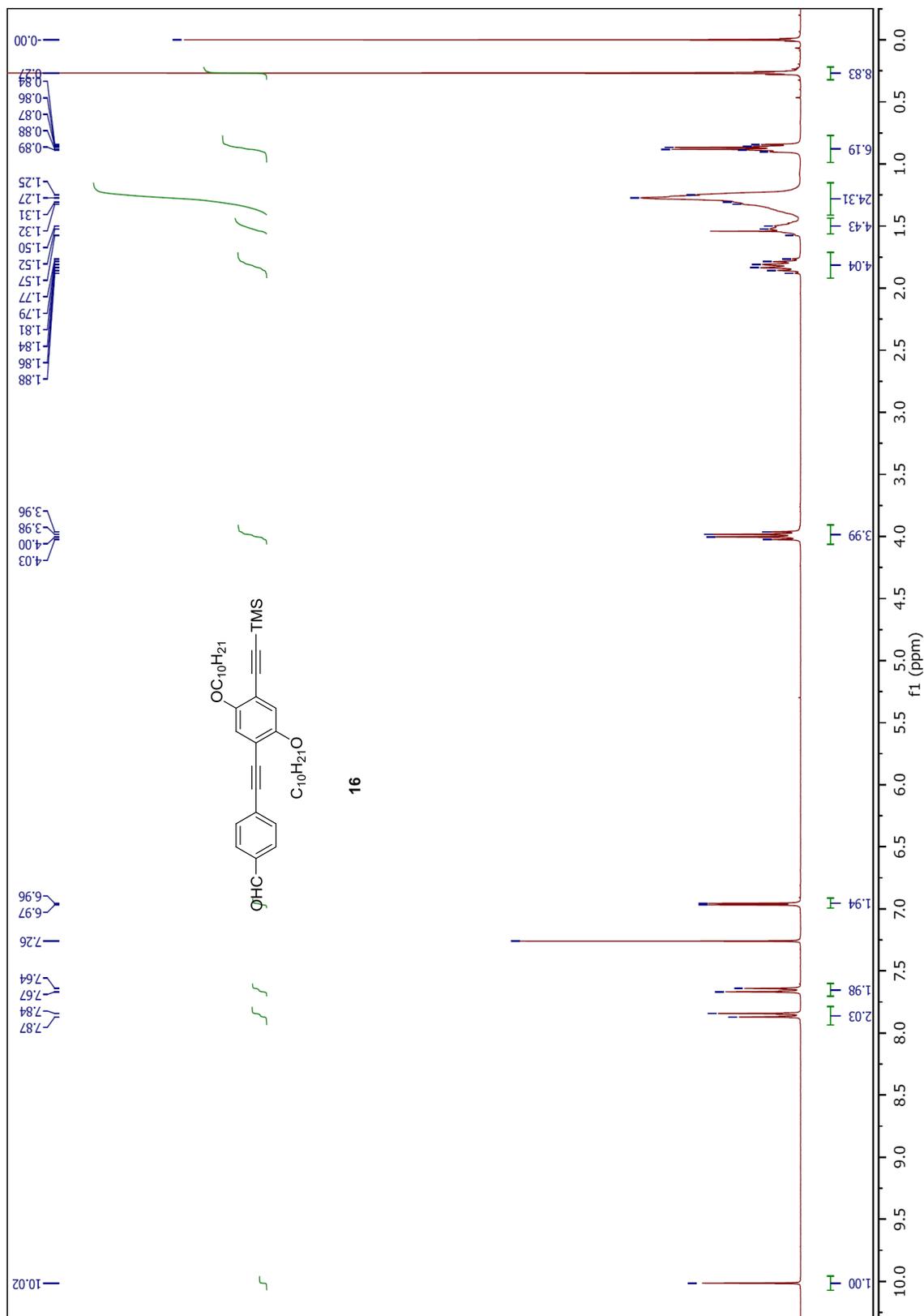
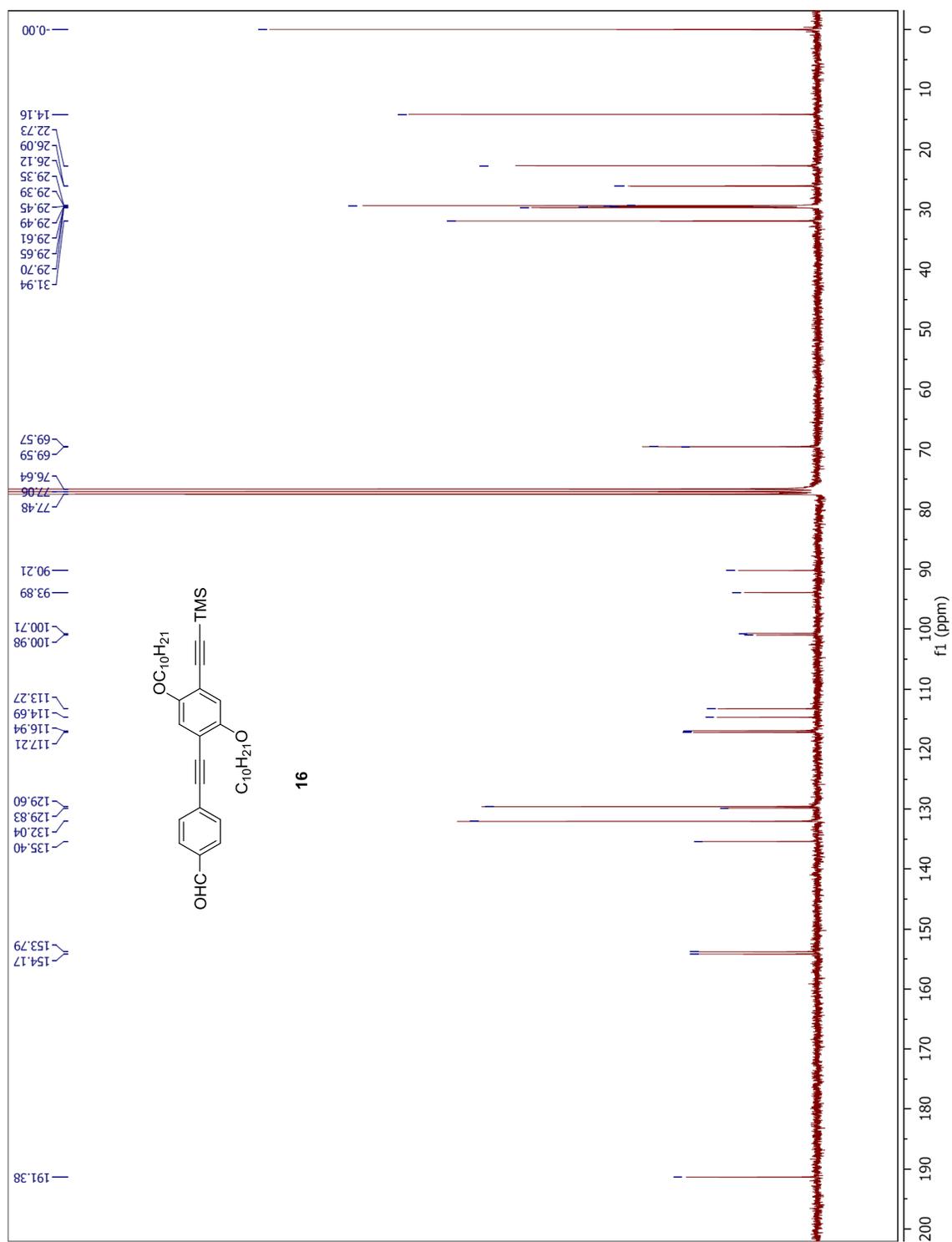
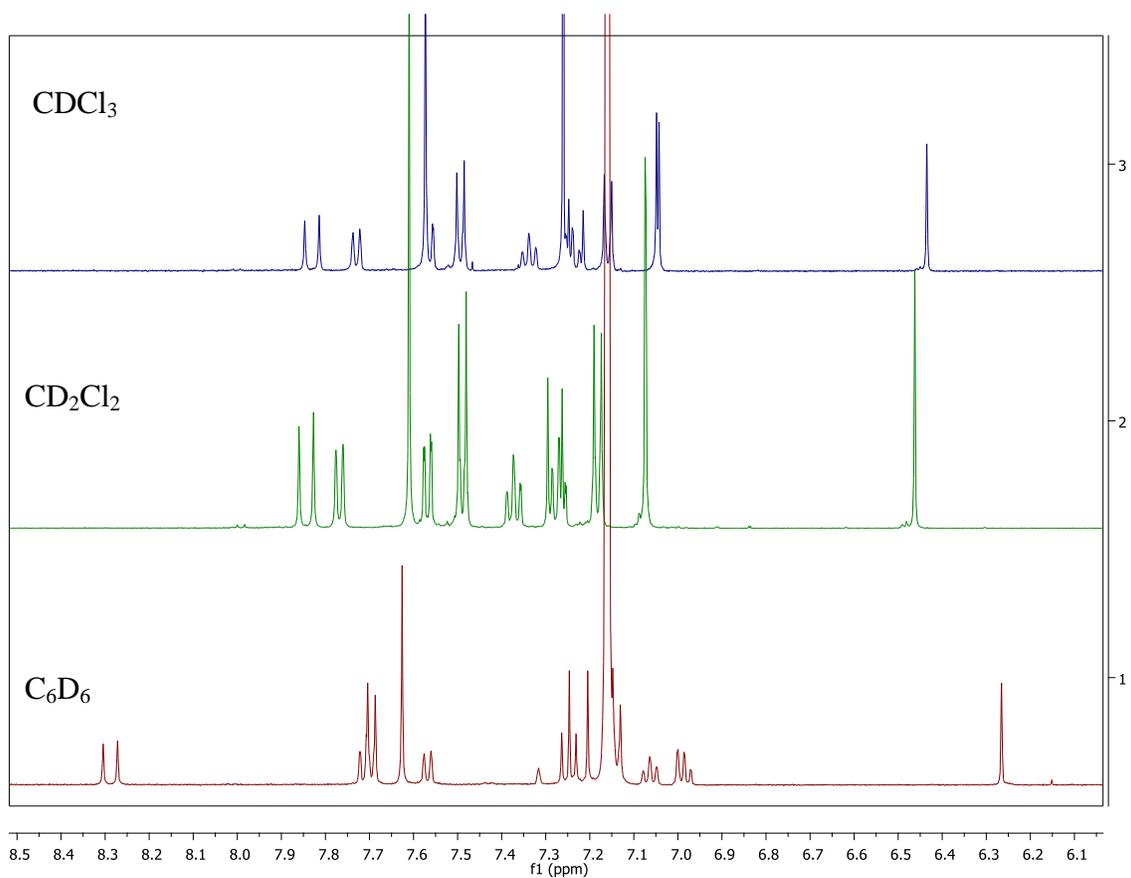


Fig. S-17.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectrum of compound 15.

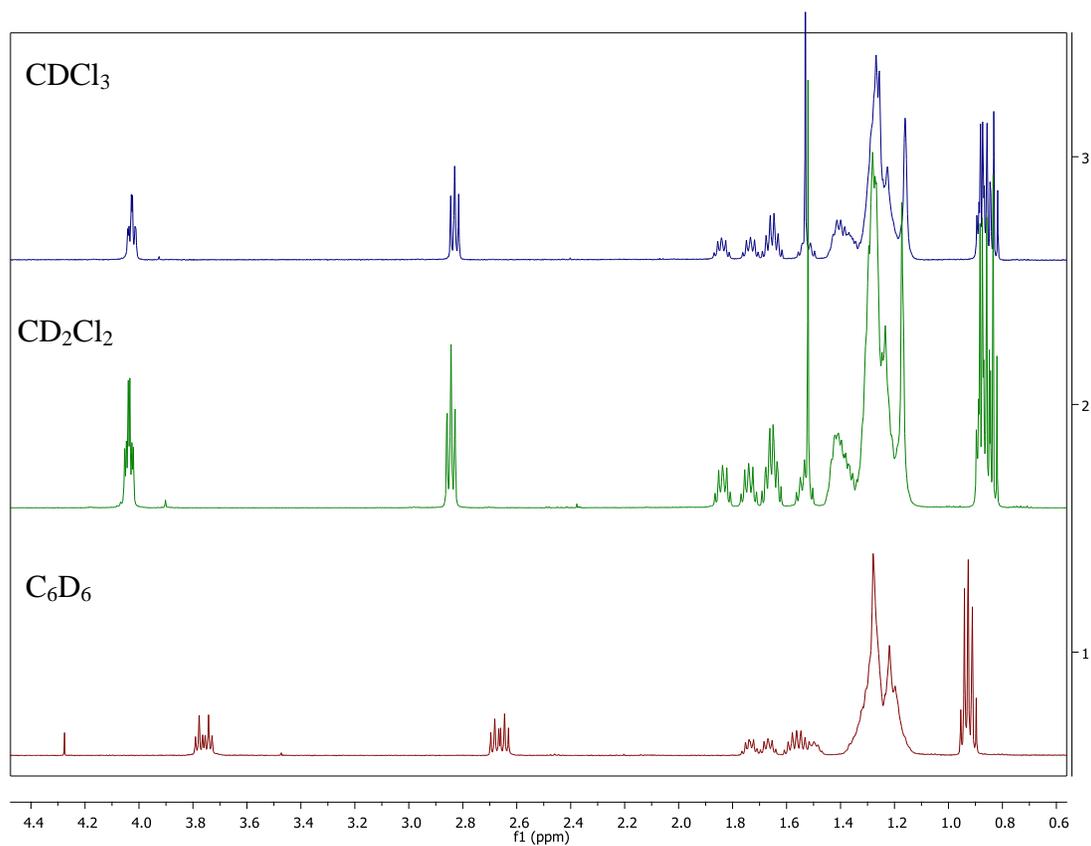


**Fig. S-18.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of compound **16**.





**Fig. S-20.** <sup>1</sup>H NMR spectra of **15** in different solvents (showing the aromatic region).



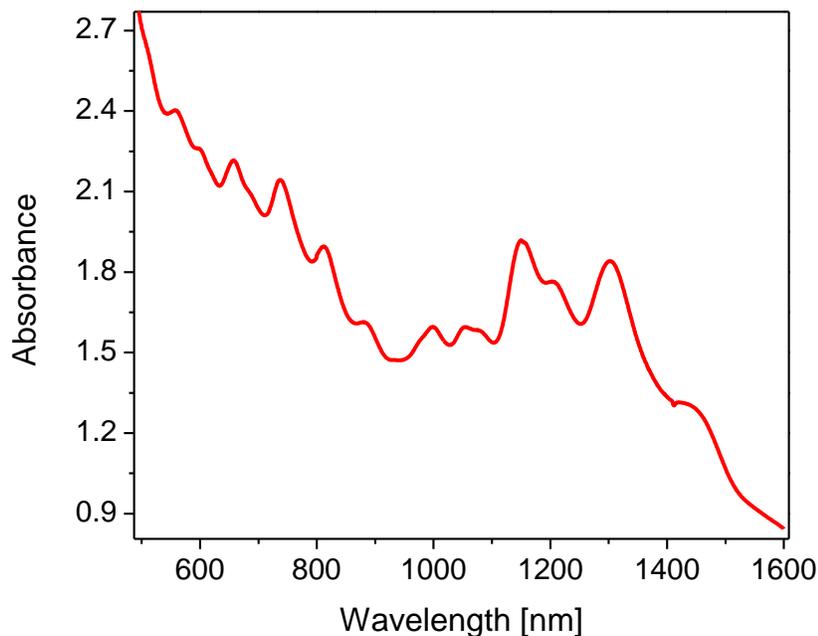
**Fig. S-21.** <sup>1</sup>H NMR spectrum of **15** in different solvents (showing the aliphatic region).

## 2. Dispersion and Release of SWNTs with DTF-Oligomers

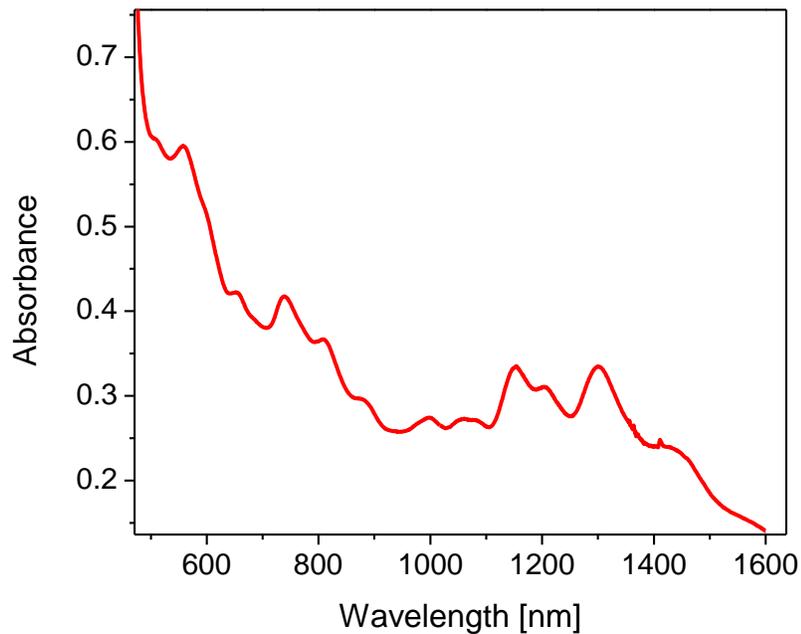
### General procedure for dispersion and release of SWNTs with DTF-oligomers.

DTF-oligomer (ca. 3 mg) and SWNTs (ca. 3 mg) were mixed in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$  (1.5 mL). The resulting mixture was ultrasonicated for 1 h at rt and filtered through a cotton plug to remove undissolved materials. The resulting black solution was then centrifuged for 10 min and filtered through the cotton plug again to afford SWNT suspension. The suspension was analyzed by UV-Vis-NIR spectroscopy to check the amount of SWNTs dispersed in chloroform.

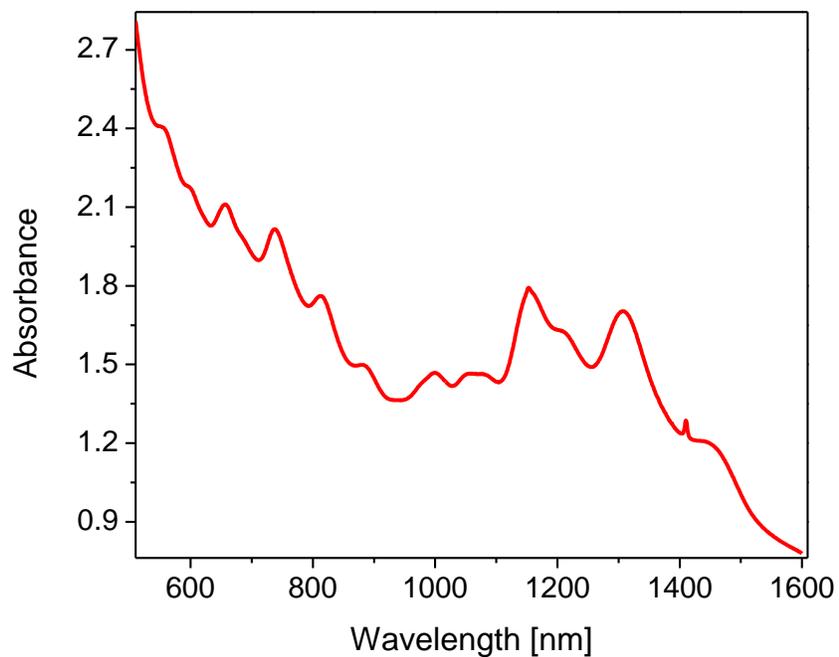
To release SWNTs, hexanes (1.0 mL) was added to the SWNT suspension in  $\text{CHCl}_3$  (1.0 mL) obtained via the above procedure. Precipitation of SWNTs was immediately observed. The mixture was filtered through a filter paper to separate the released SWNTs from the DTF-oligomer solution.



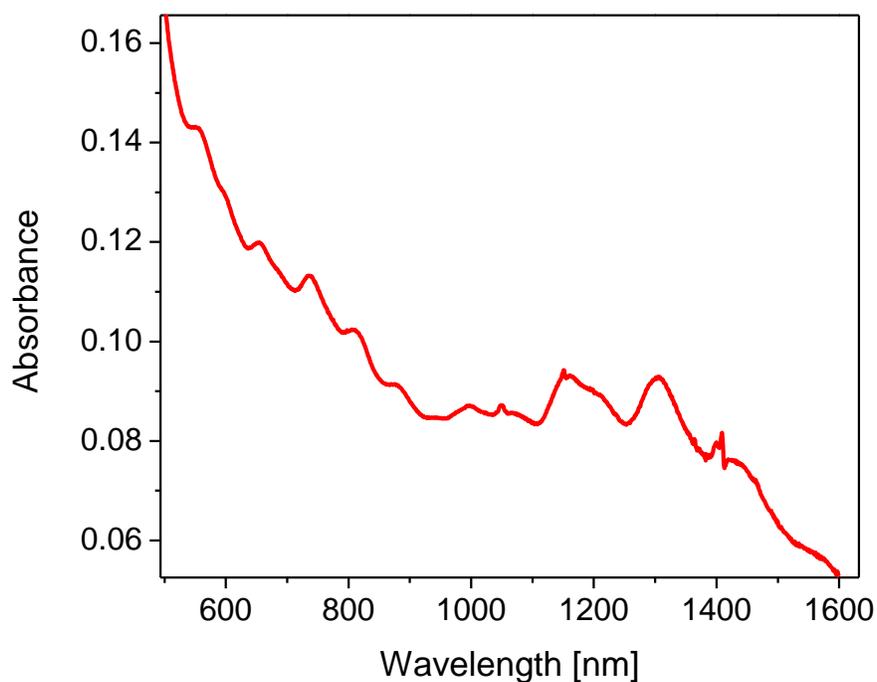
**Fig. S-22.** UV-Vis-NIR spectrum of HiPCO SWNTs dispersed with **15** in  $\text{CHCl}_3$ .



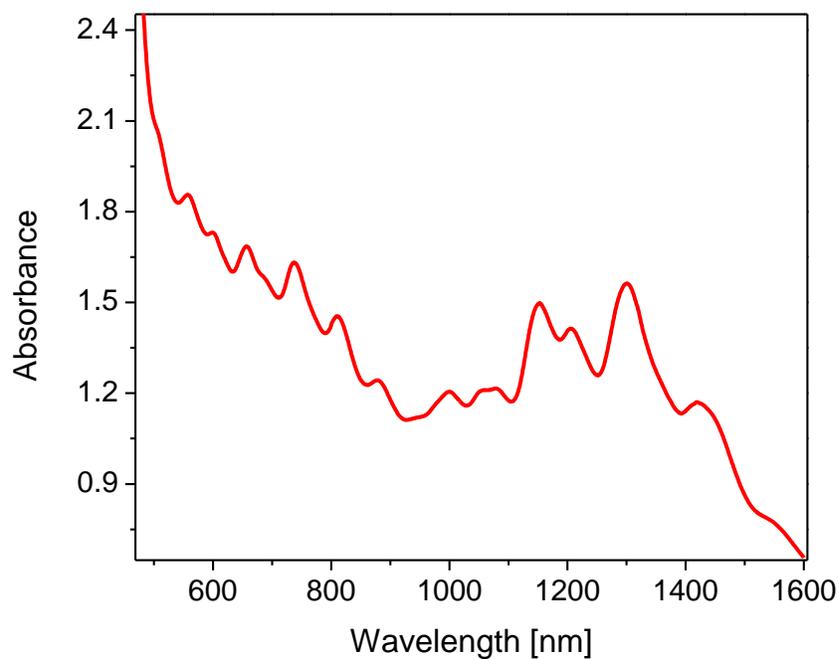
**Fig. S-23.** UV-Vis-NIR spectrum of HiPCO SWNTs dispersed with **13** in  $\text{CHCl}_3$ .



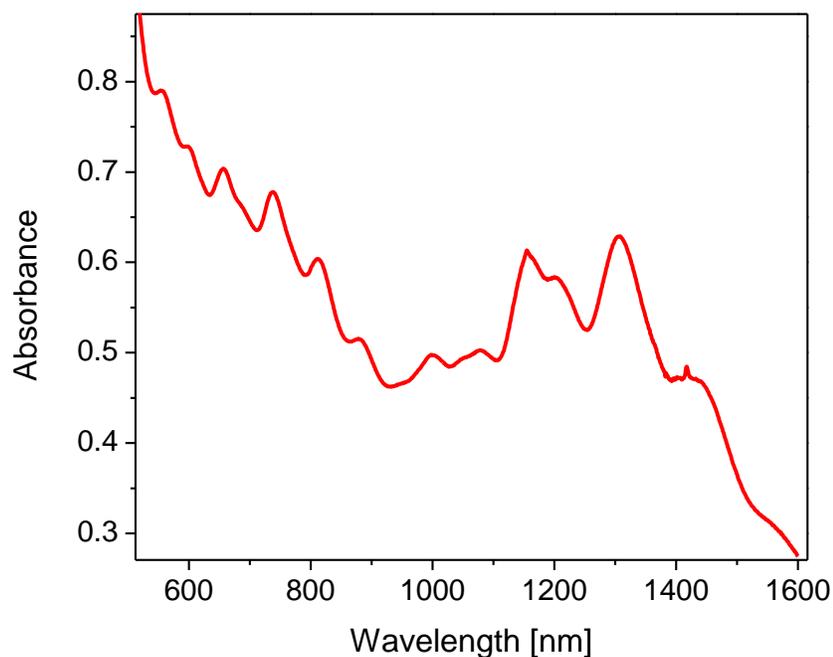
**Fig. S-24.** UV-Vis-NIR spectrum of HiPCO SWNTs dispersed with **8** in  $\text{CHCl}_3$ .



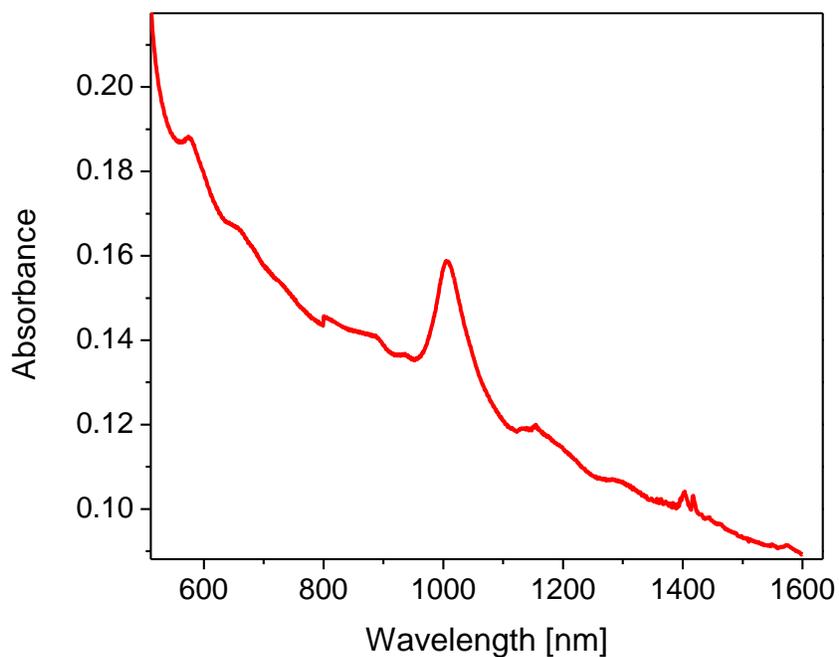
**Fig. S-25.** UV-Vis-NIR spectrum of HiPCO SWNTs dispersed with **5** in CHCl<sub>3</sub>.



**Fig. S-26.** UV-Vis-NIR spectrum of HiPCO SWNTs dispersed with **15** in CH<sub>2</sub>Cl<sub>2</sub>.



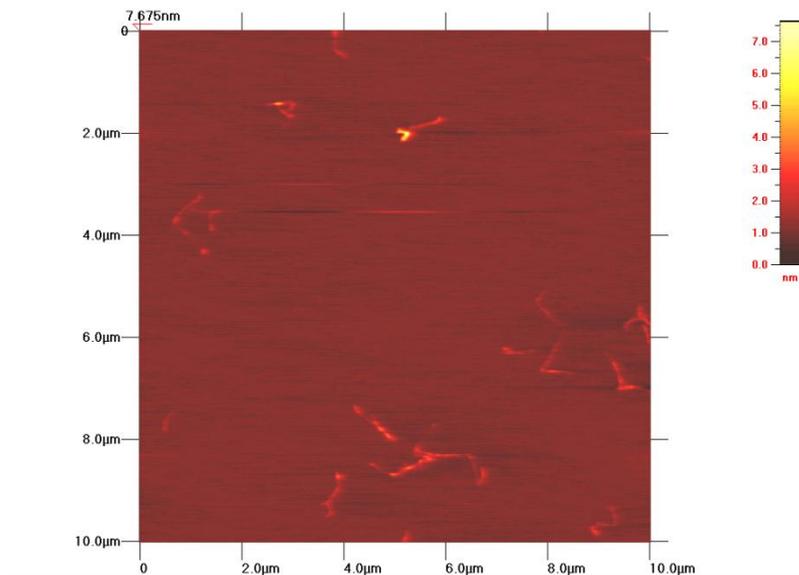
**Fig. S-27.** UV-Vis-NIR spectrum of HiPCO SWNTs dispersed with **8** in CH<sub>2</sub>Cl<sub>2</sub>.



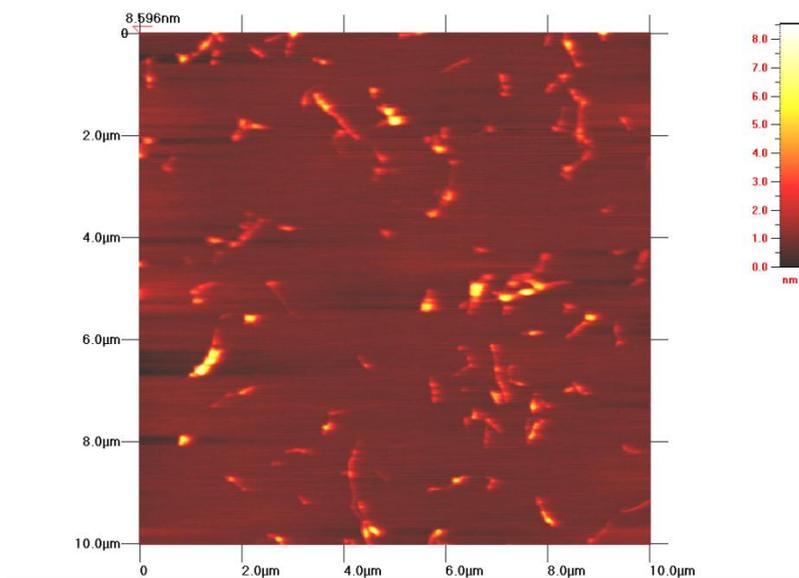
**Fig. S-28.** UV-Vis-NIR spectrum of CoMoCAT SWNTs dispersed with **8** in CH<sub>2</sub>Cl<sub>2</sub>.

### 3. Atomic Force Microscopic Analysis

The samples for AFM measurement were prepared by either drop-casting or spin-coating on a freshly cleaved mica surface. Before spin coating on the mica surface, the nanotubes dispersed solution from above step was diluted 10 times the original volume. The excess DTF-oligomers rinsed off with chloroform followed by drying with nitrogen flow. AFM image was measured out in non counter mode.

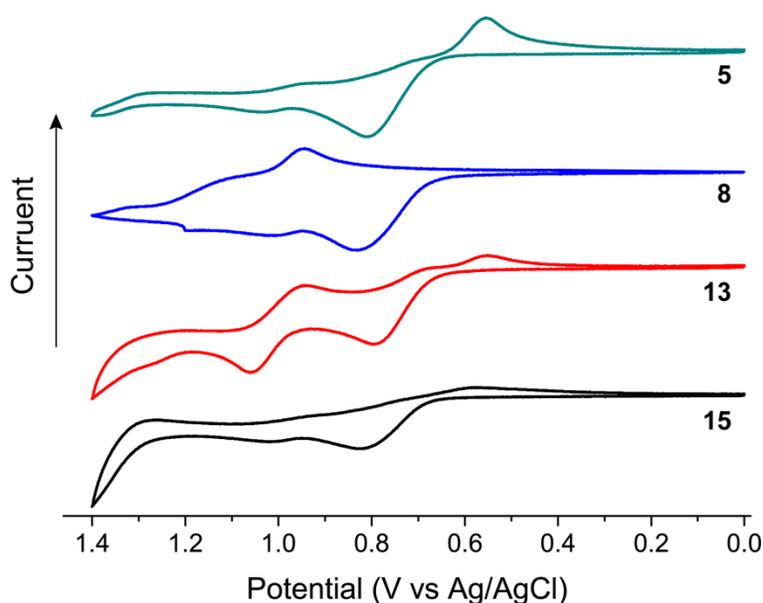


**Fig. S-29.** AFM image (tapping mode) of HiPCO SWNTs dispersed with **13**.

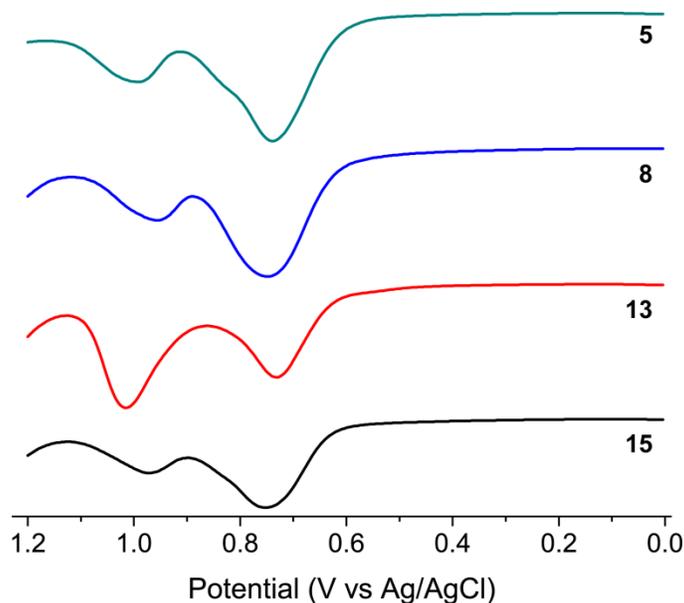


**Fig. S-30.** AFM image (tapping mode) of HiPCO SWNTs dispersed with **15**.

#### 4. Electrochemical Properties



**Fig. S-31.** Cyclic voltammograms of **5** ( $1.33 \times 10^{-3}$  M), **8** ( $0.98 \times 10^{-3}$  M), **13** ( $1.45 \times 10^{-3}$  M), and **15** ( $0.94 \times 10^{-3}$  M). Experimental conditions:  $\text{Bu}_4\text{NBF}_4$  (0.1 M) as the supporting electrolyte,  $\text{CH}_2\text{Cl}_2$  as the solvent, glassy carbon as the working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode, and the scan rate:  $50 \text{ mV s}^{-1}$ .



**Fig. S-32.** Differential pulse voltammogram of **5** ( $1.33 \times 10^{-3}$  M), **8** ( $0.98 \times 10^{-3}$  M), **13** ( $1.45 \times 10^{-3}$  M), and **15** ( $0.94 \times 10^{-3}$  M). Experimental conditions:  $\text{Bu}_4\text{NBF}_4$  (0.1 M) as the supporting electrolyte,  $\text{CH}_2\text{Cl}_2$  as the solvent, glassy carbon as the working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode, scan rate:  $20 \text{ mV s}^{-1}$ , pulse width: 20 mV, pulse period: 200 ms, pulse amplitude: 50 mV, and step: 4 mV.

## 5. Photophysical Characterization

**Quantum yield measurements.** Emission quantum yields were measured in N<sub>2</sub> saturated chloroform solutions at 295 ± 3 K. The absorbance of the samples < 0.3 at the excitation wavelength ( $\lambda_{\text{exc}} = 370$  nm) to prevent distortion of the emission spectral data by inner-filter effects. The radiative quantum yields for all compounds ( $\lambda_{\text{em}}$ ) were determined using quinine bisulfate in 0.1 M aqueous sulfuric acid solution as the actinometer ( $\phi_{\text{std}} = 0.52$  at  $\lambda_{\text{exc}} = 370$  nm) and calculated according to equation ,

$$\phi_{em} = \phi_{std} \left( \frac{A_{std}}{A_{un}} \right) \left( \frac{I_{un}}{I_{std}} \right) \left( \frac{n_{un}}{n_{std}} \right)^2$$

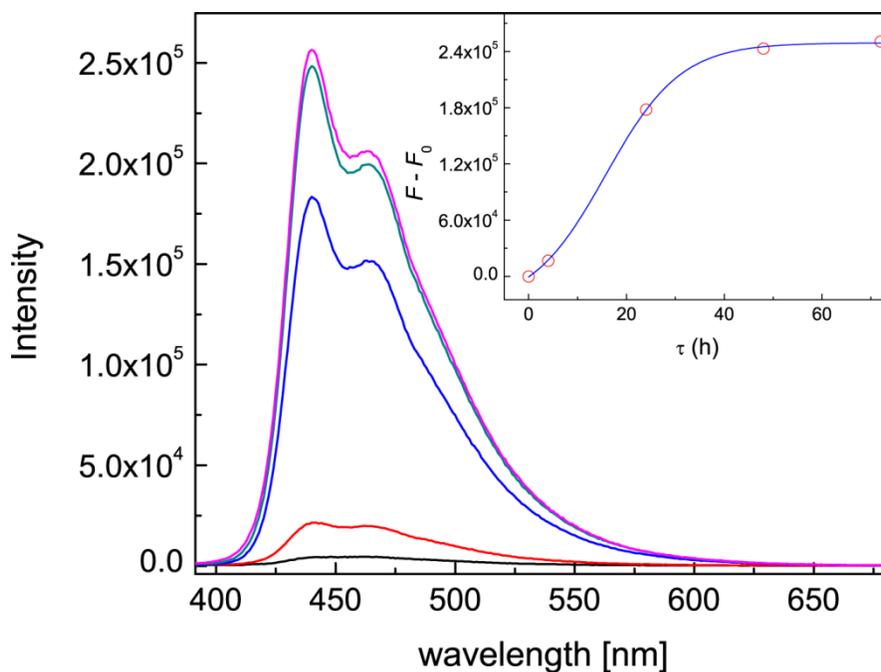
where  $A$  is the solution absorbance,  $I$  the emission intensity,  $n$  the refraction index of the solvent, and the subscripts  $un$  and  $std$  refers to the unknown and standard respectively.

**Fluorescence Spectroscopic Analysis.** Emission spectra were measured on Photon Technology International (PTI) Quantamaster 6000 spectrofluorometer equipped with a continuous xenon arc lamp as the excitation source. The emitting light was collected at 90° to the excitation beam and detected by a Hamamatsu R-928 photomultiplier tube (PMT) in photon counting mode. The PMT was housed in a water-cooled PMT housing supplied by Products for Research Inc. All emission spectra were corrected for instrumental light loss using correction factors supplied by PTI. Experiments were performed in spectral grade benzene (Sigma Aldrich > 99% pure) as solvent.

**Experimental conditions.** Concentration of oligomer **15** was kept at  $1.8 \times 10^{-6}$  M for both the experiments, in which concentration of C<sub>60</sub> fullerene  $5.4 \times 10^{-6}$  M and C<sub>70</sub> fullerene  $5.4 \times 10^{-6}$  M were added. Fluorescence spectra were measured with different time intervals at the excitation wavelength of 370 nm.

## 6. Evidence for Singlet Oxygen in the C=C Bond Cleavage

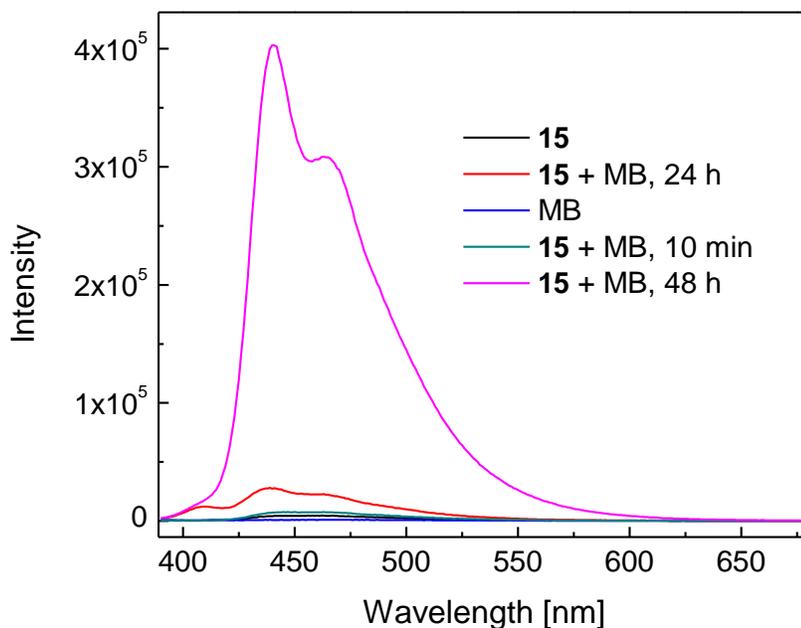
The experimental observations substantiating the involvement of singlet oxygen as oxidant in the C=C bond cleavage of DTF-oligomers are given below. As can be seen from Figure S-33, after the solution of **15** and C<sub>60</sub> in benzene was deoxygenated by three cycles of free-pump-thaw and then placed under argon, the fluorescence spectral monitoring shows a much slower reaction rate in comparison with that observed in the presence of oxygen (see Figure 5A in the paper). This result clearly shows that oxygen in the air is the oxidant of the reaction.



**Fig. S-33.** Fluorescence spectra of **15** ( $1.8 \times 10^{-6}$  M) with C<sub>60</sub> under argon in benzene at varied times. The solution was subjected to three cycles of free-pump-thaw under argon before fluorescence spectroscopic analysis. Inset plot: fluorescence enhancement ( $F - F_0$ ) as a function of time ( $\tau$ ).  $F_0$  and  $F$  denote fluorescence intensities measured at initial and later stages at 440 nm. Excitation wavelength = 370 nm.

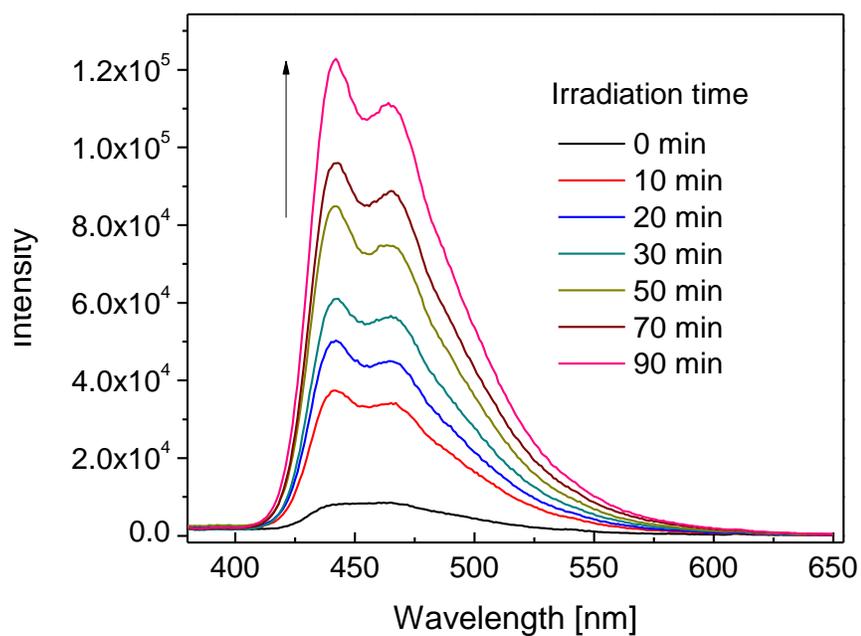
Figure S-34 show the use of a classical singlet oxygen sensitizer, methylene blue (MB), in place of C<sub>60</sub> to promote the C=C bond cleavage of DTF-oligomer **15**. As shown in the fluorescence spectra, after mixing with methylene blue under air for 48 h, the fluorescence intensity grew significantly, indicating the occurrence of C=C bond cleavage leading to highly fluorescent aldehyde product **14**. The result suggests singlet

oxygen is the active oxidant to induce C=C bond cleavage in **15**; however, the reaction under this condition proceeded relatively slower than the case where C<sub>60</sub> is used as the sensitizer, indicating that methylene blue is a poorer sensitizer than fullerenes.



**Fig. S-34.** Fluorescence spectra of **15** ( $1.8 \times 10^{-6}$  M) in benzene upon addition of methylene blue (MB) under air for varied times and the fluorescence spectrum of pure MB in benzene. Excitation wavelength = 370 nm.

Finally, a photochemical condition to induce singlet oxygen was applied. As shown in Figure S-35, the solution of **15** in benzene under air was subjected to UV light irradiation at 365 nm and monitored by fluorescence spectroscopy at varied times. The results show a steady increase in the fluorescence intensity similar to the case of Figure 5A, indicating that **15** underwent oxidative cleavage reaction in the presence of singlet oxygen.



**Fig. S-35.** Fluorescence spectra of **15** ( $1.8 \times 10^{-6}$  M) in benzene upon UV light irradiation (at 365 nm) under air for varied times. Excitation wavelength = 370 nm.