Supplementary Information (SI) for Green Chemistry.
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Supplementary Information for

A Green and Recyclable Approach for Synthesizing Disulfides

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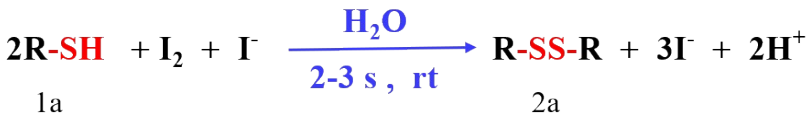
Contents：

1.General procedure for synthesis of disulfides



1a 2a

Add 1 ml of water, 0.5 mmol I_2, 1.5 mmol KI in a 10 ml tube, sonicate for 2 min waiting for the iodine to dissolve completely, add 1 mmol 1a, shake for 3-5 s.

2.Research on post-processing methods

In order to further separate the products and iodide ions for subsequent reoxidation of iodide ions to iodine, we compared various separation methods.

Table S1. post-processing methods

Method	Procedure	Advantages and disadvantages
Extraction method	Extract the reaction mixture three times with an equal volume of ethyl acetate, then remove the ethyl acetate by rotary evaporation to obtain pure disulfide. Note that the extraction should be carried out in a glove box.	The extraction and separation process is efficient and simple, and ethyl acetate is easily recoverable for reuse.
Ion exchange column	When the reaction mixture passes through an anion exchange column, iodide ions are adsorbed onto the resin, releasing hydroxide ions. The solution is then evaporated to dryness, and the residue is washed with ethanol to obtain pure disulfide.	This method offers high yield, low cost, and minimal use of organic solvents. However, the co-elution of hydroxide ions with iodides complicates subsequent reactions.
C18 reverse phase column	After concentration, the reaction mixture is passed through a C18 reverse-phase column. Pure water first elutes the polar iodide ions, followed by the elution of the less polar disulfides.	This method achieves high separation yield, avoids the use of large amounts of organic solvents, and allows iodide ions to be eluted with hydrogen ions, facilitating subsequent reactions. However, the high cost of the C18 reverse-phase column makes it unfavorable for cost control.

3.General process of cyclic reactions

$$2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$$

In order to ensure the effectiveness of this recycling system, we analyzed the conversion rate of iodide ions oxidized by hydrogen peroxide, and Figure.S1(a) shows the relational curve of the yield of iodide ions oxidized with the variation of the I^-:H_2O_2 ratio. As the I^-:H_2O_2 ratio increases, the yield shows a nonlinear increase, which is attributed to the fact that iodine monomers can effectively catalyze the decomposition of hydrogen peroxide. The oxidative conversion of iodide ions reached 40% when I^-: H_2O_2=0.46, which is the iodine concentration before the reaction (KI: I_2=3:1). This result verified the high efficiency and stability of hydrogen peroxide as a regenerative oxidant, and provided a strong support for realizing the recycling of the reaction system. To investigate the regeneration efficiency of iodine during multiple cycles, titration experiments were conducted on the iodide ion solution after each cycle to monitor its concentration variation. A 0.5 M ascorbic acid solution was employed as the titrant, and the molar quantity of iodide ions was determined through stoichiometric calculations. As shown in Figure.S2(b), the retention of iodide ions exhibited remarkable stability throughout five consecutive cycles, with negligible concentration decrement ($\Delta C < 0.8\%$). This persistent conservation of iodine species demonstrates the complete recyclability of the proposed methodology.

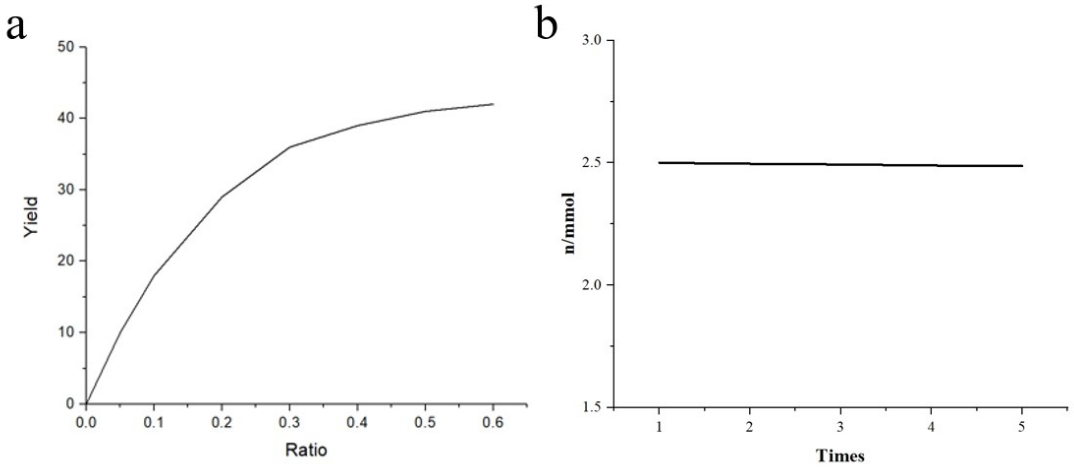


Figure S1. (a) Oxidation yield curve of iodide ions; (b) I^- cycling-regeneration efficiency

4. structural analysis

We carried out structural analysis of the prepared disulfide, as shown in the IR pattern shown in Figure.S2(a), mercaptoethanol has a distinct mercapto absorption peak at 2556 cm^{-1}, and the mercapto absorption peak at 2556 cm^{-1} disappears after oxidation with hydrogen peroxide, which proves that mercaptoethanol was successfully oxidized. However, it is noteworthy that a new absorption peak appeared at 1658 cm^{-1}, which corresponds to the stretching vibration of the carbonyl (C=O) bond. The appearance of this absorption peak indicates that the oxidizing power of hydrogen peroxide was too strong, which not only oxidized mercaptoethanol to disulfide, but also led to the overoxidation of some of the mercaptoethanol to produce carbonyl compounds. The infrared spectra after iodine oxidation showed a clear disappearance of the mercapto absorption peak at 2556 cm^{-1}, a change that clearly indicated that the mercapto group of mercaptoethanol had been oxidized to produce disulfide (-S-S-). Moreover, no additional absorption peaks appeared during this oxidation process, indicating that iodine as an oxidizing agent did not produce other by-products when oxidizing mercaptoethanol. The disulfide oxidized with iodine was subjected to Raman microscopic spectroscopy, as shown in Figure.S2(b), the characteristic peak at 510 cm^{-1} is that of disulfide bonding, which indicates that mercaptoethanol has been oxidized to disulfide.

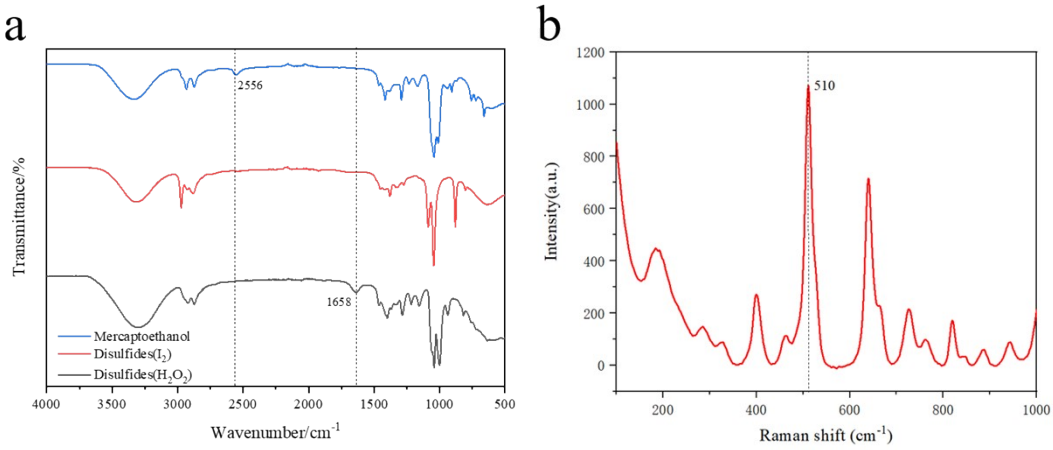


Figure S2. (a) Infrared spectrum of disulfides; (b) Raman spectrum of disulfides

5.^{1}H NMR Spectra for Compounds

The ^{1}H NMR spectra of all compounds were recorded using a Bruker Avance III HD 400 MHz superconducting nuclear magnetic resonance (NMR) spectrometer system and dissolved in deuterated chloroform ($CDCl_3$) for analysis.

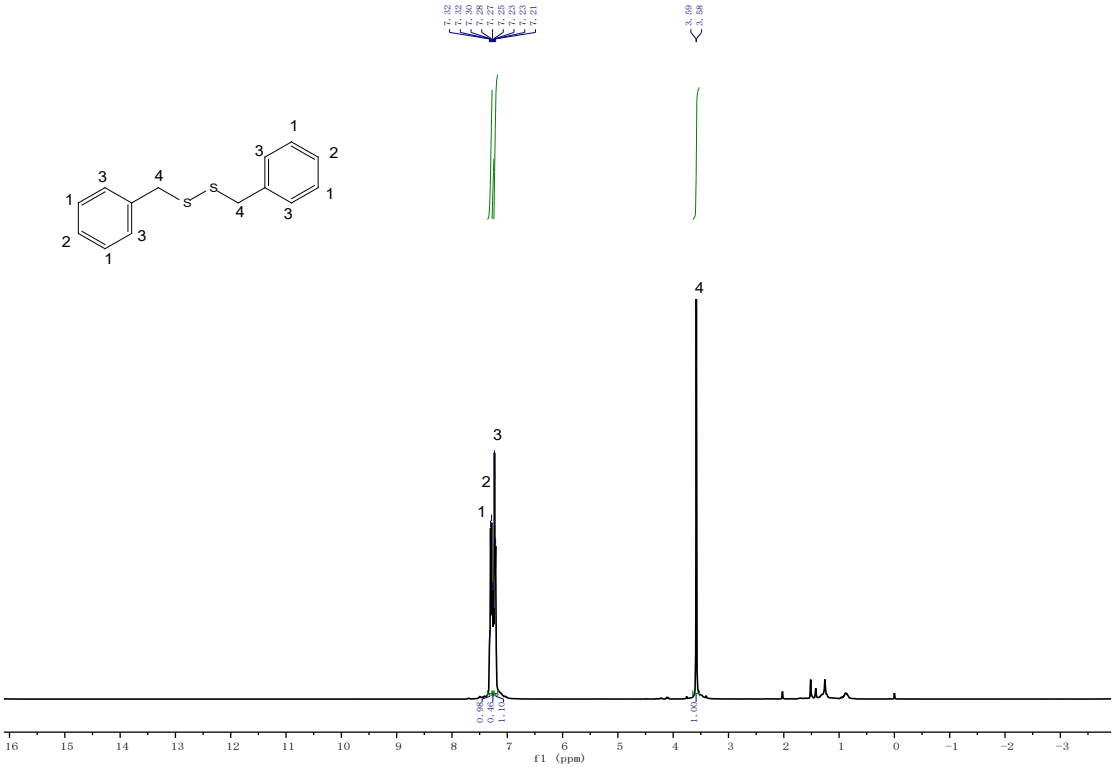


Figure S3. The ^{1}H NMR spectrum of 1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32, 7.32, 7.30, 7.28, 7.27, 7.25, 7.23, 7.23, 7.21, 3.59, 3.58.

The peaks at chemical shifts δ 7.32, 7.28, and 7.23 correspond to aromatic protons on the benzene ring, while the peak at δ 3.58 is assigned to the methylene protons.

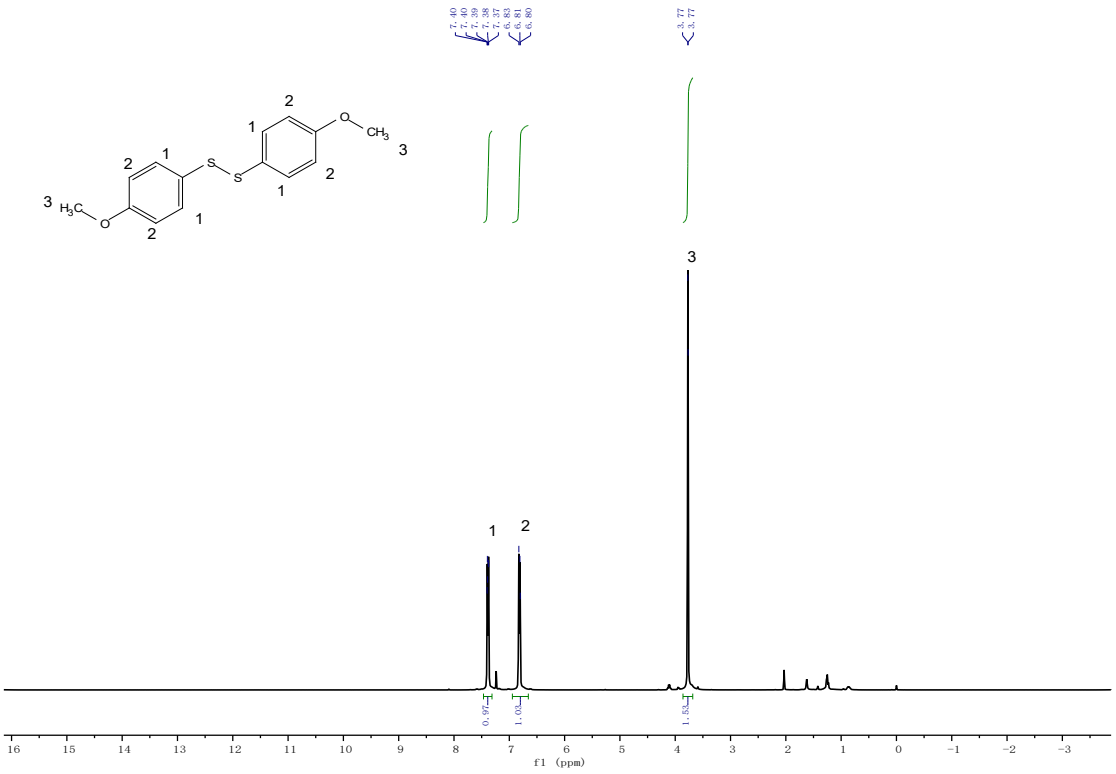


Figure S4. The ^{1}H NMR spectrum of 2a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40, 7.40, 7.39, 7.38, 7.37, 6.83, 6.81, 6.80, 3.77, 3.77.

The peaks at chemical shifts δ 7.40 and 6.81 correspond to aromatic protons on the benzene ring, while the peak at δ 3.77 is assigned to the methyl protons adjacent to an oxygen atom.

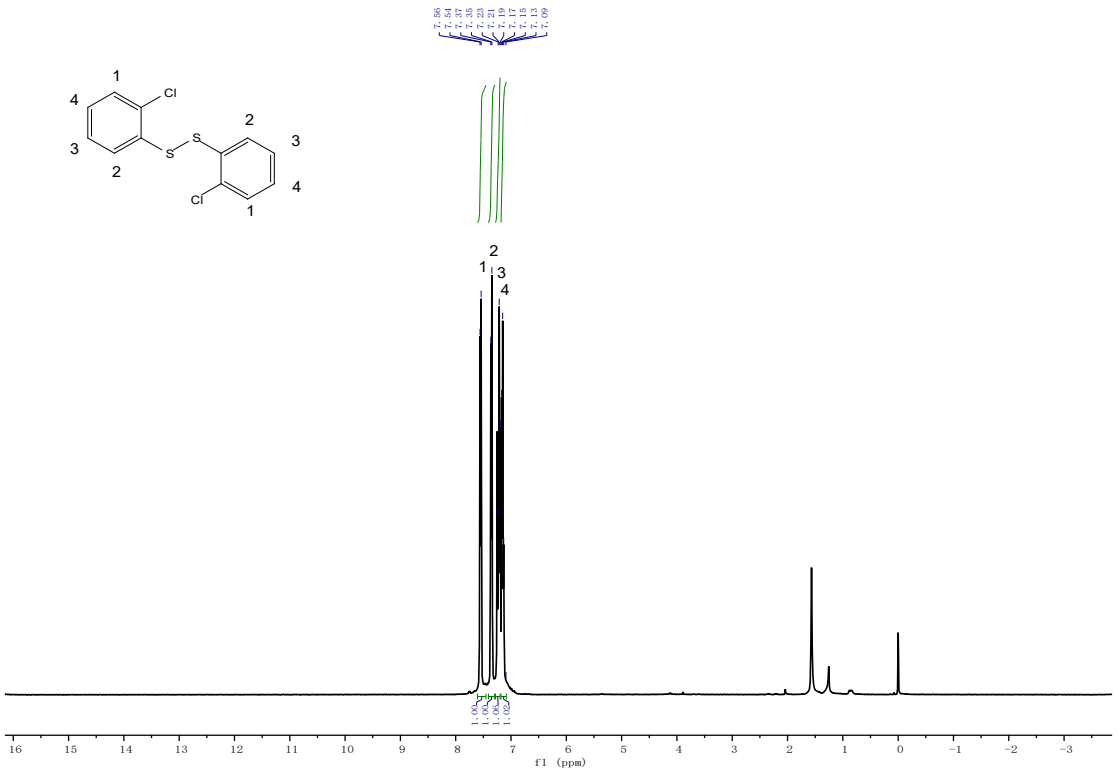


Figure S5. The ^{1}H NMR spectrum of 3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56, 7.54, 7.37, 7.35, 7.23, 7.21, 7.19, 7.17, 7.15, 7.13, 7.09.

The peaks observed at chemical shifts δ 7.56, 7.37, 7.23, 7.15, and 7.09 are all characteristic of aromatic protons in the benzene ring.

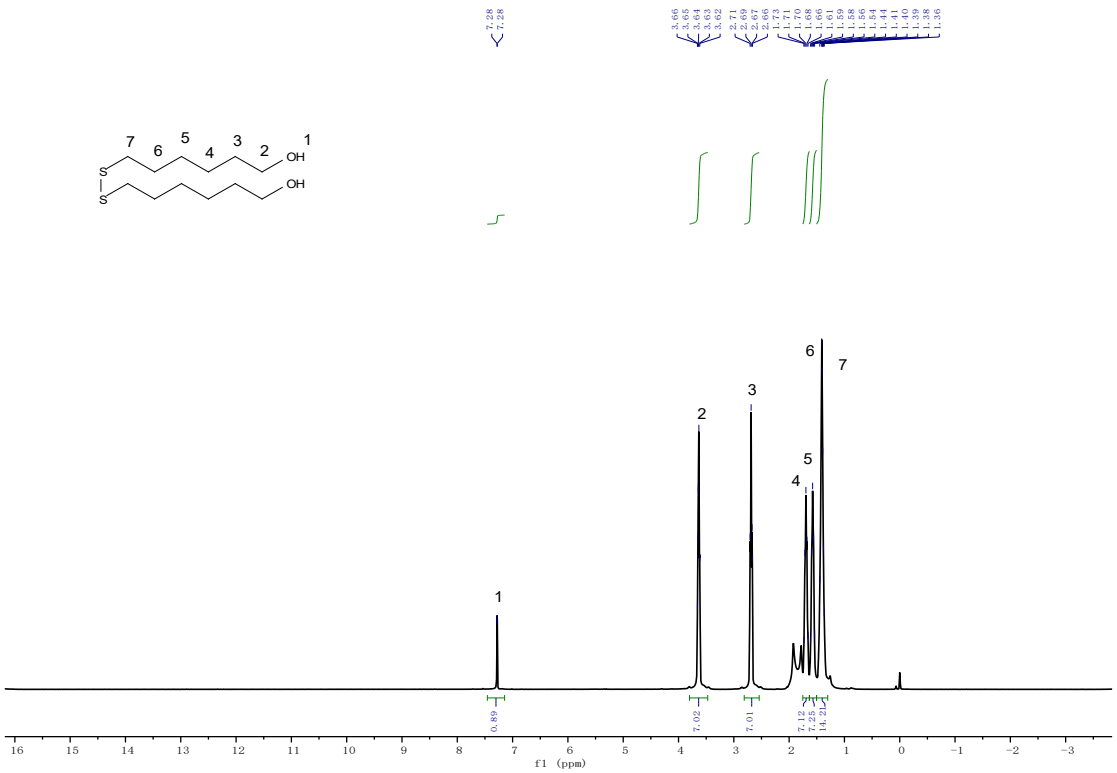


Figure S6. The ^{1}H NMR spectrum of 1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28, 7.28, 3.66, 3.65, 3.64, 3.63, 3.62, 2.71, 2.69, 2.67, 2.66, 1.73, 1.71, 1.70, 1.68, 1.66, 1.61, 1.59, 1.58, 1.56, 1.54, 1.44, 1.41, 1.40, 1.39, 1.38, 1.36.

The peak at chemical shift δ 7.28 is attributed to methyl protons, while the signals at δ 3.65, 2.69, 1.71, 1.61, 1.41, and 1.38 are all characteristic of methylene protons.

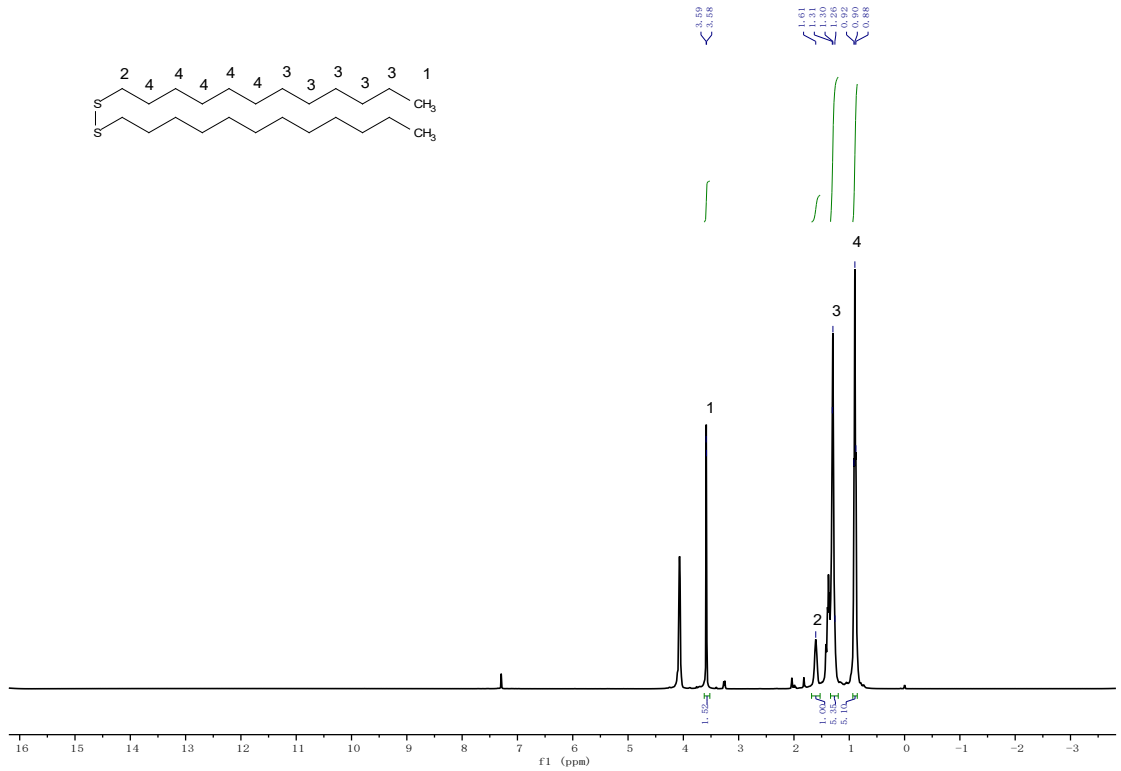


Figure S7. The ^{1}H NMR spectrum of 2c

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59, 3.58, 1.61, 1.31, 1.30, 1.26, 0.92, 0.90, 0.88.

The peak at chemical shift δ 3.59 is attributed to methyl protons, while the signals at δ 1.61,1.30, 0.90 are all characteristic of methylene protons.

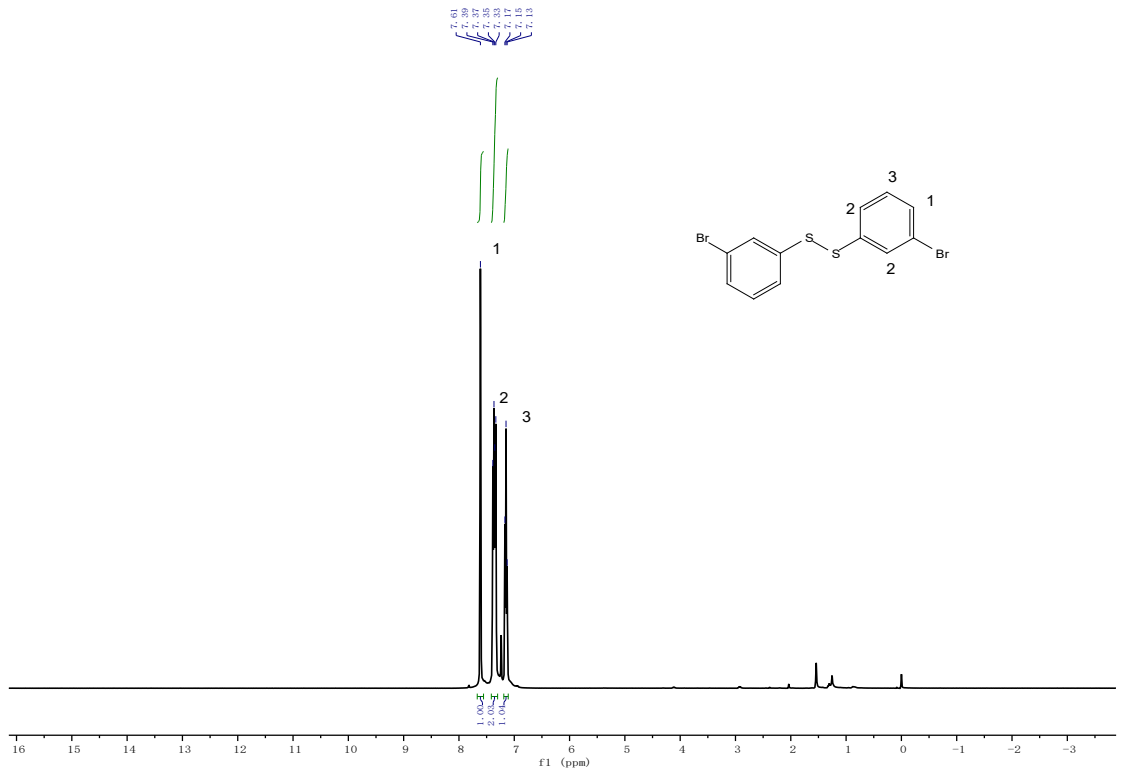


Figure S8. The ^{1}H NMR spectrum of 3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61, 7.39, 7.37, 7.35, 7.33, 7.17, 7.15, 7.13.

The peaks at chemical shifts δ 7.61, 7.37, and 7.15 are all indicative of aromatic protons in the benzene ring.

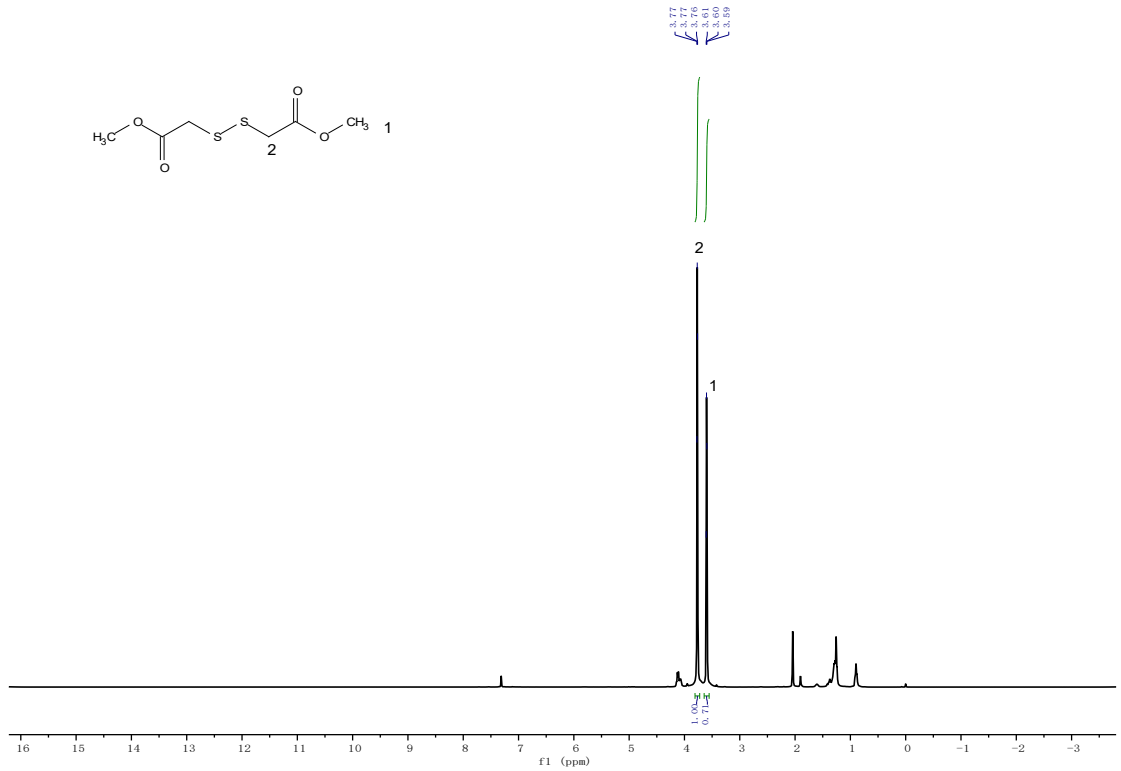


Figure S9. The ^{1}H NMR spectrum of 2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77, 3.77, 3.76, 3.61, 3.60, 3.59.

The peak at chemical shift δ 3.60 is assigned to methyl protons, whereas the signal at δ 3.77 corresponds to methylene protons.

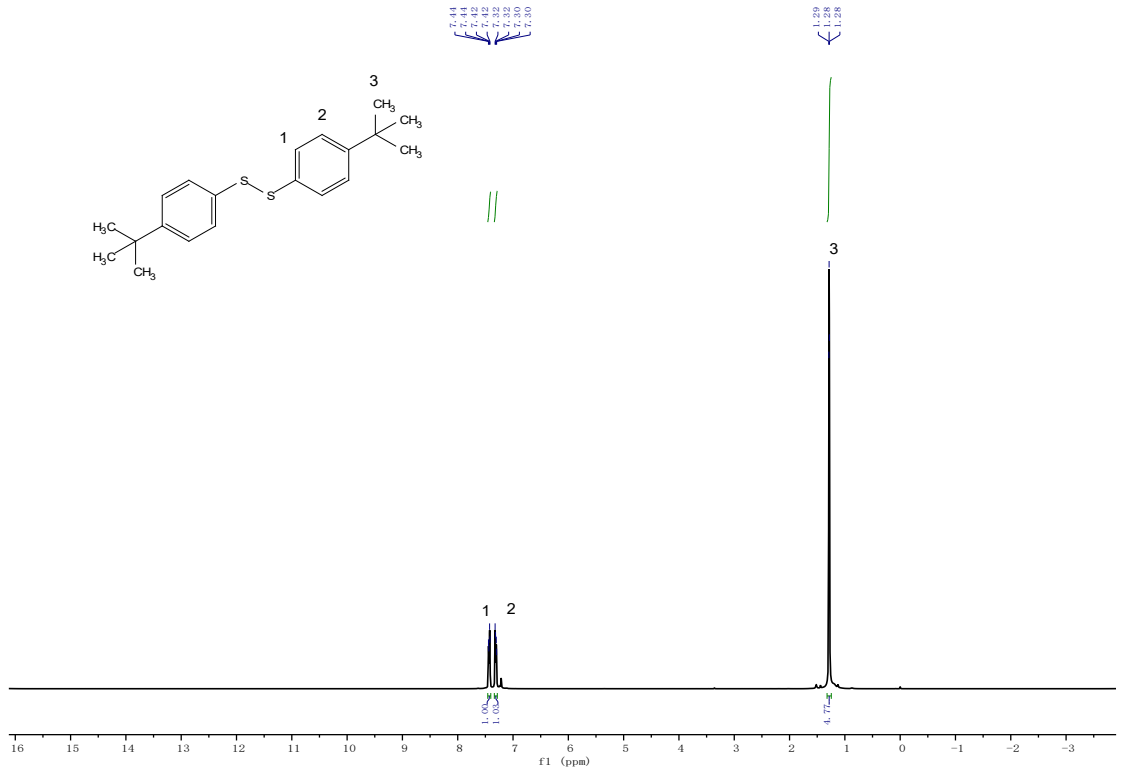


Figure S10. The ^{1}H NMR spectrum of 3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44, 7.44, 7.42, 7.42, 7.32, 7.32, 7.30, 7.30, 1.29, 1.28, 1.28.

The peaks at chemical shifts δ 7.44 and 7.32 are characteristic of aromatic protons in the benzene ring, while the signal at δ 1.28 is diagnostic of methyl protons.