Catalyst- and additive-free light-induced oxidative polymerization of diphenyl disulfides for the facile synthesis of polyphenylene sulfides

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1. Experimental

1.1 Materials

Unless otherwise specified, all chemical reagents and solvents used in the whole process were obtained from commercial suppliers and used without further purification.

For monomer synthesis: 2,6-Dimethylthiophenol (Bide, 97%), di-tert-butyl azodicarboxylate (Adamas, 98%), 2,5-dimethylthiophenol (Leyan, 98%), potassium carbonate (Macklin, LR), cyclic octaatomic sulfur (Bide, 95%), magnesium (Yonghua), 1-bromo-2,6-dimethoxybenzene (Leyan, 98%), iodine (Macklin, LR), 2,5-dimethoxythiophenol (Leyan, 98%), thionyl chloride (Macklin, LR), anhydrous sodium sulfate (Aladdin, LR), sodium bicarbonate (Aladdin, BR), *N*, *N*-dimethylformamide (DMF: ultradry, Aladdin, 99.8%), tetrahydrofuran (THF: ultradry, Energy, 99.5%), acetonitrile (Macklin, LR), chloroform (Yonghua, AR), dichloromethane (Energy, AR), ethyl acetate (EA), petroleum ether (PE), methanol (MeOH) and ethanol (EtOH). Column chromatography was performed over silica gel FCP 200-300 mesh and analytical thin layer chromatography (TLC) was GF 254 (0.20-0.25 mm thickness) visualized by irradiation with UV light (254 nm).

For polymerization: Diphenyl disulfide (Adamas, 98%), hexamethylphosphoramide (HMPA: Adamas, 98%), *N*-methyl-2-pyrrolidone (NMP, Energy, 99%), *N*, *N*-dimethylformamide (DMF: Macklin, LR), *N*, *N*-dimethylacetamide (DMA: Macklin, LR), 1,4-dioxane (Macklin, LR), pyridine (Macklin, LR), tetrahydrofuran (THF: Energy, AR), dichloromethane (DCM, Macklin, LR), 1,2-dichloroethane (DCE, Energy, AR), 1,1,2,2-tetrachloroethane (TCE, Macklin, LR), hydrochloric acid (Yonghua, AR), ethyl acetate (EtOAc), petroleum ether (PE), methanol (MeOH) and ethanol (EtOH). The 40W Blue LEDs (400 nm), 40W Blue LEDs (460 nm) and 40W Green LEDs were purchased from Hengyang Duoshang Trading Co., Ltd. UV photochemical reactions were performed on 50 W LEDs (365 nm) purchased from Beijing Nuozhi Technology Co., Ltd equipped with a 10 ^{o}C circulating water cooling system.

1.2 Measurements

Nuclear magnetic resonance (NMR) spectroscopy. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AVANCE III 400 MHz spectrometer (400 and 101 MHz, respectively) at room temperature. Chloroform-*d* (Energy, 99.8% D + 0.03% TMS) and methylene chloride-d_2 (CIL, 99.8% D+0.05% TMS) were used as the solvent, with tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. Multiplicities are reported as singlet (s), doublet (d), triplet (t), or doublet of doublets (dd). Coupling constants (J) are reported in Hertz (Hz).

Fourier transform infrared (FT-IR) spectroscopy. FT-IR spectra were recorded using a Nicolet iS8 spectrometer. Samples were prepared as potassium bromide (KBr: Macklin, 99.9%) pellets.

Elementary analysis (EA). Elemental analysis (C, H, N, S) was performed on an Elementar UNICUBE analyzer operating in CHNS mode.

Ultraviolet-visible (UV-Vis) and fluorescence emission spectroscopy. The ultraviolet to visible (UV–vis) absorption spectra and fluorescence emission spectra were acquired by a TU-1900 UV and Hitachi-F-4600 fluorescence spectrophotometer, respectively.

Electron paramagnetic resonance (EPR). The EPR measurements were carried out with a Bruker Model A200 spectrometer at 25 ^{o}C. The spin trap 2,2,6,6-tetramethylpiperidine (TEMP) was as the trapping agent to monitor $^{1}O_2$. Briefly, 40 μL reaction solution obtained under standard conditions was mixed with TEMP/acetone solution (v/v = 1:1) prior to measurement.

Gel permeation chromatography (GPC). GPC test was performed in THF solution at 35 ^{o}C with an elution rate of 1.0 mL/min on Agilent Technologies 1260 Infinity II GPC system equipped with a refractive index detector. The apparent molecular weights were determined on a PLgel Mixed-B and a PLgel Mixed-C columns using linear poly(methyl methacrylate) as standard. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the dispersity ($Đ = M_w/M_n$) are the key parameters for characterizing polymer molecular weight distribution.

Intrinsic viscosity measurement.[1-4] The viscosity measurements were performed using a standard Ubbelohde viscometer (capillary diameter: 0.38 mm) immersed in a custom-built constant temperature water bath maintained at 25.0 ± 0.3 ^{o}C. The custom-built constant temperature water bath for determining the intrinsic viscosity of polymers using the Ubbelohde viscosity method, calibrated against a standard thermometer, comprises the components shown in Fig. S1. Heating, mechanical stirring and temperature control were achieved using electric heating coils (Yancheng Leigu Technology Co., Ltd.), accurate strengthen electronic stirrer (Nanjing Dawei Corporation) and a ZNHW-II electronic intelligent temperature controller (Nanjing Wen'er Corporation), respectively. Polymer solutions were prepared at a concentration of 0.1 g/mL in trichloromethane ($CHCl_3$, 10 mL). All solutions and pure solvents were filtered through a sandcore funnel (G3) to remove micro-impurities. After charging the sample (7 mL), the viscometer was aligned vertically and equilibrated for 15 min to reach thermal equilibrium. The efflux time (t) of the liquid passing between the upper and lower marks was recorded in triplicate using a digital stopwatch. Subsequently, 2 mL, 2 mL, 3 mL, 5 mL chloroform were sequentially added to the viscometer to adjust the solution concentration. After each addition, the mixture was thermostated for 15 min before the measurements were repeated in triplicate.

The intrinsic viscosity [η] was determined by the following equations:

Relative viscosity (η_r):

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

Specific viscosity (η_{sp}):

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

Intrinsic viscosity ([η]): The intrinsic viscosity [η] was obtained by extrapolating the reduced viscosity (η_{sp}/c) and the inherent viscosity ($\ln\eta_r/c$) to zero concentration ($c\rightarrow0$) based on the Huggins and Kraemer equations:

$$\frac{\eta_{sp}}{c} = [\eta] + k^{'}[\eta]^2 c$$

$$\frac{ln\eta_r}{c} = [\eta] + k^{"}[\eta]^2 c$$

Where:
t and t_0 are the efflux times of the solution and the pure solvent, respectively.
c is the concentration of
k' and k'' are the Huggins vely.

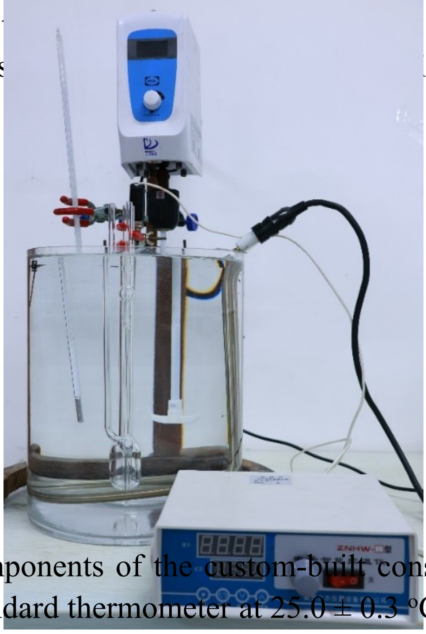


Figure S1 Diagram and components of the custom-built constant temperature water bath (calibrated against a standard thermometer at 25.0 ± 0.3 °C).

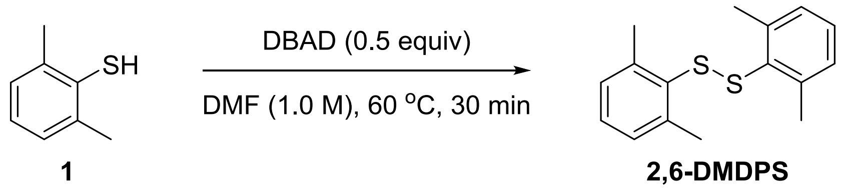
1.3 General procedure for synthesis of polyphenylene sulfides

General procedure (take Table 1, entry 6 for example): Diphenyl disulfide (**DPS**) (1.75 g, 8 mmol) was added to a 25 mL quartz tube and dissolved in HMPA (8 mL) with stirring. The atmosphere was replaced with oxygen, and this process was repeated three times. The reaction mixture was then irradiated under 50 W UV LEDs (365 nm) for 5 days. After the reaction was complete, the mixture was added dropwise to methanol solution containing 5% hydrochloric acid (250 mL) to precipitate the product. The solid was collected by suction filtration, washed alternately with methanol and water, and dried under vacuum at 40 °C to afford **PPS** as a pale yellow powdery solid.

1.4 Procedures for synthesis of monomers

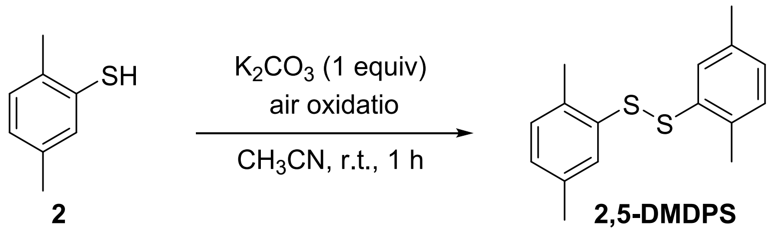
DPS was purchased from Adamas and used as received. Bis(2,6-dimethylphenyl)disulfide **(2,6-DMDPS),** bis(2,5-dimethylphenyl)disulfide **(2,5-DMDPS)** bis(2,6-methoxyphenyl)disulfide **(2,6-DMODPS)** bis(2,5-methoxyphenyl)disulfide **(2,5-DMODPS)** were synthesized according a procedure reported in the literatures.

1.4.1 Synthesis of **2,6-DMDPS**



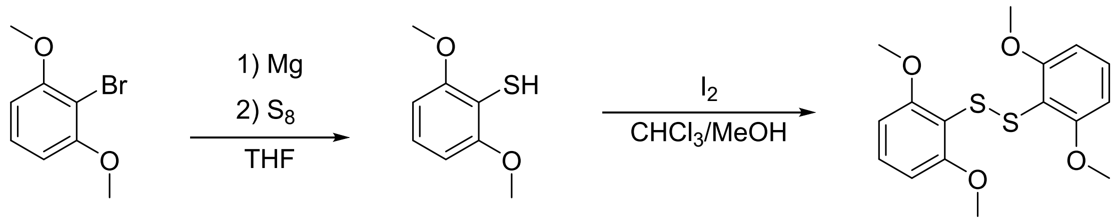
Synthesis of bis(2,6-dimethylphenyl)disulfide (2,6-DMDPS) (Scheme S1)[5]: 2,6-Dimethylbenzenethiol **1** (0.99 g, 7.2 mmol), di-tert-butyl azodicarboxylate (DBAD) (1.06 g, 3.6 mmol) and degassed DMF (7 mL) were placed in a dried 25mL vial with a magnetic stirrer. The reaction mixture was heated at 60 °C for 30 min. After completion of the reaction, the mixture was cooled to room temperature. The reaction mixture was quenched with brine (50 mL) and the aqueous phase was extracted with ethyl acetate (3×50 mL). The organic phase was washed with brine (3×100mL), dried over anhydrous sodium sulfate (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product **2,6-DMDPS** (0.92 g, 94%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, J = 7.6 Hz, 2H), 7.01 (d, J = 8.1 Hz, 4H), 2.24 (s, 12H). ^{13}C ((101 MHz, $CDCl_3$) δ 143.45, 134.74, 129.30, 128.07, 21.48.

1.4.2 Synthesis of **2,5-DMDPS**



Synthesis of bis(2,5-dimethylphenyl)disulfide (2,5-DMDPS) (Scheme S2)[6,7]: A solution of 2,5-dimethylthiophenol **2** (1.38 g, 10 mmol) and potassium carbonate (1.38 g, 10 mmol) in acetonitrile (20 mL) in a 50 mL pressure tube with a magnetic stirring bead was stirred at room temperature until the starting material was consumed. After the completion (as indicated by TLC), the reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution and extracted with EtOAc (3×20 mL). The collected organic layer was washed with brine and dried with Na_2SO_4. Finally, the organic solvent was removed under reduced pressure, and the obtained residue was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EtOAc = 30:1) to provide white solid product **2,5-DMDPS** (0.98 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.11 (d, J = 7.6 Hz, 2H), 7.02 (d, J = 7.5 Hz, 2H), 2.45 (s, 6H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.28, 135.25, 134.56, 130.18, 129.71, 128.30, 20.99, 19.61.

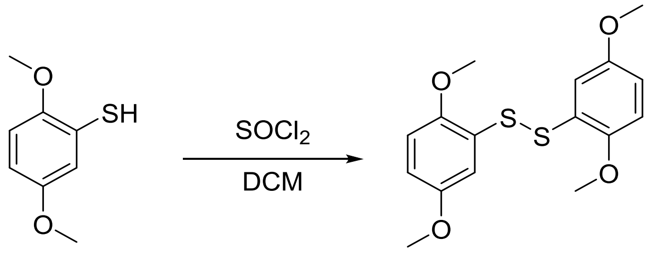
1.4.3 Synthesis of **2,6-DMODPS**



3 **4** **2,6-DMODPS**

Synthesis of bis(2,6-methoxyphenyl)disulfide (2,6-DMODPS) (Scheme S3)[8]: To a 100 mL two necked flask, Mg turnings (1.16 g, 48 mmol) was dispersed in THF (20 mL) and was purged with nitrogen after the addition of two drops of 1,2-dibromoethane. Then the solution of 2-bromo-1,3-dimethoxybenzene **3** (8.68 g, 40 mmol) dissolved in THF (10 mL) was added dropwise and heated with a hair dryer to reflux until the reaction solution turns black. Continue to react at room temperature for 2 hours. Then,the solution was cooled to 0 °C, was added sulfur (0.70 g, 22 mmol), and was stirred at room temperature for another 3 hours. The reaction was quenched with 10 vol% hydrochloric acid (50 mL) and was extracted with chloroform (3×50 mL). The solvent was then removed by rotary evaporator to give a crude product for 2,6-dimethoxybenzenethiol **4**. Without further purification, the crude was dissolved in chloroform (100 mL), was added 0.5 mM iodine solution in methanol (15 mL) dropwise, and was stirred for 1 hour. The reaction was quenched with 15 wt% sodium thiosulfate aqueous (added until the brownish color of unreacted iodine faded) and the solvent was removed by rotary evaporator. The product was extracted with chloroform and was purified by recrystallization with chloroform/methanol [= 1/10 (v/v)] to give **2,6-DMODPS** as a pale-yellow solid (4.26 g, 63%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 (t, J = 8.3 Hz, 2H), 6.50 (d, J = 8.3 Hz, 4H), 3.69 (s, 12H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.24, 130.90, 113.92, 103.79, 56.05.

1.4.4 Synthesis of **2,5-DMODPS**



5 **2,5-DMODPS**

Synthesis of bis(2,5-methoxyphenyl)disulfide (2,5-DMODPS) (Scheme S4)[9]: To a solution containing thionyl chloride (2.38 g, 20 mmol) dissolved in dichloromethane (40 mL), 2,5-dimethoxythiophenol **5** (2.29 g, 13.3 mmol) was added dropwise. The yellow solution was stirred for 0.5 h followed by addition of a saturated NaHCO$_3$ aqueous solution (50 mL). The organics were extracted with DCM (25 mL) and dried over brine and Na_2SO_4. Flash column chromatography (EtOAc/PE = 1:4) afforded **2,5-DMODPS** in the form of a yellowish foam (1.89 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 2.9 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.69 (dd, J = 8.8, 3.0 Hz, 2H), 3.85 (s, 6H), 3.70 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.30, 150.87, 125.72, 113.51, 112.42, 111.70, 56.60, 55.77.

2. Optimization conditions

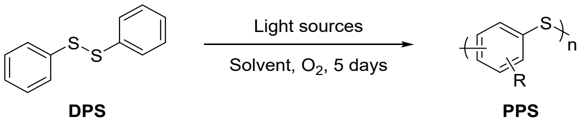


Table S1 Screening of **DPS** concentration

Entry	Concentration (M)	Yield (%)	[η] (mLg^{-1})
1	0.5	39	0.3585
2	1.0	84	0.5279
3	1.5	85	0.4939
4	2.0	89	0.4649
5	2.5	91	0.4401
6	3.0	86	0.4171

Polymerization conditions: **DPS** (1.75 g, 8 mmol), the reaction was carried out under UV LEDs(365 nm) in HMPA (8 mL) with exposure to O_2 for 5 days at 25 °C.

Table S2 Screening of polymerization time

Entry	Polymerization time (days)	Yield (%)	[η] (mLg^{-1})
1	1	74	0.3379
2	2	83	0.3928
3	3	83	0.4532
4	4	83	0.4974
5	5	84	0.5279
6	6	86	0.4508

Polymerization conditions: **DPS** (1.75 g, 8 mmol), [**DPS**] = 1.0 M, the reaction was carried out under UV LEDs(365 nm) in HMPA (8 mL) with exposure to O_2 at 25 °C.

3. Mechanism verification experiments

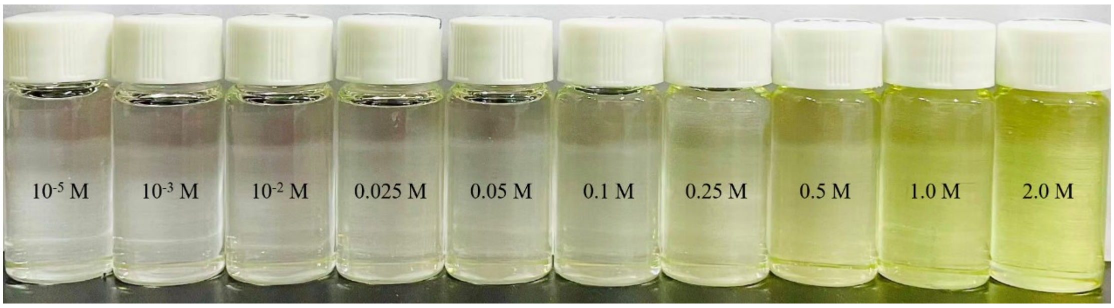


Figure S2 Color changes of **DPS** solutions in HMPA with increasing concentration from 10^{-5} M to 2.0 M.

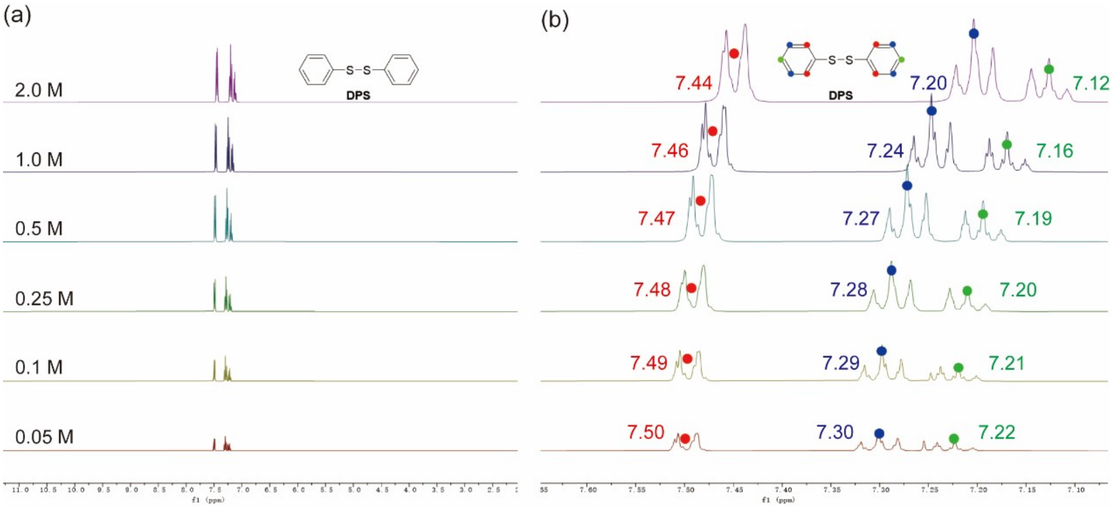


Figure S3 Evolution of ^{1}H NMR chemical shifts for aromatic protons in **DPS** with increasing concentration. (a) Full spectra and (b) amplified spectra (red, blue, and green balls in b respectively correspond to the ortho, meta, and para hydrogen atoms on the benzene ring).

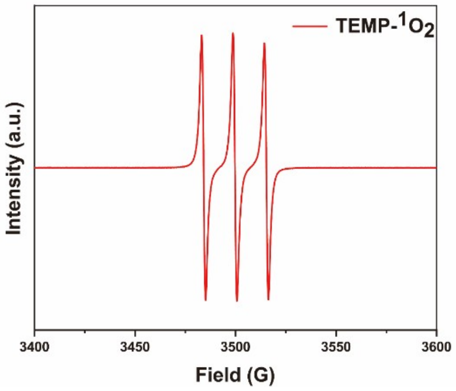
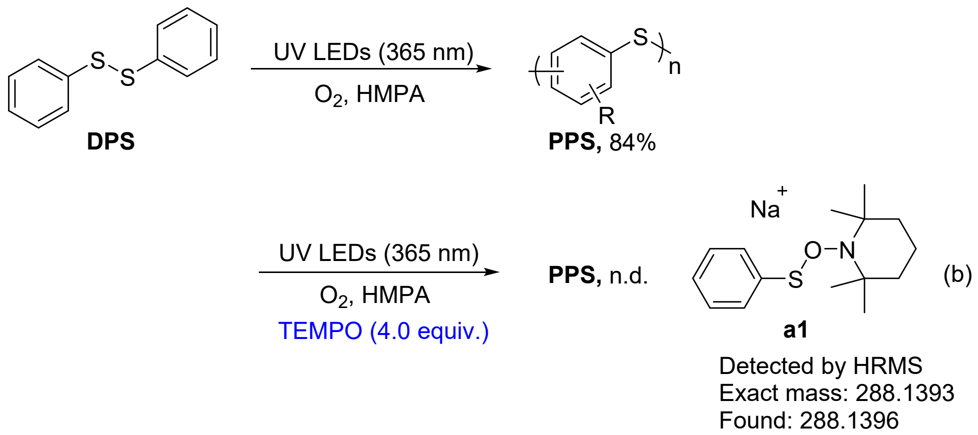


Figure S4 EPR spectrum of TEMP-$^1O_2$ adducts capture from the reaction solution under standard conditions. Polymerization conditions: **DPS** (1.75 g, 8 mmol), [**DPS**] = 1.0 M, the reactions were carried out in HMPA solution under UV LEDs(365 nm) at 25 °C with exposure to O_2 for 5 days.



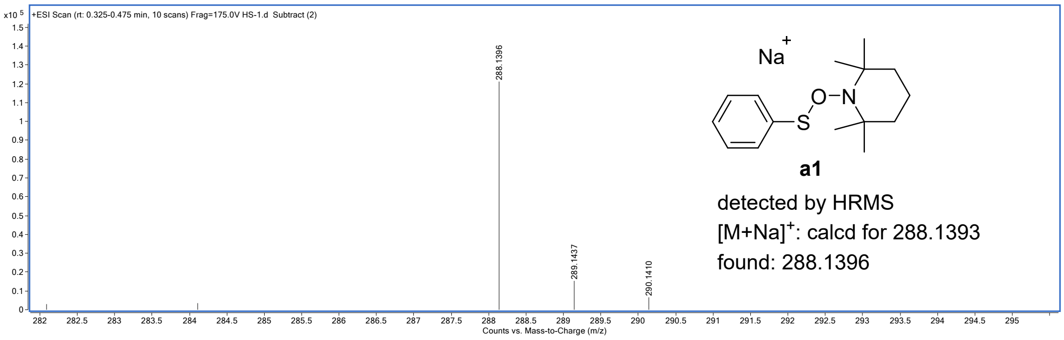


Figure S5 The positive-ion ESI mass spectrum of the adduct **a1** of TEMPO and phenyl thiyl radical **a** (standard conditions: **DPS** (1.75 g, 8 mmol), [**DPS**] = 1.0 M, the reactions were carried out in HMPA solution under UV LEDs (365 nm) at 25 °C with exposure to O_2 for 5 days, n.d. = no detected).

HRMS (ESI) *m/z* Calcd. for $C_{15}H_{23}NOSNa^+$ $[M+Na]^+$: 288.1393; found: 288.1396.

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4. Characterization of polymers

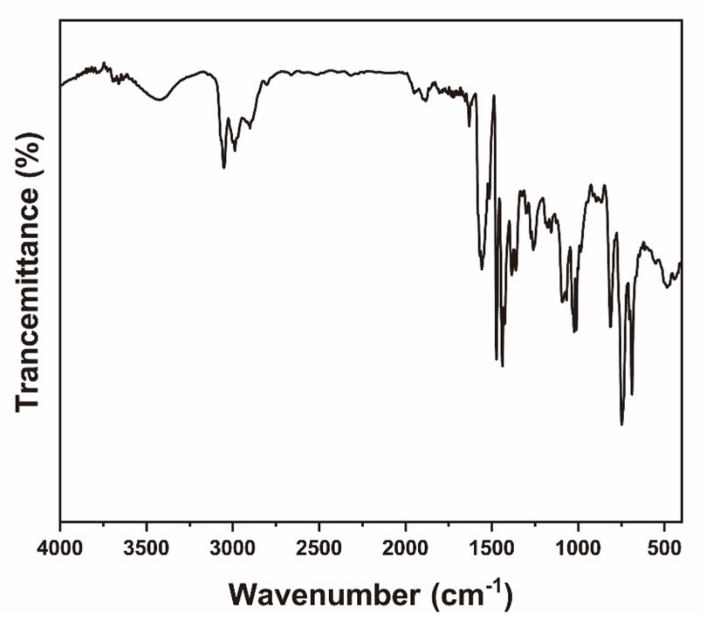

Figure S6 FT-IR spectrum of **PPS**.

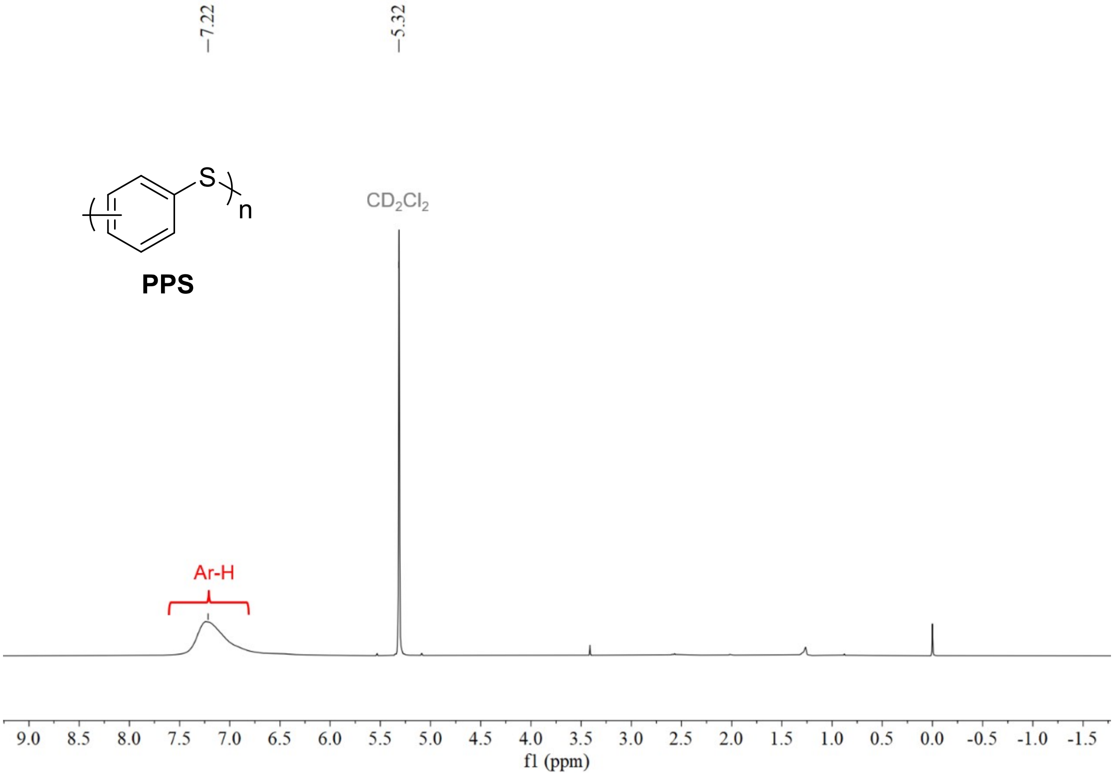

Figure S7 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **PPS**.

Table S3 EA results of **PPS**

Formula	C (%)	H (%)	S (%)
Calcd.	66.67	3.70	29.63
Found	64.21	3.60	28.90

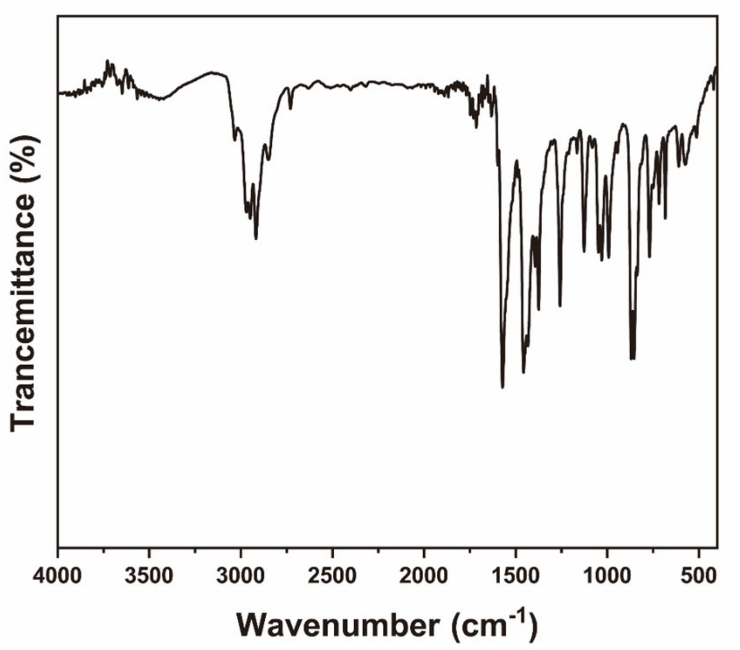

Figure S8 FT-IR spectrum of **2,6-DMPPS**.

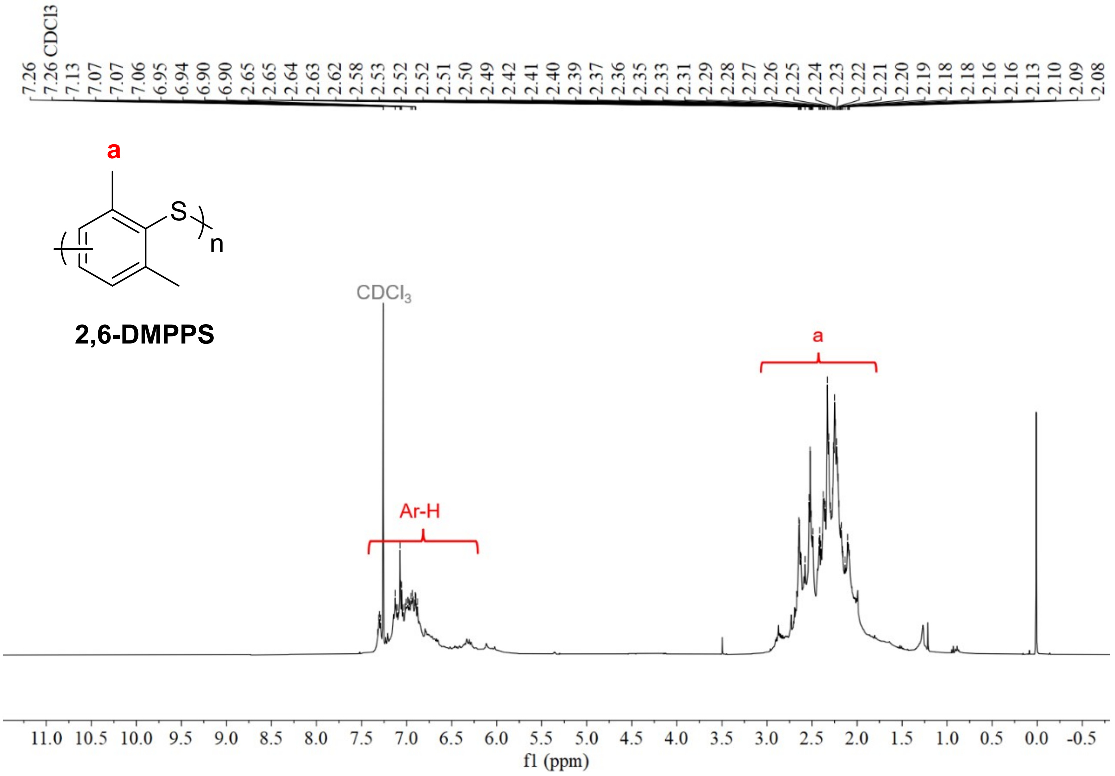

Figure S9 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **2,6-DMPPS**.

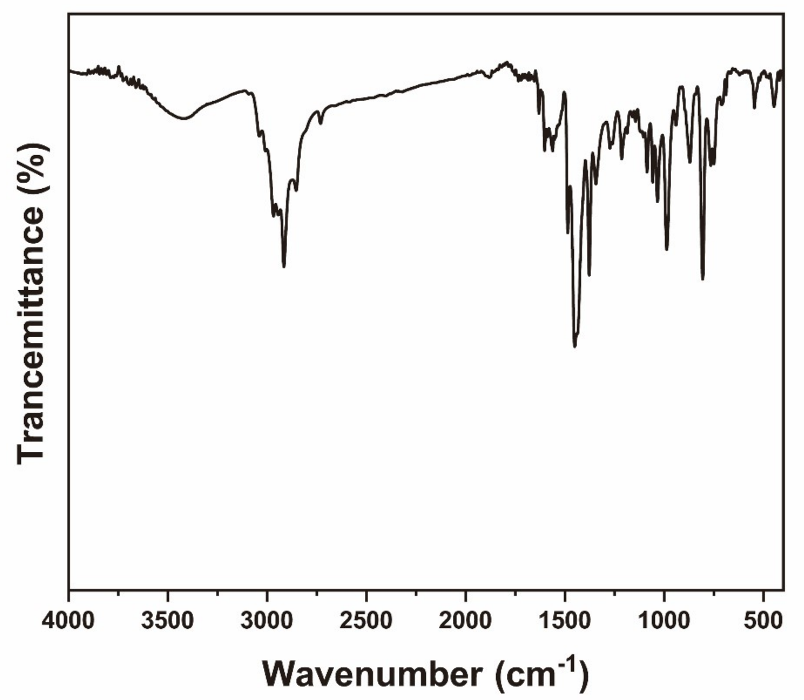

Figure S10 FT-IR spectrum of **2,5-DMPPS**.

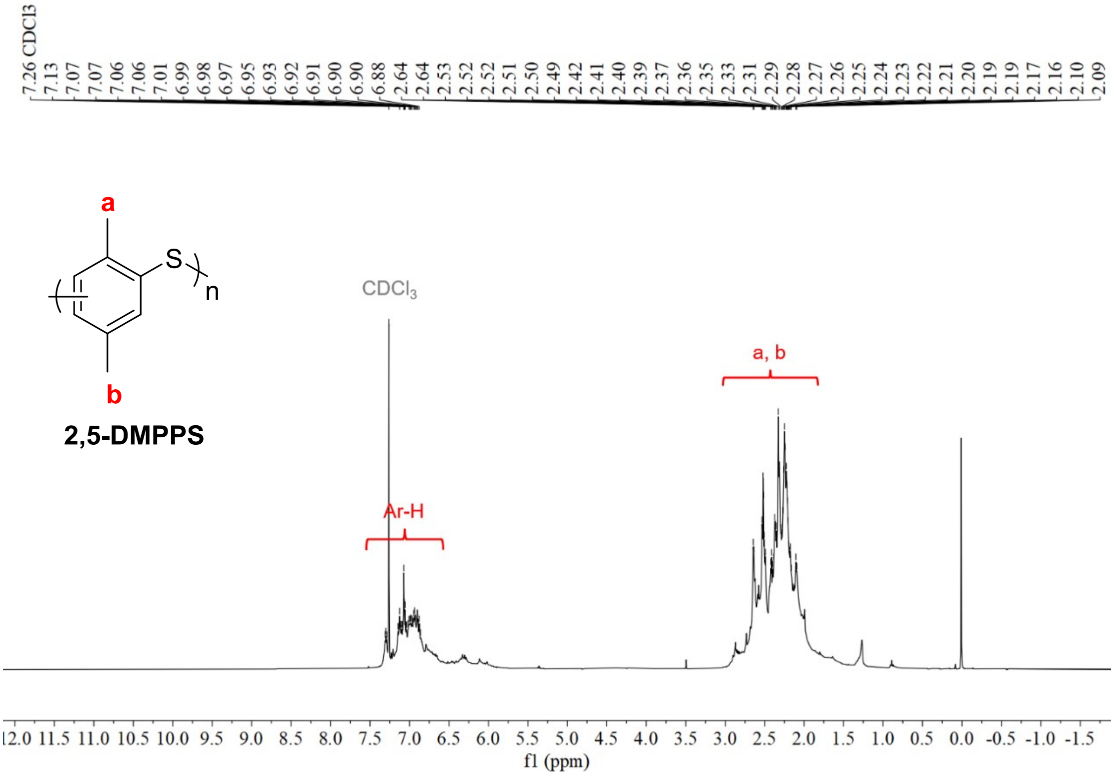

Figure S11 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2,5-DMPPS**.

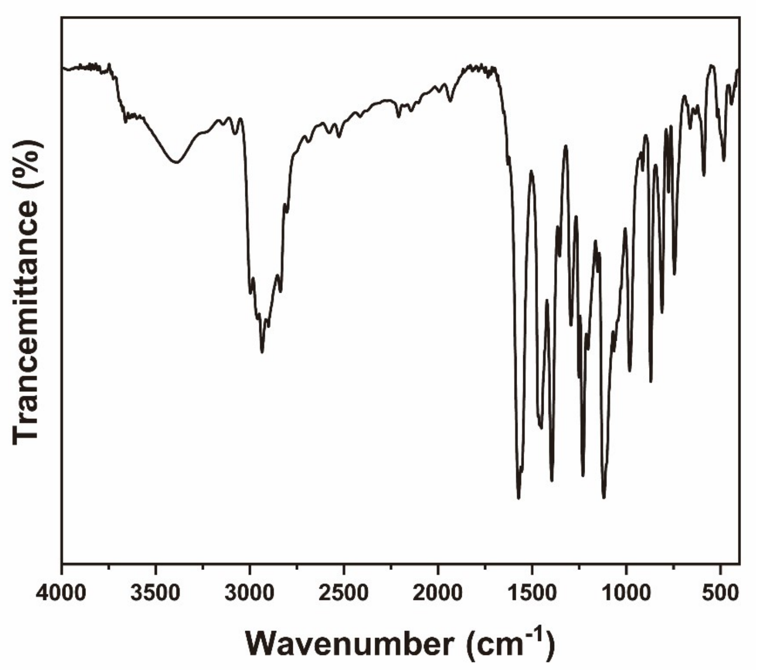

Figure S12 FT-IR spectrum of **2,6-DMOPPS**.

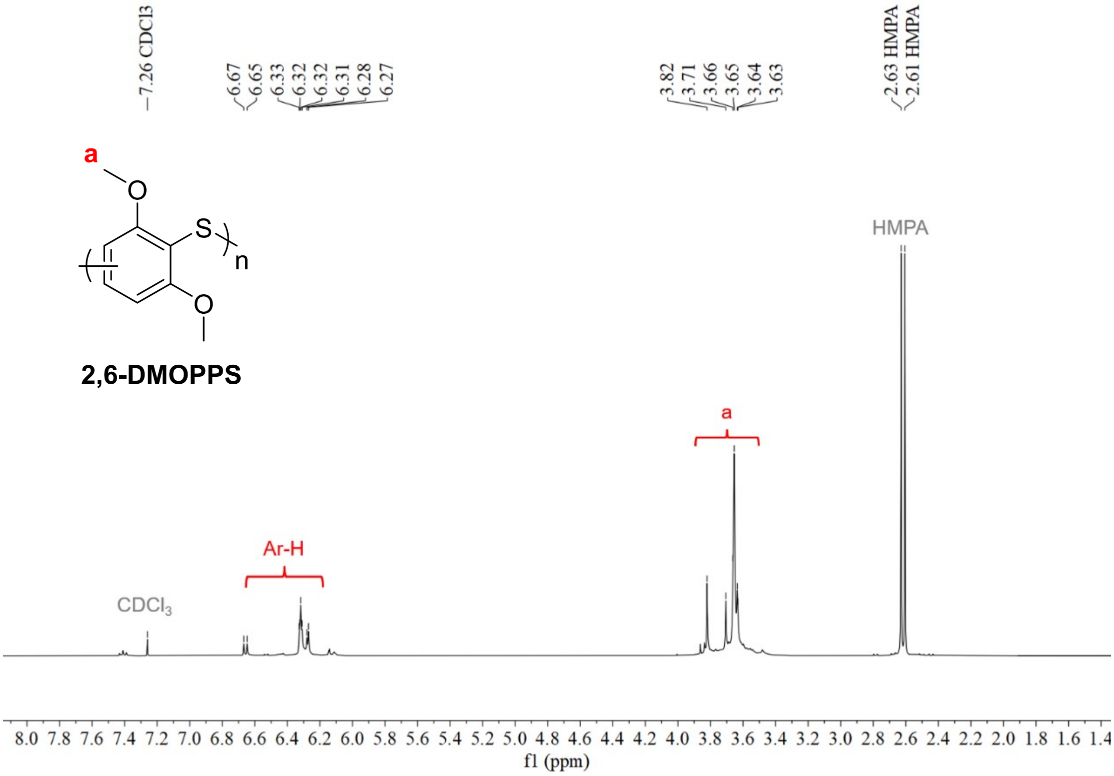

Figure S13 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2,6-DMOPPS**.

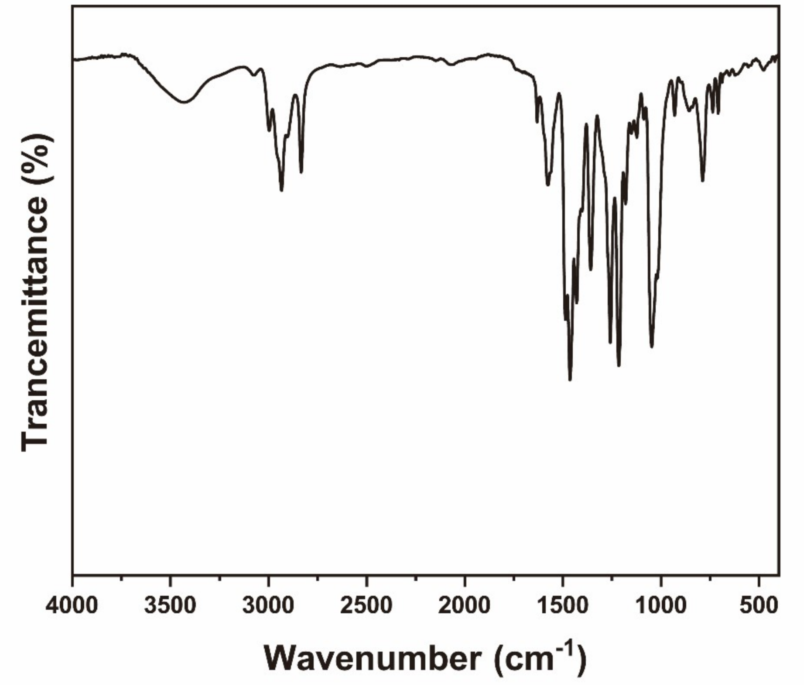

Figure S14 FT-IR spectrum of **2,5-DMOPPS**.

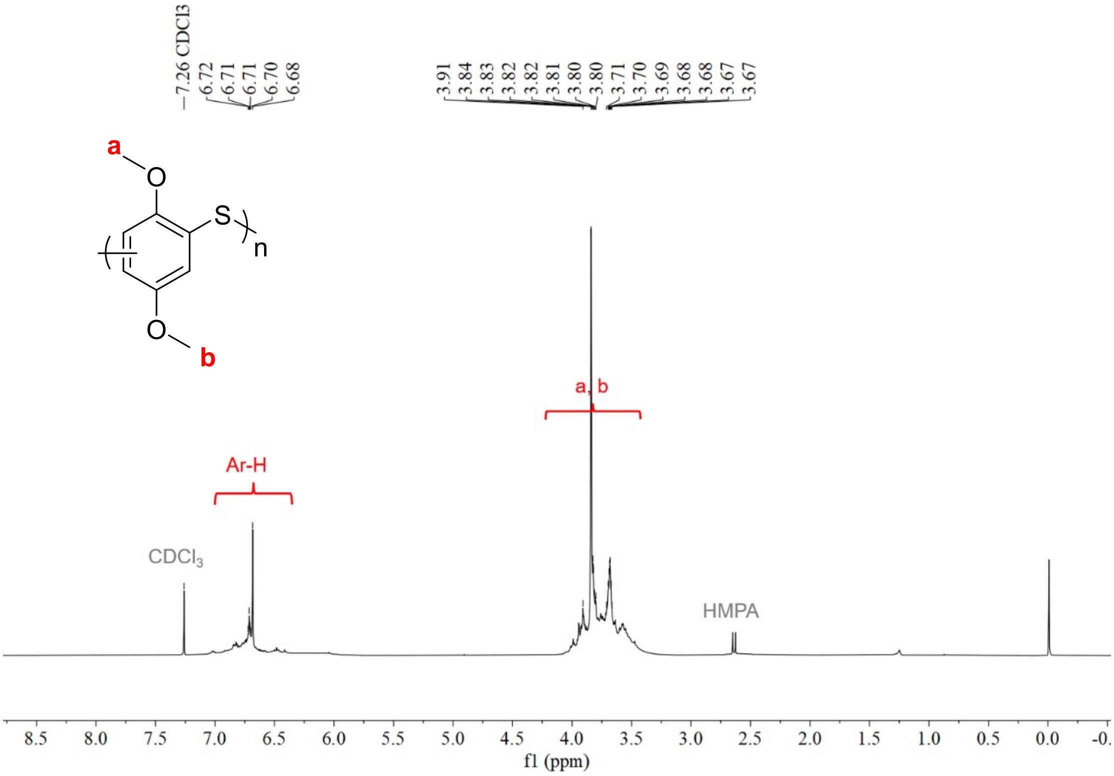

Figure S15 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **2,5-DMOPPS**.

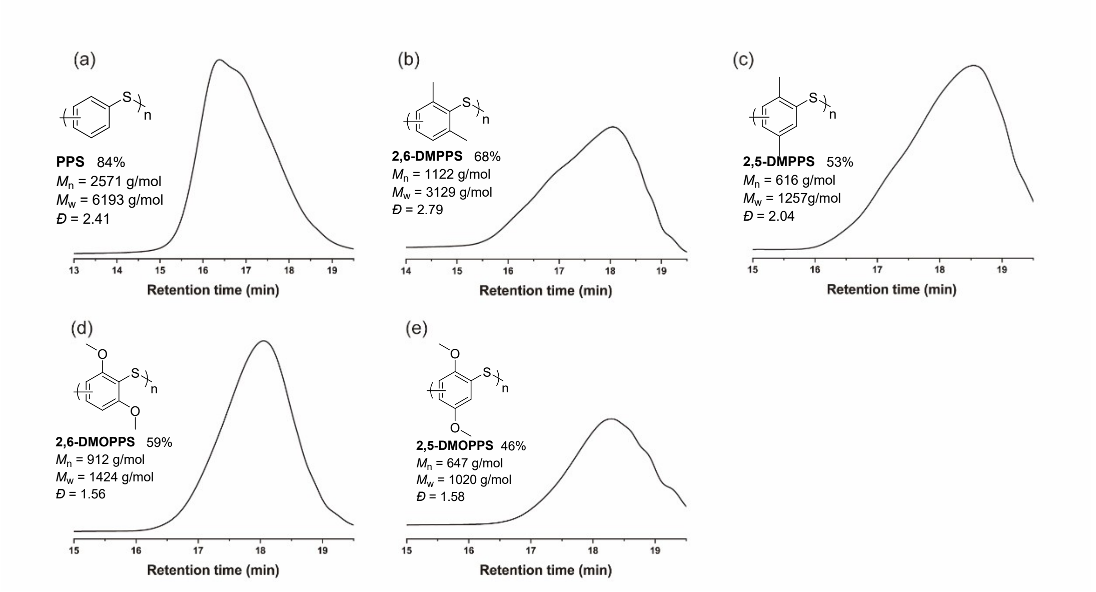

Figure S16 GPC spectra of (a) **PPS**, (b) **2,6-DMPPS**, (c) **2,5-DMPPS**, (d) **2,6-DMOPPS**, and **2,5-DMOPPS** (e).

5. NMR of monomers

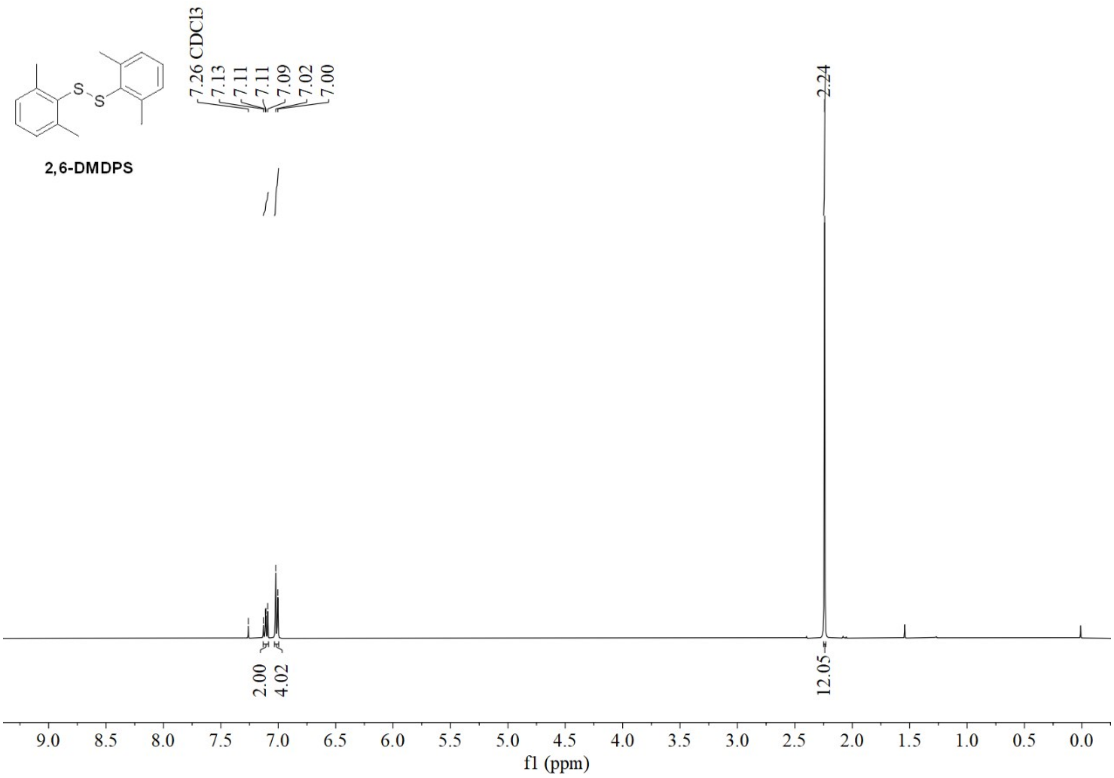

Figure S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2,6-DMDPS**.

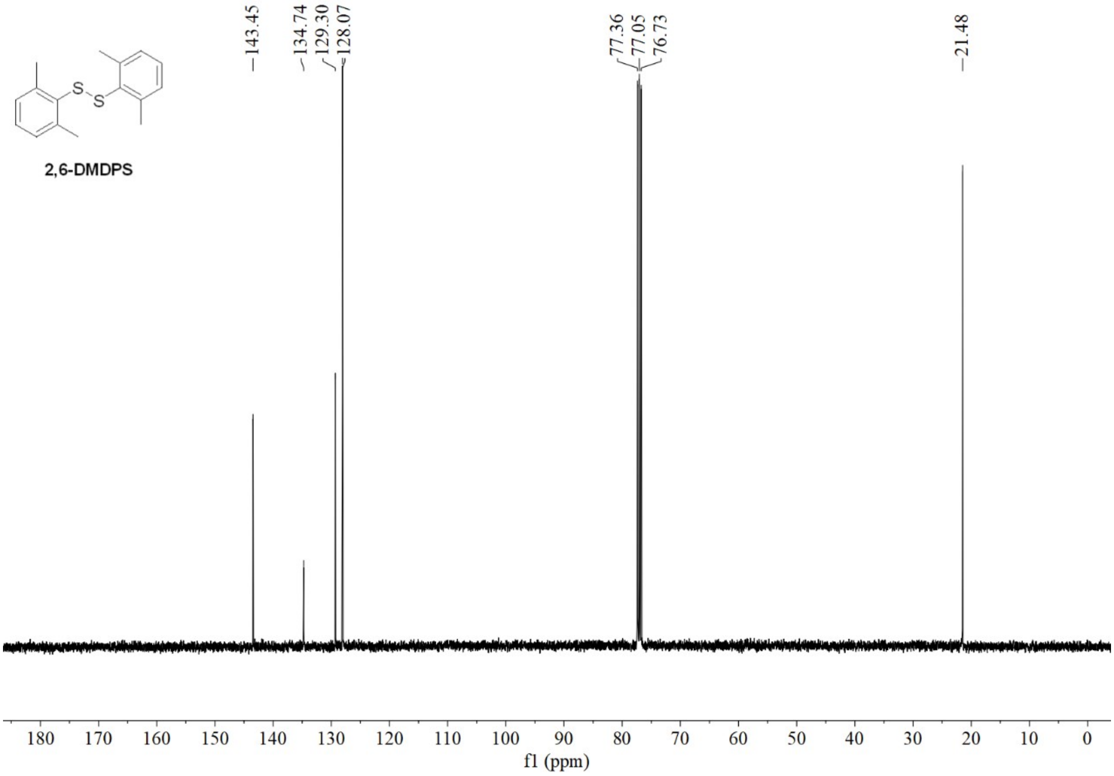

Figure S18 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2,6-DMDPS**.

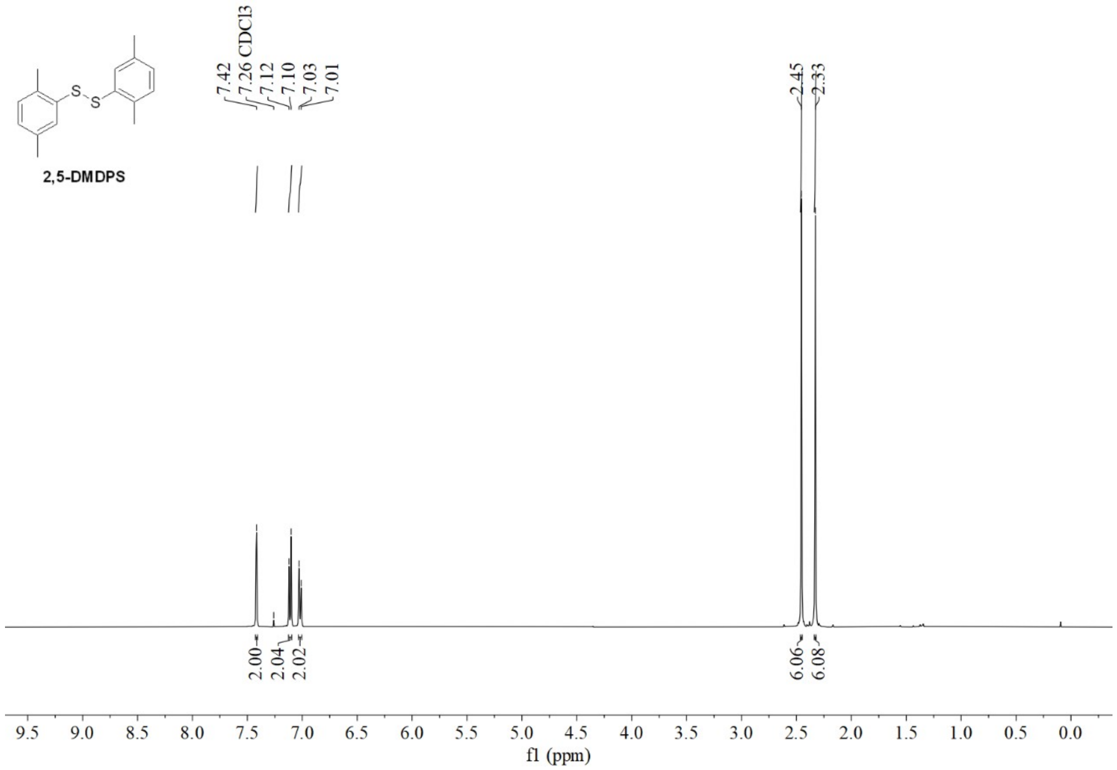

Figure S19 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **2,5-DMDPS**.

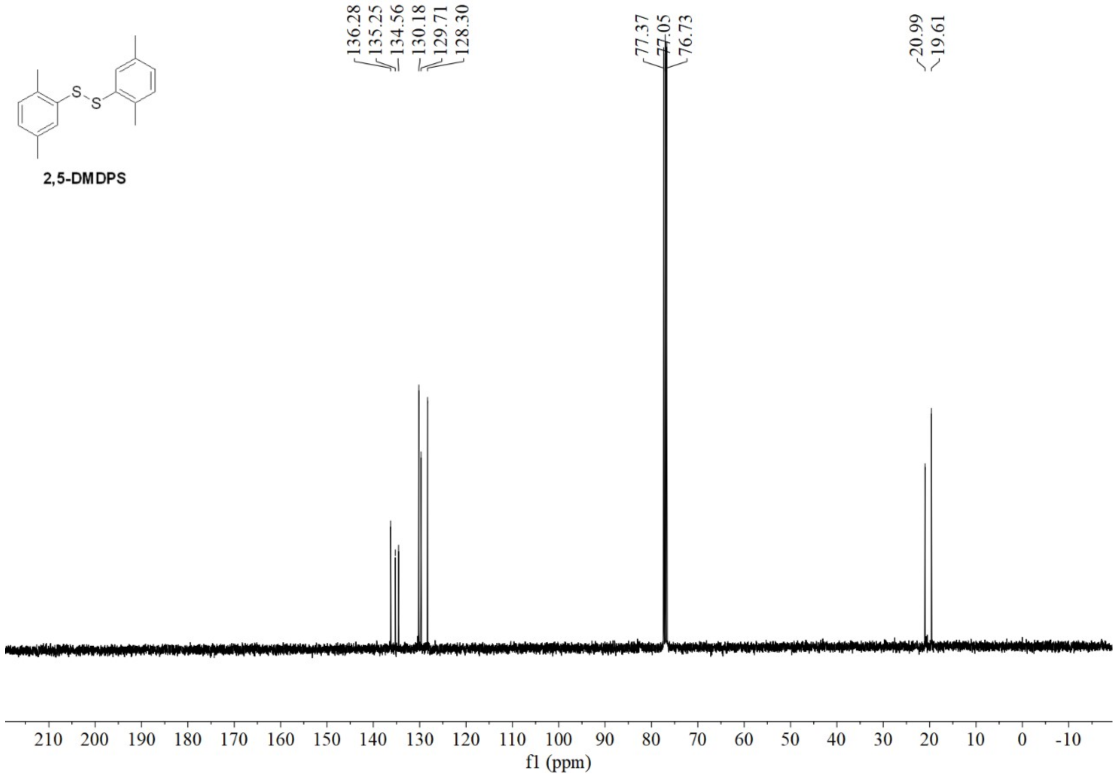

Figure S20 ^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **2,5-DMDPS**.

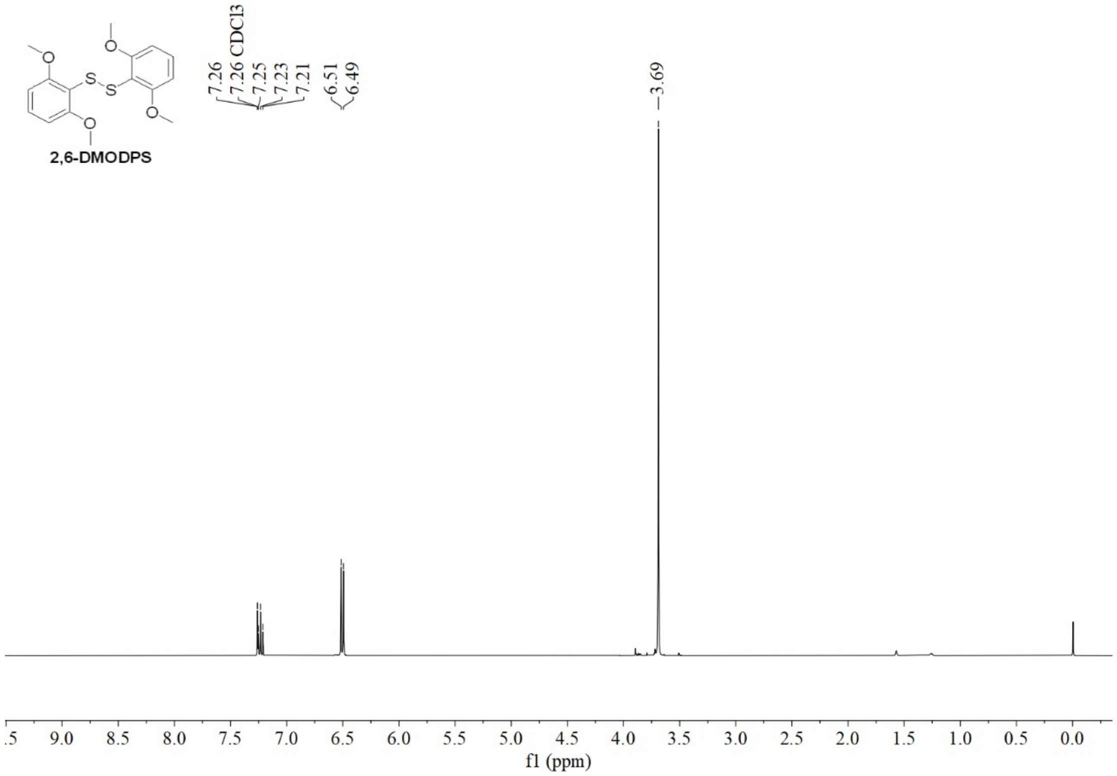

Figure S21 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2,6-DMODPS**.

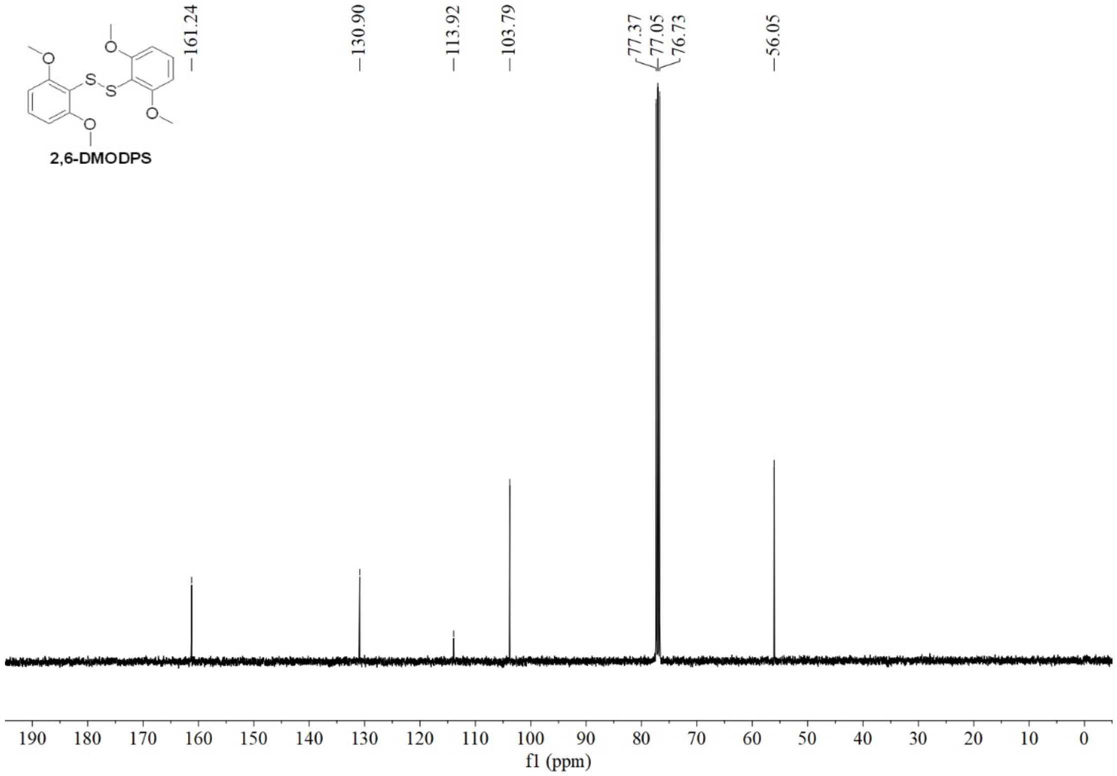

Figure S22 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2,6-DMODPS**.

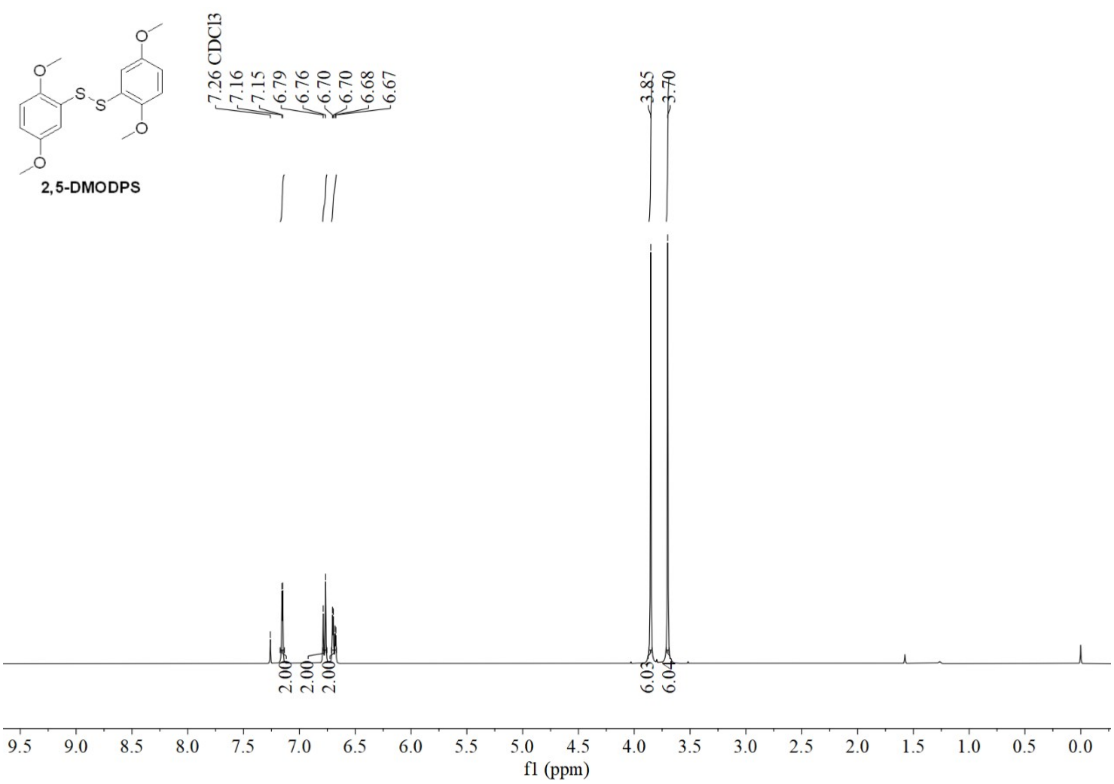

Figure S24 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **2,5-DMODPS**.

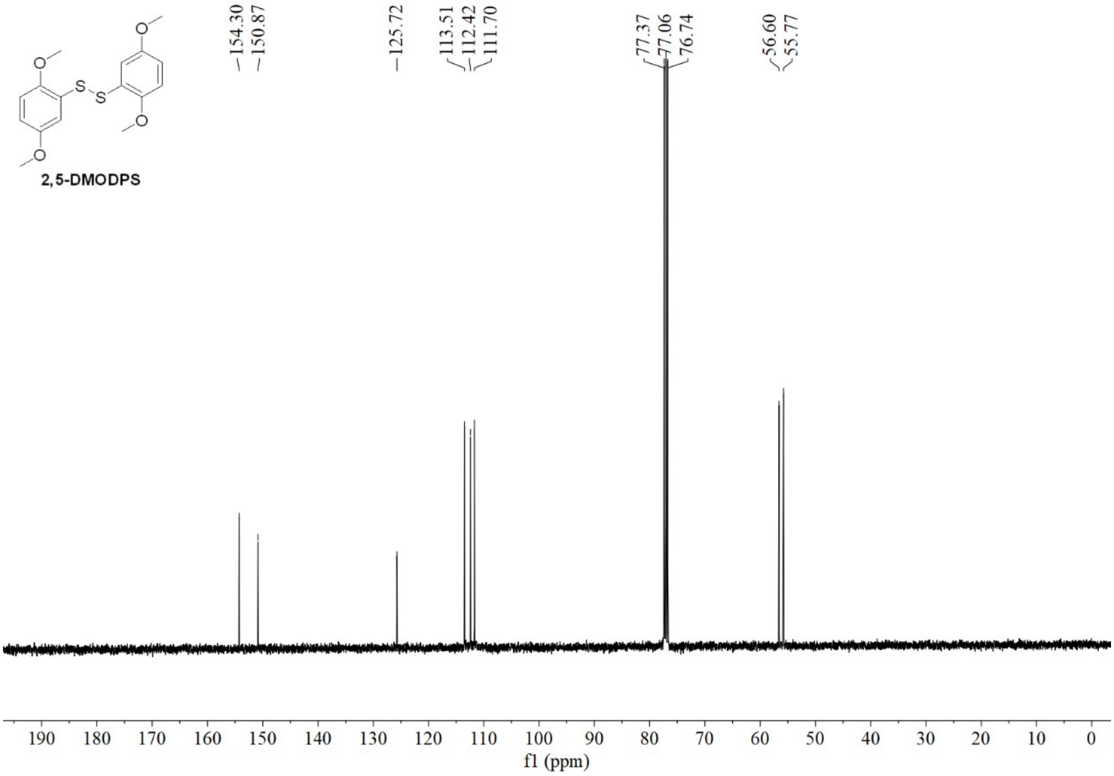

Figure S25 ^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **2,5-DMODPS**.

6. References

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