

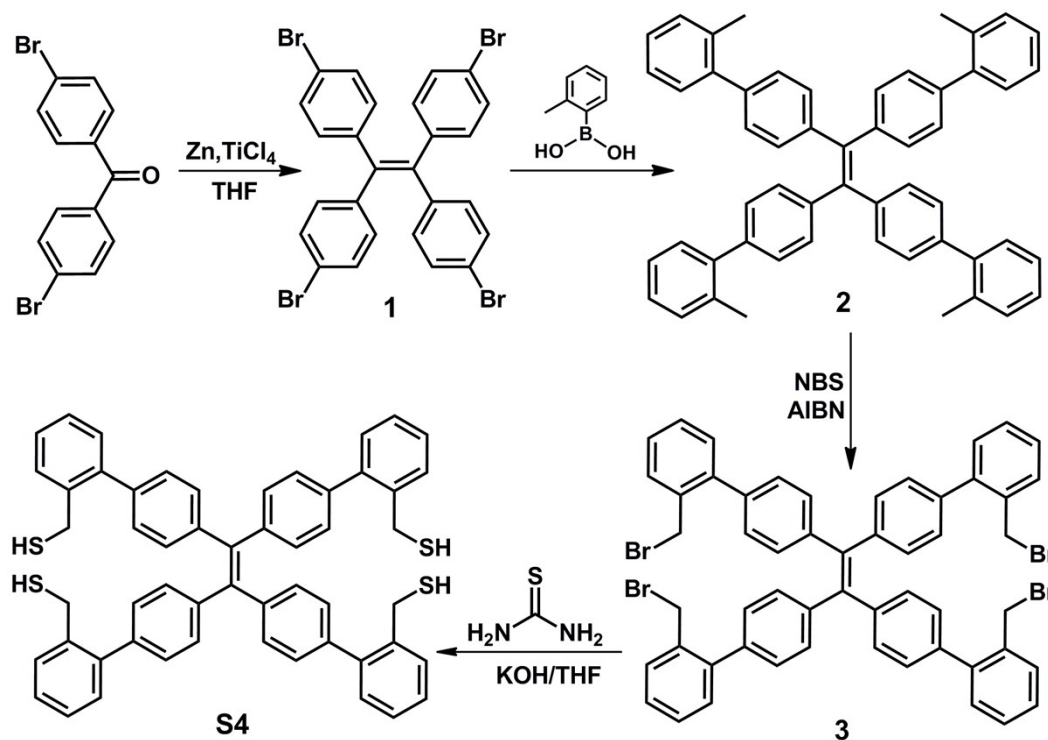
Electronic Supplementary Information for

Mercaptomethylphenyl Modified Tetraphenylethene as Multifunctional Luminophor: Stimuli-responsive Luminescence Color Switching and AIE-active Chemdosimeter for Sulfur Mustard Simulant

Hui Wang, Dong-En Wang, Jianping Guan, Xiang Han, Wenming Liu, Mao-Sen Yuan* and Jinyi Wang*

1. Synthesis.....	S2
2. Choice of metal ions.....	S4
3. Detection limit.....	S5
4. AIE property.....	S5
5. Fluorescence decay.....	S6
6. X-ray Single-Crystal Structure.....	S7
7. DSC determination.....	S8
8. Mass spectrometry.....	S9
9. ¹ H NMR and ¹³ C NMR.....	S10

1. Synthesis



Scheme S1. The Synthetic routes of compound S4.

Synthesis of 1,1,2,2-tetrakis(4-bromophenyl)ethane (1).

4,4'-Dibromobenzophenone (13.4 g, 10 mmol) and Zn powder (2.62 g, 40 mmol) were added to a 500 mL pre-dried three necked round-bottom flask. The flask was evacuated under vacuum and flushed with nitrogen for three times. Then, THF (20 mL) was injected into the flask and the mixture was stirred under an ice-bath for 0.5 h. TiCl_4 (1 mL, 8 mmol) of was injected drop-wise into the flask and the mixture was stirred again for 0.5 h on an ice bath. The mixture was refluxed at 70 °C overnight. After cooling and solvent evaporation, the mixture was extracted with dichloromethane (DCM) and the organic layer was obtained. Compound **1** was obtained by DCM evaporation as a white solid, yield: 85%. ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 7.25 (t, J = 11.4 Hz, 8H), 6.85 (t, J = 8.1 Hz, 8H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 141.47, 139.64, 132.72, 131.30, 128.05, 121.29. MS (FAB): m/z = 647.79 $[\text{M}^+\text{H}]^+$. IR (KBr): 3425, 2921, 1746, 1691, 1636, 1553, 1535, 1470, 1389, 1113, 1067, 1003, 819, 782, 672 cm^{-1} .

Synthesis of 1,1,2,2-tetrakis(2'-methyl-[1,1'-biphenyl]-4-yl)-ethene (2).

Compound **1** (684 mg, 1 mmol) and 2-methylphenylboronic acid (816 mg, 6 mmol) were dissolved in toluene (80 mL), and then an aqueous solution of K₂CO₃ (1.66 g, 12 mmol) in water (15 mL) and anhydrous ethanol (10 mL) were added. Next, Pd(PPh₃)₄ catalyst (10 mg) was added and the reaction mixture was stirred at 85 °C for 6 h. After cooling to room temperature, The crude product was then purified using flash chromatography on silica gel (with petroleum ether and dichloromethane as eluent) to yield compound **2** (616 mg, 89%). ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.41–7.28 (m, 24H), 7.24 (d, *J* = 8.1 Hz, 8H), 2.44–2.29 (m, 12H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 142.28, 141.87, 141.14, 140.23, 135.43, 131.28, 130.39, 129.76, 128.63, 127.27, 125.84, 20.57. TOF-MS-EI: *m/z* 692.3 [M]⁺. Elemental anal. calcd. for C₅₄H₄₄: C, 93.60; H, 6.40. Found: C, 93.80; H, 6.25.

Synthesis of 1,1,2,2-tetrakis(2'- bromomethyl-[1,1'-biphenyl]-4-yl)-ethene (3).

4.5 equivalents of *N*-bromosuccinimide (NBS) and azodiisobutyronitrile (AIBN) (0.16 g, 0.972 mmol) were added to a solution of **2** (1.02 g, 1.44 mmol) in dry carbon tetrachloride (100 mL). The resulting mixture was refluxed for 2 h under argon atmosphere. After cooling, the succinimide was removed by filtration and the filtrate was concentrated under vacuum. Then the crude product was purified by dissolving in chloroform and hexane to obtain compound **3** (0.87 g) in a yield of 69%. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.55 – 6.97 (m, 32H), 4.54 (s, 8H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 142.67, 141.93, 141.15, 138.70, 135.25, 131.46, 131.00, 130.49, 128.62, 128.57, 128.01, 32.51.

Synthesis of 1,1,2,2-tetrakis(2'-(ethylthio)propyl-[1,1'-biphenyl]-4-yl)-ethene (S4).

A solution of compound **3** (2 g, 1.98 mmol) and thiourea (1.5 g, 19.6 mmol) in THF (150 mL) was heated at reflux for 5 h. After removal of THF under reduced pressure, the residue was treated with 0.36 M KOH solution (100 mL), and the mixture was heated at reflux for 5 h. The solution was acidified with dilute HCl at 0~5 °C and then extracted with CH₂Cl₂ (150 mL). The organic layer was washed with water, dried, and evaporated. The residue was chromatographed on silica gel to give the compound **S4** (49.11%) as white solid. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.47 (d, *J* = 7.4 Hz, 4H), 7.41 – 7.31

(m, 8H), 7.29 (dt, $J = 15.0, 5.3$ Hz, 20H), 3.75 (d, $J = 7.6$ Hz, 8H), 1.70 (t, $J = 7.6$ Hz, 4H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 142.50, 141.08, 141.07, 139.32, 138.70, 131.42, 130.32, 129.36, 128.67, 127.90, 127.12, 26.82. HRMS $m/z = 820.2235$. ($\text{M}-\text{H}^+$), calculated 820.23. Elemental anal. for $\text{C}_{54}\text{H}_{44}\text{S}_4$: C, 78.98; H, 5.40; S, 15.62. Found: C, 79.13; H, 5.52; S, 15.47.

Procedure for prepared of CEES spiked soil sample.

Soil sample (2.0 g) was mixed with **CEES** in THF (2 mL) and this was allowed to stand for 20 min. The solvent from soil sample was evaporated by nitrogen blow down. **CEES** spiked soil sample was reacted with aqueous solution of **S4** (1 μM) in 1 mL of buffer solution (bicarbonate-hydroxide buffer, pH 9.5) at 80 $^\circ\text{C}$ for 5 mins to give a solution of podand **L**. The suspension solution was centrifuged and aqueous solution was carefully decanted. The pH of this solution goes down which was maintained at 9 by the addition of 0.1M NaOH solution. The sample was then divided into two equal portions, one of which was treated with a solution of Hg^{2+} and the other remained unchanged. Moreover, the soil sample without spiked **CEES** was also treated with **S4** in a similar manner.

2. Choice of metal ions

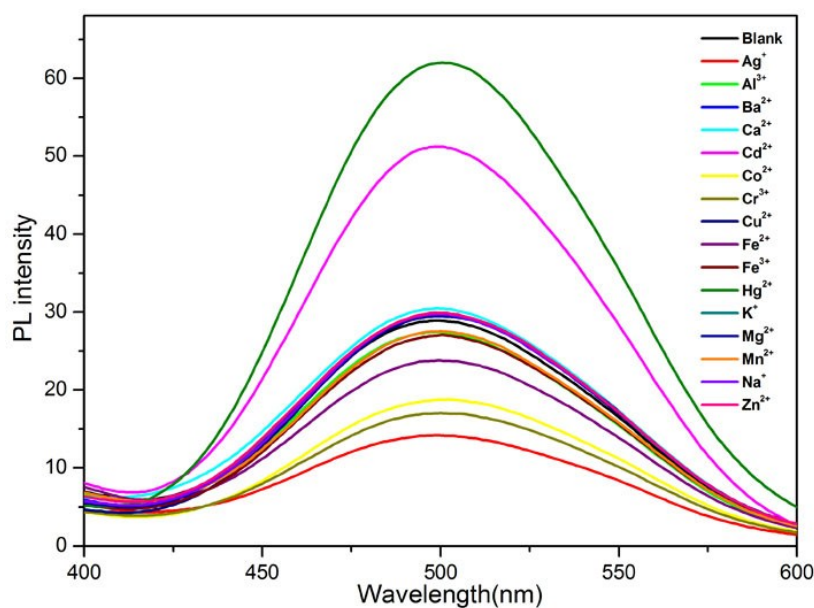


Figure S1. The fluorescent change of **L** to different metal ions (6 equivalents).

3. Detection limit

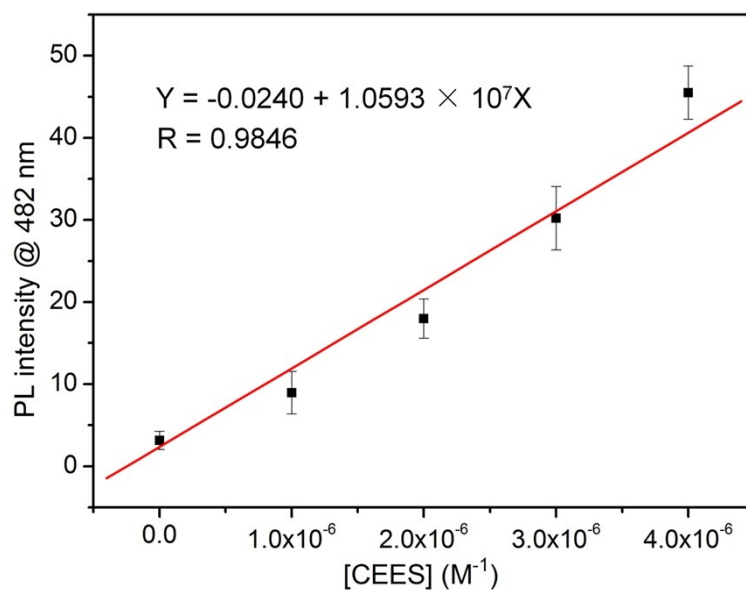


Figure S2. Plot of fluorescence intensity (at 482 nm) of **S4** versus the concentrations of **CEES** in the range of 0 – 4.0 μM [slope (S) = 1.06×10^7 , $\sigma = 3.87$, Detection limit = 1.10 μM].

4. AIE property

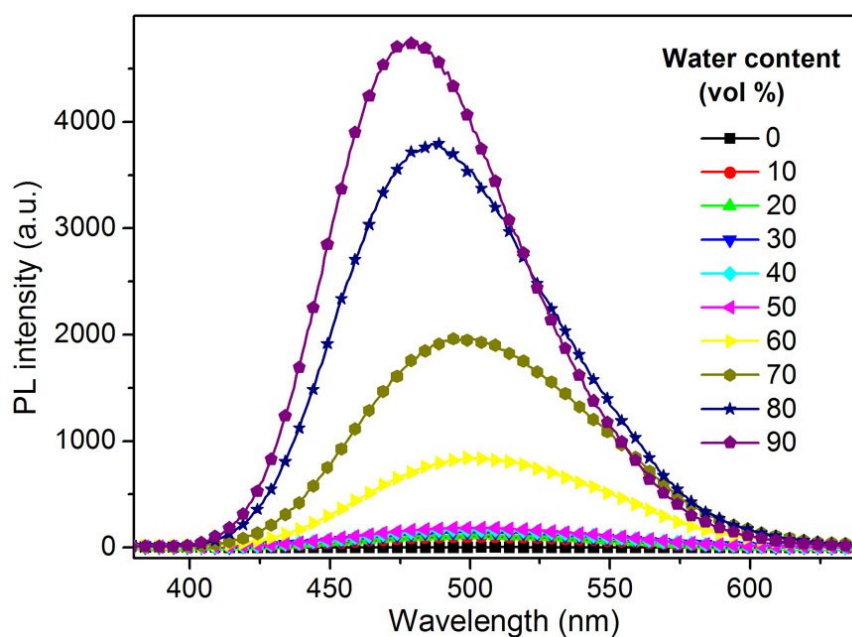


Figure S3. PL spectra changes of **S4** (10 μM) depending on the water fractions in THF.

5. Fluorescence decay

To gain more insight into the luminescence mechanism, PL decay measurements of the THF solution (20 μM) of **S4**, the blue crystal **B-S4** and the CH_2Cl_2 -fumed **S4** were employed, as shown in Fig. S3. Compared to the two solid-state samples, the THF solution of **S4** exhibits a short decay time. It is worth pointing out that the PL decay curve of the THF solution of **S4** can be fitted to a second-order exponential decay. The decay times of the fast and slow components are respectively 0.68, 3.49 and 5.67 ns, with a calculated average lifetime of 2.84 ns. Evidently, the shorter lifetime (0.68 ns) should be attributed to the free **S4** single molecule, whose excited state is mainly deactivated by nonradiative decay. The longer lifetime (5.67 ns) is caused by the greater structural rigidity of the casually aggregated **S4** molecules, which is more consistent with the lifetime of the CH_2Cl_2 -fumed **S4** (5.67 ns). On the other hand, the two solid-state samples, the blue crystal and the CH_2Cl_2 -fumed **S4** also show different decay times, which indicates that they undergo different relaxation routes or pathways from the molecular excited state to the ground state.

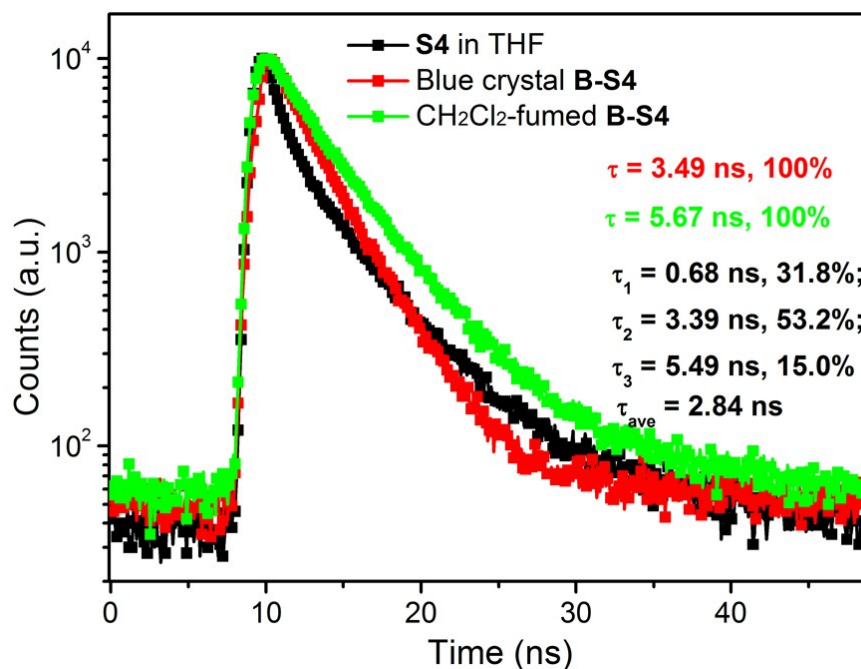


Figure S4. Fluorescence decay profiles of the blue crystal, CH_2Cl_2 -fumed sample and THF solution (20 μM) of **S4**.

6. X-ray single-crystal structure

Table S1. Selected crystallographic data for **S4**.

crystals	S4
formula	C ₅₄ H ₄₄ S ₄
fw[g·mol ⁻¹]	821.13
crystal color	Colorless
crystal system	Triclinic
space group	P-1
<i>a</i> [Å]	11.2121(16)
<i>b</i> [Å]	13.2318(18)
<i>c</i> [Å]	16.716(2)
β [°]	82.894(5)
<i>V</i> [Å ³]	2199.6(5)
<i>Z</i>	2
ρ_{calcd} [Mg/m ³]	1.240
μ [mm ⁻¹]	0.252
<i>T</i> [K]	296
$\theta_{\text{min}}\text{--}\theta_{\text{max}}$ [°]	1.302 to 25.649
<i>R</i> / <i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.1850/0.2957

7. DSC determination

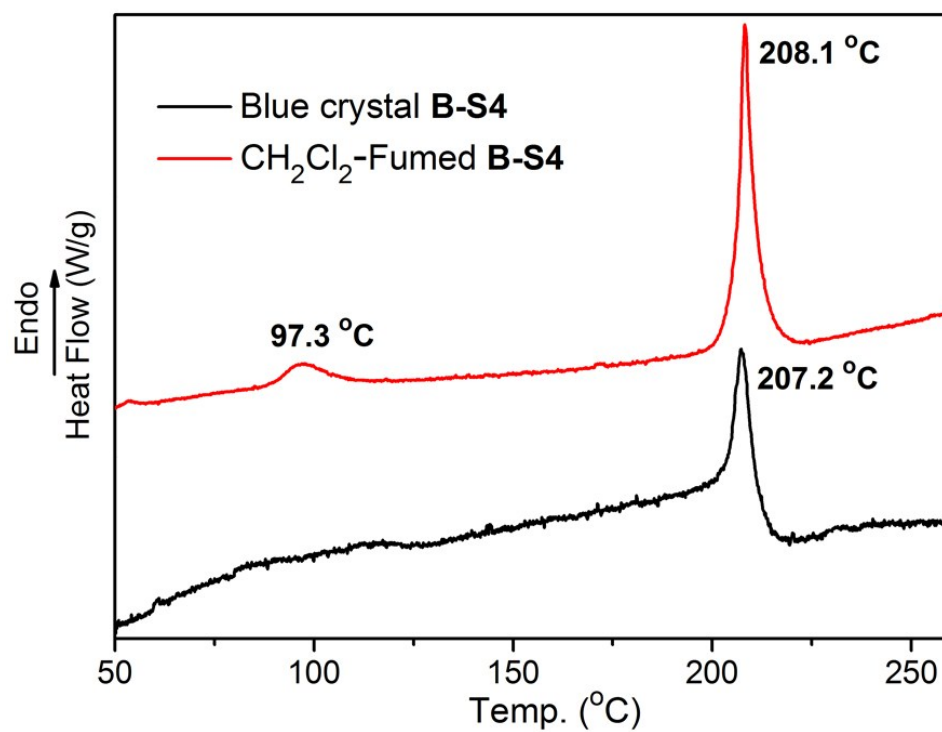


Figure S5. DSC profiles of the blue crystal **B-S4** and CH₂Cl₂ fumed **B-S4** sample.

8. Mass spectrometry of compounds S4 and L (X=H)

+TOF MS: 1.8351 min from Sample 1 (TuneSampleID) of MT20170414101319.wiff
a=7.02790960018750710e-004, t0=-2.37910443388647810e-001 (DuoSpray ())

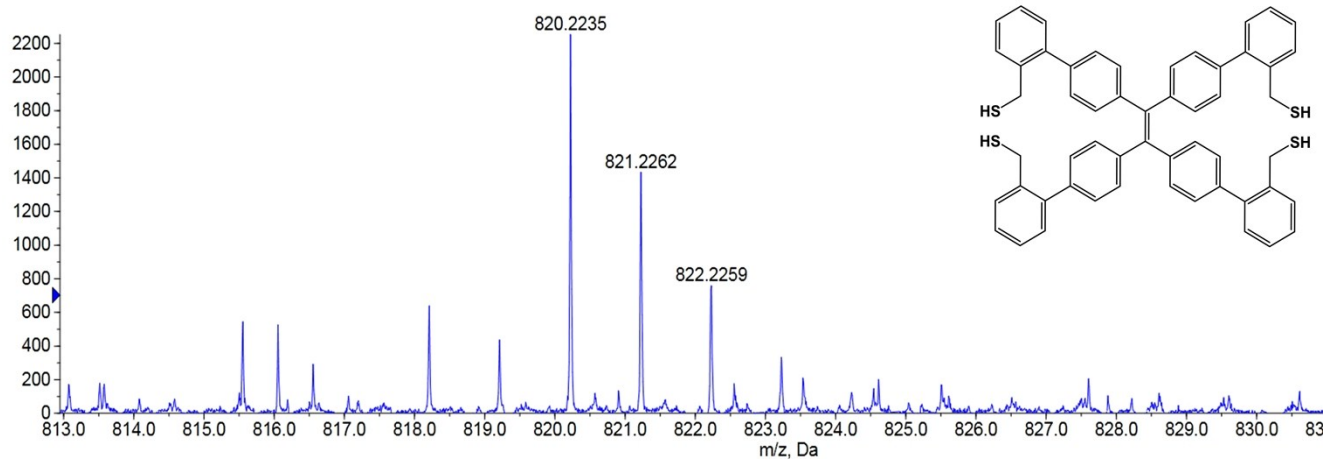


Figure S6. HRMS of compound S4 (m/z 820.23).

Y2 #165-168 RT: 0.67-0.71 AV: 4 NL: 4.10E2
T: ITMS - c ESI Full ms [100.00-1200.00]

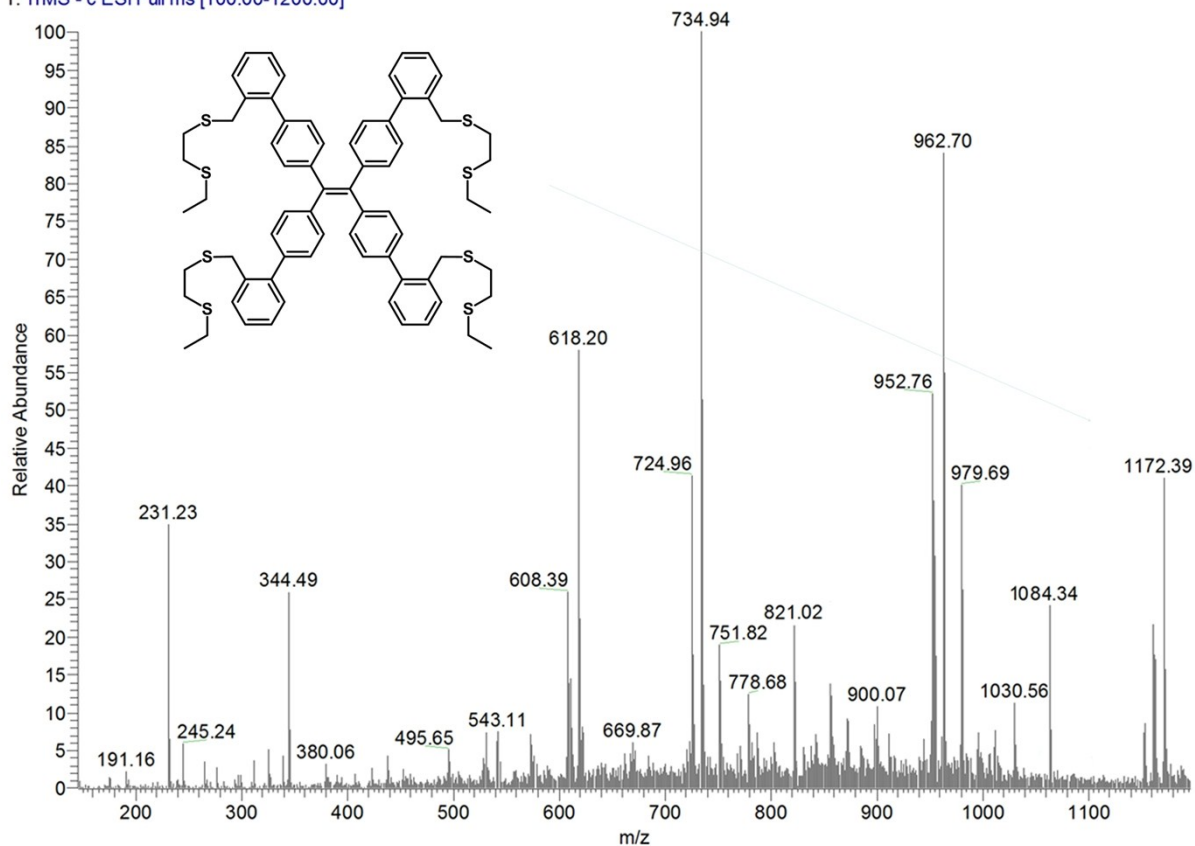


Figure S7. EI-MS of compound L (X=H) (m/z 1172.39).

9. ^1H NMR and ^{13}C NMR

YMS-20160622-WH-85-1
C13CPD CDC13 {D:\2016-1} ZHL 42

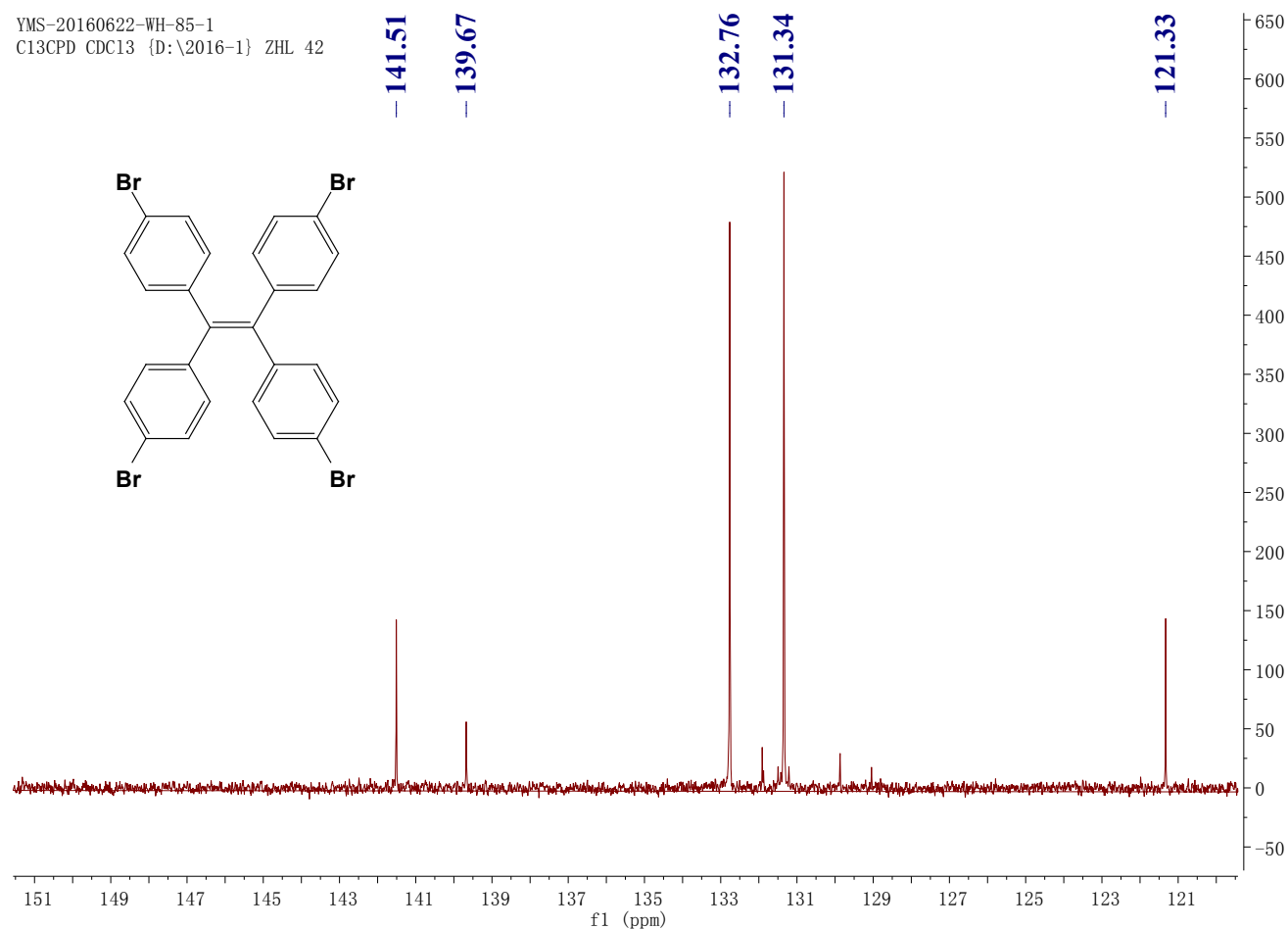


Figure S8. ^{13}C NMR spectrum (125 MHz, CDCl_3) of compound 1.

YMS-20170728-WH-86-2
PROTON CDC13 {D:\2017-2} ZHL 14

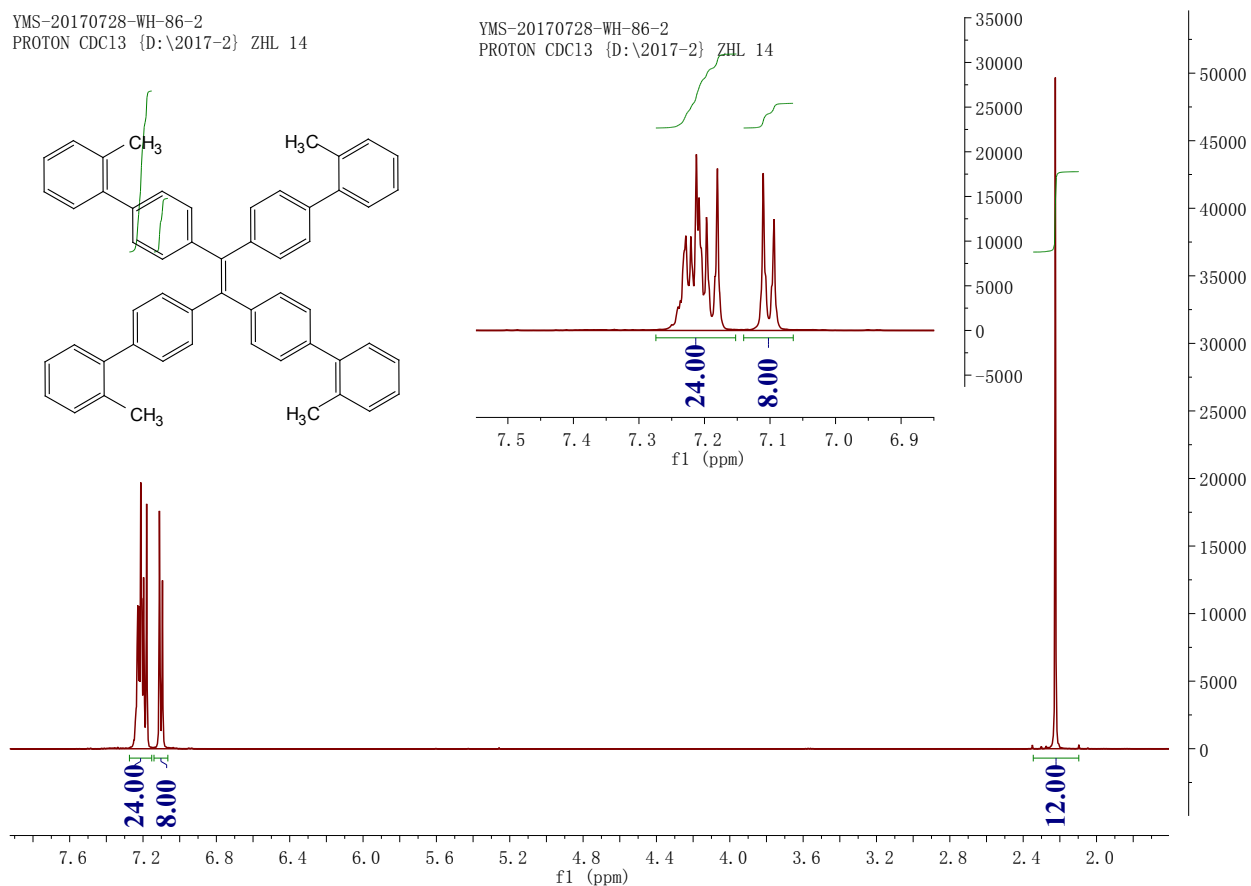


Figure S9. ¹H NMR spectrum (500 MHz, CDCl₃) of compound 2.

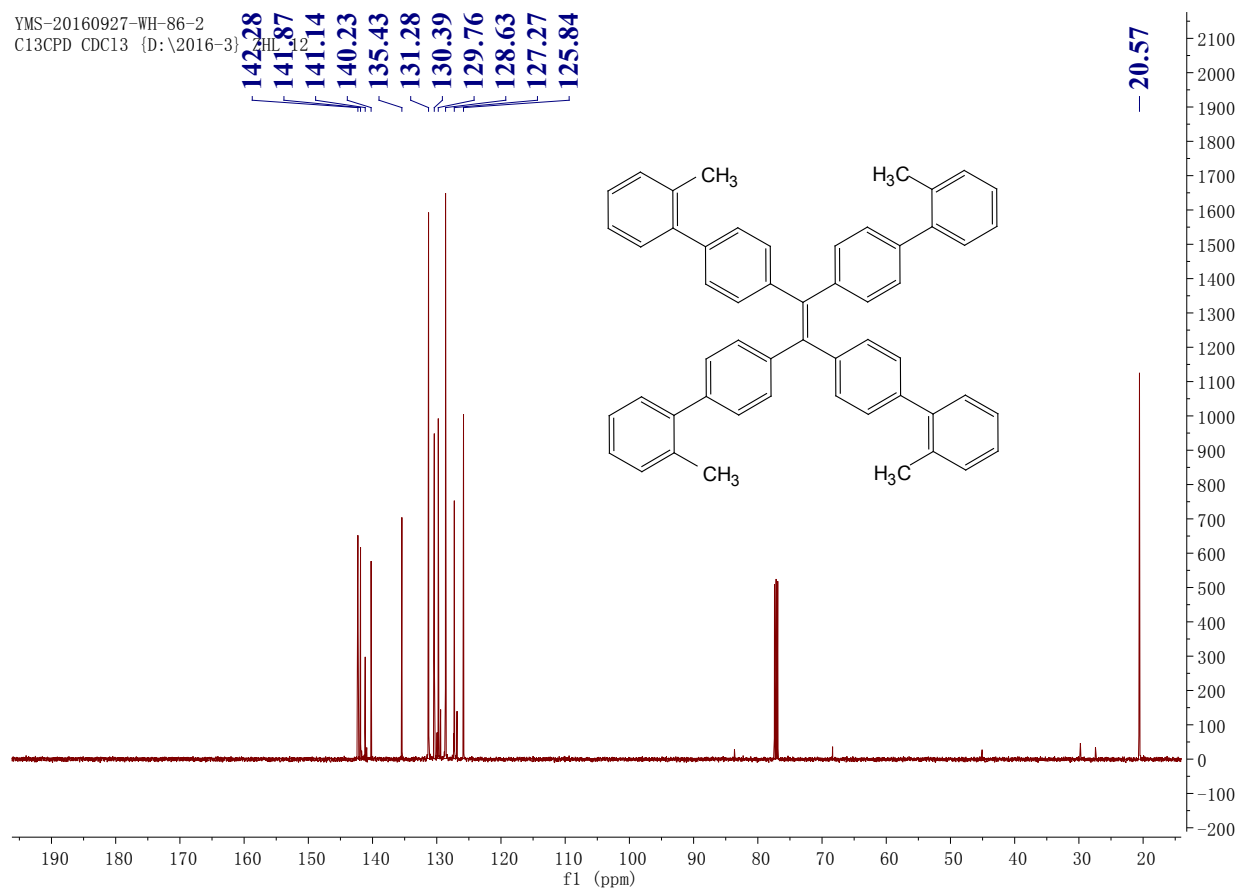


Figure S10. ¹³C NMR spectrum (125 MHz, CDCl₃) of compound 2.

YMS-20160927-WH-87-3
 PROTON CDC13 {D:\2016-3} ZHL 13

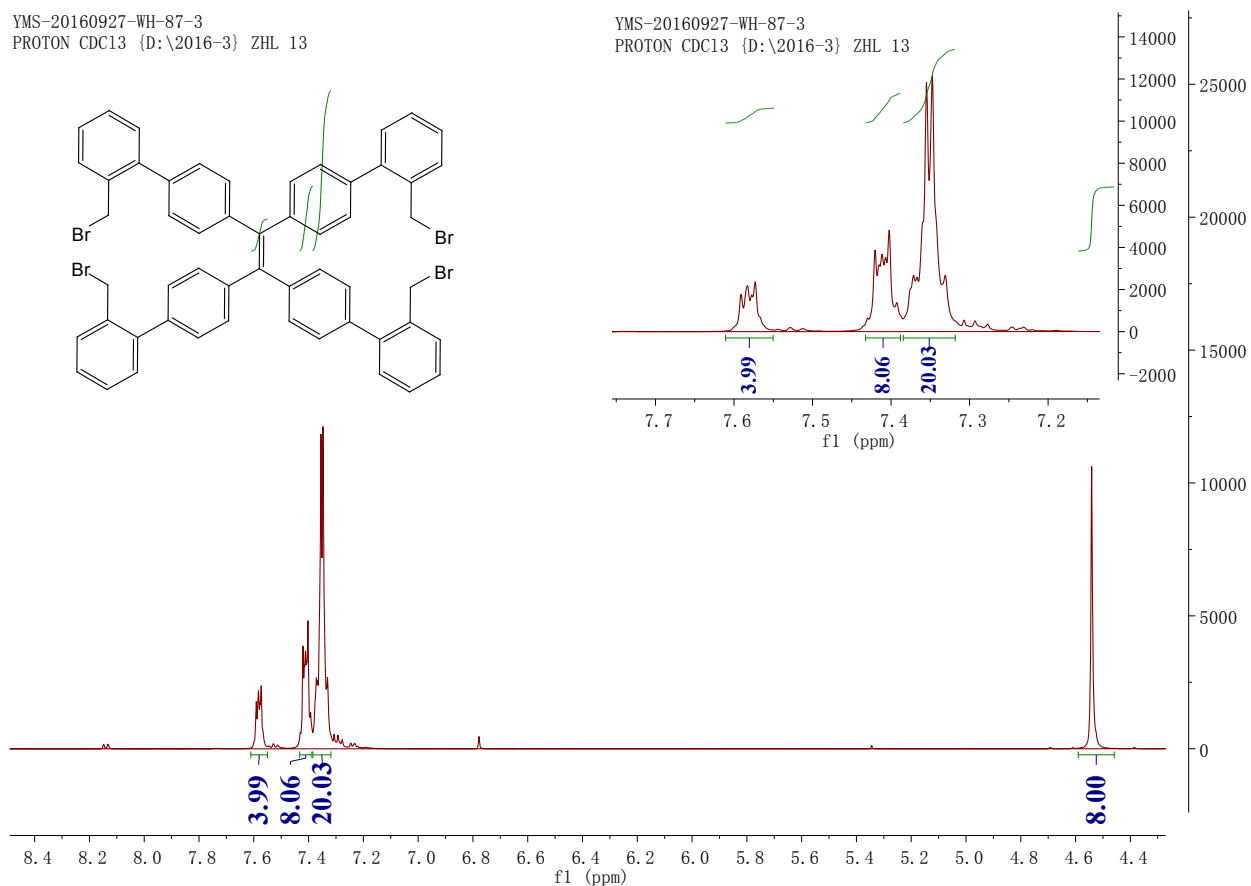


Figure S11. ¹H NMR spectrum (500 MHz, CDCl₃) of compound 3.

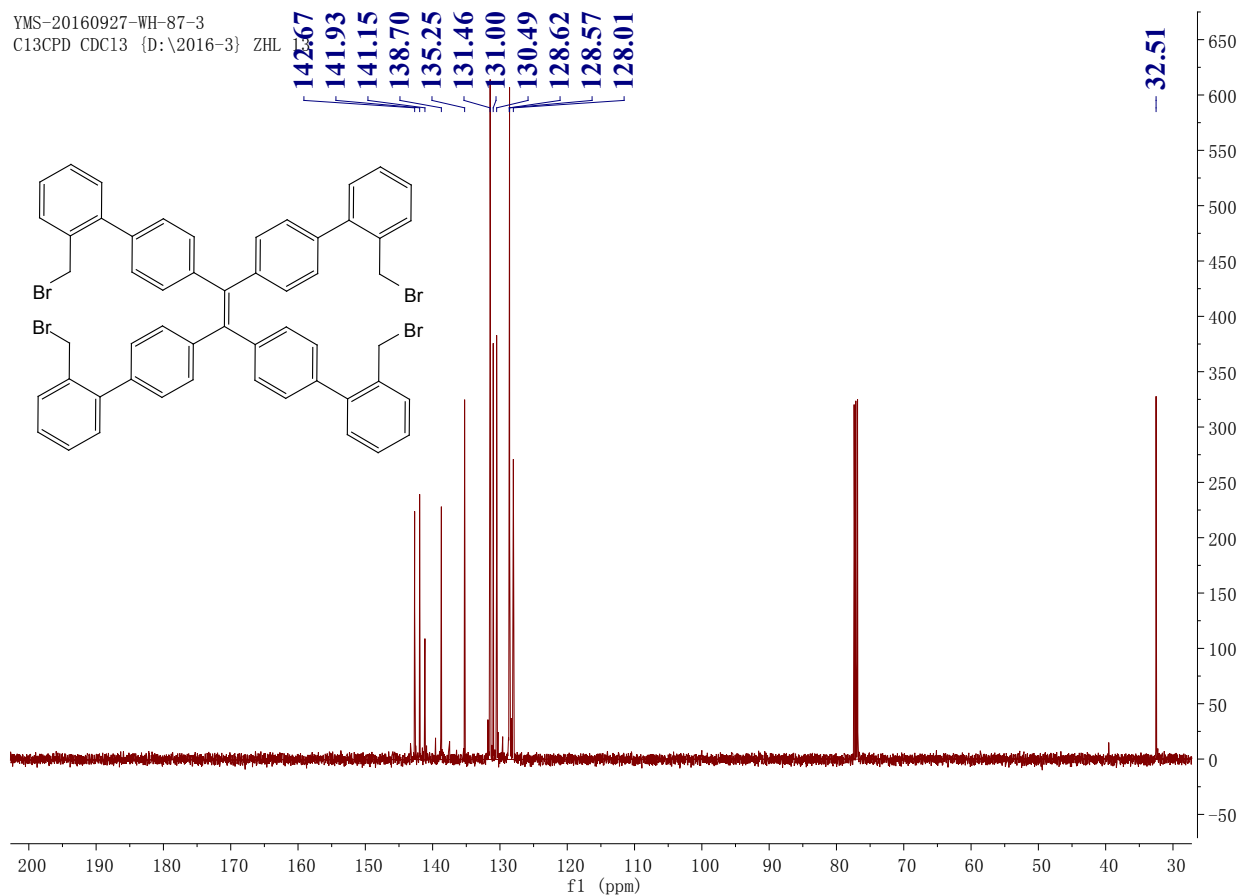


Figure S12. ¹³C NMR spectrum (125 MHz, CDCl₃) of compound 3.

YMS-20160927-WH-94-2
PROTON CDC13 {D:\2016-3} ZHL 14

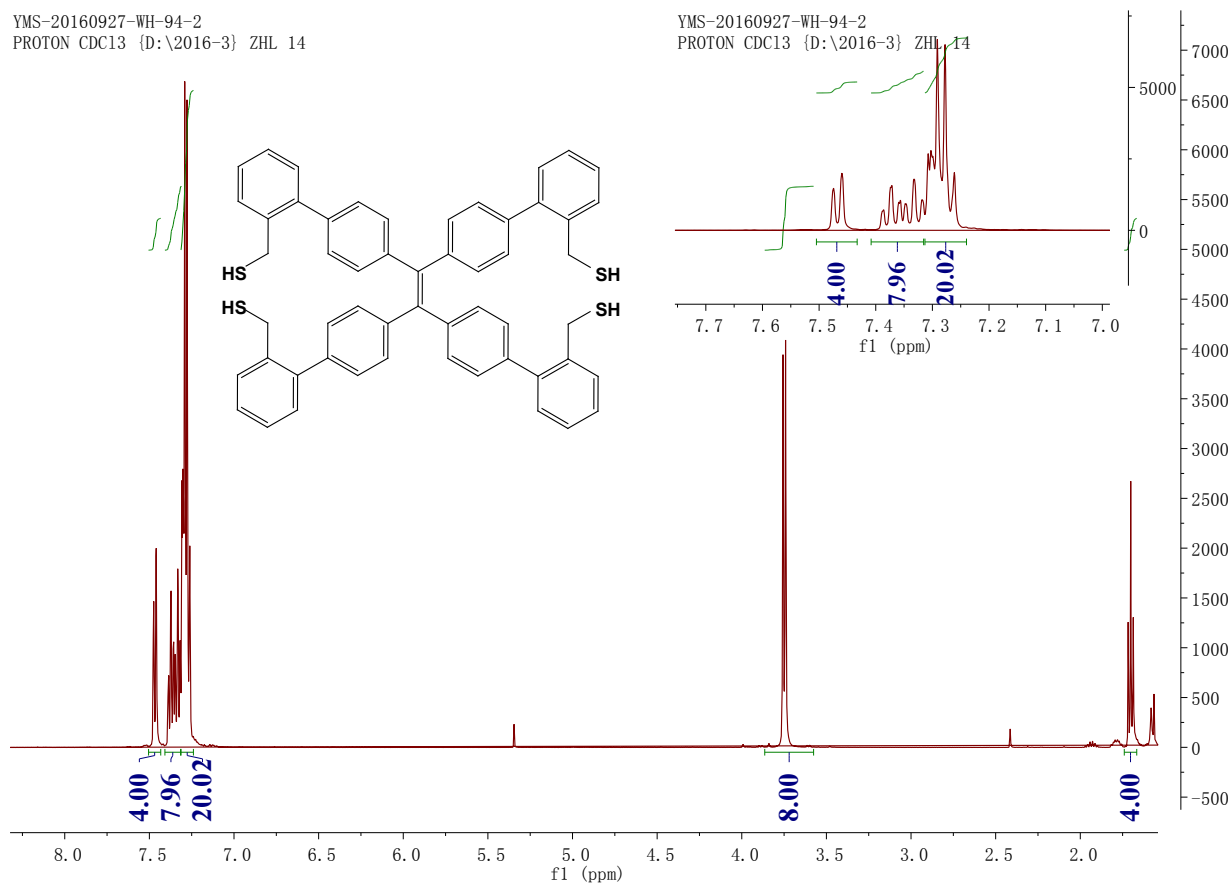


Figure S13. ¹H NMR spectrum (500 MHz, CDCl₃) of compound S4.

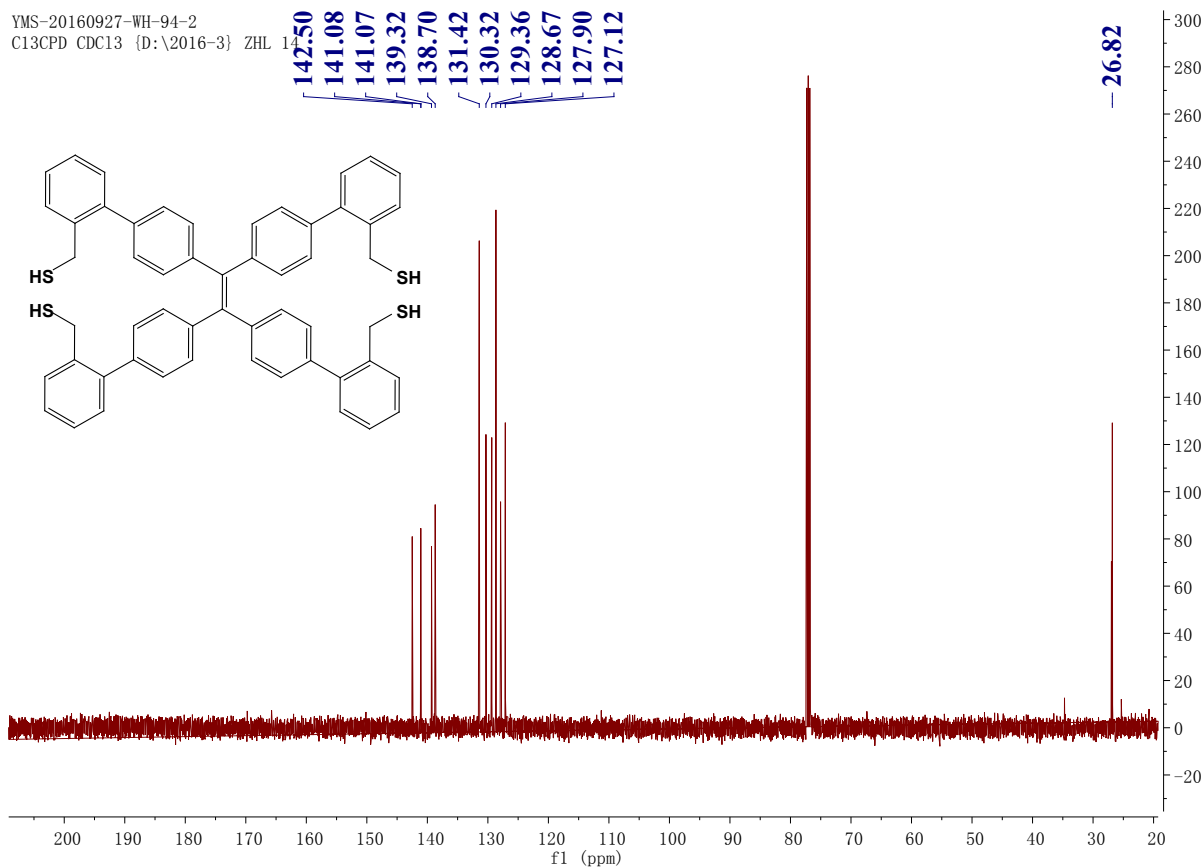


Figure S14. ¹³C NMR spectrum (125 MHz, CDCl₃) of compound S4.