Supporting Imformation

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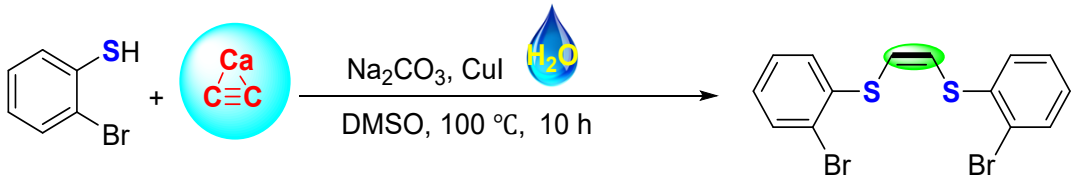
1. General information

Unless otherwise noted, all reactions were carried out in high boron silicon withstand voltage tubes. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer at room temperature. Chemical shift (ppm) were referenced to tetramethylsilane (TMS, delta =0ppm) in $CDCl_3$ as internal standard. ^{19}F NMR spectra were obtained on a Bruker AVANCEIII 400 spectrometer at room temperature; ^{13}C NMR spectra were obtained on a Bruker AVANCEIII 500 spectrometer at room temperature and calibrate with $CDCl_3$ (delta = 77.00 ppm). Data for ^{1}H NMR were reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved), coupling constant (Hz) and integration. Data for ^{13}C NMR were reported in terms of chemical shift and multiplicity where appropriate. High-Resolution Mass Spectrometry (HRMS) were performed on a Thermo Fisher LTQ Orbit rap XL. Anhydrous solvents were from J&K Scientific Ltd or Adamas and dried by standard procedures. The water comes from the Wahaha Company. All other commercially available reagents were from Innochem Chemicals or Bidepharm and used as received. Calcium carbide was purchased fromMacklin Chemical Company(China, purity: 98%), and ground into powder (ca. 50-100 mesh) in aceramic mortarprior to use. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. The crude product was purifed by reverse phase flash with the following conditions (lineal gradient of 0-100% MeCN in H_2O in 30 min. flux of 40 mL/min, in a symmetry column ^{18}C (30g), detection at 254 nm and 220 nm) to afford Products.

2. Experimental Section

1) Optimization of reaction conditions.



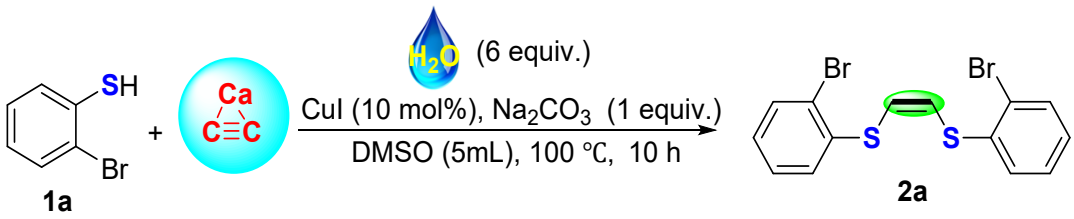
1a **2a**

Entry	Catalyst (10 mol%)	Base (2 eq.)	H_2O (x eq.)	Solvent (1 mL)	Yield/%
1	-	Na_2CO_3	3	DMSO	0
2	CuI	Na_2CO_3	3	DMSO	48
3	CuOTf	Na_2CO_3	3	DMSO	30
4	$Cu(OAc)_2$	Na_2CO_3	3	DMSO	11
5	CuI	t-BuOK	3	DMSO	Trace
6	CuI	Cs_2CO_3	3	DMSO	43

7	CuI	NaOH	3	DMSO	Trace
8	CuI	DBU	3	DMSO	Trace
9	CuI	Na_2CO_3	10	DMSO	28
10	***CuI***	Na_2CO_3	***6***	***DMSO***	***87***
11	CuI	Na_2CO_3	6	EA	51
12	CuI	Na_2CO_3	6	MeCN	34
13	CuI	Na_2CO_3	6	DMF	60

Reaction conditions: 1a (0.3 mmol), CaC_2 (1.2 mmol), H_2O (1.8 mmol), base (0.3 mmol), and a copper catalyst (0.03 mmol) in 5 mL of solvent stirred at 100 ℃ for 10 h under an air atmosphere.

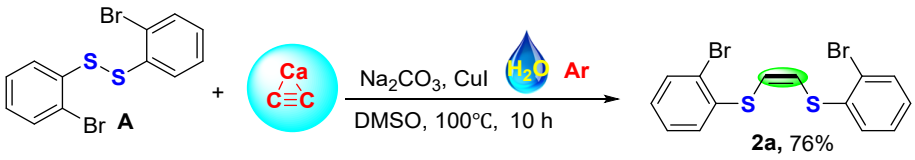
2) General procedure for synthesis of compound 2 :



To a 25 mL high boron silicon withstand voltage tube was charged with 2-bromo-phenylthiophenol **1a** (0.3 mmol), CaC_2 (1.2 mmol),CuI (0.03 mmol), Na_2CO_3 (0.3 mmol),H_2O (1.8 mmol), finally add 5 ml DMSO. The mixture was then stirred at 100℃ for 10 hours. After completion, the mixture was quenched with water (5 mL), and extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **2a**.

3) Mechanistic Studies

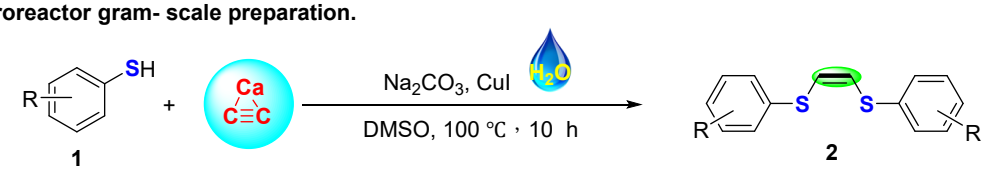
Reaction of 1,2-bis(2-bromophenyl)disulfane and CaC_2 under Argon.

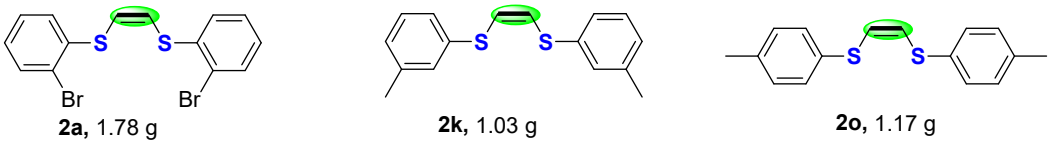


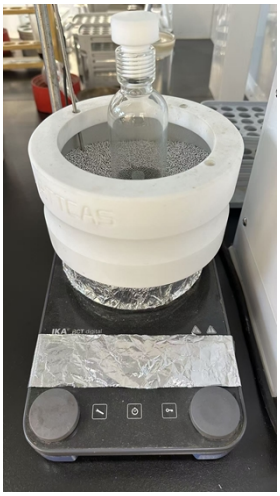
To a 25 mL high boron silicon withstand voltage tube was charged with 1,2-bis(2-bromophenyl)disulfane **A** (0.2 mmol), CaC_2 (1.2 mmol), CuI (0.03 mmol), Na_2CO_3 (0.3 mmol), H2O (1.8 mmol), 5 ml DMSO, finally, the apparatus was purged with argon via a long needle. The mixture was then stirred at 100℃ for 10 hours. After completion, the mixture was quenched with water (5 mL), and extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **2a**.

4) Microreactor gram- scale preparation.

Microreactor gram- scale preparation.

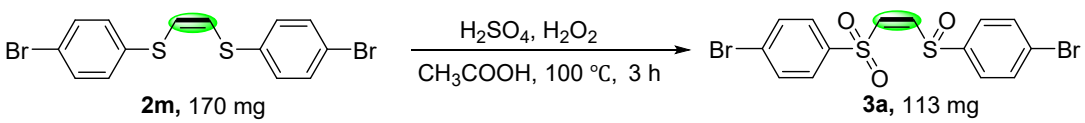






To a 100 mL high boron silicon withstand voltage tube was charged with 4-bromobenzenethiol **1o** (13.7 mmol), CaC_2 (54.8 mmol), CuI (1.37 mmol), Na_2CO_3 (13.7 mmol), finally add 5 ml DMSO and H_2O (82.2mmol). The mixture was then stirred at 100℃for 10 hours. After completion, the mixture was extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **2o** (63% yield). Employing an analogous synthetic method, reaction of **1a** and **1k** provided **2a** (65% yield) and **2k** (55% yield), respectively.

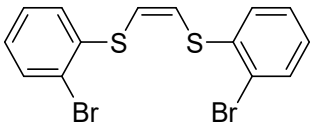
5) Synthsis of (Z)-1,2-bis((4-bromophenyl)thio)ethene derivative.



A mixture of (*Z*)-1,2-bis((4-bromophenyl)thio)ethene **2m** (0.4 mmol) and glacial acetic acid (3 mL)

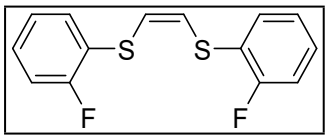
was stirred in a 5 mL round-bottom flask. The mixture was cooled to 0 ℃, followed by the addition of 30% H_2O_2 (0.02 mmol) and concentrated H_2SO_4 (0.07 mL). After the addition, the ice bath was removed and the reaction mixture was heated to 100 ℃ in a sand bath for 3 hours. Upon completion, the mixture was cooled, and any remaining oxidizer was quenched with sodium hydrosulfite. The mixture was then neutralized with sodium carbonate and extracted with dichloromethane (3 × 5 mL).The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **3a**.

3. Spectroscopic data



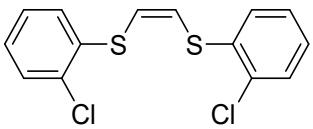
(Z)-1,2-bis((2-bromophenyl)thio)ethene (2a)

Yellow solid (52 mg, 87% yield); (***Z***:***E***>99:1) **^{1}HNMR (500MHz,Chloroform-d)** δ 7.58 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.38 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.30 (td, *J* = 7.8, 1.0 Hz, 2H), 7.11 (td, *J* = 8.0, 1.5 Hz, 2H), 6.61 (s, 2H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 136.5, 133.4, 130.0, 128.1, 128.1, 126.2, 124.02 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}Br_2S_2}$+H]$^+$: 400.8669; Found: 400.8663.



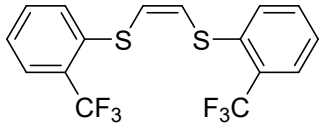
(Z)-1,2-bis((2-fluorophenyl)thio)ethene (2b)

Colorless liquid (42 mg, 77% yield); (***Z***:***E***>97:3) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.38 – 7.31 (m, 2H), 7.21 – 7.16 (m, 2H), 7.04 (dt, *J* = 17.5, 8.1 Hz, 4H), 6.41 (s, 2H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 161.9, 159.9, 132.0 (d, *J* =1.1 Hz), 129.3 (d, *J* =12.7 Hz), 125.0 (d, *J* = 1.9 Hz), 124.9 (d, *J* = 3.8 Hz), 122.1 (d, *J* = 17.3 Hz), 116.1 (d, *J* = 21.9 Hz); **^{19}F NMR (376 MHz, Chloroform-d)** δ -109.66 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}F_2S_2}$+H]$^+$: 281.0265; Found: 281.0271.



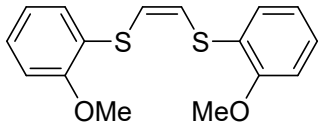
(Z) -1,2-bis((2-chlorophenyl)thio)ethene (2c)

Colorless liquid (44 mg, 82% yield); (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.44 – 7.35 (m, 4H), 7.25 (td, *J* = 7.5, 1.0 Hz, 2H), 7.19 (td, *J* = 7.5, 1.5 Hz, 2H), 6.61 (s, 2H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 134.3, 133.9, 130.0, 130.0, 127.9, 127.4, 125.7 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}Cl_2S_2}$+H]$^+$: 312.9679; Found: 312.9677.



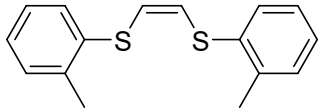
(Z)-1,2-bis((2-(trifluoromethyl)phenyl)thio)ethene (2d)

White solid (33 mg, 61%); (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.69 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.49 (m, 4H), 7.37 (t, *J* = 7.2 Hz, 2H), 6.55 (s, 2H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 134.6, 132.4, 130.1 (q, *J* =30.24 Hz), 127.2, 127.0 (q, *J* = 6.3 Hz), 126.5, 123.8 (d, *J* = 274.48 Hz), 120.5; **^{19}F NMR (376 MHz, Chloroform-d)** δ -60.64 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{10}F_6S_2}$+H]$^+$: 381.0206; Found: 381.0207.



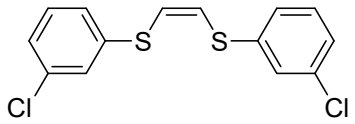
(Z)-1,2-bis((2-methoxyphenyl)thio)ethene (2e)

White solid (27 mg, 50% yield); (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.25 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.16 – 7.11 (m, 2H), 6.88 – 6.84 (m, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 6.45 (s, 2H), 3.80 (s, 6H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 157.2, 130.1, 128.1, 125.0, 123.7, 121.3, 111.0, 56.0 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{16}O_2S_2}$+H]$^+$: 305.0664; Found: 305.0657.



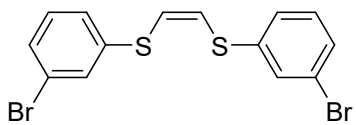
(Z)-1,2-bis(o-tolylthio)ethene (2f)

Yellow liquid (39 mg, 72% yield); (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.31 – 7.27 (m, 2H), 7.12 – 7.05 (m, 6H), 6.33 (s, 2H), 2.34 (s, 6H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 138.4, 134.5, 130.5, 130.2, 127.3, 126.8, 125.2, 20.7 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{16}S_2}$+H]$^+$: 273.0766; Found: 273.0763.



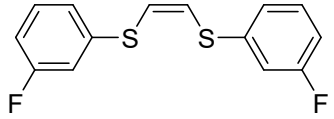
(Z)-1,2-bis((3-chlorophenyl)thio)ethene (2g)

Yellow liquid (44 mg, 82% yield); (***Z***:***E***>96:4) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.29 (s, 2H), 7.19 – 7.12 (m, 6H), 6.47 (s, 2H), 6.45 (s, 0.08H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 137.1, 135.1, 130.3, 129.0, 127.0, 127.3, 125.4 ppm; HRMS (ESI): HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}Cl_2S_2}$+ H]$^+$: 312.9673; Found: 312.9666.



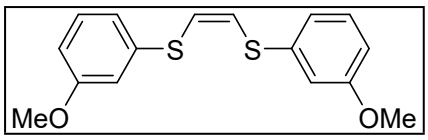
(Z)-1,2-bis((3-bromophenyl)thio)ethene (2h)

Yellow liquid (46 mg, 77% yield); (***Z***:***E***>91:9) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.53 (s, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.55 (s, 2H), 6.54 (s, 0.21H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 137.3, 131.8, 130.5, 130.1, 127.9, 125.4, 123.2 ppm; HRMS (ESI): HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}Br_2S_2}$+H]$^{+}$: 400.8663; Found: 400.8656.



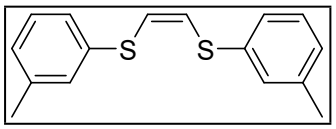
(Z)-1,2-bis((3-fluorophenyl)thio)ethene (2i)

Yellow liquid (40 mg, 74% yield); (***Z***:***E***>96:4) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.22 (td, *J* = 8.0, 6.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.02 (dt, *J* = 9.3, 1.9 Hz, 2H), 6.87 (td, *J* = 8.4, 2.3 Hz, 2H), 6.50 (s, 2H), 6.48 (s, 0.25H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 163.0 (d, *J* = 249.5 Hz), 137.3 (d, *J* = 7.8 Hz), 130.6 (d, *J* = 8.4 Hz), 125.3, 124.9 (d, *J* = 3.0 Hz), 116.2 (d, *J* = 23.4 Hz), 114.1 (d, *J* = 21.3 Hz); **^{19}F NMR (376 MHz, Chloroform-d)** δ -111.57 ppm; HRMS (ESI): HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}F_2S_2}$+H]$^{+}$: 279.0119; Found: 279.0117.



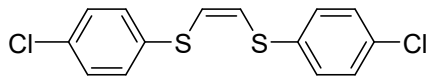
(Z)-1,2-bis((3-methoxyphenyl)thio)ethene (2j)

Yellow liquid (35 mg, 65% yield); (***Z***:***E***>70:30) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.26 – 7.17 (m, 4H), 7.11 – 7.03 (m, 2H), 7.02 – 6.87 (m, 6H), 6.81 – 6.73 (m, 4H), 6.53 (s, 2H), 6.53 (s, 1H), 3.80 (s, 6H), 3.79 (s, 3H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 160.1, 160.1, 136.0, 130.0, 130.1, 130.0, 125.4, 125.0, 121.7, 121.6, 119.6, 114.8, 114.7, 113.2, 112.8, 112.6, 55.4, 55.4, 55.4 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{16}O_2S_2}$+H]$^{+}$: 305.0664; Found: 305.0659.



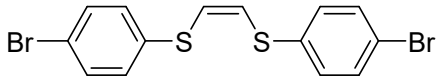
(Z)-1,2-bis(m-tolylthio)ethene (2k)

Yellow liquid (44 mg, 82% yield); (***Z***:***E***>91:9) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.15 – 7.05 (m, 6H), 6.96 (d, *J* = 5.5 Hz, 2H), 6.41 (s, 2H), 2.25 (s, 6H), 2.22 (s, 0.25H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 139.2, 139.1, 135.1, 134.8, 130.2, 130.1, 129.1, 129.1, 127.9, 127.9, 126.6, 126.6, 125.3, 125.0, 21.4 ppm; HRMS (ESI): HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{16}S_2}$+H]$^{+}$: 273.0766; Found: 273.0762.



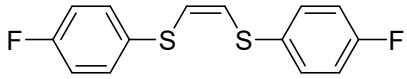
(Z)-1,2-bis((4-chlorophenyl)thio)ethene (2l)

White solid (45 mg, 84% yield); (***Z***:***E***>96:4); **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.23 – 7.17 (m, 8H), 6.38 (s, 2H), 6.36 (s, 0.12H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 133.6, 133.3, 130.9, 129.41, 125.3 ppm; HRMS (ESI-TOF)calc. for [$\mathbf{C_{14}H_{10}Cl_2S_2}$+H]$^+$: 312.9674; Found: 312.9666.



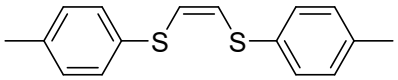
(Z)-1,2-bis((4-bromophenyl)thio)ethene (2m)

White solid (48 mg, 80% yield); (***Z***:***E***>96:4) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.40 – 7.35 (m, 4H), 7.20 – 7.16 (m, 4H), 6.41 (s, 2H), 6.39 (s, 0.09H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 134.3, 132.4, 131.1, 125.4, 121.2 ppm. HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}Br_2S_2}$+H]$^+$: 402.8648; Found: 402.8648.



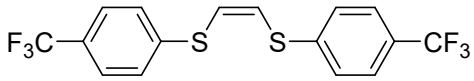
(Z)-1,2-bis((4-fluorophenyl)thio)ethene (2n)

White solid (41 mg, 76%); (***Z***:***E***>76:24) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.47 – 7.37 (m, 4H), 7.09 – 7.01 (m, 4H), 6.50 – 6.40 (m, 2H), 6.41 – 6.23 (m, 0.65H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 162.4 (d, *J* = 247.8 Hz), 132.2 (d, *J* = 8.2 Hz), 130.3 (d, *J* = 3.28 Hz), 125.4, 116.4 (d, *J* = 22.18 Hz); **^{19}F NMR (376 MHz, Chloroform-d)** δ -114.36 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}F_2S_2}$ +H]$^+$: 280.0191; Found: 280.0181.



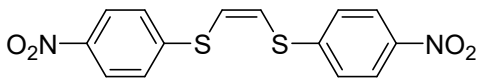
(Z)-1,2-bis(p-tolylthio)ethene (2o)

White solid(40 mg, 85%); (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.34 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 6.46 (s, 2H), 2.36 (s, 6H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 137.1, 131.8, 130.0, 130.0, 125.0, 21.2 ppm. HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{16}S_2}$+H]$^+$: 273.0766, Found: 273.0761.



(Z)-1,2-bis((4-(trifluoromethyl)phenyl)thio)ethene (2q)

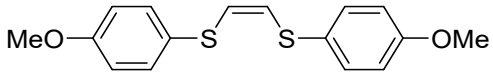
White solid (32 mg, 60%), (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.51 (d, *J* = 8.5 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 4H), 6.59 (s, 2H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 140.0, 129.1 (q, *J* = 32.9 Hz), 128.8, 126.2 (q, *J* = 3.7 Hz), 125.5, 124.1 (d, *J* = 272.4 Hz); **^{19}F NMR (376 MHz, Chloroform-d)** δ -111.57 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{10}F_6S_2}$+H]$^+$: 381.0201, Found:381.0197.



(Z)-1,2-bis((4-nitrophenyl)thio)ethene (2r)

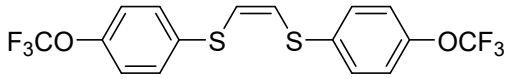
Yellow solid (34 mg, 63%); (***Z***:***E***>92:8) **^{1}H NMR (500 MHz, Chloroform-d)** δ 8.14 – 8.11 (m, 4H), 7.43 – 7.39 (m, 4H), 6.73 (s, 2H), 6.72 (s, 0.18H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 146.6,

144.0, 128.2, 125.8, 124.5 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_{10}N_2O_4S_2}$ +H]$^+$: 334.0082; Found:334.0088.



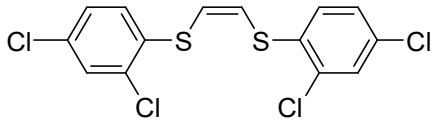
(Z)-1,2-bis((4-methoxyphenyl)thio)ethene (2s)

Yellow liquid(43 mg, 80%); (***Z***:***E***>97:3) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.41 – 7.36 (m, 4H), 6.90 – 6.86 (m, 4H), 6.32 (s, 2H), 6.27 (s, 0.07H), 3.81 (s, 6H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 159.5, 132.5, 126.0, 125.3, 114.9, 55.5 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{16}O_2S_2}$+H]$^+$: 305.0664; Found: 305.0660.



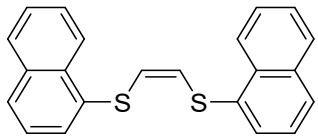
(Z)-1,2-bis((4-(trifluoromethoxy)phenyl)thio)ethene (2t)

White solid (44 mg, 83%); (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.43 (d, *J* = 9.0 Hz, 4H), 7.19 (d, *J* = 8.5 Hz, 4H), 6.52 (s, 2H); **^{13}C NMR (126 MHz, Chloroform-d)** δ148.5, 133.8, 131.1, 125.6, 121.9, 120.6 (q, *J* = 258.0 Hz); **^{19}F NMR (376 MHz, Chloroform-d)** δ -109.66 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{16}H_{10}F_6O_2S_2}$ +H]$^+$: 412.0026, Found: 412.0030.



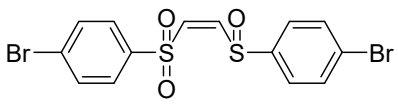
(Z)-1,2-bis((2,4-dichlorophenyl)thio)ethene (2u)

White solid (34 mg, 63%) ; (***Z***:***E***>98:2) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.43 (d, *J* = 2.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 8.5, 2.1 Hz, 2H), 6.56 (s, 2H), 6.48 (s, 0.04H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 134.8, 133.5, 132.8, 131.0, 129.9, 127.8, 126.0 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{14}H_8Cl_4S_2}$+H]$^+$: 379.8821; Found: 379.8819.



(Z)-1,2-bis(naphthalen-1-ylthio)ethene (2v)

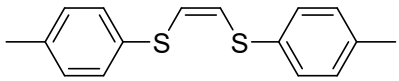
White liquid (27 mg, 50%); (***Z***:***E***>94:6) **^{1}H NMR (500 MHz, Chloroform-d)** δ 8.45 (d, J = 8.4 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.6 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 6.48 (s, 2H), 6.38 (s, 0.15H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 134.2, 133.0, 132.3, 129.8, 128.7, 128.6, 126.9, 126.6, 125.8, 125.7, 125.5 ppm; HRMS (ESI-TOF) calc. for [$\mathbf{C_{22}H_{16}S_2}$ +H]$^+$: 345.0766, Found: 345.0760.

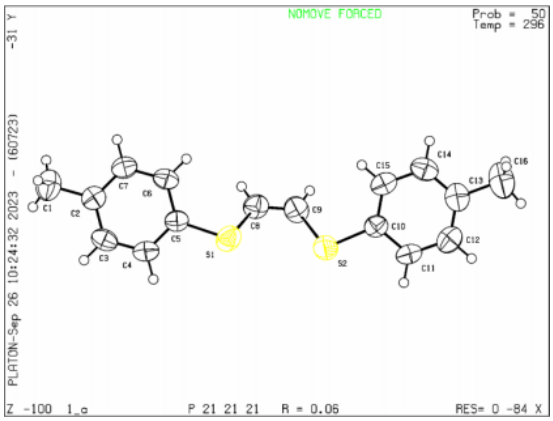


(Z)-1-bromo-4-((2-((4-bromophenyl)sulfinyl)vinyl)sulfonyl)benzene(3a)

White solid (113 mg, 70%); (***Z***:***E***>99:1) **^{1}H NMR (500 MHz, Chloroform-d)** δ 7.86 – 7.69 (m, 8H), 6.77 (d, *J* = 10.0 Hz, 1H), 6.67 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (126 MHz, Chloroform-d)** δ 152.5, 141.7, 137.9, 133.9, 133.4, 133.3, 133.1, 130.6, 129.7, 126.8 ppm; HRMS (ESI-TOF) calc. for [$C_{14}H_{10}Br_2O_3S_2$ +H]$^{+}$: 448.8511, Found: 448.8508.

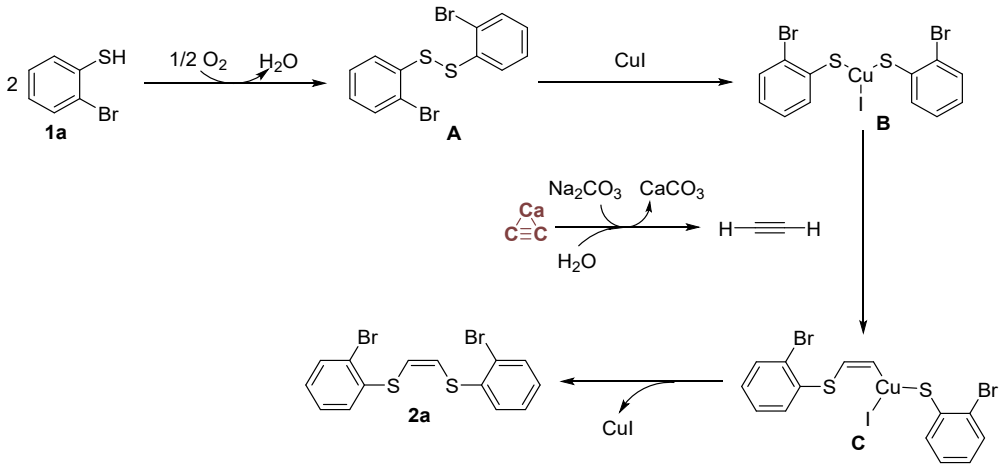
4. X-ray Single Crystal Diffraction Data of 2o（CCDC 2441924）





```
Bond precision:   C-C = 0.0059 A          Wavelength=0.71073

Cell:               a=5.4800(13)      b=7.981(2)      c=33.787(9)
                    alpha=90          beta=90         gamma=90
Temperature:        296 K

                  Calculated                Reported
Volume            1477.7(6)                 1477.6(7)
Space group       P 21 21 21                P 21 21 21
Hall group        P 2ac 2ab                 P 2ac 2ab
Moiety formula    C16 H16 S2                ?
Sum formula       C16 H16 S2                C16 H16 S2
Mr                272.41                    272.41
Dx,g cm-3         1.224                     1.225
Z                 4                         4
Mu (mm-1)         0.341                     0.341
F000              576.0                     576.0
F000'             577.15
h,k,lmax          6,9,40                    6,9,40
Nref              2647[ 1590]               2623
Tmin,Tmax         0.928,0.940               0.864,0.864
Tmin'             0.928

Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864
AbsCorr = MULTI-SCAN

Data completeness= 1.65/0.99        Theta(max)= 25.119

R(reflections)= 0.0632( 1583)                    wR2(reflections)=
                                                 0.1421( 2623)
S = 1.024                  Npar= 141
```

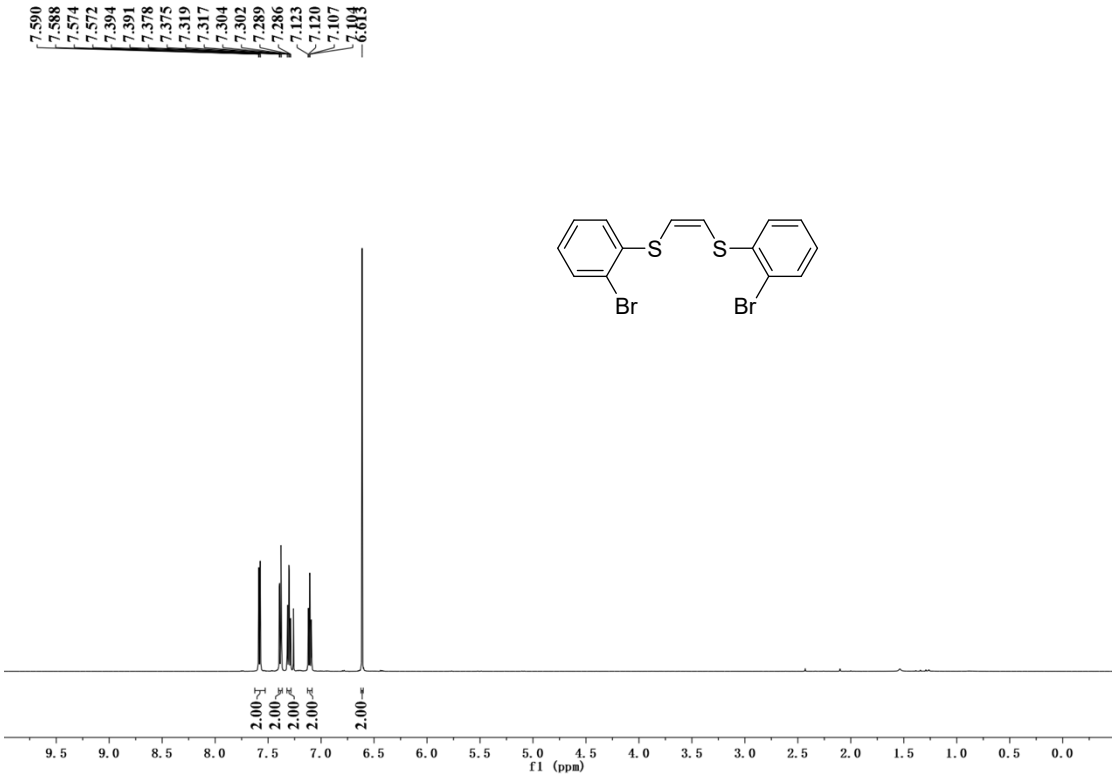
5. Proposed mechanism conclusions



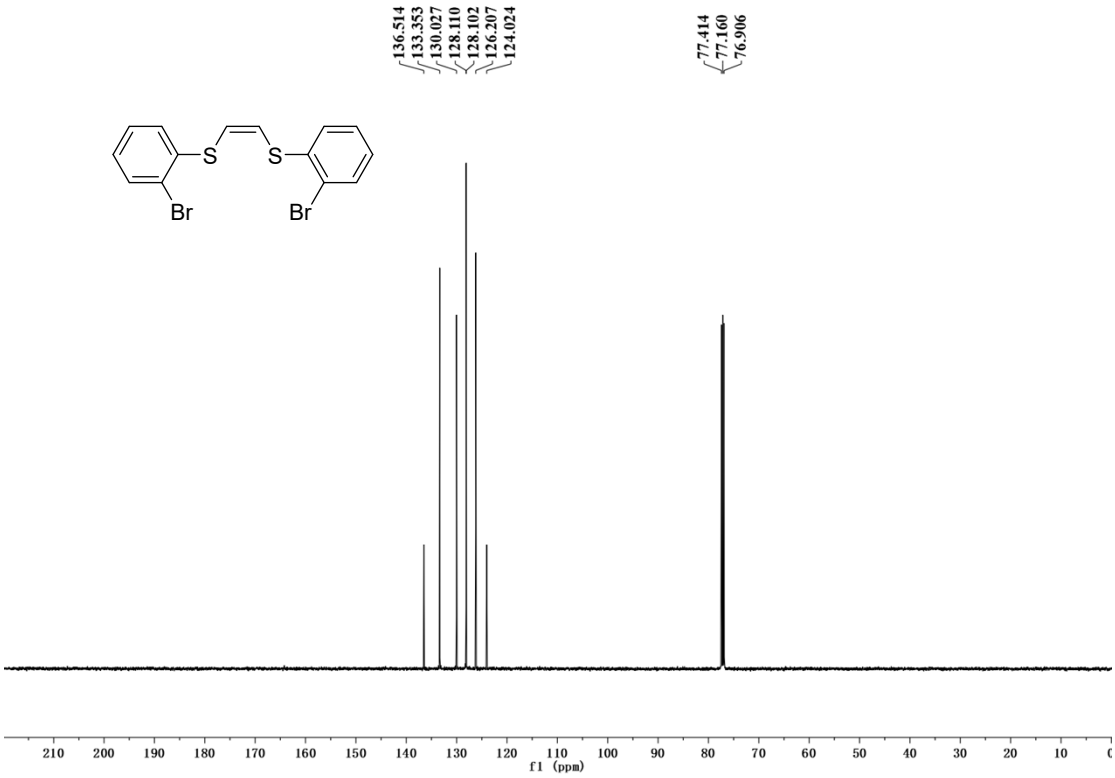
Based on prior studies and mechanistic considerations, a plausible reaction pathway for the formation of **2a** is proposed. Intermediate **A** was formed from two molecules of 2-bromobenzenethiol in the presence of sodium carbonate and oxygen. The high-valent copper(III) complex **B** was subsequently formed via an addition reaction of copper(I) iodide to **A**. Concurrently, calcium carbide undergoes in situ hydrolysis to yield acetylene, which inserts into **B** via π-coordination, producing the alkyne-bound transition state **C**. Reductive elimination of **C** then furnishes product **2a**, with concurrent regeneration of the Cu(I) catalyst, thereby proceeding to complete the catalysis.

6. NMR spectra

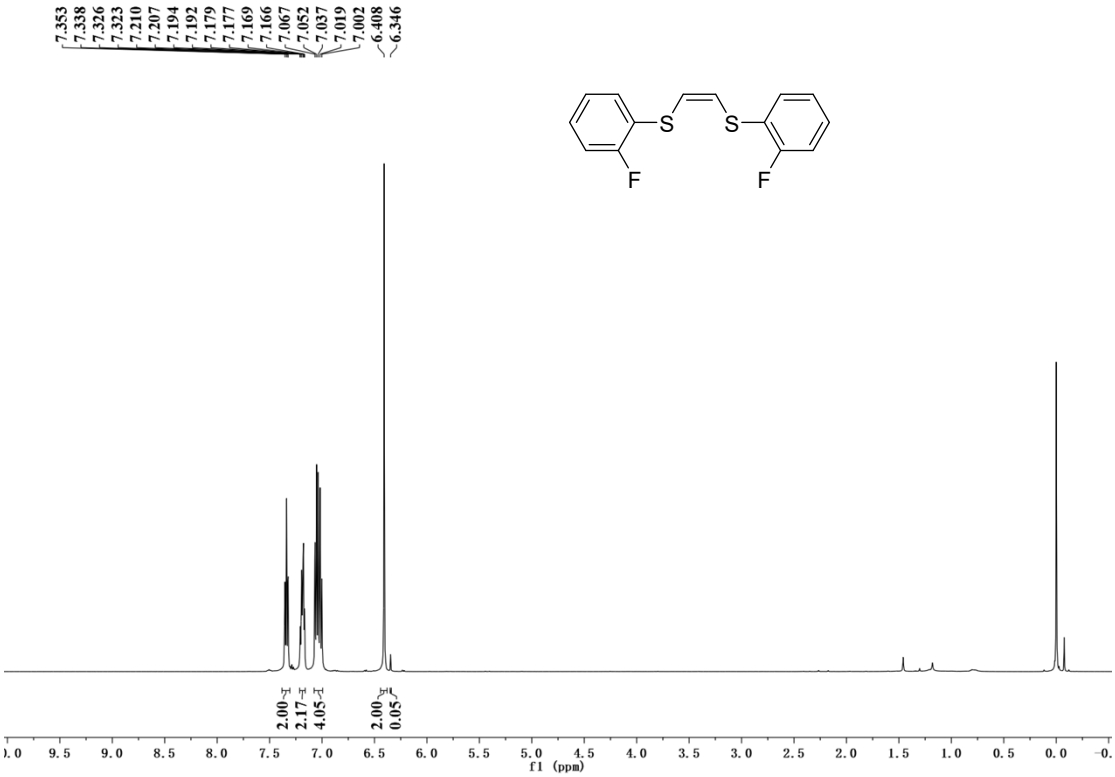
2a ^{1}H NMR (500 MHz, $CDCl_3$)



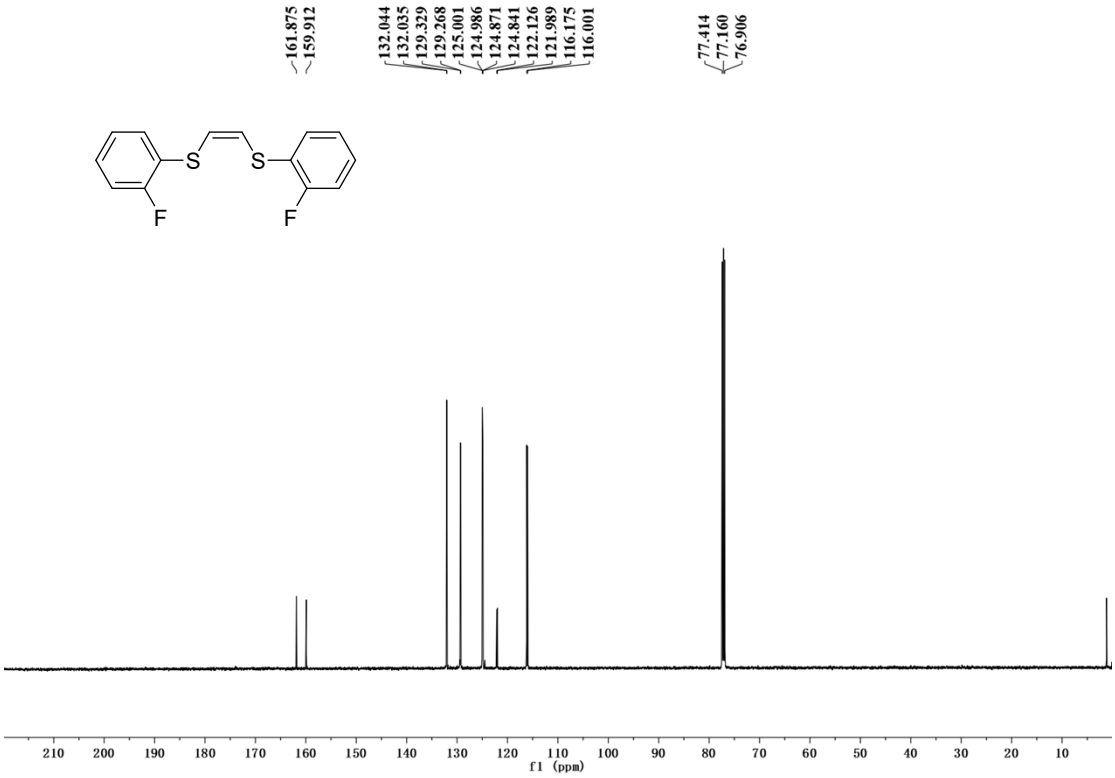
2a ^{13}C NMR (126 MHz, $CDCl_3$)



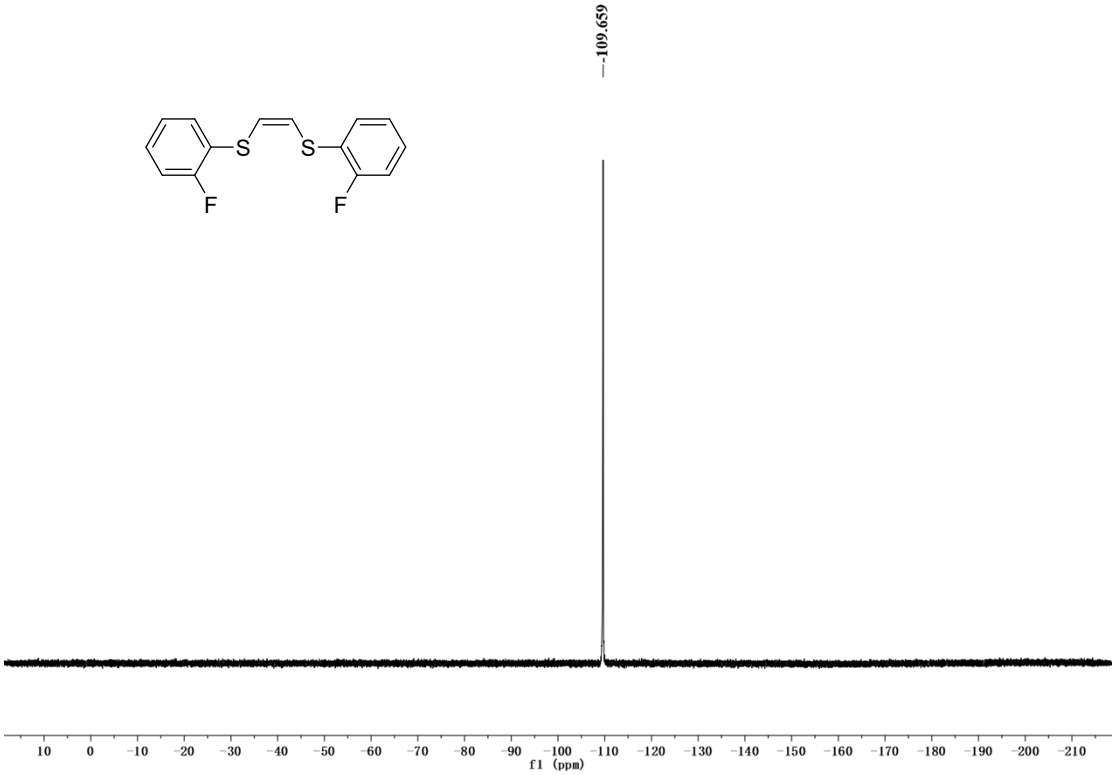
2b ^{1}H NMR (500 MHz, $CDCl_3$)



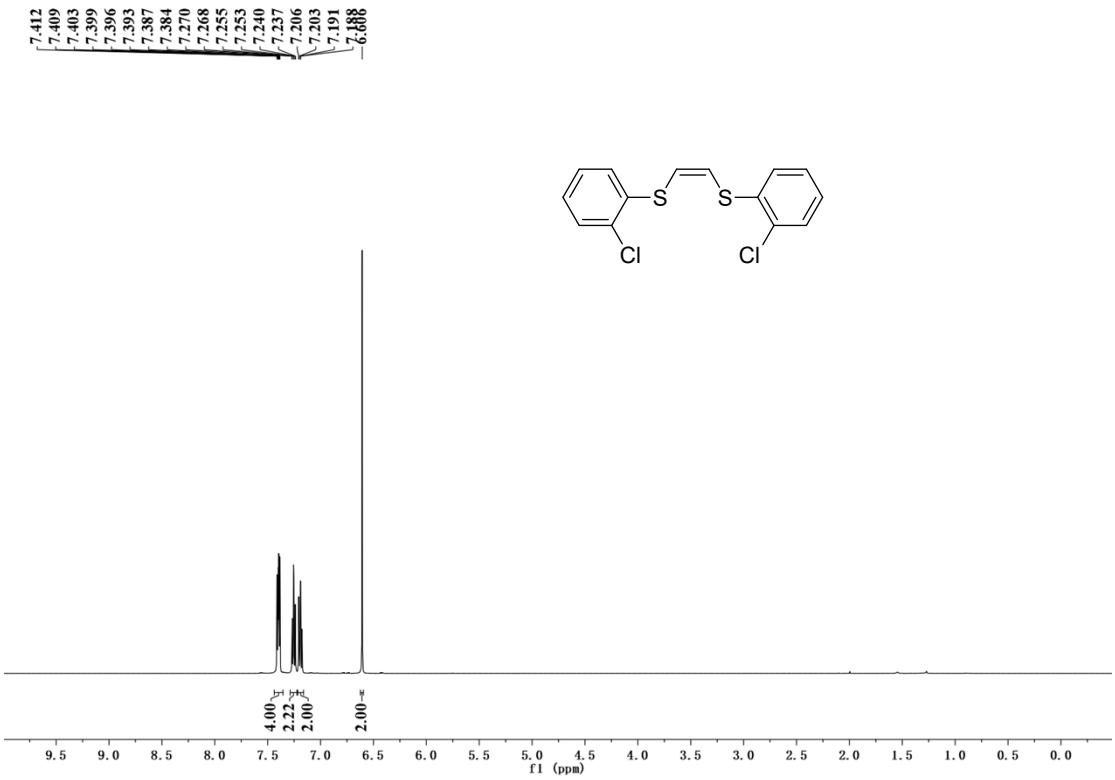
2b ^{13}C NMR (500 MHz, $CDCl_3$)



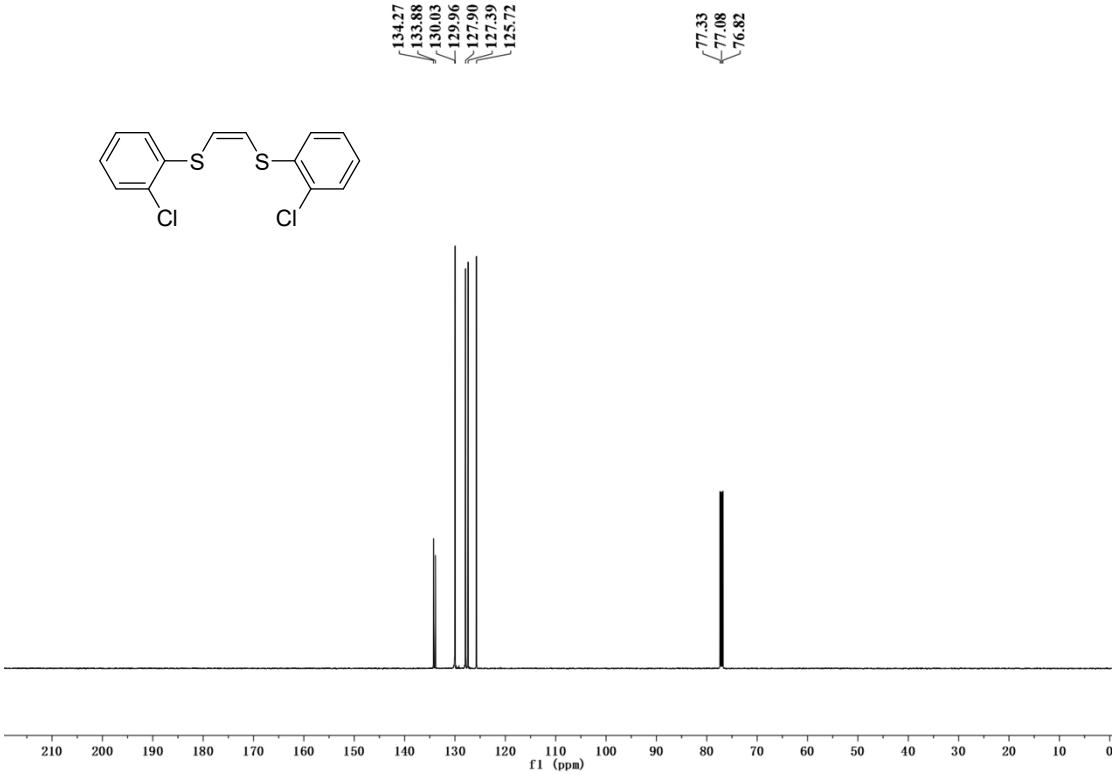
2b ^{19}F NMR (376 MHz, $CDCl_3$)



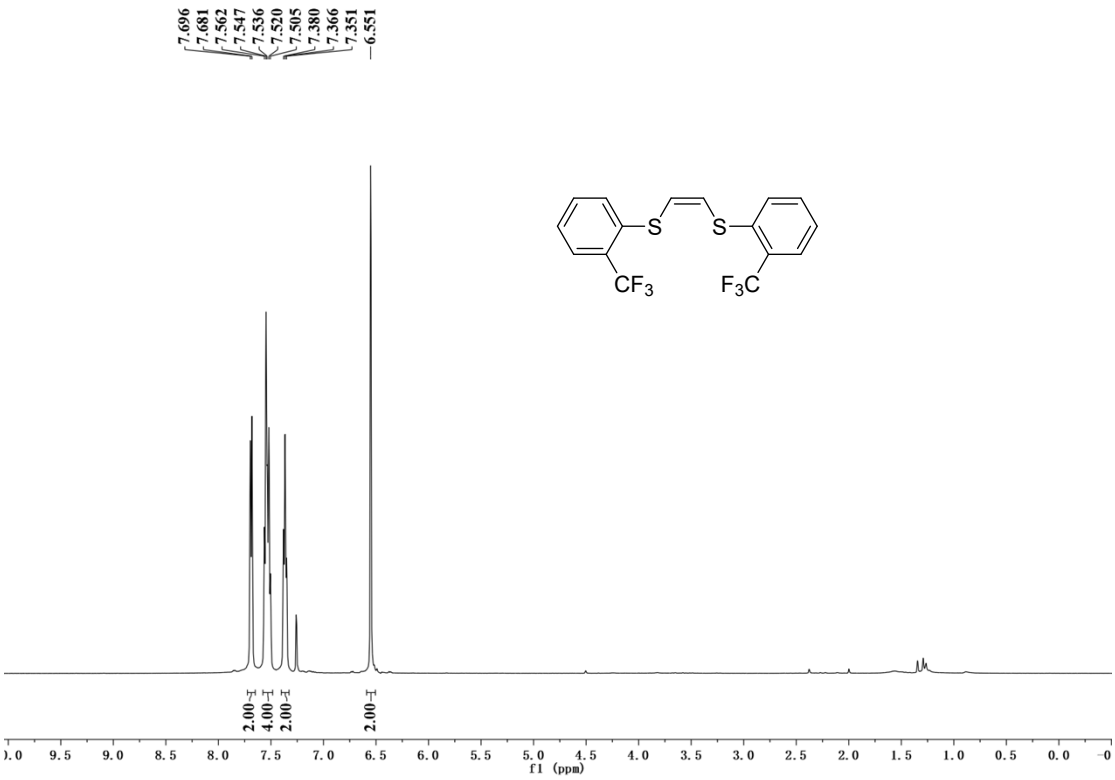
2c ^{1}H NMR (500 MHz, $CDCl_3$)



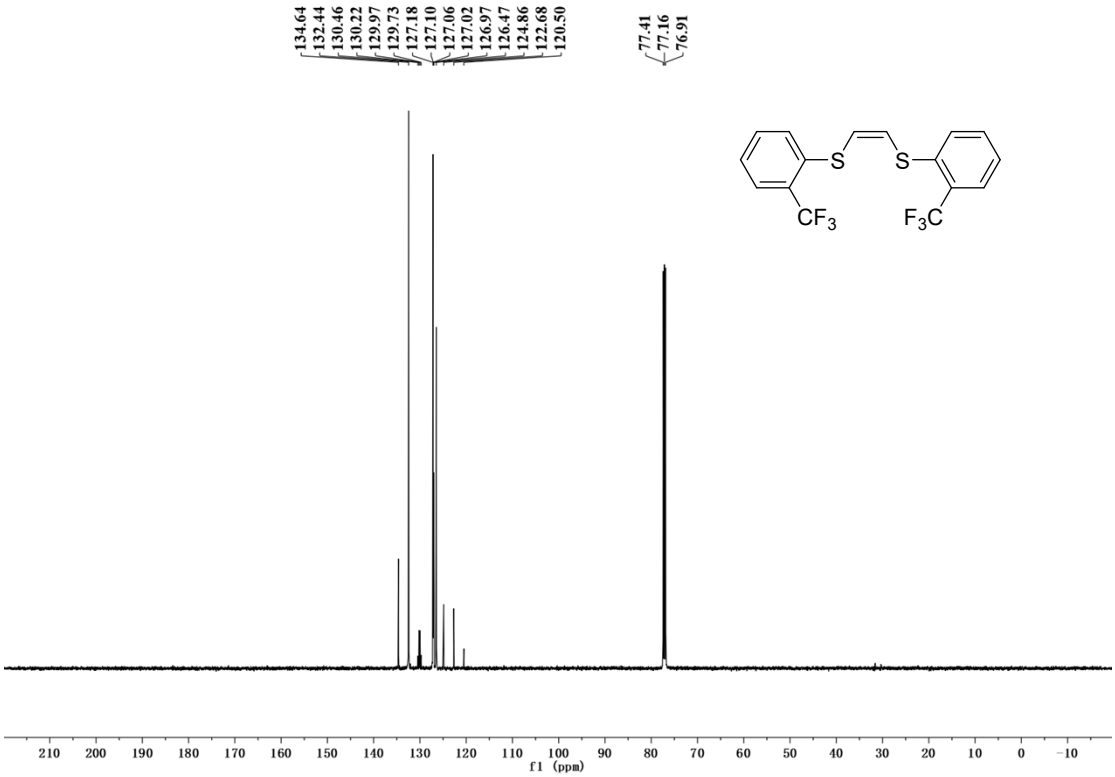
2c ^{13}C NMR (126 MHz, $CDCl_3$)



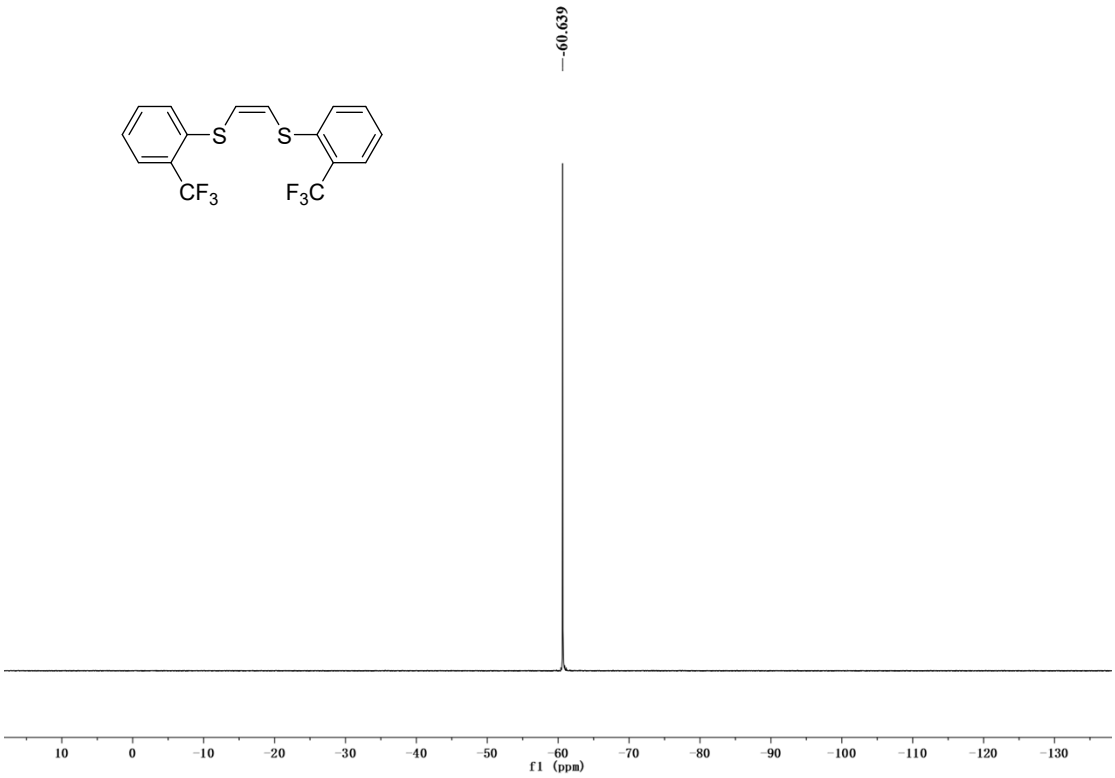
2d ^{1}H NMR (500 MHz, $CDCl_3$)



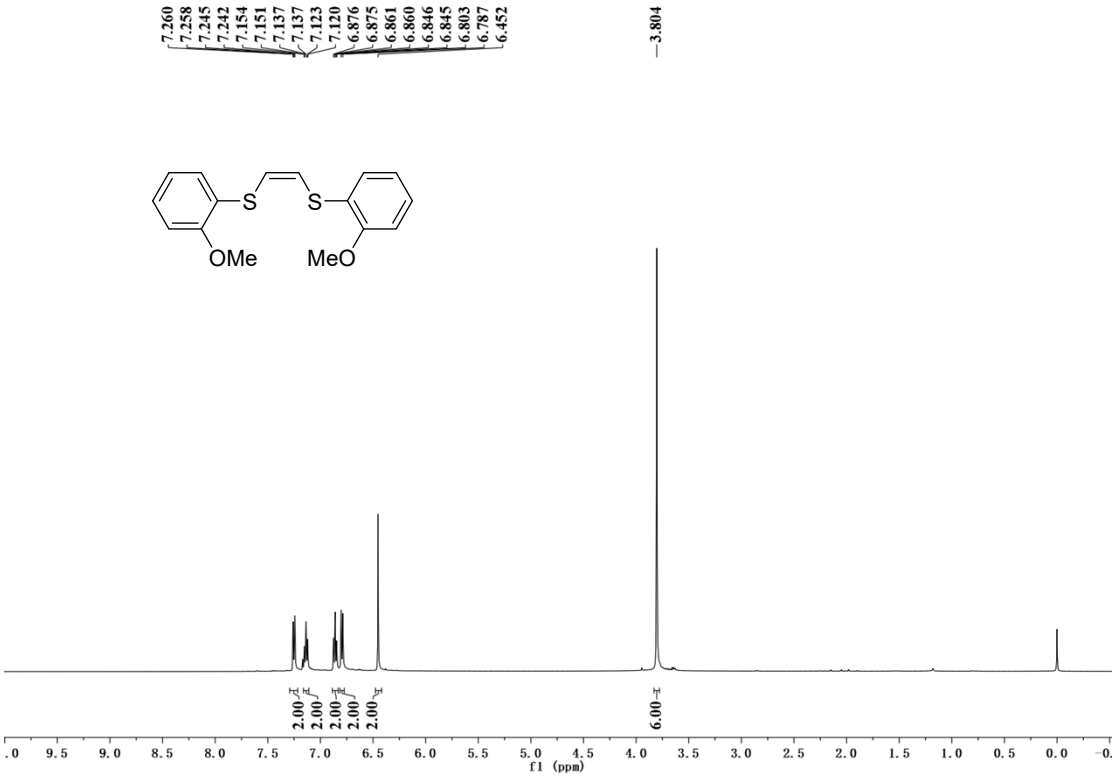
2d ^{13}C NMR (126 MHz, $CDCl_3$)



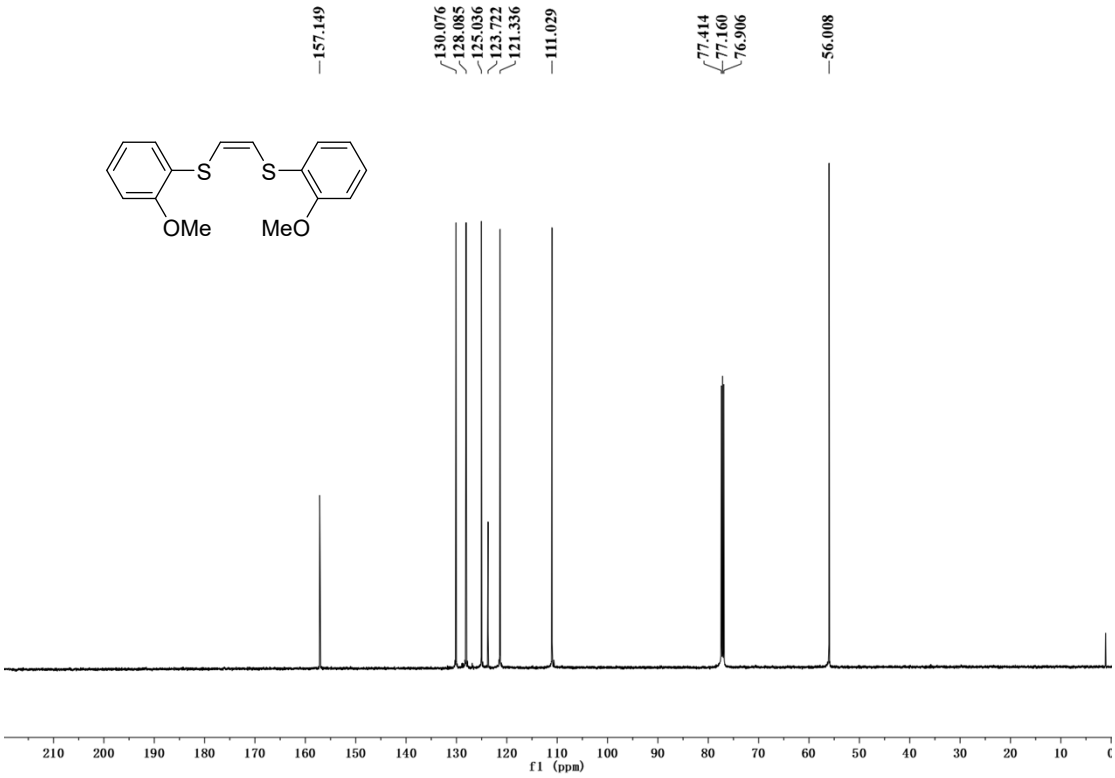
2d ^{19}F NMR (376 MHz, $CDCl_3$)



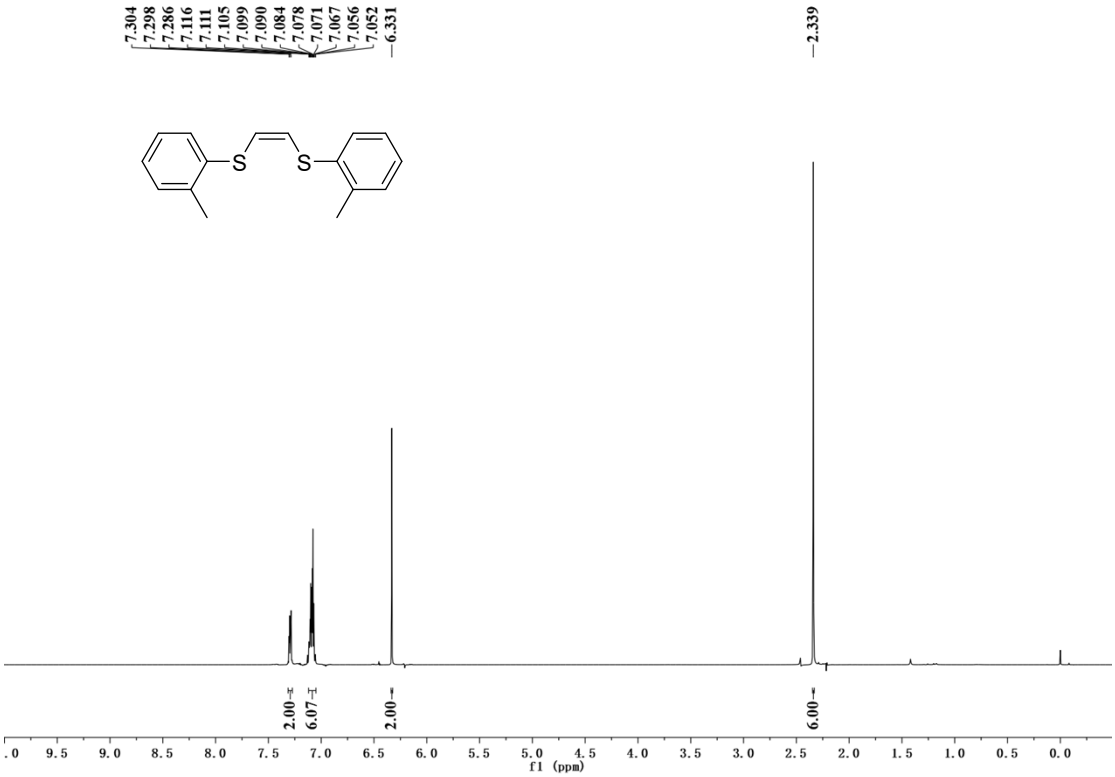
2e ^{1}H NMR (500 MHz, $CDCl_3$)



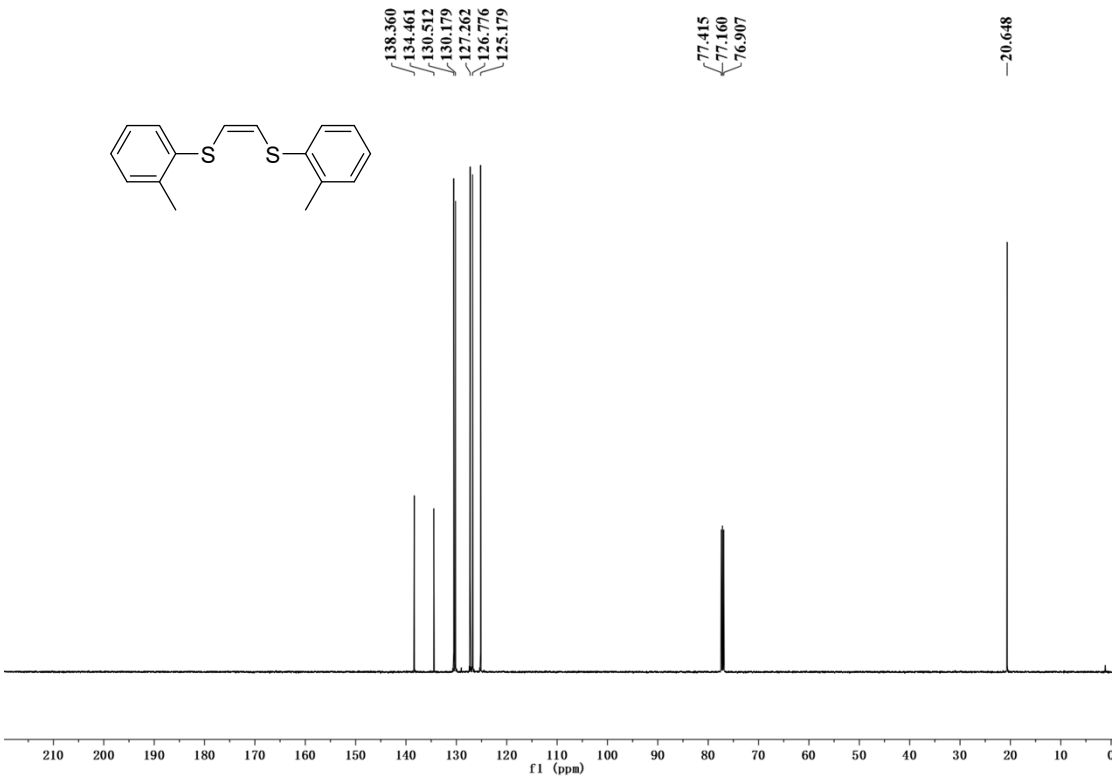
2e ^{13}C NMR (126 MHz, $CDCl_3$)



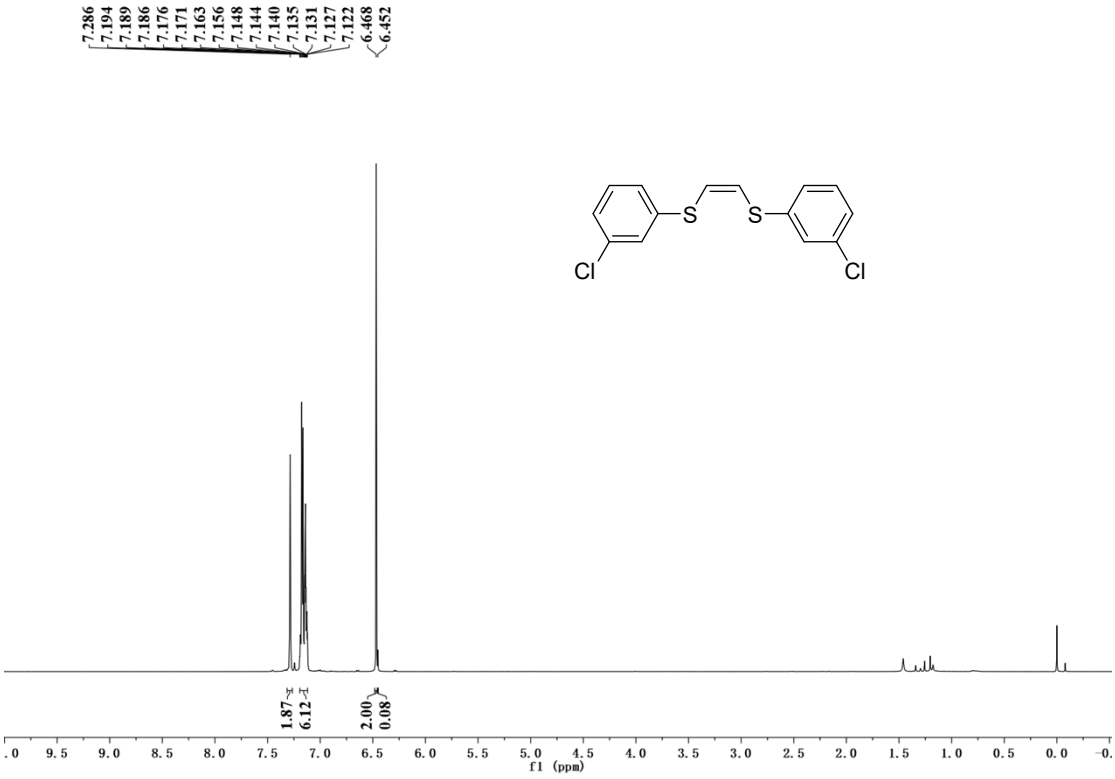
2f ^{1}H NMR (500 MHz, $CDCl_3$)



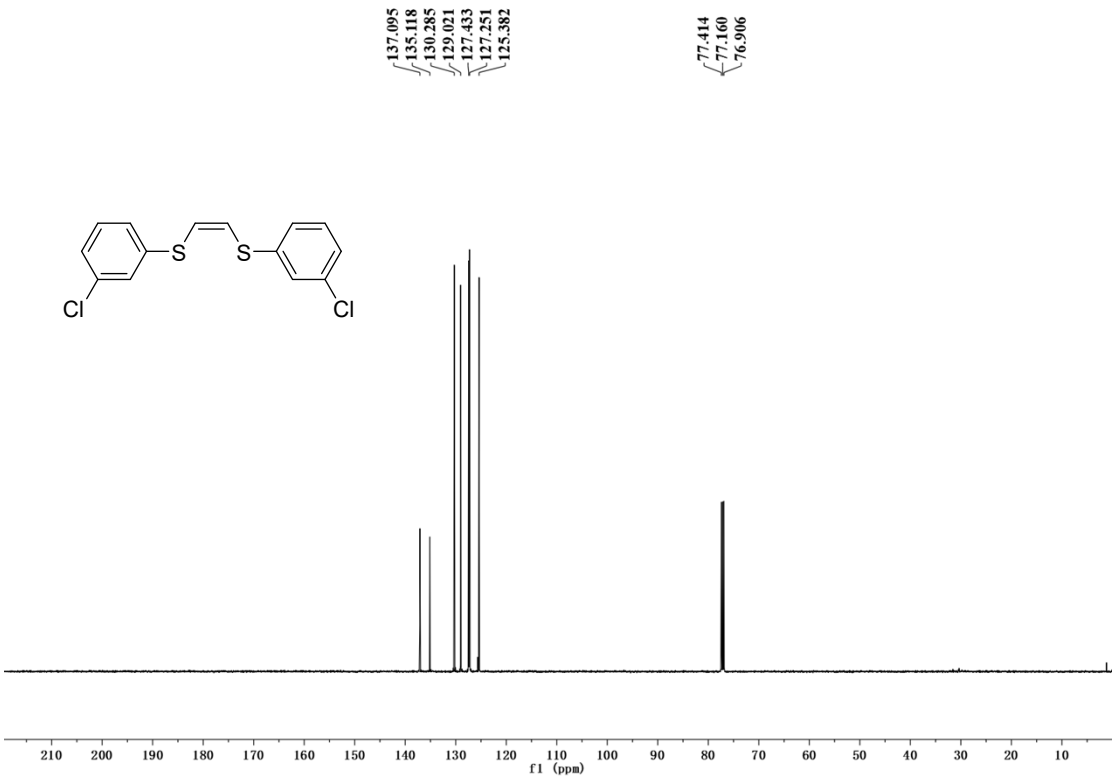
2f ^{13}C NMR (126 MHz, $CDCl_3$)



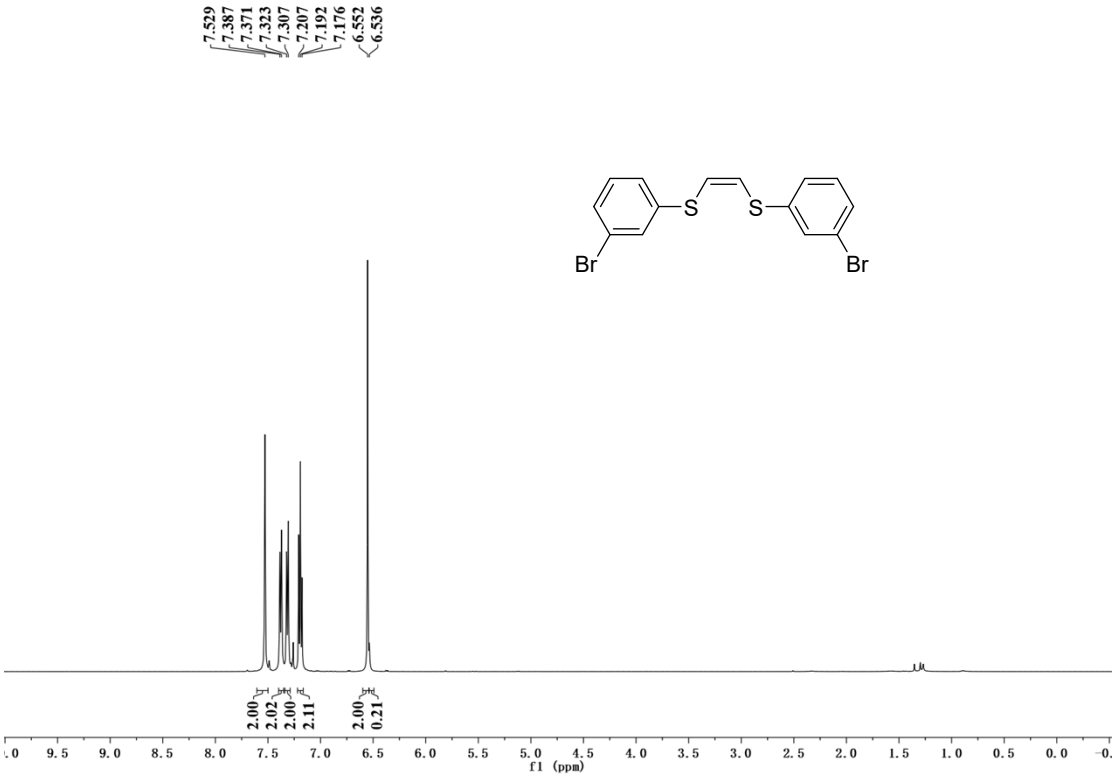
2g ^{1}H NMR (500 MHz, $CDCl_3$)



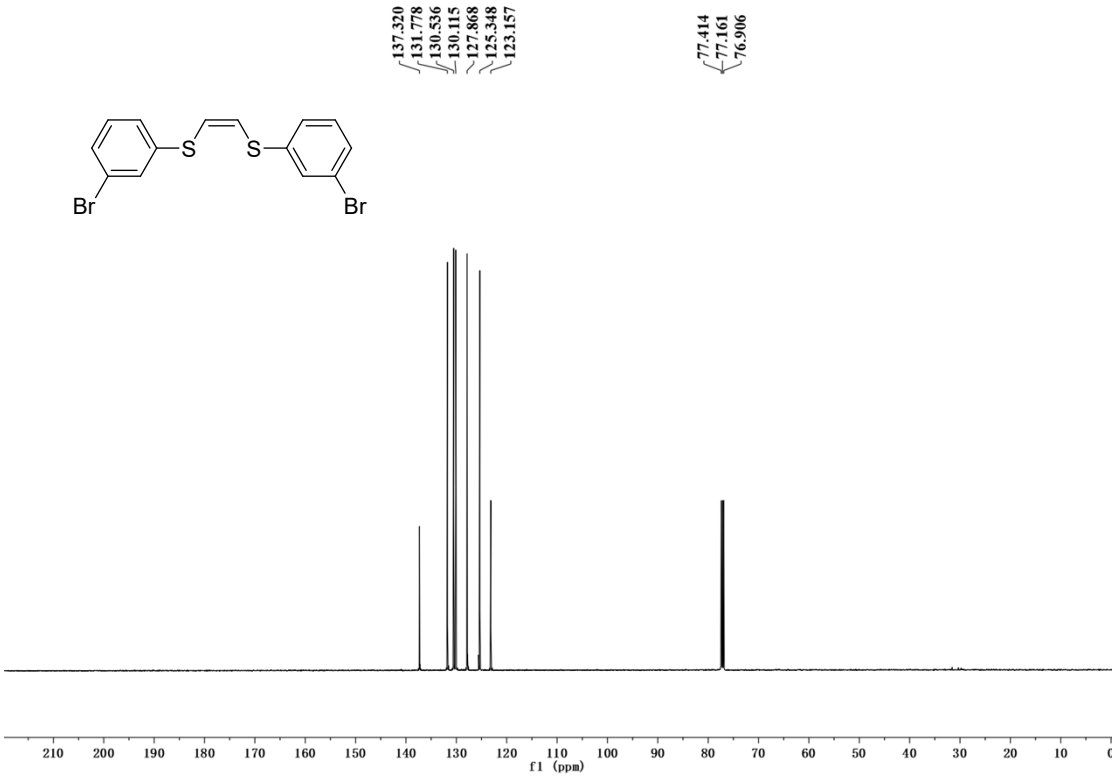
2g ^{13}C NMR (126 MHz, $CDCl_3$)



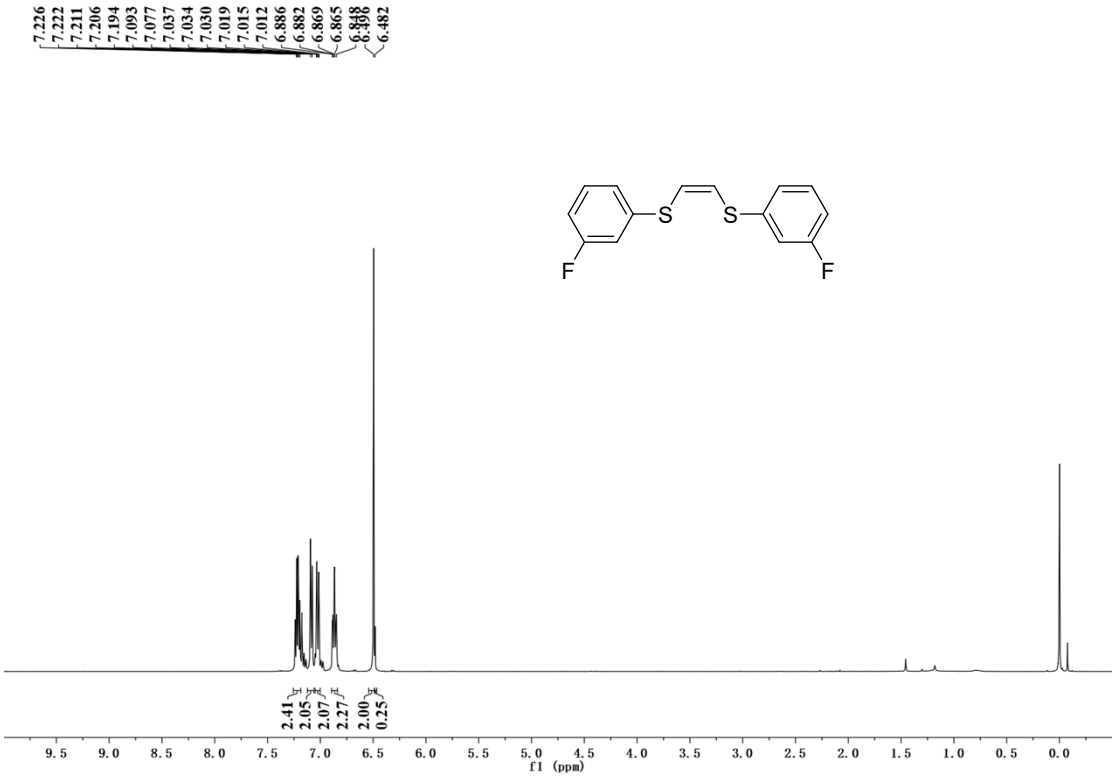
2h ^{1}H NMR (500 MHz, $CDCl_3$)



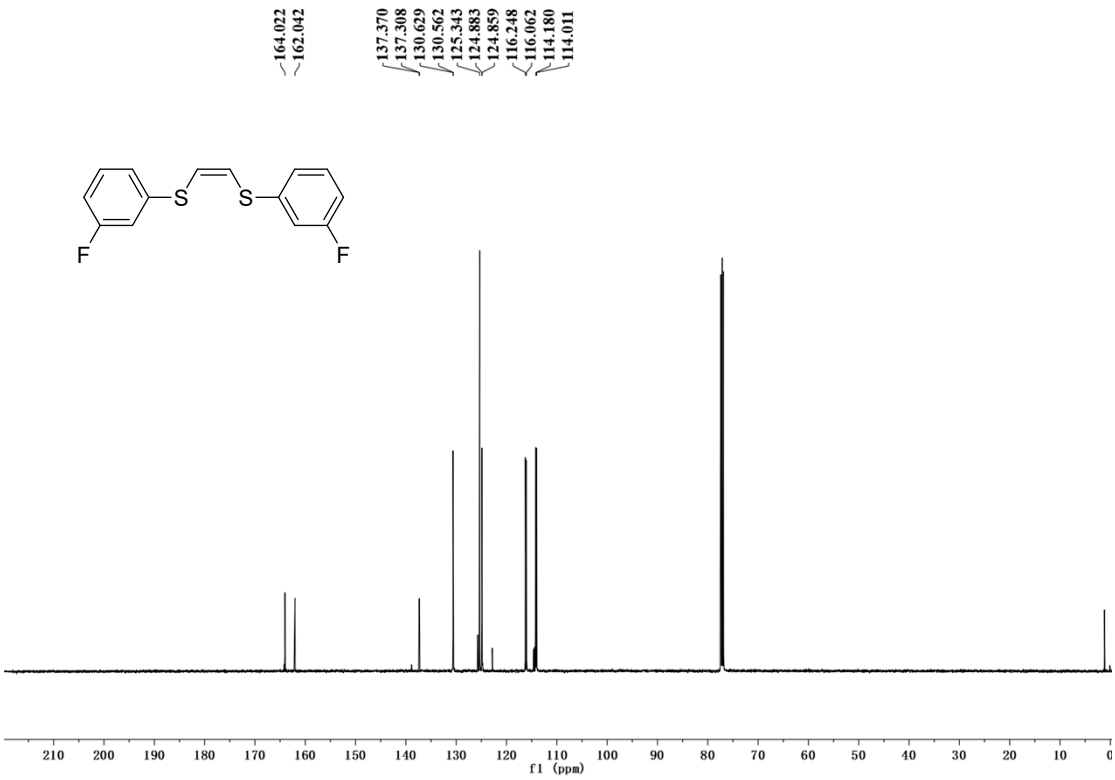
2h ^{13}C NMR (126 MHz, $CDCl_3$)



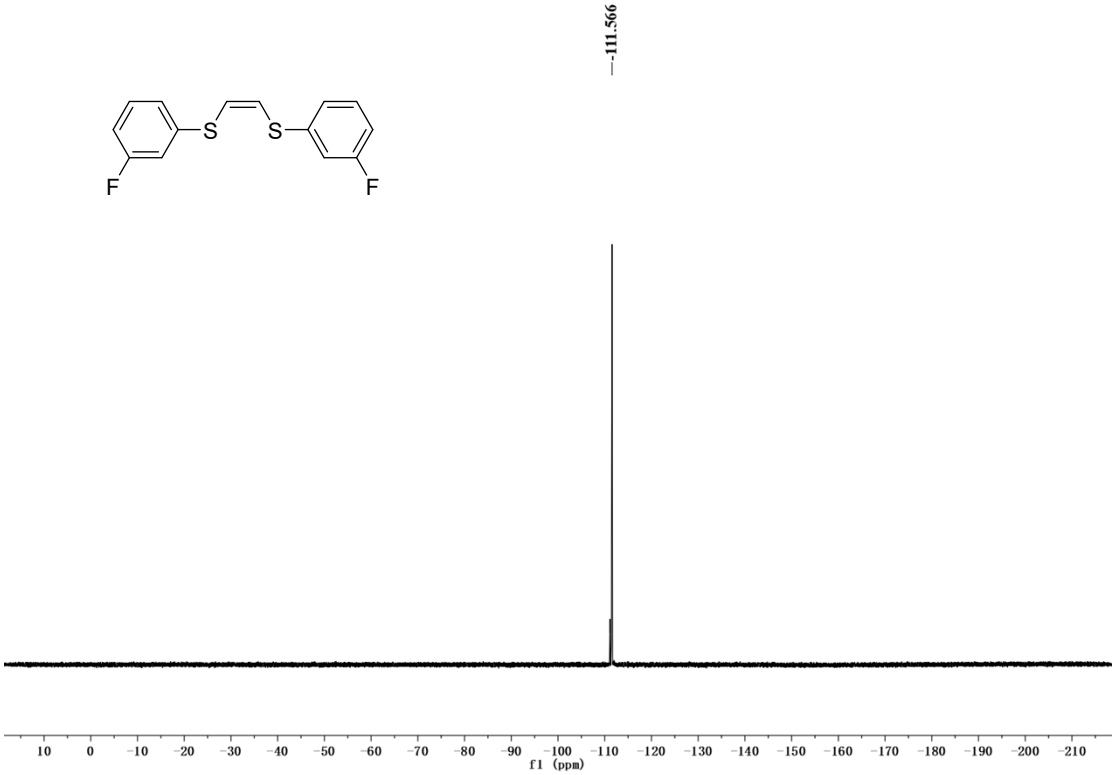
2i ^{1}H NMR (500 MHz, $CDCl_3$)



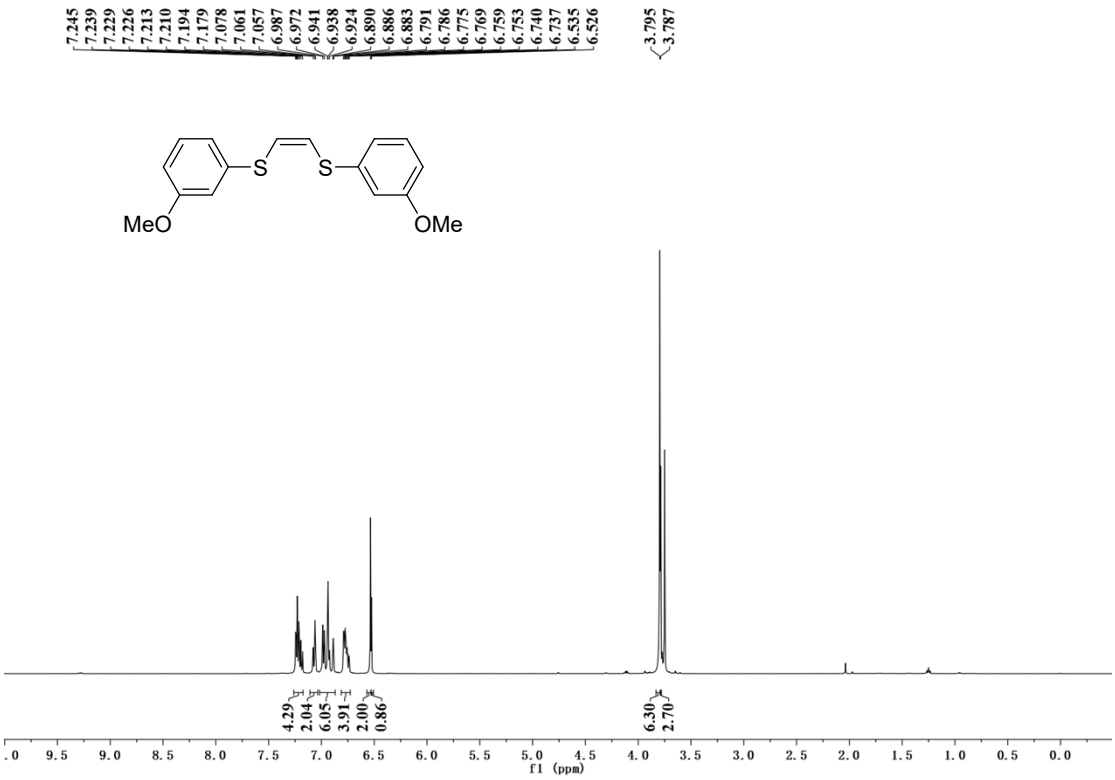
2i ^{13}C NMR (126 MHz, $CDCl_3$)



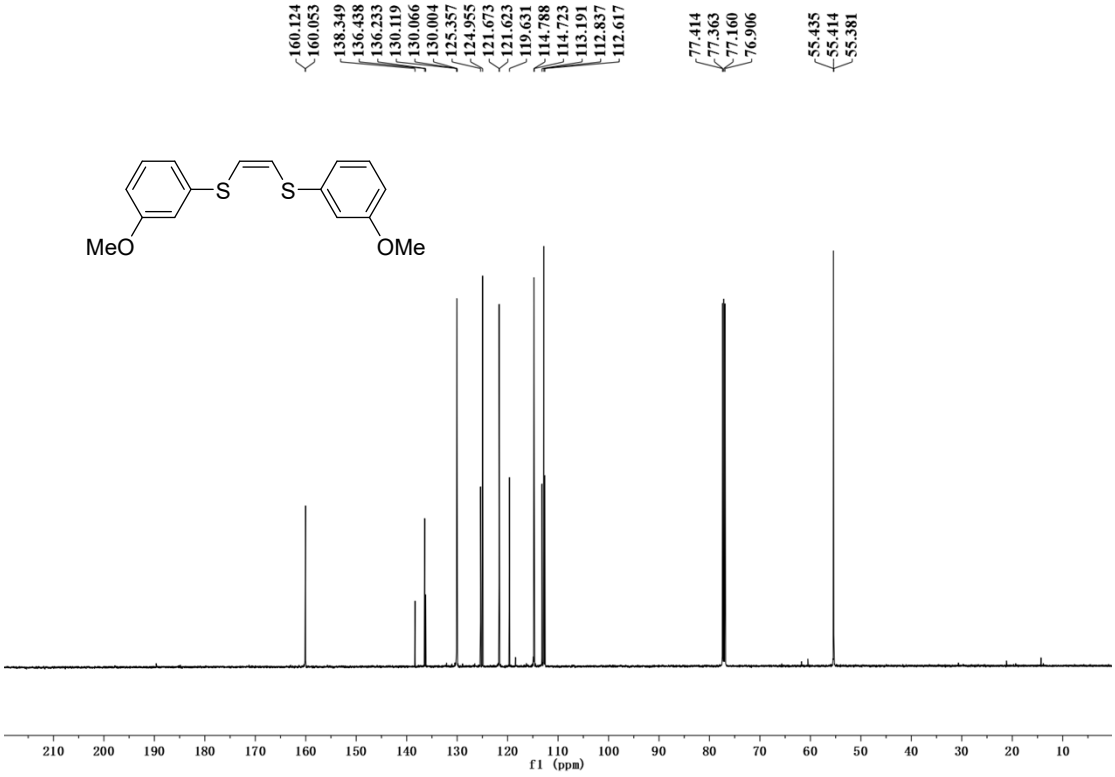
2i ^{19}F NMR (376 MHz, $CDCl_3$)



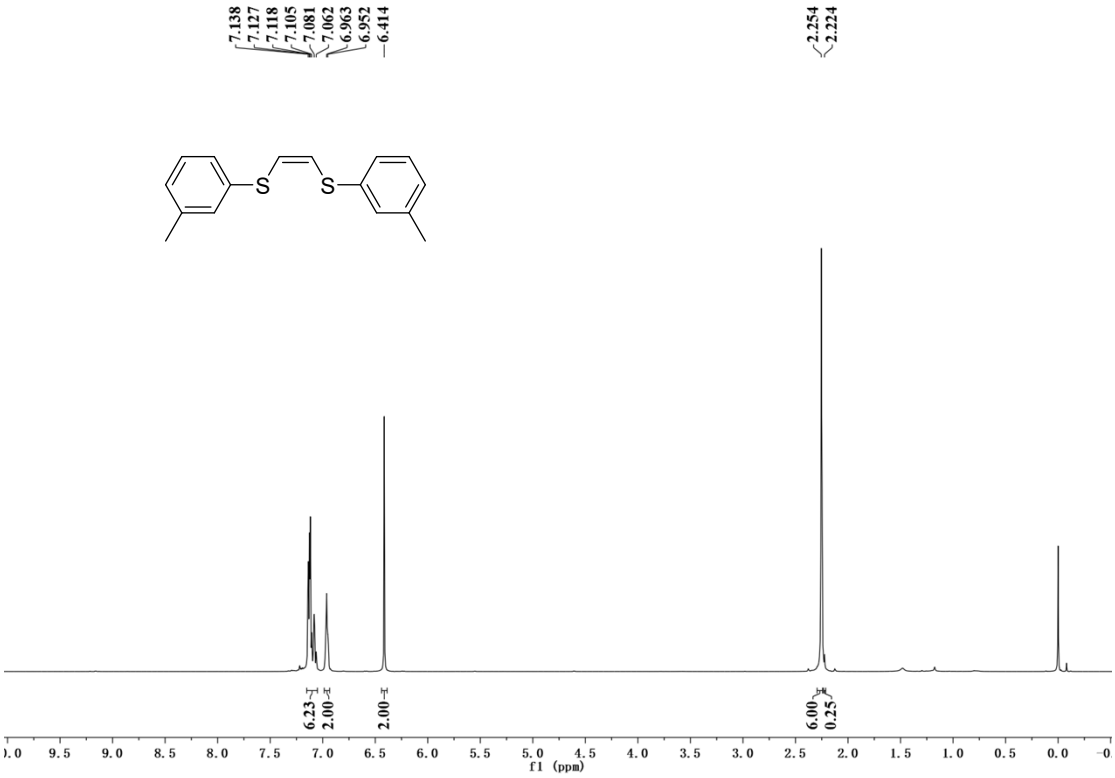
2j ^{1}H NMR (500 MHz, $CDCl_3$)



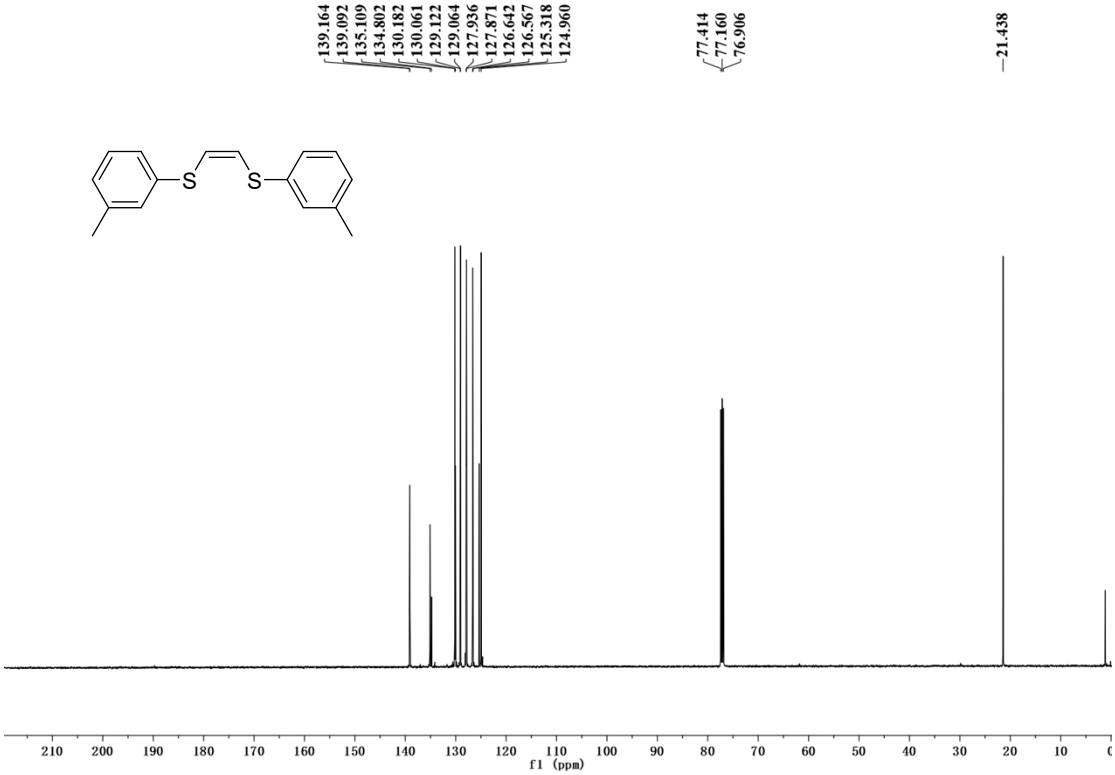
2j ^{13}C NMR (126 MHz, $CDCl_3$)



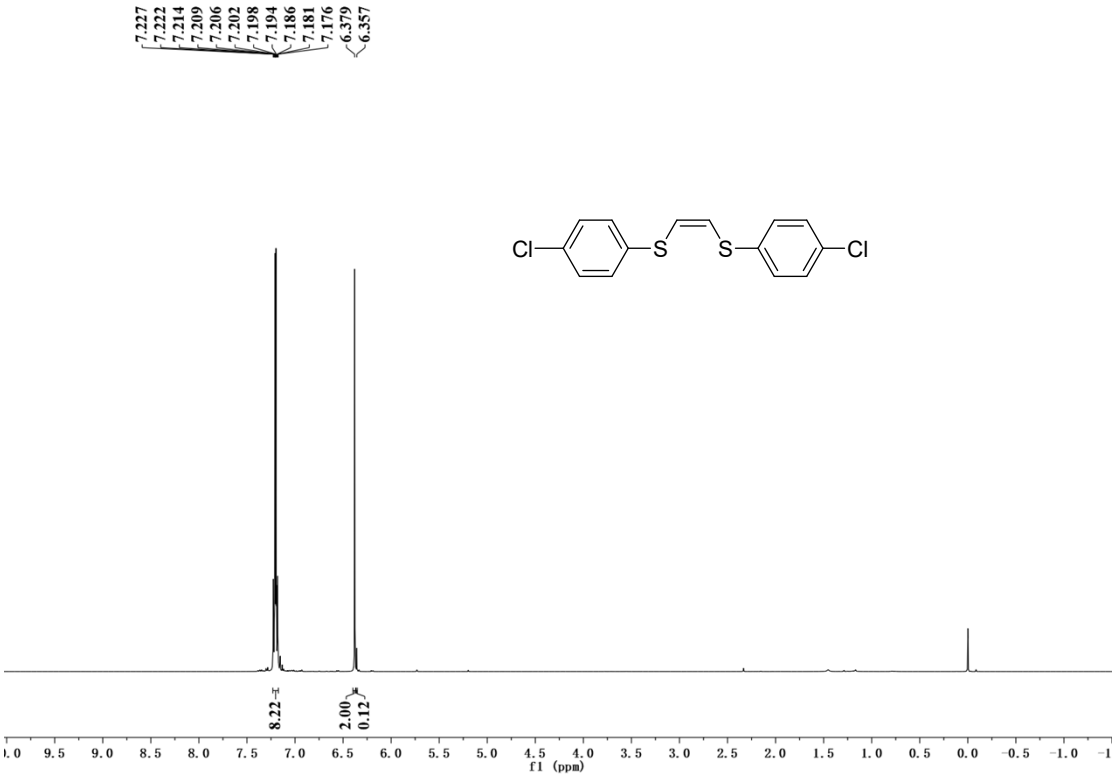
2k ^{1}H NMR (500 MHz, $CDCl_3$)



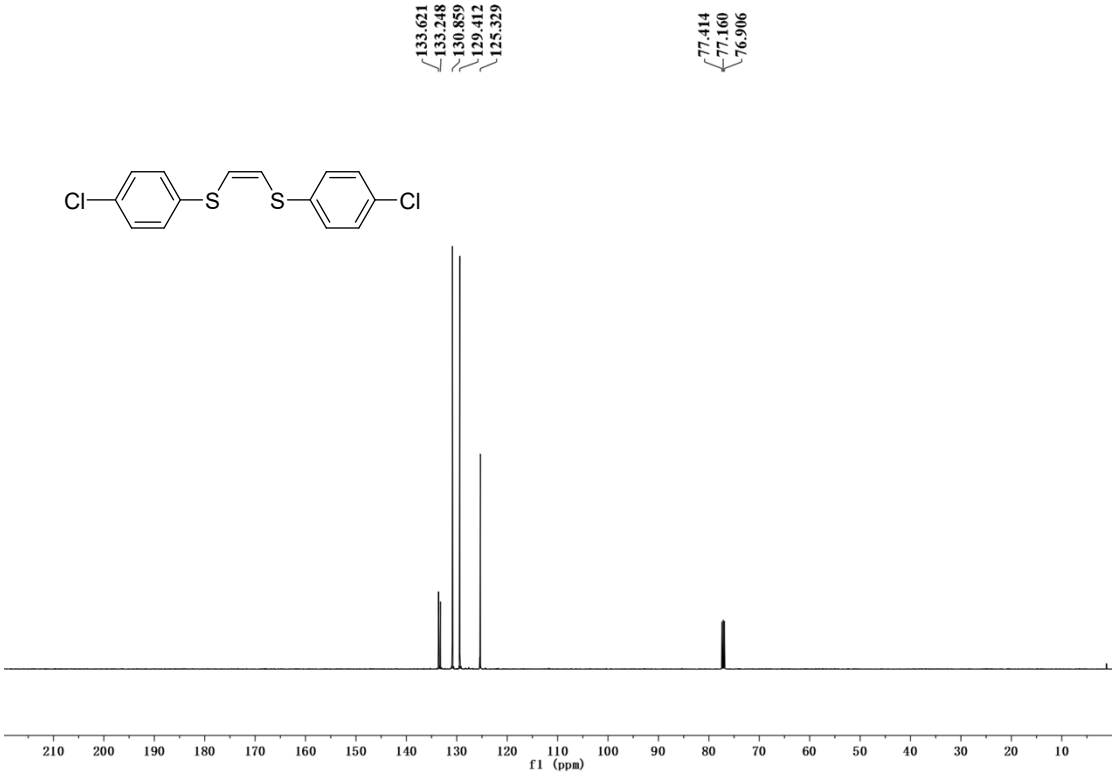
2k ^{13}C NMR (126 MHz, $CDCl_3$)



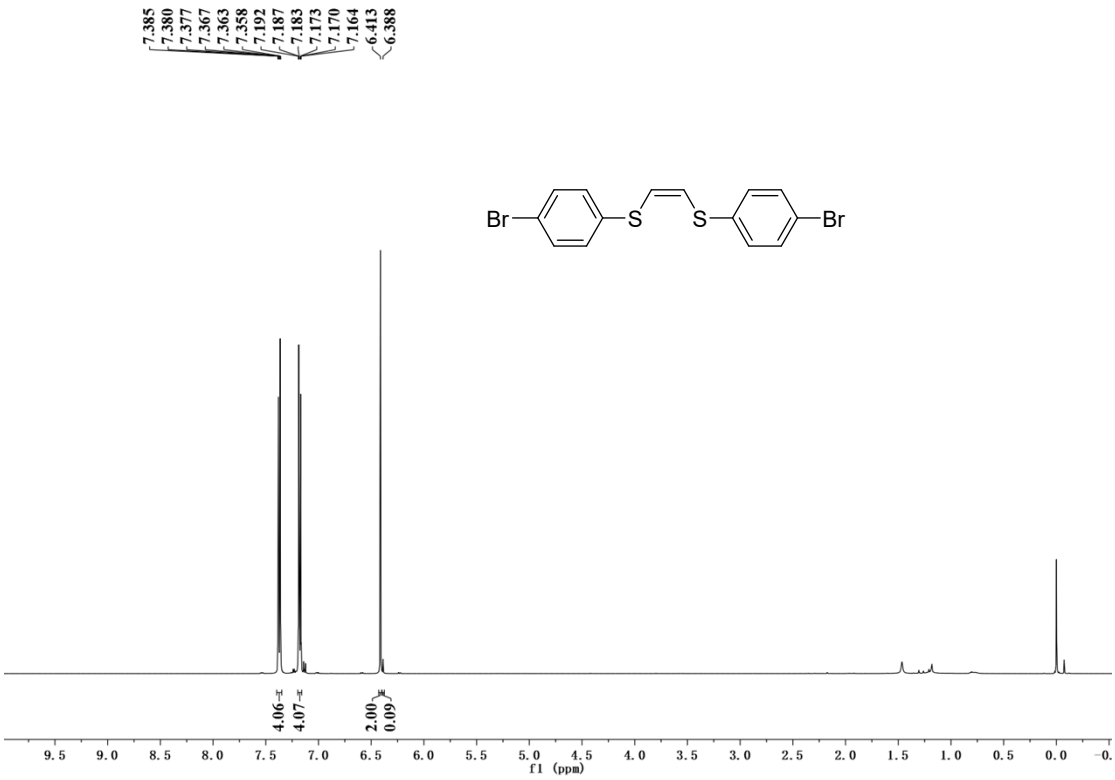
2l ^{1}H NMR (500 MHz, $CDCl_3$)



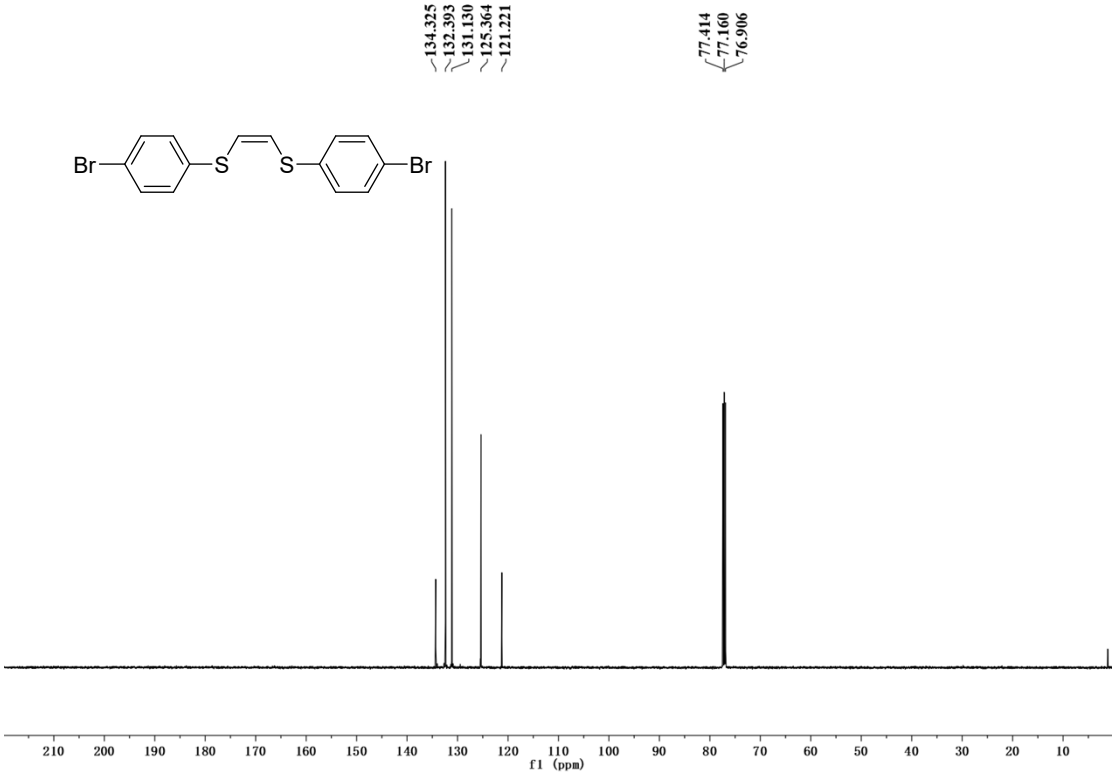
2l ^{13}C NMR (126 MHz, $CDCl_3$)



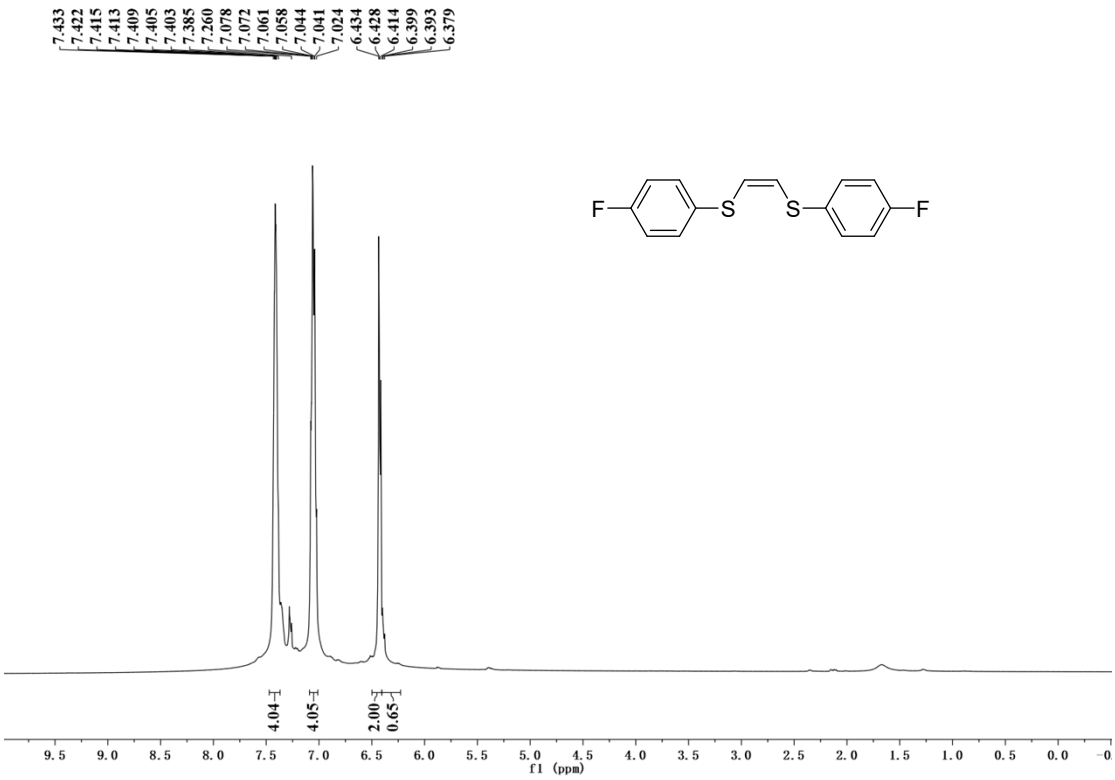
2m ^{1}H NMR (500 MHz, $CDCl_3$)



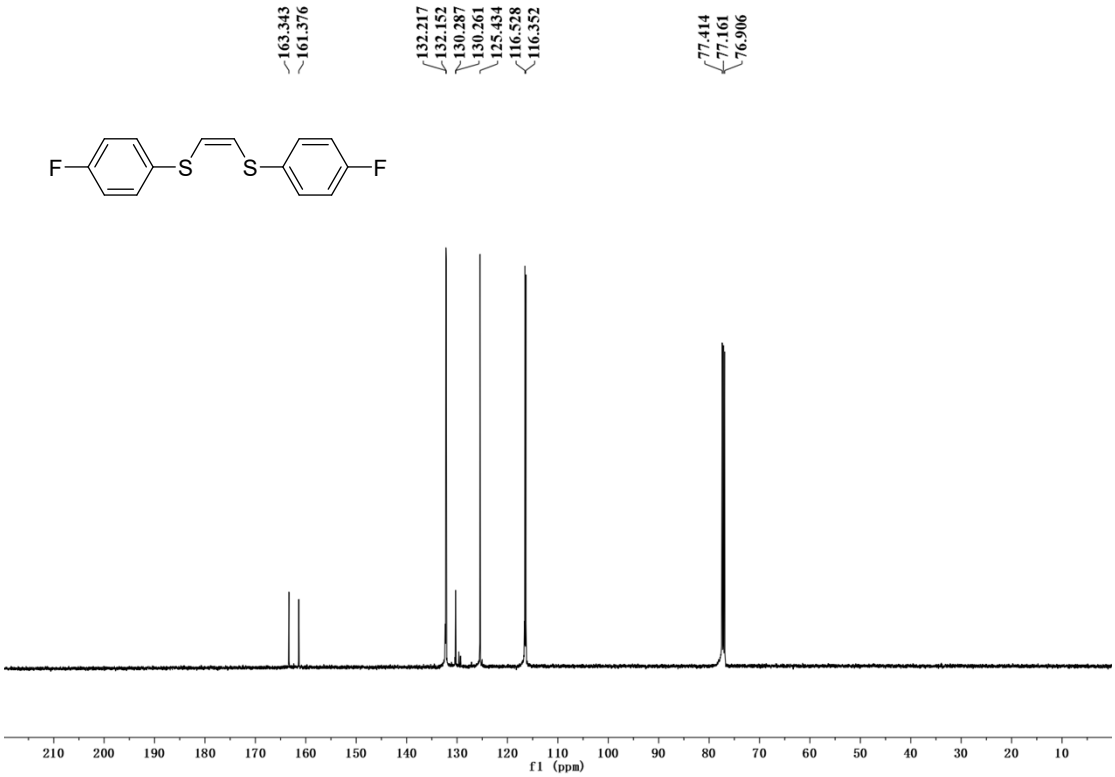
2m ^{13}C NMR (126 MHz, $CDCl_3$)



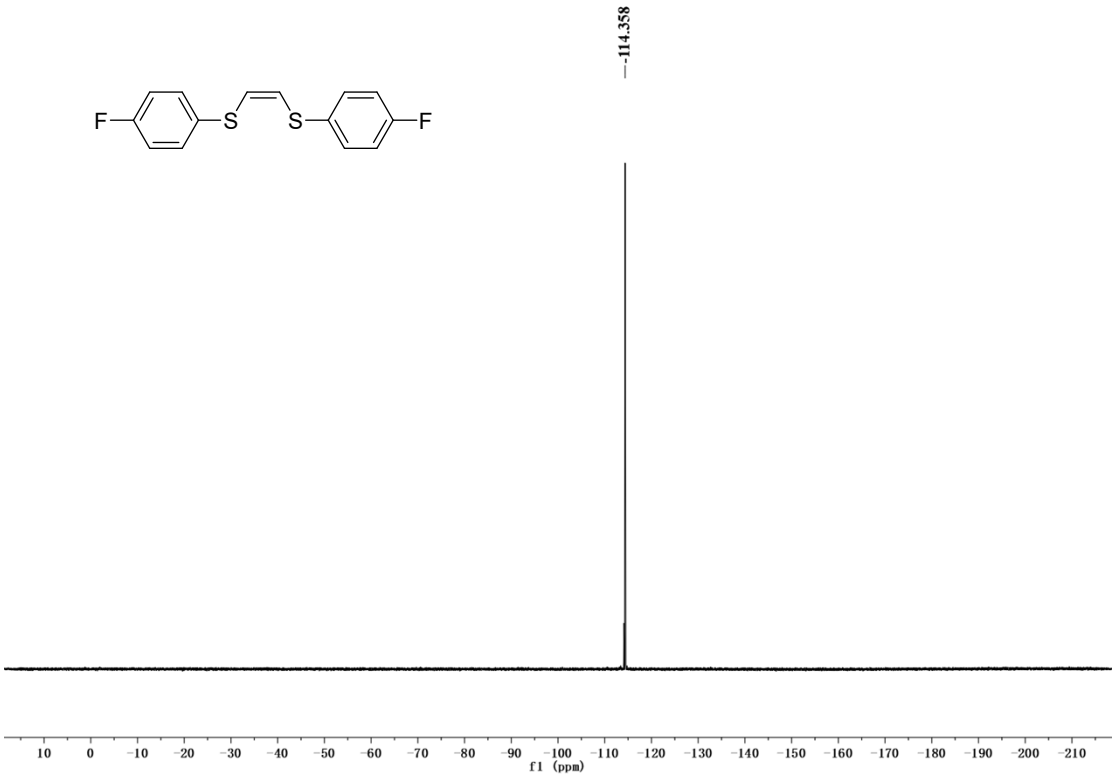
2n ^{1}H NMR (500 MHz, $CDCl_3$)



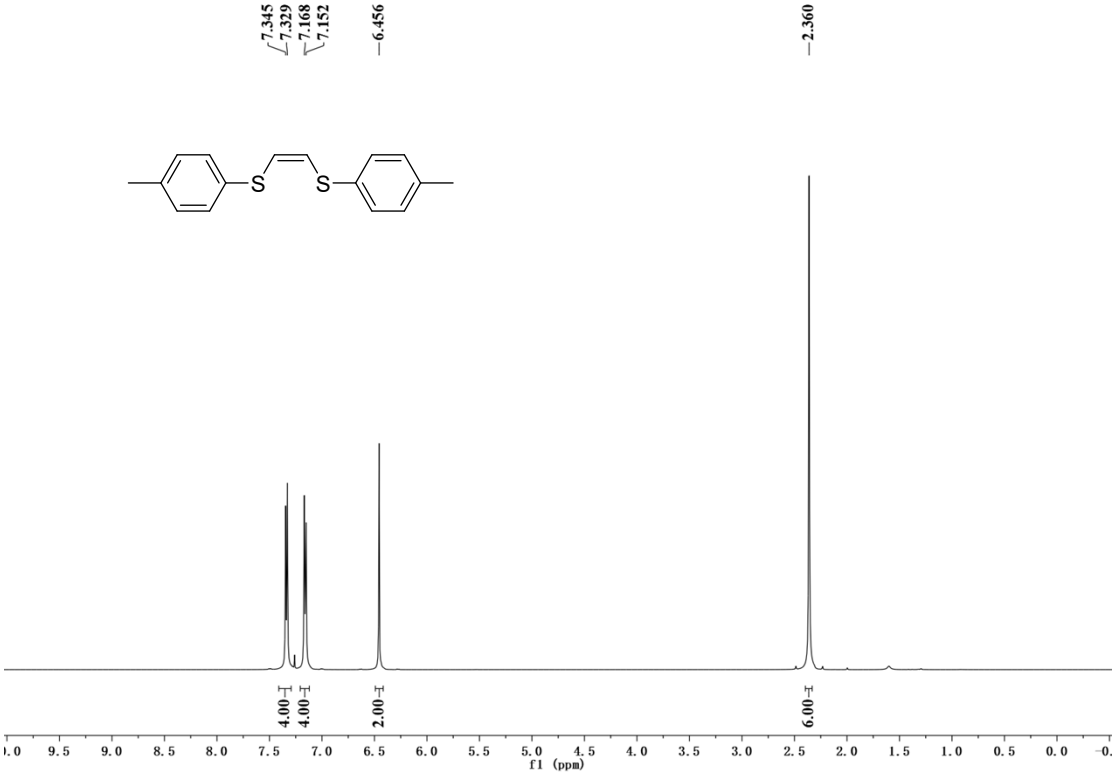
2n ^{13}C NMR (126 MHz, $CDCl_3$)



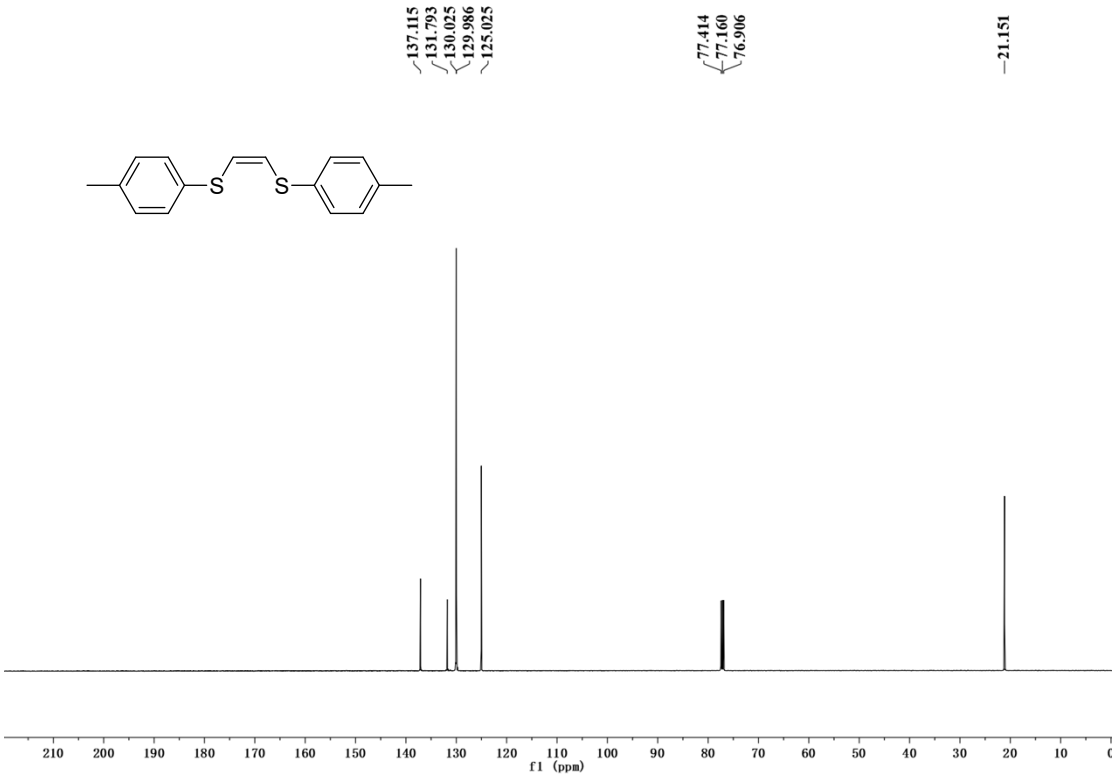
2n ^{19}F NMR (376 MHz, $CDCl_3$)



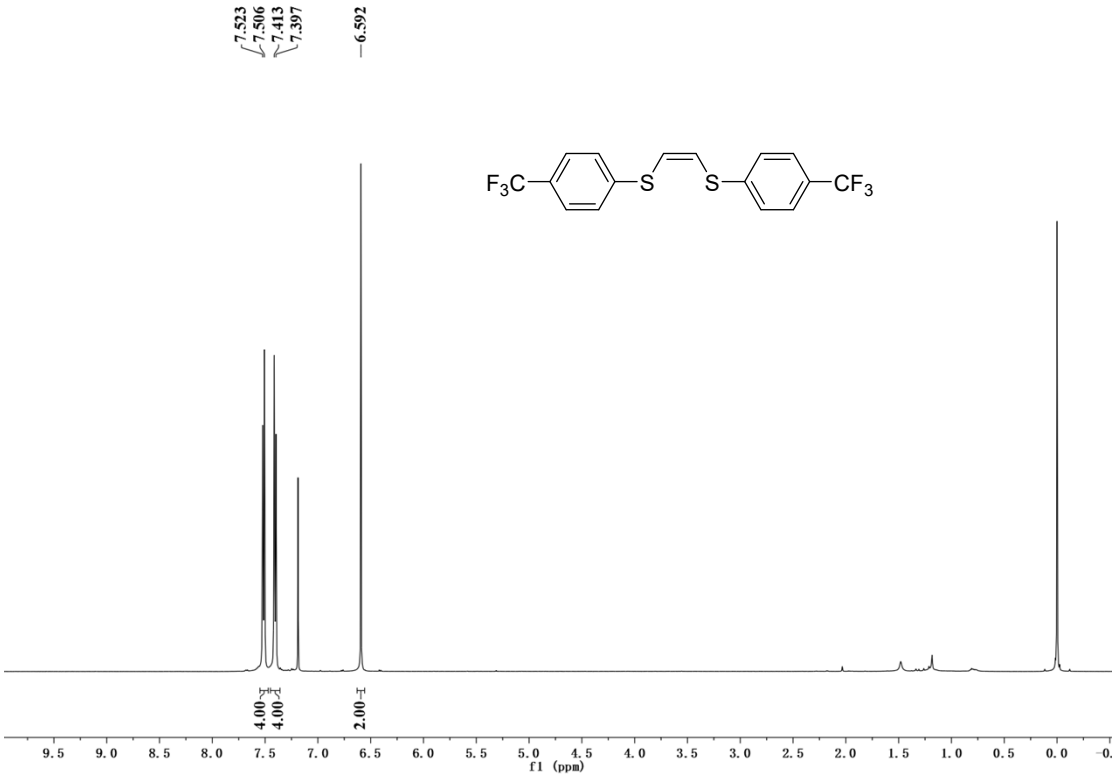
2o ^{1}H NMR (500 MHz, $CDCl_3$)



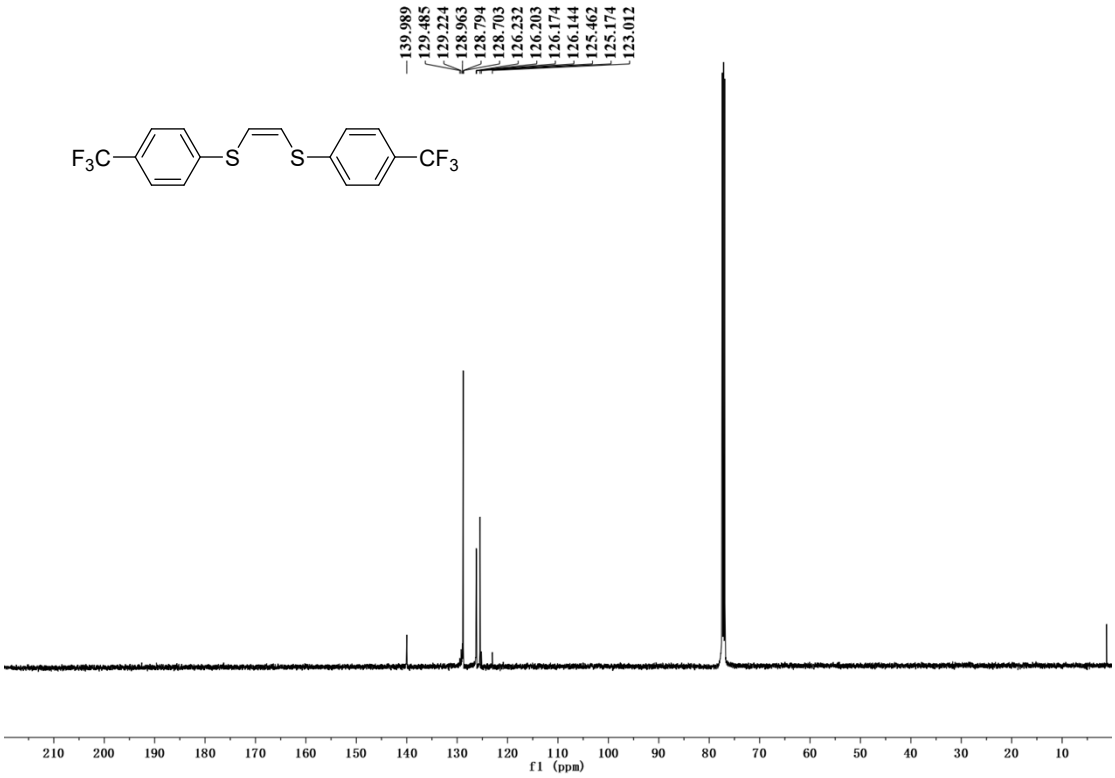
2o ^{13}C NMR (126 MHz, $CDCl_3$)



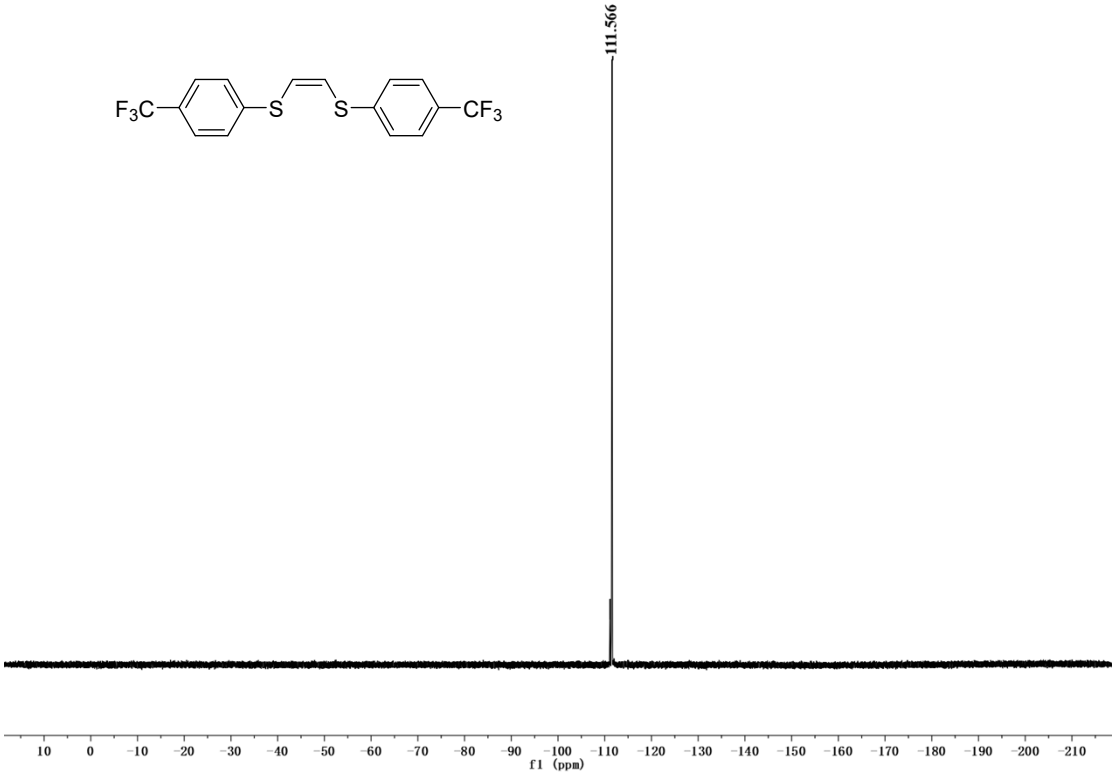
2q ^{1}H NMR (500 MHz, $CDCl_3$)



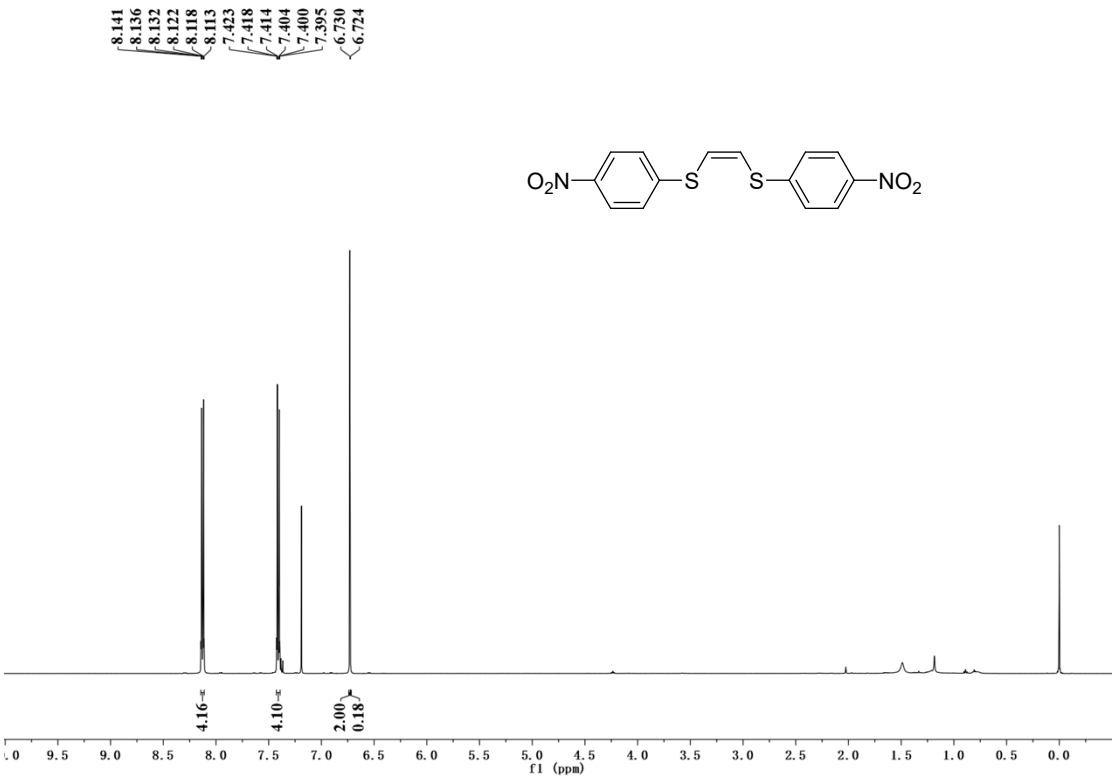
2q ^{13}C NMR (126 MHz, $CDCl_3$)



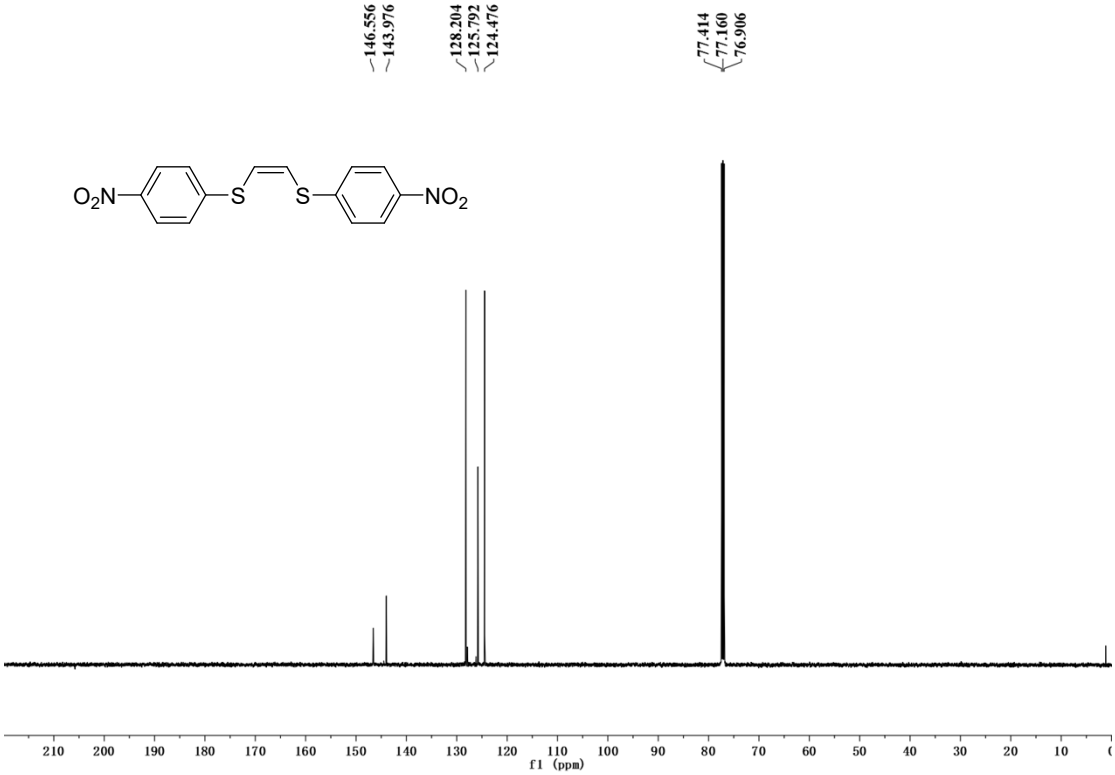
2q ^{19}F NMR (376 MHz, $CDCl_3$)



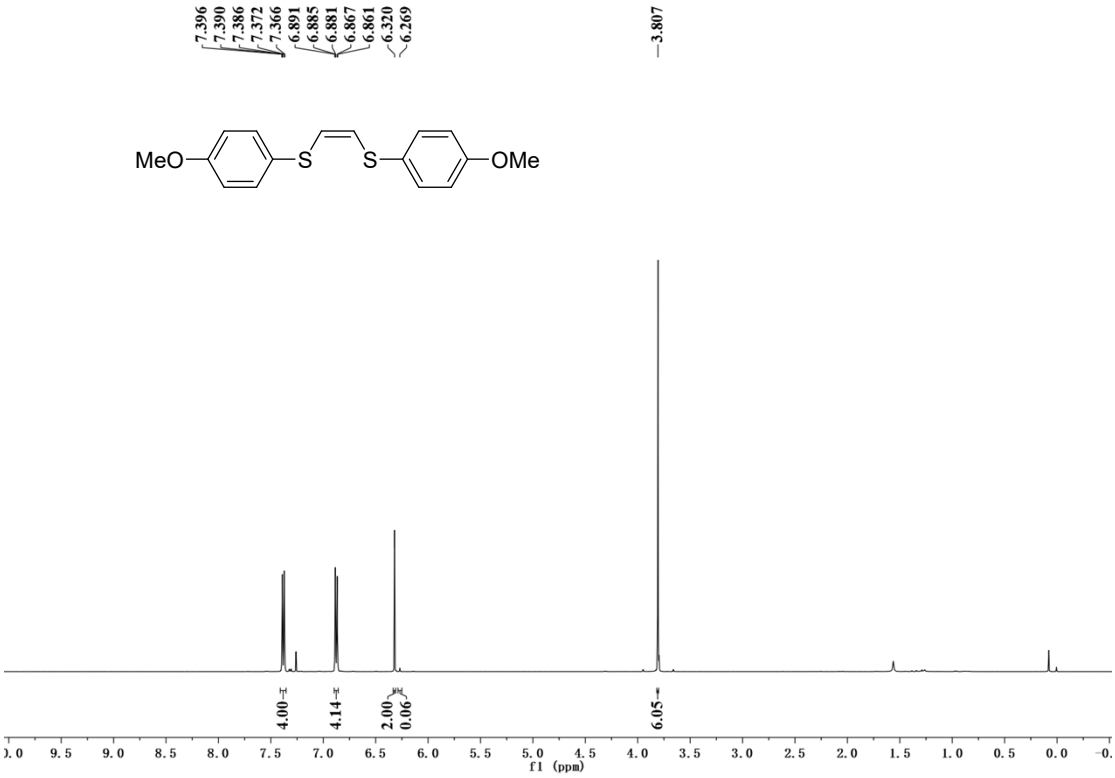
2r ^{1}H NMR (500 MHz, $CDCl_3$)



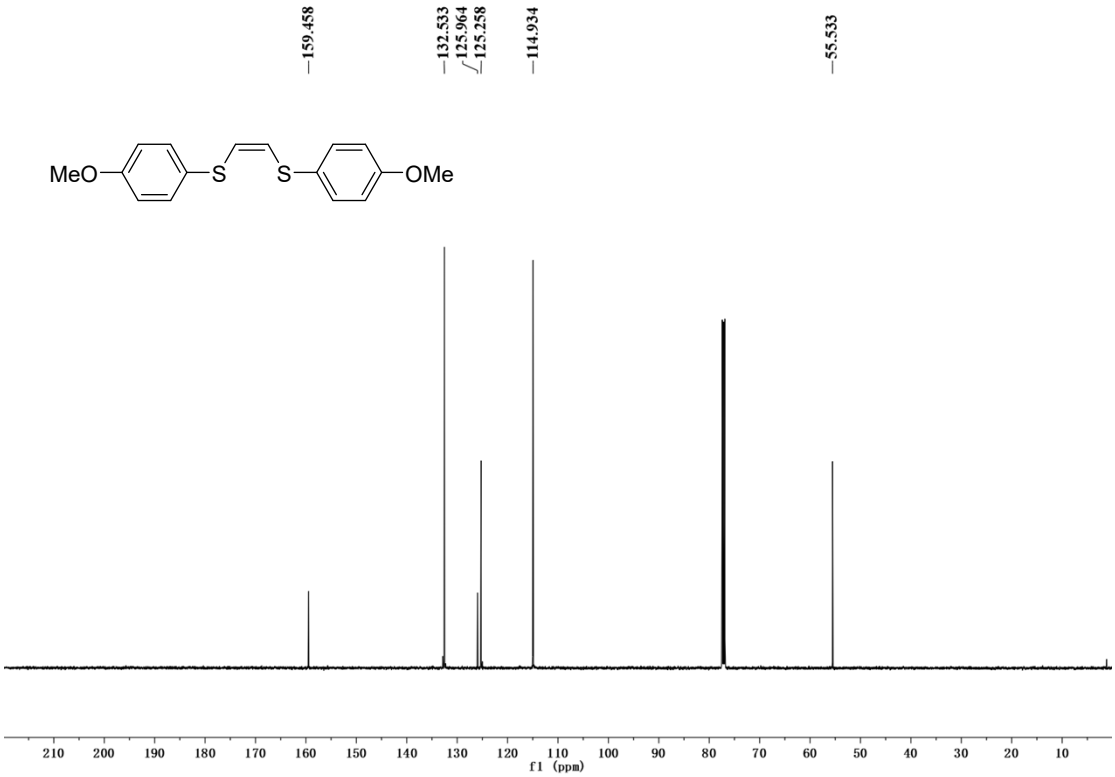
2r ^{13}C NMR (126 MHz, $CDCl_3$)



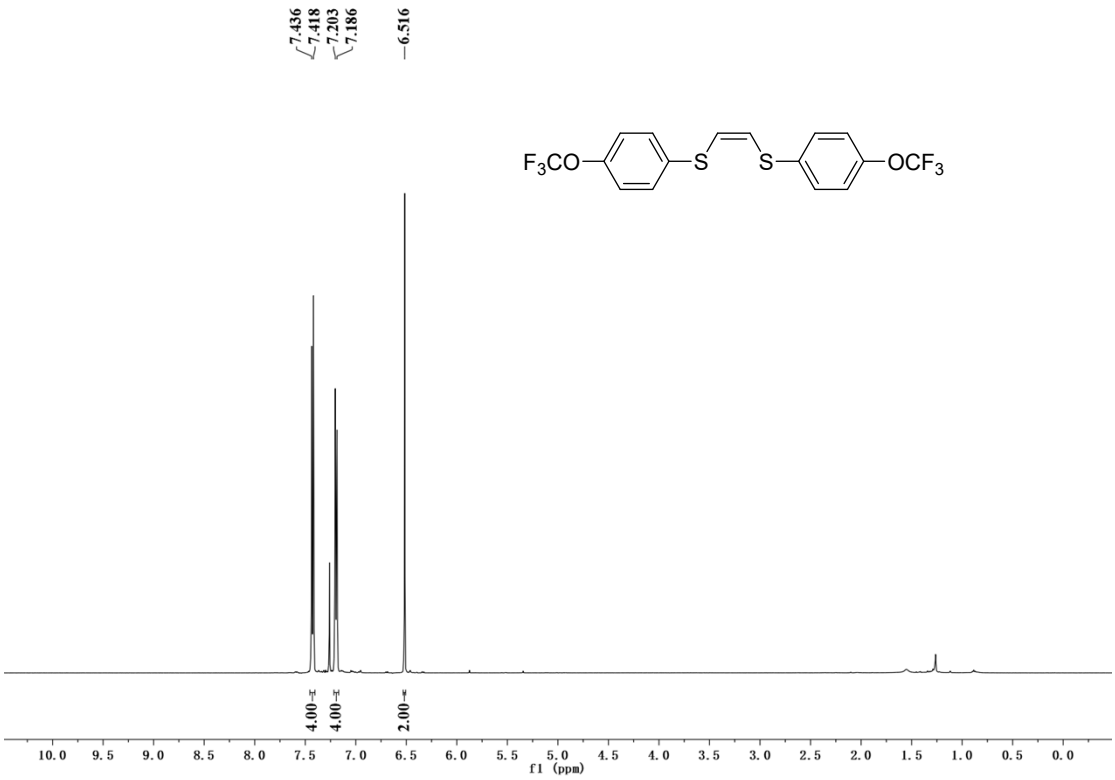
2s ^{1}H NMR (500 MHz, $CDCl_3$)



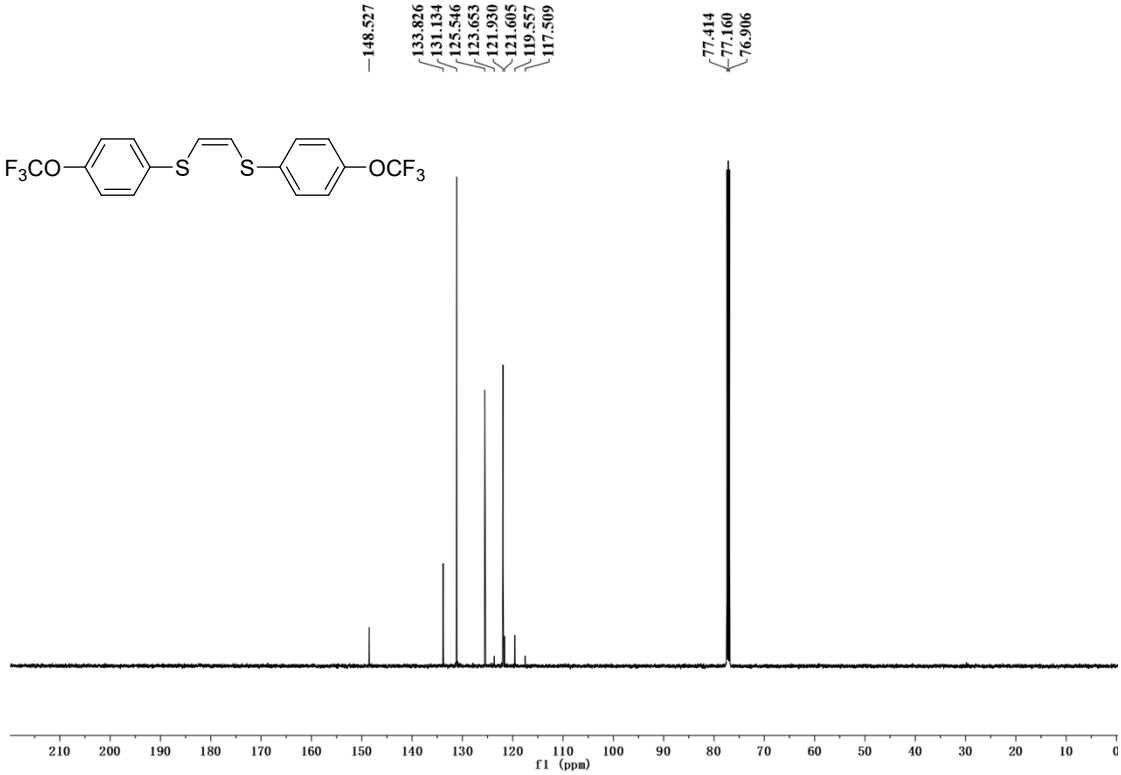
2s ^{13}C NMR (126 MHz, $CDCl_3$)



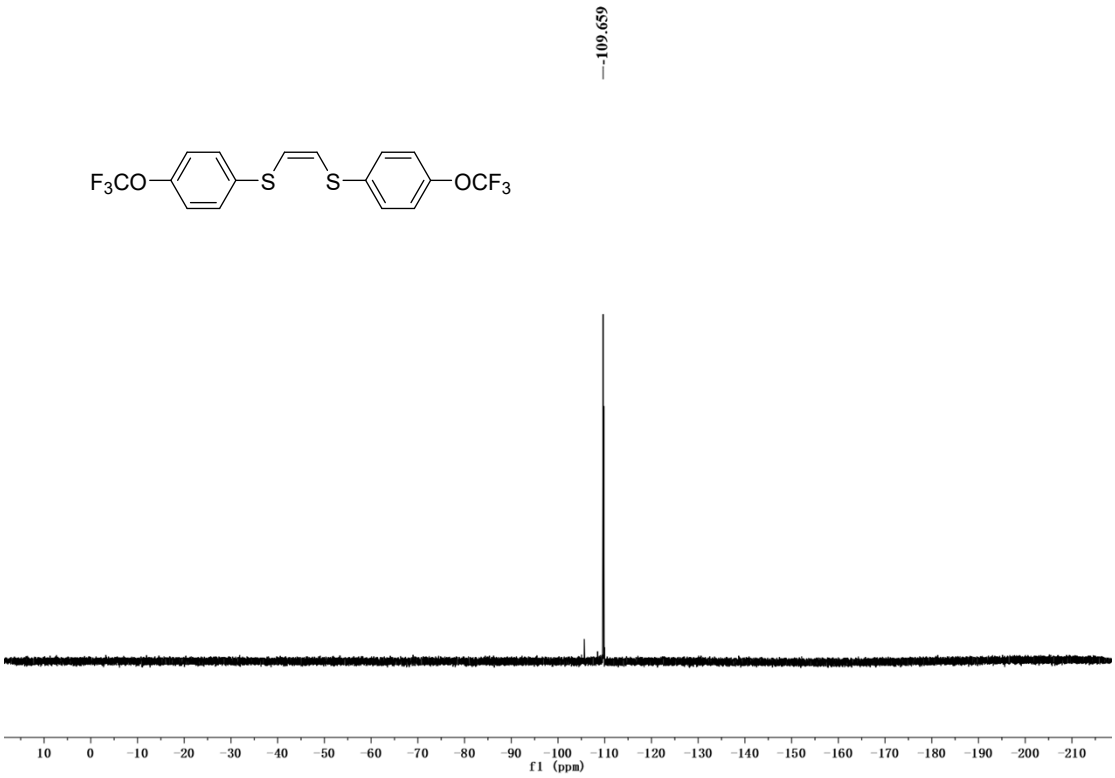
2t ^{1}H NMR (500 MHz, $CDCl_3$)



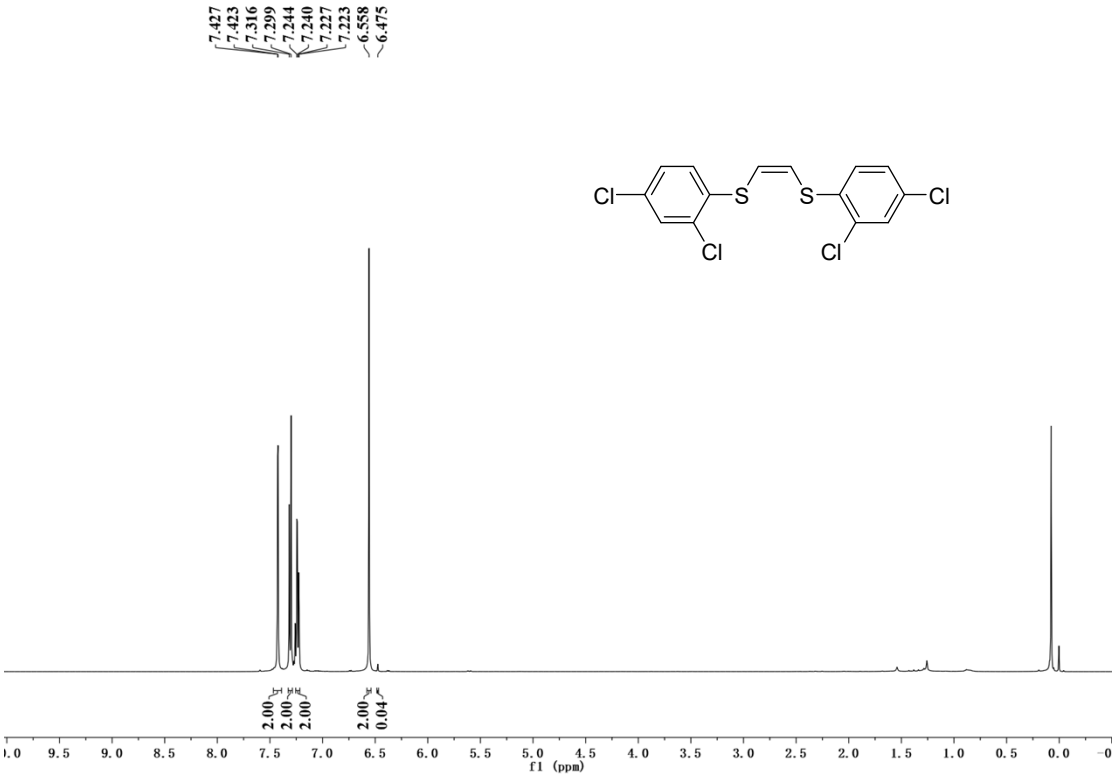
2t ^{13}C NMR (126 MHz, $CDCl_3$)



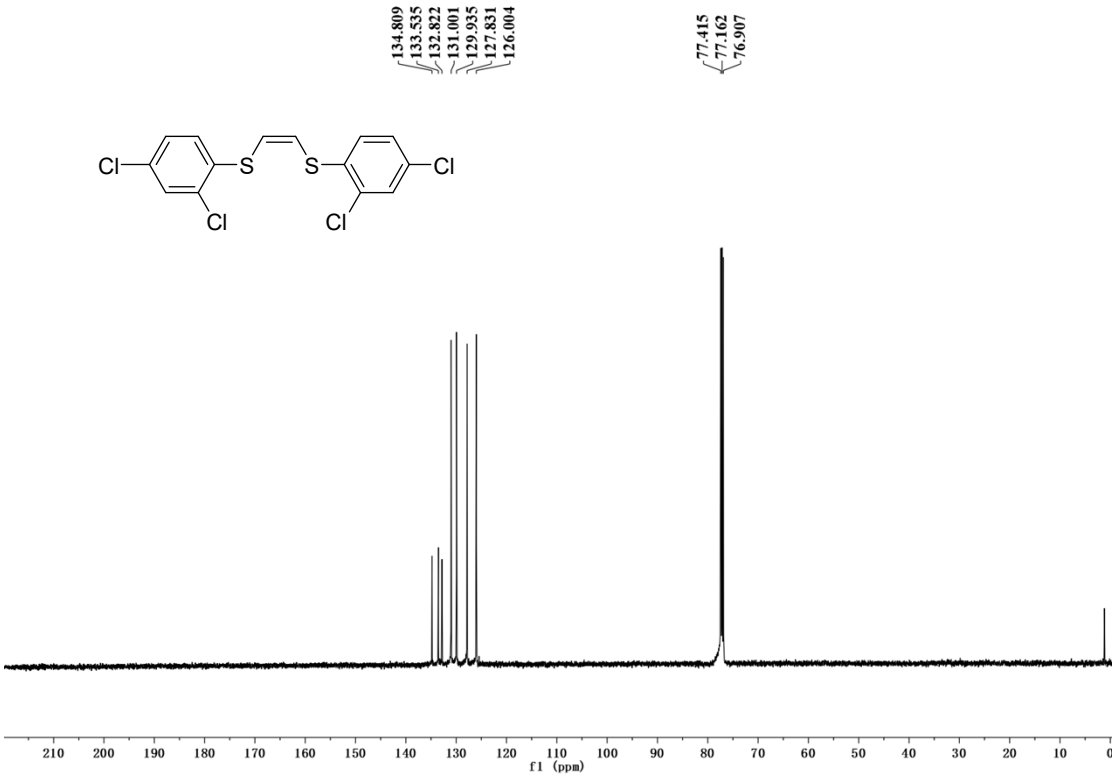
2t ^{19}F NMR (376 MHz, $CDCl_3$)



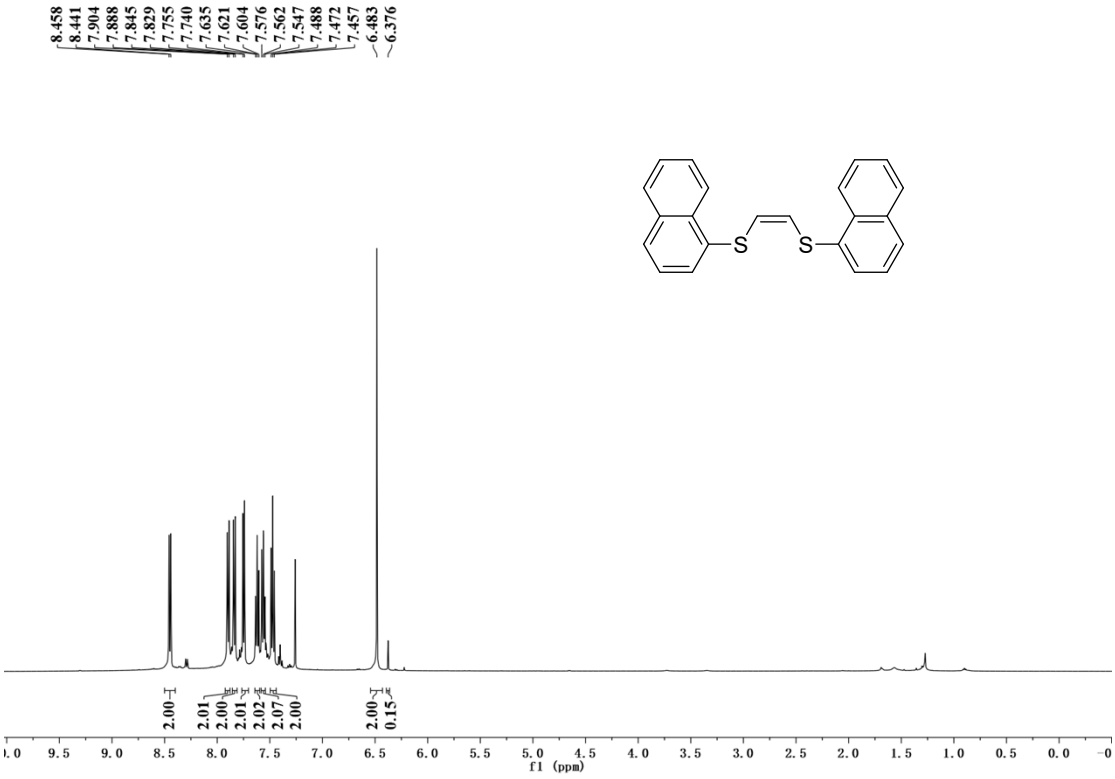
2u ^{1}H NMR (500 MHz, $CDCl_3$)



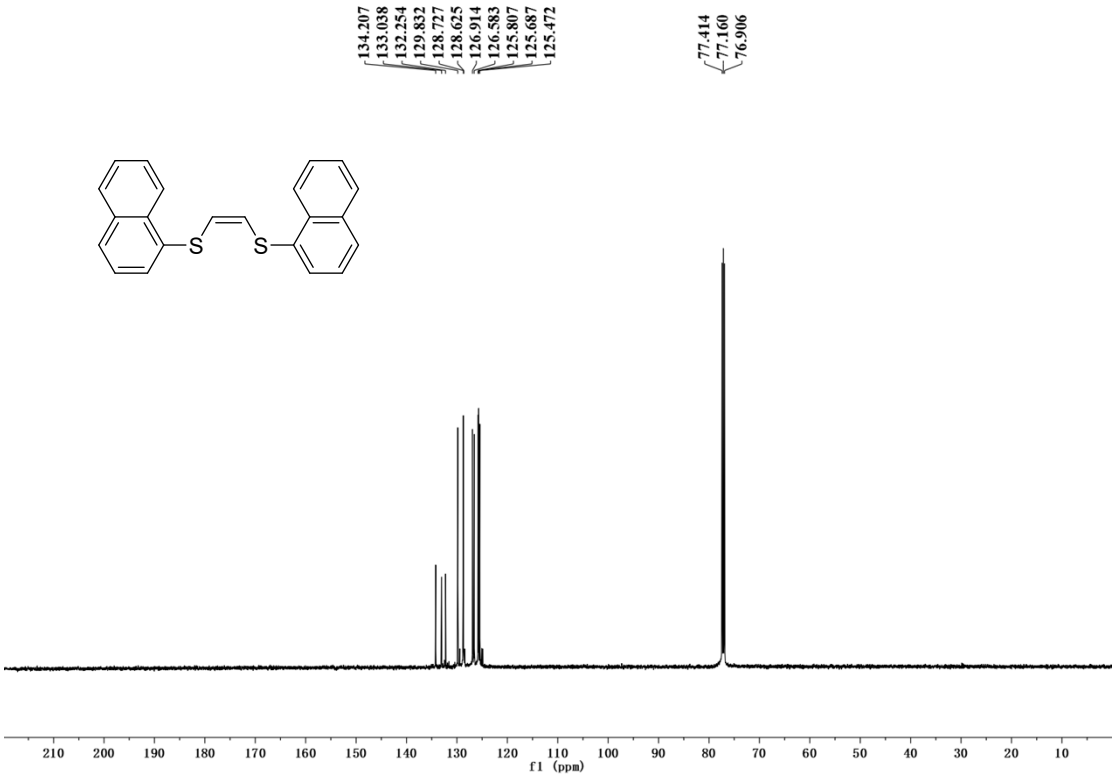
2u ^{13}C NMR (126 MHz, $CDCl_3$)



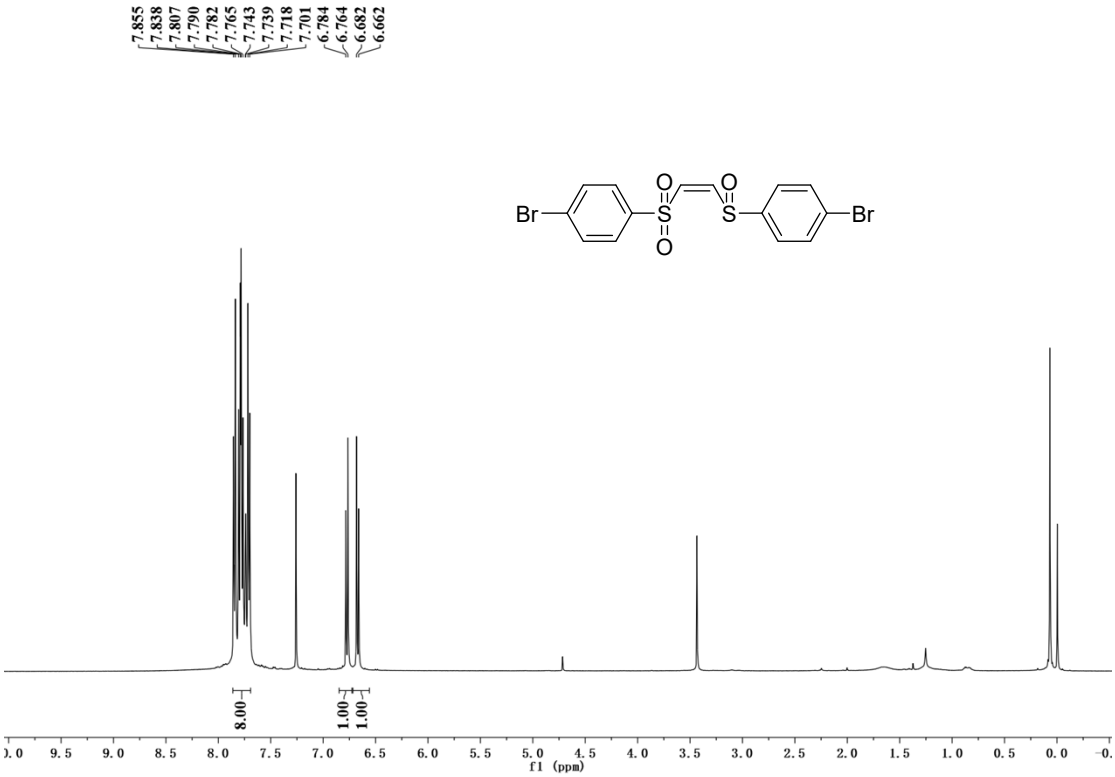
2v ^{1}H NMR (500 MHz, $CDCl_3$)



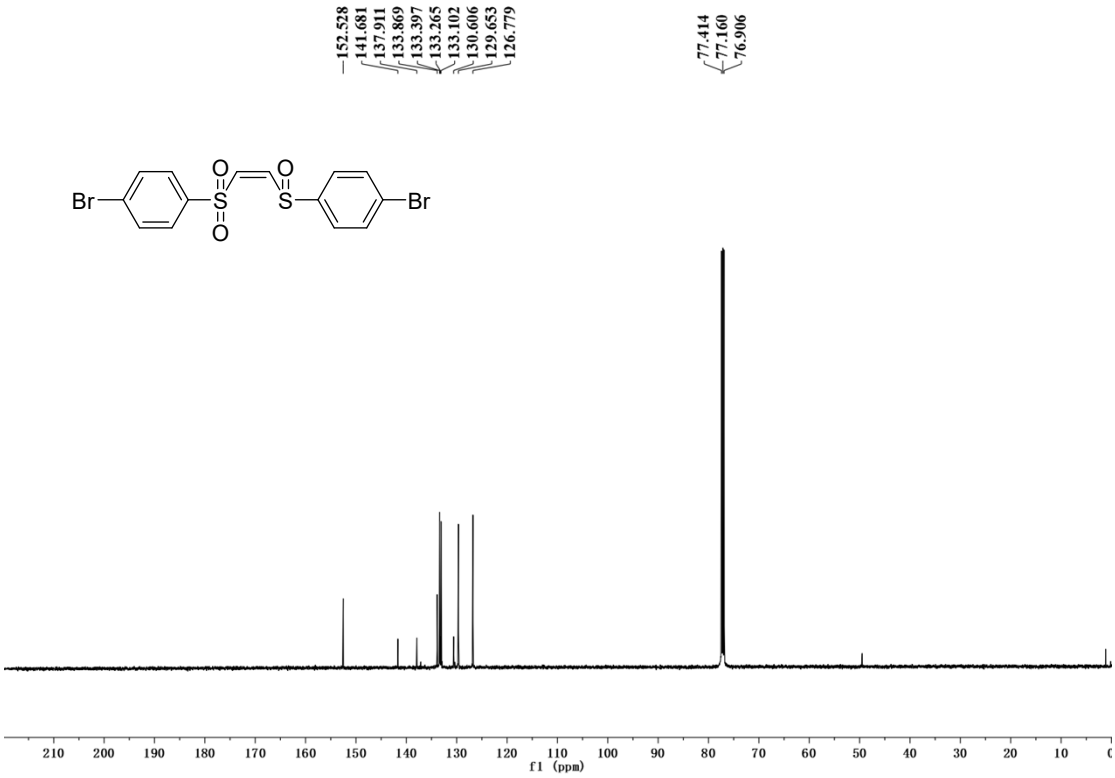
2v ^{13}C NMR (126 MHz, $CDCl_3$)



3a ^{1}H NMR (500 MHz, $CDCl_3$)



3a ^{13}C NMR (126 MHz, $CDCl_3$)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141.681
137.911
133.869
133.397
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133.102
130.606
129.653
126.779
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77.160
76.906
Br
Br
f1 (ppm)