

Supporting Information

Dithioacetalization or thioetherification of benzyl alcohols using 9-mesityl-10-methylacridinium perchlorate photocatalyst

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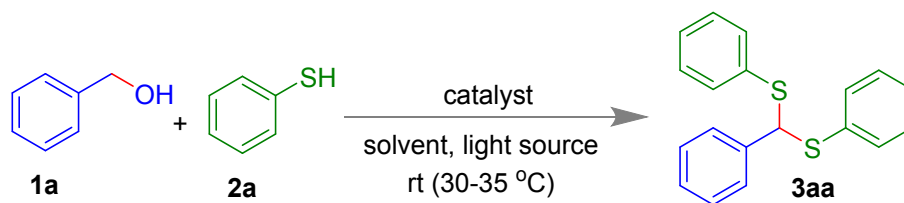
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EXPERIMENTAL SECTION

General Aspects. All the chemicals were purchased from the commercial sources and used as received. All the reactions were generally carried out under open atmosphere unless otherwise noted. The reactions were monitored by TLC on aluminum sheets pre-coated with silica gel. Chromatographic purifications of the compounds were performed using silica gel (Mess 230-400) and ethyl acetate/hexane as an eluent. ^1H and ^{13}C spectra of the compounds were recorded on Bruker 400 and 700 MHz instrument at 25 °C. The chemical shift value (δ , ppm) were reported with respect to the residual chloroform (7.26 for ^1H and 77.16 ppm for ^{13}C). Mass spectra were recorded as ESI-TOF (HRMS). Infrared spectra were recorded on neat solids using KBr pellets and described in wave number (cm^{-1}). Digital melting point apparatus were used to record the Melting Point of the compound in degree centigrade (°C) and are uncorrected.

Representative procedure for the preparation of Sulfanes. In an oven dried Schlenk tube benzylic alcohol **1a** (0.555 mmol, 60 mg) and Mes-Acr-MeClO₄ (5 mol %, 0.027 mmol, 11 mg) were dissolved in 1.0 mL acetonitrile solvent (*for solid thiophenols 5.0 equiv was used*). Following, Thiophenol **2a** (0.5 mL) was added to the reaction mixture and irradiated by 3W Blue LEDs light for 24 h at room temperature (30-35 °C). After completion of the reaction, acetonitrile was removed under reduced pressure. The pure product **3aa** was isolated through column chromatography using ethyl acetate and hexane as eluent. Generally, for 60 mg (0.555 mmol) of **1a**, 0.5 ml of **2a** was used and after reaction, approximately 0.3 mL of **2a** was recovered by column chromatography.

Table S1. Optimization of Reaction Conditions.^a

Entry	Catalyst (mol %)	Solvent	Light Source	Yield (%)
1	Mes-Acr-MeBF ₄ (5)	CH ₃ CN	Blue LED (3W)	32
2	Rose Bengal(5)	CH ₃ CN	Blue LED (3W)	-
3	Eosin Y(5)	CH ₃ CN	Blue LED (3W)	-
4	Ru(bipy) ₃ (PF ₆) ₂	CH ₃ CN	Blue LED (3W)	26
5	Mes-Acr-MeBF ₄ (5)	CHCl ₃	Blue LED (3W)	21
6	Mes-Acr-MeBF ₄ (5)	DCE	Blue LED (3W)	29
7	Mes-Acr-MeBF ₄ (5)	Toluene	Blue LED (3W)	-
8	Mes-Acr-MeBF ₄ (5)	DMSO	Blue LED (3W)	-
9	Mes-Acr-MeBF ₄ (5)	CH ₃ CN	White LED (14W)	31
10	Mes-Acr-MeBF ₄ (5)	CH ₃ CN	Green LED (26W)	-
11	Mes-Acr-MeClO ₄ (5)	CH ₃ CN	Blue LED (3W)	74 ^b
12	Mes-Acr-MeClO ₄ (5)	CH ₃ CN	Blue LED (3W)	96
13	Mes-Acr-MeClO ₄ (2)	CH ₃ CN	Blue LED (3W)	77
14	Mes-Acr-MeClO ₄ (5)	CH ₃ CN	Blue LED (3W)	68 ^c
15	-----	CH ₃ CN	Blue LED (3W)	-
16	Mes-Acr-MeClO ₄ (5)	CH ₃ CN	-----	-

Reaction Condition^a: **1a** (0.555 mmol, 60 mg), Mes-Acr-MeClO₄ (5 mol %, 0.027 mmol, 11 mg) 0.5 mL thiol and 1.0 mL CH₃CN in O₂ atmosphere for 24 h at rt in Blue LEDs;

^b4.0 equiv of thiophenol; ^cafter 12 h.

Light ON-OFF-ON Experiment. Benzylic alcohol derivatives **1a** (0.555 mmol, 60 mg), and Mes-Acr-MeClO₄ (5 mol %, 0.027 mmol, 11 mg) were dissolved in 1.0 mL acetonitrile. Following, Thiophenol **2a** (0.5 mL) was added to the reaction mixture and irradiated by 3W Blue LEDs light for 24 h. Successive progress of the reaction was monitored in every 4 h and 6 h in presence light and absence of light by ¹H NMR experiment using dibromomethane as internal standard.

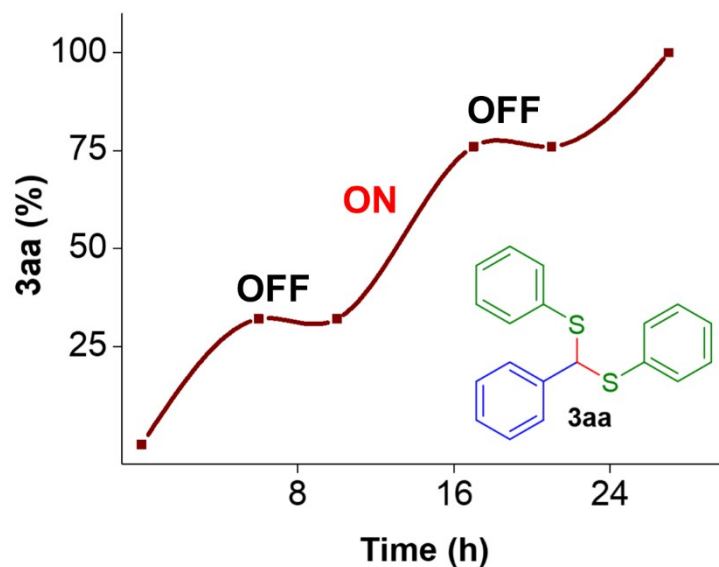


Fig. S1. Conversion of **3aa** vs. Time in presence and absence of light.

EPR Experiments.

EPR spectra was recorded at 298 K using EPR spectrometer derived at 9.4335 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3480.00 G; time constant: 0.16 ms; scan time: 122.88 s; modulation amplitude: 20.0 G; modulation frequency: 100 kHz; receiver gain: 2.00×10^2 ; microwave power: 7.14×10^{-1} mW.

Spin-trapping experiment in presence DMPO.¹ A mixture of benzyl alcohol (0.555 mmol), thiophenol (0.5 mL), Mes-Acr-MeClO₄ (5 mol %), and DMPO (20 μ L) were stirred in 1.0 mL

CH₃CN and irradiated in 3W Blue LEDs for 10 min. Afterwards, 20 μL solution was quickly transferred into EPR tube and 200 μL toluene was added to analyze EPR. Similar experiment was performed without thiophenol.

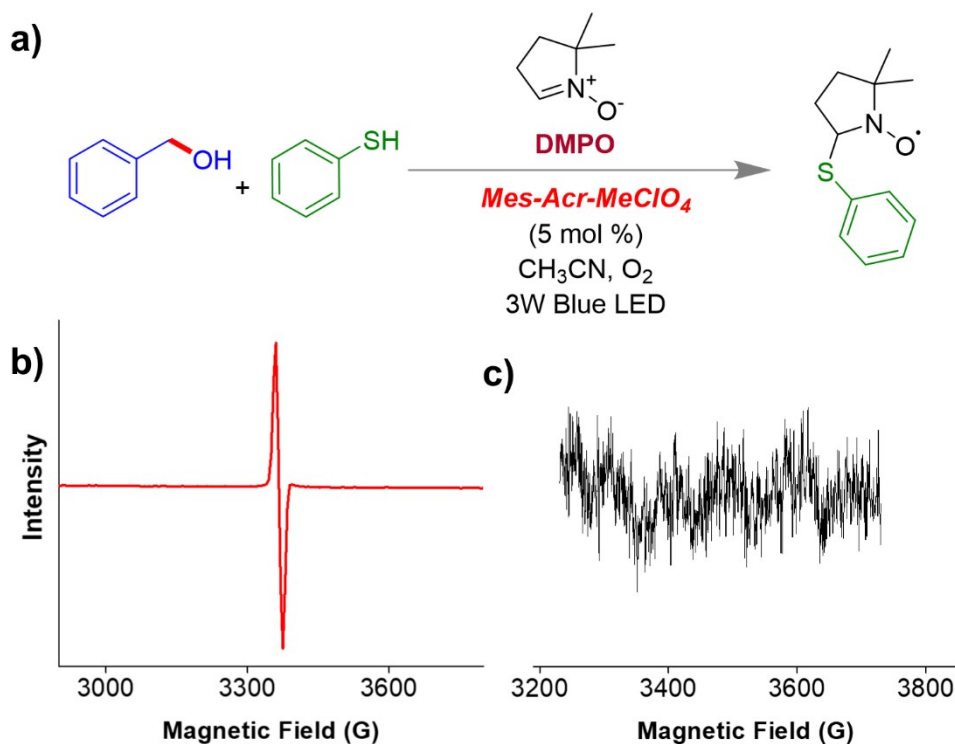


Fig. S2. a) EPR experiment with DMPO; b) under standard condition; c) absence of thiophenol.

Fluorescence quenching studies. The photocatalyst Mes-Acr-MeClO₄ was excited at 440 nm. After irradiation of Mes-Acr-MeClO₄ (4×10^{-5} M in MeCN) at 440 nm under N₂ atmosphere, maximum emission was observed at 615 nm. Increasing the amount of benzyl alcohol under saturated air and oxygen, fluorescence intensity was gradually decreased.

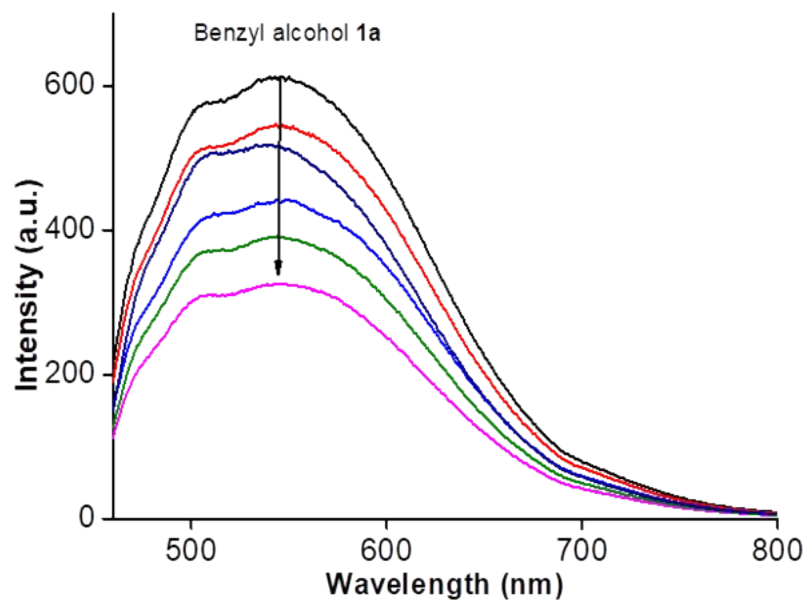


Fig. S3. Fluorescence spectra of Mes-Acr-MeClO₄ upon gradual addition of benzyl alcohol **1a**.

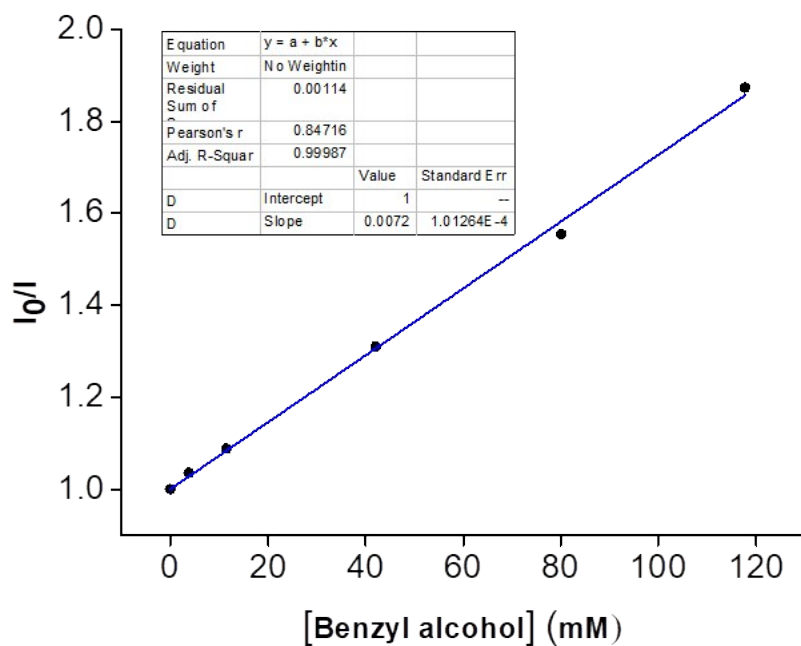


Fig. S4. Stern-Volmer plot for benzyl alcohol **1a**.

After irradiation of Mes-Acr-MeClO₄ (4×10^{-5} M in MeCN) at 440 nm under N₂ atmosphere, maximum emission was observed at 648 nm. Increasing the amount of thiophenol, fluorescence intensity was gradually decreased.

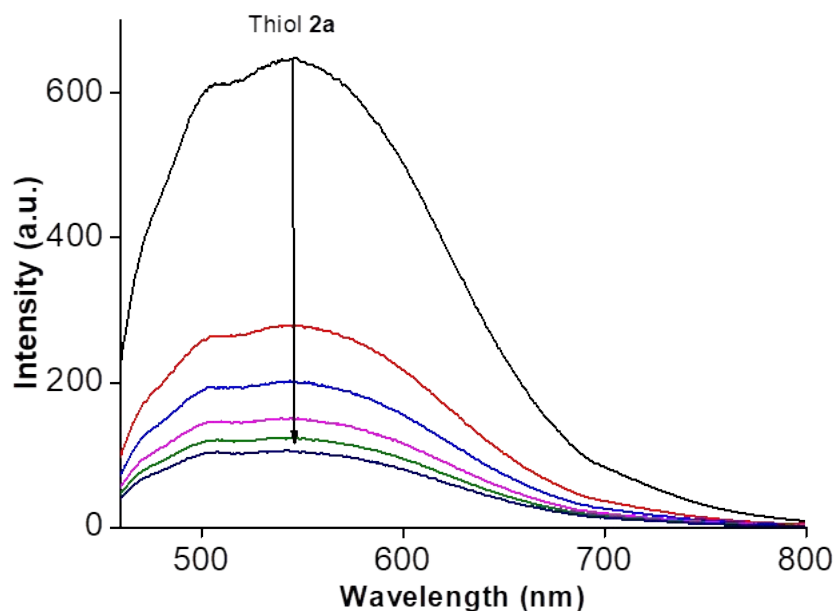


Fig. S5. Fluorescence spectra of Mes-Acr-MeClO₄ upon gradual addition of thiophenol **2a**.

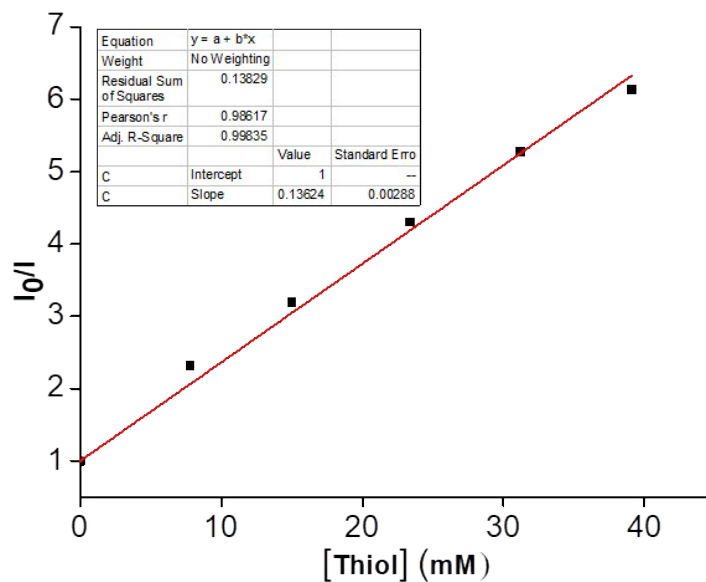
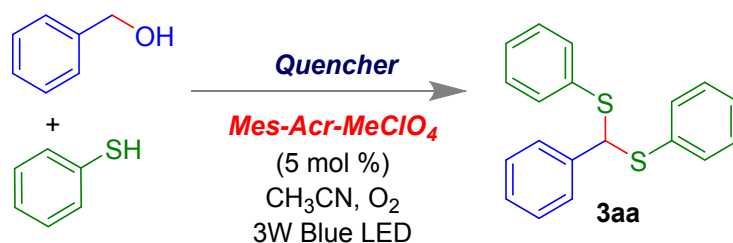


Fig. S6. Stern-Volmer plot for thiophenol **2a**.

Table S2. Quenching Experiments.^a



Entry	Quencher (equiv)	Purpose	Yield (%) ^b
1	BHT (2)	Radical scavenger	0
2	NaN_3 (1)	Singlet oxygen scavenger	0
3	DABCO (1)	Singlet oxygen scavenger	21
4	Benzoquinone (1)	Super oxide radical anion scavenger	19

Reaction condition: **1a** (0.277 mmol, 30 mg), Mes-Acr-MeClO₄ (0.0135 mmol, 5 mg) 0.2 mL thiol and 0.5 mL CH₃CN in O₂ atmosphere for 24 h using Blue LEDs. Yield was determined by ¹H NMR using dibromomethane as internal standard.

Unsuccessful substrates

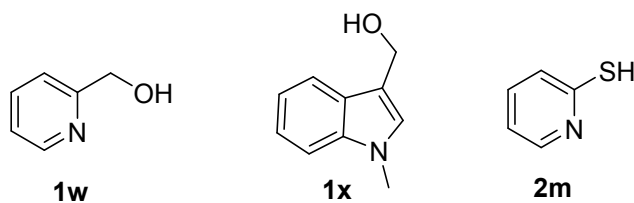
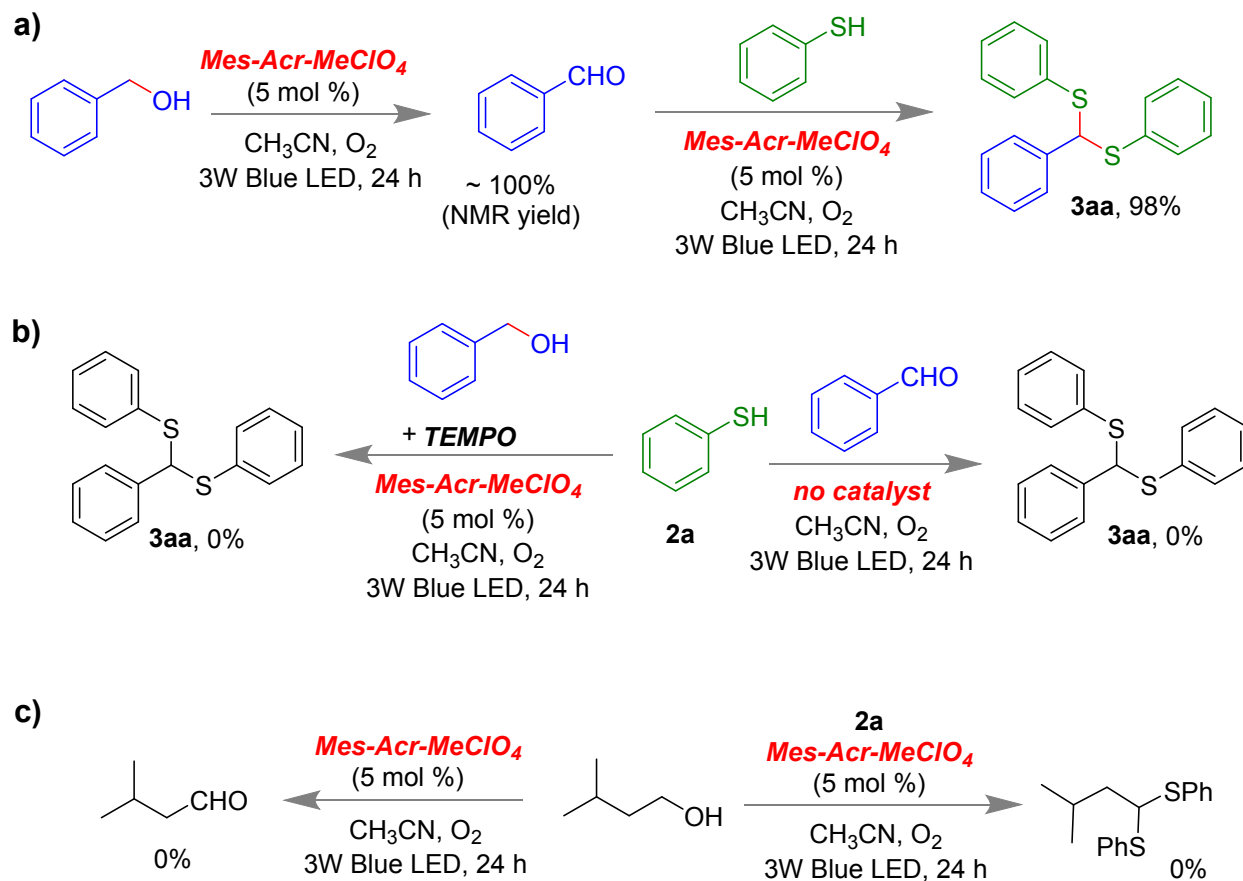


Chart S1. The alcohols and thiol were not compatible with the methodology.



Scheme S1. Control experiments.

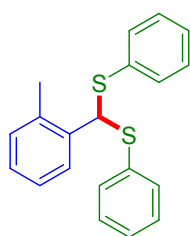
CHARATERIZATION DATA

(Phenylmethylene)bis(phenylsulfane) (3aa).² $R_f = 0.4$ (hexane); colorless liquid; yield 96% (164 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.33 (m, 6H), 7.28-7.26 (m, 2H), 7.24-7.22 (m, 7H), 5.42 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 134.7, 132.7, 129.0, 128.6, 128.2, 128.0, 127.9, 60.6.

(*p*-Tolylmethylene)bis(phenylsulfane) (3ba). $R_f = 0.45$ (hexane); white solid; yield 89% (140 mg); mp 55-57 °C (lit.² 56-58 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.34 (m, 4H), 7.27 (d, $J = 7.8$ Hz, 2H), 7.26-7.23 (m, 6H), 7.08 (d, $J = 7.8$ Hz, 2H),

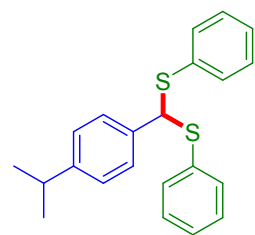
5.42 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 136.8, 134.9, 132.4, 129.3, 128.9, 127.9, 127.8, 60.3, 21.3.

(*o*-Tolylmethylene)bis(phenylsulfane) (3ca).² $R_f = 0.5$ (hexane); colorless liquid; yield 84%



(133 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.63 (m, 1H), 7.35-7.33 (m, 4H), 7.26-7.22 (m, 6H), 7.19-7.15 (m, 2H), 7.13-7.09 (m, 1H), 5.66 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 135.2, 135.0, 132.4, 130.5, 129.0, 128.4, 128.0, 127.8, 126.6, 57.2, 19.4.

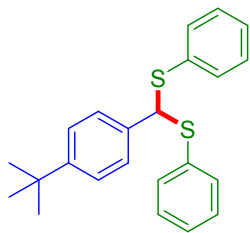
((4-Isopropylphenyl)methylene)bis(phenylsulfane) (3da).² $R_f = 0.45$ (hexane); colorless liquid;



yield 84% (118 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.34 (m, 2H), 7.34-7.32 (m, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 7.26-7.22 (m, 6H), 7.13 (d, $J = 8.2$ Hz, 2H), 5.43 (s, 1H), 2.88 (sept, $J = 7.0$ Hz, 1H), 1.23 (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 137.1, 135.0, 132.5, 128.9, 127.8,

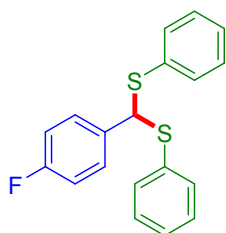
127.8, 126.7, 60.4, 33.9, 24.0.

((4-(Tert-butyl)phenyl)methylene)bis(phenylsulfane) (3ea).² $R_f = 0.3$ (hexane); white semi



solid; yield 76% (101 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.35 (m, 2H), 7.34-7.32 (m, 2H), 7.31-7.28 (m, 4H), 7.26-7.24 (m, 3H), 7.24-7.22 (m, 3H), 5.44 (s, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.2, 136.7, 135.0, 132.4, 128.9, 127.7, 127.6, 125.6, 60.4, 34.7, 31.4

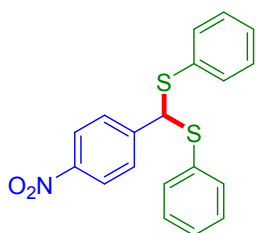
((4-Fluorophenyl)methylene)bis(phenylsulfane) (3fa).² $R_f = 0.4$ (hexane); colorless liquid; yield



65% (101 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36-7.33 (m, 4H), 7.32-7.29 (m, 2H), 7.27-7.24 (m, 6H), 6.94 (t, $J = 8.6$ Hz, 2H), 5.42 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.4 (d, $^1J_{\text{C-F}} = 247.2$ Hz), 135.6 (d, $^4J_{\text{C-F}} = 3.0$ Hz), 134.3, 132.9, 129.7 (d, $^3J_{\text{C-F}} = 8.3$ Hz), 129.0, 128.12, 115.5 (d, $^2J_{\text{C-F}} = 21.8$

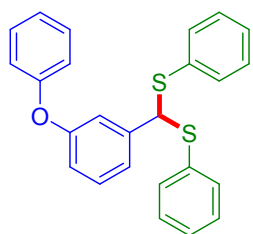
Hz), 59.8.

((4-Nitrophenyl)methylene)bis(phenylsulfane) (3ga).² $R_f = 0.45$ (5% ethyl acetate in hexane);



yellow liquid; yield 42% (58 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 8.6$ Hz, 2H), 7.35-7.34 (m, 2H), 7.34-7.32 (m, 2H), 7.29-7.25 (m, 6H), 5.44 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.2, 133.4, 129.2, 129.2, 128.9, 128.7, 127.7, 123.8, 59.9.

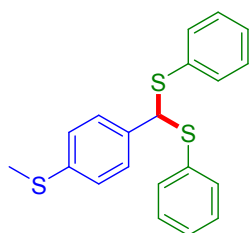
((3-Phenoxyphenyl)methylene)bis(phenylsulfane) (3ha): $R_f = 0.2$ (hexane); colorless liquid;



yield 98% (117 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37-7.35 (m, 4H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 1H), 7.27-7.23 (m, 7H), 7.15 (d, $J = 7.6$ Hz, 1H), 7.10 (t, $J = 7.4$ Hz, 1H), 6.99 (s, 1H), 6.89 (d, $J = 8.0$ Hz, 3H), 5.39 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.2, 157.1, 141.7, 134.4,

132.9, 130.0, 129.8, 129.0, 128.0, 123.3, 123.0, 118.8, 118.76, 118.68, 60.2; IR (KBr) $\bar{\nu}$ 2923, 1489, 1248, 1024, 689 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M-SC}_6\text{H}_5]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{OS}$ 291.0838; found 291.0815.

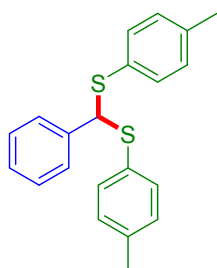
((4-(Methylthio)phenyl)methylene)bis(phenylsulfane) (3ia). $R_f = 0.4$ (2% ethyl acetate in



hexane); white solid; yield 74% (102 mg); mp 86-90 °C (lit.² 88-90 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.33 (m, 4H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.26-7.23 (m, 6H), 7.14 (d, $J = 8.4$ Hz, 2H), 5.40 (s, 1H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.5, 136.5, 134.6, 132.6, 129.0, 128.4, 127.9, 126.4,

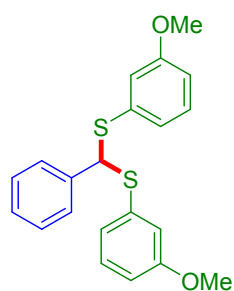
60.1, 15.8.

(Phenylmethylene)bis(p-tolylsulfane) (3ab). $R_f = 0.2$ (hexane); white solid; yield 84% (156 mg);



mp 66-67 °C (lit.² 64-66 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, $J = 7.4$ Hz, 2H), 7.25 (d, $J = 6.8$ Hz, 3H), 7.24 (d, $J = 7.8$ Hz, 4H), 7.05 (d, $J = 7.8$ Hz, 4H), 5.31 (s, 1H), 2.31 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 138.1, 133.3, 131.0, 129.7, 128.5, 128.0 (×2), 61.4, 21.3.

(Phenylmethylene)bis((3-methoxyphenyl)sulfane) (3ac): $R_f = 0.4$ (5% ethyl acetate in hexane);



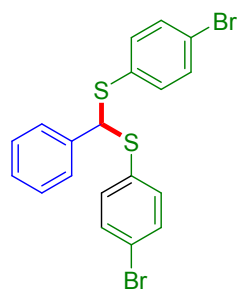
colorless liquid; yield 70% (142 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.37 (m, 2H), 7.30-7.29 (m, 1H), 7.28-7.26 (m, 1H), 7.24-7.23 (m, 1H), 7.15 (t, $J = 8.0$ Hz, 2H), 6.95 (d, $J = 7.8$ Hz, 2H), 6.86-6.84 (m, 2H), 6.77 (d, $J = 8.2$ Hz, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 5.45 (s, 1H), 3.70 (s, 6H); ¹³C NMR (100 MHz,

CDCl₃) δ 159.7, 141.4, 135.9, 129.7, 128.7, 128.2, 128.1, 124.5, 117.3, 114.0, 60.1, 55.4; IR (KBr)

$\bar{\nu}$ 2833, 2359, 1590, 1283, 685 cm⁻¹; HRMS (ESI/Q-TOF) m/z : $[M + Na]^+$ calcd for C₂₁H₂₀O₂S₂Na

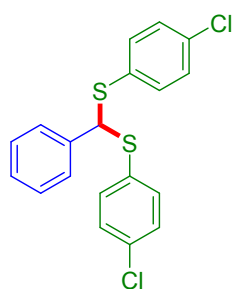
391.0797; found 391.0770.

(Phenylmethylene)bis((4-bromophenyl)sulfane) (3ad): $R_f = 0.4$ (2% ethyl acetate in hexane);



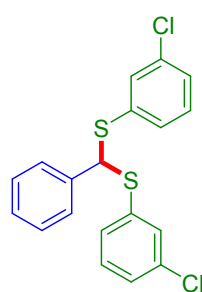
white solid; yield 77% (200 mg); mp 64-66 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.4$ Hz, 4H), 7.34-7.31 (m, 2H), 7.30-7.26 (m, 3H), 7.18 (d, $J = 8.4$ Hz, 4H), 5.35 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.0, 134.4, 133.3, 132.1, 128.8, 128.5, 128.0, 122.5, 60.6; IR (KBr) $\bar{\nu}$ 3059, 1471, 1088, 695, 592 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{14}\text{Br}_2\text{S}_2\text{Na}$ 488.8775; found 488.8753.

(Phenylmethylene)bis((4-chlorophenyl)sulfane) (3ae).² $R_f = 0.5$ (2% ethyl acetate in hexane);



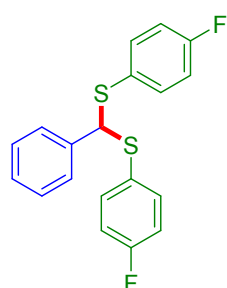
colorless liquid; yield 94% (197 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34-7.32 (m, 2H), 7.31-7.28 (m, 2H), 7.28-7.26 (m, 5H), 7.23-7.21 (m, 4H), 5.36 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.0, 134.4, 134.3, 132.6, 129.1, 128.7, 128.4, 127.9, 60.9.

(Phenylmethylene)bis((3-chlorophenyl)sulfane) (3af): $R_f = 0.55$ (2% ethyl acetate in hexane);



colorless liquid; yield 91% (191 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38-7.36 (m, 2H), 7.33-7.31 (m, 2H), 7.31-7.28 (m, 3H), 7.25-7.15 (m, 6H), 5.45 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 138.8, 136.3, 134.6, 132.2, 130.5, 130.0, 128.8, 128.6, 128.2, 128.0, 60.3; IR (KBr) $\bar{\nu}$ 3069, 1574, 1083, 778, 679 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M}-\text{C}_6\text{H}_4\text{ClS}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{ClS}$ 233.0186; found 233.0177.

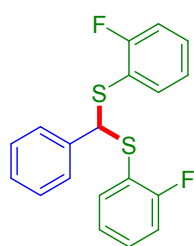
(Phenylmethylene)bis((4-fluorophenyl)sulfane) (3ag).² $R_f = 0.4$ (hexane); colorless liquid; yield



88% (168 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34-7.29 (m, 5H), 7.26-7.23

(m, 4H), 6.94 (t, $J = 8.6$ Hz, 4H), 5.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.0 (d, $^1J_{\text{C-F}} = 248.9$ Hz), 139.4, 136.0 (d, $^3J_{\text{C-F}} = 8.3$ Hz), 129.3 (d, $^4J_{\text{C-F}} = 3.4$ Hz), 128.6, 128.3, 128.0, 116.1 (d, $^2J_{\text{C-F}} = 21.8$ Hz), 62.3.

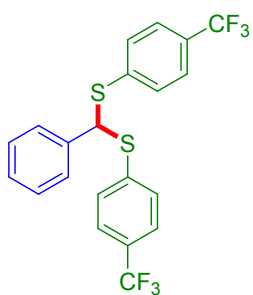
(Phenylmethylene)bis((2-fluorophenyl)sulfane) (3ah): $R_f = 0.35$ (hexane); colorless liquid;



yield 79% (151 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.4$ Hz, 2H), 7.37 (d, $J = 7.4$ Hz, 2H), 7.28-7.22 (m, 5H), 7.02 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 5.71 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.5 (d, $^1J_{\text{C-F}} = 246.8$ Hz), 139.0, 135.4, 130.5 (d, $^3J_{\text{C-F}} = 8.3$ Hz), 128.7, 128.5, 128.0, 124.6 (d, $^4J_{\text{C-F}} = 3.9$

Hz), 121.4 (d, $^2J_{\text{C-F}} = 18.3$ Hz), 115.9 (d, $^2J_{\text{C-F}} = 23.0$ Hz), 57.9; IR (KBr) $\bar{\nu}$ 3065, 1671, 1471, 1226, 697 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{14}\text{F}_2\text{S}_2\text{Na}$ 367.0397; found 367.0372.

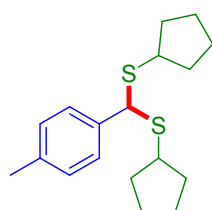
(Phenylmethylene)bis((4-(trifluoromethyl)phenyl)sulfane) (3ai): $R_f = 0.35$ (hexane); colorless



liquid; yield 61% (86 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.2$ Hz, 4H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.41 (d, $J = 8.2$ Hz, 4H), 7.36-7.30 (m, 3H), 5.60 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.5, 138.2, 131.2, 129.5 (q, $^2J_{\text{C-F}} = 32.5$ Hz), 129.0, 128.9, 128.0, 125.9 (q, $^4J_{\text{C-F}} = 3.6$ Hz), 125.4 (q, $^1J_{\text{C-F}} = 272.4$ Hz), 58.6; IR (KBr) $\bar{\nu}$ 2925, 1606, 1166, 1674, 702 cm^{-1} ; HRMS

(ESI/Q-TOF) m/z : $[\text{M}-\text{C}_7\text{H}_4\text{F}_3\text{S}]^+$ calcd for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{S}$ 267.0450; found 267.0442.

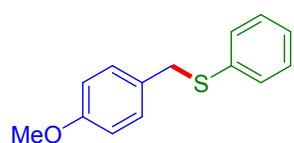
(*p*-Polymethylene)bis(cyclopentylsulfane) (3bj): $R_f = 0.6$ (hexane); colorless liquid; yield 54%



(81 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 7.8$ Hz, 2H), 7.12 (d, $J =$

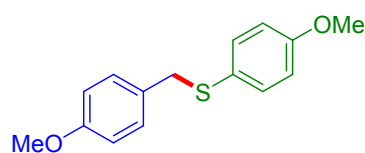
7.8 Hz, 2H), 4.86 (s, 1H), 3.12-3.07 (m, 2H), 2.33 (s, 3H), 1.98-1.88 (m, 4H), 1.71-1.63 (m, 4H), 1.53-1.48 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 137.5, 129.3, 127.7, 52.7, 44.4, 33.7, 25.0, 21.3; IR (KBr) $\bar{\nu}$ 2954, 1652, 1509, 459, 667 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{26}\text{S}_2\text{Na}$ 329.1368; found 329.1377.

(4-Methoxybenzyl)(phenyl)sulfane (4ma). $R_f = 0.4$ (5% ethyl acetate in hexane); white solid;



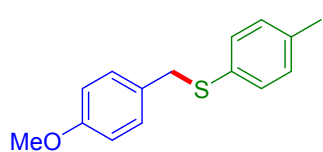
yield 85% (85 mg); mp 83-85 °C (lit.³ 85 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.24-7.23 (m, 2H), 7.21-7.16 (m, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 4.09 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 136.7, 130.1, 129.9, 129.5, 128.9, 126.4, 114.0, 55.4, 38.6.

(4-Methoxybenzyl)(4-methoxyphenyl)sulfane (4mk). $R_f = 0.65$ (5% ethyl acetate in hexane);



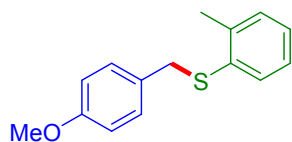
white solid; yield 93% (105 mg); mp 89-90 °C (lit.⁴ 89 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 8.6$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 8.6$ Hz, 4H), 3.95 (s, 2H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 158.8, 134.2, 130.3, 130.1, 126.4, 114.5, 113.9, 55.4, 55.4, 40.8.

(4-Methoxybenzyl)(p-tolyl)sulfane (4mb). $R_f = 0.65$ (5% ethyl acetate in hexane); white solid;



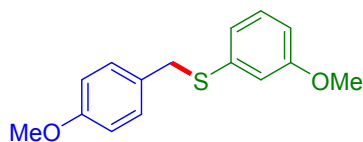
yield 72% (76 mg); mp 63-65 °C (lit.³ 66 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 4.03 (s, 2H), 3.79 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 136.6, 132.9, 130.8, 130.1, 129.9, 129.7, 114.0, 55.4, 39.3, 21.2.

(4-Methoxybenzyl)(o-tolyl)sulfane (4ml).⁵ $R_f = 0.65$ (5% ethyl acetate in hexane); white solid;



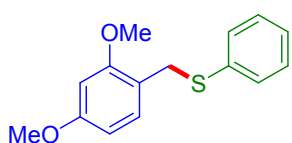
yield 70% (74 mg); mp 62-64 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 (d, $J = 7.4$ Hz, 1H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.16 (t, $J = 6.8$ Hz, 2H), 7.13-7.09 (m, 1H), 6.84 (d, $J = 8.2$ Hz, 2H), 4.06 (s, 2H), 3.80 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.9, 137.9, 136.1, 130.14, 130.10, 129.3, 128.9, 126.5, 126.1, 114.0, 55.4, 37.8, 20.4.

(4-Methoxybenzyl)(3-methoxyphenyl)sulfane (4mc): $R_f = 0.3$ (5% ethyl acetate in hexane);



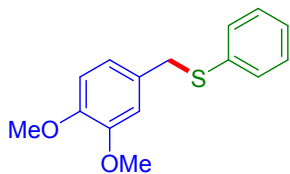
colorless liquid; yield 63% (70 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24 (d, $J = 8.6$ Hz, 2H), 7.17 (t, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 3H), 6.72 (dd, $J = 8.2, 2.2$ Hz, 1H), 4.09 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.8, 158.9, 138.1, 130.1, 129.7, 129.4, 121.8, 114.8, 114.1, 112.2, 55.4, 55.3, 38.3; IR (KBr) $\bar{\nu}$ 2924, 1634, 1511, 1034, 686 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{SNa}$ 283.0763; found 283.0755.

(2,4-Dimethoxybenzyl)(phenyl)sulfane (4na): $R_f = 0.4$ (5% ethyl acetate in hexane); colorless



liquid; yield 81% (75 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34-7.32 (m, 2H), 7.27-7.25 (m, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.19-7.16 (m, 1H), 7.09 (d, $J = 8.2$ Hz, 1H), 6.45-6.44 (m, 1H), 6.39 (dd, $J = 8.2, 2.4$ Hz, 1H), 4.10 (s, 2H), 3.80 (s, 3H), 3.79 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.6, 158.4, 137.3, 130.8, 129.9, 128.8, 126.1, 118.3, 104.2, 98.8, 55.6, 55.5, 33.1; IR (KBr) $\bar{\nu}$ 2934, 2358, 1505, 1209, 691 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{SNa}$ 283.0763; found 283.0762.

(3,4-Dimethoxybenzyl)(phenyl)sulfane (40a).⁶ $R_f = 0.35$ (5% ethyl acetate in hexane); white



solid; yield 53% (49 mg); mp 78-80 °C; ¹H NMR (400 MHz, CDCl₃) δ

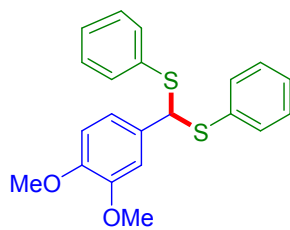
7.32 (d, $J = 7.8$ Hz, 2H), 7.26 (t, $J = 7.4$ Hz, 2H), 7.19 (t, $J = 6.8$ Hz, 1H),

6.82 (d, $J = 8.4$ Hz, 1H), 6.79-6.76 (m, 2H), 4.08 (s, 2H), 3.86 (s, 3H),

3.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 148.3, 136.5, 130.2, 130.0, 128.9, 126.5, 121.1,

112.0, 111.1, 56.0, 55.9, 39.2.

((3,4-Dimethoxyphenyl)methylene)bis(phenylsulfane) (30a).⁷ $R_f = 0.3$ (5% ethyl acetate in



hexane); colorless liquid; yield 26% (41 mg); ¹H NMR (400 MHz,

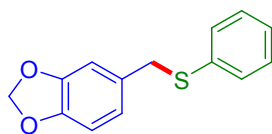
CDCl₃) δ 7.38-7.36 (m, 4H), 7.28-7.25 (m, 6H), 6.91 (s, 1H), 6.88 (d, $J =$

8.4 Hz, 1H), 6.74 (d, $J = 8.2$ Hz, 1H), 5.42 (s, 1H), 3.86 (s, 3H), 3.81 (s,

3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 148.8, 134.6, 132.7, 132.1,

128.9, 127.9, 120.3, 110.9, 110.8, 60.2, 55.9(×2).

5-((Phenylthio)methyl)benzo[d][1,3]dioxole (4pa).⁸ $R_f = 0.55$ (2% ethyl acetate in hexane);



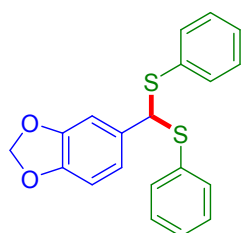
colorless liquid; yield 52% (50 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.32-

7.30 (m, 2H), 7.28-7.24 (m, 2H), 7.21-7.17 (m, 1H), 6.82 (s, 1H), 6.73-6.69

(m, 2H), 5.93 (s, 2H), 4.04 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 147.9,

146.9, 136.4, 131.3, 130.0, 129.0, 126.5, 122.2, 109.3, 108.2, 101.1, 39.2.

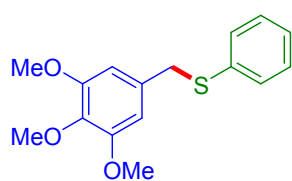
5-(Bis(phenylthio)methyl)benzo[d][1,3]dioxole (3pa).⁷ $R_f = 0.5$ (2% ethyl acetate in hexane);



colorless liquid; yield 45% (62 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.36

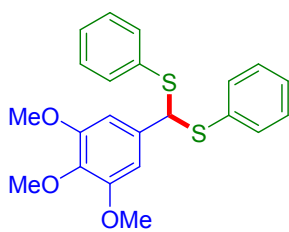
(m, 4H), 7.29-7.26 (m, 6H), 6.99 (d, $J = 1.7$ Hz, 1H), 6.79 (dd, $J = 8.0, 1.8$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 5.97 (s, 2H), 5.37 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 147.5, 134.7, 133.7, 132.5, 129.0, 127.9, 121.6, 108.4, 108.0, 101.4, 60.3.

Phenyl(3,4,5-trimethoxybenzyl)sulfane (4qa).⁹ $R_f = 0.25$ (5% ethyl acetate in hexane); colorless



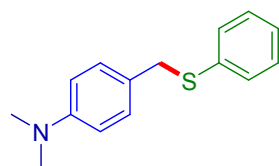
liquid; yield 29% (25 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.32 (m, 2H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.26-7.23 (m, 1H), 7.22-7.18 (m, 1H), 6.47 (s, 2H), 4.05 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.3, 137.3, 136.3, 133.2, 130.5, 129.0, 126.7, 105.9, 61.0, 56.2, 39.9.

((3,4,5-Trimethoxyphenyl)methylene)bis(phenylsulfane) (3qa).¹⁰ $R_f = 0.2$ (5% ethyl acetate in



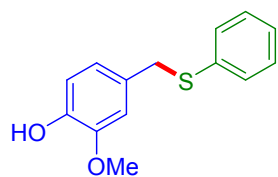
hexane); colorless liquid; yield 59% (71 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.36 (m, 4H), 7.27-7.25 (m, 6H), 6.55 (s, 2H), 5.36 (s, 1H), 3.83 (s, 3H), 3.77 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.1, 137.7, 135.2, 134.4, 132.9, 129.0, 128.0, 105.0, 61.0, 60.9, 56.2;

N,N-dimethyl-4-((phenylthio)methyl)aniline (4ra).¹¹ $R_f = 0.65$ (10% ethyl acetate in hexane);



white solid; yield 97% (93 mg); mp 95-97 °C (lit. 95-105 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 7.8$ Hz, 2H), 7.26 (t, $J = 7.4$ Hz, 2H), 7.17 (t, $J = 8.2$ Hz, 3H), 6.67 (d, $J = 8.2$ Hz, 2H), 4.09 (s, 2H), 2.93 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 137.3, 129.8, 129.5, 128.9, 126.1, 124.9, 112.7, 40.8, 38.6.

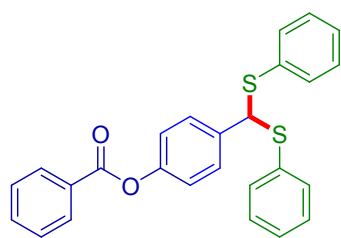
2-Methoxy-4-((phenylthio)methyl)phenol (4sa): $R_f = 0.5$ (10% ethyl acetate in hexane); white



solid; yield 79% (76 mg); mp 94-96 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33-7.30 (m, 2H), 7.28-7.26 (m, 1H), 7.26-7.24 (m, 1H), 7.21-7.17 (m, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 6.78-6.75 (m, 2H), 5.54 (s, 1H), 4.06 (s, 2H),

3.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 146.6, 144.9, 136.5, 130.2, 129.4, 129.0, 126.5, 121.9, 114.3, 111.4, 56.0, 39.3; IR (KBr) $\bar{\nu}$ 2996, 1601, 1279, 1034, 748, 699 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{SNa}$ 269.0607; found 269.0605.

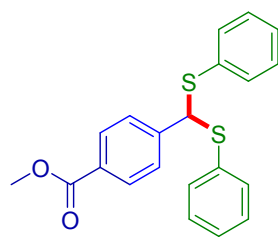
4-(bis(phenylthio)methyl)phenyl benzoate (3ja).¹² $R_f = 0.4$ (5% ethyl acetate in hexane); white



solid; yield 72% (81 mg); mp 116-118 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (d, $J = 7.8$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.38-7.36 (m, 4H), 7.27-7.26 (m, 6H), 7.14 (d, $J = 8.4$ Hz, 2H), 5.45 (s, 1H); $^{13}\text{C NMR}$ (100 MHz,

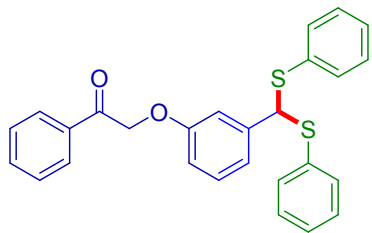
CDCl_3) δ 165.3, 150.7, 137.4, 134.4, 133.8, 132.9, 130.3, 129.6, 129.2, 129.1, 128.7, 128.1, 121.8, 60.1.

Methyl 4-(bis(phenylthio)methyl)benzoate (3ka).² $R_f = 0.45$ (5% ethyl acetate in hexane);



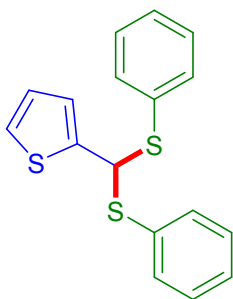
colorless liquid; yield 58% (76 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.35-7.34 (m, 4H), 7.26-7.24 (m, 6H), 5.44 (s, 1H), 3.91 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.8, 144.9, 133.9, 133.1, 129.9, 129.8, 129.1, 128.3, 128.1, 60.3, 52.3.

2-(3-(Bis(phenylthio)methyl)phenoxy)-1-phenylethan-1-one (3la).¹² $R_f = 0.55$ (5% ethyl acetate in hexane); white solid; yield 80% (87 mg); mp 89-91 °C;



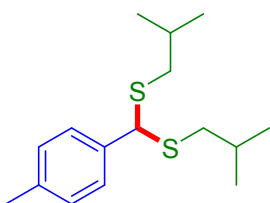
¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, $J = 7.8$ Hz, 1H), 7.97 (s, 1H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.35-7.32 (m, 4H), 7.24-7.23 (m, 6H), 7.18 (t, $J = 7.8$ Hz, 1H), 6.98 (d, $J = 7.8$ Hz, 1H), 6.97-6.95 (m, 1H), 6.84 (dd, $J = 8.2, 2.4$ Hz, 1H), 5.37 (s, 1H), 5.18 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 194.5, 158.1, 141.5, 134.8, 134.5, 134.0, 132.8, 129.8, 129.0 ($\times 2$), 128.3, 128.0, 121.4, 115.0, 114.3, 71.0, 60.4.

(2-(Bis(phenylthio)methyl)thiophene) (3ta):² $R_f = 0.35$ (hexane); colorless liquid; yield 68%



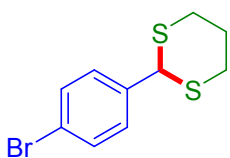
(112 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.39 (m, 4H), 7.29-7.26 (m, 6H), 7.23-7.21 (m, 1H), 6.95-6.94 (m, 1H), 6.86-6.84 (m, 1H), 5.71 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 134.3, 132.9, 129.0, 128.2, 126.64, 126.63, 125.9, 55.7.

(p-tolylmethylene)bis(isobutylsulfane) (3bk): $R_f = 0.4$ (hexane); colorless liquid; yield 62% (86



mg); ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 4.80 (s, 1H), 2.49-2.38 (m, 4H), 2.34 (s, 3H), 1.85-1.72 (m, 2H), 0.98-0.94 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 137.8, 137.6, 129.3, 127.7, 54.0, 41.4, 28.5, 22.2, 21.3; IR (KBr) $\bar{\nu}$ 2835, 2366, 1587, 1278, 688 cm⁻¹; HRMS (ESI/Q-TOF) m/z : [M + Na]⁺ calcd for C₁₆H₂₆S₂Na 305.1368; found 305.1355.

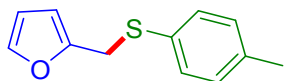
2-(4-bromophenyl)-1,3-dithiane (3ul): $R_f = 0.45$ (2% ethyl acetate in hexane); white solid; yield



69% (61 mg); mp 88-90 °C (lit.¹³ 93-94 °C); ¹H NMR (400 MHz, CDCl₃) δ

7.46 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 5.11 (s, 1H), 3.08-3.00 (m, 2H), 2.93-2.87 (m, 2H), 2.19-2.13 (m, 1H), 1.99-1.86 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 132.0, 129.6, 122.4, 50.7, 32.1, 25.1.

(2-((p-tolylthio)methyl)furan) (4vb): $R_f = 0.45$ (hexane); colorless liquid; yield 59% (74 mg); ^1H



NMR (400 MHz, CDCl_3) δ 7.35-7.34 (m, 1H), 7.26 (d, $J = 7.8$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.27 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.07 (d, $J = 3.2$

Hz, 1H), 4.05 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 142.2, 137.2, 131.8, 131.6, 129.8, 110.5, 107.9, 32.5, 21.2; IR (KBr) $\bar{\nu}$ 2923, 2358, 1547, 1298, 699 cm^{-1} ; HRMS (ESI/Q-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{OSNa}$ 227.0501; found 227.0497.

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NMR SPECTRA

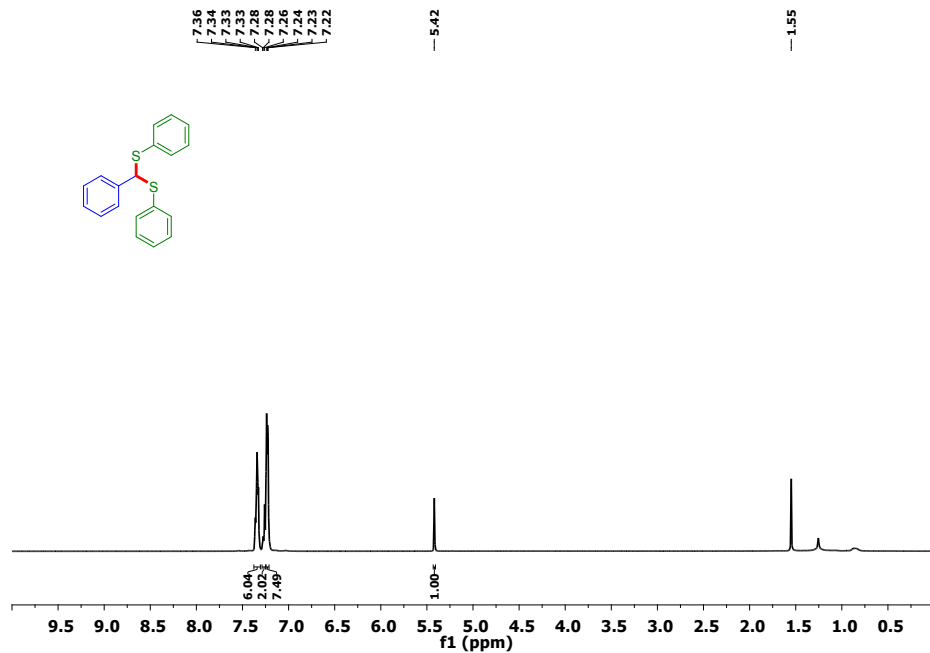


Fig. S7. ¹H NMR spectrum of (phenylmethylene)bis(phenylsulfane) (**3aa**)

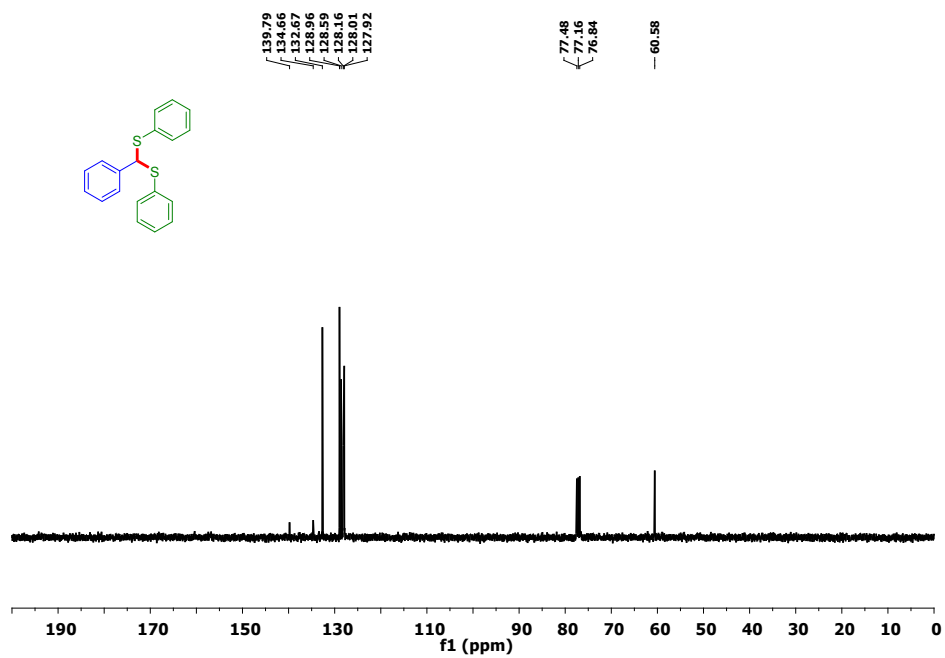


Fig. S8. ¹³C NMR spectrum of (phenylmethylene)bis(phenylsulfane) (**3aa**)

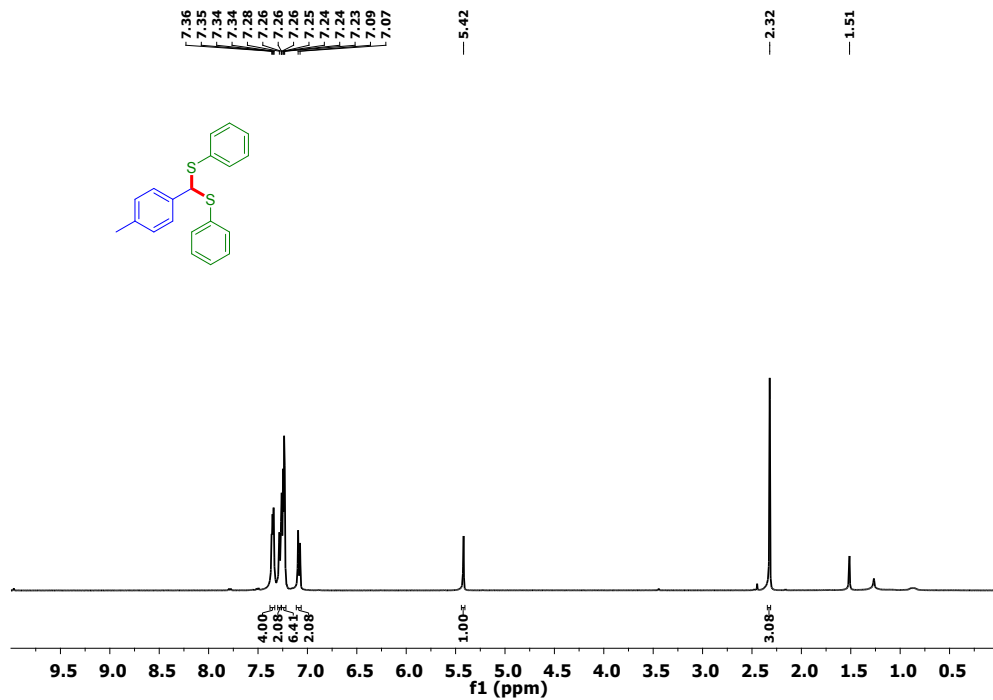


Fig. S9. ^1H NMR spectrum of (p-tolylmethylene)bis(phenylsulfane) (**3ba**)

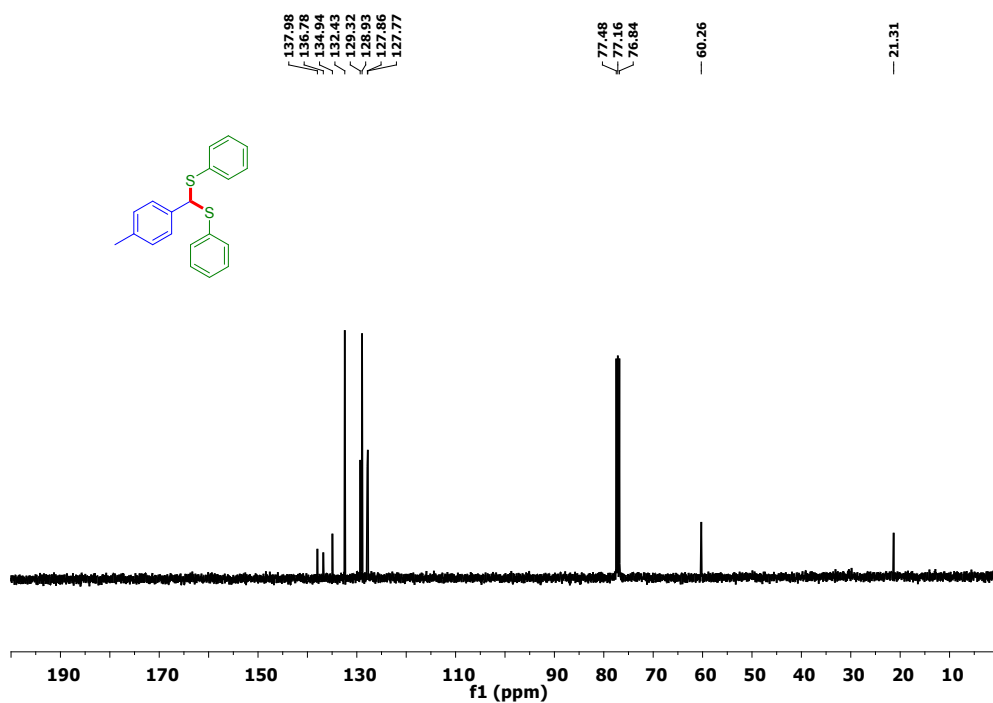


Fig. S10. ^{13}C NMR spectrum of (phenylmethylene)bis(phenylsulfane) (**3ba**)

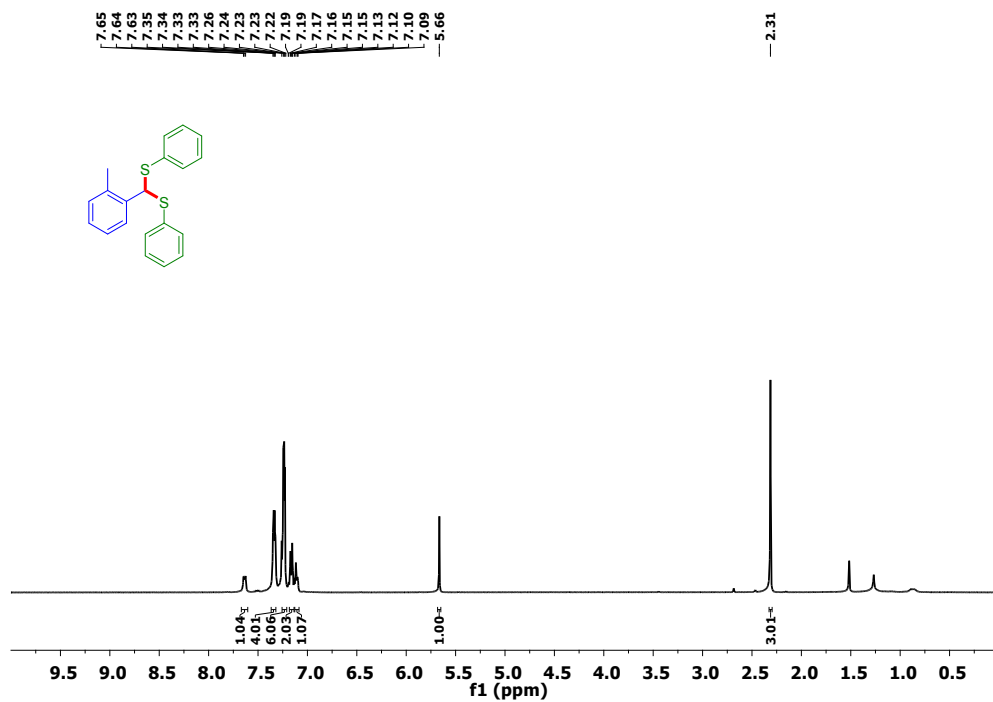


Fig. S11. ¹H NMR spectrum of (o-tolylmethylene)bis(phenylsulfane) (3ca)

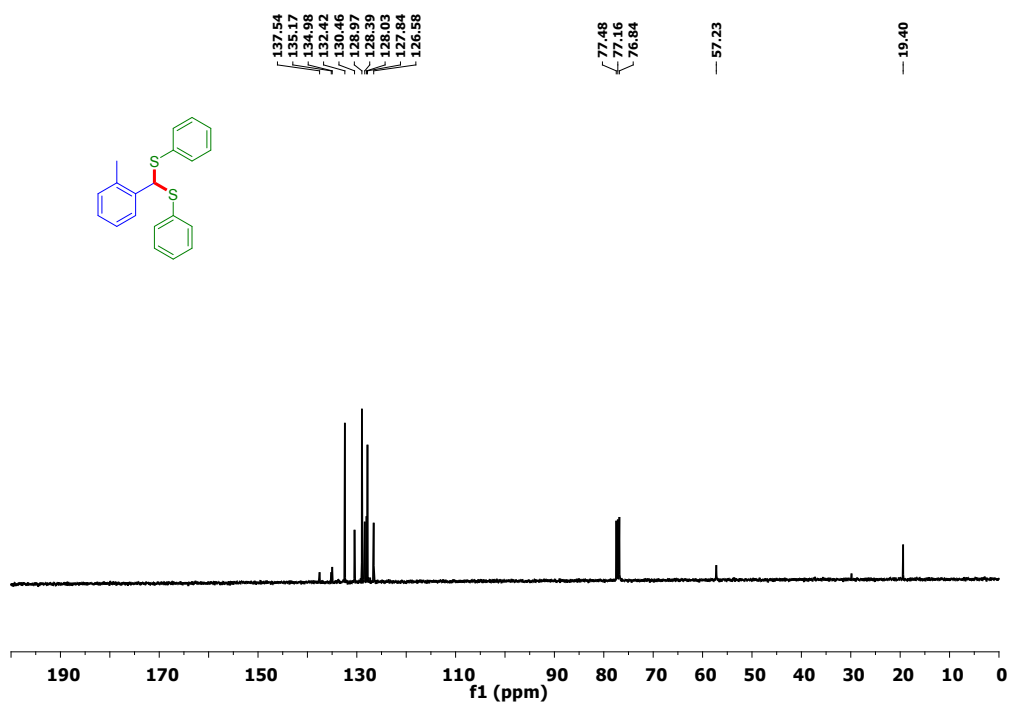


Fig. S12. ¹³C NMR spectrum of (o-tolylmethylene)bis(phenylsulfane) (3ca)

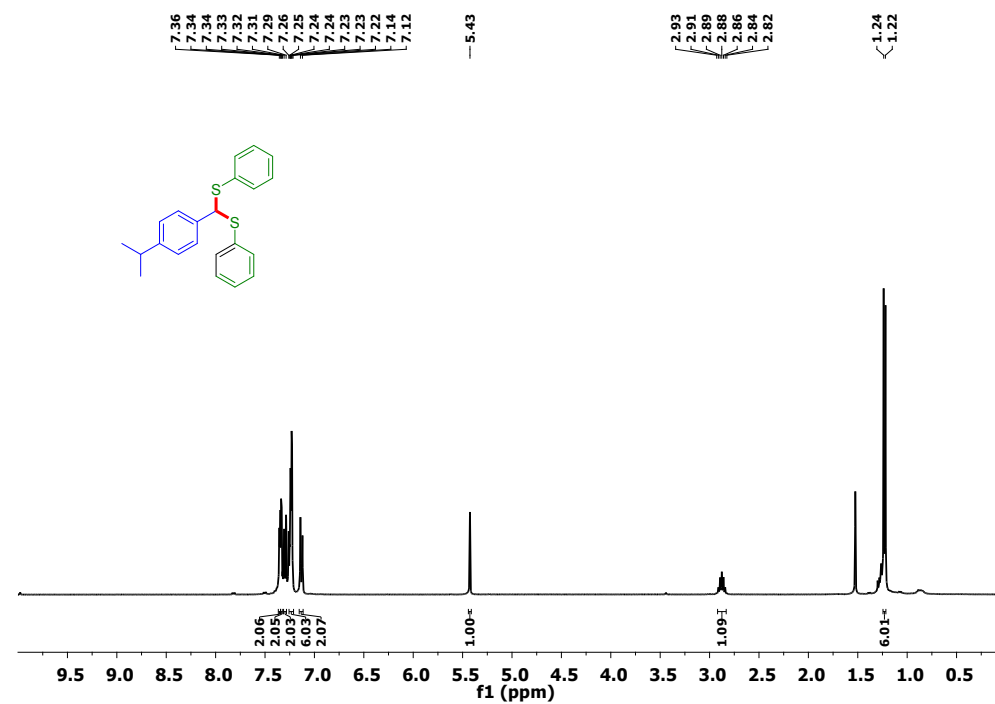


Fig. S13. ^1H NMR spectrum of ((4-isopropylphenyl)methylene)bis(phenylsulfane) (**3da**)

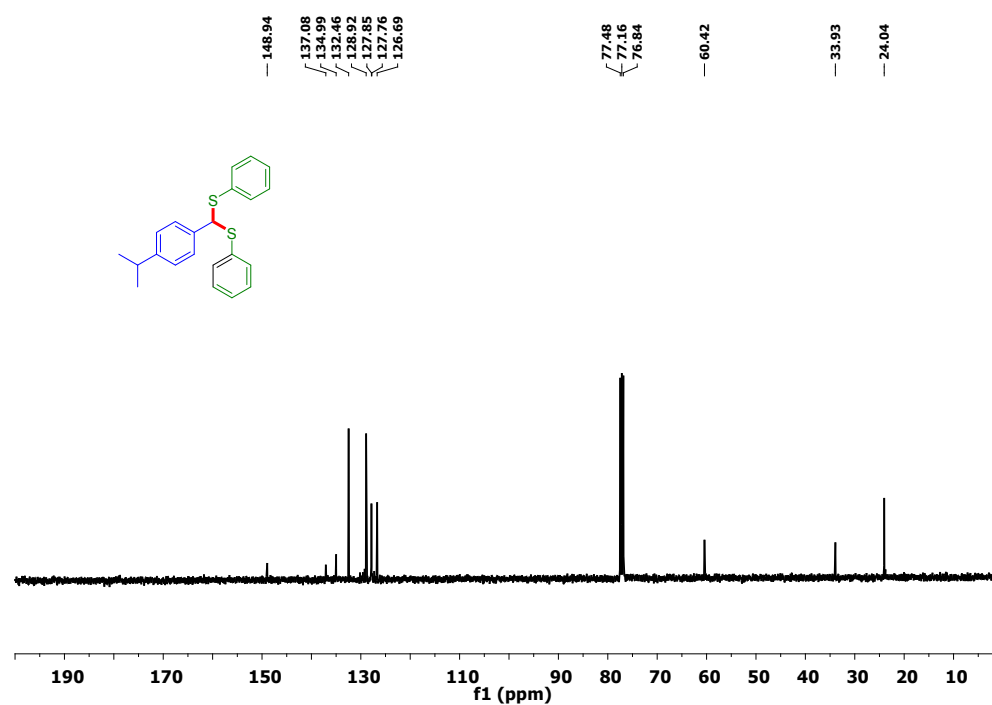


Fig. S14. ^{13}C NMR spectrum of ((4-isopropylphenyl)methylene)bis(phenylsulfane) (**3da**)

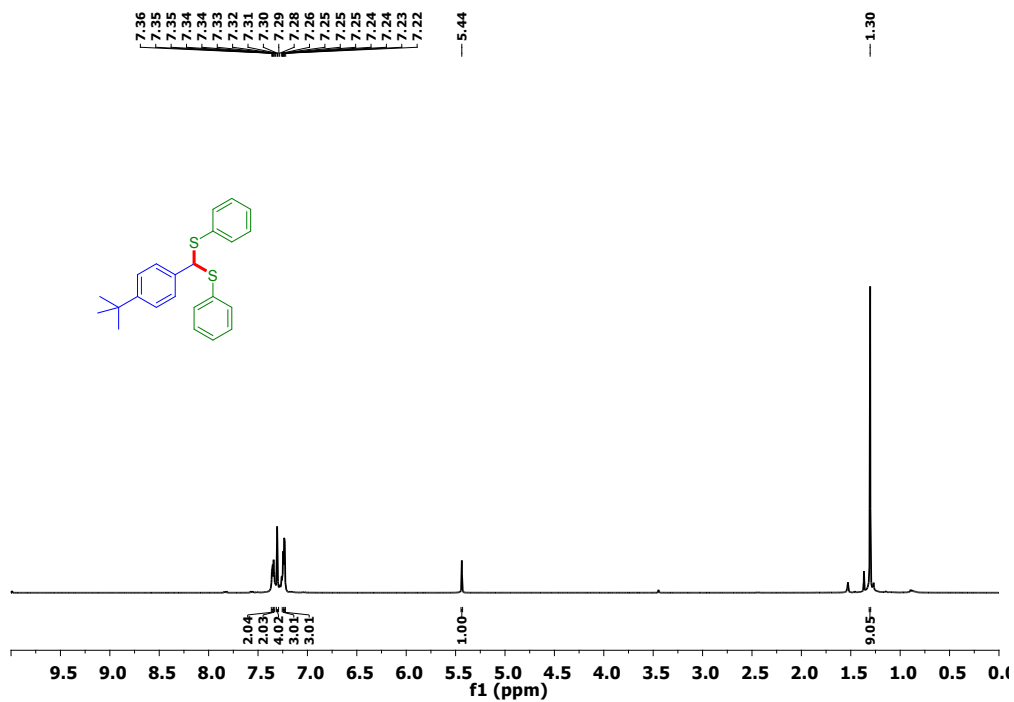


Fig. S15. ¹H NMR spectrum of ((4-(tert-butyl)phenyl)methylene)bis(phenylsulfane) (**3ea**)

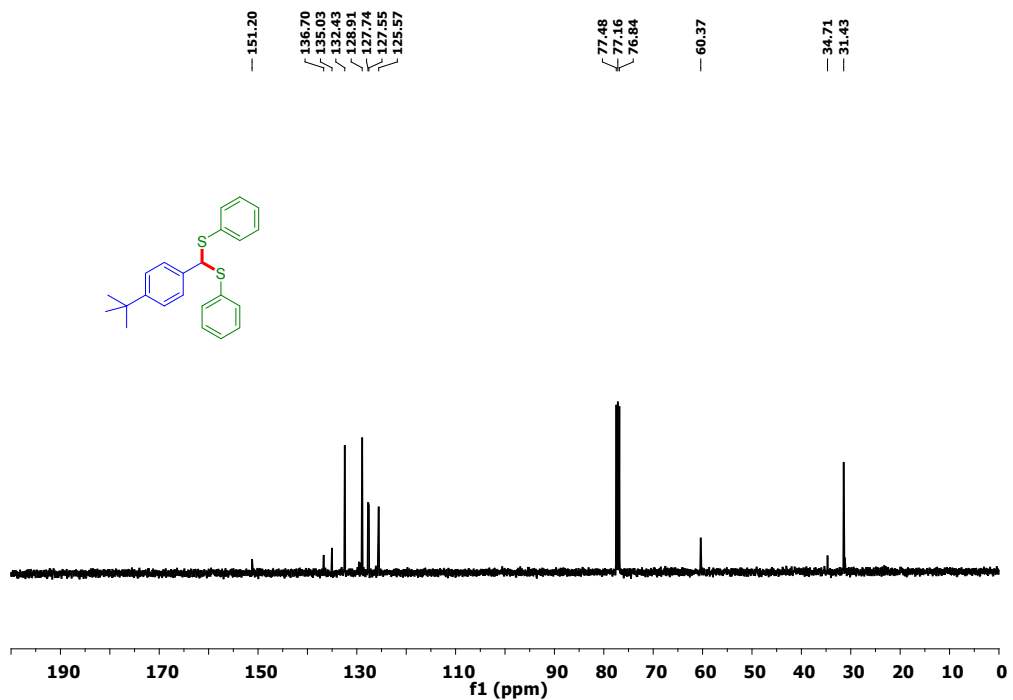


Fig. S16. ¹³C NMR spectrum of ((4-(tert-butyl)phenyl)methylene)bis(phenylsulfane) (**3ea**)

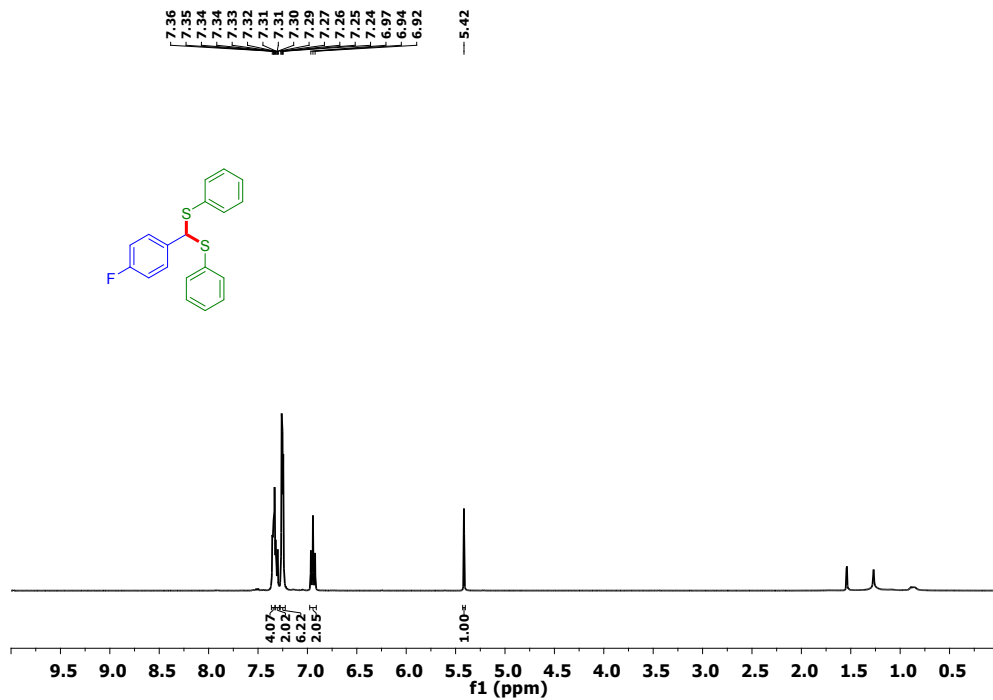


Fig. S17. ¹H NMR spectrum of ((4-fluorophenyl)methylene)bis(phenylsulfane) (**3fa**)

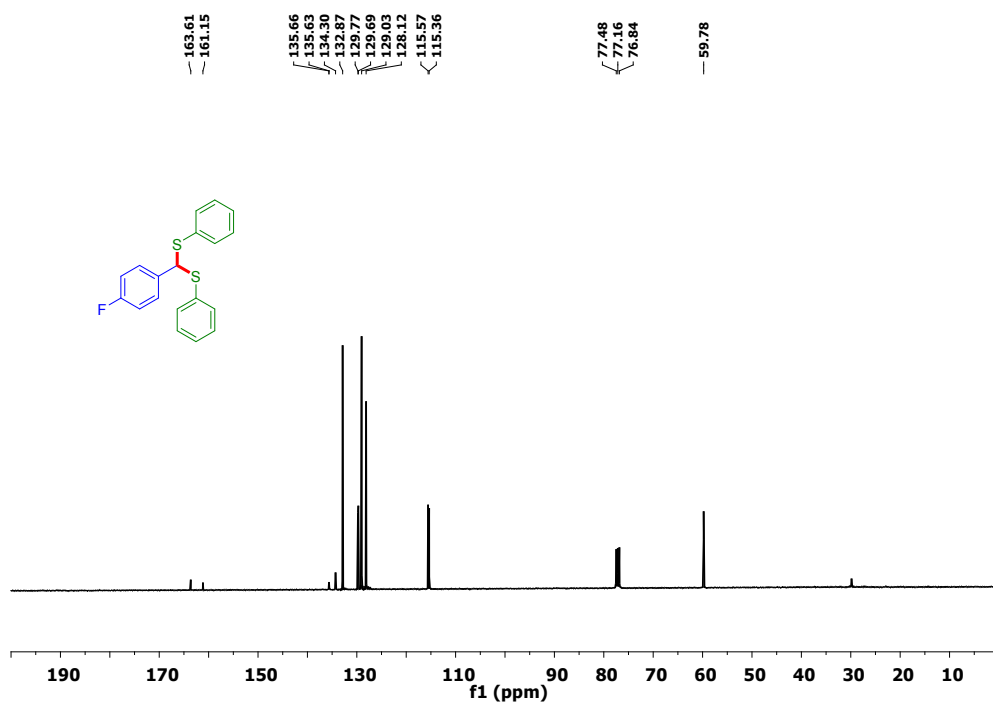


Fig. S18. ¹³C NMR spectrum of ((4-fluorophenyl)methylene)bis(phenylsulfane) (**3fa**)

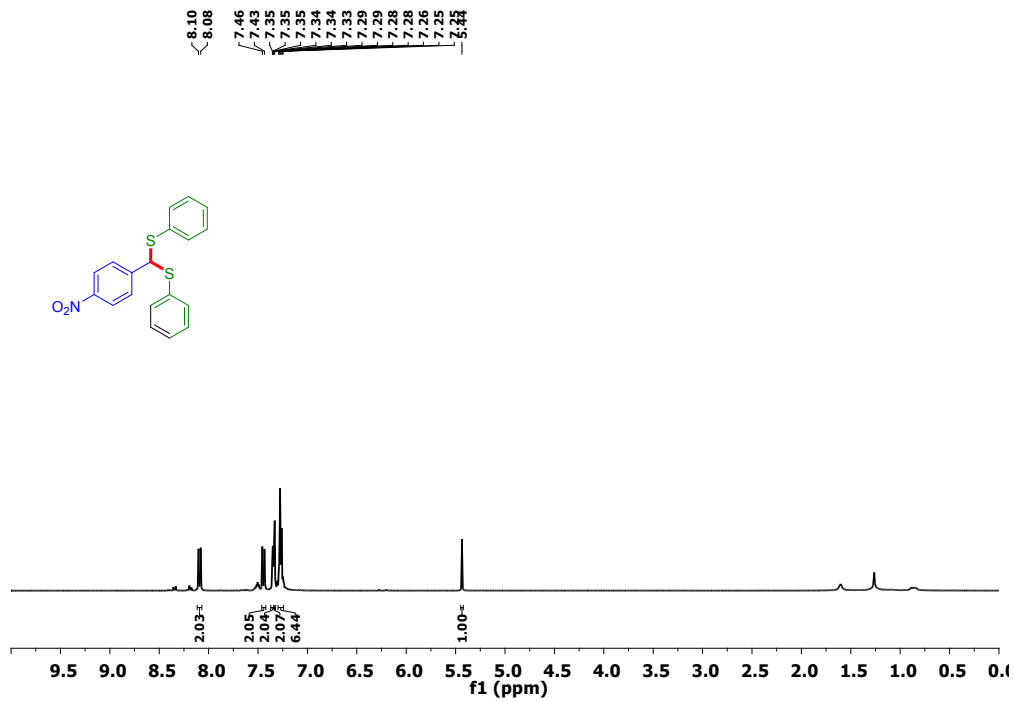


Fig. S19. ¹H NMR spectrum of ((4-nitrophenyl)methylene)bis(phenylsulfane) (**3ga**)

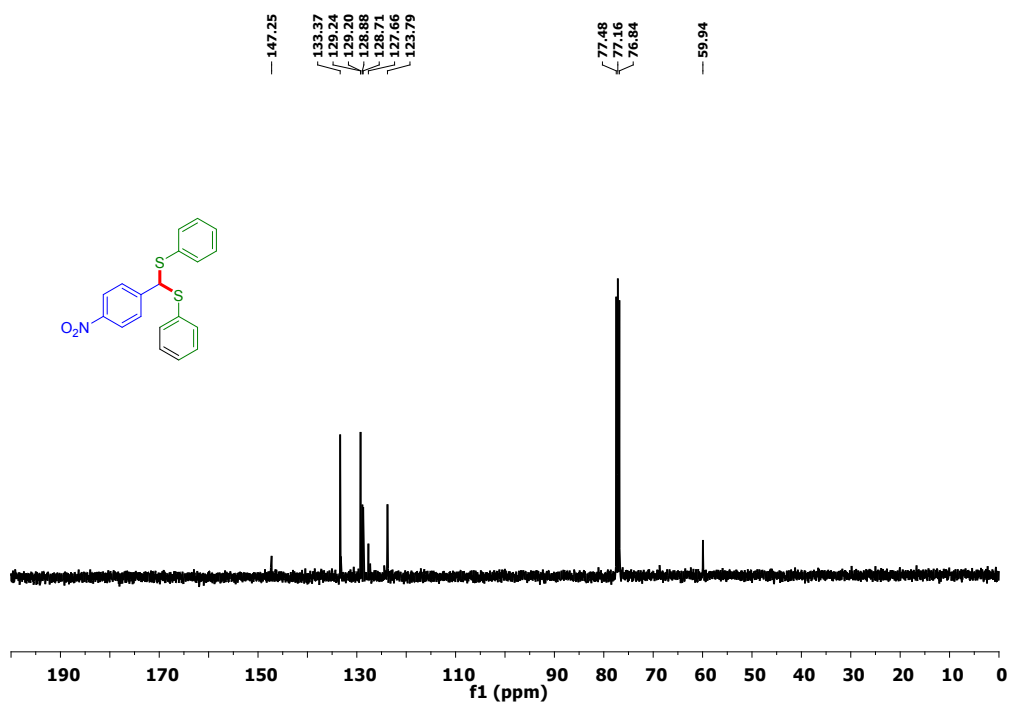


Fig. S20. ¹³C NMR spectrum of ((4-nitrophenyl)methylene)bis(phenylsulfane) (**3ga**)

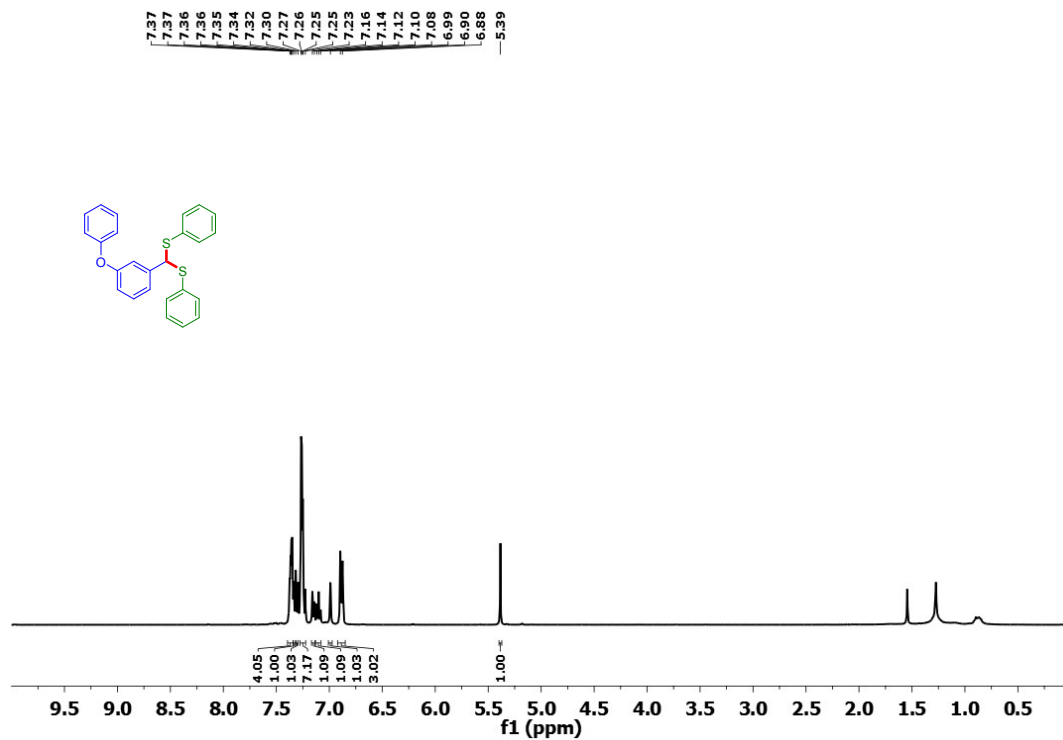


Fig. S21. ¹H NMR spectrum of ((3-phenoxyphenyl)methylene)bis(phenylsulfane) (**3ha**)

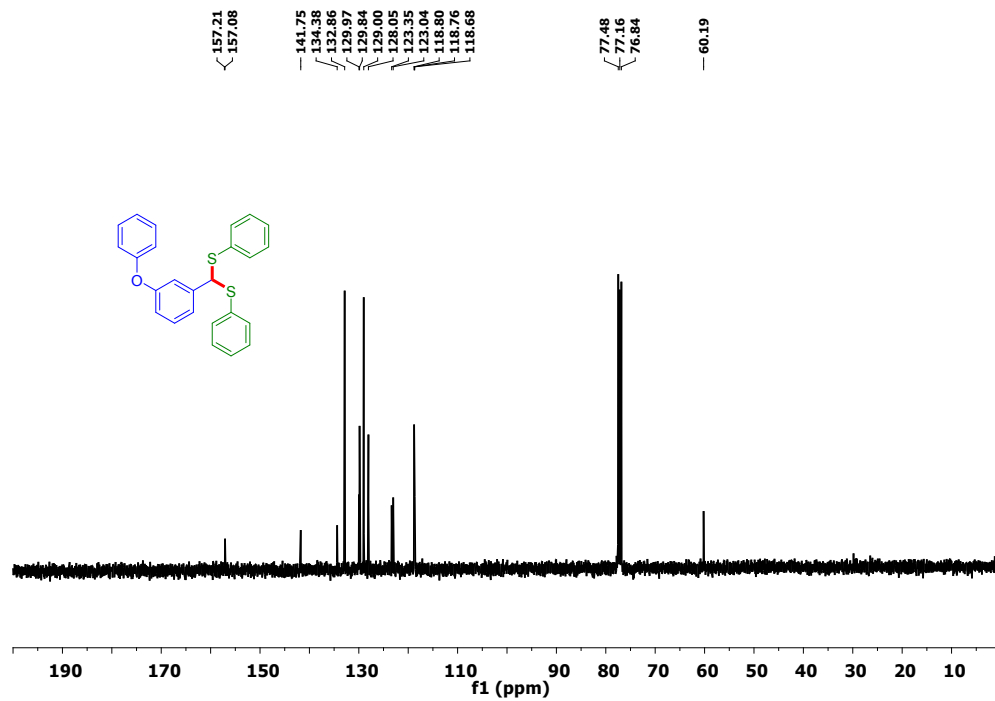


Fig. S22. ¹³C NMR spectrum of ((3-phenoxyphenyl)methylene)bis(phenylsulfane) (**3ha**)

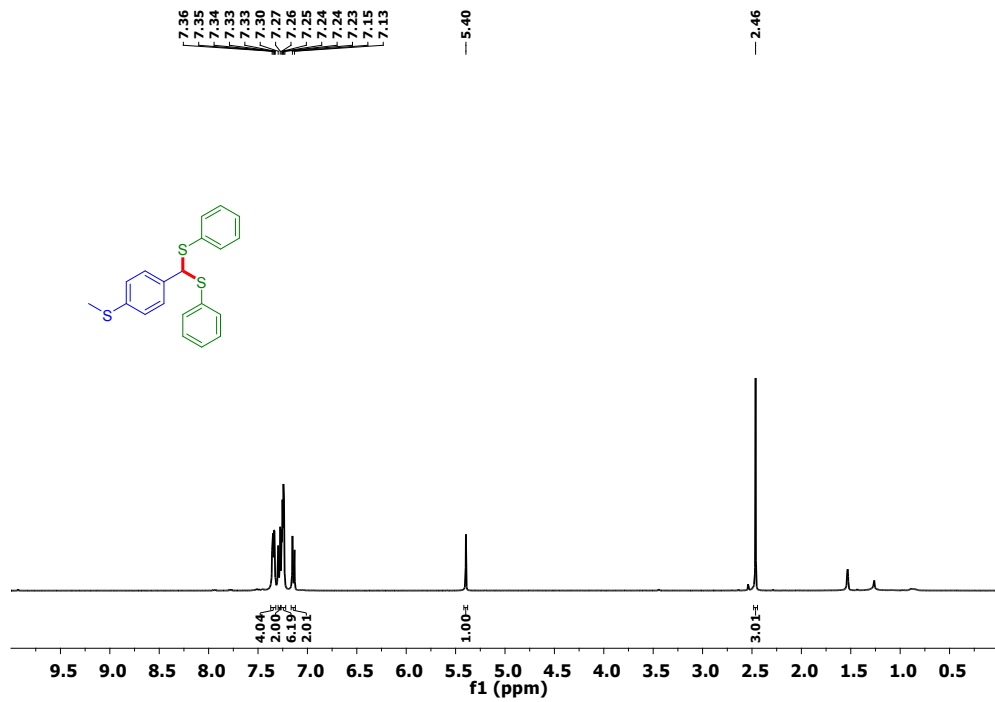


Fig. S23. ¹H NMR spectrum of ((4-(methylthio)phenyl)methylene)bis(phenylsulfane) (**3ia**)

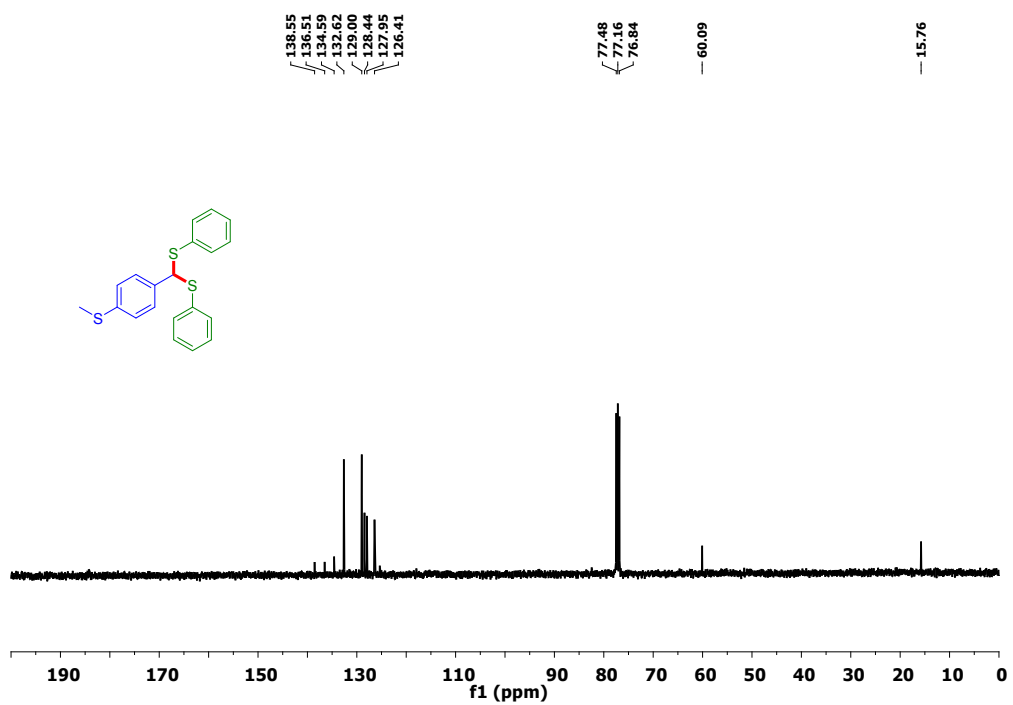


Fig. S24. ¹³C NMR spectrum of ((4-(methylthio)phenyl)methylene)bis(phenylsulfane) (**3ia**)

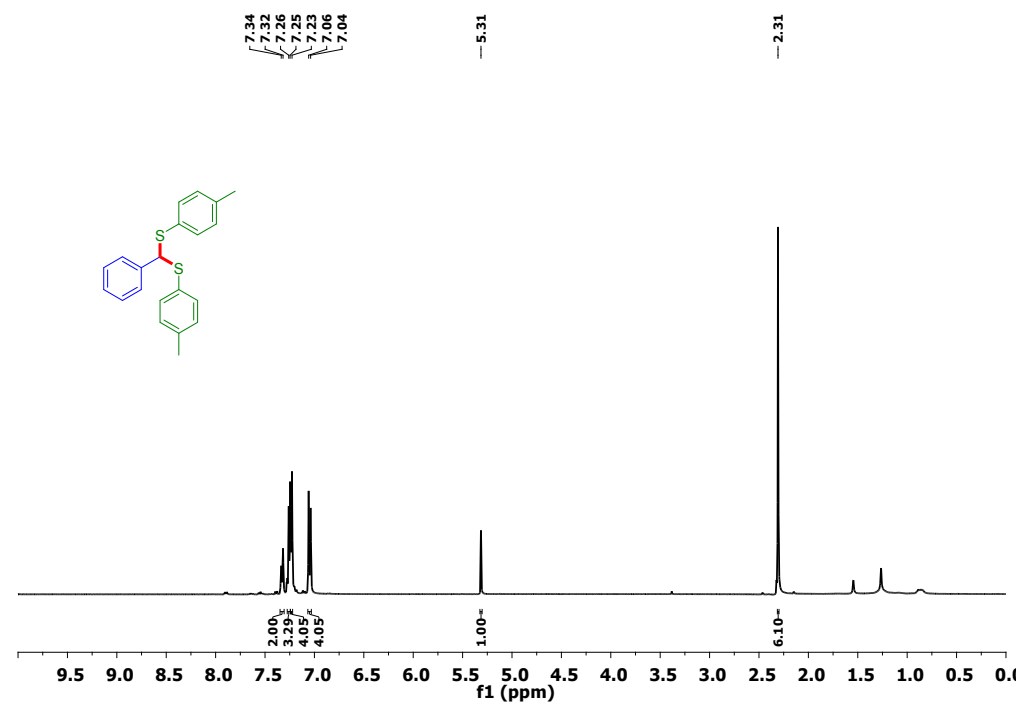


Fig. S25. ¹H NMR spectrum of (phenylmethylene)bis(p-tolylsulfane) (**3ab**)

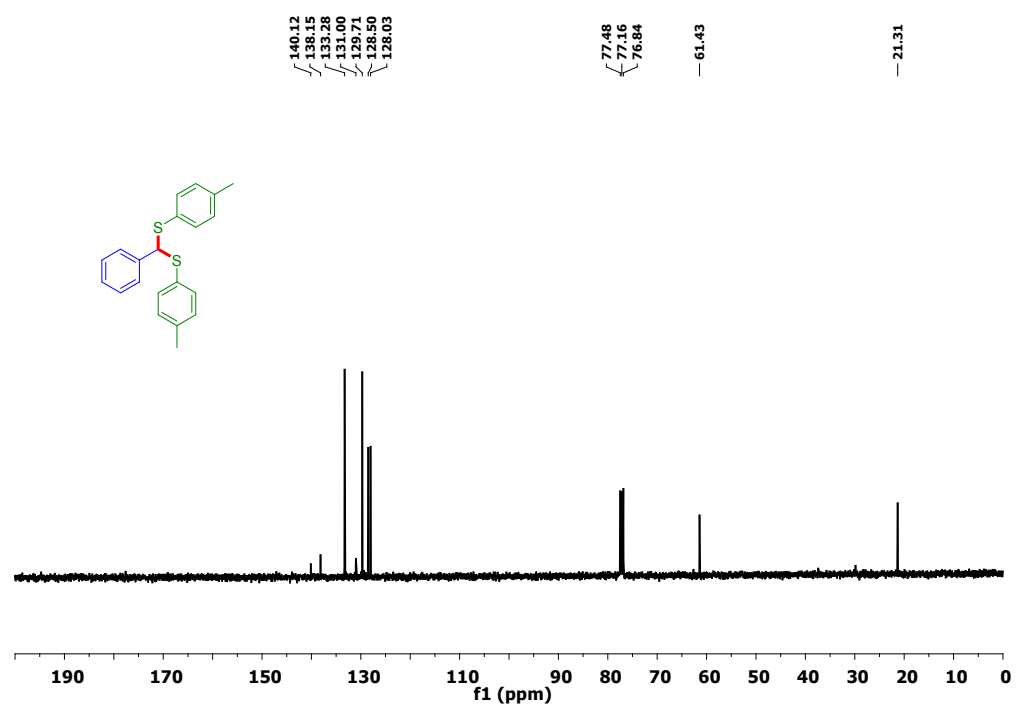


Fig. S26. ¹³C NMR spectrum of (phenylmethylene)bis(p-tolylsulfane) (**3ab**)

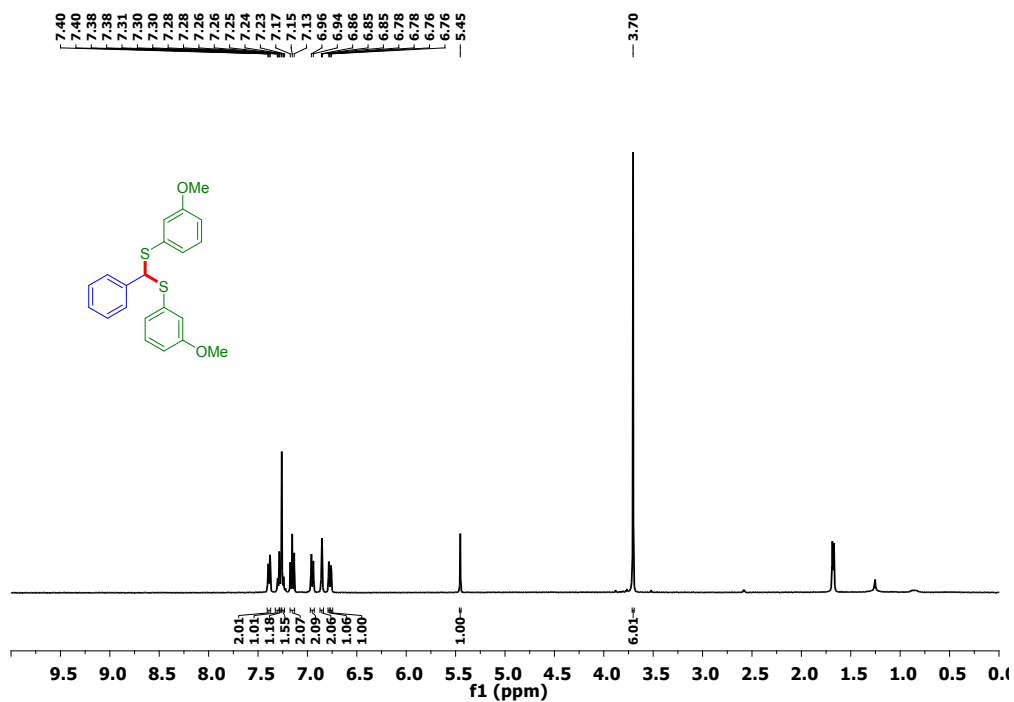


Fig. S27. ¹H NMR spectrum of (phenylmethylene)bis((3-methoxyphenyl)sulfane) (**3ac**)

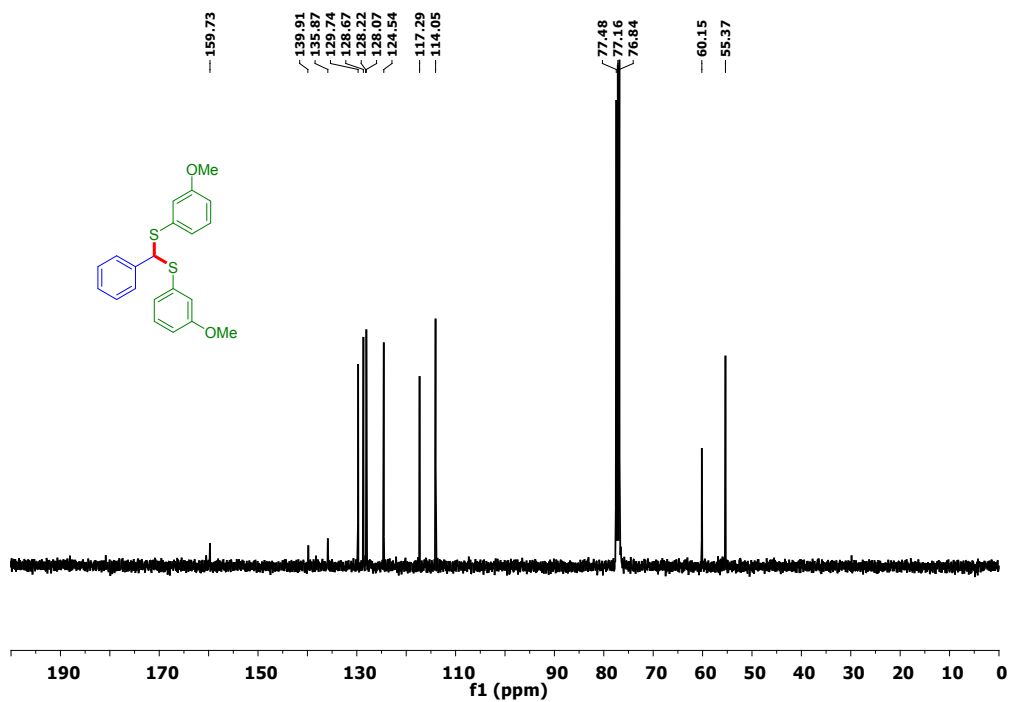


Fig. S28. ¹³C NMR spectrum of (phenylmethylene)bis((3-methoxyphenyl)sulfane) (**3ac**)

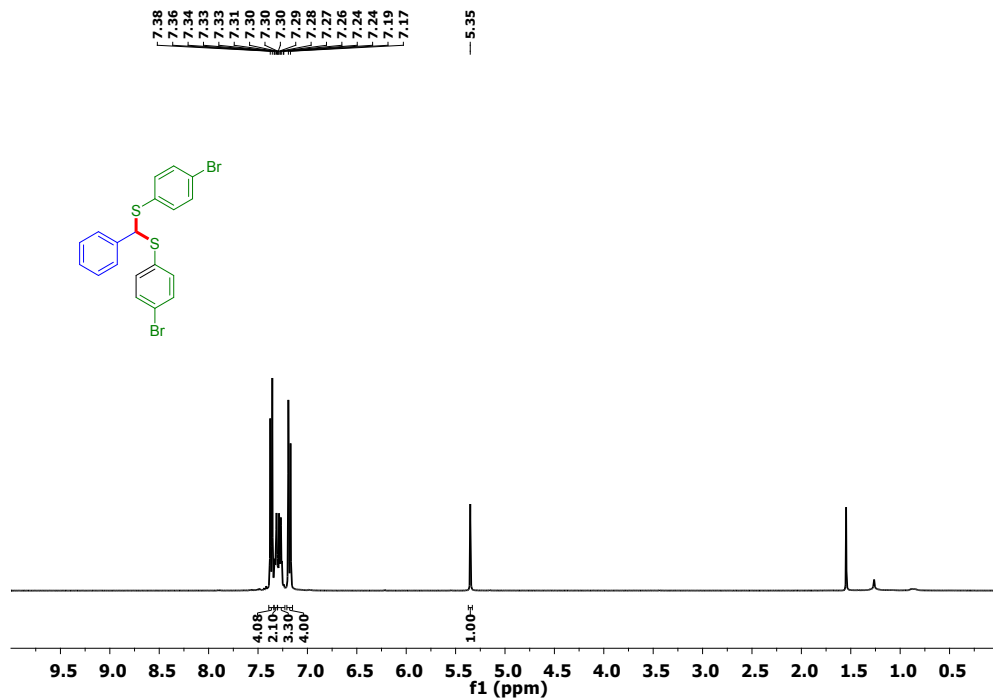


Fig. S29. ¹H NMR spectrum of (phenylmethylene)bis((4-bromophenyl)sulfane) (**3ad**)

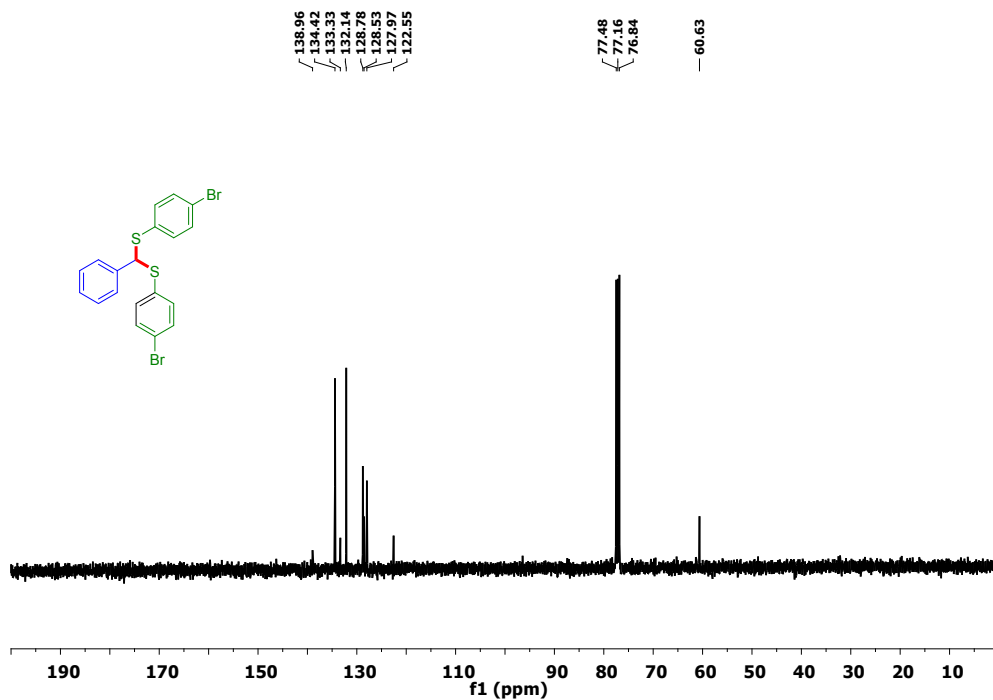


Fig. S30. ¹³C NMR spectrum of (phenylmethylene)bis((4-bromophenyl)sulfane) (**3ad**)

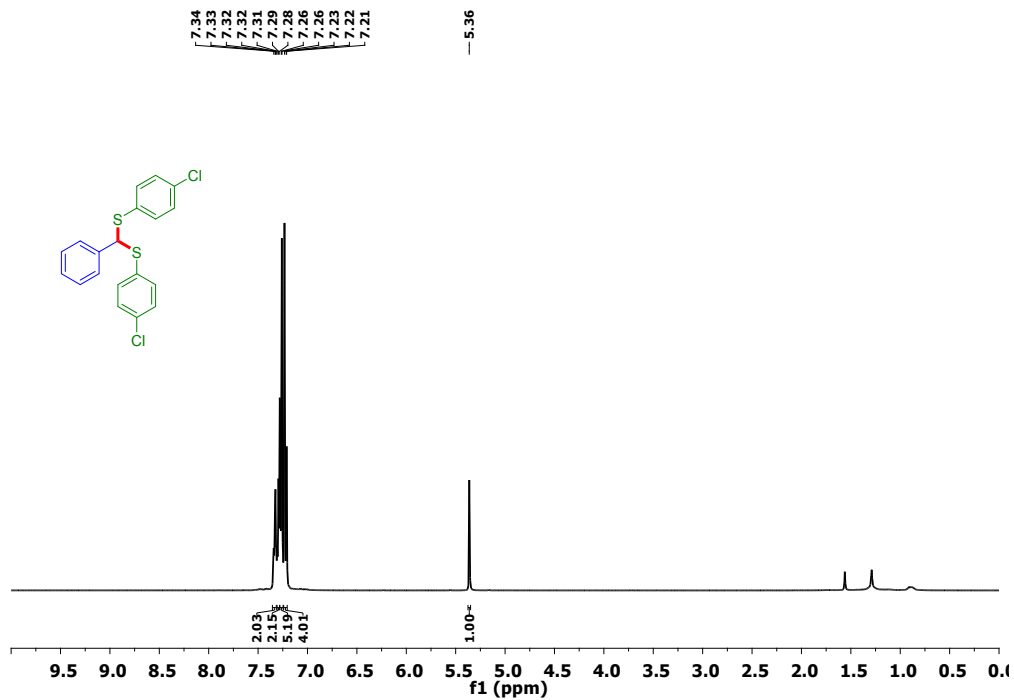


Fig. S31. ¹H NMR spectrum of (phenylmethylene)bis((4-chlorophenyl)sulfane) (**3ae**)

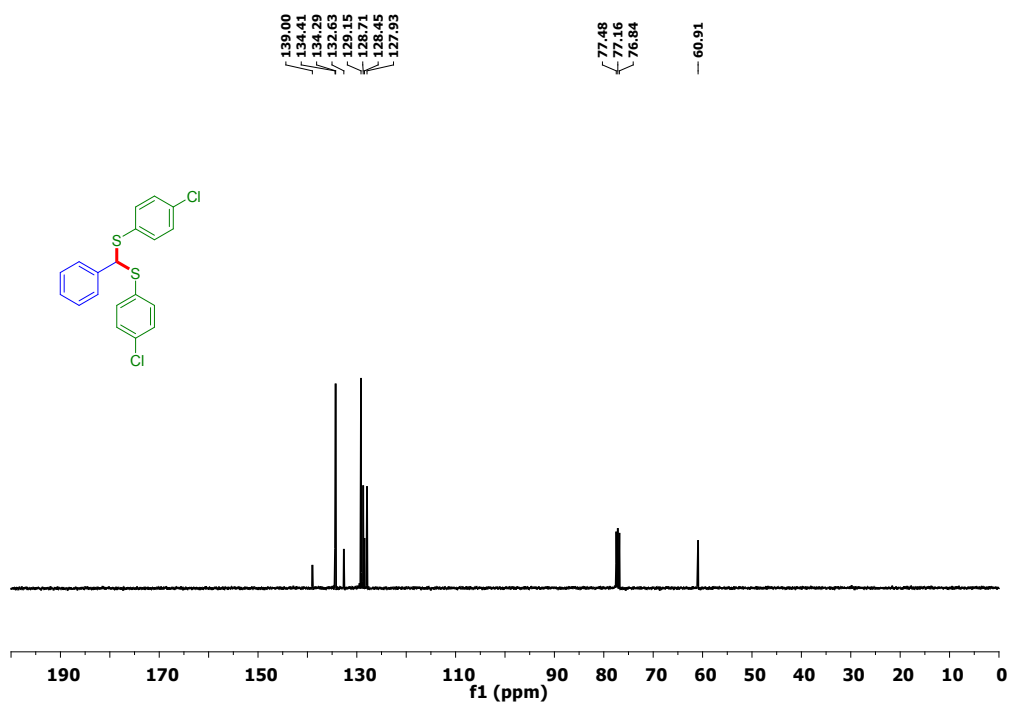


Fig. S32. ¹³C NMR spectrum of (phenylmethylene)bis((4-chlorophenyl)sulfane) (**3ae**)

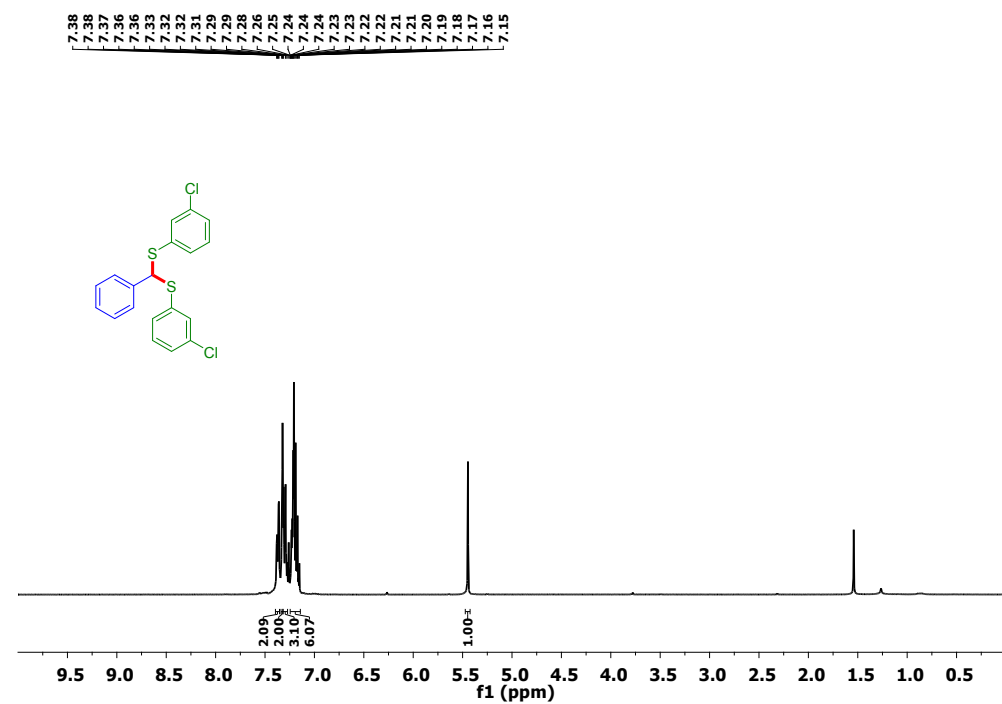


Fig. S33. ¹H NMR spectrum of (phenylmethylene)bis((3-chlorophenyl)sulfane) (**3af**)

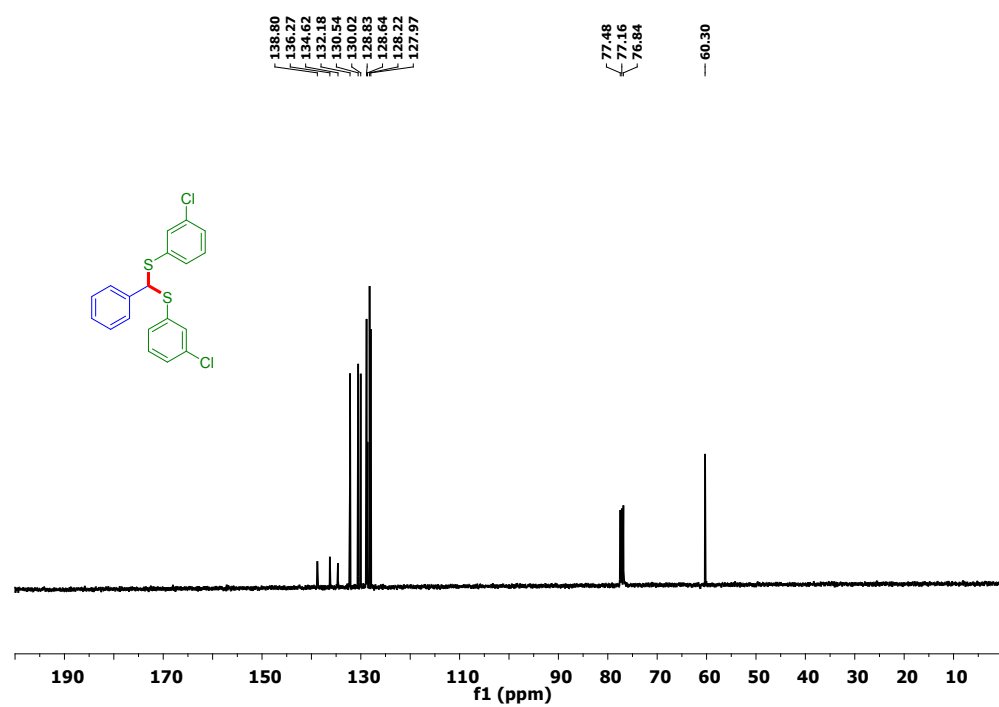


Fig. S34. ¹³C NMR spectrum of (phenylmethylene)bis((3-chlorophenyl)sulfane) (**3af**)

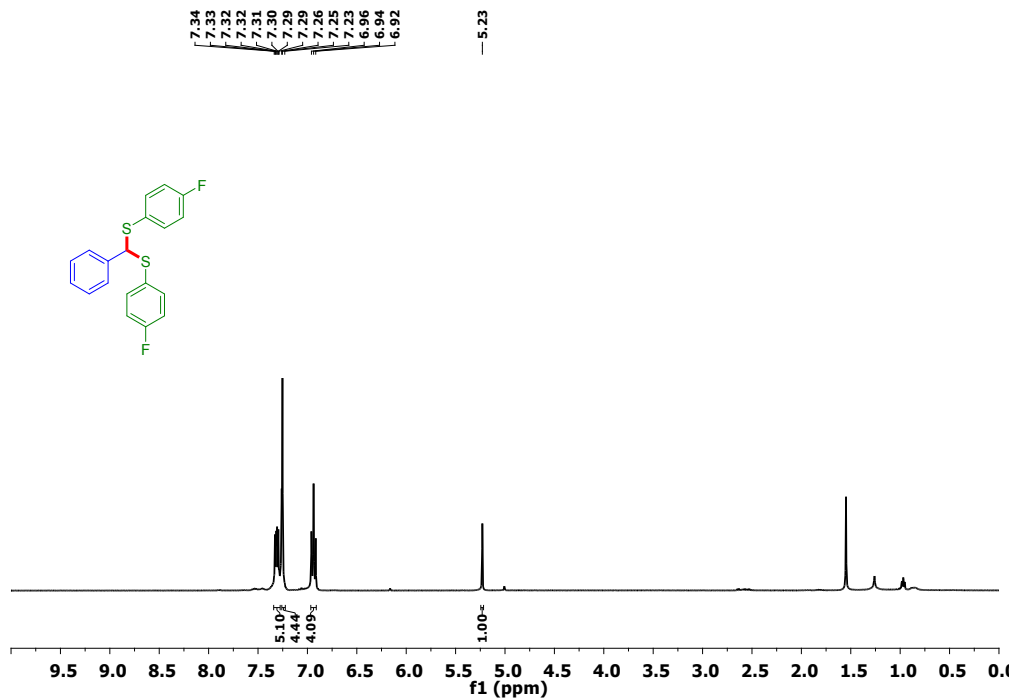


Fig. S35. ¹H NMR spectrum of (phenylmethylene)bis((4-fluorophenyl)sulfane) (**3ag**)

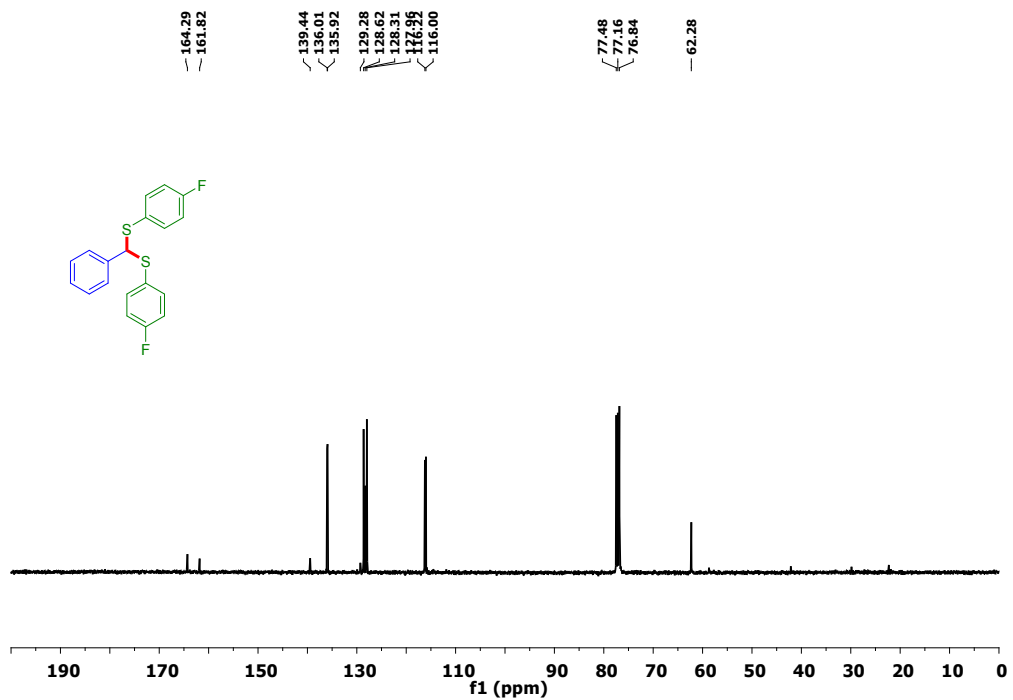


Fig. S36. ¹³C NMR spectrum of (phenylmethylene)bis((4-fluorophenyl)sulfane) (**3ag**)

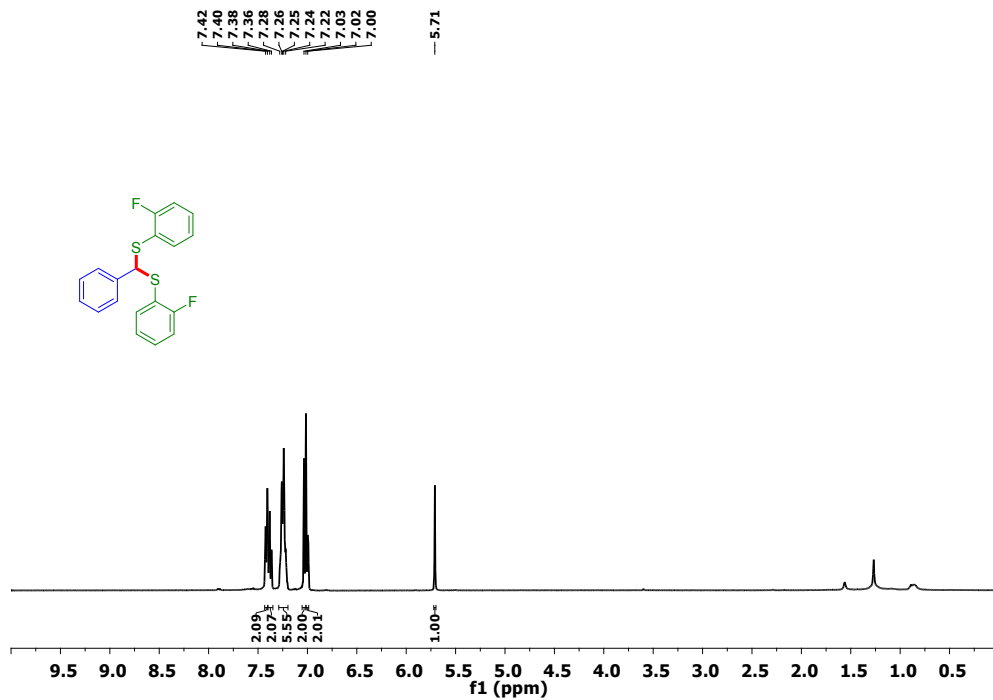


Fig. S37. ¹H NMR spectrum of (phenylmethylene)bis((2-fluorophenyl)sulfane) (**3ah**)

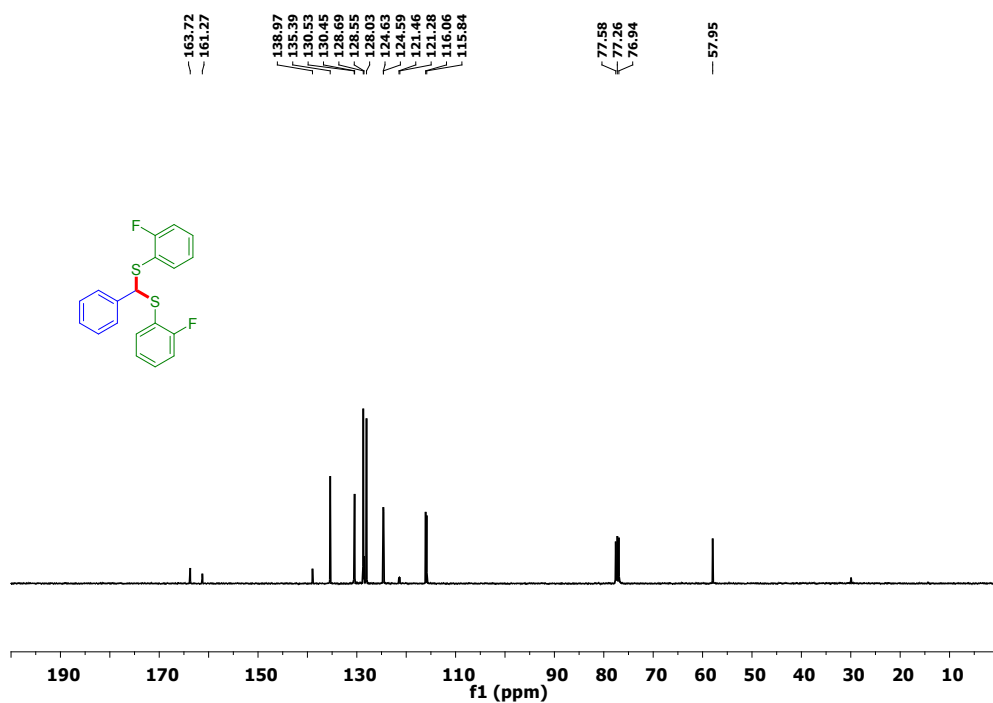


Fig. S38. ¹³C NMR spectrum of (phenylmethylene)bis((2-fluorophenyl)sulfane) (**3ah**)

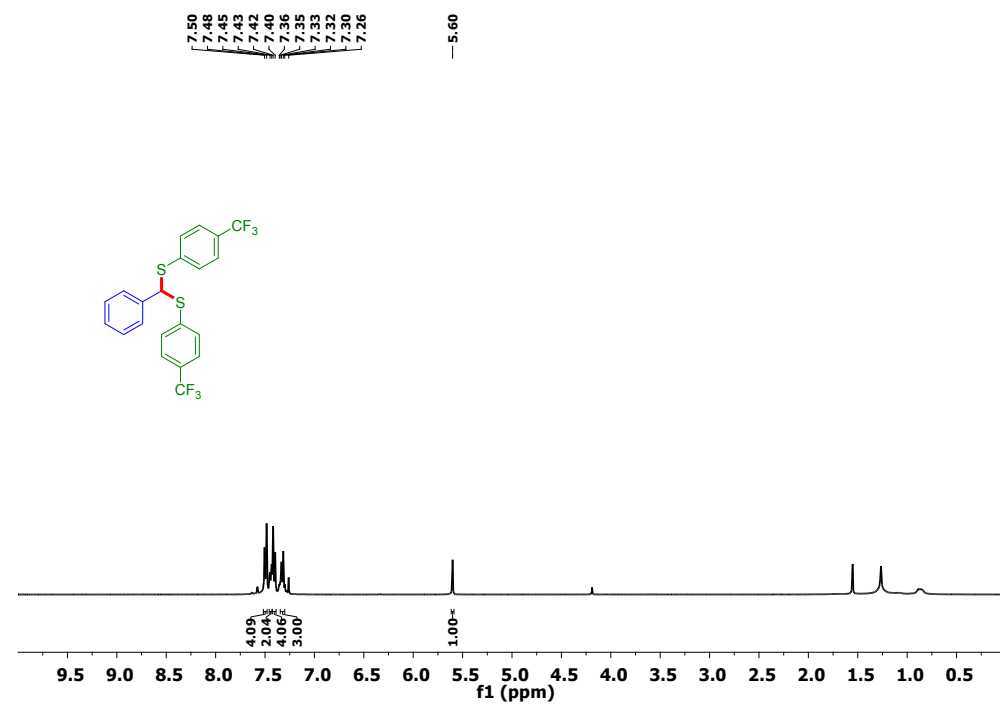


Fig. S39. ¹H NMR spectrum of (phenylmethylene)bis((4-(trifluoromethyl)phenyl)sulfane) (**3ai**)

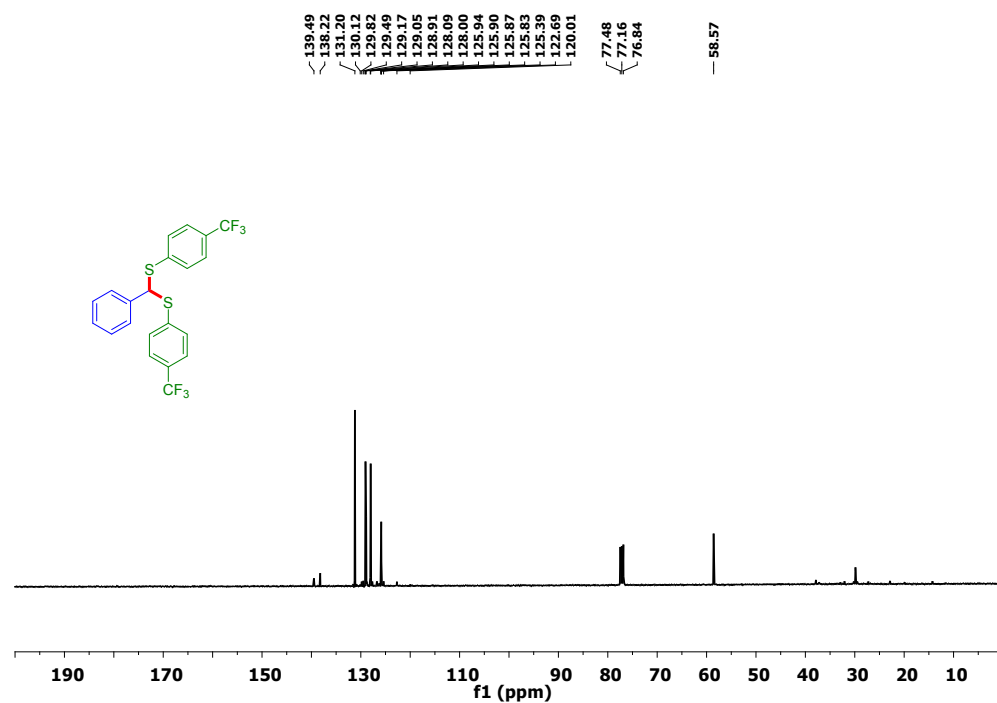


Fig. S40. ¹³C NMR spectrum of (phenylmethylene)bis((4-(trifluoromethyl)phenyl)sulfane) (**3ai**)

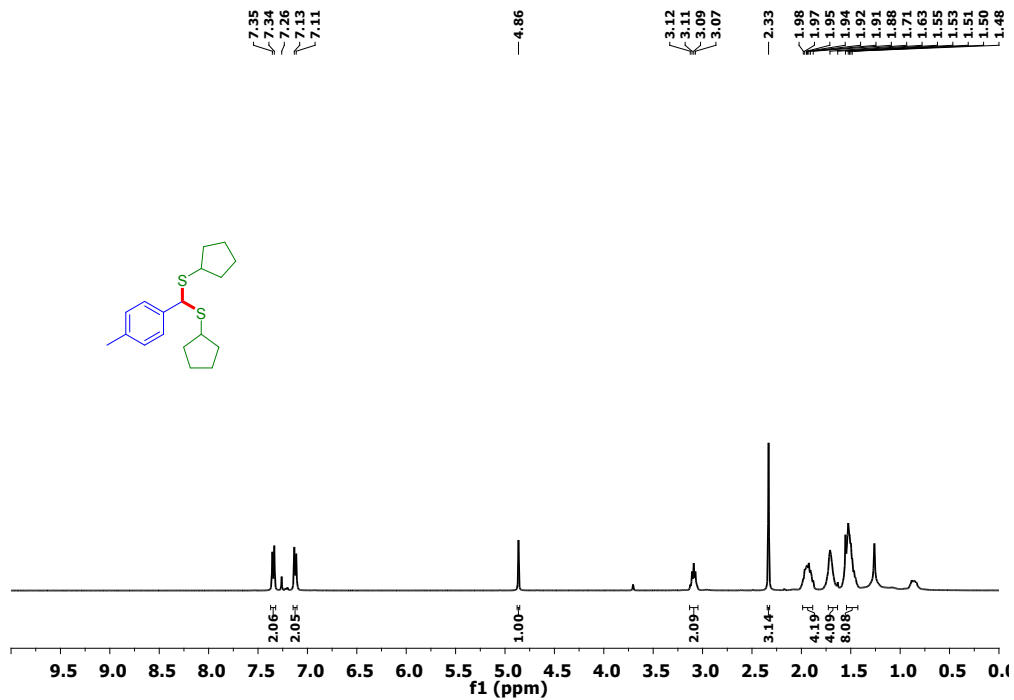


Fig. S41. ¹H NMR spectrum of (p-tolylmethylene)bis(cyclopentylsulfane) (**3bj**)

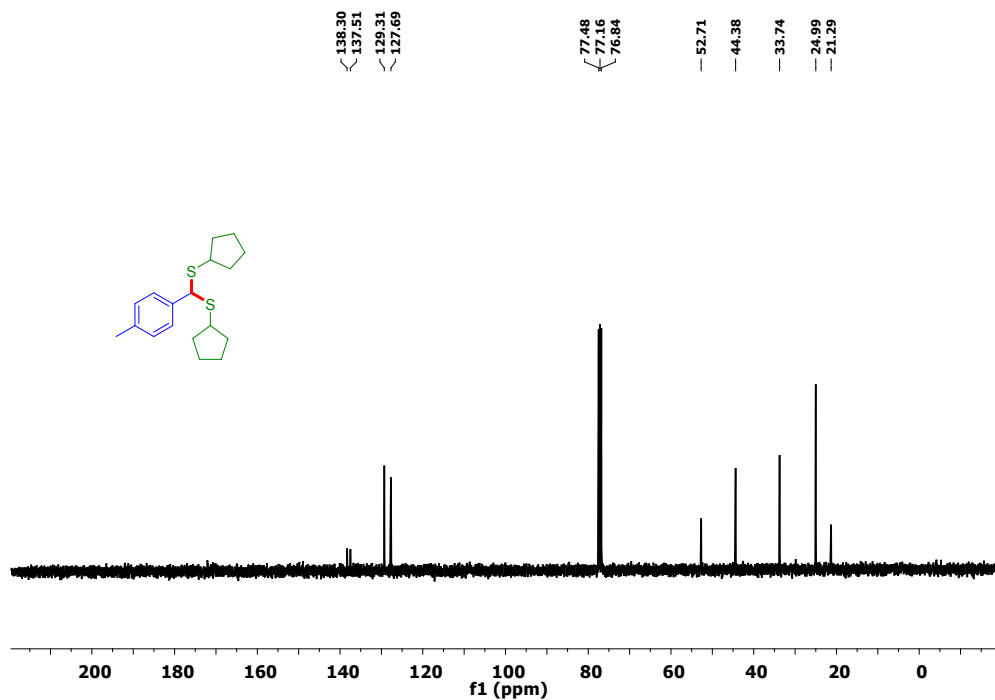


Fig. S42. ¹³C NMR spectrum of (p-tolylmethylene)bis(cyclopentylsulfane) (**3bj**)

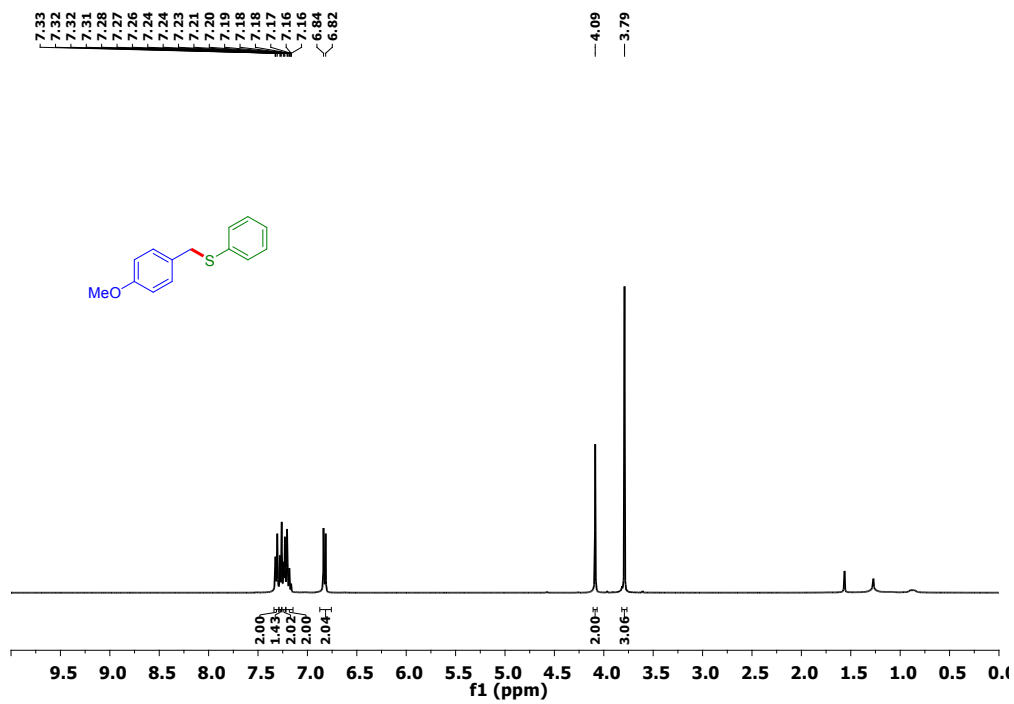


Fig. S43. ¹H NMR spectrum of (4-methoxybenzyl)(phenyl)sulfane (**4ma**)

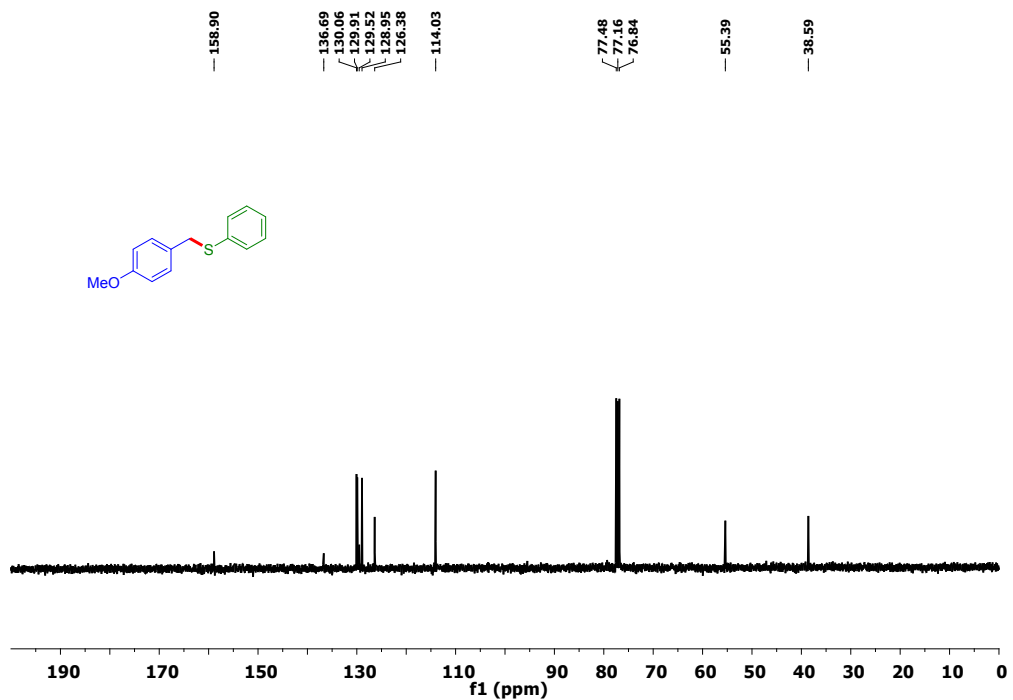


Fig. S44. ¹³C NMR spectrum of (4-methoxybenzyl)(phenyl)sulfane (**4ma**)

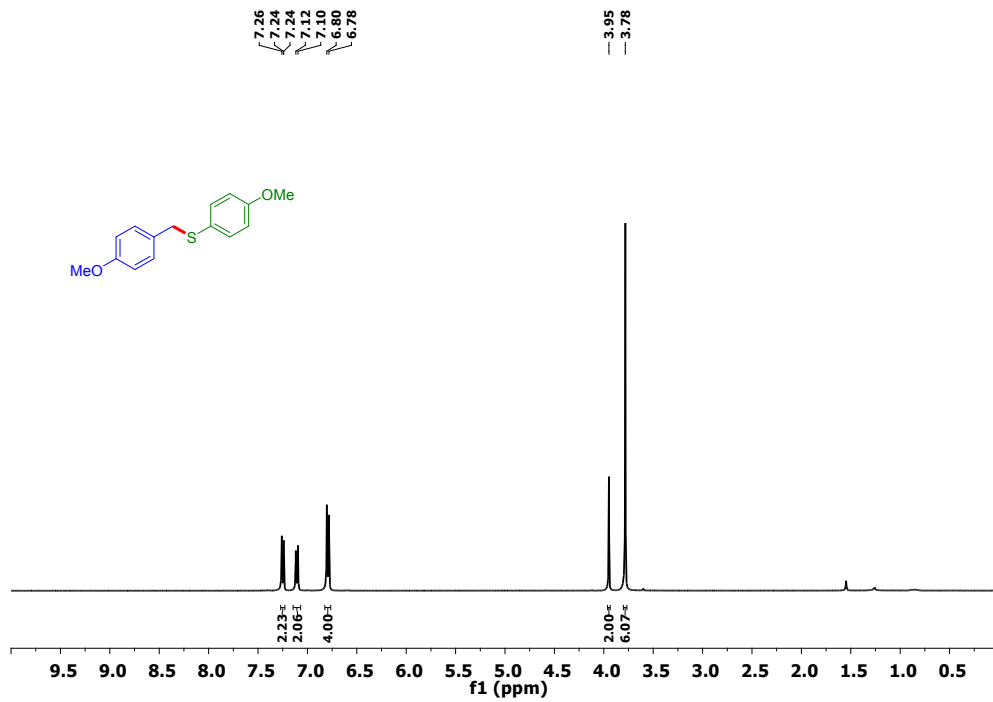


Fig. S45. ¹H NMR spectrum of (4-methoxybenzyl)(4-methoxyphenyl)sulfane (**4mk**)

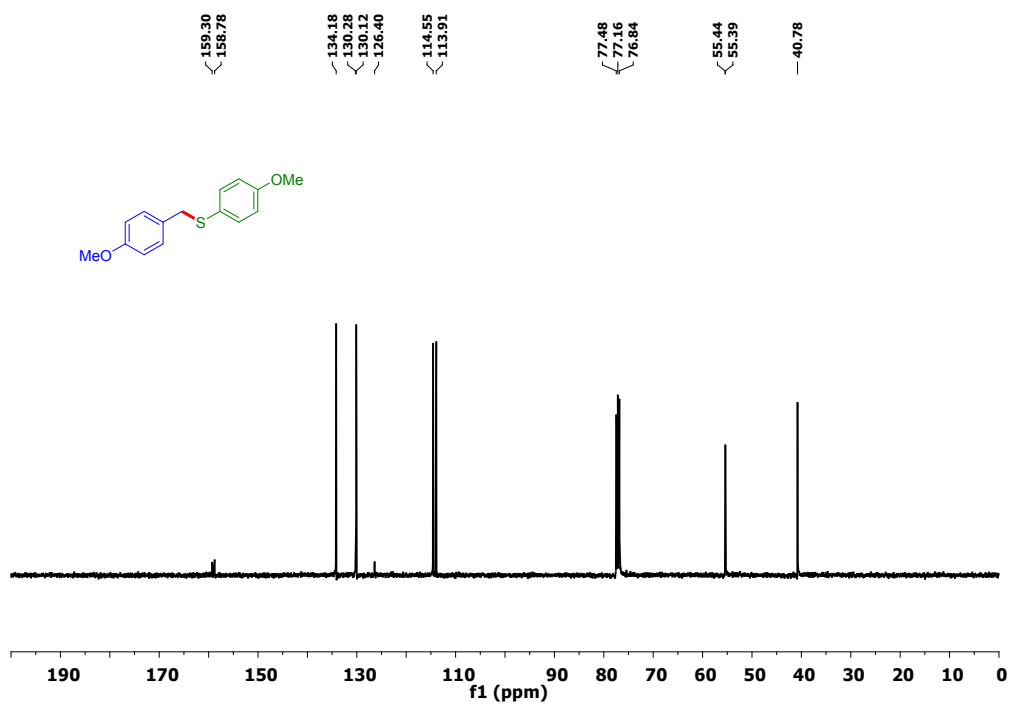


Fig. S46. ¹³C NMR spectrum of (4-methoxybenzyl)(4-methoxyphenyl)sulfane (**4mk**)

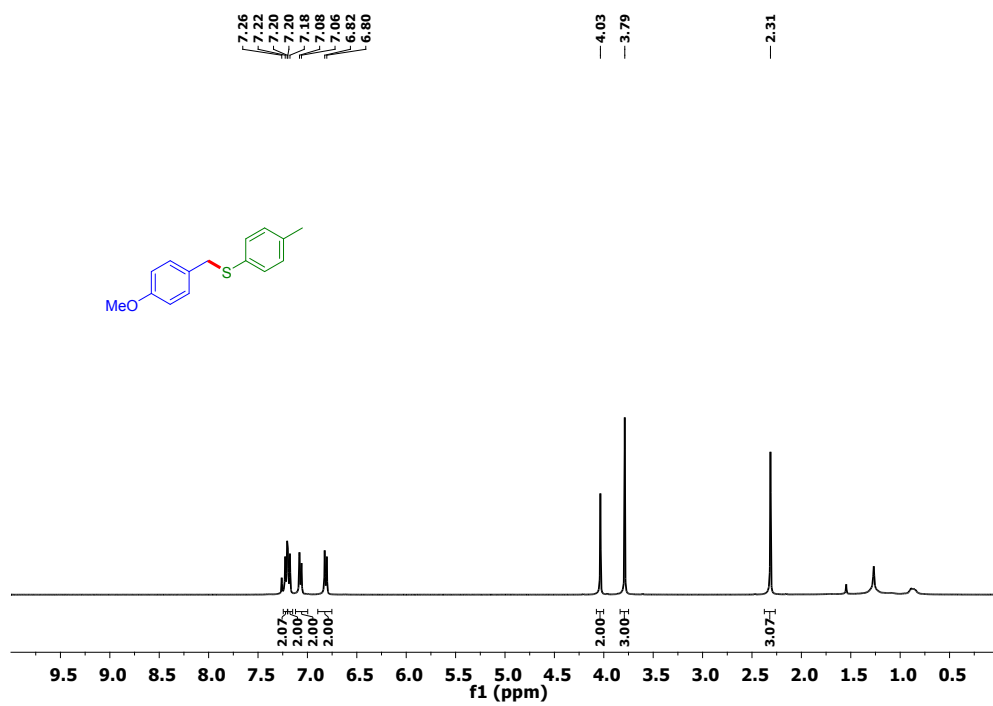


Fig. S47. ¹H NMR spectrum of (4-methoxybenzyl)(p-tolyl)sulfane (**4mb**)

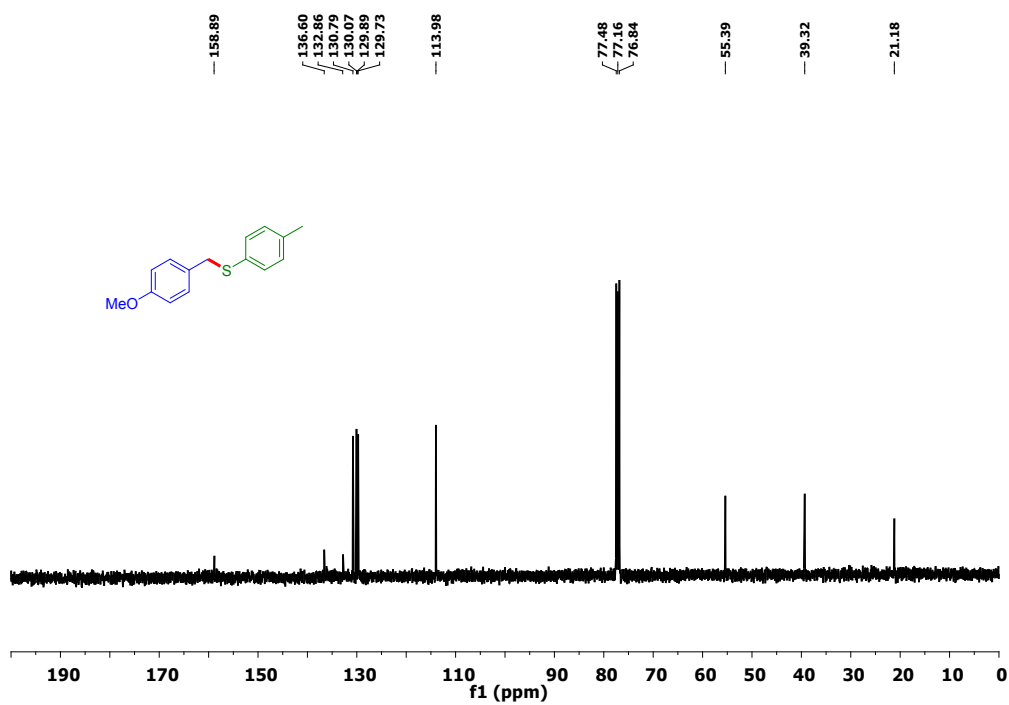


Fig. S48. ¹³C NMR spectrum of (4-methoxybenzyl)(p-tolyl)sulfane (**4mb**)

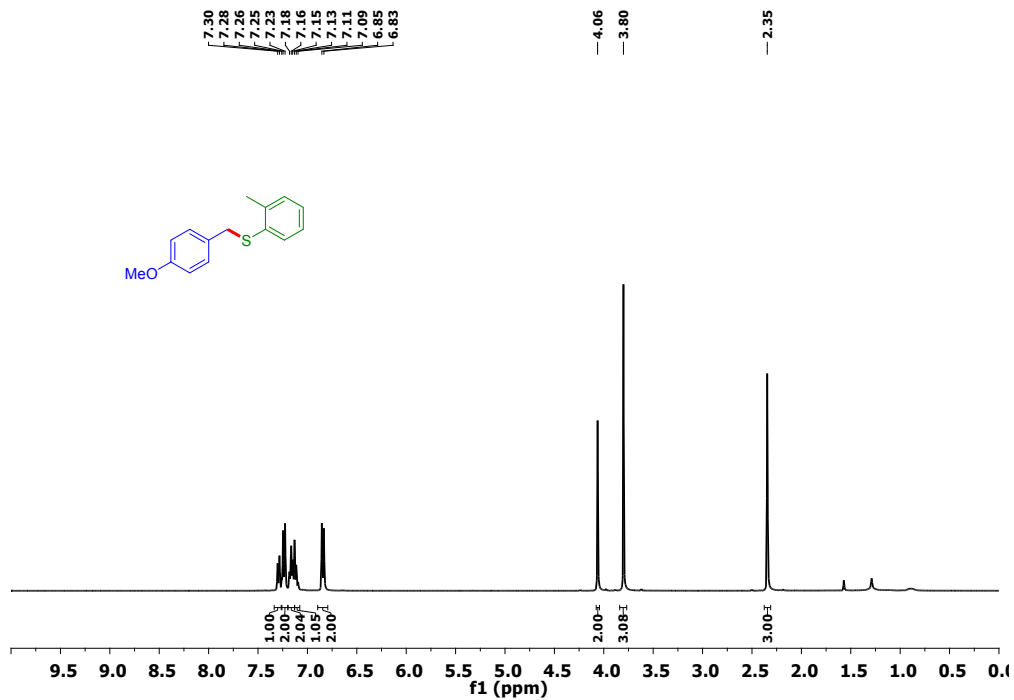


Fig. S49. ¹H NMR spectrum of (4-methoxybenzyl)(o-tolyl)sulfane (**4ml**)

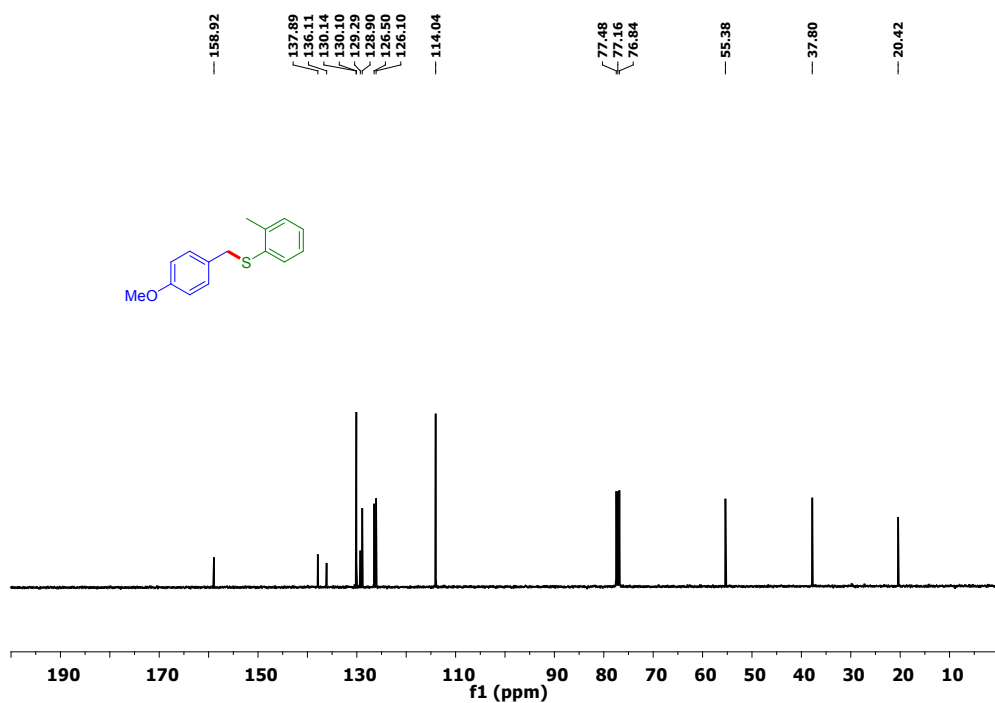


Fig. S50. ¹³C NMR spectrum of (4-methoxybenzyl)(o-tolyl)sulfane (**4ml**)

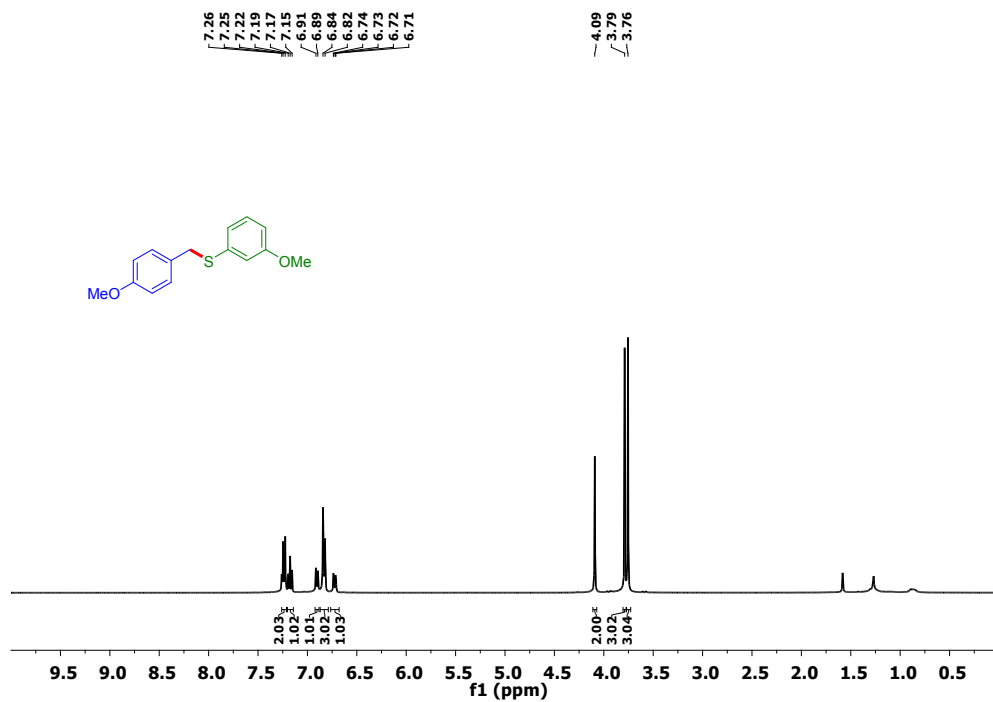


Fig. S51. ¹H NMR spectrum of (4-methoxybenzyl)(3-methoxyphenyl)sulfane (**4mc**)

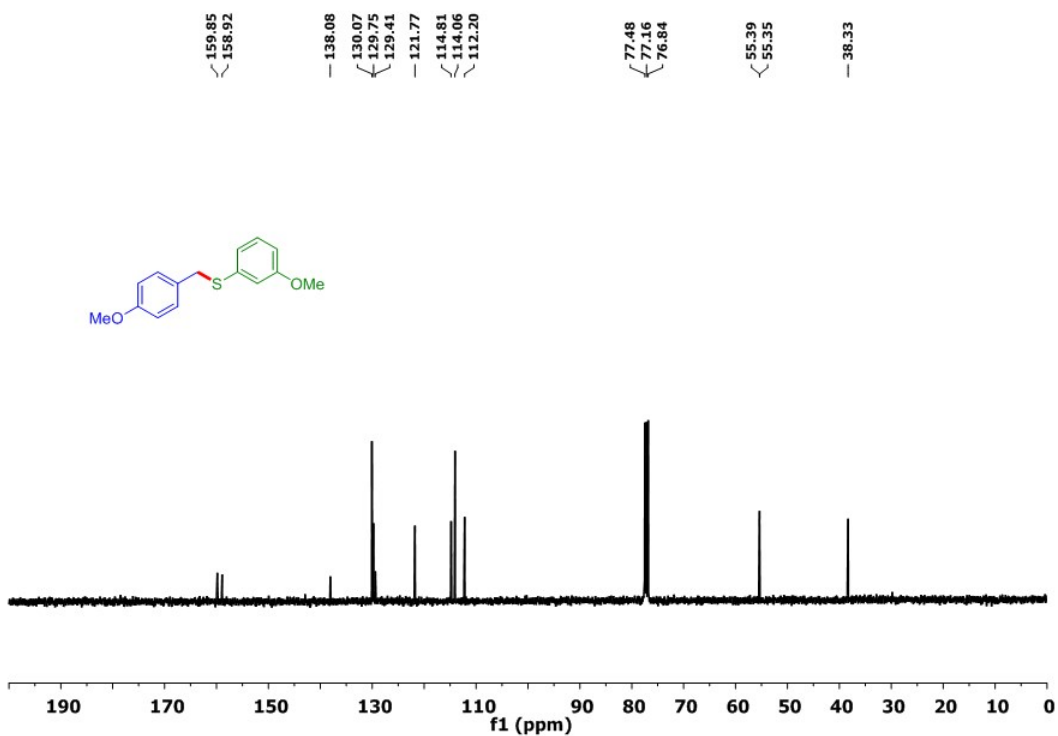


Fig. S52. ¹³C NMR spectrum of (4-methoxybenzyl)(3-methoxyphenyl)sulfane (**4mc**)

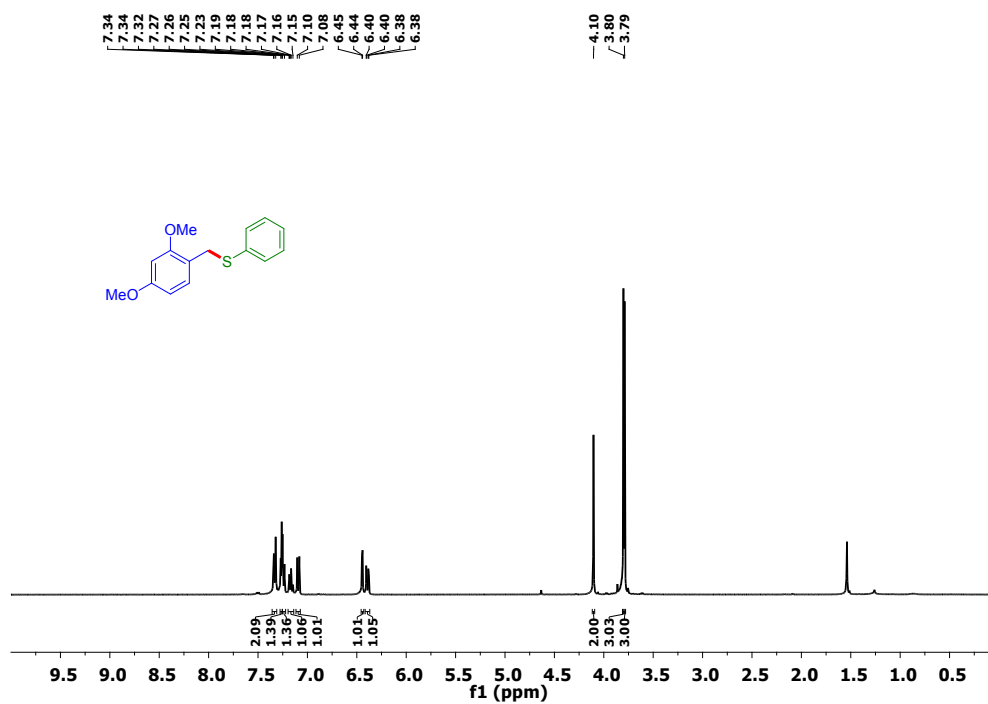


Fig. S53. ¹H NMR spectrum of (2,4-dimethoxybenzyl)(phenyl)sulfane (4na)

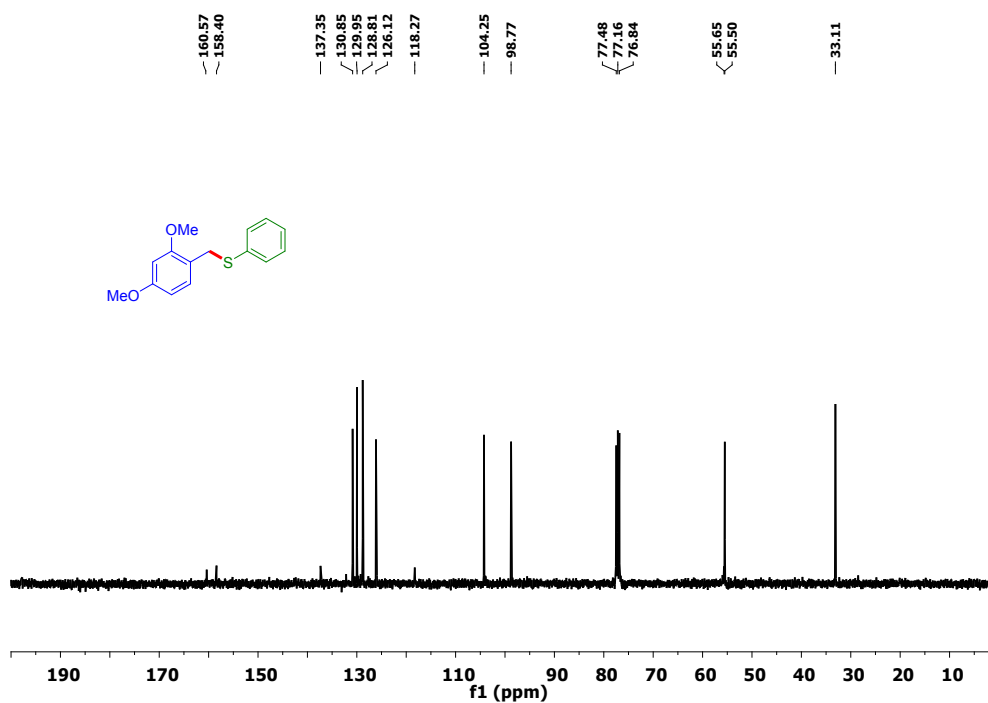


Fig. S54. ¹³C NMR spectrum of (2,4-dimethoxybenzyl)(phenyl)sulfane (4na)

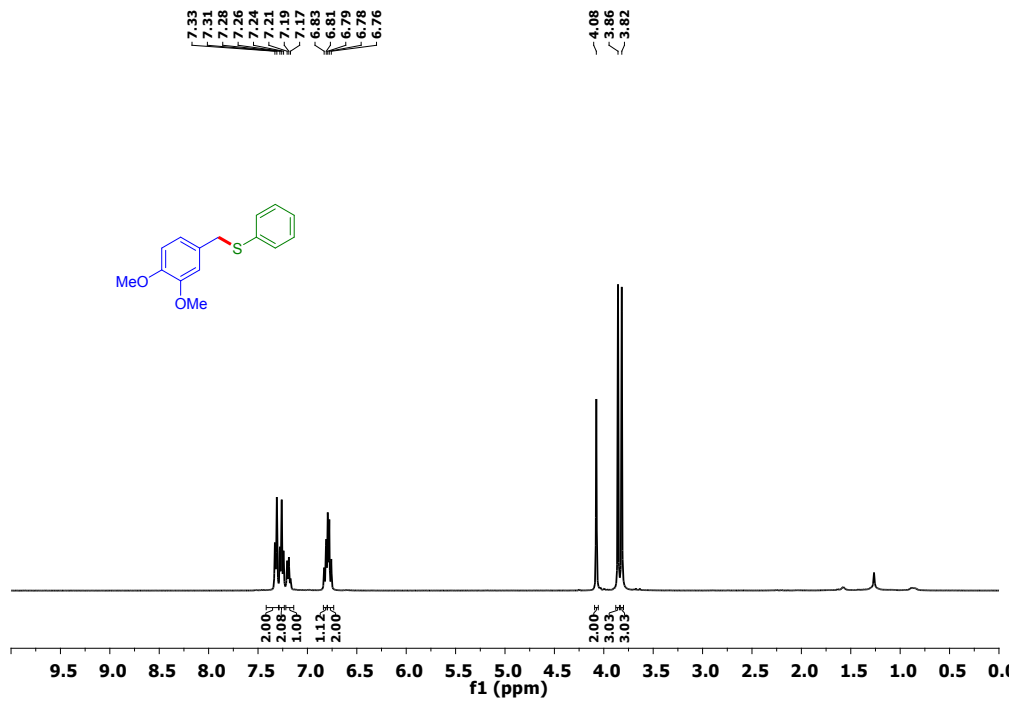


Fig. S55. ¹H NMR spectrum of (3,4-dimethoxybenzyl)(phenyl)sulfane (40a)

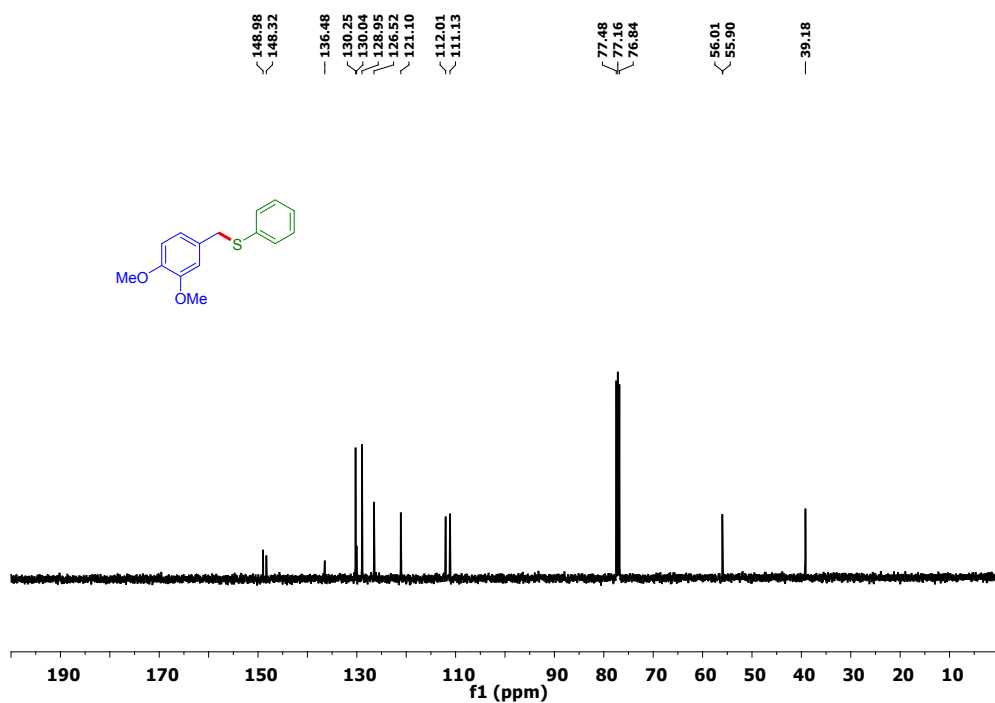


Fig. S56. ¹³C NMR spectrum of (3,4-dimethoxybenzyl)(phenyl)sulfane (40a)

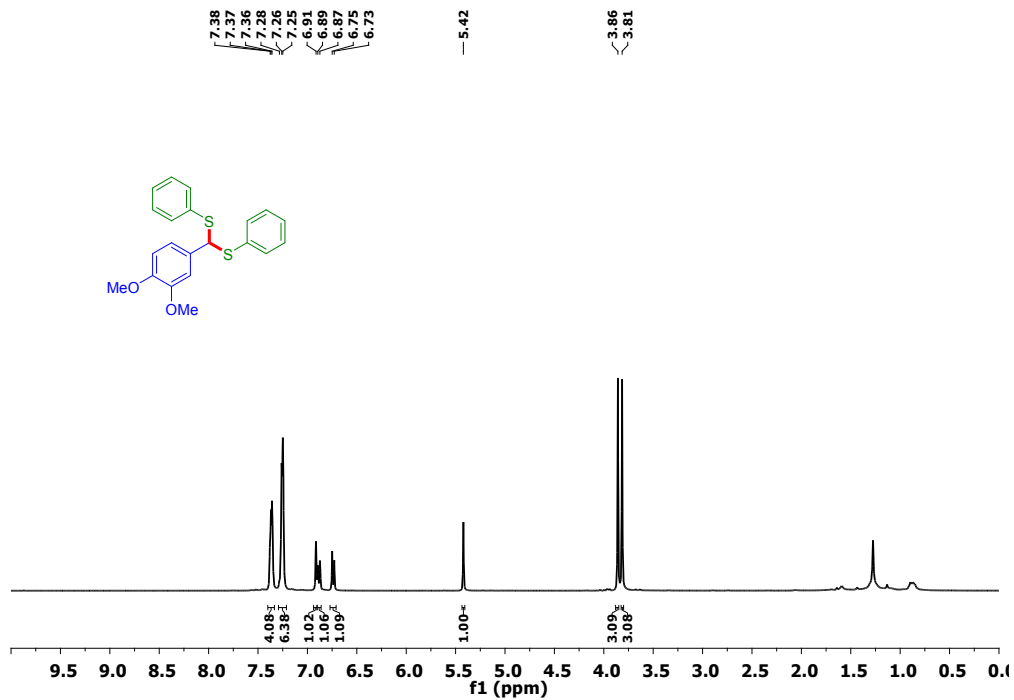


Fig. S57. ¹H NMR spectrum of ((3,4-dimethoxyphenyl)methylene)bis(phenylsulfane) (**30a**)

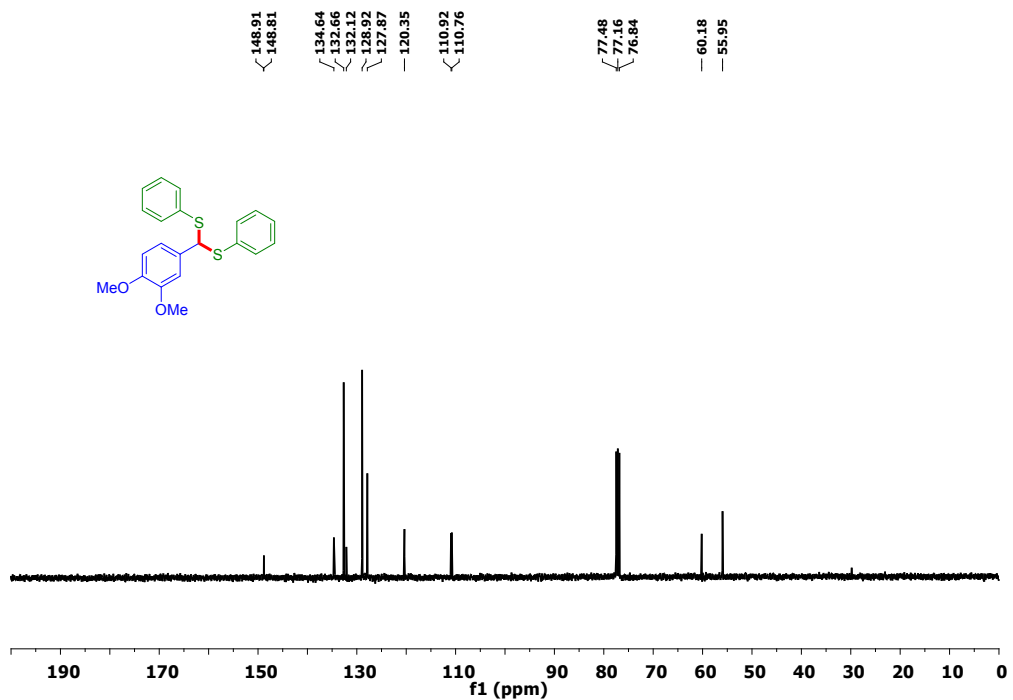


Fig. S58. ¹³C NMR spectrum of ((3,4-dimethoxyphenyl)methylene)bis(phenylsulfane) (**30a**)

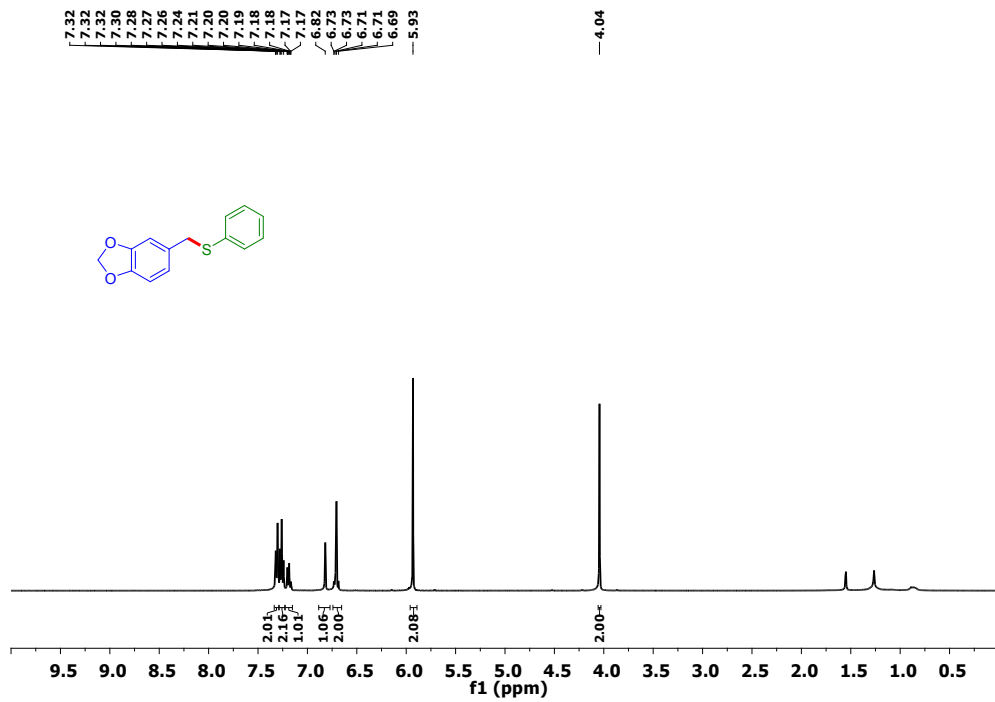


Fig. S59. ^1H NMR spectrum of 5-((phenylthio)methyl)benzo[d][1,3]dioxole (**4pa**)

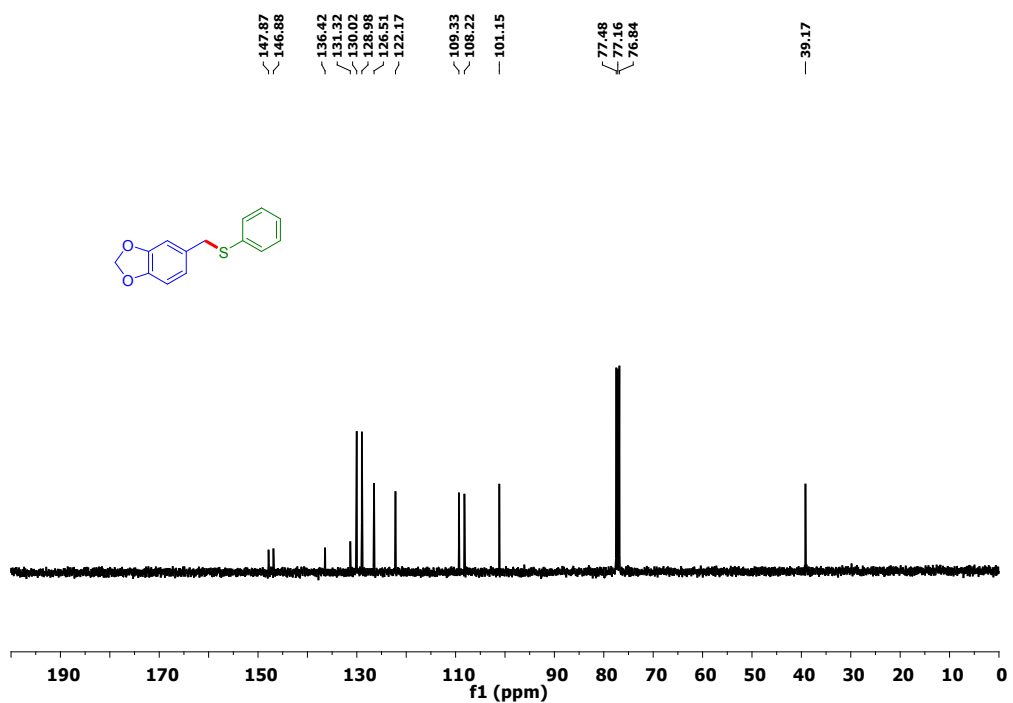


Fig. S60. ^{13}C NMR spectrum of 5-((phenylthio)methyl)benzo[d][1,3]dioxole (**4pa**)

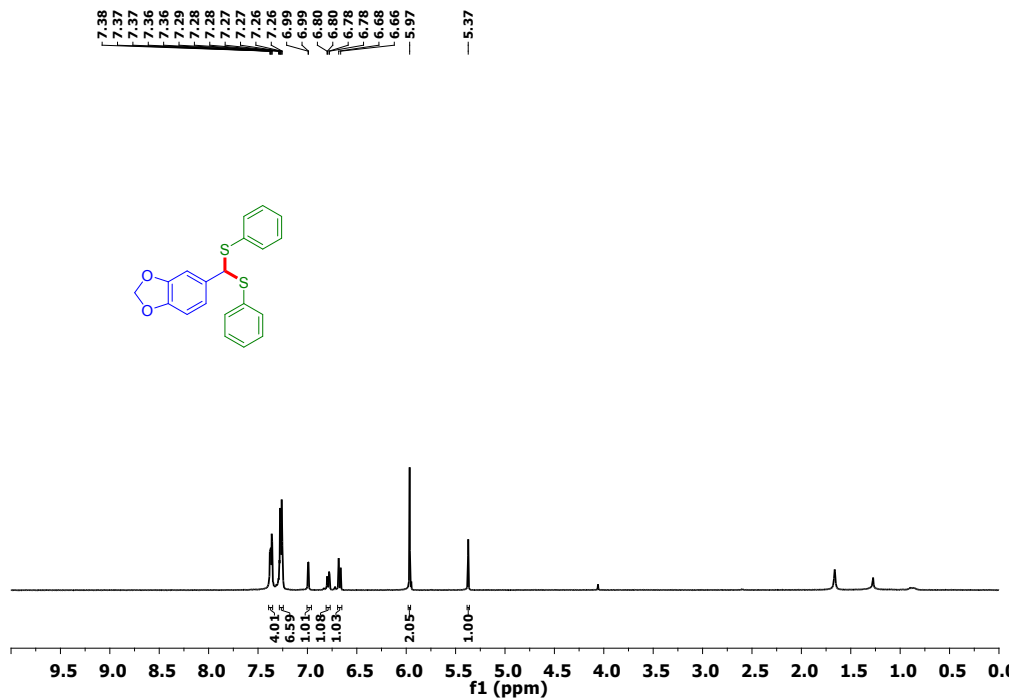


Fig. S61. ¹H NMR spectrum of 5-(bis(phenylthio)methyl)benzo[d][1,3]dioxole (**3pa**)

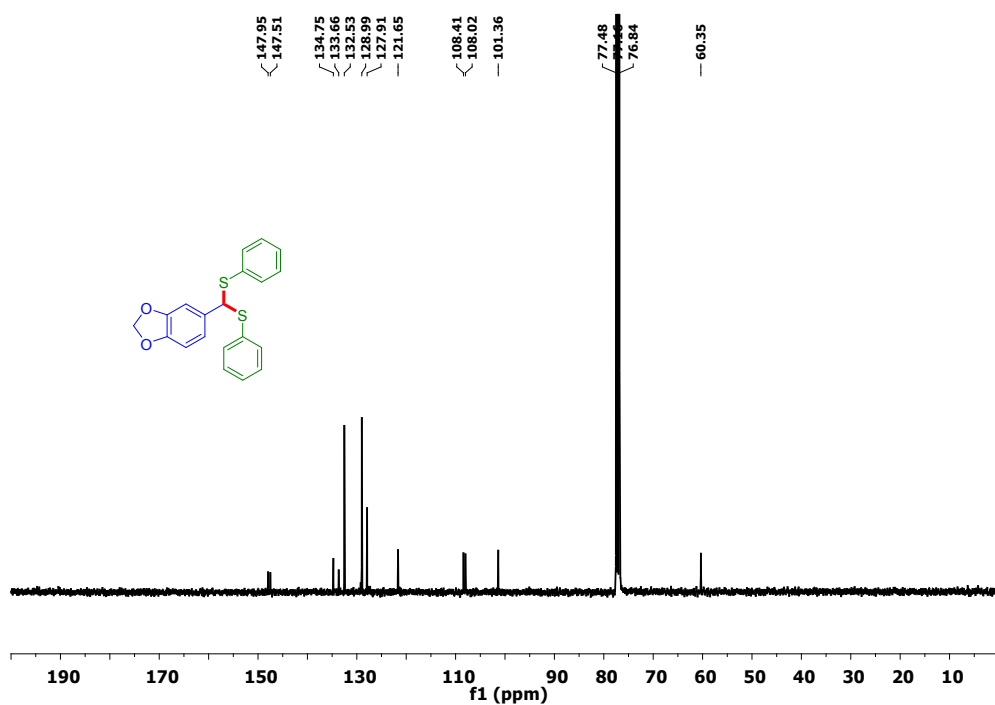


Fig. S62. ¹³C NMR spectrum of 5-(bis(phenylthio)methyl)benzo[d][1,3]dioxole (**3pa**)

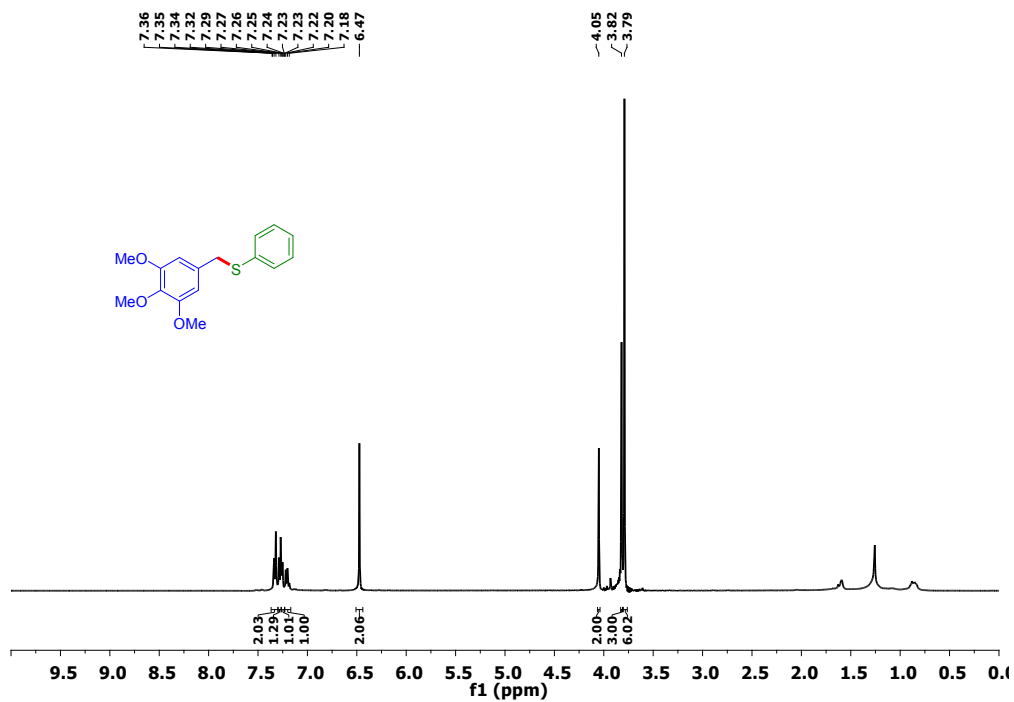


Fig. S63. ¹H NMR spectrum of phenyl(3,4,5-trimethoxybenzyl)sulfane (4qa)

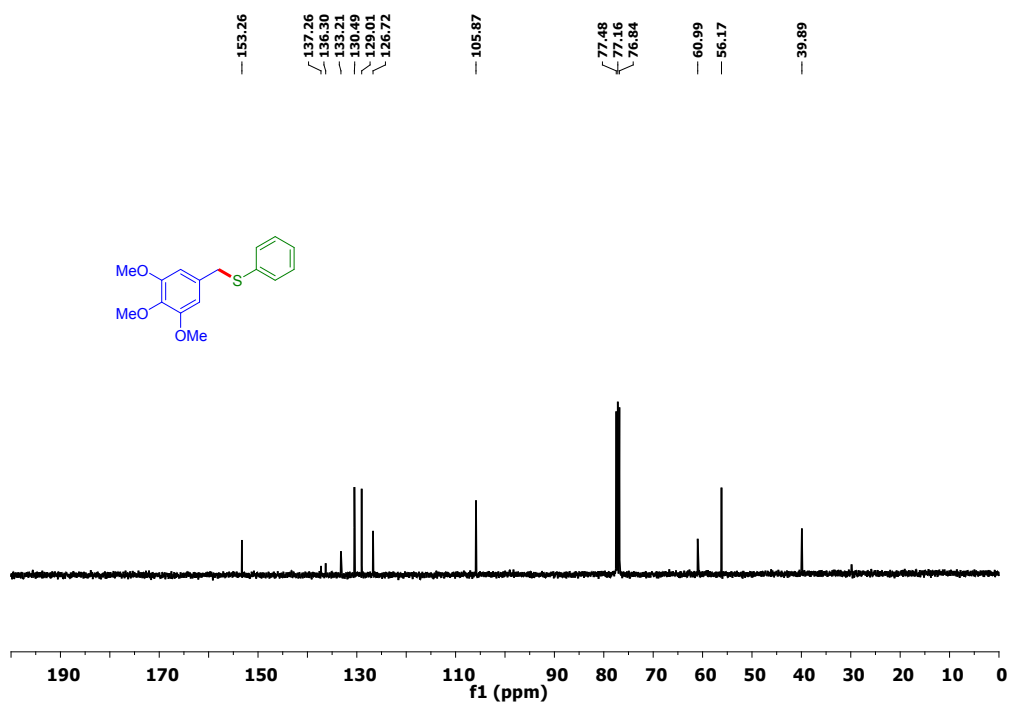


Fig. S64. ¹³C NMR spectrum of phenyl(3,4,5-trimethoxybenzyl)sulfane (4qa)

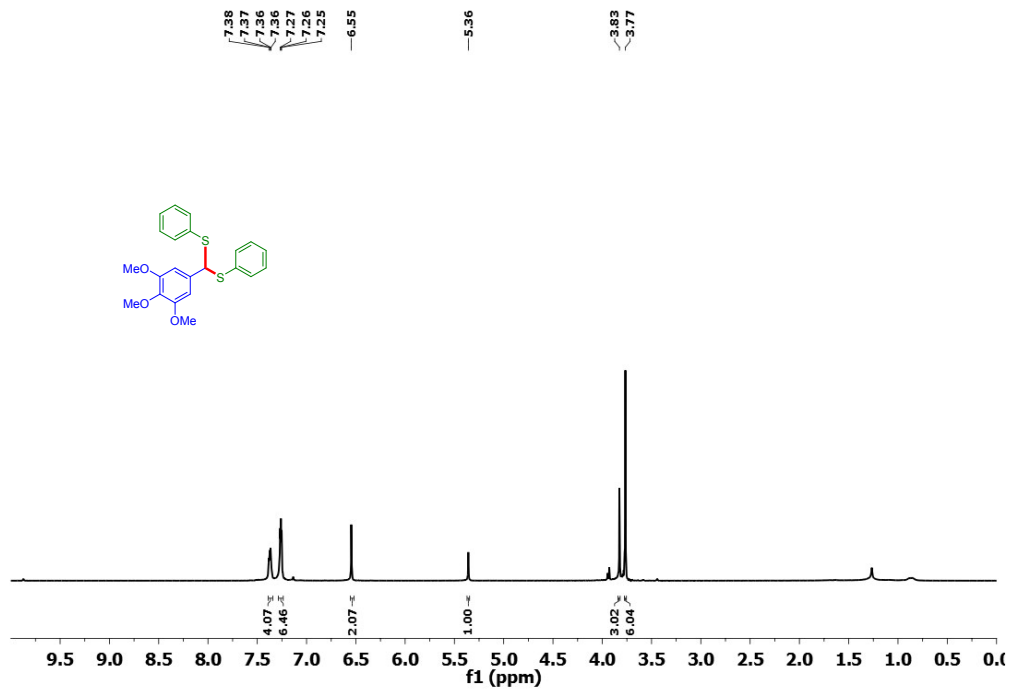


Fig. S65. ¹H NMR spectrum of ((3,4,5-trimethoxyphenyl)methylene)bis(phenylsulfane) (**3qa**)

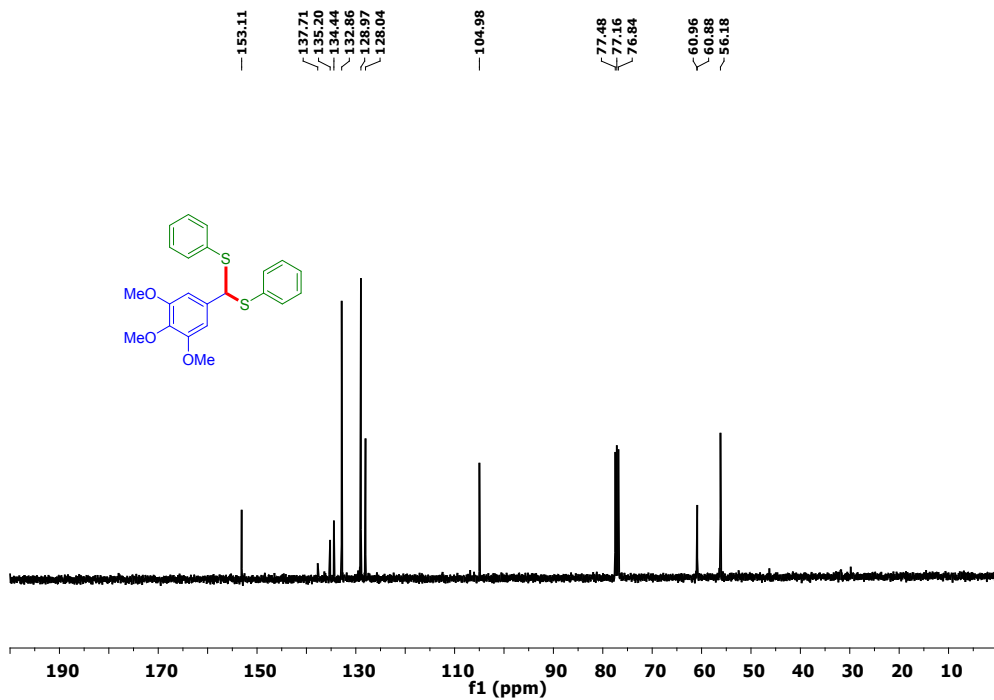


Fig. S66. ¹³C NMR spectrum of ((3,4,5-trimethoxyphenyl)methylene)bis(phenylsulfane) (**3qa**)

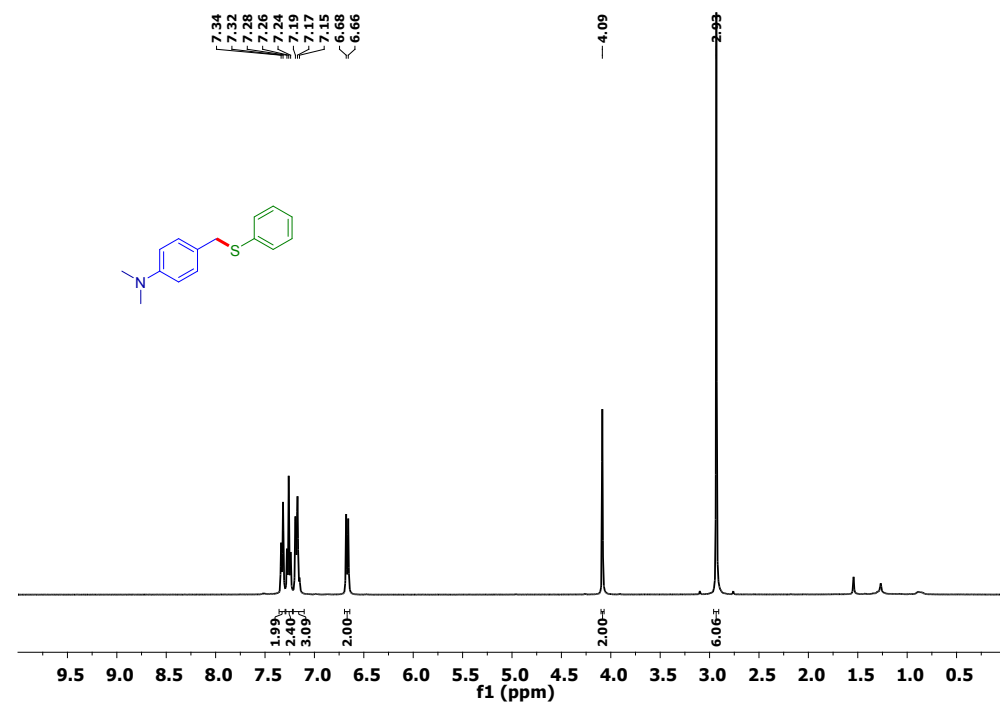


Fig. S67. ^1H NMR spectrum of N,N-dimethyl-4-((phenylthio)methyl)aniline (**4ra**)

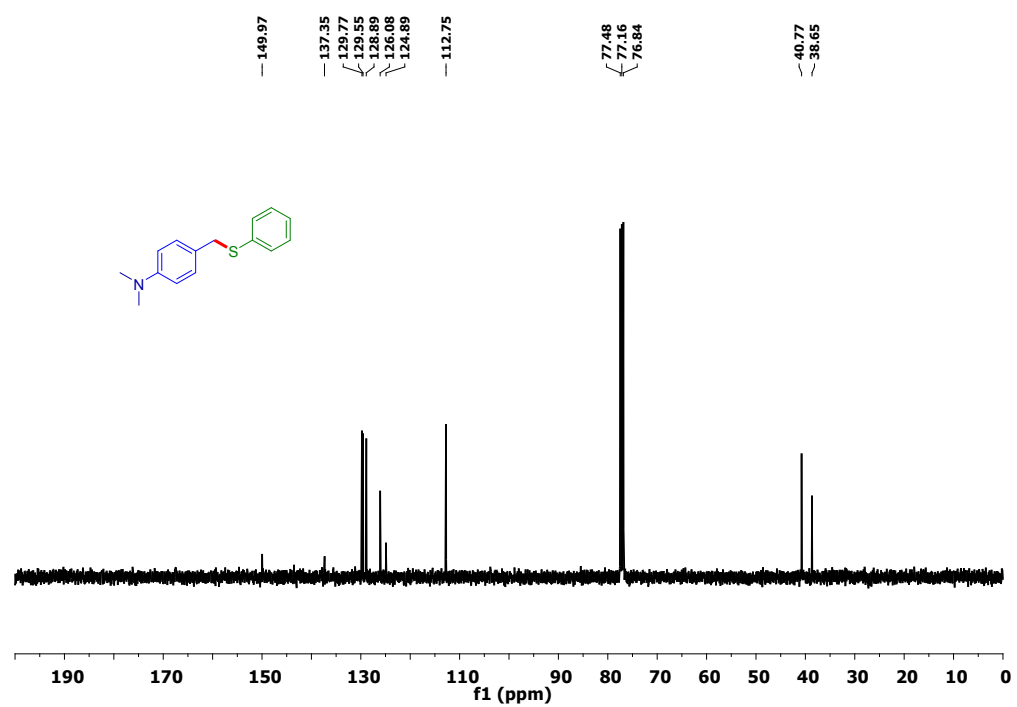


Fig. S68. ^{13}C NMR spectrum of N,N-dimethyl-4-((phenylthio)methyl)aniline (**4ra**)

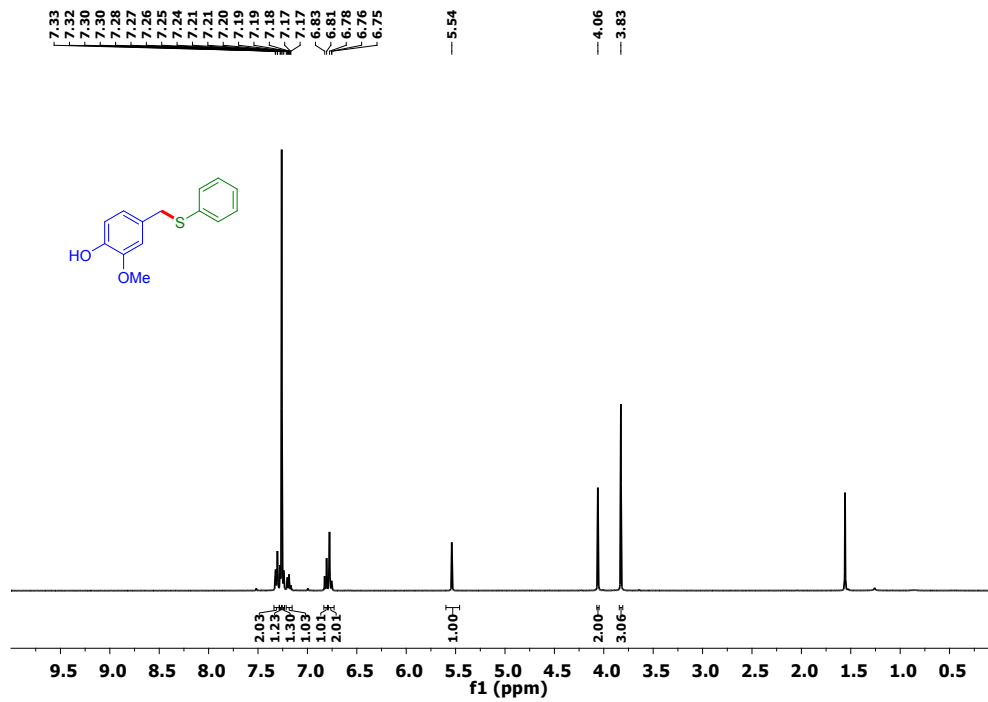


Fig. S69. ¹H NMR spectrum of 2-methoxy-4-((phenylthio)methyl)phenol (**4sa**)

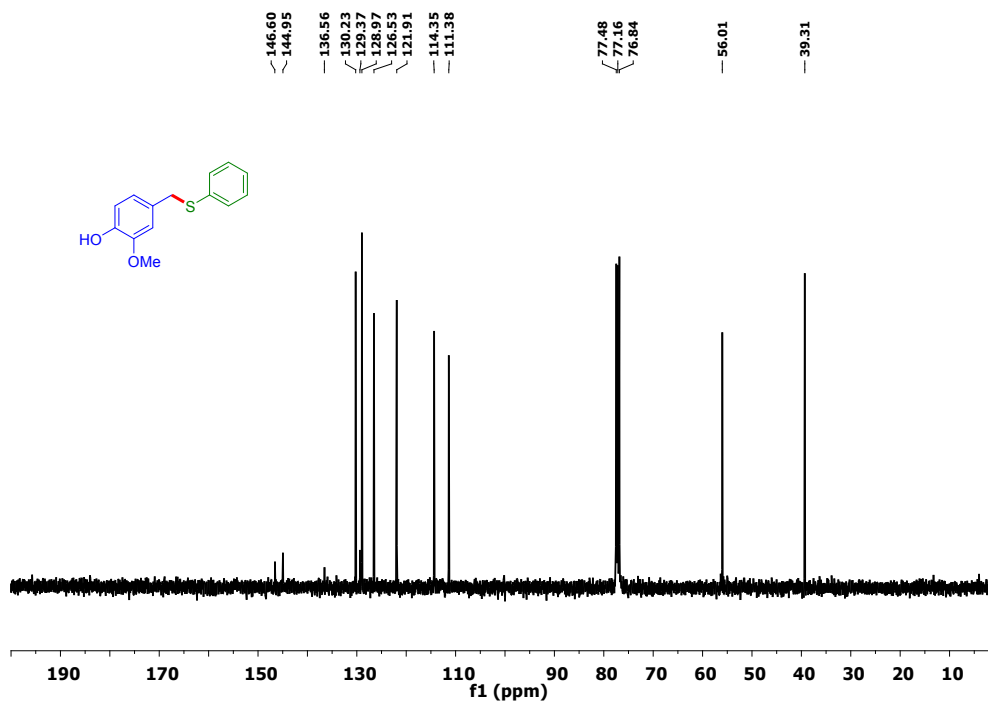


Fig. S70. ¹³C NMR spectrum of 2-methoxy-4-((phenylthio)methyl)phenol (**4sa**)

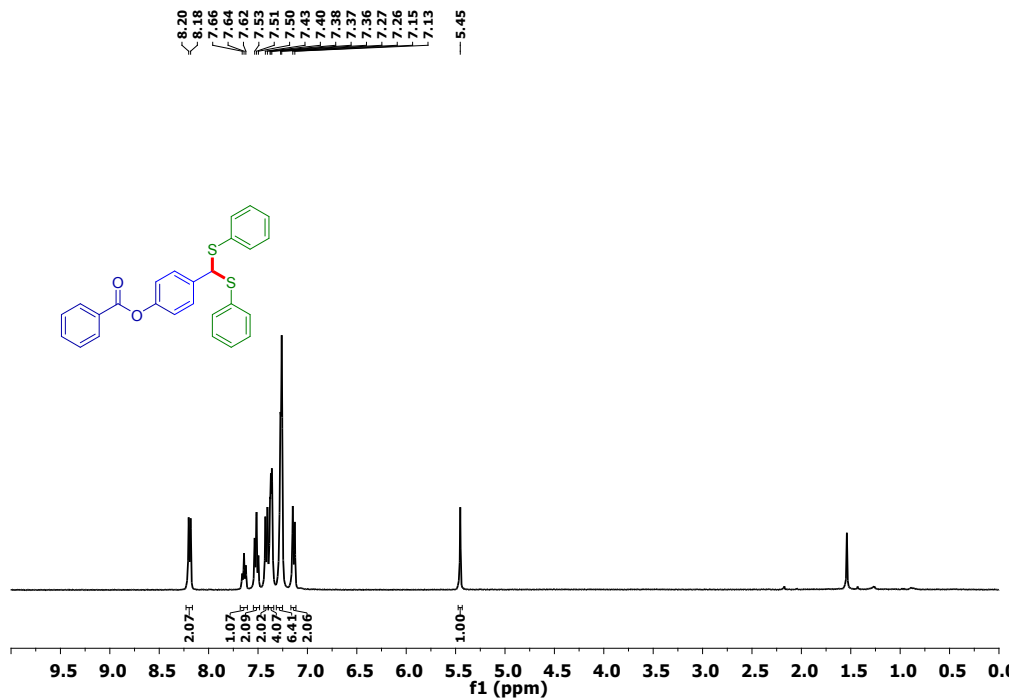


Fig. S71. ^1H NMR spectrum of 4-(bis(phenylthio)methyl)phenyl benzoate (**3ja**)

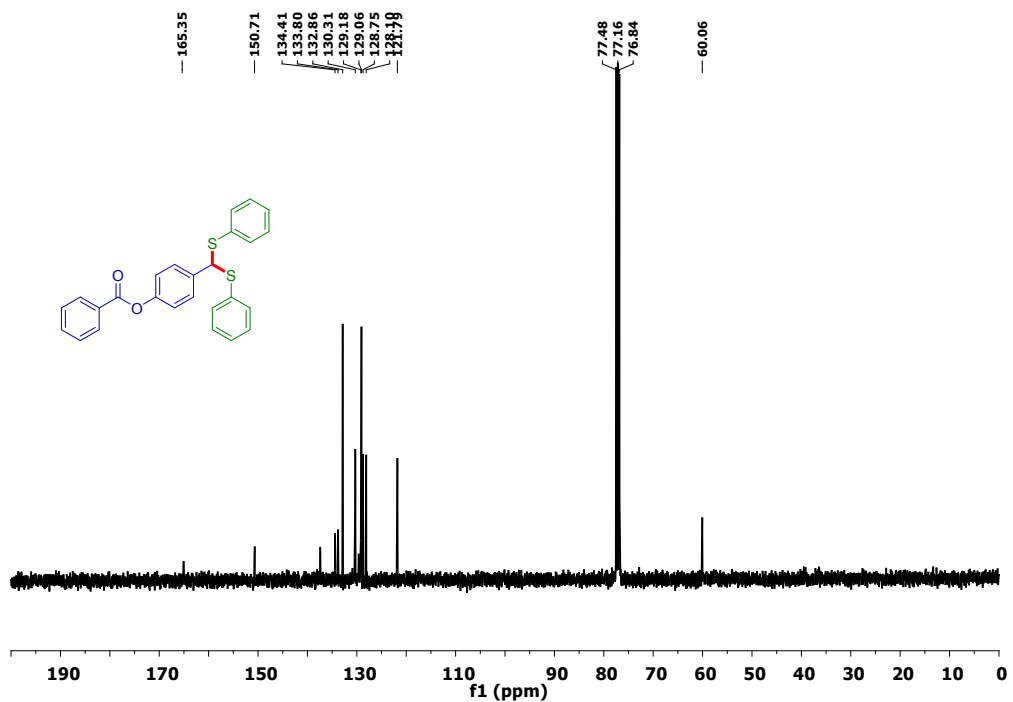


Fig. S72. ^{13}C NMR spectrum of 4-(bis(phenylthio)methyl)phenyl benzoate (**3ja**)

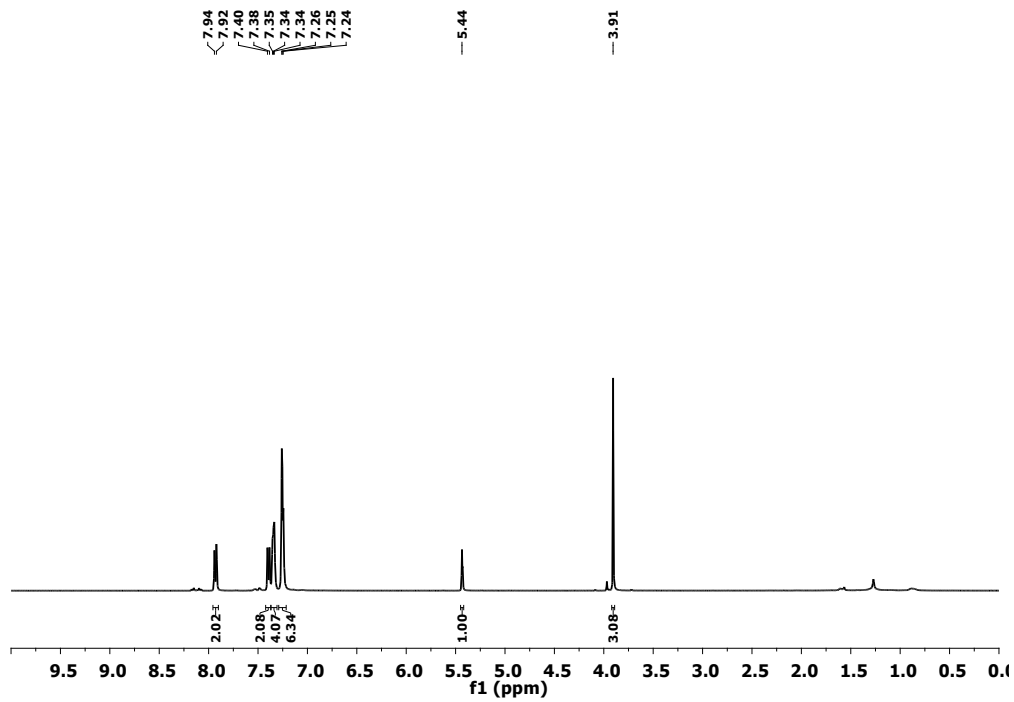


Fig. S73. ^1H NMR spectrum of methyl 4-(bis(phenylthio)methyl)benzoate (**3ka**)

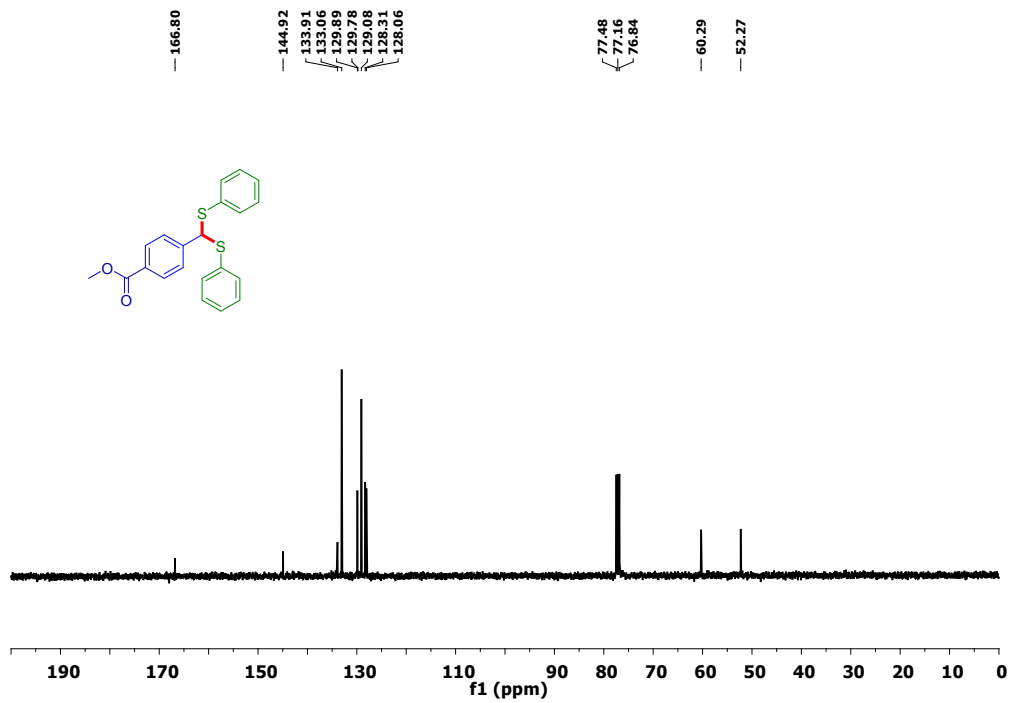


Fig. S74. ^{13}C NMR spectrum of methyl 4-(bis(phenylthio)methyl)benzoate (**3ka**)

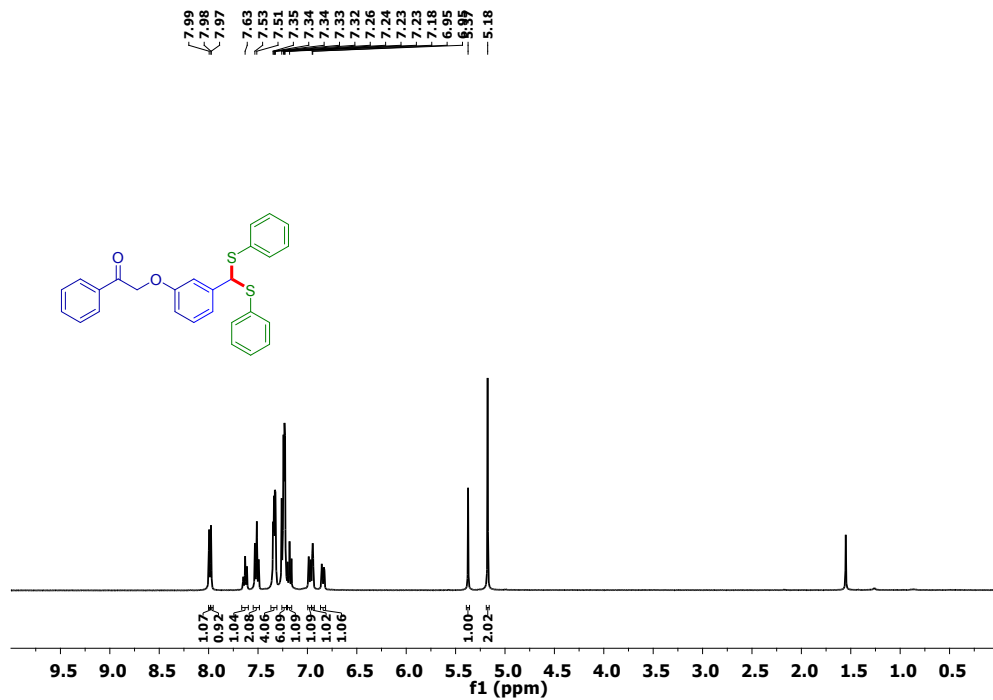


Fig. S75. ^1H NMR spectrum of 2-(3-(bis(phenylthio)methyl)phenoxy)-1-phenylethan-1-one (**3la**)

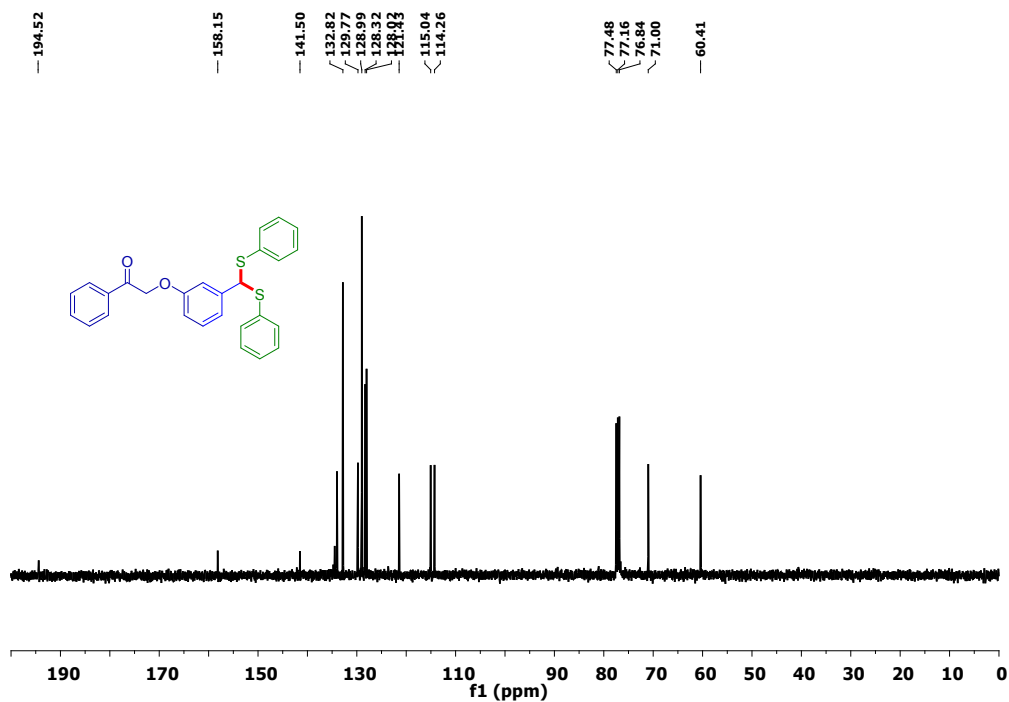


Fig. S76. ^{13}C NMR spectrum of 2-(3-(bis(phenylthio)methyl)phenoxy)-1-phenylethan-1-one (**3la**)

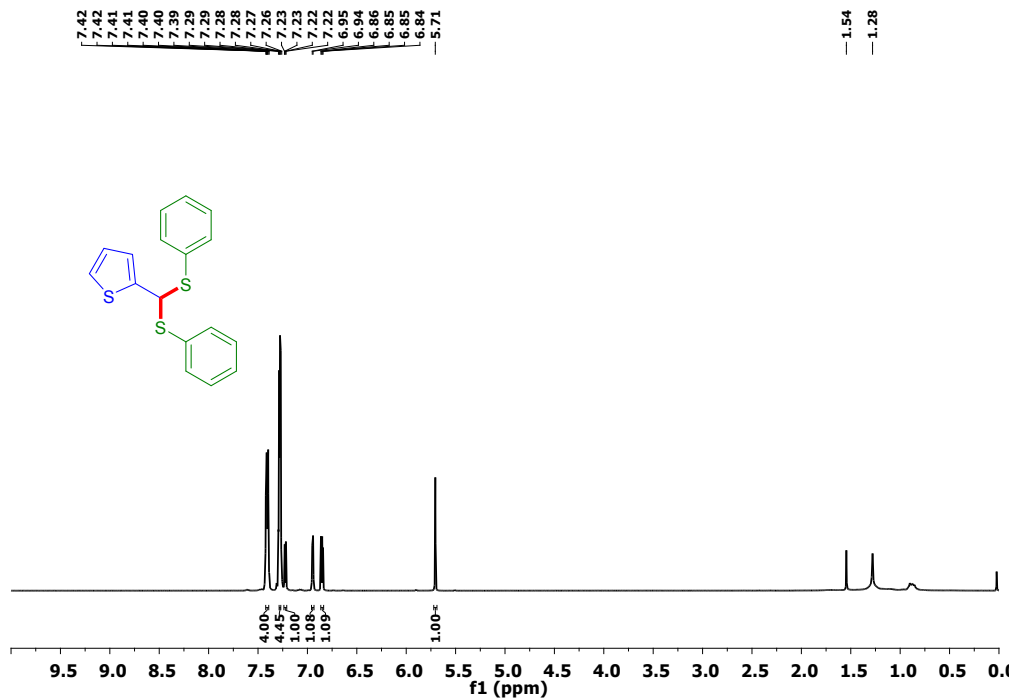


Fig. S77. ¹H NMR spectrum of (2-(Bis(phenylthio)methyl)thiophene) (**3ta**)

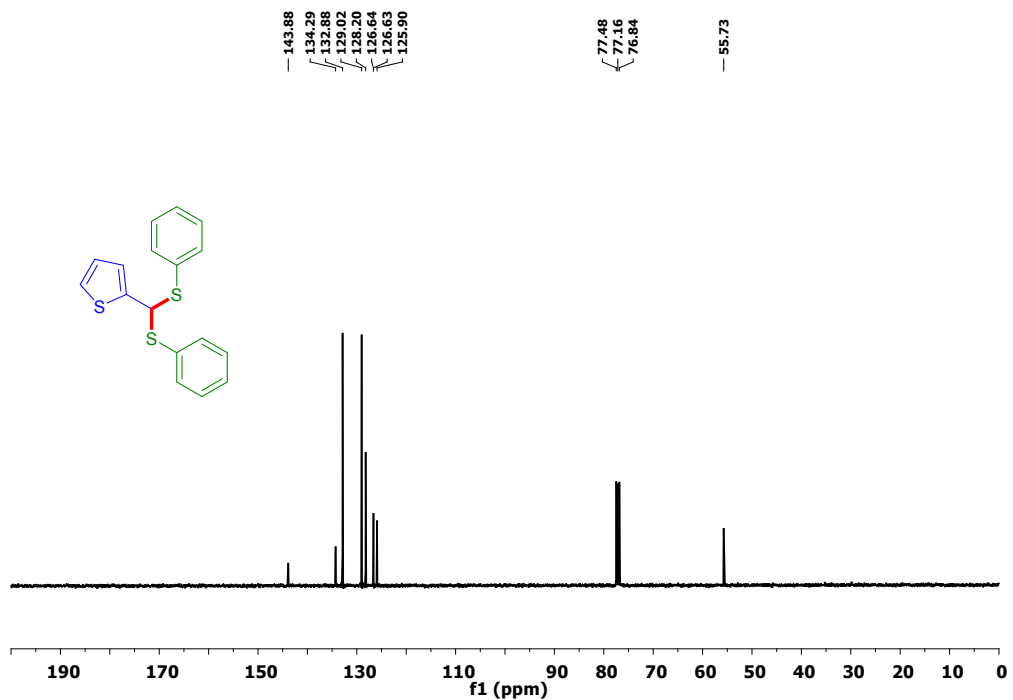


Fig. S78. ¹³C NMR spectrum of (2-(Bis(phenylthio)methyl)thiophene) (**3ta**)

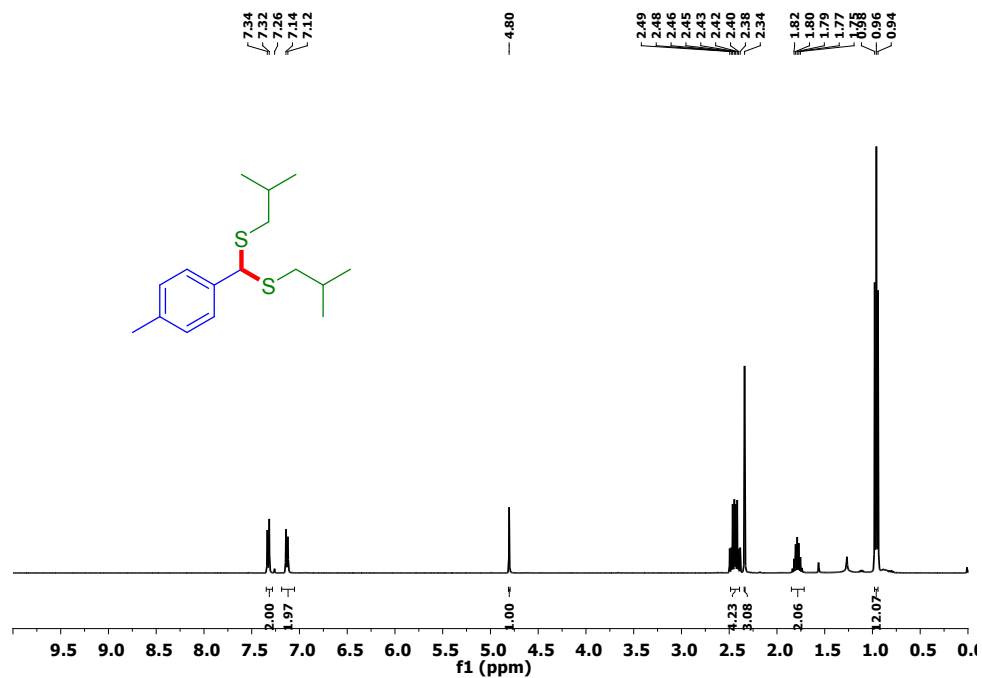


Fig. S79. ^1H NMR spectrum of (p-tolylmethylene)bis(isobutylsulfane) (**3bk**)

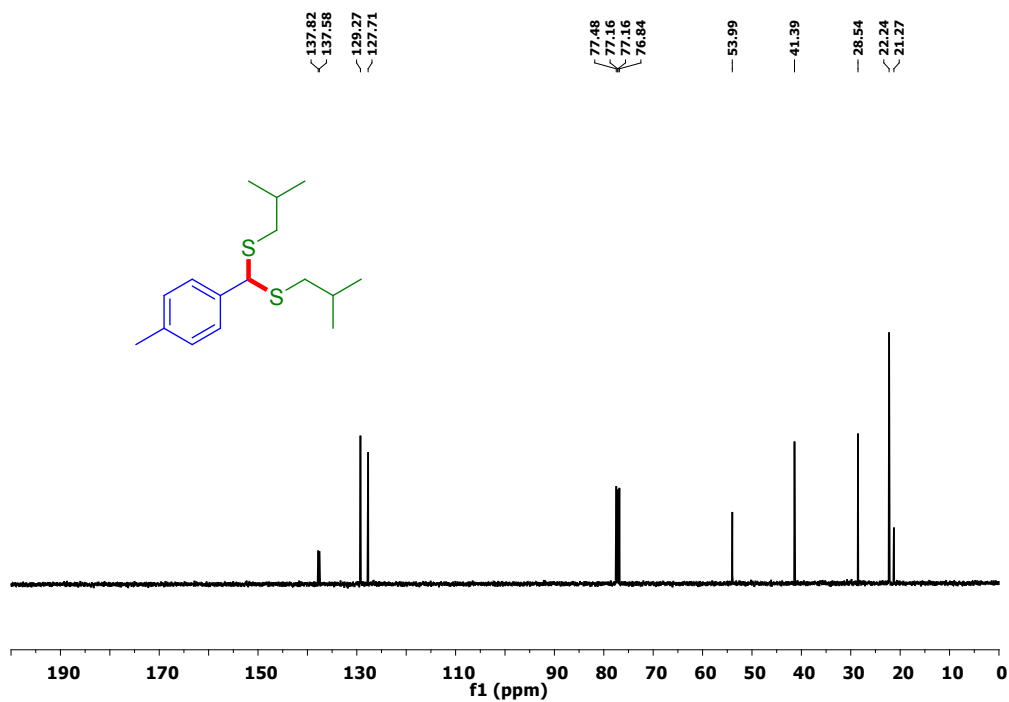


Fig. S80. ^{13}C NMR spectrum of (p-tolylmethylene)bis(isobutylsulfane) (**3bk**)

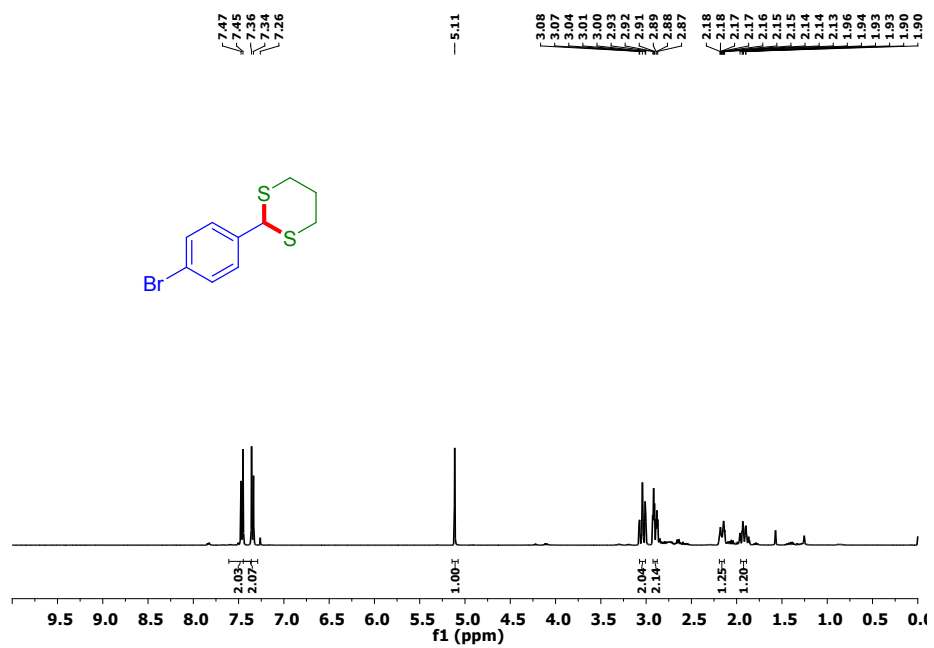


Fig. S81. ¹H NMR spectrum of (2-(4-bromophenyl)-1,3-dithiane) (**3ul**)

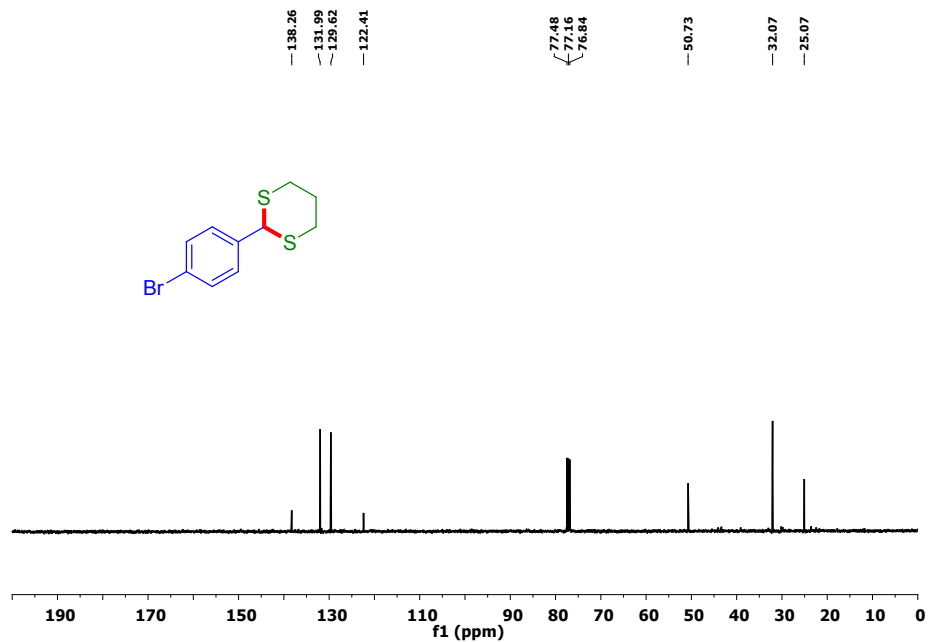


Fig. S82. ¹³C NMR spectrum of 2-(4-bromophenyl)-1,3-dithiane (**3ul**)

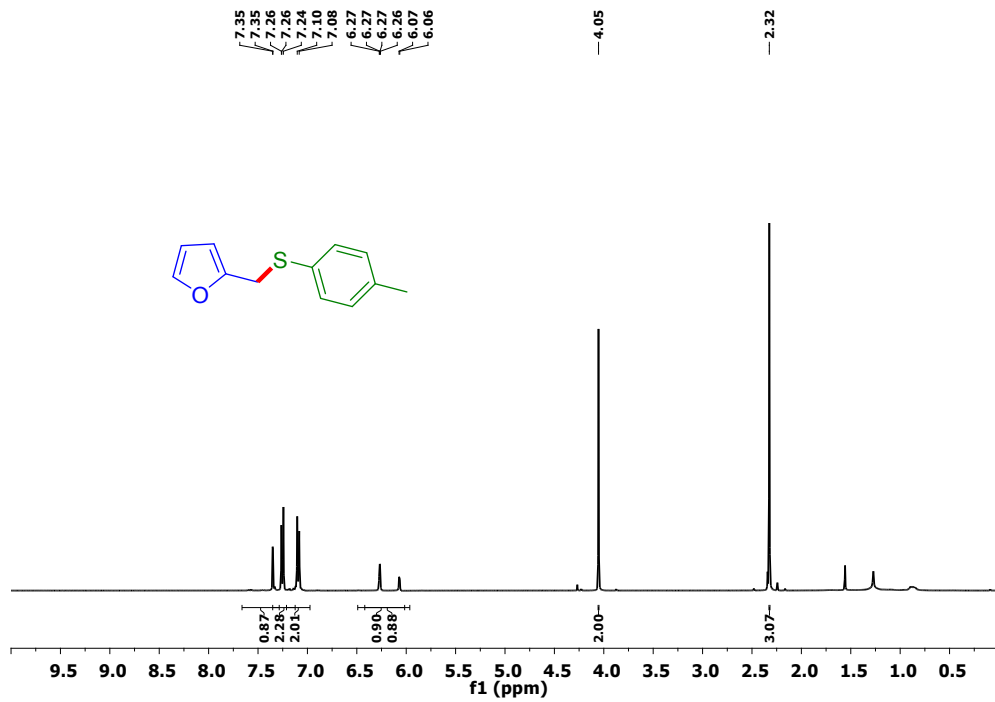


Fig. S83. ¹H NMR spectrum of 2-((p-tolylthio)methyl)furan (4vb)

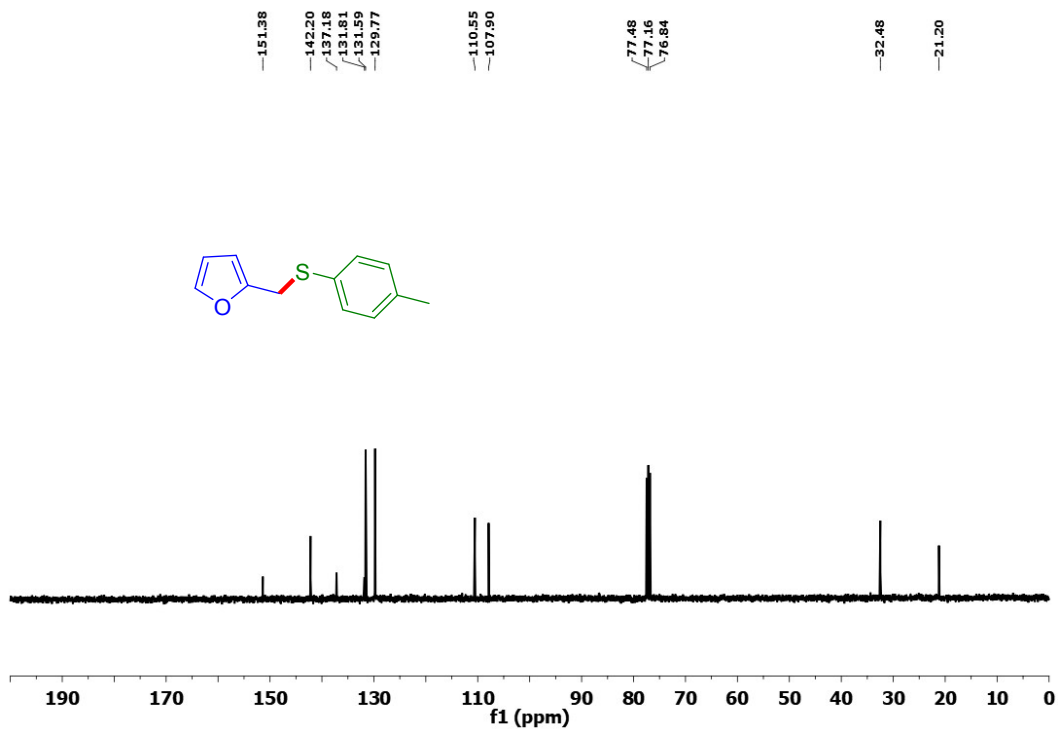


Fig. S84. ¹³C NMR spectrum of 2-((p-tolylthio)methyl)furan (4vb)