Supporting Information

Enhancing Photocatalytic Efficiency and Stability of $CsPbBr_3$ Nanocrystals for Visible-Light Driven Aerobic Diaryl Thio/Seleno Etherification

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Content

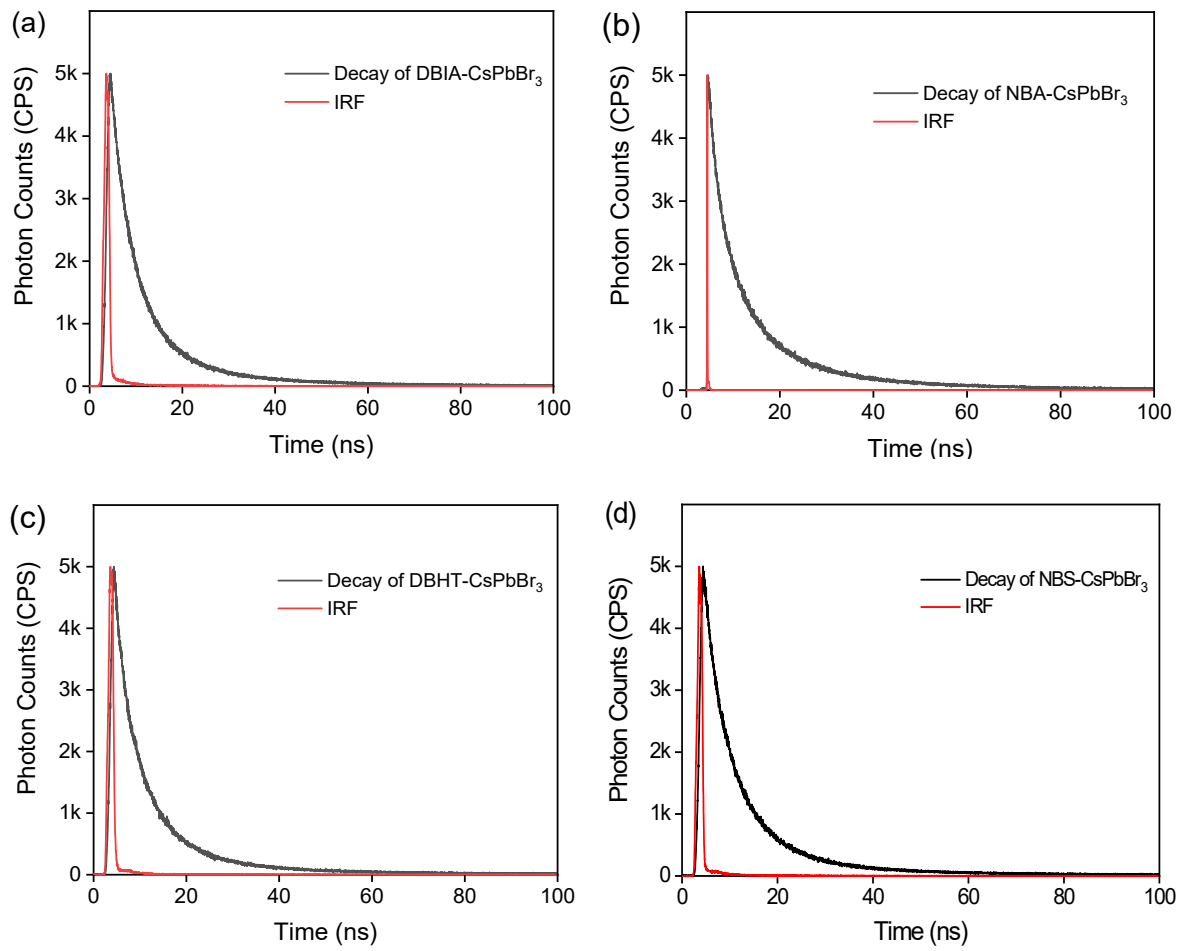


Fig. S1. PL lifetime decay of (a) DBIA-$CsPbBr_3$ (b) NBA-$CsPbBr_3$ (c) DBHT-$CsPbBr_3$ (d) NBS-$CsPbBr_3$

Table S1. Summary of fitting results for $CsPbBr_3$ perovskites.

Sample Name	**α_1**	**τ_1 (ns)**	**α_2**	**τ_2 (ns)**	**α_3**	**τ_3 (ns)**	**τ_{av} (ns)**
DBIA-$CsPbBr_3$	0.263 (37.1%)	1.85	0.321 (45.3%)	6.71	0.125 (17.6%)	19.41	12.5
NBA-$CsPbBr_3$	0.094 (50.0%)	0.7	0.082 (43.6%)	2.71	0.012 (6.4%)	20.9	10.2
DBHT-$CsPbBr_3$	0.185 (92.5%)	0.85	0.011 (5.5%)	4.17	0.004 (2.0%)	21.27	7.4
NBS-	0.011	0.93	0.084	3.72	0.103	17.93	9.7

$CsPbBr_3$	(5.5%)		(42.4%)		(52.0%)		

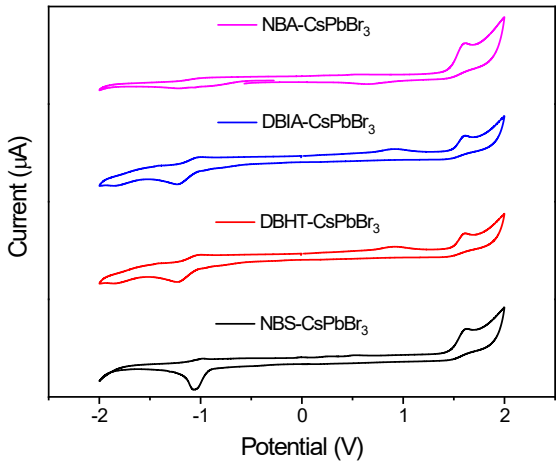


Fig. S2. Cyclic voltammetry of $CsPbBr_3$

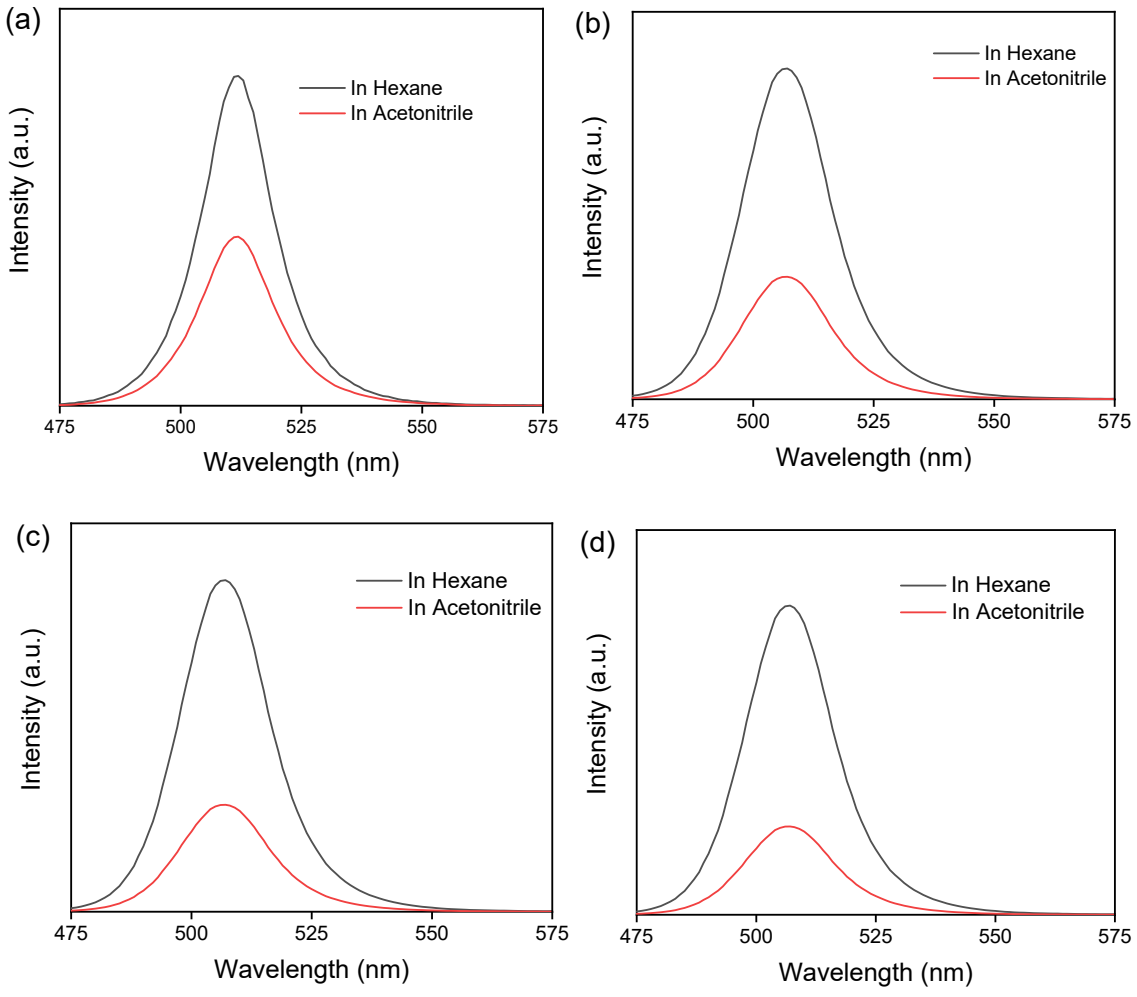


Fig. S3. PL spectra of (a) DBIA-$CsPbBr_3$, (b) NBA-$CsPbBr_3$, (c) DBHT-$CsPbBr_3$, (d) NBS-$CsPbBr_3$ in Hexane and Acetonitrile

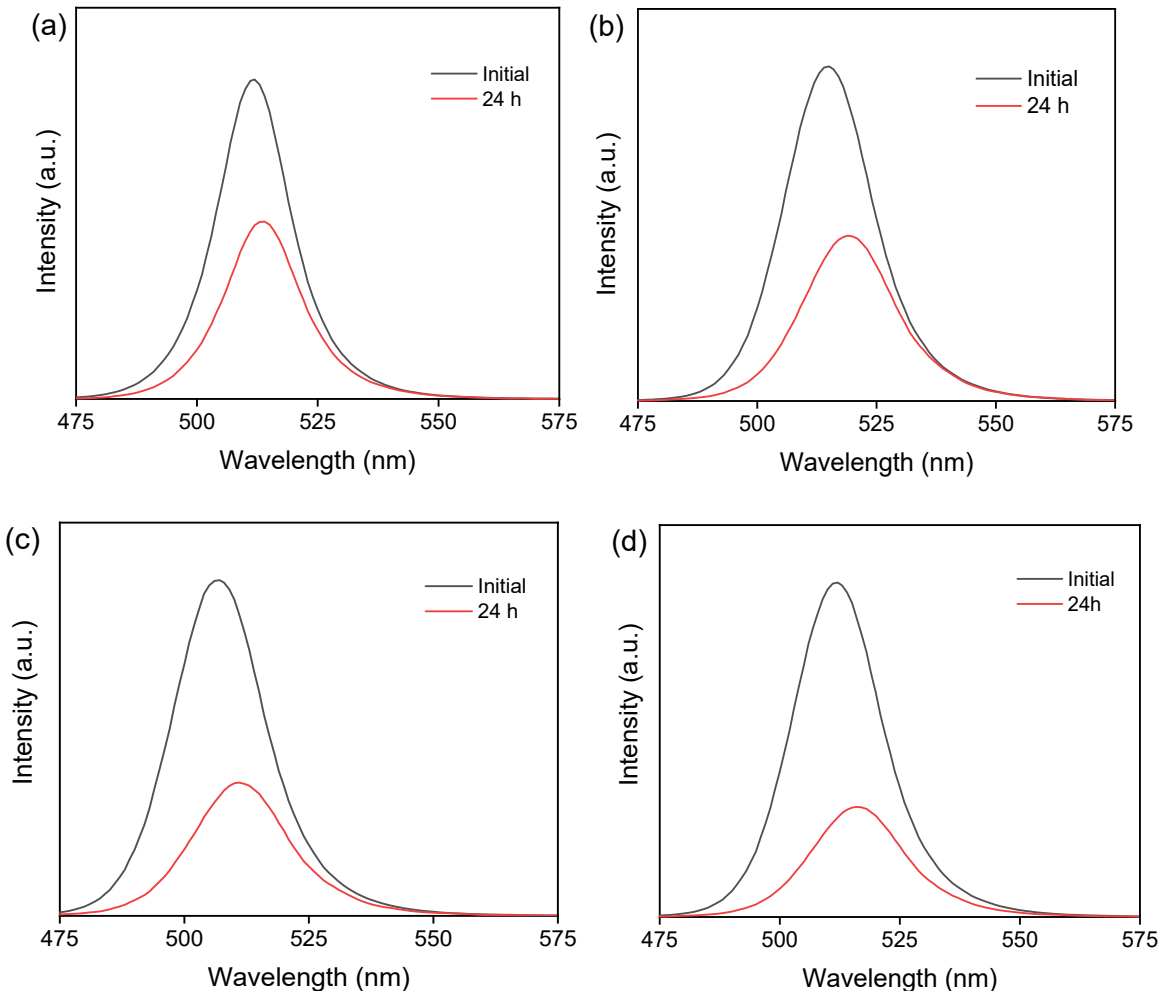


Fig. S4. PL quenching of (a) DBIA-$CsPbBr_3$, (b) NBA-$CsPbBr_3$, (c) DBHT-$CsPbBr_3$, (d) NBS-$CsPbBr_3$ in ACN.

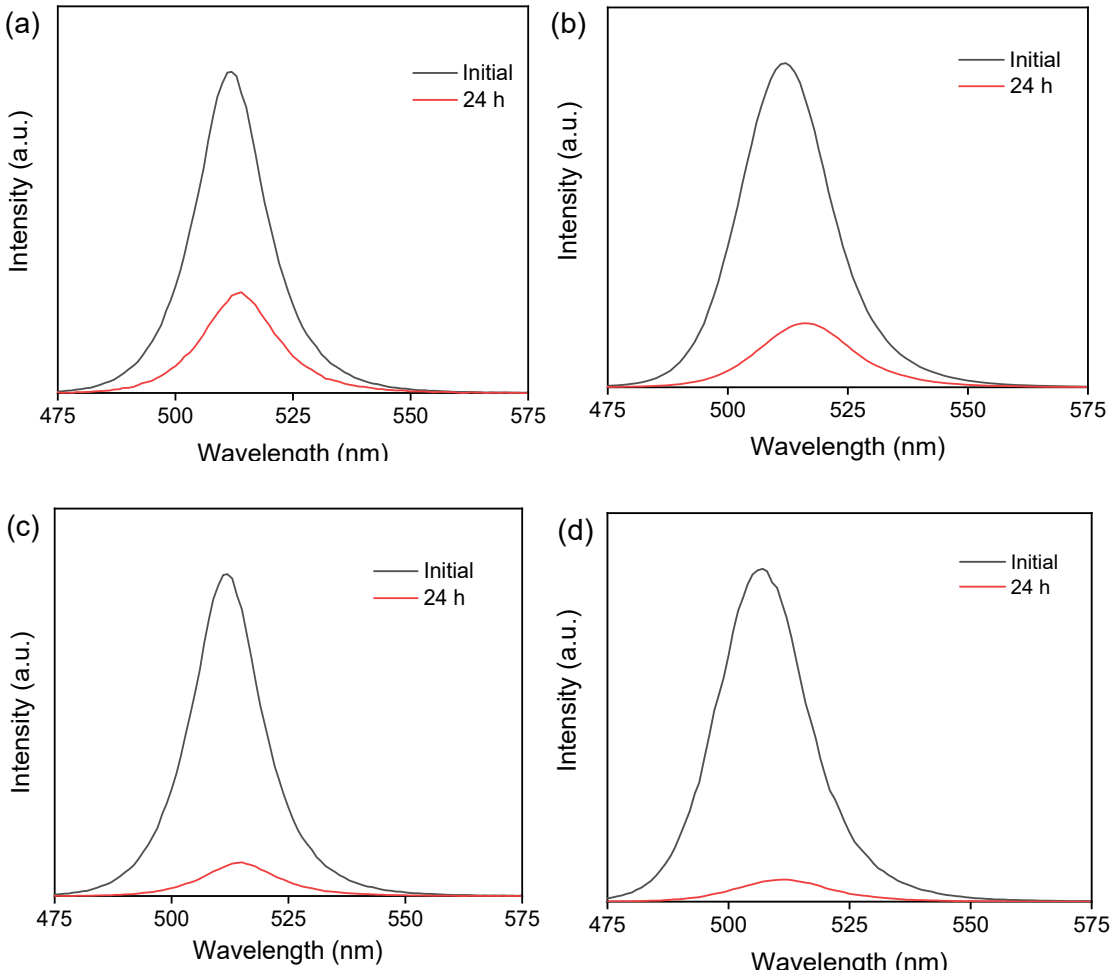


Fig. S5. PL quenching of (a) DBIA-$CsPbBr_3$, (b) NBA-$CsPbBr_3$, (c) DBHT-$CsPbBr_3$, (d) NBS-$CsPbBr_3$ in ACN and O_2 atmosphere.

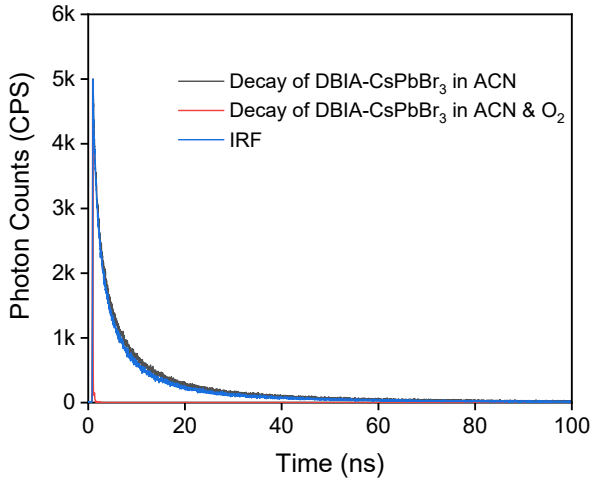


Fig. S6. PL lifetime decay of DBIA-$CsPbBr_3$ in ACN and O_2.

Table S2. Summary of fitting results for $CsPbBr_3$ perovskites.

Experiments	α_1	τ_1 (ns)	α_2	τ_2 (ns)	α_3	τ_3 (ns)	α_4	τ_4 (ns)	τ_{av} (ns)
DBIA-CPB in ACN	0.094	0.697	0.082	2.71	0.049	8.15	0.012	26.98	12.63
DBIA-CPB in ACN +O_2	0.167	0.72	0.094	2.65	0.046	7.88	0.011	24.93	10.43

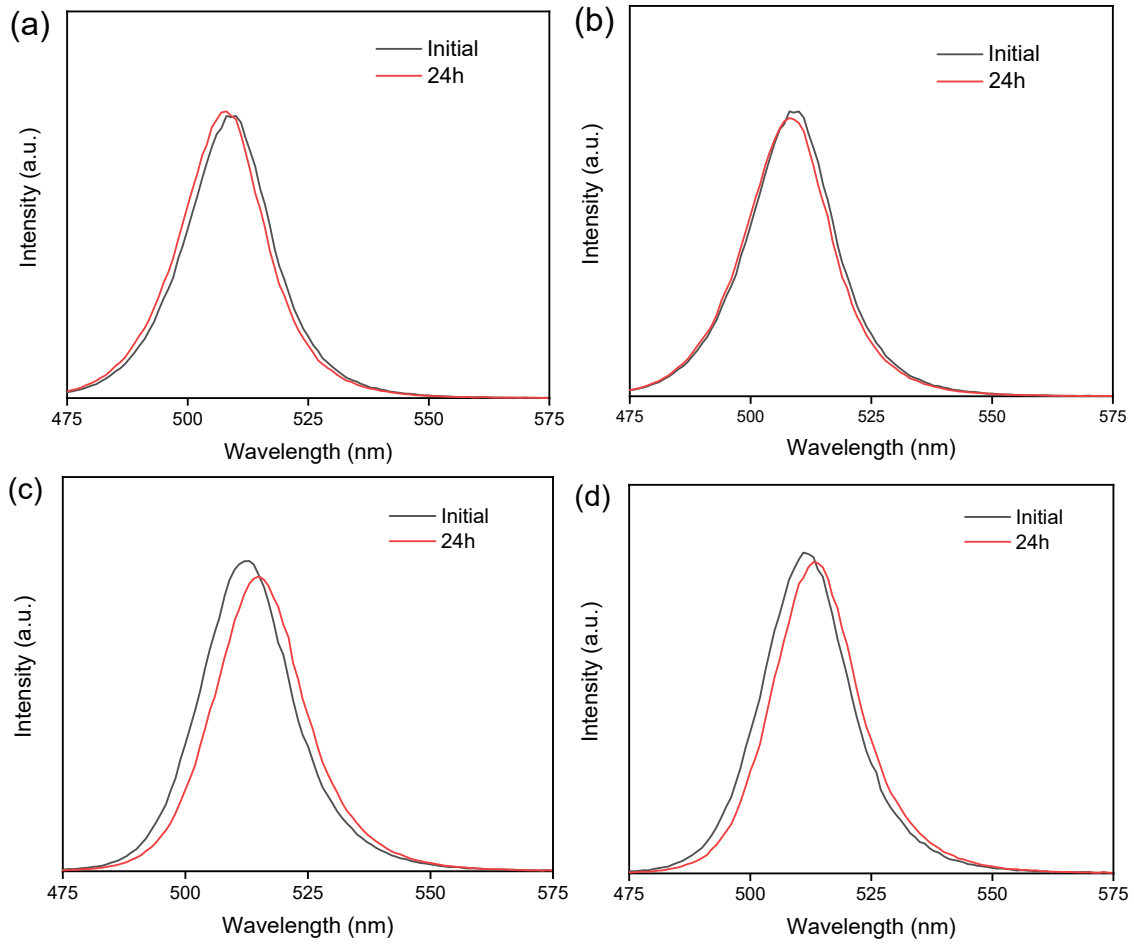


Fig. S7. PL quenching of (a) DBIA-$CsPbBr_3$, (b) NBA-$CsPbBr_3$, (c) DBHT-$CsPbBr_3$, (d) NBS-$CsPbBr_3$ in ACN and 1,3,5-Trimethoxybenzene.

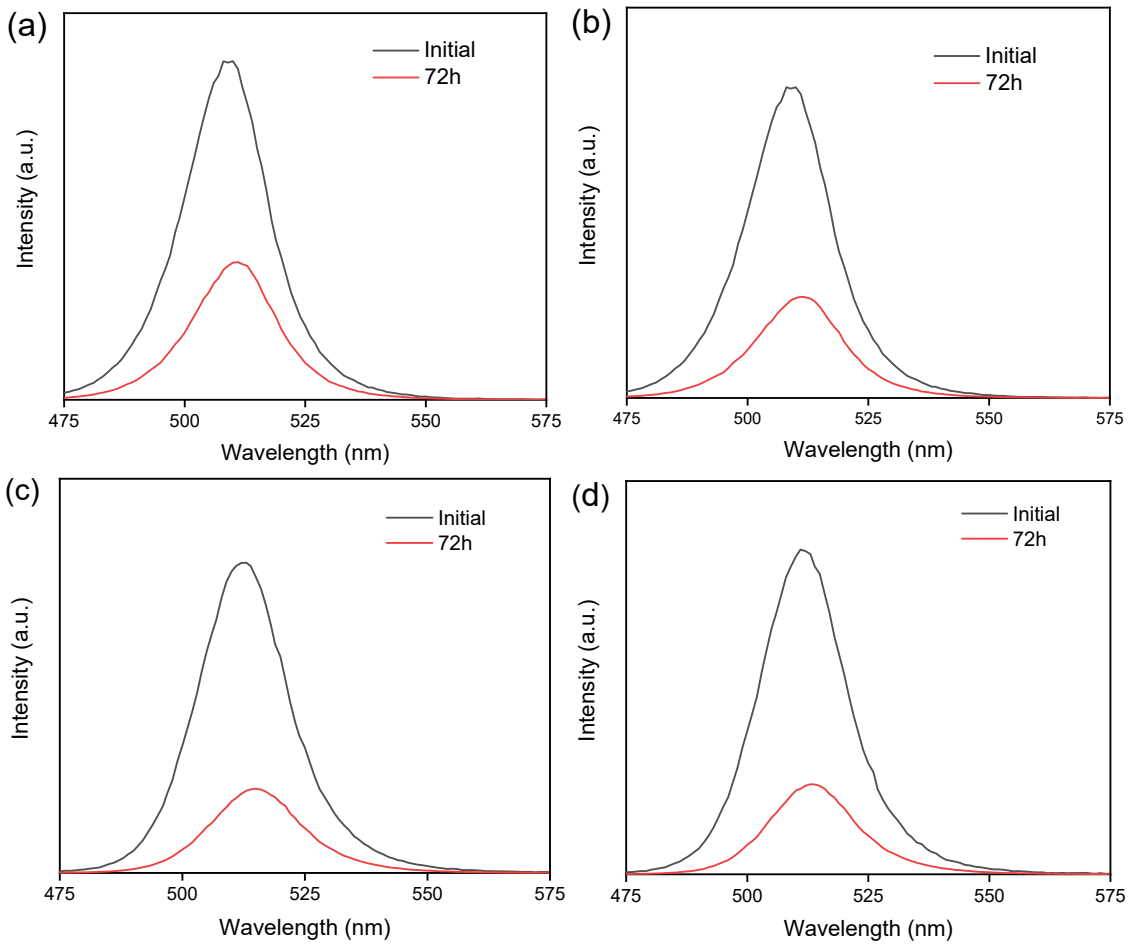


Fig. S8. PL quenching of (a) DBIA-$CsPbBr_3$, (b) NBA-$CsPbBr_3$, (c) DBHT-$CsPbBr_3$, (d) NBS-$CsPbBr_3$ in ACN and 1,3,5-Trimethoxybenzene.

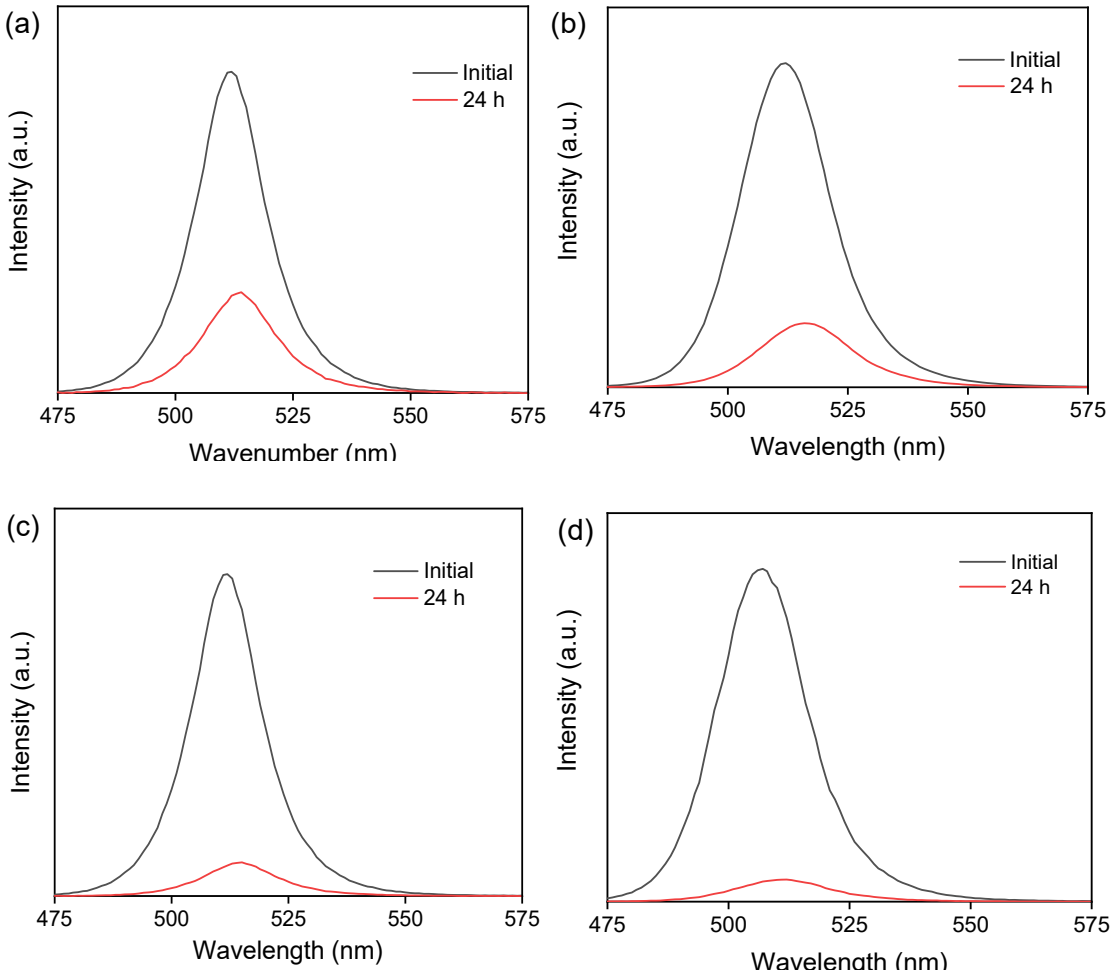


Fig. S9. PL quenching of (a) DBIA-$CsPbBr_3$, (b) NBA-$CsPbBr_3$, (c) DBHT-$CsPbBr_3$, (d) NBS-$CsPbBr_3$ in ACN, 1,3,5-Trimethoxybenzene and O_2 atmosphere.

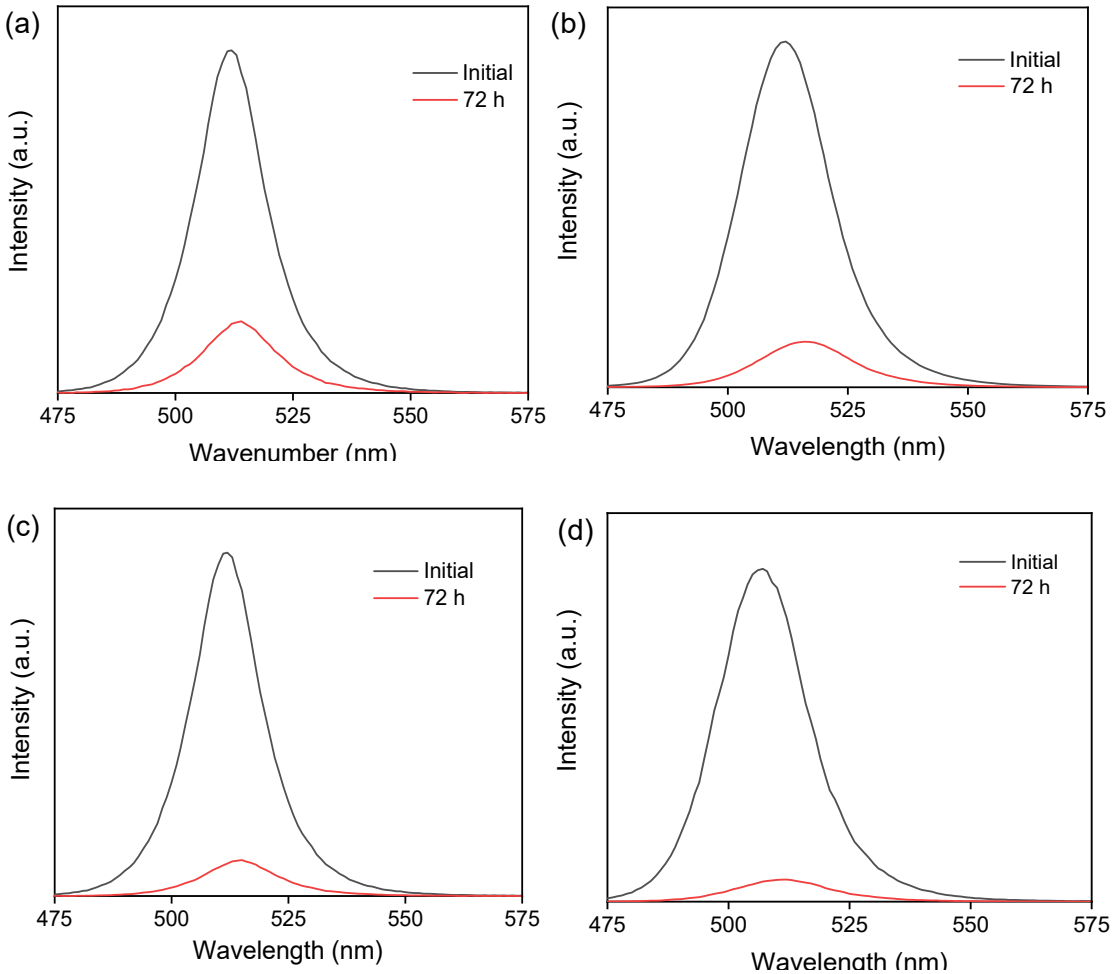


Fig. S10. PL quenching of (a) DBIA-$CsPbBr_3$, (b) NBA-$CsPbBr_3$, (c) DBHT-$CsPbBr_3$, (d) NBS-$CsPbBr_3$ in ACN, 1,3,5-Trimethoxybenzene and O_2 atmosphere.

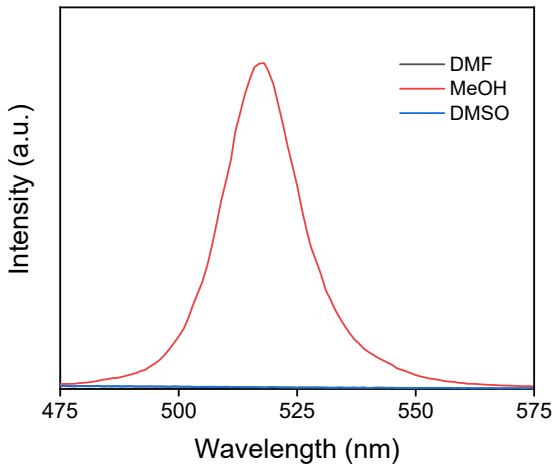


Fig. S11. Stability of $CsPbBr_3$-DBIA in different polar solvents.

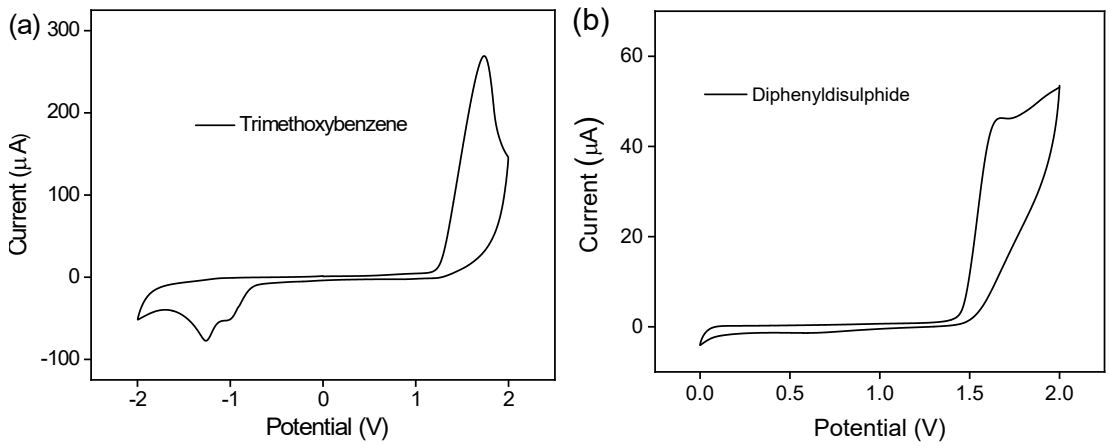


Fig. S12. Cyclic voltammetry of (a) TMB and (b) Disulphide

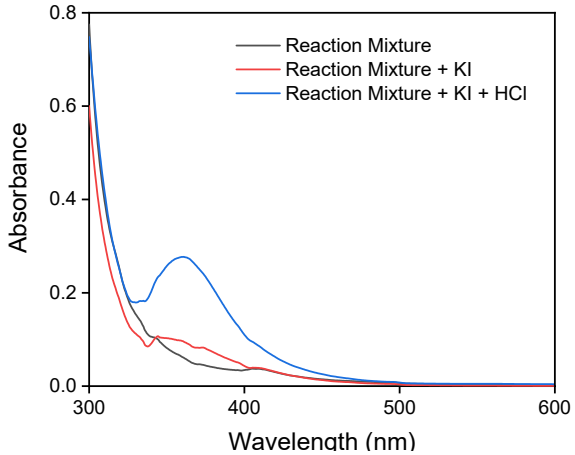


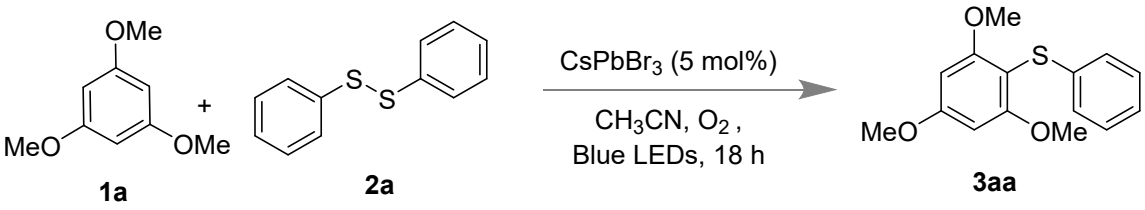
Fig. S13. UV-Vis spectroscopy for H_2O_2 generation

SYNTHESIS

Representative procedure for the preparation of Phenyl(2,4,6-trimethoxyphenyl)sulfane (3aa).

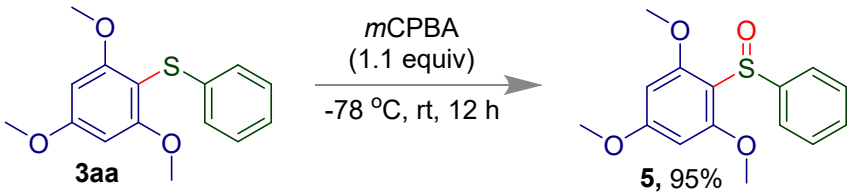
In an oven dried quartz tube 1,3,5-trimethoxybenzene **1a** (0.35 mmol, 60 mg), 1,2-diphenyldisulfane (0.43 mmol, 94 mg), and $CsPbBr_3$ (5 mol %, 0.0178 mmol) were dissolved in 2.0 mL dry acetonitrile solvent. After that, the reaction mixture was irradiated by visible light (wavelength 450-455 nm) for 18 h in the presence of an oxygen balloon. After completion of the reaction, acetonitrile was removed under reduced pressure. Then, the crude mixture was

diluted in dichloromethane (CH_2Cl_2) and extracted with brine solution. The resulting organic solution was dried over anhydrous sodium sulfate and concentrated to obtain a crude mixture which was further purified by silica−gel column chromatography using distilled ethyl acetate and hexane as the eluent to afford the pure product.



Scheme S1. Synthesis of **3aa**.

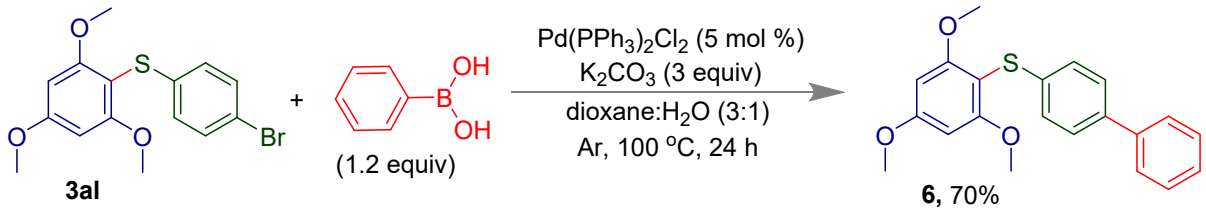
Synthetic procedure for compound 5. A 20 mL Schlenk tube holding a magnetic bar was charged with a 2 mL DCM solution of phenyl(2,4,6-trimethoxyphenyl)sulfane **3aa** (60 mg, 0.217 mmol) and *m*CPBA(41 mg, 0.24 mmol) was added under argon atmosphere and stirred at -78 °C for 12 h. After the completion of the reaction, solution was quenched with H_2O and then extracted with DCM, dried over Na_2SO_4 and concentrated in rotary evaporator. The crude mixture was further purified by column chromatography to afford 1,3,5-trimethoxy-2-(phenylsulfinyl)benzene **5** (35 mg, 67%) as a white solid.



Scheme S2. Synthesis of compound **5**

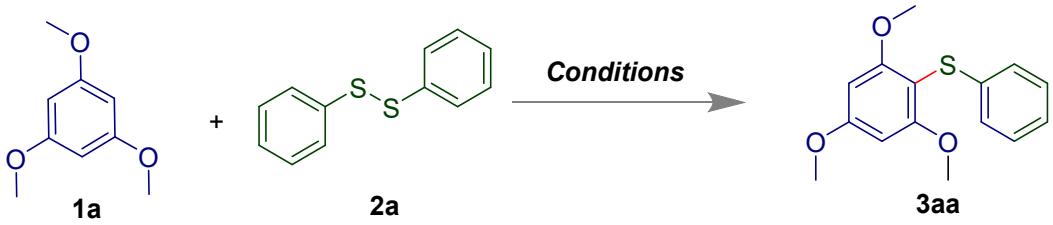
Synthetic procedure for compound 6. A 20 mL Schlenk tube holding a magnetic bar was charged with (4-bromophenyl)(2,4,6-trimethoxyphenyl)sulfane **3 al** (0.169 mmol, 60 mg), phenyl boronic acid (0.203 mmol, 25 mg), K_2CO_3 (0.507 mmol, 70 mg), and $Pd(PPh_3)_2Cl_2$ (0.08 mmol, 6 mg) in dioxane/H_2O (1.5 mL/0.5 mL) under inert atmosphere. Then the reaction

mixture was placed into a preheated oil bath at 100 °C for 24 h. After that, the crude mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated in rotary evaporator. The crude mixture was further purified by column chromatography to afford **6** (29 mg, 52%) as a white solid.



Scheme S3. Synthesis of compound **6**

Table S3. The Reaction Condition Optimization[b]



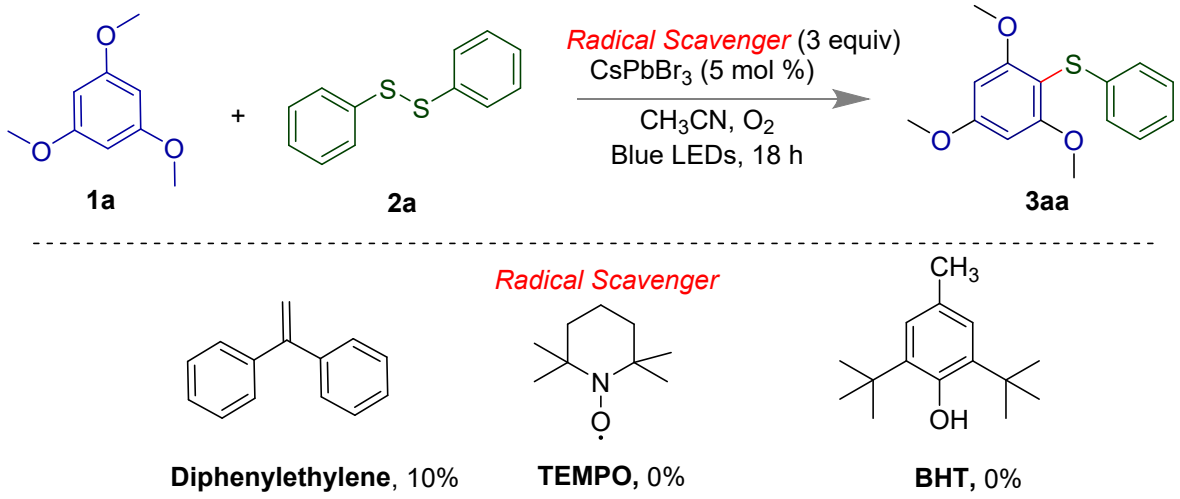
entry	2a (equiv)	$CsPbBr_3$ (mol%)	solvent	light source	yield[a] (%)
1	1.2	3 (DBIA-$CsPbBr_3$)	CH_3CN	Blue LED	75
2	1.2	3 (DBIA-$CsPbBr_3$)	DMSO	Blue LED	0
3	1.2	3 (DBIA-$CsPbBr_3$)	DMF	Blue LED	0
4	1.2	3 (DBIA-$CsPbBr_3$)	Toluene	Blue LED	0
5	1.2	3 (DBIA-$CsPbBr_3$)	THF	Blue LED	0

6	1.2	3 (DBIA-$CsPbBr_3$)	MeOH	Blue LED	30
7	1.2	3 (DBIA-$CsPbBr_3$)	DCE	Blue LED	70
8	0.6	3 (DBIA-$CsPbBr_3$)	CH_3CN	Blue LED	40
9	0.6	5 (DBIA-$CsPbBr_3$)	CH_3CN	Blue LED	50
10	1.2	5 (DBIA-$CsPbBr_3$)	CH_3CN	Blue LED	80
11	1.2	5 (DBIA-$CsPbBr_3$)	CH_3CN	Blue LED	88[c]
12	1.2	5 (NBA-$CsPbBr_3$)	CH_3CN	Blue LED	75
13	1.2	5 (DBHT-$CsPbBr_3$)	CH_3CN	Blue LED	51
14	1.2	5 (NBS-$CsPbBr_3$)	CH_3CN	Blue LED	57
16	1.2	5 (DBIA-$CsPbBr_3$)	CH_3CN	Blue LED	25 [d]

[a]Isolated yields after column chromatography, [b]Reaction conditions: **1a** (60 mg, 0.35 mmol), **2a** (94 mg, 0.43 mmol) and $CsPbBr_3$ (5 mol%) in 1.5 mL of CH_3CN for 18 h, [c]In dry CH_3CN, [d]Reaction under normal air condition.

Radical trapping experiment with TEMPO/BHT/Diphenylethelene. In an oven dried quartz tube 1,3,5-trimethoxybenzene **1a** (0.35 mmol, 60 mg), 1,2-diphenyldisulfane **2a** (0.43 mmol, 94 mg), and $CsPbBr_3$ (5 mol %, 0.0178 mmol) were dissolved in 2.0 mL dry acetonitrile (ACN) solvent and TEMPO (1.07 mmol, 167 mg) were dissolved in 1.0 mL dry acetonitrile (ACN) solvent. After that, the reaction mixture was irradiated by Blue LEDs light for 18 h in the presence of an oxygen balloon. The reaction was monitored by TLC. After the reaction time, no desired product was found. The same experiment was carried out using BHT (235 mg,

1.07 mmol) and 1,1-diphenylethylene (193 mg, 1.07 mmol). However, the addition of BHT led to no product formation whereas diphenylethylene reduced the yield of the product **3aa** giving only 10% (5 mg).



Scheme S4. Various radical scavengers under standard condition.

Crystal measurement

Crystals of compound **3ah** was achieved after slow evaporation of $CHCl_3$ and water mixture (1:0.5). The crystals data were collected with Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Mo-Kα radiation, λ = 0.71073 Å). ORTEP drawing of the compound **3ah** show ellipsoid contour at the 50% probability level.

Compound 3ah (CCDC 2205394)

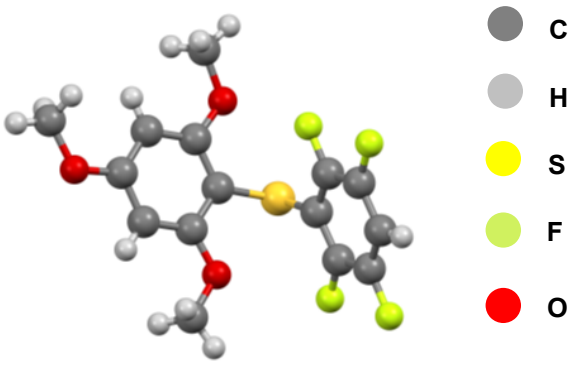


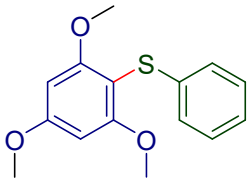
Fig. S14. Crystal structure of **3ah** (CCDC 2205394). Ellipsoids are drawn at the 50% probability level.

Crystallographic Data for (3ah)

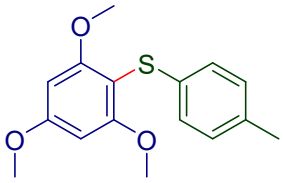
Empirical formula	$C_{15}H_{12}F_4O_3S$
Formula weight	348.31
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.9500(4)
b/Å	9.8071(6)
c/Å	11.6221(5)
α/°	90.667(4)
β/°	105.074(4)

γ/°	107.794(5)
Volume/Å3	724.72(7)
Z	2
ρcalcg/cm^3	1.596
μ/mm^{-1}	0.280
F(000)	356.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
Reflections collected	13243
Independent reflections	3515 [R_{int} = 0.0378, R_{sigma} = 0.0319]
Goodness-of-fit on F2	0.992
Final R indexes [I>=2σ (I)]	R_1 = 0.0313, wR_2 = 0.0803
Final R indexes [all data]	R_1 = 0.0356, wR_2 = 0.0827
Largest diff. peak/hole / e Å^{-3}	0.36/-0.31

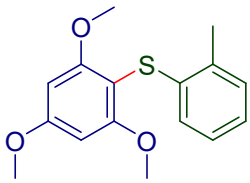
CHARATERIZATION DATA



Phenyl(2,4,6-trimethoxyphenyl)sulfane (3aa): R_f = 0.45 (5% ethyl acetate in hexane); white solid; yield 88% (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.13 (m, 2H), 7.05-7.01 (m, 3H), 6.22 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.1, 162.7, 138.8, 128.6, 125.8, 124.5, 98.9, 91.3, 56.4 , 55.6.



***p*-Tolyl(2,4,6-trimethoxyphenyl)sulfane (3ab):[1]** R_f = 0.5 (5% ethyl acetate in hexane); white solid; yield 91% (95 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98-6.93 (m, 4H), 6.21 (s, 2H), 3.86 (s, 3H), 3.81 (s, 6H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9, 162.6, 135.1, 134.2, 129.4, 126.1, 99.5, 91.3, 56.4, 55.5, 21.0.



***o*-Tolyl(2,4,6-trimethoxyphenyl)sulfane (3ac):[2]** R_f = 0.45 (5% ethyl acetate in hexane); white solid; yield 89% (92 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.08 (m, 1H), 6.97-6.91 (m, 2H), 6.59- 6.56 (m, 1H), 6.23

(s, 2H), 3.88 (s, 3H), 3.80 (s, 6H), 2.46 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.1, 162.7, 137.7, 134.84, 129.8, 126.1, 124.6, 124.2, 98.5, 91.4, 56.4, 55.5, 20.1.

(4-Methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane(3ad):[2] R_f = 0.55 (10% ethyl acetate in hexane); white solid; yield 94% (105 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.07-7.06 (m, 2H), 6.74-6.72 (m, 2H), 6.19 (s, 2H), 3.85 (s, 3H), 3.81 (s, 6H), 3.74 (s, 3H); $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) δ 162.7, 162.4, 157.6, 129.3, 128.68, 114.3, 100.7, 91.3, 56.4, 55.5, 55.4.

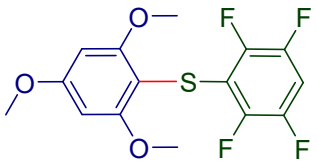
(2-Methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane (3ae):[2] R_f = 0.55 (10% ethyl acetate in hexane); white solid; yield 92% (100 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.02-7.00 (m, 1H), 6.80-6.79 (m, 1H), 6.72-6.70 (m, 1H), 6.48-6.47 (m, 1H), 6.23 (s, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.79 (s, 6H); $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) δ 163.1, 163, 155.6, 127.3, 124.9, 124.8, 120.9, 109.9, 97.4, 91.3, 56.4, 55.7, 55.5.

(4-Fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3af):[2] R_f = 0.5 (5% ethyl acetate in hexane); white solid; yield 72% (76 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.03-7.01 (m, 2H), 6.87-6.85 (m, 2H), 6.20 (s, 2H), 3.86 (s, 3H), 3.81 (s, 6H); $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) δ 163, 162.4, 160.88 (d, J = 243.2 Hz), 133.72 (d, J = 3.0 Hz), 127.97 (d, J = 7.7 Hz), 115.63 (d, J = 22.0 Hz), 99.4, 91.3, 56.4, 55.5.

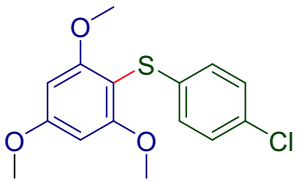
(2-Fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3ag): R_f = 0.4 (5% ethyl acetate in hexane); white solid; yield 69% (73 mg); mp 115-118 ºC; ^{1}H NMR (700

MHz, $CDCl_3$) δ 7.05-6.96 (m, 2H), 6.89-6.87 (m, 1H), 6.68-6.65 (m, 1H), 6.22 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 163.2, 162.8, 159.60 (d, J = 243.6 Hz), 127.42 (d, J = 2.7 Hz), 126.10 (d, J = 16.7 Hz), 125.81 (d, J = 7.4 Hz), 124.17 (d, J = 3.4 Hz), 115.16 (d, J = 21.2 Hz), 96.9, 91.4, 56.4, 55.5; IR (KBr) ῡ 2967, 2940, 1582, 815; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{15}FO_3SNa$ 317.0607; found 317.0624.

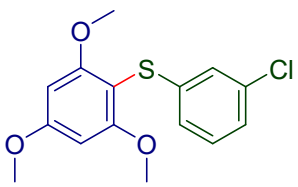
(2,3,5,6-Tetrafluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3ah): R_f = 0.4 (5% ethyl acetate in hexane); white solid; yield 68% (85 mg); mp 102-104 ºC; ^1H NMR (700 MHz, $CDCl_3$) δ 6.92-6.87 (m, 1H), 6.12 (s, 2H), 3.82 (s, 9H); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 162.7, 161.6, 146.9(m), 146.30 (m), 145.5(m), 144.9 (m), 117.4, 104.3(m), 98.0, 91.0, 56.1, 55.3; IR (KBr) ῡ 2916, 2847, 2359, 1584, 709; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{12}F_4O_3SNa$ 371.0341; found 371.0319.

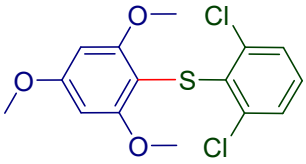


(4-Chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3ai):[1] R_f = 0.4 (5% ethyl acetate in hexane); white solid; yield 77% (85 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2H), 6.90-6.89 (m, 2H), 6.23 (s, 2H), 3.89 (s, 3H), 3.82 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 162.5, 138.2, 131.5, 127.4, 117.9, 98.2, 91.3, 56.4, 55.6.



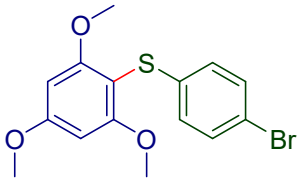
(3-Chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3aj):[2] R_f = 0.45 (5% ethyl acetate in hexane); white solid; yield 75% (82 mg); ^1H NMR (700 MHz, $CDCl_3$) δ 7.09-7.06 (m, 1H), 7.00-6.99 (m, 1H), 6.93-6.92 (m, 2H), 6.22 (s, 2H), 3.88 (s, 3H), 3.81 (s, 6H). $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 163.4, 162.6, 141.2, 134.5, 129.6, 125.2, 124.6, 123.8, 97.7, 91.4, 56.4, 55.6.



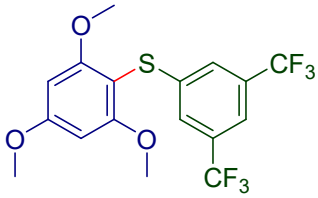


(2,6-Dichlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3ak): R_f = 0.4 (5% ethyl acetate in hexane); white solid; yield 65% (80 mg); mp 85-90 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.27-7.26 (m, 2H), 7.06-7.03 (m, 1H), 6.10 (s, 2H), 3.80 (s, 3H), 3.73 (s, 6H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 161.8, 160.9, 139.2, 134.4, 128.4, 128.1, 101.5, 91.3, 56.1, 55.4; IR (KBr) ῡ 2921, 2848, 2360, 1582, 731; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{14}Cl_2O_3SNa$ 366.9859; found 366.9838.

(4-Bromophenyl)(2,4,6-trimethoxyphenyl)sulfane(3al):[1] R_f = 0.45 (5% ethyl acetate in hexane); white solid; yield 79% (100 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.10 (m, 2H), 6.95-6.94 (m, 2H), 6.21 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 163.1, 162.4, 137.4, 130.0, 128.5, 126.9, 98.3, 91.2, 56.3, 55.4.

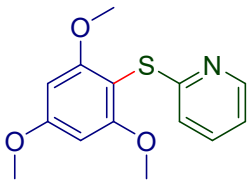


(4-(Trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane(3am):[3] R_f = 0.5 (5% ethyl acetate in hexane); white solid; yield 61% (75 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38-7.37 (m, 2H), 7.06-7.05 (m, 2H), 6.23 (s, 2H), 3.89 (s, 3H), 3.81 (s, 6H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 163.6, 162.7, 144.3, 127.6, 126.3, 125.4 (q, J = 3.7 Hz), 125.2, 97.1, 91.4, 56.5, 55.6.

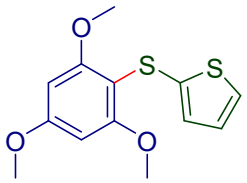


(3,5-Bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (3an): R_f = 0.4 (5% ethyl acetate in hexane); white solid; yield 57% (84 mg); mp 88-91 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38 (s, 2H), 6.24 (s,

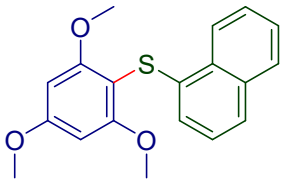
2H), 3.90 (s, 3H), 3.81 (s, 6H); $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) δ 163.9, 162.5, 142.7, 131.7 (q, J = 33.1 Hz), 125.3, 124.2, 122.6, 118.0 (q, J = 3.7 Hz), 95.9, 91.5, 56.4, 55.6; IR (KBr) ῡ 2918, 2850, 2360, 1582, 736; HRMS (ESI/Q-TOF) m/z: [M]$^+$ calcd for $C_{17}H_{14}F_6O_3S$ 412.0568; found 412.0562.



2-((2,4,6-Trimethoxyphenyl)thio)pyridine (3ao): R_f = 0.6 (30% ethyl acetate in hexane); white solid; yield 50% (49 mg); mp 120-125 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.35 (m, 1H), 7.38-7.34 (m, 1H), 6.92-6.88 (m, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.23 (s, 2H), 3.87 (s, 3H), 3.80 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 162.5, 161.9, 149.4, 136.2, 119.5, 119.0, 97.9, 91.4, 56.4, 55.6; IR (KBr) ῡ 2920, 2848, 2364, 1582, 761; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO_3S$ 278.0851; found 278.0828.



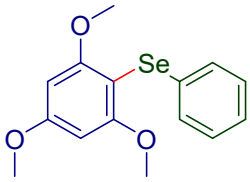
2-((2,4,6-Trimethoxyphenyl)thio)thiophene (3ap):[4] R_f = 0.5 (5% ethyl acetate in hexane); white solid; yield 48% (49 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.15 (m, 1H), 7.12-7.10 (m, 1H), 6.86-6.85 (m, 1H), 6.14 (s, 2H), 3.88 (s, 6H), 3.82 (s, 3H); $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) δ 162.8, 161.9, 137.2, 130.6, 127.2, 126.9, 102.8, 91.2, 56.3, 55.5.



Naphthalen-1-yl(2,4,6-trimethoxyphenyl)sulfane(3aq):[1] R_f = 0.45 (5% ethyl acetate in hexane); white solid; yield 75% (87 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.46 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 6.84 (d, J = 7.3 Hz, 1H), 6.25 (s, 2H), 3.89 (s, 3H), 3.79 (s, 6H);

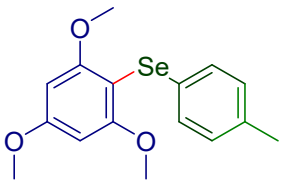
$^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) δ 163.18, 162.8, 135.8, 133.8, 131.2, 128.3, 126.0, 125.8, 125.7, 125.0, 124.6, 122.5, 98.3, 91.5, 56.4, 55.5.

Phenyl(2,4,6-trimethoxyphenyl)selane (3as):[5] R_f = 0.5 (5% ethyl acetate in hexane); white



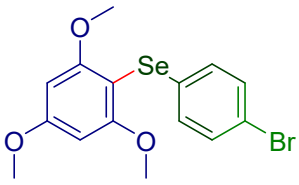
solid; yield 79% (91 mg); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.21-7.19 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.09-7.07 (m, 1H), 6.21 (s, 2H), 3.86 (s, 3H), 3.78 (s, 6H); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 163.2, 162.2, 133.8, 129.2, 128.8, 125.4, 97.7, 91.5, 56.4, 55.6.

***p*-Tolyl(2,4,6-trimethoxyphenyl)selane (3at):**[6] R_f = 0.5 (5% ethyl



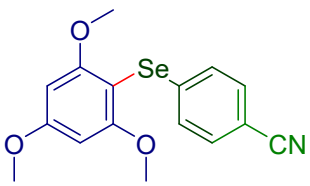
acetate in hexane); white solid; yield 60% (72 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.20 (s, 2H), 3.86 (s, 3H), 3.79 (s, 6H), 2.25 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.9, 162.0, 135.2, 129.7, 129.6, 129.3, 97.7, 91.2, 56.4, 55.5, 21.1.

(4-Bromophenyl)(2,4,6-trimethoxyphenyl)selane (3au):[6] R_f = 0.5 (5% ethyl acetate in



hexane); white solid; yield 56% (80 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 161.9, 132.8, 131.8, 130.5, 119.2, 96.7, 91.3, 56.4, 55.6.

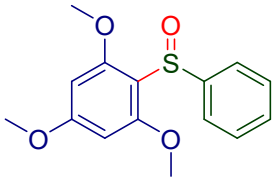
4-((2,4,6-Trimethoxyphenyl)selanyl)benzonitrile (3av): R_f = 0.5 (10% ethyl acetate in



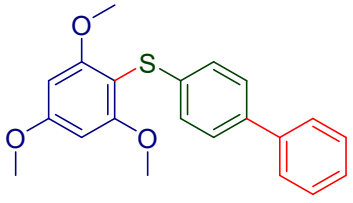
hexane); white solid; yield 85% (106 mg); mp 121-125 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.23 (s, 2H), 3.89 (s, 3H), 3.79 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100

MHz, $CDCl_3$) δ 163.8, 162.1, 142.4, 132.1, 128.3, 119.4, 108.3, 95.1, 91.3, 56.5, 55.6; IR (KBr) ῡ 3006, 2927, 1581, 1227, 821; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}NO_3Se$ 350.0323; found 350.0348.

1,3,5-Trimethoxy-2-(phenylsulfinyl)benzene (5):[7] R_f = 0.5 (40% ethyl acetate in hexane);

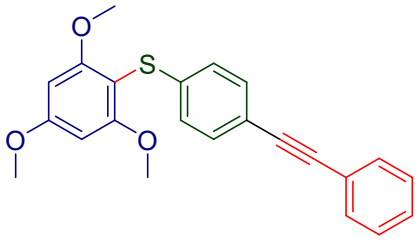


white solid; yield 95% (60 mg); ^1H NMR (700 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 2H), 7.38-7.36 (t, J = 7.6 Hz, 2H), 7.33-7.31 (t, J = 7.2 Hz, 1H), 6.04 (s, 2H), 3.79 (s, 3H), 3.67 (s, 6H); $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 165.2, 161.5, 145.4, 129.0, 128.1, 124.3, 112.8, 91.3, 56.0, 55.6.



[1,1'-Biphenyl]-4-yl(2,4,6-trimethoxyphenyl)sulfane (6):[8] R_f = 0.5 (5% ethyl acetate in hexane); white solid; yield 70% (42 mg); ^1H NMR (700 MHz, $CDCl_3$) δ 7.33-7.26 (m, 6H), 7.05-7.03 (m, 3H), 6.22 (s, 2H), 3.88 (s, 3H), 3.81 (s, 6H); $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 163.1, 162.7, 137.7, 137.1, 131.4, 126.9, 126.59, 126.58, 126.5, 126.1, 98.7, 91.4, 56.5, 55.6.

(4-(Phenylethynyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (7): R_f = 0.5 (5% ethyl acetate



in hexane); white solid; yield 75% (48 mg); mp 127-131 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.32-7.26 (m, 5H), 6.98-6.96 (m, 2H), 6.23 (s, 2H), 3.89 (s, 3H), 3.81 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 162.6, 139.9, 131.8, 131.6, 128.4, 128.2, 125.4, 123.6, 119.0, 98.0, 91.4, 89.7, 89.2, 56.5, 55.6; IR

(KBr) ῡ 3100, 2928, 1589, 1226, 728; HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{20}O_3SNa$ 399.1031; found 399.1048.

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NMR SPECTRA

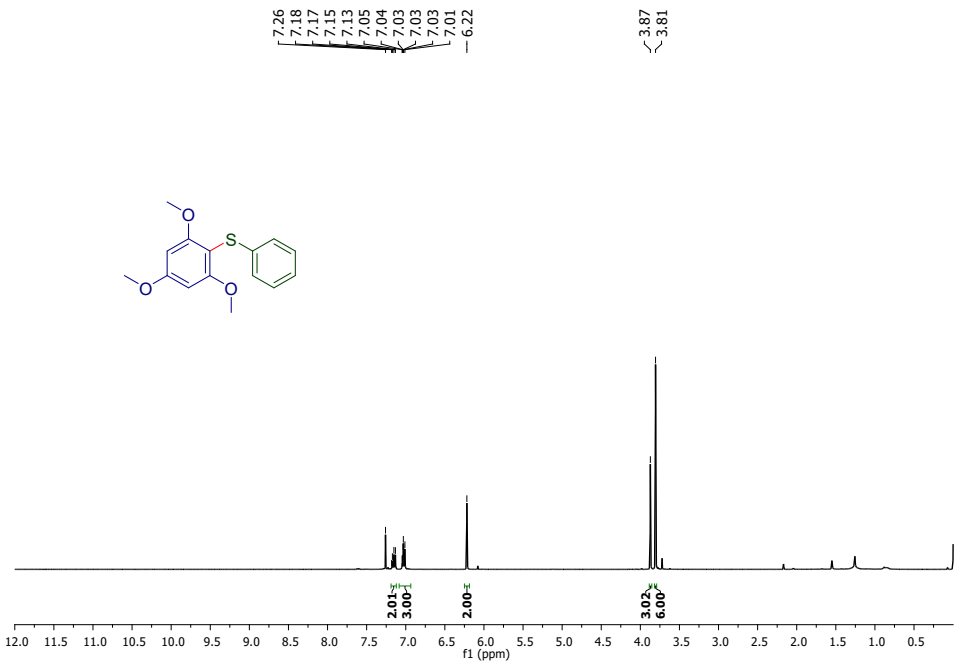


Fig. S15. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of phenyl(2,4,6-trimethoxyphenyl)sulfane (**3aa**)

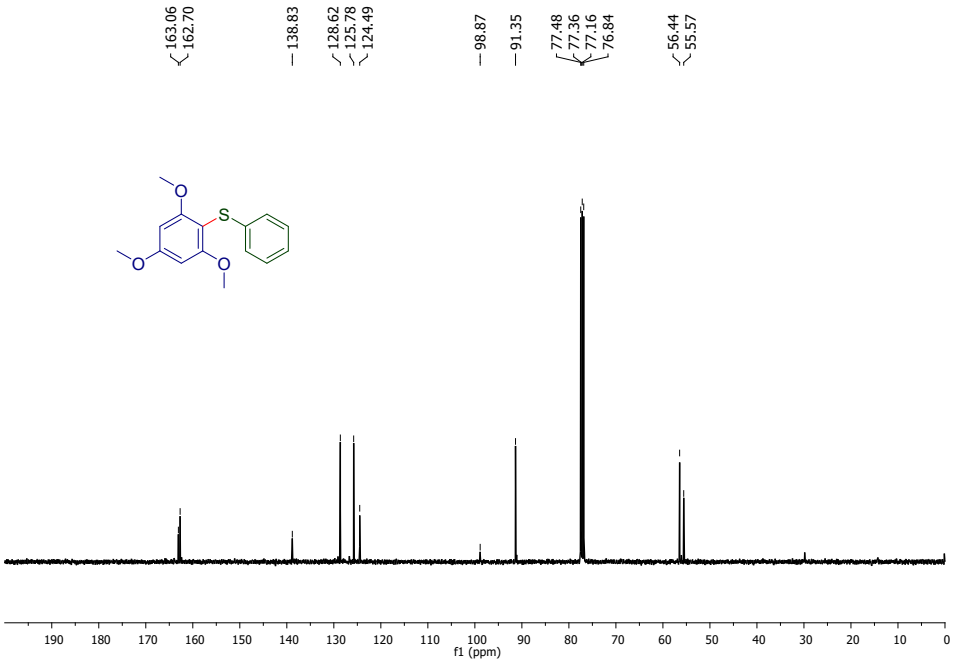


Fig. S16. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of phenyl(2,4,6-trimethoxyphenyl)sulfane (**3aa**)

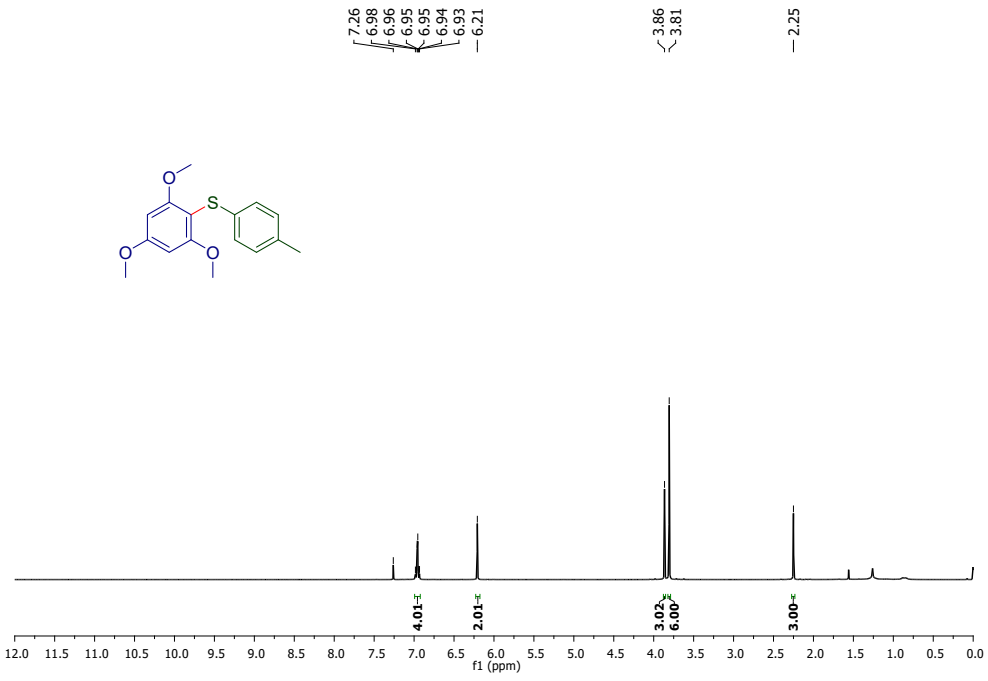


Fig. S17. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of p-tolyl(2,4,6-trimethoxyphenyl)sulfane (**3ab**)

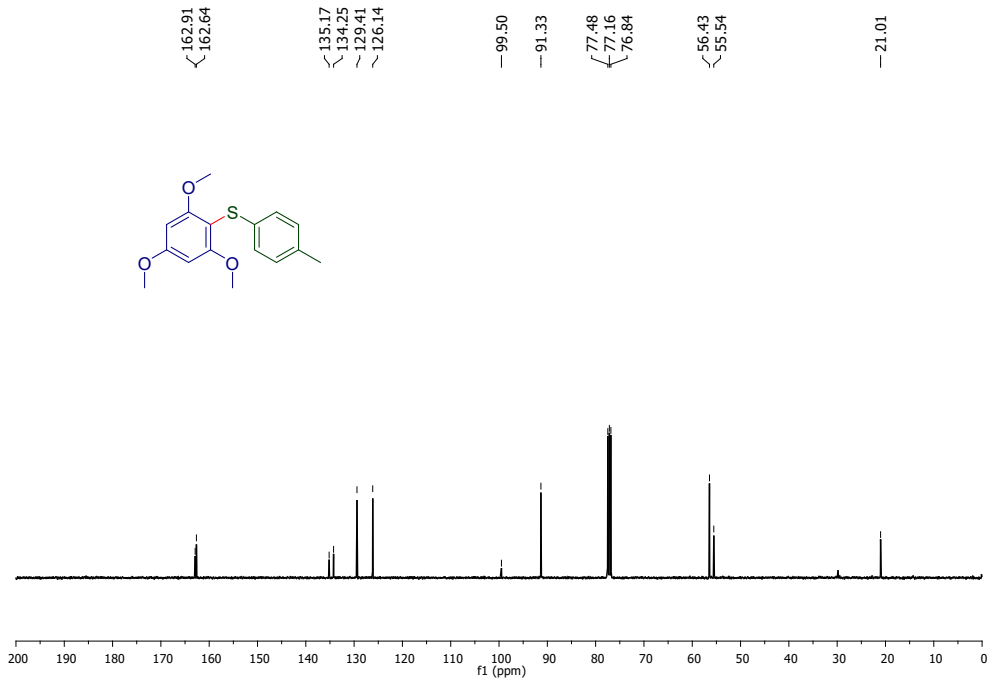


Fig. S18. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of p-tolyl(2,4,6-trimethoxyphenyl)sulfane (**3ab**)

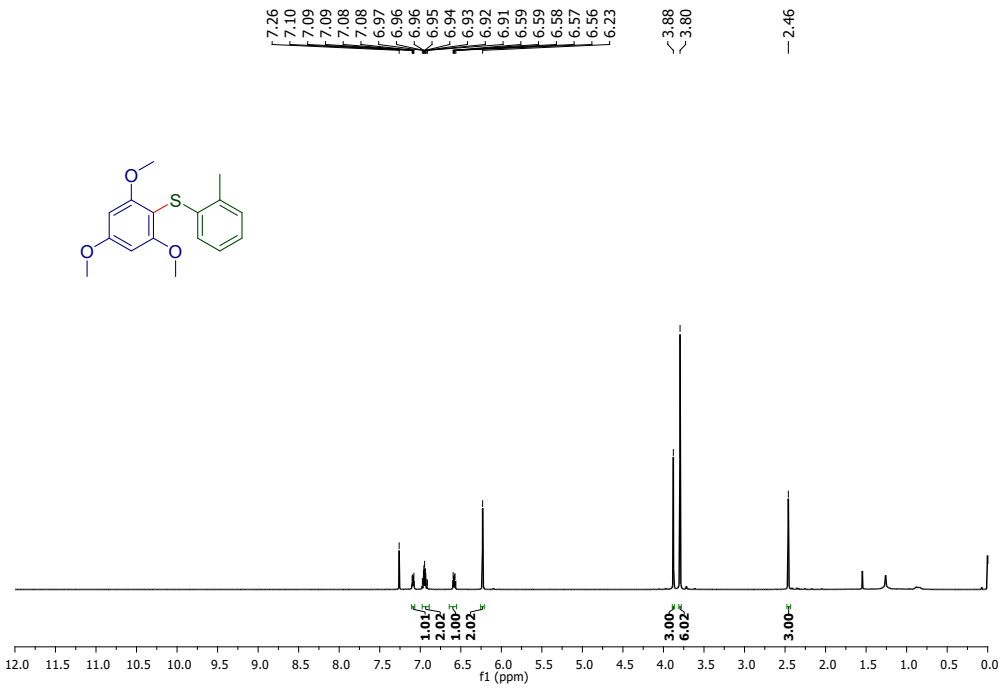


Fig. S19. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of o-tolyl(2,4,6-trimethoxyphenyl)sulfane (**3ac**)

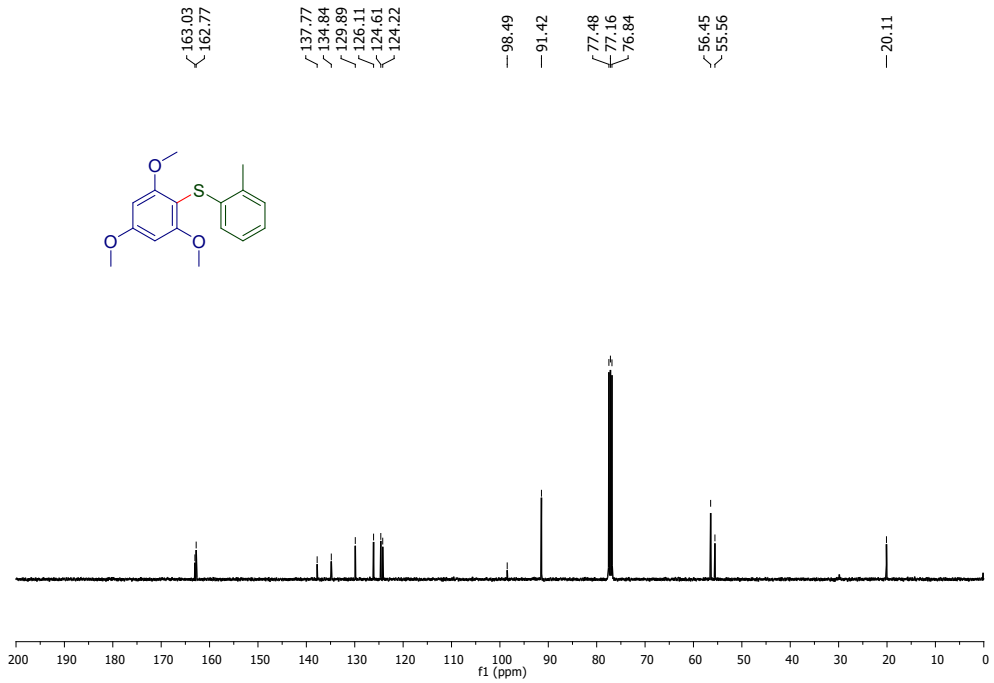


Fig. S20. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of o-tolyl(2,4,6-trimethoxyphenyl)sulfane (**3ac**)

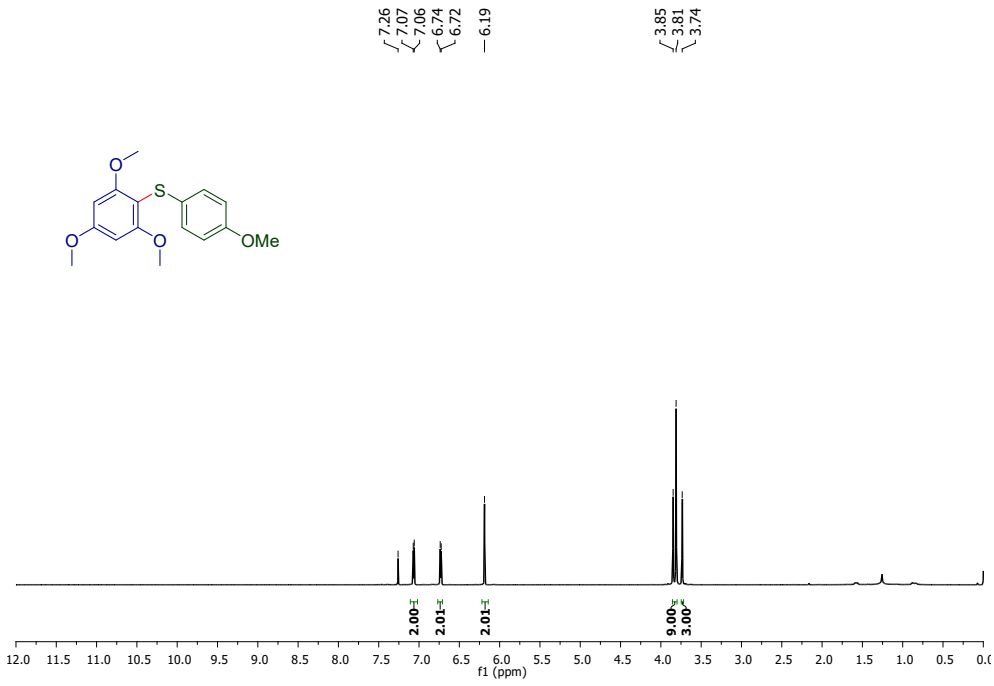


Fig. S21. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (4-methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ad**)

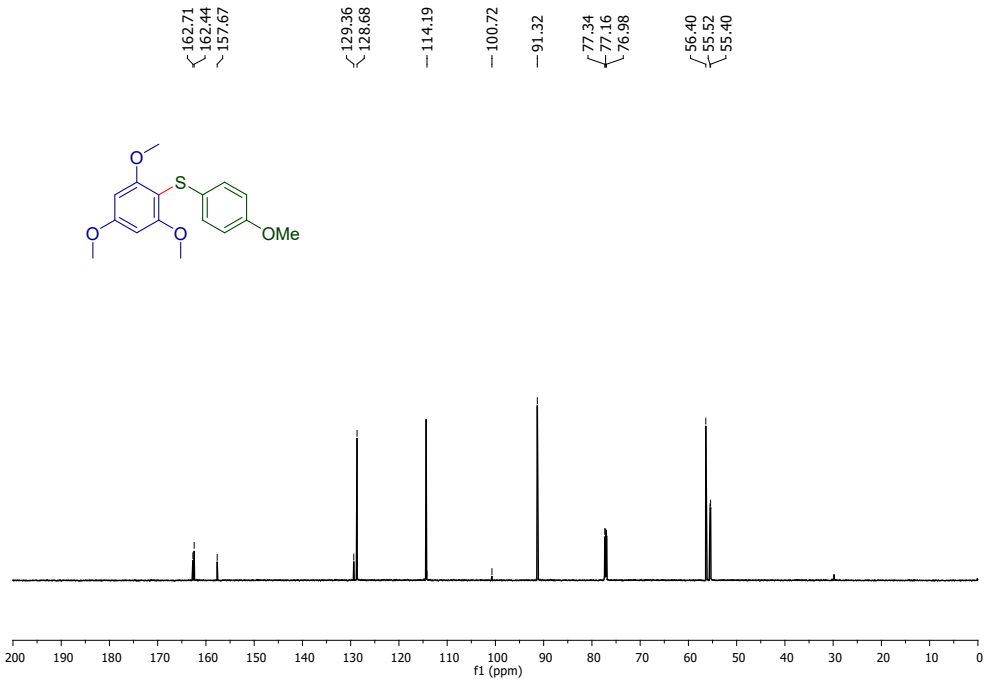


Fig. S22. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (4-methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ad**)

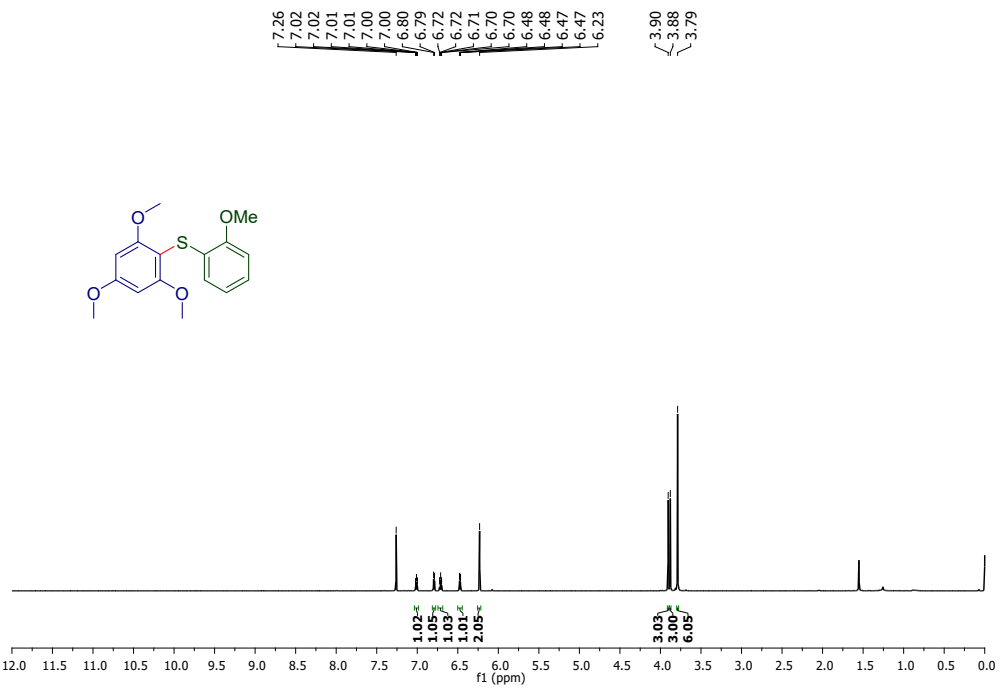


Fig. S23. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (2-methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ae**)

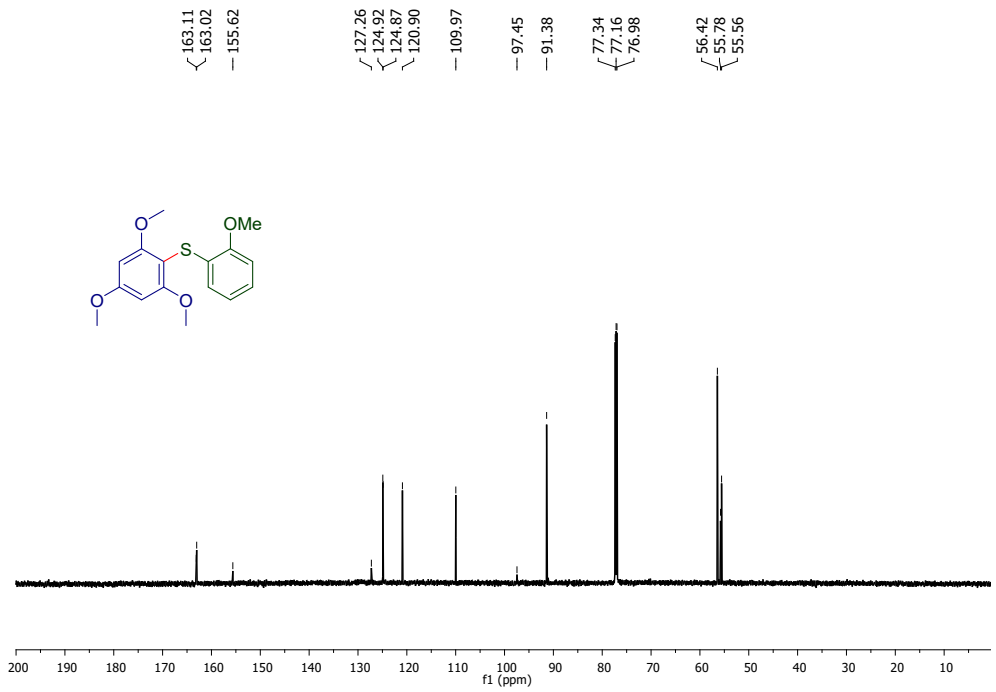


Fig. S24. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (2-methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ae**)

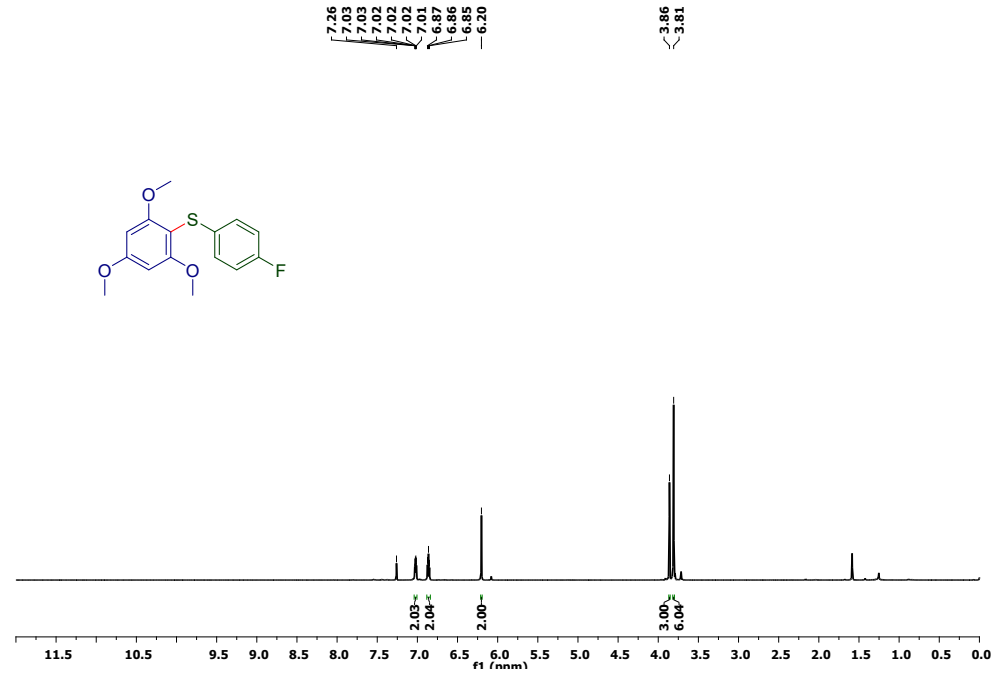


Fig. S25. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (4-fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3af**)

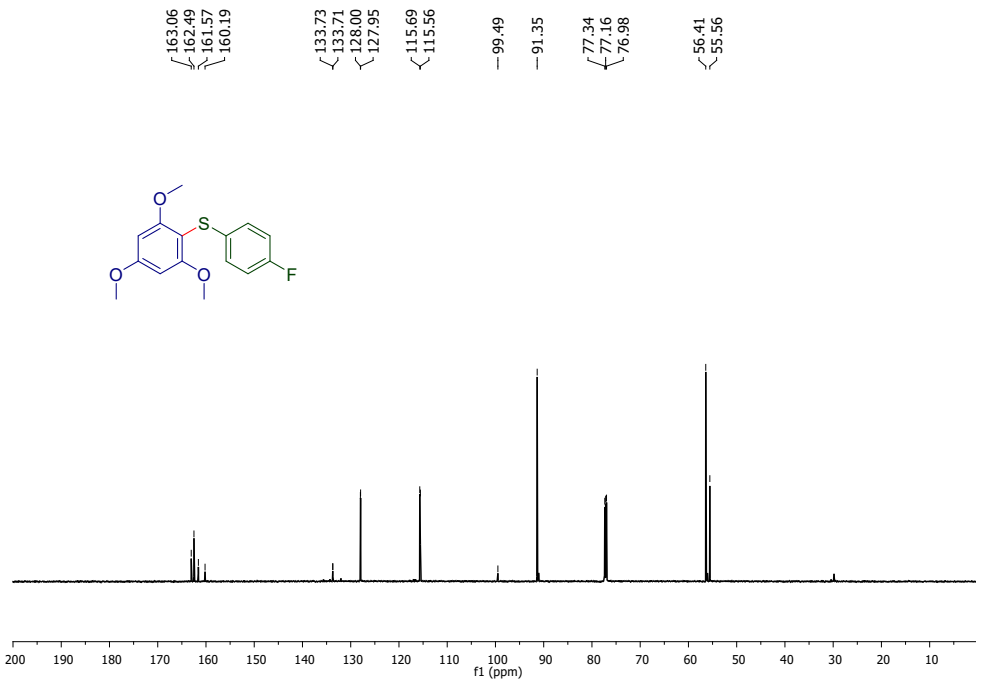


Fig. S26. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (4-fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3af**)

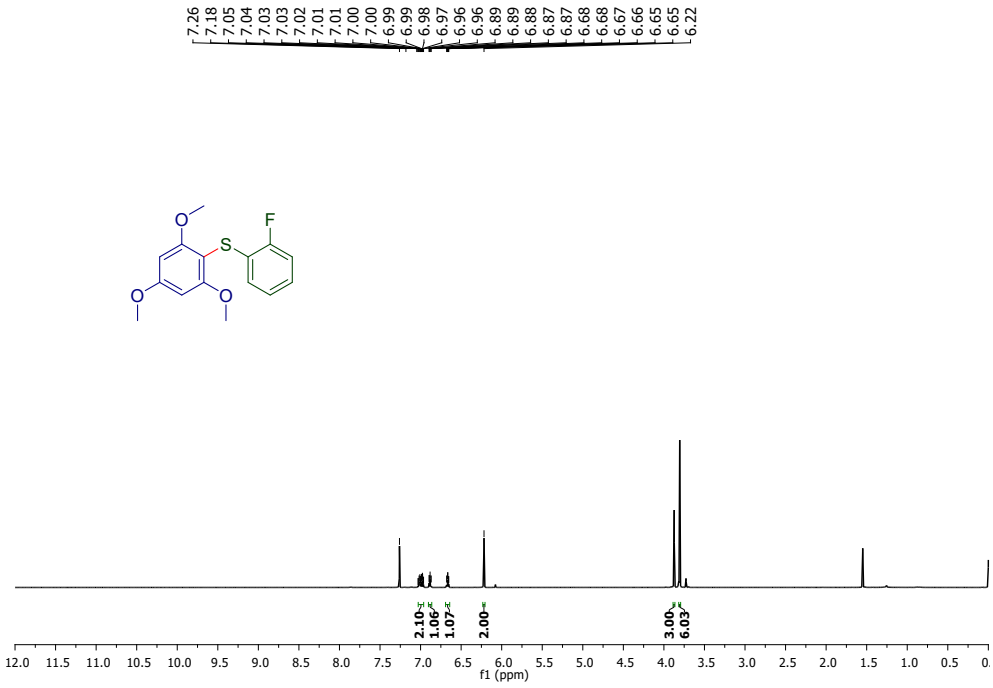


Fig. S27. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (2-fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ag**)

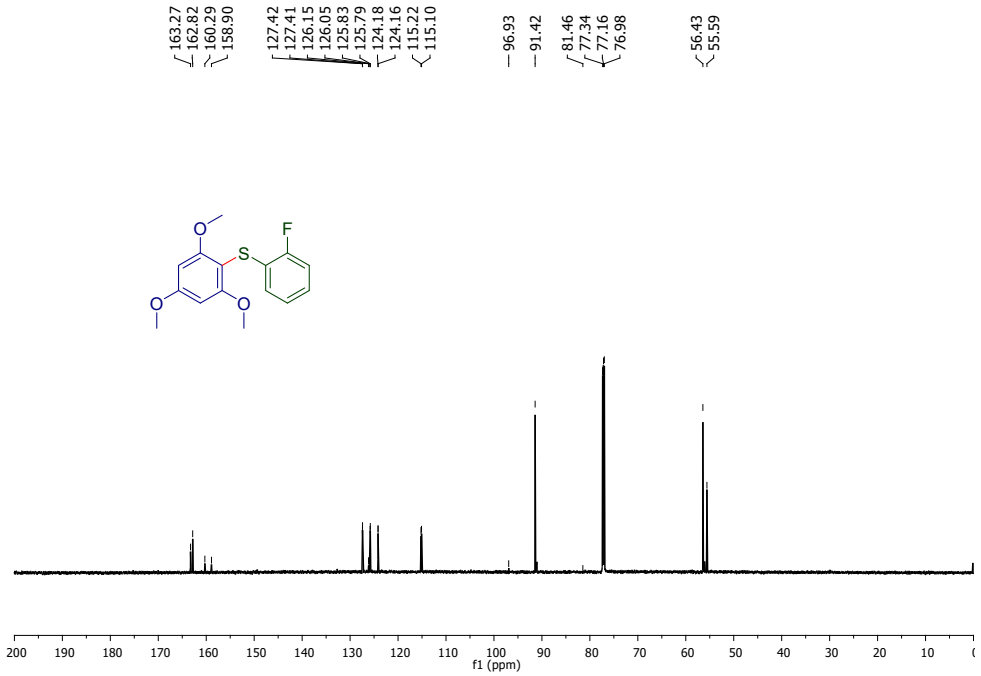


Fig. S28. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (2-fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ag**)

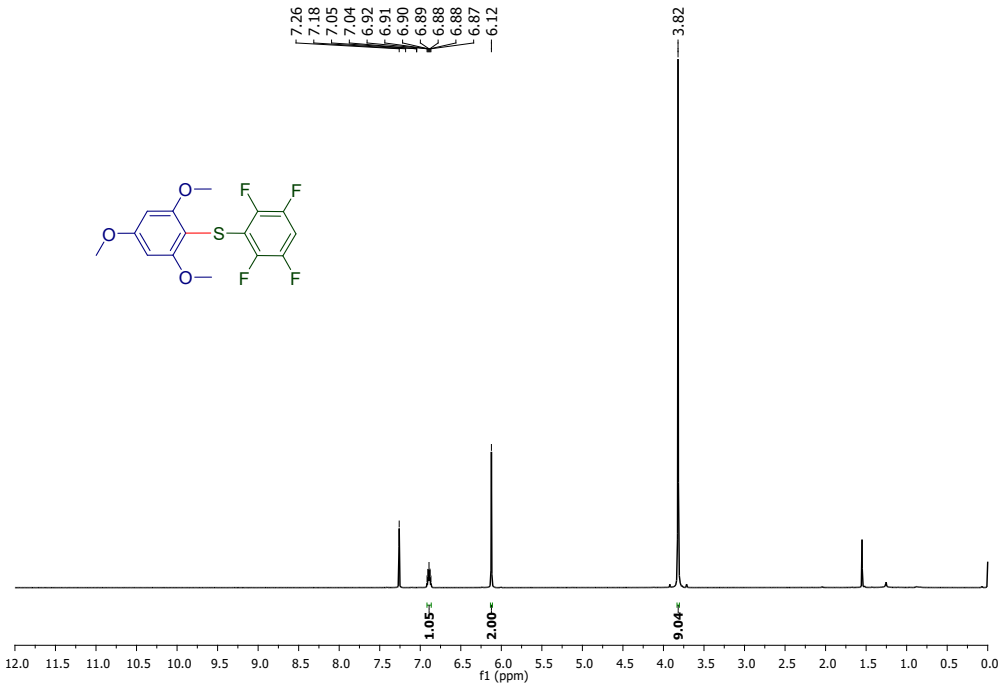


Fig. S29. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (2,3,5,6-tetrafluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ah**)

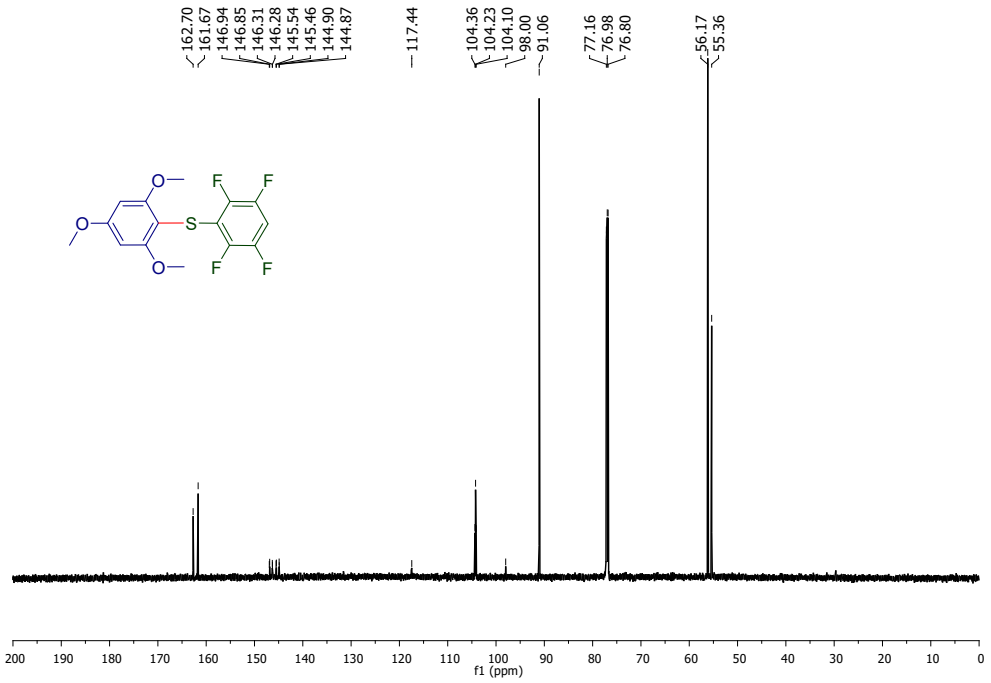


Fig. S30. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (2,3,5,6-tetrafluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ah**)

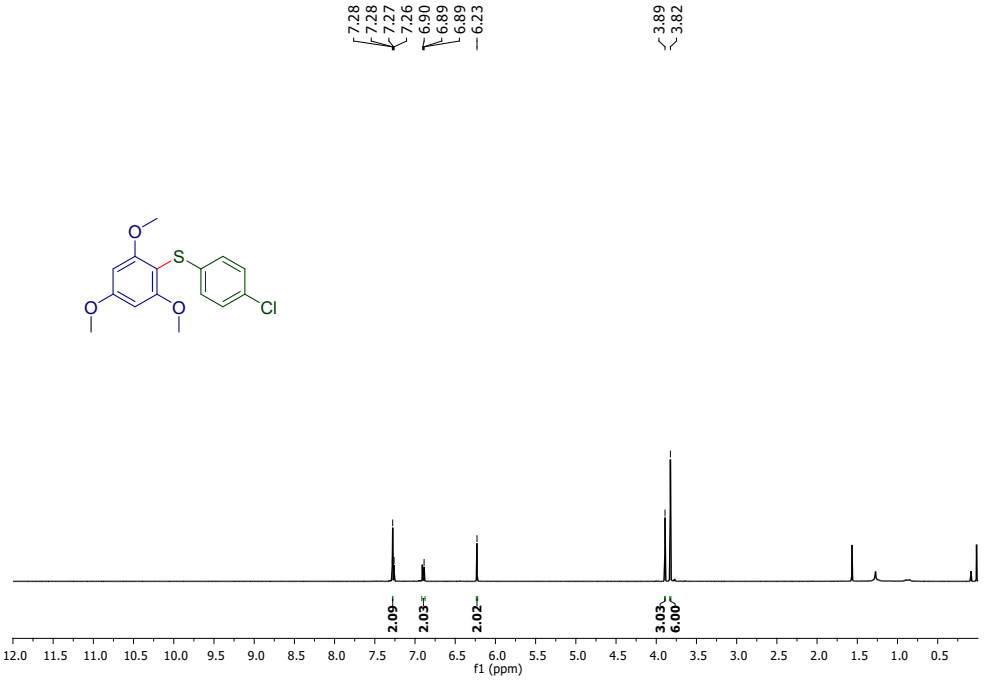


Fig. S31. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (4-chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ai**)

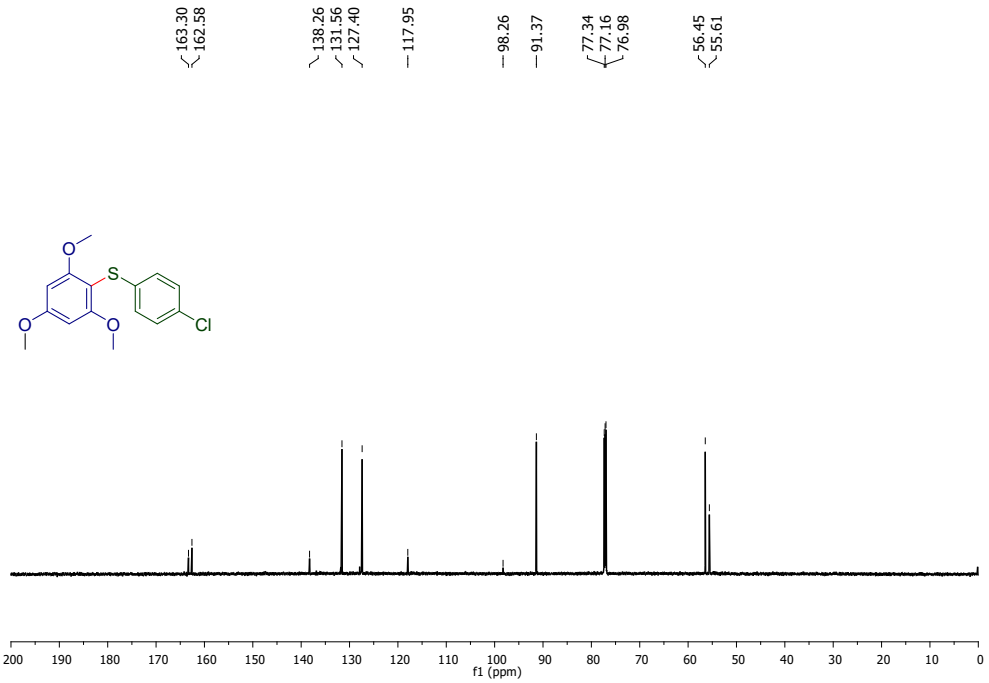


Fig. S32. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (4-chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ai**)

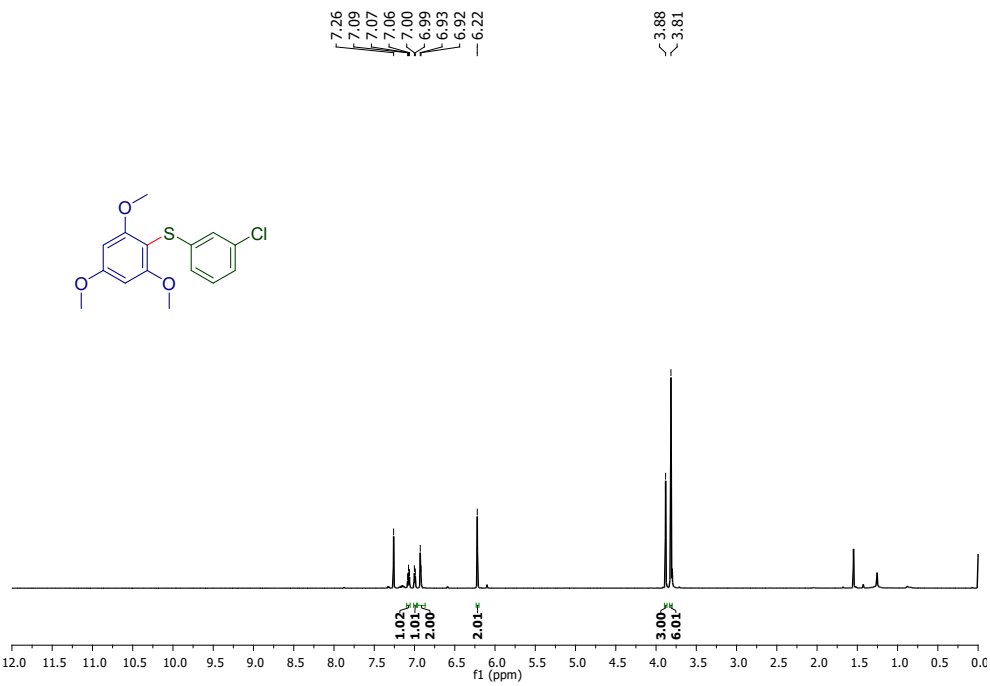


Fig. S33. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (3-chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3aj**)

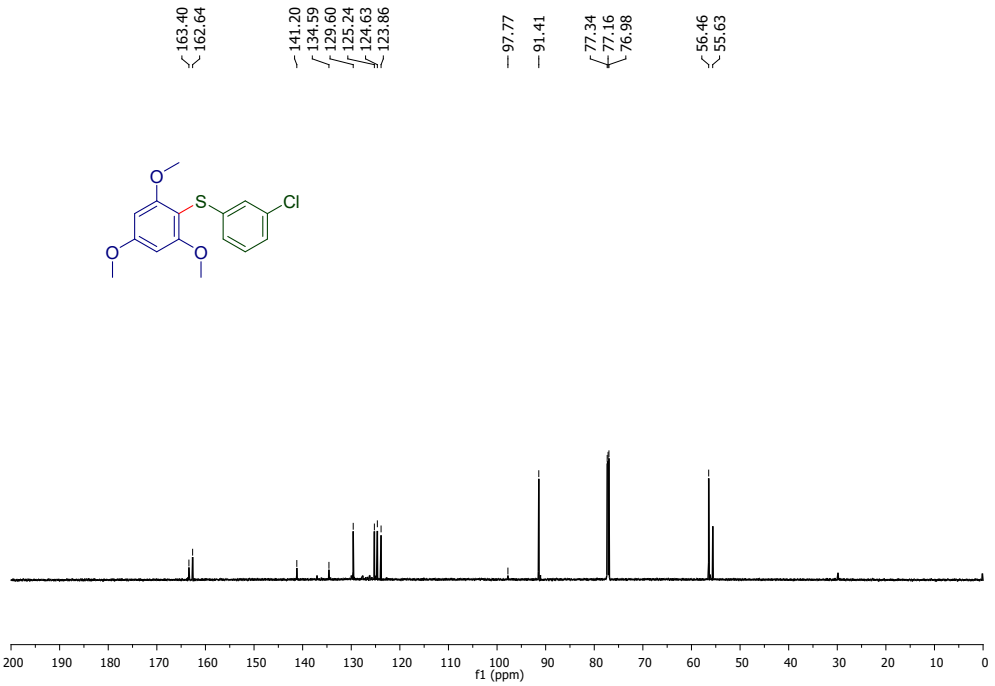


Fig. S34. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (3-chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3aj**)

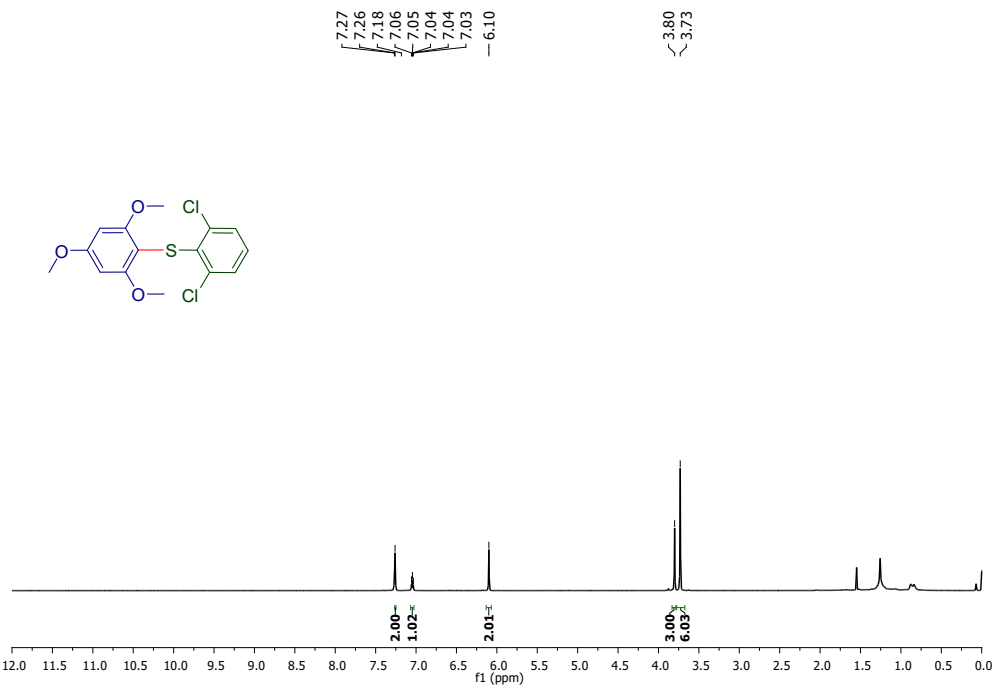


Fig. S35. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (2,6-dichlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ak**)

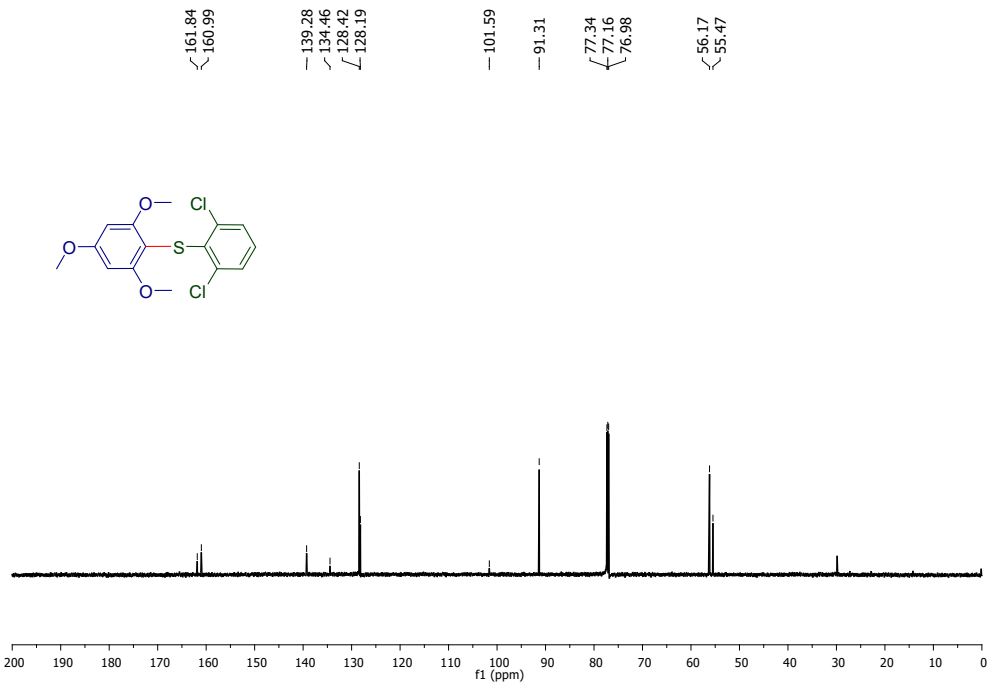


Fig. S36. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (2,6-dichlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3ak**)

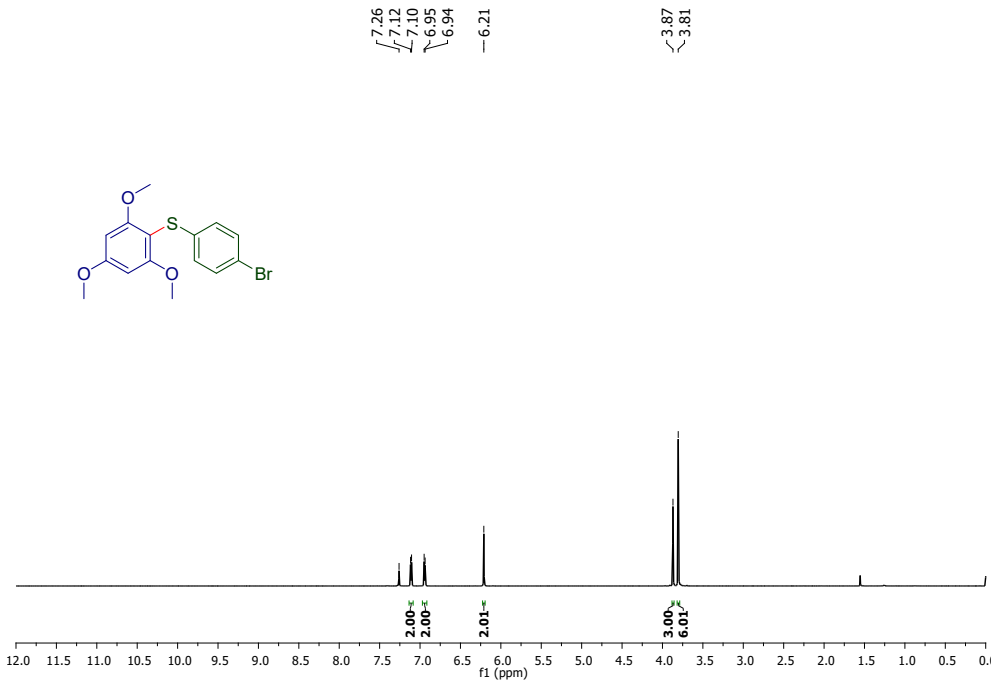


Fig. S37. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (4-bromophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3al**)

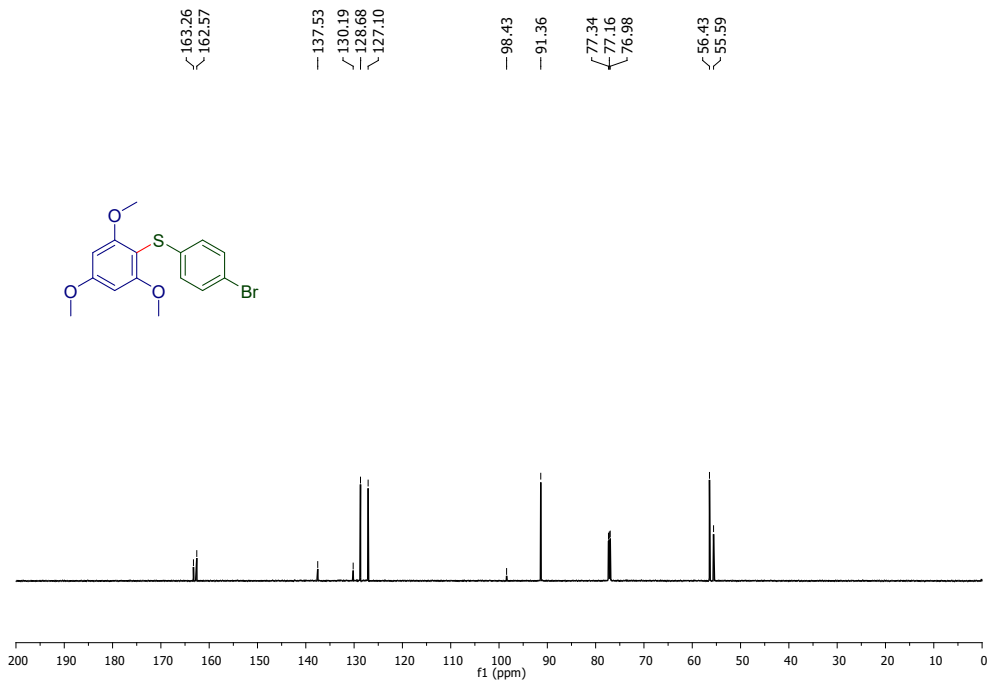


Fig. S38. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (4-bromophenyl)(2,4,6-trimethoxyphenyl)sulfane (**3al**)

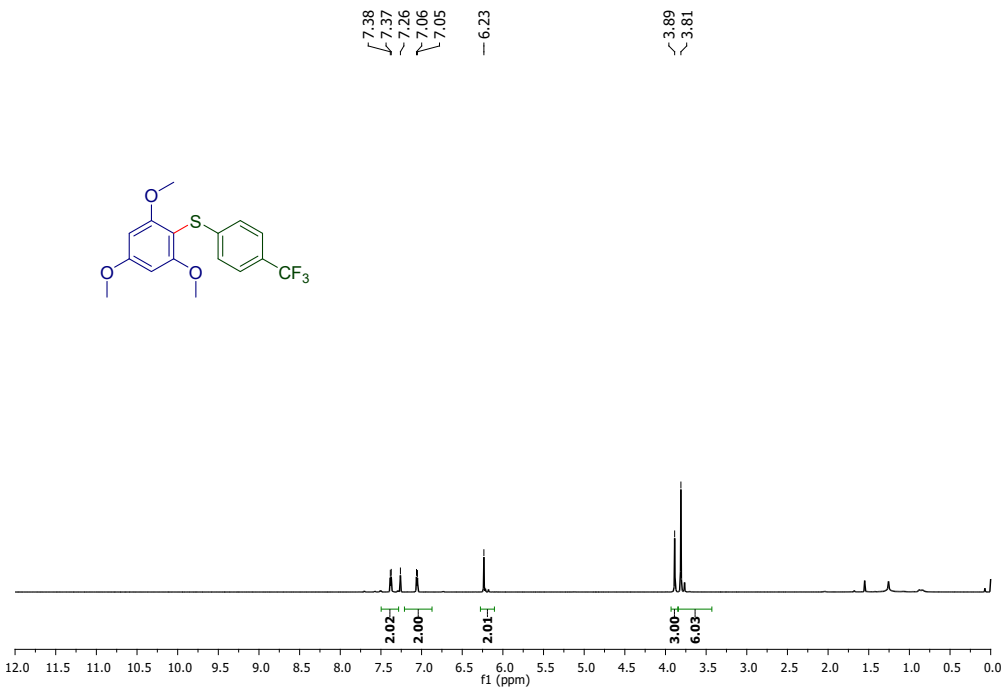


Fig. S39. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (4-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (**3am**)

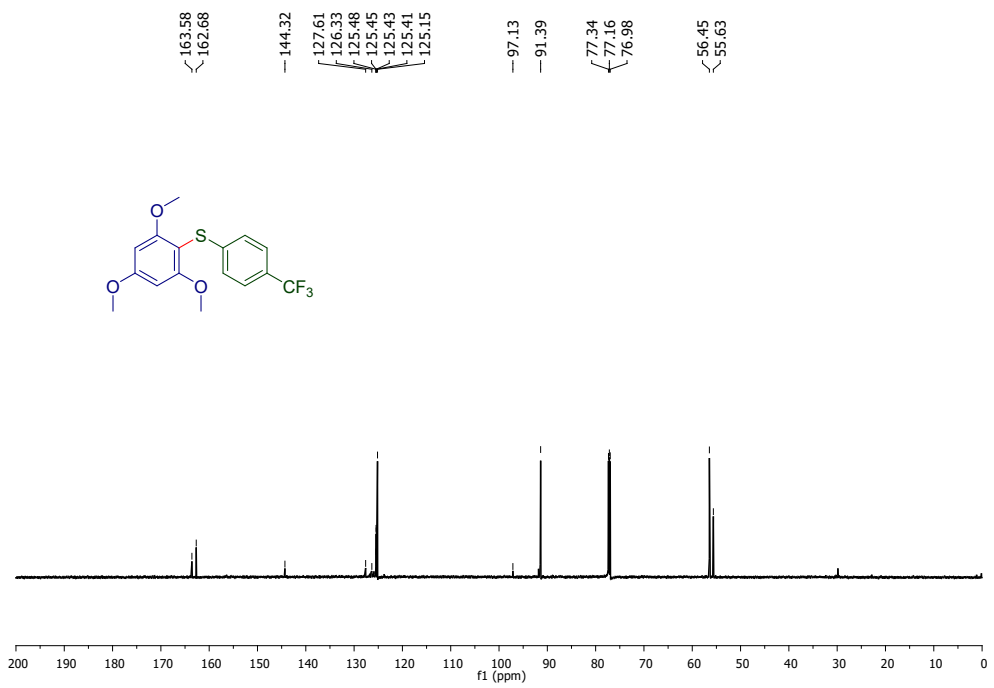


Fig. S40. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (4-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (**3am**)

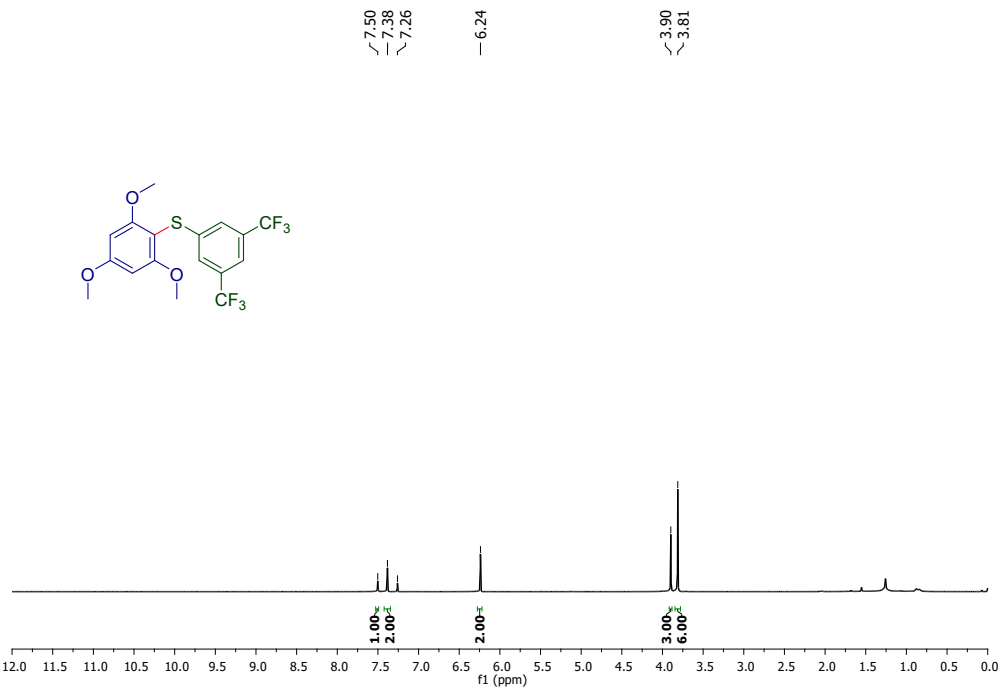


Fig. S41. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of (3,5-bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (**3an**)

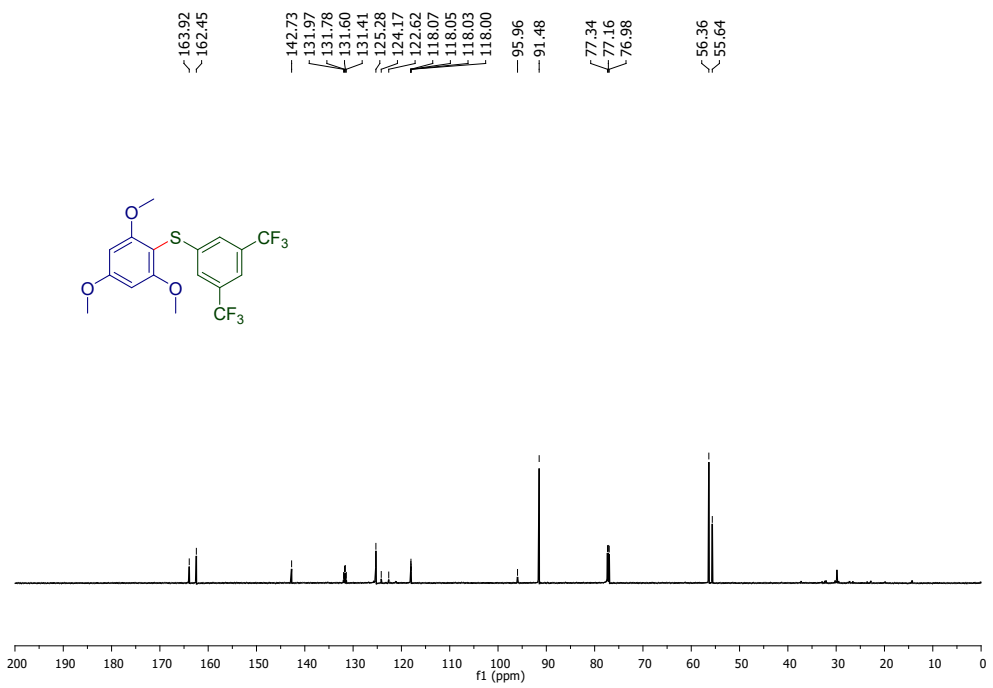


Fig. S42. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of (3,5-bis(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (**3an**)

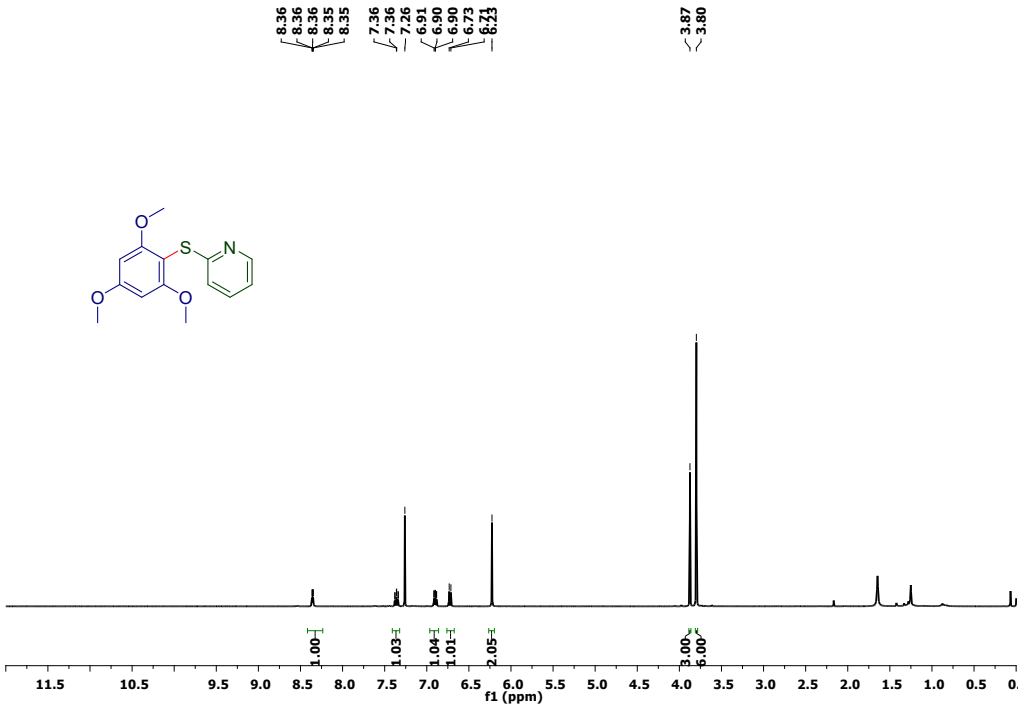


Fig. S43. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of 2-((2,4,6-trimethoxyphenyl)thio)pyridine (**3ao**)

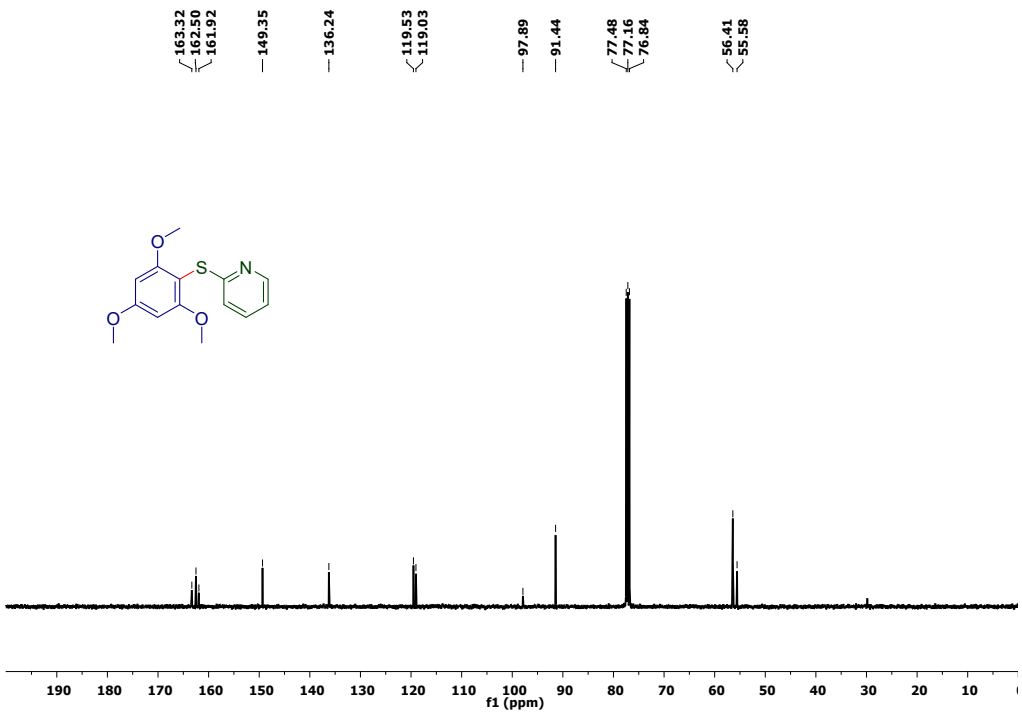


Fig. S44. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-((2,4,6-trimethoxyphenyl)thio)pyridine (**3ao**)

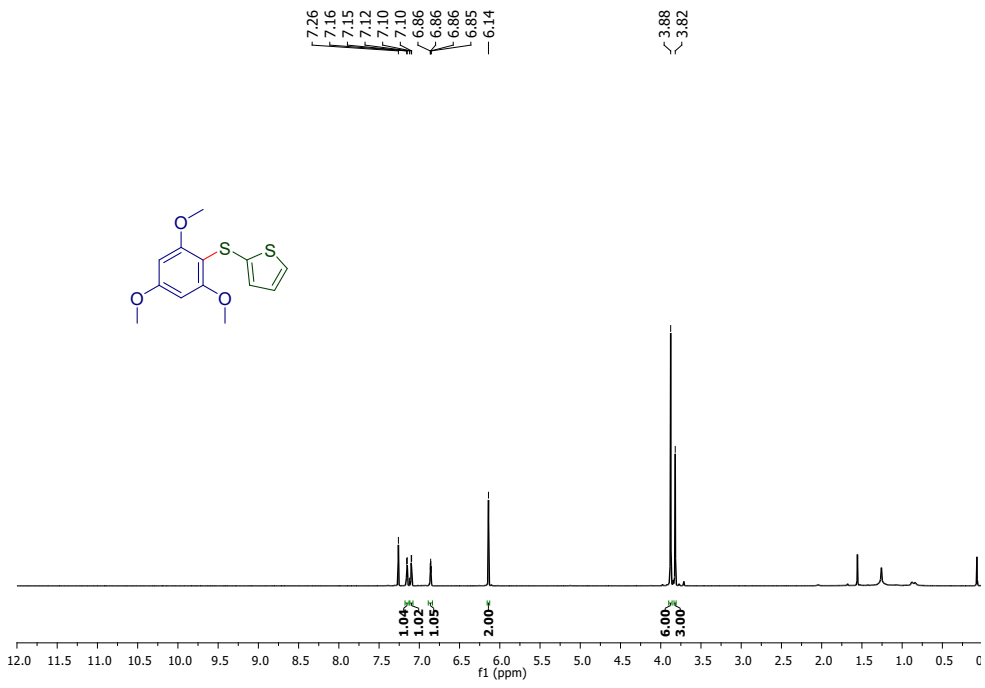


Fig. S45. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of 2-((2,4,6-trimethoxyphenyl)thio)thiophene (**3ap**)

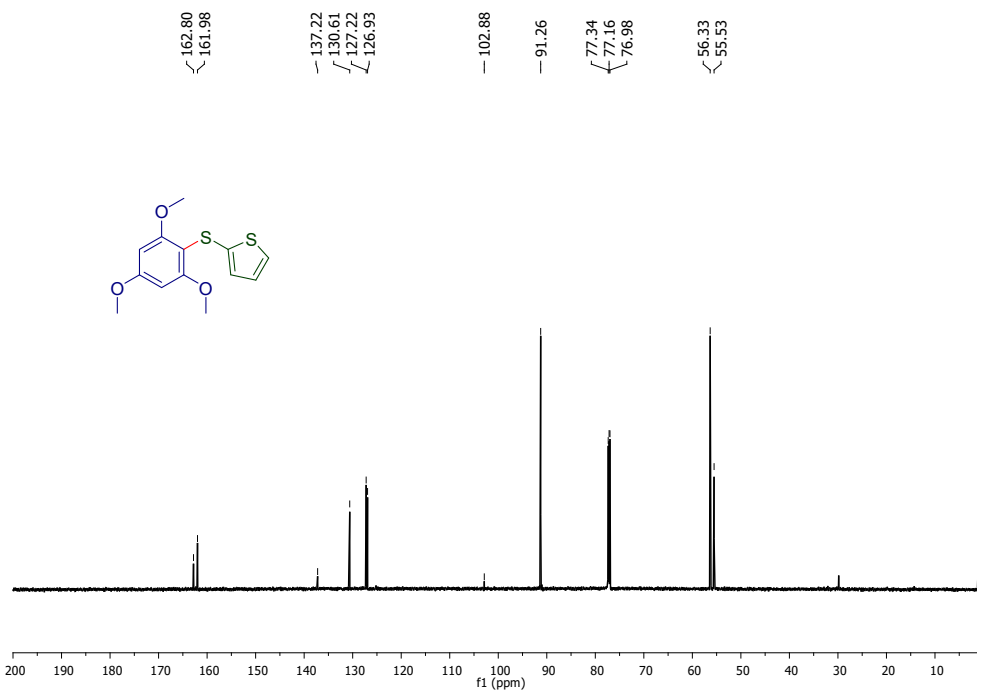


Fig. S46. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of 2-((2,4,6-trimethoxyphenyl)thio)thiophene (**3ap**)

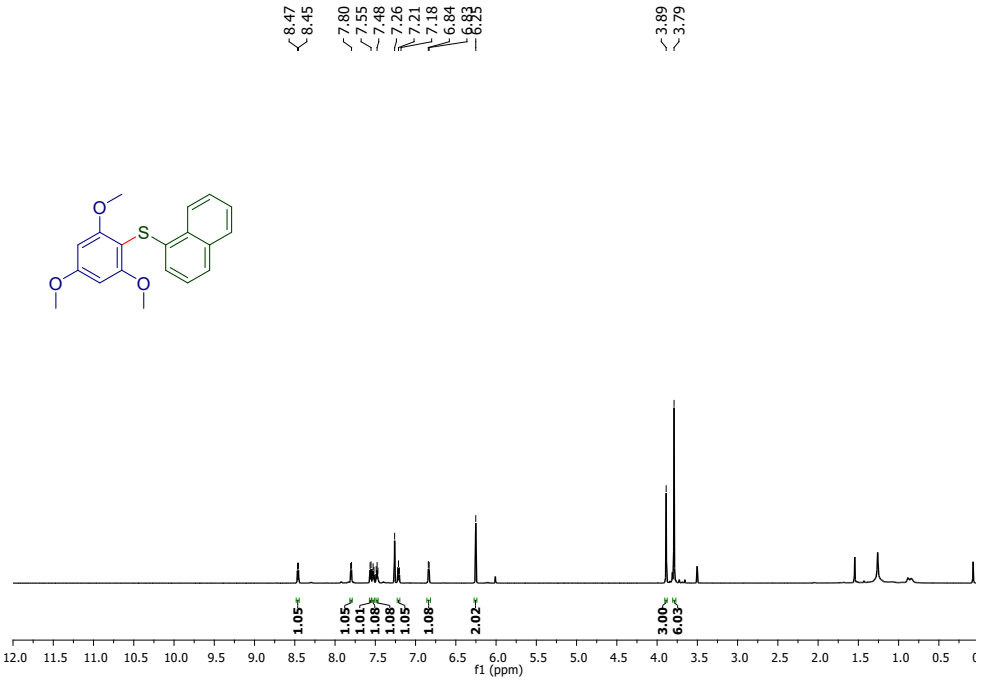


Fig. S47. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of naphthalen-1-yl(2,4,6-trimethoxyphenyl)sulfane (**3aq**)

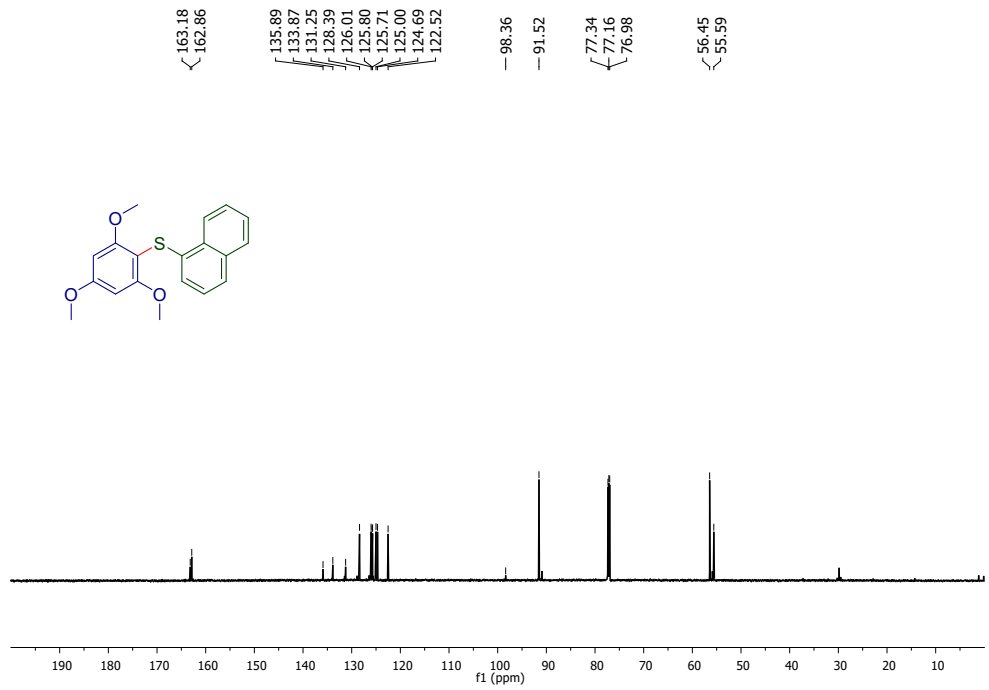


Fig. S48. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of naphthalen-1-yl(2,4,6-trimethoxyphenyl)sulfane (**3aq**)

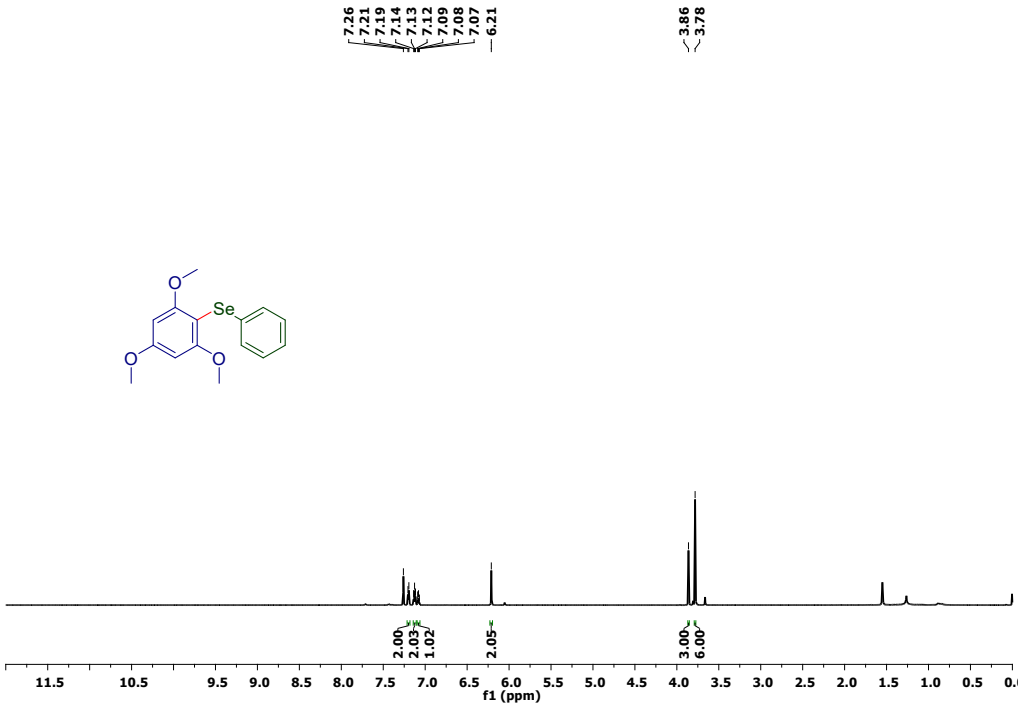


Fig. S49. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of phenyl(2,4,6-trimethoxyphenyl)selane (**3as**)

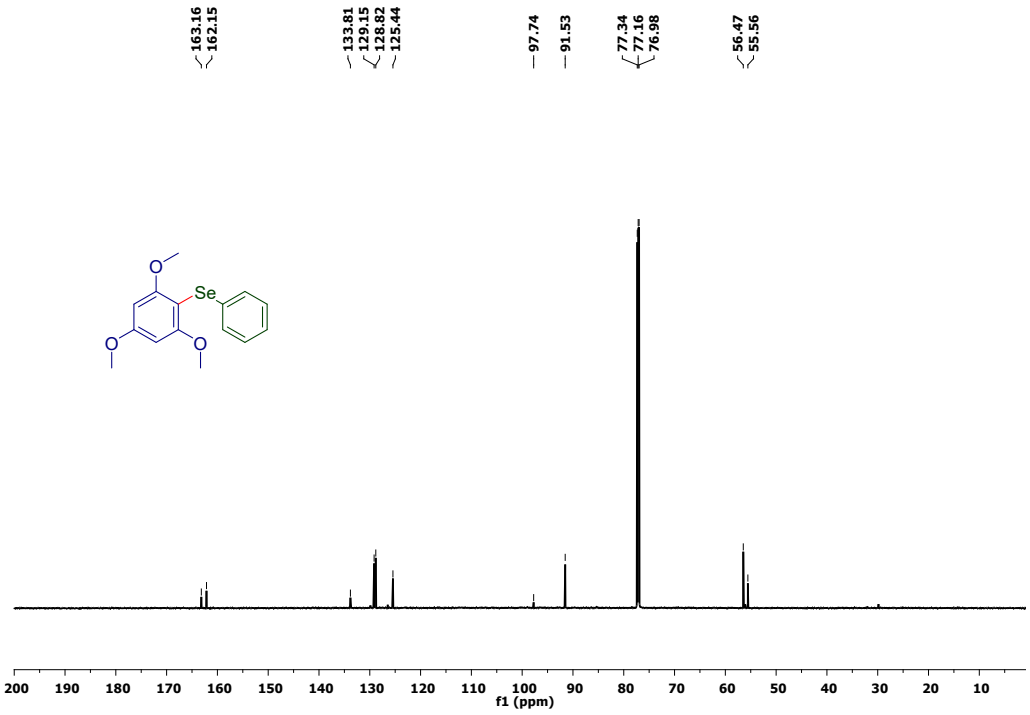


Fig. S50. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of phenyl(2,4,6-trimethoxyphenyl)selane (**3as**)

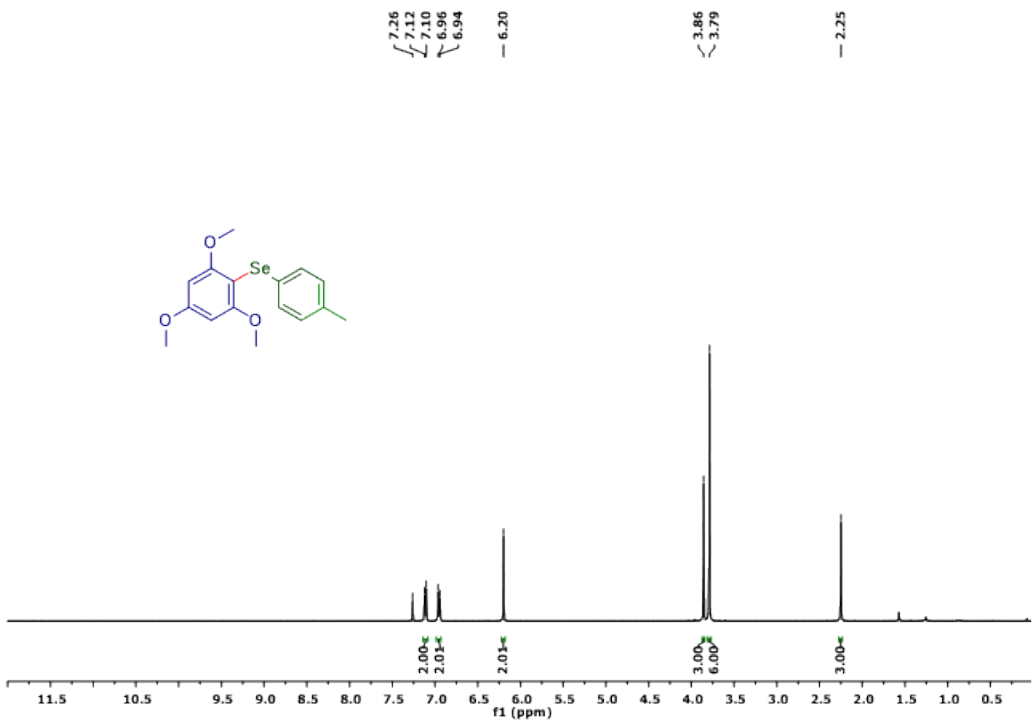


Fig. S51. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of *p*-tolyl(2,4,6-trimethoxyphenyl)selane (**3at**)

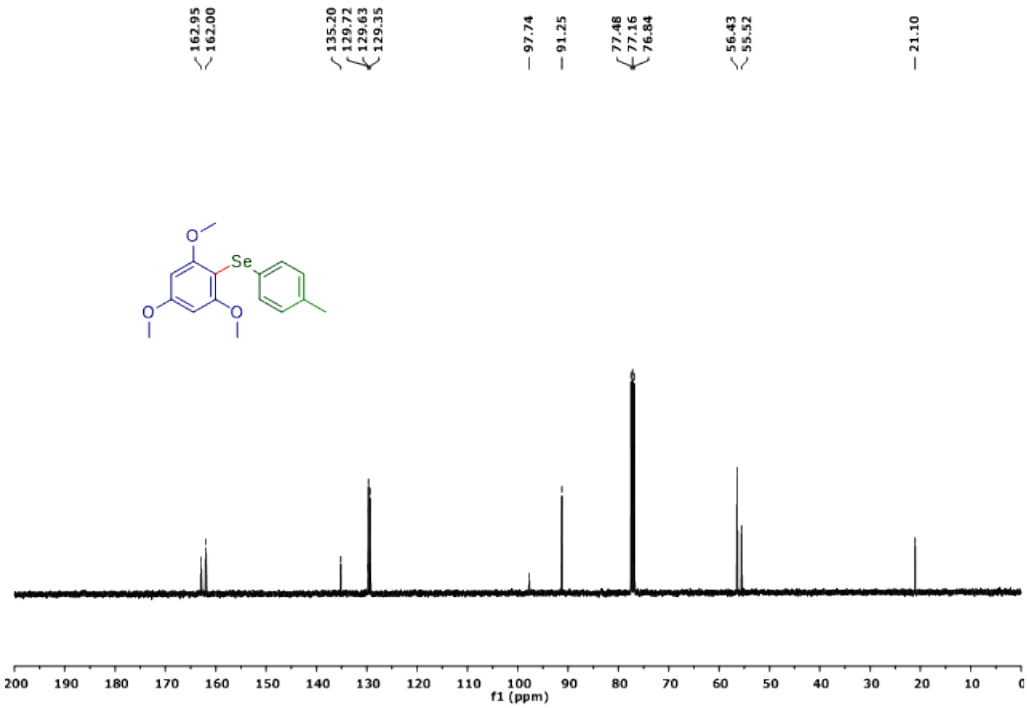


Fig. S52. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of *p*-tolyl(2,4,6-trimethoxyphenyl)selane (**3at**)

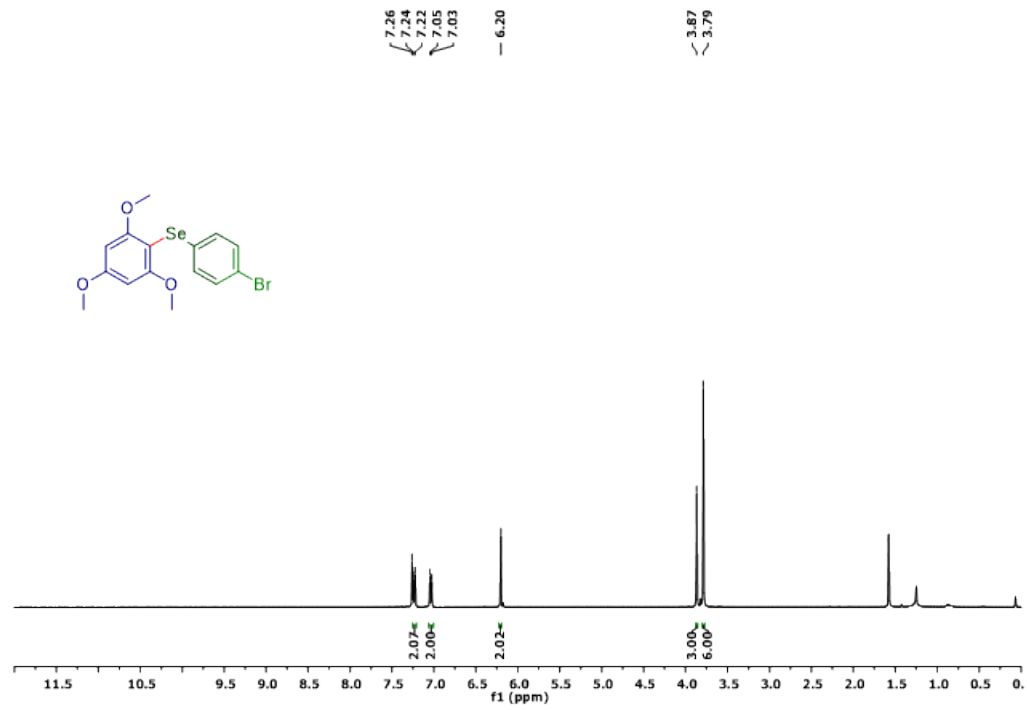


Fig. S53. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of (4-bromophenyl)(2,4,6-trimethoxyphenyl)selane (**3au**)

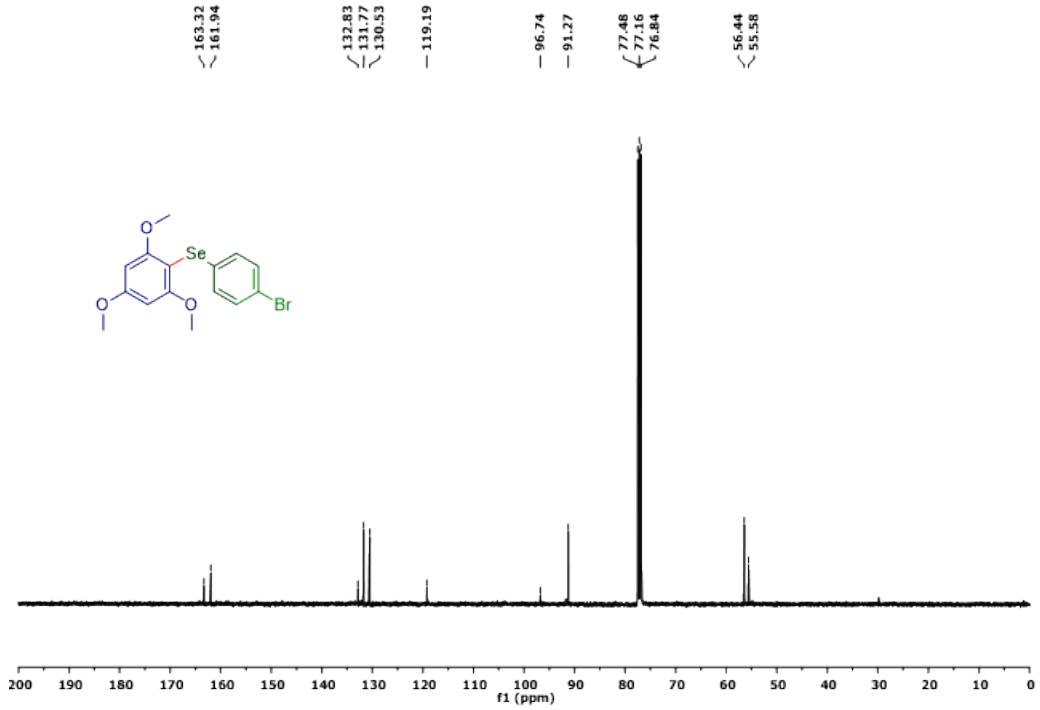


Fig. S54. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (4-bromophenyl)(2,4,6-trimethoxyphenyl)selane (**3au**)

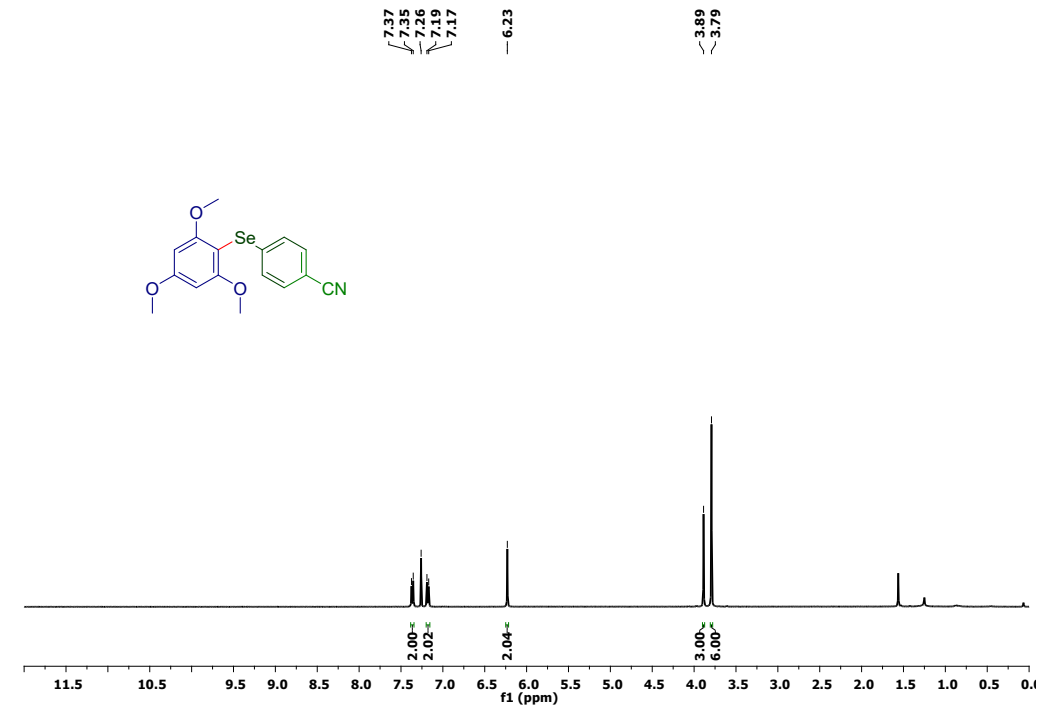


Fig. S55. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of 4-((2,4,6-trimethoxyphenyl)selanyl)benzonitrile (**3av**)

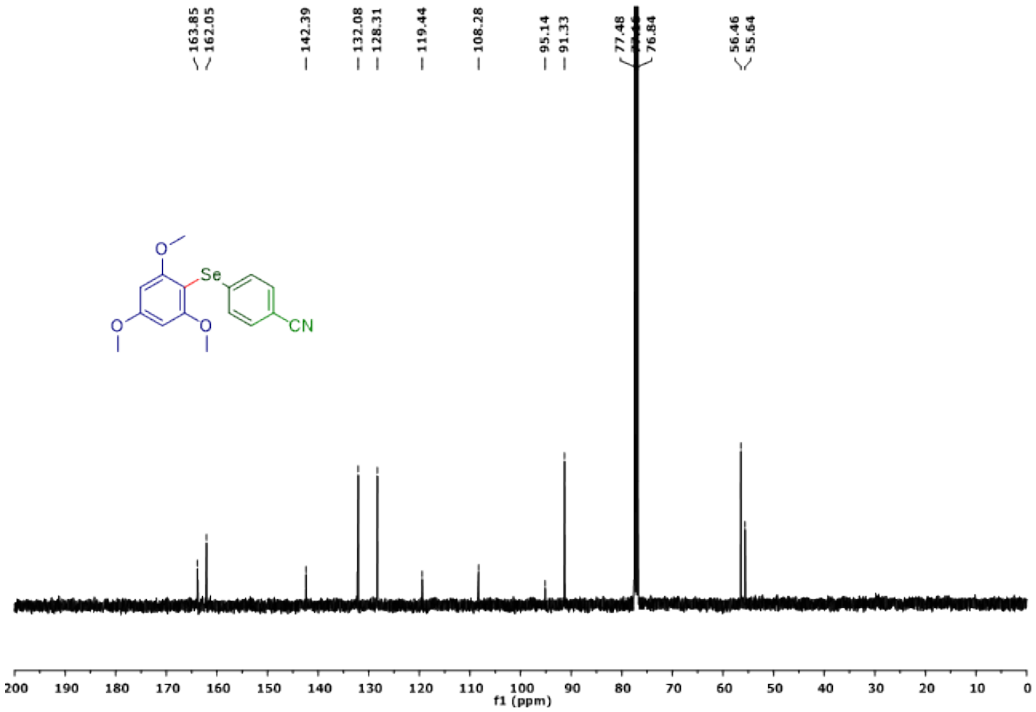


Fig. S56. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-((2,4,6-trimethoxyphenyl)selanyl)benzonitrile (**3av**)

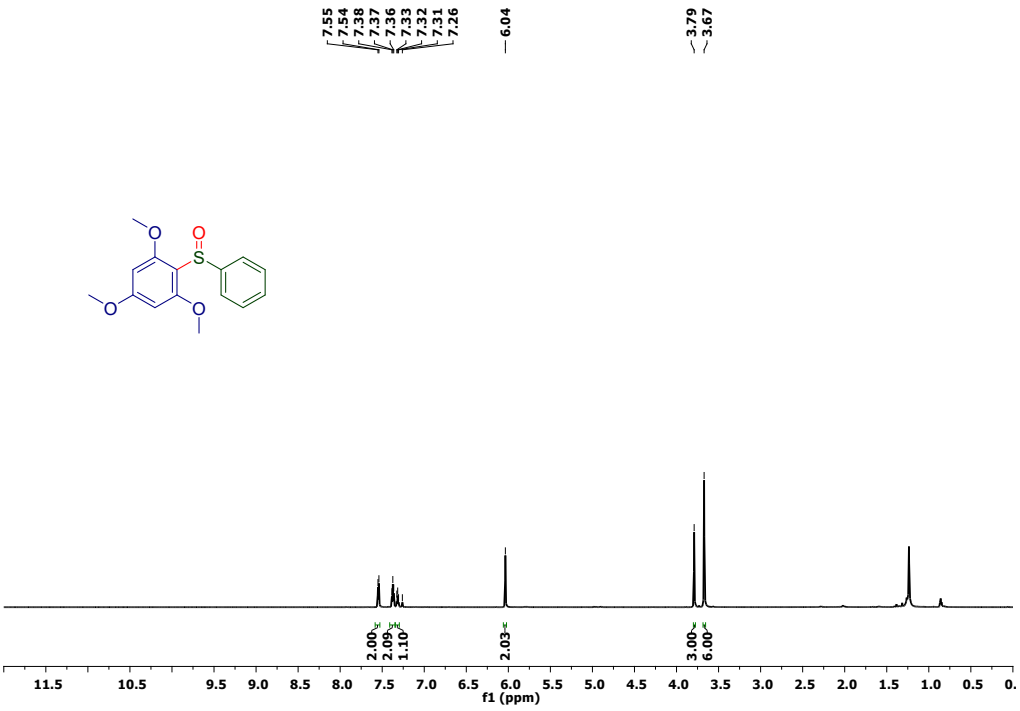


Fig. S57. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of 1,3,5-trimethoxy-2-(phenylsulfinyl)benzene (**5**)

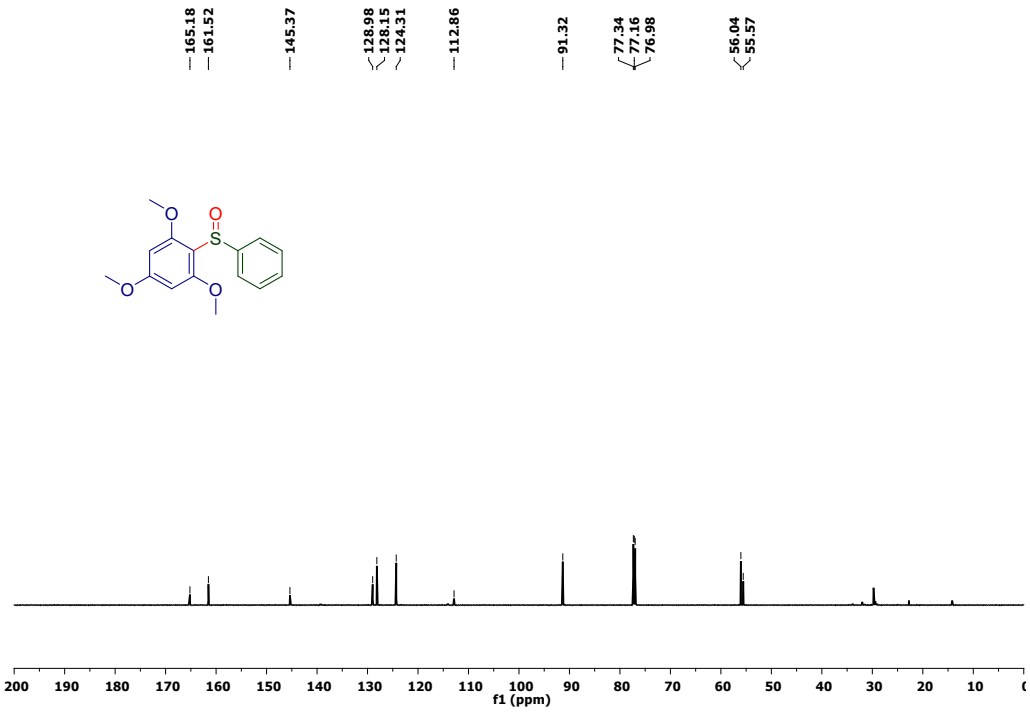


Fig. S58. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of 1,3,5-trimethoxy-2-(phenylsulfinyl)benzene (**5**)

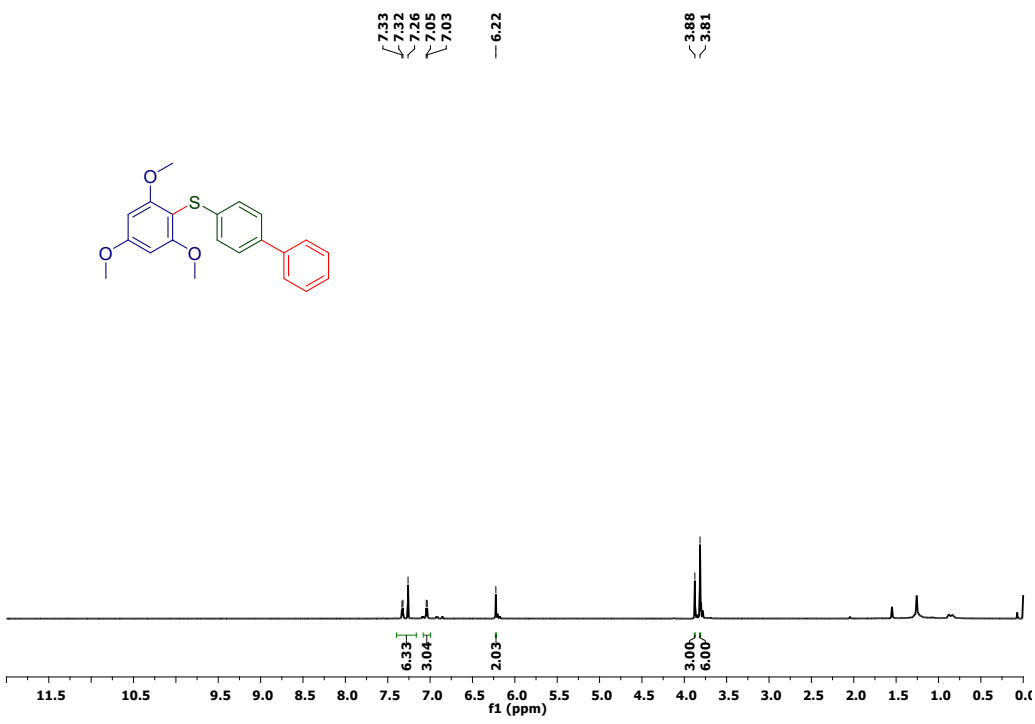


Fig. S59. ^{1}H NMR(700 MHz, $CDCl_3$) spectrum of [1,1'-biphenyl]-4-yl(2,4,6-trimethoxyphenyl)sulfane (**6**)

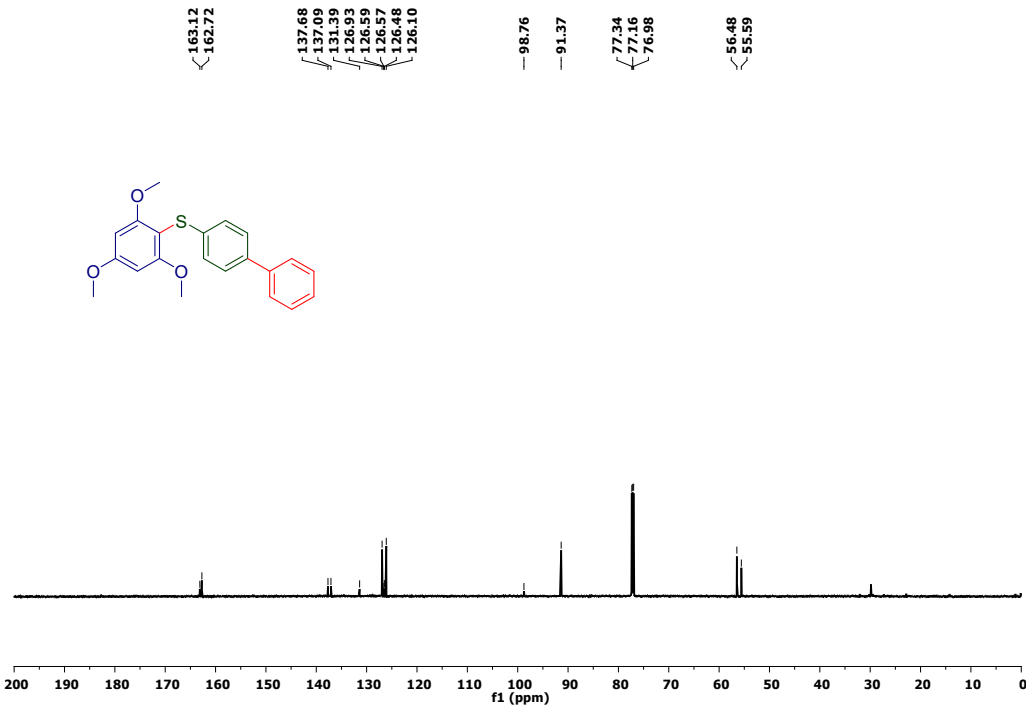


Fig. S60. $^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$) spectrum of [1,1'-biphenyl]-4-yl(2,4,6-trimethoxyphenyl)sulfane (**6**)

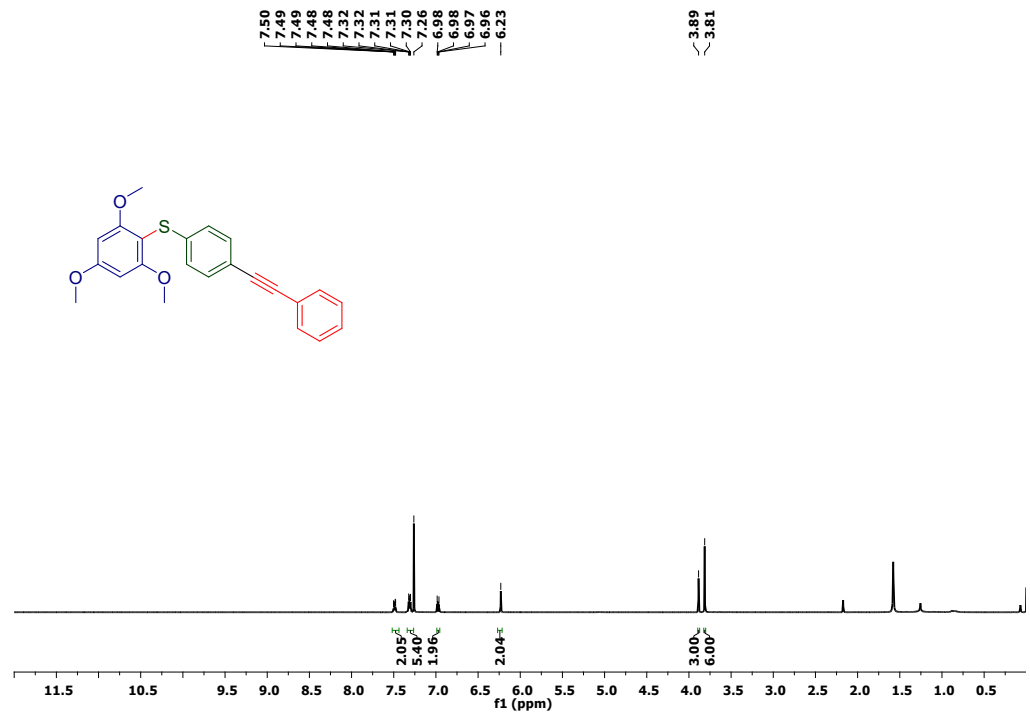


Fig. S61. ^{1}H NMR(400 MHz, $CDCl_3$) spectrum of (4-(phenylethynyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (**7**)

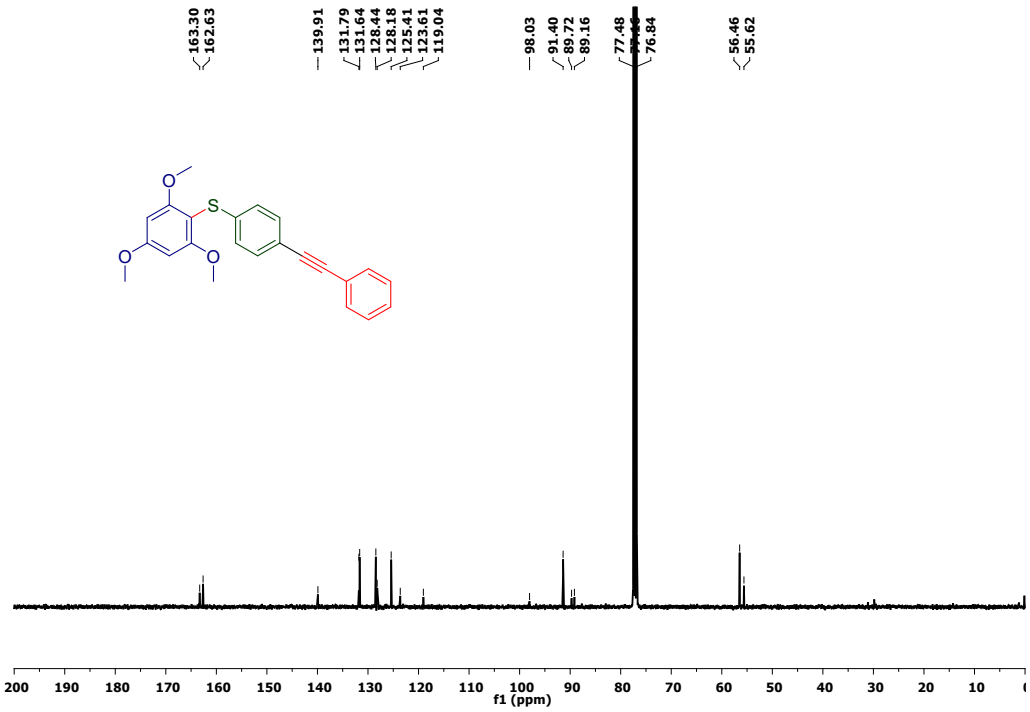


Fig. S62. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (4-(phenylethynyl)phenyl)(2,4,6-trimethoxyphenyl)sulfane (**7**)

Description of Light Source. Blue LED set up (Led Photochemical Reactor) was purchased from commercial source CRYONANO VL-PHOTON. The intensity of the blue LED was (417 × 100) lx (measured by Sigma-Digital Lux Meter 101, Model: 20036176). Quartz glass (brand name: Luzchem) was used as reaction vessel. No filter was used for the reaction. Other features of the photoreactor are as follows:

CRYONANO Labs LED Photochemical Reactor - CNPHOTON 101

The CN-Photon LED Photochemical Reactor from CRYONANO Labs is a compact desktop instrument for conducting research in areas of Photo-biology, Inorganic, Organometallic and Organic Photochemistry (e.g., Drug-DNA Interaction) etc. It has a ventilated illumination chamber with tunable high intensity LEDs and fully automatic operation with countdown timer for setting the reaction time and switching it off automatically. The intensity of light can also be automatically controlled using inbuilt microprocessors.

The reactor includes a controller in a separate housing for light intensity control and automation with display. It also comes with a carousel for liquid samples.

Main Features of the reactor are:

- High flux per LED
- Blue led - 2100 lumens
- White led - 10000 lumens
- Good color uniformity
- Industry best moisture sensitivity level
- JEDEC Level 1
- Low Voltage DC operated
- Instant light (less than 100ns)
- No UV Component
- Dimensions: Internal : 5.5" Diameter, 7" height, Anodized aluminium enclosure
- Power Rating: 220 V AC, 50 Hz, 2Amp

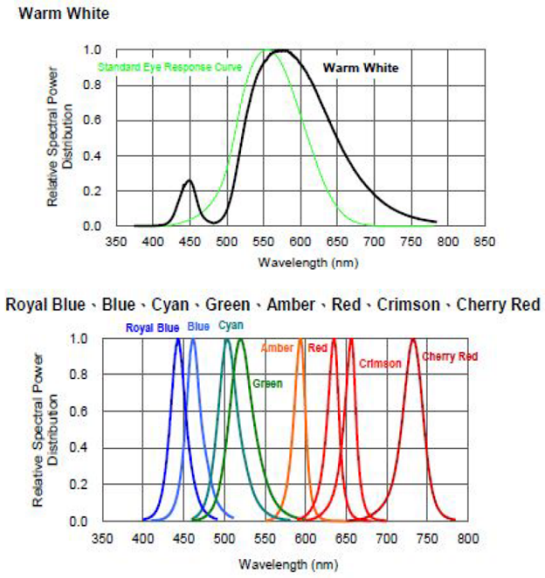
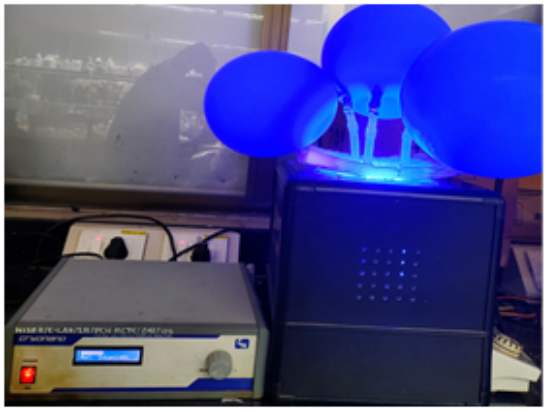


Fig. S63. The instrument configuration details provided by the manufacturer (CRYONANO VL-PHOTON). The full-width-at-half-maximum (FWHM) of the Blue LED is 450-470 nm.

a) Light on

b) Light power intensity



c) Reaction setup

d) Digital LUX Meter

Fig. S64. Light setup.