Supplementary Information

Selectivity control in thiol-yne click reactions via visible light induced associative electron upconversion

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Contents:

Optimization of reaction conditions

Products **3aa**[1], **4aa**[2], **5aa**[1], **6aa**[1] were identified according to published data. HMDSO was used as an internal standard.

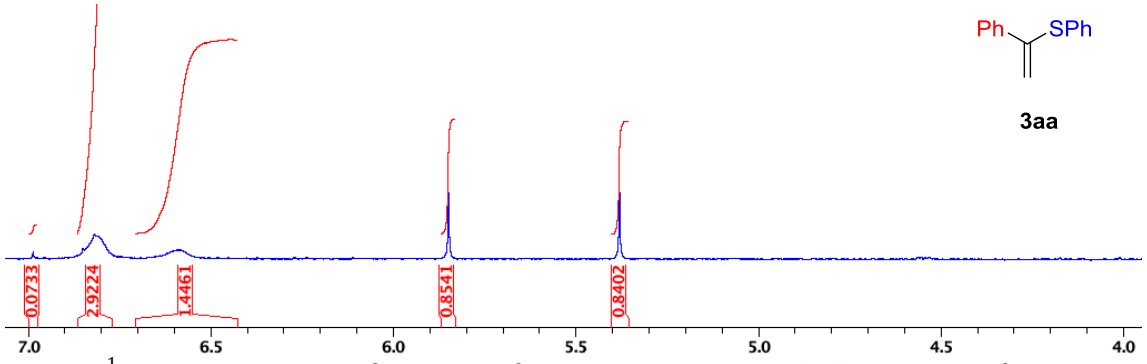


Figure S1. ^{1}H NMR spectrum fragment of reaction mixture with dominance of **3aa** (Entry 7, Table 1 in the manuscript).

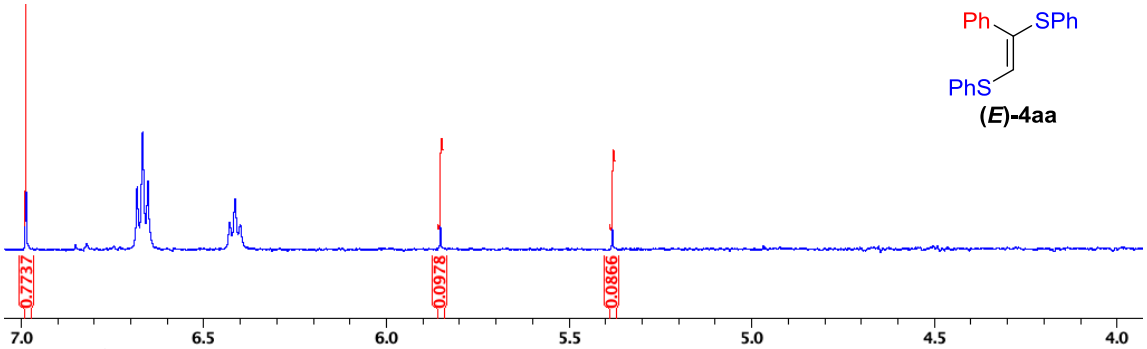


Figure S2. ^{1}H NMR spectrum fragment of reaction mixture with dominance of (*E*)-**4aa** (Entry 8, Table 1 in the manuscript).

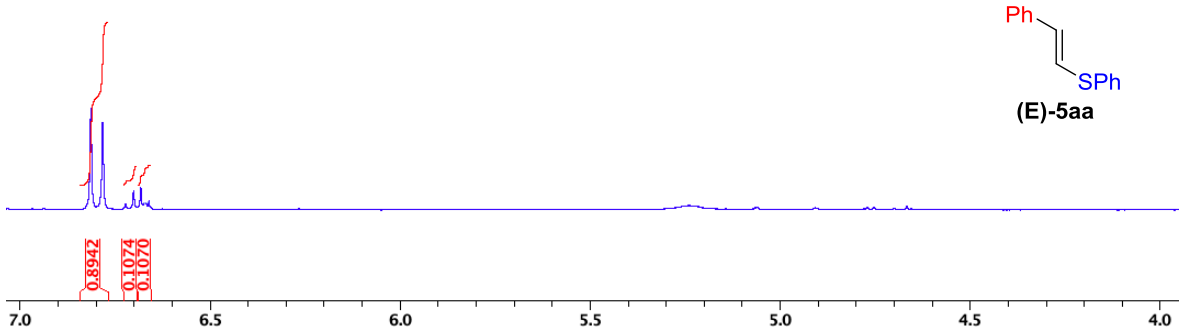


Figure S3. ^{1}H NMR spectrum fragment of reaction mixture with dominance of **5aa** (Entry 1, Table 1 in the manuscript).

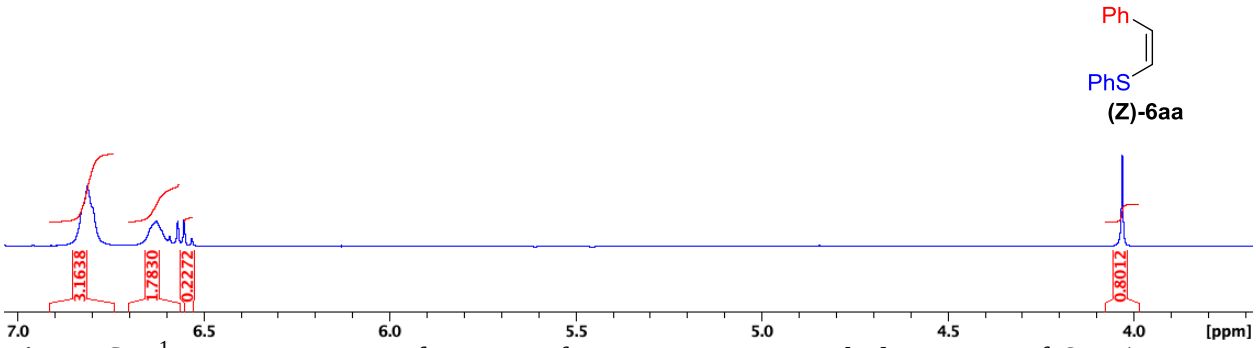
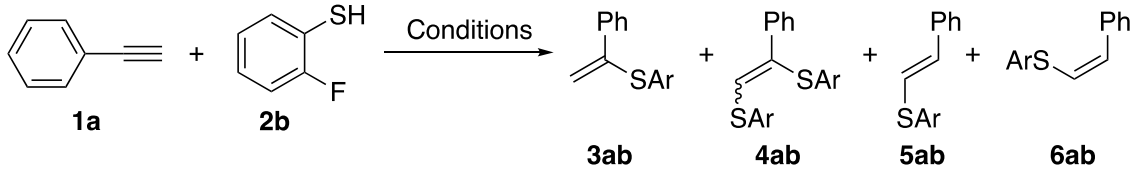


Figure S4. ^{1}H NMR spectrum fragment of reaction mixture with dominance of **6aa** (Entry 11, Table 1 in the manuscript). Signal at 4 ppm is **1a**.

Table S1. **Variation of reaction conditions**



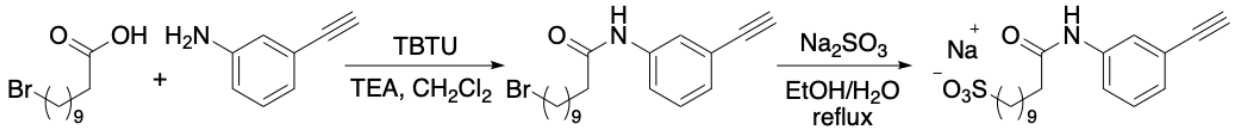
1a **2b** **3ab** **4ab** **5ab** **6ab**

#	**1a**:**2b** ratio	Solvent	Catalyst/hν	**3ab**, %	**4ab**, %	**5ab**, %	**6ab**, %
1	1:2	DMF	Eosin/540 nm	**95**	5	0	0
2	1:2	DMSO	Eosin/540 nm	67	7	2	5
3	1:2	MeCN	Eosin/540 nm	53	6	0	10
4	1:2	MeOH	Eosin/540 nm	0	0	23	13
5	1:2	DMA	Eosin/540 nm	**90**	6	1	3
6	1:2	DMF	Rh6G/540 nm	41	2	1	3
7	1:2	DMF	Fluoresceine/450 nm	58	3	1	1
8	1:2	DMF	$Ru(bpy)_3^{2+}$/450 nm	24	0	2	1
9	1:2	DMF	$Ru(bpz)_3^{2+}$/450 nm	0	0	2	10
10	1:1	DMF	Eosin/540 nm	75	3	6	4
11	1:4	DMF	Eosin/540 nm	27	8	46	6

[a] 0.15 mmol **1a**, DBU 1.1 equiv. corresponding to **2a**, solvent – 3 ml, green LEDs (1.25 W), reaction time – 24 h.

Electrospray ionization mass-spectrometry investigations

Synthesis of sodium 11-((3-ethynylphenyl)amino)-11-oxoundecane-1-sulfonate (1q)



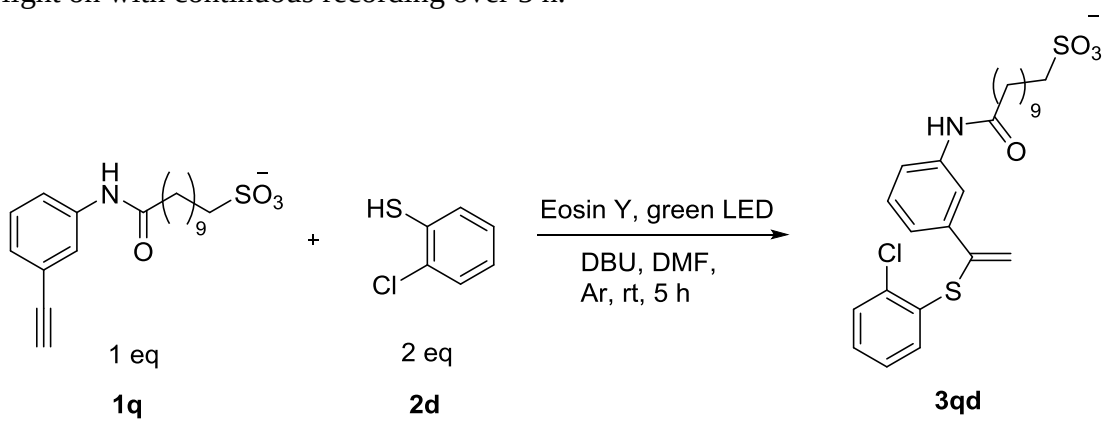
1. Trimethylamine (170 µl) was added to a solution of 11-bromodecanoic acid (265 mg, 1 mmol) and TBTU (320 mg, 1 mmol) in DCM (2 ml) under cooling (0 °C). The reaction mixture was stirred at 0 °C for 30 minutes; after that 3-acetylenephenylamine (105 µl, 1 mmol) was added to the reaction mixture and stirred overnight at room temperature. The solvent was evaporated under reduced pressure and a brown oily residue was dissolved in ethyl acetate (10 ml). This phase was washed with 10% aqueous citric acid solution (3*10 ml), water (10ml), aqueous $NaHCO_3$ (3*10ml) and then brine. The organic layer was dried over $MgSO_4$ and evaporated. Yield of the amide was 361 mg (99%). This compound was used without further purification for the second step.

2. The amide (361 mg, 0.99 mmol) was suspended in a mixture of 2 ml of ethanol and 3 ml of water. 630 mg (5 mmol) of anhydrous sodium sulfite was added to this suspension and the mixture was stirred under reflux for 16 hours. Upon completion of the reaction, 25 ml of ethanol was added to the mixture and filtered from an excess of sodium sulfite. The solvent was evaporated under reduced pressure. The product (**1q**) was a light yellow powder, 352 mg (91%) yield.

^{1}H NMR (DMSO-d_6, 300 MHz): 9.96 (1H, s), 7.81-7.78 (1H, t, J = 1.8 Hz), 7.58-7.53 (1H, d, J = 7.8 Hz), 7.32-7.26 (1H, t, J = 7.8 Hz), 7.15-7.09 (1H, d, J = 7.8 Hz), 4.14 (1H, s), 2.39-2.25 (4H, m), 1.63-1.47 (4H, m), 1.34-1.19 (12H, m). ^{13}C{^{1}H} NMR (DMSO-*d*6, 75 MHz): 171.6, 139.5, 129.1, 126.1, 121.9, 121.8, 119.6, 83.4, 80.4, 51.5, 36.4, 28.8, 28.7, 28.6, 28.4, 25.1, 25.0.

ESI-(–)MS online monitoring of the photocatalytic thiol-yne click reaction

Alkyne (**1q**) (11.6 mg, 3*10^{-5} mol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (10 µl, 6.6*10^{-5} mol), arylthiol (**2d**) (7 µl, 6.2*10^{-5} mol) and 4ml of dimethylformamide were mixed in a round-bottom flask. A Schleck tube (10 ml), equipped with magnetic stir bar was filled with 400 µl of the prepared solution and 3 mg (4.3*10^{-6} mol) of eosin Y were added followed by 3.6 ml of DMF. A neck was closed with a silicon septum and the side tap was connected to an argon double balloon. A PEEK capillary connected to the ESI source was pulled into the flask through the septum and immersed into the reaction mixture. The tube was placed into the setup equipped with green LED 1.25 W (λ_{max}=533 nm) and the reaction monitoring was started after the stabilization of total ion current. The reaction was stirred at room temperature for 5 h, spectra were recorded in negative ion mode, for 4.25 min without light irradiation, followed by green LED light on with continuous recording over 5 h.



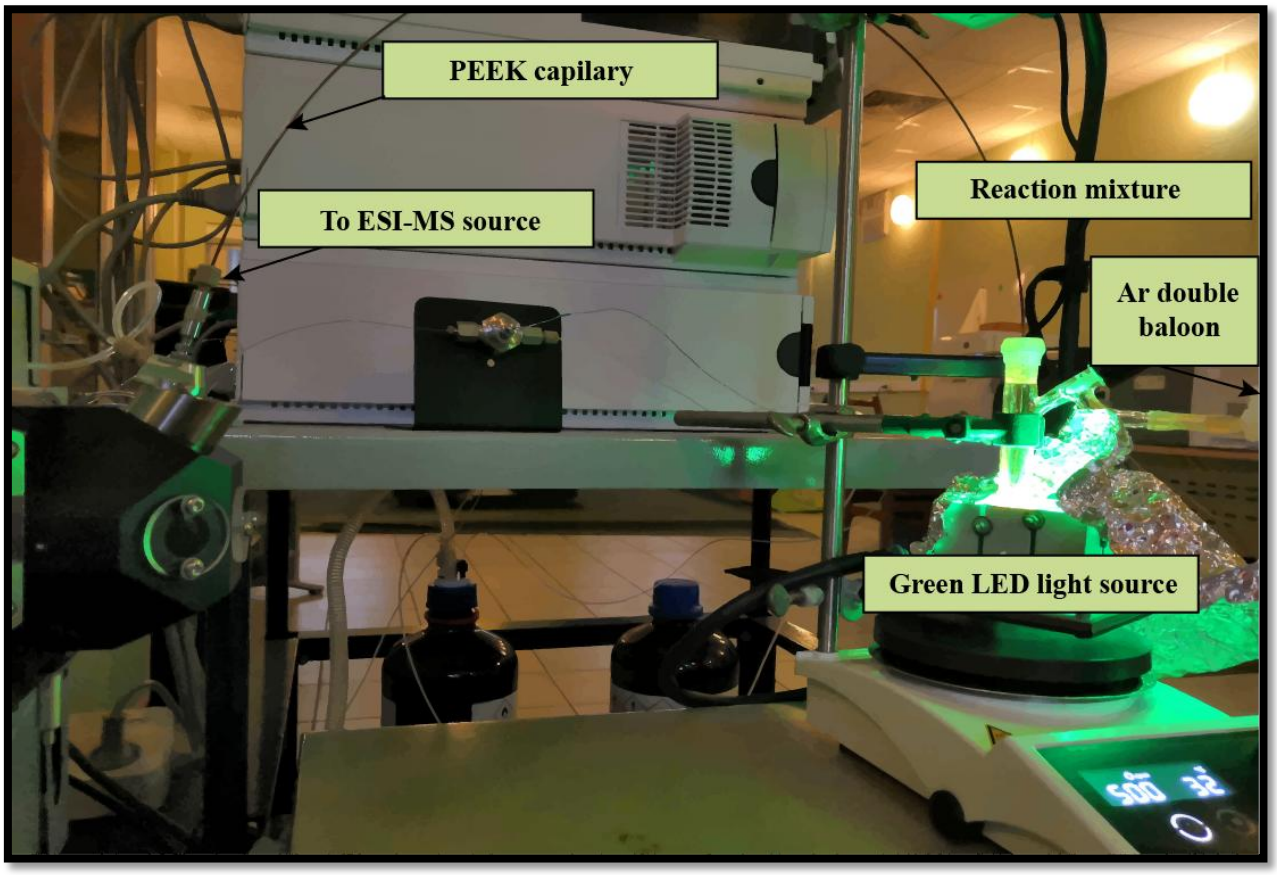


Figure S5. Online MS reaction setup for photocatalytic thiol-yne click reaction.

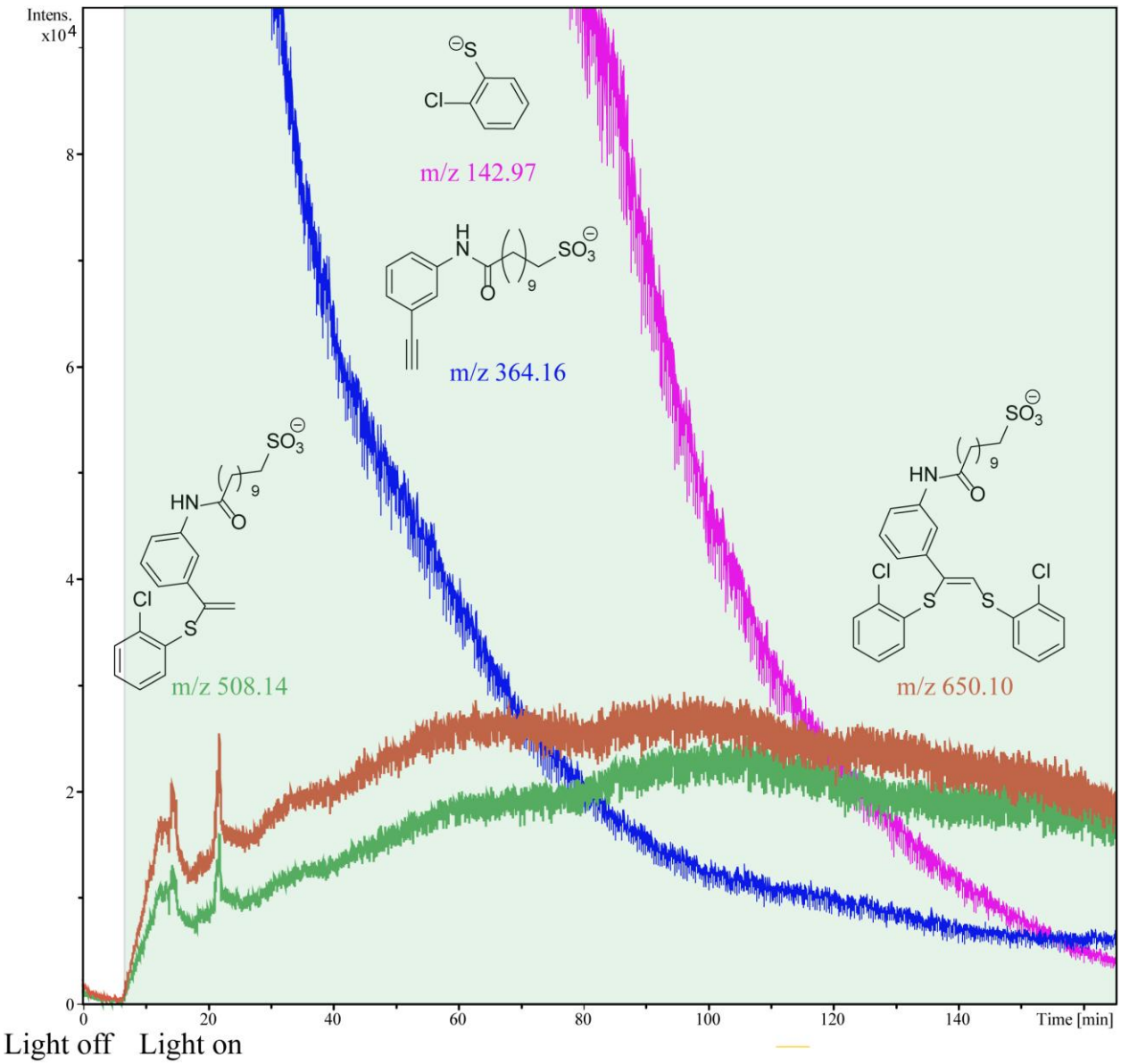


Figure S6. Real-time abundance of initial reagents (**1q;2d**), products (**3qd, 4qd**) of photocatalytic thiol-yne click reaction in the presence of 14 mol% of Eosin Y. Green light was turn on at 4.25 min from the beginning.

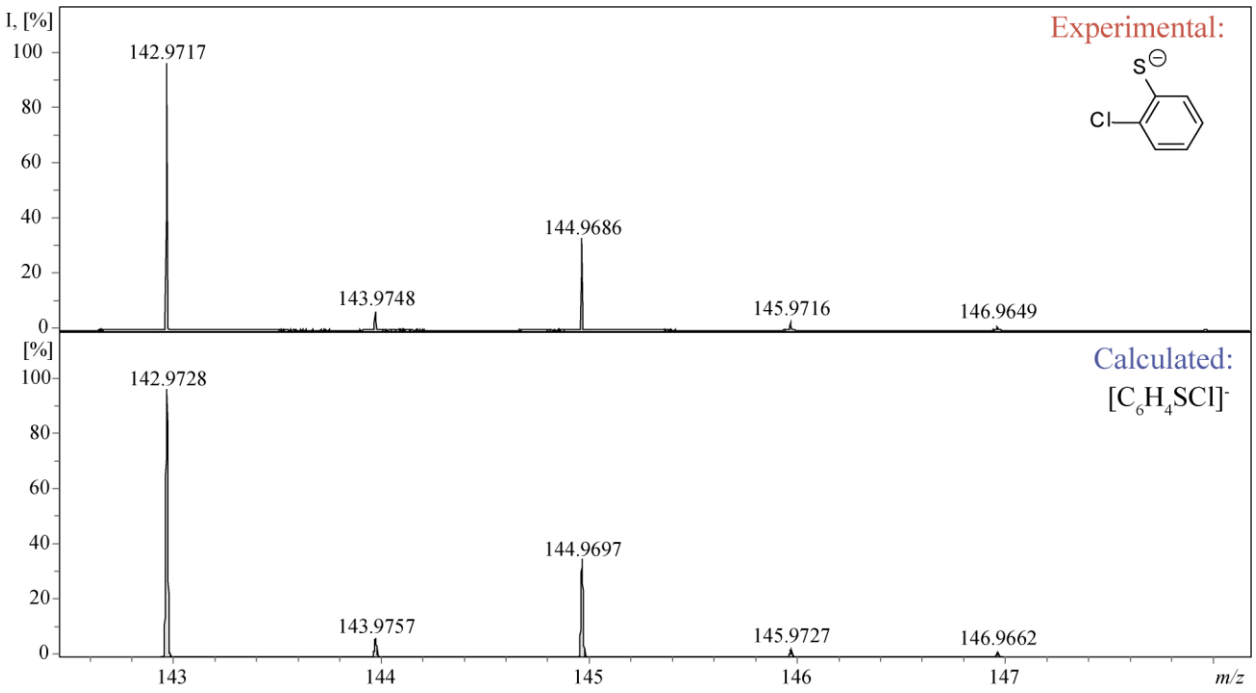


Figure S7. Experimentally detected and theoretical ESI-(-)MS spectrum of **2d** from reaction mixture under online monitoring; main experimental peak $[M\text{-}H]^-$ = 142.9714 Da, calculated for C_6H_4SCl = 142.9728 Da, Δ = 9.8 ppm.

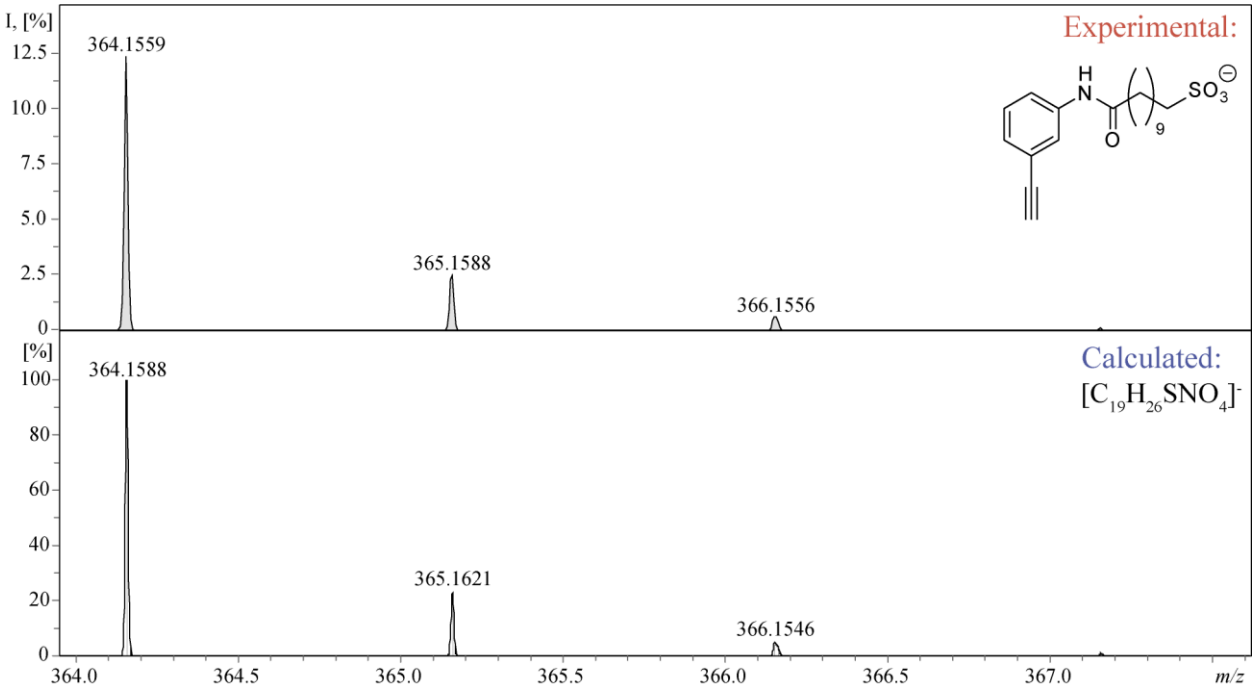


Figure S8. Experimentally detected and theoretical ESI-(-)MS spectrum of **1q** from reaction mixture under online monitoring; main experimental peak $[M]^-$ = 364.1574 Da, calculated for $C_{19}H_{26}SNO_4$ = 364.1588 Da, Δ = 3.8 ppm.

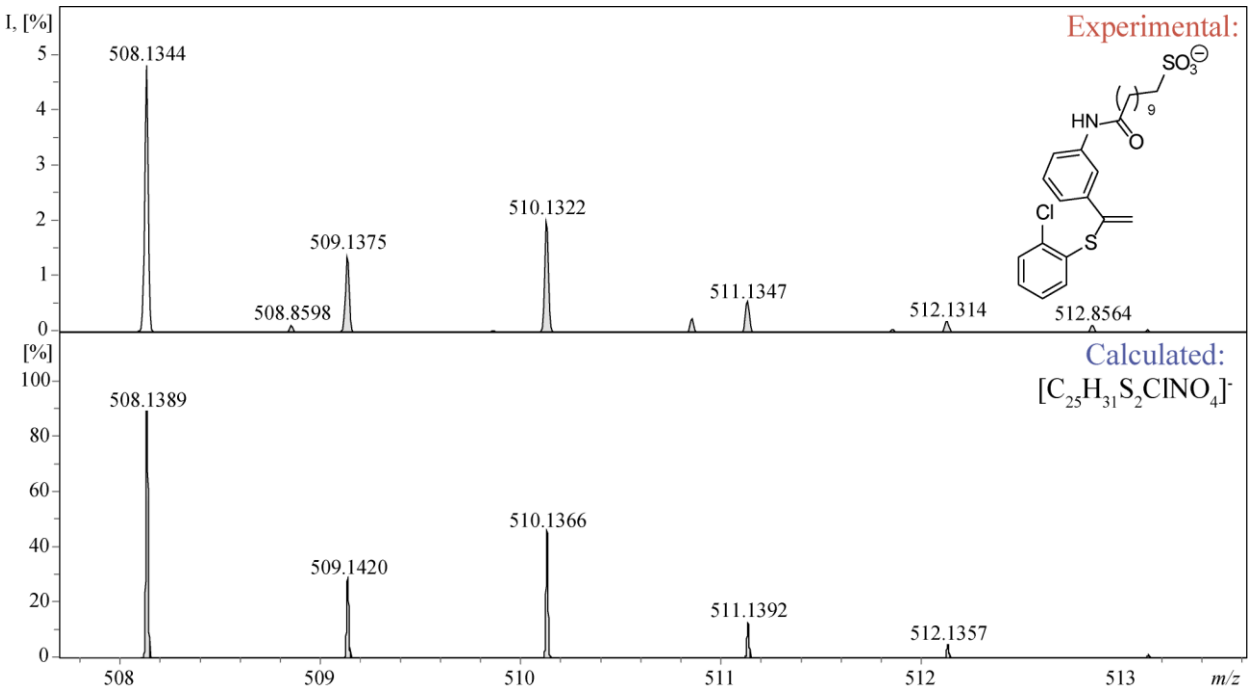


Figure S9. Experimentally detected and theoretical ESI-(-)MS spectrum of **3qd** from reaction mixture under online monitoring; main experimental peak $[M]^-$ =508.1348 Da, calculated for $C_{25}H_{31}S_2ClNO_4$ = 508.1389 Da, Δ = 8.0 ppm.

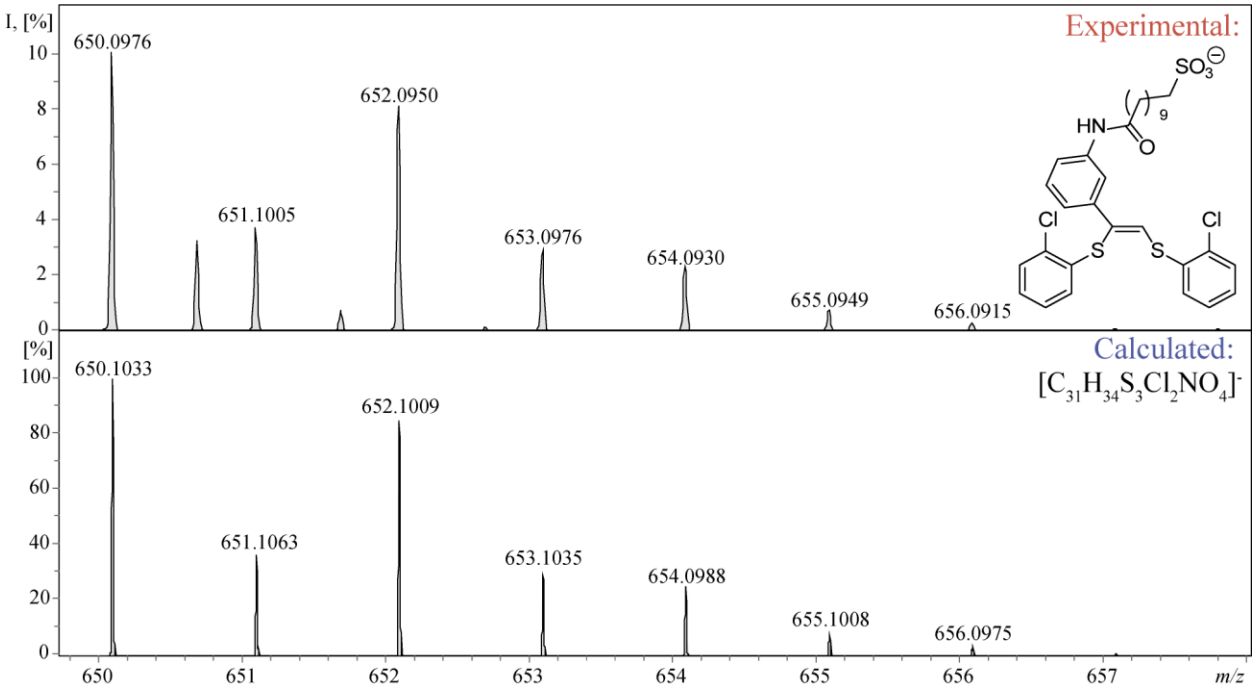


Figure S10. Experimentally detected and theoretical ESI-(-)MS spectrum of **4qd** from reaction mixture under online monitoring; main experimental peak $[M]^-$ = 650.0976 Da, calculated for $C_{31}H_{35}S_3Cl_2NO_4$= 650.1033 Da, Δ = 8.6 ppm.

Computational studies

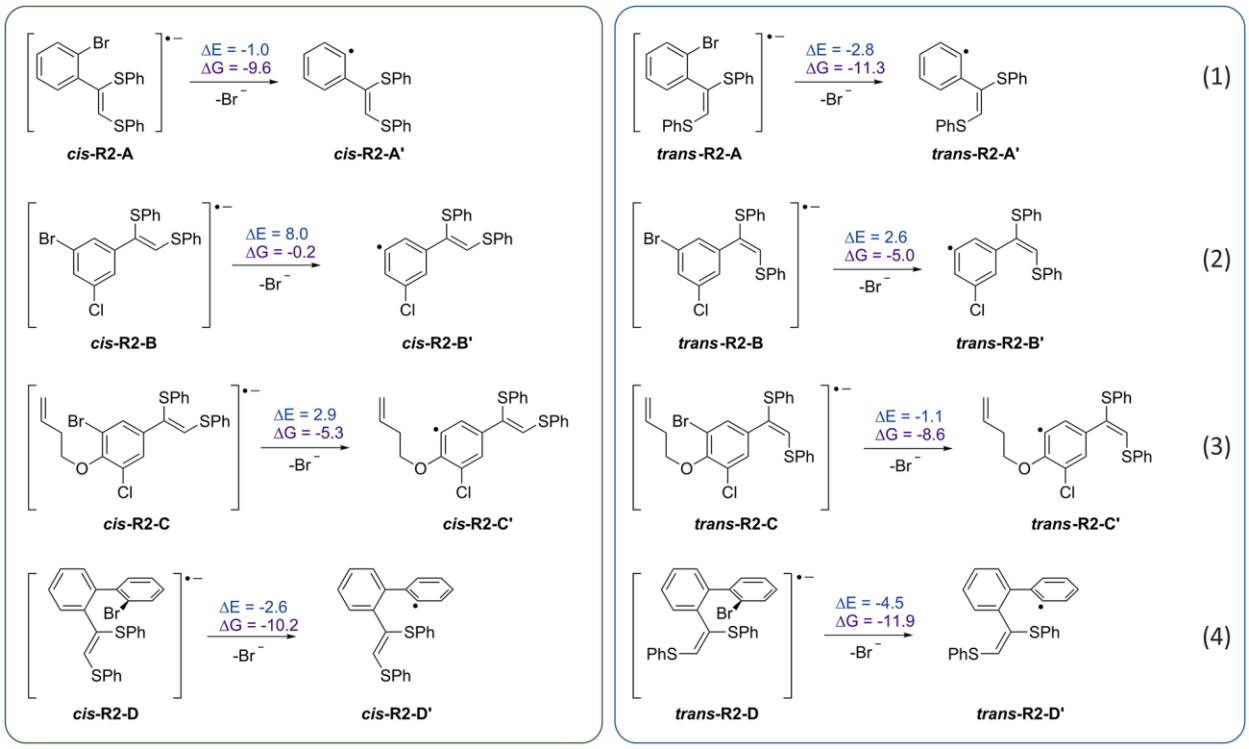


Figure S11. Debromination total energies (ΔE, kcal/mol) and Gibbs free energies (ΔG, kcal/mol) for Z- and E-isomers of radical-anions, UBMK/6-311+G(d,p) GD3BJ SMD(DMF).

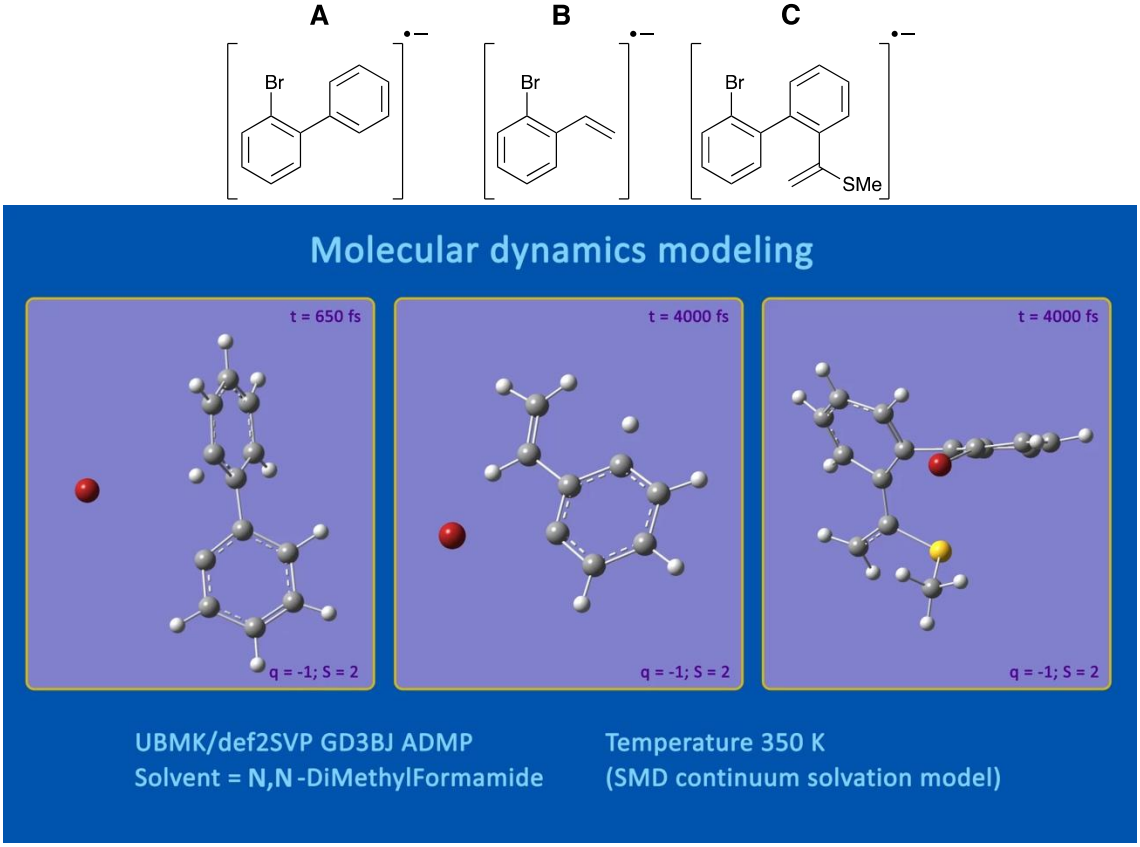
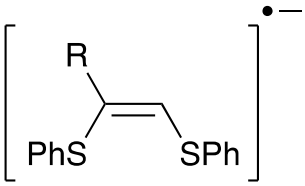


Figure S12. Structures of model Br-containing radical-anions and snapshot from molecular dynamics simulations of debromination step. Debromination step for radical-anion **C** is kinetically impeded as revealed by molecular dynamics.



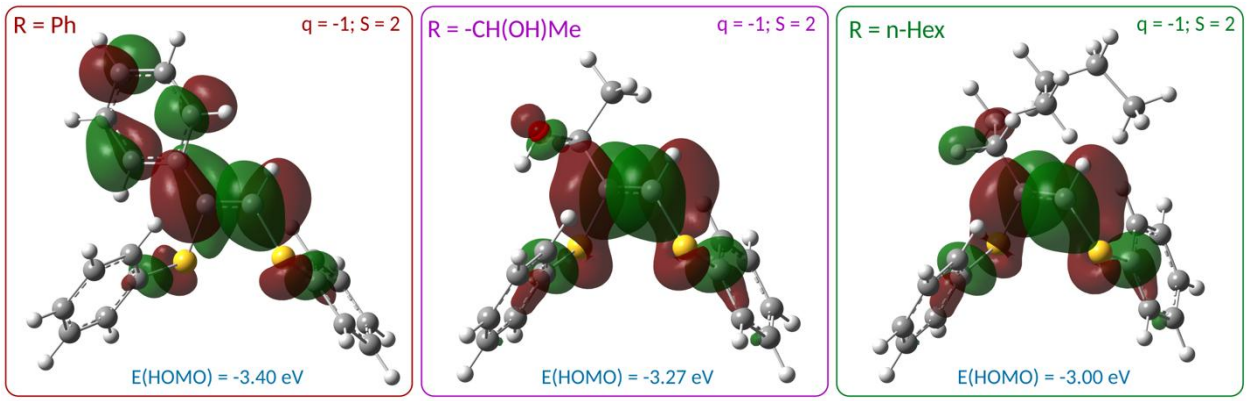


Figure S13. HOMO spatial structures and energies for radical-anions with respect to substituents on alkyne precursor.

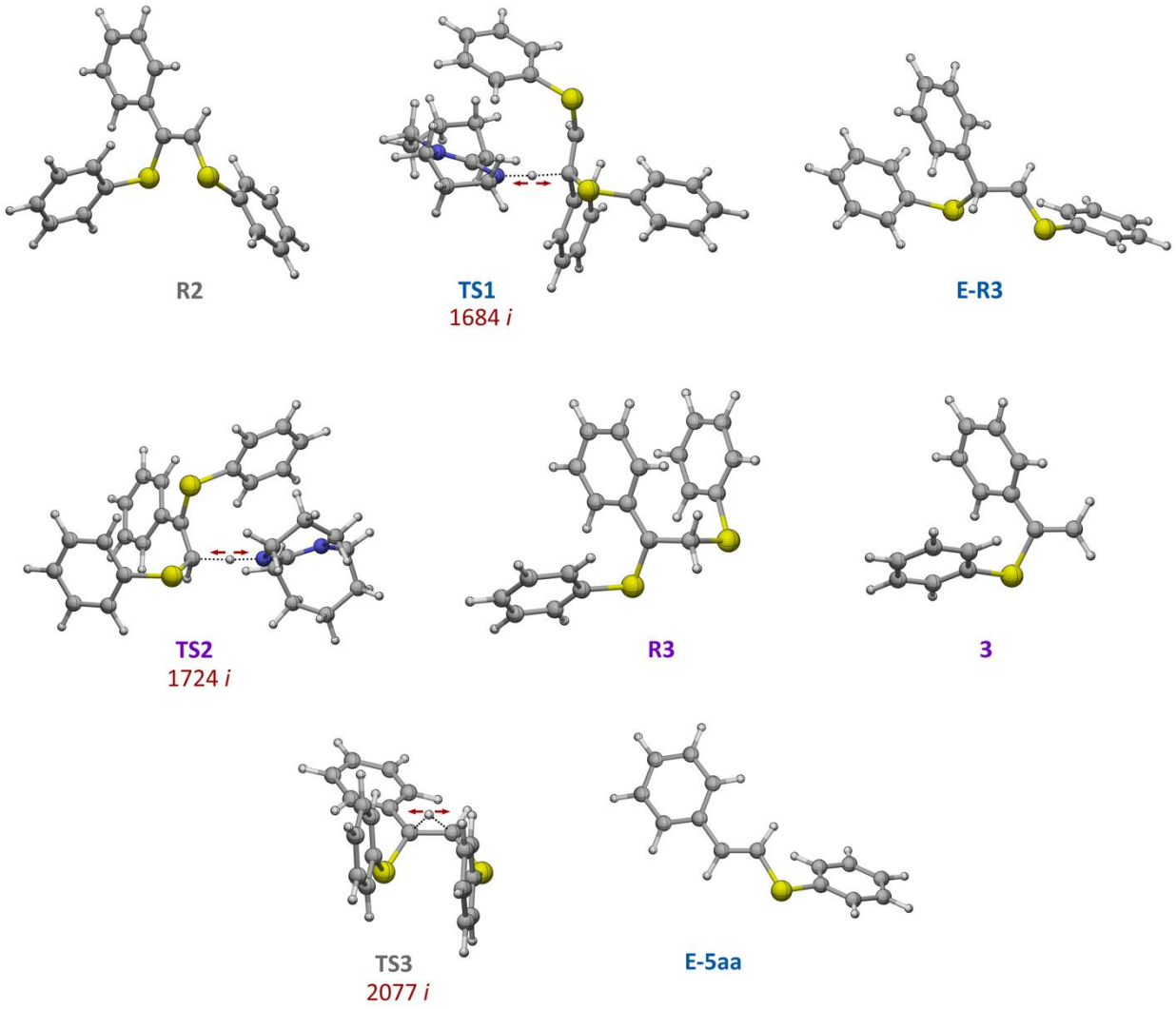


Figure S14. Optimized molecular structures of intermediates, transition states and products for product **3** formation reaction stating from **R2** radical-anion (see Figure 2 in the manuscript). The imaginary frequencies for transition states are denoted by red colour and atomic movements corresponding to each imaginary frequency are denoted by red arrows; UBMK/6-311+G(d,p) D3BJ SMD(DMF).

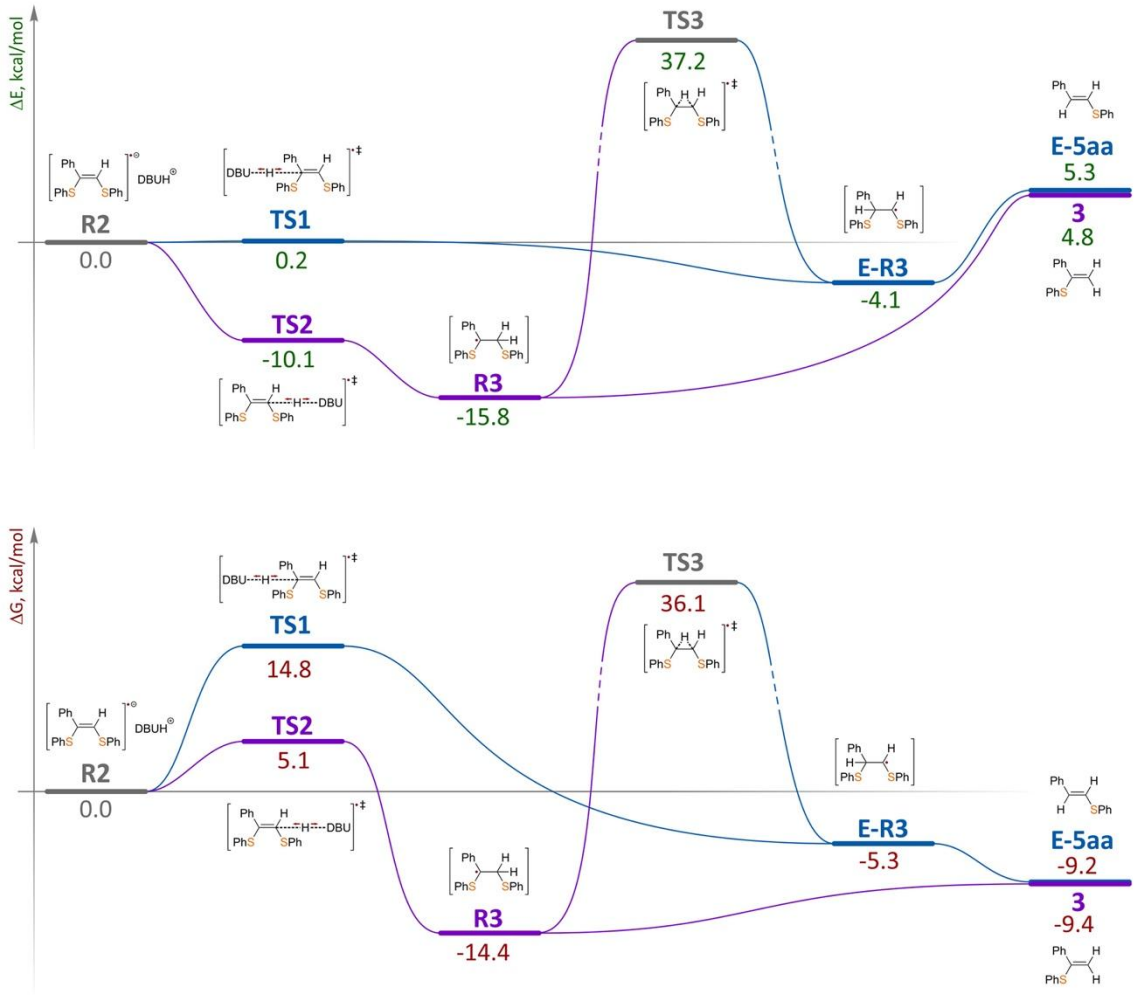
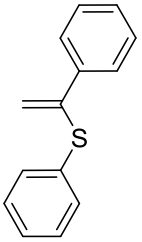


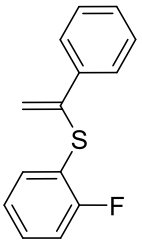
Figure S15. Total energy profile (ΔE) and free energy profile (ΔG) for mechanism of product **3** formation starting from intermediate **R2**, which is taken as a reference point, UBMK/6-311+G(d,p) D3BJ SMD(DMF).

Characterization data of products (3, 4, 5, 6)

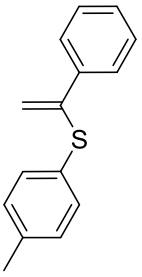
Products **3aa**[1], **3ab**[1], **3ac**[1], **3ad**[3], **3ai**[4], **(E)-4aa**[2], **(Z)-4aa**[5], **5aa**[1], **6aa**[1] and **3-6sa**[6] were identified according to published data.



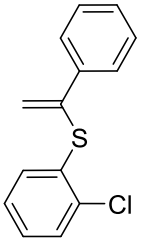
phenyl(1-phenylvinyl)sulfane (3aa)
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 300 MHz): 7.66-7.59 (2H, m), 7.39-7.25 (8H, m), 5.84 (1H, s), 5.38 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 142.8, 137.8, 133.1, 131.1, 129.3, 128.7, 128.5, 127.4, 126.8, 117.6. HRMS (ESI): *m/z* = 318.9707, calcd for $C_{14}H_{12}SAg$: 318.9705 $[M+Ag]^+$ (Δ = 0.6 ppm).



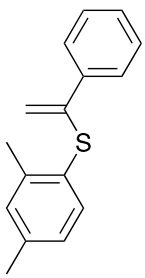
(2-fluorophenyl)(1-phenylvinyl)sulfane (3ab)
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 500 MHz): 7.65-7.57 (2H, m), 7.41-7.30 (5H, m), 7.29-7.22 (1H, m), 7.19-7.10 (1H, m), 5.80 (1H, s), 5.31 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 160.7 (d, *J*(C-F) = 245.5 Hz), 141.6, 137.5, 134.1, 130.4 (d, *J*(C-F) = 7.8 Hz), 128.8, 128.5, 126.7, 125.2 (d, *J*(C-F) = 3.3 Hz), 119.7 (d, *J*(C-F) = 17.6 Hz), 116.7, 116.0 (d, *J*(C-F) = 22.0 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -109.4-(-109.2) (m). HRMS (ESI): *m/z* = 229.0481, calcd for $C_{14}H_{11}FS$: 229.0482 $[M - H]^+$ (Δ = 0.4 ppm).



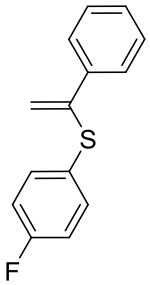
(1-phenylvinyl)(*p*-tolyl)sulfane (3ac)
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 300 MHz): 7.64-7.57 (2H, m), 7.40-7.31 (3H, m), 7.31-7.25 (2H, d, J = 8.1 Hz), 7.20-7.13 (2H, d, J = 8.1 Hz), 5.73 (1H, s), 5.22 (1H, s), 2.27 (3H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 143.7, 137.9, 137.5, 131.9, 130.1, 129.0, 128.7, 128.5, 126.7, 115.7, 20.6. HRMS (ESI): *m/z* = 225.0732, calcd for $C_{15}H_{14}S$: 225.0732 $[M - H]^+$ (Δ = 0.0 ppm).



(2-chlorophenyl)(1-phenylvinyl)sulfane (3ad)
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 500 MHz): 7.68-7.61 (2H, m), 7.54-7.48 (1H, m), 7.40-7.30 (3H, m), 7.28-7.20 (3H, m), 6.02 (1H, s), 5.58 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 140.5, 137.3, 133.1, 132.8, 131.7, 129.8, 128.8, 128.6, 127.8, 126.7, 120.7. HRMS (ESI): *m/z* = 245.0192, calcd for $C_{14}H_{11}ClS$: 245.0186 $[M-H]^+$ (Δ = 2 ppm).



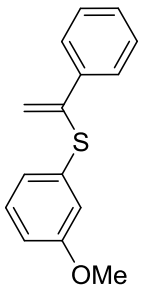
(2,4-dimethylphenyl)(1-phenylvinyl)sulfane (3ae)
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 300 MHz): 7.62-7.54 (2H, m), 7.42-7.29 (3H, m), 7.27 (1H, d, J = 7.8 Hz), 7.14 (1H, d, J = 1.1 Hz), 7.00 (1H, dd, J = 7.82 Hz, J = 1.13 Hz), 5.56 (1H, s), 4.79 (1H, s), 2.35 (3H, s), 2.25 (3H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 143.8, 140.4, 138.7, 138.2, 134.4, 131.6, 128.8, 128.6, 127.8, 127.5, 126.6, 112.3, 20.7, 19.9. HRMS (ESI): *m/z* = 347.0016, calcd for $C_{16}H_{16}SAg$: 347.0018 $[M]^+$ (Δ = 2.4 ppm).



(4-fluorophenyl)(1-phenylvinyl)sulfane (3af)

Isolation protocol A.

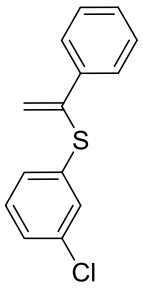
^{1}H NMR (DMSO-d_6, 500 MHz): 7.63-7.57 (2H, m), 7.46-7.40 (2H, m), 7.39-7.32 (3H, m), 7.24-7.17 (2H, m) 5.77 (1H, s), 5.26 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 161.7 (d, *J*(C-F) = 244.5 Hz), 143.5, 137.7, 134.2 (d, *J*(C-F) = 8.3 Hz), 128.8, 128.5, 128.3 (d, *J*(C-F) = 2.8 Hz), 126.8, 116.5 (d, *J*(C-F) = 22.0 Hz), 116.2. ^{19}F NMR (DMSO-d_6, 470.5 MHz): -113.7 (1F, tt, J(F-H) = 8.9 Hz, J(F-H) = 5.1 Hz). HRMS (ESI): *m/z* = 336.9611, calcd for $C_{14}H_{11}FSAg$: 336.9611 $[M + Ag]^+$ (Δ = 0 ppm).



(3-methoxyphenyl)(1-phenylvinyl)sulfane (3ag)

Isolation protocol B.

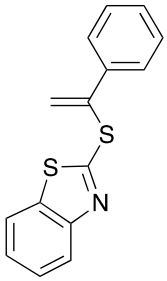
^{1}H NMR (DMSO-d_6, 500 MHz): 7.67-7.60 (2H, m), 7.37-7.29 (3H, m), 7.25-7.18 (1H, dd, J = 8.0, 7.9 Hz), 6.93-6.89 (1H, d, J = 7.9 Hz), 6.88-6.85 (1H, t J = 1.8 Hz), 6.80 (1H, dd, J = 8.0, 1.8 Hz), 5.87 (1H, s), 5.50 (1H, s), 3.68 (3H, s). ^{13}C{^{1}H} NMR (DMSO -d_6, 125 MHz): 159.6, 142.3, 137.9, 134.6, 130.1, 128.6, 128.4, 126.8, 122.6, 118.5, 115.7, 113.0, 55.0. HRMS (ESI): *m/z* = 241.0690, calcd for $C_{15}H_{14}S$: 241.0682 $[M - H]^+$ (Δ = 3.3 ppm).



(3-chlorophenyl)(1-phenylvinyl)sulfane (3ah)

Isolation protocol A.

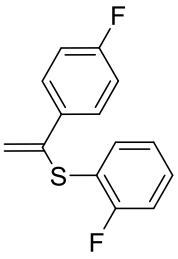
^{1}H NMR (DMSO-d_6, 500 MHz): 7.66-7.60 (2H, m), 7.40-7.30 (5H, m), 7.30-7.24 (2H, m), 5.99 (1H, s), 5.63 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 141.2, 137.4, 136.2, 133.6, 130.9, 129.1, 128.8, 128.5, 126.9, 126.9, 120.6. HRMS (ESI): *m/z* = 245.0192, calcd for $C_{14}H_{11}ClS$: 245.0186 $[M-H]^-$ (Δ = 2.4 ppm).



2-((1-phenylvinyl)thio)benzo[d]thiazole (3ai)

Isolation protocol B.

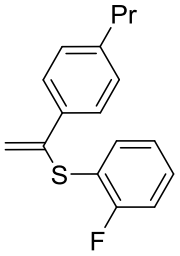
^{1}H NMR (DMSO-d_6, 500 MHz): 7.95-7.90 (1H, d, J = 8.2 Hz), 7.88-7.82 (1H, d, J = 8.1 Hz), 7.78-7.71 (2H, d, J = 7.5 Hz), 7.47-7.42 (1H, dd, J = 7.5, 7.6 Hz), 7.42-7.31 (4H, m), 6.39 (1H, s), 6.19 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 165.7, 153.0, 138.0, 137.0, 135.3, 129.2, 128.7, 127.1, 126.9, 126.4, 124.7, 121.7, 121.6. HRMS (ESI): *m/z* = 270.0404, calcd for $C_{15}H_{11}NS_2$: 270.0406 $[M + H]^+$ (Δ = 0.7 ppm).



(2-fluorophenyl)(1-(4-fluorophenyl)vinyl)sulfane (3bb)

Isolation protocol A.

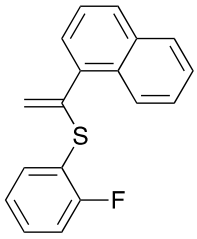
^{1}H NMR (DMSO-d_6, 500 MHz): 7.68-7.61 (2H, m), 7.41-7.35 (2H, m), 7.31-7.25 (1H, m), 7.23-7.15 (3H, m), 5.81 (1H, s), 5.35 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 162.2 (d, *J*(C-F) = 245.9 Hz), 160.6 (d, *J*(C-F) = 244.7 Hz), 140.4, 134.0, 130.6 (d, *J*(C-F) = 8.0 Hz), 129.0 (d, *J*(C-F) = 8.5 Hz), 125.3 (d, *J*(C-F) = 3.6 Hz), 119.6 (d, *J*(C-F) = 17.9 Hz), 117.4, 116.1 (d, *J*(C-F) = 22.3 Hz), 115.4 (d, *J*(C-F) = 21.6 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -109.6 (1F, m), -112.8 (1F, tt, J(F-H) = 8.7 Hz, J(F-H) = 5.4 Hz). HRMS (ESI): *m/z* = 247.0393, calcd for $C_{14}H_{10}F_2S$: 247.0388 $[M - H]^+$ (Δ = 2.0 ppm).



(2-fluorophenyl)(1-(4-propylphenyl)vinyl)sulfane (3cb)

Isolation protocol A.

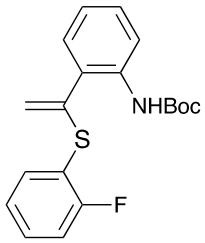
^{1}H NMR (DMSO-d_6, 500 MHz): 7.55-7.48 (2H, m), 7.41-7.34 (2H, m), 7.31-7.24 (1H, m), 7.21-7.14 (3H, m), 5.78 (1H, s), 5.24 (1H, s), 2.53 (2H, t, J = 7.4 Hz), 1.61-1.52 (2H, tq, J = 7.4, 7.3 Hz), 0.87 (3H, t, J = 7.3 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 160.6 (d, J(C-F) = 245.2 Hz), 143.0, 141.4, 134.9, 134.0, 130.5 (d, J(C-F) = 7.8 Hz), 128.5, 126.6, 125.3 (d, J(C-F) = 3.5 Hz), 119.8 (d, J(C-F) = 17.8 Hz), 116.05 (d, J(C-F) = 22.1 Hz), 116.01, 36.8, 23.8, 13.5. ^{19}F NMR (DMSO-d_6, 470.5 MHz): -109.0 (ddd, J = 9.7, 7.2, 5.8 Hz). HRMS (ESI): *m/z* = 273.1107, calcd for $C_{17}H_{17}FS$: 273.1108 $[M + H]^+$ (Δ = 0.4 ppm).



(2-fluorophenyl)(1-(naphthalen-1-yl)vinyl)sulfane (3db)

Isolation protocol A.

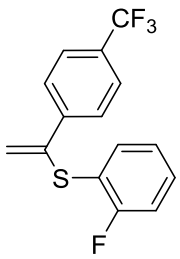
^{1}H NMR (DMSO-d_6, 300 MHz): 8.33-8.23 (1H, m), 7.97-7.84 (2H, m), 7.65-7.38 (6H, m), 7.29 (1H, td, J = 8.9 Hz, 1.2 Hz), 7.17 (1H, td, J = 7.5 Hz, 1.2 Hz), 5.37 39 (1H, s), 5.25 (1H, s). ^{13}C{^{1}H} (DMSO-d_6, 75 MHz): 161.7 (d, J(C-F) = 246.8 Hz), 141.9, 136.6, 136.0, 133.1, 132.1 (d, J(C-F) = 7.8 Hz), 130.4, 128.8, 128.2, 126.6, 126.4, 126.1, 125.3 (d, J(C-F) = 3.9 Hz), 125.1, 125.0, 116.3 (d, J(C-F) = 18.1 Hz), 114.7. ^{19}F NMR (DMSO-d_6, 470.5 MHz): -107.2 (ddd, J(F-H) = 9.3 Hz, 7.3 Hz, 5.3 Hz). HRMS (ESI): *m/z* = 281.0791, calcd for $C_{18}H_{13}FS$ $[M + H]^+$ = 281.0795 (Δ = 1.4 ppm).



***tert*-butyl (2-(1-((2-fluorophenyl)thio)vinyl)phenyl)carbamate (3eb)**

Isolation protocol B.

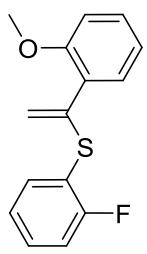
^{1}H NMR (DMSO-d_6, 500 MHz): 8.02 (1H, s), 7.62-7.55 (1H, m), 7.55-7.48 (1H, m), 7.47-7.39 (1H, m), 7.31-7.24 (3H, m), 7.22-7.16 (1H, m), 7.10-7.03 (1H, m), 5.41 (1H, s), 5.22 (1H, s) 1.48 (9H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 161.3 (d, J(C-F) = 246.0 Hz), 152.8, 140.2, 135.8, 135.5, 131.6 (d, J(C-F) = 8.1 Hz), 130.6, 129.5, 129.0, 125.3 (d, J(C-F) = 3.3 Hz), 123.7, 122.9, 118.4 (d, J(C-F) = 18.0 Hz), 116.7, 116.1 (d, J(C-F) = 22.6 Hz), 79.3, 28.0. ^{19}F NMR (DMSO-d_6, 470.5 MHz): -107.9-(-108.1) (m). HRMS (ESI): *m/z* = 346.1270, calcd for $C_{19}H_{20}FNO_2S$ $[M + H]^+$ = 346.1272 (Δ = 0.5 ppm).



(2-fluorophenyl)(1-(4-(trifluoromethyl)phenyl)vinyl)sulfane (3fb)

Isolation protocol A.

^{1}H NMR (DMSO-d_6, 500 MHz): 7.82 (2H, d, J = 8.2 Hz), 7.74 (2H, d, J = 8.4 Hz), 7.43-7.36 (2H, m), 7.33-7.26 (1H, m), 7.22-7.15 (1H, m), 5.99 (1H, s), 5.53 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 160.5 (d, J(C-F) = 245.9 Hz), 141.6, 140.1, 133.9, 130.7 (d, J(C-F) = 8.1 Hz), 129.0 (q, J(C-F) = 30.6 Hz), 127.6, 125.5 (q, J(C-F) = 3.7 Hz), 125.4 (d, J(C-F) = 3.5 Hz), 124.0 (q, J(C-F) = 272.3 Hz), 120.0, 119.3 (d, J(C-F) = 17.4 Hz), 116.2 (d, J(C-F) = 22.0 Hz). ^{19}F NMR ((DMSO-d_6, 470.5 MHz): -61.1 (3F, s), -109.4-(-109.5) (1F, m). HRMS (ESI): *m/z* = 404.9487, calcd for $C_{15}H_{10}F_4S$ $[M+Ag]^+$ = 404.9485 (Δ = 0.5 ppm).

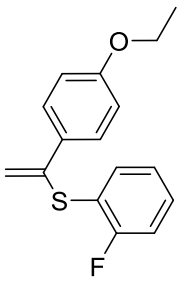


(2-fluorophenyl)(1-(2-methoxyphenyl)vinyl)sulfane (3gb)

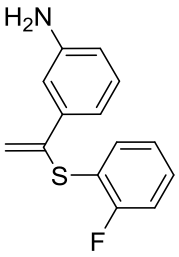
Isolation protocol B.

^{1}H NMR (DMSO-d_6, 400 MHz): 7.42 (1H, td, J = 7.7 Hz, 1.8 Hz), 7.39-7.16 (4H, m), 7.14 (1H, td, J = 7.7 Hz, 1.4 Hz), 6.97 (1H, d, J = 8.3 Hz), 6.88 (1H, td, J = 7.4 Hz, 1.1 Hz), 5.49 (1H, s), 5.32 (1H, s), 3.75 (3H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): 160.9 (d, J(C-F) = 245.8 Hz), 156.4, 139.2, 134.7, 130.6 (d, J(C-F) = 8.2 Hz), 129.9, 129.8, 127.2, 125.0 (d, J(C-F) = 3.7 Hz), 120.2, 120.0 (d, J(C-F) = 18.2

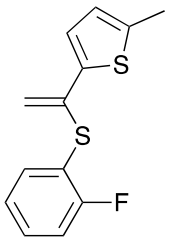
Hz), 118.3, 115.9 (d, *J*(C-F) = 22.3 Hz), 111.6, 55.6. ^{19}F NMR (DMSO-d_6, 376.5 MHz): -108.6 (ddd, J(C-F) = 9.2 Hz, 7.4 Hz, 5.1 Hz). HRMS (ESI): *m/z* = 366.9712, calcd for $C_{15}H_{13}OFSAg$: 366.9717 $[M + Ag]^+$ (Δ = 1.3 ppm).



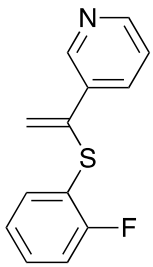
(1-(4-ethoxyphenyl)vinyl)(2-fluorophenyl)sulfane (3hb)
Isolation protocol B.
^{1}H NMR (DMSO-d_6, 300 MHz): 7.56-7.50 (2H, m), 7.39-7.32 (2H, m), 7.29-7.23 (1H, m), 7.19-7.12 (1H, m), 6.93-6.85 (2H, m), 5.72 (1H, s), 5.23 (1H, s), 4.01 (2H, q, *J* = 6.9 Hz), 1.31 (3H, t, *J* = 6.9 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): 160.5 (d, *J*(C-F) = 245.3 Hz), 159.0, 140.9, 133.8 (d, *J*(C-F) = 1 Hz), 133.2 (d, *J*(C-F) = 8.1 Hz), 129.6, 128.0, 125.2 (d, *J*(C-F) = 3.4 Hz), 120.1 (d, *J*(C-F) = 17.8 Hz), 116.0 (d, *J*(C-F) = 22.0 Hz), 115.4, 114.3, 63.1, 14.5. ^{19}F NMR (DMSO-d_6, 470.5 MHz): -109.3-(-109.1) (m). HRMS (ESI): *m/z* = 273.0750, calcd for $C_{16}H_{14}FOS$ $[M-H]^+$ = 273.0744 (Δ = 2.2 ppm).



3-(1-((2-fluorophenyl)thio)vinyl)aniline (3ib)
Isolation protocol B.
^{1}H NMR (DMSO-d_6, 500 MHz): 7.42-7.36 (2H, m), 7.29 (1H, t, J = 9.2 Hz), 7.19 (1H, t, J = 7.7 Hz), 7.00 (1H, t, J = 7.7 Hz), 6.84 (1H, s), 6.74 (1H, d, J = 7.5 Hz), 6.53 (1H, d, J = 7.5 Hz), 5.64 (1H, s), 5.18 (2H, br.s), 5.10 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 160.7 (d, *J*(C-F) = 245.3 Hz), 148.8, 142.5, 138.3, 134.2, 130.5 (d, *J*(C-F) = 8.0 Hz), 129.0, 125.3 (d, *J*(C-F) = 3.3 Hz), 120.0 (d, *J*(C-F) = 17.8 Hz), 116.1 (d, *J*(C-F) = 22.1 Hz), 114.8, 114.5, 114.3, 112.0. ^{19}F NMR (DMSO-d_6, 470.5 MHz): -109.3 (ddd, J(C-F) = 9.6 Hz, 7.5 Hz, 5.5 Hz). HRMS (ESI): *m/z* = 246.0748, calcd for $C_{14}H_{12}FNS$ $[M + H]^+$ = 246.0747 (Δ = 0.4 ppm).

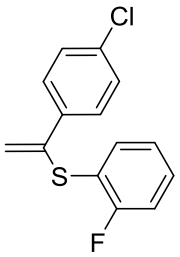


2-(1-((2-fluorophenyl)thio)vinyl)-5-methylthiophene (3jb)
(+ 10% of 5jb)
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 300 MHz): 7.42-7.34 (2H, m, **3jb**), 7.31-7.25 (1H, m, **3jb**), 7.21-7.16 (1H, td, J = 7.6, 1.4 Hz, **3jb**) 7.08 (1H, d, *J* = 3.6 Hz, **3jb**), 6.95 (1H*0.1, d, *J* = 3.7, **5jb**), 6.91 (1H*0.1, d, *J* = 15.2, **5jb**), 6.70 (1H, dq, *J* = 3.6, 1.1 Hz, **3jb**), 6.64 (1H*0.1, d, *J* = 15.2, **5jb**), 5.76 (1H, s, **3jb**), 5.15 (1H, s, **3jb**), 2.42 (1H*0.1, s, **5jb**), 2.40 (3H, d, *J* = 1.1 Hz, **3jb**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 160.4 (d, *J*(C-F) = 245.4 Hz), 140.7, 139.0, 134.1, 133.4, 130.5 (d, *J*(C-F) = 8.0 Hz), 126.2, 126.1, 125.4 (d, *J*(C-F) = 3.6 Hz), 119.8 (d, *J*(C-F) = 17.6 Hz), 116.1 (d, *J*(C-F) = 21.9 Hz), 115.4, 15.0. ^{19}F NMR (DMSO-d_6, 470.5 MHz): -109.6 (1F, m, **3jb**), -111.3 (1F*0.1, m, **5jb**). HRMS (ESI): *m/z* = 356.9330, calcd for $C_{13}H_{11}FSAg$ $[M]^+$ = 356.9332 (Δ = 0.6 ppm).

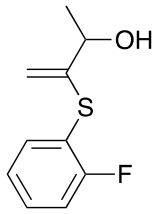


3-(1-((2-fluorophenyl)thio)vinyl)pyridine (3kb)
(+ 20% of 4kb)
Isolation protocol B.
^{1}H NMR (DMSO-d_6, 400 MHz): 8.76 (1H, d, J = 2.3 Hz, **3kb**), 8.64 (1H*0.2, d, J = 2.3 Hz, **4kb**), 8.50 (1H, dd, J = 4.7, 1.3 Hz, **3kb**), 8.46 (1H*0.2, dd, J = 4.8, 1.7 Hz, **4kb**), 7.95 (1H, dt, J = 7.9, 1.9 Hz, **3kb**), 7.87 (1H*0.2, dt, J = 8.0, 1.7 Hz, **4kb**), 7.53 (1H*0.2, td, J = 8.0, 1.6 Hz, **4kb**), 7.44-7.31 (3H, m, **3kb** + 3H*0.2, **4kb**), 7.31-7.19 (1H, m, **3kb** + 3H*0.2, **4kb**), 7.18-7.08 (1H, m, **3kb** + 2H*0.2, **4kb**), 7.03 (1H*0.2, s, **4kb**), 5.93 (1H, s), 5.50 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): 160.7 (d, *J*(C-F) = 245.4 Hz), 149.7, 147.6, 134.3, 134.0, 133.2, 130.7 (d, *J*(C-F) = 8.1 Hz), 125.4 (d, *J*(C-F) = 3.5 Hz), 123.4, 119.24, 119.16 (d 17.4Hz) 116.1 (d, *J*(C-F) = 22.0 Hz). ^{19}F

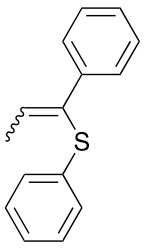
NMR (DMSO-d_6, 375.5 MHz): -109.4 (ddd, J(C-F) = 9.6, 7.5, 5.5 Hz, **3kb**), -110.0 (1F*0.2, ddd, J(C-F) = 9.9, 7.7, 5.2 Hz, **4kb**), -110.6 (1F*0.2, ddd, J(C-F) = 9.8, 7.6, 5.3 Hz, **4kb**) HRMS (ESI): *m/z* = 232.0602, calcd for $C_{13}H_{10}FNS$ $[M + H]^+$ = 232.0591 (Δ = 4.7 ppm).



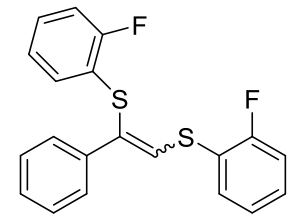
(1-(4-chlorophenyl)vinyl)(2-fluorophenyl)sulfane (3lb)
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 500 MHz): 7.62 (2H, d, J = 8.4 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.40-7.35 (2H, m), 7.30-7.24 (1H, m), 7.20-7.14 (1H, m), 5.87 (1H, s), 5.41 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 160.5 (d, *J*(C-F) = 245.3 Hz), 140.2, 136.3, 133.8, 133.4, 130.5 (d, *J*(C-F) = 8.4 Hz), 128.5, 125.3 (d, *J*(C-F) = 3.2 Hz), 119.5 (d, *J*(C-F) = 17.6 Hz), 118.2, 116.1 (d, *J*(C-F) = 22.0 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -109.4 (ddd, *J* (C-F) = 9.6, 7.5, 5.2 Hz). HRMS (ESI): *m/z* = 372.9264, calcd for $C_{14}H_{10}ClFSAg$: 372.9215 $[M + Ag]^+$ (Δ = 13 ppm).



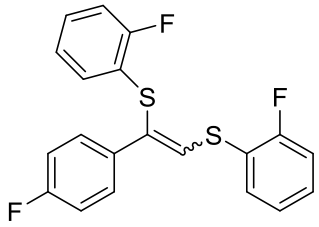
3-((2-fluorophenyl)thio)but-3-en-2-ol (3mb)
Isolation protocol B.
^{1}H NMR (DMSO-d_6, 300 MHz): 7.51-7.45 (1H, m, **3mb**), 7.45-7.40 (1H, m, **3mb**), 7.32-7.26 (1H, m, **3mb**), 7.26-7.21 (1H, m, **3mb**), 5.61 (1H*0.08, d, *J* = 4.0 Hz, **4mb**), 5.60 (1H*0.08, s, **4mb**), 5.43 (1H, s), 5.33 (1H, d, *J* = 4.6 Hz, **3mb**), 4.84 (1H*0.08, qd, *J* = 6.3, 4.0 Hz, **4mb**), 4.64 (1H, s, **3mb**), 4.22 (1H, quint, J = 5.7 Hz, **3mb**), 1.29 (3H*0.08, d, *J* = 6.3 Hz, **4mb**), 1.26 (3H, d, *J* = 6.5 Hz, **3mb**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 161.3 (d, *J*(C-F) = 245.5 Hz), 149.4, 135.3, 130.9 (d, *J*(C-F) = 8.0 Hz), 125.4 (d, *J*(C-F) = 3.6 Hz), 119.3 (d, *J*(C-F) = 18.2 Hz), 116.2 (d, *J*(C-F) = 22.4 Hz), 110.6, 68.6, 23.3. ^{19}F NMR (DMSO-d_6, 376.5 MHz): -108.4-(-108.6) (1F, m, **3mb**), -108.7-(-108.8) (1F*0.08, m, **4mb**), -111.7-(-111.8) (1F*0.08, m, **4mb**). HRMS (ESI): *m/z* = 304.9559, calcd for $C_{10}H_{11}FSO$ $[M+Ag]^+$ = 304.9560 (Δ = 0.3 ppm).



Phenyl(1-phenylprop-1-en-1-yl)sulfane (3sa)
Mixture E/Z: 14:1
Isolation protocol A.
^{1}H NMR (DMSO-d_6, 300 MHz): 7.61-7.49 (2H, m, **E**), 7.46-7.00 (8H, m, **E** + 10H*0.07, m, **Z**), 6.64 (1H, q, J = 6.7 Hz, **E**), 6.28 (1H*0.07, q, J = 7.1 Hz, **Z**), 2.05 (3H, d, J = 6.7 Hz, **E**), 1.75 (3H*0.07, d, J = 7.1 Hz, **E**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 139.9, 135.3, 135.1, 132.8, 129.0, 128.3, 127.53, 127.52, 127.0, 125.6, 16.8. HRMS (ESI): *m/z* = 226.0810, calcd for $C_{15}H_{14}S$ $[M]^+$ = 226.0811 (Δ = 0.4 ppm).



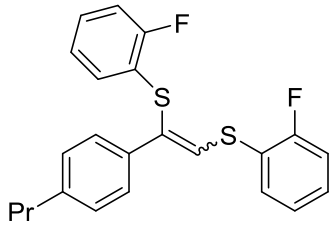
(1-phenylethene-1,2-diyl)bis((2-fluorophenyl)sulfane) (4ab)
Mixture E/Z: 1:2
^{1}H NMR (DMSO-d_6, 300 MHz): 7.78-7.68 (1H*2, td, J = 7.7, 1.6 Hz, **Z**), 7.66-7.57 (2H*2, m, **Z**), 7.56-7.03 (13H, m, **E** + 11H*2, m, **Z**), 6.82 (1H, s, **E**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 160.13 (d, *J*(C-F) = 244.2 Hz), 160.12 (d, *J*(C-F) = 244.2 Hz), 159.6 (d, *J*(C-F) = 242.7 Hz), 159.5 (d, *J*(C-F) = 243.5 Hz), 137.3, 135.9, 135.1, 133.0, 132.5, 132.5, 131.3, 130.2 (d, *J*(C-F) = 7.9 Hz), 130.1 (d, *J*(C-F) = 7.9 Hz), 130.03, 129.96, 129.8 (d, *J*(C-F) = 7.9 Hz), 128.8, 128.70, 128.67, 128.5, 128.4, 128.0, 126.6, 125.9, 125.5 (d, *J*(C-F) = 3.2 Hz), 125.1 (d, *J*(C-F) = 3.2 Hz), 121.3 (d, *J*(C-F) = 16.7 Hz), 120.6 (d, *J*(C-F) = 16.6 Hz), 120.5 (d, *J*(C-F) = 17.1 Hz), 120.4 (d, *J*(C-F) = 17.1 Hz), 116.1 (d, *J*(C-F) = 21.5 Hz), 116.0 (d, *J*(C-F) = 21.5 Hz), 115.9 (d, *J*(C-F) = 21.5 Hz), 115.7 (d, *J*(C-F) = 21.1 Hz). ^{19}F NMR ((DMSO-d_6, 376.5 MHz): -110.17, (-110.21) (1F*2, m, **Z** + 1F, m, **E**), -110.8 (1F, ddd, J(C-F) = 9.8, 7.8, 5,6 Hz, **E**), -111.7 (1F*2, m, **Z**). HRMS (ESI): *m/z* = 462.9550, calcd for $C_{20}H_{14}F_2S_2$ $[M+H]^+$ = 462.9550 (Δ = 0 ppm).



(1-(4-fluorophenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) (4bb)

Mixture E/Z: 3:1

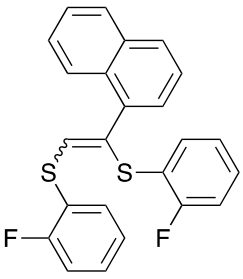
^{1}H NMR (DMSO-d_6, 300 MHz): 7.76-7.68 (1H*0.33, td, J = 7.8, 1.6 Hz, **Z**), 7.68-7.60 (2H*0.33, m, **Z**),7.59-7.52 (2H, m, **E**), 7.52-7.05 (10H, m, **E** + 10H*0.33, m, **Z**), 6.85 (1H, s, **E**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 161.8 (d, *J*(C-F) = 245.9 Hz), 161.7 (d, *J*(C-F) = 245.9 Hz), 160.2 (d, *J*(C-F) = 244.9 Hz), 160.1 (d, *J*(C-F) = 244.9 Hz), 159.6 (d, *J*(C-F) = 243.8 Hz), 159.5 (d, *J*(C-F) = 243.8 Hz), 134.9, 133.8 (d, *J*(C-F) = 2.8 Hz), 133.1, 132.5, 132.2 (d, *J*(C-F) = 3.1 Hz), 131.6, 131.4, 131.0 (d, *J*(C-F) = 8.6 Hz), 130.2 (d, *J*(C-F) = 8.0 Hz), 130.1, 129.9 (d, *J*(C-F) = 7.9 Hz), 128.8 (d, *J*(C-F) = 7.9 Hz), 128.7 (d, *J*(C-F) = 8.4 Hz), 127.0, 126.1, 125.5 (d, *J*(C-F) = 3.3 Hz), 125.2 (d, *J*(C-F) = 3.4 Hz), 121.1 (d, *J*(C-F) = 17.0 Hz), 120.2 (d, *J*(C-F) = 17.2 Hz), 116.1 (d, *J*(C-F) = 21.5 Hz), 116.0 (d, *J*(C-F) = 21.7 Hz), 115.9 (d, *J*(C-F) = 21.9 Hz), 115.8 (d, *J*(C-F) = 21.0 Hz), 115.4 (d, *J*(C-F) = 21.7 Hz), 115.3 (d, *J*(C-F) = 21.7 Hz). ^{19}F NMR (DMSO-d_6, 376.5 MHz): -110.1-(-110.2) (1F*0.33, m, **Z** + 1F, m, **E**), -110.7 (1F, m, **E**), -111.6 (1F*0.33, m, **Z**), -112.0 (1F, m, **E**), -113.9 (1F*0.33, m, **Z)**. HRMS (ESI): *m/z* = 375.0494, calcd for $C_{20}H_{14}F_3S_2$ $[M]^+$ = 375.0484 (Δ = 2.7 ppm).



(1-(4-propylphenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) (4cb)

Mixture E/Z: 9:1

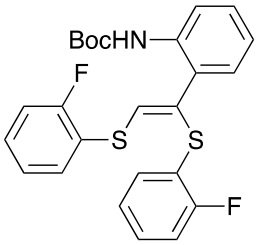
^{1}H NMR (DMSO-d_6, 300 MHz): 7.75-7.67 (1H*0.11, m, **Z**), 7.54-7.50 (2H*0.11, m, **Z**), 7.50-7.08 (10H*0.11, m, **Z** + 12H, m, **E**), 6.75 (1H*0.89, s, **E**), 2.59-2.43 (2H*0.11, t, **Z** + 2H, t, **E**), 1.61-1.47 (2H*0.11, m, **Z** + 2H, m, **E**), 0.88-0.79 (3H*0.11, t, **Z** + 3H, t, **E**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 160.1 (d, *J*(C-F) = 243.8 Hz), 159.6 (d, *J*(C-F) = 244.3 Hz), 143.0, 133.3, 132.9, 132.5, 130.0 (d, *J*(C-F) = 7.9 Hz), 129.8 (d, *J*(C-F) = 7.8 Hz), 128.6, 128.3, 125.5 (d, *J*(C-F) = 3.4 Hz), 125.21, 125.18 (d, *J*(C-F) = 3.2 Hz), 121.4 (d, *J*(C-F) = 16.9 Hz), 120.6 (d, *J*(C-F) = 17.3 Hz), 116.0 (d, *J*(C-F) = 21.7 Hz), 115.9 (d, *J*(C-F) = 21.7 Hz), 36.9, 23.7, 13.6. ^{19}F NMR (DMSO-d_6, 376.5 MHz): -108.3 (1F*0.11, m, **Z**), -110.3 (1F, ddd, J(C-F) = 9.9, 7.8, 5.7 Hz, **E**), -110.9 (1F, ddd, J(C-F) = 9.9, 7.7, 5.5 Hz, **E**), -111.9 (1F*0.11, m, **Z**). HRMS (ESI): *m/z* = 505.0026, calcd for $C_{23}H_{20}F_2S_2Ag$ $[M]^+$ = 505.0020 (Δ = 2.7 ppm).



(1-(naphthalen-1-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) (4db)

Mixture E/Z: 6:1

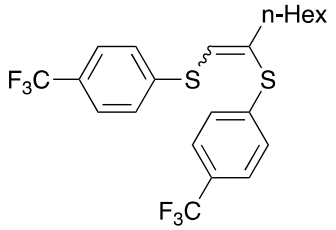
^{1}H NMR (DMSO-d_6, 500 MHz): 8.25-8.21 (1H*0.15, m, **Z**), 8.10-8.04 (1H, m, **E**), 7.98-7.94 (1H, m, **E**), 7.94-7.90 (1H, m, **E**), 7.87-7.83 (1H*0.15, m, **Z**), 7.79-7.75 (1H*0.15, m, **Z**), 7.69-7.64 (1H*0.15, m, **Z**), 7.64-7.10 (9H*0.15, m **Z** + 12H, m, **E**), 7.04-6.98 (1H*0.15, m, **Z**), 6.95 (1H*0.15, s, **Z**), 6.91-6.86 (1H*0.15, m, **Z**), 6.7 (1H, s, **E**). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 161.4 (d, *J*(C-F) = 246.1 Hz), 159.3 (d, *J*(C-F) = 244.4 Hz), 135.9, 133.8, 133.3, 133.2, 131.8 (d, *J*(C-F) = 7.9 Hz), 130.5, 129.8, 129.2 (d, *J*(C-F) = 8.1 Hz), 129.1, 128.4, 127.3, 126.7, 126.2, 125.4 (d, *J*(C-F) = 3.0 Hz), 125.2, 124.6, 122.9, 121.5 (d, *J*(C-F) = 16.8 Hz), 118.2 (d, *J*(C-F) = 18.0 Hz), 116.1 (d, *J*(C-F) = 22.2 Hz), 115.8 (d, *J*(C-F) = 21.6 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -107.6 (1F, m, **E**), -108.1 (1F*0.15, m, **Z**), -110.5 (1F*0.15, m, **Z**), -111.2 (1F, m, **E**). HRMS (ESI): *m/z* =407.0723 calcd for $C_{24}H_{16}F_2S_2$ $[M+H]^+$ = 407.0734 (Δ = 2.7 ppm).



tert-butyl(2-(1,2-bis((2-fluorophenyl)thio)vinyl)phenyl)carbamate (4eb)

Mixture E/Z: 1:3

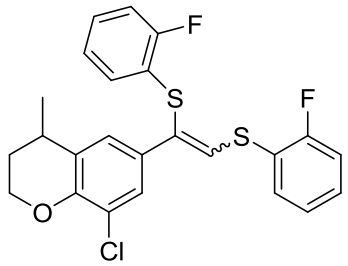
^{1}H NMR (DMSO-d_6, 300 MHz): 8.49 (1H, br s, **E**), 7.98 (1H*3, br s, **Z**), 7.71-7.10 (10H*3, m, **Z** + 11H, m, **E**) 7.08-6.99 (2H*3, m, **Z** + 1H, m, **E**), 6.63 (1H*3, s, **Z**), 5.76 (1H, s, **E**), 1.45 (9H, s, **E**), 1.44 (9H*3, s, **Z**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 161.1 (d, *J*(C-F) = 245.9 Hz), 159.9 (d, *J*(C-F) = 244.0 Hz), 159.8 (d, *J*(C-F) = 244.0 Hz), 159.3 (d, *J*(C-F) = 244.0 Hz), 153.3, 152.7, 135.7, 135.6, 135.0, 133.3, 132.0, 131.82, 131.78, 131.5, 131.3, 131.2, 130.8, 129.9, 129.7, 129.4, 129.2, 128.4, 128.1, 126.9, 125.4 (d, *J*(C-F) = 3.6 Hz), 125.3 (d, *J*(C-F) = 3.5 Hz), 125.2 (d, *J*(C-F) = 3.5 Hz), 125.0, 124.8 (d, *J*(C-F) = 3.4 Hz), 124.3, 123.3, 122.3, 121.5 (d, *J*(C-F) = 16.9 Hz), 121.0 (d, *J*(C-F) = 16.2 Hz), 119.7 (d, *J*(C-F) = 16.9 Hz), 119.0 (d, *J*(C-F) = 17.7 Hz), 116.0 (d, *J*(C-F) = 22.1 Hz), 115.8 (d, *J*(C-F) = 21.6 Hz), 115.6 (d, *J*(C-F) = 22.5 Hz), 79.3, 79.0, 28.1, 27.9. ^{19}F NMR ((DMSO-d_6, 376.5 MHz): -108.8 (1F*3, m, **Z**), -110.5 (1F, m, **E**), -110.6 (1F, m, **E**), -111.3 (1F*2, m, **Z**). HRMS (ESI): *m/z* = 472.1206, calcd for $C_{25}H_{23}F_2NO_2S_2$ $[M+H]^+$ = 472.1211 (Δ = 1.1 ppm).



Oct-1-ene-1,2-diylbis((4-(trifluoromethyl)phenyl)sulfane) (4rj)

Mixture E/Z: 11:1

^{1}H NMR (DMSO-d_6, 400 MHz): 7.74-7.67 (4H, m, **E**), 7.64-7.61 (4H*0.09, m, **Z**), 7.58-7.52 (4H, m, **E**), 7.51-7.43 (4H*0.09, m, **Z**), 7.21 (1H*0.09, s, **Z**), 6.81 (1H, s, **E**), 2.39 (2H, t, *J* = 7.5 Hz, **E**), 1.52-1.44 (2H, m, **E**), 1.31-1.14 (8H, m **E**), 0.82-0.77 (3H, t, *J* = 6.8 Hz, **E** + 3H*0.09, m, **Z**). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): 140.4 (q, *J*(C-F) = 1.3 Hz), 139.8 (q, *J*(C-F) = 1.3 Hz), 136.9, 129.8, 127.9, 127.3 (q, *J*(C-F) = 32.2 Hz), 126.9 (q, *J*(C-F) = 32.1 Hz), 126.15 (q, *J*(C-F) = 3.8 Hz), 126.07, 126.05 (q, *J*(C-F) = 3.8 Hz), 124.09 (q, *J*(C-F) = 272.1 Hz), 124.08 (q, *J*(C-F) = 272.1 Hz), 32.4, 30.8, 27.9, 27.4, 21.9, 13.8. ^{19}F NMR ((DMSO-d_6, 376.5 MHz): -60.60 (3F*0.09, **Z**), -60.61 (3F*0.09, **Z**), -60.63 (3F, **E**), -60.67 (3F, **E**). HRMS (ESI): *m/z* = 464.1067, calcd for $C_{22}H_{22}F_6S_2$ $[M]^+$ = 464.1062 (Δ = 1.2 ppm).

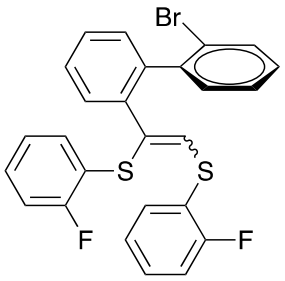


6-(1,2-bis((2-fluorophenyl)thio)vinyl)-8-chloro-4-methylchromane

(4ob')

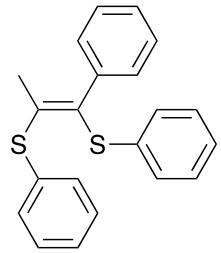
Mixture E/Z: 1:1.25

^{1}H NMR (DMSO-d_6, 300 MHz): 7.75-7.68 (1H*0.8, m, **E**), 7.54-7.07 (10H, m, **Z** + 9H*0.8, m, **E**), 6.78 (1H, s, **Z**), 5.76 (1H*0.8, s, **E**), 4.25 (2H, t, *J* = 5.3 Hz, **Z**), 4.20 (2H*0.8, t, *J* = 5.3 Hz, **E**), 3.01-2.83 (1H, m, **Z** + 1H*0.8, m, **E**), 2.09-1.91 (1H, m, **Z** + 1H*0.8, m, **E**), 1.73-1.54 (1H, m, **Z** + 1H*0.8, m, **E**), 1.23 (3H, d, *J* = 6.9 Hz, **Z**), 1.18 (3H*0.8, d, *J* = 7.0 Hz, **E**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 160.28 (d, *J*(C-F) = 244.7 Hz), 160.32 (d, *J*(C-F) = 244.1 Hz), 159.8 (d, *J*(C-F) = 243.6 Hz), 159.8 (d, *J*(C-F) = 244.1 Hz), 149.9, 149.4, 133.7, 133.4, 132.7, 131.6, 131.5, 130.5, 130.4 (d, *J*(C-F) = 7.7 Hz), 130.3 (d, *J*(C-F) = 7.5 Hz), 130.1 (d, *J*(C-F) = 7.9 Hz), 129.7, 129.5, 129.4, 129.0 (d, *J*(C-F) = 7.7 Hz), 128.3, 128.0, 127.6, 127.0, 126.0, 125.59, 125.61, 125.5, 125.4 (d, *J*(C-F) = 3.3 Hz), 121.2 (d, *J*(C-F) = 17.0 Hz), 120.6 (d, *J*(C-F) = 16.6 Hz), 120.39 (d, *J*(C-F) = 16.8 Hz), 120.41, 120.3 (d, *J*(C-F) = 17.2 Hz), 120.1, 116.2 (d, *J*(C-F) = 21.9 Hz), 116.1 (d, *J*(C-F) = 21.5 Hz), 116.0 (d, *J*(C-F) = 21.9 Hz), 116.0 (d, *J*(C-F) = 21.5 Hz), 64.5, 64.3, 28.9, 28.8, 28.0, 27.2. ^{19}F NMR ((DMSO-d_6, 470.5 MHz): -110.1 (1F*0.8, m, **E**), -110.2 (1F, m, **Z**), -110.7 (1F, m, **Z**), -111.6 (1F*0.8, m, **E**). HRMS (ESI): *m/z* = 461.0603, calcd for $C_{24}H_{19}ClF_2OS_2$ $[M+H]^+$ = 461.0607 (Δ = 0.8 ppm).



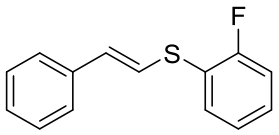
E-(1-(2'-bromo-[1,1'-biphenyl]-2-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) (4pb)

^{1}H NMR (DMSO-d_6, 300 MHz): 7.75-7.67 (1H, m), 7.51-7.11 (15H, m), 6.26 (1H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 160.9 (d, *J*(C-F) = 246.9 Hz), 159.3 (d, *J*(C-F) = 244.6 Hz), 140.1, 139.4, 134.9, 134.5, 132.7, 131.3, 131.2, 131.1, 130.3, 130.2, 129.5, 129.4, 129.3, 128.6, 127.9, 127.0, 125.3 (d, *J*(C-F) = 3.5 Hz), 125.2 (d, *J*(C-F) = 3.4 Hz), 123.0, 121.5 (d, *J*(C-F) = 16.3 Hz), 119.1 (d, *J*(C-F) = 17.6 Hz), 116.1 (d, *J*(C-F) = 21.7 Hz), 115.8 (d, *J*(C-F) = 21.4 Hz), ^{19}F NMR (DMSO-d_6, 470.5 MHz): -108.3-(-108.7) (1F, m), -110.9-(-111.7) (1F, m). HRMS (ESI): *m/z* = 510.9995, calcd for $C_{26}H_{17}F_2S_2$ $[M+H]^+$ = 510.9996 (Δ = 0.2 ppm).



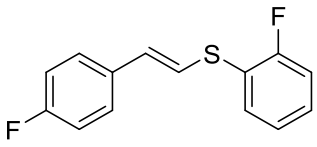
(Z)-(1-phenylprop-1-ene-1,2-diyl)bis(phenylsulfane) (4sa)

^{1}H NMR (DMSO-d_6, 300 MHz): 7.40-7.28 (7H, m), 7.25-7.10 (8H, m), 2.21 (3H, s). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 139.1, 135.5, 134.0, 133.4, 133.3, 131.5, 129.7, 129.6, 129.5, 129.3, 128.9, 127.7, 127.6, 127.5, 126.6, 22.3.



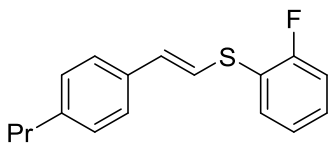
(E)-(2-fluorophenyl)(styryl)sulfane (5ab)

^{1}H NMR (DMSO-d_6, 500 MHz): 7.57-7.49 (3H, m), 7.43-7.37 (1H, m), 7.37-7.30 (3H, m), 7.30-7.24 (2H, m), 7.18 (1H, d, *J* = 15.5 Hz), 6.80 (1H, d, *J* = 15.5 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 159.6 (d, *J*(C-F) = 243.7 Hz), 135.9, 132.5, 131.3, 129.3 (d, *J*(C-F) = 8.1 Hz), 128.6, 127.8, 126.2, 125.4 (d, *J*(C-F) = 2.8 Hz), 121.3 (d, *J*(C-F) = 17.3 Hz), 120.7, 115.8 (d, *J*(C-F) = 21.3 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -111.1 (ddd, J(C-F) = 10.0, 7.9, 5.5 Hz). HRMS (ESI): *m/z* = 230.0550 calcd for $C_{14}H_{11}FS$ $[M]^+$ = 230.0560 (Δ = 4.3 ppm).



(E)-(2-fluorophenyl)(4-fluorostyryl)sulfane (5bb)
(+ 6% of 6bb)

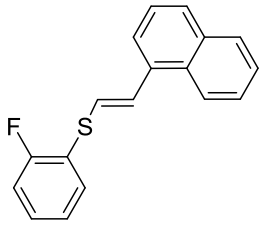
^{1}H NMR (DMSO-d_6, 500 MHz): 7.60-7.56 (2H, m, **5bb**), 7.55-7.49 (1H, m, **5bb**), 7.41-7.35 (1H, m, **5bb**), 7.33-7.23 (2H, m, **5bb**), 7.17 (2H, t, *J* = 8.8 Hz, **5bb**), 7.13 (1H, d, *J* = 15.5 Hz, **5bb**), 6.81 (1H, d, *J* = 15.5 Hz, **5bb**), 6.75 (1H*0.06, d, *J* = 10.7 Hz, **6bb**), 6.57 (1H*0.06, d, *J* = 10.7 Hz, **6bb**). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 161.7 (d, *J*(C-F) = 245.5 Hz), 160.5 (d, *J*(C-F) = 243.5 Hz), 132.5 (d, *J*(C-F) = 2.8 Hz), 131.5, 131.2, 129.2 (d, *J*(C-F) = 7.9 Hz), 128.2 (d, *J*(C-F) = 8.1 Hz), 125.4 (d, *J*(C-F) = 3.3 Hz), 121.3 (d, *J*(C-F) = 16.7 Hz), 120.5, 115.8 (d, *J*(C-F) = 21.5 Hz), 115.5 (d, *J*(C-F) = 21.5 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -110.4-(-110.5) (1F*0.06, m, **6bb**), -111.0-(-111.1) (1F, m, **5bb**), -113.6-(-113.7) (1F*0.06, m, **6bb**), -113.7-(-113.9) (1F, m, **5bb**). HRMS (ESI): *m/z* = 354.9523 calcd for $C_{14}H_{10}F_2SAg$ $[M]^+$ = 354.9517 (Δ = 1.7 ppm).



(E)-(2-fluorophenyl)(4-propylstyryl)sulfane (5cb)
(+ 12% of 6cb)

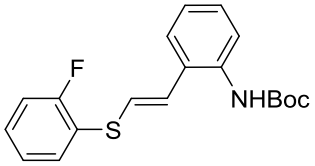
^{1}H NMR (DMSO-d_6, 300 MHz): 7.59 (1H*0.12, td, *J* = 7.7, 1.6 Hz, **6cb**), 7.51 (1H, td, *J* = 7.8, 1.6 Hz, **5cb**), 7.47-7.38 (2H, m, **5cb**), 7.38-7.23 (3H, m, **5cb**), 7.16 (2H, d, *J* = 8.0 Hz, **5cb**), 7.08 (1H, d, *J* = 15.5 Hz, **5cb**), 6.80 (1H, d, *J* = 15.5 Hz, **5cb**), 6.72 (1H*0.12, d, *J* = 10.7 Hz, **6cb**), 6.52 (1H*0.12, d, *J* = 10.7 Hz, **6cb**), 2.53 (2H, t, *J* = 7.4 Hz, **5cb**), 1.57 (2H, qt, *J* = 7.4, 7.3 Hz, **5cb**),

0.88 (3H, t, *J* = 7.3 Hz, **5cb**). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz): 159.4 (d, *J*(C-F) = 244.6 Hz), 142.1, 133.4, 133.2, 131.0, 129.1 (d, *J*(C-F) = 7.8 Hz), 128.7, 126.3, 125.4 (d, *J*(C-F) = 3.0 Hz), 121.7 (d, *J*(C-F) = 17.0 Hz), 119.2, 115.8 (d, *J*(C-F) = 21.5 Hz), 36.9, 23.9, 13.6. ^{19}F NMR (DMSO-d_6, 376.5 MHz): -110.7 (1F*0.12, ddd, *J*(F-H) = 10.2, 8.1, 5.3 Hz, **6cb**), -111.4 (1F, ddd, *J*(F-H) = 9.9, 7.8, 5.3 Hz, **5cb**). HRMS (ESI): *m/z* = 379.0081, calcd for $C_{17}H_{17}FSAg$ $[M]^+$ = 379.0080 (Δ = 0.3 ppm).



(E)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane (5db)

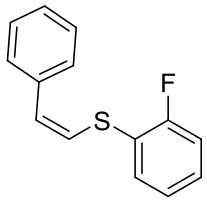
^{1}H NMR (DMSO-d_6, 500 MHz): 8.17-8.11 (1H, m), 7.98-7.92 (1H, m), 7.89 (1H, d, *J* = 8.2 Hz), 7.81 (1H, d, *J* = 7.2 Hz), 7.65-7.48 (5H, m), 7.45-7.39 (1H, m), 7.35 (1H, m), 7.30 (1H, t, *J* = 7.5 Hz), 7.20 (1H, d, *J* = 15.1 Hz). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 125 MHz): 159.7 (d, *J*(C-F) = 244.2 Hz), 133.2, 132.9, 131.5, 130.0, 129.4 (d, *J*(C-F) = 7.9 Hz), 128.7, 128.4, 128.1, 126.4, 126.0, 125.7, 125.5 (d, *J*(C-F) = 3.1 Hz), 123.68, 123.63, 123.3, 121.2 (d, *J*(C-F) = 17.2 Hz), 115.9 (d, *J*(C-F) = 21.6 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -110.8-(-111.0) (m). HRMS (ESI): *m/z* = 281.0795, calcd for $C_{18}H_{13}FS$ $[M + H]^+$ = 281.0795 (Δ = 0.0 ppm).



***tert*-butyl (E)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate (5eb)**

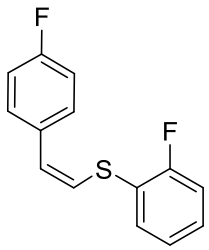
(+ 10% of 6eb)

^{1}H NMR (DMSO-d_6, 400 MHz): 8.84 (1H, br s, **5eb**), 8.65 (1H*0.1, br s, **6eb**), 7.65 (1H, d, *J* = 7.8 Hz, **5eb**), 7.58-7.52 (1H, t, *J* = 7.7 Hz, **5eb**), 7.42-7.35 (1H, m, **5eb**), 7.34-7.21 (4H, m, **5eb**), 7.18-7.11 (1H, m, **5eb**), 7.05 (1H, d, *J* = 15.3 Hz, **5eb**), 6.95 (1H, d, *J* = 15.3 Hz, **5eb**), 6.87 (1H*0.1, d, *J* = 10.5 Hz, **6eb**), 6.63 (1H*0.1, d, *J* = 10.5 Hz, **6eb**), 1.46 (9H*0.1, s, **6eb**), 1.44 (9H, s, **5eb**). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 125 MHz): 159.5 (d, *J*(C-F) = 243.4 Hz), 153.7, 135.0, 131.1, 130.6, 129.12, 129.06, 128.0, 126.1, 125.9, 125.3 (d, *J*(C-F) = 3.1 Hz), 125.1, 121.5 (d, *J*(C-F) = 17 Hz), 121.2, 115.7 (d, *J*(C-F) = 21.5 Hz), 78.8, 28.0. ^{19}F NMR (DMSO-d_6, 376.5 MHz): -110.8-(-110.9) (1F*0.1, ddd, *J*(H-F) = 9.9, 7.7, 5.8 Hz, **6eb**), -111.2 (1F, ddd, *J*(H-F) = 10.1, 8.1, 5,9 Hz, **5eb**), HRMS (ESI): *m/z* = 346.1280, calcd for $C_{19}H_{20}FNO_2S$ $[M + H]^+$ = 346.1272 (Δ = 2.6 ppm).



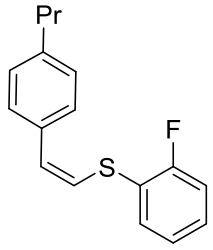
(Z)-(2-fluorophenyl)(styryl)sulfane (6ab)

^{1}H NMR (DMSO-d_6, 300 MHz): 7.61 (1H, td, *J* = 7.7, 1.5 Hz), 7.53 (2H, d, *J* = 7.5 Hz), 7.49-7.38 (3H, m), 7.38-7.25 (3H, m), 6.76 (1H, d, *J* = 10.7 Hz), 6.59 (1H, d, *J* = 10.7 Hz). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz): 159.9 (d, *J*(C-F) = 242.2 Hz), 135.8, 131.8, 129.9 (d, *J*(C-F) = 7.9 Hz), 128.5, 128.0, 127.4, 125.5 (d, *J*(C-F) = 3.8 Hz), 123.7, 121.7 (d, *J*(C-F) = 16.3 Hz), 116.0 (d, *J*(C-F) = 21.8 Hz). ^{19}F NMR (DMSO-d_6, 376.5 MHz): -110.6 (ddd, *J*(F-H) = 9.9, 7.8, 5.5 Hz). HRMS (ESI): *m/z* = 336.9621, calcd for $C_{14}H_{11}FSAg$ $[M]^+$ = 336.9611 (Δ = 3.0 ppm).

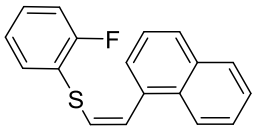


(Z)-(2-fluorophenyl)(4-fluorostyryl)sulfane (6bb)

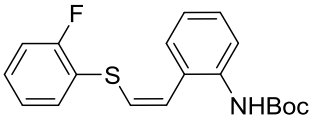
^{1}H NMR (DMSO-d_6, 300 MHz): 7.62-7.53 (3H, m), 7.48-7.21 (5H, m), 6.75 (1H, d, *J* = 10.8 Hz), 6.56 (1H, d, *J* = 10.8 Hz). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75 MHz): 160.9 (d, *J*(C-F) = 246.2 Hz), 159.7 (d, *J*(C-F) = 243.7 Hz), 132.4 (d, *J*(C-F) = 3.1 Hz), 131.8, 130.6 (d, *J*(C-F) = 8.2 Hz), 129.9 (d, *J*(C-F) = 7.9 Hz), 127.0, 125.5 (d, *J*(C-F) = 3.6 Hz), 123.3, 121.5 (d, *J*(C-F) = 17.0 Hz), 116.0 (d, *J*(C-F) = 21.6 Hz), 115.4 (d, *J*(C-F) = 21.6 Hz). ^{19}F NMR (DMSO-d_6, 376.5 MHz): -110.6 (1F, ddd, *J*(F-H) = 9.7, 7.7, 5.3 Hz), -113.7 (1F, tt, *J*(F-H) = 8.8, 5.6 Hz). HRMS (ESI): *m/z* = 354.9514, calcd for $C_{14}H_{10}F_2SAg$ $[M]^+$ = 354.9517 (Δ = 0.8 ppm).



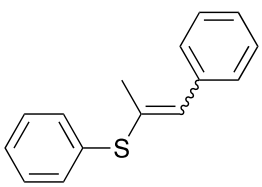
(Z)-(2-fluorophenyl)(4-propylstyryl)sulfane (6cb)
(+ 10 % of 5cb)
^{1}H NMR (DMSO-d_6, 300 MHz): 7.57 (1H, td, *J*(F-H) = 7.7, 1.6 Hz, **6cb**), 7.48-7.35 (3H, m, **6cb**), 7.35-7.19 (4H, m, **6cb**), 7.08 (1H*0.06, d, *J* = 15.5 Hz, **5cb**), 6.80 (1H*0.06, d, *J* = 15.5 Hz, **5cb**), 6.71 (1H, d, *J* = 10.6 Hz, **6cb**), 6.49 (1H, d, *J* = 10.6 Hz, **6cb**), 2.55 (2H, t, *J* = 7.6 Hz, **6cb**), 1.58 (2H, qt, *J* = 7.6, 7.3 Hz, **6cb**), 0.88 (3H, t, *J* = 7.3 Hz, **6cb**). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 159.8 (d, *J*(C-F) = 244.3 Hz), 141.5, 133.3, 131.6, 129.7 (d, J(C-F) = 7.9 Hz), 128.5, 128.4, 128.0, 125.5 (d, *J*(C-F) = 3.6 Hz), 122.4, 121.9 (d, *J*(C-F) = 16.9 Hz), 116.0 (d, *J*(C-F) = 21.6 Hz). ^{19}F NMR (DMSO-d_6, 376.5 MHz): -110.6-(-110.7) (1F, m, **6cb**), -111.3-(-111.4) (1F*0.06, m, **5cb**). HRMS (ESI): *m/z* = 379.0082, calcd for $C_{17}H_{17}FSAg$ $[M]^+$ = 379.0080 (Δ = 0.5 ppm).



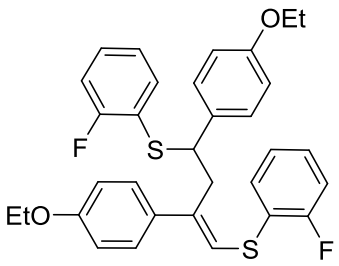
(Z)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane (6db)
(+ 17% of 5db)
^{1}H NMR (DMSO-d_6, 500 MHz): 8.17-8.11 (1H*0.17, m, **5db**), 8.09-8.04 (1H, m, **6db**), 8.00-7.95 (1H, m, **6db**), 7.94-7.90 (1H, d, *J* = 7.8 Hz, **6db**), 7.90-7.86 (1H*0.17, m, **5db**), 7.8 (1H*0.17, d, *J* = 7.1 Hz, **5db**), 7.67-7.53 (5H, m, **6db**), 7.50 (1H*0.17, t, *J* = 7.8 Hz, **5db**), 7.42 (1H, d, *J* = 10.3 Hz, **6db**), 7.41-7.35 (1H, m, **6db**), 7.35-7.25 (2H, m, **6db**), 7.20 (1H*0.17, d, *J* = 15.2 Hz, **5db**), 6.84 (1H, d, *J* = 10.3 Hz, **6db**). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 159.8 (d, *J*(C-F) = 243.2 Hz), 133.2, 132.4, 131.5, 130.7, 129.6 (d, *J*(C-F) = 7.9 Hz), 128.5, 128.1, 126.5, 126.4, 126.14, 126.13, 125.8, 125.4 (d, *J*(C-F) = 3.0 Hz), 125.3, 124.0, 121.8 (d, *J*(C-F) = 17.0 Hz), 115.9 (d, *J*(C-F) = 21.8 Hz). ^{19}F NMR (DMSO-d_6, 470.5 MHz): -110.6 (1F, ddd, *J*(F-H) = 9.9, 7.8, 5.6 Hz, **6db**), -110.9 (1F*0.17, ddd, *J*(F-H) = 9.8, 7.8, 5.7 Hz, **5db**). HRMS (ESI): *m/z* = 281.0795, calcd for $C_{18}H_{13}FS$ $[M + H]^+$ = 281.0795 (Δ = 0.0 ppm).



***tert*-butyl (Z)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate (6eb)**
^{1}H NMR (DMSO-d_6, 300 MHz): 8.64 (1H, br s), 7.62-7.54 (1H, m), 7.52-7.43 (2H, m), 7.43-7.35 (1H, m), 7.35-7.24 (3H, m), 7.20 (1H, td, *J* = 7.4, 1.4 Hz), 6.86 (1H, d, *J* = 10.6 Hz), 6.63 (1H, d, *J* = 10.6 Hz), 1.45 (9H, s). ^{13}C NMR (DMSO-d_6, 75 MHz): 159.7 (d, *J*(C-F) = 244.2 Hz), 153.4, 136.0, 131.4, 129.6, 129.5 (d, *J*(C-F) = 7.8 Hz), 128.4, 127.9, 125.8, 125.4 (d, *J*(C-F) = 3.3 Hz), 124.9, 124.3, 124.2, 122.0 (d, *J*(C-F) = 17.1 Hz), 115.9 (d, *J*(C-F) = 21.7 Hz), 78.9, 28.1. ^{19}F NMR (DMSO-d_6, 376.5 MHz): -110.9 (ddd, *J*(F-H) = 9.8, 7.8, 5.4 Hz). HRMS (ESI): *m/z* = 346.1270, calcd for $C_{19}H_{20}FNO_2Sa$ [M + H] = 346.1272 (Δ = 0.6 ppm).

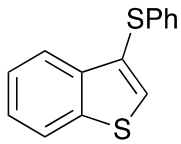


Phenyl(1-phenylprop-1-en-2-yl)sulfane (5sa+6sa)
Mixture E(5ya)/Z(6ya) = 1:1
^{1}H NMR (DMSO-d_6, 400 MHz): 7.53 (2H, d, *J* = 7.6 Hz, **E**), 7.48-7.30 (8H, m, **Z** + 8H, m, **E**), 7.29-7.22 (2H, m, **Z**), 6.83 (1H, s, **E**), 6.70 (1H, s, **Z**), 2.09 (3H, s), 1.98 (3H, s). ^{13}C NMR (DMSO-d_6, 100 MHz): 136.4, 136.3, 133.1, 132.8, 132.5, 131.7, 131.4, 130.7, 130.64, 130.61, 129.4, 129.2, 128.7, 128.5, 128.3, 128.1, 127.6, 127.5, 127.0, 25.1, 19.4.



(E)-(2,4-bis(4-ethoxyphenyl)but-1-ene-1,4-diyl)bis((2-fluorophenyl)sulfane) (7hb)

^{1}H NMR (DMSO-d_6, 500 MHz): 7.31-7.25 (2H, m), 7.25-7.18 (2H, m), 7.18-7.12 (3H, m),7.12-7.03 (4H, m), 6.97-6.90 (3H, m), 6.82 (2H, d, *J* = 8.6 Hz), 6.17 (1H, s), 4.22 (1H, dd, *J* = 9.3, 6.0 Hz), 4.06 (2H, q, *J* = 6.9 Hz), 3.98 (2H, q, *J* = 6.9 Hz), 3.21 (1H, dd, *J* =14.2, 9.3Hz), 3.12 (1H, dd, *J* = 14.2, 6.0 Hz), 1.35 (3H, t, *J* = 6.9 Hz), 1.32 (3H, t, *J* = 6.9 Hz). ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz): 161.1 (d, *J*(C-F) = 244.1 Hz), 158.8 (d, *J*(C-F) = 243.7 Hz), 158.1, 157.7, 141.7, 133.9, 131.7, 129.6 (d, *J*(C-F) = 2.6 Hz), 129.5, 129.2, 129.1 (d, *J*(C-F) = 2.4 Hz), 128.0 (d, *J*(C-F) = 7.8 Hz), 125.0 (d, *J*(C-F) = 2.7 Hz), 124.7 (d, *J*(C-F) = 2.9 Hz), 123.2 (d, *J*(C-F) = 16.7 Hz), 121.2 (d, *J*(C-F) = 17.9 Hz), 118.3, 115.6 (d, *J*(C-F) = 21.1 Hz), 115.4 (d, *J*(C-F) = 19.6 Hz), 114.1, 63.0, 62.9, 49.1, 44.3, 14.6 (2C). ^{19}F NMR (DMSO-d_6, 564.7 MHz): -108.8 (1F, ddd, *J*(F-H) = 9.5, 7.7, 5.5 Hz), -112.3 (1F, ddd, *J*(F-H) = 9.5, 7.5, 5.5 Hz). HRMS (ESI): *m/z* = 571.1531, calcd for $C_{32}H_{30}F_2O_2S_2Na$ $[M + Na]^+$ = 571.1547 (Δ = 2.8 ppm).



3-(phenylthio)benzo[b]thiophene (8na)

^{1}H NMR (DMSO-d_6, 300 MHz): 8.24 (1H, s), 8.13-8.06 (1H, m), 7.71-7.64 (1H, m), 7.46-7.39 (2H, m), 7.30-7.23 (2H, m), 7.20-7.11 (3H, m). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz): 139.6, 138.4, 135.9, 134.3, 129.3, 127.2, 126.1, 125.2, 125.1, 123.5, 122.4, 122.3.

NMR spectra of products (3−6)

3aa

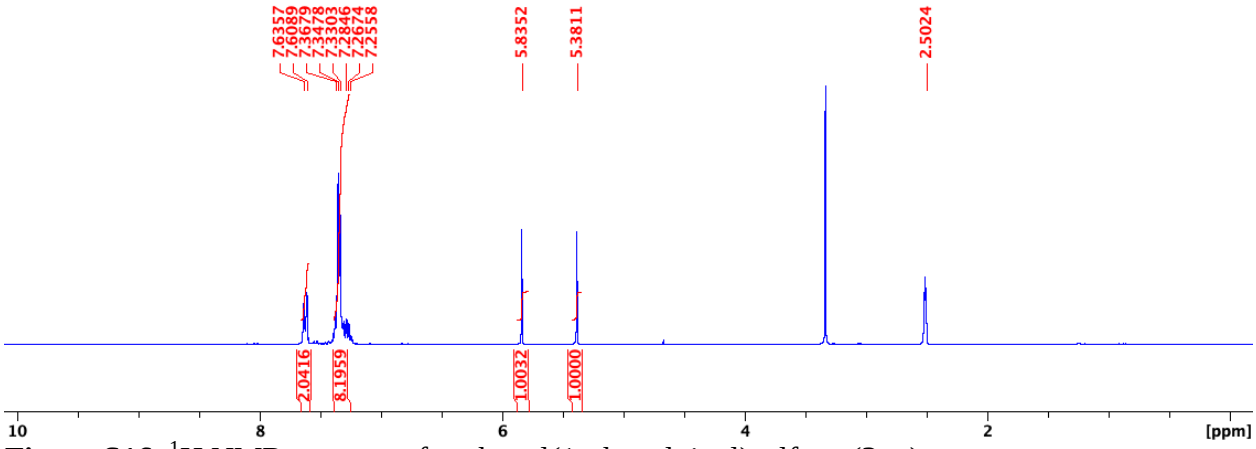


Figure S16. ^{1}H NMR spectrum for phenyl(1-phenylvinyl)sulfane (**3aa**)

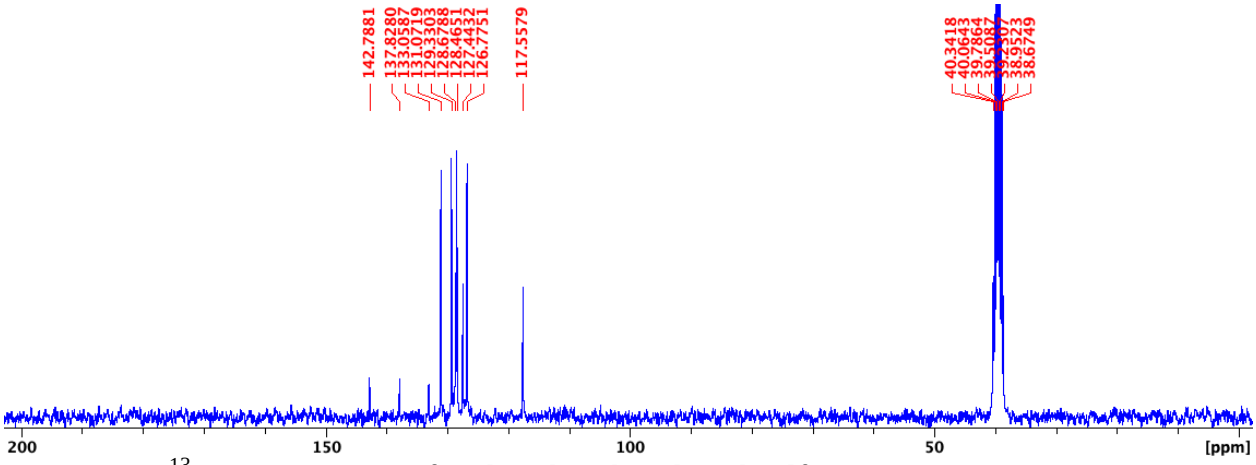


Figure S17. ^{13}C NMR spectrum for phenyl(1-phenylvinyl)sulfane (**3aa**)

3ab

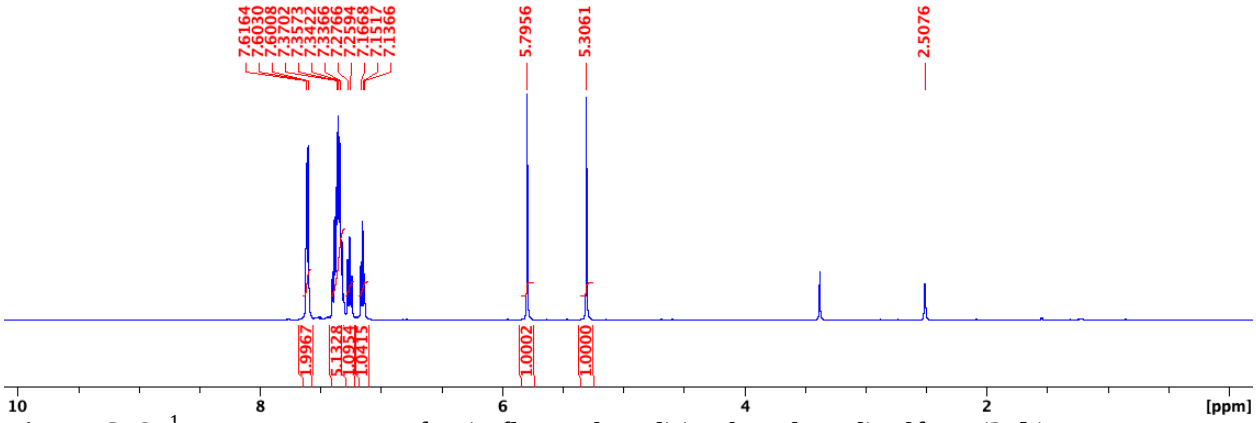


Figure S18. ^{1}H NMR spectrum for (2-fluorophenyl)(1-phenylvinyl)sulfane (**3ab**)

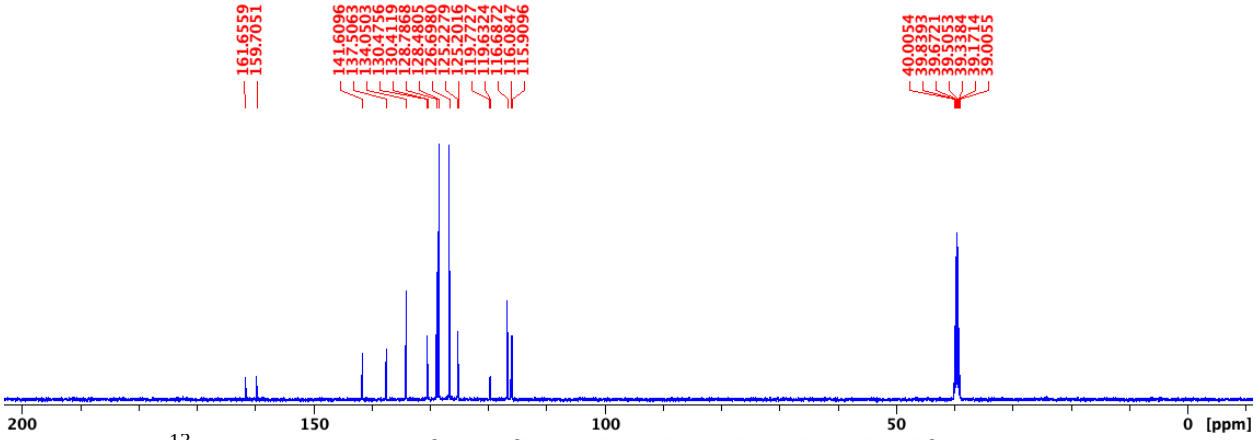


Figure S19. ^{13}C NMR spectrum for (2-fluorophenyl)(1-phenylvinyl)sulfane (**3ab**)

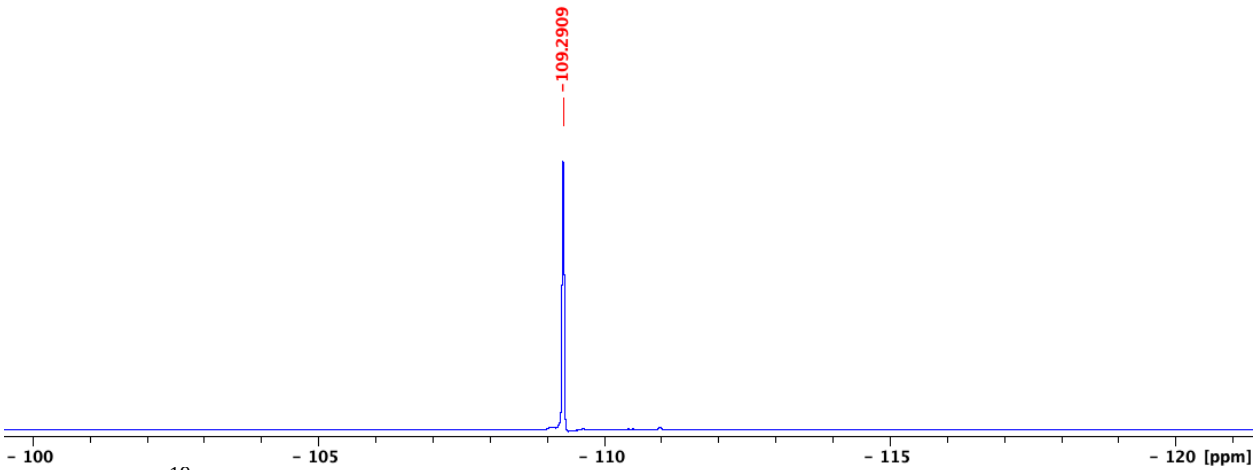


Figure S20. ^{19}F NMR spectrum for (2-fluorophenyl)(1-phenylvinyl)sulfane (**3ab**)

3ac

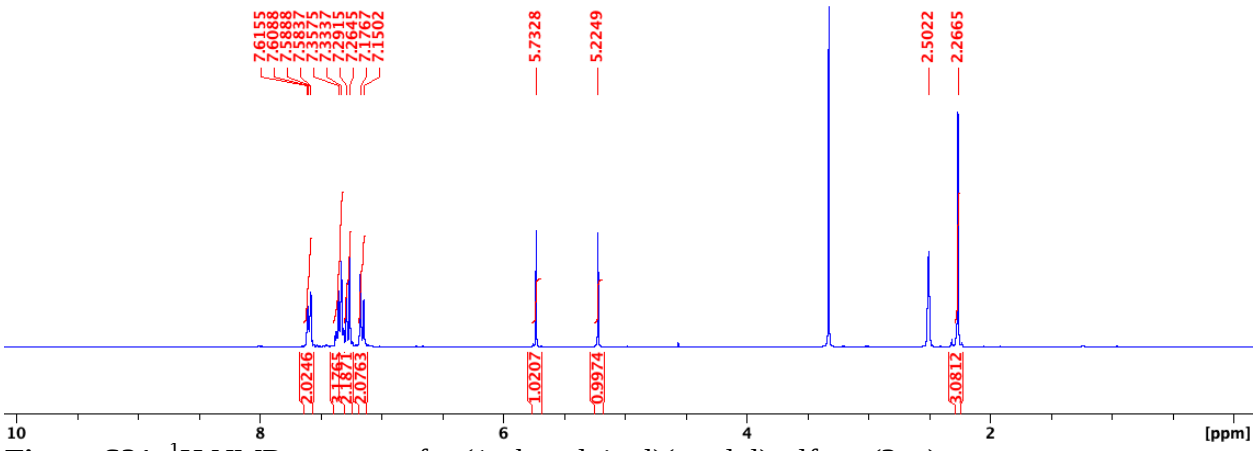


Figure S21. ^{1}H NMR spectrum for (1-phenylvinyl)(*p*-tolyl)sulfane (**3ac**)

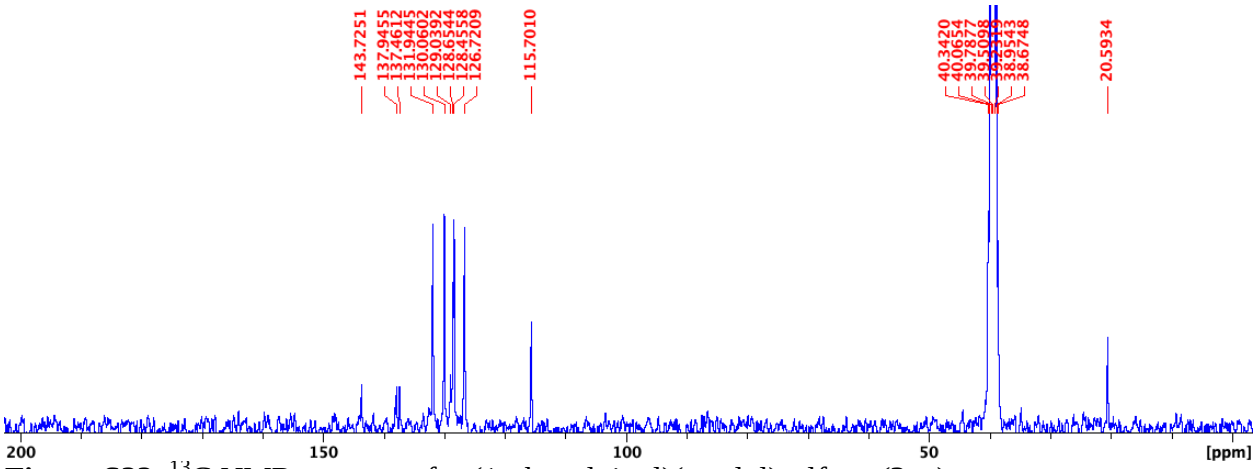


Figure S22. ^{13}C NMR spectrum for (1-phenylvinyl)(*p*-tolyl)sulfane (**3ac**)

3ad

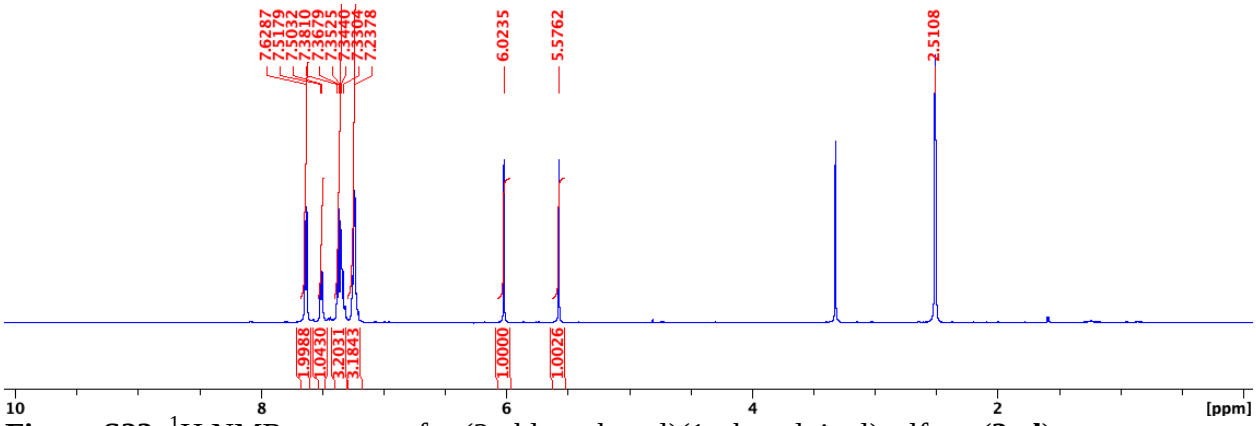


Figure S23. ^{1}H NMR spectrum for (2-chlorophenyl)(1-phenylvinyl)sulfane (**3ad**)

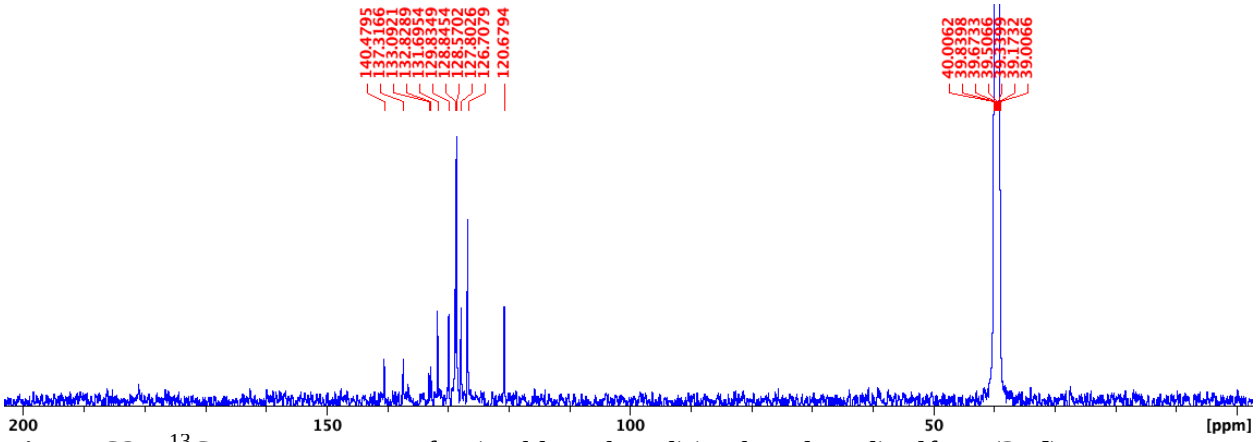


Figure S24. ^{13}C NMR spectrum for (2-chlorophenyl)(1-phenylvinyl)sulfane (**3ad**)

3ae

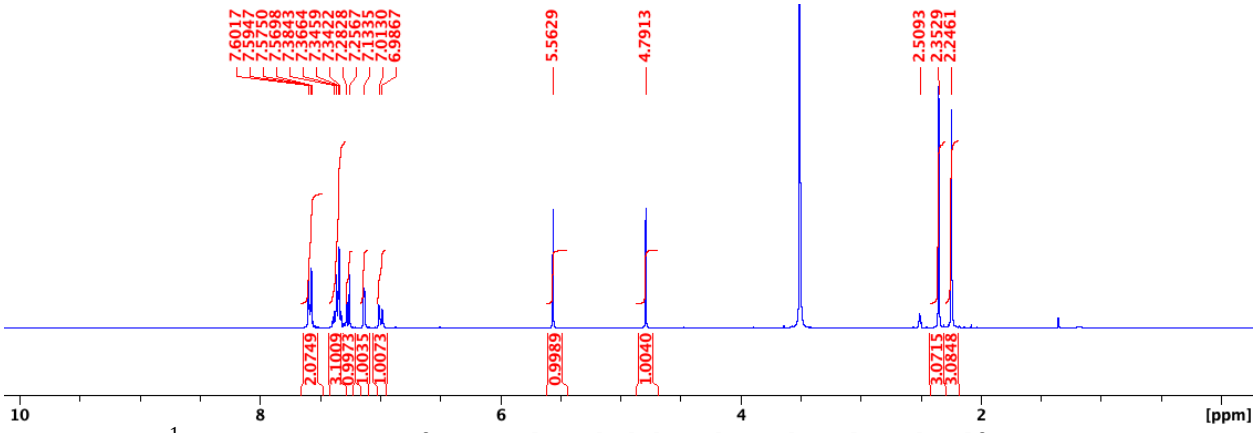


Figure S25. ^{1}H NMR spectrum for (2,4-dimethylphenyl)(1-phenylvinyl)sulfane (**3ae**)

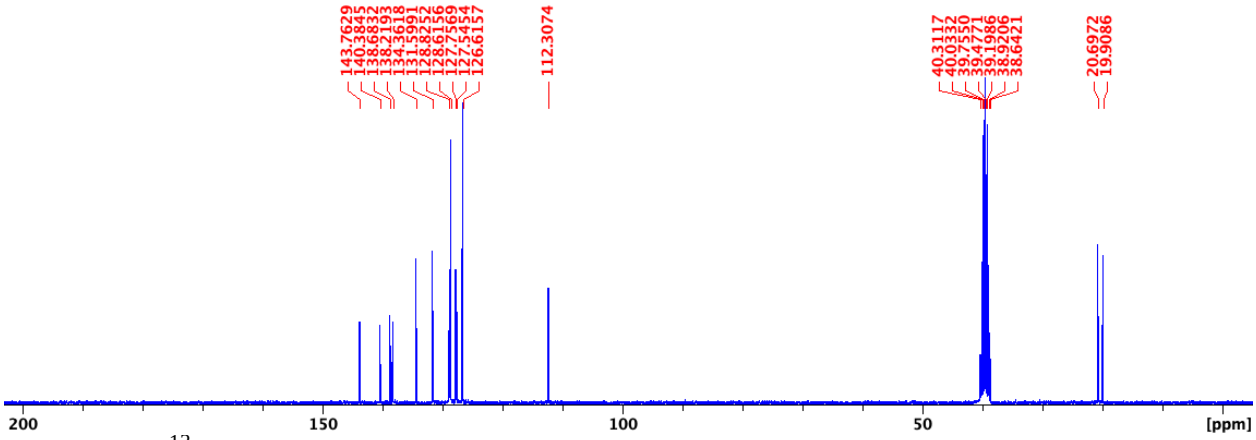


Figure S26. ^{13}C NMR spectrum for (2,4-dimethylphenyl)(1-phenylvinyl)sulfane (**3ae**)

3af

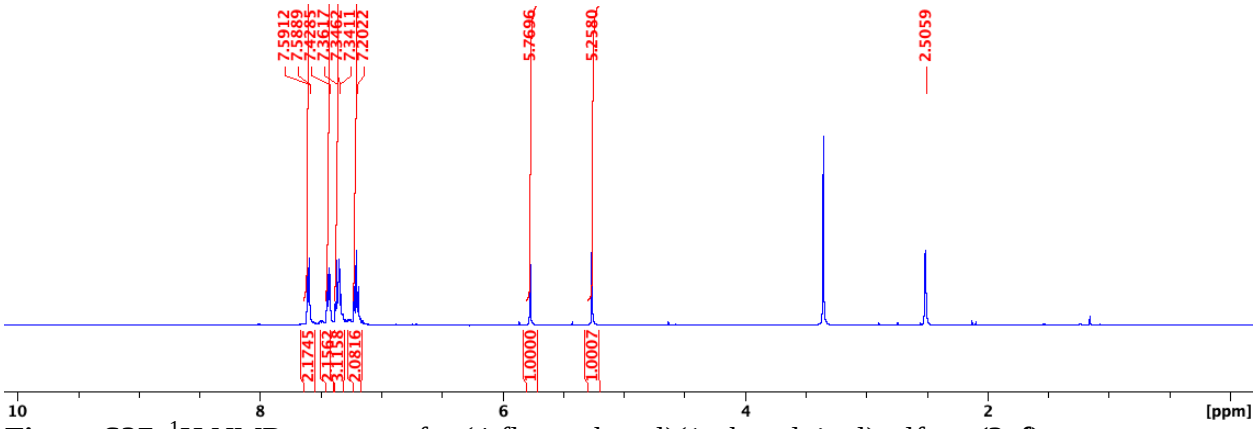


Figure S27. ^{1}H NMR spectrum for (4-fluorophenyl)(1-phenylvinyl)sulfane **(3af)**

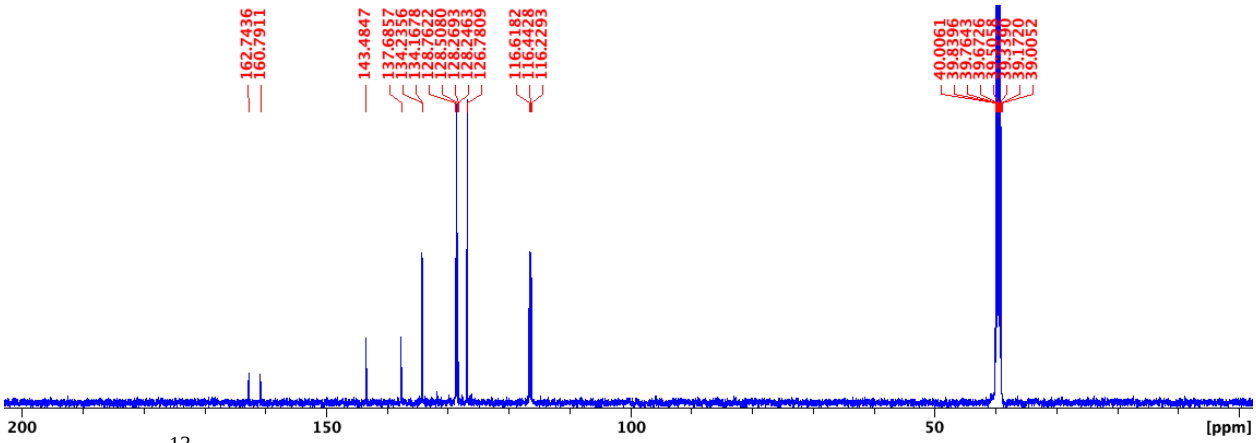


Figure S28. ^{13}C NMR spectrum for (4-fluorophenyl)(1-phenylvinyl)sulfane **(3af)**

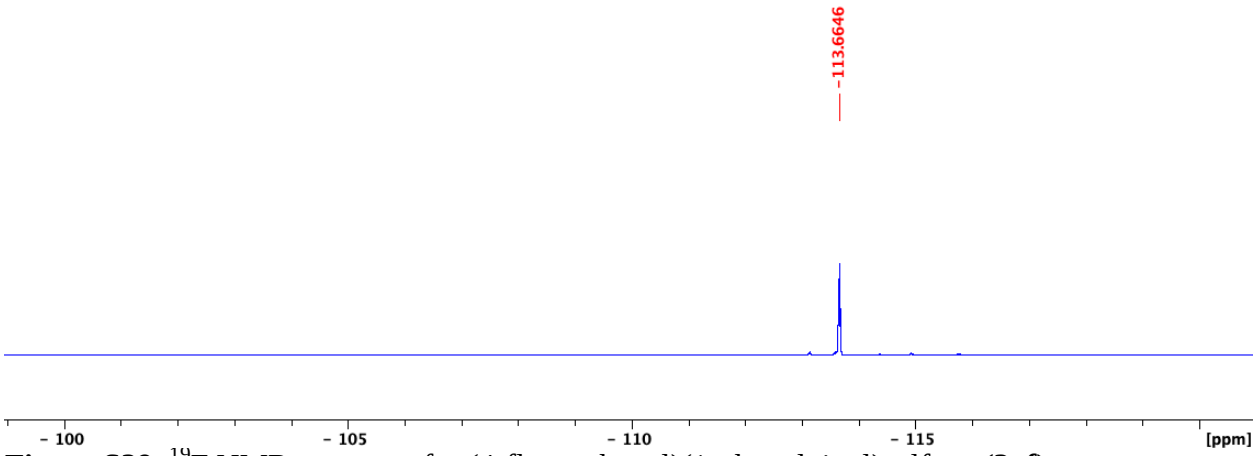


Figure S29. ^{19}F NMR spectrum for (4-fluorophenyl)(1-phenylvinyl)sulfane **(3af)**

3ag

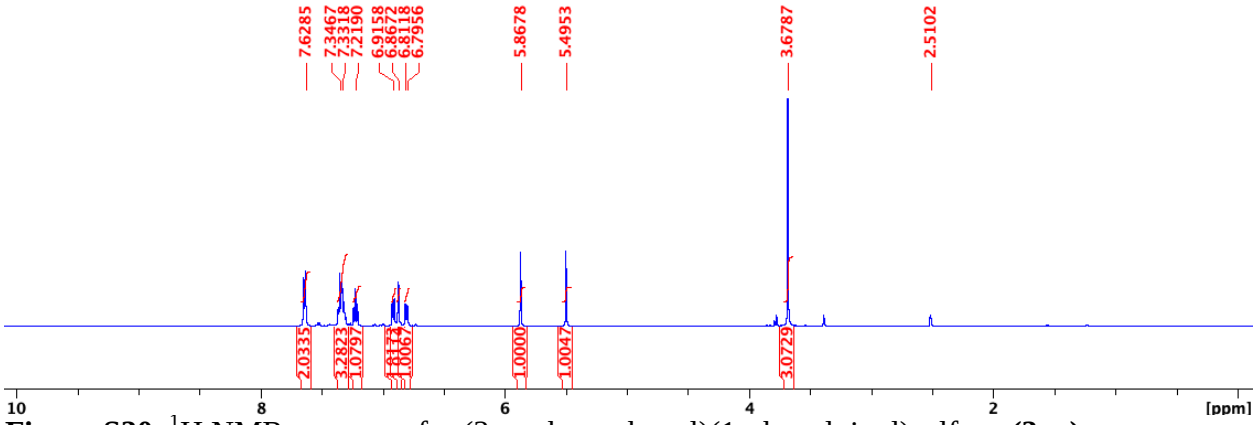


Figure S30. ^{1}H NMR spectrum for (3-methoxyphenyl)(1-phenylvinyl)sulfane **(3ag)**

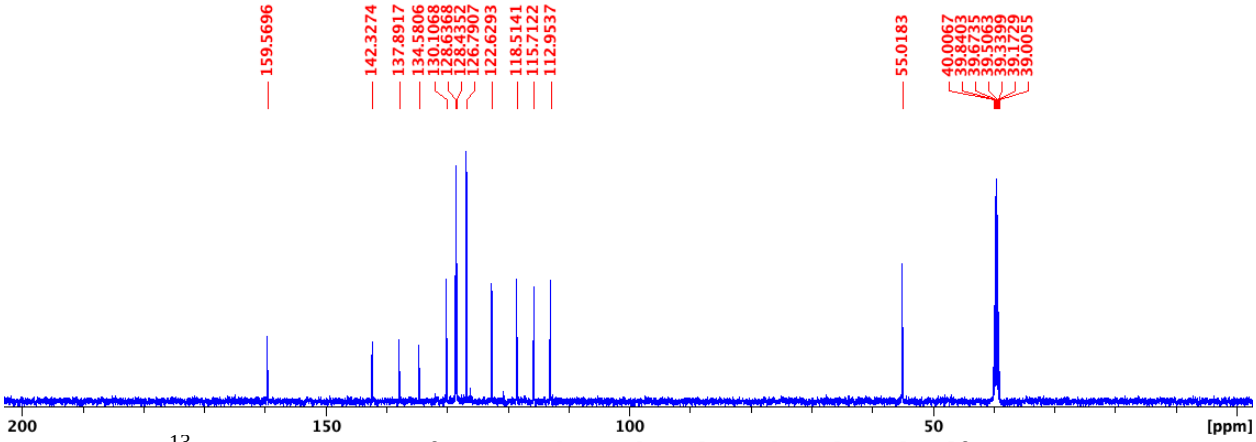


Figure S31. ^{13}C NMR spectrum for (3-methoxyphenyl)(1-phenylvinyl)sulfane **(3ag)**

3ah

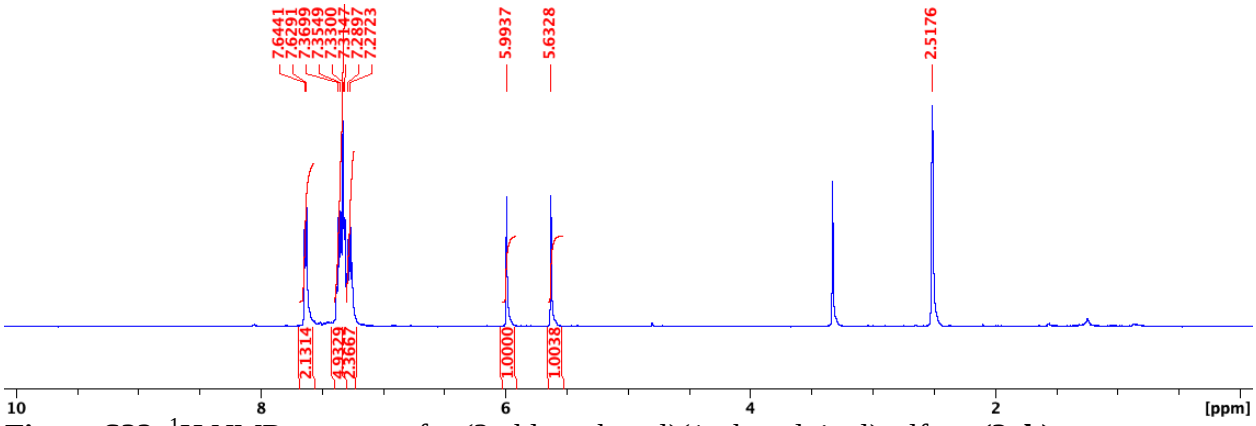


Figure S32. ^{1}H NMR spectrum for (3-chlorophenyl)(1-phenylvinyl)sulfane **(3ah)**

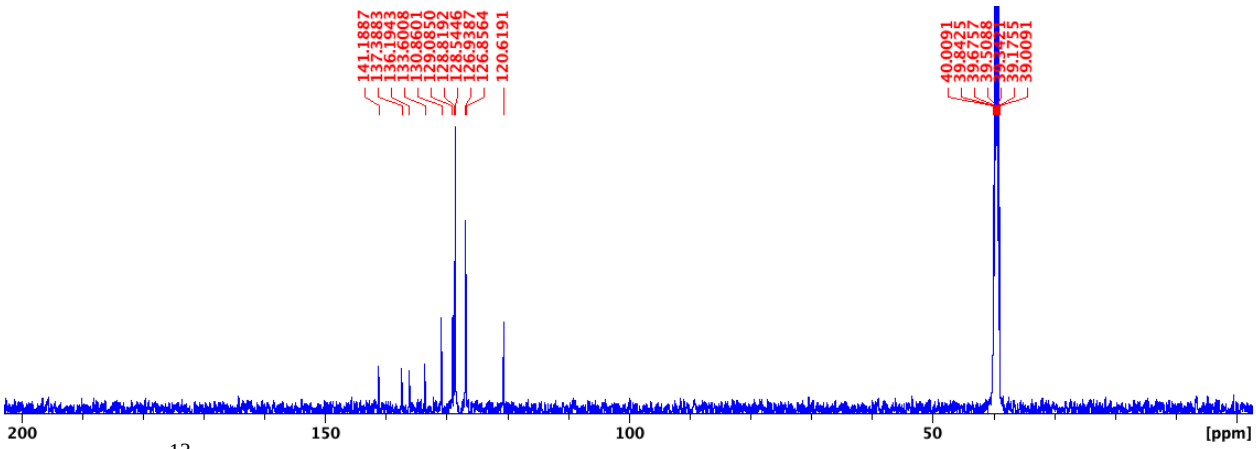


Figure S33. ^{13}C NMR spectrum for (3-chlorophenyl)(1-phenylvinyl)sulfane **(3ah)**

3ai

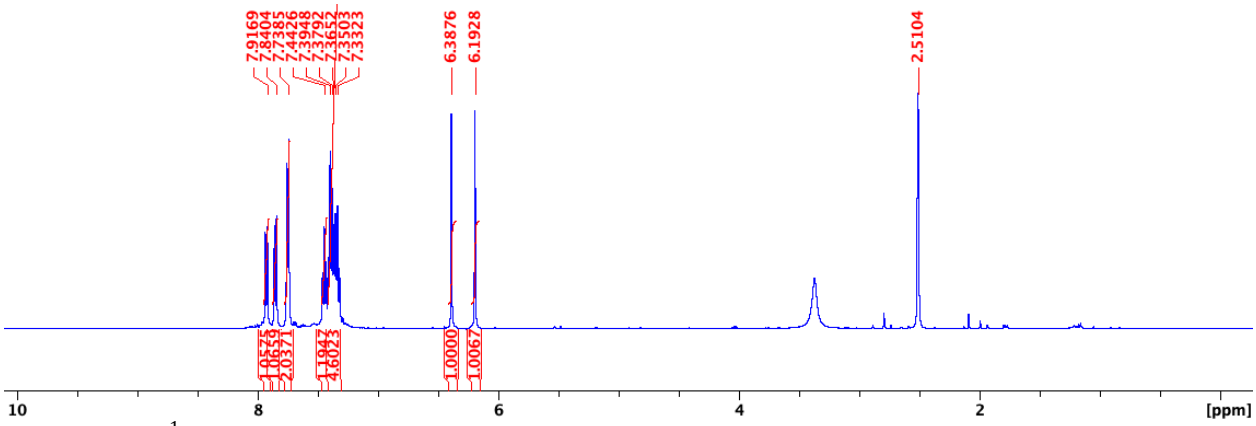


Figure S34. ^{1}H NMR spectrum for 2-((1-phenylvinyl)thio)benzo[d]thiazole **(3ai)**

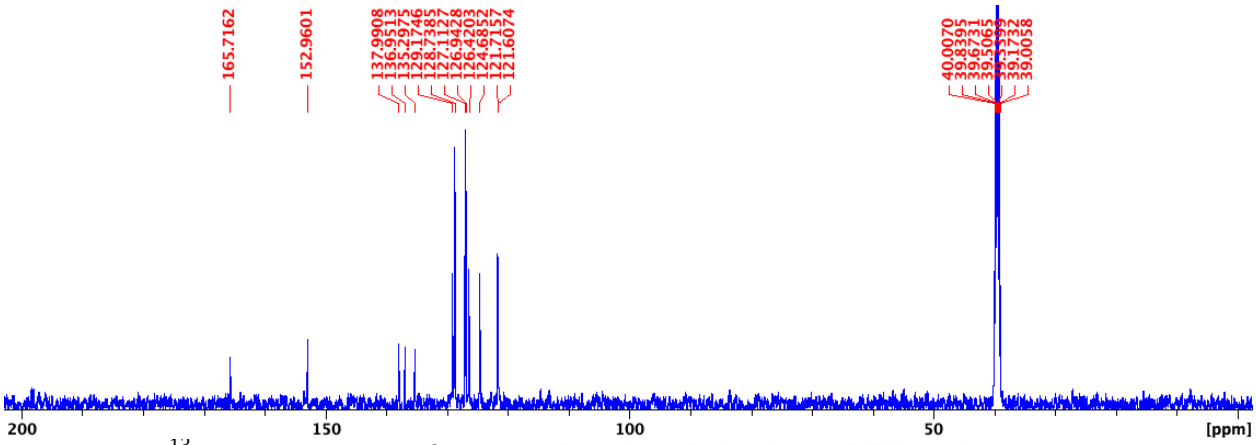


Figure S35. ^{13}C NMR spectrum for 2-((1-phenylvinyl)thio)benzo[d]thiazole **(3ai)**

3bb

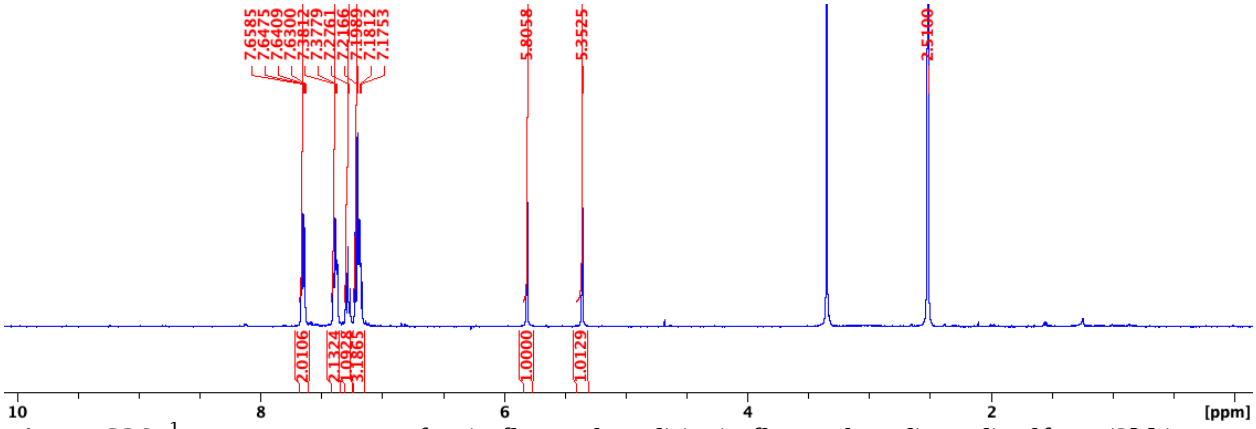


Figure S36. ^{1}H NMR spectrum for (2-fluorophenyl)(1-(4-fluorophenyl)vinyl)sulfane **(3bb)**

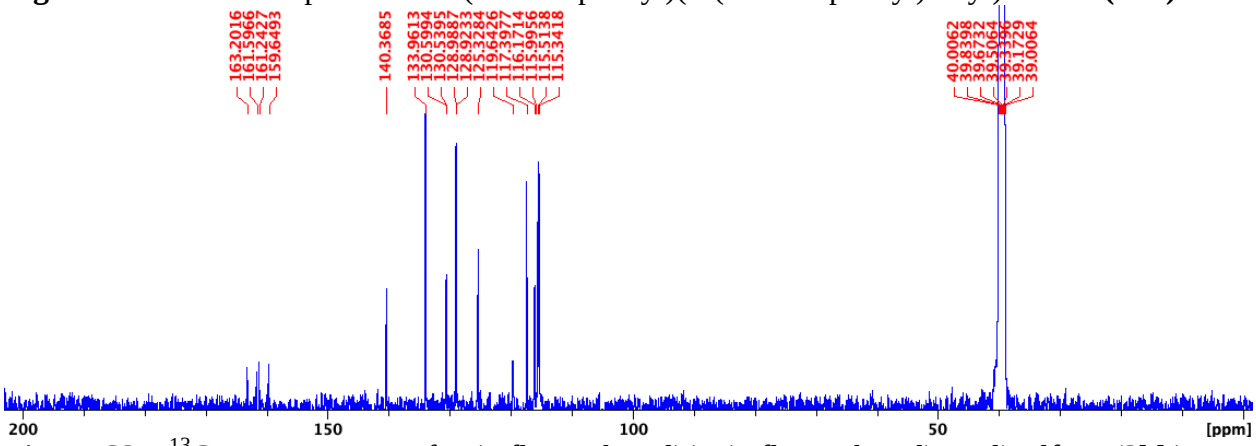


Figure S37. ^{13}C NMR spectrum for (2-fluorophenyl)(1-(4-fluorophenyl)vinyl)sulfane **(3bb)**

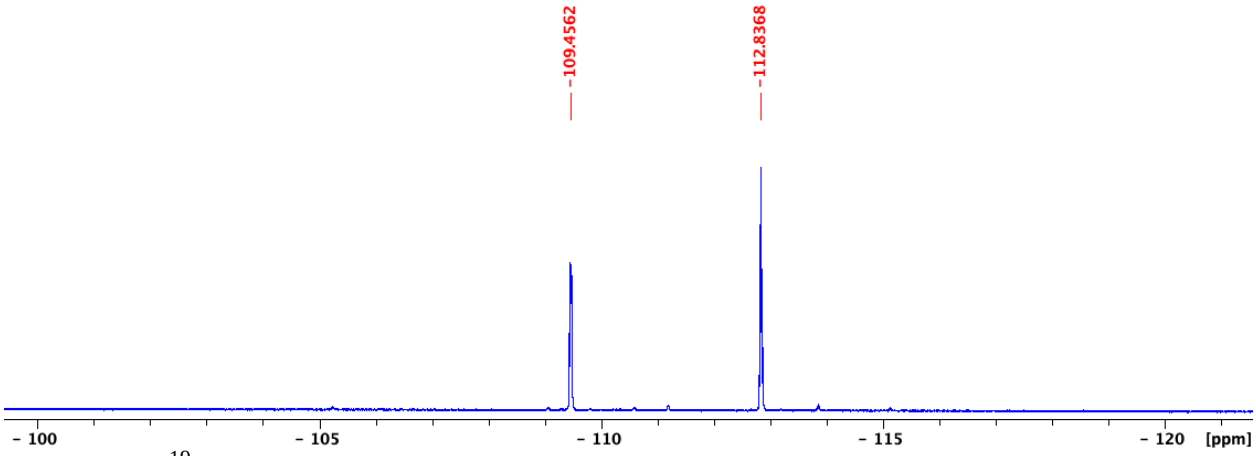


Figure S38. ^{19}F NMR spectrum for (2-fluorophenyl)(1-(4-fluorophenyl)vinyl)sulfane **(3bb)**

3cb

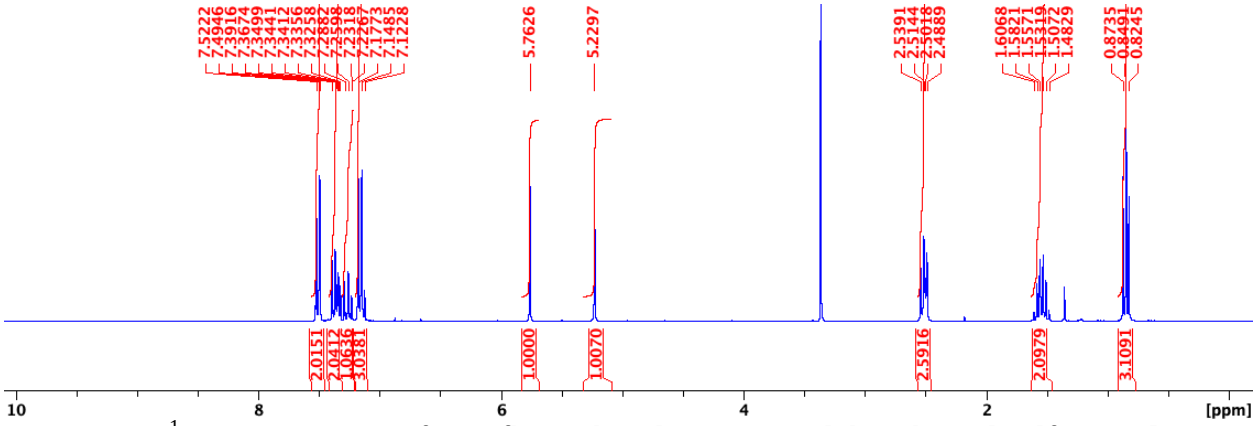


Figure S39. ^{1}H NMR spectrum for (2-fluorophenyl)(1-(4-propylphenyl)vinyl)sulfane **(3cb)**

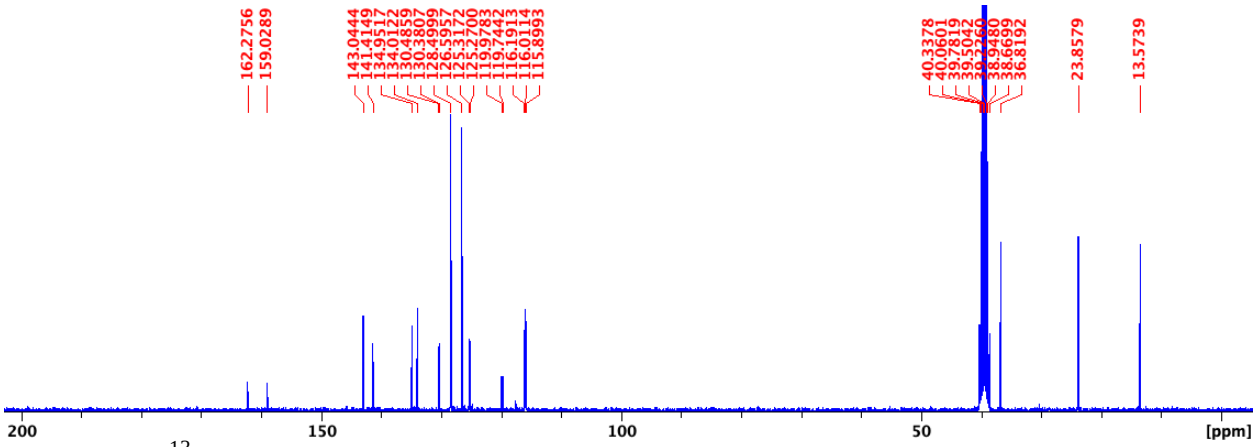


Figure S40. ^{13}C NMR spectrum for (2-fluorophenyl)(1-(4-propylphenyl)vinyl)sulfane **(3cb)**

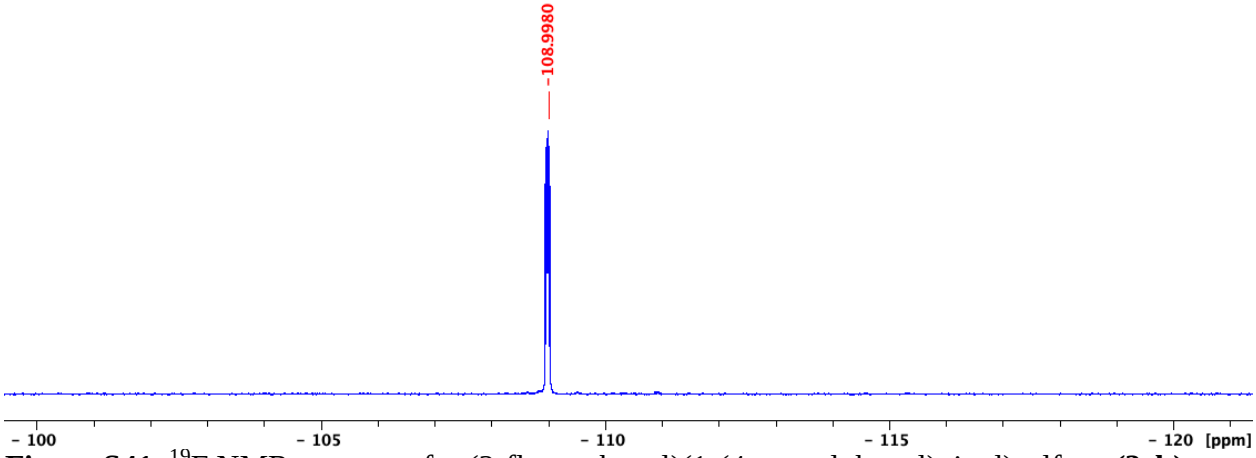


Figure S41. ^{19}F NMR spectrum for (2-fluorophenyl)(1-(4-propylphenyl)vinyl)sulfane **(3cb)**

3db

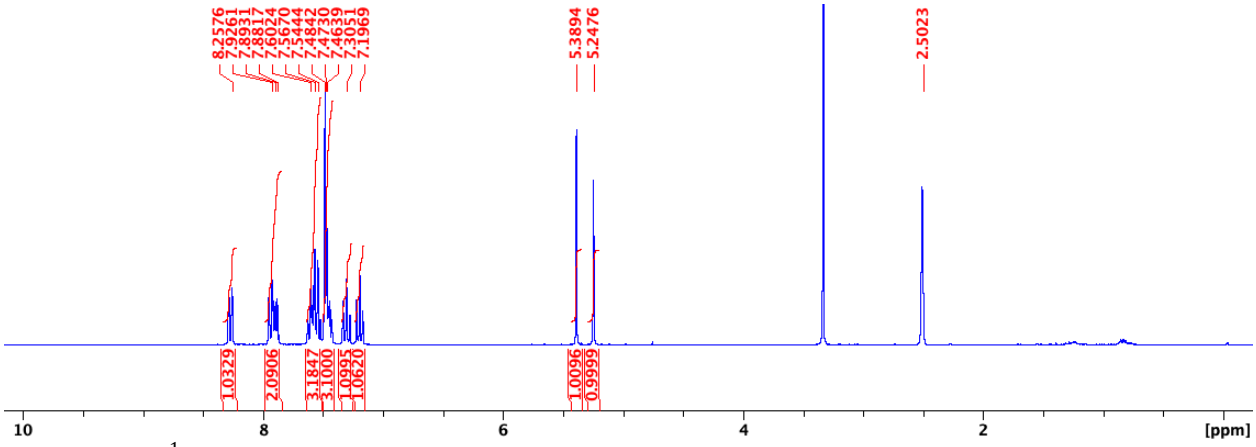


Figure S42. ^{1}H NMR spectrum for (2-fluorophenyl)(1-(naphthalen-1-yl)vinyl)sulfane **(3db)**

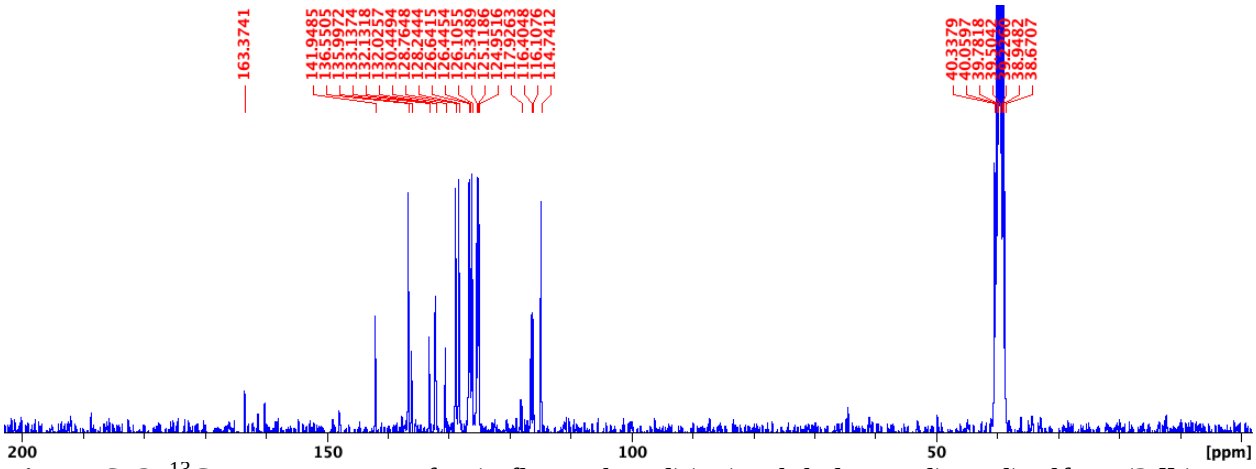


Figure S43. ^{13}C NMR spectrum for (2-fluorophenyl)(1-(naphthalen-1-yl)vinyl)sulfane **(3db)**

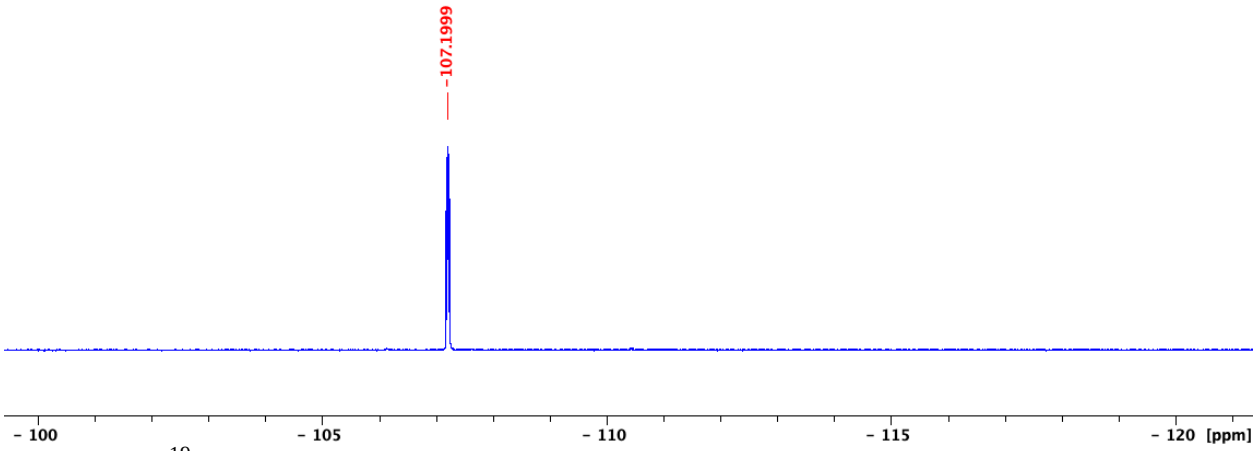


Figure S44. ^{19}F NMR spectrum for (2-fluorophenyl)(1-(naphthalen-1-yl)vinyl)sulfane **(3db)**

3eb

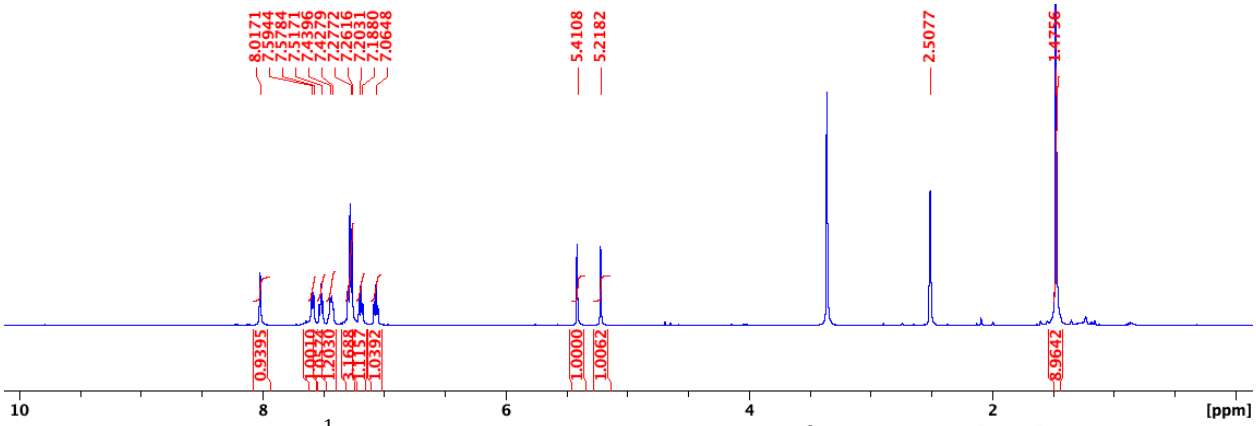


Figure S45. ^{1}H NMR spectrum for *tert*-butyl (2-(1-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(3eb)**

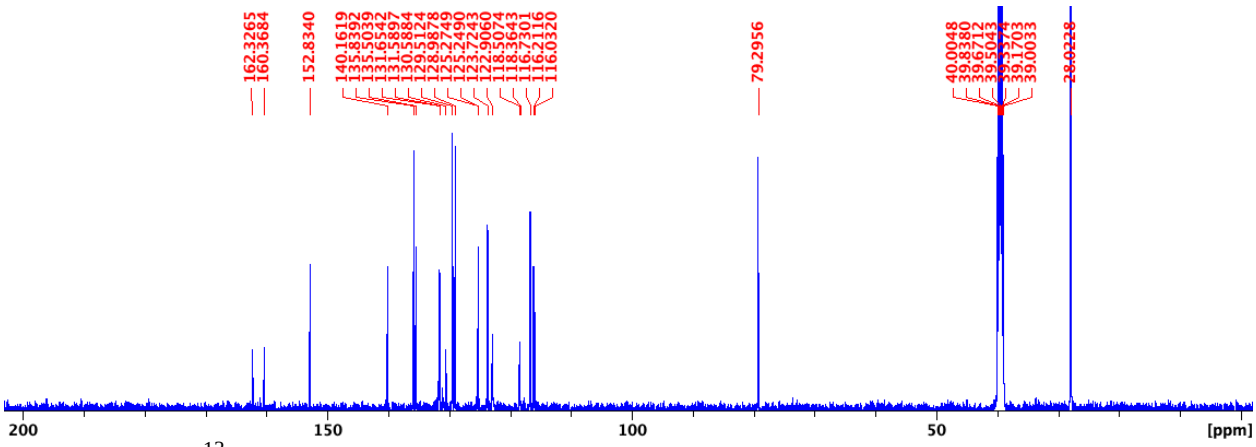


Figure S46. ^{13}C NMR spectrum for *tert*-butyl (2-(1-((2-fluorophenyl)thio)vinyl)phenyl) carbamate **(3eb)**

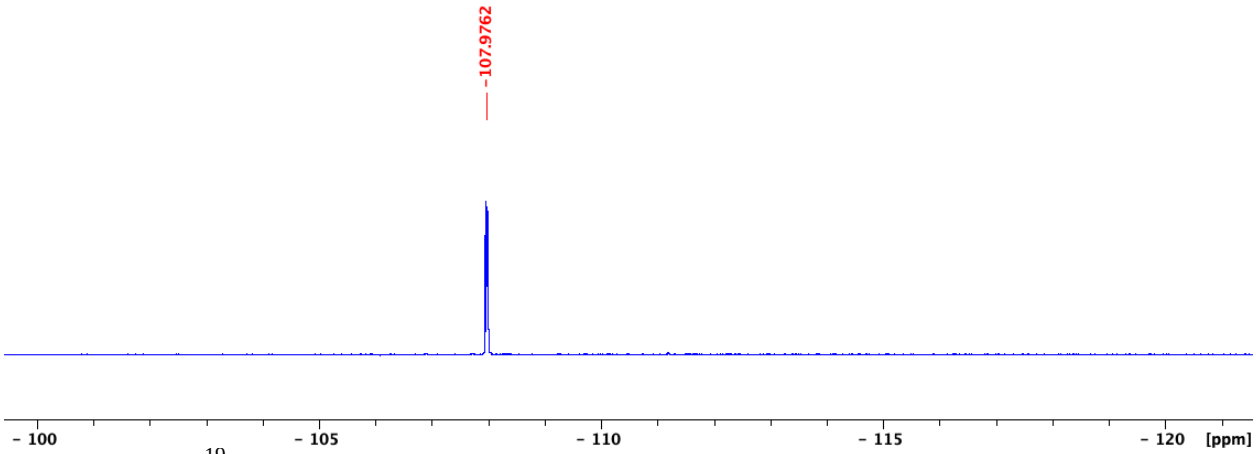


Figure S47. ^{19}F NMR spectrum for *tert*-butyl (2-(1-((2-fluorophenyl)thio)vinyl)phenyl) carbamate **(3eb)**

3fb

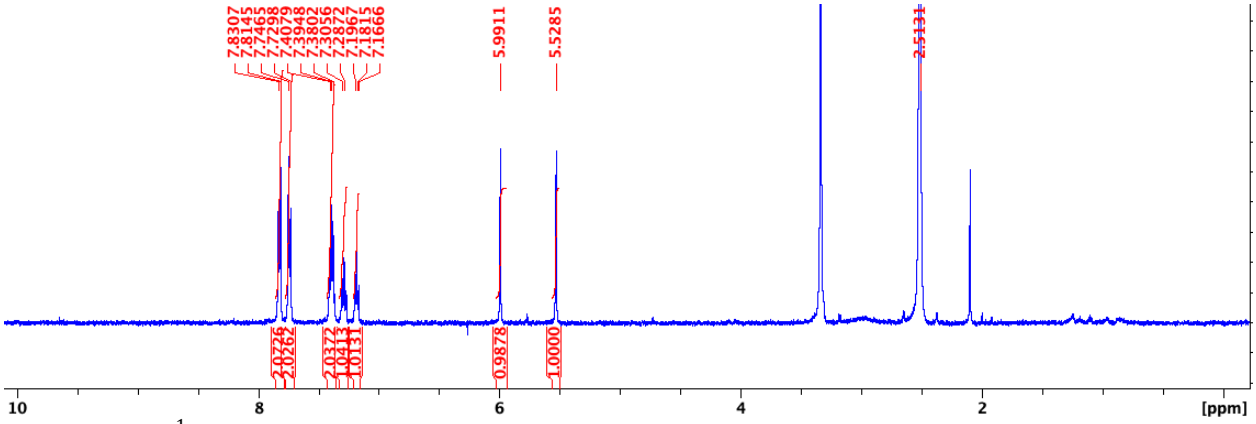


Figure S48. ^{1}H NMR spectrum for (2-fluorophenyl)(1-(4-(trifluoromethyl)phenyl)vinyl)sulfane **(3fb)**

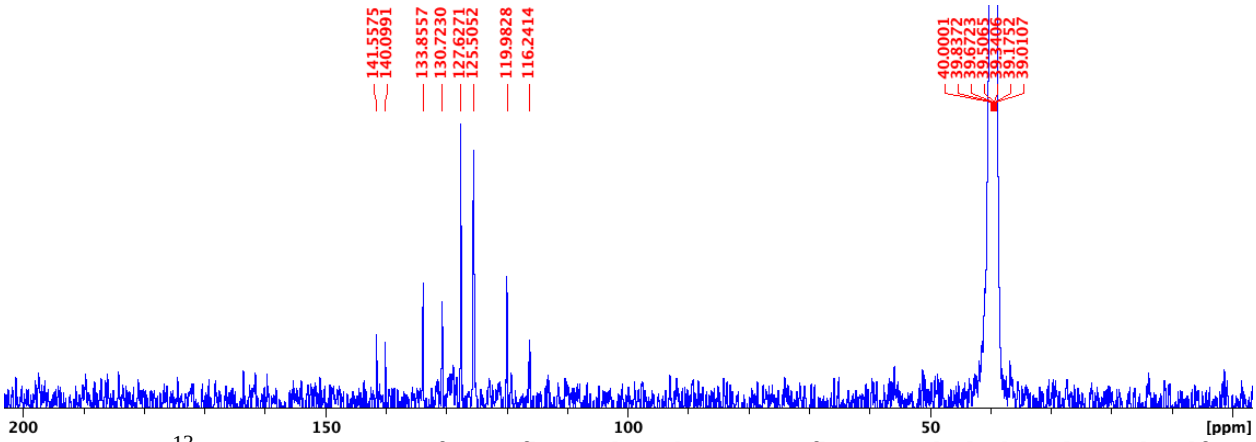


Figure S49. ^{13}C NMR spectrum for (2-fluorophenyl)(1-(4-(trifluoromethyl)phenyl)vinyl)sulfane **(3fb)**

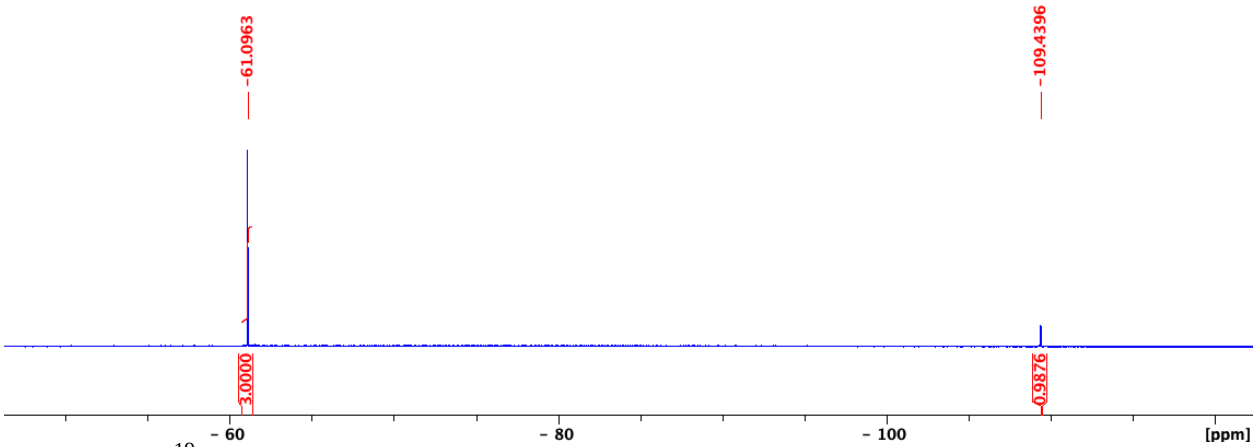


Figure S50. ^{19}F NMR spectrum for (2-fluorophenyl)(1-(4-(trifluoromethyl)phenyl)vinyl)sulfane **(3fb)**

3gb

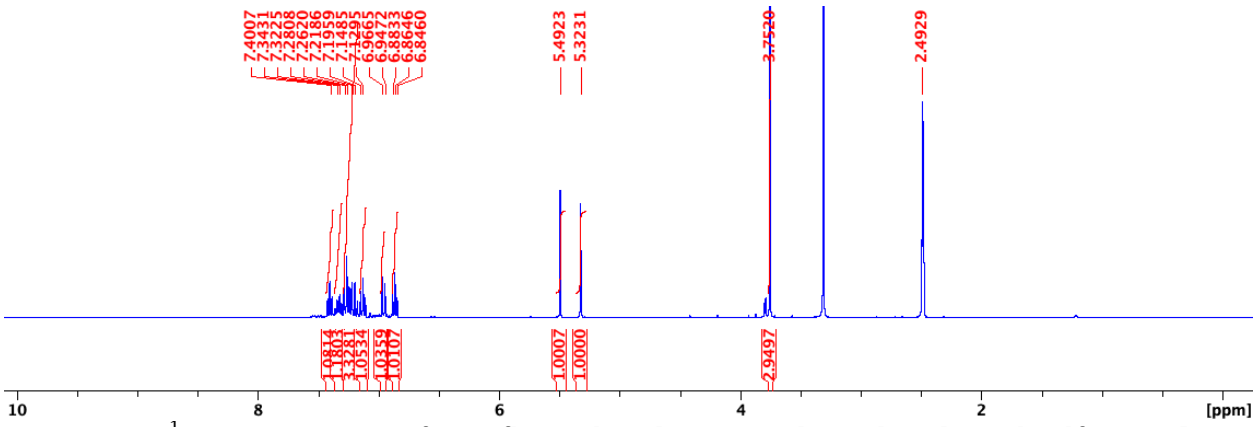


Figure S51. ^{1}H NMR spectrum for (2-fluorophenyl)(1-(2-methoxyphenyl)vinyl)sulfane **(3gb)**

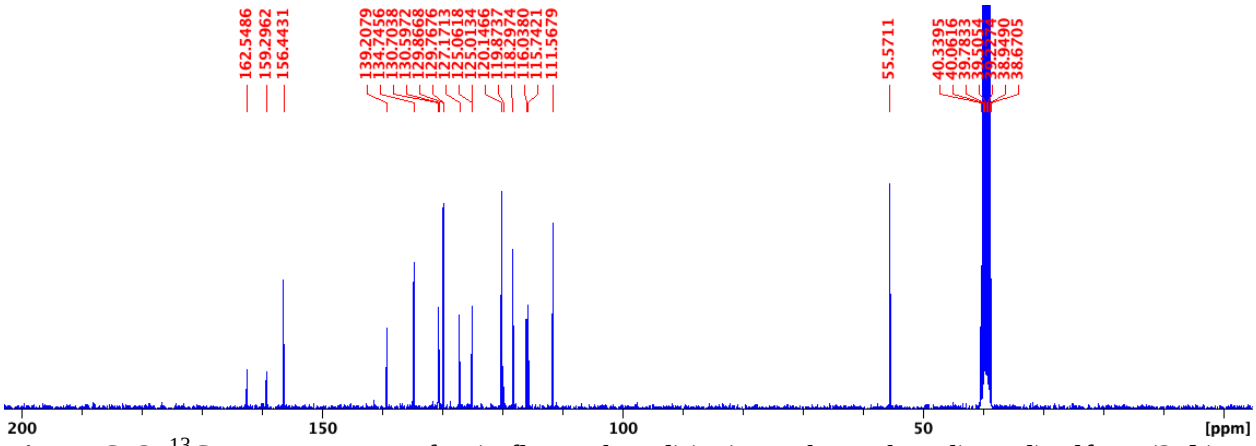


Figure S52. ^{13}C NMR spectrum for (2-fluorophenyl)(1-(2-methoxyphenyl)vinyl)sulfane **(3gb)**

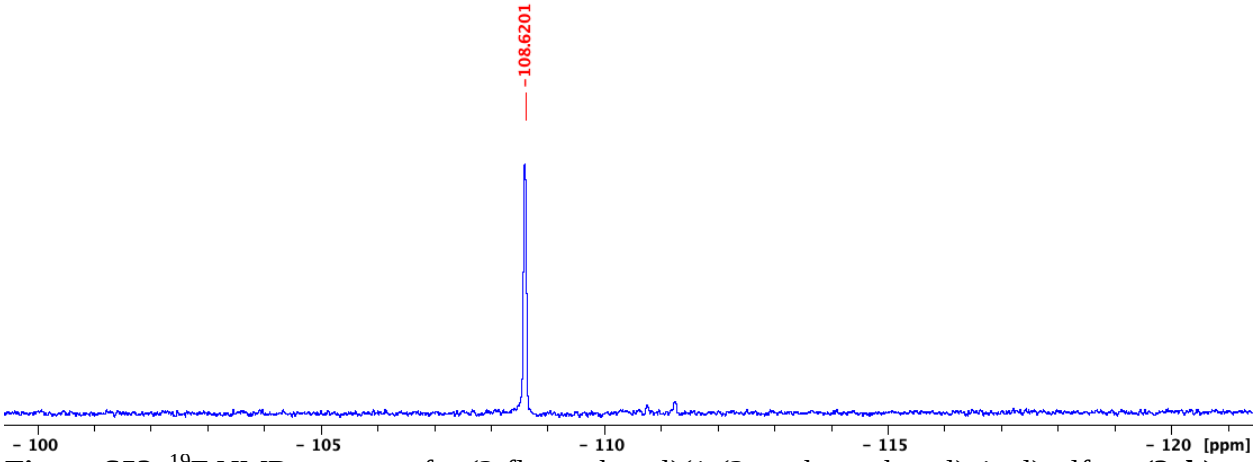


Figure S53. ^{19}F NMR spectrum for (2-fluorophenyl)(1-(2-methoxyphenyl)vinyl)sulfane **(3gb)**

3hb

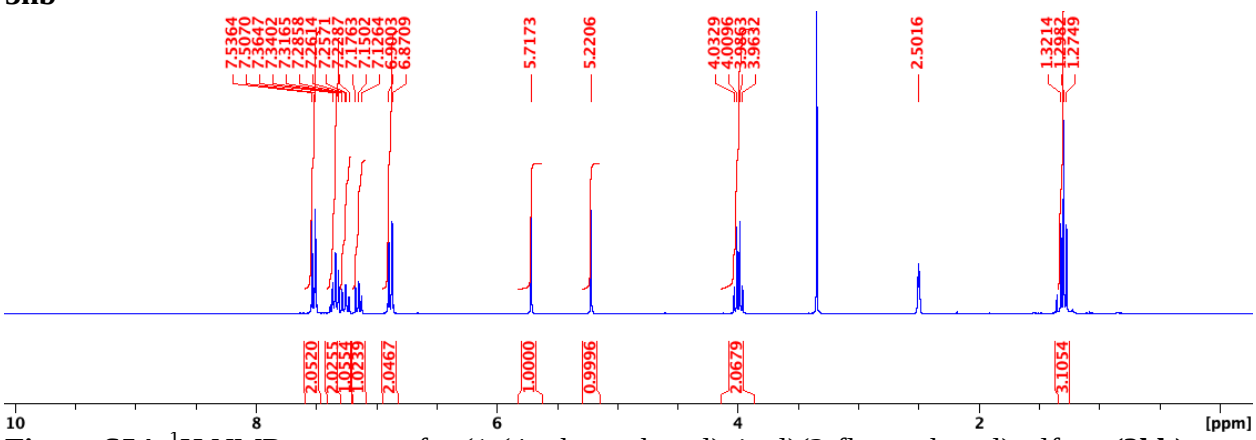


Figure S54. ^{1}H NMR spectrum for (1-(4-ethoxyphenyl)vinyl)(2-fluorophenyl)sulfane **(3hb)**

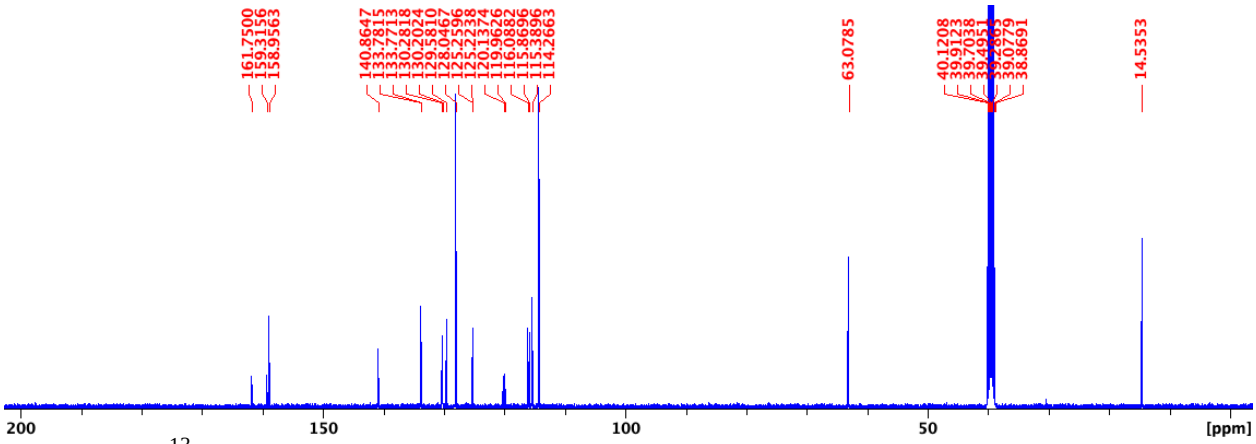


Figure S55. ^{13}C NMR spectrum for (1-(4-ethoxyphenyl)vinyl)(2-fluorophenyl)sulfane **(3hb)**

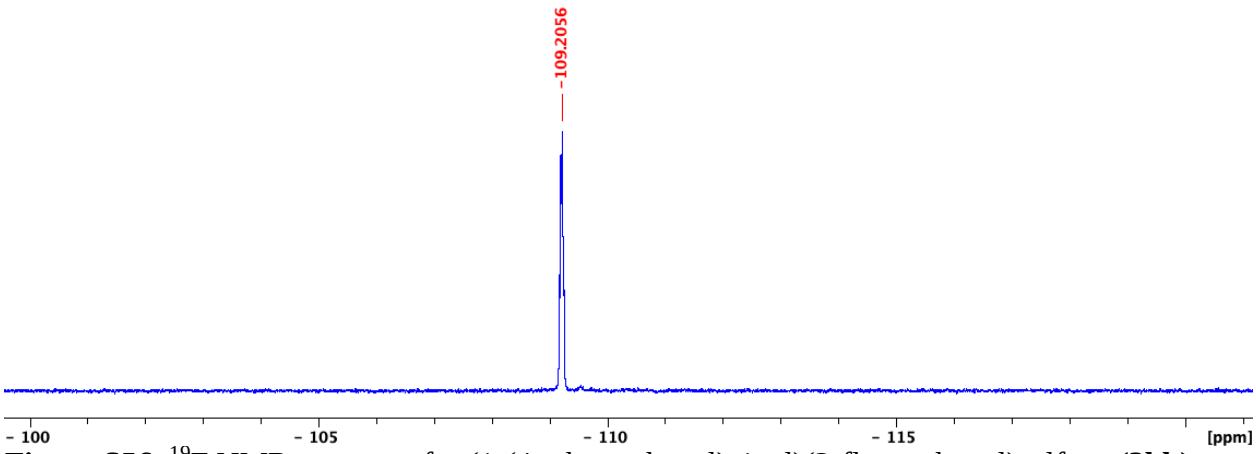


Figure S56. ^{19}F NMR spectrum for (1-(4-ethoxyphenyl)vinyl)(2-fluorophenyl)sulfane **(3hb)**

3ib

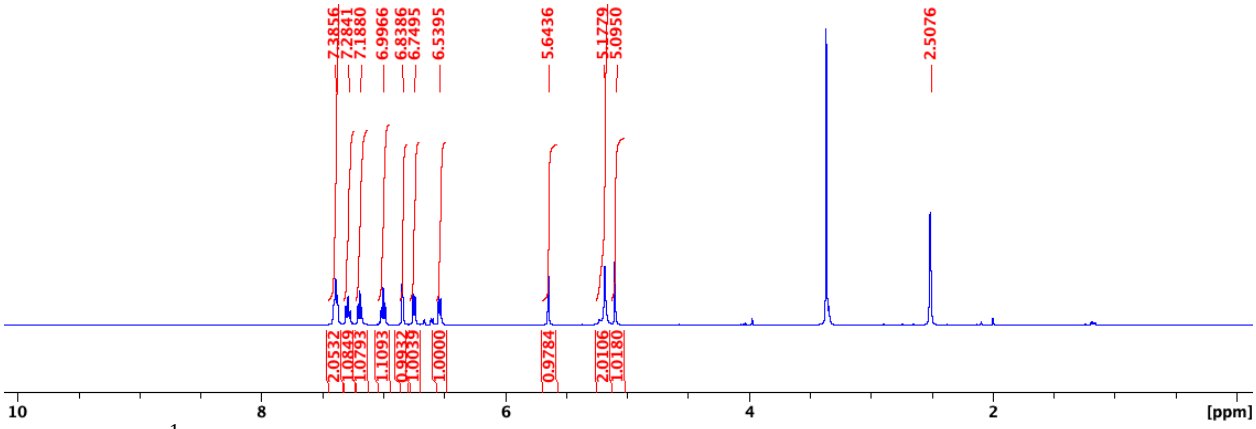


Figure S57. ^{1}H NMR spectrum for 3-(1-((2-fluorophenyl)thio)vinyl)aniline **(3ib)**

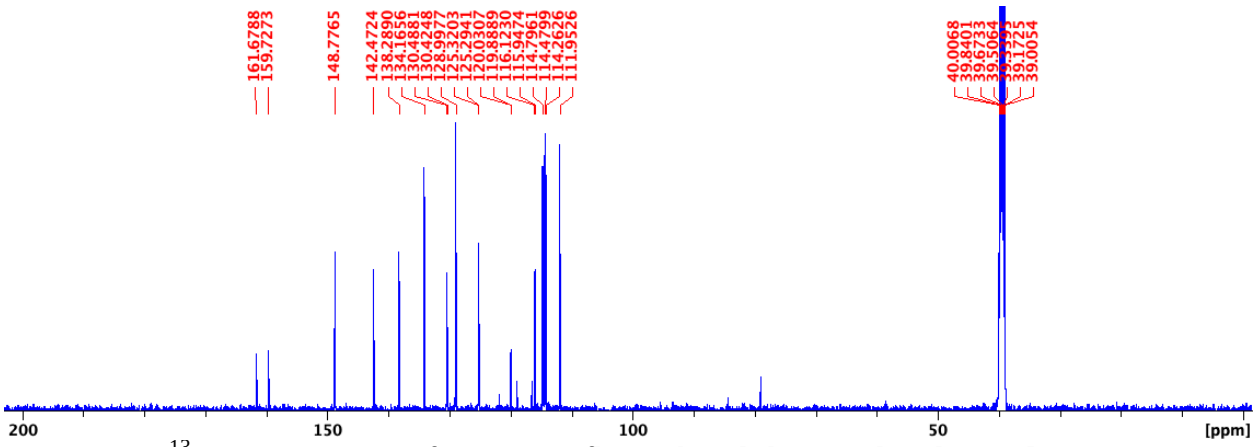


Figure S58. ^{13}C NMR spectrum for 3-(1-((2-fluorophenyl)thio)vinyl)aniline **(3ib)**

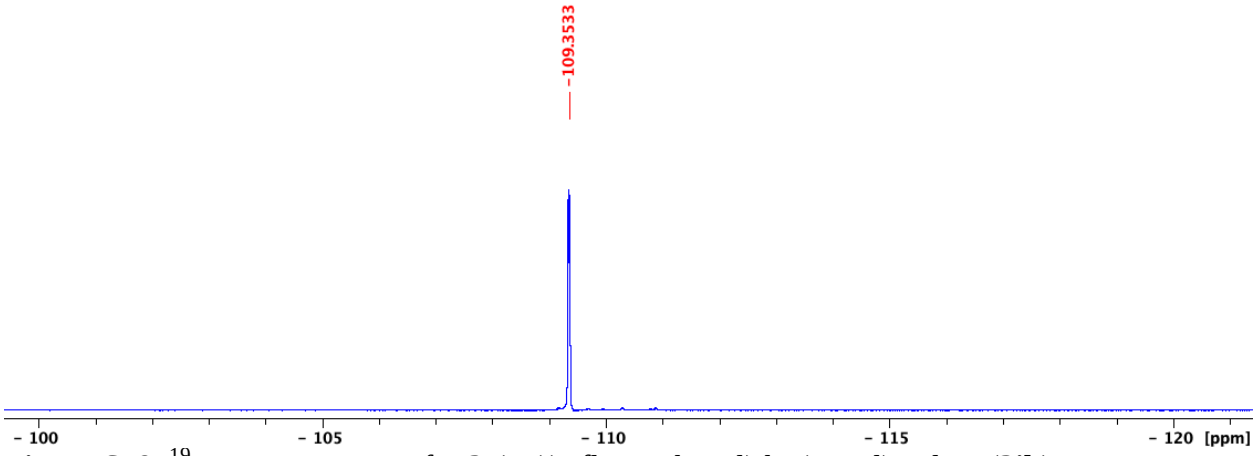


Figure S59. ^{19}F NMR spectrum for 3-(1-((2-fluorophenyl)thio)vinyl)aniline **(3ib)**

3jb

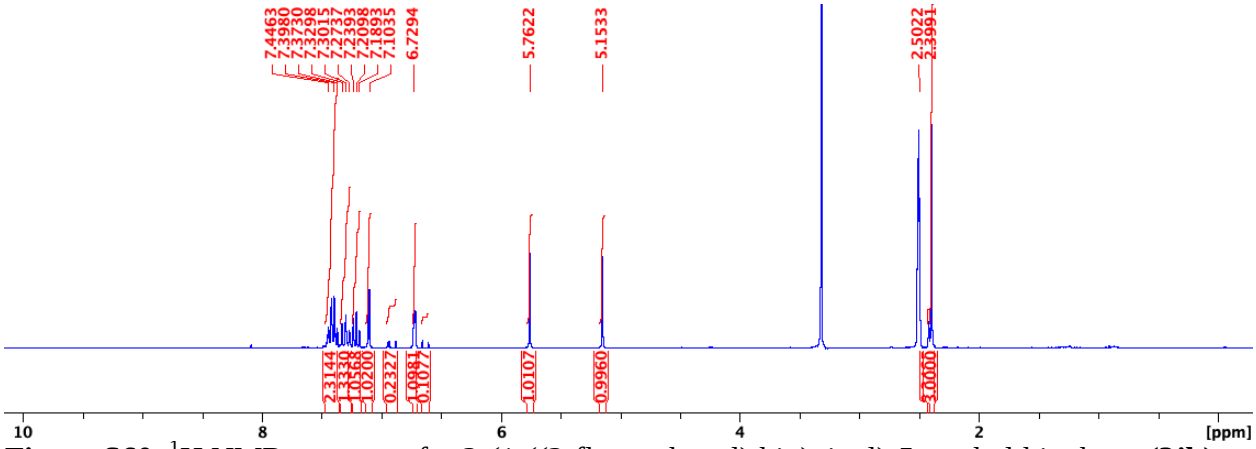


Figure S60. ^{1}H NMR spectrum for 2-(1-((2-fluorophenyl)thio)vinyl)-5-methylthiophene **(3jb),** containing (E)-2-(2-((2-fluorophenyl)thio)vinyl)-5-methylthiophene (**5jb)**: 10%.

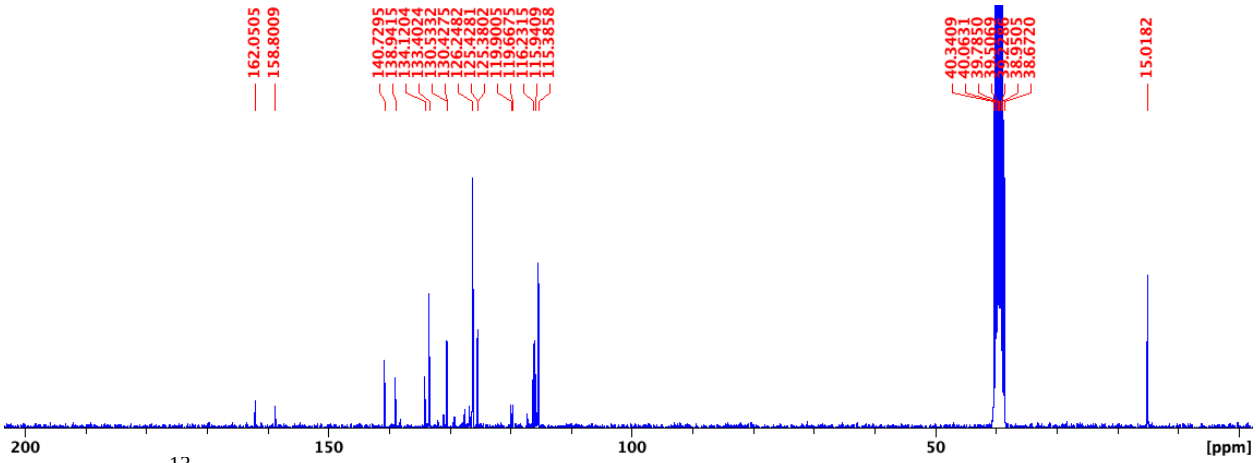


Figure S61. ^{13}C NMR spectrum for 2-(1-((2-fluorophenyl)thio)vinyl)-5-methylthiophene **(3jb)**

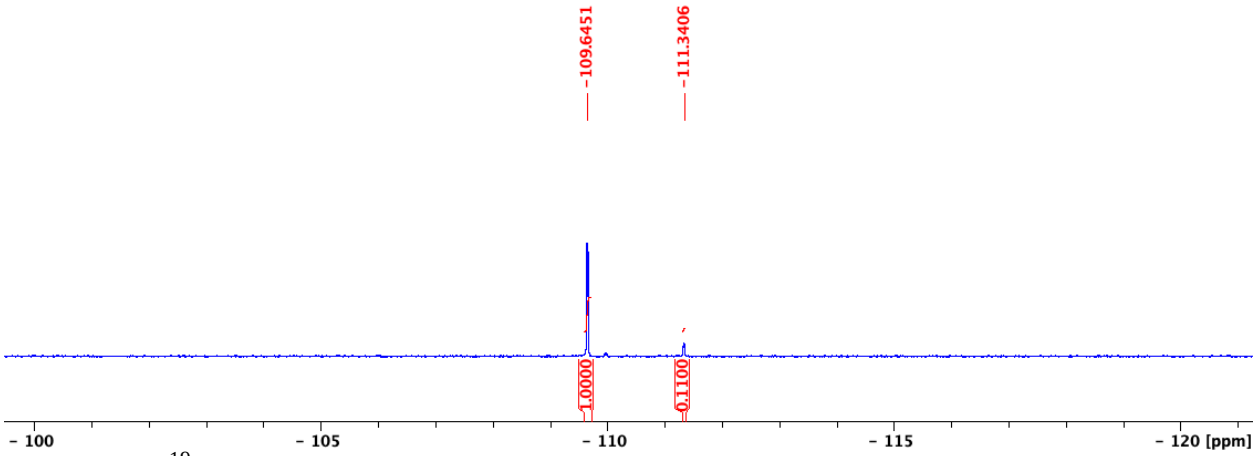


Figure S62. ^{19}F NMR spectrum for 2-(1-((2-fluorophenyl)thio)vinyl)-5-methylthiophene **(3jb),** containing (E)-2-(2-((2-fluorophenyl)thio)vinyl)-5-methylthiophene (**5jb)**: 10%.

3kb

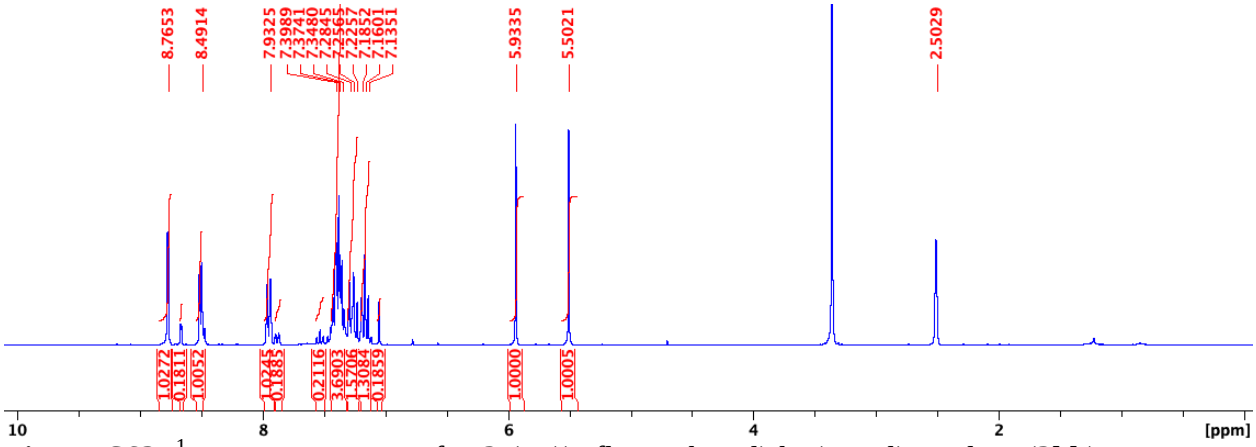


Figure S63. ^{1}H NMR spectrum for 3-(1-((2-fluorophenyl)thio)vinyl)pyridine **(3kb)**, containing (Z)-3-(1,2-bis((2-fluorophenyl)thio)vinyl)pyridine (**4kb**): 15%.

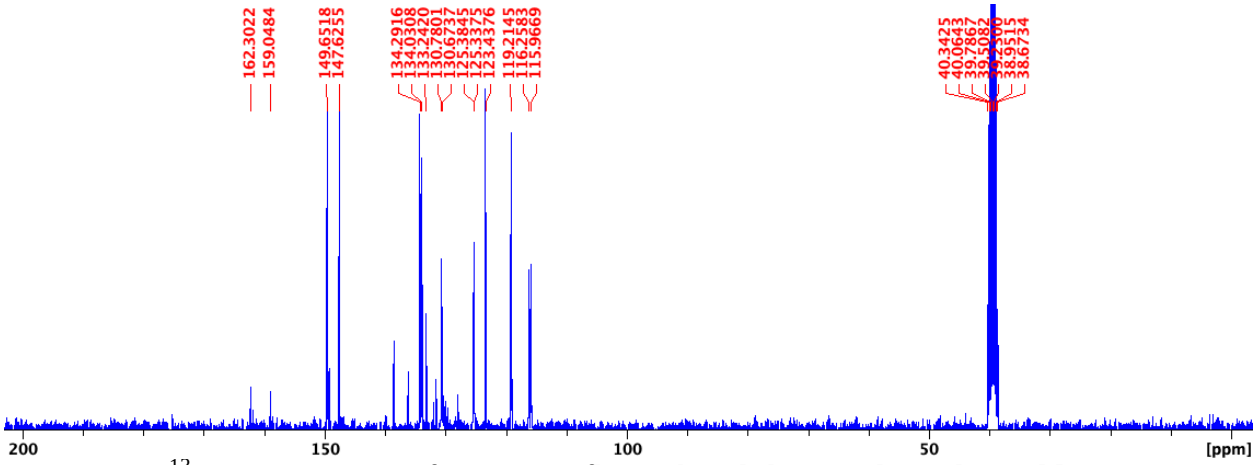


Figure S64. ^{13}C NMR spectrum for 3-(1-((2-fluorophenyl)thio)vinyl)pyridine **(3kb)**

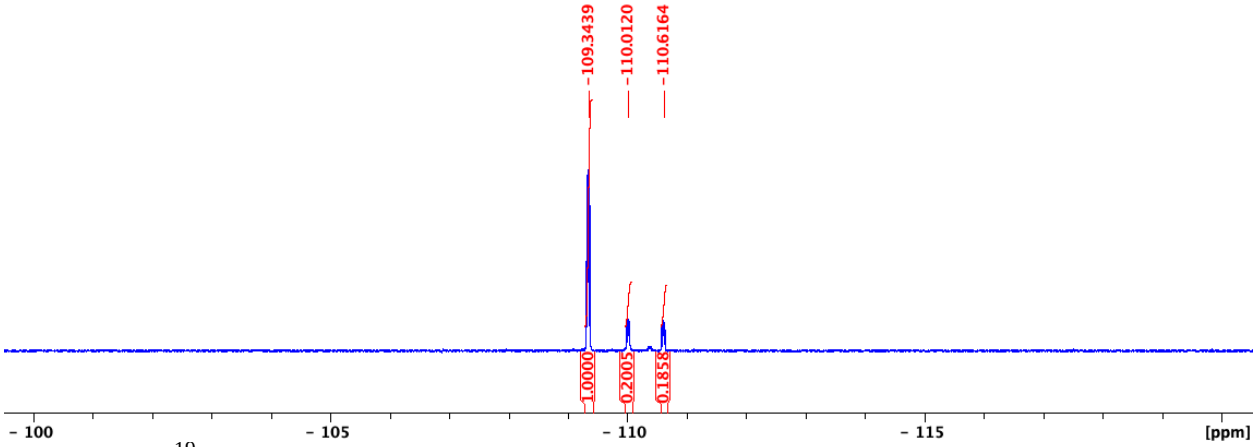


Figure S65. ^{19}F NMR spectrum for 3-(1-((2-fluorophenyl)thio)vinyl)pyridine **(3kb),** containing (Z)-3-(1,2-bis((2-fluorophenyl)thio)vinyl)pyridine (**4kb**): 15%.

3lb

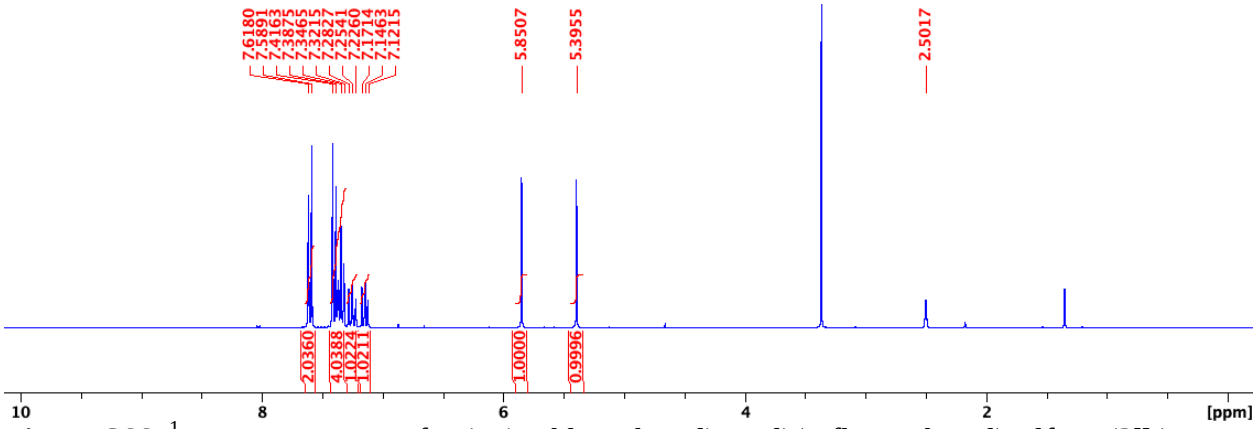


Figure S66. ^{1}H NMR spectrum for (1-(4-chlorophenyl)vinyl)(2-fluorophenyl)sulfane **(3lb)**

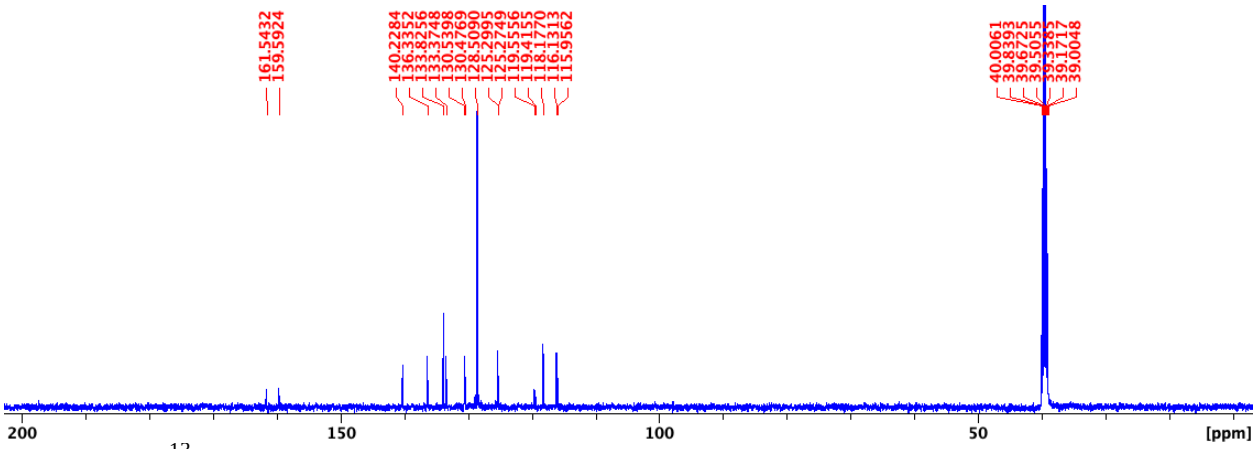


Figure S67. ^{13}C NMR spectrum for (1-(4-chlorophenyl)vinyl)(2-fluorophenyl)sulfane **(3lb)**

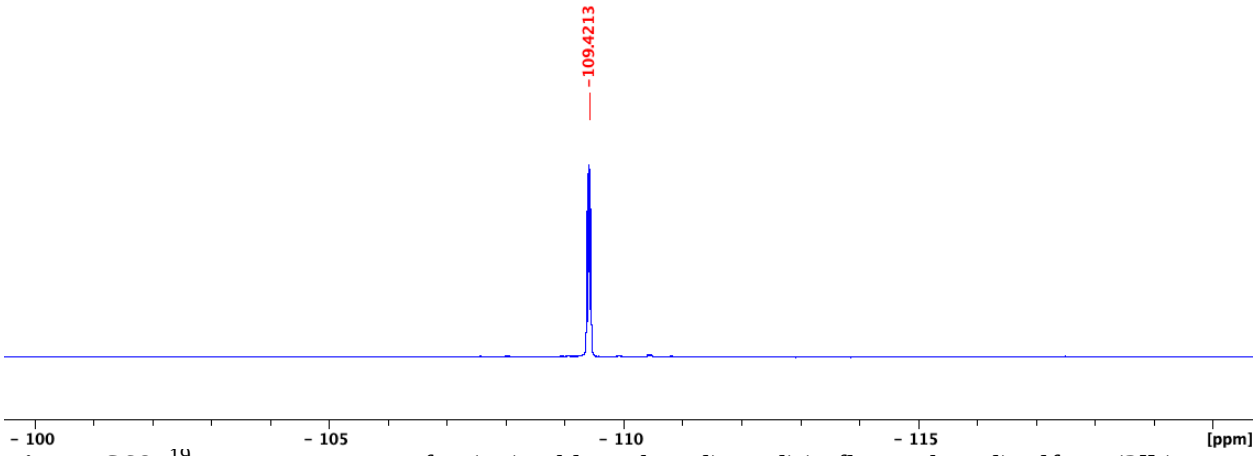


Figure S68. ^{19}F NMR spectrum for (1-(4-chlorophenyl)vinyl)(2-fluorophenyl)sulfane **(3lb)**

3mb

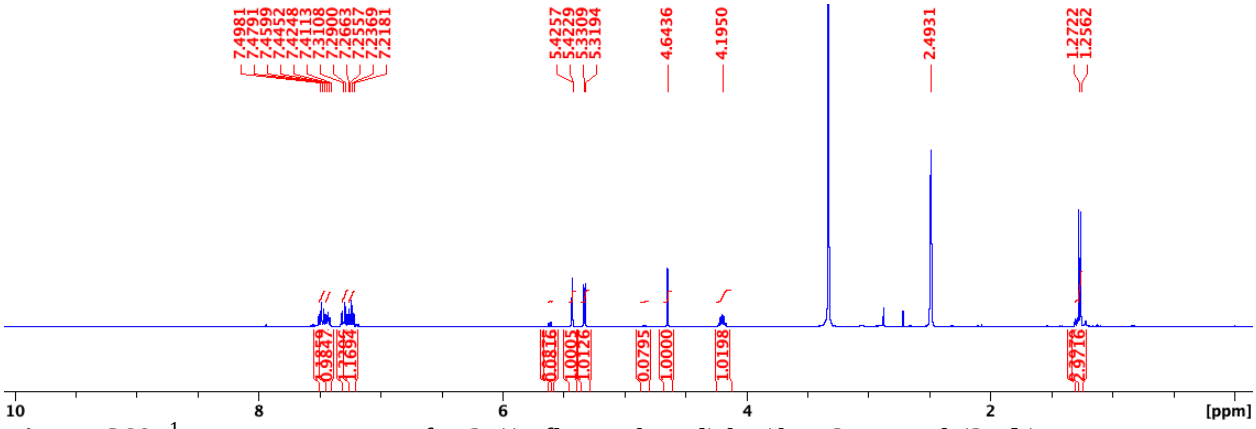


Figure S69. [1] H NMR spectrum for 3-((2-fluorophenyl)thio)but-3-en-2-ol **(3mb),** containing (Z)-3,4-bis((2-fluorophenyl)thio)but-3-en-2-ol (**4mb**): 8%.

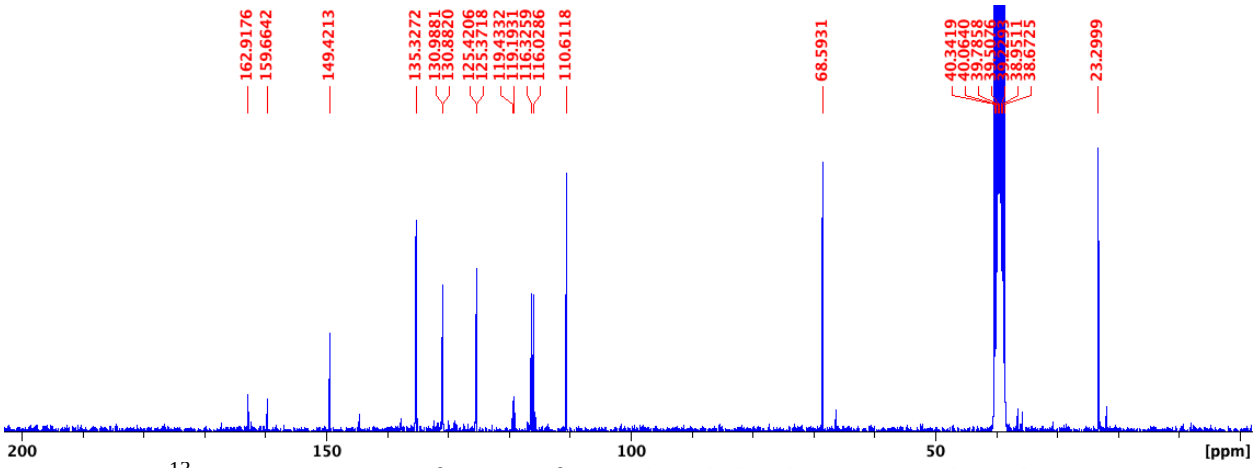


Figure S70. [13] C NMR spectrum for 3-((2-fluorophenyl)thio)but-3-en-2-ol **(3mb)**

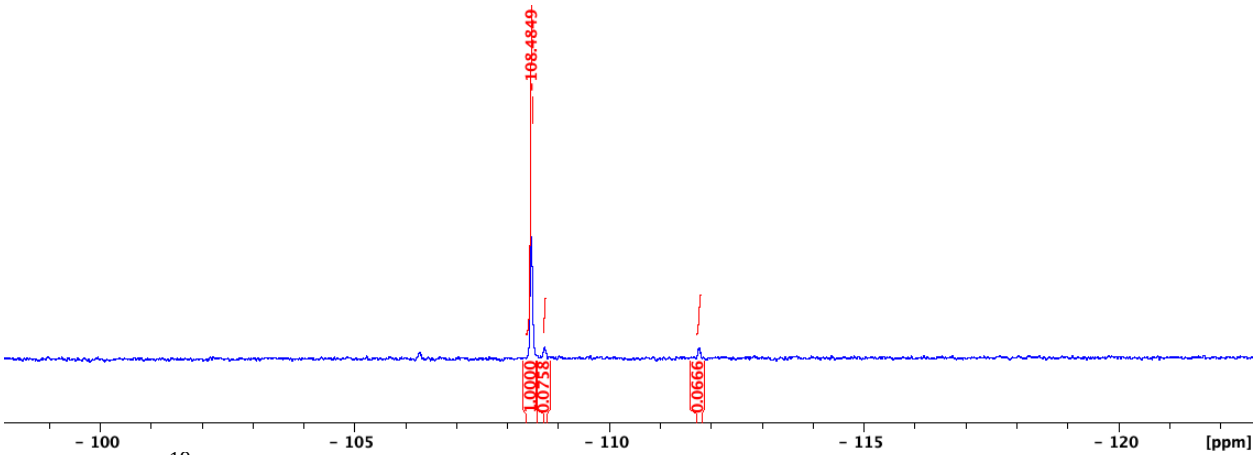


Figure S71. [19] F NMR spectrum for 3-((2-fluorophenyl)thio)but-3-en-2-ol **(3mb),** containing (Z)-3,4-bis((2-fluorophenyl)thio)but-3-en-2-ol (**4mb**): 8%.

3sa

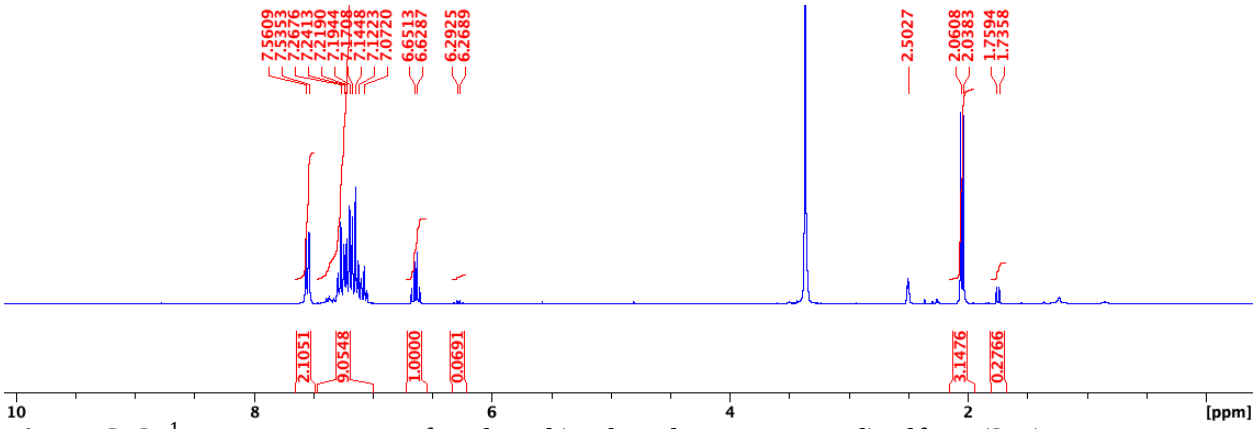


Figure S72. [1] H NMR spectrum for phenyl(1-phenylprop-1-en-1-yl)sulfane **(3sa), Mixture E/Z: 14:1**

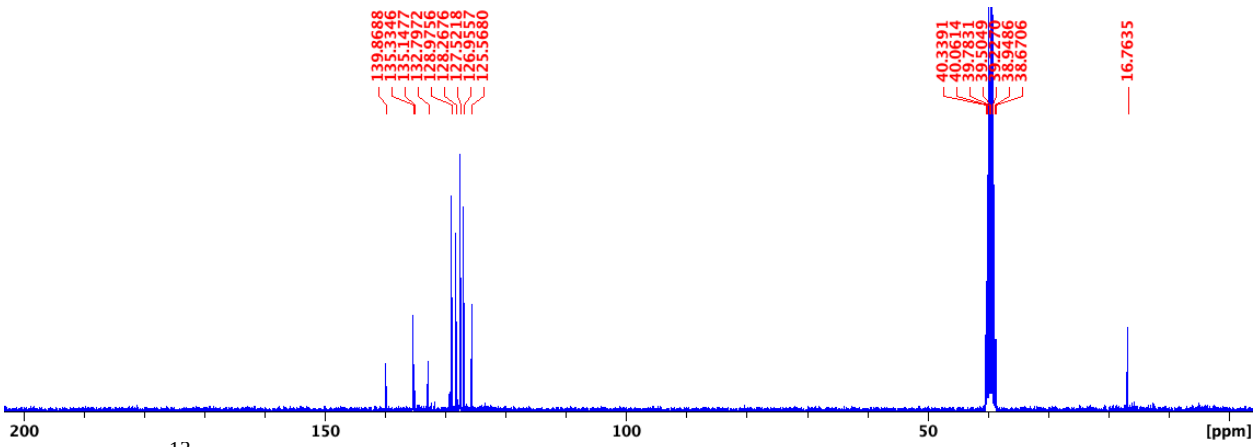


Figure S73. [13]C NMR spectrum for phenyl(1-phenylprop-1-en-1-yl)sulfane **(3sa), Mixture E/Z: 14:1**

4ab

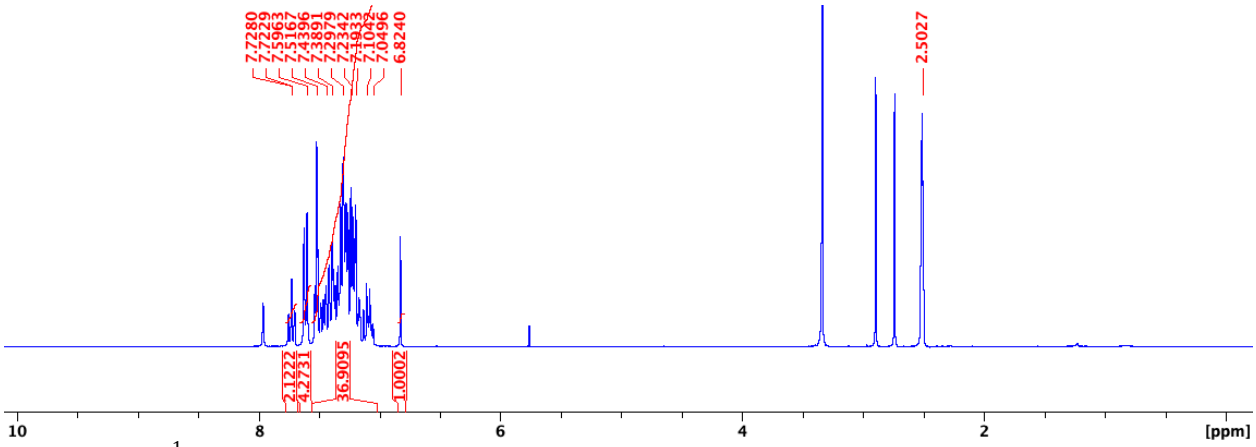


Figure S74. ^{1}H NMR spectrum for (1-phenylethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4ab), Mixture E/Z: 1:2**

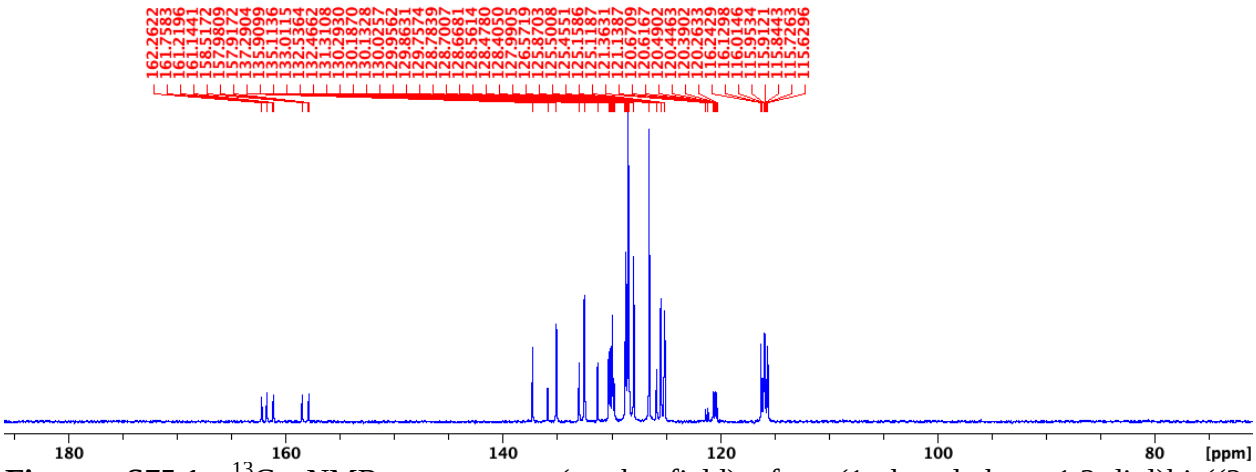


Figure S75.1 ^{13}C NMR spectrum (weak field) for (1-phenylethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4ab), Mixture E/Z: 1:2**

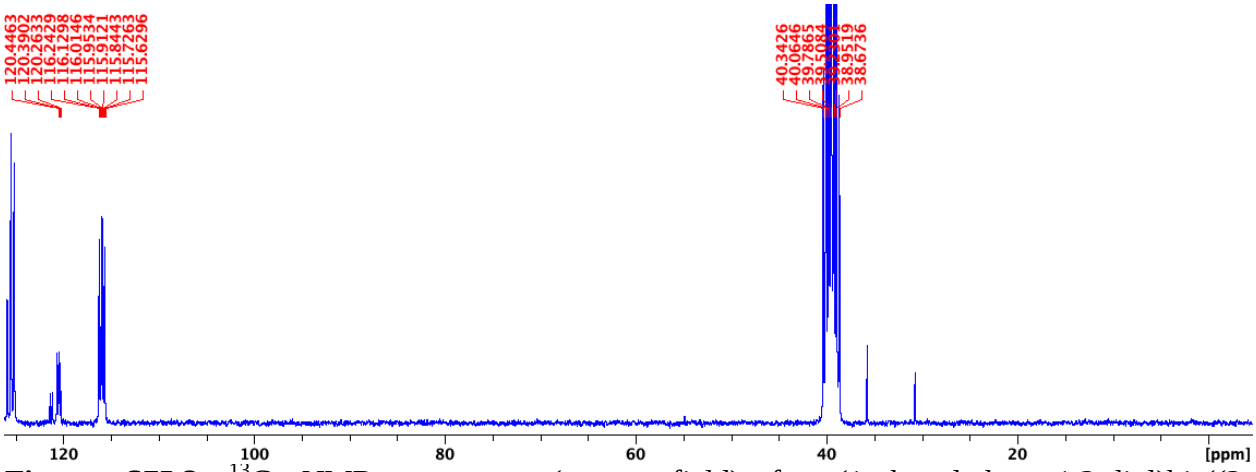


Figure S75.2 ^{13}C NMR spectrum (strong field) for (1-phenylethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4ab), Mixture E/Z: 1:2**

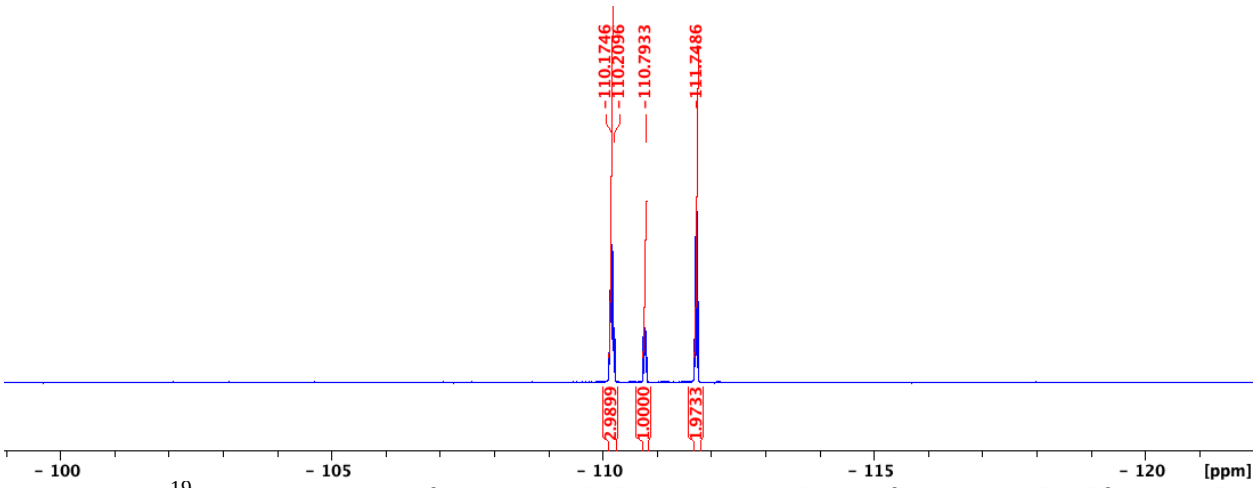


Figure S76. ^{19}F NMR spectrum for (1-phenylethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4ab), Mixture E/Z: 1:2**

4bb

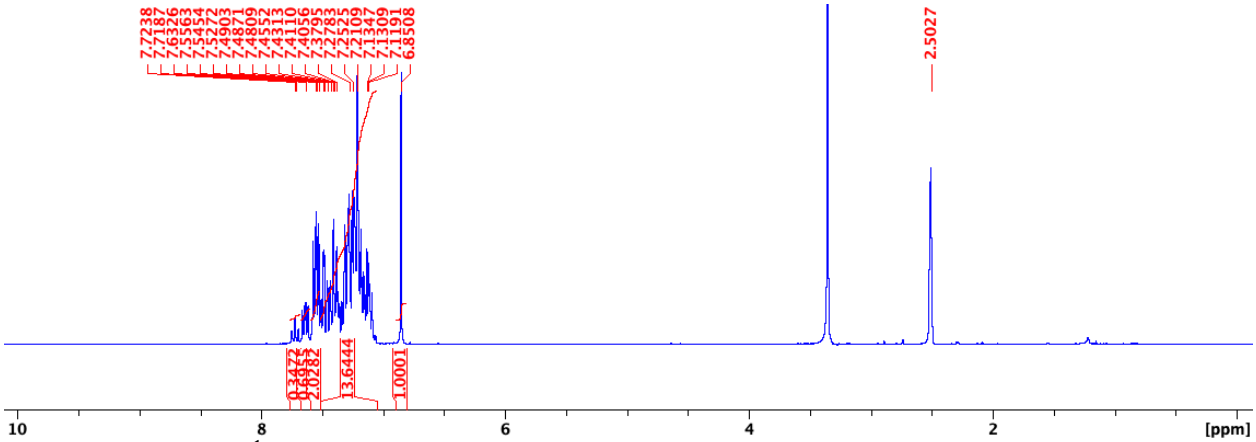


Figure S77. ^{1}H NMR spectrum for (1-(4-fluorophenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4bb), Mixture E/Z: 3:1**

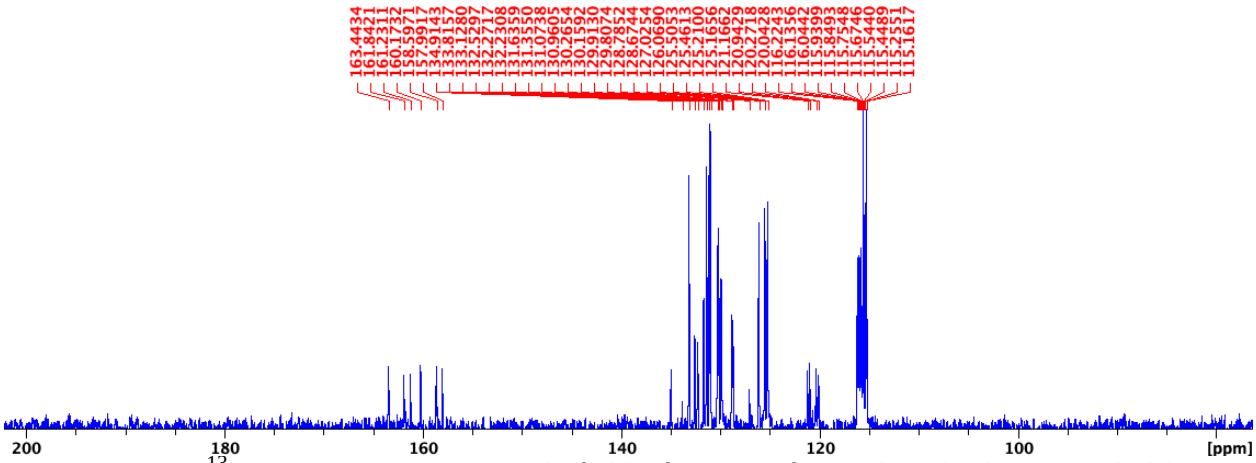


Figure S78.1. ^{13}C NMR spectrum (weak field) for (1-(4-fluorophenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4bb), Mixture E/Z: 3:1**

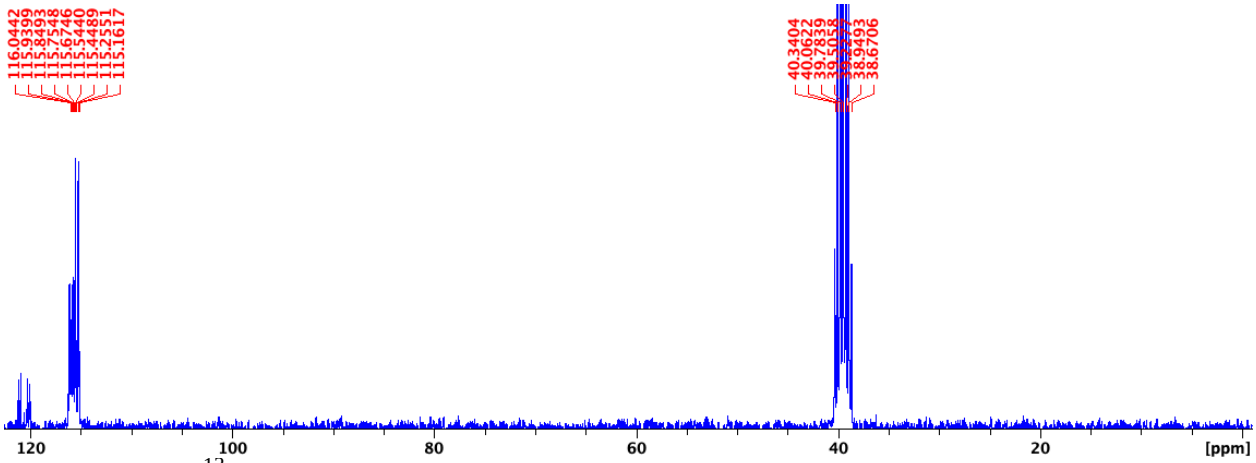


Figure S78.2. ^{13}C NMR spectrum (strong field) for (1-(4-fluorophenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4bb), Mixture E/Z: 3:1**

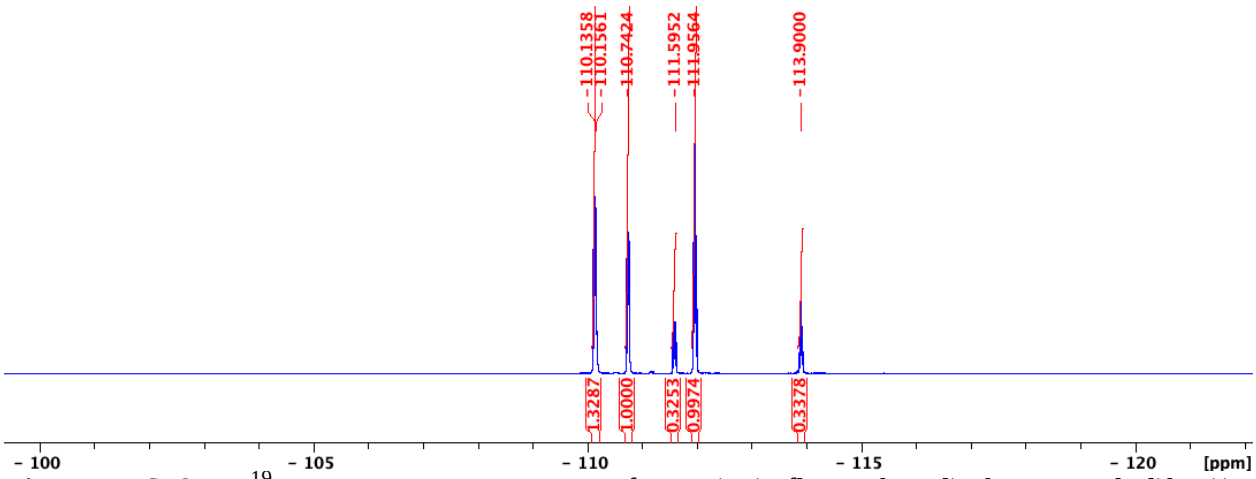


Figure S79. ^{19}F NMR spectrum for (1-(4-fluorophenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4bb), Mixture E/Z: 3:1**

4cb

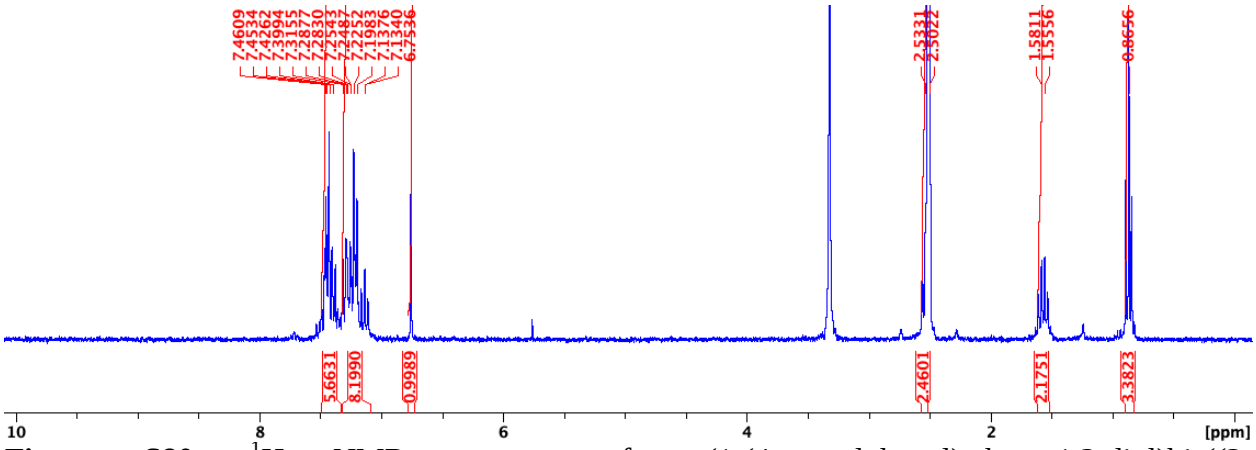


Figure S80. ^{1}H NMR spectrum for (1-(4-propylphenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4cb)**, **Mixture E/Z: 9:1**.

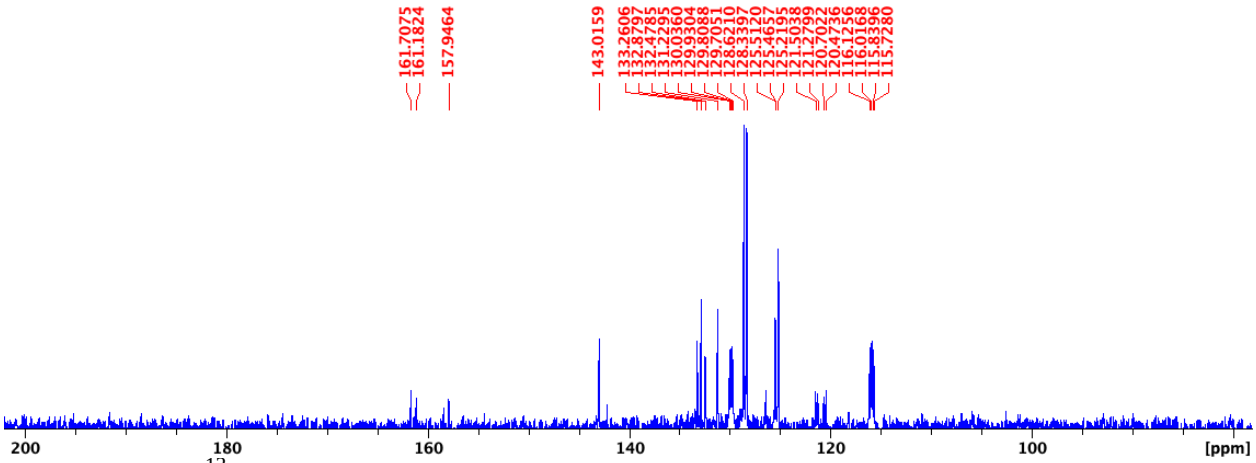


Figure S81.1. ^{13}C NMR spectrum (weak field) for (1-(4-propylphenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4cb), Mixture E/Z: 9:1**.

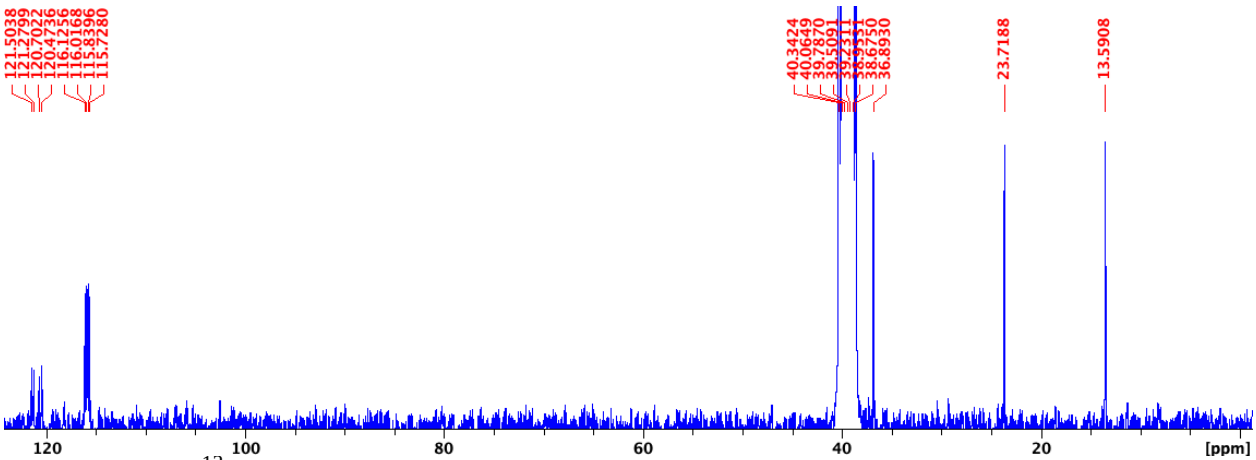


Figure S81.2. ^{13}C NMR spectrum (strong field) for (1-(4-propylphenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4cb), Mixture E/Z: 9:1**.

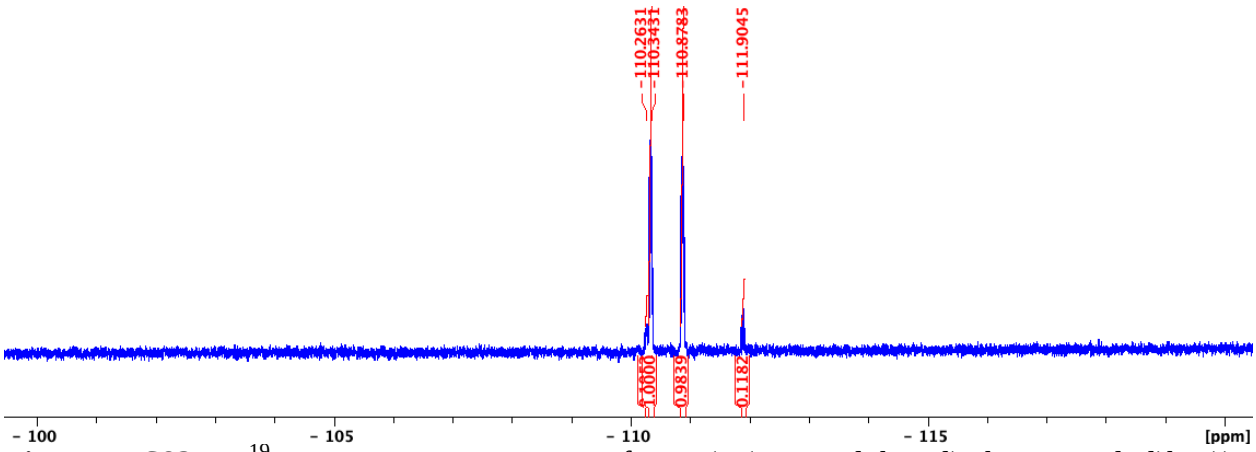


Figure S82. ^{19}F NMR spectrum for (1-(4-propylphenyl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4cb), Mixture E/Z: 9:1**.

4db

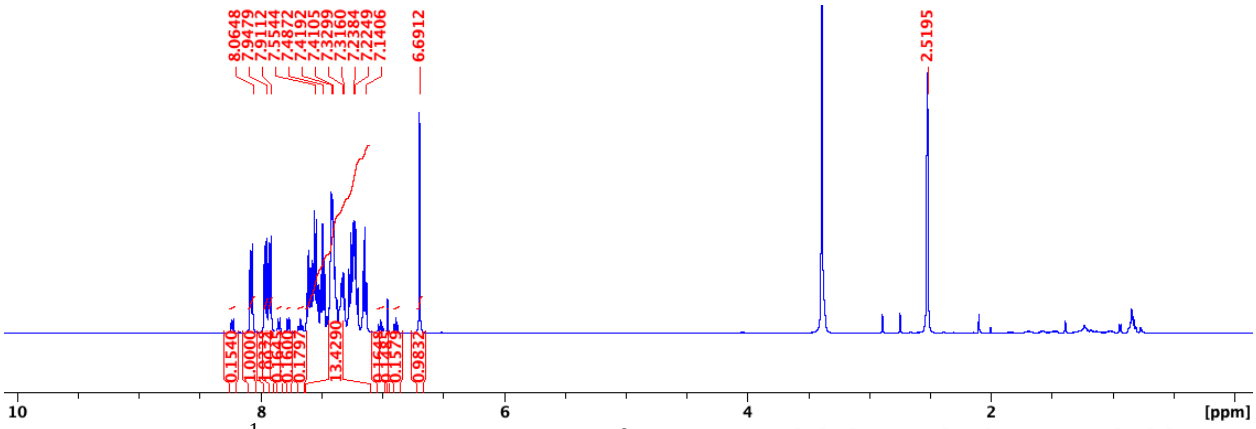


Figure S83. ^{1}H NMR spectrum for (1-(naphthalen-1-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4db), Mixture E/Z: 6:1**.

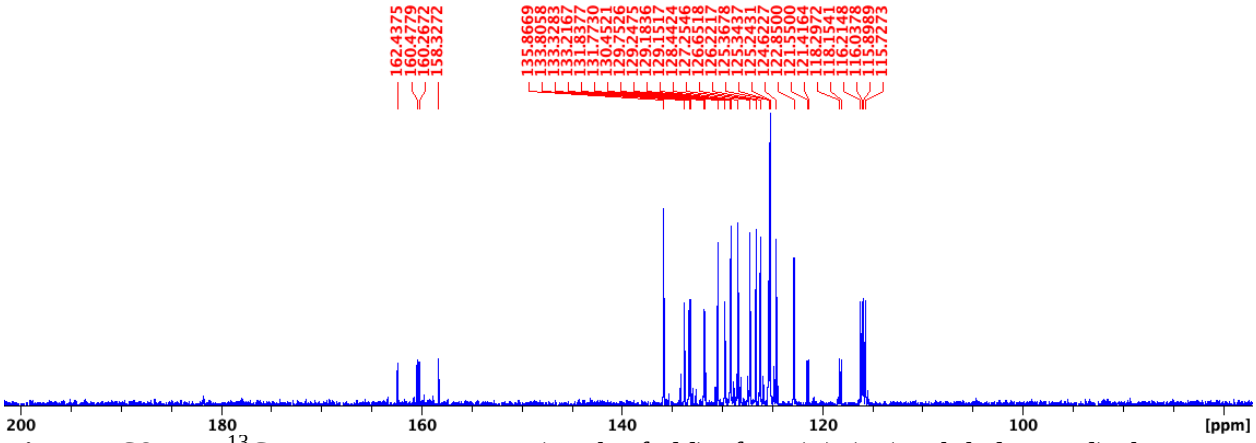


Figure S84.1. ^{13}C NMR spectrum (weak field) for (E)-(1-(naphthalen-1-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4db), Mixture E/Z: 6:1**.

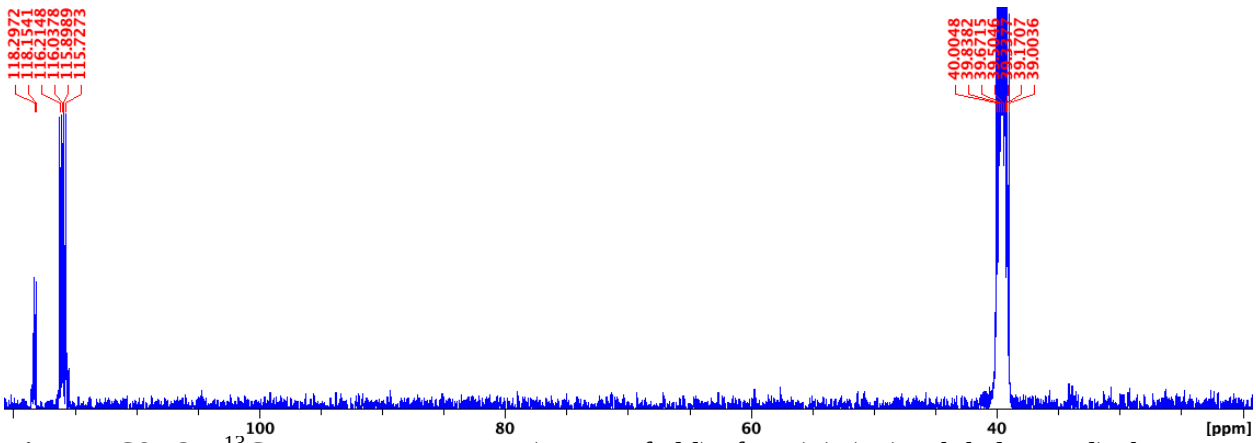


Figure S84.2. ^{13}C NMR spectrum (strong field) for (E)-(1-(naphthalen-1-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4db), Mixture E/Z: 6:1**.

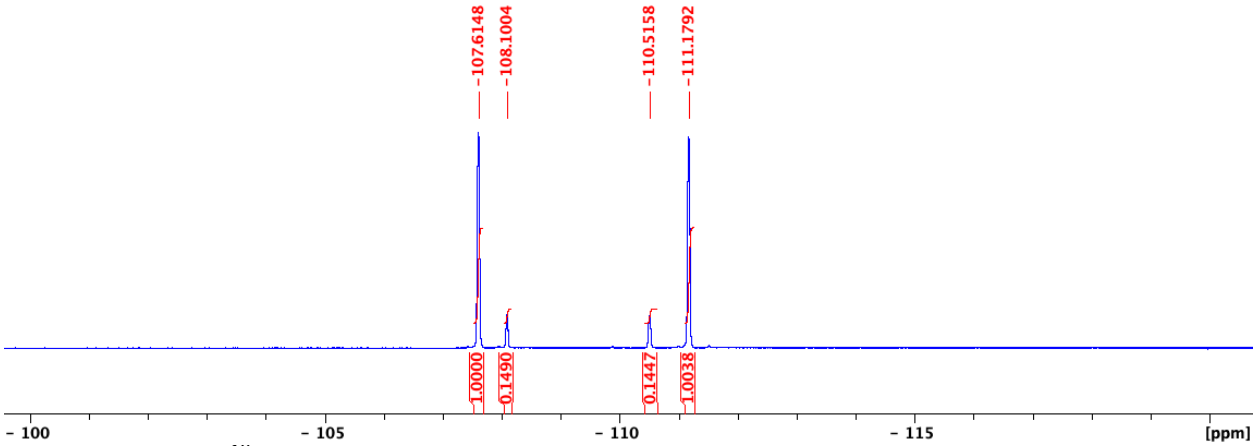


Figure S85. ^{19}F NMR spectrum for (E)-(1-(naphthalen-1-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4db), Mixture E/Z: 6:1**.

4eb

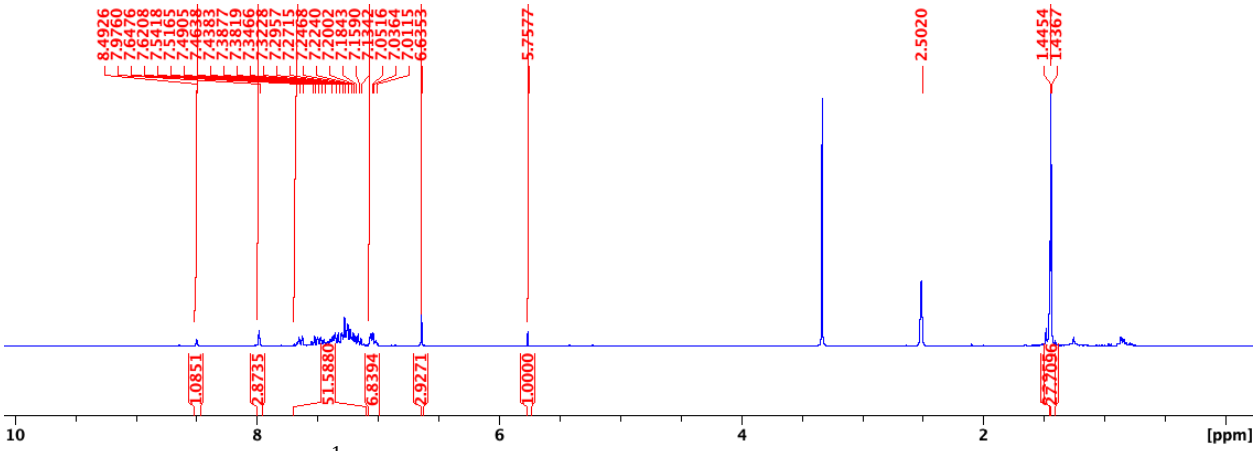


Figure S86. ^{1}H NMR spectrum for *tert*-butyl(2-(1,2-bis((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(4eb), Mixture E/Z: 1:3**

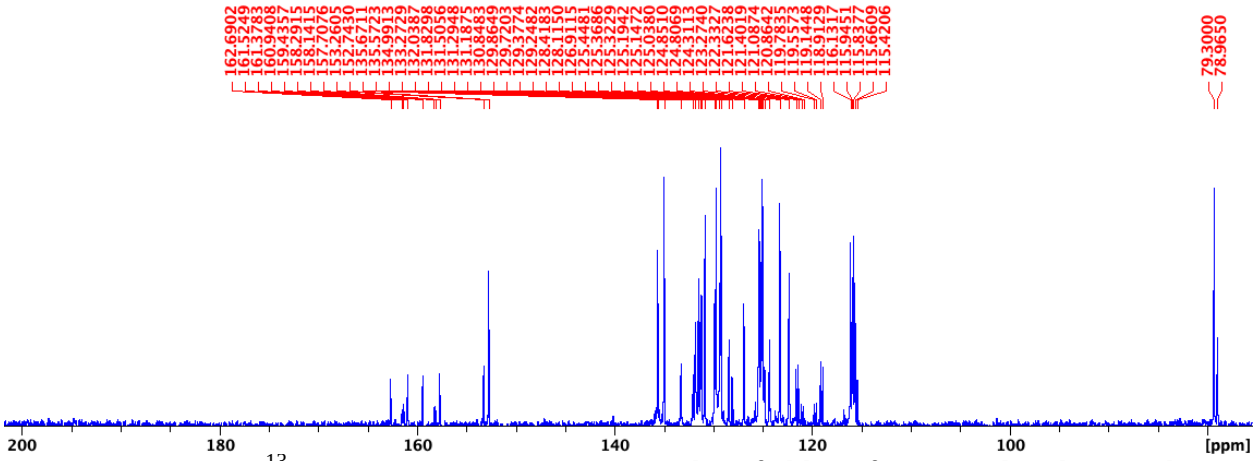


Figure S87.1. ^{13}C NMR spectrum (weak field) for *tert*-butyl(2-(1,2-bis((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(4eb), Mixture E/Z: 1:3**

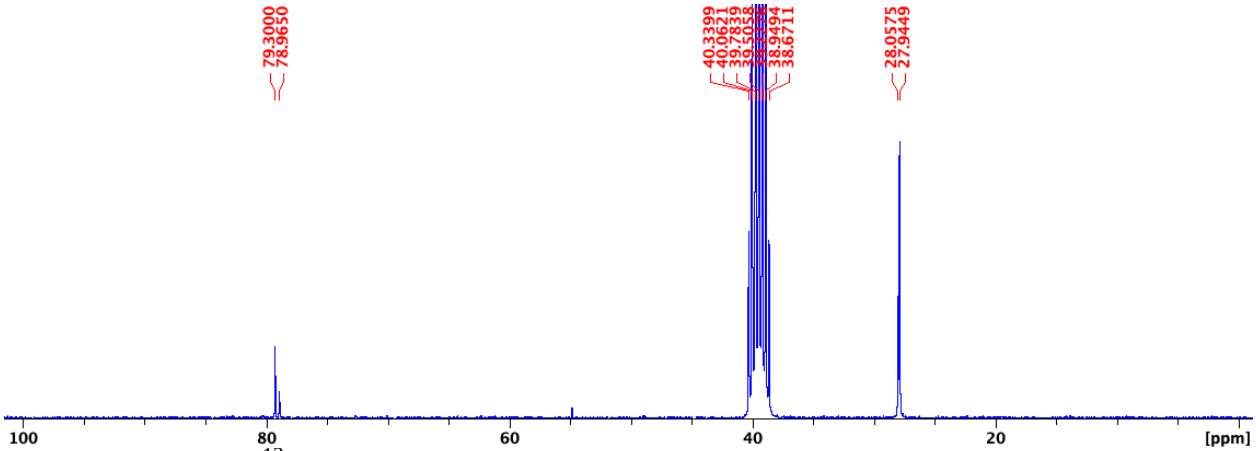


Figure S87.2. ^{13}C NMR spectrum (strong field) for *tert*-butyl(2-(1,2-bis((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(4eb), Mixture E/Z: 1:3**

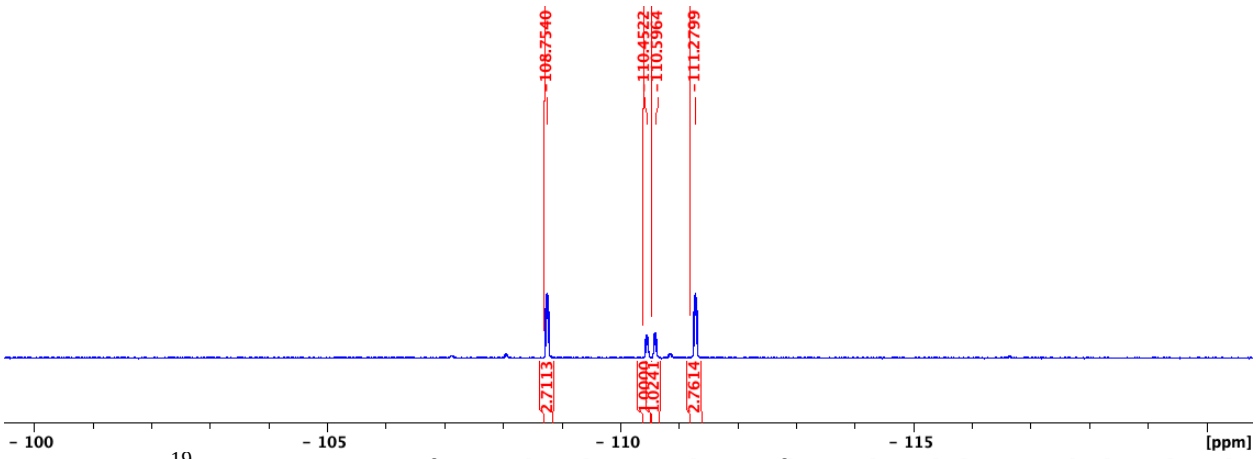


Figure S88. ^{19}F NMR spectrum for *tert*-butyl(2-(1,2-bis((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(4eb), Mixture E/Z: 1:3**

4ob’

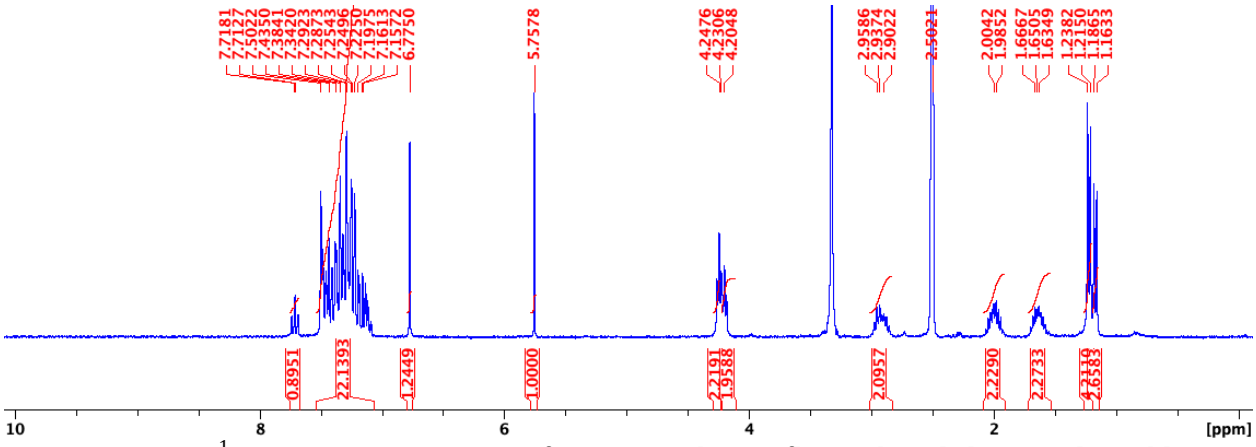


Figure S89. ^{1}H NMR spectrum for 6-(1,2-bis((2-fluorophenyl)thio)vinyl)-8-chloro-4-methylchromane **(4ob’), Mixture E/Z: 1:1.25**

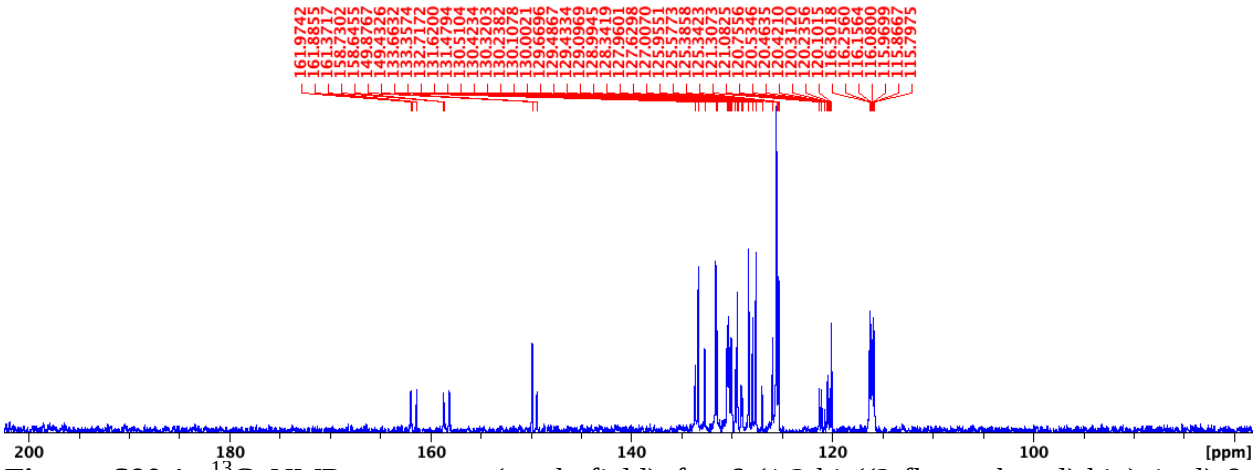


Figure S90.1. ^{13}C NMR spectrum (weak field) for 6-(1,2-bis((2-fluorophenyl)thio)vinyl)-8-chloro-4-methylchromane **(4ob’), Mixture E/Z: 1:1.25**

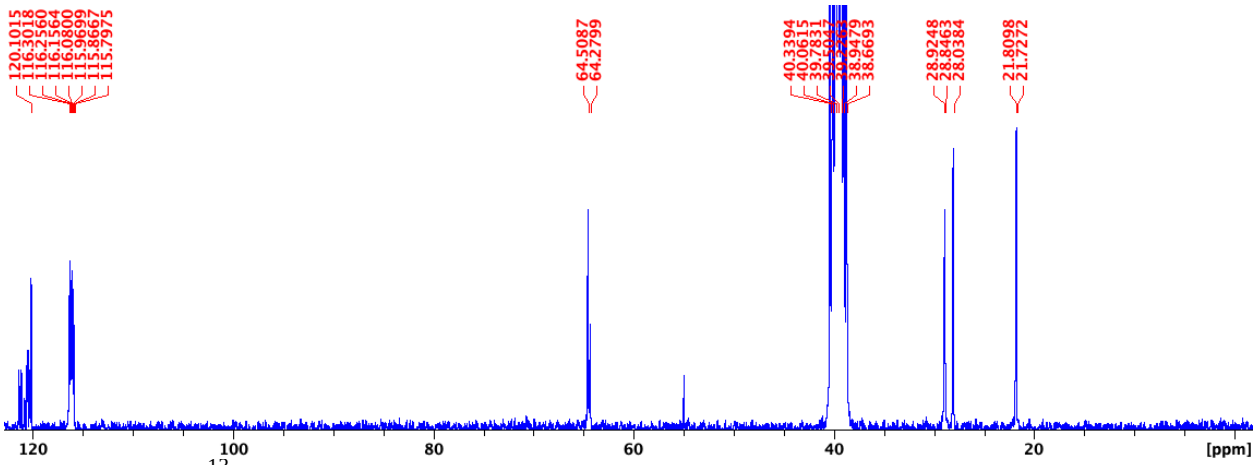


Figure S90.2. ^{13}C NMR spectrum (strong field) for 6-(1,2-bis((2-fluorophenyl)thio)vinyl)-8-chloro-4-methylchromane **(4ob’), Mixture E/Z: 1:1.25**

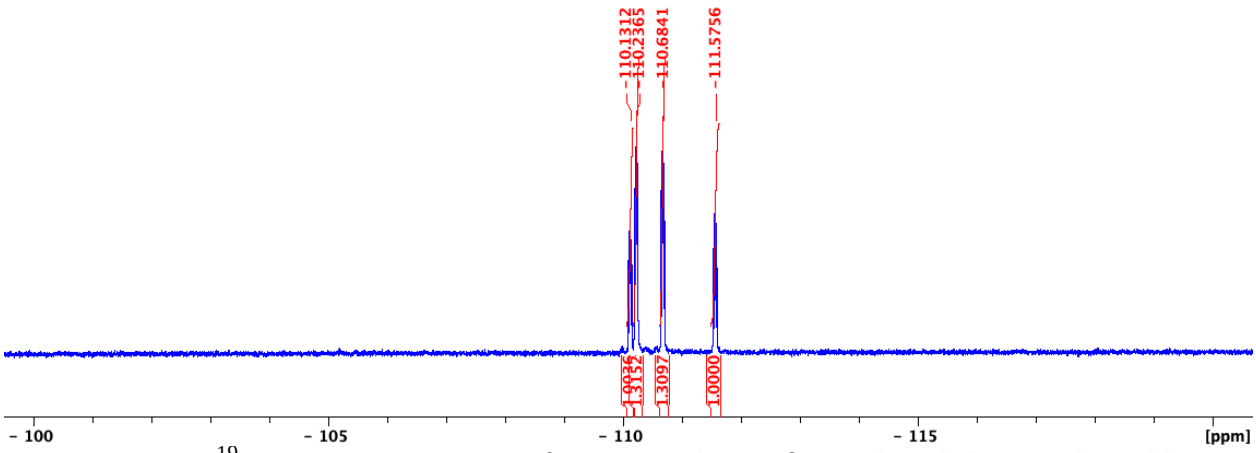


Figure S91. ^{19}F NMR spectrum for 6-(1,2-bis((2-fluorophenyl)thio)vinyl)-8-chloro-4-methylchromane **(4ob'), Mixture E/Z: 1:1.25**

4pb

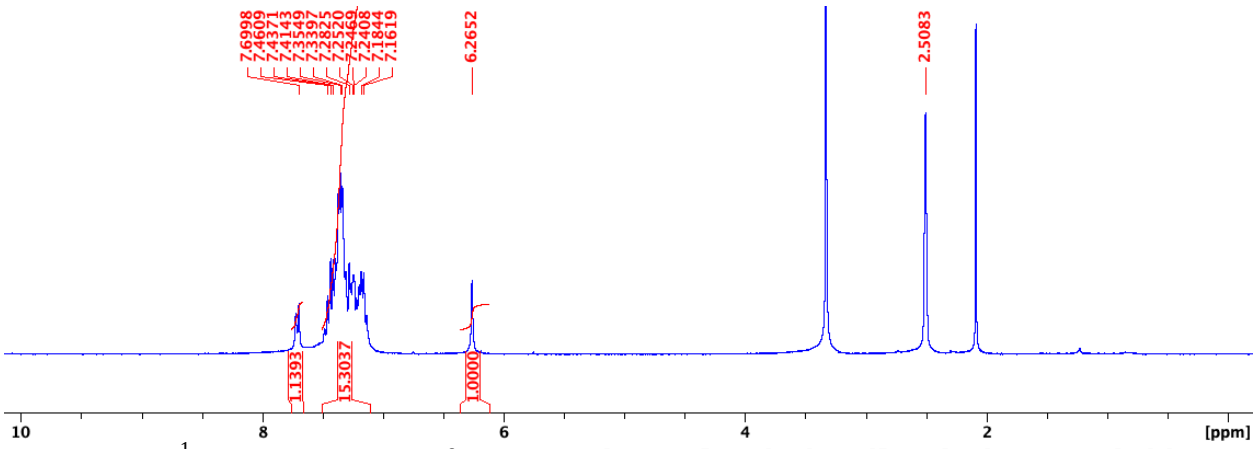


Figure S92. ^{1}H NMR spectrum for E-(1-(2'-bromo-[1,1'-biphenyl]-2-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4pb)**

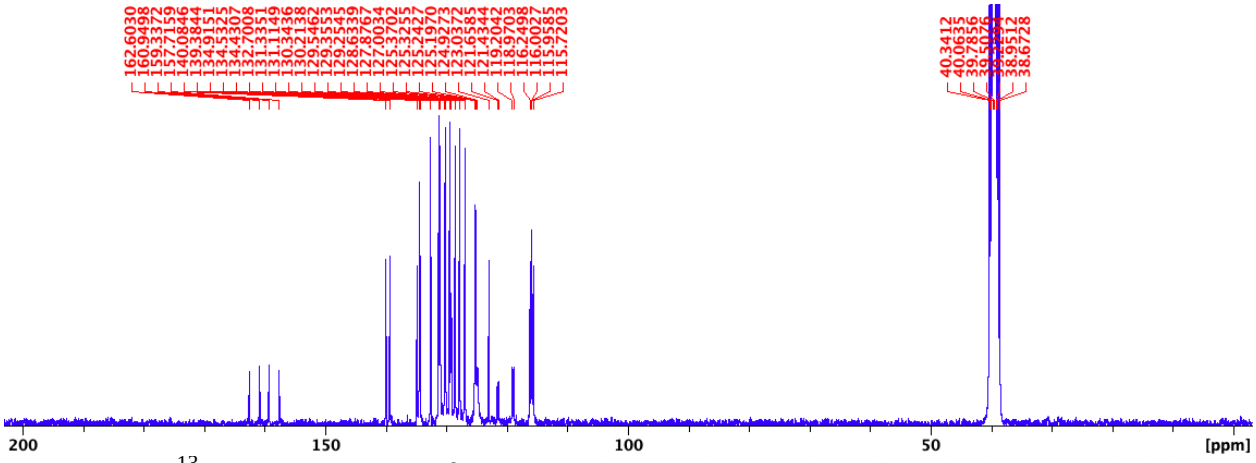


Figure S93. ^{13}C NMR spectrum for E-(1-(2'-bromo-[1,1'-biphenyl]-2-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4pb)**

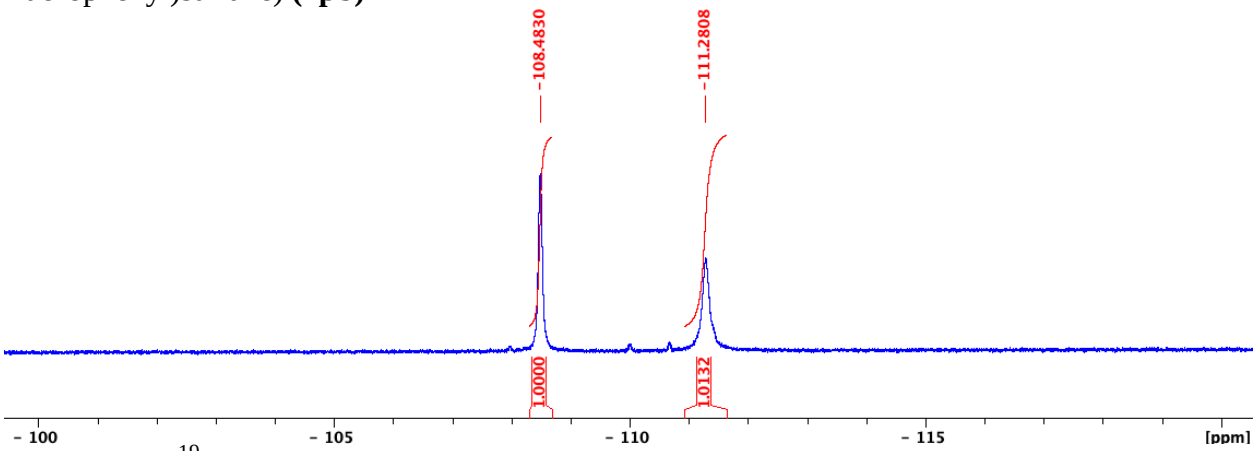


Figure S94. ^{19}F NMR spectrum for E-(1-(2'-bromo-[1,1'-biphenyl]-2-yl)ethene-1,2-diyl)bis((2-fluorophenyl)sulfane) **(4pb)**

4sa

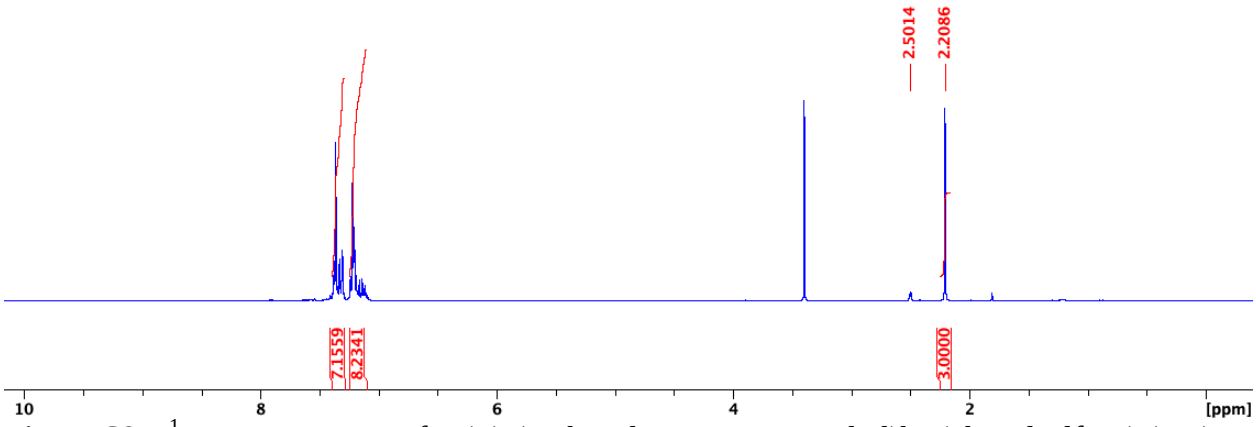


Figure S95. ^{1}H NMR spectrum for (Z)-(1-phenylprop-1-ene-1,2-diyl)bis(phenylsulfane) **(4sa)**

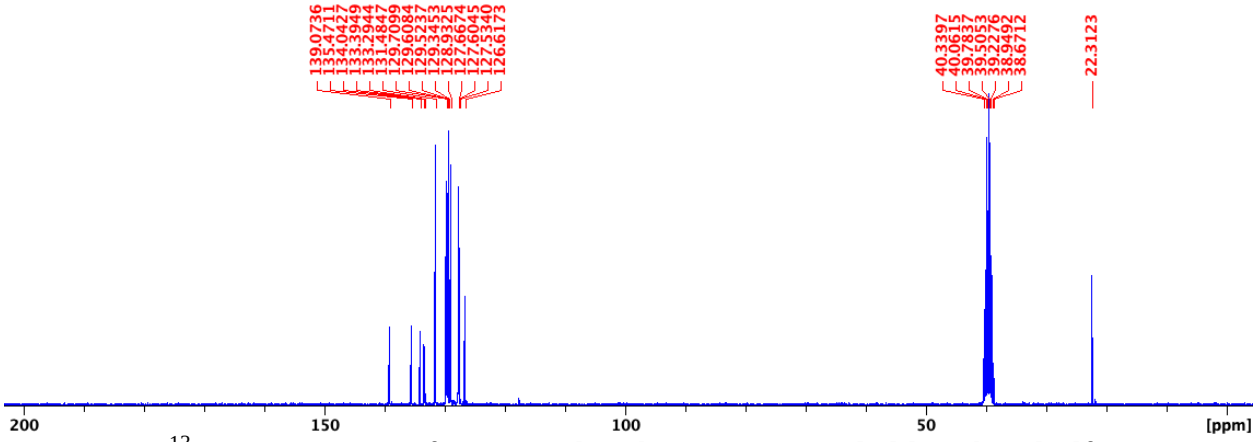


Figure S96. ^{13}C NMR spectrum for (Z)-(1-phenylprop-1-ene-1,2-diyl)bis(phenylsulfane) **(4sa)**

4rj

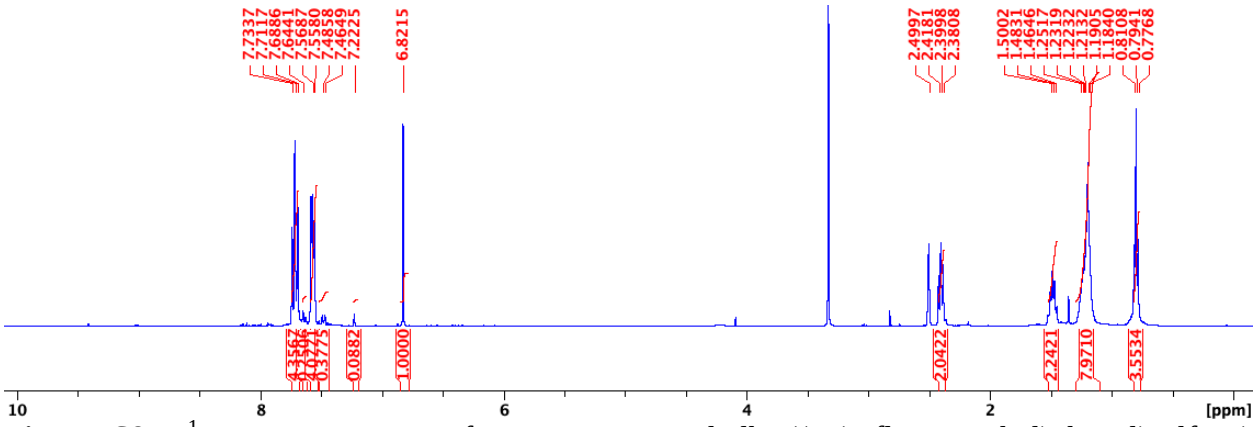


Figure S97. ^{1}H NMR spectrum for oct-1-ene-1,2-diylbis((4-(trifluoromethyl)phenyl)sulfane) **(4rj), Mixture E/Z: 11:1.**

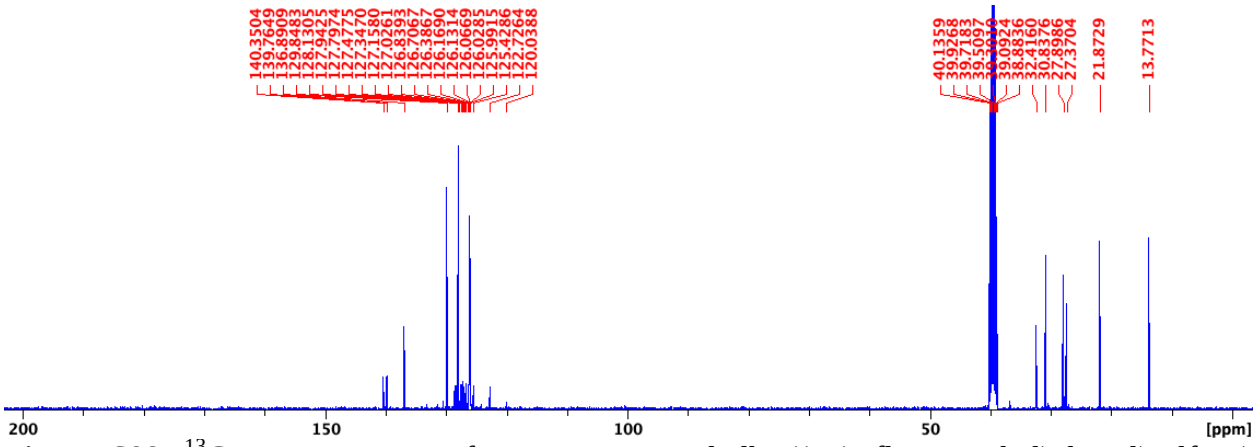


Figure S98. ^{13}C NMR spectrum for oct-1-ene-1,2-diylbis((4-(trifluoromethyl)phenyl)sulfane) **(4rj), Mixture E/Z: 11:1.**

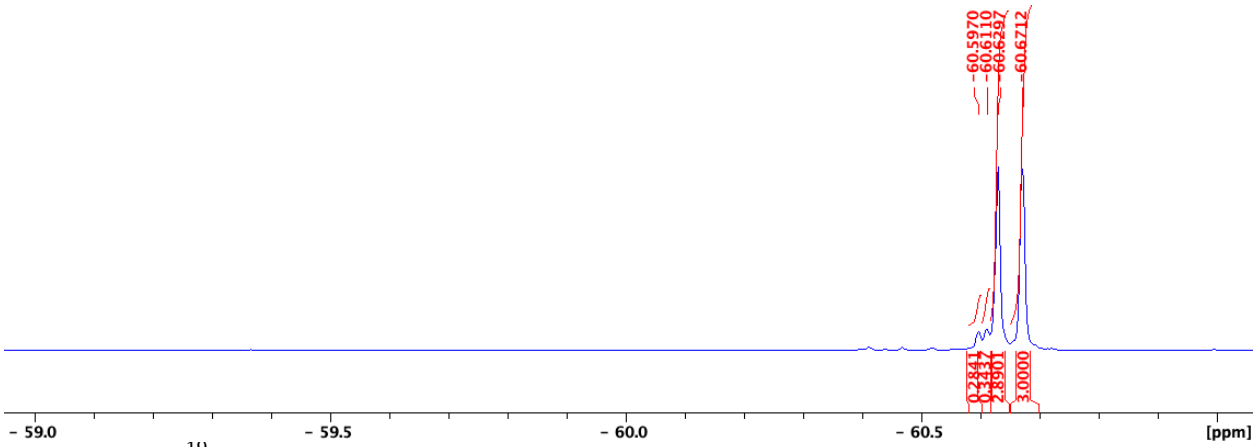


Figure S99. ^{19}F NMR spectrum for oct-1-ene-1,2-diylbis((4-(trifluoromethyl)phenyl)sulfane) **(4rj), Mixture E/Z: 11:1.**

5ab

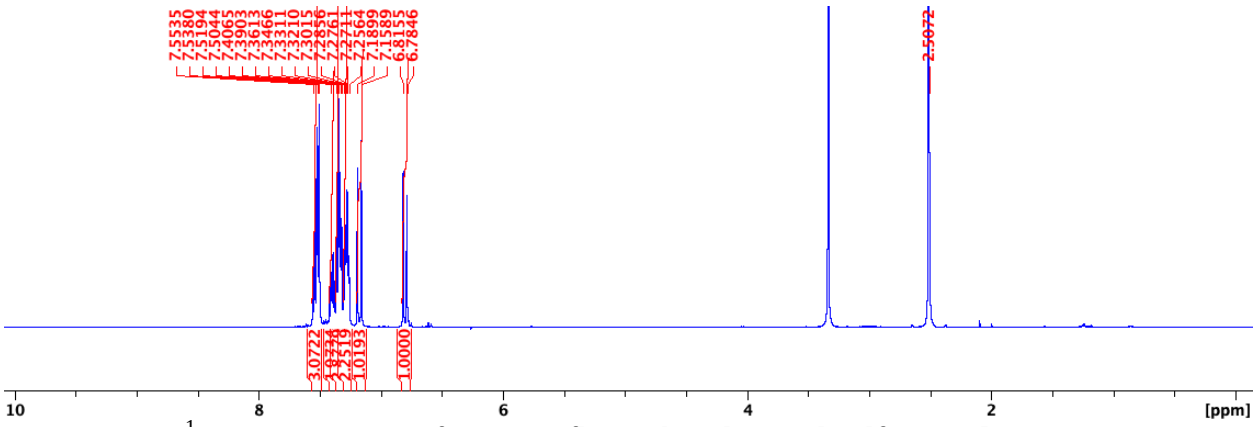


Figure S100. ^{1}H NMR spectrum for (E)-(2-fluorophenyl)(styryl)sulfane **(5ab)**

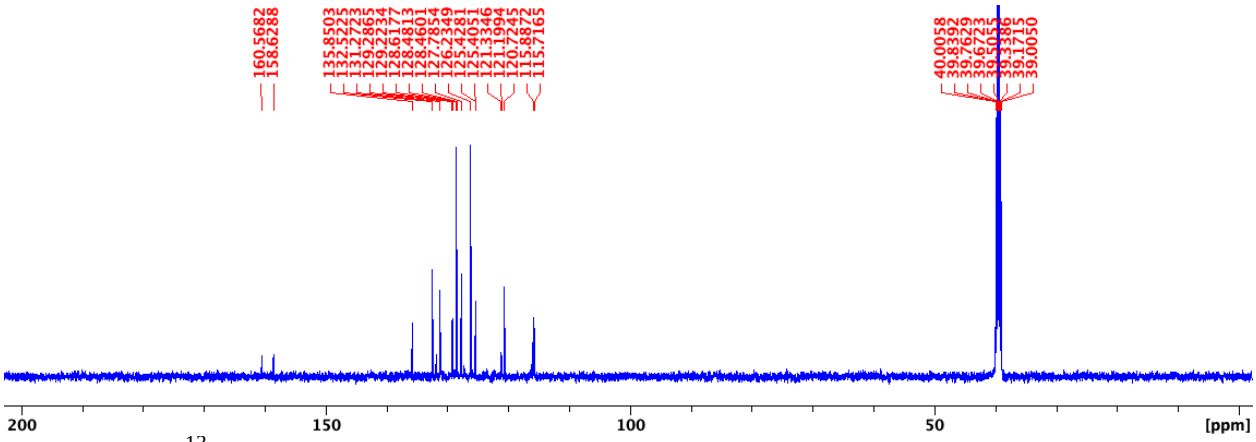


Figure S101. ^{13}C NMR spectrum for (E)-(2-fluorophenyl)(styryl)sulfane **(5ab)**

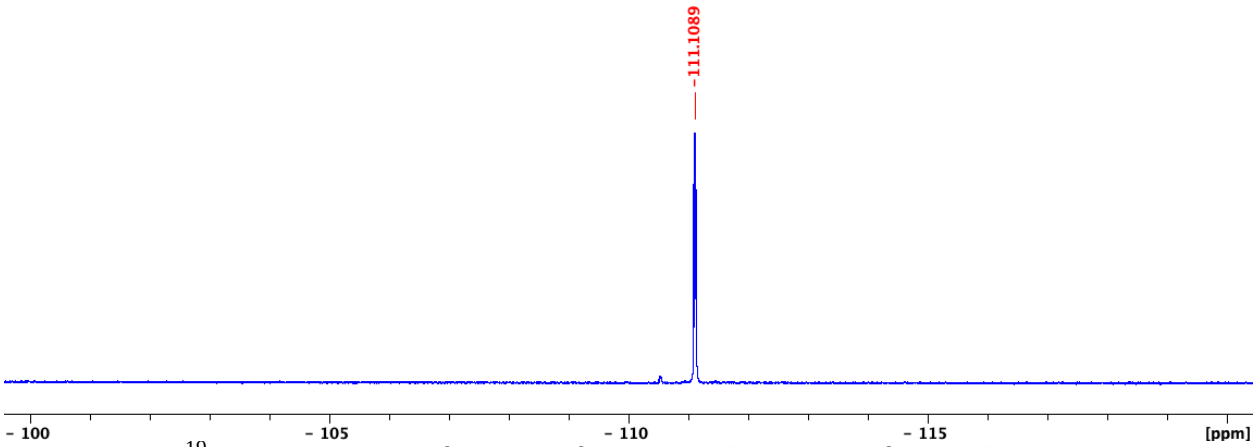


Figure S102. ^{19}F NMR spectrum for (E)-(2-fluorophenyl)(styryl)sulfane **(5ab)**

5bb

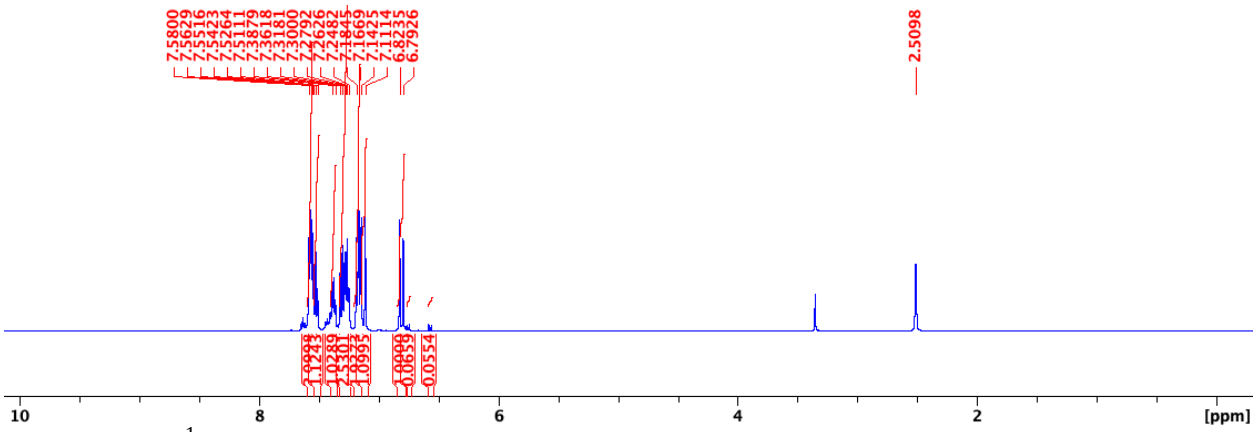


Figure S103. ^{1}H NMR spectrum for (E)-(2-fluorophenyl)(4-fluorostyryl)sulfane **(5bb),** containing (Z)-(2-fluorophenyl)(4-fluorostyryl)sulfane (**6bb**): 6%.

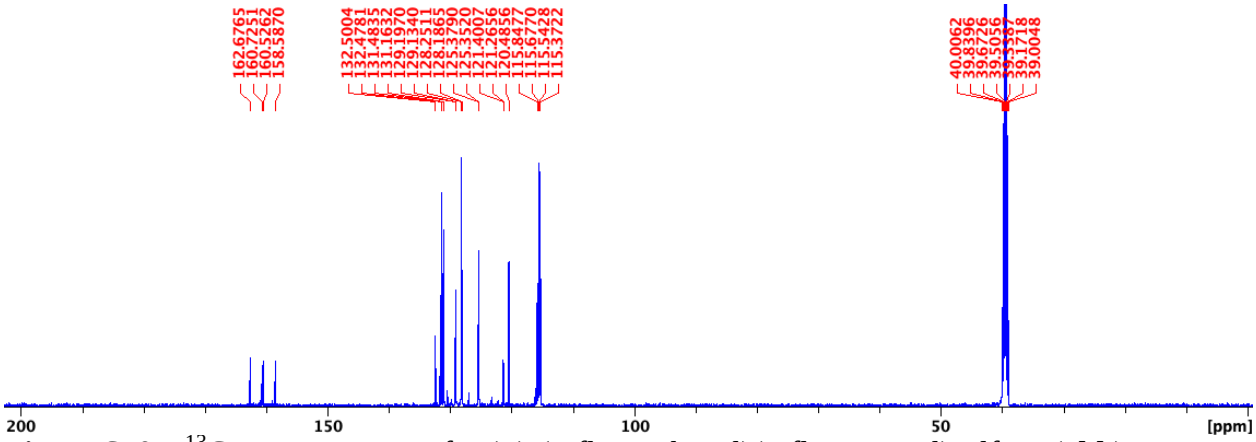


Figure S104. ^{13}C NMR spectrum for (E)-(2-fluorophenyl)(4-fluorostyryl)sulfane **(5bb)**

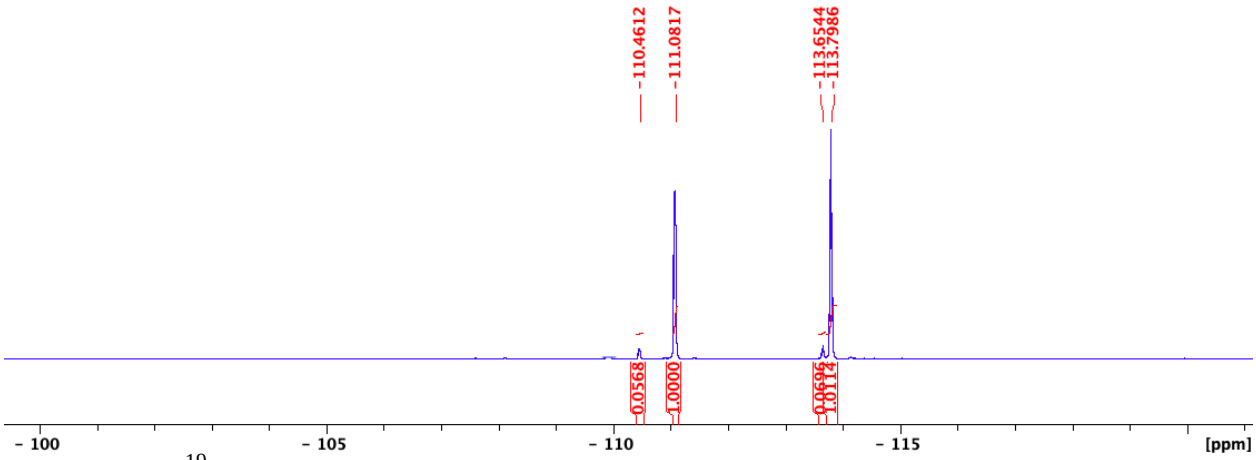


Figure S105. ^{19}F NMR spectrum for (E)-(2-fluorophenyl)(4-fluorostyryl)sulfane **(5bb),** containing (Z)-(2-fluorophenyl)(4-fluorostyryl)sulfane (**6bb**): 6%.

5cb

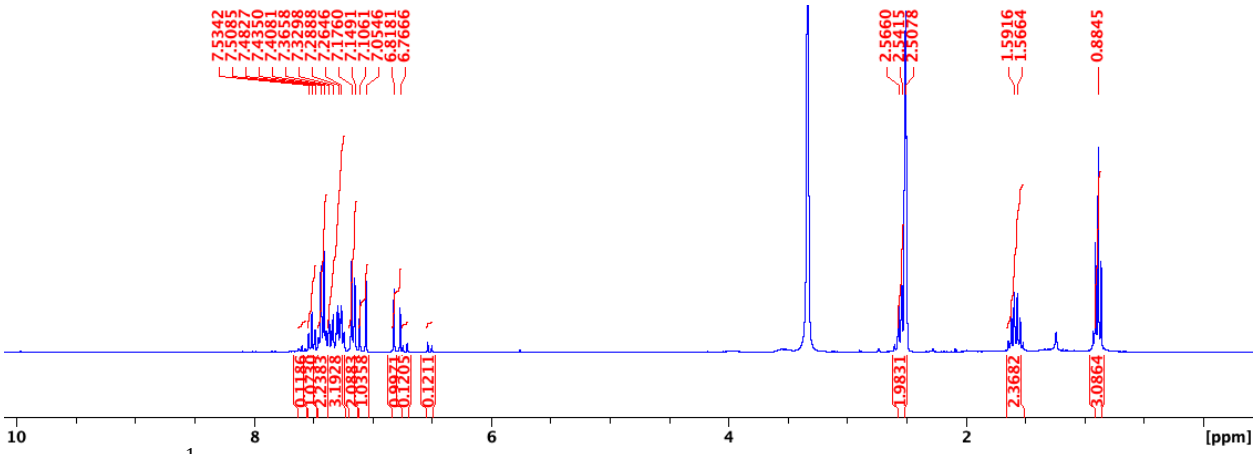


Figure S106. [1]H NMR spectrum for (E)-(2-fluorophenyl)(4-propylstyryl)sulfane **(5cb),** containing (E)-(2-fluorophenyl)(4-propylstyryl)sulfane (**6cb**): 12%.

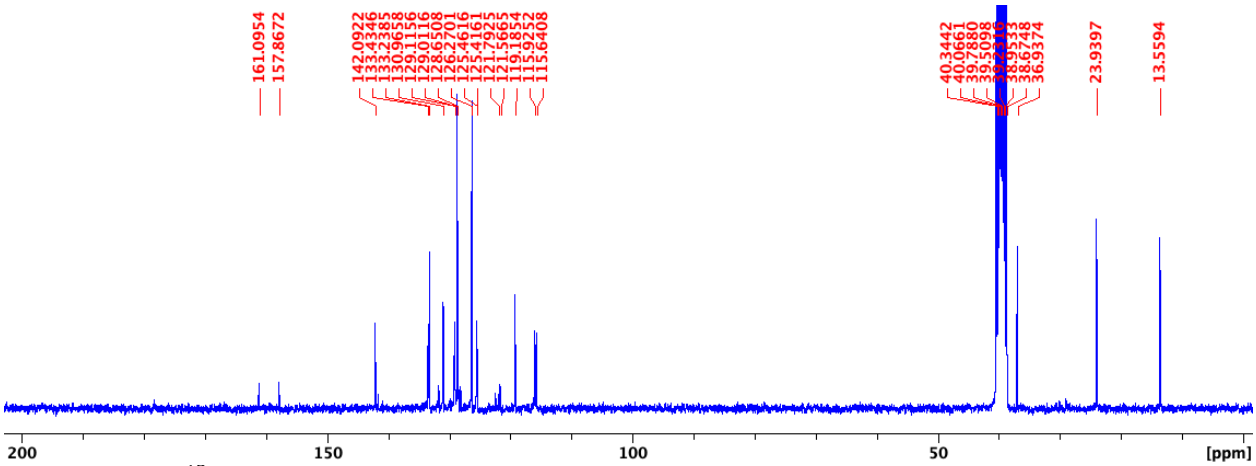


Figure S107. [13]C NMR spectrum for (E)-(2-fluorophenyl)(4-propylstyryl)sulfane **(5cb)**

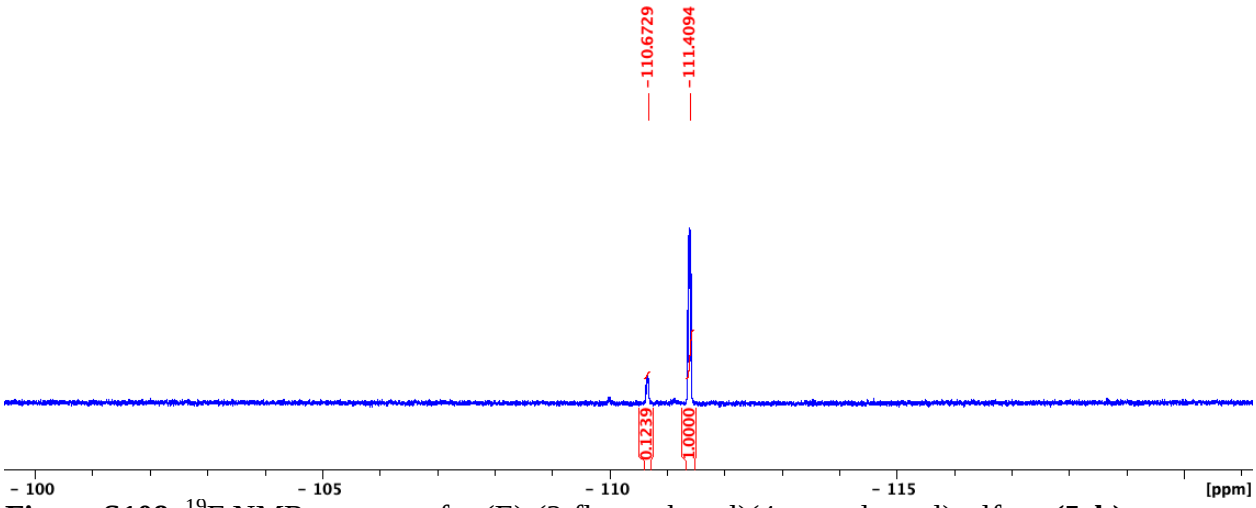


Figure S108. [19]F NMR spectrum for (E)-(2-fluorophenyl)(4-propylstyryl)sulfane **(5cb),** containing (E)-(2-fluorophenyl)(4-propylstyryl)sulfane (**6cb**): 12%.

5db

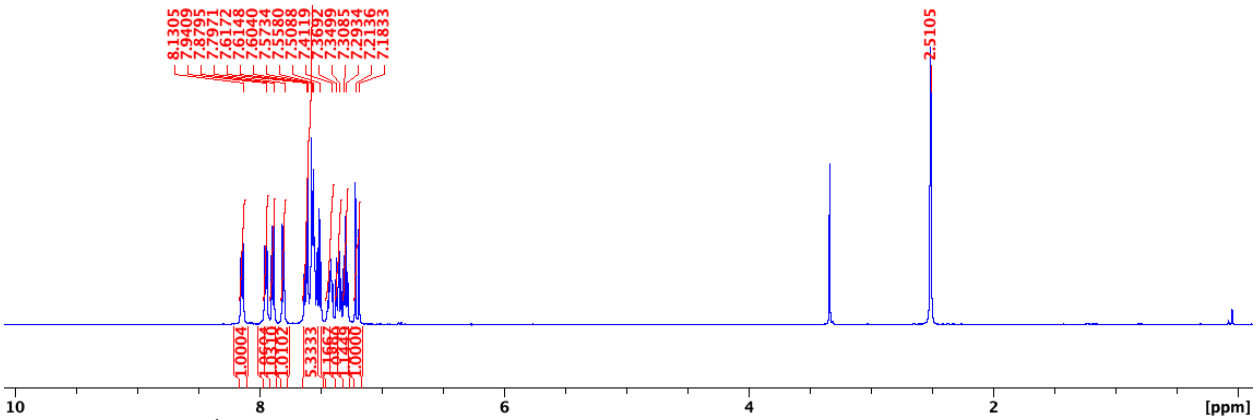


Figure S109. ^{1}H NMR spectrum for (E)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane **(5db)**

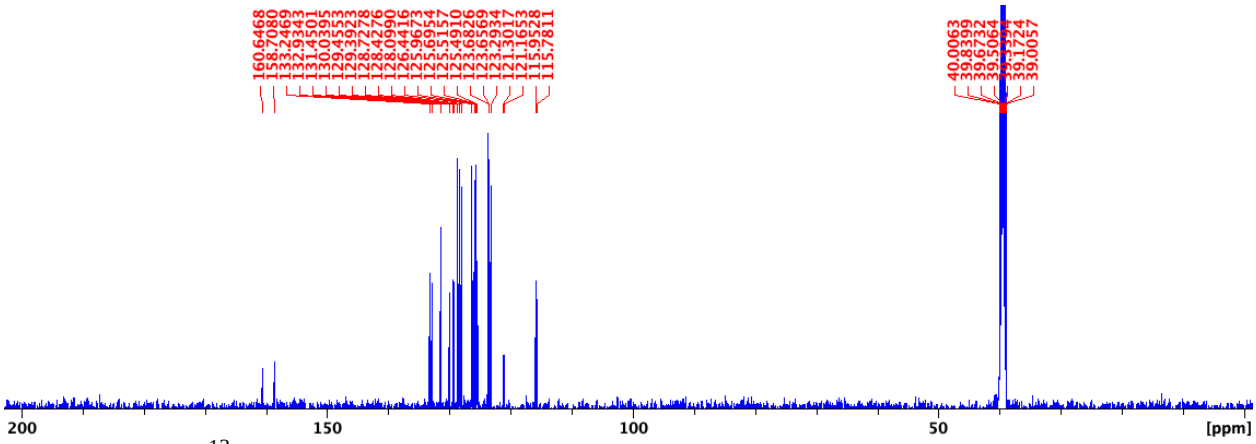


Figure S110. ^{13}C NMR spectrum for (E)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane **(5db)**

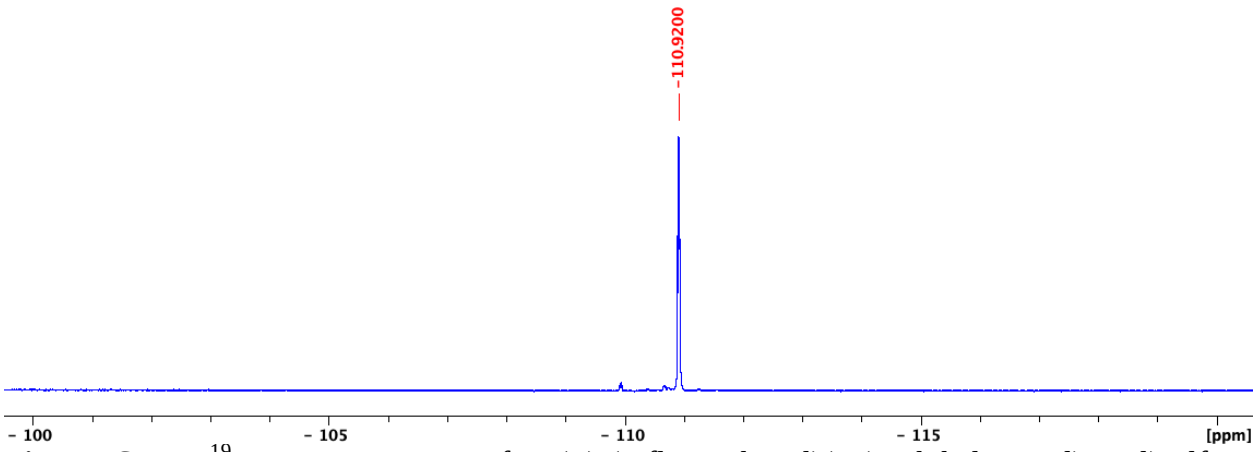


Figure S111. ^{19}F NMR spectrum for (E)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane **(5db)**

5eb

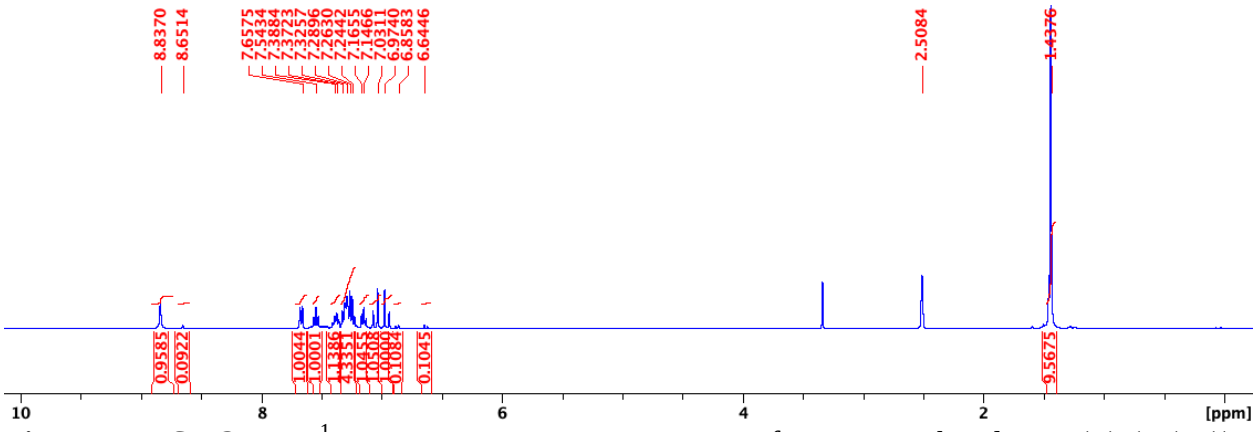


Figure S112. ^{1}H NMR spectrum for *tert*-butyl (E)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(5eb),** containing *tert*-butyl (E)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(6eb)**: 10%.

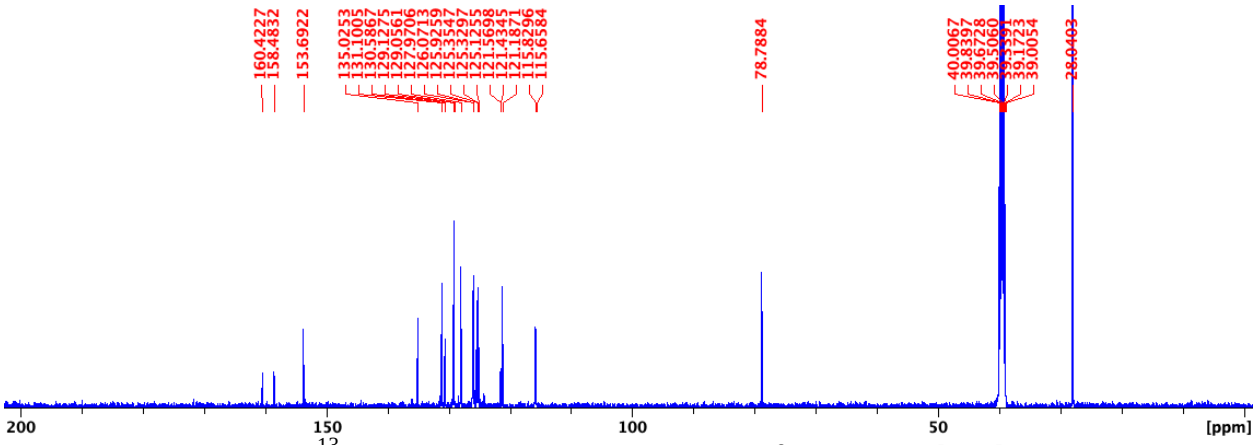


Figure S113. ^{13}C NMR spectrum for *tert*-butyl (E)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(5eb)**

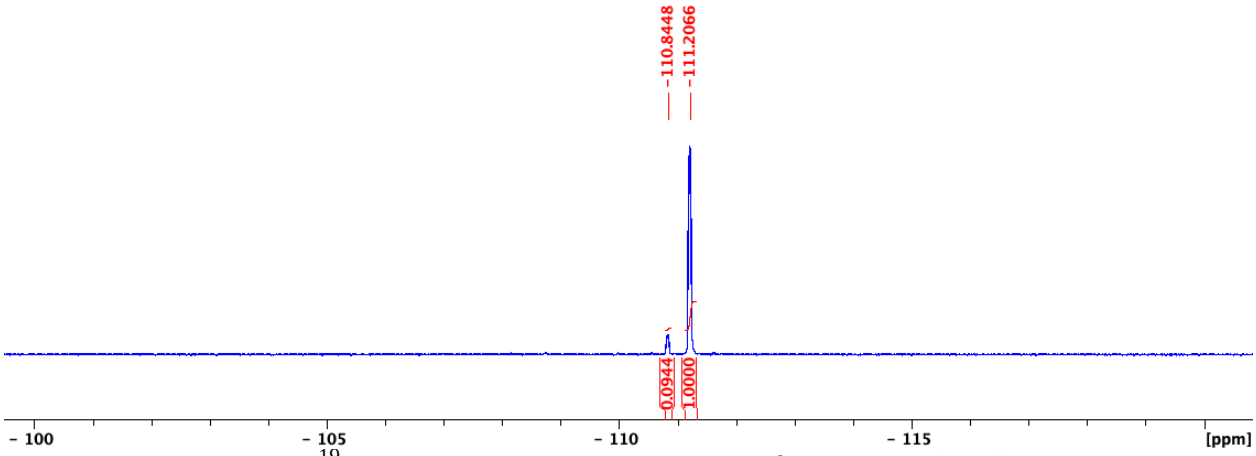


Figure S114. ^{19}F NMR spectrum for *tert*-butyl (E)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(5eb),** containing *tert*-butyl (E)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(6eb)**: 10%.

6ab

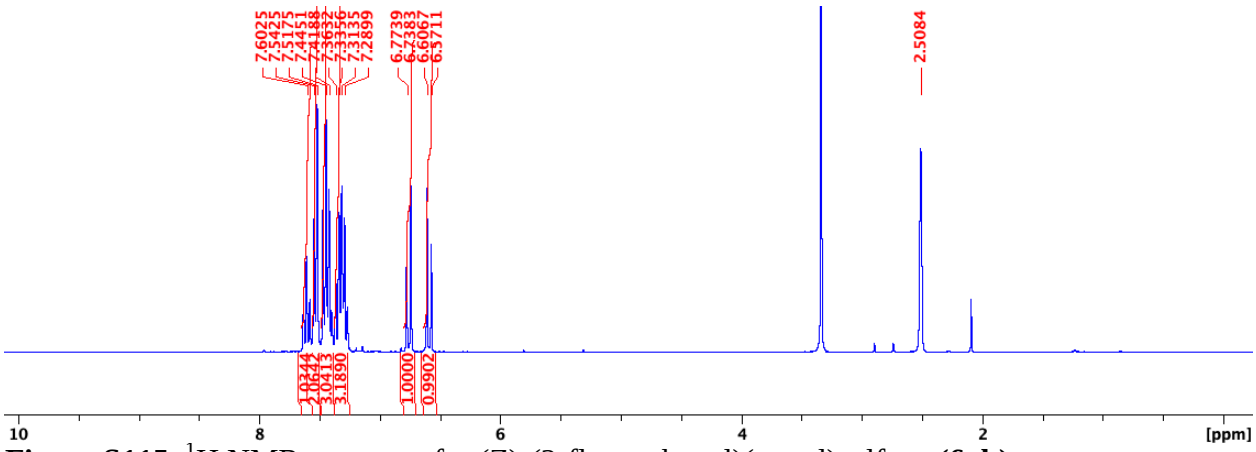


Figure S115. ^{1}H NMR spectrum for (Z)-(2-fluorophenyl)(styryl)sulfane **(6ab)**

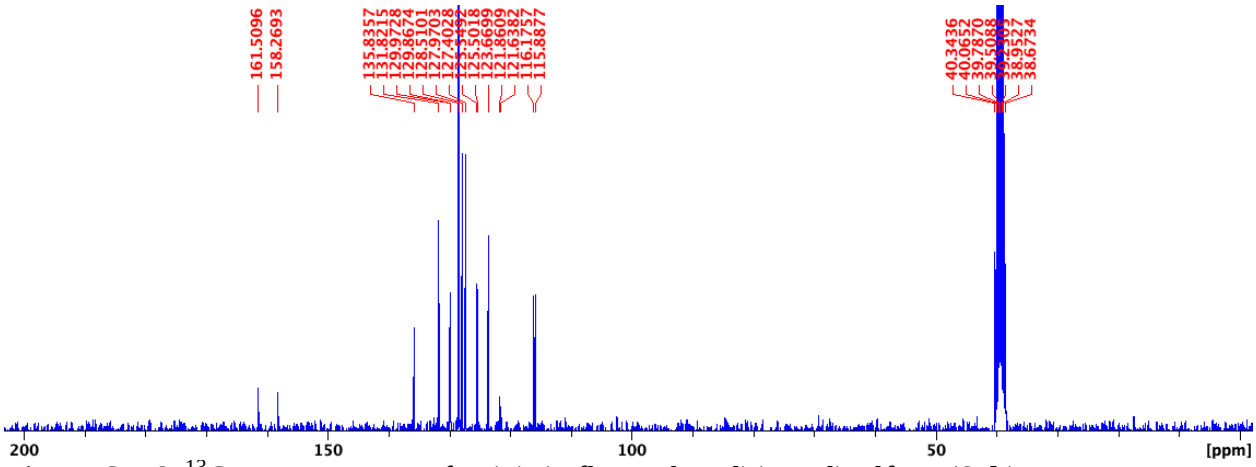


Figure S116. ^{13}C NMR spectrum for (Z)-(2-fluorophenyl)(styryl)sulfane **(6ab)**

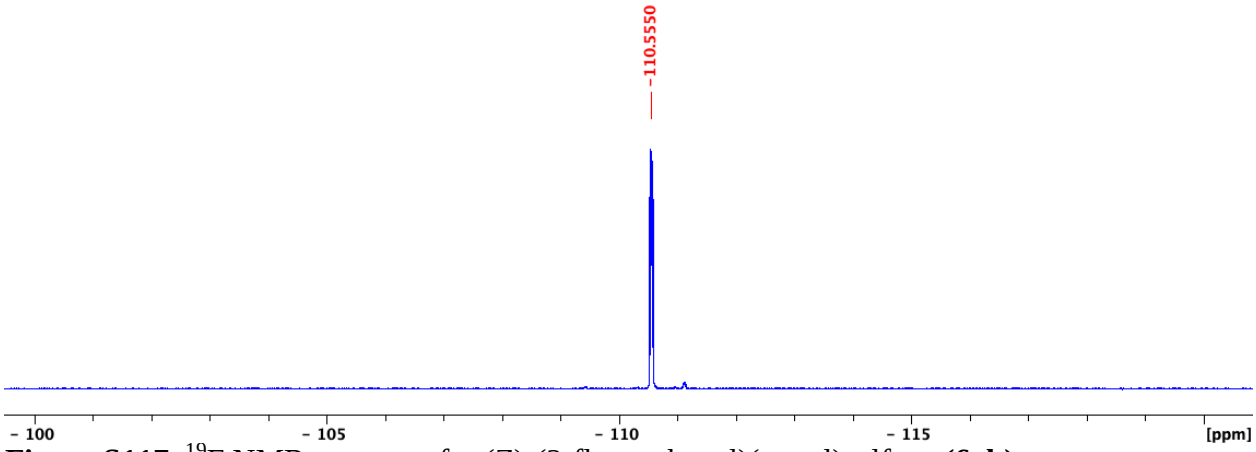


Figure S117. ^{19}F NMR spectrum for (Z)-(2-fluorophenyl)(styryl)sulfane **(6ab)**

6bb

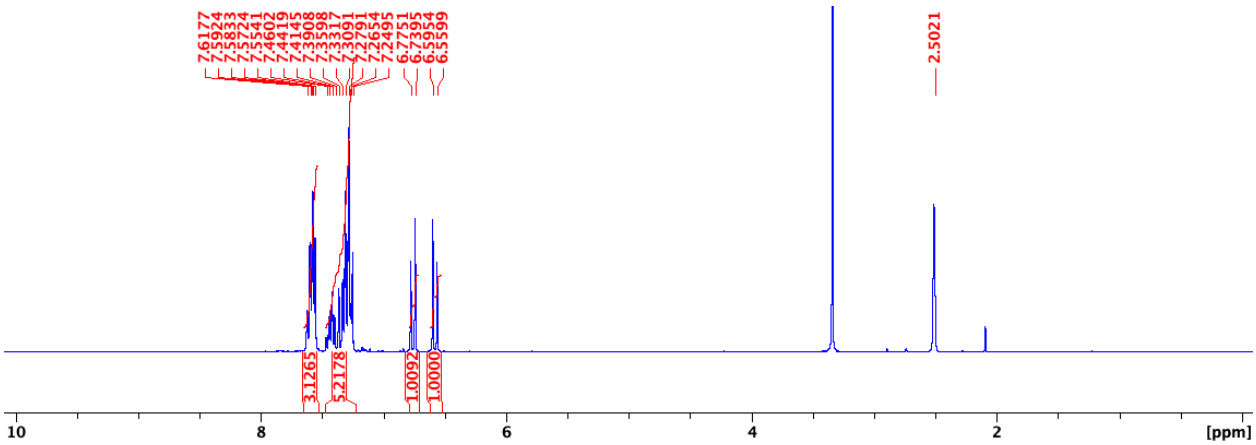


Figure S118. ^{1}H NMR spectrum for (Z)-(2-fluorophenyl)(4-fluorostyryl)sulfane **(6bb)**

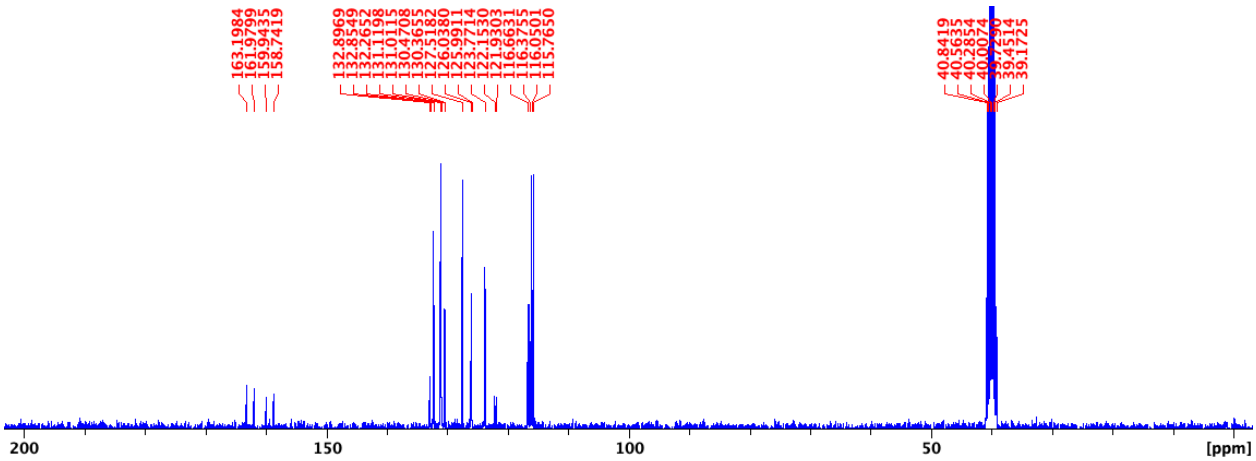


Figure S119. ^{13}C NMR spectrum for (Z)-(2-fluorophenyl)(4-fluorostyryl)sulfane **(6bb)**

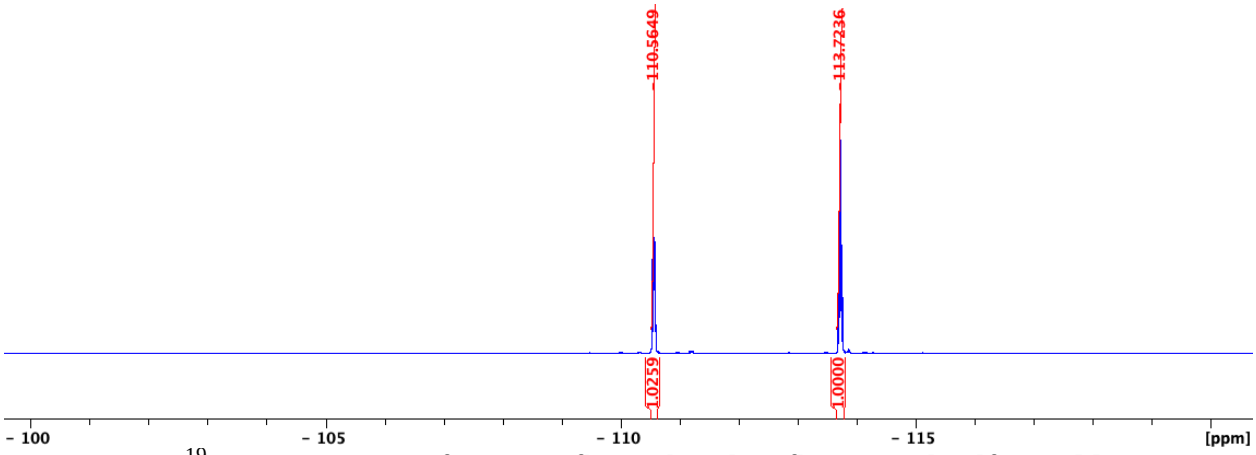


Figure S120. ^{19}F NMR spectrum for (Z)-(2-fluorophenyl)(4-fluorostyryl)sulfane **(6bb)**

6cb

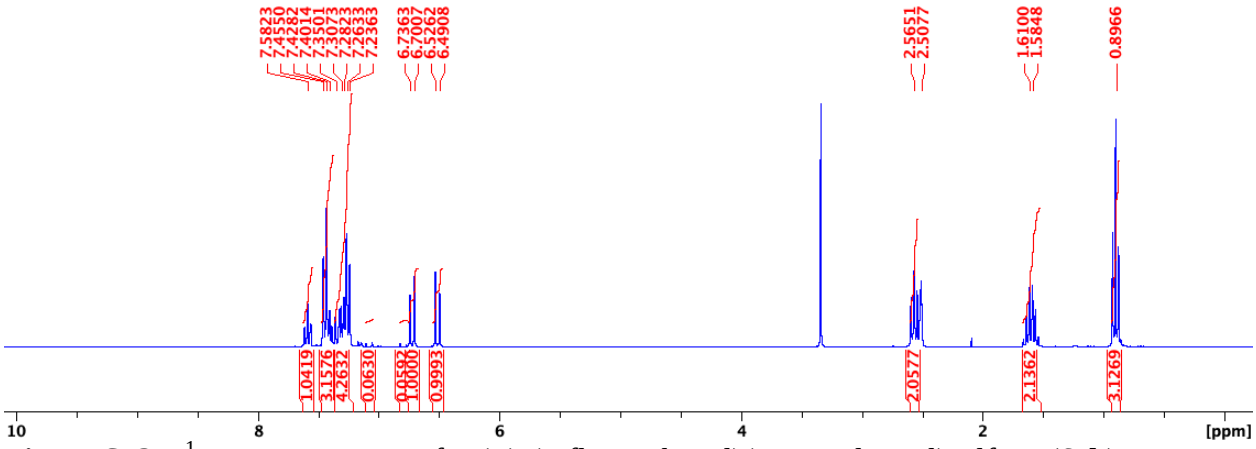


Figure S121. [1]H NMR spectrum for (Z)-(2-fluorophenyl)(4-propylstyryl)sulfane **(6cb),** containing (Z)-(2-fluorophenyl)(4-propylstyryl)sulfane **(5cb)**: 6%.

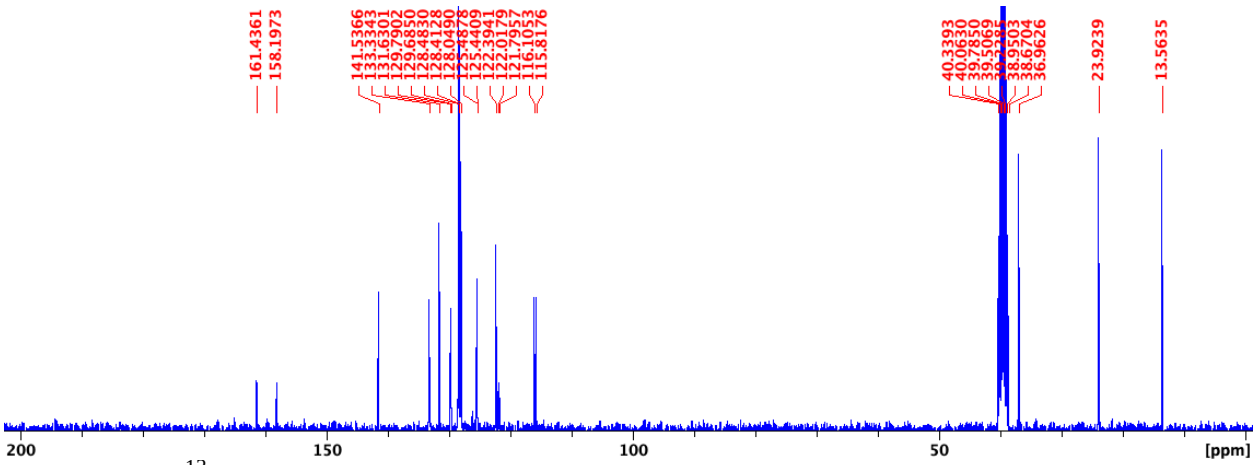


Figure S122. [13]C NMR spectrum for (Z)-(2-fluorophenyl)(4-propylstyryl)sulfane **(6cb)**

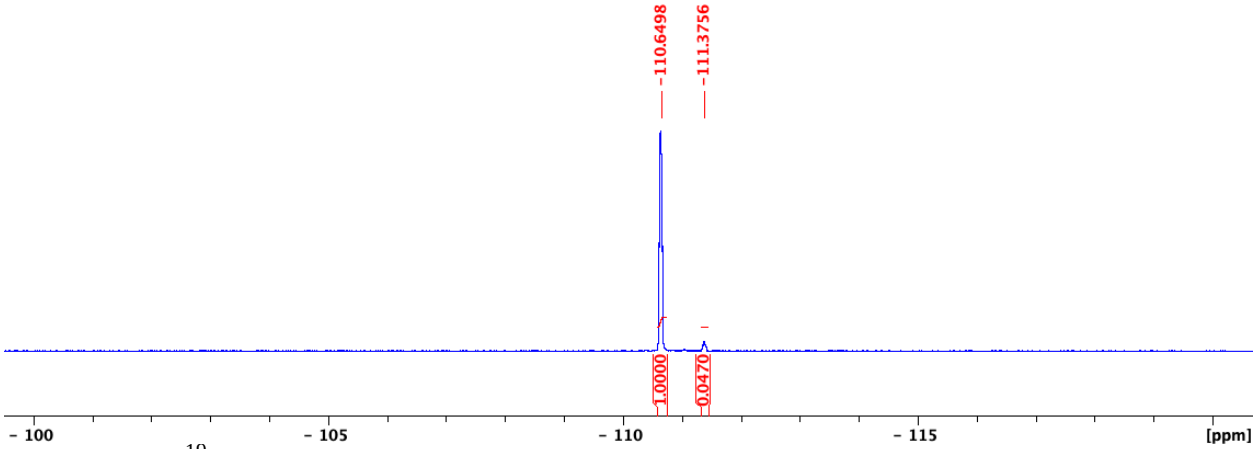


Figure S123. [19]F NMR spectrum for (Z)-(2-fluorophenyl)(4-propylstyryl)sulfane **(6cb)** Contaminated with (Z)-(2-fluorophenyl)(4-propylstyryl)sulfane **(5cb)**: 6%.

6db

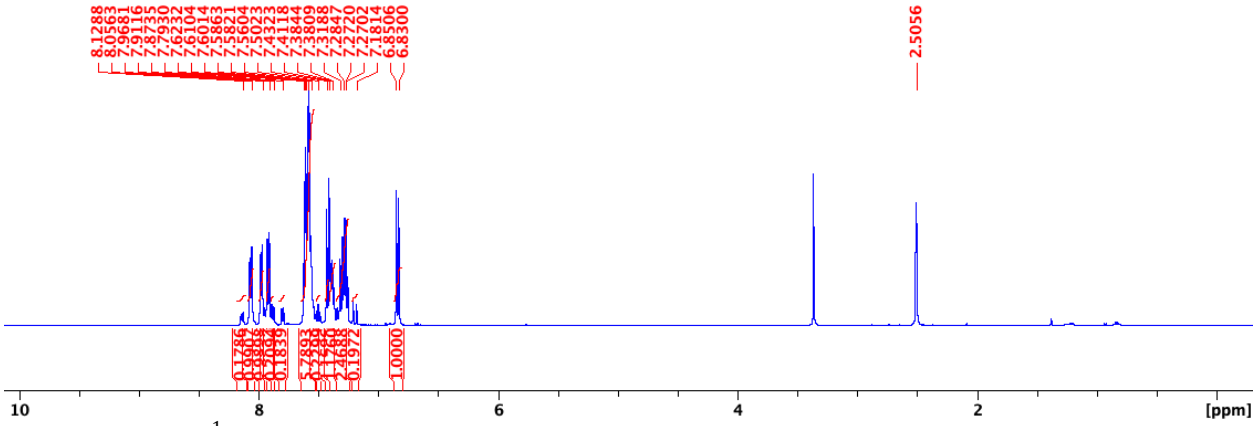


Figure S124. ^{1}H NMR spectrum for (Z)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane **(6db),** containing (Z)-(2-fluorophenyl)(4-propylstyryl)sulfane **(5db)**: 17%.

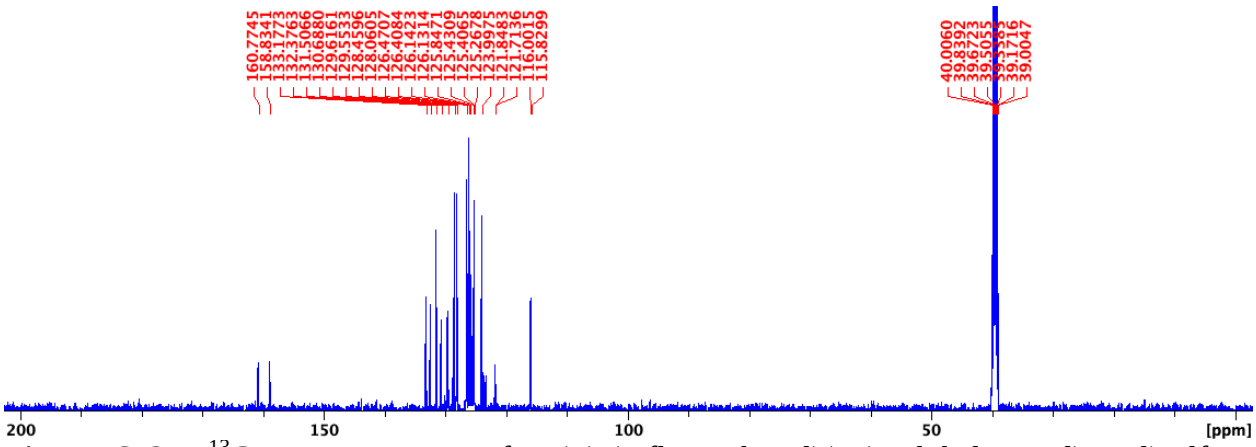


Figure S125. ^{13}C NMR spectrum for (Z)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane **(6db)**

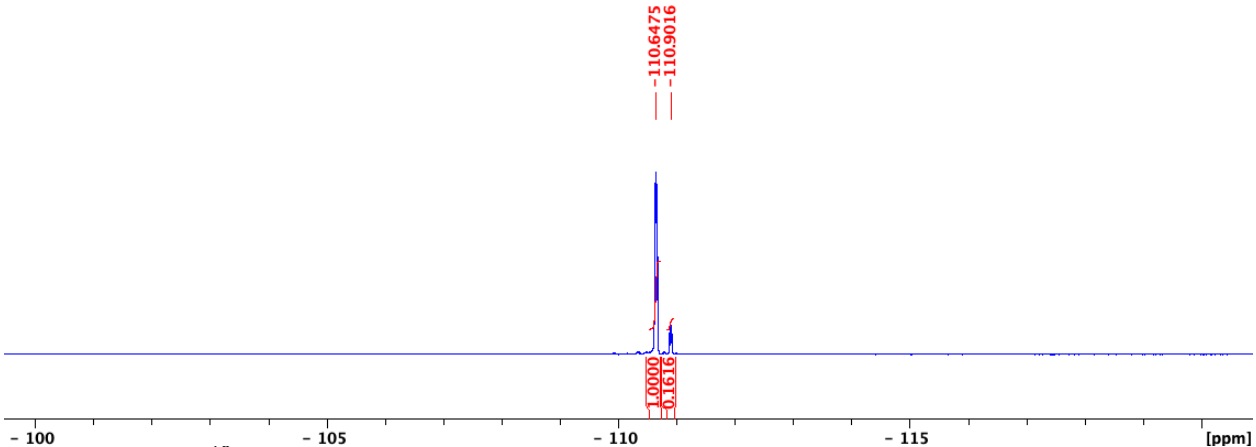


Figure S126. ^{19}F NMR spectrum for (Z)-(2-fluorophenyl)(2-(naphthalen-1-yl)vinyl)sulfane **(6db),** containing (Z)-(2-fluorophenyl)(4-propylstyryl)sulfane **(5db)**: 17%.

6eb

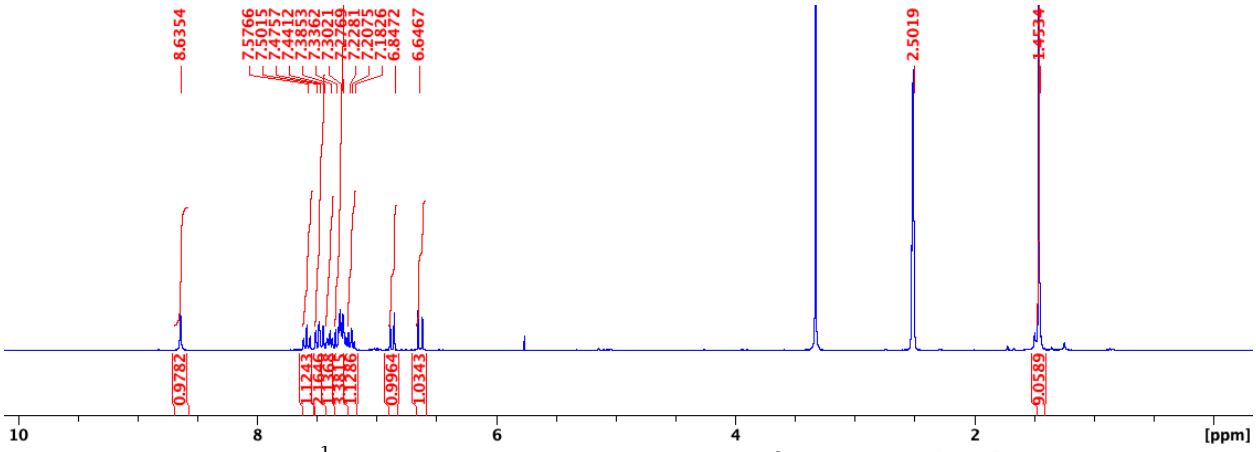


Figure S127. ^{1}H NMR spectrum for *tert*-butyl (Z)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(6eb)**

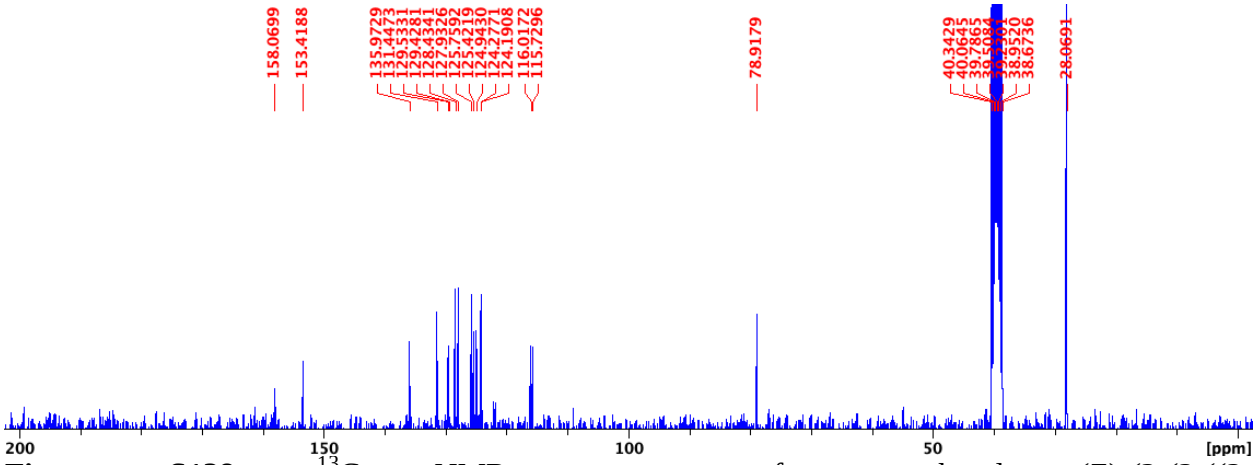


Figure S128. ^{13}C NMR spectrum for *tert*-butyl (Z)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(6eb)**

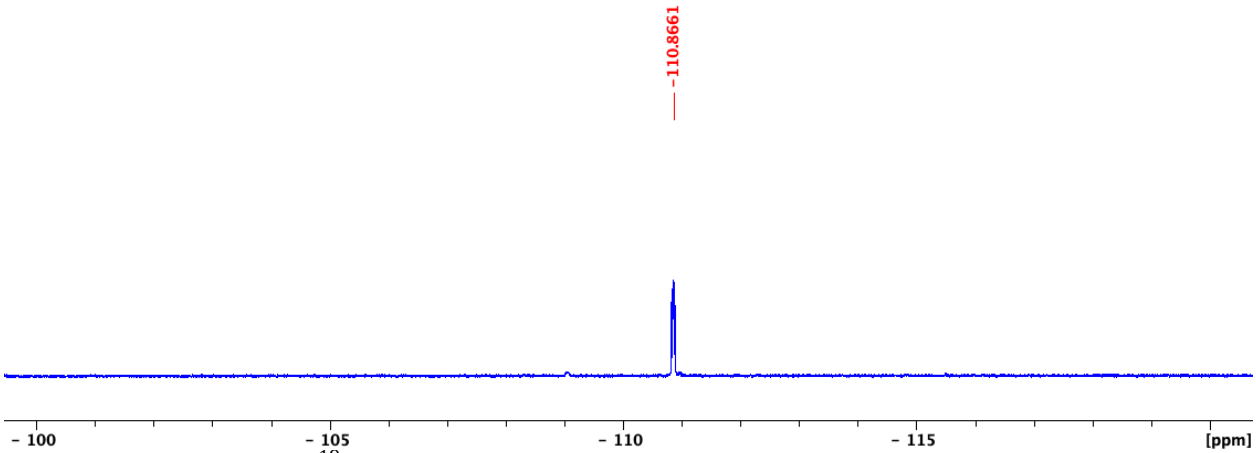


Figure S129. ^{19}F NMR spectrum for *tert*-butyl (Z)-(2-(2-((2-fluorophenyl)thio)vinyl)phenyl)carbamate **(6eb)**

5sa/6sa

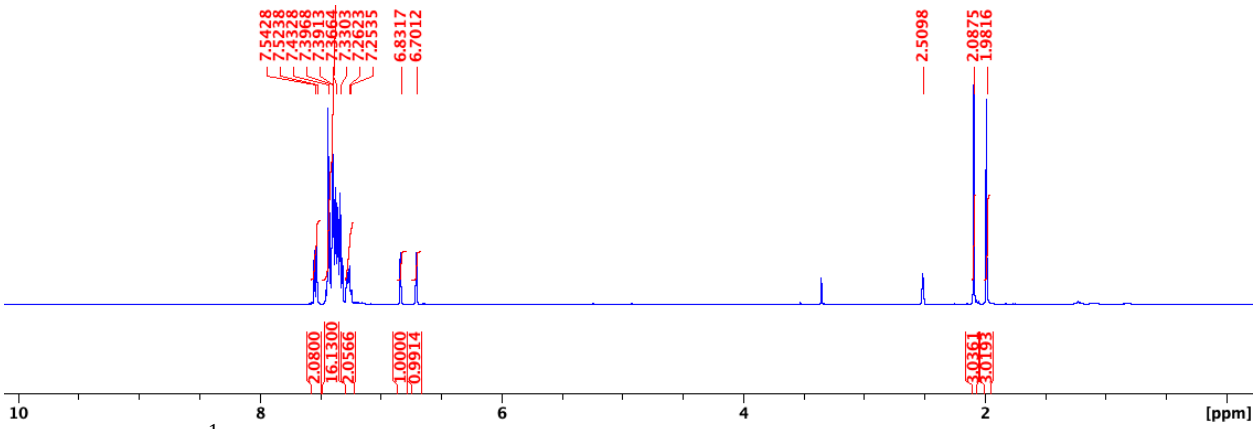


Figure S130. ^{1}H NMR spectrum for phenyl(1-phenylprop-1-en-2-yl)sulfane (**5ya** + **6ya**), **Mixture E(5sa)/Z(6sa) = 1:1**.

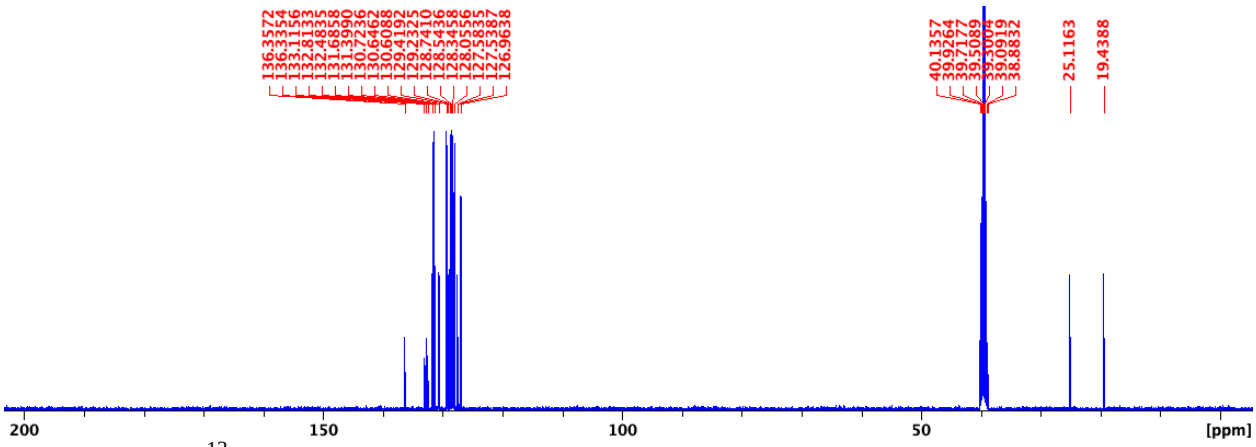


Figure S131. ^{13}C NMR spectrum for phenyl(1-phenylprop-1-en-2-yl)sulfane (**5ya** + **6ya**), **Mixture E(5sa)/Z(6sa) = 1:1**

7hb

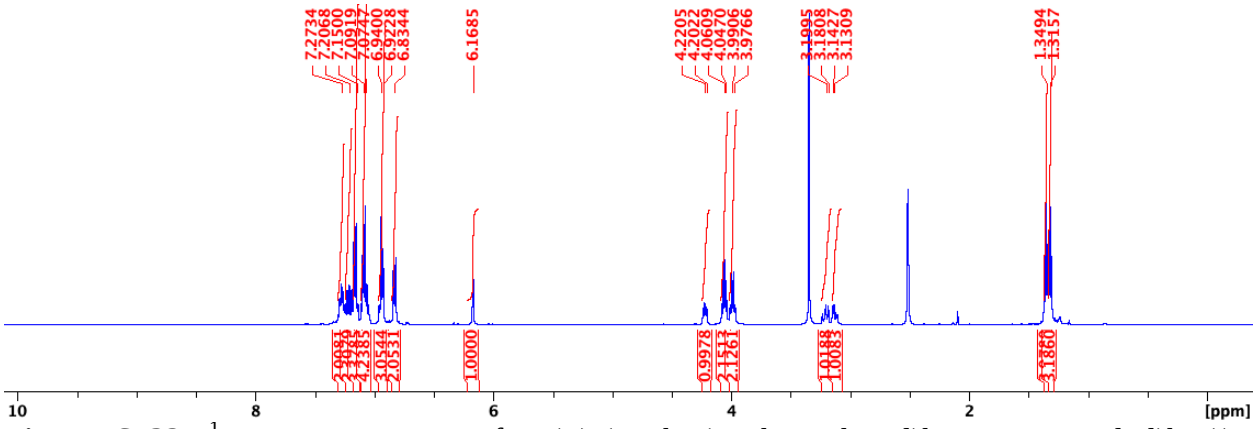


Figure S132. ^{1}H NMR spectrum for (E)-(2,4-bis(4-ethoxyphenyl)but-1-ene-1,4-diyl)bis((2-fluorophenyl)sulfane) **(7hb)**

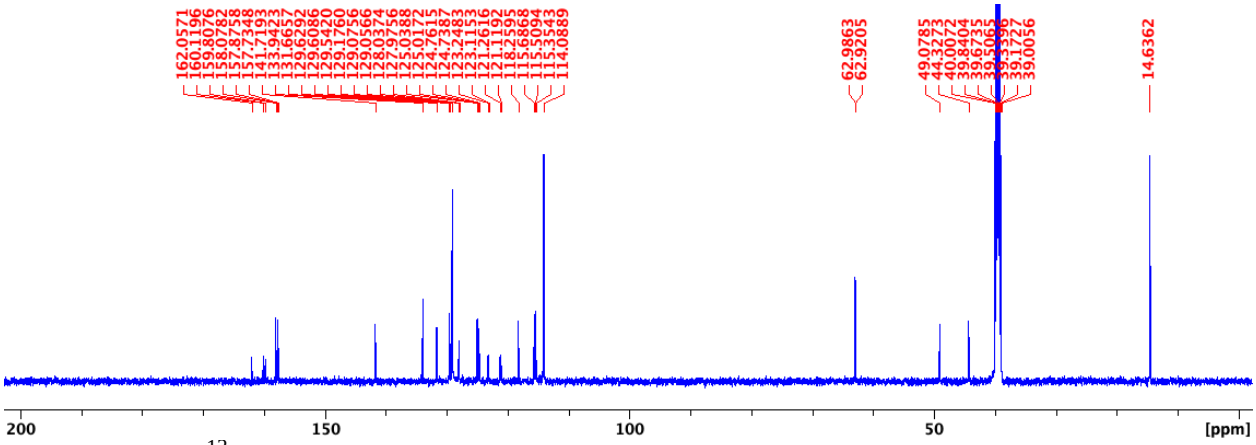


Figure S133. ^{13}C NMR spectrum for (E)-(2,4-bis(4-ethoxyphenyl)but-1-ene-1,4-diyl)bis((2-fluorophenyl)sulfane) **(7hb)**

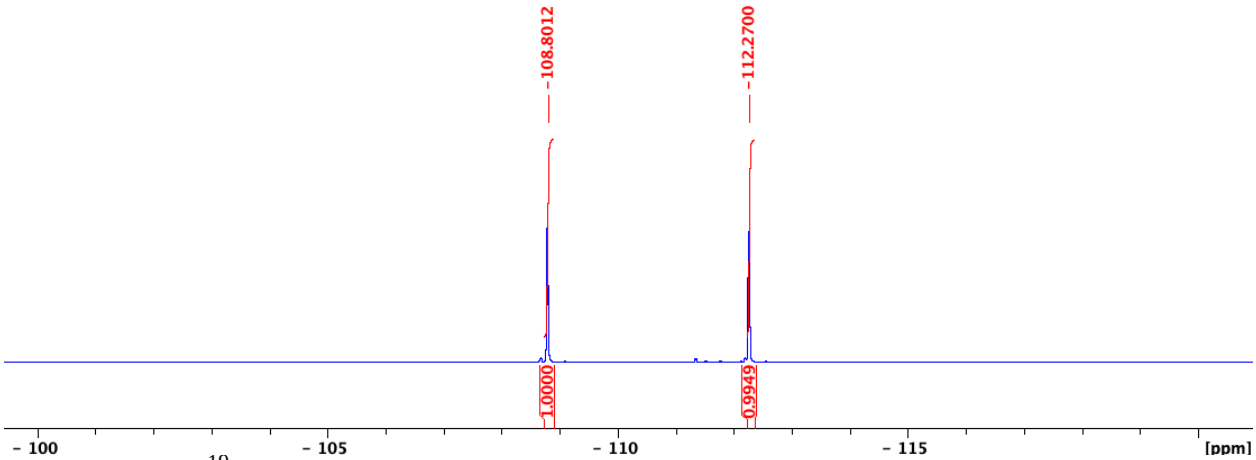


Figure S134. ^{19}F NMR spectrum for (E)-(2,4-bis(4-ethoxyphenyl)but-1-ene-1,4-diyl)bis((2-fluorophenyl)sulfane) **(7hb)**

8na

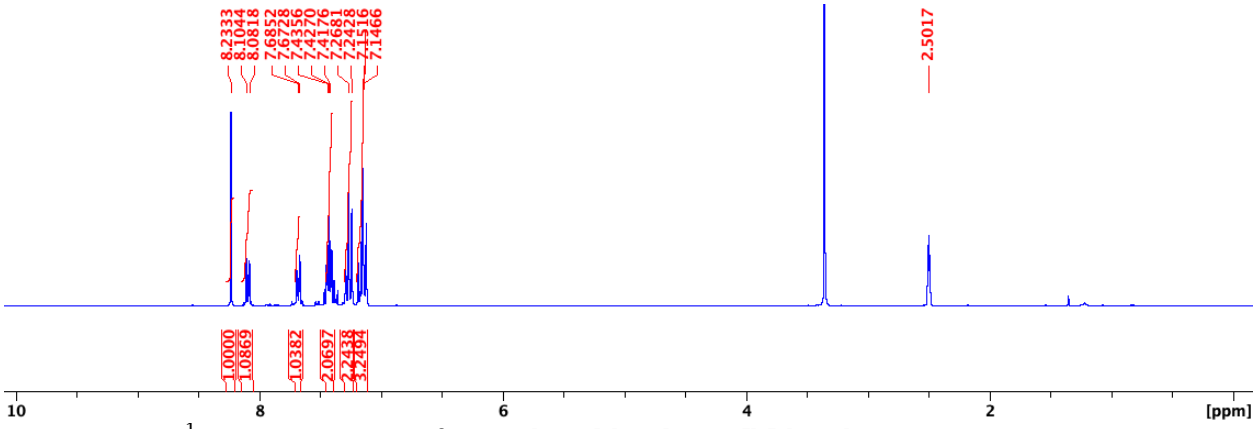


Figure S135. ^{1}H NMR spectrum for 3-(phenylthio)benzo[b]thiophene **(8na)**

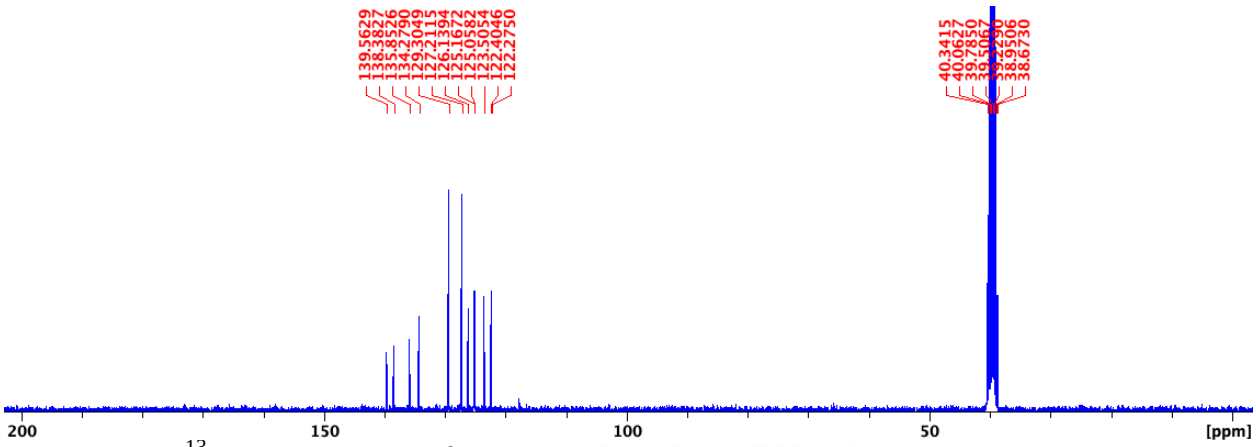


Figure S136. ^{13}C NMR spectrum for 3-(phenylthio)benzo[b]thiophene **(8na)**

ESI-HRMS spectra of products (3-7)

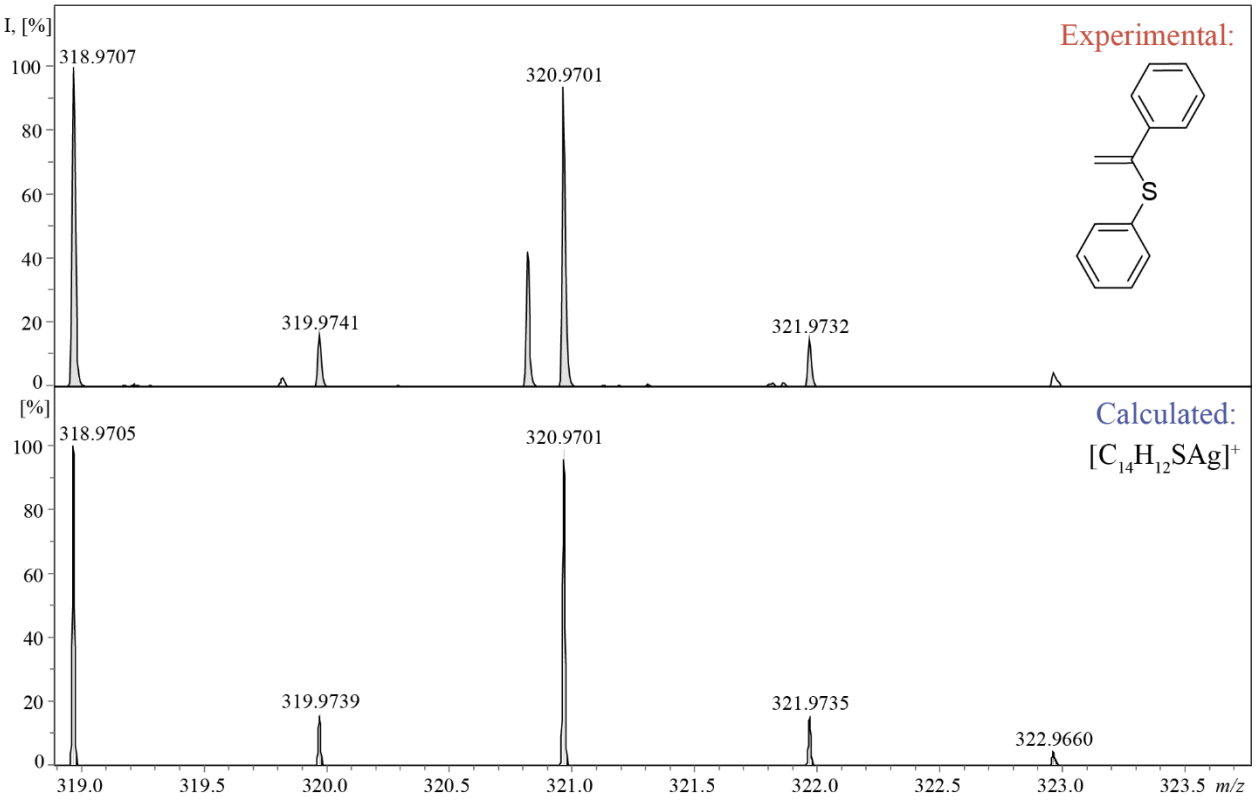


Figure S137. Experimentally detected and theoretical ESI-(+)MS spectrum of **3aa**; main experimental peak $[M+Ag]^+$ = 318.9707 Da, calculated for $C_{14}H_{12}SAg$ = 318.9705 Da, Δ = 0.6 ppm.

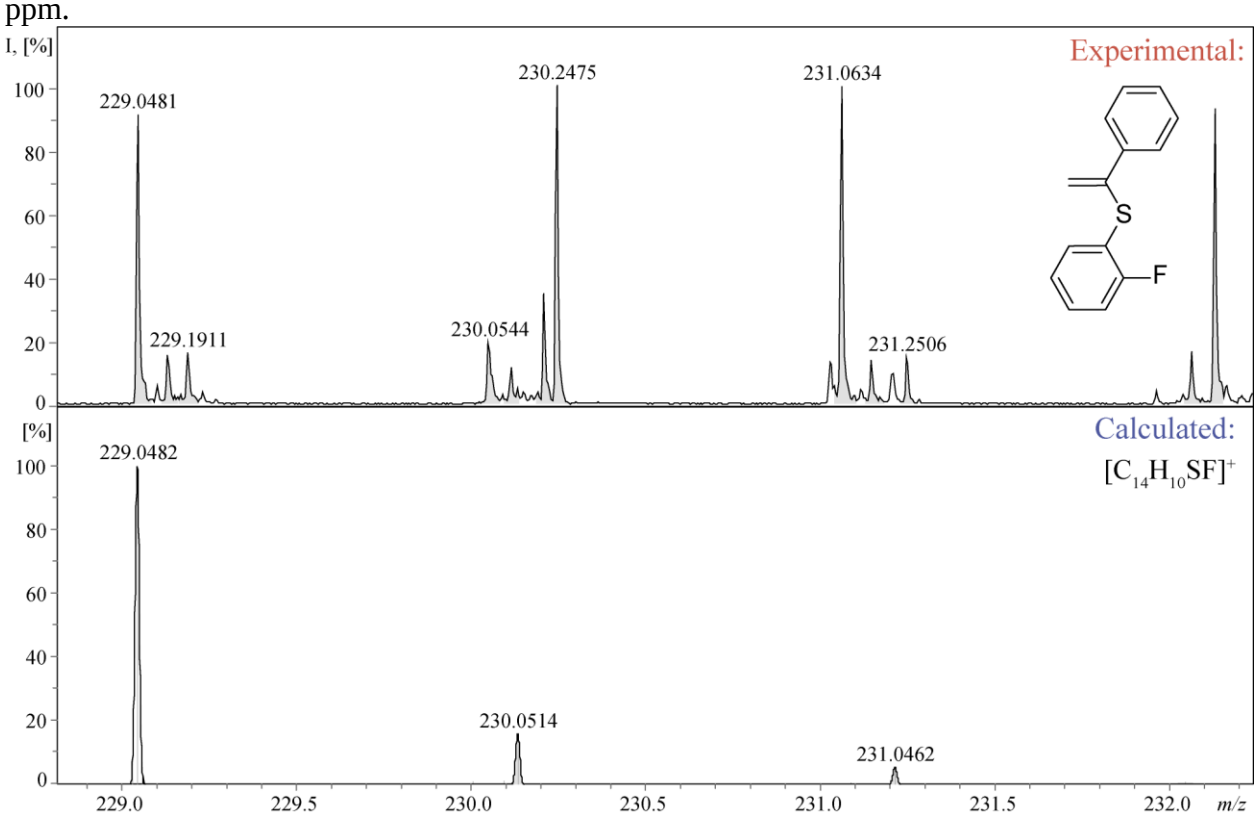


Figure S138. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ab**; main experimental peak $[M-H]^+$ = 229.0481 Da, calculated for $C_{14}H_{10}SF$ = 229.0482 Da, Δ = 0.4 ppm. Low signal-to-noise ratio was observed for these ion signals, which suggests only plausible

identification of the substance; however, in spite of low intensity isotopic pattern and accurate mass match reliably.

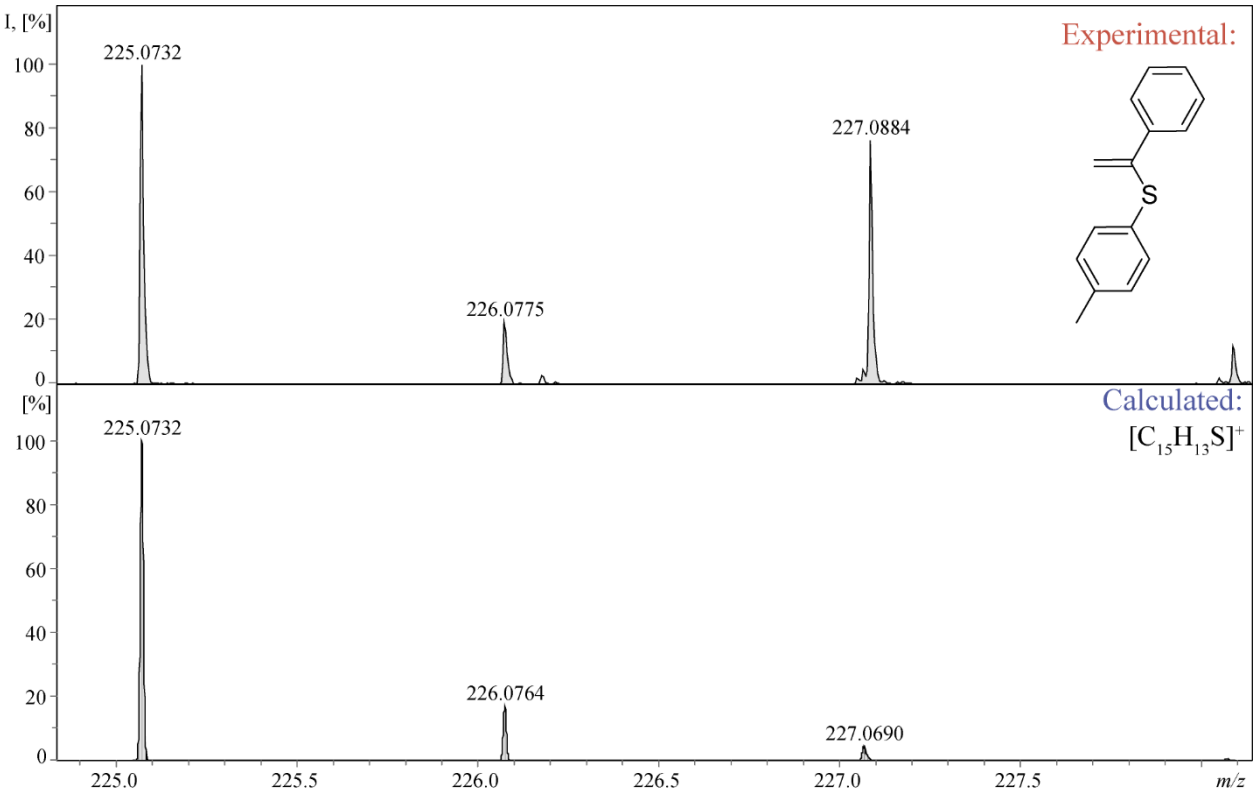


Figure S139. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ac**; main experimental peak $[M\text{-}H]^+$ = 225.0732 Da, calculated for $C_{15}H_{13}S$ = 225.0732 Da, Δ = 0.0 ppm.

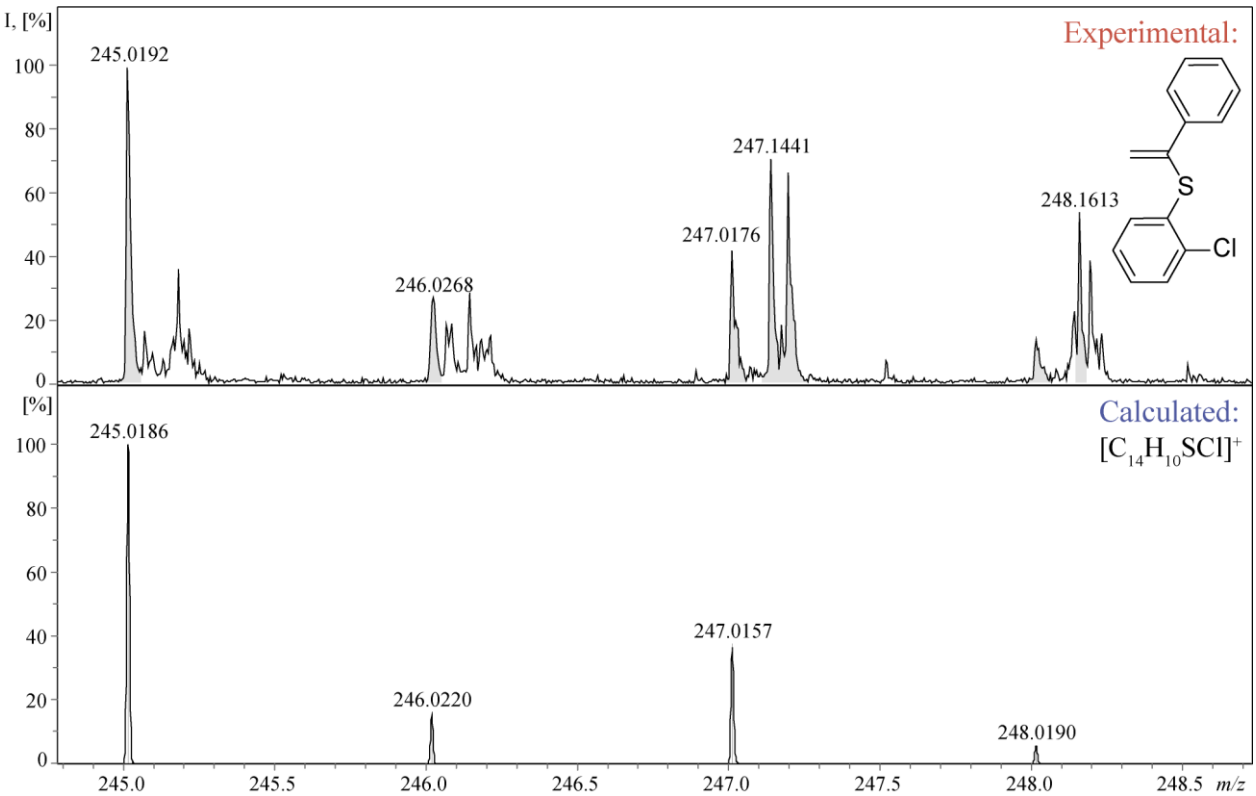


Figure S140. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ad**; main experimental peak $[M\text{-}H]^+$= 245.0192 Da, calculated for $C_{14}H_{10}SCl$ = 245.0186 Da, Δ = 2.5 ppm. Low signal-to-noise ratio was observed for these ion signals, which suggests only plausible

identification of the substance; however, in spite of low intensity isotopic pattern and accurate mass match reliably.

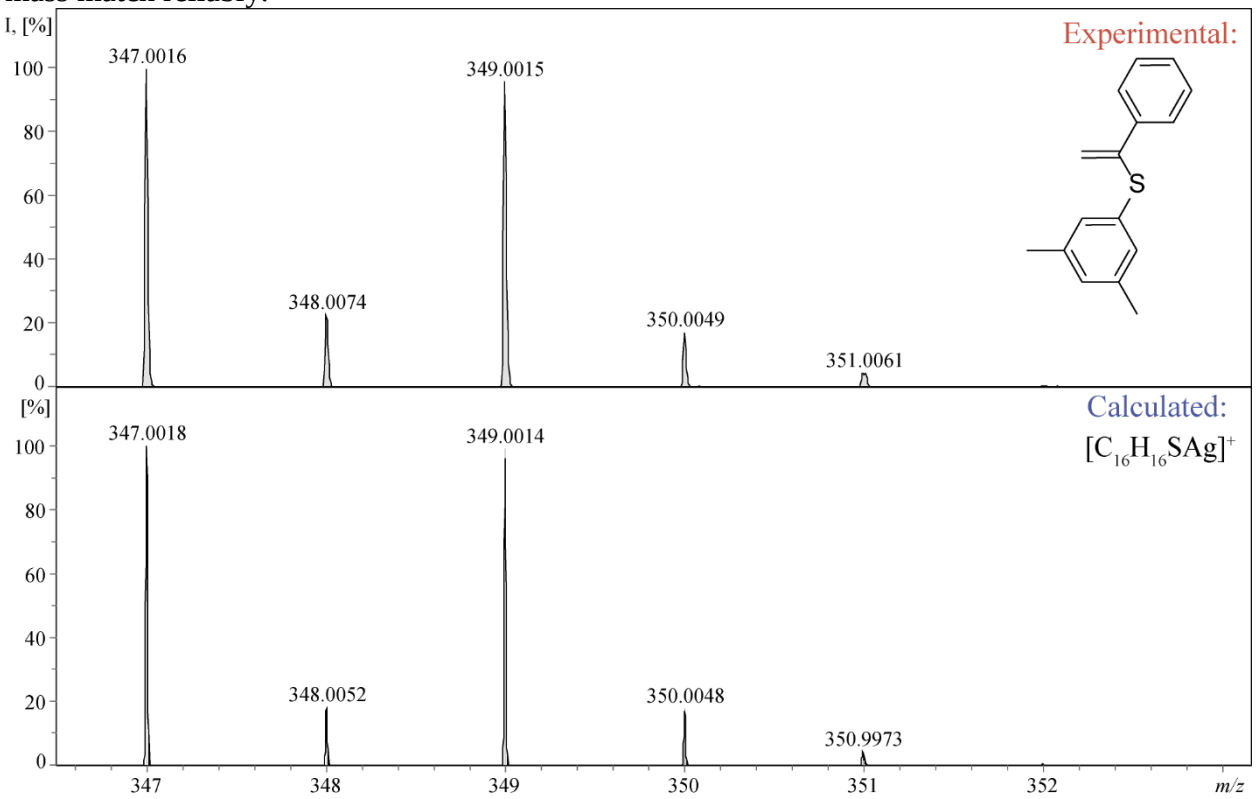


Figure S141. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ae**; main experimental peak $[M+Ag]^+$ = 347.0016 Da, calculated for $C_{16}H_{16}SAg$ = 347.0018 Da, Δ = 0.6 ppm.

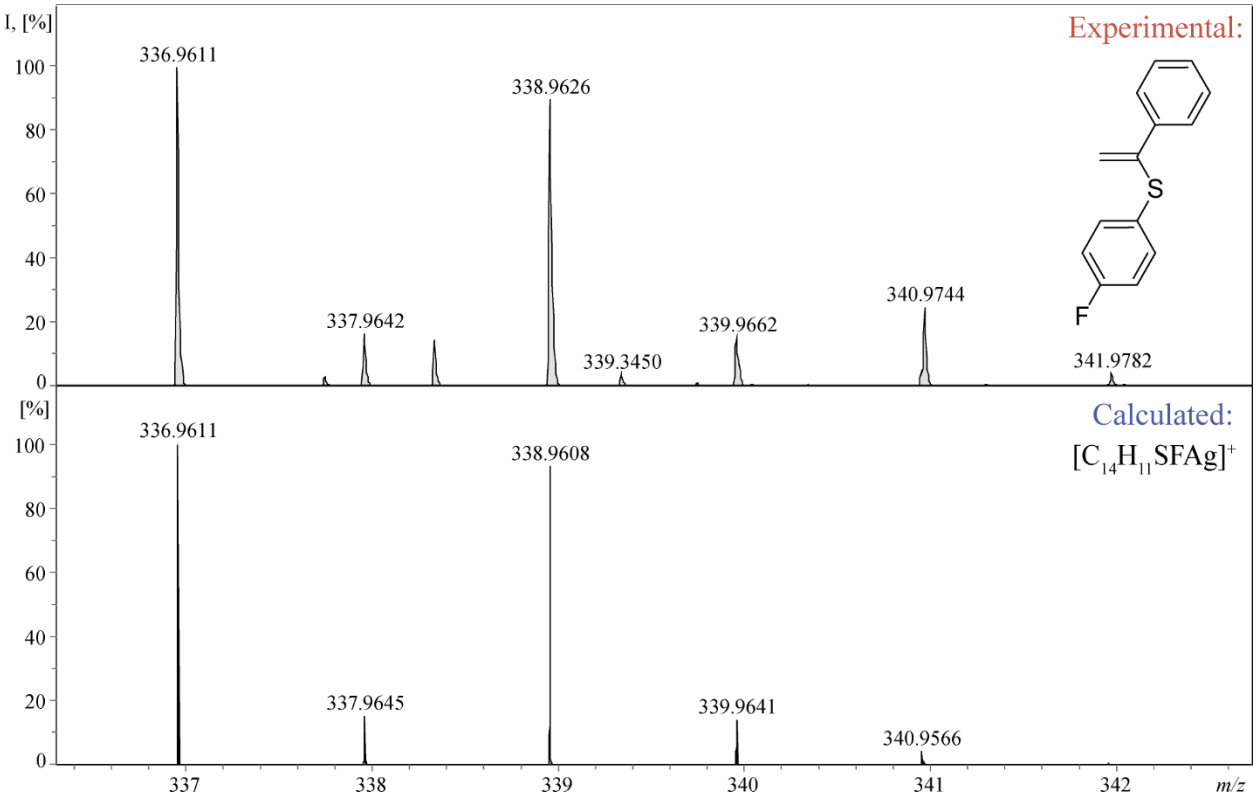


Figure S142. Experimentally detected and theoretical ESI-(+)MS spectrum of **3af**; main experimental peak $[M+Ag]^+$= 336.9611 Da, calculated for $C_{14}H_{11}SFAg$ = 336.9611 Da, Δ = 0.0 ppm.

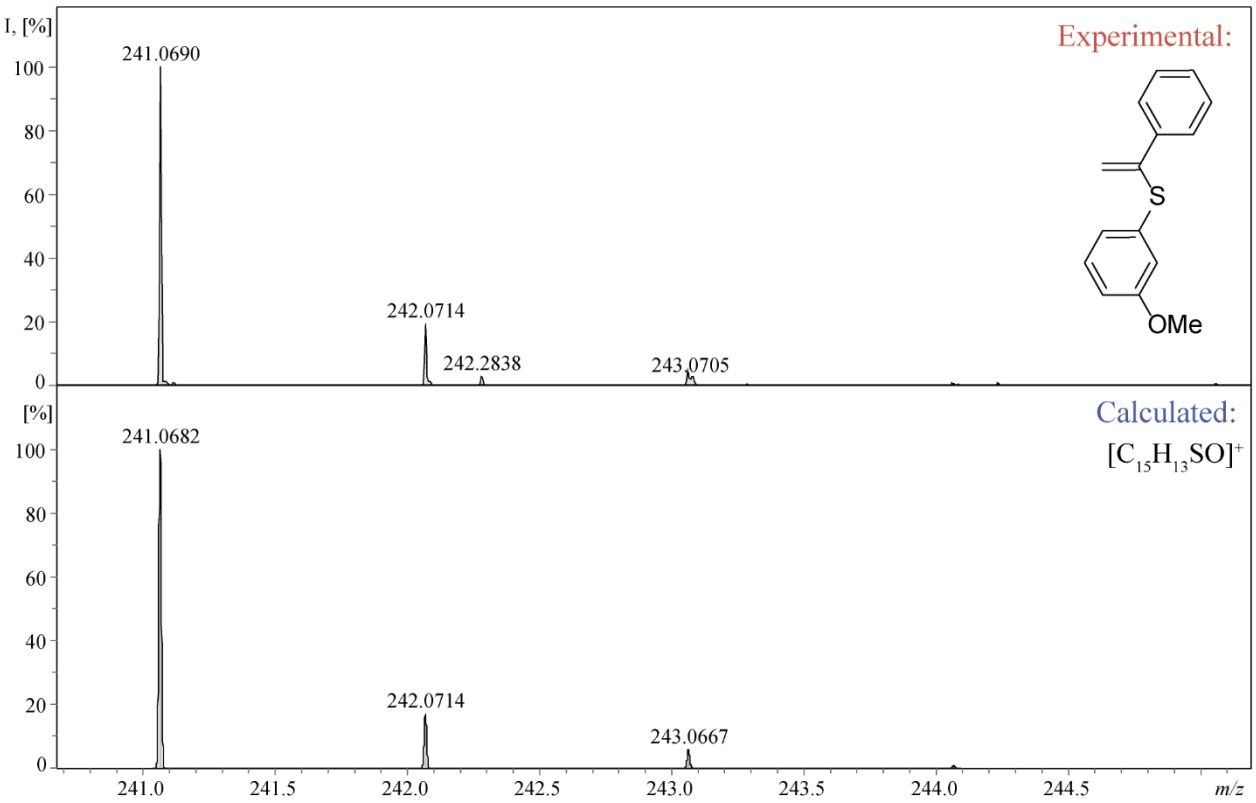


Figure S143. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ag**; main experimental peak $[M-H]^+$= 241.0690 Da, calculated for $C_{15}H_{13}SO$ = 241.0682 Da, Δ = 3.3 ppm.

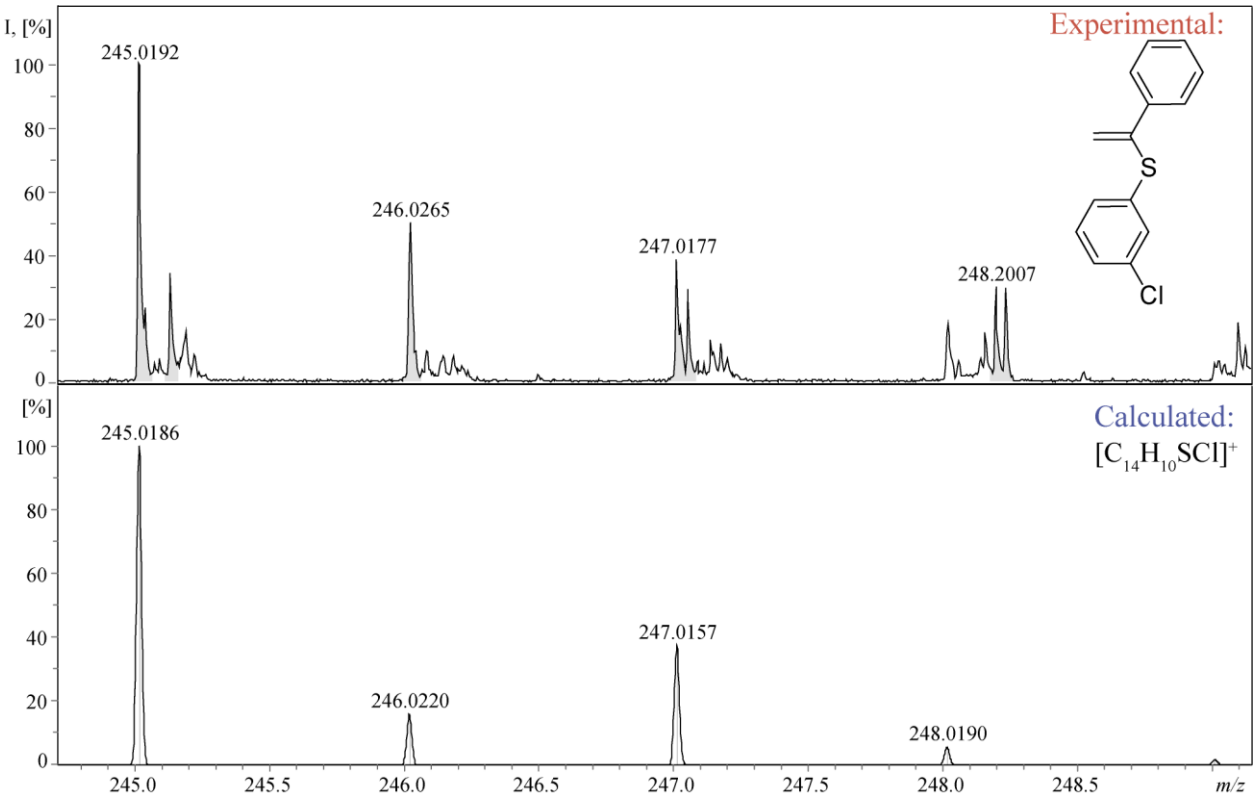


Figure S144. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ah**; main experimental peak $[M-H]^+$= 245.0192 Da, calculated for $C_{14}H_{10}SCl$ = 245.0186 Da, Δ = 2.4 ppm. Low signal-to-noise ratio was observed for these ion signals, which suggests only plausible identification of the complex; however, in spite of low intensity isotopic pattern and accurate mass match reliably.

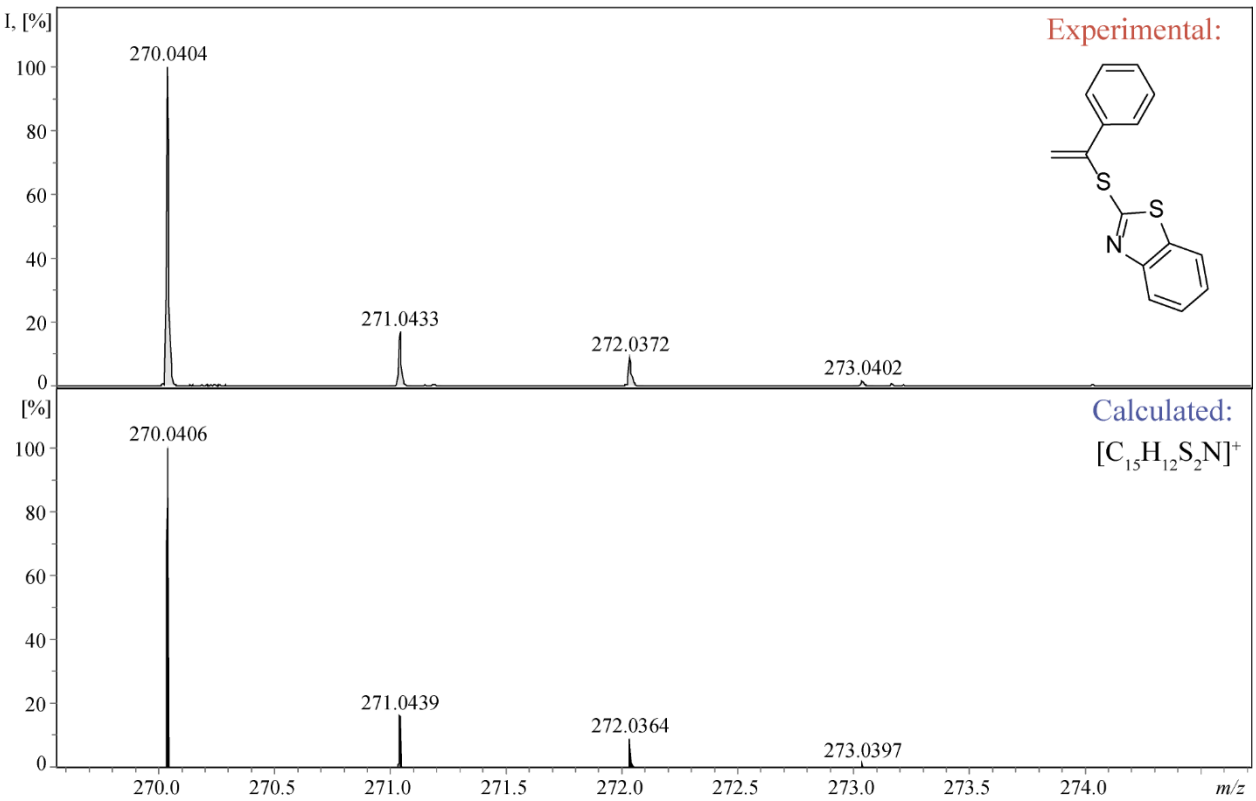


Figure S145. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ai**; main experimental peak $[M+H]^+$= 270.0404 Da, calculated for $C_{15}H_{12}S_2N$ = 270.0406 Da, Δ = 0.7 ppm.

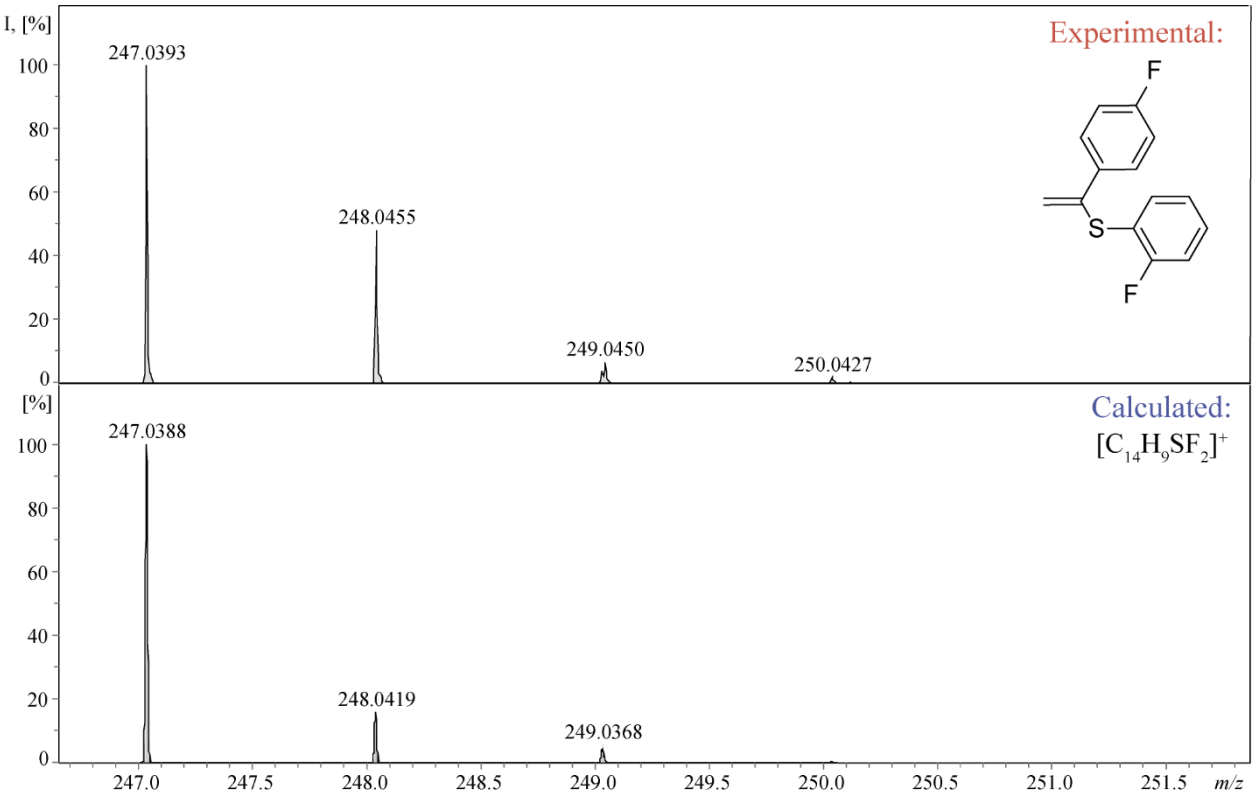


Figure S146. Experimentally detected and theoretical ESI-(+)MS spectrum of **3bb**; main experimental peak $[M-H]^+$= 247.0393 Da, calculated for $C_{14}H_9SF_2$ = 247.0388 Da, Δ = 2.0 ppm.

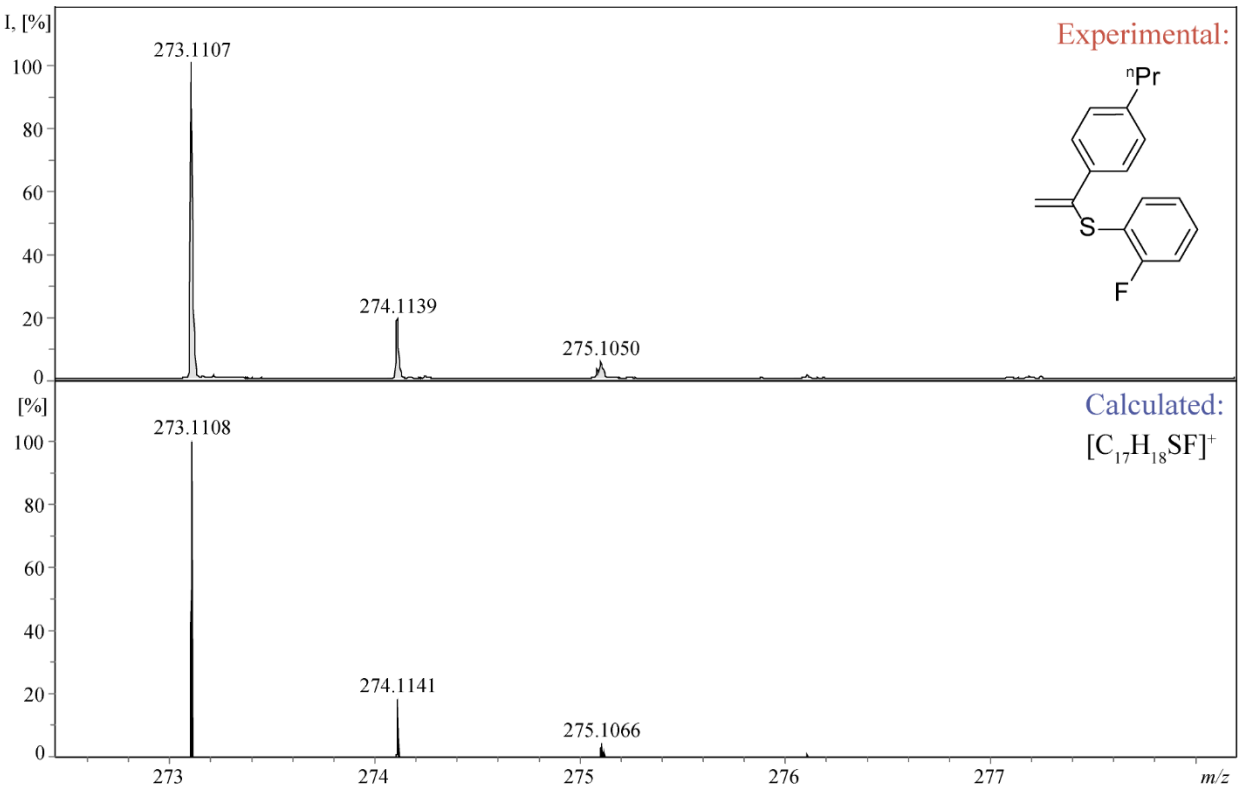


Figure S147. Experimentally detected and theoretical ESI-(+)MS spectrum of **3cb**; main experimental peak $[M+H]^+$= 273.1107 Da, calculated for $C_{17}H_{18}SF$ = 273.1108 Da, Δ = 0.4 ppm.

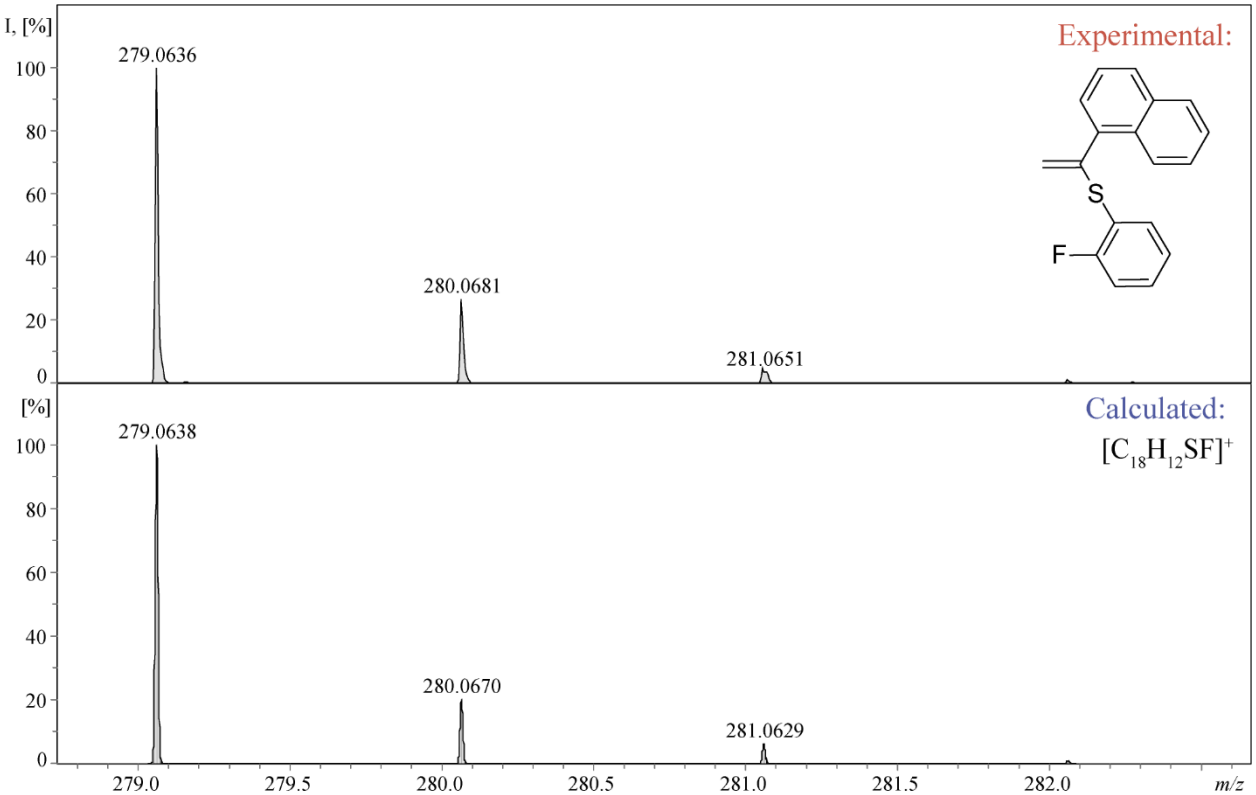


Figure S148. Experimentally detected and theoretical ESI-(+)MS spectrum of **3db**; main experimental peak $[M-H]^+$= 279.0636 Da, calculated for $C_{18}H_{12}SF$ = 279.0638 Da, Δ = 0.7 ppm.

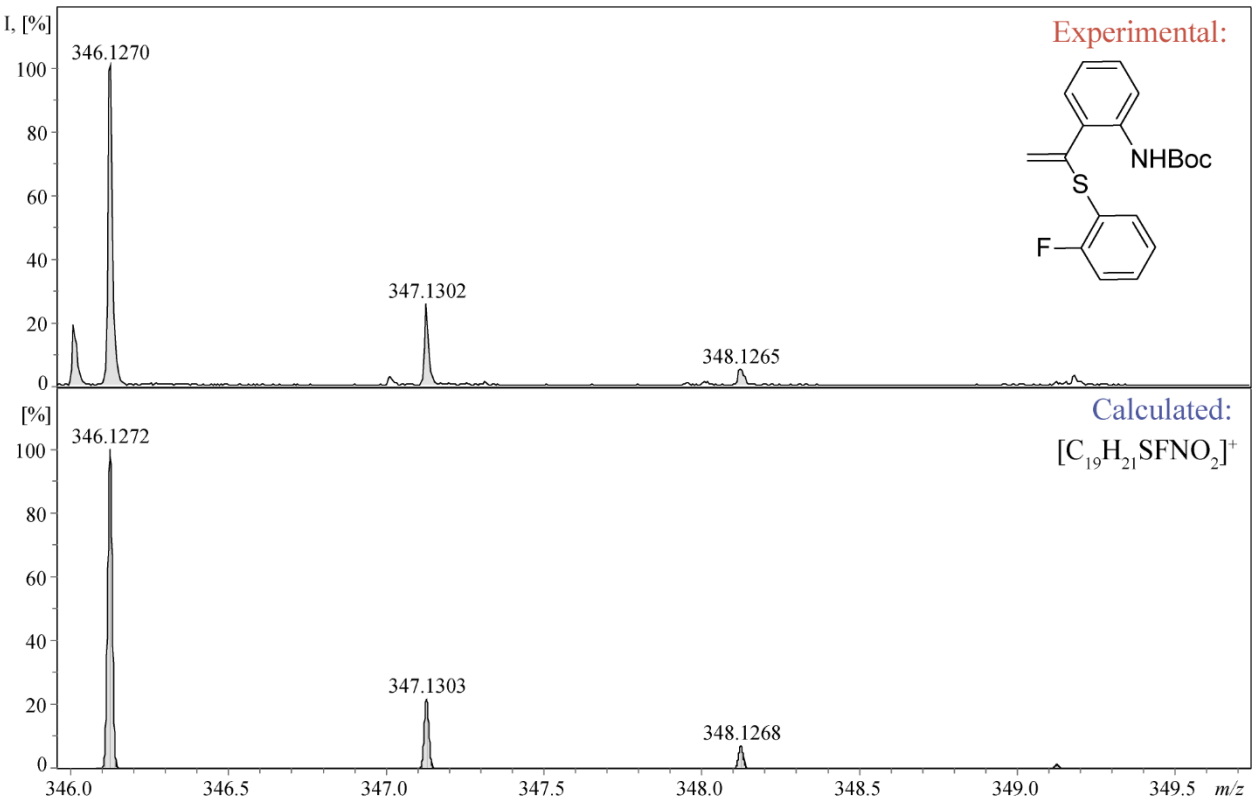


Figure S149. Experimentally detected and theoretical ESI-(+)MS spectrum of **3eb**; main experimental peak $[M+H]^+$= 346.1270 Da, calculated for $C_{19}H_{21}SFNO_2$ = 346.1272 Da, Δ = 0.6 ppm.

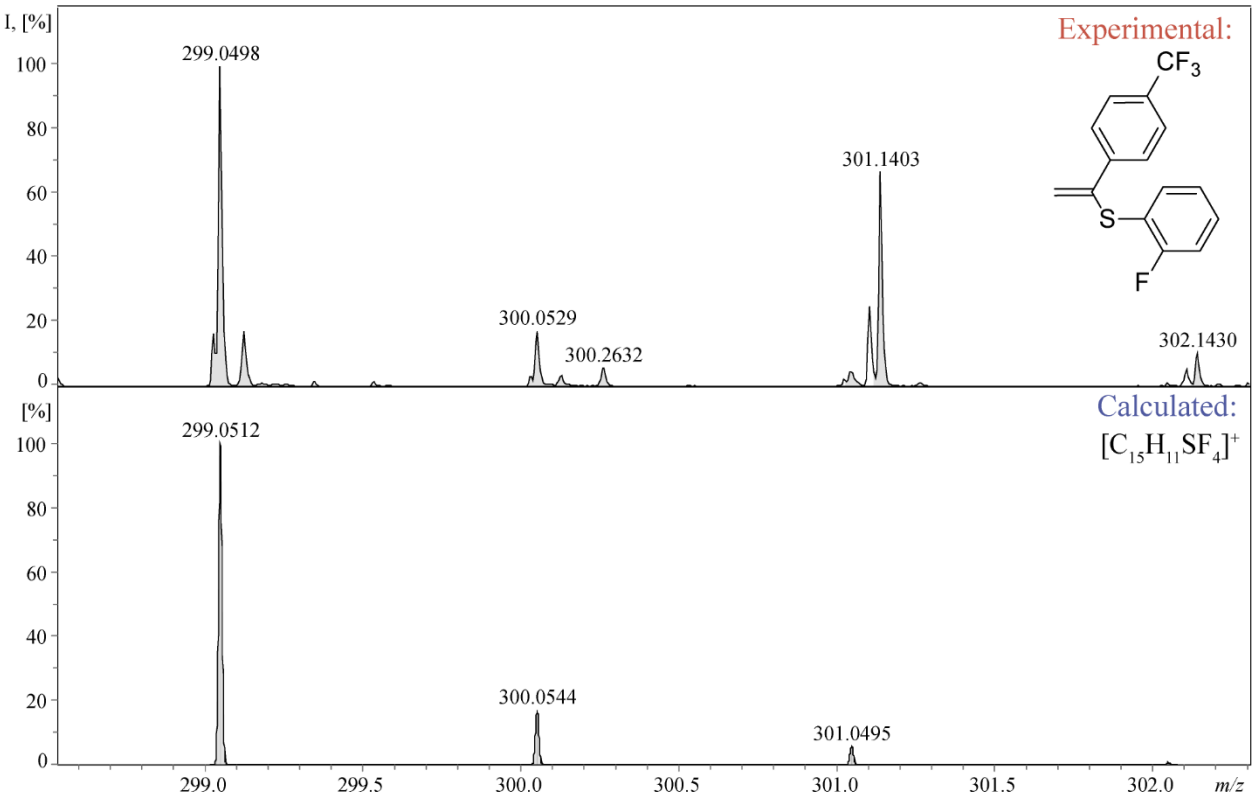


Figure S150. Experimentally detected and theoretical ESI-(+)MS spectrum of **3fb**; main experimental peak $[M+H]^+$= 299.0498 Da, calculated for $C_{15}H_{11}SF_4$ = 299.0512 Da, Δ = 4.7 ppm.

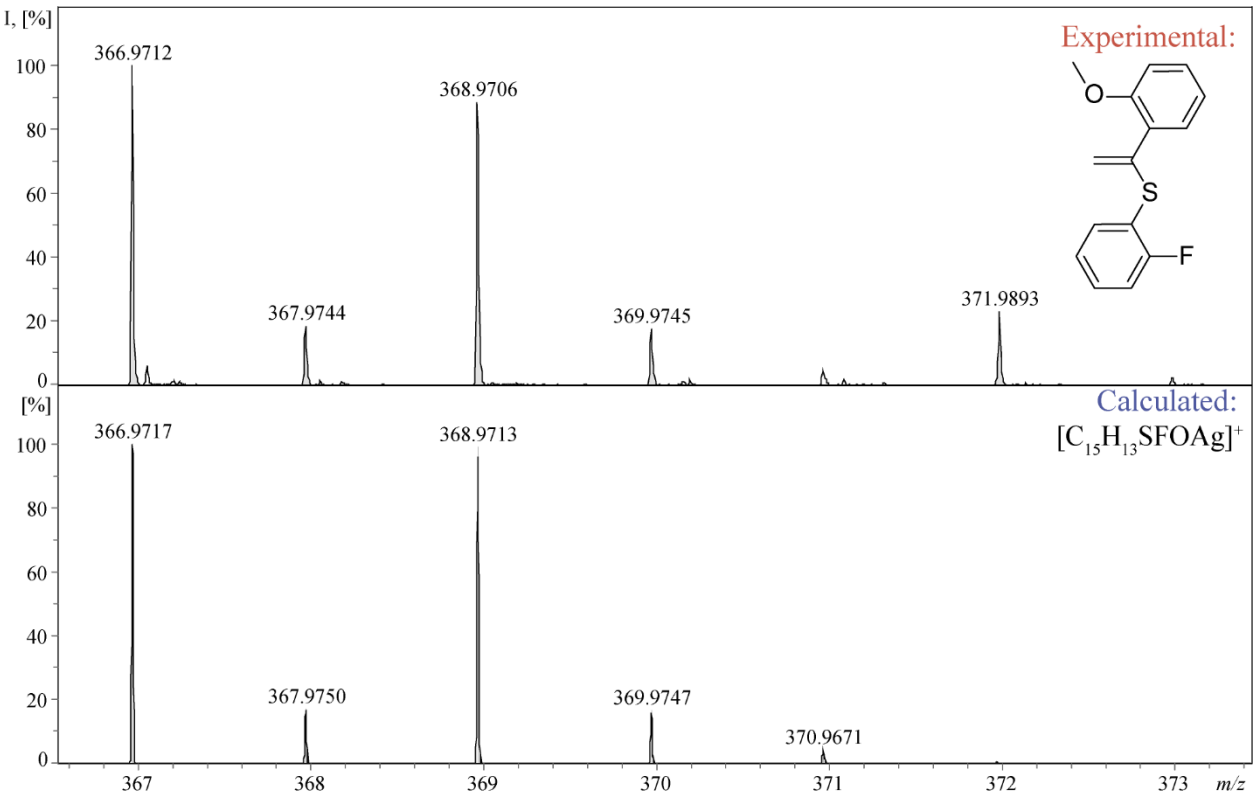


Figure S151. Experimentally detected and theoretical ESI-(+)MS spectrum of **3gb**; main experimental peak $[M+Ag]^+$= 366.9712 Da, calculated for $C_{15}H_{13}SFOAg$ = 366.9717 Da, Δ = 1.4 ppm.

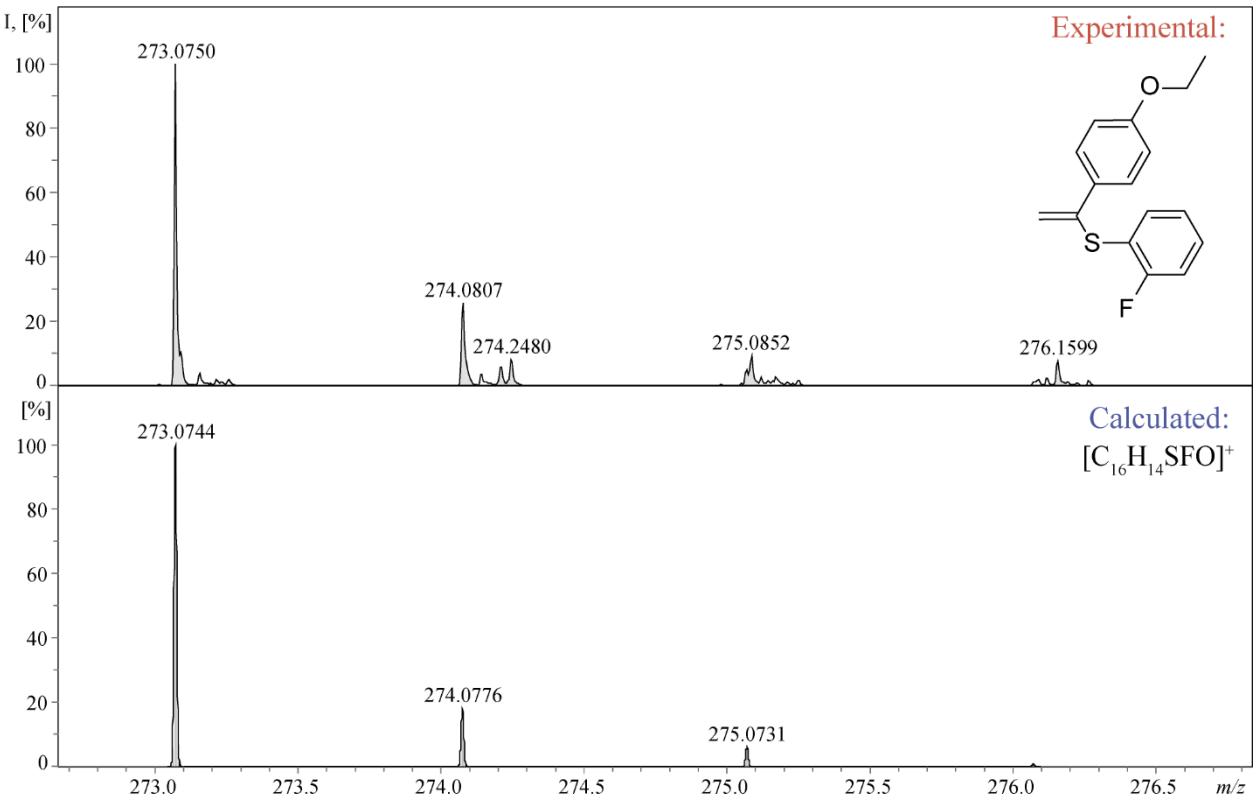


Figure S152. Experimentally detected and theoretical ESI-(+)MS spectrum of **3hb**; main experimental peak $[M-H]^+$= 273.0750 Da, calculated for $C_{16}H_{14}SFO$ = 273.0744 Da, Δ = 2.2 ppm.

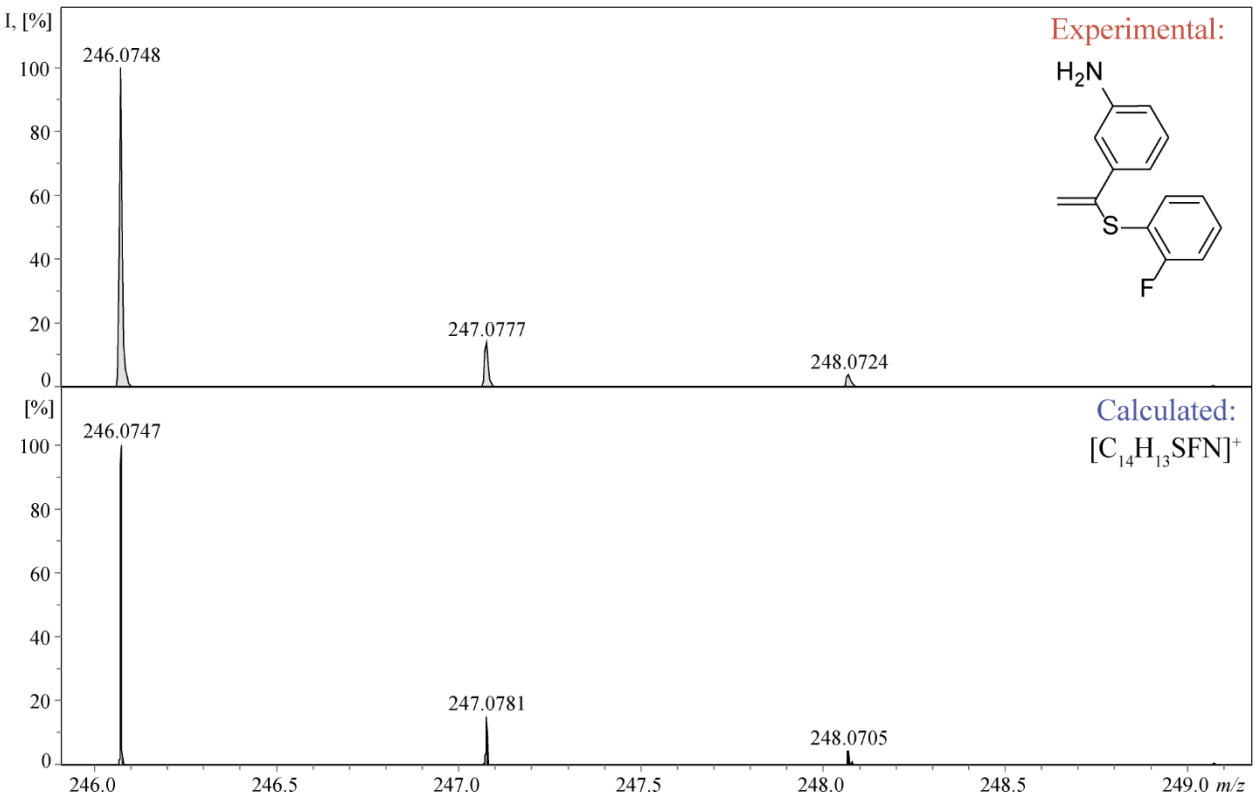


Figure S153. Experimentally detected and theoretical ESI-(+)MS spectrum of **3ib**; main experimental peak $[M+H]^+$= 246.0748 Da, calculated for $C_{14}H_{13}SFN$ = 246.0747 Da, Δ = 0.4 ppm.

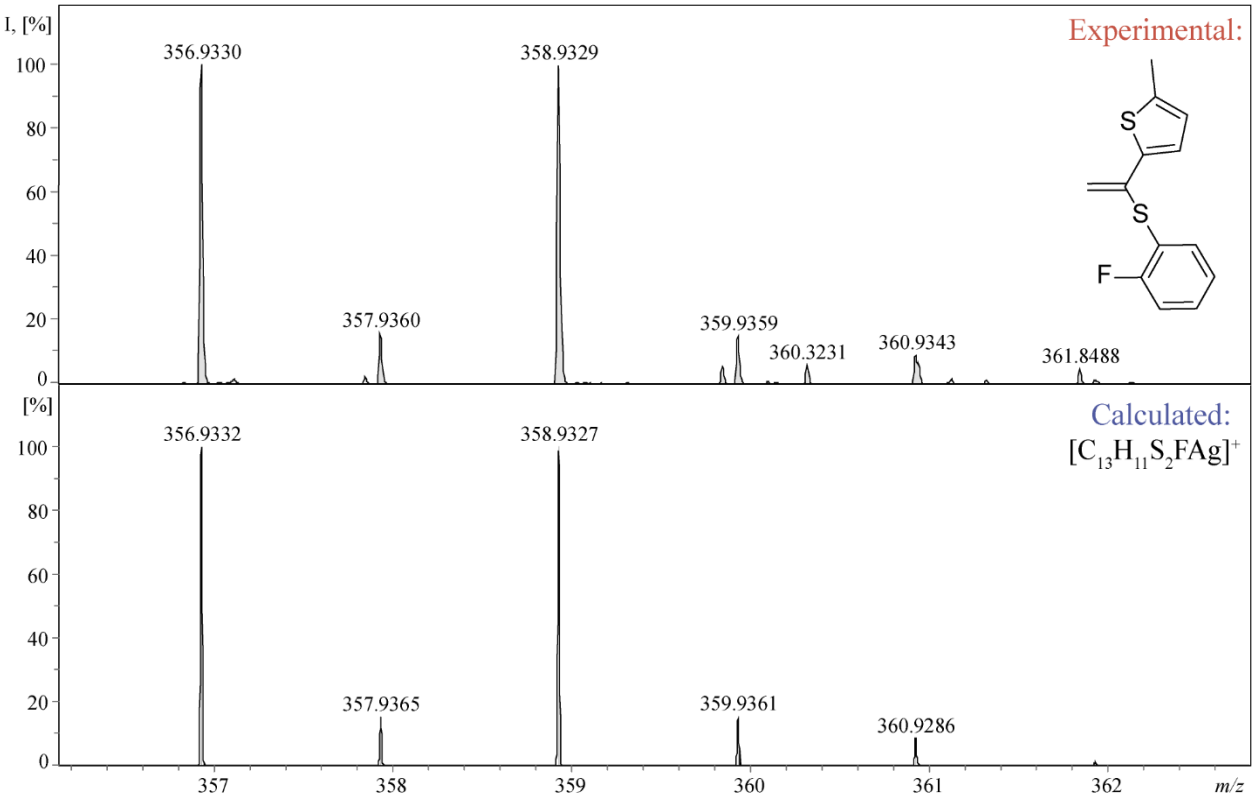


Figure S154. Experimentally detected and theoretical ESI-(+)MS spectrum of **3jb**; main experimental peak $[M+Ag]^+$= 356.9330 Da, calculated for $C_{13}H_{11}S_2FAg$ = 356.9332 Da, Δ = 0.6 ppm.

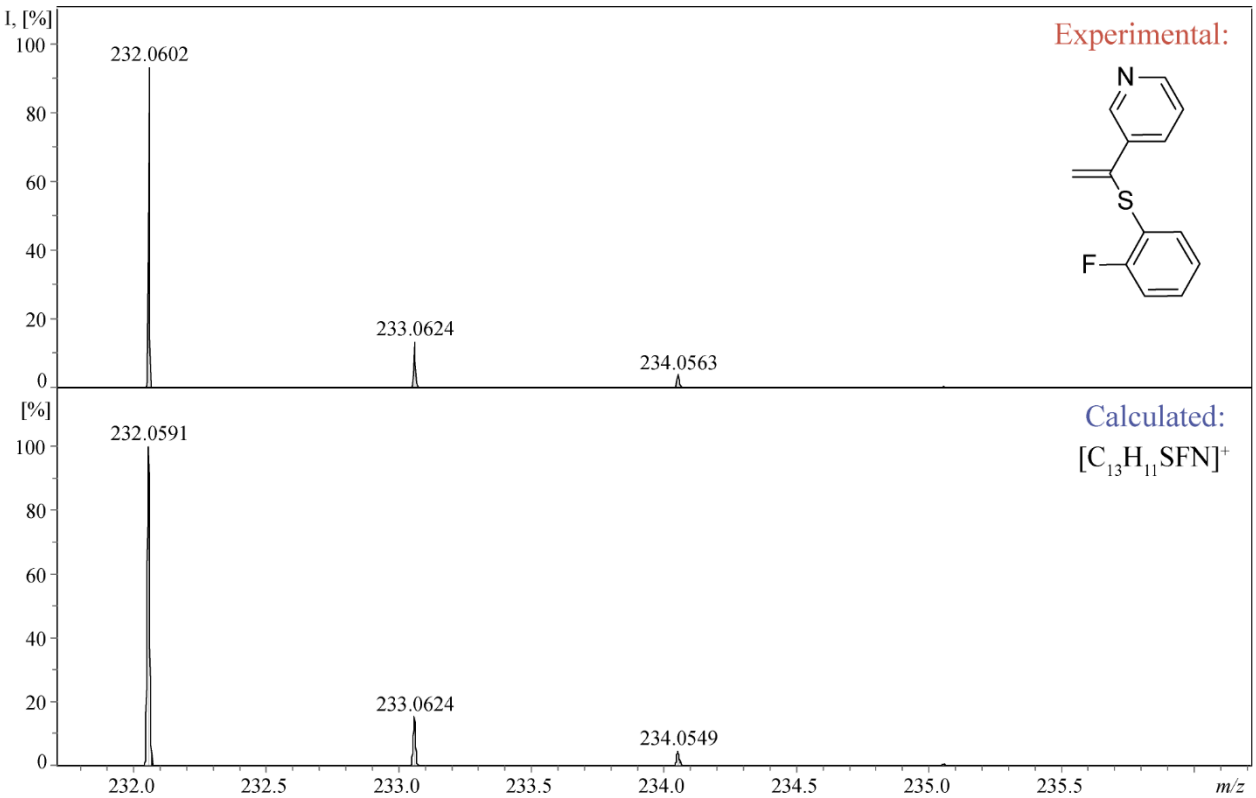


Figure S155. Experimentally detected and theoretical ESI-(+)MS spectrum of **3kb**; main experimental peak $[M+H]^+$= 232.0602 Da, calculated for $C_{13}H_{11}SFN$ = 232.0591 Da, Δ = 4.7 ppm.

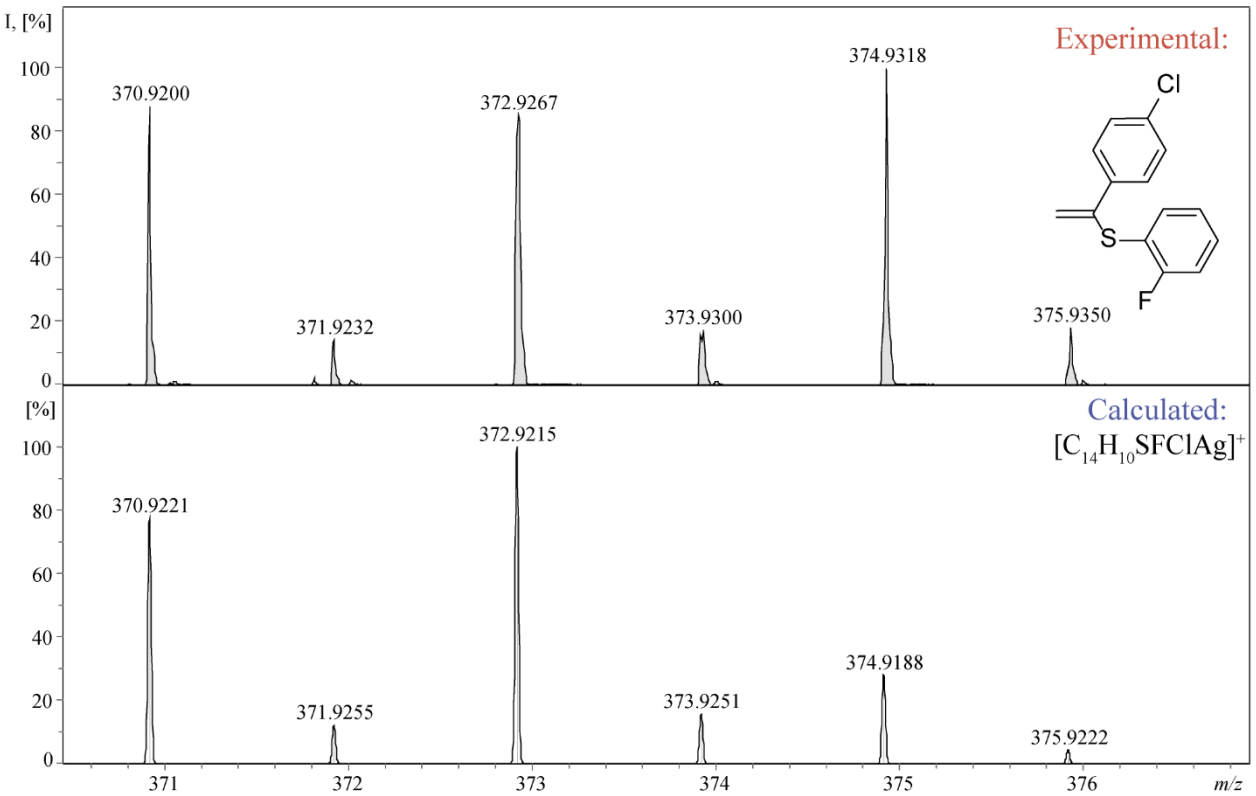


Figure S156. Experimentally detected and theoretical ESI-(+)MS spectrum of **3lb**; main experimental peak $[M+Ag]^+$= 370.9200 Da, calculated for $C_{14}H_{10}SFClAg$ = 370.9221 Da, Δ = 5.7 ppm (experimental error is high due to low resolution as a result of signal overlapping).

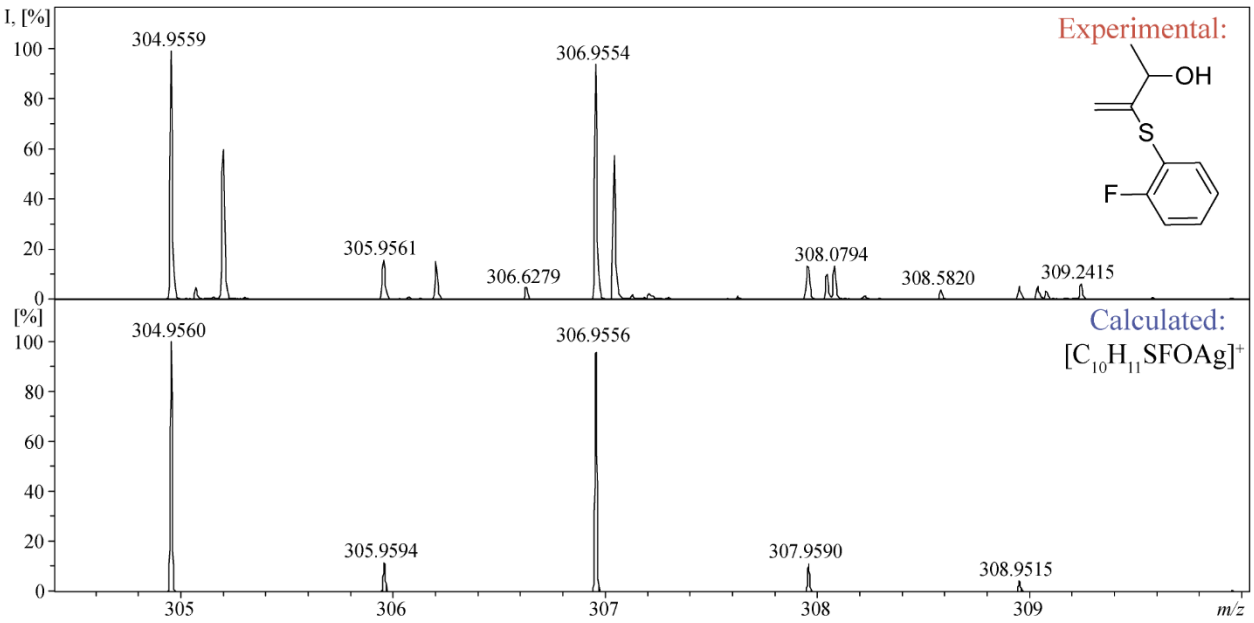


Figure S157. Experimentally detected and theoretical ESI-(+)MS spectrum of **3mb**; main experimental peak $[M+Ag]^+$= 304.9559 Da, calculated for $C_{10}H_{11}SFOAg$ = 304.9560 Da, Δ = 0.3 ppm.

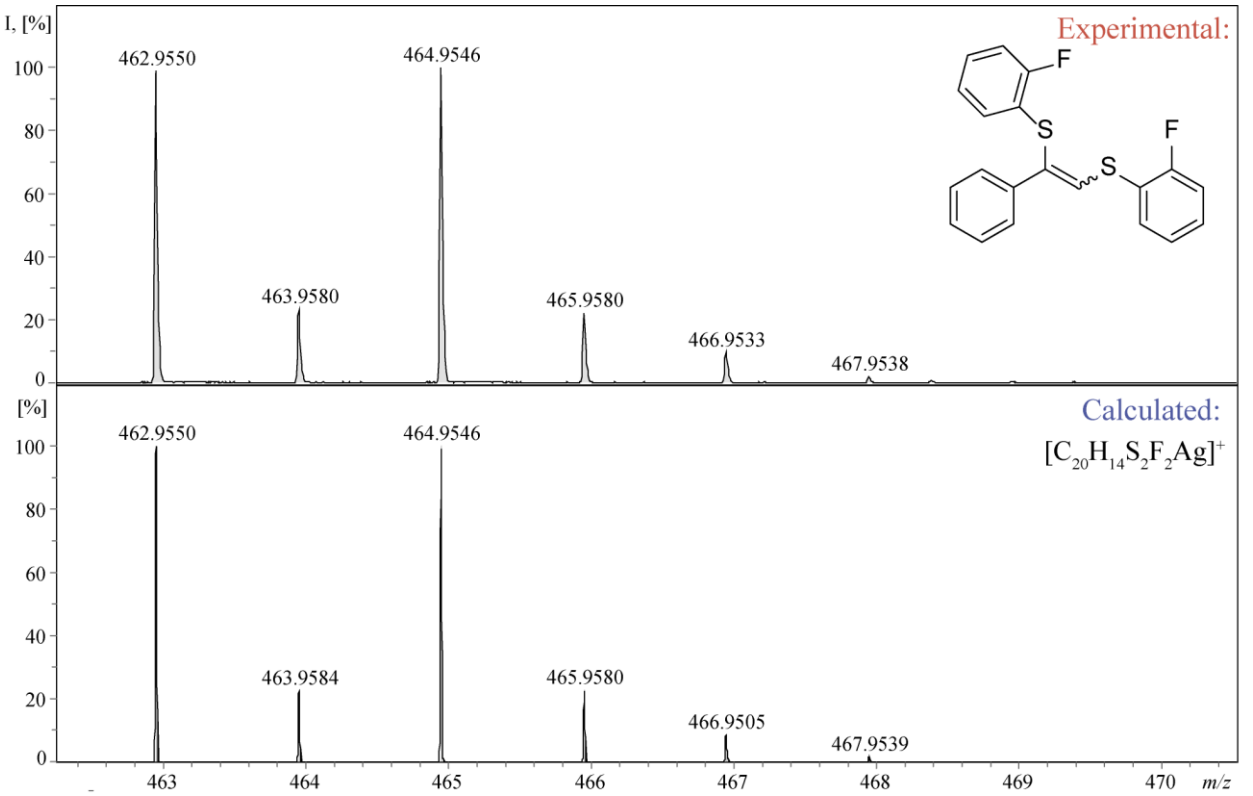


Figure S158. Experimentally detected and theoretical ESI-(+)MS spectrum of **4ab**; main experimental peak $[M+Ag]^+$= 462.9550 Da, calculated for $C_{20}H_{14}S_2F_2Ag$ = 462.9550 Da, Δ = 0.0 ppm.

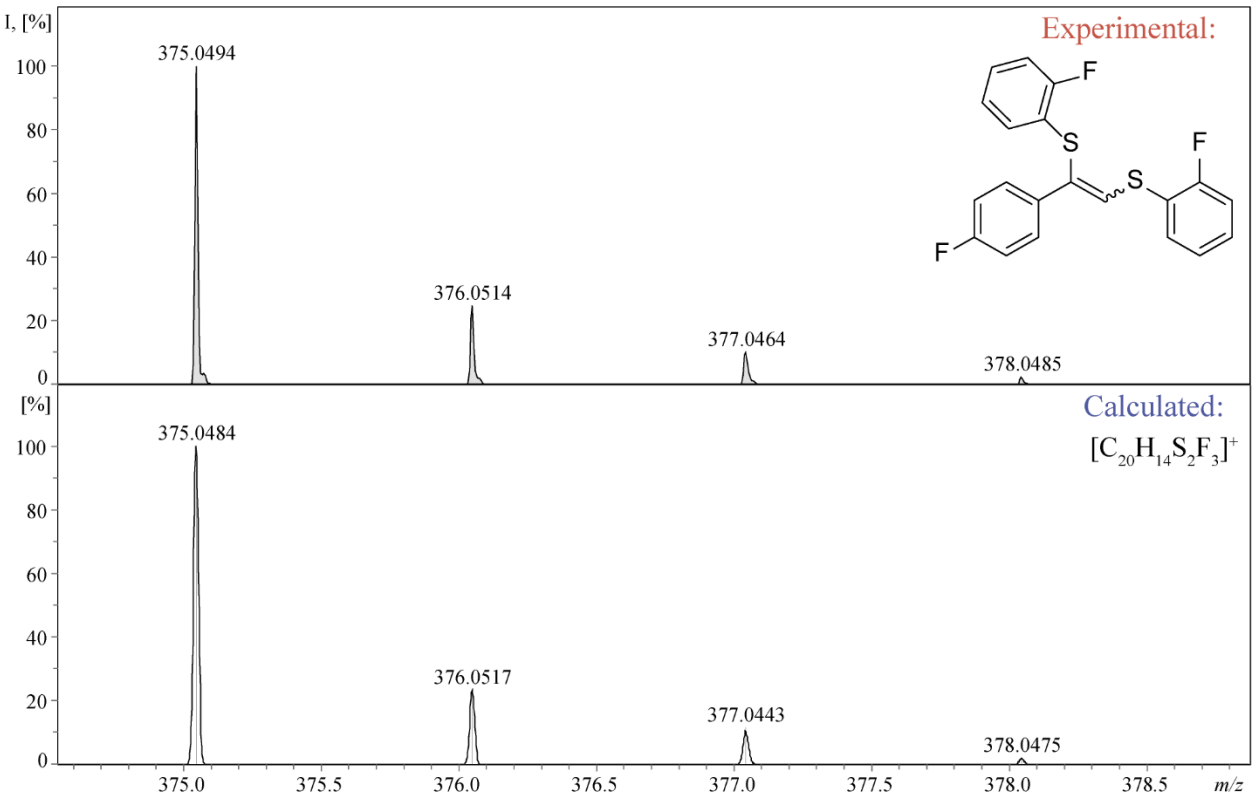


Figure S159. Experimentally detected and theoretical ESI-(+)MS spectrum of **4bb**; main experimental peak $[M+H]^+$= 375.0494 Da, calculated for $C_{20}H_{14}S_2F_3$ = 375.0484 Da, Δ = 2.7 ppm.

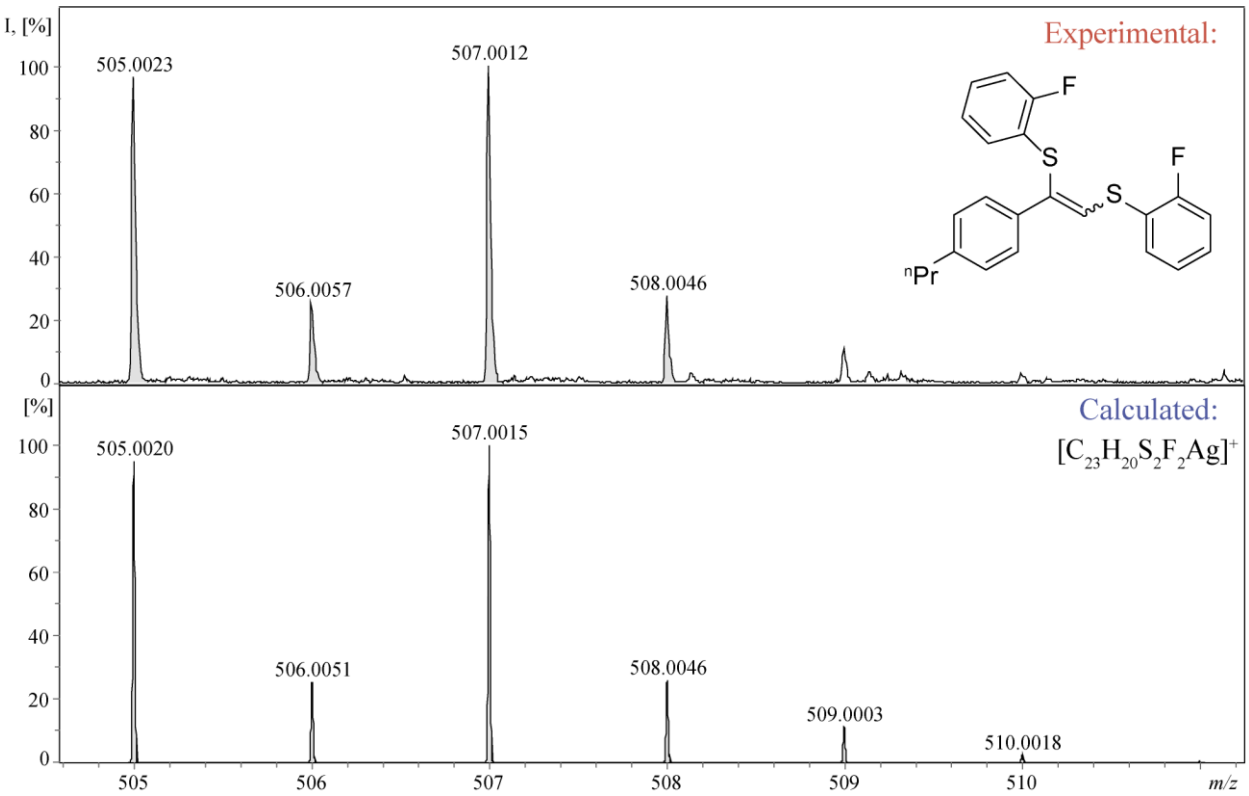


Figure S160. Experimentally detected and theoretical ESI-(+)MS spectrum of **4cb**; main experimental peak $[M+Ag]^+$= 505.0023 Da, calculated for $C_{23}H_{20}S_2F_2Ag$ = 505.0020 Da, Δ = 0.6 ppm.

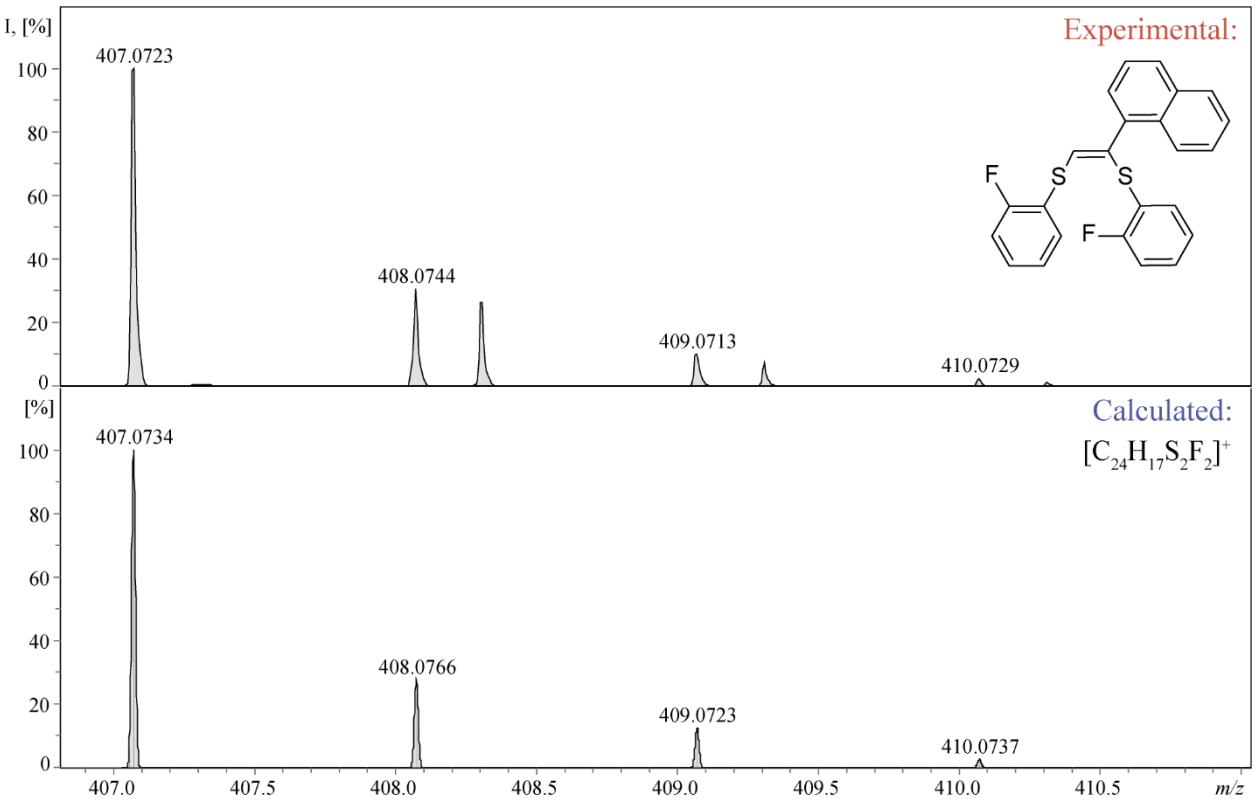


Figure S161. Experimentally detected and theoretical ESI-(+)MS spectrum of **4db**; main experimental peak $[M+H]^+$= 407.0723 Da, calculated for $C_{24}H_{17}S_2F_2$ = 407.0734 Da, Δ = 2.7 ppm.

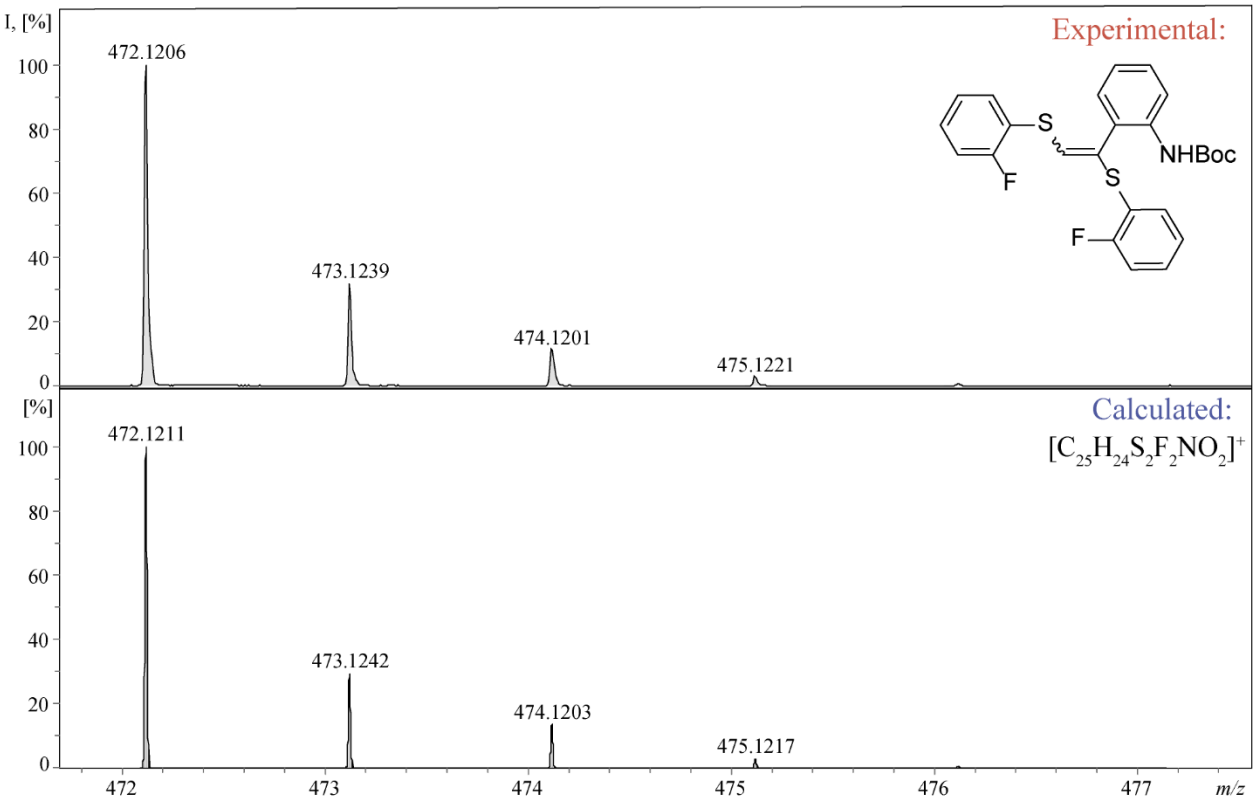


Figure S162. Experimentally detected and theoretical ESI-(+)MS spectrum of **4eb**; main experimental peak $[M+H]^+$= 472.1206 Da, calculated for $C_{25}H_{24}S_2F_2NO_2$ = 472.1211 Da, Δ = 1.1 ppm.

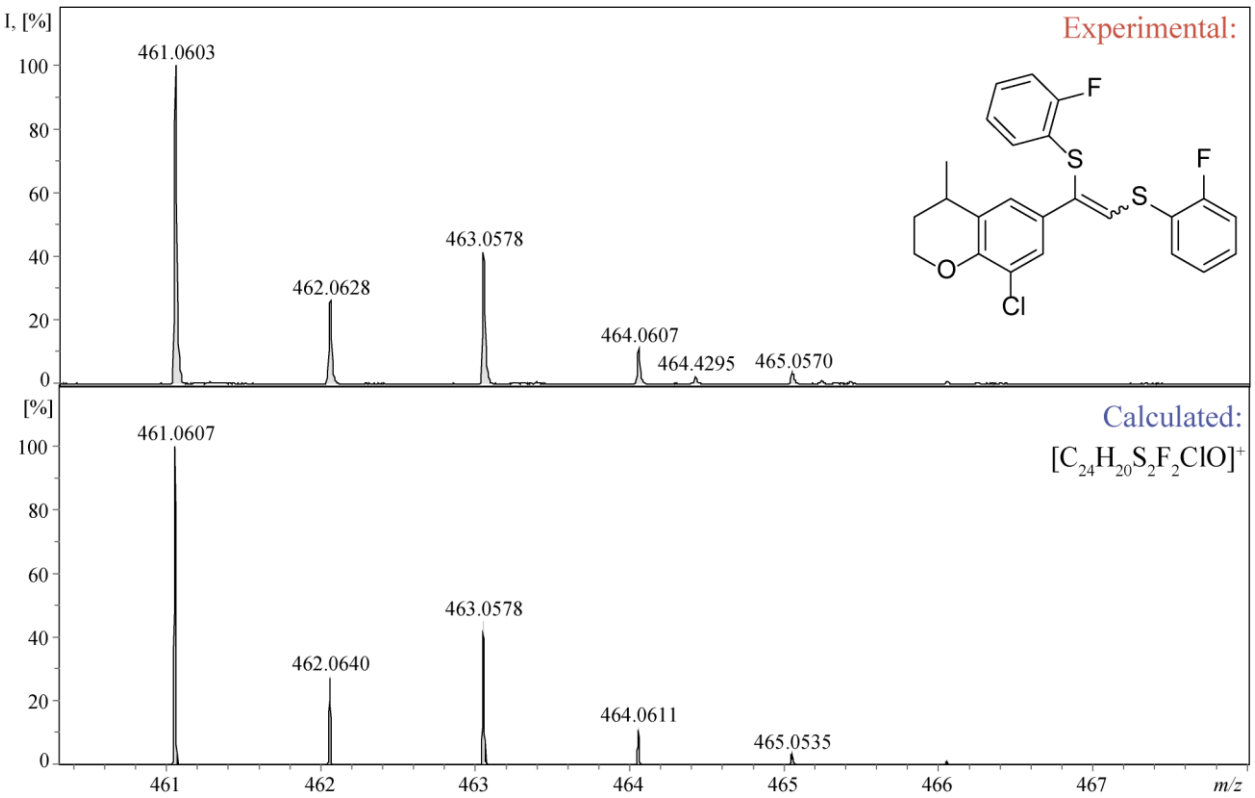


Figure S163. Experimentally detected and theoretical ESI-(+)MS spectrum of **4ob'**; main experimental peak $[M+H]^+$= 461.0603 Da, calculated for $C_{24}H_{20}S_2F_2ClO$ = 461.0607 Da, Δ = 0.9 ppm.

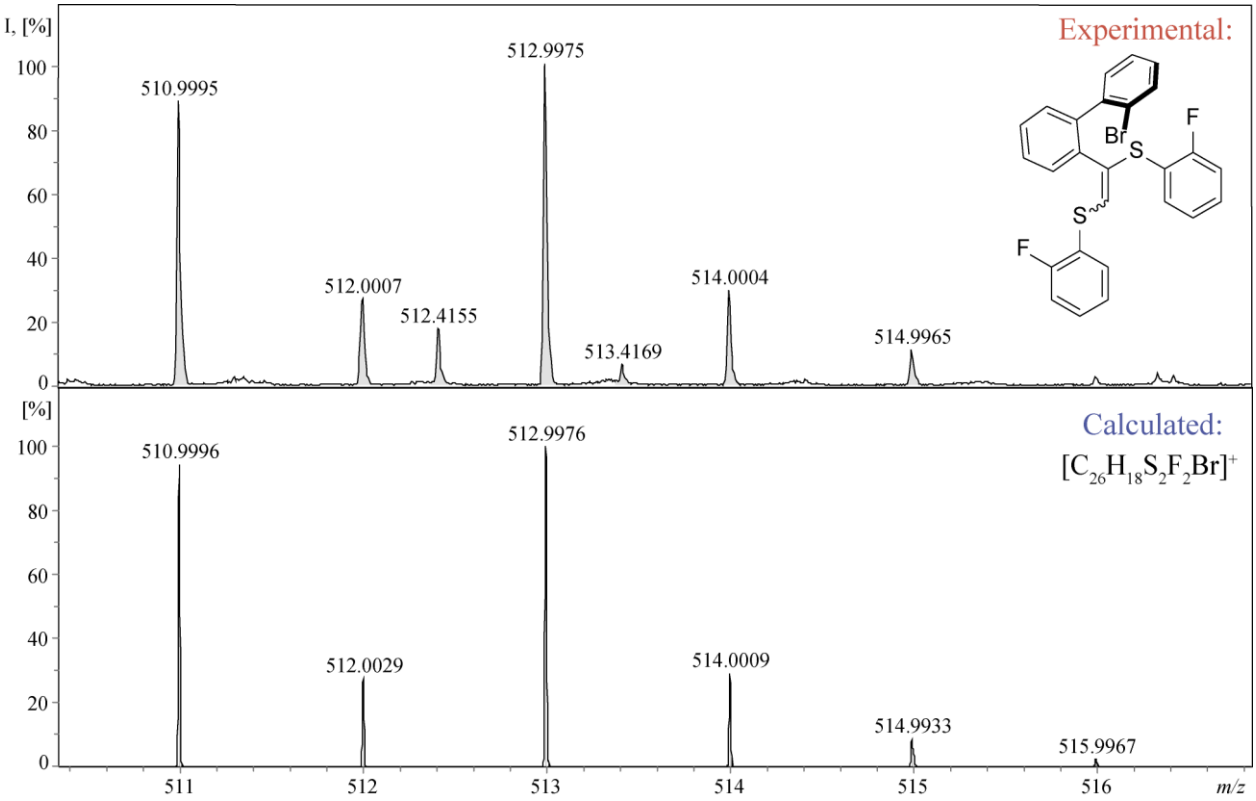


Figure S164. Experimentally detected and theoretical ESI-(+)MS spectrum of **4pb**; main experimental peak $[M+H]^+$= 510.9995 Da, calculated for $C_{26}H_{18}S_2F_2Br$ = 510.9996 Da, Δ = 0.2 ppm.

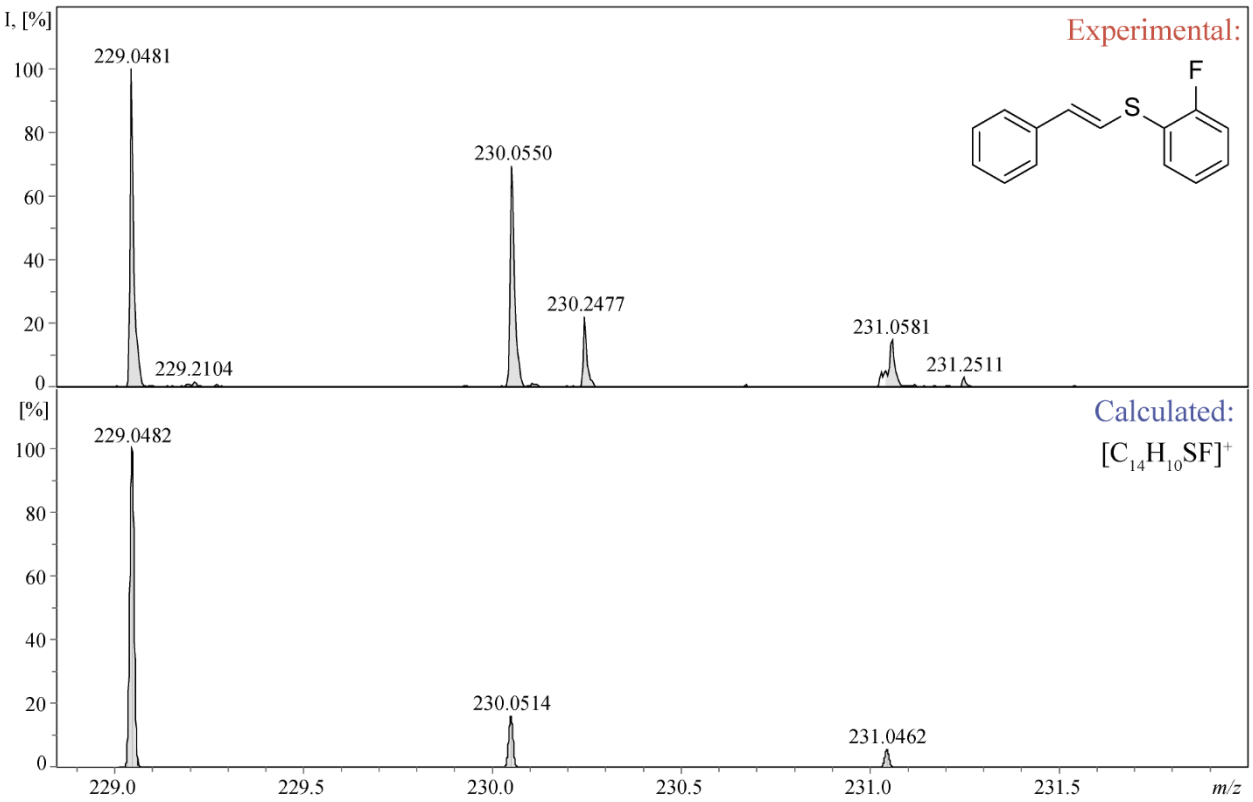


Figure S165. Experimentally detected and theoretical ESI-(+)MS spectrum of **5ab**; main experimental peak $[M-H]^+$= 229.0481 Da, calculated for $C_{14}H_{10}SF$ = 229.0482 Da, Δ = 0.4 ppm.

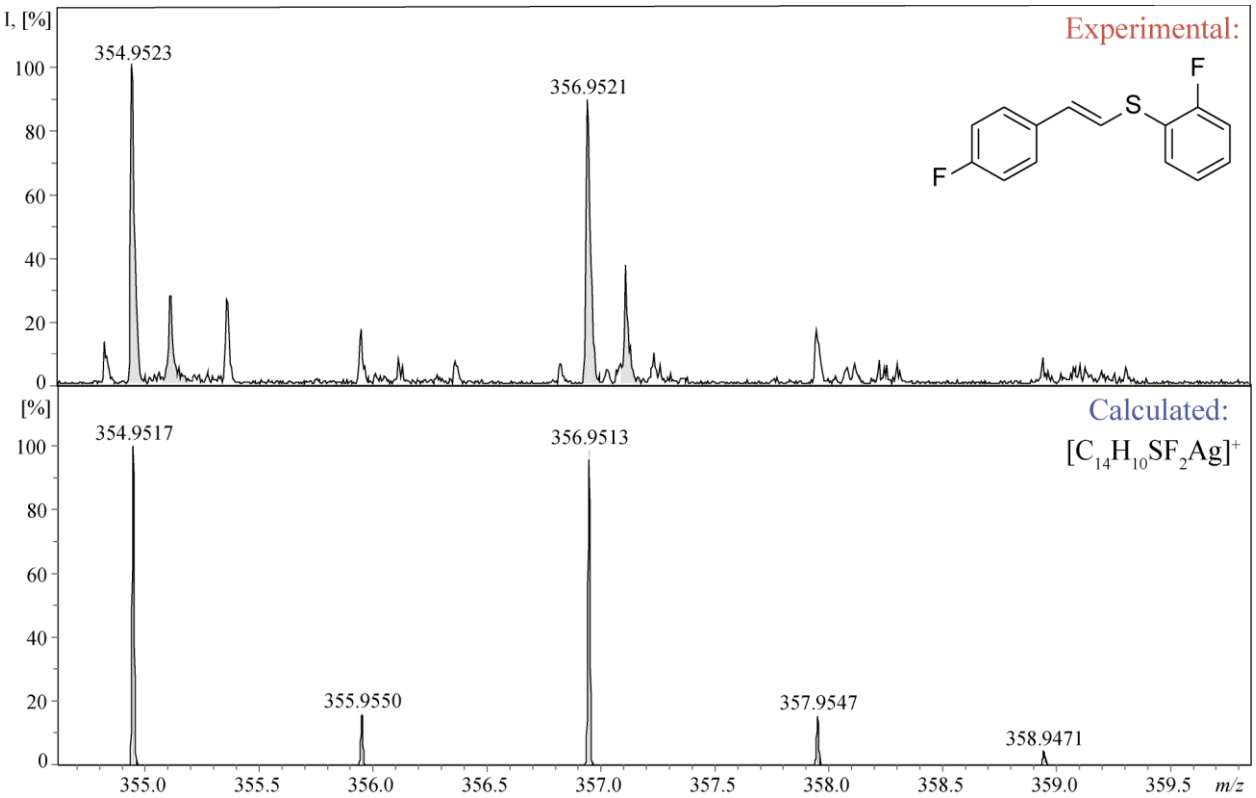


Figure S166. Experimentally detected and theoretical ESI-(+)MS spectrum of **5bb**; main experimental peak $[M+Ag]^+$= 354.9523 Da, calculated for $C_{14}H_{10}SF_2Ag$ = 354.9517 Da, Δ = 1.7 ppm.

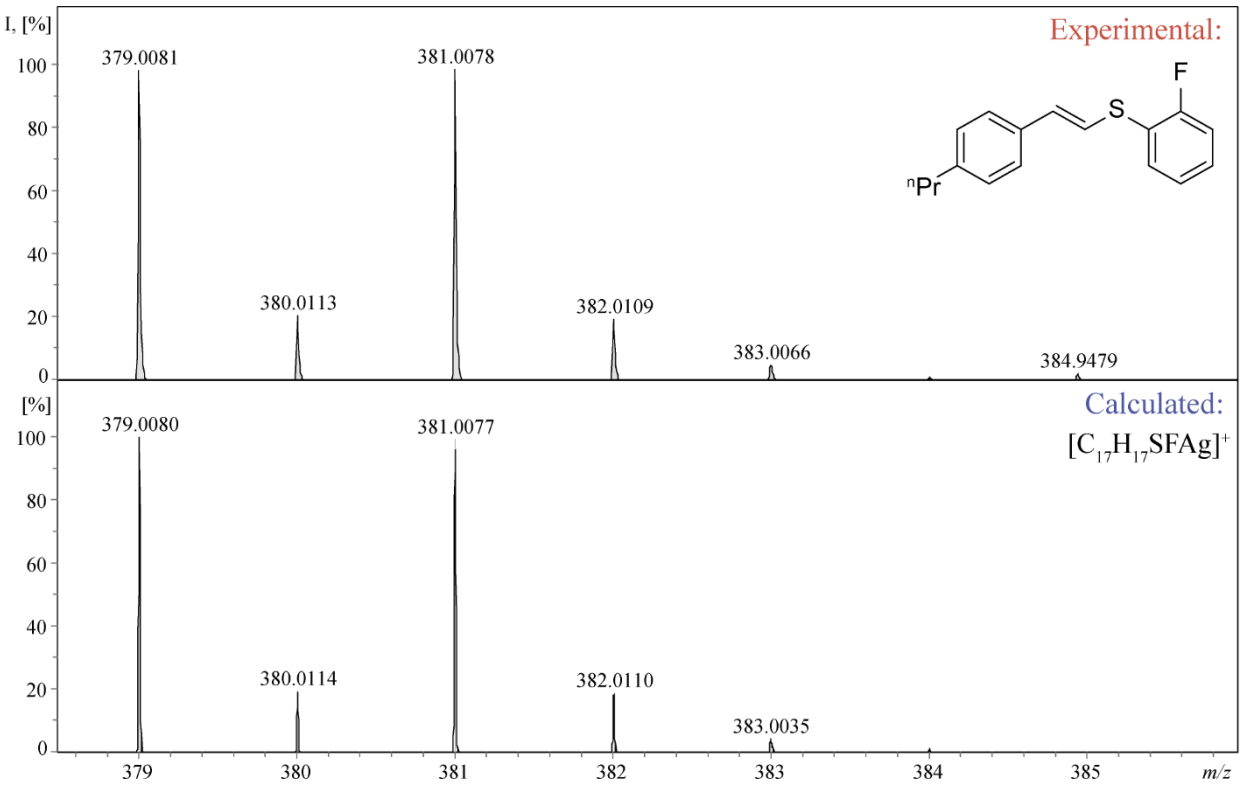


Figure S167. Experimentally detected and theoretical ESI-(+)MS spectrum of **5cb**; main experimental peak $[M+Ag]^+$= 379.0081 Da, calculated for $C_{17}H_{17}SFAg$ = 379.0080 Da, Δ = 0.3 ppm.

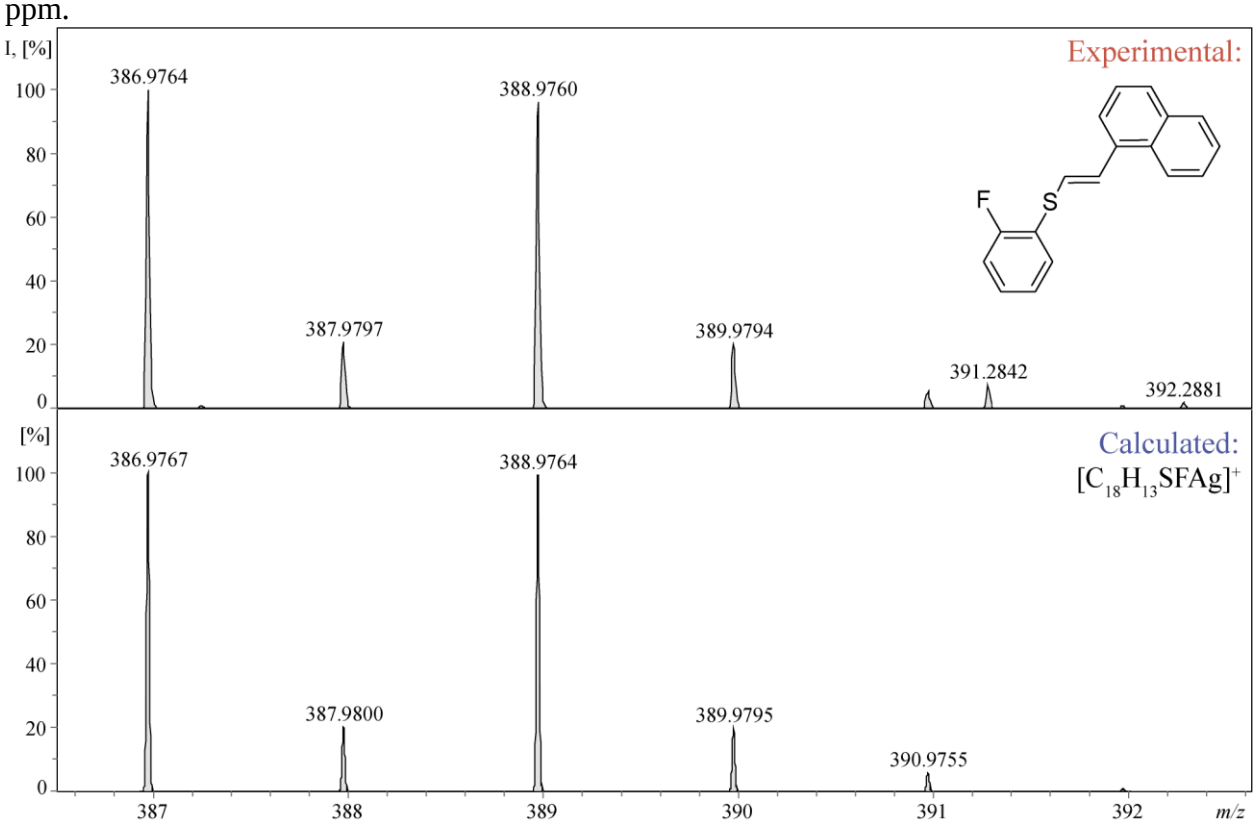


Figure S168. Experimentally detected and theoretical ESI-(+)MS spectrum of **5db**; main experimental peak $[M+Ag]^+$= 386.9764 Da, calculated for $C_{18}H_{13}SFAg$ = 386.9767 Da, Δ = 0.7 ppm.

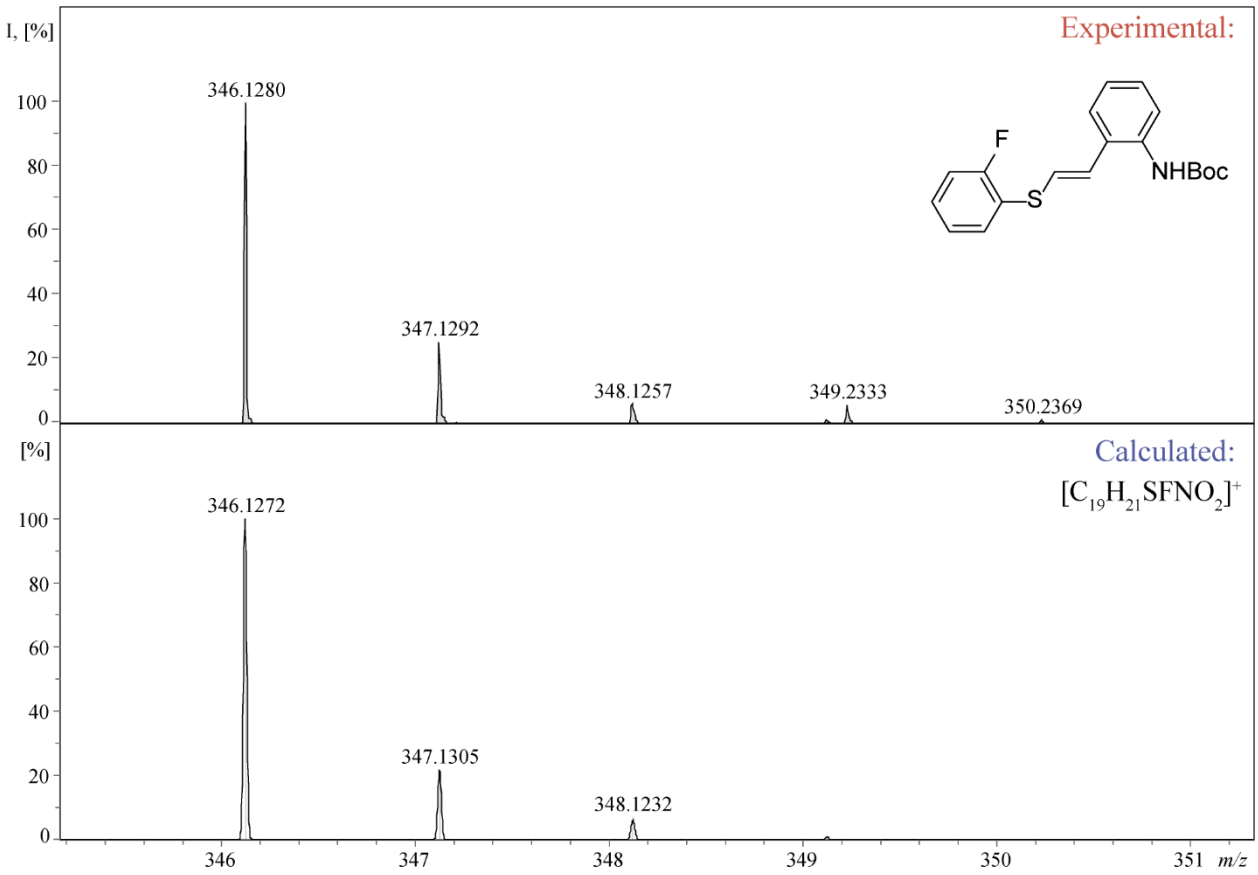


Figure S169. Experimentally detected and theoretical ESI-(+)MS spectrum of **5eb**; main experimental peak $[M+H]^+$= 346.1280 Da, calculated for $C_{19}H_{21}SFNO_2$ = 346.1272 Da, Δ = 2.3 ppm.

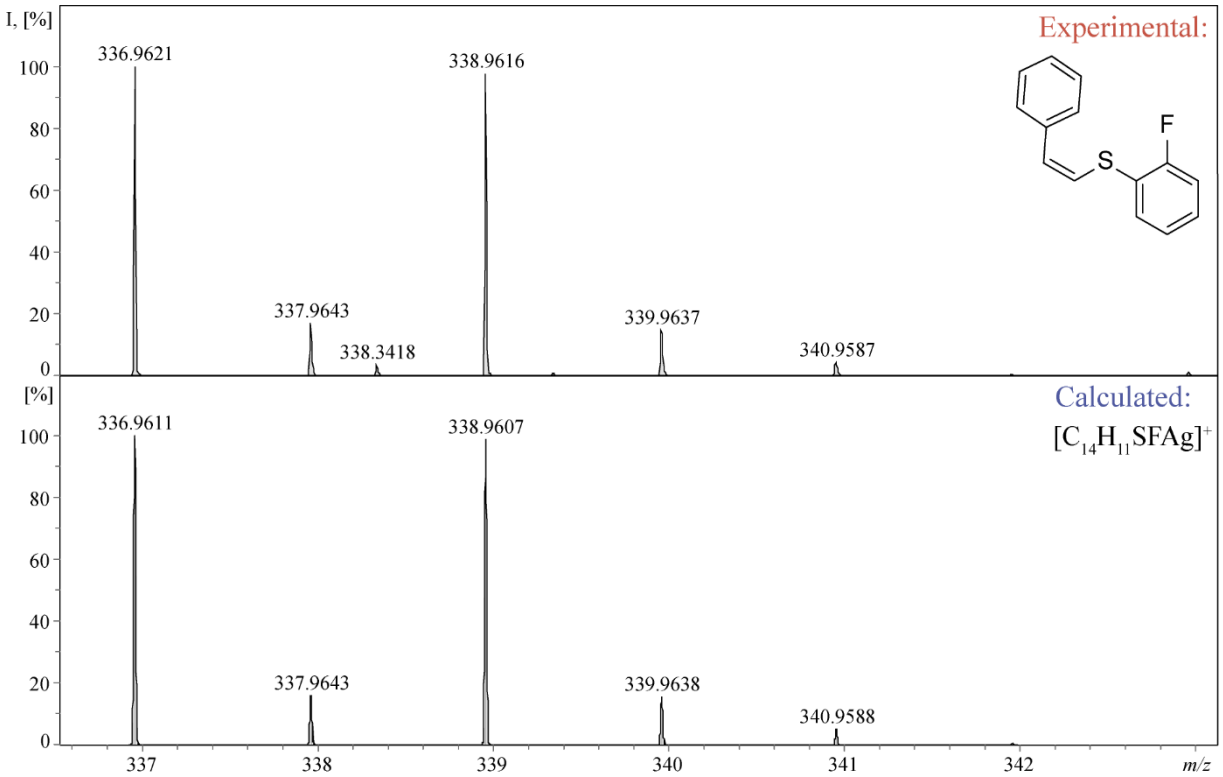


Figure S170. Experimentally detected and theoretical ESI-(+)MS spectrum of **6ab**; main experimental peak $[M+Ag]^+$= 336.9621 Da, calculated for $C_{14}H_{11}SFAg$ = 336.9611 Da, Δ = 3.0 ppm.

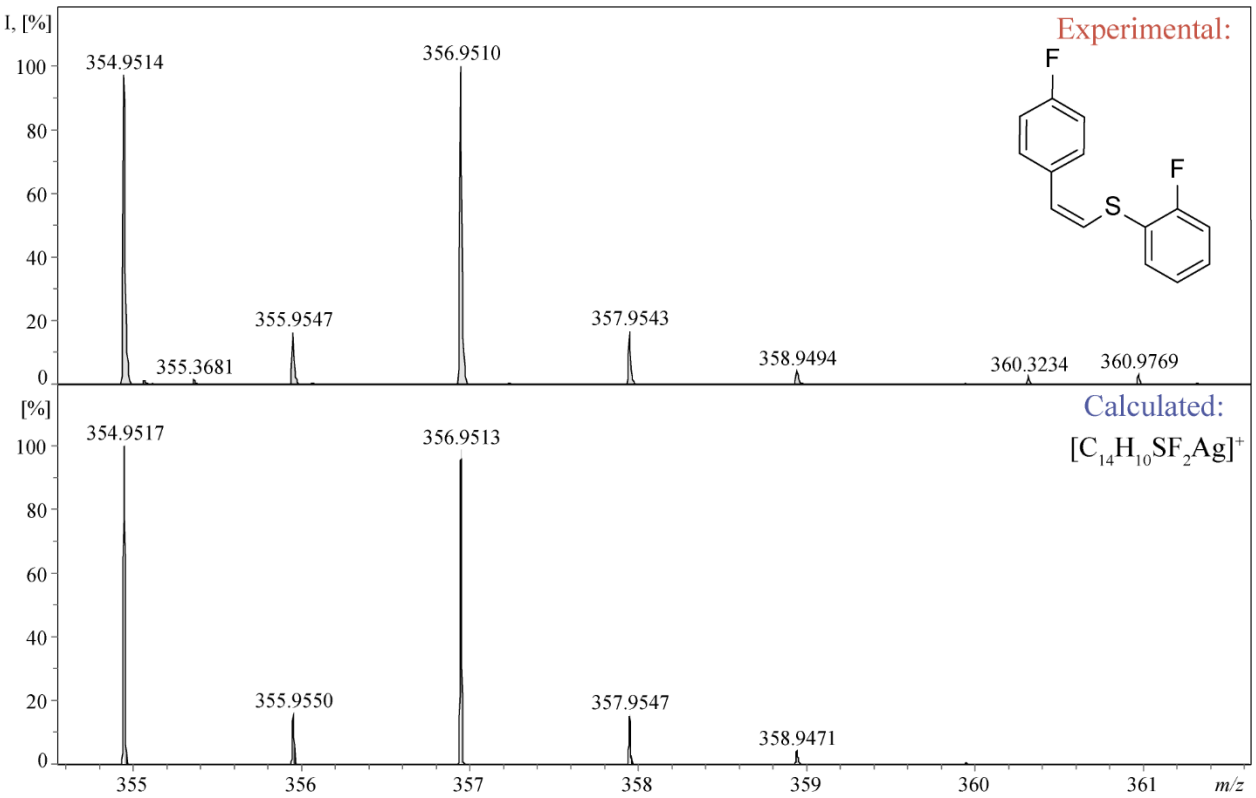


Figure S171. Experimentally detected and theoretical ESI-(+)MS spectrum of **6bb**; main experimental peak $[M+Ag]^+$= 354.9514 Da, calculated for $C_{14}H_{10}SF_2Ag$ = 354.9517 Da, Δ = 0.9 ppm.

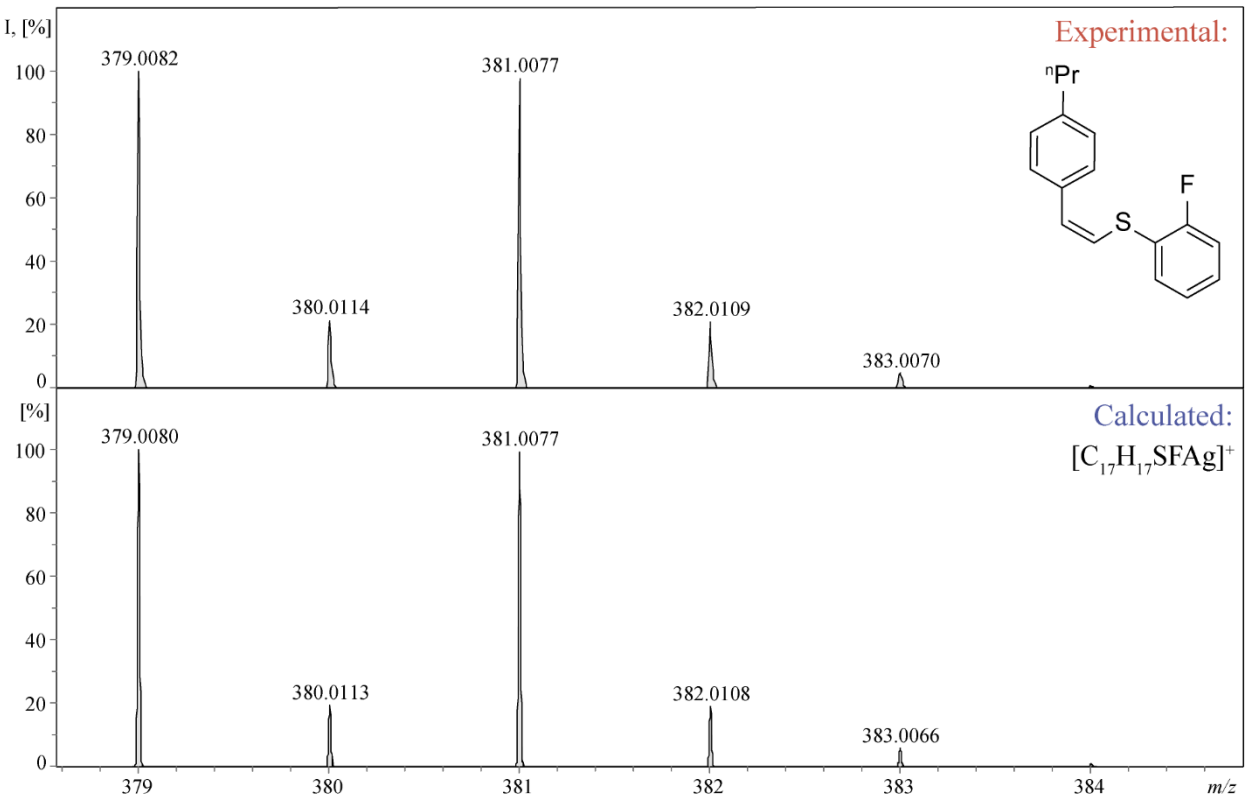


Figure S172. Experimentally detected and theoretical ESI-(+)MS spectrum of **6cb**; main experimental peak $[M+Ag]^+$= 379.0082 Da, calculated for $C_{17}H_{17}SFAg$ = 379.0080 Da, Δ = 0.5 ppm.

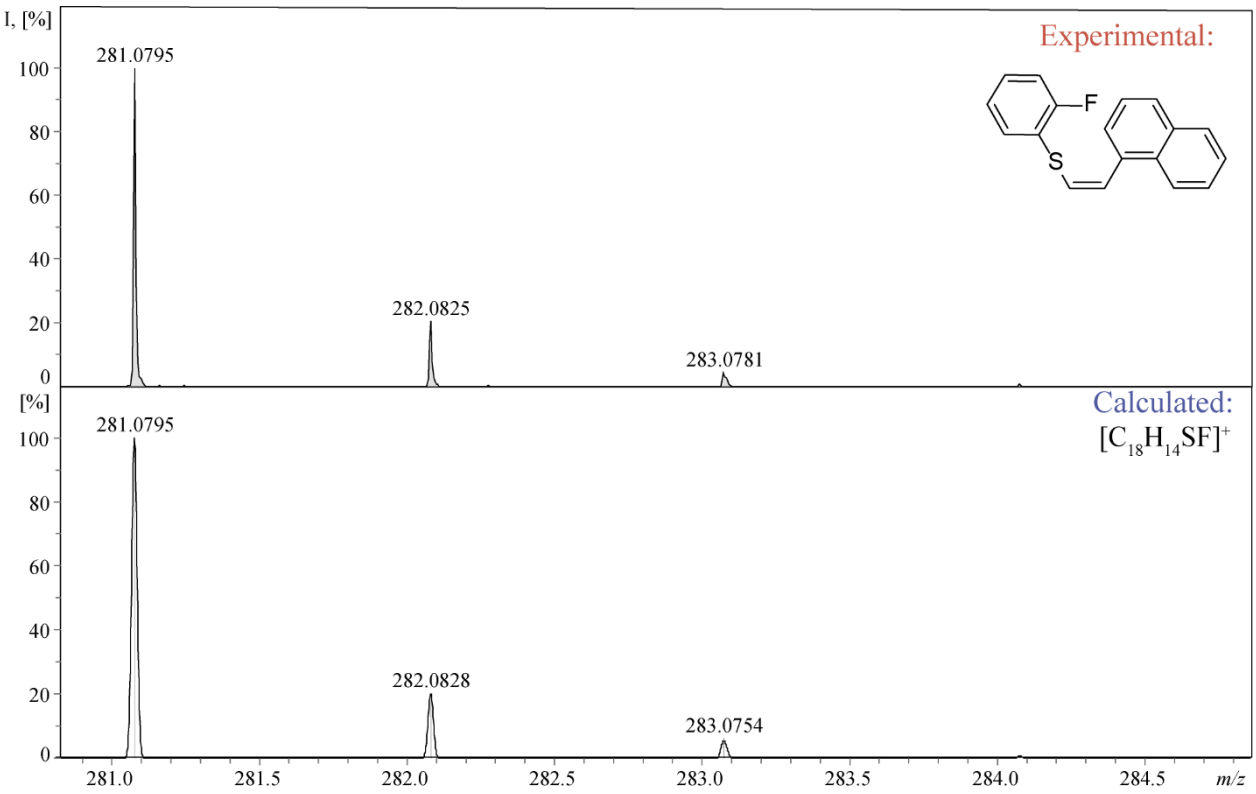


Figure S173. Experimentally detected and theoretical ESI-(+)MS spectrum of **6db**; main experimental peak $[M+H]^+$= 281.0795 Da, calculated for $C_{18}H_{14}SF$ = 281.0795 Da, Δ = 0.0 ppm.

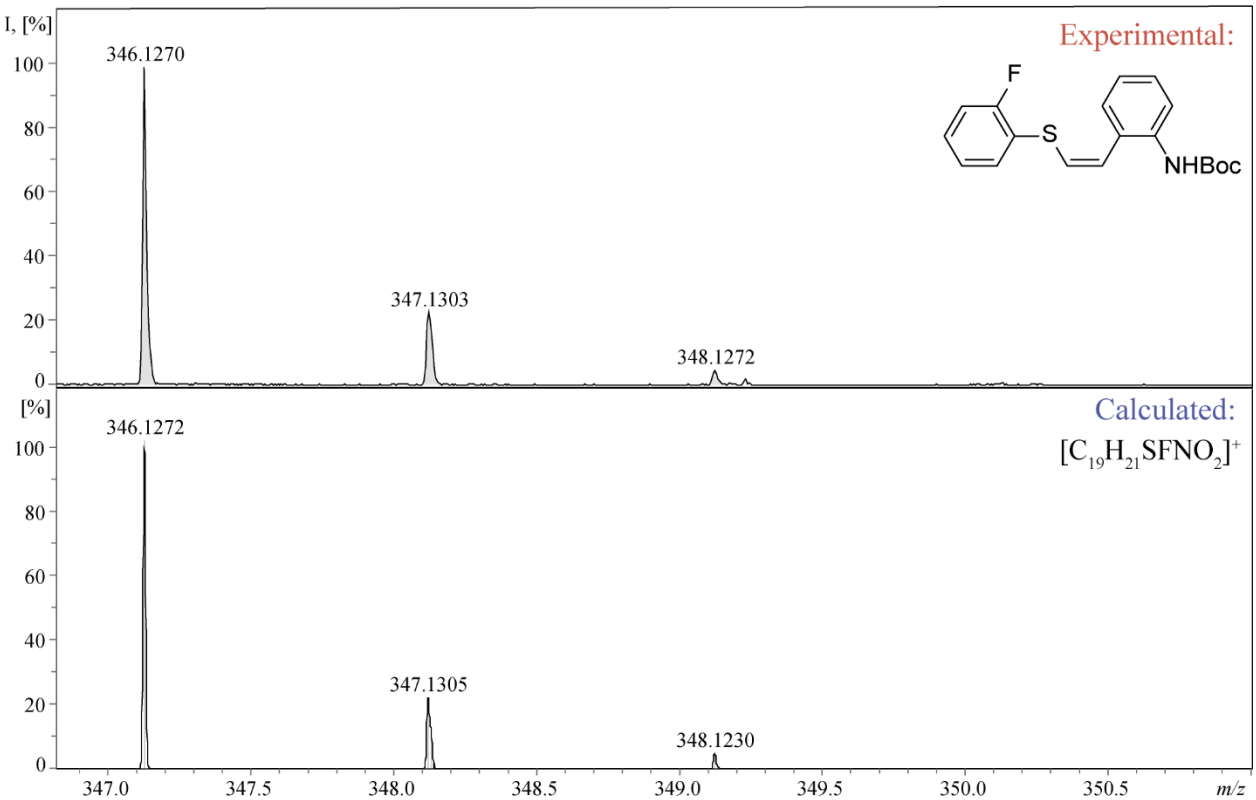


Figure S174. Experimentally detected and theoretical ESI-(+)MS spectrum of **6eb**; main experimental peak $[M+H]^+$= 346.1270 Da, calculated for $C_{19}H_{21}SFNO_2$ = 346.1272 Da, Δ = 0.6 ppm.

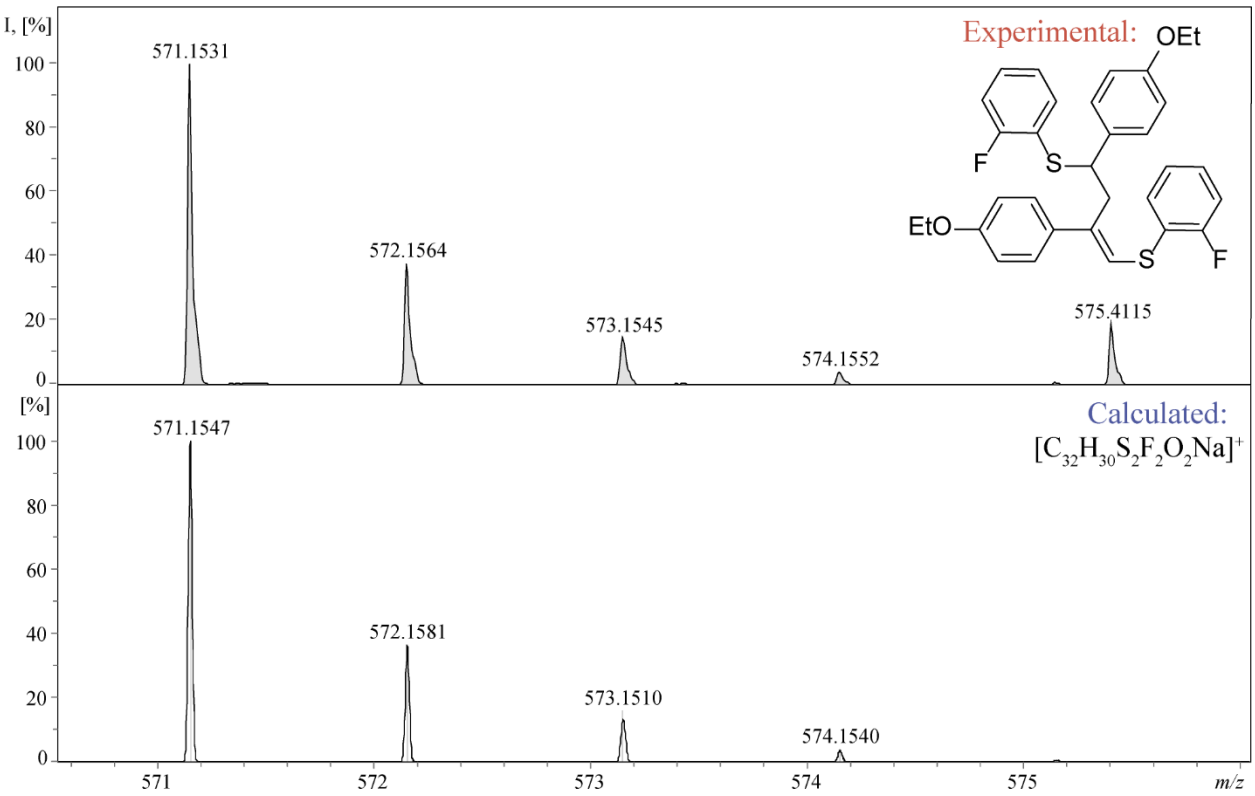


Figure S175. Experimentally detected and theoretical ESI-(+)MS spectrum of **7hb**; main experimental peak $[M+Na]^+$= 571.1631 Da, calculated for $C_{32}H_{30}S_2F_2O_2Na$ = 571.1547 Da, Δ = 2.8 ppm.

[1] K. B. Zou, X. H. Yin, W. Q. Liu, R. H. Qiu, R. X. Li, L. L. Shao, Y. H. Li, X. H. Xu and R. H. Yang, *Synth. Commun.*, 2009, **39**, 2464–2471.

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[3] N. Velasco, C. Virumbrales, R Sanz, S. Suárez-Pantiga, M. Fernández-Rodríguez, *Org. Lett.* **2018** *20*, 2848 – 2852

[4] Ma, Haojie; Ren, Xiaoyu; Zhou, Xiaoqiang; Ma, Chaowei; He, Yongqin; Huang, Guosheng *Tetrahedron Lett*. **2015** *56* 6022 – 6029

[5] K. B. Zou, X. H. Yin, W. Q. Liu, R. H. Qiu, R. X. Li, L. L. Shao, Y. H. Li, X. H. Xu and R. H. Yang, *Synth. Commun.*, **2009**, *39*, 2464–2471.

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