Supporting Information

1,2-Difunctionalization of Acetylene Enabled by Light

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1 General reagent information

All reactions were carried out in flame-dried Schlenk tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under an acetylene atmosphere or nitrogen. A part of the solvent was treated with 4 Å molecular sieves or sodium and distilled before use. All of the other reagents were purchased from Sigma-Aldrich, Alfa Aesar, Bidepharm, Energy Chemical and were used as received. Flash chromatography was performed using glass columns with silica gel (Huanghai, 300-400 mesh).

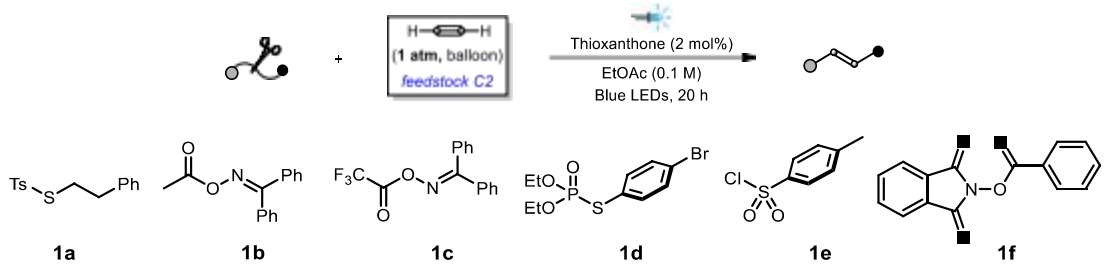
2 General analytical information

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance DPX 600 Fourier Transform spectrometer (400 MHz or 500 MHz respectively). The data of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of the doublet, dt = doublet of triplet), integration, coupling constant (Hz) and assignment. Chemical shifts (ppm) are reported in ppm using TMS as an internal standard and spin-spin coupling constants (*J*) are given in Hz. IR spectra were obtained on a Nicolet iS10 spectrophotometer and reported in terms of frequency of absorption (cm^{-1}) in the potassium bromide (KBr) pellet. High Resolution on mass spectra was obtained from an Agilent 6540 Series Q-TOF system equipped with ESI. Fluorescence spectra were recorded on Hitachi F-4500 fluorescence spectrophotometers. Enantioselectivity was measured by high-performance liquid chromatography (HPLC) using Daicel Chiral columns with *n*-hexane/*i*-PrOH as eluent. Cyclic voltammetry (CV) analysis was performed on Ingsens IGS- 1030 electrochemical workstation (Ingsens Instruments (Guangzhou) Co., Ltd., China) with a conventional three-electrode cell, using a platinum electrode as the working electrode, a Pt wire as counter electrode and saturated calomel electrode (SCE) as a reference electrode. Melting points were determined using a hot stage apparatus. Photochemical experiments have been performed in a Parallel Light Reactor (designed by WATTCAS: WP-TEC- 1020HSL, 10 W, λ_{max} = 425 nm, tube about 2 ~ 5 cm away from lights). The temperature of the reaction was maintained at approximately room temperature with the recirculated water or fans. The reaction setups can be seen below (**Supplementary Figure 1**). Kessil PR160-370 and Kessil PR160-390 lights are used for Gram-scale synthesis. Organic solutions were concentrated under reduced pressure on a Heidolph Hei-VAP rotary evaporator using a water bath. Reactions were monitored by GC-MS analysis, and thin-layer chromatography (TLC) was carried out on 0.20 mm Huanghai silica gel plates (HSGF254) using UV detection under 245 nm as a visualizing agent. X-ray crystallography analysis was performed on Rigaku Oxford Diffraction Supernova Dual Source.

Supplementary Figure 1. Emission spectra of the blue LED light source and picture of the experimental setup used within the project.

3 Optimization of 1,2-difunctionalization of acetylene with bifunctional reagents enabled by photocatalyzed insertion reaction

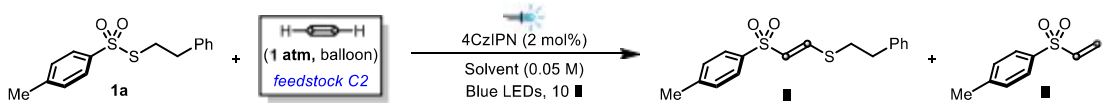
Supplementary Table 1. The screening of a series of potential bifunctional reagents on the 1,2-difunctionalization of acetylene[a]



Entry	Bifunctional reagent	Yield (%)[b]	Thioxanthone
1	**1a**	26	
2	**1b**	nd	
3	**1c**	nd	
4	**1d**	nd	
5	**1e**	nd	
6	**1f**	nd	

[a]Reaction conditions: bifunctional reagent (0. 1 mmol), acetylene gas (a balloon was filled with acetylene gas until its size was roughly 10 cm in diameter), thixanthone (2 mol%), EtOAc (0. 1 M), and irradiated with blue light-emitting diodes (LEDs) for 20 h. [b]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

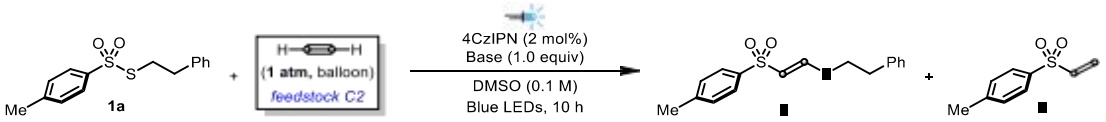
Supplementary Table 2. Effects of solvent on 1,2-difunctionalization of acetylene enabled by photocatalyzed insertion reaction[a]



Entry	solvent	Yield of **3** (%)[b]	Yield of **4** (%)[b]	4CzIPN
1	DMF	trace	n.d.	
2	DMSO	49	32	
3	THF	<10	trace	
4	1,4-Dioxane	16	trace	
5	EtOH	21	trace	
6	DME	trace	trace	
7	DMF/H_2O(100/1)	trace	trace	
8	CAN	50	13	
9	Acetone	27	11	
12	DMSO/H_2O = 10/1	63	n.d.	

[a]Reaction conditions: *S*-phenethyl 4-methylbenzenesulfonothioate (0. 1 mmol), acetylene gas (a balloon was filled with acetylene gas until its size was roughly 10 cm in diameter), solvent (0.05 M) and 4CzIPN (2 mol%), and irradiated with blue light-emitting diodes (LEDs). [b]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

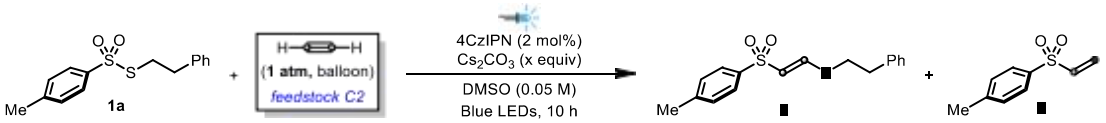
Supplementary Table 3. Effects of base type on 1,2-difunctionalization of acetylene enabled by photocatalyzed insertion reaction[a]



Entry	base	Yield of **3** (%)[b]	Yield of **4** (%)[b]	4CzIPN
1	K_2CO_3	43	16	
2	Cs_2CO_3	65	n.d.	
3	Li_2CO_3	40	21	
4	$NaHCO_3$	23	42	
5	DMAP	31	trace	
6	DIPEA	n.d.	n.d.	
7	TEA	n.d.	n.d.	
8	no	49	23	

[a]Reaction conditions: *S*-phenethyl 4-methylbenzenesulfonothioate (0. 1 mmol), acetylene gas (a balloon was filled with acetylene gas until its size was roughly 10 cm in diameter), base (1.0 equiv .), 4CzIPN (2 mol%) DMSO (0.05 M), and irradiated with blue light-emitting diodes (LEDs). [b]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

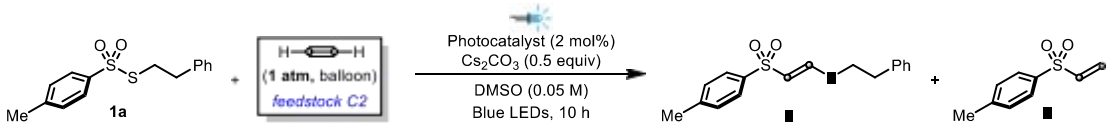
Supplementary Table 4. Effects of base equivalent on 1,2-difunctionalization of acetylene enabled by photocatalyzed insertion reaction[a]



Entry	base (X equiv.)	Yield of **3** (%)[b]	Yield of **4** (%)[b]	4CzIPN
1	0	49	21	
2	0.25	57	14	
3	0.5	65	trace	
4	0.75	63	trace	
5	1.0	66	n.d.	
6	1.25	60	n.d.	

[a]Reaction conditions: *S*-phenethyl 4-methylbenzenesulfonothioate (0. 1 mmol), acetylene gas (a balloon was filled with acetylene gas until its size was roughly 10 cm in diameter), Cs_2CO_3 (x equiv.), 4CzIPN (2 mol%), DMSO (0.05 M), and irradiated with blue light-emitting diodes (LEDs) for 20 h. [b]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

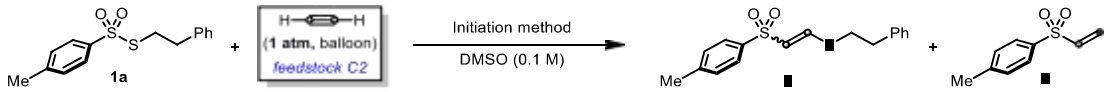
Supplementary Table 5. Effects of photocatalyst on 1,2-difunctionalization of acetylene enabled by photocatalyzed insertion reaction[a]



Entry	photocatalyst	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	[Ir(d(*t*Bu)(CF_3)ppy)$_2$(dtbbpy)](Cl)	49	n.d.
2	Benzophenone	28	12
3	Ru(bpy) $_3$ Cl_2	12	trace
4	$MesAcr^+ ClO_4^-$	n. d.	n. d.
5	TPT	n.d.	n.d.
6	Thioxanthone	34	trace
7	Eosin Y	17	11
8	4CzIPN	65	trace
9	no	trace	trace
10	Dark (26 h)	n.d.	n.d.

[a]Reaction conditions: *S*-phenethyl 4-methylbenzenesulfonothioate (0. 1 mmol), acetylene gas (a balloon was filled with acetylene gas until its size was roughly 10 cm in diameter), Cs_2CO_3 (0.5 equiv.), photocatalyst (2 mol%), DMSO (0.05 M), and irradiation from blue light-emitting diodes (LEDs). [b]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Supplementary Table 6. Effects of other modes of initiation on 1,2-difunctionalization of acetylene[a]

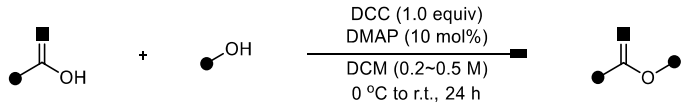


Entry	Initiation standards	Yield of **3** (%)[b]	Yield of **4** (%)[b]	Time/h
1	80 °C	n.d.	n.d.	20
2	AIBN (10 mol%), 80 °C	n.d.	n.d.	20
3	BPO (10 mol%), 90 °C	n.d.	n.d.	22
4	UV	21	11	10
5	Blue LEDs	trace	n.d.	24

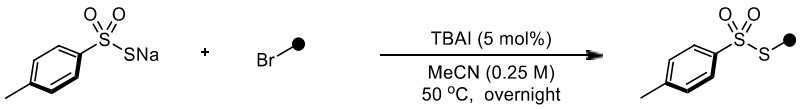
[a]Reaction conditions: *S*-phenethyl 4-methylbenzenesulfonothioate (0.2 mmol), acetylene gas (a balloon was filled with acetylene gas until its size was roughly 10 cm in diameter). [b]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

4 General Procedures and Characterization Data of Substrates

General procedure A:

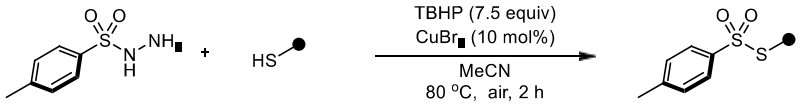


Following a slightly modified procedure[1] : to an oven-dried screw-capped Schlenk tube equipped with a Teflon-coated magnetic stir bar was sequentially added alcohol (1.0 equiv.), *N*,*N*'-dicyclohexylmethanediimine (1.0 equiv.), DMAP (0. 1 equiv.), and DCM (0.2 ~ 0.5 M) under positive N_2 pressure. The reaction mixture was stirred for 2 minutes at 0 °C, then carboxylic acid (1.0 equiv.) was then added in three potions over 2 min. The solution was warmed to room temperature and stirred for another 24 h during which a white precipitate formed. The reaction mixture was filtered through a small pad of silica gel and the precipitate was washed with EA (15 mL). The received crude material was concentrated under reduced pressure and purified by silica gel chromatography to yield the desired product.



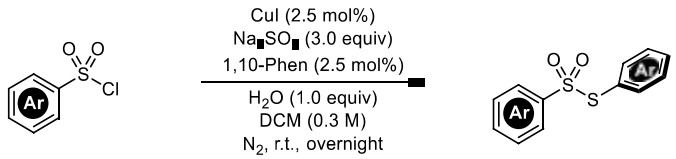
Following a slightly modified procedure[2] : to an oven-dried screw-capped Schlenk tube (25 mL) equipped with a Teflon-coated magnetic stir bar was added alkyl bromide (1.2 equiv),*p*-TolSO_2SNa (1.0 equiv.), and TBAI (5 mol%). MeCN (0.25 M) was then added to give a suspension. After the Schlenk tube was re-capped with a Teflon-screw and placed into a 50 ℃ oil bath and stirred for 12 h under a nitrogen atmosphere. Then the reaction was cooled to room temperature. The mixture was filtered and the residue was washed with EA (10 mL). The combined filtrate was concentrated under reduced pressure, then the residue was purified by flash chromatography on silica gel to afford the desired products.

General procedure B:



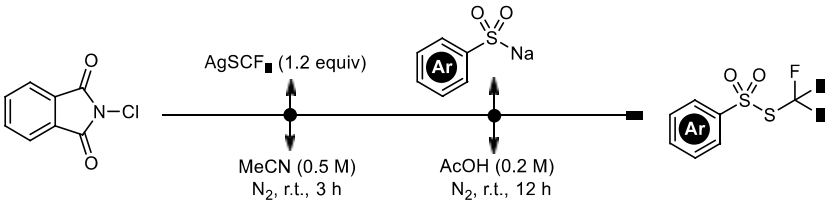
Following the reported procedure[3], an acetonitrile (5 mL) solution of sulfonylhydrazide (1 mmol), thiophenol (2 mmol, 2.0 equiv.), and $CuBr_2$ (0. 1 mmol, 0.1 equiv.) in a two-necked round-bottom flask equipped a magnetic bar and air condenser was added *tert*-butyl hydroperoxide (TBHP 70% solution in water, 7.5 mmol, 7.5 equiv.) dropwise over two minutes. The reaction mixture was stirred at 80 °C for 2 h in air. After the substrates were completely consumed, the solvent was evaporated off and the residue was purified by flash column chromatography to afford the desired thiosulfonates (Warning: Due to peroxides being involved, rigorous work-up is essential for gram-scales synthesis).

General procedure C:



Following a slightly modified procedure[4]: to an oven-dried screw-capped Schlenk tube charged with a magnetic stir bar was added aryl sulfonyl chloride (1.0 equiv.), Na_2SO_3 (3.0 equiv.), CuI (2.5 mol%), and 1,10-Phen (2.5 mol%). The flask was then evacuated and flushed with nitrogen. The degassed DCM (0.2 M) and distilled water (1.0 equiv.) were consecutively added, then the reaction was stirred at room temperature overnight. After being diluted with DCM (20 mL), the mixture was washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated by a rotary evaporator under reduced pressure. The residue was purified by flash chromatography on silica gel to afford thiosulfonates.

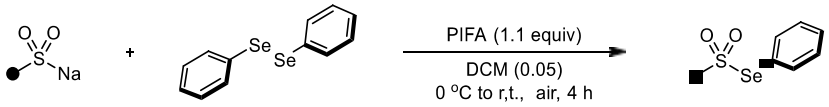
General procedure D:



Following a slightly modified procedure[5]: a mixture of *N*-bromophthalimide (1.81 g, 10 mmol, 1.0 equiv.), $AgSCF_3$ (2.51 g, 12 mmol, 1.2 equiv.) in a 50 mL of screw-capped Schlenk tube was added dried CH_3CN (0.5 M) under nitrogen atmosphere. The mixture was stirred at room temperature for 3 h. Then the solvent was evacuated under a rotary evaporator. The crude product was extracted with DCM (3 × 30 mL) and the combined organic layers were concentrated under a vacuum. The residue was added DCM (10 mL), then filtered through a short plug of silica gel, and washed by EA (10 mL). The filter was evacuated again under reduced pressure to give the title compound. The crude material was carried forward to the next step of reaction without further purification.

According to the literature procedure[6], to an oven-dried screw-capped Schlenk tube with a stir bar was added *N*-trifluoromethylthiophthalimide (247 mg, 1.0 mmol, 1.0 equiv.) and sodium benzenesulfinate (2.0 mmol, 2.0 equiv.). The contents were evacuated and backfilled three times with nitrogen. Glacial acetic acid (0.2 M) was added and the stirred solution was stirred for 2 h at room temperature, protected from light. Then the solvent was evacuated under a rotary evaporator. The crude product was extracted with DCM (3 × 15 mL) and the combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by flash column chromatography on silica gel to afford desired products as a pale-yellow oil.

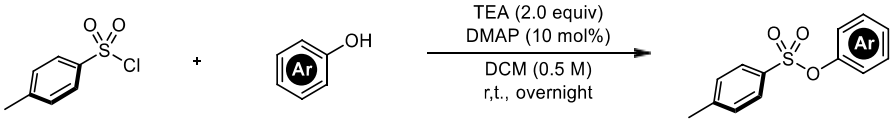
General procedure E:



Following a slightly modified procedure[7]: to an oven-dried 50 mL Teflon-screw capped Schlenk tube equipped with a magnetic stir bar were added sodium benzenesulfinate (4.0 equiv.), diselenides

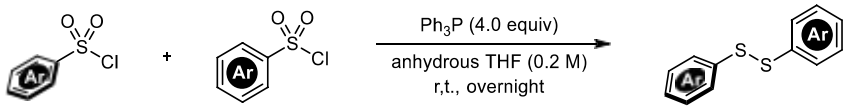
(1.0 equiv.), and DCM (15 mL) was cooled at 0 °C. Then [bis(trifluoroacetoxy)iodo]benzene (1. 1 equiv.) was dissolved in DCM (5 mL) and added dropwise. The Schlenk tube was re-capped with a Teflon-screw. The mixture was warmed to room temperature and stirred for 4 h. After the completion of the reaction, water was added; the organic layer was separated and dried over anhydrous Na_2SO_4 . The solvent DCM was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford desired products.

General procedure F:



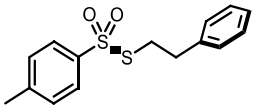
According to the literature procedure[8], an oven-dried 25 mL Teflon-screw capped Schlenk tube equipped with a magnetic stir bar was charged with phenol (5.0 mmol, 1.0 equiv.), DMAP (61 mg, 0.50 mmol, 0.10 equiv.), and triethylamine (1.0 g, 10.0 mmol, 2.0 equiv.). Dry DCM (0.5 M) was added before the Schlenk tube was capped with a rubber septum. The mixture was stirred at rt for 5 min. TsCl (1. 1g, 6.0 mmol, 1.2 equiv.) was then added in three potions over 2 minutes. The Schlenk tube was recapped by Teflon-screw, and the mixture was stirred at rt for 12 h. When the reaction was judged complete by TLC, the reaction mixture was poured into a 250 mL separatory funnel containing water (30 mL) and DCM (30 mL). The dichloromethane layer was set aside while the aqueous layer was washed further with DCM (30 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under a vacuum. The residue was purified by flash column chromatography on silica gel to afford desired products.

General procedure G:



Following a slightly modified procedure[9]: an oven-dried 25 mL Teflon-screw capped Schlenk tube equipped with a magnetic stir bar was charged with triphenylphosphine (2.0 equiv.). Then sulfonyl chloride (1.0 equiv.) was dissolved in THF (0.2 M) and added dropwise over 2 minutes. The Schlenk tube was recapped by Teflon-screw, and the mixture was stirred at rt overnight. After completion of the reaction, the solvent was removed under reduced pressure and the residue was dissolved in EA. To this solution, hexane (60 mL) was added dropwise and the byproduct triphenylphosphine oxide was precipitated and was removed by filtration. Concentration of the filtrate under reduced pressure and silica gel column chromatography using petroleum ether as eluant yielded the desired products.

***S*-Phenethyl 4-methylbenzenesulfonothioate (1a)**

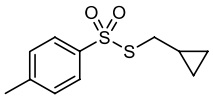


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (891 mg, 5.0 mmol, 1.0 equiv.), (2-bromoethyl)benzene (1.1 g, 6.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (92 mg, 0.25 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent:

petroleum ether/ethyl acetate = 10/1) afforded the title compound as a yellowish oil (1.04 g, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J*= 8.1 Hz, 2H), 7.34 – 7.22 (m, 3H), 7.13 (d, *J* = 6.9 Hz, 2H), 3.31 – 3.15 (t, 2H), 2.98 – 2.90 (t, 2H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.9, 142. 1, 138.8, 129.9, 128.7, 128.6, 127. 1, 126.9, 37.2, 35.2, 21.7; **IR** (KBr, cm^{-1}) 3660, 2953, 2830, 2717, 1598, 1363, 1137, 1084, 774, 585, 526; **HRMS** (ESI) calcd. $C_{15}H_{16}NaO_2S_2^+$ $[M+Na]^+$ m/z 315.0484, found: 315.0485.

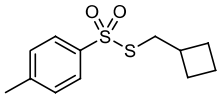
***S*-(Cyclopropylmethyl) 4-methylbenzenesulfonothioate (7a)**



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (891 mg, 5.0 mmol, 1.0 equiv.), (bromomethyl)cyclopropane (810 mg, 6.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (92 mg, 0.25 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a colorless oil (1.08 g, 89% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.95 (d, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 0.97 (tt, *J* = 7.7, 4.8 Hz, 1H), 0.56 (t, *J* = 6.3 Hz, 2H), 0.39 – 0.13 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 142.2, 129.8, 127.0, 42.0, 21.7, 9.8, 6.2; **IR** (KBr, cm^{-1}) 2829, 1633, 1593, 1363, 1142, 733, 655, 589; **HRMS** (ESI) calcd. $C_{11}H_{14}NaO_2S_2^+$ $[M+Na]^+$ m/z 265.0327, found: 265.0334.

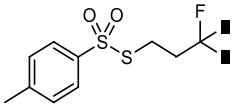
***S*-(Cyclobutylmethyl) 4-methylbenzenesulfonothioate (8a)**



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (891 mg, 5.0 mmol, 1.0 equiv.), (bromomethyl)cyclopropane (894 mg, 6.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (92 mg, 0.25 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a white solid (461 mg, 36% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.08 (d, *J* = 7.7 Hz, 2H), 2.64 – 2.49 (m, 1H), 2.47 (s, 3H), 2.15 – 2.01 (m, 2H), 1.92 – 1.77 (m, 2H), 1.71 – 1.60 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.6, 142.2, 129.8, 127.0, 42. 1, 34.0, 27.6, 21.7, 17.7; **IR** (KBr, cm^{-1}) 3751, 2830, 1633, 1591, 1362, 1325, 1142, 744, 655, 588, 521; **Mp**: 38.7 – 39.8 °C; **HRMS** (ESI) calcd. $C_{12}H_{16}NaO_2S_2^+$ $[M+Na]^+$ m/z 279.0484, found: 279.0493.

***S*-(3,3,3-Trifluoropropyl) 4-methylbenzenesulfonothioate (9a)**

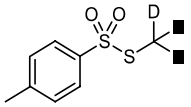


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (891 mg, 5.0 mmol, 1.0 equiv.), 1,1,1-trifluoro-3-iodopropane (1.34 g, 6.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (92 mg, 0.25 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a colorless oil (854 mg, 60%

yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J*= 8.1 Hz, 2H), 3.16 – 2.94 (m, 2H), 2.63 – 2.50 (m, 2H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.5, 141. 1, 130. 1, 127.2, 125.5 (q, ^1J =277.8), 34.2 (q, ^2J =29.3), 27.7 (q, ^3J =4.0), 21.7; **^{19}F NMR** (376 MHz, Chloroform-d) δ -66.5, -66.5, -66.6; **IR** (KBr, cm^{-1}) 2673, 2830, 2716, 1596, 1363, 1363, 1084, 774, 530; **HRMS** (ESI) calcd. $C_{10}H_{11}F_3NaO_2S_2^+$ $[M+Na]^+$ m/z 307.0045, found: 307.0041.

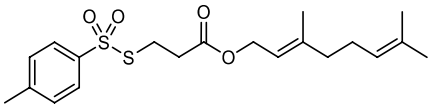
_S_-(Methyl-_d_$_3$) 4-methylbenzenesulfonothioate (10a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), iodomethane-d_3 (435 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a white solid (323 mg, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.5, 144. 1, 138.3, 129.9, 127.4, 121.6, 21.6; **HRMS** (ESI) calcd. $C_8H_7D_3NaO_2S_2^+$ $[M+Na]^+$ m/z 228.0203, found: 228.0206. The analytical datas are in agreement with the literature[10].

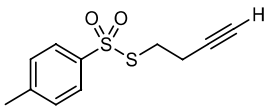
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 3-(tosylthio)propanoate (11a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), (*E*)-3,7-dimethylocta-2,6-dien- 1-yl 3-bromopropanoate (868 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 8/1) afforded the title compound as a colorless oil (763 mg, 77% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.32 (t, *J* = 7.2 Hz, 1H), 5.09 (t, *J* = 7.4 Hz, 1H), 4.61 (d, *J* = 7.1 Hz, 2H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.0 Hz, 2H), 2.47 (s, 3H), 2.09 (dt, *J* = 14.0, 6.7 Hz, 4H), 1.70 (d, *J* = 3.3 Hz, 6H), 1.62 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.0, 144.9, 142.8, 141.8, 131.9, 129.9, 127. 1, 123.7, 117.8, 61.9, 39.5, 34.2, 30.6, 26.3, 25.7, 21.6, 17.7, 16.5; **IR** (KBr, cm^{-1}) 2831, 2716, 1594, 1364, 1138, 774, 532; **HRMS** (ESI) calcd. $C_{20}H_{28}NaO_4S_2^+$ $[M+Na]^+$ m/z 419.1321, found: 419.1327.

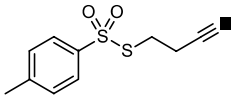
_S_-(But-3-yn-1-yl) 4-methylbenzenesulfonothioate (12a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 4-bromobut- 1-yne (399 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a colorless oil (415 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.55 (td, *J* = 7.3, 2.6 Hz, 2H), 2.47 (s, 3H), 2.03 (t, *J* = 2.6 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145. 1, 141.8, 130.0, 127. 1, 80.9, 70.6, 34.5, 21.7, 19.4; **IR** (KBr, cm^{-1}) 3751, 3647, 3612, 2830, 1599, 1363, 1138, 1083, 744, 529; **HRMS** (ESI) calcd. $C_{11}H_{12}NaO_2S_2^+$ $[M+Na]^+$ m/z 263.0171, found: 263.0178.

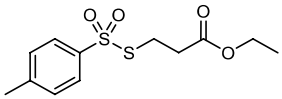
***S*-(2-Cyanoethyl) 4-methylbenzenesulfonothioate (13a)**



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropanenitrile (402 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as a light yellow liquid (495 mg, 82% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 7.1 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.8, 141.0, 130.3, 127. 1, 117.4, 31.0, 21.7, 18.5; **IR** (KBr, cm^{-1}) 3750, 3673, 2830, 1539, 1363, 1141, 774, 588, 529; **HRMS** (ESI) calcd. $C_{10}H_{11}NNaO_2S_2^+$ $[M+Na]^+$ m/z 264.0123, found: 264.0129.

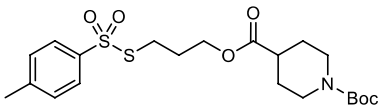
Ethyl 3-(tosylthio)propanoate (14a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), ethyl 3-bromopropanoate (543 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 6/1) afforded the title compound as a colorless oil (634 mg, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.0, 145.0, 141.7, 130.0, 127. 1, 61.0, 34. 1, 30.6, 21.7, 14. 1; **IR** (KBr, cm^{-1}) 3746, 3672, 2830, 2716, 1600, 1363, 1140, 1083, 774, 655, 587, 526; **Mp**: 39.8 – 38.4 °C; **HRMS** (ESI) calcd. $C_{12}H_{16}NaO_4S_2^+$ $[M+Na]^+$ m/z 311.0382, found: 311.0389.

1-(*tert*-Butyl) 4-(3-(tosylthio)propyl) piperidine-1,4-dicarboxylate (15a)

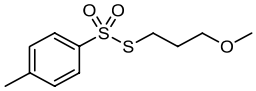


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 4-(3-bromopropyl) 1-(*tert*-butyl) piperidine- 1,4-dicarboxylate (1.05 g, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a colorless oil (1.04 g, 91% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 4.02 (d, *J* = 6.0 Hz, 2H), 3.93 (d, *J* = 13.5 Hz, 1H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 11.7 Hz, 2H), 2.46 –

2.22 (m, 4H), 1.91 (ddd, *J* = 13.2, 7.2, 6.0 Hz, 2H), 1.77 (dt, *J* = 12. 1, 3.7 Hz, 2H), 1.51 (dtd, *J* = 13.4, 11.2, 4.4 Hz, 2H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.2, 154.6, 145.0, 141.7, 129.9, 126.9, 79.5, 79.5, 62.3, 40.9, 32.5, 28.4, 28. 1, 27.9, 21.6; **IR** (KBr, cm^{-1}) 2952, 2830, 2716, 1731, 1598, 1363, 1141, 1079, 744, 653, 587, 524; **HRMS** (ESI) calcd. $C_{21}H_{31}NNaO_6S_2^+$ $[M+Na]^+$ m/z 480.1485, found: 480.1486.

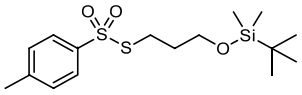
***S*-(3-Methoxypropyl) 4-methylbenzenesulfonothioate (16a)**



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 1-bromo-3-methoxypropane (459 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a light yellow oil (605 mg, 93% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.38 (t, *J* = 5.8 Hz, 2H), 3.28 (s, 3H), 3.07 (t, *J*= 7.1 Hz, 2H), 2.46 (s, 3H), 1.90 (tt, *J* = 7.7, 6.1 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 141.9, 129.9, 127.0, 70.2, 58.6, 32.9, 28.9, 21.6; **IR** (KBr, cm^{-1}) 3750, 3672, 2830, 2716, 1600, 1363, 1141, 1117, 1079, 744, 655, 589, 521; **HRMS** (ESI) calcd. $C_{11}H_{16}NaO_3S_2^+$ $[M+Na]^+$ m/z 283.0433, found: 283.0440.

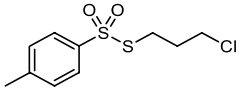
***S*-(3-((Tert-butyldimethylsilyl)oxy)propyl) 4-methylbenzenesulfonothioate (17a)**



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), (3-bromopropoxy)(*tert*-butyl)dimethylsilane (459 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 50/1) afforded the title compound as a colorless oil (563 mg, 89% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 5.7 Hz, 2H), 3.16 – 2.96 (m, 2H), 2.45 (s, 3H), 1.95 – 1.65 (m, 2H), 0.86 (s, 9H), 0.01 (s, 6H).; **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 141.9, 129.8, 127. 1, 60.8, 32.8, 31.6, 25.9, 21.6, 18.2, -5.4; **IR** (KBr, cm^{-1}) 2950, 2831,2716, 1600, 1363, 1081, 775, 586, 528; **HRMS** (ESI) calcd. $C_{16}H_{29}O_3S_2Si^+$ $[M+H]^+$ m/z 361.1322, found: 361.1325.

***S*-(3-Chloropropyl) 4-methylbenzenesulfonothioate (18a)**

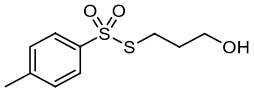


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 1-bromo-3-chloropropane (471 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a colorless oil (576 mg, 87% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.4, 1.9 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.55

(t, *J* = 6. 1, 1.8 Hz, 2H), 3.12 (t, *J* = 7.0, 1.6 Hz, 2H), 2.44 (s, 3H), 2.19 – 2.00 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-d) δ 145. 1, 141.6, 130.0, 127. 1, 42.9, 33.0, 31.4, 21.7; **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145. 1, 141.6, 130.0, 127. 1, 42.9, 33.0, 31.4, 21.7; **IR** (KBr, cm^{-1}) 2831, 2717, 1604, 1365, 1082, 775, 532; **HRMS** (ESI) calcd. $C_{10}H_{13}ClNaO_2S_2^+$ $[M+Na]^+$ m/z 286.9938, found: 286.9931.

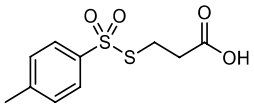
***S*-(3-Hydroxypropyl) 4-methylbenzenesulfonothioate (19a)**



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropan- 1-ol (417 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 2/1) afforded the title compound as a colorless oil (449 mg, 73% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 3.67 (t, *J* = 5.8 Hz, 2H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 2.22 (s, 1H), 2.01 – 1.75 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.0, 141.7, 129.9, 127.0, 60.2, 32.5, 31.5, 21.7; **IR** (KBr, cm^{-1}) 3647, 2948, 2830, 2716, 1599, 1364, 1324, 1139, 1077, 744, 655, 589, 521; **HRMS** (ESI) calcd. $C_{10}H_{14}NaO_3S_2^+$ $[M+Na]^+$ m/z 269.0277, found: 269.0284.

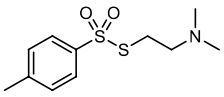
3-(Tosylthio)propanoic acid (20a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropanoic acid (459 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 1/1) afforded the title compound as a white solid (599 mg, 92% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.18 (t, *J* = 6.9 Hz, 2H), 2.78 (t, *J* = 6.9 Hz, 2H), 2.46 (s, 2H), 2.10 (d, *J* = 0.8 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.7, 145.2, 141.5, 130. 1, 127. 1, 33.9, 30. 1, 21.7; **IR** (KBr, cm^{-1}) 2951, 2831, 2716, 1600, 1364, 1138, 1079, 775, 656, 587, 525; **Mp**: 57.1 – 59.8 °C; **HRMS** (ESI) calcd. $C_{10}H_{12}NaO_4S_2^+$ $[M+Na]^+$ m/z 283.0069, found: 283.0073.

***S*-(2-(Dimethylamino)ethyl) 4-methylbenzenesulfonothioate (21a)**

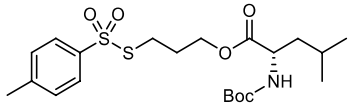


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 2-bromo-*N*,*N*-dimethylethan- 1-amine (456 mg, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as light yellow oil (253 mg, 39% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.10 (t, *J*

= 6.8 Hz, 2H), 2.54 (t, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 2.18 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 141.9, 129.8, 127.0, 57.4, 45.0, 34. 1, 21.6; **IR** (KBr, cm^{-1}) 3748, 2948, 2830, 2716, 1597, 1363, 1140, 1079, 774, 655, 588, 524; **HRMS** (ESI) calcd. $C_{11}H_{18}NO_2S_2^+$ $[M+H]^+$ m/z 260.0773, found: 260.0779.

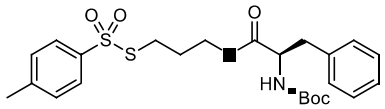
3-(Tosylthio)propyl (*tert*-butoxycarbonyl)-*L*-leucinate (22a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl (*tert*-butoxycarbonyl)-*L*-leucinate (969 mg, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as a colorless oil (873 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.99 (d, *J* = 8.6 Hz, 1H), 4.19 (dd, *J* = 9.8, 4.4 Hz, 1H), 4.08 (t, *J* = 6.0 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.95 (p, *J* = 6.7 Hz, 2H), 1.63 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.56 – 1.39 (m, 2H), 1.37 (d, *J* = 1.3 Hz, 9H), 0.88 (dd, *J* = 6.6, 2.5 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.3, 155.4, 144.9, 141.7, 129.9, 127.0, 79.7, 62.8, 52. 1, 41.4, 32.4, 28.3, 28. 1, 24.7, 22.8, 21.8, 21.6; **IR** (KBr, cm^{-1}) 2830, 2715, 1599, 1364, 1132,774, 534; **HRMS** (ESI) calcd. $C_{21}H_{33}NNaO_6S_2^+$ $[M+Na]^+$ m/z 482.1642, found: 482.1645.

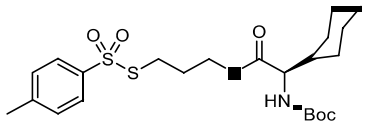
3-(Tosylthio)propyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate (23a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate (1.06 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as a colorless oil (1.0 g, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.12 (d, *J* = 6.6 Hz, 2H), 5.01 (d, *J* = 8.4 Hz, 1H), 4.53 (q, *J* = 7.0 Hz, 1H), 4.09 (td, *J* = 6.0, 2.0 Hz, 2H), 3.04 (d, *J* = 6.5 Hz, 2H), 2.87 (td, *J* = 7.2, 1.4 Hz, 2H), 2.46 (s, 3H), 1.92 (td, *J* = 6.5, 4.1 Hz, 2H), 1.43 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.8, 155. 1, 145.0, 141.8, 135.9, 130.0, 129.3, 129.2, 128.6, 127. 1, 127. 1, 80. 1, 63.0, 54.6, 38.5, 32.3, 28.3, 28. 1, 21.7; **IR** (KBr, cm^{-1}) 2830, 1601,1364, 1081, 774, 532; **HRMS** (ESI) calcd. $C_{24}H_{31}NNaO_6S_2^+$ $[M+Na]^+$ m/z 516.1485, found: 516.1475.

3-(Tosylthio)propyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate (24a)

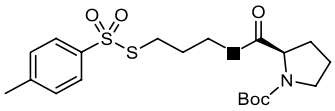


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate (1.0 g, 2.75

mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as light yellow oil (838 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.01 (d, *J* = 9.1 Hz, 1H), 4.12 (t, *J* = 6.1 Hz, 3H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.14 – 1.84 (m, 2H), 1.85 – 1.49 (m, 6H), 1.42 (s, 9H), 1.30 – 0.77 (m, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.2, 155.6, 145.0, 141.8, 129.9, 127.0, 79.8, 77.4, 62.8, 58.3, 40.9, 32.4, 29.5, 28.3, 28.2, 28. 1, 25.9, 21.6; **IR** (KBr, cm^{-1}) 3673, 2952, 2830, 2716, 1600, 1363, 1084, 774, 530; **HRMS** (ESI) calcd. $C_{23}H_{35}NO_6S_2^+$ $[M+Na]^+$ m/z 508.1798, found: 508.1802.

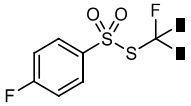
1-(*tert*-Butyl) 2-(3-(tosylthio)propyl) (*R*)-pyrrolidine-1,2-dicarboxylate (25a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 2-(3-bromopropyl) 1-(*tert*-butyl) (*R*)-pyrrolidine- 1,2-dicarboxylate (1.0 g, 3.0 mmol, 1.2 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 3/1) afforded the title compound as a colorless oil (798 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 5.7 Hz, 2H), 4.30 – 3.89 (m, 3H), 3.56 – 3.18 (m, 2H), 3.07 – 2.90 (m, 2H), 2.37 (s, 3H), 2.19 – 1.99 (m, 1H), 1.99 – 1.64 (m, 6H), 1.33 (d, *J* = 21.8 Hz, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.9, 172.7, 154.3, 153.6, 145.0, 144.9, 141.8, 141.7, 129.9, 129.9, 126.9, 79.7, 79.7, 62.6, 62.5, 59.0, 58.8, 46.5, 46.3, 32.4, 30.8, 29.9, 28.3, 28.3, 28. 1, 24.3, 23.6, 21.6; **IR** (KBr, cm^{-1}) 2831, 1601, 1364, 1139, 775; **HRMS** (ESI) calcd. $C_{20}H_{29}NNaO_6S_2^+$ $[M+Na]^+$ m/z 466.1329, found: 466.1324.

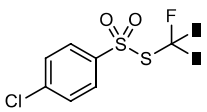
***S*-(Trifluoromethyl) 4-fluorobenzenesulfonothioate (26a)**



Prepared according to the general procedure **D**, sodium 4-fluorobenzenesulfinate (728 mg, 4.0 mmol, 2.0 equiv.), 2-((trifluoromethyl)thio)isoindoline- 1,3-dione (494 mg, 2.0 mmol, 1.0 equiv.), and AcOH (0.2 M) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a colorless oil (328 mg, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.88 (m, 2H), 7.42 – 7.11 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.7, 165.1, 140.6, 130.8 (d, ^3J =10. 1), 127.2 (q, ^1J =314. 1), 117.1 (d, ^2J =23.2); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -38.4, -38.5, -38.6, -99.8. The analytical datas are in agreement with the literature[11] .

***S*-(Trifluoromethyl) 4-chlorobenzenesulfonothioate (27a)**

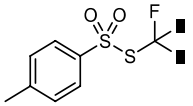


Prepared according to the general procedure **D**, sodium 4-chlorobenzenesulfinate (397 mg, 2.0 mmol, 2.0 equiv.), 2-((trifluoromethyl)thio)isoindoline- 1,3-dione (247 mg, 1.0 mmol, 1.0 equiv.), and AcOH (0.2 M) were used. Purification by column chromatography (Eluent: petroleum

ether/ethyl acetate = 50/1) afforded the title compound as a yellow oil (144 mg, 52% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.9, 141. 1, 129.0, 128. 1, 126.2 (q, ^1J =313.4); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -38.4. The analytical datas are in agreement with the literature[12] .

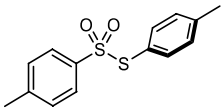
***S*-(Trifluoromethyl) 4-methylbenzenesulfonothioate (28a)**



Prepared according to the general procedure **D**, sodium 4-methylbenzenesulfinate (712 mg, 4.0 mmol, 2.0 equiv.), 2-((trifluoromethyl)thio)isoindoline- 1,3-dione (494 mg, 2.0 mmol, 1.0 equiv.), and AcOH (0.2 M) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a colorless oil (343 mg, 67% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 2.51 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 141.8, 141.8, 130.2, 127.7, 21.8; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -38.5; **HRMS** (ESI) calcd. $C_8H_7F_3NaO_2S_2^+$ $[M+Na]^+$ m/z 278.9732, found: 278.9729. The analytical datas are in agreement with the literature[13] .

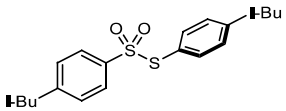
***S*-(*p*-Tolyl) 4-methylbenzenesulfonothioate (29a)**



Prepared according to the general procedure **C**, 4-methylbenzenesulfonyl chloride (1.90 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (988 mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 8.9 Hz, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 142. 1, 140.4, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5; **HRMS** (ESI) calcd. $C_{14}H_{14}NaO_2S_2^+$ $[M+Na]^+$ m/z 301.0327, found: 301.0323. The analytical datas are in agreement with the literature[14] .

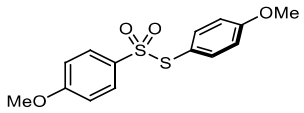
***S*-(4-(*tert*-Butyl)phenyl) 4-(*tert*-butyl)benzenesulfonothioate (30a)**



Prepared according to the general procedure **C**, 4-(*tert*-butyl)benzenesulfonyl chloride (2.33 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (1.16 g, 64% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 9H), 1.33 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.6, 155.0, 140.2, 136.3, 127.5, 126.5, 125.7, 124.7, 35.3, 34.9, 31.2, 31.1; **HRMS** (ESI) calcd. $C_{20}H_{26}NaO_2S_2^+$ $[M+Na]^+$ m/z 385.1266, found: 385.1262. The analytical datas are in agreement with the literature[14] .

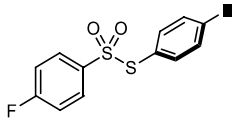
***S*-(4-Methoxyphenyl) 4-methoxybenzenesulfonothioate (31a)**



Prepared according to the general procedure **C**, 4-methoxybenzenesulfonyl chloride (2.06 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (589 mg, 38% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 9.0 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 6.87 (dd, *J* = 12.0, 8.9 Hz, 4H), 3.87 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.6, 162.3, 138.4, 134.9, 129.9, 118.9, 114.9, 113.9, 55.8, 55.5; **HRMS** (ESI) calcd. $C_{14}H_{14}NaO_4S_2^+$ $[M+Na]^+$ m/z 333.0226, found: 333.0234. The analytical datas are in agreement with the literature[14].

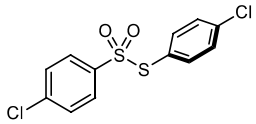
***S*-(4-Fluorophenyl) 4-fluorobenzenesulfonothioate (32a)**



Prepared according to the general procedure **C**, 4-fluorobenzenesulfonyl chloride (1.94 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (1.03 g, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.38 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 8.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.5 (d, ^2J = 74.9 Hz), 164.0 (d, ^2J = 71.9 Hz), 138.9 (d, ^3J = 9.2 Hz), 130.5 (d, ^3J = 9.7 Hz), 123.3 (d, ^3J = 3.5 Hz), 117.0 (d, ^2J = 22.3 Hz), 116.2 (d, ^2J = 22.9 Hz); **HRMS** (ESI) calcd. $C_{12}H_8F_2NaO_2S_2^+$ $[M+Na]^+$ m/z 308.9826, found: 308.9822. The analytical datas are in agreement with the literature[14].

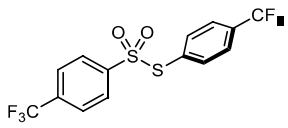
***S*-(4-Chlorophenyl) 4-chlorobenzenesulfonothioate (33a)**



Prepared according to the general procedure **C**, 4-chlorobenzenesulfonyl chloride (2.11 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (1.0 g, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.35 (q, *J* = 8.7 Hz, 4H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.3, 140.6, 138.6, 137.7, 129.9, 129.3, 129.0, 126.0; **HRMS** (ESI) calcd. $C_{12}H_8C_{l2}NaO_2S_2^+$ $[M+Na]^+$ m/z 340.9235, found: 340.9241. The analytical datas are in agreement with the literature[14].

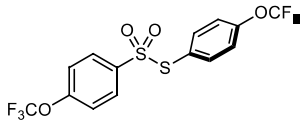
***S*-(4-(Trifluoromethyl)phenyl) 4-(trifluoromethyl)benzenesulfonothioate (34a)**



Prepared according to the general procedure **C**, 4-(trifluoromethyl)benzenesulfonyl chloride (2.44 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (966 mg, 50% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (s, 4H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146. 1, 136.7, 135.5 (q, ^2J =33.3 Hz), 133.6 (q, ^2J =33. 1 Hz), 131.7, 128.0, 126.5, 126.5 (q, ^3J =4.0 Hz), 126.3 (q, ^3J =3.7 Hz), 123.4 (d, ^1J =274.7 Hz), 123.0 (d, ^1J = 273.7 Hz); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.2, -63.3; **HRMS** (ESI) calcd. $C_{14}H_8F_6NaO_2S_2^+$ $[M+Na]^+$ m/z 386.9943, found: 386.9940. The analytical datas are in agreement with the literature[14].

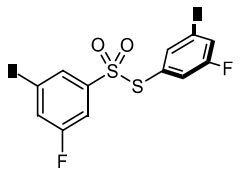
***S*-(4-(Trifluoromethoxy)phenyl) 4-(trifluoromethoxy)benzenesulfonothioate (35a)**



Prepared according to the general procedure **C**, 4-(trifluoromethoxy)benzenesulfonyl chloride (2.60 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a colorless oil (314 mg, 15% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.9 (d, ^3J = 2.5 Hz), 151.8 (d, ^3J= 2.5 Hz), 140.7, 138.3, 129.8, 125.9, 121.5, 120.6, 120.2 (q, ^1J = 259.6 Hz), 120.2 (q, ^1J = 260.8 Hz); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.8, -57.9; **IR** (KBr, cm^{-1}) 2830, 2717, 2597, 1364, 1084, 774, 534; **HRMS** (ESI) calcd. $C_{14}H_8F_6NaO_4S_2^+$ $[M+Na]^+$ m/z 440.9663, found: 440.9663. The analytical datas are in agreement with the literature[14].

***S*-(3,5-Difluorophenyl) 3,5-difluorobenzenesulfonothioate (36a)**

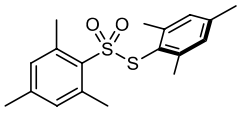


Prepared according to the general procedure **C**, 3,5-difluorobenzenesulfonyl chloride (2. 12 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a light yellow solid (853 mg, 53% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7 7.23 – 7.17 (m, 2H), 7.12 (tt, *J* = 8.3, 2.3 Hz, 1H), 7.03

(dp, *J* = 5. 1, 2.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.4 (dd, *J* = 28.8, 12.0 Hz), 162.9 – 161.1 (m), 146.03, 144.0 (t, *J* = 8.1 Hz), 132.3 (t, *J* = 9.9 Hz), 123.3, 117.5 – 114.9 (m), 112.0 – 110.4 (m), 109.1 (t, *J* = 25.0 Hz), 105.9 (t, *J* = 25.0 Hz); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ - 104.5, - 106.5; **IR** (KBr, cm^{-1}) 3747, 2830, 1597, 1364, 1132, 744; **Mp**: 59.7 – 63.1 °C; **HRMS** (ESI) calcd. $C_{12}H_7F_4O_2S_2^+$ $[M+H]^+$ m/z 322.9818, found: 322.9819.

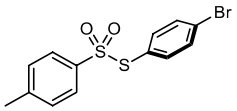
***S*-Mesityl 2,4,6-trimethylbenzenesulfonothioate (37a)**



Prepared according to the general procedure **C**, 2,4,6-trimethylbenzenesulfonyl chloride (2. 18 g, 10 mmol, 1.0 equiv.), Na_2SO_3 (3.78 g, 30 mmol, 3.0 equiv.), CuI (48 mg, 2.5 mmol, 2.5 mol%) 1,10-Phen (45 mg, 2.5 mmol, 2.5 mol%), and distilled water (180 uL, 10 mmol, 1.0 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (719 mg, 43% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.89 (d, *J* = 4.8 Hz, 4H), 2.36 (s, 6H), 2.29 (d, *J* = 9.7 Hz, 6H), 2.15 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.3, 143.6, 141.9, 139.7, 139.4, 132.0, 129.5, 123.3, 22.7, 21.5, 21.3, 21.1; **IR** (KBr, cm^{-1}) 3749, 3673, 2830, 2715, 1596, 1363, 1137, 774; **Mp**: 130.1 – 132.0 °C; **HRMS** (ESI) calcd. $C_{18}H_{22}NaO_2S_2^+$ $[M+Na]^+$ m/z 357.0953, found: 357.0951.

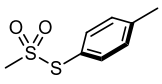
***S*-(4-Bromophenyl) 4-methylbenzenesulfonothioate (38a)**



Prepared according to the general procedure **B**, 4-methylbenzenesulfonohydrazide (931 mg, 5 mmol, 1.0 equiv.), 4-bromobenzenethiol (1.89 g, 10 mmol, 2.0 equiv.), $CuBr_2$ (111 mg, 0.5 mmol, 0.1 equiv.), *tert*-butyl hydroperoxide (TBHP 70% solution in water, 37.5 mmol, 7.5 equiv.), and CH_3CN (25 mL) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (840 mg, 49% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 3.6 Hz, 2H), 7.47 (d, *J* = 3.5 Hz, 2H), 7.24 (t, *J* = 8.2 Hz, 4H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145. 1, 140. 1, 137.9, 132.7, 129.6, 127.6, 127. 1, 126.7, 21.7; **HRMS** (ESI) calcd. $C_{13}H_{11}BrNaO_2S_2^+$ $[M+Na]^+$ m/z 364.9276, found: 364.9272. The analytical datas are in agreement with the literature[3].

***S*-*p*-Tolyl methanesulfonothioate (39a)**

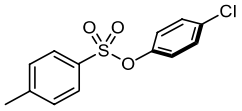


To an oven-dried screw-capped Schlenk tube (25 mL) equipped with a Teflon-coated magnetic stir bar was added sodium methanesulfinate (326 mg, 3.2 mmol, 3.2 equiv.), 1,2-di-*p*-tolyldisulfane (246 mg, 1.0 mmol, 1.0 equiv.), and DCM (5 mL). I_2 (508 mg, 2.0 mmol, 2.0 equiv.) was then added in three portions over 2 min. After the Schlenk tube was re-capped with a Teflon-screw and placed into a 45 °C metal sand bath. The mixture was stirred until the disulfide was consumed, then DCM (80 mL) was added followed by aq $Na_2S_2O_3$ (1 M) with stirring until the I_2 color disappeared. The organic layer was washed three times with water (30 mL each time), then the organic layer was dried over Na_2SO_4 and the solvent was removed at reduced pressure. Purification by column

chromatography (Eluent: petroleum ether/ethyl acetate = 6/1) afforded the title compound as a yellow solid (125 mg, 31% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 3.17 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.5, 136.2, 130.7, 124.5, 47.2, 21.5. The analytical datas are in agreement with the literature[15].

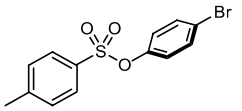
4-Chlorophenyl 4-methylbenzenesulfonate (42a)



Prepared according to the general procedure **F**, 4-chlorophenol (643 mg, 5.0 mmol, 1.0 equiv.), DMAP (61 mg, 0.50 mmol, 0.10 equiv.), triethylamine (1.0 g, 10.0 mmol, 2.0 equiv.), and DCM (10 mL) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a white solid (888 mg, 63% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 2.45 (s, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148. 1, 145.7, 132.8, 132. 1, 129.9, 129.7, 128.5, 123.8, 21.7; **HRMS** (ESI) calcd. $C_{13}H_{11}ClNaO_3S^+$ $[M+Na]^+$ m/z 305.0010, found: 305.0012. The analytical datas are in agreement with the literature[8].

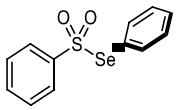
4-Bromophenyl 4-methylbenzenesulfonate (43a)



Prepared according to the general procedure **F**, 4-bromophenol (865 mg, 5.0 mmol, 1.0 equiv.), DMAP (61 mg, 0.50 mmol, 0.10 equiv.), triethylamine (1.0 g, 10.0 mmol, 2.0 equiv.), and DCM (10 mL) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a white solid (1.14 g, 70% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 2.36 (s, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.6, 145.7, 132.7, 132.0, 129.9, 128.5, 124.2, 120.6, 21.8. The analytical datas are in agreement with the literature[8].

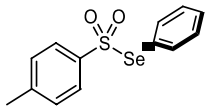
***Se*-Phenyl benzenesulfonoselenoate (44a)**



Prepared according to the general procedure **E**, sodium benzenesulfinate (656 mg, 4.0 mmol, 4.0 equiv.), 1,2-diphenyldiselane (312 mg, 1.0 mmol, 1.0 equiv.), and PIFA (473 mg, 1.1 mmol, 1.1 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a yellow solid (169 mg, 57% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.39 (t, *J* = 7.8 Hz, 4H), 7.32 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.2, 137.2, 133.6, 133.5, 131.0, 129.6, 128.8, 127.9, 127.0. The analytical datas are in agreement with the literature[16].

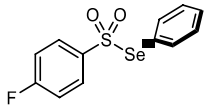
***Se*-Phenyl 4-methylbenzenesulfonoselenoate (45a)**



Prepared according to the general procedure **E**, sodium 4-methylbenzenesulfinate (712 mg, 4.0 mmol, 4.0 equiv.), 1,2-diphenyldiselane (312 mg, 1.0 mmol, 1.0 equiv.), and PIFA (473 mg, 1.1 mmol, 1.1 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a yellow solid (205 mg, 66% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.44 (m, 3H), 7.38 (s, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 142.7, 137.2, 130.9, 129.6, 129.3, 128.0, 127.0, 21.7; **HRMS** (ESI) calcd. $C_{13}H_{12}NaO_2SSe^+$ $[M+Na]^+$ m/z 334.9615, found: 334.9617. The analytical datas are in agreement with the literature[7].

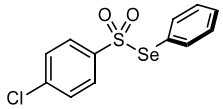
***Se*-Phenyl 4-fluorobenzenesulfonoselenoate (46a)**



Prepared according to the general procedure **E**, sodium 4-fluorobenzenesulfinate (728 mg, 4.0 mmol, 1.0 equiv.), 1,2-diphenyldiselane (312 mg, 1.0 mmol, 1.0 equiv.), and PIFA (473 mg, 1.1 mmol, 1.1 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a yellow solid (104 mg, 33% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.44 (m, 5H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.4 (d, ^1J = 256.8 Hz), 141.3 (d, ^3J = 3.1 Hz), 137.2, 131. 1, 129.9 (d, ^3J = 9.6 Hz), 129.7, 127.8, 116.0, 115.8; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ - 103. 1; **HRMS** (ESI) calcd. $C_{12}H_{10}FO_2SSe^+$ $[M+H]^+$ m/z 316.9545, found: 316.9545. The analytical datas are in agreement with the literature[7].

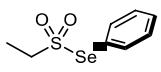
***Se*-Phenyl 4-chlorobenzenesulfonoselenoate (47a)**



Prepared according to the general procedure **E**, sodium 4-chlorobenzenesulfinate (794 mg, 4.0 mmol, 4.0 equiv.), 1,2-diphenyldiselane (312 mg, 1.0 mmol, 1.0 equiv.), and PIFA (473 mg, 1.1 mmol, 1.1 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a yellow solid (136 mg, 41% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.45 (m, 2H), 7.42 (d, *J* = 10.8 Hz, 2H), 7.38 – 7.28 (m, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143.6, 140. 1, 137.2, 131.2, 129.8, 129.0, 128.4, 127.7; **HRMS** (ESI) calcd. $C_{12}H_9ClNaO_2SSe^+$ $[M+H]^+$ m/z 354.9069, found: 354.9064. The analytical datas are in agreement with the literature[7].

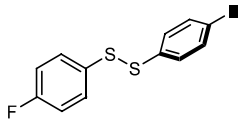
***Se*-Phenyl ethanesulfonoselenoate (48a)**



Prepared according to the general procedure **E**, sodium ethanesulfinate (464 mg, 4.0 mmol, 4.0 equiv.), 1,2-diphenyldiselane (312 mg, 1.0 mmol, 1.0 equiv.), and PIFA (473 mg, 1.1 mmol, 1.1 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a yellow solid (92 mg, 37% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J*= 7.1 Hz, 1H), 7.44 (t, *J*= 7.6 Hz, 2H), 3.24 (q, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 136.9, 131.0, 129.9, 127.5, 57.7, 8.6; **IR** (KBr, cm^{-1}) 3745, 3672, 2952, 2830, 2716, 1599, 1363, 1084, 774, 533; **Mp**: 51.1 – 52.9 °C; **HRMS** (ESI) calcd. $C_8H_{10}NaO_2SSe^+$ $[M+H]^+$ m/z 250.9639, found: 250.9637.

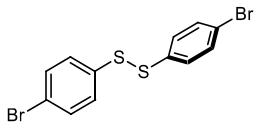
1,2-Bis(4-fluorophenyl)disulfane (51a)



Prepared according to the general procedure **G**, 4-fluorobenzenesulfonyl chloride (584 mg, 3.0 mmol, 1.0 equiv.), triphenylphosphine (1.57 g, 6.0 mmol, 2.0 equiv.), and THF (15 mL) were used. Purification by column chromatography (Eluent: petroleum ether) afforded the title compound as a light yellow liquid (324 mg, 85% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.4, 5.3 Hz, 4H), 7.00 (t, *J* = 8.5 Hz, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.6 (d, ^1J = 248.2 Hz), 132.2 (d, ^3J = 3.2 Hz), 131.3 (d, ^3J = 8.3 Hz), 116.3 (d, ^2J = 22.3 Hz); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ - 113.5. The analytical datas are in agreement with the literature[17].

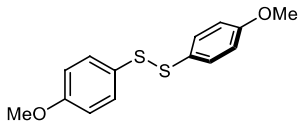
1,2-Bis(4-bromophenyl)disulfane (53a)



Prepared according to the general procedure **G**, 4-bromobenzenesulfonyl chloride (767 mg, 3.0 mmol, 1.0 equiv.), triphenylphosphine (1.57 g, 6.0 mmol, 2.0 equiv.), and THF (15 mL) were used. Purification by column chromatography (Eluent: petroleum ether) afforded the title compound as a white solid (423 mg, 75% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 4H), 7.32 (d, *J* = 8.2 Hz, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 135.8, 132.3, 129.4, 121.6. The analytical datas are in agreement with the literature[17].

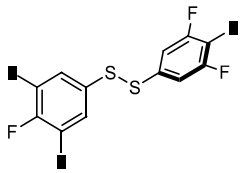
1,2-Bis(4-methoxyphenyl)disulfane (54a)



Prepared according to the general procedure **G**, 4-bromobenzenesulfonyl chloride (620 mg, 3.0 mmol, 1.0 equiv.), triphenylphosphine (1.57 g, 6.0 mmol, 2.0 equiv.), and THF (15 mL) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 100/1) afforded the title compound as a light yellow liquid (371 mg, 89% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.7 Hz, 4H), 6.81 (d, *J* = 8.7 Hz, 4H), 3.76 (s, 6H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.0, 132.7, 128.5, 114.7, 55.4; **HRMS** (ESI) calcd. $C_{14}H_{14}NaO_2S_2^+$ $[M+Na]^+$ m/z 301.0327, found: 301.0328. The analytical datas are in agreement with the literature[17].

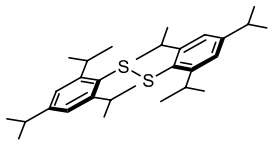
1,2-Bis(3,4,5-trifluorophenyl)disulfane (55a)



Prepared according to the general procedure **G**, 3,4,5-trifluorobenzenesulfonyl chloride (692 mg, 3.0 mmol, 1.0 equiv.), triphenylphosphine (1.57 g, 6.0 mmol, 2.0 equiv.), and THF (15 mL) were used. Purification by column chromatography (Eluent: petroleum ether) afforded the title compound as a light yellow solid (323 mg, 66% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 – 7.06 (m, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 151.5 (ddd, *J* = 254.5, 10.6, 4.0 Hz), 139.4 (dt, *J* = 253.9, 15.4 Hz), 131.8 – 131.7 (m), 111.8 (dd, *J* = 17.7, 6.0 Hz); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ - 131.4, - 131.5, - 159.6, - 159.6, - 159.7; **IR** (KBr, cm^{-1}) 3750, 3647, 2830, 1600, 1362, 1130, 774, 535; **Mp**: 71.6 – 72.3 °C; **HRMS** (ESI) calcd. $C_{12}H_4F_6NaS_2^+$ $[M+Na]^+$ m/z 348.9551, found: 348.9554.

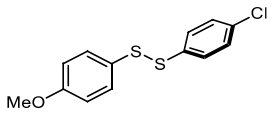
1,2-Bis(2,4,6-triisopropylphenyl)disulfane (56a)



Prepared according to the general procedure **G**, 2,4,6-triisopropylbenzenesulfonyl chloride (908 mg, 3.0 mmol, 1.0 equiv.), triphenylphosphine (1.57 g, 6.0 mmol, 2.0 equiv.) and THF (15 mL) were used. Purification by column chromatography (Eluent: petroleum ether) afforded the title compound as a light yellow solid (550 mg, 78% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.92 (s, 4H), 3.55 (p, *J* = 6.9 Hz, 4H), 2.82 (p, *J* = 6.9 Hz, 2H), 1.20 (d, *J* = 6.9 Hz, 11H), 1.00 (d, *J* = 7.5 Hz, 23H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.4, 150.5, 129.3, 121.8, 34.5, 31.4, 23.9, 23.9; **HRMS** (ESI) calcd. $C_{30}H_{46}NaS_2^+$ $[M+Na]^+$ m/z 493.2933, found: 493.2927. The analytical datas are in agreement with the literature[18].

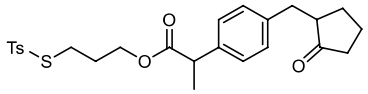
1-(4-Chlorophenyl)-2-(4-methoxyphenyl)disulfane (57a)



Prepared according to the general procedure **G**, 4-methoxybenzenesulfonyl chloride (1.03 g, 5.0 mmol, 1.0 equiv.), triphenylphosphine (5.24 g, 20 mmol, 2.0 equiv.), 4-chlorobenzenesulfonyl chloride (1.05 g, 5.0 mmol, 1.0 equiv.), and THF (20 mL) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 100/1) afforded the title compound as a colorless oil (323 mg, 23% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (dd, *J*= 12.2, 8.1 Hz, 4H), 7.27 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 2H), 3.78 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160. 1, 136. 1, 133.4, 132.2, 129.8, 129.2, 127.6, 114.8, 55.4. The analytical datas are in agreement with the literature[19].

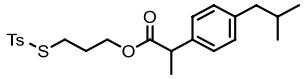
3-(Tosylthio)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (58a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (1.01 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as a colorless oil (925mg, 78% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.68 (m, 2H), 7.34 (d, *J*= 8.1 Hz, 2H), 7.19 (d, *J*= 8.2 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.07 (td, *J* = 6. 1, 3.0 Hz, 2H), 3.67 (d, *J*= 7.1 Hz, 1H), 3.13 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.91 (dd, *J* = 8.0, 6.6 Hz, 2H), 2.59 – 2.44 (m, 4H), 2.34 (dddd, *J*= 12.2, 7.7, 6. 1, 3.1 Hz, 2H), 2.19 – 2.03 (m, 2H), 2.02 – 1.86 (m, 3H), 1.83 – 1.50 (m, 3H), 1.48 (d, *J*= 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.4, 144.9, 141.9, 139. 1, 138.2, 129.9, 129.2, 127.5, 127.0, 62.4, 51.0, 45. 1, 38.2, 35.2, 32.4, 29.2, 28. 1, 21.7, 20.5, 18.3; **IR** (KBr, cm^{-1}) 3857, 3747, 3453, 2805, 1672, 1587, 1392, 802, 749; **HRMS** (ESI) calcd. $C_{25}H_{30}NaO_5S_2^+$ $[M+Na]^+$ m/z 497.1427, found: 497.1426.

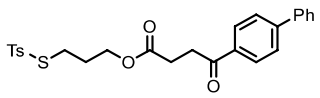
3-(Tosylthio)propyl 2-(4-isobutylphenyl)propanoate (59a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 2-(4-isobutylphenyl)propanoate (899 mg, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a white solid (826 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J*= 8.1 Hz, 2H), 4.08 (td, *J* = 5.6, 4.3 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.16 – 2.66 (m, 2H), 2.62 – 2.26 (m, 5H), 2.09 – 1.67 (m, 3H), 1.49 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.4, 144.9, 141.9, 140.7, 137.6, 129.9, 129.4, 127. 1, 127.0, 62.3, 45. 1, 45.0, 32.4, 30.2, 28. 1, 22.4, 21.7, 18.3; **IR** (KBr, cm^{-1}) 2831, 2716, 1599, 1364, 1140, 774, 532; **Mp**: 39.6 – 42.0 °C; **HRMS** (ESI) calcd. $C_{23}H_{30}NaO_4S_2^+$ $[M+Na]^+$ m/z 457.1478, found: 457.1483.

3-(Tosylthio)propyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (60a)

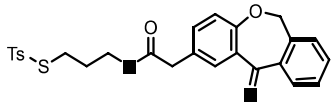


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (1.03 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as a white solid (1.09 g, 90% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.48 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.35 (d, *J*= 8.1 Hz, 2H), 4.14 (t, *J* = 6.0 Hz, 2H), 3.34 (t, *J* = 6.5 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* =

6.5 Hz, 2H), 2.44 (s, 3H), 2.01 (h, *J* = 6.1 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.7, 172.7, 145.9, 145.0, 141.8, 139.8, 135.2, 130.0, 129.0, 128.7, 128.3, 127.3, 127. 1, 62.5, 33.4, 32.6, 28.2, 21.7; **IR** (KBr, cm^{-1}) 3670, 2830, 1600, 1364, 1140, 775, 589; **Mp**: 61.8 – 62.9 °C; **HRMS** (ESI) calcd. $C_{26}H_{26}NaO_5S_2^+$ $[M+Na]^+$ m/z 505.1114, found: 505.1082.

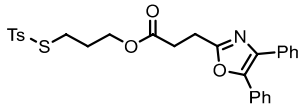
3-(Tosylthio)propyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (61a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (1.07 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as a yellow liquid (894 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 2.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.34 (dd, *J* = 11.8, 7.6 Hz, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H), 4.11 (t, *J* = 6.0 Hz, 2H), 3.62 (s, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.97 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.7, 171. 1, 160.5, 145.0, 141.8, 140.4, 136.3, 135.6, 132.9, 132.4, 130.0, 129.9, 129.5, 129.3, 128.0, 127.9, 127.6, 127.0, 125.2, 121.2, 73.6, 62.8, 40. 1, 32.5, 28. 1, 21.7; **IR** (KBr, cm^{-1}) 2952, 2831, 2716, 1600, 1364, 1135, 1081, 774, 530; **HRMS** (ESI) calcd. $C_{26}H_{25}O_6S_2^+$ $[M+H]^+$ m/z 497.1087, found: 497.1085.

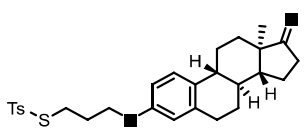
3-(Tosylthio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate (62a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 3-(4,5-diphenyloxazol-2-yl)propanoate (1. 1 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 6/1) afforded the title compound as a colorless oil (704 mg, 54% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 – 7.73 (m, 2H), 7.64 – 7.57 (m, 2H), 7.57 – 7.52 (m, 2H), 7.39 – 7.29 (m, 8H), 4.14 (t, *J* = 6.0 Hz, 2H), 3.16 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J*= 7.1 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 2H), 1.99 (p, *J* = 6.5 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.8, 161.6, 145.5, 144.9, 141.8, 135. 1, 132.4, 129.9, 128.9, 128.7, 128.6, 128.5, 128. 1, 127.9, 127. 1, 126.5, 62.6, 32.5, 31.0, 28.2, 23.5, 21.6; **IR** (KBr, cm^{-1}) 3665, 2953, 2831, 2716, 1598, 1363, 1080, 775, 530; **HRMS** (ESI) calcd. $C_{28}H_{28}NO_5S_2^+$ $[M+H]^+$ m/z 522. 1403, found: 522.1404.

***S*-(3-(((8*S*,9*R*,13*R*,14*R*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)propyl) 4-methylbenzenesulfonothioate (63a)**

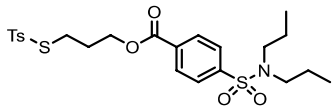


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol,

1.0 equiv.), (8*S*,9*R*,13*R*,14*R*)-3-(3-bromopropoxy)- 13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro- 17*H*-cyclopenta[*a*]phenanthren- 17-one (1.07 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 7/1) afforded the title compound as a white solid (910 mg, 73% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.69 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 1H), 6.64 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 3.94 (t, *J* = 5.8 Hz, 2H), 3.16 (t, *J*= 7.1 Hz, 2H), 2.87 (dd, *J* = 7.4, 3.2 Hz, 2H), 2.58 – 2.31 (m, 5H), 2.26 – 1.83 (m, 7H), 1.70 – 1.36 (m, 6H), 0.90 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 156.5, 144.8, 141.9, 137.8, 132.4, 129.9, 127. 1, 126.4, 114.6, 112. 1, 65.4, 50.4, 48.0, 44.0, 38.4, 35.9, 32.8, 31.6, 29.7, 28.7, 26.5, 26.0, 21.7, 21.6, 13.9; **IR** (KBr, cm^{-1}) 3448, 2831, 1601, 1363, 1084, 775, 534; **Mp**: 112.0 – 113.2 °C; **HRMS** (ESI) calcd. $C_{28}H_{34}NaO_4S_2^+$ $[M+Na]^+$ m/z 521.1791, found: 521.1784.

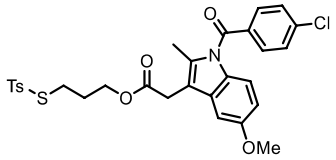
3-(Tosylthio)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (64a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1. 1 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 4/1) afforded the title compound as a white solid (848 mg, 66% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.37 (t, *J* = 6.0 Hz, 2H), 3.29 – 2.92 (m, 6H), 2.43 (s, 3H), 2.15 (p, *J* = 7. 1, 6.6 Hz, 2H), 1.55 (h, *J* = 7.4 Hz, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.0, 145.0, 144.5, 141.7, 133.2, 130.2, 129.9, 127.0, 127.0, 63.4, 50.0, 32.6, 28.3, 21.9, 21.6, 11.1; **IR** (KBr, cm^{-1}) 3655, 2957, 2831, 2716, 1601, 1363, 1267, 1082, 986, 775, 651. 527; **Mp**: 50.3 – 52.1 °C; **HRMS** (ESI) calcd. $C_{23}H_{31}NNaO_6S_3^+$ $[M+Na]^+$ m/z 536.1206, found: 536.1201.

3-(Tosylthio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (65a)

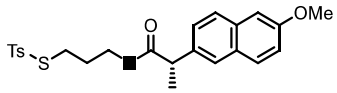


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl- 1*H*-indol-3-yl)acetate (1.3 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a light yellow solid (1.23 g, 77% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.14 (t, *J* = 6.0 Hz, 2H), 3.84 (s, 3H), 3.67 (s, 2H), 2.98 (t, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 2.39 (s, 3H), 2.07 – 1.88 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.6, 168.3, 156. 1, 145.0, 141.8, 139.3, 136.0, 133.9, 131.2, 130.8, 130.6, 129.9, 129.2, 127.0, 115.0, 112.3,

111.7, 101.3, 62.8, 55.8, 32.5, 30.3, 28.2, 21.7, 13.4; **IR** (KBr, cm^{-1}) 2830, 2716, 1601, 1364, 1137, 774, 531; **HRMS** (ESI) calcd. $C_{29}H_{28}ClNO_6S_2^+$ $[M+H]^+$ m/z 586.1119, found: 586.1112.

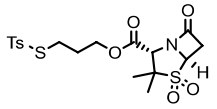
3-(Tosylthio)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (66a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (966 mg, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 6/1) afforded the title compound as a white solid (803 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.70 (m, 4H), 7.67 (s, 1H), 7.39 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.21 – 7.07 (m, 2H), 4.10 (t, *J* = 6.0 Hz, 2H), 3.93 (s, 3H), 3.85 (q, *J* = 7.1 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.99 – 1.85 (m, 2H), 1.59 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.4, 157.7, 144.9, 141.9, 135.5, 133.8, 129.9, 129.3, 128.9, 127.3, 127.0, 126. 1, 125.9, 119. 1, 105.7, 62.6, 55.3, 45.4, 32.5, 28. 1, 21.6, 18.4; **IR** (KBr, cm^{-1}) 3650, 2953, 2830, 2716, 1599, 1363, 1084, 774, 530; **Mp**: 78.0 – 80.6 °C; **HRMS** (ESI) calcd. $C_{24}H_{26}NaO_5S_2^+$ $[M+H]^+$ m/z 481.1114, found: 481.1118.

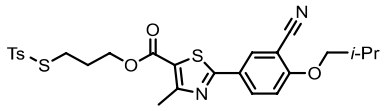
3-(Tosylthio)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (67a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia- 1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (974 mg, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 2/1) afforded the title compound as a white solid (876 mg, 76% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (dd, *J*= 8.4, 1.6 Hz, 2H), 7.37 (d, *J*= 8.0 Hz, 2H), 4.63 (dd, *J* = 4.8, 2.0 Hz, 1H), 4.36 (d, *J* = 1.6 Hz, 1H), 4.25 (dqd, *J* = 15.4, 5.4, 2.7 Hz, 2H), 3.68 – 3.33 (m, 2H), 3.07 (td, *J* = 7. 1, 1.4 Hz, 2H), 2.46 (s, 3H), 2.23 – 1.93 (m, 2H), 1.59 (d, *J*= 1.8 Hz, 3H), 1.41 (d, *J* = 1.7 Hz, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.7, 166.8, 145.2, 141.7, 130.0, 127.0, 64. 1, 63.2, 62.7, 61. 1, 38.4, 32.2, 28.0, 21.7, 20.3, 18.6; **IR** (KBr, cm^{-1}) 3476, 2802, 1387, 1342, 797, 749; **Mp**: 130.1 – 132.8 °C; **HRMS** (ESI) calcd. $C_{18}H_{24}NO_7S_3^+$ $[M+H]^+$ m/z 462.0709, found: 462.0710.

3-(Tosylthio)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (68a)

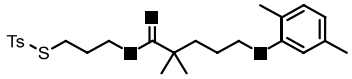


Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (1.2 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 3/1) afforded

the title compound as a white solid (1.10 g, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 2.2 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J*= 8.1 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 4.30 (t, *J* = 5.9 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.72 (s, 3H), 2.43 (s, 3H), 2.19 (dq, *J* = 14.7, 8.0, 7.4 Hz, 1H), 2.10 (q, *J* = 6.6 Hz, 2H), 1.09 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 162.6, 161.7, 161.5, 145.0, 141.7, 132.6, 132.0, 130.0, 127.0, 125.8, 121.2, 115.4, 112.7, 102.9, 75.7, 63. 1, 32.6, 28.2, 28.2, 21.7, 19.0, 17.5; **IR** (KBr, cm^{-1}) 2831, 2716, 1604, 1364, 1083, 775; **Mp**: 114.5 – 115.1 °C; **HRMS** (ESI) calcd. $C_{26}H_{28}N_2O_5S_3^+$ $[M+H]^+$ m/z 545.1233, found: 545.1223.

3-(Tosylthio)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (69a)



Prepared according to the general procedure **A**, 4-methylbenzenesulfonotioate (446 mg, 2.5 mmol, 1.0 equiv.), 3-bromopropyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (1.02 g, 2.75 mmol, 1.1 equiv.), and tetrabutylammonium iodide (46 mg, 0.0125 mmol, 0.05 equiv.) were used. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a colorless oil (1.0 g, 84% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.68 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.63 (d, *J*= 1.7 Hz, 1H), 4.10 (t, *J* = 6.0 Hz, 2H), 3.93 (t, *J* = 3.0 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 2.33 (s, 3H), 2.18 (s, 3H), 2.08 – 1.91 (m, 2H), 1.72 (d, *J* = 3.0 Hz, 4H), 1.22 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.5, 156.9, 144.9, 141.8, 136.5, 130.3, 129.9, 127. 1, 123.5, 120.8, 112.0, 67.8, 62.3, 42. 1, 37. 1, 32.6, 28.2, 25.2, 25. 1, 21.6, 21.4, 15.8; **IR** (KBr, cm^{-1}) 2950, 2830, 2716, 1603, 1364, 1081, 774, 531; **HRMS** (ESI) calcd. $C_{25}H_{34}NaO_5S_2^+$ $[M+Na]^+$ m/z 501.1740, found: 501.1744.

5 General Procedure of 1,2-difunctionalization of acetylene with bifunctional reagents enabled by photocatalyzed insertion chemistry

Method 1:

An oven-dried 25 mL Schlenk tube (sythware brand, 25 mL, part #F580050) equipped with a Teflon-coated magnetic stir bar was charged with 4CzIPN (2.0 mol %) and Cs_2CO_3 (0.25 ~ 0.5 equiv.) under N_2. Then, a solution ofbifunctional reagents (0.25 mmol, 1.0 equiv.) in dry dimethyl sulfoxide (5.0 mL) was added by pipettor. The tube was degassed through three freeze-pump-thaw cycles under acetylene and then an acetylene gas balloon was attached through a three-way-stopcok. After that, the tube was placed in the Parallel Light Reactor, which cooled with the recirculated cooling water. The reaction mixture was detected by TLC, quenched via exposure to air, diluted with brine (5 mL), and then extracted by EtOAc (2 × 10 mL). The combined organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel to obtain the product (Warning: Perform the reaction in a well-ventilated fume hood because of its explosivity, flammability, and strong diffusivity, which may raise serious safety

concerns).

Method 2:

An oven-dried Teflon-screw capped Schlenk tube containing a stirrer bar was charged with the 4CzIPN (2 mol %) and Cs_2CO_3 (0.25 ~ 0.5 equiv.) through the side-neck under positive N_2 flow. Then, a solution of bifunctional reagents (0.25 mol, 1.0 equiv.) in dry dimethyl sulfoxide (5.0 mL) was added by pipettor. The reaction mixture was then cooled to -78 ºC and connected to a Schlenk line degas via vacuum evacuation, backfilled with acetylene gas, and warmed to room temperature. The Schlenk tube was re-capped with a Teflon-screw and placed in the Parallel Light Reactor, which cooled with the recirculated cooling water. The corresponding reaction mixture was detected according to TLC. Finally, the reaction mixture was diluted with brine (5 mL) and extracted by EtOAc (2 × 10 mL). The combined organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel gave title compound.

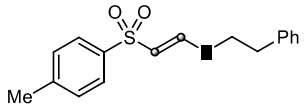
Method 3:

The reaction mixture was stirred under two 400 ~ 425 nm Kessil lamps at room temperature for 10 ~ 14 hours (flask about 10 cm away from lights, fan for cooling) until the reaction completed and then quenched with brine (5 mL). The organic phases were diluted with EtOAc (3 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated to obtain the corresponding residue, which was then purified through flash chromatography on silica gel to afford the desired products.

6 Characterization Data for the Products and Scope Limitations

6.1 Characterization Data for the Products

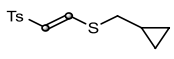
(*E*)-Phenethyl(2-tosylvinyl)sulfane (3)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-phenethyl 4-methylbenzenesulfonothioate (73 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a light yellow liquid (52 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 14.7 Hz, 1H), 7.37 – 7.26 (m, 5H), 7.19 (d, J = 8.3 Hz, 2H), 6.14 (d, J = 14.7 Hz, 1H), 3.09 – 3.00 (m, 2H), 3.00 – 2.93 (m, 2H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 144. 1, 138.8, 138.3, 129.9, 128.7, 128.5, 127.4, 126.9, 122.3, 34.7, 33.8, 21.6; **IR** (KBr, cm^{-1}) 3651, 2830, 2717, 1600, 1363, 1082, 775, 531; **HRMS** (ESI) calcd. For $C_{17}H_{18}NaO_2S_2^+$ $[M+Na]^+$ m/z 341.0640, found:341.0646.

(*E*)-(Cyclopropylmethyl)(2-tosylvinyl)sulfane (7)

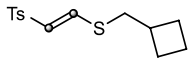


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(cyclopropylmethyl) 4-methylbenzenesulfonothioate (61 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a light

yellow liquid (28 mg, 41% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.68 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.15 (d, *J* = 14.7 Hz, 1H), 2.73 (d, *J*= 7.1 Hz, 2H), 2.44 (s, 3H), 1.12 – 0.94 (m, 1H), 0.68 – 0.60 (m, 2H), 0.29 (q, *J* = 4.9 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.4, 144.0, 138.4, 129.9, 127.4, 122. 1, 38. 1, 21.6, 9.6, 5.8; **IR** (KBr, cm^{-1}) 3449, 2830, 1603, 1364, 1082, 775, 530; **HRMS** (ESI) calcd. For $C_{13}H_{16}NaO_2S_2^+$ $[M+Na]^+$ m/z 291.0484, found:291.0489.

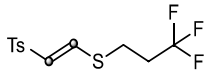
(*E*)-(Cyclobutylmethyl)(2-tosylvinyl)sulfane (8)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(cyclopropylmethyl) 4-methylbenzenesulfonothioate (61 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a light yellow solid (30 mg, 43% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 14.6 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J*= 14.6 Hz, 1H), 2.84 (d, *J* = 7.5 Hz, 2H), 2.57 (dt, *J*= 15.5, 7.8 Hz, 1H), 2.44 (s, 3H), 2.21 – 2.08 (m, 2H), 1.96 – 1.80 (m, 2H), 1.79 – 1.62 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.5, 144.0, 138.4, 129.9, 127.4, 122. 1, 38.8, 34.2, 27.8, 21.6, 17.9; **IR** (KBr, cm^{-1}) 3461, 2830, 1596, 1362, 1084, 774, 530; **Mp**: 48.6 – 49.5 °C; **HRMS** (ESI) calcd. For $C_{14}H_{18}NaO_2S_2^+$ $[M+Na]^+$ m/z 305.0640, found:305.0644.

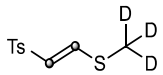
(*E*)-(2-Tosylvinyl)(3,3,3-trifluoropropyl)sulfane (9)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(3,3,3-trifluoropropyl) 4-methylbenzenesulfonothioate (71 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a light yellow liquid (48 mg, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 14.7 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.20 (d, *J* = 14.7 Hz, 1H), 3.16 – 2.86 (m, 2H), 2.56 – 2.35 (m, 5H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.4, 142.8, 137.9, 130.0, 127.5, 123.5, 33.4 (q, ^2J = 30.3 Hz), 24.4 (q, ^3J = 3.4 Hz), 21.6; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -66.3; **IR** (KBr, cm^{-1}) 3651, 2831, 1601, 1364, 1083, 755, 530; **HRMS** (ESI) calcd. For $C_{12}H_{13}F_3NaO_2S_2^+$ $[M+Na]^+$ m/z 333.0201, found: 333.0209.

(*E*)-(Methyl-d_3)(2-tosylvinyl)Sulfane (10)

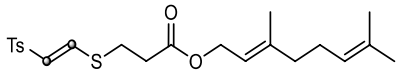


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(methyl-d_3) 4-methylbenzenesulfonothioate (51 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 15/1) afforded the title compound as a white solid (47 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.59 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.06 (d, *J* = 14.4 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.5, 144. 1, 138.3, 129.9, 127.4,

121.6, 21.6; **IR** (KBr, cm^{-1}) 3564, 2831, 2717, 1604, 1364, 1084, 775, 531; **Mp**: 59.0 – 51.7 °C; **HRMS** (ESI) calcd. For $C_{10}H_9D_3NaO_2S_2^+$ $[M+Na]^+$ m/z 254.0359, found: 254.0364.

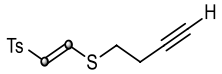
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 3-(((*E*)-2-tosylvinyl)thio)propanoate (11)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), (*E*)-3,7-dimethylocta-2,6-dien- 1-yl 3-(tosylthio)propanoate (99 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a colorless oil (57 mg, 54% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J*= 14.7 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.19 (d, *J* = 14.7 Hz, 1H), 5.33 (t, *J* = 6.2 Hz, 1H), 5.08 (t, *J* = 6.5 Hz, 1H), 4.63 (d, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.08 (dt, *J* = 13.7, 6.6 Hz, 4H), 1.70 (d, *J* = 8.5 Hz, 6H), 1.61 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 144. 1, 144. 1, 143.0, 138. 1, 131.9, 129.9, 129.9, 127.4, 127.4, 123.7, 122.7, 117.8, 62.0, 39.5, 33.4, 27.3, 26.3, 25.7, 21.6, 17.7, 16; **IR** (KBr, cm^{-1}) 3449, 2831, 1602, 1363, 1082, 775, 531; **HRMS** (ESI) calcd. For $C_{22}H_{30}NaO_4S_2^+$ $[M+Na]^+$ m/z 445.1478, found: 445.1479.

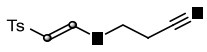
(*E*)-But-3-yn-1-yl(2-tosylvinyl)sulfane (12)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(but-3-yn- 1-yl) 4-methylbenzenesulfonothioate (60 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.) and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 8/1) afforded the title compound as a light yellow solid (17 mg, 26% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 14.7 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.21 (d, *J* = 14.7 Hz, 1H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.56 (td, *J* = 7. 1, 2.6 Hz, 2H), 2.44 (s, 3H), 2.06 (t, *J* = 2.6 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.3, 144.2, 138. 1, 129.9, 129.8, 127.4, 126.8, 122.8, 80.9, 70.9, 31.3, 21.6, 19.0; **IR** (KBr, cm^{-1}) 2830, 1603, 1366, 1081, 775; **Mp**: 57.3 – 58.6 °C; **HRMS** (ESI) calcd. For $C_{13}H_{14}NaO_2S_2^+$ $[M+Na]^+$ m/z 289.0327, found: 289.0333.

(*E*)-3-((2-Tosylvinyl)thio)propanenitrile (13)

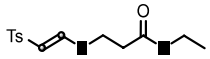


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(2-cyanoethyl) 4-methylbenzenesulfonothioate (60 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a light yellow liquid (40 mg, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J*= 14.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.29 (d, *J* = 14.8 Hz, 1H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.5, 142.5, 137.6, 130.0, 127.5, 124.3, 117.2, 28. 1, 21.6, 18.2; **IR** (KBr, cm^{-1}) 3448, 2830, 1601, 1363, 1082, 775, 531; **HRMS** (ESI) calcd. For

$C_{12}H_{13}NNaO_2S_2^+$ $[M+Na]^+$ m/z 290.0280, found: 290.0286.

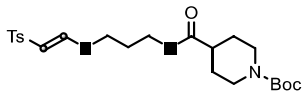
Ethyl (*E*)-3-((2-tosylvinyl)thio)propanoate (14)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), ethyl 3-(tosylthio)propanoate (72 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a a colorless oil (46 mg, 59% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 14.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.19 (d, *J* = 14.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 144.2, 138. 1, 129.9, 127.4, 122.7, 61. 1, 33.4, 27.3, 21.6, 14.1; **IR** (KBr, cm^{-1}) 2952, 2831, 2716, 1598, 1364, 1081, 775, 530; **HRMS** (ESI) calcd. For $C_{14}H_{18}NaO_4S_2^+$ $[M+Na]^+$ m/z 337.0539, found: 337.0547.

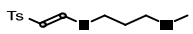
(*E*)-1-(*tert*-Butyl) 4-(3-((2-tosylvinyl)thio)propyl) piperidine-1,4-dicarboxylate (15)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 1-(*tert*-butyl) 4-(3-(tosylthio)propyl) piperidine- 1,4-dicarboxylate (114 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a light yellow liquid (79 mg, 66% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 6.2 Hz, 2H), 7.65 (d, *J* = 14.7 Hz, 1H), 7.31 (d, *J* = 6.9 Hz, 2H), 6.15 (d, *J* = 13.4 Hz, 1H), 4.14 (t, *J* = 5.0 Hz, 2H), 4.04 – 3.98 (m, 2H), 2.83 (t, *J* = 7.2 Hz, 4H), 2.41 (s, 4H), 2.00 – 1.91 (m, 2H), 1.83 (s, 2H), 1.58 (d, *J* = 11.2 Hz, 2H), 1.43 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.3, 154.7, 144.4, 144.2, 138. 1, 129.9, 127.4, 122.6, 79.6, 62.4, 43.0, 41.0, 29.0, 28.4, 27.9, 27.7, 21.6; **IR** (KBr, cm^{-1}) 3752, 3649, 3443, 2830, 1602, 1363, 1081, 774, 532; **HRMS** (ESI) calcd. For $C_{23}H_{33}NNaO_6S_2^+$ $[M+Na]^+$ m/z 506.1642, found: 506.1643.

(*E*)-(3-Methoxypropyl)(2-tosylvinyl)sulfane (16)

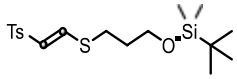


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(3-methoxypropyl) 4-methylbenzenesulfonothioate (65 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a light yellow liquid (46 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 14.6 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.20 (d, *J*= 14.7 Hz, 2H), 3.43 (t, *J* = 5.8 Hz, 2H), 3.31 (s, 3H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.90 (tt, *J* = 7.2, 5.8 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.0, 144.0, 138.4, 129.9, 127.4, 122. 1, 70.2, 58.7, 29. 1, 28.7, 21.6; **IR** (KBr, cm^{-1}) 3751, 3655, 2830, 1601, 1363, 1081, 775, 532; **HRMS** (ESI) calcd. For $C_{13}H_{18}NaO_3S_2^+$ $[M+Na]^+$ m/z 309.0590, found:

309.0595.

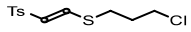
(*E*)-*tert*-Butyldimethyl(3-((2-tosylvinyl)thio)propoxy)silane (17)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(3-((*tert*-butyldimethylsilyl)oxy)propyl) 4-methylbenzenesulfonothioate (90 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 20/1) afforded the title compound as a light yellow liquid (47 mg, 49% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J*= 14.6 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.18 (d, *J* = 14.6 Hz, 1H), 3.68 (t, *J* = 5.7 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.85 (p, *J* = 6.0 Hz, 2H), 0.88 (s, 9H), 0.05 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145. 1, 144.0, 138.4, 129.9, 127.4, 121.9, 60.8, 31.3, 28.7, 25.9, 21.6, 18.3, -5.4; **IR** (KBr, cm^{-1}) 3456, 2830, 1599, 1362, 1083, 774, 533; **HRMS** (ESI) calcd. For $C_{18}H_{30}NaO_3S_2Si^+$ $[M+Na]^+$ m/z 409.1298, found: 409.1299.

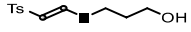
(*E*)-(3-Chloropropyl)(2-tosylvinyl)sulfane (18)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(3-chloropropyl) 4-methylbenzenesulfonothioate (62 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.) and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a colorless oil (42 mg, 59% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J*= 14.7 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 14.7 Hz, 1H), 3.54 (t, *J* = 6.1 Hz, 2H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 2.03 (p, *J* = 6.6 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.2, 138. 1, 129.9, 129.9, 129.7, 129.5, 127.4, 122.8, 42.9, 31. 1, 29.3, 21.6; **IR** (KBr, cm^{-1}) 3454, 1595, 1384, 1353, 1084, 534; **HRMS** (ESI) calcd. For $C_{12}H_{15}ClNaO_2S_2^+$ $[M+Na]^+$ m/z 313.0094, found: 313.0093.

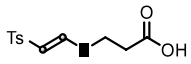
(*E*)-3-((2-Tosylvinyl)thio)propan-1-ol (19)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(3-hydroxypropyl) 4-methylbenzenesulfonothioate (62 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 2/1) afforded the title compound as a colorless oil (37 mg, 55% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 14.7 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.22 (d, *J*= 14.6 Hz, 1H), 3.73 (t, *J* = 5.9 Hz, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.91 (dt, *J* = 13.3, 6.5 Hz, 2H), 1.86 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145. 1, 144. 1, 138.3, 129.9, 127.4, 122. 1, 60.6, 31. 1, 28.8, 21.6; **IR** (KBr, cm^{-1}) 3449, 2830, 1602, 1364, 1081, 775, 530; **HRMS** (ESI) calcd. For $C_{12}H_{16}NaO_3S_2^+$ $[M+Na]^+$ m/z 295.0433, found: 295.0437.

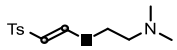
(*E*)-3-((2-Tosylvinyl)thio)propanoic acid (20)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propanoic acid (65 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (100 mg, 0.31 mmol, 1.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 1/1) afforded the title compound as a colorless oil (14 mg, 19% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 14.7 Hz, 0H), 7.35 (d, *J* = 8.0 Hz, 1H), 6.22 (d, *J*= 14.7 Hz, 0H), 3.85 (s, 0H), 3.07 (t, *J* = 7.0 Hz, 1H), 2.75 (t, *J*= 7.1 Hz, 1H), 2.45 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.0, 144.3, 144.0, 138.0, 130.0, 127.4, 122.9, 33. 1, 27. 1, 21.6; **IR** (KBr, cm^{-1}) 3561, 2831, 1603, 1363, 1082, 775, 532; **HRMS** (ESI) calcd. For $C_{12}H_{14}NaO_4S_2^+$ $[M+Na]^+$ m/z 309.0226, found: 309.0229.

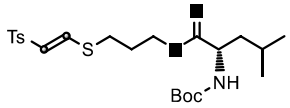
(*E*)-*N*,*N*-Dimethyl-2-((2-tosylvinyl)thio)ethan-1-amine (21)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(2-(dimethylamino)ethyl) 4-methylbenzenesulfonothioate (65 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 1/1) afforded the title compound as a brow solid (35 mg, 49% yield based on recovering starting materials).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 14.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 14.6 Hz, 1H), 2.90 (t, *J* = 6.9 Hz, 2H), 2.59 (d, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.26 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.0, 144.3, 144.0, 138.0, 130.0, 127.4, 122.9, 33. 1, 27. 1, 21.6; **IR** (KBr, cm^{-1}) 3562, 2951, 2830, 2717, 1603, 1364, 1139, 1082, 775, 531; **Mp**: 55.3 – 56.4 °C; **HRMS** (ESI) calcd. For $C_{14}H_{19}NO_2S_2^+$ $[M+H]^+$ m/z 286.0930, found: 286.0936.

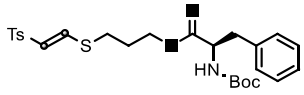
(*E*)-3-((2-Tosylvinyl)thio)propyl (*tert*-butoxycarbonyl)-*L*-leucinate (22)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl (*tert*-butoxycarbonyl)-*L*-leucinate (115 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a colorless oil (62 mg, 51% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 14.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.18 (d, *J* = 14.7 Hz, 1H), 4.97 (d, *J* = 8.5 Hz, 1H), 4.55 – 3.91 (m, 3H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.16 – 1.93 (m, 2H), 1.76 – 1.49 (m, 3H), 1.42 (s, 9H), 0.92 (d, *J* = 6.5 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.4, 155.5, 144.4, 144. 1, 138. 1, 130.0, 129.9, 127.4, 122.6, 79.9, 62.9, 52.2, 41.4, 28.8, 28.3, 27.7, 24.8, 22.8, 21.8, 21.6; **IR** (KBr, cm^{-1}) 3448, 2830, 1602, 1363, 1084, 775, 531; **HRMS** (ESI) calcd. For $C_{23}H_{35}NNaO_6S_2^+$ $[M+Na]^+$ m/z 508.1798, found: 508.1795.

(*E*)-3-((2-Tosylvinyl)thio)propyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate (23)

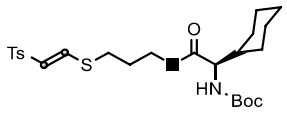


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02

equiv.), 3-(tosylthio)propyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate (123 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a colorless oil (60 mg, 46% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.58 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.26 (dt, *J* = 15.3, 6.8 Hz, 2H), 7.14 (d, *J* = 6.9 Hz, 3H), 6.14 (d, *J*= 14.7 Hz, 1H), 5.06 (d, *J* = 7.4 Hz, 1H), 4.54 (d, *J* = 7.0 Hz, 1H), 4.13 (t, *J* = 5.9 Hz, 2H), 3.05 (p, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.99 – 1.79 (m, 2H), 1.42 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.0, 155. 1, 144.3, 144. 1, 138.2, 136.0, 129.9, 129.3, 129.2, 128.6, 127.4, 127. 1, 122.7, 80. 1, 63. 1, 54.7, 38.5, 29.7, 28.6, 28.3, 27.5, 21.6; **IR** (KBr, cm^{-1}) 3451, 2830, 1600, 1361, 1082, 774, 533; **HRMS** (ESI) calcd. For $C_{26}H_{33}NNaO_6S_2^+$ $[M+Na]^+$ m/z 542.1642, found: 542.1637.

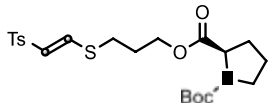
(*E*)-3-((2-Tosylvinyl)thio)propyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate (24)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate (121 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a yellow oil (77 mg, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.58 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.26 (dt, *J* = 15.3, 6.8 Hz, 2H), 7.14 (d, *J* = 6.9 Hz, 3H), 6.14 (d, *J*= 14.7 Hz, 1H), 5.06 (d, *J* = 7.4 Hz, 1H), 4.54 (d, *J* = 7.0 Hz, 1H), 4.13 (t, *J* = 5.9 Hz, 2H), 3.05 (p, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.99 – 1.79 (m, 2H), 1.42 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.0, 155. 1, 144.3, 144. 1, 138.2, 136.0, 129.9, 129.3, 129.2, 128.6, 127.4, 127. 1, 122.7, 80. 1, 63. 1, 54.7, 38.5, 29.7, 28.6, 28.3, 27.5, 21.6; **IR** (KBr, cm^{-1}) 3449, 2831, 1603, 1365, 1082, 775, 531; **HRMS** (ESI) calcd. For $C_{26}H_{33}NNaO_6S_2^+$ $[M+Na]^+$ m/z 534.1955, found: 534.1956.

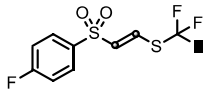
(*E*)-1-(*tert*-Butyl) 2-(3-((2-tosylvinyl)thio)propyl) (*R*)-pyrrolidine-1,2-dicarboxylate (25)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 1-(*tert*-butyl) 2-(3-(tosylthio)propyl) (*R*)-pyrrolidine- 1,2-dicarboxylate (111 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a light yellow liquid (50 mg, 43% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 14.7 Hz, 1H), 7.33 (s, 2H), 6.17 (dd, *J* = 14.7, 6.9 Hz, 1H), 4.27 (d, *J* = 8.7 Hz, 1H), 4.25 – 4.12 (m, 2H), 3.60 – 3.37 (m, 2H), 2.85 (q, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 2.20 (dt, *J* = 19. 1, 9.4 Hz, 2H), 1.96 (dd, *J* = 33.3, 9.8 Hz, 6H), 1.41 (dd, *J* = 19.7, 9.0 Hz, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.0, 155. 1, 144.3, 144. 1, 138.2, 136.0, 129.9, 129.3, 129.2, 128.6, 127.4, 127. 1, 122.7, 80. 1, 63. 1, 54.7, 38.5, 29.7, 28.6, 28.3, 27.5, 21.6; **IR** (KBr, cm^{-1}) 3454, 2830, 1599, 1360, 1083, 773, 536; **HRMS** (ESI) calcd. For $C_{22}H_{31}NNaO_6S_2^+$ $[M+Na]^+$ m/z 492.1485, found: 429.1486.

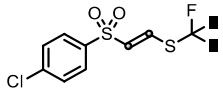
(*E*)-(2-((4-Fluorophenyl)sulfonyl)vinyl)(trifluoromethyl)sulfane (26)



Prepared following the general procedure outlined above using Mes-Acr^{+}-Me ClO_4^{-} (2.1 mg, 5.0 μmol, 0.02 equiv.), *S*-(trifluoromethyl) 4-fluorobenzenesulfonothioate (65 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a white solid (36 mg, 50% yield). Reaction times = 20 h.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 8.7, 5.0 Hz, 2H), 7.62 (d, *J*= 15.1 Hz, 1H), 7.26 – 7.08 (m, 2H), 6.52 (d, *J* = 15.1 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.0 (d, ^{1}J = 257.4 Hz), 135.5 (d, ^{3}J = 3.8 Hz) 132.9 (q, ^{3}J = 3.8 Hz), 130.8 (d, ^{3}J = 9.7 Hz), 128.1 (d, ^{1}J = 310.0 Hz), 117.0 (d, ^{2}J = 22.7 Hz); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -41. 1, - 102.6; **IR** (KBr, cm^{-1}) 3474, 2831, 1598, 1362, 1084, 775; **Mp**: 60.2 – 62.9 °C; **HRMS** (ESI) calcd. For $C_9H_6F_4NaO_2S_2^{+}$ $[M+Na]^{+}$ m/z 308.9638, found: 308.9635.

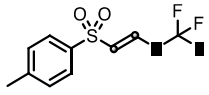
(*E*)-(2-((4-Chlorophenyl)sulfonyl)vinyl)(trifluoromethyl)sulfane (27)



Prepared following the general procedure outlined above using Mes-Acr^{+}-Me ClO_4^{-} (2. 1 mg, 5.0 μmol, 0.02 equiv.), *S*-(trifluoromethyl) 4-chlorobenzenesulfonothioate (69 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a white solid (30 mg, 40% yield). Reaction times = 20 h.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 15.1 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 6.58 (d, *J* = 15.0 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 140.9, 137.9, 133.3 (q, ^{1}J = 3.7 Hz), 130.0, 129.3, 126.9; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -41.1; **IR** (KBr, cm^{-1}) 3672, 2830, 2716, 1601, 1363, 1084, 774, 540; **Mp**: 65.7 – 68.7 °C; **HRMS** (ESI) calcd. For $C_9H_6ClF_3O_2S_2^{+}$ $[M+Na]^{+}$ m/z 324.9342, found: 324.9436.

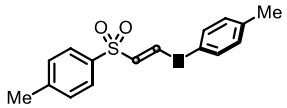
(*E*)-(2-Tosylvinyl)(trifluoromethyl)sulfane (28)



Prepared following the general procedure outlined above using Mes-Acr^{+}-Me ClO_4^{-} (2. 1 mg, 5.0 μmol, 0.02 equiv.), *S*-(trifluoromethyl) 4-methylbenzenesulfonothioate (64 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a white solid (30 mg, 43% yield). Reaction times = 20 h.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 15.1 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 15.1 Hz, 1H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.2, 136.4, 131.9 (q, ^{3}J = 3.7 Hz), 131.0, 130.2, 128.2 (d, ^{1}J = 310.1 Hz), 127.9, 21.7; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -41.2; **IR** (KBr, cm^{-1}) 3500, 2830, 1598, 1364, 1083, 775; **Mp**: 57.7 – 59.4 °C; **HRMS** (ESI) calcd. For $C_{10}H_9F_3NaO_2S_2^{+}$ $[M+Na]^{+}$ m/z 304.9888, found: 304.9888.

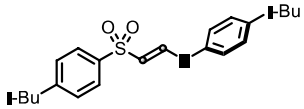
(*E*)-*p*-Tolyl(2-tosylvinyl)sulfane (29)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (70 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a yellow solid (52 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J*= 14.5 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 12.8, 8.1 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.94 (d, *J*= 14.5 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.2, 144.0, 140.3, 138.2, 133.6, 130.8, 129.9, 127.4, 125.4, 123.2, 21.6, 21.3; **IR** (KBr, cm^{-1}) 3449, 2831, 1601, 1363, 1137, 1082, 775, 529; **Mp**: 59.1 – 61.9 °C; **HRMS** (ESI) calcd. For $C_{16}H_{16}NaO_2S_2^+$ $[M+Na]^+$ m/z 327.0484, found: 327.0486.

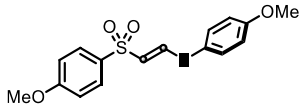
(*E*)-(4-(*tert*-Butyl)phenyl)(2-((4-(*tert*-butyl)phenyl)sulfonyl)vinyl)sulfane (30)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(4-(*tert*-butyl)phenyl) 4-(*tert*-butyl)benzenesulfonothioate (91 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a yellow solid (68 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 14.5 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.42 (q, *J* = 8.5 Hz, 4H), 6.06 (d, *J* = 14.5 Hz, 1H), 1.36 (s, 9H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.0, 153.3, 146.4, 138. 1, 133.2, 127.2, 127. 1, 126.3, 125.7, 123. 1, 35.2, 34.8, 31.2, 31.1; **IR** (KBr, cm^{-1}) 2956, 2831, 1598, 1364, 1144, 775, 535; **Mp**: 108.9 – 111.2 °C; **HRMS** (ESI) calcd. For $C_{22}H_{28}NaO_2S_2^+$ $[M+Na]^+$ m/z 411.1423, found: 411.1423.

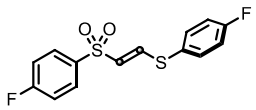
(*E*)-(4-Methoxyphenyl)(2-((4-methoxyphenyl)sulfonyl)vinyl)sulfane (31)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(4-(*tert*-butyl)phenyl) 4-(*tert*-butyl)benzenesulfonothioate (91 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a yellow solid (55 mg, 57% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 5.3 Hz, 2H), 7.72 (d, *J* = 11.1 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.85 (d, *J* = 14.4 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.3, 161. 1, 146.2, 135.7, 132.7, 129.5, 123.2, 119.0, 115.6, 114.4, 55.7, 55.5; **IR** (KBr, cm^{-1}) 2952, 2831, 2716, 1599, 1364, 1082, 775, 532; **Mp**: 90.2 – 92.1 °C; **HRMS** (ESI) calcd. For $C_{16}H_{16}NaO_4S_2^+$ $[M+Na]^+$ m/z 359.0382, found: 359.0384.

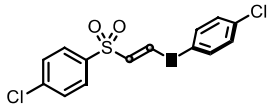
(*E*)-(4-Fluorophenyl)(2-((4-fluorophenyl)sulfonyl)vinyl)sulfane (32)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(4-fluorophenyl) 4-fluorobenzenesulfonothioate (72 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a yellow solid (47 mg, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 8.8, 5.1 Hz, 2H), 7.79 (d, *J*= 14.5 Hz, 1H), 7.47 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 5.91 (d, *J*= 14.5 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.5 (d, ^1J = 256.5 Hz), 163.8 (d, ^1J = 252.5 Hz), 146.5, 137.0 (d, ^3J = 3.1 Hz), 136.05 (d, ^3J = 8.6 Hz), 130.24 (d, ^3J = 9.5 Hz), 123.94 (d, ^3J = 3.5 Hz), 123. 1, 117.4 (d, ^2J = 22.2 Hz), 116.6 (d, ^2J = 22.7 Hz); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ - 104.2, - 109.4; **IR** (KBr, cm^{-1}) 3450, 2831, 1599, 1362, 1083, 774, 529; **Mp**: 95.9 – 97.3 °C; **HRMS** (ESI) calcd. For $C_{14}H_{10}F_2NaO_2S_2^+$ $[M+Na]^+$ m/z 334.9982, found: 334.9987.

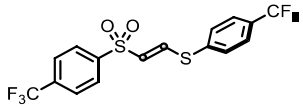
(*E*)-(4-Chlorophenyl)(2-((4-chlorophenyl)sulfonyl)vinyl)sulfane (33)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (80 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a yellow solid (56 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.71 (m, 3H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.41 (s, 4H), 5.96 (d, *J*= 14.5 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.2, 140.0, 139.3, 136.6, 134.8, 130.4, 129.6, 128.9, 127.2, 123.2; **IR** (KBr, cm^{-1}) 3447, 2831, 1602, 1363, 1083, 775, 531; **Mp**: 109.9 – 111.2 °C; **HRMS** (ESI) calcd. For $C_{14}H_{10}Cl_2NaO_2S_2^+$ $[M+Na]^+$ m/z 366.9391, found: 366.9393.

(*E*)-(4-(Trifluoromethyl)phenyl)(2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane (34)

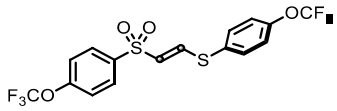


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(4-(trifluoromethyl)phenyl) 4-(trifluoromethyl)benzenesulfonothioate (97 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 20/1) afforded the title compound as a yellow solid (64 mg, 62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 14.6 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 6.14 (d, *J* = 14.6 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146. 1, 144.2, 135.1 (q, ^2J = 33.1 Hz), 134.0, 133.0, 131.9 (q, ^2J = 33.0 Hz), 128. 1, 26.9 (q, ^3J = 3.7 Hz), 126.5 (q, ^3J = 3.7 Hz), 123.5, 123.5 (d, ^1J = 273.7 Hz), 123.2 (d, ^1J = 293.9 Hz); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.0, -63.2; **IR** (KBr, cm^{-1}) 3563,

2831, 1602, 1363, 1127, 839, 775, 535; **Mp**: 141.7 – 143.5 °C; **HRMS** (ESI) calcd. For $C_{16}H_{10}F_6NaO_2S_2^+$ $[M+Na]^+$ m/z 434.9919, found: 434.9918.

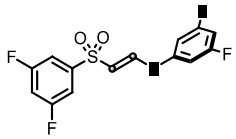
(*E*)-(4-(Trifluoromethoxy)phenyl)(2-((4-(trifluoromethoxy)phenyl)sulfonyl)vinyl)sulfane (35)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(4-(trifluoromethoxy)phenyl) 4-(trifluoromethoxy)benzenesulfonothioate (104 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 15/1) afforded the title compound as a white solid (62 mg, 56% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 14.5 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 5.94 (d, *J* = 14.5 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 151.5 (d, ^3J = 2.5 Hz), 151.6 (d, ^3J = 1.3 Hz), 146.4, 139. 1, 135.1, 129.7, 127.4, 123.2, 122.3, 121.1, 120.3 (q, ^1J = 259.6 Hz), 120.2 (q, ^1J = 259.6 Hz); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.7, -57.9; **IR** (KBr, cm^{-1}) 3647, 2830, 1608, 1364, 1084, 775, 537; **Mp**: 81.6 – 85.8 °C; **HRMS** (ESI) calcd. For $C_{16}H_{10}F_6NaO_4S_2^+$ $[M+Na]^+$ m/z 466.9817, found: 466.9813.

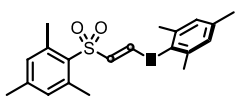
(*E*)-(3,5-Difluorophenyl)(2-((3,5-difluorophenyl)sulfonyl)vinyl)sulfane (36)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(3,5-difluorophenyl) 3,5-difluorobenzenesulfonothioate (81 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.) and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 20/1) afforded the title compound as a yellow solid (44 mg, 51% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J*= 14.6 Hz, 1H), 7.41 (dd, *J* = 6.2, 2.1 Hz, 2H), 7.13 – 7.01 (m, 3H), 6.93 (tt, *J* = 8.7, 2.3 Hz, 1H), 6.15 (d, *J* = 14.6 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.4 (dd, *J* = 28.8, 12.0 Hz), 162.9 – 161.1 (m), 146.0, 144.0 (t, *J*= 8.1 Hz), 132.3 (t, *J* = 9.9 Hz), 123.3, 117.5 – 114.9 (m), 112.0 – 110.4 (m), 109.1 (t, *J* = 25.0 Hz), 105.9 (t, *J* = 25.0 Hz); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ - 104.8, - 106.2; **IR** (KBr, cm^{-1}) 3451, 2831, 1601, 1363, 1082, 774, 528; **Mp**: 110.8 – 111.9 °C; **HRMS** (ESI) calcd. For $C_{14}H_8F_4NaO_2S_2^+$ $[M+Na]^+$ m/z 370.9794, found: 370.9796.

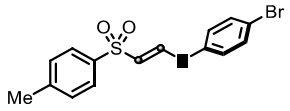
(*E*)-Mesityl(2-(mesitylsulfonyl)vinyl)sulfane (37)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-mesityl 2,4,6-trimethylbenzenesulfonothioate (84 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a gray solid (29 mg, 32% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J*= 14.3 Hz, 1H), 6.89 (s, 2H), 6.83 (s, 2H), 5.57 (d, *J* = 14.3 Hz, 1H), 2.47 (s, 6H), 2.25 (s, 6H), 2.21 (s, 6H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143.3, 142.8, 142.7, 140.6, 139.4, 134.5, 132. 1, 129.8, 123.4, 122.9, 22.7, 21.2, 21. 1, 21.0; **IR** (KBr, cm^{-1}) 3453, 2829, 1598, 1359, 1083, 773, 533; **Mp**: 117.2 – 118.9 °C; **HRMS** (ESI) calcd. For $C_{20}H_{24}NaO_2S_2^+$ $[M+Na]^+$ m/z 383.1110, found: 383.1107.

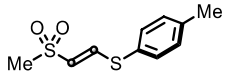
(*E*)-(4-Bromophenyl)(2-tosylvinyl)sulfane (38)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(4-bromophenyl) 4-methylbenzenesulfonothioate (86 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a light yellow solid (45 mg, 49% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.64 (m, 3H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J*= 8.5 Hz, 4H), 6.02 (d, *J*= 14.5 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.4, 144.3, 137.8, 134.9, 133.2, 130.0, 128.3, 127.5, 124.5, 124.2, 21.6; **IR** (KBr, cm^{-1}) 3448, 2831, 1600, 1363, 1081, 775, 530; **Mp**: 116.9 – 118.5 °C; **HRMS** (ESI) calcd. For $C_{15}H_{13}BrNaO_2S_2^+$ $[M+Na]^+$ m/z 390.9433, found: 390.9434.

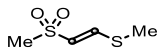
(*E*)-(2-(Methylsulfonyl)vinyl)(*p*-tolyl)sulfane (39)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-*p*-tolyl methanesulfonothioate (51 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (20 mg, 0.06 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a yellow solid (34 mg, 60% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 14.4 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 5.93 (d, *J* = 14.5 Hz, 1H), 2.88 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.4, 140.6, 133.9, 130.9, 125.0, 121.7, 43.5, 21.3; **IR** (KBr, cm^{-1}) 3747, 3648, 2830, 2717, 1599, 1363, 1129, 184, 774, 527; **Mp**: 96.4 – 100.9 °C; **HRMS** (ESI) calcd. For $C_{10}H_{12}NaO_2S_2^+$ $[M+Na]^+$ m/z 251.0171, found: 251.0176.

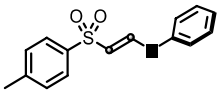
(*E*)-Methyl(2-(methylsulfonyl)vinyl)sulfane (40)



Prepared following the general procedure outlined above using 4CzIPN (7.8 mg, 10 μmol, 0.02 equiv.), *S*-methyl methanesulfonothioate (63 mg, 0.5 mmol, 1.0 equiv.), Cs_2CO_3 (40 mg, 0.12 mmol, 0.25 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a brown solid (36 mg, 48% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J*= 14.5 Hz, 1H), 6.14 (d, *J*= 14.5 Hz, 1H), 2.97 (d, *J* = 1.1 Hz, 3H), 2.37 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 147.6, 120.3, 43.6, 14.7; **IR** (KBr, cm^{-1}) 3459, 1597, 1359, 1084, 771; **Mp**: 53.6 – 55.7 °C; **HRMS** (ESI) calcd. For $C_4H_8NaO_2S_2^+$ $[M+Na]^+$ m/z 174.9858, found: 174.9856.

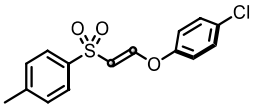
(*E*)-1-Methyl-4-((2-phenoxyvinyl)sulfonyl)benzene (41)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), phenyl 4-methylbenzenesulfonate (62 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a white solid (21 mg, 33% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 (d, *J*= 11.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J*= 8.1 Hz, 2H), 6.00 (d, *J* = 11.9 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 157.6, 155.4, 144.0, 139.0, 130. 1, 129.9, 129.6, 127. 1, 125.7, 120.6, 118.3, 115.3, 112.2, 21.6; **IR** (KBr, cm^{-1}) 2830, 1599, 1364, 1139, 1084, 774, 534; **Mp**: 92.8 – 95.4 °C; **HRMS** (ESI) calcd. For $C_{15}H_{14}NaO_3S^+$ $[M+Na]^+$ m/z 297.0556, found: 297.0561.

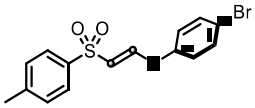
(*E*)-1-Chloro-4-((2-tosylvinyl)oxy)benzene (42)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 4-chlorophenyl 4-methylbenzenesulfonate (71 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a brow solid (22 mg, 29% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (t, *J* = 9.8 Hz, 3H), 7.34 (t, *J*= 7.1 Hz, 4H), 7.00 (d, *J*= 8.6 Hz, 2H), 6.01 (d, *J* = 11.9 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 157.0, 153.8, 144.2, 138.7, 131.0, 130.2, 129.9, 129.5, 127.2, 119.7, 116.7, 112.8, 21.6; **IR** (KBr, cm^{-1}) 2830, 1601, 1364, 1139, 1083, 774; **Mp**: 86.0 – 88.6 °C; **HRMS** (ESI) calcd. For $C_{15}H_{13}ClNaO_3S^+$ $[M+Na]^+$ m/z 331.0166, found: 331.0173.

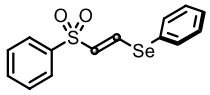
(*E*)-1-Bromo-4-((2-tosylvinyl)oxy)benzene (43)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 4-bromophenyl 4-methylbenzenesulfonate (71 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the mixture as a colorless oil (24 mg, 27% yield based on ^{1}H NMR). Since the desired product is co-polar with the by-product (4-bromophenol) and cannot be separated by column chromatography, the yield of the product is determined by ^{1}H NMR using mesitylene as an internal standard.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 14.9 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.35 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.22 (d, *J* = 14.9 Hz, 1H), 2.43 (s, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 157.0, 154.9, 144.4, 138.4, 133.2, 130.0, 127.2, 120.0, 118.6, 21.6; **IR** (KBr, cm^{-1}) 2955, 2831, 2716, 1602, 1364, 1084, 775, 531; **Mp**: 54.5 – 57.7 °C; **HRMS** (ESI) calcd. For $C_{15}H_{13}ClNaO_3S^+$ $[M+Na]^+$ m/z 374.9661, found: 374.9666.

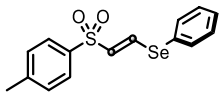
(*E*)-Phenyl(2-(phenylsulfonyl)vinyl)selane (44)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *Se*-phenyl benzenesulfonoselenoate (74 mg, 0.25 mmol, 1.0 equiv.), pyridine (20 mg, 0.25 mmol, 1.0 equiv.), and CH_3CN (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a light yellow solid (52 mg, 65% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, *J*= 15.0 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.38 (dt, *J* = 14.8, 7.1 Hz, 3H), 6.21 (d, *J* = 14.9 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143. 1, 140.7, 135.2, 133.2, 130. 1, 129.7, 129.3, 129.3, 127.5, 127.2, 125.4; **IR** (KBr, cm^{-1}) 3447, 2831, 2716, 1604, 1364, 1084, 775, 533; **Mp**: 42.4 – 74.4 °C;**HRMS** (ESI) calcd. For $C_{14}H_{12}NaO_2SSe^+$ $[M+Na]^+$ m/z 346.9615, found: 346.9615.

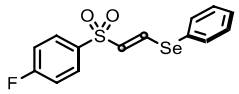
(*E*)-Phenyl(2-tosylvinyl)selane (45)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *Se*-phenyl 4-methylbenzenesulfonoselenoate (78 mg, 0.25 mmol, 1.0 equiv.), pyridine (20 mg, 0.25 mmol, 1.0 equiv.), and CH_3CN (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a white solid (56 mg, 67% yield).

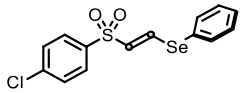
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, *J*= 15.0 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.38 (dt, *J* = 14.8, 7.1 Hz, 3H), 6.21 (d, *J* = 14.9 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143. 1, 140.7, 135.2, 133.2, 130. 1, 129.7, 129.3, 129.3, 127.5, 127.2, 125.4; **IR** (KBr, cm^{-1}) 3784, 3719, 2830, 2717, 1603, 1364, 1084, 775, 531; **Mp**: 98.1 – 99.2 °C; **HRMS** (ESI) calcd. For $C_{15}H_{14}NaO_2SSe^+$ $[M+Na]^+$ m/z 360.9772, found: 360.9774.

(*E*)-(2-((4-Fluorophenyl)sulfonyl)vinyl)(phenyl)selane (46)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *Se*-phenyl 4-fluorobenzenesulfonoselenoate (79 mg, 0.25 mmol, 1.0 equiv.), pyridine (20 mg, 0.25 mmol, 1.0 equiv.), and CH_3CN (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a yellow solid (64 mg, 75% yield).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 14.9 Hz, 1H), 7.84 – 7.64 (m, 2H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.33 (dd, *J*= 16.3, 7.5 Hz, 3H), 7.10 (q, *J* = 8.4 Hz, 2H), 6.10 (d, *J*= 14.9 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.5 (d, ^1J = 257.4 Hz), 143.4, 136.8 (d, ^3J = 3.8 Hz), 135.2 (d, ^3J = 2.5 Hz), 130.3, 130.3, 129.8, 127.0, 125.3, 116.6 (d, ^2J = 22.7 Hz); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ - 104.2; **IR** (KBr, cm^{-1}) 3648, 2955, 2830, 2717, 1605, 1365, 1083, 775, 530; **Mp**: 56.5 – 57.8 °C; **HRMS** (ESI) calcd. For $C_{14}H_{11}FNaO_2SSe^+$ $[M+Na]^+$ m/z 364.9521, found: 364.9526.

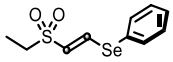
(*E*)-(2-((4-Chlorophenyl)sulfonyl)vinyl)(phenyl)selane (47)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *Se*-phenyl 4-chlorobenzenesulfonoselenoate (83 mg, 0.25 mmol, 1.0 equiv.), pyridine (20 mg, 0.25 mmol, 1.0 equiv.), and CH_3CN (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a colorless oil (62 mg, 70% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 14.9 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.39 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.36 – 7.26 (m, 3H), 6.08 (d, *J*= 14.9 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.0, 139.9, 139.2, 135.3, 130.2, 129.8, 129.6, 129.0, 126.7, 125.2; **IR** (KBr, cm^{-1}) 3649, 2830, 2716, 1600, 1363, 1084, 774, 532; **Mp**: 75.3 – 76.9 °C; **HRMS** (ESI) calcd. For $C_{14}H_{11}ClNaO_2SSe^+$ $[M+Na]^+$ m/z 380.9226, found: 380.9227.

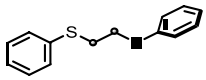
(*E*)-(2-(Ethylsulfonyl)vinyl)(phenyl)selane (48)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *Se*-phenyl ethanesulfonoselenoate (62 mg, 0.25 mmol, 1.0 equiv.), pyridine (20 mg, 0.25 mmol, 1.0 equiv.) and CH_3CN (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a colorless oil (38 mg, 57% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, *J*= 15.0 Hz, 1H), 7.60 (d, *J*= 7.1 Hz, 2H), 7.43 (dq, *J* = 14.4, 7.0 Hz, 3H), 6.11 (d, *J* = 15.0 Hz, 1H), 2.93 (q, *J* = 7.4 Hz, 2H), 1.30 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.6, 135.4, 130.2, 129.8, 125.3, 124. 1, 49.3, 7.2; **IR** (KBr, cm^{-1}) 2830, 2717, 1600, 1363, 1084, 774, 533; **HRMS** (ESI) calcd. For $C_{10}H_{12}NaO_2SSe^+$ $[M+Na]^+$ m/z 298.9615, found: 298.9620.

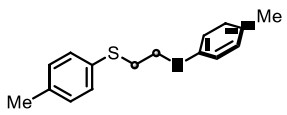
1,2-Bis(phenylthio)ethane (49)



Prepared following the general procedure outlined above using 1,2-diphenyldisulfane (55 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 100/1) afforded the title compound as a white solid (35 mg, 57% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 6.6 Hz, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.12 (t, *J*= 7.0 Hz, 2H), 3.00 (s, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 135. 1, 130. 1, 129. 1, 126.6, 33.4. The analytical datas are in agreement with the literature[20].

1,2-Bis(*p*-tolylthio)ethane (50)

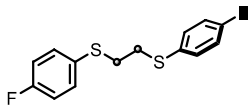


Prepared following the general procedure outlined above using 1,2-diphenyldisulfane (62 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 100/1) afforded the title compound as a white solid (43 mg, 63% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.2 Hz, 4H), 7.08 (d, *J* = 7.9 Hz, 4H), 3.01 (s,

4H), 2.32 (s, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 136.8, 131.3, 130.8, 129.8, 34.0, 21.0. The analytical datas are in agreement with the literature[20].

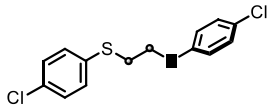
1,2-Bis((4-fluorophenyl)thio)ethane (51)



Prepared following the general procedure outlined above using 1,2-bis(4-fluorophenyl)disulfane (64 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 100/1) afforded the title compound as a white solid (38 mg, 54% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.23 (dd, *J* = 8.5, 5.2 Hz, 4H), 6.90 (t, *J* = 8.6 Hz, 4H), 2.90 (s, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.1 (d, ^{1}J = 247.3 Hz), 133.2 (d, ^{3}J = 8.2 Hz), 129.8 (d, ^{3}J = 3.4 Hz), 116.2 (d, ^{2}J = 22.0 Hz); **^{19}F NMR** (471 MHz, Chloroform-*d*) δ - 114.5. The analytical datas are in agreement with the literature[20].

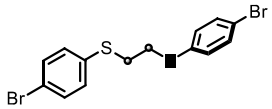
1,2-Bis((4-chlorophenyl)thio)ethane (52)



Prepared following the general procedure outlined above using 1,2-bis(4-chlorophenyl)disulfane (72 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 100/1) afforded the title compound as a white solid (49 mg, 62% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.01 (m, 8H), 2.96 (s, 8H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 133.4, 132.9, 131.6, 129.2, 33.7. The analytical datas are in agreement with the literature[20].

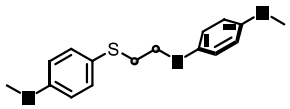
1,2-Bis((4-bromophenyl)thio)ethane (53)



Prepared following the general procedure outlined above using 1,2-bis(4-bromophenyl)disulfane (94 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 100/1) afforded the title compound as a white solid (69 mg, 69% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.5 Hz, 4H), 7.16 (d, *J* = 8.5 Hz, 4H), 3.04 (s, 8H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134. 1, 132.2, 131.7, 120.7, 33.5. The analytical datas are in agreement with the literature[20].

1,2-Bis((4-methoxyphenyl)thio)ethane (54)

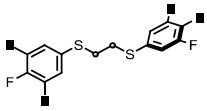


Prepared following the general procedure outlined above using 1,2-bis(4-bromophenyl)disulfane (70 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M).

Purification by column chromatography (Eluent: petroleum ether/EtOAc = 50/1) afforded the title compound as a white solid (47 mg, 62% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 4H), 3.79 (s, 6H), 2.92 (s, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.2, 133.7, 125.2, 114.7, 55.4, 35.3. The analytical datas are in agreement with the literature[20].

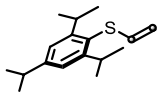
1,2-Bis((3,4,5-trifluorophenyl)thio)ethane (55)



Prepared following the general procedure outlined above using 1,2-bis(3,4,5-trifluorophenyl)disulfane (82 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 100/1) afforded the title compound as a white solid (53 mg, 60% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.94 (t, *J* = 6.8 Hz, 4H), 3.07 (s, 4H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 151.3 (ddd, *J* = 253.2, 10.4, 4.3 Hz), 138.8 (dt, *J* = 252.6, 15.3 Hz), 130.9 (td, *J* = 7.9, 4.9 Hz), 114.1 (dd, *J* = 17.0, 5.5 Hz), 33.6; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ - 132.7, - 132.7, - 132.8, - 161.3, - 161.3, - 161.3; **IR** (KBr, cm^{-1}) 3747, 3648, 2830, 2716, 1600, 1363, 1083, 774, 531; **Mp**: 55.0 – 56.6 °C; **HRMS** (ESI) calcd. For $C_{14}H_8F_6NaS_2^+$ $[M+Na]^+$ m/z 376.9864, found:376.2410.

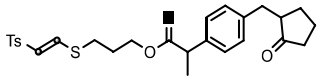
(2,4,6-Triisopropylphenyl)(vinyl)sulfane (56)



Prepared following the general procedure outlined above using 1,2-bis(2,4,6-triisopropylphenyl)disulfane (117 mg, 0.25 mmol, 1.0 equiv.), hantzsch ester (63 mg, 0.25 mmol, 1.0 equiv.), and DMC (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 150/1) afforded the title compound as a colorless oil (52 mg, 40% yield)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (s, 2H), 6.35 (dd, *J*= 16.3, 9.8 Hz, 1H), 5.04 (d, *J*= 9.8 Hz, 1H), 4.58 (d, *J* = 16.3 Hz, 1H), 3.66 (p, *J* = 6.9 Hz, 2H), 3.10 – 2.79 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.3, 150.5, 134. 1, 134. 1, 124.0, 122.0, 109.4, 34.4, 31.6, 31.6, 24.4, 23.9.

(*E*)-3-((2-Tosylvinyl)thio)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (58)

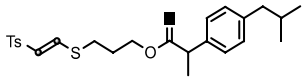


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (119 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a colorless liquid (49 mg, 39% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 14.7 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.12 (d, *J* = 15.9 Hz, 1H), 4.27 – 3.98 (m, 2H), 3.70 (q, *J* = 7.1 Hz, 1H), 3.12 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.51 (dd, *J*= 13.9, 9.6 Hz, 1H), 2.45 (s, 3H), 2.35 (dd, *J*= 16.4, 7.1 Hz, 2H), 2.10 (dd, *J*= 18.3, 9.5

Hz, 3H), 2.00 – 1.86 (m, 3H), 1.77 (s, 2H), 1.63 – 1.43 (m, 5H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.4, 144.5, 144.2, 139. 1, 138.2, 129.9, 129.2, 127.5, 127.5, 127.4, 122.5, 62.4, 50.9, 45. 1, 38.2, 35.2, 29.2, 28.7, 27.7, 21.6, 20.5, 18.2; **IR** (KBr, cm^{-1}) 3652, 2830, 1603, 1363, 1082, 775; **HRMS** (ESI) calcd. $C_{27}H_{32}NaO_5S_2^+$ $[M+Na]^+$ m/z 523.1583, found: 523.1584.

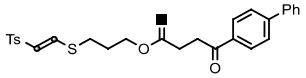
(*E*)-3-((2-Tosylvinyl)thio)propyl 2-(4-isobutylphenyl)propanoate (59)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 2-(4-isobutylphenyl)propanoate (109 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 7/1) afforded the title compound as a light yellow liquid (69 mg, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 14.7 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.12 (d, *J* = 14.7 Hz, 1H), 4.25 – 4.01 (m, 2H), 3.70 (d, *J* = 7.1 Hz, 1H), 2.64 (t, *J* = 7.3 Hz, 2H), 2.54 – 2.36 (m, 5H), 2.03 – 1.76 (m, 3H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.5, 144.6, 144. 1, 140.7, 138.3, 137.6, 129.9, 129.9, 129.4, 127.4, 127. 1, 122.4, 62.4, 45. 1, 45.0, 30.2, 28.7, 27.7, 22.4, 21.6, 18.2; **IR** (KBr, cm^{-1}) 3448, 2830, 2717, 1603, 1364, 1084, 775, 531; **HRMS** (ESI) calcd. $C_{25}H_{32}NaO_4S_2^+$ $[M+Na]^+$ m/z 483.1634, found: 483.1640.

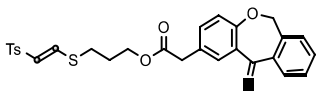
(*E*)-3-((2-Tosylvinyl)thio)propyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (60)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (121 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a white solid (65 mg, 51% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.73 – 7.68 (m, 3H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J*= 14.7 Hz, 1H), 4.21 (t, *J* = 6.0 Hz, 2H), 3.37 (t, *J* = 6.4 Hz, 2H), 2.89 (t, *J*= 7.3 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 2.02 (p, *J* = 6.5 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 197.7, 172.8, 146.0, 144.6, 144. 1, 139.8, 138.2, 135. 1, 129.9, 129.0, 128.7, 128.3, 127.4, 127.3, 127.3, 122.5, 62.5, 33.4, 28.9, 28.2, 27.8, 21.6; **IR** (KBr, cm^{-1}) 3452, 2829, 1596, 1355, 1083, 775, 531; **Mp**: 78.4 – 81.1 °C; **HRMS** (ESI) calcd. $C_{28}H_{28}NaO_5S_2^+$ $[M+Na]^+$ m/z 531.1270, found: 531.1263.

(*E*)-3-((2-Tosylvinyl)thio)propyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (61)

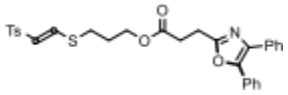


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (124 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a

light yellow liquid (68 mg, 52% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 14.7 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.31 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.19 (d, *J* = 14.7 Hz, 1H), 5.17 (s, 2H), 4.17 (t, *J* = 6.2 Hz, 2H), 3.64 (s, 2H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.98 (dq, *J* = 12.3, 6.3 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.8, 190.7, 171.3, 171.2, 160.5, 160.5, 144.5, 144. 1, 140.4, 140.4, 138.2, 136.4, 136.3, 135.6, 132.8, 132.5, 132.4, 132.4, 129.9, 129.5, 129.3, 127.9, 127.9, 127.6, 127.4, 125.2, 125.2, 122.6, 121.2, 121. 1, 73.6, 62.9, 40.2, 40. 1, 28.9, 27.6, 21.6; **IR** (KBr, cm^{-1}) 3449, 2830, 1600, 1362, 1082, 775, 531; **HRMS** (ESI) calcd. $C_{28}H_{26}NaO_6S_2^+$ $[M+Na]^+$ m/z 545.1063, found: 545.1060.

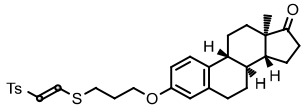
(*E*)-3-((2-Tosylvinyl)thio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate (62)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate (130 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a white solid (59 mg, 43% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 14.7 Hz, 1H), 7.61 (d, *J* = 6.8 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.33 (dt, *J* = 22.0, 8.0 Hz, 8H), 6.15 (d, *J*= 14.7 Hz, 1H), 4.20 (t, *J* = 6.0 Hz, 2H), 3.18 (t, *J* = 7.4 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.98 (p, *J* = 6.7 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 171.8, 161.6, 145.5, 144.4, 144. 1, 138.2, 135. 1, 132.4, 129.9, 128.9, 128.7, 128.6, 128.5, 128. 1, 127.9, 127.4, 126.5, 122.6, 62.6, 31.0, 28.9, 27.8, 23.5, 21.6; **IR** (KBr, cm^{-1}) 3451, 1595, 1385, 1353, 1083, 768, 531; **Mp**: 82.2 – 86.2 °C; **HRMS** (ESI) calcd. $C_{30}H_{29}NNaO_5S_2^+$ $[M+Na]^+$ m/z 570.1379, found: 570.1371.

(8*S*,9*R*,13*R*,14*R*)-13-Methyl-3-(3-(((*E*)-2-tosylvinyl)thio)propoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (63)

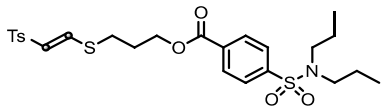


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-(3-(((8*S*,9*R*,13*R*,14*R*)- 13-methyl- 17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)propyl) 4-methylbenzenesulfonothioate (125 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a light yellow solid (48 mg, 37% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 2H1), 7.69 (d, *J*= 14.7 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 1H), 6.76 – 6.57 (m, 2H), 6.20 (d, *J* = 14.7 Hz, 1H), 4.00 (t, *J* = 5.7 Hz, 2H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.89 (dt, *J* = 7. 1, 4.4 Hz, 2H), 2.60 – 2.34 (m, 5H), 2.30 – 1.88 (m, 6H), 1.73 – 1.40 (m, 8H), 0.90 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) ^{13}C NMR (126 MHz, Chloroform-d) δ 156.5, 144.7, 144.0, 138.3, 137.9, 132.5, 129.9, 127.4, 126.4, 122.4, 114.6, 112.0, 65.5, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 29.6, 29.0, 28.3, 26.5, 25.9, 21.6, 13.9; **IR**

(KBr, cm^{-1}) 3648, 3452, 1596, 1385, 1353, 1083, 767, 534; **Mp**: 99.2 – 101.3 °C; **HRMS** (ESI) calcd. $C_{30}H_{36}NaO_4S_2^+$ $[M+Na]^+$ m/z 547.1947, found: 547.1938.

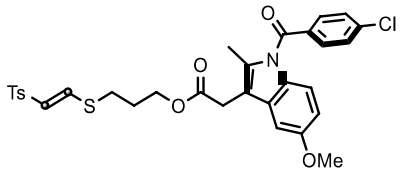
(*E*)-3-((2-Tosylvinyl)thio)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (64)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (128 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a white solid (84 mg, 62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.71 (s, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.19 (d, *J* = 14.7 Hz, 1H), 4.43 (t, *J* = 6.0 Hz, 2H), 3.23 – 3.01 (m, 4H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.24 – 2.04 (m, 2H), 1.68 – 1.46 (m, 4H), 0.86 (t, *J*= 7.4 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.5, 144.7, 144.0, 138.3, 137.9, 132.5, 129.9, 127.4, 126.4, 122.4, 114.6, 112.0, 65.5, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 29.6, 29.0, 28.3, 26.5, 25.9, 21.6, 13.9; **IR** (KBr, cm^{-1}) 3451, 2807, 1644, 1588, 1386, 1349, 789, 557; **Mp**: 60.3 – 61.2 °C; **HRMS** (ESI) calcd. $C_{25}H_{33}NNaO_6S_3^+$ $[M+Na]^+$ m/z 562.1362, found: 562.1356.

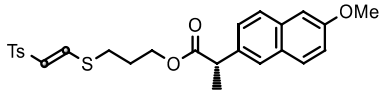
(*E*)-3-((2-Tosylvinyl)thio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (65)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl- 1*H*-indol-3-yl)acetate (147 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a light yellow liquid (87 mg, 57% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.70 – 7.60 (m, 3H), 7.48 (d, *J*= 8.4 Hz, 2H), 7.33 (s, 2H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.13 (d, *J* = 14.7 Hz, 1H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 3.69 (s, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.41 (d, *J* = 15.4 Hz, 6H), 1.98 (p, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 168.3, 156.0, 144.4, 144.2, 139.3, 138. 1, 136.0, 133.9, 131.2, 130.8, 130.5, 129.9, 129. 1, 127.4, 122.6, 115.0, 112.3, 111.6, 101.4, 62.9, 55.7, 30.3, 28.9, 27.6, 21.6, 13.4; **IR** (KBr, cm^{-1}) 3451, 2829, 1598, 1359, 1084, 775, 532; **HRMS** (ESI) calcd. $C_{31}H_{30}ClNNaO_6S_2^+$ $[M+Na]^+$ m/z 634.1095, found: 634.1088.

(*E*)-3-((2-Tosylvinyl)thio)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (66)

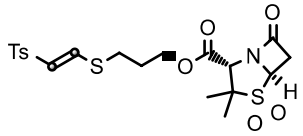


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02

equiv.), 3-(tosylthio)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (114 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 7/1) afforded the title compound as a white solid (57 mg, 46% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.69 (m, 4H), 7.67 (s, 1H), 7.62 (d, *J* = 14.7 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.09 (d, *J* = 14.7 Hz, 1H), 4.30 – 4.05 (m, 2H), 3.94 (s, 3H), 3.87 (q, *J* = 7.1 Hz, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.91 (p, *J* = 6.4 Hz, 2H), 1.60 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.5, 157.7, 144.6, 144. 1, 138.2, 135.5, 133.8, 129.9, 129.2, 128.9, 127.4, 127.3, 126. 1, 125.9, 122.4, 119. 1, 105.7, 62.5, 55.3, 45.4, 28.8, 27.6, 21.6, 18.3; **IR** (KBr, cm^{-1}) 3446, 2831, 2717, 1603, 1364, 1081, 775, 532; **Mp**: 95.1 – 96.9 °C; **HRMS** (ESI) calcd. $C_{26}H_{28}NaO_5S_2^+$ $[M+Na]^+$ m/z 507.1270, found: 507.1270.

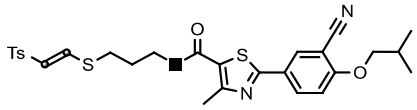
3-(((*E*)-2-Tosylvinyl)thio)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0] heptane-2-carboxylate 4,4-dioxide (67)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia- 1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (115 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 2/1) afforded the title compound as a colorless liquid (22 mg, 18% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 14.7 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.22 (d, *J*= 14.7 Hz, 1H), 4.66 (dd, *J* = 4.4, 2.1 Hz, 1H), 4.41 (s, 1H), 4.31 (td, *J*= 6.3, 1.6 Hz, 2H), 3.50 (qd, *J*= 16.2, 3.2 Hz, 2H), 3.04 – 2.72 (m, 2H), 2.45 (s, 3H), 2.13 – 2.00 (m, 2H), 1.61 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.9, 166.9, 144.3, 144.0, 138.0, 130.0, 127.4, 123.0, 64. 1, 63.2, 62.8, 61.2, 38.4, 28.7, 27.5, 21.6, 20.3, 18.6; **IR** (KBr, cm^{-1}) 3468, 2830, 1602, 1364, 1082, 775, 535; **HRMS** (ESI) calcd. $C_{20}H_{25}NNaO_7S_3^+$ $[M+Na]^+$ m/z 510.0685, found: 510.0680.

(*E*)-3-((2-Tosylvinyl)thio)Propyl 2-(3-cyano-4-isopropoxyphenyl)-4-methylthiazole-5-carbo xylate (68)

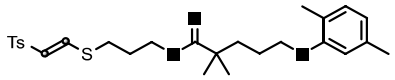


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (136 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 3/1) afforded the title compound as a light yellow solid (69 mg, 49% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J*= 1.9 Hz, 1H), 8.15 – 8.06 (m, 1H), 7.83 – 7.57 (m, 3H), 7.30 (s, 2H), 7.10 – 6.84 (m, 1H), 6.38 – 5.98 (m, 1H), 4.36 (t, *J* = 5.9 Hz, 2H), 3.89 (d, *J* = 6.4 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.73 (s, 3H), 2.40 (s, 3H), 2.19 (dt, *J*= 13.3, 6.6 Hz, 1H), 2.11

(p, *J* = 6.4 Hz, 2H), 1.08 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 162.6, 161.7, 161.7, 144.4, 144.2, 138. 1, 132.8, 132.0, 129.9, 127.3, 125.8, 122.6, 120.9, 115.4, 112.7, 102.9, 75.7, 63.2, 33.9, 28.9, 28. 1, 27.8, 25.6, 25.0, 21.6, 19. 1, 17.5; **IR** (KBr, cm^{-1}) 3449, 2831, 1602, 1363, 1084, 775, 532; **Mp**: 108.5 – 112.1 °C; **HRMS** (ESI) calcd. $C_{28}H_{30}N_2NaO_5S_3^+$ $[M+Na]^+$ m/z 593.1209, found: 593.1202.

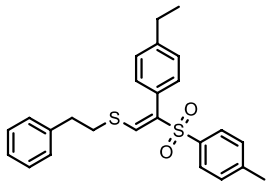
(*E*)-3-((2-Tosylvinyl)thio)Propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (69)



Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), 3-(tosylthio)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (120 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 8/1) afforded the title compound as a colorless liquid (64 mg, 51% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 14.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 6.19 (d, *J* = 14.7 Hz, 1H), 4.15 (t, *J* = 6.1 Hz, 2H), 3.94 (s, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H), 2.19 (s, 3H), 2.09 – 1.95 (m, 2H), 1.74 (s, 4H), 1.24 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.6, 156.9, 144.5, 144. 1, 138.2, 136.5, 130.3, 129.9, 127.4, 123.5, 122.6, 120.8, 112.0, 67.8, 62.3, 42. 1, 37. 1, 29.0, 27.8, 25.2, 25.2, 21.6, 21.4, 15.8; **IR** (KBr, cm^{-1}) 3448, 2831, 1602, 1363, 1082, 775, 531; **HRMS** (ESI) calcd. $C_{27}H_{36}NaO_5S_2^+$ $[M+Na]^+$ m/z 527.1896, found: 527.1899.

(*E*)-(2-(4-ethylphenyl)-2-tosylvinyl)(phenethyl)sulfane (3b)

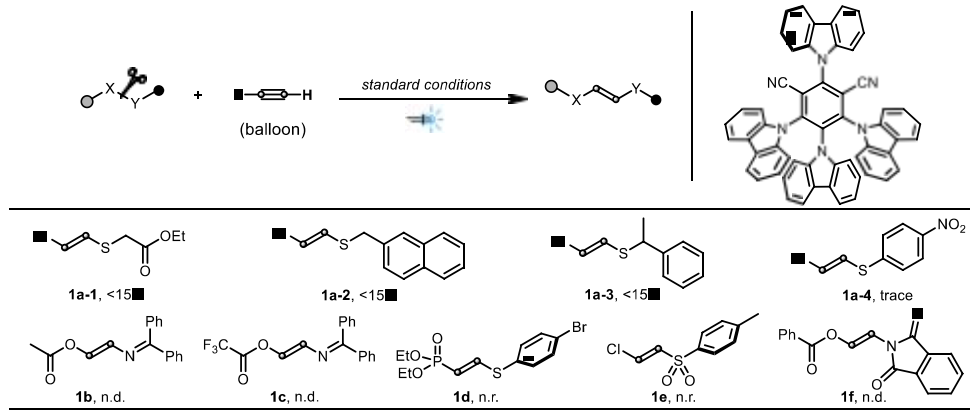


Prepared following the general procedure outlined above using 4CzIPN (3.9 mg, 5.0 μmol, 0.02 equiv.), *S*-phenethyl 4-methylbenzenesulfonothioate (73 mg, 0.25 mmol, 1.0 equiv.), 1-ethyl-4-ethynylbenzene (33 mg, 0.25 mmol, 1.0 equiv.), Cs_2CO_3 (41 mg, 0.125 mmol, 0.5 equiv.), and DMSO (0.05 M). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 10/1) afforded the title compound as a yellow liquid (31 mg, 29% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.28 (s, 1H), 7.22 (t, *J* = 7.3 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.3, 143.8, 143.7, 139.0, 136.6, 135.5, 130. 1, 129.4, 128.7, 128.7, 128.2, 128. 1, 126.8, 77.5, 77.2, 76.9, 36.9, 36.0, 28.7, 21.7, 15.2; **IR** (KBr, cm^{-1}) 3857, 3747, 3449, 2809, 1747, 1714, 1597, 1515, 1303, 803, 741, 670, 587; **HRMS** (ESI) calcd. $C_{25}H_{26}NaO_2S_2^+$ $[M+Na]^+$ m/z 445.1266, found: 445.1254.

6.2 Limitation of reaction

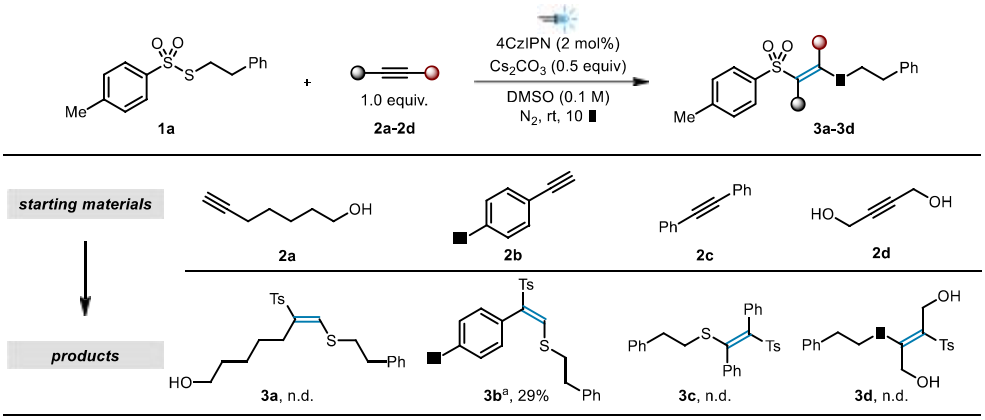
a) The following bifunctional reagents failed to give satisfactory levels of insertion product (<15%)[a].



[a]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

The current limitation of the methodology is that using α-benzyl/ester-substituted bifunctional reagents, a significant drop in yield was seen (**1a-1**-**1a-4**). Meanwhile, other types of bifunctional reagents did not give the desired product (**1b**-**1f**), even with prolonged reaction times.

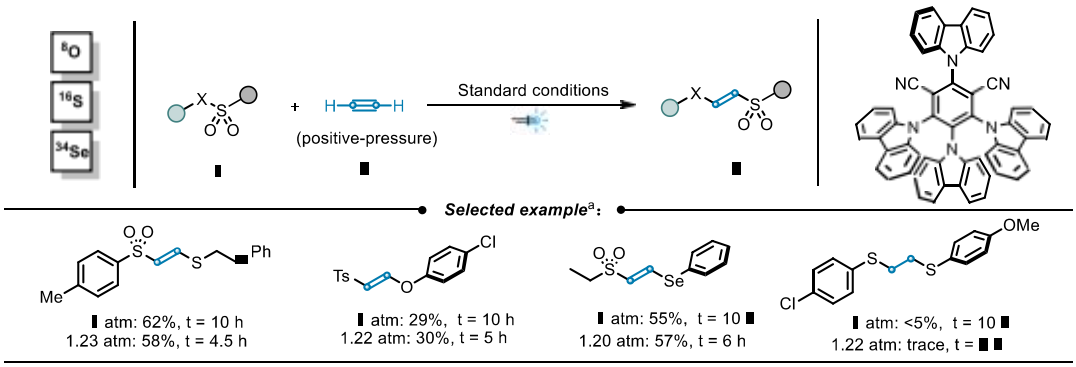
b) To better understand this insertion reaction, we subjected several other terminal and internal alkynes to the catalytic conditions.



[a] Isolated yield.

Unfortunately, 1,2-diphenylethyne (**2c**), but-2-yne- 1,4-diol (**2d**), or hept-6-yn- 1-ol (**2a**) failed to give insertion products, while by-product 1,2-diphenethyldisulfane could be detected by GC-MS. In contrast, we gratifyingly found that 1-ethyl-4-ethynylbenzene (**2b**) delivers the desired product **3b** in 29% yield under standard reaction conditions, albeit in a relatively lower yield. These results have been incorporated into the supporting information, along with a sentence in the text of the paper briefly summarising these results.

c) The influence of pressure of acetylene on the reaction efficiency and product yields. A simple positive-pressure reaction device as shown below.

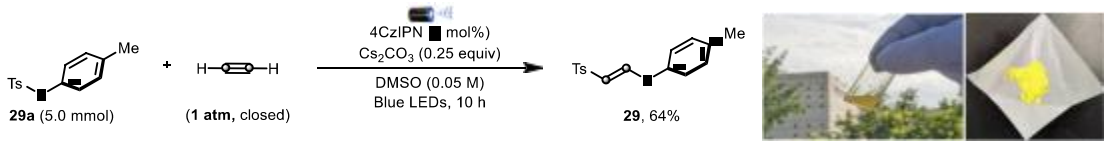


[a] Isolated yield.

In order to explore the influence of pressure of acetylene on the reaction efficiency and product yields, especially for the low yielding substrates. (As one of the anonymous reviewers suggested) The use of a positive-pressure photoreactor failed to improve the selected products yielding, but it could accelerate the reactions and shorten the reaction time. The employment of a positive-pressure photoreactor, for example, has enabled the total disappearance of raw material in less than 6 hours, whereas the previous reaction in 1 atm required more than 9 hours.

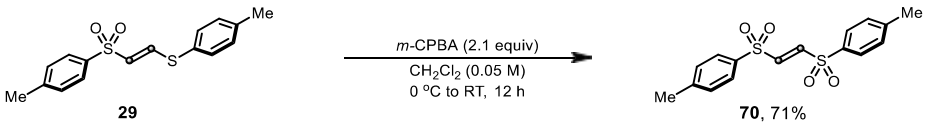
7 Gram-Scale Reaction and Synthetic Transformation

7.1 Gram-Scale synthesis



A 250 mL Schlenk round bottom flask equipped with a magnetic stir bar was charged with 4CzIPN (79 mg, 0.1 mmol, 0.2 mol%), **29a** (1.39 g, 5 mmol, 1.0 equiv.), and Cs_2CO_3 (407 mg, 1.25 mmol, 0.25 equiv.). The vessel was evacuated with three-way valve and refilled with acetylene gas. Subsequently, DMSO (100 mL) was added to the tube under positive acetylene flow. The resulting mixture was degassed by using a "freeze–pump–thaw" procedure three times. Finally, a balloon was filled with acetylene gas through three-way valve until its size was roughly 30 cm in diameter. The reaction mixture was stirred in front of two Kessil lamps at environment temperature for 10 hours (flask about 10 cm away from lights, fan for cooling) and then diluted with brine (80 mL) and extracted by EtOAc (3 × 30 mL). The combined organic layer was dried over Na_2SO_4, filtered, and evaporated. Purification by flash column chromatography on silica gel (Eluent: petroleum ether/EtOAc = 10/1) gave **29** (974 mg, 3.2 mmol, 64%) as a yellow viscous liquid.

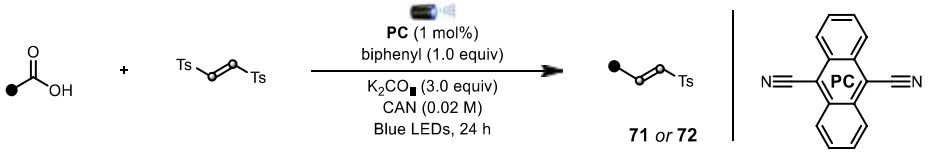
7.2 Synthetic Transformation



To an oven-dried 10 mL Teflon-screw capped Schlenk tube equipped with a stirring bar was added (*E*)- 1,2-ditosylethene **29** (304 mg, 1.0 mmol, 1.00 equiv.), 10 mL of DCM and cooled to 0 °C. Then

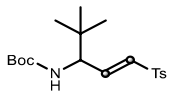
m-CPBA (85%) (426 mg, 2.1 mmol, 2.1 equiv.) was dissolved in DCM (10 mL) and added dropwise. The resultant mixture was stirred at 0 °C for 30 minutes, warmed up to room temperature, and stirred for an additional 12 h. The reaction was monitored by TLC. Next, saturated $NaHCO_3$ solution (10 mL) and water (10 mL) were added carefully, and the product was extracted into DCM (3 × 15 mL). The organic layers were combined, dried with $MgSO_4$, and filtered, and the volatiles was removed under reduced pressure. The (*E*)- 1,2-ditosylethene was isolated after flash chromatography (Eluent: DCM/CH_3OH = 200/1) as a white solid (234 mg, 0.71 mmol, 71%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.2 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.32 (s, 2H), 2.48 (s, 6H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 146.3, 140. 1, 134.7, 130.5, 128.5, 21.8; **IR** (KBr, cm^{-1}) 3403, 2831, 1609, 1366, 1080, 775, 539; **Mp**: 226.4 – 228.9 °C; **HRMS** (ESI) calcd. $C_{16}H_{17}O_4S_2^+$ $[M+H]^+$ m/z 337.0563, found: 337.0561.



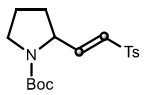
Following a slightly modified procedure[21] : To an oven-dried screw-capped Schlenk tube (25 mL) equipped with a Teflon-coated magnetic stir bar was added with (*E*)- 1,2-ditosylethene (100 mg, 0.3 mol 1.0 equiv.), *N*-(*tert*-butoxycarbonyl)-L-*tert*-leucine (208 mg, 0.9 mol 1.0 equiv.), K_2CO_3 (124 mg, 0.9 mmol, 3.00 equiv.), 9,10-dicyanoanthracene (1.36 mg, 3 μmol, 1 mol %), and biphenyl (47 mg, 0.3 mmol, 1.00 equiv.) under an inert nitrogen atmosphere, followed by the addition of degassed CH_3CN (0.02 M). After the Schlenk tube was re-capped with a Teflon-screw and irradiated with two 34 W blue LED lamps from a distance of approximately 5 cm for 24 h. The reaction mixture was diluted with DCM (15 mL) and a saturated aqueous solution of $NaHCO_3$ (15 mL) was added. Upon phase separation, the aqueous layer was extracted with DCM (2 x 15 mL). The combined organic extracts were washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel ((Eluent: petroleum ether/EtOAc = 6/1)) gave **71** (89 mg, 0.24 mmol, 81%) as a light yellow solid.

***tert*-Butyl (*E*)-(4,4-dimethyl-1-tosylpent-1-en-3-yl)carbamate (71)**



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.97 (dd, *J* = 14.9, 5.4 Hz, 1H), 6.44 (d, *J* = 15.0 Hz, 1H), 4.79 – 4.45 (m, 1H), 4.13 (t, *J* = 8.1 Hz, 1H), 2.43 (d, *J*= 1.7 Hz, 3H), 1.39 (s, 9H), 0.94 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.2, 144.4, 143.7, 137.4, 132.0, 129.9, 127.6, 79.9, 59.6, 35.0, 28.2, 26.3, 21.6; **IR** (KBr, cm^{-1}) 2965, 2832, 1701, 1606, 1366, 1146, 1086, 775, 544; **Mp**: 118.2 – 113.7 °C; **HRMS** (ESI) calcd. For $C_{19}H_{29}NaNO_4S^+$ $[M+Na]^+$ m/z 390.1710, found: 390.1710.

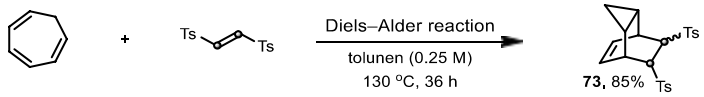
***tert*-Butyl (*E*)-2-(2-tosylvinyl)pyrrolidine-1-carboxylate (72)**



Prepared following the general procedure outlined above using (*E*)- 1,2-ditosylethene (100 mg, 0.3

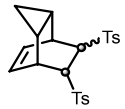
mol 1.0 equiv.), *N*-Boc-$_D$-prolin (100 mg, 0.9 mol 1.0 equiv.), K_2CO_3 (124 mg, 0.9 mmol, 3.00 equiv.), 9,10-dicyanoanthracene (1.36 mg, 3 μmol, 1 mol %), and biphenyl (47 mg, 0.3 mmol, 1.00 equiv.). Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a white solid (81 mg, 0.23 mmol, 77% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 6.79 (dd, *J* = 14.9, 5.8 Hz, 1H), 6.28 (d, *J* = 14.8 Hz, 1H), 4.43 (d, *J* = 65.5 Hz, 1H), 3.41 (s, 2H), 2.43 (s, 3H), 2.28 – 2.05 (m, 1H), 1.83 (dd, *J* = 20.5, 9.6 Hz, 3H), 1.40 (s, 3H), 1.19 (s, 6H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.0, 146.0, 145.4, 144.5, 137.5, 130.6, 130.2, 130.0, 127.7, 127.5, 79.8, 57.2, 56.9, 46.6, 46.4, 31.4, 28.3, 28.0, 23.7, 22.9, 21.6; **IR** (KBr, cm^{-1}) 3465, 2832, 1605, 1365, 1146, 775; **Mp**: 51.4 – 56.3 °C; **HRMS** (ESI) calcd. For $C_{18}H_{25}NaNO_4S^+$ $[M+Na]^+$ m/z 374.1397, found: 374.1397.

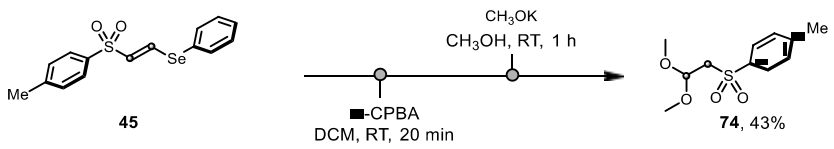


Following a slightly modified procedure[22] : to an oven-dried screw-capped Schlenk tube (10 mL) equipped with a Teflon-coated magnetic stir bar was charged with freshly distilled 1,3-cyclohexadiene (23 mg, 0.25 mmol, 1.0 equiv.) and (*E*)- 1,2-ditosylethene (84 mg, 0.25 mmol, 1.0 equiv.) in 1 mL of toluene. Then the Schlenk tube was re-capped with a Teflon-screw and immersed into a sand bath at 130 °C. The reaction mixture was stirred for 36 hours at this temperature before being cooled to room temperature and the solvent toluene was removed under decreased pressure. Purification by column chromatography (Eluent: petroleum ether/EtOAc = 4/1) afforded the title compound as a white solid (91 mg, 0.21 mmol, 85% yield).

8,9-Ditosyltricyclo[3.2.2.02,4]non-6-ene (73)



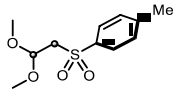
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J*= 8.1 Hz, 2H), 5.61 (p, *J* = 6.4 Hz, 2H), 3.83 (dd, *J* = 5.5, 2.3 Hz, 1H), 3.53 (dd, *J* = 5.5, 2.2 Hz, 1H), 3.36 – 3.23 (m, 1H), 3.20 – 3.09 (m, 1H), 2.26 (d, *J* = 7.1 Hz, 6H), 1.45 (dq, *J* = 7.6, 3.9 Hz, 1H), 0.88 (tt, *J* = 7.6, 3.8 Hz, 1H), 0.21 – -0.08 (m, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.9, 136.7, 136.0, 129.8, 128.7, 128.6, 126.8, 66. 1, 65.6, 33.8, 33.5, 21.8, 21.7, 9.0, 6. 1, 3.6; **IR** (KBr, cm^{-1}) 2830, 1609, 1365, 1144, 774, 742; **Mp**:190.7 – 193.2 °C; **HRMS** (ESI) calcd. For $C_{23}H_{25}O_4S_2^+$ $[M+H]^+$ m/z 429.1189, found: 429.1191.



Following a slightly modified procedure[23] : An oven-dried screw-capped Schlenk tube (25 mL) equipped with a Teflon-coated magnetic stir bar was charged with *m*-CPBA (85%) (122 mg, 0.6 mmol, 1.2 equiv.), DCM (2 mL), and hexane (15 mL). After adding (*E*)-phenyl(2-tosylvinyl)selane (169 mg, 0.5 mmol, 1.0 equiv.), the mixture was stirred for 20 min. Then filtering the mixture, the white solid washed with ether and dried for 6 h in a vacuum drying chamber. The crude material

was carried forward to the next step of reaction without further purification. The (*E*)- 1-methyl-4-((2-(phenylseleninyl)vinyl)sulfonyl)benzene in 10 mL of THF was treated with methanolic KOH for 1 h. Diluted with saturated ether and extracted with brine (3 x 10 mL). The combined organic phase was dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (Eluent: petroleum ether/EtOAc = 6/1) afforded the title compound as a light yellow solid (51 mg, 0.21 mmol, 41% yield).

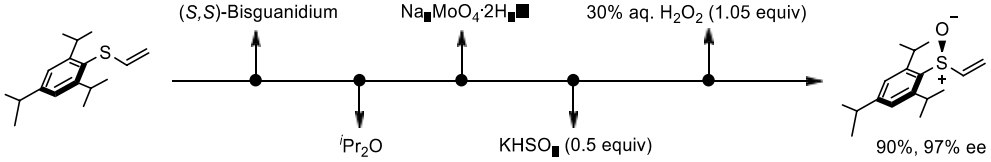
1-((2,2-Dimethoxyethyl)Sulfonyl)-4-methylbenzene (74)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J*= 8.1 Hz, 2H), 4.93 – 4.72 (m, 1H), 3.42 (d, *J* = 5.3 Hz, 2H), 3.24 (s, 6H), 2.45 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.8, 136.9, 129.7, 128.2, 99. 1, 58.8, 53.4, 21.7. The analytical datas are in agreement with the literature.[23]

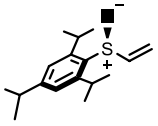
7.3 Synthesis of Chiral sulfoxide ligands (S-S, S-P, S-N, S-O).

(2,4,6-Triisopropylphenyl)(vinyl)Sulfane



According to the literature procedure[24], a 250 mL round flask equipped with a Teflon-coated magnetic stir bar was charged with (2,4,6-triisopropylphenyl)(vinyl)sulfane (1.31 g, 5 mmol), bisguanidinium phase-transfer catalyst (*S*,*S*)-Bisguanidium (17.6 mg, 0.0125 mmol), $^{i}Pr_2O$ (100 ml) solvent, $Na_2MoO_4 \cdot 2H_2O$ (30 mg, 0.125 mmol), $KHSO_4$ (340 mg, 2.5 mmol). The solution was cooled to -6 °C, when 30% aq. H_2O_2 (525 ml, 5.21 mmol) was added dropwise. The reaction mixture was stirred at -6 °C overnight. Subsequently, the organic layer was dried over Na_2SO_4, filtered through a pad of silica gel, and concentrated in vacuo, then directly used in the next step without further purification. Bisguanidinium phase-transfer catalyst (*S,S*)-Bisguanidium (developed by *Choon-Hong Tan Groups, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore*). We gratefully acknowledge Tan group for providing this phase-transfer catalyst, which provides great help for the synthesis application of this work.

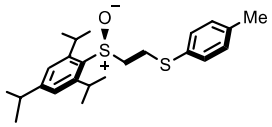
(*S*)-1,3,5-Triisopropyl-2-(vinylsulfinyl)benzene (75)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 6.77 (dd, *J*= 16.5, 9.9 Hz, 1H), 6.10 (d, *J*= 16.5 Hz, 1H), 5.94 (d, *J* = 9.8 Hz, 1H), 3.88 (dt, *J* = 13.5, 6.7 Hz, 2H), 2.89 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.24 (dd, *J* = 9.3, 6.9 Hz, 18H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.0, 150.7, 142.3, 133.0, 123.2, 119.6, 34.4, 28.2, 24.9, 23.8, 23.7; **IR** (KBr, cm^{-1}) 3698, 3135, 1655, 1395, 1075; **Mp**: 74.5 – 76.6 °C; **HR-MS** (ESI) calcd. For $C_{17}H_{26}NaOS^+$ $[M+Na]^+$ m/z 301. 1597, found 301. 1595;

Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 98/2, flow rate: 0.8 mL/min, back pressure: 2.1 MPa, detection at 254 nm, retention time = 6.6 min (major) and 7.3 min (minor), ee = 97%.

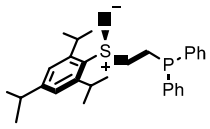
(*S*)-*p*-Tolyl(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)sulfane (76)



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), 4-methylbenzenethiol (0.25 mmol, 31 mg), *N*, *N*-diisopropylethylamine (29 mg, 0.22 mmol, 1.1 equiv.) in THF (1 mL) at 70 ℃ for 20 h, afforded 33 mg (41%) of **76** as pale yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 5.4 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.05 (s, 2H), 4.38 – 3.47 (broad, 3H), 3.35 (d, *J* = 9.7 Hz, 1H), 3.20 (dd, *J* = 17.8, 10.9 Hz, 1H), 2.88 (dt, *J* = 13.7, 12.7 Hz, 2H), 2.31 (s, 3H), 1.27 – 1.14 (m, 18H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.5, 137.3, 131.3, 130.4, 130.0, 124.0, 123.8, 122.7, 122.4, 121.9, 121.6, 53.7, 34.3, 29. 1, 24.6, 24.5, 24.4, 24.2, 23.8, 23.7, 21.1; **IR** (KBr, cm^{-1}) 3854, 3745, 3671, 3130, 1655, 1399, 1385, 1132, 676; **Mp**: 88.6 – 89.4 °C; **HR-MS** (ESI) calcd. For $C_{24}H_{34}NaOS_2^+$ $[M+Na]^+$ m/z 425. 1943, found 425. 1945; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 0.8 mL/min, back pressure: 2.1 MPa, detection at 254 nm, retention time = 7.9 min (major) and 9.9 min (minor), ee = 96%.

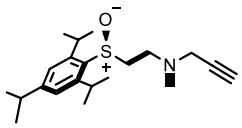
(*S*)-Diphenyl(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)phosphane (77)



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), diphenylphosphane (0.25 mmol, 46 mg), K_2CO_3 (30 mg, 0.22 mmol, 1.1 equiv.) in THF (1 mL) at 70 ℃ for 21 h, afforded 65 mg (70%) of **77** as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dddd, *J* = 13.4, 9.8, 7.9, 4.8 Hz, 5H), 7.39 – 7.32 (m, 5H), 7.07 (s, 2H), 4.51 – 3.51 (broad, 2H), 3.47 – 3.32 (m, 1H), 2.97 – 2.84 (m, 1H), 2.84 – 2.67 (m, 2H), 2.38 (ddd, *J* = 13. 1, 8.4, 3.1 Hz, 1H), 1.27 (t, *J* = 5.4 Hz, 6H), 1.19 (dd, *J* = 12.8, 6.5 Hz, 12H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153.2, 152.4, 137.2, 137. 1, 137.0, 136.9, 133.9, 132.9, 132.8, 132.7, 132.5, 132.0, 130.7, 130.6, 129. 1, 129.0, 128.8, 128.7, 128.7, 128.6, 121.9, 50.5, 50.3, 34.3, 31.5 29.7, 28.3, 28.2, 28.0, 24.4, 24. 1, 23.8, 23.7, 22.7, 22.5; **^{31}P NMR** (202 MHz, $CDCl_3$) δ - 16.4; **IR** (KBr, cm^{-1}) 3855, 3746, 3672, 3122, 1681, 1556, 1385, 1066, 678; **Mp**: 117.0 – 118.4 °C; **HR-MS** (ESI) calcd. For $C_{29}H_{38}OPS$ $[M+H]^+$ m/z 465.2375, found 465.2377; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 0.8 mL/min, back pressure: 2.1 MPa, detection at 254 nm, retention time = 9.3 min (major) and 10 min (minor), ee = 96%. Note: This compound is quickly metamorphosed, requires rapid characterization, and is protected by an inert gas.

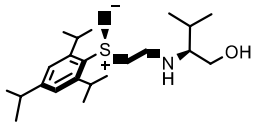
(*S*)-*N*-(2-((2,4,6-Triisopropylphenyl)sulfinyl)ethyl)prop-2-yn-1-amine (78)



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), prop-2-yn- 1-amine (0.25 mmol, 14 mg), in CH_3OH (1 mL) at 80 ℃ for 24 h, afforded 55 mg (83%) of **78** as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 4.71 – 3.65 (broad, 3H), 3.64 – 3.55 (m, 1H), 3.51 (s, 1H), 3.38 – 3.20 (m, 2H), 3.04 – 2.80 (m, 2H), 2.63 (s, 1H), 2.26 (d, *J* = 1.8 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.6 Hz, 12H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.5, 150.5, 150.0, 149.2, 133.8, 124.5, 123.3, 122.8, 122.3, 81.1, 77.4, 77. 1, 76.8, 72.3, 53.9, 43.7, 38.0, 34.3, 28.2, 28. 1, 28.0, 24.7, 24.3, 23.8, 23.8; **IR** (KBr, cm^{-1}) 3854, 3745, 3672, 3132, 1645, 1398, 1129, 673; **Mp**: 64.1 – 65.1 °C; **HR-MS** (ESI) calcd. For $C_{20}H_{31}NaNOS^+$ $[M+Na]^+$ m/z 356.2019, found 356.2016; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 0.8 mL/min, back pressure: 2.1 MPa, detection at 254 nm, retention time = 9.3 min (major) and 10 min (minor), ee = 97%.

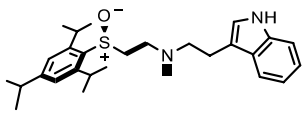
(*S*)-3-Methyl-2-((2-((*S*)-(2,4,6-triisopropylphenyl)sulfinyl)ethyl)amino)butan-1-ol (79)



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), (*S*)-2-amino-3-methylbutan- 1-ol (0.25 mmol, 26 mg), CH_3ONa ((5.4 mol/L (30 t%) in methanol) 136 ul, 0.22 mmol, 1.1 equiv) in methanol (1 mL) at 80 ℃ for 16 h, afforded 53 mg (69%) of **79** as a white solid, ee = 95%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 4.25 – 3.75 (broad, 2H), 3.71 – 3.26 (m, 4H), 3.26 – 3.04 (m, 1H), 2.99 – 2.78 (m, 2H), 2.59 – 2.16 (m, 2H), 2.02 (d, *J* = 22.5 Hz, 1H), 1.82 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.24 (t, *J* = 5.7 Hz, 12H), 0.99 (dd, *J* = 6.8, 1.8 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171. 1, 170.0, 167.0, 152.4, 136.4, 134. 1, 134.0, 122.9, 64.9, 64.6, 61.3, 60.8, 55.2, 55.0, 43.2, 41.5, 29.5, 29.4, 29.0, 28.2, 24.7, 24.2, 23.7, 23.3, 19.6, 19.5, 18.7, 18.6; **IR** (KBr, cm^{-1}) 3856, 3744, 3672, 3133, 1682, 1399, 1385,1129; **Mp**: 77.6 – 81.5 °C; **HR-MS** (ESI) calcd. For $C_{22}H_{39}NaNO_2S^+$ $[M+Na]^+$ m/z 404.2594, found 404.2592; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 0.8 mL/min, back pressure: 2.1 MPa, detection at 254 nm, retention time = 11.03 min (major) and 10.2 min (minor).

(*S*)-*N*-(2-(1*H*-Indol-3-yl)ethyl)-2-((2,4,6-triisopropylphenyl)sulfinyl)ethan-1-amine (80)

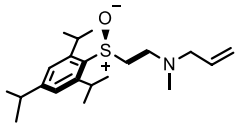


The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), 2-(1*H*-indol-3-yl)ethan- 1-amine (0.25 mmol, 40 mg), in methanol (1 mL) at 80 ℃ for 22 h, afforded 83 mg (95%) of **80** as a pale yellow solid, ee = 96%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.0 Hz,

1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.97 (s, 1H), 4.77 – 3.63 (broad, 2H), 3.53 (dd, *J* = 12.3, 5.8 Hz, 1H), 3.22 (dt, *J* = 12.9, 10.8 Hz, 1H), 3.14 – 3.05 (m, 1H), 2.97 (s, 4H), 2.94 – 2.82 (m, 2H), 1.81 (s, 1H), 1.20 (ddd, *J* = 48.5, 26.4, 8.5 Hz, 18H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.5, 150.3, 136.6, 133.9, 127.4, 123.5, 122.3, 121.8, 119.1, 118.7, 113.2, 111.7, 54.6, 50.0, 45.0, 34.35, 28.2, 25.7, 24.7, 24.3, 23.8, 23.8; **Mp**: 103.6 – 12.3 °C; **HR-MS** (ESI) calcd. For $C_{27}H_{38}N_2OSH$ $[M+H]^+$ m/z 439.2778, found 439.2773; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 3μL, mobile phase: hexane/isopropanol = 90/10, flow rate: 0.8 mL/min, back pressure: 2.6 MPa, detection at 254 nm, retention time = 6.27 min (major) and 7.95 min (minor).

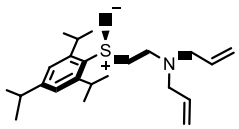
(*S*)-*N*-Methyl-N-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-en-1-amin (81)



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), *N*-methylprop-2-en- 1-amine (0.25 mmol, 19 mg), in methanol (1 mL) at 75 ℃ for 20 h, afforded 63 mg (91%) of **81** as a white solid, ee = 97%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 5.84 (ddt, *J*= 16.8, 10. 1, 6.5 Hz, 1H), 5.17 (dd, *J* = 23.4, 5.9 Hz, 2H), 3.96 (broad, 2H), 3.53 – 3.40 (m, 1H), 3.07 (qd, *J* = 13.6, 6.5 Hz, 2H), 3.00 – 2.91 (m, 2H), 2.87 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.79 (td, *J* = 11.0, 7.5 Hz, 1H), 2.28 (s, 3H), 1.30 (d, *J* = 6.9 Hz, 6H), 1.24 (dd, *J* = 6.7, 2.6 Hz, 12H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.2, 135.0, 134.2, 122.7, 117.9, 67.2, 60.6, 57.6, 52.5, 51.2, 48.9, 42.0, 36.6, 34.3, 33.7, 28.0, 24.3, 23.7; **IR** (KBr, cm^{-1}) 3855, 3745, 3672, 3135, 1682, 1398, 1385,1133, 677; **Mp**: 56.7 – 57.7 °C; **HR-MS** (ESI) calcd. For $C_{21}H_{35}NaNOS^+$ $[M+Na]^+$ m/z 372.2332, found 372.2324; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 98/2, flow rate: 0.8 mL/min, back pressure: 2.1 MPa, detection at 254 nm, retention time = 8.6 min (major) and 12 min (minor).

(*S*)-*N*-Allyl-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-en-1-amine (82)

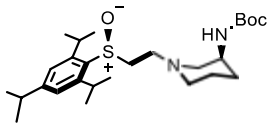


The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), diallylamine (0.25 mmol, 24 mg), in methanol (1 mL) at 75 ℃ for 20 h, afforded 62 mg (83%) of **82** as a colorless liquid, ee = 97%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 5.85 (ddt, *J*= 16.7, 10. 1, 6.4 Hz, 2H), 5.18 (dd, *J* = 23.8, 6.2 Hz, 4H), 3.95 (broad, 2H), 3.45 (dt, *J* = 12.0, 6.5 Hz, 1H), 3.16 (ddd, *J* = 31.0, 14. 1, 6.5 Hz, 4H), 3.08 – 3.00 (m, 1H), 3.00 – 2.83 (m, 3H), 1.31 (d, *J* = 6.9 Hz, 6H), 1.25 (t, *J* = 5.9 Hz, 12H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152. 1, 149.8, 149.0, 135.2, 134.3, 123.8, 122.9, 122.4, 117.79, 57.0, 52.8, 47.7, 34.3, 28.0, 24.6, 24.3, 23.8, 23.7; **IR** (KBr, cm^{-1}) 3855, 3746, 3672, 3131, 2961, 1517, 1396, 1099, 677; **HR-MS** (ESI) calcd. For $C_{23}H_{37}NNaOS^+$ $[M+Na]^+$ m/z 398.2488, found 398.2489; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 90/10, flow rate: 0.8 mL/min, back

pressure: 2.2 MPa, detection at 254 nm, retention time = 7.4 min (major) and 10 min (minor).

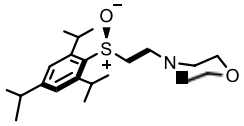
***tert*-Butyl((*S*)-1-(2-((*S*)-(2,4,6-triisopropylphenyl)sulfinyl)ethyl)piperidin-3 yl)carbamate (83)**



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), tert-*butyl* (*S*)-piperidin-3-ylcarbamate (0.25 mmol, 50 mg), in methanol (1 mL) at 75 ℃ for 22 h, afforded 73 mg (76%) of **83** as a white solid, ee = 96%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 5.17 (d, *J* = 22.2 Hz, 1H), 3.79 (s, 3H), 3.55 – 3.36 (m, 1H), 3.07 – 2.82 (broad, 3H), 2.72 (ddd, *J* = 22.5, 11.5, 5.9 Hz, 2H), 2.30 (t, *J* = 58.1 Hz, 3H), 1.83 – 1.49 (m, 4H), 1.43 (t, *J* = 11.0 Hz, 9H), 1.31 (d, *J* = 6.9 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.2, 152.3, 134.1, 134.0, 122.4, 79.1, 79.0, 77.3 60.4, 58.5, 57.8, 54.48, 53.7, 52.8, 52.38, 51.88, 46.28, 46.0, 34.3, 29.2, 28.5, 28.5, 24.3, 23.8, 23.8, 22.0, 21.75, 21.0, 14.2; **IR** (KBr, cm^{-1}) 3855, 3781, 3702, 3628, 3594, 3190, 2930, 2336, 1562, 1101; **Mp**: 110.1 – 113.4 °C; **HR-MS** (ESI) calcd. For $C_{27}H_{47}N_2O_3S^+$ [M+H]$^+$ m/z 479.3302, found 479.3296; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 1 mL/min, back pressure: 2.8 MPa, detection at 254 nm, retention time = 7.7 min (major) and 10.1 min (minor).

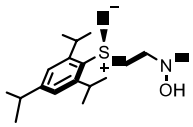
(*S*)-4-(2-((2,4,6-Triisopropylphenyl)sulfinyl)ethyl)morpholine (84)



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), morpholine (0.25 mmol, 22 mg), in methanol (1 mL) at 75 ℃ for 20 h, afforded 58 mg (80%) of **84** as a white solid, ee = 97%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 4.34 – 3.79 (m, 2H), 3.81 – 3.63 (m, 4H), 3.60 – 3.38 (m, 1H), 3.07 – 2.84 (broad, 3H), 2.79 (dd, *J* = 12.7, 5.3 Hz, 1H), 2.52 (s, 4H), 1.31 (d, *J* = 6.9 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 152.4, 149.4, 134.0, 123.6, 66.8, 53.5, 53.0, 51.8, 34.3, 28.2, 28. 1, 28.1, 28.0, 24.3, 23.8, 23.7; **IR** (KBr, cm^{-1}) 3855, 3744, 36723, 3143, 1516, 1396, 1130, 676; **Mp**: 59.3 – 61.6 °C; **HR-MS** (ESI) calcd. For $C_{21}H_{35}NaNO_2S^+$ [M+Na]$^+$ m/z 388.2281, found 388.2277; Resolution of enantiomers: **HPLC** (FLM chiral INA column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 90/10, flow rate: 0.8 mL/min, back pressure: 2.2 MPa, detection at 254 nm, retention time = 6.5 min (major) and 7.7 min (minor).

(*S*)-*N*-Methyl-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)hydroxylamine (85)

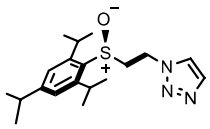


The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), *N*-Methylhydroxylamine hydrochloride (0.25 mmol, 22 mg), *N*, *N*-diisopropylethylamine (29 mg, 0.22

mmol, 1.1 equiv.) in THF (1 mL) at 65 ℃ for 20 h, afforded 33 mg (76%) of **85** as white solid, ee = 97%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (s, 2H), 6.45 (s, 1H), 4.50 – 3.54 (broad, 3H), 3.29 – 2.99 (m, 3H), 2.90 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.74 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.23 (dd, *J* = 24.9, 17.4 Hz, 12H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.4, 149.8, 134.0, 123.5, 56.7, 52.5, 48.7, 34.3, 29.7, 28.2, 24.6, 24.3, 23.8, 23.7; **IR** (KBr, cm^{-1}) 3854, 3813, 3745, 3672, 3165, 1678, 1520, 1397, 1134, 675; **Mp**: 101.5 – 105.5 °C; **HR-MS** (ESI) calcd. For $C_{18}H_{31}NNaO_2S^+$ $[M+Na]^+$ m/z 348. 1968, found 348. 1969; Resolution of enantiomers: **HPLC** (FLM chiral: INA, column size: 250*4.6 mm I.D., injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 0.8 mL/min, back pressure: 2.1 MPa, detection at 254 nm, retention time = 8.16 min (major) and 9.72 min (minor).

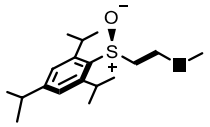
(*S*)-1-(2-((2,4,6-Triisopropylphenyl)sulfinyl)ethyl)-1*H*-1,2,3-triazole (86)



The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), 1*H*- 1,2,3-triazole (0.3 mmol, 20 mg), *t*-BuOK ((1 mol/L in *t*-BuOH) 0.22 mmol, 1.1 equiv, 220 ul) in *t*-BuOH (1.5 mL) at 70 ℃ for 14 h, afforded 52 mg (75%) of **86** as a white solid, ee = 89%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.77 (s, 1H), 7.08 (s, 2H), 5.09 – 4.85 (m, 2H), 3.84 (dd, *J* = 9.2, 4.3 Hz, 3H), 3.49 – 3.27 (m, 1H), 2.88 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.24 (dt, *J* = 35.5, 17.6 Hz, 18H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 153. 1, 150.4, 149.7, 149.0, 134.0, 132.5, 124.9, 123. 1, 122.6, 53.6, 44.7, 34.3, 28.2, 24.7, 24.0, 23.7 23.7; **IR** (KBr, cm^{-1}) 3779, 3699, 3628, 3591, 3139, 1657, 1396, 1128, 622; **Mp**: 67.6 – 69.1 °C; **HR-MS** (ESI) calcd. For $C_{19}H_{29}N_3NaOS^+$ $[M+Na]^+$ m/z 370. 1924, found 370.1917; Resolution of enantiomers: **HPLC** (Chiralcel chiral: Lot No. ODHǾCE-NLǾ85, column size: 250*4.6 mm I.D, injection: 5μL, mobile phase: hexane/isopropanol = 90/10, flow rate: 0.8 mL/min, back pressure: 3.0 MPa, detection at 254 nm, retention time = 13.36 min (major) and 10.74 min (minor).

(*S*)-1,3,5-Triisopropyl-2-((2-methoxyethyl)sulfinyl)benzene (87)

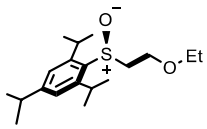


The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **75** (0.2 mmol, 54 mg), K_2CO_3 (0.22 mmol, 30 mg), in CH_3OH (1 mL) at 80 ℃ for 20 h, afforded 38 mg (62%) of **87** as a brown solid, ee = 96%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 3.90 (ddd, *J* = 23.5, 14.5, 5.8 Hz, 3H), 3.79 – 3.63 (m, 1H), 3.54 (dt, *J*= 13.2, 4.4 Hz, 1H), 3.40 (broad, 3H), 3.06 (ddd, *J*= 13.8, 9.0, 5.0 Hz, 1H), 2.88 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.3, 149.8, 133.9, 122.7, 66.5, 62.6, 59.1, 55.6, 54.8, 39.68, 34.3, 32.7, 28.0, 24.5, 24.31, 23.7; **IR** (KBr, cm^{-1}) 3779, 3695, 3631, 3148, 1658, 1394, 1115; **Mp**: 67.9 – 70.6 °C; **HR-MS** (ESI) calcd. For $C_{18}H_{30}NaO_2S^+$ $[M+Na]^+$ m/z 333. 1859, found 333.1849; Resolution of enantiomers: **HPLC** (FLM chiral: INC, column size: 250*4.6 mmI.D., injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 1 mL/min, back pressure: 2.2 MPa, detection

at 254 nm, retention time = 17.32 min (major) and 20.28 min (minor).

(*S*)-2-((2-Ethoxyethyl)sulfinyl)-1,3,5-triisopropylbenzene (88)



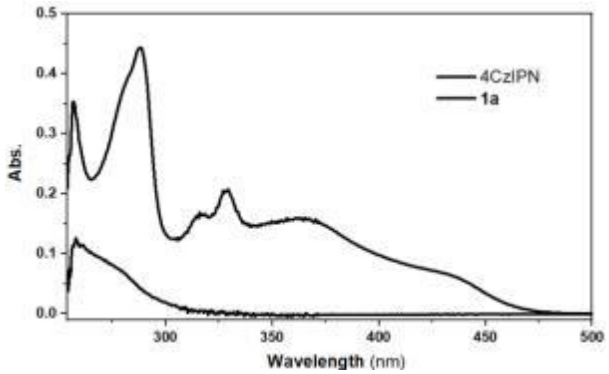
The reaction of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene 91 (0.2 mmol, 54 mg), K_2CO_3 (0.22 mmol, 30 mg), in dried ethanol (1 mL) at 80 ℃ for 20 h, afforded 43 mg (66%) of **88** as a pale yellow solid, ee = 96%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 3.93 (ddd, *J* = 10.3, 9. 1, 4.4 Hz, 3H), 3.75 (dt, *J* = 10.4, 5.1 Hz, 1H), 3.65 – 3.47 (broad, 3H), 3.09 (ddd, *J*= 13.8, 8.9, 5.2 Hz, 1H), 2.88 (hept, *J*= 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H), 1.23 (dd, *J* = 15.9, 7.0 Hz, 15H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.3, 150.0, 149.8, 134.0, 122.7, 122.4, 114.4, 66.8, 64.4, 55. 1, 34.3, 28.0, 24.5, 24.3, 23.7, 15.0; **IR** (KBr, cm^{-1}) 3854, 3745, 3133, 3672, 1556, 1398, 1128, 676; **Mp**: 59.2 – 60.1 °C; **HR-MS** (ESI) calcd. For $C_{19}H_{32}NaO_2S^+$ $[M+Na]^+$ m/z 347.2015, found 347.2012; Resolution of enantiomers: **HPLC** (FLM chiral: INC, column size: 250*4.6 mmI.D, injection: 5μL, mobile phase: hexane/isopropanol = 95/5, flow rate: 1 mL/min, back pressure: 2.2 MPa, detection at 254 nm, retention time = 14.27 min (major) and 16.80 min (minor).

8 Mechanistic Studies

8.1 UV/Vis Absorption Spectroscopy

UV–Vis absorption spectra were recorded on a Jasco V-730 spectrophotometer at 25 °C. The samples were measured in Starna® fluorescence quartz cuvettes (type: 29-F, chamber volume = 1.400 mL, H ×W ×D = 48 mm × 12.5 mm × 12.5 mm, path length = 10 mm).



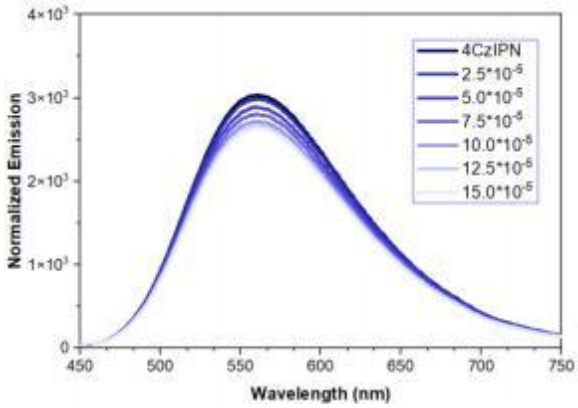
Supplementary Figure 2. UV–Vis absorption spectra of the starting materials.

Supplementary Figure 17 reveals that the 4CzIPN is the only species, which absorbs light at around λ = 450 nm (intensity maximum of the used blue LEDs λ_{max} = 425 nm), implying that no other species is directly excited by the irradiation under the current reaction conditions.

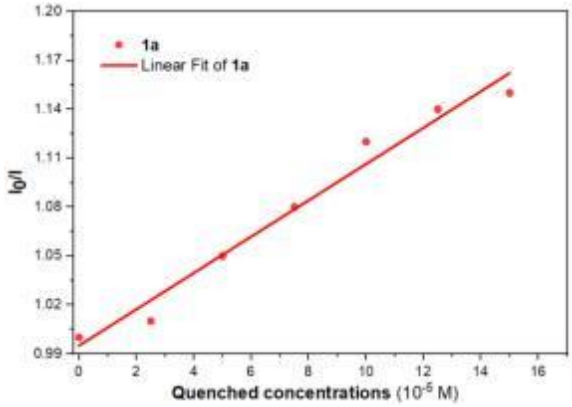
8.2 Stern–Volmer Luminescence Quenching Analysis

Steady-state emission spectra were acquired using a Hitachi F-4500 fluorescence spectrophotometer, equipped with a temperature control unit at 25 °C. In a typical experiment, a solution of

photocatalyst 4CzIPN (6.5 mg) in degassed DMSO (5 mL) was added with an appropriate amount of quencher in a quartz cuvette. Then the emission of the sample was collected. The results are listed below:



Supplementary Figure 3. Luminescence quenching of 4CzIPN with various concentrations of Sub.**1a**.

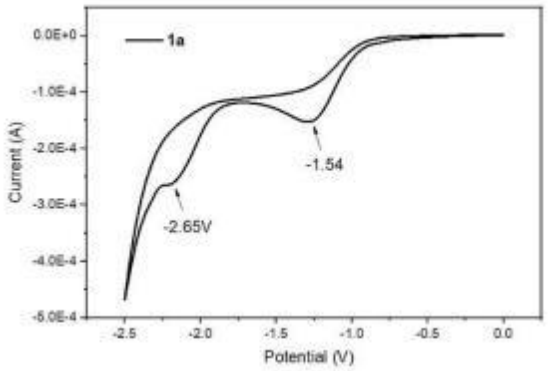


Supplementary Figure 4. Overlay of the quenching experiment.

Stern–Volmer fluorescence quenching analysis suggested that photoexcited *4CzIPN was quenched by Sub.**1a**.

8.3 Cyclic Voltammetry Experiment

The cyclic voltammogram (CV) was recorded with a standard three-electrode cell set-up (reference electrode: Ag/AgCl (3 M KCl), working electrode: 3 mm glassy carbon disc electrode, and counter electrode: platinum wire) on IGS- 1030 electrochemical workstation (Ingsens Instruments (Guangzhou) Co., Ltd., China). The scan rate was set to 100 mV/s. The electrolyte solution contains 0.10 M tetrabutylammonium perchlorate (nBu$_4$NClO$_4$) and 0.01 M **1a** in MeCN, which was preliminarily degassed by freeze-pump-thaw process. Before testing, argon gas was bubbled through the solution for 5 mins to avoid the interference of atmospheric oxygen during the test.

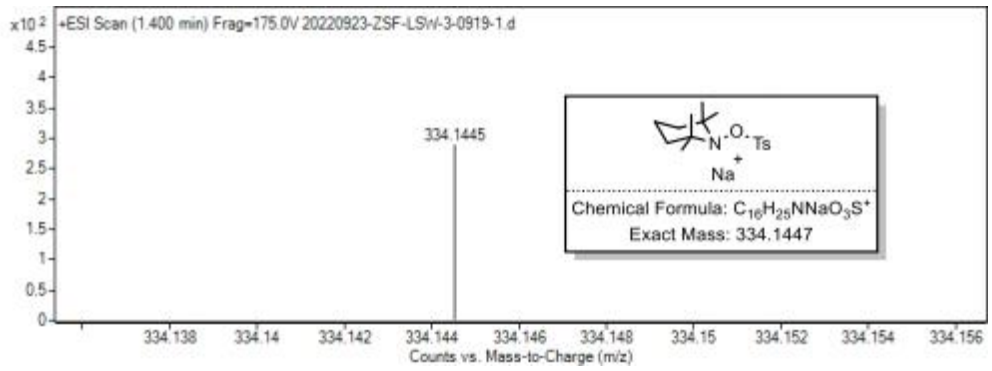


Supplementary Figure 5. Cyclic voltammogram of **1a** (0.01 M) in MeCN (0. 10 M *n*Bu4NClO4).

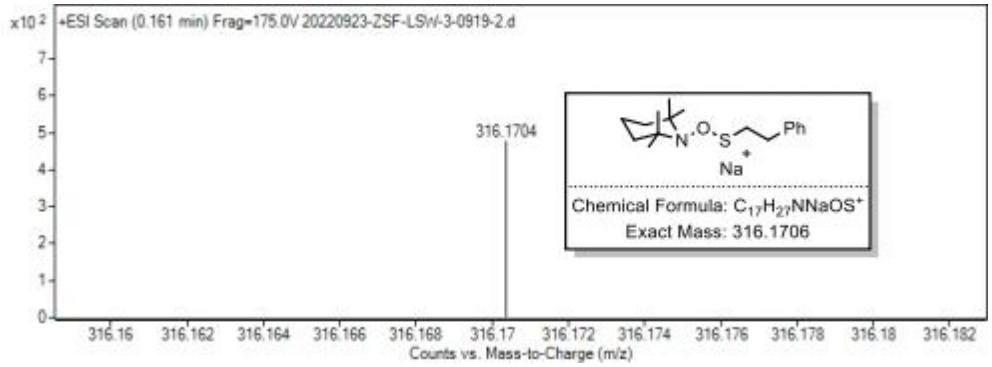
Given the redox potentials ofthe employed photocatalyst 4CzIPN ($E_{1/2}(PC^+/PC^*)$ = - 1.04 V vs SCE; $E_{1/2}(PC^*/PC^-)$ = +1.32 V vs SCE) in comparison with **1a**, neither a reductive nor an oxidative quenching towards it appears possible, therefore ruling- out the operativity of a single- electron transfer pathway.

8.4 Radical Trapping Experiment

An oven-dried 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with 4CzIPN (2.0 mol %), TEMPO (78 mg, 0.5 mmol, 2.0 equiv.) and Cs_2CO_3 (0.5 equiv.) under N_2 . Then, a solution of bifunctional reagent **1** (0.25 mol, 1.0 equiv.) in dry dimethyl sulfoxide (5.0 mL) was added by pipettor. The tube was degassed through three freeze-pump-thaw cycles under acetylene and then an acetylene gas balloon was attached through a three-way- valve. After that, the tube was placed in the Parallel Light Reactor, which cooled with the recirculated cooling water. After completion, the corresponding reaction mixture was detected by HRMS. The reaction was significantly suppressed, as no observable **3** was afforded, and some possible TEMPO- adducts (**Supplementary Figures 6 and 7**) could be observed in HRMS spectrum. This result means the involvement of thiol radical and sulfuryl radical species in this transformation.



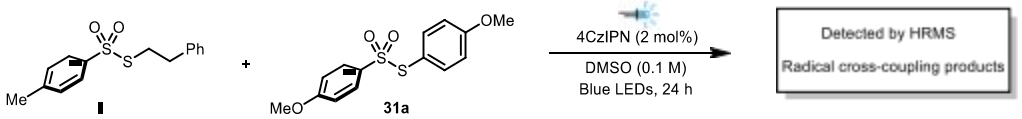
Supplementary Figure 6. High-resolution mass spectra of TEMPO adduct to sulfuryl radical.



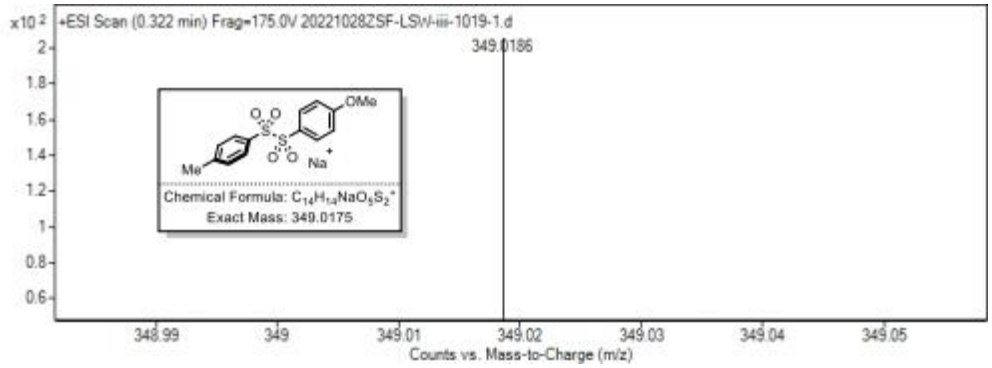
Supplementary Figure 7. High-resolution mass spectra of TEMPO adduct to thiol radical.

8.5 Radical crossover experiment

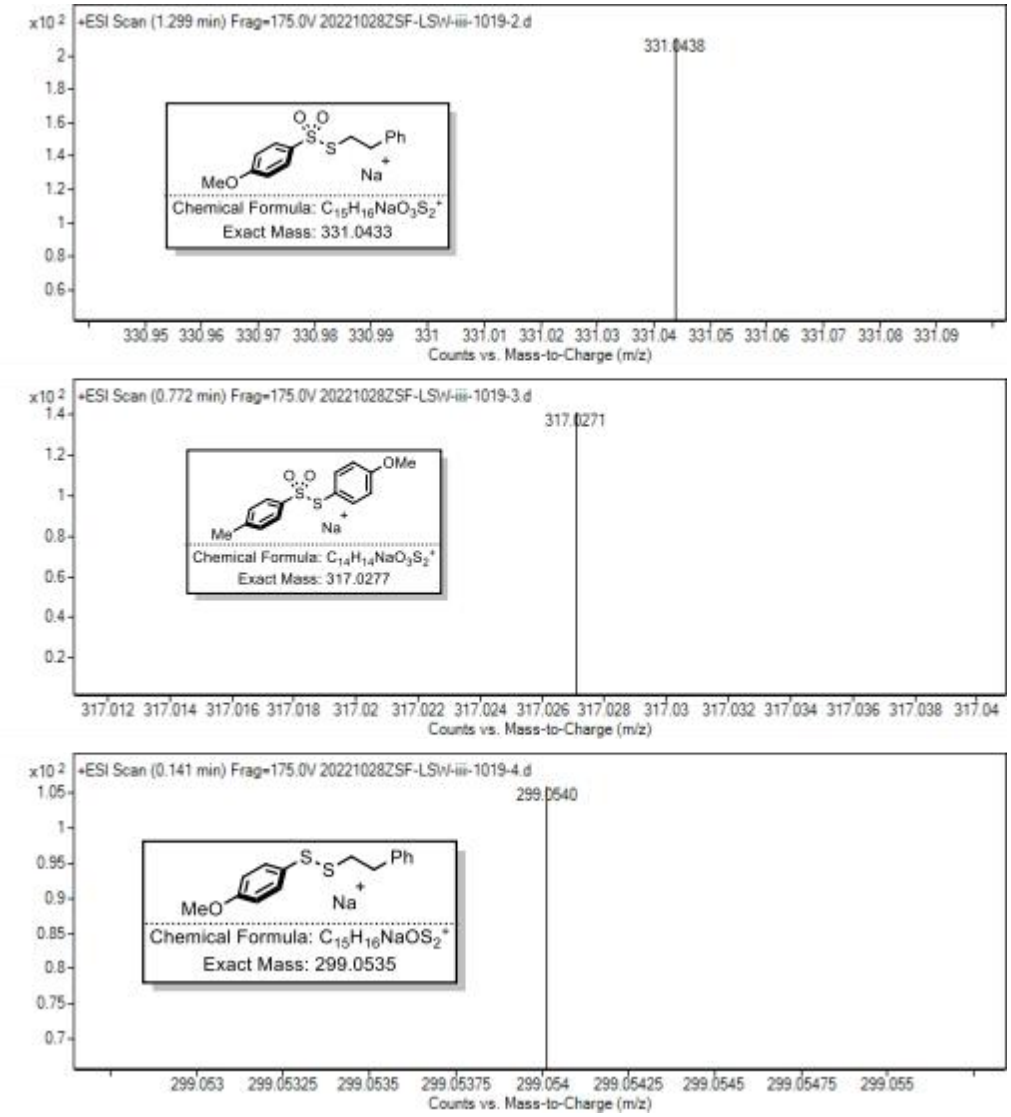
To examine whether both thiol and sulfonyl radical intermediates, generated via homolytic cleavage of the -O_2 S-S- bond of the thiosulfonate, are involved in this proposal mechanism, a crossover experiment was conducted.



An oven-dried Teflon-screw capped Schlenk tube containing a stirrer bar was charged with the 4CzIPN (1.6 mg, 0.002 mmol, 2 mol %) and *S*-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate **3a** (31 mg, 0.1 mmol, 1.0 equiv.) through the side-neck under positive N_2 flow. Then, a solution of *S*-phenethyl 4-methylbenzenesulfonothioate **1** (29 mg, 0.1 mol, 1.0 equiv) in dry dimethyl sulfoxide (2 mL) was added by pipettor. The reaction mixture was then cooled to -78 ºC and connected to a Schlenk line degas via vacuum evacuation, backfilled with N_2, and Schlenk tube re-capped with a Teflon-screw. The Schlenk tube was warmed to room temperature and placed in the Parallel Light Reactor, which cooled with the recirculated cooling water. After 24 h, the corresponding reaction mixture was detected by HRMS. This crossover experiment strongly supports the homolytic cleavage of the thiosulfonate bond under visible light, thereby generating a thiol radical and sulfenyl radical.



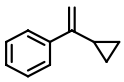
Supplementary Figure 9. HRMS of two different sulfuryl radicals cross-coupling product.



Supplementary Figure 10. HRMS of radicals cross-coupling product.

8.6 Radical Clock Experiments

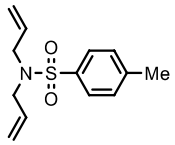
(1-Cyclopropylvinyl)Benzene (95)



According to a reported procedure[25], an oven-dried Schlenk flask (100 mL) was charged with methyltriphenylphosphonium bromide (3.57 g, 10 mmol, 4 equiv.) and anhydrous THF (30 mL, 0.3 M). After cooling to 0 °C *n*-buthyllithium (4 mL, 2.5 M in hexanes, 10 mmol, 2.0 equiv.) was dropwise added over 15 min by syringe needle. The resulting yellow suspension was stirred at 0 °C for 0.5 ~ 1 h. Then cyclopropyl(phenyl)methanone (1.46 g, 10.0 mmol, 1.0 equiv.) was added to the yellow suspension. The reaction mixture was heated to 65 °C and stirred for 24 h. After complete conversion, the reaction was diluted with pentane (20 ml) and aq. NH_4Cl (15 mL) was added. The layers were separated and the organic layer was washed with brine (20 mL) three times. The organic layer was then dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (Eluent: petroleum ether/EtOAc = 30/1) provided 894 mg of (1-cyclopropylvinyl)benzene **97** (6.2 mmol, 62% yield) as a colorless oil.

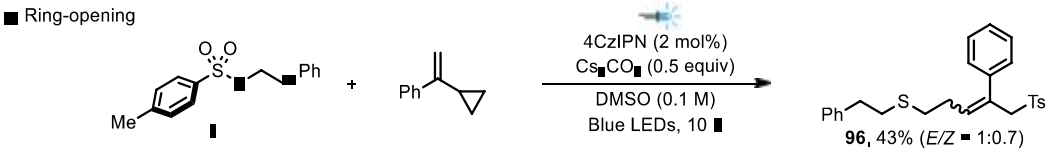
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J*= 7.2 Hz, 1H), 5.35 (s, 1H), 5.01 (s, 1H), 1.85 – 1.63 (m, 1H), 1.07 – 0.81 (m, 2H), 0.67 (q, *J* = 5.5, 4.9 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.4, 141.7, 128.2, 127.5, 126.2, 109. 1, 15.7, 6.7. The analytical datas are in agreement with the literature.

***N,N*-Diallyl-4-methylbenzenesulfonamide (97)**



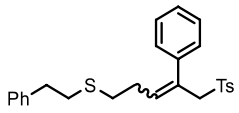
According to a reported procedure[26], to an oven-dried round bottom flask was added diallylamine (485 mg, 5 mmol, 1.0 equiv.), dry DCM (15 mL), and triethylamine (560 mg, 5.5 mmol, 1.1 equiv.). The dropwise addition of 4-toluenesulfonyl chloride (1.05 g, 5.5 mmol, 1.1 equiv.) dissolved in an additional 10 mL of DCM over 5 min. The mixture was allowed to stir at room temperature until full conversion, as monitored by TLC. The reaction mixture was diluted with 20 mL DCM and 20 mL water. The organic layer was separated and the resulting aqueous solution was extracted twice with DCM (20 mL). The organic layer was then dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (Eluent: petroleum ether/EtOAc = 15/1) provided *N,N*-diallyl-4-methylbenzenesulfonamide **97** (1. 13 g, 4.5 mmol, 90% yield) as a clear liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.62 (ddt, *J* = 16.5, 9.9, 6.3 Hz, 2H), 5.16 (d, *J* = 3.8 Hz, 2H), 5.13 (s, 2H), 3.81 (d, *J* = 6.3 Hz, 4H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.3, 137.4, 132.7, 129.7, 127.2, 119.0, 49.3, 21.5. The analytical datas are in agreement with the literature.

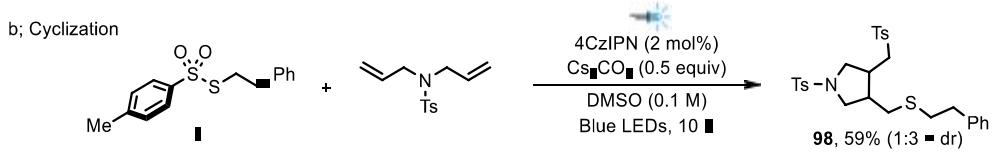


An oven-dried Teflon-screw capped Schlenk tube containing a stirrer bar was charged with the 4CzIPN (3.2 mg, 2 mol%), and Cs_2CO_3 (33 mg, 0.1 mol, 0.5 equiv.) through the side-neck under positive N_2 flow. Then, a solution of (1-cyclopropylvinyl)benzene (29 mg, 0.20 mol, 1.0 equiv.) and *S*-phenethyl 4-methylbenzenesulfonothioate **1** (61 mg, 0.22 mmol, 1.1 equiv.) in dry DMSO (5.0 mL) was added by pipettor. The reaction mixture was then cooled to -78 ºC and connected to a Schlenk line degas via vacuum evacuation, backfilled with N_2 gas, and warmed to room temperature. The Schlenk tube was re-capped with a Teflon-screw and placed in the Parallel Light Reactor, which cooled with the recirculated cooling water. The corresponding reaction mixture was detected according to TLC. Finally, the reaction mixture was diluted with brine (5 mL) and extracted by EtOAc (2 × 10 mL). The combined organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (Eluent: petroleum ether/EtOAc = 10:1) gave the ring-opening product (38 mg, 0.086 mmol, 43% yield) as a clear liquid.

Phenethyl(4-phenyl-5-tosylpent-3-en-1-yl)sulfane (96)

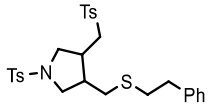


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 35. 1, 8.1 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.03 (m, 8H), 7.02 – 6.96 (m, 2H), 6.00 – 5.64 (m, 1H), 4.18 (d, *J*= 67.1 Hz, 2H), 2.89 – 2.66 (m, 2H), 2.64 – 2.45 (m, 2H), 2.27 (d, *J* = 16.2 Hz, 3H), 2.37 – 2.09 (m, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.6, 140.7, 140.5, 136. 1, 135.9, 135.5, 134.8, 132.7, 129.7, 129.5, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 127.6, 127.3, 127.2, 126.5, 126.5, 126.4, 126.4, 125.9, 123.2, 60.0, 58.0, 36.3, 33.7, 31.5, 29.7, 27.8, 23.4, 21.6, 21.6; **IR** (KBr, cm^{-1}) 3747, 2829, 1597, 1364, 1135, 774, 535; **HRMS** (ESI) calcd. $C_{26}H_{28}NaO_2S_2^+$ $[M+Na]^+$ m/z 459.1423, found: 459.1427.



An oven-dried Teflon-screw capped Schlenk tube containing a stirrer bar was charged with the 4CzIPN (3.2 mg, 2 mol%) and Cs_2CO_3 (33 mg, 0.1 mol, 0.5 equiv.) through the side-neck under positive N_2 flow. Then, a solution of *N*,*N*-diallyl-4-methylbenzenesulfonamide (50 mg, 0.20 mol, 1.0 equiv.) and *S*-phenethyl 4-methylbenzenesulfonothioate **1** (61 mg, 0.22 mmol, 1.1 equiv.) in dry DMSO (5.0 mL) was added by pipettor. The tube was degassed through three freeze-pump-thaw cycles under N_2 gas and then warmed to room temperature. The Schlenk tube was re-capped with a Teflon-screw and placed in the Parallel Light Reactor, which cooled with the recirculated cooling water. The corresponding reaction mixture was detected according to TLC. Finally, the reaction mixture was diluted with brine (5 mL) and extracted by EtOAc (2 × 10 mL). The combined organic layer was dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash column chromatography on silica gel (Eluent: petroleum ether/EtOAc = 10/1) gave the ring-opening product **98** (64 mg, 0.12 mmol, 59% yield) as a clear liquid.

3-((Phenethylthio)methyl)-1-Tosyl-4-(tosylmethyl)pyrrolidine (98)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 5.5 Hz, 2H), 7.70 (d, *J* = 5.8 Hz, 2H), 7.33 (dd, *J* = 12.0, 8.2 Hz, 4H), 7.29 – 7.23 (m, 2H), 7.16 (t, *J* = 8.2 Hz, 2H), 3.62 – 3.39 (m, 1H), 3.36 – 3.16 (m, 2H), 3.17 – 2.98 (m, 1H), 2.95 – 2.74 (m, 3H), 2.74 – 2.53 (m, 3H), 2.44 (s, 3H), 2.41 (s, 3H), 2.37 – 2.15 (m, 2H), 2.10 – 1.82 (m, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.3, 143.8, 140.2, 136. 1, 133.5, 130. 1, 130. 1, 129.9, 129.8, 128.6, 128.5, 128.5, 127.9, 127.7, 127.5, 126.5, 126.5, 54.2, 51.3, 50.8, 40.8, 36.3, 35.7, 33.8, 30.3, 21.7, 21.6, 21.6; **IR** (KBr, cm^{-1}) 2830, 2716, 1597, 1364, 1084, 774, 534; **HRMS** (ESI) calcd. $C_{28}H_{33}NNaO_4S_3^+$ $[M+Na]^+$ m/z 544.1644, found: 544.1636.

9 Computational studies

General details

All calculations were conducted using Gaussian16 software package.[27] Optimization of all

stationary points was carried out at B3LYP/def2-SVP theoretical level.[28-30] Empirical dispersion was included using the D3 version of Grimme's dispersion with Becke–Johnson damping.[31] Frequency calculations were performed at the same level to verify whether the stationary points are minima (0 imaginary frequency) or saddle points (only 1 imaginary frequency). Single point calculations were carried out with Truhlar's M06-2X functional with def2-TZVPP basis set for all atoms.[32] Solvation effects of dimethylsulfoxide for all calculations were considered using Truhlar's SMD solvent model.[33] The Gibbs free energy of each point was obtained by adding the thermal correction from frequency calculation at B3LYP-D3(BJ)/def2-SVP-SMD(DMSO) level to the electronic energy from single point energy calculation at M06-2X/def2-TZVPP-SMD(DMSO) theoretical level. Computed structures were illustrated by CYL view software.[34] The minimum energy crossing points (MECPs) were located with the program developed by J. N. Harvey.[35]

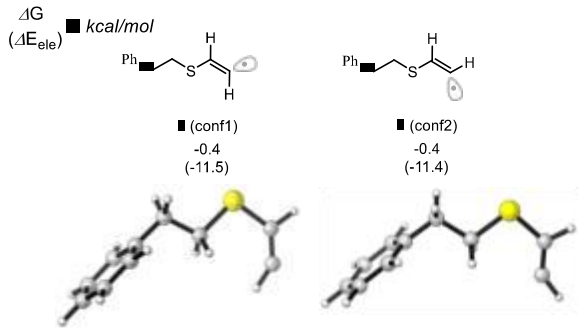
9.1 Tables of energies and other thermodynamic parameters

Supplementary Table 7. Energies and other thermodynamic parameters.

Structures	E_{ele}	E_{ele}(SP)	E_0	E	H	G
sulfonyl radical	-819.13597	-819.54026	-819.01040	-819.00091	-818.99997	-819.04713
thiyl radical	-708.13862	-708.40061	-707.99203	-707.98382	-707.98288	-708.02704
ethyne	-77.27627	-77.32748	-77.24911	-77.24637	-77.24543	-77.26806
TS1	-785.41232	-785.72061	-785.23774	-785.22599	-785.22504	-785.28164
II	-785.43782	-785.74644	-785.26059	-785.24948	-785.24854	-785.30027
MECP-1		- 1605.28855				
TS2	-896.40477	-896.85697	-896.25188	-896.23915	-896.23820	-896.29527
III	-896.41643	-896.87623	-896.26022	-896.24823	-896.24728	-896.30011
3	- 1604.69438	- 1605.41968	- 1604.38504	- 1604.36403	- 1604.36308	- 1604.44199
^{3}3	- 1604.60964	- 1605.32512	- 1604.30389	- 1604.28257	- 1604.28163	- 1604.35839
MECP-2		- 1605.29528				
3'	- 1604.69280	- 1605.41706	- 1604.38320	- 1604.36250	- 1604.36155	- 1604.43791

Notes: E_{ele}, ZPE, E_0, H, and G(T) were the electronic energies, zero-point energies, sum of electronic and zero-point energies, sum of electronic and thermal ethalpies, and sum of electronic and thermal free energies, respectively, which were given at the B3LYP-D3(BJ)/def2-SVP-SMD(DMSO) level. E_{ele}(SP) were electronic energies with solvent correction at the M06-2X/def2-TZVPP-SMD(DMSO) level.

9.2 Stability comparison of different vinyl radical conformations.



Supplementary Figure 11. Conformations of vinyl radical **II**. Energies were calculated relative to intermediate **I**, shown in kcal/mol.

It is similar to the inversion of amines in that the trans or cis conformation of vinyl radical is not static. The unpaired electron could quickly move through the nucleus to realize the conformation

change from **II (conf1)** to **II (conf2)**

9.3 Coordinates of all stationary points

ethyne

C	0.0000	0.0000	0.6053
H	0.0000	0.0000	1.6835
C	0.0000	0.0000	-0.6053
H	0.0000	0.0000	- 1.6835

Thiyl radical

S	-2.5279	-0.8645	-0.5739
C	-2.1031	0.8278	-0.0968
H	-3.0538	1.2848	0.2381
H	- 1.8229	1.3748	- 1.0144
C	- 1.0217	0.9713	0.9817
H	-0.9479	2.0424	1.2342
H	- 1.3467	0.4410	1.8901
C	0.3259	0.4608	0.5326
C	0.7403	-0.8475	0.8282
C	1.1693	1.2699	-0.2462
C	1.9655	- 1.3340	0.3601
H	0.0955	- 1.4895	1.4327
C	2.3939	0.7875	-0.7155
H	0.8610	2.2921	-0.4843
C	2.7960	-0.5185	-0.4142
H	2.2727	-2.3546	0.6035
H	3.0385	1.4338	- 1.3171
H	3.7545	-0.8968	-0.7789

Sulfonyl radical

S	-2.1579	-0.0014	-0.2447
O	-2.6649	- 1.2999	0.2882
O	-2.6703	1.2931	0.2925
C	-0.3615	0.0019	-0.0931
C	0.3128	1.2239	-0.0789
C	0.3183	- 1.2199	-0.0778
C	1.7065	1.2136	-0.0131
H	-0.2396	2.1643	-0.1052
C	1.7090	- 1.2044	-0.0121
H	-0.2318	-2.1616	-0.1027
C	2.4250	0.0071	0.0209
H	2.2466	2.1631	0.0128
H	2.2534	-2.1519	0.0147
C	3.9260	-0.0033	0.0995
H	4.3445	1.0080	-0.0040
H	4.2606	-0.4148	1.0671
H	4.3583	-0.6440	-0.6860

3

S	-2.4198	- 1.5152	-0.6848
O	-3.1159	-2.8078	-0.5393
O	- 1.7251	- 1.1966	- 1.9492
C	-3.6117	-0.2178	-0.3669
C	-3.3416	1.0833	-0.8048
C	-4.7878	-0.5217	0.3188
C	-4.2676	2.0888	-0.5415
H	-2.4198	1.3000	- 1.3475
C	-5.7056	0.4998	0.5740
H	-4.9823	- 1.5456	0.6417
C	-5.4625	1.8157	0.1516
H	-4.0659	3.1081	-0.8816
H	-6.6300	0.2688	1.1094
C	-6.4500	2.9178	0.4206
H	-5.9752	3.7462	0.9718
H	-6.8315	3.3411	-0.5238
H	-7.3081	2.5591	1.0068
C	- 1.2608	- 1.3725	0.6435
C	-0.0011	-0.9893	0.3783
H	0.2745	-0.7519	-0.6557
H	- 1.6598	- 1.6348	1.6269
S	1.2604	-0.8404	1.5664
C	2.6584	-0.3012	0.4984
H	2.3758	0.6411	0.0067
H	2.8197	- 1.0681	-0.2733
C	3.9156	-0.1142	1.3499
H	3.7197	0.6371	2.1315
H	4.1588	- 1.0624	1.8553
C	5.0803	0.3254	0.4939
C	5.9141	-0.6218	-0.1207
C	5.3205	1.6876	0.2560
C	6.9658	-0.2184	-0.9485
H	5.7375	- 1.6865	0.0565
C	6.3713	2.0945	-0.5713
H	4.6781	2.4360	0.7288
C	7.1976	1.1420	- 1.1766
H	7.6086	-0.9694	- 1.4152
H	6.5474	3.1598	-0.7419
H	8.0211	1.4588	- 1.8216

^{3}3

S	-3.1970	-2.2962	-1.0273
O	-4.4968	-2.6556	-0.4268
O	-3.0340	-2.3809	-2.4951
C	-2.7422	-0.6476	-0.5141
C	-1.8712	0.0994	-1.3086
C	-3.1899	-0.1711	0.7208
C	-1.4346	1.3420	-0.8481
H	-1.5388	-0.2906	-2.2714
C	-2.7472	1.0733	1.1633
H	-3.8706	-0.7723	1.3260
C	-1.8557	1.8438	0.3946
H	-0.7516	1.9323	-1.4632
H	-3.0934	1.4552	2.1272
C	-1.3452	3.1609	0.9104
H	-0.5255	3.0002	1.6320
H	-0.9532	3.7894	0.0980
H	-2.1346	3.7176	1.4384
C	-1.9381	-3.3211	-0.2822
C	-0.5627	-2.8964	-0.2952
H	0.0282	-2.8985	-1.2196
H	-2.3384	-4.2667	0.1074
S	0.0686	-2.0269	1.0671
C	1.3360	-0.9602	0.2720
H	0.8733	-0.5166	-0.6201
H	2.1835	-1.5879	-0.0431
C	1.7876	0.1308	1.2457
H	0.9083	0.7068	1.5735
H	2.2343	-0.3333	2.1396
C	2.7861	1.0521	0.5856
C	4.1566	0.7491	0.5883
C	2.3532	2.2032	-0.0910
C	5.0731	1.5779	-0.0653
H	4.5074	-0.1448	1.1121
C	3.2671	3.0345	-0.7449
H	1.2892	2.4493	-0.0992
C	4.6309	2.7238	-0.7347
H	6.1376	1.3296	-0.0497
H	2.9127	3.9297	-1.2626
H	5.3470	3.3737	-1.2441

3'

S	-2.6721	-1.8089	-0.0675
O	-3.7560	-2.7085	0.3685
O	-2.0069	-2.0273	-1.3680
C	-3.3059	-0.1350	-0.0556
C	-2.6969	0.8366	-0.8575
C	-4.3866	0.1806	0.7700
C	-3.1788	2.1429	-0.8160
H	-1.8619	0.5672	-1.5053
C	-4.8574	1.4943	0.7961
H	-4.8550	-0.5949	1.3783
C	-4.2628	2.4941	0.0095
H	-2.7100	2.9082	-1.4404
H	-5.7050	1.7484	1.4375
C	-4.7690	3.9102	0.0341
H	-3.9653	4.6107	0.3154
H	-5.1243	4.2174	-0.9638
H	-5.5979	4.0316	0.7461
C	-1.4406	-1.8148	1.2024
C	-0.1461	-1.4994	1.0079
H	0.5072	-1.5151	1.8883
H	-1.8293	-2.0638	2.1923
S	0.6544	-1.0644	-0.4779
C	2.2802	-0.5412	0.2077
H	2.7111	-1.3845	0.7676
H	2.1179	0.2965	0.9016
C	3.2042	-0.1228	-0.9380
H	3.3270	-0.9673	-1.6349
H	2.7383	0.7032	-1.4991
C	4.5525	0.3100	-0.4120
C	4.7754	1.6395	-0.0209
C	5.5931	-0.6191	-0.2575
C	6.0087	2.0329	0.5064
H	3.9731	2.3740	-0.1362
C	6.8281	-0.2292	0.2690
H	5.4326	-1.6585	-0.5579
C	7.0397	1.0989	0.6531
H	6.1666	3.0737	0.8010
H	7.6292	-0.9651	0.3775
H	8.0055	1.4057	1.0627

II

S	2.8386	-0.7865	-0.0630
C	1.1685	-0.0424	-0.0015
H	1.0682	0.6669	-0.8379
H	1.0686	0.5219	0.9388
C	0.1014	-1.1374	-0.0907
H	0.2351	-1.7019	-1.0274
H	0.2326	-1.8446	0.7436

C	- 1.2861	-0.5413	-0.0443
C	- 1.9424	-0.3475	1.1813
C	- 1.9248	-0.1206	- 1.2214
C	-3.2065	0.2473	1.2303
H	- 1.4562	-0.6708	2.1062
C	-3.1888	0.4747	- 1.1764
H	- 1.4250	-0.2658	-2.1835
C	-3.8338	0.6612	0.0507
H	-3.7047	0.3863	2.1934
H	-3.6732	0.7922	-2.1036
H	-4.8231	1.1245	0.0872
C	3.8725	0.6627	0.0552
C	3.4931	1.9176	0.1585
H	2.6051	2.5452	0.2112
H	4.9361	0.3832	0.0316

III

S	- 1.6981	0.2942	-0.3220
O	-2.0381	1.7251	-0.4222
O	-2.1732	-0.6532	- 1.3442
C	0.0752	0.1439	-0.1773
C	0.6832	- 1.0776	-0.4855
C	0.8201	1.2405	0.2589
C	2.0639	- 1.1925	-0.3501
H	0.0813	- 1.9201	-0.8301
C	2.2034	1.1051	0.3883
H	0.3248	2.1855	0.4870
C	2.8455	-0.1070	0.0886
H	2.5501	-2.1416	-0.5907
H	2.7963	1.9584	0.7268
C	4.3366	-0.2515	0.2177
H	4.5973	- 1.1378	0.8184
H	4.8010	-0.3900	-0.7736
H	4.7906	0.6336	0.6858
C	-2.3014	-0.2748	1.3084
C	-3.0037	- 1.3693	1.3943
H	-2.0268	0.4064	2.1231
H	-3.3925	-2.1781	0.7766

MECP-1

S	-2.1764	-0.8794	0.0645
O	- 1.7204	-0.9389	1.4440
O	- 1.9168	- 1.9983	-0.8266
C	-3.9185	-0.5369	0.0568
C	-4.6908	-0.9843	- 1.0048
C	-4.4560	0.2281	1.0858
C	-6.0463	-0.6892	- 1.0079
H	-4.2477	- 1.5649	- 1.8018
C	-5.8095	0.5121	1.0597
H	-3.8298	0.5772	1.8962
C	-6.6232	0.0563	0.0182
H	-6.6660	- 1.0484	- 1.8197
H	-6.2482	1.0930	1.8617
C	-8.0907	0.3659	0.0197
H	-8.2558	1.4410	0.1015
H	-8.5720	0.0080	-0.8883
H	-8.5800	-0.1015	0.8764
C	-0.8592	1.6694	-0.2031
C	0.3622	1.3509	0.1245
H	0.5734	0.5795	0.8631
H	- 1.3971	2.3467	-0.8472
S	1.8041	2.1465	-0.5223
C	3.0292	0.8390	-0.2197
H	2.8655	0.0239	-0.9235
H	2.8814	0.4657	0.7939
C	4.4360	1.4100	-0.3758
H	4.5603	1.8075	- 1.3845
H	4.5686	2.2313	0.3298
C	5.4628	0.3391	-0.1167
C	5.9401	0.1155	1.1733
C	5.9165	-0.4771	- 1.1510
C	6.8549	-0.8989	1.4251
H	5.5936	0.7454	1.9846
C	6.8310	- 1.4929	-0.9030
H	5.5517	-0.3107	-2.1580
C	7.3021	- 1.7067	0.3865
H	7.2201	- 1.0573	2.4316
H	7.1776	-2.1164	- 1.7172
H	8.0151	-2.4972	0.5809

MECP-2

S	-3.5390	0.0580	-0.3350
O	-4.5485	0.4959	0.6159
O	-3.8556	0.0415	- 1.7535
C	-2.0699	1.0279	-0.0902
C	- 1.2349	1.2768	- 1.1688
C	- 1.7612	1.4609	1.1930
C	-0.0833	2.0199	-0.9563
H	- 1.4887	0.9143	-2.1552
C	-0.6024	2.1951	1.3824

H	-2.4234	1.2439	2.0203
C	0.2492	2.4881	0.3146
H	0.5636	2.2469	-1.7946
H	-0.3567	2.5555	2.3737
C	1.5013	3.2814	0.5448
H	2.2098	2.7054	1.1435
H	1.9839	3.5456	-0.3947
H	1.2835	4.1980	1.0950
C	-2.9529	-2.1798	1.3864
C	-1.6688	-2.3281	1.2257
H	-1.0099	-2.5408	2.0706
H	-3.6909	-2.2122	2.1716
S	-0.8695	-2.2790	-0.3453
C	0.6699	-1.4628	0.1630
H	1.0916	-2.0269	0.9958
H	0.4385	-0.4515	0.5032
C	1.6479	-1.4279	-1.0069
H	1.7818	-2.4409	-1.3922
H	1.2367	-0.8140	-1.8106
C	2.9739	-0.8740	-0.5560
C	3.2984	0.4650	-0.7526
C	3.8815	-1.6923	0.1159
C	4.5042	0.9787	-0.2888
H	2.6021	1.1086	-1.2777
C	5.0867	-1.1842	0.5790
H	3.6384	-2.7371	0.2735
C	5.4011	0.1552	0.3783
H	4.7419	2.0225	-0.4506
H	5.7822	-1.8333	1.0957
H	6.3407	0.5526	0.7390

TS1

S	2.7978	-0.9740	0.0036
C	1.1617	-0.1666	-0.0061
H	1.0675	0.4626	-0.9049
H	1.0699	0.4860	0.8760
C	0.0437	-1.2219	0.0094
H	0.1478	-1.8756	-0.8711
H	0.1526	-1.8539	0.9050
C	-1.3171	-0.5653	0.0052
C	-1.9486	-0.2167	1.2095
C	-1.9538	-0.2423	-1.2036
C	-3.1866	0.4325	1.2074
H	-1.4637	-0.4618	2.1589
C	-3.1919	0.4069	-1.2098
H	-1.4731	-0.5074	-2.1496
C	-3.8128	0.7466	-0.0033
H	-3.6660	0.6917	2.1552
H	-3.6753	0.6461	-2.1607
H	-4.7818	1.2522	-0.0066
C	4.1315	1.0283	0.0058
H	5.0690	0.4887	0.0323
C	3.4266	2.0395	-0.0217
H	2.6720	2.8104	-0.0478

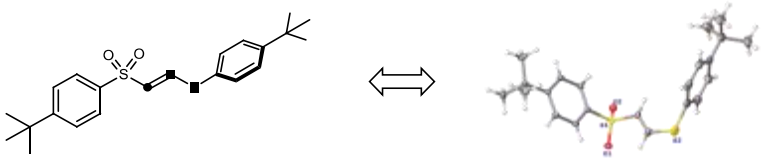
TS2

S	1.6916	0.4114	-0.3440
O	2.1753	-0.3574	-1.5125
O	2.0208	1.8517	-0.2006
C	-0.0854	0.2216	-0.2249
C	-0.6831	-0.9218	-0.7583
C	-0.8280	1.1817	0.4701
C	-2.0595	-1.0921	-0.6051
H	-0.0829	-1.6598	-1.2926
C	-2.2004	0.9916	0.6118
H	-0.3379	2.0660	0.8804
C	-2.8380	-0.1448	0.0803
H	-2.5395	-1.9783	-1.0275
H	-2.7930	1.7404	1.1441
C	-4.3206	-0.3293	0.2494
H	-4.8742	0.5107	-0.2025
H	-4.6689	-1.2620	-0.2166
H	-4.5938	-0.3529	1.3174
C	2.9093	-1.7629	1.2586
H	3.2735	-2.6529	0.7665
C	2.4115	-0.6515	1.5150
H	2.1478	0.0960	2.2586

X-ray structure analysis

Single crystals for X-ray studies were grown by slow evaporation of a solution of the compound in a mixture of ethyl acetate and hexane at room temperature. Compounds were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation.

The X-ray data of **35** is deposited in the Cambridge Crystallographic Data Centre with CCDC 2224851.

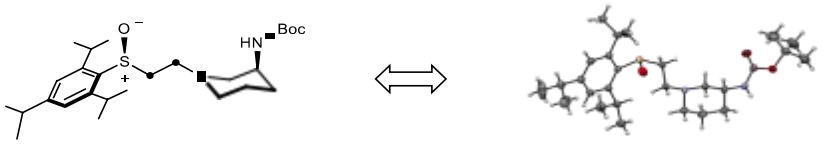


Supplementary Figure 12. ORTEP view of the crystal structure of (*E*)-(4-(*tert*-butyl)phenyl)(2-((4-(*tert*-butyl)phenyl)sulfonyl)vinyl)sulfane (The ellipsoids are shown at 30% probability levels)

Supplementary Table 8. Crystal data and structure refinement for **35**

Identification code	LSW-3-A
Empirical formula	$C_{22}H_{28}O_2S_2$
Formula weight	388.56
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.5979(5)
b/Å	10.9236(7)
c/Å	11.6364(7)
α/°	110.347(6)
β/°	105.035(5)
γ/°	100.724(5)
Volume/Å^3	1052.05(12)
Z	2
ρ_{calc}g/cm^3	1.227
μ/mm^{-1}	2.385
F(000)	416.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.658 to 147.99
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 10, -14 ≤ l ≤ 14
Reflections collected	7243
Independent reflections	4136 [R_{int} = 0.0219, R_{sigma} = 0.0275]
Data/restraints/parameters	4136/3/273
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0361, wR_2 = 0.1001
Final R indexes [all data]	R_1 = 0.0384, wR_2 = 0.1024
Largest diff. peak/hole / e Å^{-3}	0.35/-0.43

The X-ray data of **X** is deposited in the Cambridge Crystallographic Data Centre with CCDC 2215390.



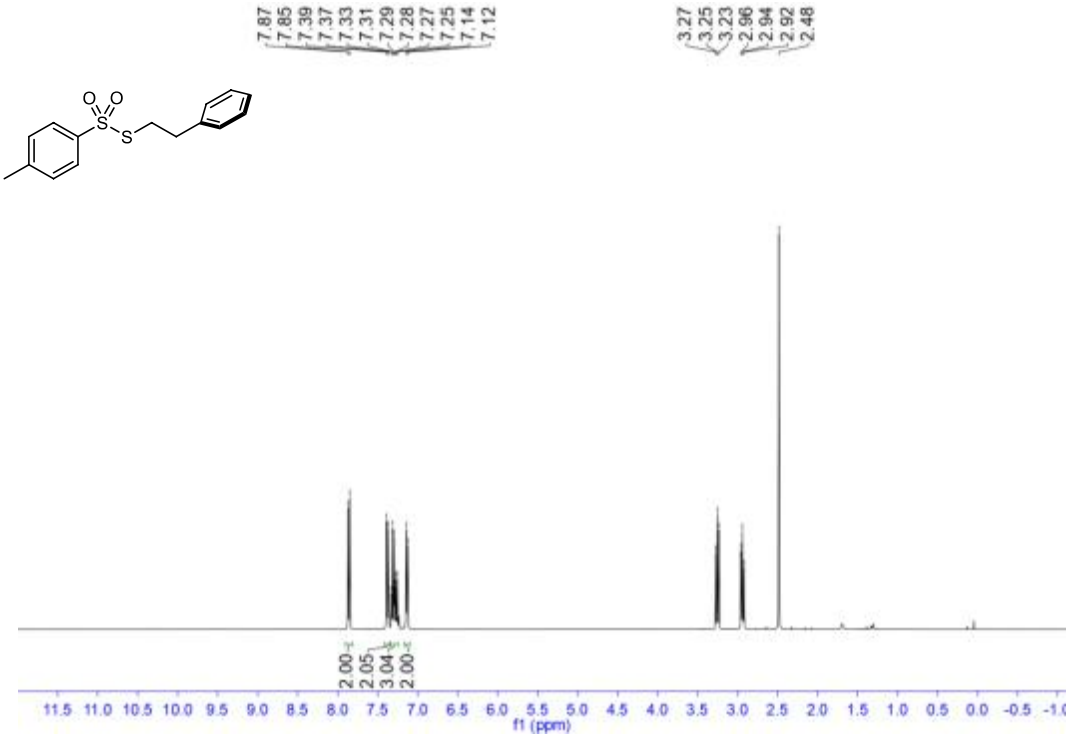
Supplementary Figure 12. ORTEP view of the crystal structure of *tert*-butyl((*S*)- 1-(2-((*S*)-(2,4,6-triisopropylphenyl)sulfinyl)ethyl)piperidin-3yl)carbamate (The ellipsoids are shown at 30% probability levels)

Supplementary Table 9. Crystal data and structure refinement for **83**

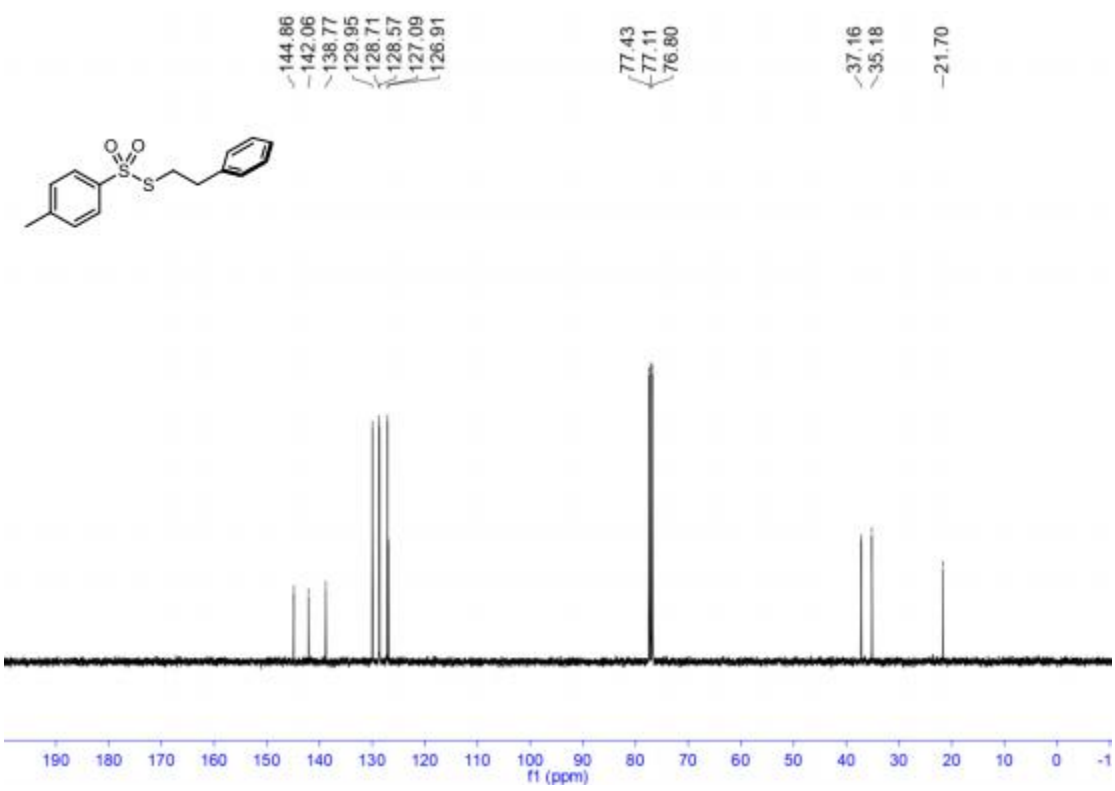
Identification code	exp_2677
Empirical formula	$C_{27}H_{46}N_2O_3S$
Formula weight	478.72
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P1
a/Å	8.8333(2)
b/Å	10.5515(2)
c/Å	16.2430(3)
α/°	108.378(2)
β/°	91.566(2)
γ/°	95.637(2)
Volume/Å^3	1427.03(5)
Z	2
ρ_{calc}g/cm^3	1.114
μ/mm^{-1}	1.217
F(000)	524.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.744 to 148.064
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 13$, $-20 \le l \le 20$
Reflections collected	22556
Independent reflections	10529 [R_{int} = 0.0238, R_{sigma} = 0.0264]
Data/restraints/parameters	10529/3/613
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0950
Final R indexes [all data]	R_1 = 0.0372, wR_2 = 0.0972
Largest diff. peak/hole / e Å^{-3}	0.46/-0.36
Flack/Hooft parameter	0.005(6)/-0.008(3)

Supplementary NMR Spectra and HPLC Spectra

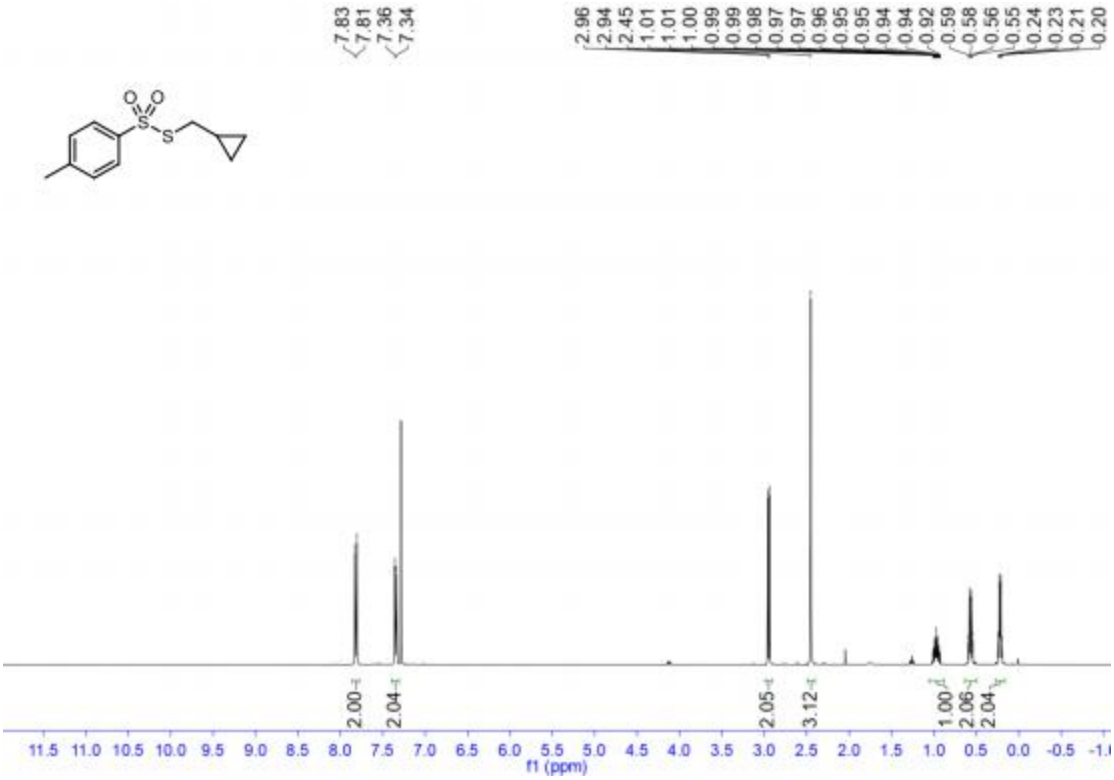
Supplementary Figure 14 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-phenethyl 4-methylbenzenesulfonothioate **(1a)**



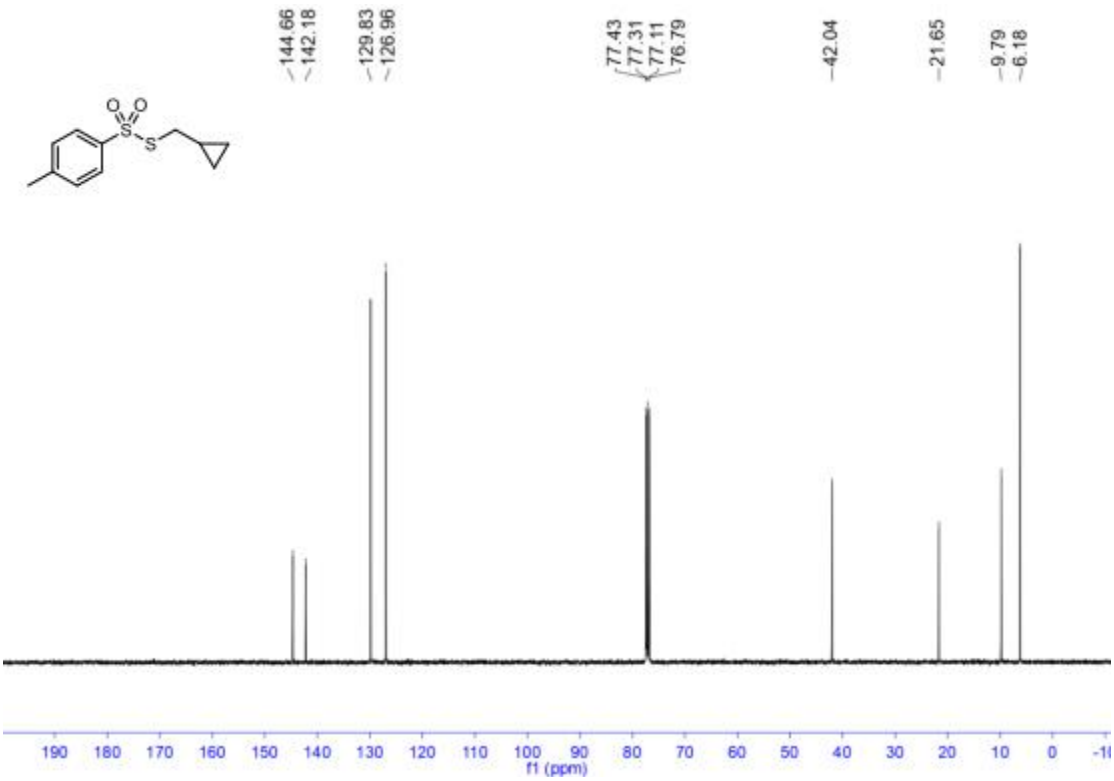
Supplementary Figure 15 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-phenethyl 4-methylbenzenesulfonothioate **(1a)**



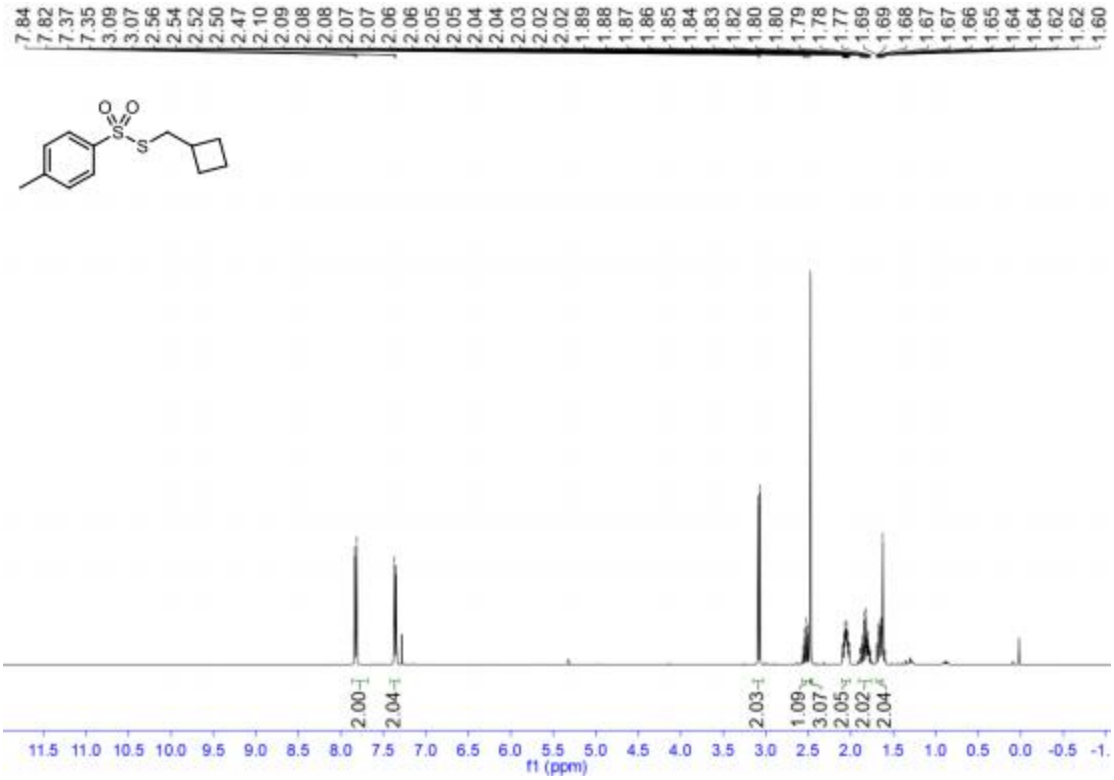
Supplementary Figure 16 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(cyclopropylmethyl) 4-methylbenzenesulfonothioate **(7a)**



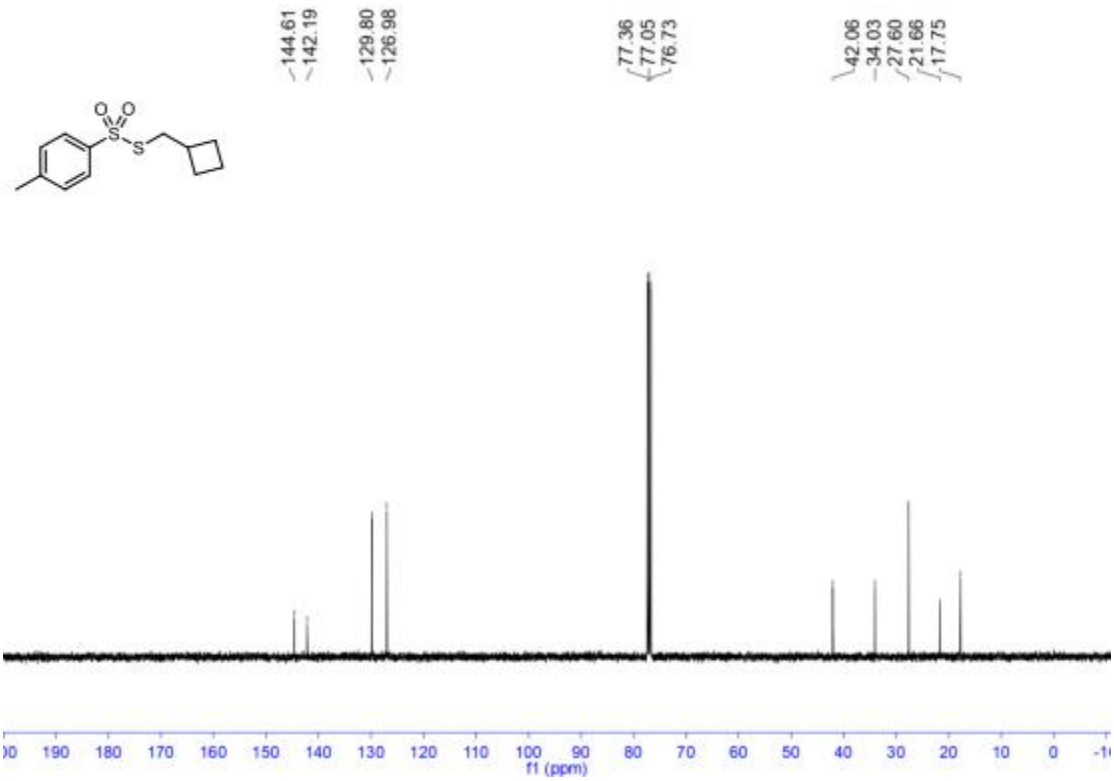
Supplementary Figure 16 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(cyclopropylmethyl) 4-methylbenzenesulfonothioate **(7a)**



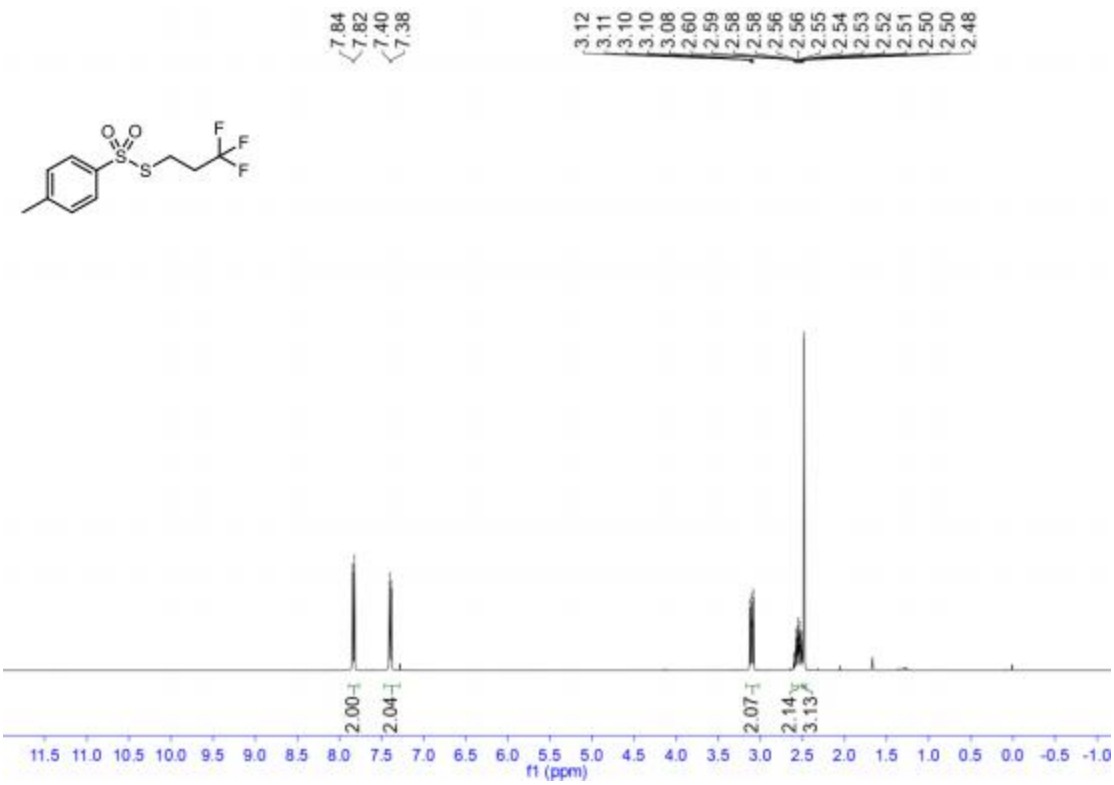
Supplementary Figure 18 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(cyclobutylmethyl) 4-methylbenzenesulfonothioate **(8a)**



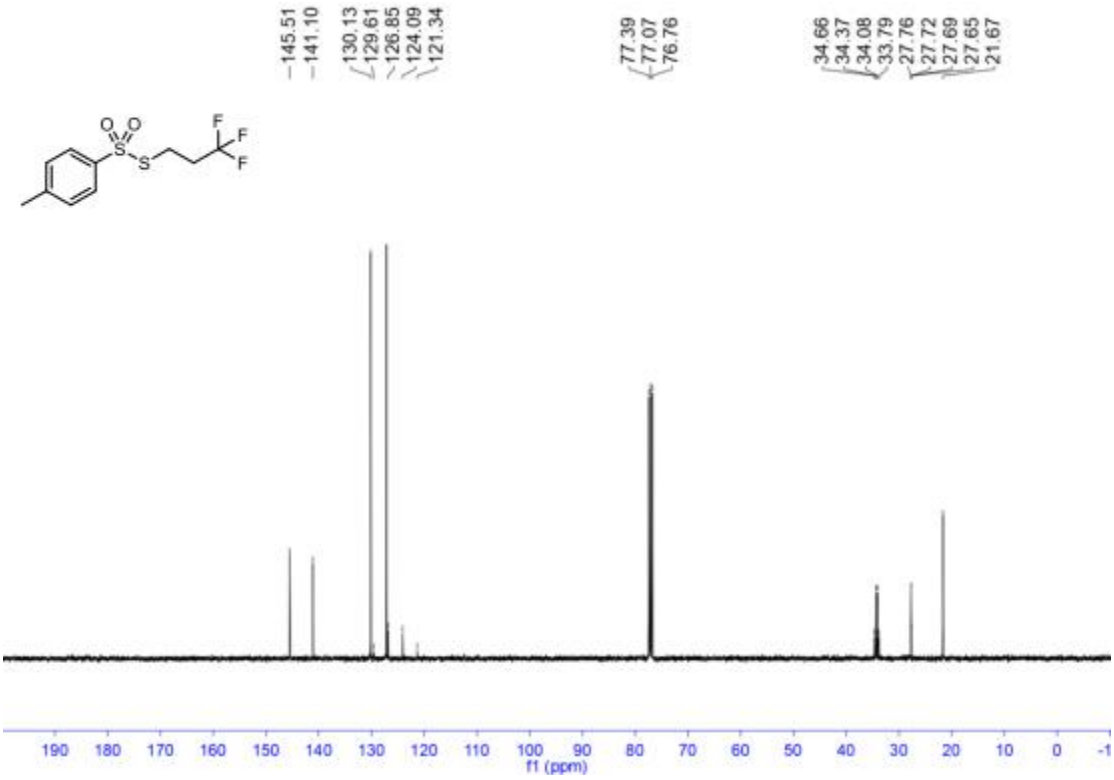
Supplementary Figure 19 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(cyclobutylmethyl) 4-methylbenzenesulfonothioate **(8a)**



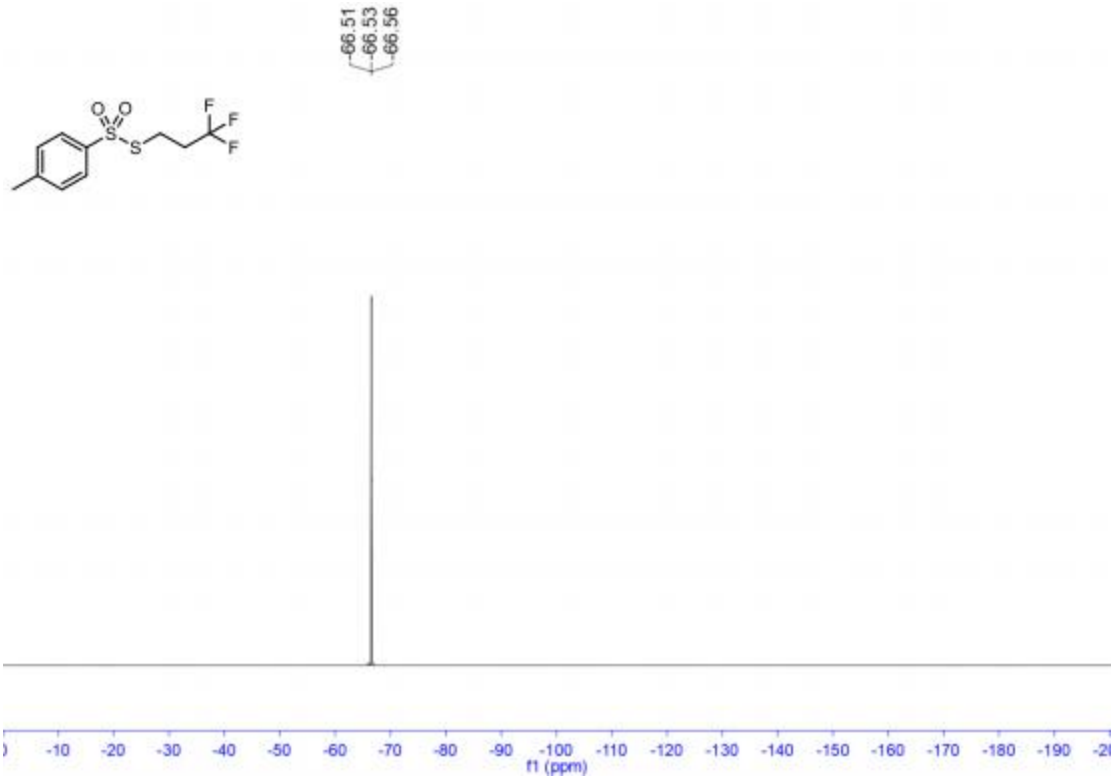
Supplementary Figure 20 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(3,3,3-trifluoropropyl) 4-methylbenzenesulfonothioate **(9a)**



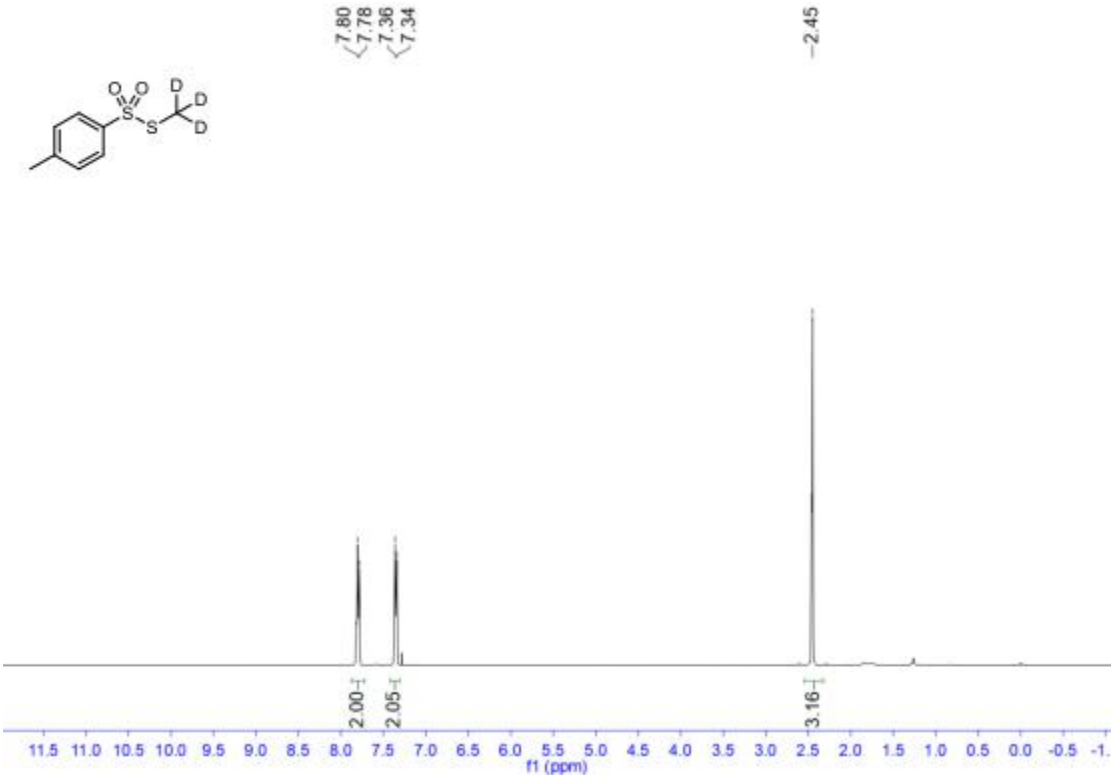
Supplementary Figure 21 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(3,3,3-trifluoropropyl) 4-methylbenzenesulfonothioate **(9a)**



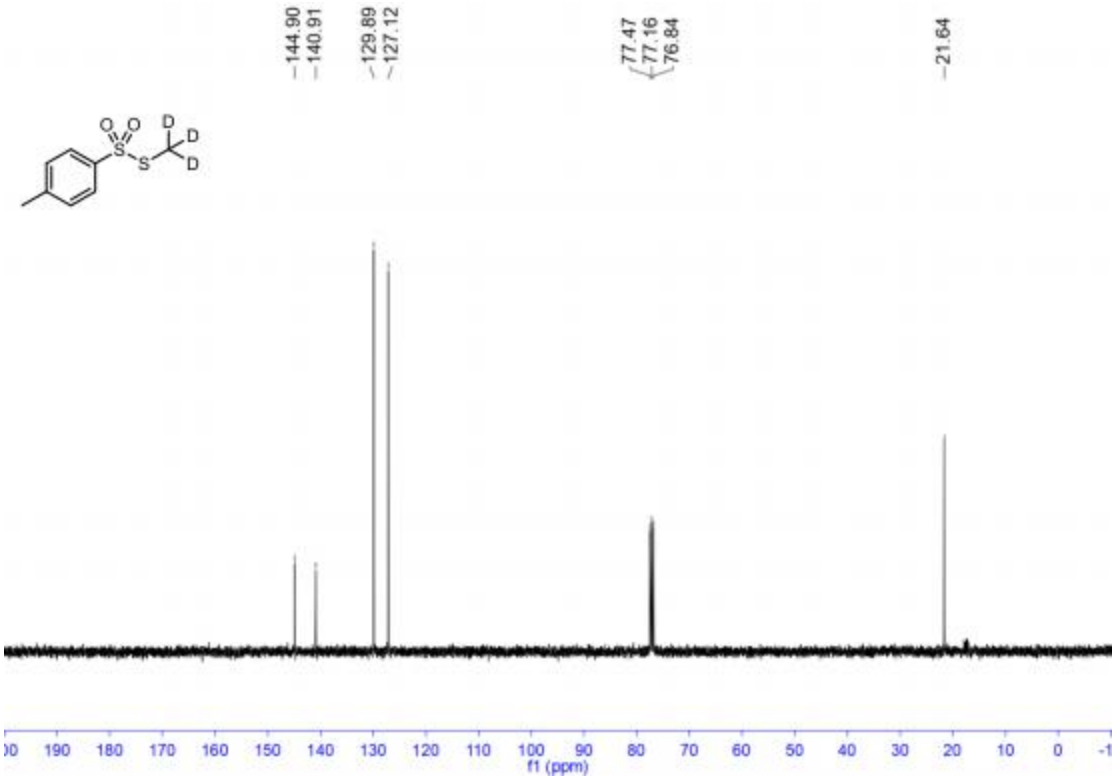
Supplementary Figure 22 | ^{19}F NMR (376MHz, 298K, Chloroform-*d*) of *S*-(3,3,3-trifluoropropyl) 4-methylbenzenesulfonothioate **(9a)**



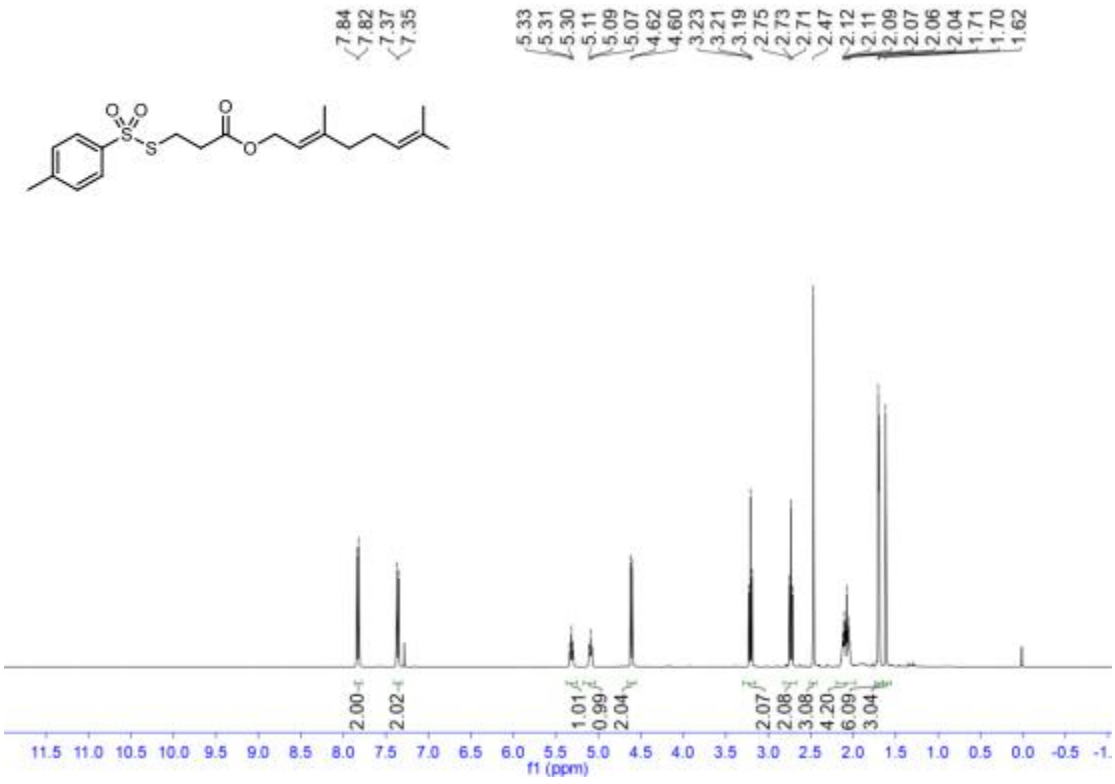
Supplementary Figure 23 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(methyl-d_3) 4-methylbenzenesulfonothioate **(10a)**



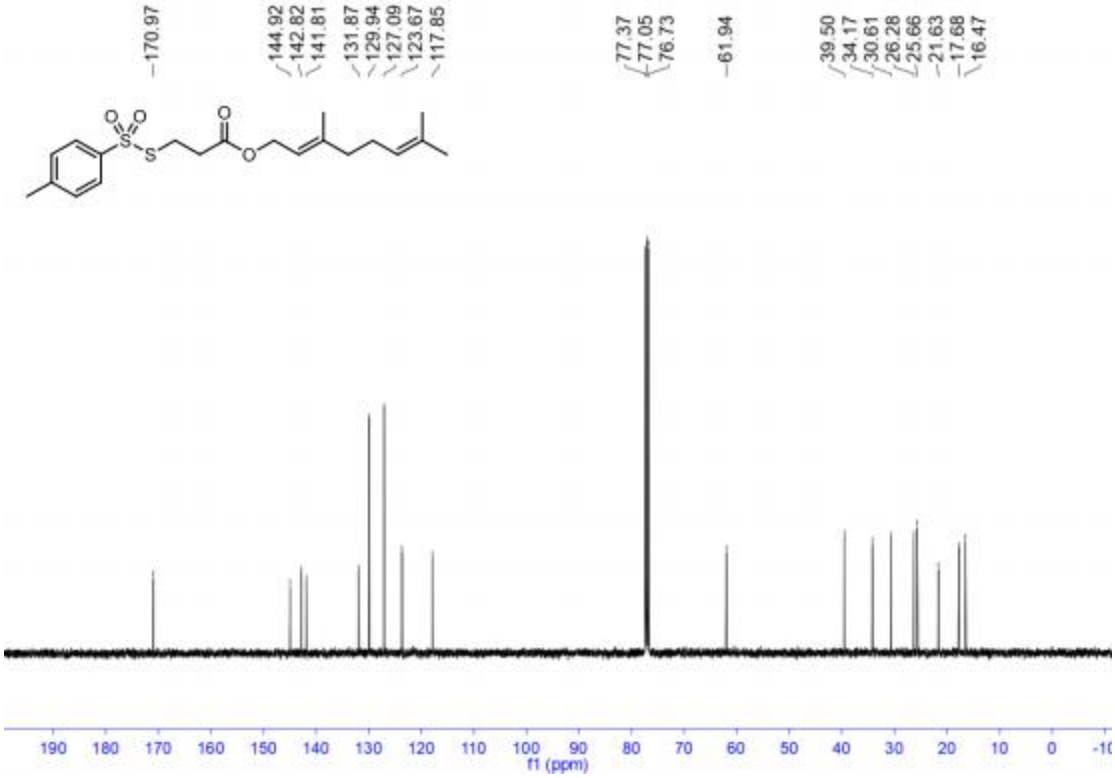
Supplementary Figure 24 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(methyl-d_3) 4-methylbenzenesulfonothioate **(10a)**



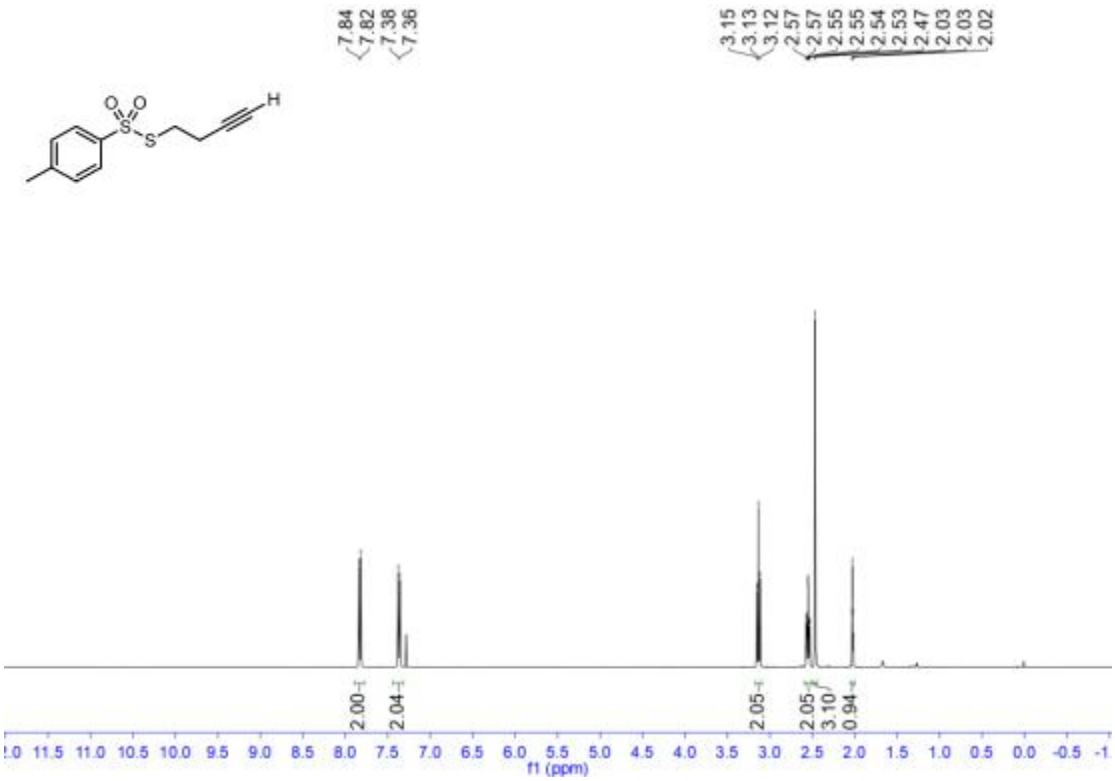
Supplementary Figure 25 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3,7-dimethylocta-2,6-dien- 1-yl 3-(tosylthio)propanoate **(11a)**



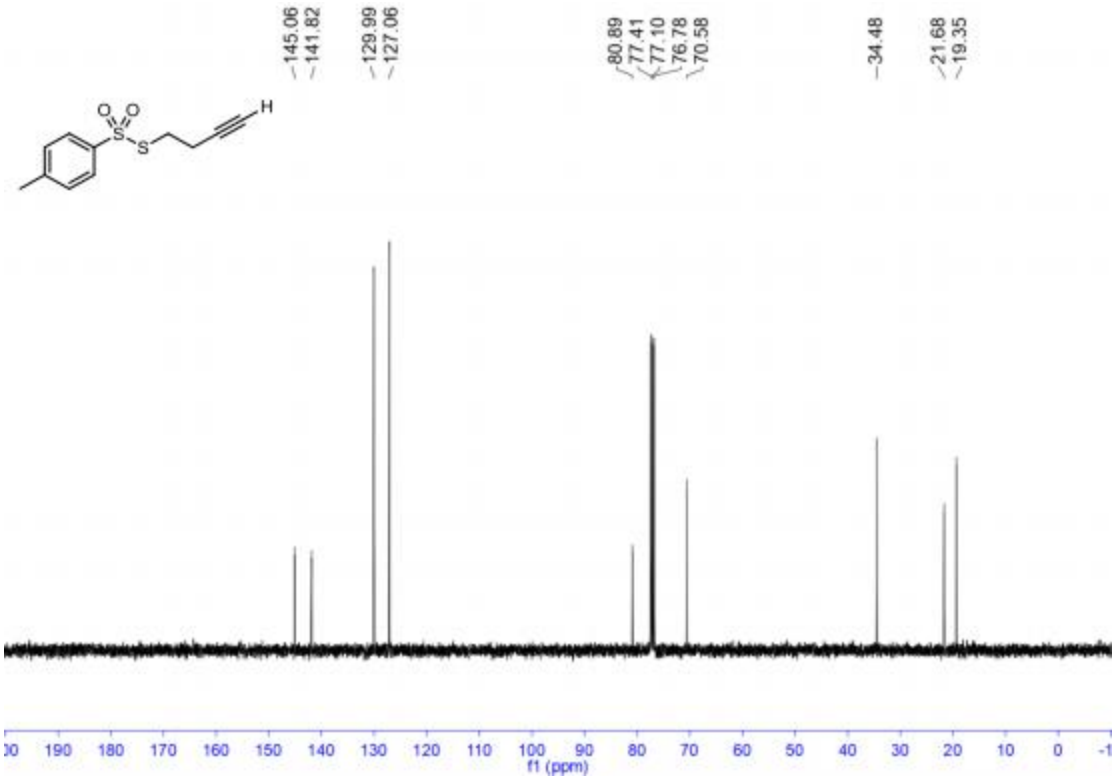
Supplementary Figure 26 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of (*E*)-3,7-dimethylocta-2,6-dien- 1-yl 3-(tosylthio)propanoate **(11a)**



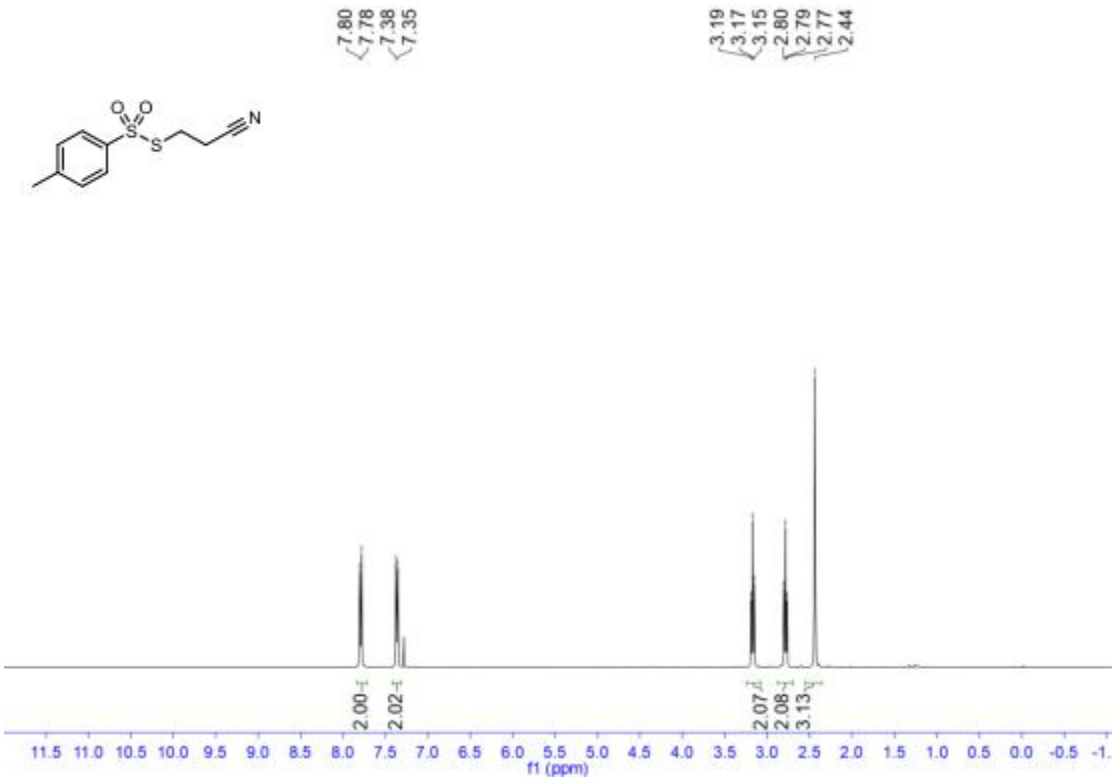
Supplementary Figure 27 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(but-3-yn- 1-yl) 4-methylbenzenesulfonothioate **(12a)**



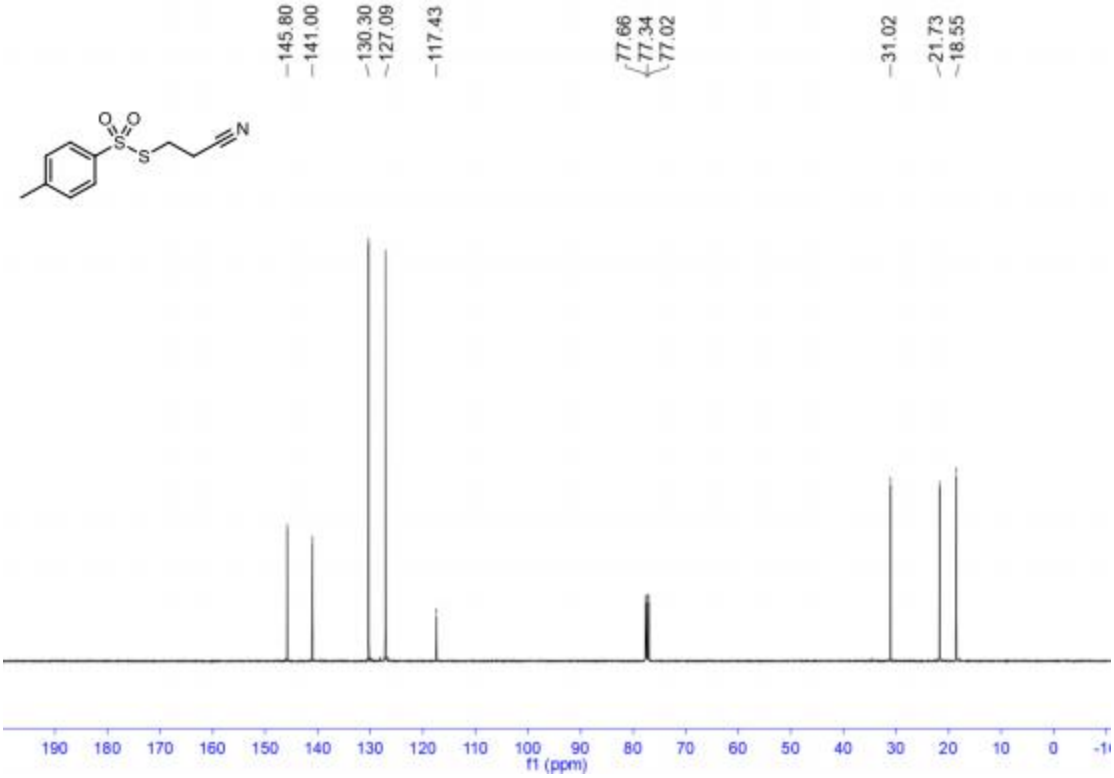
Supplementary Figure 28 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(but-3-yn- 1-yl) 4-methylbenzenesulfonothioate **(12a)**



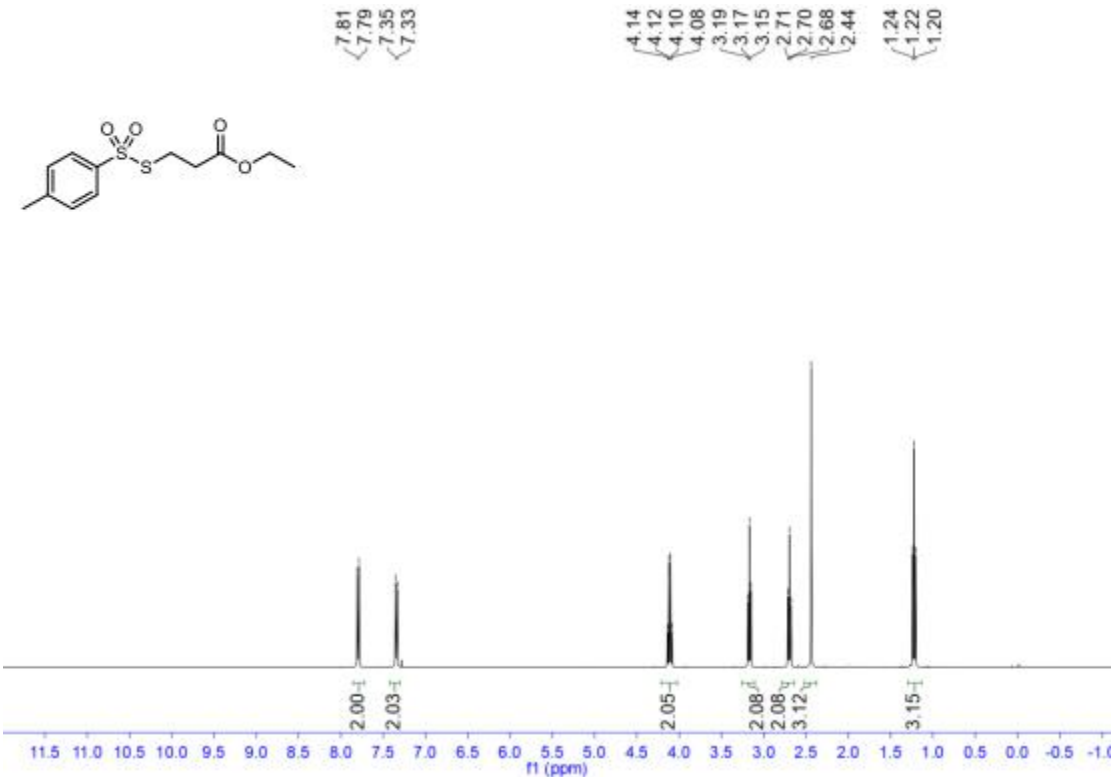
Supplementary Figure 29 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(2-cyanoethyl) 4-methylbenzenesulfonothioate **(13a)**



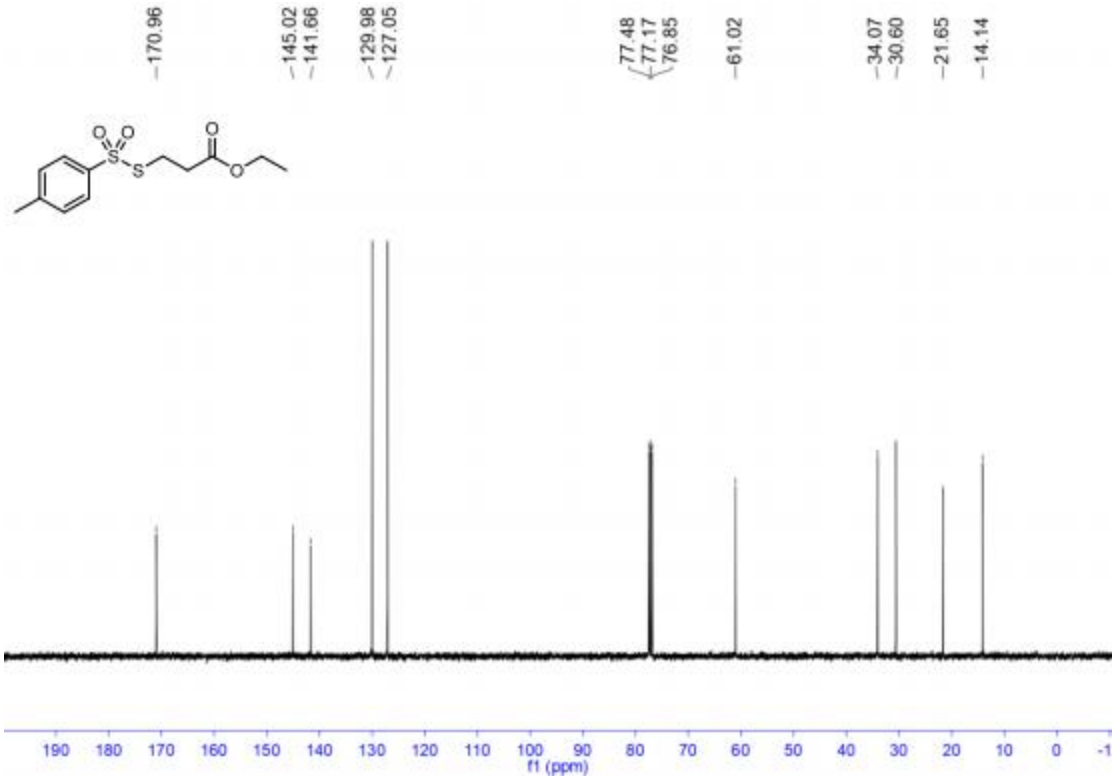
Supplementary Figure 30 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(2-cyanoethyl) 4-methylbenzenesulfonothioate **(13a)**



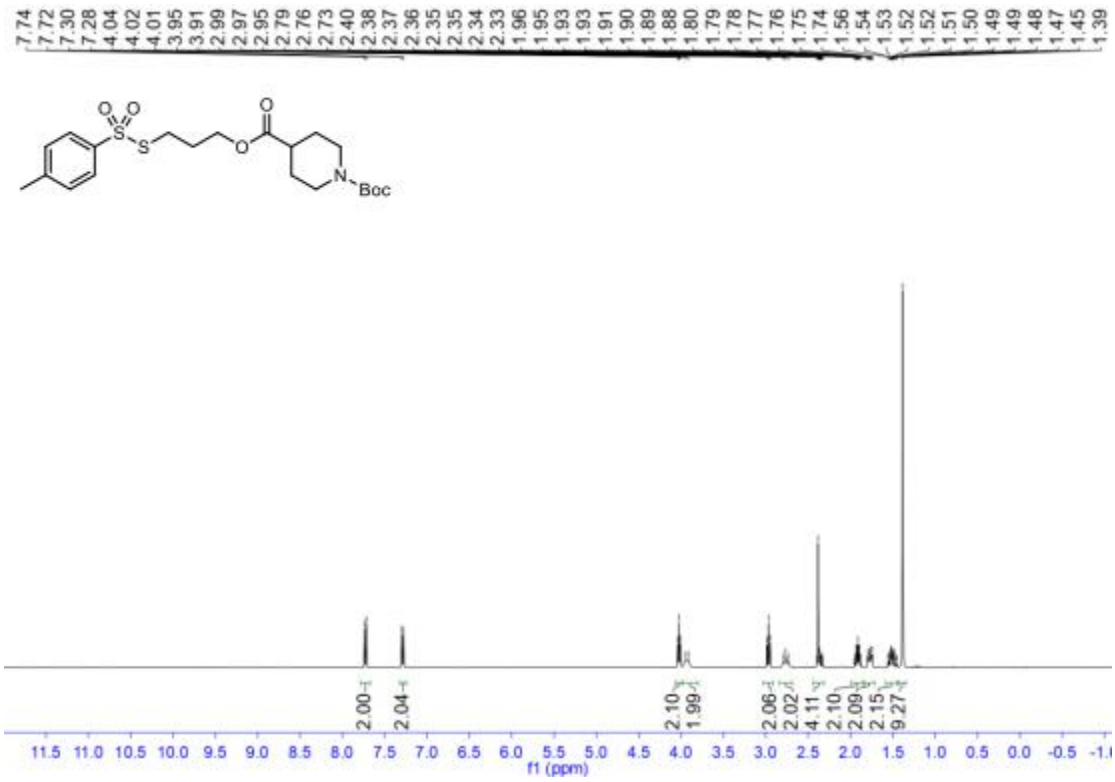
Supplementary Figure 31 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of ethyl 3-(tosylthio)propanoate **(14a)**



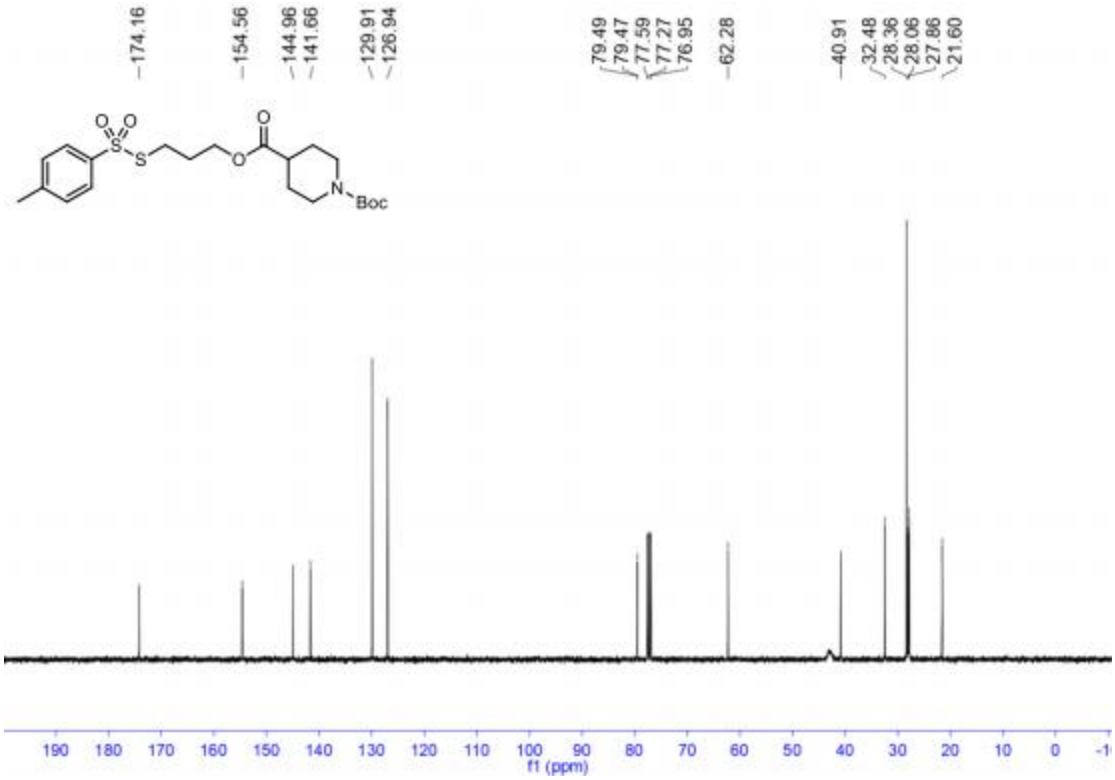
Supplementary Figure 32 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of ethyl 3-(tosylthio)propanoate **(14a)**



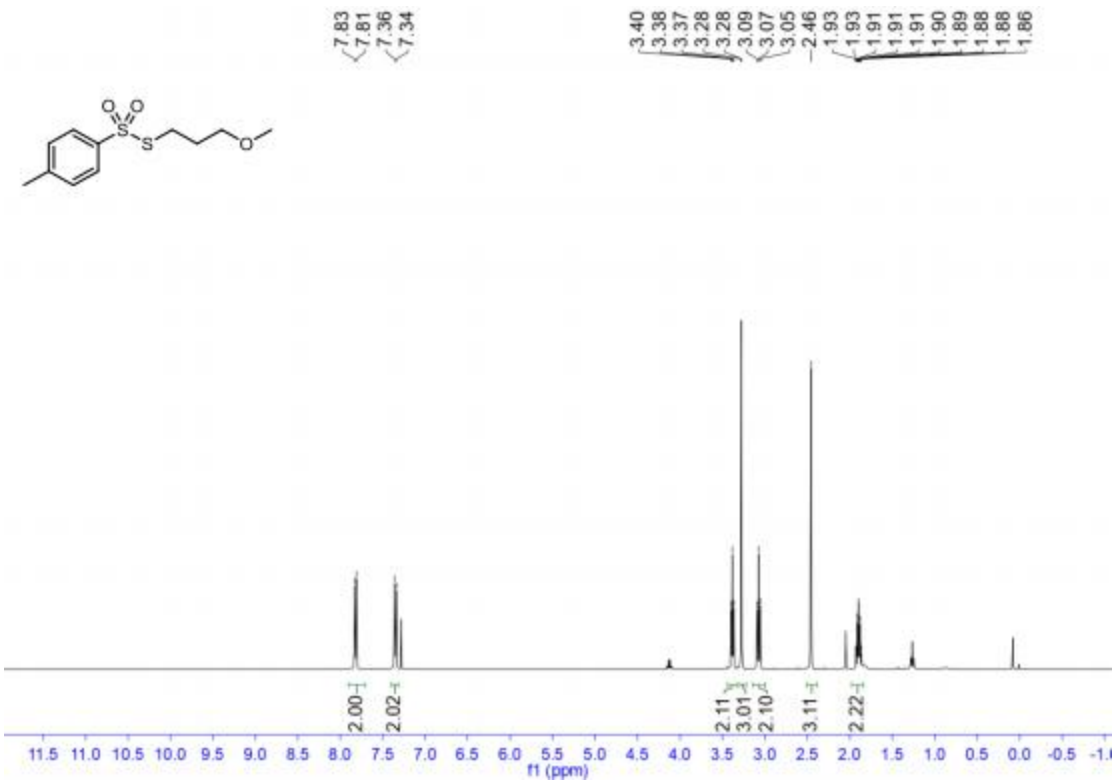
Supplementary Figure 33 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 1-(*tert*-butyl) 4-(3-(tosylthio)propyl) piperidine- 1,4-dicarboxylate **(15a)**



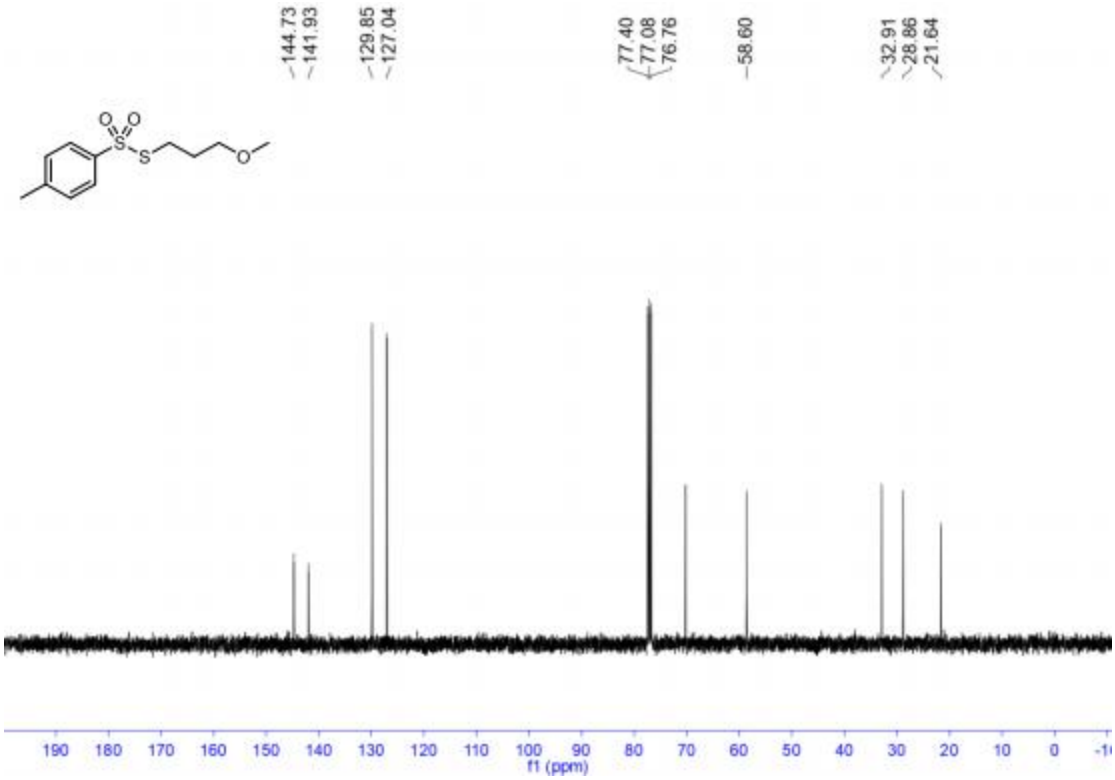
Supplementary Figure 34 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of 1-(*tert*-butyl) 4-(3-(tosylthio)propyl) piperidine- 1,4-dicarboxylate **(15a)**



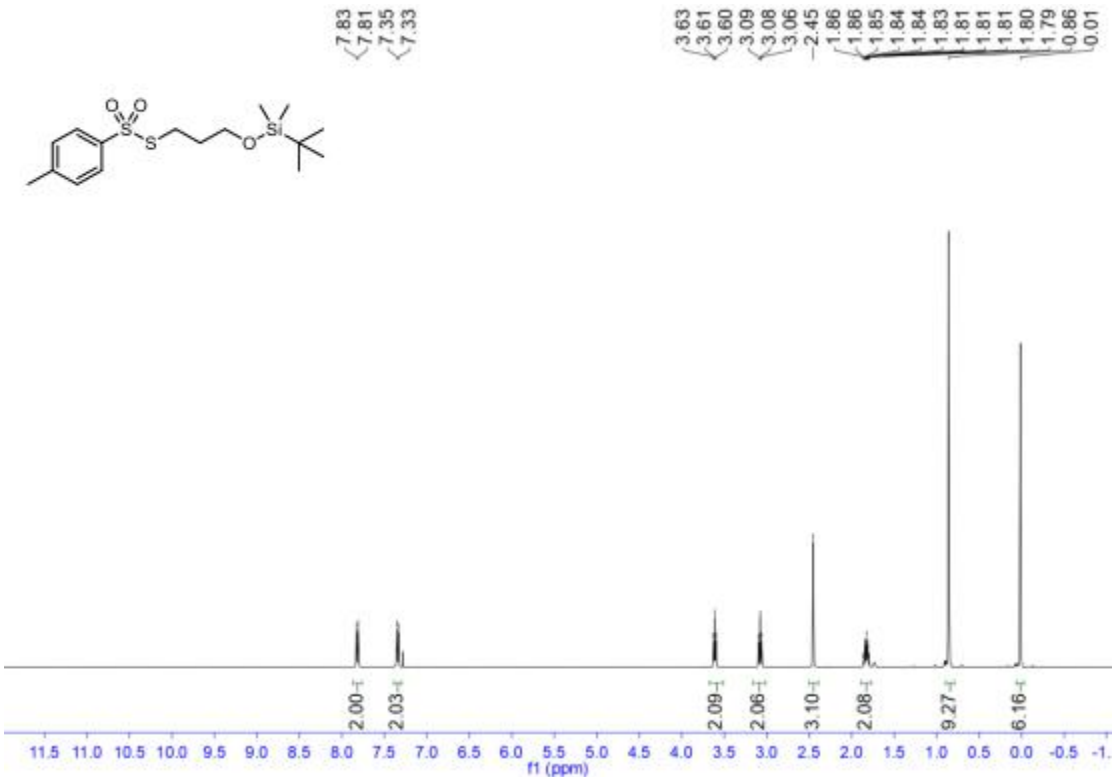
Supplementary Figure 35 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(3-methoxypropyl) 4-methylbenzenesulfonothioate **(16a)**



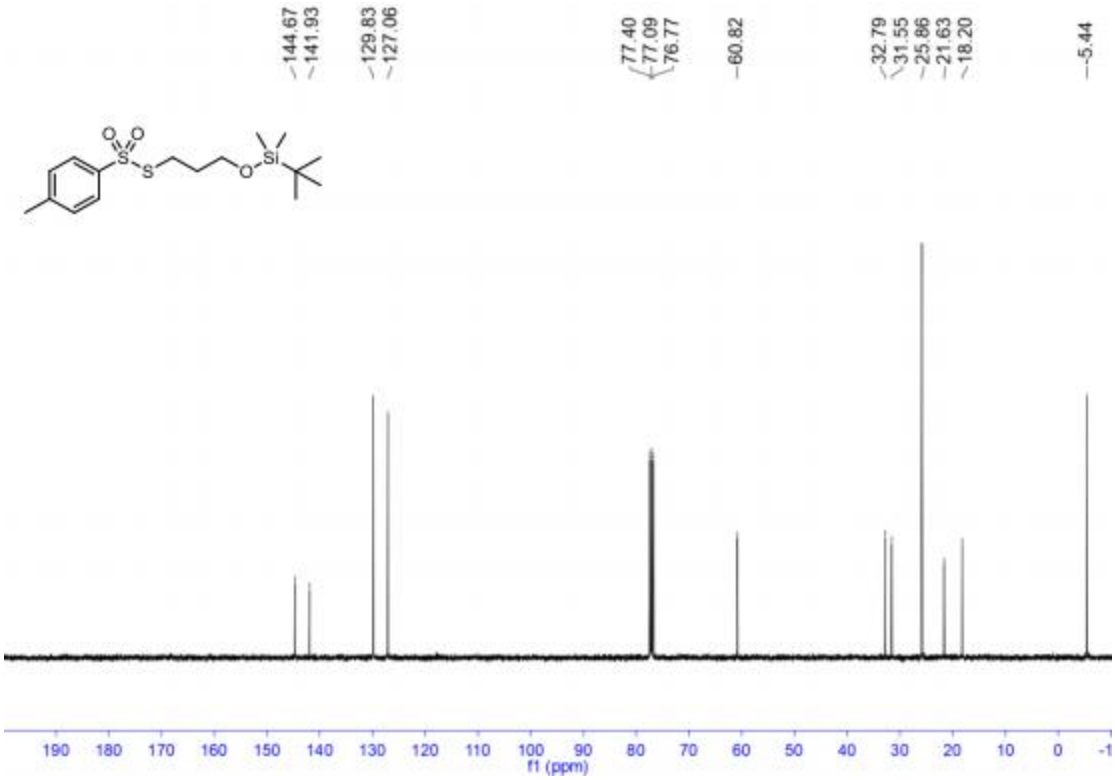
Supplementary Figure 36 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(3-methoxypropyl) 4-methylbenzenesulfonothioate **(16a)**



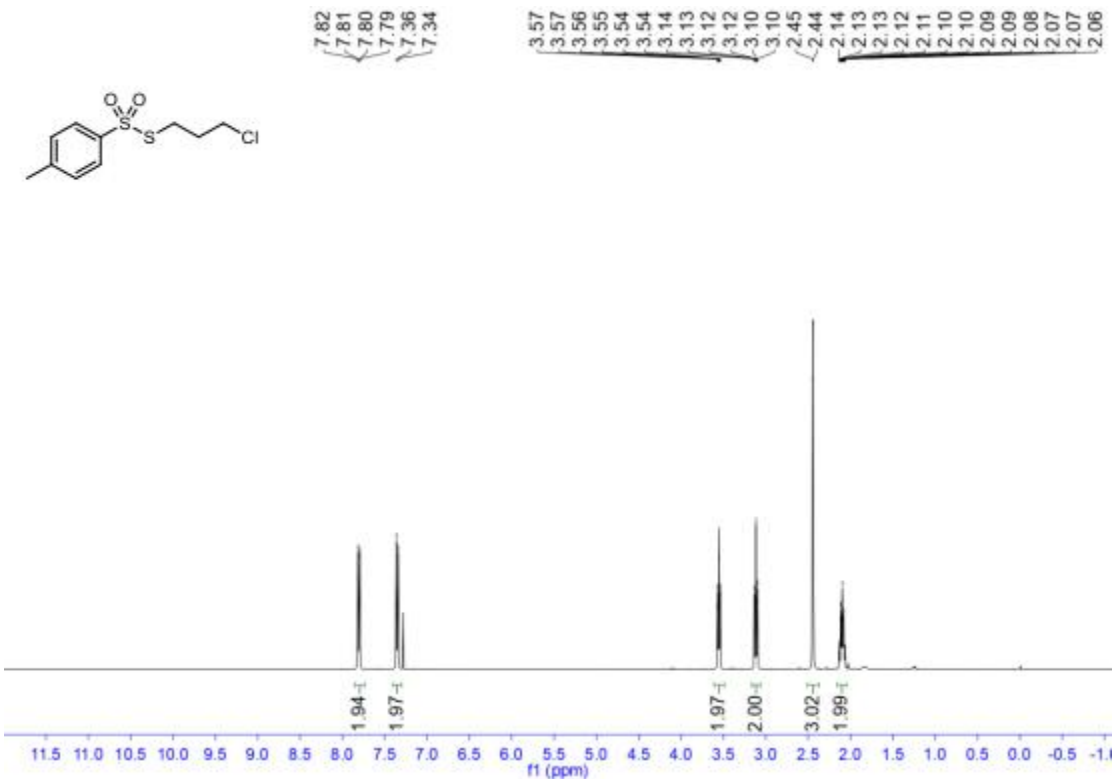
Supplementary Figure 37 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(3-((tert-butyldimethylsilyl)oxy)propyl) 4-methylbenzenesulfonothioate **(17a)**



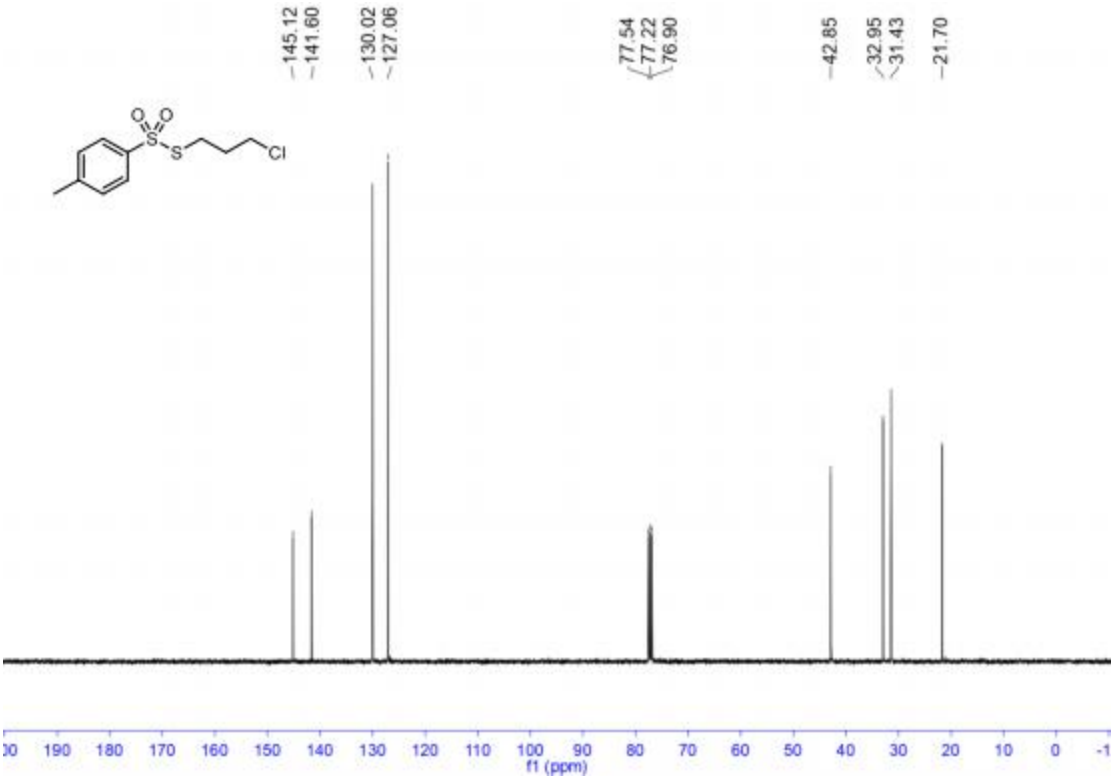
Supplementary Figure 38 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(3-((tert-butyldimethylsilyl)oxy)propyl) 4-methylbenzenesulfonothioate **(17a)**



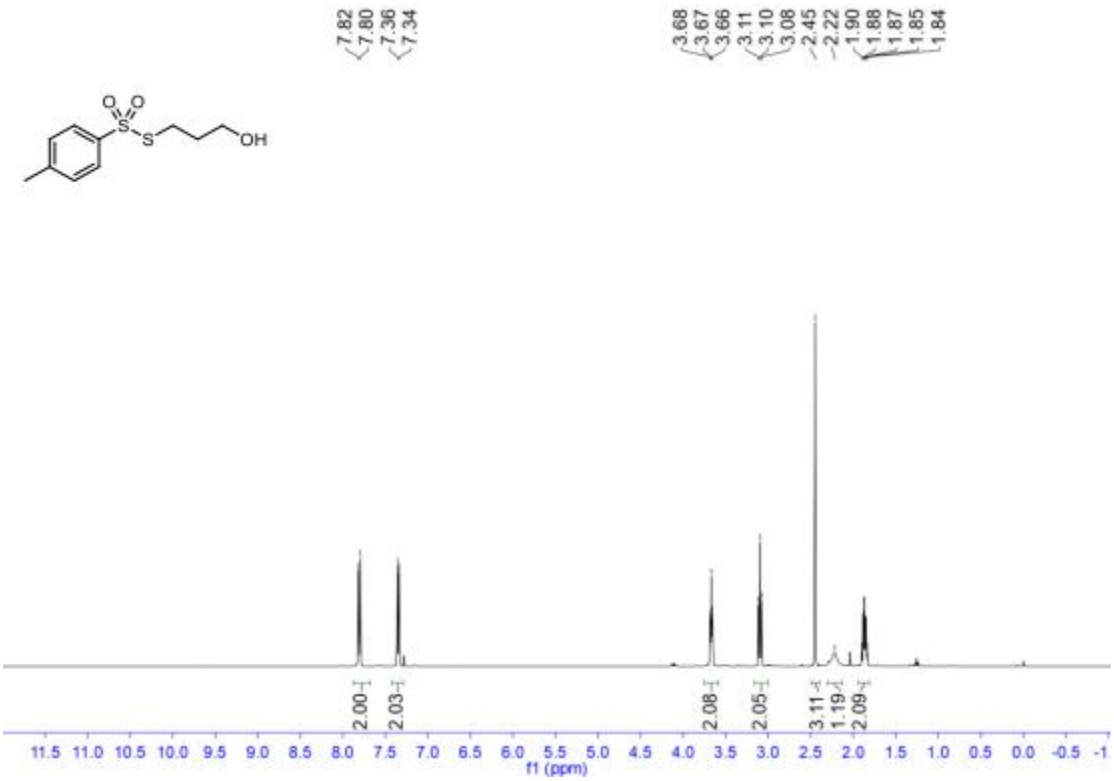
Supplementary Figure 39 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(3-chloropropyl) 4-methylbenzenesulfonothioate **(18a)**



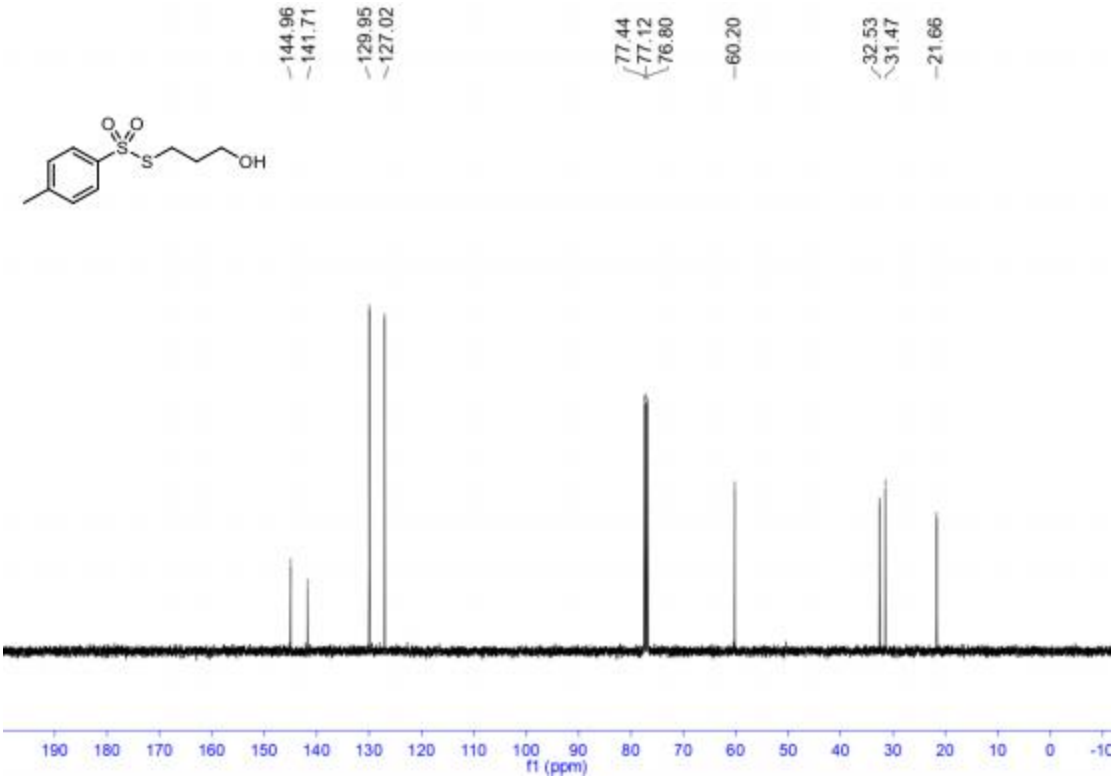
Supplementary Figure 40 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(3-chloropropyl) 4-methylbenzenesulfonothioate **(18a)**



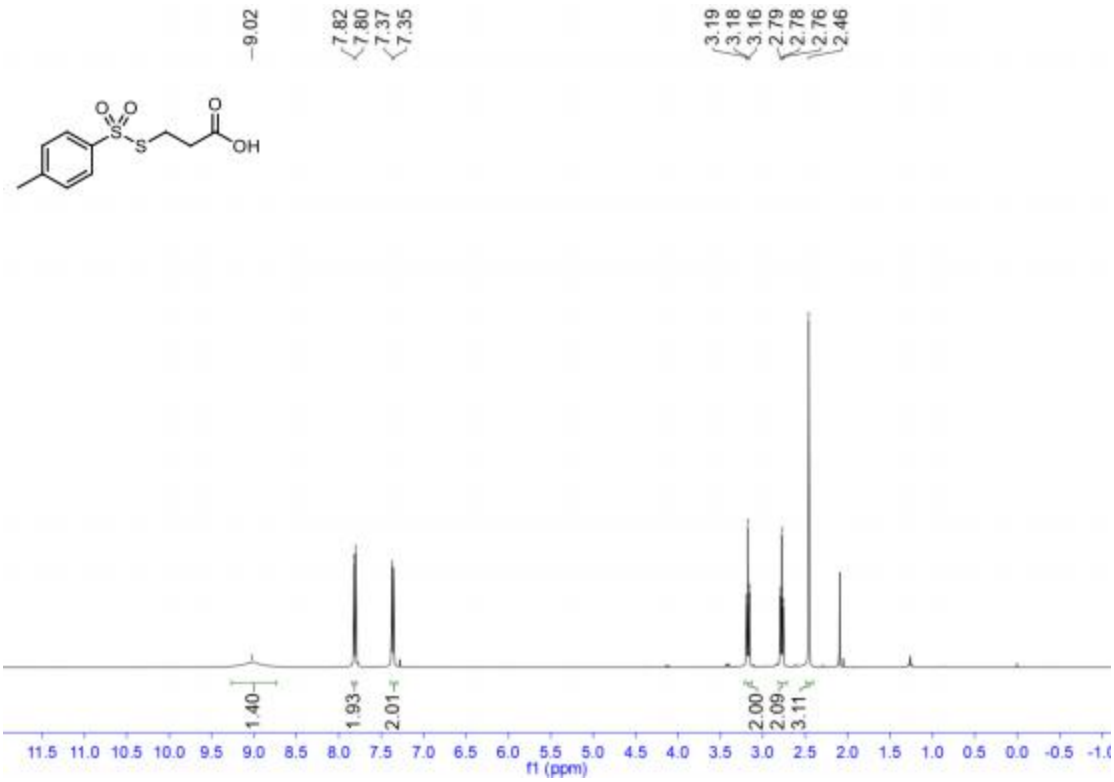
Supplementary Figure 41 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(3-hydroxypropyl) 4-methylbenzenesulfonothioate **(19a)**



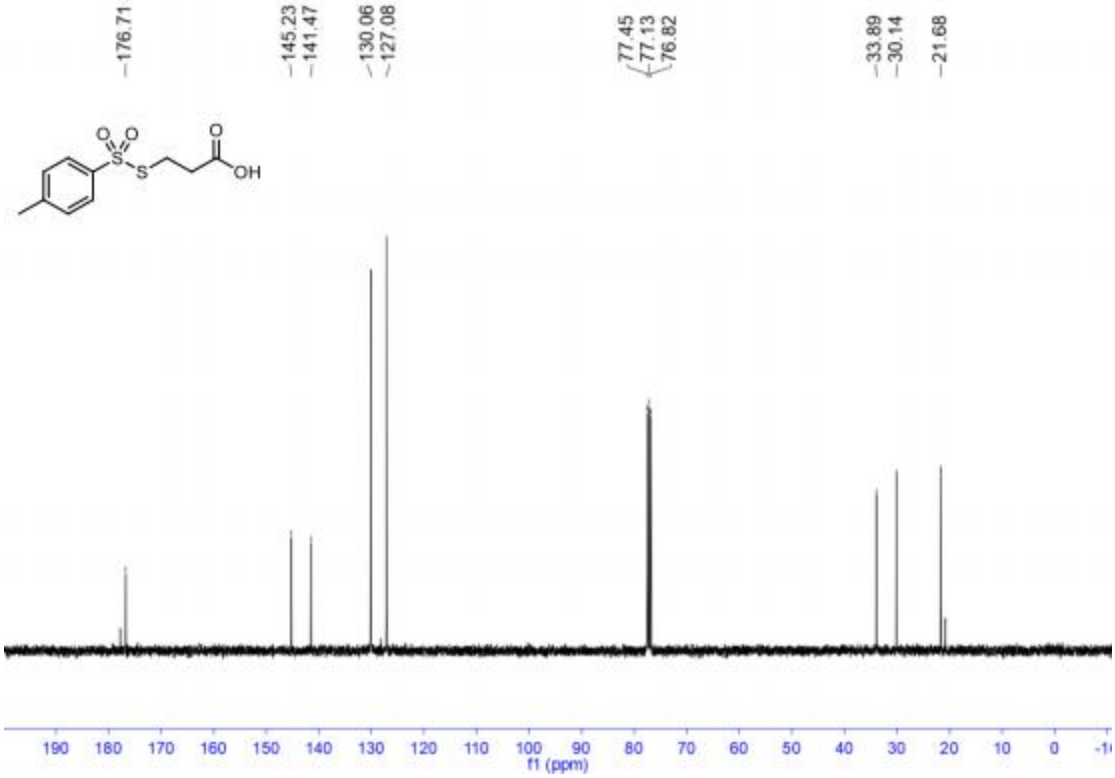
Supplementary Figure 42 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(3-hydroxypropyl) 4-methylbenzenesulfonothioate **(19a)**



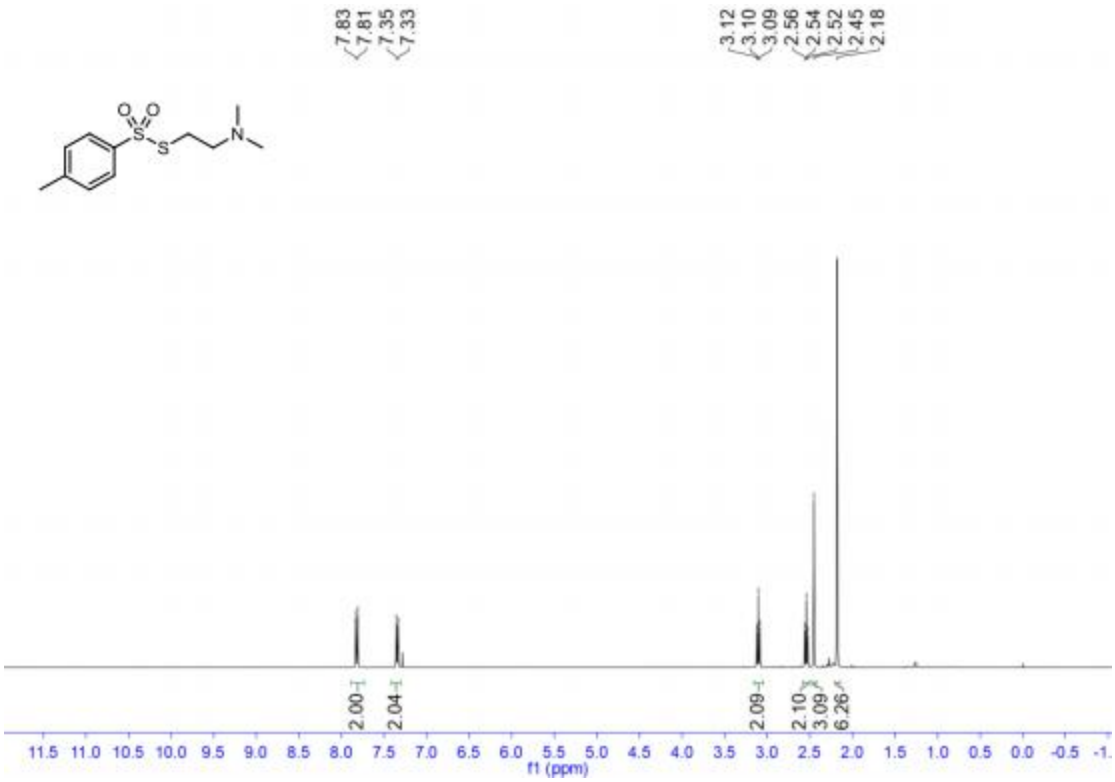
Supplementary Figure 43 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propanoic acid **(20a)**



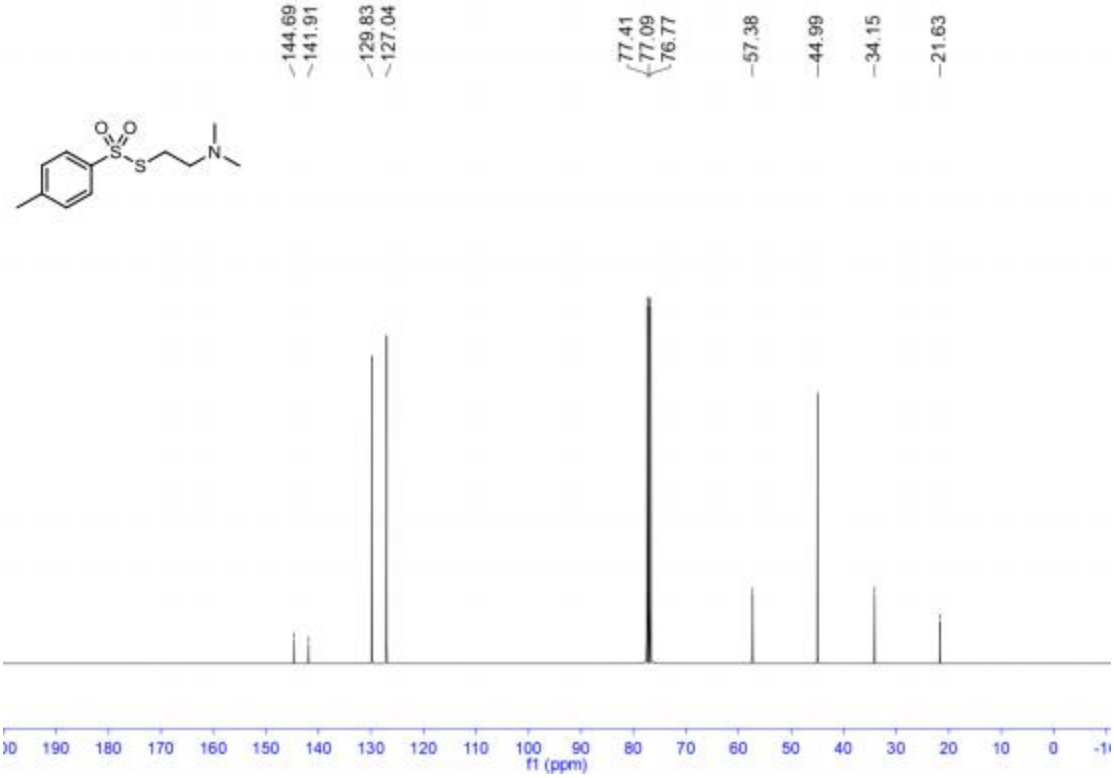
Supplementary Figure 44 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propanoic acid **(20a)**



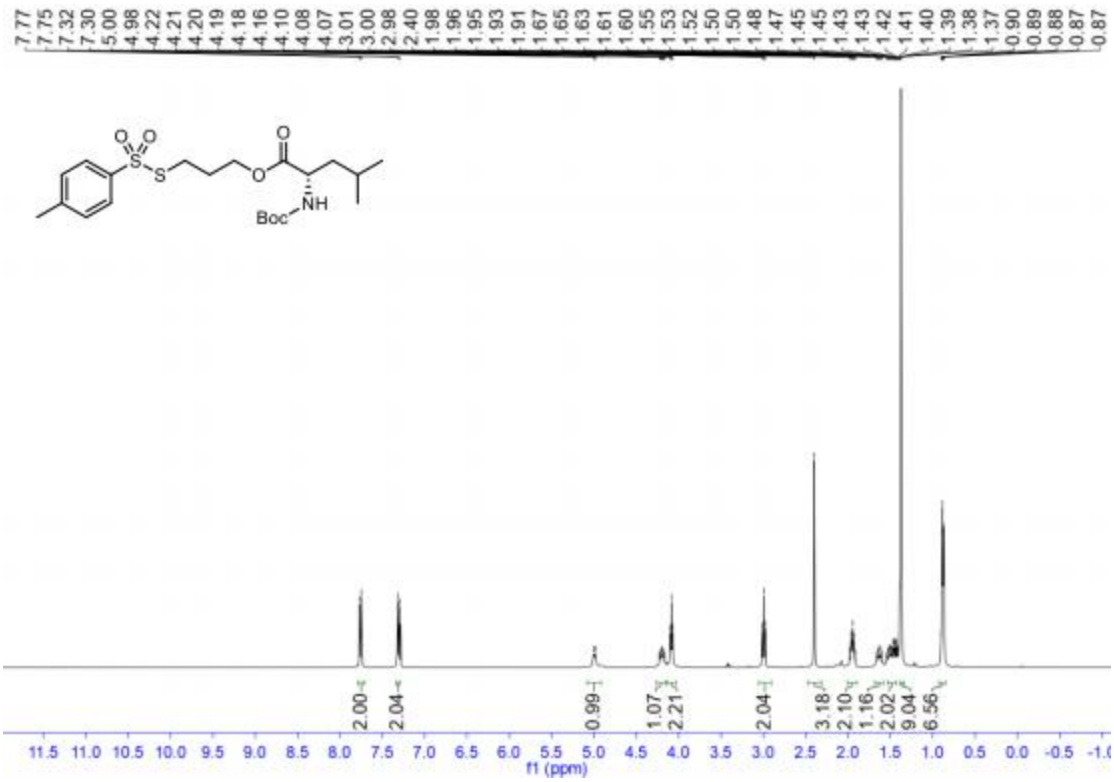
Supplementary Figure 45 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(2-(dimethylamino)ethyl) 4-methylbenzenesulfonothioate **(21a)**



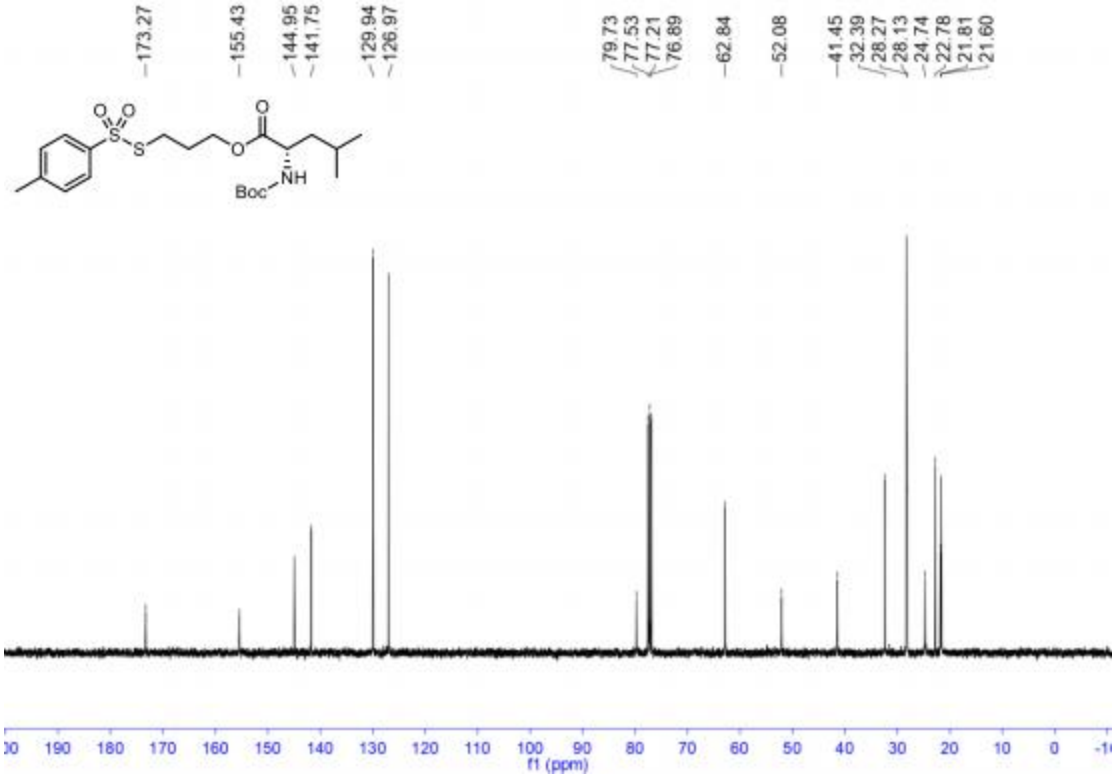
Supplementary Figure 46 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(2-(dimethylamino)ethyl) 4-methylbenzenesulfonothioate **(21a)**



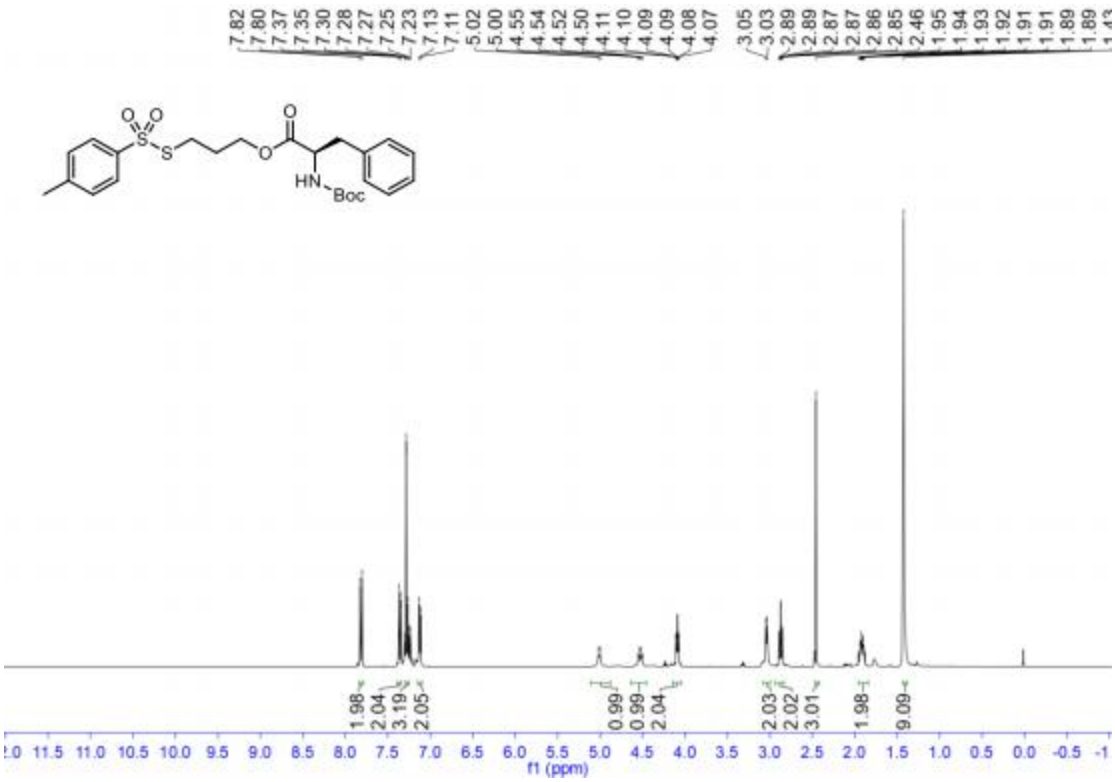
Supplementary Figure 47 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (*tert*-butoxycarbonyl)-*L*-leucinate **(22a)**



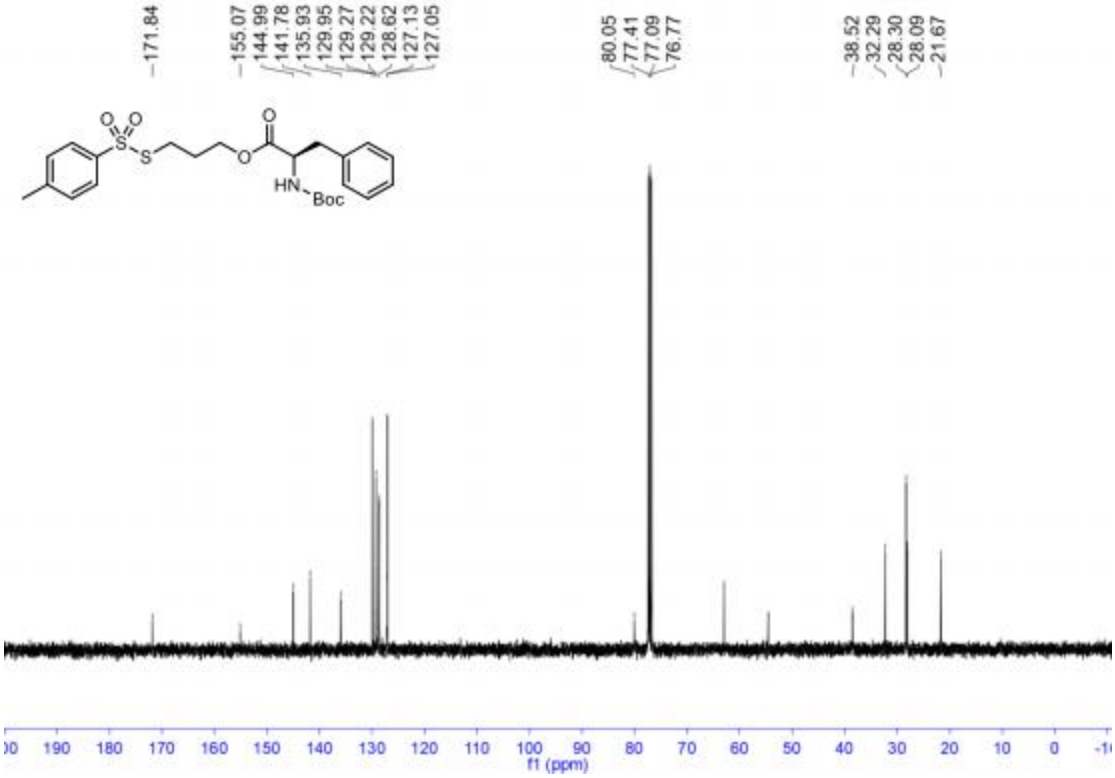
Supplementary Figure 48 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (*tert*-butoxycarbonyl)-*L*-leucinate **(22a)**



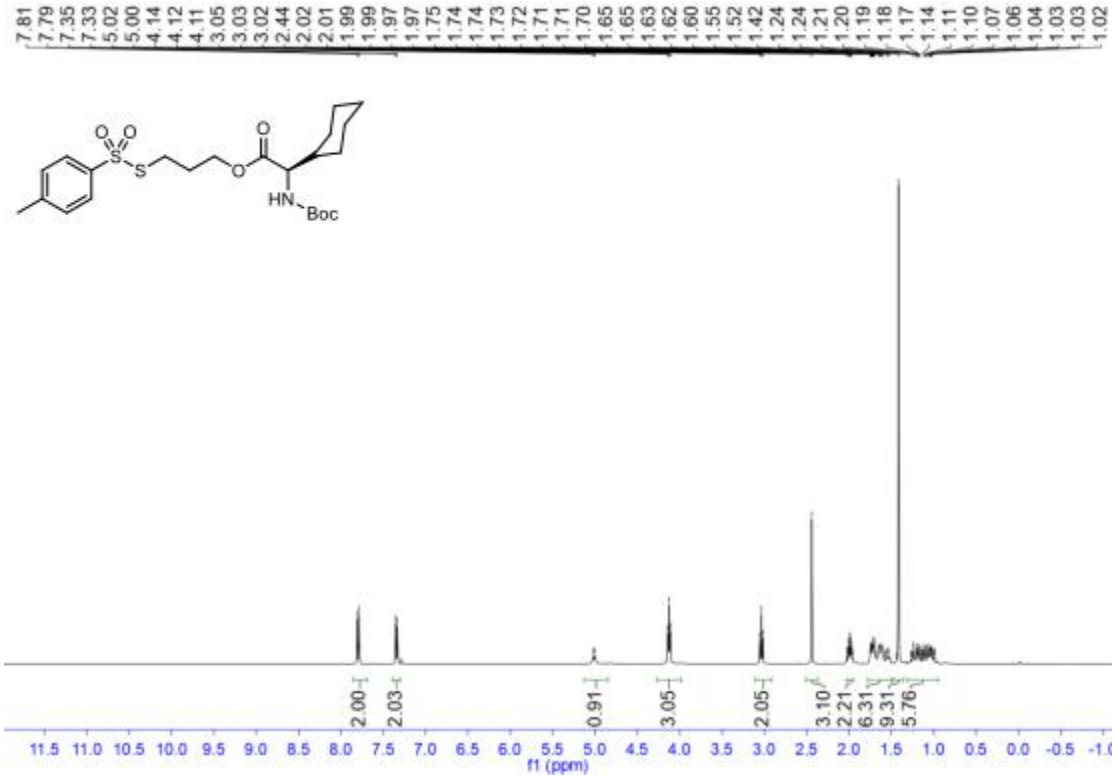
Supplementary Figure 49 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate **(23a)**



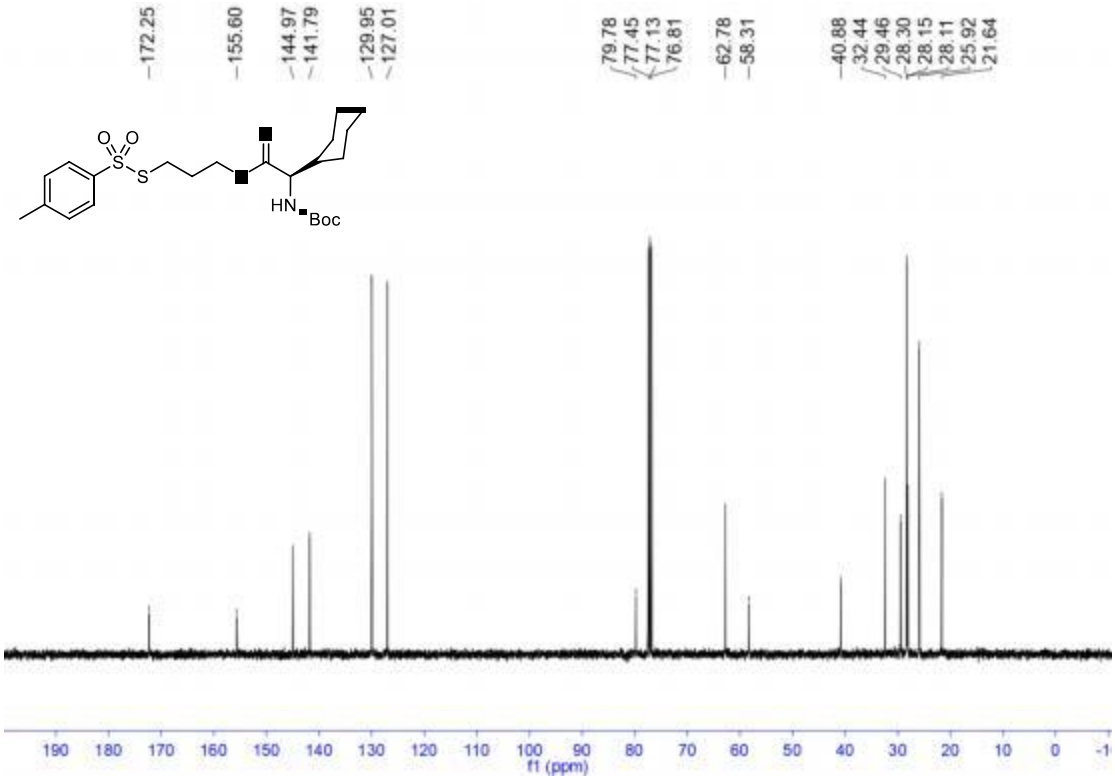
Supplementary Figure 50 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate **(23a)**



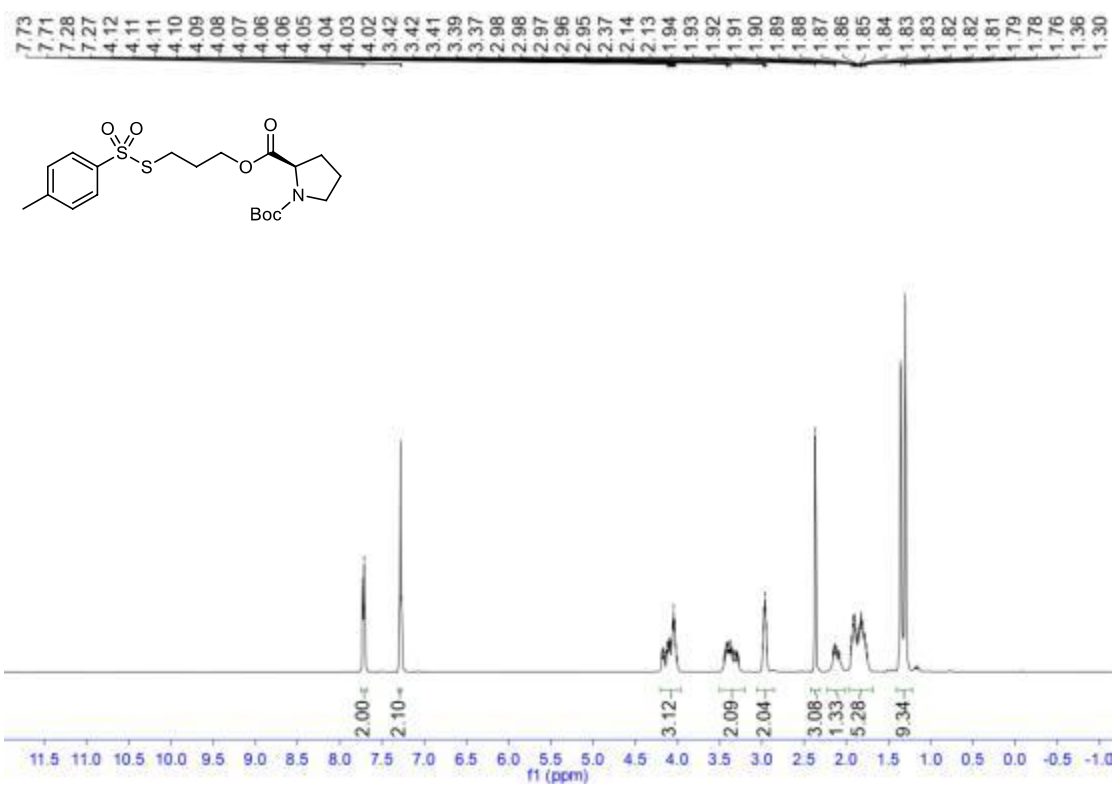
Supplementary Figure 51 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate **(24a)**



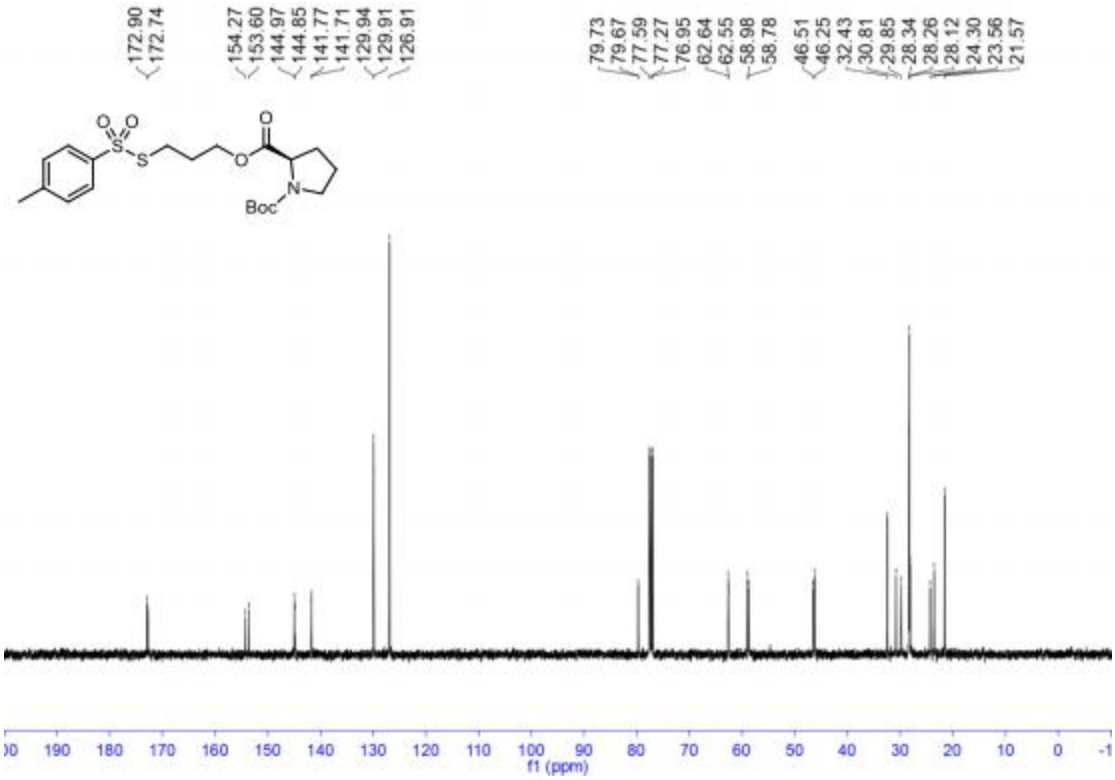
Supplementary Figure 51 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate **(24a)**



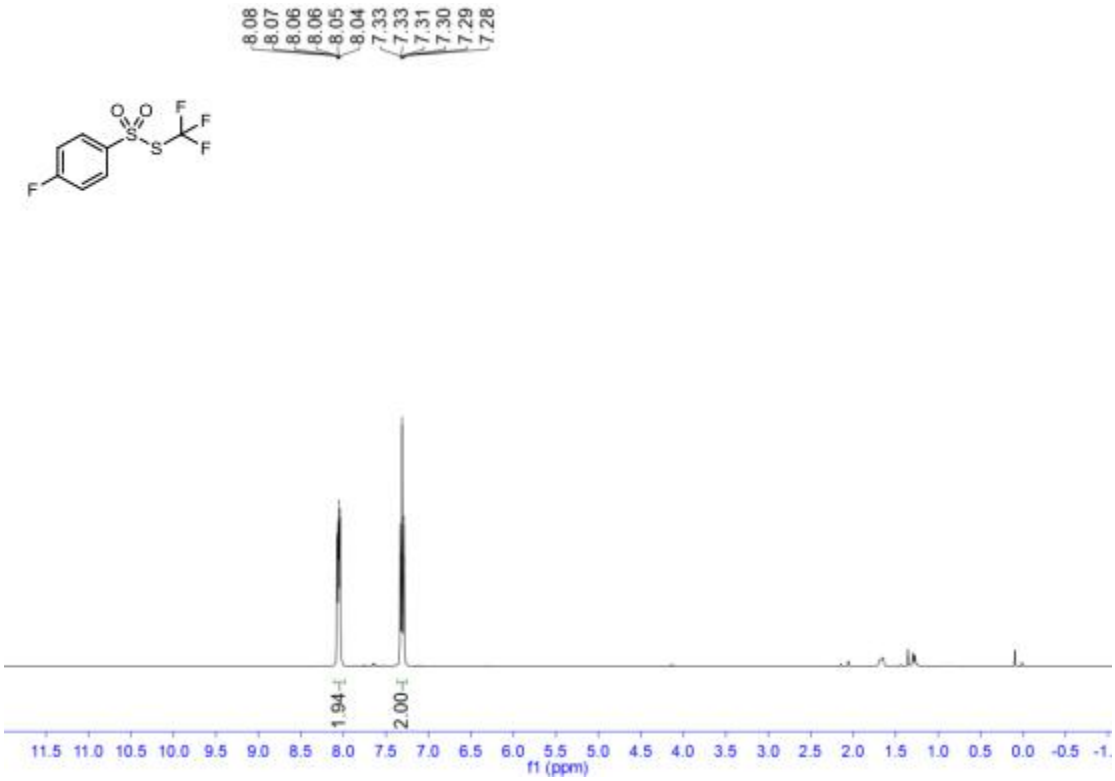
Supplementary Figure 53 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 1-(*tert*-butyl) 2-(3-(tosylthio)propyl) (*R*)-pyrrolidine- 1,2-dicarboxylate **(25a)**



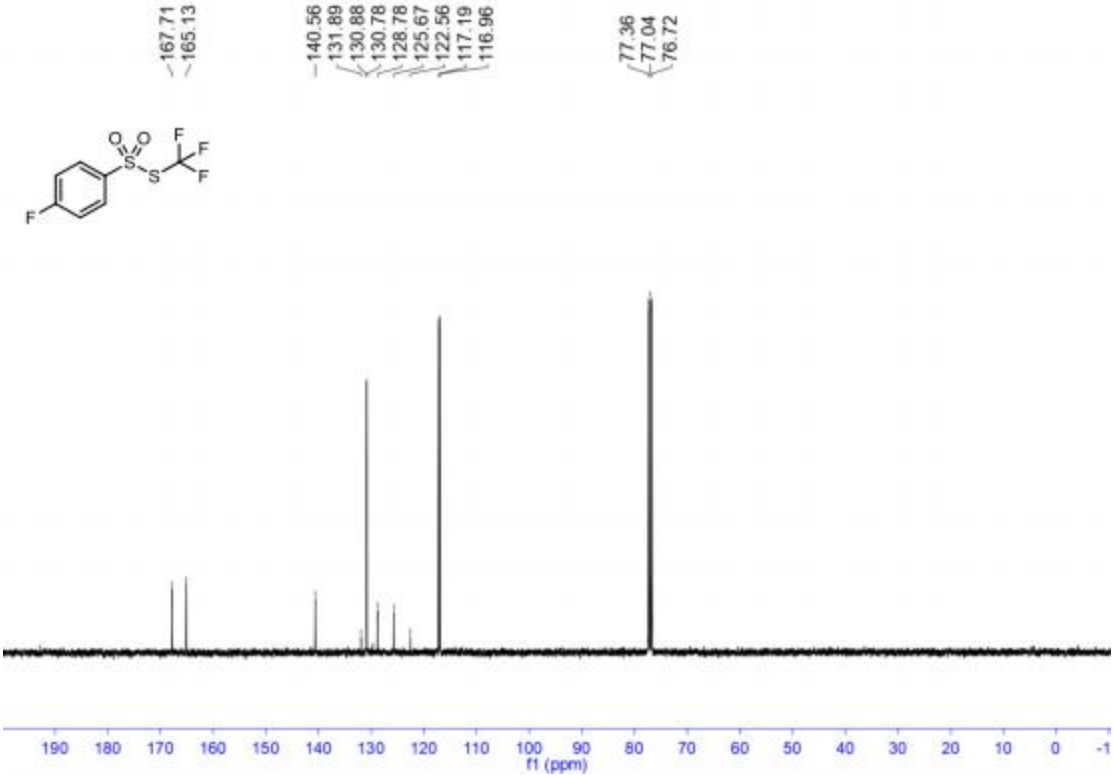
Supplementary Figure 54 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of 1-(*tert*-butyl) 2-(3-(tosylthio)propyl) (*R*)-pyrrolidine- 1,2-dicarboxylate **(25a)**



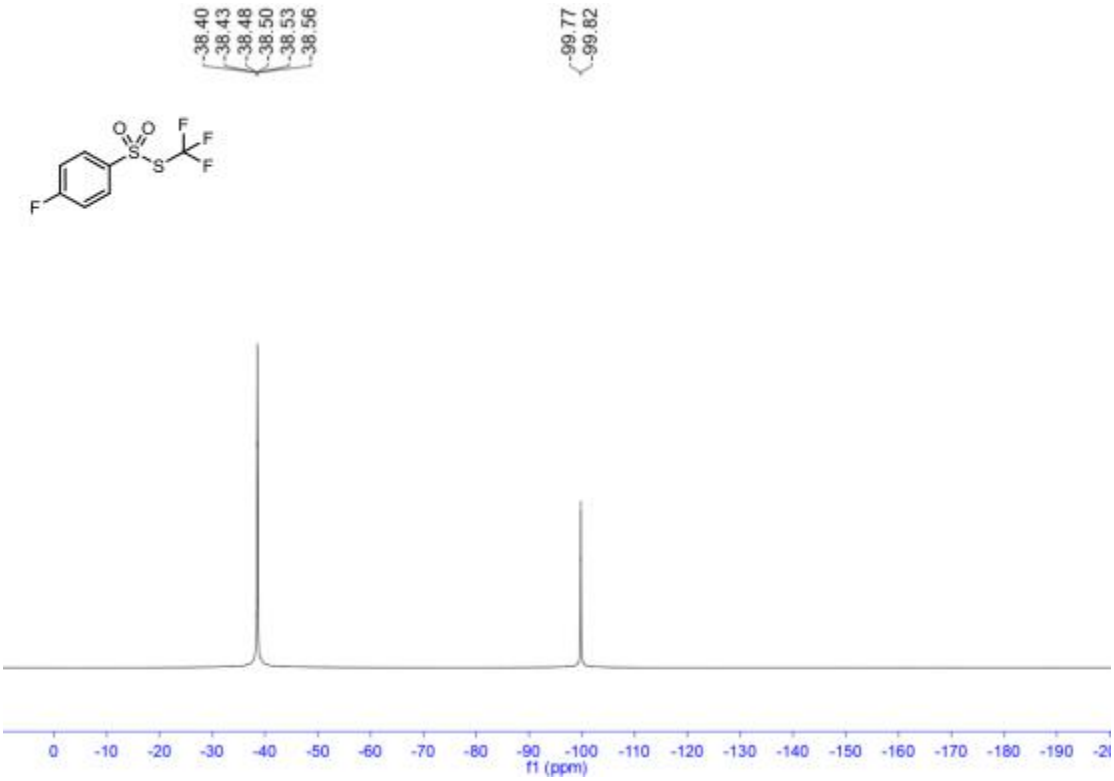
Supplementary Figure 55 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-fluorobenzenesulfonothioate **(26a)**



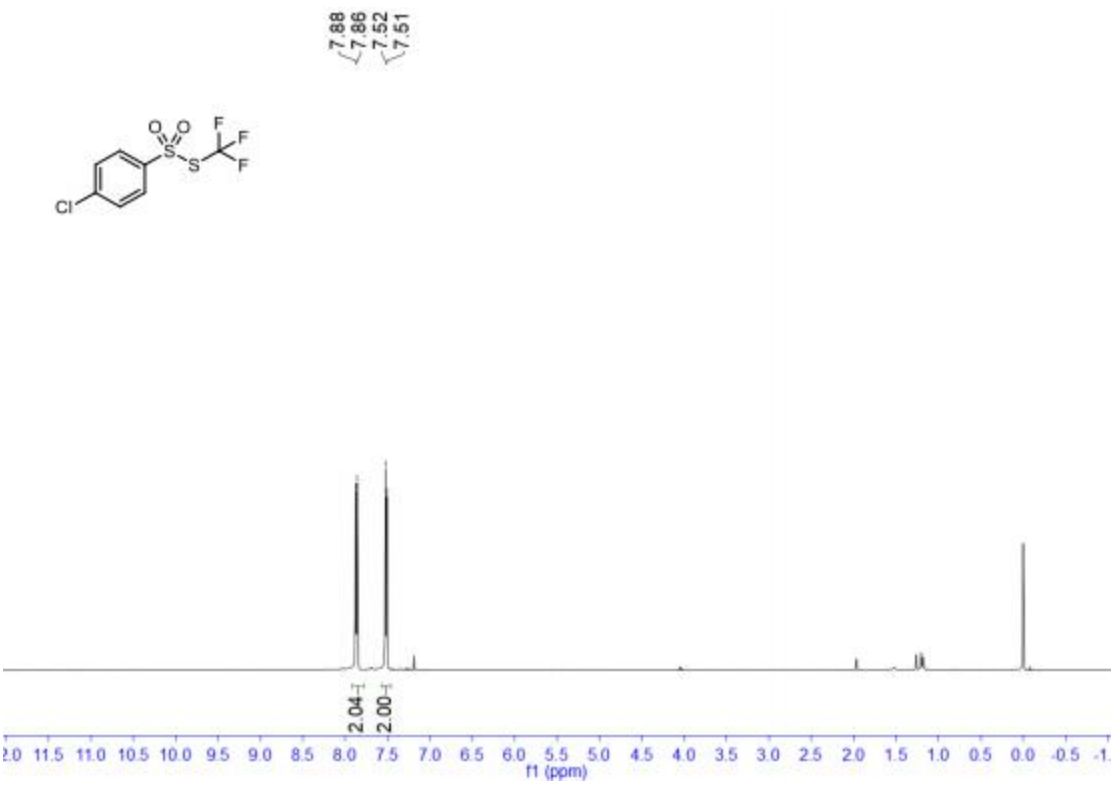
Supplementary Figure 56 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-fluorobenzenesulfonothioate **(26a)**



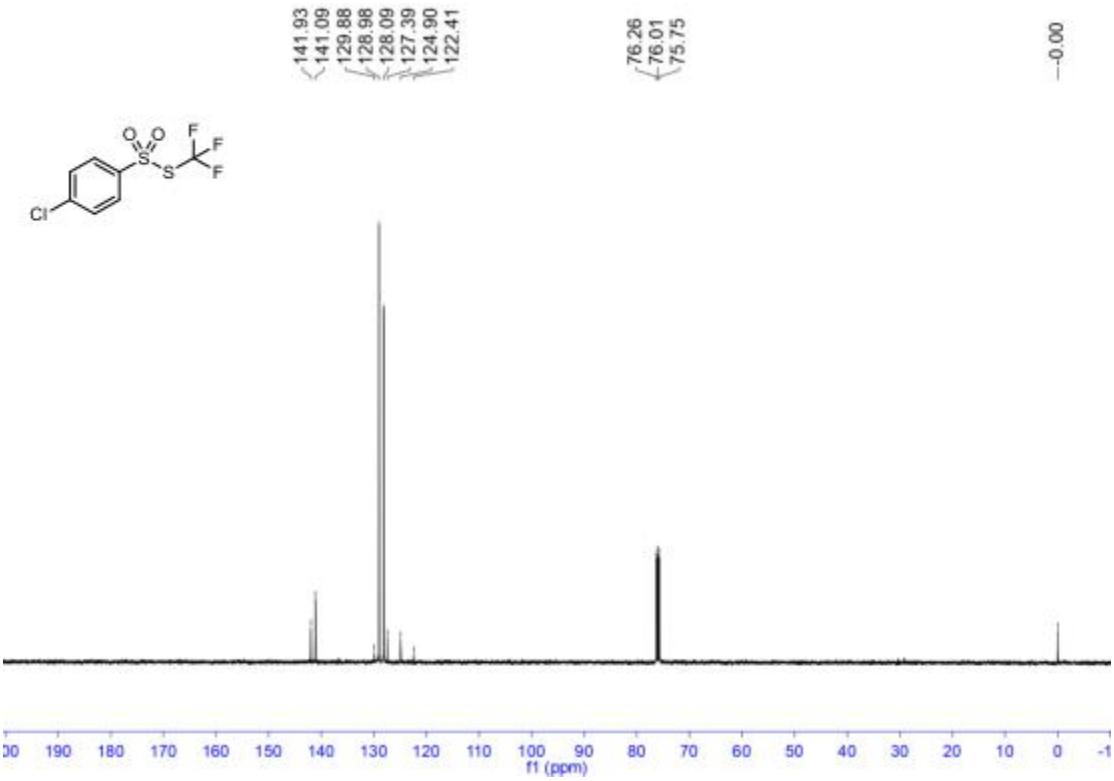
Supplementary Figure 57 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-fluorobenzenesulfonothioate **(26a)**



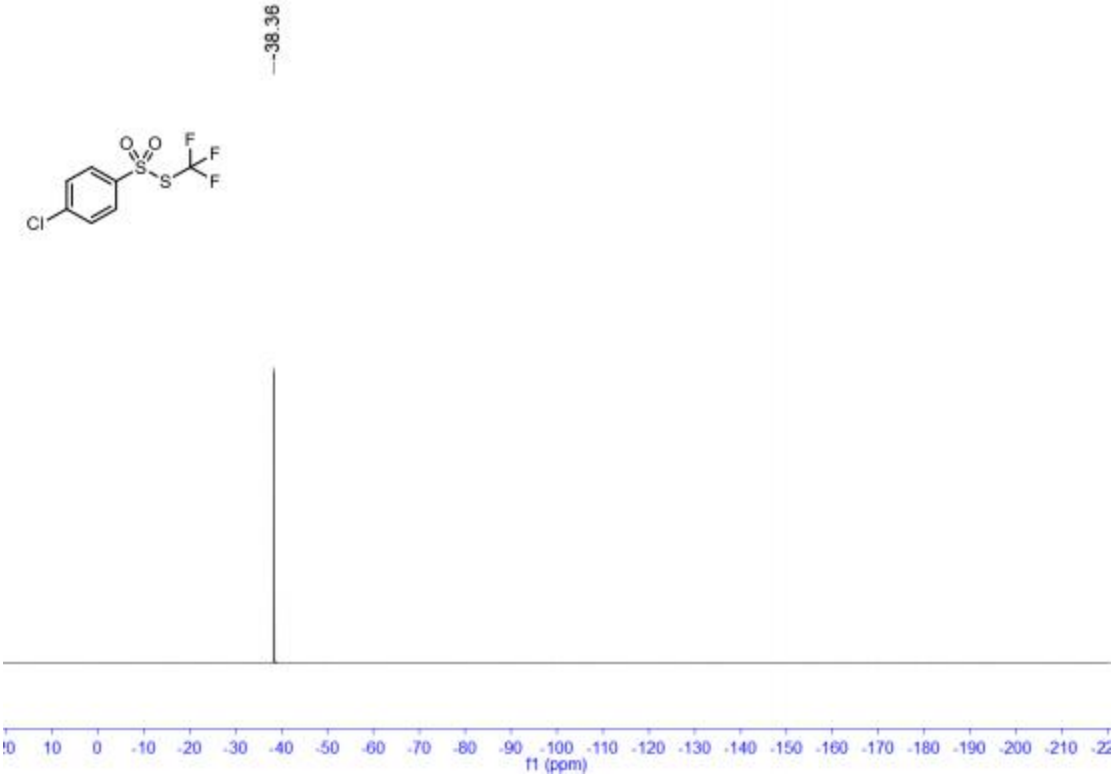
Supplementary Figure 58 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-chlorobenzenesulfonothioate **(27a)**



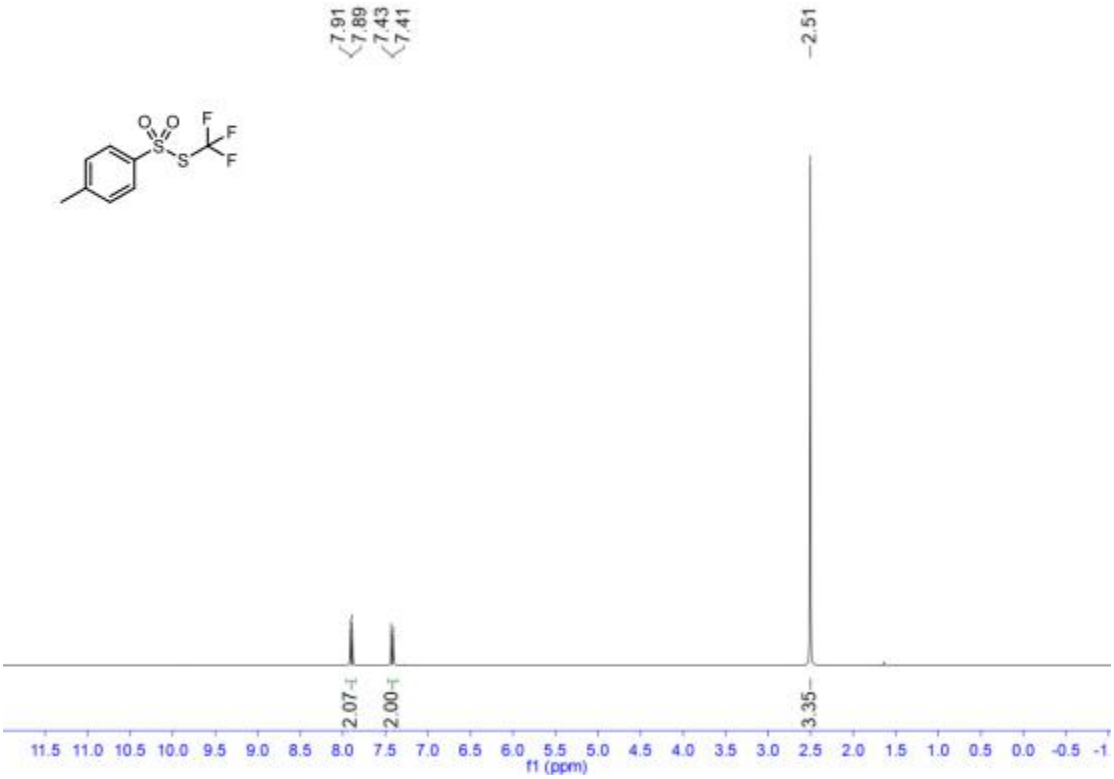
Supplementary Figure 59 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-chlorobenzenesulfonothioate **(27a)**



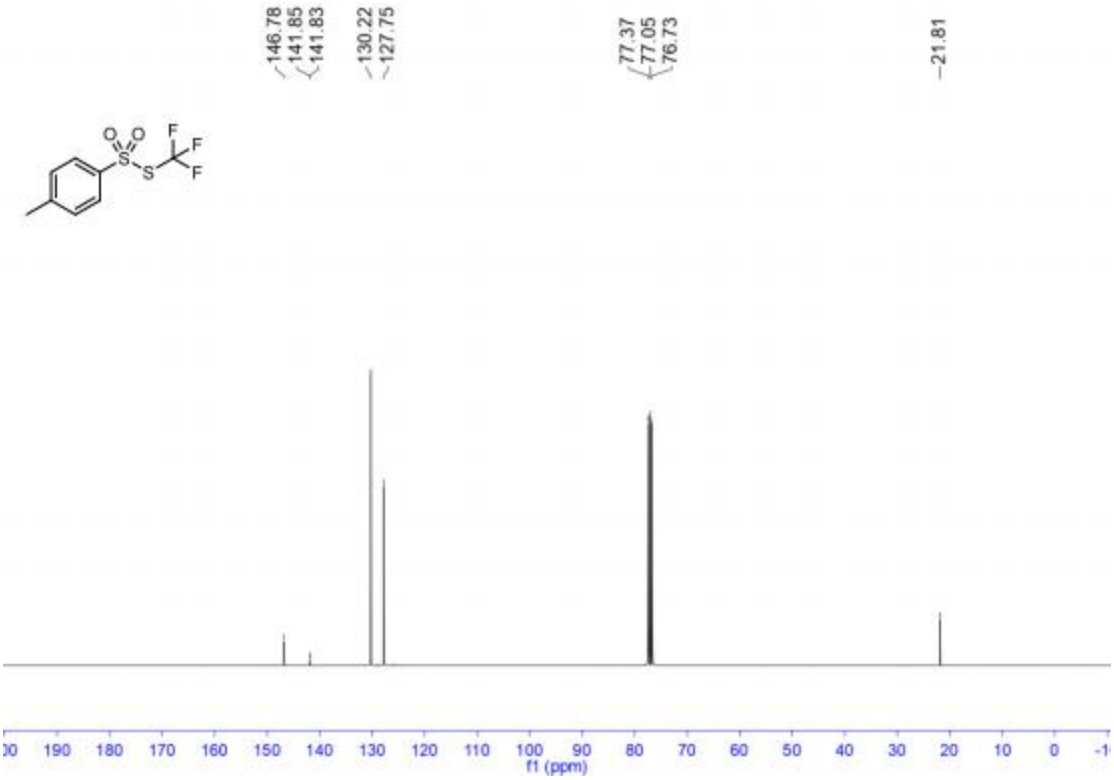
Supplementary Figure 60 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-chlorobenzenesulfonothioate **(27a)**



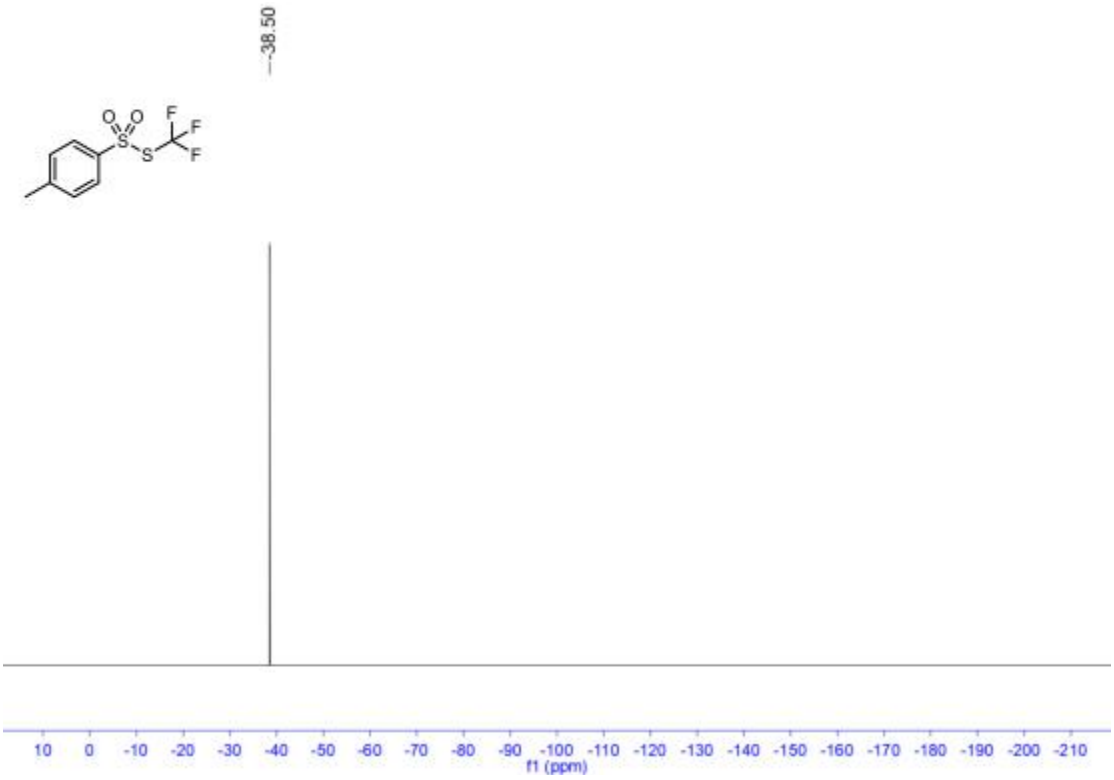
Supplementary Figure 61 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-methylbenzenesulfonothioate **(28a)**



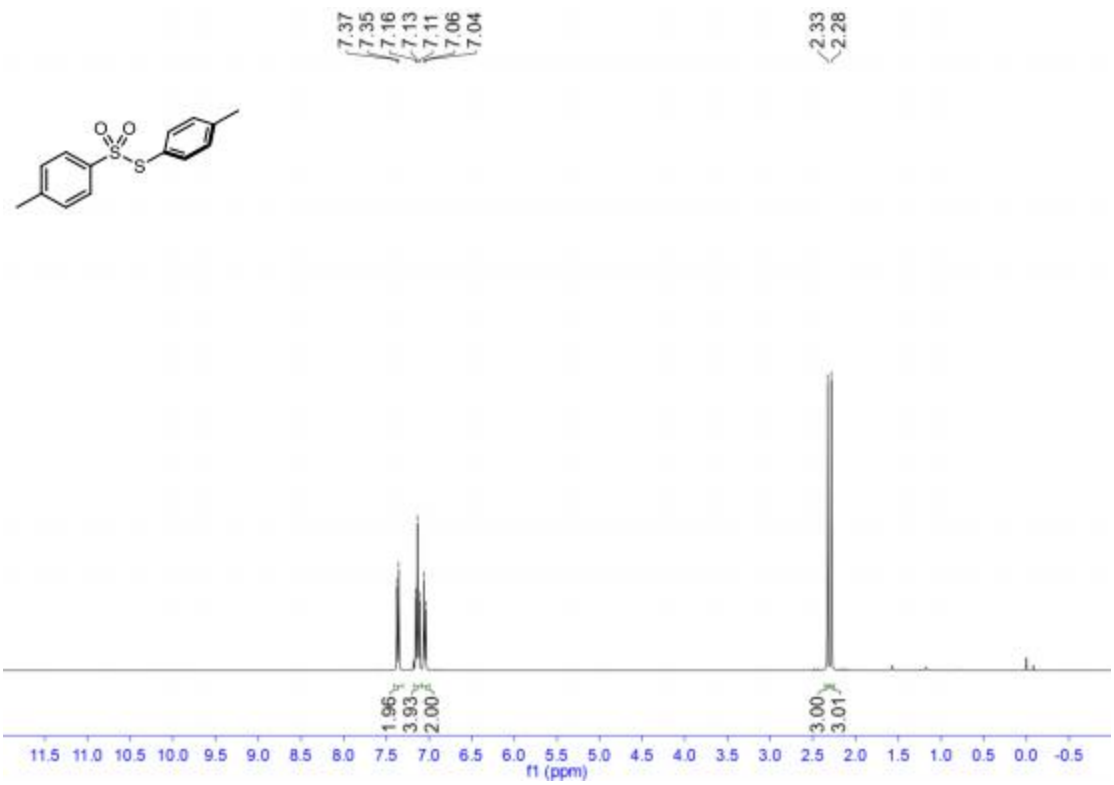
Supplementary Figure 61 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-methylbenzenesulfonothioate **(28a)**



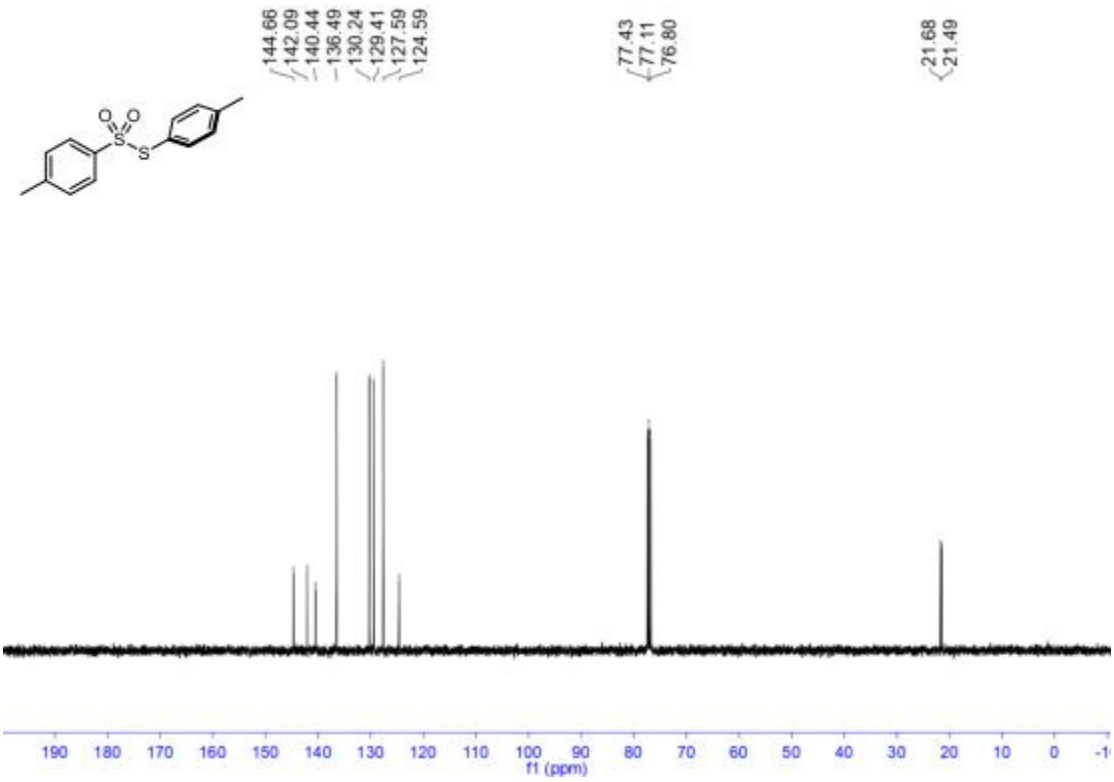
Supplementary Figure 63 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of *S*-(trifluoromethyl) 4-methylbenzenesulfonothioate **(28a)**



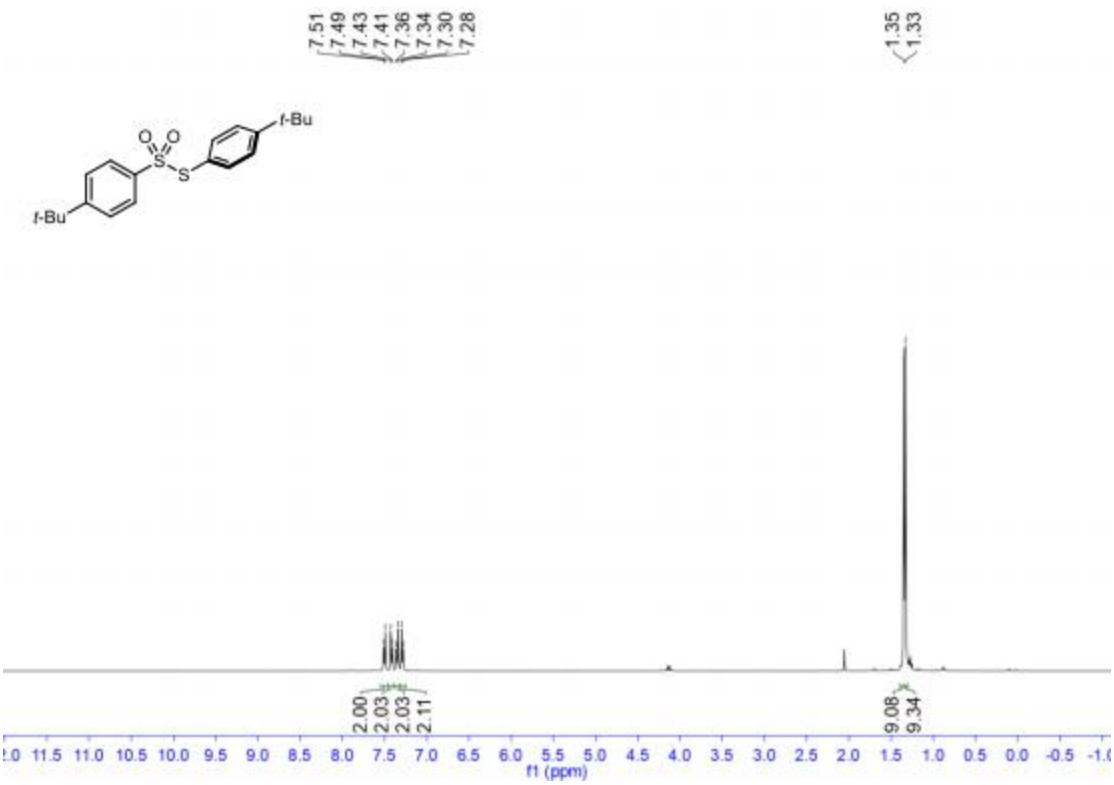
Supplementary Figure 64 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate **(29a)**



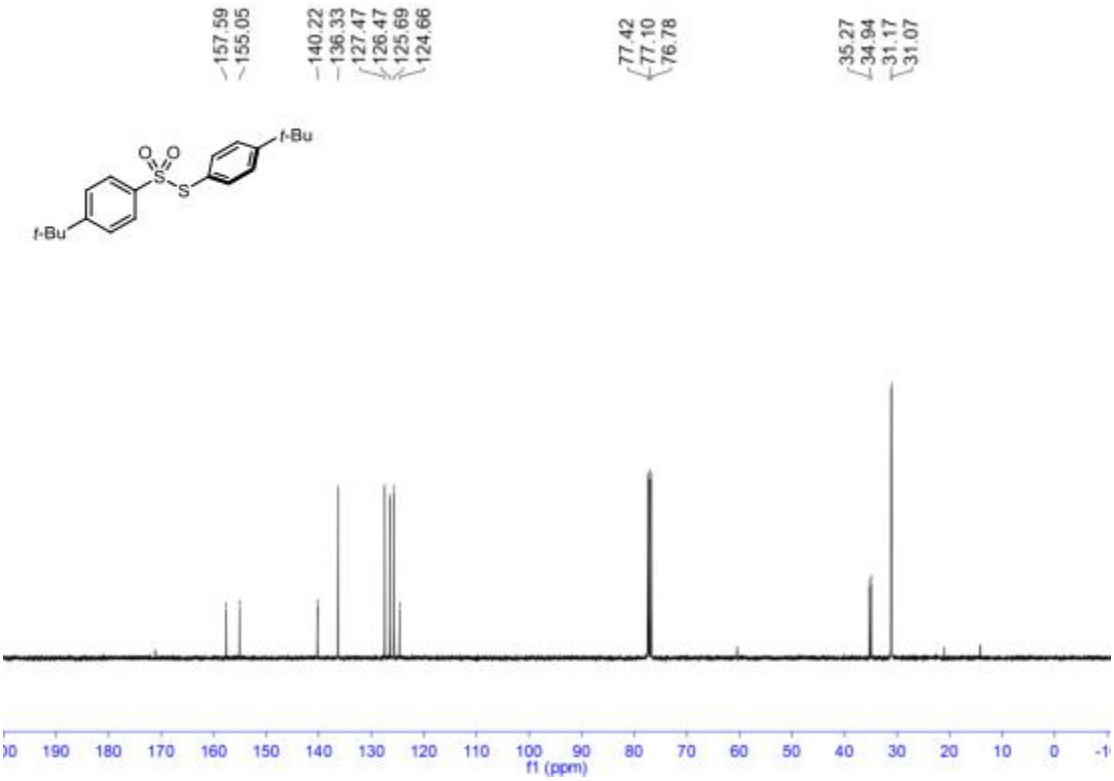
Supplementary Figure 65 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate **(29a)**



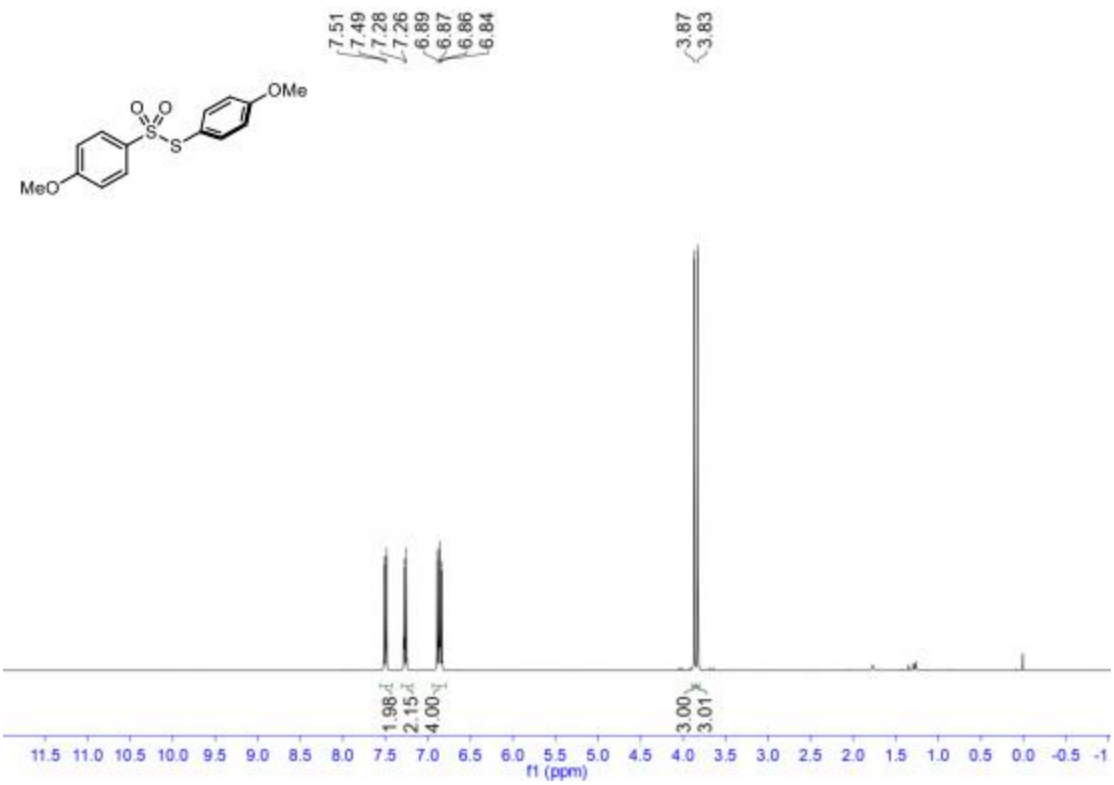
Supplementary Figure 66 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(4-(*tert*-butyl)phenyl) 4-(*tert*-butyl)benzenesulfonothioate **(30a)**



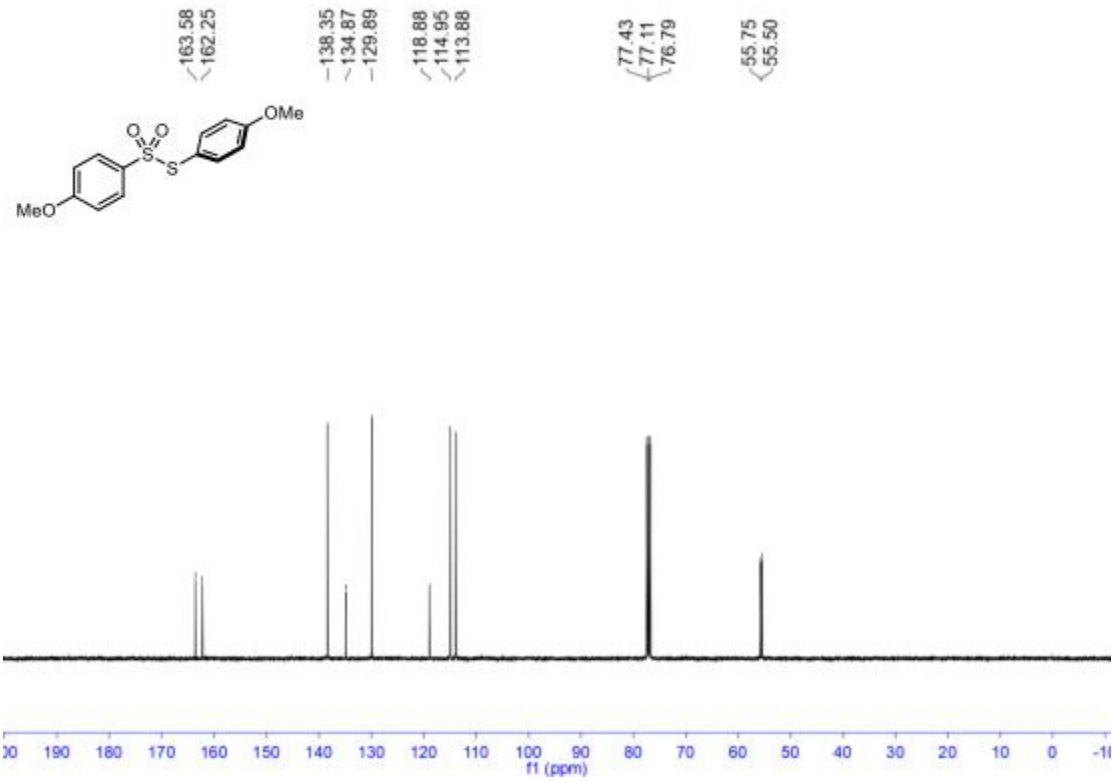
Supplementary Figure 67 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(4-(*tert*-butyl)phenyl) 4-(*tert*-butyl)benzenesulfonothioate **(30a)**



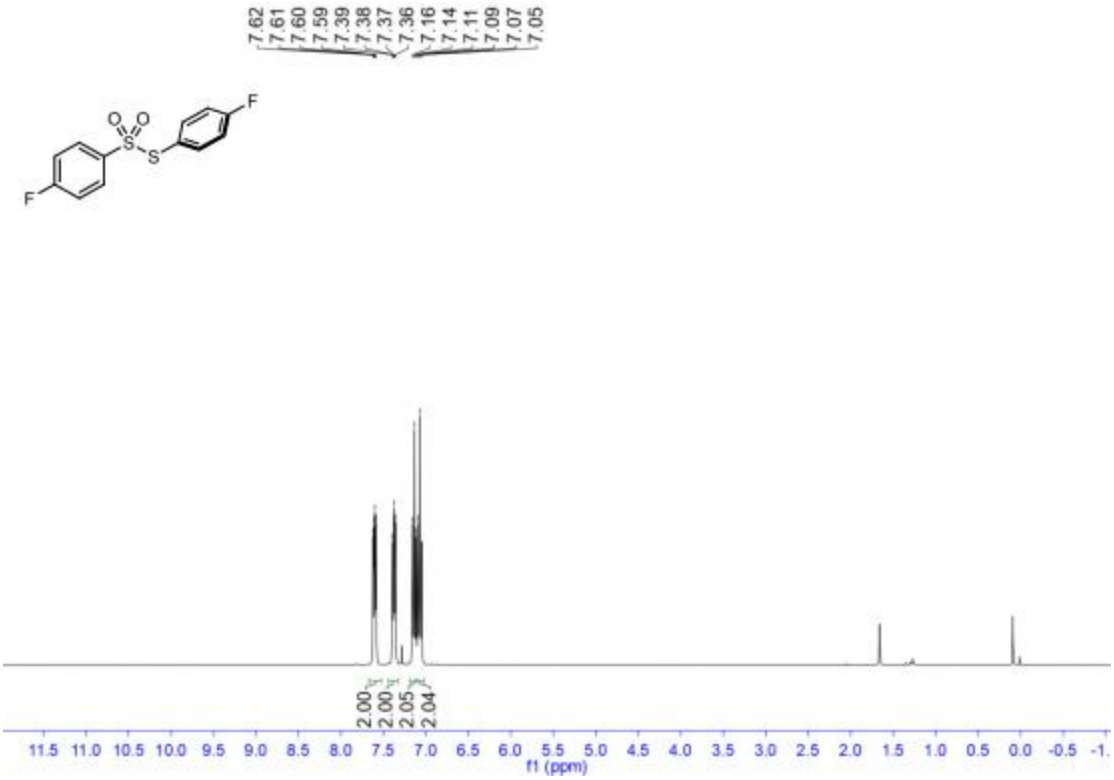
Supplementary Figure 68 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate **(31a)**



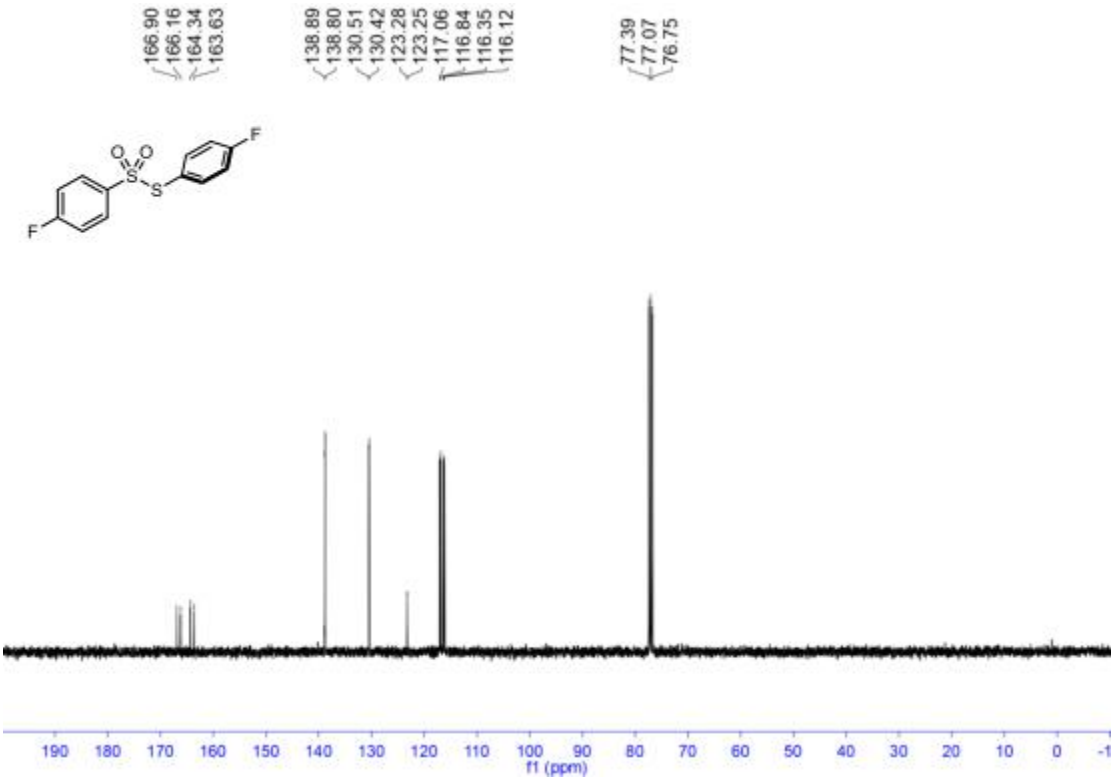
Supplementary Figure 69 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate **(31a)**



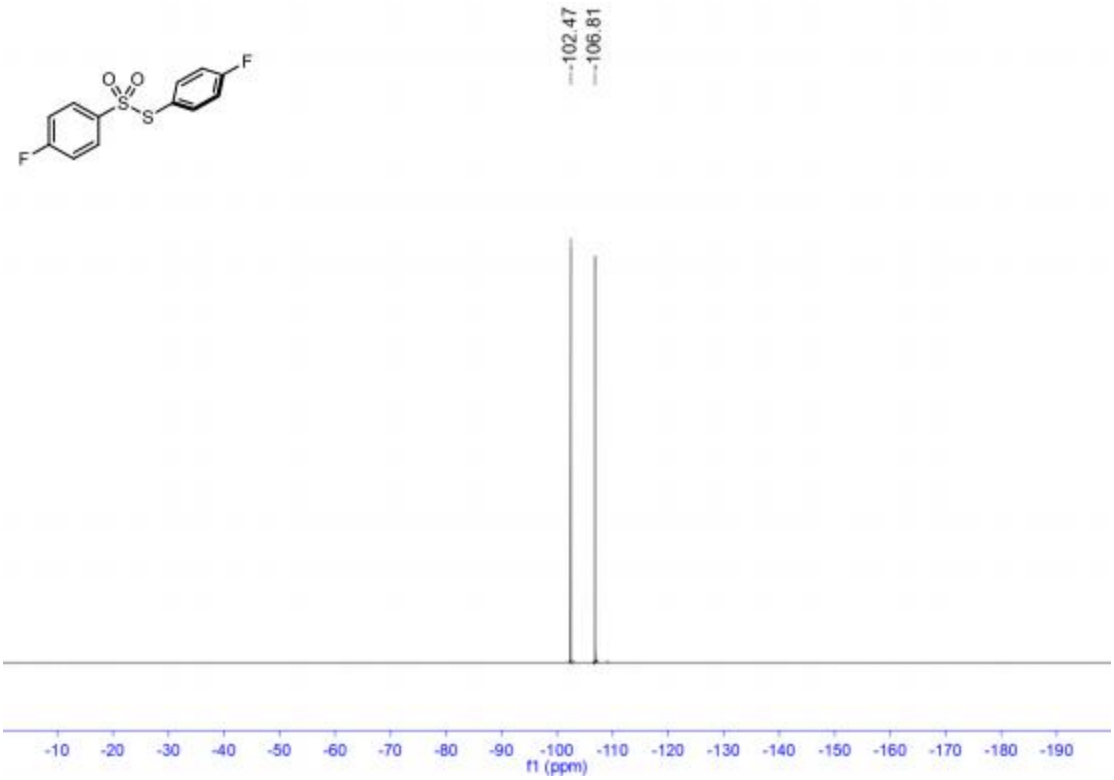
Supplementary Figure 70 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(4-fluorophenyl) 4-fluorobenzenesulfonothioate **(32a)**



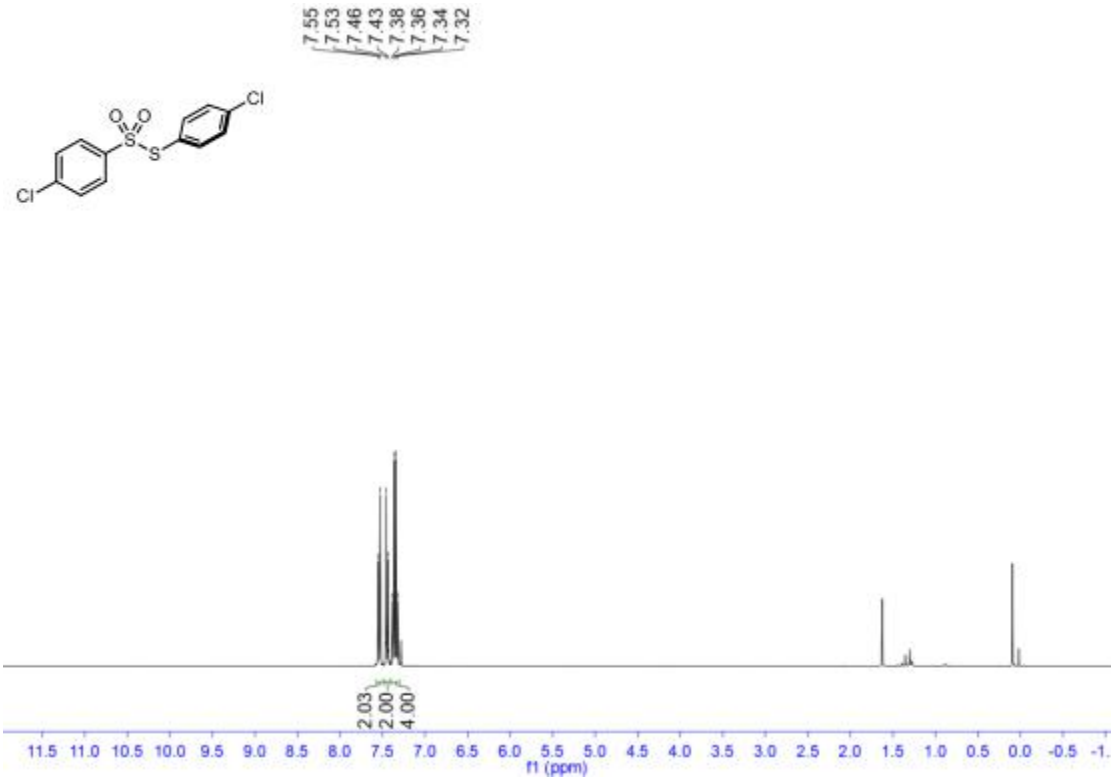
Supplementary Figure 71 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(4-fluorophenyl) 4-fluorobenzenesulfonothioate **(32a)**



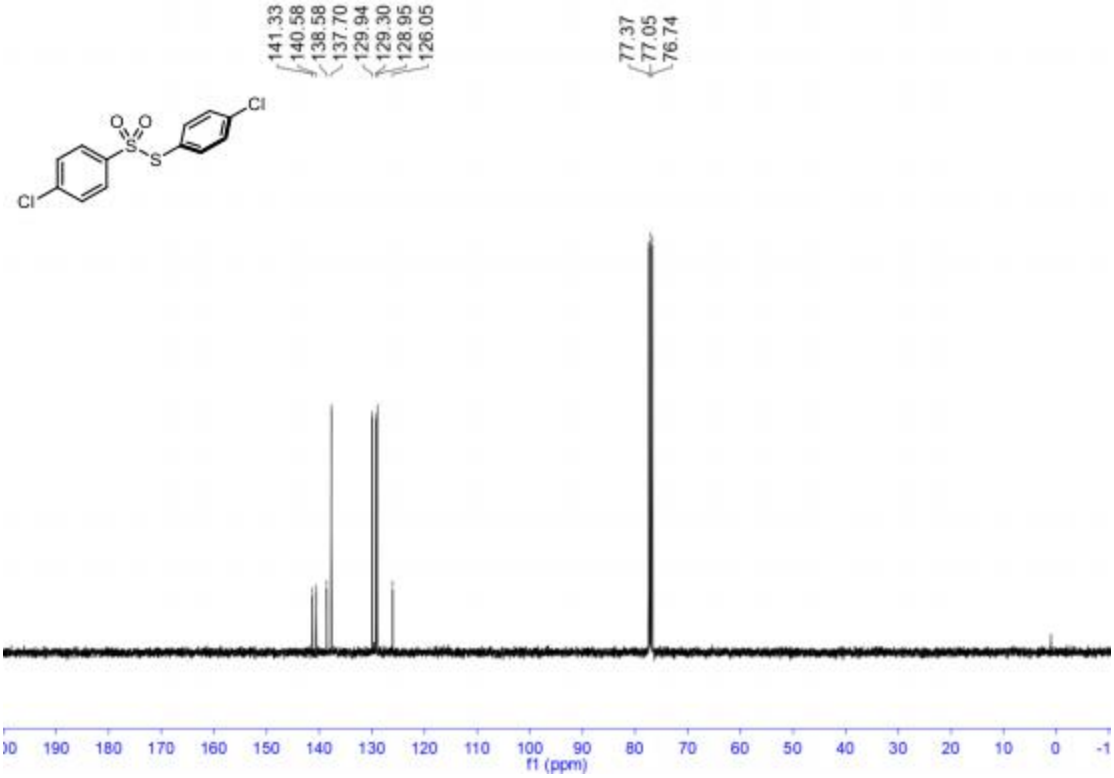
Supplementary Figure 72 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of *S*-(4-fluorophenyl) 4-fluorobenzenesulfonothioate **(32a)**



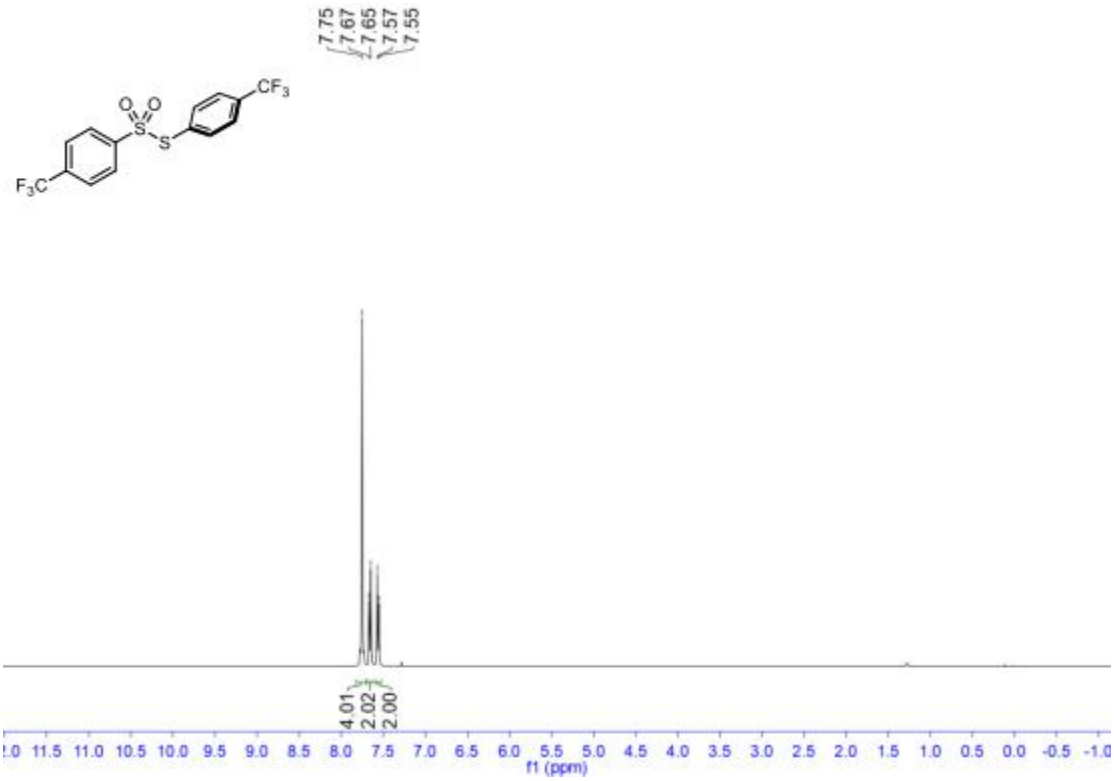
Supplementary Figure 73 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(4-chlorophenyl) 4-chlorobenzenesulfonothioate **(33a)**



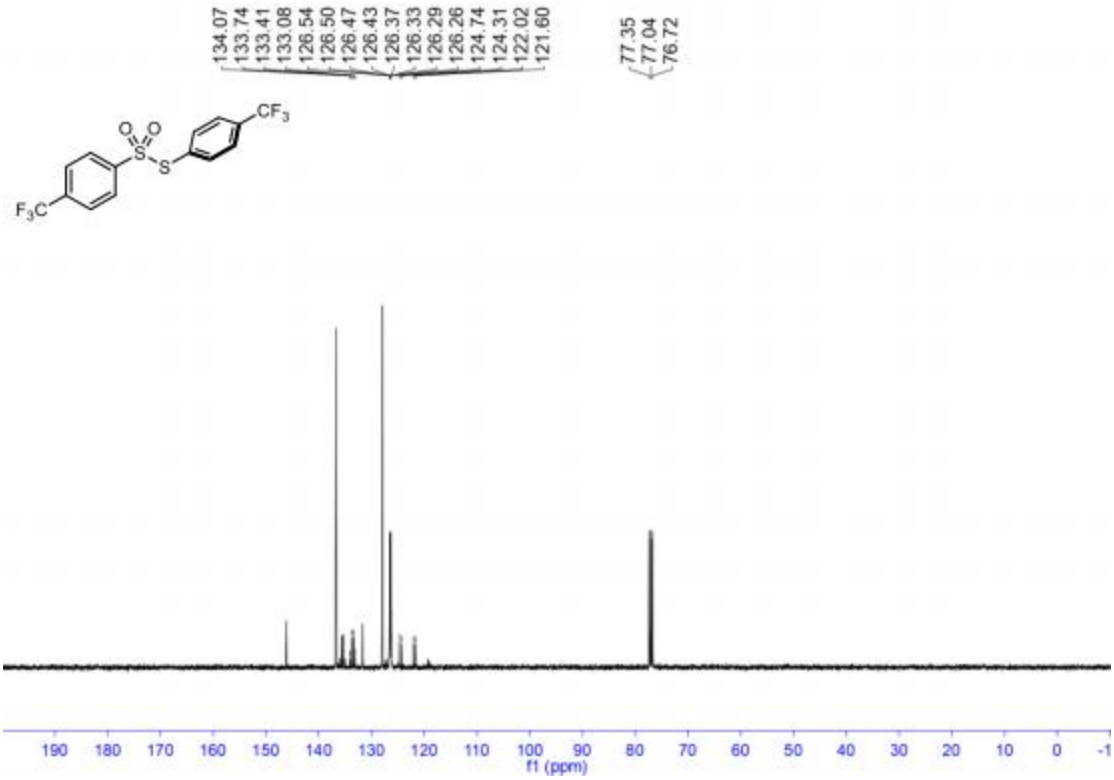
Supplementary Figure 74 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(4-chlorophenyl) 4-chlorobenzenesulfonothioate **(33a)**



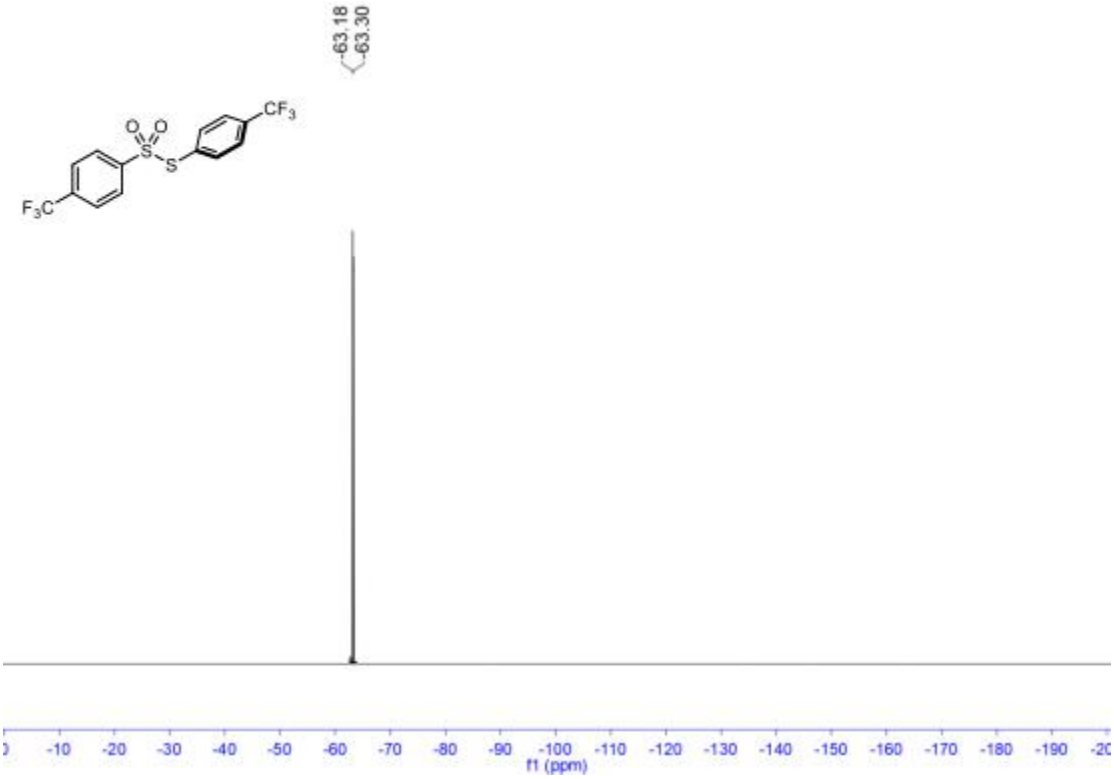
Supplementary Figure 75 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(4-(trifluoromethyl)phenyl) 4-(trifluoromethyl)benzenesulfonothioate **(34a)**



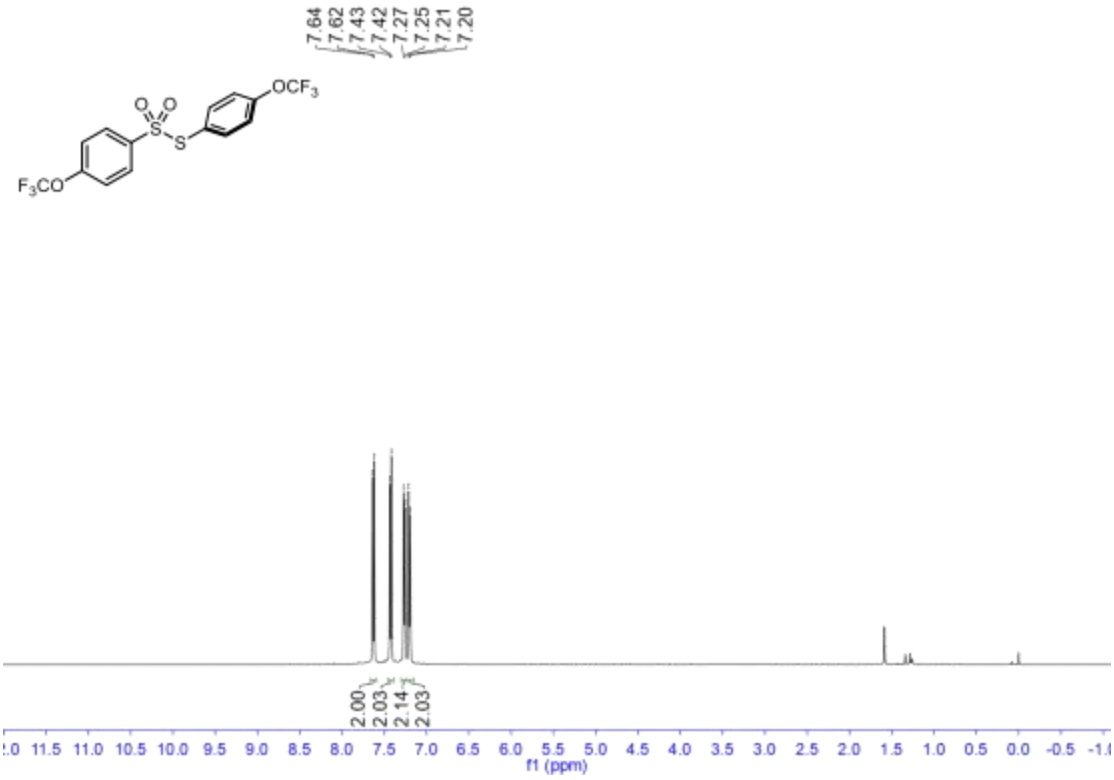
Supplementary Figure 76 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(4-(trifluoromethyl)phenyl) 4-(trifluoromethyl)benzenesulfonothioate **(34a)**



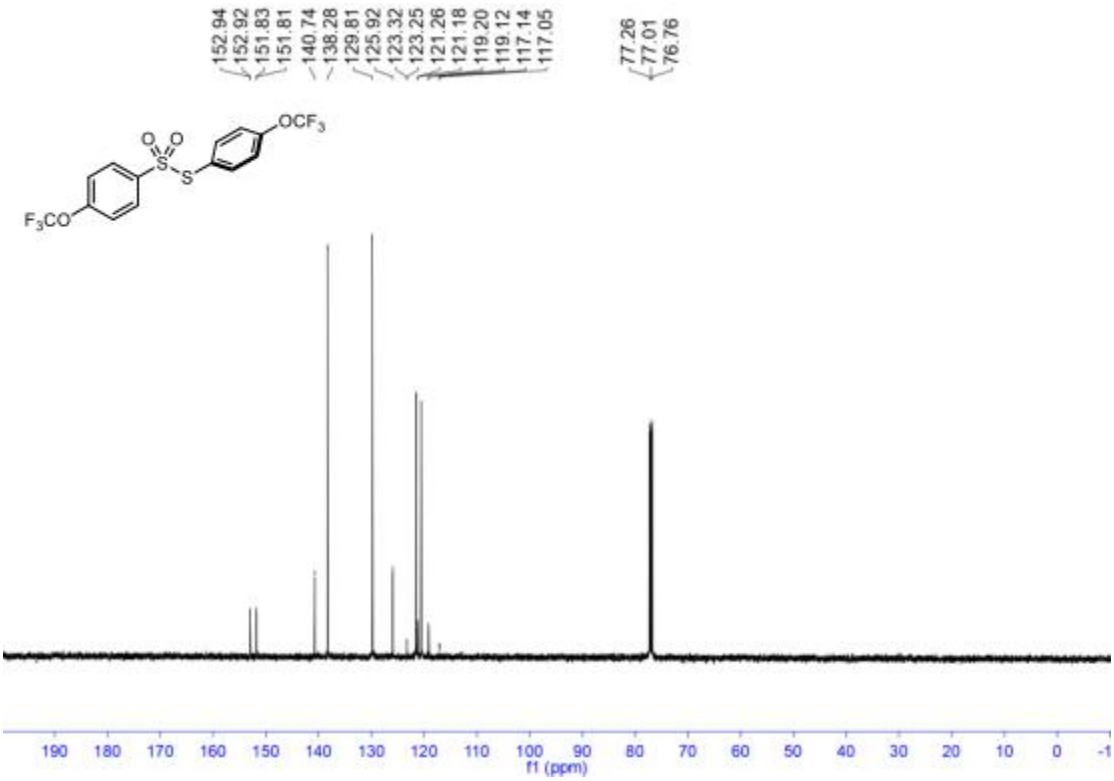
Supplementary Figure 77 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of *S*-(4-(trifluoromethyl)phenyl) 4-(trifluoromethyl)benzenesulfonothioate **(34a)**



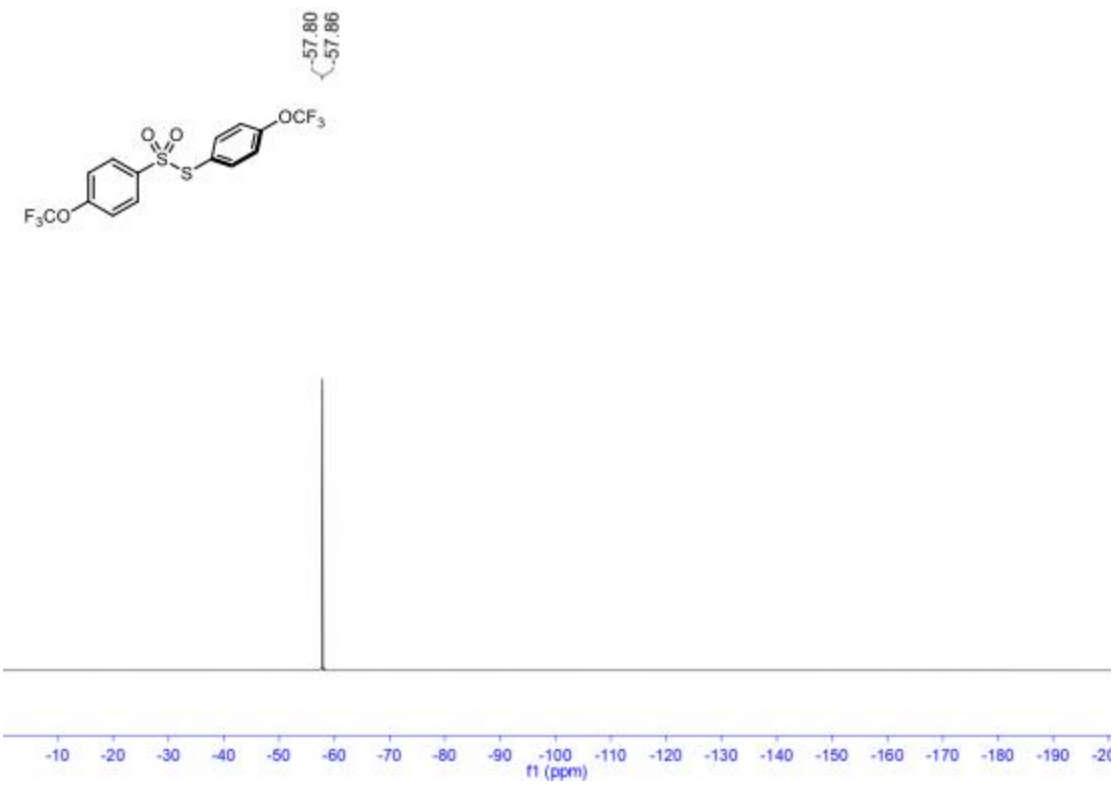
Supplementary Figure 78 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *S*-(4-(trifluoromethoxy)phenyl) 4-(trifluoromethoxy)benzenesulfonothioate **(35a)**



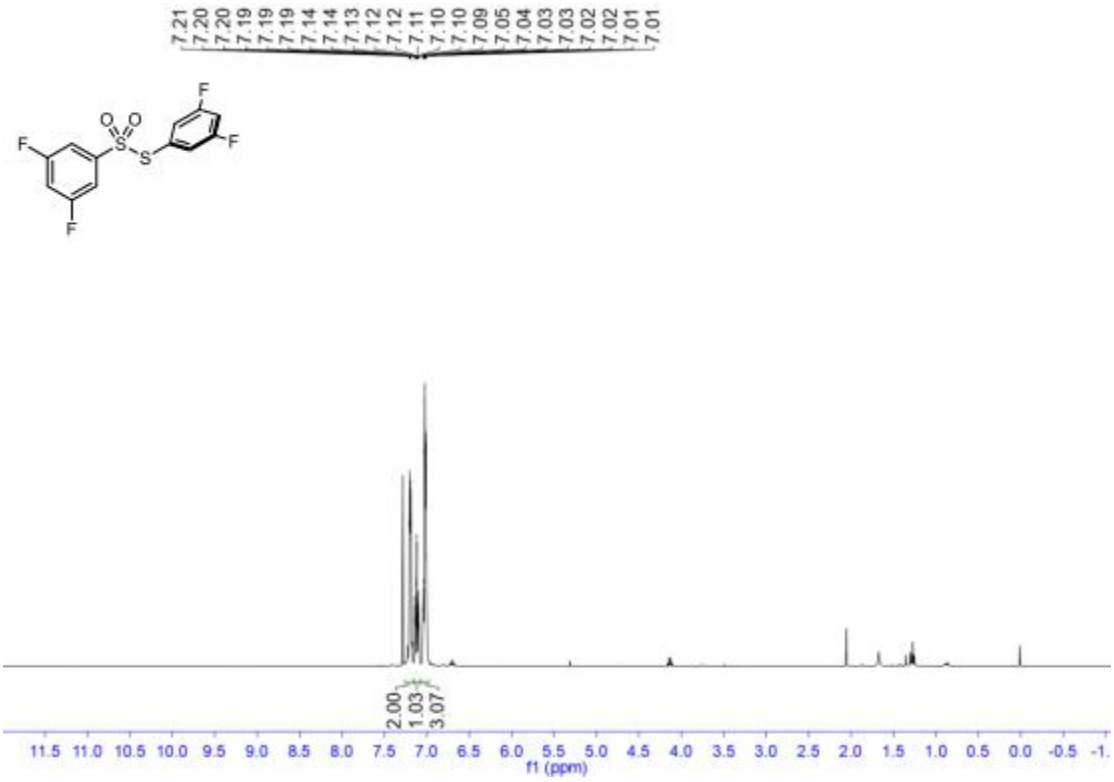
Supplementary Figure 79 | ^{13}C NMR (126MHz, 298K, Chloroform-*d*) of *S*-(4-(trifluoromethoxy)phenyl) 4-(trifluoromethoxy)benzenesulfonothioate **(35a)**



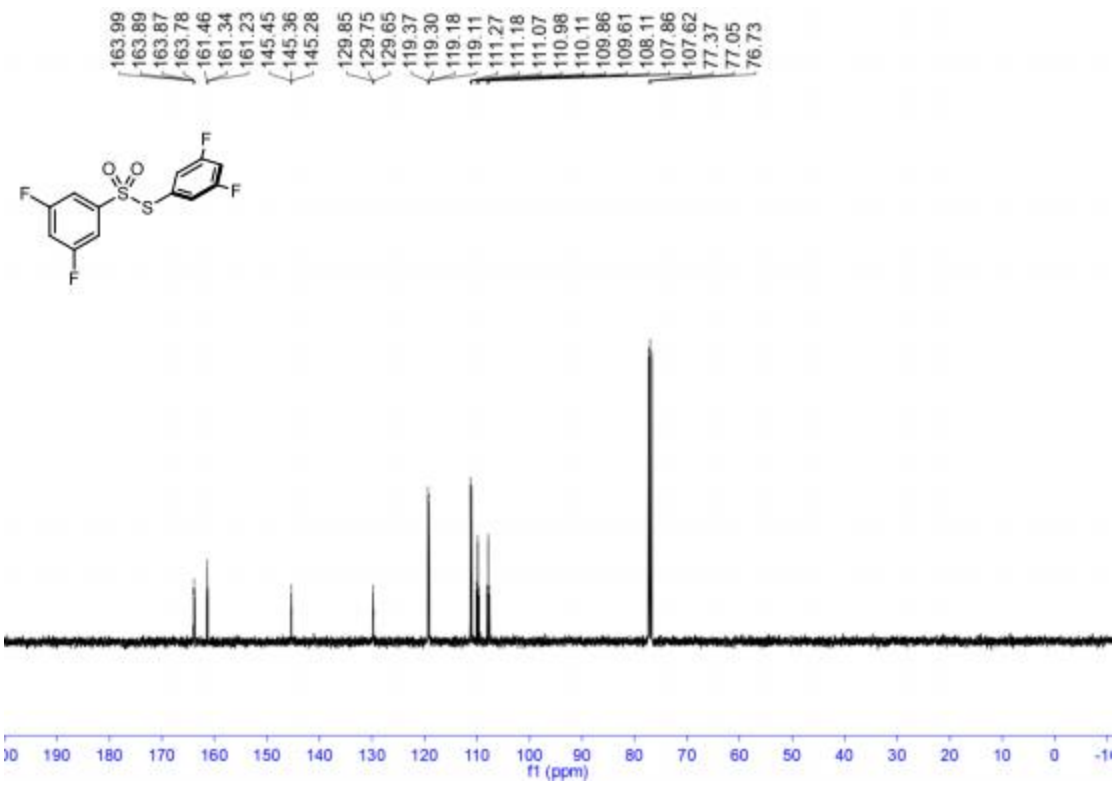
Supplementary Figure 80 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of *S*-(4-(trifluoromethoxy)phenyl) 4-(trifluoromethoxy)benzenesulfonothioate **(35a)**



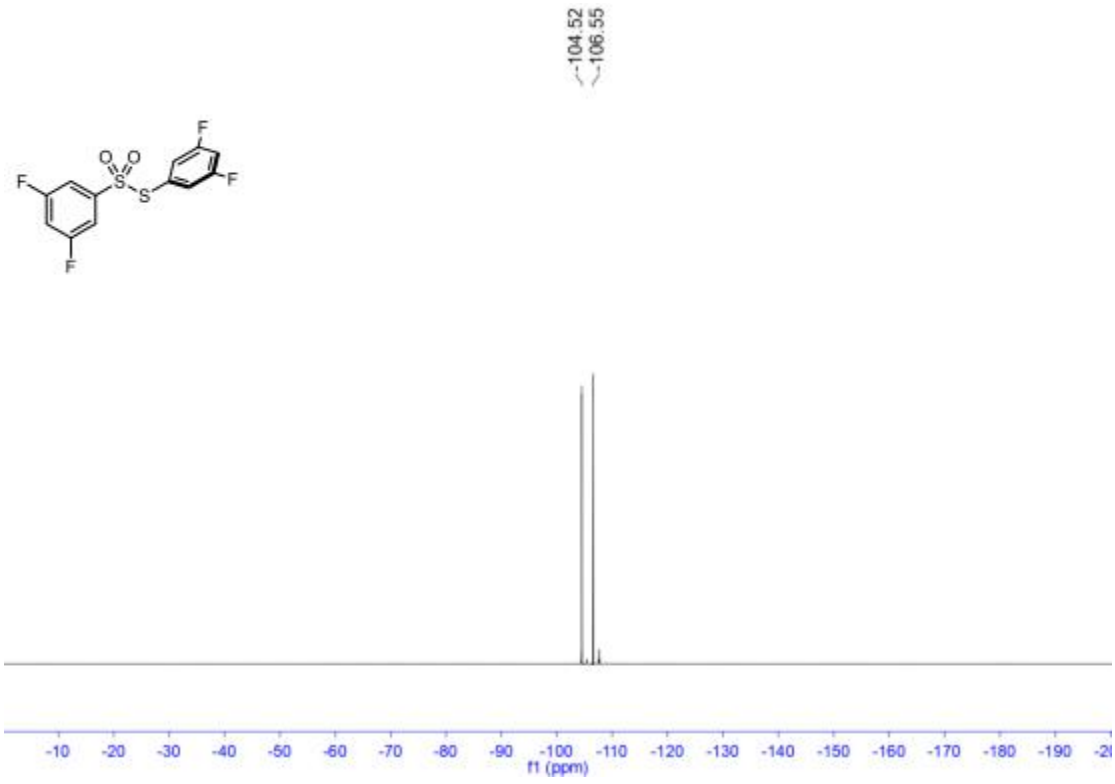
Supplementary Figure 81 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(3,5-difluorophenyl) 3,5-difluorobenzenesulfonothioate **(36a)**



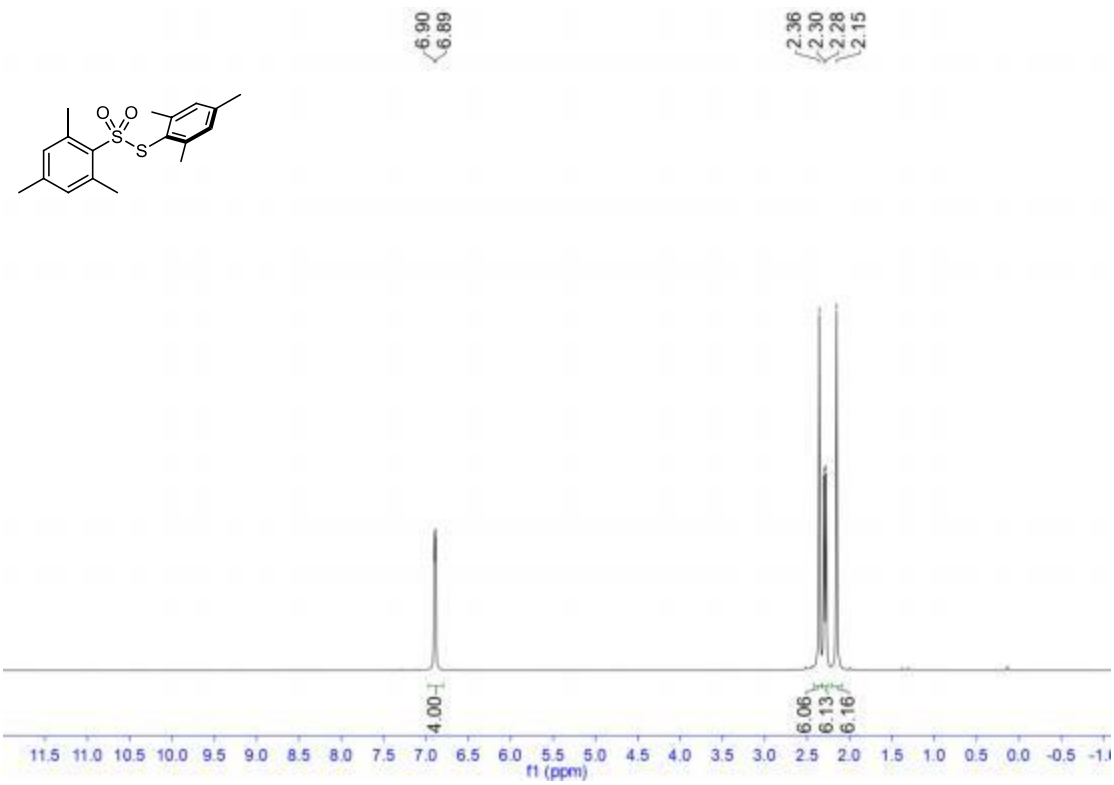
Supplementary Figure 82 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(3,5-difluorophenyl) 3,5-difluorobenzenesulfonothioate **(36a)**



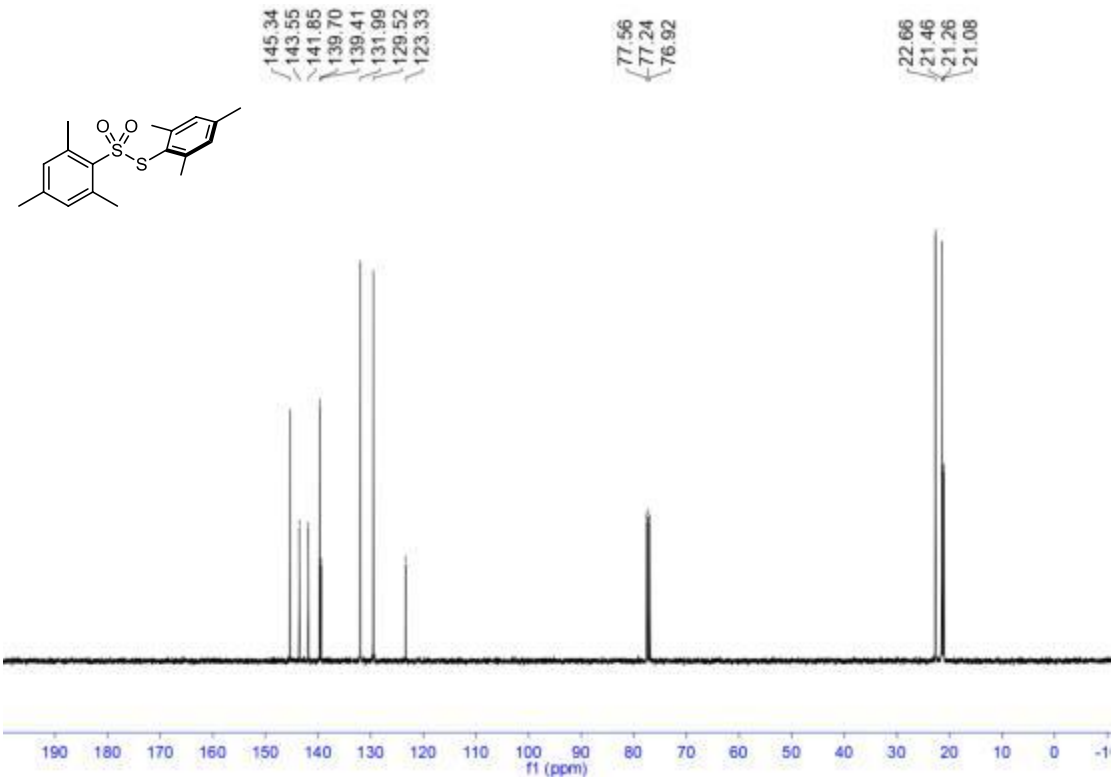
Supplementary Figure 83 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of *S*-(3,5-difluorophenyl) 3,5-difluorobenzenesulfonothioate **(36a)**



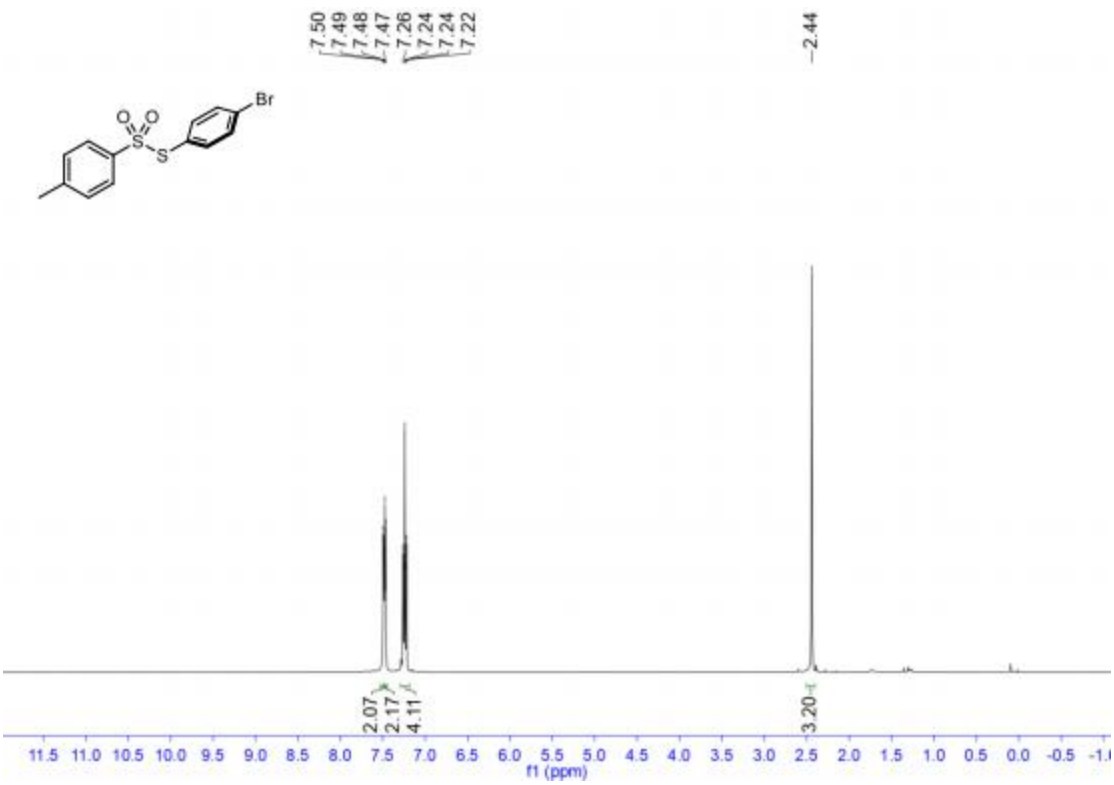
Supplementary Figure 84 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-mesityl 2,4,6-trimethylbenzenesulfonothioate **(37a)**



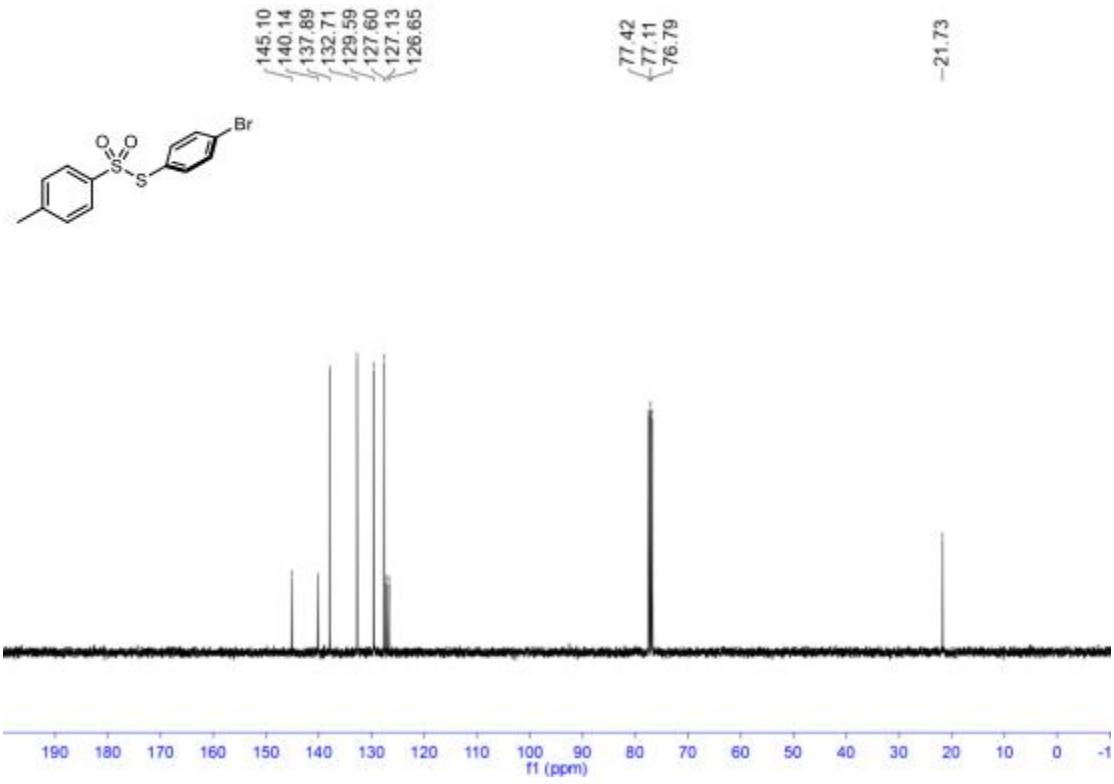
Supplementary Figure 85 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-mesityl 2,4,6-trimethylbenzenesulfonothioate **(37a)**



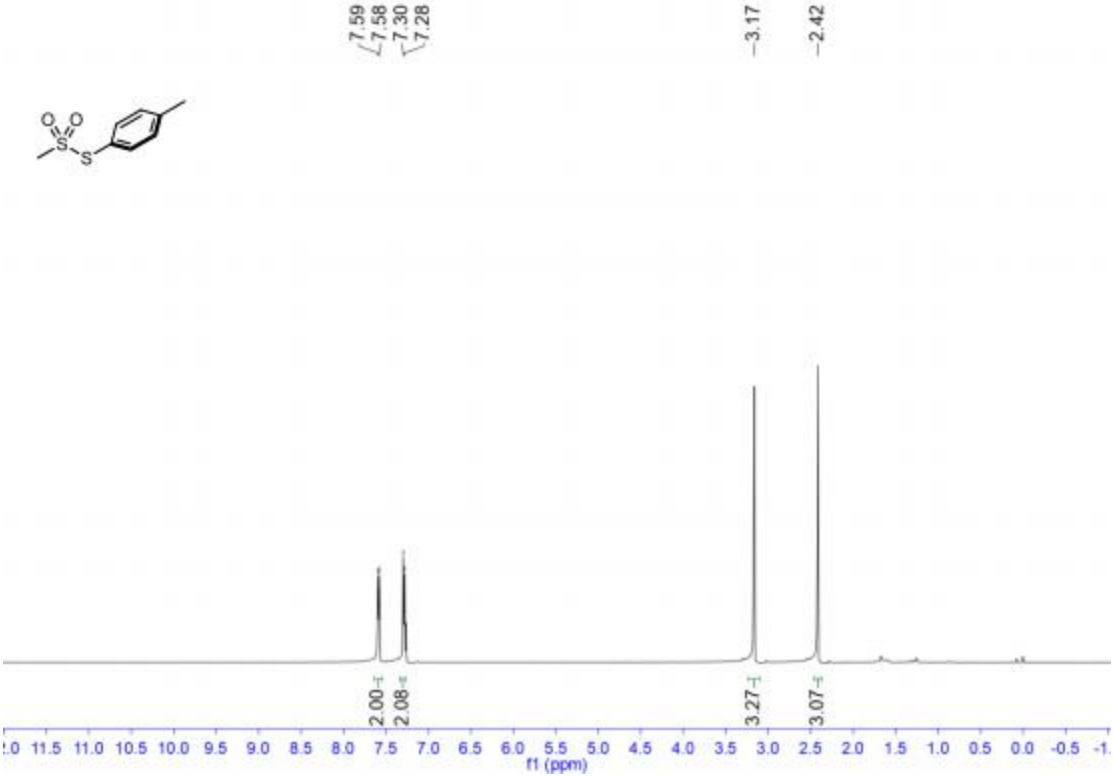
Supplementary Figure 86 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *S*-(4-bromophenyl) 4-methylbenzenesulfonothioate **(38a)**



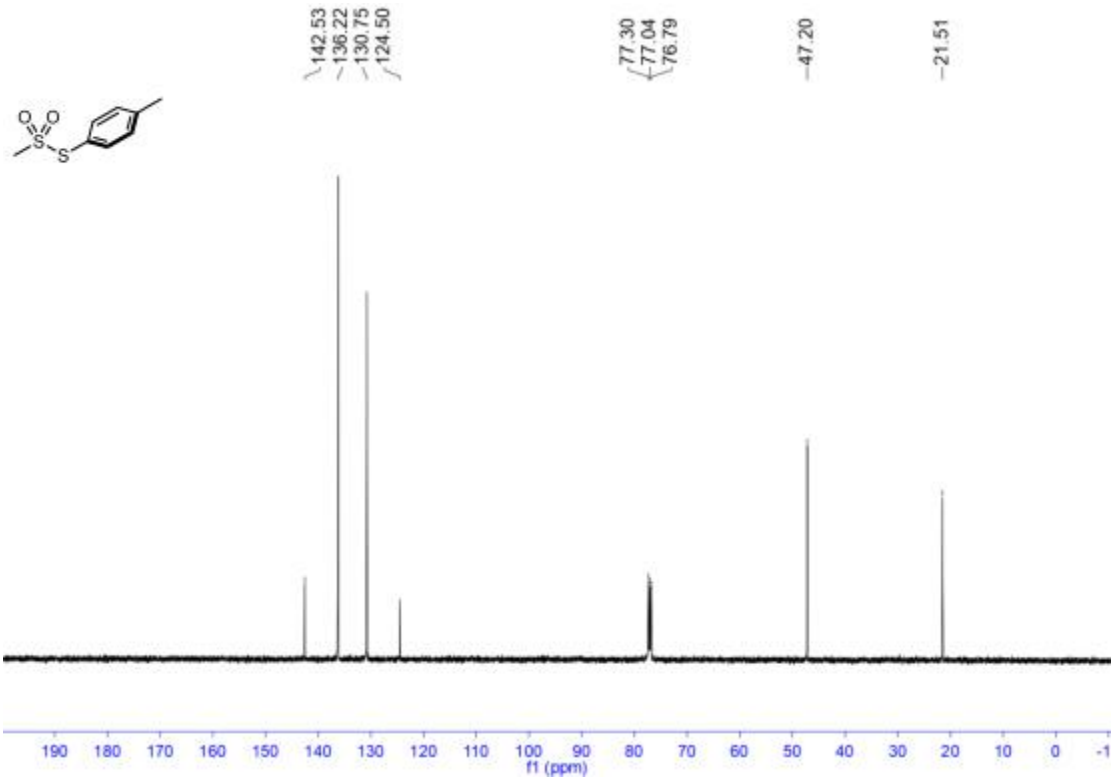
Supplementary Figure 87 | ^{13}C NMR (101MHz, 298K, Chloroform-*d*) of *S*-(4-bromophenyl) 4-methylbenzenesulfonothioate **(38a)**



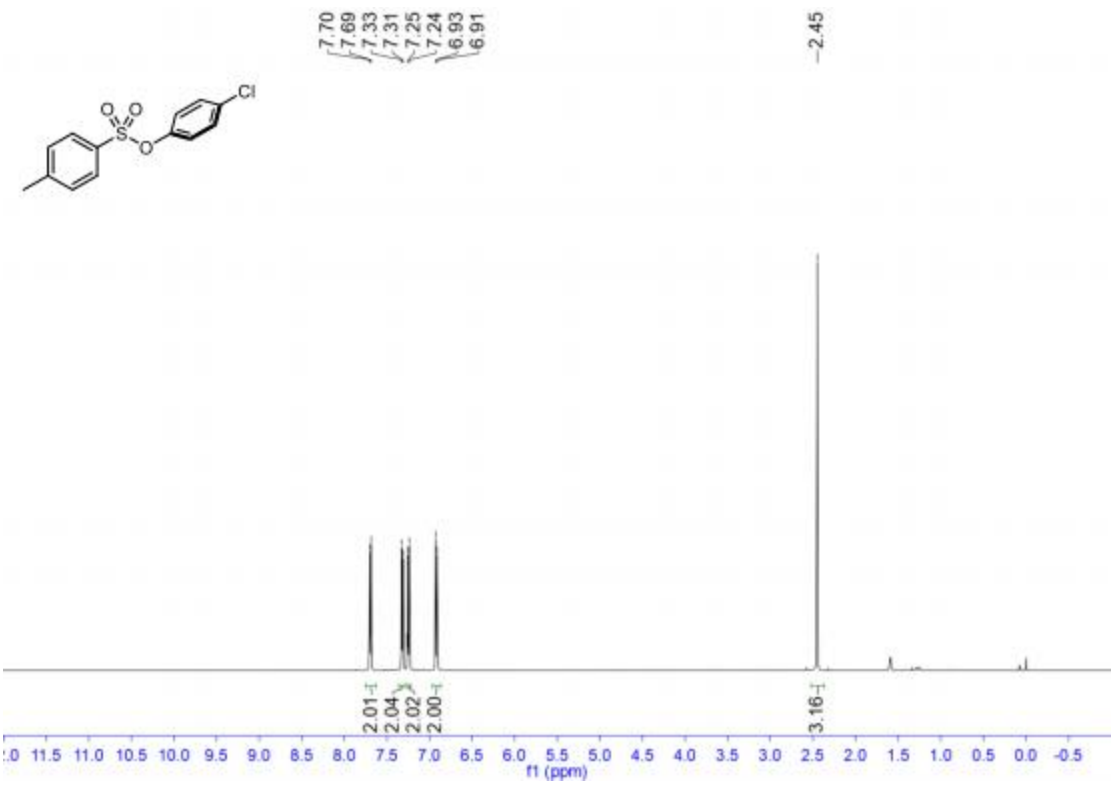
Supplementary Figure 88 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *S*-*p*-tolyl methanesulfonothioate **(39a)**



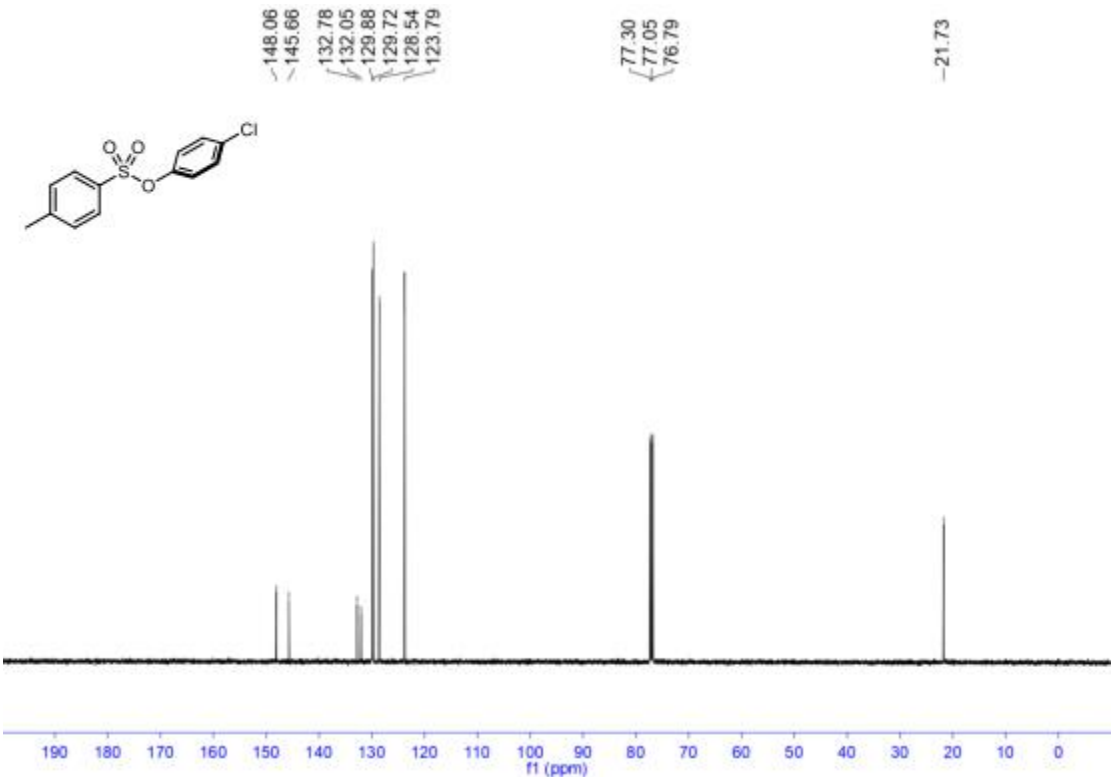
Supplementary Figure 89 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of *S*-*p*-tolyl methanesulfonothioate **(39a)**



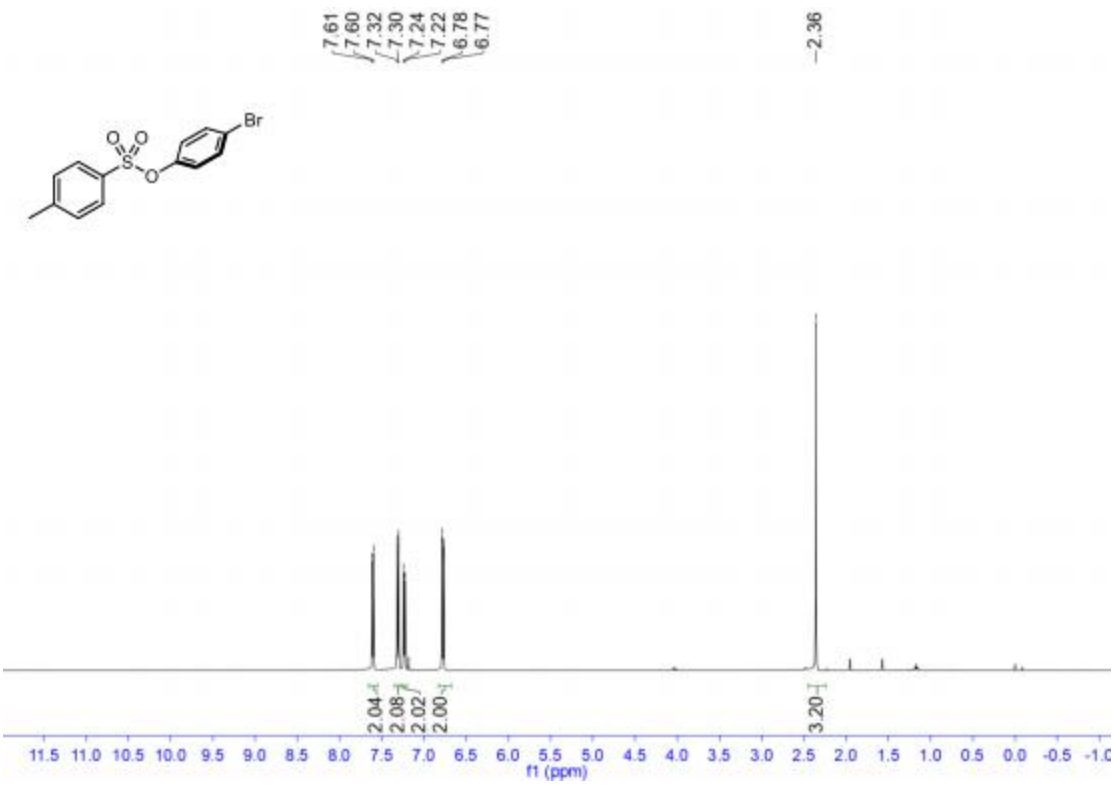
Supplementary Figure 90 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 4-chlorophenyl 4-methylbenzenesulfonate **(42a)**



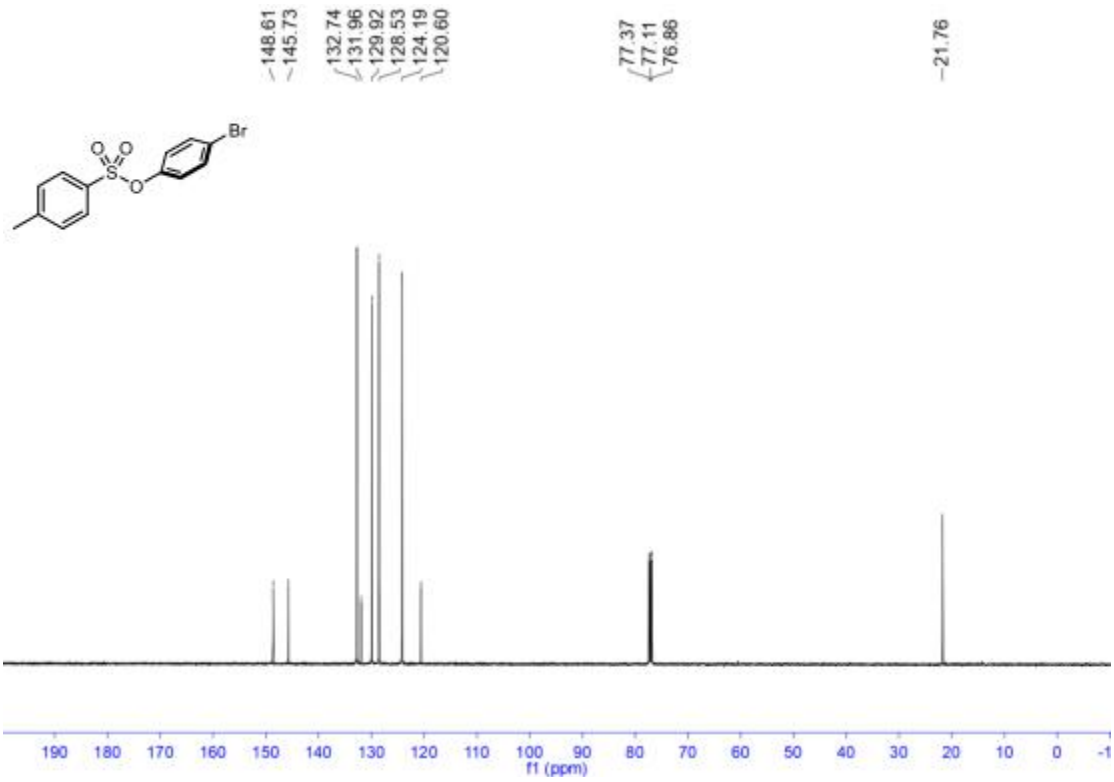
Supplementary Figure 91 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 4-chlorophenyl 4-methylbenzenesulfonate **(42a)**



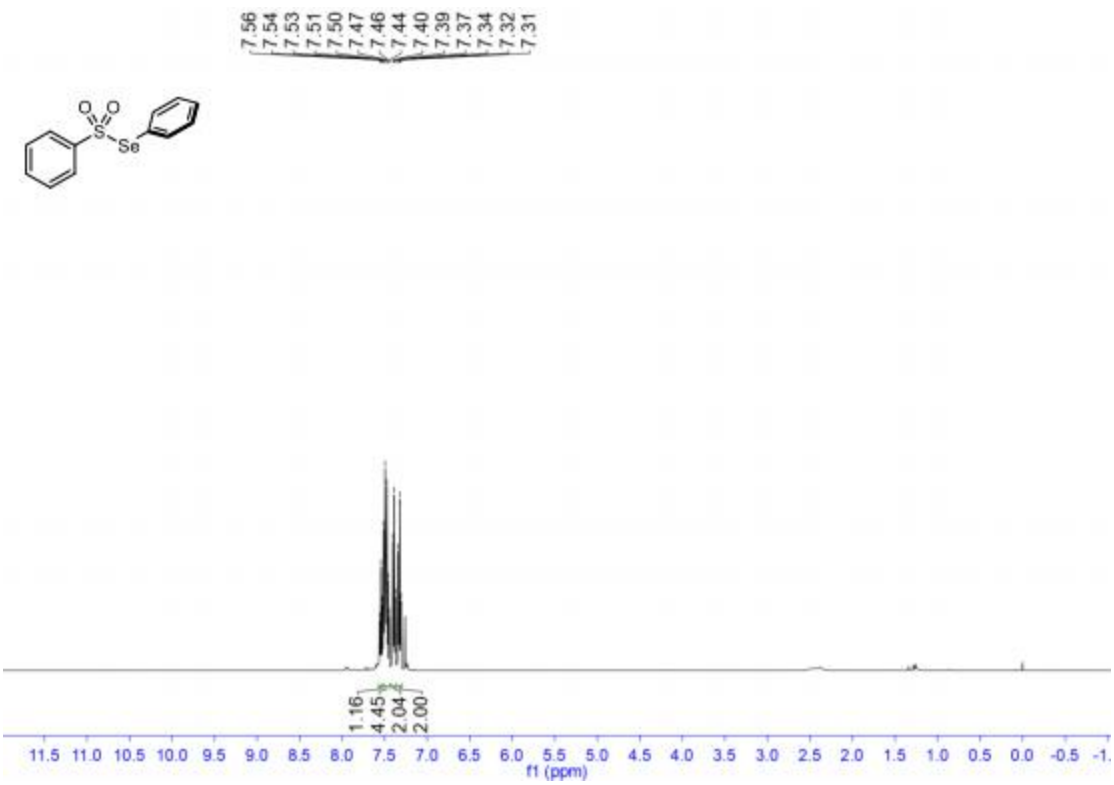
Supplementary Figure 92 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 4-bromophenyl 4-methylbenzenesulfonate **(43a)**



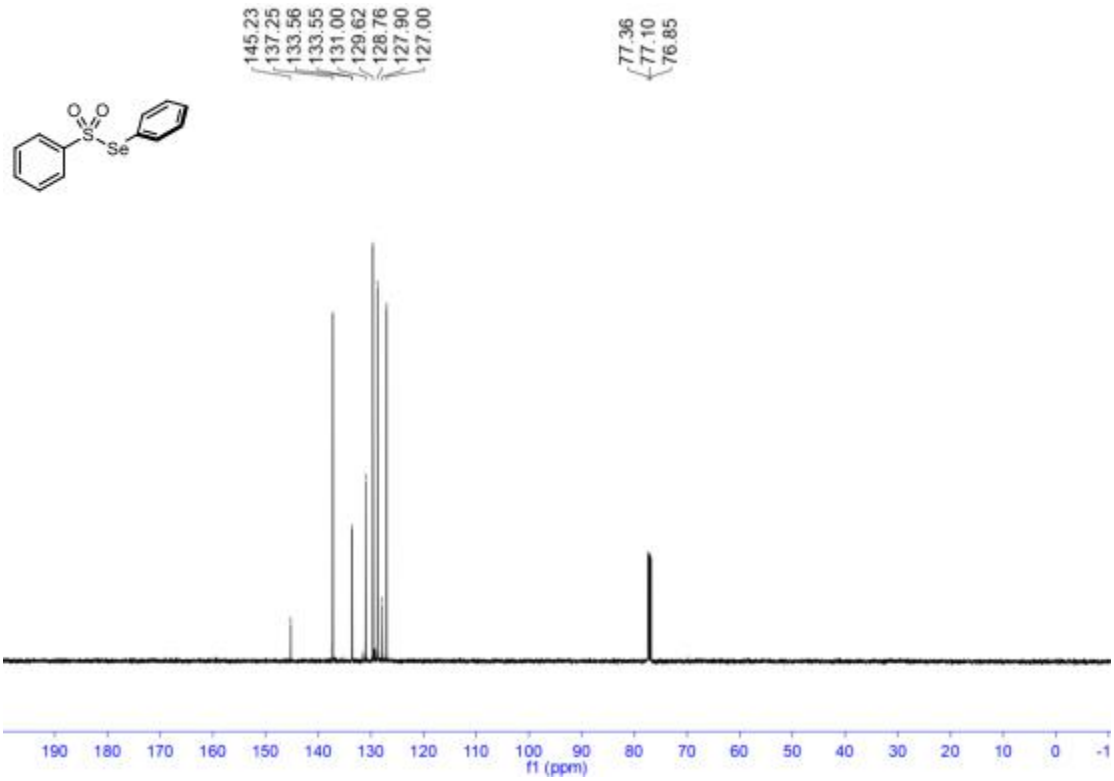
Supplementary Figure 93 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 4-bromophenyl 4-methylbenzenesulfonate **(43a)**



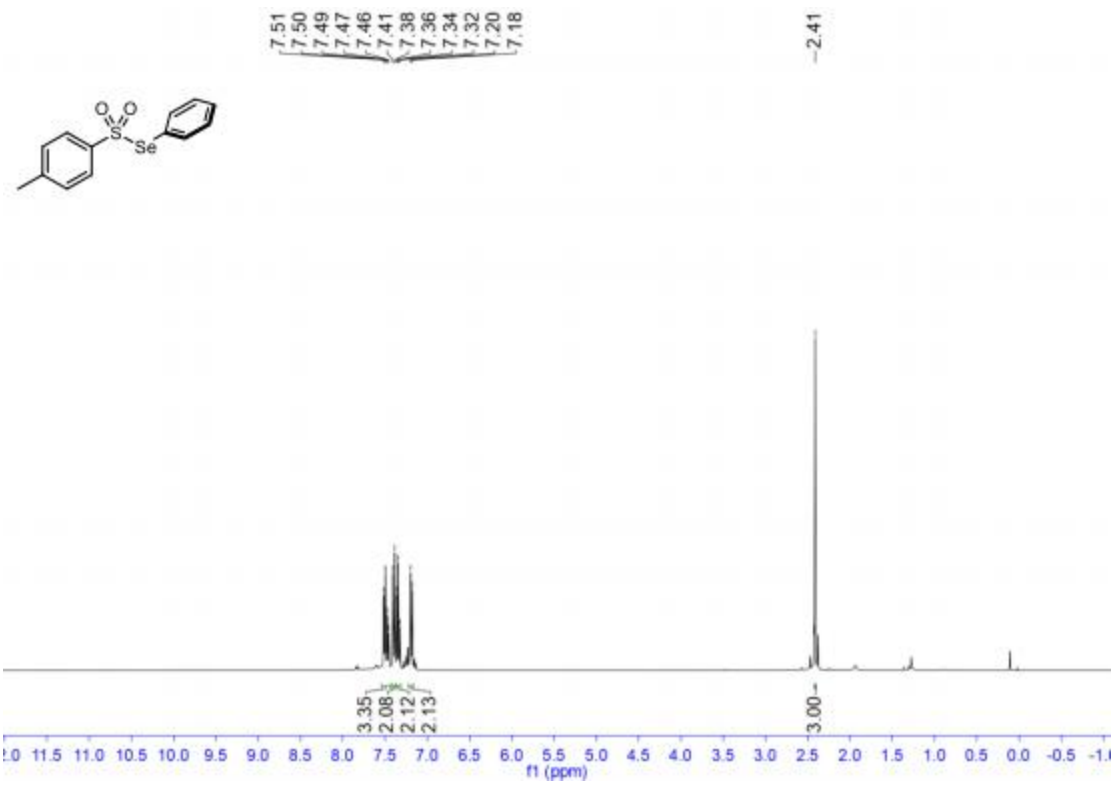
Supplementary Figure 94 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *Se*-phenyl benzenesulfonoselenoate **(44a)**



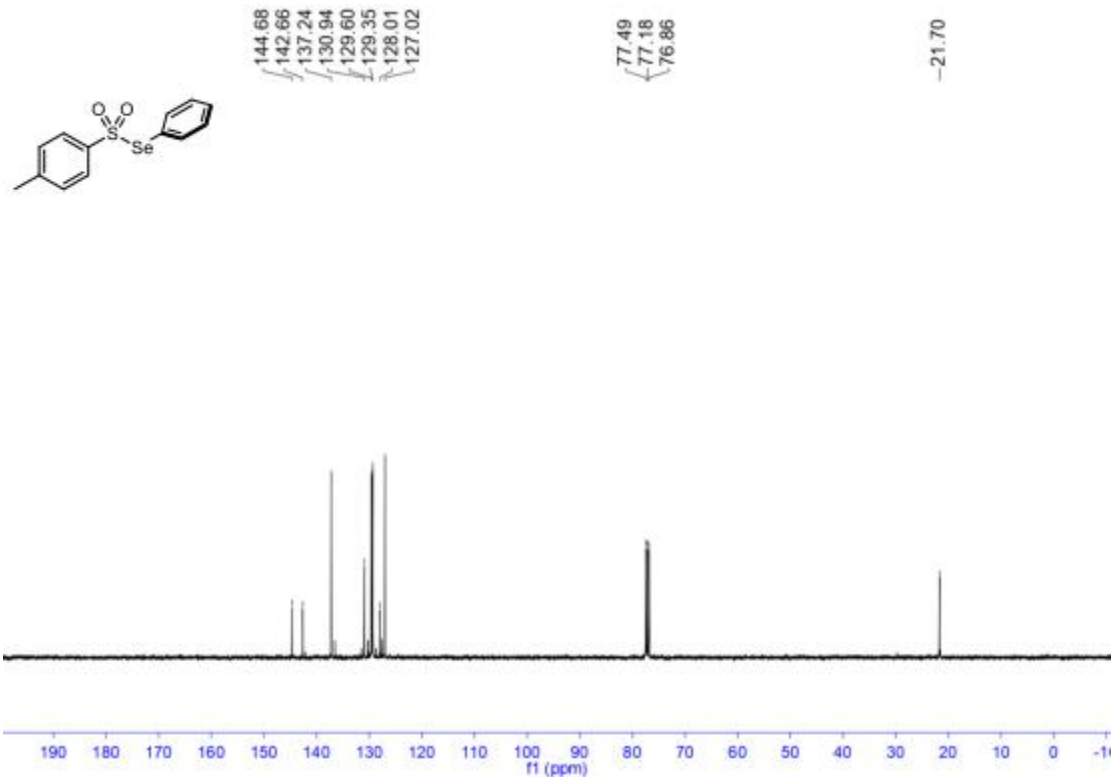
Supplementary Figure 95 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of *Se*-phenyl benzenesulfonoselenoate **(44a)**



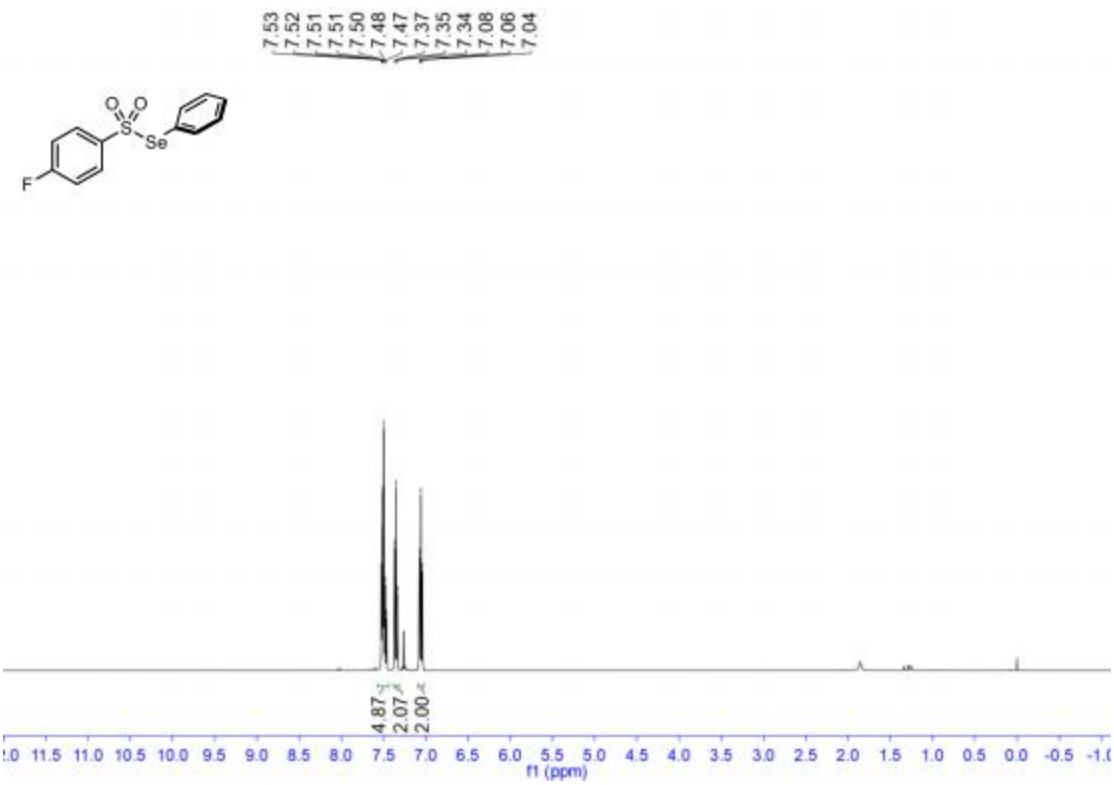
Supplementary Figure 96 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *Se*-phenyl 4-methylbenzenesulfonoselenoate **(45a)**



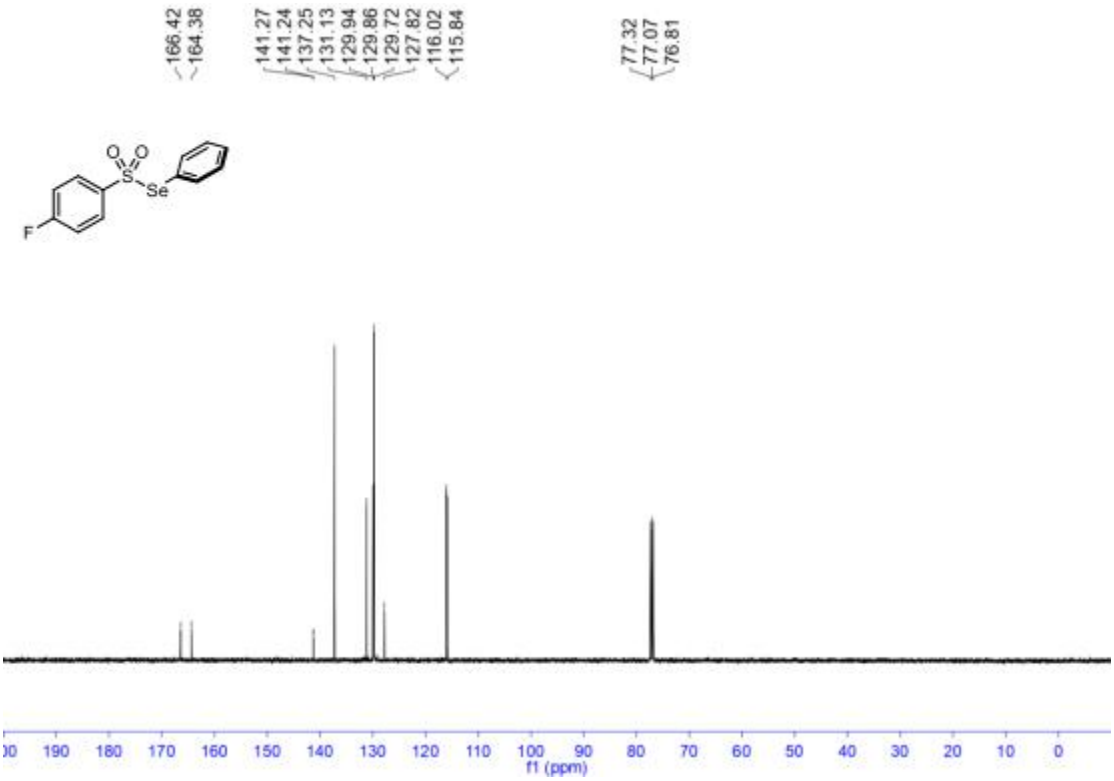
Supplementary Figure 97 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of *Se*-phenyl 4-methylbenzenesulfonoselenoate **(45a)**



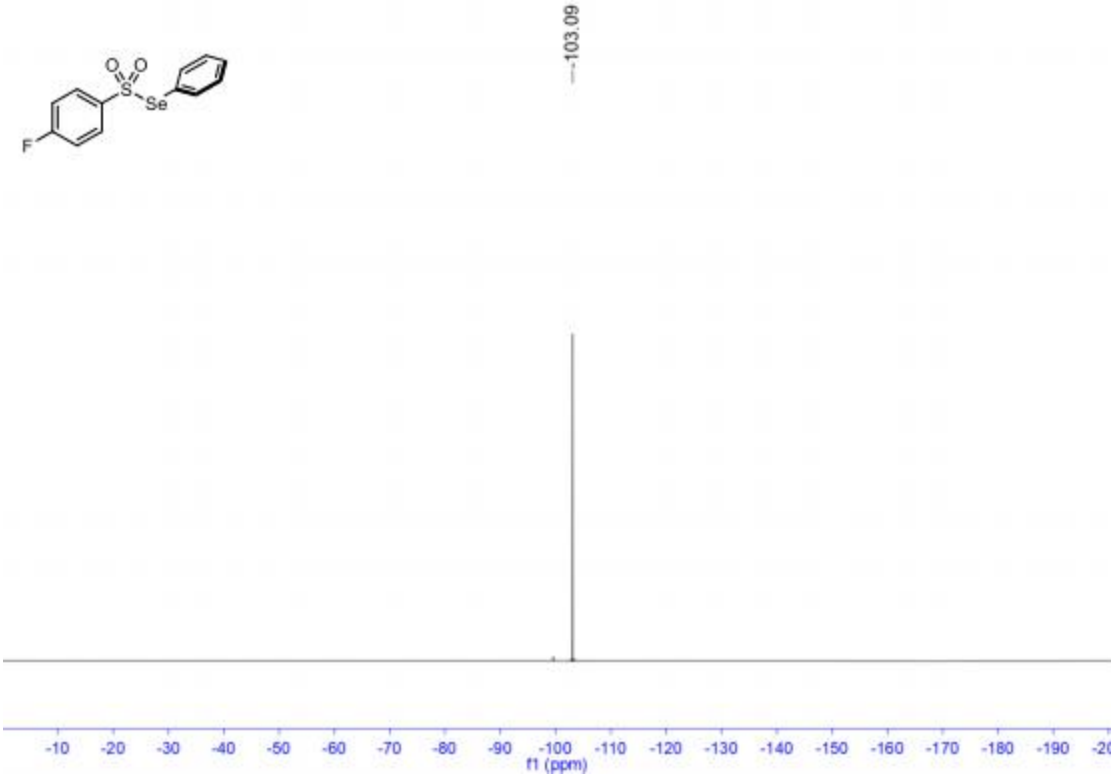
Supplementary Figure 98 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *Se*-phenyl 4-fluorobenzenesulfonoselenoate **(46a)**



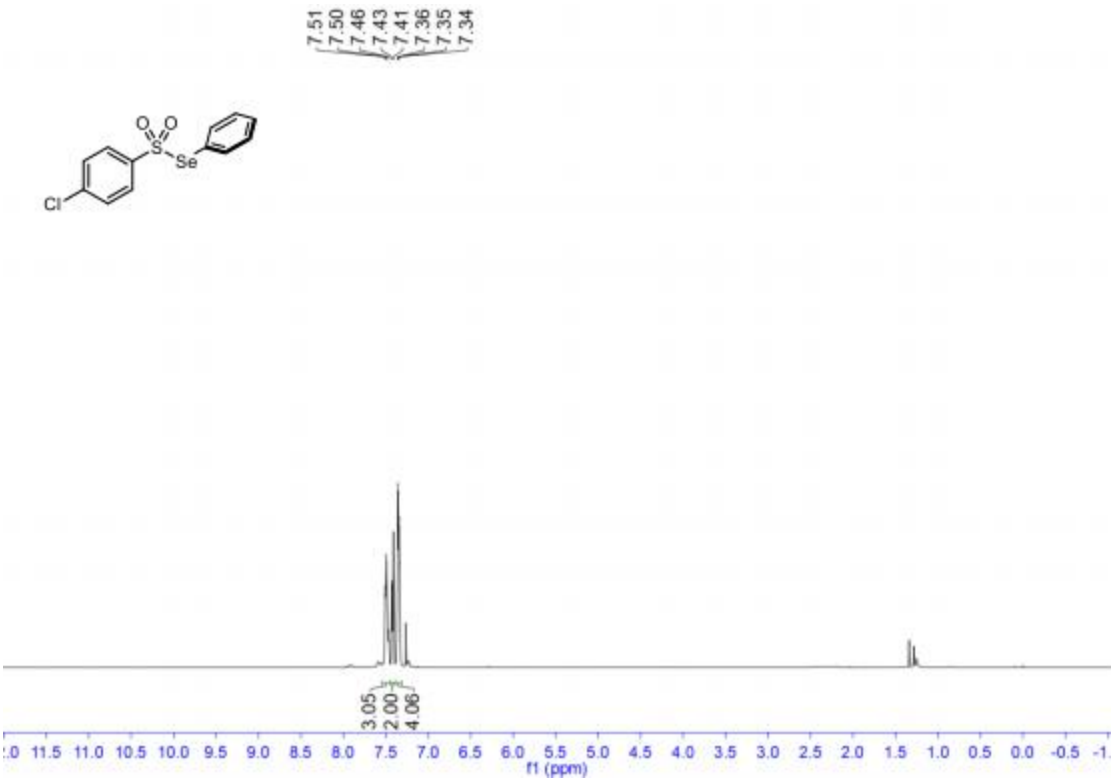
Supplementary Figure 99 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of *Se*-phenyl 4-fluorobenzenesulfonoselenoate **(46a)**



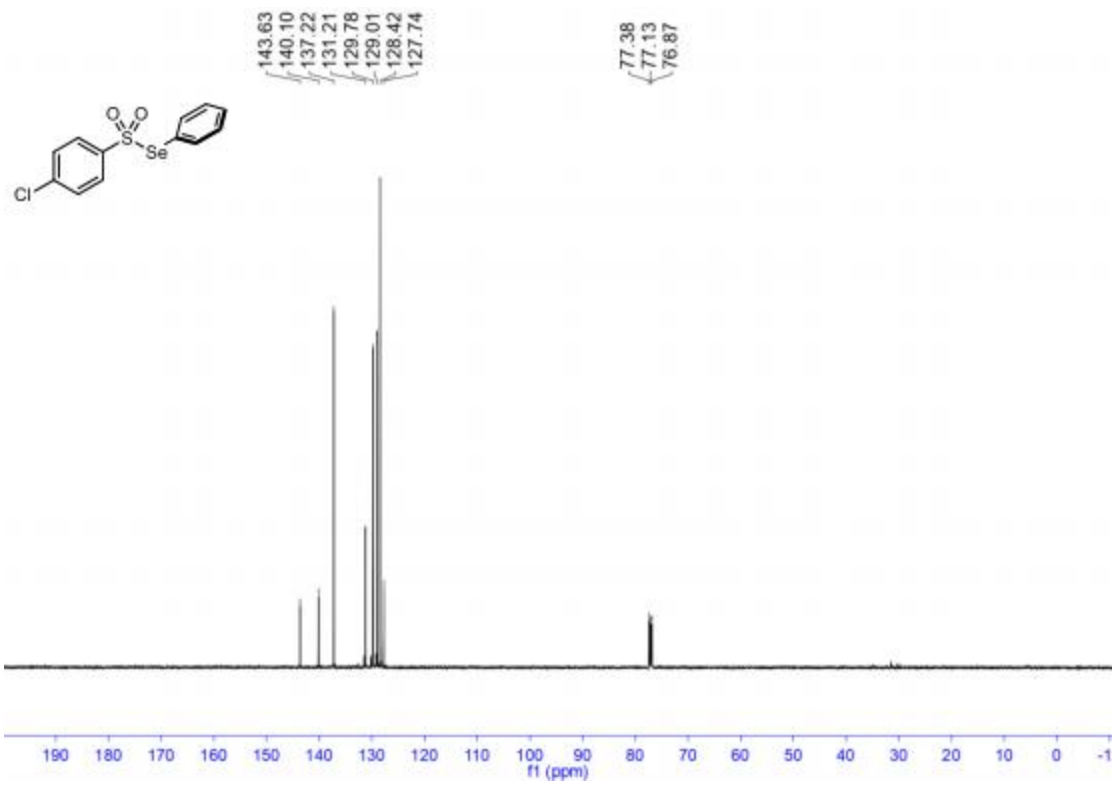
Supplementary Figure 100 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of *Se*-phenyl 4-fluorobenzenesulfonoselenoate **(46a)**



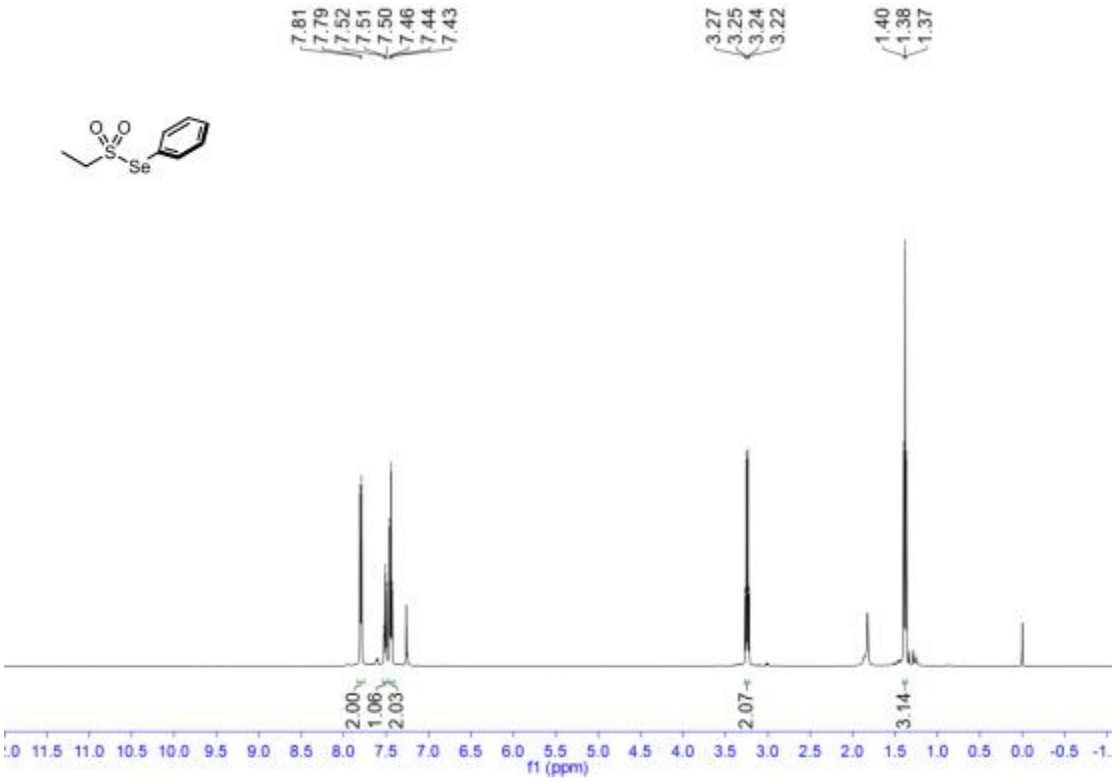
Supplementary Figure 101 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *Se*-phenyl 4-chlorobenzenesulfonoselenoate **(47a)**



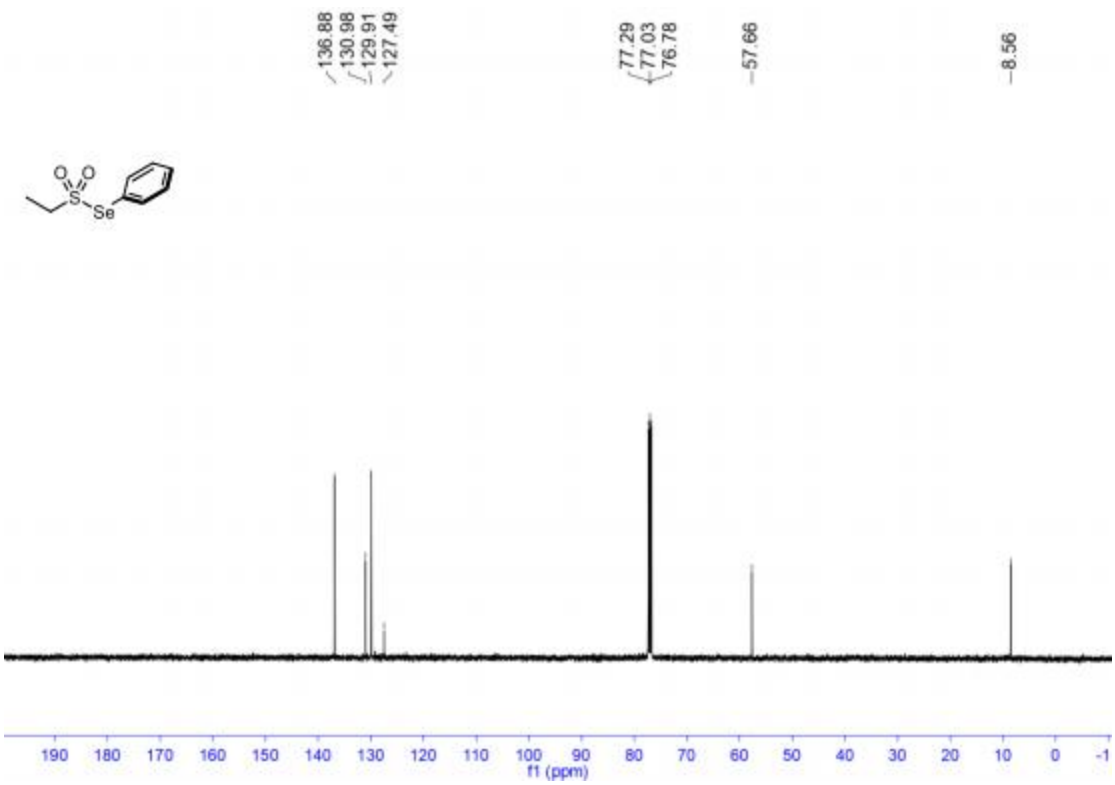
Supplementary Figure 102 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of *Se*-phenyl 4-chlorobenzenesulfonoselenoate **(47a)**



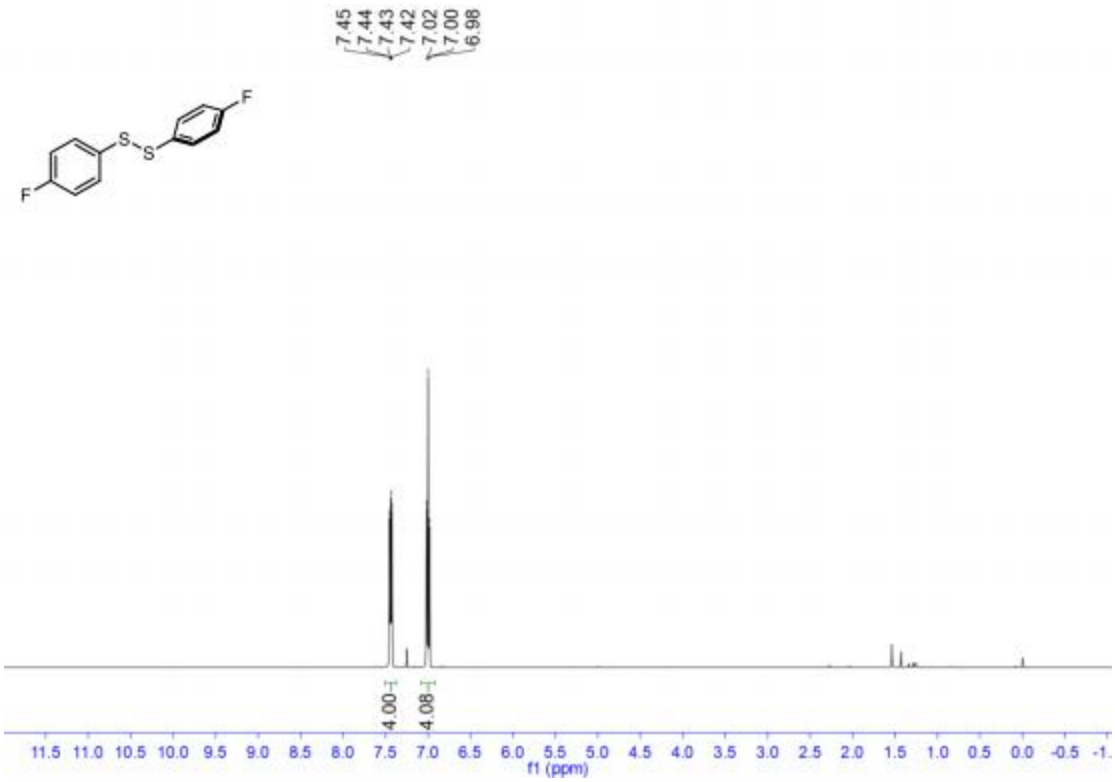
Supplementary Figure 103 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *Se*-phenyl ethanesulfonoselenoate **(48a)**



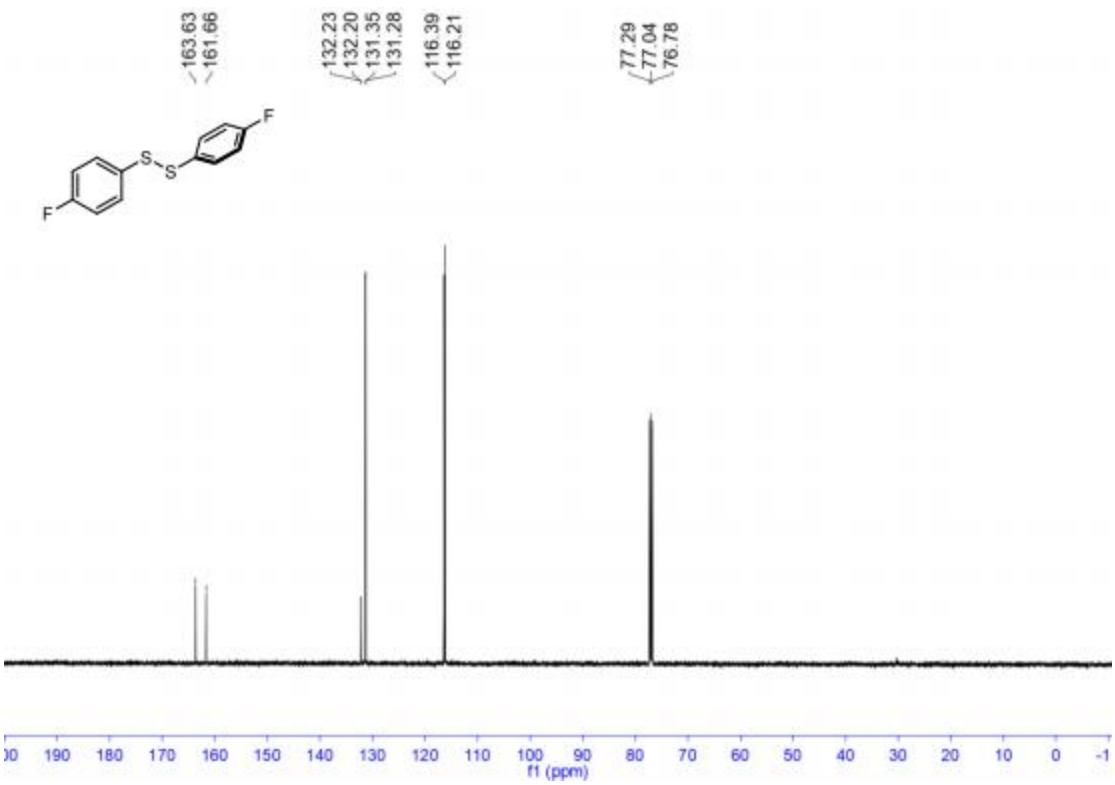
Supplementary Figure 104 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of *Se*-phenyl ethanesulfonoselenoate **(48a)**



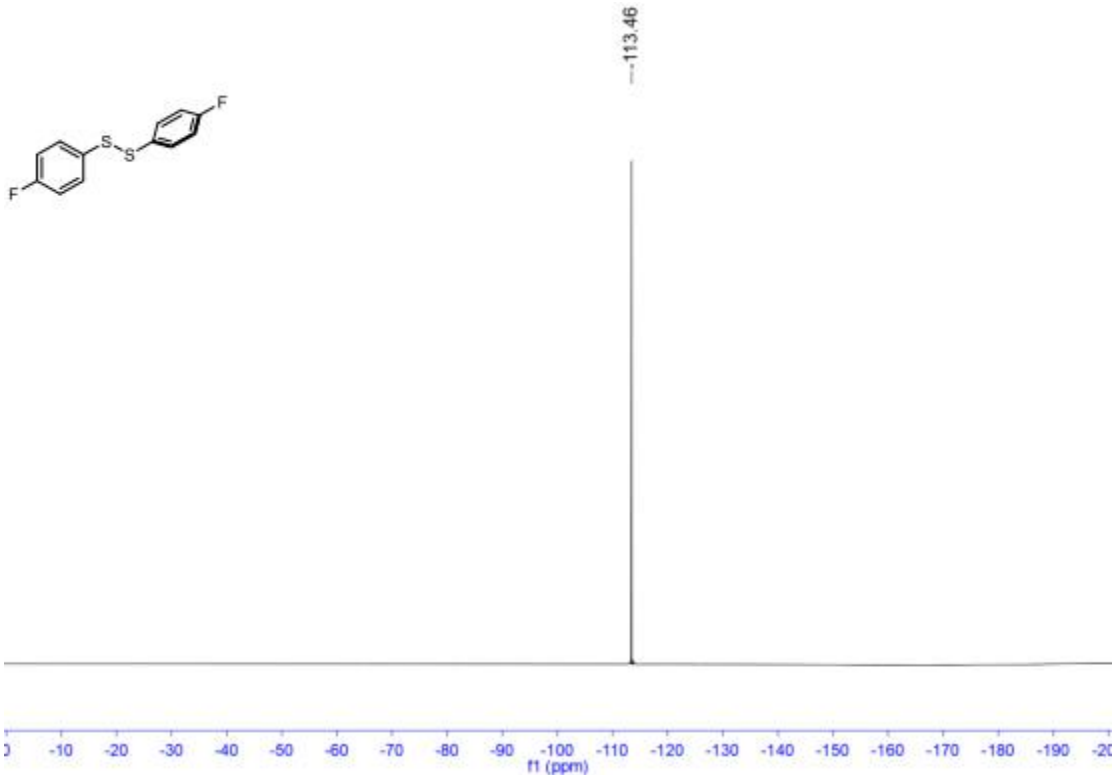
Supplementary Figure 105 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-Bis(4-fluorophenyl)disulfane **(51a)**



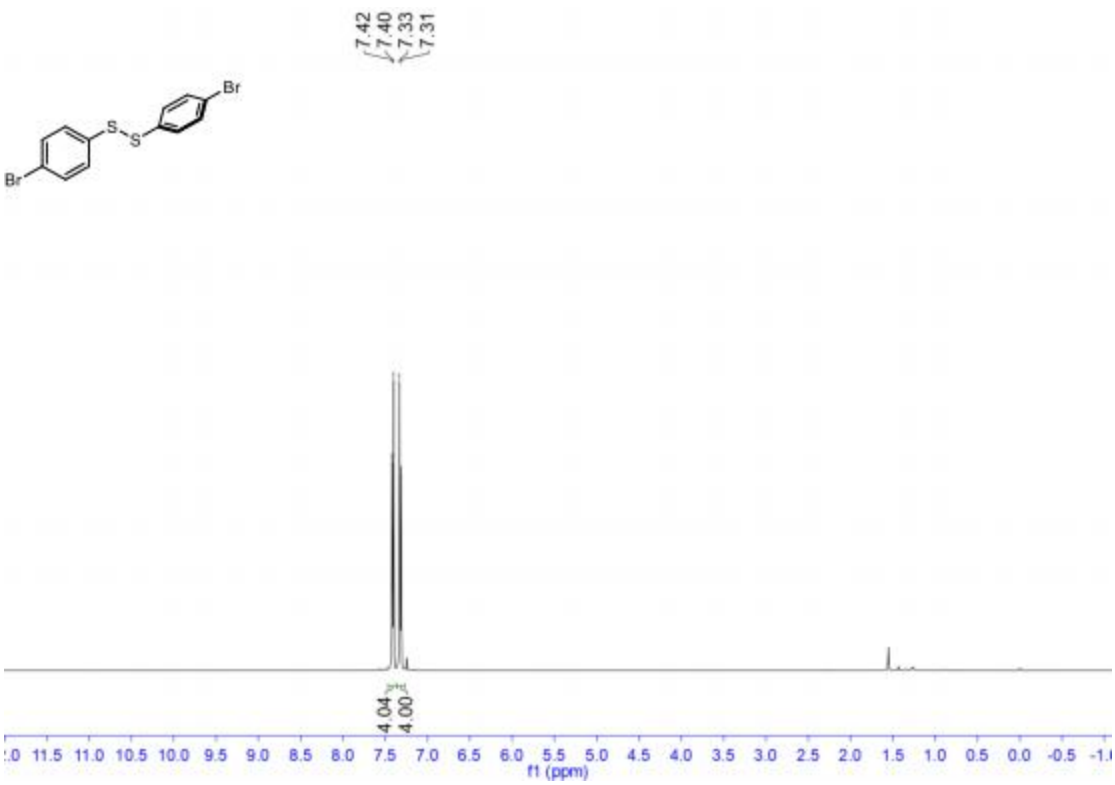
Supplementary Figure 106 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis(4-fluorophenyl)disulfane **(51a)**



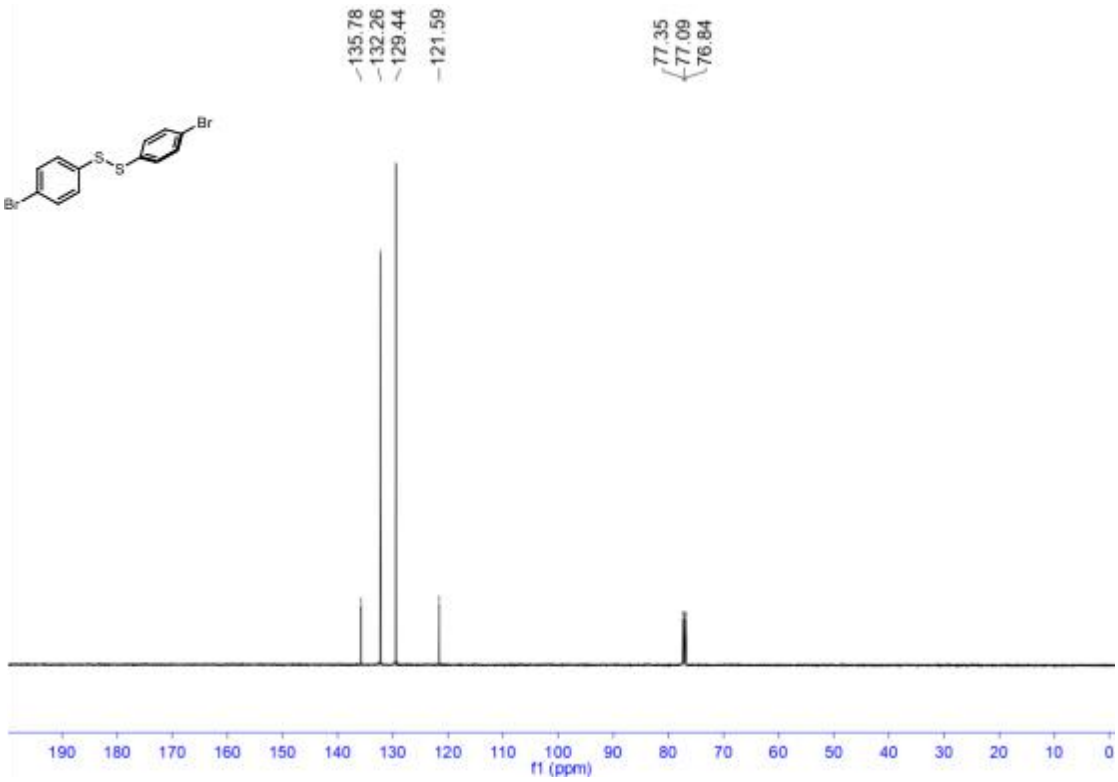
Supplementary Figure 107 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of 1,2-bis(4-fluorophenyl)disulfane **(51a)**



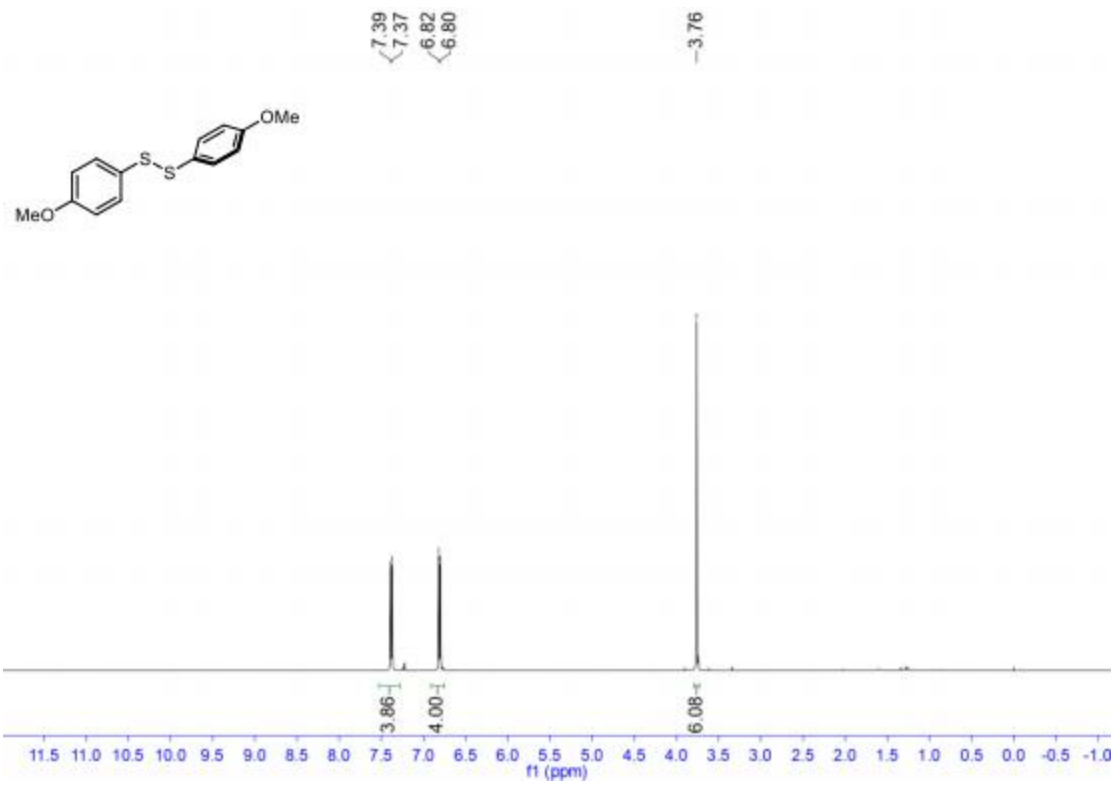
Supplementary Figure 108 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis(4-bromophenyl)disulfane **(53a)**



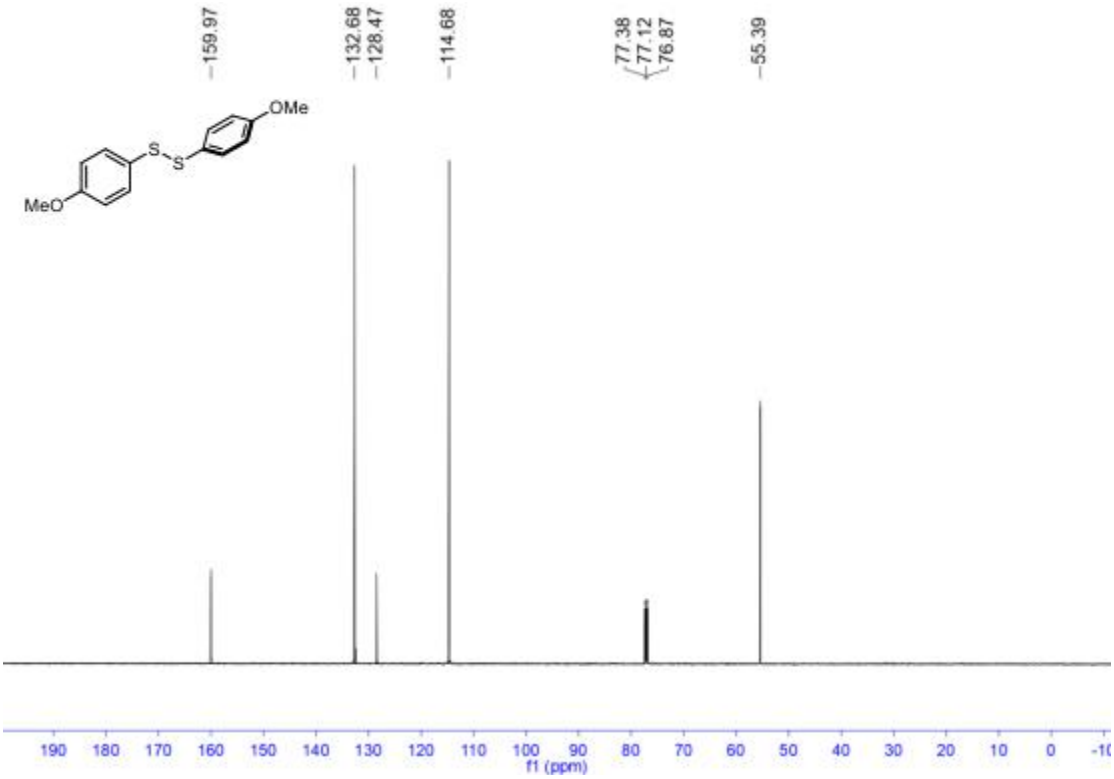
Supplementary Figure 109 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis(4-bromophenyl)disulfane **(53a)**



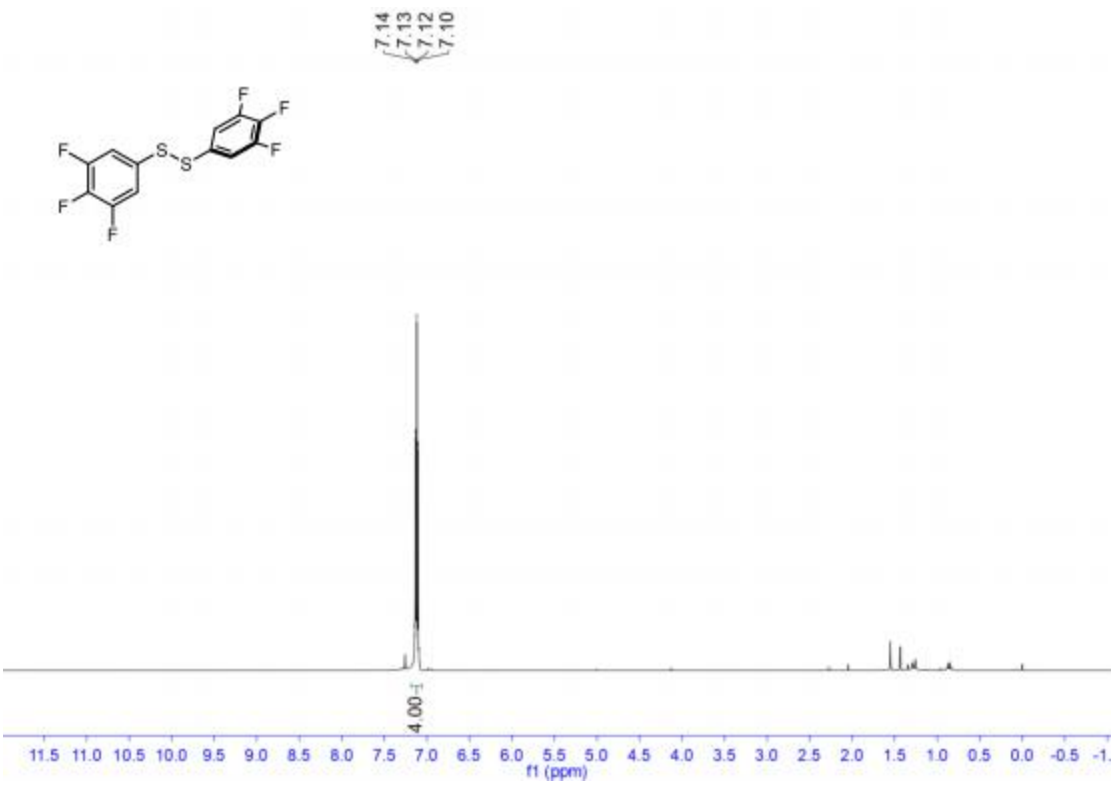
Supplementary Figure 110 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis(4-methoxyphenyl)disulfane **(54a)**



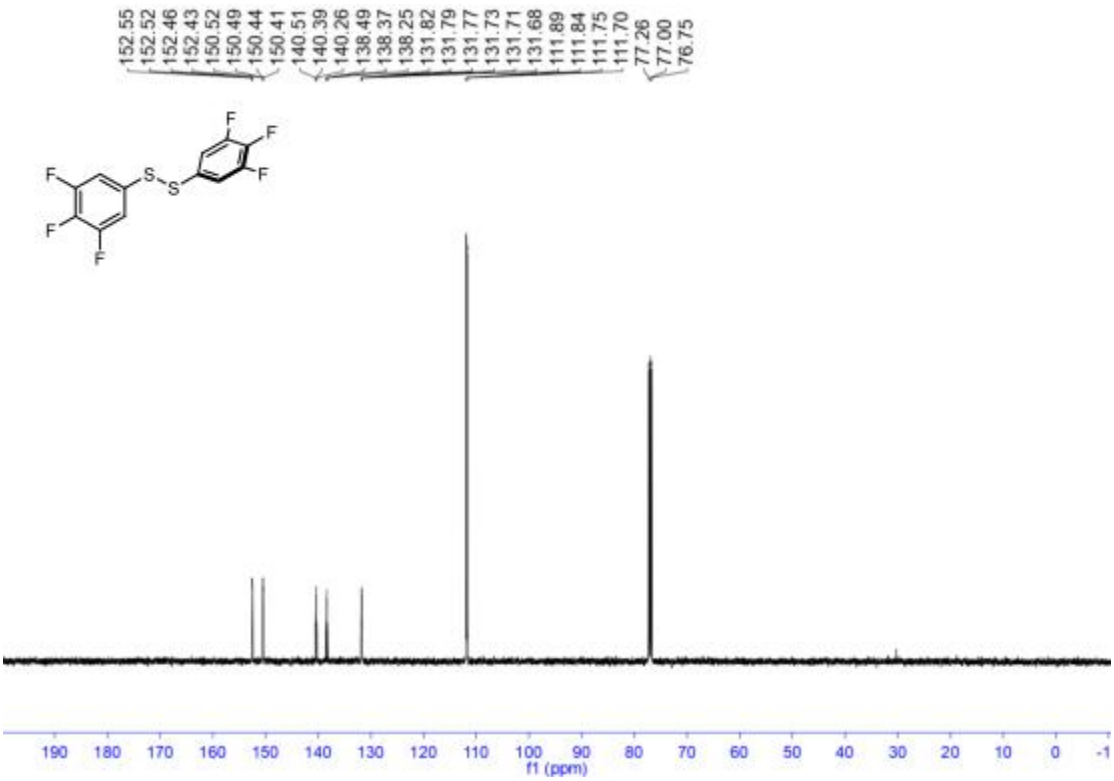
Supplementary Figure 111 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis(4-methoxyphenyl)disulfane **(54a)**



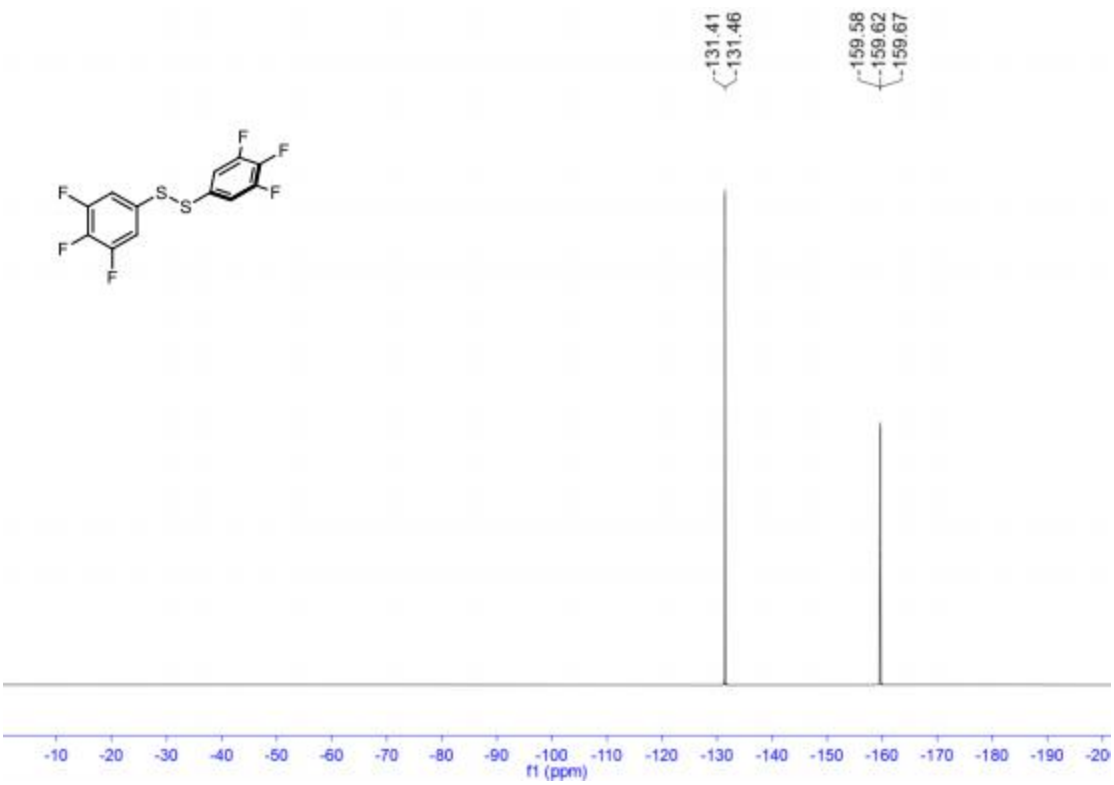
Supplementary Figure 112 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis(3,4,5-trifluorophenyl)disulfane **(55a)**



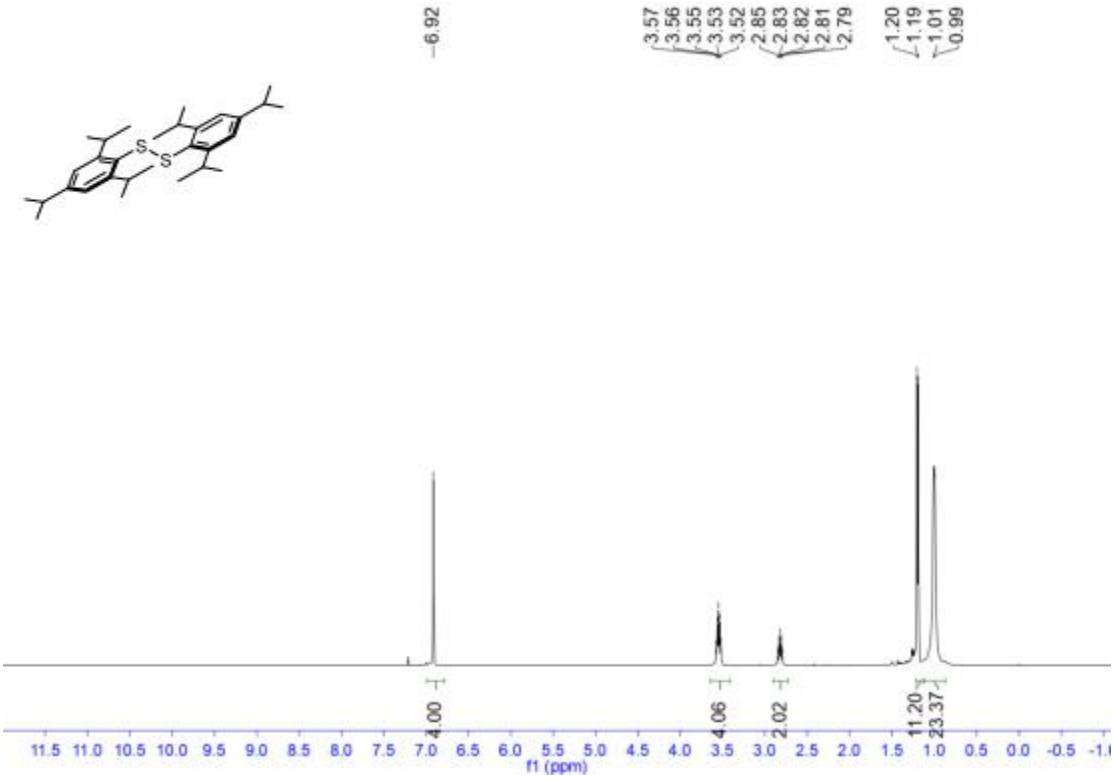
Supplementary Figure 113 | ^{13}C NMR (126 MHz, 298K, Chloroform-d) of 1,2-bis(3,4,5-trifluorophenyl)disulfane **(55a)**



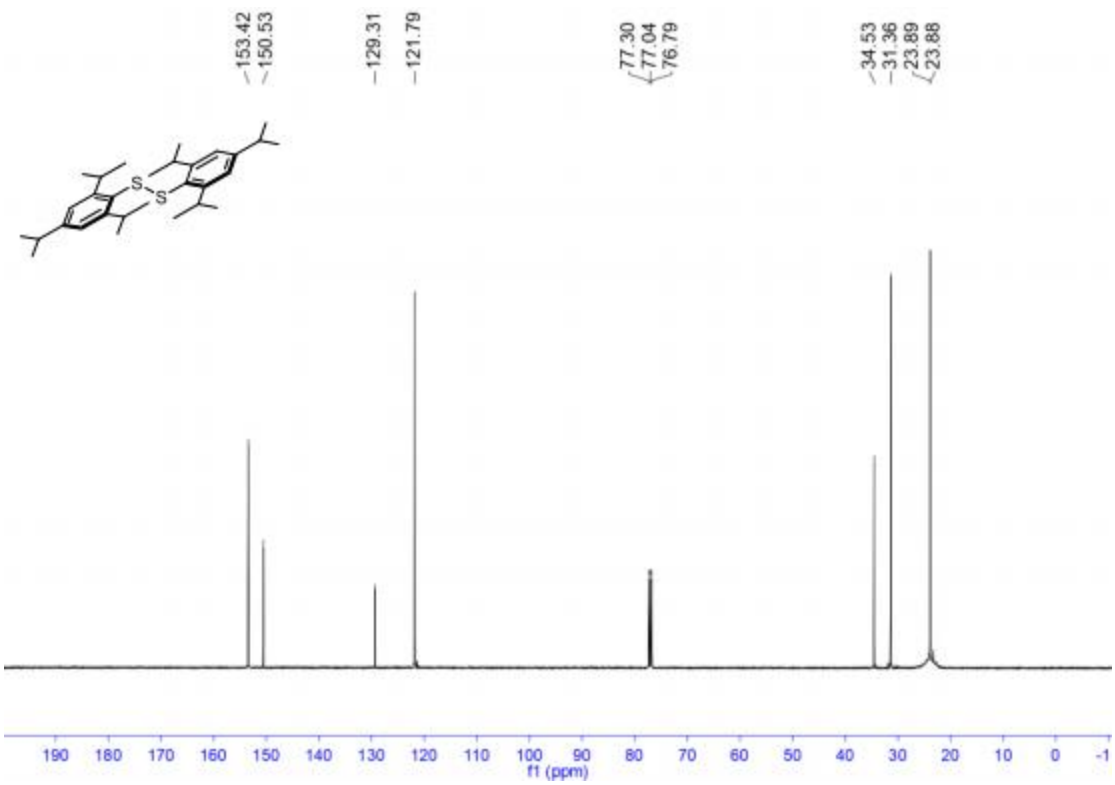
Supplementary Figure 114 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of 1,2-bis(3,4,5-trifluorophenyl)disulfane **(55a)**



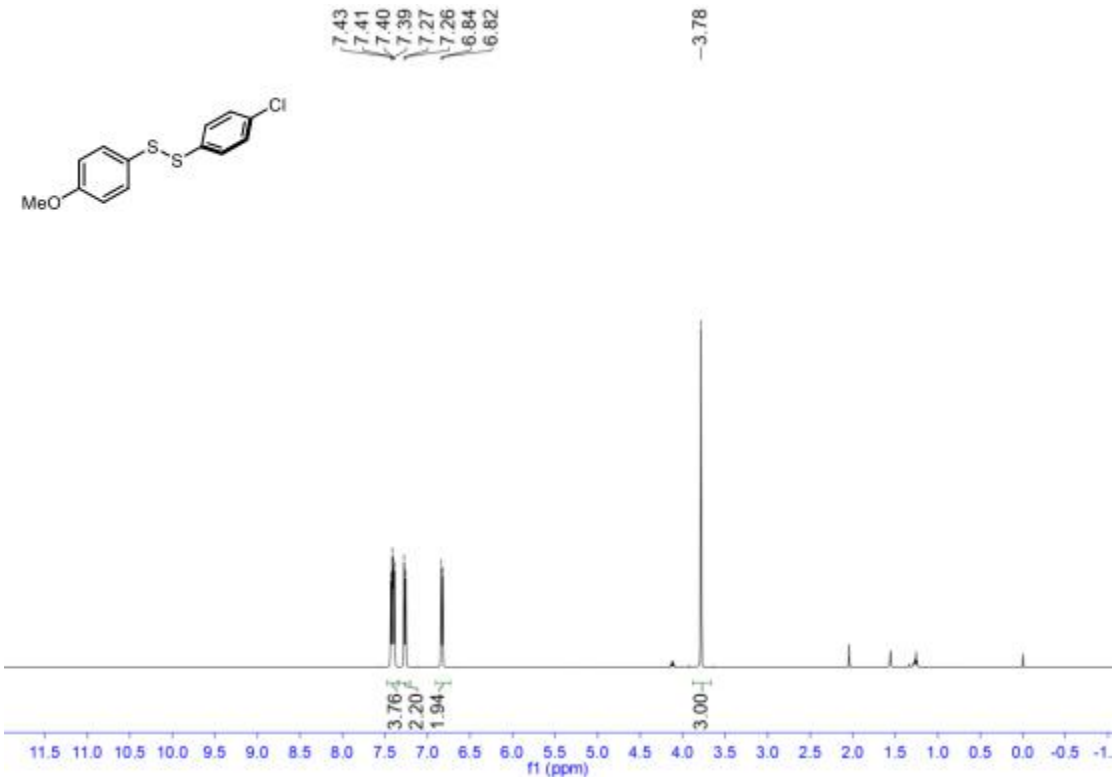
Supplementary Figure 115 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis(2,4,6-triisopropylphenyl)disulfane **(56a)**



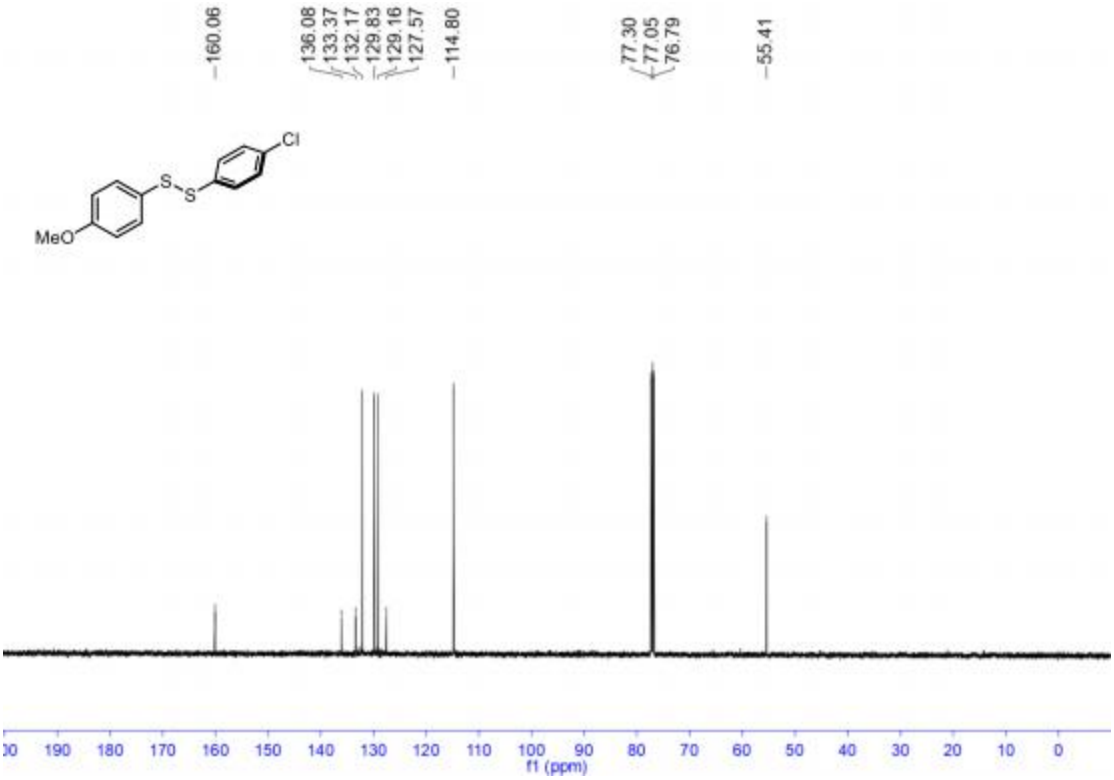
Supplementary Figure 116 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis(2,4,6-triisopropylphenyl)disulfane **(56a)**



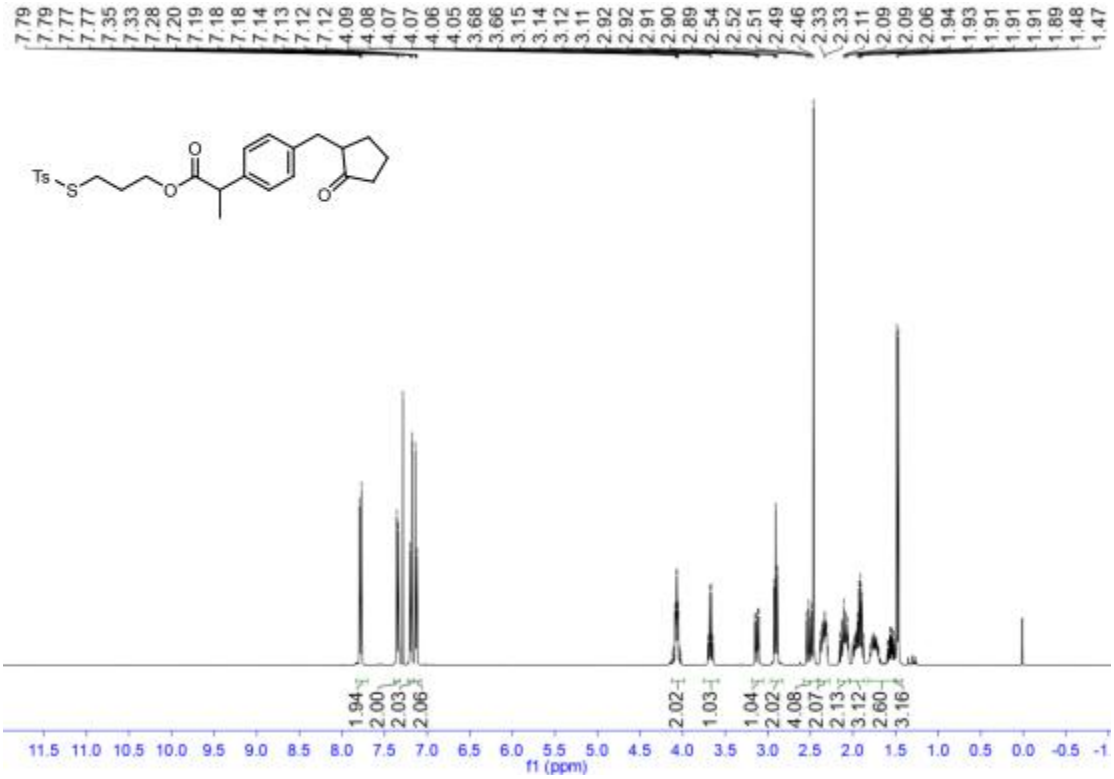
Supplementary Figure 117 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1-(4-chlorophenyl)-2-(4-methoxyphenyl)disulfane **(57a)**



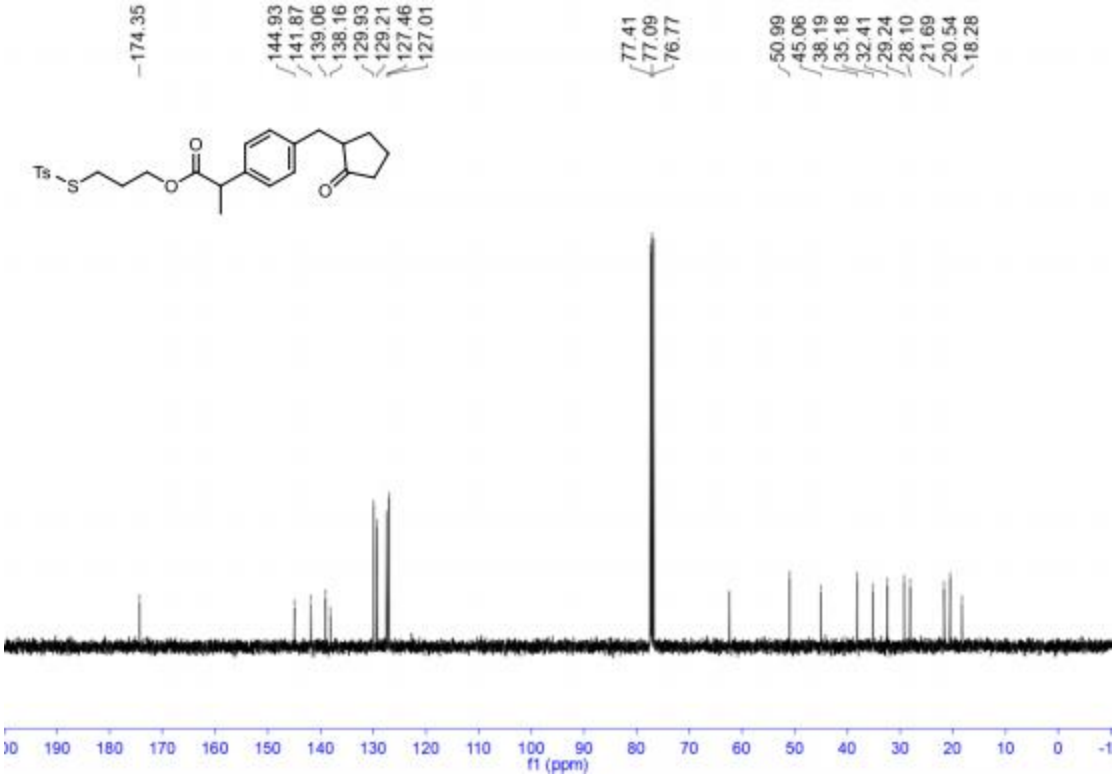
Supplementary Figure 118 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1-(4-chlorophenyl)-2-(4-methoxyphenyl)disulfane **(57a)**



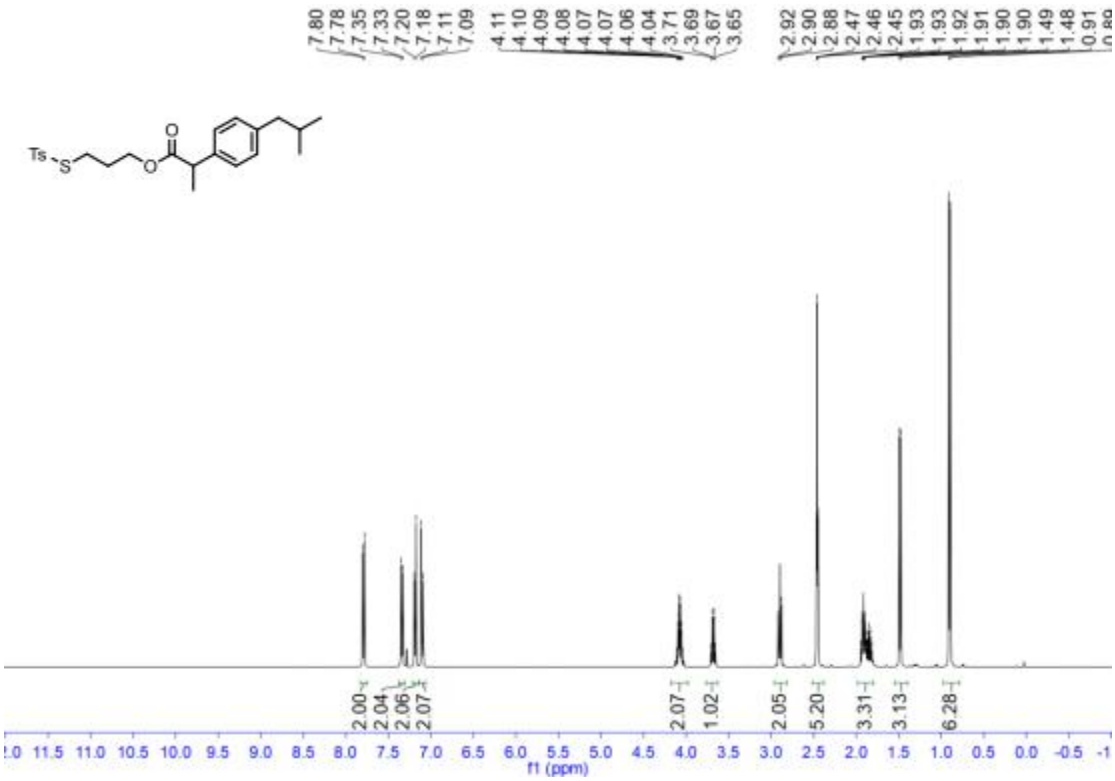
Supplementary Figure 119 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate **(58a)**



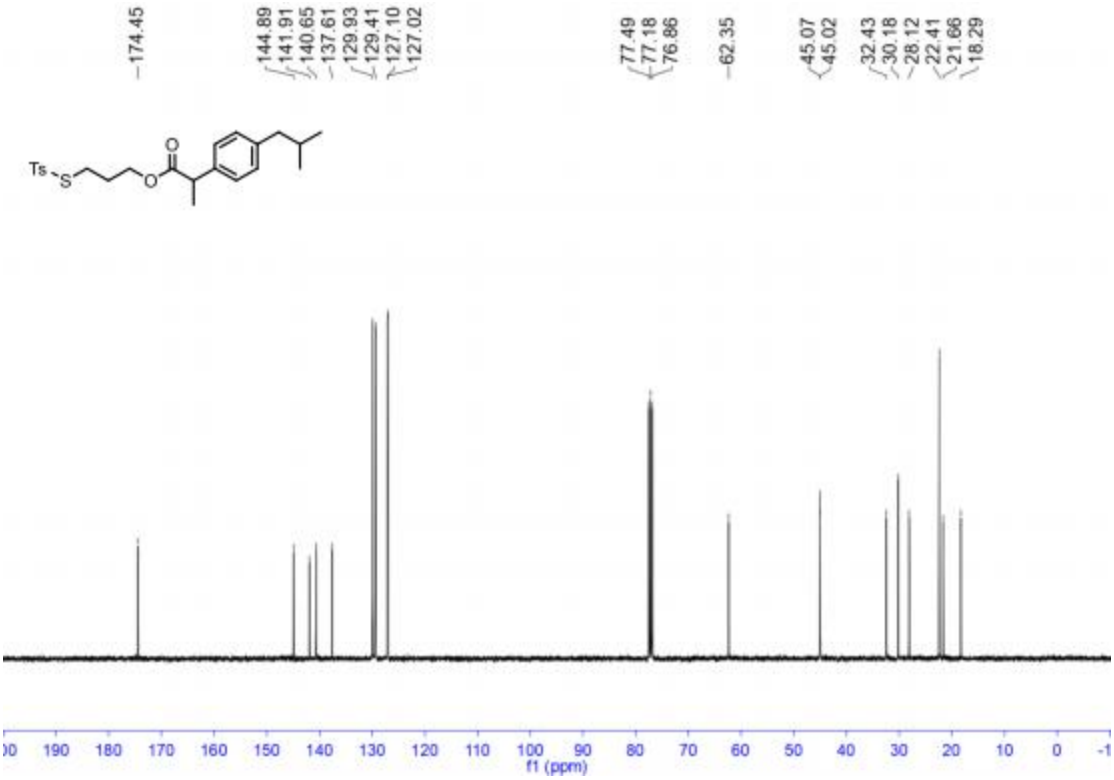
Supplementary Figure 120 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate **(58a)**



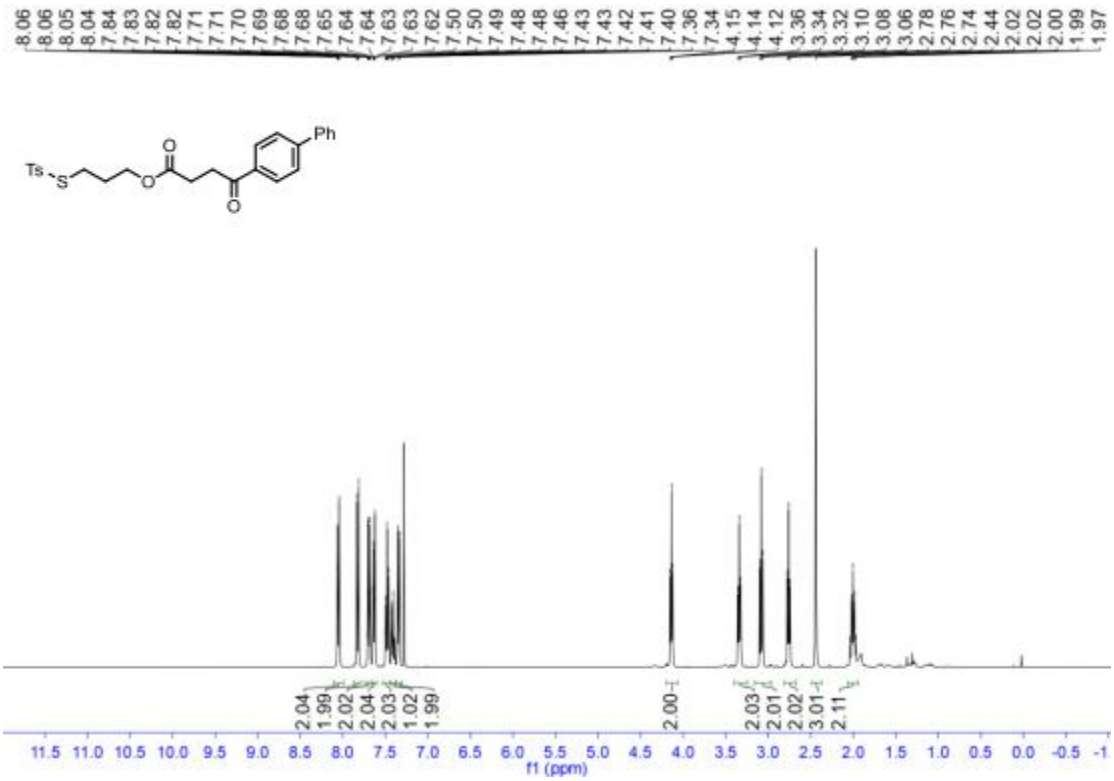
Supplementary Figure 121 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(4-isobutylphenyl)propanoate **(59a)**



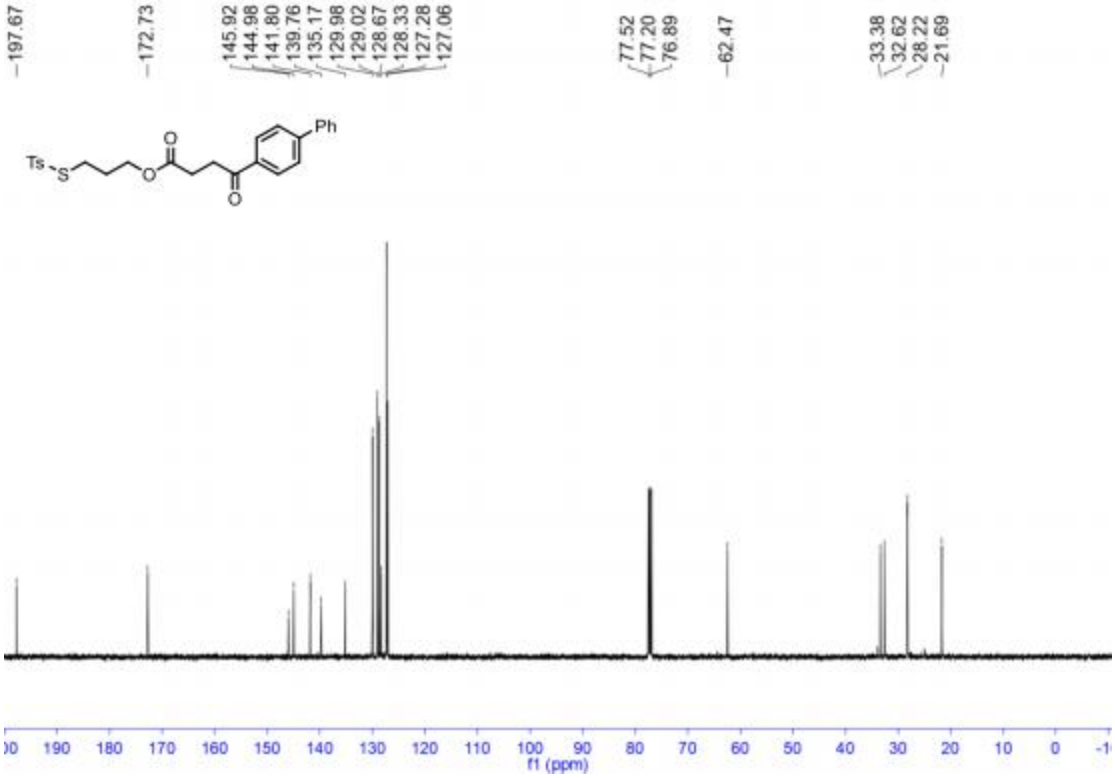
Supplementary Figure 122 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(4-isobutylphenyl)propanoate **(59a)**



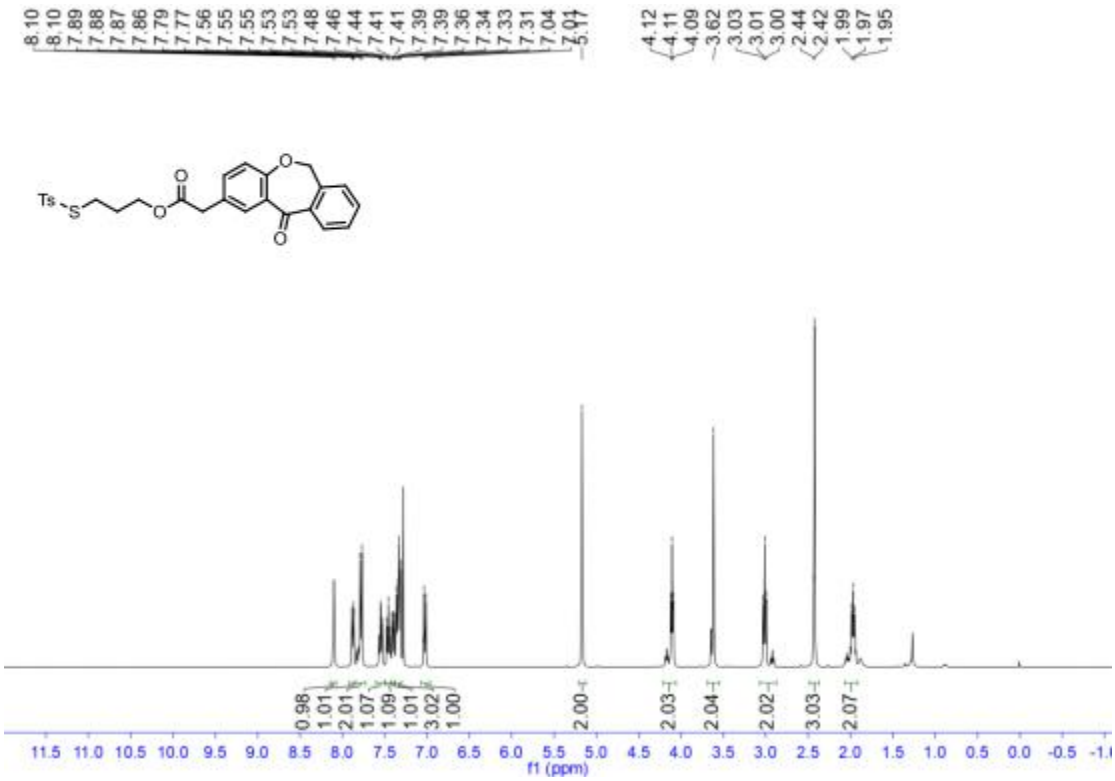
Supplementary Figure 123 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate **(60a)**



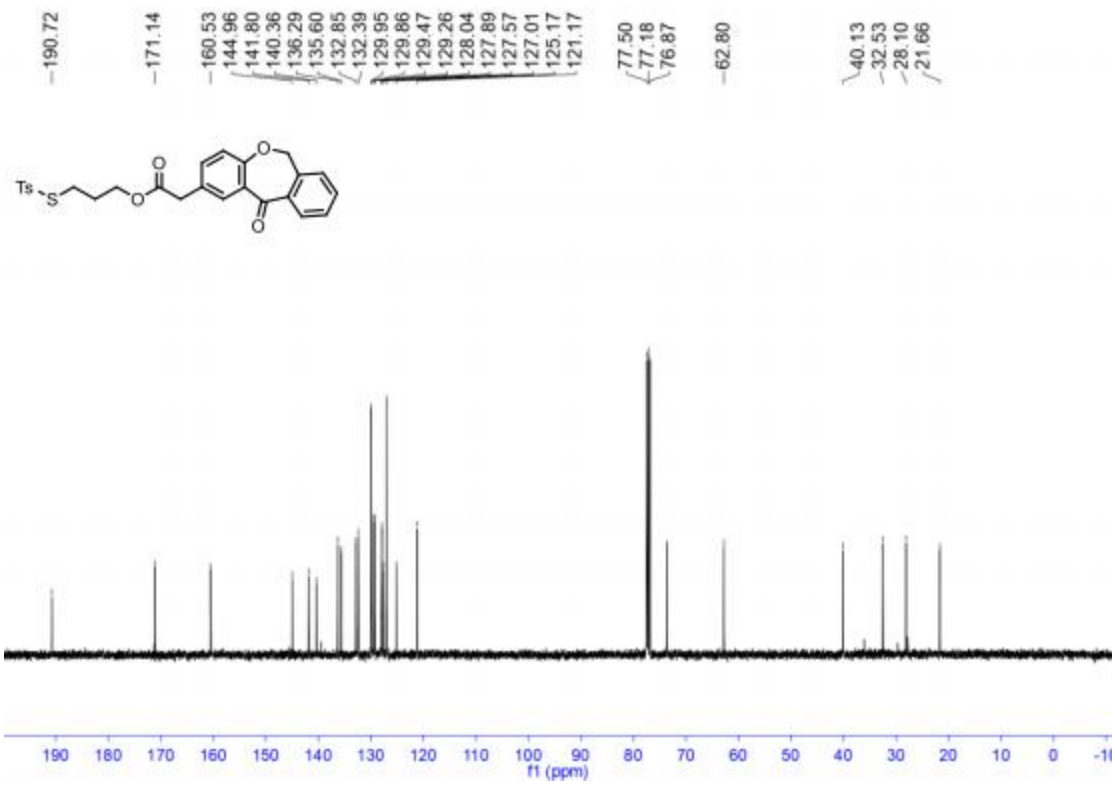
Supplementary Figure 124 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate **(60a)**



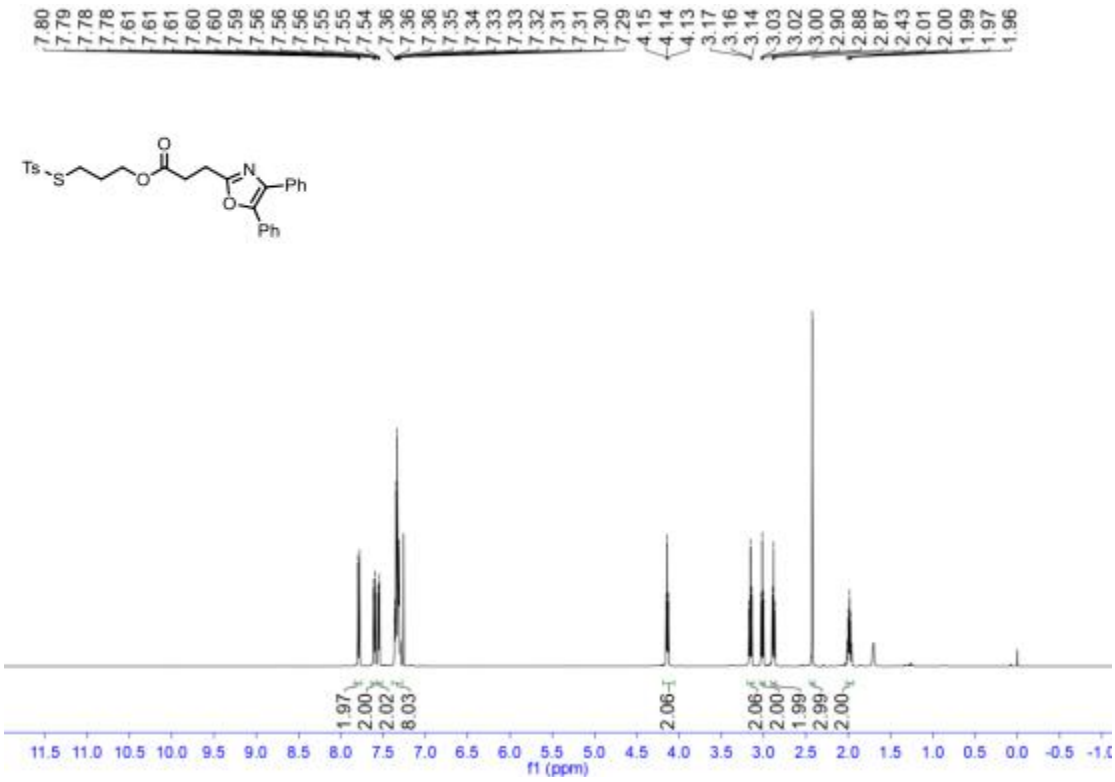
Supplementary Figure 125 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate **(61a)**



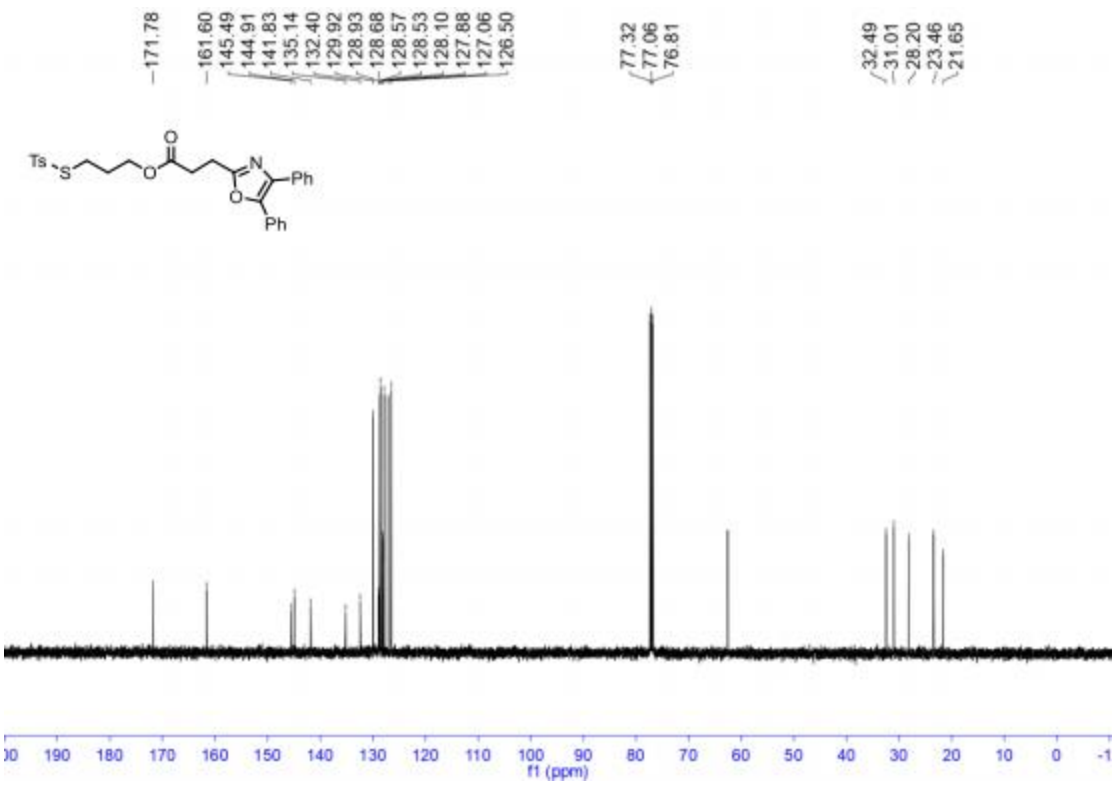
Supplementary Figure 126 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate **(61a)**



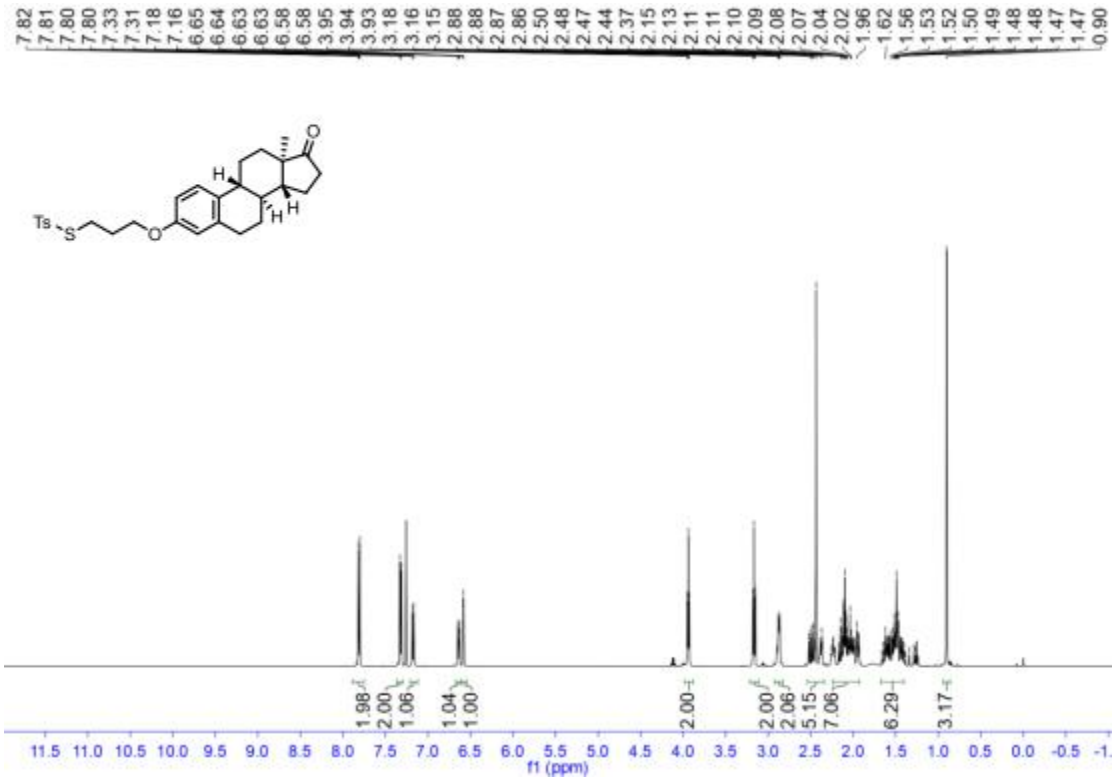
Supplementary Figure 127 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate **(62a)**



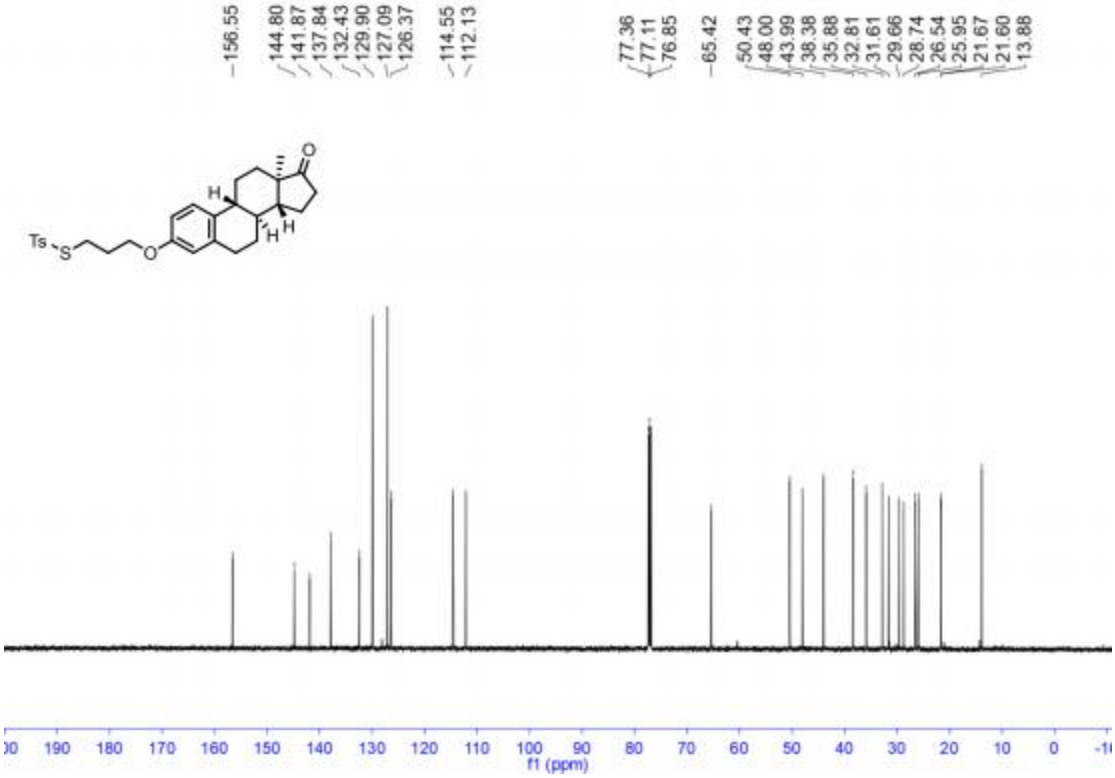
Supplementary Figure 128 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate **(62a)**



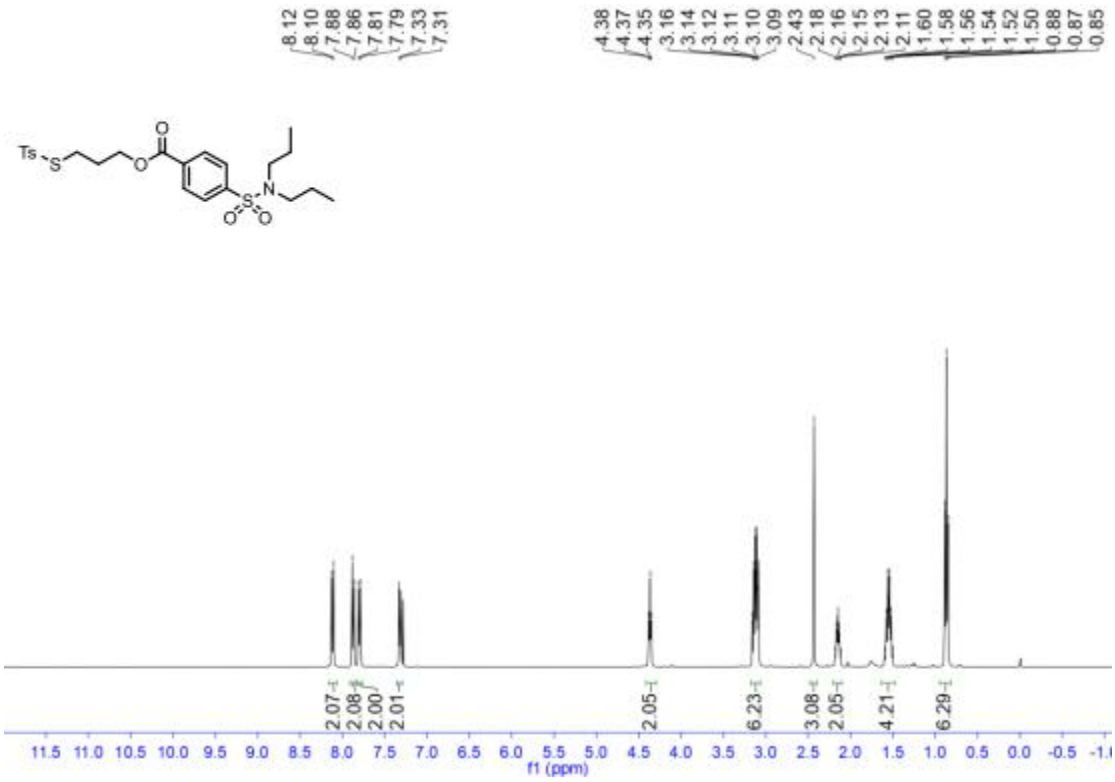
Supplementary Figure 129 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *S*-(3-(((8*S*,9*R*,13*R*,14*R*)- 13-Methyl- 17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)propyl) 4-methylbenzenesulfonothioate **(63a)**



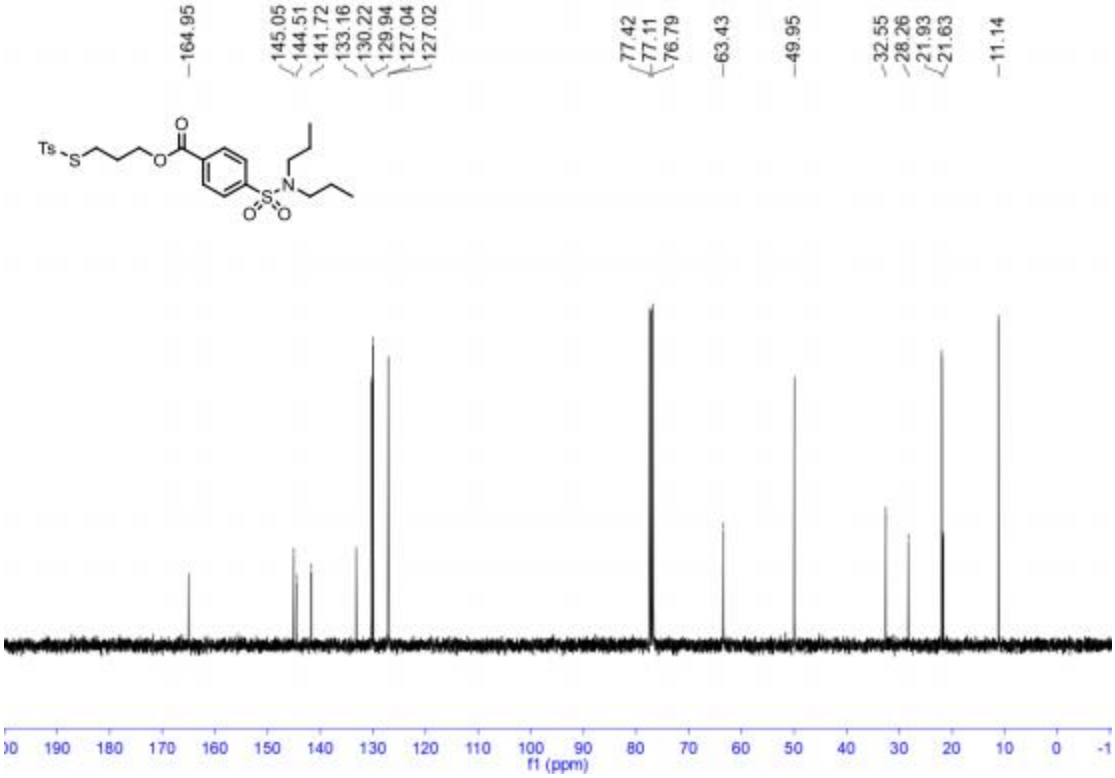
Supplementary Figure 130 | ^{13}C NMR (126 MHz, 298K, Chloroform-d) of *S*-(3-(((8*S*,9*R*,13*R*,14*R*)- 13-Methyl- 17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)propyl) 4-methylbenzenesulfonothioate **(63a)**



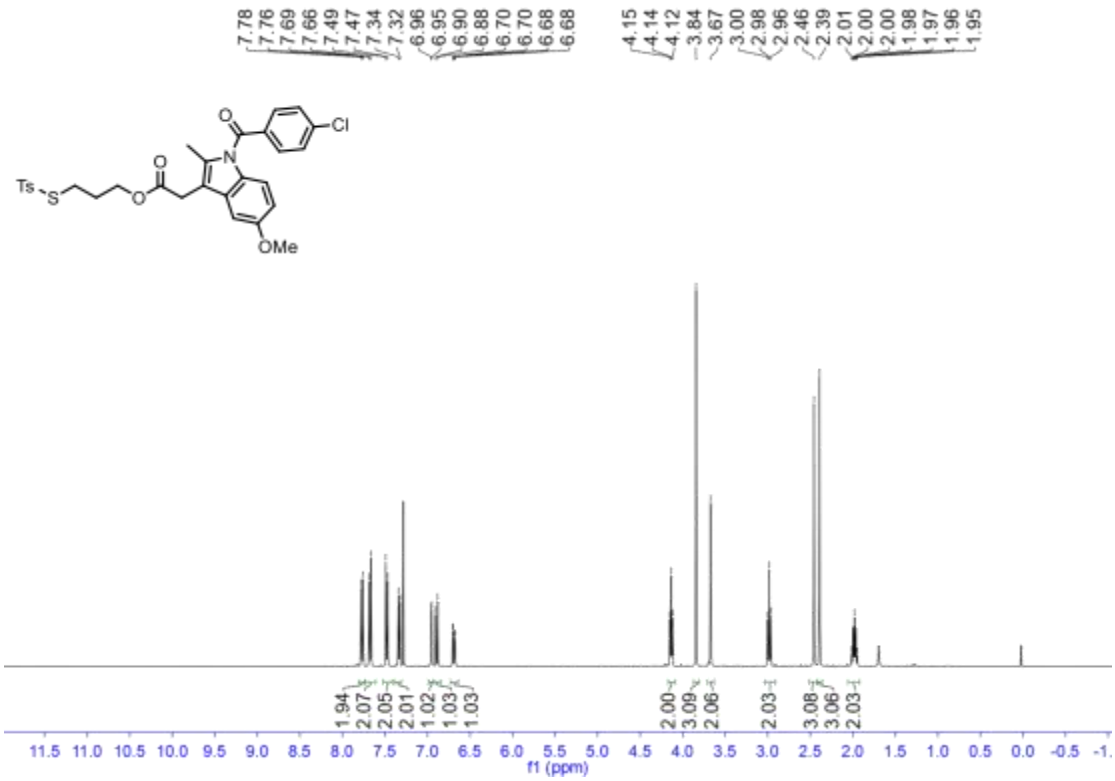
Supplementary Figure 131 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate **(64a)**



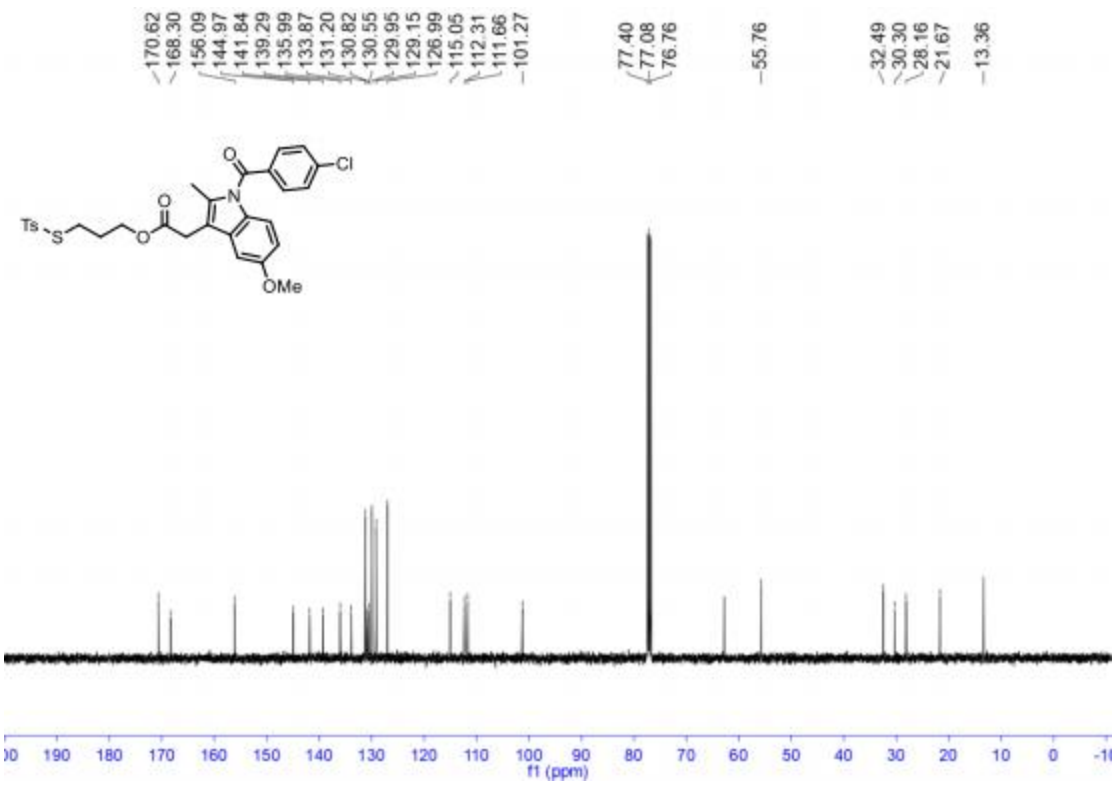
Supplementary Figure 132 | ^{13}C NMR (101 MHz, 298K, Chloroform-d) of 3-(tosylthio)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate **(64a)**



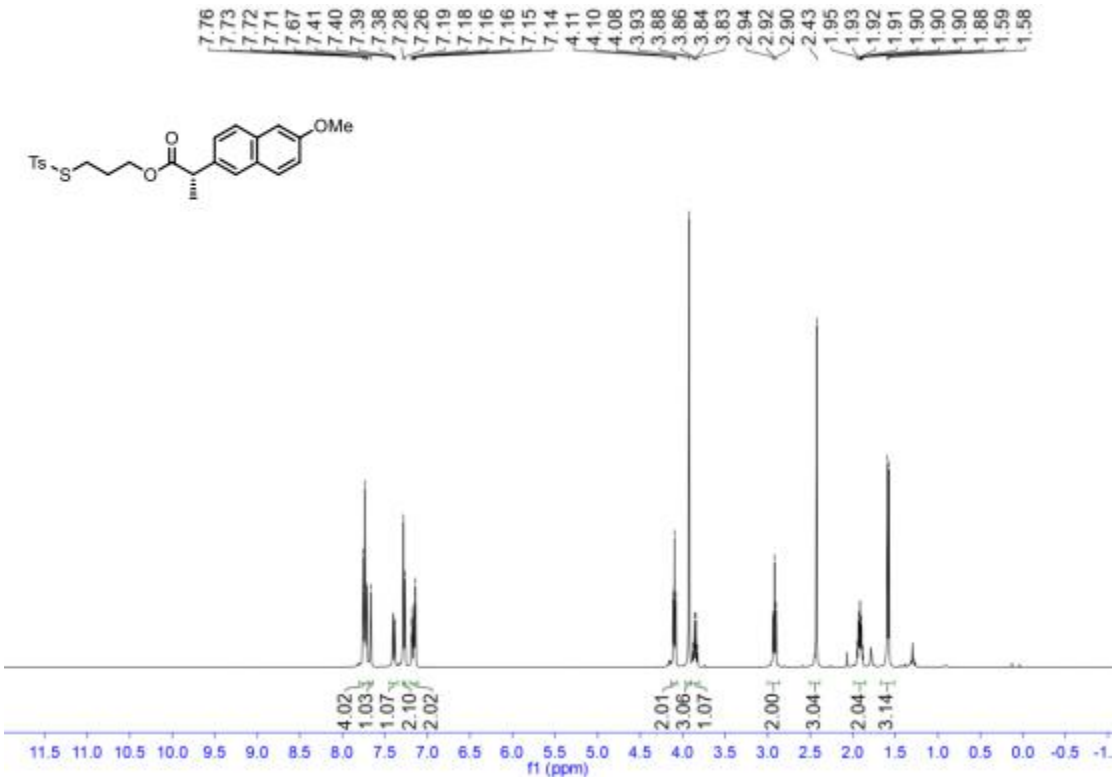
Supplementary Figure 133 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl- 1*H*-indol-3-yl)acetate **(65a)**



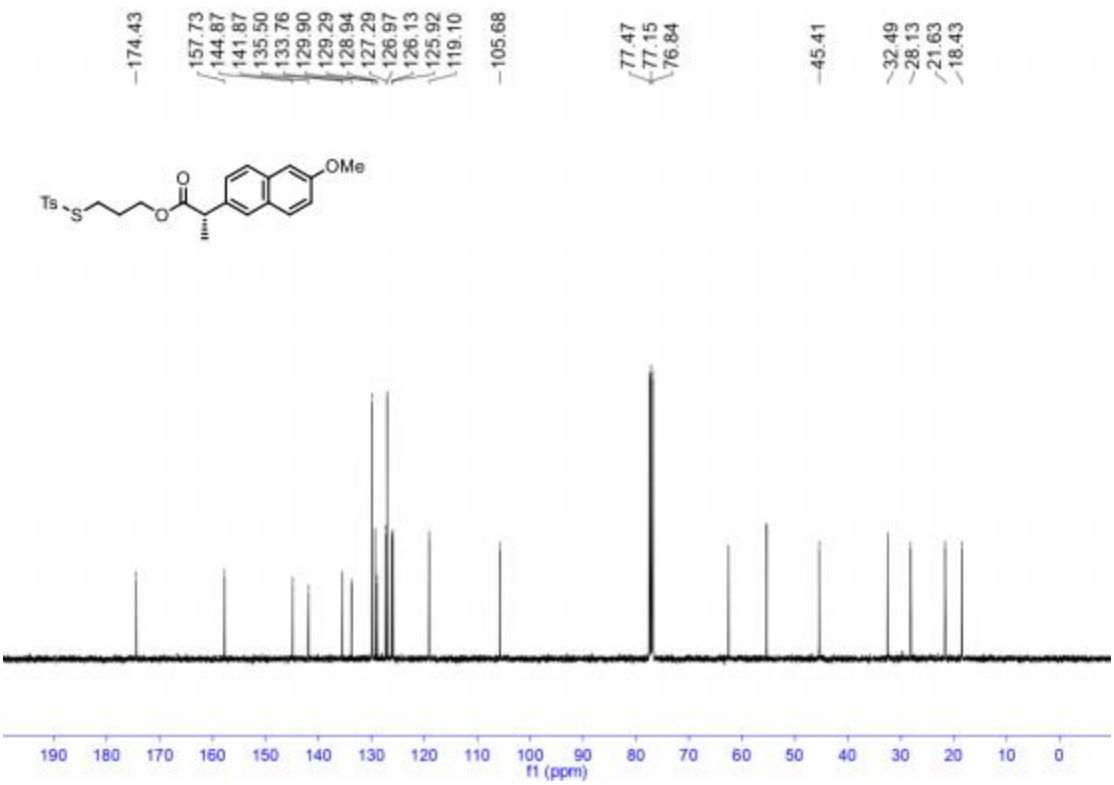
Supplementary Figure 134 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl- 1*H*-indol-3-yl)acetate **(65a)**



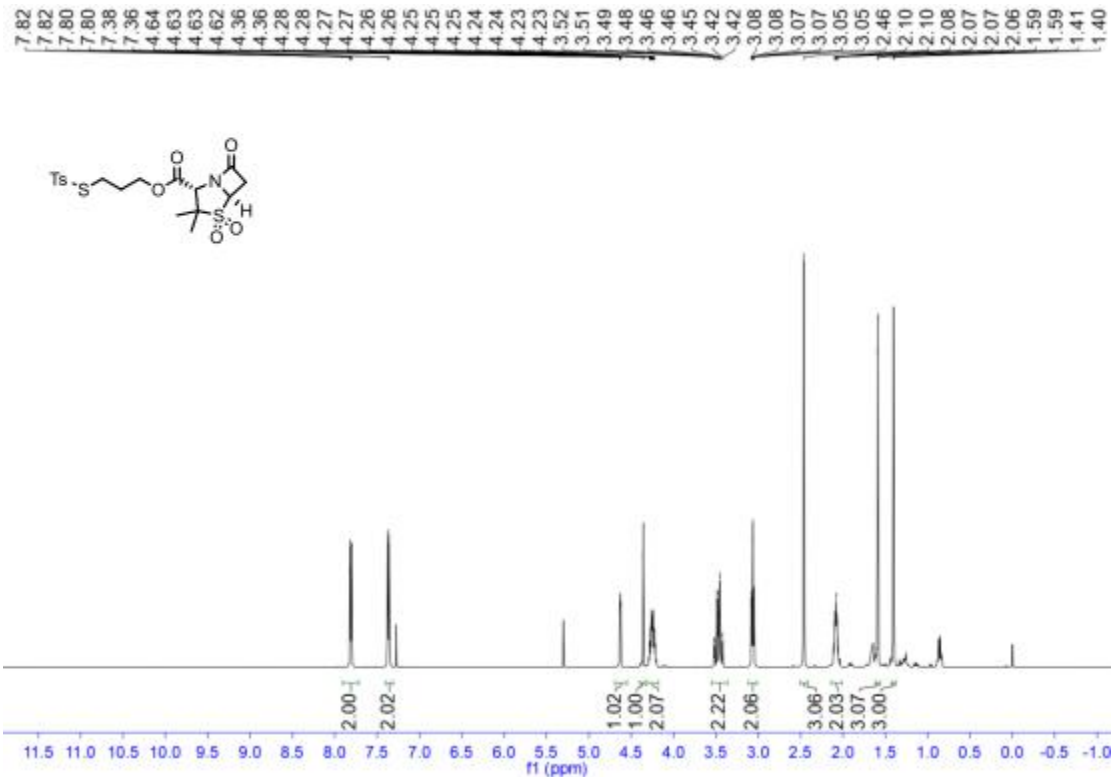
Supplementary Figure 135 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate **(66a)**



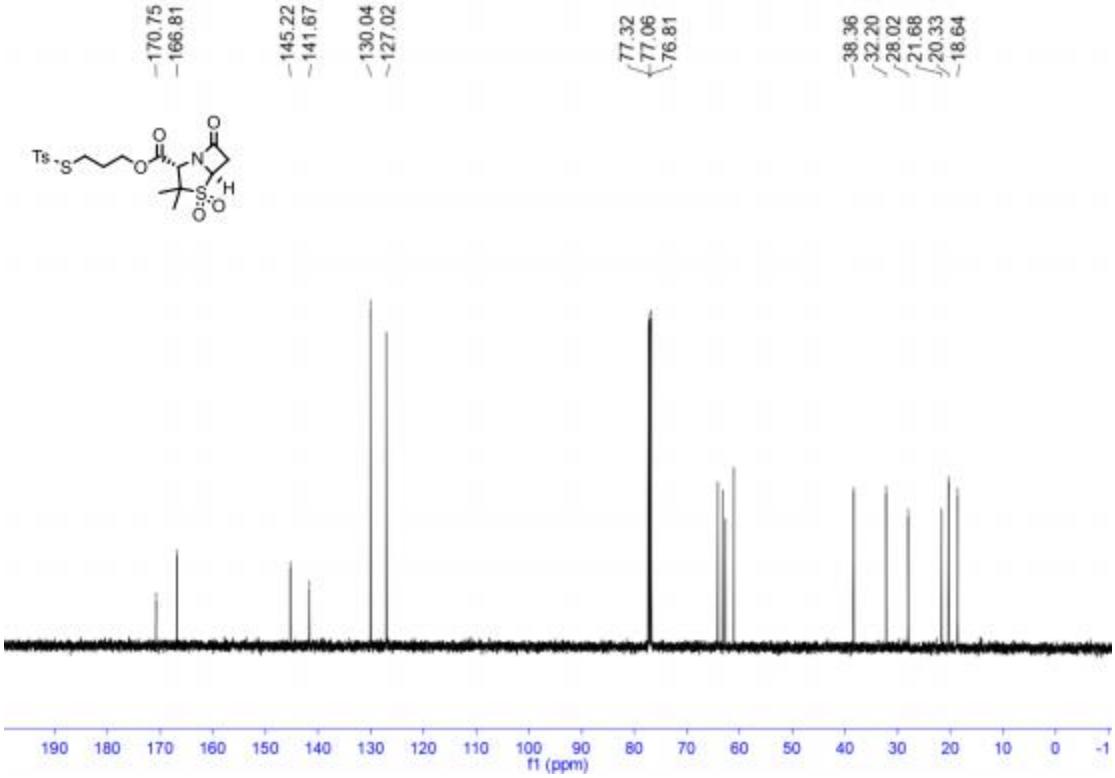
Supplementary Figure 136 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate **(66a)**



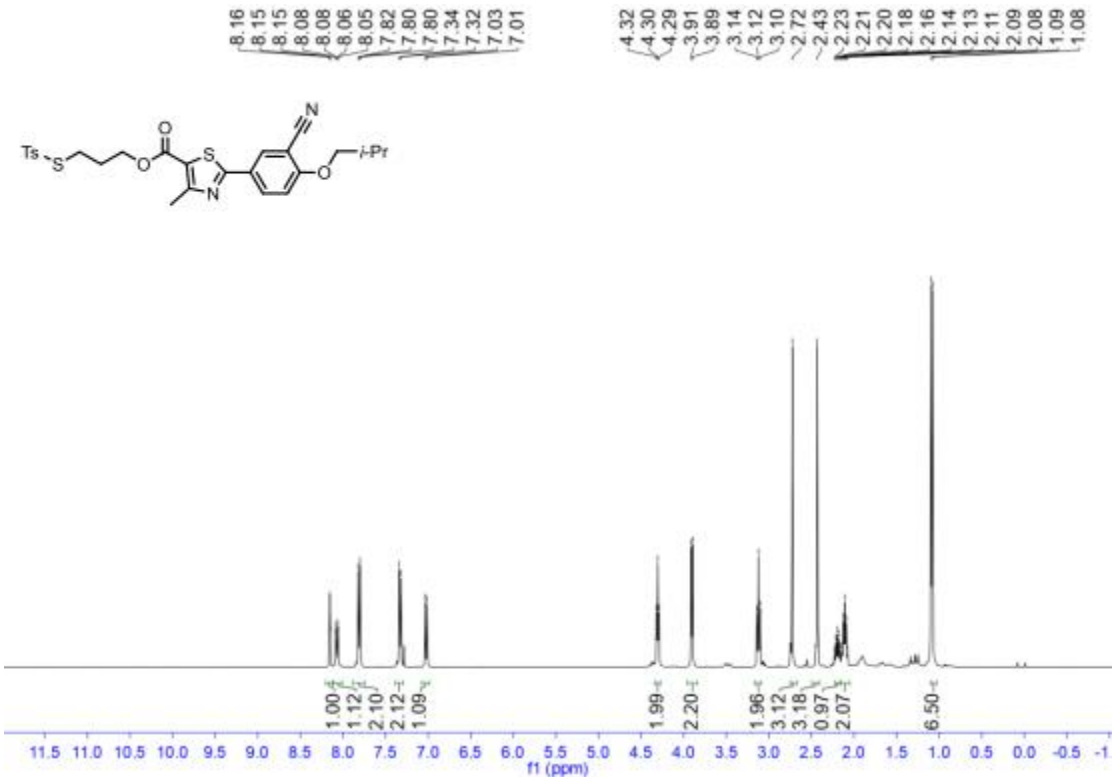
Supplementary Figure 137 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia- 1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide **(67a)**



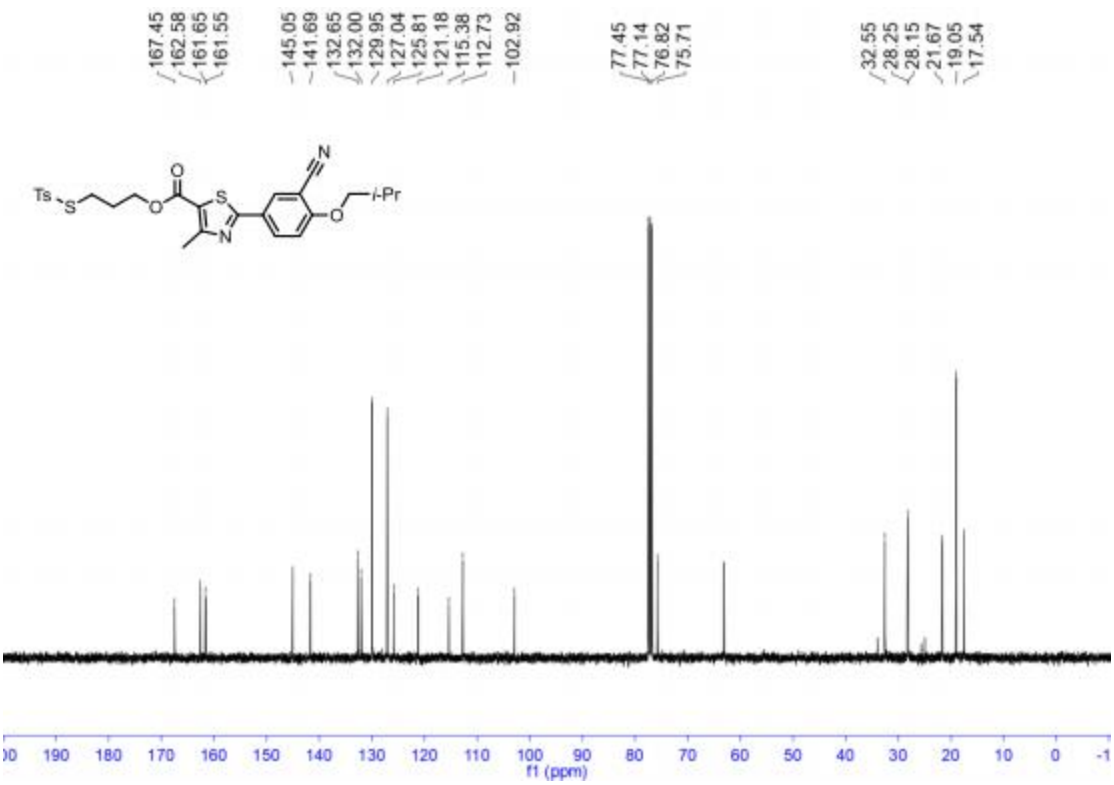
Supplementary Figure 138 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia- 1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide **(67a)**



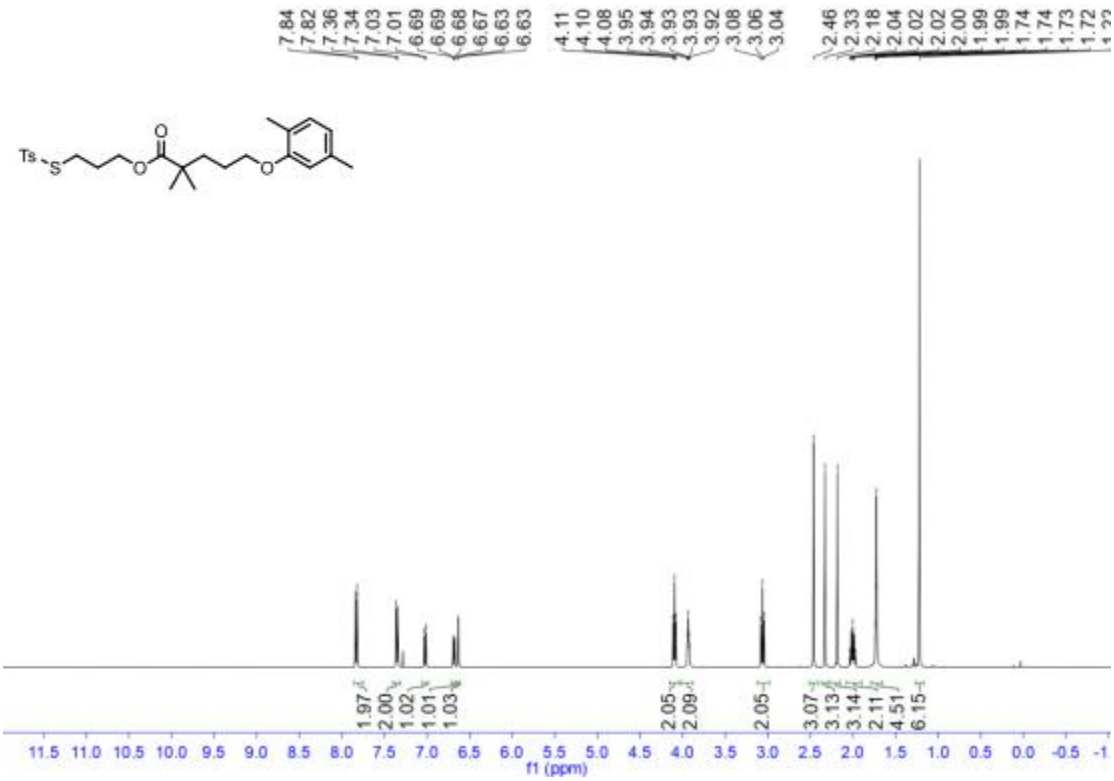
Supplementary Figure 139 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate **(68a)**



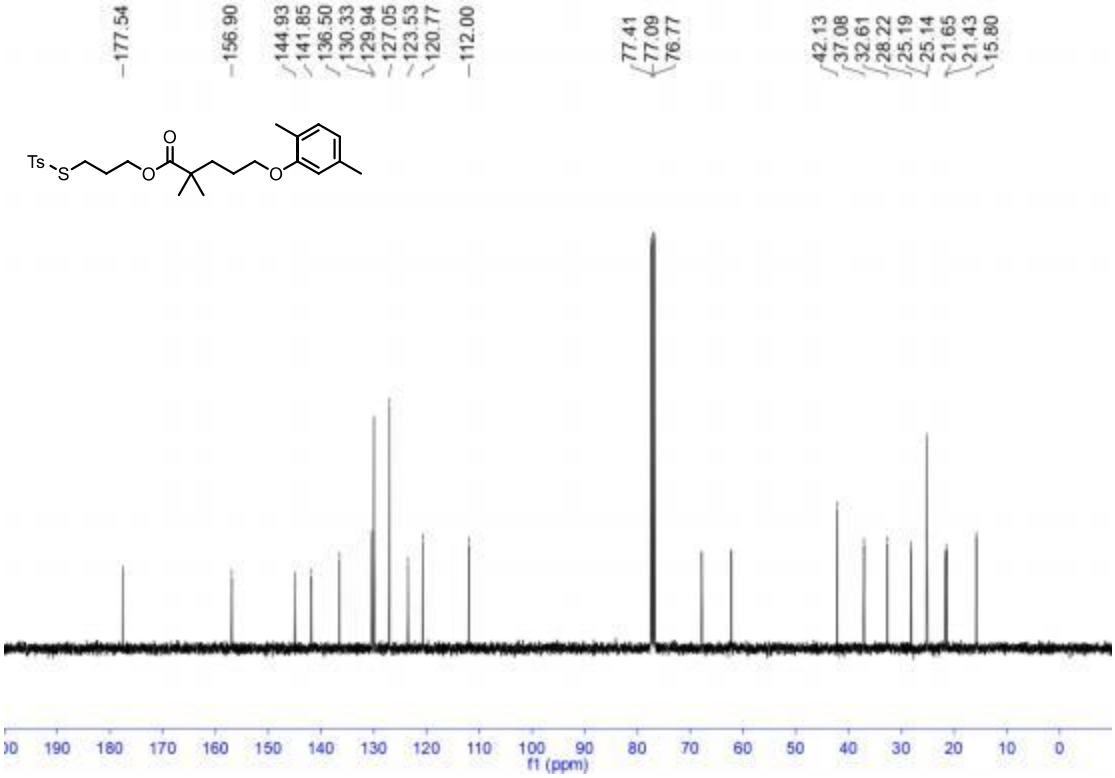
Supplementary Figure 140 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate **(68a)**



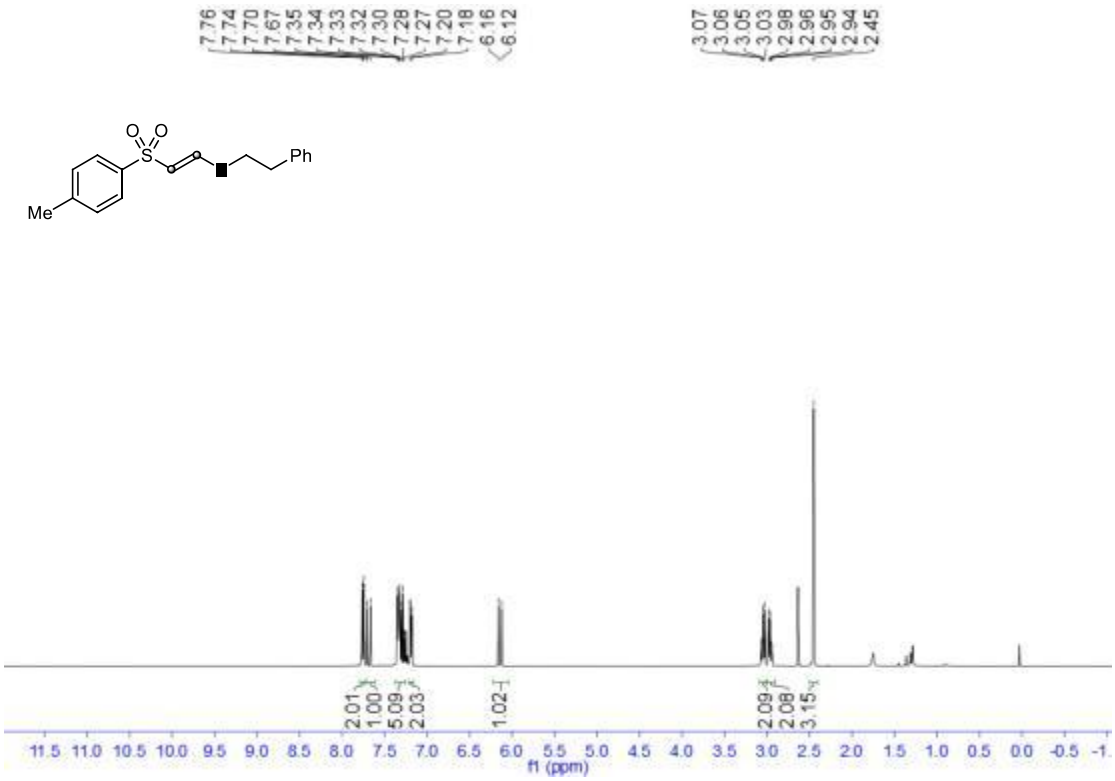
Supplementary Figure 141 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **(69a)**



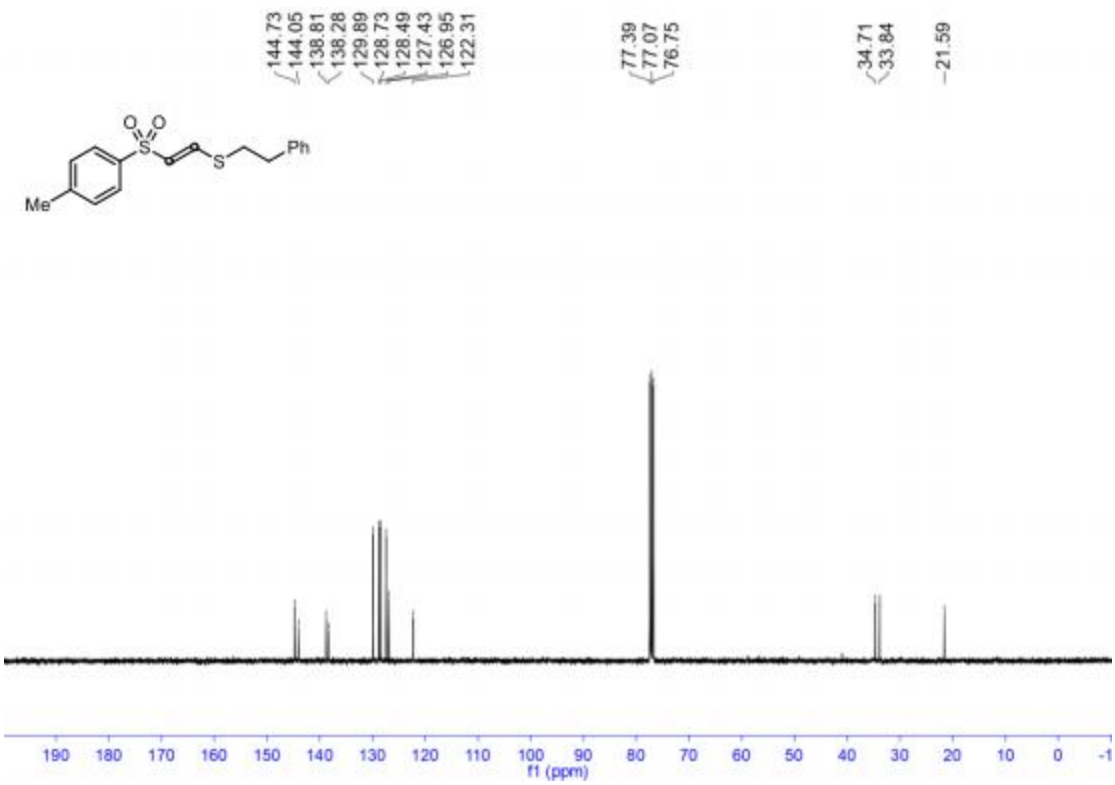
Supplementary Figure 142 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(tosylthio)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **(69a)**



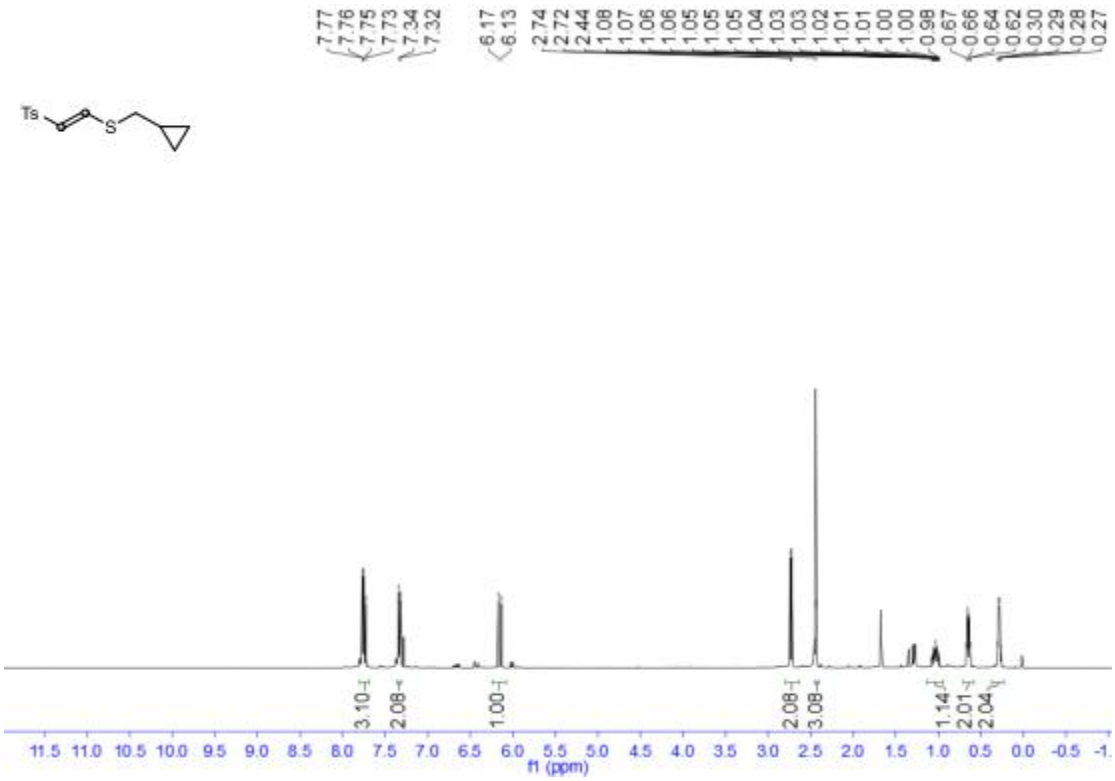
Supplementary Figure 143 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-phenethyl(2-tosylvinyl)sulfane **(3)**



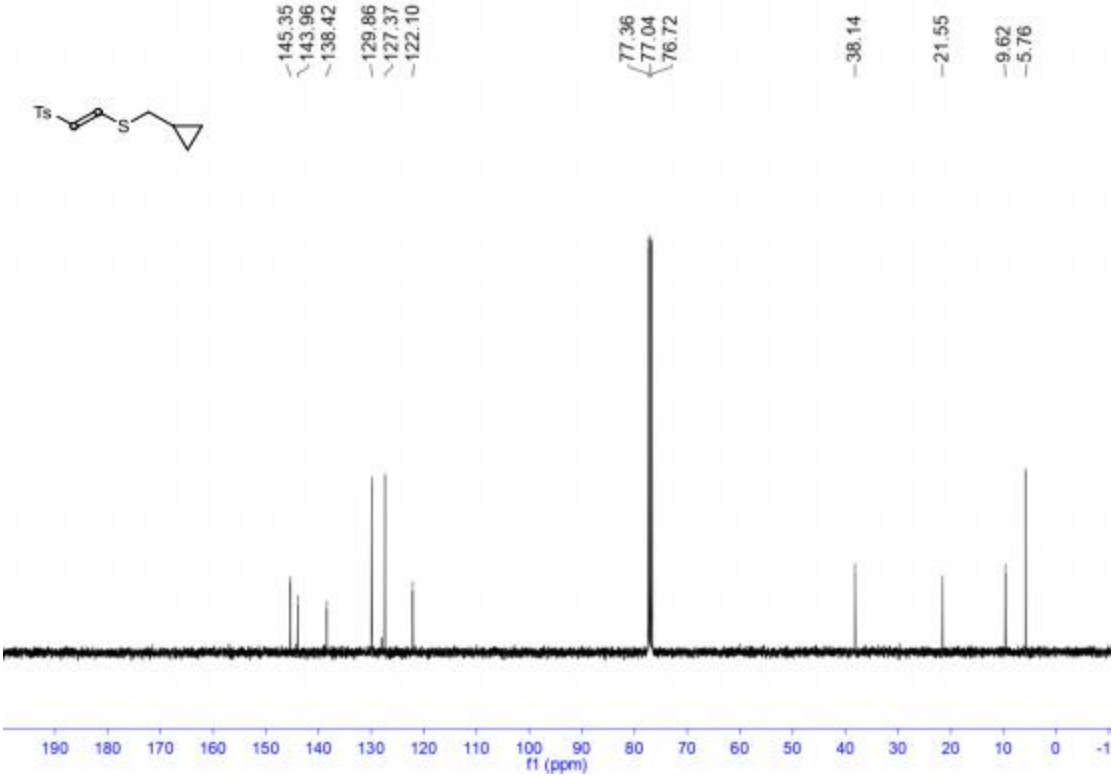
Supplementary Figure 144 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-phenethyl(2-tosylvinyl)sulfane **(3)**



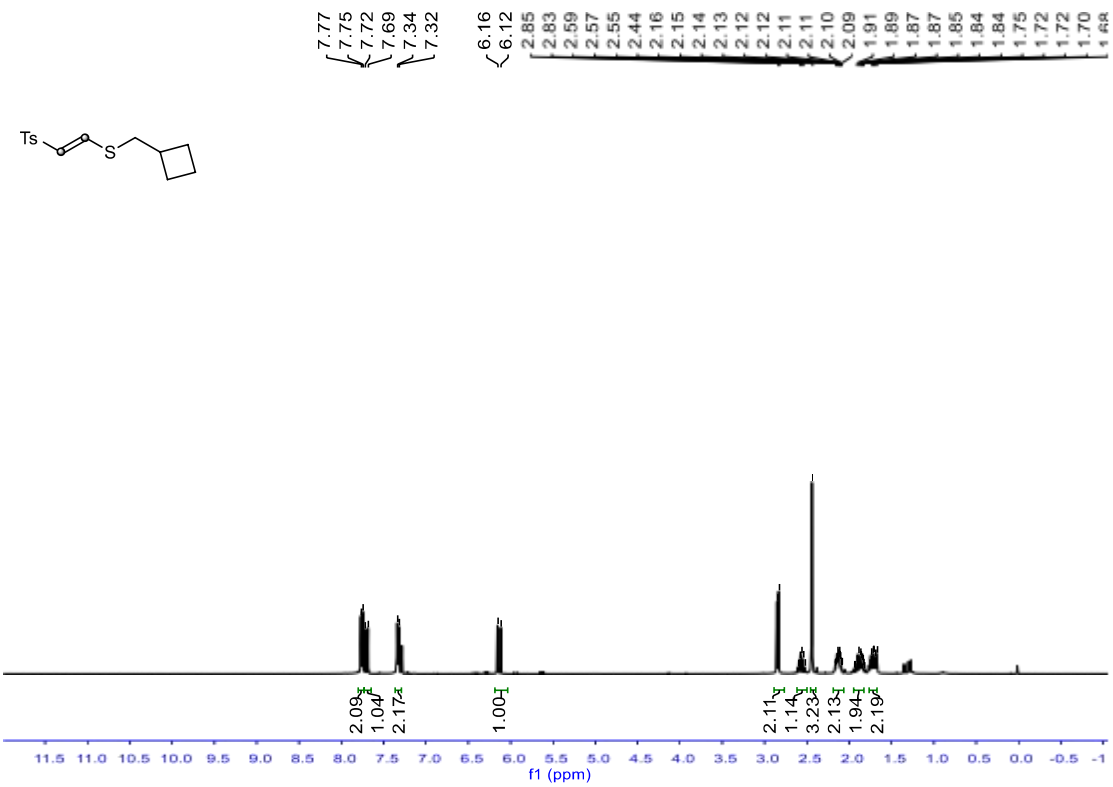
Supplementary Figure 145 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(cyclopropylmethyl)(2-tosylvinyl)sulfane **(7)**



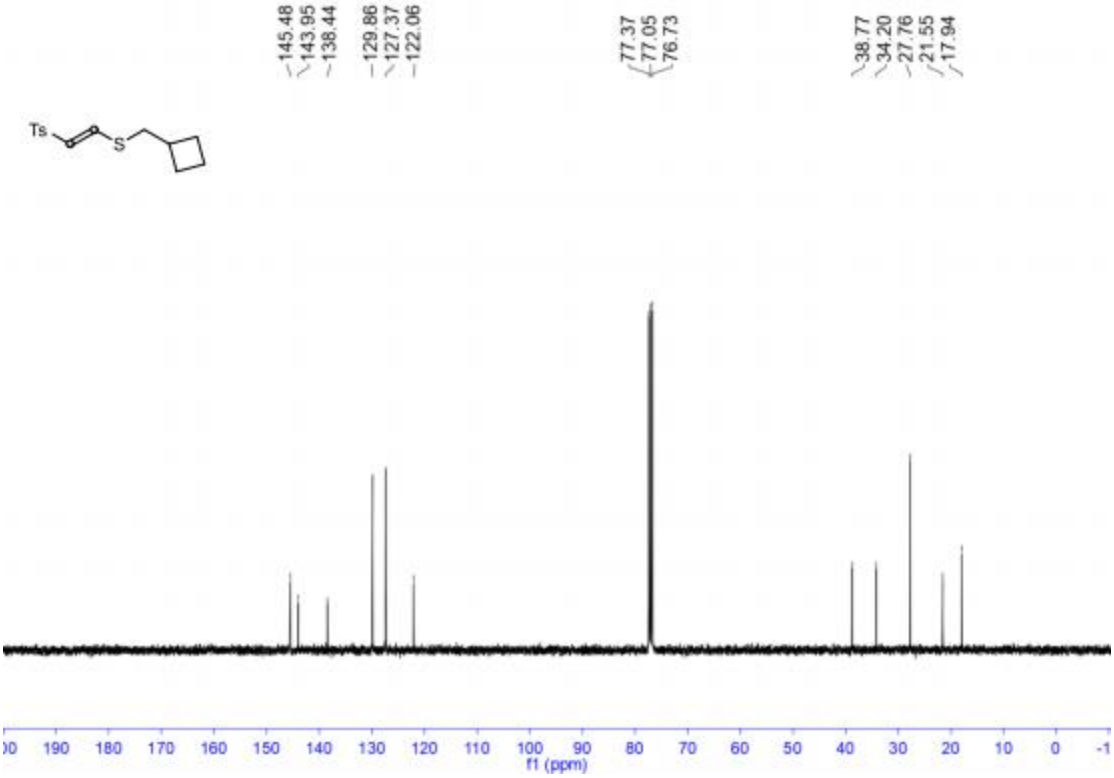
Supplementary Figure 146 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(cyclopropylmethyl)(2-tosylvinyl)sulfane **(7)**



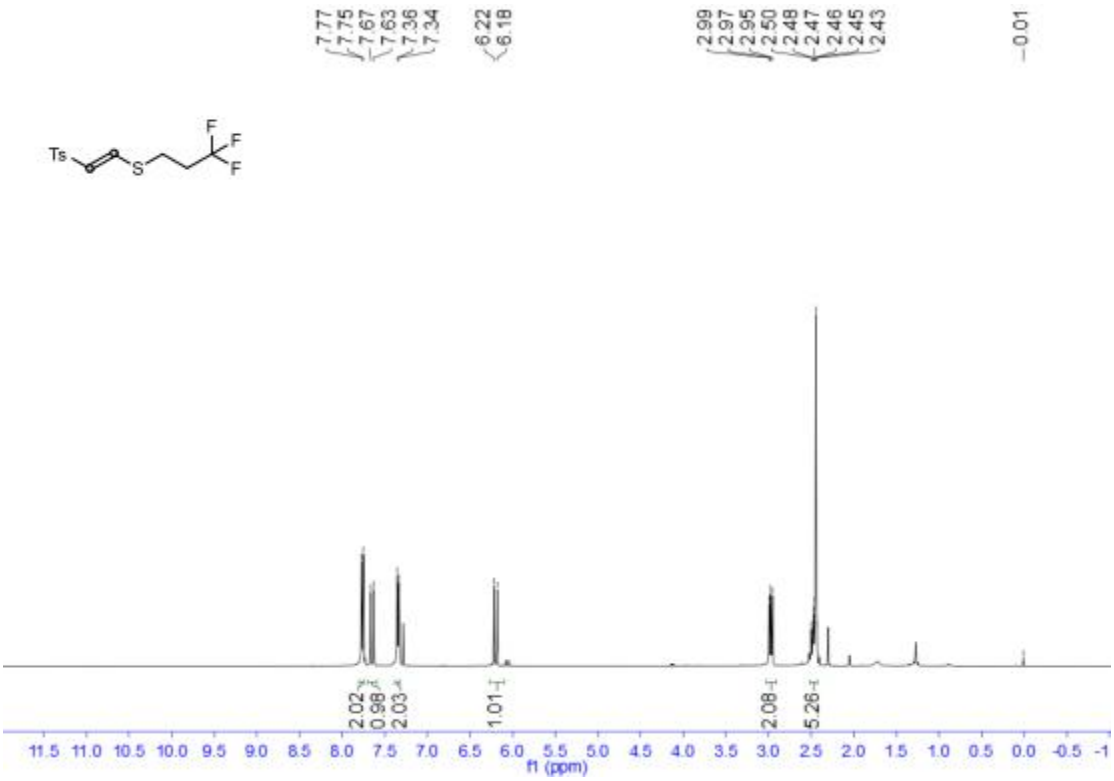
Supplementary Figure 147 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(cyclobutylmethyl)(2-tosylvinyl)sulfane **(8)**



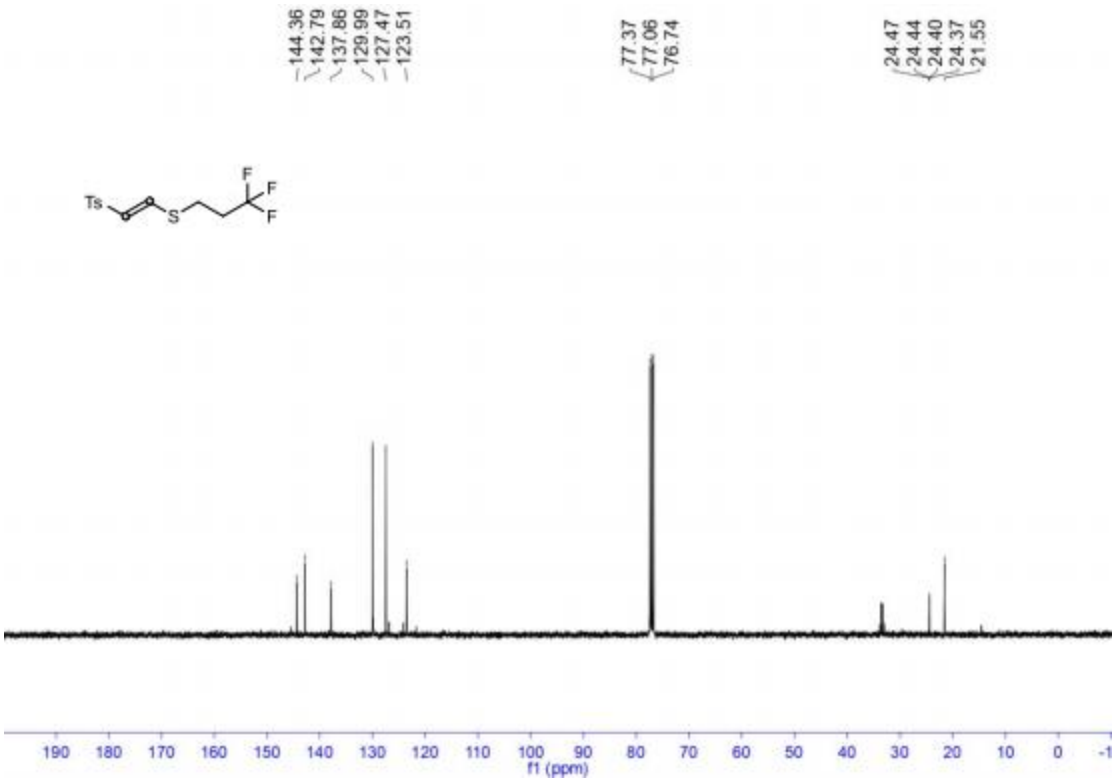
Supplementary Figure 148 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(cyclobutylmethyl)(2-tosylvinyl)sulfane **(8)**



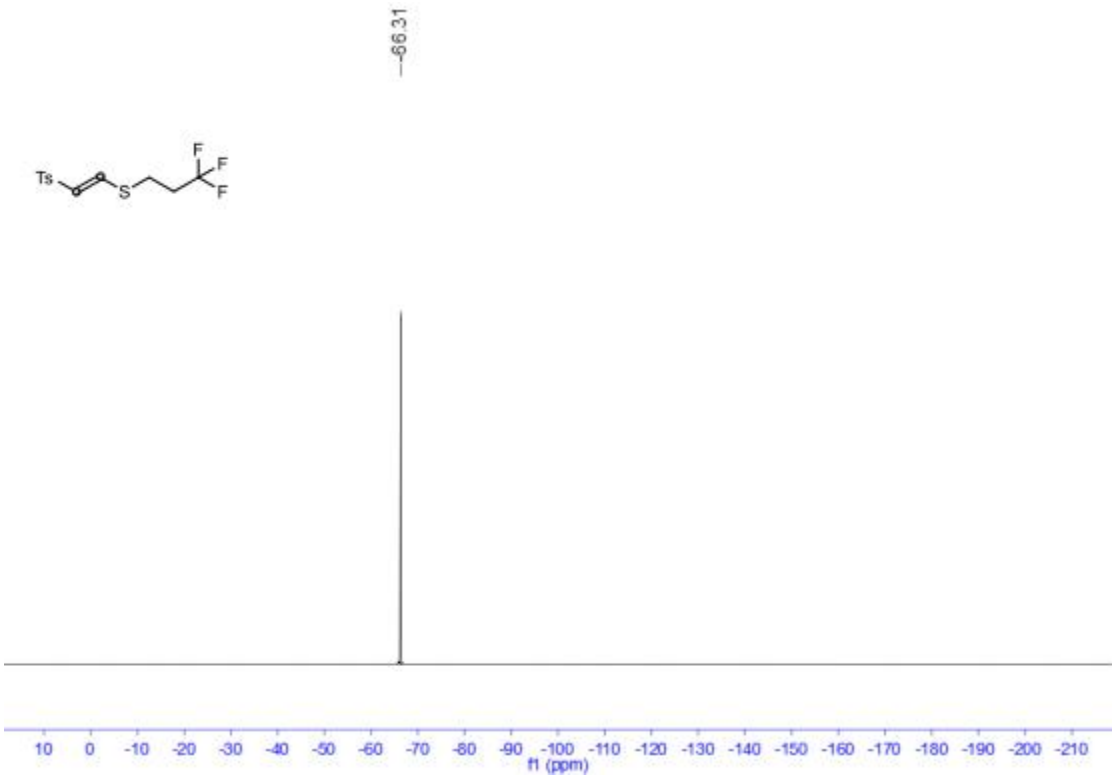
Supplementary Figure 149 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(2-tosylvinyl)(3,3,3-trifluoropropyl)sulfane **(9)**



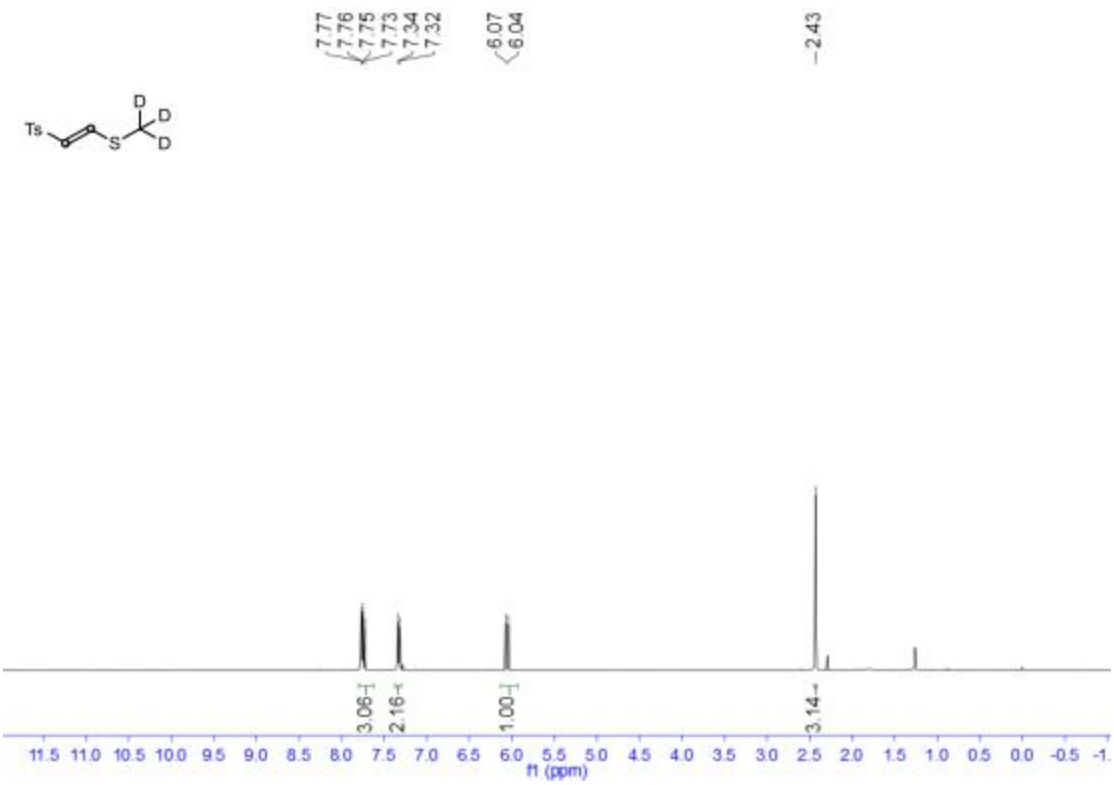
Supplementary Figure 150 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(2-tosylvinyl)(3,3,3-trifluoropropyl)sulfane **(9)**



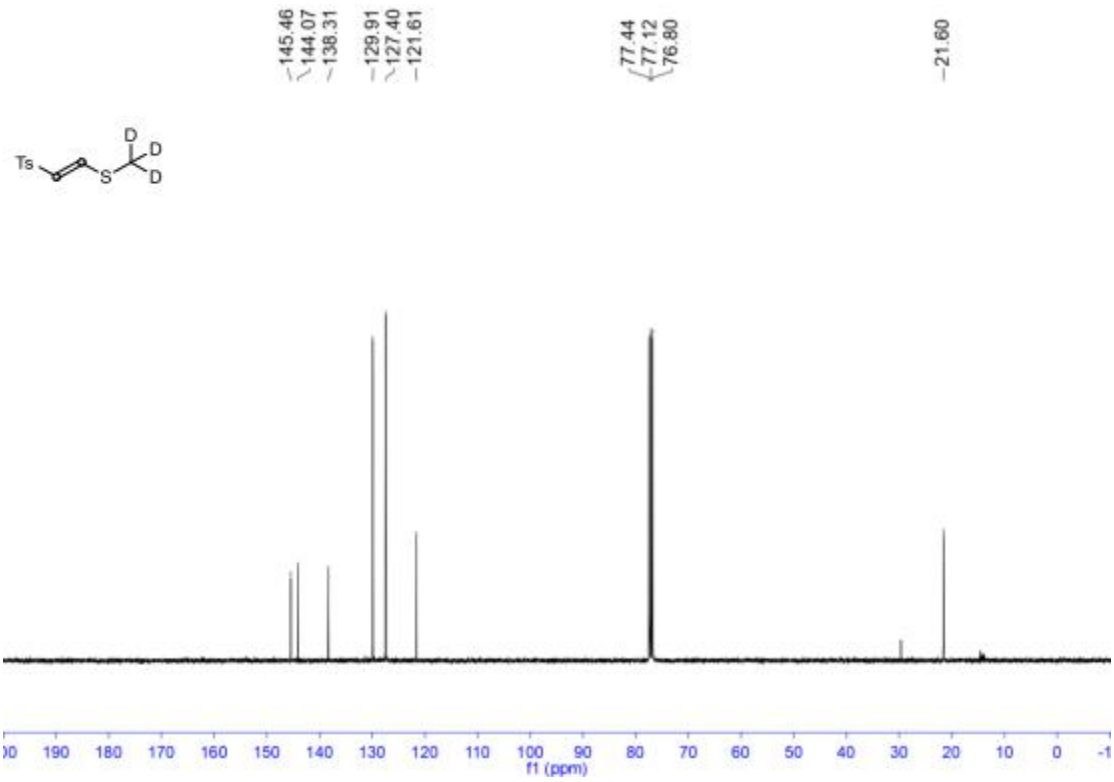
Supplementary Figure 151 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of (*E*)-(2-tosylvinyl)(3,3,3-trifluoropropyl)sulfane **(9)**



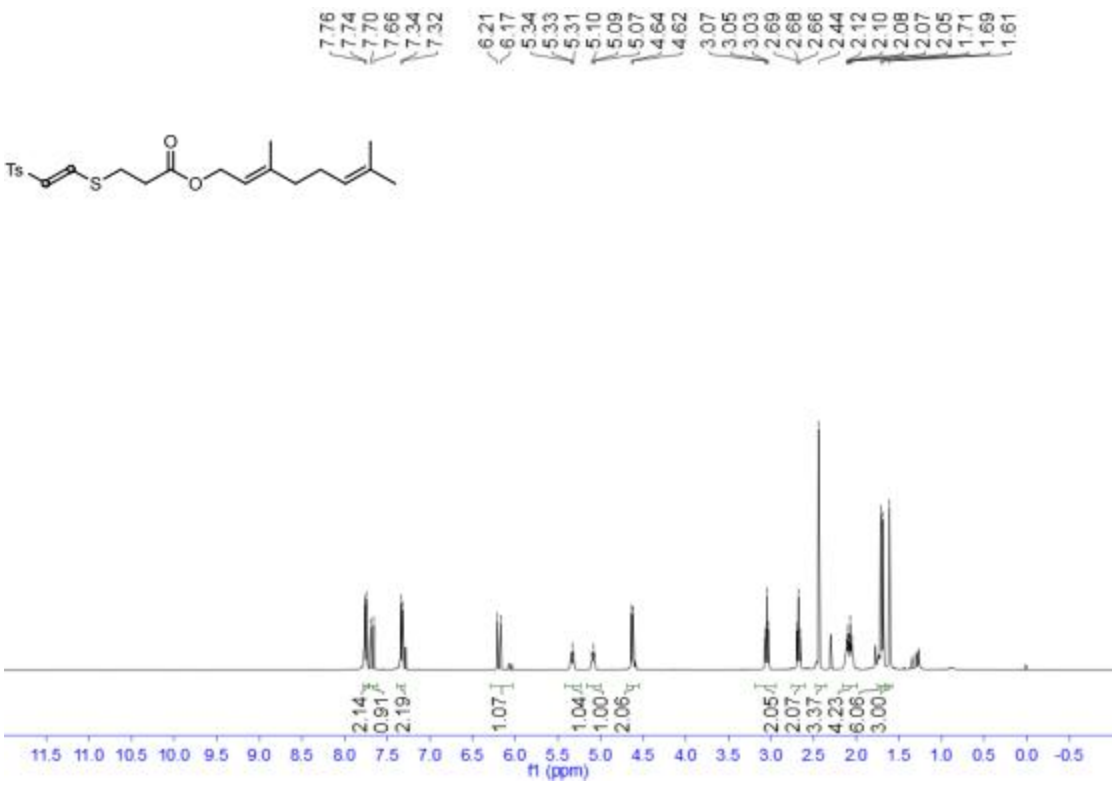
Supplementary Figure 152 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(methyl-d_3)(2-tosylvinyl)sulfane **(10)**



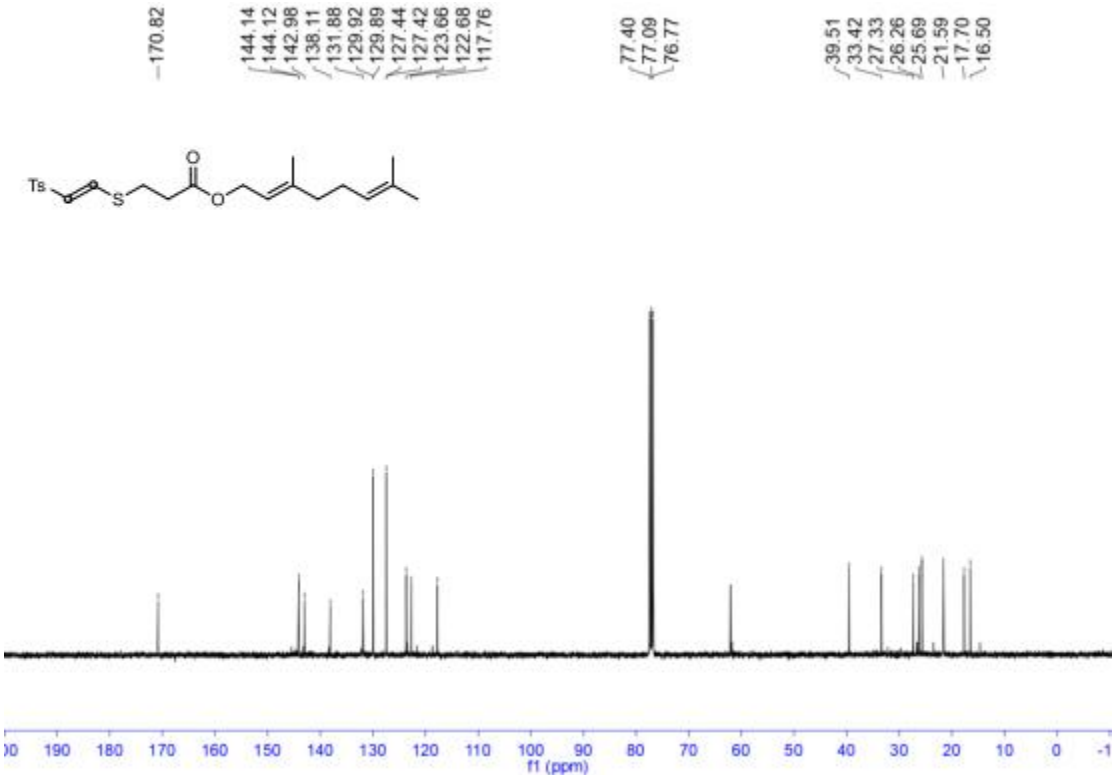
Supplementary Figure 153 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(methyl-d_3)(2-tosylvinyl)sulfane **(10)**



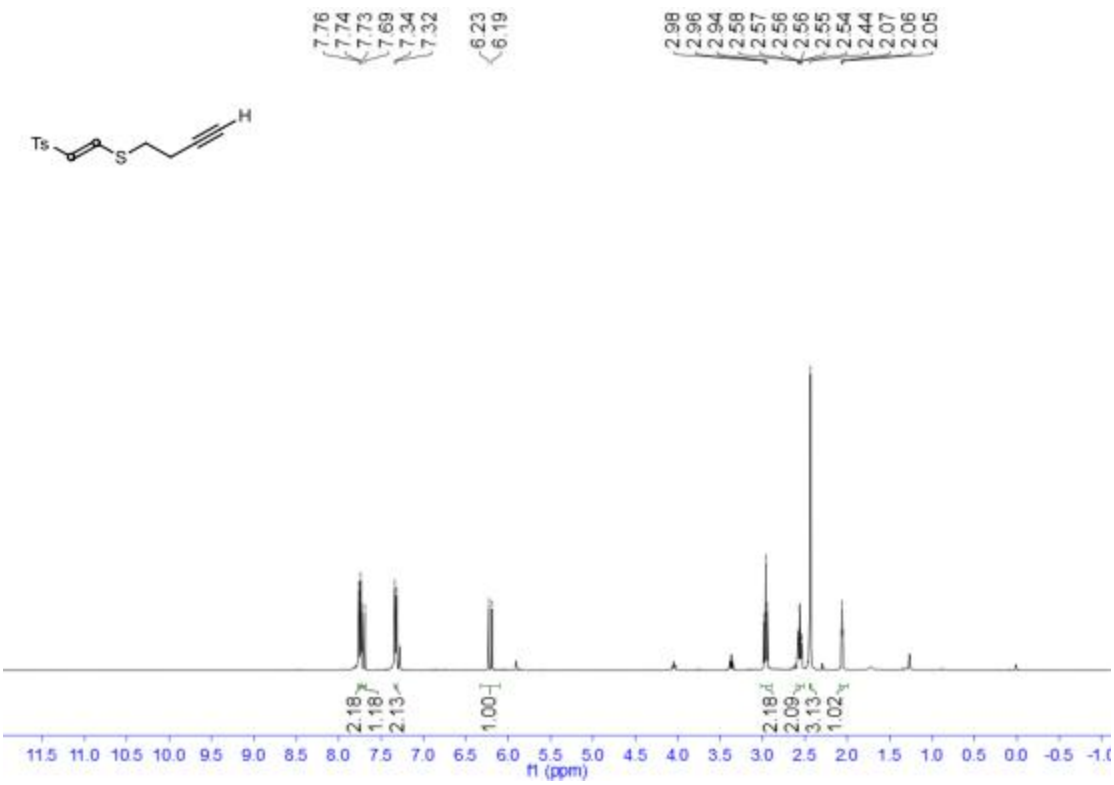
Supplementary Figure 154 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3,7-dimethylocta-2,6-dien- 1-yl 3-(((*E*)-2-tosylvinyl)thio)propanoate **(11)**



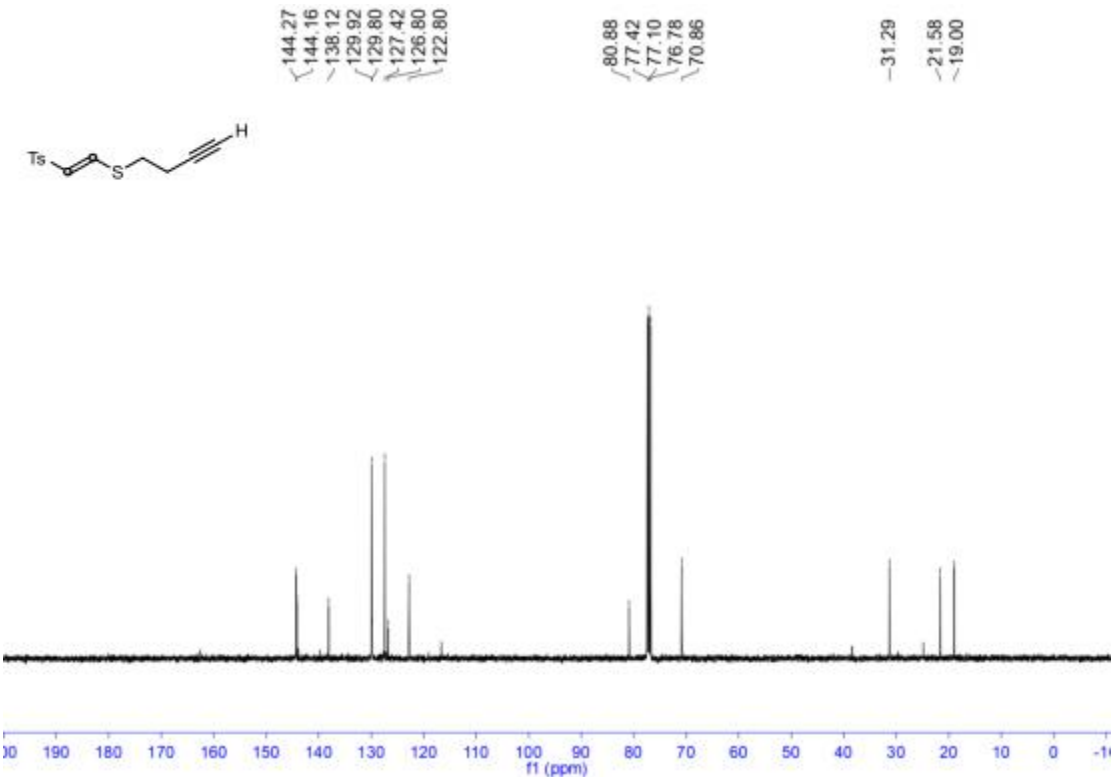
Supplementary Figure 155 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3,7-dimethylocta-2,6-dien- 1-yl 3-(((*E*)-2-tosylvinyl)thio)propanoate **(11)**



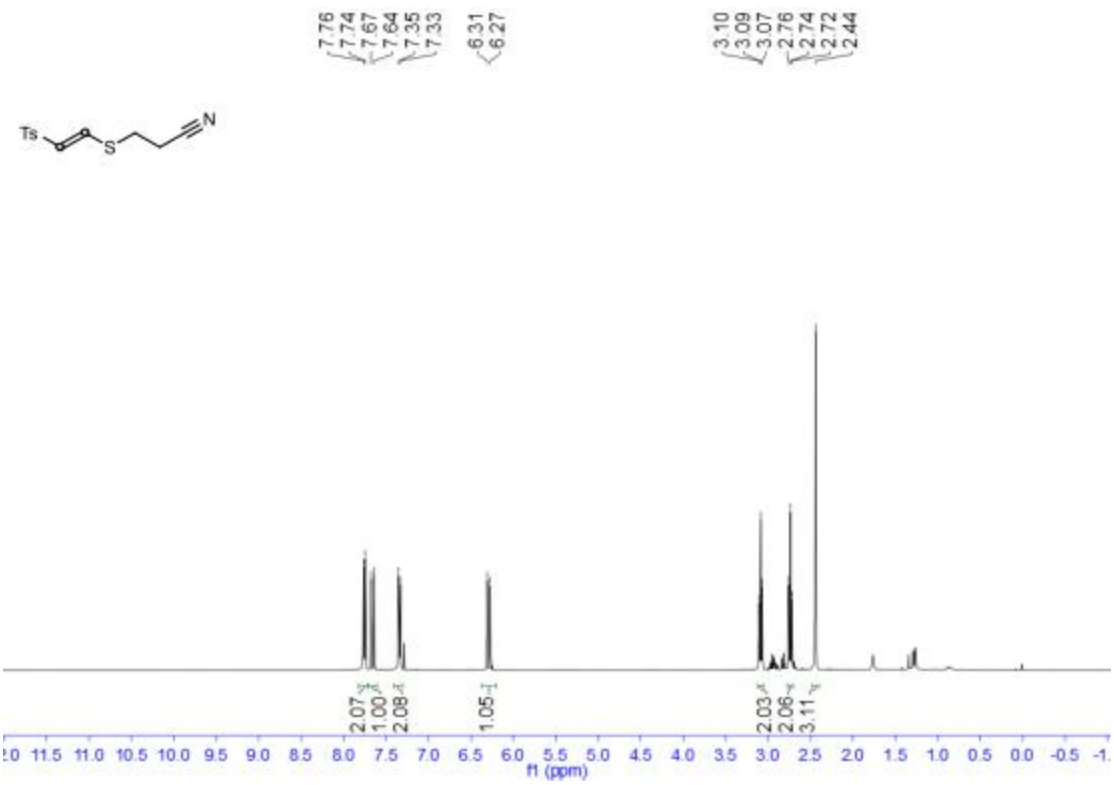
Supplementary Figure 156 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-but-3-yn- 1-yl(2-tosylvinyl)sulfane **(12)**



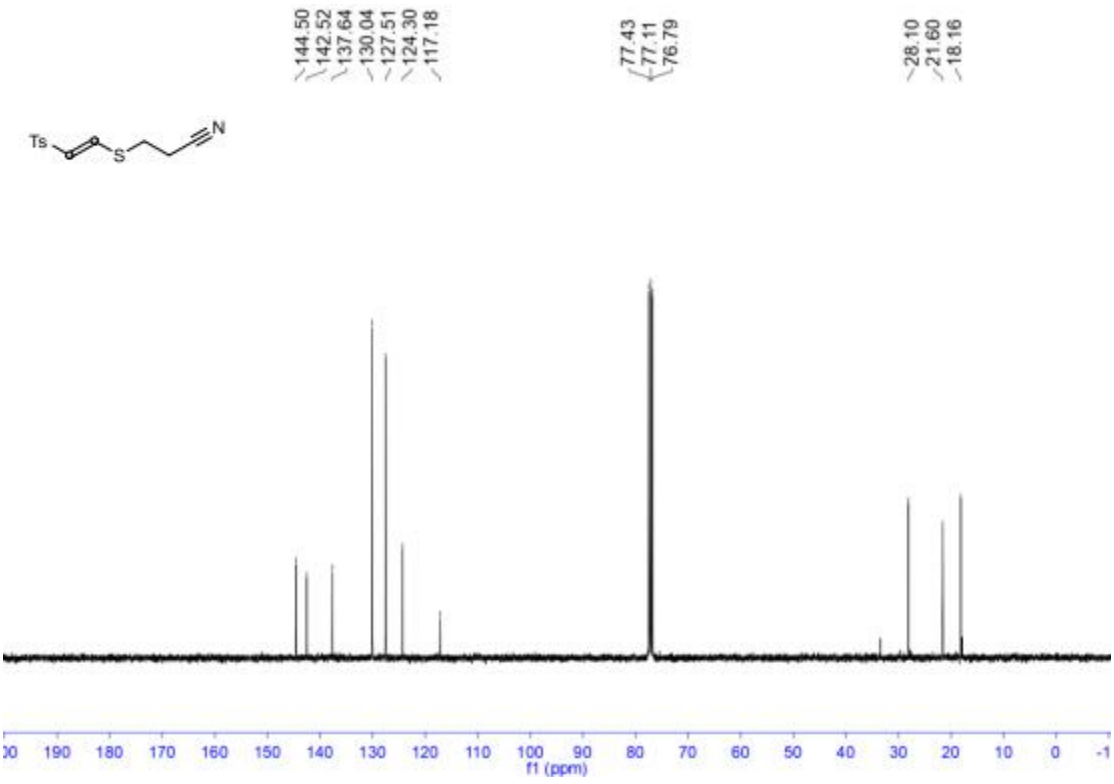
Supplementary Figure 157 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-but-3-yn- 1-yl(2-tosylvinyl)sulfane **(12)**



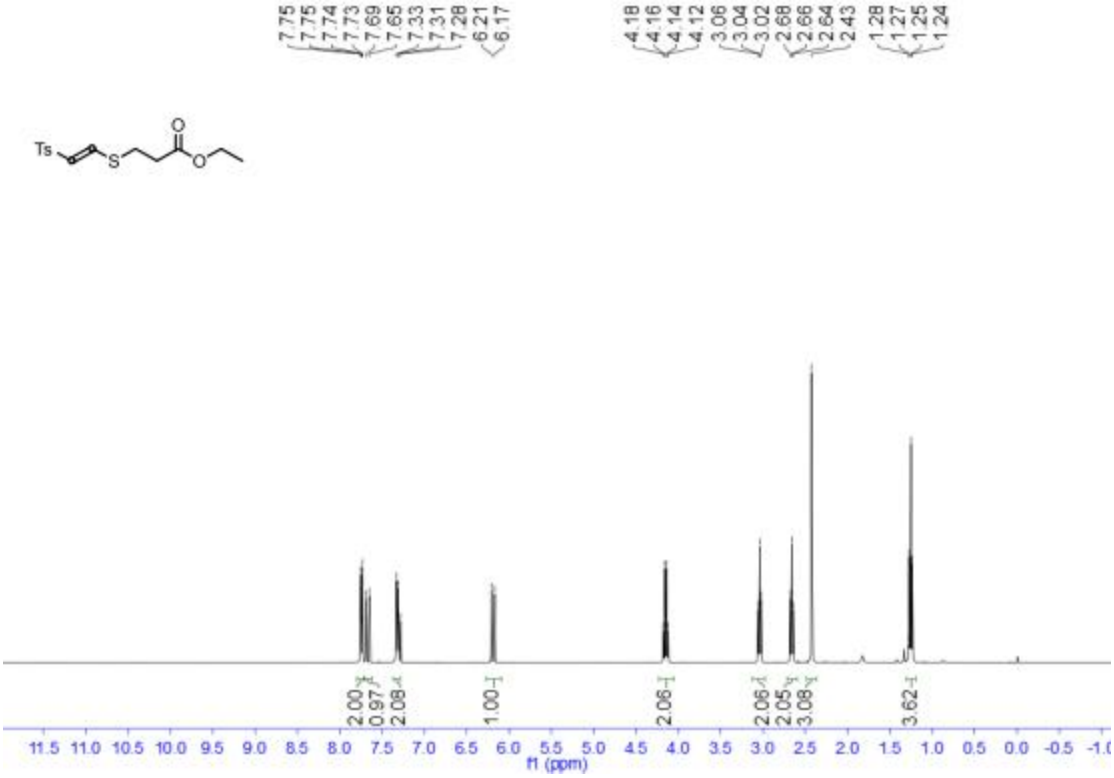
Supplementary Figure 158 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propanenitrile **(13)**



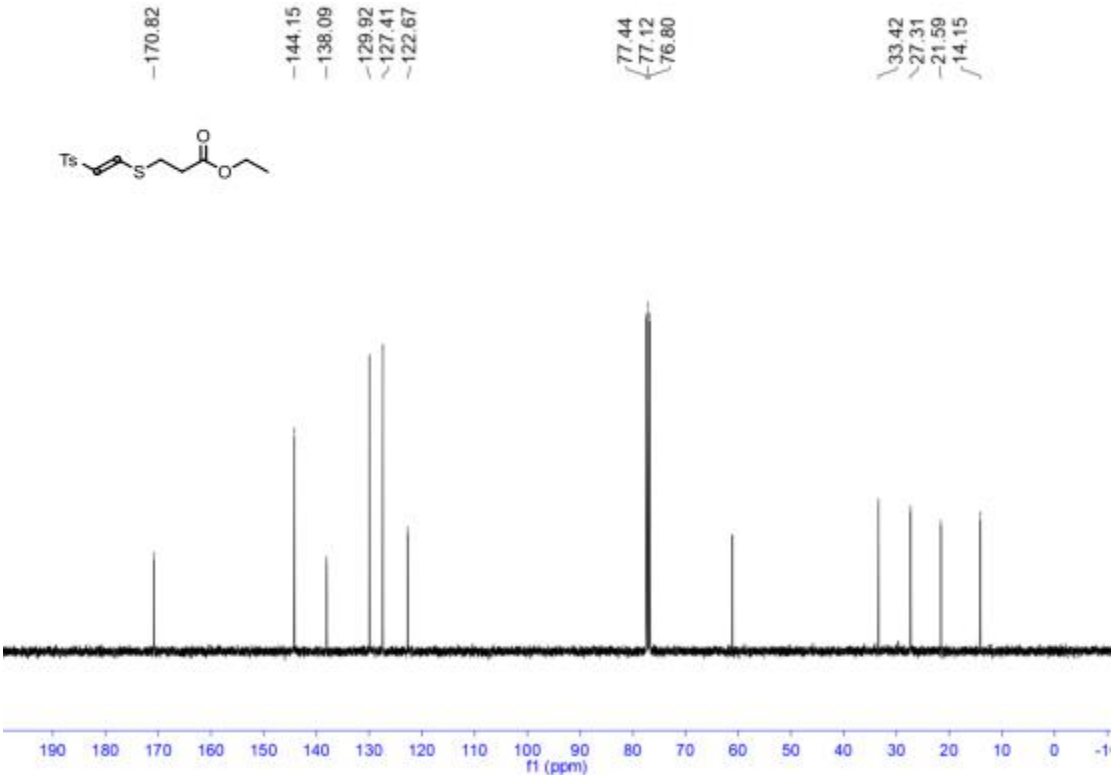
Supplementary Figure 159 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propanenitrile **(13)**



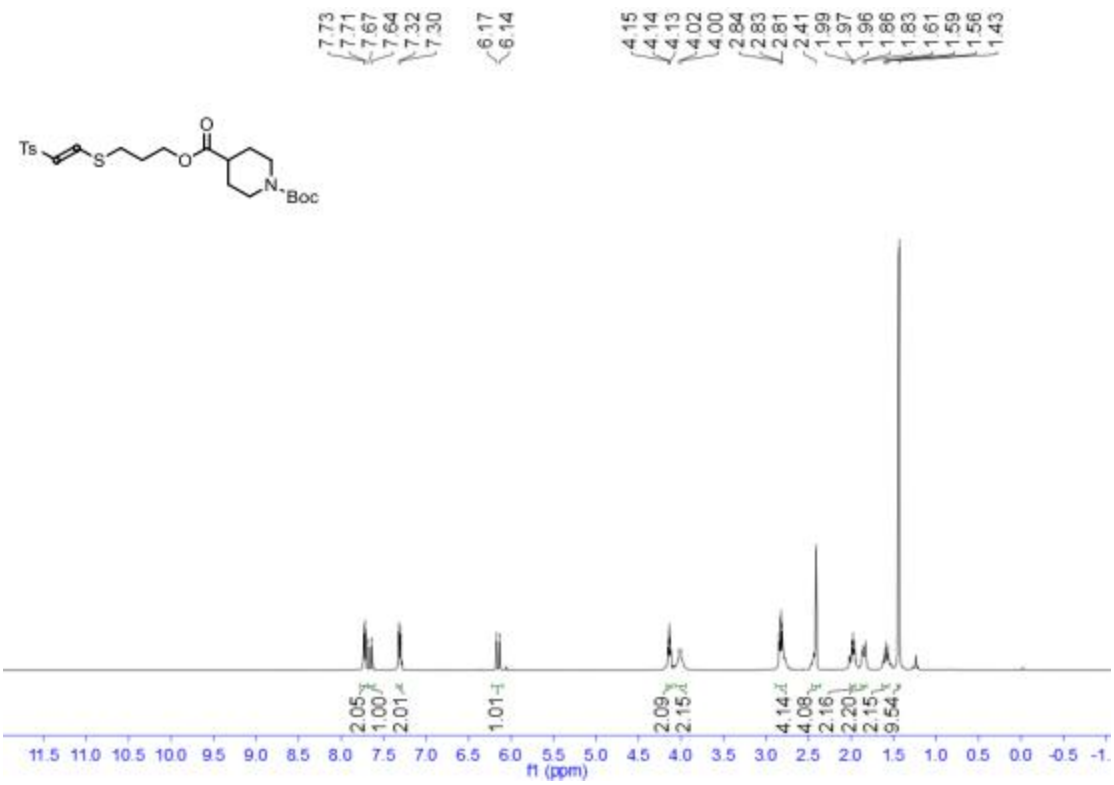
Supplementary Figure 160 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of ethyl (*E*)-3-((2-tosylvinyl)thio)propanoate **(14)**



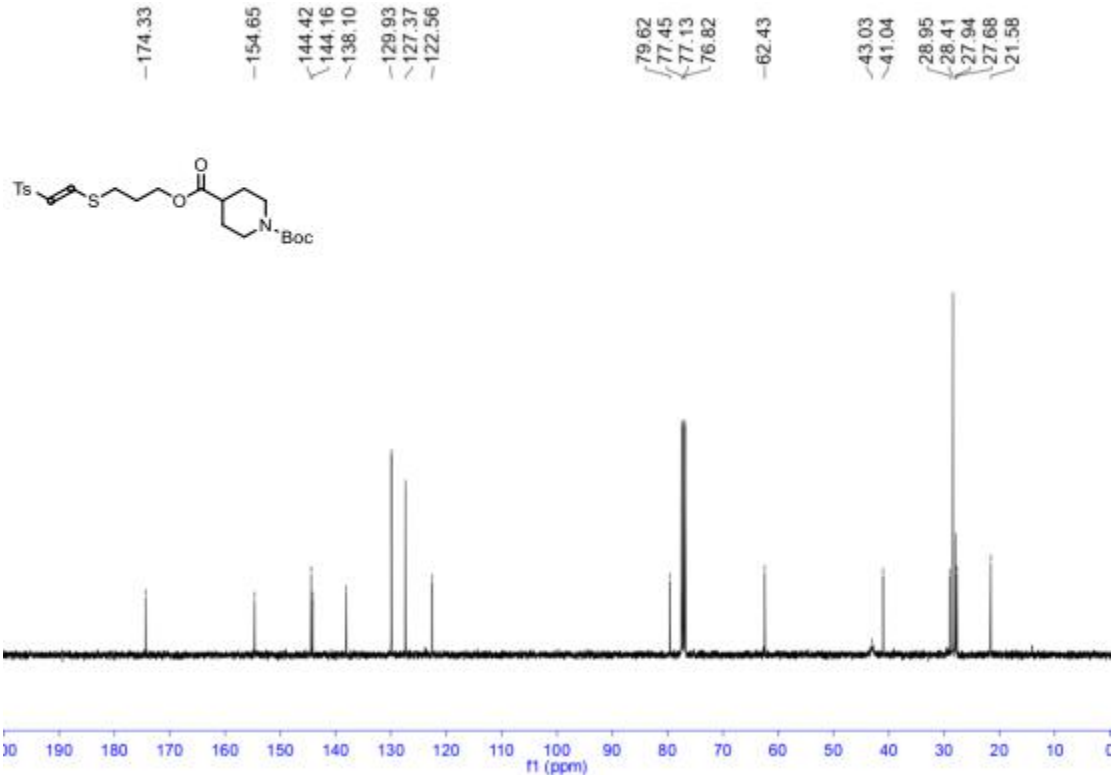
Supplementary Figure 161 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of ethyl (*E*)-3-((2-tosylvinyl)thio)propanoate **(14)**



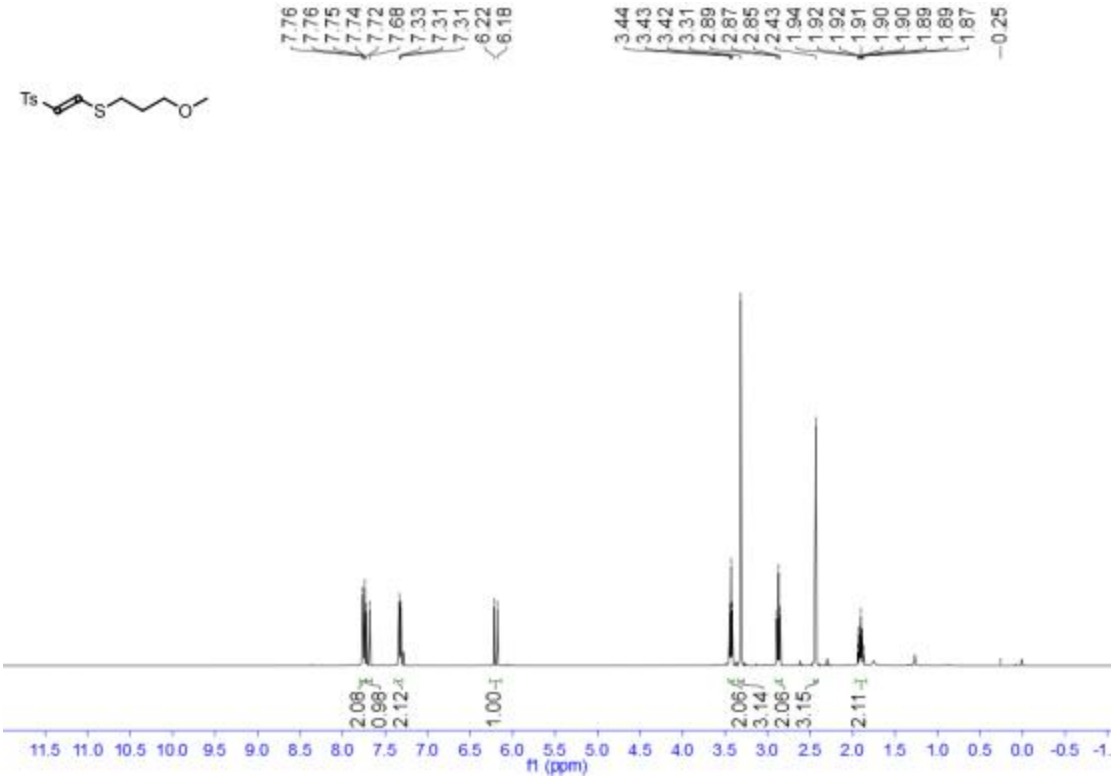
Supplementary Figure 162 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)- 1-(*tert*-butyl) 4-(3-((2-tosylvinyl)thio)Propyl) piperidine- 1,4-dicarboxylate **(15)**



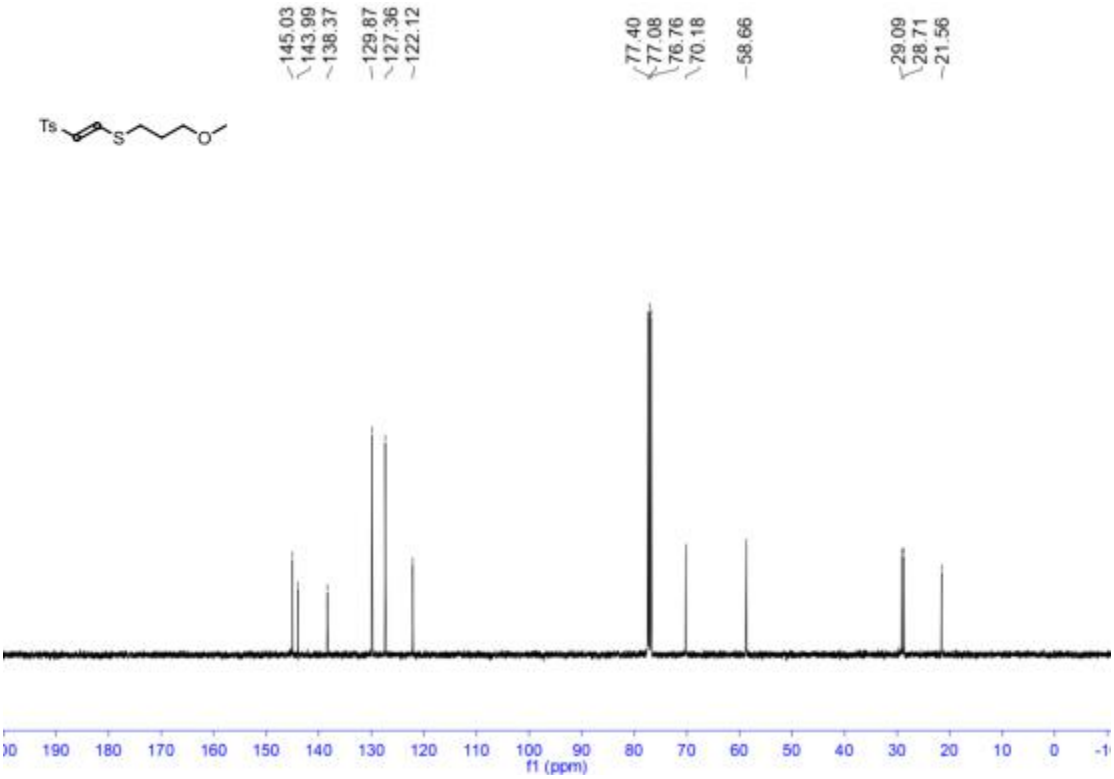
Supplementary Figure 163 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)- 1-(*tert*-butyl) 4-(3-((2-tosylvinyl)thio)Propyl) piperidine- 1,4-dicarboxylate **(15)**



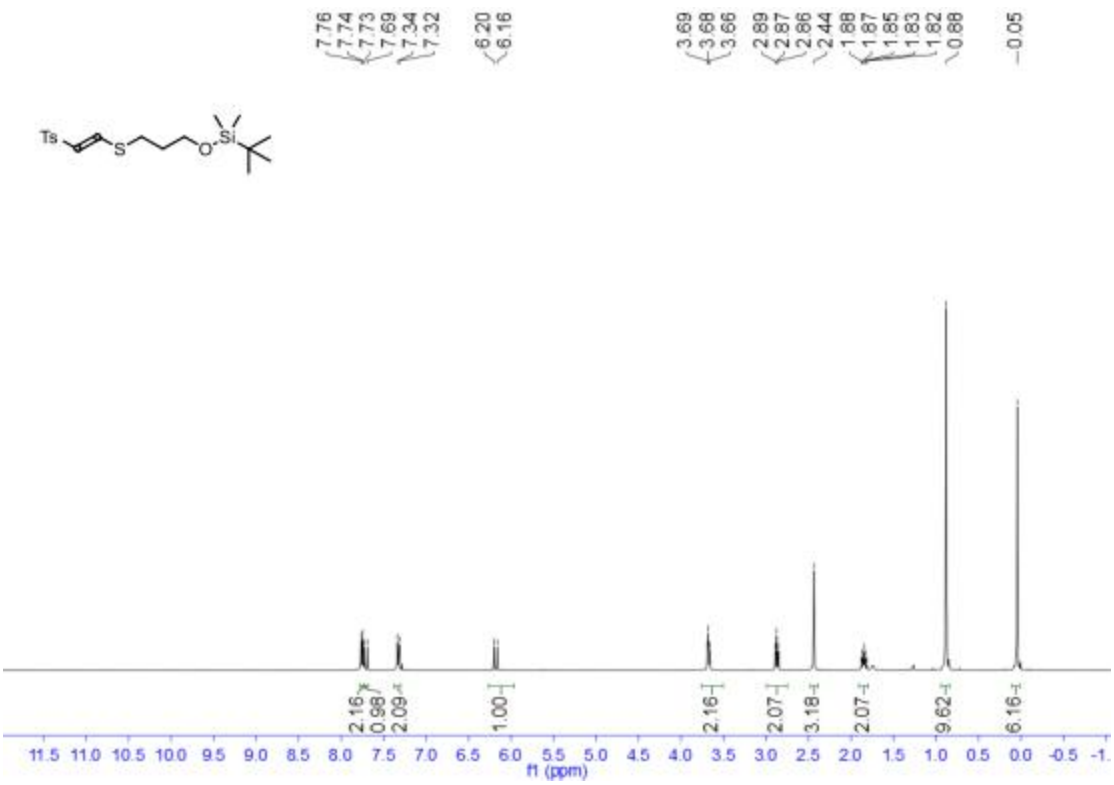
Supplementary Figure 164 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(3-methoxypropyl)(2-tosylvinyl)sulfane **(16)**



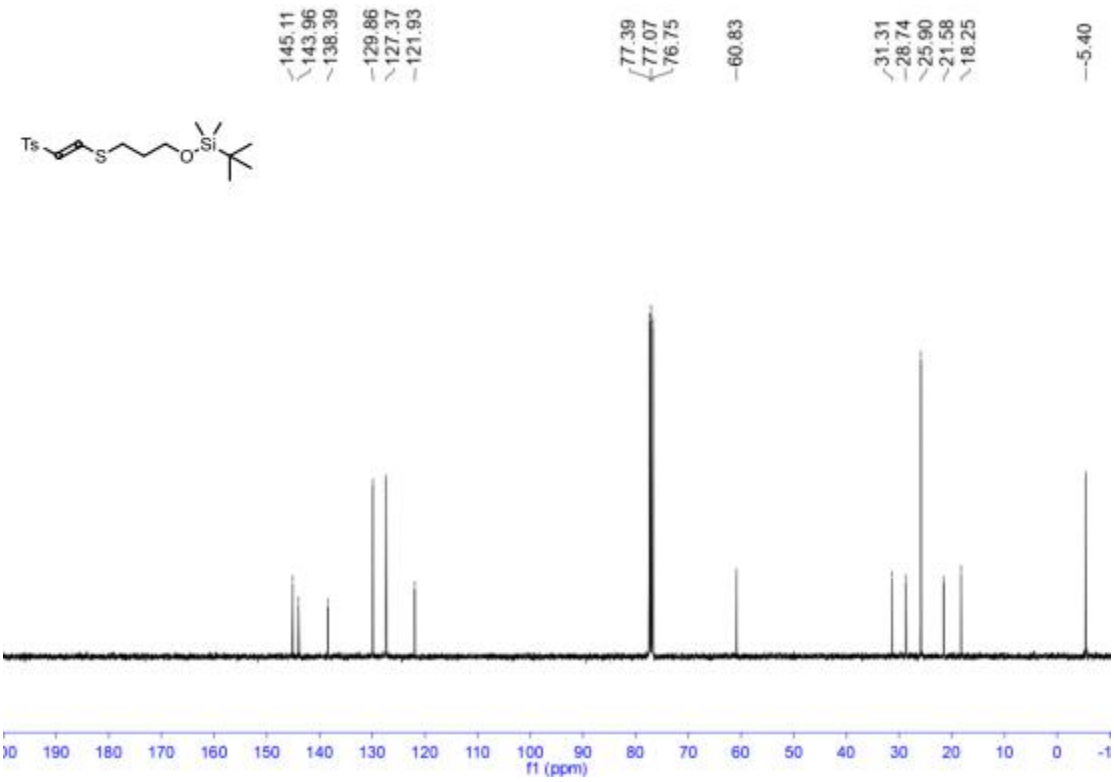
Supplementary Figure 165 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(3-methoxypropyl)(2-tosylvinyl)sulfane **(16)**



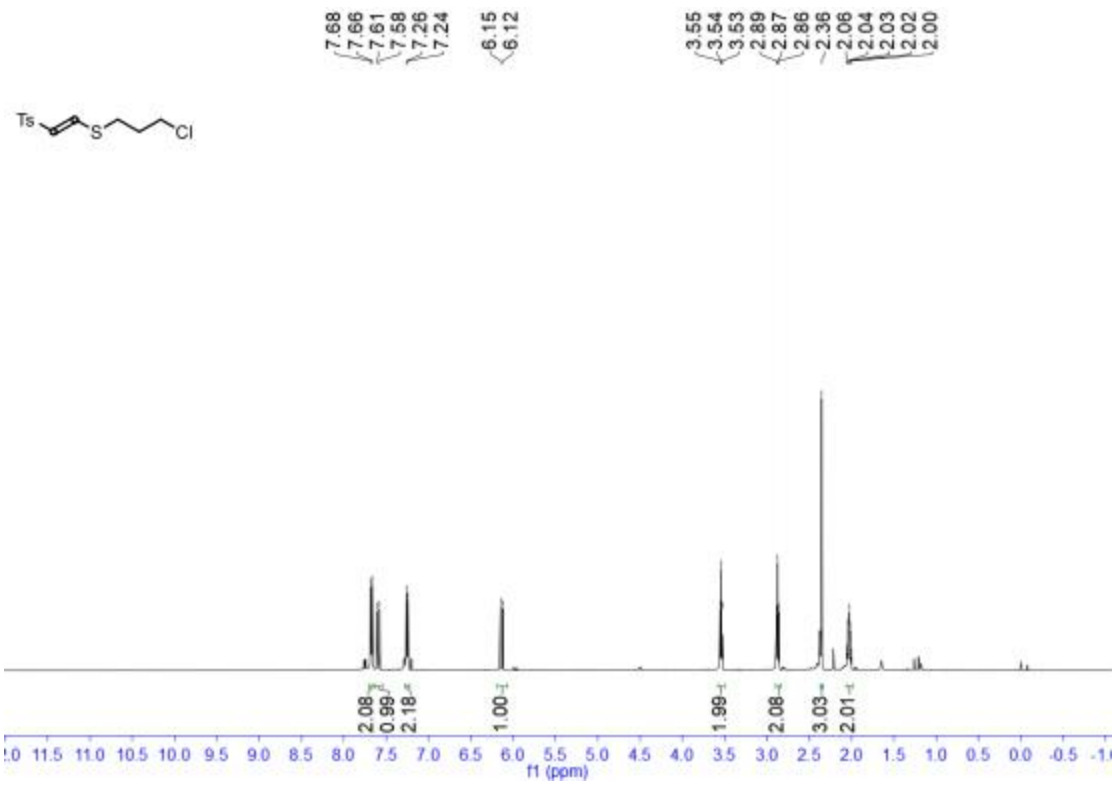
Supplementary Figure 166 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-*tert*-butyldimethyl(3-((2-tosylvinyl)thio)propoxy)silane **(17)**



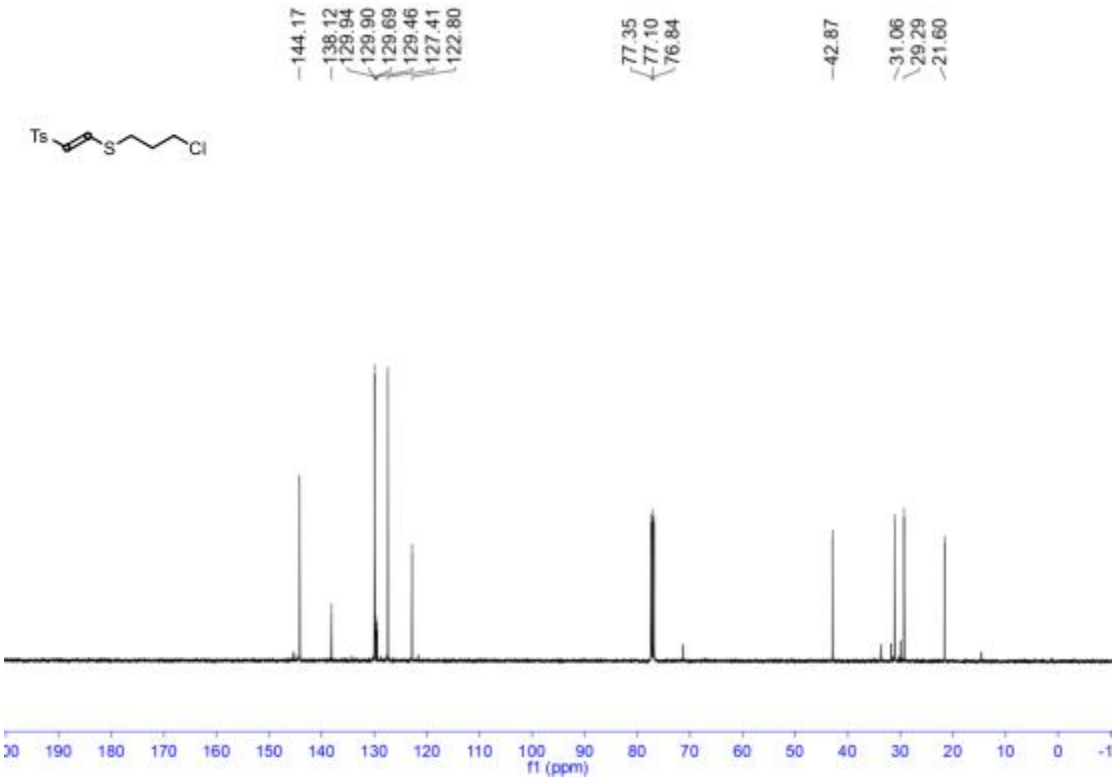
Supplementary Figure 167 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-*tert*-butyldimethyl(3-((2-tosylvinyl)thio)propoxy)silane **(17)**



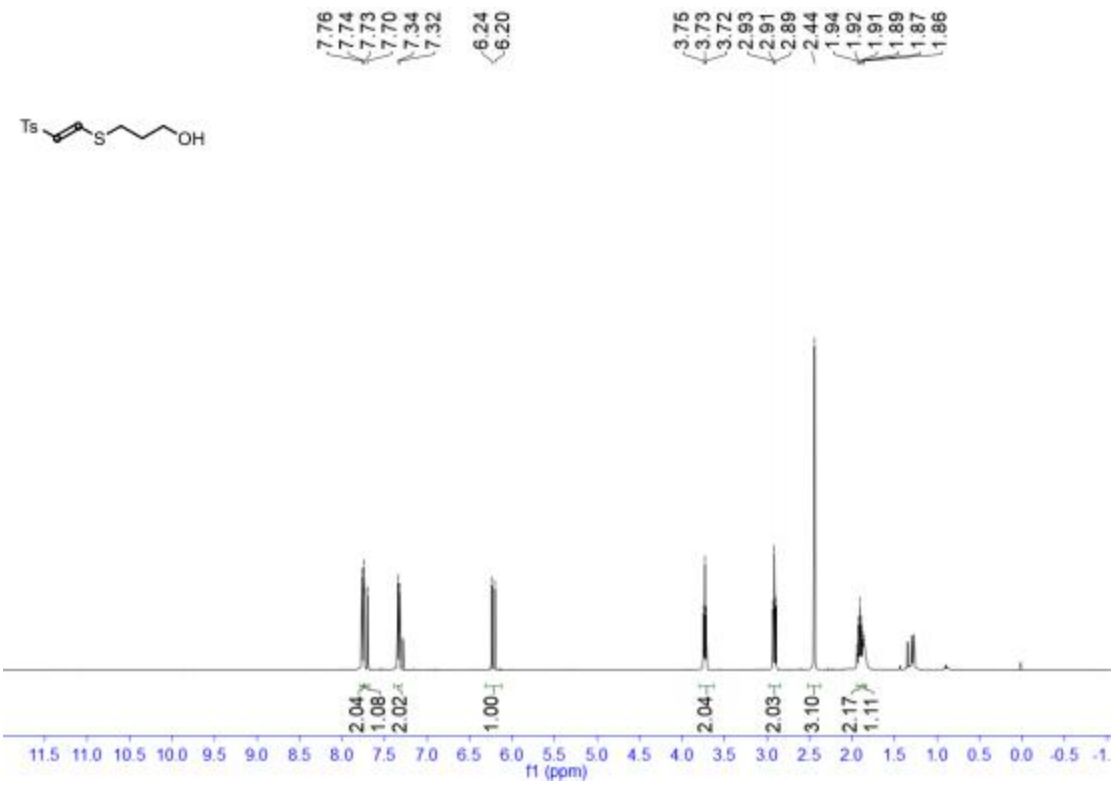
Supplementary Figure 168 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-(3-chloropropyl)(2-tosylvinyl)sulfane **(18)**



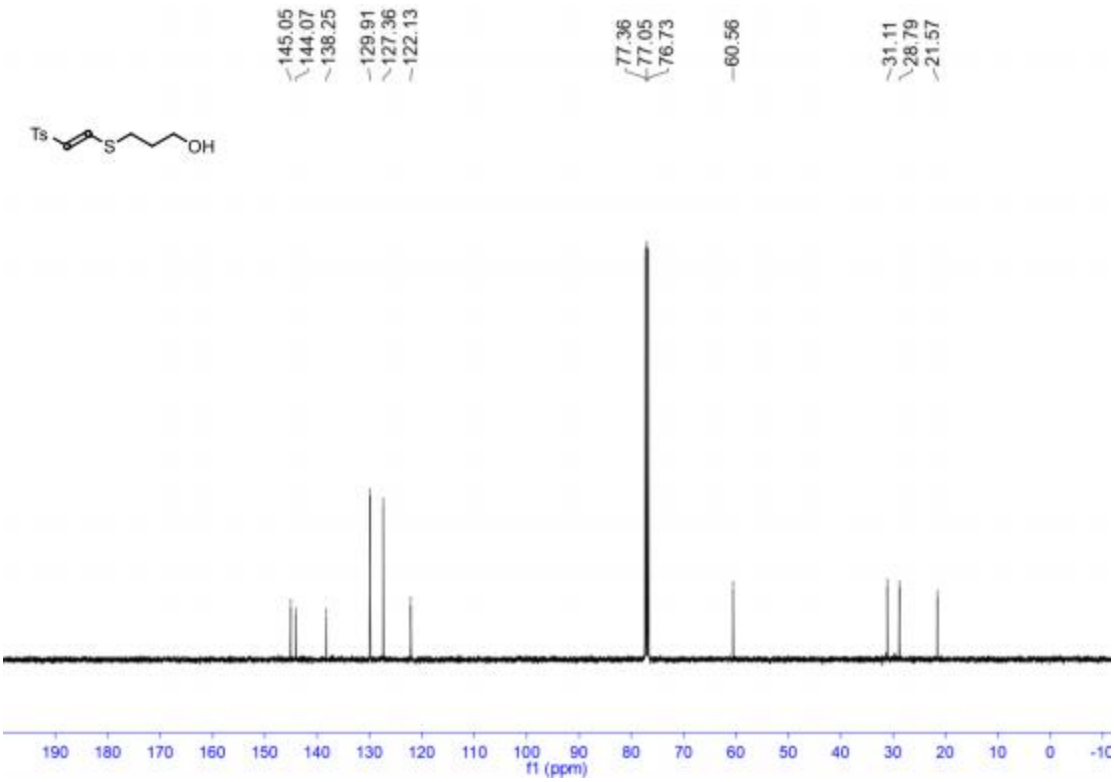
Supplementary Figure 169 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(3-chloropropyl)(2-tosylvinyl)sulfane **(18)**



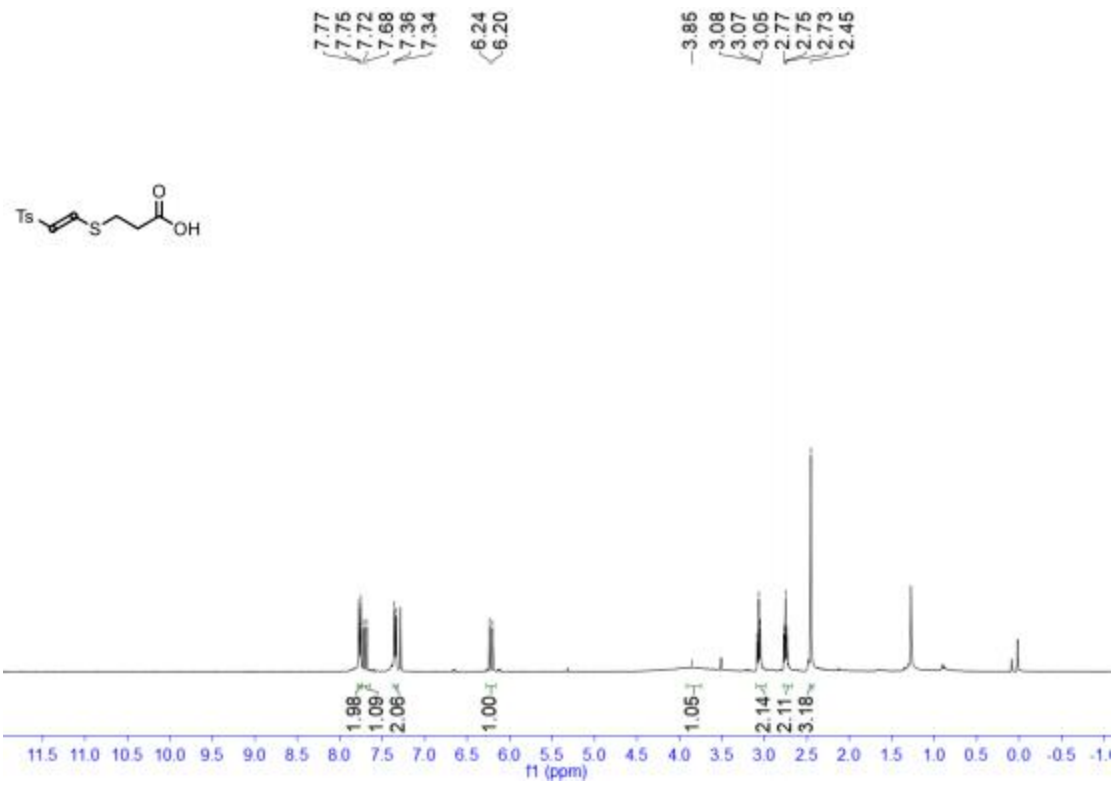
Supplementary Figure 170 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(3-chloropropyl)(2-tosylvinyl)sulfane **(19)**



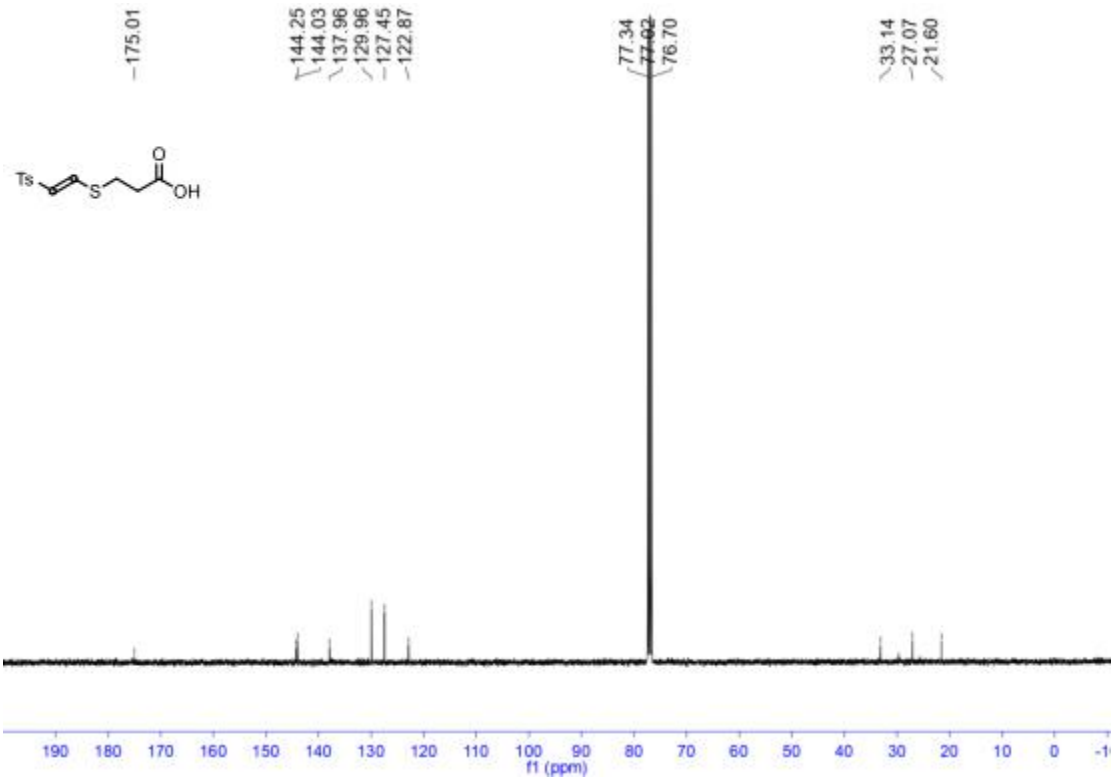
Supplementary Figure 171 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(3-chloropropyl)(2-tosylvinyl)sulfane **(19)**



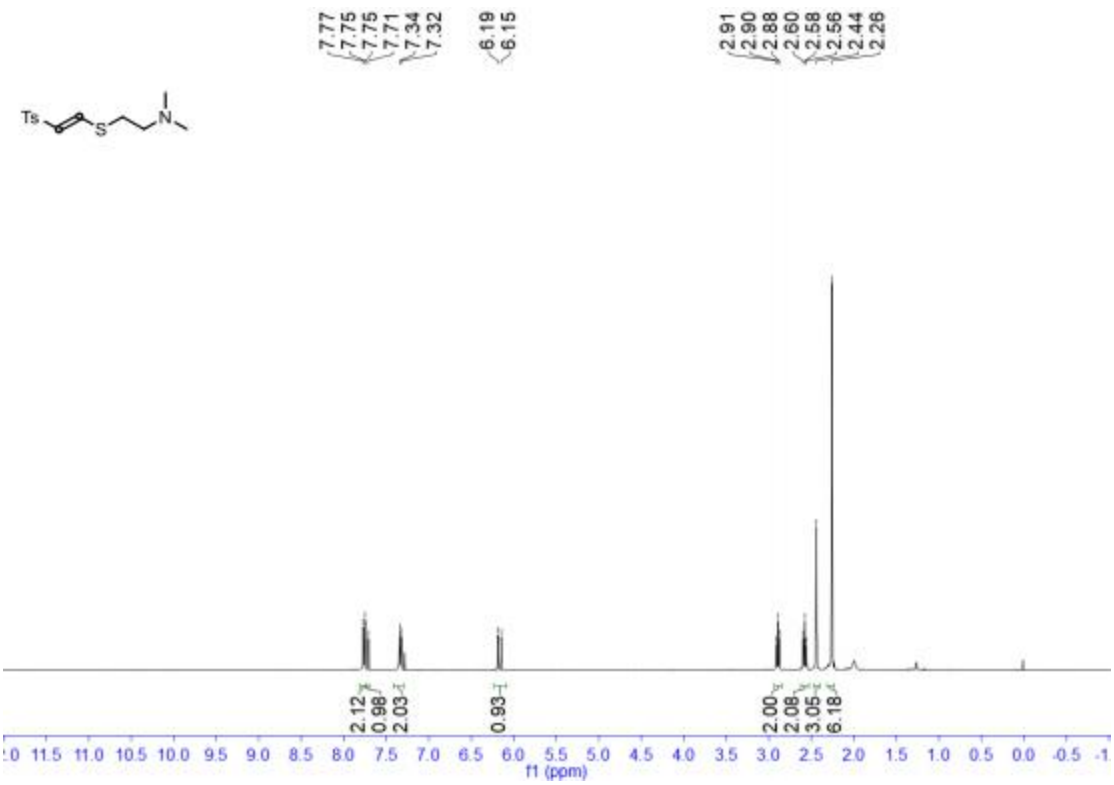
Supplementary Figure 172 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propanoic acid **(20)**



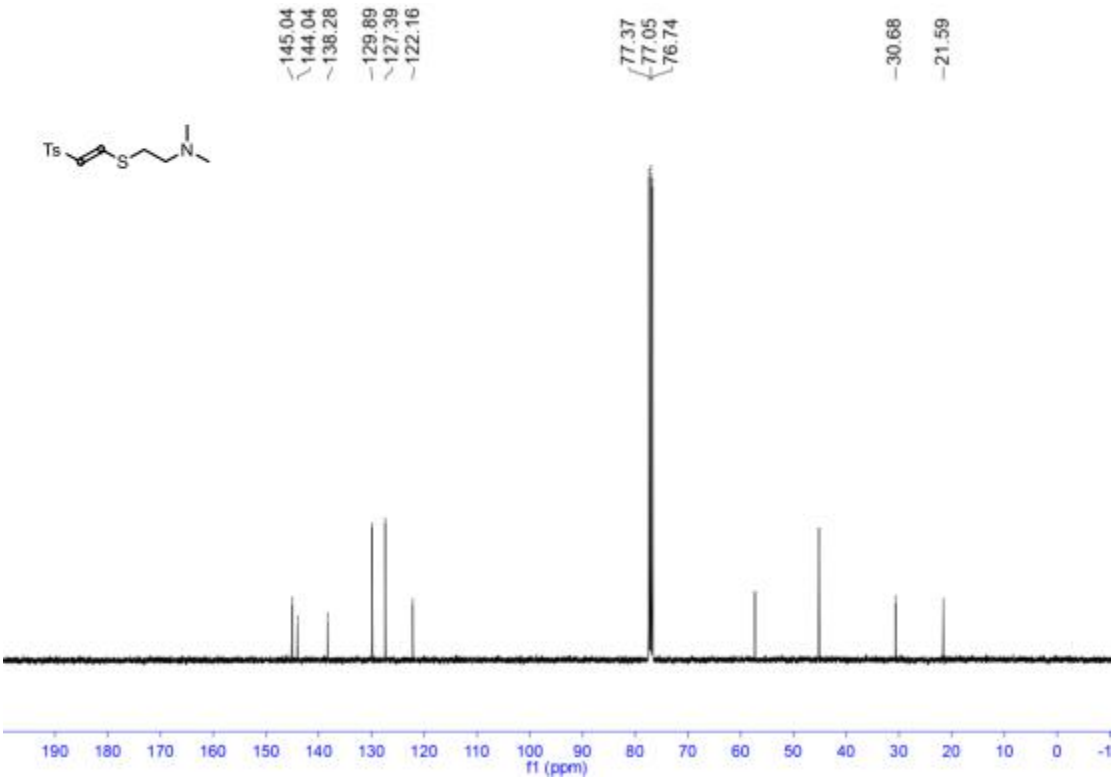
Supplementary Figure 173 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propanoic acid **(20)**



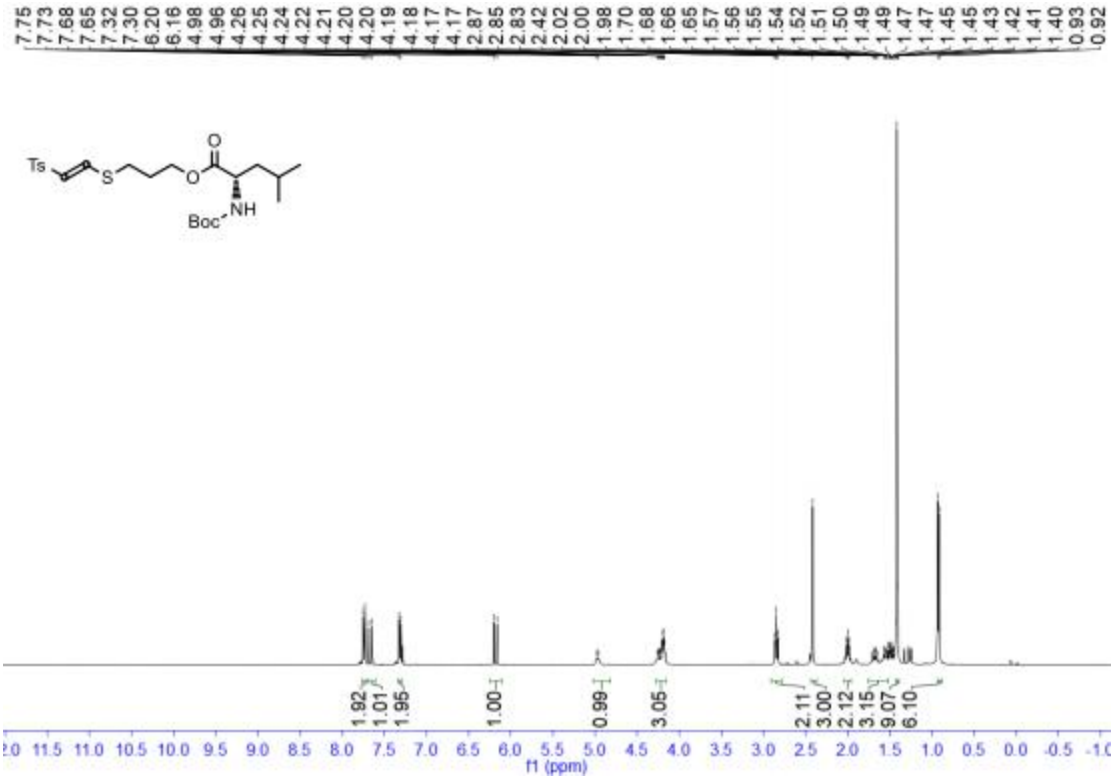
Supplementary Figure 174 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-*N*,*N*-dimethyl-2-((2-tosylvinyl)thio)ethan- 1-amine **(21)**



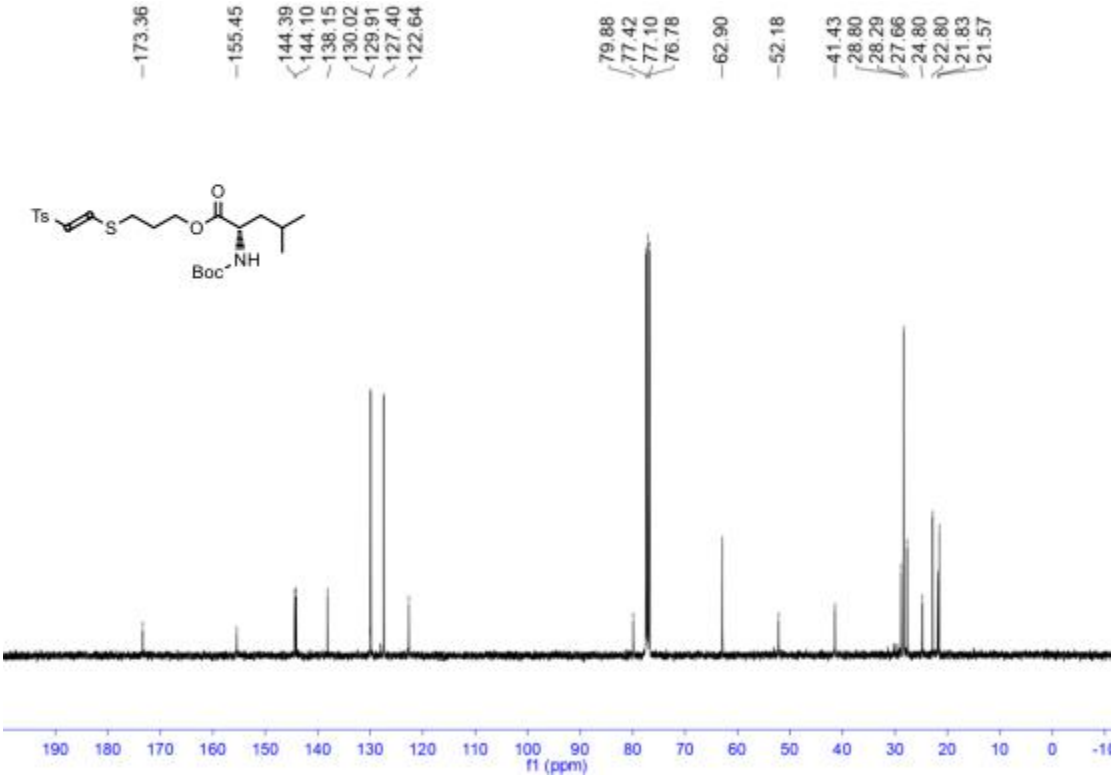
Supplementary Figure 175 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-*N*,*N*-dimethyl-2-((2-tosylvinyl)thio)ethan- 1-amine **(21)**



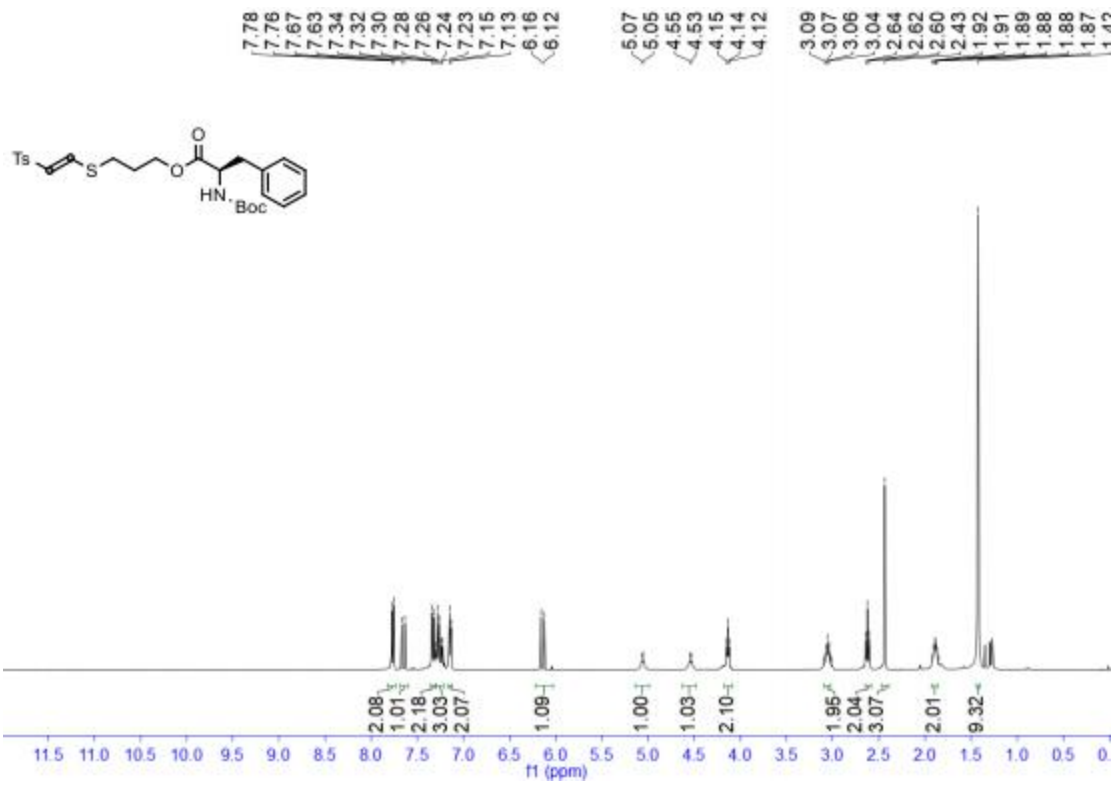
Supplementary Figure 176 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*tert*-butoxycarbonyl)-*L*-leucinate **(22)**



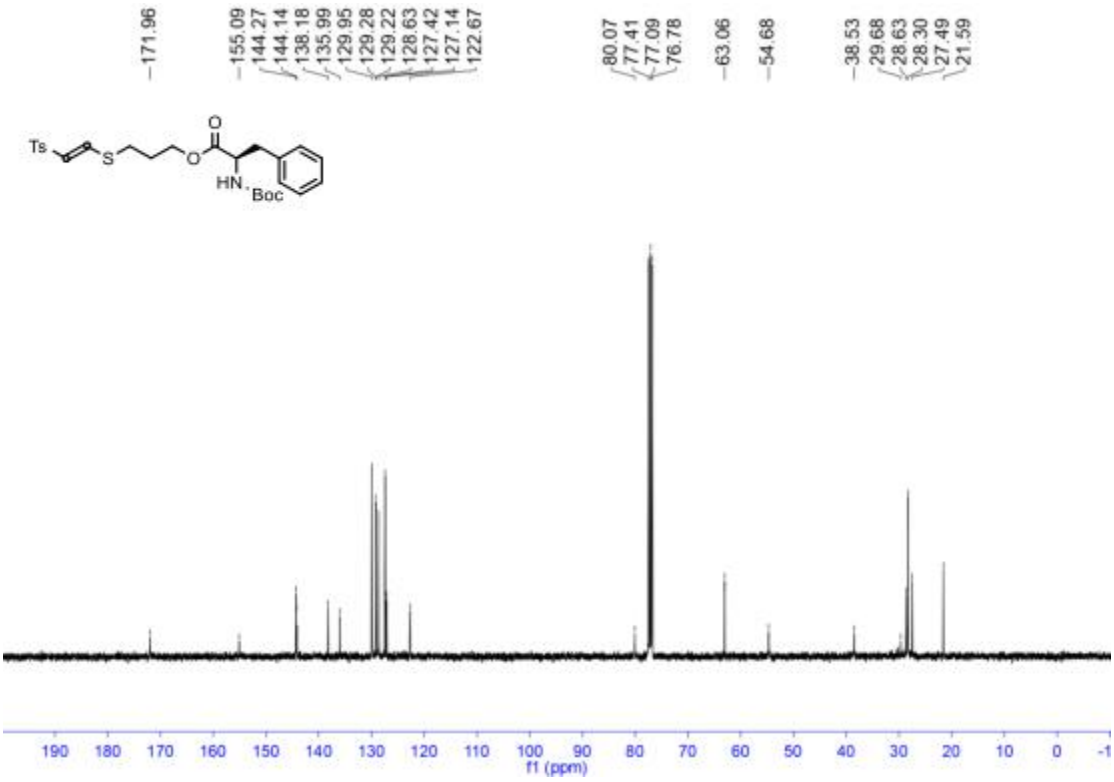
Supplementary Figure 177 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*tert*-butoxycarbonyl)-*L*-leucinate **(22)**



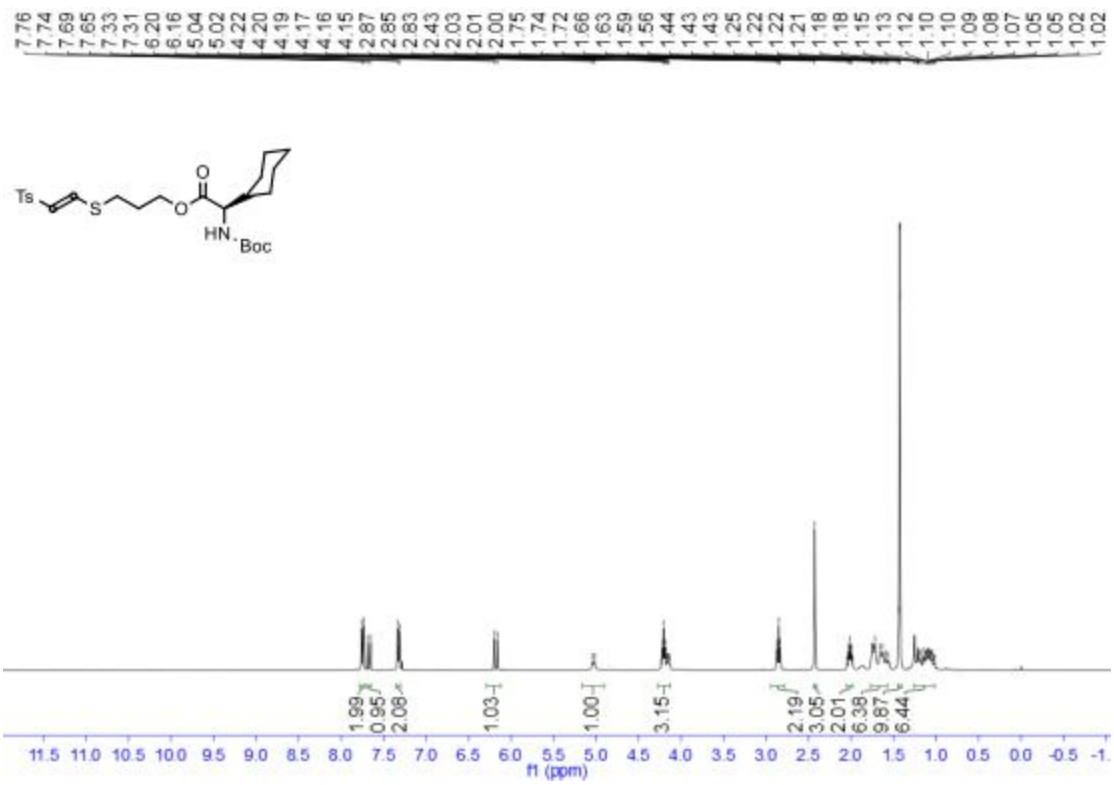
Supplementary Figure 178 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate **(23)**



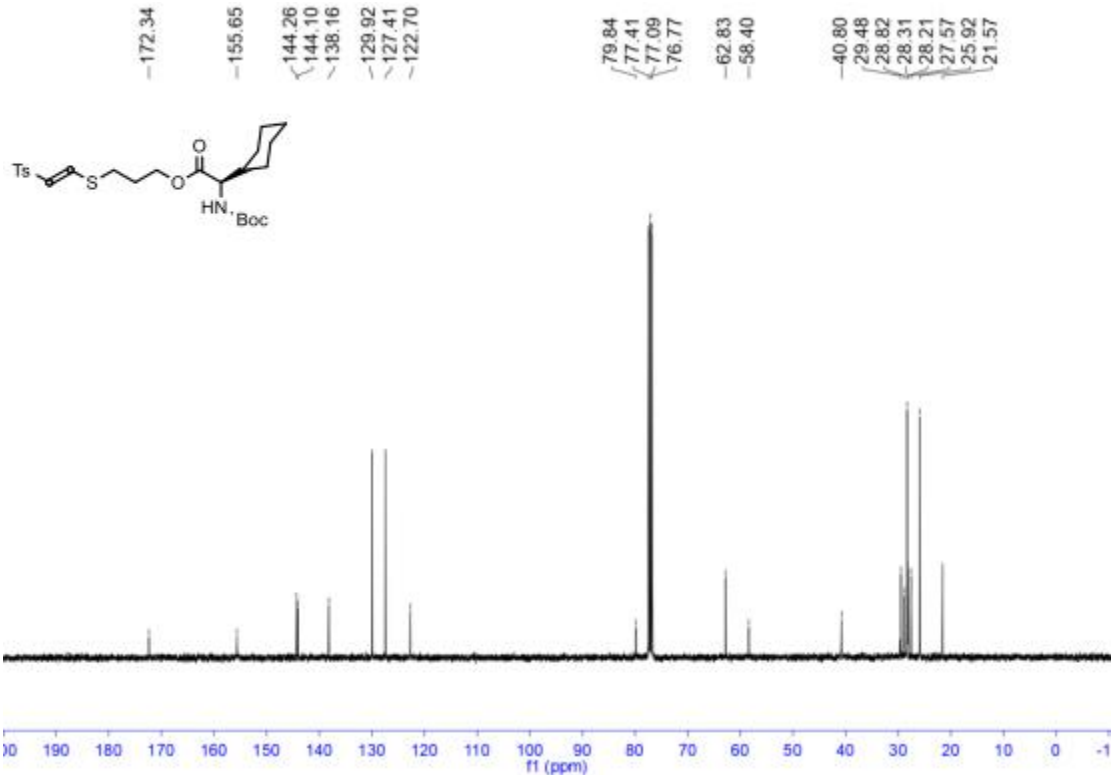
Supplementary Figure 179 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*tert*-butoxycarbonyl)-*D*-phenylalaninate **(23)**



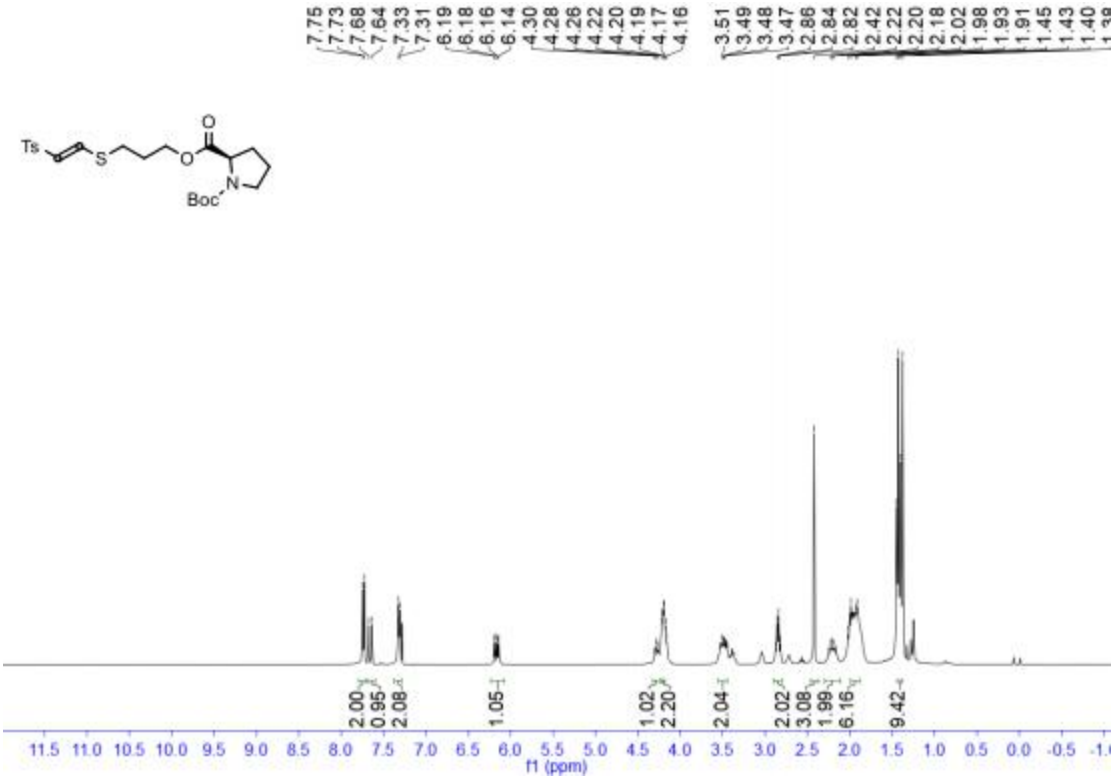
Supplementary Figure 180 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate **(24)**



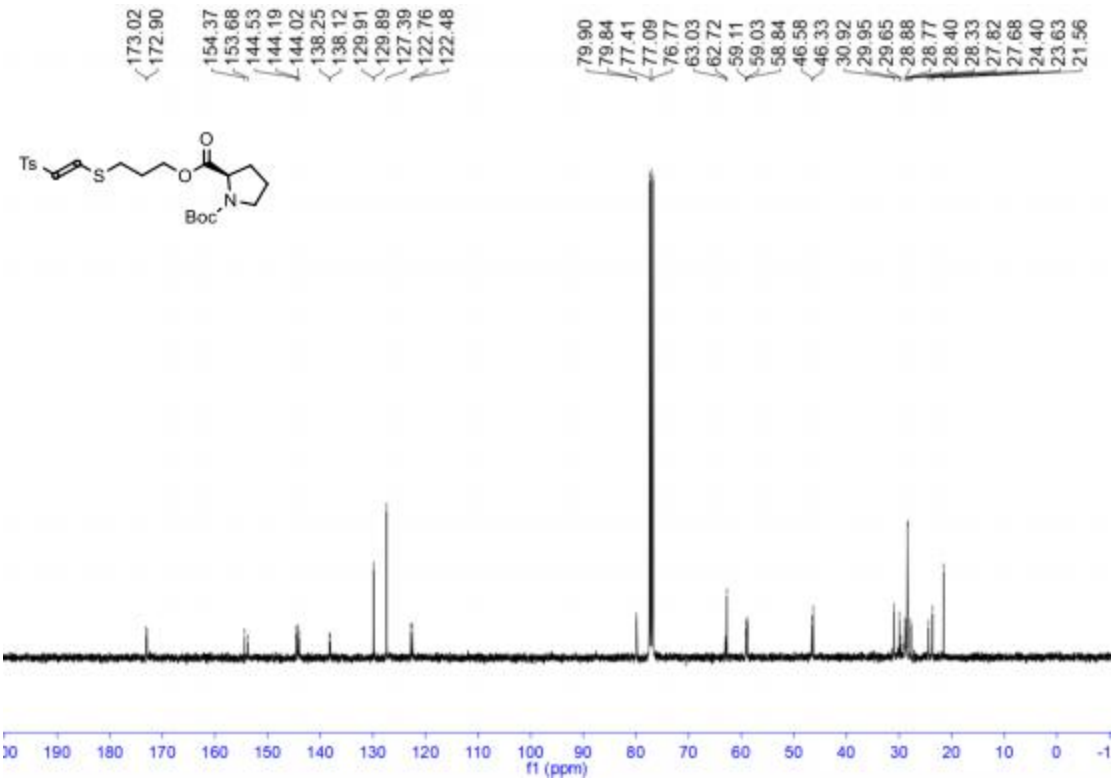
Supplementary Figure 181 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*R*)-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate **(24)**



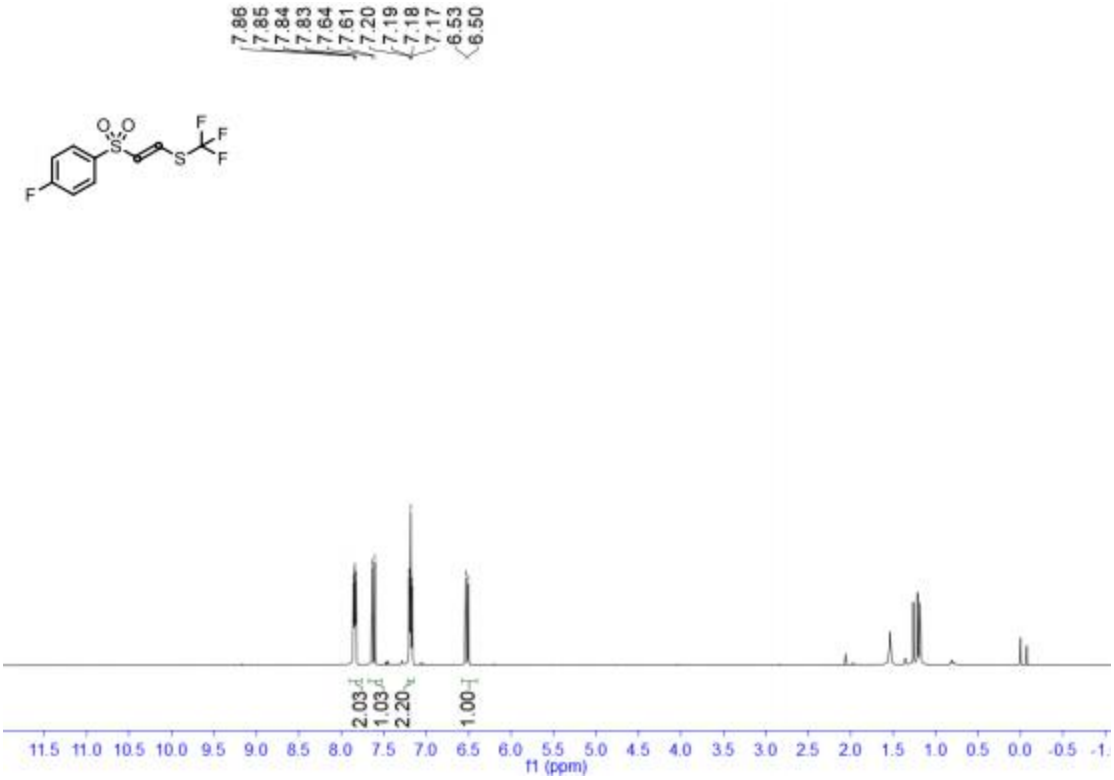
Supplementary Figure 182 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)- 1-(*tert*-butyl) 2-(3-((2-tosylvinyl)thio)propyl) (*R*)-pyrrolidine- 1,2-dicarboxylate **(25)**



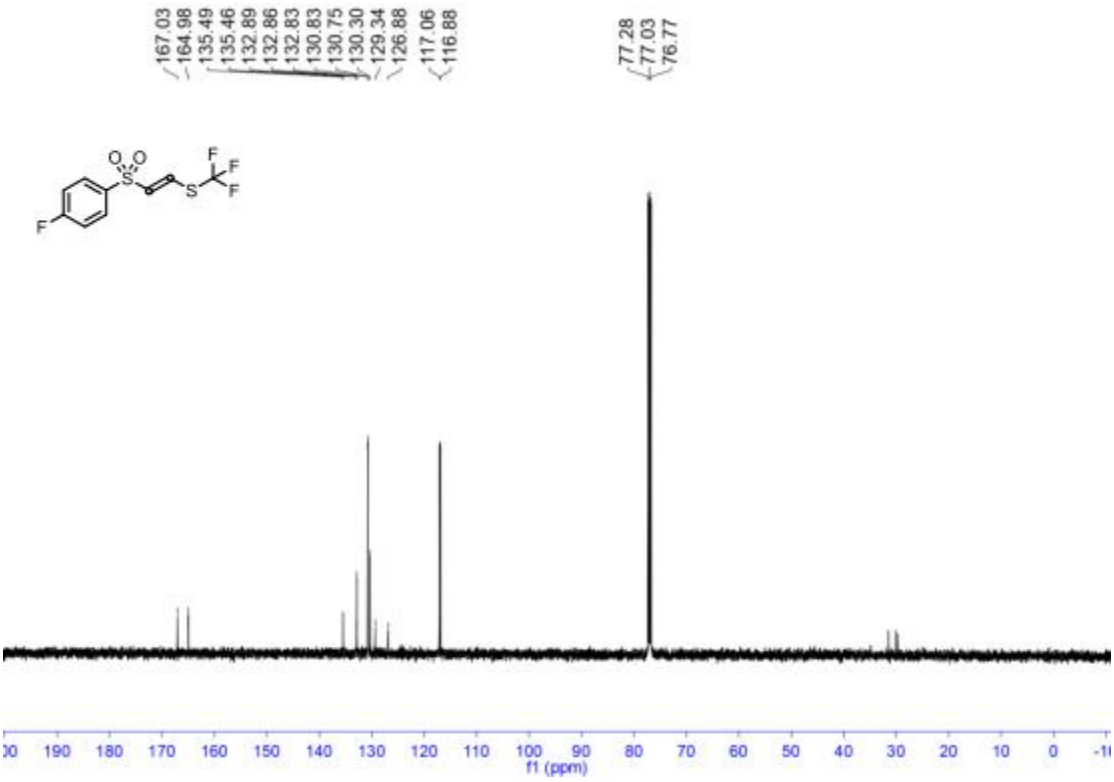
Supplementary Figure 183 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)- 1-(*tert*-butyl) 2-(3-((2-tosylvinyl)thio)propyl) (*R*)-pyrrolidine- 1,2-dicarboxylate **(25)**



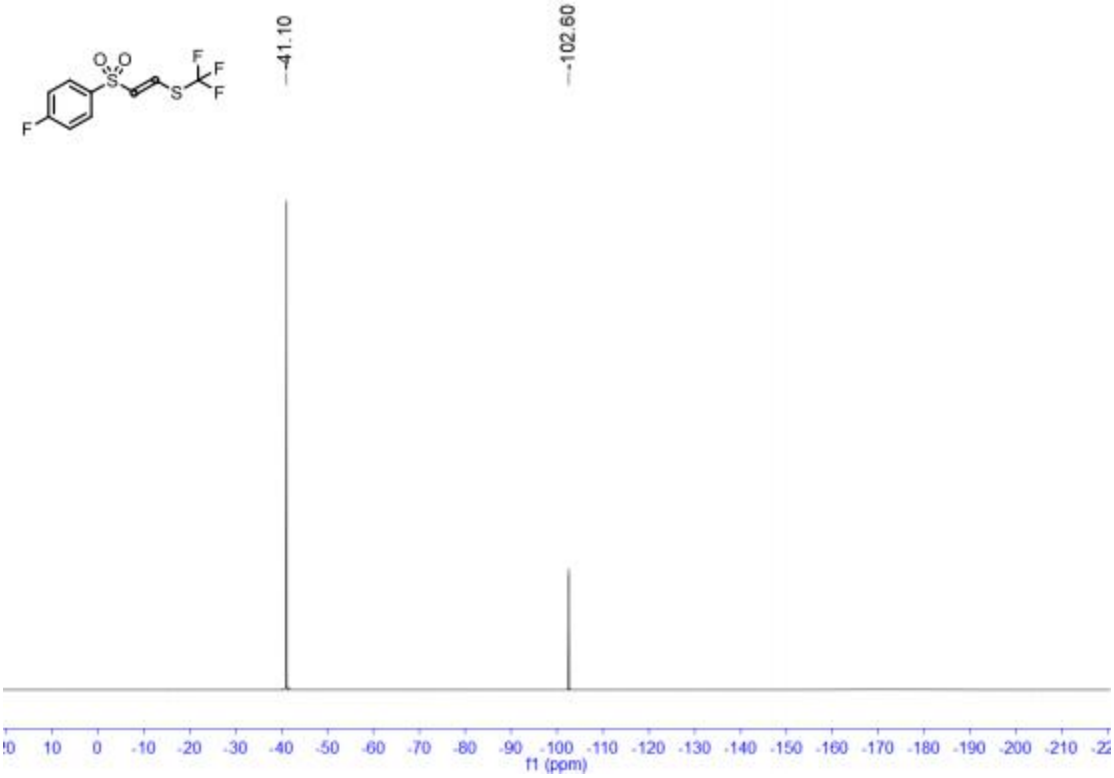
Supplementary Figure 184 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)- 1-(*tert*-butyl) 2-(3-((2-tosylvinyl)thio)propyl) (*R*)-pyrrolidine- 1,2-dicarboxylate **(26)**



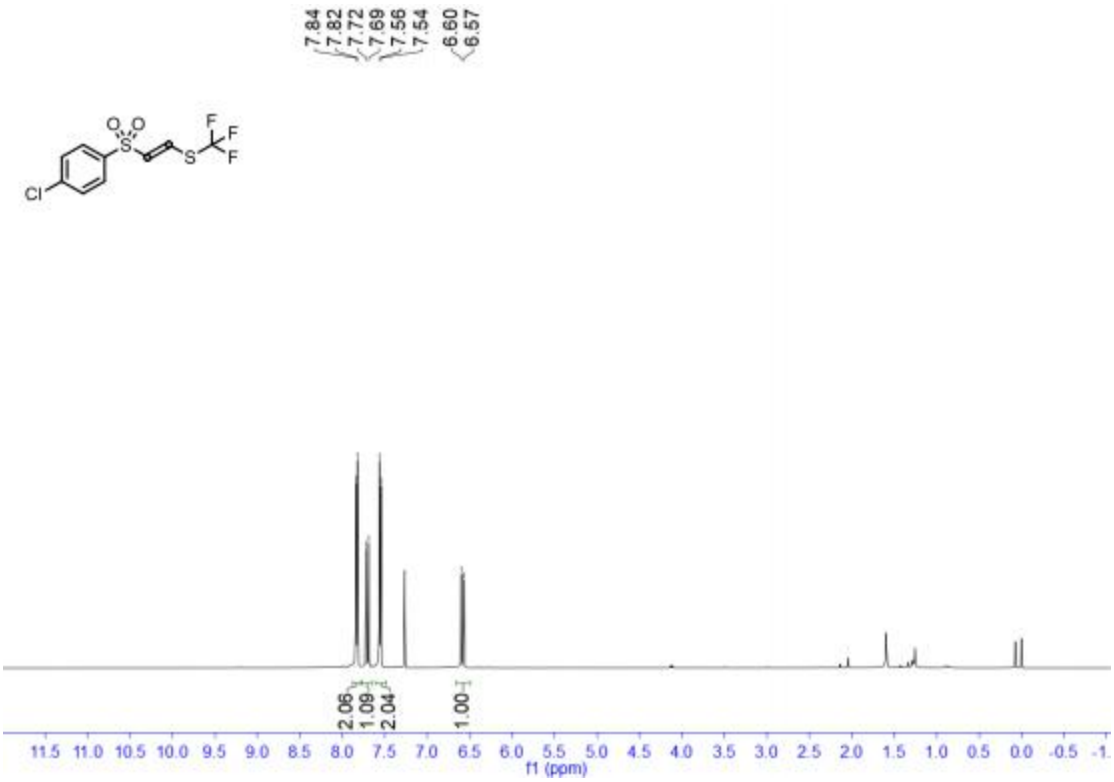
Supplementary Figure 185 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-fluorophenyl)sulfonyl)vinyl)(trifluoromethyl)sulfane **(26)**



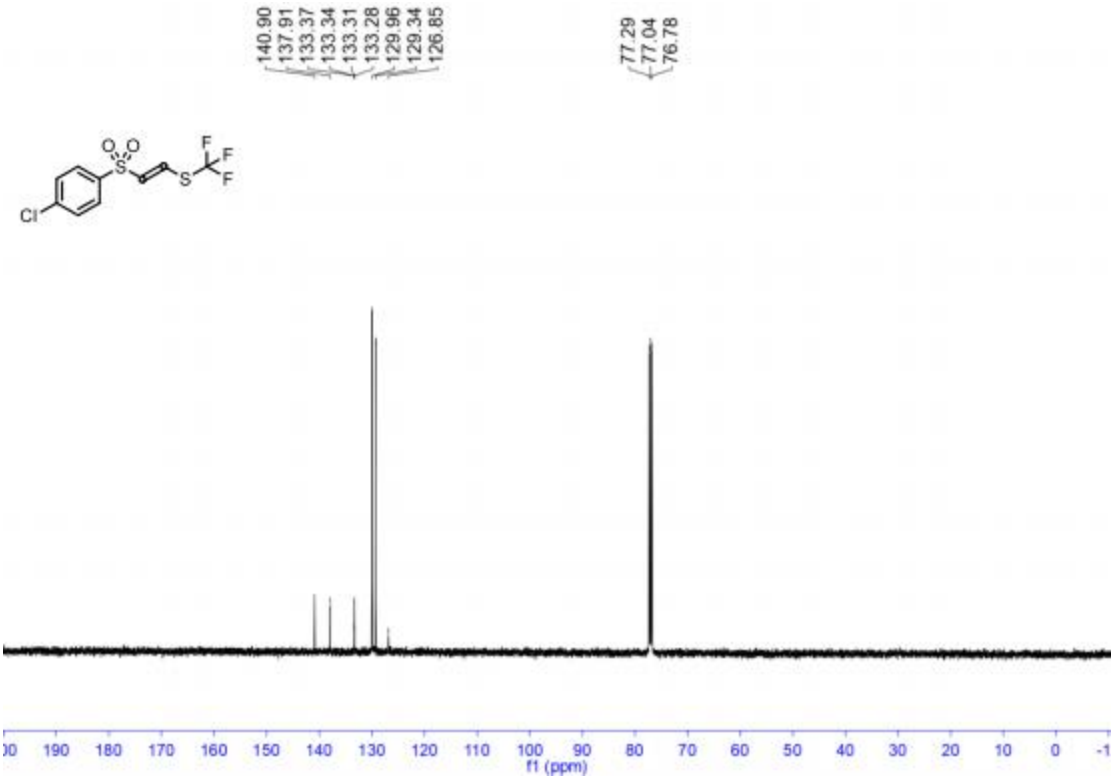
Supplementary Figure 186 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-fluorophenyl)sulfonyl)vinyl)(trifluoromethyl)sulfane **(26)**



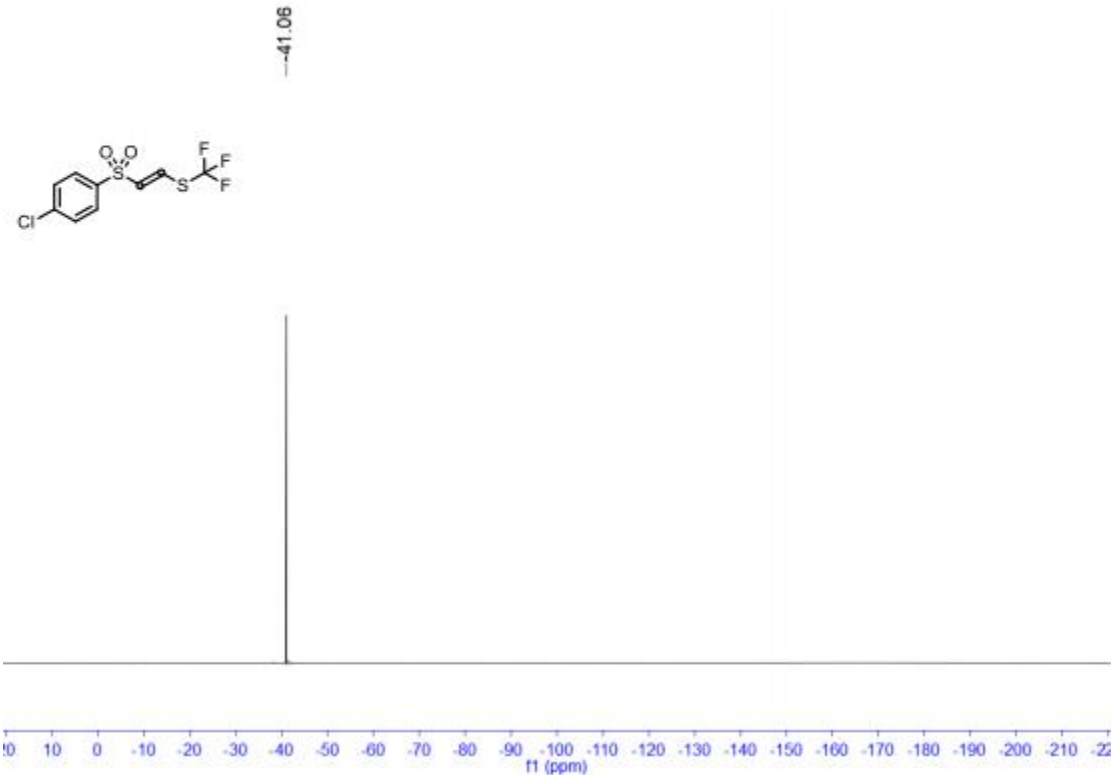
Supplementary Figure 187 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-chlorophenyl)sulfonyl)vinyl)(trifluoromethyl)sulfane **(27)**



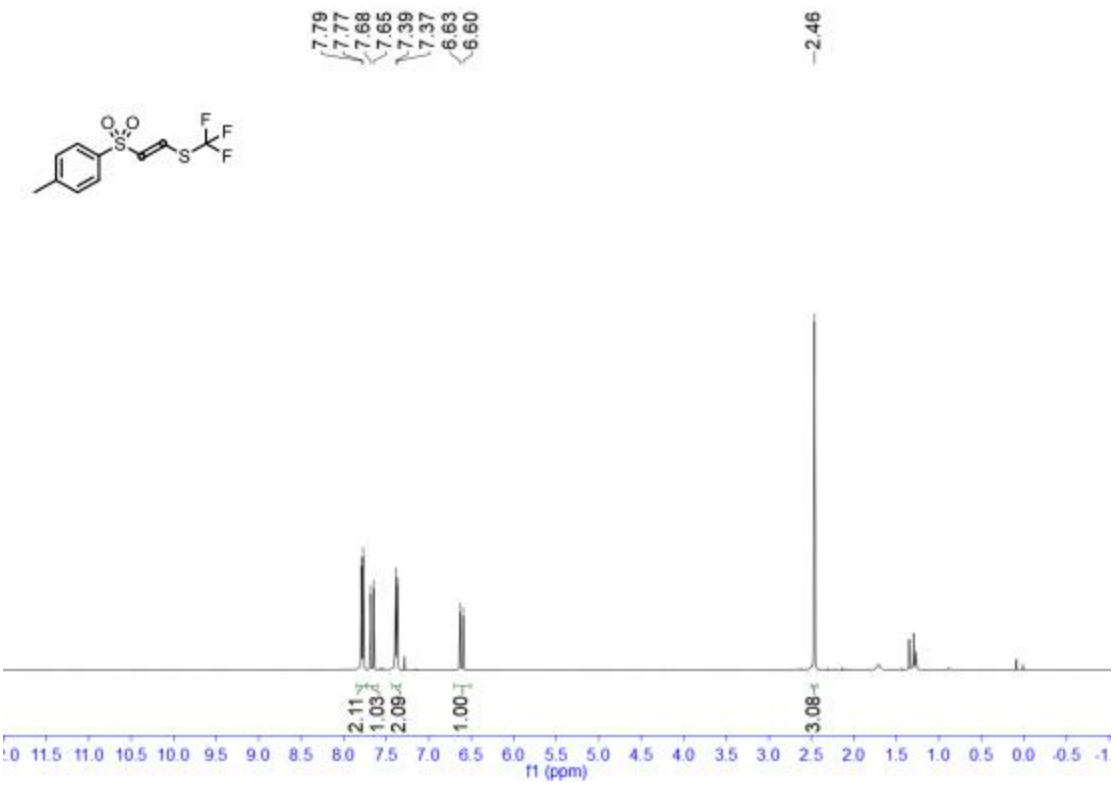
Supplementary Figure 188 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-chlorophenyl)sulfonyl)vinyl)(trifluoromethyl)sulfane **(27)**



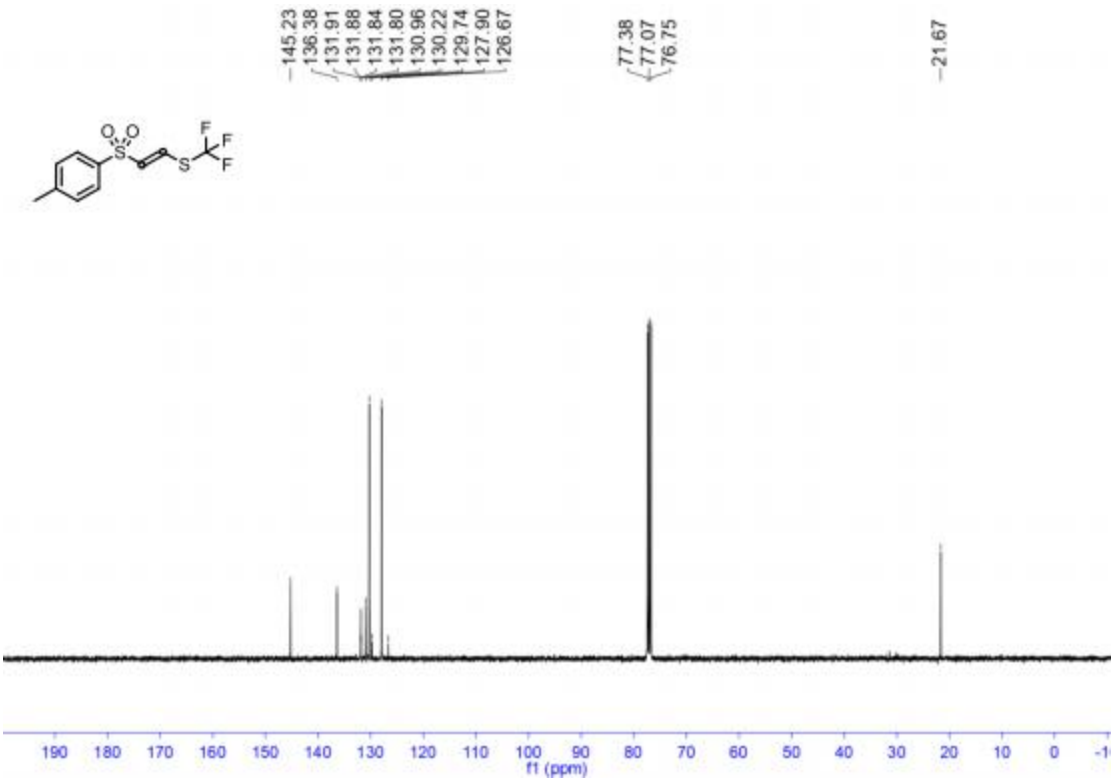
Supplementary Figure 189 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-chlorophenyl)sulfonyl)vinyl)(trifluoromethyl)sulfane **(27)**



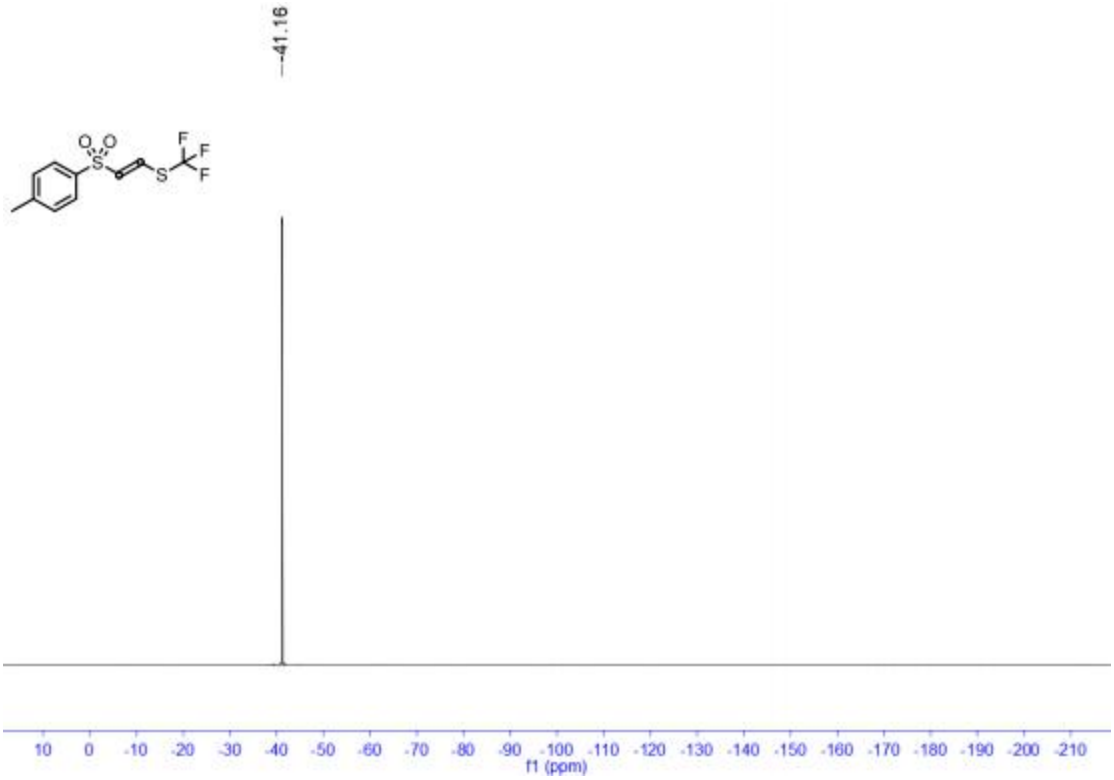
Supplementary Figure 190 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(2-tosylvinyl)(trifluoromethyl)sulfane **(28)**



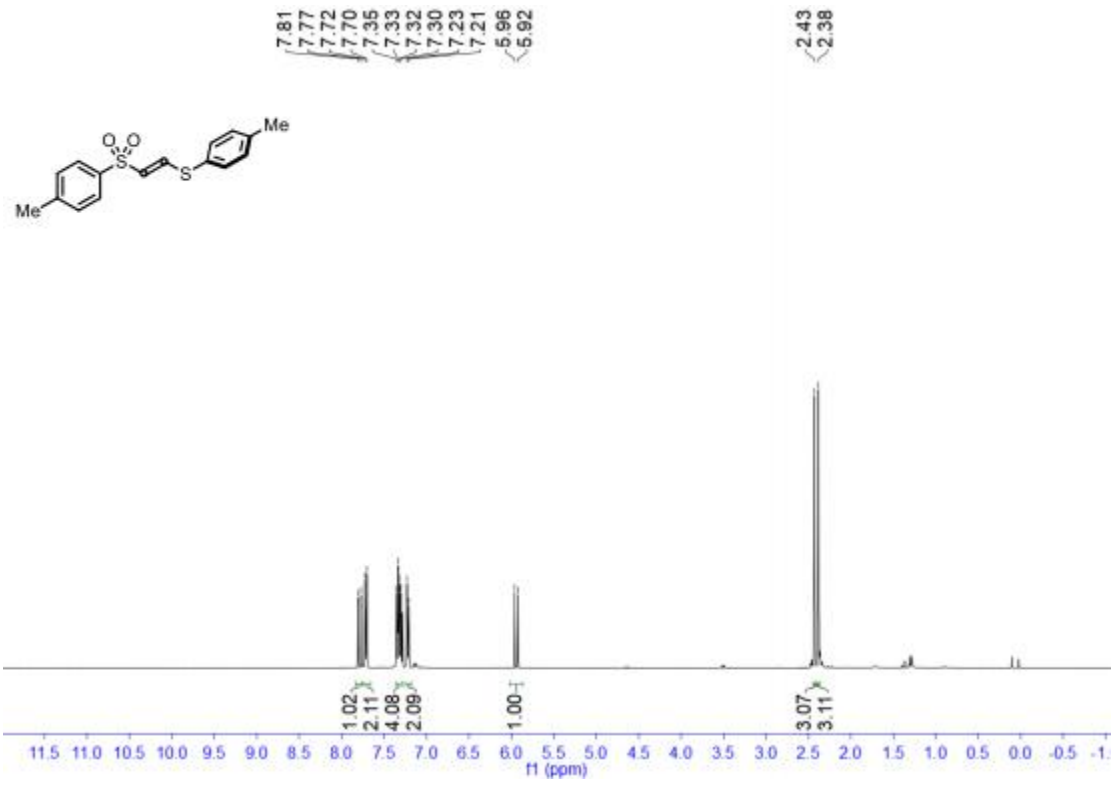
Supplementary Figure 191 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(2-tosylvinyl)(trifluoromethyl)sulfane **(28)**



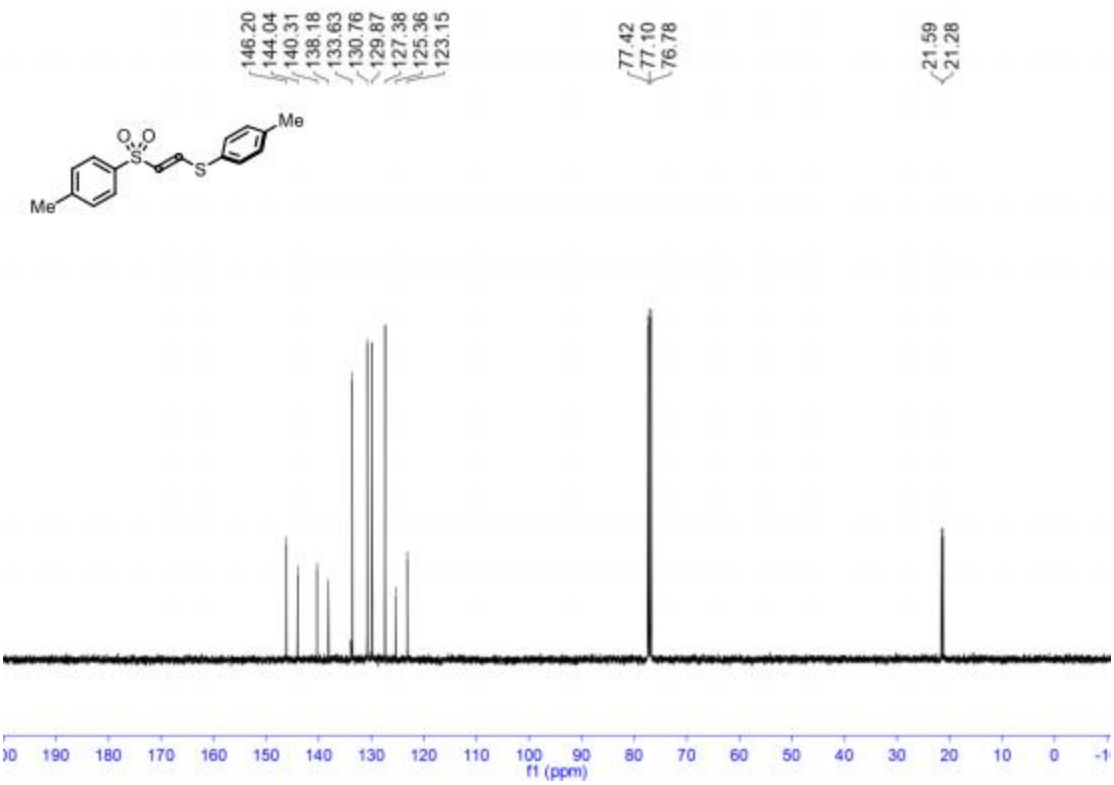
Supplementary Figure 192 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of (*E*)-(2-tosylvinyl)(trifluoromethyl)sulfane **(28)**



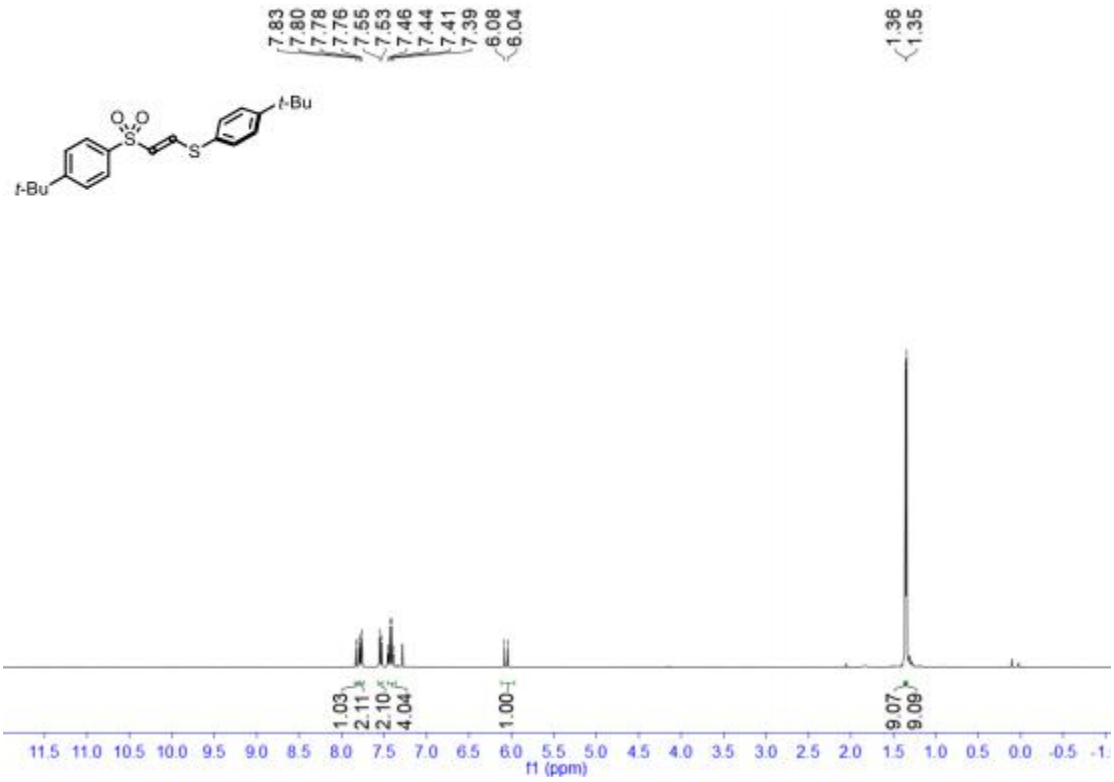
Supplementary Figure 193 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-*p*-tolyl(2-tosylvinyl)sulfane **(29)**



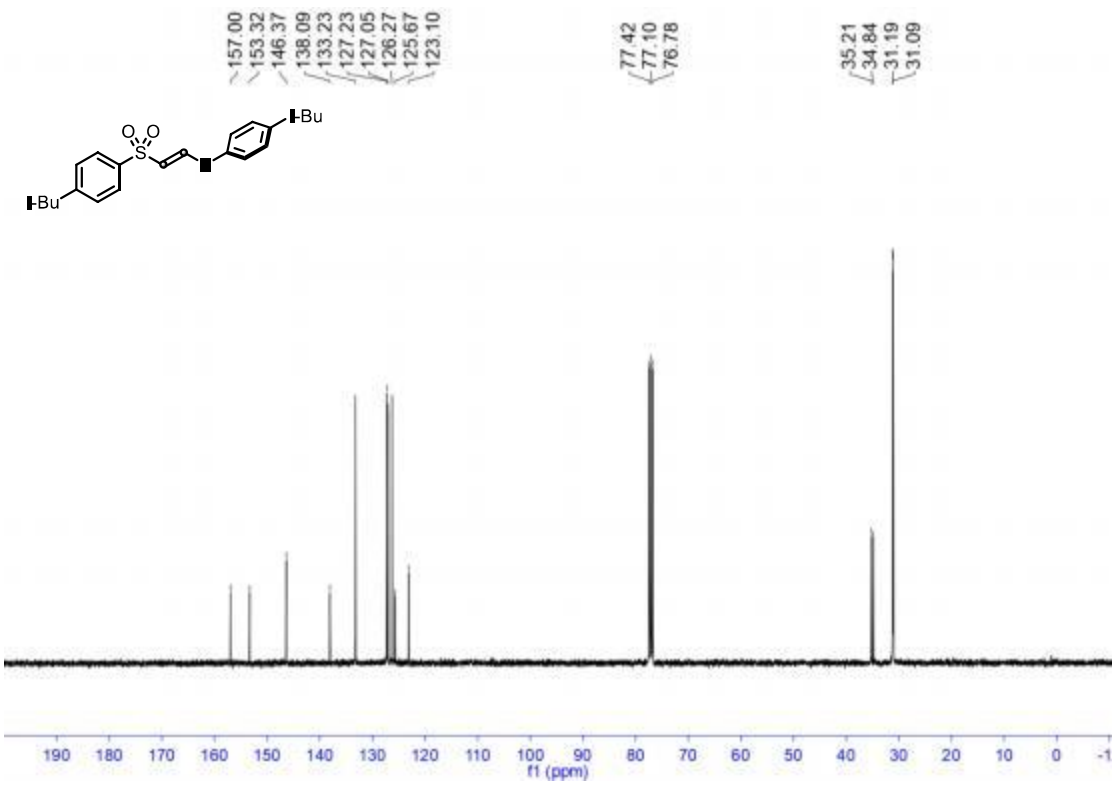
Supplementary Figure 194 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-*p*-tolyl(2-tosylvinyl)sulfane **(29)**



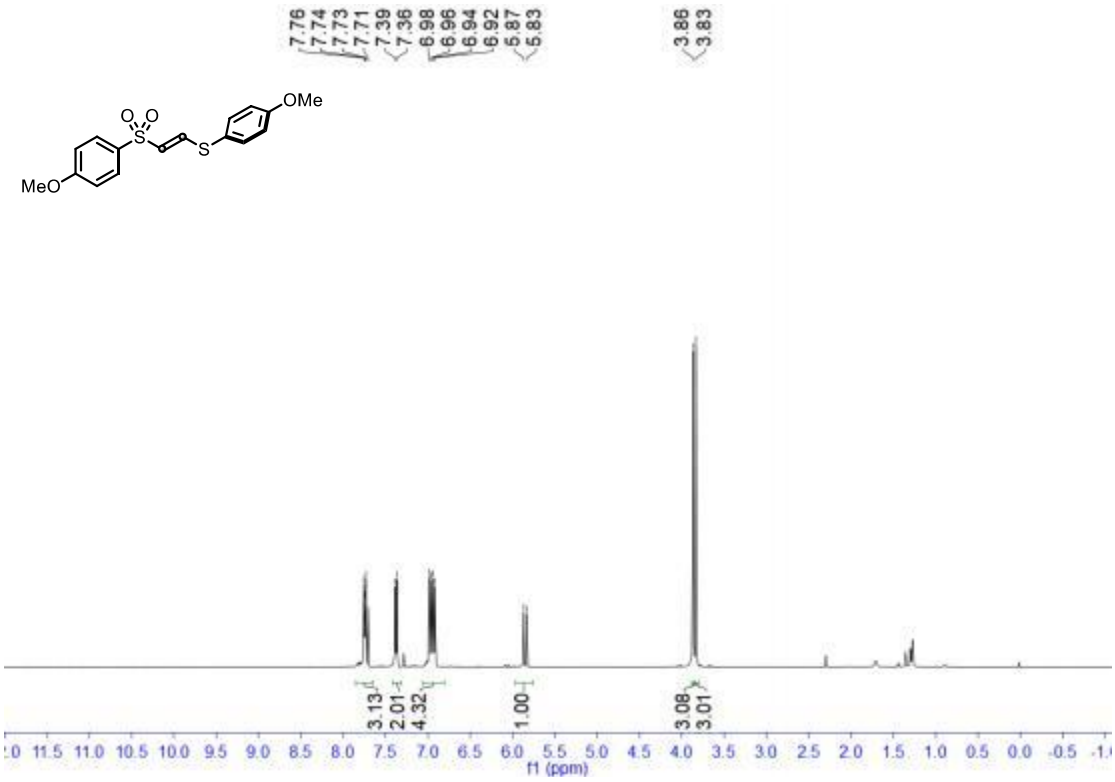
Supplementary Figure 195 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(*tert*-butyl)phenyl)(2-((4-(*tert*-butyl)phenyl)sulfonyl)vinyl)sulfane **(30)**



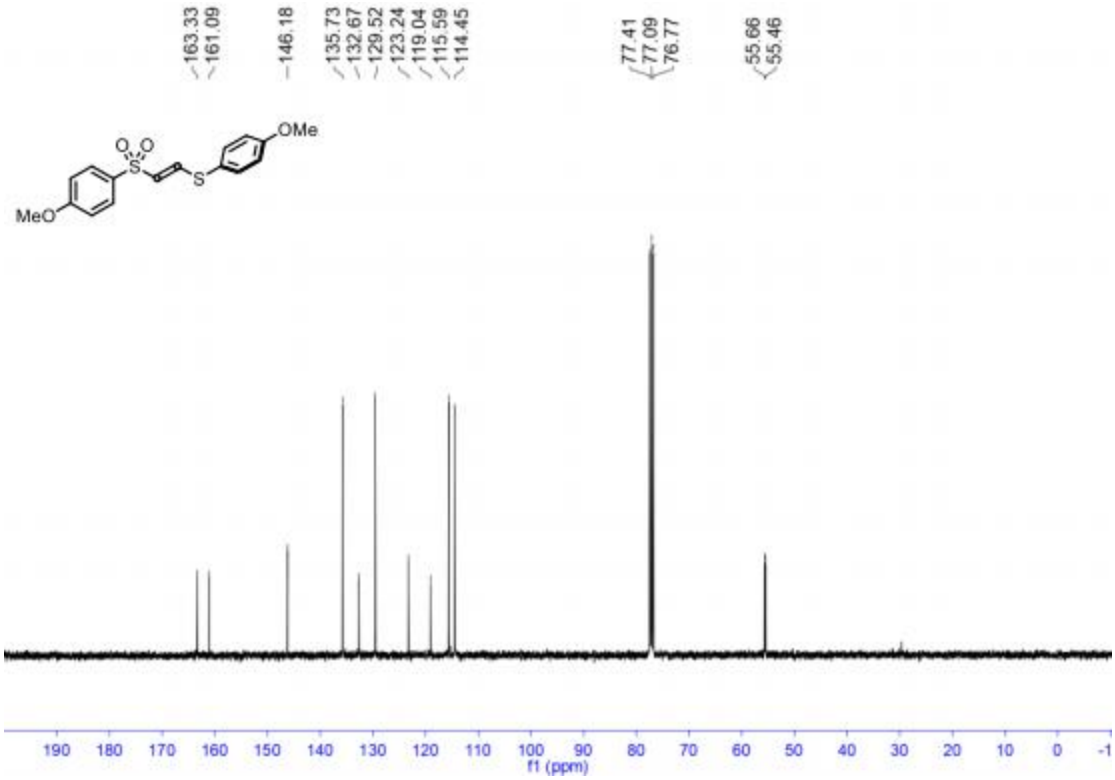
Supplementary Figure 196 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(*tert*-butyl)phenyl)(2-((4-(*tert*-butyl)phenyl)sulfonyl)vinyl)sulfane **(30)**



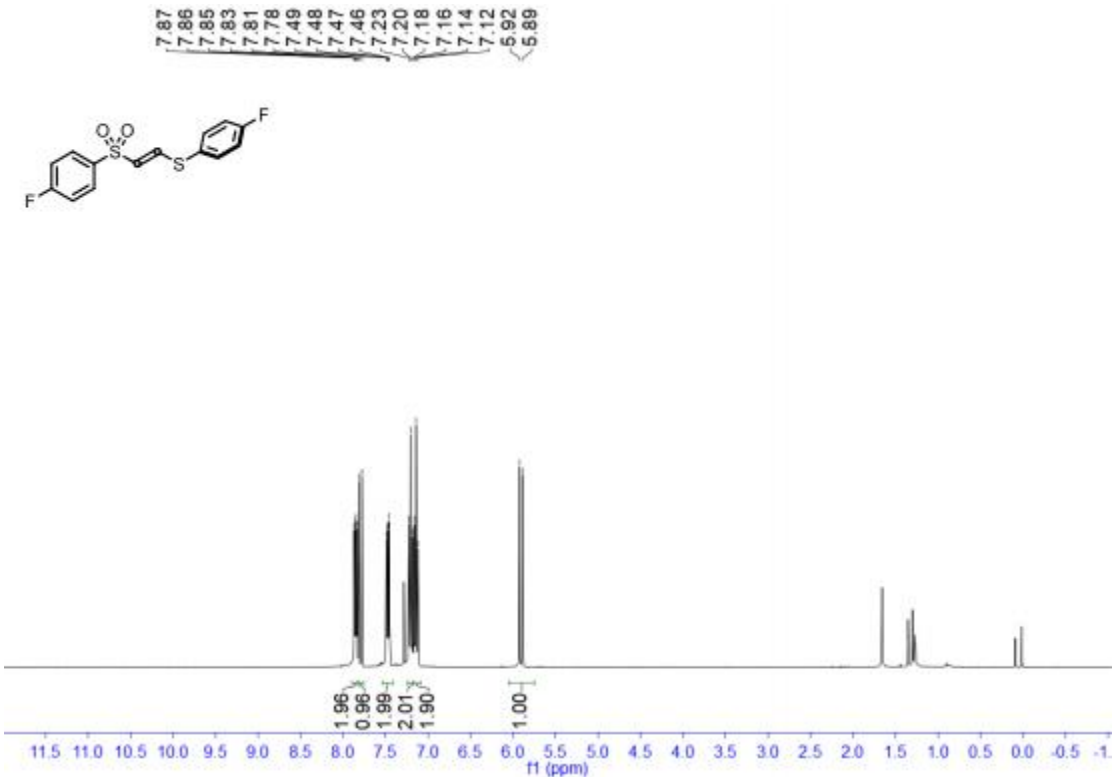
Supplementary Figure 197 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(4-methoxyphenyl)(2-((4-methoxyphenyl)sulfonyl)vinyl)sulfane **(31)**



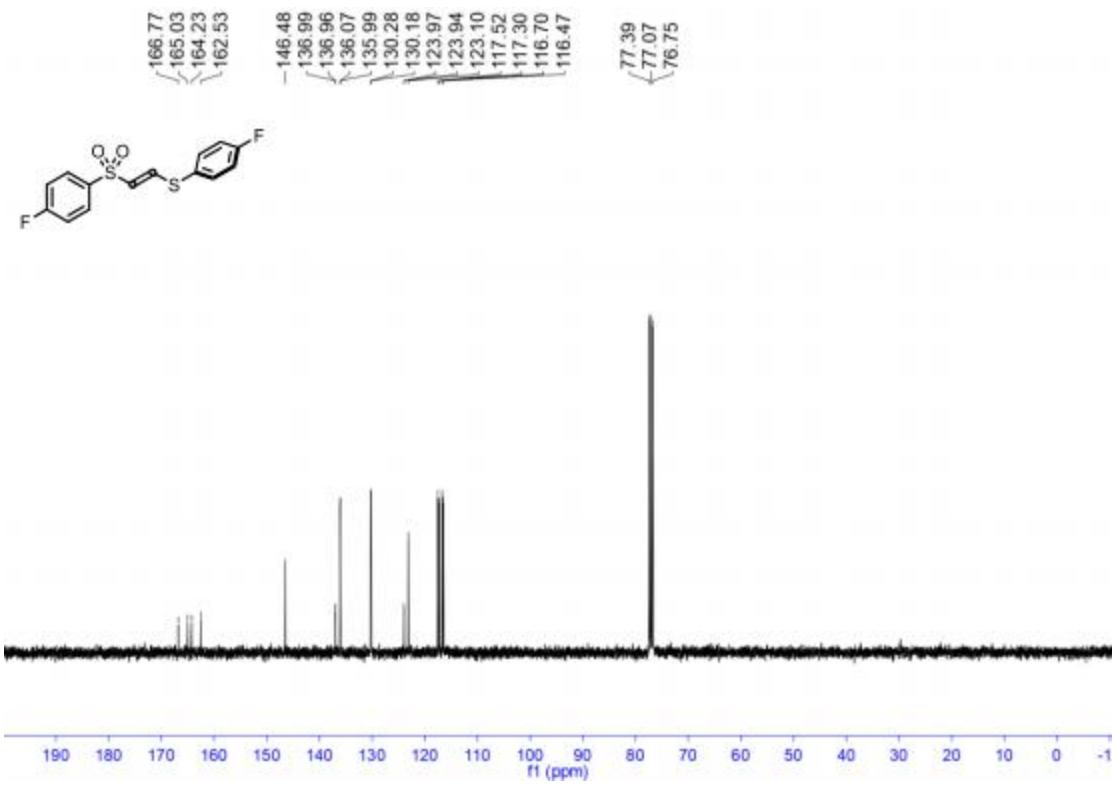
Supplementary Figure 198 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(4-methoxyphenyl)(2-((4-methoxyphenyl)sulfonyl)vinyl)sulfane **(31)**



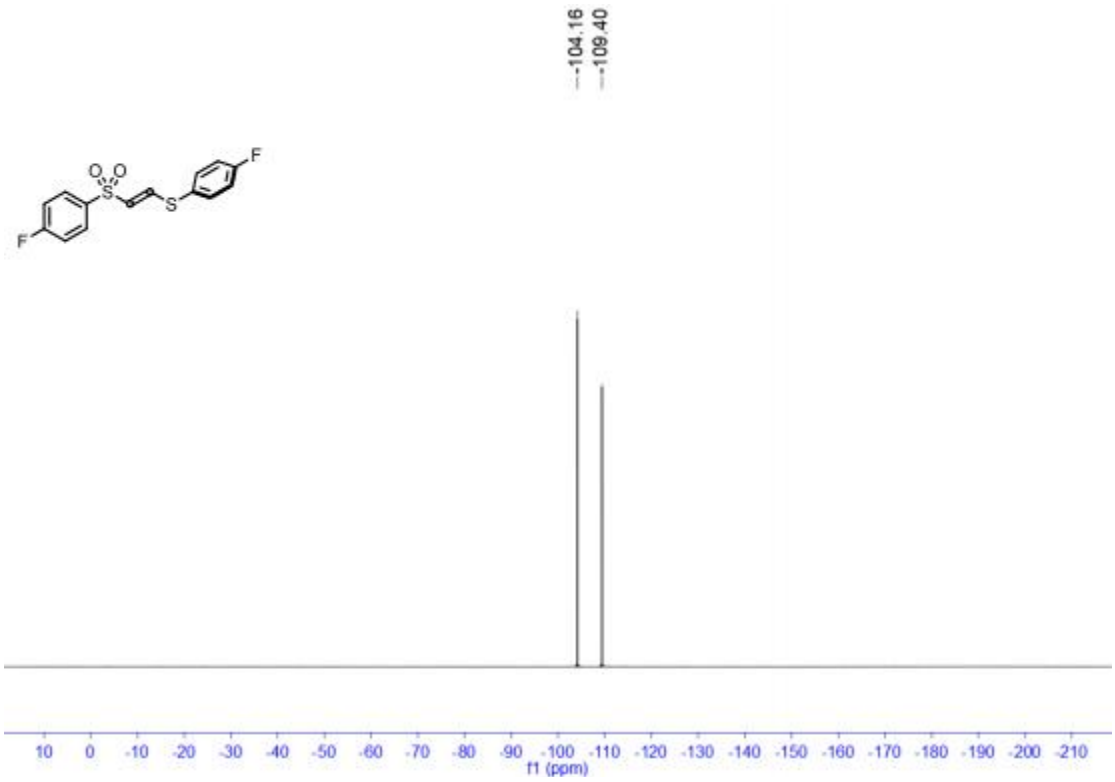
Supplementary Figure 199 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(4-fluorophenyl)(2-((4-fluorophenyl)sulfonyl)vinyl)sulfane **(32)**



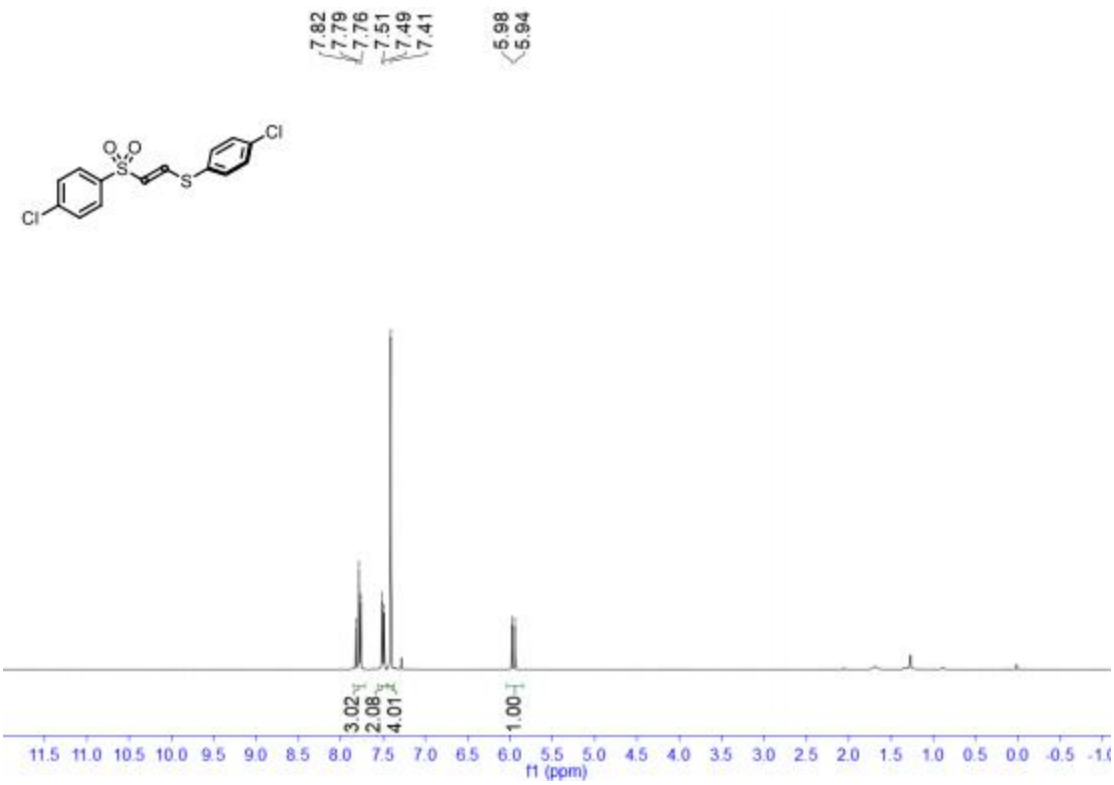
Supplementary Figure 200 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(4-fluorophenyl)(2-((4-fluorophenyl)sulfonyl)vinyl)sulfane **(32)**



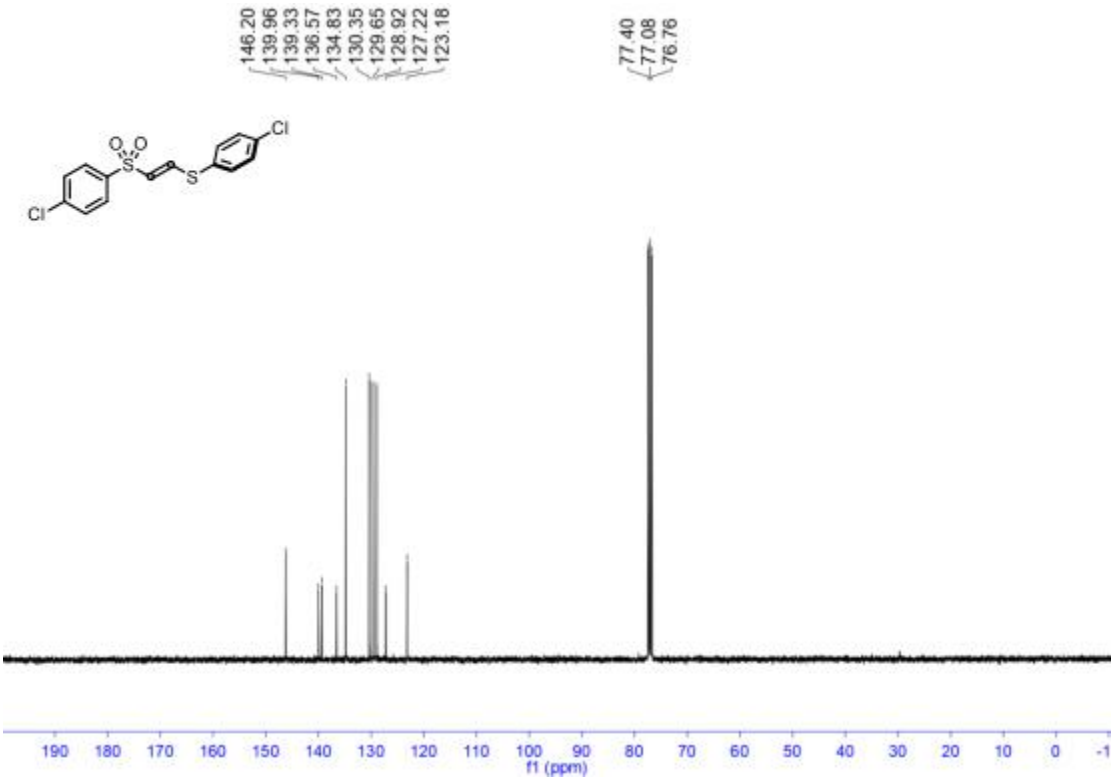
Supplementary Figure 201 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of (*E*)-(4-fluorophenyl)(2-((4-fluorophenyl)sulfonyl)vinyl)sulfane **(32)**



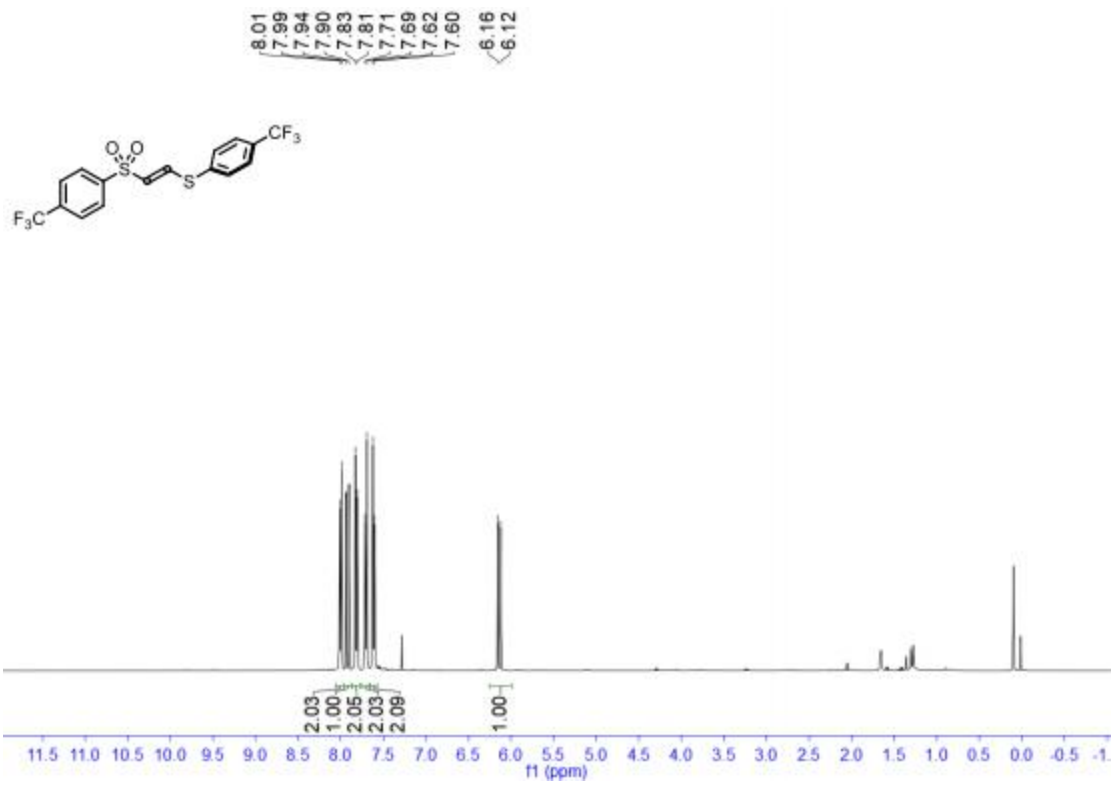
Supplementary Figure 202 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(4-chlorophenyl)(2-((4-chlorophenyl)sulfonyl)vinyl)sulfane **(33)**



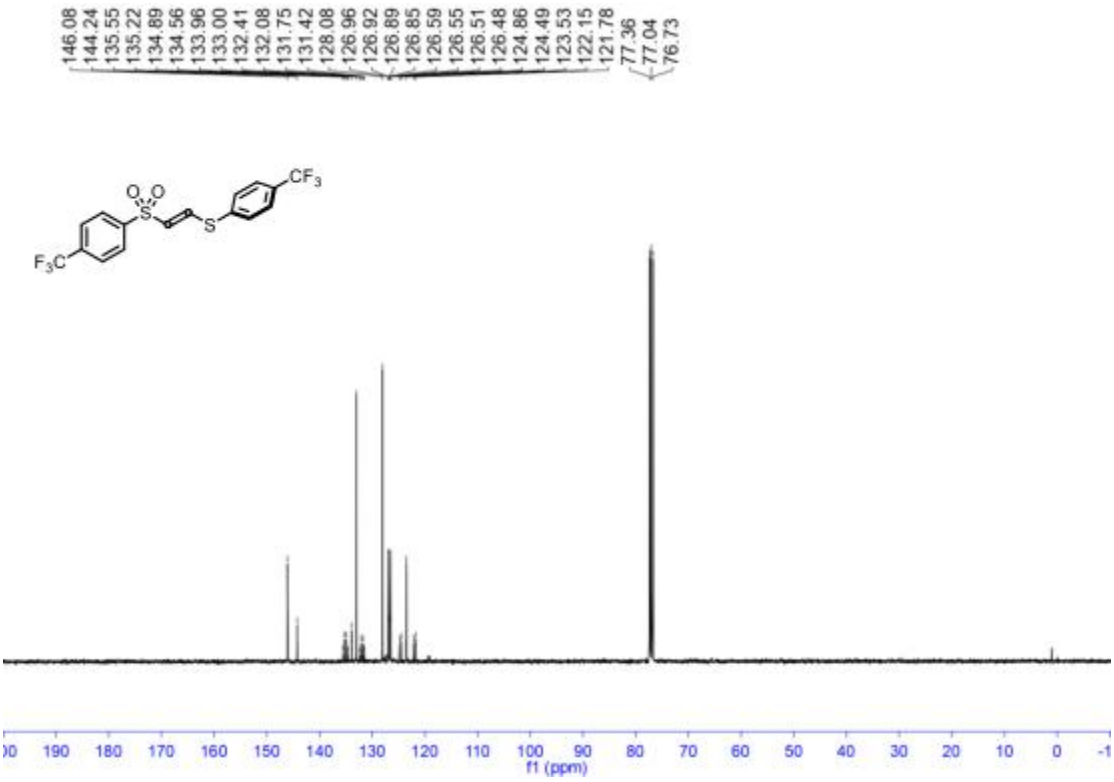
Supplementary Figure 203 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(4-chlorophenyl)(2-((4-chlorophenyl)sulfonyl)vinyl)sulfane **(33)**



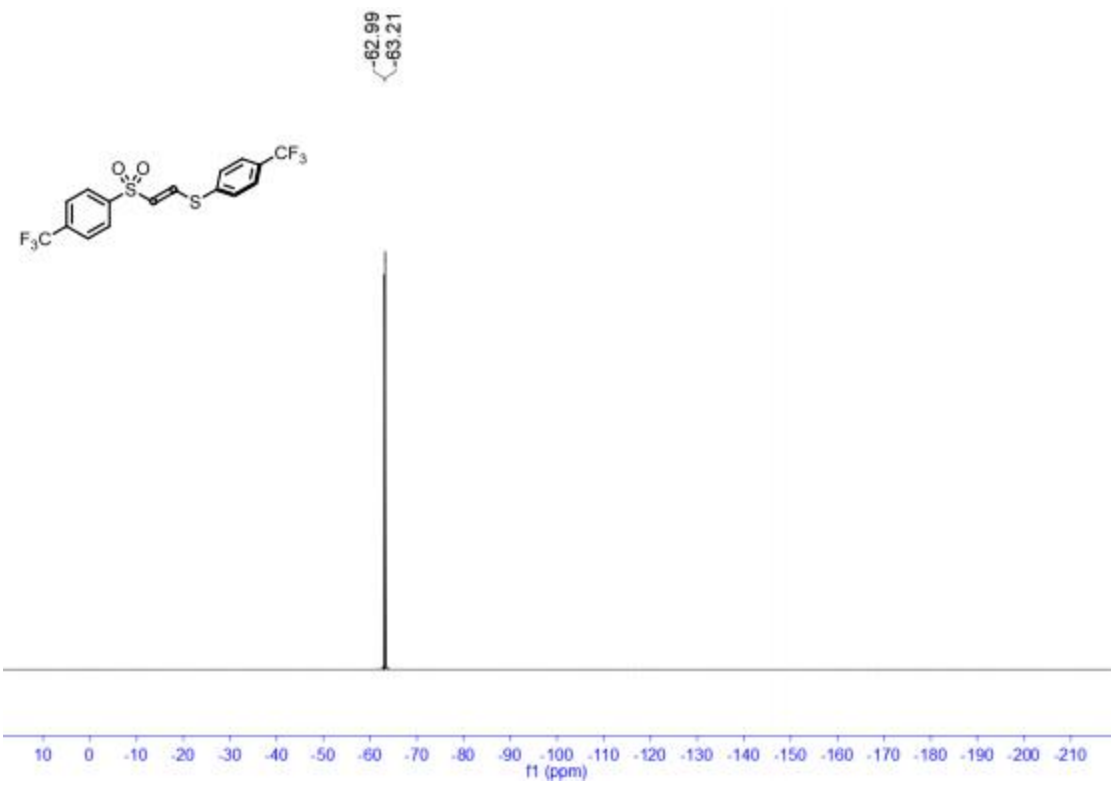
Supplementary Figure 204 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(trifluoromethyl)phenyl)(2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane **(34)**



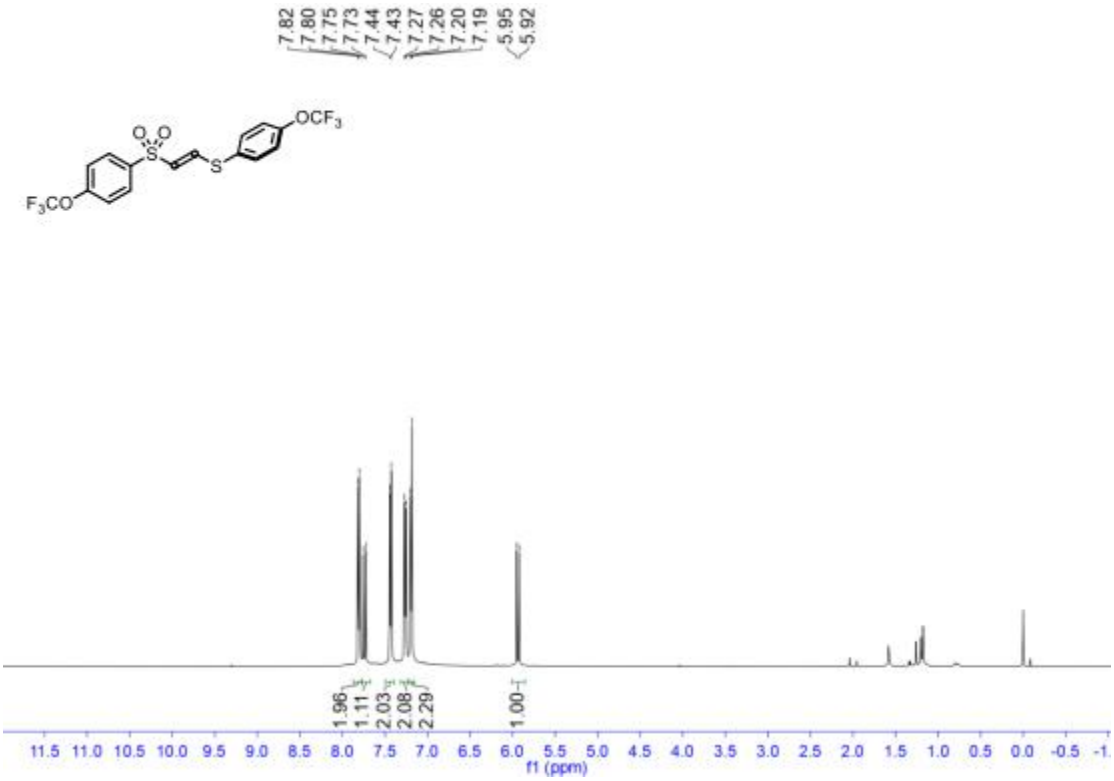
Supplementary Figure 205 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(trifluoromethyl)phenyl)(2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane **(34)**



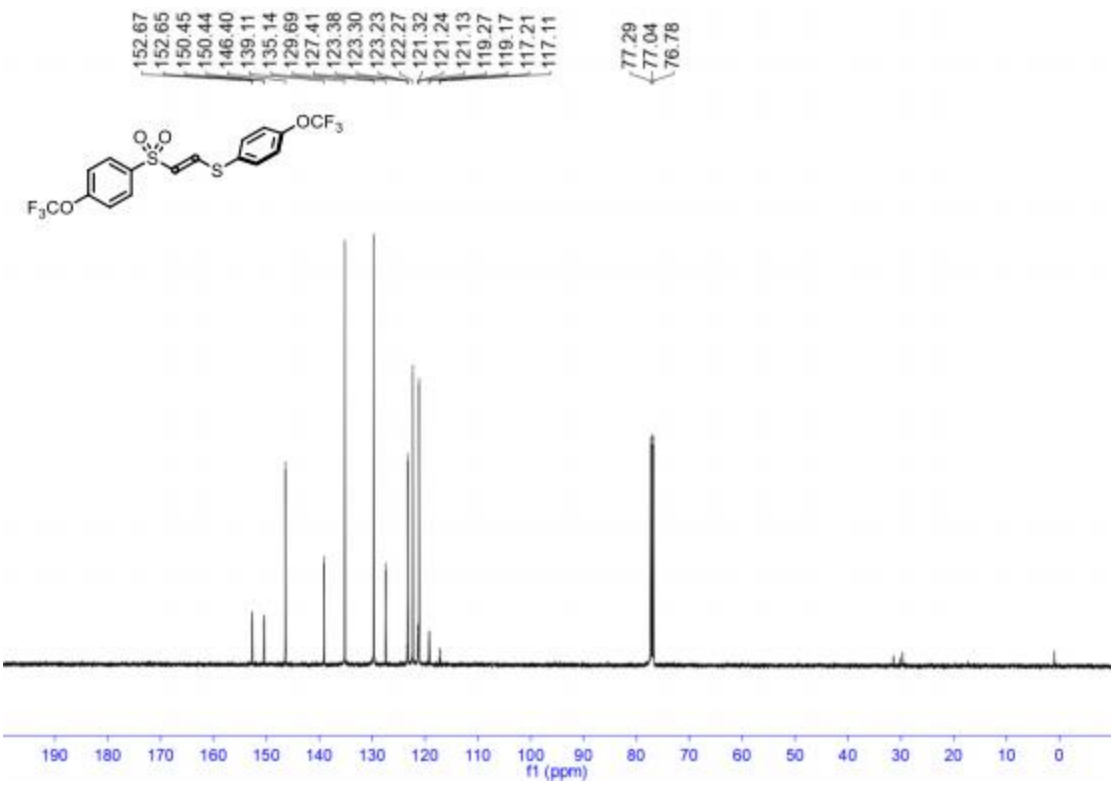
Supplementary Figure 206 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(trifluoromethyl)phenyl)(2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)sulfane **(34)**



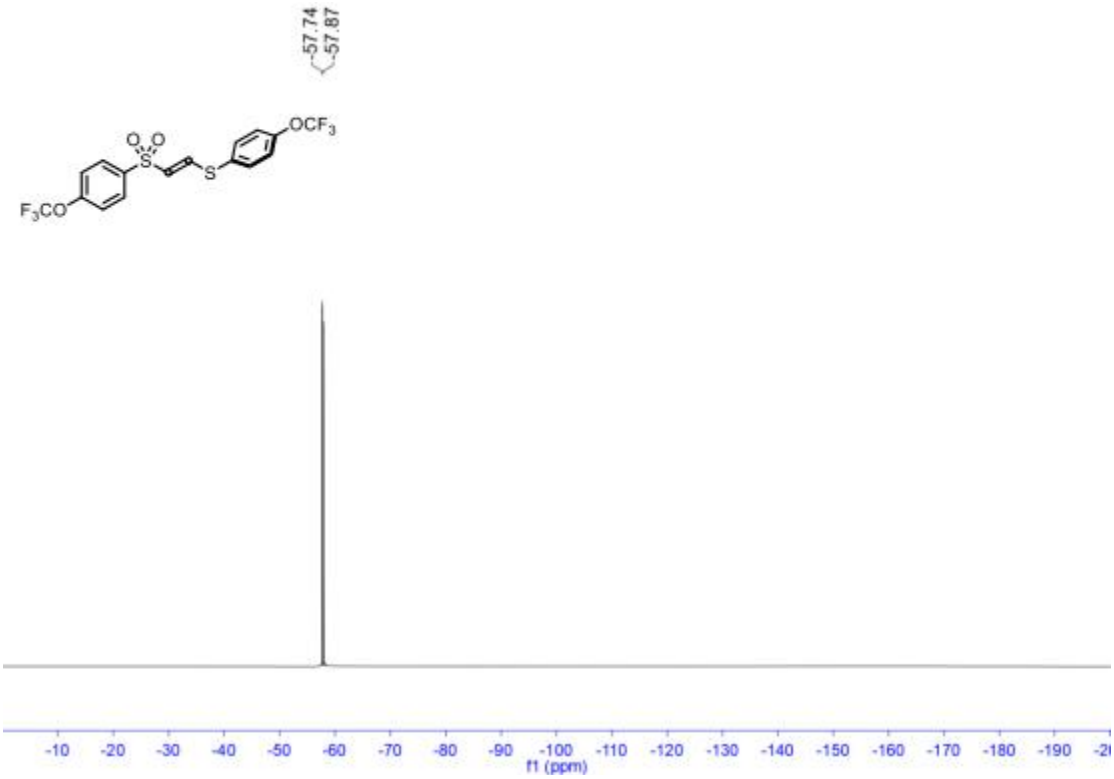
Supplementary Figure 207 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(trifluoromethoxy)phenyl)(2-((4-(trifluoromethoxy)phenyl)sulfonyl)vinyl)sulfane **(35)**



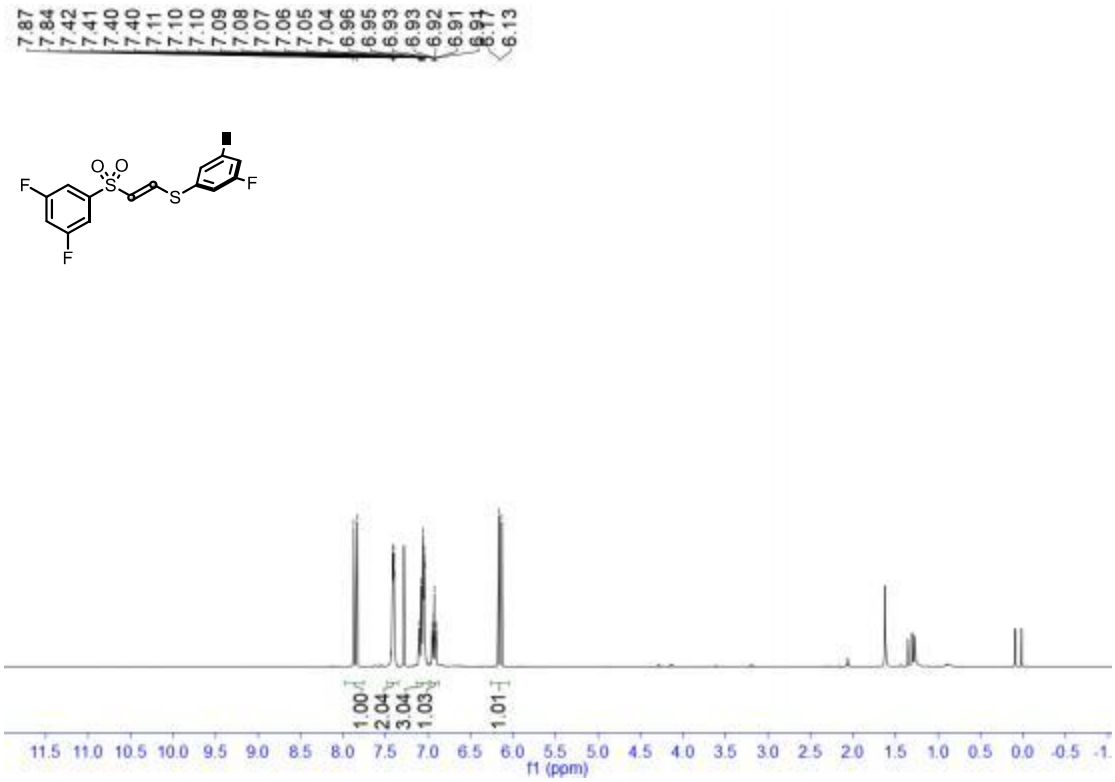
Supplementary Figure 208 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(trifluoromethoxy)phenyl)(2-((4-(trifluoromethoxy)phenyl)sulfonyl)vinyl)sulfane **(34)**



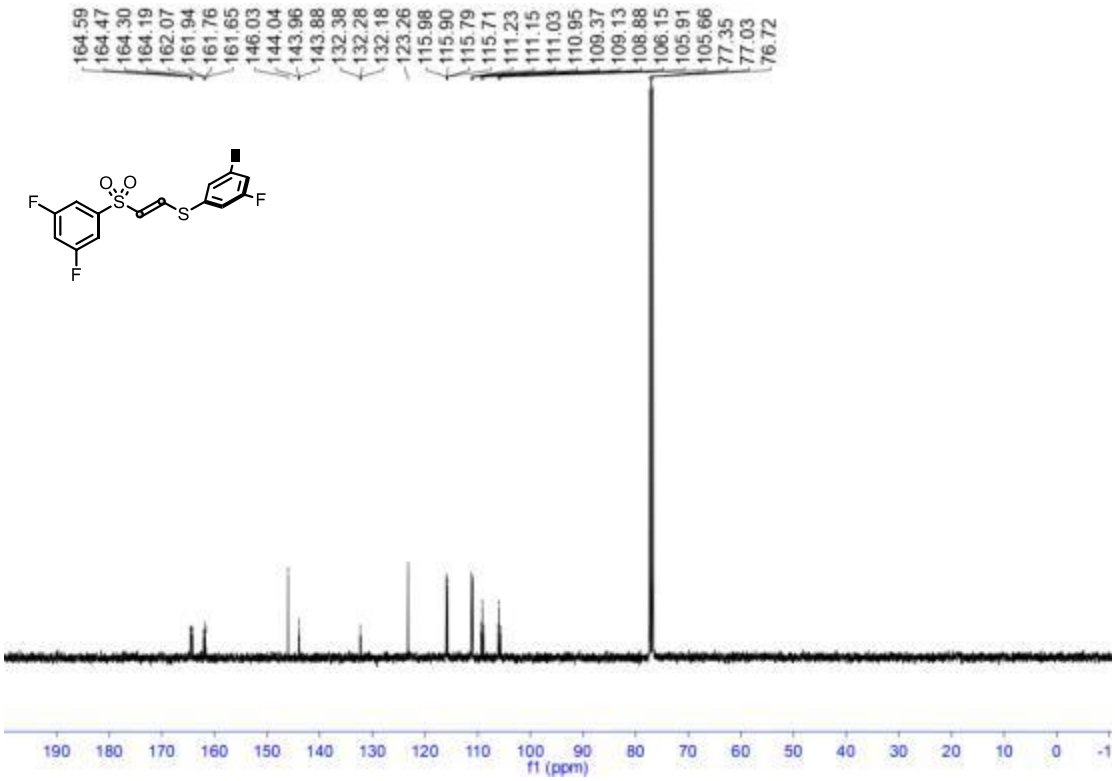
Supplementary Figure 209 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of (*E*)-(4-(trifluoromethoxy)phenyl)(2-((4-(trifluoromethoxy)phenyl)sulfonyl)vinyl)sulfane **(35)**



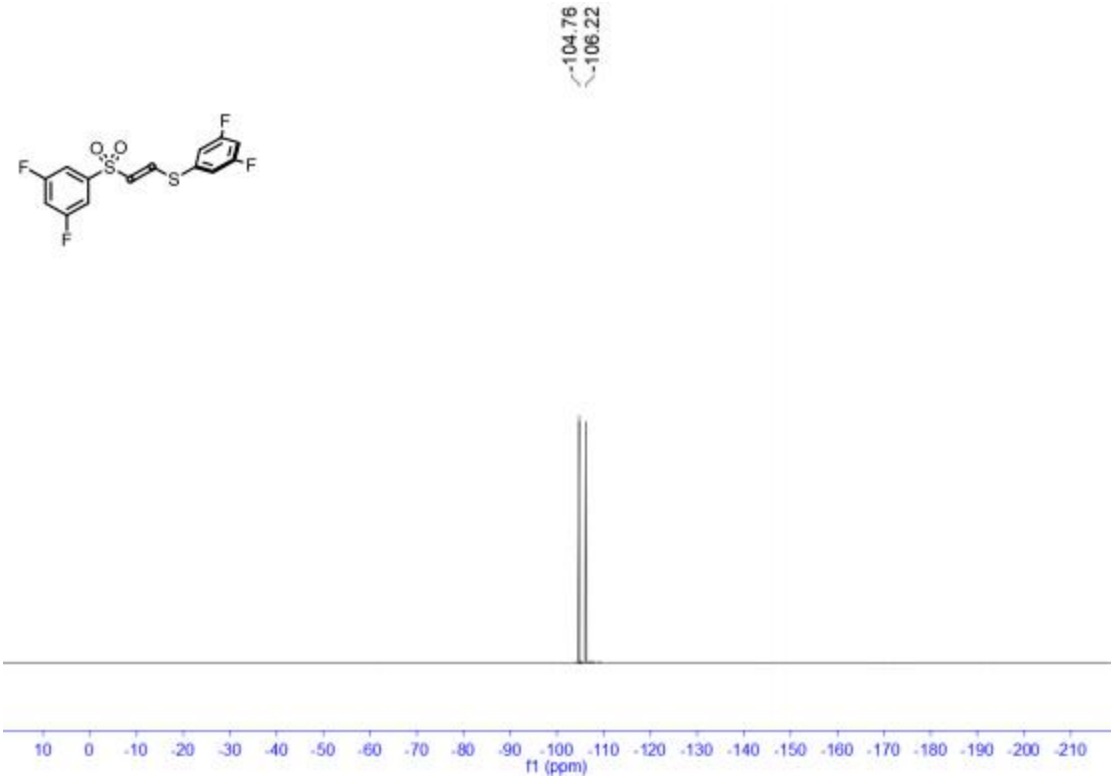
Supplementary Figure 210 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-(3,5-difluorophenyl)(2-((3,5-difluorophenyl)sulfonyl)vinyl)sulfane **(36)**



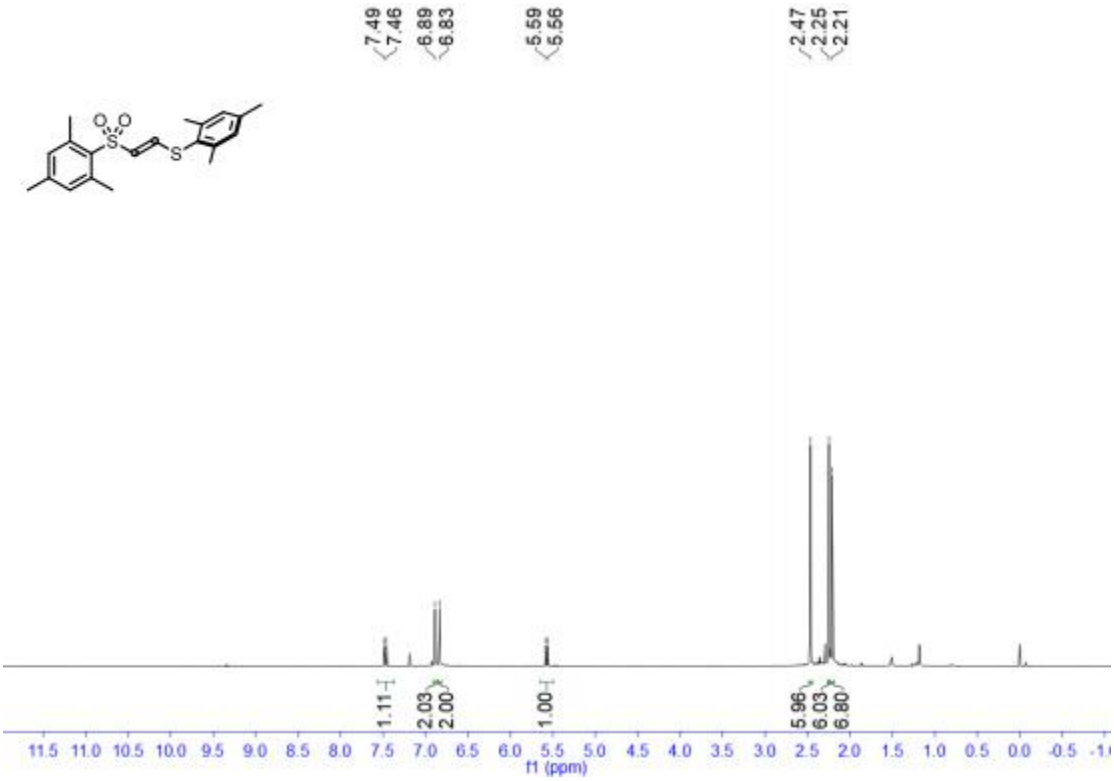
Supplementary Figure 211 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(3,5-difluorophenyl)(2-((3,5-difluorophenyl)sulfonyl)vinyl)sulfane **(36)**



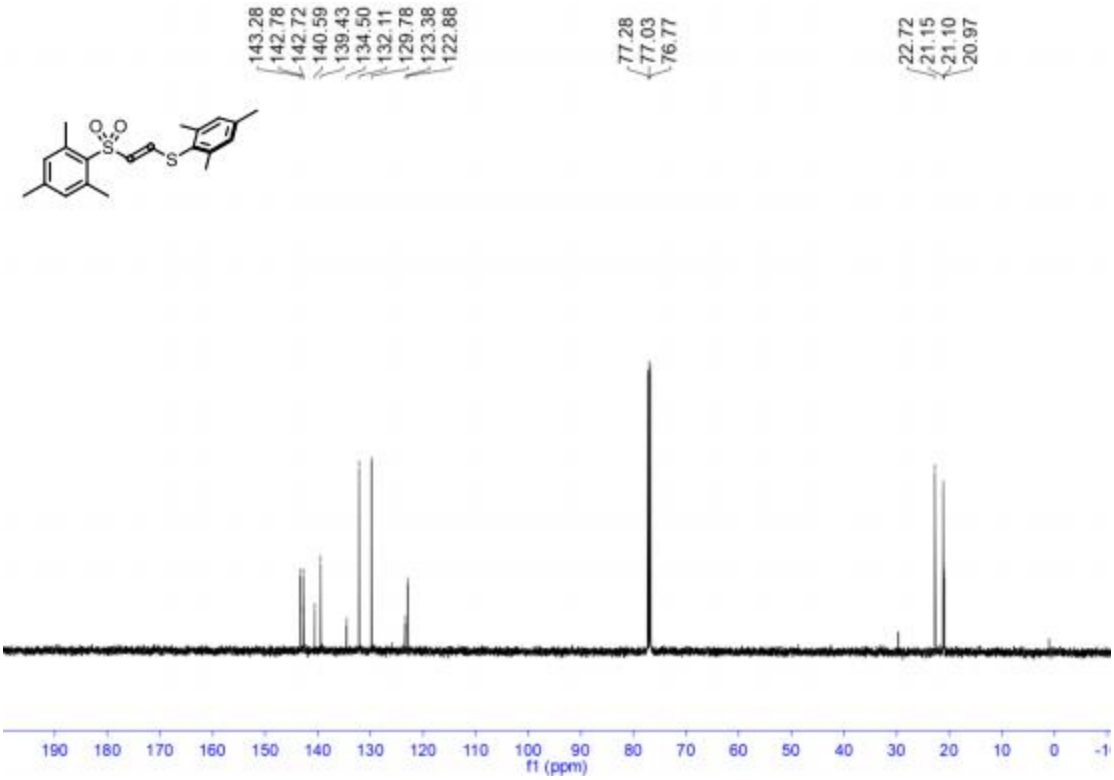
Supplementary Figure 212 | ^{19}F NMR (376 MHz, 298K, Chloroform-*d*) of (*E*)-(3,5-difluorophenyl)(2-((3,5-difluorophenyl)sulfonyl)vinyl)sulfane **(36)**



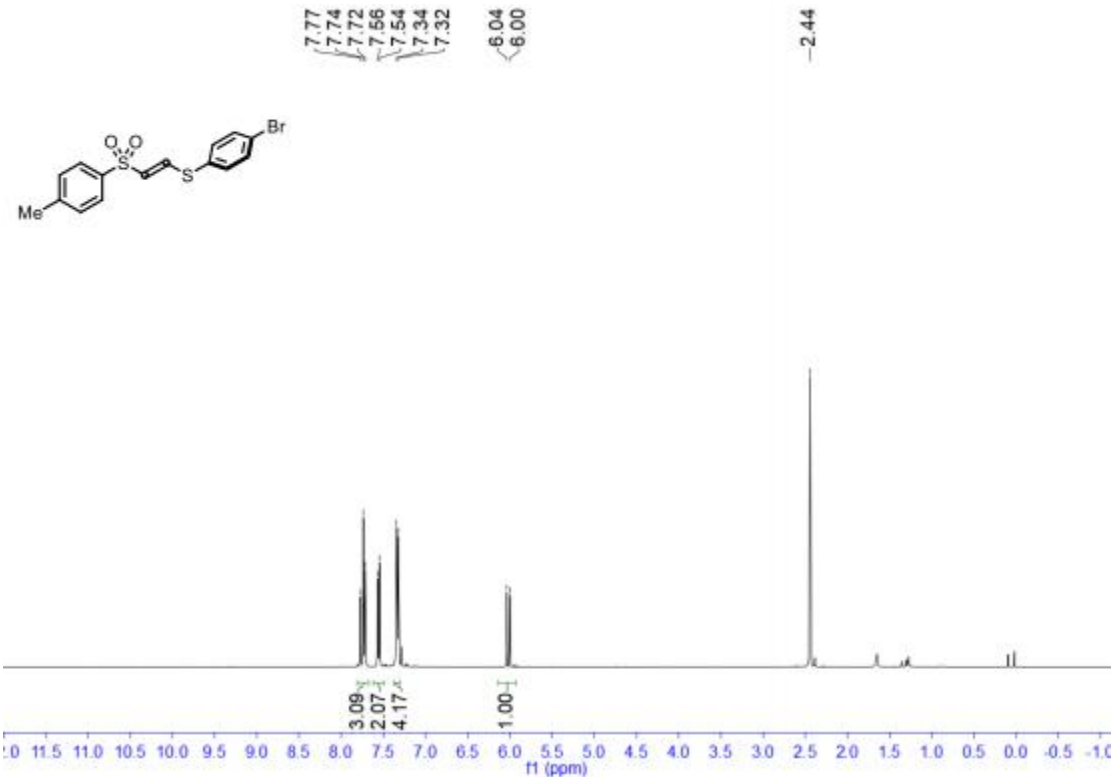
Supplementary Figure 213 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-mesityl(2-(mesitylsulfonyl)vinyl)sulfane **(37)**



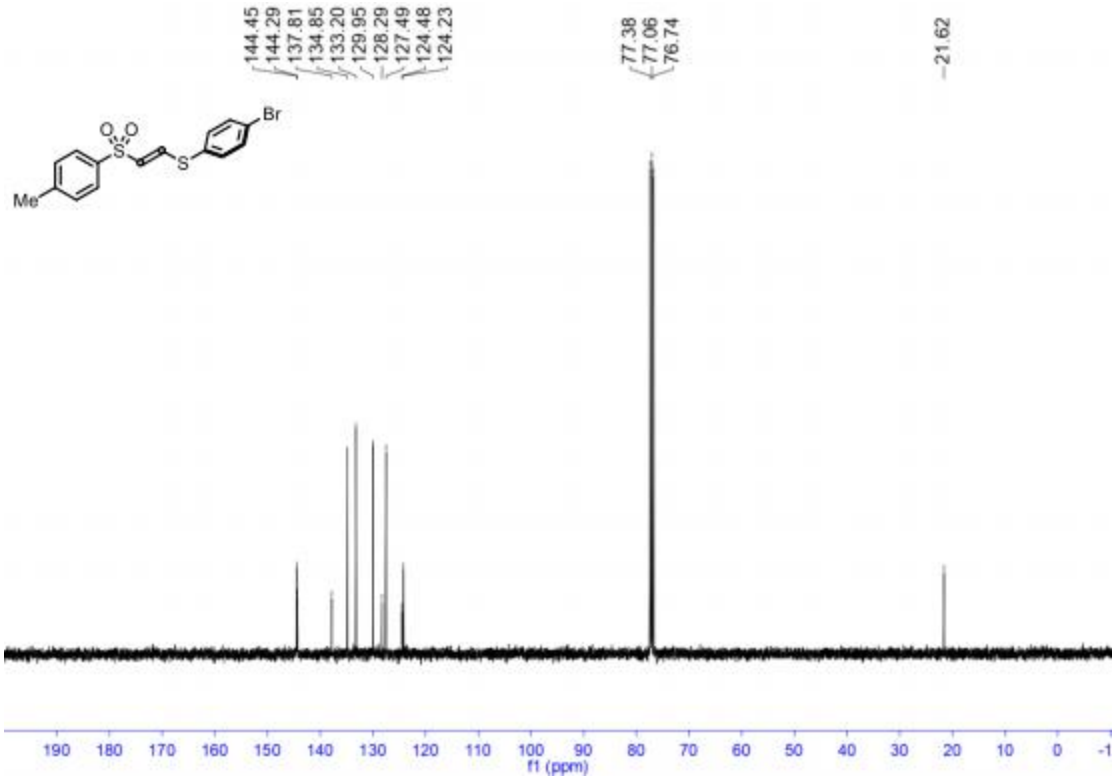
Supplementary Figure 214 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-mesityl(2-(mesitylsulfonyl)vinyl)sulfane **(37)**



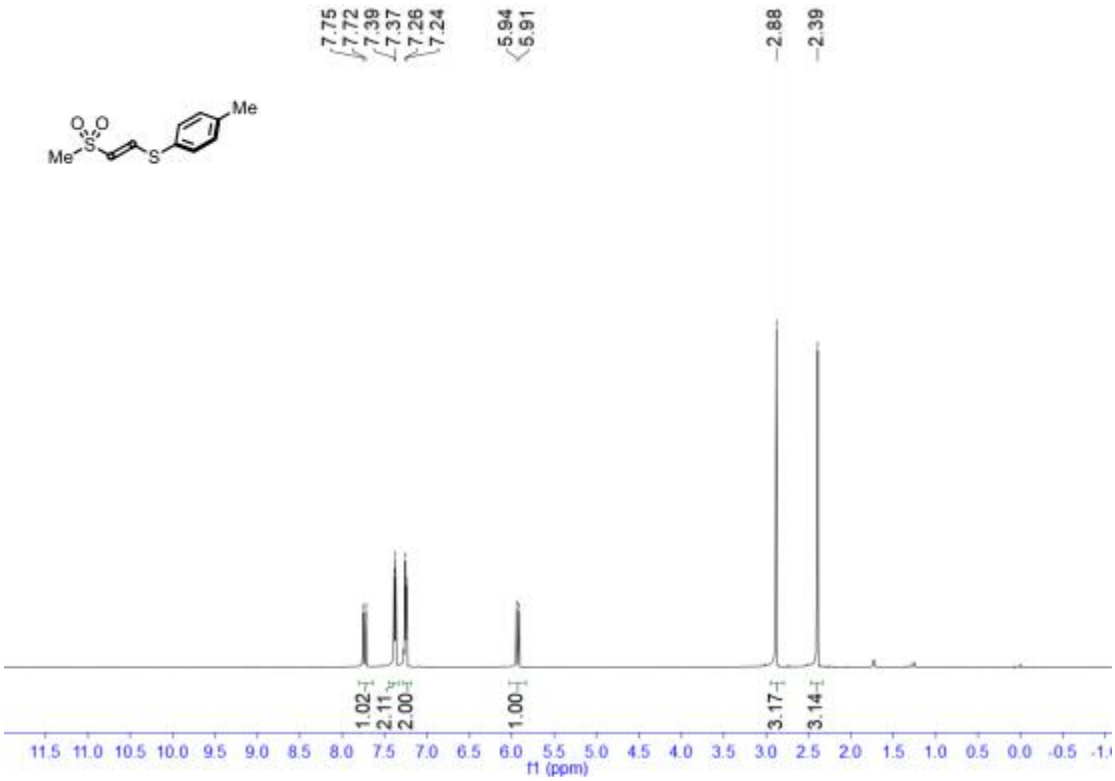
Supplementary Figure 215 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(4-bromophenyl)(2-tosylvinyl)sulfane **(38)**



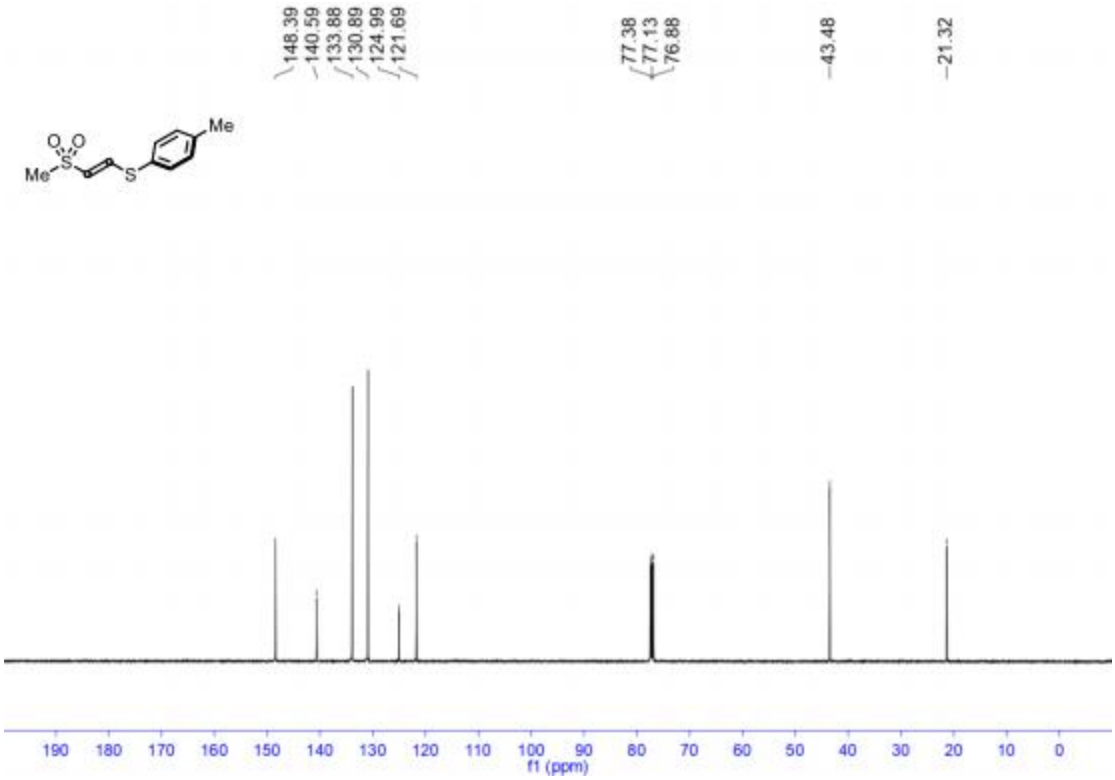
Supplementary Figure 216 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(4-bromophenyl)(2-tosylvinyl)sulfane **(38)**



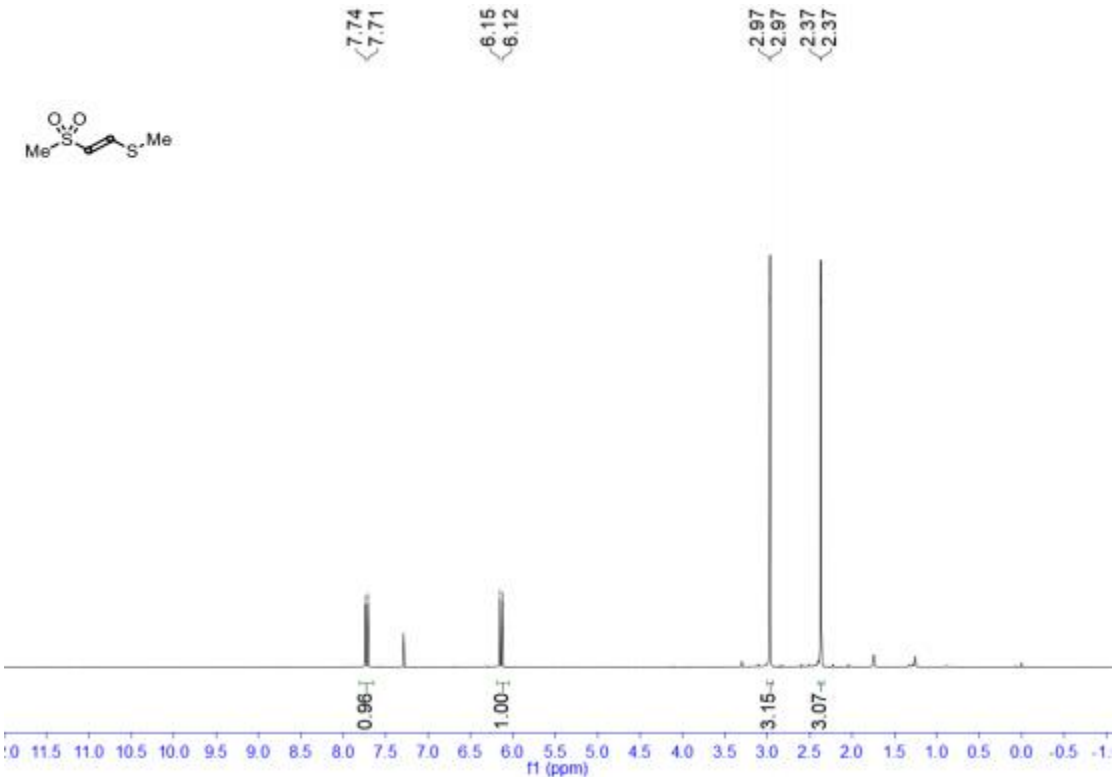
Supplementary Figure 217 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-(2-(methylsulfonyl)vinyl)(*p*-tolyl)sulfane **(39)**



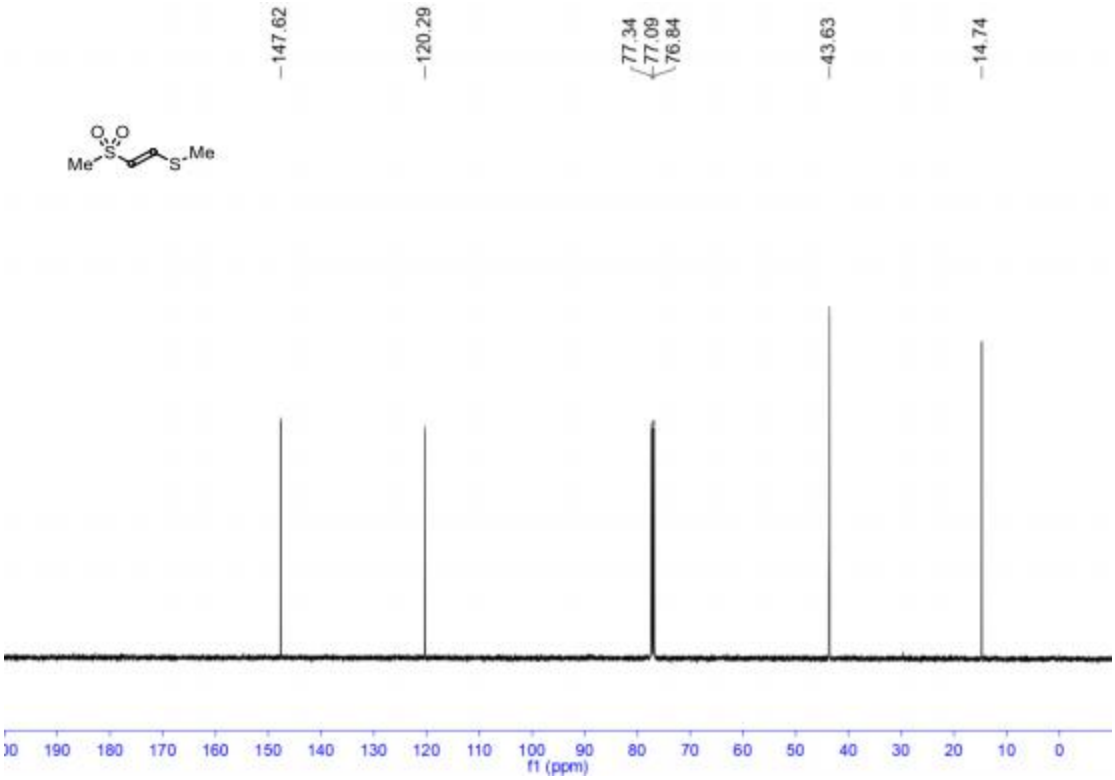
Supplementary Figure 218 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(2-(methylsulfonyl)vinyl)(*p*-tolyl)sulfane **(39)**



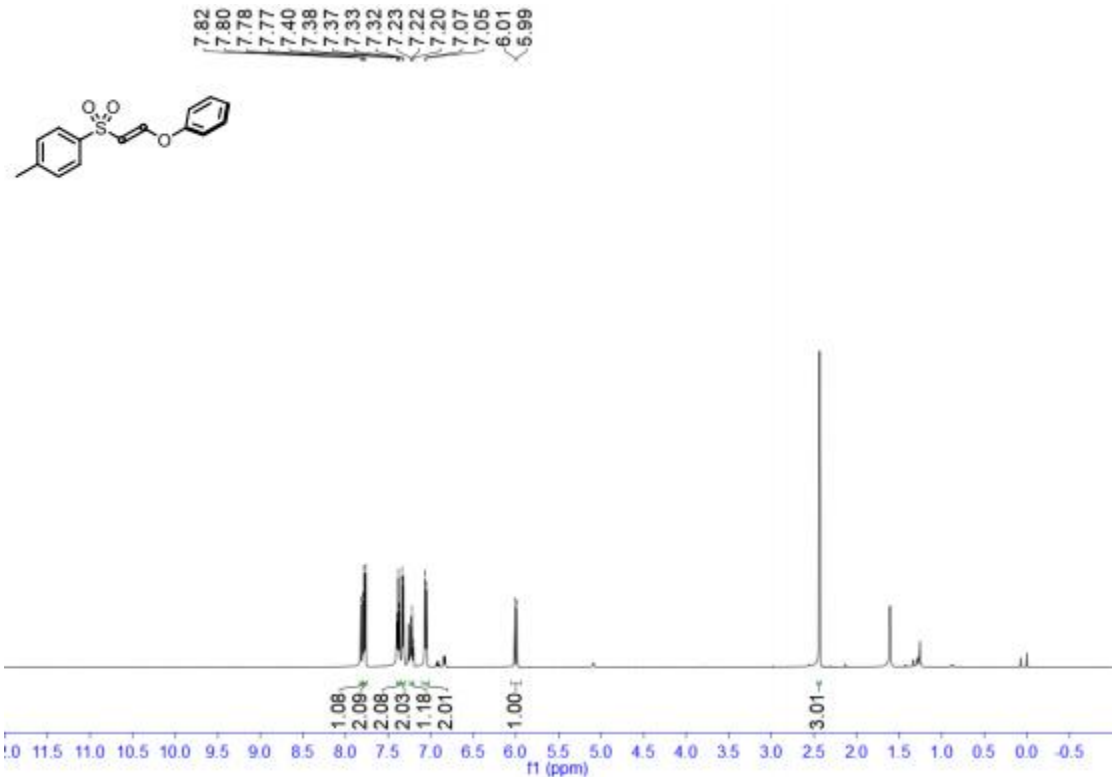
Supplementary Figure 219 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-methyl(2-(methylsulfonyl)vinyl)sulfane **(40)**



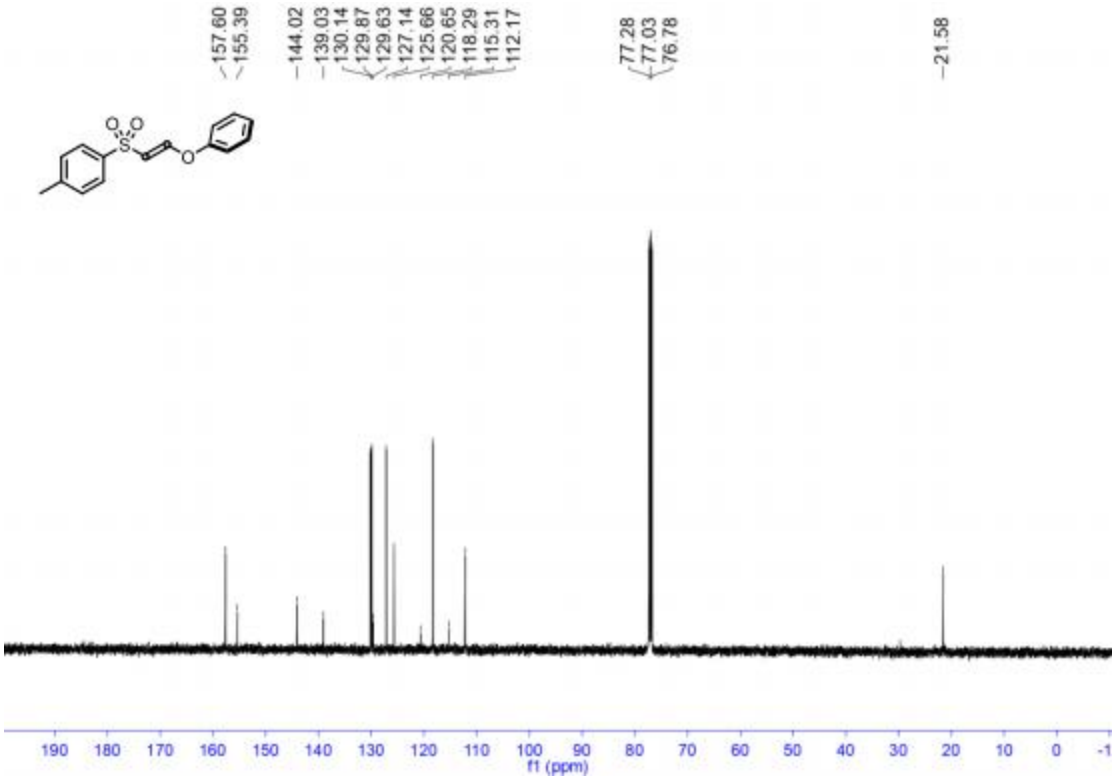
Supplementary Figure 220 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-methyl(2-(methylsulfonyl)vinyl)sulfane **(40)**



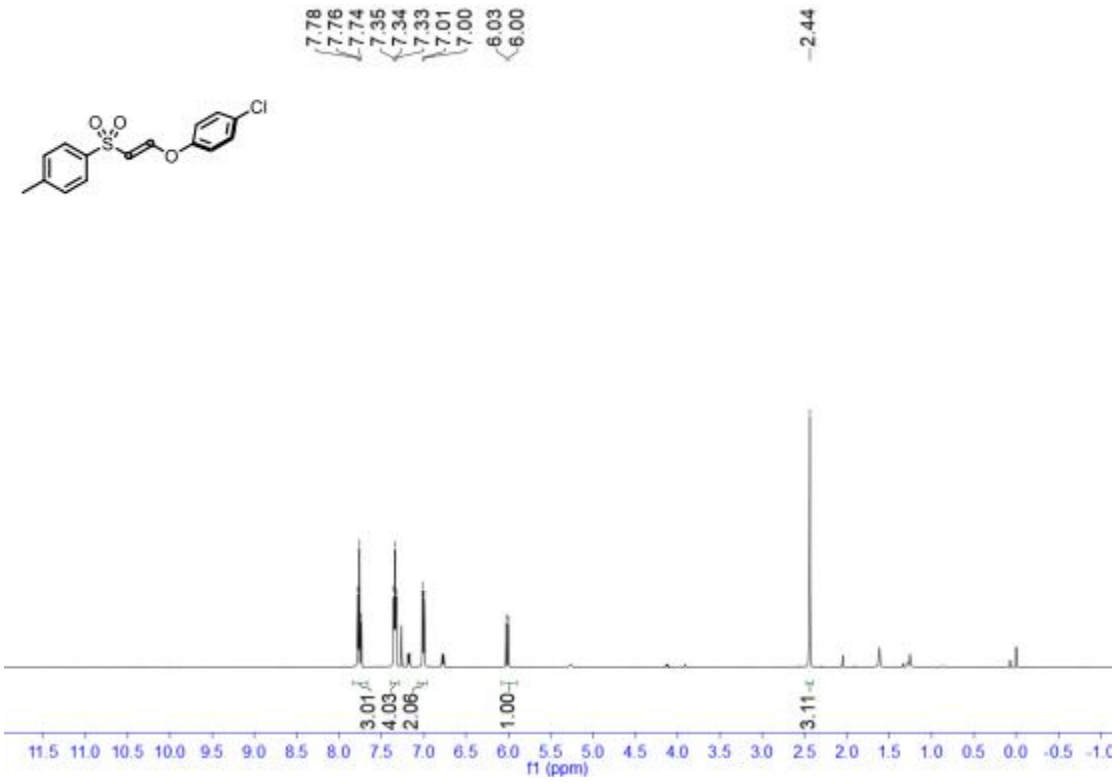
Supplementary Figure 221 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)- 1-methyl-4-((2-phenoxyvinyl)sulfonyl)benzene **(41)**



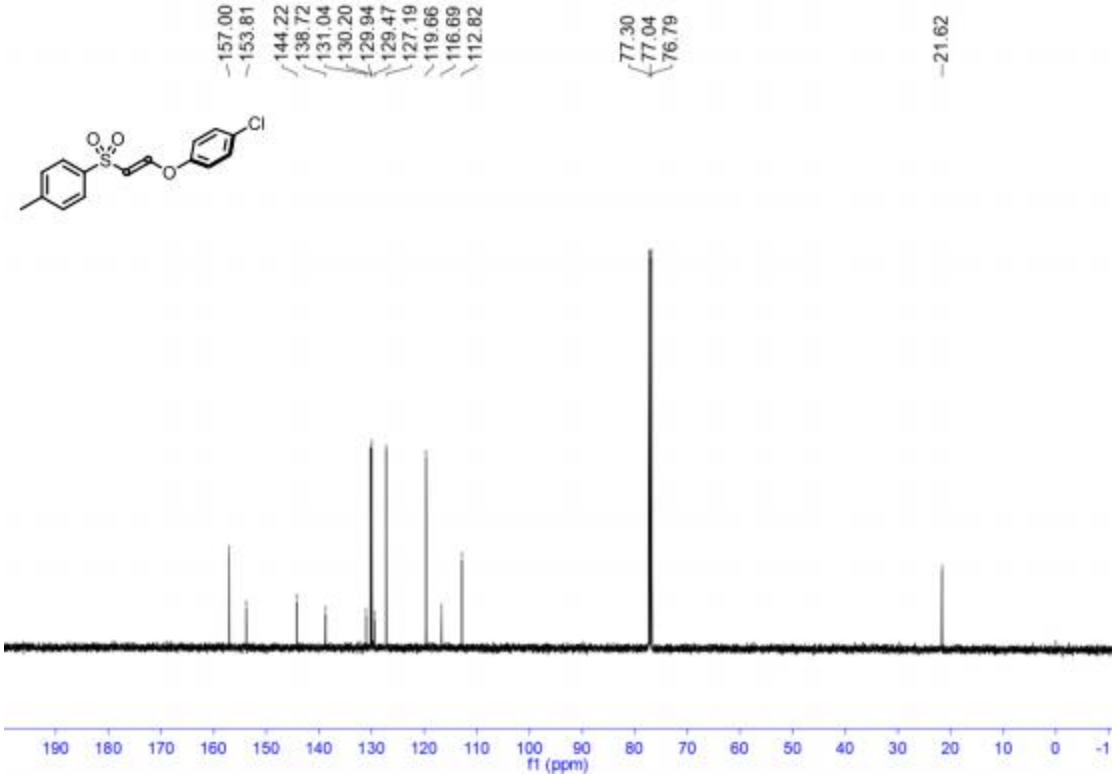
Supplementary Figure 222 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)- 1-methyl-4-((2-phenoxyvinyl)sulfonyl)benzene **(41)**



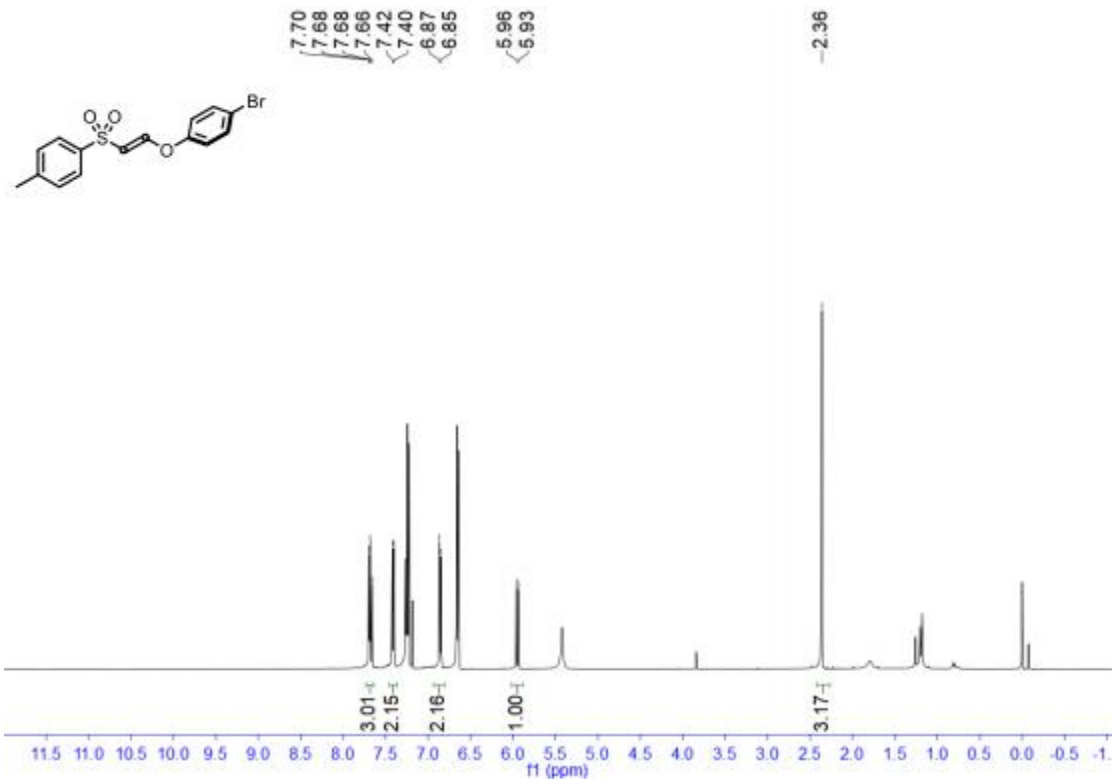
Supplementary Figure 223 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)- 1-chloro-4-((2-tosylvinyl)oxy)benzene **(42)**



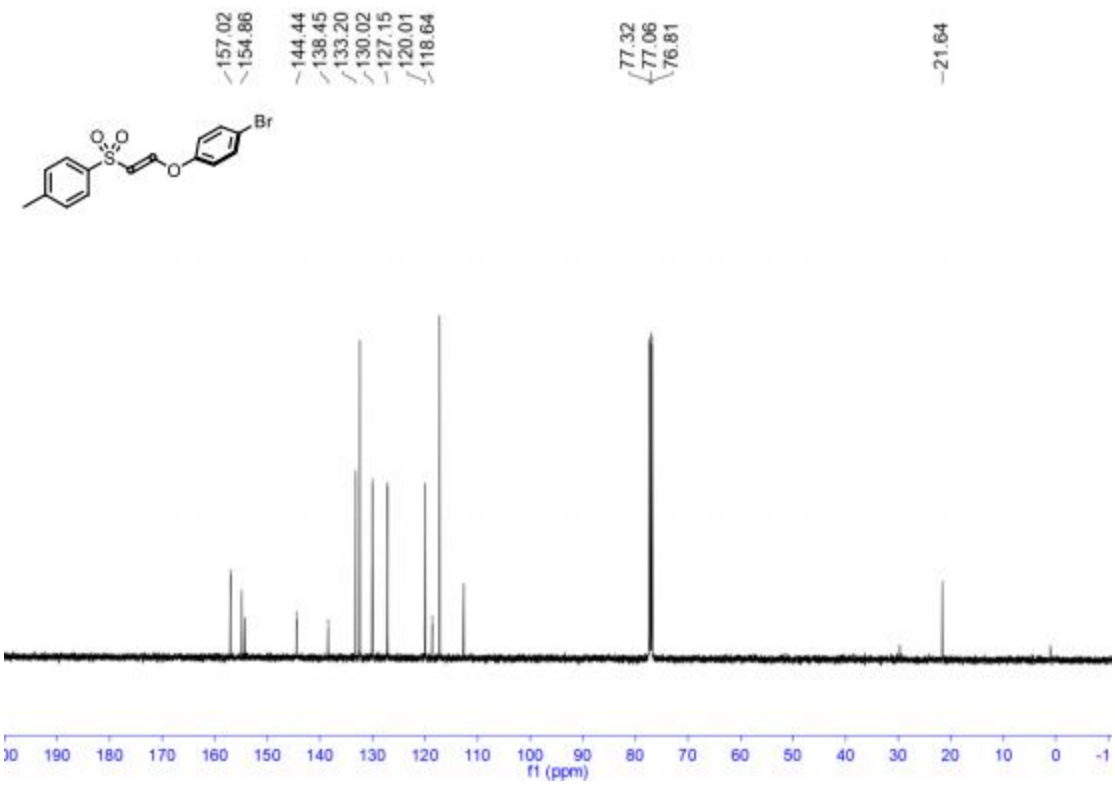
Supplementary Figure 224 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)- 1-chloro-4-((2-tosylvinyl)oxy)benzene **(42)**



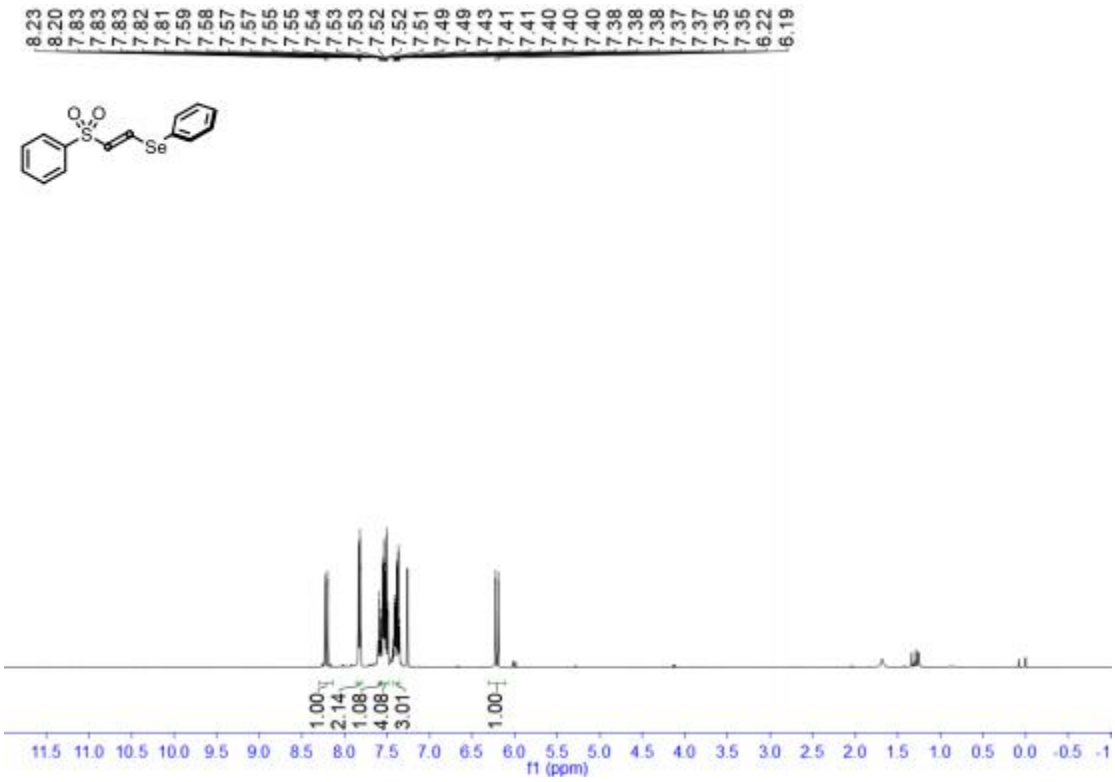
Supplementary Figure 225 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)- 1-bromo-4-((2-tosylvinyl)oxy)benzene **(43)**



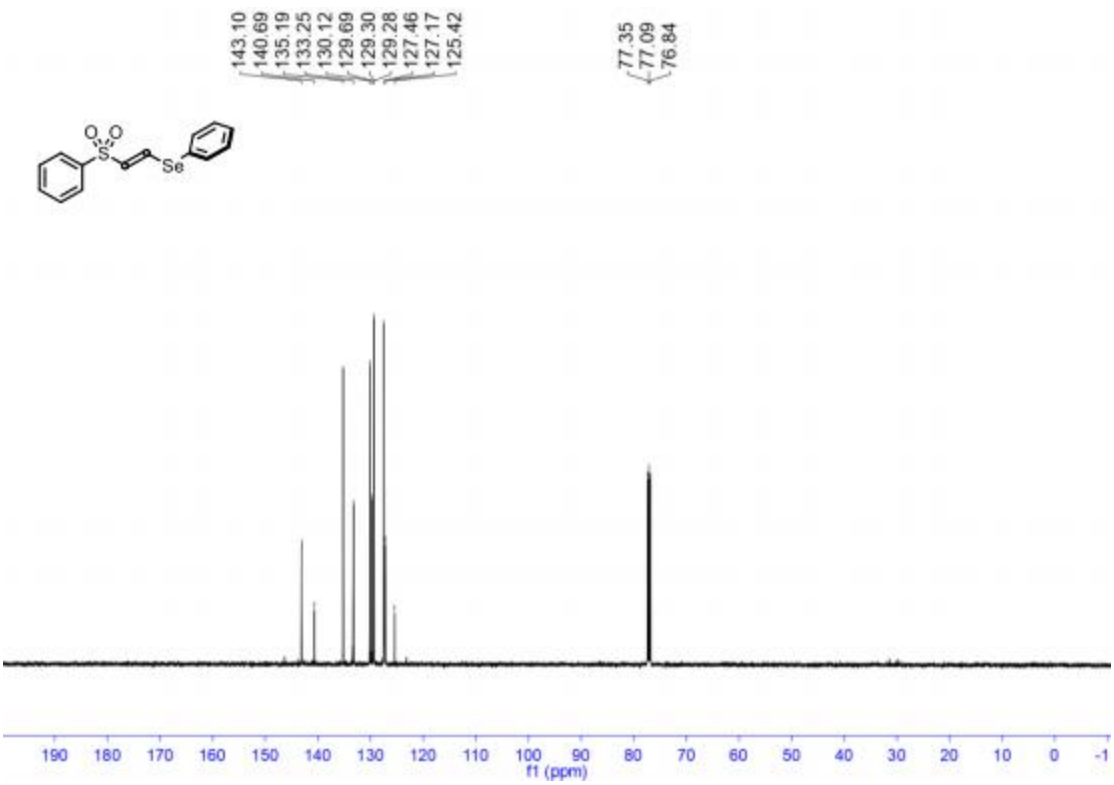
Supplementary Figure 226 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)- 1-bromo-4-((2-tosylvinyl)oxy)benzene **(43)**



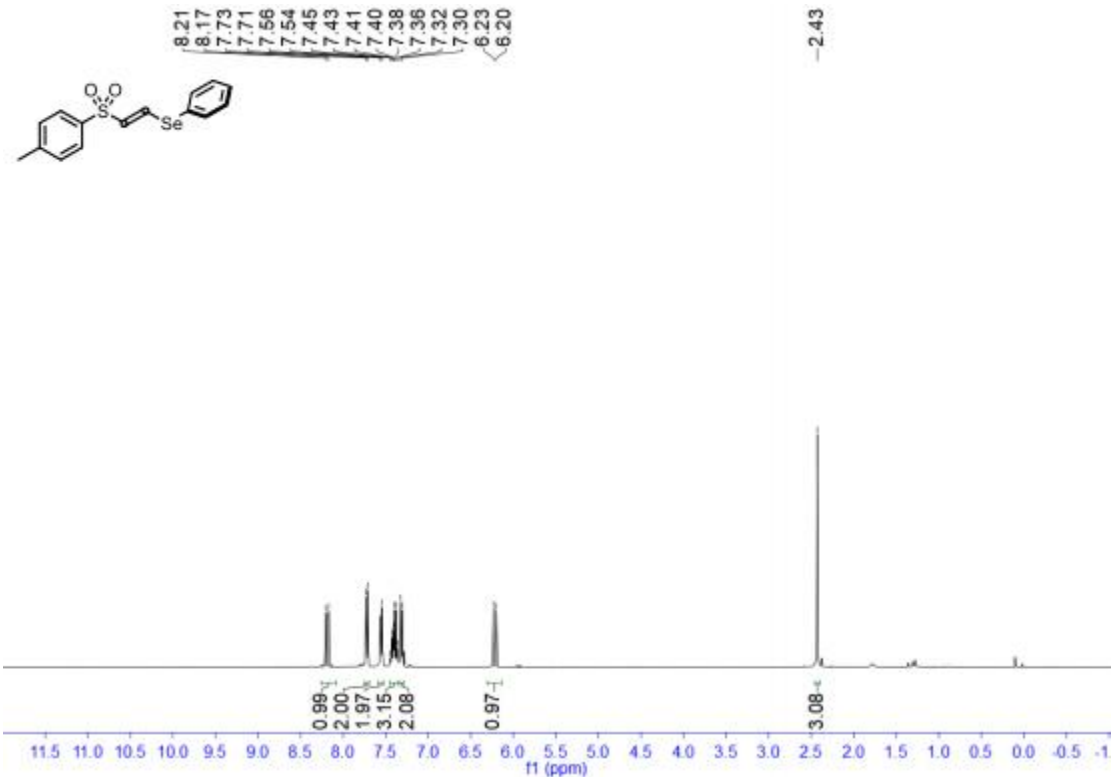
Supplementary Figure 227 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-phenyl(2-(phenylsulfonyl)vinyl)selane **(44)**



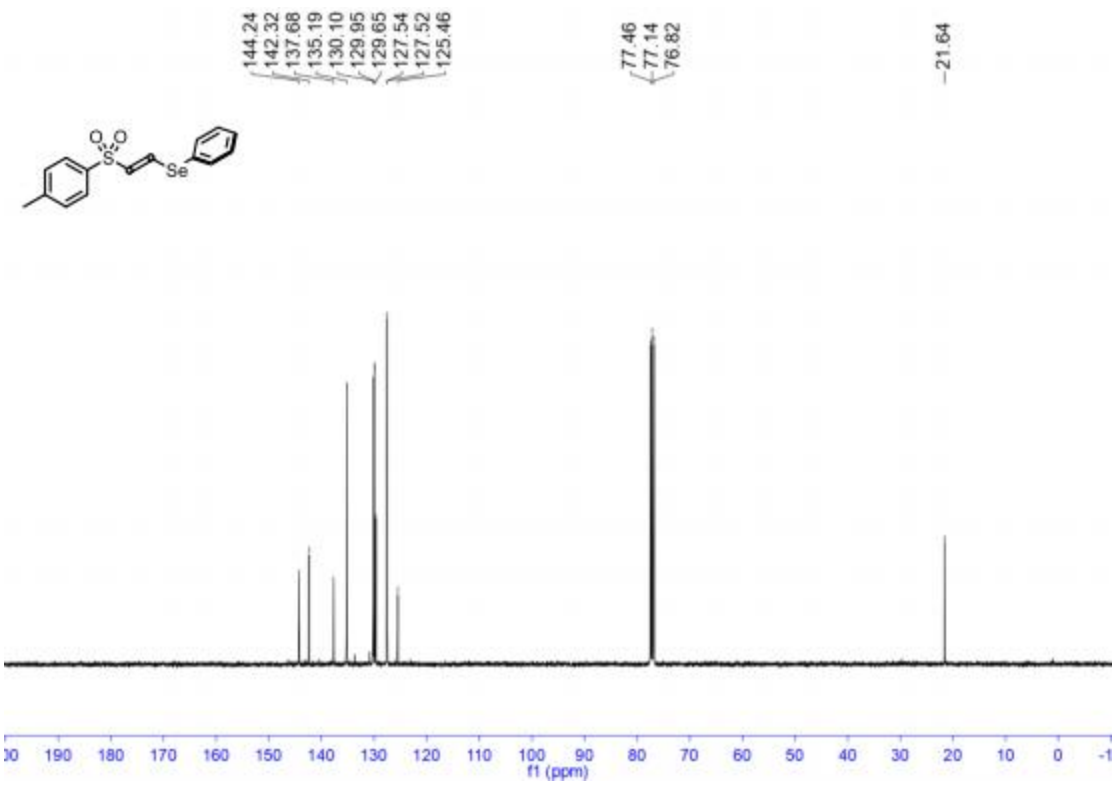
Supplementary Figure 228 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-phenyl(2-(phenylsulfonyl)vinyl)selane **(44)**



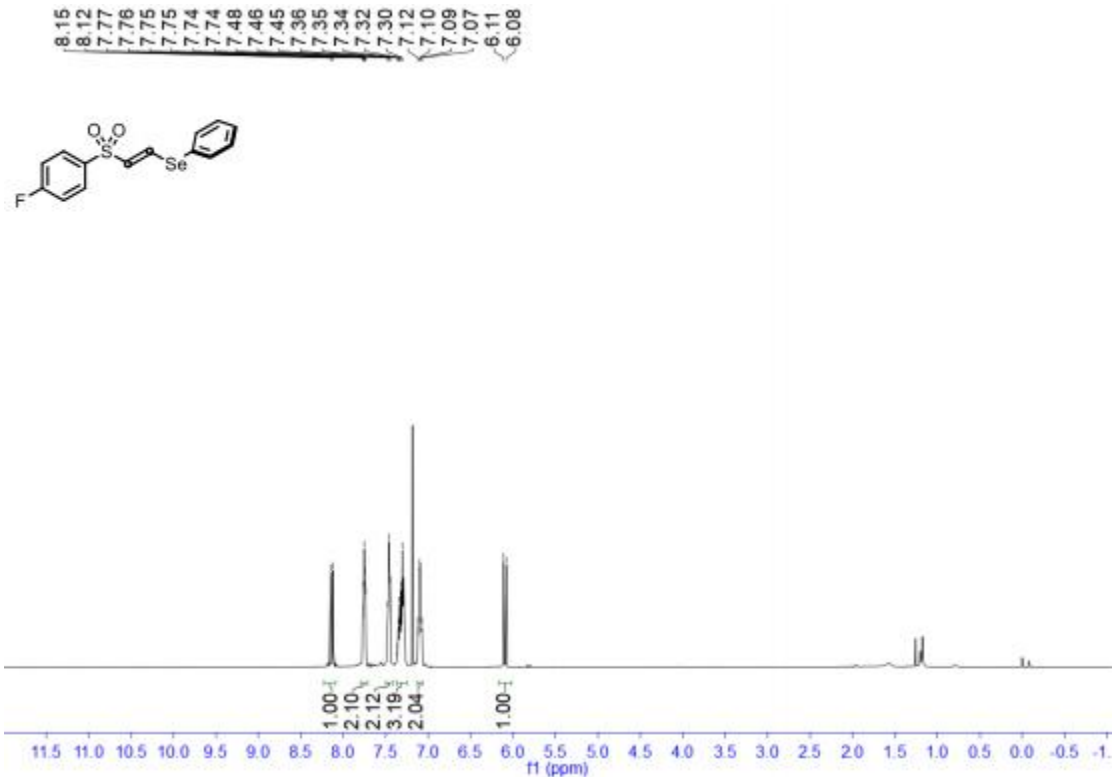
Supplementary Figure 229 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-phenyl(2-tosylvinyl)selane **(45)**



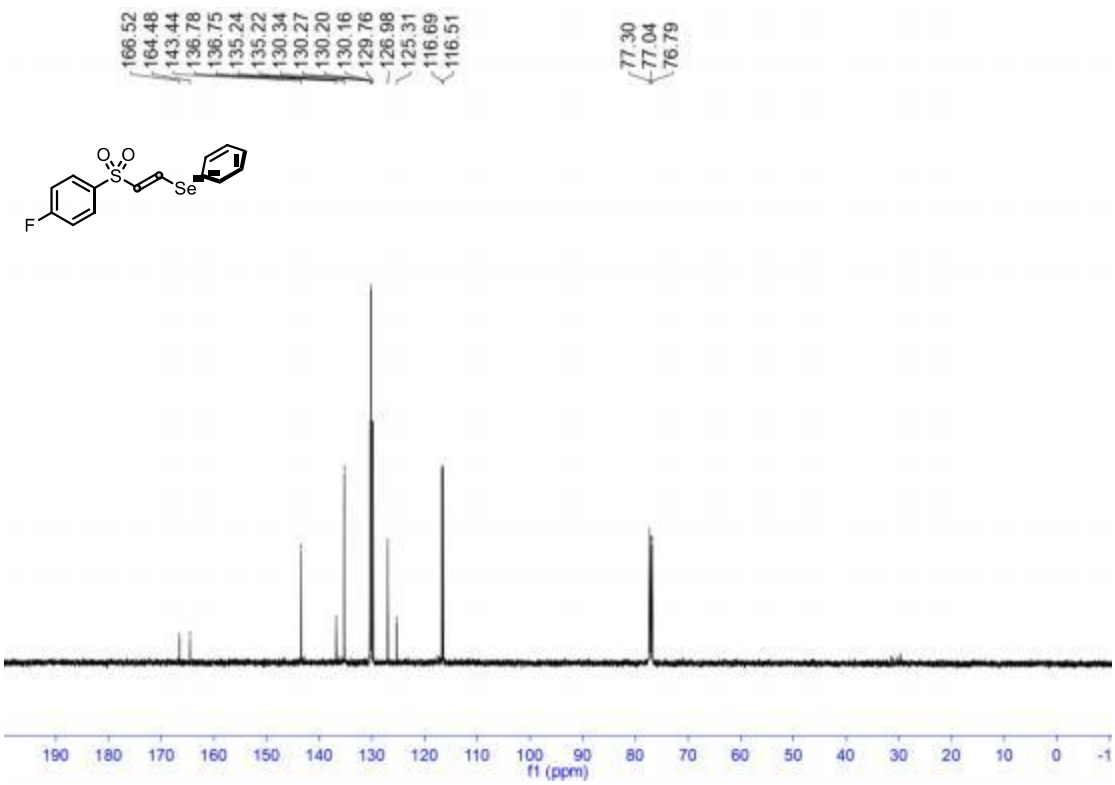
Supplementary Figure 230 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-phenyl(2-tosylvinyl)selane **(45)**



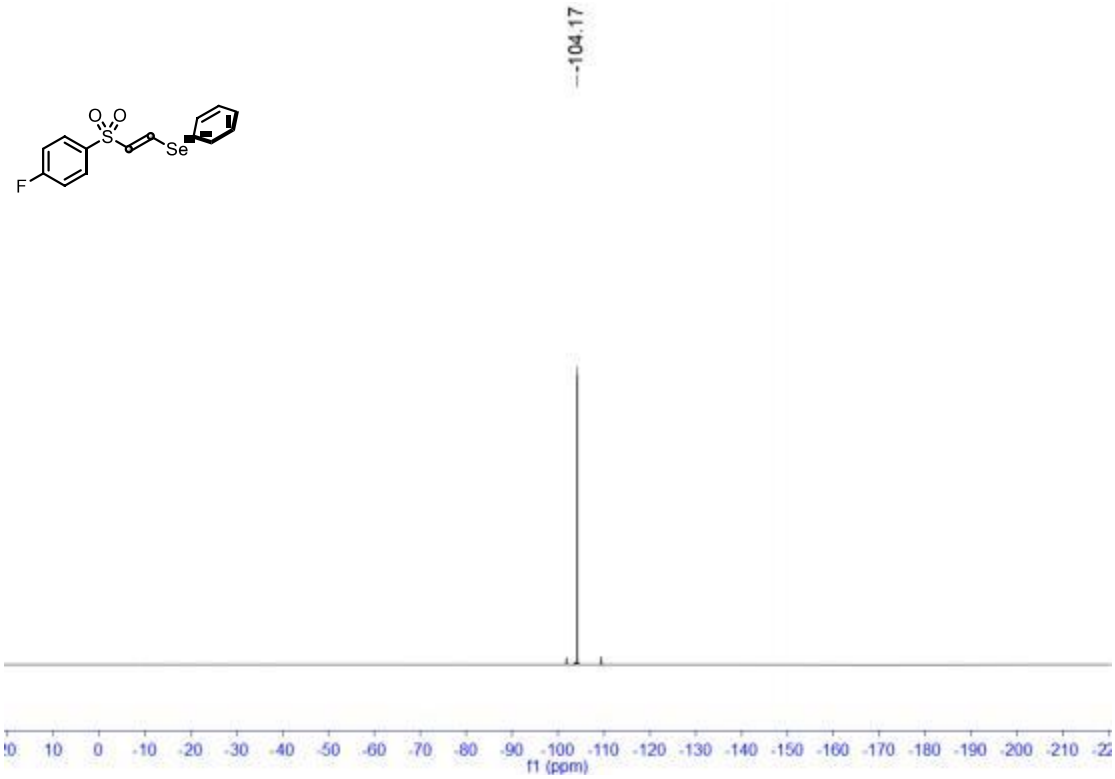
Supplementary Figure 231 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-fluorophenyl)sulfonyl)vinyl)(phenyl)Selane **(46)**



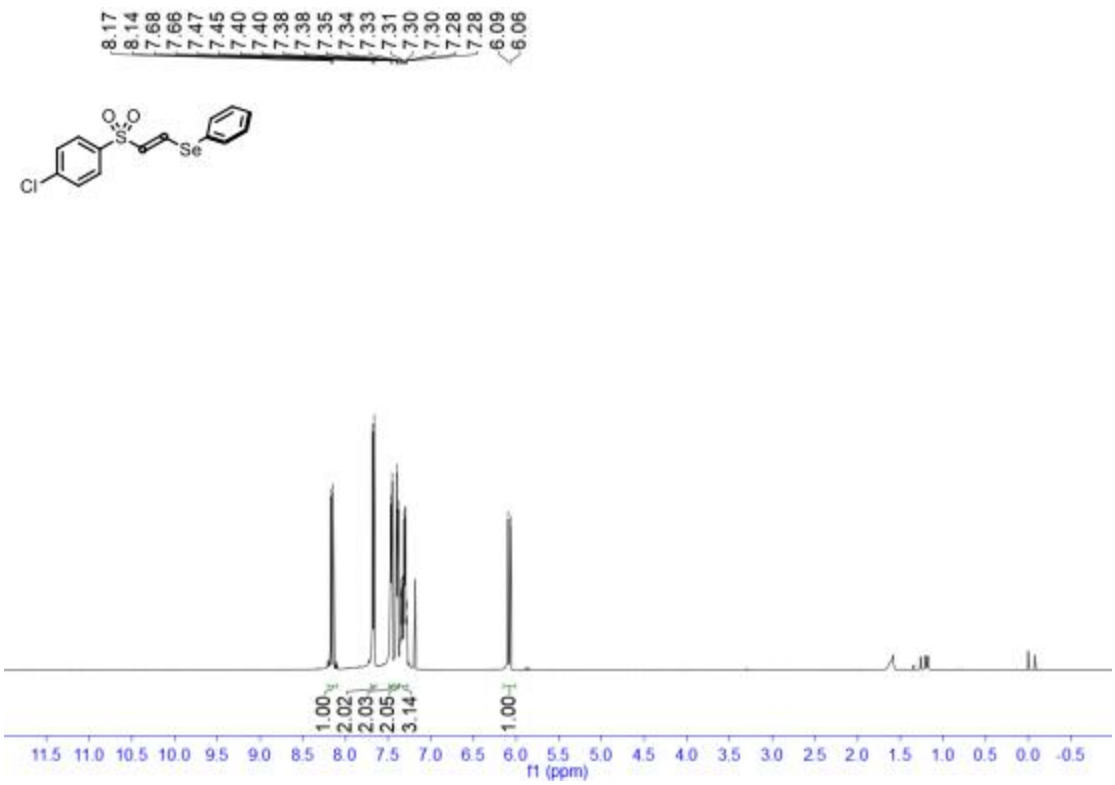
Supplementary Figure 232 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-fluorophenyl)sulfonyl)vinyl)(phenyl)Selane **(46)**



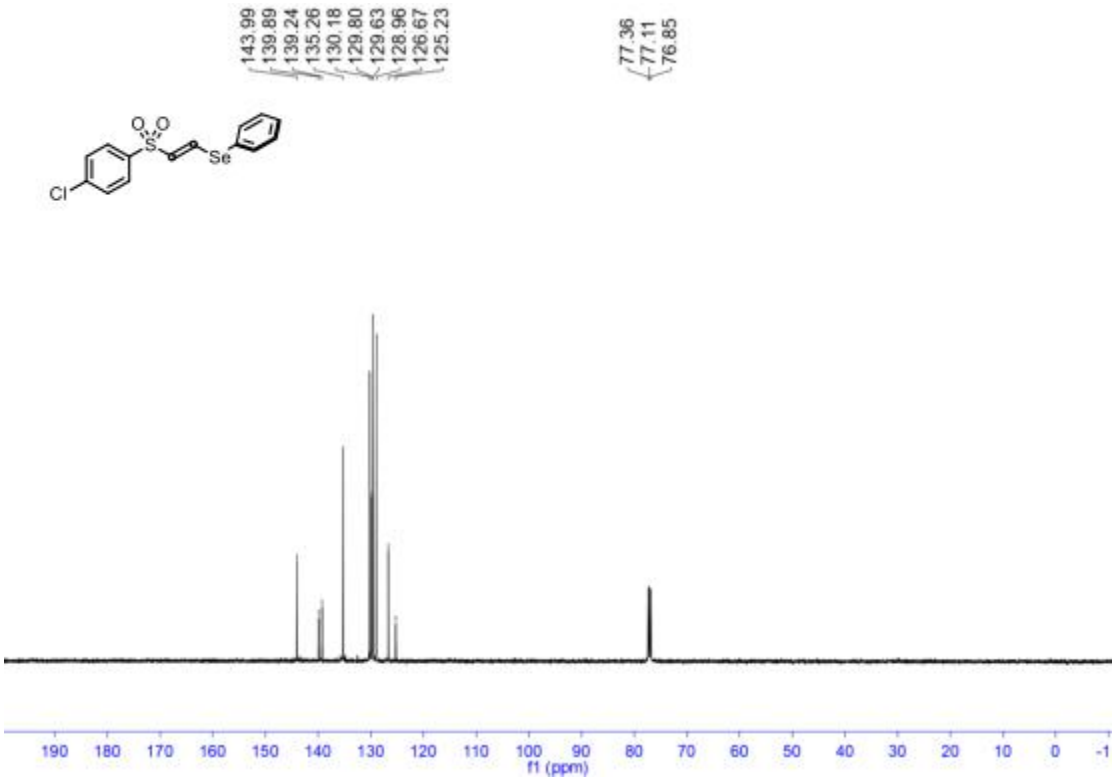
Supplementary Figure 233 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-fluorophenyl)sulfonyl)vinyl)(phenyl)Selane **(46)**



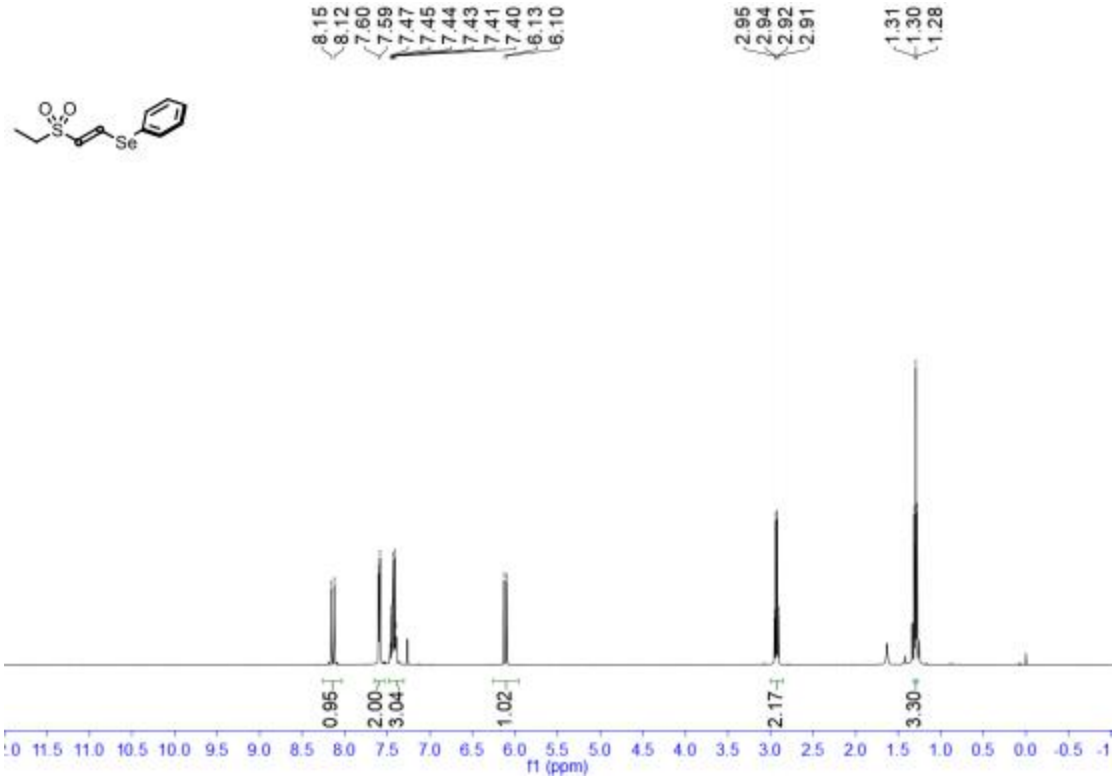
Supplementary Figure 234 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-chlorophenyl)sulfonyl)vinyl)(phenyl)Selane **(47)**



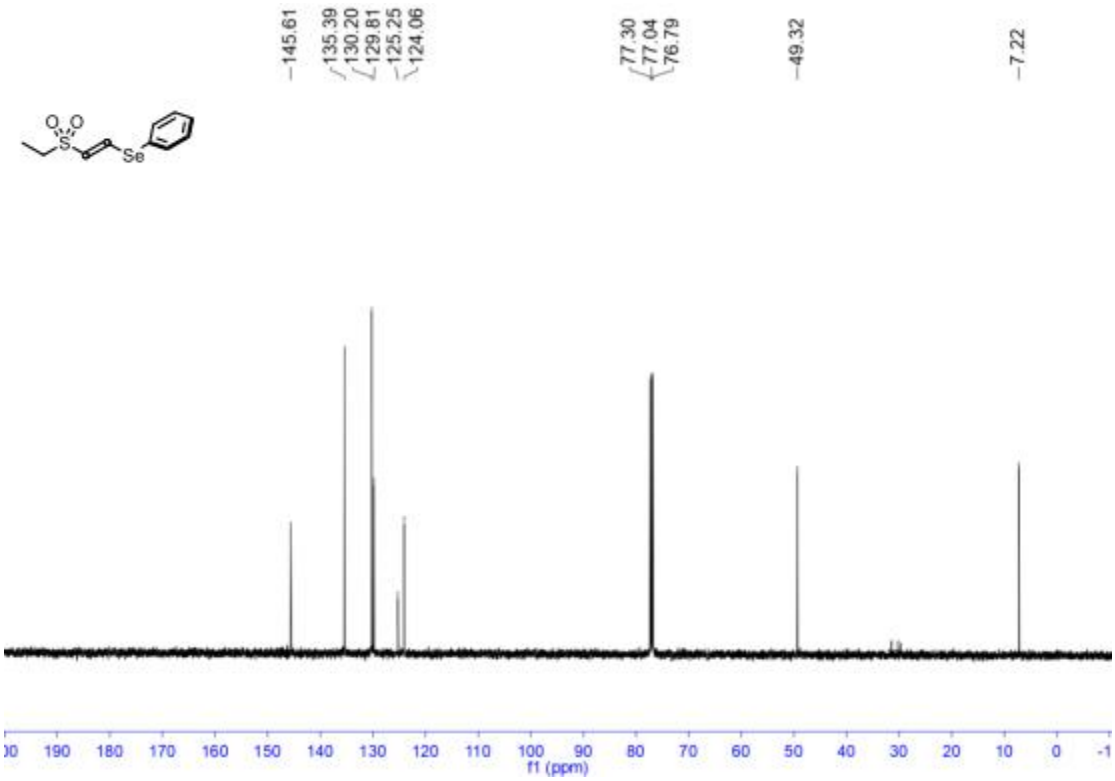
Supplementary Figure 235 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(2-((4-chlorophenyl)sulfonyl)vinyl)(phenyl)Selane **(47)**



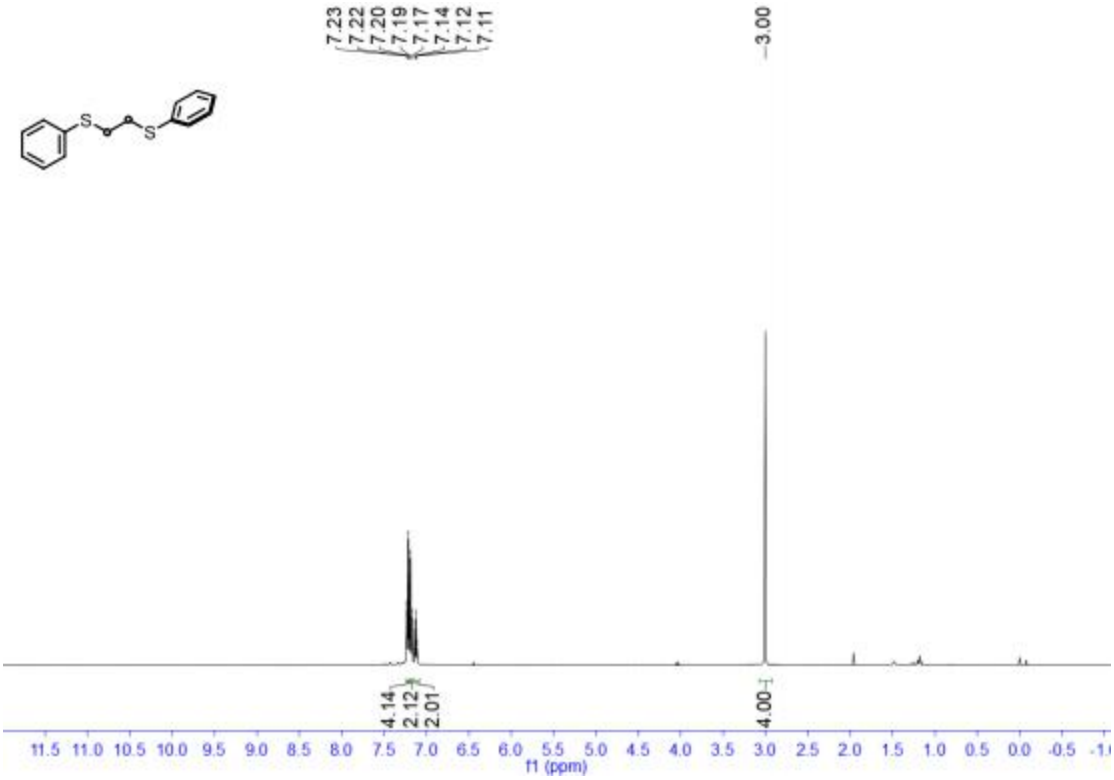
Supplementary Figure 236 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-(2-(ethylsulfonyl)vinyl)(phenyl)Selane **(48)**



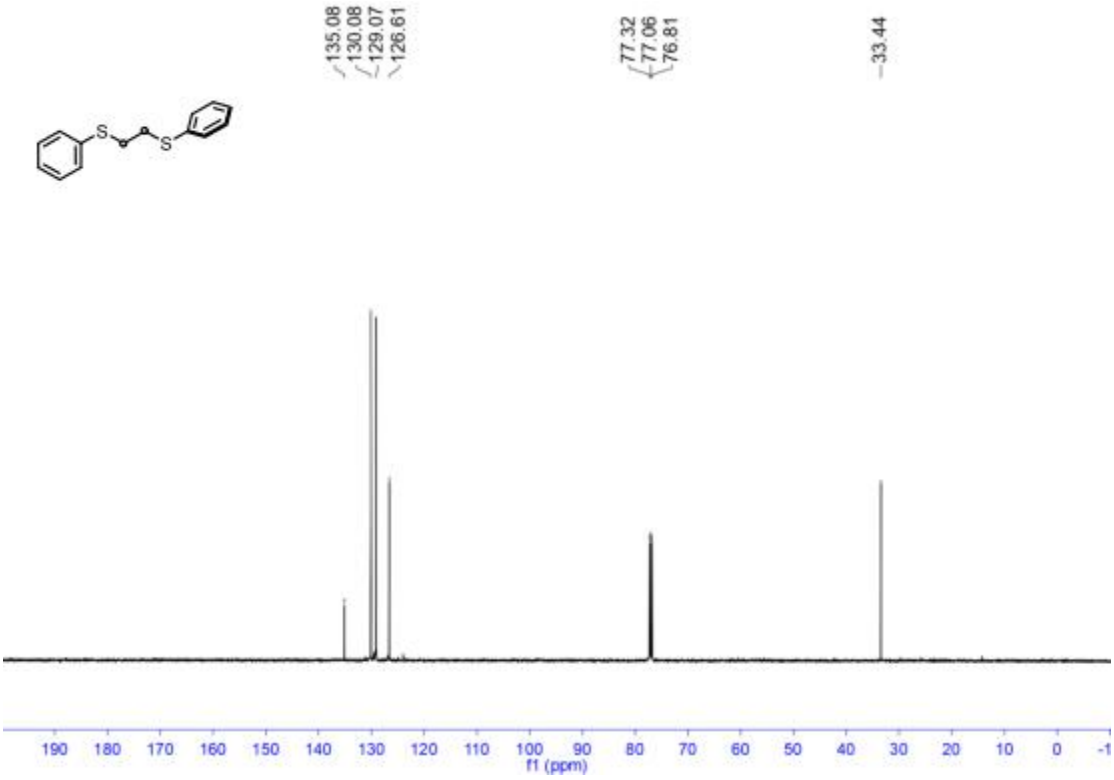
Supplementary Figure 237 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-(2-(ethylsulfonyl)vinyl)(phenyl)Selane **(48)**



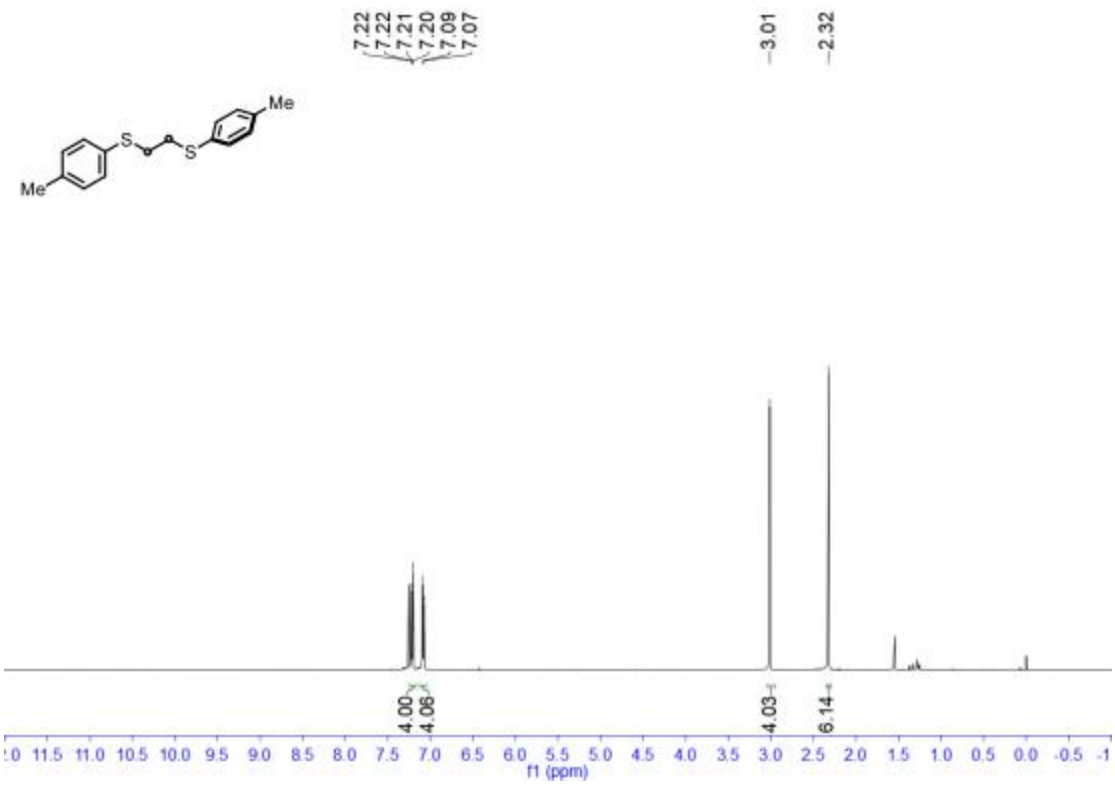
Supplementary Figure 238 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis(phenylthio)ethane **(49)**



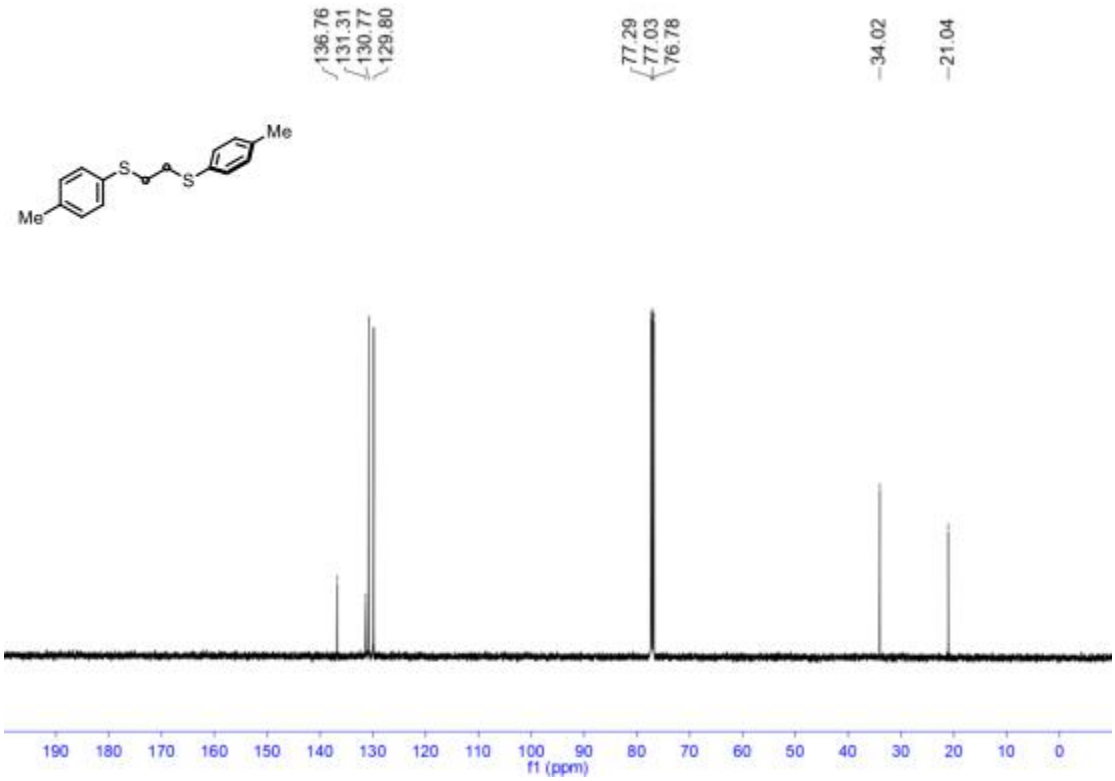
Supplementary Figure 239 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis(phenylthio)ethane **(49)**



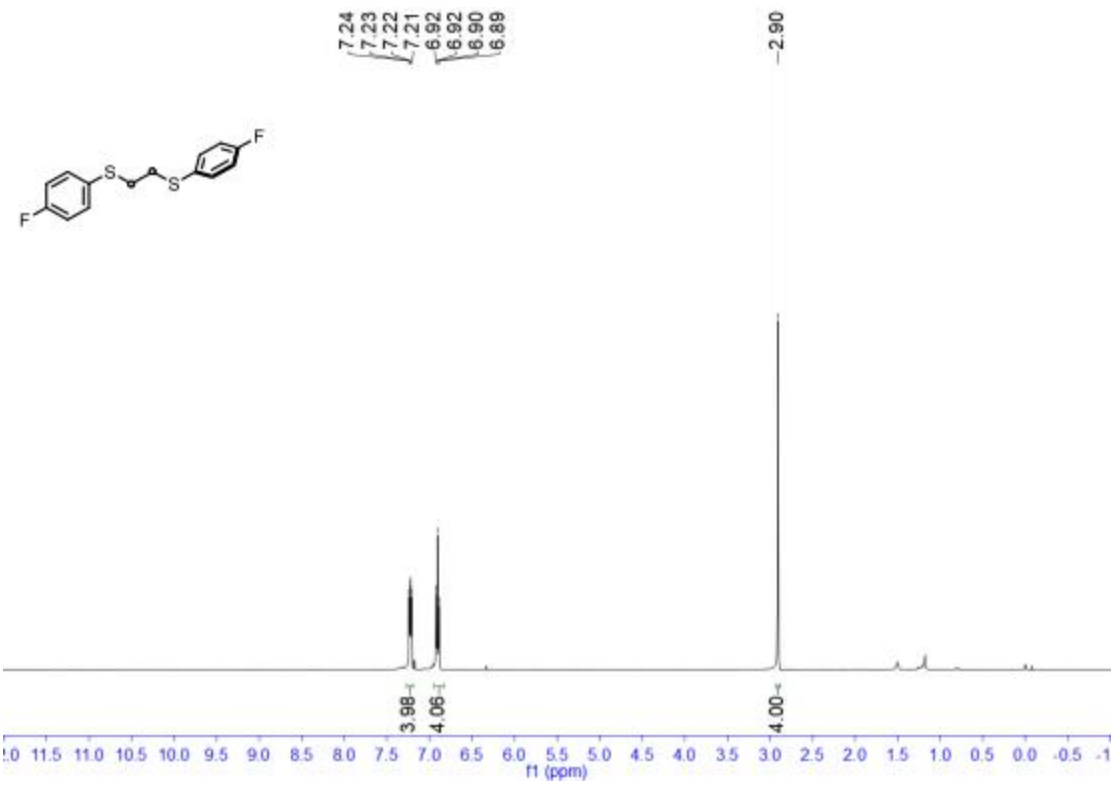
Supplementary Figure 240 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis(*p*-tolylthio)ethane **(50)**



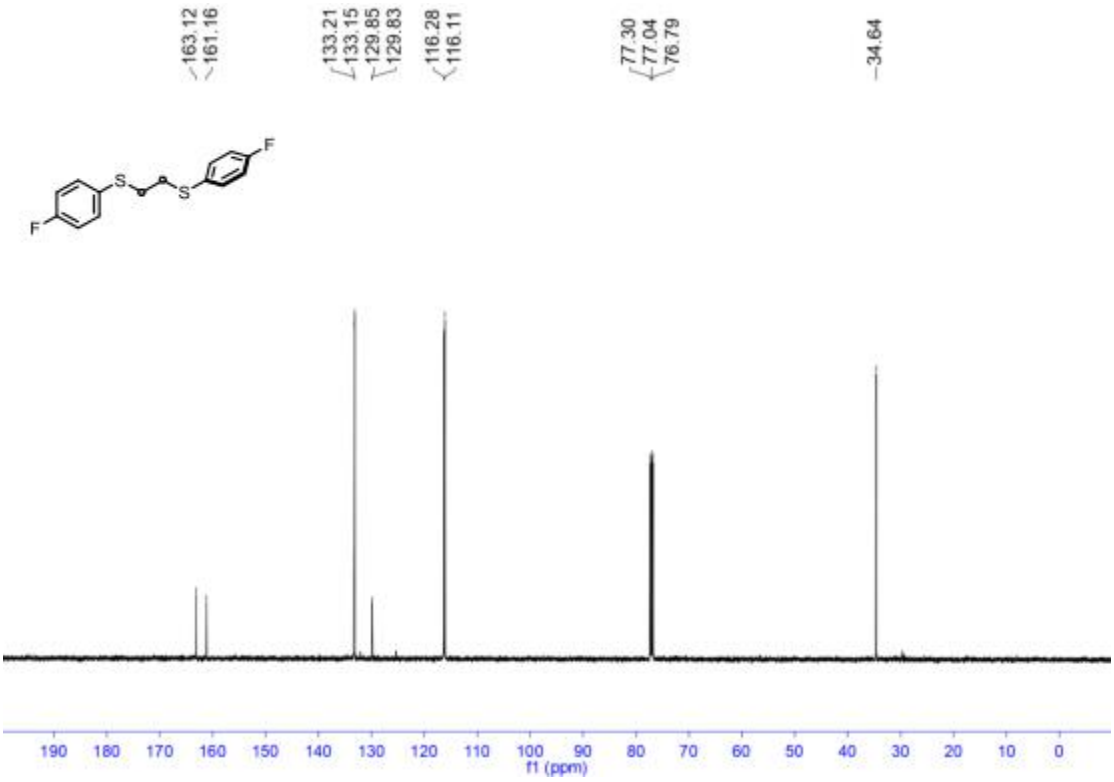
Supplementary Figure 241 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis(*p*-tolylthio)ethane **(50)**



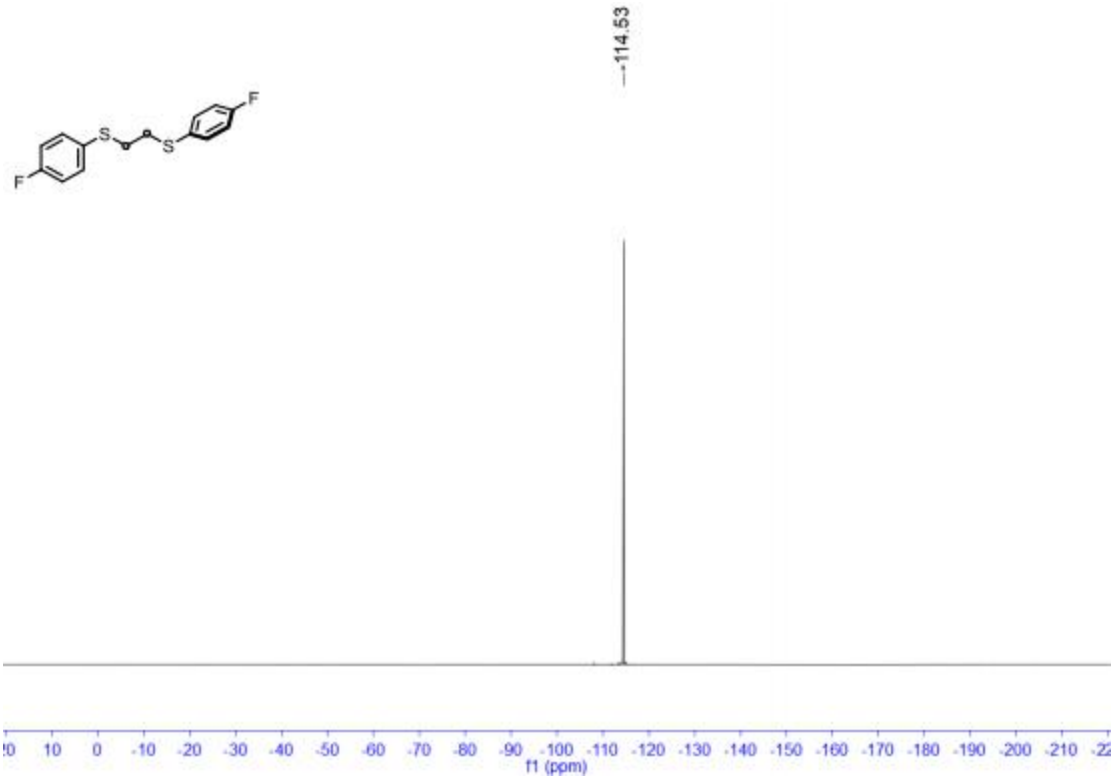
Supplementary Figure 242 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-fluorophenyl)thio)ethane **(51)**



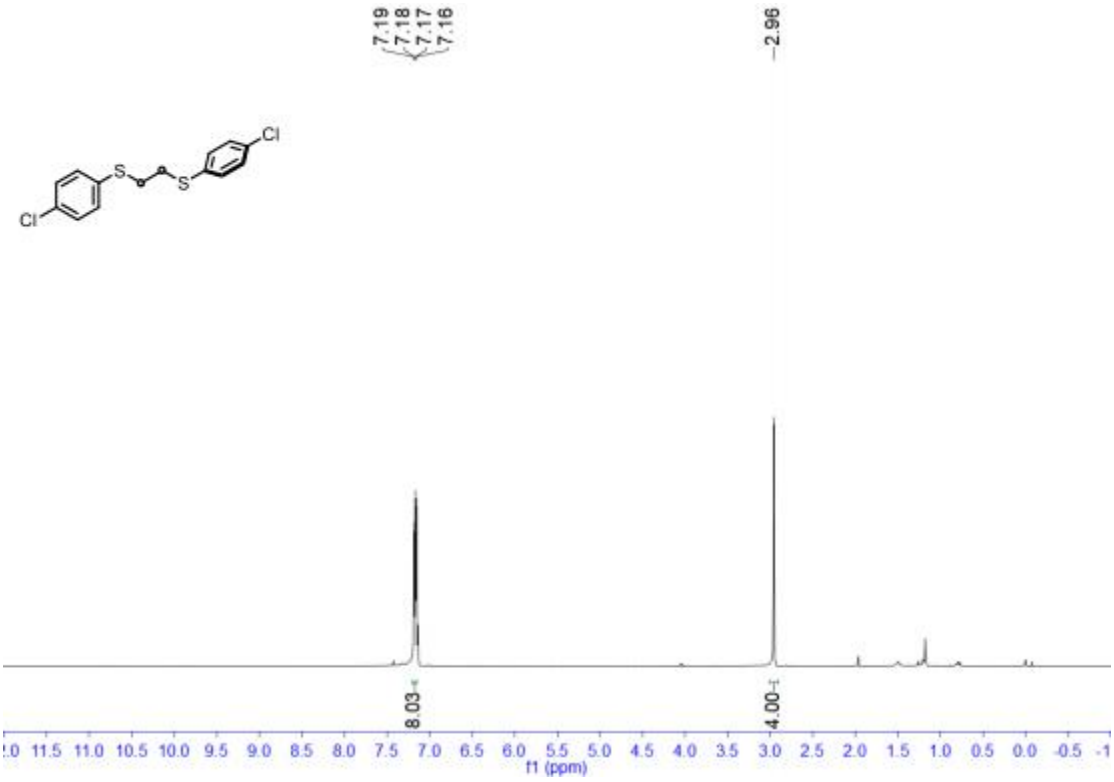
Supplementary Figure 243 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-fluorophenyl)thio)ethane **(51)**



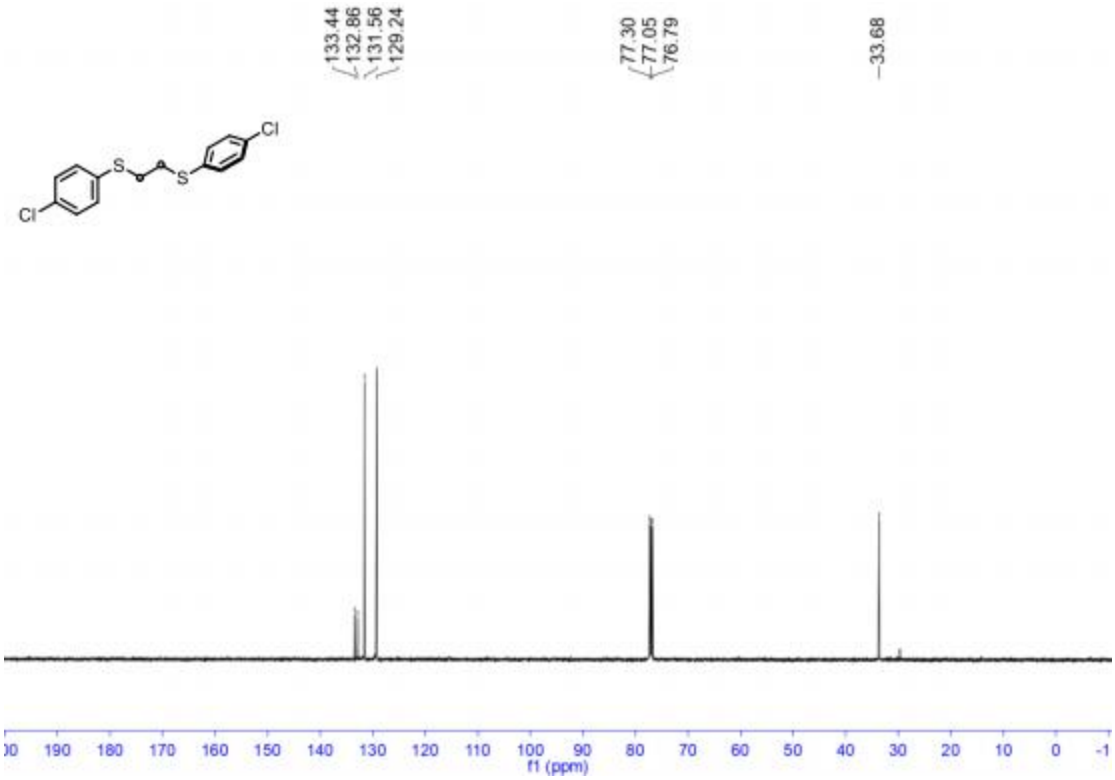
Supplementary Figure 244 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-fluorophenyl)thio)ethane **(51)**



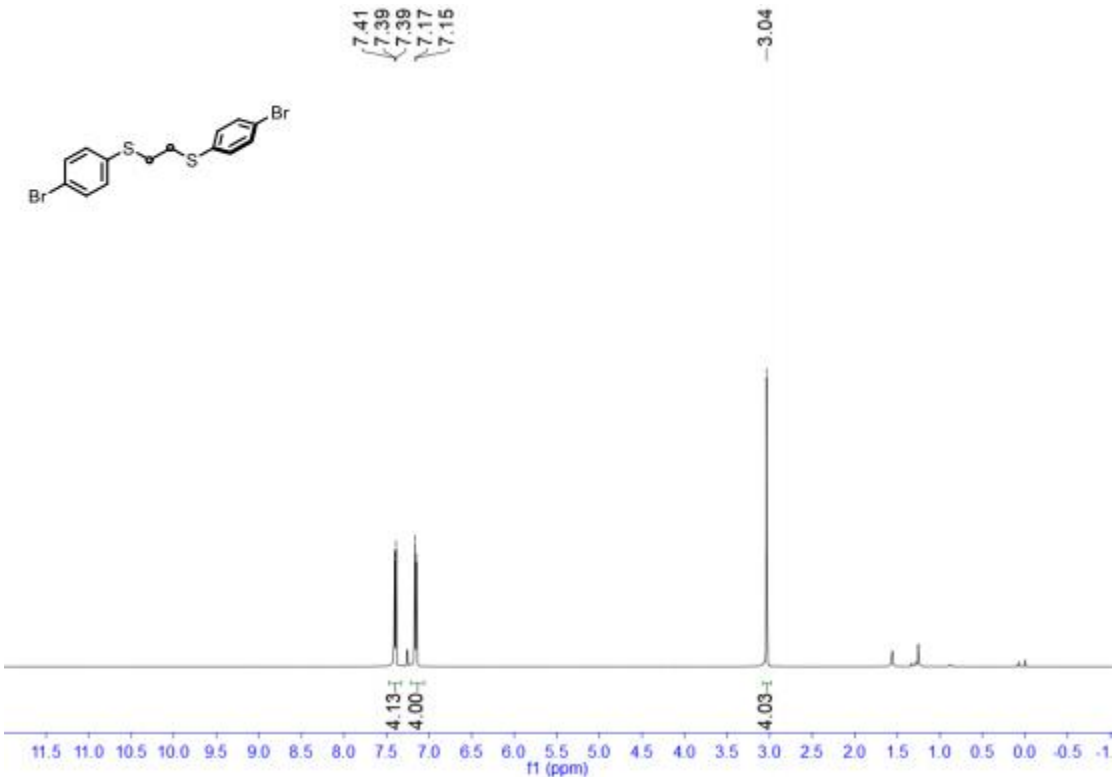
Supplementary Figure 245 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-chlorophenyl)thio)ethane **(52)**



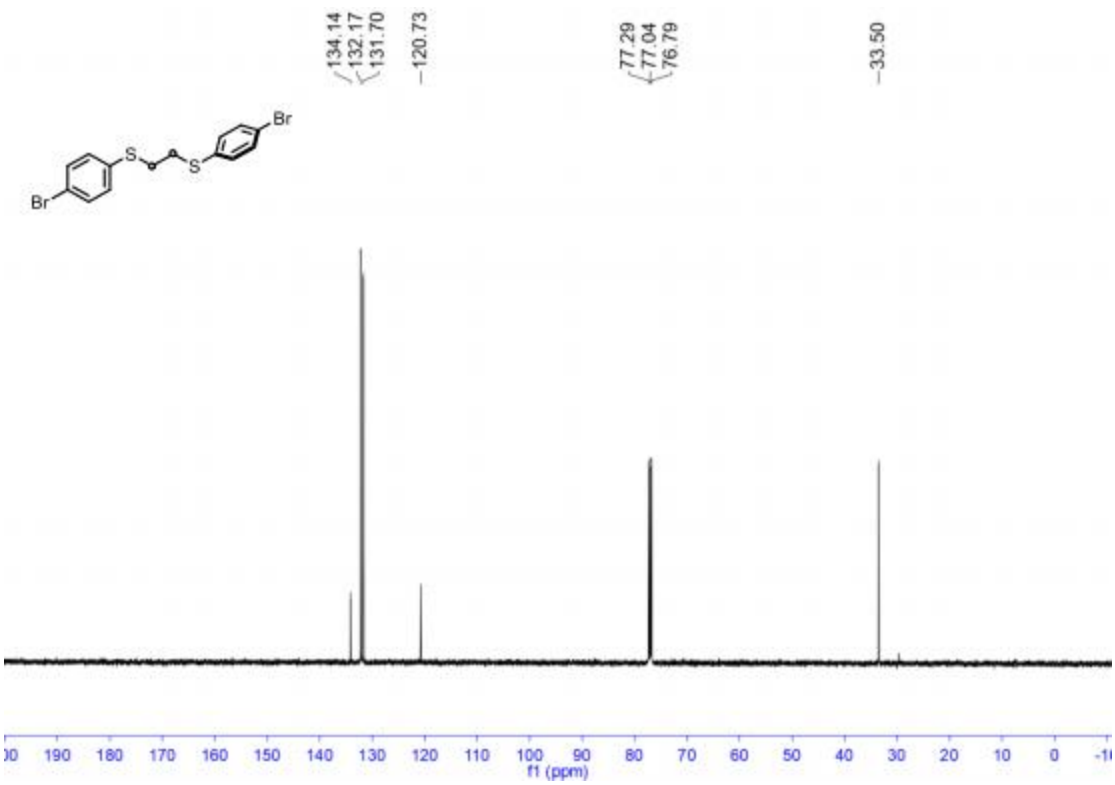
Supplementary Figure 246 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-chlorophenyl)thio)ethane **(52)**



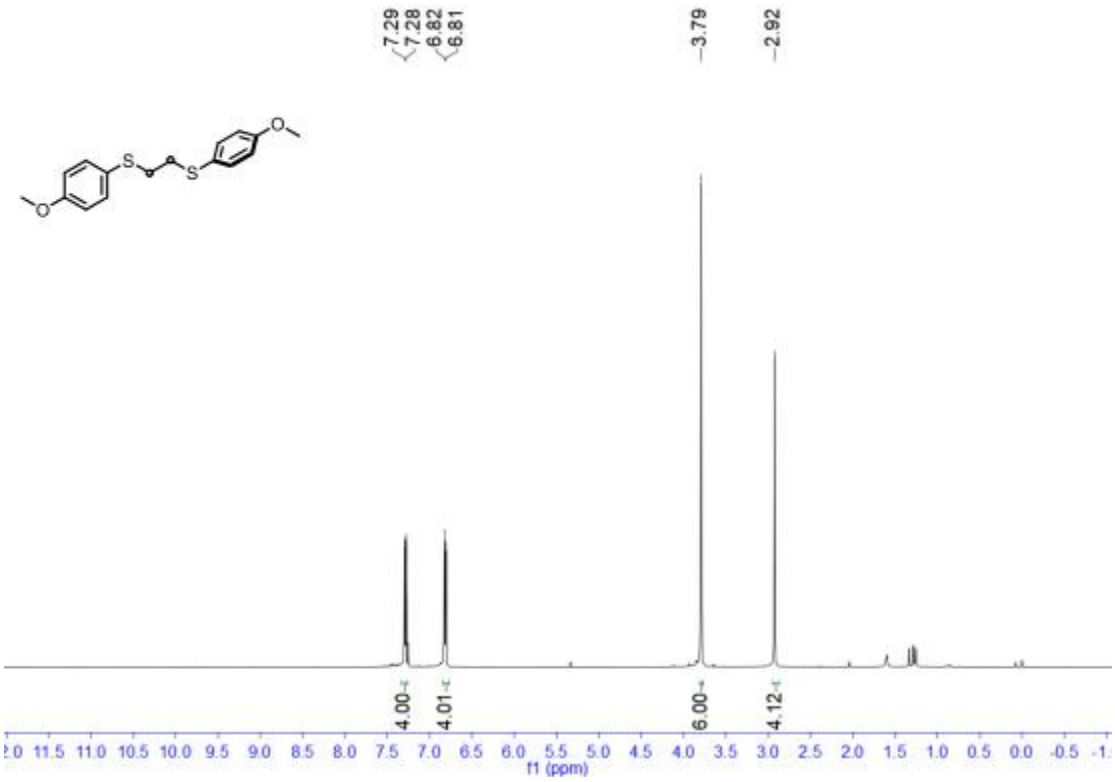
Supplementary Figure 247 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-bromophenyl)thio)ethane **(53)**



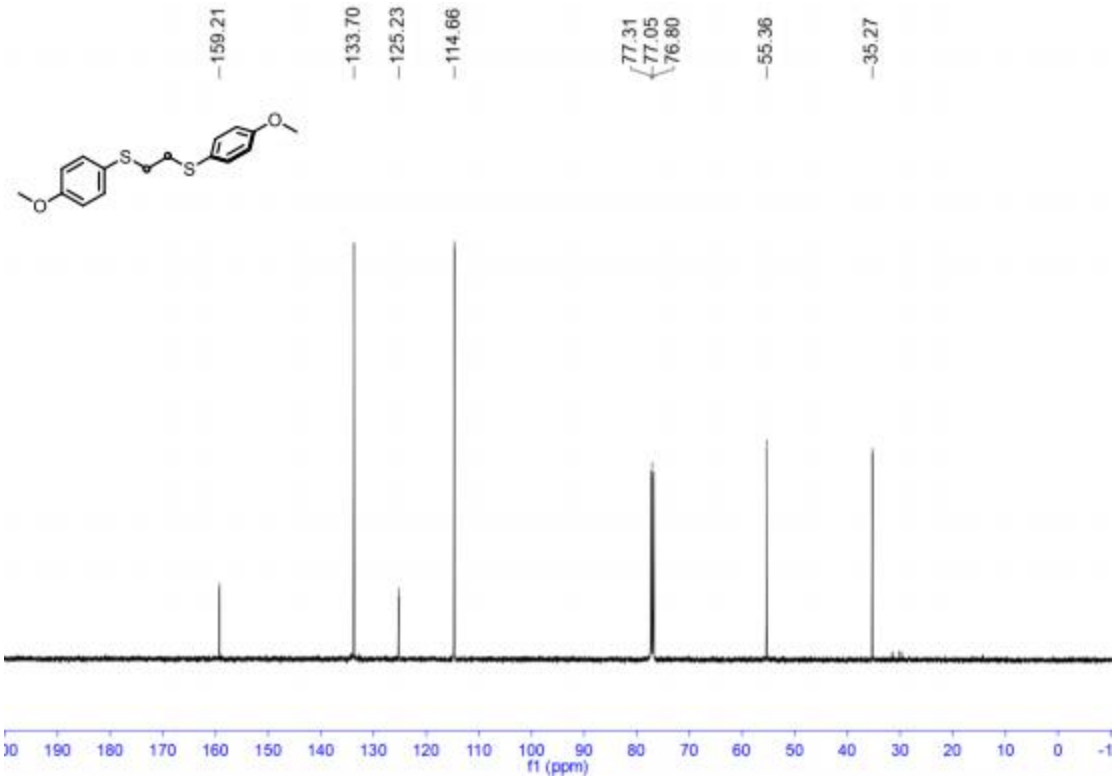
Supplementary Figure 248 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-bromophenyl)thio)ethane **(53)**



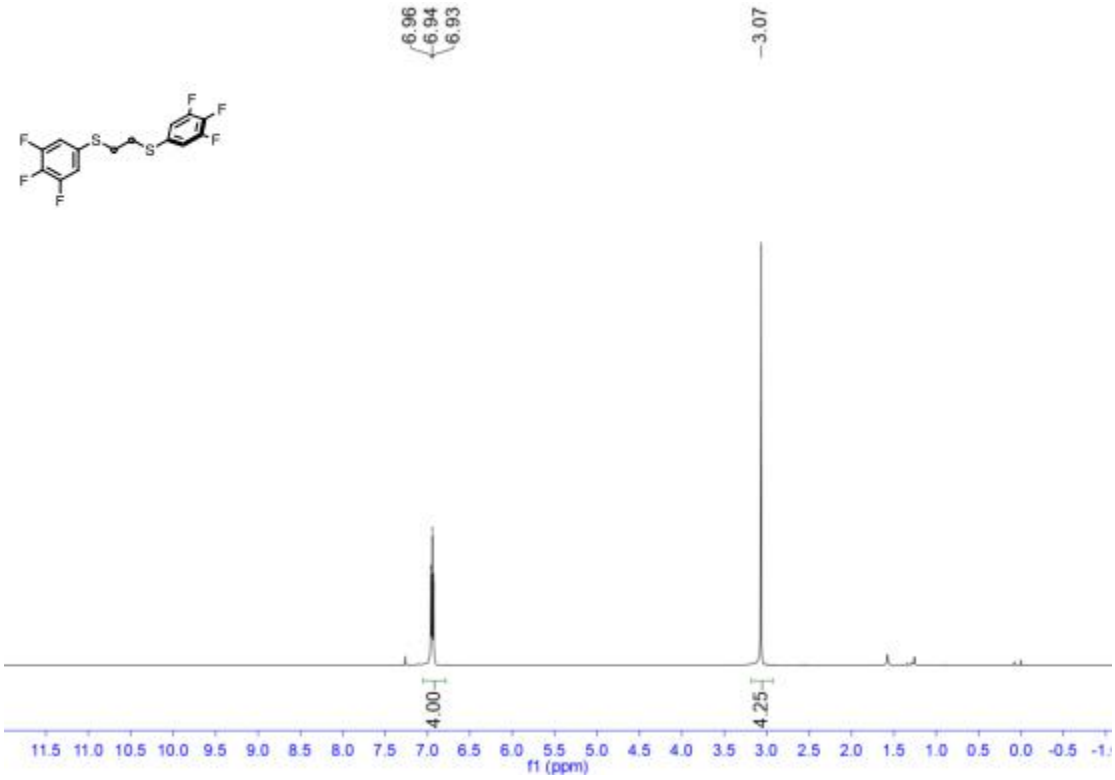
Supplementary Figure 249 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-methoxyphenyl)thio)ethane **(54)**



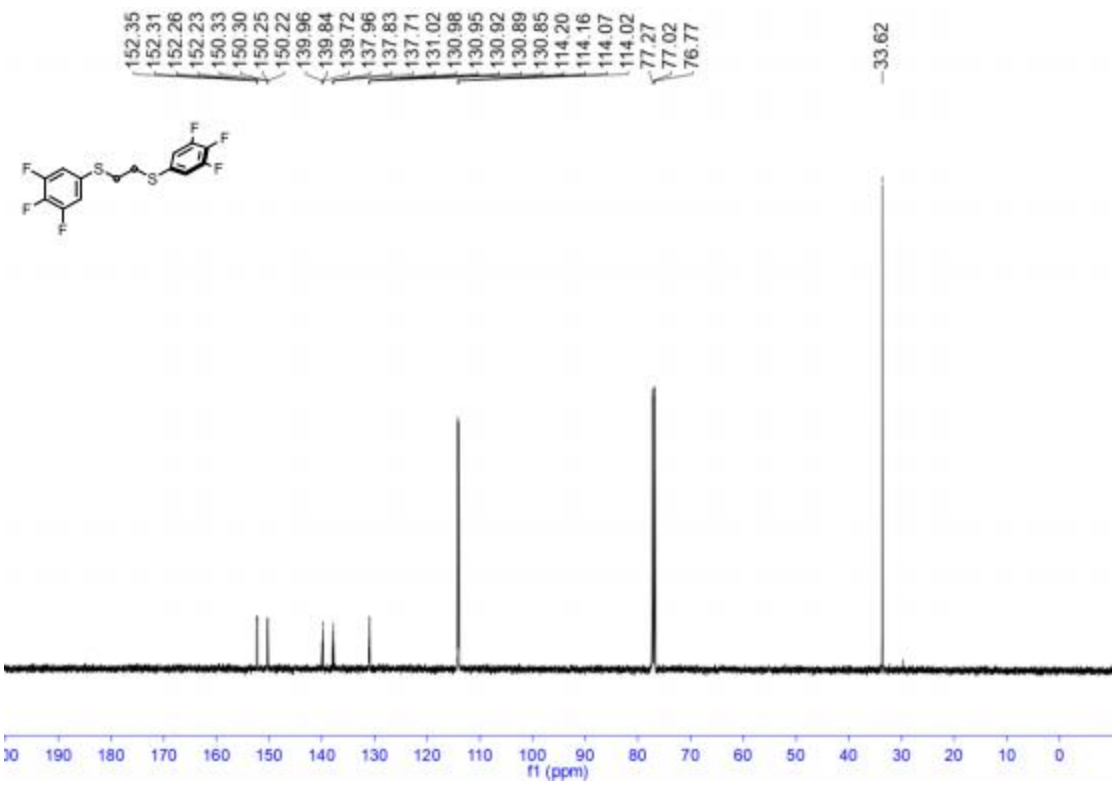
Supplementary Figure 250 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis((4-methoxyphenyl)thio)ethane **(54)**



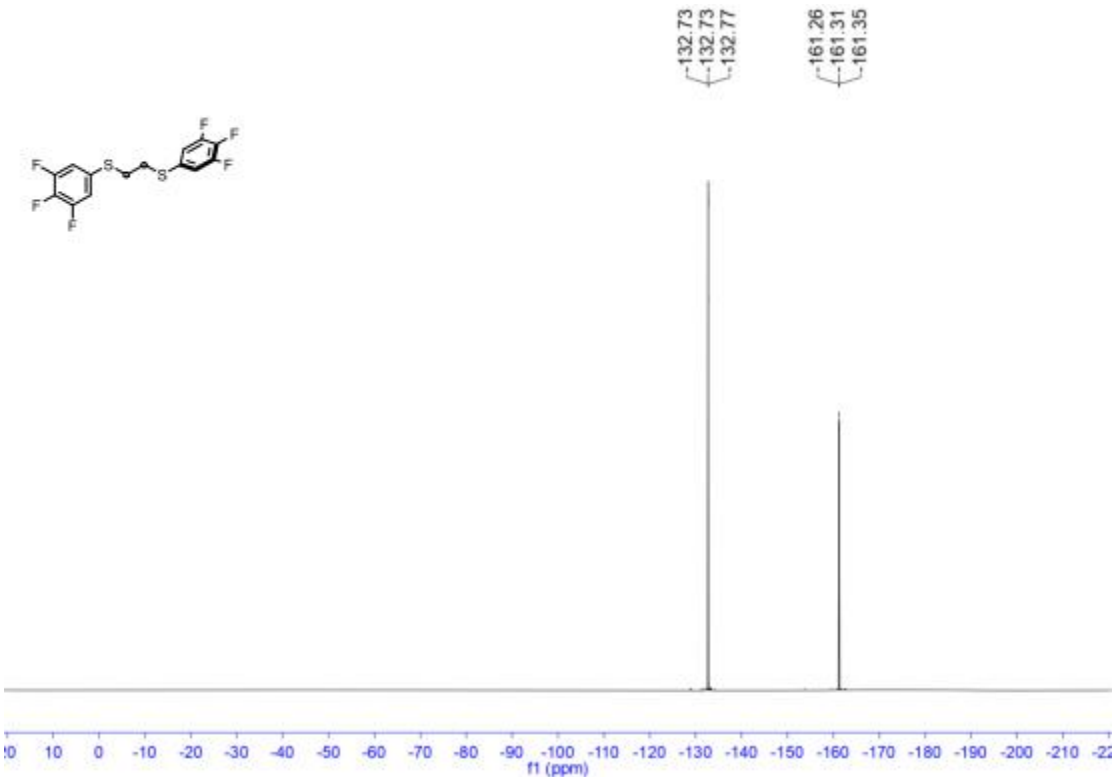
Supplementary Figure 251 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1,2-bis((3,4,5-trifluorophenyl)thio)ethane **(55)**



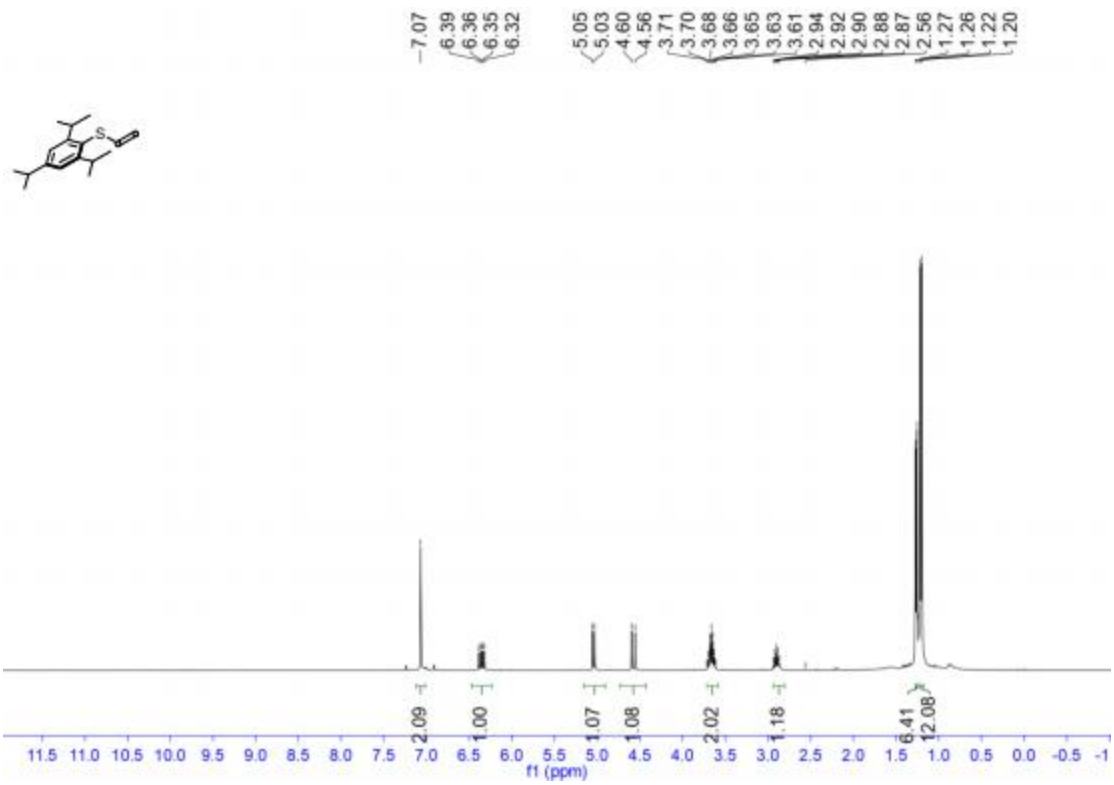
Supplementary Figure 252 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1,2-bis((3,4,5-trifluorophenyl)thio)ethane **(55)**



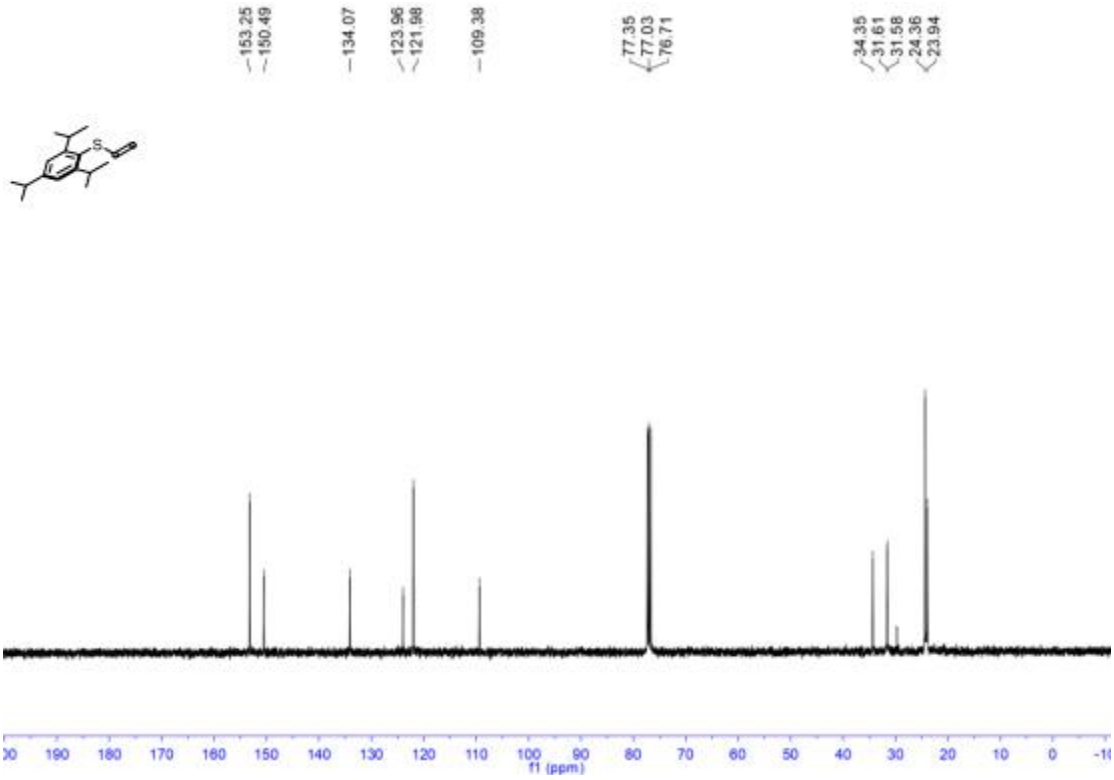
Supplementary Figure 253 | ^{19}F NMR (471 MHz, 298K, Chloroform-*d*) of 1,2-bis((3,4,5-trifluorophenyl)thio)ethane **(55)**



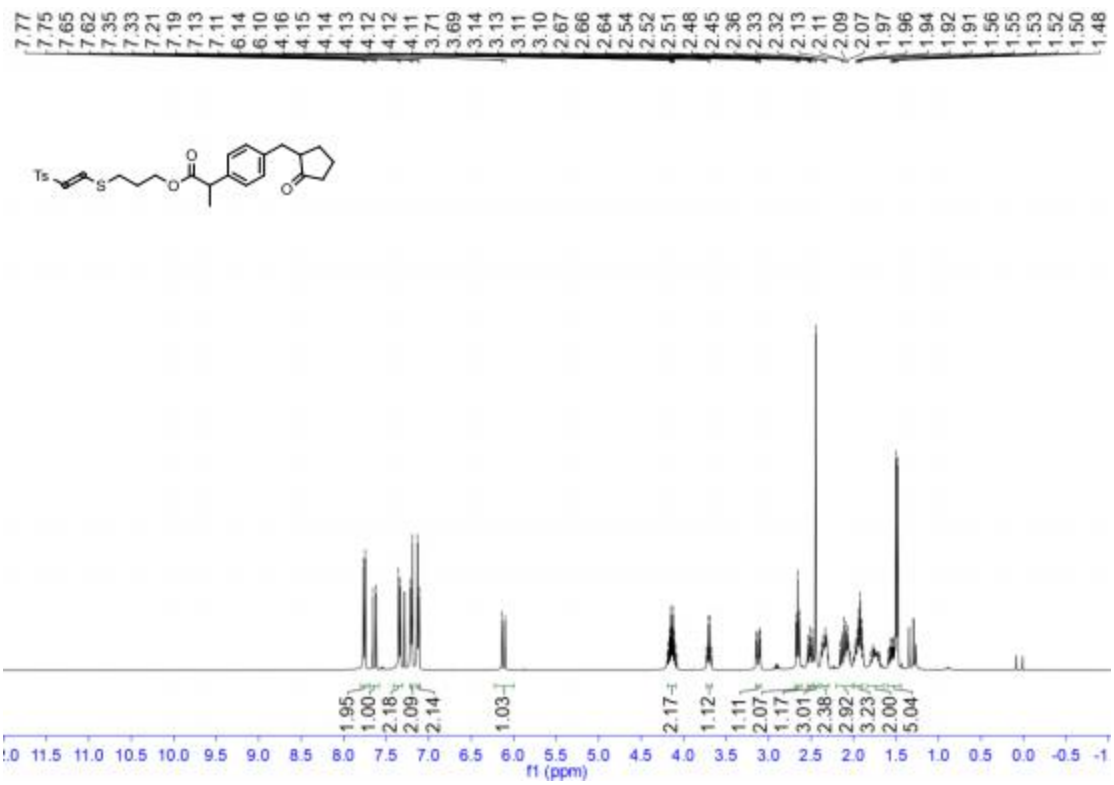
Supplementary Figure 254 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (2,4,6-triisopropylphenyl)(vinyl)sulfane **(56)**



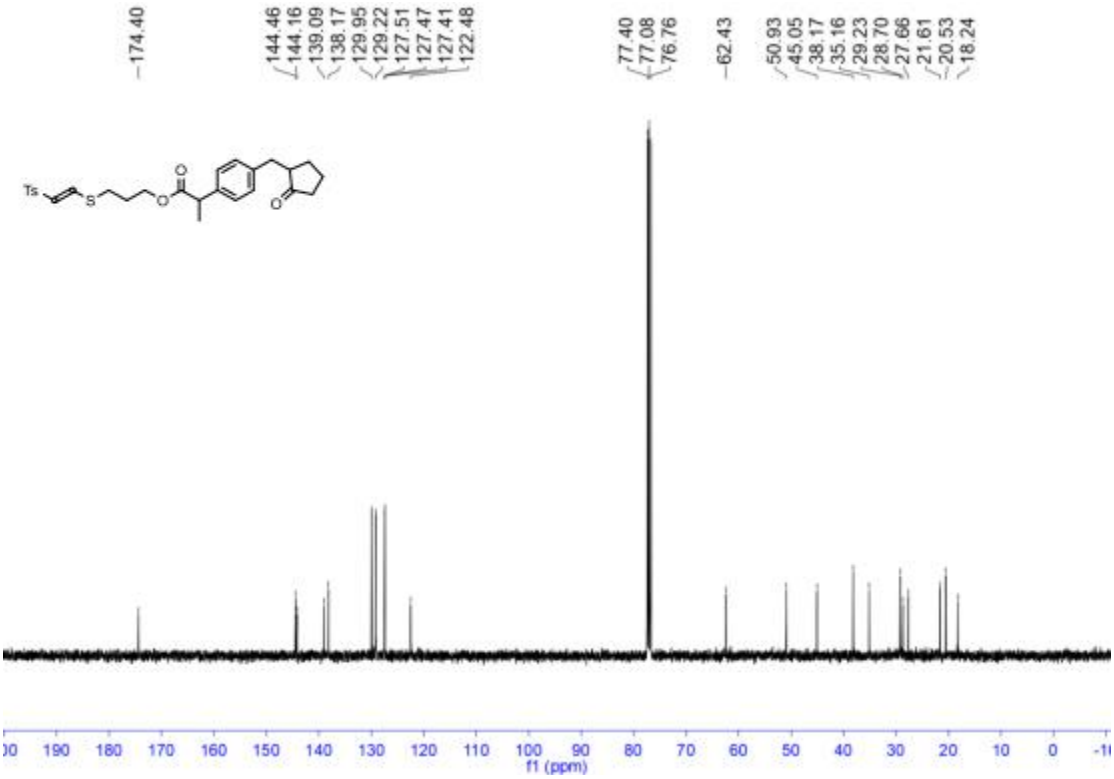
Supplementary Figure 255 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (2,4,6-triisopropylphenyl)(vinyl)sulfane **(56)**



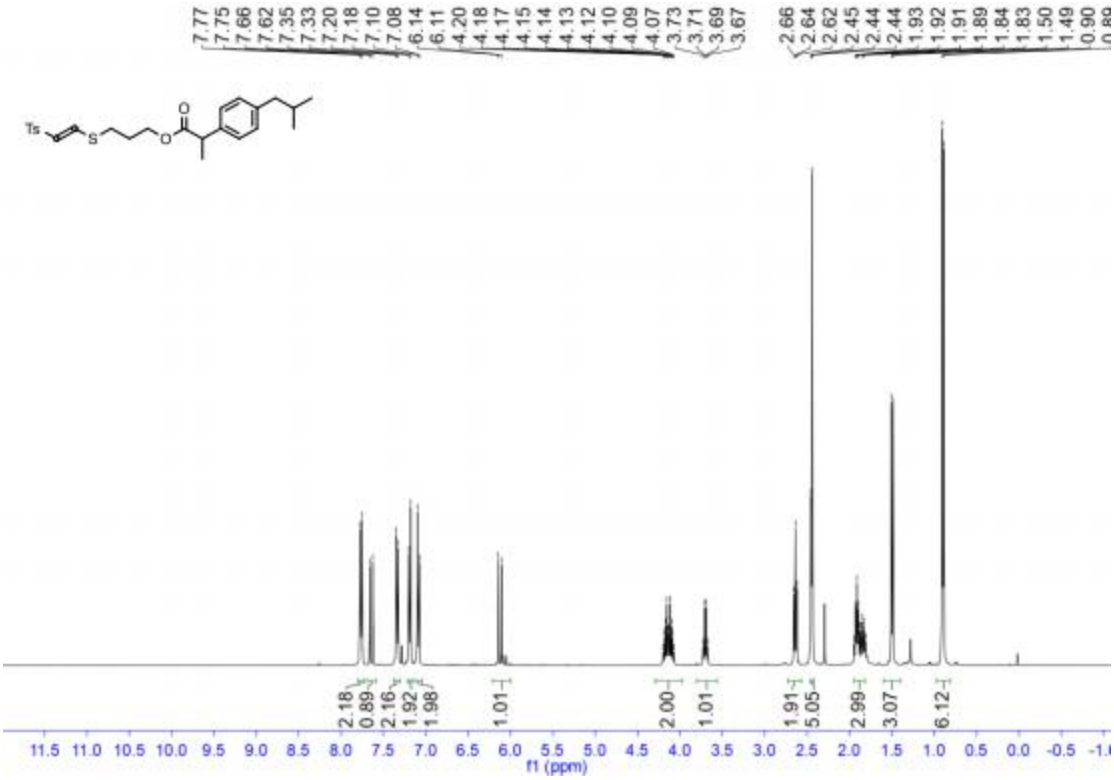
Supplementary Figure 256 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate **(58)**



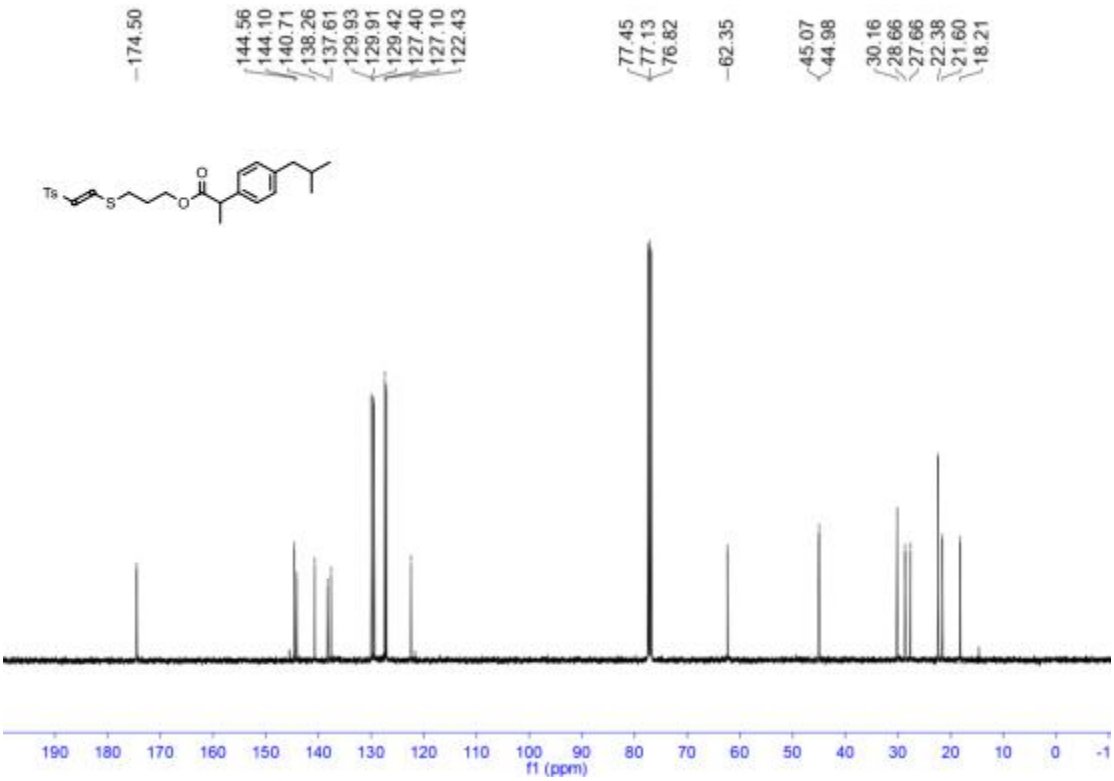
Supplementary Figure 257 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate **(58)**



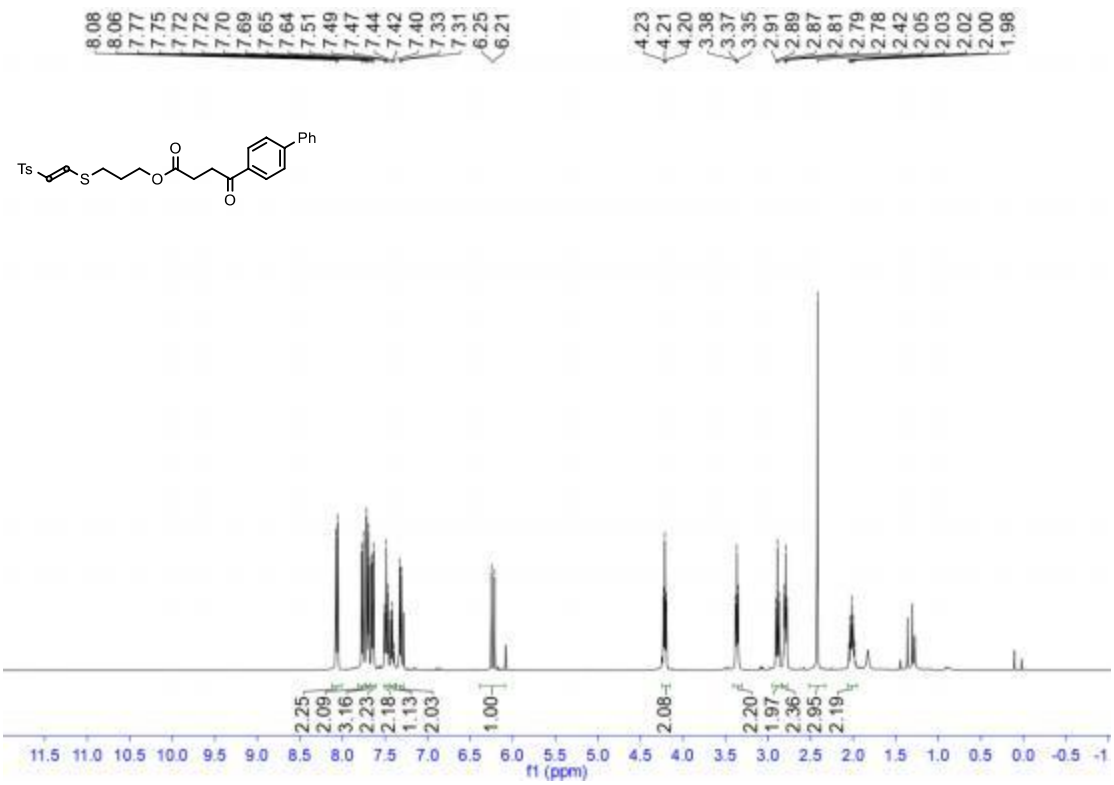
Supplementary Figure 258 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(4-isobutylphenyl)propanoate **(59)**



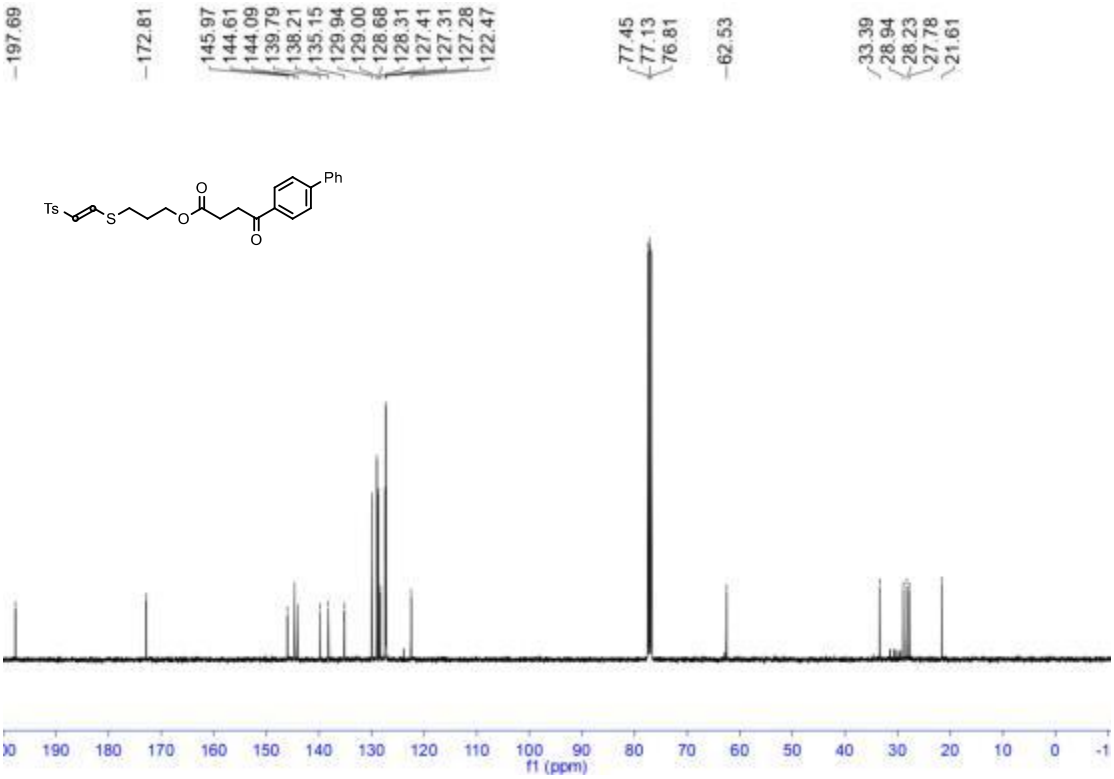
Supplementary Figure 259 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(4-isobutylphenyl)propanoate **(59)**



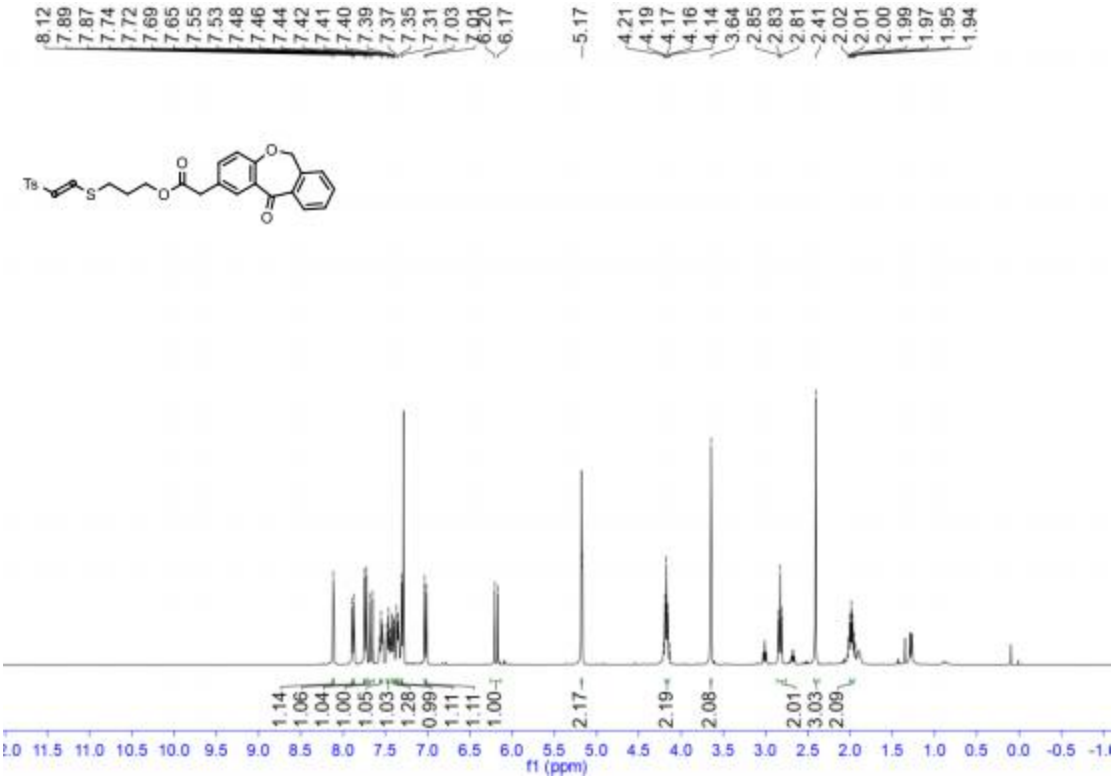
Supplementary Figure 260 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate **(60)**



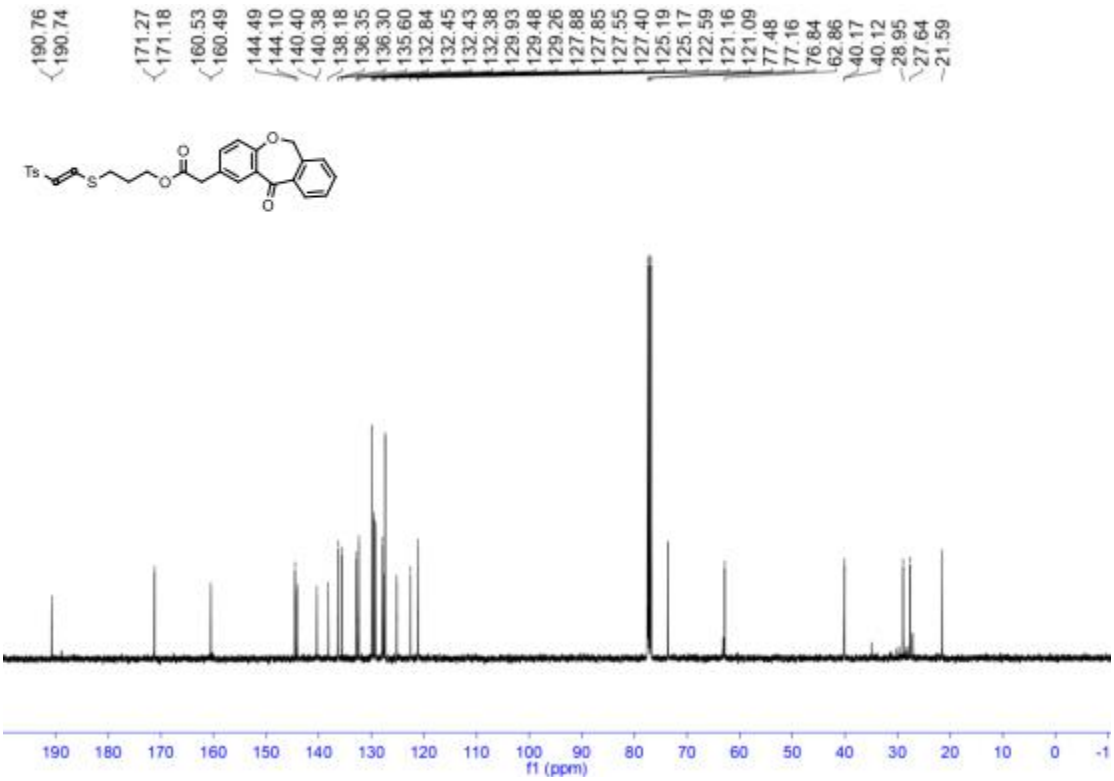
Supplementary Figure 261 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate **(60)**



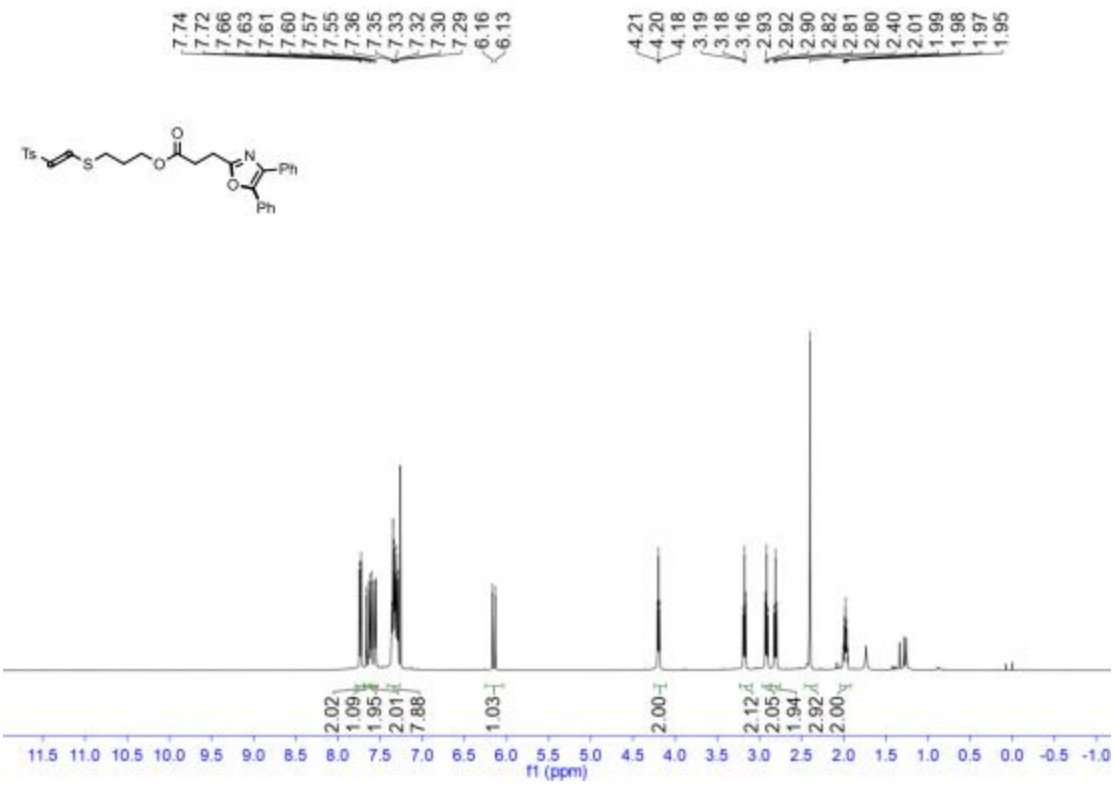
Supplementary Figure 262 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate **(61)**



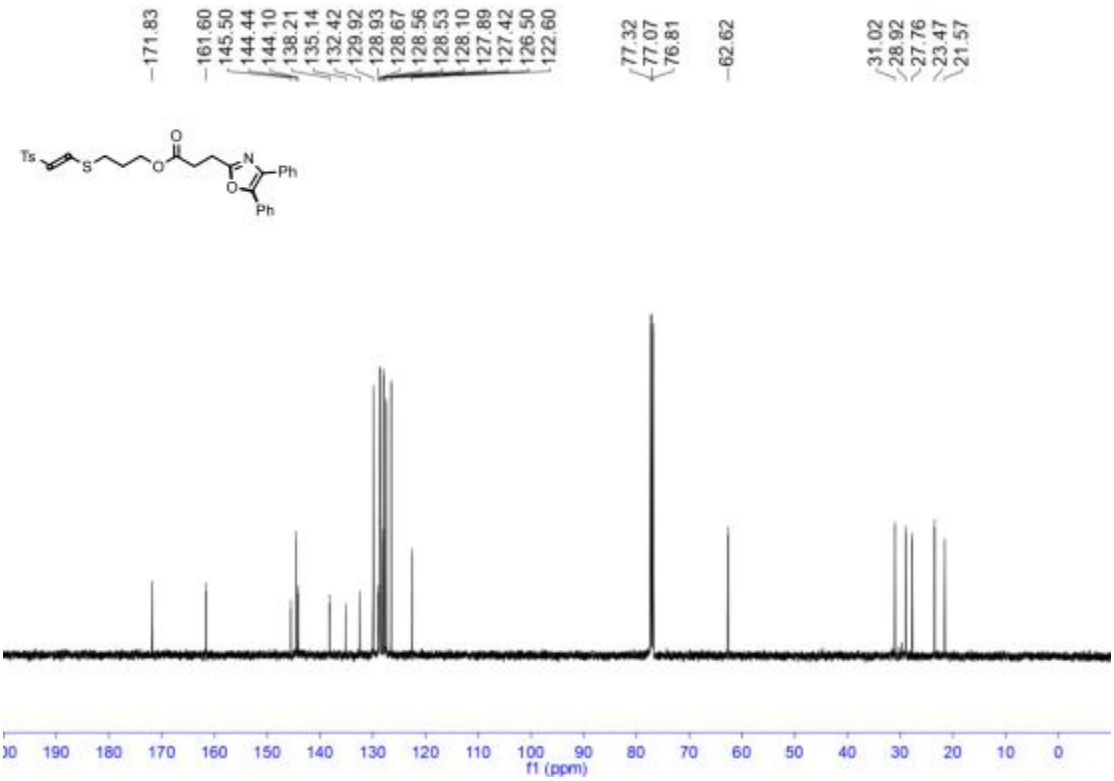
Supplementary Figure 263 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate **(61)**



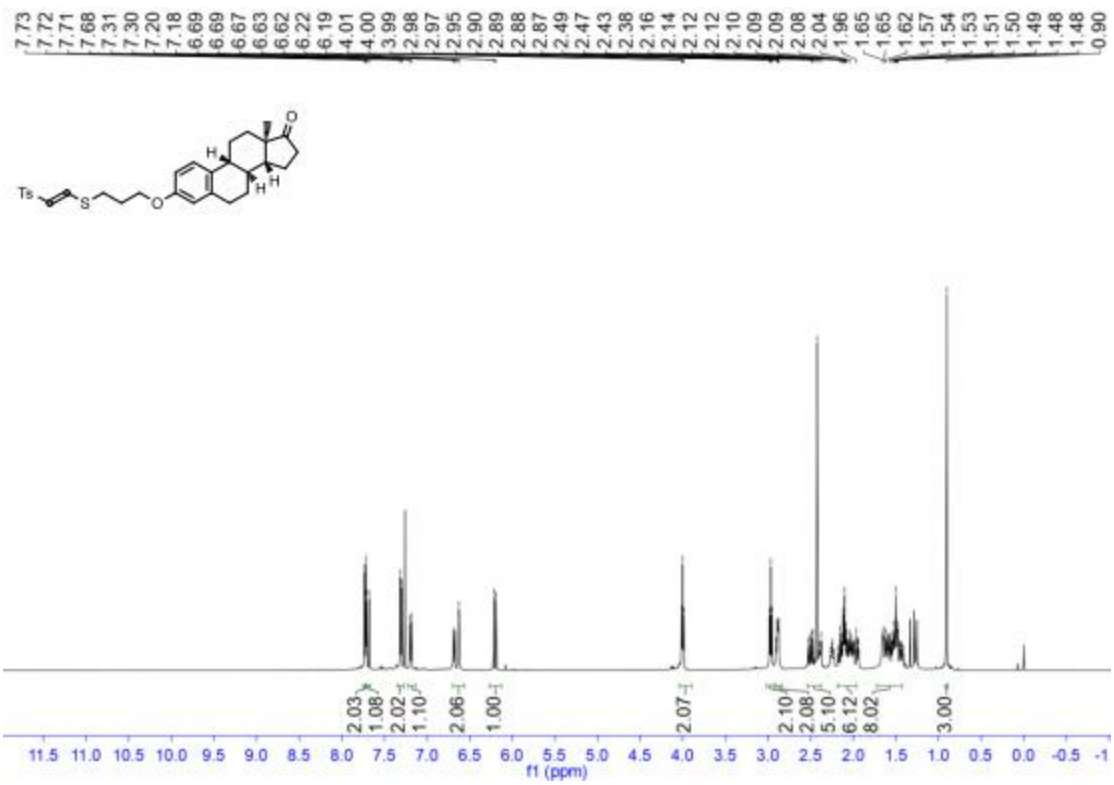
Supplementary Figure 264 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate **(62)**



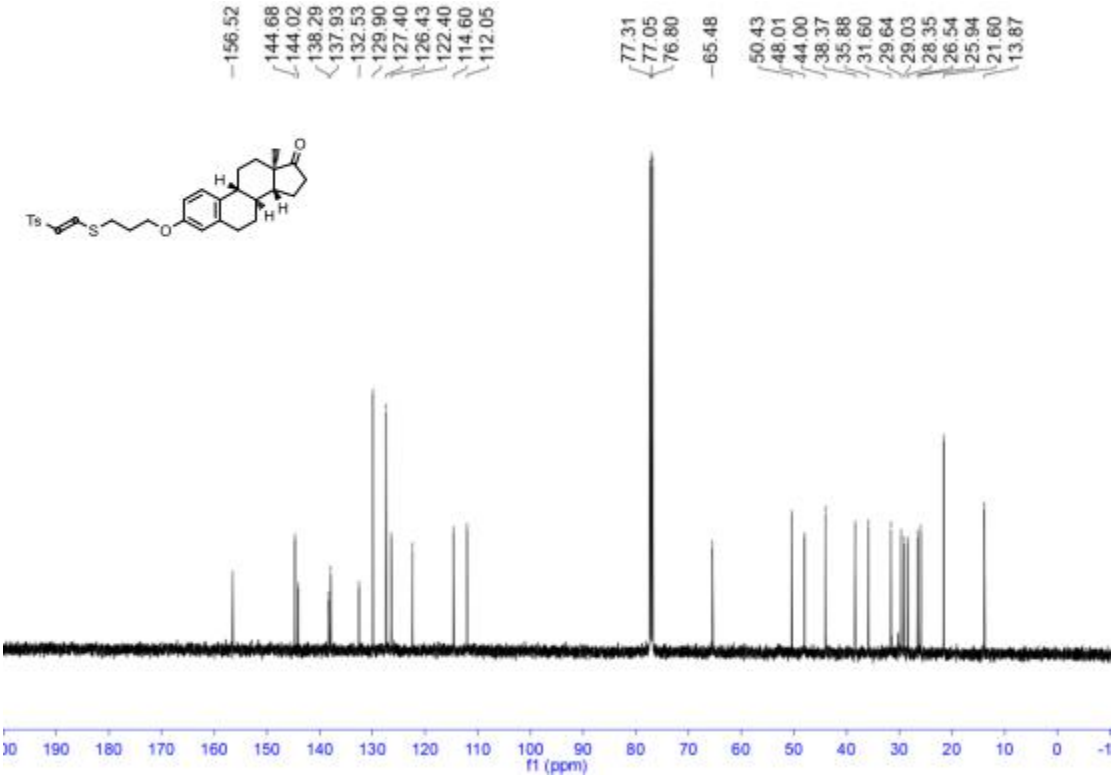
Supplementary Figure 265 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate **(62)**



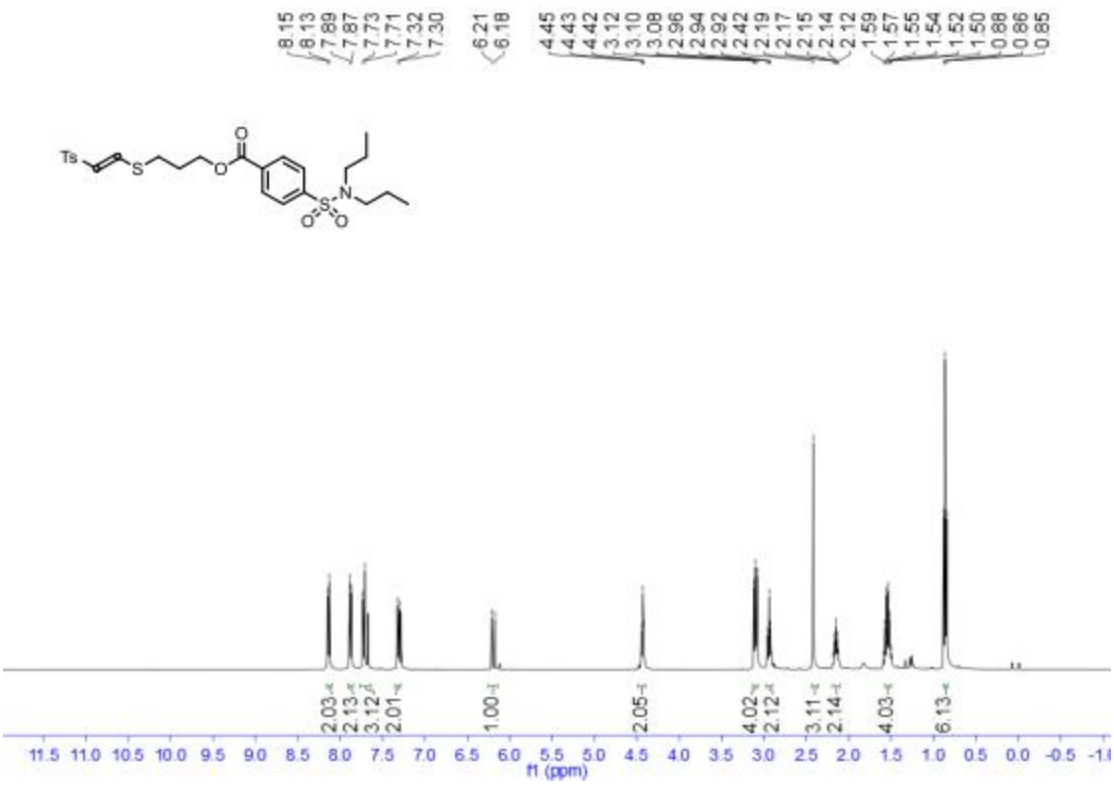
Supplementary Figure 266 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (8*S*,9*R*,13*R*,14*R*)- 13-methyl-3-(3-(((*E*)-2-tosylvinyl)thio)propoxy)-6,7,8,9,11,12,13,14,15,16-decahydro- 17H-cyclopenta[a]phenanthren- 17-one **(63)**



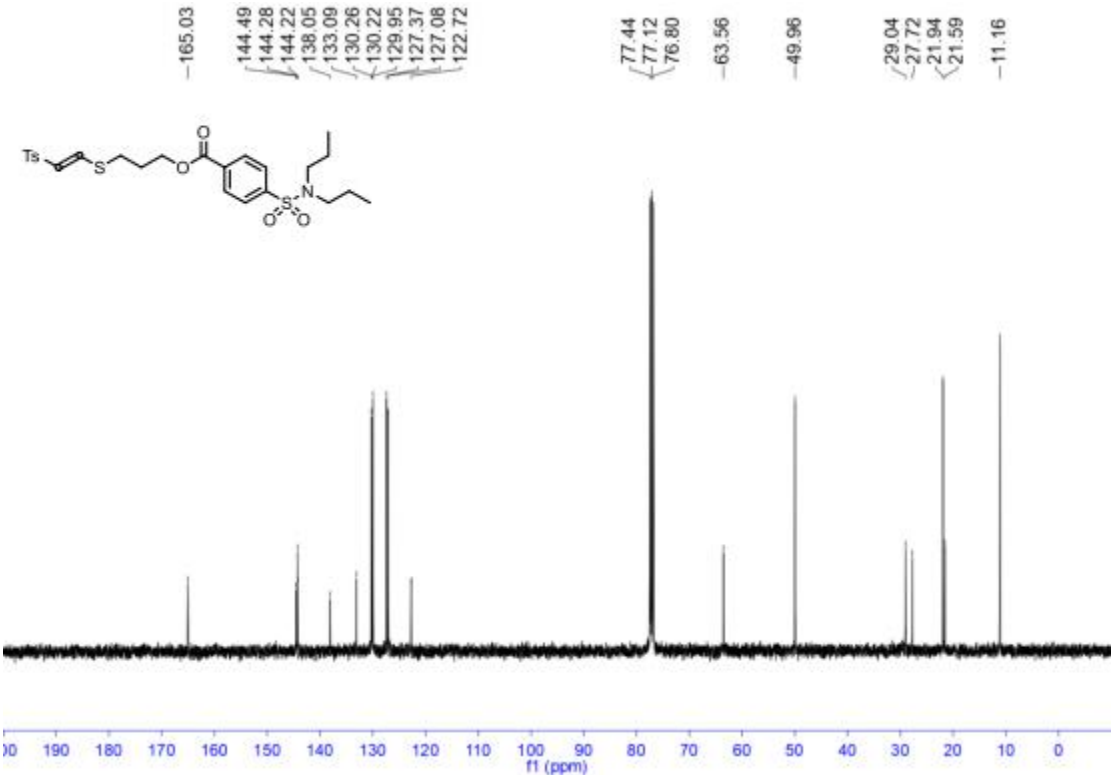
Supplementary Figure 267 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (8*S*,9*R*,13*R*,14*R*)- 13-methyl-3-(3-(((*E*)-2-tosylvinyl)thio)propoxy)-6,7,8,9,11,12,13,14,15,16-decahydro- 17H-cyclopenta[a]phenanthren- 17-one **(63)**



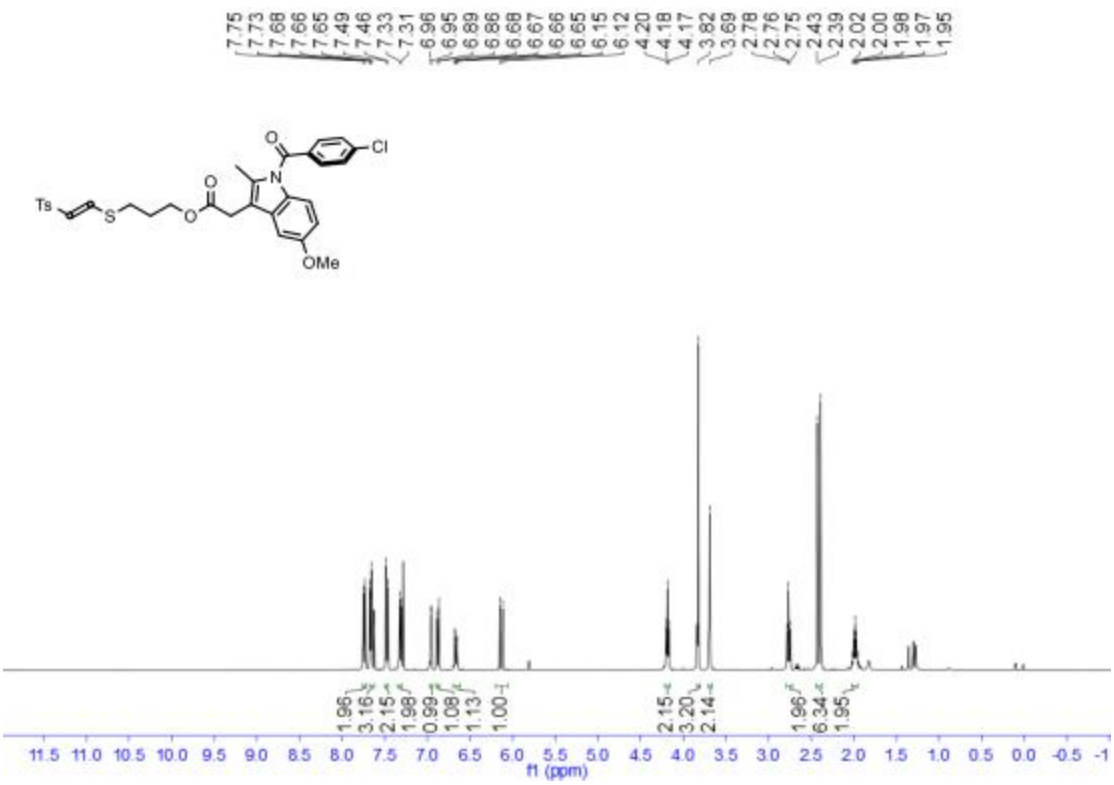
Supplementary Figure 268 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate **(64)**



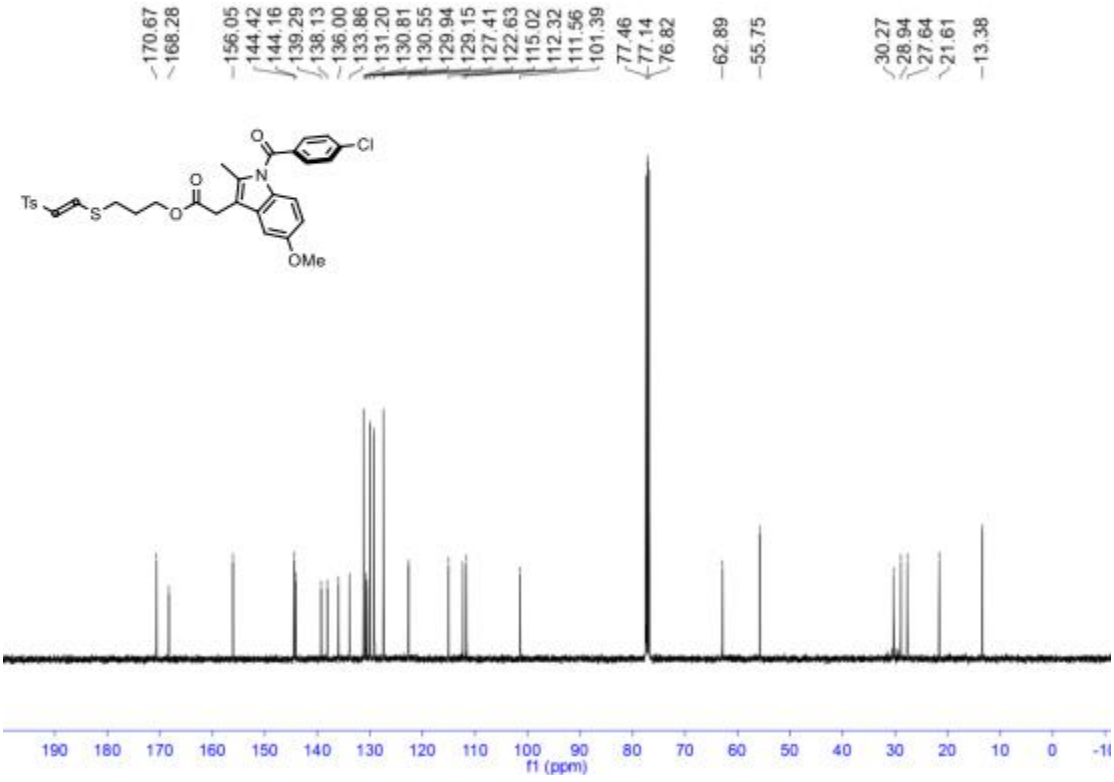
Supplementary Figure 269 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate **(64)**



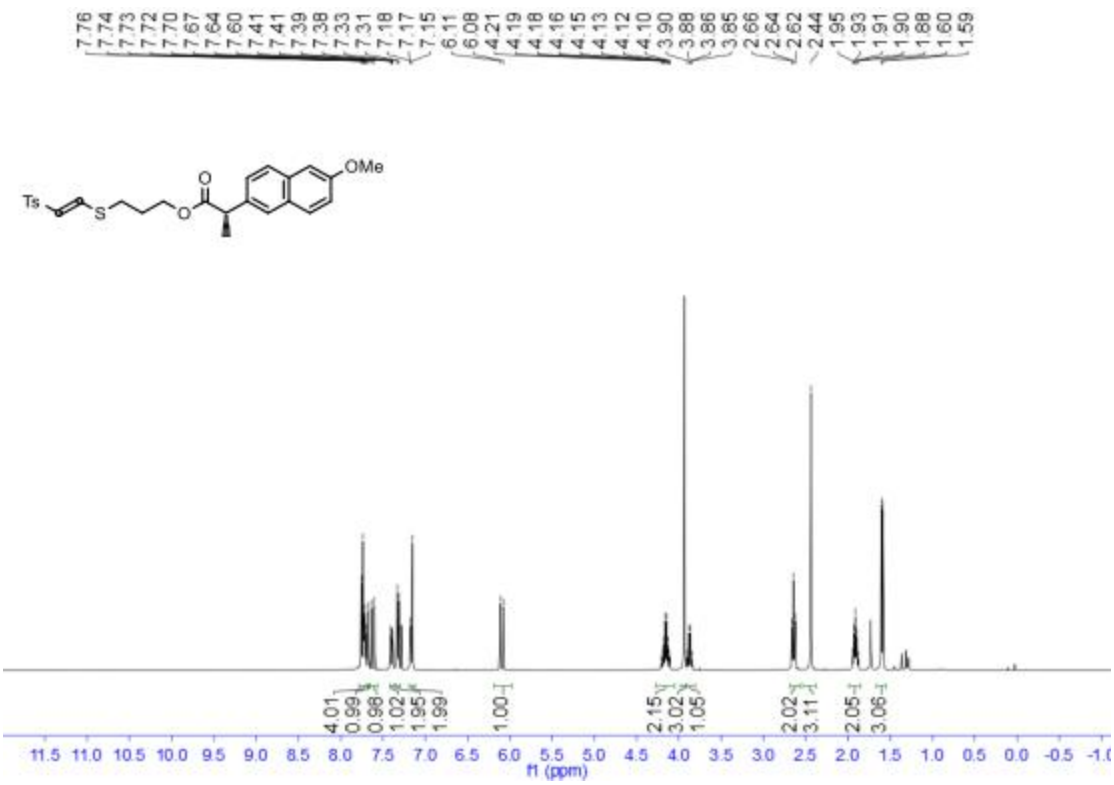
Supplementary Figure 270 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl- 1H-indol-3-yl)acetate **(64)**



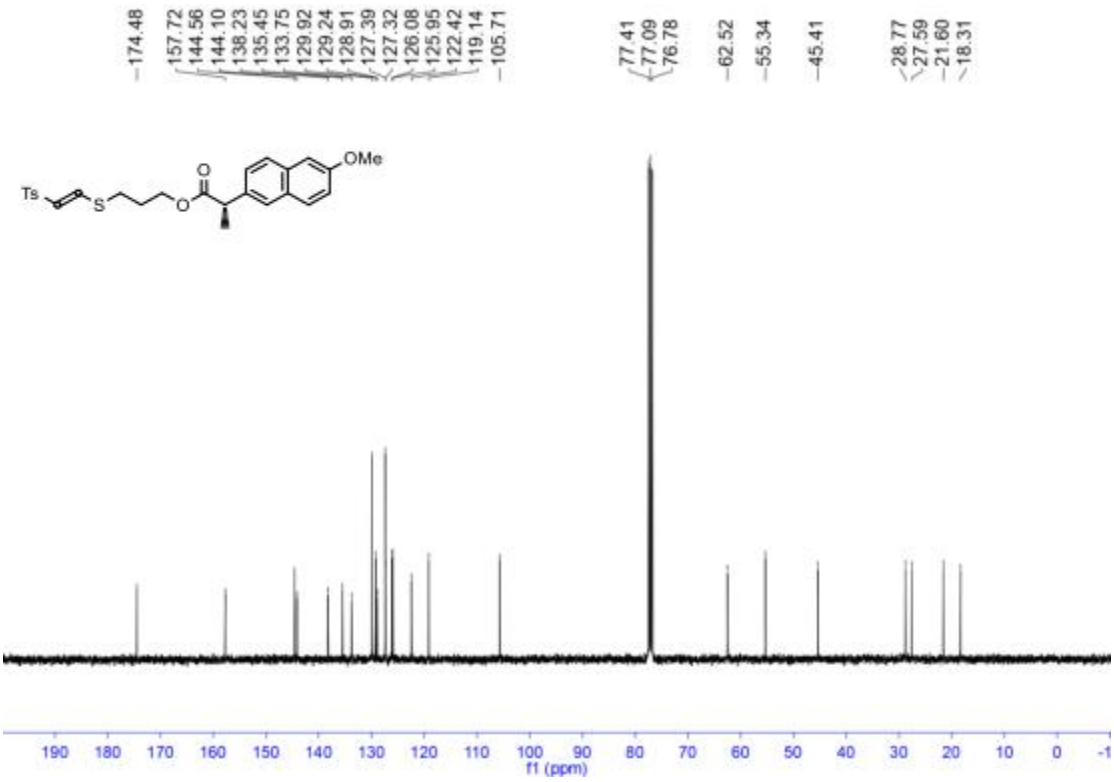
Supplementary Figure 271 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl- 1H-indol-3-yl)acetate **(65)**



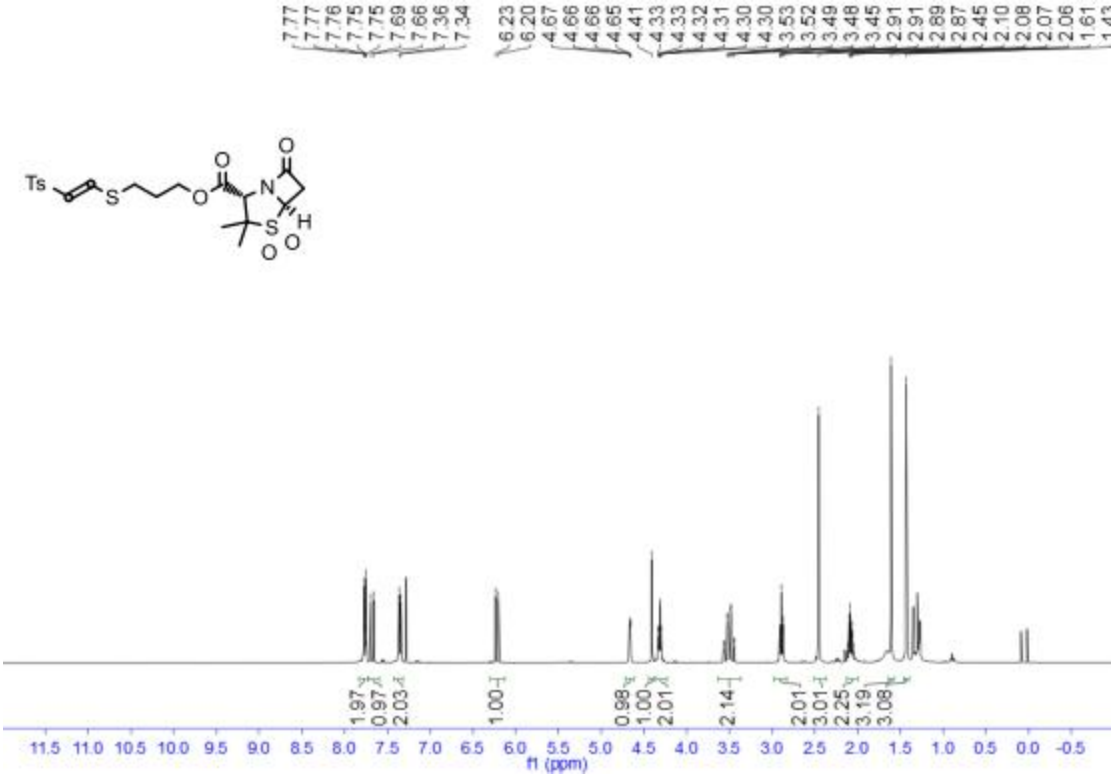
Supplementary Figure 272 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate **(66)**



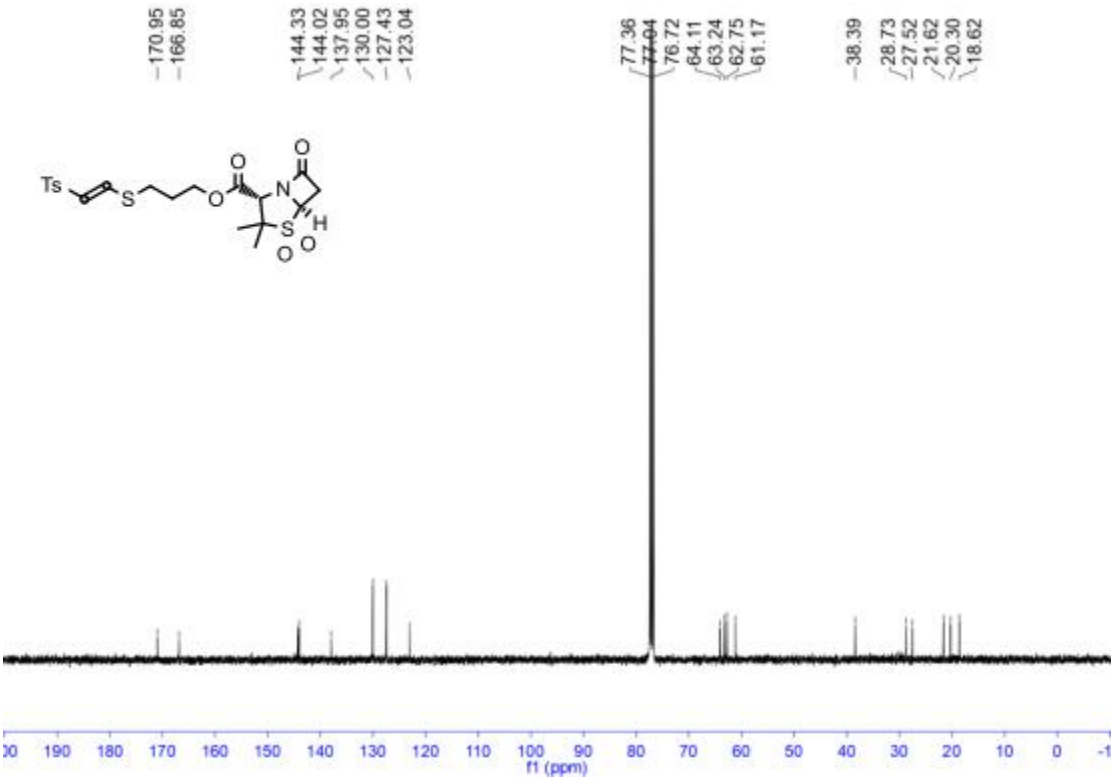
Supplementary Figure 273 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate **(66)**



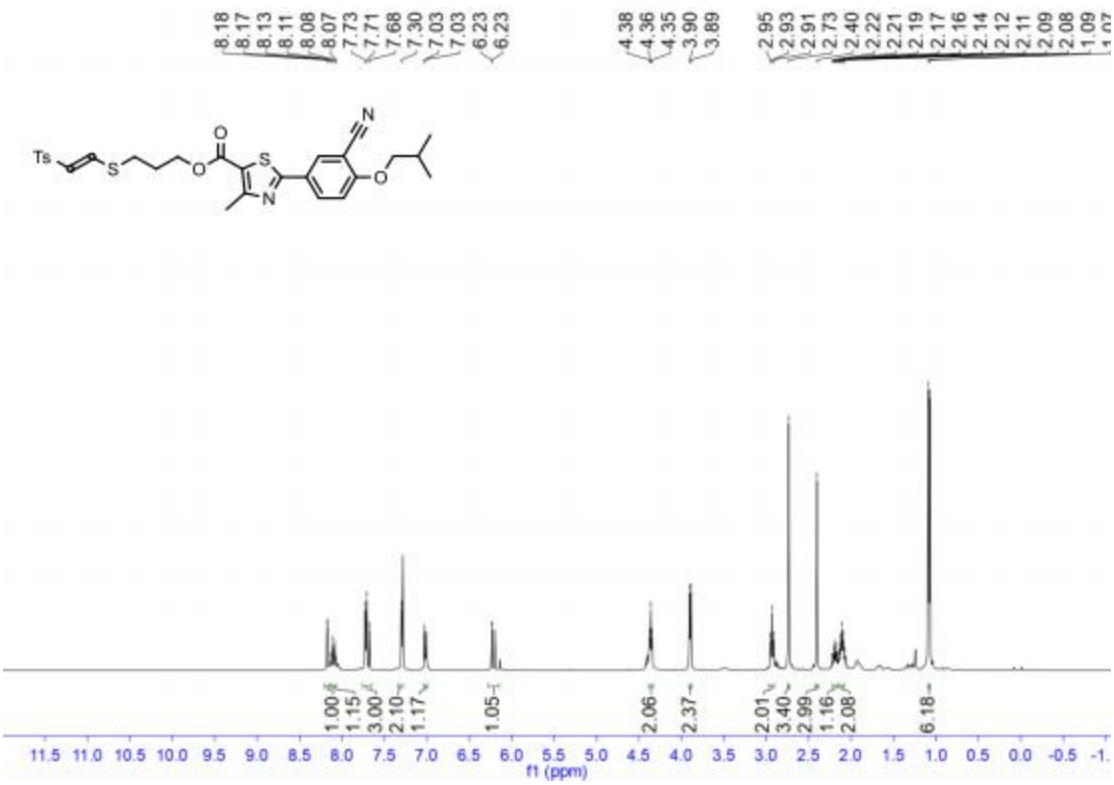
Supplementary Figure 274 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of 3-(((*E*)-2-tosylvinyl)thio)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia- 1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide **(67)**



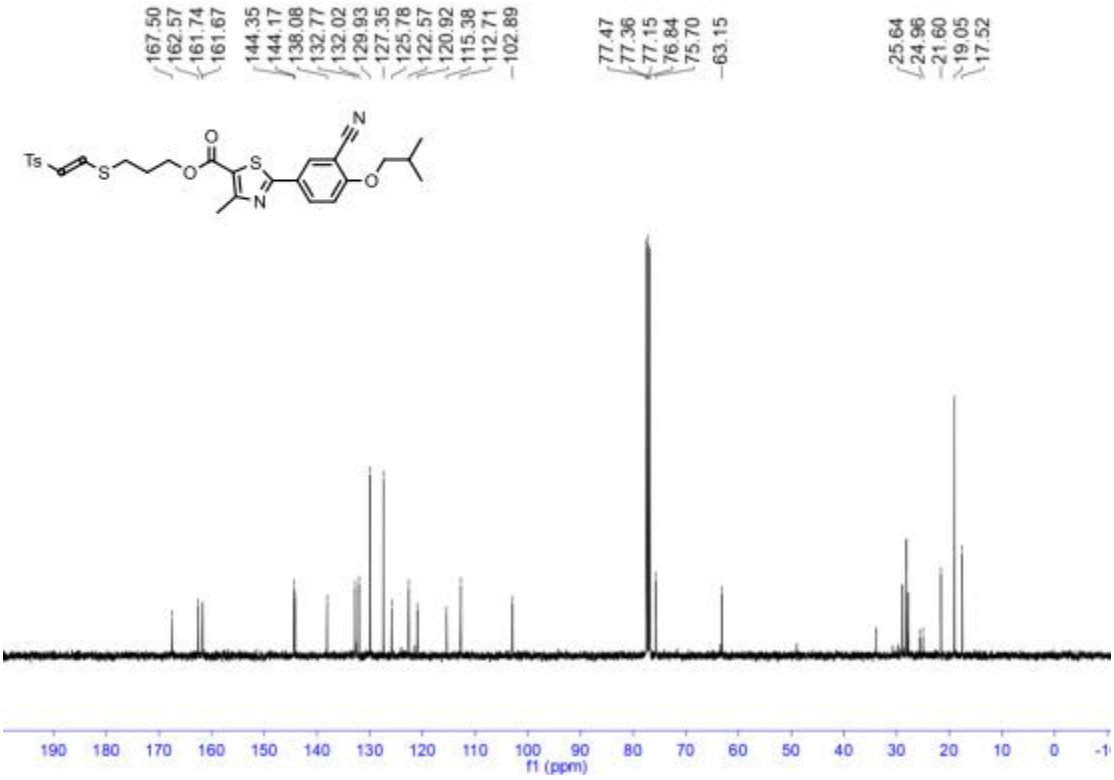
Supplementary Figure 275 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of 3-(((*E*)-2-tosylvinyl)thio)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia- 1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide **(67)**



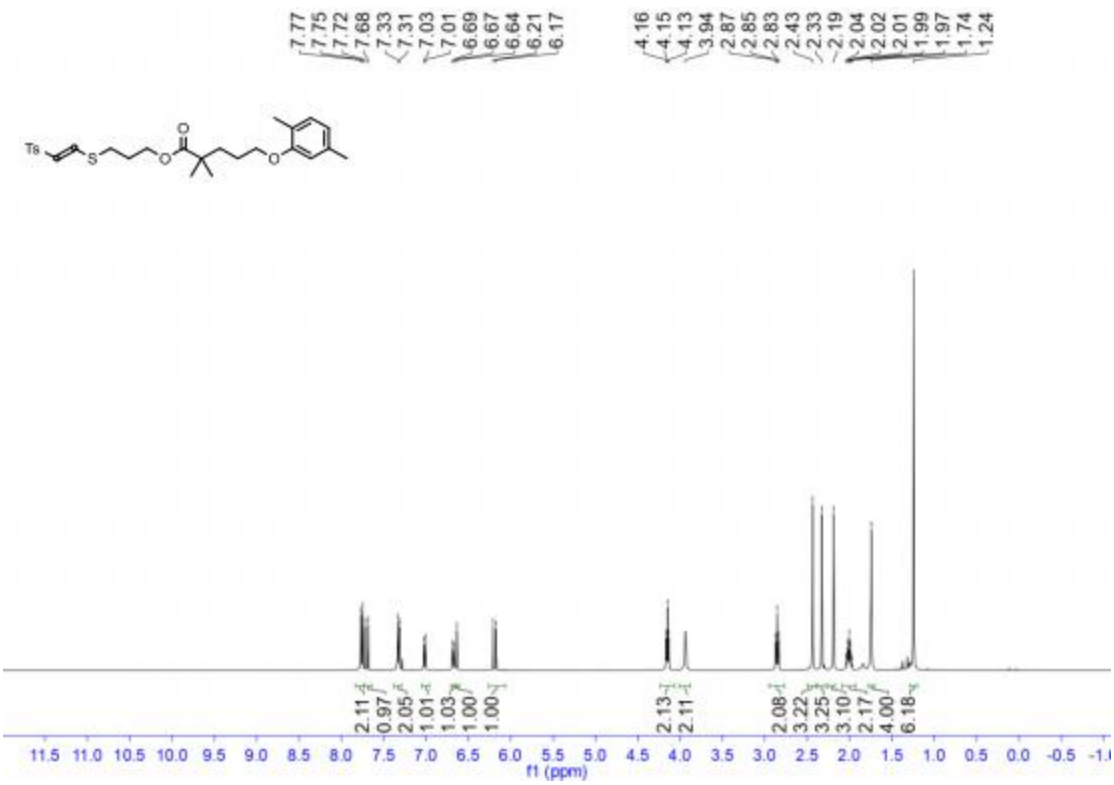
Supplementary Figure 276 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate **(68)**



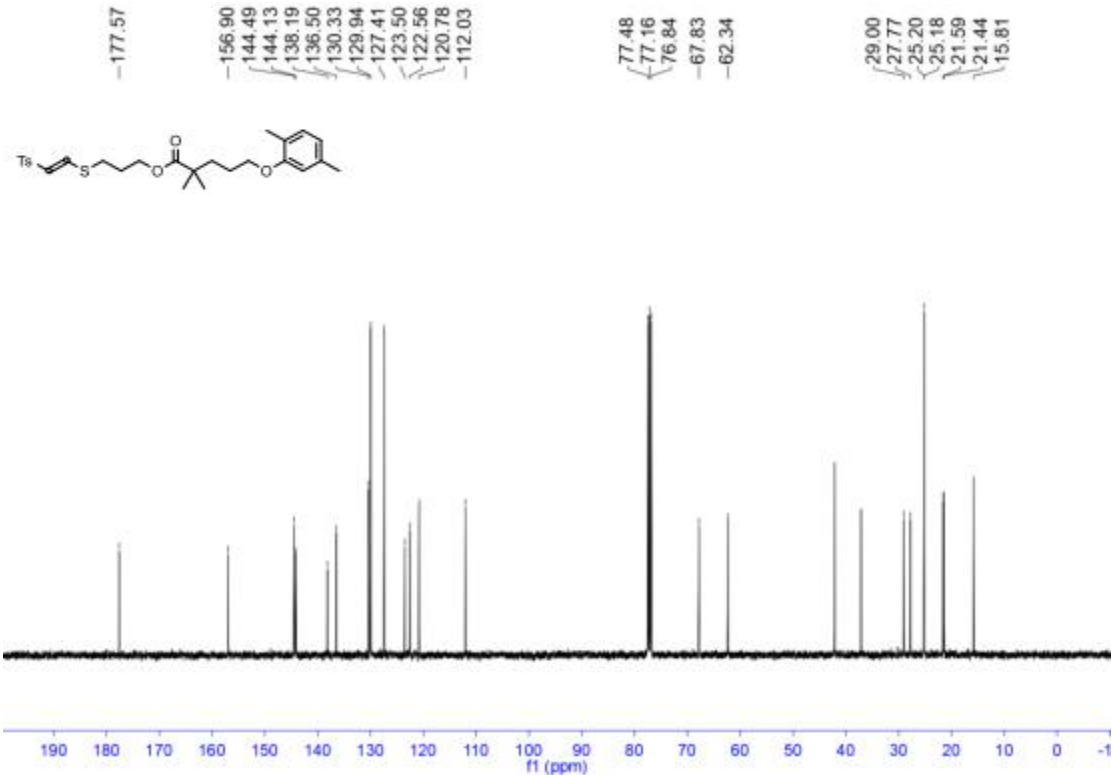
Supplementary Figure 277 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate **(68)**



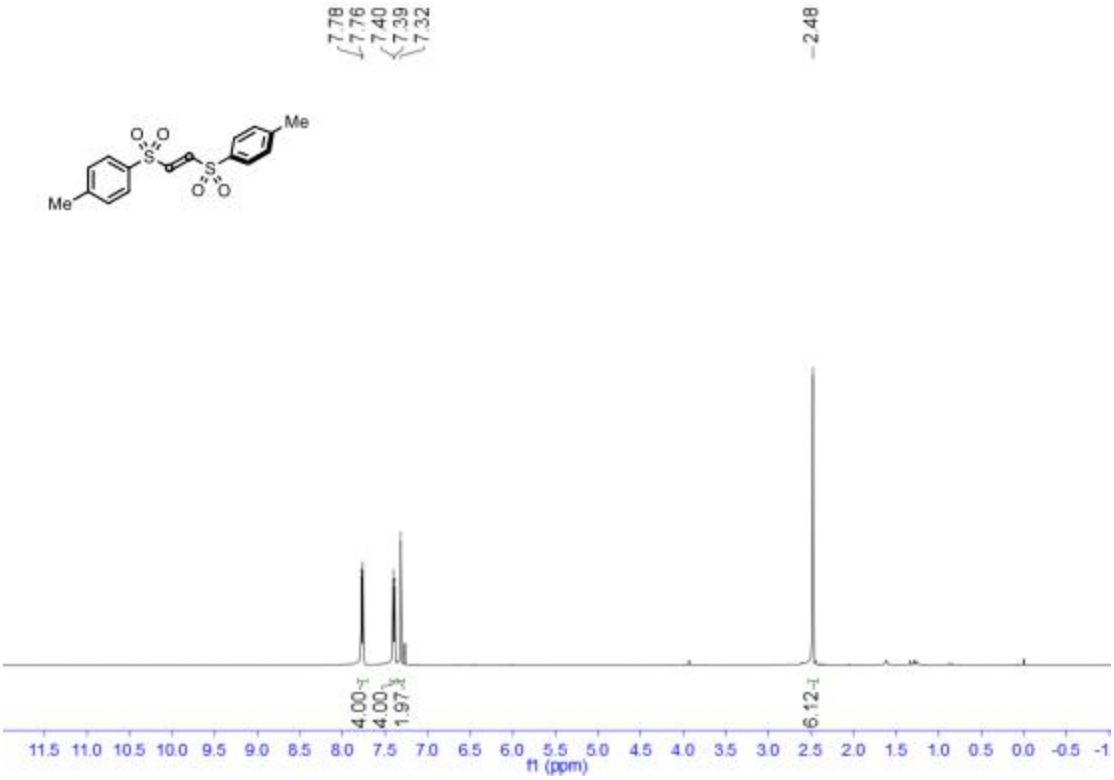
Supplementary Figure 278 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **(69)**



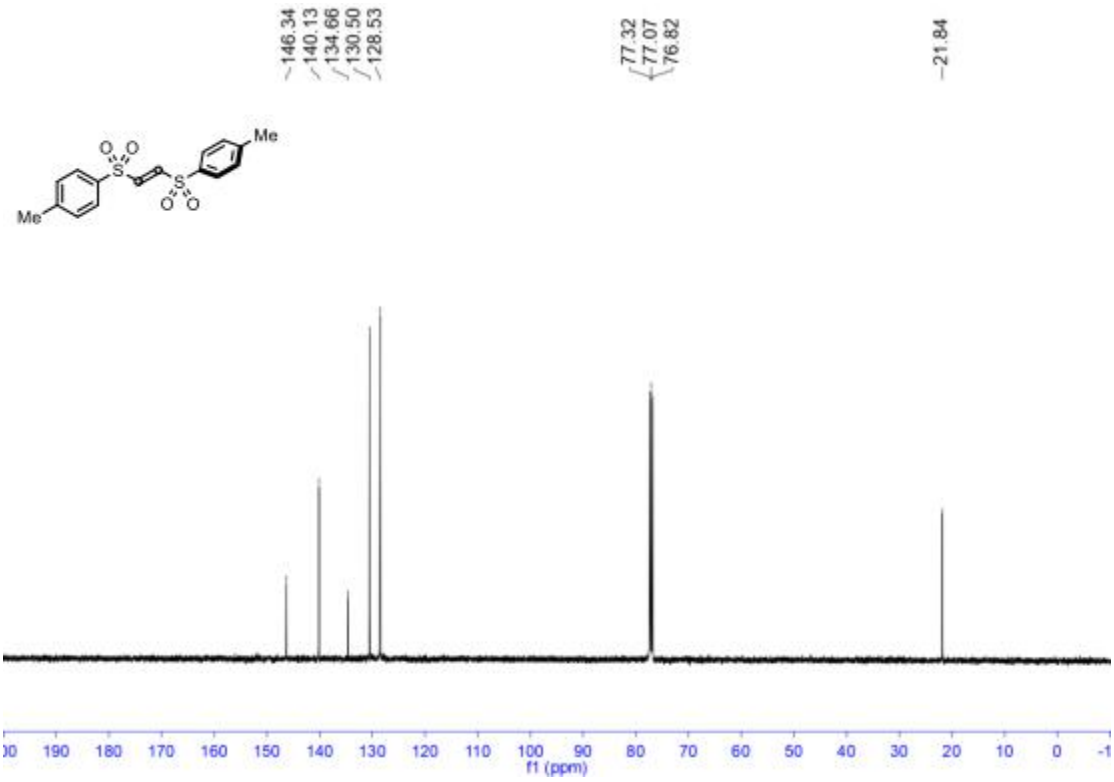
Supplementary Figure 279 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-3-((2-tosylvinyl)thio)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **(69)**



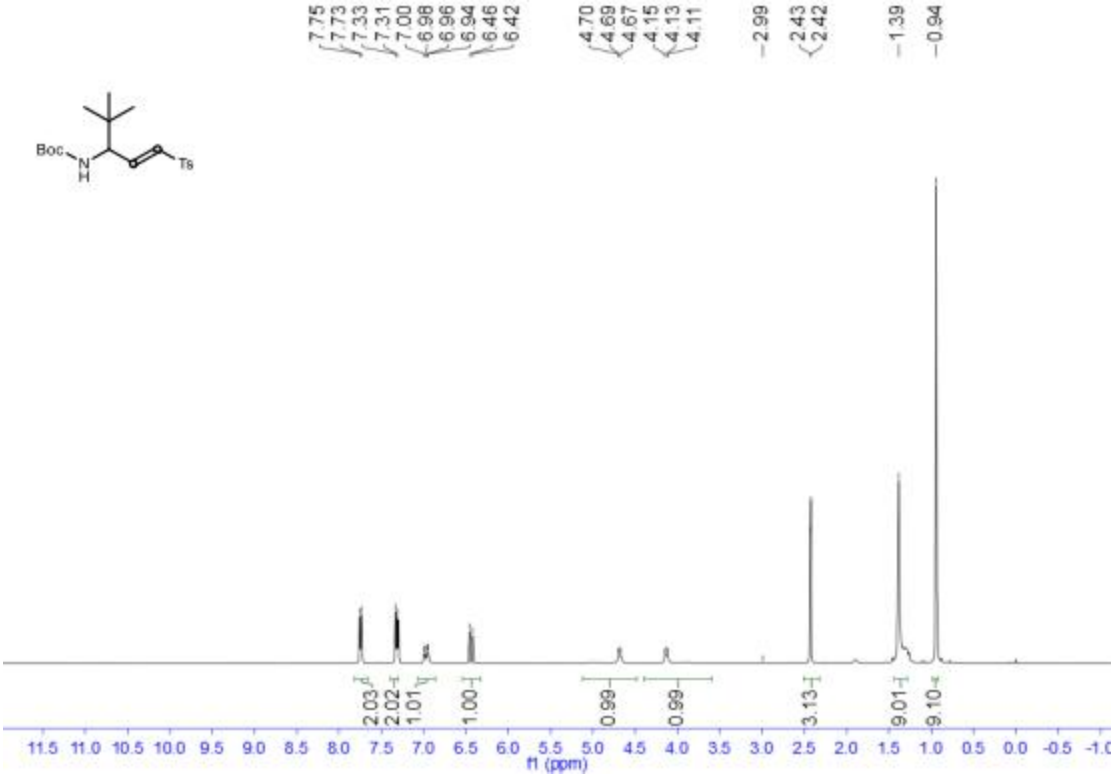
Supplementary Figure 280 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*E*)- 1,2-ditosylethene **(70)**



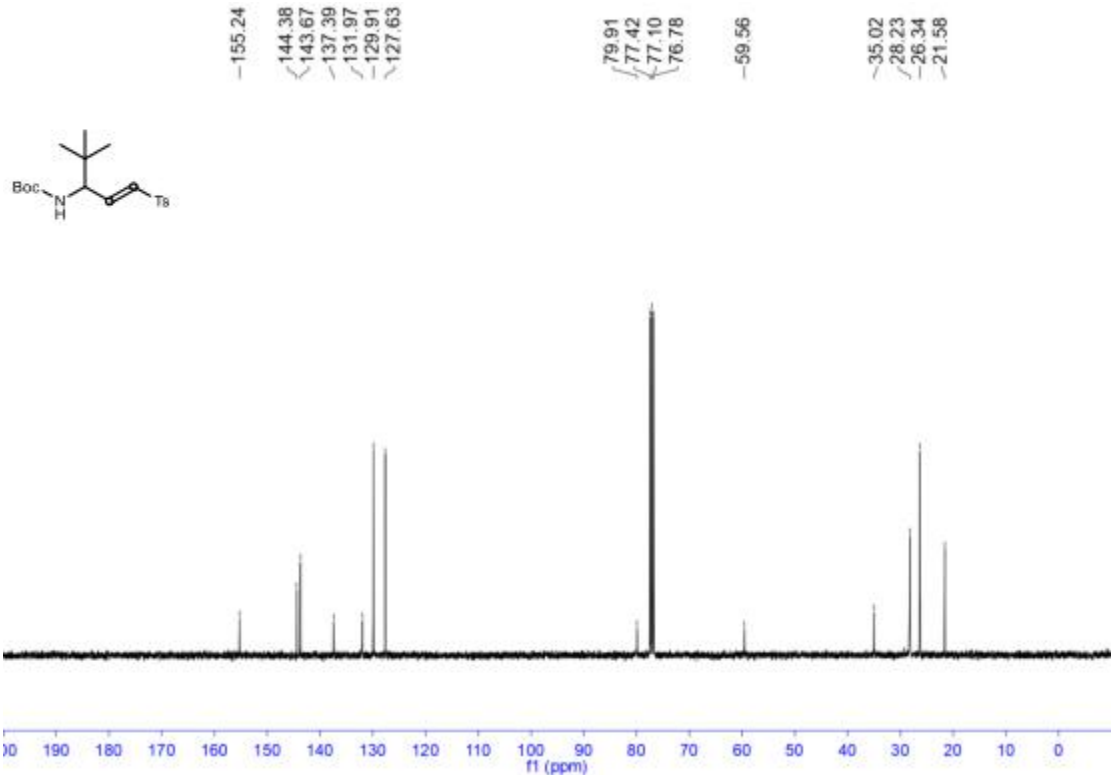
Supplementary Figure 281 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*E*)- 1,2-ditosylethene **(70)**



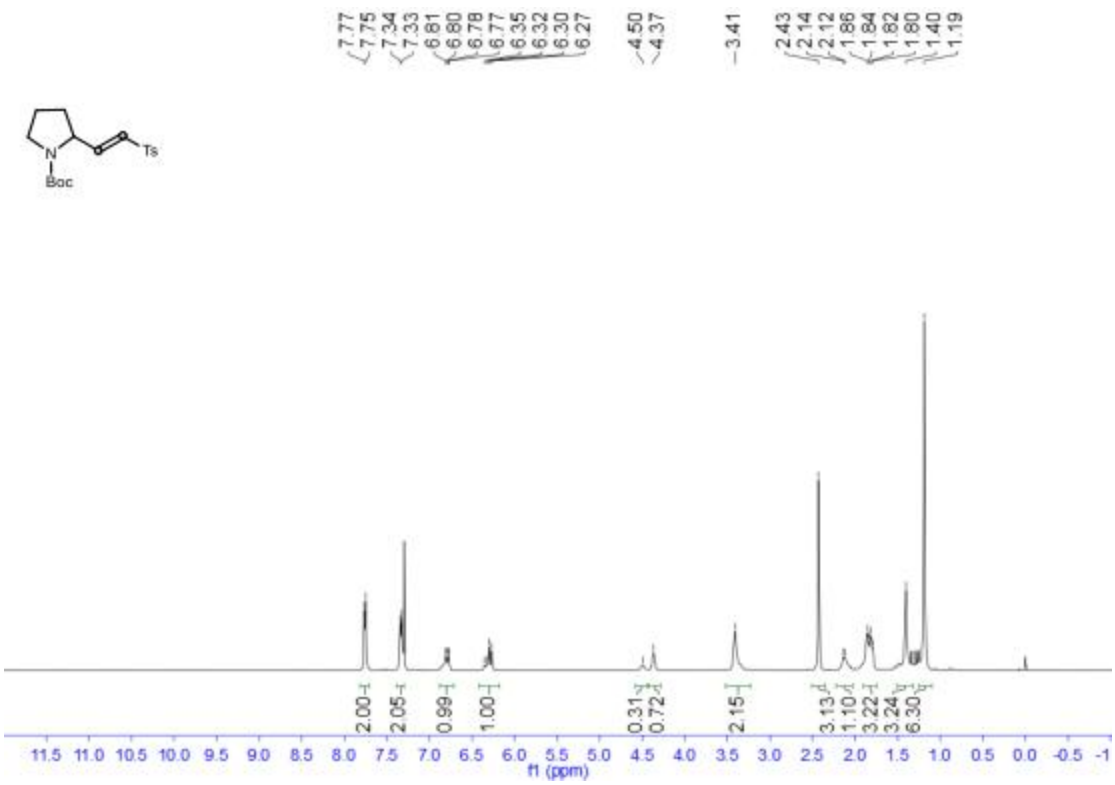
Supplementary Figure 282 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *tert*-butyl (*E*)-(4,4-dimethyl- 1-tosylpent- 1-en-3-yl)carbamate **(71)**



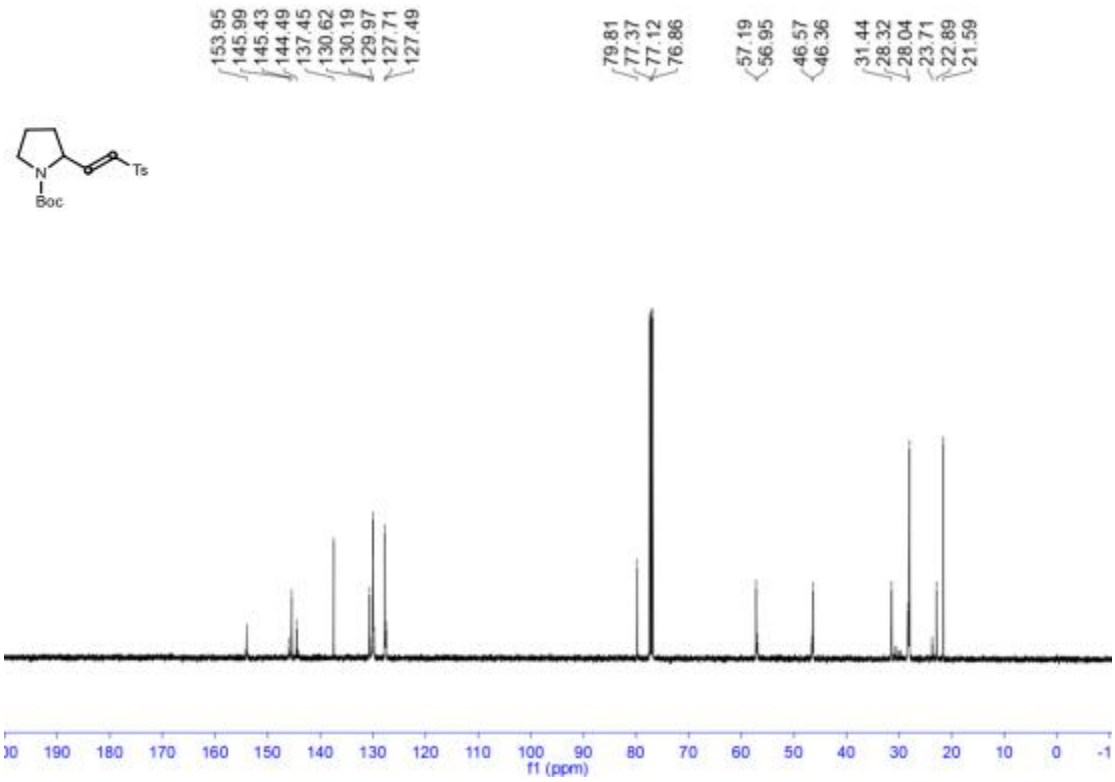
Supplementary Figure 283 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of *tert*-butyl (*E*)-(4,4-dimethyl- 1-tosylpent- 1-en-3-yl)carbamate **(71)**



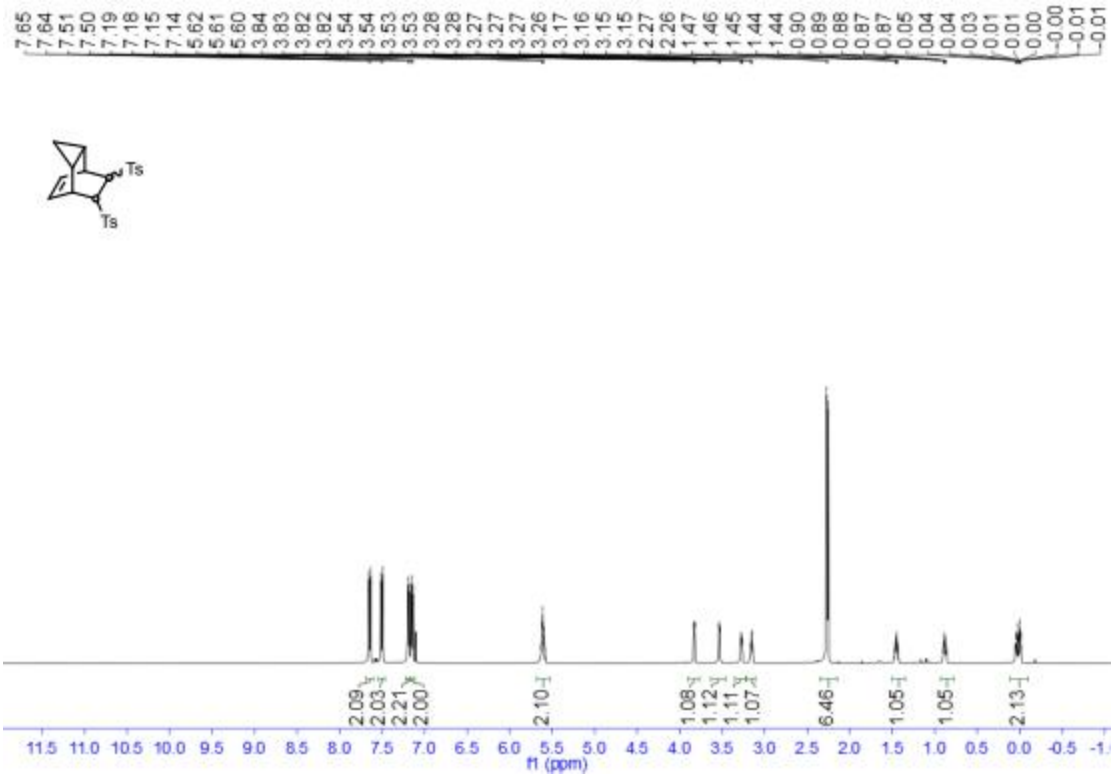
Supplementary Figure 284 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of *tert*-butyl (*E*)-2-(2-tosylvinyl)pyrrolidine- 1-carboxylate **(72)**



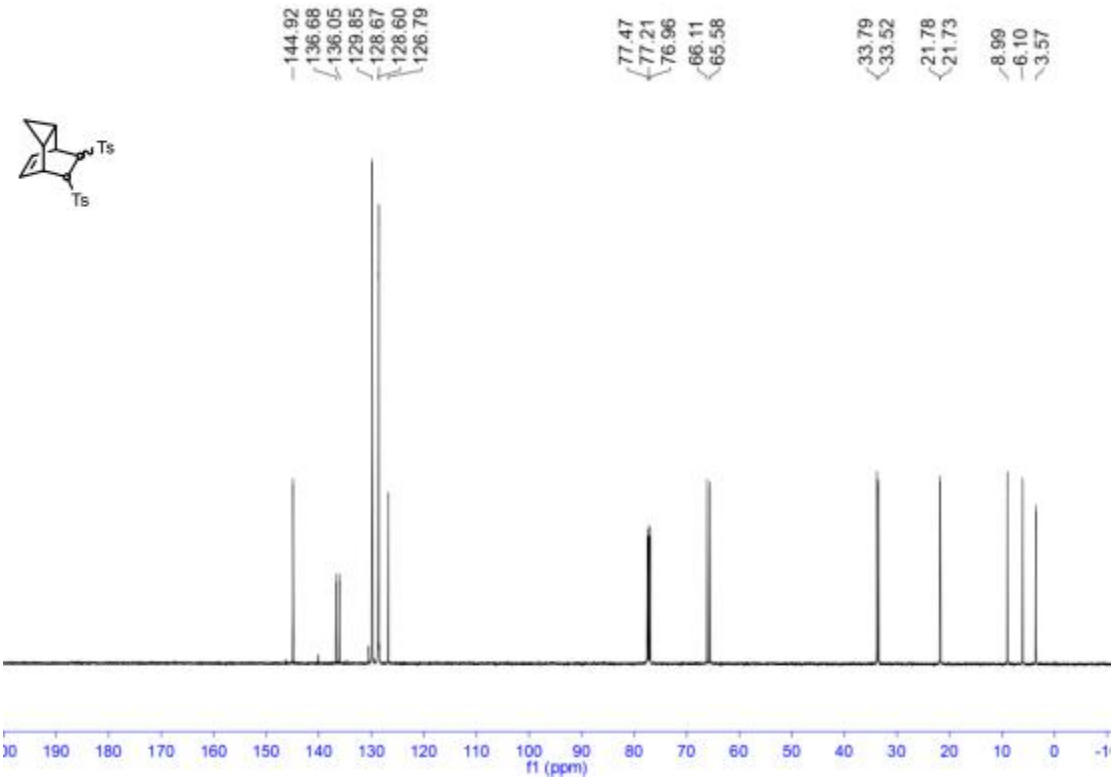
Supplementary Figure 285 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of *tert*-butyl (*E*)-2-(2-tosylvinyl)pyrrolidine- 1-carboxylate **(72)**



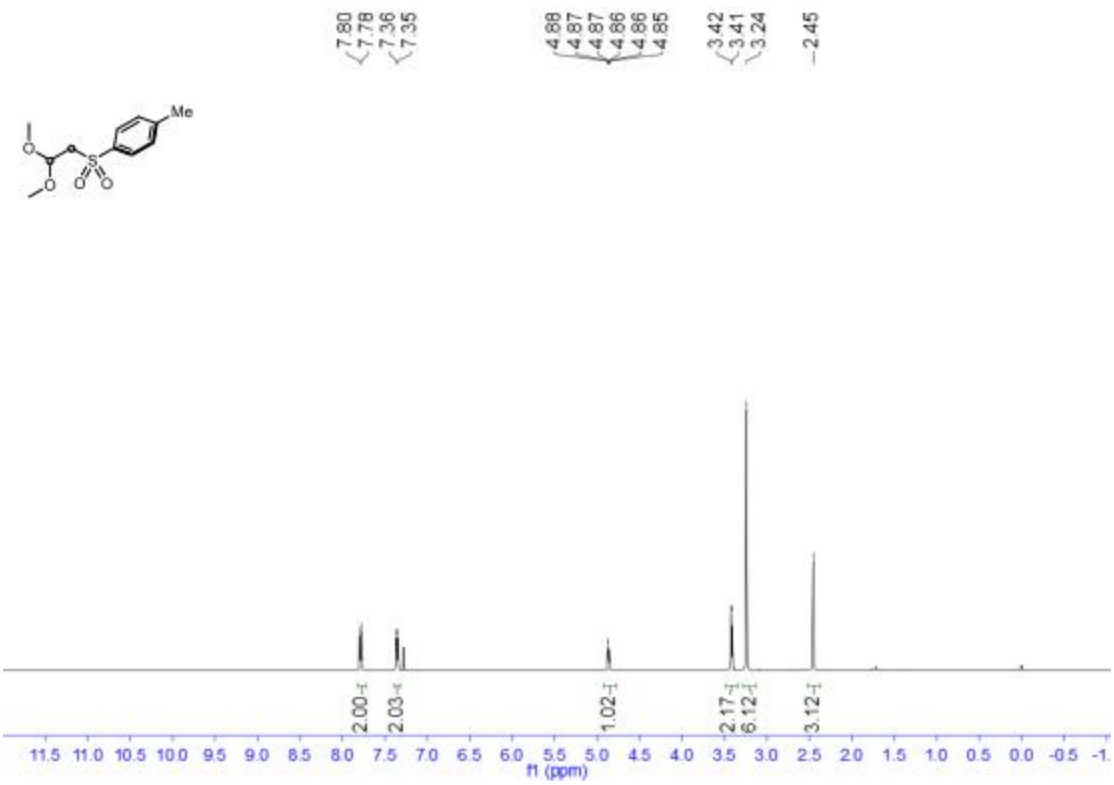
Supplementary Figure 286 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 8,9-ditosyltricyclo[3.2.2.0$_{2,4}$]non-6-ene **(73)**



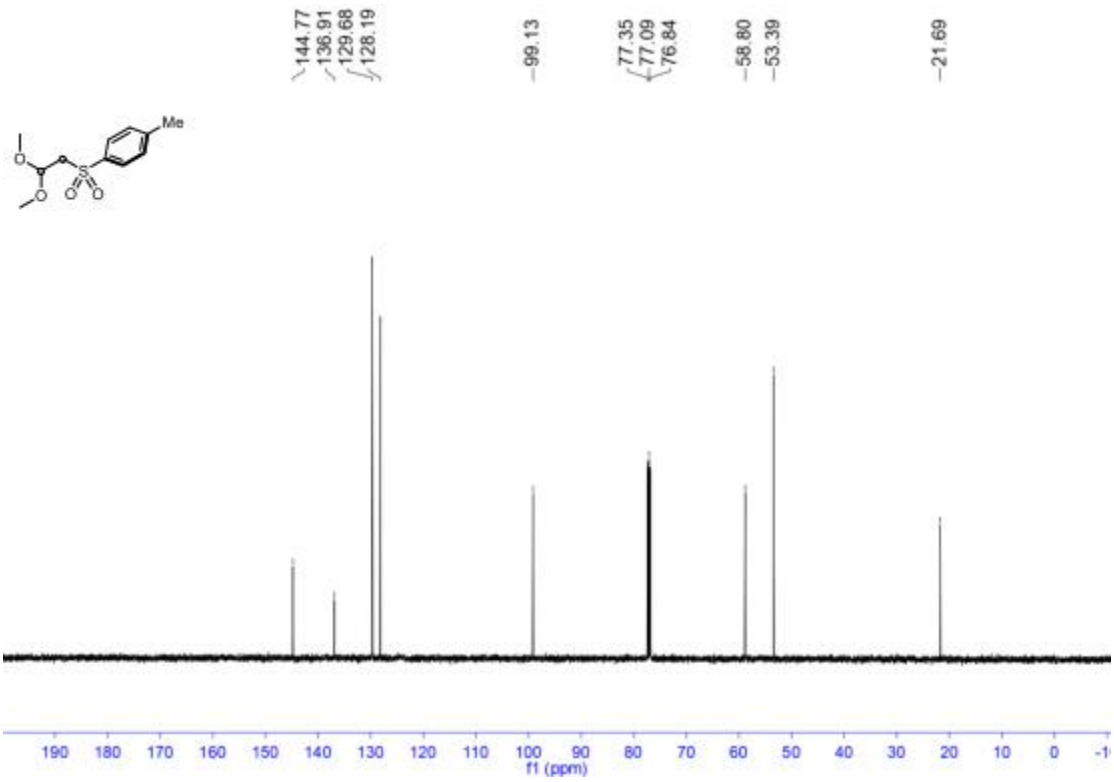
Supplementary Figure 287 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 8,9-/ditosyltricyclo[3.2.2.0$_{2,4}$]non-6-ene **(73)**



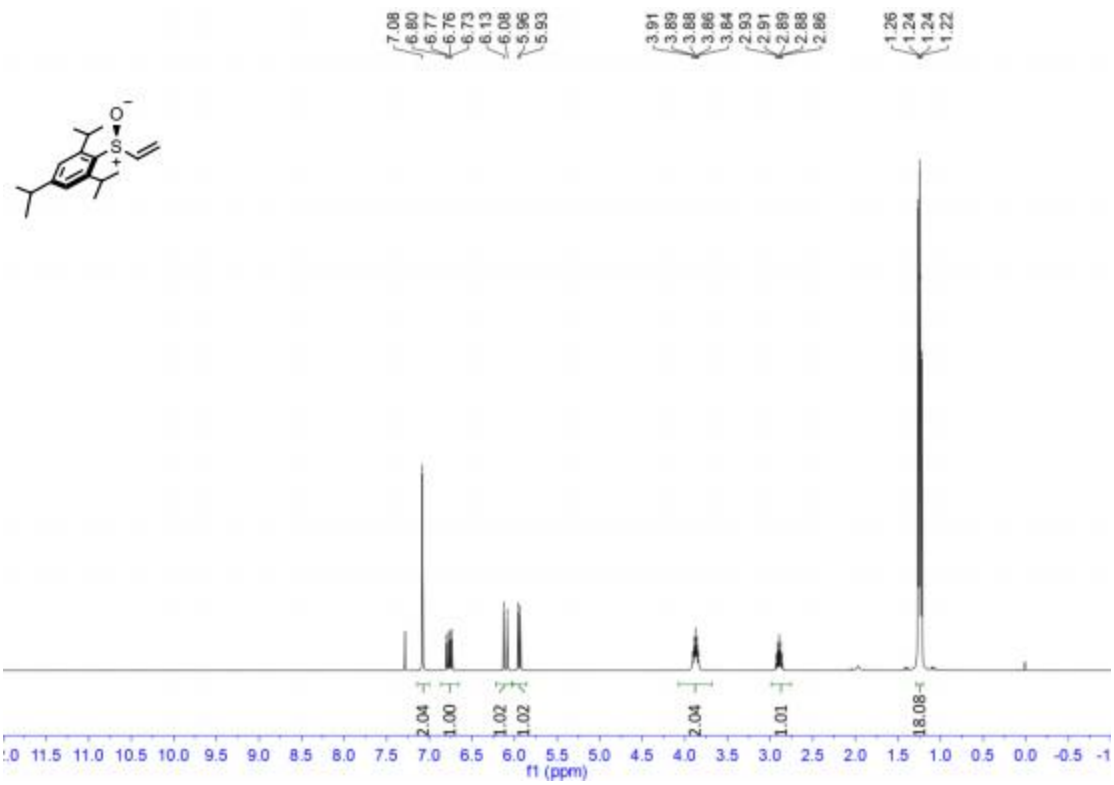
Supplementary Figure 288 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 1-((2,2-dimethoxyethyl)sulfonyl)-4-methylbenzene **(74)**



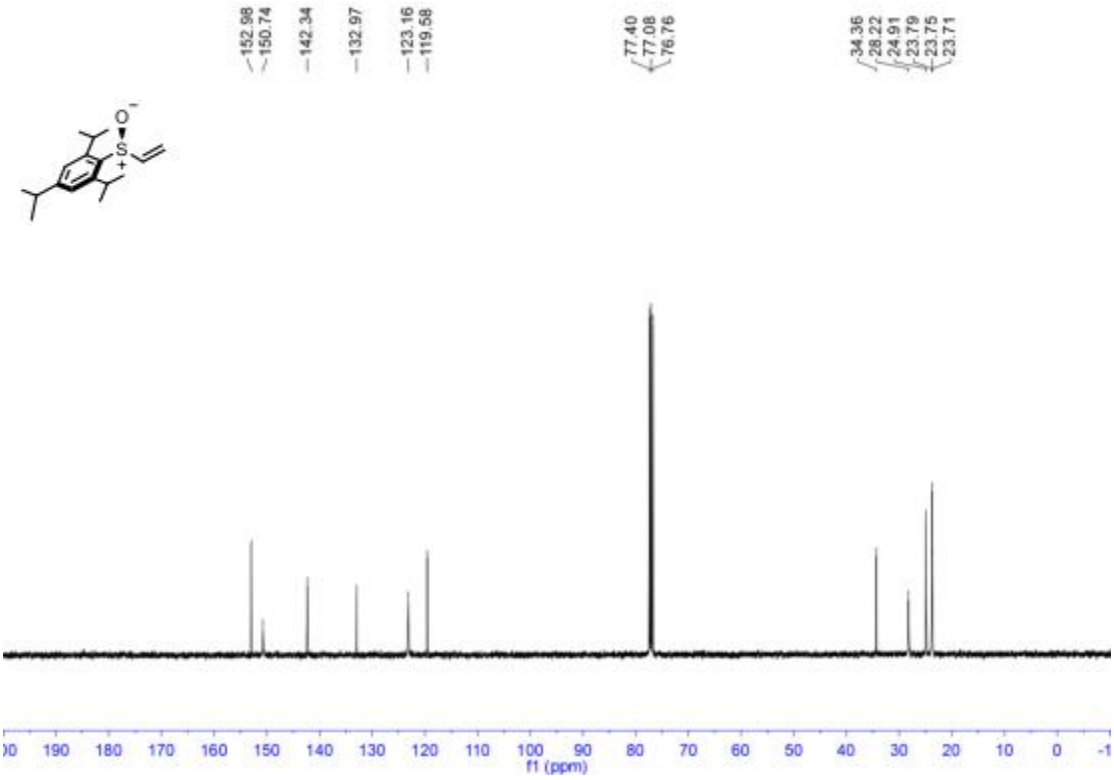
Supplementary Figure 289 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 1-((2,2-dimethoxyethyl)sulfonyl)-4-methylbenzene **(74)**



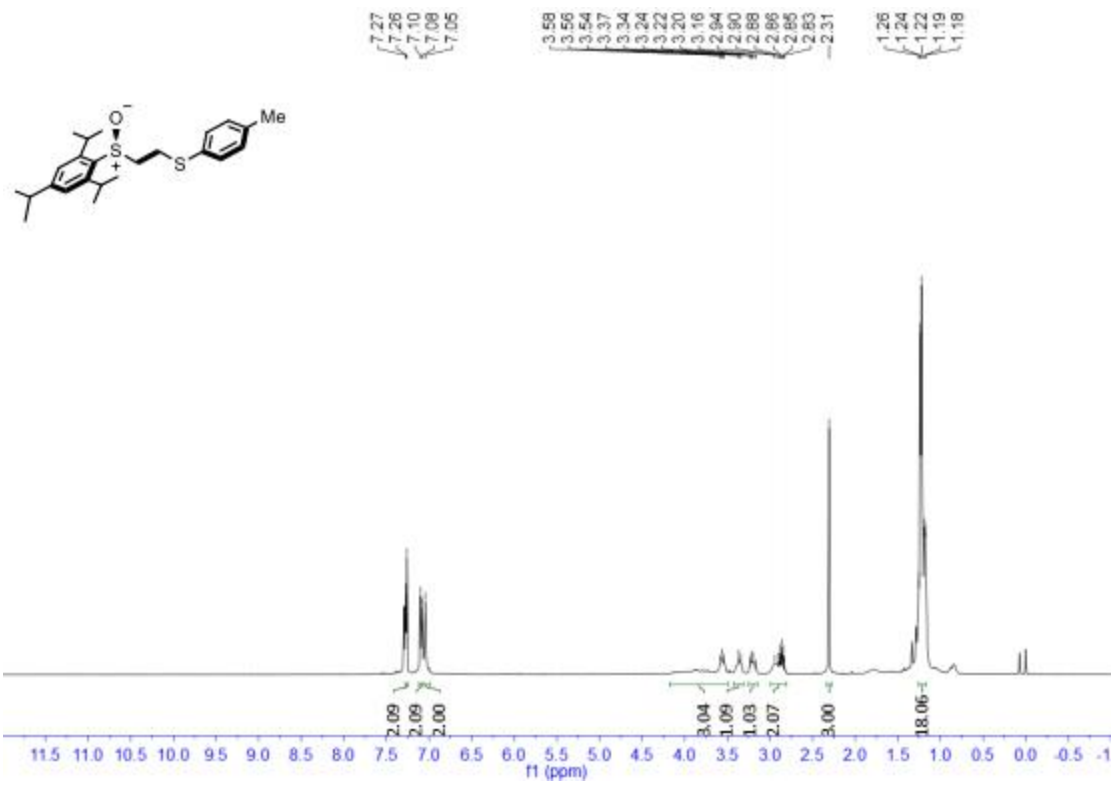
Supplementary Figure 290 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **(75)**



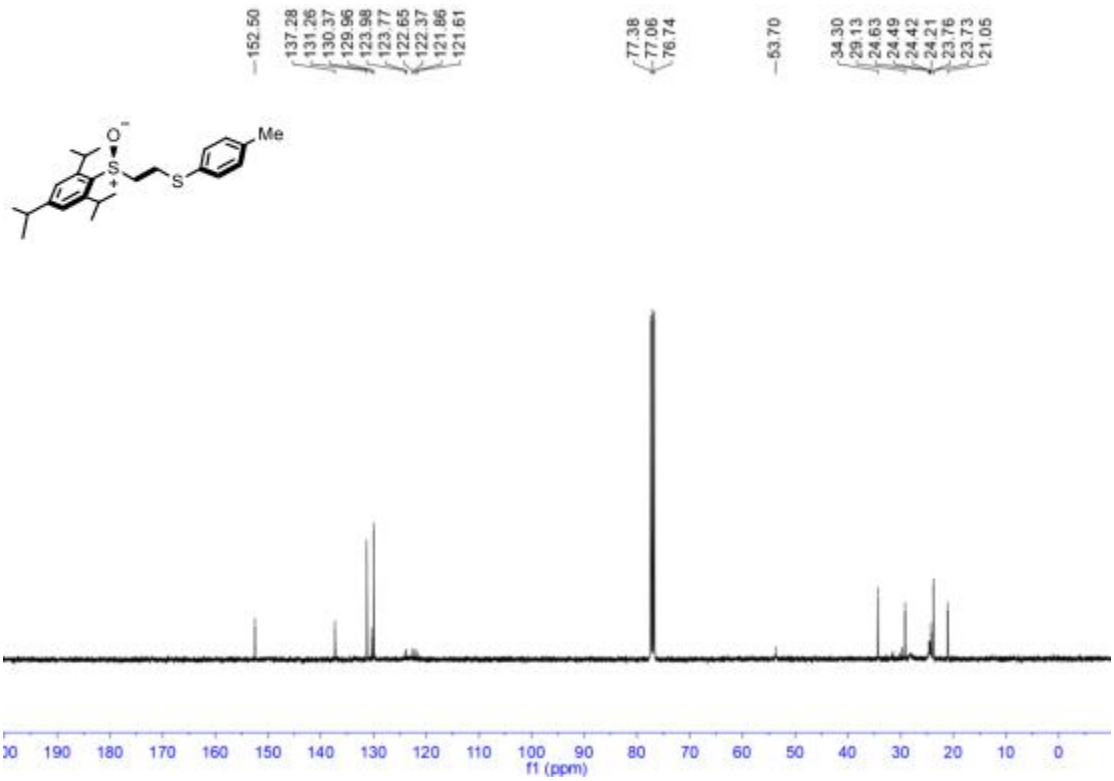
Supplementary Figure 291 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)- 1,3,5-triisopropyl-2-(vinylsulfinyl)benzene **(75)**



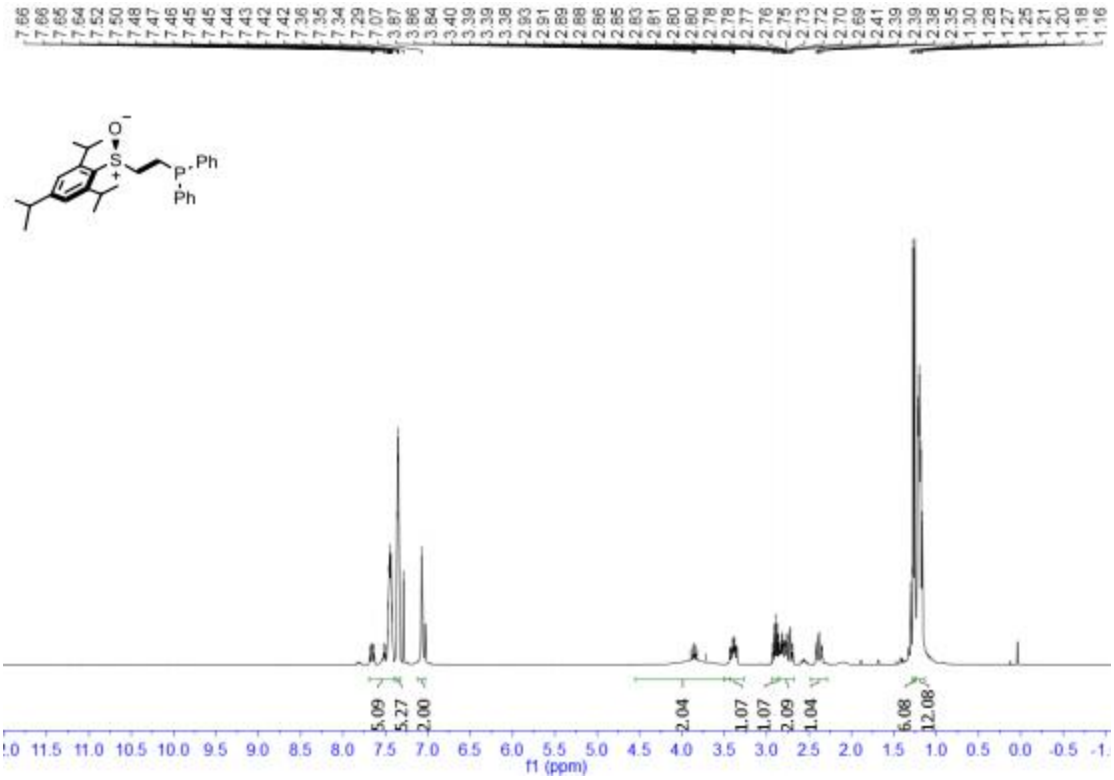
Supplementary Figure 292 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-*p*-tolyl(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)sulfane **(76)**



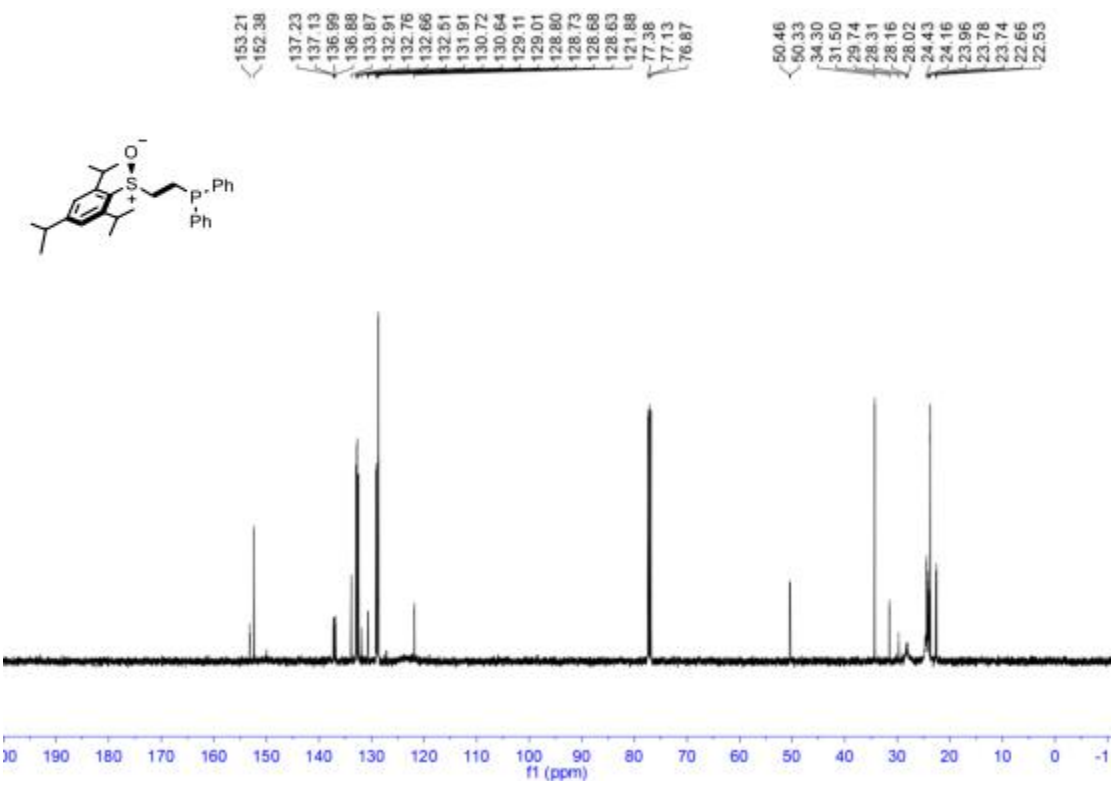
Supplementary Figure 293 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-*p*-tolyl(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)sulfane **(76)**



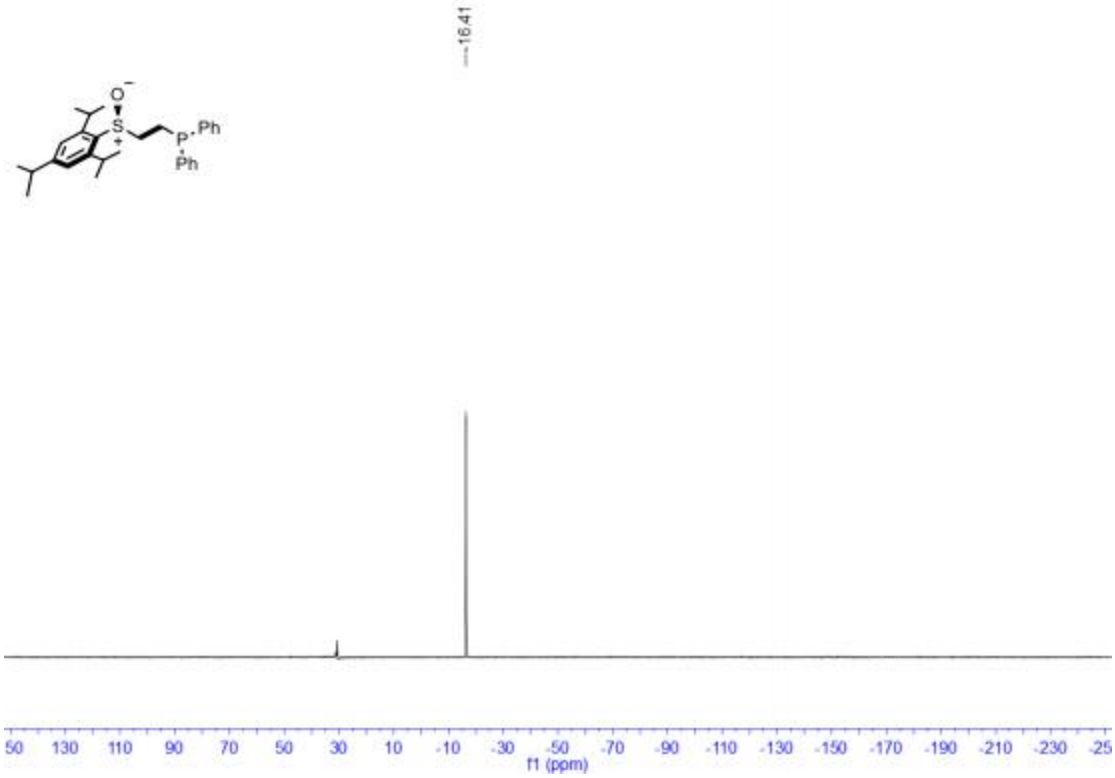
Supplementary Figure 294 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-diphenyl(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)phosphane **(77)**



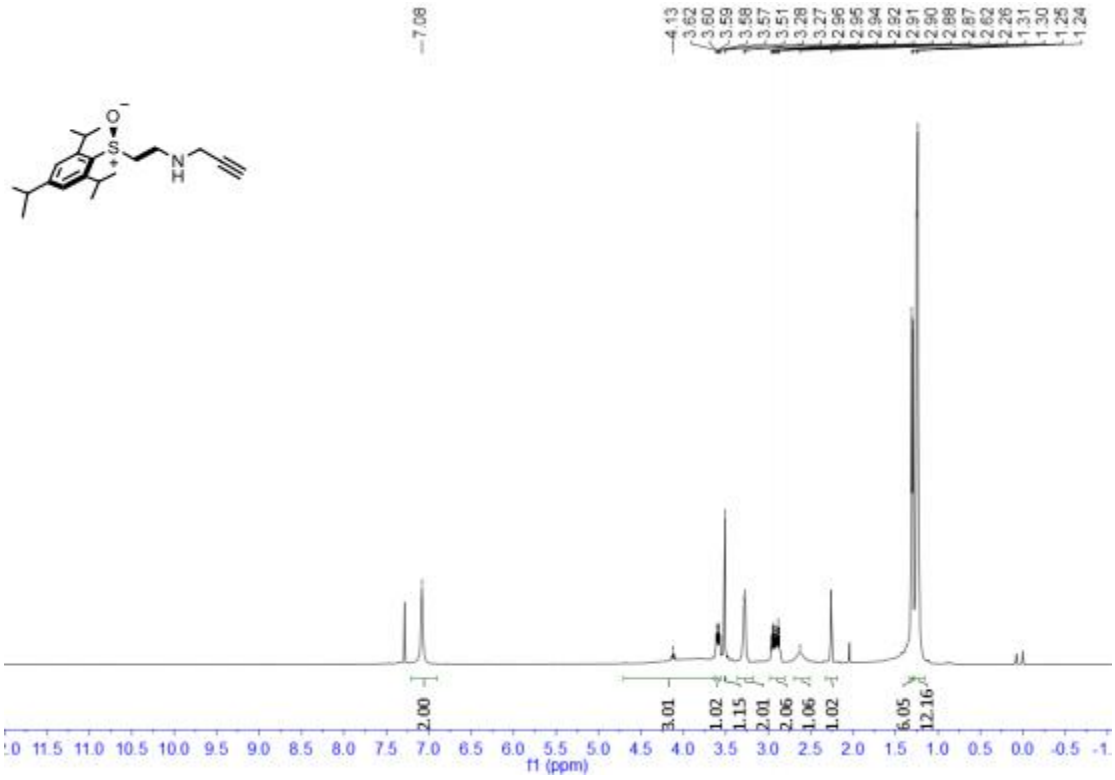
Supplementary Figure 295 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-diphenyl(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)phosphane **(77)**



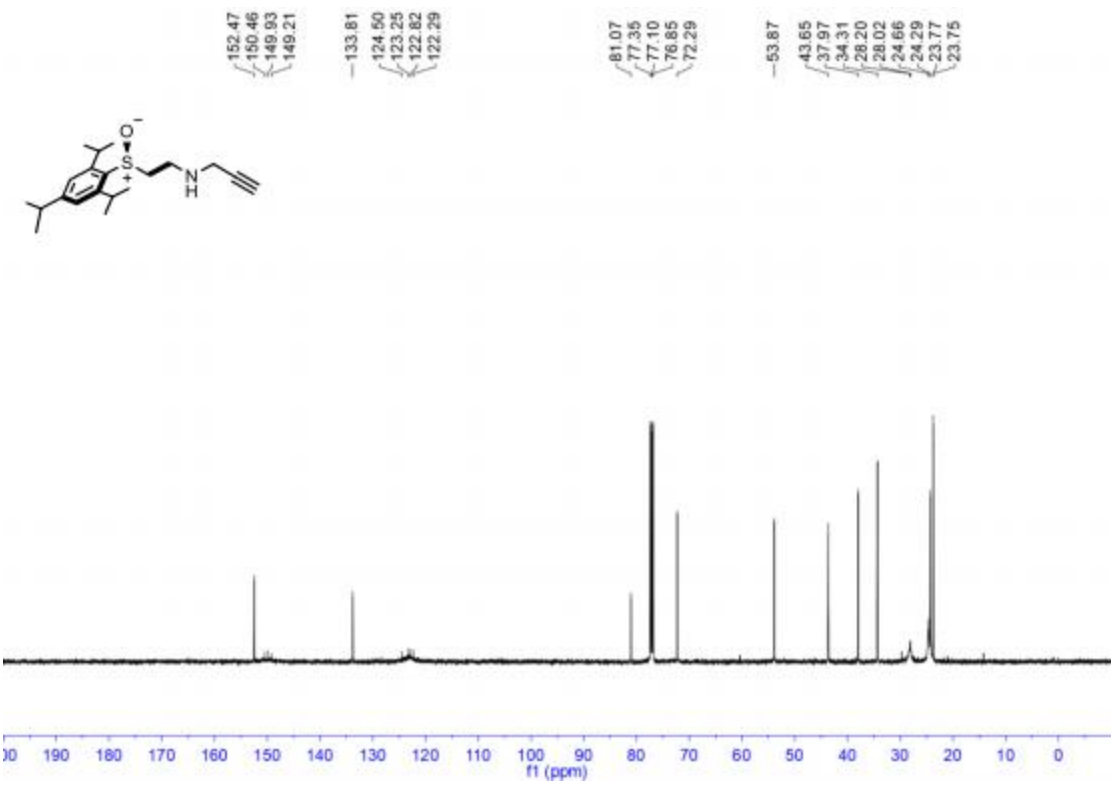
Supplementary Figure 296 | ^{31}P NMR (202 MHz, 298K, Chloroform-*d*) of (*S*)-diphenyl(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)phosphane **(77)**



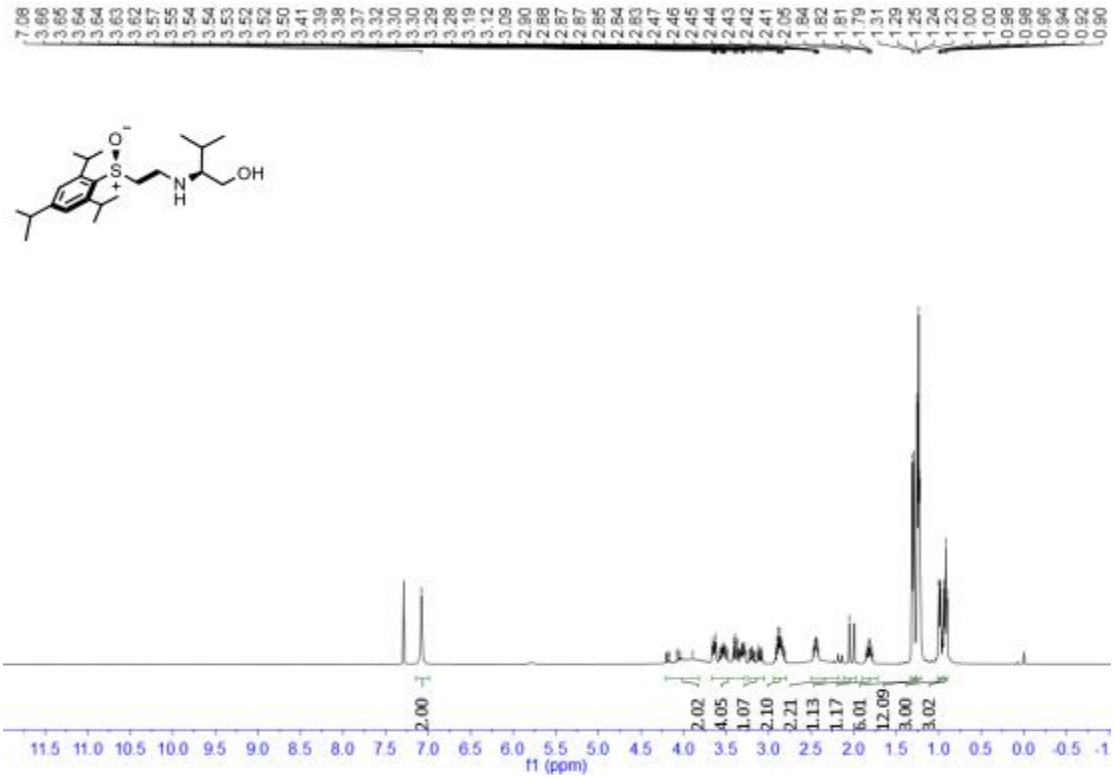
Supplementary Figure 297 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-yn- 1-amine **(78)**



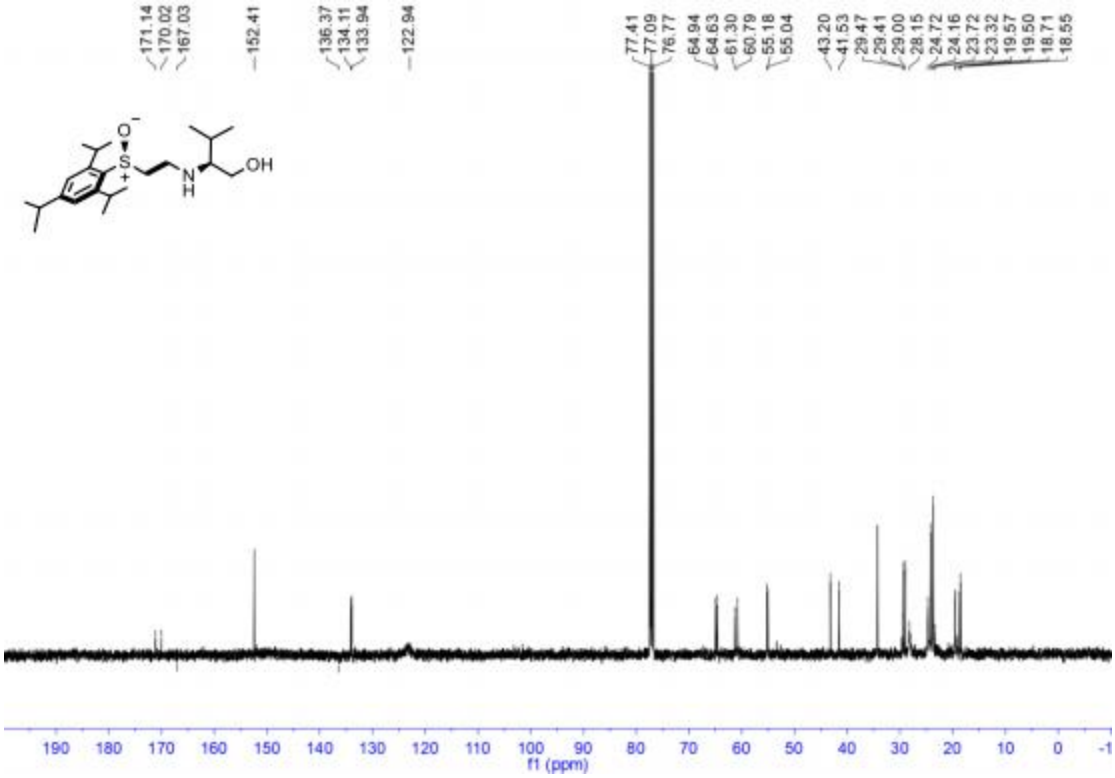
Supplementary Figure 298 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-yn- 1-amine **(78)**



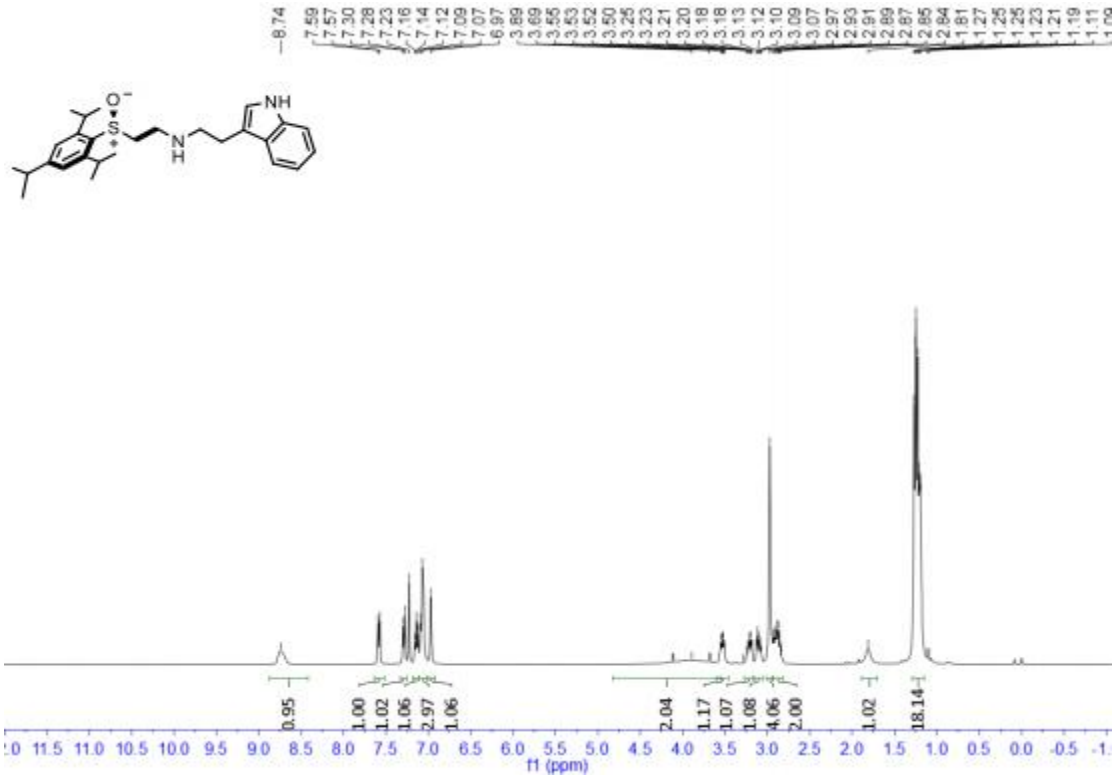
Supplementary Figure 299 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-3-methyl-2-((2-((*S*)-(2,4,6-triisopropylphenyl)sulfinyl)ethyl)amino)butan- 1-ol **(79)**



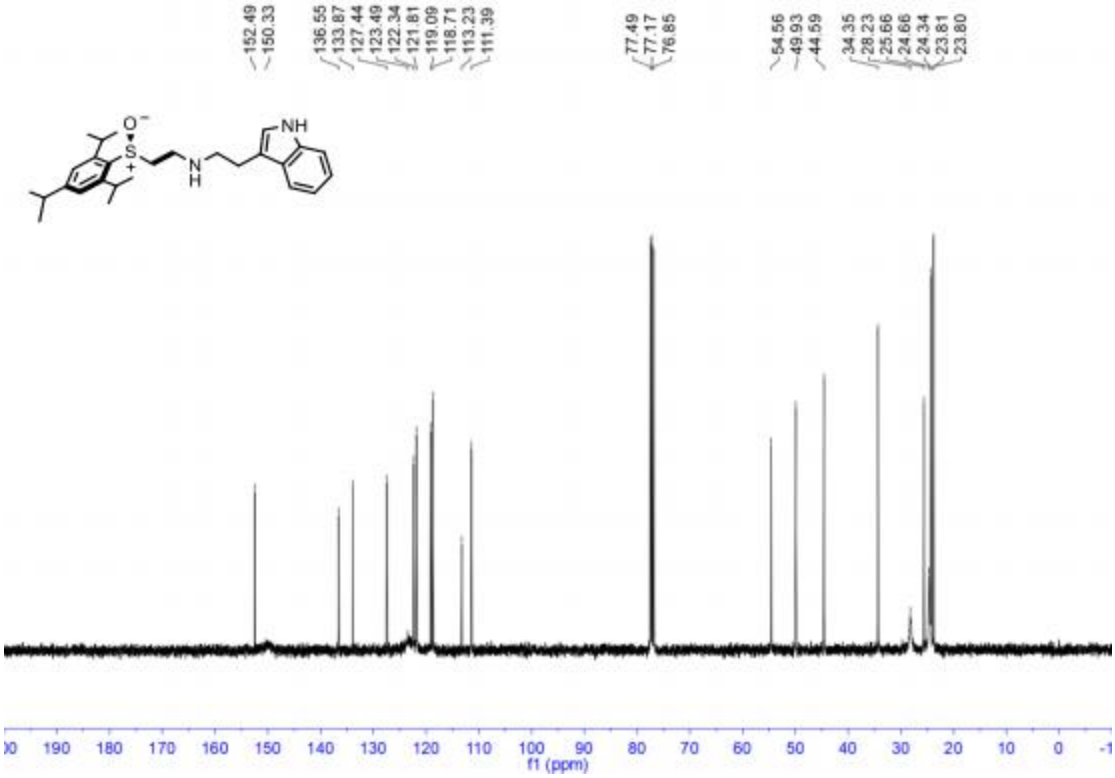
Supplementary Figure 300 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-3-methyl-2-((2-((*S*)-(2,4,6-triisopropylphenyl)sulfinyl)ethyl)amino)butan- 1-ol **(79)**



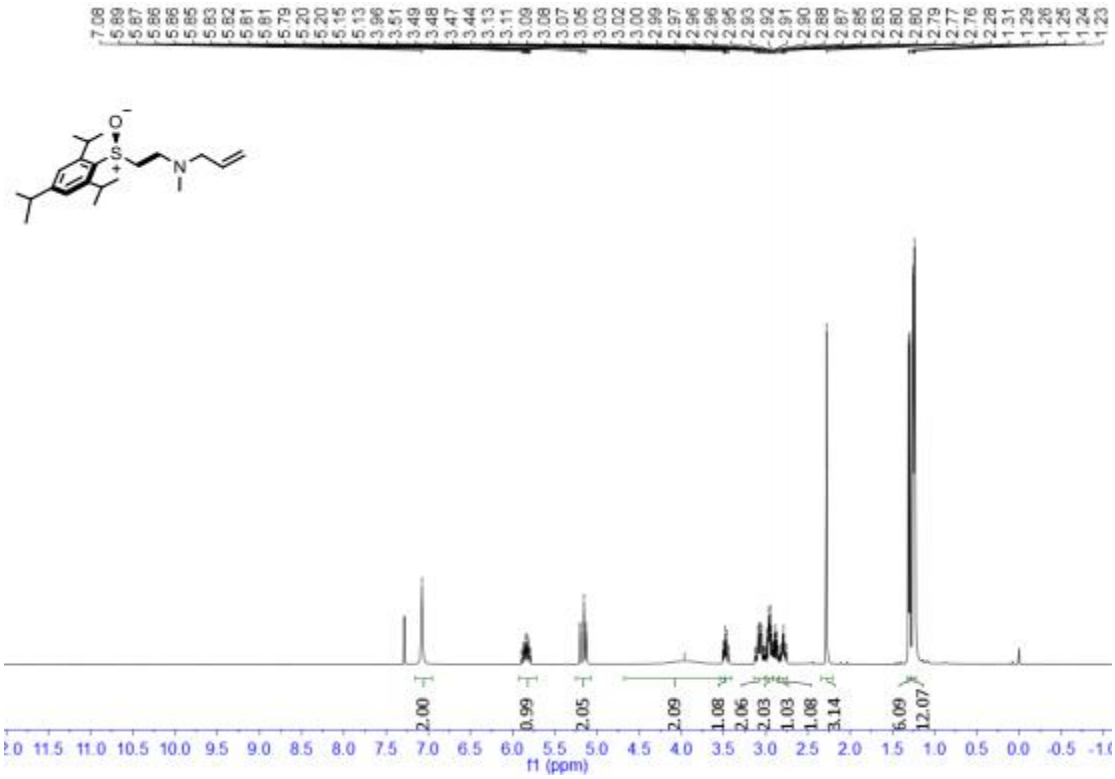
Supplementary Figure 301 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-(2-(1*H*-indol-3-yl)ethyl)-2-((2,4,6-triisopropylphenyl)sulfinyl)ethan- 1-amine **(80)**



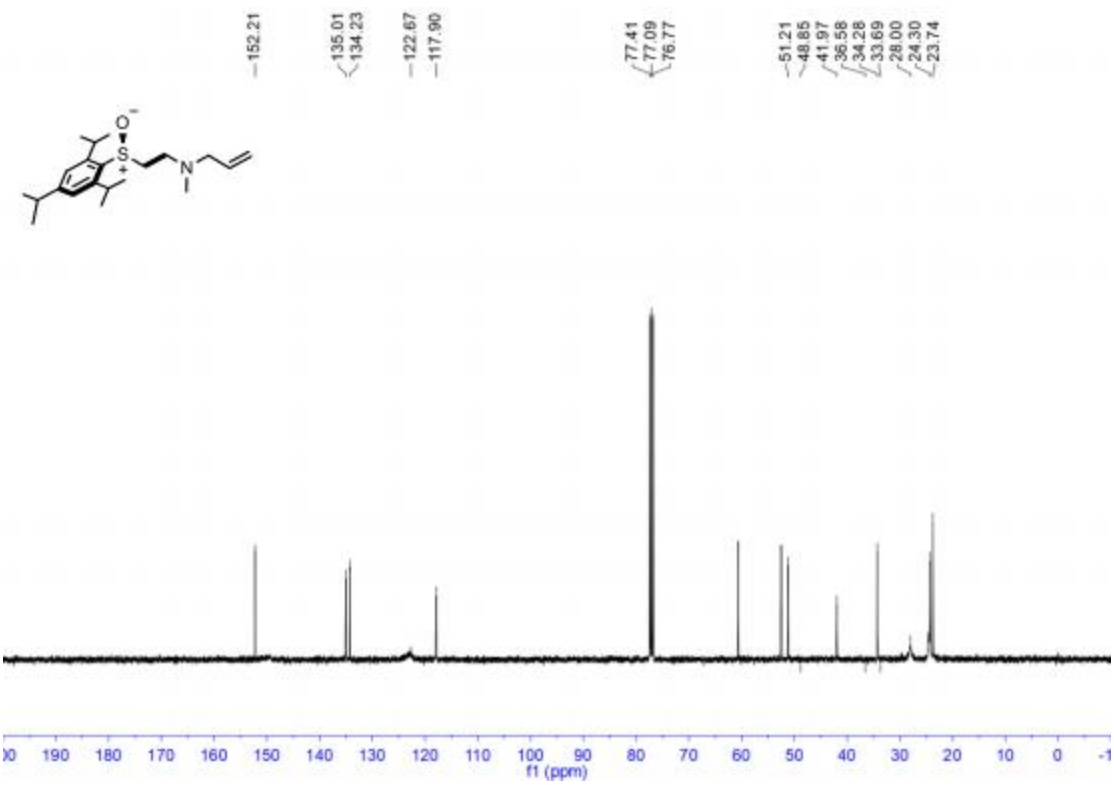
Supplementary Figure 302 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-(2-(1*H*-indol-3-yl)ethyl)-2-((2,4,6-triisopropylphenyl)sulfinyl)ethan- 1-amine **(80)**



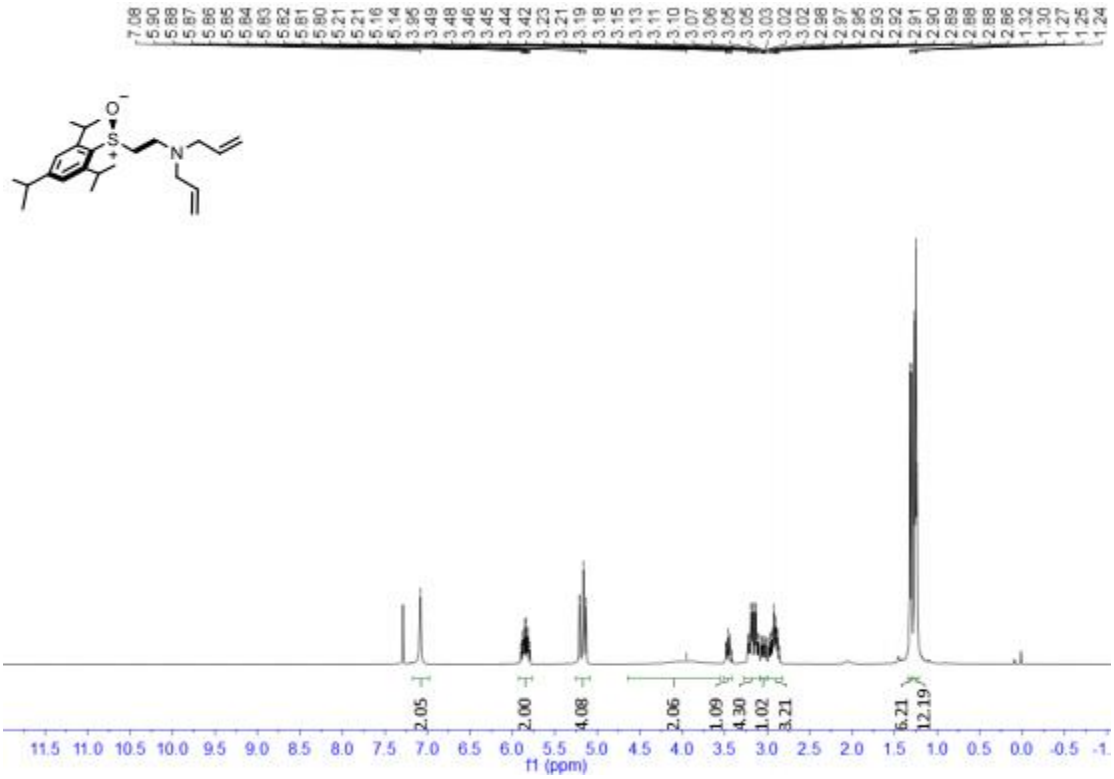
Supplementary Figure 303 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-methyl-N-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-en- 1-amin **(81)**



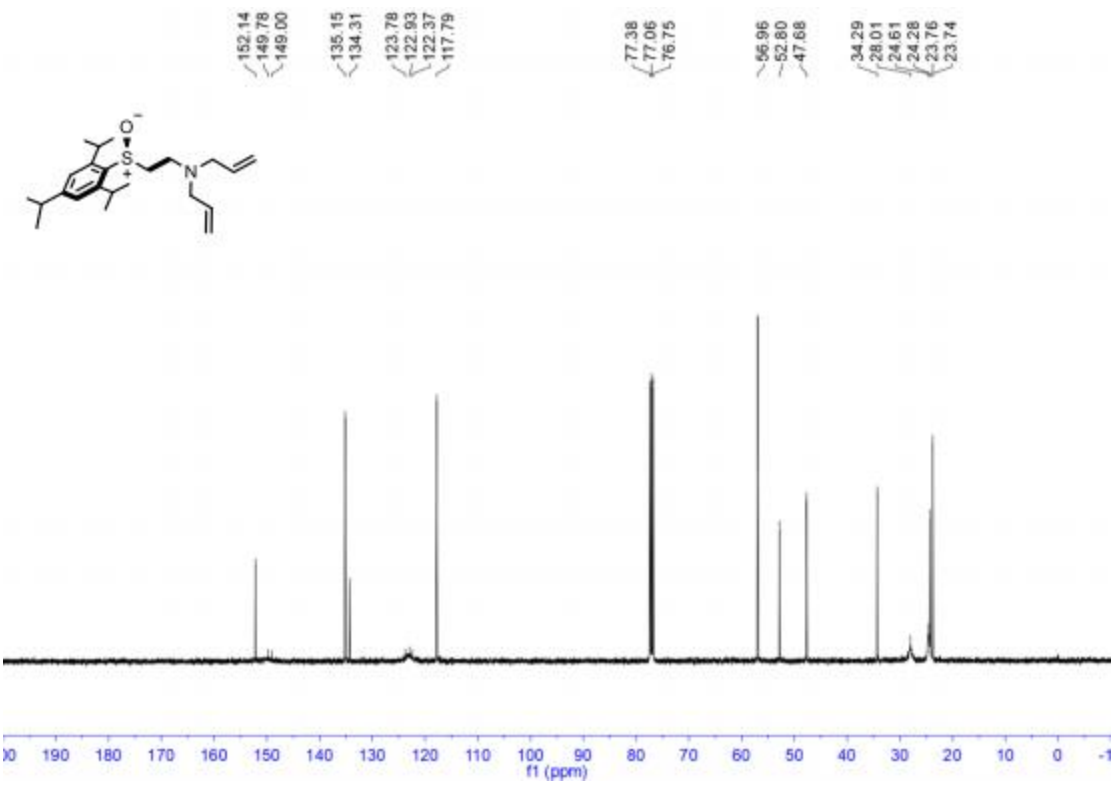
Supplementary Figure 304 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-methyl-N-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-en- 1-amin **(81)**



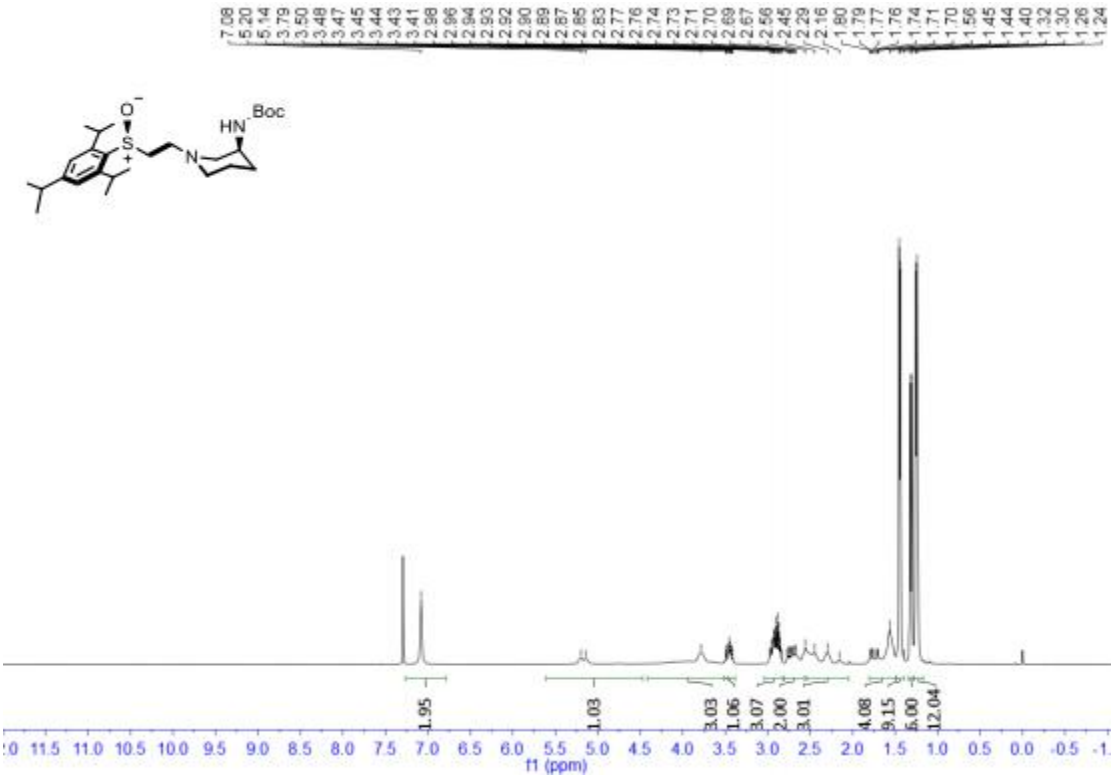
Supplementary Figure 305 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-allyl-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-en- 1-amine **(82)**



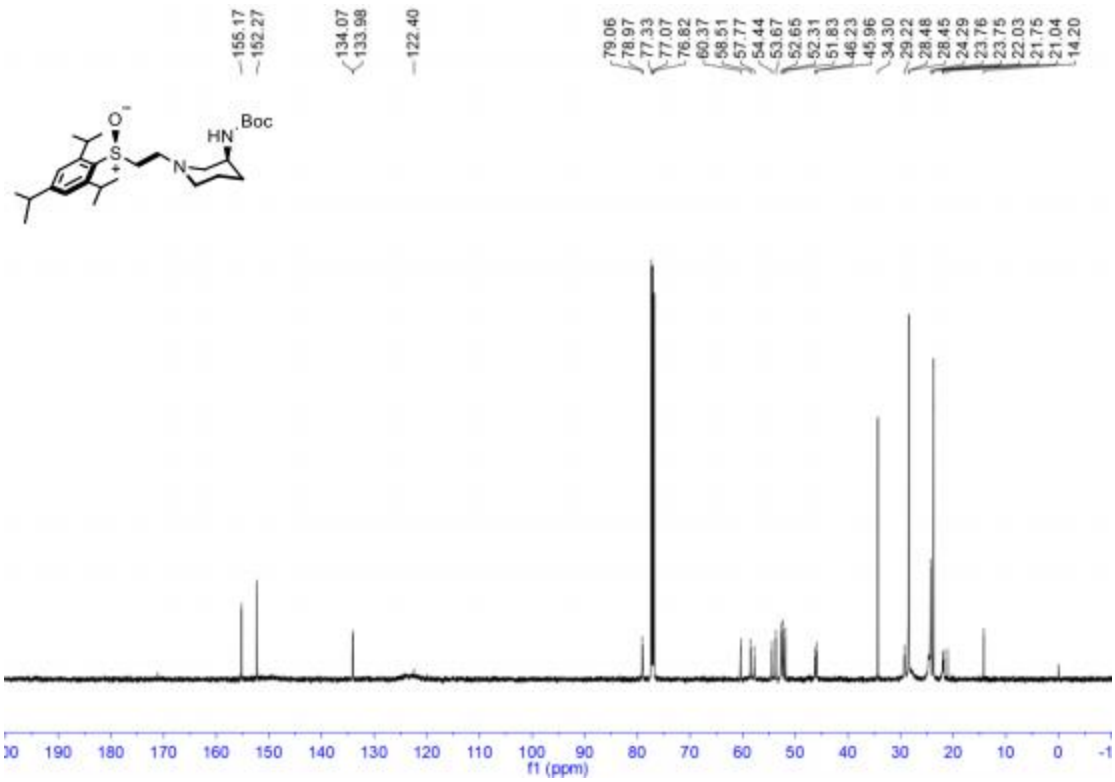
Supplementary Figure 306 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-allyl-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)prop-2-en- 1-amine **(82)**



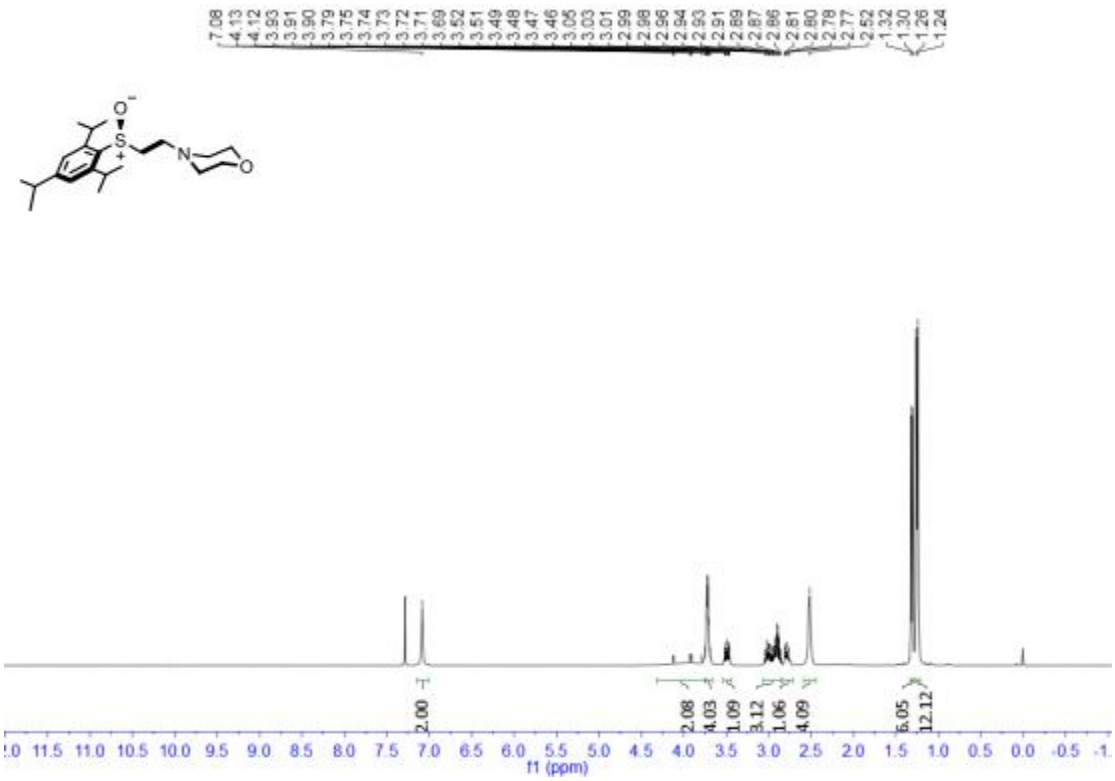
Supplementary Figure 307 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *tert*-butyl((*S*)- 1-(2-((*S*)-(2,4,6-triisopropylphenyl)sulfinyl)ethyl)piperidin-3 yl)carbamate **(83)**



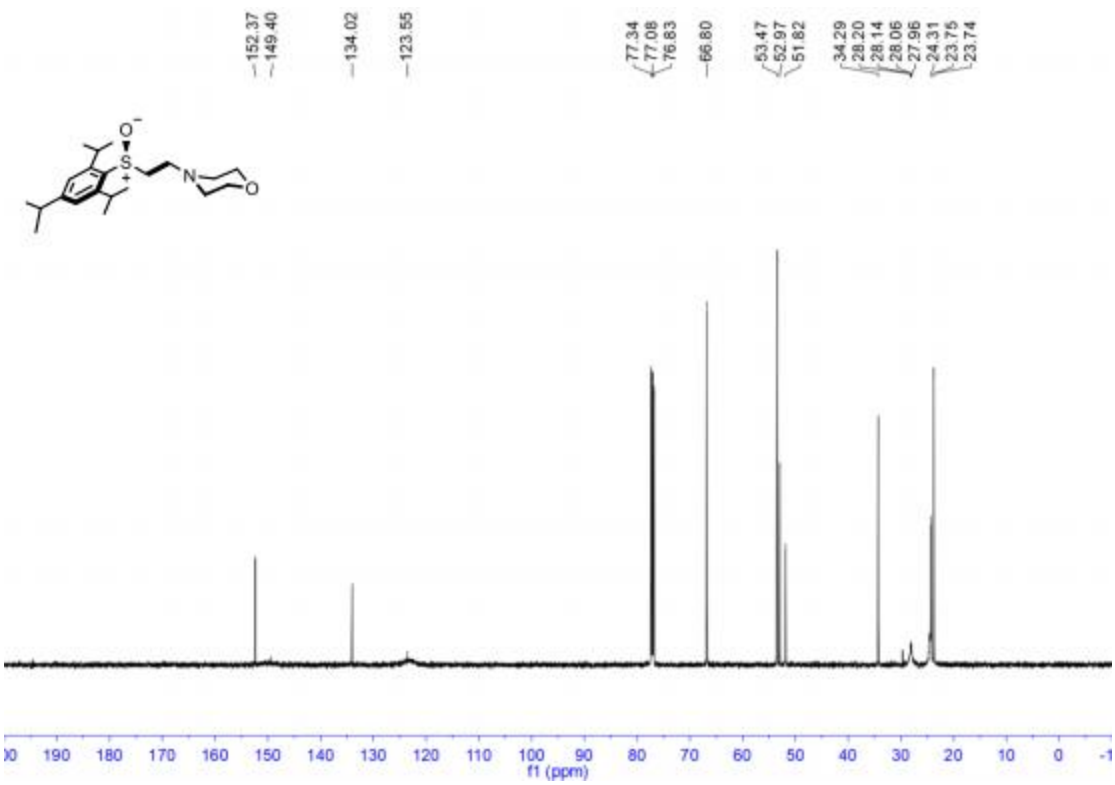
Supplementary Figure 308 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of *tert*-butyl((*S*)- 1-(2-((*S*)-(2,4,6-triisopropylphenyl)sulfinyl)ethyl)piperidin-3 yl)carbamate **(83)**



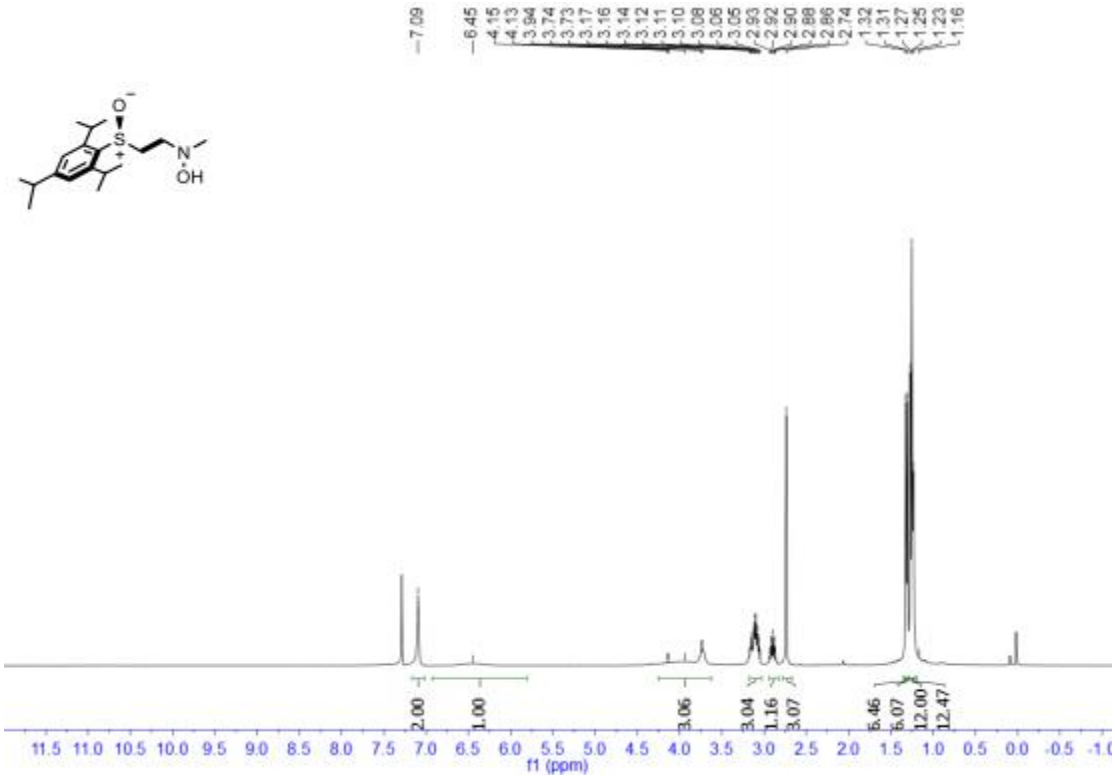
Supplementary Figure 309 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-4-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)morpholine **(84)**



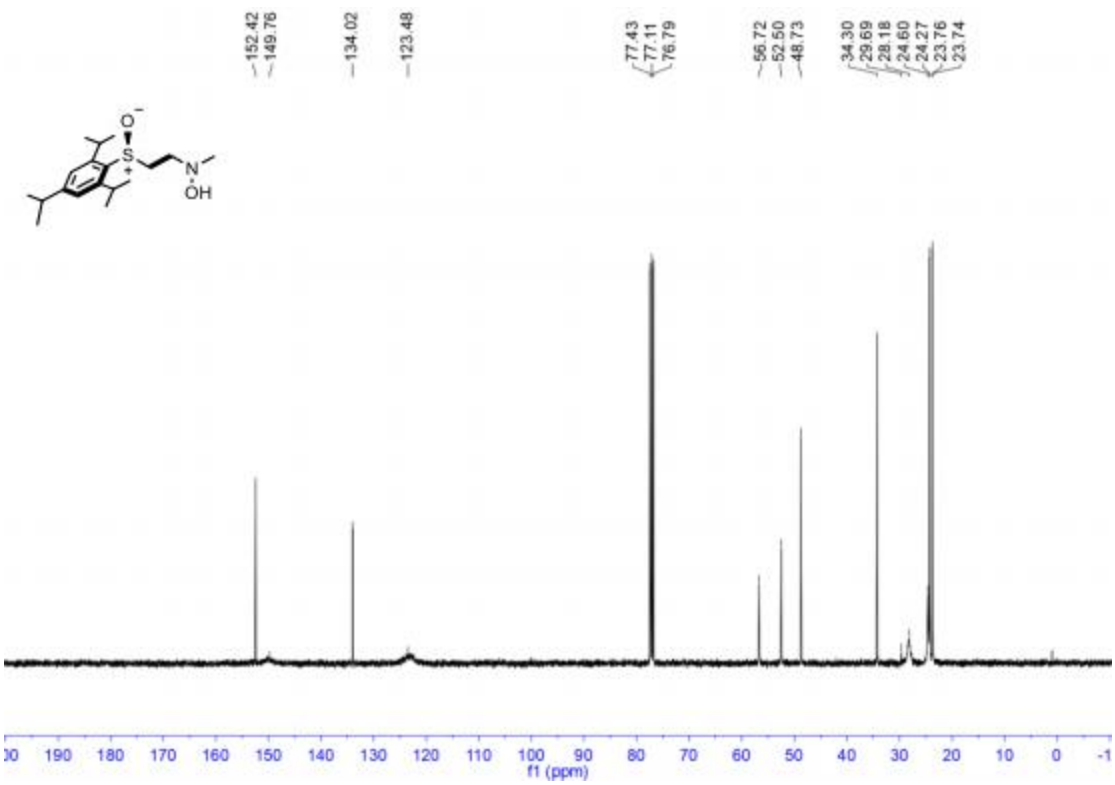
Supplementary Figure 310 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-4-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)morpholine **(84)**



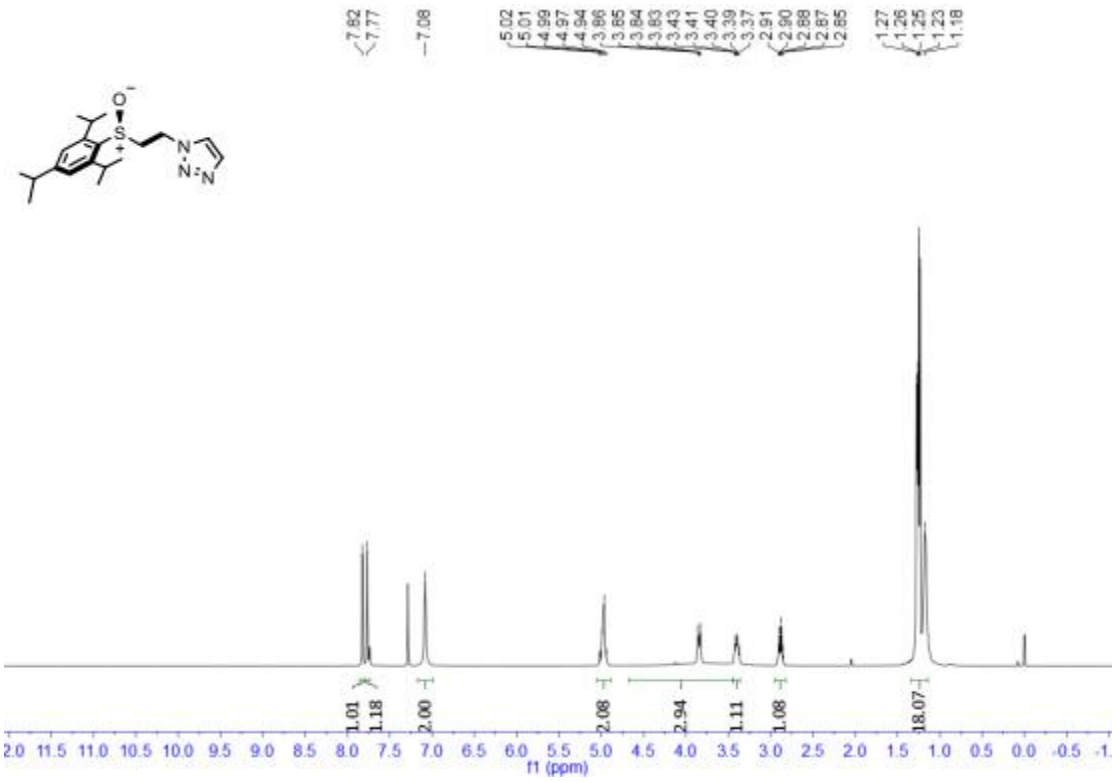
Supplementary Figure 311 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-methyl-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)hydroxylamine **(85)**



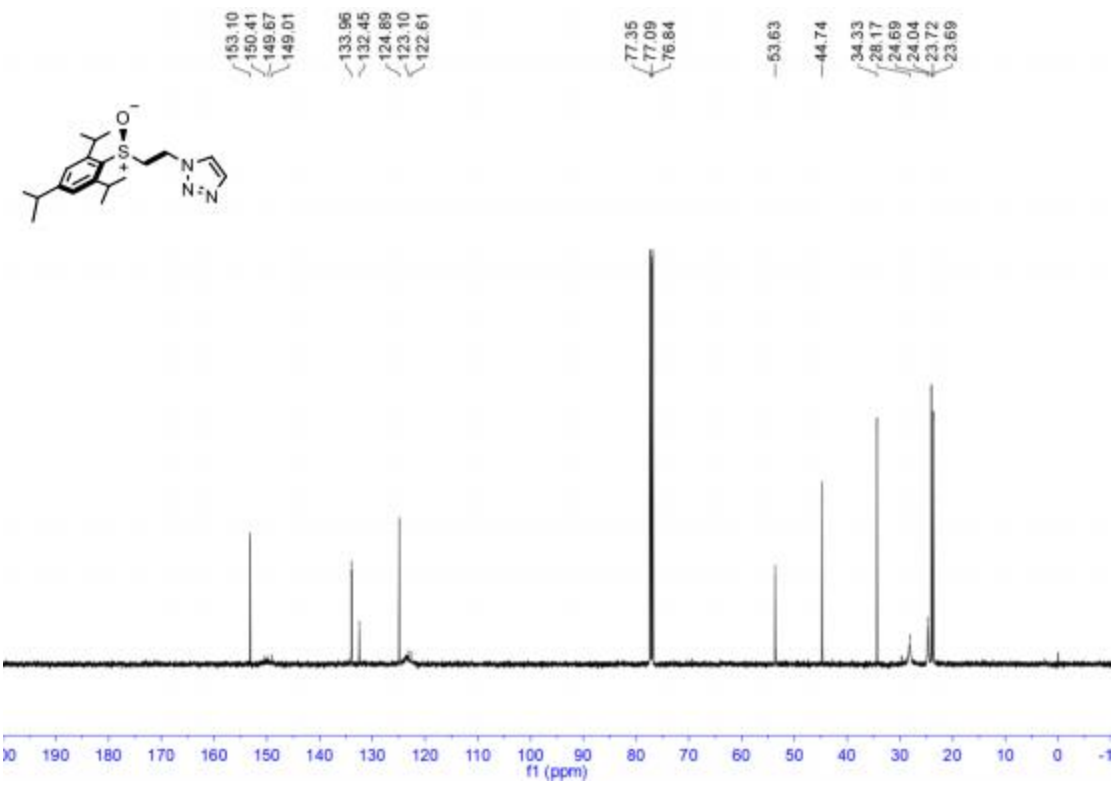
Supplementary Figure 312 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-*N*-methyl-*N*-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)hydroxylamine **(85)**



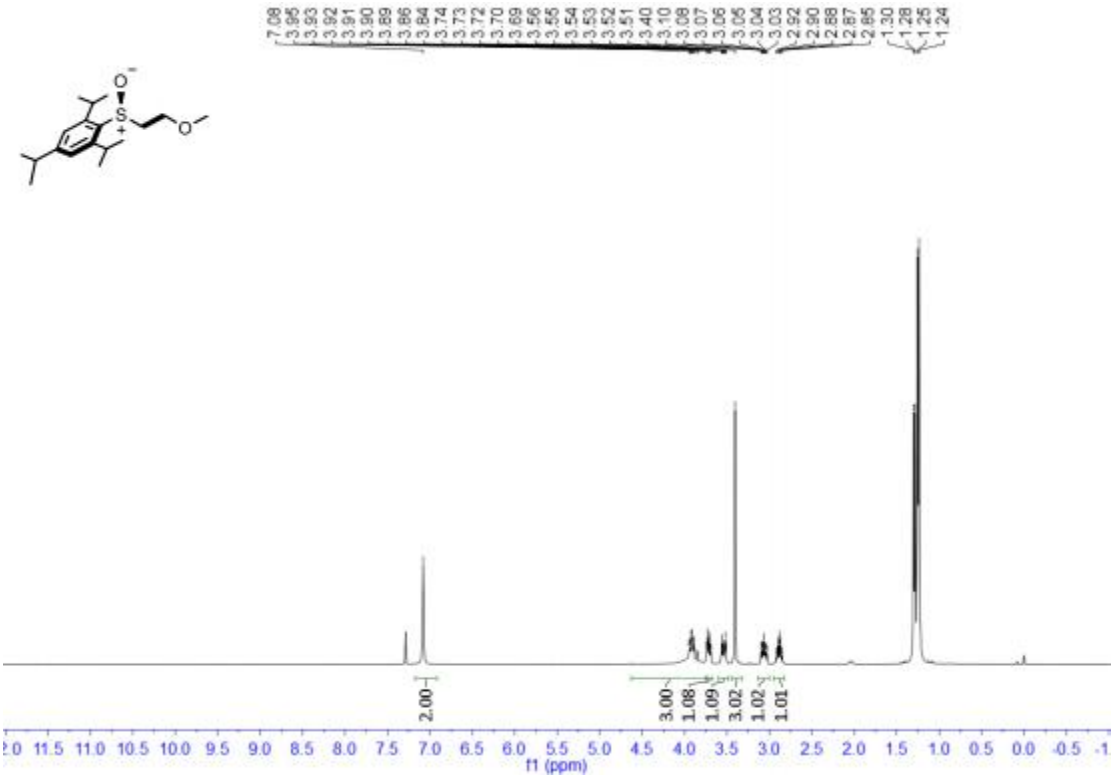
Supplementary Figure 313 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of (*S*)- 1-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)- 1*H*- 1,2,3-triazole **(86)**



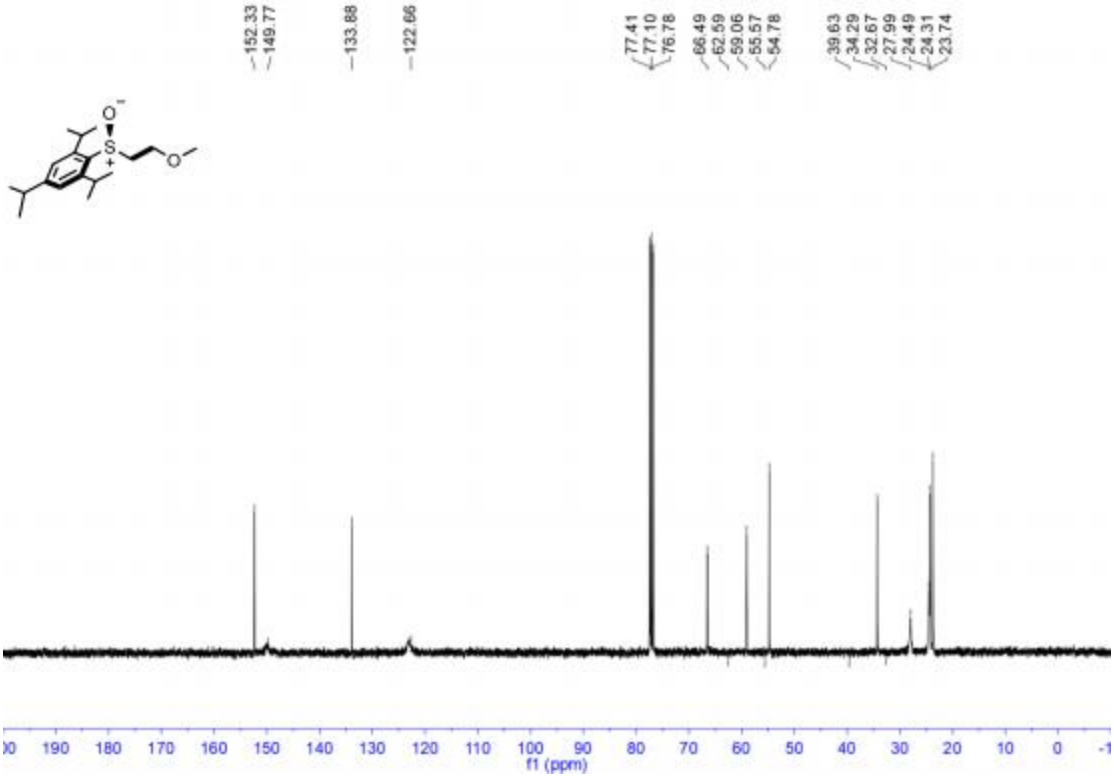
Supplementary Figure 314 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of (*S*)- 1-(2-((2,4,6-triisopropylphenyl)sulfinyl)ethyl)- 1*H*- 1,2,3-triazole **(86)**



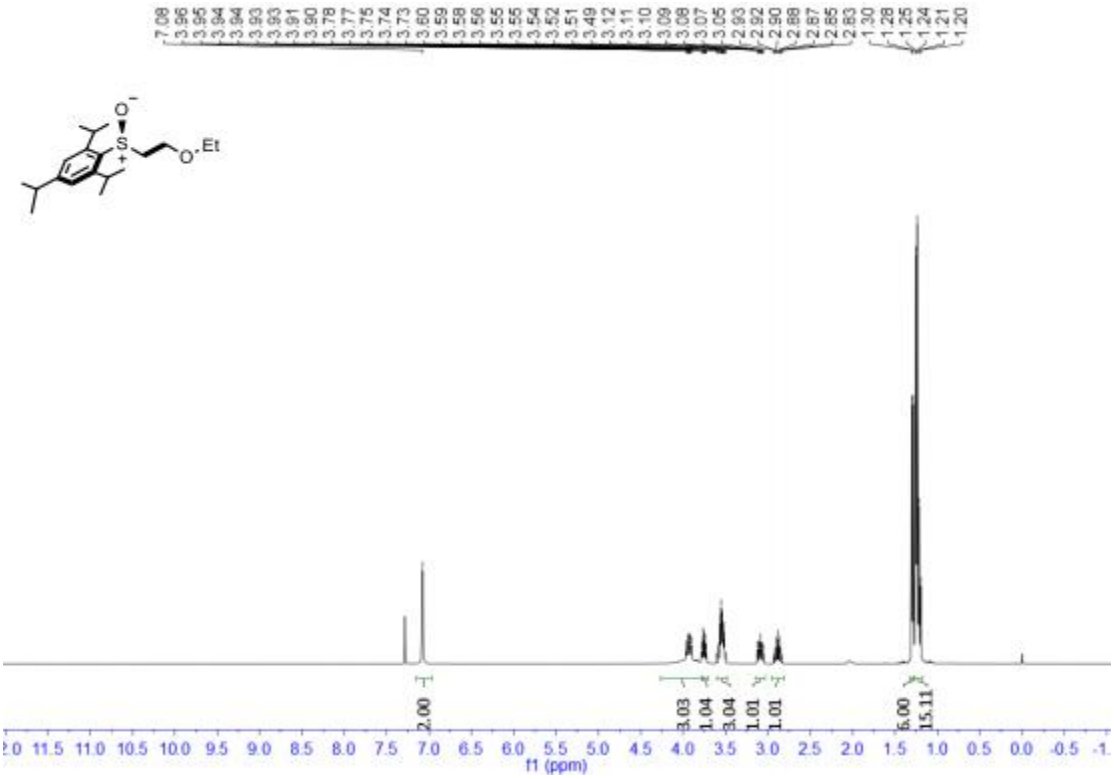
Supplementary Figure 315 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)- 1,3,5-Triisopropyl-2-((2-methoxyethyl)sulfinyl)benzene **(87)**



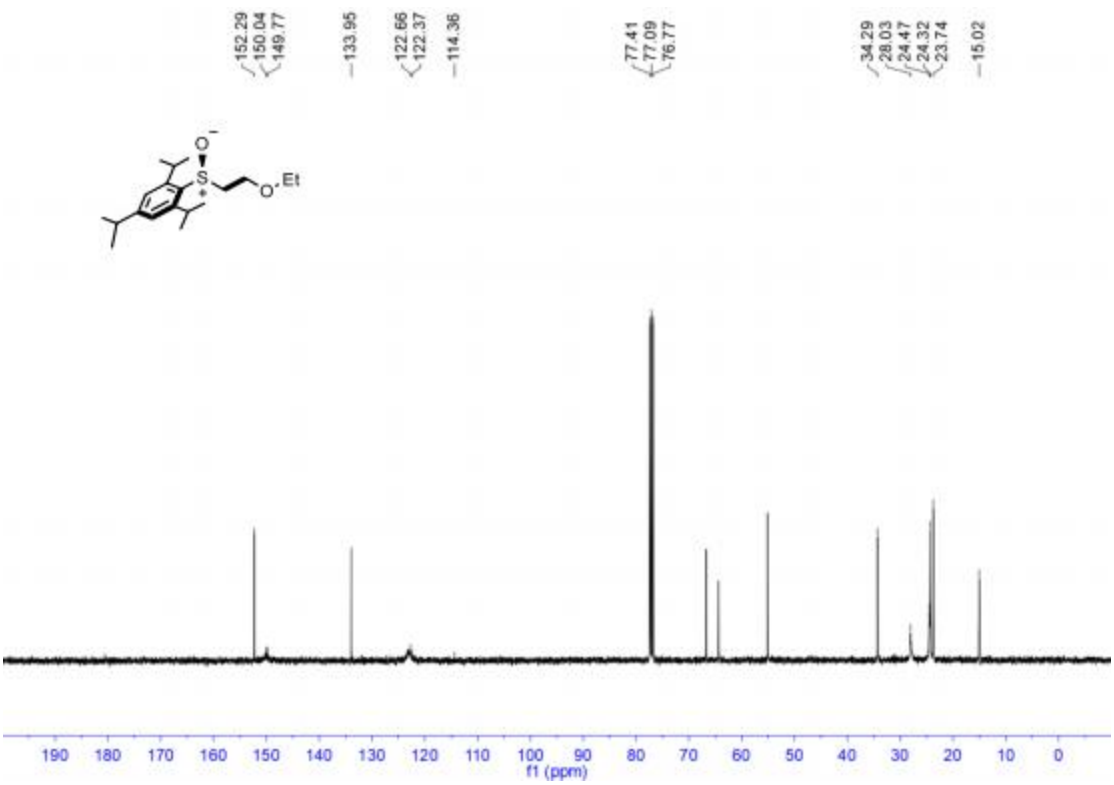
Supplementary Figure 316 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)- 1,3,5-Triisopropyl-2-((2-methoxyethyl)sulfinyl)benzene **(87)**



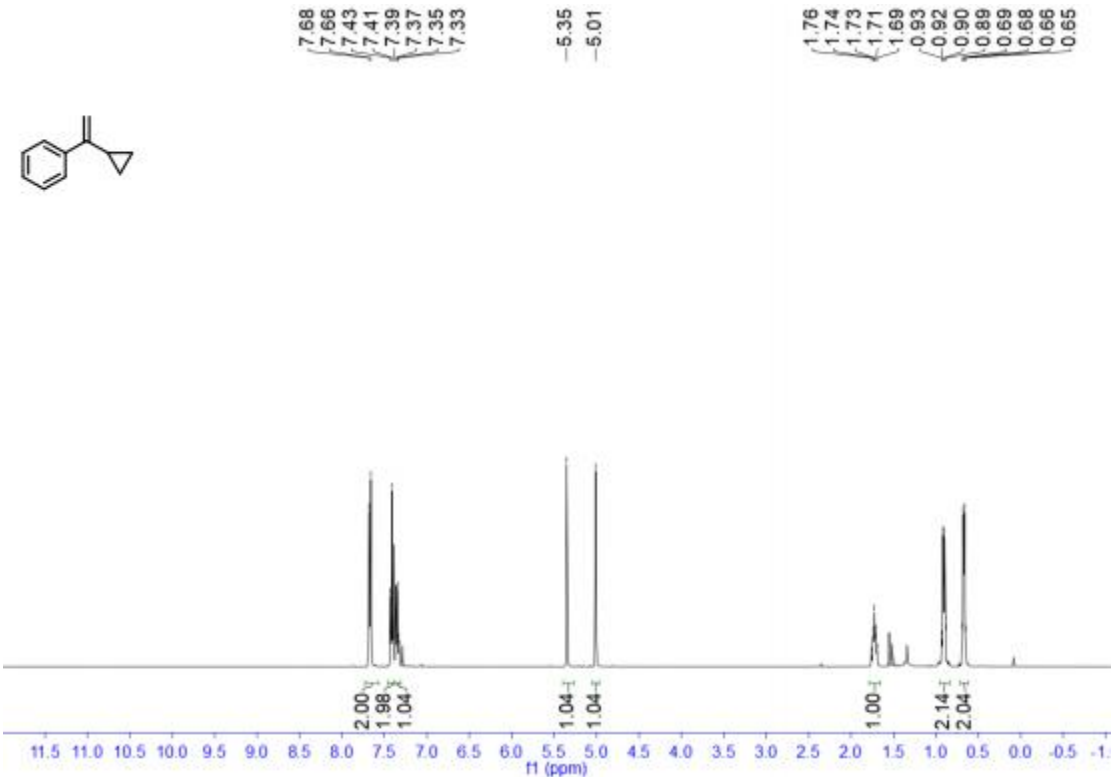
Supplementary Figure 317 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*S*)-2-((2-ethoxyethyl)sulfinyl)- 1,3,5-triisopropylbenzene **(88)**



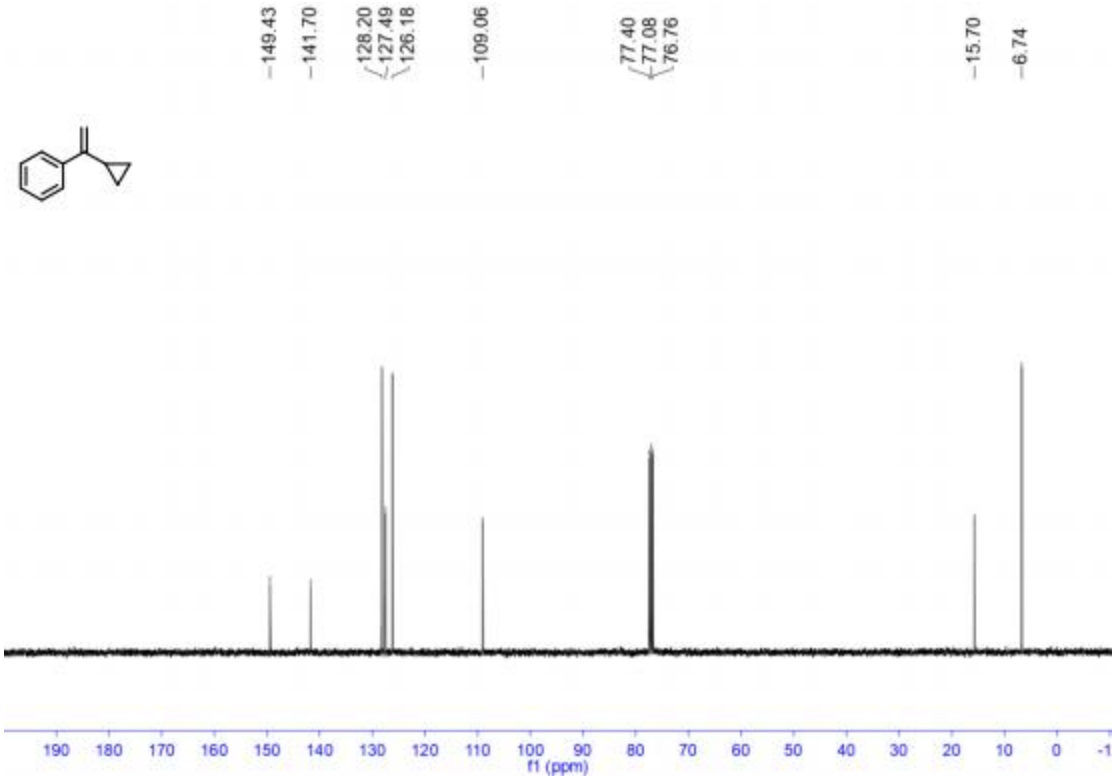
Supplementary Figure 318 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*S*)-2-((2-ethoxyethyl)sulfinyl)- 1,3,5-triisopropylbenzene **(88)**



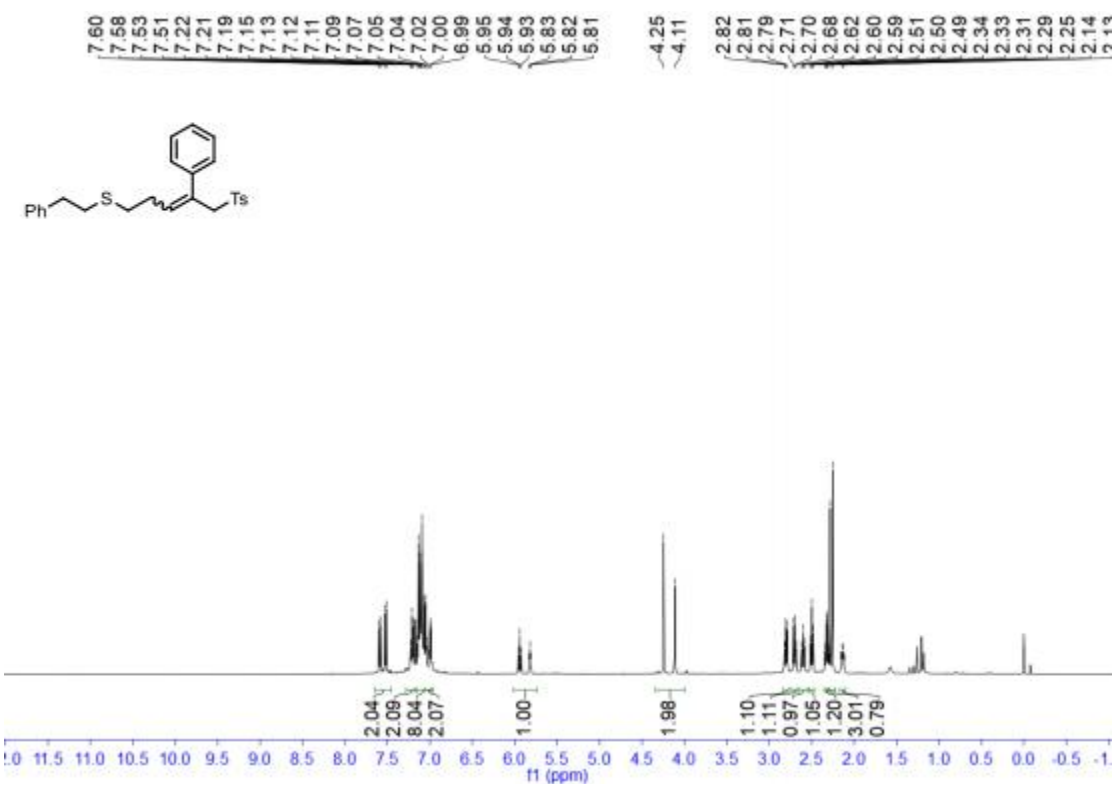
Supplementary Figure 319 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (1-cyclopropylvinyl)benzene **(95)**



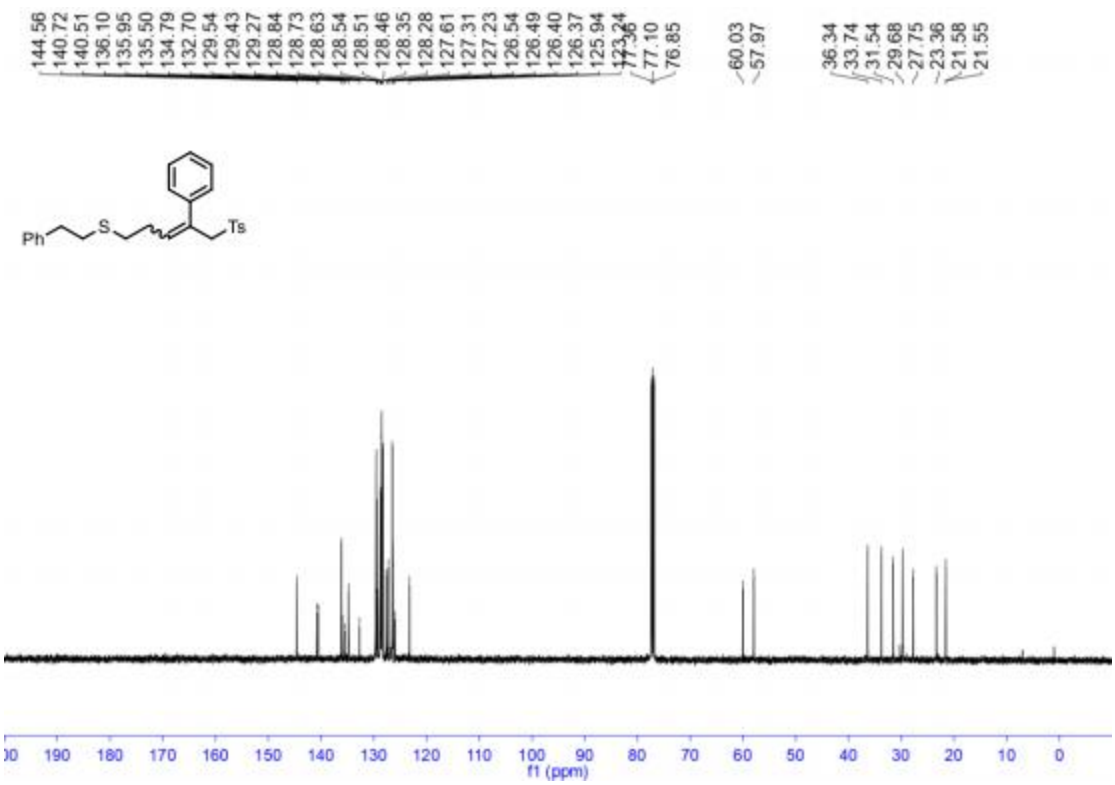
Supplementary Figure 320 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (1-cyclopropylvinyl)benzene **(95)**



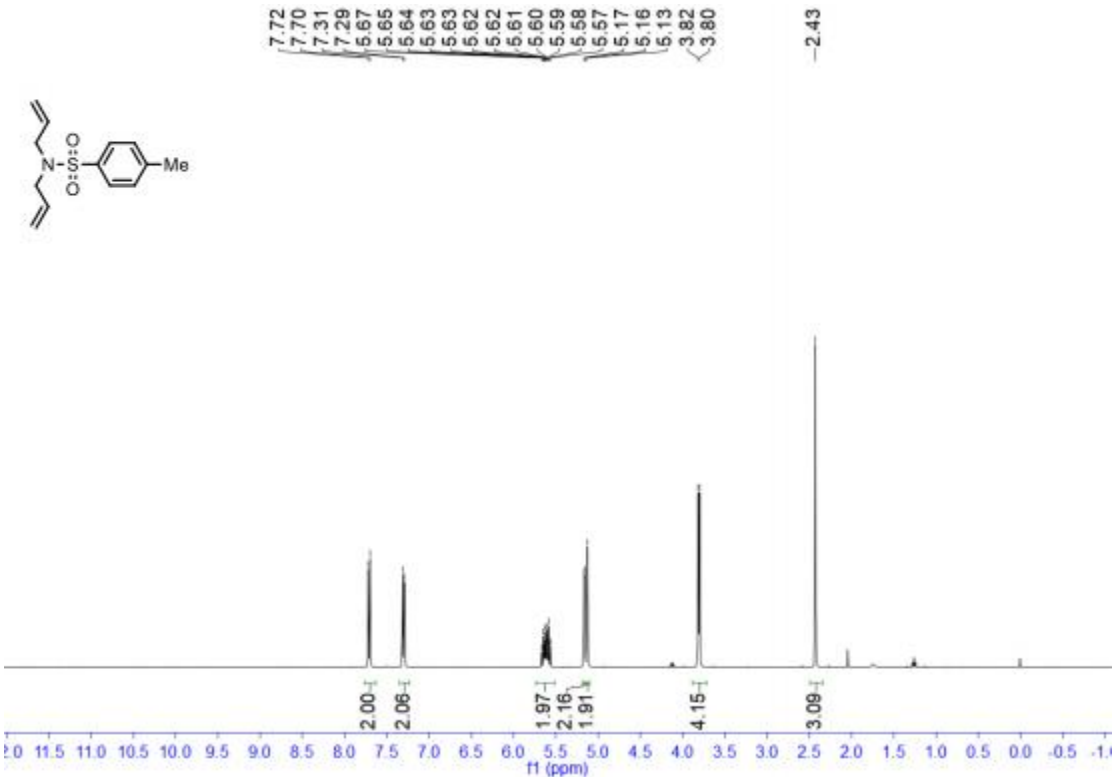
Supplementary Figure 321 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of phenethyl(4-phenyl-5-tosylpent-3-en- 1-yl)sulfane **(96)**



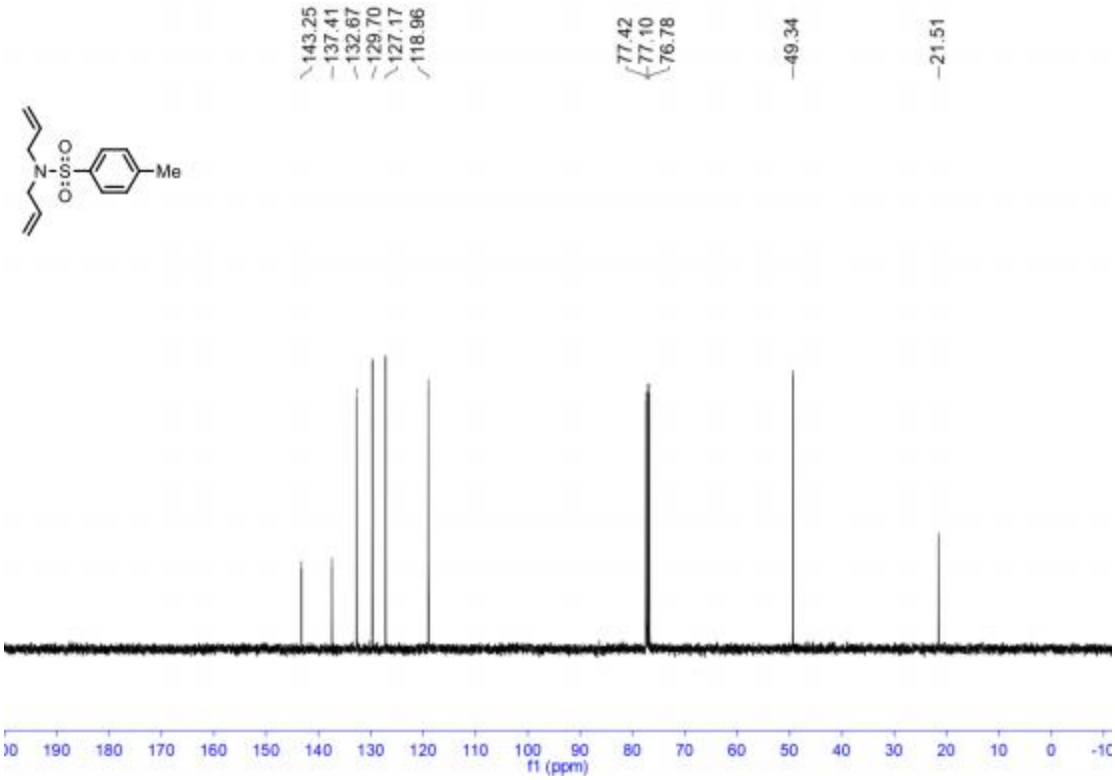
Supplementary Figure 322 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of phenethyl(4-phenyl-5-tosylpent-3-en- 1-yl)sulfane **(96)**



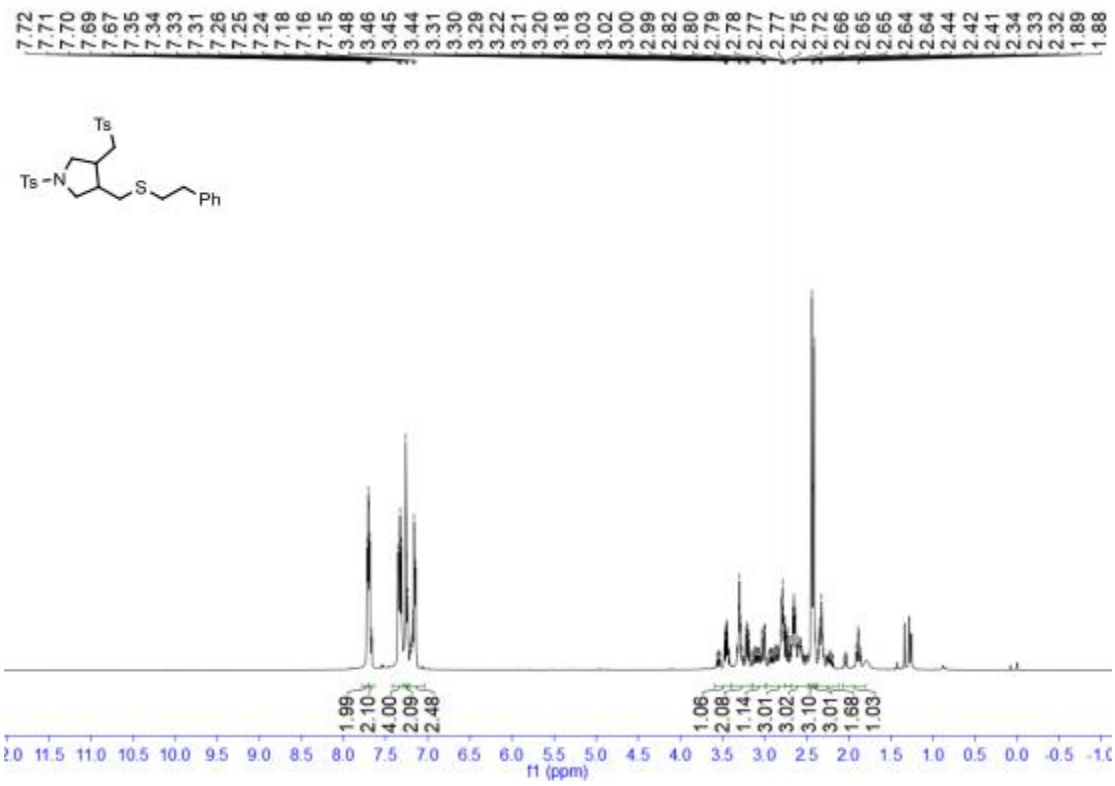
Supplementary Figure 323 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of *N,N*-diallyl-4-methylbenzenesulfonamide **(97)**



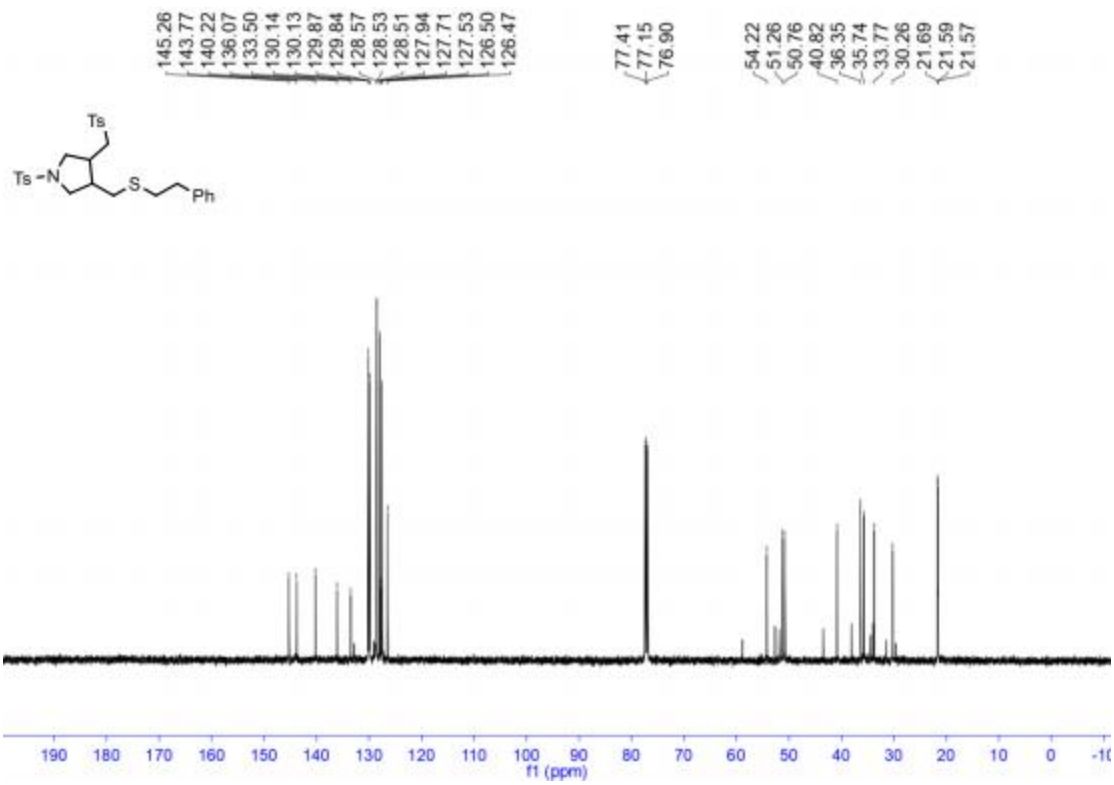
Supplementary Figure 324 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of *N,N*-diallyl-4-methylbenzenesulfonamide **(97)**



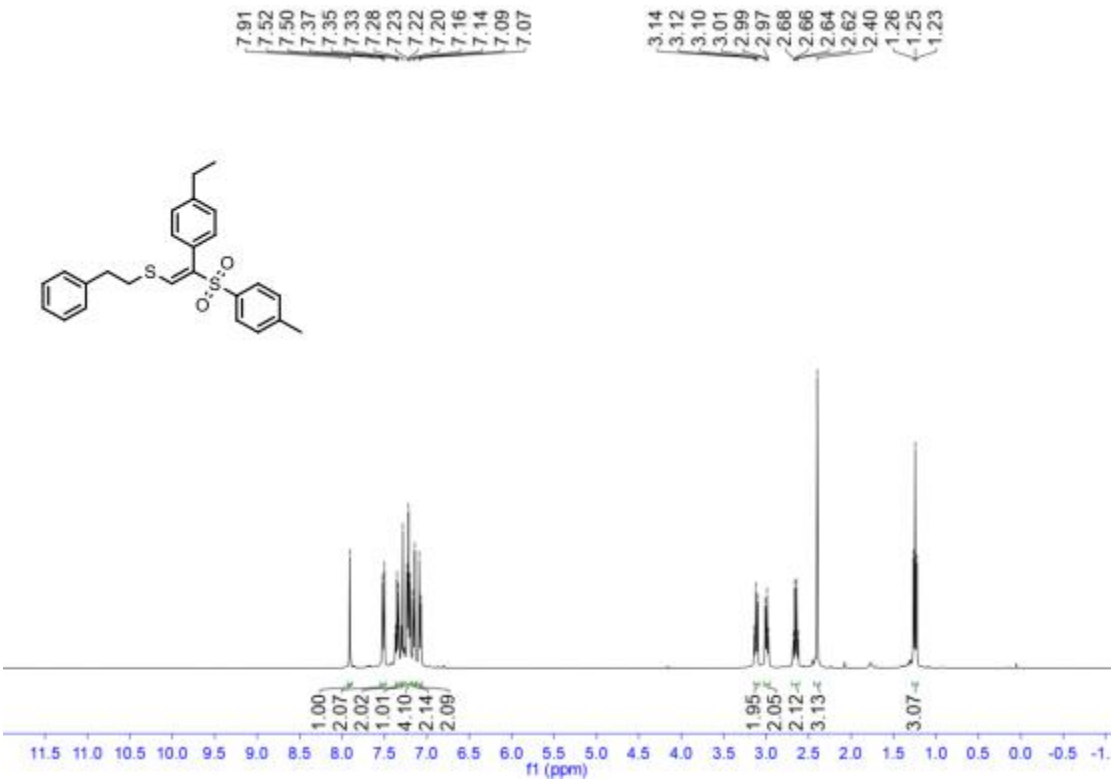
Supplementary Figure 325 | ^{1}H NMR (500 MHz, 298K, Chloroform-*d*) of 3-((phenethylthio)methyl)- 1-tosyl-4-(tosylmethyl)pyrrolidine **(98)**



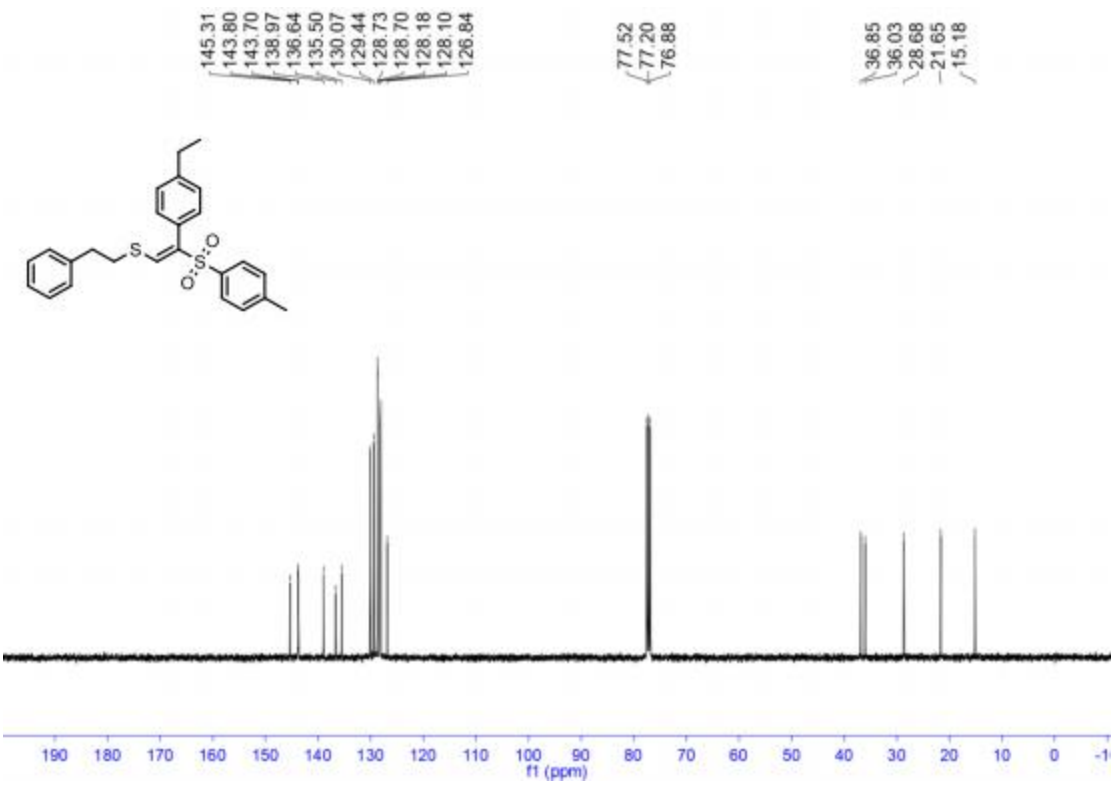
Supplementary Figure 326 | ^{13}C NMR (126 MHz, 298K, Chloroform-*d*) of 3-((phenethylthio)methyl)- 1-tosyl-4-(tosylmethyl)pyrrolidine **(98)**



Supplementary Figure 327 | ^{1}H NMR (400 MHz, 298K, Chloroform-*d*) of (*E*)-(2-(4-ethylphenyl)-2-tosylvinyl)(phenethyl)sulfane (**3b**)

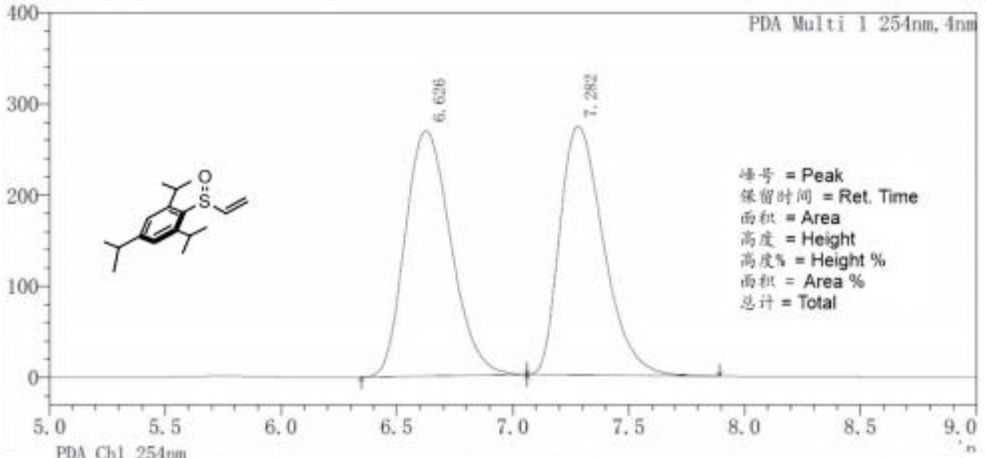


Supplementary Figure 328 | ^{13}C NMR (101 MHz, 298K, Chloroform-*d*) of (*E*)-(2-(4-ethylphenyl)-2-tosylvinyl)(phenethyl)sulfane (**3b**)



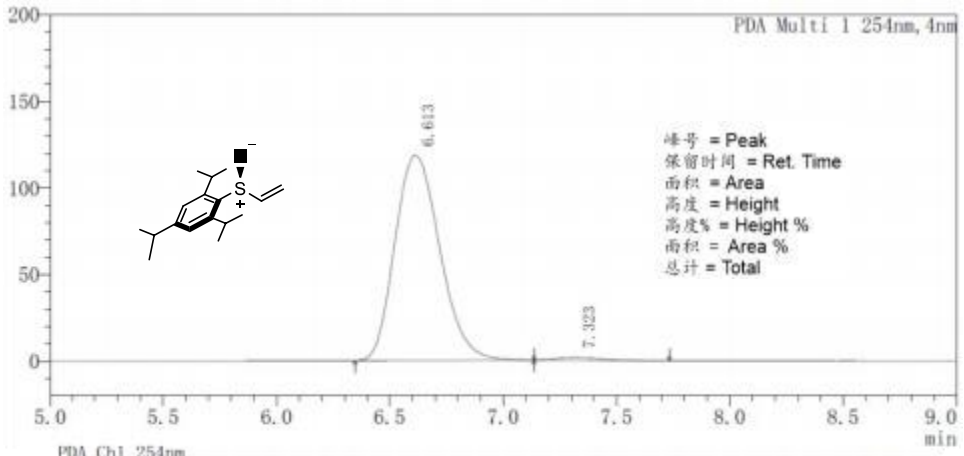
HPLC Data

Supplementary Figure 329 | HPLC of **(75)**



PDA Ch1 254nm

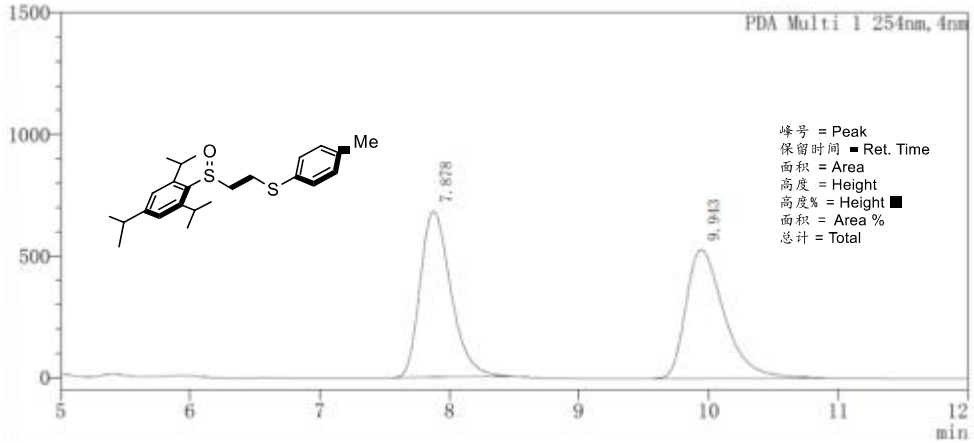
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.626	3699345	269009		50.705	49.626
2	7.282	3596421	273063		49.295	50.374
总计		7295766	542072		100.000	100.000



PDA Ch1 254nm

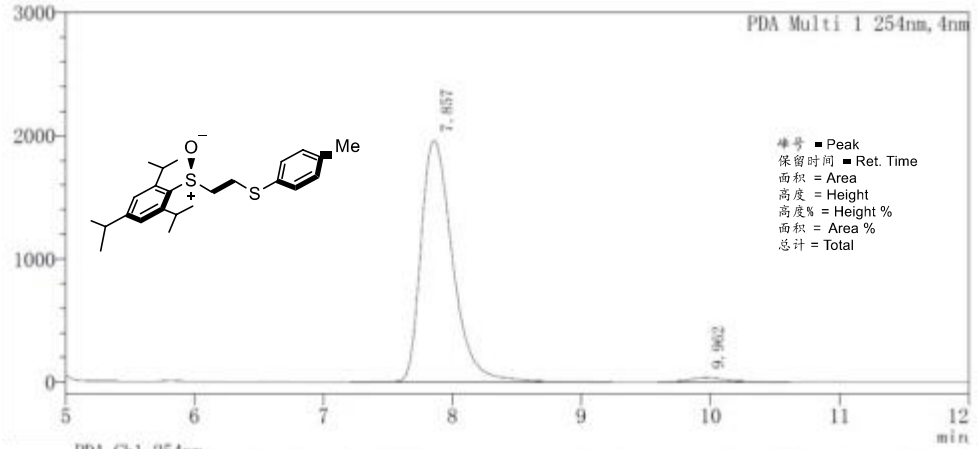
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.613	1633234	118485		98.774	98.620
2	7.323	20267	1659		1.226	1.380
总计		1653501	120143		100.000	100.000

Supplementary Figure 330 | HPLC of **(76)**



PDA Ch1 254nm

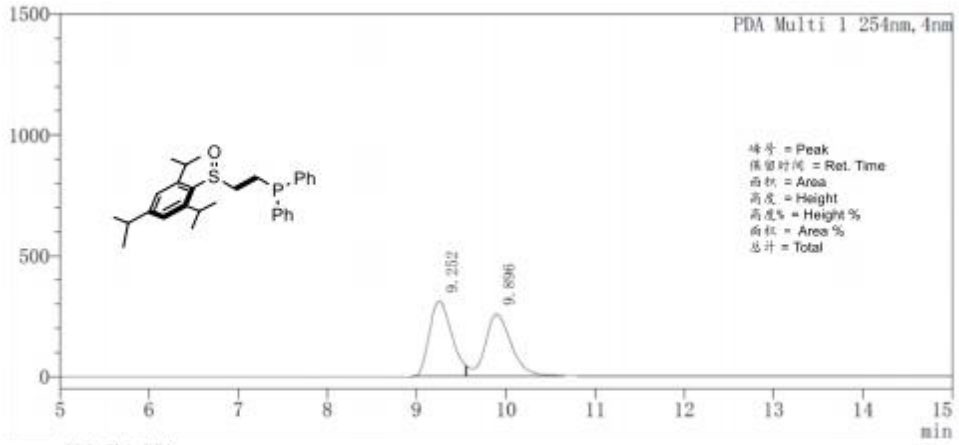
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.878	11225528	681188		56.275	50.824
2	9.943	10861397	529280		43.725	49.176
总计		22086924	1210469		100.000	100.000



PDA Ch1 254nm

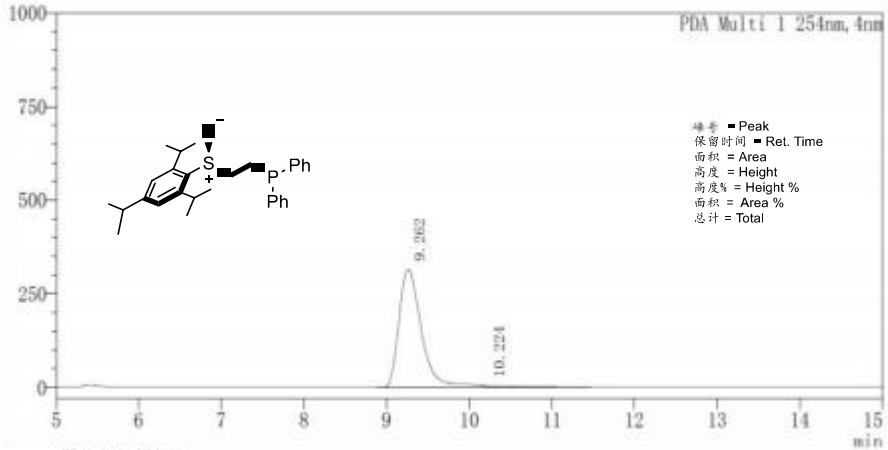
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.857	33433777	1960274		98.252	98.026
2	9.962	673329	34881		1.748	1.974
总计		34107106	1995155		100.000	100.000

Supplementary Figure 331 | HPLC of **(77)**



PDA Ch1 254nm

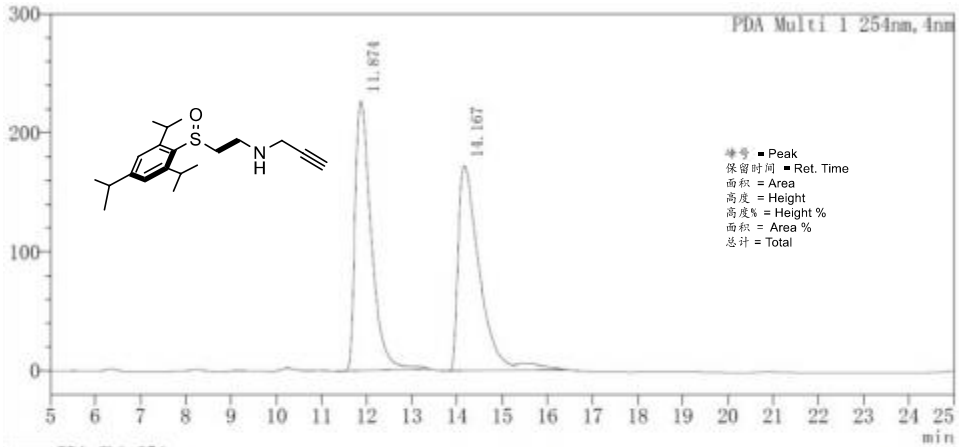
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.252	5356245	308826		54.727	50.754
2	9.896	5197188	255481		45.273	49.246
总计		10553432	564308		100.000	100.000



PDA Ch1 254nm

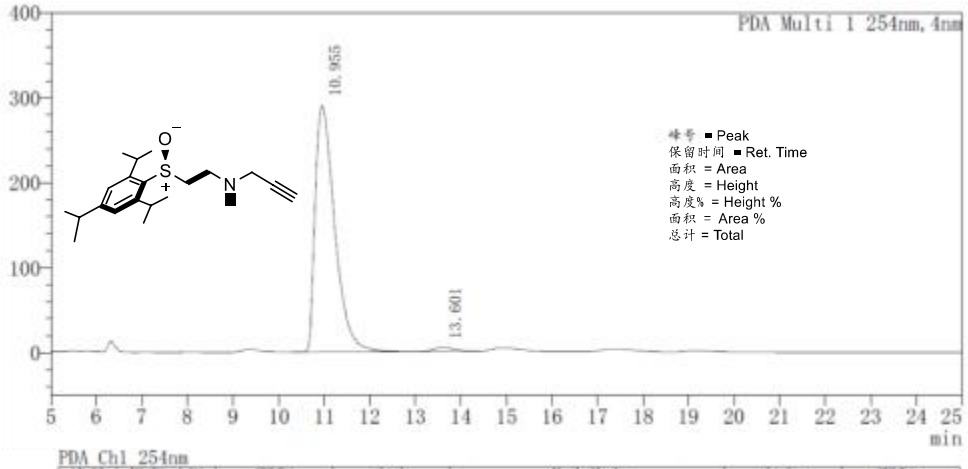
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.262	5920917	314391		98.972	98.134
2	10.224	112606	3267		1.028	1.866
总计		6033523	317658		100.000	100.000

Supplementary Figure 332 | HPLC of **(78)**



PDA Ch1 254nm

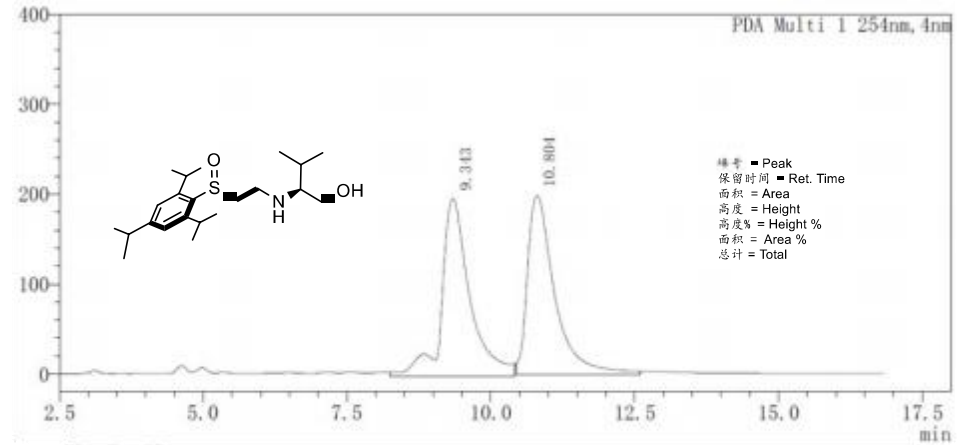
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.874	5645451	226421		56.826	49.739
2	14.167	5704713	172023		43.174	50.261
总计		11350164	398444		100.000	100.000



PDA Ch1 254nm

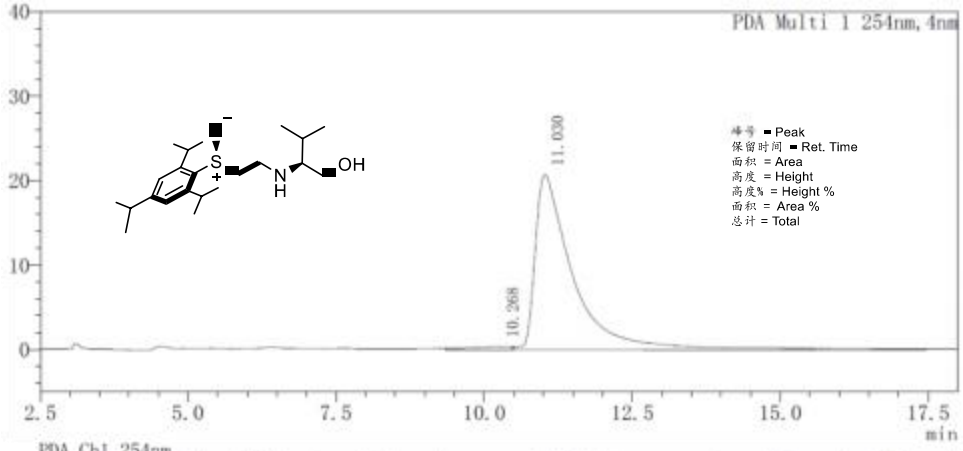
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.955	8662164	290230		98.468	98.379
2	13.601	142738	4514		1.532	1.621
总计		8804902	294744		100.000	100.000

Supplementary Figure 333 | HPLC of **(79)**



PDA Ch1 254nm

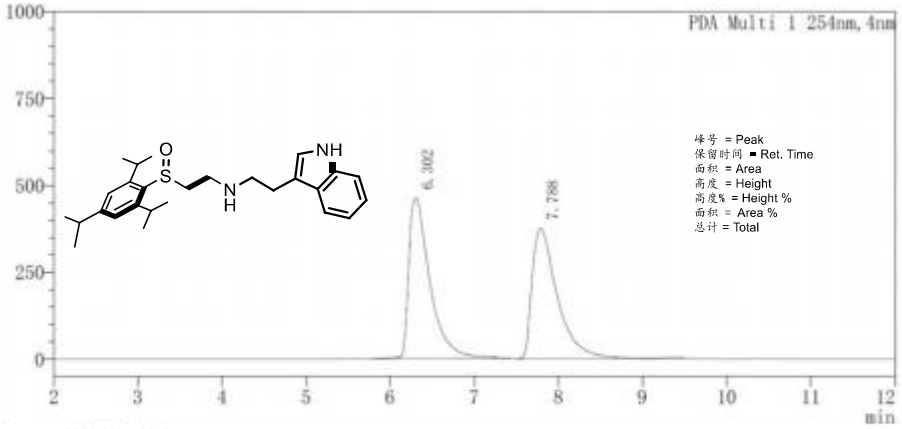
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.343	6821367	198029		49.772	50.589
2	10.804	6662638	199842		50.228	49.411
总计		13484005	397871		100.000	100.000



PDA Ch1 254nm

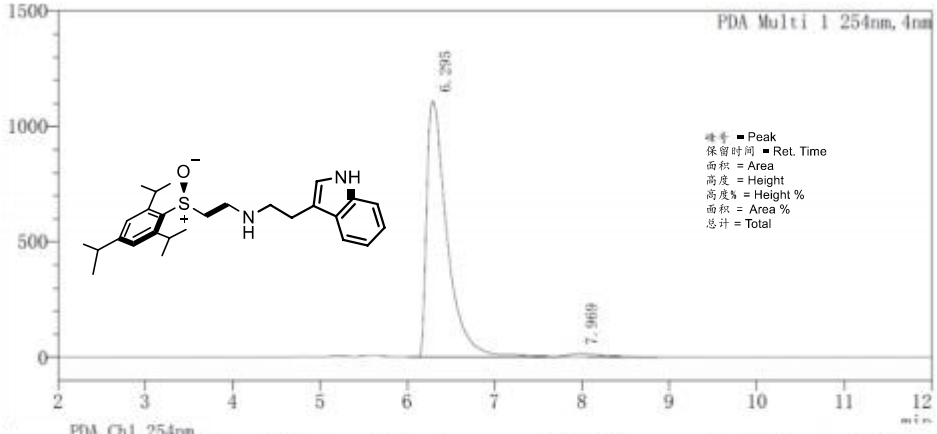
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.268	23940	465		2.193	2.463
2	11.030	947974	20755		97.807	97.537
总计		971914	21220		100.000	100.000

Supplementary Figure 334 | HPLC of **(80)**



PDA Ch1 254nm

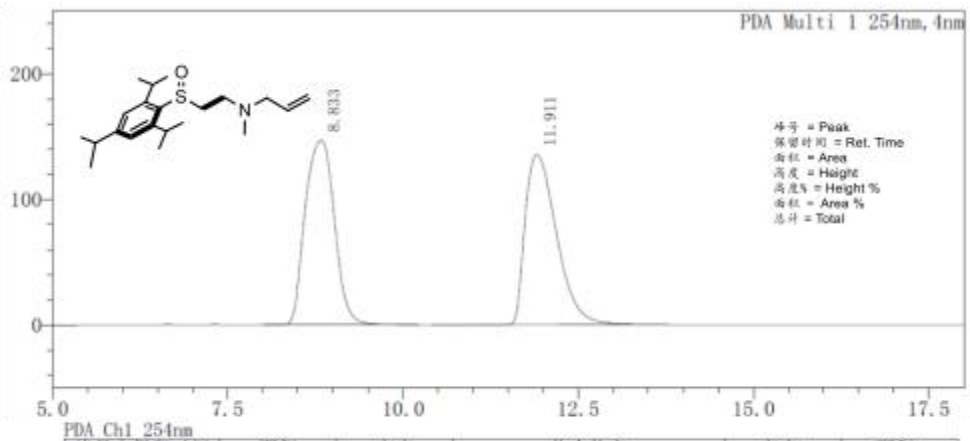
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.302	8131259	463145		55.236	51.111
2	7.788	7777611	375332		44.764	48.889
总计		15908870	838477		100.000	100.000



PDA Ch1 254nm

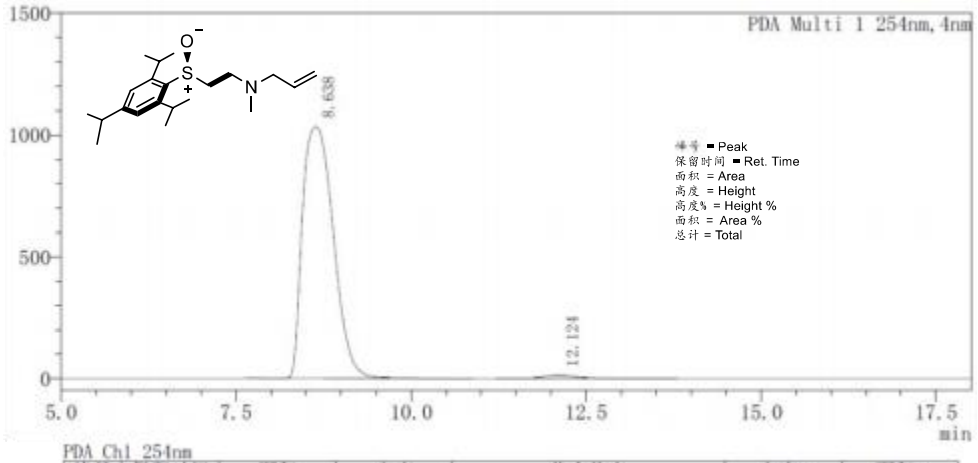
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.295	17879502	1107214		98.771	98.179
2	7.969	331559	13779		1.229	1.821
总计		18211061	1120994		100.000	100.000

Supplementary Figure 335 | HPLC of **(81)**



PDA Ch1 254nm

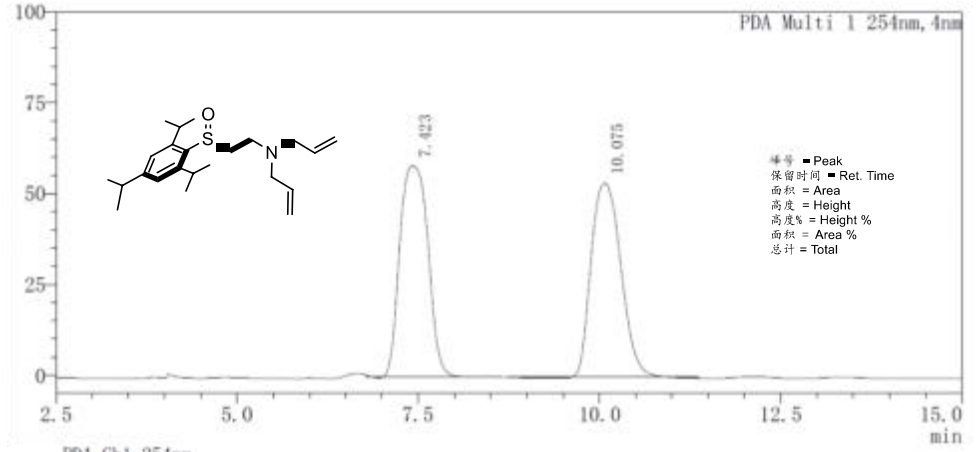
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.833	4271552	146900		52.030	50.337
2	11.911	4214342	135436		47.970	49.663
总计		8485894	282336		100.000	100.000



PDA Ch1 254nm

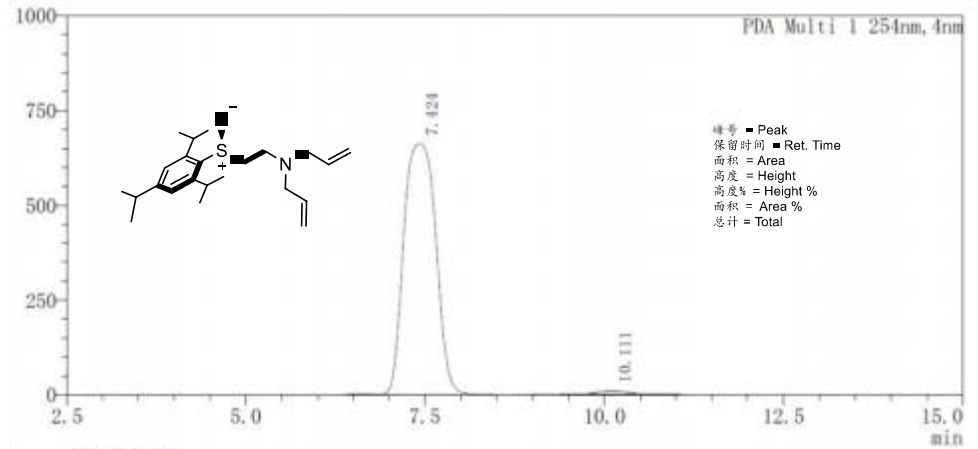
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.638	31807783	1033539		98.586	98.476
2	12.124	492189	14821		1.414	1.524
总计		32299972	1048360		100.000	100.000

Supplementary Figure 336 | HPLC of **(82)**



PDA Ch1 254nm

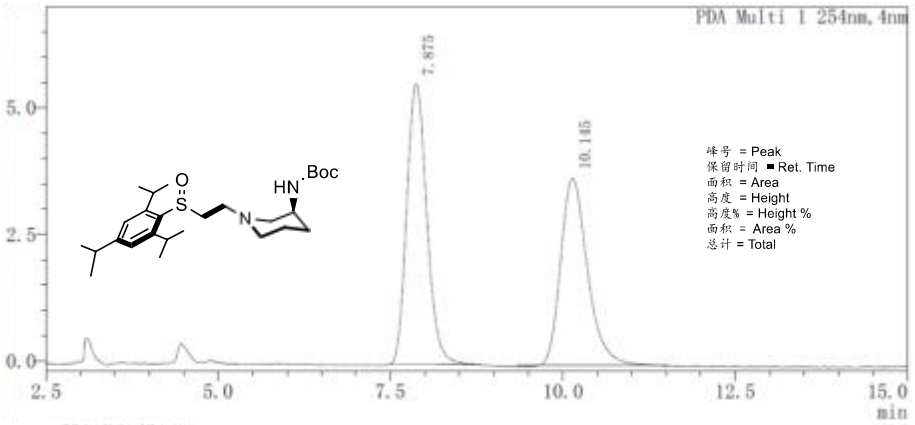
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.423	1584364	58200		52.137	50.963
2	10.075	1524495	53428		47.863	49.037
总计		3108859	111628		100.000	100.000



PDA Ch1 254nm

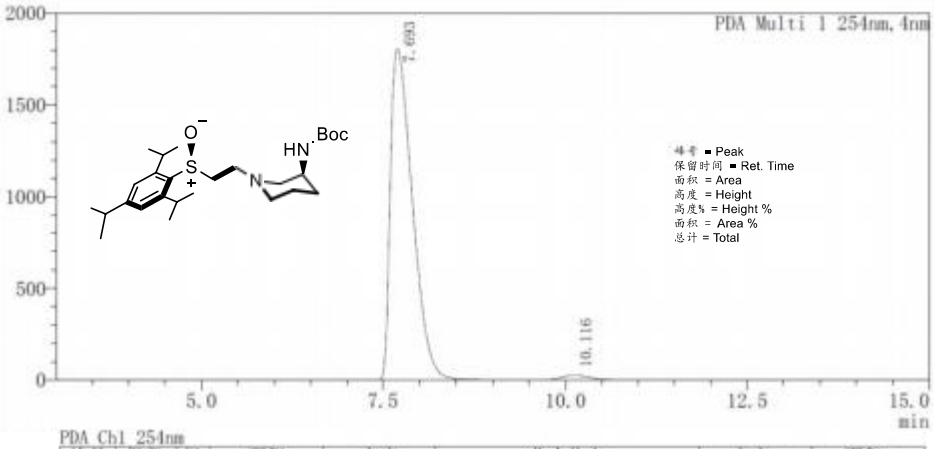
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.424	20591274	660717		98.856	98.548
2	10.111	238267	9738		1.144	1.452
总计		20829540	670455		100.000	100.000

Supplementary Figure 337 | HPLC of **(83)**



PDA Ch1 254nm

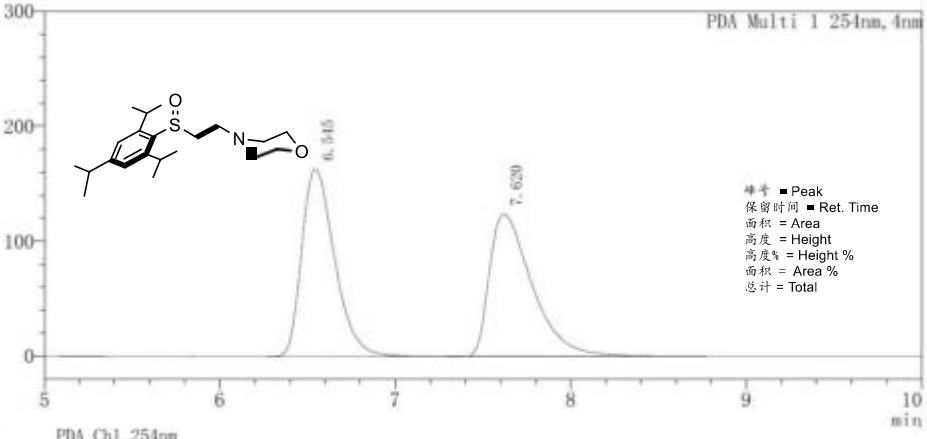
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.875	112354	5550		59.934	52.661
2	10.145	101001	3710		40.066	47.339
总计		213356	9260		100.000	100.000



PDA Ch1 254nm

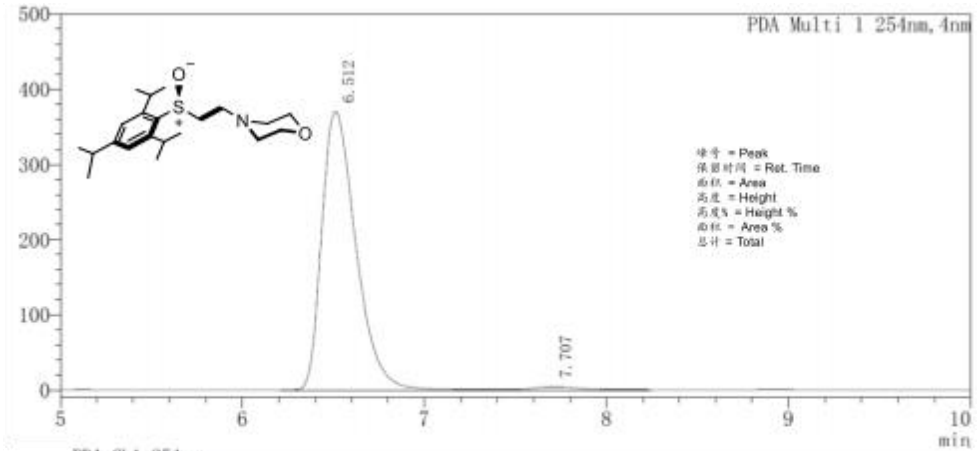
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.693	38354942	1806605		98.506	97.879
2	10.116	831000	27399		1.494	2.121
总计		39185942	1834004		100.000	100.000

Supplementary Figure 338 | HPLC of **(84)**



PDA Ch1 254nm

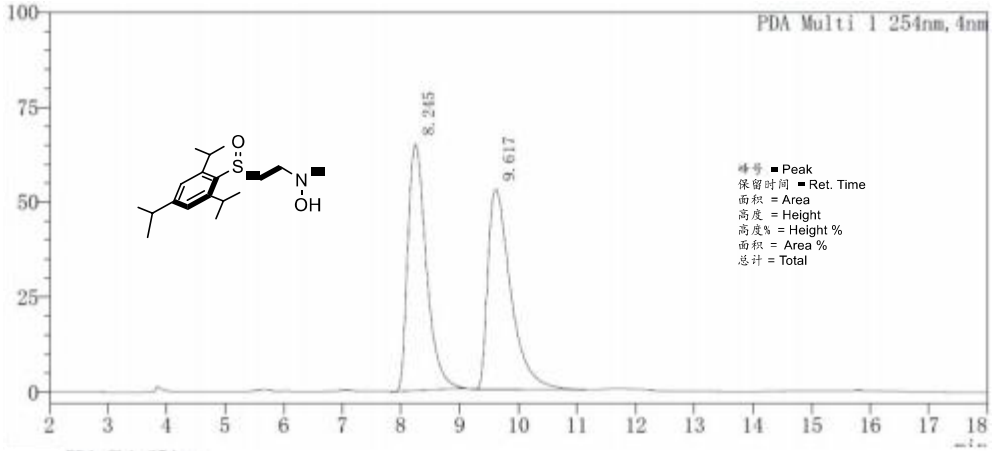
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.545	2111692	163182		56.942	50.457
2	7.620	2073451	123393		43.058	49.543
总计		4185143	286575		100.000	100.000



PDA Ch1 254nm

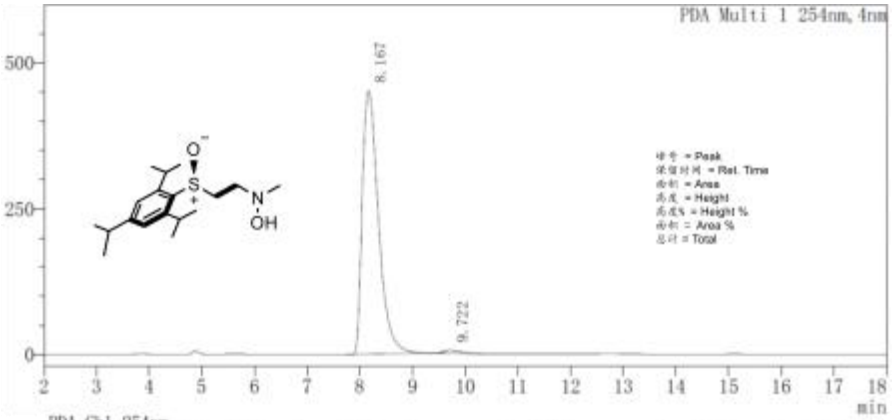
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.512	4836160	370380		98.270	98.851
2	7.707	85154	4306		1.730	1.149
总计		4921314	374686		100.000	100.000

Supplementary Figure 339 | HPLC of **(85)**



PDA Ch1 254nm

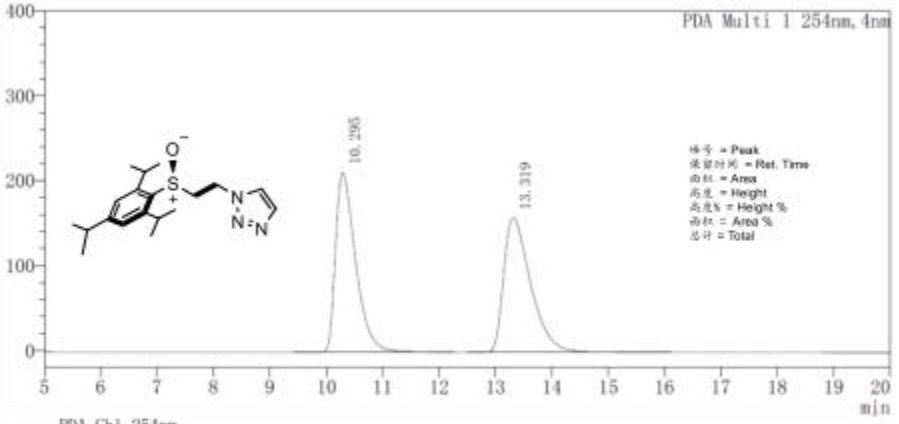
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.245	1427209	64808		55.151	49.869
2	9.617	1434684	52703		44.849	50.131
总计		2861893	117510		100.000	100.000



PDA Ch1 254nm

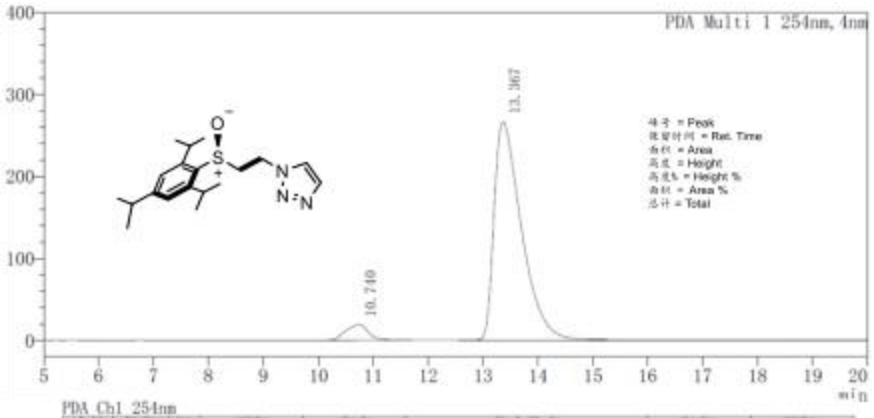
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.167	9679595	451502		98.822	98.640
2	9.722	133454	5384		1.178	1.360
总计		9813049	456887		100.000	100.000

Supplementary Figure 340 | HPLC of **(86)**



PDA Ch1 254nm

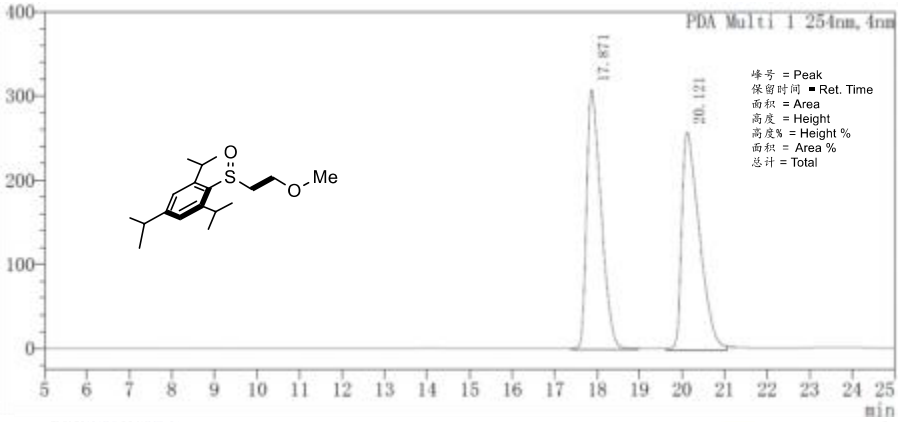
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.295	5282819	211869		57.180	49.987
2	13.319	5285647	158658		42.820	50.013
总计		10568466	370528		100.000	100.000



PDA Ch1 254nm

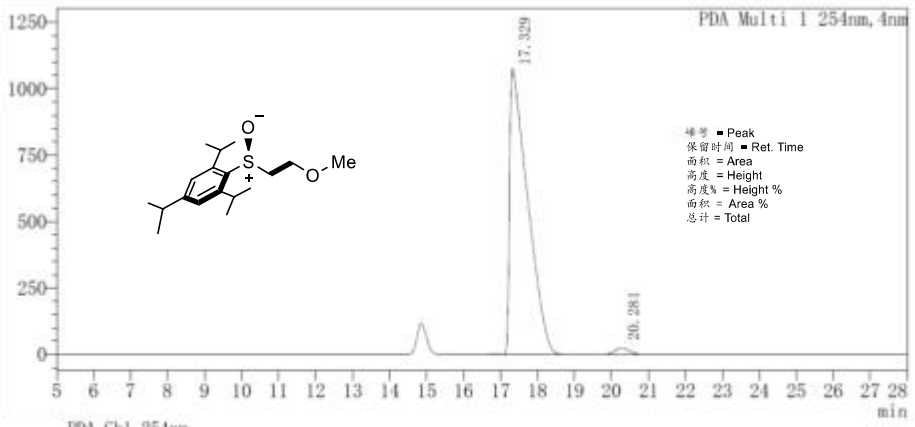
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.740	537289	19296		6.747	5.474
2	13.367	9278758	266705		93.253	94.526
总计		9816047	286001		100.000	100.000

Supplementary Figure 341 | HPLC of **(87)**



PDA Ch1 254nm

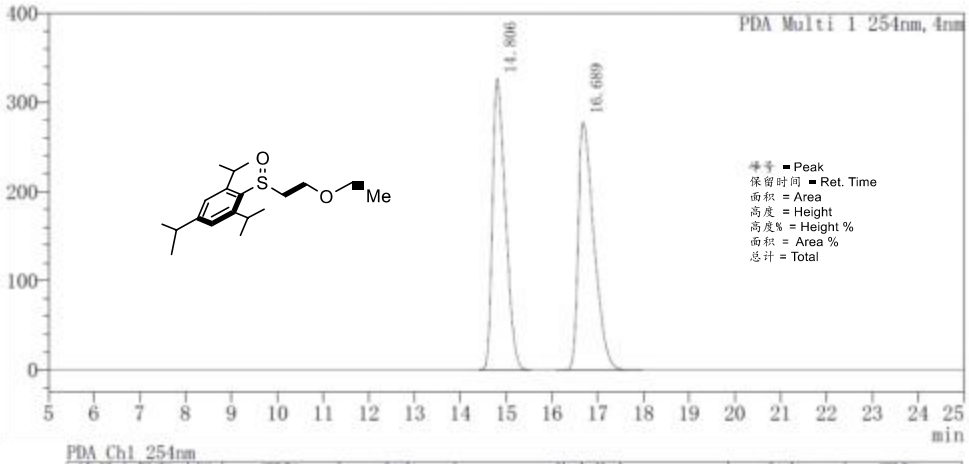
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.871	7329033	308619		54.414	49.608
2	20.121	7444923	258550		45.586	50.392
总计		14773955	567169		100.000	100.000



PDA Ch1 254nm

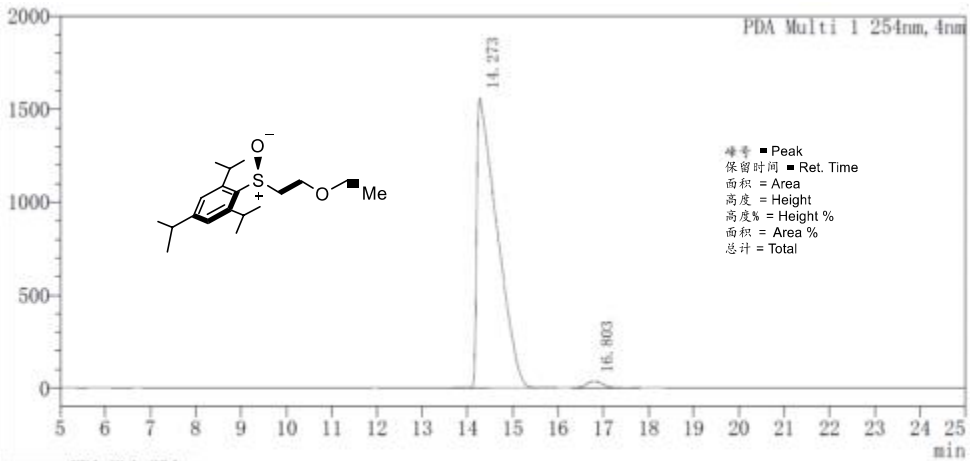
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.329	36566841	1074339		97.784	98.031
2	20.281	734442	24345		2.216	1.969
总计		37301283	1098684		100.000	100.000

Supplementary Figure 342 | HPLC of **(88)**



PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	14.806	6436232	327088		54.082	49.272
2	16.689	6626474	277710		45.918	50.728
总计		13062706	604798		100.000	100.000



PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	14.273	48672823	1558850		97.807	98.283
2	16.803	850407	34954		2.193	1.717
总计		49523230	1593804		100.000	100.000

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