Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Efficient Metal-Free Pathway to Vinyl Thioesters with Calcium Carbide as the Acetylene Source

Konstantin S. Rodygin, and Valentine P. Ananikov*

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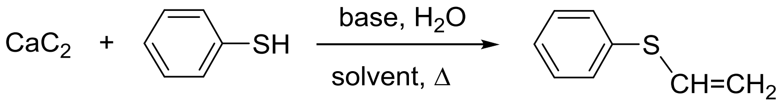
1. Materials and methods

Calcium carbide was purchased from Acros (97+% purity) and preparation for the reaction was performed as shown on Figure S4. Solvents were dried and purified according to standard procedures. GCMS was performed using a Shimadzu GC-2010Ultra coupled to a GCMS-QP2010 with an “RTX-5ms column” employing helium gas as the mobile phase. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer. The data were processed using MestReNova (version 6.0.2) desktop NMR data processing software. Microanalyses (C, H, N) were carried out on a Euro EA3028-HT analyzer. The FE-SEM observations were performed using a Hitachi SU8000 field-emission scanning electron microscope.

2. Optimization of reaction conditions

Table S1. Optimization of reaction conditions in the synthesis of vinyl thioesters.[a]



Entry	Solvent	Base	Yield (%)[b]
1	DMF	Na_2CO_3	45
2	DMF	K_2CO_3	55
3	DMF	NaOH	89
4	DMF	Pyridine	57
5	DMF	No base	Trace
6	EtOH	KOH	5
7	^{t}BuOH	KOH	84
8	DCE	KOH	Trace
9	Dioxane	KOH	58
10	THF	KOH	Trace
11	No solvent	KOH	Trace

[a] Experimental conditions: powdered CaC_2 (2 mmol); benzenethiol (1 mmol); dried solvent; H_2O (3 mmol); 100 °C, 3 h; [b] Isolated yields.

3. Synthetic procedure of scaling experiment

KOH (60 mmol, 3.36 g), benzenethiol (40 mmol, 4.08 mL), and water (120 mmol, 2.16 mL) were added to a sealed reaction flask (250 mL) with 150 mL DMF under inert atmosphere. After stirring at room temperature for 30 min, powdered calcium carbide (80 mmol, 5.12 g) was added, and the mixture was heated to 100 °C with vigorous stirring for 3 h. Then, the mixture was filtered, diluted with aqueous alkaline solution (50 mL), and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with ether (3 × 50 mL). The organic fractions were combined, washed with water (100 mL), and dried with sodium sulfate. The mixture was filtered, and the solvent was evaporated under reduced pressure. The evaporation temperature was maintained as low as possible to avoid product loss due to volatility of phenyl vinyl sulfide. Distillation of the residue afforded 4.9 g (91-92%) of phenyl vinyl sulfide, bp 80-84 °C/11-12 mm.

Caution! A care should be taken with dosing of water and calcium carbide to avoid excessive pressure in the reaction vessel. Acetylene should be slowly released and reacted.

4. Mechanistic studies

(a) Thiovinylation with gaseous acetylene dissolved in DMSO-d6.

A modest flow of gaseous acetylene was bubbled through 1 mL of DMSO-d6 for 20 min at room temperature. Then, ^{1}H and ^{13}C NMR spectra were recorded for the dissolved acetylene (Figure S1 and S2). Spectral data: ^{1}H NMR (DMSO-d6, 400 MHz) 2.81 (s). ^{13}C NMR (DMSO-d6, 100 MHz) 75.43.

Next, KOH (1.5 mmol), benzenethiol (1 mmol), and water (3 mmol) were added to the acetylene solution under inert atmosphere. The mixture was heated to 100 °C with vigorous stirring for 3 h. Then, the mixture was analyzed by NMR and GCMS, and formation of phenyl vinyl sulfide **1** was detected.

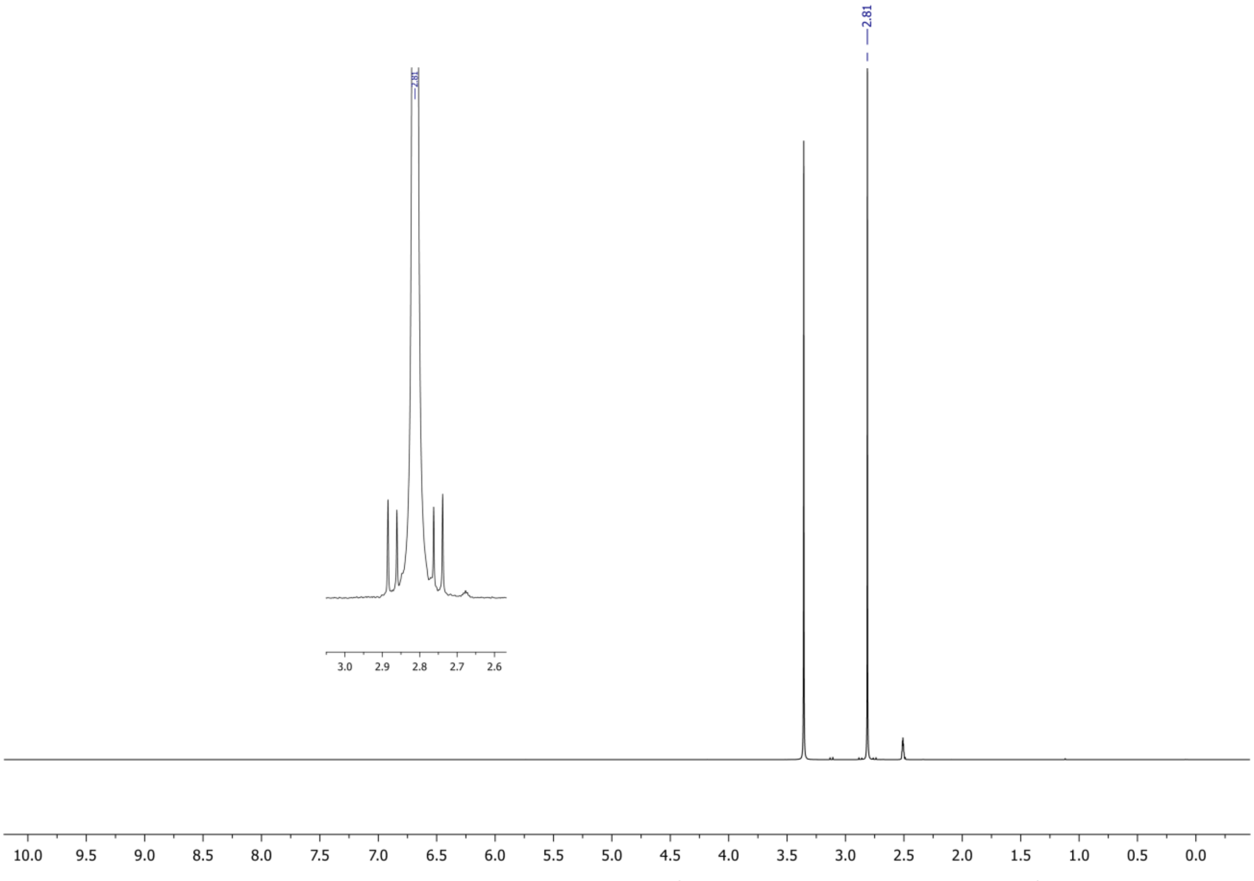


Figure S1. ^{1}H NMR spectrum of acetylene with $^3J_{HH}$= 9 Hz measured in ^{13}C satellites.

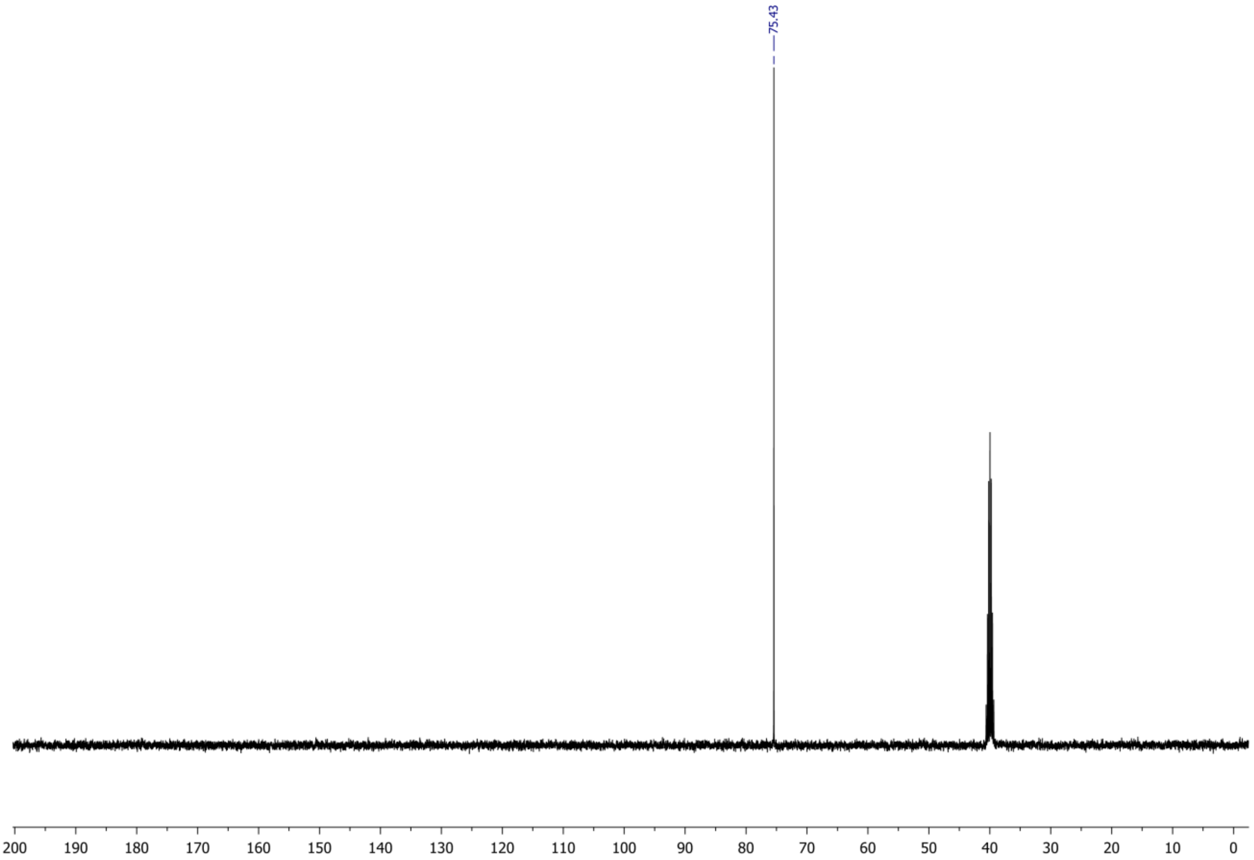


Figure S2. ^{13}C NMR spectrum of acetylene.

(b) Use of molecular sieves and 1,2-bis(phenylthio)-ethene formation.

KOH (1.5 mmol), benzenethiol (1 mmol) and molecular sieves were added to a reaction tube (10 mL) with 1 mL dry DMF under inert atmosphere. After stirring at room temperature for 30 min, powdered calcium carbide (2 mmol) was added, and the mixture was heated to 100 °C with vigorous stirring for 3 h. Then, the mixture was diluted with aqueous alkaline solution (10 mL), and the aqueous layer was extracted with diethyl ether (2 × 10 mL), dried over Na_2SO_4, and concentrated under vacuum to give a crude product that was analyzed by NMR and GCMS.

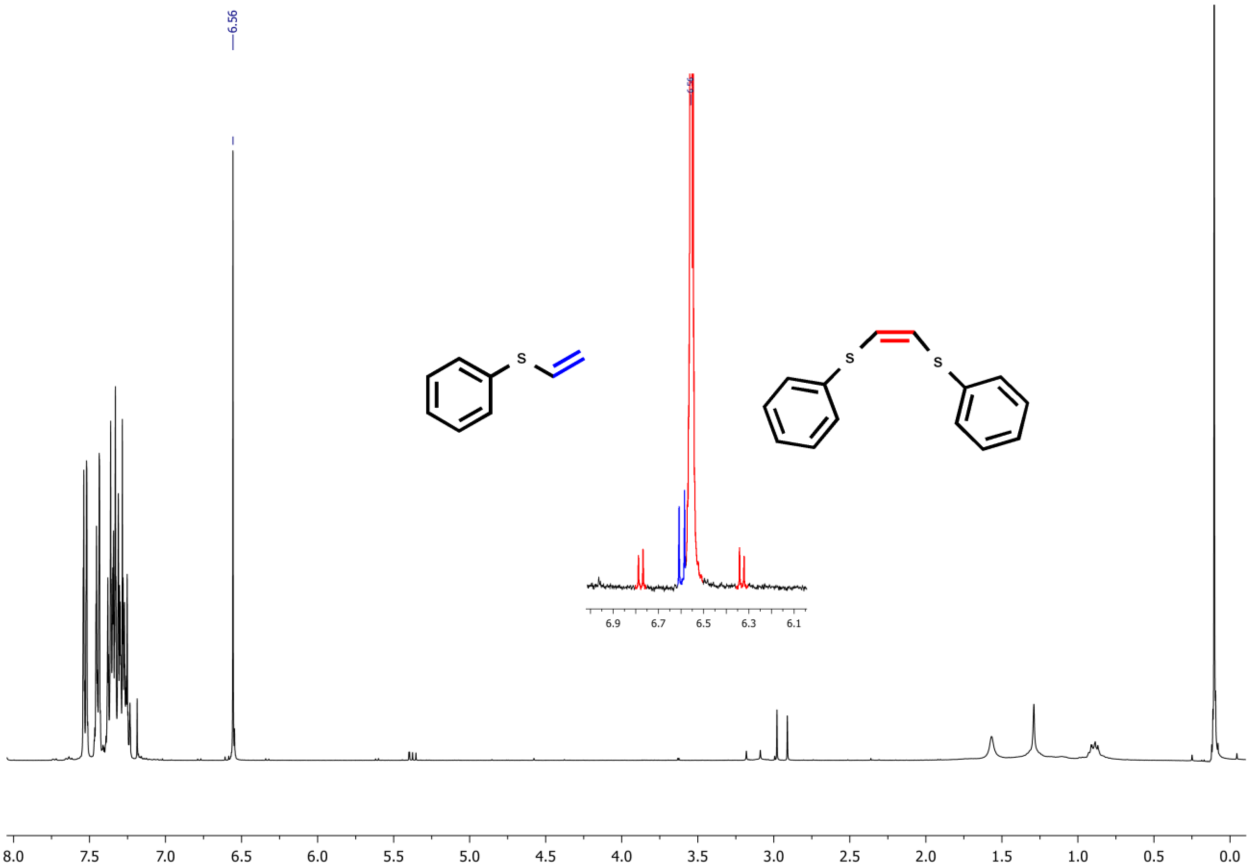
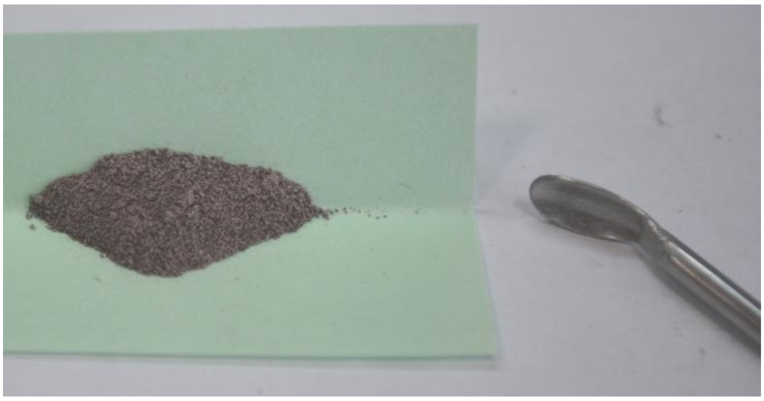


Figure S3. ^{1}H NMR spectrum of the reaction mixture containing 1,2-bis(phenylthio)ethene.

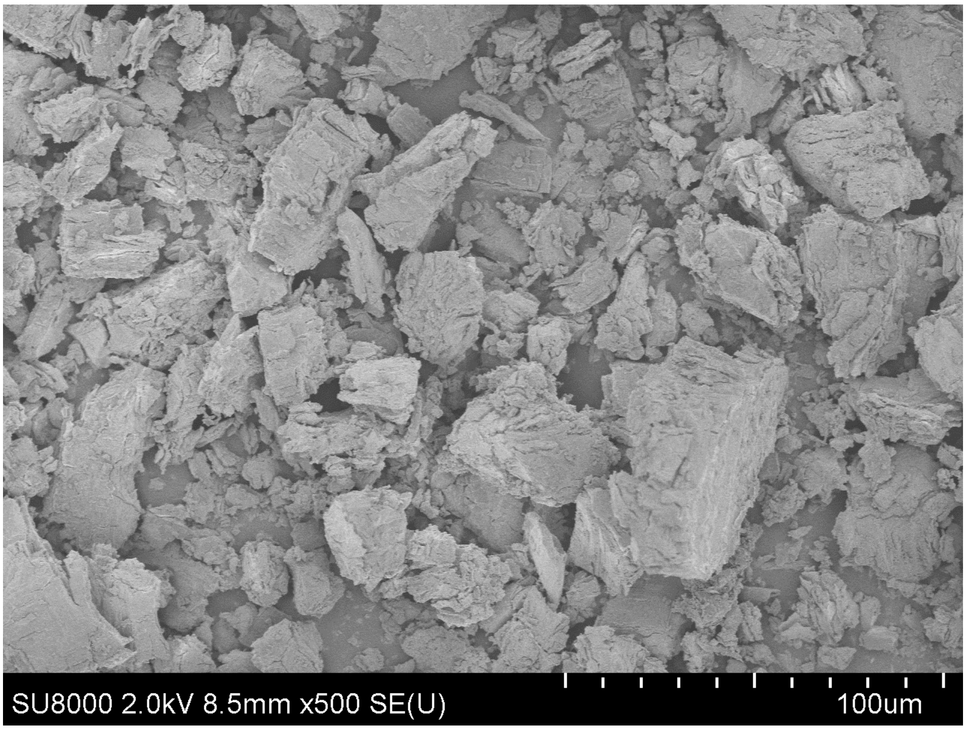
Blue signals indicate the trace amount of phenyl vinyl sulfide formed due to a remaining trace amount of water in the reaction mixture. Red signals correspond to the CH=CH protons; $^3J_{HH}$ = 8.2 Hz measured in ^{13}C satellites indicates *cis*-geometry of the double bond. The obtained spectra agree with the literature data.[1]

5. Preparation of calcium carbide

Calcium carbide as received.



Calcium carbide after grinding.



Field-Emission Scanning Electron Microscopy (FE-SEM) image of calcium carbide after grinding.

Figure S4. Preparation of CaC_2 for the reaction.

6. Spectral data and characterization

phenyl vinyl sulfide (1).

^{1}H NMR (CDCl$_3$, 400 MHz) 7.43 (2H, d, J = 7 Hz), 7.36 (2H, t, J = 7 Hz), 7.29 (1H, tt, J = 7 Hz, 1 Hz), 6.58 (1H, dd, J = 17, 10 Hz), 5.39 (1H, d, J = 10 Hz), 5.38 (1H, d, J = 17 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) 134.3, 131.9, 130.6, 129.2, 127.1, 115.5. MS: m/z (% of max intensity) 51 (28), 58 (10), 65 (25), 66 (16), 67 (12), 69 (10), 77 (21), 91 (100), 109 (11), 135 (75), 136 (62). Anal. calcd (%) for C_8H_8S: C, 70.54; H, 5.92. Found (%): C, 70.48; H, 5.89.

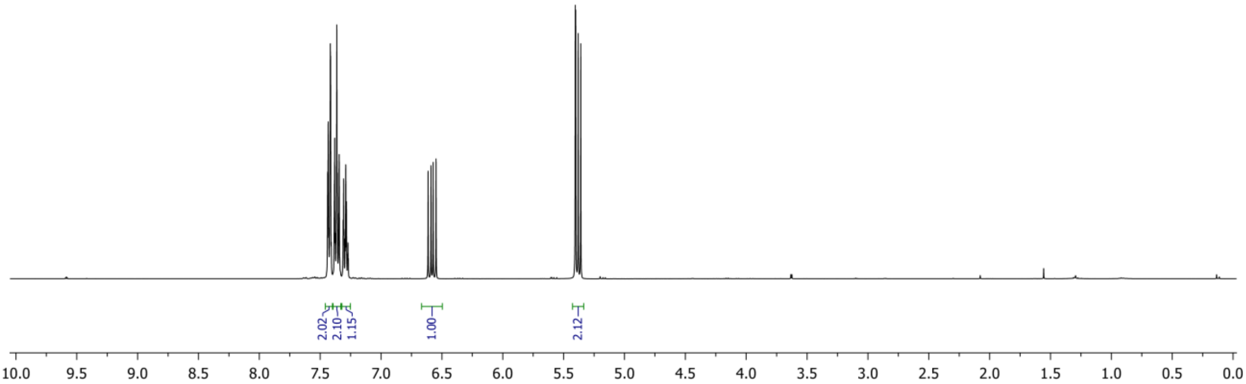


Figure S5. ^{1}H NMR spectrum of phenyl vinyl sulfide (**1**).

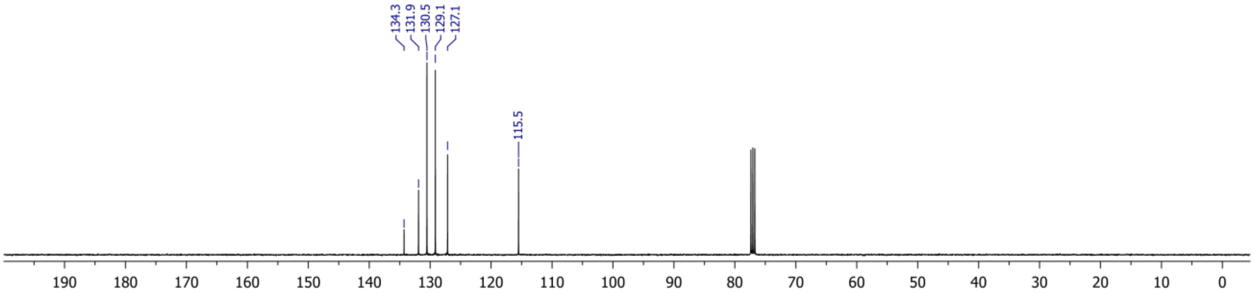


Figure S6. ^{13}C NMR spectrum of phenyl vinyl sulfide (**1**).

2-methylphenyl vinyl sulfide (2).

^{1}H NMR (CDCl$_3$, 400 MHz) 7.46-7.39 (1H, m), 7.28-7.18 (3H, m), 6.50 (1H, dd, J = 17, 10 Hz), 5.34 (1H, d, J = 10 Hz), 5.19 (1H, d, J = 17 Hz), 2.43 (3H, s). ^{13}C NMR (CDCl$_3$, 100 MHz) 139.5, 132.6, 131.9, 131.5, 130.4, 127.7, 126.7, 114.4, 20.3. MS: m/z (% of max intensity) 45 (20), 65 (17), 77 (18), 91 (53), 134 (17), 135 (100), 149 (15), 150 (59). Anal. calcd (%) for $C_9H_{10}S$: C, 71.95; H, 6.71. Found (%): C, 71.99; H, 6.78.

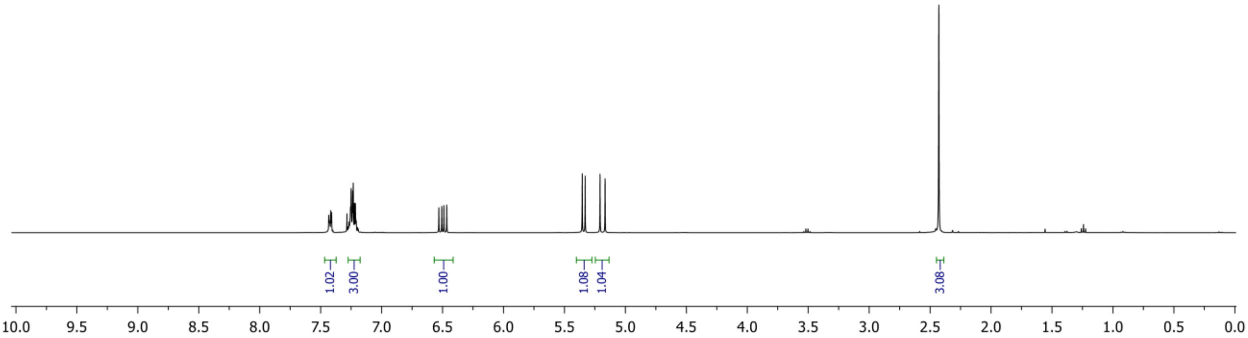


Figure S7. ^{1}H NMR spectrum of 2-methylphenyl vinyl sulfide (**2**).

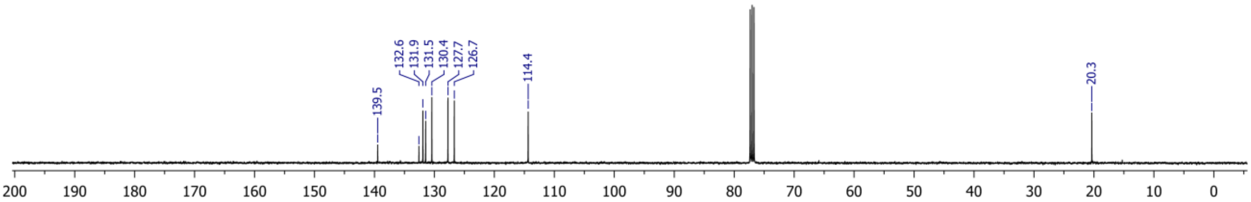


Figure S8. ^{13}C NMR spectrum of 2-methylphenyl vinyl sulfide (**2**).

3-methylphenyl vinyl sulfide (3).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.28-7.19 (3H, m), 7.13-7.07 (1H, d, *J* = 7 Hz), 6.58 (1H, dd, *J* = 17, 10 Hz), 5.38 (1H, d, *J* = 17 Hz), 5.37 (1H, d, *J* = 10 Hz), 2.37 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) 139.0, 134.0, 132.1, 131.1, 129.0, 128.0, 127.5, 115.3, 21.3. MS: m/z (% of max intensity) 65 (20), 74 (18), 77 (21), 79 (16), 91 (56), 105 (41), 134 (28), 135 (100), 149 (23), 150 (71). Anal. calcd (%) for $C_9H_{10}S$: C, 71.95; H, 6.71. Found (%): C, 71.90; H, 6.65.

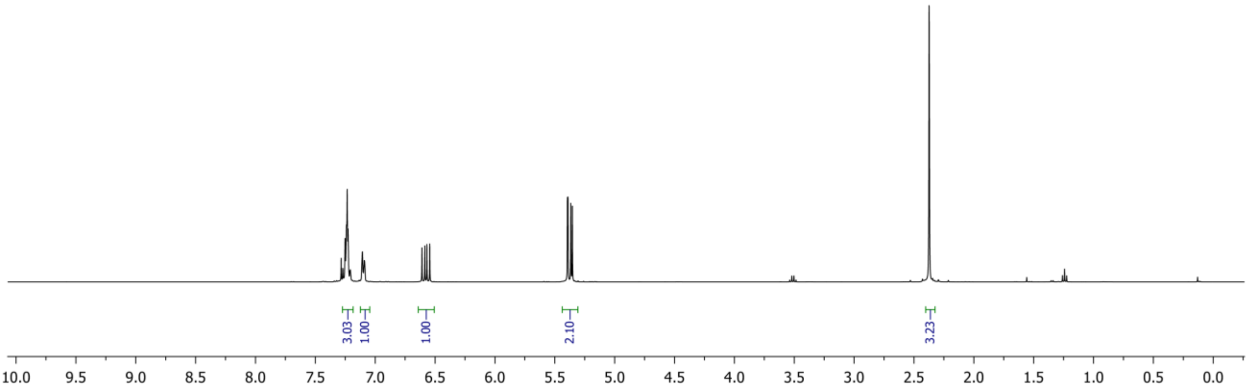


Figure S9. ^{1}H NMR spectrum of 3-methylphenyl vinyl sulfide (**3**).

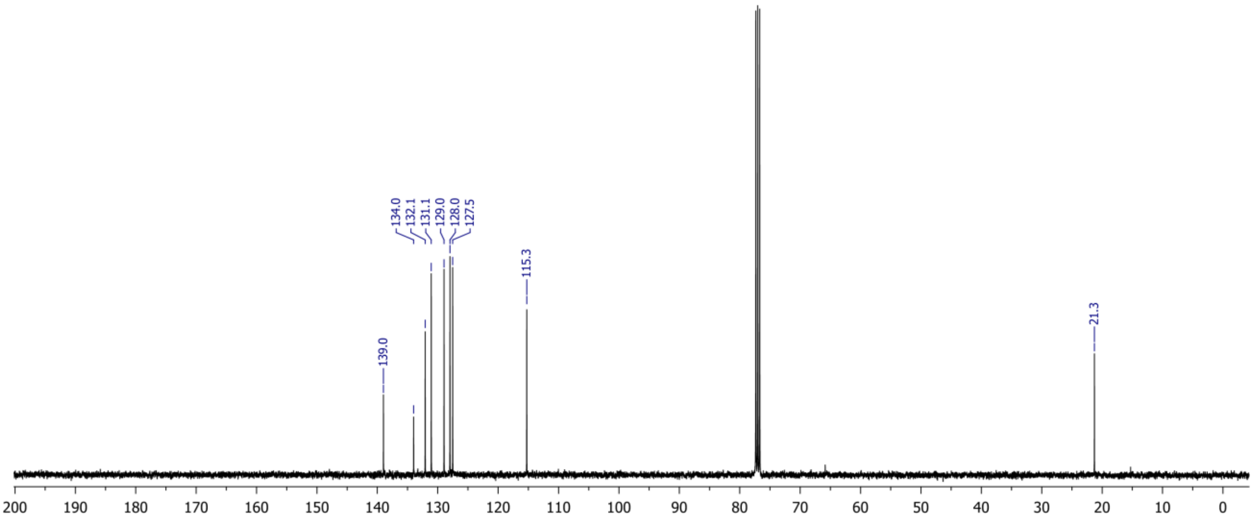


Figure S10. ^{13}C NMR spectrum of 3-methylphenyl vinyl sulfide (**3**).

4-methylphenyl vinyl sulfide (4).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.33 (2H, d, *J* = 8 Hz), 7.18 (2H, d, *J* = 8 Hz), 6.54 (1H, dd, *J* = 17, 10 Hz), 5.32 (1H, d, *J* = 10 Hz), 5.28 (1H, d, *J* = 17 Hz), 2.38 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) 137.4, 132.7, 131.3, 130.2, 129.9, 114.2, 21.1. MS: m/z (% of max intensity) 45 (7), 51 (7), 63 (7), 65 (34), 89 (8), 90 (6), 91 (100), 92 (25), 104 (8), 150 (32). Anal. calcd (%) for $C_9H_{10}S$: C, 71.95; H, 6.71. Found (%): C, 71.88; H, 6.77.

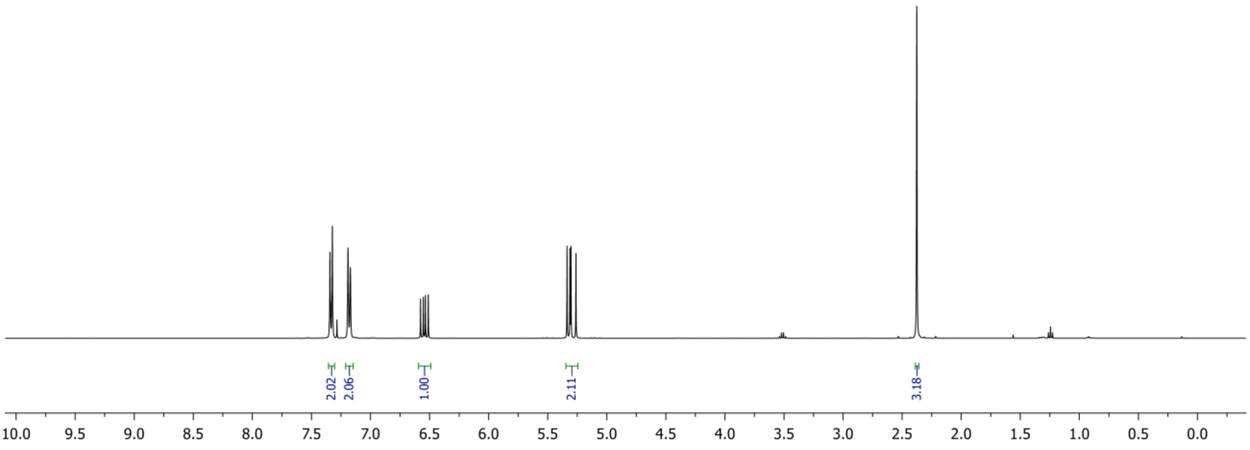


Figure S11. ^{1}H NMR spectrum of 4-methylphenyl vinyl sulfide (**4**).

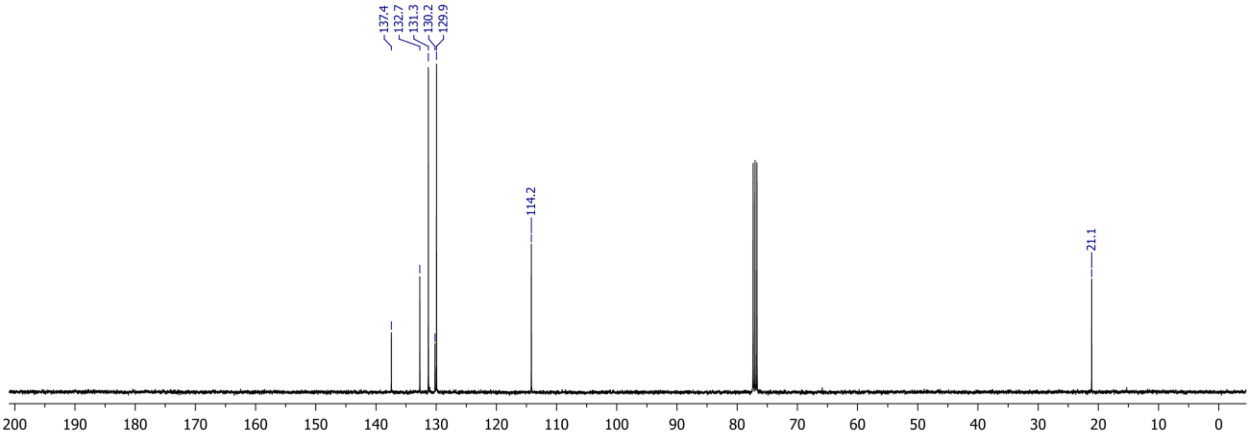


Figure S12. ^{13}C NMR spectrum of 4-methylphenyl vinyl sulfide (**4**).

2-chlorophenyl vinyl sulfide (5).

^{1}H NMR (CDCl$_3$, 400 MHz) 7.42 (1H, dd, *J* = 8 Hz, 1.5 Hz), 7.39 (1H, dd, *J* = 8 Hz, 1.5 Hz), , 7.27 (1H, td, *J* = 8 Hz, 1.5 Hz), 7.20 (1H, td, *J* = 8 Hz, 1.5 Hz), 6.54 (1H, dd, *J* = 17, 9 Hz), 5.55 (1H, d, *J* = 9 Hz), 5.53 (1H, d, *J* = 17 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) 134.3, 133.9, 130.3, 129.8, 129.5, 127.7, 127.3, 118.7. MS: m/z (% of max intensity) 67(15), 69 (12), 75 (13), 91 (48), 108 (24), 109 (14), 125 (15), 134 (26), 135 (100), 136 (11), 170 (36), 172 (14). Anal. calcd (%) for C_8H_7ClS: C, 56.30; H, 4.13. Found (%): C, 56.25; H, 4.19.

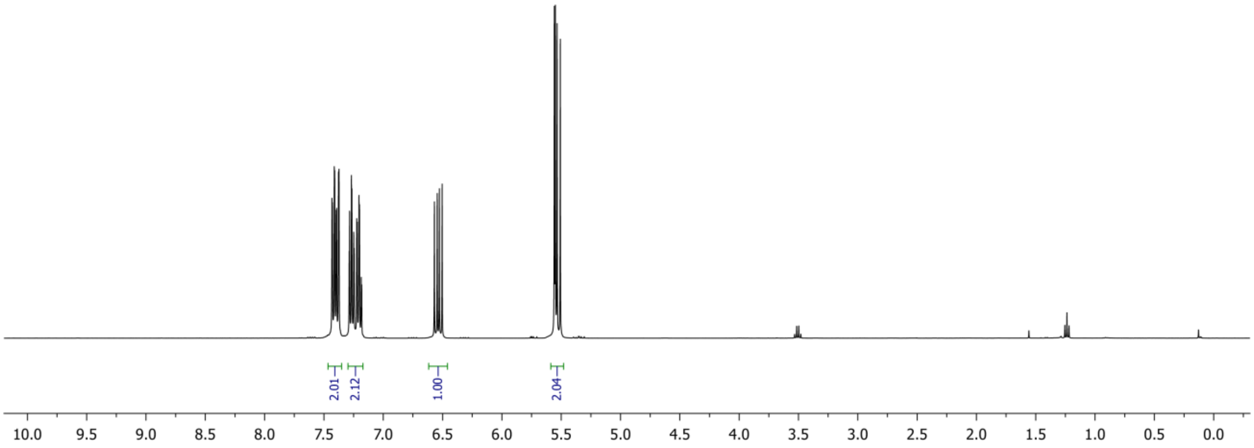


Figure S13. ^{1}H NMR spectrum of 2-chlorophenyl vinyl sulfide (**5**).

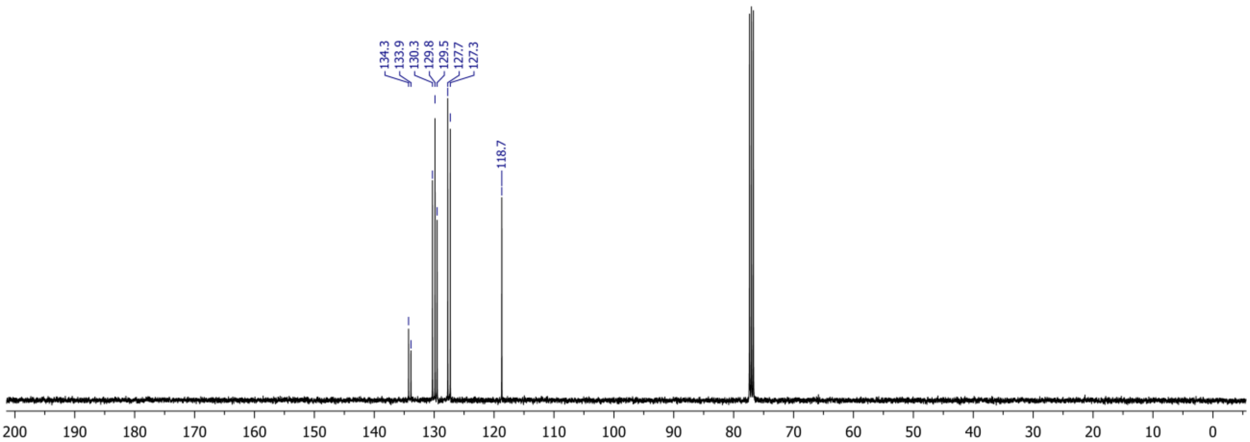


Figure S14. ^{13}C NMR spectrum of 2-chlorophenyl vinyl sulfide (**5**).

3-chlorophenyl vinyl sulfide (6).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.38 (1H, t, *J* = 2 Hz), 7.30-7.21 (3H, m), 6.54 (1H, dd, *J* = 17, 10 Hz), 5.48 (1H, d, *J* = 17 Hz), 5.48 (1H, d, *J* = 10 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 136.8, 134.9, 130.5, 130.1, 129.4, 127.8, 127.0, 117.6. MS: m/z (% of max intensity) 67 (16), 75 (19), 91 (47), 108 (19), 109 (12), 125 (21), 134 (30), 135 (100), 136 (11), 170 (37), 172 (13). Anal. calcd (%) for C_8H_7ClS: C, 56.30; H, 4.13. Found (%): C, 56.21; H, 4.05.

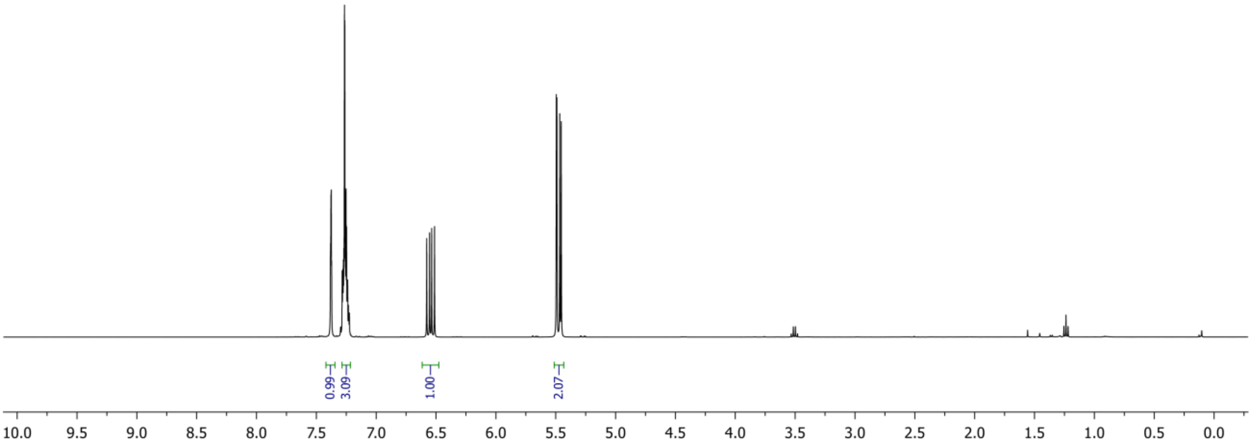


Figure S15. ^{1}H NMR spectrum of 3-chlorophenyl vinyl sulfide (**6**).

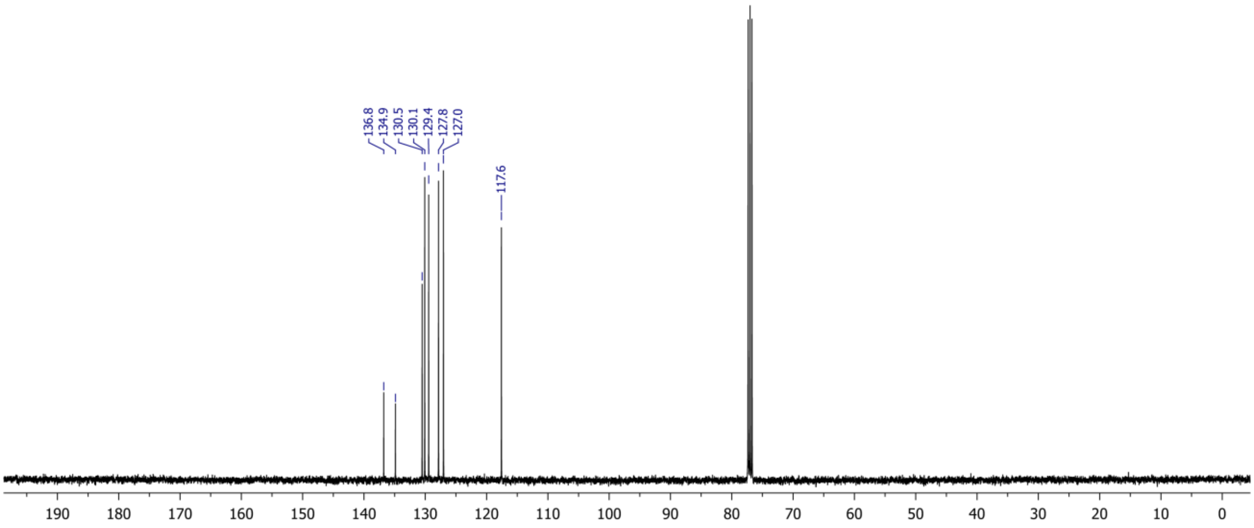


Figure S16. ^{13}C NMR spectrum of 3-chlorophenyl vinyl sulfide (**6**).

4-chlorophenyl vinyl sulfide (7).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.33 (4H, br. s), 6.51 (1H, dd, *J* = 17, 10 Hz), 5.41 (1H, d, *J* = 10 Hz), 5.38 (1H, d, *J* = 17 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 133.3, 132.8, 131.8, 131.3, 129.3, 116.2. MS: m/z (% of max intensity) 50 (11), 63 (10), 67 (15), 75 (20), 91 (46), 108 (26), 109 (15), 125 (26), 134 (28), 135 (100), 136 (11), 170 (45), 172 (16). Anal. calcd (%) for C_8H_7ClS: C, 56.30; H, 4.13. Found (%): C, 56.38; H, 4.22.

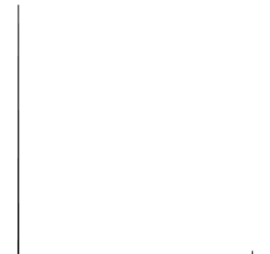


Figure S17. ^{1}H NMR spectrum of 4-chlorophenyl vinyl sulfide (**7**).

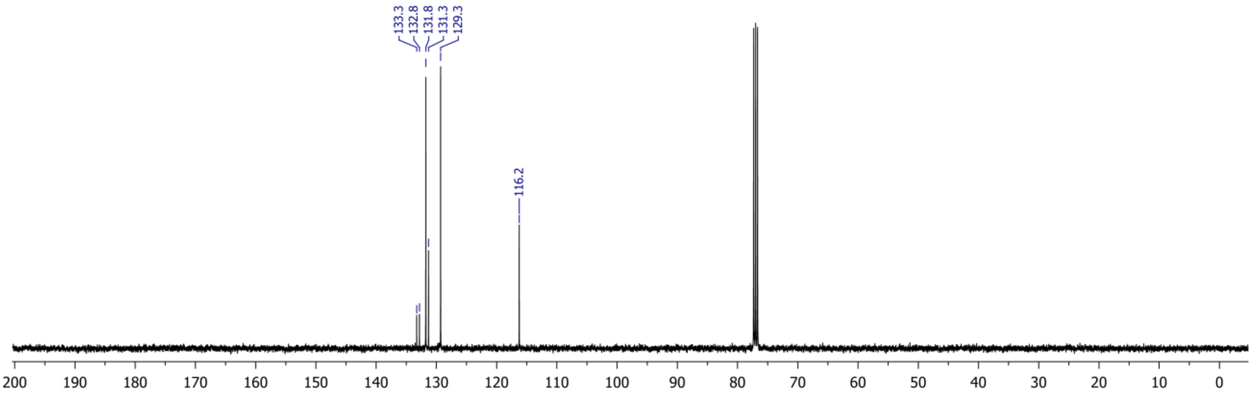


Figure S18. ^{13}C NMR spectrum of 4-chlorophenyl vinyl sulfide (**7**).

Hexyl vinyl sulfide (8).

^{1}H NMR ($CDCl_3$, 400 MHz) 6.38 (1H, dd, *J* = 17, 10 Hz), 5.20 (1H, d, *J* = 10 Hz), 5.12 (1H, d, *J* = 17 Hz), 2.72 (2H, t, *J* = 7), 1.66 (2H, quint, *J* = 7), 1.43 (2H, quint, *J* = 7 Hz), 1.38-1.27 (4H, m), 0.91 (3H, t, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 132.6, 110.3, 31.4, 31.4, 29.0, 28.6, 22.5, 14.0. MS: m/z (% of max intensity) 41 (45), 43 (82), 45 (31), 55 (37), 56 (34), 60 (100), 61 (25), 73 (30), 115 (25), 144 (27). Anal. calcd (%) for $C_8H_{16}S$: C, 66.60; H, 11.18. Found (%): C, 66.58; H, 11.23.

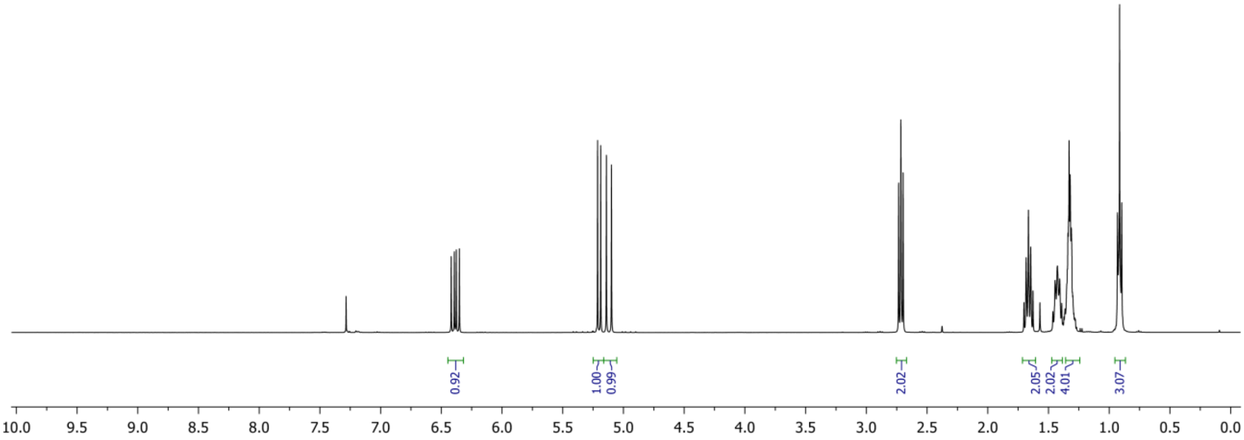


Figure S19. ^{1}H NMR spectrum of hexyl vinyl sulfide (**8**).

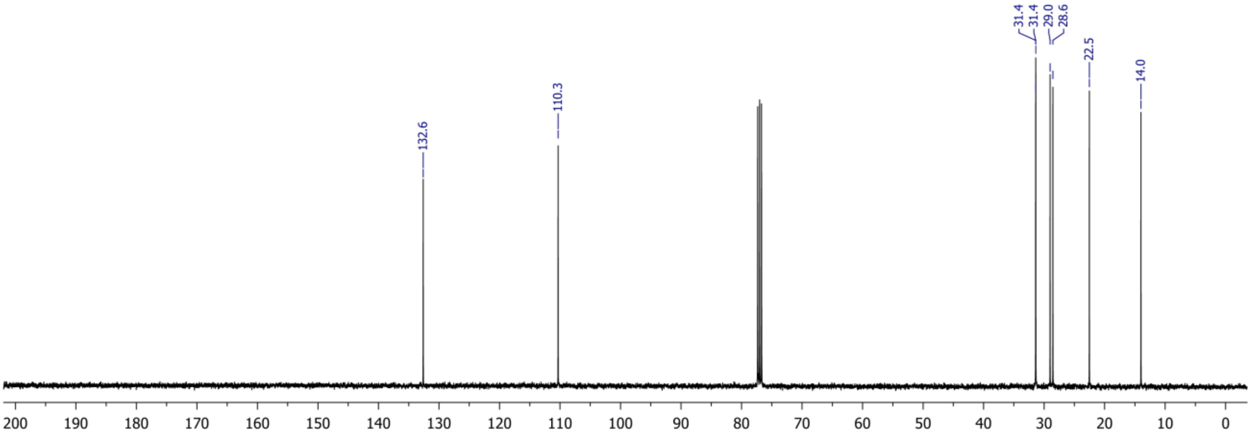


Figure S20. ^{13}C NMR spectrum of hexyl vinyl sulfide (**8**).

4-fluorophenyl vinyl sulfide (9).

^{1}H NMR (CDCl$_3$, 400 MHz) 7.41 (2H, m), 7.07 (2H, m), 6.50 (1H, dd, *J* = 17, 10 Hz), 5.34 (1H, d, *J* = 10 Hz), 5.25 (1H, d, *J* = 17 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) 162.4 (d, *J* = 247 Hz), 133.4 (d, *J* = 8 Hz), 132.4, 128.8 (d, *J* = 3 Hz), 116.3 (d, *J* = 22 Hz), 114.6. ^{19}F NMR (CDCl$_3$, 376 MHz) -114.10 (s). MS: m/z (% of max intensity) 57 (11), 69 (11), 75 (16), 83 (34), 84 (13), 108 (14), 109 (100), 153 (80), 154 (75), 155 (10). Anal. calcd (%) for C_8H_7FS: C, 63.31; H, 4.58. Found (%): C, 63.28; H, 4.50.

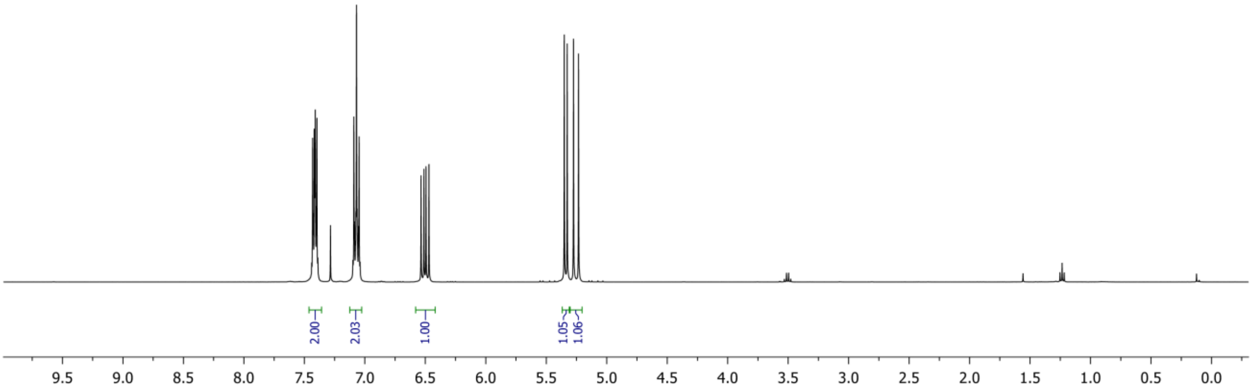


Figure S21. ^{1}H NMR spectrum of 4-fluorophenyl vinyl sulfide (**9**).

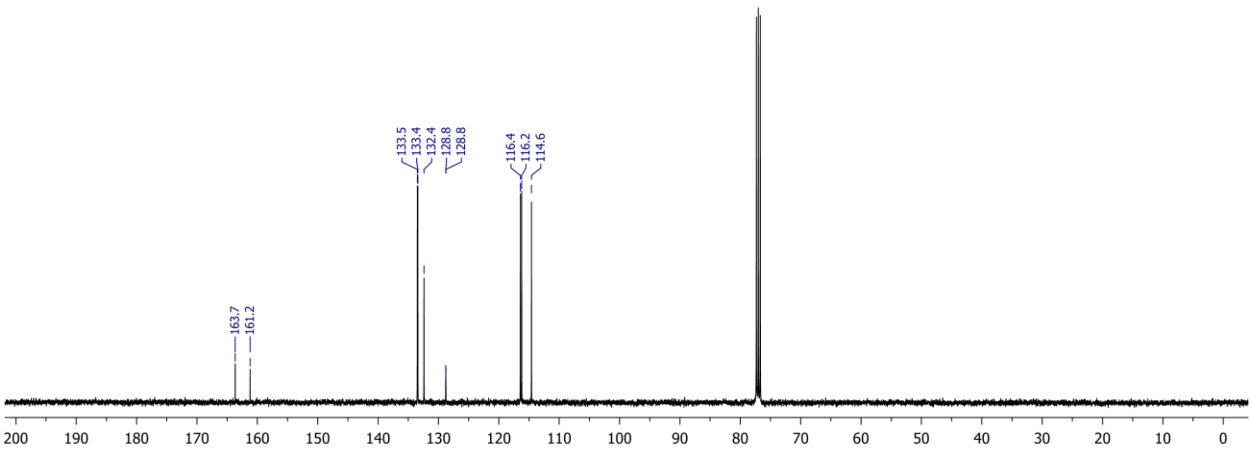


Figure S22. ^{13}C NMR spectrum of 4-fluorophenyl vinyl sulfide (**9**).

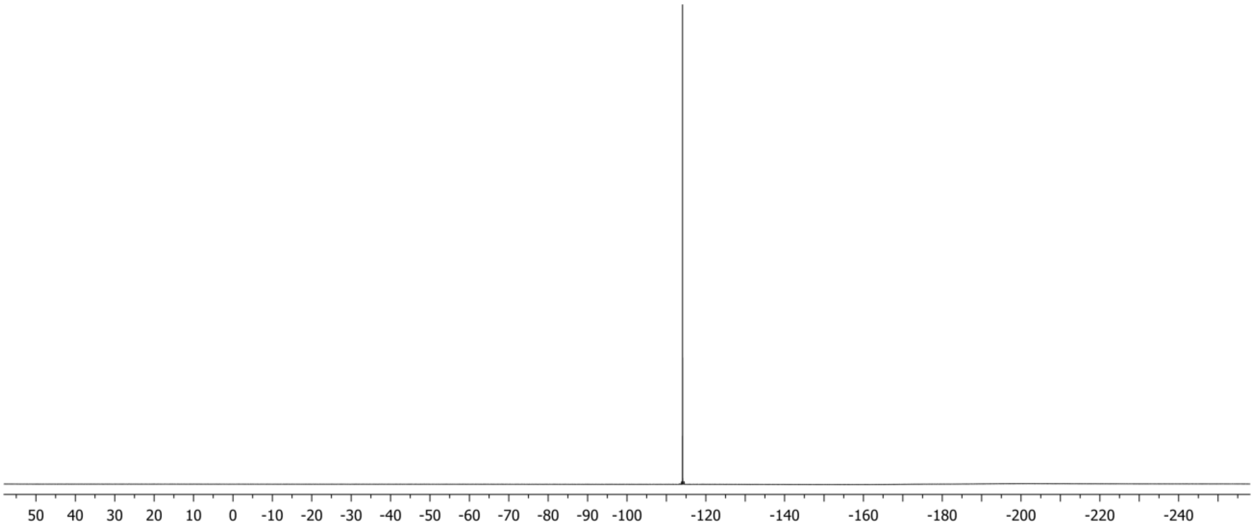


Figure S23. ^{19}F NMR spectrum of 4-fluorophenyl vinyl sulfide (**9**).

2-aminophenyl vinyl sulfide (10).

^{1}H NMR (CDCl$_3$, 400 MHz) 7.40 (1H, dd, *J* = 8 Hz, 1.5Hz), 7.22 (1H, td, *J* = 8 Hz, 1.5Hz), 6.79 (1H, d, *J* = 7 Hz) , 6.76 (1H, t, *J* = 7 Hz), 6.35 (1H, dd, *J* = 16, 10 Hz), 5.23 (1H, d, *J* = 10 Hz), 4.99 (1H, d, *J* = 16 Hz), 4.28 (2H, br. s). ^{13}C NMR (CDCl$_3$, 100 MHz) 148.2, 136.4, 131.1, 130.8, 118.8, 115.3, 113.8, 111. 9. MS: m/z (% of max intensity) 65 (21), 80 (52), 91 (17), 106 (15), 109 (17), 117 (20), 118 (17), 136 (100), 150 (18), 151 (68). Anal. calcd (%) for C_8H_9NS: C, 63.54; H, 6.00; N, 9.26. Found (%): C, 63.58; H, 6.06; N, 9.21.

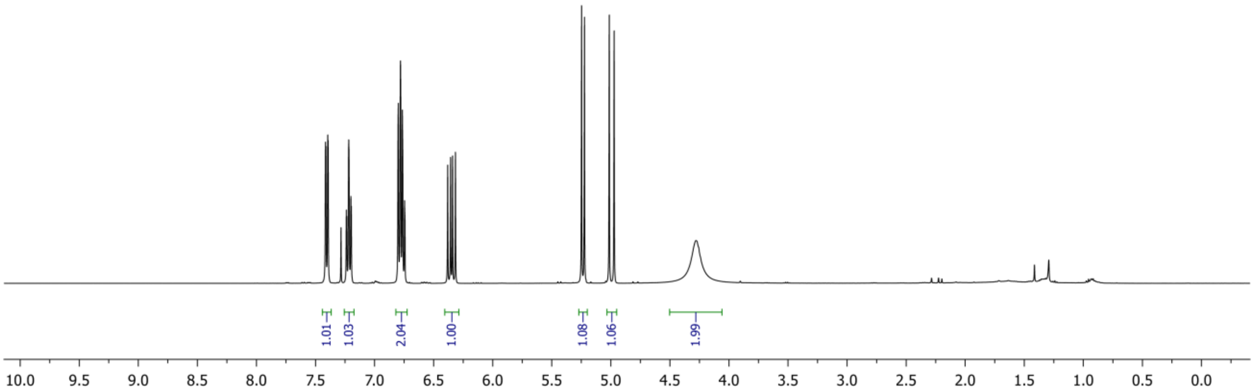


Figure S24. ^{1}H NMR spectrum of 2-aminorophenyl vinyl sulfide (**10**).

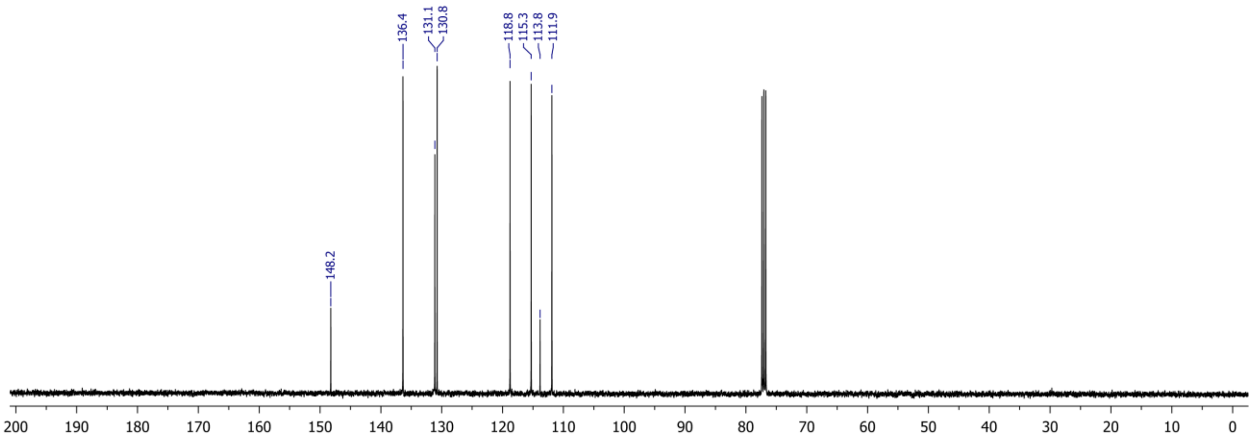


Figure S25. ^{13}C NMR spectrum of 2-aminorophenyl vinyl sulfide (**10**).

3-aminophenyl vinyl sulfide (11).

^{1}H NMR (CDCl$_3$, 400 MHz) 7.13 (1H, t, J = 8 Hz), 6.80 (1H, ddd, J = 8 Hz, 1.5 Hz, 1 Hz), 6.73 (1H, t, J = 2 Hz), 6.59 (1H, dm, J = 8 Hz, <3 Hz), 6.57 (1H, dd, J = 17, 9 Hz), 5.39 (1H, d, J = 17), 5.37 (1H, d, J = 9), 3.71 (2H, br. s). ^{13}C NMR (CDCl$_3$, 100 MHz) 147.1, 135.2, 131.9, 129.9, 120.3, 116.5, 115.5, 113.9. MS: m/z (% of max intensity) 65 (10), 80 (36), 106 (49), 118 (10), 119 (13), 124 (29), 150 (58), 151 (100), 152 (12). Anal. calcd (%) for C_8H_9NS: C, 63.54; H, 6.00; N, 9.26. Found (%): C, 63.49; H, 5.94; N, 9.25.

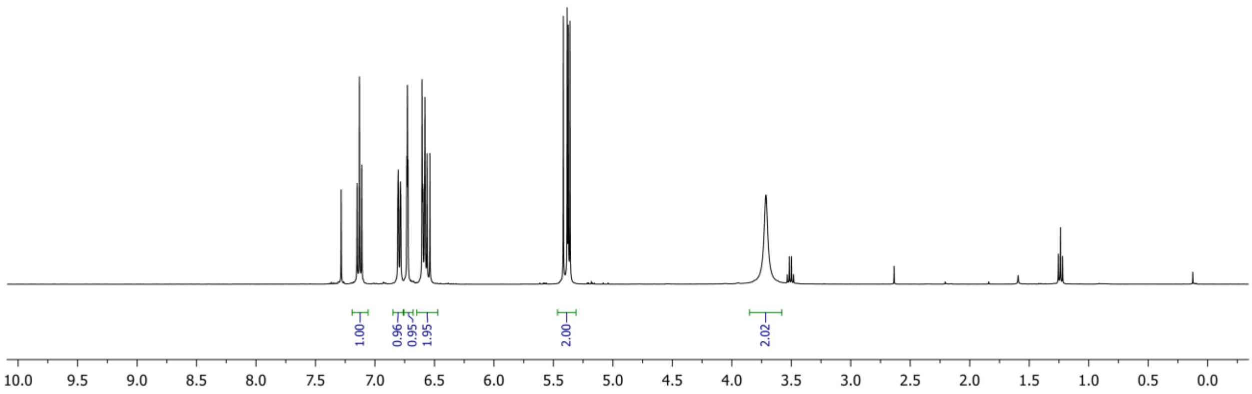


Figure S26. ^{1}H NMR spectrum of 3-aminorophenyl vinyl sulfide (**11**).

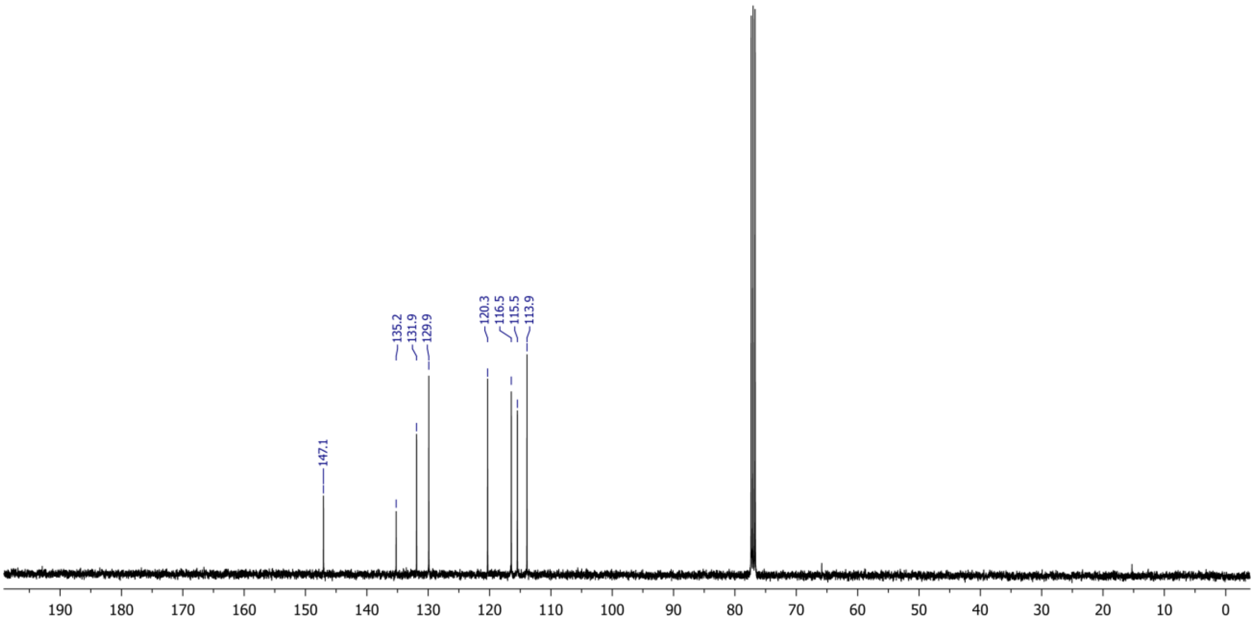


Figure S27. ^{13}C NMR spectrum of 3-aminorophenyl vinyl sulfide (**11**).

4-aminophenyl vinyl sulfide (12).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.27 (2H, d, *J* = 8 Hz), 6.69 (2H, d, *J* = 8 Hz), 6.48 (1H, dd, *J* = 16, 10 Hz), 5.19 (1H, d, *J* = 10 Hz), 5.06 (1H, d, *J* = 16 Hz), 3.80 (2H, br. s). ^{13}C NMR ($CDCl_3$, 100 MHz) 146.7, 134.7, 134.5, 120.0, 115.7, 111.5. MS: m/z (% of max intensity) 65 (24), 80 (25), 91 (13), 106 (60), 117 (17), 118 (12), 149 (14), 150 (100), 151 (97), 152 (13). Anal. calcd (%) for C_8H_9NS: C, 63.54; H, 6.00; N, 9.26. Found (%): C, 63.46; H, 5.95; N, 9.31.

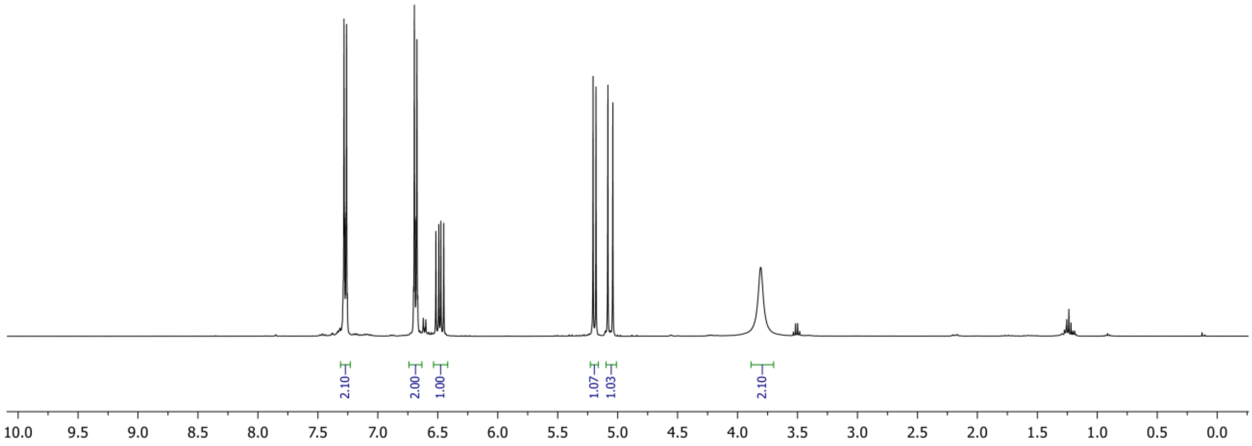


Figure S28. ^{1}H NMR spectrum of 4-aminorophenyl vinyl sulfide (**12**).

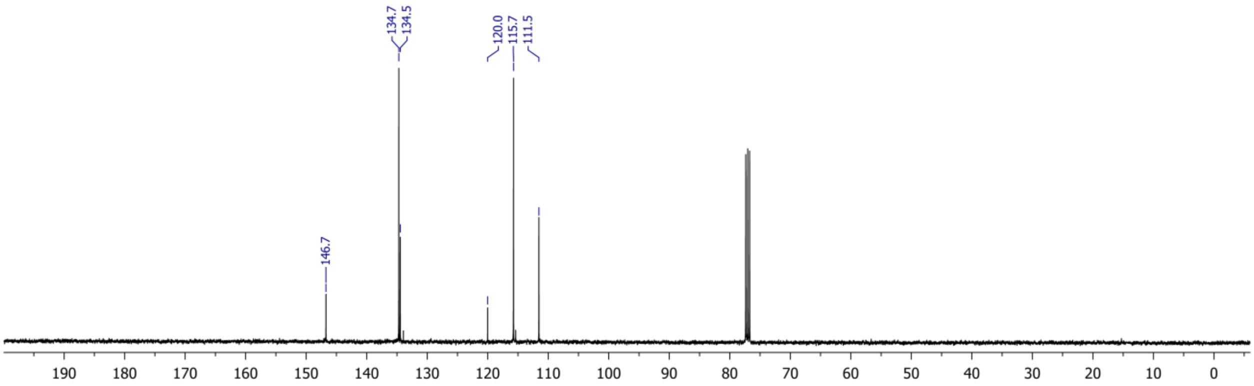


Figure S29. ^{13}C NMR spectrum of 4-aminorophenyl vinyl sulfide (**12**).

Cyclohexyl vinyl sulfide (13).

^{1}H NMR ($CDCl_3$, 400 MHz) 6.40 (1H, dd, J = 17, 10 Hz), 5.24 (1H, d, J = 17 Hz), 5.22 (1H, d, J = 10 Hz), 2.97-2.88 (1H, m), 2.07-1.99 (2H, m), 1.83-1.4 (2H, m), 1.69-1.60 (1H, m), 1.47-1.22 (5H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) 131.6, 112.4, 44.37, 33.4, 26.0, 25.7. MS: m/z (% of max intensity) 41 (51), 54 (20), 55 (100), 60 (31), 61 (16), 67 (72), 80 (20), 81 (30), 82 (83), 83 (80), 142 (36). Anal. calcd (%) for $C_8H_{14}S$: C, 67.54; H, 9.92. Found (%): C, 67.51; H, 9.98.

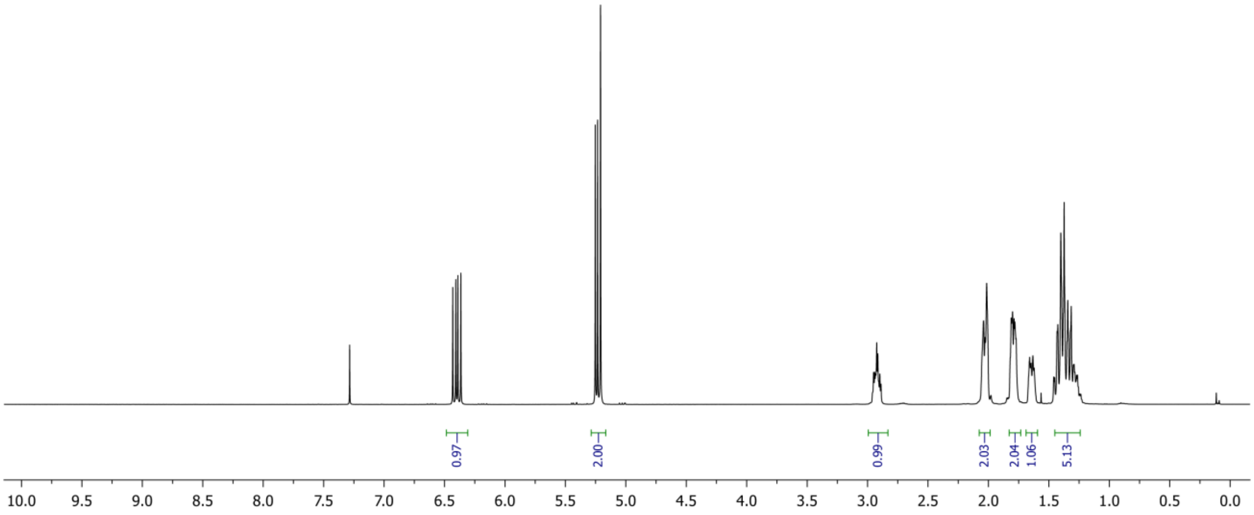


Figure S30. ^{1}H NMR spectrum of cyclohexyl vinyl sulfide (13).

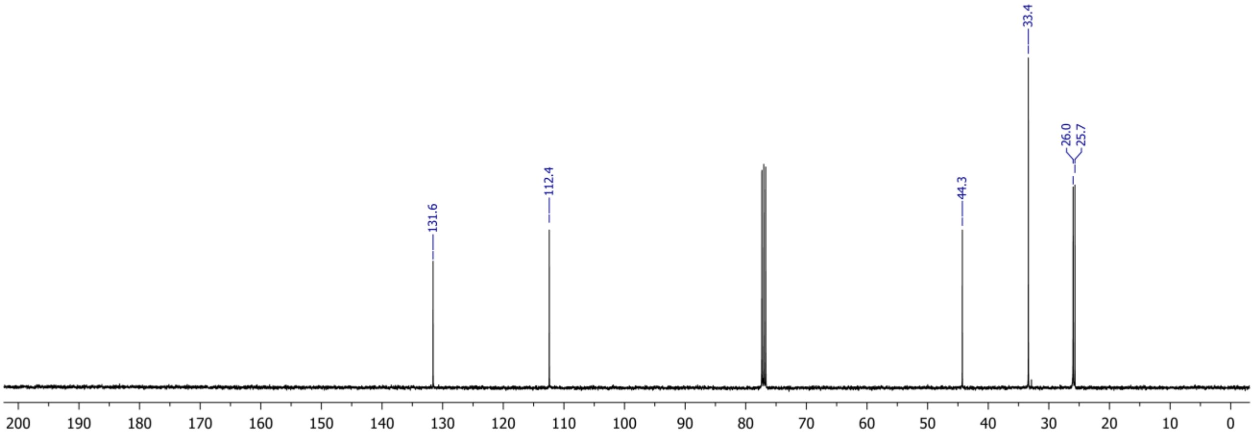


Figure S31. ^{13}C NMR spectrum of cyclohexyl vinyl sulfide (**13**).

Dodecyl vinyl sulfide (14).

^{1}H NMR ($CDCl_3$, 400 MHz) 6.39 (1H, dd, J = 17, 10 Hz), 5.20 (1H, d, J = 10 Hz), 5.12 (1H, d, J = 17 Hz), 2.72 (2H, t, J = 8), 1.67 (2H, quint, J = 8), 1.42 (2H, quint, J = 8 Hz), 1.36-1.23 (16H, m), 0.91 (3H, t, J = 7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 132.6, 110.3, 31.9, 31.4, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 14.1. MS: m/z (% of max intensity) 41 (74), 43 (82), 55 (92), 57 (61), 60 (100), 61 (35), 67 (32), 68 (36), 69 (59), 81 (32), 82 (37), 83 (35), 87 (68), 101 (48), 115 (33), 199 (45), 228 (12). Anal. calcd (%) for $C_{14}H_{28}S$: C, 73.61; H, 12.35. Found (%): C, 73.57; H, 12.38.

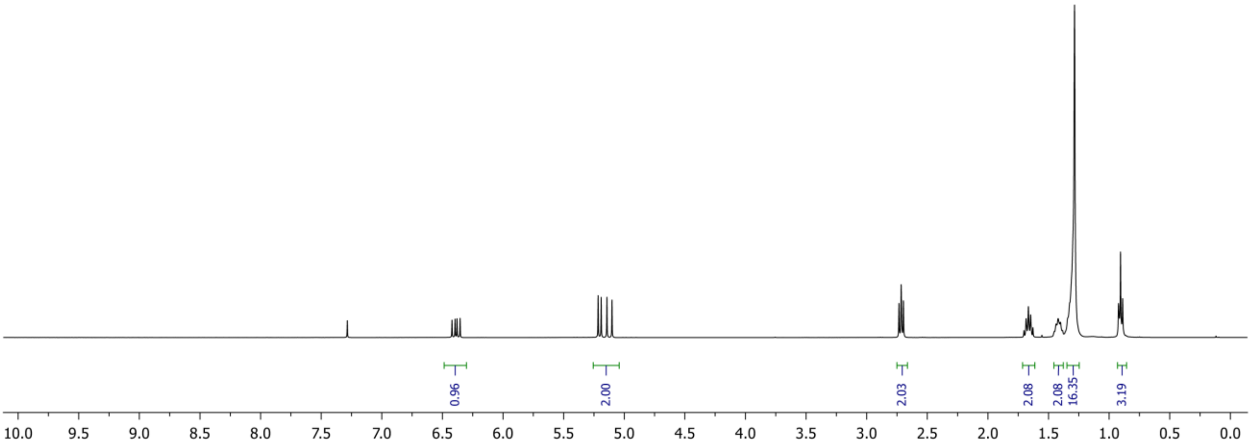


Figure S32. ^{1}H NMR spectrum of dodecyl vinyl sulfide (**14**).

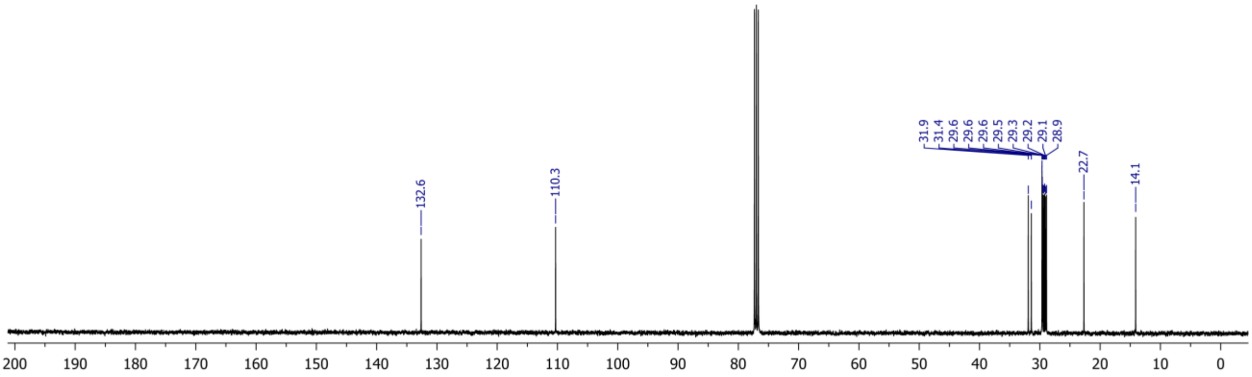


Figure S33. ^{13}C NMR spectrum of dodecyl vinyl sulfide (**14**).

Benzyl vinyl sulfide (15).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.42-7.32 (4H, m), 7.32-7.26 (1H, m), 6.40 (1H, dd, *J* = 17, 10 Hz), 5.24 (1H, d, *J* = 10 Hz), 5.21 (1H, d, *J* = 10 Hz), 3.96 (2H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) 137.2, 132.0, 128.8, 128.6, 127.3, 111.7, 36.2. MS: m/z (% of max intensity) 45 (7), 51 (7), 63 (7), 65 (34), 89 (8), 90 (6), 91 (100), 92 (25), 104 (8), 150 (32). Anal. calcd (%) for $C_9H_{10}S$: C, 71.95; H, 6.71. Found (%): C, 71.90; H, 6.69.

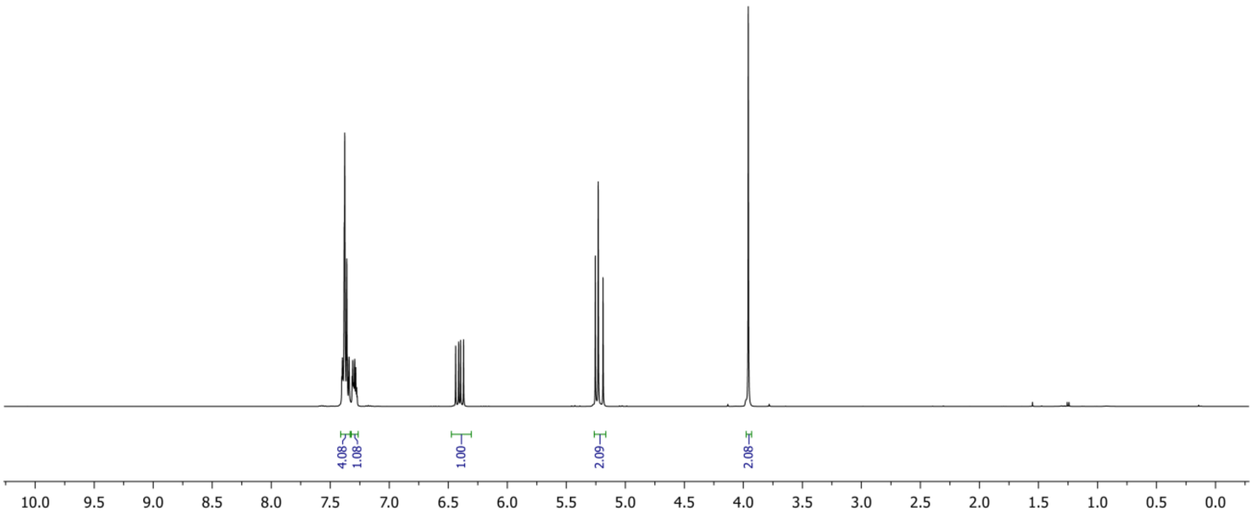


Figure S34. ^{1}H NMR spectrum of benzyl vinyl sulfide (**15**).

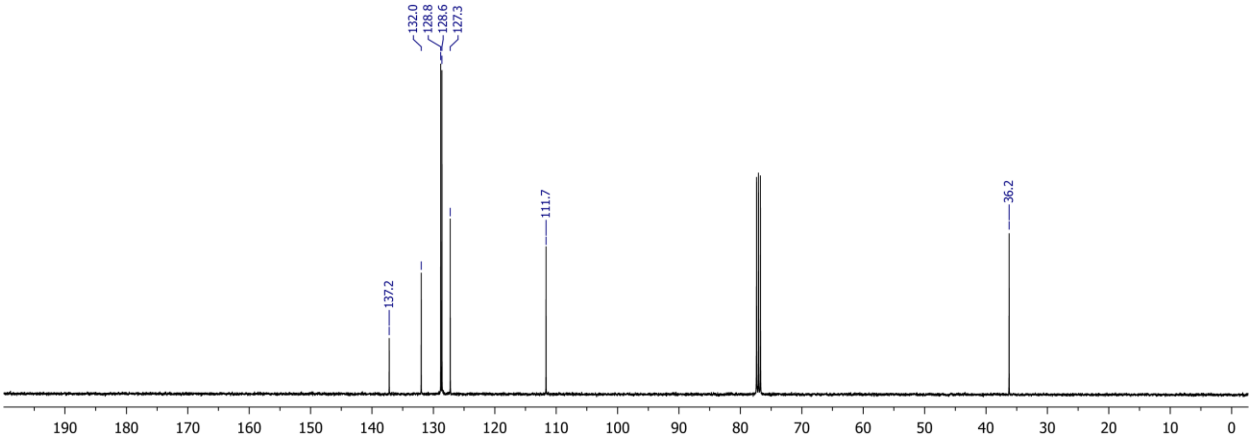


Figure S35. ^{13}C NMR spectrum of benzyl vinyl sulfide (**15**).

3-methylbutyl vinyl sulfide (16).

^{1}H NMR ($CDCl_3$, 400 MHz) 6.39 (1H, dd, *J* = 17, 10 Hz), 5.21 (1H, d, *J* = 10 Hz), 5.12 (1H, d, *J* = 17 Hz), 2.72 (2H, m, *J* = 7 Hz), 1.71 (1H, o, *J* = 7 Hz), 1.60-1.52 (2H, m), 0.95 (6H, d, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 132.5, 110.3, 37.9, 29.3, 27.5, 22.3. MS: m/z (% of max intensity) 41 (44), 42 (28), 43 (76), 45 (42), 55 (100), 59 (27), 60 (92), 70 (92), 73 (30), 74 (42), 115 (26), 130 (42). Anal. calcd (%) for $C_7H_{14}S$: C, 64.55; H, 10.83. Found (%): C, 64.50; H, 10.86.

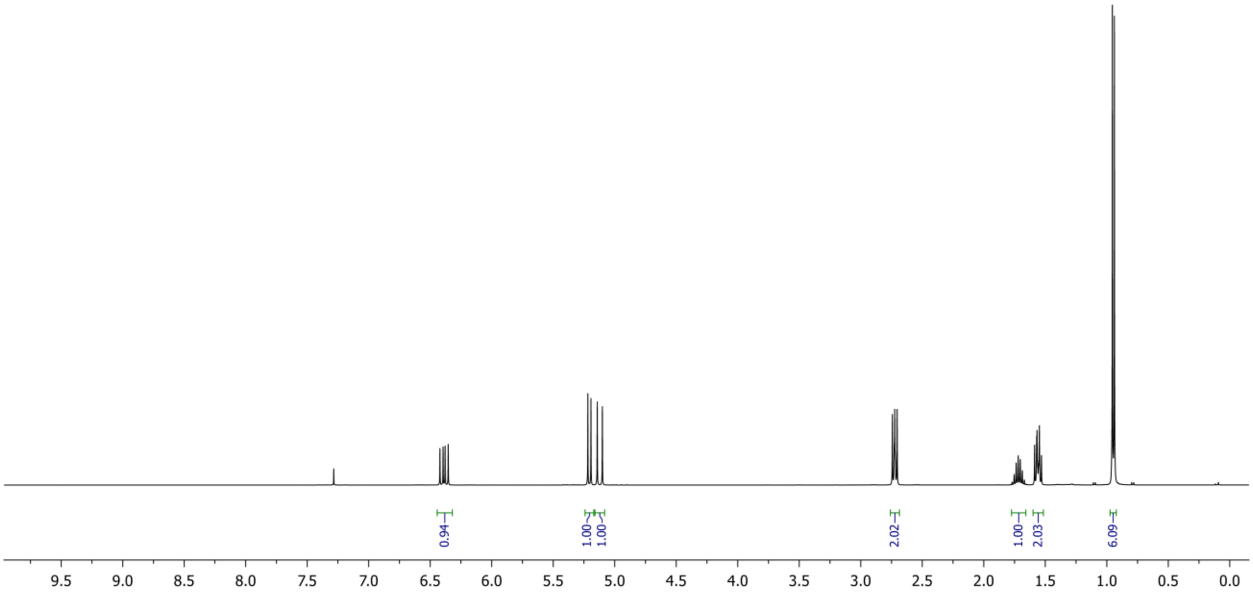


Figure S36. ^{1}H NMR spectrum of 3-methylbutyl vinyl sulfide (**16**).

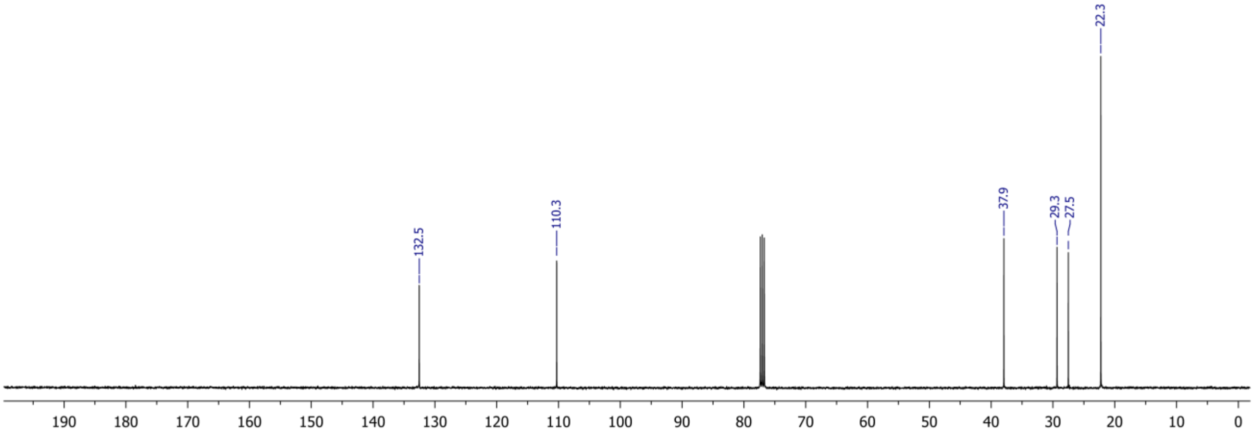


Figure S37. ^{13}C NMR spectrum of 3-methylbutyl vinyl sulfide (**16**).

2-pyridyl vinyl sulfide (17).

^{1}H NMR ($CDCl_3$, 400 MHz) 8.48 (1H, ddd, J = 5 Hz, 1.5 Hz, 1 Hz), 7.54 (1H, td, J = 8 Hz, 2 Hz), 7.21 (1H, dt, J = 8 Hz, 1 Hz), 7.14 (1H, dd, J = 17, 10 Hz), 7.05 (1H, ddd, J = 8 Hz, 5 Hz, 1 Hz), 5.61 (1H, d, J = 17 Hz), 5.54 (1H, d, J = 10 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 157.7, 149.8, 136.4, 128.1, 122.1, 120.2, 117.0. MS: m/z (% of max intensity) 51 (23), 52 (19), 58 (8), 67 (18), 78 (25), 79 (29), 111 (10), 136 (100), 137.32, 138 (7). Anal. calcd (%) for C_7H_7NS: C, 61.28; H, 5.14; N, 10.21. Found (%): C, 61.22; H, 5.18; N, 10.19.

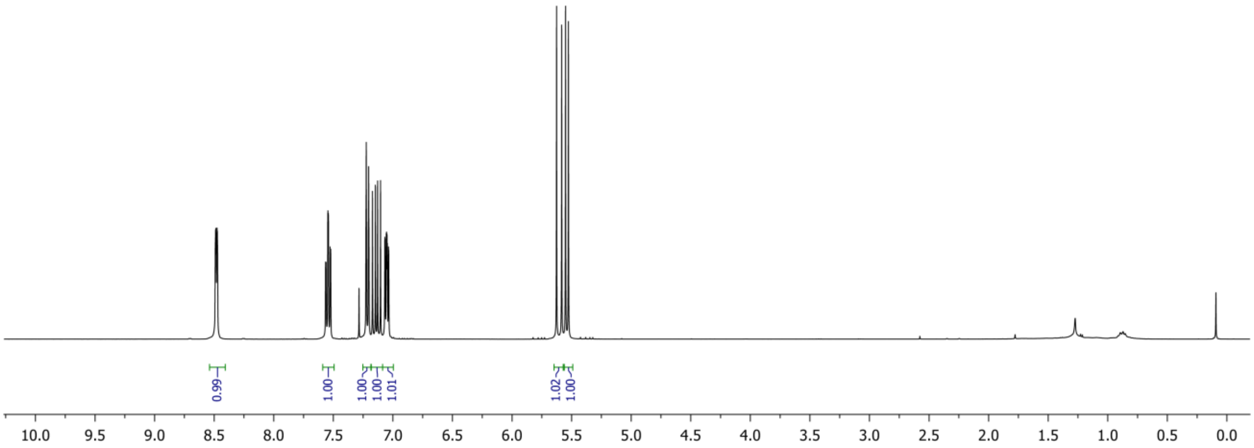


Figure S38. ^{1}H NMR spectrum of 2-pyridyl vinyl sulfide (**17**).

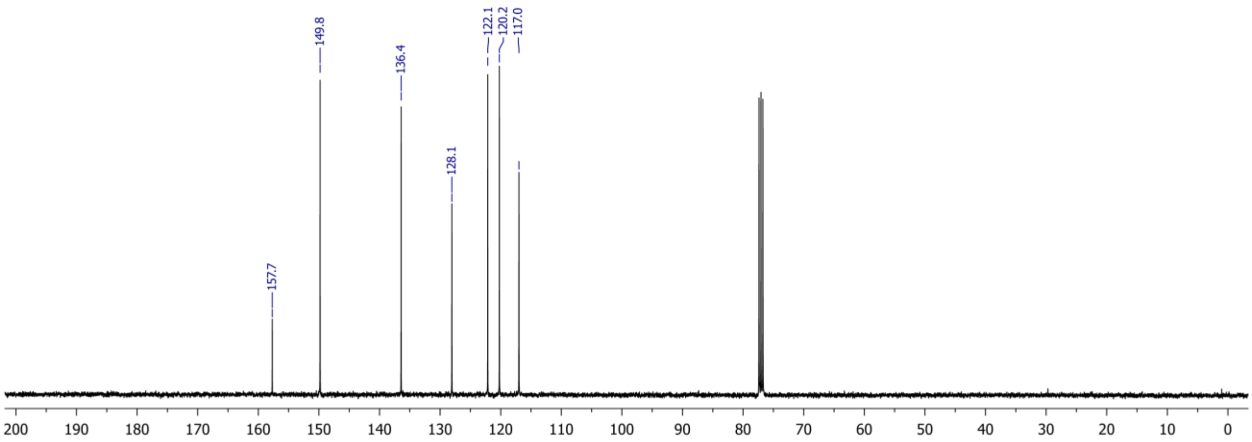


Figure S39. ^{13}C NMR spectrum of 2-pyridyl vinyl sulfide (**17**).

3-fluorophenyl vinyl sulfide (18).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.31 (1H, td, *J* = 7 Hz, 6 Hz), 7.16 (1H, ddd, *J* = 8 Hz, 1 Hz, <1Hz), 7.11 (1H, dt, *J* = 9 Hz, 2 Hz), 6.96 (1H, tdd, *J* = 8 Hz, 2.5 Hz, 1 Hz), 6.56 (1H, dd, *J* = 17, 9 Hz), 5.49 (1H, d, *J* = 17 Hz), 5.48 (1H, d, *J* = 9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) 162.9 (d, *J* = 248 Hz), 137.1 (d, *J* = 8 Hz), 130.5, 130.4 (d, *J* = 8 Hz), 125.2 (d, *J* = 3 Hz), 117.6, 116.5 (d, *J* = 23 Hz), 113.8 (d, *J* = 21 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) -112.00 (s). MS: m/z (% of max intensity) 75 (17), 83 (49), 84 (16), 108 (18), 109 (100), 153 (89), 154 (97). Anal. calcd (%) for C_8H_7FS: C, 63.31; H, 4.58. Found (%): C, 63.24; H, 4.50.

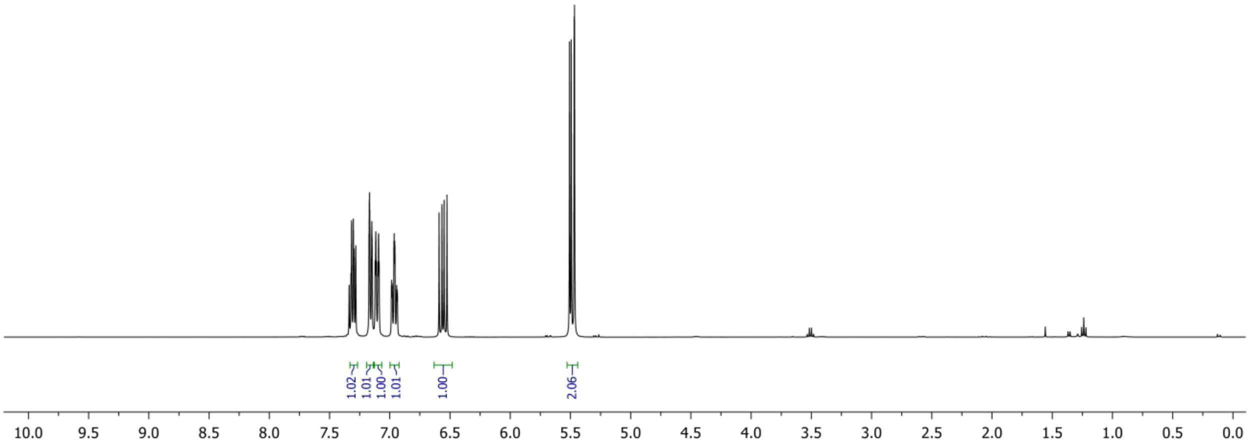


Figure S40. ^{1}H NMR spectrum of 3-fluorophenyl vinyl sulfide (1**8**).

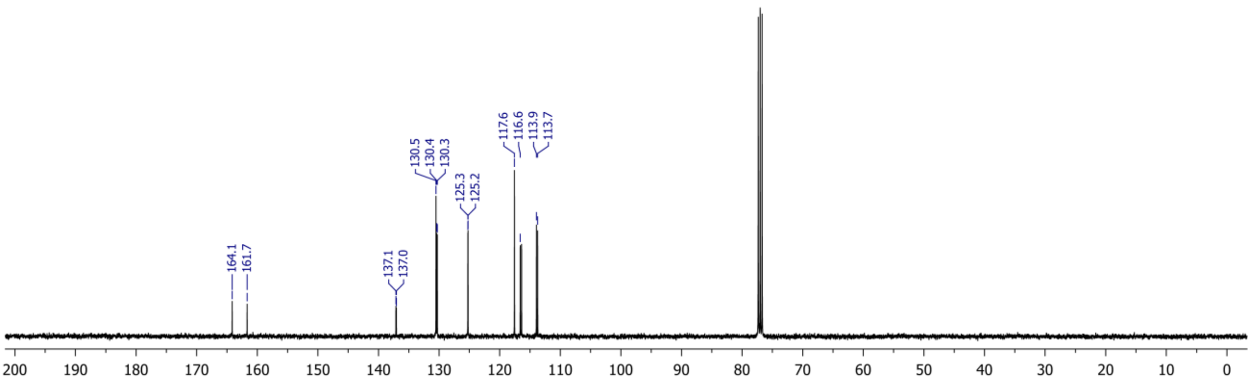


Figure S41. ^{13}C NMR spectrum of 3-fluorophenyl vinyl sulfide (1**8**).

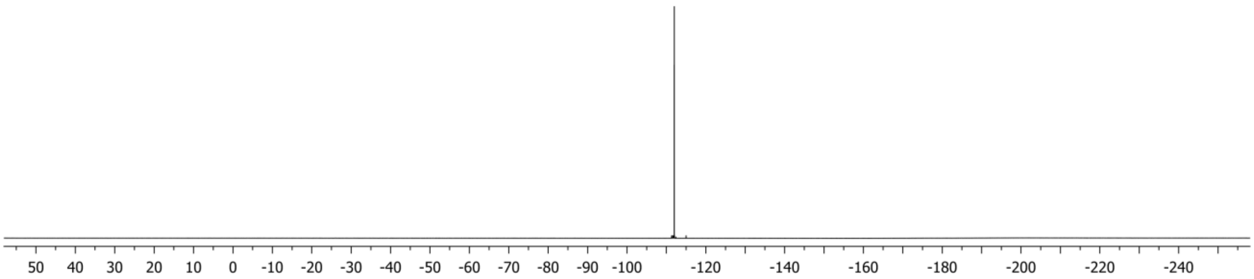


Figure S43. ^{19}F NMR spectrum of 3-fluorophenyl vinyl sulfide (1**8**).

Phenyl vinyl selenide (19).

^{1}H NMR (CDCl$_3$, 400 MHz) 7.58-7.52 (2H, m), 7.38-7.31 (3H, m), 6.87 (1H, dd, *J* = 17, 9 Hz), 5.81 (1H, d, *J* = 9 Hz; $^2J_{SeH}$ = 16 Hz), 5.57 (1H, d, *J* = 17 Hz; $^2J_{SeH}$ = 5 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) 133.1, 129.3, 127.7, 127.5, 119.4. MS: m/z (% of max intensity) 50 (21), 51 (48), 77 (100), 78 (99), 91 (37), 102 (15), 103 (57), 104 (87), 180 (22), 181 (36), 182 (36), 183 (57), 184 (66). Anal. calcd (%) for C_8H_8Se: C, 52.47; H, 4.40. Found (%): C, 52.41; H, 4.34.

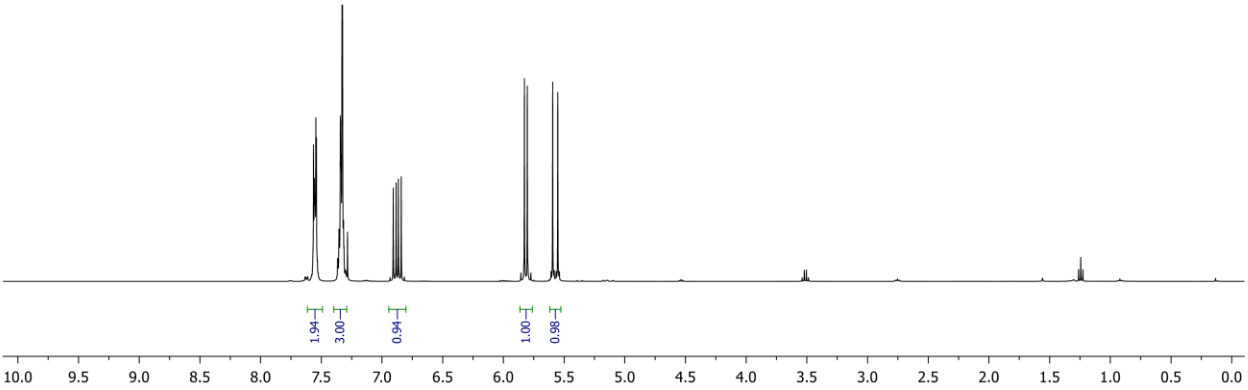


Figure S44. ^{1}H NMR spectrum of phenyl vinyl selenide (**19**).

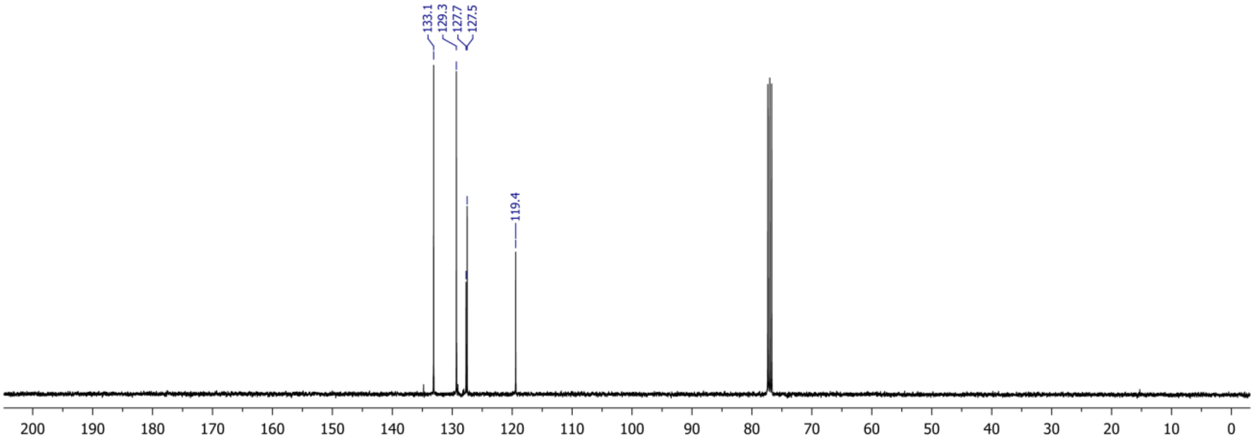


Figure S45. ^{13}C NMR spectrum of phenyl vinyl selenide (**19**).

7. Literature

[1] (a) C. Gómez, B. Maciá, M. Yus, *Tetrahedron* **2005**, *16*, 9325-9330. (b) A. L. J. Beckwith, P. E. Pigou, *Aust. J. Chem*. **1986**, *39*, 77-87.