Supplementary Information (SI) for Chemical Science.

Supplementary Information for:

Hydroselenation of Simple Olefins: Elucidating the β-Selenide Radical Effect

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1. General

Commercial reagents were purchased from Sigma Aldrich, Strem, Alfa Aesar, Acros Organics, Combi-Blocks or TCI and used without further purification. Dry 1,2-dichloroethane (DCE) was purified using CaH_2, degassed by three freeze-pump-thaw cycles, and stored within a N_2 filled glove box. All experiments were performed in oven-dried or flame-dried glassware. Irradiation was performed with Kessil A160WE Tuna Blue LED lights, at the lowest wavelength and highest intensity settings. Reactions were monitored using either thin-layer chromatography (TLC) or gas chromatography using an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Purification and isolation of products were performed via silica gel chromatography (both column and preparative thinlayer chromatography). Column chromatography was performed with Silicycle Silica-P Flash Silica Gel using glass columns. Solvents were purchased from Fisher. ^{1}H NMR, ^{2}H NMR, ^{13}C NMR, and ^{77}Se NMR spectra were recorded on Bruker AVANCE600, CRYO500, GN500 or DRX400 spectrometer. ^{1}H NMR spectra were internally referenced to the residual solvent signal or TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Data for ^{2}H NMR, ^{13}C NMR, and ^{31}P NMR are reported in terms of chemical shift (δ ppm). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI). Static UV-Visible spectra were obtained using a quartz cuvette and a Cary-60 absorption spectrometer, and are reported in terms of wavelength (nm). Diselenides **3b**-**3d** used here were known compounds and synthesized according to the reported methods.[1]

2. General procedure for synthesis of alkene starting materials

Wittig reaction

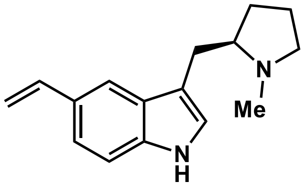
A flame-dried two-necked flask was equipped with a stir bar and the corresponding triphenylphosphonium bromide (1.0 equiv.). THF (0.2 M) was added and the solution was cooled to 0 °C under nitrogen. n-BuLi (2.5 M in hexanes, 1.0 equiv.) was added dropwise and the solution was stirred for two hours at 0 °C. The corresponding aldehyde (1.0 equiv.) was added dropwise as a solution (1.25 M). The solution was allowed to warm to room temperature, and monitored by TLC until all starting material was consumed. The solution was quenched using silica gel, then solvent was removed using rotary evaporation. The corresponding oil was dissolved in ethyl acetate and was washed with water and brine and dried with sodium sulfate. The solution was decanted and solvent was removed using rotary evaporation, and the resulting residue was purified via column chromatography to afford the alkene.

The following alkenes were synthesized using this procedure, and NMR spectra of the products matched literature reports: **1b**,[2] **1c**,[2] **1e**,[3] **1f**,[4] **1h**,[2] **1i**,[4] **1j**,[4] **1l**,[4] **1m**,[3] **1p**,[4] **1s**,[5] **1t,**[4] **1u**,[6] **1x**,[4] **1y**,[7] **1ac.**[8] Other substrates were purchased.

Suzuki coupling

A mixture of (*R*)-5-Br-3-((1-methylpyrrolidin-2-yl)methyl)-1H-indole (1 equiv.), potassium trifluorovinylborate (3 equiv.), Pd(dppf)Cl_2•DCM (10 mol%) and triethylamine (3 equiv.) were dissolved in ethanol (0.100 M) in a 1-dram vial in a nitrogen-filled glovebox. The reaction was sealed and refluxed in the glovebox for 20 hours. After cooling to room temperature and removing from the glovebox, acetonitrile (0.23 M), trimercaptotriazine (0.3 equiv.), and decolorizing charcoal (6 equiv.) were added. This solution was stirred for at room temperature for 1 hour. The solution was filtered through celite and solvent removed by rotary evaporation. The crude mixture was dissolved in ethyl acetate and washed with water and brine. The organic phase was dried with sodium sulfate, then decanted and solvent was removed using rotary evaporation. The resulting product was purified by preparatory TLC (90:9:1 DCM:MeOH:AcOH).

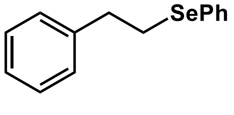
(*R*)-3-((1-methylpyrrolidin-2-yl)methyl)-5-vinyl-1H-indole (1ad)



Yellow-brown oil, 61% yield. **^{1}H NMR** (499 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.49 (s, 1H), 7.41 – 7.32 (m, 3H), 6.83 (dd, J = 17.5, 10.9 Hz, 1H), 5.71 (dd, J = 17.5, 0.9 Hz, 1H), 5.17 (dd, J = 10.9, 0.8 Hz, 1H), 3.94 – 3.79 (m, 1H), 3.59 – 3.42 (m, 2H), 3.23 (dd, J = 13.8, 6.8 Hz, 1H), 2.82 (dd, J = 18.8, 8.1 Hz, 1H), 2.63 (s, 3H), 2.27 – 2.12 (m, 2H), 2.06 – 1.88 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.70, 136.31, 129.85, 126.86, 124.62, 124.59, 120.53, 116.52, 111.88, 111.45, 69.15, 56.98, 40.27, 30.93, 27.12, 21.79.

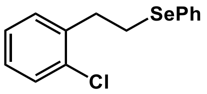
3. General procedure for *anti*-Markovnikov hydroselenation

phenethyl(phenyl)selane (4aa)[9]



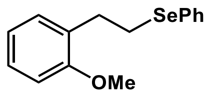
Light yellow oil, 98% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.39 – 7.28 (m, 6H), 7.26 (t, *J* = 6.8 Hz, 2H), 3.25 – 3.19 (m, 2H), 3.10 – 3.03 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.01, 132.61, 130.20, 129.07, 128.49, 128.37, 126.84, 126.39, 36.59, 28.68. **IR** (ATR): 22928, 1577, 1476, 1436, 1072, 1022, 732, 690 cm^{-1}.

(2-chlorophenethyl)(phenyl)selane (4ab)



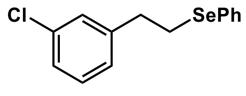
Light yellow oil, 97% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.41 – 7.37 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.29 – 7.20 (m, 3H), 3.25 – 3.14 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.49, 133.85, 132.65, 130.65, 129.97, 129.59, 129.05, 127.93, 126.89, 126.84, 34.68, 26.57. **IR** (ATR): 2929, 1577, 1473, 1437, 1051, 1022, 732 cm^{-1}. **HRMS** calculated for $C_{14}H_{13}ClSe$ $[M]^+$ 295.9871, found 295.9867.

(2-methoxyphenethyl)(phenyl)selane (4ac)



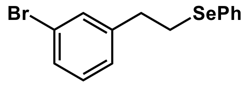
Light yellow oil, 95% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.36 – 7.25 (m, 4H), 7.18 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 3.24 – 3.19 (m, 2H), 3.11 – 3.05 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.43, 132.01, 130.74, 130.06, 129.34, 128.94, 127.74, 126.43, 120.42, 110.31, 55.15, 31.80, 26.96. **IR** (ATR): 2935, 1578, 1491, 1436, 1241, 1029, 751, 731, 690 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}OSe$ $[M]^+$ 292.0366, found 292.0365.

(3-chlorophenethyl)(phenyl)selane (4ad)



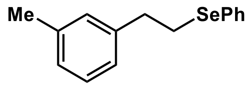
Light yellow oil, 88% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.21 (m, 3H), 7.12 (d, *J* = 6.7 Hz, 1H), 3.21 – 3.16 (m, 2H), 3.06 – 3.00 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.91, 134.21, 132.83, 129.84, 129.70, 129.12, 128.53, 127.04, 126.60, 126.58, 36.23, 28.27. **IR** (ATR): 3056, 2929, 1596, 1574, 1476, 1436, 1073, 1022, 862, 733, 689 cm^{-1}. **HRMS** calculated for $C_{14}H_{13}ClSe$ $[M]^+$ 295.9871, found 295.9870.

(3-bromophenethyl)(phenyl)selane (4ae)



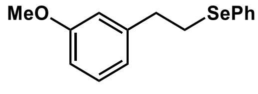
Light yellow oil, 91% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 3H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 3.18 (t, *J* = 7.5 Hz,, 2H), 3.02 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.21, 132.84, 131.45, 130.01, 129.81, 129.51, 129.12, 127.07, 127.05, 122.50, 36.21, 28.29. **IR** (ATR): 2927, 1577, 1567, 1474, 1436, 1425, 1071, 1022, 997, 780, 732 cm^{-1}. **HRMS** calculated for $C_{14}H_{13}BrSe$ $[M]^+$ 339.9366, found 339.9363.

(3-methylphenethyl)(phenyl)selane (4af)



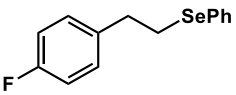
Light yellow oil, 90% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.38 – 7.29 (m, 3H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.13 – 7.04 (m, 3H), 3.24 – 3.18 (m, 2H), 3.07 – 3.00 (m, 2H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.95, 138.07, 132.57, 130.28, 129.14, 129.04, 128.38, 127.13, 126.80, 125.36, 36.55, 28.67, 21.36. **IR** (ATR): 2923, 1578, 1477, 1436, 1072, 1022, 774, 733, 690 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}Se$ $[M]^+$ 276.0417, found 276.0418.

(3-methoxyphenethyl)(phenyl)selane (4ag)



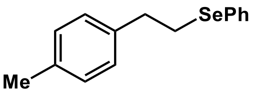
Light yellow oil, 88% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.38 – 7.31 (m, 3H), 7.28 (t, *J* = 7.9 Hz, 1H), 6.83 (dd, *J* = 10.2, 4.5 Hz, 2H), 6.79 (s, 1H), 3.86 (s, 3H), 3.25 – 3.17 (m, 2H), 3.08 – 2.99 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.71, 142.60, 132.62, 130.19, 129.46, 129.06, 126.85, 120.73, 114.21, 111.63, 55.15, 36.64, 28.52. **IR** (ATR): 2934, 1600, 1583, 1489, 1436, 1262, 1150, 1046, 734, 690 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}OSe$ $[M]^+$ 292.0366, found 292.0365.

(4-fluorophenethyl)(phenyl)selane (4ah)



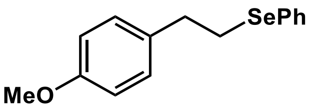
Light yellow oil, 91% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.36 – 7.30 (m, 3H), 7.22 – 7.16 (m, 2H), 7.06 – 7.00 (m, 2H), 3.18 (t, *J* = 7.5 Hz, 2H), 3.02 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.56 (d, *J* = 244.4 Hz), 136.62, 132.73, 130.02, 129.81 (d, *J* = 7.6 Hz), 129.10, 126.95, 115.24 (d, *J* = 21.4 Hz), 35.73, 28.85. **IR** (ATR): 2925, 1508, 1476, 1437, 1220, 1157, 1022, 823, 734, 690 cm^{-1}. **HRMS** calculated for $C_{14}H_{13}FSe$ $[M]^+$ 280.0167, found 280.0166.

(4-methylphenethyl)(phenyl)selane (4ai)



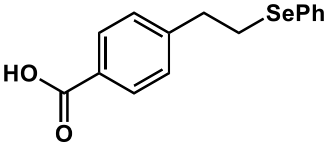
Light yellow oil, 93% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.36 – 7.29 (m, 3H), 7.15 (q, *J* = 8.1 Hz, 4H), 3.22 – 3.17 (m, 2H), 3.05 – 2.99 (m, 2H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.96, 135.92, 132.55, 130.28, 129.17, 129.05, 128.24, 126.78, 36.13, 28.86, 21.03. **IR** (ATR): 2922, 1577, 1514, 1476, 1436, 1022, 806, 733, 689 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}Se$ $[M]^+$ 276.0417, found 276.0412.

(4-methoxyphenethyl)(phenyl)selane (4aj)



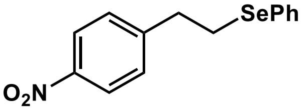
Light yellow oil, 95% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.36 – 7.29 (m, 3H), 7.19 – 7.14 (m, 2H), 6.92 – 6.87 (m, 2H), 3.85 (s, 3H), 3.22 – 3.16 (m, 2H), 3.03 – 2.97 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.18, 133.14, 132.56, 130.28, 129.33, 129.05, 126.79, 113.89, 55.25, 35.68, 29.08. **IR** (ATR): 2931, 1609, 1510, 1477, 1437, 1243, 1177, 1034, 818, 734, 690 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}OSe$ $[M]^+$ 292.0366, found 292.0362.

4-(2-(phenylselanyl)ethyl)benzoic acid (4ak)



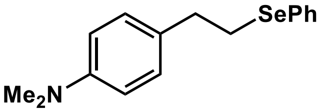
Yellow-white solid, 44%, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 5H), 3.17 (t, *J* = 7.8 Hz, 2H), 3.07 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.05, 147.44, 133.04, 130.63, 129.90, 129.30, 128.76, 127.63, 127.26, 36.74, 28.22. **IR** (ATR): 2924, 2549, 1674, 1609, 1420, 1314, 1286, 1175, 741, 691 cm^{-1}. **HRMS** calculated for $C_{15}H_{14}O_2Se$ $[M-H]^-$ 305.0081, found 305.0078

(4-nitrophenethyl)(phenyl)selane (4al)



*24 hours, orange oil, 25% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.49 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.27 (dd, *J* = 6.6, 4.1 Hz, 3H), 3.19 – 3.13 (m, 2H), 3.12 – 3.05 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.58, 146.83, 133.21, 129.56, 129.47, 129.36, 127.45, 123.88, 36.43, 28.00. **IR** (ATR): 2928, 1514, 1477, 1342, 853, 734, 690, 669 cm^{-1}. **HRMS** calculated for $C_{14}H_{13}NO_2Se$ $[M]^+$ 307.0112, found 307.0110.

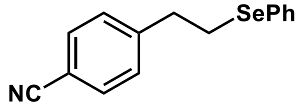
N,N-dimethyl-4-(2-(phenylselanyl)ethyl)aniline (4am)



Clear colorless oil, 70% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 3.13 (dd, *J* = 9.0, 7.0 Hz, 2H), 2.97 – 2.87

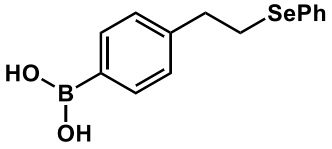
(m, 8H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 149.44, 132.54, 130.64, 129.36, 129.16, 129.14, 126.79, 113.08, 40.97, 35.74, 29.34. . **IR** (ATR): 2926, 2798, 1613, 1519, 1476, 1345, 1162, 805, 733, 690 cm^{-1}. **HRMS** calculated for C$_{16}$H$_{19}$NSeH [M+H]$^+$ 306.0761, found 306.0776.

4-(2-(phenylselanyl)ethyl)benzonitrile (4an)



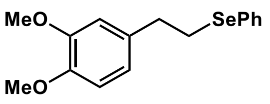
Light yellow oil, 77% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.55 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.33 (td, *J* = 4.3, 1.1 Hz, 5H), 3.22 – 3.16 (m, 2H), 3.13 – 3.06 (m, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 149.91, 149.75, 133.13, 129.62, 129.31, 127.37, 123.91, 35.88, 27.31. **IR** (ATR): 3054, 2930, 2226, 1477, 1436, 1021, 818, 735, 690, 669 cm^{-1}. **HRMS** calculated for C$_{15}$H$_{13}$NSe [M]$^+$ 287.0214, found 287.0221.

(4-(2-(phenylselanyl)ethyl)phenyl)boronic acid (4ao)



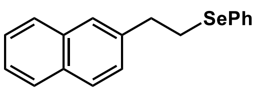
Yellow-white solid, 61%, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.16 (d, *J* = 7.9 Hz, 2H), 7.55 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.38 – 7.28 (m, 5H), 3.21 (t, *J* = 7.9 Hz, 2H), 3.09 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 145.93, 136.05, 132.88, 130.21, 129.27, 128.25, 127.11, 36.96, 28.52. IR: 2925, 1608, 1407, 1339, 1307, 1181, 1020, 733, 690 cm^{-1}. **HRMS** calculated for C$_{14}$H$_{14}$BO$_2$Se [M-H]$^-$ 305.0255, found 305.0263.

(3,4-dimethoxyphenethyl)(phenyl)selane (4ap)



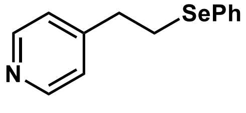
Light yellow oil, 95% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.60 – 7.54 (m, 2H), 7.37 – 7.28 (m, 3H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.76 (s, 1H), 3.92 (s, 6H), 3.24 – 3.16 (m, 2H), 3.05 – 2.98 (m, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 148.89, 147.61, 133.62, 132.60, 130.27, 129.03, 126.81, 120.27, 111.72, 111.26, 55.90, 55.82, 36.17, 28.98. **IR** (ATR): 2932, 1511, 1256, 1234, 1141, 1026, 804, 734, 690 cm^{-1}. **HRMS** calculated for C$_{16}$H$_{18}$O$_2$Se [M]$^+$ 322.0472, found 322.0474.

(2-(naphthalen-2-yl)ethyl)(phenyl)selane (4aq)



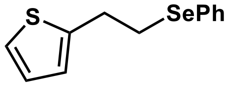
Light yellow oil, 92% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.85 – 7.75 (m, 3H), 7.62 (s, 1H), 7.57 – 7.52 (m, 2H), 7.48 – 7.41 (m, 2H), 7.35 – 7.27 (m, 4H), 3.28 – 3.21 (m, 2H), 3.20 – 3.14 (m, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 138.45, 133.55, 132.72, 132.22, 130.18, 129.09, 128.12, 127.63, 127.50, 126.93, 126.90, 126.63, 126.04, 125.41, 36.76, 28.59. **IR** (ATR): 2924, 1577, 1507, 1476, 1436, 1072, 1022,815,733, 690 cm^{-1}. **HRMS** calculated for C$_{18}$H$_{16}$Se [M]$^+$ 312.0417, found 312.0411.

4-(2-(phenylselanyl)ethyl)pyridine (4ar)



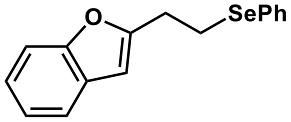
Light yellow oil, 90% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.56 (s, 2H), 7.64 – 7.51 (m, 2H), 7.33 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.16 (d, *J* = 5.1 Hz, 2H), 3.19 (t, *J* = 7.8 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 149.91, 149.75, 133.13, 129.62, 129.31, 127.37, 123.91, 35.88, 27.31. **IR** (ATR): 3054, 2930, 2226, 1477, 1436, 1021, 818, 735, 690, 669 cm^{-1}. **HRMS** calculated for C$_{13}$H$_{13}$NSe [M]$^+$ 262.0302, found 262.0309.

2-(2-(phenylselanyl)ethyl)thiophene (4as)



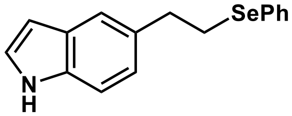
Light yellow oil, 70% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.12 (m, 5H), 6.40 (d, *J* = 0.6 Hz, 1H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.76, 133.00, 129.93, 129.27, 127.18, 126.96, 124.92, 123.74, 30.91, 28.93. **IR** (ATR): 3069, 2929, 1577, 1476, 1436, 1232, 1022, 850, 823, 733, 688, 669 cm^{-1}. **HRMS** calculated for $C_{12}H_{12}SSe$ $[M]^+$ 263.9852, found 263.9846.

2-(2-(phenylselanyl)ethyl)benzofuran (4at)



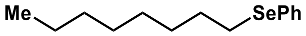
Light yellow oil, 88% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.3, 2.1 Hz, 2H), 7.57 (d, J = 7.3 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.39 – 7.23 (m, 5H), 6.51 (d, J = 0.6 Hz, 1H), 3.33 (t, J = 7.4 Hz, 2H), 3.28 – 3.20 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.48, 154.80, 133.14, 129.67, 129.25, 128.79, 127.26, 123.61, 122.68, 120.58, 110.95, 103.05, 29.79, 25.03. **IR** (ATR): 3056, 2931, 1540, 1474, 1455, 1436, 1255, 734, 690 cm^{-1}. **HRMS** calculated for $C_{16}H_{14}OSe$ $[M]^+$ 302.0211, found 302.0199.

5-(2-(phenylselanyl)ethyl)-1H-indole (4au)



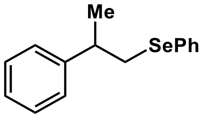
Bright yellow oil, 69% yield, >20:1 *rr*. Ran reaction for 16 hours. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.52 (d, *J* = 6.7 Hz, 2H), 7.44 (s, 1H), 7.33 – 7.20 (m, 4H), 7.16 (t, *J* = 2.8 Hz, 1H), 7.02 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.49 (s, 1H), 3.19 (dd, *J* = 9.6, 6.7 Hz, 2H), 3.08 (dd, *J* = 9.1, 6.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.17, 133.10, 132.98, 131.11, 129.62, 128.66, 127.24, 125.08, 123.35, 120.56, 111.55, 102.94, 37.35, 30.12. **IR** (ATR): 3412 (br), 2925, 1577, 1475, 1436, 1415, 1066, 1022, 908, 795, 755, 723, 690, 669 cm^{-1}. **HRMS** calculated for $C_{16}H_{14}NSe$ $[M-H]^-$ 300.0292, found 300.0293.

octyl(phenyl)selane (4av)



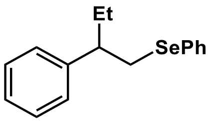
Light yellow oil, 87% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.28 – 7.20 (m, 3H), 2.95 – 2.88 (m, 2H), 1.75 – 1.64 (m, 2H), 1.44 – 1.36 (m, 2H), 1.34 – 1.19 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.36, 130.72, 128.95, 126.56, 31.78, 30.14, 29.83, 29.14, 29.03, 27.95, 22.62, 14.07. **IR** (ATR): 2923, 2852, 1476, 1457, 1437, 732, 690 cm^{-1}. **HRMS** calculated for $C_{14}H_{22}Se$ $[M]^+$ 270.0887, found 270.0884.

(±)-phenyl(2-phenylpropyl)selane (4aw)



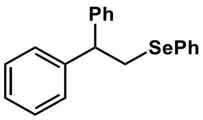
Light yellow oil, 94% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.24 (m, 6H), 3.29 (dd, *J* = 11.6, 6.3 Hz, 1H), 3.15 (dd, *J* = 11.6, 6.3 Hz, 1H), 3.13 – 3.05 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.88, 132.50, 130.78, 128.99, 128.48, 126.85, 126.69, 126.53, 40.29, 36.66, 21.72. **IR** (ATR): 2962, 2925, 1578, 1477, 1451, 1436, 1072, 1022, 733, 760, 699 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}Se$ $[M]^+$ 276.0417, found 276.0410.

(±)-phenyl(2-phenylbutyl)selane (4ax)



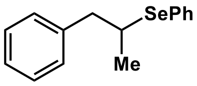
Light yellow oil, 90% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.50 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.22 (d, *J* = 7.2 Hz, 2H), 3.25 (d, *J* = 7.4 Hz, 2H), 2.86 – 2.79 (m, 1H), 2.05 – 1.93 (m, 1H), 1.77 – 1.67 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 144.09, 132.41, 130.97, 128.96, 128.39, 127.58, 126.61, 126.55, 47.98, 35.10, 29.10, 12.07. **IR** (ATR): 2960, 2924, 1577, 1476, 1436, 1072, 1022, 732, 690 cm^{-1}. **HRMS** calculated for $C_{16}H_{18}Se$ [M]$^+$ 290.0574, found 290.0570.

(±)-(2,2-diphenylethyl)(phenyl)selane (4ay)



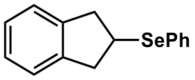
Light yellow oil, 92% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.56 – 7.50 (m, 2H), 7.39 – 7.34 (m, 4H), 7.33 – 7.25 (m, 9H), 4.34 (t, *J* = 8.0 Hz, 1H), 3.66 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 143.54, 132.77, 130.70, 129.05, 128.54, 127.81, 126.89, 126.68, 51.53, 33.72. **IR** (ATR): 3026, 1577, 1491, 1476, 1450, 1436, 1022, 731, 690 cm^{-1}. **HRMS** calculated for $C_{20}H_{18}Se$ [M]$^+$ 338.0574, found 338.0572.

(±)-phenyl(1-phenylpropan-2-yl)selane (4az)



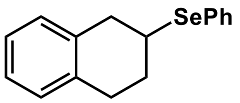
Light yellow oil, 82% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.66 – 7.60 (m, 2H), 7.39 – 7.31 (m, 5H), 7.31 – 7.25 (m, 1H), 7.24 – 7.19 (m, 2H), 3.64 – 3.54 (m, 1H), 3.15 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.83 (dd, *J* = 13.7, 9.2 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 139.77, 134.92, 129.35, 129.07, 128.94, 128.31, 127.47, 126.36, 44.08, 40.03, 21.05. **IR** (ATR): 2920, 1578, 1495, 1476, 1453, 1436, 1022, 736, 691 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}Se$ [M]$^+$ 276.0417, found 276.0415.

(2,3-dihydro-1H-inden-2-yl)(phenyl)selane (4aaa)



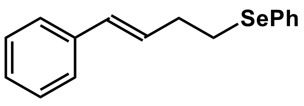
Light yellow oil, 93% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.59 – 7.54 (m, 2H), 7.32 – 7.27 (m, 3H), 7.22 – 7.13 (m, 4H), 4.17 – 4.10 (m, 1H), 3.40 (dd, *J* = 16.4, 7.4 Hz, 2H), 3.08 (dd, *J* = 16.4, 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 141.98, 133.98, 130.09, 129.03, 127.28, 126.59, 124.39, 40.74, 40.24. **IR** (ATR): 2942, 1578, 1476, 1436, 1224, 1022, 734, 690 cm^{-1}. **HRMS** calculated for $C_{15}H_{14}Se$ [M]$^+$ 274.0261, found 274.0260.

(±)-phenyl(1,2,3,4-tetrahydronaphthalen-2-yl)selane (4aab)



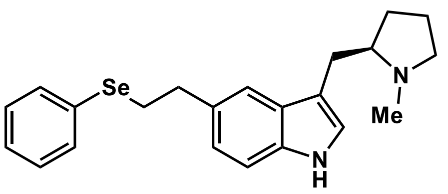
Light yellow oil, 79%, >20:1 *rr*. **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.62 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.31 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.17 – 7.06 (m, 3H), 7.04 (d, *J* = 6.4 Hz, 1H), 3.66 (tdd, *J* = 10.3, 5.0, 3.1 Hz, 1H), 3.23 (dd, *J* = 16.5, 4.9 Hz, 1H), 2.99 (dd, *J* = 17.0, 9.3 Hz, 1H), 2.93 – 2.99 (m, 1H), 2.85 (ddd, *J* = 20.3, 13.1, 8.1 Hz, 1H), 2.29 (dddd, *J* = 8.7, 7.5, 5.2, 3.8 Hz, 1H), 1.95 (dtd, *J* = 13.1, 10.2, 5.7 Hz, 1H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 135.70, 135.60, 135.03, 129.14, 129.08, 128.97, 128.85, 127.69, 126.13, 125.92, 39.15, 36.96, 30.45, 29.33. **IR** (ATR): 3057, 3016, 2924, 1578, 1494, 1476, 1451, 1435, 1022, 738, 690, 670 cm^{-1}. **HRMS** calculated for $C_{16}H_{16}Se$ [M]$^+$ 288.0418, found 288.0412.

(*E*)-phenyl(4-phenylbut-3-en-1-yl)selane (4aac)



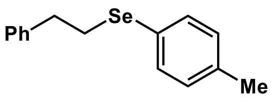
Light yellow oil, 87% yield, >20:1 *rr*. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.17 (d, *J* = 7.3 Hz, 2H), 3.17 – 3.09 (m, 2H), 3.02 – 2.93 (m, 2H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 137.33, 132.78, 131.24, 130.20, 129.05, 128.91, 128.49, 127.16, 126.86, 126.07, 33.70, 27.18. **IR** (ATR): 2921, 1633, 1578, 1477, 1436, 1072, 1022, 963, 733, 690 cm^{-1}. **HRMS** calculated for C$_{16}$H$_{16}$Se [M]$^+$ 288.0417, found 288.0412.

(R)-3-((1-methylpyrrolidin-2-yl)methyl)-5-(2-(phenylselanyl)ethyl)-1H-indole (4aad)



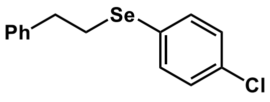
Light yellow solid, 31% yield, >20:1 *rr*. Purified by crystallization from DCM/hexanes. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.24 (s, 1H), 7.51 (dd, J = 7.8, 1.7 Hz, 2H), 7.37–7.16 (m, 5H), 7.04 (dd, J = 8.3, 1.5 Hz, 1H), 3.66 (dd, J = 10.6, 7.2 Hz, 1H), 3.40 (dd, J = 14.3, 5.4 Hz, 1H), 3.26–3.19 (m, 2H), 3.12 (dd, J = 9.5, 5.2 Hz, 3H), 3.02 (dd, J = 14.2, 8.7 Hz, 1H), 2.60 (s, 3H), 2.14–1.96 (m, 3H), 1.96–1.77 (m, 2H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 135.41, 132.67, 132.47, 130.77, 129.27, 127.43, 126.95, 123.78, 123.20, 117.97, 111.67, 111.63, 68.29, 56.97, 40.41, 37.00, 31.24, 29.93, 27.90, 21.89. **IR** (ATR): 3231, 2922, 1575, 1477, 1436, 1402, 1022, 800, 736, 691, 650 cm^{-1}. **HRMS** calculated for C$_{22}$H$_{26}$SeN$_2$H [M+H]$^+$ 395.1367, found 395.1383.

phenethyl(*p*-tolyl)selane (4ba)



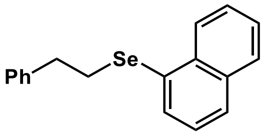
Light yellow oil, 68% yield, >20:1 *rr*. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.18 – 3.04 (m, 2H), 3.04 – 2.91 (m, 2H), 2.34 (s, 3H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 141.28, 137.11, 133.35, 130.04, 128.62, 128.53, 126.49, 126.37, 36.81, 29.16, 21.23. **IR** (ATR): 3024.97, 2921.01, 1488.51, 1452.60, 1015.50, 800.05, 749.51, 697.21 cm^{-1}. **HRMS** calculated for C$_{15}$H$_{16}$Se [M]$^+$ 276.0418, found 276.0425.

(4-chlorophenyl)(phenethyl)selane (4ca)



Light yellow oil, 46% yield, >20:1 *rr*. ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.17 (d, J = 7.3 Hz, 2H), 3.17 – 3.10 (m, 2H), 3.02 – 2.95 (m, 2H). ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 140.87, 134.20, 133.46, 133.26, 129.36, 128.69, 128.53, 126.65, 36.66, 29.27. **IR** (ATR): 3025.42, 2929.07, 1472.20, 1088.07, 1009.58, 808.59, 697.51 cm^{-1}. **HRMS** calculated for C$_{14}$H$_{13}$Se [M]$^+$ 295.9869, found 295.9876.

naphthalen-1-yl(phenethyl)selane (4da)



Light yellow oil, 33% yield, >20:1 *rr*. Product could not be separated fully from diselenide, sample contains 69% dinaphthyl diselenide. ^{1}**H NMR** (499 MHz, CDCl$_3$) δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.86-7.77 (m, 5H) 7.53 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 3.27 – 3.12 (m, 2H), 3.06 – 2.92 (m, 2H). ^{13}**C NMR** (125 MHz,

$CDCl_3$) δ 141.15, 134.48, 134.15, 132.33, 129.64, 128.77, 128.61, 128.52, 128.41, 127.76, 126.73, 126.51, 126.34, 125.90, 36.72, 29.09. **IR** (ATR): 3047.23, 1499.77, 787.04, 763.90, 651.44 cm^{-1}. **HRMS** calculated for $C_{18}H_{16}Se$ $[M]^+$ 312.0418, found 312.0417.

3.1 Scope limitations

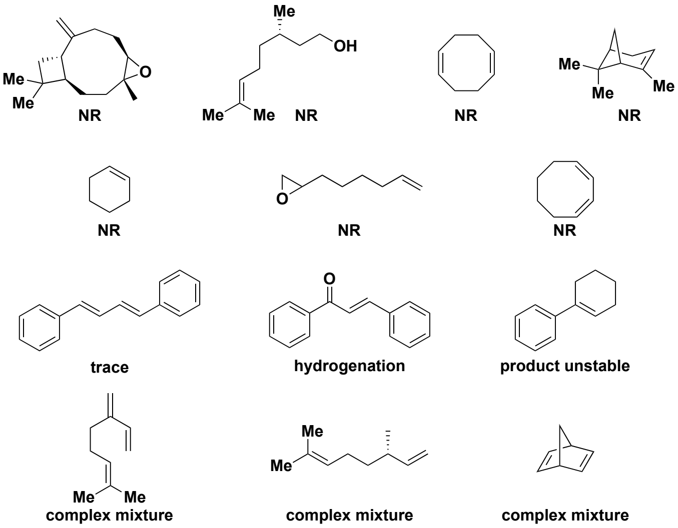


Fig. S1 Table of substrates which exhibited poor reactivity or strong side-reactivity.

4. Sensitivity assessment

In order to check the reproducibility and limitations of the presented transformation, a series of sensitivity tests are presented.[10]

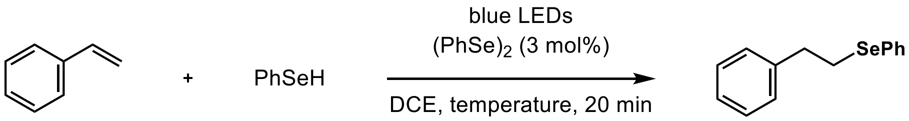
For most reactions a stock solution was prepared.

Stock Solution: In a N_2-filled glovebox, benzeneselenol (2a, 1.20 mmol, 1.5 equiv.) containing 3 mol% diphenyl diselenide (3a) was added to a solution of styrene (0.80 mmol, 1.0 equiv.) in DCE (1.34 mL) in a 1-dram vial.

Standard Conditions: All reactions were performed on a 0.10 mmol scale. To 8 different oven-dried 1-dram vials equipped with Teflon-coated magnetic stir bars, 167 uL of stock solution were added. An additional vial was prepared using degassed starting material for the low oxygen parameter. All vials were treated as mentioned in Table S1 and then stirred under irradiation with blue LEDs for 20 min. Solvent was removed by rotary evaporation. Triphenylmethane (24.4 mg, 0.10 mmol, 1.0 equiv.) was added as an internal standard and the crude ^{1}H NMR was measured.

Large Scale Reaction: In a N_2-filled glovebox, benzeneselenol (2a, 3.00 mmol, 1.5 equiv.) containing 3 mol% diphenyl diselenide (3a) was added to a solution of styrene (2.00 mmol, 1.0 equiv.) in DCE (6.7 mL) in a 2-dram vial. The reaction was stirred under irradiation with blue LEDs for 20 min. Solvent was removed by rotary evaporation. 1.0 mL $CDCl_3$ was added and 5% of the resulting solution was added to an NMR tube. Triphenylmethane (24.4 mg, 0.10 mmol, 1.0 equiv.)

was added as an internal standard and the crude ^{1}H NMR was measured.



entry	modification	execution	% yield^a	% deviation
1	high *c*	no additional solvent	97	0
2	low *c*	+0.5 mL DCE	80	-17
3	high H_2O	+0.13 mL DCE, + 4 uL H_2O	85	-12
4	low O_2	+0.13 mL DCE, all material degased	97	0
5	high O_2	+0.13 mL DCE, + 4 mL air	71	-26
6	**control**	+0.13 mL DCE	97	--
7	high *I*	+0.13 mL DCE, 2.75 cm away from light	99	+2
8	low *I*	+0.13 mL DCE, 44 cm away from light	83	-14
9	low *T*	+0.13 mL DCE, 20^{0}C	55	-42
10	high *T*	+0.13 mL DCE, 70^{0}C	59	-38
11	large scale	2.0 mmol scale	69	-28

^{a}crude NMR yield

Table S1. Parameters screened for sensitivity analysis.

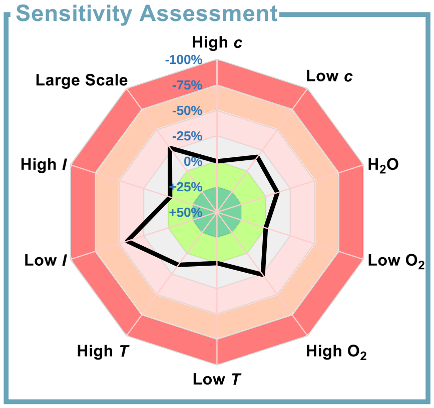


Fig. S2 Graphical depiction of Sensitivity Assessment.

5. Mechanistic studies

5.1 UV-Vis studies

In an N_2-filled glovebox, 1.00 mL stock solutions of PhSeH (**1a,** 50.0 mM), styrene (**2a,** 50.0 mM), $(PhSe)_2$ (**3a,** 1.5 mM) and $Rh(cod)_2BF_4$ (5.0 mM) in DCE were prepared in 1-dram vials. The solutions were removed from the glove box in order to take spectra. Solutions of each of the starting materials were diluted tenfold, and an additional $(PhSe)_2$ solution was made by diluting threefold.

The PhSeH solution's peak at 330 nm had an intensity close to that of the 0.15 mM $(PhSe)_2$, and less than that of the 0.5 mM solution. This was consistent with approximately 3% $(PhSe)_2$ in the PhSeH solution, which is what was observed *via* ^{1}H NMR. Previous studies of purified PhSeH taken in inert atmosphere and without ambient light have found that there is no absorption above 300 nm, consistent with our findings.[11] The $Rh(cod)_2BF_4$ spectrum offers insight into why the facile photocatalytic background reaction shuts down for the Markovnikov adduct, even with irradiation. At 330 nm, $Rh(cod)_2BF_4$ absorption intensity was nearly seven times that of the $(PhSe)_2$; therefore, it is likely that the competitive $Rh(cod)_2BF_4$ absorption precludes $(PhSe)_2$ excitation.

Fluorescence spectroscopy was also attempted, however none of the reactants nor the reaction mixture were fluorescent. This ruled out the possibility of conducting Stern-Volmer quenching studies.

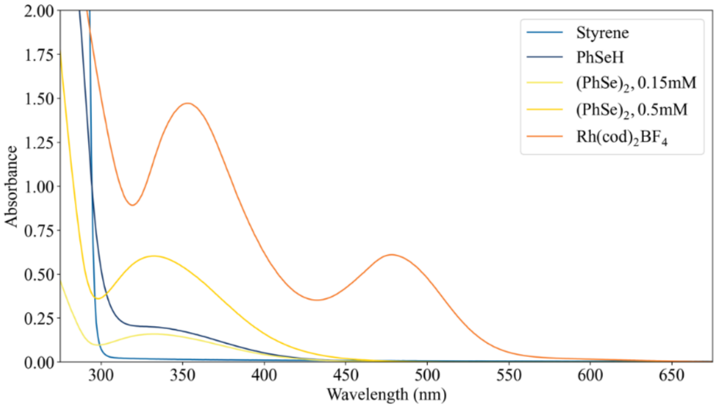


Fig. S3 UV-Visible spectra of PhSeH (**1a,** 5.0 mM), styrene (**2a,** 5.0 mM), $(PhSe)_2$ (**3a,** 0.15 and 0.5 mM) and $Rh(cod)_2BF_4$.

5.2 Ultrafast Transient Absorption (TA) Spectroscopy

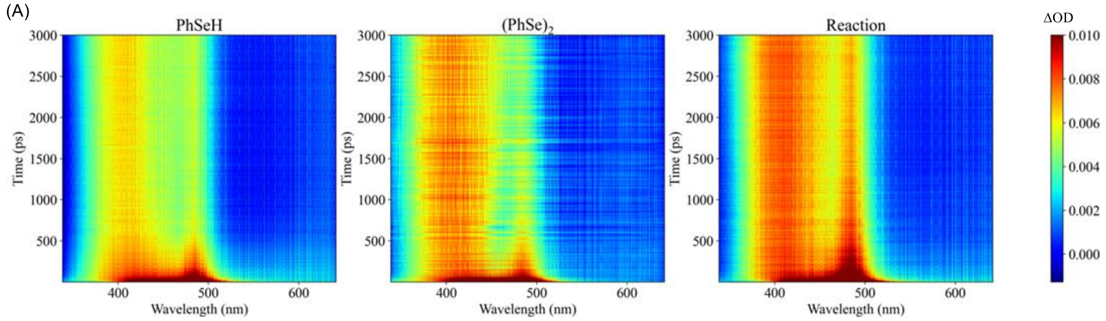
In an N_2-filled glovebox, solutions of **1a** (15 mM), **2a** (15 mM), **3a** (0.45 mM), as well as a solution reflecting hydroselenation reaction conditions (1.0 eq. **1a** (10 mM), 1.5 eq. **2a** (15 mM)) in DCE were made such that the maximum absorbance at 330 nm was below 0.3. Each solution was placed in a 1 mL quartz cuvette and sealed prior to removal from the glovebox.

Ultrafast time-resolved absorption has been performed in standard pump-probe geometry utilizing amplified femtosecond (fs) laser system. Femtosecond oscillator (MaiTai, Spectra Physics) was used to seed regenerative amplified system (Spitfire Ace, Spectra Physics) to produce high energy 80 fs pulses at 800 nm at 1 kHz repetition rate. The beam has been split to multiple beamlines, with one going through optical parametric generator/amplifier (Topas, Light Conversion) to generate strong pulse at 660 nm. The frequency of this pulse has been doubled using BBO crystal to generate pump pulse at 330 nm (1 mJ at sample). Another beam has been used to generate broad white-light continuum in 2 mm thick CaF_2 crystal, covering spectral range from 320 nm to 900 nm. The probe has been fiber-coupled to CCD based spectrometer and transient absorption spectrum has been recorded at different position of time delay.

Data from 480 nm was fit using SciPy's optimize least squares function, with exponential decay equation:

$$y = A_1 * e^{-x/\tau_1} + A_2 * e^{-x/\tau_2} + b$$

TA spectra for styrene exhibited no deviations from the ground state spectra. For $(PhSe)_2$, PhSeH, and the reaction mixture, excited state absorption peaks can be observed with maxima around approximately 380 and 480 nm. Because there may be significant influence from the pump bleaching region on the peak at 380 nm, analysis was focused on the 480 nm peak. For the $(PhSe)_2$ data at 480 nm, the decay of a singlet state within first several hundred picoseconds (ps) can be observed, coming to a plateau (Fig. S4). This plateau is likely the spin-forbidden plateau, associated with spin-forbidden transition to the triplet state. The slope of the plateau suggests that the $(PhSe)_2$ triplet lifetime is at least several tens of nanoseconds (ns). A second-degree exponential fit results in a second time constant of 388 ps, which is attributed to ISC time. Therefore, the TA spectra indicate that the $(PhSe)_2$ triplet can be formed within a few hundred. The PhSeH and reaction mixture solutions produced similar time constants. Thus, it can be concluded that the three solutions did not exhibit significant deviations for the first three ns, and so it is likely that $(PhSe)_2$ is excited the photoactive species, and undergoes homolytic bond cleavage to form free selenide radicals following the formation of a triplet state.



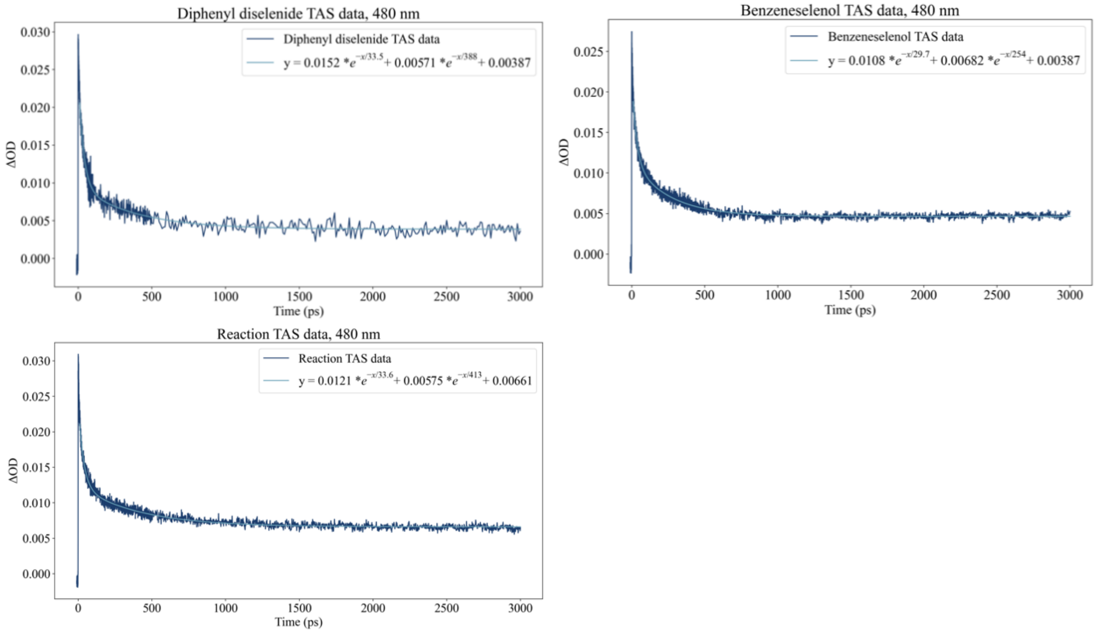
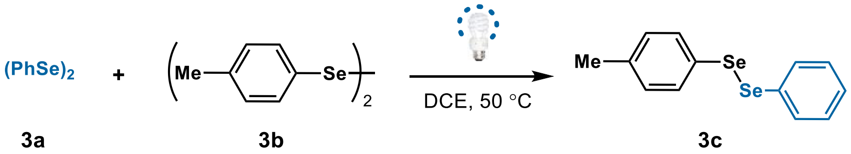


Fig. S4 (A) False color maps of the TA spectra for PhSeH (**2a**), (PhSe)$_2$ (**3a**), and the reaction mixture. **B** (PhSe)$_2$ (**3a**), **C.** PhSeH (**2a**), and **D.** reaction mixture second-degree exponential fits for 480 nm data.

5.3 Reaction with AIBN

In a N$_2$-filled glovebox, AIBN (9.9 mg, 0.6 equiv.) and triphenylmethane (16.2 mg) were weighed into a 1-dram vial, and triphenylmethane (12.6 mg) was weighed into a second vial. 0.400 mL DCE was added, then styrene (**1a**, 11.5 µL, 0.100 mmol), PhSeH (**2a**, 15.9 µL, 0.150 mmol) and a stir bar. The vials were capped and wrapped in aluminum foil, then placed in a 70 ºC heating mantle and stirred for four hours. The resulting mixture was then cooled to room temperature and the solvent was evaporated by rotary evaporation. ^{1}H NMR analysis of the unpurified reaction mixture indicated a 54% yield for the AIBN reaction, and a 15% yield for the control.

5.4 Crossover experiment



observed via ^{77}Se NMR

Scheme S1 Crossover study with two unique diselenides.

In an N$_2$-filled glovebox, diphenyl diselenide (**3a,** 31.2 mg, 99.9 µmol) and 1,2-di-*p*-tolyl-diselenide (**3b,** 33.7 mg, 99.1 µmol) were combined in a 1-dram vial, dissolved in DCE-*d4* (0.60 mL) and added to a J. Young NMR tube. The J. Young tube was capped, removed from the glovebox and irradiated with blue LEDs for 30 minutes. In a second vial, diphenyl diselenide (**3a,** 31.7 mg, 102 µmol), 1,2-di-*p*-tolyl-diselenide (**3b,** 37.6 mg, 111 µmol) and azobisisobutyronitrile (AIBN, 16.4 mg, 99.9 µmol) were combined in a 1-dram vial, dissolved in DCE-*d4* (0.60 mL) stirred at 70 ºC for 30 minutes. The solution was then transferred to a J. Young NMR tube and removed from the glovebox. Crossover product was observed based on crude ^{77}Se NMR (similarly to previous diselenide crossover studies, crossover product could not be observed by GCMS).[12] **^{77}Se NMR** (95 MHz, DCE) δ 471.89, 467.83, 458.70, 454.71. Peaks at δ 458.70 and 467.83 correspond to **3a** and **3b**, respectively.

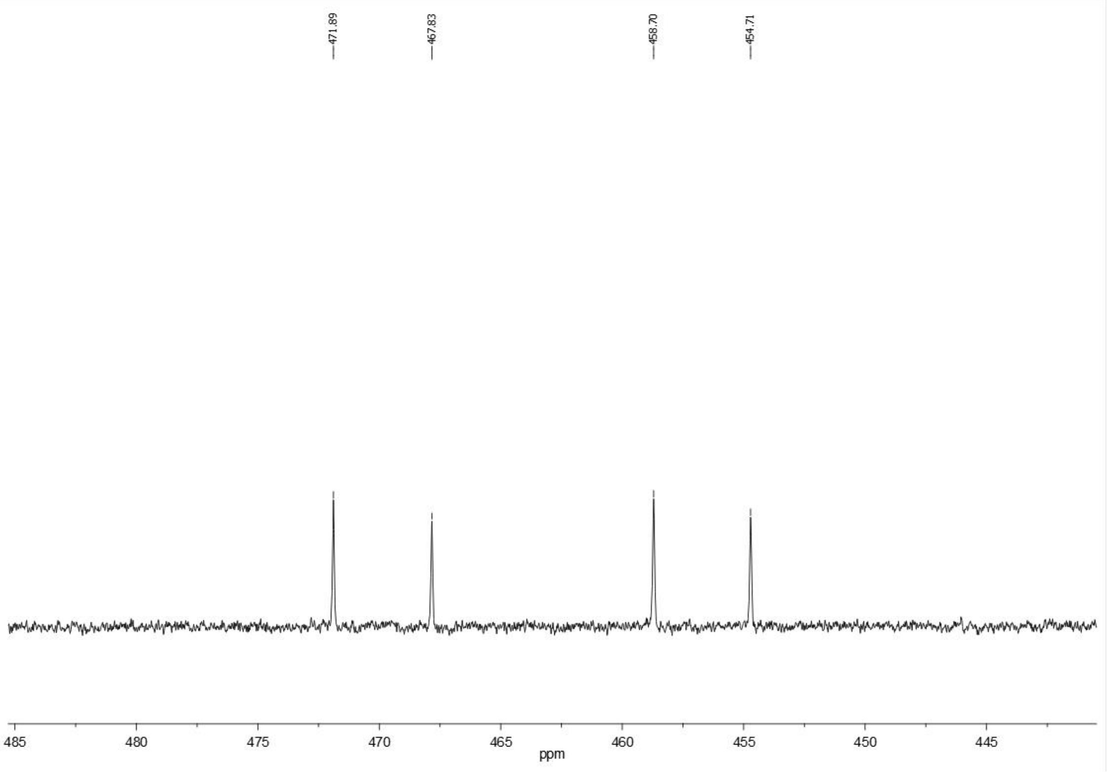


Fig. S5 ^{77}Se NMR of crude crossover reaction.

5.5 Dark-Light experiment

In an N_2-filled glovebox, 1,3,5-trimethoxybenzene (17.3 mg, 0.103 mmol), **1a** (24.0 mg, 0.150 mmol), and **2a** (11.7 mg, 0.112 mmol) were combined in a 1-dram vial and dissolved in DCE (0.80 mL). The vial was sealed with a septa cap, removed from the glovebox. While stirring, the vial was irradiated; the light was turned on and off incrementally every 5 minutes for 25 minutes. Aliquots of the reaction mixture (100 µL) were taken every two minutes, diluted with ethyl acetate, and removed from light. The reaction halts without light, and 1,3,5-trimethoxybenzene was determined to have no effect on the reaction yield. The amount of **4aa** was monitored by GC-FID analysis.

Time (min)	0	5	10	15	20	25
Conversion (%)	0	21.5	21.6	35.9	36.6	47.5

Table S2 Reaction progress during dark-light experiment.

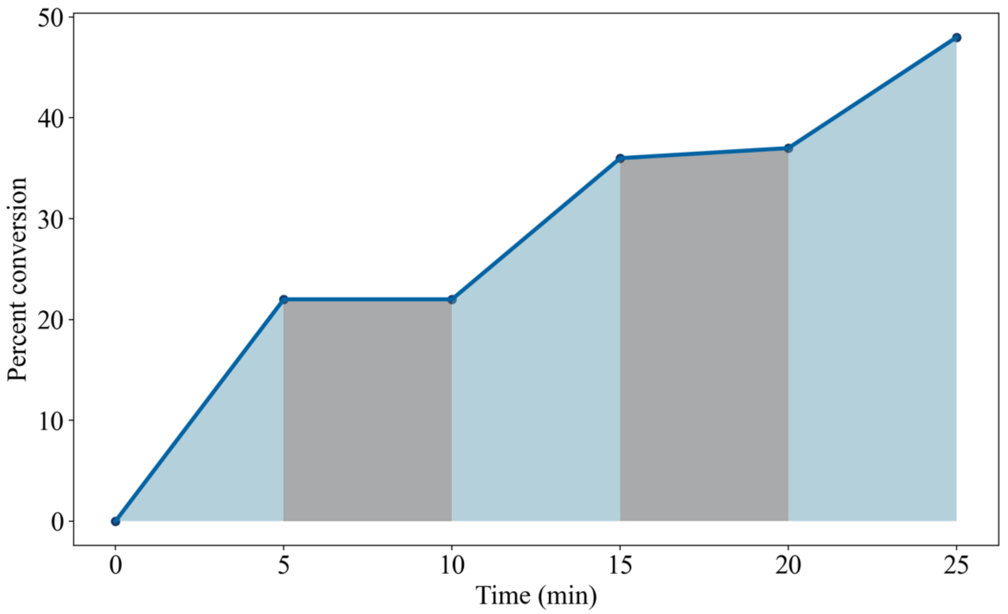
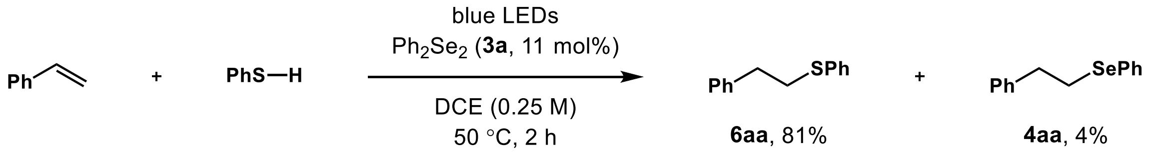


Fig. S6 Reaction progress during dark-light experiment. Blue-shaded sections represent the light being on, gray-shaded sections represent the light being off.

5.6 Hydrothiolation



Scheme S2 Diselenide-catalyzed hydrothiolation of styrene **1a**.

In an N_2-filled glovebox, a 1-dram vial was charged with **3a** (3.3 mg, 0.011 mmol, 0.11 equiv.) and DCE (0.4 mL). Styrene **1a** (10.2 mg, 0.979 mmol, 1.0 equiv.) and thiophenol (15.3 µL, 150 mmol, 1.5 equiv.) were added to the solution, which was then capped and removed from the glovebox. This solution was irradiated with stirring for 2 hours. DCE was evaporated and a mixture of sulfide **6aa** (81% yield) and **4aa** (4%) was obtained after preparative thin-layer chromatography as a faint yellow oil.

5.7 Diastereoselectivity studies

5.7.1 Cyclic system

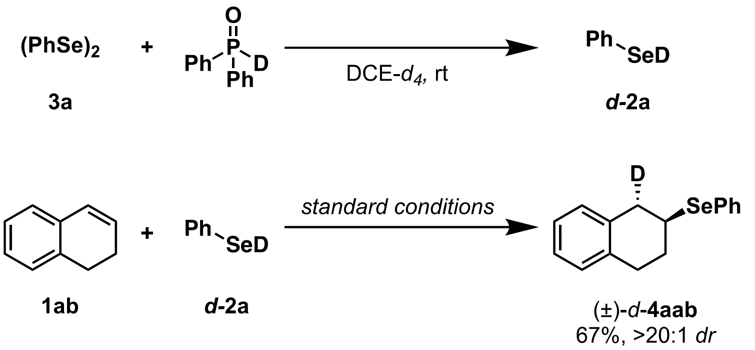


Fig. S7 Formation of deuterated selenol and addition to substrate **1ab**.

In an N$_2$-filled glovebox, deuterated diphenylphosphine oxide (60.9 mg, 0.3 mmol, 3.0 eq., 80% D-incorporation) was adding to a solution of **3a** (94.2 mg, 0.3 mmol, 3.0 eq.) in DCE-d_4 (0.4 mL) in a 1-dram vial. The reaction mixture was stirred under room temperature and monitor by GC-FID until **3a** disappeared (1 h). Alkene **1ab** (13 mg, 0.1 mmol, 1.0 eq.) was added to the solution and the vial was brought out from glovebox and irradiated with blue LEDs for 30 min. DCE was evaporated and the pure **d-4aab** (67% yield) was obtained after preparative thin-layer chromatography (hexane) as a faint yellow oil. D-incorporation was only observed at a single site (δ 3.21), and was approximately 60%, with additional H-incorporation likely due to trace adventitious water. The vicinal coupling constant (4.9 Hz) indicates that this proton is *syn* to the neighboring proton, and therefore is *anti* to the selenide. Thus, only *anti*-addition product ***d*-4aab** was observed based on the ^{1}H NMR (Fig. S8) and ^{2}H NMR (Fig. S9). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.64 – 7.58 (m, 2H), 7.33 – 7.25 (m, 3H), 7.14 – 7.05 (m, 3H), 7.02 (d, *J* = 6.7 Hz, 1H), 3.68 – 3.60 (m, 1H), *3.21 (dd, J = 16.6, 4.9 Hz, 0.4H)*, 3.01 – 2.91 (m, 2H), 2.89 – 2.79 (m, 1H), 2.32 – 2.24 (m, 1H), 1.99 – 1.88 (m, 1H). **^{2}H NMR** (500 MHz, CDCl$_3$) δ 3.21. **^{13}C NMR** (126 MHz, CDCl$_3$) δ 135.56, 135.46, 134.88, 128.99, 128.92, 128.82, 128.73, 127.54, 125.98, 125.76, 39.01, 36.82, 30.31, 29.18. **IR** (ATR): 3066, 2925, 1578, 1494, 1476, 1435, 1021, 733 cm^{-1}.

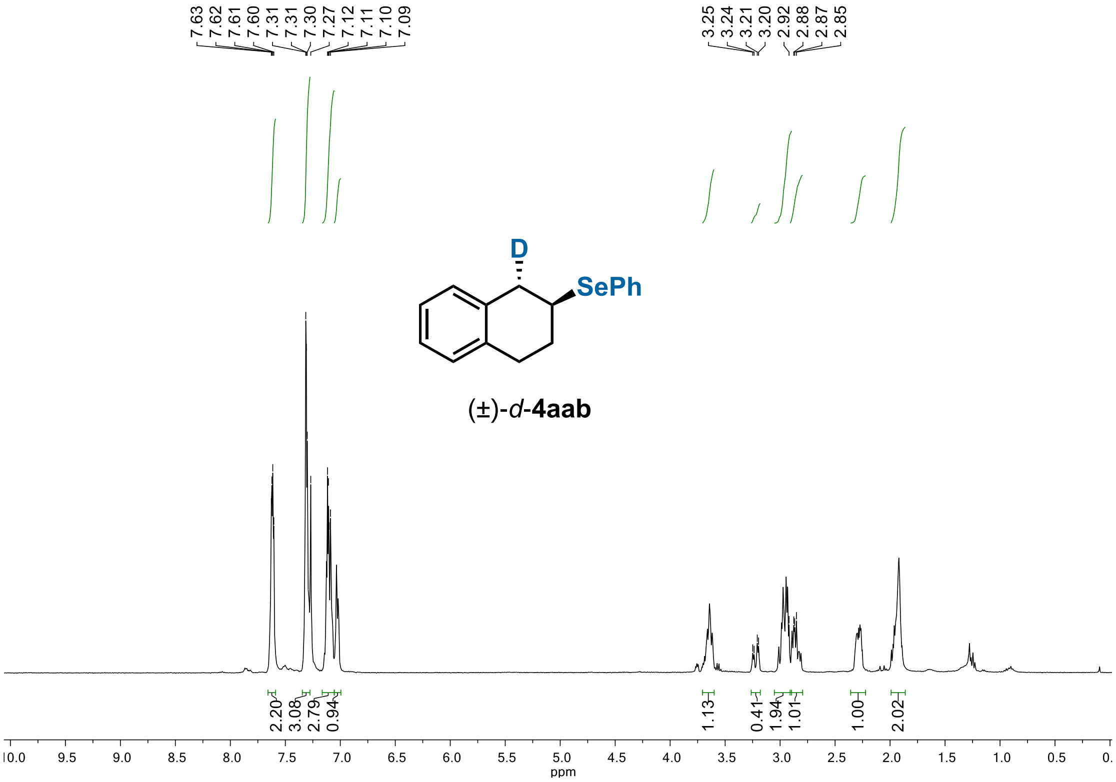


Fig. S8 ^{1}H NMR for ***d*-4aab**

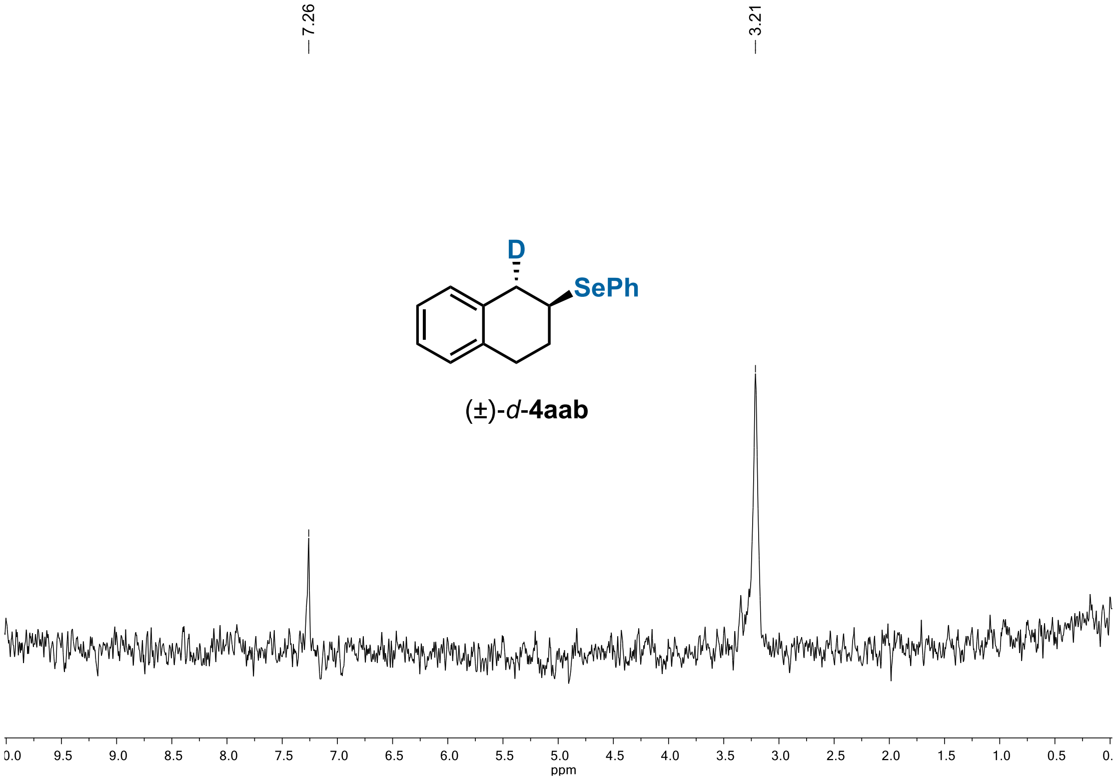


Fig. S9 ^{2}H NMR for ***d*-4aab**

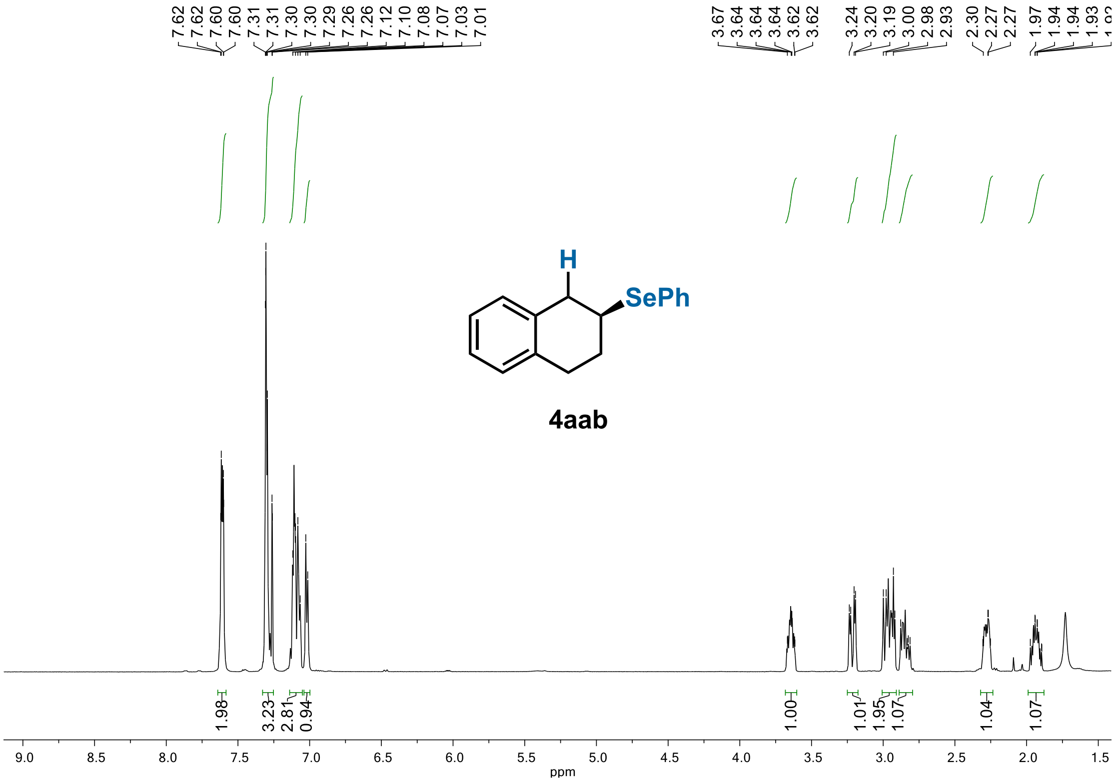


Fig. S10 ^{1}H NMR for **4aab**

5.7.2 Cyclic hydrothiolation system

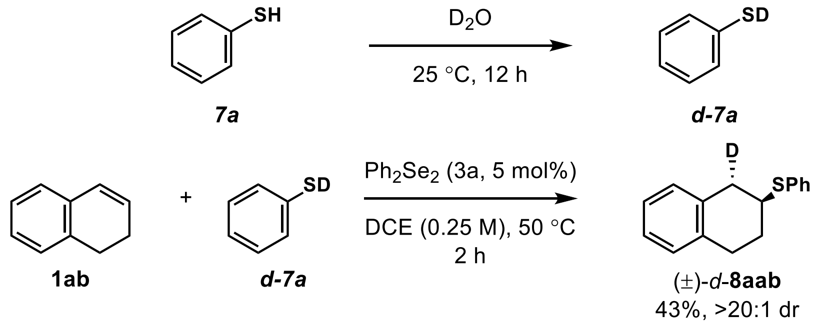


Fig. S11 Formation of deuterated benzenethiol and addition to substrate **1ab**

Benzenethiol **5a** (500 mg, 4.54 mmol, 1 equiv.) was dissolved in D_2O (0.821 mL, 45.4 mmol, 10 equiv.) and vigorously stirred for 12 hours at room temperature. The solution was concentrated *in vacuo* and resulted in **d-5a** with 69% D incorporation which was determined by ^{1}H NMR. Colorless oil, 49% yield. **^{1}H NMR** (500 MHz, d_6-benzene) δ 7.08 – 7.07 (m, 2H), 7.00 – 6.93 (m, 3fH), 3.13 (s, 0.31 H). In an N_2-filled glovebox, a 1-dram vial was charged with **3a** (1.56 mg, 0.005 mmol, 0.05 equiv.) and DCE (0.4 mL). Alkene 1**ab** (13.0 mg, 0.100 mmol, 1.0 equiv.) and ***d*-5a** (14.3 mg, 0.150 mmol, 1.5 equiv.) were added to the solution, which was then capped and removed from the glovebox. This solution was irradiated with stirring for 2 hours. DCE was evaporated and the pure d-8aab (43% yield) was obtained after preparative thin-layer chromatography (hexane) as a colorless oil. D-incorporation was only observed at a single site (δ 3.17), and was approximately 20%, with additional H-incorporation likely due to trace adventitious water. The vicinal coupling constant (4.7 Hz) indicates that this proton is *syn* to the neighboring proton, and therefore is *anti* to the selenide. Thus, only *anti*-addition product ***d*-8aab** was observed based on the ^{1}H NMR (Fig. S12) and ^{2}H NMR (Fig. S13). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 3.6 Hz, 1H), 7.17 – 7.01 (m, 4H), 3.62 – 3.52 (m, 1H), *3.17 (dd, J = 16.2, 4.7 Hz, 0.81H)*, 2.98 (dt, *J* = 16.1, 5.0 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.27 – 2.21 (m, 1H), 1.90 – 1.79 (m, 1H). **^{2}H NMR** (600 MHz, CDCl$_3$) δ 3.16. **^{13}C NMR** (101 MHz, CDCl$_3$) δ 135.73, 135.21 134.71, 132.22, 129.10, 129.06, 129.00, 127.11, 126.19, 125.96, 43.32, 36.23, 29.64, 28.75. **IR** (ATR) 3058, 2917, 1581, 1479, 1452, 1437, 1024, 736, 690 cm^{-1}.

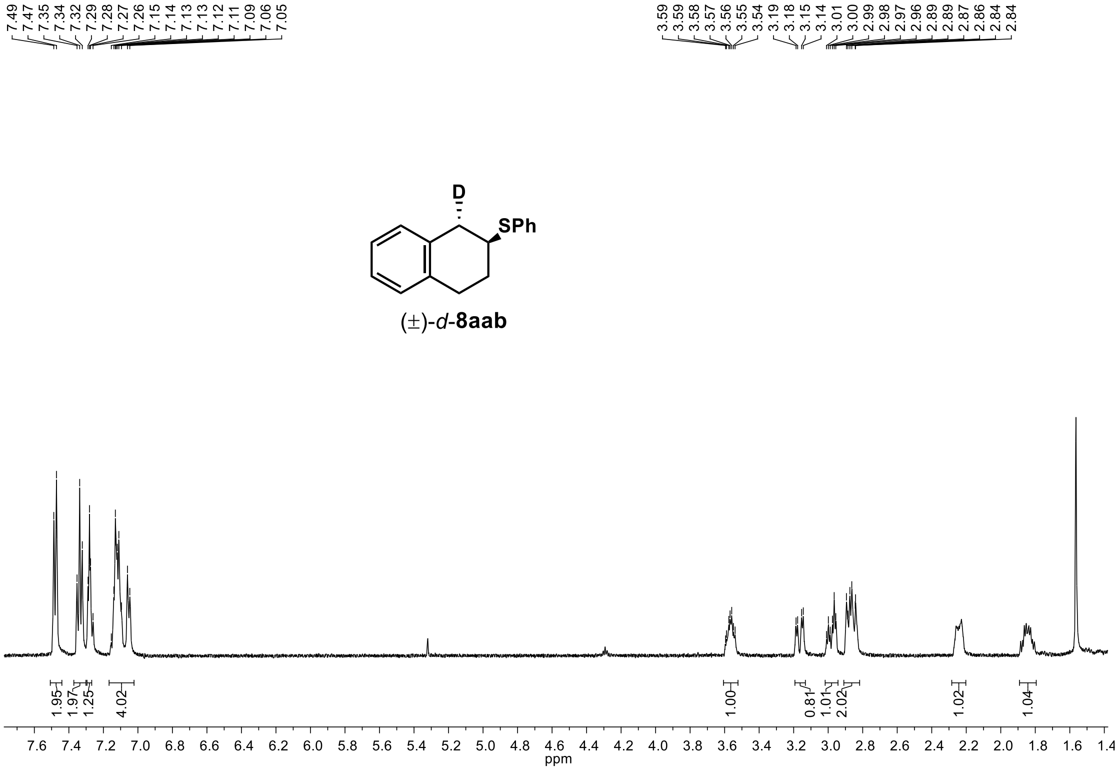


Fig. S12 ^{1}H NMR for *d*-**8aab**

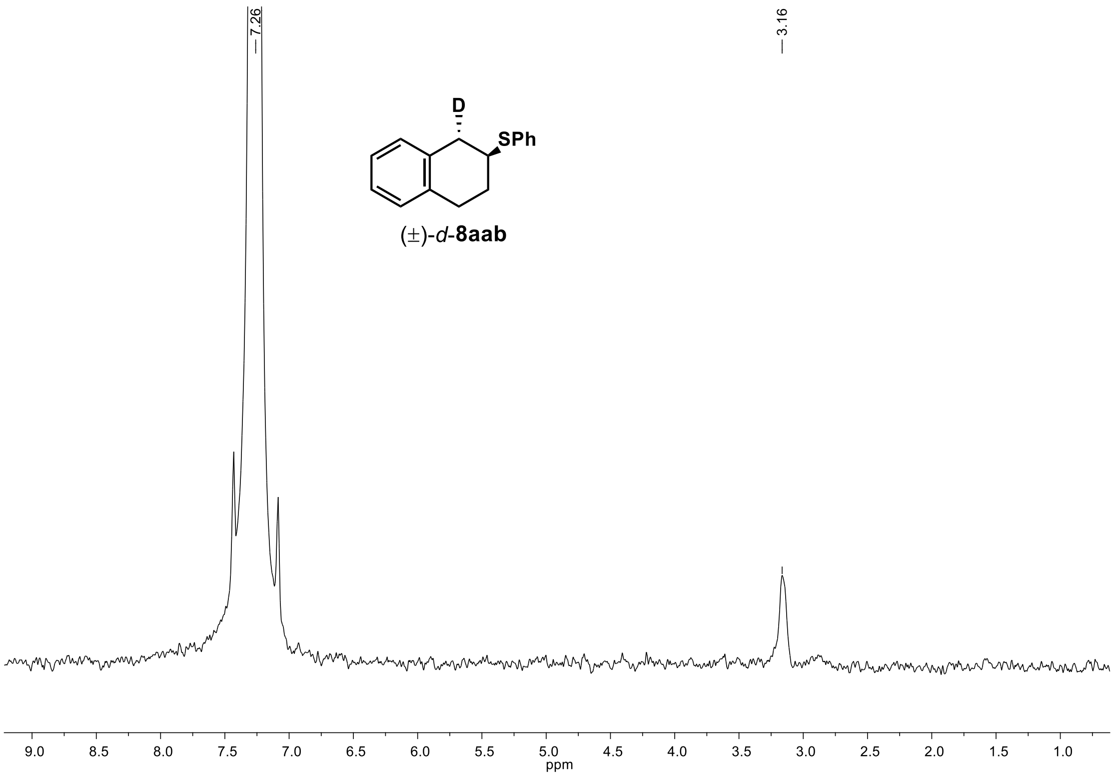


Fig. S13. ^{2}H NMR for *d*-**8aab**

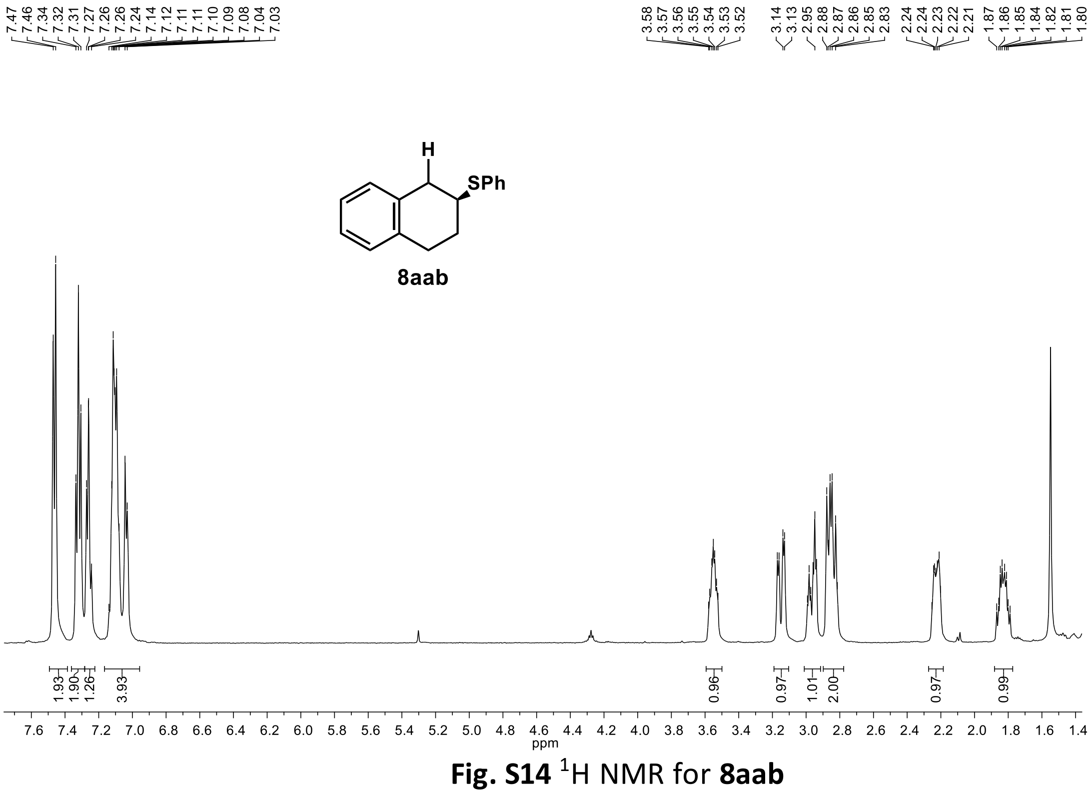
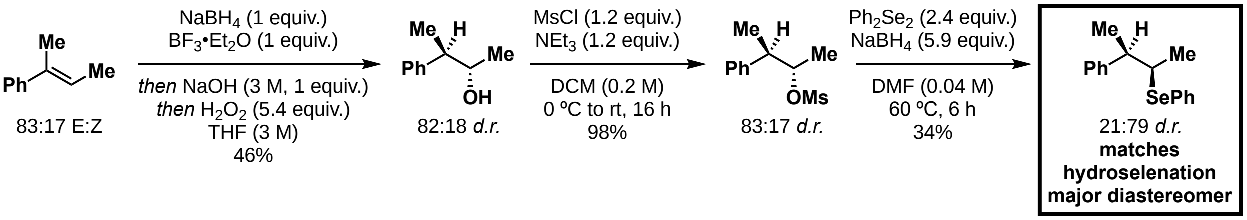


Fig. S14 ^{1}H NMR for **8aab**

5.7.3 Trisubstituted system

Diastereoselectivity for (±)-**4aae** was confirmed by independently synthesizing the diastereo-enriched product.



Scheme S3 Synthesis of **4aae** by hydroboration-oxidation, mesylation, and S$_N$2 displacement.

Hydroboration-oxidation of the diastereo-enriched tri-substituted alkene was performed following literature precedence,[13] and matched literature spectra.[14] Then, the alcohol was mesylated and matched literature spectra.[15] The mesylate was then displaced with *in-situ*-generated phenyl selenide anion following literature procedure for this type of reaction.[16]

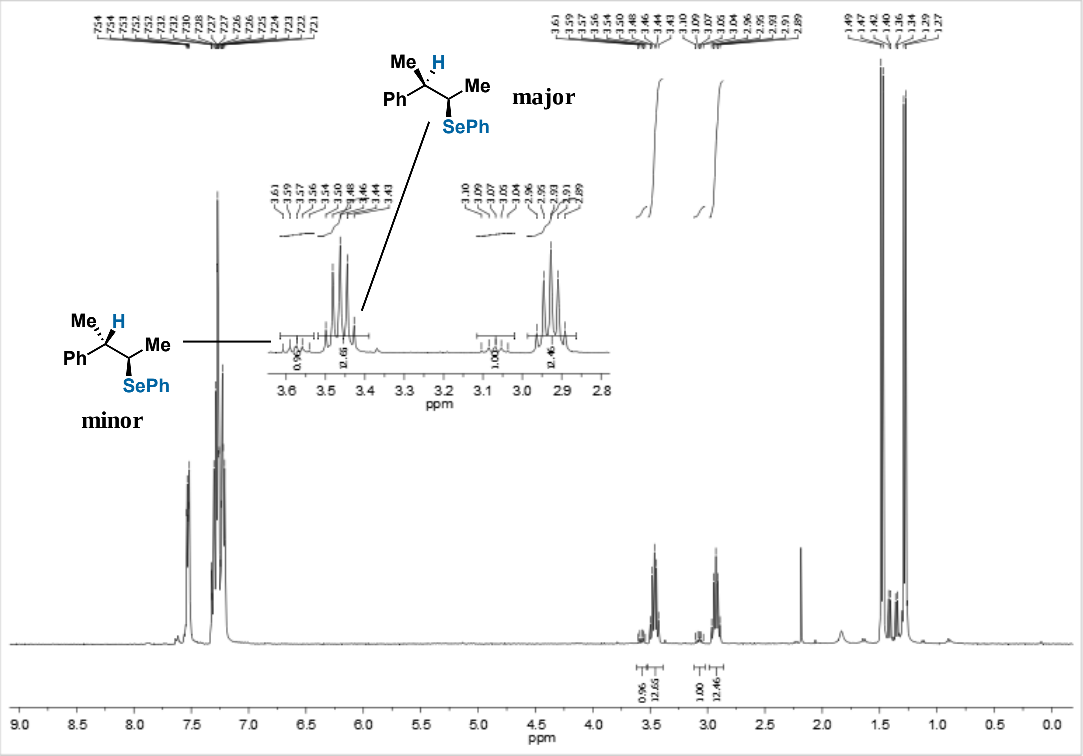


Fig. S15 ^{1}H NMR for (±)-**4aae**.

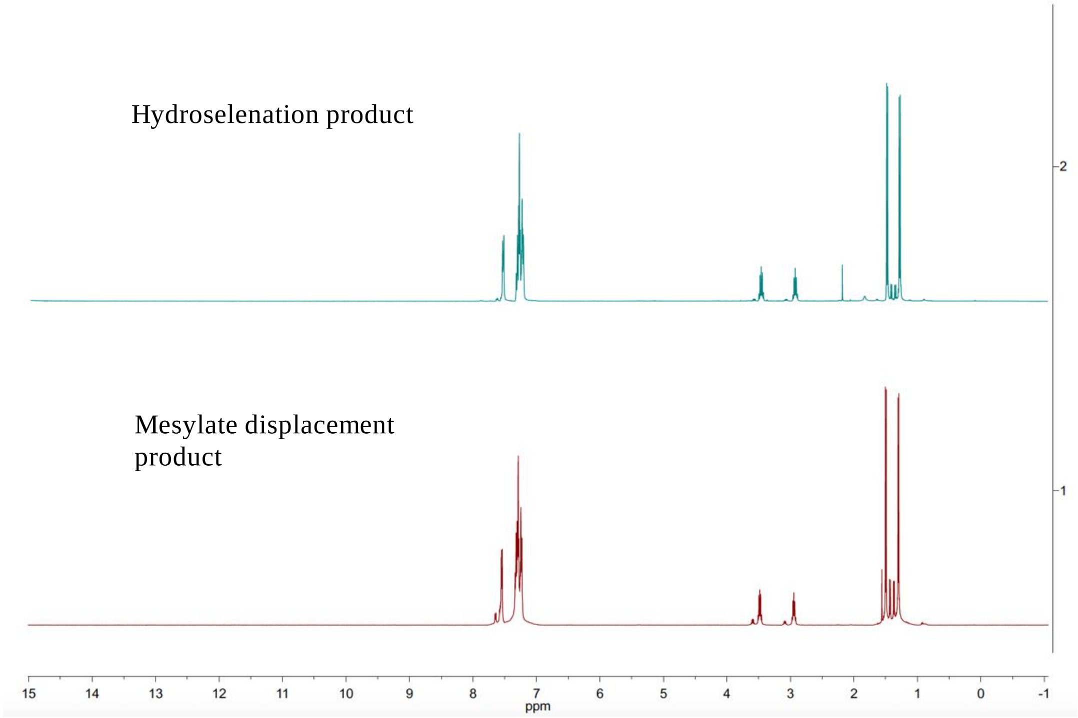


Fig. S16 Comparison of (±)-**4aae** ^{1}H NMR spectra from hydroselenation and independent synthesis.

For the hydroselenation product, standard reaction protocol was followed for (±)-**4aae**. Reaction was run for 24 hours. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 2H), 7.35–7.17 (m, 8H), 3.52–3.39 (m, 1H), 2.93 (p, J = 7.1 Hz, 1H), 1.48 (d, J = 7.0 Hz, 3H), 1.28 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.83, 135.07, 129.79, 129.02, 128.40, 127.79, 127.47, 126.61, 47.56, 46.28, 21.42, 20.86. **IR** (ATR): 3058, 3026, 2961, 2923, 1475, 1451, 1436, 1022, 759, 736, 699, 692 cm^{-1}. **HRMS** calculated for $C_{16}H_{18}Se$ $[M]^+$ 286.0601, found 286.0614.

The percent (*E*)-alkene was also monitored over time, both when mixed with $(PhSe)_2$ (**3a**) and during hydroselenation reaction. To mix with **3a**, **3a** (1.6 mg, 5.0 µmol) was dissolved in 0.600 mL d_2-DCM. Alkene **1ae** (14.4 µL, 100.0 µmol) was added to the solution, and this was transferred to an NMR tube, capped, and sealed with parafilm. The solution was irradiated with blue LEDs and NMR spectra taken at various time points. For the hydroselenation conditions, d_2-DCM, **2a** (15.9 µL, 150.0 µmol), and **1ae** (14.4 µL, 100.0 µmol) were combined and transferred to an NMR tube. The tube was capped and sealed with parafilm. The solution was irradiated with blue LEDs and NMR spectra taken at various time points.

Trial	1, isomerization	2, isomerization	3, isomerization	4, hydroselenation
time	%E	%E	%E	%E
0	76	53	33	88
1	78	56	40	88
2	79	60	47	87
3	80	64	53	86
5	81	70	62	85
7	83	74	68	85
9	-	76	72	-
11	-	78	74	-
19	85	-	-	85
21	-	82	80	-
24	83	81	80	86
29	-	80	79	-
44	-	79	-	-

Table S3 Percent (*E*)-**1ae** over time under isomerization (5 mol% **3a**) or hydroselenation (1.5 equiv. **2a**) conditions.

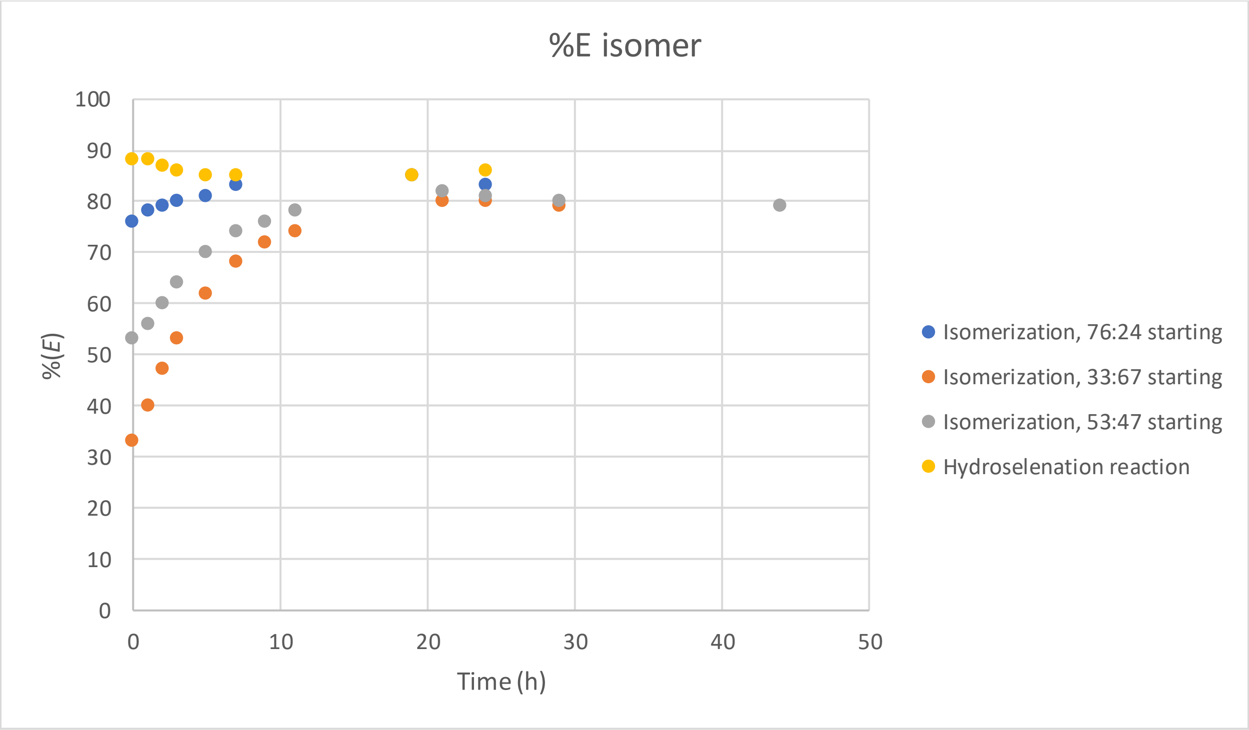


Fig. S17 Percent (*E*)-**1ae** over time under isomerization (5 mol% **3a**) or hydroselenation (1.5 equiv. **2a**) conditions.

5.8 O_2 studies

In an N_2-filled glovebox, triphenylmethane (41.4 mg, 169 µmol) was weighed into a 4-dram vial. d4-DCE (1.8 mL), styrene (**1a**, 34.4 µL, 300 µmol) and PhSeH (**2a**, 47.8 µL, 450 µmol) were added to the vial. All liquid reagents were sparged with Ar prior to use. 0.6 mL of the stock solution was added to a J. Young tube and two regular NMR tubes, which were then capped and brought out of the glovebox. One NMR tube was uncapped briefly and recapped to expose to atmosphere. A balloon of O_2 was prepared and equipped with a needle, which was inserted to the top of the standard NMR cap of the other tube. The NMR tubes were then irradiated for five minutes, then kept out of the light and subjected to NMR analysis.

Trial	Inert	Air	O_2
µmol product	72.1 ± 4.5	73.2 ± 4.6	74.4 ± 4.6

Table S4 Yield of reactions run under inert, air, and O_2 conditions.

5.9 Solvent studies

In an N_2-filled glovebox, triphenyl methane was added to six vials in the indicated amounts. Solvents were added to each vial, then styrene (**1a**, 11.5 µL, 0.100 mmol), PhSeH (**2a**, 15.9 µL, 0.150 mmol) and a stir bar. Vials were capped with a septa cap and removed from the glovebox. Reactions were stirred under blue LEDs for five minutes then subjected to GCFID analysis.

Trial	Solvent	Dielectric constant	Triphenylmethane (mg)	Yield 4aa (µmol)
1	Heptane	2.38	8.7	38.7
2	THF	7.58	10.2	1.4
3	DCE	10.66	10.1	42.4
4	α,α,α-trifluorotoluene	9.18	7.6	28.8
5	Acetonitrile	37.5	10.3	2.3

Table S5 Results of solvent studies.

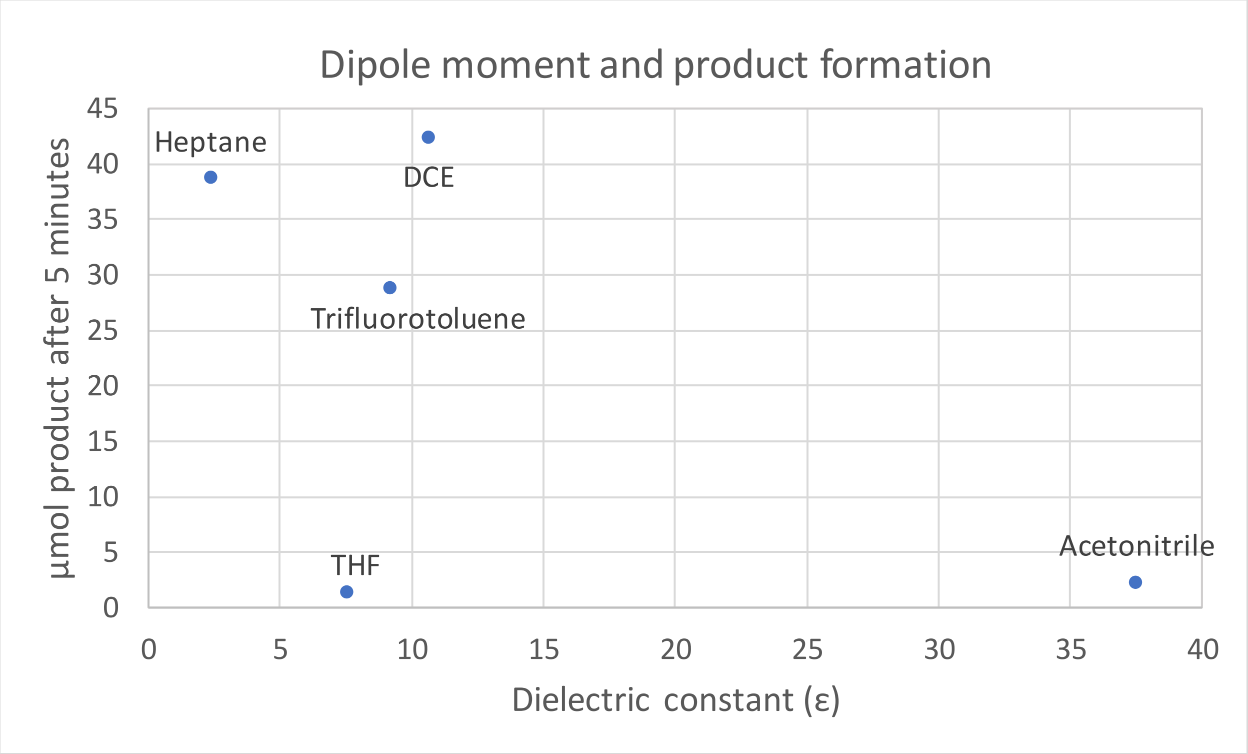
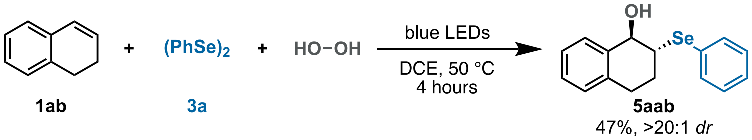


Fig. S18 Graph of product formation versus solvent dielectric constant (ε).

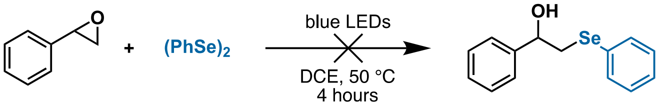
5.10 Trapping with H_2O_2

In an N_2-filled glovebox, Ph_2Se_2 (**3a**, 37.5 mg, 0.120 mmol) was weighed into a 1-dram vial. DCE (0.4 mL), 1,2-dihydronaphthalene (**1aab**, 13.0 mg, 0.100 mmol) and a stir bar were added. The vial was sealed with a septa cap and removed from the glovebox. Sparged 30 weight% H_2O_2 (12.3 μL, 0.120 mmol) was added, and the vial was irradiated for four hours. The solvent was evaporated by rotary evaporation. The diastereoselectivity was determined by ^{1}H NMR analysis of the crude reaction mixture. Product **5aab** was isolated using preparatory TLC. ^{1}H NMR matches literature report.[17]



Scheme S4 Trapping C-radical with hydrogen peroxide.

To check whether this product could be formed from epoxide formation and ring opening, reactivity between styrene oxide and diphenyl selenide was investigated as well. In an N_2-filled glovebox, Ph_2Se_2 (**3a**, 37.5 mg, 0.120 mmol) was weighed into a 1-dram vial. DCE (0.4 mL), styrene oxide (11.4 μL, 0.100 mmol) and a stir bar were added. The vial was sealed and removed from the glovebox. The reaction was allowed to run for 24 hours. No reactivity was observed.



Scheme S5 Control reaction with styrene oxide.

6. Computational Studies

6.1 Starting material absorbances of diselenide (3a)

Styrene (**1a**)			
Excitation Energy (eV)	Excitation Wavelength (nm)	Oscillator Strength	Assignment
2.79	445	0	
4.11	302	0	
4.34	286	0	
4.70	264	0	
4.80	258	0	
4.92	252	1.38E-01	ππ*

Table S6 Vertical excitations computed with PBE0 TDDFT in the def2-TZVP basis set for **1a**.

PhSeH (**2a**)			
Excitation Energy (eV)	Excitation Wavelength (nm)	Oscillator Strength	Assignment
3.46	358	0	
4.19	296	0	
4.35	285	0	
4.49	276	0	
4.81	257	4.4E-07	πσ*
4.83	256	9.3E-03	ππ*

Table S7 Vertical excitations computed with PBE0 TDDFT in the def2-TZVP basis set for **2a**.

Diphenyl diselenide (**3a**)			
Excitation Energy (eV)	Excitation Wavelength (nm)	Oscillator Strength	Assignment
3.25	382	0	
3.25	381	0	
3.57	348	0	
3.59	346	0	
3.82	325	9.54E-03	πσ*
3.89	319	2.46E-02	nσ*
4.30	288	0	
4.32	287	0	
4.52	274	0	
4.52	274	0	

Table S8 Vertical excitations computed with PBE0 TDDFT in the def2-TZVP basis set for **3a**.

6.2 Homolytic bond cleavage of diselenide (3a)

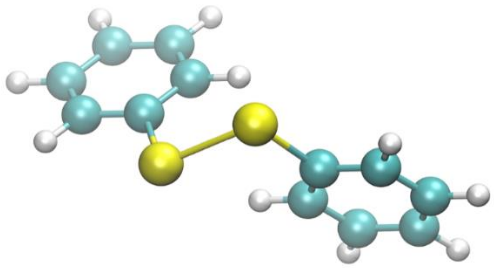


Fig. S19 Diphenyl diselenide (**3a**) ground state optimized geometry.

24
S0 minimum Energy = -5265.481061830

C	-4.5568318	2.9848966	-0.0508021
C	-4.5529729	1.9962601	0.9230888
C	-3.5730953	3.0077271	-1.0310123
C	-2.5850703	2.0324230	-1.0349593
C	-3.5613976	1.0193349	0.9080840

C	-2.5778171	1.0331765	-0.0707483
H	-3.5753116	3.7844065	-1.7869916
H	-5.3295293	3.7453719	-0.0348744
H	-5.3187379	1.9938946	1.6920928
Se	-3.6955564	-0.3407651	2.2631293
H	-1.8012442	0.2766171	-0.0804370
H	-1.8125914	2.0420564	-1.7958637
Se	-1.5946247	-1.2799289	2.2939689
C	-1.6856758	-2.6329726	0.9283298
C	-2.6392988	-2.6430920	-0.0797245
C	-2.6018308	-3.6375452	-1.0481728
C	-1.6131850	-4.6117899	-1.0192753
C	-0.6936900	-3.6087925	0.9682719
C	-0.6593775	-4.5926542	-0.0098443
H	-3.4160871	-1.8872682	-0.1091316
H	-3.3510539	-3.6442638	-1.8320208
H	-1.5873202	-5.3847529	-1.7786177
H	0.1134447	-5.3523437	0.0256429
H	0.0487047	-3.6093358	1.7598672

Table S9 Diselenide-diphenyl (**3a**) coordinates for the ground state optimized geometry.

24

S1 minimum Energy =-5265.439900990

C	-4.4574697	3.4952728	0.7343034
C	-4.5948232	2.1267423	0.8859581
C	-3.5378562	4.0132264	-0.1698912
C	-2.7553749	3.1519238	-0.9240941
C	-3.7997952	1.2553846	0.1361012
C	-2.8812509	1.7790947	-0.7773211
H	-3.4381628	5.0856860	-0.2896684
H	-5.0731677	4.1628264	1.3263472
H	-5.3120775	1.7262547	1.5928519
Se	-4.0042449	-0.6057780	0.3755040
H	-2.2814215	1.1089687	-1.3805494
H	-2.0424687	3.5482381	-1.6382422
Se	-1.2648819	-1.0056131	0.4486796
C	-1.4398819	-2.8649490	0.1774789
C	-2.3274870	-3.3883170	-0.7664748
C	-2.4318166	-4.7604652	-0.9337472
C	-1.6584290	-5.6217119	-0.1700334
C	-0.6523367	-3.7362169	0.9357806
C	-0.7688651	-5.1042050	0.7640232
H	-2.9192591	-2.7180026	-1.3773912
H	-3.1201587	-5.1563703	-1.6718080

H	-1.7411368	-6.6936741	-0.3061206
H	-0.1599752	-5.7716686	1.3631401
H	0.0421910	-3.3359868	1.6651735

Table S10 Diselenide-diphenyl (**3a**) coordinates for the S1 optimized geometry.

6.3 C-radical mechanism (M1)

6.3.1 Cyclic System

Table S11 Relative Free Energies (kCal/mol)

	I	TS2
cyclic *anti*	0	14.9859
cyclic *syn*	1.51495	23.0129

Table S12 Electronic Energies (RPA) (Hartrees)

	I	TS2
cyclic *anti*	-5651.284940	-5651.286337
cyclic *syn*	-5651.282941	-5651.274946

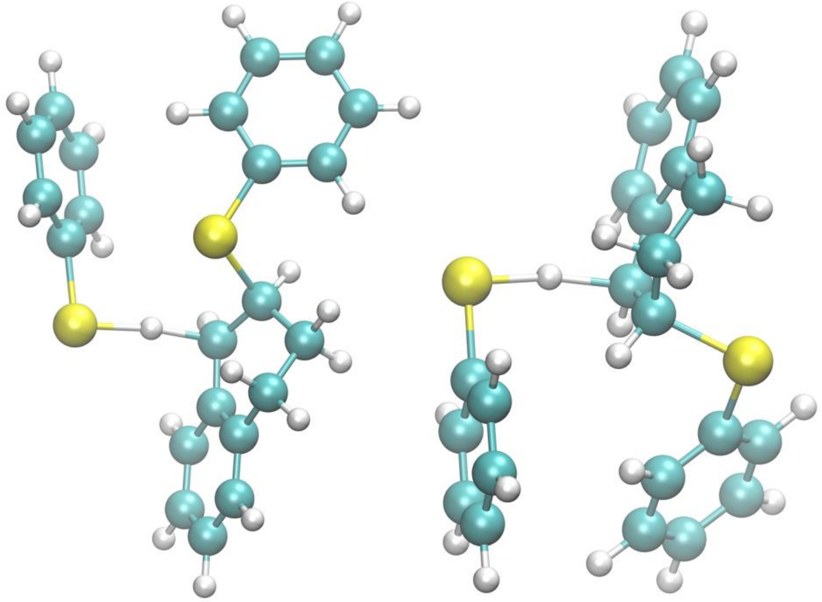


Fig. S20 cyclic-*syn* and cyclic-*anti* 2nd transition state geometries.

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cyclic anti TS2

C	-1.6203257	0.3371793	4.3365474
C	-1.8396266	-0.9679851	4.7587570
C	-1.1612189	0.6143176	3.0567008
H	-1.8109099	1.1608931	5.0176886
C	-1.6019936	-2.0291683	3.8876465

H	-2.1945202	-1.1584787	5.7652759
C	-1.1447133	-1.7750991	2.6109547
H	-1.7734857	-3.0495381	4.2110407
C	-0.9151263	-0.4588006	2.1725327
H	-0.9521048	-2.5950558	1.9263688
C	-0.3945740	-0.2210580	0.8554869
C	-0.2762960	1.1572815	0.3358020
Se	-1.9792721	1.6586751	-0.5969221
C	-1.9436200	0.3160152	-1.9590435
C	-0.8260877	0.1364747	-2.7699997
C	-3.0725383	-0.4752978	-2.1507463
C	-0.8391790	-0.8376476	-3.7572678
H	0.0581019	0.7504913	-2.6386513
C	-1.9690628	-1.6202922	-3.9578138
H	0.0389817	-0.9784741	-4.3766945
C	-3.0865583	-1.4332996	-3.1559704
H	-3.9368450	-0.3489478	-1.5087632
H	-1.9765118	-2.3754979	-4.7354820
H	-3.9708147	-2.0437727	-3.3014441
H	-0.4983022	-1.0212616	0.1267986
C	0.0082377	2.1552381	1.4434357
H	0.4814257	1.2219236	-0.4436778
H	1.1385669	-0.5287700	1.0581475
Se	2.7194217	-0.7594116	1.0024472
C	2.8247160	-0.3176074	-0.8585304
C	2.6755887	-1.3095593	-1.8244855
H	2.5004876	-2.3351610	-1.5215660
H	3.1736469	1.7736226	-0.5038922
C	3.0513030	1.0000546	-1.2533405
C	2.7467907	-0.9836287	-3.1719615
H	2.6296502	-1.7620700	-3.9175986
C	2.9604627	0.3309220	-3.5638488
H	3.0092596	0.5836549	-4.6169289
H	3.2806761	2.3504822	-2.9008678
C	3.1123314	1.3218984	-2.6021014
C	-0.9791177	2.0315183	2.5938957
H	0.0174794	3.1743965	1.0513303
H	1.0202815	1.9406642	1.8062976
H	-1.9571042	2.4216853	2.2837279
H	-0.6588581	2.6560141	3.4314251

Table S13 Cyclic-*anti* coordinates for 2nd transition state optimized geometry.

cyclic *syn* TS2

C	-0.5906193	-4.9236173	-1.4241065
C	0.3475184	-5.5266322	-0.5904753
C	-0.5832267	-3.5515900	-1.5851569
H	-1.3238550	-5.5276851	-1.9461842
C	1.2876352	-4.7485802	0.0754286
H	0.3486512	-6.6032227	-0.4625351
C	1.3058938	-3.3701848	-0.0707491
H	2.0221802	-5.2226818	0.7188070
C	0.3645401	-2.7568186	-0.9219567
H	-1.3136679	-3.0734996	-2.2297793
C	0.3225259	-1.3174299	-1.0362553
C	1.5270263	-0.5020643	-0.6740011
Se	1.0901805	0.8324268	0.7541312
C	1.7727975	2.4064381	-0.0866042
C	3.0450415	2.4585535	-0.6509799
C	0.9612532	3.5381268	-0.1045306
C	3.4927760	3.6316692	-1.2422045
C	2.6882348	4.7644495	-1.2503354
H	4.4815793	3.6630267	-1.6863771
H	-0.0397342	3.4893138	0.3100089
H	3.0449176	5.6815123	-1.7052279
H	0.7887296	5.5936134	-0.6841137
H	-0.2787809	-0.9176354	-1.8499774
C	2.7246378	-1.3619275	-0.2963493
H	1.7711123	0.1533028	-1.5115188
H	-0.7935536	-1.0931684	-0.0739443
C	1.4254718	4.7157585	-0.6749297
H	3.6920224	1.5890619	-0.6262455
Se	-2.1471667	-1.0529463	0.8650283
C	-2.4763862	0.8120977	0.6500640
C	-2.5224907	1.6428416	1.7669689
H	-2.3615698	1.2279266	2.7551992
C	-2.7573590	3.0022192	1.6137608
H	-2.7940567	3.6412729	2.4891594
C	-2.9266817	3.5451969	0.3466188
H	-3.0973680	4.6092555	0.2282413
C	-2.8731971	2.7186388	-0.7688261
H	-3.0026668	3.1351808	-1.7616562
H	-2.6374441	0.7127141	-1.4918516
C	-2.6621555	1.3556734	-0.6194596
C	2.3110085	-2.5012888	0.6215422
H	3.5003093	-0.7495874	0.1657140
H	3.1444109	-1.7849712	-1.2170606

H	1.8757677	-2.0861682	1.5409772
H	3.1765471	-3.0933588	0.9256824

Table S14 Cyclic *syn* coordinates for 2nd transition state optimized geometry.

6.3.2 Trisubstituted system

Table S15 Relative Electronic Energies (RPA) (kCal/mol).

	R	TS1	I	TS2	P
E-*anti*	19.7107	19.1588	16.6543	24.7282	4.91207
E-*syn*	21.8401	21.3149	17.8569	26.2603	0.
Z-*anti*	20.5424	21.2457	19.1323	24.424	1.67759
Z-*syn*	19.5841	20.1164	18.6564	27.2417	1.50291

Table S16 Absolute Free Energy Corrections (kCal/mol).

	R	TS1	I	TS2	P
E-*anti*	203.968	206.063	204.888	205.875	208.396
E-*syn*	204.51	206.805	204.928	205.959	209.848
Z-*anti*	203.956	204.907	204.79	206.063	208.241
Z-*syn*	205.746	206.237	204.897	205.838	208.927

Table S17 Relative Free Energies (kCal/mol).

	R	TS1	I	TS2	P
E-*anti*	13.8313	15.3744	11.6939	20.7554	3.46058
E-*syn*	16.5019	18.2725	12.9368	22.371	0.
Z-*anti*	14.6504	16.3049	14.0747	20.6395	0.0703964
Z-*syn*	15.4826	16.5053	13.7055	23.2319	0.582545

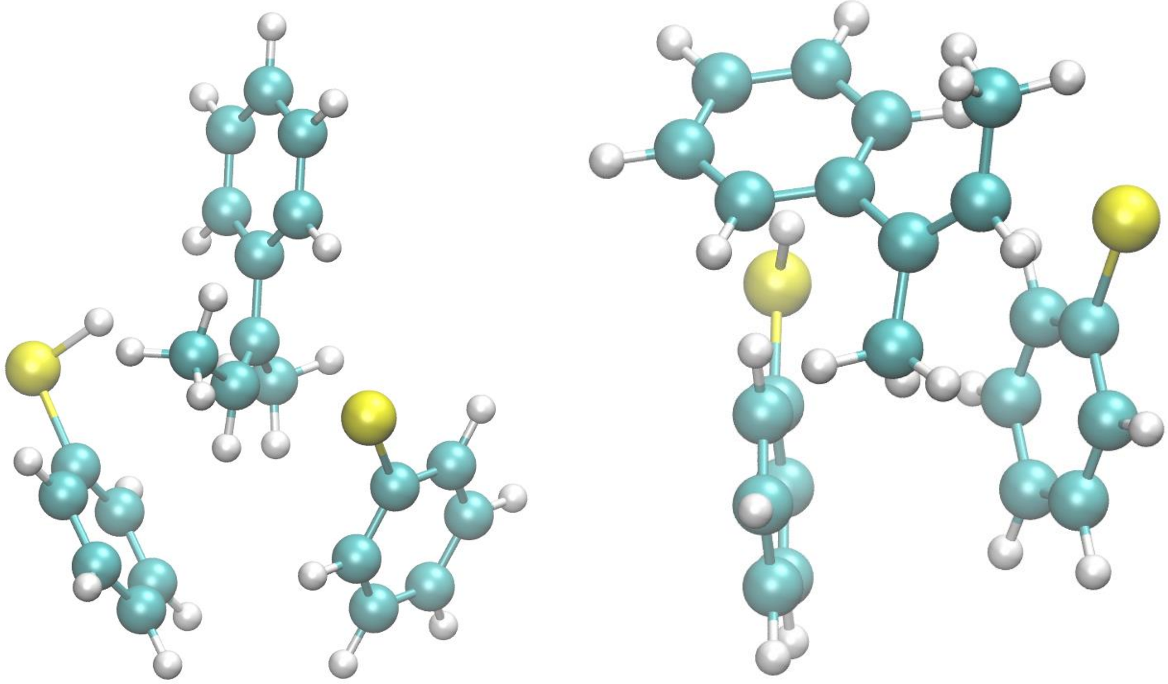

Fig. S21 (*Z*)-*syn* and (*Z*)-*anti* 1st transition state geometries.

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(*Z*)-*anti* 1st Energy =-5652.50510221133

C	0.6883194	0.4580729	4.7437970
C	1.6983890	-0.4461096	5.0786268
C	0.1981836	0.5151301	3.4415048
H	0.2703813	1.1200100	5.5067933
C	2.2024202	-1.3047373	4.1007294
H	2.0844482	-0.4875270	6.1002924
C	1.7036925	-1.2578033	2.8005066
H	2.9898092	-2.0202741	4.3515120
C	0.7052248	-0.3333908	2.4402563
H	2.1119270	-1.9368090	2.0478274
H	-0.6188773	1.1977026	3.1977304
C	0.1897179	-0.2998989	1.0578543
C	-0.0262164	0.8792993	0.3547621
Se	-2.4720989	1.3187042	0.8296196
C	-3.0779649	-0.1325974	-0.2258004
C	-2.9626903	-0.0884931	-1.6254361
C	-3.6178775	-1.2797617	0.3792251
C	-3.3645169	-1.1750654	-2.3995459
H	-2.5441280	0.8003099	-2.1040298
C	-3.8990171	-2.3129346	-1.7906025
H	-3.2622891	-1.1321980	-3.4872652

C	-4.0295964	-2.3589600	-0.4008058
H	-3.7017068	-1.3238307	1.4678542
H	-4.2150664	-3.1636379	-2.3997346
H	-4.4469773	-3.2469393	0.0813168
C	-0.1237600	-1.6172283	0.4201257
H	0.8001075	-2.1968257	0.2468182
H	-0.6221484	-1.4876494	-0.5488504
H	-0.7675897	-2.2297845	1.0716121
C	0.5851943	2.2099458	0.6793613
H	-0.2830517	0.7426694	-0.7011420
H	0.6308970	2.4210105	1.7545431
H	0.0391595	3.0238708	0.1831078
H	1.6204138	2.2257943	0.2958976
H	2.7679982	-0.0657657	0.2904966
Se	3.5588228	-0.3175861	-0.9289875
C	2.1209153	0.0909401	-2.1418520
C	1.3170251	-0.9381223	-2.6419964
H	1.5137830	-1.9729377	-2.3538802
H	2.5172675	2.2173834	-2.1478827
C	1.8778866	1.4147775	-2.5224968
C	0.2517076	-0.6382960	-3.4913624
H	-0.3828090	-1.4446951	-3.8670418
C	-0.0092028	0.6852041	-3.8484461
H	-0.8491283	0.9191629	-4.5075959
H	0.6125297	2.7470440	-3.6513588
C	0.8077537	1.7097019	-3.3681588

Table S18 (*Z*)-*anti* coordinates for 1st transition state optimized geometry.

47

(*Z*)-*syn* 1st Energy =-5652.50690100032

C	-3.7501081	0.5160507	-0.8661996
C	-3.9259112	0.4094525	0.5145035
C	-2.7816037	-0.2505312	-1.5117109
H	-4.3700855	1.2041516	-1.4463832
C	-3.1216227	-0.4698565	1.2431225
H	-4.6792620	1.0167929	1.0222513
C	-2.1582453	-1.2427753	0.5972110
H	-3.2378476	-0.5481550	2.3271914
C	-1.9765943	-1.1543992	-0.7946251
H	-1.5121001	-1.9101674	1.1733878
H	-2.6634216	-0.1601276	-2.5943464
C	-0.9504471	-1.9587818	-1.4917482
C	-0.7903947	-3.3124106	-1.2880651
Se	0.9988504	-3.3420956	0.6118912

C	1.8942353	-1.7117026	0.2758507
C	2.9376576	-1.6483930	-0.6648079
C	1.5128170	-0.5390152	0.9511208
C	3.5728346	-0.4371792	-0.9307266
C	3.1839890	0.7233646	-0.2576181
H	4.3753392	-0.3982331	-1.6721158
H	0.6994336	-0.5745369	1.6795709
H	3.6724896	1.6762752	-0.4748164
H	1.8471007	1.5695992	1.2164313
C	-0.0325993	-1.2254746	-2.4189648
H	-0.5976549	-0.7143385	-3.2169891
H	0.6912814	-1.9021662	-2.8924500
H	0.5256064	-0.4447854	-1.8753566
C	-1.7877851	-4.2419849	-0.6666426
H	-0.0540422	-3.7971239	-1.9381087
H	-2.4603436	-3.7447009	0.0429165
H	-1.2942408	-5.0803956	-0.1526762
H	-2.4064017	-4.6820176	-1.4682193
H	-1.6231066	1.7447913	0.8866428
C	2.1592017	0.6662513	0.6884058
H	3.2390181	-2.5556505	-1.1942664
Se	-0.9619095	2.9909360	1.3000642
C	0.1013310	3.1645983	-0.2765314
C	1.1418087	4.1012963	-0.2732662
H	1.3307788	4.7162460	0.6111473
C	1.9543749	4.2414459	-1.3981540
H	2.7666385	4.9729796	-1.3847710
C	1.7417716	3.4500097	-2.5278028
H	2.3858018	3.5560563	-3.4040252
C	0.7018862	2.5201965	-2.5272580
H	0.5270691	1.8916269	-3.4043936
H	-0.9286368	1.6423991	-1.4199093
C	-0.1208840	2.3775655	-1.4110928

Table S19 (*Z*)-*syn* coordinates for 1st transition state optimized geometry.

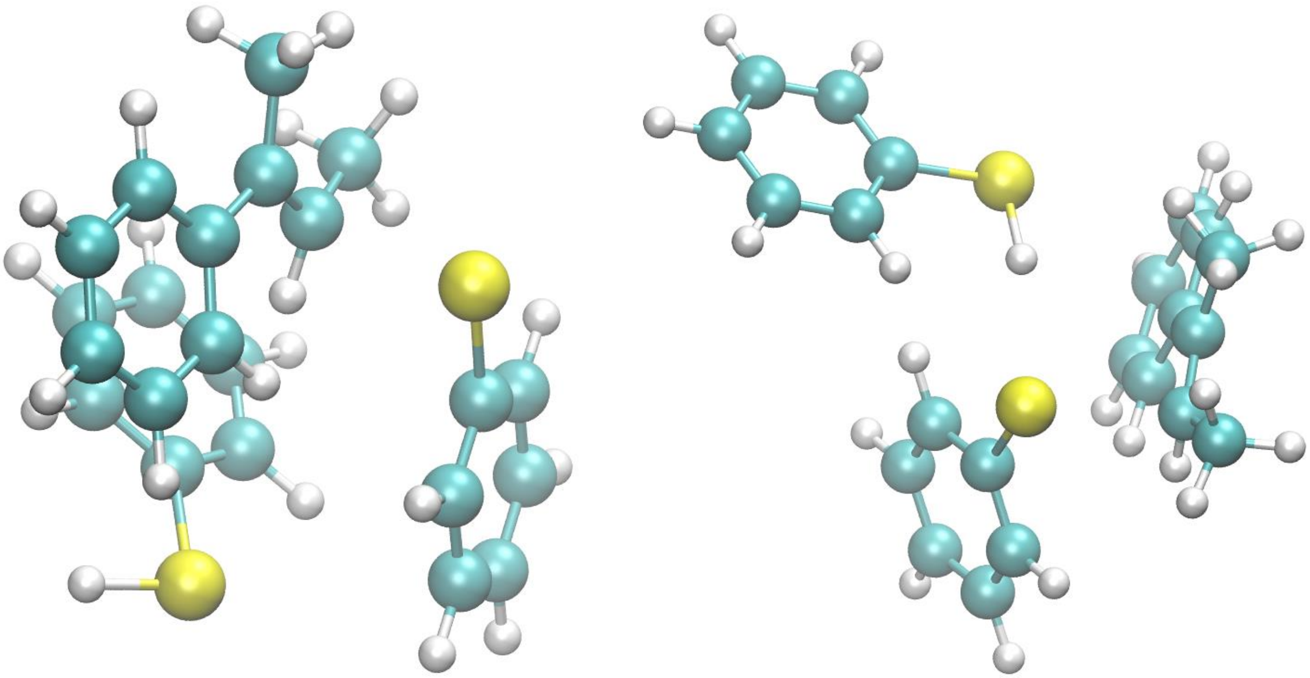

Fig. S22 (*E*)-*anti* and (*E*)-*syn* 1st transition state geometries.

47

(*E*)-*anti* 1st Energy =-5652.50842635526

C	-3.8439926	-0.8580057	2.8104584
C	-3.5362809	-1.9372627	1.9807832
C	-3.0121112	0.2580466	2.8507079
H	-4.7411662	-0.8839348	3.4345394
C	-2.3845165	-1.8831434	1.1909012
H	-4.1852494	-2.8162865	1.9528453
C	-1.5581008	-0.7669137	1.2228790
H	-2.1216810	-2.7200939	0.5388544
C	-1.8517728	0.3390769	2.0505270
H	-0.6594895	-0.7662798	0.6046650
H	-3.2833011	1.0883878	3.5050213
C	-1.0034263	1.5309203	2.0885327
C	-0.0239776	1.7512418	1.1107700
Se	1.9069559	0.3846240	1.9497841
C	2.5650446	-0.0912141	0.2348860
C	2.2826978	-1.3558906	-0.3098775
C	3.3620675	0.8027514	-0.5018534
C	2.8009309	-1.7217565	-1.5515909
H	1.6572987	-2.0555864	0.2495027
C	3.5939901	-0.8277870	-2.2748164
H	2.5798526	-2.7116563	-1.9590977

C	3.8675404	0.4370529	-1.7482308
H	3.5949743	1.7853369	-0.0842981
H	3.9969461	-1.1160788	-3.2489602
H	4.4863909	1.1423662	-2.3091133
C	-1.1914560	2.5035137	3.2107729
H	-2.1195243	3.0872246	3.0780674
H	-0.3650360	3.2213529	3.2759557
H	-1.2760039	1.9889793	4.1807395
C	0.6351764	3.0785879	0.8855402
H	-0.0857743	1.1250840	0.2153876
H	1.0380894	3.5228843	1.8057585
H	-0.0992739	3.7837891	0.4581583
H	1.4542435	2.9823861	0.1607022
H	-2.1710713	-2.2562963	-2.3515845
Se	-0.7264474	-1.9871680	-2.3139130
C	-0.9141969	-0.0866164	-2.2406157
C	0.2026653	0.7012783	-2.5457497
C	-2.1169688	0.5269574	-1.8703956
C	-2.2023550	1.9183568	-1.8302834
C	0.1069991	2.0915280	-2.4977295
C	-1.0955030	2.7063174	-2.1485239
H	-2.9866388	-0.0774496	-1.6028572
H	-3.1458470	2.3876545	-1.5401396
H	-1.1676830	3.7959649	-2.1144884
H	0.9863687	2.6954671	-2.7356183
H	1.1515861	0.2340314	-2.8191187

Table S20 (*E*)-*anti* coordinates for 1st transition state optimized geometry.

47

(*E*)-*syn* 1st Energy =-5652.50499206035

C	3.8028343	1.1707272	-1.0012361
C	3.1548893	2.3556024	-1.3502956
C	3.1974372	-0.0599586	-1.2403596
H	4.7890485	1.2021339	-0.5312062
C	1.8960722	2.2917553	-1.9522184
H	3.6254657	3.3221335	-1.1536774
C	1.2940483	1.0645887	-2.2008164
H	1.3698666	3.2099849	-2.2248955
C	1.9242480	-0.1489050	-1.8460702
H	0.3047394	1.0608186	-2.6580386
H	3.7308317	-0.9664856	-0.9516819
C	1.3022349	-1.4578614	-2.0703453
C	0.1181162	-1.5864954	-2.8002870
Se	-1.5960985	-1.2573666	-0.9688805

C	-1.9327976	0.5779054	-1.2955657
C	-2.4479338	0.9901040	-2.5373162
C	-1.6511793	1.5461885	-0.3170079
C	-2.6477925	2.3434138	-2.8014924
H	-2.6851146	0.2430240	-3.2994445
C	-2.3589185	3.3008122	-1.8255140
H	-3.0377769	2.6524503	-3.7748416
C	-1.8706184	2.8962744	-0.5814756
H	-1.2460824	1.2411280	0.6500646
H	-2.5179840	4.3617430	-2.0342130
H	-1.6449420	3.6392472	0.1878224
C	1.9506595	-2.6603016	-1.4577654
H	2.9242520	-2.8725118	-1.9313023
H	1.3332064	-3.5601326	-1.5584415
H	2.1458993	-2.5004312	-0.3846600
C	-0.3729311	-2.8783232	-3.3835748
H	-0.2300226	-0.6953543	-3.3307295
H	-0.3688851	-3.7089933	-2.6641292
H	0.2773270	-3.1690618	-4.2276373
H	-1.3955579	-2.7664143	-3.7670816
H	0.4369246	-0.5441597	0.6371412
Se	1.3883794	-0.0169537	1.6438071
C	0.1622329	-0.1370127	3.1057468
C	-1.1206673	-0.6819203	2.9643524
C	0.5726044	0.3481106	4.3547841
C	-0.2922859	0.2870394	5.4468684
C	-1.9800752	-0.7337393	4.0620836
C	-1.5724817	-0.2519390	5.3067311
H	1.5707447	0.7783799	4.4782173
H	0.0399223	0.6681860	6.4162571
H	-2.2488539	-0.2961211	6.1638558
H	-2.9797957	-1.1588130	3.9380925
H	-1.4509765	-1.0656320	1.9950362

Table S21 (*E*)-*syn* coordinates for 1st transition state optimized geometry.

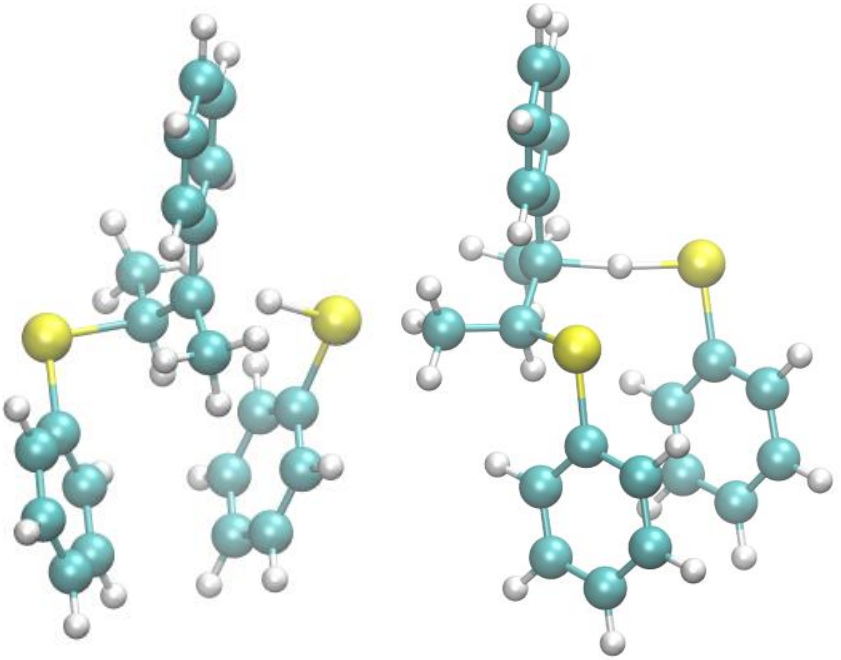

Fig. S23 (*Z*)-*anti* and (*Z*)-*syn* 2nd transition state geometries.

47

(*Z*)-*anti* 2nd Energy =-5652.50003976996

C	-0.7601950	0.6437552	4.7930076
C	-1.7296477	-0.2688973	5.1893458
C	-0.2788112	0.6361677	3.4943545
H	-0.3671139	1.3623549	5.5035732
C	-2.1994561	-1.2019716	4.2739876
H	-2.1075575	-0.2596547	6.2053691
C	-1.7095342	-1.2191386	2.9784536
H	-2.9531869	-1.9230770	4.5704857
C	-0.7512187	-0.2878381	2.5503870
H	-2.0938647	-1.9524591	2.2802956
H	0.5038761	1.3312157	3.2226867
C	-0.2443141	-0.3388505	1.1740622
C	-0.2542069	0.8513214	0.2784196
Se	-2.0855729	1.0016109	-0.5676086
C	-1.8515407	-0.1767775	-2.0541731
C	-0.7748547	-0.0297240	-2.9249051
C	-2.7898810	-1.1802835	-2.2796519
C	-0.6276551	-0.8962283	-3.9972771
H	-0.0448962	0.7570325	-2.7696350
C	-1.5660855	-1.8948357	-4.2260921

H	0.2211015	-0.7831038	-4.6624428
C	-2.6507322	-2.0287831	-3.3697871
H	-3.6222612	-1.3059475	-1.5962788
H	-1.4514915	-2.5662434	-5.0694203
H	-3.3864121	-2.8070539	-3.5396492
C	-0.2910587	-1.6638150	0.4747017
H	0.0597516	-2.4662002	1.1257651
H	0.3242692	-1.6464649	-0.4262746
H	-1.3102402	-1.9119788	0.1559309
C	0.0793188	2.2158444	0.8422937
H	0.3847026	0.6463022	-0.5808599
H	-0.6410994	2.5450648	1.5928580
H	0.0924906	2.9508049	0.0366589
H	1.0702309	2.1976071	1.3034849
H	1.4054891	-0.3230927	1.4697274
Se	2.9726626	-0.3114364	1.4523865
C	3.0372678	-0.0006068	-0.4400541
C	2.9579471	-1.0701903	-1.3287838
H	2.8866102	-2.0826765	-0.9491046
H	3.2073173	2.1324149	-0.2430107
C	3.1403324	1.2983884	-0.9315226
C	2.9583787	-0.8380651	-2.6971376
H	2.8853734	-1.6753150	-3.3819980
C	3.0456603	0.4586448	-3.1857740
H	3.0407329	0.6386089	-4.2548739
H	3.2128592	2.5397319	-2.6764774
C	3.1413573	1.5249850	-2.3012920

Table S22 (*Z*)-*anti* coordinates for 2nd transition state optimized geometry.

47

(*Z*)-*syn* 2nd Energy =-5652.49555160079

C	-3.1886728	-4.4014596	0.3445523
C	-2.3815238	-4.9180875	1.3510139
C	-2.7503237	-3.3444114	-0.4326846
H	-4.1699277	-4.8257198	0.1635962
C	-1.1269604	-4.3609929	1.5661003
H	-2.7252644	-5.7467727	1.9592529
C	-0.6888928	-3.3005647	0.7930950
H	-0.4809319	-4.7574527	2.3412990
C	-1.4865694	-2.7601823	-0.2300576
H	0.3027630	-2.9080699	0.9826722
H	-3.4055236	-2.9635481	-1.2051250
C	-1.0731536	-1.6077309	-1.0241301
C	0.3441098	-1.0828193	-0.9743111

Se	0.9235022	-0.4516613	0.8137000
C	1.9037852	1.1122514	0.3208046
C	2.4670693	1.3186743	-0.9348500
C	2.0870225	2.0662575	1.3192968
C	3.1945264	2.4738632	-1.1872698
C	3.3855803	3.4195645	-0.1902001
H	3.6220714	2.6261605	-2.1723317
H	1.6325195	1.9264816	2.2940382
H	3.9580279	4.3178685	-0.3909819
H	2.9604343	3.9445011	1.8496096
C	-1.7147346	-1.4169487	-2.3739936
H	-1.4469026	-2.2429389	-3.0429067
H	-1.3771421	-0.4890439	-2.8367259
H	-2.8028607	-1.3789598	-2.3175406
C	1.3368835	-2.0663317	-1.5889218
H	0.3535984	-0.1563900	-1.5505875
H	1.3782214	-2.9973860	-1.0232600
H	2.3412082	-1.6417360	-1.6165493
H	1.0376001	-2.3049530	-2.6139058
H	-1.8922219	-0.5415371	-0.2587532
C	2.8315097	3.2071634	1.0649486
H	2.3541770	0.5888574	-1.7265017
Se	-2.9208388	0.4822904	0.4412501
C	-1.8545766	2.0412496	0.1708767
C	-1.6323354	2.9089047	1.2372987
H	-2.0384416	2.6787891	2.2157640
C	-0.8791640	4.0590542	1.0509189
H	-0.7097188	4.7276254	1.8877800
C	-0.3204859	4.3388146	-0.1883309
H	0.2897925	5.2238500	-0.3240516
C	-0.5339228	3.4697566	-1.2489634
H	-0.0952534	3.6757545	-2.2187365
H	-1.4971197	1.6759414	-1.9180533
C	-1.3114977	2.3340685	-1.0774033

Table S23 (*Z*)-*syn* coordinates for 2nd transition state optimized geometry.

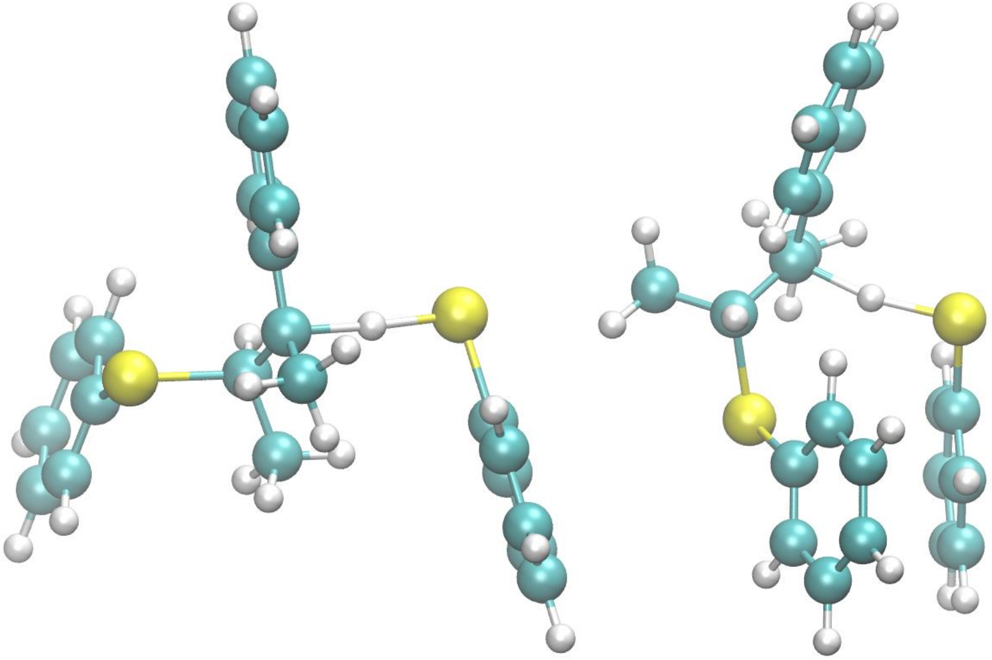

Fig. S24 (*E*)-*anti* and (*E*)-*syn* 2nd transition state geometries.

47

(*E*)-*anti* 2nd Energy =-5652.49955519706

C	-0.7596167	0.6956446	4.6786991
C	-0.2120348	-0.5321242	5.0263322
C	-0.7974339	1.0969197	3.3533139
H	-1.1599739	1.3489625	5.4459079
C	0.2982104	-1.3557996	4.0288871
H	-0.1859365	-0.8471638	6.0631795
C	0.2679017	-0.9533260	2.7065070
H	0.7200547	-2.3214110	4.2842688
C	-0.2745409	0.2876331	2.3338781
H	0.6569668	-1.6266339	1.9526761
H	-1.2215739	2.0634381	3.1138911
C	-0.3331312	0.7017538	0.9296516
C	0.7454984	0.2258755	0.0082389
Se	2.4313018	1.2133648	0.5066229
C	3.6501974	0.0091509	-0.3453608
C	3.8760785	-1.2521724	0.2007573
C	4.3150207	0.3901960	-1.5069557
C	4.7526211	-2.1301183	-0.4201067
H	3.3706555	-1.5451163	1.1145477
C	5.4209210	-1.7472105	-1.5767239
H	4.9213799	-3.1122598	0.0072114

C	5.2046469	-0.4863065	-2.1154019
H	4.1340296	1.3686381	-1.9365985
H	6.1107946	-2.4320457	-2.0567128
H	5.7228509	-0.1834182	-3.0184066
C	-0.9842191	2.0100310	0.5972496
H	-1.1779784	2.0957366	-0.4708648
H	-0.3376909	2.8495336	0.8847594
H	-1.9341387	2.1314977	1.1182365
C	0.4849838	0.3602517	-1.4761350
H	1.0070002	-0.8069186	0.2349616
H	0.3697135	1.3999068	-1.7832391
H	-0.4221537	-0.1855504	-1.7502785
H	1.3176739	-0.0649293	-2.0386301
H	-1.4660331	-0.2684784	0.5109967
Se	-2.6457352	-1.3062443	0.1566396
C	-3.1608743	-0.4679135	-1.4830884
C	-2.9298135	-1.1155677	-2.6947344
C	-3.7750670	0.7827545	-1.4764109
C	-4.1347046	1.3865520	-2.6726516
C	-3.3068516	-0.5140539	-3.8876091
C	-3.9036862	0.7396616	-3.8801567
H	-3.9695076	1.2835450	-0.5352701
H	-4.6039779	2.3640420	-2.6593724
H	-4.1903546	1.2112482	-4.8132763
H	-3.1249017	-1.0254502	-4.8263160
H	-2.4476494	-2.0863240	-2.7041720

Table S24 (*E*)-*anti* coordinates for 2nd transition state optimized geometry.

47

(*E*)-*syn* 2nd Energy = -5652.49711478066

C	-5.0221472	-0.6452631	-0.2777745
C	-5.0139402	-1.7044344	-1.1766936
C	-3.9237111	0.1895761	-0.1668296
H	-5.8928771	-0.4665193	0.3432391
C	-3.8882049	-1.9166118	-1.9638021
H	-5.8738991	-2.3586650	-1.2621809
C	-2.7898027	-1.0827506	-1.8561023
H	-3.8645060	-2.7410308	-2.6675996
C	-2.7777818	-0.0004137	-0.9585517
H	-1.9321967	-1.2866427	-2.4843672
H	-3.9616019	1.0075042	0.5405274
C	-1.6071393	0.8611342	-0.7903610
C	-0.6463613	0.9758675	-1.9489671
Se	1.2102981	1.3763663	-1.4066474

C	2.0358920	-0.3388511	-1.5116263
C	1.3437852	-1.5442211	-1.4986560
C	3.4297533	-0.3483792	-1.5484575
C	2.0410279	-2.7451113	-1.5276760
H	0.2647394	-1.5677143	-1.4306747
C	3.4277610	-2.7563118	-1.5539743
H	1.4883728	-3.6780967	-1.5123505
C	4.1186718	-1.5502296	-1.5619951
H	3.9801901	0.5865759	-1.5586209
H	3.9672465	-3.6962908	-1.5676486
H	5.2028659	-1.5427105	-1.5832555
C	-1.7490560	2.0968168	0.0512779
H	-2.4632698	2.7954106	-0.3992009
H	-0.7887452	2.6058777	0.1485176
H	-2.1006568	1.8648692	1.0573040
C	-1.1022958	2.0598539	-2.9241626
H	-0.5593775	0.0384331	-2.4923270
H	-1.0561747	3.0533312	-2.4736384
H	-2.1381205	1.8731120	-3.2222821
H	-0.4747117	2.0568592	-3.8161887
H	-0.9183386	-0.0255188	0.2842716
Se	-0.5290199	-0.9291543	1.5675091
C	1.0792972	-0.0135969	2.0352543
C	1.0259343	1.2421972	2.6373560
C	2.3131887	-0.6098437	1.7905812
C	3.4833837	0.0489641	2.1406139
C	2.1983259	1.9010960	2.9742103
C	3.4298088	1.3056555	2.7275326
H	2.3577305	-1.5777193	1.3056099
H	4.4407859	-0.4188642	1.9401480
H	4.3457073	1.8213451	2.9938217
H	2.1499581	2.8817774	3.4347140
H	0.0657368	1.7036038	2.8365871

Table S25 (*E*)-*syn* coordinates for 2nd transition state optimized geometry.

6.4 Seleniranium mechanism (M2)

12

PhSe• Optimized Geometry RPA Energy = -2631.80127217438

C	1.4300166	6.4504545	0.6198760
C	2.0710535	5.5505553	1.4512217
C	1.7666893	6.5162688	-0.7424118
C	2.7599210	5.6602054	-1.2465442
C	3.3974412	4.7654397	-0.4069318
C	3.0548504	4.7081116	0.9410660
H	0.6644948	7.1098822	1.0113215
Se	0.9036496	7.7277566	-1.8700978
H	3.0213525	5.7086547	-2.2969804
H	4.1640714	4.1082190	-0.8009069
H	3.5561066	4.0046599	1.5961258
H	1.8064531	5.5031022	2.5012718

Table S26 PhSe• coordinates for ground state optimized geometry.

28

II• Optimized Geometry RPA Energy =-2941.99691669796

C	-3.5340481	-1.2720549	1.1639179
C	-3.4480415	-2.4761429	1.8617297
C	-2.5923456	-0.9529275	0.2076517
H	-4.3432989	-0.5812890	1.3739992
C	-2.4019668	-3.3547333	1.5863601
H	-4.1871665	-2.7259987	2.6140898
C	-1.4559560	-3.0449728	0.6291275
H	-2.3266336	-4.2902616	2.1299047
C	-1.5255410	-1.8318810	-0.0942432
H	-0.6470043	-3.7405140	0.4397132
H	-2.6619938	-0.0132002	-0.3308960
C	-0.5850293	-1.4722967	-1.0864252
C	0.5792953	-2.2653640	-1.4747922
Se	2.1334464	-1.9721947	-0.2411283
C	2.2902401	-0.0740174	-0.4161400
C	2.3364344	0.5363308	-1.6665824
C	2.3867322	0.7016321	0.7347835
C	2.4623104	1.9145450	-1.7609452
C	2.5681575	2.6893511	-0.6121877
H	2.4888572	2.3836270	-2.7383251
H	2.3344581	0.2317182	1.7104409
H	2.6736152	3.7654953	-0.6894881
H	2.6154212	2.6760142	1.5355300
H	-0.6884949	-0.4909471	-1.5374711

H	0.9320578	-2.0269836	-2.4758528
C	2.5372516	2.0788382	0.6337611
H	2.2780250	-0.0603709	-2.5698896
H	0.4315880	-3.3436516	-1.4012124

Table S27 II• coordinates for ground state optimized geometry.

6.5 Dexter energy transfer (DET) mechanism

Geometry structure optimizations using the PBE0 hybrid density functional,[18,19] Grimme's D3 dispersion correction,[20] and the Conductor-like Screening Model (COSMO)[21] with the dielectric constant of 1,2-Dichloroethane (ϵ =10.45) were performed. The polarized triple ζ def2-TZVP basis set,[22] the Resolution-of-the-identity approximation (RI),[23] and a DFT quadrature grid of size m4[24] were used. Unrestricted vertical excitations using TDDFT[25] and without COSMO were done on ground state orbitals with COSMO. The energy gap between the lowest triplet and ground state was computed from the difference of the electronic energies at the minimized geometry of the ground state. The rigid-rotor harmonic oscillator approximation at a temperature of 298.15 K and a pressure of 0.1 MPa was used to compute free energies. The 2D triplet and singlet potential energy surfaces were obtained by constraining the H–C and Se–C bond lengths and optimizing in a triplet configuration.

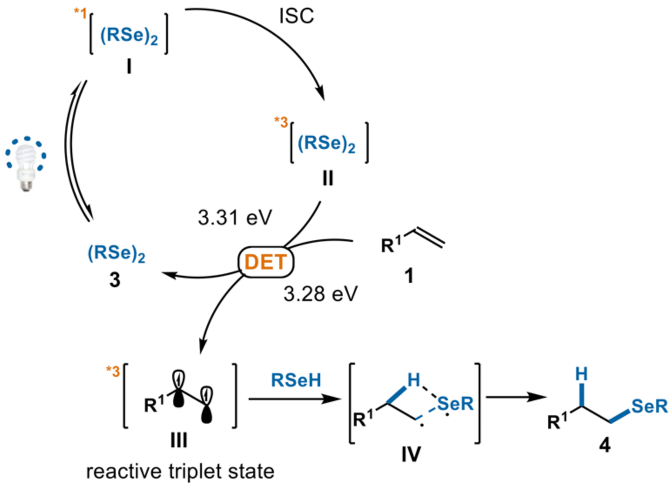

Fig. S25 Proposed DET mechanism for *syn*-addition *anti*-Markovnikov hydroselenation

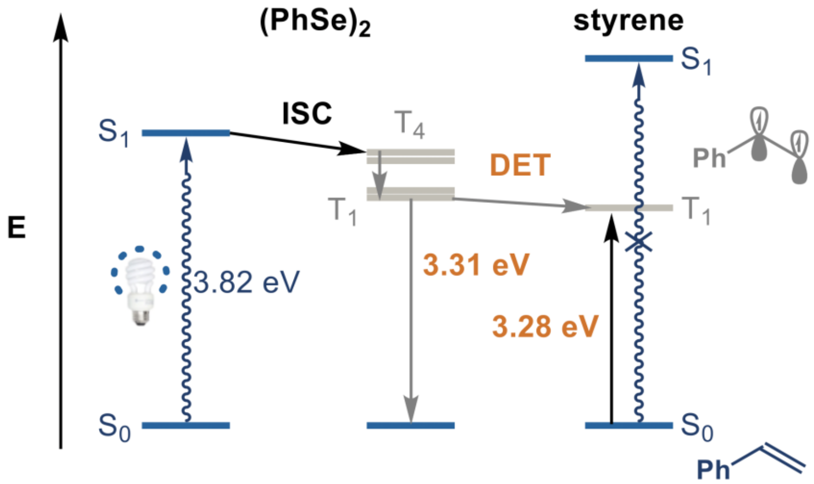

Fig. S26. Energy diagram for photocatalyzed hydroselenation reaction based on DFT results.

	T_1 TDDFT excitation (eV)	T_1 - S_0 excitation (eV)	Character
PhSeH (**1a**)	3.46	3.92	ππ*
Styrene (**2a**)	2.78	3.28	ππ*
Ph_2Se_2 (**3a)**	3.25	3.31	πσ*
Styrene & Ph_2Se_2 complex	T_1: 2.79 T_2: 3.00		ππ* πσ*

Table S28 First triplet excitation energy computed from the difference of the electronic energies at the minimized geometry of the ground state. Vertical excitations computed with TDDFT. PBE0 and the def2-TZVP basis set were used. The energetically similar excitations between styrene and diphenyl diselenide support DET.

Styrene (**1a**) & PhSeH (**2a**)	Relative Singlet energy (eV)	Relative Triplet energy (eV)
Singlet optimized geometry	0	3.29
Triplet optimized geometry	3.45	2.31

Table S29 Excitation energies were computed from the difference of the electronic energies at the minimized geometry. All energies are relative to ground state optimized geometry. PBE0 and the def2-TZVP basis set were used.

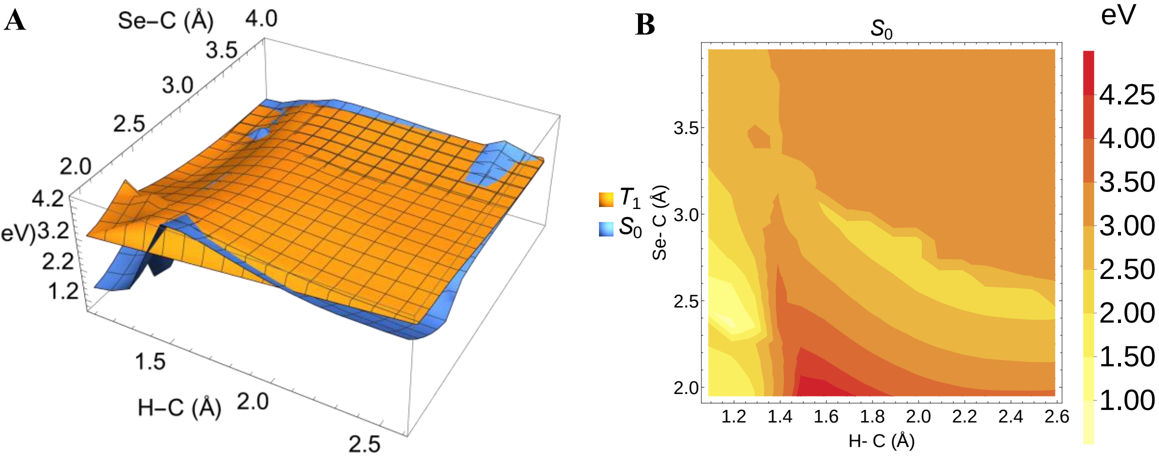

Fig. S27 2D T_1 and S_0 potential energy surfaces (A) and contour plot of the ground state (B) for styrene (**1a**)-PhSeH (**2a**) addition. The geometries were obtained by constraining the H–C and Se–C bond lengths and optimizing in a triplet configuration. All electronic energies are relative to the ground state optimized geometry of the *anti*-Markovnikov product. The relatively flat triplet surface suggests the addition occurs on the ground state surface. The intersections of the two surfaces support intersystem crossing. The energy of T_1 at the ground state reactant geometry relative to the *anti*-Markovnikov product is 4.14 eV which suggests that some of the geometries are energetically inaccessible. This barrier impedes the Se before H pathway while the H before Se pathway is relatively downhill.

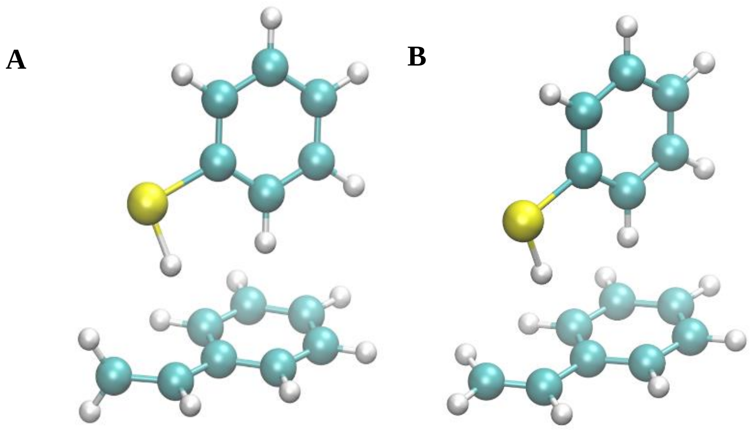

Fig. S28. Complexes of styrene (**1a**) & PhSeH (**2a**) triplet (A) and singlet (B) optimized geometries.

A. Triplet

Energy = -2942.634219707

C	1.1199528	-2.2267107	0.1922596
C	-0.2278805	-2.5464588	-0.1031664
C	1.5277313	-2.0105065	1.4925268
C	0.6192837	-2.1052608	2.5458057
C	-1.1336957	-2.6365010	0.9828376
C	-0.7134224	-2.4198710	2.2785394
H	1.8306115	-2.1452111	-0.6231037
H	2.5631614	-1.7596097	1.6948824
H	0.9447122	-1.9296619	3.5644644
H	-1.4255605	-2.4905135	3.0933584
H	-2.1725188	-2.8758256	0.7797865
C	-0.6744682	-2.7599645	-1.4268159
C	0.1644057	-2.7104312	-2.6092892
H	-0.3949356	-0.1866531	-1.4146355
H	-1.7295787	-3.0045185	-1.5569344
Se	0.0001810	1.1691786	-1.8198161
H	0.2482511	-1.8077423	-3.2089574
H	0.6503666	-3.6031081	-2.9937054
C	-0.1076767	1.9131797	-0.0637542
C	0.0867744	3.2844057	0.0789017
C	-0.2275698	3.0819197	2.4596521
C	-0.4218225	1.7152795	2.3100732
C	-0.3614748	1.1264550	1.0550706
C	0.0276795	3.8620481	1.3392914
H	0.2831235	3.9053380	-0.7887586
H	0.1807272	4.9306224	1.4423457
H	-0.5045625	0.0572017	0.9578502
H	-0.2744146	3.5364771	3.4424560
H	-0.6184625	1.0934128	3.1766246

B. Singlet

Energy = -2942.719057498

C	1.1486184	-2.3386533	0.2761690
C	-0.1647500	-2.5949562	-0.1338354
C	1.4429745	-2.1169280	1.6106182
C	0.4343417	-2.1455901	2.5682336
C	-1.1670523	-2.6204553	0.8398026
C	-0.8731568	-2.3964154	2.1772221
H	1.9501654	-2.3189104	-0.4532981
H	2.4665613	-1.9192400	1.9083198
H	0.6687322	-1.9696642	3.6118826
H	-1.6680548	-2.4159814	2.9141979

H	-2.1911785	-2.8156407	0.5383764
C	-0.5320404	-2.8329162	-1.5331455
C	0.2537248	-2.6916828	-2.6000548
H	-0.3099593	-0.2204751	-1.3255312
H	-1.5646805	-3.1382579	-1.6873115
Se	-0.3957368	1.1707789	-1.7846901
H	-0.1249670	-2.8900907	-3.5955392
H	1.2879992	-2.3726862	-2.5261219
C	-0.2523449	1.9446786	-0.0446079
C	-0.2094726	3.3323803	0.0586830
C	-0.0356397	3.1493875	2.4557468
C	-0.0807798	1.7658283	2.3458870
C	-0.1916428	1.1600054	1.1026675
C	-0.1027031	3.9279684	1.3076885
H	-0.2561741	3.9520373	-0.8305824
H	-0.0692259	5.0094348	1.3800354
H	-0.2259032	0.0795415	1.0338129
H	0.0510201	3.6180896	3.4291418
H	-0.0297569	1.1453832	3.2340227

Table S30 Coordinates for styrene (**1a**)-PhSeH (**2a**) addition, for triplet (A) and singlet (B) optimized geometries.

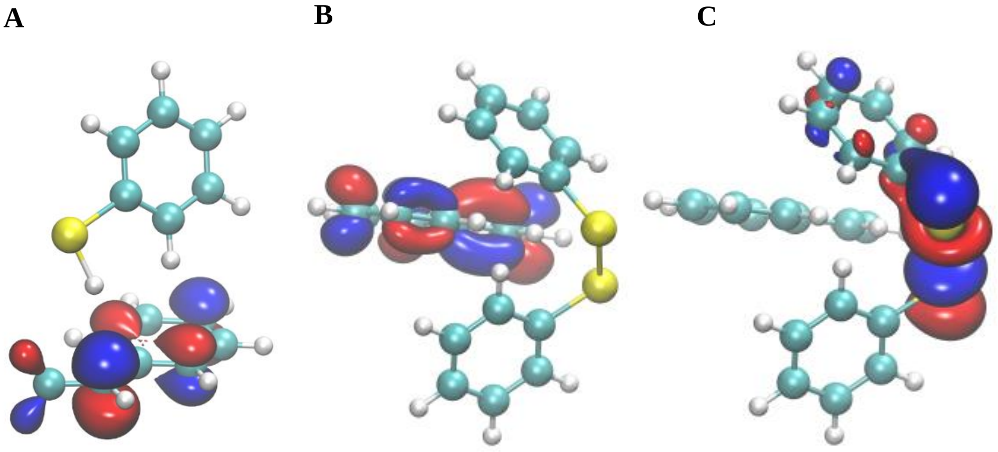

Fig. S29 Styrene (**1a**) & PhSeH (**2a**) SOMO at triplet ground state optimized geometry (A). The dominant virtual orbitals involved in the T_1 (B) and T_2 (C) excitations of a styrene and diphenyl diselenide complex.

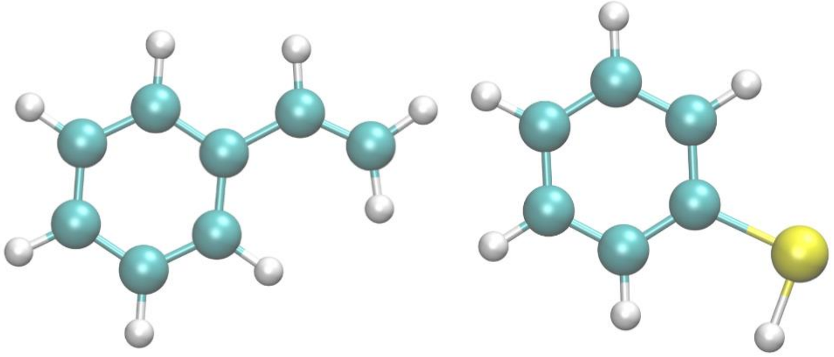

Fig. S30 Styrene (**1a**) and PhSeH (**2a**) ground state optimized geometry.

A. Styrene (**1a**) coordinates

Energy = -309.3875009213

C	-1.8108392	2.5027199	-0.0000342
C	-1.9188968	1.1195948	0.0003671
C	-0.5589633	3.1011697	-0.0005146
H	-2.7029903	3.1190437	0.0000058
C	-0.7647452	0.3422599	-0.0000307
H	-2.8946378	0.6470790	0.0011230
C	0.4830368	0.9410229	-0.0002941
H	-0.8406175	-0.7395307	-0.0002600
C	0.6088456	2.3344631	-0.0003606
H	1.3696475	0.3171990	-0.0003345
H	-0.4796806	4.1837967	-0.0011322
C	1.9039854	3.0202329	0.0002913
C	3.1117920	2.4580234	0.0001384
H	1.8421308	4.1066334	0.0008862
H	3.2569186	1.3828855	-0.0005890
H	4.0062040	3.0696370	0.0007380

B. PhSeH (**2a**) coordinates

Energy = -2633.324525208

C	-3.4695997	4.8511798	-0.0000731
C	-3.4027210	3.4642989	0.0000207
C	-2.2948893	5.5917333	0.0000169
H	-4.4309153	5.3516388	-0.0002266
C	-2.1748351	2.8169138	0.0001152
H	-4.3130419	2.8749381	-0.0000121
C	-1.0005637	3.5637946	0.0000958
H	-2.1380263	1.7335214	0.0002956
C	-1.0622022	4.9548166	0.0001009
H	-2.3334867	6.6753949	-0.0000007
H	-0.1520377	5.5451933	0.0000659

Se	0.7263969	2.7483827	-0.0000361
H	0.2273319	1.3690140	-0.0003623

Table S31 Ground state optimized geometry coordinates for styrene (**1a,** A) and PhSeH (**2a,** B).

6.6 Alkene radical cation mechanism

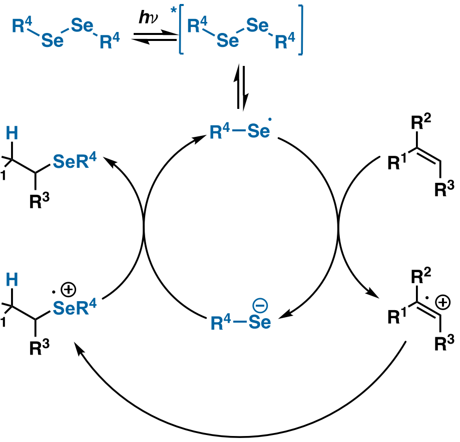

Fig. S31 Proposed mechanism involving alkenyl radical cation.

	S_1 TDDFT excitation (eV)
Ph_2Se_2 (**3a**)	3.82

	Energy (eV)
Styrene → Styrene$^+$	6.74
PhSe → PhSe$^-$	-4.27
Electrostatic Energy of q^+ and q^-	0.11
Total Energy	2.57

Table S32 The energetic feasibility of cationic radical styrene formation based on the energy of the photon which is absorbed by diphenyl diselenide. The electrostatic energy of the separation of the positive and negative charge is assumed to be in DCE (ϵ = 10.45) with a distance of ~13 Å separating them. The formation is energetically accessible, however, the mechanism is expected to be concerted which would favor the *syn* products over the *anti*.

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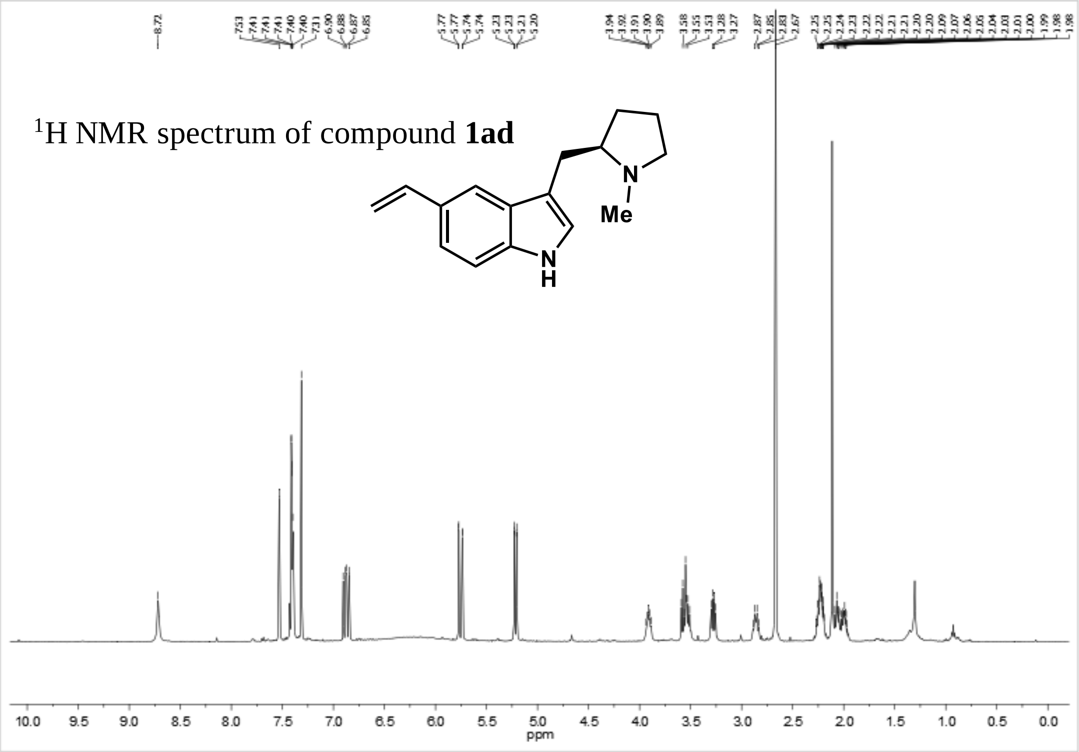
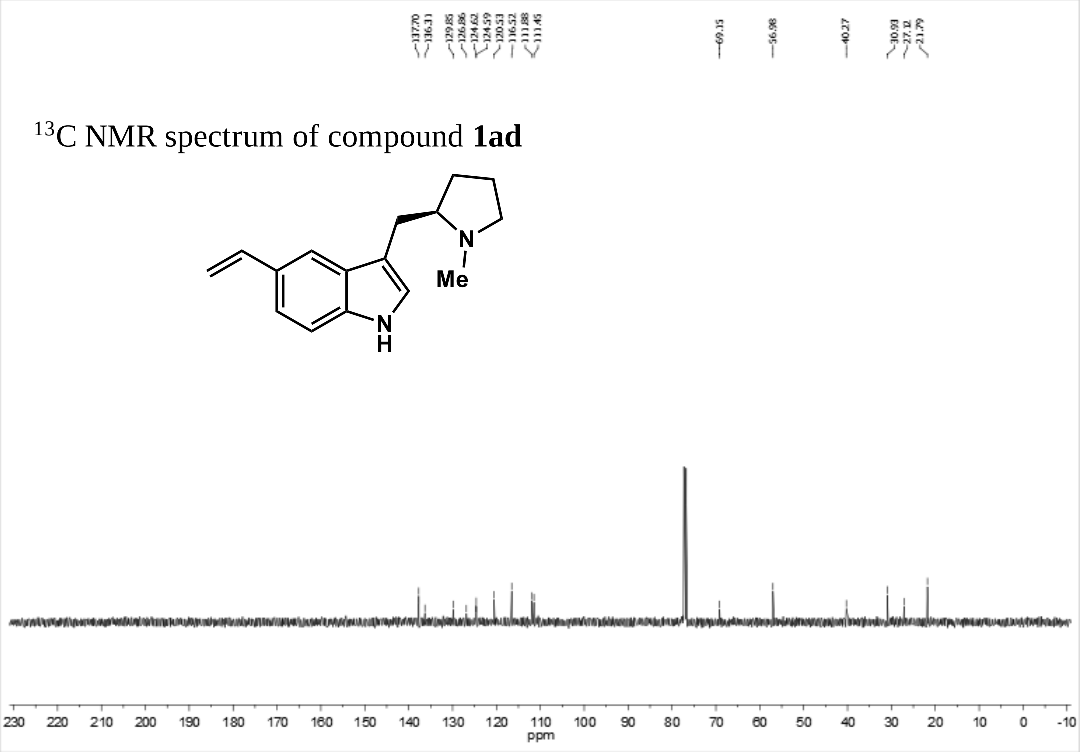
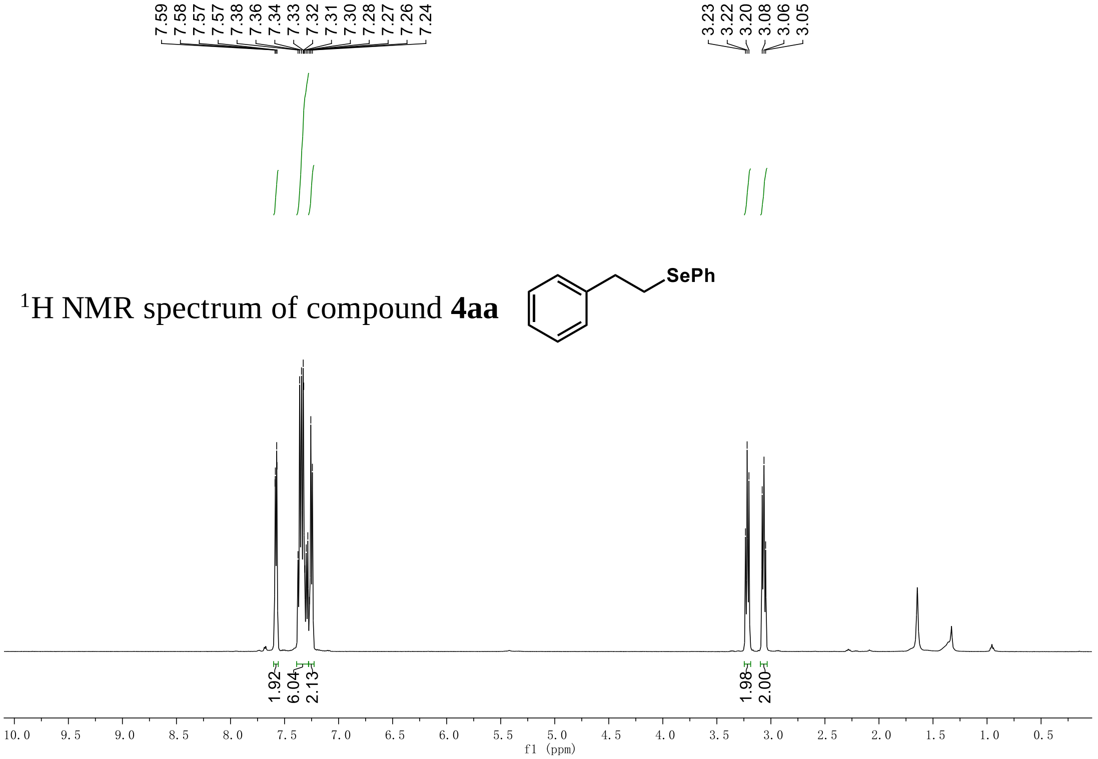
8. NMR spectra of unknown compounds

(*R*)-3-((1-methylpyrrolidin-2-yl)methyl)-5-vinyl-1H-indole (1ad)

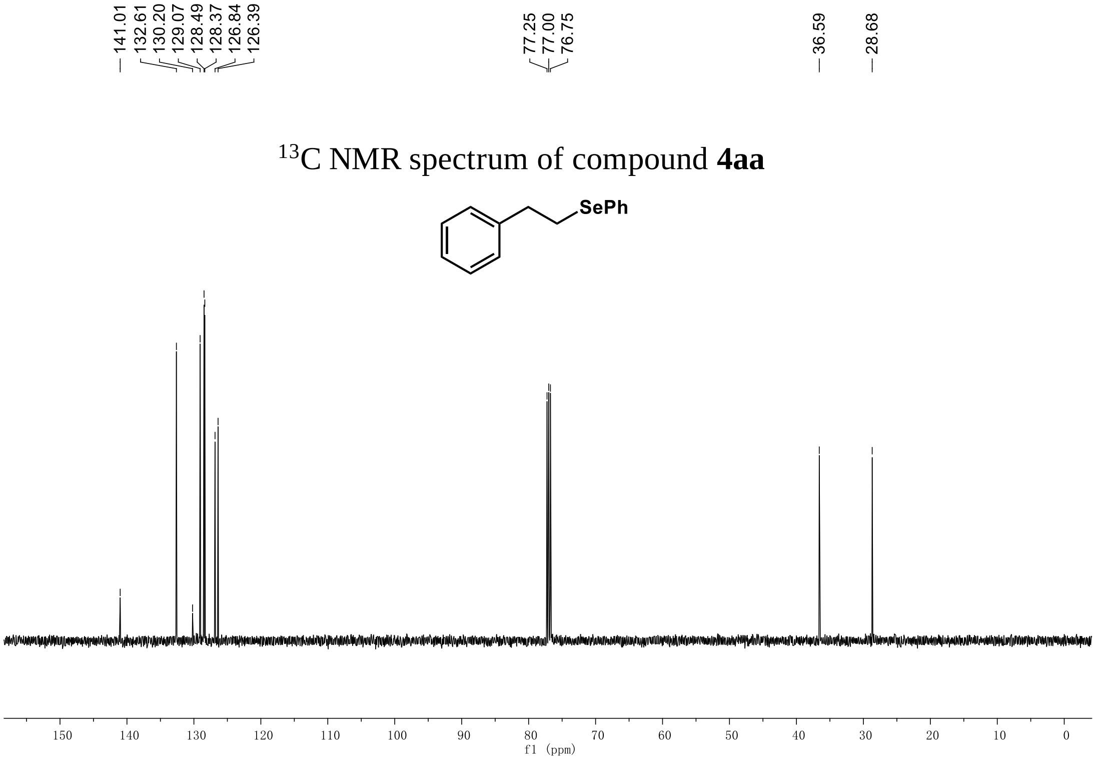




phenethyl(phenyl)selane (4aa)

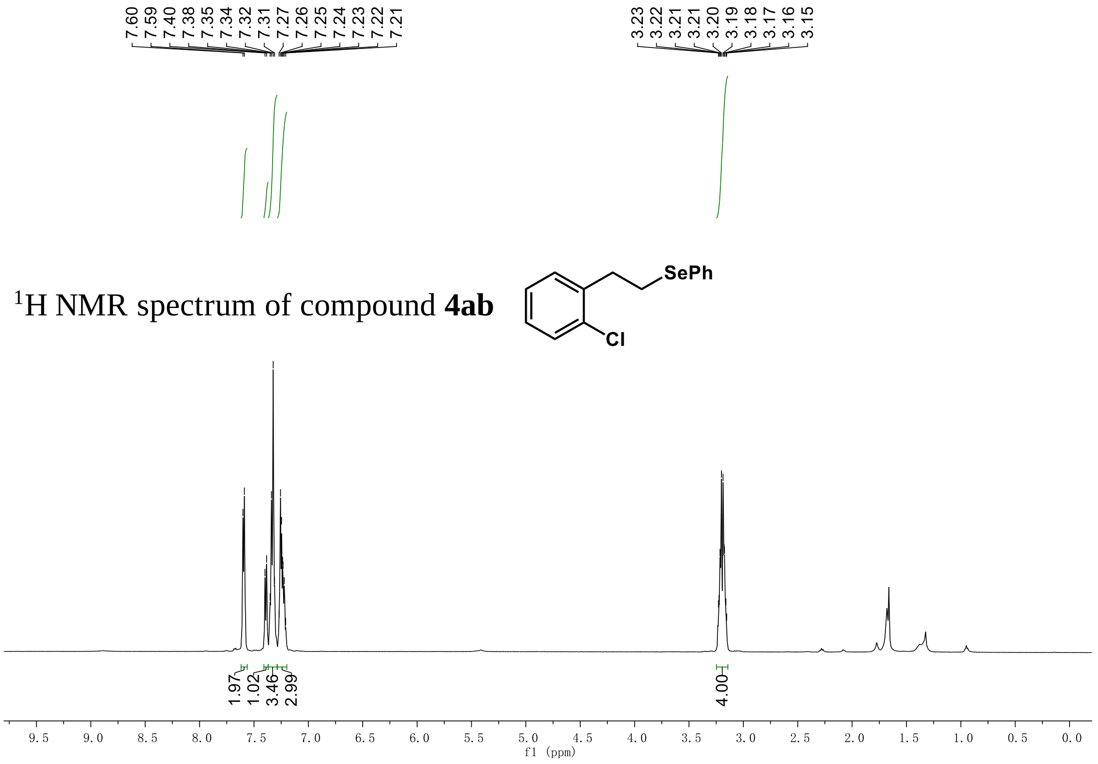


^{1}H NMR spectrum of compound **4aa**

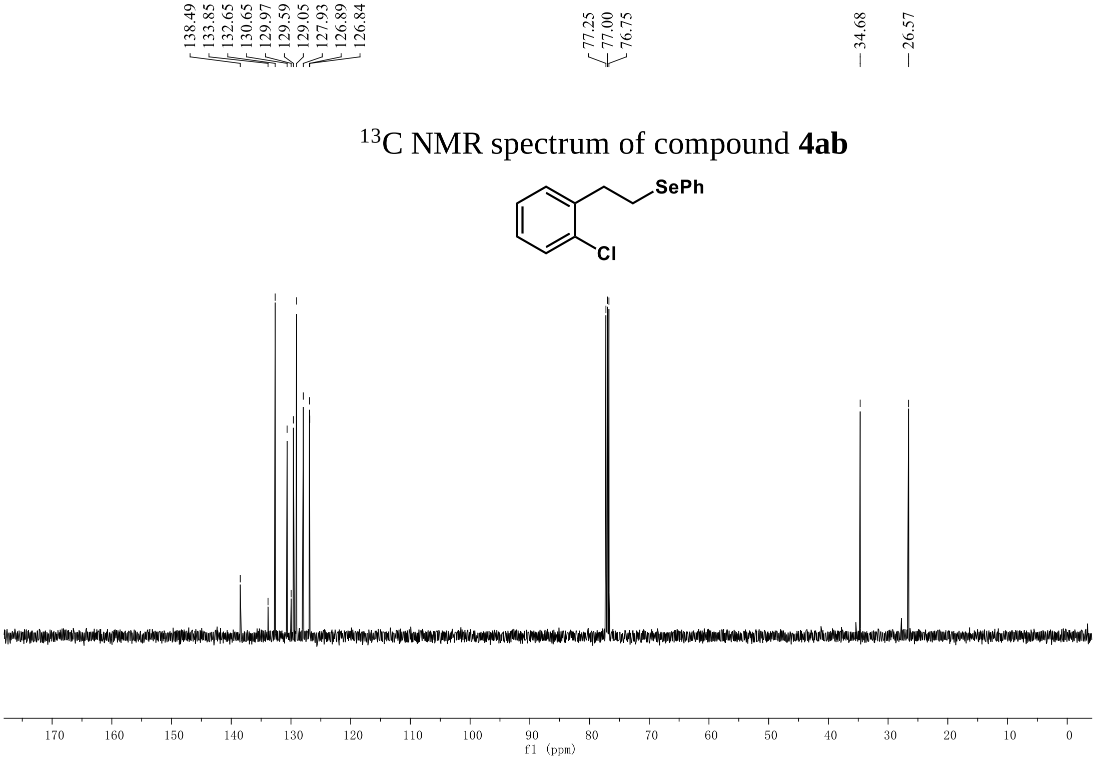


^{13}C NMR spectrum of compound **4aa**

(2-chlorophenethyl)(phenyl)selane (4ab)

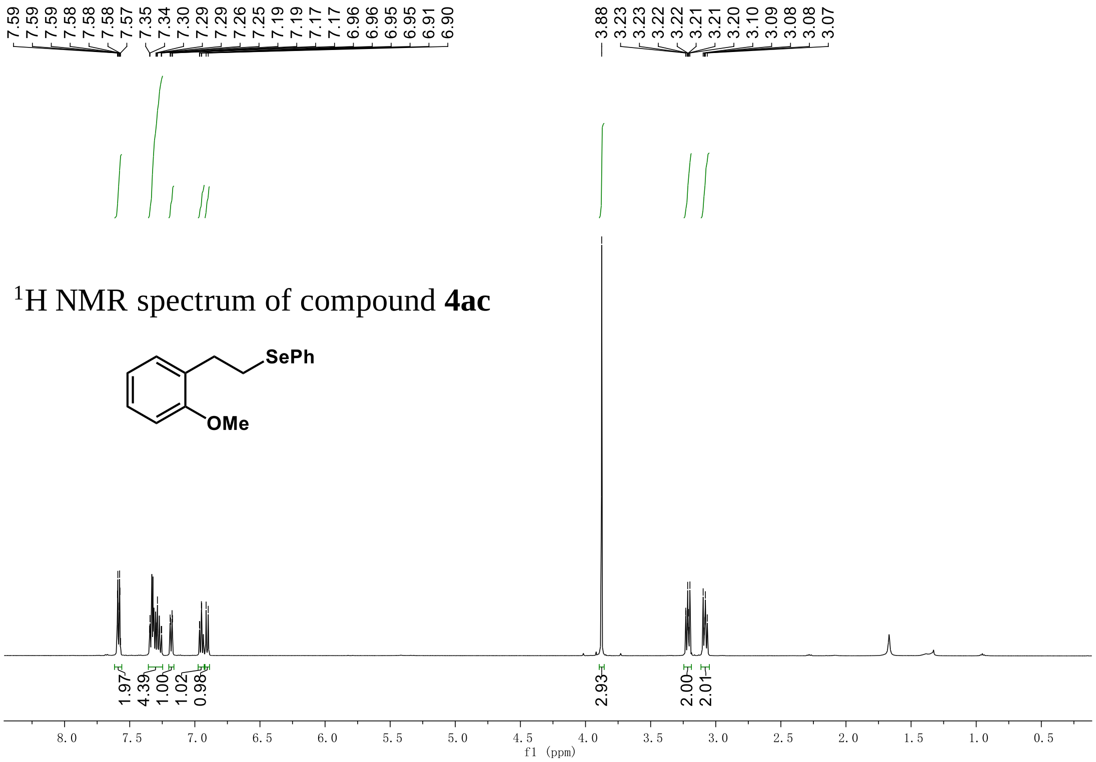


^{1}H NMR spectrum of compound **4ab**

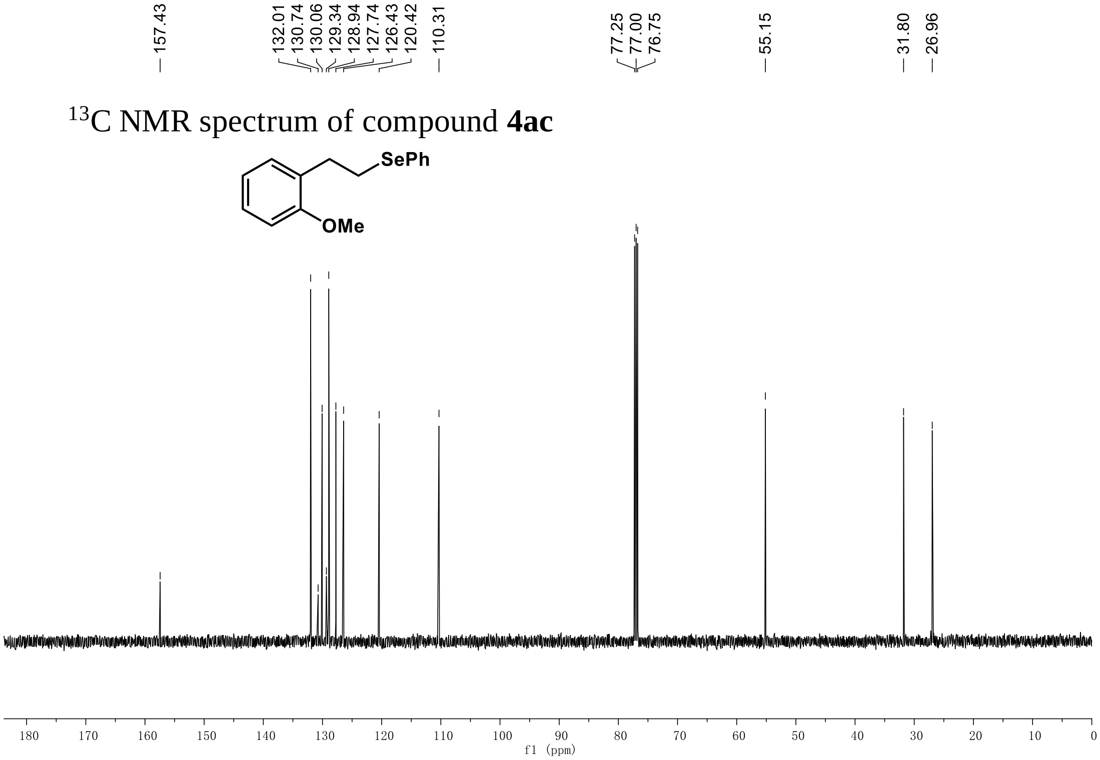


^{13}C NMR spectrum of compound **4ab**

(2-methoxyphenethyl)(phenyl)selane (4ac)

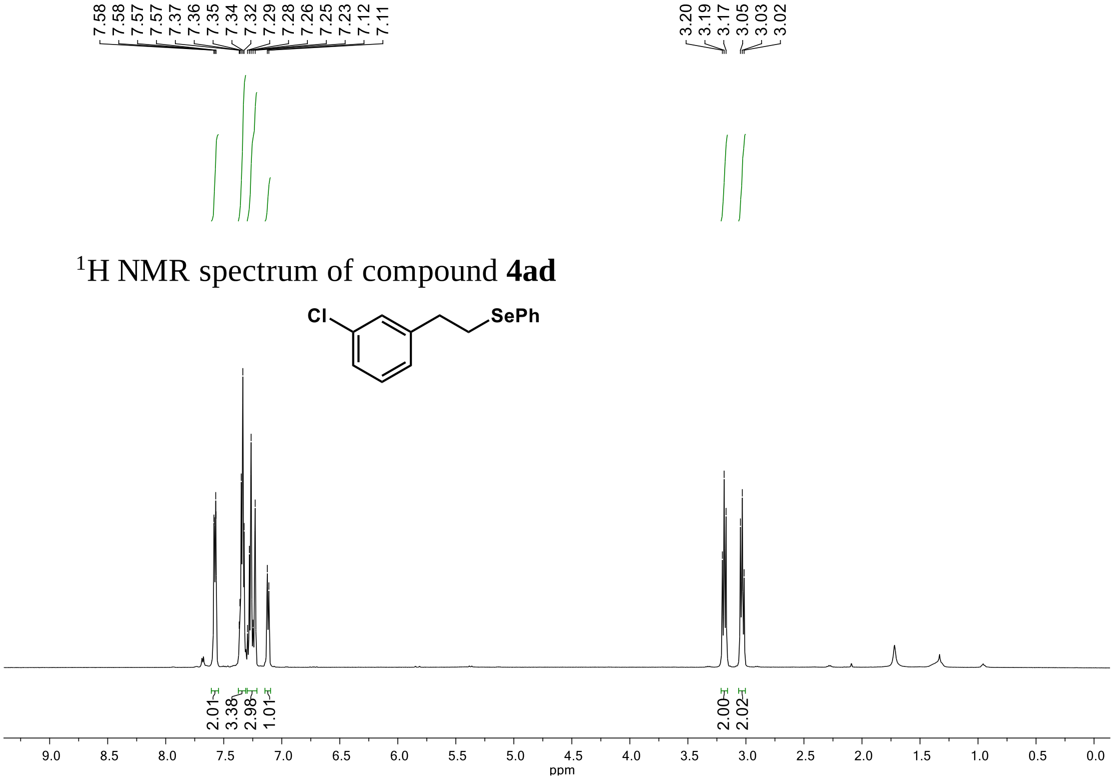


^{1}H NMR spectrum of compound **4ac**

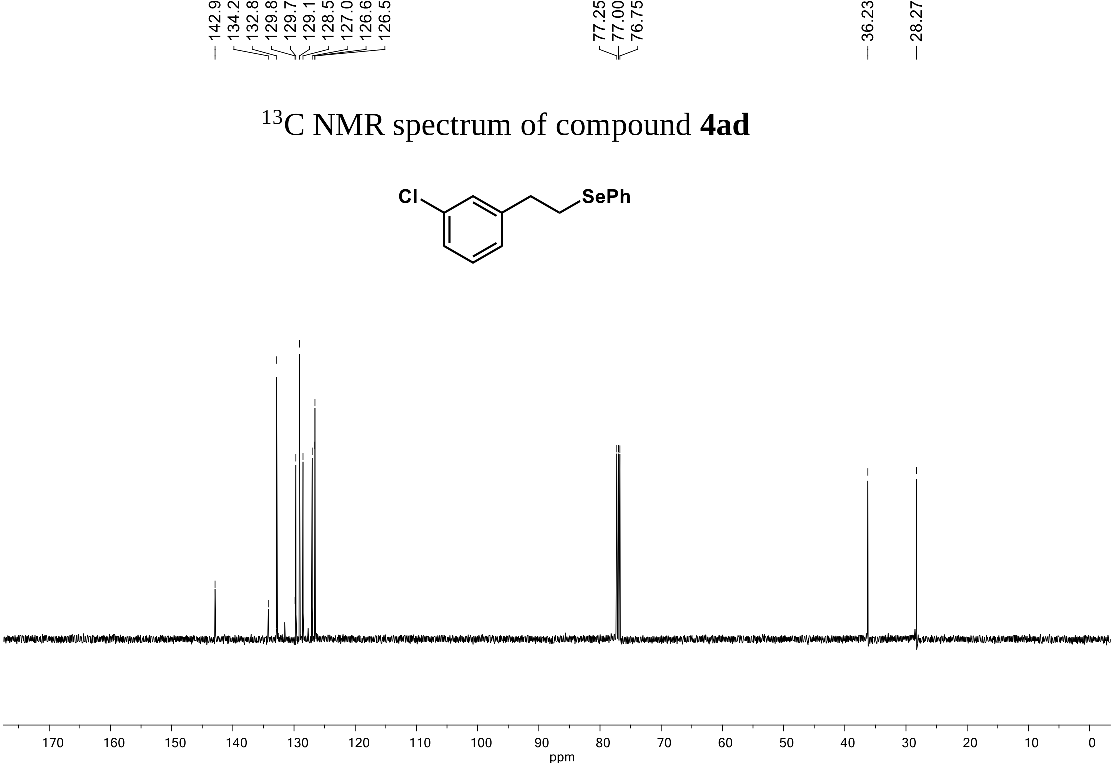


^{13}C NMR spectrum of compound **4ac**

(3-chlorophenethyl)(phenyl)selane (4ad)

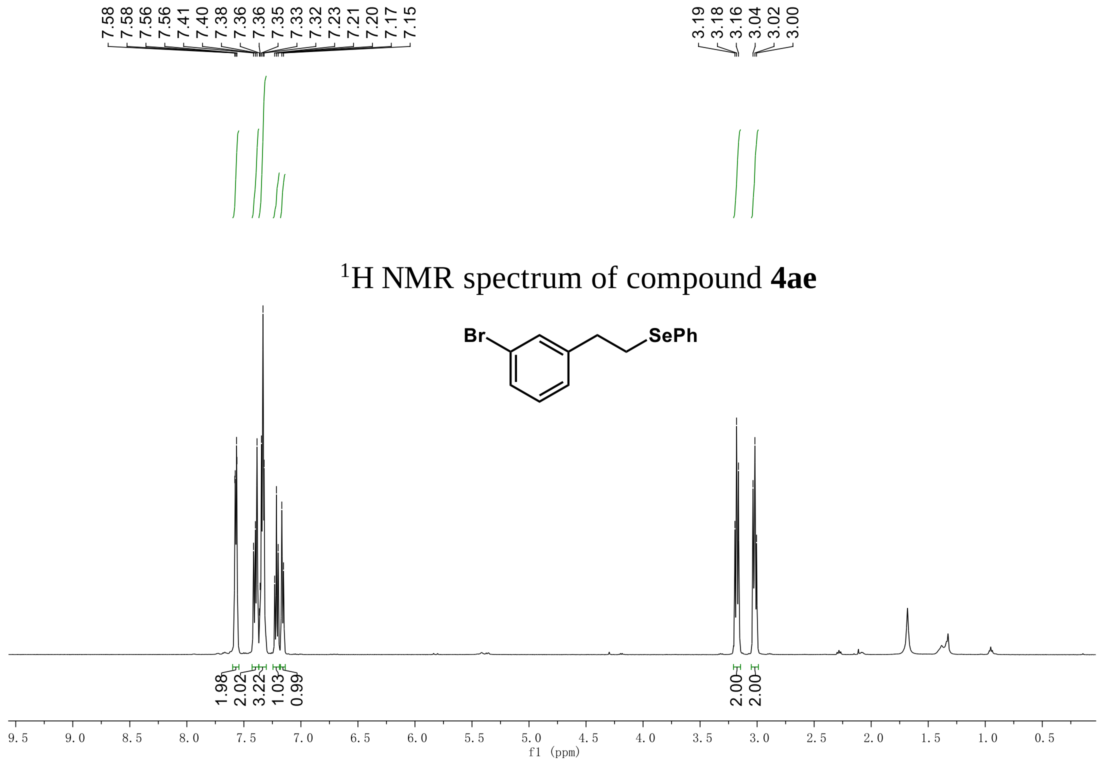


^{1}H NMR spectrum of compound **4ad**

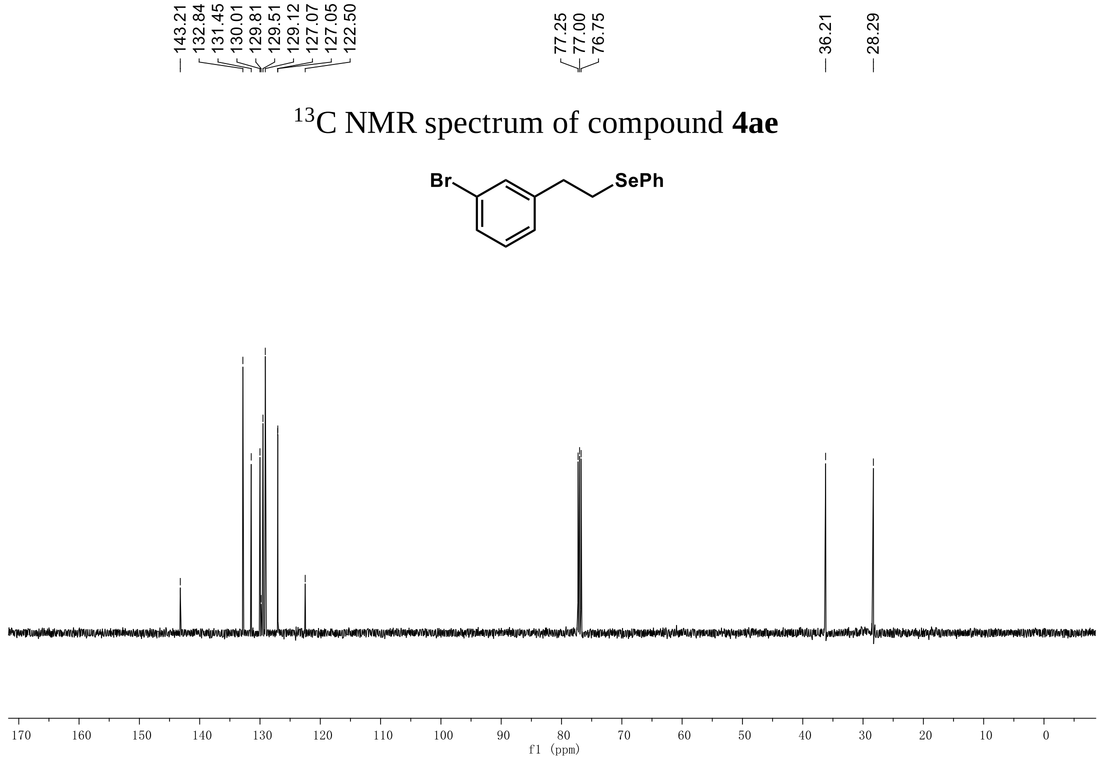


^{13}C NMR spectrum of compound **4ad**

(3-bromophenethyl)(phenyl)selane (4ae)

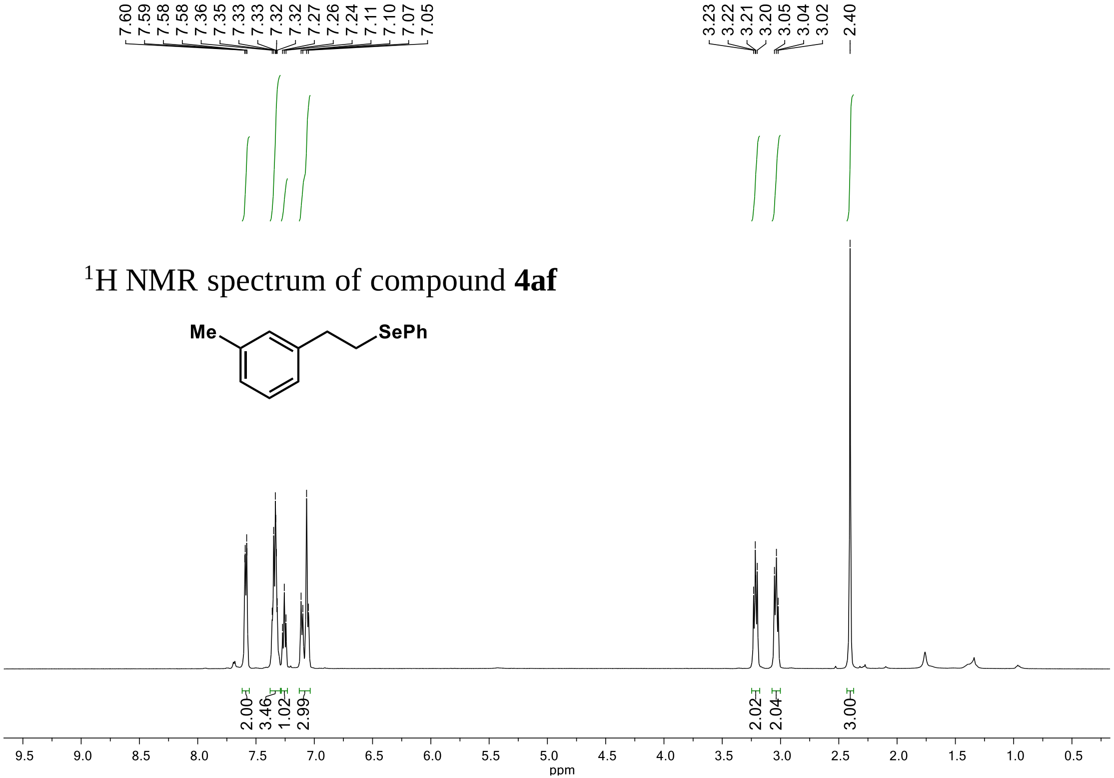


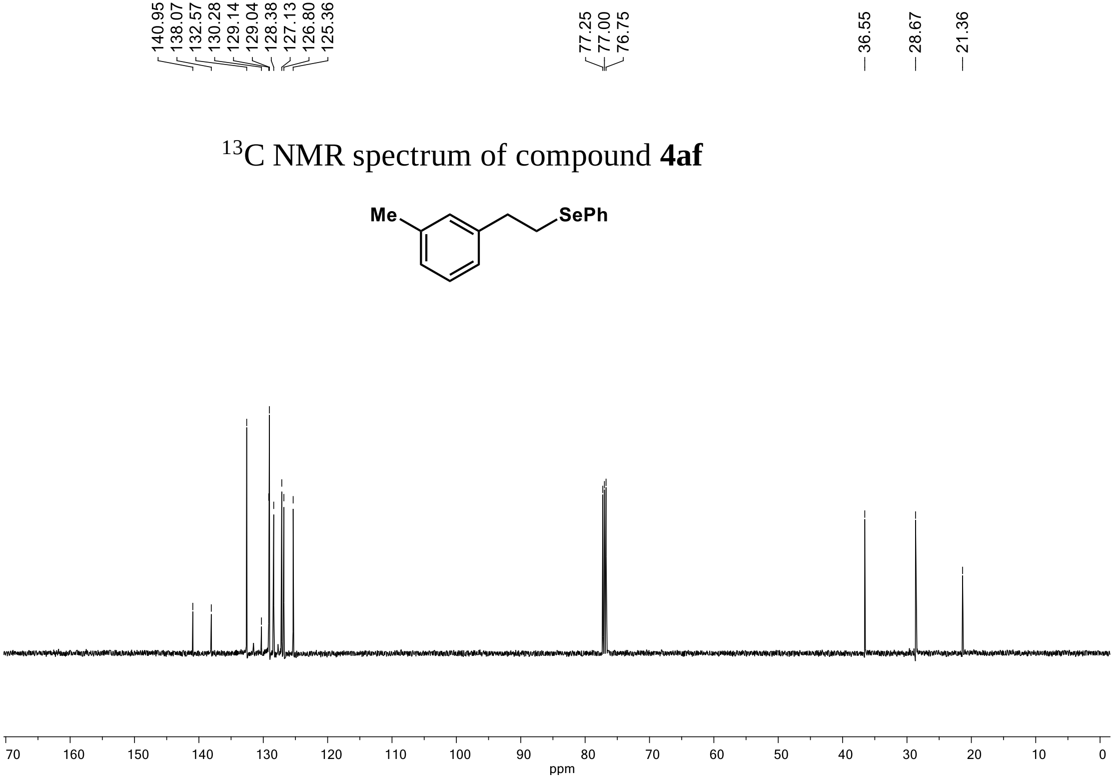
^{1}H NMR spectrum of compound **4ae**



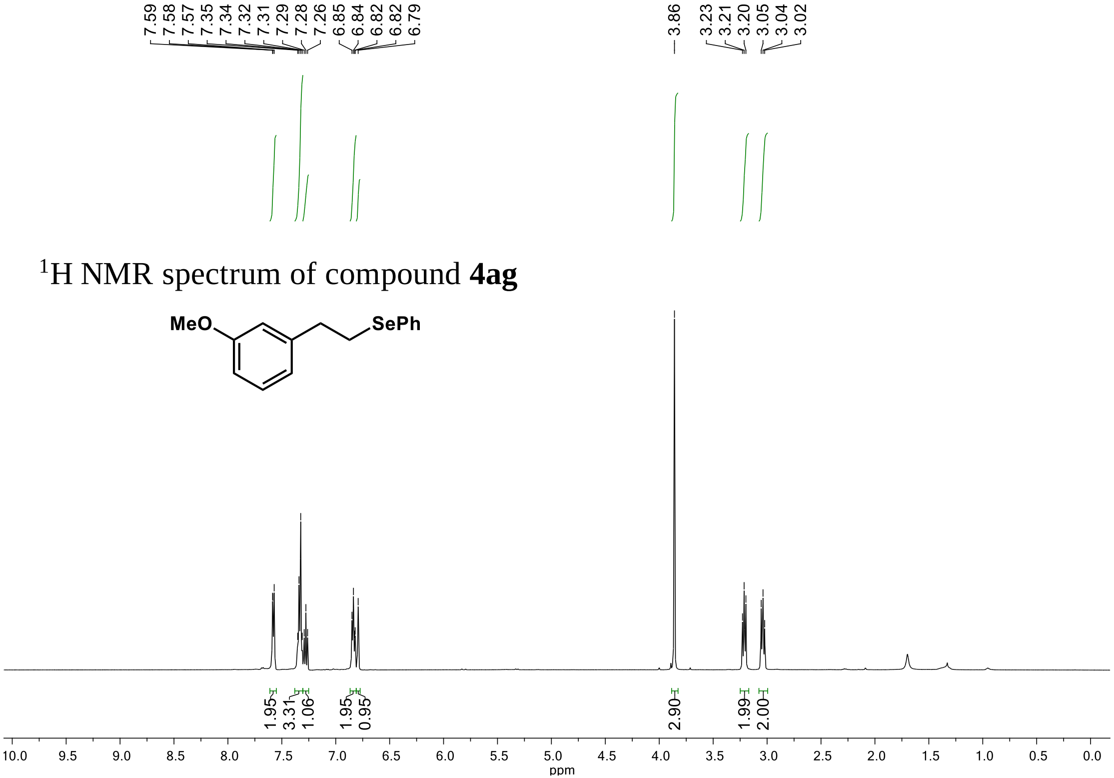
^{13}C NMR spectrum of compound **4ae**

(3-methylphenethyl)(phenyl)selane (4af)

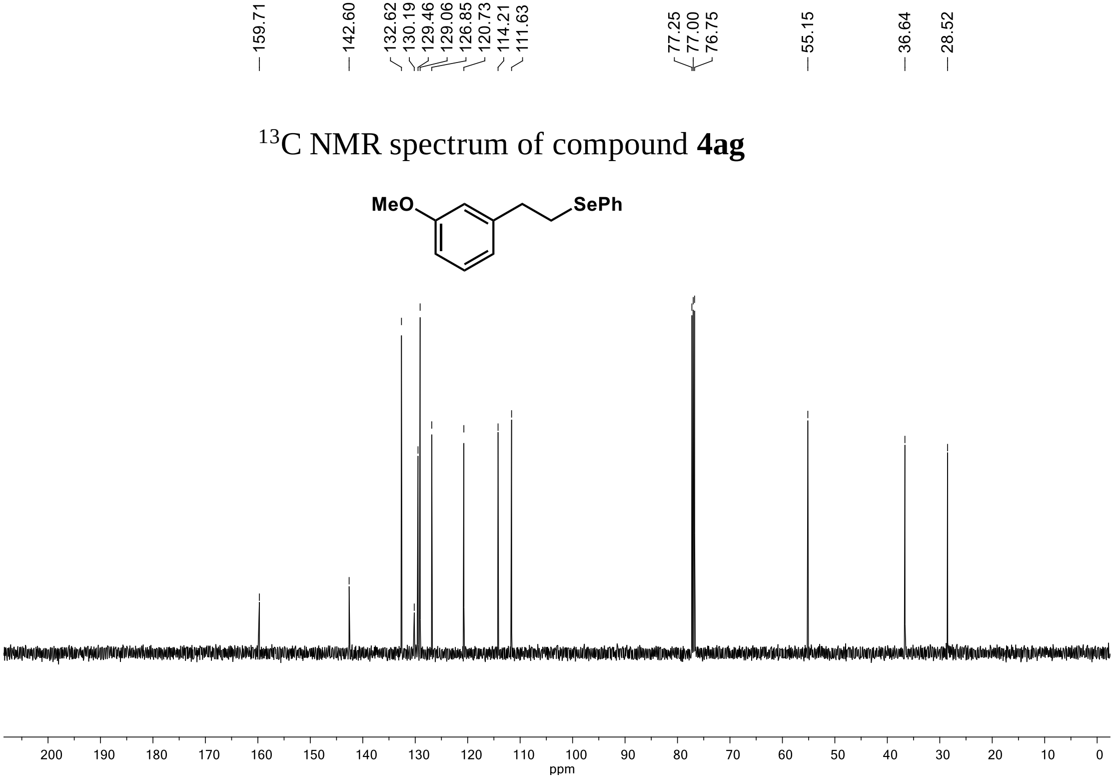

^{1}H NMR spectrum of compound **4af**


^{13}C NMR spectrum of compound **4af**

(3-methoxyphenethyl)(phenyl)selane (4ag)

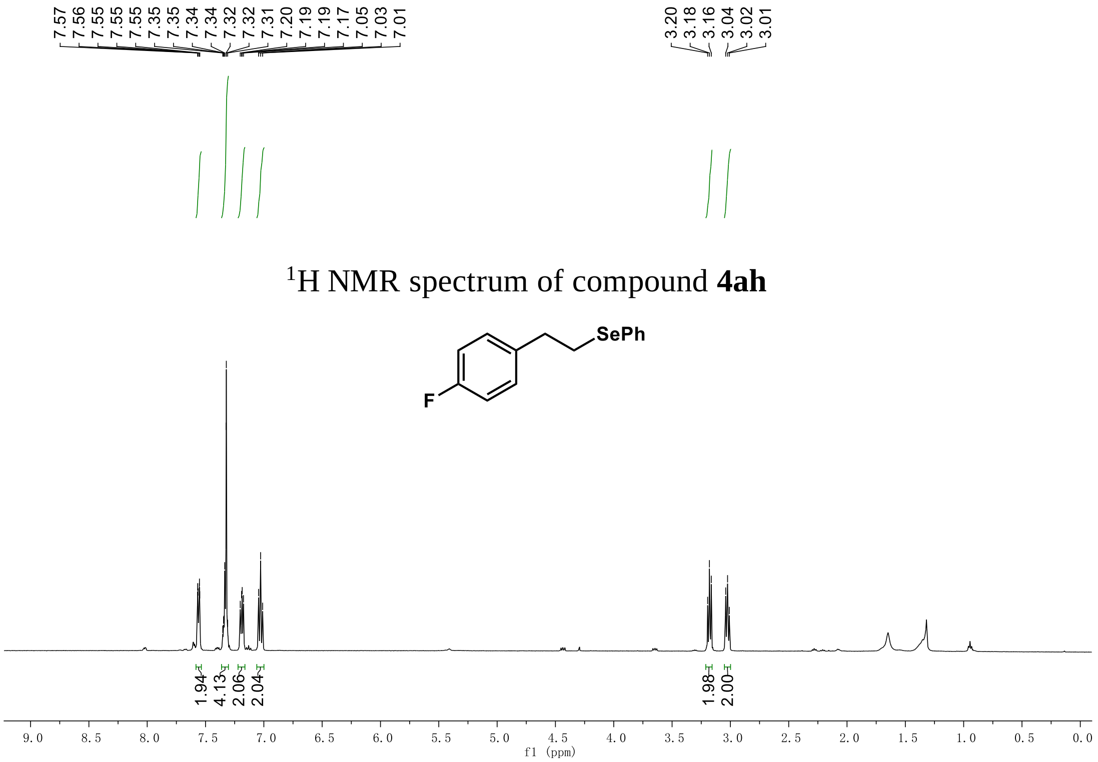


^{1}H NMR spectrum of compound **4ag**

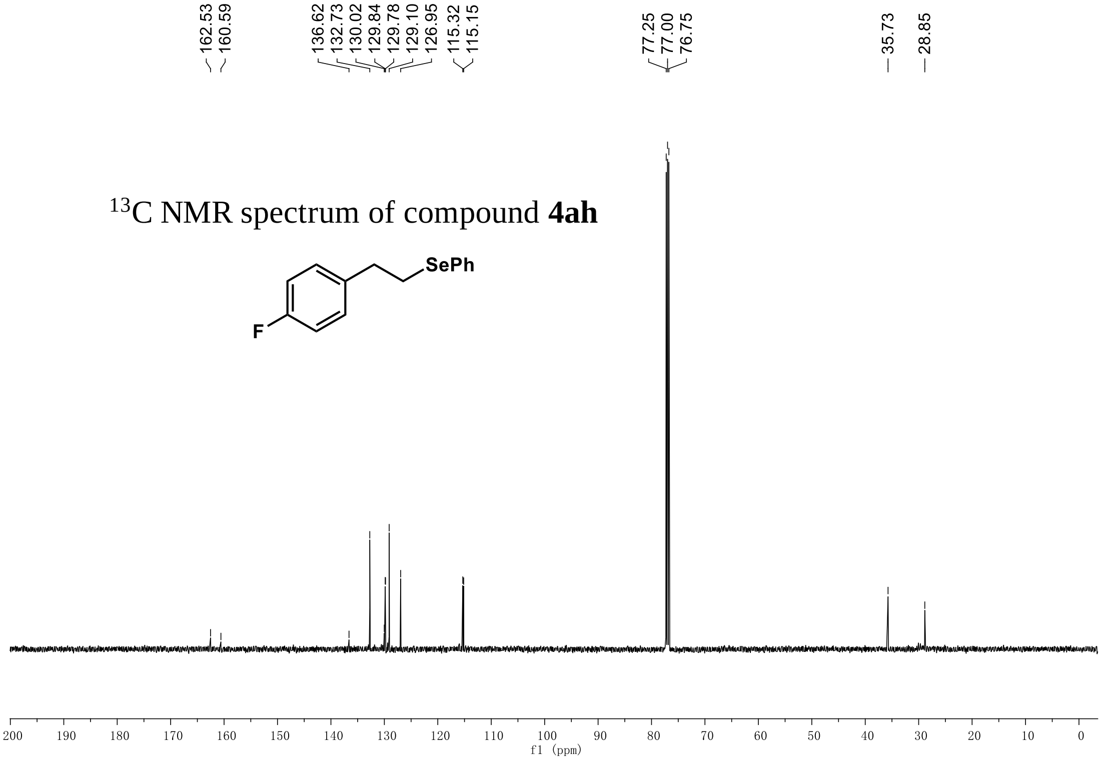


^{13}C NMR spectrum of compound **4ag**

(4-fluorophenethyl)(phenyl)selane (4ah)

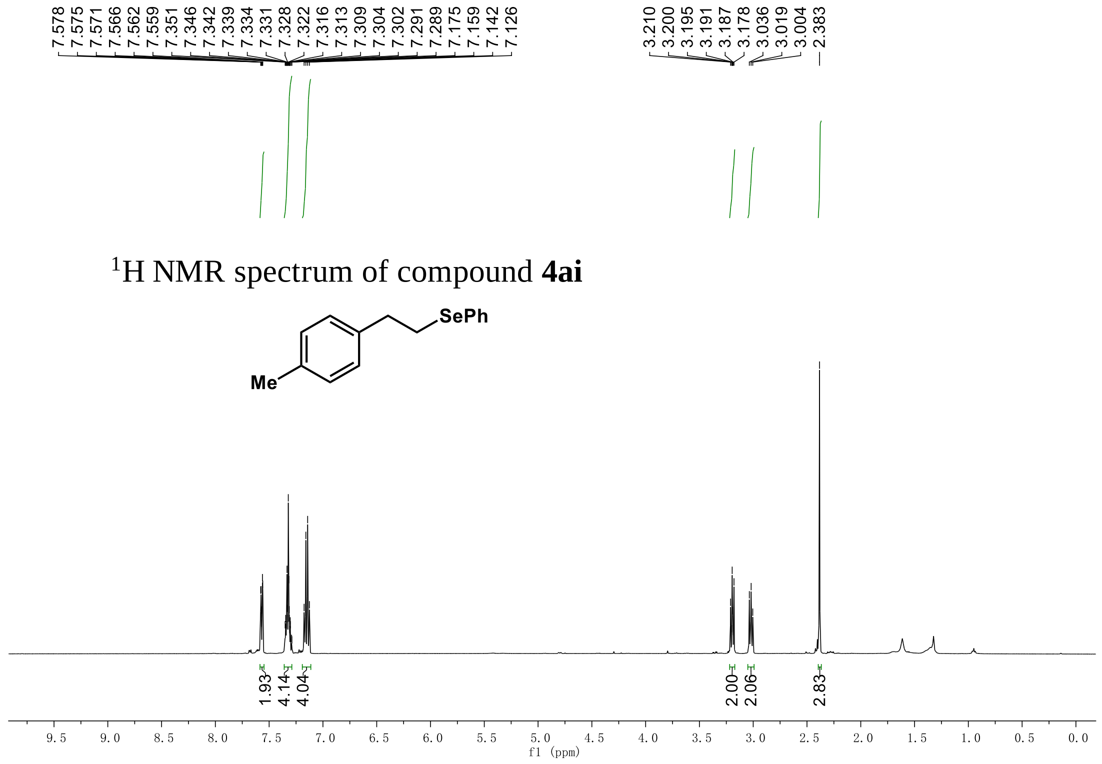


^{1}H NMR spectrum of compound **4ah**

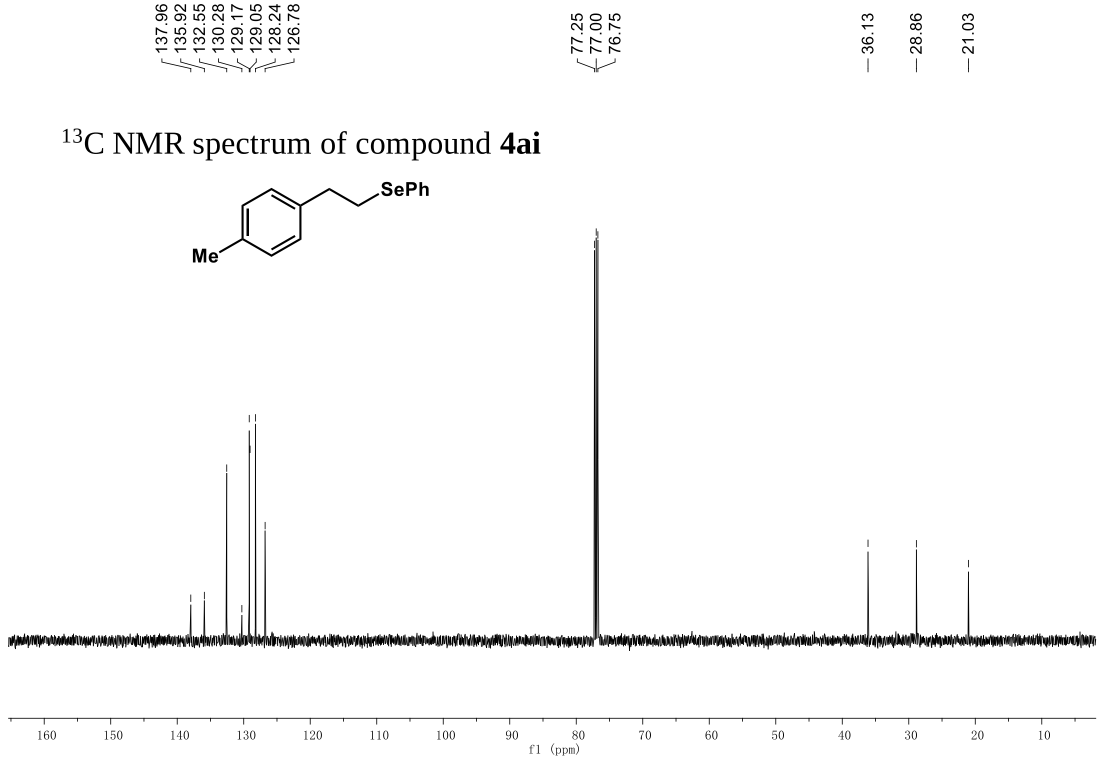


^{13}C NMR spectrum of compound **4ah**

(4-methylphenethyl)(phenyl)selane (4ai)

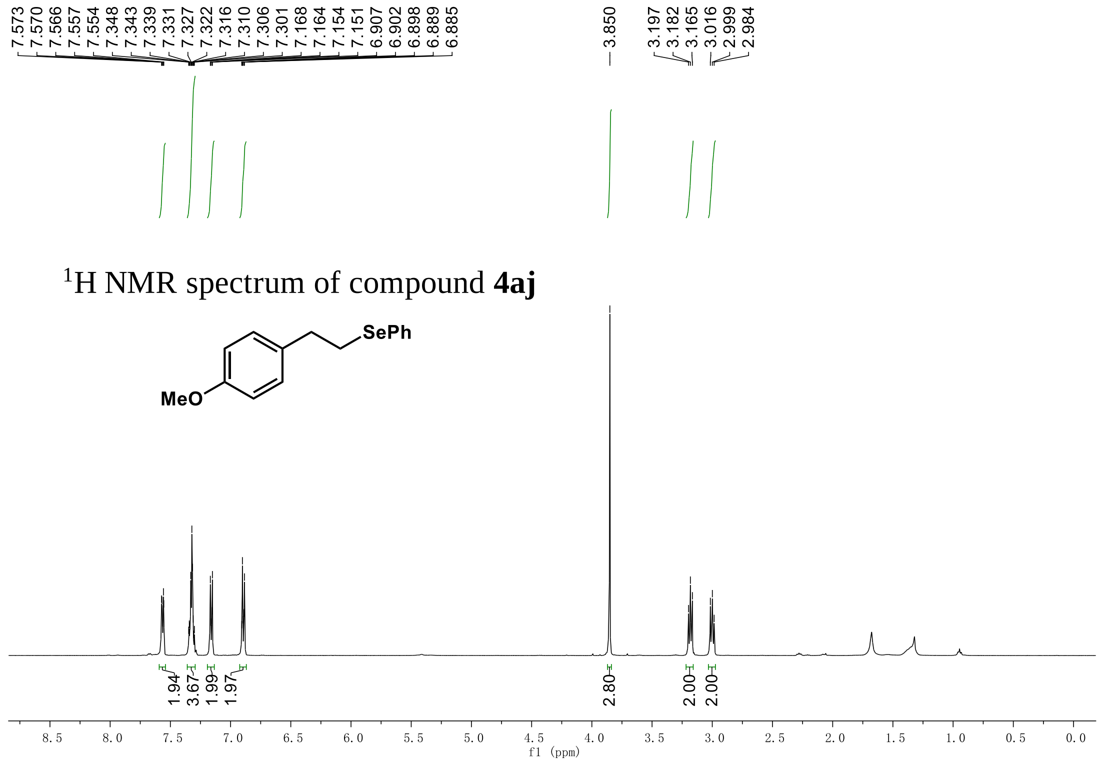


^{1}H NMR spectrum of compound **4ai**

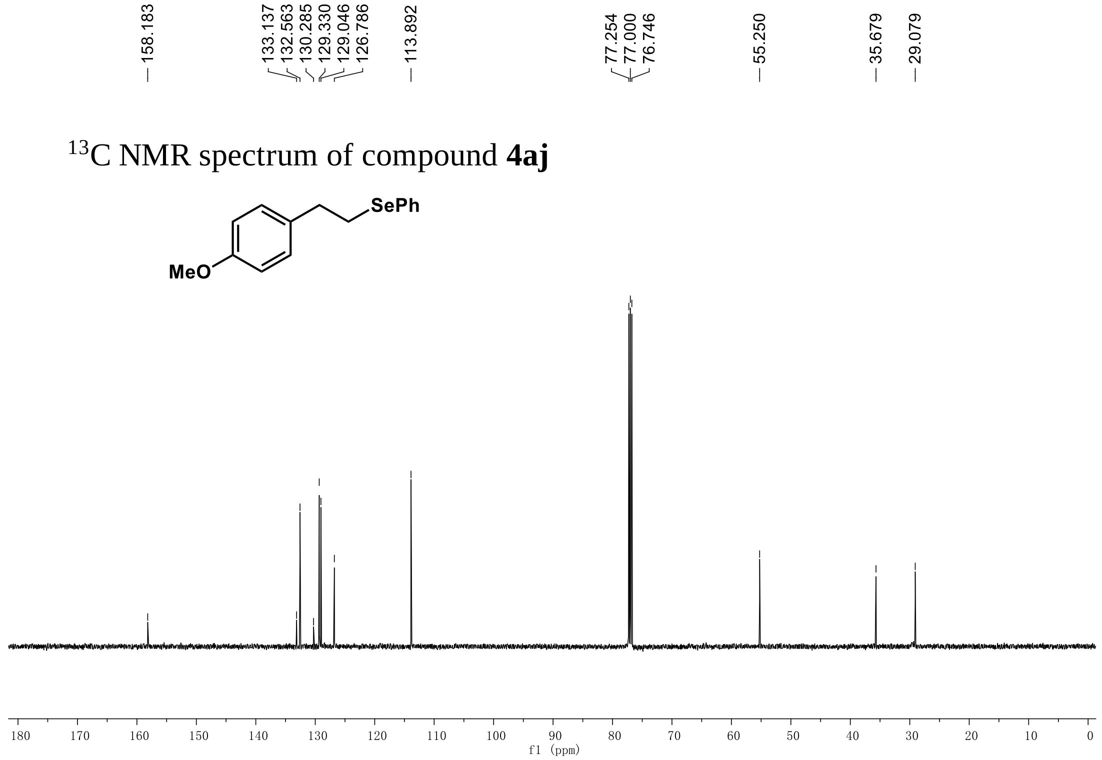


^{13}C NMR spectrum of compound **4ai**

(4-methoxyphenethyl)(phenyl)selane (4aj)

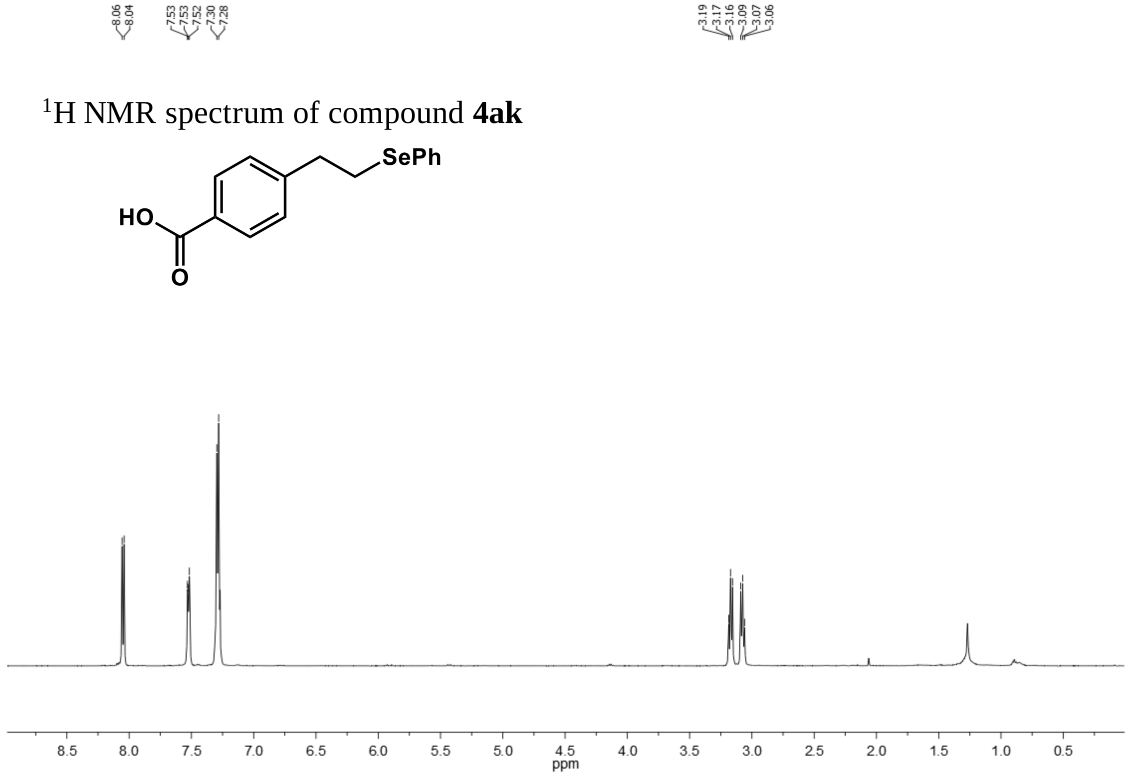


^{1}H NMR spectrum of compound **4aj**

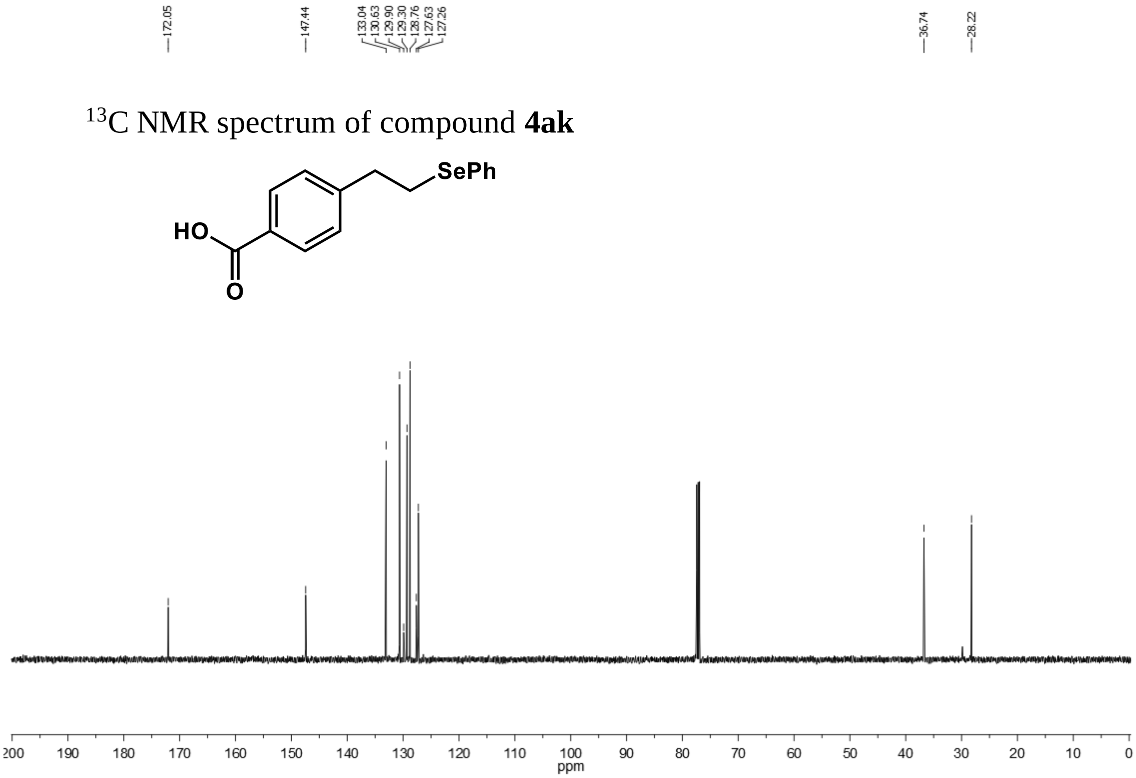


^{13}C NMR spectrum of compound **4aj**

4-(2-(phenylselanyl)ethyl)benzoic acid (4ak)



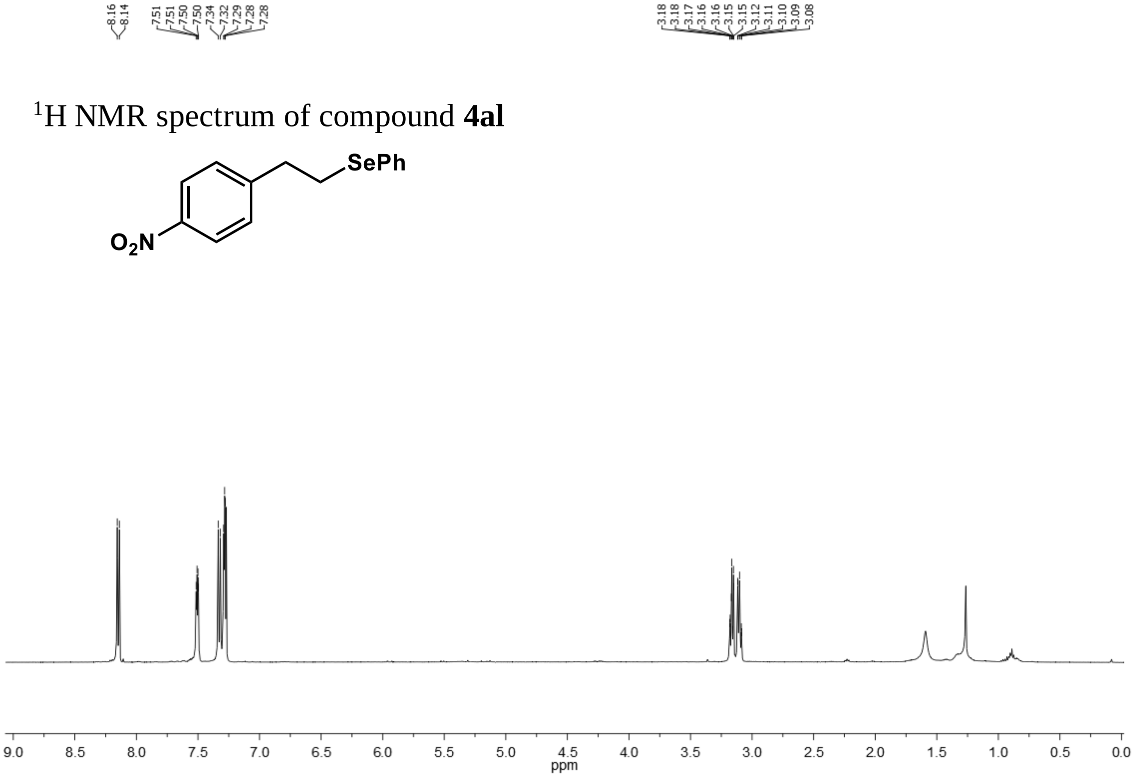
^{1}H NMR spectrum of compound **4ak**



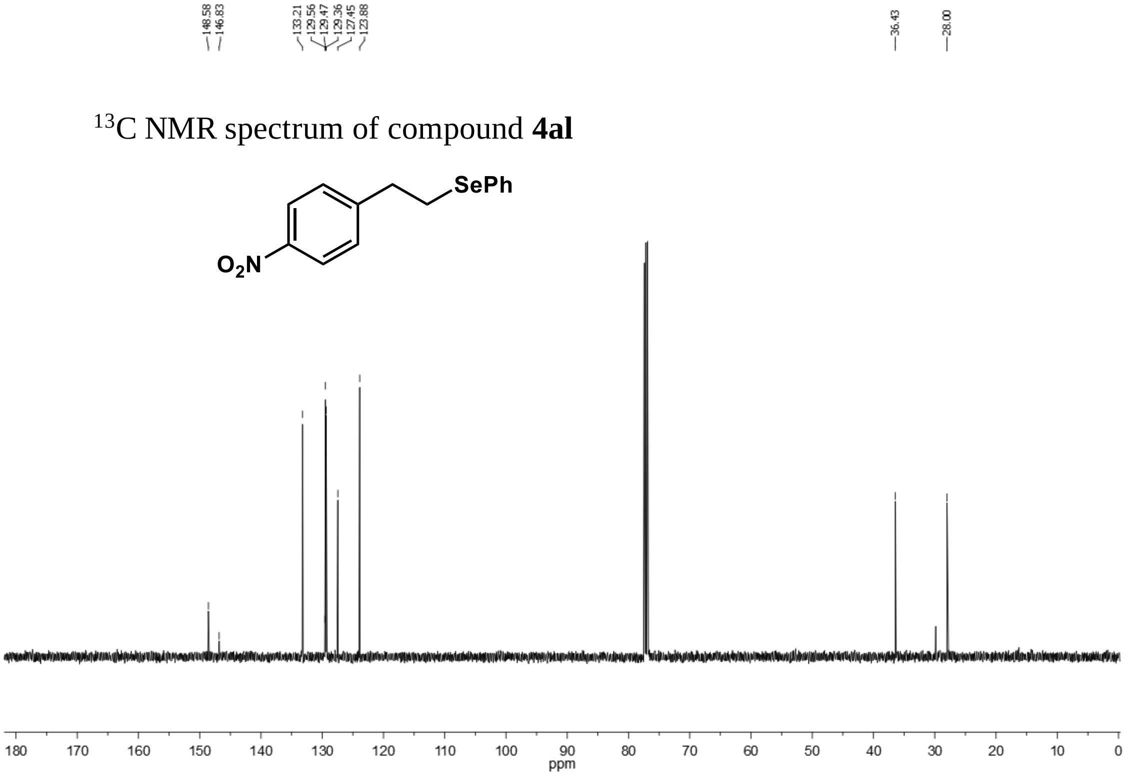
^{13}C NMR spectrum of compound **4ak**

(4-nitrophenethyl)(phenyl)selane (4al)

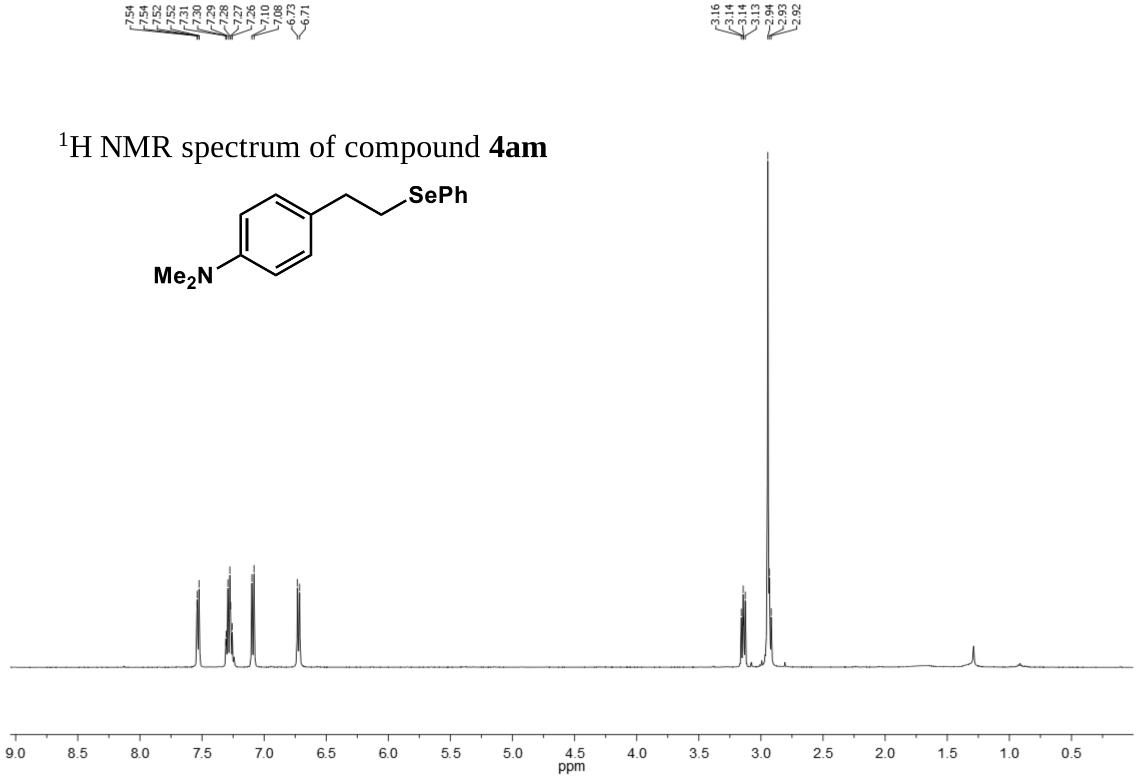
^{1}H NMR spectrum of compound **4al**

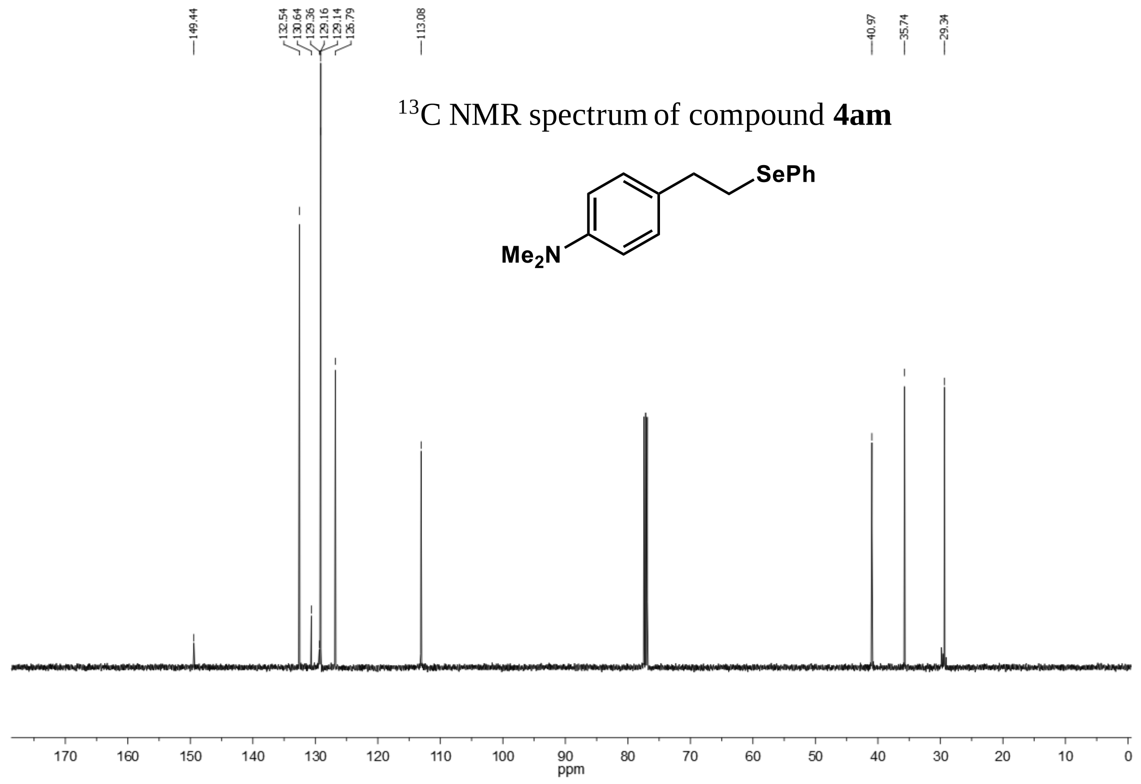


^{13}C NMR spectrum of compound **4al**

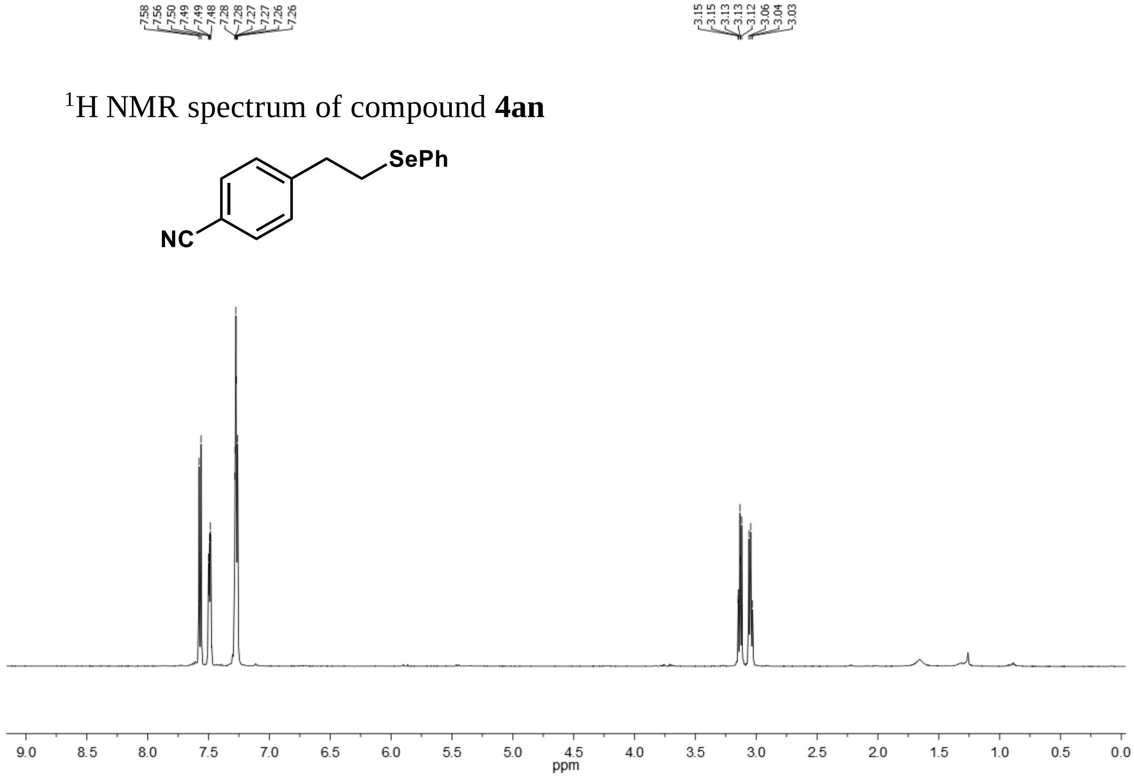


N,N-dimethyl-4-(2-(phenylselanyl)ethyl)aniline (4am)

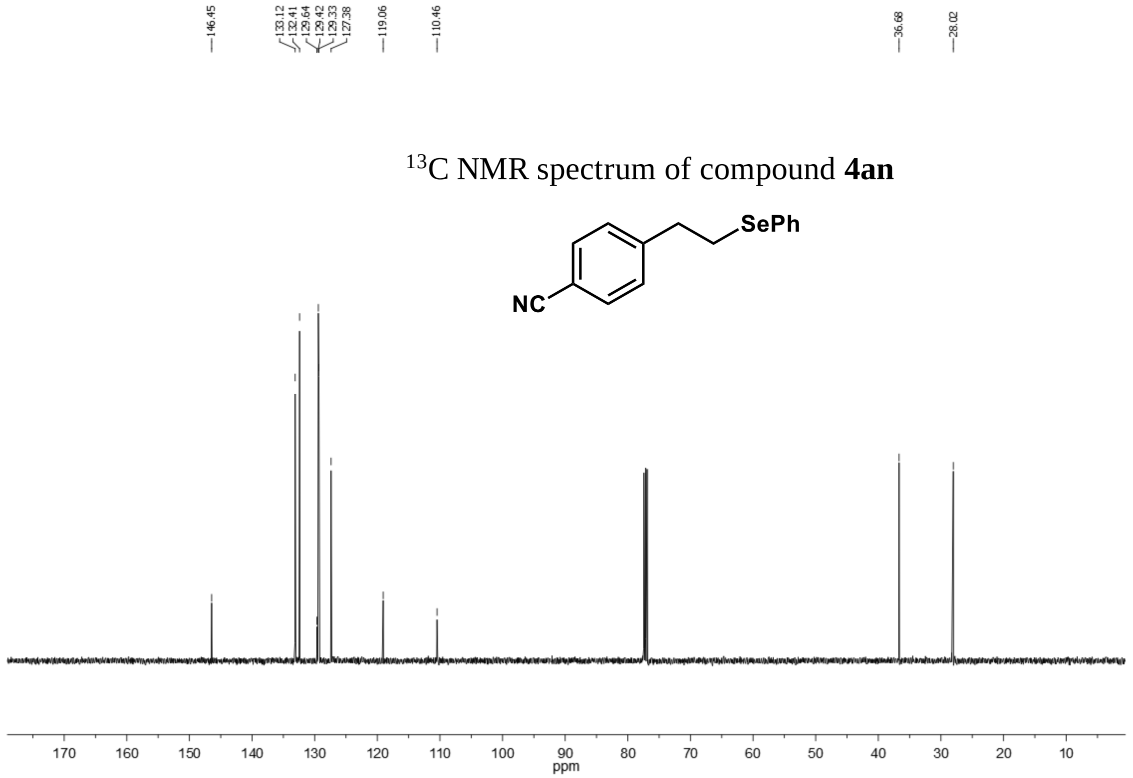

^{1}H NMR spectrum of compound **4am**


^{13}C NMR spectrum of compound **4am**

4-(2-(phenylselanyl)ethyl)benzonitrile (4an)



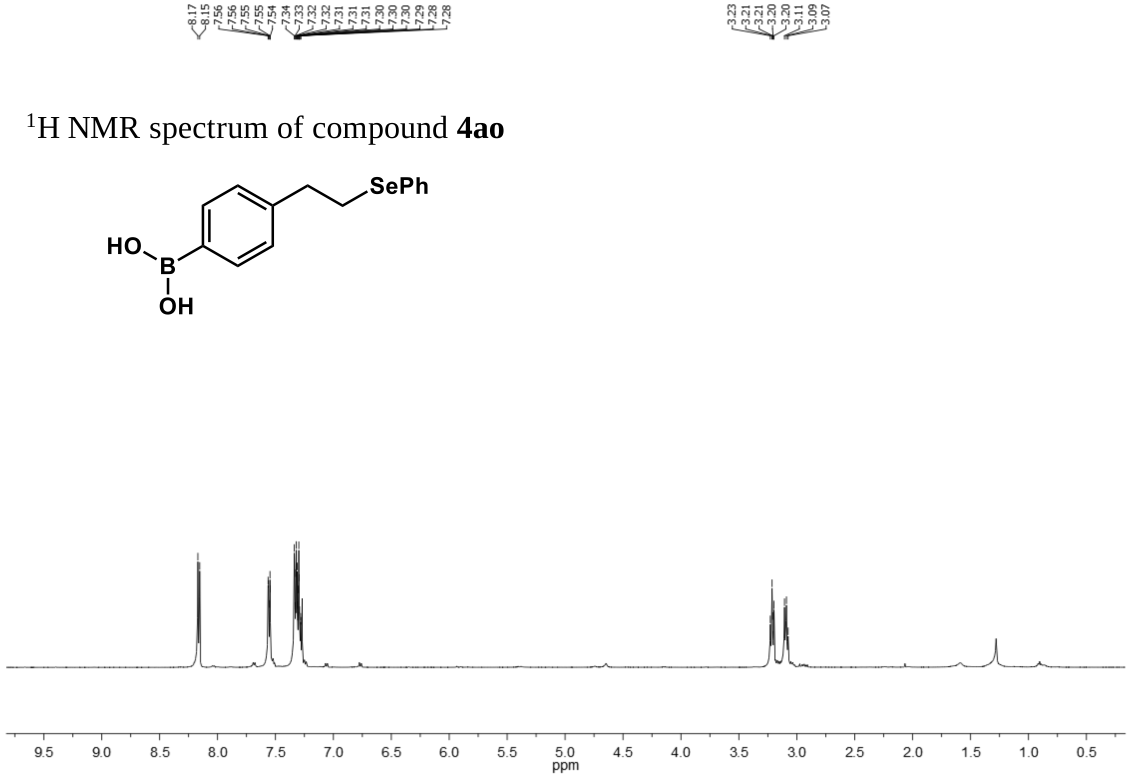
^{1}H NMR spectrum of compound **4an**



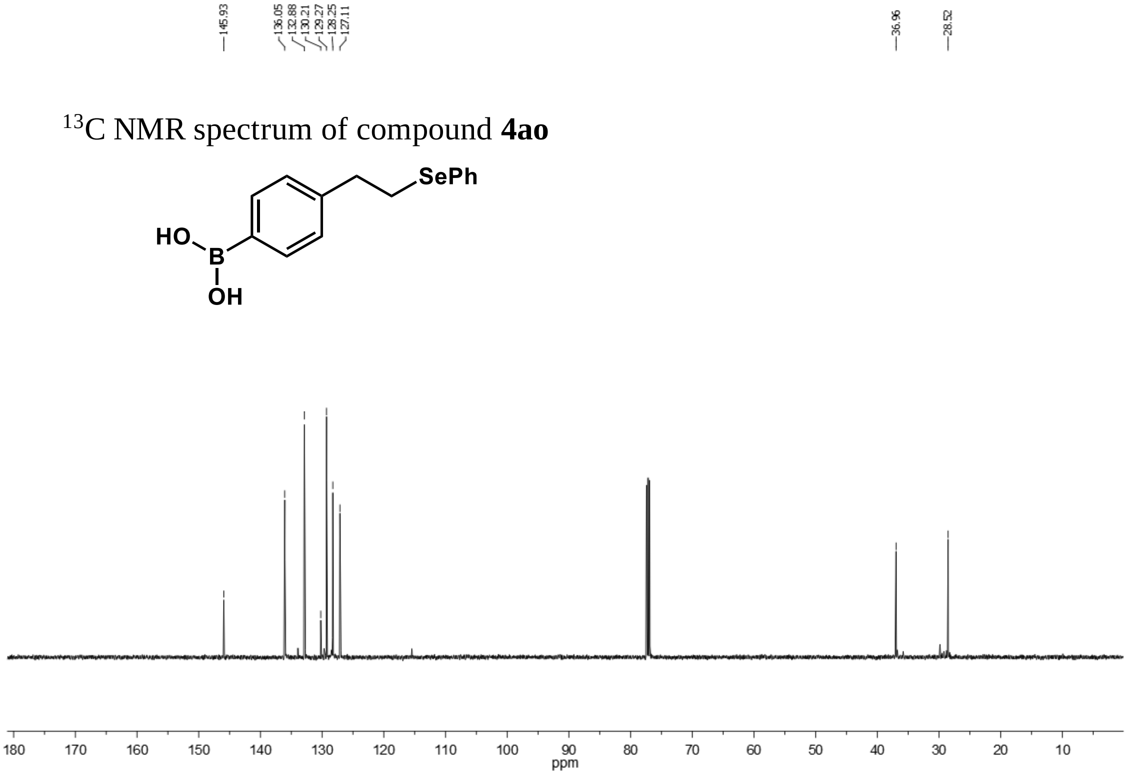
^{13}C NMR spectrum of compound **4an**

(4-(2-(phenylselanyl)ethyl)phenyl)boronic acid (4ao)

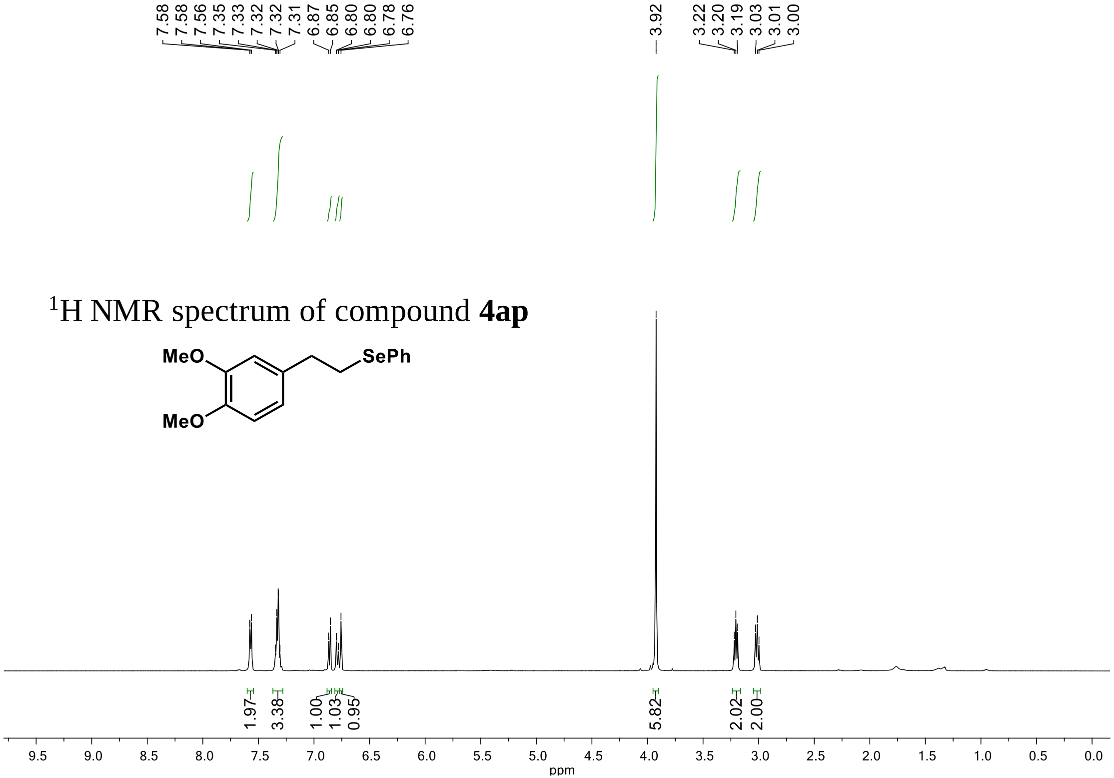
^{1}H NMR spectrum of compound **4ao**



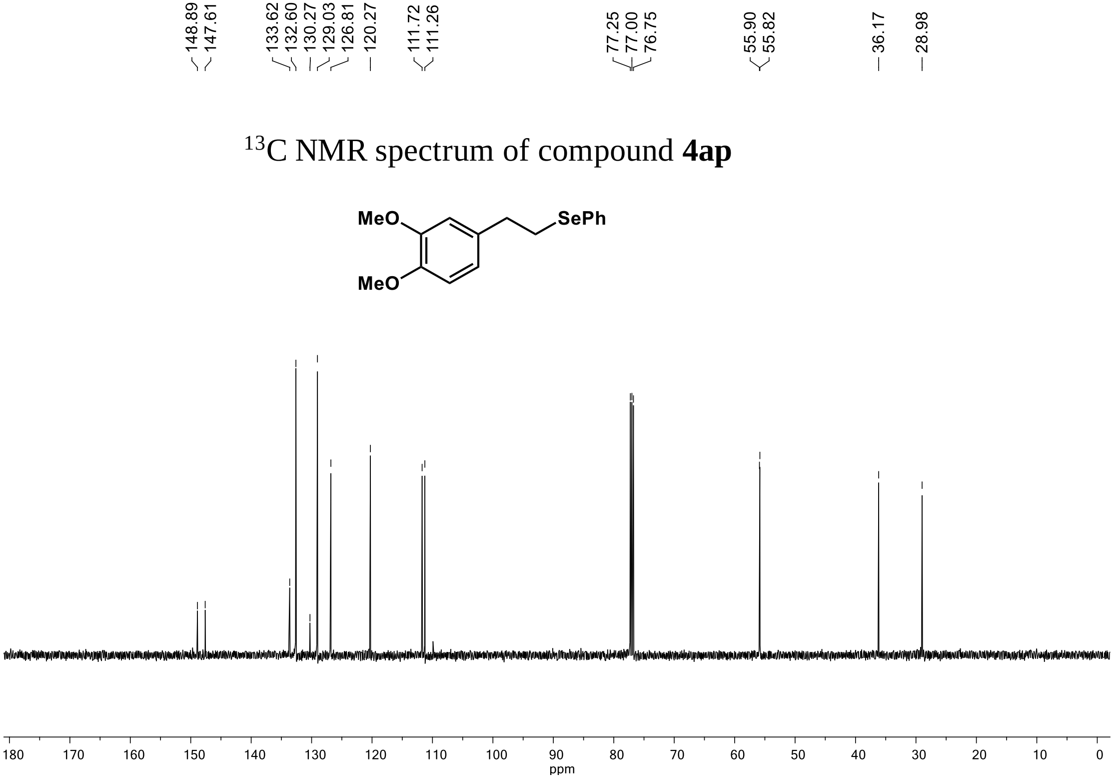
^{13}C NMR spectrum of compound **4ao**



(3,4-dimethoxyphenethyl)(phenyl)selane (4ap)

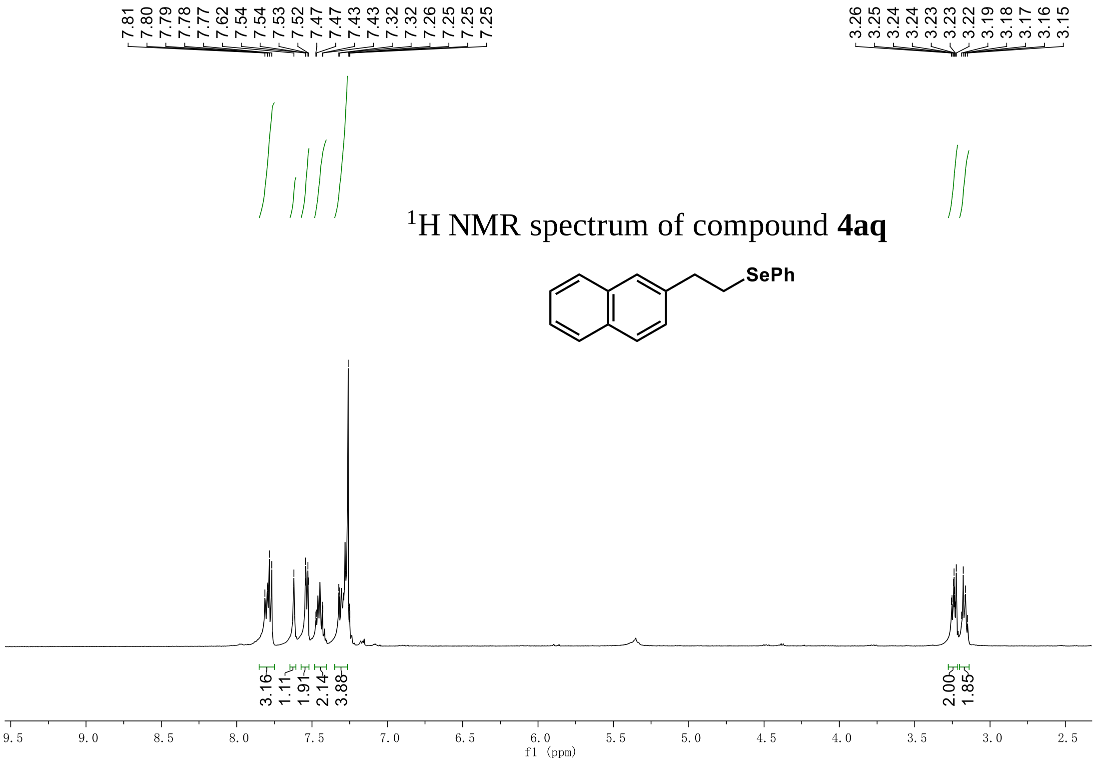


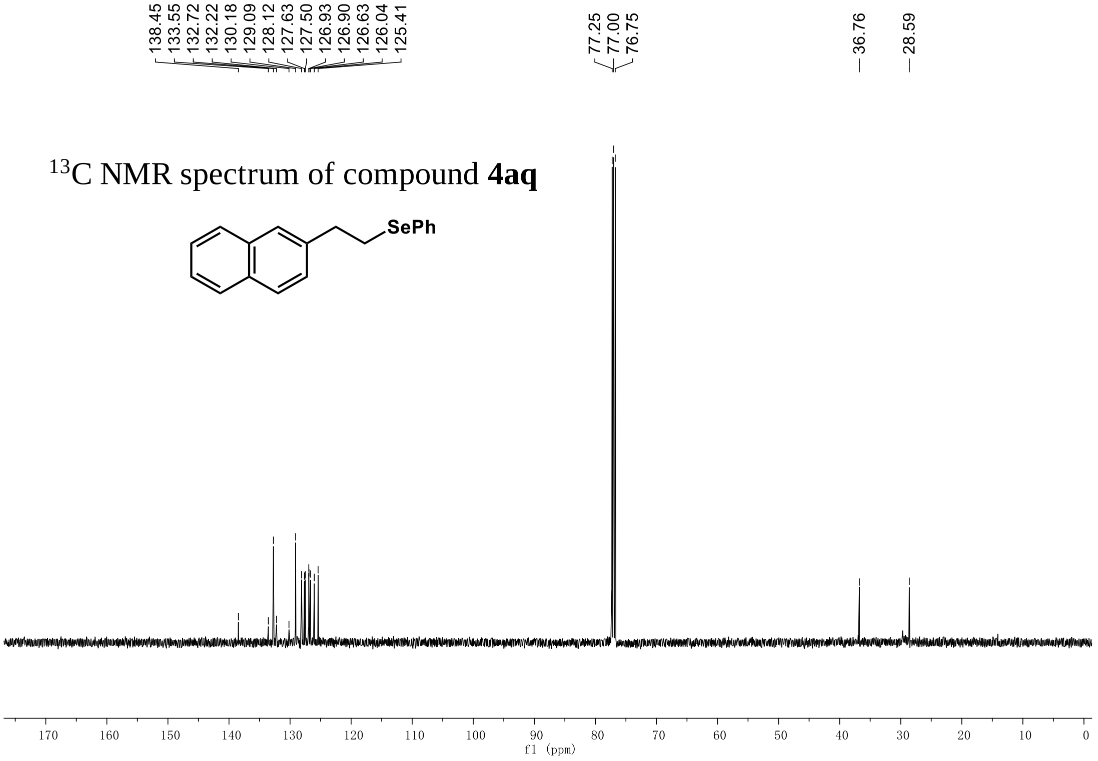
^{1}H NMR spectrum of compound **4ap**



^{13}C NMR spectrum of compound **4ap**

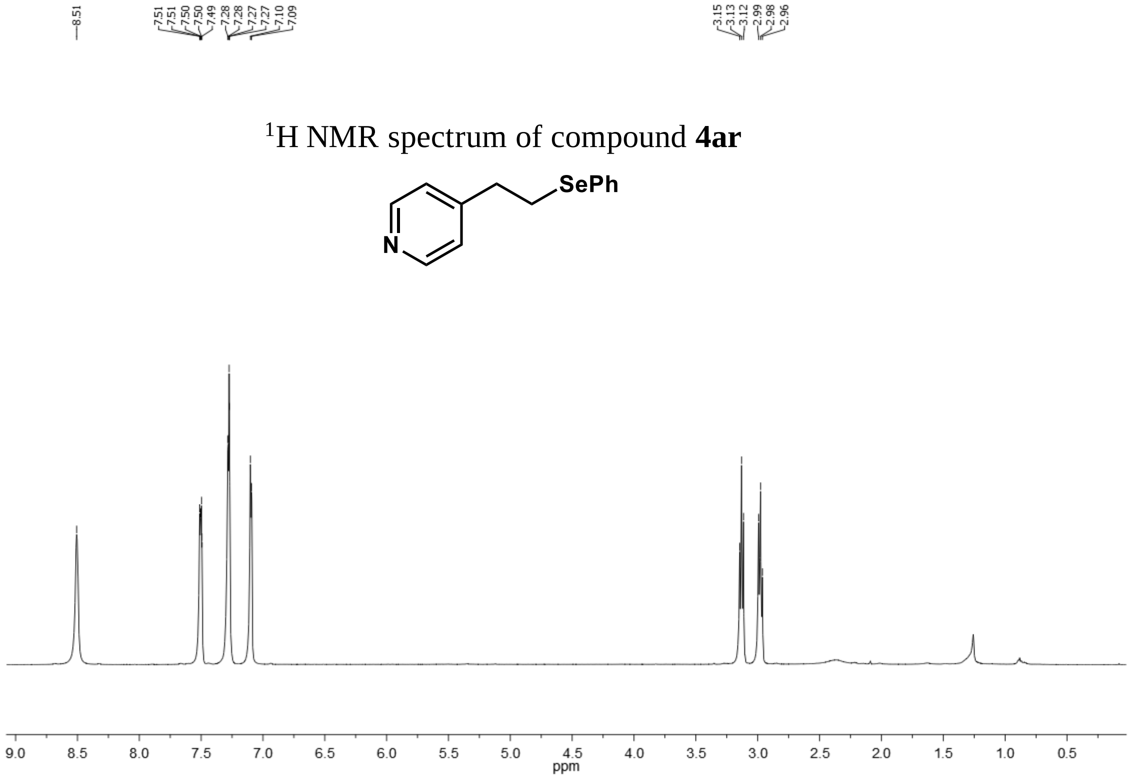
(2-(naphthalen-2-yl)ethyl)(phenyl)selane (4aq)


^{1}H NMR spectrum of compound **4aq**

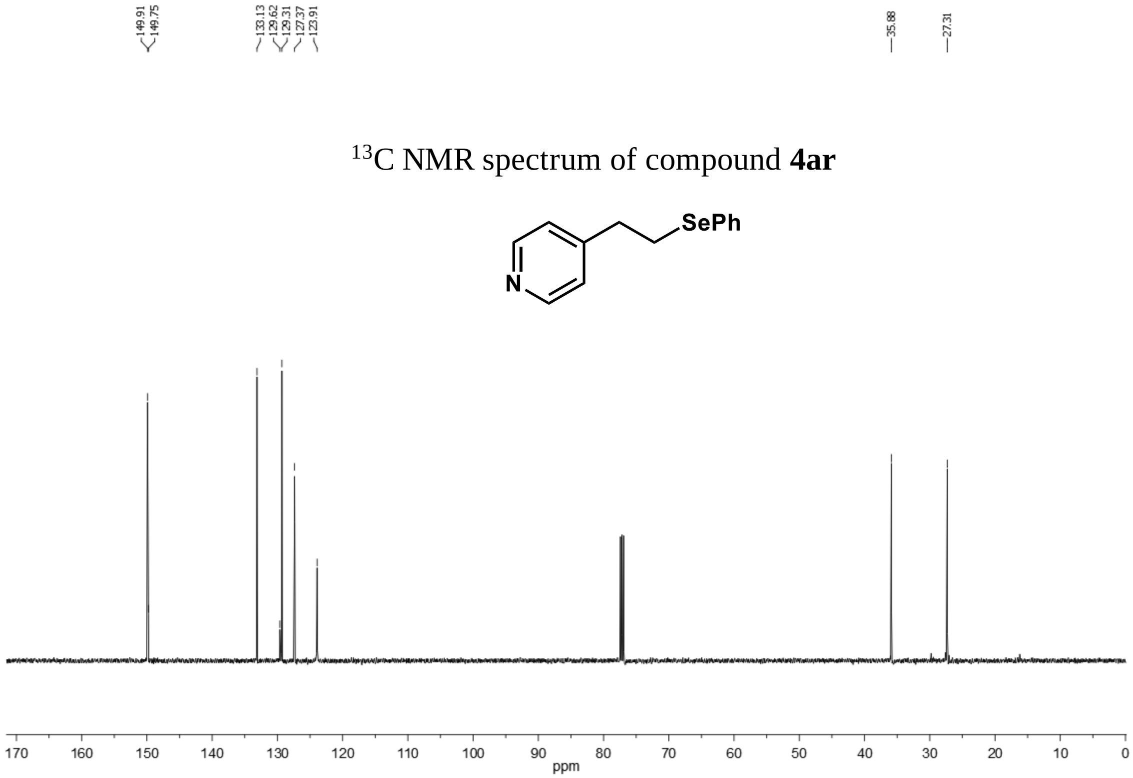

^{13}C NMR spectrum of compound **4aq**

4-(2-(phenylselanyl)ethyl)pyridine (4ar)

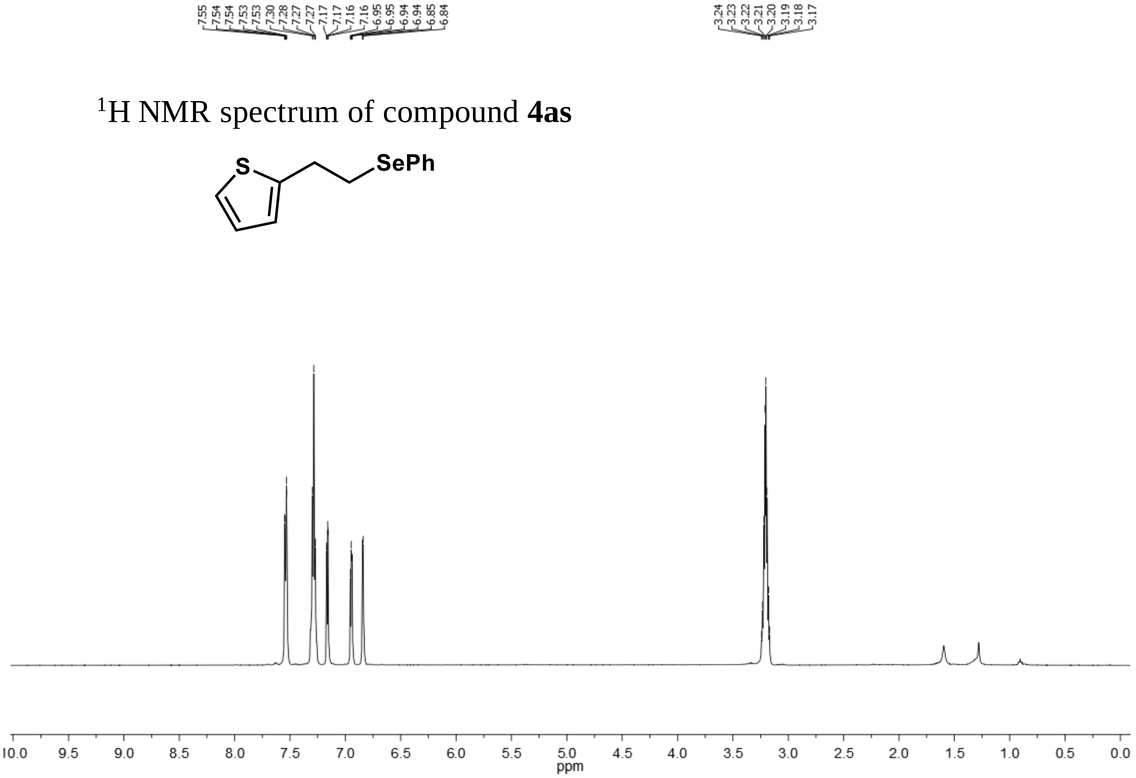
^{1}H NMR spectrum of compound **4ar**



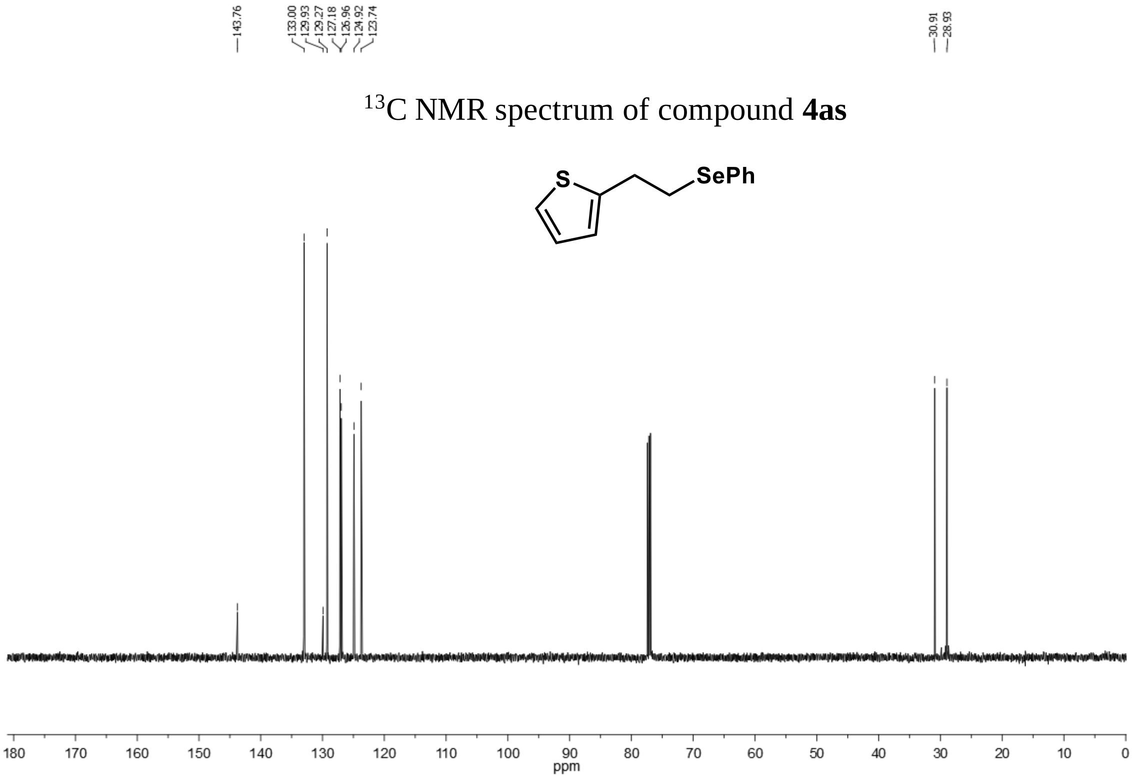
^{13}C NMR spectrum of compound **4ar**



2-(2-(phenylselanyl)ethyl)thiophene (4as)

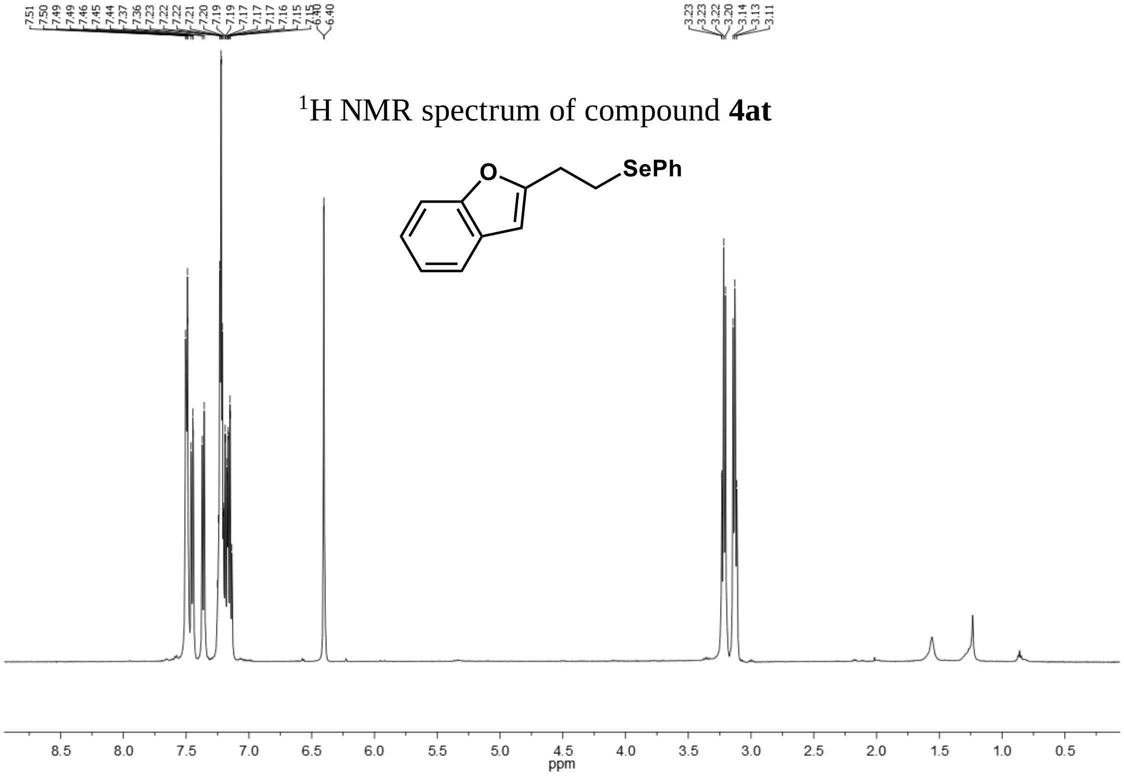


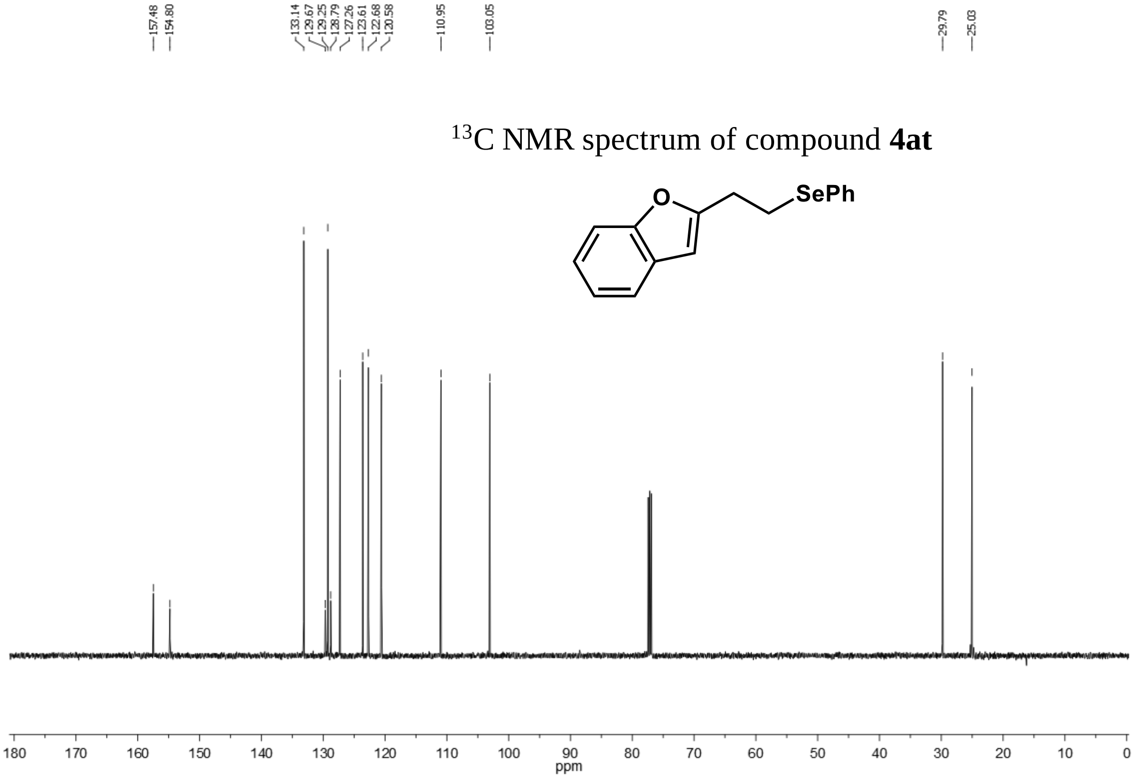
^{1}H NMR spectrum of compound **4as**



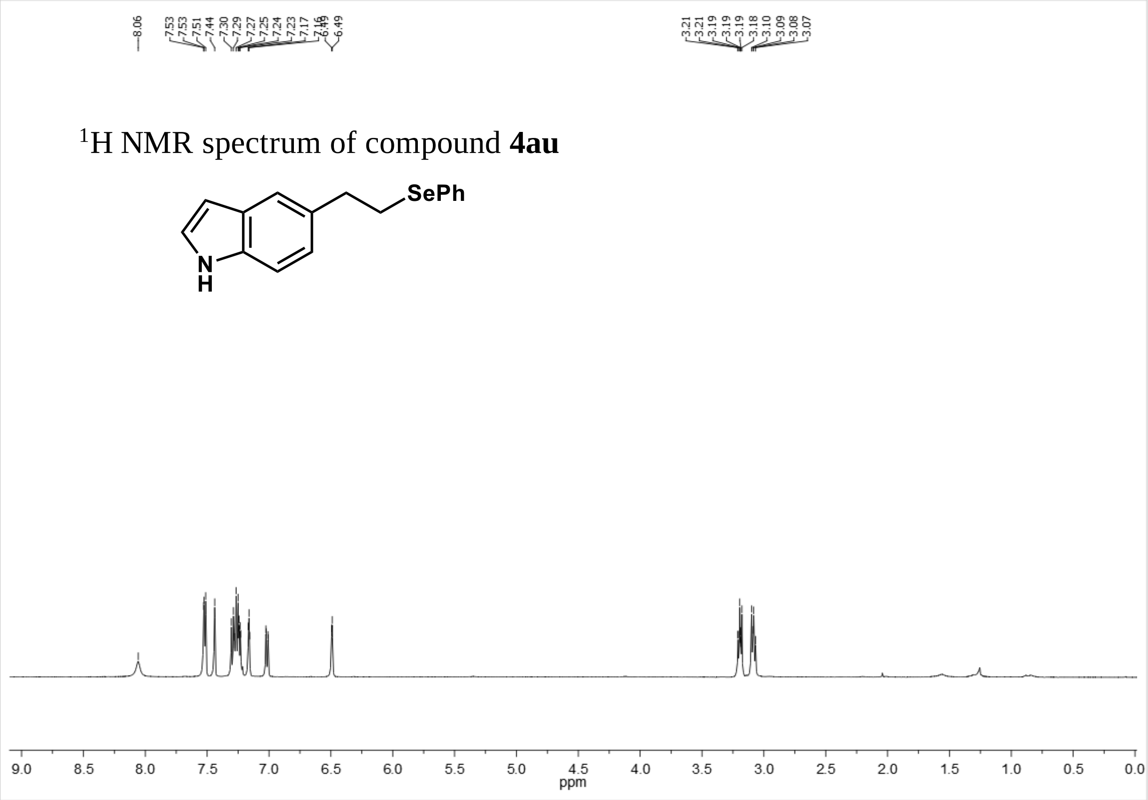
^{13}C NMR spectrum of compound **4as**

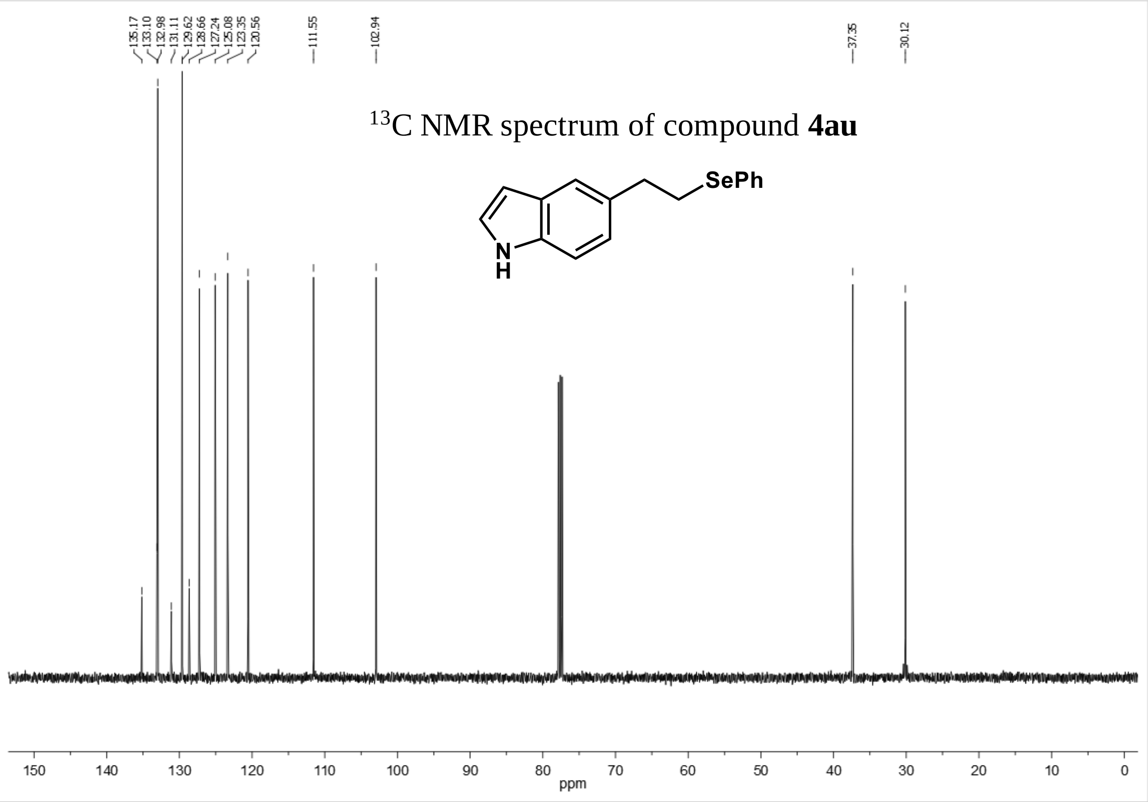
2-(2-(phenylselanyl)ethyl)benzofuran (4at)


^{1}H NMR spectrum of compound **4at**

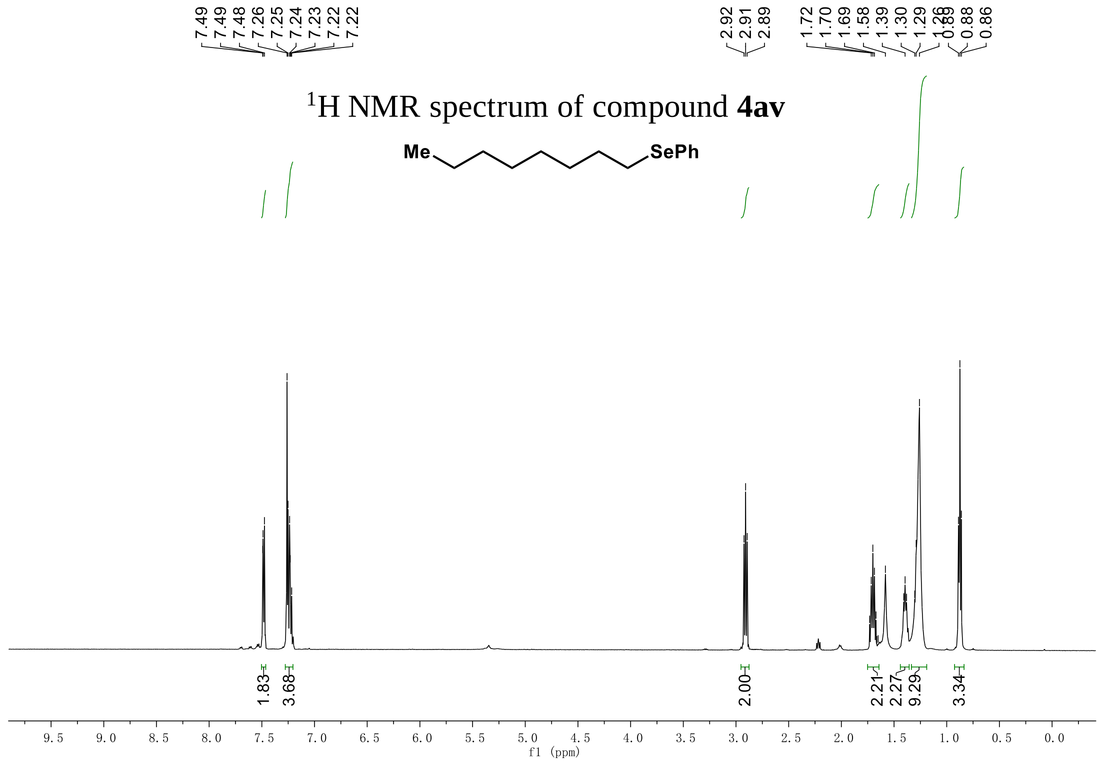

^{13}C NMR spectrum of compound **4at**

5-(2-(phenylselanyl)ethyl)-1H-indole (4au)

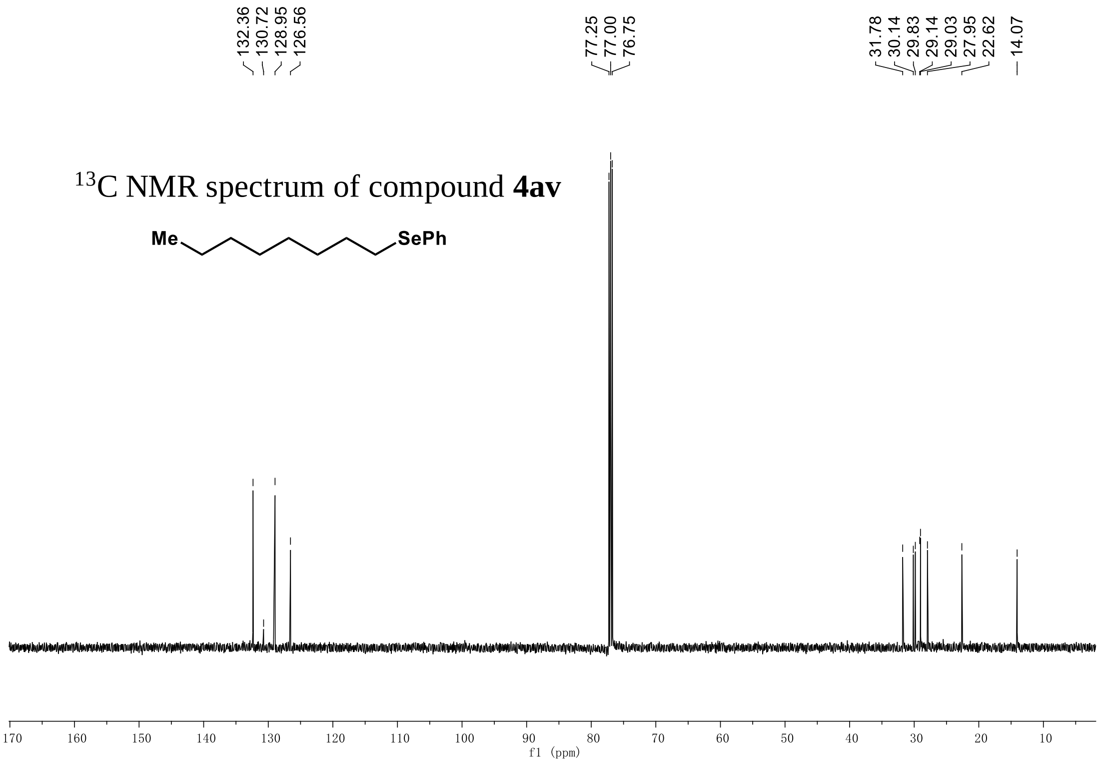

^{1}H NMR spectrum of compound **4au**


^{13}C NMR spectrum of compound **4au**

octyl(phenyl)selane (4av)

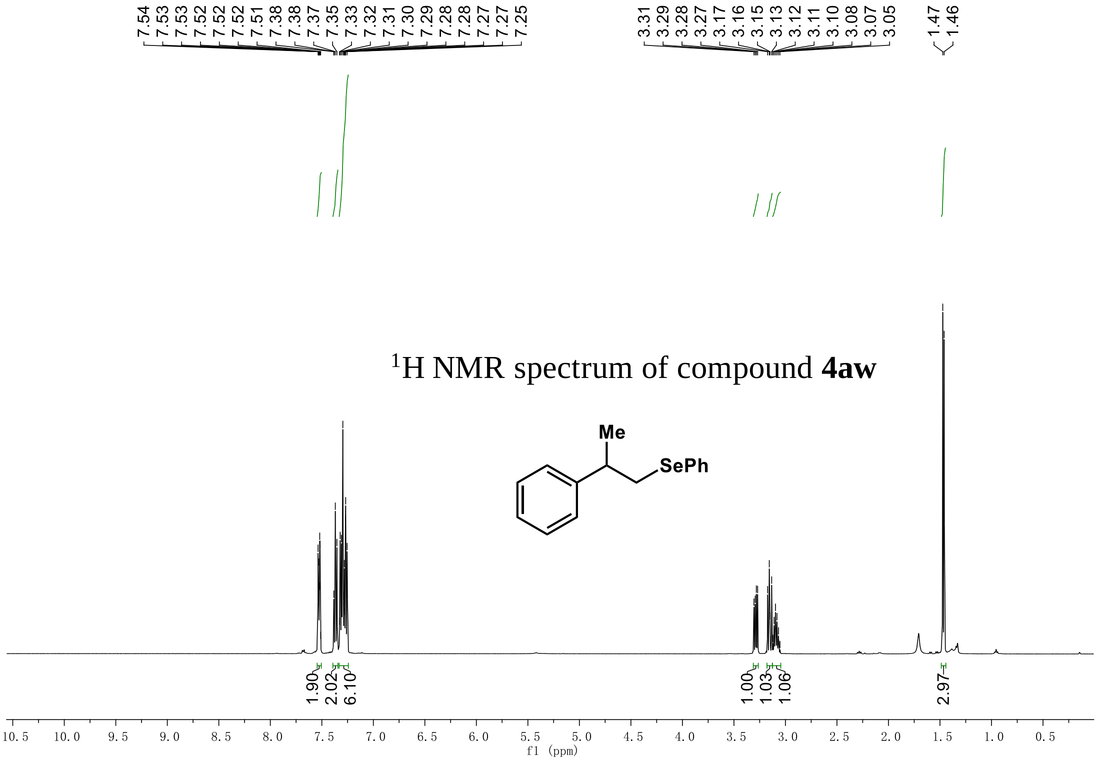


^{1}H NMR spectrum of compound **4av**

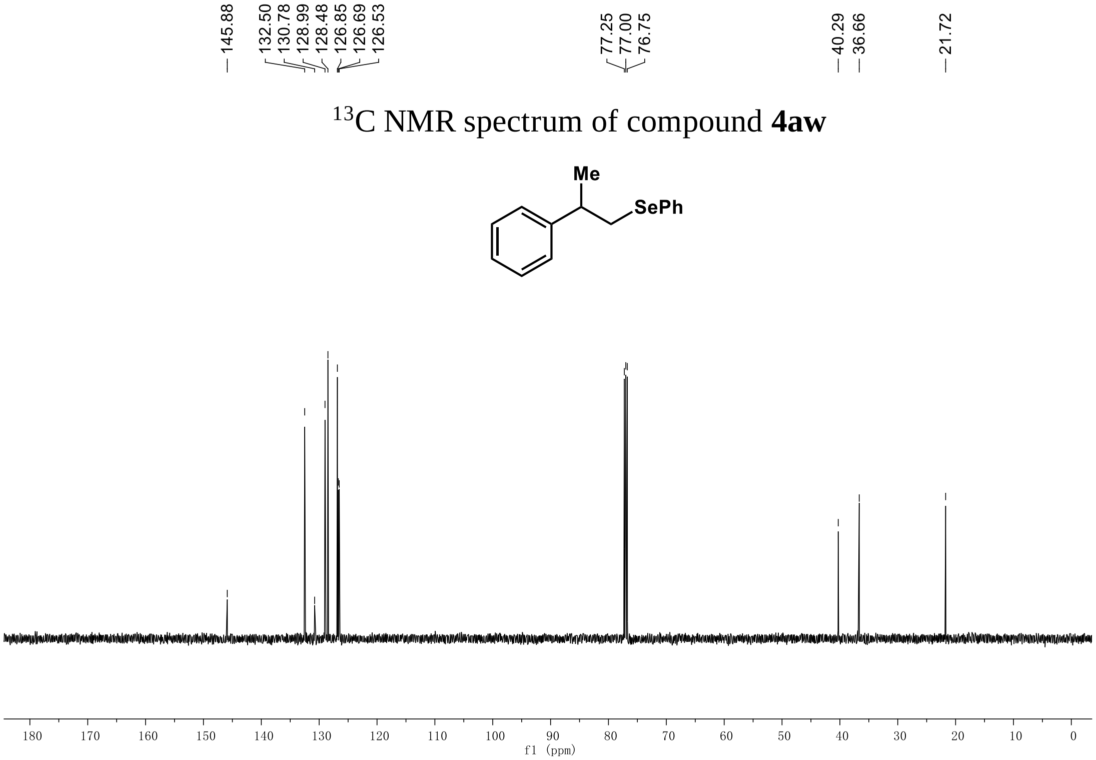


^{13}C NMR spectrum of compound **4av**

(±)-phenyl(2-phenylpropyl)selane (4aw)

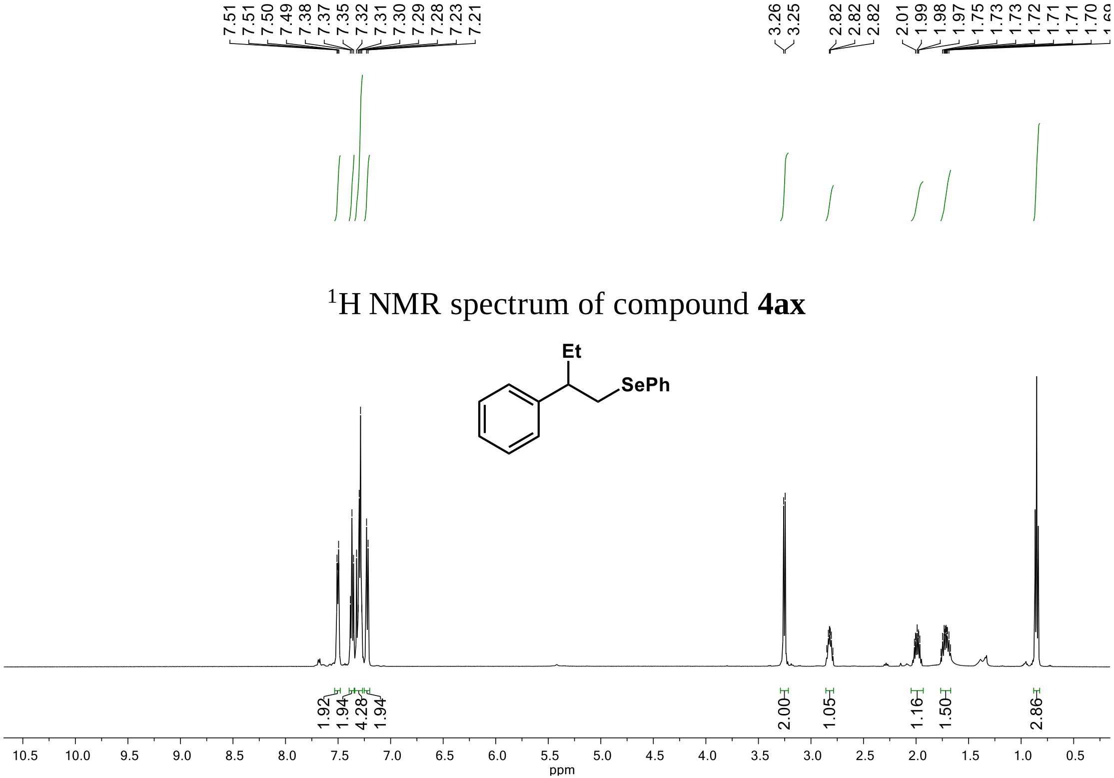


^{1}H NMR spectrum of compound **4aw**

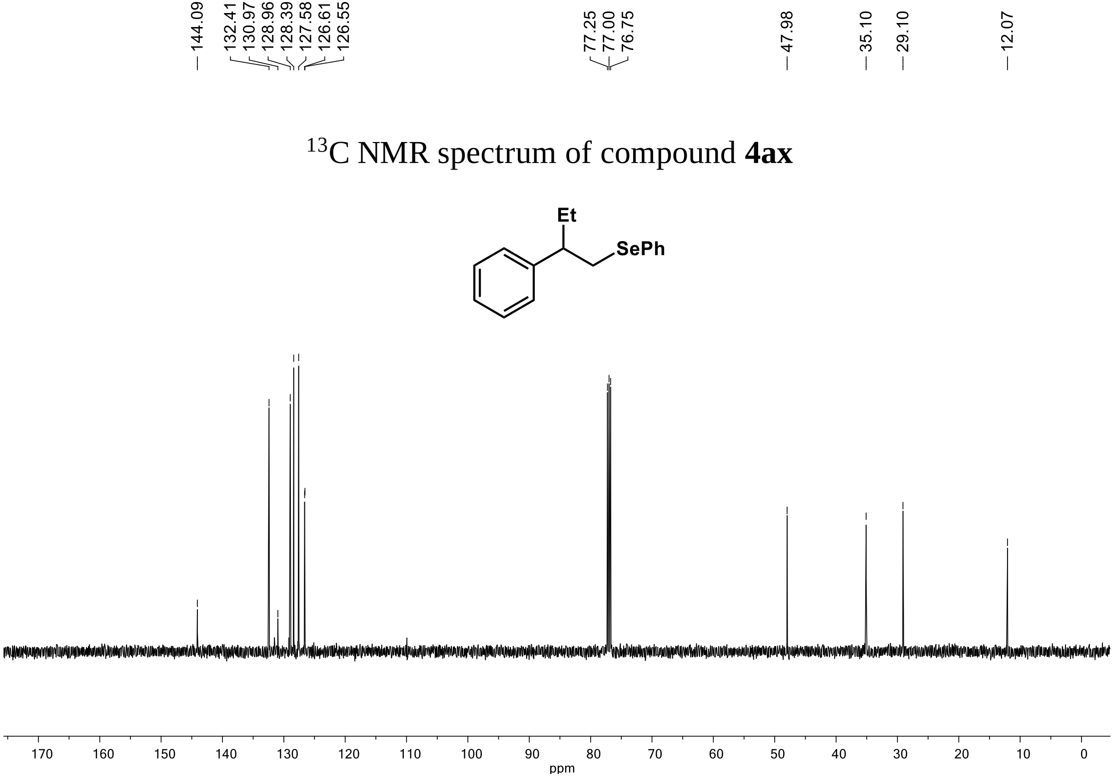


^{13}C NMR spectrum of compound **4aw**

(±)-phenyl(2-phenylbutyl)selane (4ax)

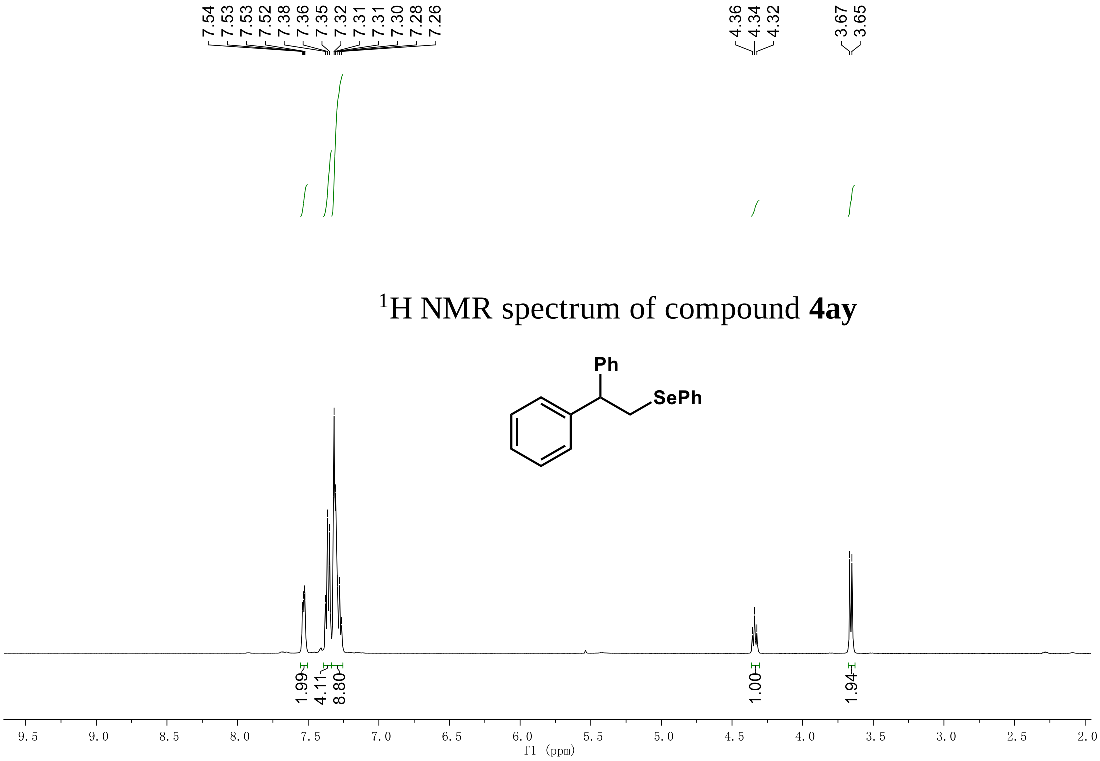


^{1}H NMR spectrum of compound **4ax**

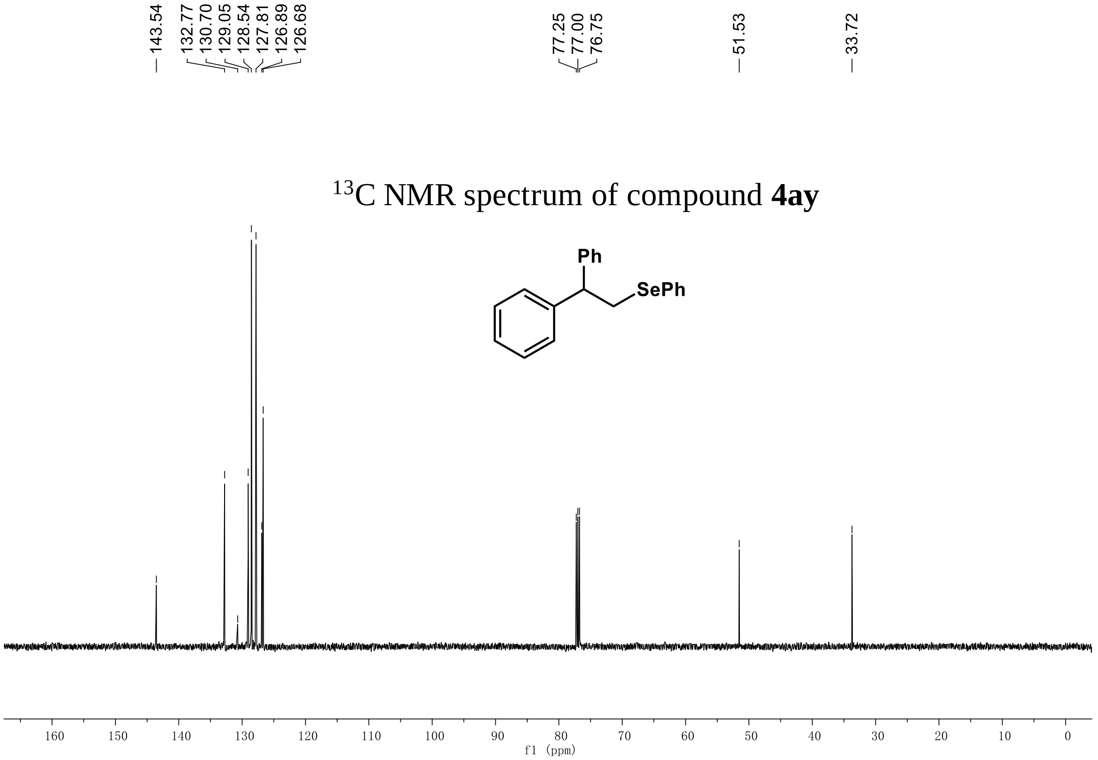


^{13}C NMR spectrum of compound **4ax**

(±)-(2,2-diphenylethyl)(phenyl)selane (4ay)

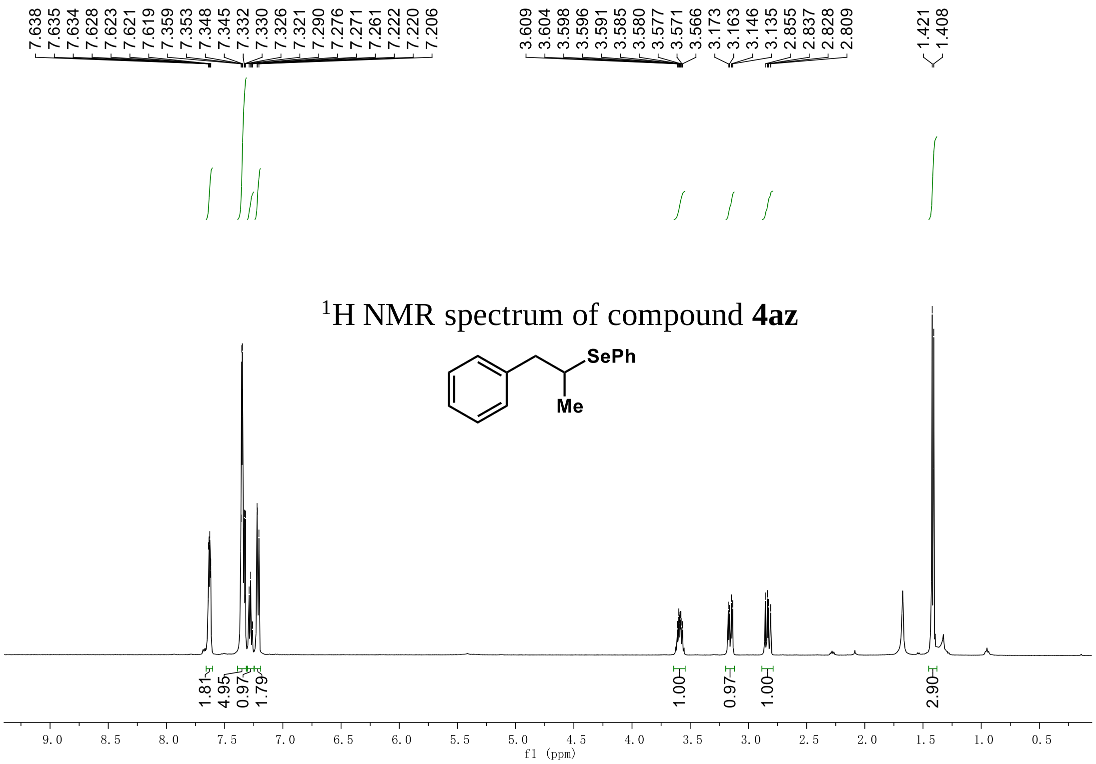


^{1}H NMR spectrum of compound **4ay**

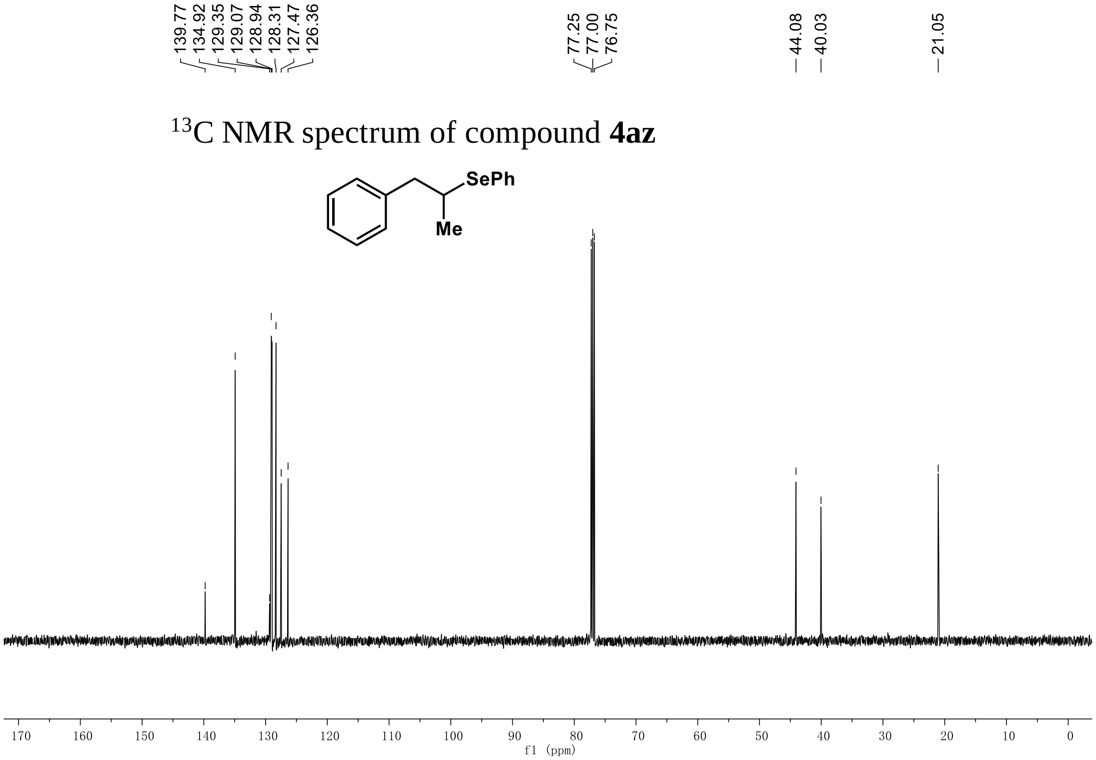


^{13}C NMR spectrum of compound **4ay**

(±)-phenyl(1-phenylpropan-2-yl)selane (4az)

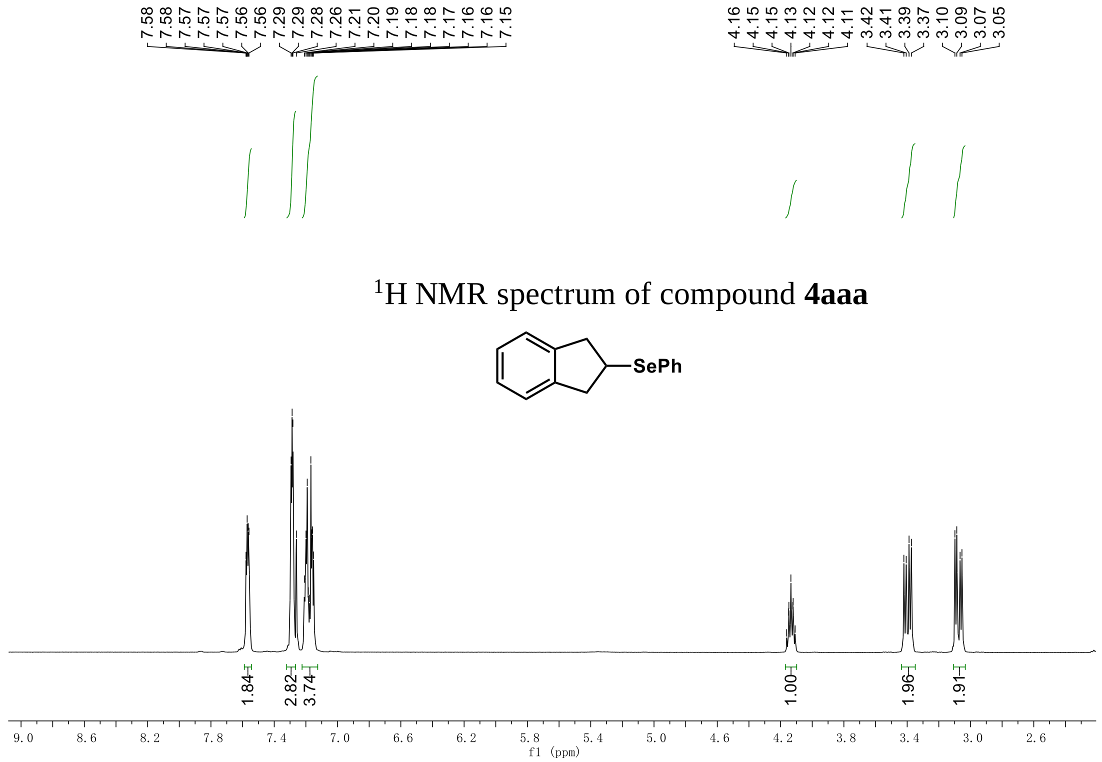


^{1}H NMR spectrum of compound **4az**

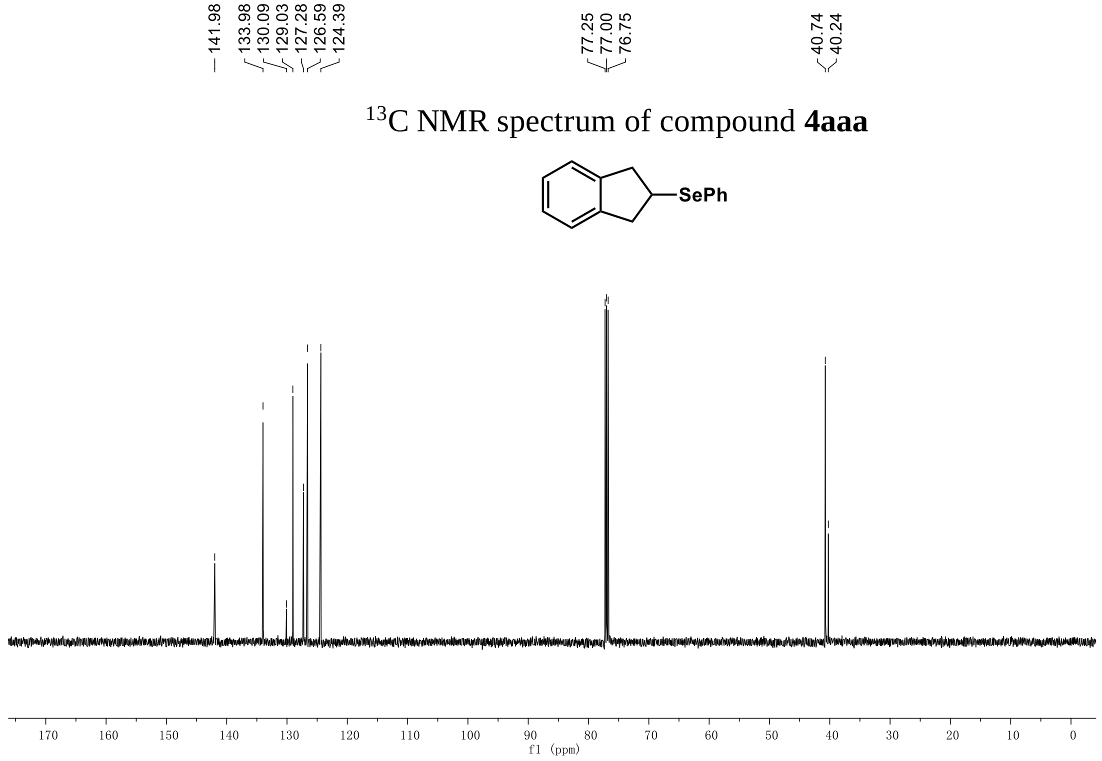


^{13}C NMR spectrum of compound **4az**

(2,3-dihydro-1H-inden-2-yl)(phenyl)selane (4aaa)

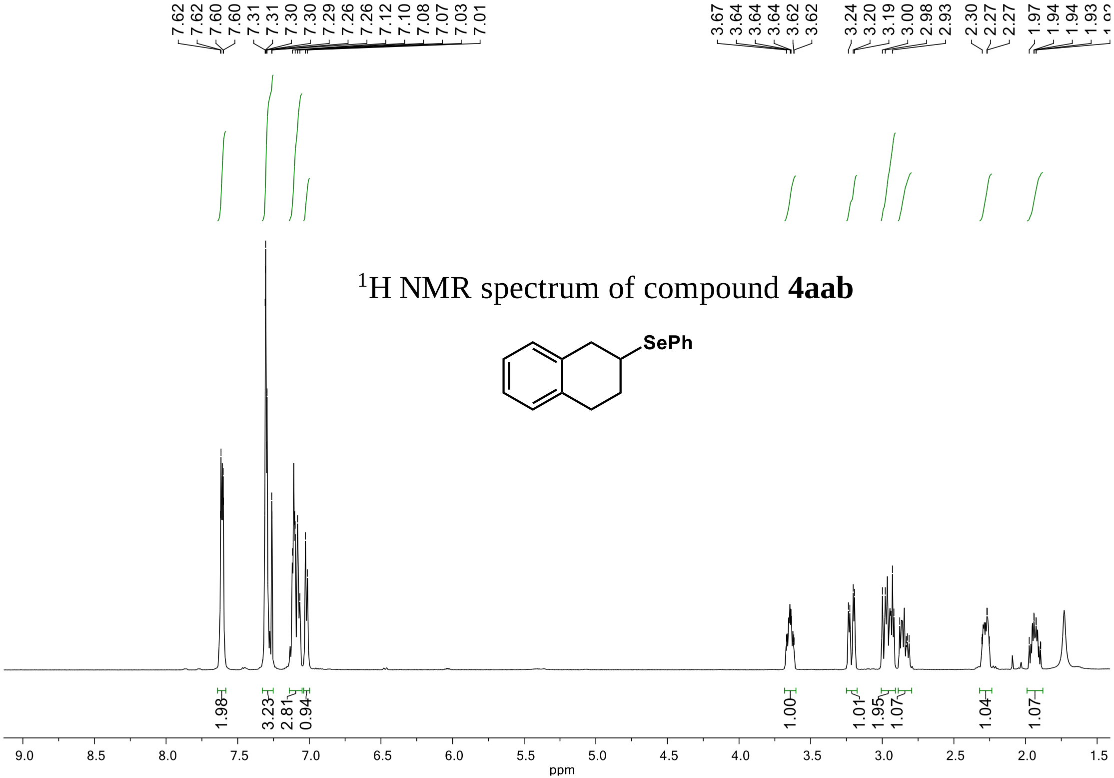


^{1}H NMR spectrum of compound **4aaa**

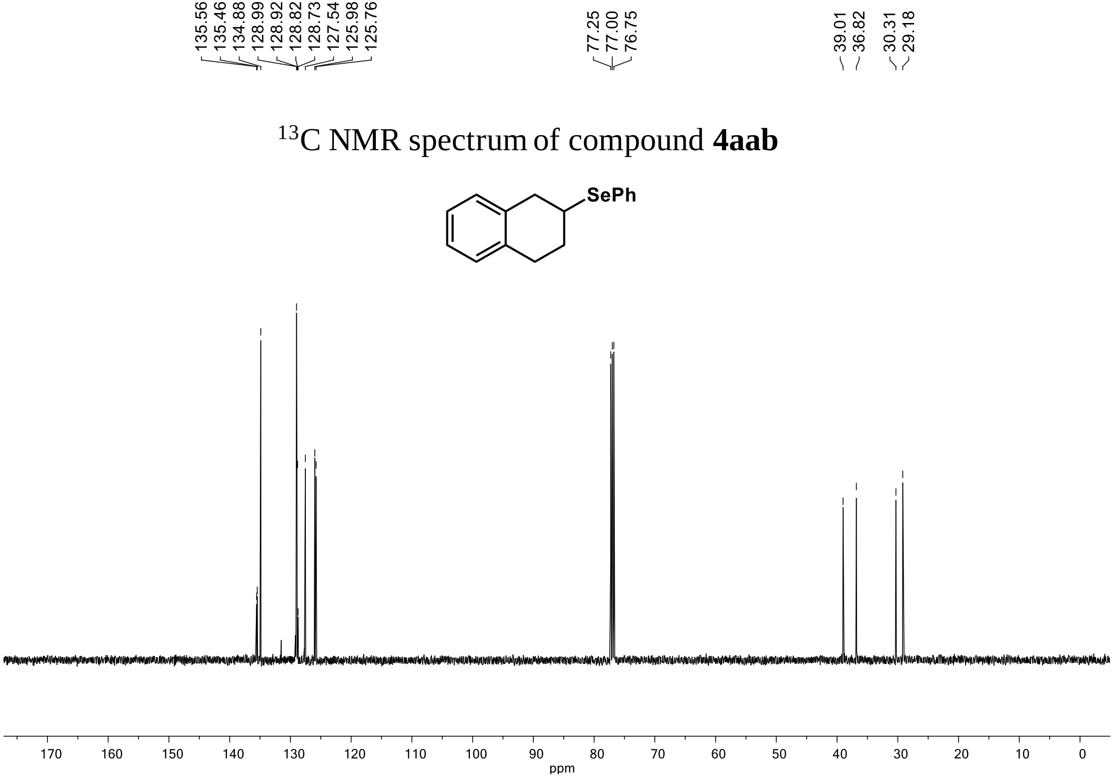


^{13}C NMR spectrum of compound **4aaa**

(±)-phenyl(1,2,3,4-tetrahydronaphthalen-2-yl)selane (4aab)

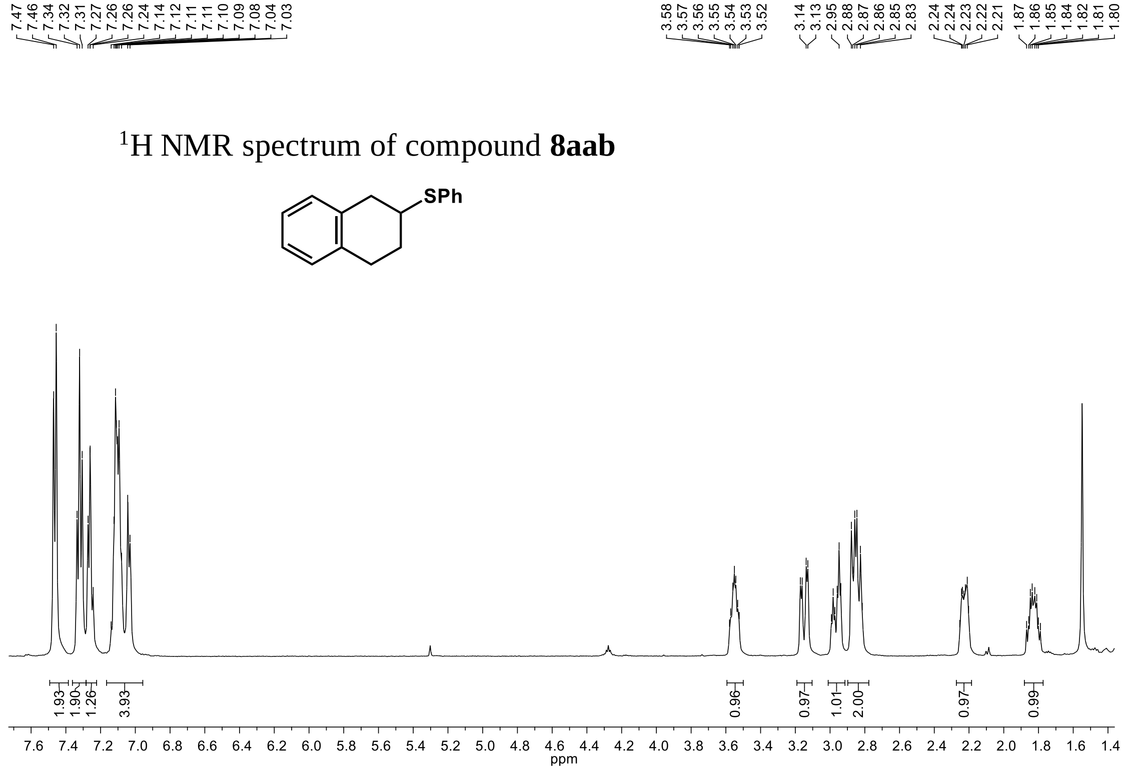


^{1}H NMR spectrum of compound **4aab**

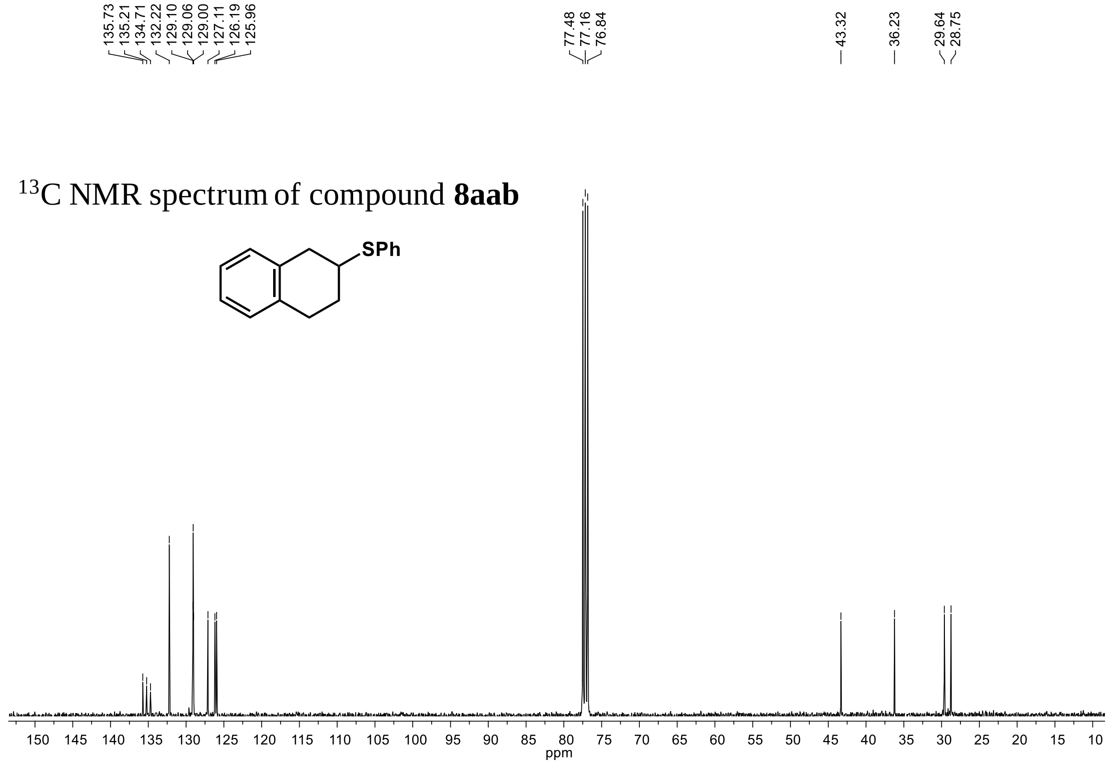


^{13}C NMR spectrum of compound **4aab**

(±)-phenyl(1,2,3,4-tetrahydronaphthalen-2-yl)sulfane (8aab)

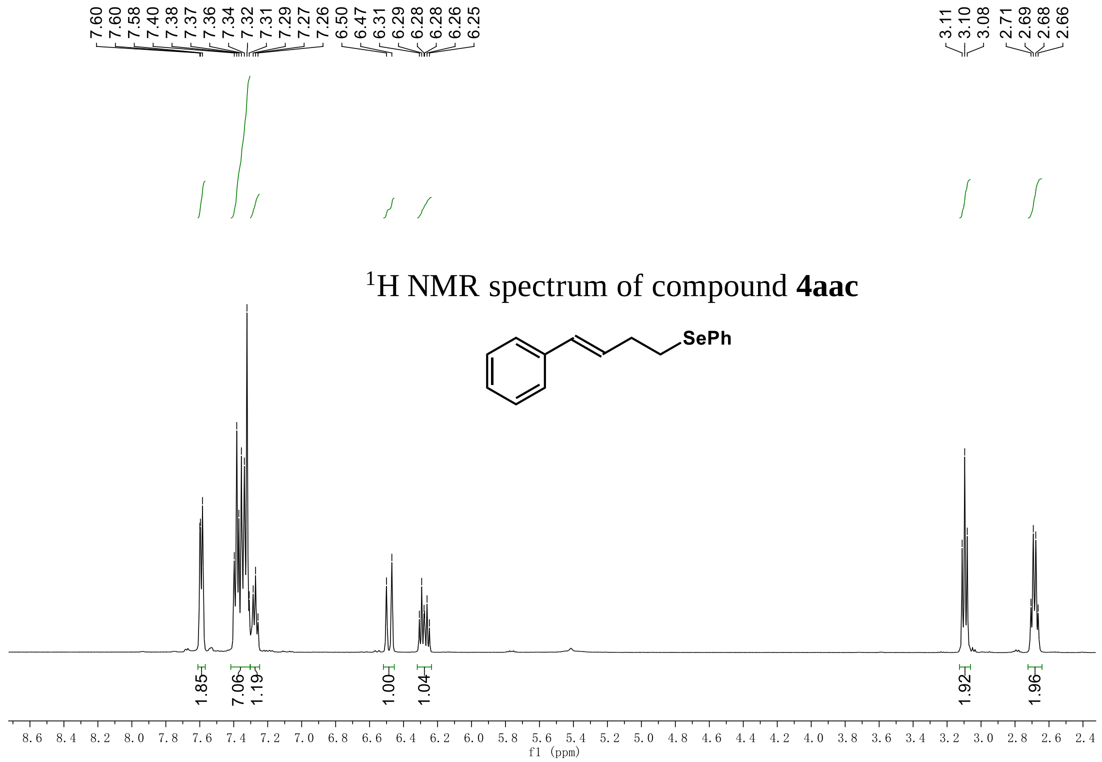


^{1}H NMR spectrum of compound **8aab**

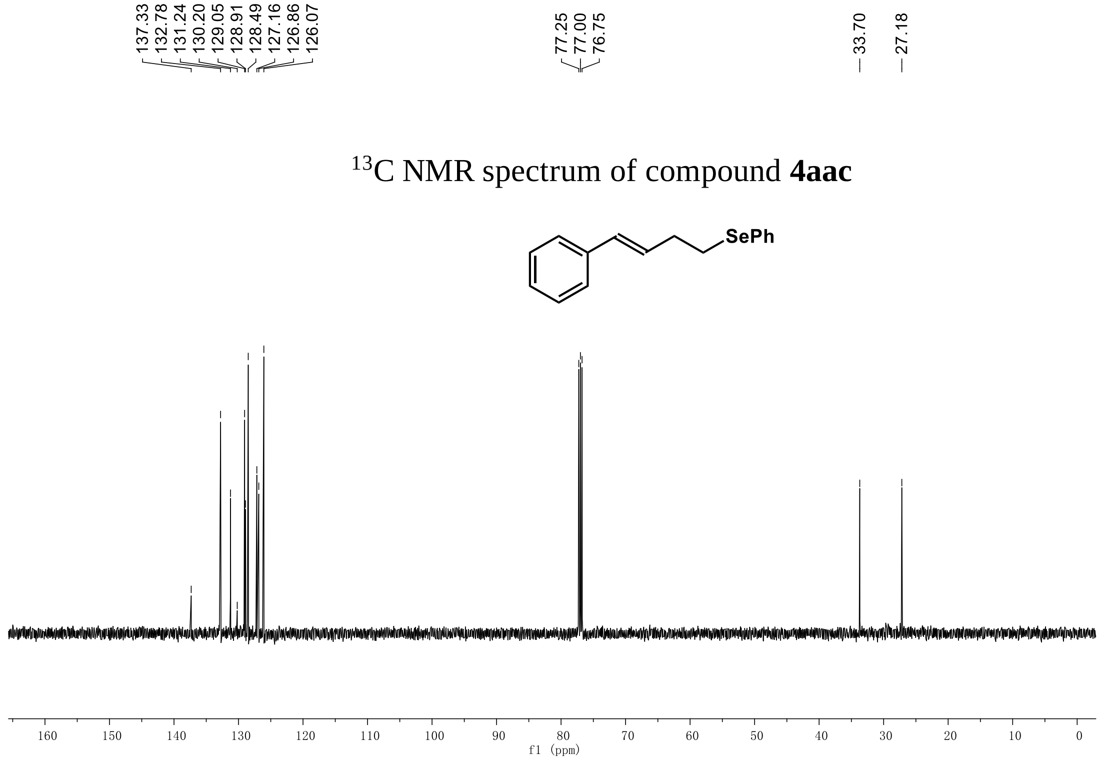


^{13}C NMR spectrum of compound **8aab**

(*E*)-phenyl(4-phenylbut-3-en-1-yl)selane (4aac)

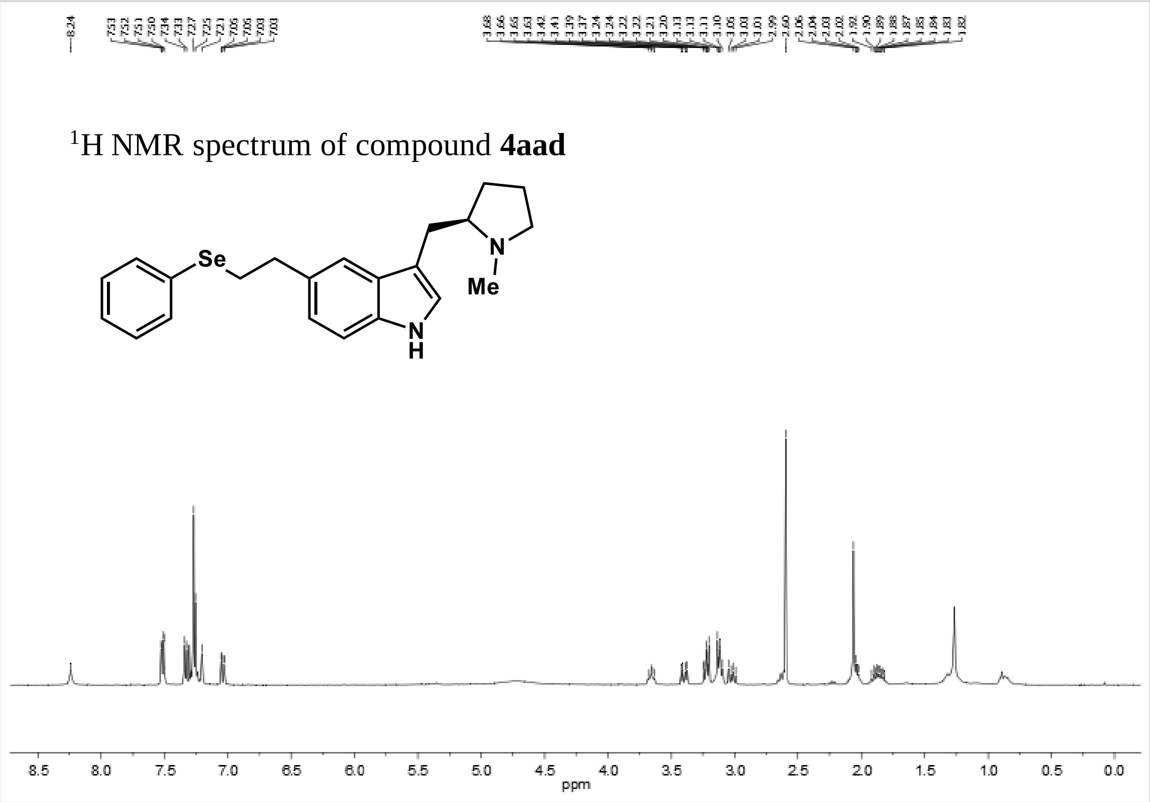


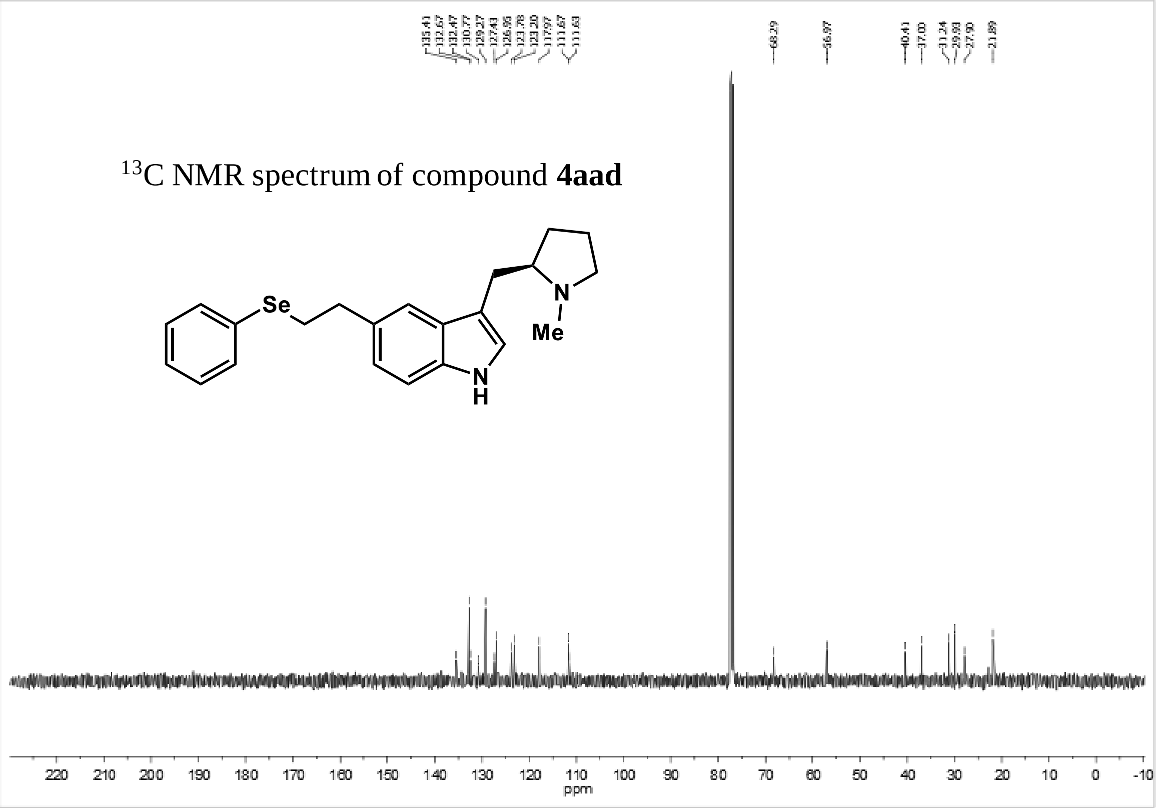
^{1}H NMR spectrum of compound **4aac**



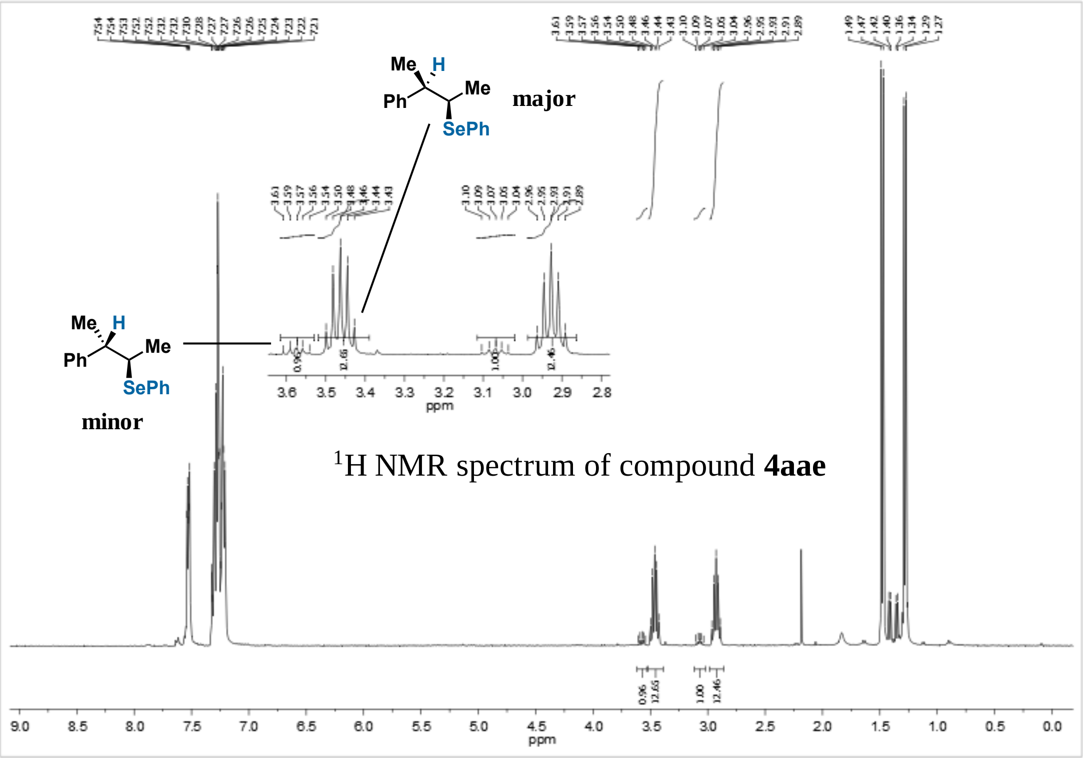
^{13}C NMR spectrum of compound **4aac**

(R)-3-((1-methylpyrrolidin-2-yl)methyl)-5-(2-(phenylselanyl)ethyl)-1H-indole (4aad)

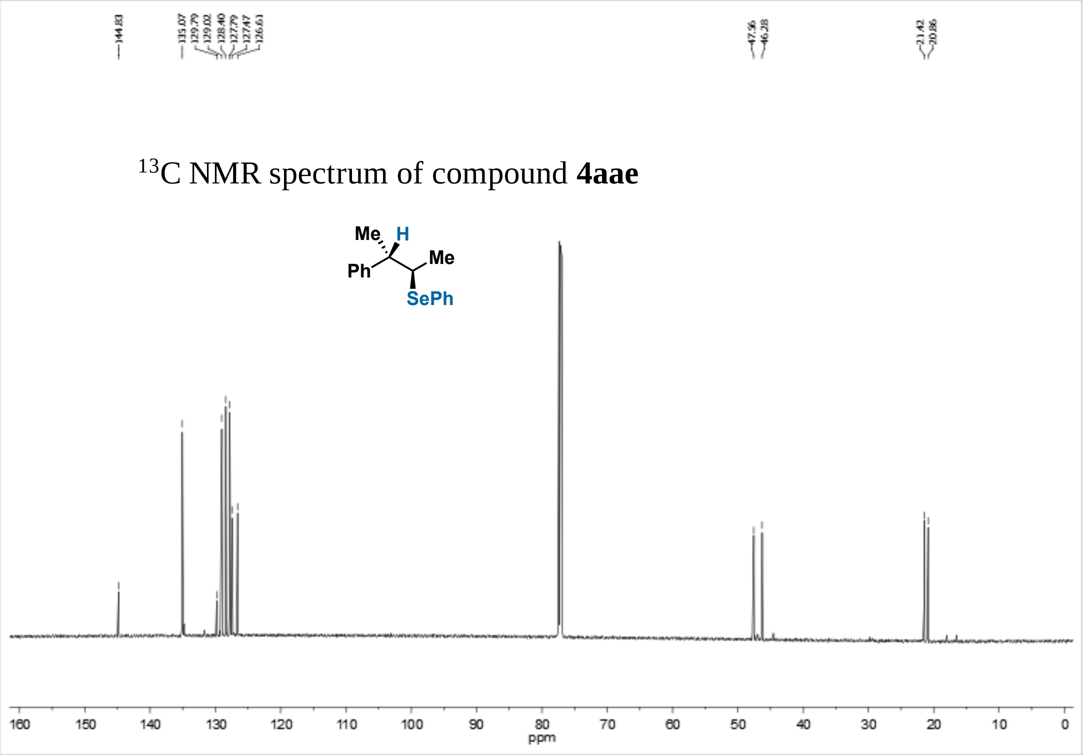

^{1}H NMR spectrum of compound **4aad**


^{13}C NMR spectrum of compound **4aad**

(±)-phenyl((2*R*,3*R*)-3-phenylbutan-2-yl)selane (4aae)

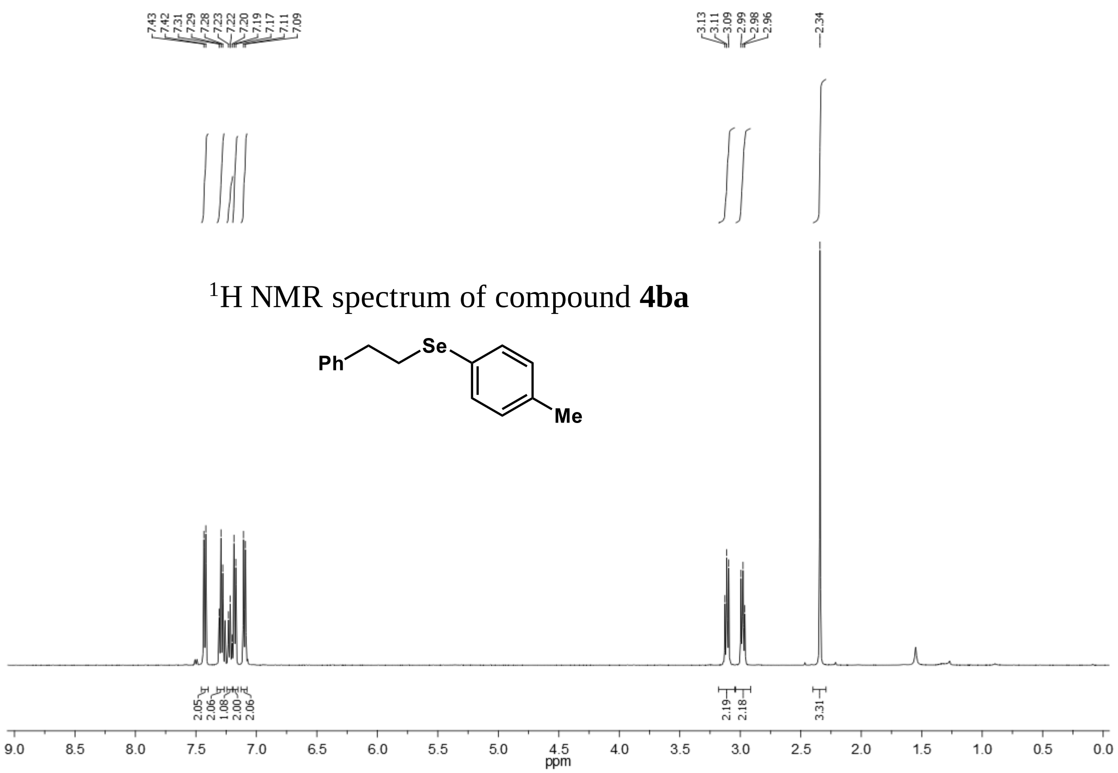


^{1}H NMR spectrum of compound **4aae**

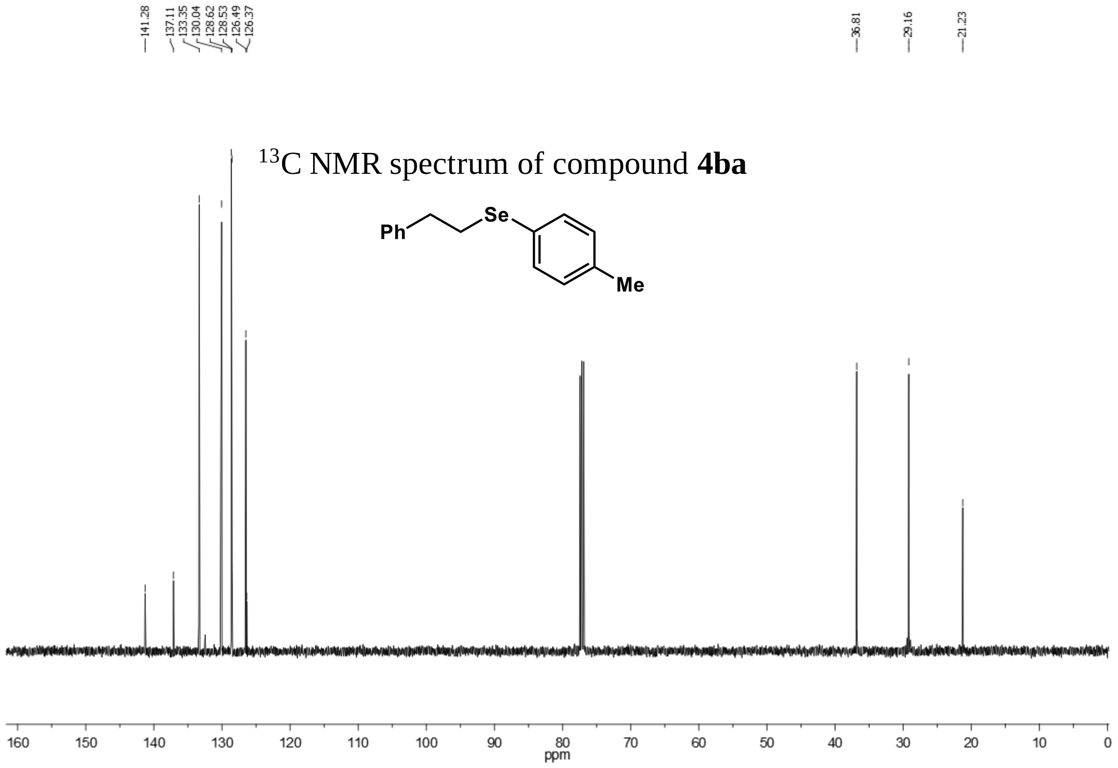


^{13}C NMR spectrum of compound **4aae**

phenethyl(*p*-tolyl)selane (4ba)

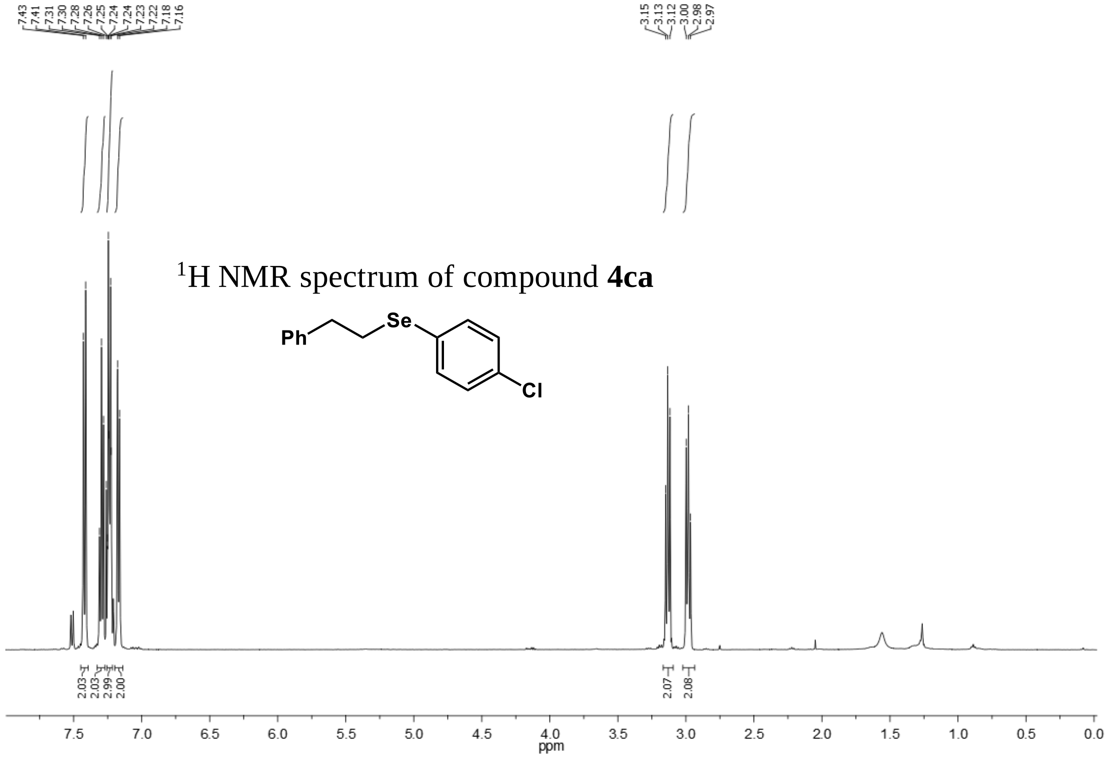


^{1}H NMR spectrum of compound **4ba**

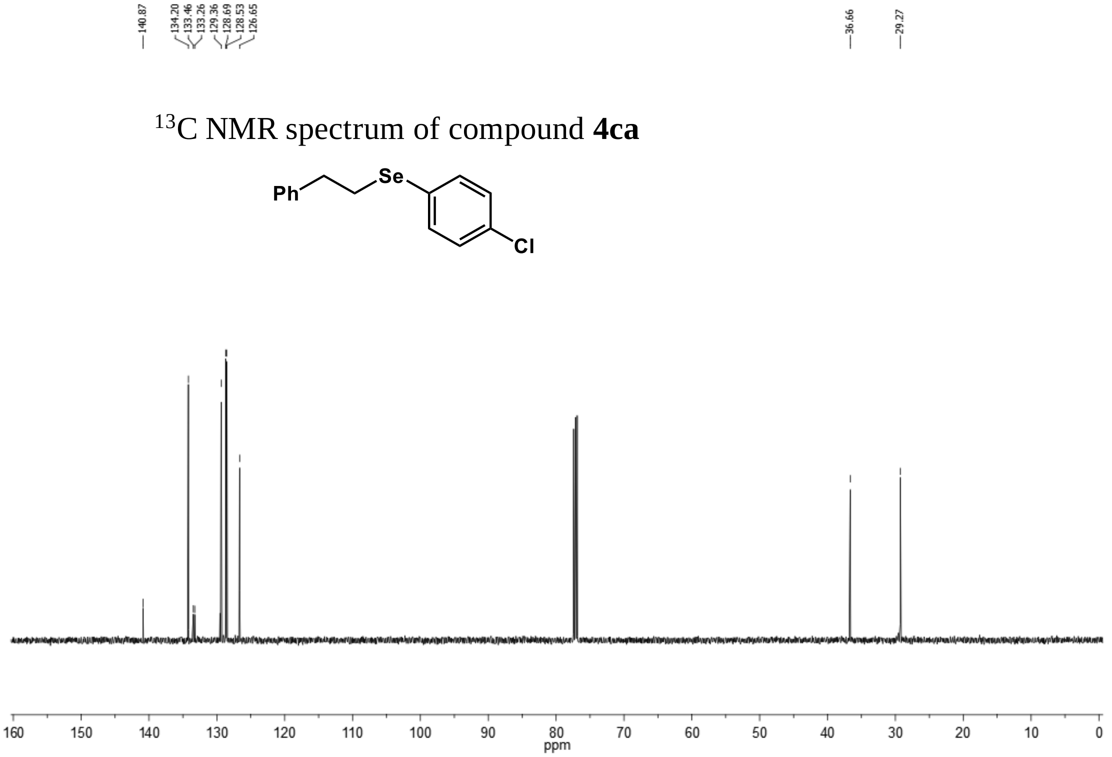


^{13}C NMR spectrum of compound **4ba**

(4-chlorophenyl)(phenethyl)selane (4ca)

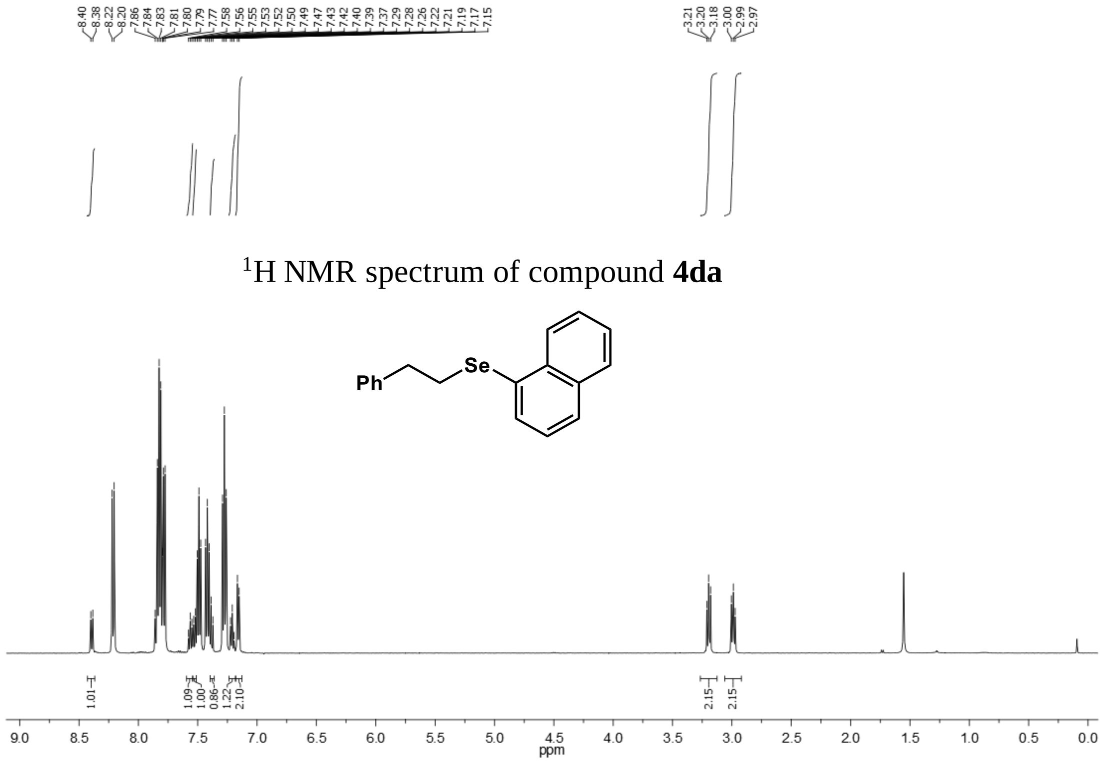


^{1}H NMR spectrum of compound **4ca**

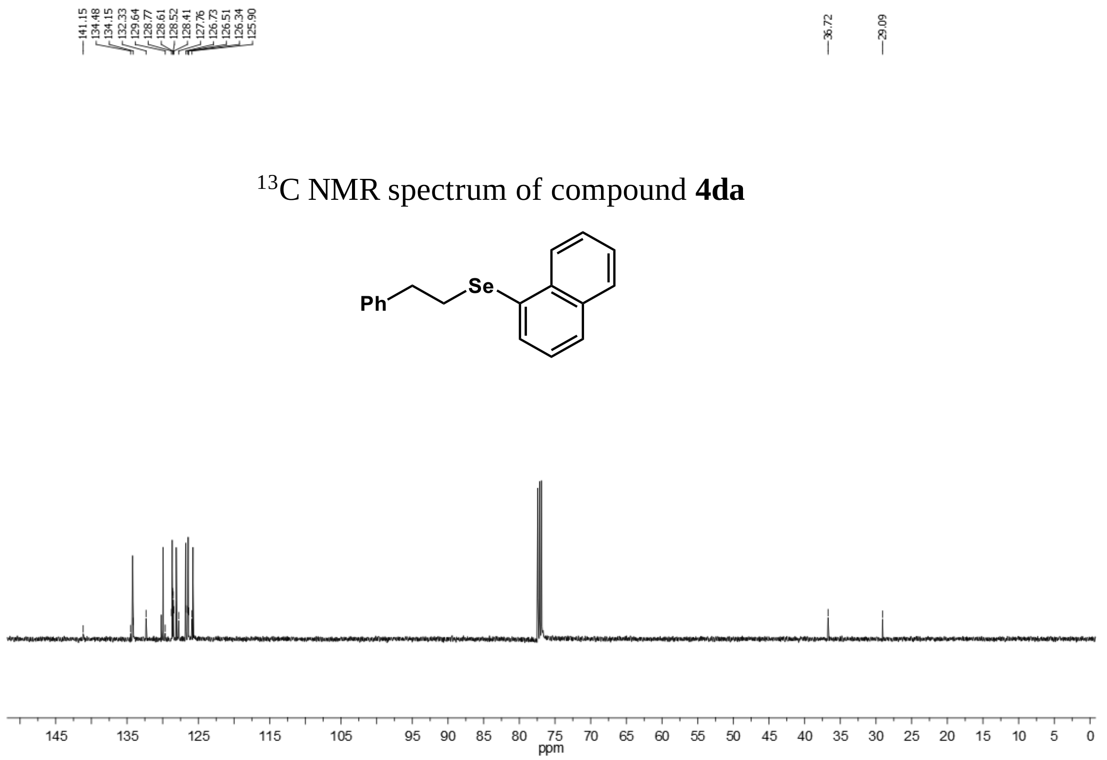


^{13}C NMR spectrum of compound **4ca**

naphthalen-1-yl(phenethyl)selane (4da)



^{1}H NMR spectrum of compound **4da**



^{13}C NMR spectrum of compound **4da**