Electronic supplementary materials

Efficient Oxyselenation and Aminoselenation Utilizing a Selenenyl Iodide Based on the Characteristic Thermodynamics of Its Reaction with Olefins

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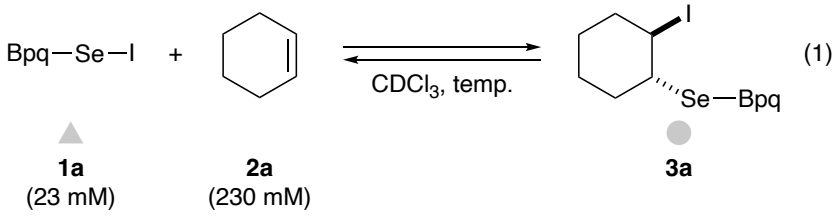
Contents

Experimental section

General

All synthetic experiments were performed under an argon atmosphere. $CHCl_3$ was purchased from commercial sources, distilled over CaH_2, and dried over 4ÅMS. MeCN was purchased from commercial sources, distilled over CaH_2, and dried over 3ÅMS. Other chemicals were purchased from commercial sources and used as received. Silica gel column chromatography was performed using Kanto Chemical silica gel N60. Preparative thin layer chromatography (PTLC) was performed using Merck silica gel 60 PF254. ^{1}H NMR spectra were recorded on a JEOL JNM-AL400, a JEOL LAMBDA-400, JEOL ECX-400, or a JEOL ECX-500, and the chemical shifts of ^{1}H are referenced to the residual proton signal of $CDCl_3$ (δ 7.25). $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL ECX-400 or a JEOL ECX-500, and the chemical shifts are given relative to $CDCl_3$ (δ 77.0) as internal standards. $^{77}Se\{^1H\}$ NMR spectra were recorded on a JEOL ECX-400 or a JEOL ECX-500, and the chemical shifts of ^{77}Se are referenced to Ph_2Se_2 (δ 480) as an external standard. All spectra were assigned with the aid of DEPT, COSY, HMQC, and HMBC NMR experiments. IR spectra were recorded on a JASCO FT/IR- 4100. High-resolution FD-TOF mass spectra were measured on a JEOL JMS-T100GCv "AccuTOF GCv". Melting points (m.p.) were measured with a Yanaco MP-S3 (uncorrected).

^{1}H NMR study of a reaction of BpqSeI and cyclohexene



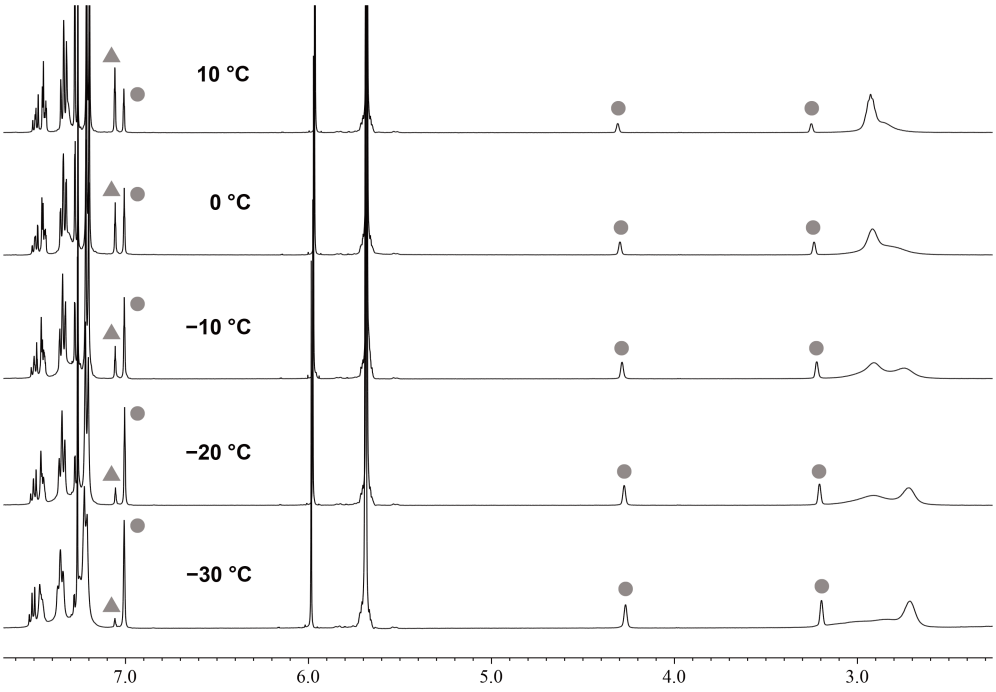
BpqSeI (15 mg) and 1,1,2,2-tetrachloroethane (internal standard) (2 μL) were added to a J. Young NMR tube. The mixture was dissolved in $CDCl_3$ (0.6 mL) and cyclohexene (14 μL) was added. For measurements, the mixture was pre-cooled at the desired temperature until equilibrium was reached. After pre-cooling, the mixture was analyzed using a JEOL ECX-500 MHz spectrometer at 10 °C intervals in the temperature range of 10 to −30 °C, and the compound ratios were determined from the signal intensities. Measurements were made at least 10 times at the temperature consecutively, and the average of the signal intensity ratios was used to determine the equilibrium constant. The thermodynamic parameters $\Delta H°$ and $\Delta S°$ were calculated based on the equilibrium constant.

Equilibrium Equations

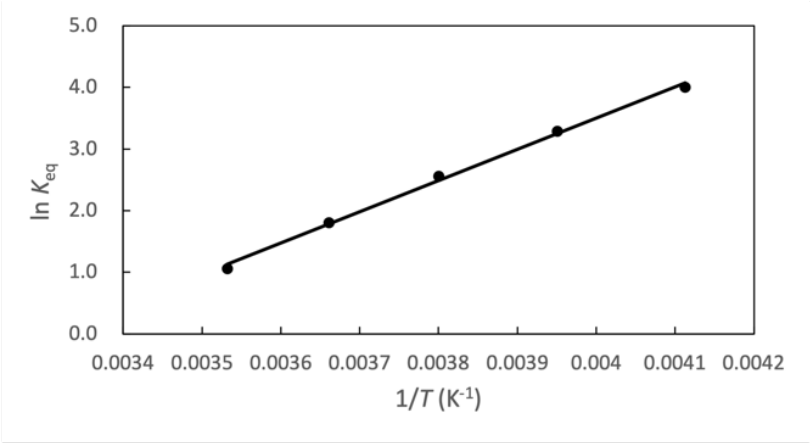
1) $K_{eq} = \frac{[3a]}{[1a][2a]}$

2) $-RTlnK_{eq} = \Delta H° - \Delta S°$

Variable-temperature (VT) ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



van't Hoff plot for the VT-NMR studies



General procedure for oxyselenation of olefin (2)

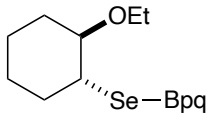
To a solution of BpqSeI (**1a**) (1.0 eq) in $CHCl_3$ and MeCN (1:1) were added NIS (1.0 eq), olefin (**2**) (6.0 eq), and ROH **4** (5.0 eq). The resulting reaction mixture was stirred at 25 °C for 30 min before saturated aq. Na_2SO_3 was added. The two layers were separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo and the crude mixture was purified by preparative TLC (hexane/$CHCl_3$ = 1:1) to give product **5**.

General procedure for aminoselenation of olefin (2)

To a solution of BpqSeI (**1a**) (1.0 eq) in $CHCl_3$ and MeCN (1:1) were added NIS (0.9 eq), olefin (**2**) (1.0 eq), and amine **9** (1.0 eq). The resulting reaction mixture was stirred at 25 °C for 10 or 60 min before saturated aq. Na_2SO_3 was added. The two layers were separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo and the crude mixture was purified by preparative TLC (hexane/$CHCl_3$ = 1:1) to give product **10**.

Analytical data of new compounds

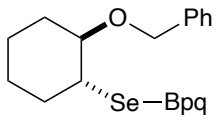
(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)(*trans*-2-ethylcyclohyxyl)selane (5b)



5b

35.3 mg (32.8 μmol) of **1a** was used, and 29.2 mg of **5b** was obtained (83% yield). **5b**: white solids; m.p. >290 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.38-7.36 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 4H), 7.27 (s, 4H), 7.16 (d, *J* = 7.7 Hz, 8H), 6.97 (t, *J* = 1.8 Hz, 2H), 3.08-3.00 (m, 2H), 2.91-2.83 (m, 10H), 1.74-1.69 (m, 1H), 1.65-1.60 (m, 1H), 1.46-1.40 (m, 1H), 1.29-1.24 (m, 2H), 1.19-1.12 (m, 27H), 1.06 (d, *J* = 6.9 Hz, 24H), 0.87 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 148.9 (s), 146.9 (s), 146.8 (s), 142.8 (s), 139.6 (s), 139.2 (s), 129.6 (d), 129.5 (d), 129.4 (d), 128.8 (d), 128.0 (d), 127.8 (s), 122.4 (d), 77.8 (d), 63.4 (t), 46.4 (d), 30.4 (d), 27.5 (t), 27.2 (t), 24.5 (q), 24.4 (q), 24.1 (q), 24.0 (q), 23.2 (t), 21.4 (t), 15.3 (q); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 309; **IR** (KBr); 3059, 2960, 2928, 2867, 1597, 1459 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1076.6323 $[M]^+$ (calcd for $C_{74}H_{92}OSe$, 1076.6313).

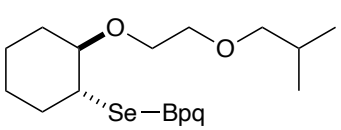
(*trans*-2-(benzyl)cyclohyxyl)(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selane (5c)



5c

50.0 mg (46.5 μmol) of **1a** was used, and 51.8 mg of **5c** was obtained (95% yield). **5c**: white solids; m.p. 254-255 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.36-7.33 (m, 1H), 7.28-7.22 (m, 6H), 7.11-7.06 (m, 12H), 6.92-6.90 (m, 3H), 6.88 (t, *J* = 1.7 Hz, 2H), 6.76-6.75 (m, 2H), 4.08 (d, *J* = 12.6 Hz, 1H), 3.88 (d, *J* = 12.6 Hz, 1H), 2.90-2.78 (m, 10H), 1.74-1.68 (m, 1H), 1.58-1.53 (m, 1H), 1.39-1.34 (m, 1H), 1.27-1.25 (m, 2H), 1.18-1.06 (m, 27H), 0.97 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 148.9 (s), 146.8 (s), 146.7 (s), 142.6 (s), 139.5 (s), 139.1 (s), 138.4 (s), 129.7 (d), 129.6 (d), 129.5 (d), 128.8 (s), 128.2 (d), 128.1 (d), 127.8 (d), 127.5 (d), 127.1 (d), 122.4 (d), 75.6 (d), 70.0 (t), 46.4 (d), 30.3 (d), 27.0 (t), 26.2 (t), 24.6 (q), 24.4 (q), 24.0 (q), 22.8 (t), 20.9 (t); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 305; **IR** (KBr); 3062, 3031, 2960, 2926, 2867, 1596, 1458 cm^{-1}; **HRMS** (ESI-TOF) *m/z* 1161.6376 $[M]^+$ (calcd for $C_{79}H_{94}NaOSe$, 1161.6362).

(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)(*trans*-2-(2-isobutoxyethan-1-)cyclohyxyl)selane (5d)

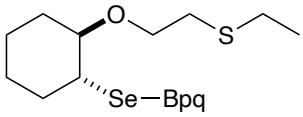


5d

17.7 mg (16.4 μmol) of **1a** was used, and 18.1 mg of **5d** was obtained (96% yield). **5d**: white solids; m.p. 273-274 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40-7.38 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 4H), 7.28 (s, 4H), 7.20 (d, *J* = 7.4 Hz, 8H), 6.99 (t, *J* = 1.7 Hz, 2H), 3.24-3.22 (m, 2H), 3.17-3.14 (m, 2H), 3.03-2.99 (m, 2H), 2.92-2.85 (m, 10H), 1.71-1.65 (m, 3H), 1.47-1.44 (m, 2H), 1.36-1.07 (m, 53H), 0.76 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ148.8 (s), 146.8 (s),

146.8 (s), 142.8 (s), 139.6 (s), 139.2 (s), 129.5 (d), 129.4 (d), 128.7 (s), 128.0 (d), 127.8 (d), 122.4 (d), 78.7 (d), 78.2 (t), 69.9 (t), 67.7 (t), 46.5 (d), 30.4 (d), 28.3 (d), 27.3 (t), 26.8 (t), 24.5 (q), 24.4 (q), 24.1 (q), 24.0 (q), 23.1 (d), 21.2 (d), 19.2 (t); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 293; **IR** (KBr); 3060, 2958, 2929, 2867, 1597, 1460 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1148.6936 $[M]^+$ (calcd for $C_{78}H_{100}O_2Se$, 1148.6889).

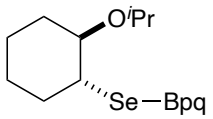
(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl) (*trans*-2-(2-(ethylthio)ethan-1-)cyclohyxyl)selane (5e)



5e

17.7 mg (16.4 μmol) of **1a** was used, and 14.1 mg of **5e** was obtained (76% yield). **5e**: white solids; m.p. 252-253 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42-7.39 (m, 3H), 7.33 (t, *J* = 7.9 Hz, 4H), 7.29 (s, 4H), 7.20 (d, *J* = 7.9 Hz, 8H), 6.99 (s, 2H), 3.18-3.10 (m, 4H), 2.92-2.84 (m, 10H), 2.37-2.32 (m, 4H), 1.75-1.66 (m, 2H), 1.45-1.43 (m, 1H), 1.34-1.31 (m, 1H), 1.26-1.07 (m, 55H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ148.8 (s), 146.8 (s), 146.7 (s), 142.7 (s), 139.6 (s), 139.1 (s), 129.6 (d), 129.4 (d), 128.7 (s), 128.1 (d), 127.8 (d), 122.4 (d), 78.3 (d), 68.3 (t), 46.4 (d), 31.0 (t), 30.4 (d), 27.3 (t), 26.7 (t), 26.3 (t), 24.5 (q), 24.4 (q), 24.1 (q), 24.1 (q), 23.1 (t), 21.2 (t), 14.8 (q); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 314; **IR** (KBr); 3059, 3033, 2961, 2927, 2866, 1739, 1462 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1136.6364 $[M]^+$ (calcd for $C_{76}H_{96}OSSe$, 1136.6347).

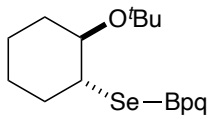
(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)(*trans*-2-isopropoxycyclohyxyl)selane (5f)



5f

17.7 mg (16.4 μmol) of **1a** was used, and 15.8 mg of **5f** was obtained (88% yield). **5f**: colorless crystals; m.p. 267-270 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40 (s, 3H), 7.33 (t, *J* = 7.7 Hz, 4H), 7.29 (s, 4H), 7.20 (d, *J* = 7.7 Hz, 8H), 6.98 (s, 2H), 3.20-3.15 (m, 1H), 3.01 (d, *J* = 3.2 Hz, 1H), 2.89 (s, 8H), 2.82 (d, *J* = 3.2 Hz, 1H), 1.70-1.15 (m, 32H), 1.07 (d, *J* = 6.9 Hz, 24H), 0.76 (d, *J* = 6.0 Hz, 3H), 0.72 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.2 (s), 147.0 (s), 146.9 (s), 142.8 (s), 139.7 (s), 139.3 (s), 129.8 (d), 129.7 (d), 129.5 (d), 129.2 (s), 128.2 (d), 127.9 (d), 122.5 (d), 73.9 (d), 68.4 (d), 47.8 (d), 30.4 (d), 27.4 (t), 27.1 (t), 24.6 (q), 24.5 (q), 24.2 (q), 23.3 (t), 22.3 (q), 21.2 (t); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 282; **IR** (KBr); 3059, 3033, 2960, 2967, 2867, 1459, 1382, 1362, 803, 763, 753 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1090.6475 $[M]^+$ (calcd for $C_{75}H_{94}OSe$, 1090.6470).

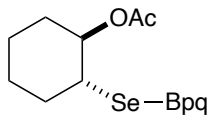
(*trans*-2-(*tert*-butoxy)cyclohyxyl)(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selane (5g)



5g

17.7 mg (16.4 μmol) of **1a** was used, and 9.8 mg of **5g** was obtained (54% yield). **5g**: colorless crystals; m.p. 269-273 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.41 (s, 3H), 7.32 (t, *J* = 7.7 Hz, 8H), 7.21-7.19 (m, 8H), 6.98 (t, *J* = 1.4 Hz, 2H), 3.11 (d, *J* = 2.6 Hz, 1H), 2.90 (s, 8H), 2.72 (s, 1H), 1.90-1.84 (m, 1H), 1.74-1.69 (m, 1H), 1.27-1.02 (m, 54H), 0.67 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ147.1 (s), 146.9 (s), 142.7 (s), 139.6 (s), 139.3 (s), 129.8 (d, two signals were overlapped), 129.3 (d, s two signals were overlapped), 128.4 (d), 127.9 (d), 122.5 (d), 73.1 (s), 67.8 (d), 50.5 (d), 30.4 (d), 27.9 (a), 27.6 (t), 26.7 (t), 24.7 (q), 24.5 (q), 24.2 (q), 24.1 (q), 22.7 (t), 20.7 (t); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 306; **IR** (KBr); 2959, 2926, 2866, 1458, 1362, 1021, 752 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1104.6616 $[M]^+$ (calcd for $C_{76}H_{96}OSe$, 1104.6626).

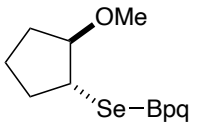
(*trans*-2-acetylcyclohyxyl)(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selane (5h)



5h

17.7 mg (16.4 μmol) of **1a** was used, and 16.5 mg of **5h** was obtained (92% yield). **5h**: colorless crystals; m.p. 285-287 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42-7.39 (m, 3H), 7.34-7.27 (m, 8H), 7.20-7.18 (m, 8H), 6.98 (t, *J* = 1.4 Hz, 2H), 4.39 (d, *J* = 3.2 Hz, 1H), 2.89 (s, 9H), 1.83-1.77 (m, 1H), 1.73 (s, 3H), 1.66-1.63 (m, 1H), 1.44-1.41 (m, 1H), 1.29-1.21 (m, 5H), 1.17-1.14 (m, 24H), 1.08-1.06 (m, 24H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ169.7 (s), 148.9 (s), 146.8 (s), 142.8 (s), 139.9 (s), 139.7 (s), 139.2 (s), 139.1 (s), 129.9 (d), 129.8 (d), 129.7 (d), 128.4 (d), 127.9 (d), 127.3 (s), 122.6 (d), 122.5 (d), 30.5 (d), 27.5 (t), 26.8 (t), 24.6 (q), 24.5 (q), 24.14 (q), 24.08 (t), 22.9 (t), 21.5 (t), 21.1 (q); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 317; **IR** (KBr); 3058, 3033, 2961, 2927, 2867, 1741, 1459, 1362, 1233, 1032, 884, 804, 753 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1090.6091 $[M]^+$ (calcd for $C_{74}H_{90}O_2Se$, 1090.6106).

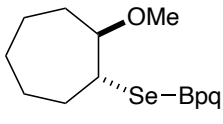
(5',5'''-bis(2,6-diisopropylphenyl)-2,2'''',6,6''''-tetraisopropyl-[1,1':3',1'':3'',1''':3''',1''''-quinquephenyl]-2''-yl)(2-methoxycyclopentyl)selane (5i)



5i

20.1 mg (18.7 μmol) of **1a** was used, and 19.1 mg of **5i** was obtained (97% yield). **5i**: white solids; m.p. >290 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.47-7.41 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 8H), 7.19 (d, *J* = 7.9 Hz, 8H), 7.00 (s, 2H), 3.18 (d, *J* = 5.1 Hz, 1H), 2.92-2.88 (m, 9H), 2.71 (s, 3H), 1.72-1.66 (m, 1H), 1.63-1.57 (m, 1H), 1.51-1.43 (m, 3H), 1.16-1.03 (m, 48H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 148.7, 146.9, 146.8, 142.4, 139.7, 139.1, 129.7, 129.5, 129.4, 128.4, 127.8, 122.5, 88.6, 55.7, 46.6, 30.8, 30.4, 30.2, 24.4, 24.1, 24.0, 23.5; **^{77}Se NMR** (75 MHz, $CDCl_3$): δ ; **IR** (KBr); 3059, 2960, 2868, 1597, 1460, 753 cm^{-1}; **HRMS** (ESI-TOF) *m/z* 1071.5888 $[M+Na]^+$ (calcd for $C_{72}H_{88}NaOSe$, 1071.5893).

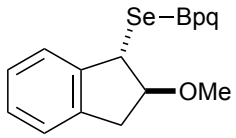
(5',5'''-bis(2,6-diisopropylphenyl)-2,2'''',6,6''''-tetraisopropyl-[1,1':3',1'':3'',1''':3''',1''''-quinquephenyl]-2''-yl)(2-methoxycycloheptyl)selane (5j)



5j

20.4 mg (20.0 μmol) of **1a** was used, reaction time is 6 h, and 11.1 mg of **5j** was obtained (54% yield). **5j**: white solids; m.p. 220 °C (decomp.); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.41 (s, 3H), 7.33 (t, *J* = 7.7 Hz, 8H), 7.20 (d, *J* = 7.4 Hz, 8H), 7.00 (s, 2H), 3.04-2.81 (m, 10H), 2.68 (s, 3H), 1.75-1.70 (m, 1H), 1.65-1.60 (m, 1H), 1.54-1.50 (m, 1H), 1.44-1.40 (m, 4H), 1.35-1.24 (m, 3H), 1.18-1.07 (m, 48H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.2, 146.9, 146.8, 142.6, 139.6, 139.2, 129.8, 129.6, 129.5, 128.5, 128.2, 127.8, 122.5, 84.0, 55.7, 49.5, 30.4, 30.0, 29.3, 28.6, 25.6, 24.5, 24.5, 24.0, 21.1; **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 295; **IR** (KBr); 3060, 2961, 2926, 2867, 1460, 754 cm^{-1}; **HRMS** (ESI-TOF) *m/z* 1099.6200 $[M+Na]^+$ (calcd for $C_{74}H_{92}NaOSe$, 1099.6206).

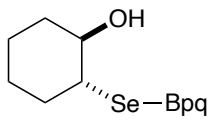
(5',5'''-bis(2,6-diisopropylphenyl)-2,2'''',6,6''''-tetraisopropyl-[1,1':3',1'':3'',1''':3''',1''''-quinquephenyl]-2''-yl)(-2-methoxy-2,3-dihydro-1*H*-inden-1-yl)selane (5k)



5k

20.0 mg (18.6 μmol) of **1a** was used, reaction time is 18 h, and 12.1 mg of **5k** was obtained (59% yield). **5j**: white solids; m.p. >290 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.54-7.47 (m, 3H), 7.43-7.29 (m, 9H), 7.23-7.05 (m, 12H), 6.83 (d, *J* = 7.4 Hz, 1H), 4.24 (s, 1H), 3.41 (d, *J* = 5.7 Hz, 1H), 2.95-2.83 (m, 9H), 2.66 (s, 3H), 2.63 (d, *J* = 17.0 Hz, 1H), 1.16-0.92 (m, 48H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.1, 146.7, 141.6, 139.8, 138.9, 129.6, 129.5, 129.0, 128.9, 127.9, 126.3, 125.0, 124.8, 122.5, 86.5, 55.8, 51.7, 37.5, 30.6, 30.4, 24.5, 24.3, 24.2; **IR** (KBr); 2960, 1459, 1092, 729 cm^{-1}; **HRMS** (ESI-TOF) *m/z* 1119.5877 $[M]^+$ (calcd for $C_{76}H_{88}OSe$, 1119.5893).

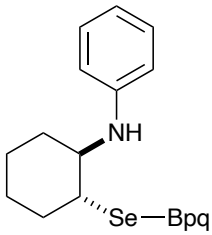
(5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴,6‴-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗-quinquephenyl-2″-yl)(*trans*-2-hydroxy)selane (7)



7

17.7 mg (16.4 μmol) of **1a** was used, and 16.9 mg of **7** was obtained (98% yield). **7**: white solids; m.p. >290 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42-7.39 (m, 3H), 7.33-7.29 (m, 8H), 7.18 (d, *J* = 7.8 Hz, 8H), 6.99 (s, 2H), 3.11 (s, 1H), 2.88 (s, 8H), 2.55-2.50 (m, 1H), 1.82-1.79 (m, 1H), 1.58-1.54 (m, 2H), 1.35 (s, 1H), 1.25-1.06 (m, 53H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.3 (s), 146.8 (s), (s), 142.7 (s), 139.8 (s), 139.0 (s), 129.8 (d), 129.7 (d), 128.5 (d), 127.8 (s), 126.8 (d), 127.9 (d), 122.5 (d), 73.5 (d), 53.2 (d), 32.9 (t), 30.8 (t), 30.4 (d), 25.8 (t), 24.6 (q), 24.2 (q), 23.5 (t); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 297; **IR** (KBr); 3481, 3060, 2961, 2927, 2867, 1596, 1459 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1048.6020 $[M]^+$ (calcd for $C_{72}H_{88}OSe$, 1048.6000).

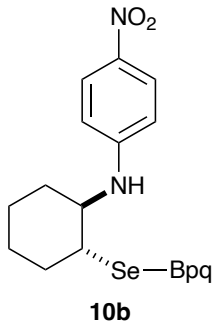
***N*-(*trans*-2-((5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴,6‴-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗-quinquephenyl-2″-yl)selanyl)cyclohexyl)aniline (10a)**



10a

8.8 mg (8.2 μmol) of **1a** was used, and 8.5 mg of **10a** was obtained (92% yield). **10a**: colorless crystals; m.p. >300 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52-7.44 (m, 3H), 7.29 (t, *J* = 7.7 Hz, 4H), 7.22 (s, 4H), 7.16 (d, *J* = 7.7 Hz, 8H), 6.96 (s, 2H), 6.83 (t, *J* = 7.9 Hz, 2H), 6.46 (t, *J* = 7.3 Hz, 1H), 5.89 (d, *J* = 7.7 Hz, 2H), 3.46 (s, 1H), 3.12 (s, 1H), 2.88-2.84 (m, 9H), 2.01-1.95 (m, 1H), 1.56 (t, *J* = 4.6 Hz, 1H), 1.42-1.35 (m, 2H), 1.27-0.98 (m, 52H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.5. 146.8, 146.7, 146.4, 142.8, 139.6, 139.1, 129.6, 129.5, 129.0, 128.7, 128.0, 127.8, 122.4, 117.1, 112.6, 60.4, 46.7, 30.3, 27.5, 26.2, 24.5, 24.4, 24.0, 23.8, 22.4, 15.4; **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 280; **IR** (KBr); 3400, 3057, 2962, 2927, 2867, 1601, 1503, 1460, 1362, 885, 803, 753 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1123.6504 $[M]^+$ (calcd for $C_{77}H_{93}NSe$, 1123.6473).

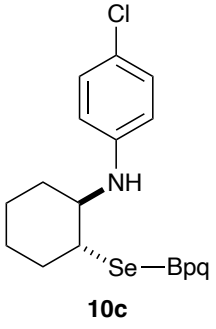
***N*-(*trans*-2-((5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴,6‴-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1⁗:3⁗-quinquephenyl-2″-yl)selanyl)cyclohexyl)-4-nitroaniline (10b)**



10b

50.0 mg (46.5 μmol) of **1a** was used, and 38.4 mg of **10b** was obtained (71% yield). **10b**: yellow crystals; m.p. >300 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.9 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 4H), 7.24 (s, 4H), 7.18-7.16 (m, 8H), 7.03-7.00 (m, 2H), 5.70 (d, *J* = 8.0 Hz, 2H), 4.43 (d, *J* = 4.9 Hz, 1H), 3.23 (s, 1H), 2.86 (s, 9H), 2.06-2.01 (m, 1H), 1.68-1.27 (m, 7H), 1.20-0.88 (m, 48H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.6 (s), 149.4 (s), 146.6 (s), 146.5 (s), 142.3 (s), 139.8 (s), 138.8 (s), 137.8 (s), 129.9 (d, two signals were overlapped), 129.8 (d), 128.9 (d), 128.6 (s), 127.9 (d), 126.3 (d), 122.5 (d), 122.2 (d), 110.4 (d), 53.0 (d), 46.5 (d), 30.4 (d), 27.8 (t), 27.1 (t), 24.5 (q), 24.3 (q), 24.0 (q), 23.2 (t), 21.5 (t); **^{77}Se NMR** (75 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C): δ 322; **IR** (KBr); 3410, 3060, 2960, 2926, 2866, 1600, 1324, 1112, 803, 752 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1168.6320 $[M]^+$ (calcd for $C_{78}H_{92}N_2O_2Se$, 1168.6324).

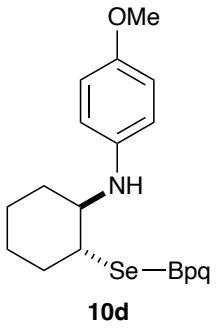
4-chloro-*N*-(*trans*-2-((5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selanyl)cyclohexyl)aniline (10c)



10c

50.0 mg (46.5 μmol) of **1a** was used, and 49.9 mg of **10c** was obtained (93% yield). **10c**: white crystals; m.p. >300 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.57-7.48 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 4H), 7.25 (s, 4H), 7.18 (d, *J* = 8.0 Hz, 8H), 6.99 (t, *J* = 1.4 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.77 (d, *J* = 8.6 Hz, 2H), 3.56 (s, 1H), 3.08 (d, *J* = 4.0 Hz, 1H), 2.88-2.82 (m, 9H), 1.21-1.94 (m, 1H), 1.63-1.58 (m, 1H), 1.39-1.06 (m, 54H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ149.4 (s), 146.71 (s), 146.66 (s), 145.1 (s), 142.6 (s), 139.6 (s), 139.0 (s), 129.8 (d), 129.6 (d), 128.9 (d), 128.8 (s), 128.4 (d), 127.8 (d), 122.47 (d), 122.46 (d), 121.4 (s), 113.2 (d), 53.6 (d), 46.9 (d), 30.4 (d), 28.3 (t), 28.0 (t), 24.5 (q), 24.4 (q), 24.0 (q), 23.6 (t), 21.8 (t); **^{77}Se NMR** (75 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C): δ 322; **IR** (KBr); 3402, 3059, 2960, 2867, 1597, 1496, 1362, 1055, 885, 813, 752 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1157.6065 $[M]^+$ (calcd for $C_{78}H_{92}ClNSe$, 1157.6084).

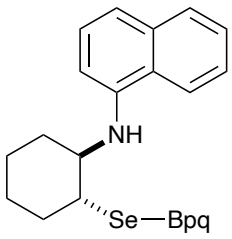
***N*-(*trans*-2-((5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selanyl)cyclohexyl)-4-methoxyaniline (10d)**



10d

50.0 mg (46.5 μmol) of **1a** was used, and 33.4 mg of **10d** was obtained (62% yield). **10d**: pale yellow crystals; m.p. >300 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.48-7.41 (m, 3H), 7.31-7.28 (m, 4H), 7.20-7.15 (m, 12H), 6.96 (s, 2H), 6.44 (d, *J* = 8.9 Hz, 2H), 5.86 (d, *J* = 8.3 Hz, 2H), 3.53 (s, 3H), 3.02 (d, *J* = 4.9 Hz, 1H), 2.93-2.78 (m, 9H), 1.33-1.03 (m, 56H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.9 (s), 149.5 (s), 146.9 (s), 146.8 (s), 142.9 (s), 140.9 (s), 139.7 (s), 139.2 (s), 129.8 (d, two signals were overlapped), 129.6 (d), 129.0 (s), 128.3 (d), 127.9 (d), 122.5 (d), 114.9 (d), 114.2 (d), 55.9 (d), 46.9 (d), 30.5 (d), 29.8 (t), 28.5 (t), 24.6 (q), 24.1 (q), 23.9 (t), 22.1 (t); **^{77}Se NMR** (75 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C): δ 323; **IR** (KBr); 3056, 2959, 2927, 2866, 1509, 1459, 1241, 885, 805, 754 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1153.6585 $[M]^+$ (calcd for $C_{79}H_{95}NOSe$, 1153.6579).

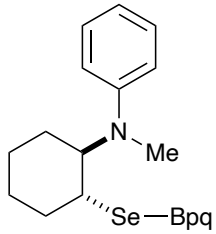
***N*-(*trans*-2-((5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selanyl)cyclohexyl)naphthalen-1-amine (10e)**



10e

50.0 mg (46.5 μmol) of **1a** was used, and 27.8 mg of **10e** was obtained (51% yield). **10e**: pale yellow crystals; m.p. 175-180 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60-7.57 (m, 2H), 7.53-7.49 (m, 3H), 7.33-7.25 (m, 11H), 7.19-7.10 (m, 8H), 6.97-6.94 (m, 3H), 6.81-6.78 (m, 1H), 5.26 (d, *J* = 7.4 Hz, 1H), 3.37 (s, 1H), 3.08 (s, 1H), 2.89 (s, 8H), 2.11-2.05 (m, 1H), 1.78-1.71 (m, 1H), 1.53-1.27 (m, 6H), 1.17-1.01 (m, 48H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.7 (s), 146.9 (s), 146.8 (s), 142.7 (s), 141.4 (s), 139.7 (s), 139.2 (s), 134.4 (s), 130.1 (d, two signals were overlapped), 129.8 (d), 129.7 (d), 129.0 (s), 128.7 (d), 127.9 (d), 126.5 (d), 125.3 (d), 124.3 (d), 123.4 (s), 122.5 (d), 119.4 (d), 117.1 (d), 103.6 (d), 52.2 (d), 46.7 (d), 30.5 (d), 30.4 (d), 27.8 (t), 27.3 (t), 24.6 (q), 24.4 (q), 24.1 (q), 23.9 (q), 23.4 (t), 21.7 (t); **^{77}Se NMR** (75 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C): δ 324; **IR** (KBr); 3565, 3060, 2960, 2866, 1459, 1362, 884, 805, 753 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1173.6606 $[M]^+$ (calcd for $C_{82}H_{95}NSe$, 1173.6630).

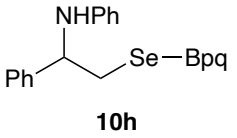
***N*-(*trans*-2-((5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selanyl)cyclohexyl)-*N*-methylaniline (10f)**



10f

50.0 mg (46.5 μmol) of **1a** was used, and 51.4 mg of **10f** was obtained (97% yield). **10f**: pale yellow crystals; m.p. 290-295 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.32-7.29 (m, 7H), 7.21-7.15 (m, 14H), 6.99 (t, *J* = 1.4 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 2H), 3.37-3.25 (m, 1H), 3.03-2.98 (m, 1H), 2.88-2.83 (m, 8H), 2.46 (s, 3H), 1.57-1.53 (m, 4H), 1.41 (d, *J* = 11.7 Hz, 1H), 1.17-1.01 (m, 51H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ150.6 (s), 150.3 (s), 147.0 (s), 146.9 (s), 143.9 (s), 139.9 (s), 139.3 (s), 137.8 (s), 129.3 (d), 129.1 (d), 128.9 (d), 127.9 (d), 127.7 (d), 127.5 (s), 122.5 (d), 117.7 (d), 114.7 (d), 64.7 (d), 45.4 (d), 33.2 (t), 30.5 (d), 30.2 (q), 27.5 (t), 27.0 (t), 25.2 (t), 24.5 (q), 24.4 (q), 24.2 (q); **^{77}Se NMR** (75 MHz, 1,1,2,2-tetrachloroethane-d_2, 120 °C): δ 308; **IR** (KBr); 3058, 2959, 2925, 2866, 1597, 1459, 1362, 882, 753 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1137.6656 $[M]^+$ (calcd for $C_{79}H_{95}NSe$, 1137.6630).

***N*-(2-((5′,5‴-bis(2,6-diisopropylphenyl)-2,6,2‴″,6‴″-tetraisopropyl-1,1′:3′,1″:3″,1‴:3‴,1‴″-quinquephenyl-2″-yl)selanyl)-1-phenylethyl)aniline (10h)**



10h

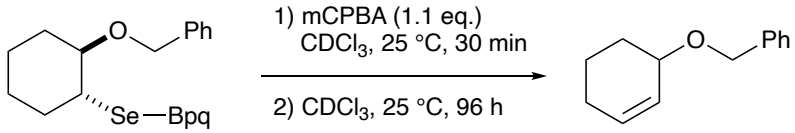
8.9 mg (8.2 μmol) of **1a** was used, and 8.5 mg of **10h** was obtained (90% yield). **10h**: white crystals; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35-7.41 (m, 11H), 7.24 (d, *J* = 8.0 Hz, 8H), 7.16-7.20 (m, 3H), 7.08-7.10 (m, 4H), 6.96 (t, *J* = 7.0 Hz, 2H), 6.58 (t, *J* = 7.0 Hz, 1H), 6.22 (d, *J* = 7.5 Hz, 2H), 4.42-4.39 (m, 1H), 4.09 (d, *J* = 3.0 Hz, 1H), 2.84-2.75 (m, 8H), 2.83 (d, *J* = 5.0 Hz, 2H), 1.12-1.16 (m, 48H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.2 (s), 146.9 (d), 146.4 (s), 142.5 (s), 141.8 (s), 140.3 (s), 139.0 (s), 129.9 (s), 129.8 (s), 129.5 (s), 129.1 (d), 128.5 (s), 128.0 (s), 127.8 (s), 127.3 (s), 126.2 (s), 122.6 (d), 117.6 (s), 113.5 (s), 58.0 (s), 37.5 (s), 30.5 (s), 24.5 (d), 24.1 (d); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 211; **IR** (KBr); 3418, 3060, 2960, 2867, 1600, 1504, 885, 805, 753 cm^{-1}; **HRMS** (FD-TOF) *m/z* 1145.6603 $[M]^+$ (calcd for $C_{80}H_{91}NSe$, 1145.6331).

Attempted oxyselenation of methyl acrylate

1a (1.0 eq.) (6.0 eq.) **4a** (5.0 eq.) not obtained not obtained

To a solution of BpqSeI (**1a**) (20.4 mg, 18.9 μmol, 1.0 eq) in 0.8 mL of $CHCl_3$ and MeCN (1:1) were added NIS (4.2. mg, 18.6 μmol,1.0 eq), methyl acrylate (10.0 μL, 18.6 μmol, 6.0 eq), and methanol (4.0 μL, 98.6 μmol, 5.0 eq). The resulting reaction mixture was stirred at 25 °C for 18 h before saturated aq. Na_2SO_3 was added. The two layers were separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo. The crude product contained a complex mixture, and target compounds were not obtained.

Selenoxide elimination

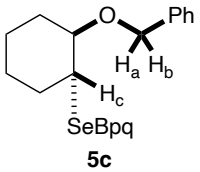


5c (1.0 eq.) **8** 64% yield

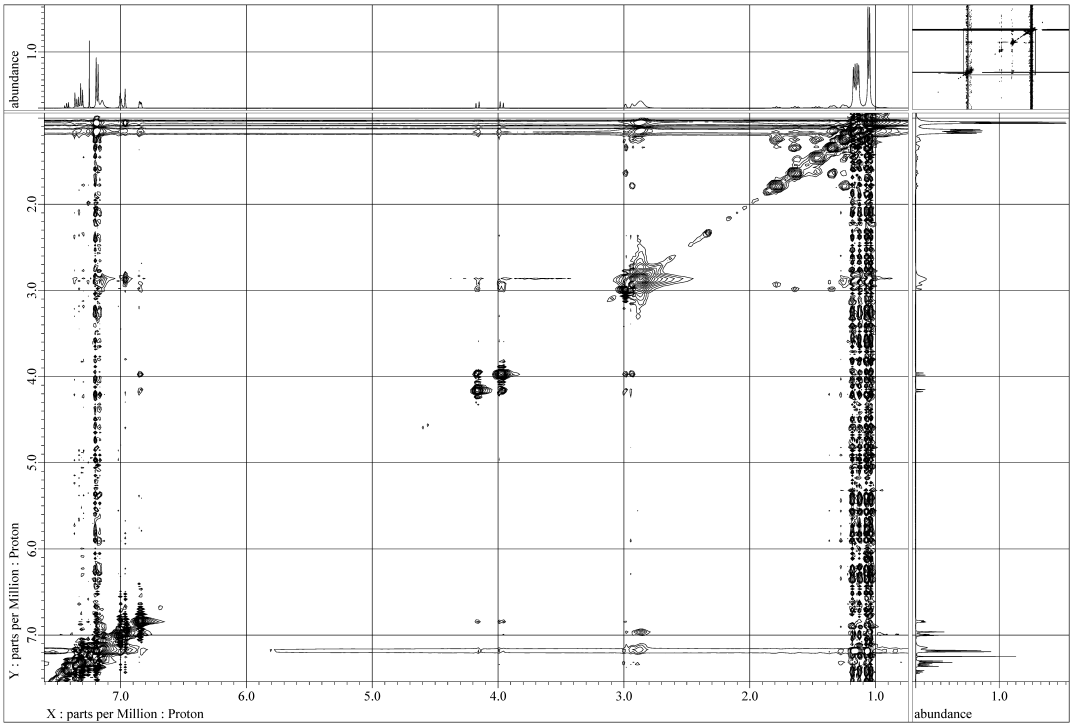
To a solution of **5c** (15.0 mg, 13.2 μmol, 1.0 eq), triphenylmethane (internal standard, 1.60 mg, 6.59 μmol, 0.5 eq) and $CDCl_3$ (0.6 mL) in vial was added mCPBA (77%, 3.1 mg, 1.1 eq). The resulting mixture was transferred to J-Young NMR tube and monitored at 25 °C. After 30 min, sat. aq. $NaHCO_3$ was added. The two layers were separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were dried over Na_2SO_4 and filtered. To the filtrate in vial, $CDCl_3$ (0.6 mL) was added. The resulting mixture was transferred to J-Young NMR tube and monitored at 25 °C. After 96 h, the mixture was concentrated in vacuo. The crude mixture was purified by preparative TLC (hexane/$CHCl_3$ = 3:2) to give product **8** (1.6 mg, 64% yield). ^{1}H NMR spectrum data was identical to that reported (A. B. Pulipaka and S. C. Bergmeier, *Synthesis*, 2008, 1420.).

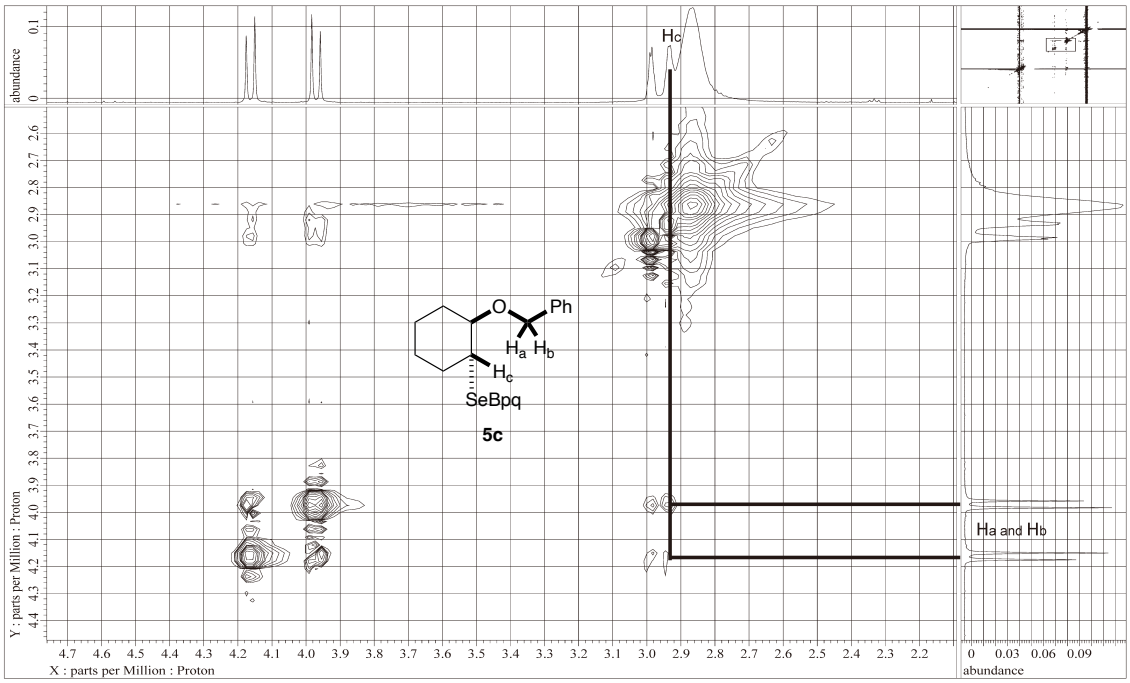
NOESY spectrum (500 MHz, $CDCl_3$) of 5c

The NOESY spectrum showed cross peaks of Ha/Hc and Hb/Hc, which supported the *anti*-configurations of the products.



5c





NMR spectra

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5b**.

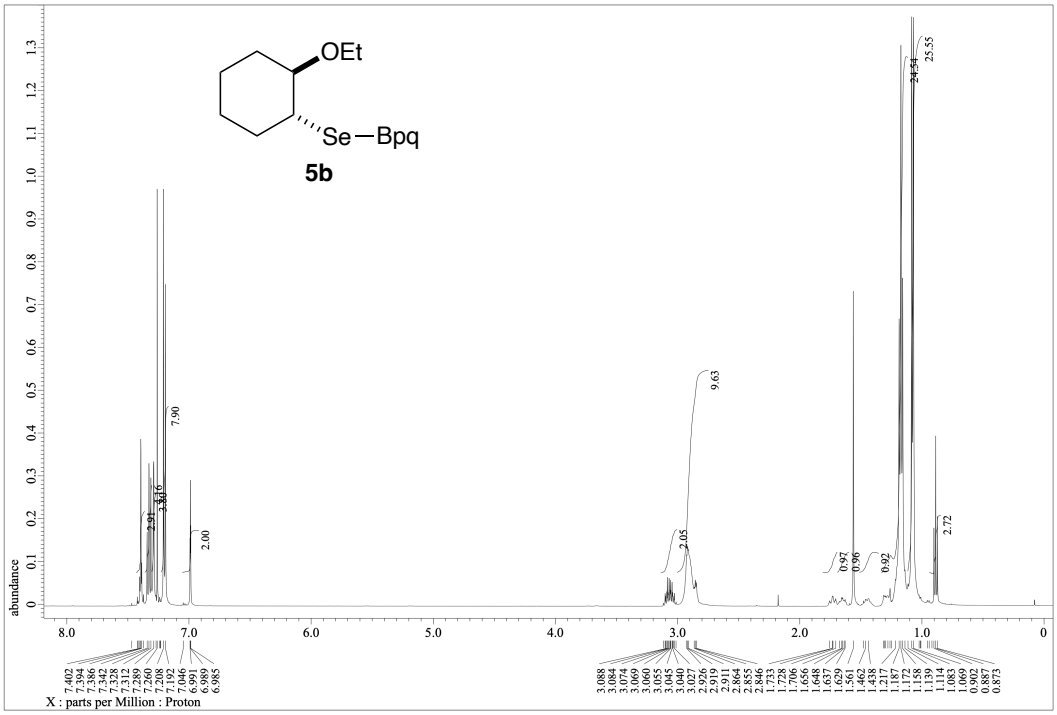


Figure S2. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5b**.

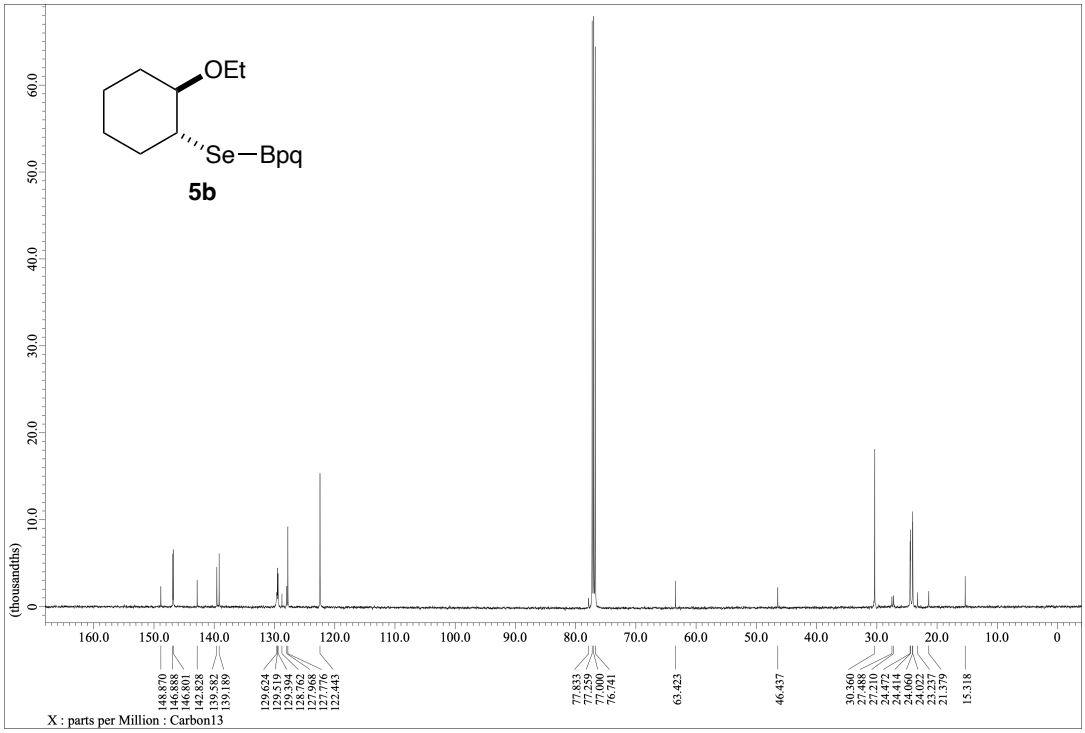


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5c**.

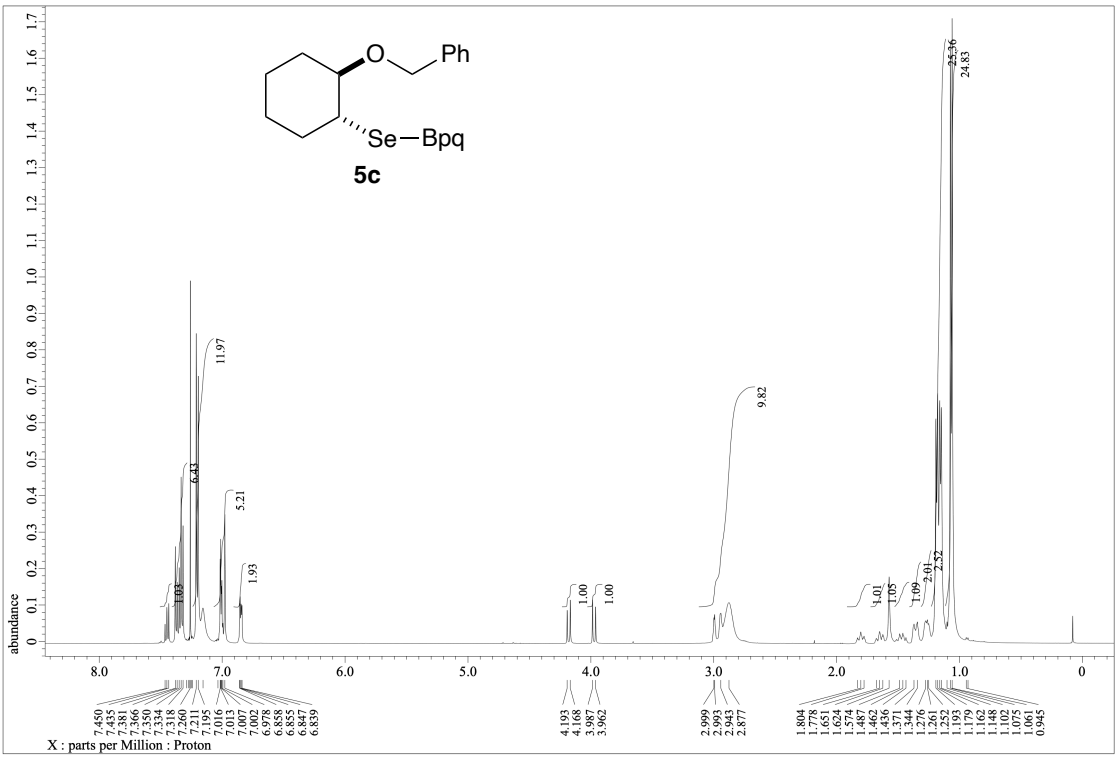


Figure S4. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5c**.

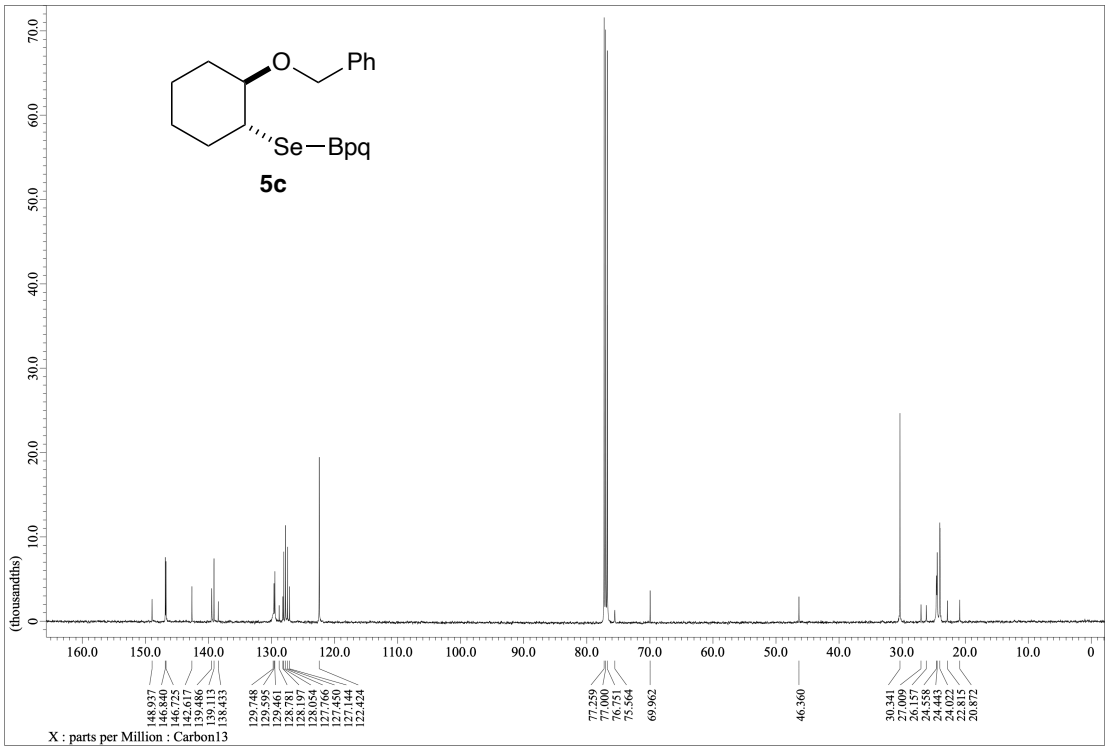


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5d**.

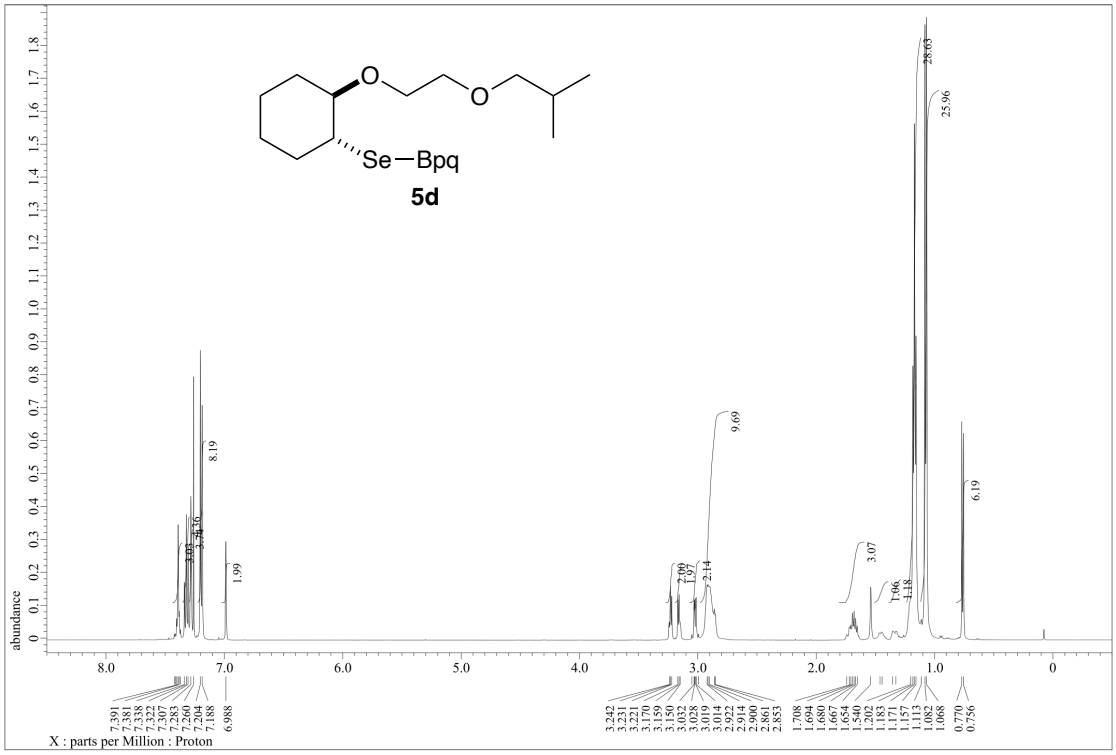


Figure S6. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5d**.

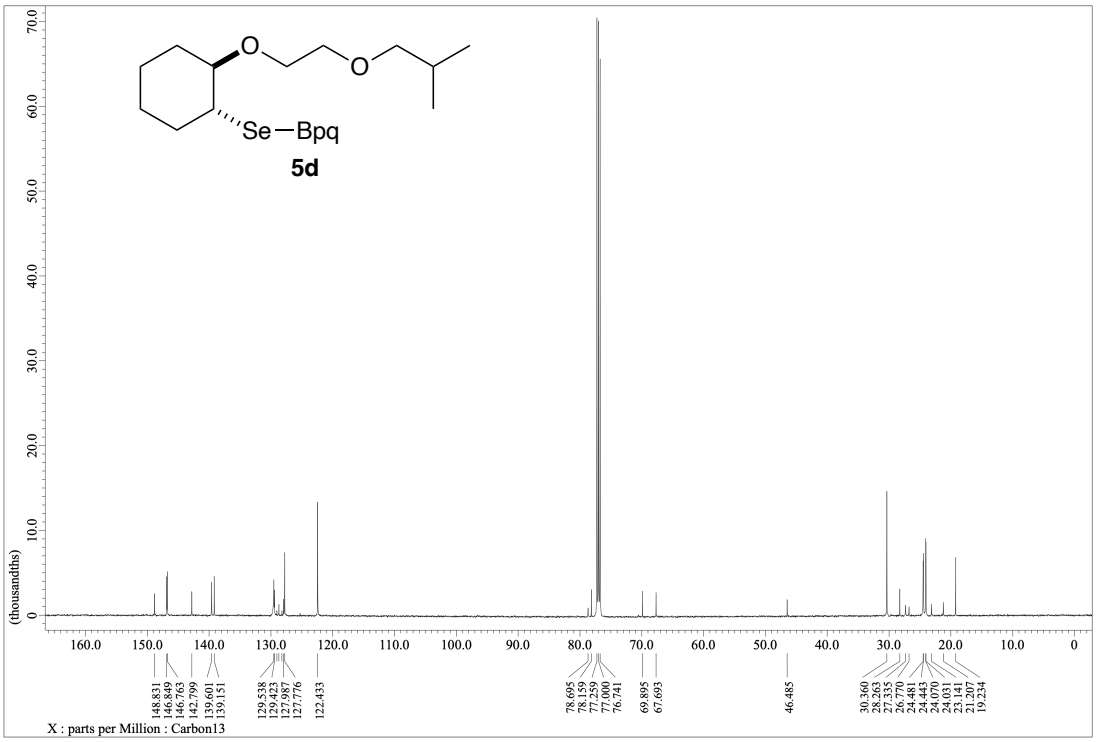


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5e**.

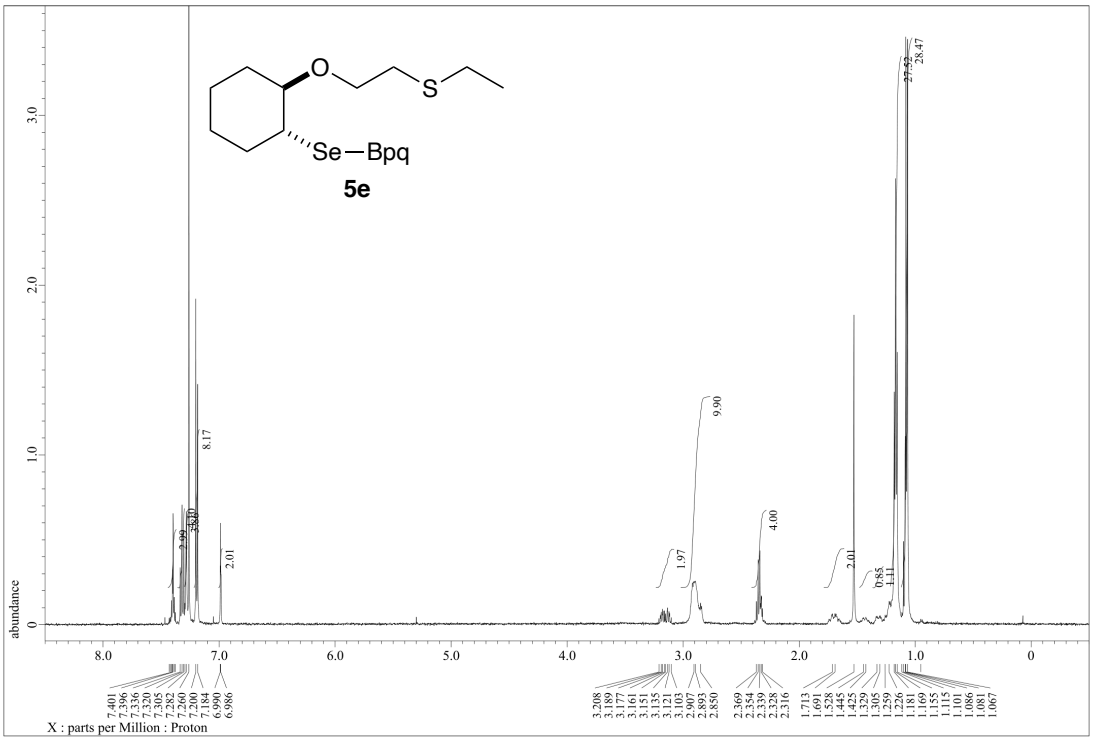


Figure S8. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5e**.

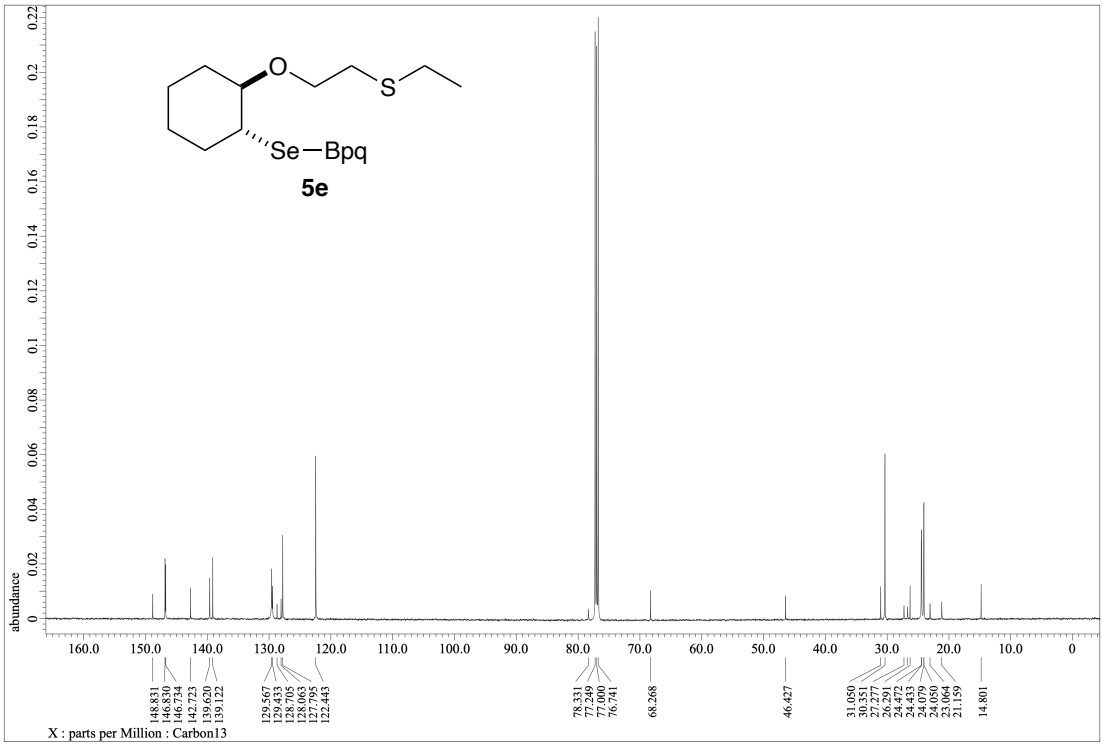


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5f**.

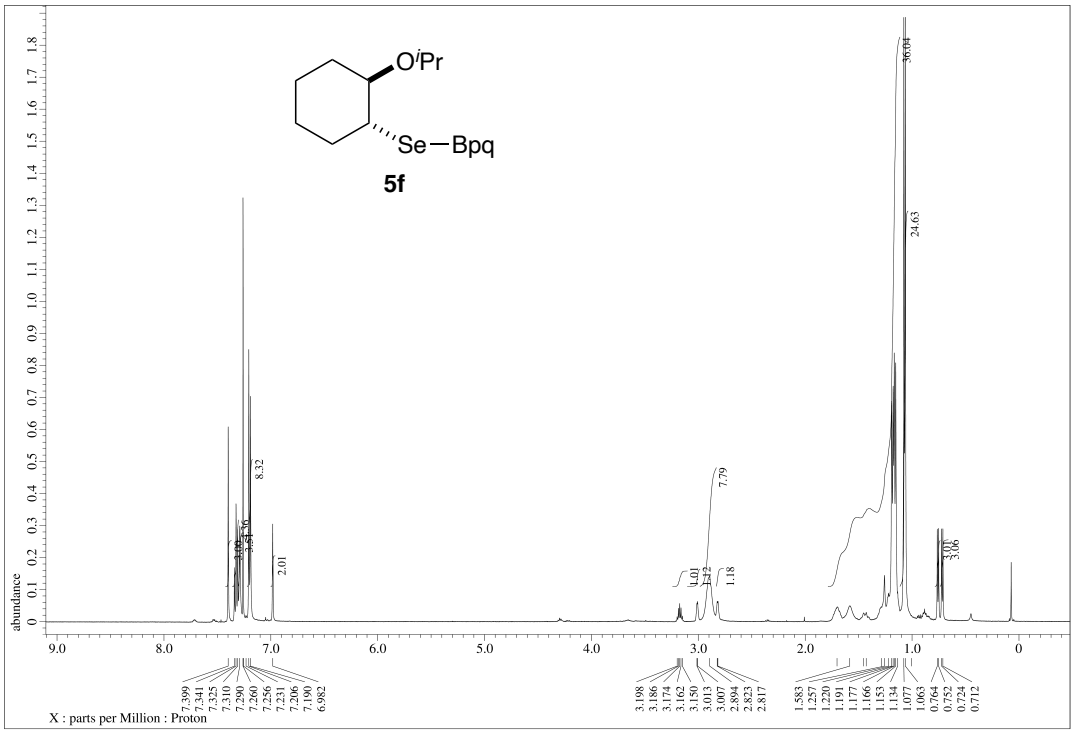


Figure S10. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5f**.

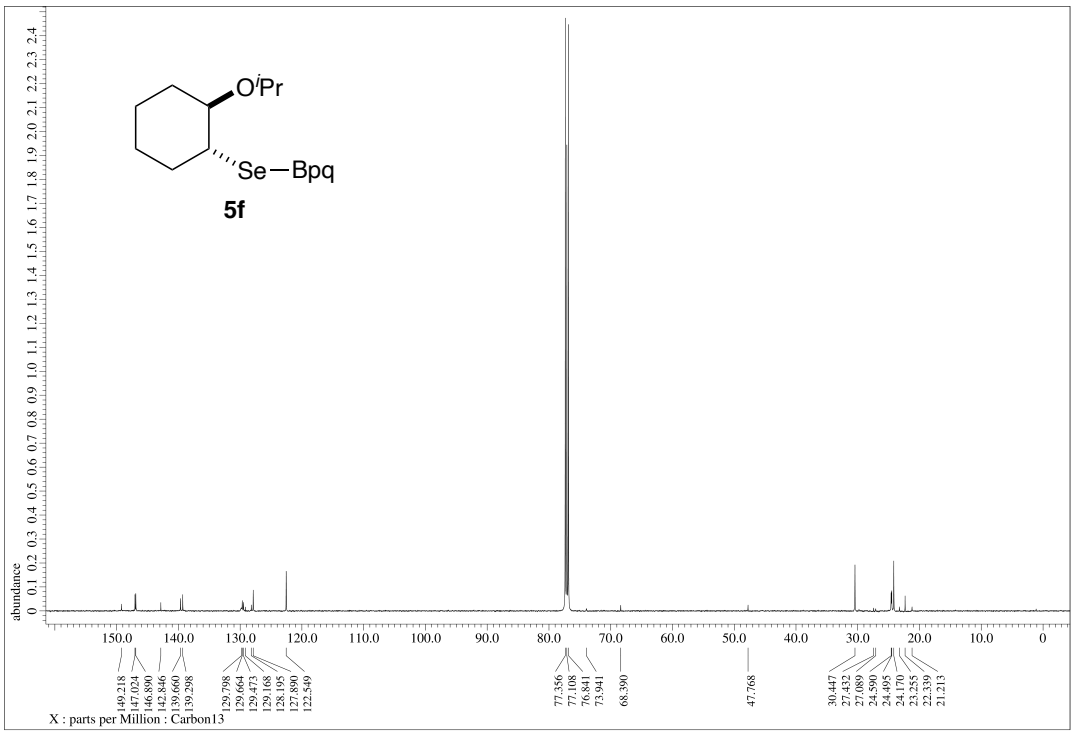


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5g**.

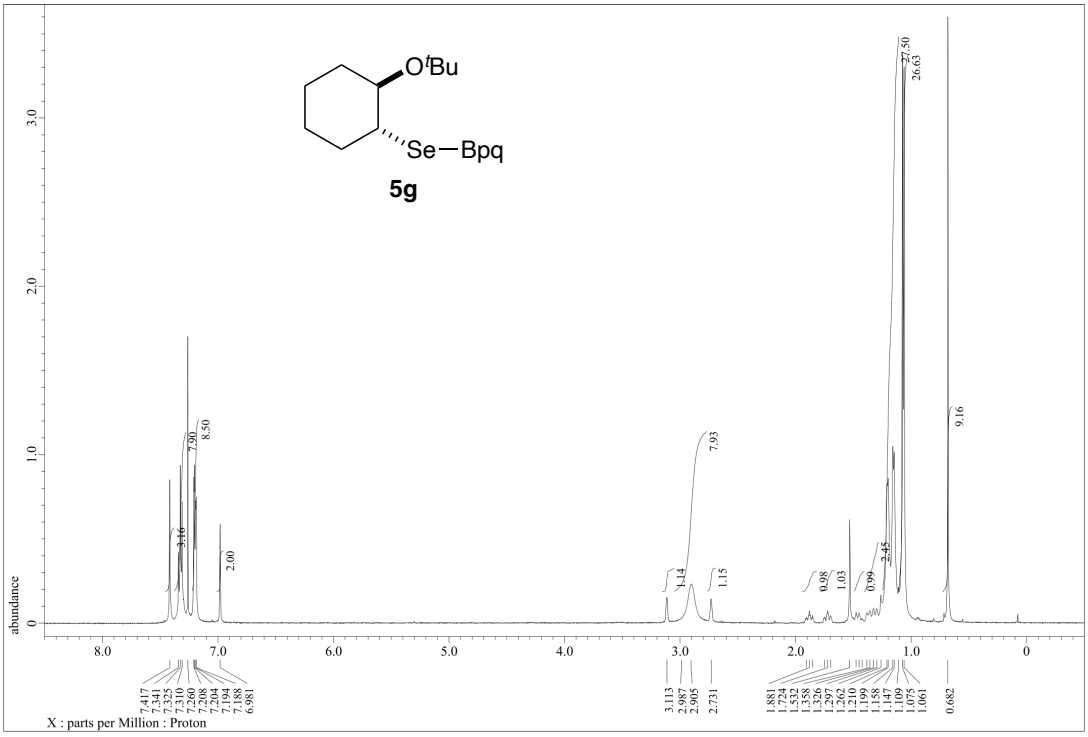


Figure S12. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5g**.

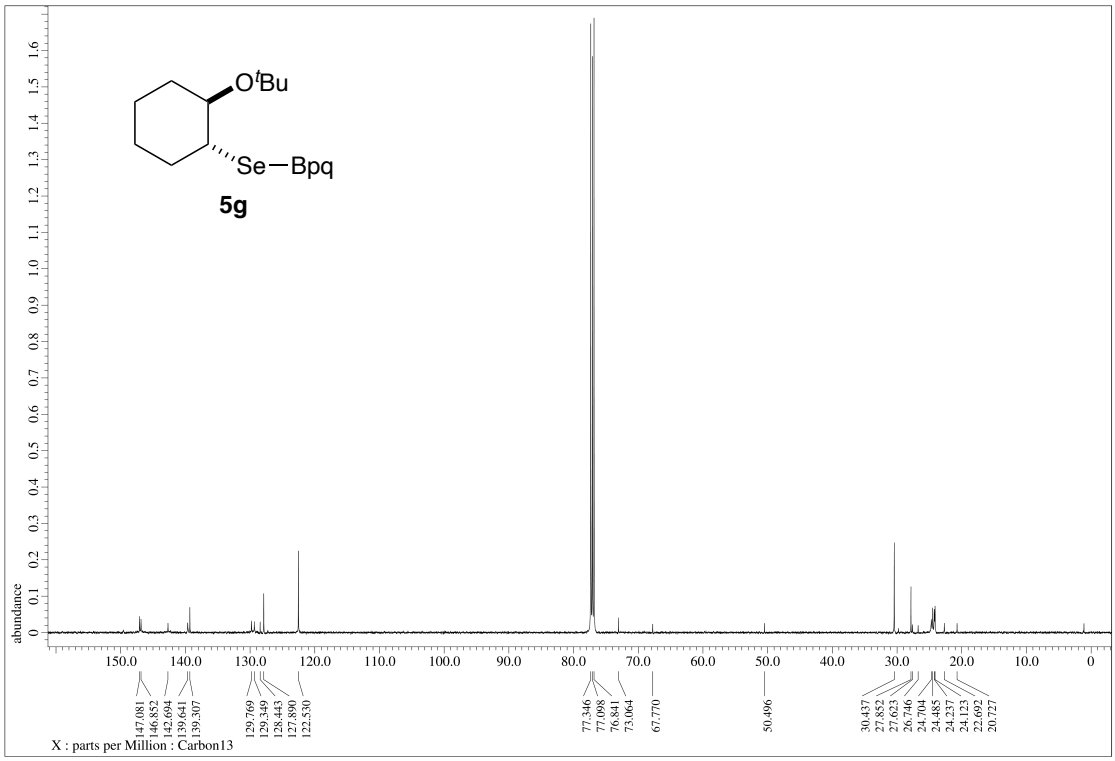


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5h**.

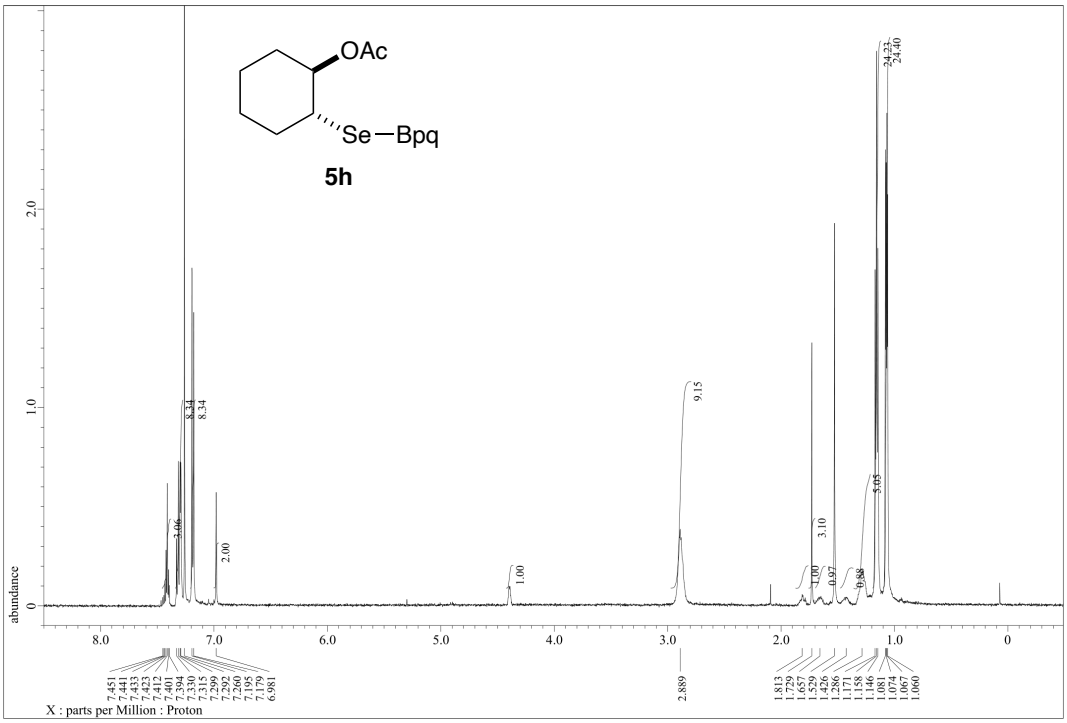


Figure S14. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5h**.

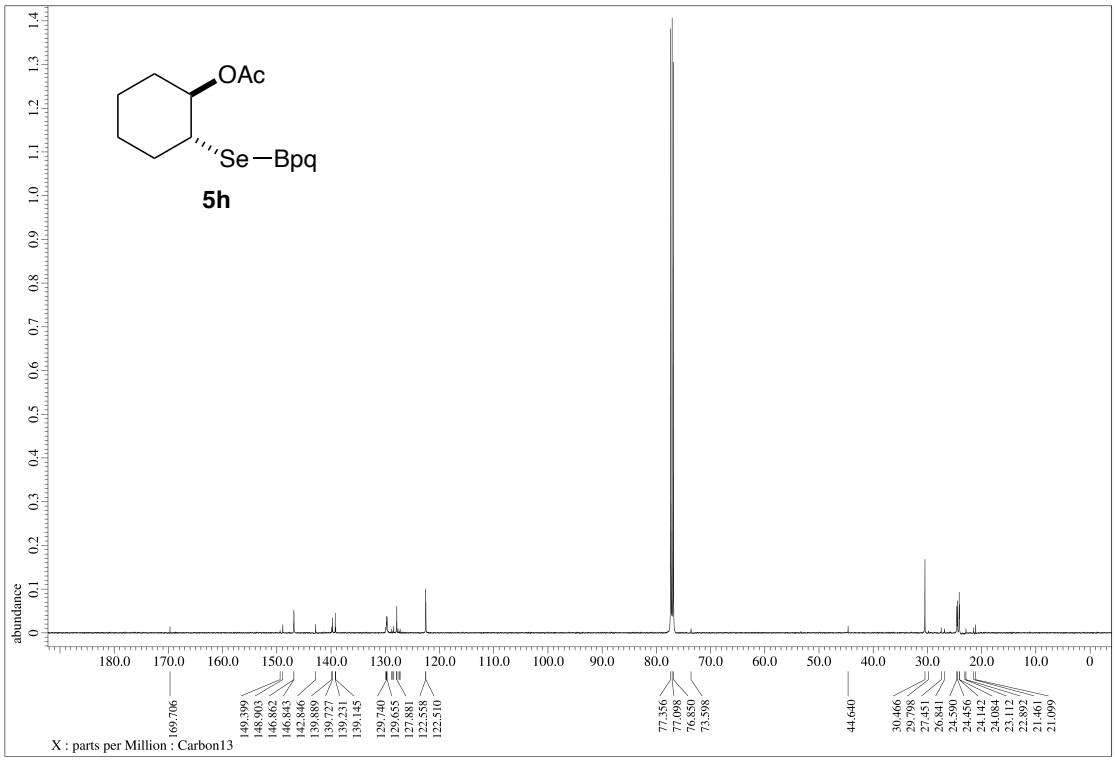


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5i**.

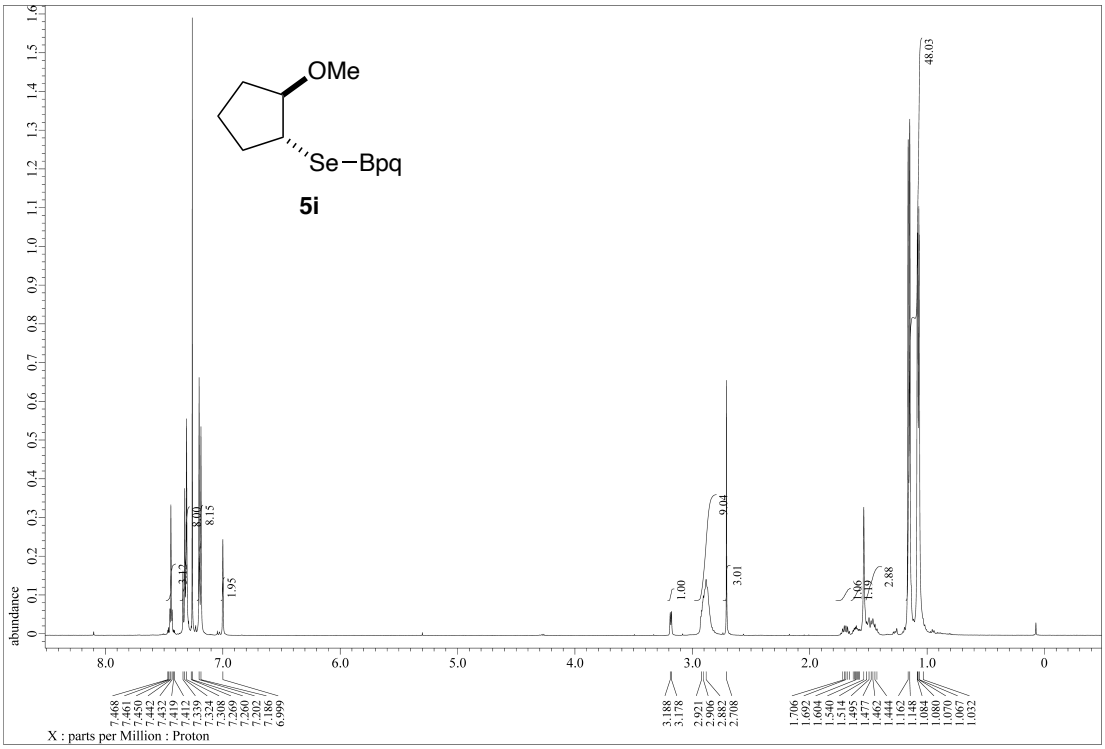


Figure S16. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5i**.

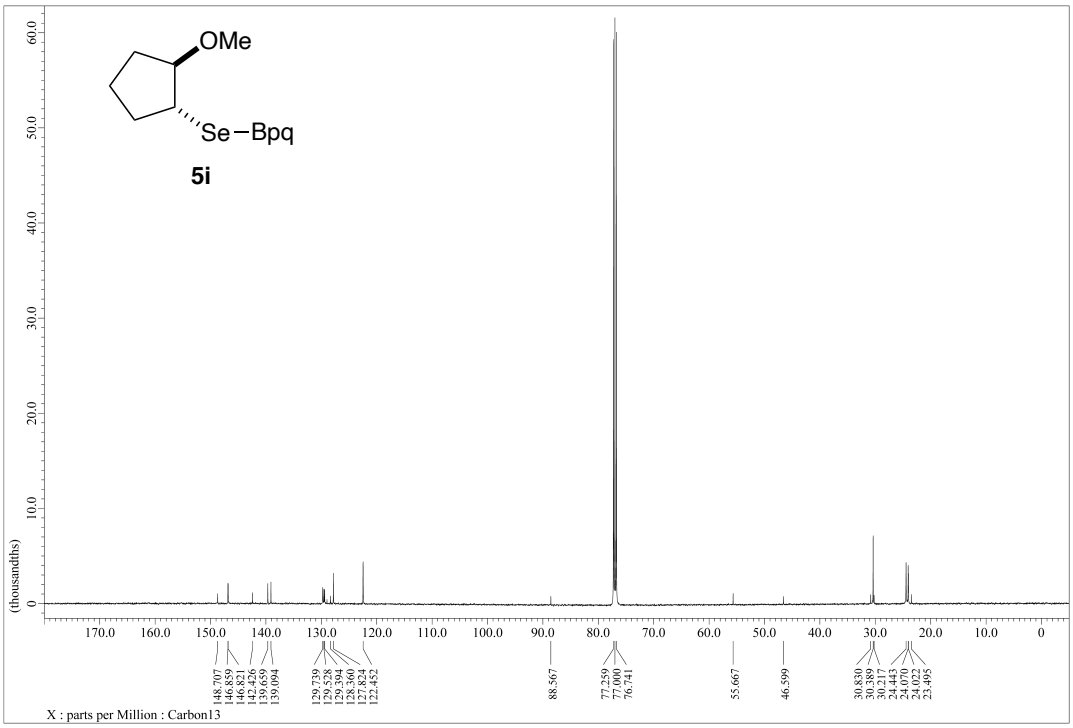


Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5j**.

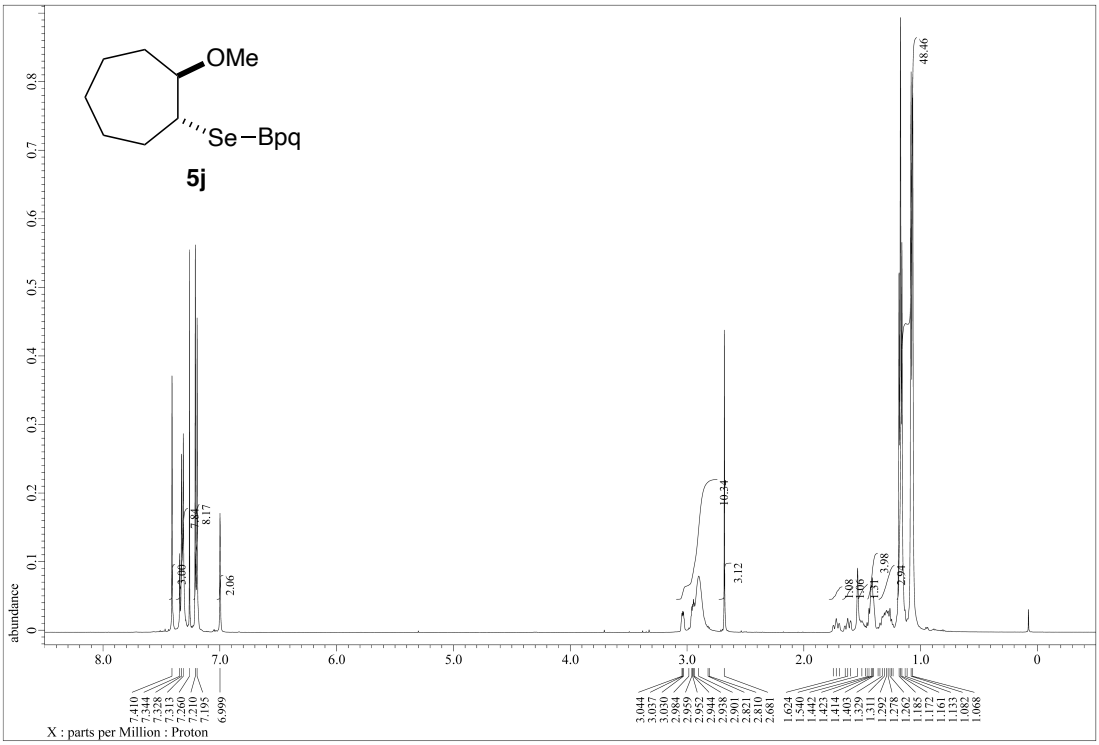


Figure S18. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5j**.

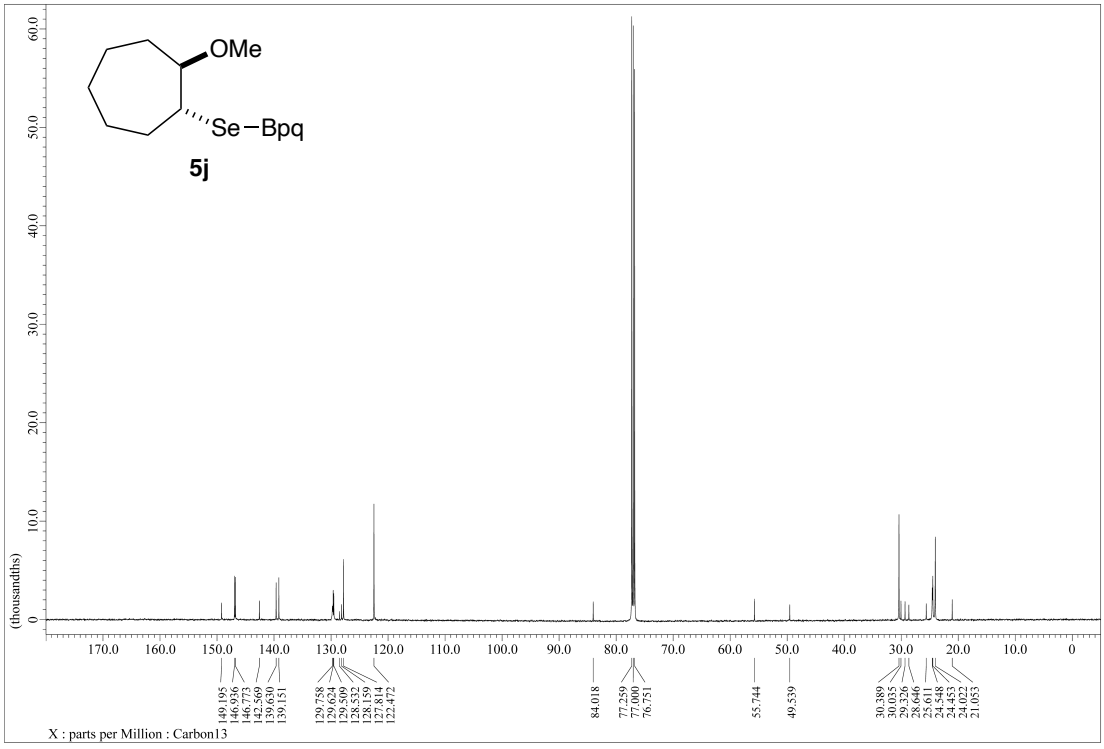


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5k**.

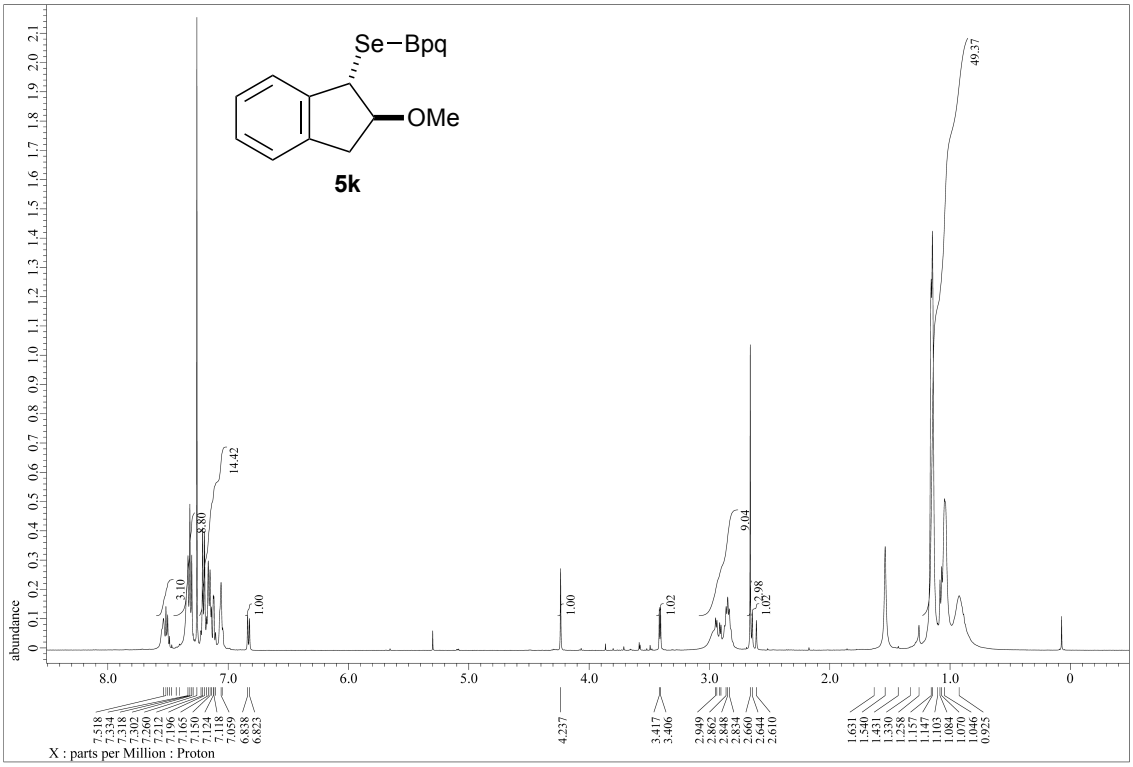


Figure S20. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **5k**.

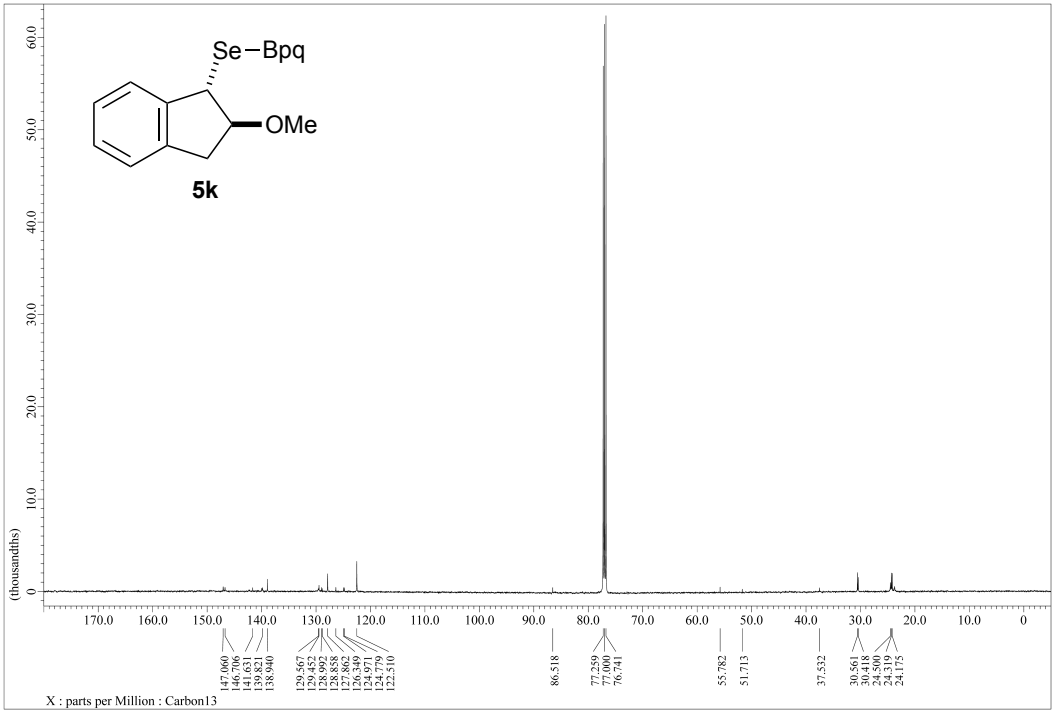


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7**.

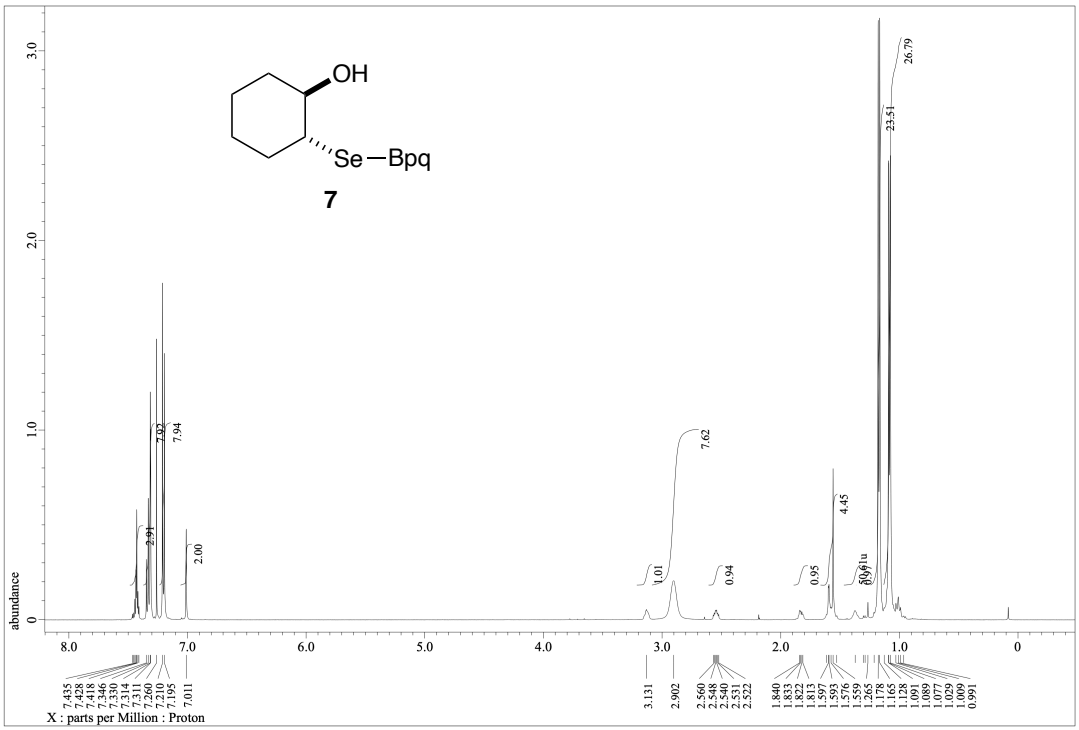


Figure S22. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **7**.

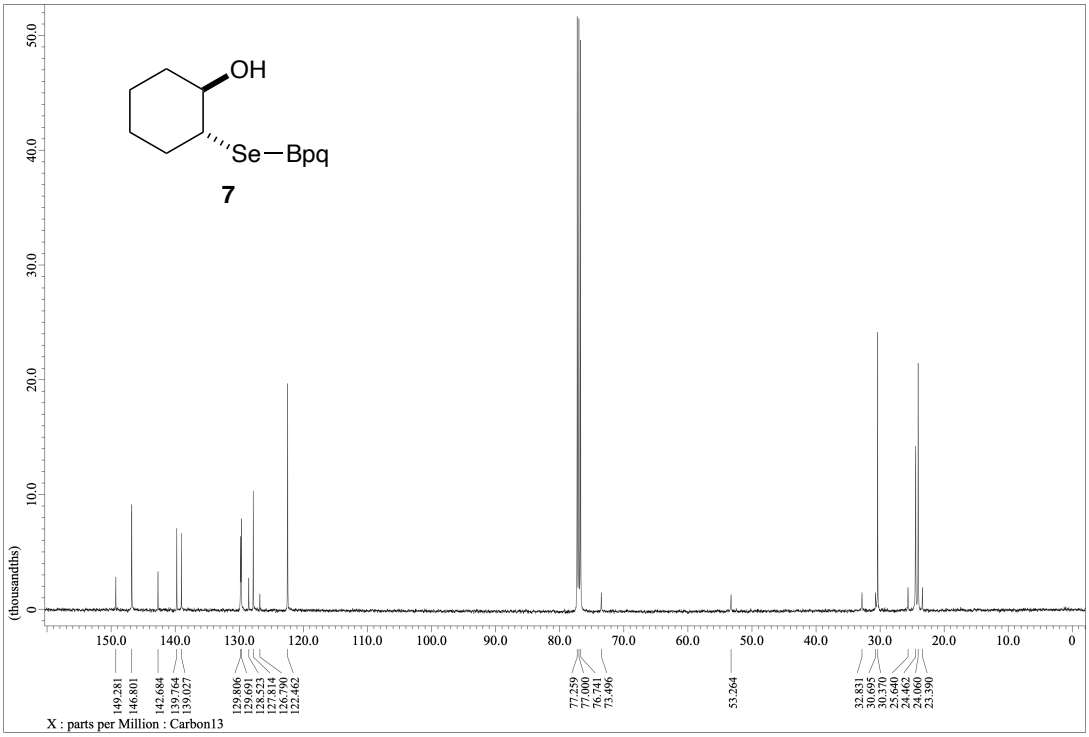


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10a**.

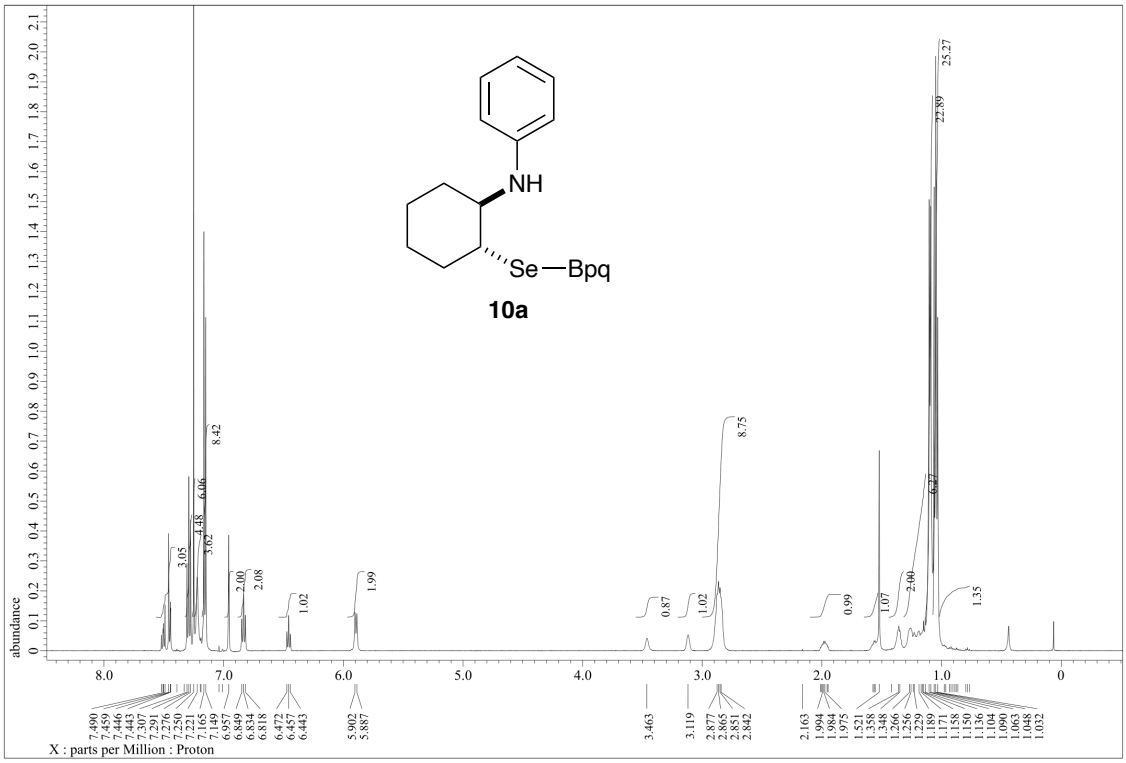


Figure S24. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10a**.

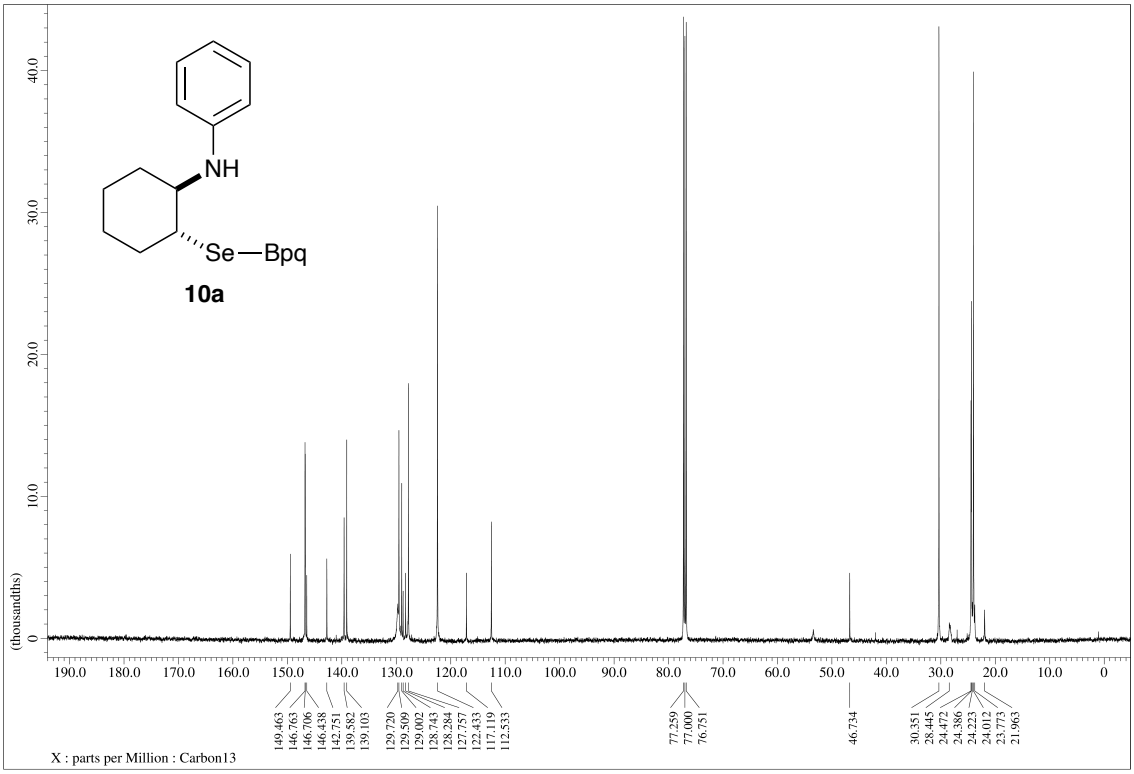


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10b**.

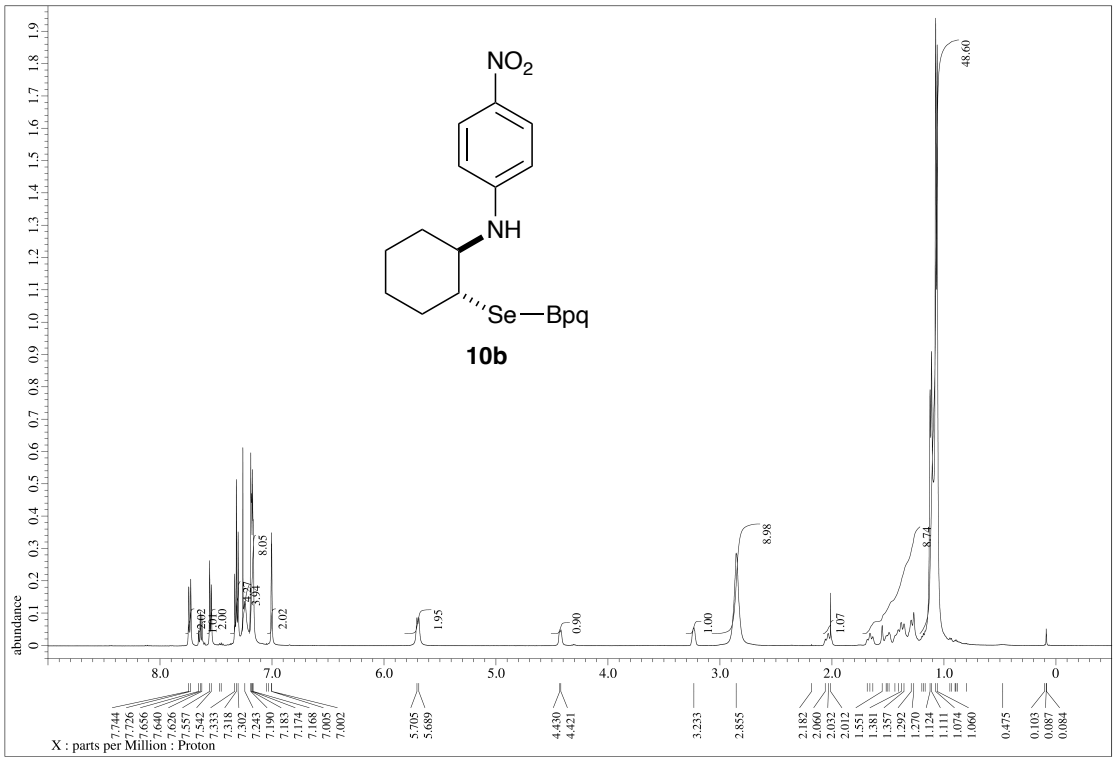


Figure S26. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10b**.

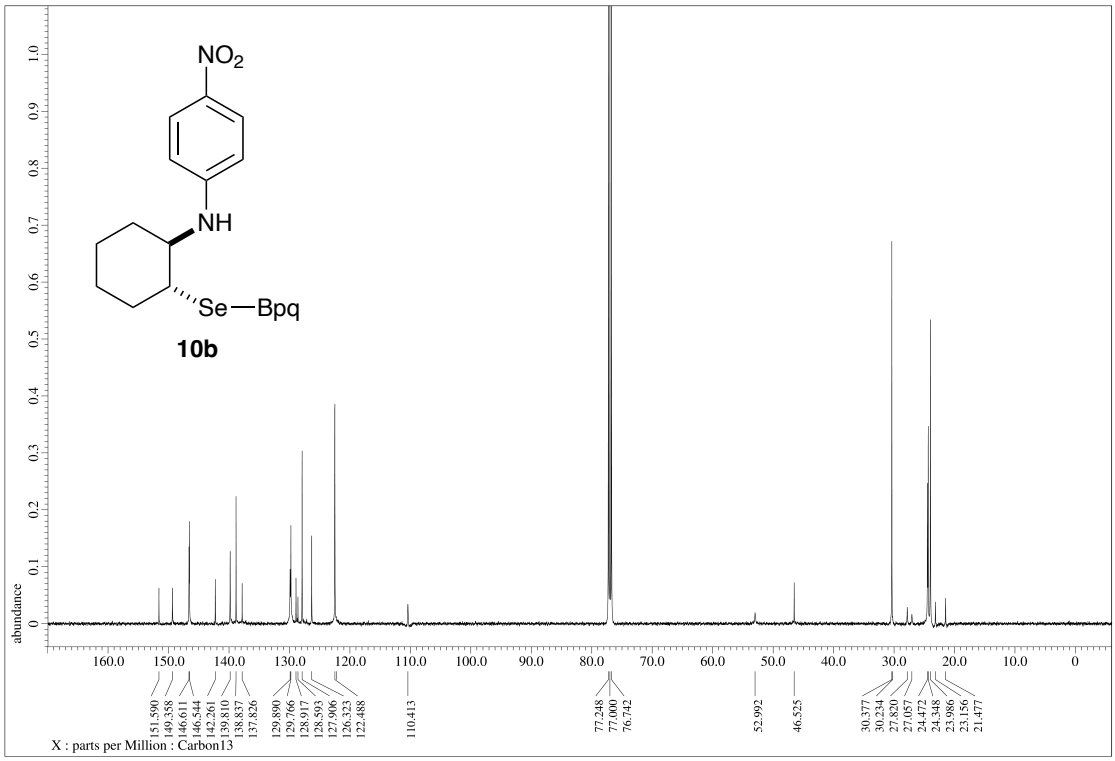


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10c**.

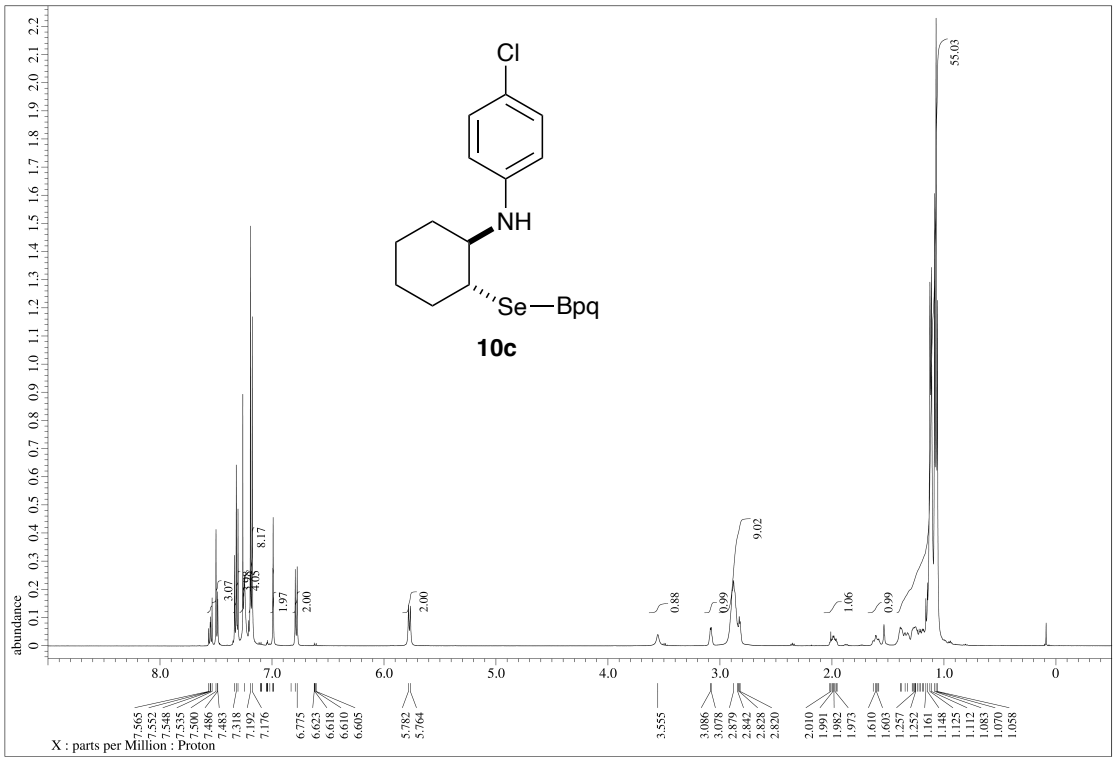


Figure S28. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10c**.

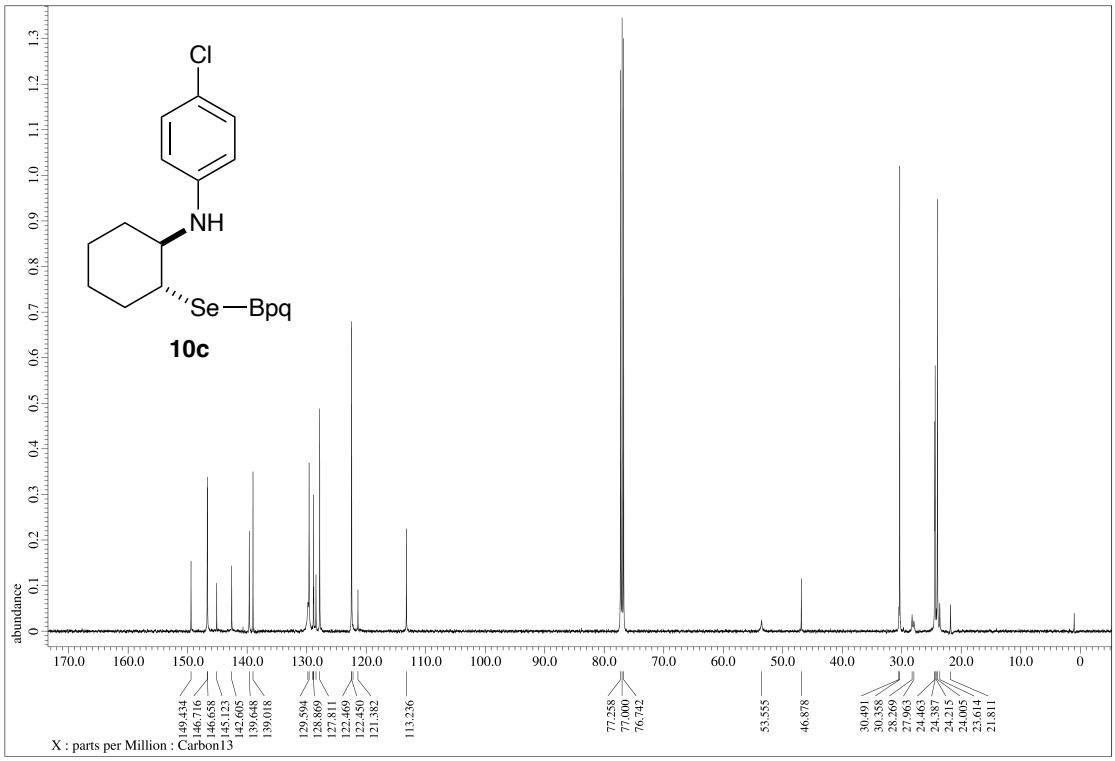


Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10d**.

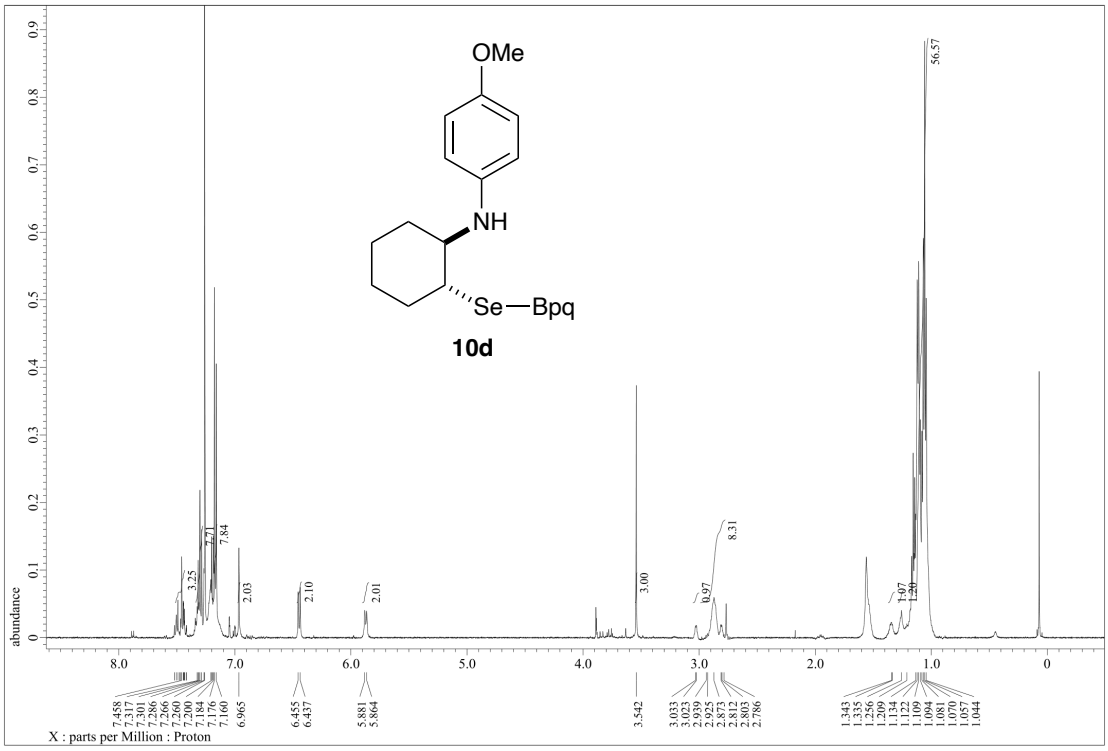


Figure S30. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10d**.

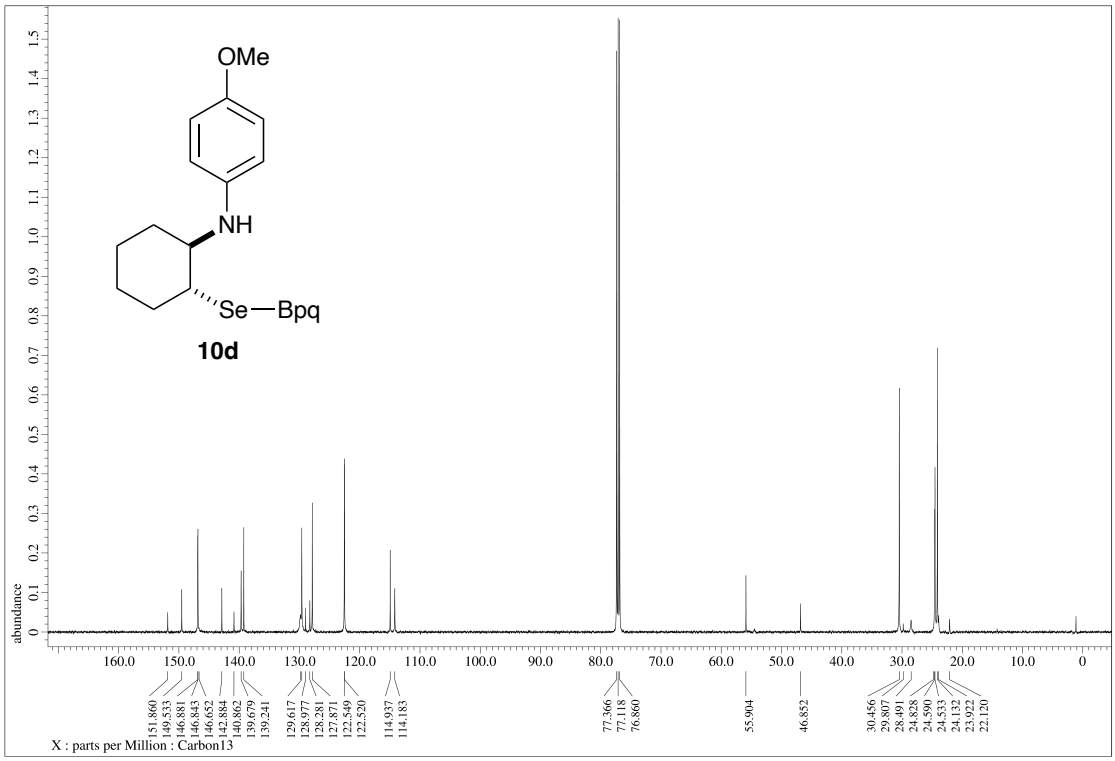


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10e**.

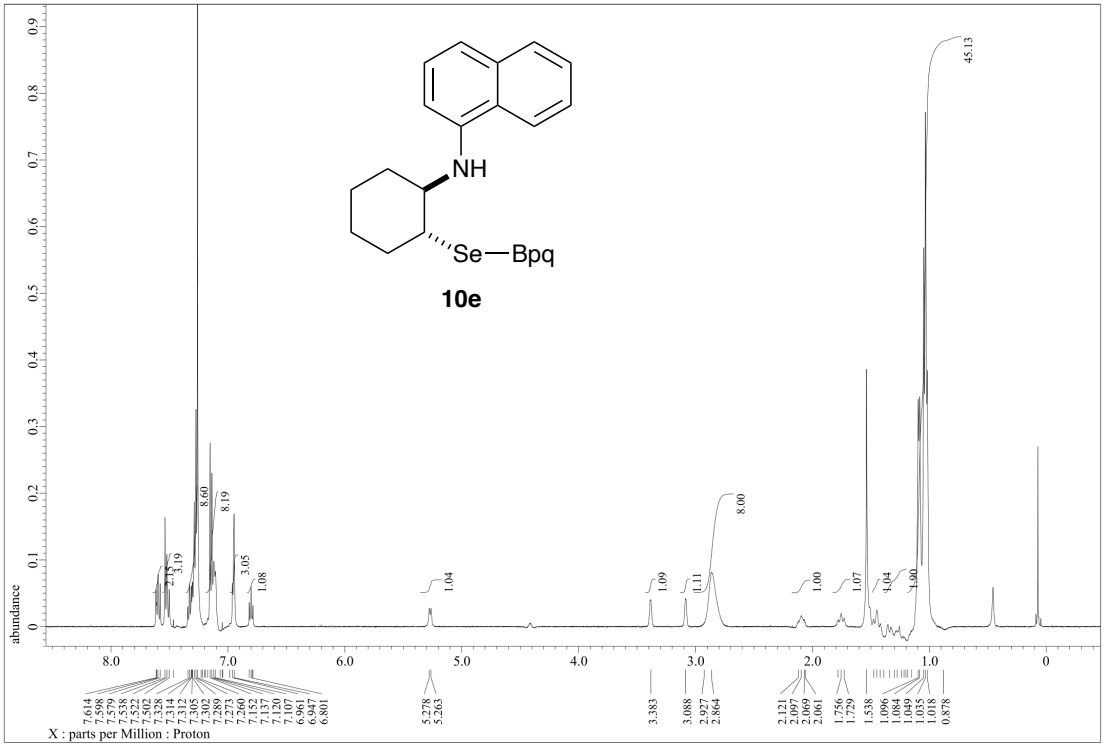


Figure S32. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10e**.

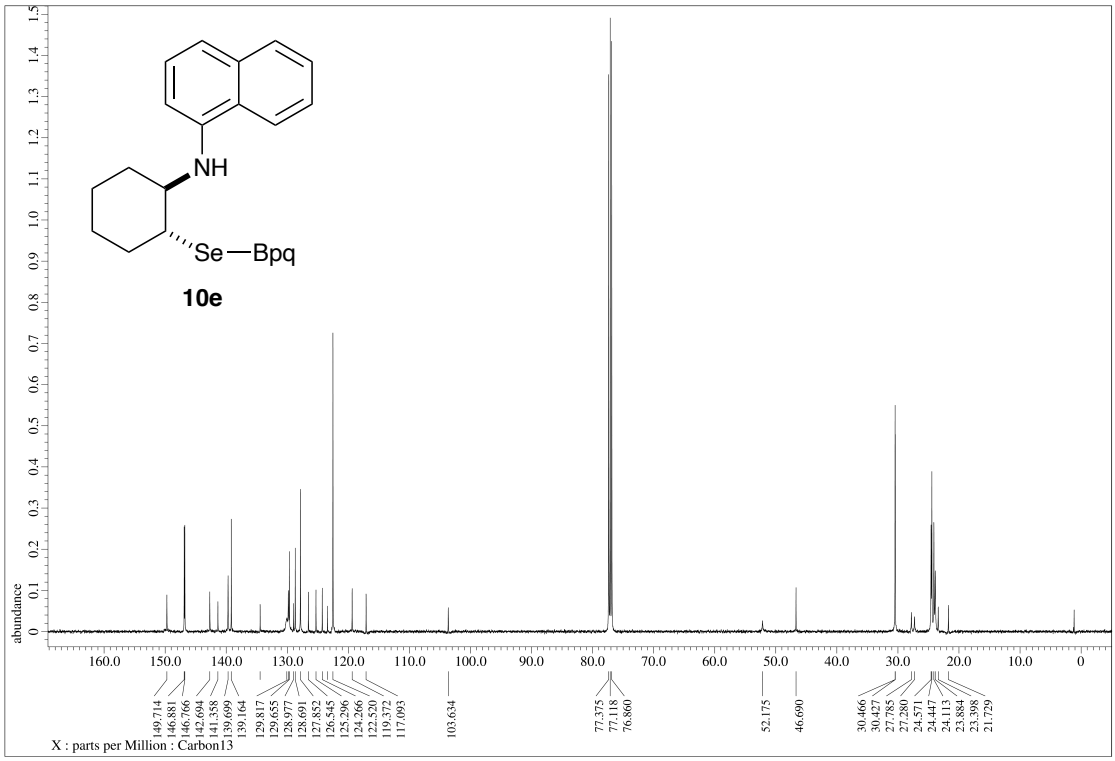


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10f**.

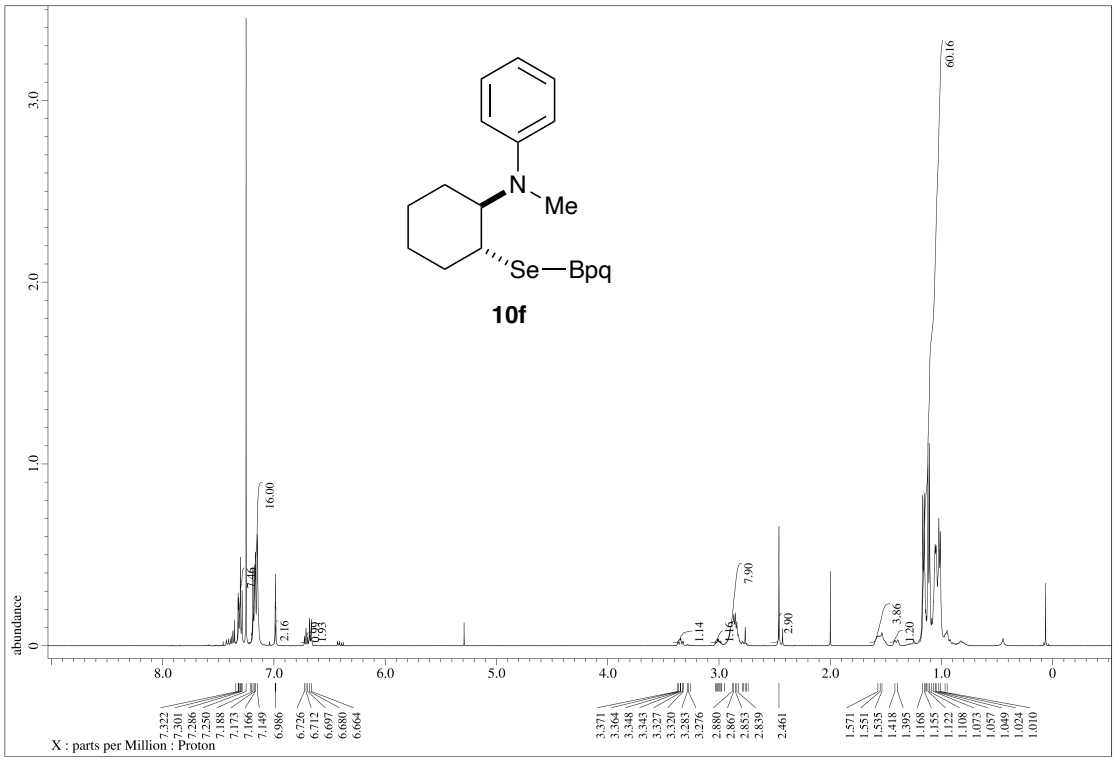


Figure S34. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10f**.

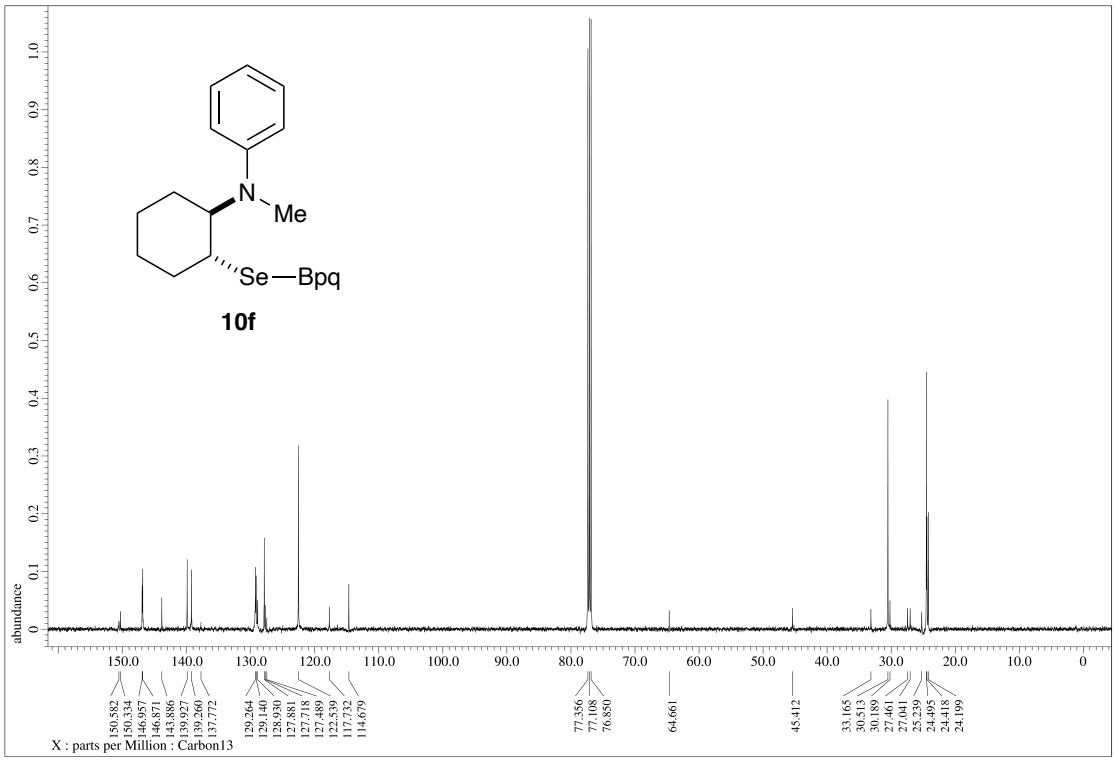


Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10h**.

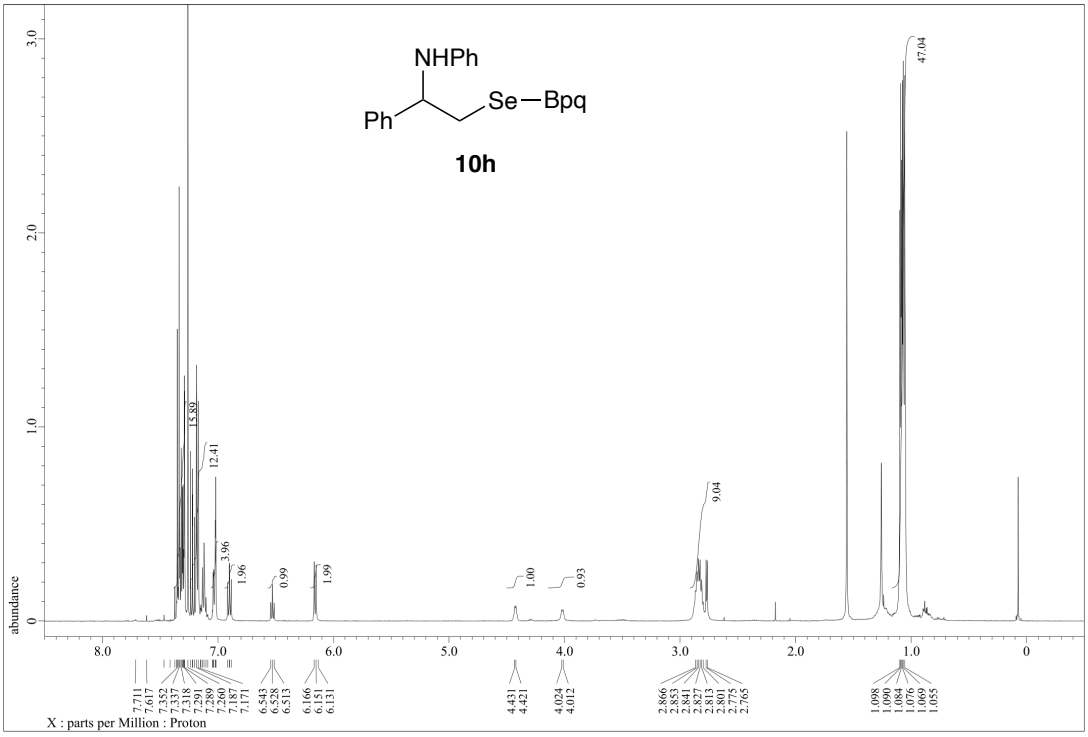


Figure S36. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10h**.