

Supporting Information

**A Stable Bis(methylene)- λ^4 -selane with a $>\text{C}=\text{Se}=\text{C}<$
bond containing Se(IV)**

Table of Contents

General Procedure	2
NMR Spectroscopic Analysis	3
X-ray Crystallographic Analysis of 1, 12, 13, and 14	12
Computational Details	15
Kinetic Experiment	16
Electrochemical experiments	17
References	18

General Procedure

Unless otherwise noted, all experiments were performed under an argon atmosphere. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in CDCl_3 and $\text{C}_6\text{D}_5\text{CD}_3$ on a JEOL JNM ECS-400SS spectrometer. A signal arising from residual CHCl_3 (7.26 ppm) in benzene- d_6 and $\text{C}_6\text{D}_5\text{CD}_2\text{H}$ (2.08 ppm) in toluene- d_8 were used as an internal standard for the ^1H NMR spectra, respectively, and that of CDCl_3 (77.26 ppm) and $\text{C}_6\text{D}_5\text{CD}_3$ (20.43 ppm) for the ^{13}C NMR spectra. ^{29}Si NMR (79 MHz) spectra were measured in C_6D_6 using $\text{Si}(\text{CH}_3)_4$ (0 ppm) as an external standard. ^{77}Se NMR (76 MHz) spectra were measured in C_6D_6 using Me_2Se (0 ppm) as an external standard.

High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-T100LP (ESI) mass spectrometer. All melting points were measured on a SMP-300CT capillary melting point apparatus and are uncorrected.

Synthesis of Bis(methylene)- λ^4 -selane (1): A THF solution (6 mL) of (MePh₂Si)₂CBr₂ (572 mg, 1.01 mmol) at -78 °C was treated dropwise with *t*-BuLi (1.64 M in pentane, 1.21 mL, 2.00 mmol) under vigorous stirring. After stirring for 5 min at this temperature, selenium powder (36 mg, 0.46 mmol) was added and the reaction mixture was allowed to warm to room temperature, where stirring was continued for 1 h. Subsequently, all volatiles were removed under reduced pressure, and the residue was dissolved in CH₂Cl₂ and filtered through Celite®. The filtrate was evaporated to dryness, and the residue was re-precipitated from CH₃CN to afford **1** as a purple solid (265 mg, 0.30 mmol, 59 %). mp. 130 °C (dec.); ¹H NMR (400 MHz, toluene-*d*₈, 298 K) δ 0.42 (brs, 12H), 7.0–7.2 (m, 24H, Ar-H), 7.3–7.5 (m, 16H, Ar-H); ¹³C NMR (100 MHz, toluene-*d*₈, 298 K), δ -0.24 , 127.9, 129.2, 135.8, 138.2, 166.7 (¹*J*_{Se-C} = 215 Hz, ¹*J*_{Si-C} = 51 Hz, >C=Se); ²⁹Si NMR (79 MHz, toluene-*d*₈, 298 K), δ -11.1 ; ⁷⁷Se NMR (76 MHz, toluene-*d*₈, 298 K), δ 1501; Anal. Calcd for C, 72.69; H, 5.87; found: C, 71.16; H, 5.95; HRMS (DART) found: *m/z* = 893.2393 ([M+H]⁺). Calcd for C₅₄H₅₂SSi₄ 893.2397 ([M+H]⁺). UV-vis (toluene): λ = 523 nm (ϵ 6,700).

Reaction of 1 with HCl: A CH₂Cl₂ solution (10 mL) of **1** (104 mg, 0.12 mmol) at -78 °C was treated with HCl (0.8 M in dioxane, 0.60 mL, 0.12 mmol). After 30 min, all volatiles were removed under reduced pressure, and the residue was recrystallized from Et₂O to afford **12** as a colorless solid (86 mg, 0.093 mmol, 79%). HCl-adduct **12**: mp. 79 °C (dec.); ¹H NMR (400 MHz, CDCl₃, 298 K) δ -0.26 (s, 6H), 0.22 (s, 6H), 2.77 (s, 1H), 7.04 (d, 4H), 7.13(t, 4H), 7.15–7.30 (m, 16 H), 7.41 (t, 2H), 7.47 (t, 4H), 7.45–7.55 (m, 6H), 7.77 (d, 4H); ¹³C NMR (100 MHz, CDCl₃, 298 K), δ -3.55 , -1.10 , 10.6 (s, ¹*J*_{Se-C} = 90 Hz, ¹*J*_{Si-C} = 44 Hz), 52.1, 127.3, 127.3, 127.4, 127.8, 128.9, 129.0, 129.6, 129.9, 135.2, 135.4, 136.0, 136.1, 136.4, 137.1, 137.3, 137.5; ⁷⁷Se NMR (76 MHz, CDCl₃), δ 375.

Reaction of 1 with SO₂Cl₂: A CH₂Cl₂ solution (5 mL) of **1** (57 mg, 0.064 mmol) at -78 °C was treated with SO₂Cl₂ in CH₂Cl₂ (0.12 M, 0.5 mL, 0.064 mmol). After stirring for 30 min at room temperature, all volatiles were removed under reduced pressure, and the residue was recrystallized from Et₂O to afford **13** as a colorless solid (46 mg, 0.048 mmol, 75%). mp. 107 °C (dec.); ¹H NMR (400 MHz, CDCl₃) δ 0.07 (s, 12H), 7.20–7.30 (m, 16H), 7.43 (t, 8H), 7.50 (d, 8H), 7.58 (d, 8H); ¹³C NMR (100 MHz, CDCl₃) δ -2.42 , 56.4 (s, ¹*J*_{Se-C} = 134 Hz, ¹*J*_{Si-C} = 42 Hz), 127.3, 127.4, 129.4, 129.7, 135.0, 136.3, 136.6, 137.1; ⁷⁷Se NMR (76 MHz, CDCl₃), δ 621.

Reaction of 1 with Br₂: A CH₂Cl₂ solution (13 mL) of **1** (135 mg, 0.15 mmol) at -78 °C was treated with Br₂ in CH₂Cl₂ (0.10 M, 1.5 mL, 0.15 mmol). After stirring for 30 min at room temperature, all volatiles were removed under reduced pressure, and the residue was recrystallized from Et₂O to afford **14** as a colorless solid (160 mg, 0.15 mmol, 99%). mp. 128 °C (dec.); ¹H NMR (400 MHz, CDCl₃) δ 0.21 (s, 12H), 7.25-7.35 (m, 16H), 7.40-7.50 (m, 8H), 7.50-7.60 (m, 16H); ¹³C NMR (100 MHz, CDCl₃), δ -0.58, 48.6 (s, ¹J_{Se-C} = 142 Hz, ¹J_{Si-C} = 39 Hz), 127.2, 127.3, 129.3, 129.7, 135.1, 136.3, 136.8, 137.5; ⁷⁷Se NMR (76 MHz, CDCl₃), δ 511.

NMR Spectroscopic Analysis

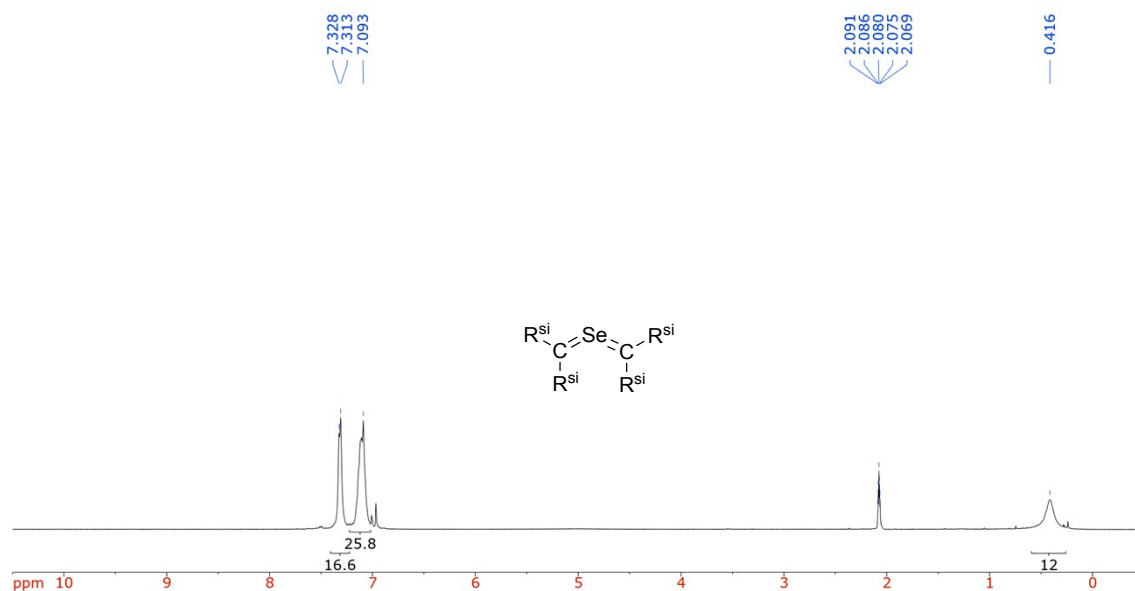


Figure S1. ^1H NMR spectrum of **1** (400 MHz, toluene- d_8 , 298 K)

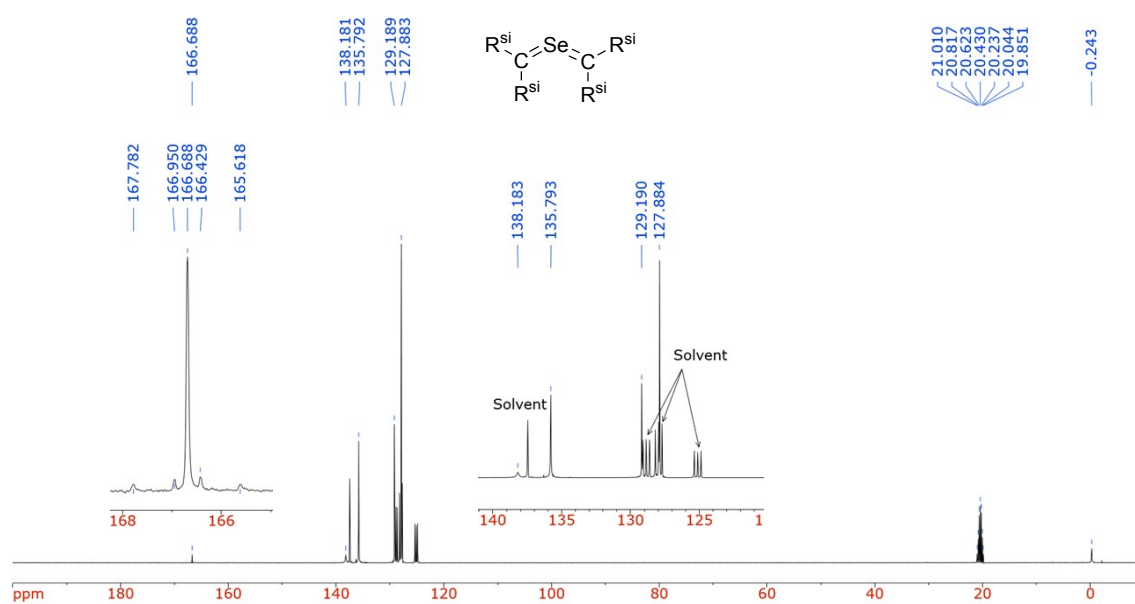


Figure S2. ^{13}C NMR spectrum of **1** (100 MHz, toluene- d_8 , 298 K)

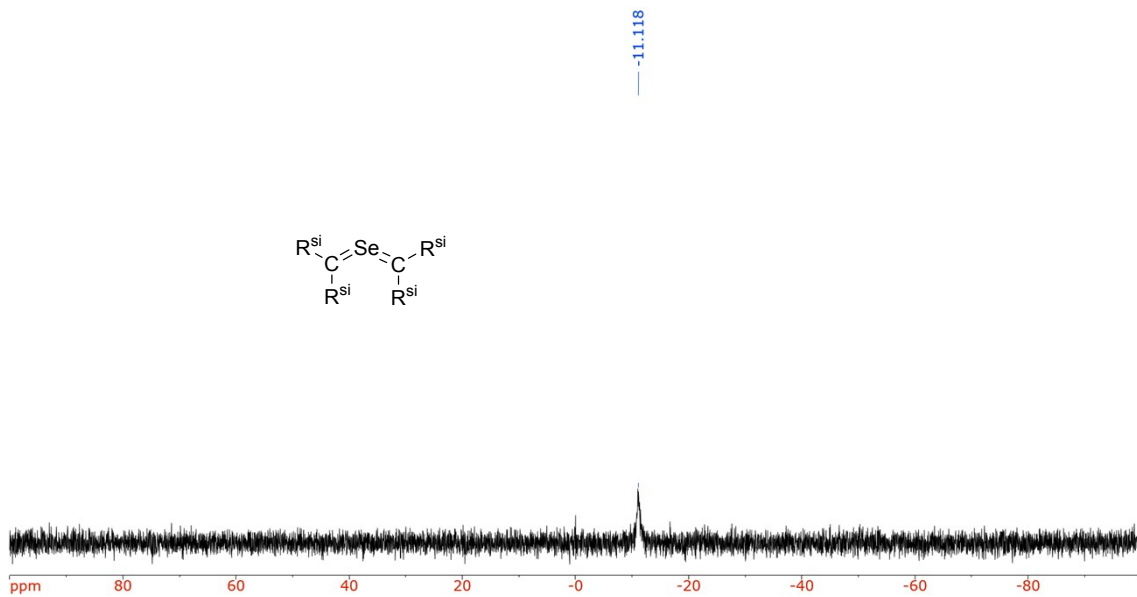


Figure S3. ^{29}Si NMR spectrum of **1** (79 MHz, toluene- d_8 , 298 K)

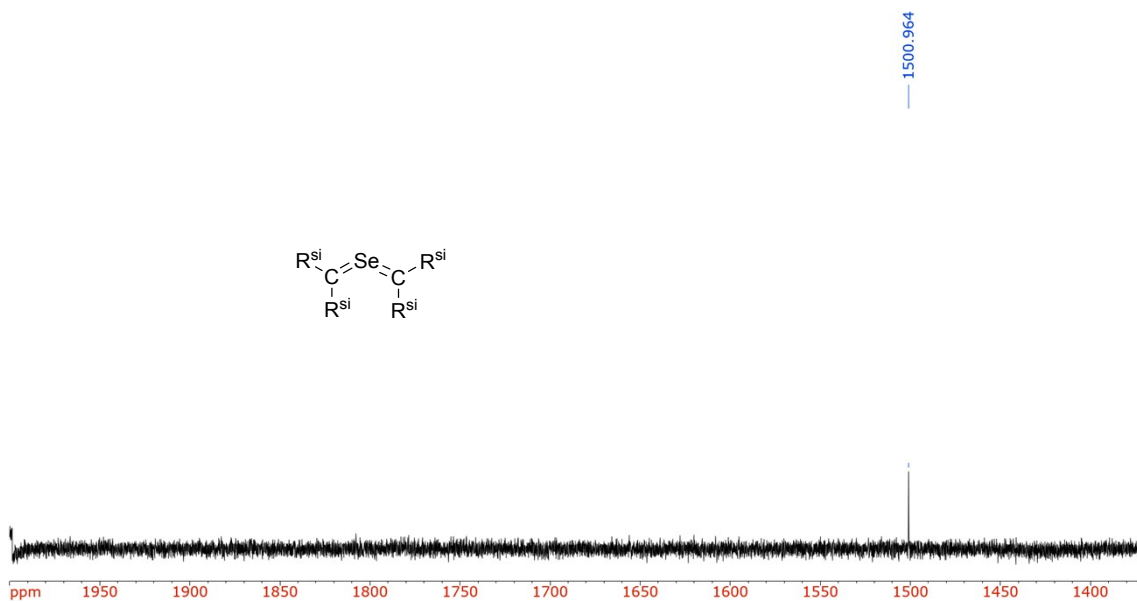


Figure S4. ^{77}Se NMR spectrum of **1** (76 MHz, toluene- d_8 , 298 K)

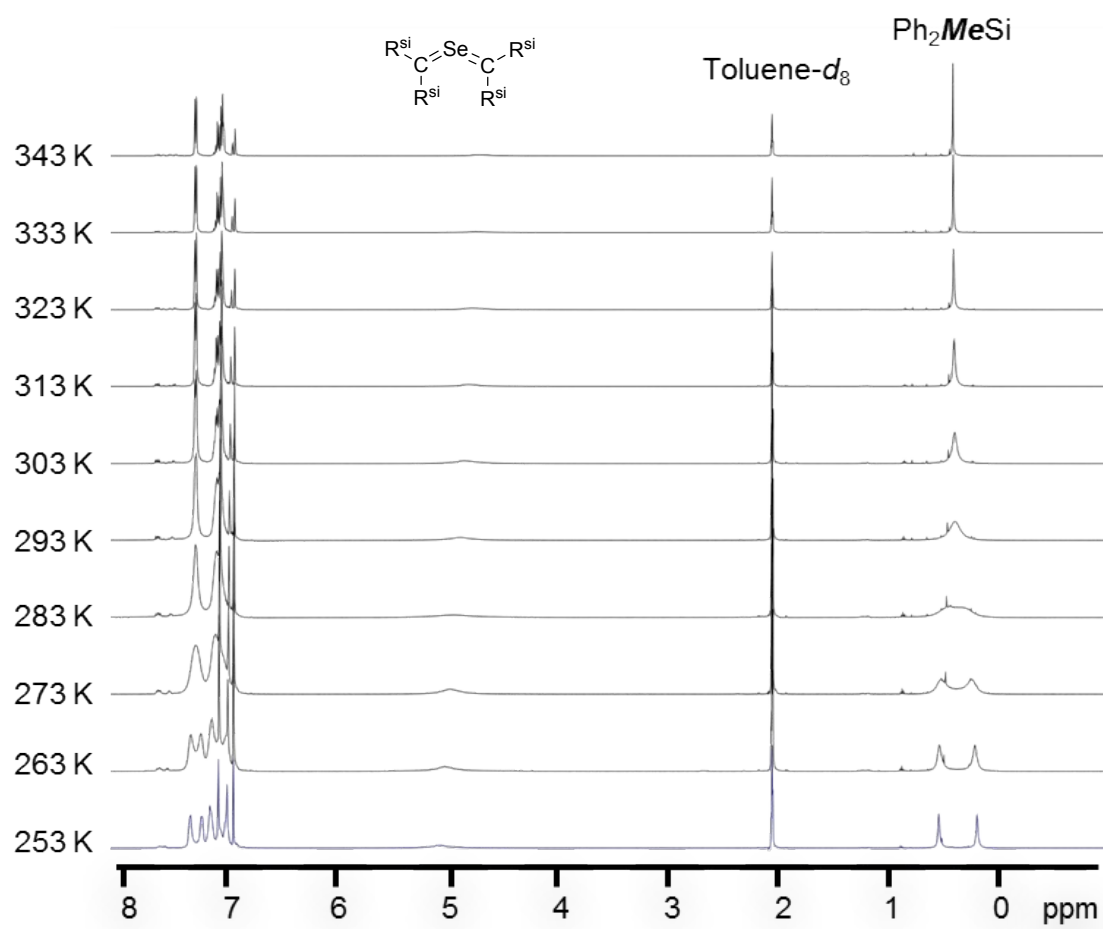
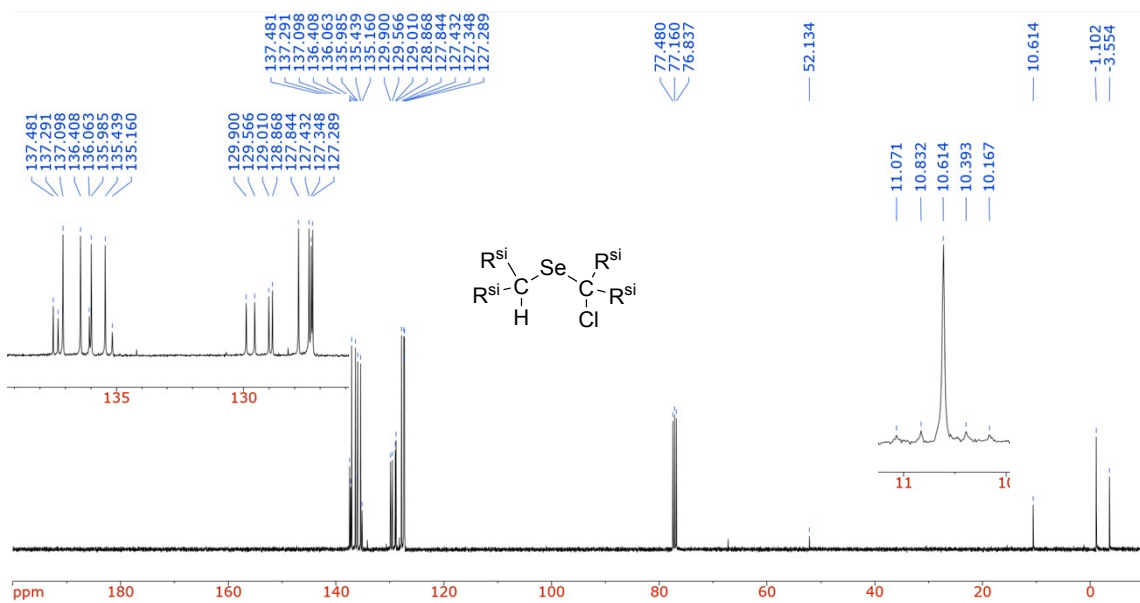
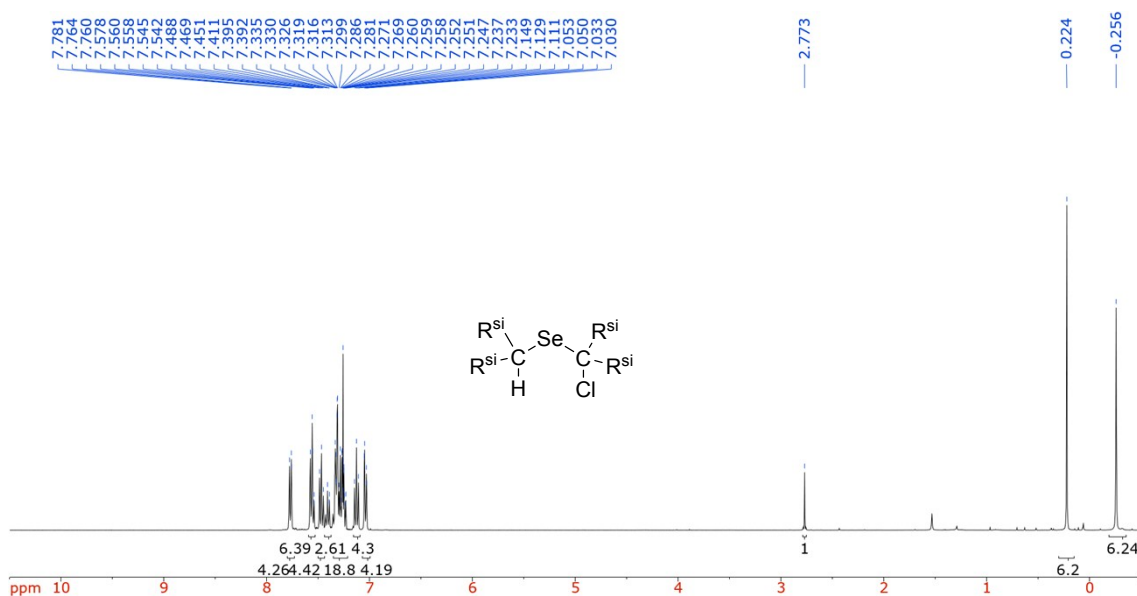


Figure S5. VT-¹H NMR spectrum for **1** in toluene- d_8 (400 MHz)



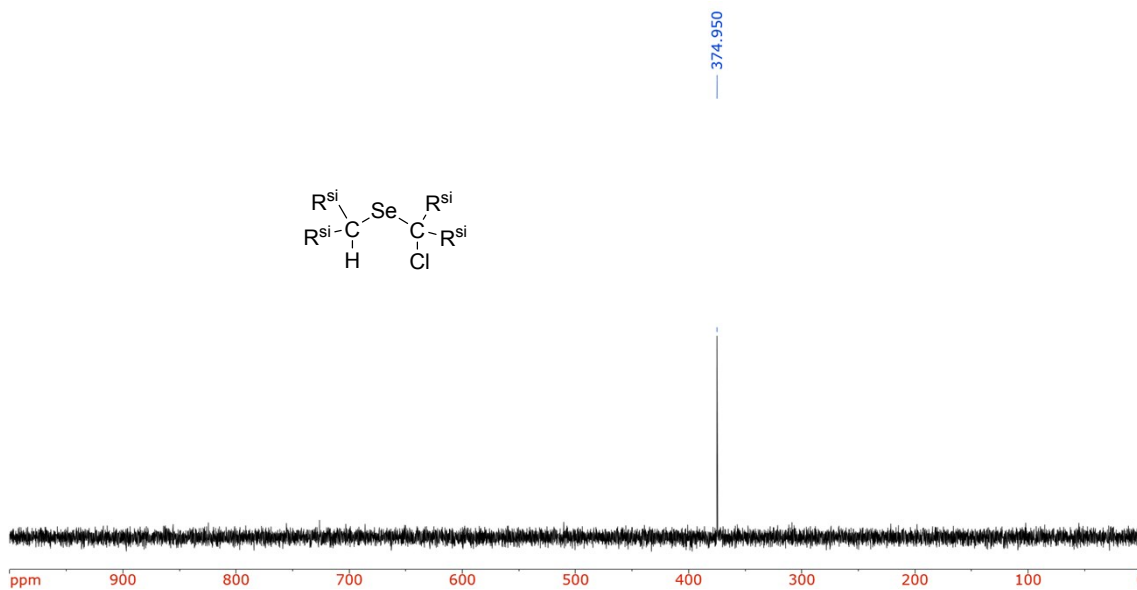


Figure S8. ^{77}Se NMR spectrum for **12** in CDCl_3 (76 MHz)

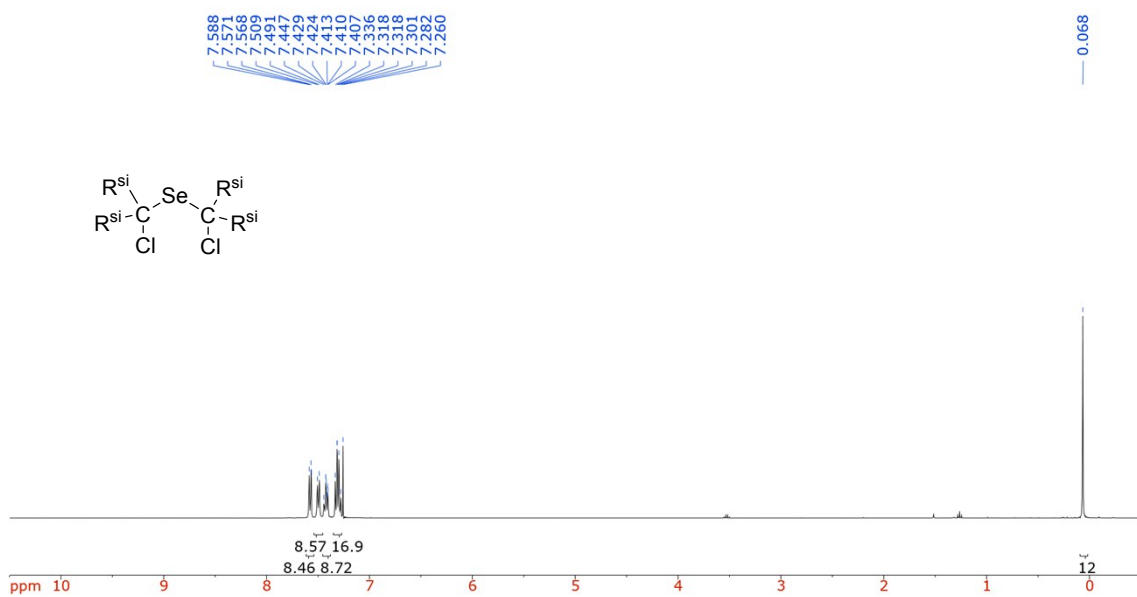


Figure S9. ^1H NMR spectrum for **13** in CDCl_3 (400 MHz)

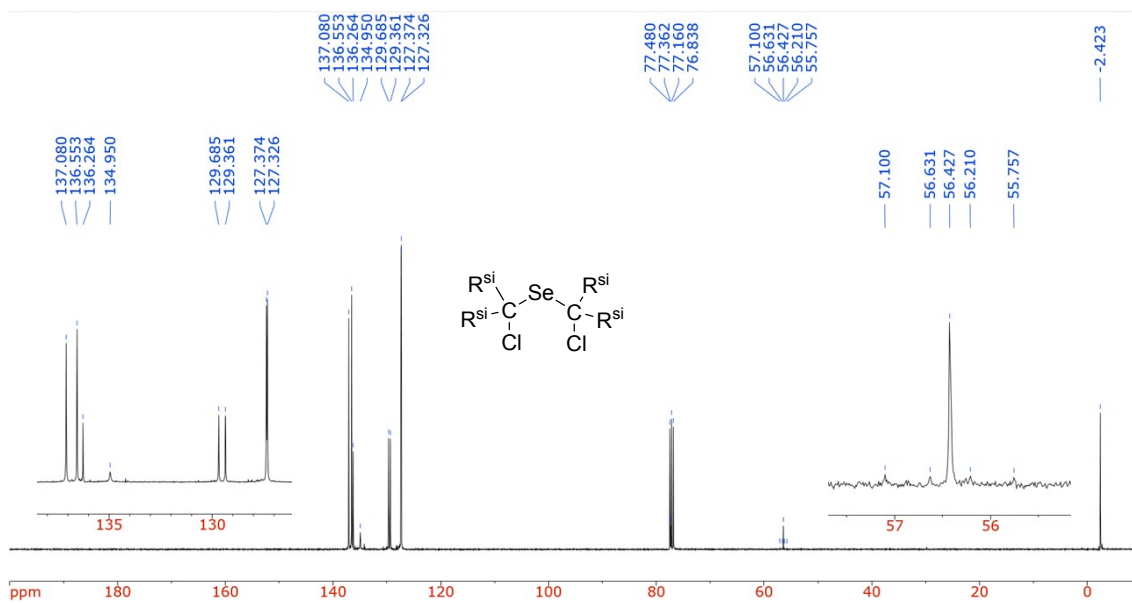


Figure S10. ^{13}C NMR spectrum for **13** in CDCl_3 (100 MHz)

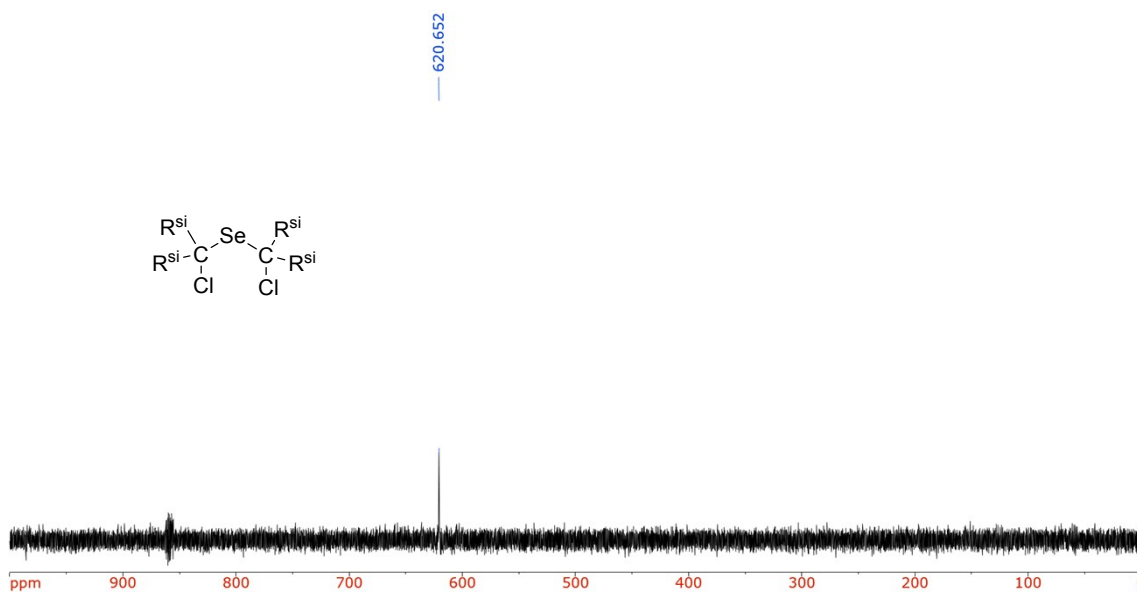


Figure S11. ^{77}Se NMR spectrum for **13** in CDCl_3 (76 MHz)

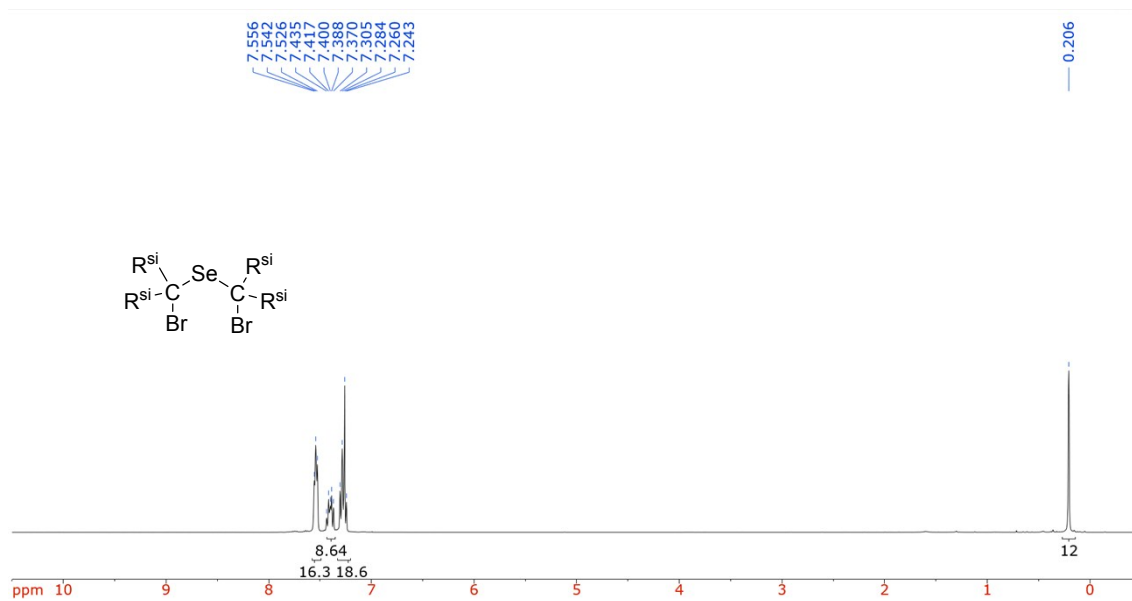


Figure S12. ¹H NMR spectrum for **14** in CDCl₃ (400 MHz)

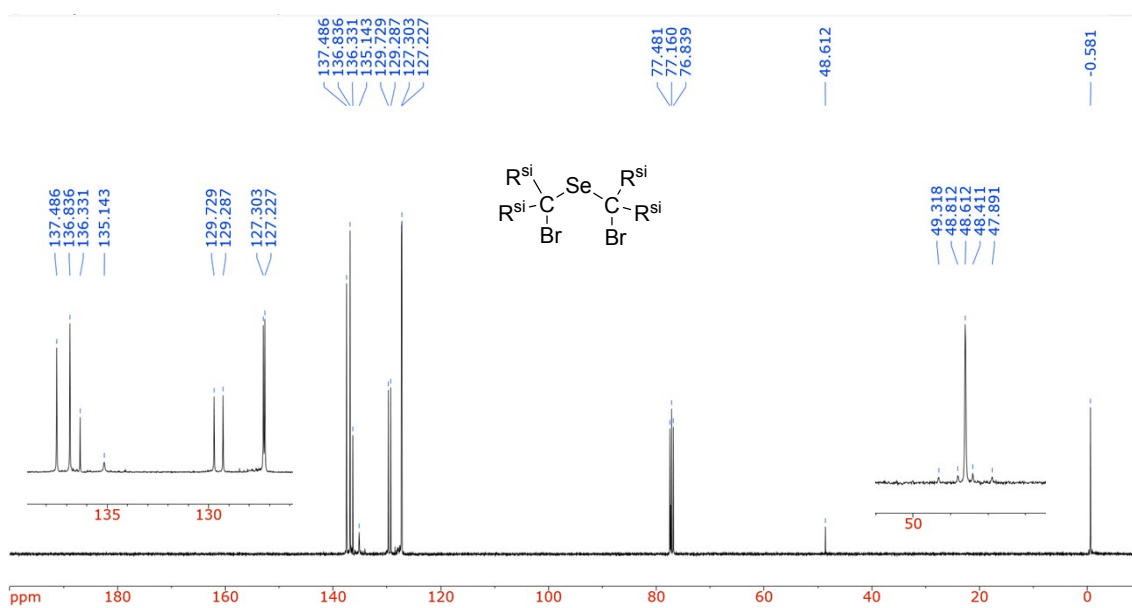


Figure S13. ¹³C NMR spectrum for **14** in CDCl₃ (100 MHz)

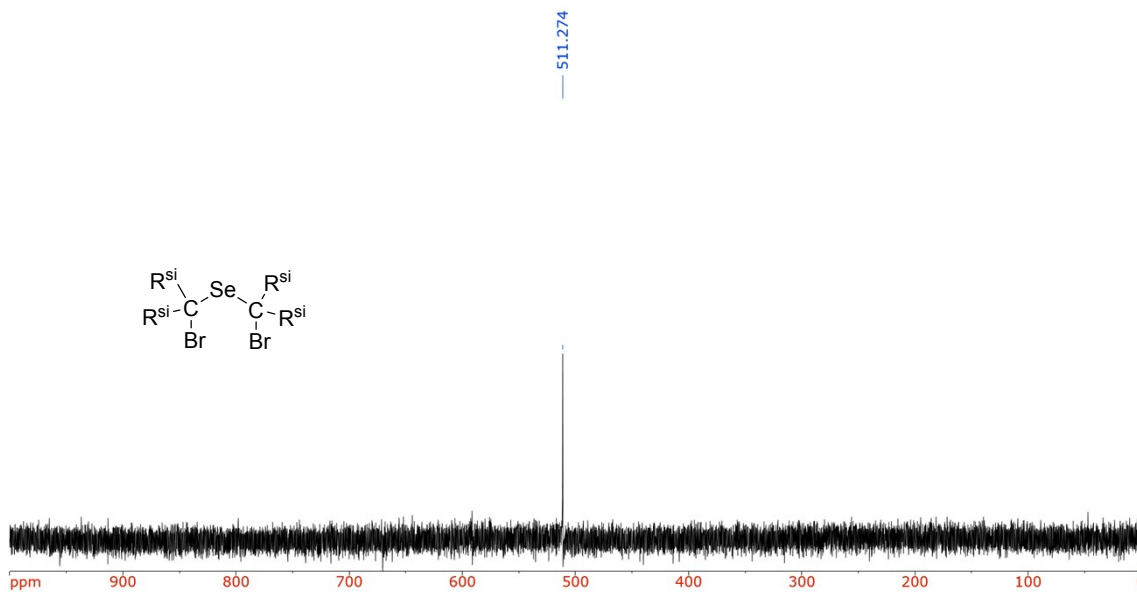


Figure S14. ^{77}Se NMR spectrum for **14** in CDCl_3 (76 MHz)

X-ray Crystallographic Analysis of **1**, **12**, **13**, and **14**

Single crystals of **1** was grown by slow recrystallization of the Hexane solutions at -4 °C. Suitable single crystals of **12**, **13**, and **14** were grown by slow recrystallization of the Et₂O solutions at room temperature. The structures were solved by a direct method (SHELXT)^[S2] and refined by full-matrix least square method on F² for all reflections (SHELXL-2016).^[S3] All hydrogen atoms were placed using AFIX instructions, while the other atoms were refined anisotropically. The supplementary crystallographic information for this paper has been deposited at The Cambridge Crystallographic Data Centre (CCDC) under the reference numbers CCDC-1916133 (**1**), CCDC-1916134 (**12**), CCDC-1916132 (**13**), CCDC-1916135 (**14**).

Table S1 Crystal data and data collections of **1**, **12**, **13**, and **14**.

	CSeC (1)	HCl adduct (12)	Cl ₂ adduct (13)	Br ₂ adduct (14)
empirical formula	C ₅₄ H ₅₂ SeSi ₄	C ₅₄ H ₅₃ ClSeSi ₄	C ₅₄ H ₅₂ Cl ₂ SeSi ₄	C ₅₄ H ₅₂ Br ₂ SeSi ₄ •Et ₂ O
formula weight	892.27	928.73	963.17	1126.21
color	purple	colourless	colourless	colourless
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>c</i> (#14)
unit-cell dimensions				
<i>a</i> (Å)	12.7354(8)	17.3177(13)	17.4721(5)	12.0334(4)
<i>b</i> (Å)	21.5853(14)	13.0257(8)	13.4080(5)	20.0424(6)
<i>c</i> (Å)	17.4791(10)	21.8104(15)	21.0645(7)	22.4788(6)
α (°)	90	90	90	90
β (°)	102.496(2)	105.764(8)	104.8770(10)	91.4760(10)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	4691.1(5)	4734.8(6)	4769.3(3)	5419.6(3)
<i>Z</i>	4	4	4	4
<i>D</i> (g/cm ³)	1.263	1.303	1.341	1.380
independent reflections	8658	9304	8865	12402
parameters	536	555	554	601
<i>R</i> 1, <i>wR</i> 2	0.0544, 0.1446	0.0626, 0.1428	0.0315, 0.0697	0.0382, 0.0760
goodness-of-fit on <i>F</i> ²	1.025	1.058	1.025	1.024
CCDC	1916133	1916134	1916132	1916135

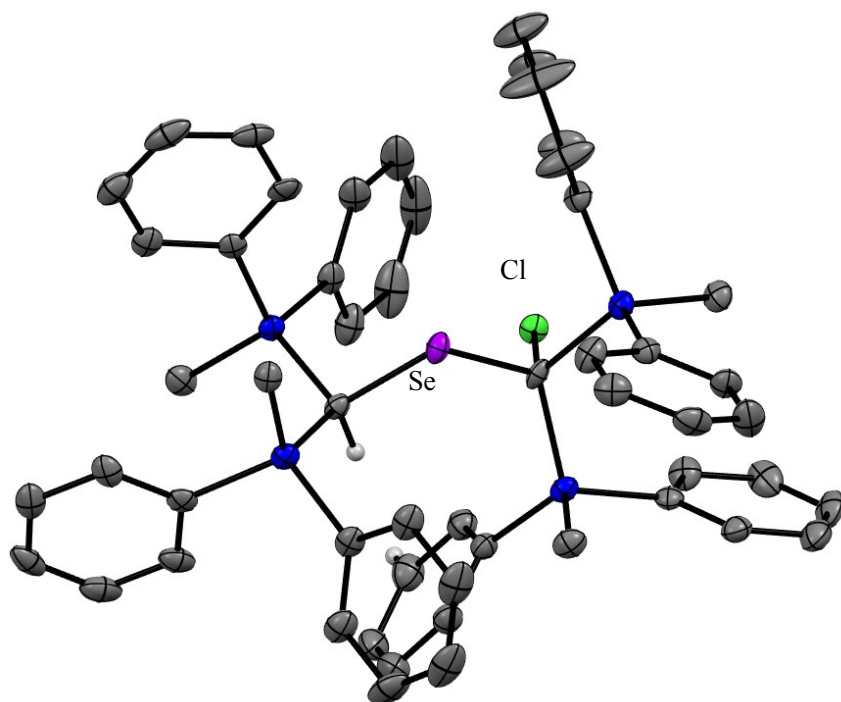


Figure S15. Structure of Compound 12

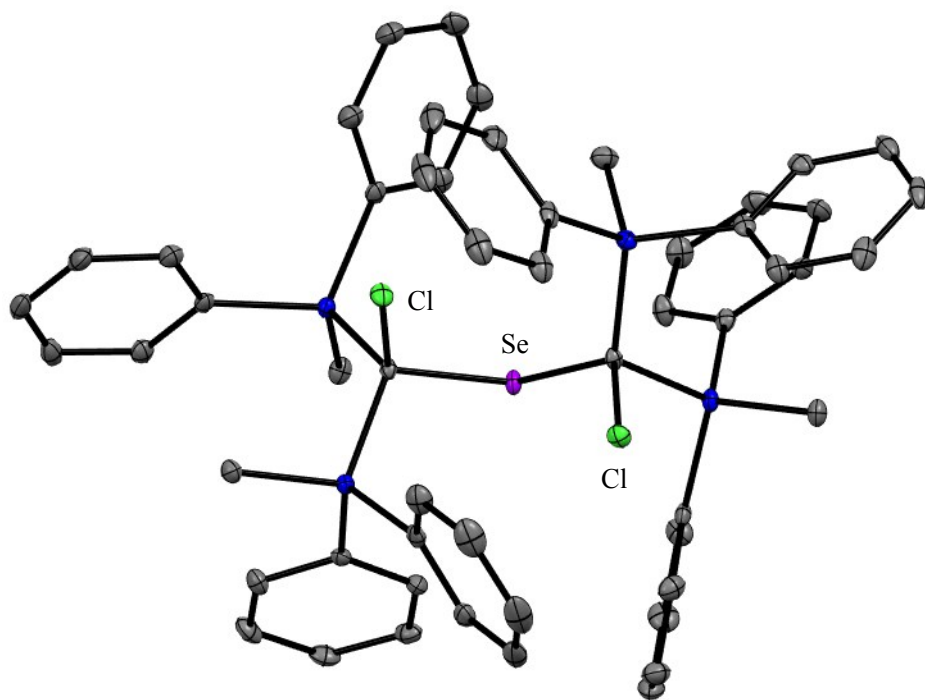


Figure S16. Structure of Compound 13

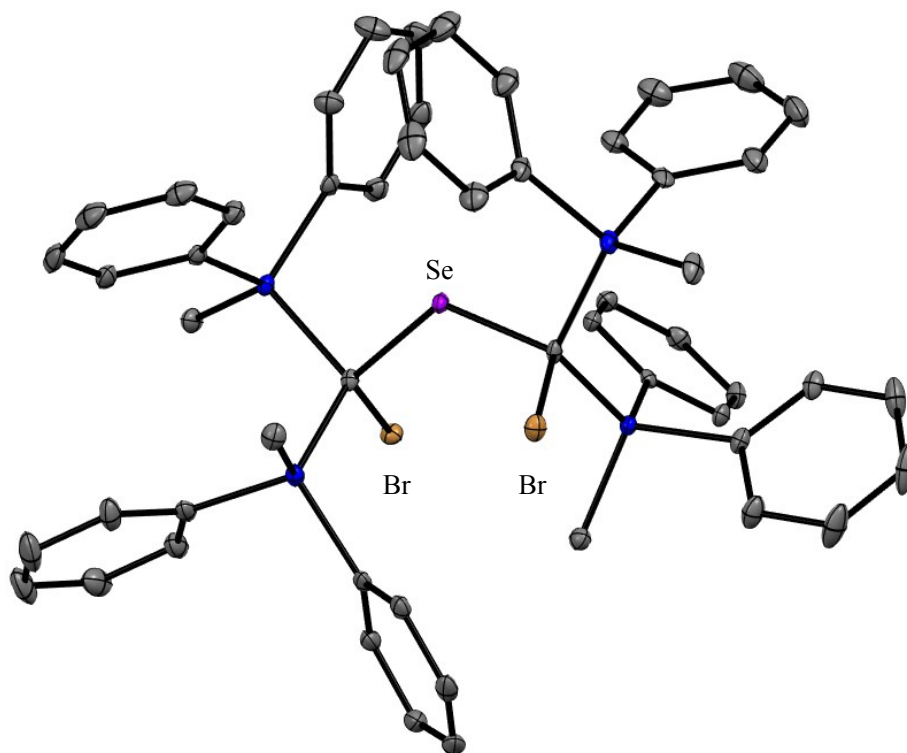


Figure S17. Structure of Compound 14 (All hydrogens and solvent molecule are omitted for clarity.)

Computational Details

All calculations were performed using the Gaussian 09 suite of programs, revision E 01.^[S1] The geometry optimization and harmonic vibration frequency calculations of **1**, **1a-e** were performed in DFT method at B3PW91/6-311G(2d,p) level of theory. The frequency calculations confirmed minimum energies for the optimized structures. The optimized geometry of **1** is shown in Figure S6, and the selected optimized structural parameters are given in Table S1. Optimized structures are provided as a xyz file. Frontier orbitals of **1** is shown in Figures S6.

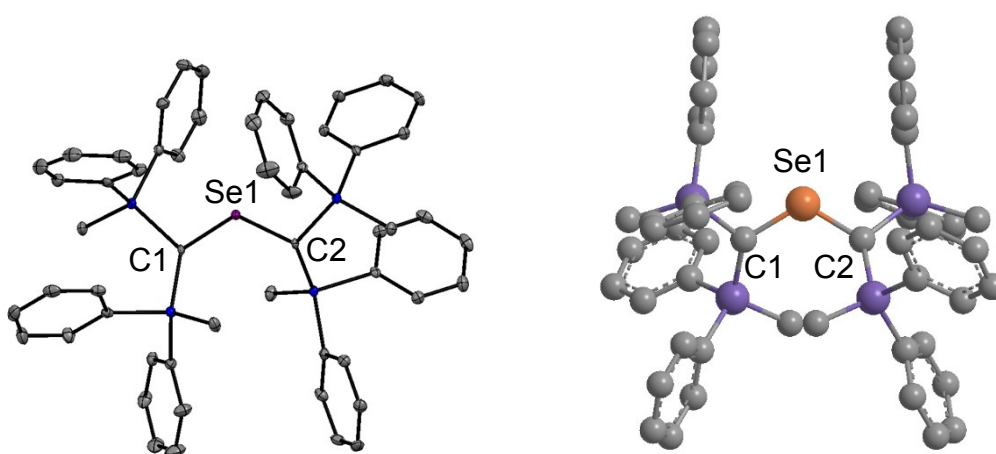


Figure S18. Molecular structure of **1** with ellipsoids at the 50% probability and calculated geometry for **1** at B3PW91/6-311G(2d,p) level. Hydrogen atoms omitted for clarity. For the comparison of the structural parameters obtained experimentally with those calculated, see Table S1.

Table S2. The bond parameters of the experimental and calculated values for compound **1**.

	Experimental values (Å, deg)	Calculated values(Å, deg)
Se1-C1	1.811(4)	1.846
Se1-C2	1.808(3)	1.846
C1-Si1	1.886(4)	1.883
C1-Si2	1.862(4)	1.871
C2-Si3	1.886(4)	1.871
C2-Si4	1.867(4)	1.883
C1-Se1-C2	120.82(16)	117.97
Se1-C1-Si1	104.82(18)	109.42

Se1-C1-Si2	124.24(19)	124.82
Si1-C1-Si2	125.7(2)	124.14
Se1-C2-Si3	124.29(18)	124.84
Se1-C2-Si4	105.34(18)	109.42
Si3-C2-Si4	124.29(19)	124.13

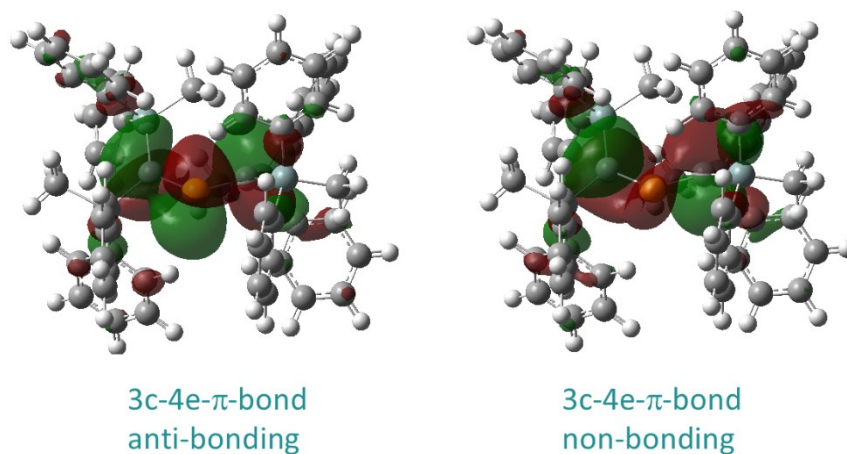


Figure S19. Frontier orbitals of **1** (B3PW91/6-311G(2d,p))

Kinetic Experiment

Kinetic experiments were conducted to ascertain the rate of bond rotation of selane **1** and sulfane **2** in toluene using temperature as a function. Line shape analysis allowed the rotation rate constant (k) values estimated at several temperatures from 243 to 323 K. The thermodynamic parameters of activation for the rotation between the carbon and chalcogen atoms were obtained from an Eyring plot analysis^{S4} of **1** and **2**.

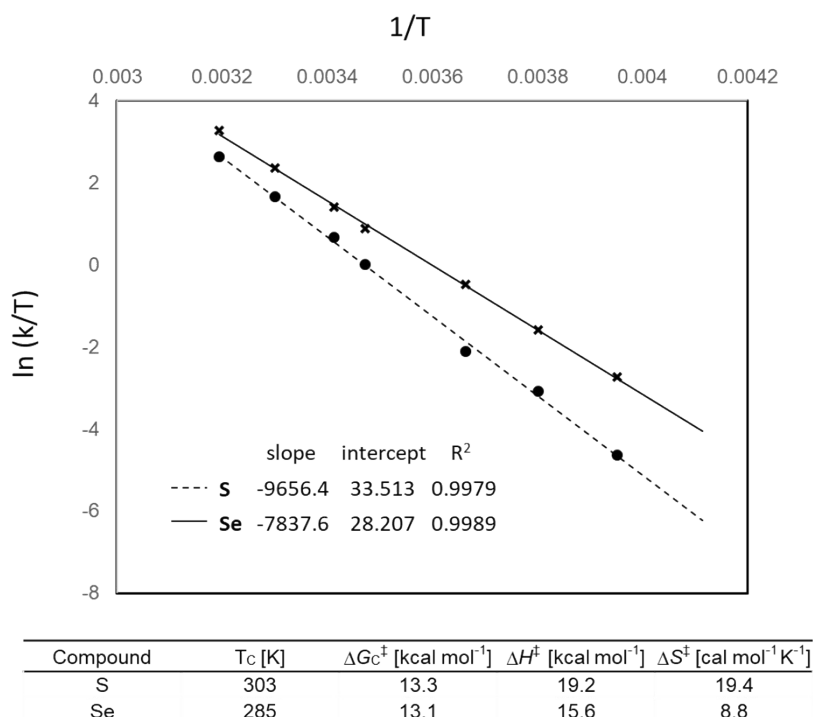


Figure S20. Eyring Plots of **1** and **2**.

Electrochemical experiments

Electrochemical experiments were carried out on an ALS 600A potentiostat/galvanostat using Pt wire electrodes. Electrochemical samples were recorded with scan rates of 50 mVs⁻¹ at room temperature. Samples solutions in CH₂Cl₂ were 1.0 mM in analyte and 0.1 M in [*n*-Bu₄N][ClO₄] as the supporting electrolyte.

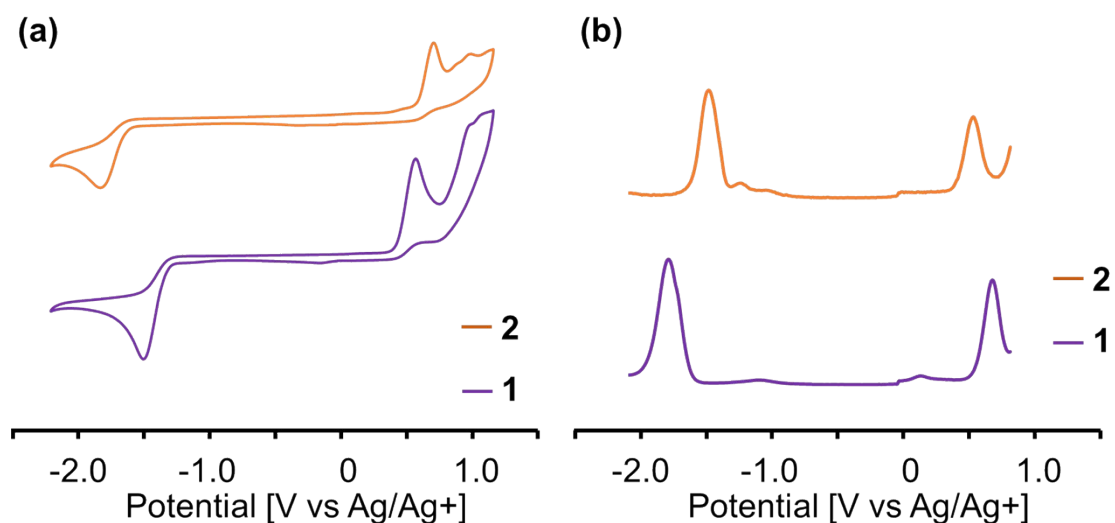


Figure S21. Cyclic and Differential Pulse Voltammograms of **1** and **2**

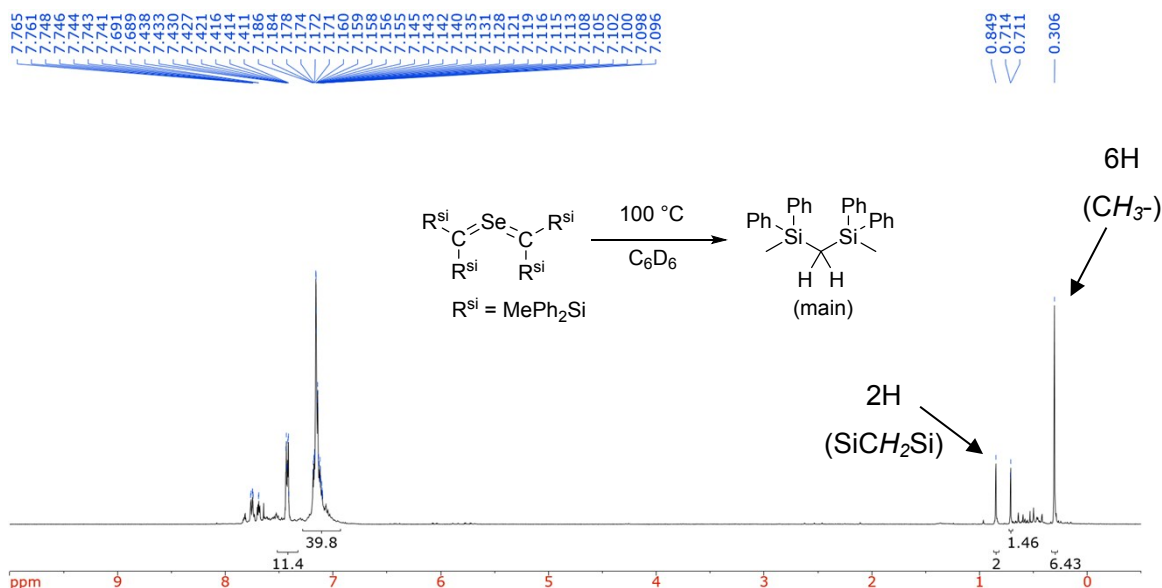


Figure S22. Thermolysis of Bis(methylene)- λ^4 -selane in C_6D_6 .

References

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- [S3] Sheldrick, G. M. *Acta Crystallogr. Sect. C*, 2015, 71, 3-8.
- [S4] Gasparro, F. P.; Kolodny, N. H. NMR Determination of the Rotational Barrier in N,N-Dimethylacetamide. *J. Chem. Educ.* **1977**, 54, 258–261.