Hydroxyselenylation and Tethered Silanoxyselenylation of Allylic Silanols

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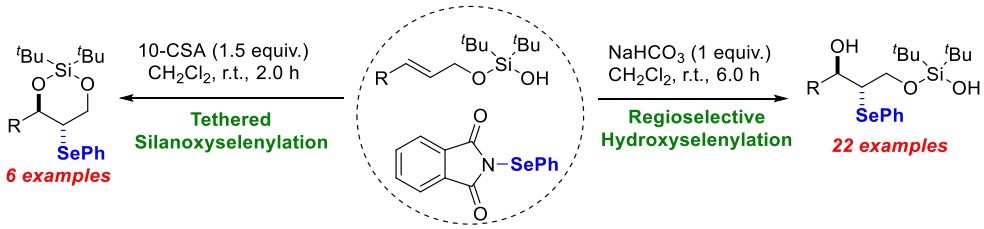
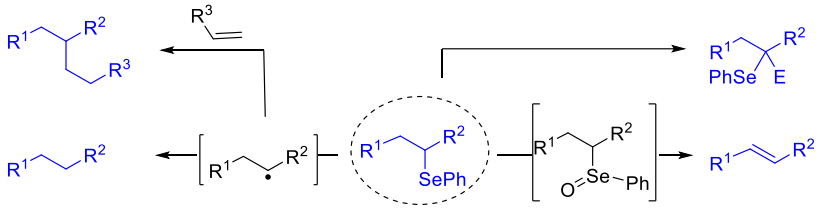


Abstract: We present protocols for the highly regioselective hydroxyselenylation and silanoxyselenylation of allylic silanols. *N*-(Phenylseleno)phthalimide acts as the selenylating agent for both transformations. Under basic conditions, hydroxyselenylation proceeds with >20:1 regioselectivity, and the products are valuable synthons for further transformations. We show that the silanol plays a critical role in maintaining the yield and regioselectivity of this reaction. Surprisingly, under acidic conditions, the hydroxyselenylation pathway is blocked, and products of a tethered silanoxyselenylation are exclusive.

The electrophilic functionalization of unactivated alkenes is an important synthetic approach for the installation of carbon-heteroatom linkages.[1] Generally, the first step in most of these reactions is the formation of a cyclic three-membered cationic intermediate, which is subsequently opened by a nucleophile.[2] In such processes, controlling the regioselectivity of nucleophilic attack is often a challenge. "Tethering" a desired nucleophile to an existing functional group in the molecule of interest allows for intramolecular attack, which often proceeds with predictable regioselectivity and high diastereocontrol.[3-10] Our laboratory has provided the first examples of the use of silanol tethers for the intramolecular ring-opening of both transient and stable electrophiles.[11-14]

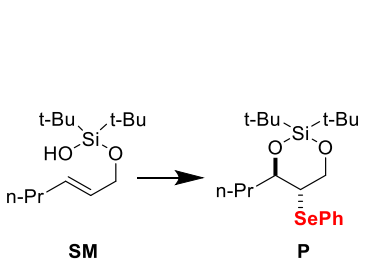
Organoselenides have many attractive properties that make them complementary to organomercurials and organohalides.[15-17] Unlike organohalides, organoselenides are stable to most common synthetic reactions, including hydrolysis, nucleophilic substitution, reduction, and Swern-type oxidations. Organoselenides are also unreactive in

the presence of nucleophilic nitrogen centers which are often present in heteroarenes of medicinal chemistry importance, and selenylation reagents are highly chemoselective for alkene functionalizations. Furthermore, much like C–Hg bonds, which can be facilely cleaved into C•, C–Se bonds are excellent radical precursors,[18] and their reduced toxicity makes organoselenides more attractive intermediates relative to organomercurials (**Scheme 1**). We were thus interested in developing a tethered silanoxyselenylation of allylic alcohols. Such a reaction would form protected 1,3-diol organoselenides in a single step from the corresponding allylic silanol starting materials. Based on precedent from selenolactonization[19, 20] and selenoetherfication chemistry,[21-23] we envisioned that such products would be valuable intermediates in the syntheses of important carbohydrate or polyketide targets.



Scheme 1. Prior art has established that organoselenides are versatile synthons.

Table 1. Optimization of a tethered silanoxyselenylation reaction.



Reagent A
$AgBF_4$/PhSeCl/$NaHCO_3$
(1.1 equiv. each)

Reagent B
$AgPF_6$/PhSeCl/$NaHCO_3$
(1.1 equiv. each)

Reagent C
$AgNO_3$/PhSeCl/$NaHCO_3$
(1.1 equiv. each)

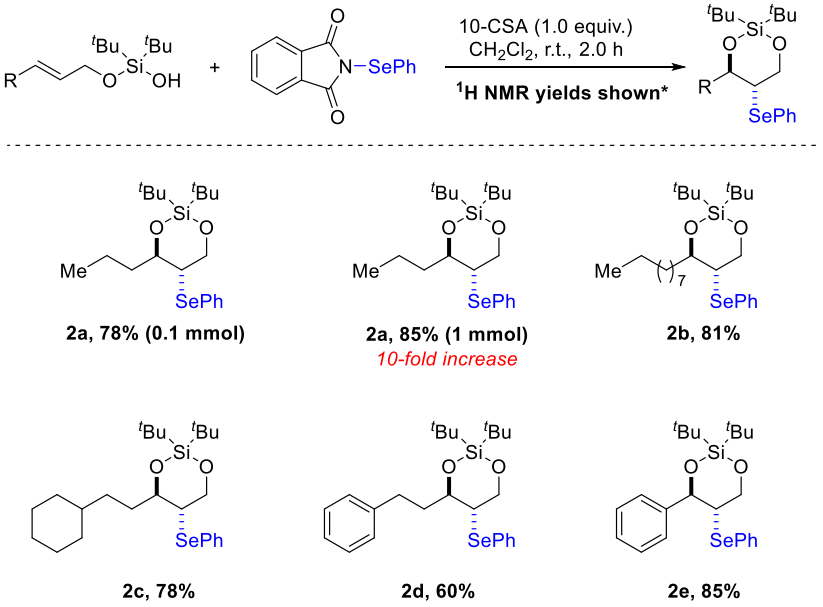
Reagent D
PhSe-Phth/10-CSA
(1.5/1.0 equiv.)

	Se^+ Reagent	Temp.	Solvent	**P** yield[a]
1	A	-40 °C	DME	12%
2	A	-40 °C	EtOAc	24%
3	A	-40 °C	MeCN	50%
4	A	-40 °C	THF	56%
5	A	0 °C	THF	30%
6	B	-40 °C	THF	38%
7	C	-40 °C	THF	0%
8	**D**	**RT**	**CH_2Cl_2**	**70%**

[a] ^1H NMR yield estimated using an internal standard

Optimization of this reaction began with (*E*)-di-*tert*-butyl(hex-2-en-1-yloxy)silanol, prepared in one step from condensation of commercially available di-*tert*-butylsilyl bis(trifluoromethanesulfonate) with *trans*-2-hexen-1-

ol (**Table 1**).[13] With $AgBF_4$/PhSeCl,[24, 25] 12% of product formed in dimethoxyethane (**Table 1**, **Entry 1**). Product yield increased when the solvent was switched to ethyl acetate, acetonitrile, and tetrahydrofuran (**Table 1**, **Entries 2-4**). In THF, warming the reaction temperature from -40 °C to 0 °C (**Table 1**, **Entry 5**) was markedly deleterious. Using $AgPF_6$ (**Table 1**, **Entry 6**) or $AgNO_3$ (**Table 1, Entry 7**) in place of $AgBF_4$ was also harmful. Abandoning silver salts completely and using Nicolaou's *N*-(phenylseleno)phthalimide[26, 27] reagent with 10-camphorsulfonic acid increased both the product yield and the reaction reproducibility (**Table 1**, **Entry 8**).



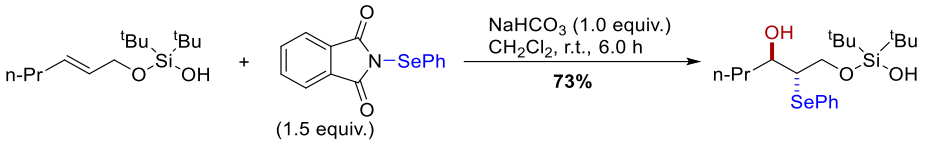
**Compounds are unstable to chromatographic purification.*

Scheme 2. Substrate scope of a tethered silanoxyselenylation reaction.

Our optimized protocol was compatible with several allylic silanols (**Scheme 2**). The reaction was also scalable 10-fold from 0.1 mmol to 1 mmol without loss of yield or selectivity (**Scheme 2**, **Compound 2a**). Unfortunately, in all cases examined, the product organoselenide heterocycles were unstable to chromatographic purification with unadulterated silica gel, triethylamine-treated silica gel, neutral alumina, Florisil, and Davisil. In general, starting material was fully consumed in these reactions with few side products. The main impurities were unreacted *N*-(phenylseleno)phthalimide reagent, phthalimide, and 10-camphorsulfonic acid. In the instances shown here (**Scheme 2**), washing with 0.5 M aqueous NaOH solution was sufficient to yield reasonably pure compound, but the inability to purify by chromatography hampered our substrate survey.

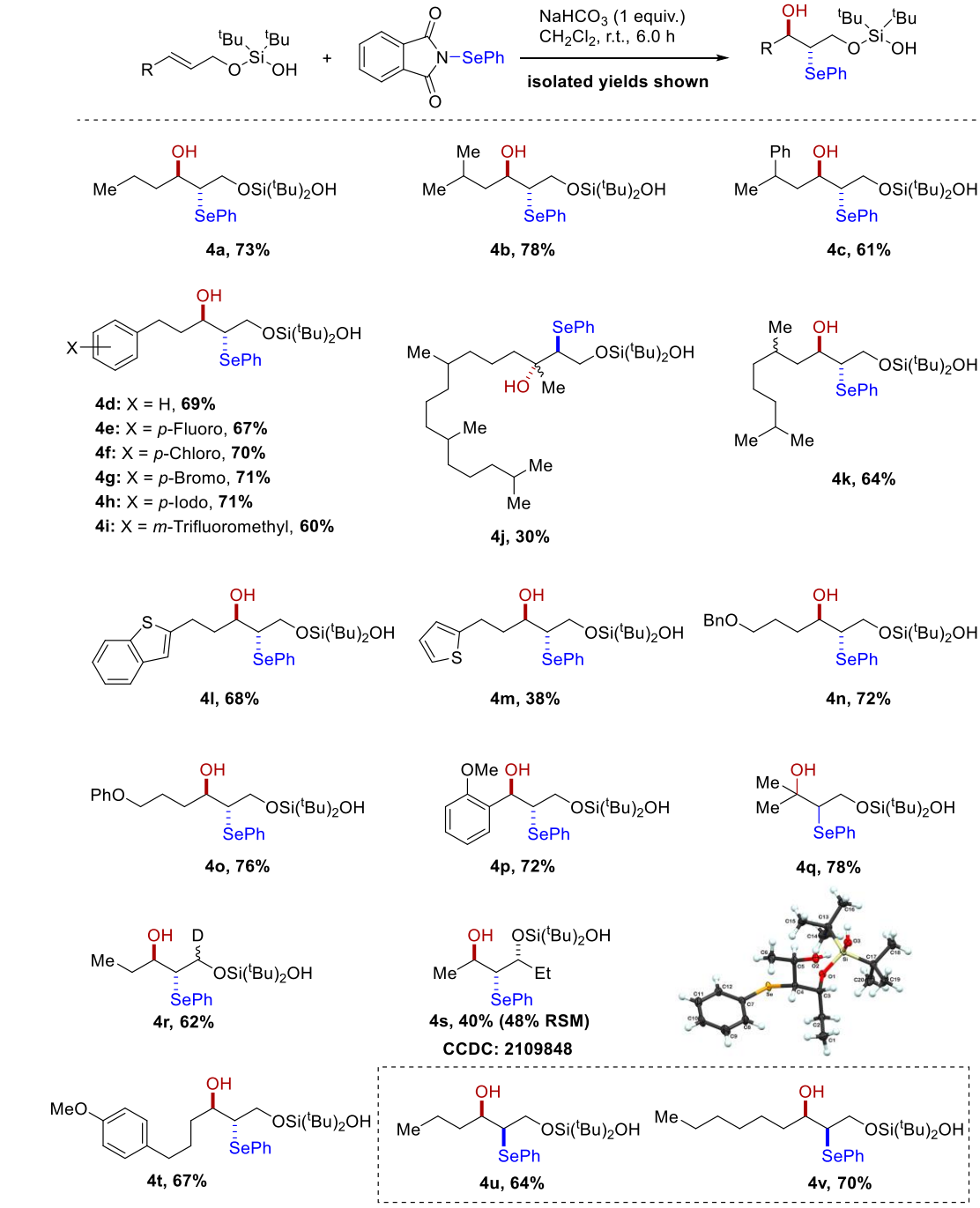
Over the course of optimization (**Table 1**), a small amount of hydroxyselenylated product formed in select reactions, and this compound was stable to silica gel chromatography. We thus wondered if we could optimize the

formation of this product (**Scheme 3**). Absent a tether, we were unsure whether perfect regiocontrol could be achieved with such a reaction. Amazingly, a simple replacement of 10-camphorsulfonic acid with 1 equivalent of $NaHCO_3$ led to a complete reversal of product selectivity, now exclusively favoring hydroxyselenylated compound. Importantly, this product was a single regioisomer, stable to chromatographic purification, and easily isolable in pure form.

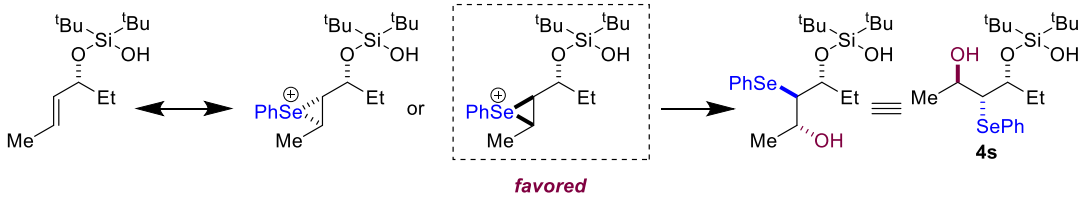


Scheme 3. A pH switch leads to a complete reversal of product selectivity!

This protocol was compatible with a variety of allylic silanols (**Scheme 4**). In all cases, reactions proceeded, with >20:1 regiocontrol. Our protocol tolerated substrates with branched alkyl chains (**Scheme 4**, **Compounds 4b-c and 4j-k**), substituted aryl rings (**Scheme 4**, **Compounds 4d-i, 4p, 4t**), heteroaryl rings (**Scheme 4**, **Compounds 4l-4m**), and aliphatic ethers (**Scheme 4**, **Compounds 4n-4o**). We were not constrained to using only *trans*-allylic silanol starting materials. *Cis*-allylic silanols reacted smoothly as well to form *syn*-selenohydrin silanol products (**Scheme 4**, **Compounds 4u-v**). Most of these investigations were conducted using primary allylic silanols. With a secondary allylic silanol, selenohydrin product (**Scheme 4**, **Compound 4s**) was formed as a single regioisomer and diastereomer in 40% yield; 48% starting material was recovered in the reaction. The relative configuration of the three stereocenters in this molecule was stablished by single crystal X-ray diffraction analysis (**CCDC: 2109848**). What accounts for the high diastereoselectivity in this case? We propose a model shown in **Scheme 5**, which suggests that the avoidance of unfavorable steric clashing between the seleniranium adduct and the bulky di-*tert*-butyl-silanol group may be a primary factor.

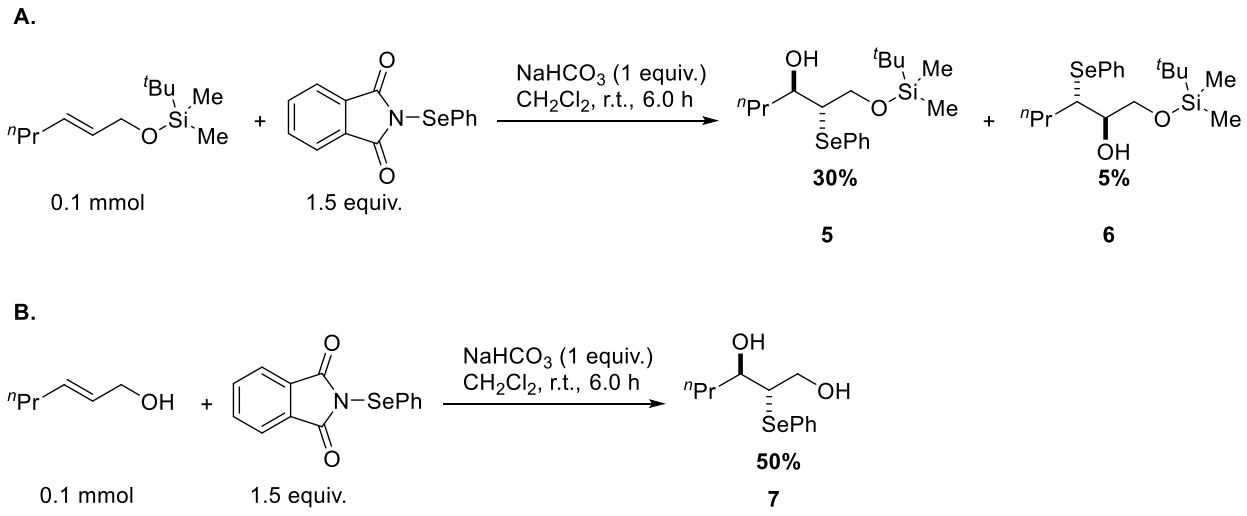


Scheme 4. Substrate scope of our hydroxyselenylation of allylic silanols.



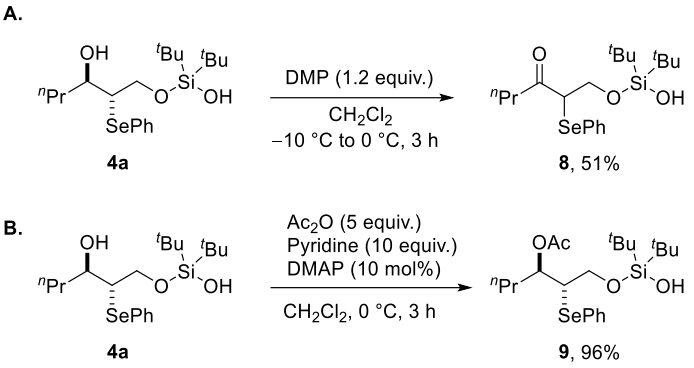
Scheme 5. Avoidance of steric clashing may be a driving force for stereoselectivity.

What is the role of the silanol auxiliary in this hydroxyselenylation? To answer this question, we conducted a series of control experiments (**Scheme 6**). With (E)-*tert*-butyl(hex-2-en-1-yloxy)dimethylsilane, regioisomeric selenohydrin products **5** and **6** formed in a combined yield of 35% (**Scheme 6A**). With *trans*-2-hexen-1-ol, selenohydrin product **7** formed in >20:1 regioselectivity and in 50% yield (**Scheme 6B**); this yield is ~20% lower than with the corresponding silanol starting material (**Scheme 4**, **Compound 4a**). Thus, a hydroxyl group is essential for regiocontrol in this and related reactions,[28-30] but a free alcohol leads to a drop in yield. Overall, we conclude that the silanol auxiliary serves as a unique protecting group, capable of maintaining >20:1 regioselectivity in the reaction due to presence of the Si–OH.



Scheme 6. The di-*tert*-butylsilanol auxiliary appears to have beneficial effects on both the yield and the regioselectivity of our hydroxyselenylation reaction.

The selenohydrin silanols are versatile synthons (**Scheme 7**). Oxidation of **4a** with Dess-Martin periodinane formed ketone **8** in 52% yield (**Scheme 7A**). Using acetic anhydride, the C–OH rather than the Si–OH is preferentially transformed into the corresponding acetate (**Scheme 7B**). We note that **9** (**Scheme 7B**) contains differentially protected primary and secondary alcohols, a marked advantage of using allylic silanols as starting materials over the analogous allylic alcohols.



Scheme 7. Selenohydrin silanols are versatile synthons.

In summary, we have developed hydroxyselenylation and silanoxyselenylation reactions of allylic silanols. *N*-(Phenylseleno)phthalimide acts as the selenylating agent for both transformations. Under basic conditions, hydroxyselenylation proceeds with >20:1 regioselectivity, and the products are valuable synthons for further transformations. The silanol plays a critical role in maintaining the yield and regioselectivity of this reaction. Surprisingly, under acidic conditions, the hydroxyselenylation pathway is blocked, and products of a tethered silanoxyselenylation are exclusive. While this latter reaction interesting from a mechanistic standpoint, the products are unfortunately unstable to chromatography on silica gel and alumina. Given the known versatility of organoselenium compounds, we expect the hydroxyselenylation of allylic silanols to be employed in the pursuit of complex, polyfunctional targets of value.

Experimental Section

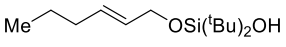
I. General Considerations

All reagents were obtained commercially unless otherwise noted. Solvents were purified by passage under 10 psi N_2 through activated alumina columns. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer; data are reported in frequency of absorption (cm^{-1}). NMR data are recorded as chemical shift in ppm referenced internally using residue solvent peaks, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances), integration, and coupling constant (Hz). ^{1}H NMR spectra were recorded at 400, 500, or 600 MHz. ^{13}C NMR spectra were recorded at 100 or 125 MHz. Exact mass spectra were recorded using an electrospray ion source (ESI) either in positive mode or negative mode with a time-of-flight (TOF) analyzer on a Waters LCT PremierTM mass spectrometer and are given in m/z. TLC was performed on precoated glass plates (Merck) and visualized either with a UV lamp (254 nm) or by dipping into a solution of $KMnO_4$– K_2CO_3

in water followed by heating. Flash chromatography was performed on silica gel (230−400 mesh) or Florisil (60−100 mesh).

II. Allylic Silanol Starting Materials

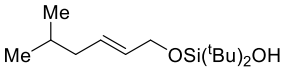
Note: Allylic silanol starting material compounds were prepared according to a previously reported procedure.[13]



1a

(*E*)-di-*tert*-butyl(hex-2-en-1-yloxy)silanol

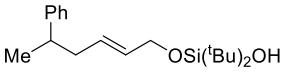
Compound 1a: Previously characterized in *Org. Lett.* **2020**, *22*, 8665–8669.



1b

(*E*)-di-*tert*-butyl((5-methylhex-2-en-1-yl)oxy)silanol

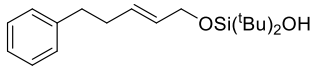
Compound 1b: Previously characterized in *Org. Chem. Front.*, **2021**, *8*, 5361-5368.



1c

(*E*)-di-*tert*-butyl((5-phenylhex-2-en-1-yl)oxy)silanol

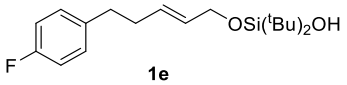
Compound 1c: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (colorless oil, 279 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.30 – 7.17 (m, 3H), 5.63 (m, 2H), 4.31 (d, *J* = 3.6 Hz, 2H), 2.83 (h, *J* = 7.0 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.38 – 2.26 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.06 (s, 9H), 1.05 (s, 9H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 147.0, 130.9, 129.1, 128.3, 127.0, 125.9, 64.0, 41.0, 40.0, 27.4, 21.6, 20.4. IR 3488, 2860, 1473, 1101, 970 cm^{-1}.; HRMS (APCI) m/z: [M–H] calculated for $C_{20}H_{33}O_2Si$ 333.2236, found 333.2255.



1d

(*E*)-di-*tert*-butyl((5-phenylpent-2-en-1-yl)oxy)silanol

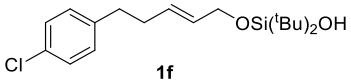
Compound 1d: Previously characterized in *Org. Lett.* **2020**, *22*, 8665–8669.



1e

(*E*)-di-*tert*-butyl((5-(4-fluorophenyl)pent-2-en-1-yl)oxy)silanol

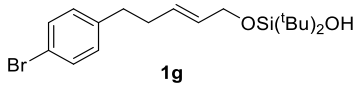
Compound 1e: Previously characterized in *Org. Chem. Front.*, **2021**, *8*, 5361-5368.



1f

(*E*)-di-*tert*-butyl((5-(4-chlorophenyl)pent-2-en-1-yl)oxy)silanol

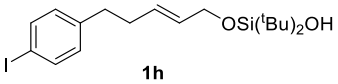
Compound 1f: Previously characterized in *Org. Chem. Front.*, **2021**, *8*, 5361-5368.



1g

(*E*)-((5-(4-bromophenyl)pent-2-en-1-yl)oxy)di-*tert*-butylsilanol

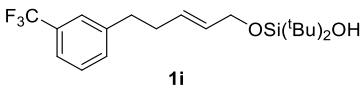
Compound 1g: Previously characterized in *Org. Chem. Front.*, **2021**, *8*, 5361-5368.



1h

(*E*)-di-*tert*-butyl((5-(4-iodophenyl)pent-2-en-1-yl)oxy)silanol

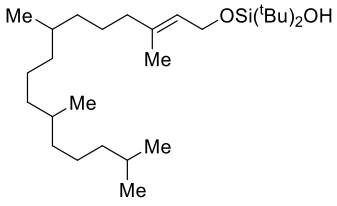
Compound 1h: Previously characterized in *Org. Chem. Front.*, **2021**, *8*, 5361-5368.



1i

(*E*)-di-*tert*-butyl((5-(3-(trifluoromethyl)phenyl)pent-2-en-1-yl)oxy)silanol

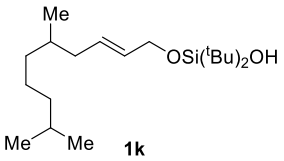
Compound 1i: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (colorless oil, 358 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 4H), 5.70 (dtt, *J* = 15.6, 6.4, 1.3 Hz, 1H), 5.65 – 5.53 (m, 1H), 4.29 (dt, *J* = 4.9, 1.4 Hz, 2H), 2.76 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.39 (tdt, *J* = 9.2, 7.9, 1.4 Hz, 2H), 1.02 (d, *J* = 1.1 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 132.0 (d, *J* = 1.7 Hz), 130.8 (q, *J* = 20 Hz), 130.6, 129.2, 128.8, 125.8 (q, *J* = 270 Hz), 125.2 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 3.9 Hz), 63.9, 35.5, 33.7, 27.5, 20.6. IR 3511, 2934, 2860, 1473, 1324, 1130, 833 cm^{-1}.; HRMS (APCI) m/z: [M–H] calculated for $C_{20}H_{30}F_3O_2Si$ 387.1967, Found 387.1955.



1j

(*E*)-di-*tert*-butyl((3,7,11,15-tetramethylhexadec-2-en-1-yl)oxy)silanol

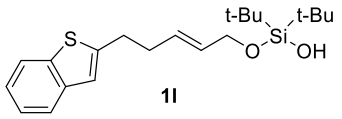
Compound 1j: Previously characterized in *J. Org. Chem.* **2021**, *86*, 9233−9243.



1k

(*E*)-di-*tert*-butyl((5,9-dimethyldec-2-en-1-yl)oxy)silanol

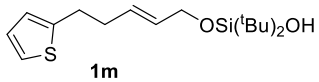
Compound 1k: Previously characterized in *Molecules* **2021**, *26*, 3829.



1l

(*E*)-((5-(benzo[*b*]thiophen-2-yl)pent-2-en-1-yl)oxy)di-*tert*-butylsilanol

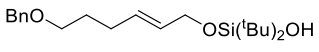
Compound 1l: Purified using a gradient of 0 to 20% Ethyl acetate/Hexanes on silica gel; (light yellow semi-solid, 225 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dq, *J* = 7.8, 0.9 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.36 – 7.22 (m, 2H), 7.04 (q, *J* = 1.0 Hz, 1H), 5.85 – 5.73 (m, 1H), 5.73 – 5.59 (m, 1H), 4.33 (dq, *J* = 5.0, 1.3 Hz, 2H), 3.09 – 2.95 (m, 2H), 2.53 (tdd, *J* = 7.5, 6.3, 1.2 Hz, 2H), 1.03 (s, 18H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 145.6, 140.1, 139.3, 130.7, 129.0, 124.0, 123.4, 122.7, 122.1, 120.7, 63.9, 33.5, 30.6, 27.4, 20.4. IR 3460, 2934, 2854, 1473, 827 cm^{-1}.; HRMS (APCI) m/z: [M–H] calculated for $C_{21}H_{31}O_2SSi$ 375.1820, found 375.1802.



1m

(*E*)-di-*tert*-butyl((5-(thiophen-2-yl)pent-2-en-1-yl)oxy)silanol

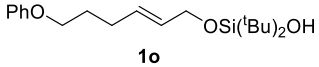
Compound 1m: Purified using a gradient of 0.5 to 5% diethyl ether/hexane on silica gel; (colorless oil, 411.7 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.82 – 6.75 (m, 1H), 5.78 – 5.68 (m, 1H), 5.68 – 5.58 (m, 1H), 4.35 – 4.24 (m, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.53 – 2.34 (m, 2H), 1.02 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.8, 130.6, 129.4, 126.8, 124.3, 123.1, 64.0, 34.3, 29.8, 27.5, 20.6. IR 3648, 2934, 2894, 2860, 1473, 1381, 1113, 1056, 970, 827, 690, 645 cm^{-1}.; HRMS (APCI) m/z: [M–H] calculated for $C_{17}H_{29}O_2SSi$ 325.1663, found 325.1665.



1n

(*E*)-((6-(benzyloxy)hex-2-en-1-yl)oxy)di-*tert*-butylsilanol

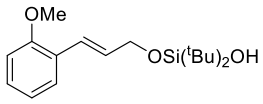
Compound 1n: Previously characterized in *Org. Chem. Front.*, **2021**, *8*, 5361-5368.



1o

(*E*)-di-*tert*-butyl((6-phenoxyhex-2-en-1-yl)oxy)silanol

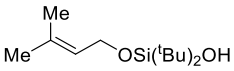
Compound 1o: Previously characterized in *Org. Chem. Front.*, **2021**, *8*, 5361-5368.



1p

(*E*)-di-*tert*-butyl((3-(2-methoxyphenyl)allyl)oxy)silanol

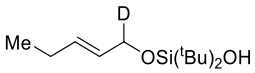
Compound 1p: Previously characterized in *Org. Lett.* **2020**, *22*, 8665–8669.



1q

di-*tert*-butyl((3-methylbut-2-en-1-yl)oxy)silanol

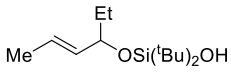
Compound 1q: Previously characterized in *Org. Lett.* **2020**, *22*, 8665–8669.



1r

(*E*)-di-*tert*-butyl((pent-2-en-1-yl-1-*d*)oxy)silanol

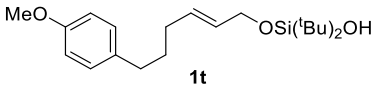
Compound 1r: Previously characterized in *Org. Lett.* **2020**, *22*, 8665–8669.



1s

(*E*)-di-*tert*-butyl(hex-4-en-3-yloxy)silanol

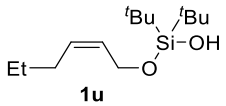
Compound 1s: Previously characterized in *Org. Lett.* **2020**, *22*, 8665–8669.



1t

(*E*)-di-*tert*-butyl((6-(4-methoxyphenyl)hex-2-en-1-yl)oxy)silanol

Compound 1t: Purified using a gradient of 0 to 2% acetone/DCM on silica gel; (colorless oil, 339 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 8.7, 2.2 Hz, 2H), 6.93 – 6.79 (m, 2H), 5.80 – 5.67 (m, 1H), 5.62 (ddddd, *J* = 15.3, 5.2, 4.0, 2.6, 1.3 Hz, 1H), 4.34 (ddt, *J* = 5.3, 4.0, 1.2 Hz, 2H), 3.82 (s, 3H), 2.60 (td, *J* = 7.8, 2.3 Hz, 2H), 2.16 – 2.05 (m, 2H), 1.77 – 1.63 (m, 2H), 1.10 – 0.98 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 134.5, 130.7, 129.7, 129.3, 113.7, 64.1, 55.2, 34.4, 31.6, 31.2, 27.4, 20.5. IR 3522, 2951, 2854, 1513, 1473, 1244, 1044 cm^{-1}.; HRMS (APCI) m/z: [M+] calculated for $C_{21}H_{36}O_3Si$ 364.2434, Found 364.2422.

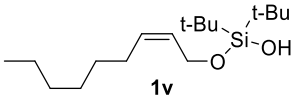


1u

(*Z*)-di-*tert*-butyl(hex-2-en-1-yloxy)silanol

Compound 1u: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (colorless oil, 252 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (dtt, *J* = 11.0, 6.1, 1.5 Hz, 1H), 5.51 – 5.40 (m, 1H), 4.47 – 4.36 (m, 2H), 2.05 (qd, *J* = 7.4, 1.4 Hz, 2H), 1.41 (h, *J* = 7.4 Hz, 2H), 1.05 (s, 18H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (100 MHz,

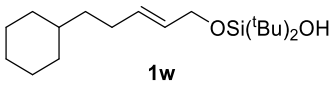
$CDCl_3$) δ 130.7, 129.7, 59.6, 29.5, 27.4, 22.7, 20.4, 13.7. IR 3494, 2951, 2854, 1467, 1090, 833 cm^{-1}.; HRMS (APCI) m/z: [M–H] calculated for $C_{14}H_{29}O_2Si$ 257.1937, found 257.1935.



1v

(*Z*)-di-*tert*-butyl(non-2-en-1-yloxy)silanol

Compound 1v: Purified using a gradient of 0 to 0.2% acetone/DCM on silica gel; (colorless oil, 324 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (dtt, *J* = 11.0, 6.0, 1.5 Hz, 1H), 5.52 – 5.38 (m, 1H), 4.42 (ddt, *J* = 6.1, 1.6, 0.8 Hz, 2H), 2.12 – 2.02 (m, 2H), 1.44 – 1.25 (m, 8H), 1.05 (s, 18H), 0.95 – 0.85 (m, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 131.0, 129.5, 59.6, 31.7, 29.5, 28.9, 27.5, 27.4, 22.6, 20.4, 14.0. IR 3500, 2946, 2866, 1473, 1096, 822 cm^{-1}.; HRMS (APCI) m/z: [M + H^+] calculated for $C_{17}H_{37}O_2Si$ 301.2557, found 301.2549.



1w

(*E*)-di-*tert*-butyl((5-cyclohexylpent-2-en-1-yl)oxy)silanol

Compound 1w: Purified using a gradient of 0.5 to 5% diethyl ether/hexane on silica gel; (colorless oil, 592 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 – 5.61 (m, 1H), 5.61 – 5.50 (m, 1H), 4.33 – 4.23 (m, 2H), 2.09 – 1.98 (m, 2H), 1.83 (s, 1H), 1.73 – 1.60 (m, 5H), 1.27 – 1.13 (m, 6H), 1.02 (s, 18H), 0.89 – 0.84 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 131.8, 129.1, 64.3, 37.2, 37.0, 33.4, 29.6, 27.5, 26.8, 26.5, 20.6. IR 3494, 2923, 2854, 1473, 1450, 1381, 1364, 1113, 1056, 970, 827, 645 cm^{-1}.; HRMS (APCI) m/z: [M + H^+] calculated for $C_{19}H_{39}O_2Si$ 327.2719, found 327.2719.

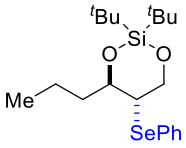
III. General Procedure for Tethered Silanoxyselenylation

0.1 mmol scale: An oven dried tube equipped with a magnetic stir bar was charged with allylic silanol starting material (0.1 mmol) and 0.5 mL CH_2Cl_2. Next, 10-camphorsulfonic acid (0.1 mmol, 23 mg, 1.0 equiv.), *N*-(Phenylseleno)phthalimide (0.15 mmol, 45 mg, 1.5 equiv.), and 0.5 mL CH_2Cl_2 were added to the above solution sequentially (Final reaction concentration: 0.1 M). The mixture was stirred at room temperature and monitored by thin layer chromatography (TLC). After 2.0 h, the reaction mixture was diluted with 5 mL CH_2Cl_2, transferred to a separatory funnel, and washed with 0.5 M aqueous NaOH solution. The organic layer was separated, dried over $MgSO_4$, concentrated in vacuo.

1 mmol scale: An oven dried tube equipped with a magnetic stir bar was charged with allylic silanol starting material **1a** (1 mmol, 258 mg, 1 equiv.) and 5.0 mL of CH_2Cl_2. 10-camphorsulfonic acid (1 mmol, 232 mg, 1.0 equiv.) and *N*-(Phenylseleno)phthalimide (1.5 mmol, 453 mg, 1.5 equiv.) were added sequentially. An additional 5.0 mL CH_2Cl_2

were added (0.1 M final concentration) and the heterogenous mixture was stirred for 3 h. Next, the reaction mixture was diluted with 25 mL CH_2Cl_2, transferred to a separatory funnel, and washed with 0.5 M aqueous NaOH solution. The organic layer was separated, dried over $MgSO_4$, concentrated in vacuo.

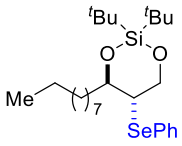
IV. Tethered Silanoxyselenylation Product Characterization (Scheme 2 Compounds)



2a

2,2-di-*tert*-butyl-5-(phenylselanyl)-4-propyl-1,3,2-dioxasilinane

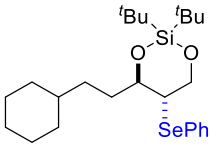
Compound 2a: Synthesized using the general procedure; single diastereomer; (pale yellow oil, 78% NMR yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.23 – 7.17 (m, 3H), 4.06 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.97 (t, *J* = 11.5 Hz, 1H), 3.90 (ddd, *J* = 10.7, 8.4, 2.4 Hz, 1H), 3.12 (ddd, *J* = 11.6, 10.7, 4.6 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.53 – 1.33 (m, 3H), 0.92 (s, 9H), 0.90 (s, 9H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.2, 129.3, 128.2, 127.2, 76.9, 69.1, 47.4, 39.0, 27.6, 27.1, 22.8, 19.9, 18.1, 14.0. IR 2957, 2934, 2860, 1473, 1141, 1073, 1022, 827, 787, 736, 650 cm^{-1}.; HRMS (APCI) m/z: [M+H$^+$] calculated for $C_{20}H_{35}O_2SeSi$ 415.1566, found 415.1563.



2b

2,2-di-*tert*-butyl-5-(phenylselanyl)-4-propyl-1,3,2-dioxasilinane

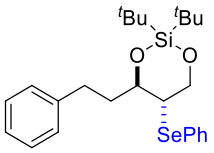
Compound 2b: Synthesized using the general procedure; single diastereomer; (pale yellow oil, 81% NMR yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.21 – 7.17 (m, 3H), 4.06 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.96 (t, *J* = 11.5 Hz, 1H), 3.88 (ddd, *J* = 10.7, 8.4, 2.4 Hz, 1H), 3.12 (ddd, *J* = 11.6, 10.8, 4.6 Hz, 1H), 2.08 – 1.91 (m, 1H), 1.49 – 1.42 (m, 1H), 1.20 (s, 14H), 0.92 (s, 9H), 0.90 (s, 9H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.2, 129.3, 128.2, 127.3, 77.3, 69.0, 47.5, 36.8, 32.1, 29.8, 29.7, 29.5, 27.6, 27.2, 24.8, 22.9, 22.8, 19.9, 14.3. IR 2929, 2854, 1575, 1473, 1136, 1101, 1044, 827, 787, 736, 690, 650 cm^{-1}.; HRMS (APCI) m/z: [M + H$^+$] calculated for $C_{26}H_{47}O_2SeSi$ 499.2511, found 499.2521.



2c

2,2-di-*tert*-butyl-4-(2-cyclohexylethyl)-5-(phenylselanyl)-1,3,2-dioxasilinane

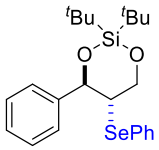
Compound 2c: Synthesized using the general procedure; single diastereomer; (pale yellow oil, 78% NMR yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.21 – 7.17 (m, 3H), 4.05 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.97 (t, *J* = 11.5 Hz, 1H), 3.85 (ddd, *J* = 10.8, 8.6, 2.3 Hz, 1H), 3.12 (ddd, *J* = 11.6, 10.8, 4.6 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.69 – 1.54 (m, 6H), 1.50 – 1.42 (m, 1H), 1.27 – 1.03 (m, 7H), 0.92 (s, 9H), 0.90 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.3, 129.3, 128.2, 127.3, 77.6, 69.1, 47.5, 37.5, 34.2, 33.9, 33.4, 32.6, 27.6, 27.2, 26.9, 26.6, 26.5, 22.89, 19.9. IR 2923, 2854, 1473, 1364, 1113, 1033, 964, 827, 782, 736, 690, 650 cm^{-1}.; HRMS (APCI) m/z: [M + H^{+}] calculated for $C_{25}H_{43}O_2SeSi$ 483.2198, found 483.2203.



2d

2,2-di-*tert*-butyl-4-phenethyl-5-(phenylselanyl)-1,3,2-dioxasilinane

Compound 2d: Synthesized using the general procedure; single diastereomer; (pale yellow oil, 60% NMR yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 1H), 7.22 – 7.13 (m, 9H), 4.08 (dd, *J* = 11.3, 4.4 Hz, 1H), 3.90 (t, *J* = 11.6 Hz, 1H), 3.86 – 3.80 (m, 1H), 3.09 (ddd, *J* = 11.8, 10.8, 4.5 Hz, 1H), 2.84 – 2.76 (m, 1H), 2.72 – 2.63 (m, 1H), 2.47 – 2.41 (m, 1H), 1.82 – 1.72 (m, 1H), 0.93 (s, 9H), 0.91 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.4, 129.3, 129.2, 128.8, 128.4, 128.2, 127.8, 125.8, 76.0, 68.9, 47.1, 38.7, 31.1, 27.5, 27.2, 22.8, 19.9. IR 2929, 2860, 1473, 1119, 1044, 976, 827, 787, 736, 696, 650 cm^{-1}; HRMS (APCI) m/z: [M + H^{+}] calculated for $C_{25}H_{37}O_2SeSi$ 477.1728, found 477.1725.



2e

2,2-di-*tert*-butyl-4-phenyl-5-(phenylselanyl)-1,3,2-dioxasilinane

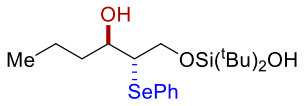
Compound 2e: Synthesized using the general procedure; single diastereomer; (pale yellow oil, 85% NMR yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.28 – 7.23 (m, 3H), 7.14 – 7.09 (m, 3H), 7.08 – 7.03 (m, 2H), 4.93 (d, *J* = 10.7 Hz, 1H), 4.22 – 4.07 (m, 2H), 3.45 – 3.37 (m, 1H), 1.00 (s, 9H), 0.98 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.2, 129.3, 129.0, 128.3, 128.2, 128.0, 127.8, 127.4, 80.9, 69.5, 49.2, 27.7, 27.3, 23.0, 20.2. IR 2934,

2860, 1473, 1273, 1261, 1101, 1033, 827, 747, 696, 650 cm^{-1}.; HRMS (APCI) m/z: [M + H^+] calculated for $C_{23}H_{33}O_2SeSi$ 449.1415, found 449.1413.

V. General Procedure for Hydroxyselenylation

An oven dried tube equipped with a magnetic stir bar was charged with allylic silanol (0.1 mmol) and 0.5 mL CH_2Cl_2. Next, sodium bicarbonate (0.1 mmol, 8 mg, 1.0 equiv.), *N*-(phenylseleno)phthalimide (0.15 mmol, 45 mg, 1.5 equiv.), and 0.5 mL CH_2Cl_2 were added sequentially (Final reaction concentration: 0.1 M). The mixture was stirred at room temperature and monitored by thin layer chromatography (TLC). After 6 h, the reaction mixture was diluted with 5 mL of CH_2Cl_2, transferred to a separatory funnel, and washed with water. The organic layer was separated, dried over $MgSO_4$, concentrated *in vacuo*, and purified by chromatography on Florisil (specific conditions are associated with each product).

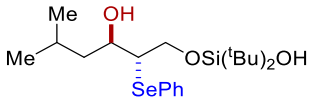
VI. Hydroxyselenylation Product Characterization (Scheme 4 Compounds)



4a

di-*tert*-butyl((3-hydroxy-2-(phenylselanyl)hexyl)oxy)silanol

Compound 4a: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 30 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 2H), 7.33 – 7.17 (m, 3H), 4.36 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.11 (dd, *J* = 11.1, 6.2 Hz, 1H), 3.93 (ddd, *J* = 9.0, 5.8, 3.4 Hz, 1H), 3.29 (td, *J* = 6.0, 3.7 Hz, 1H), 1.76 – 1.64 (m, 1H), 1.53 (dddt, *J* = 17.3, 8.9, 5.5, 4.3 Hz, 2H), 1.45 – 1.34 (m, 1H), 1.03 (s, 9H), 1.01 (s, 9H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.3, 129.2, 129.1, 127.6, 72.7, 64.7, 54.4, 37.1, 27.5, 27.4, 20.6, 20.4, 19.0, 13.9. IR 3374, 2957, 2854, 1473, 1096 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] Calculated for $C_{20}H_{35}O_2SeSi$ 415.1566, found 415.1587.

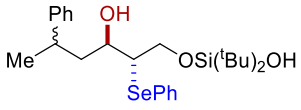


4b

di-*tert*-butyl((3-hydroxy-5-methyl-2 (phenylselanyl)hexyl)oxy)silanol

Compound 4b: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 33 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.36 – 7.23 (m, 3H), 4.38 (dd, *J* = 11.1, 3.8 Hz, 1H), 4.18 – 4.08 (m, 1H), 4.08 – 4.00 (m, 1H), 3.31 (td, *J* = 6.0, 3.8 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.58 – 1.43 (m, 2H), 1.06 (s, 9H), 1.04 (s, 9H), 0.93 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.3, 129.3, 129.1, 127.6, 70.8, 64.5, 55.2, 44.0, 27.5, 27.4, 24.7, 23.6, 21.6, 20.6, 20.4. IR 3385, 2957,

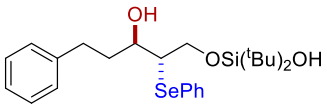
2860, 2358, 1473, 1096 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{21}H_{37}O_2SeSi$ 429.1723, found 429.1744.



4c

di-*tert*-butyl((3-hydroxy-5-phenyl-2-(phenylselanyl)hexyl)oxy)silanol

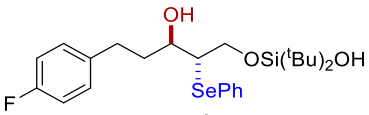
Compound 4c: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; ~1:1 mixture of diastereomers; (colorless oil, 30 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 4H), 7.32 – 7.15 (m, 16H), 4.38 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.32 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.16 – 4.10 (m, 1H), 4.07 (td, *J* = 5.8, 2.9 Hz, 1H), 4.01 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.62 (ddd, *J* = 10.4, 6.3, 2.4 Hz, 1H), 3.30 (td, *J* = 5.9, 3.7 Hz, 1H), 3.17 (td, *J* = 6.1, 3.6 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.12 – 2.02 (m, 1H), 1.98 (ddd, *J* = 13.9, 9.3, 3.5 Hz, 1H), 1.86 – 1.80 (m, 1H), 1.75 (ddd, *J* = 14.1, 10.3, 4.0 Hz, 1H), 1.32 – 1.23 (m, 6H), 1.05 (s, 9H), 1.03 (s, 9H), 0.97 (s, 9H), 0.93 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.7, 146.4, 134.4, 134.3, 129.4, 129.3, 129.2, 128.7, 128.6, 127.8, 127.7, 127.4, 127.0, 126.2, 126.1, 71.0, 70.6, 64.7, 64.6, 54.9, 54.8, 43.6, 43.5, 36.6, 36.2, 27.7, 27.6, 27.58, 27.51, 23.4, 21.2, 20.8, 20.7, 20.6, 20.5. IR 3391, 2940, 2860, 1473, 1261, 1016 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{26}H_{39}O_2SeSi$ 491.1879, found 491.1879.



4d

di-*tert*-butyl((3-hydroxy-5-phenyl-2-(phenylselanyl)pentyl)oxy)silanol

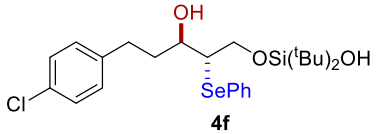
Compound 4d: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 32 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.34 – 7.25 (m, 5H), 7.20 (ddt, *J* = 6.9, 5.8, 1.5 Hz, 3H), 4.39 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.21 – 4.06 (m, 1H), 3.97 (ddd, *J* = 9.2, 6.2, 3.0 Hz, 1H), 3.32 (td, *J* = 6.2, 3.7 Hz, 1H), 2.90 (ddd, *J* = 14.3, 9.8, 5.0 Hz, 1H), 2.80 – 2.65 (m, 1H), 2.20 – 2.02 (m, 1H), 1.86 (dtd, *J* = 14.2, 9.4, 5.1 Hz, 1H), 1.04 (s, 9H), 1.02 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.9, 134.4, 129.2, 129.1, 128.5, 128.3, 127.7, 125.8, 72.2, 64.9, 54.1, 36.7, 32.0, 27.5, 27.4, 20.6, 20.4. IR 3397, 2946, 2854, 1473, 1022, 833 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{25}H_{37}O_2SeSi$ 477.1723, found 477.1741.



4e

di-*tert*-butyl((5-(4-fluorophenyl)-3-hydroxy-2-(phenylselanyl)pentyl)oxy)silanol

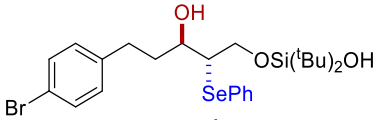
Compound 4e: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 33 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 2H), 7.35 – 7.22 (m, 3H), 7.14 (ddd, *J* = 8.7, 5.5, 2.6 Hz, 2H), 7.03 – 6.89 (m, 2H), 4.40 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.17 – 4.06 (m, 1H), 3.93 (ddd, *J* = 9.3, 6.3, 2.9 Hz, 1H), 3.30 (td, *J* = 6.3, 3.7 Hz, 1H), 2.86 (ddd, *J* = 14.2, 9.5, 5.0 Hz, 1H), 2.70 (ddd, *J* = 14.6, 9.5, 7.6 Hz, 1H), 2.12 – 2.01 (m, 1H), 1.83 (dtd, *J* = 14.1, 9.3, 5.0 Hz, 1H), 1.04 (s, 9H), 1.02 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.4 Hz), 137.6 (d, *J* = 2.8 Hz), 134.5, 130.0 (d, *J* = 7.0 Hz), 129.3, 129.1, 127.9, 115.2 (d, *J* = 20.9 Hz), 72.0, 65.0, 54.1, 36.8, 31.2, 27.6, 27.5, 20.7, 20.5. IR 3397, 2940, 2854, 1507, 1473, 1221, 1107 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{25}H_{36}FO_2SeSi$ 495.1628, found 495.1646.



4f

di-*tert*-butyl((5-(4-chlorophenyl)-3-hydroxy-2-(phenylselanyl)pentyl)oxy)silanol

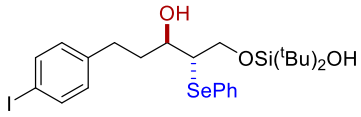
Compound 4f: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 37 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.36 – 7.16 (m, 5H), 7.13 – 7.06 (m, 2H), 4.37 (dd, *J* = 11.0, 3.7 Hz, 1H), 4.18 – 4.03 (m, 1H), 3.89 (ddd, *J* = 9.3, 6.4, 2.9 Hz, 1H), 3.26 (td, *J* = 6.4, 3.6 Hz, 1H), 2.82 (ddd, *J* = 14.1, 9.5, 4.9 Hz, 1H), 2.68 (ddd, *J* = 14.2, 9.3, 7.6 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.80 (dtd, *J* = 14.1, 9.2, 5.0 Hz, 1H), 1.01 (s, 9H), 0.99 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.4, 134.5, 131.6, 130.0, 129.3, 129.0, 128.5, 127.9, 72.0, 65.1, 54.1, 36.6, 31.4, 27.6, 27.5, 20.7, 20.5. IR 3391, 2940, 2860, 1473, 1090, 1016 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{25}H_{36}ClO_2SeSi$ 511.1333, found 511.1353.



4g

Compound 4g: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 39 mg, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.28 – 7.23 (m, 2H), 7.20 – 7.11 (m, 3H), 6.93 (d, *J* = 8.3 Hz, 2H), 4.25 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.77 (ddd, *J* = 9.4, 6.4, 2.8 Hz, 1H), 3.14 (td, *J* = 6.4, 3.6 Hz, 1H), 2.69 (ddd, *J* = 14.1, 9.4, 4.9 Hz, 1H), 2.60 – 2.50 (m, 1H), 1.96 – 1.87 (m, 1H), 1.68 (dtd, *J* = 14.0, 9.2, 4.9 Hz, 1H), 0.90 (s, 9H), 0.88 – 0.84 (m, 9H). ^{13}C{^{1}H}

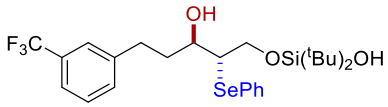
NMR (125 MHz, $CDCl_3$) δ 140.8, 134.4, 131.4, 130.3, 129.2, 128.9, 127.8, 119.5, 71.8, 64.9, 53.9, 36.4, 31.3, 27.5, 27.3, 20.6, 20.4. IR 3408, 2934, 2860, 1473, 1267, 1107 cm^{-1}.; HRMS (APCI) m/z: [$M–H_2O+H^+$] calculated for $C_{25}H_{36}BrO_2SeSi$ 555.0828, found 555.0854.



4h

di-*tert*-butyl((3-hydroxy-5-(4-iodophenyl)-2-(phenylselanyl)pentyl)oxy)silanol

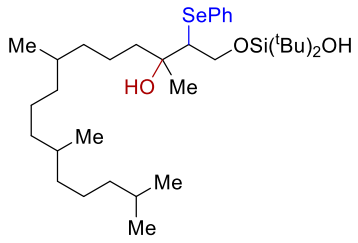
Compound 4h: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 44 mg, 71% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.47 (m, 4H), 7.34 – 7.19 (m, 3H), 6.99 – 6.86 (m, 2H), 4.36 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.09 (td, *J* = 11.7, 6.8 Hz, 1H), 3.87 (ddd, *J* = 9.3, 6.3, 2.8 Hz, 1H), 3.25 (td, *J* = 6.4, 3.7 Hz, 1H), 2.79 (ddd, *J* = 13.9, 9.3, 4.8 Hz, 1H), 2.72 – 2.56 (m, 1H), 2.08 – 1.97 (m, 1H), 1.79 (dtd, *J* = 14.1, 9.2, 5.0 Hz, 1H), 1.01 (s, 9H), 0.98 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 137.3, 134.4, 130.7, 129.2, 128.9, 127.8, 90.8, 71.8, 65.0, 53.9, 36.4, 31.4, 27.5, 27.4, 20.6, 20.4. IR 3397, 2946, 2860, 1473, 1101 cm^{-1}.; HRMS (APCI) m/z: [$M–H_2O+H^+$] calculated for $C_{25}H_{36}IO_2SeSi$ 603.0689, found 603.0710.



4i

di-*tert*-butyl((3-hydroxy-2-(phenylselanyl)-5-(3-(trifluoromethyl)phenyl)pentyl)oxy)silanol

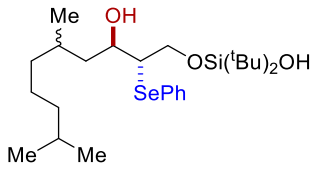
Compound 4i: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 34 mg, 60% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.51 – 7.36 (m, 4H), 7.34 – 7.24 (m, 3H), 4.42 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.13 (dd, *J* = 11.0, 6.3 Hz, 1H), 3.94 (ddd, *J* = 9.4, 6.6, 2.8 Hz, 1H), 3.30 (td, *J* = 6.4, 3.6 Hz, 1H), 2.93 (ddt, *J* = 17.5, 12.5, 6.3 Hz, 1H), 2.79 (ddd, *J* = 13.8, 9.4, 7.1 Hz, 1H), 2.17 – 2.06 (m, 1H), 1.86 (dtd, *J* = 14.2, 9.4, 4.9 Hz, 1H), 1.04 (s, 9H), 1.01 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.8, 134.4, 131.9, 130.6 (q, *J* = 31.8 Hz), 129.2, 128.9, 128.7, 127.8, 125.6 (q, *J* = 270 Hz), 125.3 – 125.1 (m), 122.8 – 122.6 (m), 71.9, 65.0, 53.9, 36.4, 31.7, 27.5, 27.4, 20.6, 20.4. IR 3391, 2934, 2860, 1478, 1330, 1130 cm^{-1}.; HRMS (APCI) m/z: [$M–H_2O+H^+$] calculated for $C_{26}H_{36}F_3O_2SeSi$ 545.1602, found 545.1625.



4j

di-*tert*-butyl((3-hydroxy-3,7,11,15-tetramethyl-2 (phenylselanyl)hexadecyl)oxy)silanol

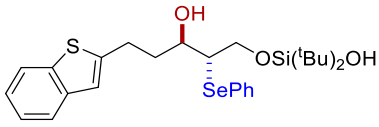
Compound 4j: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; mixture of diastereomers; (colorless oil, 18 mg, 30% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.54 (m, 2H), 7.37 – 7.18 (m, 3H), 4.37 – 4.25 (m, 2H), 3.36 – 3.27 (m, 1H), 1.78 – 1.08 (m, 24H), 1.06 (s, 9H), 1.01 (s, 9H), 0.93 – 0.82 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.2, 129.9, 129.2, 127.6, 75.3, 65.6, 57.3, 41.9, 39.3, 37.6, 37.5, 37.48, 37.46, 37.3, 32.8, 32.7, 27.9, 27.4, 25.1, 24.8, 24.52, 24.51, 22.7, 22.6, 20.9, 20.5, 20.4, 19.7. IR 3408, 2929, 2860, 1467, 1376, 827 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{34}H_{63}O_2SeSi$ 611.3757, found 611.3786.



4k

di-*tert*-butyl((3-hydroxy-5,9-dimethyl-2-(phenylselanyl)decyl)oxy)silanol

Compound 4k: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; mixture of diastereomers; (colorless oil, 33 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 2H), 7.34 – 7.25 (m, 3H), 4.39 (ddd, *J* = 11.1, 3.7, 1.0 Hz, 1H), 4.17 – 4.01 (m, 2H), 3.34 – 3.26 (m, 1H), 1.72 – 1.11 (m, 10H), 1.05 (m, 18H), 0.94 – 0.85 (m, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.4, 134.3, 129.4, 129.2, 127.7, 71.0, 70.6, 64.6, 64.4, 55.4, 55.1, 42.5, 42.3, 39.4, 39.3, 38.2, 36.3, 29.8, 29.3, 28.0, 27.9, 27.6, 27.5, 27.4, 24.7, 24.5, 22.8, 22.7, 22.6, 22.5, 20.6, 20.5, 20.4, 19.0. IR 3391, 2934, 2860, 1473, 1107, 827 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{26}H_{47}O_2SeSi$ 499.2511, found 499.2521.

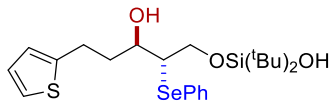


4l

((5-(benzo[*b*]thiophen-2-yl)-3-hydroxy-2-(phenylselanyl)pentyl)oxy)di-*tert*-butylsilanol

Compound 4l: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 36 mg, 68% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz,

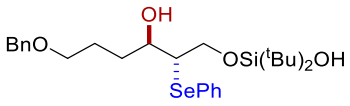
1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.58 (dt, *J* = 7.0, 1.5 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 – 7.21 (m, 4H), 7.03 (s, 1H), 4.43 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.15 (dd, *J* = 11.3, 6.4 Hz, 1H), 4.03 (ddd, *J* = 9.6, 6.4, 2.9 Hz, 1H), 3.32 (td, *J* = 6.3, 3.6 Hz, 1H), 3.17 (ddd, *J* = 14.4, 9.1, 5.1 Hz, 1H), 3.06 (dt, *J* = 15.4, 8.1 Hz, 1H), 2.25 (dddd, *J* = 13.8, 9.0, 7.6, 2.8 Hz, 1H), 1.97 (dtd, *J* = 13.9, 9.1, 5.0 Hz, 1H), 1.03 (s, 9H), 1.01 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.7, 140.2, 139.4, 134.4, 129.2, 128.9, 127.7, 124.0, 123.4, 122.7, 122.1, 121.0, 71.9, 65.0, 53.9, 36.3, 27.4, 27.3, 27.0, 20.6, 20.4. IR 3402, 2934, 2860, 1473, 1107, 827 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O] calculated for $C_{27}H_{36}O_2SSeSi$ 532.1370, found 532.1406.



4m

di-*tert*-butyl((3-hydroxy-2-(phenylselanyl)-5-(thiophen-2-yl)pentyl)oxy)silanol

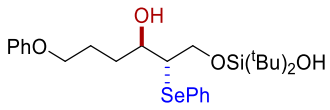
Compound 4m: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 19.1 mg, 38% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.21 – 7.17 (m, 3H), 7.03 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.82 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.72 – 6.68 (m, 1H), 4.31 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.03 (dd, *J* = 11.1, 6.2 Hz, 1H), 3.93 – 3.87 (m, 1H), 3.25 – 3.16 (m, 1H), 3.04 – 2.95 (m, 1H), 2.91 – 2.81 (m, 1H), 2.12 – 2.02 (m, 1H), 1.85 – 1.74 (m, 1H), 0.94 (s, 9H), 0.92 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.8, 134.5, 129.3, 127.8, 126.8, 124.5, 123.1, 72.1, 64.9, 54.1, 37.1, 27.6, 27.5, 26.3, 20.7, 20.5. IR 3380, 2929, 2854, 1473, 1107, 827, 690 cm^{-1}.; HRMS (APCI) m/z: [M–H] calculated for $C_{23}H_{35}O_3SSeSi$ 499.1241, found 499.1230.



4n

((6-(benzyloxy)-3-hydroxy-2-(phenylselanyl)hexyl)oxy)di-*tert*-butylsilanol

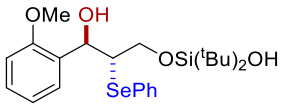
Compound 4n: Synthesized using the general procedure; Purified using a gradient of 0 to 40% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 37 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 2H), 7.41 – 7.24 (m, 8H), 4.53 (s, 2H), 4.40 (dd, *J* = 11.0, 3.6 Hz, 1H), 4.19 – 4.09 (m, 1H), 4.00 (ddd, *J* = 9.2, 6.3, 3.0 Hz, 1H), 3.58 – 3.45 (m, 2H), 3.32 (td, *J* = 6.1, 3.6 Hz, 1H), 1.97 (dddd, *J* = 13.6, 8.3, 6.7, 3.1 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.77 – 1.68 (m, 1H), 1.68 – 1.50 (m, 1H), 1.05 (s, 9H), 1.04 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 138.1, 134.3, 129.4, 129.1, 128.4, 127.7, 127.65, 127.60, 72.9, 72.4, 70.1, 64.5, 54.5, 31.8, 27.6, 27.5, 26.1, 20.6, 20.5. IR 3397, 2934, 2866, 1473, 1101, 833 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{27}H_{41}O_3SeSi$ 521.1985, found 521.2015.



4o

di-*tert*-butyl((3-hydroxy-6-phenoxy-2-(phenylselanyl)hexyl)oxy)silanol

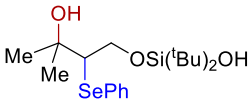
Compound 4o: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 38 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.34 – 7.25 (m, 5H), 6.97 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.94 – 6.87 (m, 2H), 4.42 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.22 – 4.11 (m, 1H), 4.02 (dddd, *J* = 14.6, 12.3, 6.8, 4.0 Hz, 3H), 3.34 (td, *J* = 6.2, 3.6 Hz, 1H), 2.03 (ddt, *J* = 13.1, 8.8, 2.6 Hz, 2H), 1.99 – 1.85 (m, 1H), 1.74 – 1.59 (m, 1H), 1.05 (s, 9H), 1.04 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.9, 134.4, 129.4, 129.2, 129.1, 127.7, 120.6, 114.5, 72.6, 67.6, 64.8, 54.2, 31.5, 27.5, 27.4, 25.7, 20.6, 20.5. IR 3397, 2934, 2860, 1495, 1238, 827 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{26}H_{39}O_3SeSi$ 507.1828, found 507.1837.



di-*tert*-butyl(3-hydroxy-3-(2-methoxyphenyl)-2-(phenylselanyl)propoxy)silanol

4p

Compound 4p: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 36 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.23 – 7.12 (m, 4H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.72 – 6.65 (m, 1H), 5.22 (d, *J* = 6.5 Hz, 1H), 4.41 (dd, *J* = 10.9, 2.6 Hz, 1H), 4.16 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.61 (s, 3H), 1.08 (s, 9H), 1.06 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.5, 134.5, 130.0, 129.6, 128.8, 128.74, 128.72, 127.2, 120.6, 110.4, 73.6, 64.4, 55.0, 52.7, 27.7, 27.6, 20.8, 20.7. IR 3425, 2929, 2854, 1490, 1467, 1438, 1238, 1107, 1073, 1027, 827, 742 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{24}H_{35}O_3SeSi$ 479.1515, found 479.1516.

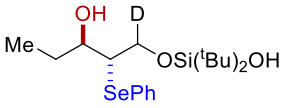


4q

di-*tert*-butyl(3-hydroxy-3-methyl-2-(phenylselanyl)butoxy)silanol

Compound 4q: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; (white solid, 31 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 2H), 7.32 – 7.21 (m, 3H), 4.35 (dd, *J* = 11.3, 3.8 Hz, 1H), 4.25 (dd, *J* = 11.3, 6.7 Hz, 1H), 3.26 (dd, *J* = 6.7, 3.8 Hz, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 1.04 (s, 9H), 1.00 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.2, 130.2, 129.3, 127.7, 73.7, 66.0, 59.7, 29.3,

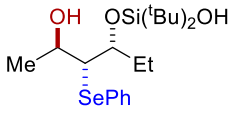
27.5, 20.6, 20.5. IR 3391, 2934, 2860, 1473, 1072 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{19}H_{33}O_2SeSi$ 401.1410, found 401.1427.



4r

di-*tert*-butyl((3-hydroxy-2-(phenylselanyl)pentyl-1-*d*)oxy)silanol

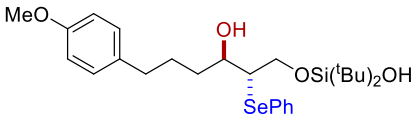
Compound 4r: Synthesized using the general procedure; Purified using a gradient of of 0 to 30% EtOAc/hexanes on Florisil; ~1:1 mixture of diastereomers; (colorless oil, 25 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.48 (m, 4H), 7.33 – 7.20 (m, 6H), 4.35 (d, *J* = 3.6 Hz, 1H), 4.11 (dd, *J* = 10.5, 6.6 Hz, 1H), 3.84 (ddd, *J* = 8.6, 6.1, 3.6 Hz, 2H), 3.29 (td, *J* = 5.3, 1.4 Hz, 2H), 1.86 – 1.66 (m, 2H), 1.63 – 1.49 (m, 2H), 1.01 (m, 42H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 134.4, 129.4, 129.3, 127.8, 74.6, 64.6 (dd, *J* = 22.3, 14.8 Hz), 53.9, 53.8, 28.0, 27.6, 27.5, 20.7, 20.6, 10.3. IR 3385, 2934, 2860, 1461, 827 cm^{-1}.; HRMS (APCI) m/z: [M + H^+] calculated for $C_{19}H_{32}DO_2SeSi$ 402.1472, found 402.1482.



4s

di-*tert*-butyl((5-hydroxy-4-(phenylselanyl)hexan-3-yl)oxy)silanol

Compound 4s: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (crystalline solid, 16 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.32 – 7.21 (m, 3H), 4.35 (ddd, *J* = 9.4, 4.1, 1.2 Hz, 1H), 4.08 (p, *J* = 6.4 Hz, 1H), 3.12 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.26 – 2.13 (m, 1H), 1.80 – 1.72 (m, 1H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.06 (s, 9H), 1.04 (s, 9H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 134.0, 132.4, 130.1, 127.7, 74.0, 70.0, 61.3, 29.9, 28.2, 28.0, 22.8, 21.5, 21.4, 10.6.; IR 3334, 2940, 2860, 1473, 1061, 827 cm^{-1}.; HRMS (APCI) m/z: [M–H_2O+H^+] calculated for $C_{20}H_{35}O_2SeSi$ 415.1566, found 415.1583.

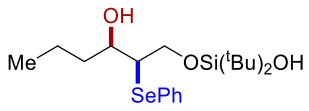


4t

di-*tert*-butyl((3-hydroxy-6-(4-methoxyphenyl)-2 (phenylselanyl)hexyl)oxy)silanol

Compound 4t: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 36 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 2H), 7.35 – 7.23 (m, 3H), 7.13 – 7.06 (m, 2H), 6.88 – 6.80 (m, 2H), 4.38 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.12 (dd, *J* = 11.1, 6.1 Hz, 1H), 3.97 (ddd, *J* = 8.7, 6.0, 3.1 Hz, 1H), 3.81 (s, 3H), 3.29 (td, *J* = 6.0, 3.6 Hz, 1H), 2.61 – 2.51 (m, 2H), 1.89 –

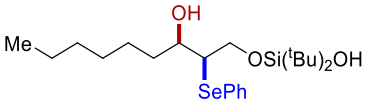
1.71 (m, 2H), 1.71 – 1.62 (m, 1H), 1.62 – 1.49 (m, 1H), 1.05 (s, 9H), 1.03 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.7, 134.4, 129.3, 129.23, 129.20, 127.7, 113.7, 72.9, 64.7, 55.2, 54.2, 34.7, 34.4, 27.8, 27.5, 27.4, 20.6, 20.4. IR 3408, 1513, 1473, 1244, 1033, 827 cm^{-1}.; HRMS (APCI) m/z: [$M–H_2O+H^+$] calculated for $C_{27}H_{41}O_3SeSi$ 521.1990, found 521.2012.



4u

di-*tert*-butyl((3-hydroxy-2-(phenylselanyl)hexyl)oxy)silanol

Compound 4u: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 30 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.29 – 7.18 (m, 3H), 4.25 – 4.02 (m, 3H), 3.26 (ddd, *J* = 7.6, 4.3, 2.6 Hz, 1H), 1.75 (dddd, *J* = 13.4, 9.7, 8.1, 5.2 Hz, 1H), 1.61 (dddd, *J* = 13.5, 9.5, 6.2, 5.0 Hz, 1H), 1.46 (dddd, *J* = 12.8, 9.7, 7.4, 5.4 Hz, 1H), 1.40 – 1.27 (m, 1H), 1.02 (s, 9H), 1.01 (s, 9H), 0.90 (t, *J* = 7.3 Hz, 3H).; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 134.4, 129.6, 129.3, 127.6, 71.6, 65.9, 55.5, 37.8, 27.7, 27.6, 20.8, 20.6, 19.2, 14.1. IR 3397, 2934, 2860, 1473, 827 cm^{-1}.; HRMS (APCI) m/z: [$M–H_2O+H^+$] calculated for $C_{20}H_{35}O_2SeSi$ 415.1566, found 415.1590.

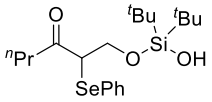


4v

di-*tert*-butyl((3-hydroxy-2-(phenylselanyl)nonyl)oxy)silanol

Compound 4v: Synthesized using the general procedure; Purified using a gradient of 0 to 30% EtOAc/hexanes on Florisil; single diastereomer; (colorless oil, 33 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.19 (m, 3H), 4.15 (dd, *J* = 10.8, 7.7 Hz, 1H), 4.10 (dd, *J* = 10.8, 4.2 Hz, 1H), 3.99 (ddd, *J* = 7.9, 5.3, 2.6 Hz, 1H), 3.21 (dt, *J* = 7.2, 3.1 Hz, 1H), 1.68 (dtd, *J* = 13.5, 8.7, 5.0 Hz, 1H), 1.58 (ddt, *J* = 14.7, 10.1, 5.1 Hz, 1H), 1.35 (m, 1H), 1.28 – 1.09 (m, 7H), 0.96 (s, 9H), 0.95 (s, 9H), 0.80 (t, *J* = 6.7 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 134.2, 129.4, 129.1, 127.5, 71.8, 65.8, 55.4, 35.6, 31.7, 29.1, 27.6, 27.4, 25.8, 22.6, 20.7, 20.4, 14.0. IR 3397, 2934, 2871, 1473, 1090, 827 cm^{-1}.; HRMS (APCI) m/z: [$M–H_2O+H^+$] calculated for $C_{23}H_{41}O_2SeSi$ 457.2041, found 457.2060.

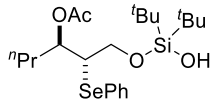
VII. Derivatization Reactions (Scheme 7)



8

1-((di-*tert*-butyl(hydroxy)silyl)oxy)-2-(phenylselanyl)hexan-3-one

An oven dried tube with a magnetic stir-bar was charged with compound **4a** (0.1 mmol, 43 mg, 1.0 equiv.) and CH_2Cl_2 (2 mL). The solution was cooled to -10 °C using a cryogenic cooler, and Dess-Martin periodinane (0.12 mmol, 51 mg, 1.2 equiv.) was added in one portion. The suspension was stirred for 15 minutes at -10 °C, and then allowed to warm to 0 °C. After 3 h at 0 °C, the reaction mixture was diluted with CH_2Cl_2 and filtered through a short pad of celite. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography (gradient of 2-5% ethyl acetate/hexanes) to afford **8** as a colorless oil (22 mg, 0.051 mmol, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.39 – 7.27 (m, 3H), 4.24 (t, *J* = 10.5 Hz, 1H), 4.05 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.83 (dd, *J* = 10.3, 4.3 Hz, 1H), 2.79 (dt, *J* = 17.1, 7.4 Hz, 1H), 2.49 (dt, *J* = 17.2, 7.1 Hz, 1H), 1.70 – 1.53 (m, 2H), 1.01 – 0.87 (m, 21H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.0, 135.5, 129.4, 129.0, 127.2, 62.8, 51.6, 43.8, 27.6, 27.3, 20.8, 20.3, 17.4, 13.9. IR 3499, 2963, 2934, 2860, 1695, 1473, 1364, 1107, 1084, 1016, 856, 827, 742, 690, 650 cm^{-1}.; HRMS (APCI) m/z: [M+H$^+$] calculated for $C_{20}H_{35}O_3SeSi$ 431.1521, found 431.1507.



9

1-((di-*tert*-butyl(hydroxy)silyl)oxy)-2-(phenylselanyl)hexan-3-yl acetate

A solution of compound **4a** (0.1 mmol, 43 mg, 1 equiv.) in CH_2Cl_2 (1 mL) was cooled to 0 °C using an ice-water bath. Pyridine (1.0 mmol, 82 µL, 10 equiv.), acetic anhydride (0.5 mmol, 47 µL, 5 equiv.) and DMAP (catalytic, ~1.0 mg) were sequentially added. The mixture was stirred at 0 °C for 3 h. Next, the reaction mixture was diluted with 5 mL CH_2Cl_2, transferred to a separatory funnel, and washed with water. The organic layer was collected and concentrated after drying over Na_2SO_4. The residue was purified by silica gel column chromatography (gradient of 2-5% ethyl acetate/hexanes) to afford **9** (colorless oil, 46 mg, 0.096 mmol, 96% yield)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.21 – 7.14 (m, 3H), 5.25 (ddd, *J* = 9.1, 5.6, 3.2 Hz, 1H), 4.08 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.96 (dd, *J* = 11.0, 7.4 Hz, 1H), 3.46 (ddd, *J* = 7.3, 5.6, 4.3 Hz, 1H), 1.89 (s, 3H), 1.75 – 1.54 (m, 2H), 1.33 – 1.14 (m, 2H), 0.95 (s, 9H), 0.93 (s, 9H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 134.4, 129.6, 129.2, 127.7, 74.2, 64.2, 52.0, 33.4, 27.7, 27.5, 21.1, 20.6, 20.5, 18.9, 13.8. IR 3505, 2963, 2934, 2860, 1712, 1473, 1370, 1256, 1101, 1022, 827, 742, 690, 645 cm^{-1}.; HRMS (APCI) [M$^+$] calculated for $C_{22}H_{38}O_4SeSi$ 474.1705, found 474.1702.

Associated Content

Copies of ^{1}H and ^{13}C NMR spectra of new compounds, crystallographic data, further experimental details

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