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Silylene Transfer to Allylic Sulfides: Formation of Substituted Silacyclobutanes

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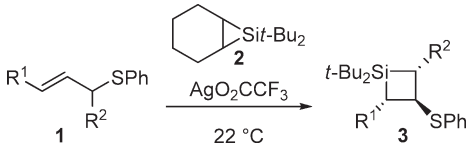
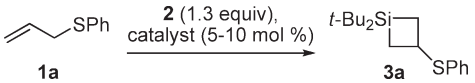


Silylene transfer to allylic sulfides results in a formal 1,2-sulfide migration. The rearrangement yields substituted silacyclobutanes, not the expected silacyclopropanes. The silacyclobutanes were elaborated by insertions of carbonyl compounds selectively into one carbon−silicon bond. A mechanism for the 1,2-sulfide migration is proposed involving an episulfonium ion intermediate.

Silacyclobutanes are unique strained-ring compounds[1] that have been used in a variety of chemical applications, including ring-opening polymerization.[2] These silanes are synthesized conventionally by intramolecular Wurtz-type coupling[3−6] or [2+2] cycloaddition reactions,[7,8] making additional synthetic routes desirable. Unlike three-membered-ring silanes, silacyclobutanes are often air stable, which facilitates their handling and manipulation.[9] Carbonyl insertions with strained silacyclobutanes provide a variety of synthetically useful transformations.[6,10−13]

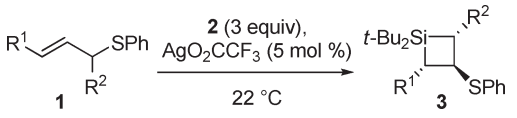
TABLE 1. Metal Catalysts Utilized for Silylene Transfer to Allylic Sulfide 1a



entry	catalyst	*T* (°C)	yield (%)[a]
1	AgO_2CCF_3	22	72
2	AgOTf	22	61
3	Ag_3PO_4	22	70
4	$(CuOTf)_2 \cdot PhMe$	22	42
5	CuBr	22	63
6	CuI	22	35
7	$AuBr_3$	22	58
8	none	70	43

[a]As determined by ^{1}H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$).

TABLE 2. Silylene Transfer to Substituted Allylic Sulfides



entry	substrate	R^1	R^2	product	dr[a,b]	yield (%)[a]
1	**1b**	H	Me	**3b**	92:8	41
2	**1c**	H	*i*-Pr	**3c**	100:0	17
3	**1d**	Me	H	**3d**	86:14	55
4	**1e**	Me	Me	**3e**	66:34	19[c]

[a]As determined by ^{1}H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$). [b]Relative stereochemistry was determined by NOE analysis of the products. Details are provided as Supporting Information. [c]Five equivalents of cyclohexene silacyclopropane **2** were required for this reaction to proceed to completion.[20]

In the course of exploring silylene transfer reactions, we discovered that our silylene transfer conditions[14−16] provided a synthesis of four-membered-ring silanes when applied to allylic sulfides (Table 1). In contrast to metal-catalyzed silylene insertion reactions with allylic ethers,[17,18] no carbon−sulfur bond insertion products were observed. Instead, the products resulted from formal 1,2-sulfur migration.[19] A variety of metal salts catalyzed the silylene transfer reaction at ambient temperature in moderate yields. AgO_2CCF_3 was found to be the optimal catalyst (entry 1). Silylene transfer with silacyclobutane formation occurred in the absence of catalyst, but elevated temperatures were required (entry 8).

The reaction was general for a variety of substituted allylic sulfides, although yields were lower (Table 2). Silylene transfer to α-methyl-substituted allylic sulfide **1b** afforded silacyclobutane *trans*-**3b** with high diastereoselectivity (entry 1).

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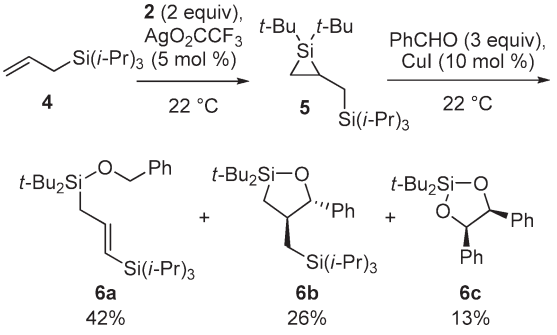
An increase in steric hindrance at the α position was observed to increase diastereoselectivity in the reaction, but resulted in low yield of the desired silacyclobutane (entry 2). Silylene transfer to crotyl sulfide **1d** gave silacyclobutane *trans*-**3d** with lower diastereoselectivity (entry 3). When the reaction was attempted with α-methyl substituted crotyl sulfide **1e**, product **3e** was obtained in low yield and with low diastereoselectivity (entry 4).

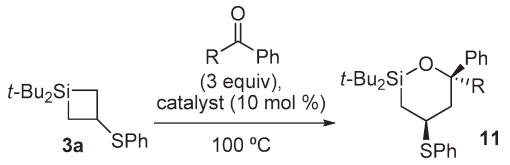
To assess if other functional groups could undergo 1,2-migration,[21−23] the silylene transfer conditions were applied to allylic silane **4** and allyl bromide. Silylene transfer to allylic silane **4** did not provide 1,2-silyl migration and afforded silacyclopropane **5**, which was subjected to the two-step, one-flask carbonyl insertion reaction[24] to afford a mixture of products **6a**−**c** (Scheme 1). Allylic silane **6a** can result from hydrogen atom transfer processes,[25,26] and dioxasilacyclopentane **6c** is the product of silylene transfer to 2 equiv of benzaldehyde.[27,28] The same conditions with allyl bromide resulted in decomposition of the starting materials.

SCHEME 1. Silylene Transfer to an Allylic Silane



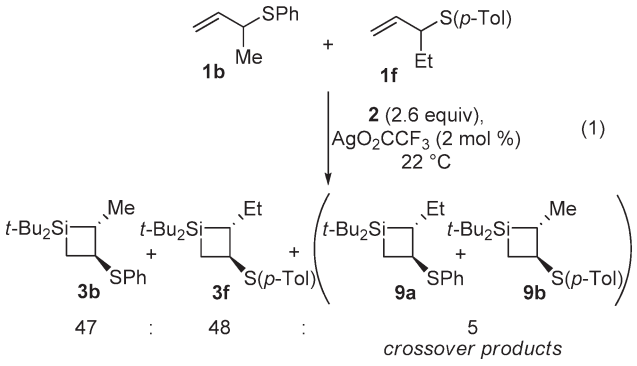
A crossover experiment was performed with allylic sulfides **1b** and **1f** to provide insight into the mechanism for the allylic sulfide rearrangement (eq 1). Only trace amounts of crossover products were observed, indicating that the 1,2-sulfide migration occurs through a stepwise mechanism in which fragments largely combine intramolecularly. The likely mechanism involves episulfonium ion formation[29−33] with the electrophilic silylenoid[15,34,35] to give intermediate **10**. The silver-bound silyl species could open the episulfonium ion concurrent to four-membered ring closure to afford silacyclobutane **3** (Scheme 2). The trace crossover products could arise from loss and recombination of the sulfide group on intermediate **10**.[36]

TABLE 3. Carbonyl Insertion Reactions with Silacyclobutane 3a

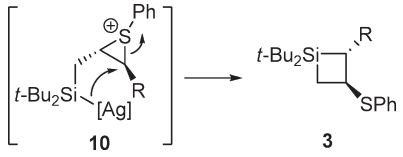


entry	R	catalyst	product	yield (%)[a]	dr[a]
1	H	$(CuOTf)_2 \cdot PhMe$	**11a**	68	100:0
2	H	ZnI_2	**11a**	70	100:0
3	H	$Zn(OTf)_2$	**11a**	70	100:0
4	Me	ZnI_2	**11b**	63	96:4

[a]As determined by ^1H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$).



SCHEME 2. Episulfonium Ion Formation in the 1,2-Sulfide Migration Mechanism



Carbonyl insertion reactions were performed with silacyclobutane **3a** to afford oxasilacyclohexanes as single diastereomers (Table 3).[6,11−13] Various metal catalysts were employed in the insertion reaction with silacyclobutane **3a**, and zinc catalysts were observed to be optimal (entry 2). No reaction was observed in the absence of catalyst. Benzaldehyde and acetophenone were competent in the insertion reaction, but both linear and branched aliphatic aldehydes and ketones were not.[25] The observed diastereoselectivity could occur to minimize the unfavorable 1,3-diaxial interaction that would arise between the phenyl group of the carbonyl and a *tert*-butyl group on silicon.

(20) Silacyclobutanes *trans*-**3e** and *cis*-**3e** were the only identifiable products of this reaction. Details are provided as Supporting Information.

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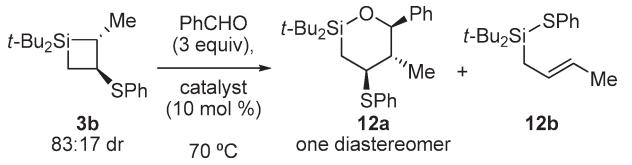
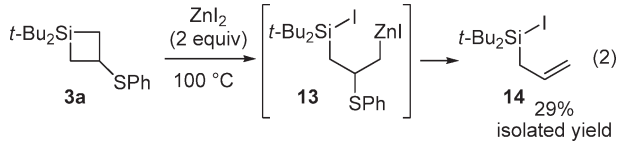
TABLE 4. Carbonyl Insertion Reactions with Silacyclobutane 3b



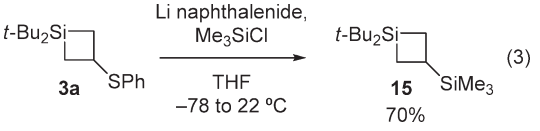
entry	catalyst	yield **12a** (%)[a]
1	$(CuOTf)_2 \cdot PhMe$	25
2	ZnI_2	35
3	$Zn(OTf)_2$	29

[a]As determined by ^1H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$).

The increased ring substitution on silacyclobutane **3b** decreased the efficiency of the carbonyl insertion reaction (Table 4). The most competent catalyst in the benzaldehyde insertion reaction was ZnI_2. The yield was moderate, however, and isolation of the product proved difficult due to the significant number of unidentifiable decomposition products. Carbonyl insertion occurred into the more substituted carbon−silicon bond in moderate yield to afford oxasilacyclohexane **12a** as a single diastereomer. Allyl silane **12b** was observed as a minor product resulting from metal-mediated rearrangement of the starting material.[37] The regiochemistry is in contrast to that observed for analogous zinc-catalyzed carbonyl insertions into silacyclopropanes.[38] The formation of allylic silane **14** from silacyclobutane **3a** in the absence of aldehyde supports the existence of transmetalation intermediate **13** (eq 2). The regioselectivity of this reaction is analogous to the copper-mediated transmetalation observed for silacyclopropanes.[39,40]



To increase the general utility of the 1,1-di-*tert*-butyl-3-thiophenyl-1-silacyclobutanes, lithiation reactions were performed to see if the sulfide moiety could be functionalized selectively. Silacyclobutane **3a** underwent lithium−sulfide exchange[41−45] followed by trapping with chlorotrimethylsilane to afford silacyclobutane **15** (eq 3). Silacyclobutane **15** did not undergo carbonyl insertion when subjected to the zinc-catalyzed conditions.[46]



In conclusion, metal-catalyzed silylene transfer conditions were utilized in a rearrangement reaction with allylic sulfides to afford silacyclobutanes. The resulting four-membered-ring compounds were subjected to carbonyl insertion reaction conditions to afford substituted oxasilacyclohexanes. A mechanism for the 1,2-sulfide migration was proposed utilizing a sulfonium ion intermediate.

Experimental Section

Silylene Transfer to Allylic Sulfides (Procedure A). Silacyclobutane 3a. To a solution of allylic sulfide **1a** (5.00 g, 33.3 mmol) in toluene (140 mL) was added cyclohexene silacyclopropane **2**[15,47] (8.96 g, 39.9 mmol) and AgO_2CCF_3 (0.073 g, 0.33 mmol). The reaction mixture was stirred overnight, filtered through a pad of SiO_2 with hexanes to remove residual catalyst, and concentrated in vacuo. Purification by column chromatography (hexanes) afforded silacyclobutane **3a** as a white solid (6.2 g, 64%): mp 36−38 °C; ^1H NMR (400 MHz, C_6D_6) δ 7.40 (d, J = 7.2 Hz, 2H), 7.10 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 3.88 (quint, J = 9.2 Hz, 1H), 1.57−1.50 (m, 2H), 1.32−1.25 (m, 2H), 0.93 (s, 9H), 0.92 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 130.0, 128.7, 125.8, 37.8, 28.0, 27.8, 19.3, 18.9, 18.7; ^{29}Si NMR (99.3 MHz, $CDCl_3$) δ 18.9; IR (thin film) 3082, 3059, 2935, 2854, 1583, 1464 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{17}H_{29}SSi$ $(M + H)^+$ 293.1759, found 293.1759. Anal. Calcd for $C_{17}H_{28}SSi$: C, 69.79; H, 9.65. Found: C, 69.89; H, 9.65.

Silacyclobutane 3b. Procedure A was employed using allylic sulfide **1b** (4.01 g, 24.4 mmol), AgO_2CCF_3 (0.53 g, 2.4 mmol), and cyclohexene silacyclopropane **2**[15,47] (16.4 g, 73.1 mmol). Purification by column chromatography (hexanes) afforded a mixture of silacyclobutanes *trans*-**3b** and *cis*-**3b** (83:17 dr) as a pale yellow oil (1.0 g, 15%). **Silacyclobutane *trans*-3b:** ^1H NMR (400 MHz, C_6D_6) δ 7.53 (d, J = 7.1 Hz, 2H), 7.08 (t, J = 7.4 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 3.51 (dt, J = 10.6, 9.8 Hz, 1H), 1.66 (dq, J = 11.3, 7.3 Hz, 1H), 1.54 (dd, J = 14.6, 8.9 Hz, 2H), 1.26 (d, J = 7.4 Hz, 3H), 0.98 (s, 9H), 0.85 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 136.4, 132.57, 128.6, 126.4, 48.4, 29.3, 28.4, 28.1, 19.8, 19.5, 18.2, 14.5; ^{29}Si NMR (119.2 MHz, C_6D_6) 17.1; IR (neat) 3059, 2931, 2858, 1583, 1471, 1265 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{18}H_{31}SSi$ $(M + H)^+$ 307.1916, found 307.1912. **Silacyclobutane *cis*-3b:** ^1H NMR (400 MHz, C_6D_6, distinctive peaks) δ 7.34 (d, J = 7.3 Hz, 2H), 4.19 (q, J = 9.7 Hz, 1H), 2.14−2.05 (m, 1H), 1.37 (d, J = 8.2 Hz, 3H), 1.01 (s, 9H), 0.96 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6, distinctive peaks) δ 135.3, 132.56, 128.7, 124.7, 42.9, 28.7, 28.0, 17.2, 12.9.

Silacyclobutane 3c. Procedure A was employed using allylic sulfide **1c** (0.55 mL, 0.24 M in C_6D_6, 0.13 mmol), AgO_2CCF_3 (0.001 g, 0.005 mmol), and cyclohexene silacyclopropane **2**[15,47] (0.085 g, 0.38 mmol). After 24 h, the reaction had afforded silacyclobutane **3c** as a single diastereomer in 17% yield as determined by ^1H NMR spectroscopy relative to an internal standard ($PhSiMe_3$) using a single scan: ^1H NMR (400 MHz, C_6D_6, distinctive peaks) δ 3.57 (q, J = 9.5 Hz, 1H), 0.94 (s, 9H), 0.88 (s, 9H); LRMS (GC-MS) R_t = 19.3 min; m/z calcd for $C_{20}H_{34}SSi$ $(M)^+$ 334.22, found 334.17; m/z calcd for $C_{16}H_{25}SSi$ $(M - C_4H_9)^+$ 277.14, found 277.19.

(37) Allyl silane **12b** was isolated in 6% yield when the reaction was performed on preparative scale, although it was present in such small amounts that it was not observed by ^1H NMR spectroscopic analysis of the unpurified reaction mixture.

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(40) The thiophenyl silane analogue of compound **14** was observed as a minor product due to rearrangement of the starting material . Details are provided as Supporting Information.

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(46) The lithiation reaction with silacyclobutane **3a** suffered from irreproducibility. Attempts to trap the alkyllithium intermediate with a carbon electrophile were unsuccessful, as were attempts to lithiate the sulfide functionality on oxasilacyclohexane **11a**.

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Silacyclobutane 3d (same as compound 3b). Procedure A was employed using crotyl sulfide **1d** (0.62 g, 3.7 mmol), cyclohexene silacyclopropane **2**[15,47] (2.53 g, 11.3 mmol), and AgO_2CCF_3 (0.038 mg, 0.19 mmol). Purification by column chromatography (hexanes—1:99 EtOAc/hexanes) afforded silacyclobutanes *trans*-**3d** and *cis*-**3d** (80:20 dr) as a colorless oil (0.28 g, 24%). Full characterization data were reported for silacyclobutane **3b**, vide supra.

Silacyclobutane 3e. Procedure A was employed using crotyl sulfide **1e** (0.372 g, 2.09 mmol), cyclohexene silacyclopropane **2**[15,47] (2.36 g, 10.5 mmol), and AgO_2CCF_3 (0.023 g, 0.10 mmol). The crude mixture contained a mixture of silacyclobutanes *trans*-**3e**/*cis*-**3e** (66:34 dr). Purification by column chromatography (hexanes—1:99 EtOAc/hexanes) afforded an impure yellow oil containing silacyclobutane *cis*-**3e** (0.06 g, 10%) in addition to an impure mixture containing silacyclobutanes *trans*-**3e**/*cis*-**3e** (55:45 dr) as a yellow oil (0.22 g, 32%). **Silacyclobutane *trans*-3e:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 7.58 (dd, J = 8.0, 2.0 Hz, 2H), 3.07 (t, J = 11.5 Hz, 1H). **Silacyclobutane *cis*-3e:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 7.37 (d, J = 7.3 Hz, 2H), 7.07 (t, J = 7.7 Hz, 2H), 3.96 (dd, J = 12.6, 9.3 Hz, 1H), 2.06 (quint, J = 8.8 Hz, 1H), 1.87−1.78 (m, 1H), 1.36 (d, J = 8.2 Hz, 3H), 1.29 (d, J = 5.7 Hz, 3H),[48] 1.03 (s, 9H), 0.98 (s, 9H); ^{29}Si NMR (119.2 MHz, C_6D_6) δ 14.1; IR (neat) 3059, 2935, 2860, 1581, 1473, 1363 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{19}H_{31}SSi$ $(M - H)^+$ 319.1916, found 319.1920.

Carbonyl Insertion into Silacyclobutanes (Procedure B). Oxasilacyclohexane 11a. To a solution of silacyclobutane **3a** (1.4 g, 4.8 mmol) in toluene (22 mL) was added benzaldehyde (1.5 mL, 15 mmol) and ZnI_2 (0.16 g, 0.50 mmol). The reaction mixture was heated to 100 °C. After 30 h, the reaction mixture was filtered through a pad of SiO_2/Celite (1:9) with hexanes to remove residual catalyst and concentrated in vacuo. Benzaldehyde was removed in vacuo at 100 °C (0.4 mmHg). Purification by column chromatography (1:99 EtOAc/hexanes) afforded oxasilacyclohexane **11a** as a white solid (0.69 g, 36%): mp 56−58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 2H), 7.35−7.32 (m, 6H), 7.28−7.24 (m, 2H), 4.99 (appar d, J = 11.2 Hz, 1H), 3.73 (tdd, J = 12.7, 4.2, 2.3 Hz, 1H), 2.17 (appar dd, J = 13.9, 1.7 Hz, 1H), 1.60 (dt, J = 13.7, 11.7 Hz, 1H), 1.34 (ddd, J = 14.4, 4.5, 2.1 Hz, 1H), 1.09 (s, 9H), 1.07 (s, 9H), 0.89 (appar t, J = 13.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 134.6, 132.4, 129.0, 128.3, 127.2, 127.1, 125.2, 77.3, 45.0, 44.7, 28.2, 27.6, 22.2, 20.2, 13.8; IR (thin film) 3061, 2931, 1601, 1583, 1471, 1092 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{24}H_{35}OSSi$ $(M + H)^+$ 399.2178, found 399.2180. Anal. Calcd for $C_{24}H_{34}OSSi$: C, 72.30; H, 8.60. Found: C, 72.04; H, 8.59.

Oxasilacyclohexane 11b. Procedure B was employed using silacyclobutane **3a** (0.29 g, 1.0 mmol), acetophenone (0.35 mL, 3.0 mmol), and ZnI_2 (0.035 g, 0.11 mmol). Acetophenone was removed in vacuo at 100 °C (0.4 mmHg). Purification by column chromatography (1:99 EtOAc/hexanes) afforded oxasilacyclohexane **11b** as a colorless oil (0.22 g, 54%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.31−7.26 (m, 3H), 7.20 (t, J = 7.3 Hz, 1H), 3.78 (appar td, J = 12.7, 3.5 Hz, 1H), 2.45 (appar d, J = 13.7 Hz, 1H), 1.85 (appar t, J = 12.9 Hz, 1H), 1.46 (s, 3H), 1.30 (ddd, J = 14.2, 4.2, 2.2 Hz, 1H), 1.10 (s, 9H), 0.87 (s, 9H), 0.78 (appar t, J = 13.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 135.2, 131.5, 129.0, 127.9, 126.9, 126.3, 124.2, 76.4, 45.2, 40.6, 32.0, 27.6, 27.4, 20.9, 20.6, 14.6; IR (neat) 3058, 2967, 1601, 1583, 1471, 1011 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{25}H_{37}OSSi$ $(M + H)^+$ 413.2334, found 413.2328. Anal. Calcd for $C_{25}H_{36}OSSi$: C, 72.76; H, 8.79. Found: C, 72.55; H, 8.85.

(48) An NOE enhancement was applied to resolve the splitting of this peak.

Oxasilacyclohexane 12a and Allyl Silane 12b. Procedure B was employed using silacyclobutane **3b** (0.319 g, 1.04 mmol, 83:17 dr), benzaldehyde (0.32 mL, 3.1 mmol), and ZnI_2 (0.032 g, 0.10 mmol). The reaction mixture was heated to 70 °C. Benzaldehyde was removed in vacuo at 100 °C (0.4 mmHg). Purification by column chromatography (1:199 EtOAc/hexanes) afforded oxasilacyclohexane **12a** as a white solid (0.072 g, 16%) and allyl silane **12b** as a colorless oil (0.019 g, 6%). **Oxasilacyclohexane 12a:** mp 80−82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.7 Hz, 2H), 7.40−7.34 (m, 8H), 4.61 (d, J = 9.5 Hz, 1H), 3.58 (ddd, J = 11.9, 10.5, 4.4 Hz, 1H), 1.88 (tq, J = 10.3, 6.7 Hz, 1H), 1.40 (dd, J = 14.9, 4.5 Hz, 1H), 1.15 (dd, J = 15.1, 11.9 Hz, 1H), 1.08 (s, 9H), 1.04 (s, 9H), 0.90 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 135.2, 132.8, 128.9, 128.2, 127.6, 127.2, 127.0, 84.4, 53.0, 45.7, 28.4, 27.6, 22.2, 20.1, 17.6, 16.2; IR (thin film) 3070, 2929, 2856, 1581, 1471, 1387 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{25}H_{37}OSSi$ $(M + H)^+$ 413.2334, found 413.2320. Anal. Calcd for $C_{25}H_{36}OSSi$: C, 72.76; H, 8.79. Found: C, 72.48; H, 8.91. **Allyl Silane 12b:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60−7.28 (m, 5H), 5.48 (dt, J = 15.1, 7.5 Hz, 1H), 5.37 (dq, J = 15.0, 6.3 Hz, 1H), 1.80 (d, J = 7.6 Hz, 2H), 1.67 (d, J = 6.3 Hz, 3H), 1.13 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 136.1, 128.7, 126.93, 126.87, 125.1, 28.9, 18.3, 18.1; IR (neat) 3072, 2933, 1768, 1583, 1473, 1389 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{18}H_{34}NSSi$ $(M + NH_4)^+$ 324.2181, found 324.2171.

Lithiation of the Sulfide Functionality. Silacyclobutane 15. A procedure reported by Cohen[42] was adapted to prepare silacyclobutane **15**. A cooled (−78 °C) solution of Li pellets (0.030 g, 4.3 mmol) in THF (1.0 mL) was prepared under an atmosphere of argon. A solution of naphthalene (0.014 g, 0.11 mmol) in THF (1.0 mL) was added, followed by a solution of silacyclobutane **3a** (0.24 g, 0.80 mmol) in THF (1.5 mL). After 2 h at −78 °C, Me_3SiCl (0.15 mL, 1.2 mmol) was added to the reaction mixture. After 2 h, the reaction mixture was warmed to 22 °C and diluted with pentane (10 mL). An aqueous solution of saturated NH_4Cl was added and the layers were separated. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (hexanes) afforded silacyclobutane **15** as a pale yellow oil (0.15 g, 70%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (quint, J = 10.8 Hz, 1H), 1.10 (s, 9H), 0.99 (s, 9H), 0.89 (d, J = 10.7 Hz, 4H), −0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 27.7, 20.3, 19.2, 17.3, 8.5, −3.6; IR (neat) 2951, 2858, 1470, 1248, 1115, 829 cm^{-1}; HRMS (GC-MS) m/z calcd for $C_{14}H_{36}NSi_2$ $(M + NH_4)^+$ 274.2386, found 274.2388.

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Supporting Information Available: General experimental information and additional experimental procedures and spectroscopic and analytical data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.