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Silylboranes as New Sources of Silyl Radicals for Chain-Transfer Reactions

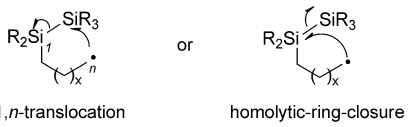
Guy Rouquet,[a] Frédéric Robert,[a] Raphaël Méreau,[a] Frédéric Castet,[a] Philippe Renaud,*[b] and Yannick Landais*[a]

Abstract: Various silylboranes, which were outfitted with a catecholborane moiety at one end and a $(Me_3Si)_3Si$ moiety at the other end of a carbon chain, were prepared through the hydroboration of the corresponding unsaturated silanes. The C-centered radical species generated from these silylboranes efficiently cyclized to provide, through a 5-*exo* intramolecular homolytic substitution at the silicon center, the corresponding silacycle and a Me_3Si radical that was subsequently trapped by sulfonyl acceptors. These cyclizations proceeded at unprecedented rates, due, in part, to a strong *gem*-dialkyl effect that was attributable to the presence of bulky substituents on a quaternary center located on the chain. In parallel, we designed arylsilylboranes that produced silyl radicals through a 1,5-hydrogen transfer. Such silyl radicals may be valuable radical chain carriers, for instance, in oximation reactions of alkyl halides. Finally, computational studies allowed calculation of activation barriers of the homolytic substitution step and additionally illustrated that the overall reaction mechanism involved a transition state in which the attacking carbon center, the central silicon atom, and the Me_3Si leaving group were collinear.

Keywords: *gem*-dialkyl effect · homolytic substitution · hydroboration · hydrogen transfer · radical reactions

Introduction

Tin reagents are widely used in radical chemistry and exhibit unique and unequalled reactivity.[1] Amongst them, Bu_3SnH and ditin compounds, such as $(Bu_3Sn)_2$ or $(Me_3Sn)_2$, are broadly employed in reductive and C–C bond-forming processes, respectively. Unfortunately, organotin reagents suffer from severe drawbacks, which include perceived toxicity,[2] tedious product purification, and product contamination by residual tin derivatives.[3–4] Silicon derivatives offer an attractive alternative to tin because they are nontoxic and have similar chemical properties (Group 14 elements). Silyl and tin radicals are highly reactive towards alkyl and aryl halides and form strong Si–X and Sn–X bonds. Silyl radicals have remained much less exploited than their tin analogues,[5] due to the relatively high bond-dissociation energy (BDE) of Si–H and Si–Si bonds with respect to their Sn–H and Sn–Sn analogues.[6] The release of a silyl radical, which can then efficiently sustain the radical chain, constitutes a major hurdle that is difficult to overcome. Several elegant solutions to this problem, which include the use of tris(trimethylsilyl)silane derivatives,[5,7] polarity reversal catalysis,[8] or methodologies that rely on the aromatization of silylcyclohexadienyl systems,[9] have been proposed recently. Other less common methods to generate silyl radicals,[5,10] such as intramolecular silyl group migration to C-centered radicals[11] and 1,5-hydrogen transfer,[12] have also been reported in this context. Silyl shift processes may occur through two different pathways, depending on the position of the silicon moiety and the chain length, that is 1,*n*-migration (or translocation) and homolytic ring closure (Scheme 1). In an



Scheme 1. Intramolecular homolytic substitution at silicon.

effort to generalize and conceptualize these S_Hi reactions, the groups of Matsubara and Schiesser have carried out ab initio calculations on model compounds ($R\text{-}MH_3$) that had various carbon chain lengths and contained different Group 14 elements (M = Sn, Si, Ge).[13] They were, thus, able to show that the energy of activation for these processes was quite low and that cyclizations, which occurred through frontside, backside, or hypervalent species (depending on the chain length), were favored and could produce silyl radicals. A comparison of the different systems finally

[a] Dr. G. Rouquet, Dr. F. Robert, Dr. R. Méreau, Dr. F. Castet, Prof. Dr. Y. Landais
Université de Bordeaux, Institut des Sciences Moléculaires
UMR-CNRS 5255, 351, Cours de la libération
33405 Talence Cedex (France)
Fax: (+33) 540006286
E-mail: y.landais@ism.u-bordeaux1.fr

[b] Prof. Dr. P. Renaud
Universität Bern, Departement für Chemie und Biochemie
Freiestrasse 3, CH-3012 Bern (Switzerland)
Fax: (+41) 31-631-43-59
E-mail: philippe.renaud@ioc.unibe.ch

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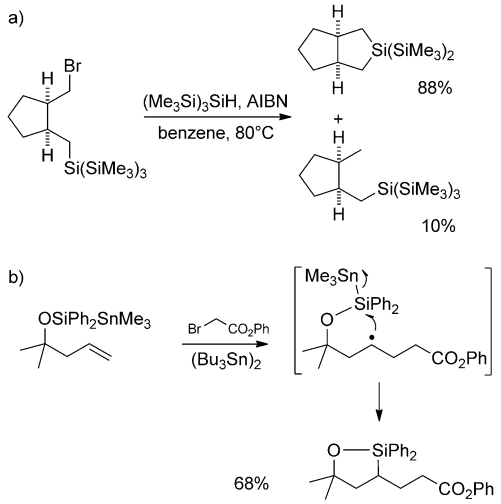
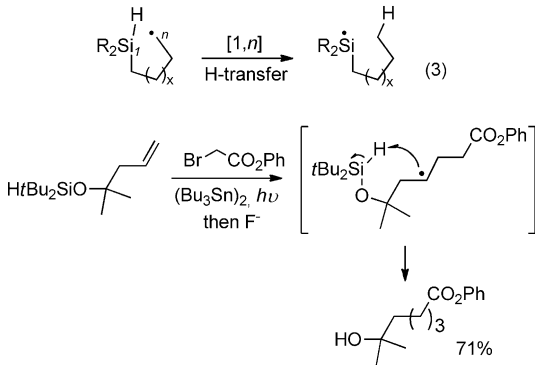
led to the conclusion that 1,4- and 1,5-transfer, as well as five-membered-ring formation, were favored processes that might be useful for synthetic purposes. Examples of such homolytic substitutions were presented as early as 1958 when Kumada and Shiina described the 1,2-migration of a silicon group onto a C-centered radical center.[11a] Since then, other examples of 1,3-, 1,4- and 1,5-silyl shifts[14] have been reported. Chatgilialogu and co-workers[11c] reported, simultaneously with Oshima and co-workers,[11d,e] an interesting 5-*exo* intramolecular homolytic substitution (Scheme 2a), in which a



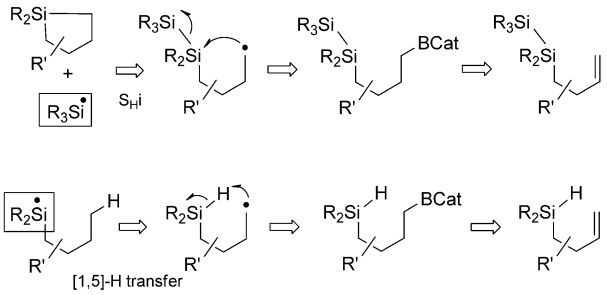
Scheme 2. Intramolecular homolytic substitution at a silicon center. AIBN = azobisisobutylonitrile.

Me_3Si radical was released and then propagated the radical chain through the abstraction of a bromine atom. Interestingly, the rate constant for the 5-*exo* cyclization was calculated to be 10^4–$10^5\ s^{-1}$. More recently, Studer and Steen showed that the efficiency of S_Hi reactions at a silicon center was greatly enhanced through the use of a tin substituent as a leaving group (cyclization rates of approximately 10^6–$10^7\ s^{-1}$ were calculated).[11g,h] The nature of the substituents on the silicon center was also of critical importance: phenyl substituents led to faster cyclizations, probably as a result of a weakening of the Si–Sn bond (Scheme 2b). Investigations into processes that involved homolytic substitution at a silicon center have led to the accumulation of a wealth of experimental and theoretical data, whereas 1,*n*-hydrogen transfer (Scheme 3, top) has attracted much less interest. The groups of Curran[12a] and Clive,[12b] however, found that a silyl radical could be generated by the migration of a hydrogen atom from a silicon atom to an sp^2 or sp^3 carbon-centered radical, (1,5-hydrogen transfer). Curran used the 1,5-hydrogen transfer as a basis for the development of an efficient strategy, termed unimolecular chain transfer (UMCT), for intermolecular carbon–carbon bond forming reactions (Scheme 3, bottom).[12a] These examples demonstrate that silyl radicals, which are formed through 1,5-migration processes, efficiently propagate radical chains. In



Scheme 3. 1,5-Hydrogen transfer from Si to C.

most cases, however, the generation of the initial carbon-centered radical requires the reaction of a stannyl or a silyl radical with an alkyl halide (Scheme 2), which limits the scope of the methodology. On the basis of recent reports about the role of organoborane compounds as alkyl radical precursors,[15] it was envisioned that the carbon-centered radical might, instead, be generated in situ from the corresponding organoborane compound, which, in turn, could be produced from a suitable olefin (Scheme 4). The boron spe-



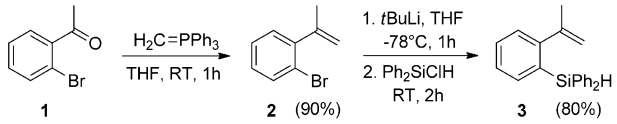
Scheme 4. Silylboranes producing silyl radicals through S_Hi and 1,5-hydrogen transfer processes. Cat = catechol.

cies would not only allow the formation of the carbon-centered radical species under mild conditions, but also serve as a radical chain-transfer agent in further transformations.[15–16] Various types of organoboranes may be used, although previous studies showed that catecholborane (CatBH) is very convenient for the selective generation of alkyl radicals from olefins under mild conditions.[15a] Moreover, previous reports[11c,d,g,h] showed that S_Hi reactions that used simple disilane precursors led to the displacement of a silyl radical at low rates. We, thus, hypothesized that it would be possible to increase cyclization rates, by simply varying the nature and the number of substituents on the carbon chain of the silylboranes. Herein, we present the first example of the generation of silyl radicals from silylboranes. The design and optimization of the structures of silylboranes and the trapping of the silyl radical species generated through 1,5-hydrogen transfer and S_Hi reactions from the corresponding carbon-centered radical precursors are, additionally, de-

scribed. Kinetic and computational studies of homolytic ring-closure processes are also provided.

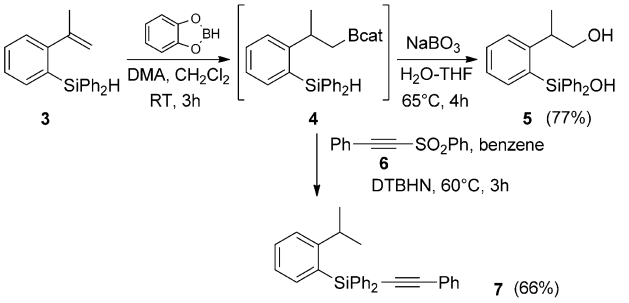
Results and Discussion

1,5-Hydrogen transfer from a silicon atom to a carbon atom as a means of manufacturing silyl radicals: Arylsilane **3** was designed as a suitable candidate to enable fast hydrogen transfer. It was foreseen that the aromatic ring in **3** would accelerate transfer due to its rigidity and the enforced proximity of both reacting centers.[11c,d,g,h] The 2-propenyl substituent also appeared to be well suited for regioselective hydroboration.[17] Compound **3** was easily synthesized in two steps from aryl bromide **1**, following the reaction sequence depicted in Scheme 5. Hydroboration of **3** was carried out



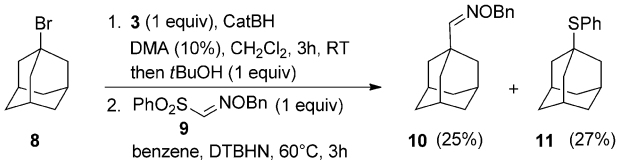
Scheme 5. Synthesis of arylsilane **3**.

by using CatBH in the presence of *N*,*N*-dimethylacetamide (DMA) as a catalyst,[18] and proceeded with complete regioselectivity as indicated by the formation of alcohol **5** after oxidation with $NaBO_3 \cdot H_2O$ (Scheme 6).[19] We, subsequently,



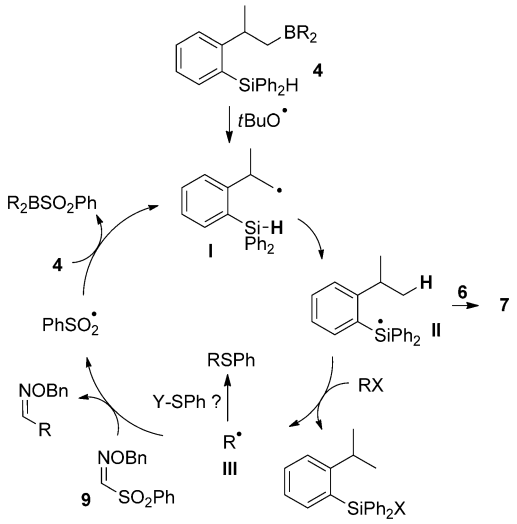
Scheme 6. 1,5-Hydrogen transfer and trapping of the silyl radical species. DTBHN = di-*tert*-butylhyponitrite.

focused on investigating the hydrogen transfer process. Our specific aim was the trapping of the resultant silyl radical with a sulfone acceptor (alkenyl and alkynyl sulfones are efficient traps for nucleophilic radicals).[20] Accordingly, the hydroboration of **3** was followed by the removal of excess borane with *t*BuOH and the addition of a solution of sulfone **6** in benzene to provide the alkynylsilane **7** in 66% yield. Interestingly, we did not observe any trace of product arising from the direct addition of the carbon-centered radical to **6**; a fact that indicates that the 1,5-hydrogen transfer is a fast process. We, then, proceeded to apply this methodology to a radical chain-transfer process. We selected the oximation of a simple alkyl halide as a model reaction.[21] Adamantyl bromide **8** reacted with sulfonyloxime **9** in the presence of the silylborane **4**, which was generated in situ from **3** and CatBH. The reaction led, as expected, to oxime **10**, albeit in low yield, and the adamantyl thioether **11** (Scheme 7). The formation of **11** was ascribed to the pres-



Scheme 7. Oximation of adamantyl bromide with silylboranes involving a 1,5-hydrogen transfer process. Bn = benzyl.

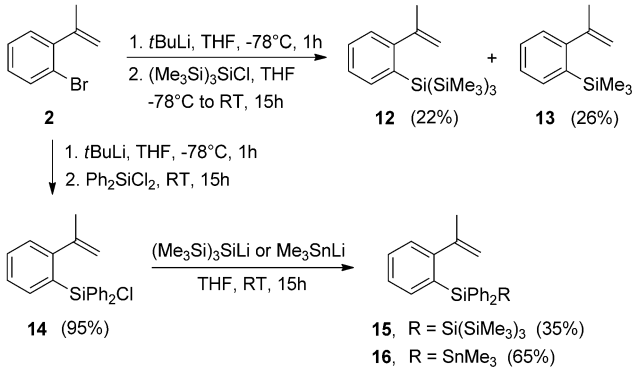
ence of $PhSO_2SPh$, which was produced by the disproportionation reaction of $PhSO_2$ radicals.[22,23] The addition of nucleophilic carbon-centered radicals to $PhSO_2SPh$ is known to result in the formation of thioethers.[24] The presence of other sulfurizing agents (denoted Y-SPh in Scheme 7), however, cannot be ruled out at this stage. In both cases, there was no evidence of products produced by the direct addition of the carbon-centered radical derived from **4** to oxime **9**. A potential reaction scheme for the overall process is depicted in Scheme 8. The decomposition of DTBHN provides the *t*BuO radical, which reacts with silyl borane **4** to provide the corresponding carbon-centered radical **I** that leads to the desired silyl radical **II** through a 1,5-hydrogen transfer. The latter may then react with a trap, such as alkynylsulfone **6**, to form **7** along with the $PhSO_2$ radical, which sustains the radical chain reaction. The presence of alkyl halide **8** in the reaction mixture results in the fast abstraction of the halide by the silyl radical and the generation of the nucleophilic carbon-centered radical species **III** that may then react further with sulfonyl oxime **9**. Again, addition–fragmentation



Scheme 8. Radical chain reaction involving a 1,5-hydrogen transfer within silylboranes.

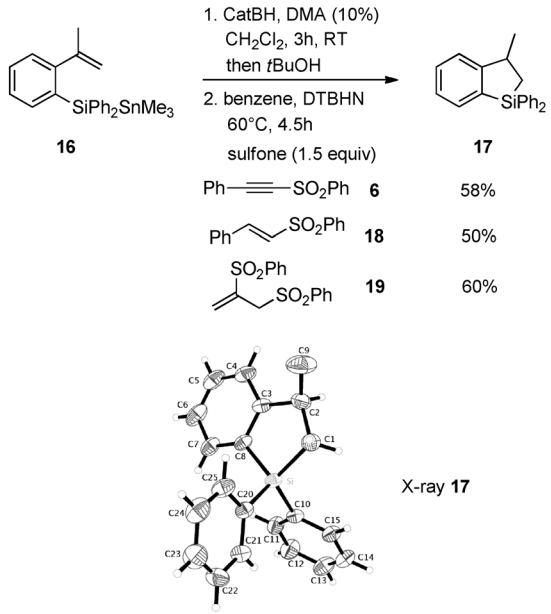
onto **9** provides the desired oxime **10** along with the $PhSO_2$ radical that can propagate the chain reaction. These results demonstrate that the 1,5-hydrogen transfer from a silicon atom to a carbon atom may be exploited to reliably manufacture silyl radicals. The direct trapping of silyl radicals proved that the process was efficient and sufficiently fast. In contrast, the modest yields of both **10** and **11** indicated that the abstraction of halogen atoms by **II** was not as efficient as expected.

Intramolecular homolytic substitution at silicon centers (S_Hi) as a source of silyl radicals: We then extended these preliminary investigations towards processes that involved homolytic substitution at silicon centers. We initially examined systems that were closely related to silane **3**. Two silanes (**12** and **15**) were prepared and tested as potential silyl radical precursors. We also synthesized model compound **16**, which possessed a Si–Sn bond, to compare systems with Si–Si and Si–Sn bonds in S_Hi processes (Scheme 9). The synthesis of

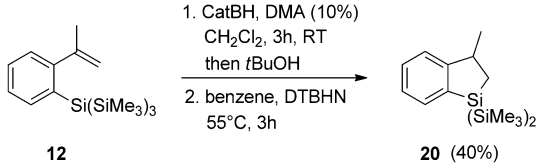


Scheme 9. Synthesis of compounds **12**–**16**.

aryltris(trimethylsilyl)silane (**12**) from aryl bromide **2** was troublesome, probably due to steric hindrance. The lithiation of **2**, followed by quenching of the reaction mixture with $(Me_3Si)_3SiCl$, gave **12** and **13** in low yield. The latter was formed through the reaction of the intermediate aryl lithium compound with the Me_3Si substituent of $(Me_3Si)_3SiX$. Our efforts to improve this strategy, by use of $(Me_3Si)_3SiBr$ or $(Me_3Si)_3SiOTf$ (Tf = triflate) proved unsuccessful. The second model compound **15**, which would provide a $(Me_3Si)_3Si$ radical through an S_Hi process, was prepared from **2**. Aryl bromide **2** underwent lithiation, followed by silylation with Ph_2SiCl_2 to afford **14**. The addition of $(Me_3Si)_3SiLi$ or Me_3SnLi to **14** in the last step afforded **15** and **16**, respectively, in modest yields. Phenyl substituents on the silicon center were introduced specifically to weaken the Si–Si and Si–Sn bonds, and thus, facilitate the S_Hi process.[11g,h] With the above aryl silanes in hand, we tested the effectiveness of the S_Hi process under the same conditions as those described above. Precursor **16** was tested first because it is known that S_Hi processes are more efficient in systems that possess Si–Sn bonds.[6,11g,h] The hydroboration of **16**, followed by treatment with DTBHN, in the presence of various sulfone traps (**6**, **18**, **19**; Scheme 10), led to the desired cyclization product **17**; the structure of which was unambiguously determined by X-ray diffraction studies. It has to be noted that ^1H NMR spectroscopic analysis of the reaction mixture showed only traces of the expected corresponding unsaturated tin compounds. We repeated the reaction with a solution of BH_3 in THF and sulfone **6** as the trapping agent and obtained **17** in 35% yield, but again without a trace of the alkynyl tin products. The formation of **17** in the presence of BH_3 ruled out the possibility that the trimethyltin radical was trapped by catechol residues and demonstrated that the S_Hi process had taken place. Therefore, we went on to apply the same protocol to silane derivatives **12** and **15**. The hydroboration of **12** and subsequent intramolecular reaction in the presence of DTBHN without a sulfone trap effectively led to the corresponding cyclization product **20**, albeit in modest yield (Scheme 11). Conversely, under identical conditions, compound **15** gave a complex mixture of products that was not analyzed further. The low yield in the synthesis of **12** and the poor efficiency in the cyclization of these aromatic systems eventually led us to turn our attention toward acyclic systems that would be more readily accessible and easier to derivatize. We designed three precur-

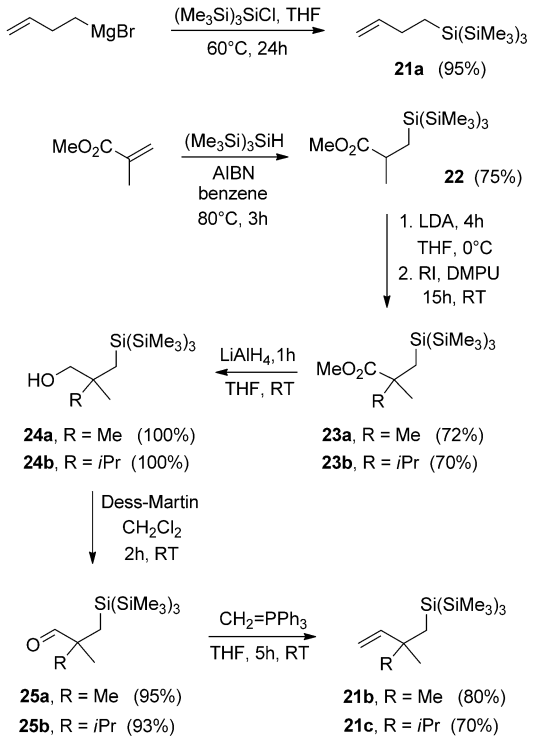


Scheme 10. Synthesis and X-ray crystal structure of **17**.



Scheme 11. Formation of cyclization product **20**.

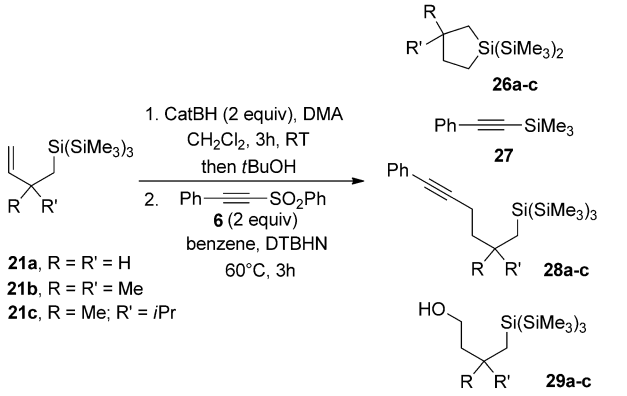
sors, **21a–c**, all of which possessed a $(Me_3Si)_3Si$ functionality. The substituents on the chain were introduced to favor cyclization through a *gem*-dialkyl effect.[25] The unsubstituted compound **21a** was thus prepared in excellent yield through the silylation of the corresponding Grignard reagent (Scheme 12). We used inexpensive methyl methacrylate as



Scheme 12. Synthesis of S_Hi precursors **21a–c**. LDA = lithium diisopropyl amide, DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone.

the starting material to synthesize precursors **21b,c** in five steps. In the first step, methyl methacrylate was silylated with $(Me_3Si)_3SiH$ (TTMSH)[7] to afford the β-silyl ester **22**. The alkylation of **22** with methyl or isopropyl iodide then allowed the introduction of the corresponding alkyl substituents on the tertiary carbon atom of **22** and, thus, the generation of **23a,b**. Finally, the reduction of the ester function into an alcohol (**24a,b**), followed by a Dess–Martin oxidation, afforded the corresponding aldehydes **25a,b**, which then underwent a Wittig olefination to give the desired unsaturated silanes **21b,c**. It is noteworthy that the whole sequence may easily be performed on a multigram scale and proceeds with only three purification steps in good overall yields (44 and 29% in five steps for **21b** and **21c**, respectively). Our first attempts to trap silyl radicals through an intramolecular homolytic substitution involved treatment of precursors **21a–c** with CatBH, followed by the addition of alkynyl sulfone **6**. The results are summarized in Table 1. We isolated four products in various amounts, depending on the nature of the precursor. Interestingly, the interposition of a quaternary carbon atom between the C-centered radical

Table 1. Intramolecular homolytic substitution on precursors **21a–c**.

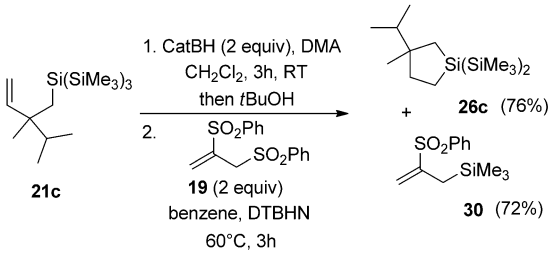


Entry	Precursor	**26a–c** [%][a]	**27** [%][a]	**28a–c** [%][a]	**29a–c** [%][a]
1	**21a**	trace[b]	trace[b]	71	–
2	**21b**	44	22	26	18
3	**21c** (0.5 M)	73	44	7	16
4	**21c** (0.25 M)	69	35	–	13
5	**21a**[c]	trace[b]	trace[b]	65	–
6	**21b**[c]	–	–	–	84
7	**21c**[d]	70	49	–	9

[a] Isolated yield. [b] Observed by using GC-MS. [c] The reaction was initiated with dry oxygen instead of DTBHN. [d] Four equivalents of sulfone **6** were used instead of two.

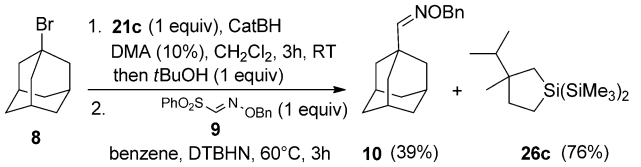
species and the silicon center (Table 1, entry 1 versus 2) resulted in enhanced yields for silacycles **26a–c** (produced through the S_Hi pathway). An increase in the size of substituents on the quaternary center also had a beneficial effect on the efficiency of these S_Hi processes (Table 1, entry 3 versus 2).[11g,h,25] Lower concentrations also favored the S_Hi mechanism at the expense of the direct alkynylation process (Table 1, entry 4 versus 3). The generation of the silyl radical was confirmed by the formation of **27**, which was produced in lower yields than **26**; a fact that indicated that the silyl radical was partially consumed in undesired competitive processes (see above). Conversely, the quantity of alkyne **28a–c**, which was formed by the direct trapping of the C-centered radical by **6**, decreased inversely proportional to the size of substituents on the quaternary center. Finally, we also synthesized alcohols **29a,b**. Notably, precursor **21a**, which lacks the quaternary center (Table 1, entry 1) does not provide **29a** under the conditions shown in Table 1. Alcohol **29a** was obtained independently in 75% yield through the hydroboration of **21a** and then the oxidation of the resultant borane with $NaBO_3$.[26] Solvents were degassed before reaction and the initiation was usually carried out with DTBHN, which provided better and more reproducible results. However, when reactions were repeated with oxygen as the initiator (Table 1, entries 5 and 6), compound **21a** led to **28a** in 65% yield without any evidence of oxidation products, whereas **21b** led exclusively to **29b**. This indicated that alcohols **29b,c** probably resulted from the oxidation of the hydroboration products by oxygen present in the solvent, although we took the necessary precautions prior to each experiment. The results above demonstrated that unsa-

turated silanes could serve as silyl radical precursors through the hydroboration and initiation of an S_Hi process by oxygenated radicals. Nevertheless, although the *gem*-dialkyl effect was remarkable and dramatically improved the cyclization rate, a large amount of silyl radical could not be trapped by **6**, as indicated by the large difference in yield between **26c** and **27**, as well as between **26b** and **27**. An increase in the concentration of sulfone (Table 1, entry 7 versus 4) slightly improved the yield of **27**, which still remained 20% lower than that of **26c**. Careful examination of the ^{1}H NMR spectrum of the crude reaction mixture also revealed that a byproduct, which had a distinct signal at $\delta =$ 0.31 ppm, characteristic of a methyl substituent at the silicon center, always formed, whatever the nature of the precursor. Although it was impossible to isolate and characterize this byproduct, it was likely that it formed through a reaction between the silyl radical and catechol residues. The reaction of **21c** under identical conditions (Table 1), but with the use of BH_3–THF as the hydroboration agent led to **26c** in 32% yield, along with **29c** and no trace of the byproduct. This indicated that in cases when slow radical traps (such as **6**) were utilized, the addition of the silyl radical onto electron-rich catechol or benzene[11f,27] was a competitive process that partly consumed the silyl radical, which was generated through the S_Hi pathway. This hypothesis was reinforced by the fact that we obtained improved results when using allylsulfone **19**. The enhanced reactivity match between this acceptor and the nucleophilic silyl radical allowed the S_Hi process to proceed smoothly and eventually produced nearly equimolar amounts of **26c** and the corresponding allylsilane **30**; both in excellent yields (Scheme 13). Interestingly, in



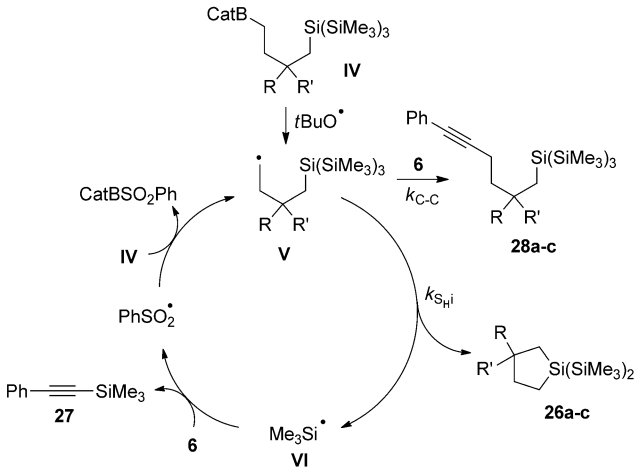
Scheme 13. Silyl radical trapping by allyl sulfone **19**.

this case, the signal at $\delta = 0.31$ ppm nearly disappeared. The potential application of this methodology to chain-transfer reactions was then studied briefly. As in the case of the 1,5-hydrogen transfer process, the oximation of an alkyl halide was studied as a model reaction. Adamantyl bromide **8** was thus treated with the silylborane prepared from **21c** to afford **10** in 39% yield (in the presence of **9**), along with **26c** in 76% yield (Scheme 14). These results indicate that chain-transfer reactions may be induced through the utilization of silyl radicals generated through a S_Hi process, although it has to be noted that the silyl radical species is partially lost in competitive pathways. Similarly, examination of the ^{1}H NMR spectrum of the reaction mixture confirmed



Scheme 14. Oximation of adamantyl bromide using silylboranes involving an S_Hi process.

the formation of the byproduct (which exhibited a SiMe signal at $\delta = 0.31$ ppm). Traces of thioether **11** and low amounts (14%) of **29c** were also observed. Finally, less reactive primary or secondary bromides led to the production of **26c** in good yield, whereas no amount of the corresponding oximes was detected. The radical chain reaction that was probably involved in this S_Hi process is depicted in Scheme 15. We envisioned that the carbon-centered free



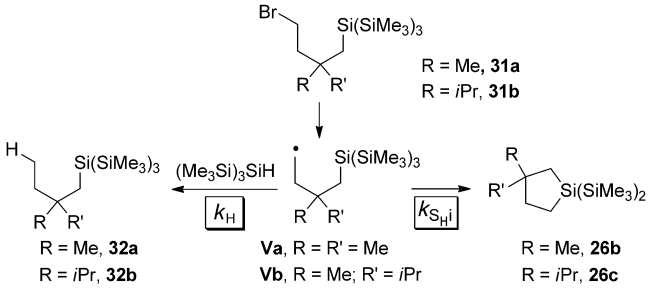
Scheme 15. Radical chain in S_Hi process from silylboranes.

radical **V**, which was generated from silylborane **IV**, possibly reacted through two competitive pathways, with respective rate constants that were dependent upon the structure of precursors **21a–c** (in compounds that have quaternary centers with bulky substituents, k_{S_Hi} is clearly higher than k_{C-C} and high yields of cyclization products relative to alkynylation products are obtained; Table 1). Dilution of the reaction mixture also favored, as expected, the formation of cyclization products **26**. Studies by Chatgilialoglu and co-workers have provided rate constant values for S_Hi processes.[11c] Our precursors have been designed to allow fast cyclization processes. Therefore, it would be interesting to compare the cyclization rates of the carbon-centered radical species generated from precursors **21a–c** with those reported in the literature.[11c]

Kinetic studies of the S_Hi process by use of silanes 21a–c: We used bromosilanes **31a**,**b** (which were prepared from the corresponding unsaturated silanes **21a–c**;[28] see the Support-

ing Information) to perform standard competition kinetic measurements. The generation of the carbon-centered radical **V** (Scheme 15) from **31a**,**b** was carried out through the use of $(Me_3Si)_3SiH$/AIBN (Table 2). Samples of the reduced

Table 2. Kinetic investigations into the S_Hi mechanism.



Precursor	[Bromide]	$[(Me_3Si)_3SiH]$	Ratio **26**/**32**[a]	k_{S_Hi} [s^{-1}][b]
31a	0.053	1.20	0.905 (±2%)	1.3×10^6
31a	0.045	1.40	0.813 (±1%)	1.4×10^6
31a	0.049	2.05	0.523 (±6%)	1.3×10^6
31b	0.067	1.43	11.05 (±4%)	1.9×10^7
31b	0.066	1.93	7.79 (±5%)	1.8×10^7
31b	0.065	2.80	5.11 (±3%)	1.7×10^7

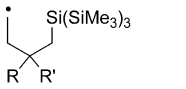
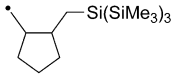
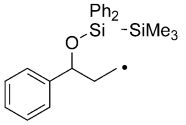
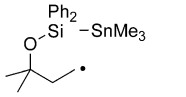
[a] Estimated ratio from GC analysis (see the Supporting Information). [b] At 80 °C

products **32a**,**b** were also prepared from **21a**–**c**.[28] The competition experiments between the intramolecular homolytic substitution reaction, which leads to **26b**,**c**, and the reduction of **V**, which affords **32a**,**b**, were performed in sealed tubes at 80 °C in the presence of AIBN and a large excess of the reducing agent ($(Me_3Si)_3SiH$) to allow the reaction to occur under pseudo-first-order conditions. For each model compound three measurements were performed; these are summarized in Table 2. By using the kinetic expression given in Equation (1), for a competition between a unimolecular (S_Hi) and a bimolecular (reduction) process,[29] rate constants were estimated by measuring the ratio between cyclized products **26b**,**c** and the reduced products **32a**,**b** (GC analysis).

$$\frac{[\mathbf{26b,c}]}{[\mathbf{32a,b}]} = \frac{k_{S_Hi}}{k_H[(Me_3Si)_3SiH]} \quad (1)$$

Based on the known value of the rate constant k_H ($1.2\times10^6\ s^{-1}$) for the reduction of primary carbon radicals by $(Me_3Si)_3SiH$ at 80 °C, the rate constant for the S_Hi reaction of radical species **Va** was calculated as $1.3\text{–}1.4\times10^6\ s^{-1}$ and that of **Vb** as $1.7\text{–}1.9\times10^7\ s^{-1}$ at 80 °C. Acyclic radical species **Va**,**b**, which have a quaternary center, are thus able to generate a silyl radical through the homolytic cleavage of a Si–Si bond, with remarkable rate constants, that are two to three orders of magnitude higher than those measured for radical precursors **VI** and **VII**[11c–e] (Table 3). Studer and Steen[11h] carried out chain transfer reactions on compounds such as **IX**, which have a Si–Sn bond. They were able to measure rate constants as high as $1\times10^7\ s^{-1}$ for these S_Hi reactions at silicon, in which a tin radical species was released. The related siloxane **VIII** (which includes a Si–Si bond), however, led to a rate constant that was in the range 10^3–$10^4\ s^{-1}$. It is noteworthy that they were able to perform chain-transfer reactions with a precursor of **IX**. This shows that rate constants of at least $10^7\ s^{-1}$ are required to carry out such radical chain reactions and, simultaneously, eliminate competitive side reactions. Our results and those reported also emphasized the critical role of the *gem*-dialkyl effect in achieving high rate constants in radical cyclizations[25] (see rate constants for **Va**,**b** and **IX** in Table 3). We should, finally, point out that the steric bulk of the substituents significantly affects rate constant values. More specifically, replacing Me with a *i*Pr group produced a difference of one order of magnitude in rate constant values (**Va** versus **Vb**).[30]

Table 3. Rate constants for S_Hi on various silanes.

Radical precursor		Rate constant [s^{-1}]	Reference
	**Va**: R = R′ = Me	$1.3\text{–}1.4\times10^6$	this work
	Vb: R = Me, R′ = *i*Pr	$1.7\text{–}1.9\times10^7$	this work
	VI: R = R′ = H[a]	1×10^4	[11d,e]
	**VII**	2.5×10^5	[11c]
	**VIII**	$0.1\text{–}1\times10^4$	[11h]
	**IX**	1×10^7	[11h]

[b] Rate constant values reported in the literature were utilized to calculate k_{S_Hi}.[11d–e]

Theoretical studies of the S_Hi process which involved radical species V–VII: Correlations between the rate constants reported above and the activation barriers of the key homolytic substitution at the silicon center were then obtained by DFT calculations. We calculated free enthalpies of activation ($\Delta G^{\neq}$) at the B3LYP/6-31G(d) and BH&HLYP/6-31G(d) levels and their relative values (Table 4). As already observed in processes that involved silyl radical species,[31] the B3LYP functional provides systematically smaller barrier heights than BH&HLYP due to a smaller amount of HF

Table 4. Free enthalpies of activation [kcal mol^{-1}] calculated at the B3LYP/6-31G(d) and BH&HLYP/6-31G(d) levels. Relative values are given in brackets.

Precursor	B3LYP	BH&HLYP	Exptl
Va (R = R′ = Me)	15.44 (0.78)	20.15 (1.19)	(1.5)
Vb (R = Me, R′ = *i*Pr)	14.66 (0.00)	18.96 (0.00)	(0.0)
VI (R = R′ = H)	22.58 (7.92)	27.92 (8.96)	(4.5)
VII	17.43 (2.77)	21.68 (2.72)	(2.5)

exchange.[32] Nevertheless, both levels of calculation follow very similar trends with respect to the relative $\Delta G^{\neq}$ values. We found that the radical species **Vb** had the lowest cyclization energy, followed by **Va** for which $\Delta G^{\neq}$ was about 1 kcal mol^{-1} higher, whereas the barrier heights for compounds **VI** and **VII** were significantly larger (by 8–9 and 3 kcal mol^{-1}, respectively). These two sets of results were fully consistent with the hierarchy of the $\Delta G^{\neq}$ values deduced from the experimental rate constants (Table 3). Accordingly, the lowest cyclization energy transition state (TS) proceeded through a 5-*exo* backside process, with a quasi-perfect collinearity between the attacking C-centered radical species and the $SiMe_3$ leaving group (at an C–Si–Si angle of 168°; Figure 1).

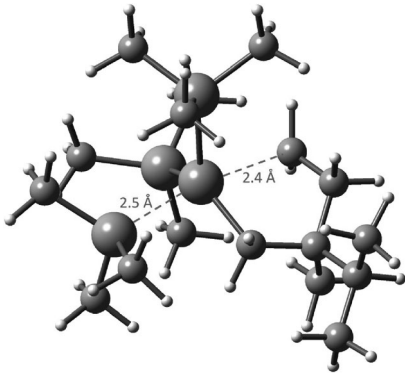


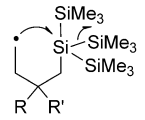
Figure 1. TS associated with the cyclization of precursor **Vb** calculated at the B3LYP/6-31G(d) level.

The analysis of the TS structure showed that the silicon center was pentacoordinated with very similar distances for the forming and breaking bonds (2.4 and 2.5 Å, respectively). Moreover, the vibrational mode associated with the imaginary frequency suggested that the cyclization at the radical center occurred simultaneously with the leaving of the $SiMe_3$ group in a single-step process. Finally, it is worth mentioning that 6-*endo* (or 1,5-translocation) reactive processes for compounds **V**–**VII** have also been modeled at the B3LYP/6-31G(d) and BH&HLYP/6-31G(d) levels. The differences in the free enthalpies of activation of the 6-*endo* and 5-*exo* reactions are compiled in Table 5. At both levels of theory, the activation barriers for the 6-*endo* reaction were 3–6 kcal mol^{-1} higher than those of the competing 5-*exo* reaction. This indicated that the 1,5-translocation product did not form, confirming Matsubara and Schiesser's calculations[13c] on simpler models (SiH_3 instead of $(Me_3Si)_3Si$) in good agreement with our experimental results.

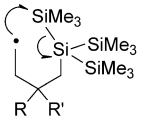
Conclusion

This study provides the first experimental evidence that silyl radicals may be generated from silylboranes and that chain-transfer processes may be induced by this approach. Thus, cyclization reactions through a homolytic substitution at a silicon center afforded high yields of the corresponding cyclic silanes, along with a trimethylsilyl radical that could be efficiently trapped with sulfonyl acceptors. We made similar observations for the 1,5-hydrogen transfer reaction, starting from the corresponding arylsilylborane. Although the release of the silyl radical was effective in both processes, we realized that the trapping of this elusive species required highly reactive traps. As a result, this strategy is limited to highly reactive alkyl halides. For instance, tertiary bromides gave oximation products, albeit in modest yields, most likely due to the high rate of reactions between the silyl radical chain carrier and catecholborane derivatives. Nevertheless, kinetic studies established that the exploitation of the *gem*-dialkyl effect, along with an increase in the size of the substituents on the quaternary center led to the fastest S_Hi processes reported to date, as far as disilanes are concerned. This work paves the way for the future development of S_Hi and 1,5-hydrogen transfer processes based on silylborane methodology.

Table 5. Differences in the free enthalpies of activation [kcal mol^{-1}] of the 6-*endo* and 5-*exo* reactions ($\Delta G^{\neq}_{endo} - \Delta G^{\neq}_{exo}$), as calculated at the B3LYP/6-31G(d) and BH&HLYP/6-31G(d) levels.



5-*exo* (S_Hi)



6-*endo* (1,5-translocation)

Precursor	B3LYP/6-31G(d)	BH&HLYP/6-31G(d)
Va (R = R′ = Me)	5.36	5.81
Vb (R = Me, R′ = *i*Pr)	6.07	5.47
VI (R = R′ = H)	3.15	2.44
VII	3.70	3.00

Experimental Section

General information: All reactions were carried out under a nitrogen atmosphere in dry solvents under anhydrous conditions, unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C) homogeneous materials, unless otherwise stated. Commercial reagents were used without further purification, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-250 FT (^{1}H: 250 MHz, ^{13}C: 62.9 MHz), Bruker AC-300 FT, and (^{1}H: 300 MHz, ^{13}C: 75.46 MHz), Bruker ARX-400 FT (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) spectrometers in $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin–Elmer 1710 spectrophotometer, on a Perkin–Elmer Paragon 500 FTIR spectrophotometer, or on a Perkin–Elmer Mattson Unicam 500 16PC FTIR. Mass spectra were recorded on a Nermag R10-10C instrument. High-resolution mass spectra were recorded on a FT-ICR Bruker 4.7T BioApex II mass spectrometer. Melting points were not corrected and determined by means of a Stuart Scientific SMP3 apparatus. Merck silica gel 60 (70–230 mesh) was used for flash chromatography. Benzene was distilled from sodium and benzophenone and dichloromethane from CaH_2. Catecholborane was distilled under a nitrogen atmosphere. DTBHN was synthesized according to a reported procedure.[33] GC was performed on a on a Fisons Instruments, GC 8000 Series, instrument. GC method: initial temperature = 50 °C; initial time = 5 min; ramp = 15 °C min^{-1}; final temperature =

300 °C; final time = 10 min; carrier gas : He; Column: 30 m, DB5; diameter: 0.25 mm; film thickness: 0.25 μm.

General procedure A: Addition of silyl radicals to sulfones: Catecholborane (2 equiv) was added dropwise at 0 °C to a solution of the olefin (1 equiv, 1 M) and DMA (0.1 equiv) in CH_2Cl_2. The mixture was stirred at 45 °C for 3 h. Then, *tert*-butanol (1 equiv) was added at 0 °C and the mixture was stirred for 15 min at room temperature. CH_2Cl_2 was then evaporated under vacuum and strictly in the absence of O_2. Benzene (degassed with freeze–pump–thaw cycles (3×), the volume depending on the desired concentration in sulfone) was transferred into the flask. The sulfone was then added and the solution was heated to 65 °C. Subsequently, DTBHN (0.1 equiv) was added every 1.5 h, until the solution turned black. Benzene was evaporated and the desired product was purified by flash column chromatography through silica gel.

Alkynylsilane (7): The general procedure A was followed. Alkene **3** (150 mg, 0.50 mmol), catecholborane (0.1 mL, 1.00 mmol), and DMA (4 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL) were used. The reaction mixture was quenched with *tert*-butanol (0.046 mL, 0.50 mmol). The radical reaction was performed with **6** (242 mg, 1.00 mmol), and DTBHN (10 mg, 0.06 mmol, 2 additions) in benzene (degassed, 0.25 M in sulfone, 4 mL). Products were purified by flash column chromatography through silica gel (petroleum ether/AcOEt : 98/2), affording **7** as a white solid (130 mg, 66 %). An analytical sample was recrystallized from methanol. $R_f = 0.5$ (petroleum ether/AcOEt 98/2); m.p. (methanol) 134 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.73$–7.71 (m, 4H), 7.59–7.56 (m, 2H), 7.48–7.17 (m, 12H), 7.15–7.13 (m, 1H), 3.36 (visible quint, $J = 6$ Hz, 1H), 1.11 ppm (d, $J = 6$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 156.4$, 137.2, 135.7, 134.4, 132.2, 131.0, 130.9, 129.8, 129.0, 128.4, 128.0, 125.9, 125.4, 123.0, 109.1, 90.2, 34.7, 24.2 ppm; IR (neat): $\tilde{\nu} = 3066.9$, 2960.8, 2156.2, 1428.4, 1109.4, 830.5, 755.9, 698.0 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{29}H_{26}SiNa$ $[M+Na]^+$: 425.1701; found: 425.1704.

Adamantyl oxime (10) and adamantyl sulfide (11): Following general procedure A was followed. Alkene **3** (150 mg, 0.50 mmol), catecholborane (0.1 mL, 1.00 mmol), and DMA (0.1 equiv) in CH_2Cl_2 (0.5 mL) were used. The reaction was quenched with *tert*-butanol (0.046 mL, 0.50 mmol). The radical reaction was conducted with **9** (137 mg, 0.50 mmol), 1-bromoadamantane (322 mg, 1.50 mmol), and DTBHN (10 mg, 0.06 mmol, 2 additions) in benzene (degassed, 0.25 M in sulfone, 2 mL). Products were purified by flash column chromatography through silica gel, affording **11** as a white solid (33 mg, 27 %) eluted with petroleum ether, and **10** as a colorless oil (33 mg, 25 %) eluted with petroleum ether/AcOEt (98/2).

Compound ***10***: $R_f = 0.35$ (petroleum ether/AcOEt 98/2); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.39$–7.28 (m, 5H), 7.22 (s, 1H), 5.04 (s, 2H), 2.01 (br s, 3H), 1.79–1.64 ppm (m, 12H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta =$ 158.9, 137.8, 128.5, 128.4, 127.9, 75.7, 40.1, 36.7, 35.8, 28.0 ppm; IR (neat) $\tilde{\nu} = 2904.4$, 2847.6, 1724.6, 1626.1, 1440.6, 1297.6, 1192.2, 1209.4, 1174.6, 1134.7, 942.4, 836.2 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{23}NONa$ $[M+Na]^+$: 292.1677; found: 292.1679.

Compound ***11***: $R_f = 0.48$ (petroleum ether); m.p. 68 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.52$–7.48 (m, 2H), 7.34–7.30 (m, 3H), 2.00 (br s, 3H), 1.80 (d, $J = 2$ Hz, 6H), 1.68–1.54 ppm (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 137.8$, 130.7, 128.6, 128., 47, 43.7, 36.3, 30.1 ppm; IR (neat): $\nu =$ 2902.6; 2848.7, 1692, 1573, 1474.3, 1441.50, 1341.0, 1295.8, 1259.2, 1037.4, 1023.5, 837.7, 826.7, 751.1 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{20}SNa$ $[M+Na]^+$: 267.1183; found: 267.1183.

Compound 27: Spectroscopic data matched those of a commercial sample. $R_f = 0.44$ (petroleum ether); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta =$ 7.49–7.44 (m, 2H), 7.32–7.27 (m, 3H), 0.25 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 132.1$, 128.6, 128.3, 123.2, 105.2, 94.2, 0.12 ppm.

Intramolecular homolytic substitution on precursor 21c: The general procedure A was followed. Alkene **21c** (100 mg, 0.27 mmol), catecholborane (0.06 mL, 0.540 mmol), and DMA (2.4 mg, 0.027 mmol) in CH_2Cl_2 (0.3 mL) were used, then quenched with *tert*-butanol (0.025 mL, 0.270 mmol). The radical reaction was performed in benzene (degassed, 0.5 M in sulfone, 2.16 mL) with **6** (131 mg, 0.540 mmol), and DTBHN (5 mg, 0.030 mmol, 2 additions). Products were purified by flash column chromatography through silica gel (petroleum ether), affording **26c** as a colorless oil (56 mg, 73 %), **28c** as a colorless oil (9 mg, 7 %), **27** as a colorless oil (20,5 mg, 44 %), and **29c** was eluted with petroleum ether/AcOEt (90/10) as a colorless oil (16 mg, 16 %). Analytical data for **27** matched those described above.

Compound ***26c***: $R_f = 1$ (petroleum ether); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.67$–1.59 (m, 1H), 1.45 (septet, $J = 6.9$ Hz, 1H), 1.29–1.18 (m, 1H), 0.89 (d, $J = 6{,}9$ Hz, 3H), 0.85 (d, $J = 6.9$ Hz, 3H), 0.86–0.81 (m, 2H), 0.68 (s, 1H), 0.64–0.56 (m, 2H), 0.12 (s, 9H), 0.09 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 46.5$, 40.0, 38.8, 20.7, 19.7, 18.7, 18.6, 6.3, −0.2, −0.6 ppm; IR (neat): $\tilde{\nu} = 2954$, 2869.2, 1456, 1387, 1059.1, 831.4, 788.94 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{14}H_{34}Si_3$ $[M]^{+\cdot}$: 286.1968; found: 286.1967.

Compound ***28c***: $R_f = 0.85$ (petroleum ether); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.40$–7.35 (m, 2H), 7.30–7.24 (m, 3H), 2.36–2.28 (m, 2H), 1.74–1.52 (m, 3H), 1.00–0.98 (m, 2H), 0.88 (d, $J = 4$ Hz, 6H), 0.83(s, 3H), 0.20 ppm (s, 27H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 131.6$, 128.3, 127.5, 124.2, 90.9, 80.6, 39.0, 37.4, 35.0, 25.1, 17.5, 17.3, 17.2, 14.3, 1.7 ppm; IR (neat): $\tilde{\nu} = 2977.6$, 2903.2, 1493, 1246.3, 831.1 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{25}H_{48}Si_4Na$ $[M+Na]^+$: 483.2730; found: 483.2731.

Compound ***29c***: $R_f = 0.3$ (petroleum ether/AcOEt, 90:10); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 3.74$–3.64 (m, 2H), 1.65–1.49 (m, 3H), 1.06 (d, $J =$ 14 Hz, 1H), 0.97 (d, $J = 14$ Hz, 1H), 0.89 (s, 3H), 0.85 (d, $J = 2.8$ Hz, 3H), 0.83 (d, $J = 2.8$ Hz, 3H), 0.19 ppm (s, 27H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 59.8$, 41.9, 37.1, 36.0, 25.7, 18.3, 17.6, 17.4, 1.7 ppm; IR (neat): $\tilde{\nu} =$ 3293.3, 2957.2, 2892.8, 1456.7, 1384.9, 1244.4, 1061.2, 1042.6, 1014.5, 827.1 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{44}OSi_4$ $[M+Na]^+$: 399.2367; found: 399.2367.

Oximation of 8 with 21c: Following the general procedure A, alkene **21c** (180 mg, 0.500 mmol), catecholborane (0.1 mL, 1.000 mmol), and DMA (4 mg, 0.050 mmol) in CH_2Cl_2 (0.5 mL), then quenched with *tert*-butanol (0.046 mL, 0.500 mmol). The radical reaction was performed with **9** (137 mg, 0.500 mmol), **8** (322 mg, 1.500 mmol), and DTBHN (10 mg, 0.060 mmol, 2 additions) in benzene (degassed, 0.25 M in sulfone, 2 mL). Products were purified by flash column chromatography through silica gel, affording **26c** as a colorless oil (108 mg, 76 %) with petroleum ether as the eluent, **10** as a colorless oil (52 mg, 39 %) with petroleum ether/AcOEt (98/2) as the eluent, and **29c** as a colorless oil (26 mg, 14 %) with petroleum ether/AcOEt (90/10) as the eluent. Analytical data for **10**, **26c**, and **29c** matched those previously reported.

General procedure B: Kinetic measurements: Bromide (1 equiv), $(Me_3Si)_3SiH$ (>10 equiv), tetradecane (≈1.5 equiv, internal standard), and AIBN (0.2 equiv) were dissolved in benzene. The solution was degassed by freeze–pump–thaw cycles (3×) then transferred into a sealed tube. The mixture was stirred (2–3 h) at 90 °C. After completion of the reaction, the solution was cooled down to room temperature and a sample was analyzed by GC.

Kinetic studies with bromide 31a (results compiled in Table 2)

Experiment A: Performed according to the general procedure B with bromide **31a** (76 mg, 0.184 mmol), tris(trimethylsilyl)silane ($(Me_3Si)_3SiH$, TTMSH; 1.022 g, 4.12 mmol, 1.2 M), tetradecane (51 mg, 0.26 mmol), and AIBN (7 mg, 0.04 mmol) in benzene (3.43 mL).

Experiment B: Performed according to the general procedure B from bromide **31a** (78 mg, 0.189 mmol), TTMSH (1.46 g, 5.88 mmol, 1.4 M), tetradecane (55.4 mg, 0.28 mmol), and AIBN (7 mg, 0.04 mmol) in benzene (4.2 mL).

Experiment C: Performed according to the general procedure B from bromide **31a** (76 mg, 0.184 mmol), TTMSH (1.89 g, 7.620 mmol, 2.05 M), tetradecane (55.4, 0.28 mmol), and AIBN (7 mg, 0.04 mmol) in benzene (3.7 mL).

Kinetic studies with bromide 31b (results collected in Table 2)

Experiment A: Performed according to the general procedure B from bromide **31b** (77 mg, 0.175 mmol), TTMSH (925 mg, 3.72 mmol, 1.43 M), tetradecane (52 mg, 0.26 mmol), and AIBN (9 mg, 0.05 mmol) in benzene (2.6 mL).

Experiment B: Performed according to the general B procedure from bromide **31b** (64 mg, 0.146 mmol), TTMSH (1.054 g, 4.25 mmol, 1.93 M),

tetradecane (43 mg, 0.22 mmol), and AIBN (7 mg, 0.04 mmol) in benzene (2.2 mL).

Experiment C: Performed according to the general procedure B from bromide **31b** (97 mg, 0.221 mmol), TTMSH (2.23 g, 9 mmol, 2.81 M), tetradecane (65 mg, 0.33 mmol), and AIBN (9 mg, 0.05 mmol) in benzene (3.2 mL).

Computational calculations: Geometry optimizations were carried out using DFT with the B3LYP and BH&HLYP exchange-correlation functionals and the 6-31G(d) basis set with a tight convergence threshold on the residual forces. Every TS was characterized by an imaginary frequency associated to one single vibrational mode. Thermal corrections were calculated from the unscaled harmonic vibrational frequencies by using standard temperature and pressure conditions. All calculations were performed with Gaussian 09.[34]

X-ray crystallography: CCDC-833211 (**17**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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