Synthetic Methods

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Reductive Carbocyclization of Homoallylic Alcohols to *syn*-Cyclobutanes by a Boron-Catalyzed Dual Ring-Closing Pathway

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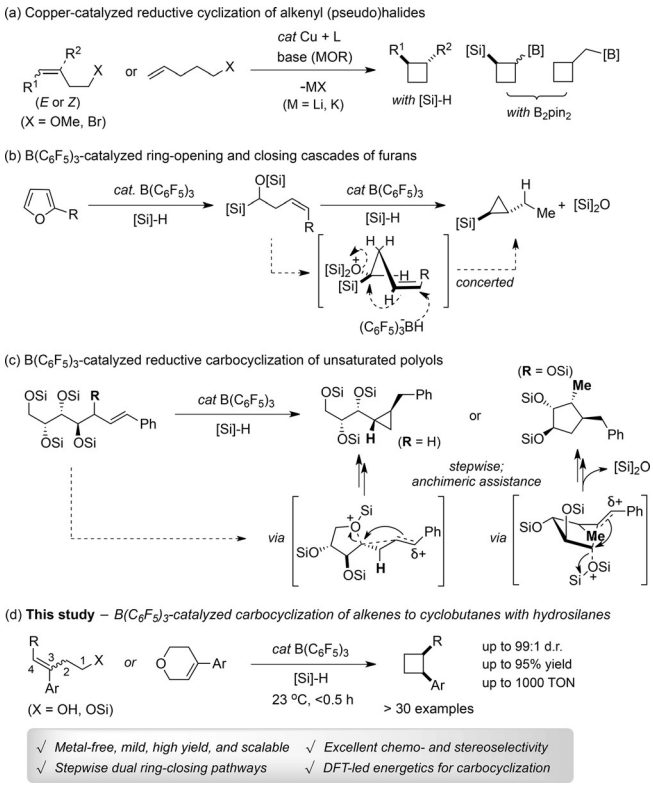
Abstract: *The organoborane-catalyzed reductive carbocyclization of homoallylic alcohols has been developed by using hydrosilanes as reducing reagents to provide a range of 1,2-disubstituted arylcyclobutanes. The reaction proceeds in a cis-selective manner with high efficiency under mild conditions. Mechanistic studies, including deuterium scrambling and Hammett studies, and DFT calculations, suggest a dual ring-closing pathway.*

Four-membered carbocycles, such as cyclobutanes and cyclobutenes, are valuable intermediates in organic synthesis because they can undergo a wide range of ring-opening, -contraction, or -expansion reactions.[1] These carbocycles provide access to many scaffolds found in biologically active molecules that are difficult to prepare by other means in drug design.[2] Conventional catalytic methods for the synthesis of such four-membered carbocycles can be largely divided into two types: 1) intra- or intermolecular [2+2] cycloadditions[3,4] and 2) ring expansion of cyclopropylcarbinyl precursors by a Wagner–Meerwein shift.[5,6] A powerful alternative to the conventional approaches has been developed independently by the groups of Ito and Buchwald, in which alkene substrates bearing (pseudo)halides undergo reductive cyclization by means of copper catalysis. This reaction was proposed to involve ring closure on organocuprate intermediates formed in situ, accompanied by the release of a (pseudo)halide salt (Scheme 1 a).[7]

Recently, we reported a $B(C_6F_5)_3$-catalyzed cascade conversion of furans providing silicon-functionalized compounds, in which a homoallylic intermediate was assumed to undergo a concerted S_N2'-type ring-closing process to furnish cyclopropanes with exclusive *trans*-selectivity (Scheme 1 b).[8] Gagné and co-workers found that $B(C_6F_5)_3$ promotes a reductive cyclization of silyl-protected unsaturated polyols to give cyclopropanes and cyclopentanes depending on the substituents adjacent to the alkenyl moiety (Scheme 1 c).[9] Unlike in our previous work,[8] Gagné suggested a stepwise pathway involving an intramolecular attack of a neighboring alkenyl group at the activated C–O bond of the silaoxonium ion. This pathway takes advantage of anchimeric assistance[10] to generate a benzylic cation with C–C bond formation. Inspired by these results, we envisioned that homoallylic alcohols bearing an aryl substituent at the C3 position may undergo a carbocyclization with anchimeric assistance from an adjacent alkenyl group to give cyclobutanes under a $B(C_6F_5)_3$/silane catalytic system. Reported herein is the first boron-catalyzed reductive cyclobutanation of homoallylic alcohols with hydrosilanes (Scheme 1 d). The present catalysis produces a range of 1,2-disubstituted (hetero)arylcyclobutanes with remarkably high efficiency and excellent *cis*-selectivity. Experimental and computational experiments strongly support a stepwise, dual ring-closing pathway.



Scheme 1. a–c) Reductive catalytic approaches towards the synthesis of carbocycles. d) $B(C_6F_5)_3$-catalyzed reductive cyclobutanation (this work).

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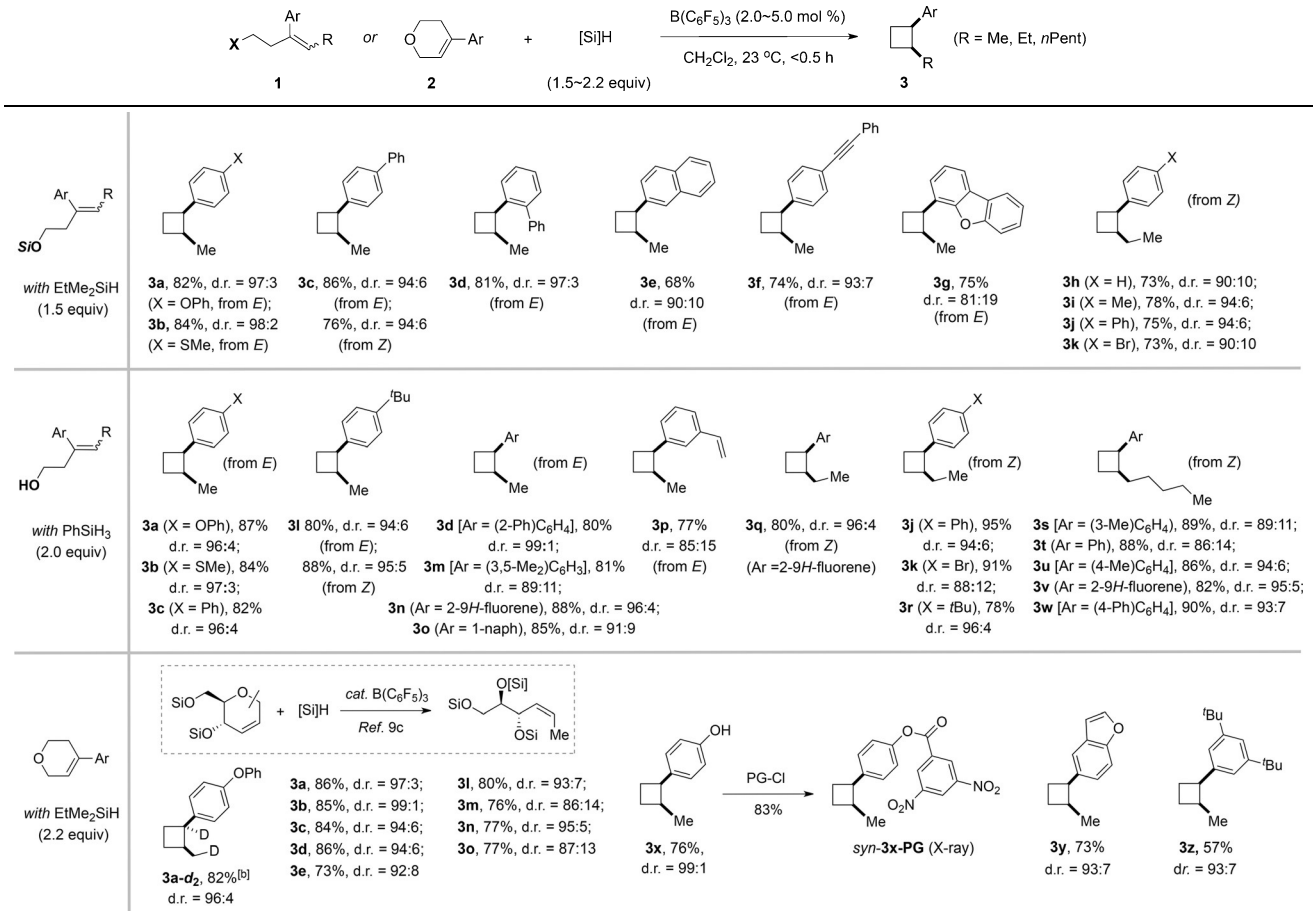
Initially, one representative homoallylic *O*-silyl ether (Scheme 1 d, R = Me; X = $OSiEt_3$) was chosen and the reaction conditions were optimized (see the Supporting Information). The substrate underwent a condensation cyclization reaction when 1.5 equivalents of $EtMe_2SiH$ were used in the presence of 2.0 mol % of $B(C_6F_5)_3$ in dichloromethane to afford the corresponding 1,2-disubstituted cyclobutane quantitatively in 0.5 h at 23 °C. The stereochemistry of the product was determined to be *syn* by 2 D NMR experiments, and its diastereomeric ratio (d.r.) was calculated by ^{1}H NMR analysis of the crude reaction mixture (d.r. > 95:5).

With the optimized conditions in hand [2.0 mol % $B(C_6F_5)_3$, 1.5 equiv of $EtMe_2SiH$, CH_2Cl_2, 23 °C], we investigated the substrate scope in the cyclobutanation of silyl-protected homoallylic alcohols (Table 1, top). In general, the reaction was highly facile, completed within 0.5 h, and the diastereoselectivity was excellent in most cases. Functional groups such as phenoxy or thioether, which are known to be labile under the reductive conditions,[11] were compatible (**3a** and **3b**, respectively). Significantly, the olefinic geometry (*E* or *Z*) of the substrates was not a stereochemistry-determining factor, as demonstrated in the formation of *syn*-cyclobutane **3c**. Analogous substrates bearing biphenyl or naphthyl groups were also reactive and selective for this transformation (**3d** and **3e**, respectively). A substrate bearing an alkynyl moiety was also smoothly cyclized leading to *syn*-**3f**. However, an *O*-silyl homoallyl ether possessing a dibenzofuranyl group underwent the desired cyclization with decreased diastereoselectivity (**3g**). As in the case of **3c**, when a series of (*Z*)-*O*-silyl homoallyl ethers with a 3-hexenyl skeleton (R = Et) were subjected to the standard conditions, the corresponding 1,2-arylethylcyclobutanes were formed with *syn*-stereochemistry (**3h**–**3k**).[12]

Next, we were curious as to whether unprotected homoallylic alcohols could be viable for the reductive cyclobutanation. This route was envisioned to be synthetically more convenient because the *O*-silyl homoallyl ethers had to be prepared from the parent alcohols. Pleasingly, the cyclization of homoallylic alcohols occurred under slightly modified conditions (Table 1, middle: 5.0 mol % $B(C_6F_5)_3$, 2 equiv of $PhSiH_3$).[13] A series of homoallylic alcohols bearing aryl groups were converted to the corresponding cyclobutanes with high *syn*-selectivity (**3a**–**3d** and **3l**–**3o**). Notably, a vinyl substituent at the phenyl moiety remained intact although the diastereoselectivity in this case was slightly decreased (**3p**). Replacing the olefinic substituent from a methyl (R = CH_3)

Table 1: Substrate scope in the ring-closing reaction of silyl-protected and parent homoallylic alcohols.[a]

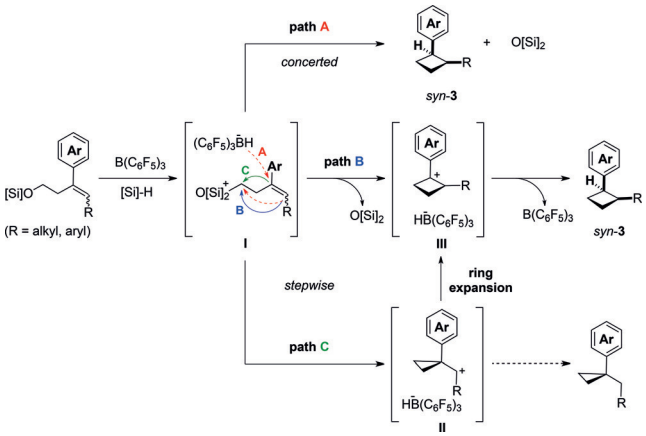


[a] $B(C_6F_5)_3$ (2.0–5.0 mol %), substrate (0.2 mmol), $EtMe_2SiH$ or $PhSiH_3$ (1.5–2.2 equiv) in CH_2Cl_2 at 23 °C for 0.5 h. Yields of isolated products are presented. Diastereomeric ratio (d.r.) was determined by ^{1}H NMR analysis of the crude reaction mixture. ***Si*** = $SiMe_3$, $SiEt_3$, or $SiMe_2tBu$. [b] 2.2 equiv of $PhMe_2SiD$ was used instead of $EtMe_2SiH$.

group to an ethyl ($R = CH_2CH_3$) or pentyl ($R = (CH_2)_4CH_3$) group did not deteriorate the reaction efficiency or diastereoselectivity (**3j**–**3k** and **3q**–**3w**).

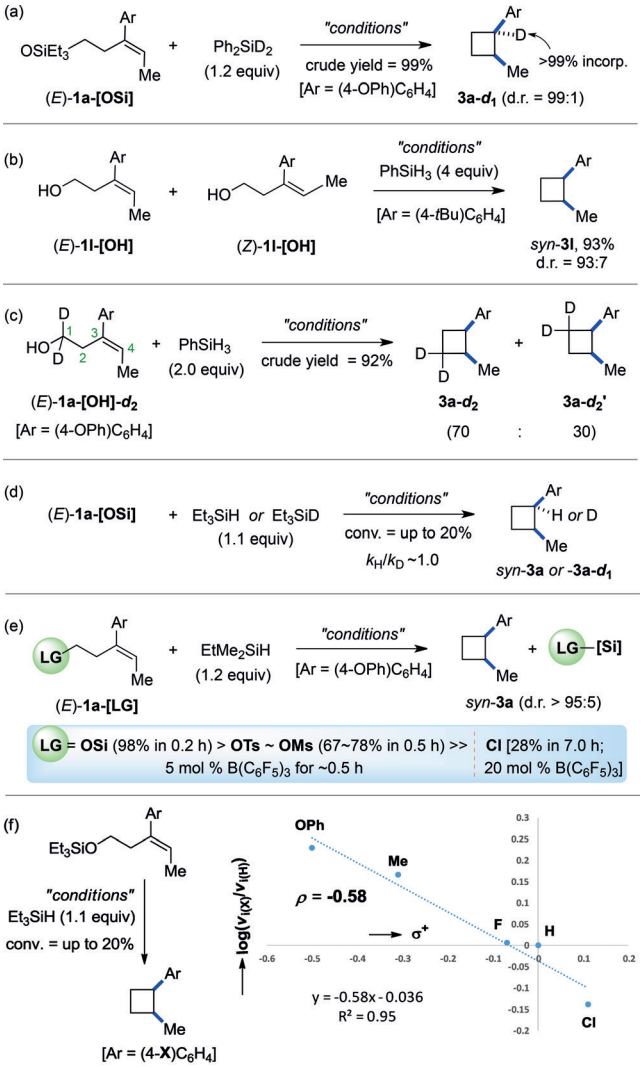
Gagné and co-workers showed that 3,6-dihydro-2*H*-pyrans undergo selective allylic C–O bond cleavage to generate silyl-protected homoallylic alcohols by $B(C_6F_5)_3$ catalysis (Table 1, bottom, inset).[9c] Inspired by this report, we tested C4 aryl-substituted dihydropyrans as substrates for the cyclobutanation. Indeed, a series of 4-aryl-dihydro-2*H*-pyrans were smoothly transformed to *syn*-cyclobutanes under similar conditions (Table 1, bottom: 2.0 mol% $B(C_6F_5)_3$, 2.2 equiv of $EtMe_2SiH$). In the same way as that for the reaction of *O*-silyl homoallyl ethers, the cyclobutanation of pyran substrates bearing electronic and/or steric variations showed good-to-excellent reactivity and *syn*-selectivity. The reaction of a pyran substrate with a deuterated hydrosilane afforded **3a**-d_2 with excellent *syn*-diastereoselectivity, demonstrating the selective ring-opening and -closing cascade of the pyran substrates. It is noteworthy that the reaction of a 2*H*-pyran possessing a benzofuranyl group cleanly gave the desired product **3y** in good yield.

Based on the selectivity and precedent in previous reports,[8,9] three cyclization pathways can be proposed (Scheme 2): 1) an S_N2'-type concerted mechanism (path A), 2) stepwise cyclobutanation (path B), and 3) a stepwise ring-closing and ring-expansion cascade (path C). All three possible pathways are assumed to be initiated by the formation of a silaoxonium ion complexed with borohydride (**I**).[14]



Scheme 2. Possible reaction pathways for cyclobutanation.

To validate the mechanistic details in the present cyclization, we performed a series of experimental mechanistic studies. The reaction of (*E*)-**1a-[OSi]** with Ph_2SiD_2 (1.2 equiv) in the presence of a $B(C_6F_5)_3$ catalyst proceeded to afford *syn*-**3a**-d_1 with complete deuterium incorporation (Scheme 3a). The $B(C_6F_5)_3$-catalyzed reaction of a 1:1 mixture of *E*/*Z* isomeric **1l-[OH]** with $PhSiH_3$ furnished a single product **3l** in 93% yield with 93:7 d.r. (Scheme 3b). This result may support the stepwise pathways B or C, in which a cyclobutyl benzylic carbocation **III** (Scheme 2) will be generated as a common



Scheme 3. Experimental mechanistic studies. "*conditions*": $B(C_6F_5)_3$ (2–10 mol%) in CH_2Cl_2 at 23 °C.

intermediate irrespective of the olefinic geometry in the homoallylic alcohol substrates.[15]

The reaction of a bis-deuterated homoallylic alcohol at the C1 position (**1a-[OH]**-d_2) was designed to investigate the involvement of pathway B and/or pathway C (Scheme 3c). In pathway C, a 1:1 mixture of cyclobutane products incorporating bis-deuterium atoms at the C3 and C4 positions (**3a**-d_2 and **3a**-d_2', respectively) is predicted, whereas only **3a**-d_2 will be obtained if pathway B is followed because the direct formation of a cyclobutyl carbocation **III** from the presupposed silaoxonium ion **I** is assumed. Intriguingly, the reaction of **1a-[OH]**-d_2 afforded an approximate 7:3 mixture of **3a**-d_2 and **3a**-d_2' in 92% crude yield, suggesting that pathways B and C are operative in a bifurcated manner for the ring-closing process.[16]

To identify the rate-determining step (RDS), the kinetic isotope effect (KIE) was measured to be 1.0 in cyclization reactions of **1a-[OSi]** with Et_3SiH and its deuterium analogue (Scheme 3d). Again, this result may suggest that a S_N2'-type nucleophilic attack of $(C_6F_5)_3BH^-$ at the C3 position of

a silaoxonium ion **I** is less likely.[17] When substrates possessing different types of leaving groups at the C1 position were allowed to react the yield of the cyclization reaction was observed to decrease in the following order: LG = $OSiEt_3$ > OTs ≈ OMs ≫ Cl (Scheme 3e). Together with KIE data, this result corroborates that the RDS would be a condensative intramolecular cyclization to form a carbocation intermediate.

Electronic effects on the cyclization rate were subsequently investigated (Scheme 3f). A plot of $v_{i(x)}/v_{i(H)}$ against the σ^+ Hammett constants provided a ρ value of −0.58 (R^2 = 0.95), indicating that substrates with more electron-rich aryl groups led to increased reaction rates.[18] This small ρ value can be taken to indicate an early transition state,[19] in which no strong resonance interaction occurs,[20] whereas there is a small positive-charge polarization at the C3 position in the RDS.

The mechanism of cyclobutane formation starting from the silaoxonium ion intermediate **A** is visualized in Figure 1 and was obtained from extensive exploration of the mechanism by using density functional calculations. For the forward reaction, the intermediate **A** first traverses the transition state **A-TS-B**, which is 16.0 kcal mol^{-1} higher in energy than **A**. From **A-TS-B**, the reaction affords the cyclopropane **B**, which is energetically downhill by −5.9 kcal mol^{-1}. However, with the given energy landscape, there is a very shallow minimum for **B** that is presumed to result in some portion of activated molecules at the transition state to directly proceed to the intermediate **C**, not via intermediate **B**.[21]

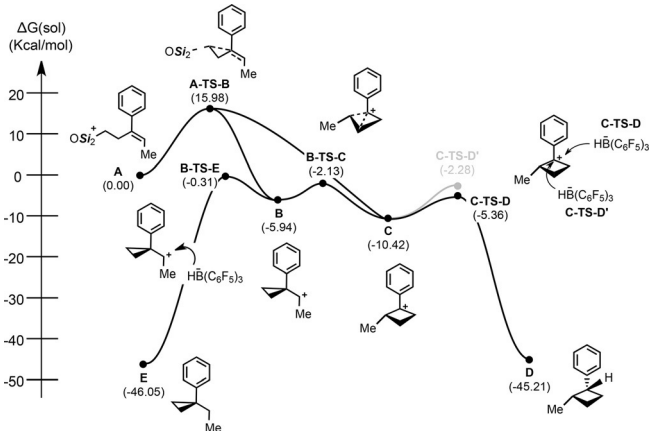
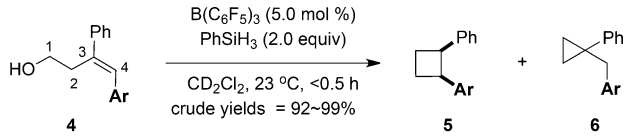


Figure 1. DFT-derived energetics of the $B(C_6F_5)_3$-mediated carbocyclization of (*E*)-3-phenylpent-3-en-1-ol with Et_3SiH (all structures were optimized at the M06/6-31G** level of theory).

Starting from intermediate **B**, the reaction may proceed through either intermolecular hydridation to form cyclopropane product **E** or intramolecular ring expansion to generate cyclobutane intermediate **C**. The barriers for both possibilities are too low at 5.6 and 3.8 kcal mol^{-1}, respectively, to infer any significant difference in the rate of these steps. It is an intermolecular process for the hydridation to proceed as shown on the left-hand side of Figure 1, whereas the ring expansion shown on the right-hand side is an entropically beneficial intramolecular event. Therefore, **C** at −10.4 kcal mol^{-1} should be formed exclusively. The intermediate **C** may then be attacked by a borohydride to give the product **D**, traversing another low barrier of 5.4 kcal mol^{-1}. Hydridation from the top is estimated to be preferred by approximately 3 kcal mol^{-1} over the bottom-side attack to give the *syn*-selective product **D**.

An additional mechanistic assumption was that if the reaction pathway involves a ring-expansion process (pathway C),[22,23] we may see a product distribution between cyclopropanes and cyclobutanes and the ratio will be susceptible to the electronic variation of substrates. Indeed, when electronically variable diaryl-3-butenols (**4**) were subjected to the standard conditions, reductive carbocyclization smoothly proceeded to afford a mixture of cyclobutanes and cyclopropanes in varied ratios (Scheme 4). Significantly,



Ar	5	:	6
= C_6H_4(4-CF_3)	96	:	4
= Ph	80	:	20
= C_6H_4(4-*t*Bu)	26	:	74
= C_6H_4(4-OPh)	11	:	89
= C_6H_4(4-OH)	<1	:	>99

Scheme 4. Electronic effects of the C4-aryl substituents on product distribution.

substrates bearing electron-rich C4-aryl groups were cyclized leading mainly to cyclopropanes. These data further support the conclusion that 1) pathway C is operative, and 2) hydride transfer to the electron-rich cyclopropylcarbinyl cation is facile. Additionally, our computed mechanistic model explains the electronic effect of the aryl groups (see the Supporting Information).

In summary, we have developed a borane-catalyzed carbocyclization of homoallylic alcohols and dihydro-2*H*-pyrans to produce *syn*-1,2-disubstituted cyclobutanes in high yields and with excellent selectivity. Mechanistic studies indicate that stepwise dual ring-closing pathways are operative, whereas the condensative intramolecular cyclization is turnover limiting. Tuning the electronic nature of the C4-aryl groups of homoallyl substrates can alter the reaction pathway to lead to cyclopropanes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbocyclization · cyclobutanes · homoallylic alcohols · neighboring-group effects · ring-closing

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[12] A gram-scale reaction of (*E*)-**1a-[OSi]** with $EtMe_2SiH$ (1.1 equiv) in the presence of $B(C_6F_5)_3$ (0.1 mol%) produced **3a** with 83% yield of isolated product (1.38 g) with >95% of *syn*-selectivity within 0.5 h at 23°C (see the Supporting Information).

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