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Synthesis of Stereodefined Trisubstituted Alkenyl Silanes Enabled by Borane Catalysis and Nickel Catalysis

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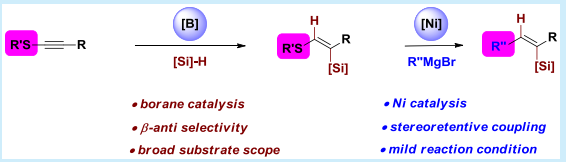
ABSTRACT: Regioselective and stereoselective synthesis of trisubstituted alkenyl silanes via hydrosilylation is challenging. Herein, we report the first *β-anti*-selective addition of silanes to thioalkynes with $B(C_6F_5)_3$ as the catalyst. The reaction shows broad substrate scope. The products were proven to be useful intermediates to other trisubstituted alkenyl silanes by Ni-catalyzed stereoretentive cross-coupling reactions of the C−S bond. A mechanism study suggests that nucleophilic attack of thioalkyne to an activated silylium intermediate might be the rate-determining step.



Organosilicon compounds are widely used in synthetic chemistry and material science.[1] Functionalized trisubstituted alkenyl silanes are of particular importance because the functional group can be used to make new chemical bonds. Catalytic hydrosilylation of internal alkynes is the most atom-economical method to prepare these alkenyl silanes (Scheme 1a).[2,3] However, there are two challenges in this chemistry: (1) control of the regioselectivity and stereoselectivity of the hydrosilylation step and (2) stereoselective transformation of the C−FG bond of the product to another useful bond.[3] Thioalkynes are stable and readily available compounds. In this context, we envisioned that the selective hydrosilylation of internal thioalkynes will provide silyl-substituted alkenyl sulfide as versatile synthetic building blocks, if both the C−S and C−Si bonds can be further functionalized (Scheme 1b).[1−4]

Scheme 1. Background of Synthesis of Trisubstituted Alkenyl Silanes via Hydrosilylation and Reaction Design

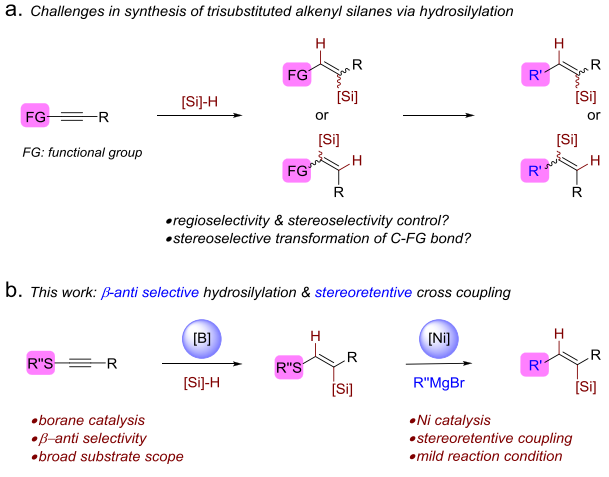
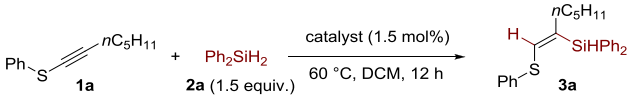


Table 1. Investigation of Reaction Conditions[a]



entry	catalyst	conv. (%)	yield (%)	Z/E	β/α
1	$AlCl_3$	<2	<1	/	/
2[b]	$AlCl_3$	40	10	>99:1	>99:1
3	$BF_3{\cdot}Et_2O$	<2	<1	/	/
4	BCl_3	<2	<1	/	/
5	BBr_3	<2	<1	/	/
6	$Zn(OTf)_2$	<2	<1	/	/
7	$CuCl_2$	<2	<1	/	/
8	$B(C_6F_5)_3$	>99	85	>99:1	>99:1
9	/	<2	<1	/	/

[a]Conditions: under N_2 protection, catalyst was added into the mixture of **1a** and **2a** in dry DCM at rt, and then the mixture was heated at 60 °C for 12 h; the conversion of **1** and the yield and selectivity of **3a** were determined by ^1H NMR with $BrCH_2CH_2Br$ as an internal standard. [b]120 mol % of $AlCl_3$ was used, instead of 1.5 mol %.

However, it is challenging to control regio- and/or stereoselectivity of the hydrosilylation of internal thioalkynes.[5] Previous hydrosilylation of internal thioalkynes all employed transition metal complexes as catalysts, and only *α-syn* addition into the triple bond was achieved in high selectivity. In 1988, Isobe and co-workers reported Pt-catalyzed *α-syn*-selective addition of tertiary silanes into the triple bonds of internal thioalkynes, and the products were converted to alkenyl

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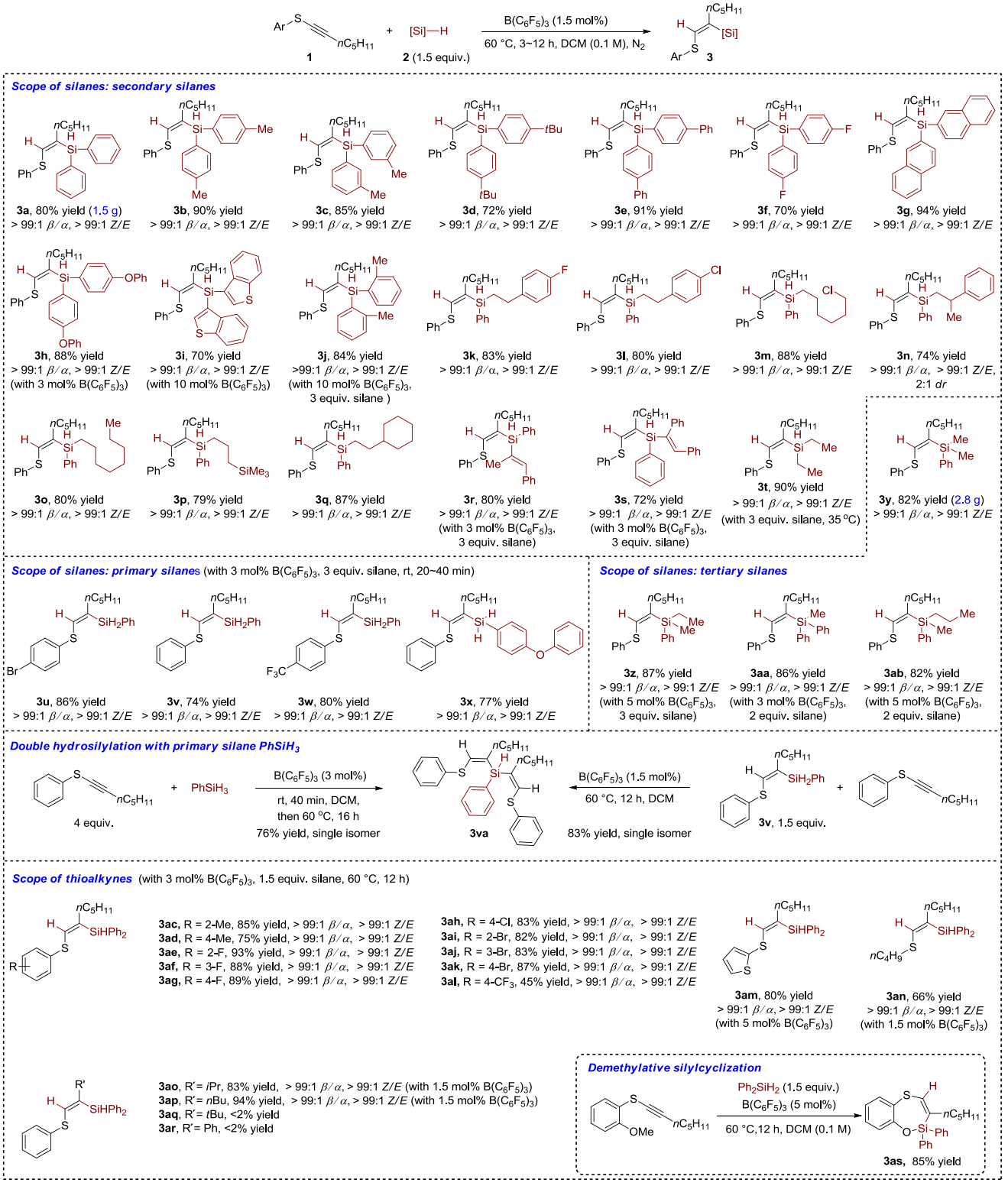
Scheme 2. Scope of *β-anti*-Selective Hydrosilylation of Thioalkynes with Silanes



sulfones for conjugate addition reactions.[5a,b] In 1999, the same group achieved *α-syn*-selective hydrosilylation reactions with a Co catalyst.[5c−f] In 2015, the Sun, Wu, Chung, and Zhang groups disclosed a Ru-catalyzed hydrosilylation system, which also afforded *α-syn* selectivity.[5g] Both the sulfenyl group and the bulky silane $(TMSO)_3SiH$ proved crucial to high regio- and stereoselectivity.[5g] Later, the Sun, Wu, and Zhang groups extended their methodology to an Ir-catalyzed system, in which *α-syn* selectivity was again obtained with tertiary silanes.[5h] To the best of our knowledge, there is no *β-anti*-selective hydrosilylation of internal thioalkynes. We are not aware of selective hydrosilylation of thioalkynes with primary and secondary silanes as agents. This is probably because it is challenging to inhibit the reaction of the hydrosilylation

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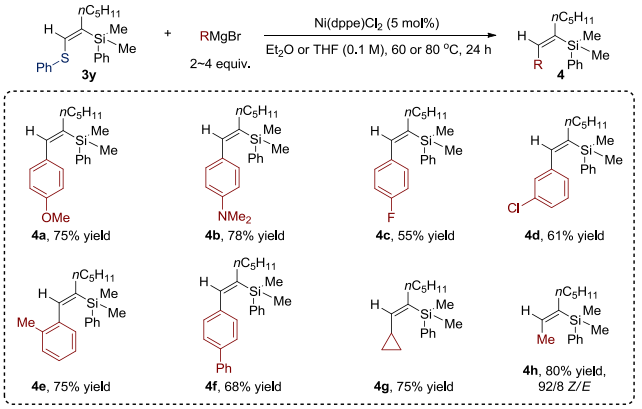
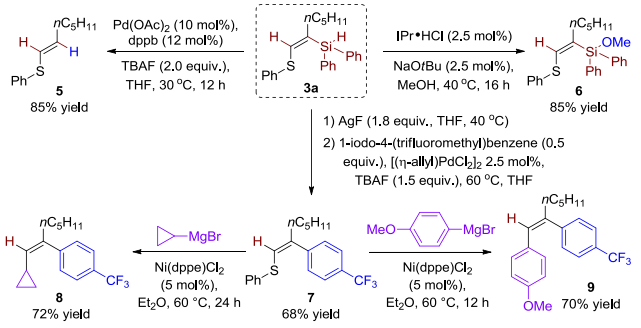
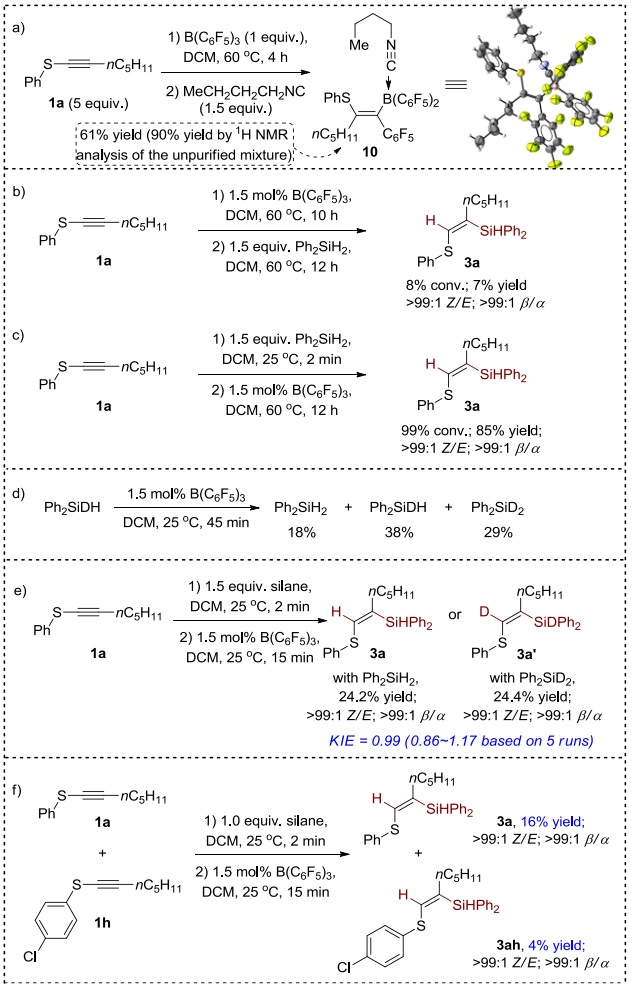
Scheme 3. Nickel-Catalyzed Cross Coupling of Silyl-Substituted Alkenyl Sulfide 3y with Various Grignard Reagents



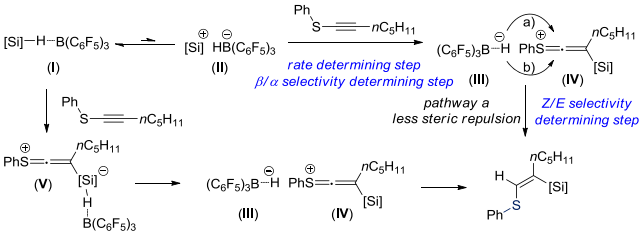
Scheme 4. Transformations of the Si−H Bond, C−Si Bond, and C−S Bond



Scheme 5. Mechanism Study



Scheme 6. Proposed Mechanism



product with another alkyne substrate. In 2017, Chang and co-workers reported a *β-anti*-selective hydrosilylation of internal yamides, but no further transformation of the C−N bond was disclosed.[6] Herein, we show that $B(C_6F_5)_3$ can efficiently catalyze the reaction of primary, secondary, and tertiary silanes with thioalkynes, affording silyl-substituted alkenyl sulfides with complete *β-anti* selectivity (Scheme 1b). The metal-free process has broad substrate scope with high functional group tolerance and can be performed under mild conditions. Stereoretentive cross coupling of the C−S bond under Ni catalysis demonstrated the unique synthetic potential compared with the C−N bond.

Initially, thioalkyne **1a** and secondary silane Ph_2SiH_2 (**2a**, 1.5 equiv) were employed as the model substrates (Table 1). We chose $AlCl_3$ as the catalyst for initial evaluation in view of its reported ability to promote hydrosilylation of electron-neutral alkynes.[7] However, the reaction with 1.5 mol % of $AlCl_3$ in DCM at 60 °C did not afford any **3a** after 12 h (Table 1, entry 1). After increasing the amount of $AlCl_3$ to 120 mol %, there was only 40% conversion of **1a**, and **3a** was isolated in 10% yield, >99:1 β/α, and >99:1 *Z*/*E* (entry 2). This excellent regioselectivity is in contrast to the previous low β/α selectivity in electron-neutral internal alkynes.[7a] The low yield of the $AlCl_3$ system led us to investigate other Lewis acids.[8] We found that $BF_3{\cdot}Et_2O$, BCl_3, BBr_3, $Zn(OTf)_2$, and $CuCl_2$ did not give any of the desired product (entries 3−7). $B(C_6F_5)_3$ was found to be optimal, and the yield of **3a** increased to 85%, with complete *β-anti*-selectivity (entry 8). Without $B(C_6F_5)_3$, **3a** was not formed (entry 9).

With the optimized conditions in hand, we explored the scope of the hydrosilylation of thioalkynes with different silanes (Scheme 2). A wide range of silanes, including primary, secondary, and tertiary silanes as well as a variety of thioalkynes reacted efficiently and with high regio- and stereoselectivity. Many functional groups, such as F, Cl, Br, CF_3, OPh, or an alkenyl unit, are tolerated. The more hindered silanes required higher catalyst loading and/or reagent loading at 60 °C, while primary silanes reacted readily at room temperature. Double hydrosilylation of thioakyne **1a** with $PhSiH_3$ was achieved in one pot (**3va**, 76% yield, >98% regioselectivity). The method is scalable: we prepared 1.5 g of **3a** and 2.8 g of **3y** in 80% yield, >99:1 β/α, >99:1 *Z*/*E* and 82% yield, >99:1 β/α, >99:1 *Z*/*E*, respectively. Unfortunately, when $HSi(OMe)_3$, $HSiMe(OEt)_2$, and $HSiMe_2(OEt)$ were used as silane reagents, no desired hydrosilylation product was found. Various thioalkynes can

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participate in the hydrosilylation reactions, affording **3ac**−**3ap** in 45−94% yield, with excellent selectivity. However, *t*Bu- and Ph-substituted thioalkynes did not work under current conditions, which might be because of the steric hindrance of these substituents. It is worthy of note that the methoxy group can serve as a removable directing group, and seven-membered silacyclic **3as** was prepared in 85% yield by demethylative silacyclization.

Next, we explored whether a sulfide-substituted alkenyl silane can be converted into other trisubstituted alkenyl silanes (Scheme 3). Although cross-coupling of alkenyl halides has been well studied,[9] the investigation of alkenyl sulfide in cross-coupling chemistry is considerably less developed.[4,10] Thus, on the basis of the seminal reports by Kumada and Takei,[10a,b] we investigated the cross-coupling of silyl-substituted *Z*-alkenyl sulfide with Grignard reagents. We were able to react a variety of aryl Grignard reagents with **3y** in the presence of $Ni(dppe)Cl_2$ (5.0 mol %) to generate the corresponding alkenyl silanes in 55−80% yield; all transformations were entirely stereoretentive. Moreover, cyclopropyl-substituted **4g** was obtained in 75% yield and as a single isomer. These stereodefined trisubstituted alkenyl silanes are difficult to synthesize by other methods. In addition, by using MeMgBr, we were able to synthesize **4h** in 80% yield and a 92:8 *Z*/*E* ratio. It is encouraging that the steric bulky silyl group did not inhibit the cross-coupling reactions.

We then investigated the selective transformation of the silyl moiety (Scheme 4). Protodesilylation reaction of compound **3a** proceeded smoothly, affording alkenyl sulfide **5** in 85% yield, with the C−S bond unchanged. The Si−H bond of compound **3a** was converted to the Si−OMe bond, and alkenyl silane **6** was synthesized in 85% yield. Pd-catalyzed Hiyama coupling afforded trisubstituted alkenyl sulfide **7** in 68% yield. An ensuing bisphosphine−Ni-catalyzed cross coupling delivered trisubstituted alkenes **8** (72% yield) and **9** (70% yield); such entities cannot be easily accessed by alternative methods.[11] It is noteworthy that an alkene's stereochemical identity was preserved in the above sequence of reactions.

We then focused on gaining some insight regarding the hydrosilylation process. The ability of $B(C_6F_5)_3$ to activate a Si−H bond is well appreciated and has been proposed in the context of catalytic hydrosilylation.[12] However, $B(C_6F_5)_3$ can also react with thioalkyne to generate carboboration product **10** (Scheme 5a).[13] The identity of **10** was determined through X-ray crystallography. The question then was: might the carboboration product be the actual catalyst in the present set of hydrosilylation reactions? To clarify, we performed the following reaction: mixing thioalkyne **1a** with 1.5 mol % of $B(C_6F_5)_3$ in CH_2Cl_2 for 10 h at 60 °C, and then 1.5 equiv of Ph_2SiH_2 was added. The resulting mixture was heated at 60 °C for another 12 h. Only 8% conversion of **1a** and 7% yield of **3a** were observed (^1H NMR analysis; Scheme 5b). However, when $B(C_6F_5)_3$ was added after mixing compound **1a** and Ph_2SiH_2, there was complete conversion, and **3a** was isolated in 85% yield, >99:1 *Z*/*E* ratio, and >99:1 β/α selectivity (Scheme 5c). These findings indicate that $B(C_6F_5)_3$ is likely the catalyst.[14]

To establish which step is rate-determining, we carried out reactions with deuterium-labeled substrates. We found H−D scrambling to be efficient in the reaction of Ph_2SiHD with $B(C_6F_5)_3$ at room temperature (Scheme 5d). The KIE value of 0.99 suggests that Si−H bond clevage is not kinetically significant (Scheme 5e). These data led us to the mechanism proposed in Scheme 6. Silylium intermediate II, generated through reaction between a silane and $B(C_6F_5)_3$, can be in equilibrium with I, in the presence of Lewis basic thioalkyne;[12] addition of thioalkyne to II then gives ketene sulfonium species IV, which may be converted to the final product after reaction with boron hydride III. The competition reaction with electronically distinct thioalkynes (Scheme 5f) reveals that an electron-withdrawing group leads to reduced reaction rates, implying that the step involving a thioalkyne and II (step 1) might be rate-determining. The high β-selectivity might be explained by the polarization property of thioalkynes. The *anti*-addition selectivity might be explained by the lower steric pressure in pathway a. However, the following possibility cannot be ruled out: sulfonium species IV and boron hydride III might be generated from intermediate V, which might be formed from the reaction between thioalkyne and complex I.

In summary, we have developed the first β-*anti*-selective addition of silanes to thioalkynes with $B(C_6F_5)_3$ as the catalyst, affording trisubstituted alkenyl silanes in excellent regio- and stereoselectivity. The reaction shows broad substrate scope and functional group tolerance. The products were proved to be useful intermediates to other trisubstituted alkenyl silanes by Ni-catalyzed stereoretentive cross-coupling reactions of the C−S bond. Mechanism study of the hydrosilylation reaction suggests that nucleophilic attack of thioalkyne to the activated silylium intermediate might be the rate-determining step, and Si−H bond cleavage is not involved in the rate-determining step.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04505.

Experimental procedures and characterization data for all new compounds (PDF)

Accession Codes

CCDC 1956653 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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