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Selectivity Control in Alkylidene Carbene-Mediated C−H Insertion and Allene Formation

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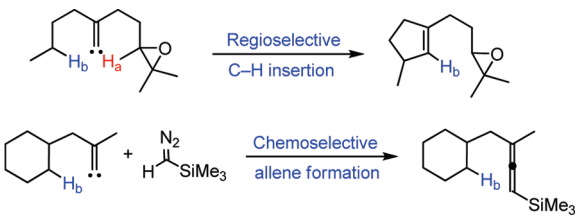

Regioselectivity of alkylidene carbene-mediated C−H insertion was explored utilizing electronic, conformational, steric, and stereoelectronic effects. Relying on these factors, highly regio- and chemoselective carbene insertion reaction of C−H bonds in different environments could be obtained. The observed selectivity clearly indicates that an electronic effect plays a more important role than steric effect. In general, C−H bonds in conformationally rigid cyclic environments are less reactive than those in acyclic systems toward carbene insertion, and in this situation, a competing intermolecular reaction between alkylidene carbene and trimethylsilyldiazomethane led to the formation of allenylsilanes. The formation of allenylsilane becomes more favorable as the concentration of reaction becomes higher, as well as the C−H bonds undergoing insertion becomes electronically and conformationally deactivated.

Introduction

Alkylidene carbenes and carbenoids are versatile intermediates widely used in organic synthesis.[1] On the basis of their high reactivity due to a strong electrophilic nature yet controllable behavior, a variety of chemoselective transformations including C−H insertion,[1] Fritsch−Buttenberg−Wiechell rearrangement,[2] nucleophilic substitution,[3] and [1 + 2] cycloaddition[4,5] reactions have been developed as powerful synthetic tools.[1] Among these reaction categories, C−H insertion has gained most significant attention due to its unique feature to generate five-membered carbocyclic or heterocyclic[6] systems with a stereochemically defined quaternary carbon center. Thus, many approaches to generate alkylidene carbene species have been developed and utilized to construct a diverse array of molecular architecture.[7,8] Wolinsky and Gilbert have extensively investigated the reactivity of alkylidene carbenes toward various types of C−H bonds for insertion including primary, secondary,

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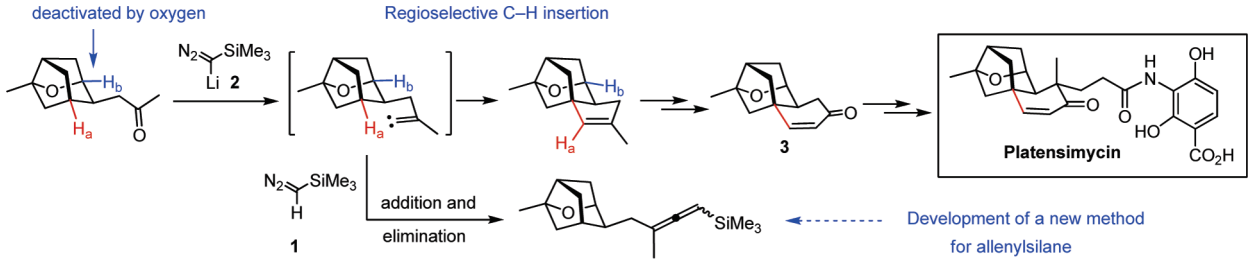
SCHEME 1



tertiary, and benzylic C−H bonds, and found a preference for insertion into the C−H bonds of higher degree.[9,10] However, the reactivity and selectivity between the same degrees of C−H bonds on structurally or conformationally biased systems are yet to be defined. For example, the extent of selectivity of insertion into C−H bonds on cyclic and acyclic systems or C−H bonds on six- and five-membered-ring systems is not easily predictable due to lack of systematic investigation. While the C−H bonds attached to a carbon carrying one or more heteroatoms are generally known to be more reactive toward carbene insertion,[11] the exact role of these heteroatoms in C−H insertion is not well characterized. Recently, an investigation of C−H insertion of variously substituted and conformationally constrained systems revealed high selectivity between two competing C−H bonds, which is believed to be the manifestation of a strong stereoelectronic effect of oxygen substituents. In the context of platensimycin[12] synthesis,[13] this regioselective C−H insertion based on the stereoelectronic effect of oxygen has led to a rapid construction of the key quaternary carbon-containing platensimycin core **3**[13a] (Scheme 1).

While optimizing the C−H insertion, we also observed allenylsilane as a byproduct, which sometimes became a predominant product. Subsequently, the formation of silylallenes was found to be a general phenomenon rather than an exception in conformationally constrained systems. Since allenes play critical roles in metal-catalyzed reactions and constitute a structural subunit in many natural products,[14,15] diverse synthetic approaches have been developed for their preparation.[16] However, the synthesis of functionalized allenes with various heteroatom substituents such as the silyl group are still in demand. The novel reaction mechanism of this allenylsilane formation and their potential utility prompted us to explore the scope and generality of this new allene-forming reaction.

In this article, we delineate two major selectivity issues in the alkylidene carbene-mediated transformations employing

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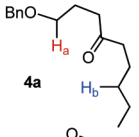
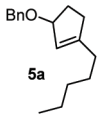
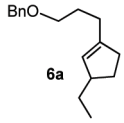
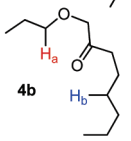
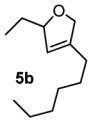
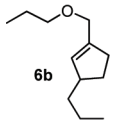
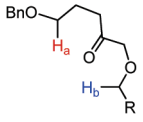
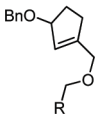
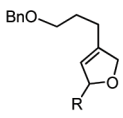
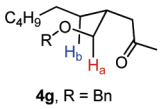
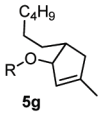
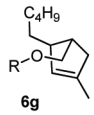
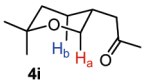
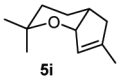
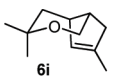
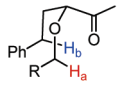
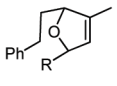
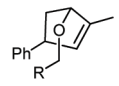
lithium trimethylsilydiazomethane (**2**): C−H insertion in structurally biased systems, and the selectivity between C−H insertion and allene formation. This systematic study revealed a profound impact of electronic, conformational, steric, and stereoelectronic effects on the regioselectivity in C−H insertion as well as the chemoselectivity between C−H insertion vs allenylsilane formation. Also, the unprecedented reaction of alkylidene carbene with trimethylsilyldiazomethane (**1**) was systematically investigated to prove its generality as a new method for the efficient synthesis of allenylsilanes.

Results and Discussion

Alkylidene carbenes are highly electrophilic species, and thus readily react with available electron sources including σ-electrons in C−H,[1] O−H,[17] N−H,[18] C−Si,[19] and O−Si[20] bonds and π-electrons in C=C bonds.[4,5] Despite their high reactivity, generally good to excellent chemo- and regioselectivity as well as stereoselectivity have been observed in their reactions. A powerful electronic influence by heteroatom substituents such as oxygen and nitrogen is well-known in carbene-mediated C−H insertion, yet the heteroatom effect is either reinforced or canceled out by structural or conformational bias in certain substrates. To gain further insight into the factors that interplay to provide these observed selectivity profiles, we explored systems that contain more than two competing C−H bonds on cyclic and acyclic systems with electronically, conformationally, and sterically differentiated environments. We envision that deconvolution and delineation of individual contributions of these factors would provide more elaborated information on carbene insertion reactions.

Electronic Effect. The regioselectivity of C−H insertion was examined by probing the contribution of an electronic effect. Especially, the extent of the activating role of an oxygen substituent to the C−H bonds on the same carbon bearing the oxygen was systematically explored (Table 1). First, the carbene insertion into an activated C−H_a and normal C−H_b on a linear ketone substrate **4a** provided a mixture of **5a** and **6a** in a 91:9 ratio and 96% yield (entry 1). Moving the activating oxygen from the terminal carbon to an internal carbon of substrate **4b**, such that the oxygen becomes an *endo* in the incipient ring, further activates the C−H_a for insertion, affording exclusively **5b** (entry 2). We surmise that the smaller C−O−C bond angle in **4b** relative to that of C−C−C in **4a** facilitates a carbene intermediate to interact with the C−H_a bond to form a lower energy transition state than that with C−H_b.[21] The extent of the activating role of the two different oxygens was explored with substrates **4c**−**f** where the electronic nature of the substituents on the oxygen connected to the carbon bearing C−H_b was varied while that of C−H_a remained constant as benzyl ether (entries 3−6). The selectivity trend between **5c**−**f** and **6c**−**f** clearly suggests that the influence of the *endo* oxygen is slightly larger than that of the *exo* oxygen if the alkyl group is attached to the oxygen (entry 3), reconfirming the observed selectivity trend with substrates **4a** and **4b**. However, the extent of contribution by the *endo* oxygen diminished

TABLE 1. Electronic Effect on C−H Insertion Selectivity[a]

entry	substrate	product		ratio	yield (%)
1	 **4a**	 **5a**	 **6a**	91 : 9	96
2	 **4b**	 **5b**	 **6b**	100 : 0	90
3	 **4c**, R = Ethyl	 **5c**	 **6c**	33 : 67	96
4	**4d**, R = Vinyl	**5d**	**6d**	40 : 60	89
5	**4e**, R = Ethynyl	**5e**	**6e**	58 : 42	82
6	**4f**, R = OMe	**5f**	**6f**	66 : 33	80
7	 **4g**, R = Bn	 **5g**	 **6g**	88 : 12	88
8	**4h**, R = TBS	**5h**	**6h**	88 : 12	76
9	 **4i**	 **5i**	 **6i**	100 : 0	69
10	 **4j**, R = Ethyl	 **5j**	 **6j**	100 : 0	82
11	**4k**, R = Vinyl	**5k**	**6k**	100 : 0	85

[a]Reaction conditions: $TMSCHN_2$ (1.6 equiv), *n*-BuLi(1.7 equiv), −78 °C to room temperature in THF over 3 h.

(16) For recent examples for allene synthesis, see: (a) Pu, X.; Ready, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 10874. (b) Zhang, W.; Xu, H.; Xu, H.; Tang, W. *J. Am. Chem. Soc.* **2009**, *131*, 3832. (c) Ogasawara, M.; Okada, A.; Nakajima, K.; Takahashi, T. *Org. Lett.* **2009**, *11*, 177. (d) Zeng, X.; Frey, G. D.; Kousar, S.; Bertrand, G. *Chem.—Eur. J.* **2009**, *15*, 3056. (e) Maity, P.; Lepore, S. D. *J. Am. Chem. Soc.* **2009**, *131*, 4196. (f) Li, J.; Kong, W.; Fu, C.; Ma, S. *J. Org. Chem.* **2009**, *74*, 5104. (g) Zheng, Z.-J.; Shu, X.-Z.; Ji, K.-G.; Zhao, S.-C.; Liang, Y.-M. *Org. Lett.* **2009**, *11*, 3214. (h) Lee, D.; Danishefsky, S. J. *Am. Chem. Soc.* **2010**, *132*, 4427. (i) Fürstner, A.; Méndez, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5355. (j) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492. (k) González, J. R.; González, A. Z.; Soderquist, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 9924. (l) Sakai, T.; Danheiser, R. L. *J. Am. Chem. Soc.* **2010**, *132*, 13203.

(17) For an example of O−H insertion, see: Kim, S.; Yoon, K.-Y.; Cho, C. M. *Chem. Commun.* **1996**, 909.

(18) For selected examples of N−H insertion, see: (a) Miyagi, T.; Aoyama, T.; Shioiri, T. *Synlett* **1997**, 1063. (b) Miyagi, T.; Hari, Y.; Shioiri, T. *Tetrahedron. Lett* **2004**, *45*, 6303. (c) Taber, D. F.; Plepys, R. A. *Tetrahedron. Lett* **2005**, *46*, 6045.

(19) For an example of C−Si insertion, see: Li, J.; Sun, C.; Lee, D. *J. Am. Chem. Soc.* **2010**, *132*, 6640.

(20) For selected examples of O−Si insertion, see: (a) Feldman, K. S.; Wrobleski, M. L. *Org. Lett.* **2000**, *2*, 2603. (b) Feldman, K. S.; Wrobleski, M. L. *J. Org. Chem.* **2000**, *65*, 8659. (c) Hari, Y.; Kondo, R.; Date, K.; Aoyama, T. *Tetrahedron* **2009**, *65*, 8708. (d) Kim, S.; Cho, C. M. *Tetrahedron Lett.* **1995**, *36*, 4845.

(21) This can be considered as a Thorp−Ingold effect induced by the two lone-pair electrons of oxygen. For a review and leading references for the Thorpe−Ingold effect, see: (a) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735. (b) Lightstone, F. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1994**, *116*, 10789. (c) Allinger, N. L.; Zalkow, V. *J. Org. Chem.* **1960**, *25*, 701. (d) Bruice, T. C.; Pandit, U. K. *J. Am. Chem. Soc.* **1960**, *82*, 5858. (e) Bruice, T. C.; Pandit, U. K. *Proc. Natl. Acad. Sci. U.S.A.* **1960**, *46*, 402. (f) Ingold, C. K.; Sako, S.; Thorpe, J. F. *J. Chem. Soc.* **1922**, *121*, 1117. (g) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305. (h) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080.

proportionally to the change from an electron-donating ethyl (entry 3) to an inductively electron-withdrawing vinyl (entry 4), ethynyl (entry 5), and methoxy (entry 6) group, ultimately providing the reversed selectivity of a 33:67 ratio for **5f**:**6f** compared to a 66:33 ratio for **5c**:**6c**. Unexpectedly, only the inductive effect of the R-substituents, but not their resonance effect through the participation of π- or lone-pair electrons, seems to contribute to the reactivity of the C−H_b bond, otherwise the proportion of **6c**−**f** should have increased relative to that of **6c**. β-Branched substrates containing different protecting groups on the oxygen **4g** and **4h** showed identical selectivity, generating a mixture of **5g**:**6g** and **5h**:**6h** both in 88:12 ratios (entries 7 and 8). On the other hand, conformationally constrained substrate **4i** with almost identical electronic bias to that of **4g** and **4h** afforded much higher selectivity, generating only **5i** albeit the yield was slightly lower (entry 9). The higher activating effect of the *endo* oxygen in α-branched substrates **4j** and **4k** relative to β-branched substrates **4g** and **4h**, where the oxygen is an *exo* to an incipient ring, was clearly demonstrated by the perfect selectivity for the formation of **5j** and **5k** over **6j** and **6k**, respectively (entries 10 and 11).

Conformational Effect. To explore the conformational effect on the regioselectivity of C−H insertion, we prepared substrates containing a pyran ring and a linear side chain that has at least two competing cyclic and acyclic C−H_γ bonds available toward carbene insertion (Table 2). The selectivity of insertion into C−H_a vs C−H_b should be the consequence of respective conformational behaviors of cyclic and acyclic portions of these molecules. The pyran substrate ***4l*** bearing a side chain where oxygen is *exo* to an incipient ring gave a mixture of **5*l*** and ***6l*** in a 5:95 ratio, where preferred insertion occurred into an acyclic C−H_b over cyclic C−H_a bond (entry 1). Replacing the benzyl-protecting group in ***4l*** with an electron-withdrawing pivalate in **4m** completely switched the insertion preference, generating C−H_a insertion product **5m** as the only observed product (entry 2). For comparison, the insertion reaction with substrate **4n** that does not contain any oxygen substituent afforded a mixture of **5n** and **6n** in a 16:84 ratio. This clearly indicates two important features: (1) the C−H_a on a conformationally rigid cyclohexane ring is less reactive than the C−H_b in the butyl group and (2) the extent of an activating role of an oxygen substituent is more pronounced in acyclic environments than in conformationally rigid systems, otherwise a similar ratio of products should have been observed from both ***4l*** and **4n**. The complete reversal of selectivity with **4m** also suggests that the conformational contribution should be subtle so that it could be easily overridden by an electronic factor.

Next, we examined a ring-size effect on the regioselectivity of insertion. We expected that C−H bonds on five- and six-membered rings would have a slightly different reaction rate as the reflection of subtle difference in their conformational behavior. However, the insertion reaction of substrate **4o** containing C−H_γ bonds on both six- and five-membered rings occurred at the C−H_b on the five-membered ring over C−H_a on the six-membered ring with remarkable selectivity of a 2:98 ratio for **5o**:**6o** in 69% combined yield (entry 4). A complete regioselectivity of insertion was observed with substrate **4p** and **4q**, where the oxygen substituent is *endo* to the incipient ring as opposed to *exo* in substrate ***4l***, provided **6p** and **6q** over **5p** and **5q** (entries 5 and 6).

TABLE 2. Conformational Effect on C−H Insertion Selectivity[a]

entry	substrate	product		ratio	yield (%)
1	**4l**, R = Benzyl	**5l**	**6l**	5 : 95	85
2	**4m**, R = Pivaloyl	**5m**	**6m**	100 : 0	56
3	**4n**	**5n**	**6n**	16 : 84	63[b]
4	**4o**	**5o**	**6o**	2 : 98	69
5	**4p**, R = Ethyl	**5p**	**6p**	0 : 100	73
6	**4q** R = Vinyl	**5q**	**6q**	0 : 100	71
7	**4r**	**5r**	**6r**	42 : 58	62
8	**4s**	**5s**	**6s**	0 : 100	66

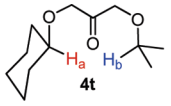
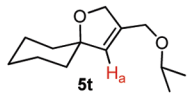
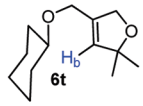
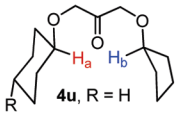
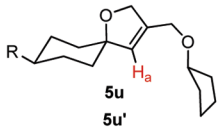
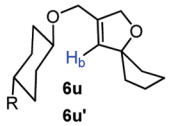
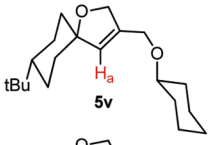
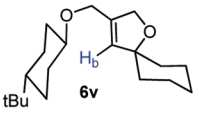
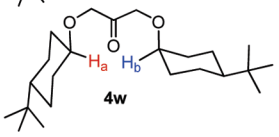
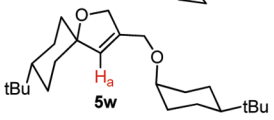
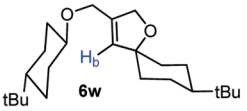
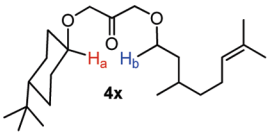
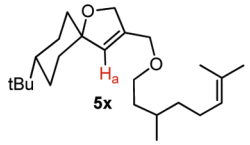
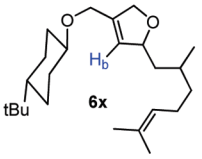
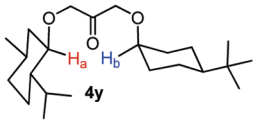
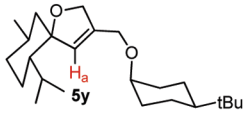
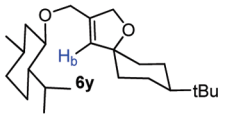
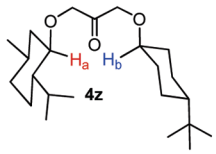
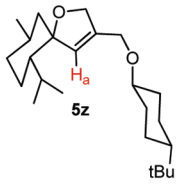
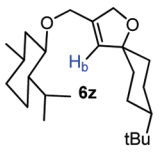
[a]Reaction conditions: $TMSCHN_2$ (1.6 equiv), *n*-BuLi(1.7 equiv), −78 °C to room temperature in THF over 3 h. [b]Combined yield including 14% of allene product.

This result is consistent with the high selectivity with substrate **4b** (entry 2 in Table 1), where the smaller C−O−C bond angle relative to that of C−C−C seems to be a key structural element.[21] To our surprise, even the unactivated acyclic C−H_b bond in **4r** appeared to be slightly more reactive than the seemingly more activated cyclic C−H_a bond by an oxygen substituent, affording a mixture of **5r** and **6r** in a 42:58 ratio (entry 7). This is another evidence that the electronic contribution of oxygen in conformationally rigid environment is diminished. The C−H_a bond on the epoxide moiety of **4s** is virtually unreactive toward carbene insertion, affording only **6s**. This is the result of not only a larger bond angle between the C−H_a and the C−C bond tethered to the carbene moiety but also stronger bond strength of the C−H_a bond due to an increased s-character of the exocyclic bond on the three-membered ring.[22]

Steric Effect. Various selectivities (chemo-, regio-, stereo-) in organic transformations are generally the consequence of interplay between electronic and steric effects. We already demonstrated the fundamentally important role of electronic and conformational/structural effects in Tables 1 and 2. The C−H insertion selectivity modulated by an electronic factor

(22) Tian, Z.; Fattahi, A.; Lis, L.; Kass, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 17087.

TABLE 3. Steric Effect for Selectivity on C−H Insertion[a]

entry	substrate	products	ratio (**5**:**6**)	yield (%)
1	 **4t**	 **5t**	 **6t**	42 : 58	55
2	 **4u**, R = H	 **5u**	 **6u**	42 : 58	56
3	**4u'**, R = tBu	**5u'**	**6u'**	33 : 67	75
4	 **4v**	 **5v**	 **6v**	45 : 55	76
5	 **4w**	 **5w**	 **6w**	42 : 58	80
6	 **4x**	 **5x**	 **6x**	40 : 60	61
7	 **4y**	 **5y**	 **6y**	26 : 74	82
8	 **4z**	 **5z**	 **6z**	39 : 61	77

[a]Reaction conditions: $TMSCHN_2$ (1.6 equiv), *n*-BuLi(1.7 equiv), −78 °C to room temperature in THF over 3 h.

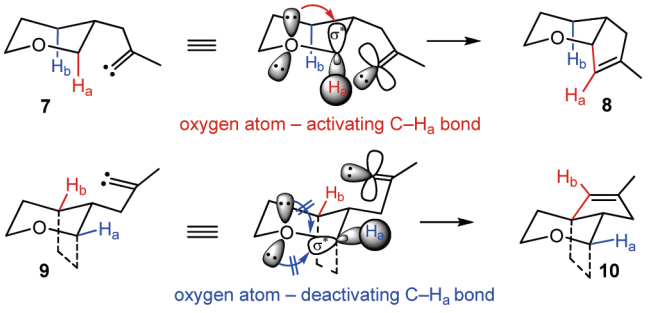
on or near the reacting C−H stems from the strongly electron-deficient nature of the reacting counterpart carbene. At this juncture, we were intrigued by the potential influence of steric factor for the selectivity. Because of the sterically unencumbered nature of the alkylidene carbene center, we predict that the effect of steric hindrance on and around the C−H bond undergoing insertion would be less important compared to that of the electronic effect, which, however, should not be neglected. To assess the contribution of steric effect to the regioselectivity of C−H insertion, a range of substrates containing at least two competing C−H bonds with sterically differentiated environments were examined (Table 3). First, the insertion into tertiary C−H bonds on cyclic and acyclic environments was compared with substrate **4t**, affording a mixture of **5t** and **6t** in a 42:58 ratio (entry 1). Coincidently, a mixture of **5u** and **6u** with an identical ratio was also observed from the reaction of substrate **4u** containing two tertiary C−H bonds on five- and six-membered rings (entry 2). On the other hand, identical substrate **4u**′ but with a 4-tertiary butyl substituent gave a slightly increased ratio (33:67) between **5u**′ and **6u**′ (entry 3). Substrate **4v** with two competing C−H bonds on cyclohexyl and 4-tertiary butyl-substituted cyclohexyl moieties showed similar insertion behavior, affording a 45:55 ratio of **5v**:**6v** (entry 4). These results strongly support the general reactivity trend that C−H bonds in more conformationally rigid environments are slightly less reactive than those in more flexible situations. The first example of steric hindrance meaningfully discriminating C−H insertion was illustrated by the substrate **4w** where equatorial and axial C−H bonds compete (entry 5). As expected, insertion into the sterically less hindered equatorial $C-H_b$ was slightly favored over $C-H_a$, generating a 42:58 mixture of **5w** and **6w**. In the case of **4x**, more favorable insertion into a secondary $C-H_b$ over a tertiary $C-H_a$ in a 40:60 ratio was observed (entry 6). This is somewhat unusual because the electronic contribution seems to be far greater that that of steric hindrance for the carbene insertion process and thus 3° $C-H_a$ was expected be more reactive than 2° $C-H_b$. Although this observed selectivity could be the consequence of steric hindrance-based control more data need to be accumulated to generalize this argument. The insertion reaction of substrate **4y** that is similar to **4w** but containing an isopropyl group near the axial $C-H_a$ bond showed significantly increased selectivity for the insertion into sterically less hindered $C-H_b$, affording a mixture of **5y** and **6y** in a 26:74 ratio (entry 7). When the

insertion into two axial C−H_a and C−H_b bonds competes in substrate **4z**, a reduced yet appreciable selectivity between **5z** and **6z** was observed (entry 8).

From the insertion behavior of substrates **4t**−**z**, an obvious selectivity trend has emerged: steric hindrance does affect the selectivity of carbene insertion by retarding the insertion into C−H bonds in sterically more congested environment but its contribution was found to be marginal.

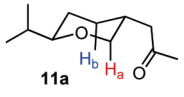
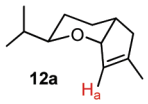
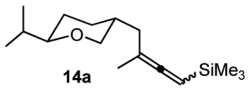
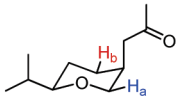
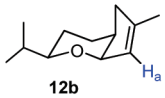
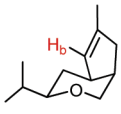
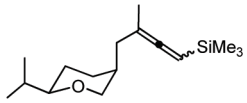
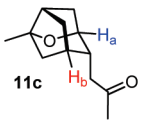
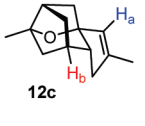
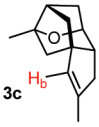
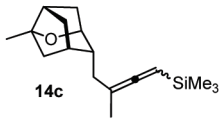
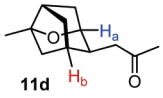
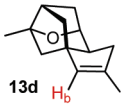
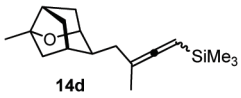
Steroelectronic Effect. The diminished electronic contribution by oxygen when constrained in a cyclic structure, for example **4*l*** and **4r** in Table 2, implies that the directionality of its lone pair electrons relative to a C−H bond undergoing insertion reaction should be important. The electronic effect of the oxygen substituent in the C−H insertion reaction of alkylidene carbenes[8a] is expected to be manifested by the specific interactions of orbitals around the reaction center.[23] The most important orbital−orbital interaction was hypothesized to be the axially oriented nonbonding orbital of oxygen and the σ^* orbital of the axial C−H_a bond (Scheme 2). We reasoned that if this stereoelectronic effect of an oxygen substituent is important, the C−H insertion of carbene **7** should generate product **8** via a selective insertion into the axial (O)C−H_a bond due to its more electron-rich nature resulting from n(O) → σ^*(C−H_a) electron delocalization. On the other hand, the insertion of carbene **9** lacking axial hydrogens should take place selectively at (C)C−H_b over the (O)C−H_a bond to generate product **10**. In this case, due to poor orbital overlap, electron delocalization via n(O) → σ^*(C−H) will be minimal, and thus the oxygen would deactivate the (O)C−H_a bond through an inductive effect.[13a,24]

SCHEME 2



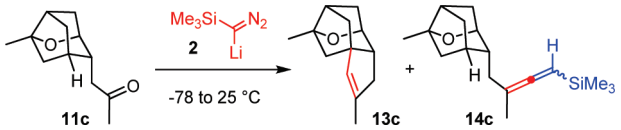
To test this stereoelectronic hypothesis for regioselective C−H insertion, we prepared two pairs of conformationally constrained diastereomers **11a/11b** and **11c/11d** that represent the insertion behavior of **7** and **9**, respectively (Table 4). Indeed, substrate **11a** underwent a selective insertion into the C−H_a bond, providing **12a** as the only insertion product when condition A (1.6 equiv of *n*-BuLi/1.7 equiv of TMSdiazomethane/THF/−78 °C, 0.06 M) was employed (entry 1). However, to our surprise a significant amount of another product was obtained, which was found not to be the expected regioisomer but allenylsilane **14a** (see Table 4 for mechanistic rationale). On the other hand, **11b**, a diastereomer of **11a**, afforded a mixture of **12b** and **13b** in a 1:11 ratio together with allenylsilane **14b** (entry 2). Similarly, reaction of substrates **11c** and **11d** that contain only equatorial hydrogens afforded a mixture of products **12c** and **13c** in 1:5 ratio and only insertion product **13d**, respectively, accompanied by allenylsilane **14c** and **14d** (entries 3 and 4). The predominant or exclusive formation of **13b** and **13d** via the insertion into seemingly less reactive C−H_b compared to C−H_a should be the consequence of the stereoelectronic effect of oxygen substituent as hypothesized in Scheme 2. The formation of allenylsilane byproducts **14a**−**d** via a competing intermolecular process is attributed to somewhat lower reactivity of C−H bonds in these systems, which further support the general trend that C−H bonds in conformationally rigid environments are less reactive than those corresponding flexible systems. We surmised that by increasing the reaction concentration, allenylsilane formation should be more favorable because the intermolecular reaction rate would increase while the intramolecular reaction rate remains constant. Indeed, under condition B (2 equiv of

TABLE 4. Stereoelectronic Effect for Selectivity on C−H Insertion[a]

entry	substrate	insertion product		allene product	condition	ratio (**12** : **13** : **14**)	yield (%)
1	 **11a**	 **12a**		 **14a**	A	75 : 0 : 25	77
					B	33 : 0 : 67	69
2	 **11b**	 **12b**	 **13b**	 **14b**	A	6 : 66 : 28	65
					B	0 : 25 : 75	76
3	 **11c**	 **12c**	 **13c**	 **14c**	A	10 : 46 : 44	86
					B	0 : 8 : 92	75
4	 **11d**		 **13d**	 **14d**	A	0 : 74 : 26	63
					B	0 : 8 : 92	63

[a]Condition A: Reaction conditions: $TMSCHN_2$ (1.6 equiv), *n*-BuLi(1.7 equiv), −78 °C to room temperature in THF over 3 h. Condition B: $TMSCHN_2$ (3 equiv), *n*-BuLi (2 equiv), −78 °C to room temperature in THF over 1 h then additional 2 h at room temperature.

TABLE 5. Optimization for Allenylsilane Formation[a]



entry	11c : BuLi : 1	concentration (M)	ratio (13c : 14c)[b]	yield of 14c (%)
1	1.0 : 1.7 : 1.6	0.009	1 : 0.7	28
2	1.0 : 1.7 : 1.6	0.02	1 : 1.6	36
3	1.0 : 2.0 : 3.0	0.02	1 : 6	68
4	1.0 : 2.0 : 3.0	0.06	1 : 12	75
5	1.0 : 2.0 : 3.0	0.10	1 : 15	53
6[c,d]	1.0 : 2.0 : 3.0	0.02	1 : 5	63
7[e]	1.0 : 3.0 : 3.0	0.02	1 : 5	58

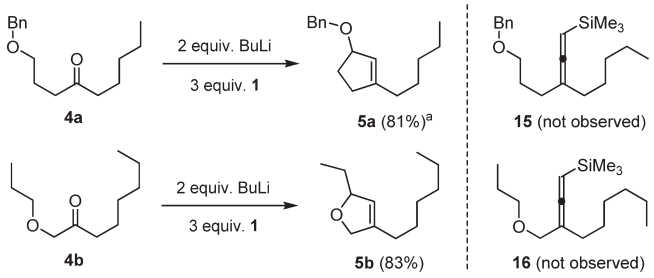
[a]Reactions were carried out in THF. [b]Determined by ^{1}H NMR. [c]Et_2O as the solvent. [d]Almost identical result in hexane. [e]Quenched with D_2O.

n-BuLi/3.0 equiv of TMS-diazomethane/THF/−78 °C, 0.06 M), the formation of allenylsilane becomes a major reaction pathway, producing allenylsilanes **14a**−**d** predominantly.

Optimization for Allenylsilane Formation. To gain more insight into the mechanism of the allene formation as well as to develop an optimal protocol for its formation, systematic variation on stoichiometry and concentration was examined (Table 5). Considering the bimolecular nature for the formation of allenylsilane, we envisioned that the relative portion of unimolecular C−H insertion could be decreased upon increasing the concentration of reaction and by employing excess amounts of **1** or **2**. As expected, at higher reaction concentration, an increased amount of allenylsilane **14c** with concomitant decrease of **13c** (entries 1 vs 2 and 3 vs 4) was obtained.[25] A maximum yield of **14c** (75%) was realized when a 3-fold excess of **1** was employed at 0.06 M (entry 4) but at a higher concentration deteriorated yield was observed (entry 5). Increasing the amount of **2** also lowered the yield (entry 7). Also, a significant solvent effect was not observed, thus changing the solvent from THF to Et_2O did not affect the yield or product ratio.[26]

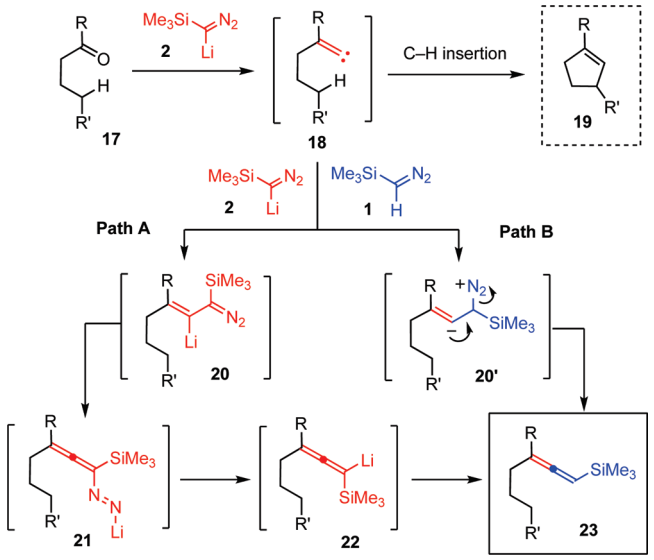
Having recognized the profound impact of concentration and stoichiometry of reagents on the selectivity, we resubjected substrates **11a**−**d** to the optimized reaction conditions (condition B) for allenylsilane formation (Table 4). Substrate **11a** containing the stereoelectronically activated axial C−H bond afforded a 33:67 ratio of **12a**:**14a**. In contrast, substrates **11b**−**d** lacking axial C−H bonds provided an increased amount of allene in 25:75, 8:92, and 8:92 ratios of **13b**:**14b**, **13c**:**14c**, and **13d**:**14d**. For comparison, we reexamined acyclic ketone substrates **4a** and **4b** under the optimized conditions for allene formation (Scheme 3). In contrast to the reactivity pattern of pyran substrates **11a**−**d**, acyclic ketones **4a** and **4b** did not generate allenes **15** and **16** at all. This is most likely the consequence of a faster

SCHEME 3



[a]Combined yield including 8% of regioisomer **6a**.

SCHEME 4. Putative Mechanisms for Allenylsilane Formation



C−H insertion that preempts the relatively slower bimolecular process leading to allene formation.

Mechanistic Considerations. The reaction between ketone **17** and lithium trimethylsilyldiazomethane **2** followed by Peterson olefination and nitrogen extrusion would generate alkylidene carbenes **18**.[27] Once generated, **18** undergoes rapid C−H insertion to form cyclopentene derivative **19** (Scheme 4). However, we surmised that if the insertion into a C−H bond becomes slower or not available, an intermolecular process starts to operate. In this scenario, the participation of **2** to generate adduct **20** (path A) seems most probable by analogy to the reaction between an alkylidene carbenoid and Grignard reagents as reported by Satoh and co-workers.[28,29] Upon formation, the extrusion of N_2 from vinyl lithium **20** via **21** would generate allenyllithium species **22**, the protonation of which would afford allenylsilane **23**. Likewise, the reaction of alkylidene carbene **18** with free trimethylsilyldiazomethane **1** will form adduct **24** (path B), the N_2 elimination of which would result in the formation of

(23) (a) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1995. (b) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 609.

(24) Wang, J.; Stefane, B.; Jaber, D.; Smith, J. A. I.; Vickery, C.; Diop, M.; Sintim, H. O. *Angew. Chem., Int. Ed.* **2010**, *49*, 3964.

(25) Selectivity control by changing reaction concentration was demonstrated in olefin metathesis reactions: Maifeld, S. V.; Miller, R. L.; Lee, D. *J. Am. Chem. Soc.* **2004**, *126*, 12228.

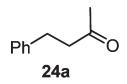
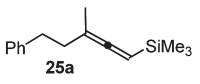
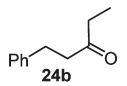
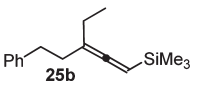
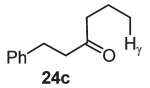
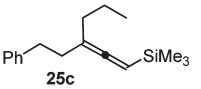
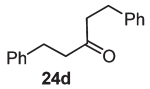
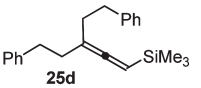
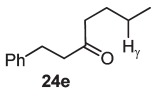
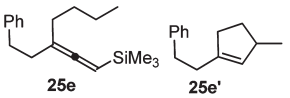
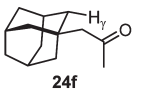
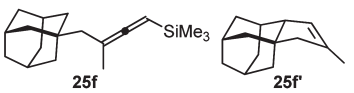
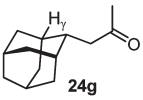
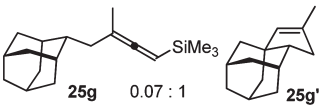
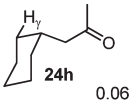
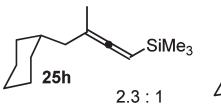
(26) Instead of free carbene, a protocol that involves carbenoid formation was also examined but the ratio remained unchanged.

(27) (a) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Chem. Commun.* **1973**, 151. (b) Ohira, S.; Ishi, S.; Shinohara, K.; Nozaki, H. *Tetrahedron Lett.* **1990**, *31*, 1039. (c) Ohira, S.; Okai, K.; Moritani, T. *J. Chem. Soc., Chem. Commun.* **1992**, 721. (d) Taber, D. F.; Walter, R.; Meagley, R. P. *J. Org. Chem.* **1994**, *59*, 6014. (e) Sakai, A.; Aoyama, T.; Shioiri, T. *Tetrahedron* **1999**, *55*, 3687.

(28) Satoh, T. *Chem. Soc. Rev.* **2007**, *36*, 1561.

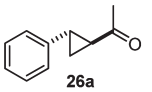
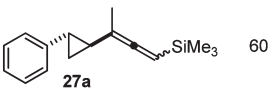
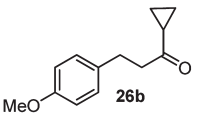
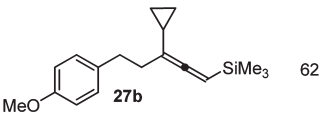
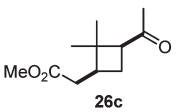
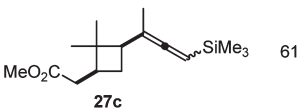
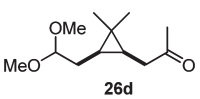
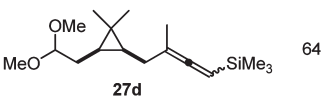
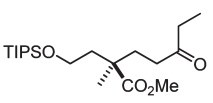
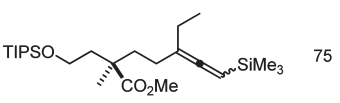
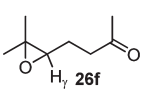
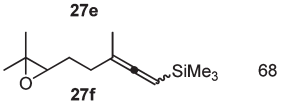
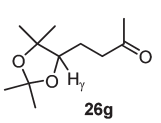
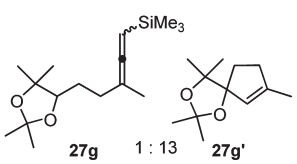
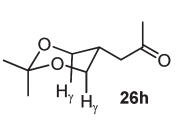
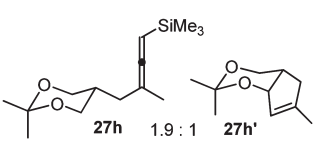
(29) Related examples of Path B: (a) Satoh, T.; Sakamoto, T.; Watanabe, M. *Tetrahedron Lett.* **2002**, *43*, 2043. (b) Satoh, T.; Sakamoto, T.; Watanabe, M.; Takano, K. *Chem. Pharm. Bull.* **2003**, *51*, 966.

TABLE 6. Allenylsilane Synthesis from Acyclic Ketones[a]

entry	substrate	product	yield of **25** (%)
1	 **24a**	 **25a**	73
2	 **24b**	 **25b**	75
3	 **24c**	 **25c**	76
4	 **24d**	 **25d**	72
5	 **24e**	 **25e** **25e'**	
	0.06 M	0.25 : 1	80
	0.10 M	0.33 : 1	76
	0.20 M	1.1 : 1	71
6	 **24f**	 **25f** **25f'**	
	0.02 M	0.14 : 1	80
	0.06 M	1.0 : 1	80
	0.10 M	2.5 : 1	76
	0.20 M	3.3 : 1	71
7	 **24g**	 **25g** 0.07 : 1 **25g'**	80
8	 **24h**	 **25h** **25h'**	
	0.06 M	2.3 : 1	62
	0.20 M	49 : 1	61

[a]Conditions: $TMSCHN_2$ (3 equiv), *n*-BuLi (2 equiv), −78 °C to room temperature in THF over 1 h then additional 2 h at room temperature.

TABLE 7. Allenylsilanes from Functinalized Acyclic Ketones[a]

entry	substrate	product[b]	yield (%)
1	 **26a**	 **27a**	60
2	 **26b**	 **27b**	62
3	 **26c**	 **27c**	61
4	 **26d**	 **27d**	64
5	 **26e**	 **27e**	75
6	 **26f**	 **27f**	68
7	 **26g**	 **27g** 1 : 13 **27g'**	86
8	 **26h**	 **27h** 1.9 : 1 **27h'**	75

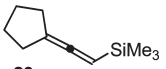
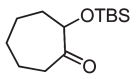
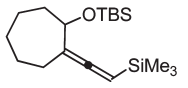
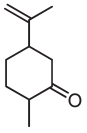
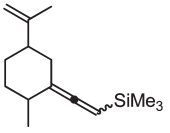
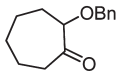
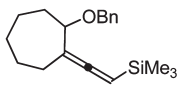
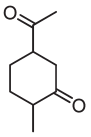
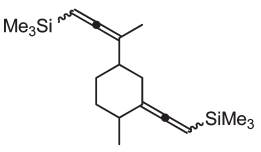
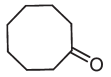
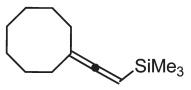
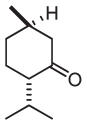
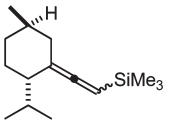
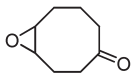
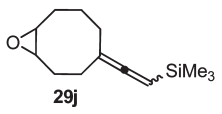
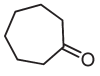
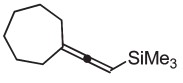
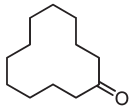
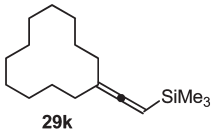
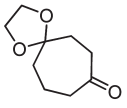
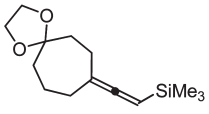
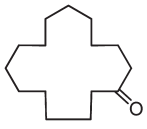
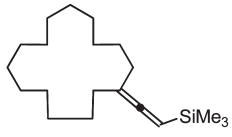
[a]Conditions: $TMSCHN_2$ (3 equiv), *n*-BuLi (2 equiv), −78 °C to room temperature in THF over 1 h then additional 2 h at room temperature. [b]Substrates with existing stereocehhmistry accorded ca. 1:1 ratio of diastereomers.

allenylsilane **23**. We observed that increasing the amount of free trimethylsilyldiazomethane **1**, but its lithated form **2**, provided proportinally increased amounts of allenylsilane **14c**, but with **2**, the yield was increased only slightly (Table 5, entries 3 vs 7). On the basis of this observation, we tentatively concluded that path B is a major-contributing pathway and path A, if it is still operating, is a minor reaction pathway. Interestingly, quenching the reaction with D_2O did not give an appreciable amount of deuterated allenylsilane (Table 5, entry 7), which also makes our mechanistic interpretation inconclusive.

Reaction Scope. Under the optimized conditions for allenylsilane formation, we examined substrate scope and reaction efficiency (Table 6). Unbranched substrates **24a**−**d** carrying methyl, ethyl, propyl, and phenethyl groups afforded allenylsilanes **25a**−**d** in good yields (entries 1−4). It was somewhat surprising that substrate **24c** that contains 1° C−H_γ bonds available for insertion still gave allenylsilane **25c** exclusively. For 1,3-dibenzyl acetone **24d**, although the aromatic C−H insertion or addition is possible,[30] only allenylsilane **25d** was obtained in good yield. However, butyl-substituted ketone **24e** provided a mixture of **25e** and **25e'** in 80% yield with 0.25:1 ratio (entry 5). Increasing the concentration to 0.10 M changed the ratio to 0.33:1. Although the ratio was further changed to 1.1:1 at higher concentration (0.20 M) the yield decreased. This series of experiments implies that the insertion into 2° C−H_γ in **24e** should be substantially more favorable than that of 1° C−H_γ in **24c** because under similar conditions no insertion but only allene formation was observed. To further explore how substrate structure and reaction concentration affect the ratio of products, we examined the behavior of adamentane-derived ketone **24f** carrying multiple 2° C−H_γ bonds available for insertion (entry 6). Under dilute conditions with 1:2:2 ratio of **24f**:BuLi:**1**, insertion product **25f'** was obtained predominantly over allenylsilane **25f**. However, at an increased concentration with the typical 1:2:3 ratio of **24f**:BuLi:**1**, the allenylsilane formation favorably competed with the insertion into a 2° C−H_γ bond, thereby providing the ratio of **25f**:**25f'** in the range of 1:1 to 3.3:1 with good yield.

(30) Ogawa, H.; Aoyama, T.; Shioiri, T. *Synlett* **1994**, 757.

TABLE 8. Allenylsilane Formation from Cyclic Ketones[a]

entry	substrate	allene product	yield (%)	entry	substrate	allene product	yield (%)
1	 **28a**	 **29a**	55	7	 **28g**	 **29g**	10[c]
2	 **28b**	 **29b**	60	8	 **28h**	 **29h**	0[c]
3	 **28c**	 **29c**	51	9	 **28i**	 **29i**	82
4	 **28d**	 **29d**	32[b]	10	 **28j**	 **29j**	62
5	 **28e**	 **29e**	72	11	 **28k**	 **29k**	63
6	 **28f**	 **29f**	74	12	 **28l**	 **29l**	43[d]

[a]Reaction conditions: $TMSCHN_2$ (3 equiv), *n*-BuLi (2 equiv), −78 °C to room temperature in THF over 2 h. at room temperature. [b]Recovered starting meterial in 40% yield. [c]Mostly ring-expansion products formed. [d]Insertion product was isolated in 17% yield.

Another adamentane-derived substrate **24g** that has 3° C−H_γ bonds available for insertion afforded insertion product **25g′** without an appreciable amount of allenylsilane **25g** (entry 7). On the other hand, **24h**, a simplified version of **24g** that contains only a single cyclohexane ring with 2° C−H_γ bonds behaved somewhat similar to **24f** such that a mixture of allenylsilane **25h** and insertion product **25h′** were generated, but at higher concentration allene formation becomes a predominant process (entry 8).

Next, we examined substrates containing a carbon or an oxygen branch either at the α-, *β*-, or *γ*-position (Table 7). Reactions with substrates **26a**−**f** consistently provided allenylsilanes **27a**−**f** in the range of 60−75% yield except for **26g**. Various oxygen functionalities such as ether, ester, acetal, and epoxide did not interfere with the formation of allenylsilanes. However, a significant influence of certain functionality was recognized. For example, the reaction of **26f** carrying a *γ*,*δ*-epoxide afforded only allenylsilane **27f** (entry 6), whereas **26g** with the corresponding dioxolane moiety yielded C−**H**$_\gamma$ insertion product **27g′** predominantly together with allenylsilane **27g** only in 6% yield in all three concentrations examined (entry 7). On the other hand, a dioxane-containing susbtrate **26h** provided a mixture of allenylsilane **27h** and insertion product **27h′** in a 1.9:1 ratio (entry 8). This indicates that a subtle environmental difference at or around C−H bonds can affect their reactivity whereby a completely different chemo- and regioselectivity may ensue.[22,31]

We expected that cyclic ketones of small- to medium-sized rings should be excellent substrates for allenylsilane formation[32] since the competing C−H insertion process will be excluded (Table 8). As expected, cyclopentanone **28a** and dihydrocarvone **28b** afforded allene **29a** (55%) and **29b** (60%), respectively, in moderate yields (entries 1 and 2). Substrate **28c** containing acyclic ketone gave corresponding bisallene **29c** as a mixture of four stereoisomers in 51% yield when an excess amount of reagents (3 equiv of BuLi and 5 equiv of **1**) was used (entry 3). The formation of allene has proven inherently sensitive to the steric encumbrance at the α-carbon of cyclic ketones, as evidenced by the low yield of menthone **28d** (entry 4) and α-substituted cycloheptanones **28g** and **28h** (entries 7 and 8). On the other hand, cyclopentanone **28e** and its derivative **28f** afforded the corresponding allenes **29e** and **29f** in respectable yields (entries 5 and 6).

(31) This is probably due to the difference of strength of C−H bonds on 3- and 5-membered rings. Alternatively, the more favourable n(O)→*σ**(C−H) electron delocalization in dioxolane may also cause this difference as described in ref 13a.

The low yields of allenylsilanes from these α-substituted ketones seem to stem from the slow elimination of $LiOSiMe_3$ from the intermediate formed between the ketone and lithium trimethylsilyldiazomethane **2**. In contrast, other cyclic ketones **28i**−***l*** not possessing bulky substituents at the α-carbon gave allenylsilanes **29i**−***l*** in good to excellent yields. It is quite surprising that there was no C−H insertion product from the 12-membered-ring ketone **28k** as opposed to the 15-membered-ring ketone **28*l***, which afforded a 2.5:1 mixture of allenylsilane **29*l*** and C−H insertion product in 60% overall yield.

Conclusions

We have examined the regioselectivity of alkylidene carbene-mediated C−H insertion utilizing electronic, conformational, steric, and stereoelectronic effects. Due to a significant rate difference caused by these factors, high regio- and chemoselectivity between C−H bonds in different environments could be obtained. It is well-known that the C−H bond connected to the same carbon bearing an ether oxygen substituent is significantly more reactive toward C−H insertion. However, in this study, we have observed that the lone-pair electrons of oxygen can either activate a C−H bond via an n(O) → σ^*(C−H) resonance effect or deactivate it via an inductive effect by the strong electronegativity of oxygen depending on their relative orientation to the C−H bonds.

We recognized that when an intramolecular C−H insertion of alkylidene carbenes is slow, an intermolecular reaction between the alkylidene carbene and free trimethylsilyldiazomethane supersedes the insertion, leading to the formation of allenylsilanes. Because of its bimolecular nature, higher efficiency of allenylsilane formation was realized by running the reaction at higher concentration as well as slowing down the competing C−H insertion with conformational and stereoelectronic effects. We also found that in general, conformationally constrained C−H bonds are less reactive than those in acyclic environments. Thus, insertion reaction of substrates containing these conformationally constrained C−H bonds was accompanied by the formation of allenylsilanes. Similarly, the allene formation is more favorable than insertion into 1° C−H bonds, providing exclusively allenylsilane. On the other hand, the competition between allene formation and insertion into acyclic 2° and 3° C−H bonds predominantly gives insertion products. Relying on this differential and controllable reactivity of C−H bonds toward alkylidene carbenes as well as an unprecedented reactivity of alkylidene carbenes toward trimethylsilyldiazomethane, we have developed a unique method for the synthesis of silyl-functionalized trisubstituted allenes.

The selectivity between the C−H insertion and allenylsilane formation observed in this study provides further insight into the relative reactivity of particular C−H bonds toward insertion by alkylidene carbenes. We expected that the reactivity and selectivity trends of various C−H bonds toward alkylidene carbenes discovered in this study will be extrapolated to other types of carbene- and carbenoid- as well as nitrene- and nitrenoid-mediated insertion processes.

Experimental Section

General Information. All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Flasks were oven-dried overnight and cooled under a stream of nitrogen. Solvents were purified based on standard procedures. Flash chromatography was performed with silica gel 60 Å (32−63 mesh). Analytical thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 (particle size 0.040−0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded in the deuterated solvents stated. ^{1}H and ^{13}C chemical shifts were referenced to internal solvent resonances and reported relative to $SiMe_4$; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in hertz. Characterization data for compounds **4a**−**k**, **5a**−**k**, **6a**−**k**, **11a**−**d**, **12a**−**c**, **13b**−**d**, **14a**−**d** were previously reported.[13a]

Typical Preparative Scale Reaction for C−H Insertion. To a solution of trimethylsilyldiazomethane (2.0 M in Et_2O, 0.19 mL, 0.38 mmol) in 10 mL of THF was added *n*-BuLi (2.5 M in hexanes, 0.16 mL, 0.4 mmol) at −78 °C. After the solution was stirred for 30 min, a substrate (0.25 mmol) in 2 mL of THF was added. The mixture was stirred for 1 h at −78 °C and gradually warmed to room temperature over 2 h. The reaction mixture was quenched by adding a few drops of water and filtered through a pad of silica gel. The filtrate was concentrated and the residue was flash chromatographed on silica gel.

Typical Preparative Scale Reaction for Allenylsilane. To a solution of trimethylsilyldiazomethane (2.0 M in Et_2O, 0.75 mL, 1.5 mmol, 3.0 equiv) in 6.0 mL of THF was added *n*-BuLi (2.5 M in hexanes, 0.4 mL, 1.0 mmol, 2.0 equiv) at −78 °C. After the mixture was stirred for 30 min, a substrate (0.5 mmol) in 1.0 mL of THF was added. The mixture was stirred for 1 h at −78 °C, then gradually warmed to room temperature over 1 h. The reaction mixture was stirred an additional 2 h at room temperature and quenched by filtering through a pad of silica gel. The filtrate was concentrated and the residue was flash chromatographed on silica gel.

4l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 5H), 4.43 (s, 2H), 3.63 (dd, J = 12, 4.5 Hz, 1H), 3.46 (t, J = 6 Hz, 2H), 3.28 (dd, J = 12, 9.5 Hz, 1H), 2.50 (t, J = 7.5 Hz, 2H), 2.32 (ABX, J_{AB} = 7 Hz, J_{AX} = 9 Hz, J_{BX} = 9.5 Hz, 2H), 2.04 (m, 1H), 1.88 (qn, J = 7 Hz, 2H), 1.68 (m, 1H), 1.47 (m, 1H), 1.32 (m, 1H), 1.29 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 138.4, 128.3, 127.6, 127.5, 72.8, 71.0, 69.2, 65.8, 45.1, 39.8, 35.3, 31.4, 29.4, 26.9, 23.8, 23.1

6l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.27 (m, 1H), 5.61 (s, 1H), 4.61 (s, 1H), 4.53 (ABq, J = 11 Hz, 2H), 3.66 (dd, J = 12, 4.5 Hz, 1H), 3.23 (dd, J = 21, 13 Hz, 1H), 2.43 (m, 1H), 2.20 (m, 2H), 2.00 (m, 2H), 1.88 (m, 1H), 1.71 (m, 2H), 1.50 (m, 2H), 1.20 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 139.0, 128.3, 127.7, 127.3, 125.8, 84.5, 71.1, 70.3, 66.7, 35.9, 34.1, 33.8, 33.4, 30.5, 30.3, 26.3, 22.3; HRMS (ESI, m/z) $[M + Na]^+$ calcd for $C_{20}H_{28}O_2Na$ 323.1987, found 323.1994.

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4m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.00 (t, J = 6 Hz, 2H), 3.60 (dd, J = 11.5, 4 Hz, 1H), 3.26 (dd, J = 12, 9.5 Hz, 1H), 2.43 (t, J = 7.5 Hz, 2H), 2.32 (m, 2H), 2.0 (m, 1H), 1.87 (qn, J = 7 Hz, 2H), 1.67 (m, 1H), 1.44 (m, 2H), 1.28 (m, 1H), 1.14 (s, 3H), 1.29 (s, 9H), 1.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 178.3, 71.0, 65.7, 63.3, 45.1, 39.3, 38.7, 35.2, 31.4, 29.2, 27.1, 25.9, 23.1, 22.7.

5m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (s, 1H), 4.46 (d, J = 5 Hz, 1H), 4.03 (t, J = 6.5 Hz, 2H), 2.22 (m, 3H), 2.12 (m, 2H), 1.82 (m, 3H), 1.51 (m, 2H), 1.20 (m, 1H), 1.20 (s, 3H), 1.17 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.5, 150.3, 125.0, 76.0, 64.0, 39.6, 38.7, 36.9, 33.6, 30.2, 27.8, 27.2, 26.5, 24.1, 22.5; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{18}H_{31}O_3$ 295.2273, found 295.2272.

4n: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (t, J = 7.5 Hz, 2H), 2.24 (d, J = 7 Hz, 2H), 1.81 (m, 1H), 1.64 (m, 5H), 1.53 (qn J = 7 Hz, 2H), 1.31 (m, 4H), 1.13 (m, 1H), 0.88 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.2, 50.5, 43.2, 33.9, 33.2, 26.2, 26.0, 25.9, 22.3, 13.8.

5n: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.21 (s, 1H), 2.70 (m, 1H), 2.36 (m, 2H), 2.11 (m, 1H), 1.96 (d, J = 6.5 Hz, 2H), 1.70 (m, 4H), 1.46 (m, 6H), 0.99 (d, J = 6.5 Hz, 3H), 0.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142. 4, 131.0, 39.8, 39.2, 35.9, 34.7, 33.4, 32.6, 26.6, 26.4, 21.4; HRMS (EI, m/z) $[M]^+$ calcd for $C_{10}H_{16}$ 136.1252, found 136.1244.

4o: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.41 (qn, J = 6 Hz, 1H), 4.14 (m, 1H), 3.62 (dd, J = 11.5, 4 Hz, 1 H), 3.51 (m, 1H), 3.28 (dd, J = 11.5, 11 Hz), 2.85 (dt, J = 16.5, 5.5 Hz, 1H), 2.53 (dd, J = 16.5, 6.5 Hz, 1H), 2.34 (m, 2H), 1.87 (m, 1H), 1.69 (m, 1H), 1.45 (m, 2H), 1.35 (s, 3H), 1.30 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 108.8, 71.6, 71.0, 69.3, 65.7, 47.3, 45.7, 35.2, 31.3, 29.3, 26.8, 25.8, 25.4, 23.3

6o: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (s, 1H), 5.03 (d, J = 6.4 Hz, 1H), 4.71 (t, J = 5.5 Hz, 1H), 3.63 (m, 1H), 3.27 (m, 1H), 2.46 (m, 2H), 1.95 (m, 2H), 1.66 (m, 2H), 1.37 (s, 3H), 1.33 (m, 1H), 1.30 (s, 3H), 1.18 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 125.5, 109.5, 85.3, 78.1, 71.1, 66.4, 41.0, 35.8, 34.0, 33.7, 30.2, 27.5, 26.4, 25.6, 22.4; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{16}H_{27}O_3$ 267.1960, found 267.1949.

4q: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (m, 1H), 5.26 (d, J = 17.5 Hz, 1H), 5.18 (d, J = 10.5 Hz, 1H), 3.99 (d, J = 6 Hz, 2H), 3.96 (s, 2H), 3.62 (dd, J = 11.5, 4.5 Hz, 1H), 3.27 (dd, J = 11.5, 9.5 Hz, 1H), 2.31 (ABX, J_{AB} = 7 Hz, J_{AX} = 9 Hz, J_{BX} = 9.5 Hz, 2H), 2.04 (m, 1H), 1.69 (m, 1H), 1.47 (m, 2H), 1.36 (m, 1H), 1.14 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.5, 133.7, 117.9, 75.2, 72.3, 71.0, 65.7, 41.1, 35.2, 31.0, 29.3, 25.9, 23.1.

6q: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (m, 1H), 5.39 (s, 1H), 5.24 (d, J = 17.5 Hz, 1H), 5.16 (br s, 1H), 5.07 (d, J = 10.5 Hz, 1H), 4.57 (m, 2H), 3.68 (dd, J = 11.5, 4.5 Hz, 1H), 3.30 (dd, J = 11.5, 9.5 Hz, 1H), 1.99 (m, 2H), 1.72 (m, 2H), 1.54 (m, 1H), 1.45 (m, 1H), 1.31 (m, 1H), 1.20 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 123.3, 111.5, 87.5, 76.7, 71.2, 66.3, 35.7, 34.1, 30.0, 29.9, 26.4, 22.5; LRMS (ESI, m/z) $[M + Na]^+$ calcd for $C_{14}H_{22}O_2Na$ 245.1, found 245.1.

4r: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.61 (m, 1H), 3.27 (m, 1H), 2.35 (m, 2H), 2.26 (m, 2H), 2.01 (m, 1H), 1.66 (m, 1H), 1.51 (m, 2H), 1.48 (m, 2H), 1.29 (m, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 0.87 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.0, 71.0, 65.8, 45.0, 42.9, 35.3, 31.4, 29.3, 25.9, 25.8, 23.0, 22.2, 13.8.

5r and **6r**: key resonances for **5r**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (s, 1H), 4.47 (d, J = 6 Hz, 1H), 1.21 (s, 3H), 1.19 (s, 3H), 0.88 (t, J = 7.2 Hz, 3H); key resonances for **6r**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23 (s, 1H), 3.63 (m, 1H), 3.26 (dd, J = 11.5, 10 Hz, 1H), 2.68 (m, 1H), 1.177 (s, 3H), 1.170 (s, 3H), 0.97 (dd, J = 6.8, 3 Hz, 3H); ^{13}C NMR for **5r** and **6r** (125 MHz, $CDCl_3$) δ 151.7, 141.1, 131.6, 124.3, 76.1, 71.1, 70.6, 66.8, 39.8, 39.6, 37.0, 36.0, 34.6, 34.5, 34.1, 33.9, 33.7, 32.5, 31.2, 30.4, 30.2, 29.5, 26.5, 24.2, 22.6, 22.2, 21.2, 13.9; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{14}H_{25}O$ 209.1905, found 209.1912.

4s: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.71 (dd, J = 8, 5 Hz, 1H), 2.58 (m, 2H), 2.41 (t, J = 7.5 Hz, 2H), 1.90 (m, 1H), 1.63 (m, 1H), 1.57 (m, 2H), 1.31 (m, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 63.4, 58.7, 42.6, 39.2, 25.9, 24.7, 22.9, 22.3, 18.7, 13.8.

6s: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (s, 1H), 2.72 (t, J = 6 Hz, 2H), 2.26 (m, 4H), 2.21 (m, 1H), 1,71 (m, 2H), 1.35 (m, 1H), 1.29 (s, 3H), 1.25 (s, 3H), 0.98 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 130.3, 64.2, 58.3, 39.8, 34.8, 32.5, 27.9, 27.2, 24.8, 21.3, 18.7; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{11}H_{19}O$ 167.1436, found 167.1441.

4t: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (s, 2H), 4.18 (s, 2H), 3.58 (m, 1H), 3.23 (m, 1H), 1.86 (m, 2H), 1.68 (m, 2H), 1.48 (m, 1H), 1.29 (m, 4H), 1.21 (m, 1H), 1.14 (d, J = 6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 78.5, 72.7, 72.2, 72.0, 31.8, 25.6, 23.9, 21.7.

5t: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (s, 1H), 4.57 (s, 2H), 4.03 (s, 2H), 3.58 (m, 1H), 1.81 (m, 2H), 1.56 (m, 2H), 1.48 (m, 1H), 1.26 (m, 5H), 1.12 (d, J = 6.5 Hz, 6H).

6t: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 (s, 1H), 4.59 (s, 2H), 4.06 (s, 2H), 3.28 (m, 1H), 1.81 (m, 2H), 1.56 (m, 2H), 1.48 (m, 1H), 1.28 (s, 6H), 1.26 (m, 5H); ^{13}C NMR for **5t** and **6t** (125 MHz, $CDCl_3$) δ 137.7, 136.9, 130.6, 129.2, 74.1, 74.6, 72.2, 71.1, 70.2, 70.0, 63.8, 63.4, 37.0, 32.1, 27.6, 25.8, 24.0, 23.8, 23.4, 21.8; HRMS (ESI, m/z) $[M + Na]^+$ calcd for $C_{13}H_{22}O_2Na$ 233.1517, found 233.1514.

4u: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (s, 2H), 4.15 (s, 2H), 3.90 (br s, 1H), 3.25 (m, 1H), 1.88 (m, 2H), 1.78−1.61 (8H), 1.50 (br s, 3H), 1.33−1.20 (5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 82.5, 78.5, 72.8, 72.0, 32.0, 25.6, 23.9, 23.4.

5u and **6u**: key resonances for **5u**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (s, 1H), 4.57 (s, 2H), 4.00 (s, 2H), 3.91 (m, 1H); HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{15}H_{25}O_2$ 237.1855, found 237.1856; **6u**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (s, 1H), 4.55 (s, 2H), 4.08 (s, 2H), 3.26 (m, 1H), 1.88 (m, 2H), 1.78−1.61 (8H), 1.50 (br s, 3H), 1.33−1.20 (5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 128.6, 98.3, 77.2, 73.9, 63.5, 38.3, 32.1, 25.7, 24.4, 24.1.

4u′: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.23 (s, 2H), 4.14 (s, 2H), 3.90 (m, 1H), 3.17 (m, 1H), 2.06 (d, J = 11.5 Hz, 2H), 1.78 (m, 2H), 1.70 (m, 6H), 1.15 (m, 2H), 1.21 (m, 2H), 0.97 (m, 3H), 0.79 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1 82.5, 79.6, 72.9, 72.1, 47.3, 32.3, 32.2, 32.0, 27.6, 25.5, 23.4.

5u′ and **6u′**: key resonances for **5u′**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (s, 1H), 4.57 (s, 2H), 4.01 (s, 2H), 3.94 (m, 1H); key resonances for **6u′**: 5.59 (s, 1H), 4.54 (s, 2H), 4.08 (s, 2H), 3.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) for **5u′** and **6u′** δ 137.6, 137.4, 128.6, 127.1, 98.3, 90.9, 81.2, 78.4, 73.9, 73.5, 64.6, 63.6, 47.4, 38.38, 38.35, 32.6, 32.29, 32.26, 27.63, 25.62, 25.51, 24.41, 23.57; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{19}H_{33}O_2$ 293.2481, found 293.2479.

4v: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26 (s, 2H), 4.22 (s, 2H), 3.27 (m, 1H), 3.18 (m,1H), 2.07 (d, J = 12 Hz, 2H), 1.89 (m, 2H), 1,79 (m, 4H), 1.52 (m, 1H), 1.34−1.17 (m, 7H), 1.09 (m, 2H), 0.83 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 79.6, 78.6, 72.1, 47.3, 32.3, 32.2, 31.8, 27.6, 25.6, 25.5, 23.9.

5v and **6v**: key resonances for **5v**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 (s, 1H), 4.58 (s, 2H), 4.08 (s, 2H), 3.25 (m, 1H); key resonances for **6v**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (s, 1H), 4.57 (s, 2H), 4.08 (s, 2H), 3.17 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) for **5v** and **6v** δ 137.8, 137.4, 129.2, 127.0, 90.9, 89.8, 78.3, 73.7, 73.5, 63.78, 63.74, 47.43, 47.40, 38.3, 37.0, 32.6, 32.2, 32.1, 27.66, 27.63, 25.77, 25.62, 25.51, 25.45, 24.12, 23.46; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{20}H_{35}O_2$ 307.2637, found 307.2635.

4w: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32 (s, 2H), 4.12 (s, 2H), 3.53 (br s, 1H), 3.19 (m, 1H), 2.07 (d, J = 12 Hz, 2H), 1.97 (d, J = 12 Hz, 2H), 1.79 (m, 2H), 1.50 (m, 2H), 1.48−1.20 (m, 6H), 1.00

(m, 4H), 0.83 (s, 9H), 0.82 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.5, 79.5, 74.3, 72.1, 71.9, 47.8, 47.3, 32.5, 32.3, 32.2, 30.2, 27.6, 27.4, 25.5, 21.3.

5w and **6w**: key resonances for **5w**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.99 (s, 1H), 4.61 (s, 2H), 4.05 (s, 2H), 3.55 (br s, 1H), 0.86 (s, 9H), 0.84 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 126.8, 90.7, 73.5, 72.4, 63.4, 47.8, 47.3, 38.3, 32.6, 32.3, 30.4, 27.6, 27.4, 25.6, 21.3; key resonances for **6w**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (s, 1H), 4.60 (s, 2H), 4.08 (s, 2H), 3.19 (m, 1H), 0.89 (s, 9H), 0.83 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 130.8, 88.7, 78.2, 73.9, 63.7, 47.4, 36.5, 32.6, 32.4, 30.4, 27.6, 27.4, 25.6, 25.5, 23.3; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{24}H_{43}O_2$ 363.3263, found 363.3264.

4x: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (t, J = 6 Hz, 1H), 4.23 (s, 2H), 4.21 (s, 2H), 3.52 (m, 2H), 3.19 (m, 1H), 2.08 (d, J = 12 Hz, 2H), 1.97 (m, 2H), 1.79 (m, 2H), 1.66 (s, 3H), 1.64 (m, 1H), 1.59 (s, 3H), 1.56 (m, 1H), 1.42 (m, 2H), 1.24 (m, 4H), 0.99 (m, 2H), 0.89 (d, J = 7 Hz, 3H), 0.83 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.0, 131.2, 124.7, 79.7, 74.7, 72.1, 70.3, 47.3, 37.1, 36.4, 32.3, 32.2, 29.5, 27.6, 25.7, 25.5, 25.4, 19.5, 17.6.

5x and **6x**: key resonances for **5x**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00 (s, 1H), 5.09 (t, J = 7 Hz, 1H), 4.59 (s, 2H), 4.01 (s, 2H), 3.46 (m, 2H); key resonances for **6x**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (d, J = 1.5 Hz, 1H), 5.09 (t, J = 7 Hz, 1H), 4.89 (br s, 1H), 4.62 (m, 2H), 4.10 (s, 2H), 3.16 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) for **5x** and **6x**: δ 138.3, 138.2, 137.2, 131.0, 127.6, 126.2, 125.9, 124.8, 124.7, 90.9, 85.0, 84.6, 78.2, 74.8, 73.4, 69.0, 66.6, 63.5, 47.4, 47.3, 43.3, 38.3, 37.7, 37.3, 36.63, 33.60, 32.6, 32.2, 30.3, 29.8, 29.6, 29.5, 27.6, 25.7, 25.6, 25.5, 25.46, 25.42, 20.1, 19.5, 19.4, 17.3; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{24}H_{43}O_2$ 363.3263, found 363.3265.

4y: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (m, 2H), 4.15 (m, 2H), 3.52 (br s, 1H), 3.09 (m, 1H), 2.22 (m, 1H), 2.01 (m, 3H), 1.62 (m, 2H), 1.48 (br s, 2H), 1.32 (m, 6H), 0.98 (m, 1H), 0.85 (m, 6H), 0.83 (s, 9H), 0.76 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 80.3, 74.2, 72.5, 72.0, 48.0, 47.7, 39.9, 34.4, 32.5, 31.4, 30.2, 27.4, 25.6, 23.3, 22.2, 21.3, 20.9, 16.2.

5y and **6y**: key resonances for **5y**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (s, 1H), 4.63 (m, 2H), 4.04 (s, 2H), 3.54 (br s, 1H); **6y**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (s, 1H), 4.62 (ABq, J = 12 Hz, 2H), 4.21 (ABq, J = 12.5 Hz, 2H), 3.07 (m, 1H), 2.17 (m, 1H), 2.08 (m, 1H), 1.75 (m, 2H), 1.64 (m, 4H), 1.42−1.24 (m, 7H), 0.96 (m, 3H), 0.91 (d, J = 9.5 Hz, 3H), 0.88 (d, J = 7 Hz, 3H), 0.84 (s, 9H), 0.75 (d, J = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137. 0, 130.9, 88.6, 79.4, 74.1, 64.2, 48.2, 47.3, 40.3, 36.5, 36.4, 34.5, 32.4, 31.5, 27.6, 25.6, 23.3, 22.3, 20.9, 16.2; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{24}H_{43}O_2$ 363.3263, found 363.3274.

4z: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (ABq, J = 17.5 Hz, 2H), 4.26 (s, 2H), 3.17 (m, 1H), 3.09 (m, 1H), 2.20 (m, 1H), 2.06 (m, 3H), 1.78 (m, 2H), 1.63 (m, 2H), 1.43 (m, 1H), 1.32 (m, 5H), 0.99 (m, 4H), 0.86 (m, 6H), 0.79 (s, 9H), 0.75 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 80.4, 79.5, 72.6, 72.0, 48.0, 47.3, 41.3, 39.9, 34.4, 32.3, 32.2, 31.4, 27.6, 27.4, 25.6, 25.5, 23.2, 22.2, 20.9, 16.2.

5z and **6z**: key resonances for **5z**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (s, 1H), 4.62 (ABq, J = 12 Hz, 2H), 4.10 (s, 2H), 3.14 (m, 1H); key resonances for **6z**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 (s, 1H), 4.62 (ABq, J = 12 Hz, 2H), 4.22 (ABq, J = 12.5 Hz, 2H), 3.08 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) for **5z** and **6z** δ 137.7, 127.2, 126.4, 94.3, 90.9, 79.4, 77.8, 74.3, 73.6, 64.4, 63.7, 52.1, 49.5, 48.2, 47.3, 40.3, 38.3, 38.2, 35.0, 34.5, 32.7, 32.4, 32.2, 31.5, 31.3, 27.65, 27.62, 25.8, 25.6, 25.58, 25.50, 24.4, 23.6, 23.4, 22.3, 20.9, 18.7, 16.2; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{24}H_{43}O_2$ 363.3263, found 363.3260.

11c: colorless liquid; R_f 0.2 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (d, J = 5.0 Hz, 1H), 2.74 (dd, J = 8.0, 17.5 Hz, 1H), 2.40 (dd, J = 5.5, 18.0 Hz, 1H), 2.12 (t, J = 6.5 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 1H), 1.98−1.94 (m, 1H), 1.91−1.86 (m, 2H), 1.70 (d, J = 10.5 Hz, 1H), 1.68−1.62 (m, 1H), 1.58 (dd, J = 3.0, 11.5 Hz, 1H), 1.27 (s, 3H), 1.21 (dd, J = 3.5, 10.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.1, 86.5, 80.1, 45.8, 43.9, 42.8, 42.0, 41.9, 41.0, 36.4, 30.6, 23.2; HRMS (EI, m/z) $[M]^+$ calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1308.

13c: colorless liquid, volatile; R_f 0.75 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (s, 1H), 4.39 (d, J = 4.5 Hz, 1H), 2.30 (t, J = 16.5 Hz, 1H), 2.25 (t, J = 6.5 Hz, 1H), 1.98−1.90 (m, 2H), 1.86−1.76 (m, 2H), 1.72 (s, 3H), 1.69 (d, J = 11.0 Hz, 2H), 1.44 (dd, J = 3.5, 10.5 Hz, 1H), 1.37 (d, J = 11.0 Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 129.2, 83.6, 77.3, 56.2, 50.2, 48.2, 45.9, 43.8, 42.5, 36.3, 23.1, 17.6; HRMS (EI, m/z) $[M]^+$ calcd for $C_{13}H_{18}O$ 190.1358, found 190.1357.

14c: 1:1 mixture of two diastereomers; colorless liquid, volatile; R_f 0.77 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.82 (m, 1H), 4.08 (br s, 1H), 2.23−2.15 (m, 3H), 2.08−1.95 (m, 3H), 1.78−1.66 (m, 2H), 1.63 (d, J = 3.5 Hz, 3H), 1.62−1.53 (m, 2H), 1.35 (d, J = 3.5 Hz, 3H), 1.27−1.22 (m, 1H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0, 208.9, 90.3, 86.4, 82.3, 80.5, 80.2, 44.3, 42.8, 42.7, 42.2, 42.1, 41.1, 40.8, 40.0, 39.7, 35.2, 23.4, 18.7, 18.6, −0.7; HRMS (EI, m/z) $[M]^+$ calcd for $C_{17}H_{28}OSi$ 276.1909, found 276.1908.

25a: colorless liquid; volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.24−7.18 (m, 3H), 4.91 (q, J = 4.0 Hz, 1H), 2.73 (t, J = 7.0 Hz, 2H), 2.24 (qn, J = 4.0 Hz, 2H), 1.71 (d, J = 3.5 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 142.4, 128.4, 128.3, 125.8, 91.7, 83.0, 35.0, 34.4, 18.3, −0.7; HRMS (EI, m/z) $[M]^+$ calcd for $C_{15}H_{22}Si$ 230.1491, found 230.1488.

25b: colorless liquid, volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2H), 7.23−7.16 (m, 3H), 5.01 (m, 1H), 2.73 (m, 2H), 2.24 (m, 2H), 1.97 (m, 2H), 1.02 (t, J = 7.5 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.9, 142.6, 128.4, 128.3, 125.7, 98.5, 85.0, 34.5, 33.7, 24.9, 12.5, −0.7; HRMS (EI, m/z) $[M]^+$ calcd for $C_{16}H_{24}Si$ 244.1647, found 244.1647.

25c: colorless liquid; volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.23−7.18 (m, 3H), 4.98 (m, 1H), 2.72 (m, 2H), 2.23 (m, 2H), 1.96 (qn, J = 4.0 Hz, 2H), 1.46 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 142.6, 128.4, 128.3, 125.6, 96.5, 84.3, 34.5, 34.2, 33.7, 21.1, 14.1, −0.7; HRMS (EI, m/z) $[M]^+$ calcd for $C_{17}H_{26}Si$ 258.1804, found 258.1804.

25d: colorless liquid, volatile; R_f 0.78 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32−7.28 (m, 4H), 7.23−7.18 (m, 6H), 5.03 (m, 1H), 2.73 (m, 4H), 2.27 (m, 4H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.1, 142.4, 128.4, 128.3, 125.8, 96.7, 85.1, 34.4, 33.8, −0.7; HRMS (EI, m/z) $[M]^+$ calcd for $C_{22}H_{28}Si$ 320.1960, found 320.1962.

25e and **25e′**: inseparable mixture; colorless liquid; volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.29 (m, 2.5H), 7.26−7.17 (m, 3.8H), 5.32 (d, J = 1.5 Hz, 1H), 5.00 (m, 0.24H), 2.80 (t, J = 7.5 Hz, 2H), 2.76−2.72 (m, 1.5H), 2.39 (t, J = 7.5 Hz, 2H), 2.34−2.24 (m, 2H), 2.14 (m, 1H), 2.00 (m, 0.5H), 1.41 (m, 2.5H), 1.03 (d, J = 7.0 Hz, 3H), 0.95 (t, J = 7.5 Hz, 0.75H), 0.12 (s, 2.3H); ^{13}C NMR (125 MHz, $CDCl_3$), characteristic peaks for allene **25e**: δ 208.2, 142.6, 128.39, 128.30, 125.7, 96.7, 84.3, 34.5, 33.7, 31.7, 30.1, 22.6, 14.1, −0.7; ^{13}C NMR (125 MHz, $CDCl_3$), characteristic peaks for alkene **25e′**: δ 143.3, 142.5, 130.2, 128.35, 128.27, 125.7, 39.9, 35.0, 34.4, 33.2, 32.6, 21.3; **25e**: HRMS (EI, m/z) $[M]^+$ calcd for $C_{18}H_{28}Si$ 272.1960, found 272.1964; **25e′**: HRMS (EI, m/z) $[M]^+$ calcd for $C_{14}H_{18}$ 186.1409, found 186.1410.

24f: colorless liquid; R_f 0.40 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 2H), 2.08 (s, 3H), 1.91 (m, 3H), 1.67−1.56 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 57.0, 42.5, 36.7, 33.4, 33.1, 28.6.

25f: colorless liquid, volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75 (m, 1H), 1.95 (br s, 3H), 1.73−1.54 (m, 17H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.9, 87.7, 80.4, 48.4, 42.7, 37.2, 34.4, 28.8, 21.4, −0.7; HRMS (EI, m/z) $[M]^+$ calcd for $C_{18}H_{30}Si$ 274.2117, found 274.2115.

25f′: colorless liquid, volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (s, 1H), 2.49 (br s, 1H), 2.05 (br s, 1H), 2.00−1.91 (m, 3H), 1.91−1.81 (m, 2H), 1.78−1.54 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 128.0, 57.1, 50.0, 42.5, 39.0, 38.4, 38.1, 32.2, 30.3, 29.8, 28.8, 28.2, 17.8; HRMS (EI, m/z) $[M]^+$ calcd for $C_{14}H_{20}$ 188.1565, found 188.1562.

25g′: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32 (s, 1H), 2.24 (m, 1H), 1.95 (m, 4H), 1.85 (m, 4H), 1.82 (m, 4H), 1.72 (s, 3H), 1.69 (m, 5H), 1.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 135.9, 53.2, 44.7, 42.2, 39.7, 38.5, 37.7, 37.6, 31.6, 30.3, 29.7, 29.4, 27.7, 17.5; HRMS (EI, m/z) $[M]^+$ calcd for $C_{14}H_{20}$ 188.1565, found 188.1558.

25h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (m, 1H), 1.82 (m, 2H), 1.79 (m, 4H), 1.62 (d, J = 3.5 Hz, 3H), 1.39 (m, 1H), 1.36 (m, 4H), 0.91 (m, 2H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.3, 90.0, 81.2, 41.3, 35.9, 33.4, 26.6, 18.2, −0.6; HRMS (EI, m/z) $[M]^+$ calcd for $C_{14}H_{26}Si$ 222.1803, found 222.1796.

26a: colorless liquid; R_f 0.24 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.5 Hz, 2H), 2.54 (ddd, J = 4.0, 7.0, 10.0 Hz, 1H), 2.31 (s, 3H), 2.23 (ddd, J = 4.0, 5.0, 8.5 Hz, 1H), 1.69 (ddd, J = 4.5, 5.0, 9.0 Hz, 1H), 1.39 (ddd, J = 4.5, 7.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.8, 140.4, 128.6, 126.6, 126.1, 32.9, 30.9, 29.0, 19.2.

27a: 1:1 mixture of two diastereomers; colorless liquid; volatile; R_f 0.81 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.25 (m, 2H), 7.18−7.15 (m, 1H), 7.15−7.08 (m, 2H), 5.00 (m, 1H), 1.89 (ddd, J = 4.5, 5.0, 9.5 Hz, 0.5H), 1.84 (ddd, J = 5.0, 5.1, 9.0 Hz, 0.5H), 1.77 (t, J = 4.0 Hz, 3H), 1.39 (m, 1H), 1.14−1.03 (m, 2H), 0.11 (d, J = 1.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.1, 208.0, 143.1, 128.3, 125.9, 125.8, 125.5, 94.2, 94.1, 84.6, 25.4, 25.3, 25.1, 24.8, 17.8, 17.7, 16.3, 15.8, −0.7, −0.8; HRMS (CI, m/z) $[M]^+$ calcd for $C_{16}H_{22}Si$ 242.1491, found 242.1492.

26b: colorless liquid; R_f = 0.23 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 3.77 (s, 3H), 2.86 (m, 4H), 1.90 (tt, J = 3.5, 8.0 Hz, 1H), 1.01 (ddt, J = 4.0, 7.5, 11.5 Hz, 2H), 0.85 (ddt, J = 3.5, 7.0, 11.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 157.9, 133.3, 129.3, 113.9, 55.3, 45.3, 29.1, 20.6, 10.7.

27b: colorless liquid; R_f = 0.75 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.00 (m, 1H), 3.78 (s, 3H), 2.70 (t, J = 7.0 Hz, 2H), 2.30 (dt, J = 4.0, 9.5 Hz, 2H), 1.09 (m, 1H), 0.63 (m, 2H), 0.37 (ddt, J = 3.5, 8.5, 12.0 Hz, 1H), 0.29 (ddt, J = 3.5, 8.5, 12.5 Hz, 1H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 157.8, 134.7, 129.2, 113.7, 85.8, 55.3, 34.2, 33.7, 11.8, 6.9, 5.5, −0.8; HRMS (EI, m/z) $[M]^+$ calcd for $C_{18}H_{26}OSi$ 286.1753, found 286.1753.

26c: colorless liquid; R_f 0.20 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.56 (s, 3H), 2.80 (dd, J = 7.5, 10.0 Hz, 1H), 2.30−2.16 (m, 3H), 1.98 (s, 3H), 1.88−1.79 (m, 2H), 1.24 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 173.1, 54.1, 51.4, 43.2, 37.9, 34.8, 30.1, 22.9, 17.2.

27c: 1:1 mixture of two diastereomers; colorless liquid; R_f 0.50 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.94−4.87 (m, 1H), 3.64 (s, 3H), 2.32−2.17 (m, 4H), 2.02−1.92 (m, 1H), 1.57 (s, 1.5H), 1.56 (s, 1.5H), 1.44−1.37 (m, 1H), 1.13 (s, 1.5H), 1.12 (s, 1.5H), 0.88 (s, 1.5H), 0.82 (s, 1.5H), 0.12 (s, 4.5H), 0.02 (s, 4.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 209.2, 173.8, 173.7, 92.9, 92.5, 83.4, 83.3, 51.4, 45.4, 45.3, 42.3, 42.1, 38.3, 38.2, 35.2, 35.1, 30.53, 30.48, 27.4, 27.1, 18.2, 18.0, 17.2, 16.9, −0.4, −0.9; HRMS (CI, m/z) $[M]^+$ calcd for $C_{16}H_{28}O_2Si$ 280.1858, found 280.1853.

26d: colorless liquid; R_f 0.23 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (m, 1H), 3.31 (s, 3H), 3.30 (s, 3H), 2.35−2.30 (m, 2H), 2.13 (s, 3H), 1.53−1.42 (m, 2H), 1.06 (s, 3H), 0.88 (s, 3H), 0.88−0.81 (m, 1H), 0.64−0.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 105.1, 53.3, 39.5, 29.7, 28.7, 28.3, 21.4, 21.1, 16.8, 15.2;

27d: 1:1 mixture of two diastereomers; colorless liquid; R_f 0.75 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.85 (m, 1H), 4.36 (m, 1H), 3.33 (s, 6H), 1.97 (dt, J = 15.5, 5.0 Hz, 0.5H), 1.90−1.80 (m, 1H), 1.77−1.71 (m, 0.5H), 1.65 (d, J = 4.0 Hz, 3H), 1.57−1.47 (m, 1.5H), 1.32−1.26 (m, 0.5H), 1.04 (s, 1.5H), 1.02 (s, 1.5H), 0.93 (s, 1.5H), 0.89 (s, 1.5H), 0.62−0.51 (m, 2H), 0.07 (s, 4.5H), 0.06 (s, 4.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.3, 209.0, 105.2, 92.1, 82.4, 53.2, 53.0, 52.9, 52.8, 29.3, 29.2, 29.1, 28.5, 28.2, 28.1, 25.1, 24.8, 21.6, 21.5, 18.5, 18.4, 17.0, 16.9, 15.2, 14.9, −0.7, −0.8; HRMS (CI, m/z) $[M - H]^+$ calcd for $C_{17}H_{31}O_2Si$ 295.2093, found 295.2090.

26e: colorless liquid; R_f 0.45 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.71−3.60 (m, 5H), 2.43−2.31 (m, 4H), 1.99−1.87 (m, 2H), 1.76−1.65 (m, 2H), 1.14 (s, 3H), 1.06−0.97 (m, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.7, 177.0, 59.9, 51.7, 43.7, 41.6, 37.6, 35.9, 33.1, 21.4, 18.0, 11.9, 7.8; HRMS (EI, m/z) $[M - C_3H_7]^+$ calcd for $C_{17}H_{33}O_4Si$ 329.2148, found 329.2156.

27e: 1:1 mixture of two diastereomers; colorless liquid; R_f 0.77 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.95 (m, 1H), 3.72−3.62 (m, 5H), 2.02−1.95 (m, 1H), 1.93−1.82 (m, 3H), 1.78−1.68 (m, 3H), 1.56−1.49 (m, 1H), 1.18 (s, 3H), 1.09−1.01 (m, 21H), 0.97 (t, J = 7.5 Hz, 3H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 177.4, 98.5, 84.9, 84.8, 60.0, 51.5, 44.2, 41.8, 41.6, 38.1, 38.0, 26.6, 24.8, 21.5, 21.4, 18.0, 12.4, 12.0, −0.8; HRMS (EI, m/z) $[M - C_3H_7]^+$ calcd for $C_{22}H_{43}O_3Si_2$ 411.2751, found 411.2751.

26f: colorless liquid; R_f 0.18 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (t, J = 4.5 Hz, 1H), 2.52 (t, J = 6.0 Hz, 2H), 2.08 (s, 3H), 1.81 (m, 1H), 1.54 (m, 1H), 1.19 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 63.2, 58.7, 40.1, 29.9, 24.7, 22.9, 18.6;

27f: 1:1 mixture of two diastereomers; colorless liquid, volatile; R_f 0.73 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (m, 1H), 2.76 (t, J = 6.5 Hz, 1H), 2.09−1.97 (m, 2H), 1.67−1.57 (m, 5H), 1.31 (s, 3H), 1.27 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 91.3, 91.2, 83.1, 83.0, 64.0, 58.4, 29.8, 27.4, 27.3, 24.9, 18.7, 18.3, −0.8; HRMS (EI, m/z) $[M - CH_3]^+$ calcd for $C_{12}H_{21}OSi$ 209.1362, found 209.1364.

26g: colorless liquid; R_f 0.15 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59 (dd, J = 2.5, 10.0 Hz, 1H), 2.75−2.67 (m, 1H), 2.55−2.47 (m, 1H), 2.14 (s, 3H), 1.74−1.62 (m, 2H), 1.37 (s, 3H), 1.28 (s, 3H), 1.23 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 106.7, 82.6, 80.2, 41.0, 30.0, 28.5, 26.9, 25.9, 23.2, 22.9;

27g: 1:1 mixture of two diastereomers; colorless liquid, volatile; R_f 0.51 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (m, 1H), 3.73 (dd, J = 2.5, 10.0 Hz, 1H), 2.13 (m, 1H), 1.95 (m, 1H), 1.67(m, 3H), 1.62 (m, 1H), 1.47 (m, 1H), 1.42 (m, 3H), 1.34 (s, 3H), 1.25 (s, 1.5H), 1.24 (s, 1.5H), 1.09 (s, 1.5H), 1.08 (s, 1.5H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 106.5, 91.7, 91.6, 83.4, 83.0, 80.2, 30.3, 29.9, 29.7, 28.6, 27.8, 27.6, 27.0, 26.9, 26.1, 22.9, 22.7, 18.5, 18.3, −0.8; HRMS (CI, m/z) $[M]^+$ calcd for $C_{16}H_{30}O_2Si$ 282.2015, found 282.2010.

27g′: colorless liquid; R_f 0.49 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (s, 1H), 2.40 (m, 1H), 2.13 (m, 2H), 1.98 (m, 1H), 1.78 (s, 3H), 1.40 (s, 6H), 1.25 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 126.3, 106.2, 97.9, 82.0, 35.0, 33.6, 29.7, 29.2, 24.7, 24.5, 17.2; HRMS (CI, m/z) $[M + H]^+$ calcd for $C_{12}H_{21}O_2$ 197.1541, found 197.1539.

26h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.93 (ddd, J = 12, 4, 1.5 Hz, 2H), 3.51 (ddd, J = 11.5, 5.5, 2 Hz, 2H), 2.55 (dd, J = 7, 1.5 Hz, 2H), 2.11 (m, 1H), 2.09 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.0, 97.9, 63.8, 43.0, 30.2, 29.7, 24.5, 23.1.

27h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84 (m, 1H), 3.88 (ddd, J = 22, 11, 5 Hz, 2H), 3.51 (ddd, J = 20.5, 11, 5 Hz, 2H), 1.96 (m, 1H), 1.83 (m, 2H), 1.63 (d, J = 3.5 Hz, 3H), 1.41(s, 3H), 1.40 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 97.9, 88.6, 64.9, 32.8, 32.5, 26.7, 21.1, 18.2, −0.8; HRMS (ESI, m/z) $[M + H]^+$ calcd for $C_{10}H_{27}O_2Si$ 255.1780, found 255.1786.

29a: colorless liquid; volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.89 (m, 1H), 2.36 (m, 4H), 1.65 (m, 4H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 95.8, 83.6, 30.7, 27.4, 0.7; HRMS (EI, m/z) $[M - H]^+$ calcd for $C_{10}H_{17}Si$ 165.1099, found 165.1112.

29b: 1:1 mixture of two diastereomers; colorless liquid, volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.94 (m, 1H), 4.71 (m, 2H), 2.34 (m, 1H), 2.07−1.18 (m, 4H), 1.73 (m, 3H), 1.36−1.21(m, 2H), 1.17−1.05 (m, 1H), 0.10 (s, 4.5H), 0.07 (s, 4.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 205.7, 150.1, 150.0, 108.5, 100.4, 83.5, 46.4, 46.1, 36.6, 36.4, 36.3, 36.0, 33.2, 33.1, 31.8, 31.8, 21.0, 20.9, 19.5, 19.4, −0.7, −0.8; HRMS (EI, m/z) $[M]^+$ calcd for $C_{15}H_{26}Si$ 234.1803, found 234.1811.

29c: colorless liquid; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.94−4.88 (m, 2H), 2.44−2.31 (m, 1H), 2.00−1.75 (m, 3H), 1.31−1.03 (m, 4H), 0.11−0.05 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.0, 207.9, 205,8, 205.8, 100.6, 96.4, 96.2, 83.53, 83.43, 83.38, 83.27, 41.8, 41.7, 41.4, 36.9, 36.4, 36.2, 36.0,33.23, 33.17, 32.0, 31.9, 29.7, 19.5, 19.4, 16.9, 16.8, 16.6, 16.5, −0.0, −0.5, −0.7, −0.8; LRMS (EI, m/z) $[M + H]^+$ calcd for $C_{19}H_{35}Si$ 319.2, found 319.2

29d: 3:2 mixture of two diastereomers; colorless liquid, volatile; R_f 0.98 (hexanes/ethyl acetate = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (m, 1H), 2.21 (m, 1H), 1.84−1.75 (m, 2H), 1.74−1.67 (m, 1H), 1.67−1.46 (m, 3H), 1.18−1.08 (m, 1H), 1.01−0.89 (m, 7H), 0.88−0.83 (m, 3H), 0.09 (s, 5.4H), 0.07 (s, 3.6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 205.9, 98.7, 98.2, 82.7, 82.6, 46.0, 45.5, 41.0, 40.3, 35.3, 34.8, 34.4, 33.5, 29.7, 29.6, 29.3, 29.2, 27.6, 22.4, 22.2, 22.1, 22.0, 19.3, 18.6, −0.7, −0.9; HRMS (EI, m/z) $[M - H]^+$ calcd for $C_{15}H_{27}Si$ 235.1882, found 235.1882.

29e: colorless liquid; volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (m, 1H), 2.21 (m, 4H), 1.64−1.54 (m, 8H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 96.5, 80.6, 31.7, 29.3, 28.9, −0.6; HRMS (EI, m/z) $[M - H]^+$ calcd for $C_{12}H_{21}Si$ 193.1413, found 193.1412.

29f: colorless liquid; R_f 0.84 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (m, 1H), 3.91 (m, 4H), 2.38−2.03 (m, 4H), 1.92−1.49 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 111.7, 95.6, 64.2, 39.0, 37.7, 31.5, 25.7, 21.3, −0.6; HRMS (EI, m/z) $[M - H]^+$ calcd for $C_{14}H_{23}O_2Si$ 251.1467, found 251.1480.

29g: colorless liquid; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (m, 1H), 4.37 (m, 1H), 2.30 (m, 1H), 2.04 (m, 1H), 1.82−1.33 (m, 8H), 0.88 (s, 9H), 0.0.09 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 100.7, 83.0, 72.7, 38.9, 28.3, 27.8, 25.9, 23.7, 18.2, −0.5, −4.6, −4.9; HRMS (ESI, m/z) $[M - H]^+$ calcd for $C_{18}H_{35}OSi_2$ 323.2226, found 323.2216.

29i: colorless liquid; volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (m, 1H), 2.14 (m, 4H), 1.64−1.52 (m, 10H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.8, 96.1, 80.9, 31.2, 27.1, 26.7, 26.2, −0.4.

29j: 5:3 mixture of two diastereomers; colorless liquid, volatile; R_f 0.79 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (m, 1H), 2.91 (m, 2H), 2.36−2.05 (m, 4H), 2.01 (m, 1H), 1.76 (m, 1H), 1.72−1.46 (m, 2H), 0.1.45−1.18 (m, 2H), 0.08 (s, 5.4H), 0.06 (s, 3.6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 209.3, 95.3, 95.1, 82.2, 82.1, 56.3, 56.0, 55.9, 55.8, 30.6, 30.5, 30.3, 27.4, 26.5, 26.2, 26.1, 26.0, −0.5, −0.6; HRMS (EI, m/z) $[M - H]^+$ calcd for $C_{13}H_{21}OSi$ 221.1361, found 221.1376.

29k: colorless liquid; volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (m, 1H), 1.98 (m, 4H), 1.48−1.36 (m, 18H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 93.8, 82.5, 28.9, 24.6, 24.3, 24.2, 23.5, 22.6, −0.5; HRMS (EI, m/z) $[M]^+$ calcd for $C_{17}H_{32}Si$ 264.2273, found 264.2276.

29l and ***29l′***: inseparable mixture; colorless liquid, volatile; R_f 0.98 (hexanes/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (m, 0.4H), 4.90 (m, 1H), 2.74 (br s, 0.4H), 2.42−2.31 (m, 0.8H), 2.15−2.02 (m, 1H), 1.99 (m, 4H), 1.52−1.32 (m, 32H), 0.13 (s, 9H, $-SiMe_3$); ^{13}C NMR (125 MHz, $CDCl_3$), characteristic peaks for allene ***29l***: δ 209.3, 96.0, 82.6, 31.2, 27.3, 27.1, 27.0, 26.8, 26.7, −0.6; ^{13}C NMR (125 MHz, $CDCl_3$), characteristic peaks for alkene ***29l′***: δ 143.6, 129.9, 44.5, 33.7, 33.6, 29.6, 29.5, 27.2, 26.3, 26.1, 26.0, 25.2, 25.0, 23.2, 21.9. ***29l***: HRMS (EI, m/z) $[M]^+$ calcd for $C_{20}H_{38}Si$ 306.2742, found 306.2737. ***29l′***: HRMS (EI, m/z) $[M]^+$ calcd for $C_{16}H_{28}$ 220.2191, found 220.2188.

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Supporting Information Available: Complete ref 12a and ^{1}H and ^{13}C NMR spectra for representative compounds. This material is available free of charge via the Internet at http://pubs.acs.org.