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Carboazidation of Chiral Allylsilanes: Experimental and Theoretical Investigations

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Abstract: The carboazidation of chiral allylsilanes has been investigated by varying the nature of the substituents at the silicon center and on the carbon framework. The influence of temperature and the nature of the sulfonyl azide, as well as the stereochemistry of the remote stereogenic center, on the 1,2-diastereocontrol of the process were considered. Good to excellent levels of diastereocontrol were generally observed, with the *syn*-β-azidosilane always being formed as the major isomer. An illustration of the value of this methodology has been provided with a short and efficient synthesis of an analogue of castanospermine. EPR spectroscopy was carried out on various β-silyl radicals providing useful information about their conformations in the ground state. Based on this experimental evidence and DFT calculations, reactant-like transition state models were finally proposed that rationalize the observed 1,2-stereoinduction.

Keywords: allylsilanes · azides · carboazidation · density functional calculations · radicals

Introduction

The azido group constitutes a versatile functional group[1] that may be involved in many important synthetic transformations,[2] including 1,3-dipolar cycloadditions onto alkynes, which have recently attracted a lot of interest through the click-chemistry concept.[1b] Numerous methods have been developed to incorporate an azido group into a carbon framework.[3–8] Amongst these, radical processes hold a special place and have recently led to useful and attractive developments. For instance, N_3 radical species were shown to add to electron-rich olefins by using a combination of hypervalent iodine reagents and $TMSN_3$.[5] Activation of the C–H bond and formation of the corresponding alkyl azide by using similar reagents[6] or IN_3 was also reported.[7] More challenging intermolecular transfer of azido groups has also been described by using sulfonyl azides following a fragmentation process.[8] Recently, we developed a useful carboazidation process, allowing the formation of both a C–C bond and a C–N bond in a one-pot operation starting from simple olefins (Scheme 1).[9] The reaction works well with radical species which have an electrophilic character that add efficiently onto olefins in a first step. This intermolecular process then generates a second radical species with nucleophilic character, which reacts with the sulfonyl azide to provide

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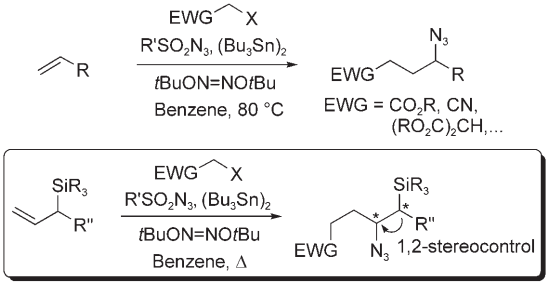


Scheme 1. The carboazidation reaction of olefins. Application to chiral allylsilanes.

the carboazidation product. The process is general and was found to be efficient for a number of radical precursors and olefins. This method is a valuable tool in organic synthesis, as illustrated by some recent applications in natural product synthesis.[10]

Allylsilanes are known to react efficiently with radical species and possess an enhanced reactivity, compared to other olefins, toward radical intermediates with electrophilic character.[11] Allylsilanes exhibit a unique reactivity towards electrophiles, and while a wealth of data is available on the 1,2-stereocontrol arising from the reaction of chiral allylsilanes with ionic electrophilic reagents,[12] little is known on the stereocontrol occurring during radical reactions of chiral allylsilanes.[13] Porter et al. first demonstrated that an allylic silicon group could control the stereochemistry of a new stereogenic center created during the radical addition (atom transfer) of α-bromo and α-iodo amides onto a chiral allylsilane.[14] Based on these premises, we started an investigation on the 1,2-stereocontrol arising from free-radical mediated carboazidation of chiral allylsilanes (Scheme 1).[15] We report here a full account of our studies, including the scope and limitations of the process, and an EPR study on the β-silyl radical species issued from the addition of the carbon radical onto chiral allylsilanes. Finally, ab initio calculations were performed, providing support for the transition state models proposed to rationalize the stereoinduction.

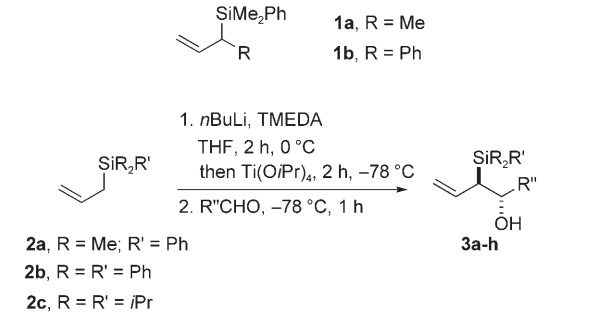
Results and Discussion

Synthesis of chiral allylsilane precursors: A series of simple allylsilanes possessing one or two stereogenic centers (bearing the silicon group) were prepared (Table 1). Racemic allylsilanes **1a**,**b** bearing a single stereogenic center were prepared through the intermediacy of a silylcuprate-mediated S_N2' displacement of the corresponding allyl chlorides (Scheme 2).[16] Allylsilanes **3a**–**h**, with two contiguous stereogenic centers, were prepared following the Yamamoto–Reetz allylation[17] procedure from allylsilanes **2a**–**c** and the corresponding aldehydes (Table 1). Good yields and high levels of *anti* stereoselectivity were generally observed using this strategy. This method is general and provided good results with most aldehydes that were tried, except glyoxal

Table 1. Synthesis of chiral β-hydroxy allylsilanes **3a**–**h** (Scheme 2).

	Product	R	R′	R″	Yield [%][a]	*anti*/*syn*[b]
1	**3a**	Me	Ph	Ph	66	>98:<2
2	**3b**	Me	Ph	*i*Pr	79	>98:<2
3	**3c**	Me	Ph	*t*Bu	69	>98:<2
4	**3d**	Me	Ph	CO_2Et	22	>98:<2
5	**3e**	Me	Ph	CH=CHMe (*E*)	68	>98:<2
6	**3f**	*i*Pr	*i*Pr	Ph	79	>98:<2
7	**3g**	Ph	Ph	Ph	63	>98:<2
8	**3h**	Ph	Ph	*i*Pr	68	>98:<2

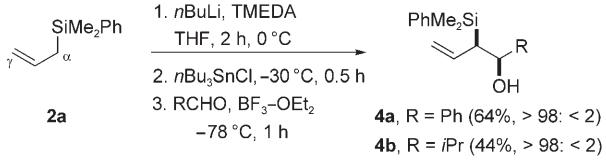
[a] Isolated yield. [b] Estimated from ^{1}H NMR analysis of the crude reaction mixture.



Scheme 2. Chiral allylsilanes **1a**,**b** and *anti*-β-hydroxy allylsilanes **3a**–**h**.

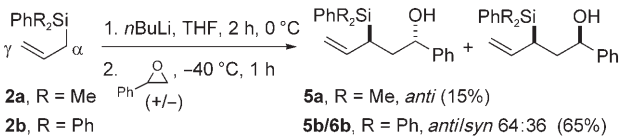
(entry 4) for which the resulting titanium alcoholate was found to be difficult to hydrolyze. The nature of the silicon moiety was also varied, with $PhMe_2Si$, Ph_3Si, and $(iPr)_3Si$ groups introduced following this approach.[18]

syn-Diastereomers of chiral allylsilanes were prepared in parallel, starting from allyltin intermediates (not shown).[19] Under Lewis acid conditions, allylsilanes **4a**,**b** were thus obtained in moderate to good yield, but with high levels of *syn*-stereocontrol (Scheme 3).



Scheme 3. Synthesis of *syn*-β-hydroxy allylsilanes **4a**,**b**.

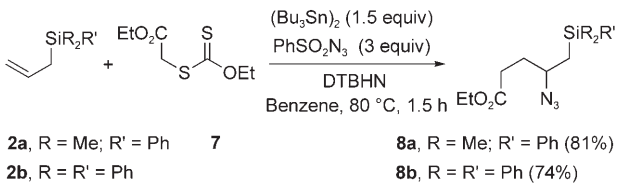
Finally, γ-hydroxyallylsilanes were prepared by reacting the lithium carbanion of allylsilanes **2a**,**b** with racemic phenyloxirane (Scheme 4).[20] While good yields of the desired and separable diastereomers **5b** and **6b** were obtained from **2b**, only the *anti* isomer **5a** could be isolated from the reaction mixture starting from **2a**. In this case, a large amount of the γ isomer was formed along with the desired α-*anti* **5a** and α-*syn* isomers.



Scheme 4. Synthesis of γ-allylsilanes **5a**,**b** and **6b**.

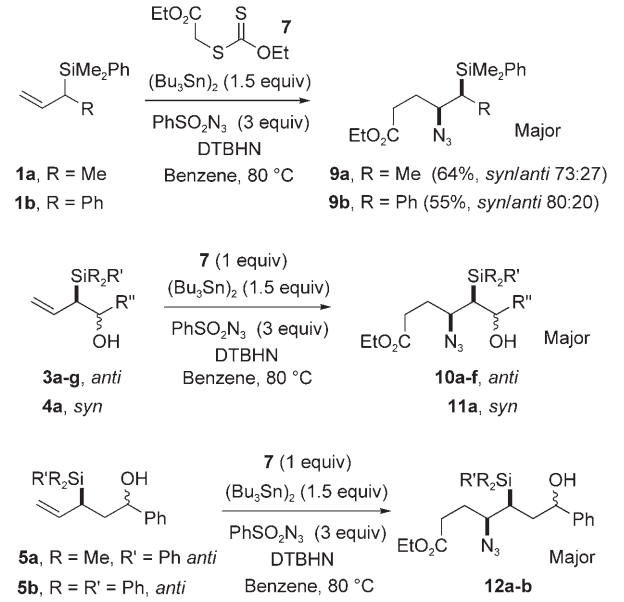
Carboazidation of achiral allylsilanes: Carboazidation was first carried out on simple allylsilanes **2a**,**b**, lacking a stereogenic center, in order to test the influence of the substituents on the silicon center on the course of the carboazidation. Xanthate **7** was used as a radical precursor,[21] and DTBHN (di-*tert*-butyl hyponitrite) as an initiator, and the reaction was carried out as previously reported.[9] Under

these conditions (1.5 h at 80 °C), **2a**,**b** provided the carboazidation products **8a**,**b** in excellent yields,[22] indicating that the nature of the silicon group has little effect on the rate of the radical process on simple allylsilanes (Scheme 5). This contrasts with observations by Hwu et al., who noticed substituent effects in the radical addition of ketones onto allylsilanes.[23] This reactivity is also very different from that of allylsilanes toward electrophiles under ionic conditions, for which **2b** is far less reactive than **2a**.[24]



Scheme 5. Carboazidation of achiral allylsilanes **2a**,**b**. Study on the effects of substituents at silicon.

Carboazidation of OH-free chiral β- and γ-hydroxyallylsilanes: With these results in hand, we then started our investigations on the carboazidation of chiral allylsilanes **1a**,**b**, **3a–c**, **3e–g**, **4a**, and **5a**,**b** (Scheme 6). Several trends emerge



Scheme 6. Carboazidation of OH-free chiral allylsilanes.

from the preliminary studies summarized in Table 2. Carboazidation of chiral allylsilanes led to moderate to good yields of the desired β-azidosilanes **9a**,**b**, **10a–f**, **11a**, and **12a**,**b** with *syn* selectivities. The moderate yields were generally ascribed to the tedious purification of the products, from excess sulfonyl azide. The diastereomer ratio was estimated from ^{1}H and ^{28}Si NMR studies after removal of tin residues through a short pad of silica, and the relative configuration of the major isomer was obtained by treating the

Table 2. Carboazidation of chiral allylsilanes **3a–h**, **4a**, and **5a**,**b**.

	Allyl-silane	Product	R	R′	R″	Yield [%][a]	*syn*/*anti*[b]
1	**3a**	**10a**	Me	Ph	Ph	71	63:37
2	**3g**	**10b**	Ph	Ph	Ph	30	90:10
3	**3f**	**10c**	*i*Pr	*i*Pr	Ph	34	>95:<5
4	**3b**	**10d**	Me	Ph	*i*Pr	56	>90:<10
5	**3c**	**10e**	Me	Ph	*t*Bu	45	>90:<10
6	**3e**	**10f**	Me	Ph	CH=CHMe	–	–
7	**4a**	**11a**	Me	Ph	Ph	47	73:27
8	**5a**	**12a**	Me	Ph	–	72	80:20
9	**5b**	**12b**	Ph	Ph	–	30	80:20

[a] Isolated yield. [b] Estimated from ^{1}H NMR and ^{28}Si NMR analysis of the crude reaction mixture.

isolated pure diastereomers with tetrabutyl ammonium fluoride (TBAF). Under these conditions, the *syn* and *anti*-β-azidosilanes led to the corresponding *Z*- and *E*-olefins, respectively, in high yield through an *anti*-stereospecific β-elimination.[25,26] The *syn* configuration of the major isomer was later confirmed through X-ray structure determination of a crystalline β-azidosilane (vide infra).

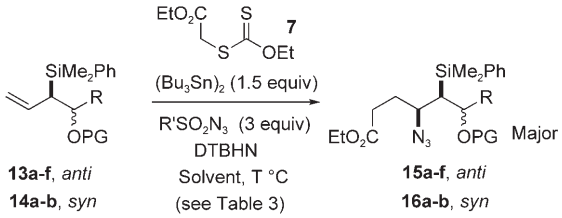
The influence on the 1,2-stereocontrol and of the nature of the substituents on the carbon backbone and the silicon center were studied, as well as the effect of the additive stereogenic centers located in the β- and γ-positions relative to the silicon group. Modest-to-high levels of *syn*-stereoselectivity were thus observed, with diastereocontrol increasing with the size of the R″ substituents (entries 1, 4, and 5). Similar observations were made by Porter et al. during their studies on the radical azidation of β-silyl Barton esters.[26]

The diastereocontrol also increased with the size of the silicon group, as shown by the good to excellent diastereomer ratio observed with $(i\text{Pr})_3\text{Si}$ and Ph_3Si groups, albeit with moderate yield (entries 2,3). It should also be noted that the Ph_3Si group always led to lower yields than other silicon groups, probably due to the decomposition of the azide product under our radical conditions. This contrasts with the results observed with the achiral allylsilane **2b** (Scheme 5). β-Fragmentation of the β-silyl radical intermediate was ruled out as no olefinic proton could be detected in the ^{1}H NMR spectrum of the crude reaction mixture. Aryl migration and homolytic aromatic substitution may also be envisioned, but are not supported by the isolation of the corresponding byproducts.

The stereocontrol appears to rely mainly on the nature of the substituents on the α-stereocenter bearing the silicon group (i.e., **1a**,**b**). Hence, the introduction of a second stereogenic center (as in **3a–g** and **4a**) did not greatly influence the level of stereocontrol (entries 1–7). The same conclusion may be drawn if the additional stereogenic center is more remote, that is, in the γ-position as in **5a**,**b** (entries 8,9). A slightly better diastereocontrol was observed with the *syn*-β-hydoxysilane **4a** than *anti*-**3a** (entries 1 and 7). However, this result should be treated with caution as the yield in this case is moderate and decomposition of the minor isomer can not be completely ruled out. Overall, we observed that β-benzylic alcohols (**3a**,**f**,**g**, **4a**) were quite sensitive to the

reaction conditions, although again no β-elimination products could be detected from the crude reaction mixture. In line with this observation, only decomposition was observed upon carboazidation of diene **3e** with an allylic alcohol moiety (entry 6).

Carboazidation of OH-protected chiral β- and γ-hydroxyallylsilanes: Although free OH groups are usually inert under radical conditions, the sometimes modest yields observed above, along with the reported failure[27] during carboazidation of olefins bearing a free hydroxyl group, led us to consider the carboazidation process onto OH-protected β-hydroxy allylsilanes (Scheme 7). As summarized in Table 3,



Scheme 7. Carboazidation of OH-protected chiral allylsilanes.

Table 3. Carboazidation of OH-protected chiral allylsilanes (Scheme 7).

	Allyl-silane	Product	R	PG	*T* [°C]	Yield [%][a]	*syn*/*anti*[b]
1	**13a**	**15a**	*i*Pr	Ac	80	67[c]	78:22
2	**13b**	**15b**	*i*Pr	$SiEt_3$	80	61[c]	50:50
3	**13a**	**15a**	*i*Pr	Ac	60	74[c]	77:23
4	**13a**	**15a**	*i*Pr	Ac	10–15[d]	44[e]	84:16
5	**13a**	**15a**	*i*Pr	Ac	−30[d]	48[e]	82:18
6	**13c**	**15c**	*t*Bu	Ac	60	72[e]	83:17
7	**13d**	**15d**	Ph	Ac	60	65[e]	>95:<5
8	**13e**	**15e**	CH=CHMe	Ac	60	–	–
9	**13f**	**15f**	CO_2Et	Ac	60	34[e]	88:12
10	**14a**	**16a**	Ph	Ac	60	78[e]	83:17
11	**14b**	**16b**	*i*Pr	Ac	80	67[e]	82:18
12	**13a**	**15a**	*i*Pr	Ac	60	74[e]	77:23
13	**13a**	**15a**	*i*Pr	Ac	60	50[f]	77:23
14	**13a**	**15a**	*i*Pr	Ac	60	64[g]	76:24

[a] Isolated yield. [b] Estimated from ^{1}H NMR analysis of the crude reaction mixture. [c] $PhSO_2N_3$ was used. [d] *hv*. [e] 3-$PyrSO_2N_3$ was used. [f] 2,4,6-$PhSO_2N_3$ (Trisyl) was used. [g] $EtSO_2N_3$ was used.

yields with acetate-protected allylsilanes were generally higher and more reproducible, indicating that in our case the OH group probably interferes with the radical process for reasons that are currently unknown. The diastereocontrol was in turn slightly lower (see Table 2, entry 4, and Table 3, entry 1). The acetate led to the best results in terms of both yield and diastereocontrol. In comparison, a triethylsilyl (TES) group, as in **13b**, led to the β-azidosilane **15b** (Entry 2) in reasonable yield, but with no stereocontrol. This may be attributed to the small size differentiation, on the allylic stereogenic center, between the large $PhMe_2Si$ group and the medium-sized substituent *i*PrCHOSiEt_3.

The influence of various parameters on the stereocontrol (nature of the substituents on the allylsilane framework and at silicon, additional stereogenic centers) was studied as above. Optimization of the carboazidation conditions, varying the temperature and the nature of the azide reagent, was also considered.

Decreasing the temperature from 80 to 60 °C led to a significant improvement of the yield of product, but with similar stereocontrol, indicating that β-azidosilanes are sensitive to thermal degradation (entries 1 and 3). The reaction was also carried out under irradiation at a lower temperature (entries 4,5). A slightly higher level of stereocontrol was obtained at the expense of the yields, with a large amount of xanthate **7** left unreacted even after 8 h of irradiation. As above for **3e**, the diene **13e** led mainly to decomposition (entry 8), and allylsilane **13f** provided the desired β-azidosilane **15f** (entry 9) with good selectivity but poor yield. *syn*-β-Hydroxy allylsilanes **14a**,**b** afforded all-*syn* azides **16a**,**b** in good yields and selectivities (entries 10,11), which compare well with those observed with *anti*-diastereomers, showing again the weak effect of the stereochemistry of the β-stereocenter on the stereochemical course of the carboazidation. As above, increasing the size of the R group improved the diastereocontrol (entries 3 and 6). The excellent diastereocontrol obtained reproducibly with benzyl acetate **13d** is misleading as a careful examination of ^{1}H and ^{28}Si NMR spectra of the crude reaction mixture led to the conclusion that a partial degradation of the minor diastereomer was likely to be the cause of the overestimation of the diastereomeric ratio. Pleasingly, β-silylazide **15d** crystallized, allowing the determination of its relative configuration through X-ray crystallography, thus confirming the *syn* configuration determined through chemical correlation[25] (Figure 1).

Optimization of the reaction conditions also led us to investigate the nature of the sulfonyl azide. Increasing the size of the aryl (or alkyl) sulfonyl group led to no improvement of the diastereocontrol (entry 13). The absence of a steric effect of the R′ sulfonyl group may be explained in the light of recent work by Masterson et al.[28] who demonstrated that the linear azide reacts with the carbon radical center,

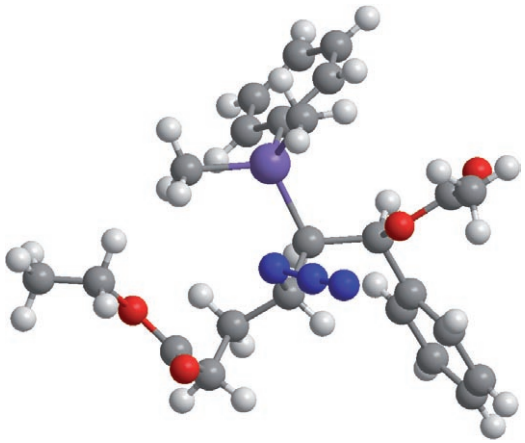
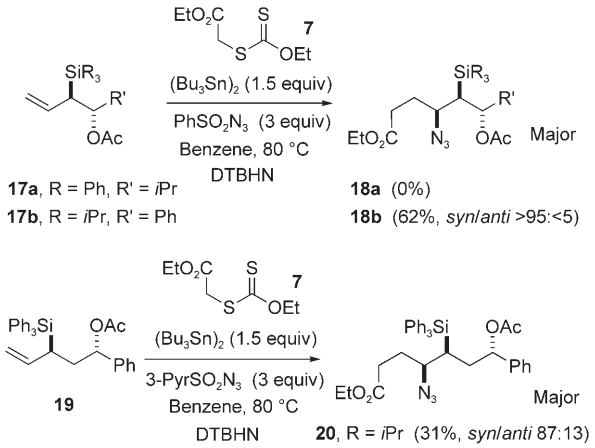


Figure 1. X-ray structure determination of β-azidosilane **15d**.

through its terminal nitrogen center, so that the R′ group is rather remote from the reacting center. In line with this, 3-pyridyl[9c] and ethylsulfonyl azides led to similar diastereocontrol, but with better yields than the trisyl azide[3] (entries 12 and 14). 3-Pyridylsulfonyl azide is, however, recommended when purification of the β-azidosilane is tedious, as the excess of azide may simply be removed through a mild acidic workup.

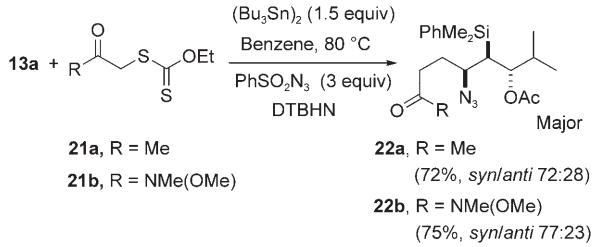
The nature of the substituents at silicon was again varied, with Ph_3Si leading invariably to lower yields (i.e., **19**, Scheme 8), and only decomposition products with β-silylacetate **17a**. In this case, we observed the formation of olefinic products probably resulting from the elimination of Ph_3SiN_3 or Ph_3SiOAc fragments. These byproducts could unfortunately not be isolated in pure form from the complex reaction mixture. Finally, triisopropylsilylallylsilane **17b** led to the corresponding β-azidosilane as a single stereoisomer, thus demonstrating that bulky silicon groups promote an optimum level of diastereocontrol. However, for the sake of simplicity, the $PhMe_2Si$ group was used in most of our studies, since it provides a reasonable level of diastereocontrol, is stable, easily available from commercial sources, and can be oxidized into the corresponding OH group[29] under mild conditions (vide infra).



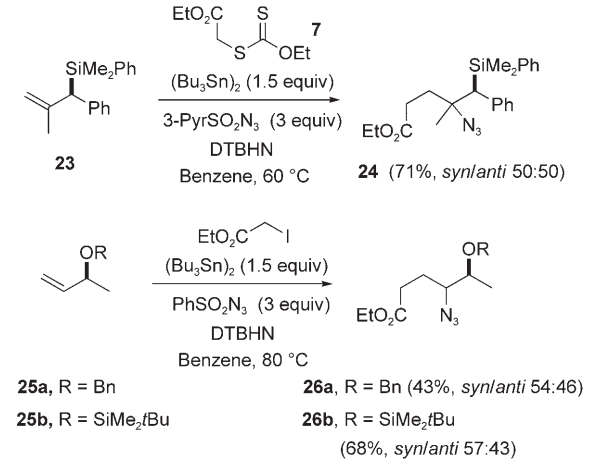
Scheme 8. Influence of the nature of the silicon group on the carboazidation.

Carboazidation with various xanthates and olefins: Interestingly, other xanthates may be added to our allylsilanes, allowing attractive further functionalization of the resulting β-azidosilanes. This is illustrated with the ketone **21a** and the Weinreb amide **21b**, both adding to allylsilane **13a** to afford the desired β-azido silanes **22a**,**b** in good yields and with reasonable selectivities (Scheme 9).

In contrast to the above results, we experienced some limitations with the carboazidation of chiral 2,2-disubstituted allylsilanes and allylic ethers (Scheme 10). Carboazidation of allylsilane **23** thus afforded, as expected, azide **24** in good yield, but without any selectivity. In parallel, it was anticipated, based on some precedent, that we could take advantage of the reversal of stereocontrol generally observed during reactions of allylsilanes and their allylic alcohol analogues with radical and ionic reagents.[11d,e,30] Carboazidation of chiral allylic ethers **25a**,**b** was thus tested, and led, surprisingly, under the above conditions, to the desired β-alkoxy azides **26a**,**b** in modest to good yield, but with very low stereocontrol, which contrasts with literature reports on closely related stereocontrolled radical processes.[31]

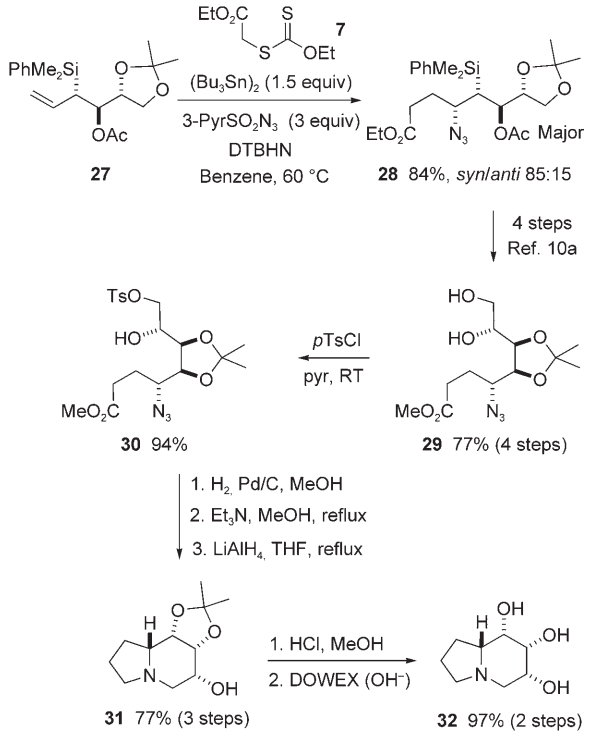


Scheme 9. Varying the nature of the xanthate fragment.

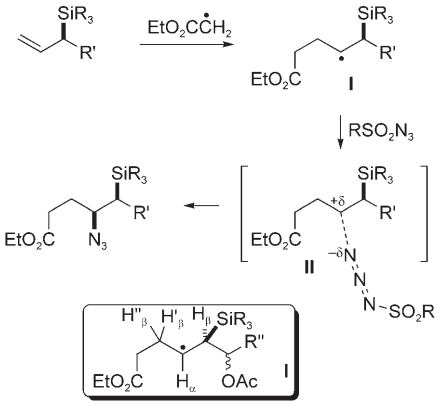


Scheme 10. Carboazidation of 2,2-disubstituted allylsilanes and allylic ethers.

Application of the carboazidation of chiral allylsilanes to the synthesis of an analogue of castanospermine: The utility of the carboazidation process applied to chiral allylsilanes has recently been illustrated with the total synthesis of hyacinthacine A1.[10a] This chemistry was also found practical for straightforward access to an analogue of indolizidine castanospermine, a potent glycosidase inhibitor (Scheme 11).[32] Carboazidation of optically pure chiral allylsilane **27**,[10a] under the optimized conditions described above, thus led to β-silylazide **28** in 85% yield and with good stereocontrol. The next four steps were similar to those developed for the synthesis of hyacinthacine A1.[10a] Thus, oxidation of the C–Si bond under Fleming buffered conditions,[29d,e] followed by saponification (MeOH, NH_3) of the resulting acetates led to a diol which was protected as a bis-acetonide. Regioselective deprotection of the latter gave the diol **29**, in which the primary alcohol function was transformed into the correspond-



Scheme 11. Synthesis of an analogue of castanospermine.



Scheme 12. Allylsilane carboazidation pathway.

ing tosylate **30**. Pd/C reduction of the azido group of **30** then led to the desired amine, which cyclized spontaneously to provide a lactam that was reduced with $LiAlH_4$ into the bicyclic intermediate **31**. Deprotection of the acetonide and treatment of the resulting chlorhydrate with basic Dowex led to 1-deoxy-6,8-diepicastanospermine **32**,[32a] a potent inhibitor of α-L-fucosidase,[32b] in 45% overall yield and in ten steps from allylsilane **27**.

Carboazidation of chiral allylsilanes—EPR and quantum chemical studies—transition-state models: The course of the carboazidation process under radical conditions is believed to follow the pathway depicted in Scheme 12,[8a,b] with the C–N bond formation as the stereochemistry-determining step. It was reasoned that during the reaction of radical **I**, which has nucleophilic character, with electrophilic sulfonyl azide, the transition state (**II**) should resemble the starting β-silyl radical **I** in the ground state.[33] Spectroscopic measurement and recent ab initio calculations have shown that the minimum energy conformations of acyclic β-silyl radicals such as **I** exhibit a σ_{C-Si} bond eclipsing the radical SOMO, the maximum energy having a σ_{C-Si} bond orthogonal to the radical orbital.[34]

EPR experiments were carried out to provide additional information relative to the conformation of radical species **I** in the ground state. Radical **I** was generated inside the EPR cavity, at room temperature, by photolytic cleavage of $(Bu_3Sn)_2$ in the presence of xanthate **7** and allylsilanes (**13a**,**d**, **14a**, and **17b**) in benzene. All the spectra were straightforwardly interpreted on the basis of the coupling of the unpaired electron with the α- and three unequivalent β-protons; the spectroscopic parameters are reported in Table 4.

Inspection of Table 4 shows that the value of $a(H_\alpha)$ is essentially unaffected by changing the nature of SiR_3 and R″ substituents in **I** (Scheme 12). Its value depends on the spin density at the α-carbon, which is expected to be close to 1 (for comparison, in the isopropyl radical, $a(H_\alpha)$ is 22.22 Gauss). In contrast, the value of $a(H_\beta)$ shows a significant dependence on the nature of substrate and a good correlation is observed between this value and the carboazidation ratio. According to the Heller–McConnel equation,[35] the value of $a(H_\beta)$ depends on the time-average value of $\cos^2\theta$, in which θ is the dihedral angle between a β-C–H bond and the axis of the p orbital on C_α. The low value of $a(H_\beta)$ indicates that $\langle\cos^2\theta\rangle$ is close to zero. On this basis, two different conformations **I-A** and **I-B** could be drawn, with eclipsing interactions between the σ_{C-Si} bond and the radical SOMO (Figure 2). These conformations are similar to those obtained through other spectroscopic methods[36] and in good agreement with our recent calculations on radical cyclizations.[34]

To further support the putative conformations of the β-silyl radicals and explain the stereochemistry of the process, we carried out a quantum chemical study on the radical azidation step. The reaction of **1a** with phenylsulfonyl azide to give **9a** was chosen as a model system (see Scheme 6). To reduce the number of conformational possibilities for the

Table 4. EPR spectral parameters [in Gauss] for radical **I** (Scheme 12) deriving from allylsilanes **13a**, **13d**, **14a**, **17b**.

	SiR_3	Allylsilane	R″	$a(H_\alpha)$	$a(H_\beta)$	$a(H'_\beta)$	$a(H''_\beta)$	*syn*/*anti*
1	$SiMe_2Ph$	**13a**	*i*Pr	20.64	8.66	25.82	25.96	78:22
2	$SiMe_2Ph$	**13d**	Ph	20.70	7.65	23.05	24.75	>95:5
3	$SiMe_2Ph$	**14a**	Ph	20.71	8.00	23.34	24.61	83:17
4	$Si(iPr)_3$	**17b**	Ph	20.82	5.75	24.63	25.58	>95:5

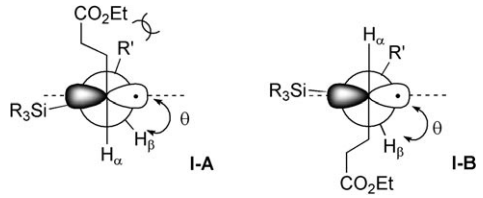


Figure 2. Conformations of the β-silyl radical obtained through EPR measurements.

ethyl group and thus lower the computational costs, we replaced the CO_2Et group by a simpler CO_2Me group, assuming that the alkyl chain on the terminal ester has no direct influence on the course of the carboazidation process. B3LYP/6–31G(d) calculations performed using the reaction temperature of 80°C (see Computational Methods) led to two stable radical conformers that confirm the putative schemes **I-A** and **I-B** in Figure 2. The radical **I-B** is 2.66 kcal mol^{-1} more stable than **I-A**, due to the weaker gauche interactions in the former, while the interconversion barrier from **I-A** to **I-B** amounts to 0.55 kcal mol^{-1}. Moreover, as suspected from EPR experiments, both radicals present an almost coplanar arrangement between the σ_{C-Si} bond and the radical SOMO, **I-B** presenting an angle of 86° between H_β and the silicon group with no pyramidalization of the carbon radical center. **I-A** presents larger deformations with an angle of 78° between H_β and $SiMe_2Ph$ and a pyramidalization of 5°, which probably account for its higher energetic level. Concerning the azide addition, we considered only an attack at the terminal nitrogen center of the azide.[28] $PhSO_2N_3$ may then approach radicals **I** *syn* or *anti* relative to the $SiMe_2Ph$ group. The *syn* approach led to much higher energetic transition states (TS) with major rearrangement of the radicals in a conformation in which the silicon group is orthogonal to the radical orbital. Thus, only transition states resulting from an *anti* approach relative to silicon were considered, the azide moiety preferring to avoid strong steric interactions with the silicon group. Two diastereomeric transition states **II-A** and **II-B**, resembling conformations **I-A** and **I-B**, thus emerged, which led to *syn* and *anti* β-azidosilanes respectively (Figure 3).

A total of eight different transition states (TS) were then considered (Figure 4), four TS named **IIA-*i*** leading to the *syn* product and four TS named **IIB-*i*** leading to the *anti* product. The structures **IIA-*i*** (**IIB-*i***) with $i=1$ and $i=2$ (or with $i=3$ and $i=4$) differ from the others by a rotation of about 120° of the sulfonyl group. The activation barriers and the relative Gibbs free energies (ΔG_i) of the eight TS, as calculated at the B3LYP and ROMP2//B3LYP levels, are reported in Table 5. The lower TS arises from the less stable radical **I-A**, and the activation barriers (between 15–19 kcal mol^{-1}), being one order of magnitude higher than the interconversion barrier between **I-A** and **I-B**, mean that the reaction should follow a Curtin–Hammett regime, in which product ratios are only controlled by the ΔG_i values. The relative populations were thus estimated by performing Maxwell–Boltzmann statistics using the relative free energies of the eight possible TS.[33b] Populations of products connected to **IIA-*i*** and **IIB-*i*** were eventually summed to

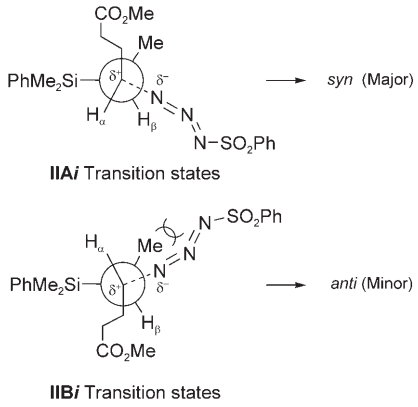


Figure 3. Transition-state models for the carboazidation of chiral allylsilanes.

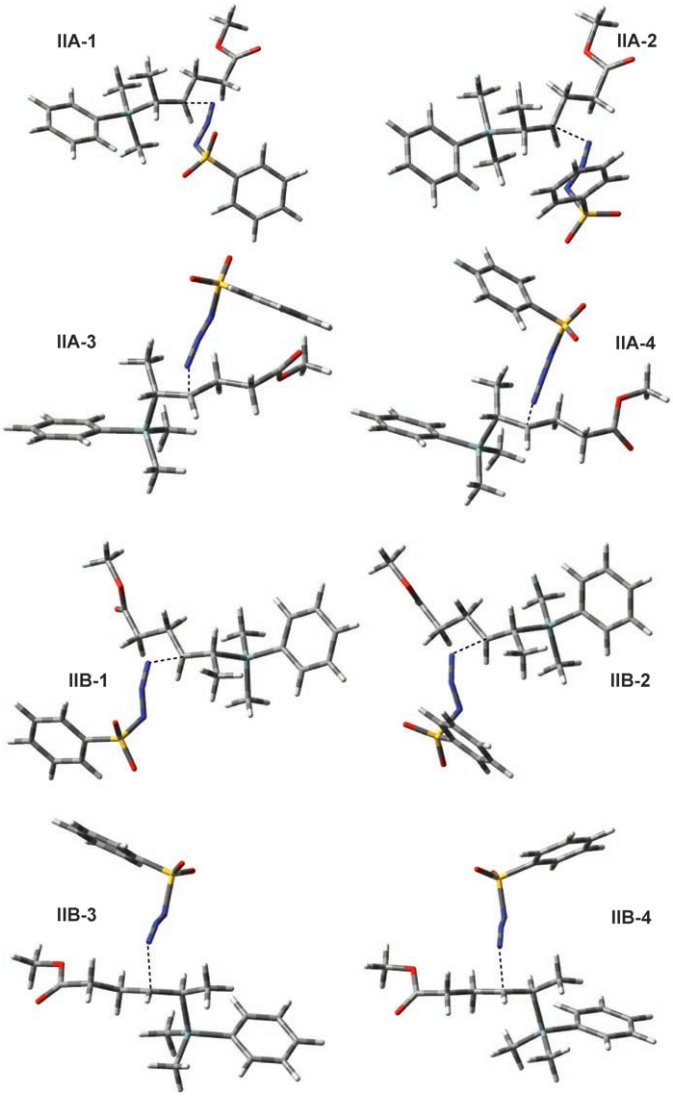


Figure 4. Representation of the eight transition structures leading to **9a**.

Table 5. Relative Gibbs free energies [ΔG, kcal mol^{-1}] of the transition structures **IIA-*i*** and **IIB-*i*** and relative product populations [Rel. pop. %], calculated at 353 K.

	B3LYP/6–31G(d)		ROMP2/6–31G(d)// B3LYP/6–31G(d)	
	ΔG	Rel. pop.	ΔG	Rel. pop.
TS *syn*				
IIA-1	0.00	60	0.00	52
IIA-2	0.83	18	0.73	18
IIA-3	2.41	2	1.16	10
IIA-4	2.46	2	2.60	1
TS *anti*				
IIB-1	1.75	5	2.19	2
IIB-2	2.07	3	2.44	1
IIB-3	2.42	2	1.87	4
IIB-4	1.46	8	1.05	12
syn/*anti* ratio	82:18		81:19	

obtain the final populations of the *syn* and *anti* β-azidosilanes, respectively (last line of Table 5). The relative energies indicate that the major product is formed through the **IIA-*i*** structure, in which the sulfonyl azide approaches on the H_β side, thus avoiding steric interactions with the methyl group (as in **IIB-*i***). It is worth noting that, as observed experimentally, increasing the size of this medium-sized group (*i*Pr, *t*Bu) led to better diastereomeric excess.

The pyramidalization of the carbon radical center amounts to 25° and the length of the incipient bond is equal to 2.30 Å, consistent with the picture of an early transition state. Besides, the dihedral angle between the σ_{C-Si} bond and the incipient C–N bond is −157.8°. All the other transition states present similar features, confirming the stabilizing effect of an eclipsed conformation between the σ_{C-Si} bond and the SOMO of the radical. Although the relative ordering of the eight transition states depends on the level of theory used to determine the electronic wave function, the B3LYP and ROMP2//B3LYP levels predict very similar *syn*/*anti* selectivities that reproduce fairly well the experimental ratio (73:27, see Scheme 6).

Interestingly, this transition-state model is reminiscent of the Felkin–Anh model[37] proposed for nucleophilic additions to chiral carbonyl compounds. Similar to Felkin–Anh model, the more favorable transition state **II-A**, that is, the approach of the reagent *anti* with respect to the largest substituent (SiR_3) on the side of the smallest group (H), occurs through the highest energy conformation of the starting radical (i.e., **I-A**), under a Curtin–Hammett regime.[37c] The partial positive charge developing at the carbon radical center at the transition state is also stabilized further by the electron-rich σ_{C-Si} bond through hyperconjugation (β-silicon effect).[38] A related model had been proposed earlier by Giese and Curran[39] to rationalize the 1,2-stereoinduction occurring in reactions of acyclic radicals. At the transition state, the largest groups are orthogonal to each other with a pronounced pyramidalization (≈25°), a key feature to explain the preference for the approach of sulfonyl azide following TS-**IIA** instead of that illustrated by TS-**IIB**.

Conclusion

Carboazidation of chiral allylsilanes provides the corresponding β-azidosilanes with 1,2-stereocontrol ranging from 7:3 to >95:5. This process is particularly powerful as it provides straightforward access to acyclic systems with several contiguous stereogenic centers, the stereochemistry of which can be controlled efficiently. EPR experiments and ab initio calculations have also been performed, which led to transition state models allowing the prediction of the stereochemical course of the carboazidation reaction. These investigations offer valuable information and better insight into the factors at the origin of the 1,2-stereocontrol in these systems. They also give information on the behavior of acyclic radical systems such as **I** (Scheme 12) that should be relevant for other transformations as well as carboazidations.[40]

Experimental Section

Computational methods: Geometry optimizations were performed in vacuum using the density functional theory (DFT) with the three-parameter hybrid functional B3LYP and the 6–31G(d) basis set. Thermal corrections were calculated from the unscaled B3LYP/6–31G(d) harmonic vibrational frequencies using experimental temperature and pressure conditions. Every transition structure was characterized by a single imaginary frequency in the diagonalized mass-weighted Hessian matrix associated with the normal mode corresponding to the formation of the C–N bond. The largest eigenvalue of the total spin operator was equal to 0.7596, which suggests no error due to spin contamination. The electronic energies were further refined by using the restricted open shell second-order Møller-Plesset (ROMP2) level of theory with the same basis set. This procedure is referred to as ROMP2/6–31G(d)//B3LYP/6–31G(d) and abbreviated as ROMP2//B3LYP. All calculations were performed using Gaussian03.[41] The geometries of all the TS are provided as Supporting Information.

EPR spectroscopy: EPR spectra were obtained using a Bruker ESP300 spectrometer equipped with an NMR gaussmeter for field calibration and a Hewlett Packard 5350B microwave frequency counter for the determination of the *g* factors. Photolysis was carried out by focusing the unfiltered light from a 500 W high pressure mercury lamp on the EPR cavity. The instrument settings were as follows: microwave power 5.0 mW, modulation amplitude 0.05 mT, modulation frequency 100 kHz, scan time 180 s.

General remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brüker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75.5 MHz) or a Brüker AC-250 FT (^{1}H: 250 MHz, ^{13}C: 62.9 MHz), with $CDCl_3$ as internal reference. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and hertz, respectively. IR spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrophotometer as neat films on NaCl windows or as KBr pellets. HRMS were recorded on a Varian MAT 311 apparatus (for EI) or a Micromass ZABSpec TOF apparatus (for ESI). Melting points were determined by using a Büchi Totolli apparatus and are uncorrected. Merck silica gel (0.043–0.063 mm) was used for flash chromatography. All reactions were carried out under a nitrogen atmosphere unless specified otherwise. CH_2Cl_2 was distilled over CaH_2. Benzene and THF were distilled from sodium/benzophenone prior to use. All reagent-grade chemicals were obtained from commercial suppliers and were used as received, unless otherwise stated. Spectroscopic data for the starting allylsilanes is available in the Supporting Information.

Preparation of β-hydroxyallylsilanes (general procedure A): 1.6 M solution of *n*-butyllithium in hexane (1.1 equiv) was added to a solution of allylsilane (1 equiv) in dry THF, followed by TMEDA (1.5 equiv) at 0 °C. The resulting pale yellow solution was stirred at 0 °C for 2 h, turning red-

dish brown, then cooled to −78 °C. Titanium isopropoxide (1 equiv) was added at −78 °C and the mixture was stirred for 1 h at this temperature. Finally, a solution of aldehyde (1 equiv) in dry THF was added at −78 °C, and the reaction mixture was then stirred for 75 min. The reaction was quenched with an aqueous solution of NH_4Cl at −78 °C. The organic layer was decanted and the aqueous layer extracted with diethyl ether. The combined organic layers were then washed with H_2O, dried over $MgSO_4$, and the solvents were removed under reduced pressure. The residue was purified by chromatography.

Acetylation of β- and γ-hydroxysilanes (general procedure B): Acetic anhydride (2 equiv), NEt_3 (2 equiv), and a catalytic amount of 4-DMAP (0.1 equiv) were added to a stirred solution of alcohol (1 equiv) in dry CH_2Cl_2 (6.5 mL mmol^{-1}). The resulting mixture was then stirred at room temperature (RT) under nitrogen for 18 h and was treated with saturated aqueous $NaHCO_3$ solution. The organic layer was decanted and the aqueous layer extracted with diethyl ether. The combined extracts were washed with brine and dried over $MgSO_4$, and the solvents were concentrated in vacuo. The crude product was purified by chromatography through silica.

Radical carboazidation (general procedure C): DTBHN (3 mol% or 18 mol%) was added every 90 min to a solution of ethyl 2-iodoacetate or xanthate (1 or 2 equiv), olefin (2 or 1 equiv), arylsulfonylazide (3 equiv) and $(Bu_3Sn)_2$ (1.5 equiv) in dry benzene (2 mL mmol^{-1}) at reflux (80 or 60 °C) under N_2. The reaction was monitored by TLC. Upon completion, the solvent was removed under reduced pressure and the crude product was filtered through silica gel (pentane, then pentane/EtOAc).

4-Azido-5-(dimethylphenylsilanyl)pentanoic acid ethyl ester (8a): Prepared according to general procedure C from ethyl ester **7** (86.8 mg, 0.42 mmol), dimethylphenylallylsilane (136.2 mg, 0.77 mmol), benzenesulfonylazide (220.3 mg, 1.20 mmol), $(Bu_3Sn)_2$ (0.29 mL, 0.57 mmol), and DTBHN (12 mg, 0.07 mmol) in dry benzene (0.8 mL). The crude product was purified by chromatography (pentane/EtOAc 95:5) to afford a yellow oil (103.9 mg, 81%). IR (neat): ν_{max} = 3069–2958, 2102, 1728, 1252, 1110 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.56–7.30 (m, 5H), 4.11 (q, J = 7.3 Hz, 2H), 3.38 (m, 1H), 2.37 (t, J = 7.0 Hz, 2H), 1.93–1.63 (m, 2H), 1.24 (t, J = 7.0 Hz, 3H), 1.21 (dd, J = 14.3, 7.3 Hz, 1H), 1.11 (dd, J = 14.6, 7.0 Hz, 1H), 0.39 (s, 3H), 0.37 ppm (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 172.8, 137.9, 133.4, 129.2, 127.9, 60.5, 59.5, 32.2, 30.8, 21.8, 14.1 ppm; MS (LSIMS): m/z (%): 328 (12) $[M+Na]^+$, 263 (100) $[M-N_3]^+$; HRMS $[M+Na]^+$ $C_{15}H_{23}N_3O_2SiNa$ calcd: 328.145911; found: 328.145725.

4-Azido-5-triphenylsilanylpentanoic acid ethyl ester (8b): Prepared according to general procedure C from ethyl ester **7** (86.7 mg, 0.42 mmol), triphenylallylsilane (233.4 mg, 0.78 mmol), benzenesulfonylazide (230.3 mg, 1.26 mmol), $(Bu_3Sn)_2$ (0.29 mL, 0.57 mmol), and DTBHN (12 mg, 0.07 mmol) in dry benzene (0.8 mL). The crude was purified by chromatography (pentane/EtOAc : 95/5) to afford a yellow oil (133.5 mg, 74%). IR (neat): ν_{max} = 3071–2910, 2101, 1728, 1110 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.58–7.30 (m, 15H), 4.07 (q, J = 7.3 Hz, 2H), 3.51 (m, 1H), 2.33 (m, 2H), 1.90–1.75 (m, 3H), 1.68 (dd, J = 14.9, 6.6 Hz, 1H), 1.20 ppm (t, J = 7.3 Hz, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 172.7, 135.6, 133.9, 129.7, 128.0, 60.5, 59.4, 32.6, 31.0, 19.6, 14.1 ppm; MS (LSIMS): m/z (%): 452 (12) $[M+Na]^+$, 387 (31) $[M-N_3]^+$, 259 (100) $[Ph_3Si]$; HRMS $[M+Na]^+$ $C_{25}H_{27}N_3O_2SiNa$ calcd: 452.175932; found: 452.177025.

4-Azido-5-(dimethyl-phenyl-silanyl)-hexanoic acid ethyl ester (9a): Prepared according to general procedure C from ethyl ester **7** (91.5 mg, 0.44 mmol), **1a** (334 mg, 0.88 mmol), benzenesulfonylazide (241 mg, 1.32 mmol), $(Bu_3Sn)_2$ (0.33 mL, 0.65 mmol), and DTBHN (13 mg, 0.06 mmol) in dry benzene (1.5 mL). The crude was purified by chromatography (pentane/EtOAc : 98/2) to afford the two diastereomers (*syn*/*anti* 73:27) as a colorless oil (90.3 mg, 64%). IR (neat): ν_{max} = 3069–2874, 2097, 1734, 1251, 1112, 702 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$), major + minor: δ = 7.60–7.30 (m, 10H), 4.11 (q, J = 7.0 Hz, 2H), 4.10 (q, J = 7.0 Hz, 2H), 3.45 (m, 1H), 3.35 (m, 1H), 2.41–2.26 (m, 4H), 1.80–1.60 (m, 4H), 1.43–1.35 (m, 2H), 1.25 (t, J = 7.0 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H), 1.02 (d, J = 7.3 Hz, 6H), 0.38 (s, 6H), 0.34 ppm (s, 6H); ^{13}C NMR (63 MHz, $CDCl_3$), major + minor: δ = 172.9, 137.4, 133.8, 129.1, 127.8, 65.4, 60.5, 31.2, 28.6, 27.4, 25.5, 25.2, 14.1, 10.4, 9.6, −3.8, −3.9, −4.4 ppm; MS (ESI): m/z (%) : 342 (100) $[M+Na]^+$, 277 (74) $[M-N_3]^+$, 135 (80) $[PhMe_2Si]$;. HRMS $[M+Na]^+$ $C_{16}H_{25}N_3O_2SiNa$ calcd: 342.1613; found: 342.1613.

4-Azido-5-(dimethylphenylsilanyl)-5-phenylpentanoic acid ethyl ester (9b): Prepared according to general procedure C from ethyl ester **7** (70.2 mg, 0.34 mmol), **1b** (161 mg, 0.64 mmol), benzenesulfonylazide (199 mg, 1.09 mmol), $(Bu_3Sn)_2$ (0.25 mL, 0.49 mmol), and DTBHN (10 mg, 0.06 mmol) in dry benzene (1 mL). The crude was purified by chromatography (EP/EtOAc : 98/2) to afford an inseparable mixture of the two diastereomers (*syn*/*anti* 80:20) as a colorless oil (74.4 mg, corrected yield 55%). IR (neat): ν_{max} = 3069–2958, 2099, 1733, 1250, 1112, 702 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$), major + minor: δ = 7.50–7.00 (m, 20H), 4.08 (q, J = 7.0 Hz, 2H), 4.06 (q, J = 7.0 Hz, 2H), 3.77 (ddd, J = 8.5, 7.3, 7.0 Hz, 1H), 3.61 (m, 1H), 2.47 (d, J = 7.3 Hz, 1H), 2.42 (d, J = 10.7 Hz, 1H), 2.30 (t, J = 7.6 Hz, 2H), 2.29 (t, J = 7.0 Hz, 2H), 1.93–1.62 (m, 4H), 1.21 (t, J = 7.0 Hz, 3H), 1.20 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR (63 MHz, $CDCl_3$), major + minor: δ = 172.6, 139.2, 137.2, 133.9, 129.3, 129.1, 128.3, 127.9, 126.7, 64.0, 60.5, 42.5, 42.0, 30.9, 30.6, 29.5, 29.1, 14.1, 13.7, −2.4, −2.6, −3.9, −3.9, −4.6 ppm; MS (ESI): m/z (%): 404 (8) $[M+Na]^+$, 339 (100) $[M-N_3]^+$; HRMS $[M+Na]^+$ $C_{21}H_{27}N_3O_2SiNa$ calcd: 404.1770; found: 404.1748.

4-Azido-6-hydroxy-6-phenyl-5-triisopropylsilanylhexanoic acid ethyl ester (10c): Prepared according to general procedure C from ethyl ester **7** (221.5 mg, 1.06 mmol), **3f** (609 mg, 2 mmol), benzenesulfonylazide (549 mg, 3 mmol), $(Bu_3Sn)_2$ (0.76 mL, 1.5 mmol), and DTBHN (30 mg, 0.18 mmol) in dry benzene (2 mL). The crude was purified by chromatography (pentane/EtOAc : 95/5) to afford a yellow oil (*syn*/*anti* > 95:5, 192.2 mg, yield 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 5H), 5.21 (m, 1H), 4.02 (q, J = 7.1 Hz, 2H), 3.69 (m, 1H$_3$), 2.39 (d, J = 4.5 Hz, 1H), 2.21–2.11 (m, 2H), 1.95–1.81 (m, 1H), 1.79 (m, 1H), 1.70–1.51 (m, 1H), 1.18 ppm (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5, 145.1, 128.5, 128.4, 125.2, 72.4, 62.0, 60.4, 37.8, 31.8, 31.3, 19.4, 19.3, 14.1, 11.7 ppm; MS (ESI): m/z (%): 456 (16) [+Na]$^+$, 391 (80) $[M-N_3]^+$, 347 (100); HRMS $[M+Na]^+$ $C_{23}H_{39}N_3O_3SiNa$ calcd: 456.265841; found: 456.265502.

4-Azido-5-(dimethylphenylsilanyl)-6-hydroxy-7,7-dimethyloctanoic acid ethyl ester (10e): Prepared according to general procedure C from ethyl ester **7** (208 mg, 1 mmol), allylsilane **3c** (524 mg, 2 mmol), benzenesulfonylazide (549 mg, 3 mmol), $(Bu_3Sn)_2$ (0.76 mL, 1.5 mmol), and DTBHN (30 mg, 0.18 mmol) in dry benzene (2 mL). The crude was purified by chromatography (pentane/EtOAc 95:5) to afford a colorless oil as an inseparable mixture of azidosilane and $PhSO_2N_3$ (*syn*/*anti* > 90:10, 360.6 mg, estimated yield 45%). IR (neat): ν_{max} = 3520, 3069–2871, 2097, 1732, 1252, 1112 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.61–7.52 (m, 2H), 7.39–7.31 (m, 3H), 4.17 (q, J = 7.3 Hz, 2H), 4.03 (m, 1H), 3.49 (d, J = 4 Hz, 1H), 2.52–2.27 (m, 2H), 1.86–1.63 (m, 2H), 1.56 (d, J = 4 Hz, 1H), 1.38 (m, 1H), 1.29 (t, J = 7.3 Hz, 3H), 0.73 (s, 9H), 0.47 (s, 3H), 0.41 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.9, 138.5, 134.3, 129.0, 127.8, 75.9, 62.4, 60.4, 37.1, 35.3, 32.2, 32.1, 26.0, 14.2, −1.8, −3.3 ppm; MS (LSIMS): m/z (%): 414 (48) $[M+Na]^+$, 364 (69), 349 (100) $[M+N_3]^+$; HRMS $[M+Na]^+$ $C_{20}H_{33}N_3O_3SiNa$ calcd: 414.218890; found: 414.218667.

Ethyl 4-azido-6-hydroxy-5-(dimethylphenylsilyl)-6-phenylhexanoate (11a): Prepared according to general procedure C from ethyl ester **7** (110 mg, 0.53 mmol), allylsilane **4a** (303.7 mg, 1.06 mmol), benzenesulfonylazide (288 mg, 1.59 mmol), $(Bu_3Sn)_2$ (0.40 mL, 0.79 mmol), and DTBHN (15 mg, 0.09 mmol) in dry benzene (1 mL). The crude was purified by chromatography (pentane/EtOAc 9:1) to afford a colorless oil (*syn*/*anti* 73:27, 102.1 mg, 47%). IR (neat): ν_{max} = 3500, 3069–2854, 2098, 1732, 1251, 1111 cm^{-1}. : ^{1}H NMR (250 MHz, $CDCl_3$), major diastereomer: δ = 7.61–7.19 (m, 10H), 4.91 (dd, J = 8.2, 3.7 Hz, 1H), 4.04 (q, J = 7.0 Hz, 2H), 3.36 (m, 1H), 2.29–2.07 (m, 3H), 1.93–1.66 (m, 2H), 1.19 (t, J = 7 Hz, 3H), 0.50 (s, 3H), 0.42 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6, 144.6, 139.1, 134.3, 128.9, 128.6, 127.7, 126.3, 74.9, 64.4, 60.4, 42.1, 31.7, 29.3, 14.1, −0.7, −1.0 ppm.

6-Acetoxy-4-azido-5-(dimethylphenylsilanyl)-7-methyloctanoic acid ethyl ester (15a): Prepared according to general procedure C from ethyl ester **7** (50 mg, 0.24 mmol), allylsilane **13a** (139.4 mg, 0.48 mmol), 3-pyridylsul-

fonylazide (132 mg, 0.72 mmol), $(Bu_3Sn)_2$ (0.18 mL, 0.36 mmol), and DTBHN (9 mg, 0.05 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (hexane/EtOAc 95:5) to afford a yellow oil (*syn*/*anti* 77:23, 75 mg, 74%). IR (neat): ν_{max} = 3070–2965, 2106, 1732, 1427, 1372, 1235, 1112, 837, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), major diastereomer: δ = 7.58–7.51 (m, 2H), 7.38–7.32 (m, 3H), 4.93 (dd, J = 8.1, 2.1 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.89 (m, 1H), 2.38 (m, 2H), 2.00 (s, 3H), 1.84 (m, 1H), 1.68 (m, 2H), 1.45 (dd, J = 2.0, 1.4 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.77 (d, J = 7.0 Hz, 3H), 0.74 (d, J = 7 Hz, 3H), 0.41 (s, 3H), 0.40 ppm (s, 3H); minor diastereomer: δ = 7.58–7.48 (m, 2H), 7.40–7.32 (m, 3H), 5.03 (dd, J = 6.7, 5.2 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.75 (m, 1H), 2.36 (m, 2H), 2.04 (s, 3H), 1.94 (m, 1H), 1.69 (m, 2H), 1.43 (m, 1H), 1.25 (t, J = 7.2 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H), 0.71 (d, J = 6.6 Hz, 3H), 0.43 (s, 3H), 0.42 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), major diastereomer: δ = 172.8, 170.7, 137.7, 134.2, 129.1, 127.7, 76.8, 63.0, 60.5, 36.5, 32.5, 32.0, 31.7, 21.6, 19.4, 18.5, 14.2, −2.1, −3.1 ppm; minor diastereomer : δ?172.7, 170.5, 137.8, 133.7, 129.2, 127.9, 77.0, 62.8, 60.4, 33.7, 32.2, 31.7, 30.3, 21.1, 19.9, 17.5, −2.3, −2.4 ppm; MS (ESI): m/z: 442 (50) $[M+Na]^+$; HRMS $[M+Na]^+$ $C_{21}H_{33}N_3O_4SiNa$ calcd: 442.2138; found: 442.2137.

4-Azido-5-(dimethylphenylsilanyl)-7-methyl-6-triethylsilanyloxyoctanoic acid ethyl ester (15b): Prepared according to general procedure C from ethoxythiocarbonylsulfanyl-acetic acid ethyl ester **7** (59 mg, 0.283 mmol), allylsilane **13b** (205 mg, 0.566 mmol), benzenesulfonylazide (161 mg, 0.849 mmol), $(Bu_3Sn)_2$ (0.21 mL, 0.424 mmol) and DTBHN (9 mg, 0.05 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (hexane/EtOAc : 98/2) to afford a yellow oil (50/50, 75 mg, 61%). IR (neat) ν_{max} = 2857, 2099, 1738, 1250, 1111 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) two diastereomers: δ = 7.54–7.49 (m, 4H), 7.39–7.30 (m, 6H), 4.17–4.04 (m, 4H), 3.98 (m, 1H), 3.87 (m, 1H), 3.85–3.79 (m, 2H), 2.48–2.23 (m, 2H), 2.21–2.00 (m, 2H), 1.92-.159 (m, 4H), 1.61-.154 (m, 2H), 1.45–1.31 (m, 2H), 1.29–1.23 (m, 6H), 1.01–0.95 (m, 18H), 0.88 (d, J = 6.8 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H), 0.68–0.59 (m, 18H), 0.46 (s, 3H), 0.44 (s, 3H), 0.43–0.41 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) two diastereomers: δ = 172.8, 172.8, 139.2, 139.1, 134.1, 133.7, 128.9, 128.8, 127.8, 127.6, 76.3, 75.1, 63.5, 63.0, 60.4, 60.3, 35.8, 35.7, 35.2, 34.8, 32.1, 32.1, 32.0, 30.5, 19.5, 17.7, 17.6, 17.6, 14.2, 7.1, 5.6, 5.6, −0.9, −1.5, −1.6, −2.7 ppm; MS (ESI): m/z (%): 514 (100) $[M+Na]^+$, 471 (40); HRMS $[M+Na]^+$ $C_{25}H_{45}N_3O_3Si_2Na$ calcd: 514.2897; found: 514.2892.

Ethyl 6-acetoxy-4-azido-7,7-dimethyl-5-(dimethylphenylsilyl)octanoate (15c): Prepared according to general procedure C from ethyl ester **7** (144 mg, 0.69 mmol), allylsilane **13c** (425 mg, 1.4 mmol), 3-pyridylsulfonylazide (386 mg, 2.1 mmol), $(Bu_3Sn)_2$ (0.53 mL, 1.05 mmol), and DTBHN (22 mg, 0.13 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (pentane/EtOAc 95:5) to afford a yellow oil (*syn*/*anti* 83:17, 108 mg, corrected yield 72%). IR (neat): ν_{max} = 3071–2872, 2106, 1738, 1370, 1235, 1113, 1051, 837 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), major + minor: δ = 7.62–7.53 (m, 2H), 7.39–7.31 (m, 3H), 5.01 (m, 1H), 4.14 (q, J = 7.2 Hz, 1H), 4.13 (q, J = 7.0 Hz, 1H), 4.07 (m, 1H), 2.51–2.28 (m, 2H), 2.13 (s, 3H), 2.10 (s, 3H) 1.83 (m, 1H), 1.67 (m, 1H), 1.38 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 0.69 (s, 9H) 0.67 (s, 9H),0.48 (s, 3H) 0.43 (s, 3H), 0.41 (s, 3H) 0.40 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), major + minor: δ = 172.8, 172.7, 170.5, 170.3, 138.0, 137.9, 134.4, 134.2, 129.3, 129.1, 127.8, 127.7, 76.7, 76.5, 63.5, 62.7, 60.5, 60.4, 37.6, 37.2, 34.9, 32.7, 32.4, 32.0, 31.7, 26.2, 26.1, 21.9, 21.0, 14.2, −2.0, −2.4, −2.5, −3.7 ppm; MS (LSIMS): m/z (%): 456 (100) $[M+Na]^+$, 391 $[M-N_3]^+$, 349, 305, 288; HRMS $[M+Na]^+$ $C_{22}H_{35}N_3O_4SiNa$ calcd: 456.229455; found: 456.230196.

Ethyl 6-acetoxy-4-azido-5-(dimethylphenylsilyl)-6-phenylhexanoate (15d): Prepared according to general procedure C from ethyl ester **7** (52 mg, 0.25 mmol), allylsilane **13d** (162 mg, 0.50 mmol), benzenesulfonylazide (137 mg, 0.75 mmol), $(Bu_3Sn)_2$ (0.18 mL, 0.37 mmol), and DTBHN (7 mg, 0.04 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (hexane/EtOAc 95:5) to afford a yellow oil (*syn*/*anti* >95:5, 74 mg, 65%). IR (neat): ν_{max} = 3440, 2105, 1737, 1373, 1229, 1112, 1033 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ =)7.42–7.35 (m, 5H), 7.31–7.18 (m, 5H), 6.05 (d, J = 3.4 Hz, 1H), 4.03 (q, J = 7.2 Hz, 1H), 4.02 (q, J = 7.1 Hz, 1H), 3.72 (m, 1H), 2.20–2.00 (m, 2H), 2.03 (s, 3H), 1.72–1.55 (m, 2H), 1.45–1.31 (m, 1H), 1.19 (t, J = 7.2 Hz, 3H), 0.47 (s, 3H), 0.39 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.4, 169.8, 140.5, 137.5, 134.0, 129.2, 128.4, 127.9, 127.5, 125.4, 74.1, 62.2, 60.4, 41.8, 31.6, 31.4, 21.4, 14.1, −2.0, −2.6 ppm; MS (ESI): m/z (%): 476 (100) $[M+Na]^+$, 433 (29), 299 (18), 217 (48); HRMS $[M+Na]^+$ $C_{24}H_{31}N_3O_4SiNa$ calcd: 476.1981; found: 476.1961.

Diethyl 2-acetoxy-4-azido-3-(dimethylphenylsilyl)heptanedioate (15f): Prepared according to general procedure C from ethyl ester **7** (73 mg, 0.35 mmol), allylsilane **13f** (213 mg, 0.66 mmol), 3-pyridylsulfonylazide (197 mg, 1.07 mmol), $(Bu_3Sn)_2$ (0.25 mL, 0.5 mmol), and DTBHN (10 mg, 0.06 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (pentane/EtOAc 9:1) to afford a yellow oil (*syn*/*anti* 88:12, 54 mg, 34%). Major diastereomer : IR (neat) ν_{max} = 3071–2950, 2109, 1740, 1731, 1373, 1113, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 2H), 7.40–7.34 (m, 3H), 5.11 (d, J = 1.9 Hz, 1H), 4.14 (m, 4H), 3.72 (m, 1H), 2.44–2.24 (m, 2H), 2.03 (s, 3H), 1.86 (m, 1H), 1.78–1.66 (m, 2H), 1.25 (m, 6H), 0.47 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6, 170.1, 170.0, 136.6, 133.9, 129.5, 128.0, 71.4, 62.9, 61.7, 60.5, 36.7, 31.5, 31.1, 20.9, 14.2, 14.0, −2.3, −2.7 ppm; MS (LSIMS): m/z (%): 472 (30) $[M+Na]^+$, 407 (65) $[M-N_3]^+$, 372 (26), 235 (22); HRMS $[M+Na]^+$ $C_{21}H_{31}N_3O_6SiNa$ calcd: 472.187984; found: 472.187837.

Ethyl 6-acetoxy-4-azido-5-(dimethylphenylsilyl)-6-phenylhexanoate (16a): Prepared according to general procedure C from ethyl ester **7** (58 mg, 0.278 mmol), allylsilane **14a** (151 mg, 0.466 mmol), 3-pyridylsulfonylazide (156 mg, 0.85 mmol), $(Bu_3Sn)_2$ (0.18 mL, 0.36 mmol), and DTBHN (16 mg, 0.09 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (hexane/EtOAc 95:5) to afford a colorless oil (*syn*/*anti* 83:17, 98 mg, 78%). IR (neat): ν_{max} = 3069–2950, 2099, 1737, 1229, 1111, 1022 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$), major + minor: δ = 7.60–7.50 (m, 2H), 7.40–7.22 (m, 5H), 6.09 (d, J = 7.0 Hz, 1H), 5.93 (d, J = 8.5 Hz, 1H), 4.04 (q, J = 7.0 Hz, 2H), 3.38 (m, 1H), 2.30–2.06 (m, 2H), 1.96 (s, 3H), 1.95 (m, 2H), 1.89 (s, 3H), 1.76–1.64 (m, 2H), 1.20 (t, J = 7.3 Hz, 3H), 1.19 (t, J = 7.3 Hz, 3H), 0.46 (s, 3H), 0.41 (s, 3H), 0.34 ppm (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) major diastereomer: δ = 172.3, 169.4, 140.5, 138.4, 133.8, 129.0, 128.5, 127.9, 127.8, 126.6, 76.2, 63.4, 60.4, 39.6, 31.5, 29.2, 21.1, 14.1, −1.2, −1.3 ppm; minor diastereomer: δ = 172.2, 169.5, 141.1, 138.4, 133.6, 126.4, 74.8, 62.3, 60.4, 38.4, 31.2, 29.3, 21.1, 13.7, −1.3, −2.3 ppm; MS (LSIMS): m/z (%): 476 (100) $[M+Na]^+$, 329 (50), 307 (36), 288 (67); HRMS $[M+Na]^+$ $C_{24}H_{31}N_3O_4SiNa$ calcd: 476.198155; found: 476.198755.

6-Acetoxy-4-azido-5-(dimethylphenylsilanyl)-7-methyloctanoic acid ethyl ester (16b): Prepared according to general procedure C from ethyl ester **7** (55 mg, 0.265 mmol), allylsilane **14b** (154 mg, 0.53 mmol), benzenesulfonylazide (145 mg, 0.795 mmol), $(Bu_3Sn)_2$ (0.20 mL, 0.4 mmol), and DTBHN (5 mg, 0.05 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (hexane/EtOAc : 95/5) to afford a yellow oil (*syn*/*anti* 82:18, 74 mg, 67%). IR (neat) ν_{max} = 2970–2874, 2100, 1732, 1427, 1372, 1236, 1112, 838, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), major + minor: δ = 7.61–7.50 (m, 2H), 7.40–7.32 (m, 3H), 5.07 (dd, J = 9.4, 1.5 Hz, 1H), 5.00 (dd, J = 9.0, 2.3 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 4.06 (q, J = 7.1 Hz, 2H), 3.52 (m, 1H), 2.33 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 1.92–1.58 (m, 7H), 1.48 (dd, J = 5.4, 1.6 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.3 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 6.4 Hz, 3H), 0.80 (m, 3H), 0.78 (d, J = 6.6 Hz, 3H), 0.52 (s, 6H), 0.51 (s, 3H), 0.50 ppm (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), major diastereomer: δ = 172.7, 170.2, 138.4, 133.8, 129.1, 127.8, 78.8, 63.9, 60.4, 36.7, 32.9, 31.3, 27.8, 21.2, 19.8, 18.2, 14.1, −0.7, −1.9 ppm; minor diastereomer: δ = 172.3, 170.4, 138.8, 133.7, 129.1, 127.9, 78.4, 63.1, 60.5, 35.2, 32.6, 31.0, 30.2, 21.2, 19.9, 18.5, 14.1, −0.3, −2.7 ppm; MS (ESI): m/z (%): 442 (75) $[M+Na]^+$; HRMS $[M+Na]^+$ $C_{21}H_{33}N_3O_4SiNa$ calcd: 442.2138; found: 442.2126.

(4*S*,5*R*,6*S*)-Ethyl 6-acetoxy-4-azido-5-(triisopropylsilyl)-6-phenylhexanoate ethyl ester (18b): Prepared according to general procedure C from ethyl ester **7** (92 mg, 0.44 mmol), allylsilane **17c** (77 mg, 0.22 mmol), 3-pyridylsulfonylazide (124 mg, 0.67 mmol), $(Bu_3Sn)_2$ (0.17 mL, 0.32 mmol), and DTBHN (14 mg, 0.08 mmol) added by 3% portion every 2 h. The crude was purified by chromatography (hexane/EtOAc 95:5) to afford a

yellow oil (*syn*/*anti* >95:<5, 65 mg, 62%). IR (neat): ν_{max}=3063–2868, 2104, 1732, 1226 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.38–7.14 (m, 5H), 6.14 (d, J=1.9 Hz, 1H), 3.81 (qd, J=7.1, 2.1 Hz, 2H), 3.54 (ddd, J=10.5, 4.1, 2.3 Hz, 1H), 2.03 (s, 1H), 1.99–1.91 (m, 2H), 1.64–1.56 (m, 2H), 1.11–0.87 ppm (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.4, 169.9, 141.3, 128.6, 127.3, 124.9, 74.9, 62.2, 60.4, 37.7, 31.8, 31.7, 21.7, 19.3, 14.1, 12.2 ppm; MS (ESI): *m*/*z*: 498 (100) $[M+Na]^+$; HRMS $[M+Na]^+$ $C_{25}H_{41}N_3O_4SiNa$ calcd: 498.2764; found: 498.2744.

Ethyl 7-acetoxy-4-azido-7-phenyl-5-(triphenylsilyl)heptanoate (20): Prepared according to general procedure C from ethyl ester **7** (102 mg, 0.48 mmol), allylsilane **19** (380 mg, 0.82 mmol), 3-pyridylsulfonylazide (265 mg, 1.44 mmol), $(Bu_3Sn)_2$ (0.36 mL, 0.72 mmol), and DTBHN (16 mg, 0.09 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (pentane/EtOAc 9:1) to afford a colorless oil (*syn*/*anti* 87:13, 89 mg, 31%). Major diastereomer : IR (neat): ν_{max}= 3070–2933, 2100, 1732, 1428, 1372, 1112 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=7.53–7.28 (m, 20H), 5.78 (m, 1H), 4.06 (q, J=6.9 Hz, 2H), 3.95 (m, 1H), 2.44–2.26 (m, 2H), 2.25–2.16 (m, 2H), 2.04 (s, 3H), 2.02–1.91 (m, 1H), 1.79–1.46 (m, 2H), 1.21 ppm (t, J=7.2 Hz, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ=172.6, 170.1, 139.4, 136.0, 133.1, 129.7, 128.5, 128.0, 127.4, 126.3, 75.9, 64.6, 60.4, 33.9, 31.8, 28.4, 26.8, 21.3, 14.1 ppm; MS (LSIMS): *m*/*z*: 614 (13) $[M+Na]^+$, 504 (11), 259 (100) $[Ph_3Si]^+$; HRMS $[M+Na]^+$ $C_{35}H_{37}N_3O_4SiNa$ calcd: 614.245105; found: 614.244118.

5-Azido-2-methyl-4-(dimethylphenylsilyl)-8-oxononan-3-yl acetate (22a): Prepared according to general procedure C from xanthate **21a** (123 mg, 0.69 mmol), allylsilane **13a** (105 mg, 0.362 mmol), 3-pyridylsulfonylazide (190 mg, 1.03 mmol), $(Bu_3Sn)_2$ (0.26 mL, 0.52 mmol), and DTBHN (12 mg, 0.06 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (hexane/EtOAc 95:5) to afford a colorless oil (*syn*/*anti* 72:28, 101 mg, 72%). IR (neat): ν_{max}=2962, 2101, 1732, 1236 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), major isomer: δ=7.54 (m, 2H), 7.33 (m, 3H), 4.93 (dd, J=8.3, 1.9 Hz, 1H), 3.85 (m, 1H), 2.61–2.40 (m, 2H), 2.12 (s, 3H), 2.00 (s, 3H), 1.85 (m, 1H), 1.75–1.49 (m, 2H), 1.47 (m, 1H), 0.78 (d, J=6.8 Hz, 3H), 0.76 (d, J=6.8 Hz, 3H), 0.40 (s, 3H), 0.39 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=207.7, 170.7, 137.7, 134.3, 129.0, 127.8, 76.8, 63.1, 40.8, 36.6, 32.0, 31.3, 29.9, 21.7, 19.4, 18.5, −2.2, −3.1 ppm; MS (ESI): *m*/*z* (%): 412 (100) $[M+Na]^+$. HRMS $[M+Na]^+$ $C_{20}H_{31}N_3O_3SiNa$ calcd: 412.2032; found: 412.2017.

7-(*N*-Methoxy-*N*-methylcarbamoyl)-5-azido-2-methyl-4-(dimethylphenylsilyl)heptan-3-yl acetate (22b): Prepared according to general procedure C from xanthate **21b** (97 mg, 0.43 mmol), allylsilane **13a** (157 mg, 0.89 mmol), 3-pyridylsulfonylazide (247 mg, 1.29 mmol), $(Bu_3Sn)_2$ (0.32 mL, 0.64 mmol), and DTBHN (13 mg, 0.07 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (pentane/EtOAc 8:2) to afford a yellow oil (*syn*/*anti* 77:23, 209 mg, estimated yield 75%). Major diastereomer: IR (neat): ν_{max}=2964, 2104, 1731, 1664, 1373, 1235, 1111 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.59–7.52 (m, 2H), 7.38–7.31 (m, 3H), 4.92 (dd, J=8.3, 2.3 Hz, 1H), 3.95 (m, 1H), 3.69 (s, 3H), 3.18 (s, 3H), 2.59–2.44 (m, 2H), 1.99 (s, 3H), 1.92–1.63 (m, 3H), 1.49 (m, 1H), 0.78 (d, J=6.8 Hz, 3H), 0.74 (d, J=6.8 Hz, 3H), 0.41 (s, 3H), 0.40 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=170.8, 137.8, 134.3, 129.0, 127.7, 76.6, 63.3, 61.2, 36.7, 32.2, 31.9, 29.1, 21.7, 19.4, 18.5, −2.0, −3.1 ppm; MS (LSIMS): m/z (%): 457 $[M+Na]^+$ (100); HRMS $[M+Na]^+$ $C_{21}H_{34}N_4O_4SiNa$ calcd: 457.2247; found: 457.2249.

Ethyl 4-azido-4-methyl-5-(dimethylphenylsilyl)-5-phenylpentanoate (24): Prepared according to general procedure C from ethyl ester **7** (62 mg, 0.3 mmol), olefin **23** (160 mg, 0.6 mmol), 3-pyridylsulfonylazide (175 mg, 0.9 mmol), $(Bu_3Sn)_2$ (0.22 mL, 0.45 mmol), and DTBHN (9 mg, 0.05 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (pentane/EtOAc 98:2) to afford a yellow oil as an inseparable of xanthate and both diastereomers (50:50, 90.2 mg, estimated yield 71%). IR (neat): ν_{max}=3070–2950, 2099, 1732, 1252, 1112 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$), major + minor: δ=7.47 (m, 4H), 7.34 (m, 6H), 7.28–7.05 (m, 10H), 4.05 (m, 4H), 2.49 (s, 1H), 2.47 (s, 1H), 2.32–2.15 (m, 4H), 1.96–1.67 (m, 4H), 1.22 (s, 3H), 1.21 (s, 3H), 1.18 (m, 6H), 0.47 (s, 3H), 0.43 (s, 3H), 0.20 (s, 3H), 0.15 ppm (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ=172.9, 172.8, 139.5, 139.3, 138.8, 138.7, 134.1, 134.0, 129.0, 128.9, 128.1, 128.0, 127.7, 127.6, 125.9, 66.7, 66.4, 60.5, 60.4, 48.3, 48.0, 35.9, 34.8, 29.4, 24.1, 23.2, 14.1, −1.0, −1.1, −2.0, −2.2 ppm; MS (LSIMS): *m*/*z* (%): 418 $[M+Na]^+$ (35), 353 (100), 318 (13), 288 (43); HRMS $[M+Na]^+$ $C_{22}H_{29}N_3O_2SiNa$ calcd: 418.192505; found: 418.192676.

Ethyl 4-azido-5-(benzyloxy)hexanoate (26a): Prepared according to general procedure C from ethyliodoacetate (222 mg, 1.04 mmol), olefin **25a** (324 mg, 2 mmol), benzenesulfonylazide (550 mg, 3 mmol), $(Bu_3Sn)_2$ (0.75 mL, 1.5 mmol) and DTBHN (5 mg, 0.03 mmol) in dry benzene (2 mL). The crude was purified by chromatography (cyclohexane then cyclohexane/*t*BuOMe 95:5) to afford a yellow oil as an inseparable mixture of $PhSO_2N_3$ and both diastereomers (54:46, 281 mg, estimated yield 43%). IR (neat): ν_{max}=3065–2871, 2127, 1732, 1449, 1372, 1170, 1087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), major + minor: δ=7.41–7.25 (m, 10H), 4.59 (m, 4H), 4.30 (m, 1H), 4.22 (m, 1H), 4.14 (q, J=7.2 Hz, 2H), 4.14 (q, J=7.2 Hz, 2H), 3.45 (m, 1H), 3.20 (m, 1H), 2.69–2.52 (m, 2H), 2.51–2.34 (m, 2H), 2.12 (m, 2H), 2.04 (m, 2H), 1.34 (d, J=6.0 Hz, 3H), 1.31–1.22 ppm (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.6, 172.5, 138.2, 138.0, 128.3, 127.7, 126.6, 77.5, 77.2, 70.8, 70.7, 60.5, 60.4, 42.0, 40.3, 34.4, 34.3, 30.8, 30.4, 18.5, 17.9, 14.2 ppm.

4-Azido-5-(*tert*-butyldimethylsilanyloxy)hexanoic acid ethyl ester (26b): Prepared according to general procedure C from ethyliodoacetate (212 mg, 0.99 mmol), olefin **25b** (373 mg, 2 mmol), benzenesulfonylazide (550 mg, 3 mmol), $(Bu_3Sn)_2$ (0.75 mL, 1.5 mmol) and DTBHN (5 mg, 0.03 mmol) added by 3% portion every 90 min. The crude was purified by chromatography (cyclohexane then cyclohexane/EtOAc 98:2) to afford a yellow oil (57:43, 214 mg, 68%). IR (neat), major diastereomer: ν_{max}=2959–2858, 2103, 1736, 1463, 1257, 1179, 837 cm^{-1}; minor diastereomer: ν_{max}=2930–2858, 2102, 1736, 1472, 1257, 837 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), major diastereomer: δ=4.15 (q, J=7.2 Hz, 2H), 3.89 (m, 1H), 3.32 (dt, J=10.6, 3.5 Hz, 1H), 2.43 (m, 2H), 1.81 (m, 1H), 1.58 (m, 1H), 1.27 (t, J=7.2 Hz, 3H), 1.17 (d, J=6.2 Hz, 3H), 0.90 (s, 9H), 0.08 ppm (s, 6H); minor diastereomer : δ=4.15 (q, J=7.1 Hz, 2H), 3.83 (m, 1H), 3.00 (dt, J=9.9, 4.8 Hz, 1H), 2.46 (m, 2H), 1.85 (m, 1H), 1.27 (t, J=7.2 Hz, 3H), 1.21 (d, J=6.2 Hz, 3H), 0.91 (s, 9H), 0.1 (s, 3H), 0.09 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), major diastereomer: δ= 172.9, 71.3, 67.6, 60.5, 31.2, 25.7, 25.4, 18.7, 17.9, 14.2, −4.5, −4.9 ppm; minor diastereomer: δ=172.9, 71.4, 66.9, 60.5, 31.1, 25.8, 25.7, 20.7, 17.9, 14.2, −4.5, −5.0 ppm; MS (LSIMS): major diastereomer *m*/*z* (%): 316 $[M+H]^+$ (17), 258 (47), 185 (16), 159 (100), 115 (34); minor diastereomer *m*/*z* (%): 316 $[M+H]^+$ (21), 258 (97), 185 (37), 159 (100), 115 (44); HRMS $[M+H]^+$ $C_{14}H_{30}N_3O_3Si$ calcd: 316.205646; found: 316.205260.

Tosylate (30): *p*-Tolylsulfonyl chloride (270 mg, 1.4 mmol) was added to a solution of diol **29** (71.5 mg, 0.236 mmol) in pyridine (3.5 mL). The mixture was stirred at RT for 5 h then quenched with brine. The aqueous layer was extracted with EtOAc and the combined extracts washed with Cu_2SO_4. The solvent was evaporated under vacuum and the crude purified through silica gel (pentane/EtOAc 8:2) to afford a colorless oil (101.5 mg, 94%). IR (neat): ν_{max}=3500, 2953, 2106, 1738, 1361, 1177, 1069 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.81 (d, J=8.2 Hz, 2H), 7.36 (d, J=7.9 Hz, 2H), 4.34 (dd, J=10.2, 2.0 Hz, 1H), 4.20 (m, 1H), 4.17 (dd, J=6.1, 4.6 Hz, 1H), 4.07 (dd, J=10.0, 6.4 Hz, 1H), 3.97 (dd, J=9.5, 6.1 Hz, 1H), 3.69 (s, 3H), 3.56 (m, 1H), 2.89 (d, J=5.5 Hz, 1H), 2.50 (m, 2H), 2.45 (s, 3H), 2.16–1.85 (m, 2H), 1.40 (s, 3H), 1.29 ppm (s, 3H); ^{13}C NMR (75 мhz, $CDCl_3$): δ=173.4, 145.1, 132.5, 129.9, 128.0, 109.1, 79.6, 75.7, 72.4, 67.8, 58.4, 51.8, 30.5, 26.9, 24.7, 21.6 ppm; MS (LSIMS): *m*/*z* (%): 480 $[M+Na]^+$ (100), 430 (35); HRMS $[M+Na]^+$ $C_{19}H_{27}N_3O_8SNa$ calcd: 480.141657; found: 480.141685.

(3a*R*,4*R*,9a*R*,9b*S*)-Octahydro-2,2-dimethyl[1,3]dioxolo[4,5-*g*]indolizin-4-ol (31): The tosylate **30** (104 mg, 0.227 mmol) was dissolved in MeOH (2.3 mL) and 10% Pd/C (2 mg) was added. The suspension was stirred at RT under H_2 (1 atm) for 2 h. The solution was filtered through Celite (MeOH, 10 mL) then the residue was concentrated under vacuum. The crude product was dissolved in MeOH (3 mL), Et_3N (0.16 mL, 1.14 mmol) was added, and the solution was heated under reflux overnight. The solvent was evaporated and the resulting crude material dissolved in THF (2.8 mL). A 1 M solution of $LiAlH_4$ in Et_2O (0.64 mL) was added dropwise at 0°C. The solution was stirred under reflux for 3 h. Water (0.03 mL), NaOH 10% (0.03 mL), and water (0.05 mL) were successively added. The residue was extracted with EtOAc. The organic

layer was dried over Na_2SO_4 and the solvent evaporated under vacuum. The crude was purified through silica gel (CH_2Cl_2/MeOH 9:1) to afford a white solid (37 mg, 77%). IR (neat): ν_{max} = 3376, 2924, 1379, 1207 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 4.31 (dd, J = 6.1, 2.7 Hz, 1H), 4.12 (dd, J = 6.4, 4.6 Hz, 1H), 3.78 (m, 1H), 3.00 (dd, J = 11.0, 6.1 Hz, 1H), 2.91 (m, 1H), 2.55 (m, 1H), 2.47–2.36 (m, 2H), 2.07–1.65 (m, 5H), 1.58 (s, 3H), 1.37 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.4, 74.7, 74.5, 66.3, 60.4, 54.1, 53.5, 26.1, 25.9, 25.3, 22.4 ppm; MS (LSIMS): m/z (%): 214 (100) $[M+H]^+$; HRMS $[M+H]^+$ $C_{11}H_{20}NO_3$ calcd: 214.144319; found: 214.143925.

(6*R*,7*R*,8*S*,8a*R*)-Octahydroindolizine-6,7,8-triol (32):[32a] The acetonide **31** (37 mg, 0.173 mmol) was dissolved in MeOH/HCl (v/v 2:1) (0.9 mL). The solution was stirred under reflux for 1 h. The solvent was evaporated and the chlorhydrate was purified through DOWEX 1X10 (OH^- form) and eluted with water to afford **32** as a colorless oil (29 mg, 97%). ^1H NMR (300 MHz, CD_3OD): δ = 3.83 (m, 2H), 3.45 (m, 1H) 3.17 (dd, J = 12.1, 2.6 Hz, 1H), 3.02 (m, 1H), 2.17 (m, 2H), 2.06 (m, 1H), 1.98–1.65 ppm (m, 4H); ^{13}C NMR (75 Mhz, CD_3OD): δ = 72.3, 71.7, 71.2, 67.9, 57.7, 54.6, 25.5, 22.4 ppm.

X-ray of (15d): CCDC 659354 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) *Chemistry of Halides, Pseudo-Halides and Azides, Part 1–2* (Eds.: S. Patai, Z. Rappoport), Chichester, UK, **1995**; b) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.

[2] a) L. Benati, P. C. Montevecchi, *J. Org. Chem.* **1981**, *46*, 4570–4573; b) S. Kim, G. H. Joe, J. Y. Do, *J. Am. Chem. Soc.* **1994**, *116*, 5521–5522; c) J. A. Murphy, M. Kizil, *J. Chem. Soc. Chem. Commun.* **1995**, 1409–1410; d) D. E. Lizos, R. Tripoli, J. A. Murphy, *Chem. Commun.* **2001**, 2732–2733; e) D. E. Lizos, J. A. Murphy, *Org. Biomol. Chem.* **2003**, *1*, 117–122.

[3] a) D. A. Evans, T. C. Britton, *J. Am. Chem. Soc.* **1987**, *109*, 6881–6883; b) D. A. Evans, T. C. Britton, J. A. Ellman, R. L. Dorow, *J. Am. Chem. Soc.* **1990**, *112*, 4011–4030.

[4] J. Waser, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 8294–8295.

[5] a) P. Magnus, J. Lacour, *J. Am. Chem. Soc.* **1992**, *114*, 767–769; b) P. Magnus, J. Lacour, P. Evans, M. B. Roe, C. Hulme, *J. Am. Chem. Soc.* **1996**, *118*, 3406–3418.

[6] a) C. M. Pedersen, L. M. Marinescu, M. Bols, *Org. Biomol. Chem.* **2005**, *3*, 816–822; b) Y. Kita, H. Tohma, T. Takada, S. Mitoh, S. Fujita, M. Gyoten, *Synlett* **1994**, 427–428; c) M. Baruah, M. Bols, *J. Chem. Soc. Perkin Trans. 1* **2002**, 509–512; d) H. Pedersen, S. Sinning, A. Bülow, O. Wiborg, L. Falborg, M. Bols, *Org. Biomol. Chem.* **2004**, *2*, 2861–2869.

[7] a) V. V. Zhdankin, A. P. Krasutsky, C. J. Kuehl, A. J. Simonsen, J. K. Woodward, B. Mismash, J. T. Bolz, *J. Am. Chem. Soc.* **1996**, *118*, 5192–5197; b) C. Viuf, M. Bols, *Angew. Chem.* **2001**, *113*, 643–645; *Angew. Chem. Int. Ed.* **2001**, *40*, 623–625; c) L. Marinescu, J. Thinggaard, I. B. Thomsen, M. Bols, *J. Org. Chem.* **2003**, *68*, 9453–9455; d) L. Marinescu, C. M. Pedersen, M. Bols, *Tetrahedron* **2005**, *61*, 123–127.

[8] a) C. Ollivier, P. Renaud, *J. Am. Chem. Soc.* **2000**, *122*, 6496–6497; b) C. Ollivier, P. Renaud, *J. Am. Chem. Soc.* **2001**, *123*, 4717–4727; c) D. S. Breslow, M. F. Sloan, N. R. Newburg, W. B. Renfrow, *J. Am. Chem. Soc.* **1969**, *91*, 2273–2279; d) R. A. Abramovitch, W. D. Holcomb, *J. Chem. Soc. D* **1969**, 1298–1299.

[9] a) P. Renaud, C. Ollivier, P. Panchaud, *Angew. Chem.* **2002**, *114*, 3610–3612; *Angew. Chem. Int. Ed.* **2002**, *41*, 3460–3462; b) P. Renaud, C. Ollivier, P. Panchaud, S. Zigmantas, *J. Org. Chem.* **2004**, *69*, 2755–2759; c) P. Panchaud, P. Renaud, *Adv. Synth. Catal.* **2004**, *34*, 925–928.

[10] a) L. Chabaud, P. Renaud, Y. Landais, *Org. Lett.* **2005**, *7*, 2587–2590; b) P. Schar, P. Renaud, *Org. Lett.* **2006**, *8*, 1569–1571.

[11] a) H. Sakurai, A. Hosomi, M. Kumada, *J. Org. Chem.* **1969**, *34*, 1764–1768; b) A. W. P. Jarvie, R. J. Rowley, *J. Chem. Soc. B* **1971**, 2439–2442; c) A. S. Gozdz, P. Maslak, *J. Org. Chem.* **1991**, *56*, 2179–2189; d) P. James, Y. Landais, *Org. Lett.* **2004**, *6*, 325–328; e) P. James, F.-X. Felpin, Y. Landais, K. Schenk, *J. Org. Chem.* **2005**, *70*, 7985–7995; f) P. James, K. Schenk, Y. Landais, *J. Org. Chem.* **2006**, *71*, 3630–3633.

[12] a) I. Fleming, J. Dunoguès, R. Smithers, *Org. React.* **1989**, *37*, 57–575; b) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063–2192; c) C. E. Masse, J. S. Panek, *Chem. Rev.* **1995**, *95*, 1293–1316; d) L. Chabaud, P. James, Y. Landais, *Eur. J. Org. Chem.* **2004**, 3173–3199.

[13] Y. Landais, *C. R. Acad. Sci. Ser. IIc* **2005**, *8*, 823–832.

[14] a) N. A. Porter, J. H. Wu, G. Zhang, A. D. Reed, *J. Org. Chem.* **1997**, *62*, 6702–6703; b) N. A. Porter, G. Zhang, A. D. Reed, *Tetrahedron Lett.* **2000**, *41*, 5773–5777.

[15] For a preliminary communication of this work, see: L. Chabaud, Y. Landais, P. Renaud, *Org. Lett.* **2002**, *4*, 4257–4260.

[16] a) B. Laycock, W. Kitching, G. Wickman, *Tetrahedron Lett.* **1983**, *24*, 5785–5788; b) I. Fleming, D. Waterson, *J. Chem. Soc. Perkin Trans. 1* **1984**, 1809–1813; c) Compound **1a** was obtained as a 93:7 mixture with 4-(phenyldimethylsilyl)but-2-ene and was used without further purification in the carboazidation process.

[17] a) Y. Ikeda, H. Yamamoto, *Bull Chem. Soc. Jpn.* **1986**, *59*, 657–658; b) M. T. Reetz, B. Wenderoth, *Tetrahedron Lett.* **1982**, *23*, 5259–5262; c) Y. Landais, C. Mahieux, K. Schenk, S. S. Surange, *J. Org. Chem.* **2003**, *68*, 2778–2789; d) J. M. Adam, L. de Fays, M. Laguerre, L. Ghosez, *Tetrahedron* **2004**, *60*, 7325–7344; e) F. Schleth, A. Studer, *Angew. Chem.* **2004**, *116*, 317–319; *Angew. Chem. Int. Ed.* **2004**, *43*, 313–315.

[18] Depending on the nature of the substituent on the silicon center, we noticed that the ease of deprotonation of the allylsilane precursor changed. With triphenylsilyl groups, deprotonation occurred smoothly with *n*BuLi at 0°C in THF while a THF/TMEDA medium and 2 h stirring was generally required with $PhMe_2Si$. With $(iPr)_3Si$ groups, deprotonation occurred only at room temperature, overnight in a hexane/TMEDA mixture.

[19] a) Y. Yamamoto, Y. Saito, K. Maruyama, *J. Chem. Soc. Chem. Commun.* **1982**, 1326–1328; b) Y. Yamamoto, H. Yatagai, Y. Ishihara, N. Maeda, K. Maruyama, *Tetrahedron* **1984**, *40*, 2239–2246.

[20] a) R. J. P. Corriu, J. Masse, D. Samate, *J. Organomet. Chem.* **1975**, *93*, 71–80; b) E. Schaumann, A. Kirschning, *Tetrahedron Lett.* **1988**, *29*, 4281–4284.

[21] α-Iodoesters are not convenient substrates for reactions with allylsilanes since the iodine atom transfer process may occur after the addition of the ester group onto the double bond, leading to β-iodosilanes that are known to β-eliminate even at low temperature.[14b]

[22] Trimethylallylsilane afforded 73% of the carboazidation product.[8a,b]

[23] J. R. Hwu, K. Y. King, I-F. Wu, G. H. Hakimelahi, *Tetrahedron Lett.* **1998**, *39*, 3721–3724.

[24] a) G. Hagen, H. Mayr, *J. Am. Chem. Soc.* **1991**, *113*, 4954–4961; b) J. Bartl, S. Steenken, H. Mayr, *J. Am. Chem. Soc.* **1991**, *113*, 7710–7716.

[25] L. Chabaud, Y. Landais, *Tetrahedron Lett.* **2003**, *44*, 6995–6998.

[26] D. S. Masterson, N. E. Porter, *Org. Lett.* **2002**, *4*, 4253–4256.

[27] C. Ollivier, Ph.D. thesis, Bern University, **2001**.

[28] D. S. Masterson, J. P. Shakleford, *Synlett* **2007**, 1302–1304.

[29] a) I. Fleming, *Chemtracts: Org. Chem.* **1996**, 1–64; b) Y. Landais, G. Jones, *Tetrahedron* **1996**, *52*, 7599–7662; c) K. Tamao, in *Advances*

in Silicon Chemistry, Vol. 3, Jai Press, **1996**, pp. 1–62; d) I. Fleming, R. Henning, D. C. Parker, H. E. Plaut, P. E. J. Sanderson, *J. Chem. Soc. Perkin Trans. 1* **1995**, 317–337; e) J. S. Panek, J. Zhang, *J. Org. Chem.* **1993**, *58*, 294–296.

[30] a) I. Fleming, A. K. Sarkar, M. J. Doyle, P. R. Raithby, *J. Chem. Soc. Perkin Trans. 1* **1989**, 2023–2030; b) R. Tripathy, R. W. Franck, K. D. Onan, *J. Am. Chem. Soc.* **1988**, *110*, 3257–3262; c) Y. Landais, D. Planchenault, V. Weber, *Tetrahedron Lett.* **1995**, *36*, 2987–2990; d) O. Andrey, Y. Landais, *Tetrahedron Lett.* **1993**, *34*, 8435–8438.

[31] The absence of $A_{1,3}$ strain in our case is likely to be responsible for the lack of stereocontrol, see: a) Y. Guindon, C. Yoakim, V. Gorys, W. W. Ogilvie, D. Delorme, J. Renaud, G. Robinson, J.-F. Lavallée, A. Slassi, G. Jung, J. Rancourt, K. Durkin, D. Liotta, *J. Org. Chem.* **1994**, *59*, 1166–1178; b) K. Durkin, D. Liotta, J. Rancourt, J.-F. Lavallée, L. Boisvert, Y. Guindon, *J. Am. Chem. Soc.* **1992**, *114*, 4912–4914; c) B. Giese, W. Damm, F. Wetterich, H.-G. Zeitz, *Tetrahedron Lett.* **1992**, *33*, 1863–1866.

[32] a) D. Hendry, L. Hough, A. C. Richardson, *Tetrahedron* **1988**, *44*, 6153–6168; b) B. Winchester, I. Cenci di Bello, A. C. Richardson, R. J. Nash, L. E. Fellows, N. G. Ramsden, G. W. Fleet, *Biochem. J.* **1990**, *269*, 227–231.

[33] a) M. J. S. Dewar, S. Olivella, *J. Am. Chem. Soc.* **1978**, *100*, 5290–5295; b) D. C. Spellmeyer, K. N. Houk, *J. Org. Chem.* **1987**, *52*, 959–974; c) N. E. Porter, B. Giese, D. P. Curran, *Acc. Chem. Res.* **1991**, *24*, 296–304.

[34] P. d'Antuono, A. Fritsch, L. Ducasse, F. Castet, P. James, Y. Landais, *J. Phys. Chem. A* **2006**, *110*, 3714–3722.

[35] C. Heller, H. M. McConnell, *J. Chem. Phys.* **1960**, *32*, 1535–1539.

[36] a) P. J. Krusic, J. K. Kochi, *J. Am. Chem. Soc.* **1971**, *93*, 846–860; b) T. Kawamura, J. K. Kochi, *J. Am. Chem. Soc.* **1972**, *94*, 648–650; c) D. Griller, K. U. Ingold, *J. Am. Chem. Soc.* **1974**, *96*, 6715–6720; d) R. A. Jackson, K. U. Ingold, D. Griller, A. S. Nazran, *J. Am. Chem. Soc.* **1985**, *107*, 208–211; e) N. Auner, R. Walsh, J. Westrup, *J. Chem. Soc. Chem. Commun.* **1986**, 207–208.

[37] a) M. Chérest, H. Felkin, N. Prudent, *Tetrahedron Lett.* **1968**, *9*, 2199–2204; b) N. T. Anh, O. Eisenstein, *Nouv. J. Chim.* **1977**, *1*, 61–70; c) for a discussion on allylic strain versus Felkin–Anh models in stereocontrolled free-radical processes, see reference [13] and B. Giese in *Radicals in Organic Synthesis, Vol. 1* (Eds: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**, Chapter 4, pp. 381–399; d) M. Roth, W. Damm, B. Giese, *Tetrahedron Lett.* **1996**, *37*, 351–354.

[38] a) M. Sugawara, J. I. Yoshida, *J. Org. Chem.* **2000**, *65*, 3135–3142; b) J. B. Lambert, *Tetrahedron* **1990**, *46*, 2677–2689, and references therein; c) J. B. Lambert, Y. Zhao, R. W. Emblide, L. A. Salvador, X. Liu, J.-H. So, E. C. Chelius, *Acc. Chem. Res.* **1999**, *32*, 183–190; d) S. Zhang, F. G. Bordwell, *J. Org. Chem.* **1996**, *61*, 51–54.

[39] G. Thoma, D. P. Curran, S. V. Geib, B. Giese, W. Damm, F. Wetterich, *J. Am. Chem. Soc.* **1993**, *115*, 8585–8591.

[40] M. E. Briggs, S. Z. Zard, *Synlett* **2005**, 334–336.

[41] Gaussian 03, Revision C.02: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

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