Pergamon

Tetrahedron 58 (2002) 8195–8203

TETRAHEDRON

Lewis acid catalyzed stereoselective hydrosilylation of ketones under the control of σ–π chelation

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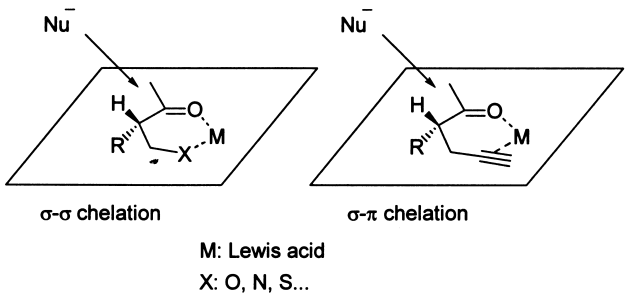
Received 16 April 2002; accepted 1 May 2002

Abstract—Hydrosilylation of 2-methyl-1-phenyl-pentan-1-one with Et_3SiH in the presence of catalytic amounts of $B(C_6F_5)_3$ gave the *anti*-product with slight predominance over *syn*-product (*syn*/*anti*=1:1.5). In contrast, the *syn*-product was obtained stereoselectively in the reaction of 2-methyl-1-phenyl-pent-4-yn-1-one bearing an ethynyl group at the β-position (*syn*/*anti*=7:1). The *syn*-selectivities were also observed in the $B(C_6F_5)_3$-catalyzed reactions of other related ketones, such as α-methyl-β-alkynyl aryl ketones and α-methyl-β-alkynyl alkyl ketones. The moderate *anti*-selectivity observed in the former case can be explained by the ordinary Felkin–Anh model. On the other hand, the unusual *syn*-selectivity in the latter cases can be accounted for by the σ–π chelation by R_3Si^+, in which both the lone pair (σ) of the carbonyl group and the π-electrons of the alkyne coordinate to the silylium ion. The σ–π chelation control was also effective for the 1,3-asymmetric induction. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Since Cram's pioneering work on chelation control in Grignard-type addition to chiral alkoxy carbonyl substrates,[1] a number of studies on related subjects have appeared.[2] Among them, the Lewis acid-mediated chelation control is one of the most fundamental and practically important concepts in modern organic chemistry.[3] It is well accepted that the chelating controlled reaction proceeds through the *σ-coordination of a lone pair of heteroatoms*, such as an oxygen of alkoxy groups and a nitrogen of amino groups, to a Lewis acid (*σ–σ chelation*). Recently, we reported the first example of chelation controlled regio- and chemoselective reaction through the *σ-coordination of carbonyl oxygen* and *π-coordination of triple bond* to a Lewis acid (*σ–π chelation*).[4] Based on this finding, we next communicated the unprecedented σ–π chelation-controlled stereoselective hydrosilylation of ketones using $B(C_6F_5)_3$ catalyst.[5,6] Herein, we wish to report the full detail on the $B(C_6F_5)_3$-catalyzed 1,2 and 1,3-stereoselective hydrosilylation of ketones (Scheme 1).

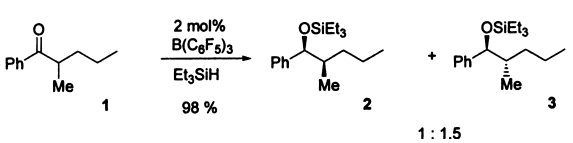


Scheme 1.

2. Results and discussion

2.1. 1,2-Stereoselective hydrosilylation

We examined the stereoselective hydrosilylation of various ketones using R_3SiH-$B(C_6F_5)_3$ as a reducing agent.[7] The reaction of 2-methyl-1-phenyl-pentan-1-one **1** with Et_3SiH in the presence of catalytic amounts of $B(C_6F_5)_3$ proceeded smoothly to give a mixture of the hydrosilylated products **2** and **3** in 98% yield (Eq. (1)). Slightly predominant formation of the *anti*-product **3** over *syn*-product **2** was observed: the ratio of **2**/**3** was 1:1.5. We next examined the hydrosilylation of 2-methyl-1-phenyl-pent-4-yn-1-one **4a** (R^1=Ph, R^2=H) under the same reaction conditions as above. Interestingly, the *syn*-product **5a** was afforded as the major product (**5a**/**6a**=7:1) (Eq. (2)). This result prompted us to examine the hydrosilylation of **4a** and related ketones **4b**–**h** to clarify the generality of this unusual diastereoselectivity. The results are summarized in Table 1.



(1)

Keywords: chelation; stereocontrol; alkynes; ketones.

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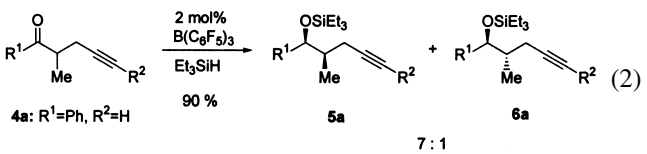
PII: S0040-4020(02)00968-7

Table 1. σ–π chelation-controlled hydrosilylation of **4**

Entry	Substrate **4**			R_3SiH	Yield **5** and **6** (%)[a]	Ratio **5**/**6**
	R^1	R^2				
1	Ph	H	**4a**	Et_3SiH	90	7.0:1
2	Ph	H	**4a**	Ph_2MeSiH	99	6.8:1
3	Ph	Me	**4b**	Et_3SiH	Quant	5.0:1
4	Ph	Ph	**4c**	Et_3SiH	Quant	3.0:1
5	Ph	TMS	**4d**	Et_3SiH	Quant	7.7:1
6	Et	H	**4e**	Et_3SiH	Quant	4.4:1
7	*c*-C_6H_{11}	H	**4f**	Et_3SiH	93	5.0:1
8	*o*-MePh	H	**4g**	Et_3SiH	94	15:1
9	^{t}Bu	H	**4h**	Et_3SiH	Quant	>30:1

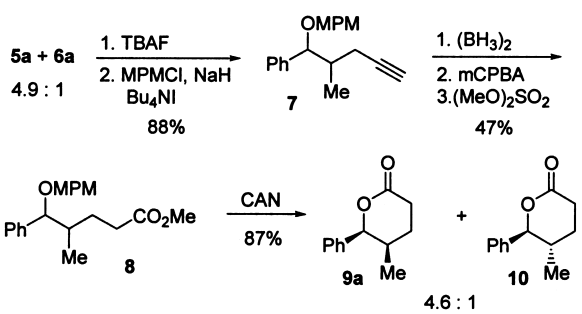
Reaction was performed with R_3SiH (1 equiv.) and $B(C_6F_5)_3$ (2 mol%) in toluene at 0°C within 1 h.
[a] Isolated yield.



(2)

The predominant formation of the *syn*-product was also observed in the reaction of **4a** with other silanes such as Ph_2MeSiH (entry 2). The reactions of **4b–d**, bearing Me, Ph, and TMS groups at the terminal position of alkyne, respectively, also gave *syn*-selectivities (entries 3–5). Not only aromatic ketones but also aliphatic ketones **4e**, **4f**, and **4h** produced *syn*-products selectively (entries 6, 7, and 9). Interestingly, stereoselectivities increased from 4.4:1 (R^1=Et) to >30:1 (R^1=^{t}Bu) as the substituents at R^1 position became bulkier. These results clearly indicate that the *syn* diastereoselectivity is widely observed in the $B(C_6F_5)_3$ catalyzed reduction of **4** with hydrosilanes.

The stereostructures of **5a** and **6a** were unambiguously determined by converting **5a** and **6a** to **9a** and **10**, respectively, as shown in Scheme 2. The treatment of a mixture of **5a** and **6a** (4.9:1) with TBAF, followed by the protection of the resulting alcohols by MPMCl under basic condition gave **7** in 88% yield. The alkynyl part of **7** was converted to a carboxylic acid by hydroboration-oxidative work-up, which was subsequently esterified to give **8** in 47% yield. Deprotection of the MPM group of **8** by CAN gave a mixture of the lactones **9a** and **10** in a ratio of 4.6:1 in 87% yield. The ^{1}H NMR spectrum of **9a** was identical to that of the known compound.[8] The stereostructure of **5h**, which was obtained from the aliphatic ketone **4h**, was also determined by converting **5h** to *cis*-6-*tert*-butyl-5-methyl-tetrahydro-pyran-2-one (**9b**) via similar routes. The stereo-



Scheme 2.

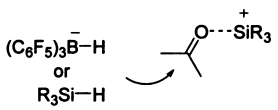
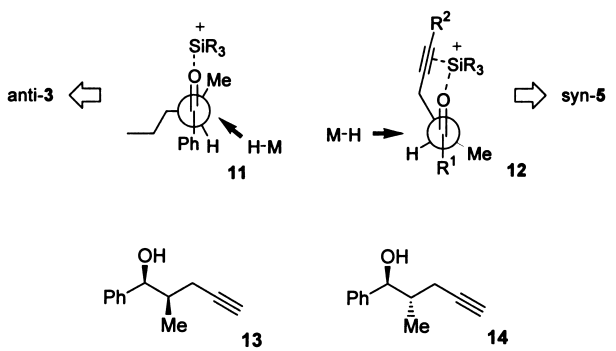


Figure 1.

structures of **5b–g** and **6b–g** were assigned by their ^{1}H NMR spectra on the analogy of those of **5a**, **6a**, and **5h**.

The difference of the diastereoselectivities between Eqs. (1) and (2) clearly shows that the acetylenic bond of **4** exerts a crucial role upon the observed *syn*-selectivity. Piers et al. proposed the interesting silane activation mechanism in the $B(C_6F_5)_3$ catalyzed hydrosilylation of aldehydes and ketones; the ordinary mechanism, in which the carbonyl oxygen of the electrophiles coordinates to $B(C_6F_5)_3$ and thus carbonyl substrates are activated, is not operative in the $B(C_6F_5)_3$ catalyzed reduction.[7] Their extensive mechanistic studies clarify that $B(C_6F_5)_3$ activates the silane via hydride abstraction to form the incipient silylium species which enhances the electrophilicity of carbonyl group, facilitating the reduction by $[HB(C_6F_5)_3]^-$ or R_3SiH (Fig. 1).

Most probably, a silylium species is generated here also, and the σ–π coordination of this species is operative in the reaction of **4**. The *anti* diastereoselectivity in the reaction of **1** can be accounted for by the ordinary Felkin–Anh model. The propyl group at the α-position is regarded as the largest group and the Me as the medium size (model **11**). Accordingly, *anti*-**3** is produced with slight preference, and the observed low stereoselectivity is due to the small steric difference between propyl and methyl group at the α-position. On the contrary, in the reaction of **4**, the reduction would proceed through the σ–π chelation of R_3Si^+ (model **12**): the hydride attack takes place from the less hindered side to produce the *syn*-isomer **5**. If the ordinary Felkin–Anh model is involved also in the case of **4**, the *anti*-diastereomer **6** should be produced predominantly, since a propargyl group is sterically larger than a Me group. Indeed, the *anti*-selectivity was observed with slight predominance when the reduction of **4a** was carried out using DIBAL-H, in which the ratio of **13**/**14** was 49:51.



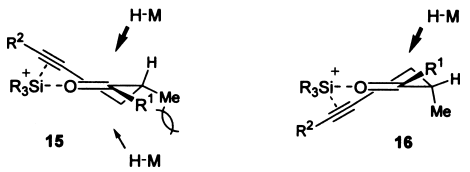
The stereoselectivities decreased as the substituents R^2 of **4** became bulky (entries 1, 3, and 4). Presumably, a bulky R^2 group would make it difficult to form strong σ–π chelation in **12**. Higher selectivity obtained in the case of **4d** may be explained by the well-known β-silyl effect, which would make the chelation more stronger.[9] The proposed chelation model also can explain the reason the *syn*-selectivity was obtained very predominantly or exclusively in the reaction

Table 2. σ−π chelation-controlled 1,3-hydrosilylation of **25**

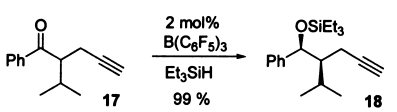
Entry	Substrate **25**				Yield **26** and **27** (%)[a]	Ratio *anti*-**26**/*syn*-**27**
	R^1	R^2	R^3			
1	Ph	Me	TMS	**25a**	Quant	6.5:1
2[b]	Ph	Me	TMS	**25a**	90	4.2:1
3[c]	Ph	Me	TMS	**25a**	Quant	4.2:1
4	Ph	Me	Ph	**25b**	90	6.5:1
5	Ph	Me	Me	**25c**	Quant	4.8:1
6	Ph	Me	H	**25d**	85	3.3:1
7	Ph	*c*-C_6H_{11}	Ph	**25e**	Quant	12:1
8	Ph	^{t}Bu	Ph	**25f**	Quant	18:1
9	*c*-C_6H_{11}	Me	TMS	**25g**	83	3.6:1
10	^{t}Bu	Me	TMS	**25h**	77	20:1

Reaction was performed with Ph_2MeSiH (1 equiv.) and $B(C_6F_5)_3$ (2 mol%) in toluene at 0°C within 1 h unless otherwise indicated.
[a] Isolated yield.
[b] Et_3SiH was used instead of Ph_2MeSiH.
[c] $PhMe_2SiH$ was used instead of Ph_2MeSiH.

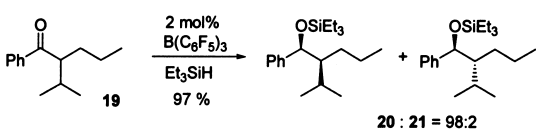
of **4g** and **4h** having bulky R^1 groups (entries 8 and 9). There is a possibility that hydride may attack from the bottom side of carbonyl group in the conformer **15**, which produces the *anti*-isomer **6**. On the other hand, the axially oriented methyl group prevents the hydride attack from the bottom side in the conformer **16**. The conformer **16** is more favored with the bulkier R^1 group because of the increased steric repulsion between R^1 and Me in **15**.[10]



The $B(C_6F_5)_3$-catalyzed hydrosilylation of **17** with Et_3SiH afforded the *syn*-isomer **18** as a sole product in 99% yield (Eq. (3)). Both the σ−π chelation and Felkin–Anh model leads to the *syn*-isomer, since isopropyl group at the α-position of **17** is sterically larger than propargyl group. On the other hand, the *syn*-selectivity was decreased (*syn*-**20**/*anti*-**21**=98:2) in the hydrosilylation of **19**, bearing a saturated propyl group instead of a propargyl group at the α-position, under the same reaction condition (Eq. (4)). These results clearly imply the σ−π chelation can be used not only for reversing the Felkin–Anh selectivity but also for increasing it by choosing the substituent at the α-position of carbonyl compounds.



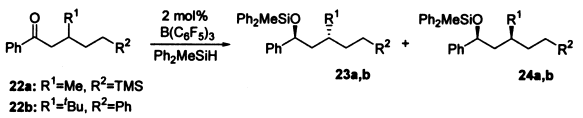
(3)



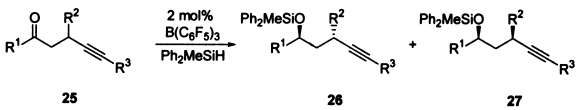
(4)

2.2. 1,3-Stereoselective hydrosilylation

The 1,2-asymmetric induction via the σ−π chelation control could be extended to the 1,3-system. First, we attempted the $(C_6F_5)_3B$ catalyzed hydrosilylation of 3-methyl-1-phenyl-5-trimethylsilyl-pentan-1-one **22a** with Ph_2MeSiH (Eq. (5)). The reaction proceeded smoothly to give a mixture of the reduced products **23a** and **24a** quantitatively, however, no selectivity was observed (**23a**/**24a**=1:1). While the *anti*-product **23b** was obtained predominantly in the reaction of **22b** bearing ^{t}Bu group at the β-position, the selectivity was not high (**23b**/**24b**=2.3:1). On the other hand, high *anti*-selectivities were observed in the reaction of **25** bearing alkynyl moieties (Eq. (6)) and the results are summarized in Table 2.



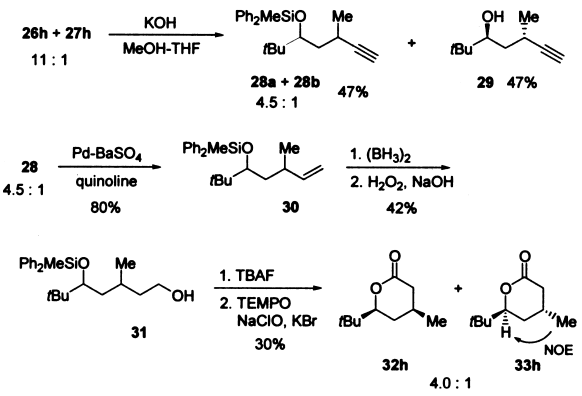
(5)



(6)

The reaction of the alkynyl ketone **25a** with Ph_2MeSiH gave the *anti*-product **26a** stereoselectively (**26a**/**27a**=6.5:1) (entry 1). The *anti*-selectivities were also observed in the reactions using other silanes although the selectivities slightly decreased (entries 2 and 3). Interestingly, stereoselectivities increased from 6.5:1 (R^2=Me) to 18:1 (R^2=^{t}Bu) as the substituent at R^2 position became bulkier (entries 4, 7, and 8). Not only aromatic ketones but also the aliphatic ketones **25g** and **25h** produced the corresponding *anti*-products selectively (entries 9 and 10). These results clearly indicate that the *anti* diastereoselectivity is widely observed in the $B(C_6F_5)_3$ catalyzed reduction of **25** with hydrosilanes.

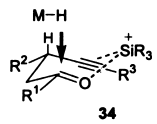
The stereostructure of **26a** was unambiguously determined by converting **26a** to *cis*-4-Methyl-6-phenyl-tetrahydropyran-2-one **32a**[11] via a similar route to that shown in Scheme 2. The stereostructures of **26h** and **27h**, which were obtained from the aliphatic ketone **25h**, were also determined by converting an 11:1 mixture of **26h** and **27h** to the 6-membered lactones **32h** and **33h**, as shown in Scheme 3. To remove the silyl group at the terminus position of alkyne, a mixture of **26h** and **27h** (11:1) was treated with KOH in MeOH–THF. The reaction gave the desired product **28** (*anti*/*syn*=4.5:1) in 47% yield together



Scheme 3.

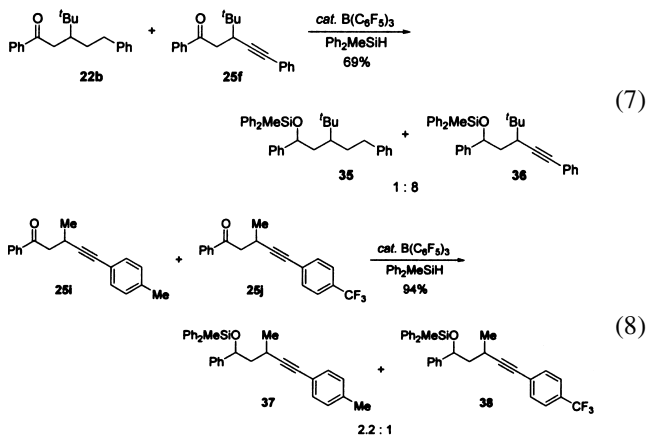
with the *anti*-alcohol **29** as a single diastereomer in 47% yield. This result indicates that the desilylation of TMS and Ph_2MeSi group of the *anti*-isomer **26h** proceeded more readily than that of the *syn*-isomer **27h**. Hydrogenation of the alkynyl part of **28** with Pd–$BaSO_4$ in the presence of quinoline gave **30** in 80% yield and the resulting alkene **30** was converted to the corresponding alcohol **31** in 42% yield by hydroboration-oxidative work-up. Deprotection of the Ph_2MeSi group of **31** by TBAF gave diol, which was subsequently oxidized with NaClO in the presence of a catalytic amount of TEMPO to give the lactones **32h** and **33h** in a ratio of 4.0:1 in 30% yield. Irradiation of the methyl group at the 4-position of pyran ring of **33h** enhanced the signal of the proton at the 6-position (2.6% NOE), whereas no enhancement was observed in the case of **32h**.

The *anti*-stereoselectivity in the reaction of **25** can be accounted for by the σ–π chelation model **34**, which involves hydride attack on the less hindered face of a conformationally locked, internally chelated intermediate.[2a] The stereoselectivities decreased as the silanes became small (entries 1–3 in Table 2). Presumably, when the sterically less-hindered silanes work as reducing agents (M–H in **34**), they would have smaller steric interactions with the chiral center rather than that in the 1,2-system since the chiral center in the present system is remote from the reaction center.



34

The proposed formation of σ–π chelation is supported not only by the 1,3-*anti* stereoselectivity observed in the reduction of **25**, but also by the chemoselectivity mentioned below. The competitive reaction of a 1:1 mixture of **22b** and **25f** with 1 equiv. of Ph_2MeSiH in the presence of catalytic amounts of $B(C_6F_5)_3$ gave selectively **36** over **35** in a ratio of 8:1 (Eq. (7)). The observed chemoselectivity suggested that the reactivity of **25f** would be enhanced by the formation of σ–π chelation.[4,12] We next examined the hydrosilylation of an equimolar mixture of **25i** and **25j**. If the electron-withdrawing effect of the alkyne is responsible for the enhanced reactivity of **25f**, **25j** would be more reactive than **25i** due to the presence of an electron-withdrawing CF_3 group at the para position, and therefore predominant formation of **38** should be observed. However, **37** was produced preferentially over **38** (Eq. (8)). Therefore, the reactivity difference in the present reaction is not due to the inductive effect but due to the coordinating effect of alkyne leading to formation of the σ–π chelation complex **34**.



Now it is clear that the σ–π chelation is operative not only in the 1,2- but also in the 1,3-asymmetric induction of certain acetylenic ketones. The *syn*-diastereoisomers obtained either exclusively or predominantly in the reaction of **4** or the *anti*-isomer in the reaction of **25** can be converted, upon reduction of the triple bond, to the *anti*-Felkin–Anh products which are not easily available through the ordinary reducing methods. We are now in a position to apply the σ–π coordination concept along with the well-known σ–σ chelation in order to control stereoselectivities.

3. Experimental

3.1. General procedures

All reactions sensitive to air or moisture were carried out under argon atmosphere in dry solvents purchased from Wako or Kanto chemicals. Analytical thin-layer chromatography (TLC) was performed using E. Merck Silica gel 60 F254 plates. Column chromatography was performed using Kanto Chemical silica gel 60N (spherical, neutral; 40–50 μm). IR spectra were recorded on a Shimazu FTIR-8200A spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer, and chemical shift values are reported in ppm (δ) downfield from tetramethylsilane with reference to internal residual $CHCl_3$ (^1H NMR, 7.26; ^{13}C NMR, 77.0). Coupling constants (*J*) are reported in hertz (Hz). Low- and high-resolution mass spectra (MS, HRMS) were recorded on a Hitachi M-2500S spectrometer.

3.2. General procedure for hydrosilylation

The preparation of **5h** is representative. To a stirred solution of **4h** (152 mg, 1 mmol) and Et_3SiH (0.16 mL, 1 mmol) in toluene (3 mL) was added a 0.05 M solution of $B(C_6F_5)_3$ in toluene (0.40 mL, 2 mol%) at 0°C. After the mixture was stirred for 60 min, the resulting solution was filtered through a short column chromatography of silica gel. The solvent was removed under reduced pressures to give a crude product, which was purified by silica gel column

chromatography using hexane/Et_2O=9/1 as eluent to give **5h** as a colorless oil (268 mg, 1 mmol) in nearly 100% yield.

3.2.1. 2-Methyl-1-phenyl-1-triethylsilyloxy-pentane (2+3). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20–7.36 (m, 5H), 4.45 (d, J=5.4 Hz, 1H, **2**), 4.37 (d, J=6.3 Hz, 1H, **3**), 0.43–1.74 (m, 26H). IR (neat); 3086, 3065, 3028, 2957, 2912, 1495, 1454, 1379, 1238, 1082, 1067, 1006, 743 cm^{-1}. MS (EI) m/z 291 (M^+-H, 0.1). HRMS calcd for $C_{18}H_{31}OSi$ (M^+-H) 291.2143, found 291.2117.

3.2.2. 4-Methyl-5-phenyl-5-triethylsilyloxy-pent-1-yne (5a+6a). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20–7.30 (m, 5H), 4.69 (d, J=5.1 Hz, 1H, **5a**), 4.47 (d, J=7.2 Hz, 1H, **6a**), 2.20–2.30 (m, 1H), 1.85–2.00 (m, 3H), 0.97 (d, J=6.6 Hz, 3H, **5a**), 0.87 (t, J=7.8 Hz, 9H), 0.51 (q, J=7.8 Hz, 6H). IR (neat); 2957, 2912, 2878, 1454, 1414, 1240, 1134, 1088, 1069, 826, 743, 702 cm^{-1}. MS (EI) m/z 259 ($M^+-C_2H_5$, 16). HRMS calcd for $C_{16}H_{23}OSi$ ($M^+-C_2H_5$) 259.1518, found 259.1529.

3.2.3. 4-Methyl-5-phenyl-5-diphenylmethylsilyloxy-pent-1-yne (5aa+6aa). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17–7.61 (m, 15H), 4.71 (d, J=5.4 Hz, 1H, **5aa**), 4.52 (d, J=7.2 Hz, 1H, **6aa**), 1.83–2.32 (m, 4H), 1.03 (d, J=6.9 Hz, 3H, **5aa**), 0.78 (d, J=6.9 Hz, 3H, **6aa**), 0.44, (s, Si-*Me*, 3H, **5aa**), 0.39 (s, Si-*Me*, 3H, **6aa**). IR (neat) 3069, 3026, 2963, 2910, 2874, 1454, 1429, 1256, 1119, 1088, 854, 739 cm^{-1}. MS (EI) m/z 330 ($M^+-C_3H_4$, 0.4). HRMS calcd for $C_{22}H_{22}OSi$ ($M^+-C_3H_4$) 330.1440, found 330.1435.

3.2.4. 5-Methyl-6-phenyl-6-triethylsilyloxy-hex-2-yne (5b+6b). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20–7.29 (m, 5H), 4.69 (d, J=4.8 Hz, 1H, **5b**), 4.47 (d, J=7.2 Hz, 1H, **6b**), 2.16–2.20 (m, 1H), 1.27–1.91 (m, 5H), 0.92 (d, J=6.6 Hz, 3H, **5b**), 0.87 (t, J=8.1 Hz, 9H), 0.78 (d, J=6.9 Hz, 3H, **6b**), 0.51 (q, J=8.1 Hz, 6H). IR (neat); 3063, 3028, 2957, 2912, 2876, 1454, 1414, 1240, 1134, 1086, 831, 742 cm^{-1}. MS (EI) m/z 273 ($M^+-C_2H_5$, 8). Anal. calcd for $C_{19}H_{30}OSi$: C, 75.43; H, 10.00. found: C, 75.44; H, 10.30.

3.2.5. 4-Methyl-1-phenyl-5-phenyl-5-triethylsilyloxy-pent-1-yne (5c+6c). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21–7.42 (m, 10H), 4.78 (d, J=5.1 Hz, 1H, **5c**), 4.55 (d, J=7.5 Hz, 1H, **6c**), 2.54 (d, J=6.0 Hz, 2H, **6c**), 2.46 (dd, J=13.5, 6.6 Hz, 1H, **5c**), 2.16 (dd, J=16.5, 6.9 Hz, 1H, **5c**), 1.93–2.04 (m, 1H), 0.83–1.05 (m, 12H), 0.45–0.57 (m, 6H). IR (neat); 3063, 3030, 2957, 2910, 2876, 1454, 1414, 1240, 1132, 1088, 827, 754 cm^{-1}. MS (EI) m/z 364 (M^+, 0.1). HRMS calcd for $C_{24}H_{32}OSi$ (M^+) 364.2222, found 364.2234. Anal. calcd for $C_{24}H_{32}OSi$: C, 79.06; H, 8.85, found: C, 78.72; H, 9.21.

3.2.6. 4-Methyl-5-phenyl-5-triethylsilyloxy-1-trimethylsilyl-pent-1-yne (5d+6d). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19–7.29 (m, 5H), 4.75 (d, J=4.8 Hz, 1H, **5d**), 4.51 (d, J=7.2 Hz, 1H, **6d**), 2.33 (m, 2H, **6d**), 2.27 (dd, J=16.5, 6.3 Hz, 1H, **5d**), 1.99 (dd, J=16.6, 6.8 Hz, 1H, **5d**), 1.84–1.90 (m, 1H), 0.94 (d, J=6.6 Hz, 3H, **5d**), 0.89 (t, J=4.1 Hz, 9H), 0.79 (d, J=6.6 Hz, 3H, **6d**), 0.51 (q, J=8.1 Hz, 6H), 0.17 (s, 9H). IR (neat); 3065, 3028, 2957, 2910, 2878, 2174, 1454, 1379, 1250, 1134, 843, 743 cm^{-1}. MS (EI) m/z 331 ($M^+-C_2H_5$, 3). Anal. calcd for $C_{21}H_{36}OSi$: C, 69.93; H, 10.06, found: C, 70.16; H, 10.33.

3.2.7. 4-Methyl-5-phenyl-5-triethylsilyloxy-hept-1-yne (5e+6e). Colorless oil; ^{1}H NMR (C_6D_6, 300 MHz) δ 3.22 (dt, J=3.6, 6.6 Hz, 1H, **5e**), 3.14 (q, J=5.4 Hz, 1H, **6e**), 1.35–1.94 (m, 4H), 0.93–1.02 (m, 2H), 0.40–1.02 (m, 15H), 0.17 (q, J=8.1 Hz, 6H). IR (neat); 2961, 2912, 2878, 1458, 1416, 1240, 1136, 1094, 1011, 841, 743 cm^{-1}. MS (EI) m/z 211 ($M^+-C_2H_5$, 42). HRMS calcd for $C_{12}H_{23}OSi$ ($M^+-C_2H_5$) 211.1518, found 211.1504.

3.2.8. 5-Cyclohexyl-4-methyl-5-triethylsilyloxy-pent-1-yne (5f+6f). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.46 (dd, J=3.2, 6.5 Hz, 1H, **5f**), 3.29 (m, 1H, **6f**), 2.03–2.36 (m, 2H), 1.95 (t, J=2.6 Hz, 1H, **5f**), 1.93 (t, J=2.6 Hz, 1H, **6f**), 1.60–1.93 (m, 6H), 0.86–1.43 (m, 12H), 0.62 (q, J=7.9 Hz, 6H). IR (neat); 2955, 2930, 1458, 1450, 1109, 1076, 1009, 738 cm^{-1}. MS (EI) m/z 265 ($M^+-C_2H_5$, 26). HRMS calcd for $C_{16}H_{29}OSi$ ($M^+-C_2H_5$) 265.2013, found: 265.1976.

3.2.9. 4-Methyl-5-*o*-methylphenyl-5-triethylsilyloxy-pent-1-yne (5g+6g). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.07–7.43 (m, 4H), 5.06 (d, J=3.9 Hz, 1H, **5g**), 4.71 (d, J=6.6 Hz, 1H, **6g**), 2.32 (s, 3H), 1.85–2.36 (m, 4H), 0.81–0.96 (m, 12H), 0.51 (q, J=8.1 Hz, 6H). IR (neat); 3067, 3024, 2957, 2912, 2878, 1460, 1414, 1240, 1136, 1076, 837, 746 cm^{-1}. MS (EI) m/z 302 (M^+, 0.1). Anal. calcd for $C_{19}H_{30}OSi$: C, 75.43; H, 10.00, found: C, 75.08; H, 10.26.

3.2.10. (4*R,5*S**)-4,6,6-Trimethyl-5-phenyl-5-triethylsilyloxy-hept-1-yne (5h).** Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.22 (d, J=1.6 Hz, 1H), 2.40–2.48 (m, 1H), 1.83–2.01 (m, 3H), 1.11 (d, J=6.5 Hz, 3H), 0.97 (t, J=7.8 Hz, 9H), 0.88 (s, 9H), 0.62 (q, J=7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 85.3, 84.1, 68.4, 36.6, 34.7, 26.7, 21.1, 21.0, 7.3, 5.7. IR (neat); 2957, 2912, 2878, 1458, 1418, 1238, 1128, 1099, 1034, 849, 808, 737 cm^{-1}. MS (EI) m/z 267 (M^+-H, 0.1). HRMS calcd for $C_{16}H_{31}OSi$ (M^+-H) 267.2143, found 267.2134.

3.3. Determination of stereostructure of 5a and 6a

To a solution of **5a** and **6a** (1.44 g, 5 mmol, **5a/6a**=4.9:1) in THF (10 mL) was added 1 M solution of TBAF in THF (10.2 mL, 10.2 mmol) at 0°C. The resulting mixture was stirred for 1 h at rt, and then H_2O was added. The mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=2/1 eluent) to give 2-methyl-1-phenyl-4-pentyn-1-ol (826 mg, 4.7 mmol) in 95% yield. To a suspension of NaH (150 mg, 6.3 mmol) in THF (10 mL) was added 2-methyl-1-phenyl-4-pentyn-1-ol (826 mg, 4.8 mmol) at rt. After the mixture was stirred for 10 min, *p*-methoxybenzyl chloride (0.8 mL, 6 mmol) and TBAI (184 mg, 0.5 mmol) were added. The resulting mixture was stirred for 2 h at 50°C, and then H_20 was added. The mixture was extracted with ether several times.

The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=19/1 eluent) to give 5-*p*-methoxybenzyloxy-4-methyl-5-phenyl-1-pentyne (**7**) (1.3 g, 4.4 mmol) in 93% yield. To a solution of **7** (885 mg, 3.0 mmol) in THF (5 mL) was added a 1 M solution of BH_3·THF in THF (3 mL, 3.0 mmol) at 0°C. The mixture was stirred for 2 h at 0°C, then excess hydride was decomposed by adding 0.5 mL of MeOH. To the resulting solution was added a solution of mCPBA (1.7 g, 10 mmol) in THF (10 mL) at 0°C and the mixture was stirred for 2 h at rt. The reaction was quenched by adding H_2O, and then the mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product. The crude product was treated with K_2CO_3 (0.76 g) and Me_2SO_4 (1.7 mL, 18 mmol) in acetone (20 mL) at rt. After the mixture was stirred for 2 h at 65°C, the reaction mixture was filtered through a pad of celite. The solvent was removed under the reduced pressure to give a crude product, which was purified by column chromatography (silica gel, hexane/ether=9/1 eluent) to give methyl 5-*p*-methoxybenzyloxy-4-methyl-5-phenyl-pentanoate (**8**) (479 mg, 1.4 mmol) in 47% yield by three steps. To a solution of **8** (72 mg, 0.21 mmol) in CH_3CN (2.0 mL) and H_2O (1.0 mL) was added CAN (230 mg, 0.42 mmol) at 0°C. After the mixture was stirred for 2 h at rt, the mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=1/1 eluent) to give a mixture of 4-methyl-6-phenyl-tetrahydro-pyran-2-one (**9a/10**=4.6:1) (35 mg, 0.18 mmol) in 87% yield.

3.3.1. 5-Methyl-6-phenyl-tetrahydro-pyran-2-one (9a+10). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26–7.41 (m, 5H), 5.50 (d, J=3.3 Hz, 1H, **9a**), 4.85 (d, J=9.6 Hz, 1H, **10**), 2.64–2.76 (m, 2H), 2.01–2.40 (m, 2H), 1.73–1.83 (m, 1H), 0.87 (d, J=6.3 Hz, 3H, **10**), 0.78 (d, J=7.2 Hz, 3H, **9a**). IR (neat); 3063, 3032, 2964, 2936, 2880, 1454, 1383, 1236, 1200, 1065, 748, 702 cm^{-1}. MS (EI) *m/z* 190 (M^+, 22). HRMS calcd for $C_{12}H_{14}O_2$ (M^+) 190.0994, found 190.0996.

3.3.2. *cis*-6-*tert*-Butyl-5-methyl-tetrahydro-pyran-2-one (9b). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.72 (d, J=7.2 Hz, 1H), 2.47 (ddd, J=4.8, 8.1, 16.8 Hz, 1H), 2.32 (ddd, J=4.5, 8.4, 17.1 Hz, 1H), 2.02 (sex, J=6.7 Hz, 1H), 1.85 (dddd, J=4.6, 5.6, 8.7, 13.1 Hz, 1H), 1.58 (dddd, J=4.8,7.5, 8.5, 13.3 Hz, 1H), 1.12 (d, J=6.6 Hz, 3H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.1, 92.5, 36.2, 28.7, 27.8, 27.7, 26.0, 21.4. IR (neat); 2961, 2874, 1740, 1464, 1244, 1082, 1061, 1005, 920, 733 cm^{-1}. MS (EI) *m/z* 170 (M^+, 1). HRMS calcd for $C_{10}H_{18}O_2$ (M^+) 170.1307, found 170.1287.

3.3.3. (4*R* *,5*R* *)-4-Isopropyl-5-phenyl-5-triethylsilyloxy-pent-1-yne (18). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.1–7.3 (m, 5H), 4.96 (d, J=5.4 Hz, 1H), 2.23 (ddd, J=2.6, 7.9, 16.9 Hz, 1H), 2.04 (ddd, J=2.7, 5.0, 16.9 Hz, 1H), 1.93 (t, J=2.7 Hz, 1H), 1.65–1.72 (m, 1H), 0.95 (d, J=6.9 Hz, 3H), 0.87 (m, 12H), 0.51 (q, J=7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.3, 127.8, 126.9, 126.6, 84.5, 75.6, 69.3, 51.1, 26.1, 22.5, 18.1, 15.6, 6.8, 4.8. IR (neat); 3030, 2957, 2912, 1456, 1238, 1099, 1070, 825, 731, 702 cm^{-1}. MS (EI) *m/z* 287 ($M^+-C_2H_5$, 5). HRMS calcd for $C_{18}H_{27}OSi$ ($M^+-C_2H_5$) 287.1830, found: 287.1848.

3.3.4. (1*R* *,2*R* *)-2-Isopropyl-1-phenyl-1-triethylsilyloxy-pentane (20). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.2–7.3 (m, 5H), 4.55 (d, J=6.6 Hz, 1H), 2.07 (m, 1H), 1.3–1.4 (m, 1H), 0.8–1.1 (m, 19H), 0.71 (t, J=6.9 Hz, 3H), 0.43 (q, J=8.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.1, 127.6, 127.0, 126.7, 77.0, 51.5, 27.7, 26.4, 22.3, 22.0, 17.2, 14.4, 6.8, 4.9. IR (neat); 3028, 2957, 2876, 1454, 1414, 1130, 1084, 827 cm^{-1}. MS (EI) *m/z* 291 ($M^+-C_2H_5$, 2). HRMS calcd for $C_{18}H_{31}OSi$ ($M^+-C_2H_5$) 291.2144, found: 291.2176.

3.3.5. 1-Diphenylmethylsilyloxy-3-methyl-1-phenyl-5-trimethylsilyl-pentane (23a+24a). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.20 (m, 15H), 4.74 (m, 1H, **22**), 4.71 (m, **21**), 1.92 (ddd, J=4.2, 9.0, 13.4 Hz, 1H, **21**), 1.69 (t, J=6.9 Hz, 1H, **22**), 1.65–0.86 (m, 4H), 0.81 (d, J=6.1 Hz, 3H, **22**), 0.73 (d, J=6.1 Hz, 3H, **21**), 0.44 (s, 3H, **22**), 0.43 (s, 3H, **21**), 0.40–0.20 (m, 2H), −0.04 (s, 9H, **21**), −0.10 (s, 9H, **22**). IR (neat); 3068, 2952, 1429, 1248, 1119, 698 cm^{-1}. MS (EI) *m/z* 446 (M^+, 0.06). HRMS calcd for $C_{28}H_{38}OSi_2$ (M^+) 446.2459, found 446.2484.

3.3.6. 3-*tert*-Butyl-1-diphenylmethylsilyloxy-1,5-diphenyl-pentane (23b+24b). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (m, 4H), 7.29 (m, 14H), 7.07 (d, J=6.9 Hz, 2H), 4.67 (dd, J=6.6, 7.7 Hz, 1H), 2.77 (ddd, J=5.1, 11.4, 13.5 Hz, 1H), 2.46 (ddd, J=5.4, 11.4, 13.8 Hz, 1H), 1.91 (ddd, J=4.2, 6.6, 14.1 Hz, 1H), 1.72 (m, 2H), 1.24 (m, 2H), 0.69 (s, 9H), 0.41 (s, 3H). IR (neat); 3069, 3026, 2961, 2868, 1494, 1454, 1429, 1367, 1253, 1119, 1065, 791, 698 cm^{-1}. MS (EI) *m/z* 492 (M^+, 0.01). HRMS calcd for $C_{34}H_{40}OSi$ 492.2848, found: 492.2816.

3.3.7. (3*R* *,5*R* *)-5-Diphenymethylsilyloxy-3-methyl-5-phenyl-1-trimethylsilyl-pent-1-yne (26a). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51 (m, 4H), 7.40–7.20 (m, 11H), 4.88 (dd, J=5.7, 7.6 Hz, 1H), 2.18 (ddq, J=5.8, 6.4, 8.7 Hz, 1H), 2.08 (ddd, J=5.7, 8.7, 12.6 Hz, 1H), 1.76 (ddd, J=5.8, 7.6, 12.6 Hz, 1H), 1.02 (d, J=6.4 Hz, 3H), 0.46 (s, 3H), 0.09 (s, 9H). ^{13}CNMR ($CDCl_3$, 75 MHz) δ 144.7, 136.3, 136.2, 134.4, 134.3, 129.5, 129.4, 128.0, 127.6, 127.4, 127.3, 126.4, 111.4, 85.0, 74.4, 48.3, 24.3, 21.3, 0.4, −2.5. IR (neat); 3069, 2961, 2168, 1429, 1250, 1119, 1082, 843, 698 cm^{-1}. MS (EI) *m/z* 442 (M^+, 2). HRMS calcd for $C_{28}H_{34}OSi_2$ (M^+) 442.2146, found 442.2133.

3.3.8. (3*R* *,5*S* *)-5-Diphenymethylsilyloxy-3-methyl-5-phenyl-1-trimethylsilyl-pent-1-yne (27a). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.20 (m, 15H), 5.00 (dd, J=2.3, 9.6 Hz, 1H), 2.80 (ddq, J=4.0, 7.0, 11.0 Hz, 1H), 1.91 (ddd, J=4.0, 9.6, 13.4 Hz, 1H), 1.62 (ddd, J=2.3, 11.0, 13.4 Hz, 1H), 1.16 (d, J=7.0 Hz, 3H), 0.54 (s, 3H), 0.15 (s, 9H). IR (neat); 3080, 2963, 2166, 1429, 1250, 1119, 1057, 843, 698 cm^{-1}. MS (EI) *m/z* 442 (M^+, 2). HRMS calcd for $C_{28}H_{34}OSi_2$ (M^+) 442.2146, found 442.2161.

3.3.9. 3-Methyl-5-phenyl-5-triethylsilyloxy-1-trimethylsilyl-pent-1-yne (26aa+27aa). Colorless oil; ^{1}H NMR

($CDCl_3$, 300 MHz) δ 7.20 (m, 5H), 4.92 (dd, J=2.4, 9.8 Hz, 1H, **27aa**), 4.85 (dd, J=5.6, 8.6 Hz, 1H, **26aa**), 2.15 (ddq, J=6.6, 6.8, 9.2 Hz,1H), 1.95 (ddd, J=5.6, 9.2, 12.0 Hz, 1H) 1.67 (ddd, J=6.8, 8.6,12.0 Hz, 1H), 1.16 (d, J=6.7 Hz, 3H, **27aa**), 1.11 (d, J=6.6 Hz, 3H, **26aa**), 0.87 (t, J=8.0 Hz, 9H), 0.52 (dq, J=3.6, 8.0 Hz,6H), 0.19 (s, 9H, **27aa**), 0.18 (s, 9H, **26aa**). IR (neat); 2957, 2878, 2168, 1493, 1456, 1416, 1250, 1086, 1057, 1005, 881, 758, 665 cm^{-1}. MS (EI) m/z 360 (M^+, 2). HRMS calcd for $C_{21}H_{36}OSi_2$ 360.2305, found: 360.2320.

3.3.10. 5-Dimethyphenylsilyloxy-3-methyl-5-phenyl-1-trimethylsilyl-pent-1-yne (26aaa+27aaa). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.48 (m, 2H), 7.29 (m, 8H), 4.95 (dd, J=2.4, 9.8 Hz, 1H, **27aaa**), 4.80 (dd, J=6.2, 7.3 Hz,1H, **26aaa**), 2.19 (ddq, J=5.8, 6.9, 8.3 Hz, 1H), 1.97 (ddd, J=6.2, 8.3, 2.3 Hz, 1H), 1.77 (ddd, J=4.1, 9.8, 12.9 Hz, **27aaa**), 1.66 (ddd, J=5.8, 7.3, 12.3 Hz, 1H, **26aaa**), 1.13 (d, J=6.9 Hz, 3H, **27aaa**), 1.03 (d, J=6.9 Hz, 3H, **26aaa**), 0.24 (d, J=9.0 Hz, 6H), 0.16 (s, 9H, **27aaa**), 0.11 (s, 9H, **26aaa**). IR (neat); 3069, 3028, 2961, 2899, 2168, 1454, 1427, 1250, 1117, 1084, 841, 700 cm^{-1}. MS (EI) m/z 380 (M^+, 0.3). HRMS calcd for $C_{23}H_{32}OSi_2$ 380.1992, found: 380.1985.

3.3.11. 5-Diphenylmethylsilyloxy-3-methyl-1,5-diphenyl-pent-1-yne (26b+27b). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.52 (m,4H), 7.32 (m,16H), 5.05 (dd, J=2.5, 9.6 Hz, 1H, **26b**), 4.97 (dd, J=5.9, 8.0 Hz, 1H, **27b**), 2.38 (ddq, J=5.6, 6.9, 8.6 Hz, 1H), 2.17 (ddd, J=5.9, 8.6, 12.6 Hz, 1H, **26b**), 2.00 (ddd, J=3.9, 9.6, 13.0 Hz, 1H, **27b**), 1.84 (ddd, J=5.6, 8.0, 12.6 Hz, 1H, **26b**), 1.72 (ddd, J=2.5, 10.1, 13.0 Hz, 1H, **27b**), 1.26 (d, J=7.2 Hz, 3H, **27b**), 1.12 (d, J=6.9 Hz, 3H, **26b**), 0.50 (s, 3H, **27b**), 0.46 (s, 3H, **26b**). IR (neat); 3069, 2966, 2361, 2443, 1489, 1456, 1429, 1256, 1119, 1082, 1053, 997, 835, 793, 698, 665 cm^{-1}. MS (EI) m/z 446 (M^+, 5). HRMS calcd for $C_{31}H_{30}OSi$ 446.2066, found: 446.2072.

3.3.12. 6-Diphenylmethylsilyloxy-4-methyl-6-phenyl-hex-2-yne (26c+27c). Colorless oil; ^1H NMR($CDCl_3$, 300 MHz) δ 7.54 (m, 6H), 7.35 (m, 9H), 4.97 (dd, J=3.0, 9.9 Hz, 1H, **27c**), 4.90 (dd, J=6.0, 7.5 Hz, 1H, **26c**) 2.77 (m, 1H), 2.15 (m, 1H), 2.07 (ddd, J=6, 8.9, 12.9 Hz, 1H), 1.91 (ddd, J=4.2, 9.9.13.8 Hz, 1H), 1.76 (d, J=2.4 Hz, 3H, **27c**), 1.74 (d, J=2.1 Hz, 3H, **26c**), 1.71 (m, 1H), 1.59 (ddd, J=3.0, 10.8, 13.5 Hz, 1H), 1.15 (d, J=6.9 Hz, 3H, **27c**), 1.02 (d, J=6.6 Hz, 3H, **26c**), 0.50 (s, 3H, **27c**), 0.48 (s, 3H, **26c**). IR (neat); 3069, 3049, 2964, 2918, 1429, 1119, 1088, 1069, 716, 793 cm^{-1}. MS (EI) m/z 384 (M^+, 3). HRMS calcd for $C_{26}H_{28}OSi$ 384.1909, found: 384.1901.

3.3.13. (3*R* *,5*R* *)-5-Diphenylmethylsilyloxy-3-methyl-5-phenyl-pent-1-yne (26d). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.52 (m, 4H), 7.32 (m, 11H), 4.88 (dd, J=6.0, 7.6 Hz, 1H), 2.21 (ddq, J=5.8, 6.6, 8.8 Hz, 1H), 2.10 (ddd, J=6.0, 8.8, 12.9 Hz, 1H), 1.97 (d, J=2.4 Hz, 1H), 1.74 (ddd, J=5.8, 7.6, 12.9 Hz, 1H), 1.04 (d, J=6.6 Hz, 3H), 0.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.9, 136.3, 136.1, 134.4, 134.3, 129.7, 129.6, 128.1, 127.7, 127.4, 126.4, 88.6, 73.8, 68.6, 47.2, 22.2, 20.6, −2.5. IR (neat); 3302, 3069, 3026, 2970, 2936, 2853, 2343, 1454, 1429, 1254, 1119, 1055, 858, 791, 739, 700 cm^{-1}. MS (EI) m/z 370 (M^+, 0.3). Anal. calcd for $C_{25}H_{26}OSi$: C, 81.03; H, 7.07. Found: C, 80.97; H, 7.23.

3.3.14. (3*R* *,5*S* *)-5-Diphenylmethylsilyloxy-3-methyl-5-phenyl-pent-1-yne (27d). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.51 (m, 4H), 7.31 (m, 11H), 4.96 (dd, J=2.7, 9.9 Hz, 1H), 2.78 (ddq, J=3.9, 7.2, 9.2 Hz, 1H), 1.99 (d, J=1.2 Hz, 1H), 1.91 (ddd, J=3.9, 9.9, 13.2 Hz, 1H), 1.63 (ddd, J=2.7, 9.2, 13.2 Hz, 1H), 1.17 (d, J=7.2 Hz, 3H), 0.48 (s, 3H.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.6, 136.4, 136.2, 134.6, 134.4, 129.6, 129.5, 128.1, 127.7, 127.6, 127.2, 126.2, 88.4, 74.0, 69.0, 48.0, 22.9, 21.2, −2.6. IR (neat); 3304, 3069, 3026, 2968, 2936, 1456, 1429, 1254, 1119, 1053, 847, 791, 734, 698 cm^{-1}. MS (EI) m/z 370 (M^+, 0.5). Anal. calcd for $C_{25}H_{26}OSi$: C, 81.03; H, 7.07, found: C, 80.88; H, 7.41.

3.3.15. 3-Cyclohexyl-1,5-diphenyl-5-diphenylmethylsilyloxy-pent-1-yne (26e+27e). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.54 (d, J=6.3 Hz, 4H), 7.32 (m, 16H), 5.01 (t, J=6.0 Hz, 1H), 2.14 (m, 2H), 1.93 (t, J=8.4 Hz, 1H), 1.71–1.54 (m, 5H), 1.26–1.11 (m, 6H), 0.46 (S, 3H). IR (neat); 2926, 2853, 1489, 1450, 1429, 1254, 1119, 1078, 1026, 854, 791 cm^{-1}. MS (EI) m/z 514 (M^+, 2). HRMS calcd for $C_{18}H_{38}OSi$ 514.2692, found: 514.2675.

3.3.16. 3-*tert*-Butyl-1,5-diphenyl-5-diphenylmethylsilyoxy-pent-1-yne (26f+27f). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (dd, J=1.5, 7.8 Hz, 4H), 7.28 (m, 16H), 5.09 (t, J=7.4 Hz, 1H), 2.04 (m, 2H), 1.74 (ddd, J=2.8, 5.8, 10.1 Hz, 1H), 0.88 (s, 9H), 0.47 (s, 3H). IR (neat); 3069, 2963, 2868, 1489, 1456, 1429, 1367, 1254, 1119, 1074, 1053, 885, 792, 737, 698 cm^{-1}. MS (EI) m/z 448 (M^+, 1). HRMS calcd for $C_{34}H_{36}OSi$ 488.2535, found: 488.2525.

3.3.17. 5-Cyclohexyl-5-diphenylmethylsilyloxy-3-methyl-1-trimethylsilyl-pent-1-yne (26g+27g). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58 (m, 4H), 7.38 (m, 6H), 3.95 (dt, J=3.0, 9.9 Hz, 1H, **27g**), 3.76 (dt, J=3.6, 9.9 Hz, 1H, **26g**), 2.5 (tq, J=6.9, 13.8 Hz, 1H) 1.70–1.43 (m, 8H) 1.21–1.04 (m, 5H), 1.09 (d, J=6.9 Hz, 3H, **27g**), 0.97 (d, J=6.9 Hz, 3H, **26g**), 0.71 (s, 3H, **27g**),0.66 (s, 3H, **26g**), 0.15 (s, 9H, **27g**) 0.13 (s, 9H, **26g**). IR (neat); 2959, 2928, 2853, 2164, 1450, 1429, 1250 cm^{-1}. MS (EI) m/z 448 (M^+, 0.4). HRMS calcd for $C_{18}H_{40}OSi_2$ 448.2618, found: 448.2598.

3.3.18. (3*R* *,5*R* *)-5-Diphenylmethylsilyloxy-3,6,6,-trimethyl-1-trimethylsilyl-hept-1-yne (26h). White crystals; mp 36–36.5°C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58 (m, 4H), 7.37 (m, 6H), 3.38 (dd, J=2.6, 8.5 Hz, 1H), 2.37 (ddq, J=2.1, 4.3, 9.8 Hz, 1H), 1.79 (ddd, J=4.3, 8.5, 13.1 Hz, 1H), 1.55 (ddd, J=2.6, 9.8, 13.1 Hz, 1H), 0.86 (s, 9H), 0.83 (d, J=2.1 Hz, 3H), 0.66 (s, 3H), 0.144 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.8, 134.6, 129.5, 127.7, 112.7, 79.0, 77.2, 40.5, 35.6, 26.3, 23.4, 19.7, 0.3, −1.7. IR (KBr); 2168, 2959, 2872, 1429, 1250, 1117, 1092, 1028, 860, 841 cm^{-1}. MS (EI) m/z 407 (M^+-CH_3, 0.7). Anal. calcd for $C_{26}H_{38}OSi_2$: C, 73.87; H, 9.06. Found: C, 73.62; H, 9.12.

3.3.19. (3*R* *,5*S* *)-5-Diphenylmethylsilyloxy-3,6,6-trimethyl-1-trimethylsilyl-hept-1-yne (27h). Colorless oil;

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59 (m, 4H), 7.35 (m, 6H), 3.76 (dd, J=0.9, 9.0 Hz, 1H), 2.31 (ddq, J=3.6, 6.9, 12.0 Hz, 1H), 1,56 (ddd, J=0.9 12.0 13.3 Hz, 1H), 1.45 (ddd, J=3.6, 9.0, 13.3 Hz, 1H), 0.98 (d, J=6.9 Hz, 3H), 0.81 (s, 9H), 0.74 (s, 3H), 0.16 (s, 9H). IR (neat); 2961, 2870, 2168, 1479, 1429, 1250, 1117, 1090, 841 cm^{-1}. MS (EI) m/z 407 (M^+-CH_3, 2). Anal. calcd for $C_{26}H_{38}OSi_2$: C, 73.87; H, 9.06, found: C, 73.68; H, 9.20.

3.4. Determination of stereostructure of 26a

To a solution of **26a** (2.2 g, 5.0 mmol) in THF (10 mL) was added a 1 M solution of TBAF in THF (10.2 mL, 10.2 mmol) at 0°C. The resulting mixture was stirred for 0.5 h at 0°C, and then H_2O was added. The mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=4/1 eluent) to give 3-methyl-1-phenyl-4-pentyn-1-ol (870 mg, 5.0 mmol) quantitatively. To a suspension of NaH (100 mg, 4.2 mmol) in DMF (5 mL) was added 3-methyl-1-phenyl-4-pentyn-1-ol (354 mg, 2.0 mmol) at rt. After the mixture was stirred for 1 h, *p*-methoxybenzyl chloride (0.4 mL, 3.0 mmol) was added. The resulting mixture was stirred for 3 h, and then NH_4Cl was added. The mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, CH_2Cl_2 eluent) to give 5-*p*-methoxybenzyloxy-3-methyl-5-phenyl-1-pentyne (532 mg, 1.8 mmol) in 90% yield. To a solution of 5-*p*-methoxybenzyloxy-3-methyl-5-phenyl-1-pentyne (294 mg, 1.0 mmol) in THF (3 mL) was added $BH_3{\cdot}SMe_2$ (0.1 mL, 1.0 mmol) at −15°C. The mixture was stirred for 3 h at 0°C, then excess hydride was decomposed by adding 0.2 mL of MeOH. To the resulting solution was added a solution of mCPBA (580 mg, 3.0 mmol) in THF (3.0 mL) at −78°C. The mixture was allowed to warm to rt and it was stirred for 2 h. The reaction was quenched by adding NH_4Cl, and then the mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was treated by sodium chlorite (325 mg, 3.6 mmol) in the presence of 2-methyl-2-butene (0.5 mL, 4.7 mmol) and NaH_2PO_4 (125 mg, 1.0 mmol) in ^{t}BuOH (7.5 mL) and H_2O (2 mL) to give crude 5-*p*-methoxybenzyl-3-methyl-5-phenyl-pentanoic acid. The crude product was treated with K_2CO_3 (1 g) and MeI (0.62 mL, 10 mmol) at rt. After the mixture was stirred for 2 h, the reaction was quenched with H_2O. The mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=5/1 eluent) to give methyl 5-*p*-methoxybenzyloxy-3-methyl-5-phenyl-pentanoate (125 mg, 0.37 mmol) in 37% yield by four steps. To a solution of methyl 5-*p*-methoxybenzyloxy-3-methyl-5-phenyl-pentanoate (124 mg, 0.36 mmol) in CH_3CN (1.5 mL) and H_2O (1.5 mL) was added CAN (394 mg, 0.72 mmol) at rt. After the mixture was stirred for 2 h, the mixture was extracted with ether several times. The combined extracts were dried (Na_2SO_4) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=1/1 eluent) to give *cis*-4-methyl-6-phenyl-tetrahydro-pyran-2-one (**32a**) (61 mg, 0.32 mmol) in 89% yield.

3.5. Determination of stereostructure of 26h and 27h

To a solution of **26h** and **27h** (2.32 g, 5.50 mmol, **26h/27h**=11:1) in MeOH (10 mL) and THF (1.5 mL) was added a 1 M solution of KOH in MeOH (6.6 mL, 6.6 mmol) at −10°C. The resulting mixture was stirred for 2.5 h at 0°C, and then H_2O was added. The mixture was extracted with ether several times. The combined extracts were dried ($MgSO_4$) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=30/1 eluent) to give **28** (898 mg, 2.57 mmol, *anti*/*syn*=4.5:1) in 47% yield together with (3R^*,5R^*)-2,2,5-Trimethyl-hept-6-yn-3-ol **29** (399 mg, 2.59 mmol) in 47% yield. To a solution of **28** (854 mg, 2.44 mmol, *anti*/*syn*=4.5:1) in AcOEt (5 mL) was added Pd−$BaSO_4$ which was poisoned with quinoline. The resulting mixture was stirred for 1 h at rt under hydrogen atmosphere, then it was filtrated through a pad of celite and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=30/1 eluent) to give 5-diphenylmethylsilyloxy-3,6,6-trimethyl-hept-1-ene **30** (686 mg, 1.95 mmol, *anti*/*syn*=4.9:1) in 80% yield. To a solution of **30** (651 mg, 1.85 mmol) in THF (5 mL) was added BH_3-Me_2S complex (17.5 mL, 1.85 mmol) at 0°C. The resulting mixture was stirred for 50 min at 0°C, and then H_2O was added. To the mixture was added 3 M solution of aqueous NaOH (2.47 mL, 7.40 mmol) and 30% H_2O_2 (1 mL, 8.80 mmol) at 0°C, successively. The resulting mixture was stirred for 1 h at rt, and then it was extracted with ether several times. The combined extracts were dried ($MgSO_4$) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=3/1 eluent) to give 5-diphenylmethylsilyloxy-3,6,6-trimethyl-heptan-1-ol **31** (287 mg, 0.78 mmol, *anti*/*syn*=5.3:1) in 42% yield. To a solution of **31** (256 mg, 0.75 mmol) in THF (3 mL) was added a 1 M solution of TBAF in THF (0.75 mL, 0.75 mmol) at 0°C. The resulting mixture was stirred for 1 h at rt, then H_2O was added. The mixture was extracted with ether several times. The combined extracts were dried ($MgSO_4$) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=1/1 eluent) to give 3,6,6-trimethyl-heptane-1,5-diol (130 mg, 0.75 mmol, *anti*/*syn*=6.4:1) quantitatively. To a solution of 3,6,6-trimethyl-heptane-1,5-diol (100 mg, 0.60 mmol) in CH_2Cl_2 (2 mL) was added a 1 M solution of aqueous KBr (0.05 mL, 0.05 mmol), TEMPO reagent (1.6 mg, 0.01 mmol), and 0.3 M solution of aqueous NaClO (2 mL, 0.60 mmol) at 0°C, successively. The resulting mixture was stirred for 1 h at rt, then it was extracted with ether several times. The combined extracts were dried ($MgSO_4$) and evaporated to leave a crude product, which was purified by column chromatography (silica gel, hexane/ether=2/1 eluent) to give a mixture of **32h** and **33h** (31 mg, 0.18 mmol, *anti*/*syn*=4.0:1) in 30 % yield.

3.5.1. 5-Diphenylmethylsilyloxy-3,6,6-trimethyl-hept-1-yne (28). Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59 (m, 4H), 7.45 (m, 6H), 3.74 (dd, J=1.4, 9.2 Hz, 1H,

28b), 3.40 (dd, *J*=2.4, 8.4 Hz, 1H, **28a**), 2.33 (dddq, *J*=2.4, 3.9, 6.6, 10.2 Hz, 1H,), 2.01 (d, *J*=2.1 Hz, 1H, **28b**), 1.98 (d, *J*=2.4 Hz, 1H, **28a**), 1.82 (ddd, *J*=3.9, 8.4, 13.2 Hz, 1H), 1.58 (ddd, *J*=2.4, 10.2, 13.2 Hz, 1H), 1.02 (d, *J*=6.9 Hz, 3H, **28b**), 0.85 (d, *J*=6.6 Hz, 3H, **28a**), 0.74 (s, 9H, **28b**), 0.68 (s, 9H, **28a**). IR (neat); 3308, 3071, 2959, 2872, 1429, 1254, 1117, 1090, 791, 737 cm^{-1}. MS (EI) *m/z* 350 (M^+, 0.1). HRMS calcd for $C_{23}H_{30}OSi$ 350.2066, found: 350.2033.

3.5.2. (3*R* *,5*R* *)-2,2,5-Trimethyl-hept-6-yn-3-ol (29). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.33 (ddd, *J*=2.1, 4.5, 9.6 Hz, 1H), 2.62 (m,1H), 2.14 (d, *J*=2.4 Hz, 1H), 2.06 (d, *J*=4.5 Hz, 1H), 1.66 (ddd, *J*=2.1, 7.5, 12.9 Hz, 1H), 1.53 (ddd, *J*=7.3, 9.6, 12.9 Hz, 1H), 1.22 (d, *J*=6.9 Hz, 3H), 0.89 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 89.7, 78.2, 69.0, 38.8, 34.8, 25.6, 23.7, 20.6. IR (neat); 3404, 3312, 2957, 2906, 2872, 2112, 1479, 1466, 1394, 1466, 1188, 980 cm^{-1}. MS (EI) *m/z* 154 (M^+, 5). HRMS calcd for $C_{10}H_{18}O$ 154.1358, found: 154.1345.

3.5.3. *cis*-4-Methyl-6-phenyl-tetrahydro-pyran-2-one (32a). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.30 (m, 5H), 5.32 (dd, *J*=2.9, 11.6 Hz, 1H), 2.82 (m, 1H), 2.32–2.12 (m, 3H), 1.53 (ddd, *J*=11.6, 13.2, 13.5 Hz, 1H), 1.09 (d, *J*=5.8 Hz, 3H). MS (EI) *m/z* 190 (M^+, 25). IR (neat); 1722, 1496, 1266, 1244, 995 cm^{-1}. HRMS calcd for $C_{12}H_{14}O_2$ (M^+) 190.0993, found 190.0993.

3.5.4. 6-*tert*-Butyl-4-methyl-tetrahydro-pyran-2-one (32h+33h). White crystals; mp 24–25°C; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.98 (dd, *J*=2.1, 7.1 Hz, 1H, **33h**), 3.95 (dd, *J*=1.8, 7.2 Hz, 1H, **32h**), 2.66 (ddd, *J*=1.2, 6.3, 13.5 Hz, 1H, **32h**), 2.51 (dd, *J*=5.4, 11.4 Hz, 1H, **33h**), 2.19 (m, 2H, **33h**), 1.99 (m, 2H, **32h**), 1.87 (m, 1H, **32h**), 1.82 (ddd, *J*=4.4, 7.1, 8.4 Hz, 1H, **33h**), 1.50 (ddt, *J*=0.6, 2.4, 8.4 Hz, 1H, **33h**), 1.18 (ddd, *J*=0.9, 7.2, 14.1 Hz, 1H, **32h**), 1.10 (d, *J*=3.9 Hz, 1H, **33h**), 1.04 (d, *J*=3.9 Hz, 1H). IR (KBr); 2959, 2874, 1481, 1458, 1367, 1242, 1207, 1074, 1003 cm^{-1}. MS (EI) *m/z* 170 (M^+, 0.01). HRMS calcd for $C_{10}H_{18}O$, found: 170.1341.

3.5.5. 5-Diphenylmethylsilyloxy-3-methyl-5-phenyl-1-*p*-tolyl-pent-1-yne (37). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (m, 6H), 7.34 (m, 9H), 7.15 (d, *J*=7.8 Hz, 2H), 7.07 (d, *J*=7.8 Hz, 2H), 5.05 (dd, *J*=3.0, 9.9 Hz, 1H, **37b**), 4.97 (dd, *J*=6.0, 8.1 Hz, 1H, **37a**), 2.36 (s, 3H), 2.35 (m, 1H), 2.34 (s, 3H), 2.16 (ddd, *J*=6.0, 9.3, 13.2 Hz, 1H), 1.83 (ddd, *J*=5.7, 8.1, 13.2 Hz, 1H), 1.24 (d, *J*=6.9 Hz, 3H), 1.11 (d, *J*=6.6 Hz, 3H), 0.50 (s, 3H, **37b**), 0.45 (s, 3H, **37a**). IR (neat); 3049, 3026, 2966, 1510, 1454, 1254, 1119, 1082, 797, 791 cm^{-1}. MS (EI) *m/z* 460 (M^+, 8). Anal. calcd for $C_{32}H_{32}OSi$: C, 83.43; H, 7.00, found: C, 83.17; H, 7.06.

3.5.6. 5-Diphenylmethylsilyloxy-3-methyl-5-phenyl-1-(4-trifluoromethylphenyl)-pent-1-yne (38). Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.48 (m, 6H), 7.27 (m, 13H), 4.95 (dd, *J*=3, 10.1 Hz, 1H, **36b**), 4.87 (dd, *J*=6.0, 7.8 Hz, 1H, **36a**), 2.48 (m, 1H, **38b**), 2.37 (ddq, *J*=5.5, 6.9, 8.9 Hz, 1H, **38a**), 2.12 (ddd, *J*=6.0, 8.9, 13.2 Hz, 1H, **38a**), 1.96 (ddd, *J*=4.1, 10.1, 13.4 Hz, 1H, **38b**), 1.79 (ddd, *J*=5.5, 7.8, 13.2 Hz, 1H, **38a**), 1.67 (ddd, *J*=3.0, 10.8, 13.4 Hz, 1H, **38b**), 1,21 (d, *J*=6.9 Hz, 3H, **38b**), 1.07 (d, *J*=6.9 Hz, 3H, **38a**), 0.41 (s, 3H, **38b**), 0.39 (s, 3H, **38a**). IR (neat); 3071, 1614, 1429, 1323, 1256, 1167, 1121, 1067, 700, 665 cm^{-1}. MS (EI) *m/z* 514 (M^+, 5). Anal. calcd for $C_{32}H_{29}F_3OSi$: C, 74.68; H, 5.68, found: C, 74.39; H, 5.68.

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