Crucial Role of the Conjugate Base for Silyl Lewis Acid Induced Mukaiyama Aldol Reactions

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The silyl Lewis acid induced Mukaiyama aldol reaction proceeds through each catalytic cycle under the influence of their conjugate bases; there is an especially significant difference between the low nucleophilic conjugate bases, $^{-}NTf_{2}$ and $^{-}CTf_{3}$, and the relatively high nucleophilic ^{-}OTf .

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Introduction

Mechanistic investigations for Lewis acid induced Mukaiyama aldol reactions have been demonstrated over the last decade.^[1-4] The possible and proposed pathways for the Lewis acid catalyzed Mukaiyama aldol reaction of silyl enol ether 2 with the aldehyde 1 are shown in Scheme 1. The reaction of the activated aldehyde 4 and the silvl enol ether 2 generates the silvloxycarbenium intermediate 5a or 5b.^[5] The intermolecular transfer of the silyl group to conjugate base X produces the metal aldolate 6 and the silvl Lewis acid ($R_{3}^{3}SiX$) derived from silvl enol ether (path A). This reaction pathway may account for the relatively high nucleophilicity of ligand X. When the metathesis between 6 and $R_{3}^{3}SiX$ is faster than the coordination of 1 to $R_{3}^{3}SiX$, the catalyst MX regenerates to give the silvl aldolate 3 (path C). On the other hand, the silvl Lewis acid catalysis eventuates from the slow metathesis (path **D**). Meanwhile, at the stage of intermediate 5a or 5b, the silvl group can be captured by the carbonyl substrate (path **B**). In this case, the Lewis acid catalyst regenerates directly. Among these possible reaction mechanisms, however, the common conclusions in notable mechanistic studies can be summarized as follows: (1) the generation of the silyl Lewis acid derived from silvl enol ether, and (2) one of the real catalysts is derived from this powerful silyl Lewis acid generated in situ rather than from the Lewis acid catalyst.^[2–4]

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Scheme 1.

Recently, we demonstrated that $Me_3SiNTf_2^{[6-9]}$ shows a strong catalytic activity for the Mukaiyama aldol reaction and the Sakurai-Hosomi allylation reaction.^[10] The conjugate base, $\neg NTf_2$, is well recognized as a strong electronwithdrawing and weakly coordinating counteranion, that is a ligand of low nucleophilicity.^[11] The counteranion of tris-(triflyl)methane ($\neg CTf_3$) is also known as a weakly coordinating counteranion, and the corresponding Brønsted acid (HCTf_3) was reported to be one of the strongest acids in the gas phase.^[12–14] To date, the mechanistic studies on Lewis acid induced Mukaiyama aldol reactions reported have lacked any focus on the role of conjugate base on the Lewis acid catalyst. Herein, we describe the diversity of the reaction mechanism, which is dependent on the conjugate base in silyl Lewis acid induced Mukaiyama aldol reactions.^[15]

Results and Discussion

Initially, we considered two extreme mechanisms for silvl Lewis acid induced Mukaiyama aldol reactions.^[4] These are illustrated in Scheme 2, where the Mukaiyama aldol reaction of $tBuMe_2Si$ -enol ether 9 with benzaldehyde (8) is an example and where a trimethylsilyl Lewis acid (Me₃SiX) is employed as the catalyst. In the first stage of the catalytic process, the addition of the silvl enol ether 9 to the aldehyde 8 should generate a siloxocarbenium ion intermediate 12a or 12b. In path A, tBuMe₂SiX is released from the intermediate 12a or 12b to give the Me₃Si aldolate 10 by intramolecular transfer of the counteranion X^- . Thus, tBuMe₂SiX emerges as the catalyst for the next reaction path. On the other hand, in path B, the Me₃SiX is released into the reaction medium to provide the *t*BuMe₂Si aldolate 11 by intramolecular transfer of tBuMe₂Si⁺. Therefore, Me₃SiX plays a role as a catalyst in path **B**. We assumed that this reaction mechanism can be expected from the ratio of the resulting silyl aldolates 10 and 11 when the reaction is conducted in the presence of 1.0 equiv. of Me₃SiX.

Mechanistic Study on the R₃SiNTf₂-Induced Mukaiyama Aldol Reaction

Firstly, the mechanistic details of the Me₃SiNTf₂-induced Mukaiyama aldol reaction were investigated. To clarify whether the transformation from 12a or 12b to a silyl aldolate occurs through X^{-} (path A) or $R_{3}Si^{+}$ transfer (path B), the aldol reaction of tBuMe₂Si enol ether 9 with benzaldehyde (8) was carried out in the presence of 1.0 equiv. Me₃-SiNTf₂ (Scheme 3). To control the strong Lewis acidity of Me₃SiNTf₂, Et₂O was used as a solvent for the experiments.^[10] Regardless of the addition of substrates and Me₃-SiNTf₂, only the tBuMe₂Si aldolate 11 was produced. In contrast, the reaction of Me₃Si enol ether 13 with 8 in the presence of 1.0 equiv. of tBuMe₂SiNTf₂ gave the exclusive formation of Me₃Si aldolate 10 in moderate yield. Furthermore, neither the silvl group of tBuMe₂Si aldolate 11 and Me₃Si aldolate 10 nor that of silvl enol ethers 9 and 13 was exchanged under similar reaction conditions.^[16] These experimental results would exclude the silyl catalysis path A derived from silvl enol ether, and indicate the possibility of path **B**.



Scheme 2.

Scheme 3.

However, the double-label crossover experiment, in a manner similar to that described by Carreira and Denmark,^[2,3] demonstrated the feasibility of path A (Scheme 4). Two silyl enol ethers of similar steric and electronic demands (9 and 14) were prepared and combined with benzal-dehyde (8) in the presence of 1 mol-% of Me₃SiNTf₂. The reaction was complete at -78 °C within 15 min, and the product composition was determined by GC analysis. A mixture of scrambled silyl aldolates was isolated in a ratio of 1:1.0:0.89:0.81 (11/15/16/17). Control experiments showed that neither the starting silyl enol ethers 9 and 14 nor the silyl aldolates 11 and 15 were exchanged under-



Total >99% yield, 11/15/16/17 = 1/1.0/0.89/0.81

Scheme 4.

Table 1. Symunic Selectivity in the Mukaiyania aluor reaction	Table 1.	syn/anti	<i>i</i> Selectivity	in the	Mukaiyama	aldol	reaction
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O Ph	+ R ² - Ca - C	atalyst (3 mol%) Et ₂ O, −78 °C	$R_3SiO O$ $Ph \xrightarrow{H^3} R^2$
8	18, 19, 20, 21		89 - 90% yield
Entry	Silyl Enol Ether	Catalyst ^[c]	syn/anti ^[d]
1	OSiMe ₃	Me ₃ SiNTf ₂	60/40
2	18	tBuMe ₂ SiN	$Tf_2 = 62/38$
3	OSi <i>t</i> BuMe ₂	Me ₃ SiNTf ₂	52/48
4	19	tBuMe ₂ SiN	Tf ₂ 51/49
5	OSiMe₃	Me ₃ SiNTf ₂	61/39
6	Ph 20	$t Bu Me_2 Si N$	Tf ₂ 58/42
7	OSi <i>t</i> BuMe₂	Me ₃ SiNTf ₂	87/13
8	Ph 21	tBuMe ₂ SiN	Tf ₂ 87/13

[a] (E)/(Z) = 1:99, determined by ¹H NMR spectroscopy. [b] (E)/(Z) = 4:96, determined by ¹H NMR spectroscopy. [c] Prepared in situ by the treatment of AgNTf₂ with the corresponding silyl chloride in Et₂O at room temp. for 0.5 h. [d] Determined by ¹H NMR spectroscopy.

similar conditions. These facts unambiguously preclude path B and suggest the silyl group transfer between intermediates.

While the intermolecular silyl group transfer is in conflict with the afore-mentioned results for the control experiments in Scheme 3, the investigations of the *synlanti* selectivities in R_3SiNTf_2 -induced aldol reactions advocates the exchange of the silyl group in the reaction course. The reactions of (*E*)- and (*Z*)-silyl enol ethers **18–21** with aldehyde **8** were conducted in the presence of 3 mol-% of R_3SiNTf_2 (Table 1). Similar *synlanti* ratios of the products were obtained, which are independent of the size of the trialkylsilyl group of the catalyst. In contrast, the diastereoselectivities correlate to the size of the silyl groups of the silyl enol ether. These experimental data indicate that the catalysis is initiated by the silyl group of silyl enol ether.

Plausible Mechanism for the R₃SiNTf₂-Induced Mukaiyama Aldol Reaction

In order to explain the results of the control experiments (Scheme 3) and the crossover experiment (Scheme 4), it was imperative to postulate another mechanism for the R₃SiNTf₂-induced Mukaiyama aldol reaction, since neither path A nor B could account for the results. With the low nucleophilicity of -NTf2 in mind, we proposed the novel reaction mechanism E for the R₃SiNTf₂-induced Mukaiyama aldol reaction (Scheme 5). In path Ea, the direct interception of the silvl group $(-SiR_{3}^{3})$ in intermediate 23a or 23b by aldehyde 1 would provide the silvloxycarbenium cation intermediate 24. Nucleophilic attack of silvl enol ether 2 on 24 would generate the other silvloxycarbenium cation intermediate 26, and the reaction would proceed in the same manner. Additionally, we considered the role of Et_2O for the alternative reaction mechanism (path Eb). Since Et₂O can coordinate to a silvl Lewis acid, a highly reactive silyloxycarbenium cation, $R_{3}^{3}Si-OEt_{2}^{+}$ [counteranion]^{-,[17]} may be generated in the reaction medium, especially with the low nucleophilic counteranion -NTf₂.

In this reaction pathway E, two possible counteranions could be possible. One is the silicate anion 25, which bears an NTf₂ group on the silvl aldolate, the other is -NTf₂, which is released from the silvl Lewis acid. In both cases, it is difficult to distinguish path E from path D. However, we envisaged that reaction path **D** could not reasonably explain the results of the control experiments in Scheme 3. The reaction in the presence of 1.0 equiv. of silvl triflylimide should produce a definite amount of silyl aldolate by path **D**, which bears the silvl group of silvl triflylimide. The real activation species in path E would be the silyloxycarbenium cation intermediate 24 or 26, and either would be expected to be a stronger Lewis acid than Me₃SiNTf₂ and tBuMe₂S $iNTf_2$.^[17] Our proposed mechanism *E* and our hypothesis satisfactorily interprets all the control experiments and the double-label crossover experiments.



Scheme 5.

Mechanistic Study on the R₃SiCTf₃-Induced Mukaiyama Aldol Reaction

Next, the mechanistic study of the R_3SiCTf_3 -induced Mukaiyama aldol reaction was inspected. Me₃SiCTf₃ and *t*BuMe₂SiCTf₃ were prepared in situ by the treatment of Me₃SiCl and *t*BuMe₂SiCl with AgCTf₃^[18] in Et₂O at room temperature, respectively, and were used without further purifications. The control experiments were conducted in a manner similar to that for R_3SiNTf_2 (Scheme 6). In the case

of the reaction of $tBuMe_2Si$ enol ether 9 with benzaldehyde (8) in the presence of 1.0 equiv. of Me_3SiCTf_3, $tBuMe_2Si$ aldolate 11 was produced exclusively in 63% yield. No Me_3Si aldolate was detected by ¹H NMR spectroscopy or MS analysis. In contrast, the use of 1.0 equiv. of $tBuMe_2SiCTf_3$ for the reaction of Me_3Si enol ether 13 with benzaldehyde (8) produced Me_3Si aldolate 10 in 34% yield.

A double-label crossover experiment was also conducted for the Me_3SiCTf_3 -induced Mukaiyama aldol reaction under the same reaction conditions as those employed for Me_3 -



Scheme 6.

SiNTf₂ (Scheme 7). Four silyl aldolates (11, 15–17) were produced in quantitative yield, and the ratio was similar to the results of Me_3SiNTf_2 . The small amount of desilylated aldol 27 was confirmed by GC analysis and may indicate



Total >99% yield, 11/15/16/17/27 = 1/1.3/1.1/0.86/0.03

Scheme 7.

Table 2. Control experiment for Me₃SiOTf-induced Mukaiyama aldol reaction.

the intermediate **25**. The same trend of products in the R_3SiCTf_3 - as in the R_3SiNTf_2 -induced Mukaiyama aldol reaction led us to the conclusion that the former also proceeds through path *E*. The low nucleophilicity of $-CTf_3$ akin to that of $-NTf_2$ probably contributes to the reaction mechanism.

Mechanistic Study on the R₃SiOTf-Induced Mukaiyama Aldol Reaction

Finally, we performed a mechanistic study of the R_3Si -OTf-induced Mukaiyama aldol reaction.^[4,19] The control reactions analogous to those of Scheme 3 were conducted using Me₃SiOTf (Table 2). When the reaction was carried out at -100 °C for 15 min, Me₃Si aldolate **10** was obtained exclusively in 24% yield, along with the starting materials (Table 2, Entry 1). With the Me₃SiNTf₂- or Me₃SiCTf₃-induced reaction, the ratio of silyl aldolates **10** and **11** was completely reversed with respect to that obtained with Me₃SiOTf. The ratio of produced silyl aldolates suggests that

	O OSi <i>t</i> BuMe ₂ Ph + Ph -	$\underbrace{\text{Me}_{3}\text{SiOTf (1.0 equiv.)}}_{\text{Et}_{2}\text{O, conditions}} \underbrace{\text{Me}_{3}\text{SiO}}_{\text{Ph}} \underbrace{\text{Ph}}_{\text{Ph}} + \underbrace{\text{HuMe}_{2}\text{SiO}}_{\text{Ph}} \underbrace{\text{O}}_{\text{Ph}} \underbrace{\text{Ph}}_{\text{Ph}} + \underbrace{\text{Ph}}_{\text{Ph}} \underbrace{\text{Ph}} \underbrace{\text{Ph}} \underbrace{\text{Ph}}_{\text{Ph}} \underbrace{\text{Ph}} \underbrace{Ph} \underbrace{\text{Ph}} \underbrace{\text{Ph}} \underbrace{\text{Ph}} \underbrace{Ph} \underbrace{Ph} \underbrace{\text{Ph}} \underbrace{Ph} $	
	8 9	10 11	
Entry	Conditions	Isolated yield [%]	Ratio 10/11 ^[a]
1	−100 °С, 0.5 h, 0.02 м	24	>99:1
2	−78 °C, 5 h, 0.06 м	61	83:17

[a] Determined by ¹H NMR spectroscopy for the mixture of **10** and **11**.



Scheme 8.

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the Me₃SiOTf-induced Mukaiyama aldol reaction proceeds through path *A*. The starting materials are not completely consumed upon prolonged stirring at -78 °C even with a concentration threefold higher than that in the reaction at -100 °C, and the mixture of **10** and **11** was obtained in 61% yield at a molar ratio of 83:17 (Table 2, Entry 2).

It seems that the result of Entry 2 does not match path A towing to the generation of tBuMe₂Si aldolate 11. However, further control experiments offered an idea to explain the reaction mechanism adequately by path A. For instance, tBuMe₂SiOTf cannot promote the reaction of tBuMe₂Si enol ether with benzaldehyde (8) under similar reaction conditions as those in Table 2. Furthermore, control experiments of the scrambling for the silvl groups among silvl aldolates 11, silvl enol ether 9 and Me₃SiOTf showed that neither 9 and Me₃SiOTf nor 11 and Me₃SiOTf were exchanged under similar conditions. On the basis of our observations and Bosnich's proposed pathway,^[4] the mechanism for the R₃SiOTf-induced Mukaiyama aldol reaction could be concluded to be an intramolecular transfer of -OTf (path A), and the tBuMe₂SiOTf catalysis is shown in Scheme 8 as a model case. From intermediate 28a or 28b, Me₃SiOTf is released into the reaction medium by the intramolecular transfer of OTf, and the reaction is promoted in the same manner. Since Me₃SiOTf possesses a stronger reactivity than tBuMe₂SiOTf, the Me₃Si aldolate 10 would be generated through Me₃SiOTf catalysis under the reaction conditions shown in Table 2. In the case of the R₃Si-OTf-induced Mukaiyama aldol reaction, the formation of Me₃Si·OEt₂⁺ with ⁻OTf can be excluded because of the relatively high nucleophilicity of -OTf.^[20]

Conclusion

We have demonstrated the diversity of the mechanism for silyl Lewis acid induced Mukaiyama aldol reactions that are dependent on the conjugate base, and have proposed a novel reaction mechanism *E*. In the case of R_3SiNTf_2 - or R_3SiCTf_3 -induced Mukaiyama aldol reactions, the low nucleophilicity of their conjugate bases prevent not only the intramolecular transfer of X⁻ (path *A*) but also that of the R_3Si group to the carbonyl oxygen atom (path *B*). On the other hand, the high nucleophilicity of $-OTf^{[17]}$ causes the intramolecular transfer of X⁻ and generates the silyl Lewis acid derived from silyl enol ether.

Experimental Section

General Remarks: Unless otherwise stated, reactions were performed in flame-dried glassware under argon. Infrared (IR) spectra were recorded with a Shimadzu FTIR-8100 spectrometer and Nicolet 20 SXB FTIR spectrometer, and are reported in reciprocal centimeters (cm⁻¹). ¹H NMR spectra were measured with Bruker DMX-500 (500 MHz), 400 (400 MHz), and Varian Gemini-300 (300 MHz) spectrometers at room temperature. Data are reported as follows: chemical shift in ppm from internal Me₄Si (δ = 0.0 ppm) on the δ scale, coupling constant *J* [Hz], integration, and assignment. ¹³C NMR spectra were recorded with Bruker DMX-500

(125 MHz) and 400 (100 MHz), and Varian Gemini-300 (75 MHz) spectrometers at room temperature. Chemical shifts are reported in ppm from the solvent resonance employed as the internal standard (CDCl₃ at δ = 77.00 ppm). Analytical gas–liquid phase chromatography (GC) was performed with a Shimadzu Model GC-17A Ver. 3 instrument with a flame-ionization detector and a capillary column of TC-1 (100% dimethylpolysiloxane, 0.25 mm×30 m, GL Sciences Inc.) using helium as carrier gas (116.0 kPa). Measurement conditions: Injection temp. 150 °C; column temp. 70 °C for 5 min, +10 °C/min for 18 min, and 250 °C for 7 min. High-resolution mass spectra data were obtained from the Research Resources Center Mass Spectrometry Laboratory at University of Illinois at Chicago. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254 0.25 mm) were used. The products were purified by flash column chromatography on silica gel (E. Merck 9325). In experiments that required dry solvents, CH₂Cl₂, Et₂O and THF were stored under dry argon after being distilled from calcium hydride (CH₂Cl₂) or sodium metal using benzophenone ketyl as an initiator (Et₂O and THF), and were then used. Simple chemicals (if not described in this Exp. Sect.) were purchased and used. AgNTf₂ and AgCTf₃ were prepared according to Shreeve's procedure.[18,21]

Preparation of Me₃SiNTf₂^[6] Me₃SiNTf₂ was prepared from freshly distilled Me₃SiCl (1.2 equiv.) and AgNTf₂ (1.0 equiv.) in CH₂Cl₂ and purified by distillation (80–84 °C, 7 Torr). Me₃SiNTf₂ was also prepared from freshly distilled Me₃SiCl (1.2 equiv.) and AgNTf₂ (1 equiv.) in Et₂O and used for the reaction without further purification.

Preparation of tBuMe₂SiNTf₂, Me₃SiCTf₃, and tBuMe₂SiCTf₃: These silyl Lewis acids were prepared in situ according to the procedure for Me₃SiNTf₂ using the corresponding silyl chloride and silver salt.

General Procedure for the Control Experiments (Schemes 3 and 6, Table 2): To a solution of in situ prepared $tBuMe_2SiNTf_2$ (1.0 mmol) in dry Et₂O (50 mL) was added freshly distilled benzaldehyde (**8**, 102 µL, 1.0 mmol) at -100 °C. Subsequently, Me₃Si enol ether **13** (281 mg, 1.2 mmol) was added in a dropwise fashion at the same temperature. After stirring for 0.5 h, pyridine (200 µL) and saturated aqueous NaHCO₃ (20 mL) were added. The mixture was warmed to room temperature and extracted with Et₂O (2×20 mL). The combined organic extracts were dried with Na₂SO₄, concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane/ EtOAc, 10:1) to give Me₃Si aldolate **10** (185 mg, 62% yield). The corresponding *t*BuMe₂Si aldolate **11** was not formed in a detectable amount (¹H NMR and GC analysis).

General Procedure for the Silyl Group Scrambling Control Experiments (Schemes 3, 4, 6 and 7, Table 2): To a solution of 3-(*tert*-butyldimethylsilyloxy)-1,3-diphenylpropan-1-one (11, 340 mg, 1.0 mmol) in Et₂O (50 mL) was added freshly distilled Me₃SiOTf (184 μ L, 1.0 mmol) at -100 °C. The reaction mixture was stirred for 0.5 h, and quenched with pyridine (200 μ L) and saturated aqueous NaHCO₃ (20 mL). The mixture was then warmed to room temperature and extracted with Et₂O (2×20 mL). The combined organic extracts were dried with Na₂SO₄, and concentrated under reduced pressure. The corresponding Me₃Si aldolate 10 was not formed in a detectable amount (¹H NMR and GC analysis).

Procedure for the Silyl Group Scrambling Control Experiments of Silyl Enol Ether 9 and 14 (Schemes 4 and 7): To a solution of 9 (1.8 mmol, 422 mg), 14 (1.8 mmol, 498 mg), and Me₃SiNTf₂ (0.03 mmol, prepared in situ by the treatment of Me₃SiCl and AgNTf₂) in Et₂O (6.0 mL) was added benzaldehyde (0.3 mmol,

30 μ L) at -78 °C. The reaction mixture was stirred at -78 °C for 15 min and quenched with pyridine (5 drops) followed by saturated aqueous NaHCO₃ (15 mL). The mixture was warmed to room temperature and extracted with EtOAc. The combined organic layers were dried with Na₂SO₄ and concentrated. No silyl group exchange was observed by ¹H NMR analysis of the residue.

General Procedure for the Double-Label Crossover Experiment (Schemes 4 and 7): To a solution of Me₃SiNTf₂ (11 mg, 0.03 mmol), silyl enol ether 9 (421 mg, 1.8 mmol), and silyl enol ether 14 (497 mg, 1.8 mmol) in Et₂O (6 mL) was added freshly distilled benzaldehyde (8, 305 µL, 3.0 mmol) at -78 °C. The reaction mixture was stirred for 15 min, quenched with pyridine (5 drops) followed by saturated aqueous NaHCO₃ (5 mL), warmed to room temperature, and extracted with Et_2O (3×10 mL). The combined organic layers were dried with Na₂SO₄, concentrated in vacuo, and purified by flash column chromatography on silica gel (hexane/ EtOAc, 50:1) to give a mixture of 11, 15, 16, and 17 (1.15 g, >99% yield). The ratio of products was determined as 1:1.0:0.89:0.81 by ¹H NMR and GC analysis. The GC peaks were assigned on the basis of the $[M - 15]^+$ or $[M + H]^+$ peak as well as expected fragmentation patterns. GC/MS: $tBuMe_2Si$ aldolate 11; $t_R = 20.5$ min, $m/z = 341 [M + H]^+$. ThexylMe₂Si aldolate **15**; $t_R = 22.8 \text{ min}, m/z$ = 383 [M + H]⁺. ThexylMe₂Si aldolate 16; $t_{\rm R}$ = 22.5 min, m/z = 353 $[M - 15]^+$. tBuMe₂Si aldolate 17; $t_R = 20.9 \text{ min}, m/z = 355 [M]$ + H]+.

General Procedure for the Mukaiyama Aldol Reaction (Table 1): To a solution of in situ prepared $tBuMe_2SiNTf_2$ (0.03 mmol) in Et₂O (2 mL) was added freshly distilled (1-cyclohexenyloxy)trimethylsilane (**18**, 233 µL, 1.2 mmol) at -78 °C, followed by benzaldehyde (**8**, 102 µL, 1.0 mmol). The reaction mixture was stirred at -78 °C for 20 min, quenched with pyridine (5 drops) and saturated aqueous NaHCO₃ (5 mL), and extracted with Et₂O (2×10 mL). The combined organic layers were dried with Na₂SO₄, concentrated in vacuo, and purified by flash column chromatography on silica gel (hexane/EtOAc, 50:1) to give a diastereomer mixture of the corresponding silyl aldolate (277 mg, >99% yield, *synlanti* = 62:38 determined by ¹H NMR). In all cases, the diastereoselectivities were determined by ¹H NMR of the diastereomer mixtures, according to reported values.

Dimethyl(thexyl)([1-(p-tolyl)vinyloxylsilane (14): To a solution of dimethyl(thexyl)silyl chloride (3.5 mL, 18 mmol) and silver trifluoromethanesulfonate (4.2 g, 16.5 mL) in CH₂Cl₂ (20 mL) was added methyl 4-methylphenyl ketone (2.0 mL, 15 mmol) and triethylamine (4.2 mL, 30 mmol) at 0 °C. The reaction mixture was warmed to room temperature, stirred for 3 h, quenched with a saturated aqueous NaHCO3 solution (10 mL), and extracted with Et2O $(3 \times 50 \text{ mL})$. The combined organic layers were dried with Na₂SO₄, concentrated in vacuo, and purified by flash column chromatography on silanized silica gel (column wrapped with a dry ice jacket, hexane/EtOAc, 50:1) to give 14 (3.36 g, 81% yield) as a colorless oil. IR (film): v = 2959, 1614, 1511, 1465, 1314, 1301, 1183, 1111, 832, 781 cm⁻¹. ¹H NMR (300 MHz, room temp., CDCl₃): $\delta = 0.23$ (s, 6 H, Me), 0.95 (m, 12 H, Me), 1.74 (m, 1 H, CH for thexyl group), 2.35 (s, 3 H, ArCH₃), 4.35 (d, J = 1.5 Hz, 1 H, CH₂), 4.83 (d, J = 1.5 Hz, 1 H, CH₂), 7.13 (d, J = 8.7 Hz, 2 H, *m*-H for *p*tolyl group), 7.50 (d, J = 8.7 Hz, 2 H, o-H for p-tolyl group) ppm. ¹³C NMR (100 MHz, room temp., CDCl₃): $\delta = -2.7$ (CH₃Si), 18.5 [(CH₃)₂CSi], 20.2 [(CH₃)₂CH], 21.2 (CH₃Ph), 25.1 [SiC(CH₃)₂CH], 33.9 [(CH₃)₂CH], 90.3 (CH₂), 125.2 (*o*-CH for *p*-tolyl group), 128.7 (m-CH for p-tolyl group), 135.2 [C-CSi(CH₂)], 137.9 (p-CH for ptolyl group), 155.9 [p-tolylC-Si(CH₂)] ppm.

3-[Dimethyl(thexyl)silyloxy]-3-phenyl-1-(*p***-tolyl)propan-1-one** (15): To a solution of in situ prepared Me₃SiNTf₂ (ca. 0.005 mmol) and

silvl enol ether 14 (166 mg, 0.6 mmol) in Et₂O (1 mL) was added freshly distilled benzaldehyde (8, 51 μ L, 0.5 mmol) at -78 °C. The reaction mixture was stirred for 15 min, quenched with pyridine (2 drops) and a saturated aqueous NaHCO₃ solution (5 mL), then warmed to room temperature, and extracted with Et_2O (3 × 50 mL). The combined organic layers were dried with Na₂SO₄, concentrated in vacuo, and purified by flash column chromatography on silica gel (hexane/EtOAc, 50:1) to give 15 (195 mg, 99% yield) as a colorless oil. TLC (hexane/EtOAc, 4:1): $R_f = 0.64$. GC: $t_R = 22.8$ min. IR (film): $\tilde{v} = 2959$, 1684, 1607, 1254, 1089, 1071, 939, 831, 810, 777 cm⁻¹. ¹H NMR (300 MHz, room temp., CDCl₃): $\delta = -0.20$ (s, 3 H, Me), -0.01 (s, 3 H, Me), 0.71 (s, 6 H, Me), 0.77 (d, J = 6.9 Hz, 3 H, Me), 0.78 (d, J = 6.9 Hz, 3 H, Me), 1.51 (sept, J = 6.9 Hz, 1 H, CH for thexyl group), 2.41 (s, 3 H, ArC H_3), 2.92 (dd, J = 3.9, 15.0 Hz, 1 H, CH₂), 3.55 (dd, J = 8.4, 15.0 Hz, 1 H, CH₂), 5.35 (dd, J = 3.9, 8.4 Hz, 1 H, CH), 7.23–7.42 (m, 7 H, Ar), 7.86 (d, J = 8.1 Hz, 2 H, Ar-*H* for phenyl) ppm. $C_{24}H_{34}O_2Si$ (382.64): calcd. C 75.34, H 8.96; found C 75.32, H 8.99.

3-(tert-Butyldimethylsilyloxy)-3-phenyl-1-(p-tolyl)propan-1-one (17): To a solution of tert-butyldimethylsilyl trifluoromethanesulfonate (1.98 mL, 8.3 mmol) and triethylamine (2.1 mL, 15 mmol) in CH_2Cl_2 (20 mL) was added methyl 4-methylphenyl ketone (1.0 mL, 7.5 mmol) at 0 °C. The reaction mixture was warmed to room temperature, stirred for 3 h, quenched with a saturated aqueous NaHCO₃ solution (10 mL), and extracted with Et_2O (3×30 mL). The combined organic layers were dried with Na₂SO₄, concentrated in vacuo, and purified by flash column chromatography on silanized silica gel (column wrapped with a dry ice jacket, pentane) to give tert-butyldimethyl(1-p-tolylvinyloxy)silane (1.16 g, 63% yield) as a colorless oil. IR (film): $\tilde{v} = 2930, 2361, 1616, 1315, 1302, 1254$, 1111, 1014, 836, 780 cm⁻¹. ¹H NMR (400 MHz, room temp., $CDCl_3$): $\delta = 0.20$ (s, 6 H, CH_3Si), 1.00 [s, 9 H, $(CH_3)C$], 2.34 (s, 3 H, ArC H_3), 4.36 (d, J = 1.6 Hz, 1 H, CH₂), 4.84 (d, J = 1.6 Hz, 1 H, CH₂), 7.12 (d, J = 6.5 Hz, 2 H, *m*-H for *p*-tolyl group), 7.50 (d, J = 6.5 Hz, 2 H, o-H for p-tolyl group) ppm. ¹³C NMR (100 MHz, room temp., CDCl₃): $\delta = -4.6$ (CH₃Si), 21,2 [(CH₃)₃CSi], 25.7 [(CH₃)₃CSi], 90.2 (CH₂), 125.2 (o-CH for p-tolyl group), 128.7 (m-CH for p-tolyl group), 135.0 [C-CSi(CH₂)], 138.0 (p-C for p-tolyl group), 156.0 (p-tolylC-Si) ppm. The title compound was synthesized according to the analoguous procedure for 15 using tert-butyldimethyl(1-p-tolylvinyloxy)silane instead of 14. TLC (hexane/ EtOAc, 4:1): $R_f = 0.74$. GC: $t_R = 20.9$ min. IR (film): $\tilde{v} = 2955$, 1686, 1607, 1256, 1092, 1071, 939, 835, 808, 779 cm⁻¹. ¹H NMR (300 MHz): $\delta = -0.18$ (s, 3 H, Me), -0.09 (s, 3 H, Me), 0.75 (s, 9 H, tBu), 2.41 (s, 3 H, ArC H_3), 2.92 (dd, J = 3.9, 15.3 Hz, 1 H, CH₂), 3.55 (dd, J = 8.7, 15.3 Hz, 1 H, CH₂), 5.35 (dd, J = 3.9, 8.7 Hz, 1 H, CH), 7.23–7.43 (m, 7 H, Ar), 7.87 (d, J = 8.1 Hz, 2 H, Ar-H for phenyl) ppm. C₂₂H₃₀O₂Si (354.56): calcd. C 74.53, H 8.53; found C 74.67, H 8.52.

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