Direct Transformation of Silyl Enol Ethers into Functionalized Allenes

Peter Langer,*[a] Manfred Döring,[b] Dietmar Seyferth,[c] and Helmar Görls[b]

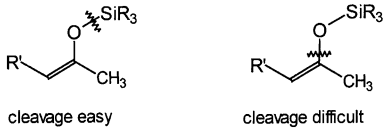
Abstract: The first elimination reactions of silyl enol ethers to lithiated allenes are reported. These reactions allow a direct transformation of readily available silyl enol ethers into functionalized allenes. The action of three to four equivalents of lithium diisopropylamide (LDA) on silyl enol ethers results in the formation of lithiated allenes by initial allylic lithiation, subsequent elimination of a lithium silanolate, and finally, lithiation of the allene thus formed. Starting with amide-derived silyl imino ethers, lithiated ketenimines are obtained. A variety of reactions of the lithiated allenes with electrophiles (chlorosilanes, trimethylchlorostannane, dimethyl sulfate and ethanol) were carried out. Elimination of silanolate is observed only for substrates that contain the hindered $SiMe_2tBu$ or $Si(iPr)_3$ moiety, but not for the $SiMe_3$ group. The reaction of 1,1-dilithio-3,3-diphenylallene with ketones provides a convenient access to novel 1,1-di(hydroxymethyl)allenes which undergo a domino Nazarov–Friedel–Crafts reaction upon treatment with *p*-toluenesulfonic acid.

Keywords: allenes · domino reactions · ketenimines · lithium · silyl enol ethers

Introduction

The allene moiety represents a versatile and useful building block in organic synthesis. Allenes can be transformed to other functional groups, such as olefins, α,β-unsaturated carbonyl compounds and alkynes,[1a] and also participate in a variety of cycloaddition reactions.[1b] The use of allenes in transition metal catalyzed cyclization reactions is of great current interest.[1c–m] Although a number of methods for the synthesis of allenes is known, more efficient procedures, which offer new synthetic pathways, need to be developed. Allenes have been prepared so far mainly from alkenes by means of the Skattebøl dibromocarbene methodology. In contrast, transformations of ketones or ketone-derived substrates into allenes are more rare.[2] This is remarkable, since carbonyl compounds are readily available starting materials. Herein, we report what we believe to be the first direct transformation of silyl enol ethers into lithiated allenes.

Until now, interest in silyl enol ethers has been focused on reactions with electrophiles that proceed with cleavage of the silicon–oxygen bond.[3a–c] Very recently, oxidative dimerizations of silyl enol ethers have been reported.[4] Surprisingly, only very few reactions, which involve cleavage of the carbon–oxygen rather than the silicon–oxygen bond, have been reported so far: for example, di- and trisubstituted olefins have been prepared by the displacement of the Me_3SiO group by Grignard reagents in the presence of a Ni^{II} catalyst.[3d] There has been only little interest in the formation and reactivity of carbanions of silyl enol ethers. Herein, we report the results of our studies in this area, which have resulted in the development of base-mediated elimination reactions of silyl enol ethers.[5] These reactions provide a method for the direct transformation of silyl enol ethers into allenes.



Results and Discussion

Optimization and mechanism of the allene synthesis: Trimethylsilyl enol ether **1**[6] was prepared by silylation (Me_3SiCl/KH) of 1,1-diphenylacetone in 88% yield (Scheme 1). Treatment of **1** with lithium diisopropylamide (LDA; 1 equiv) in THF, stirring for 4 h, and subsequent addition of Me_2HSiCl afforded a mixture of (2-silyloxy)allylsilane **2** and silyl enol ether **3** as the main products (combined yield: 76%). Based on a comparison with authentic samples of **2** and its positional isomer, the location of the silyl groups was unambiguously

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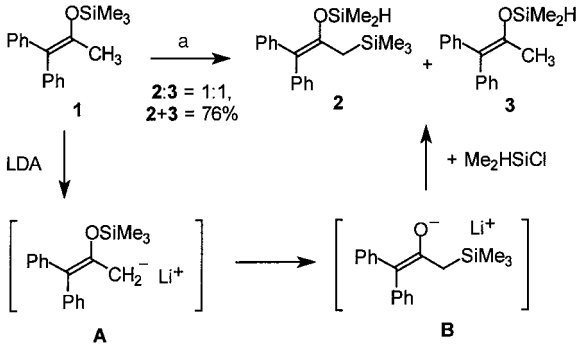
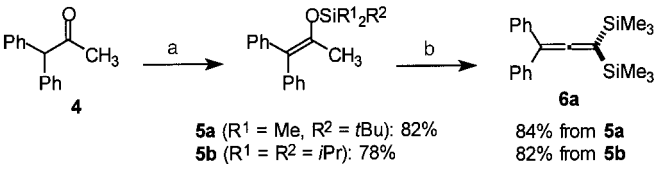


Scheme 1. Lithiation of trimethylsilyl enol ether **1**. a) 1) 1.1 equiv LDA, THF, 0 °C; 2) 1.2 equiv Me_2HSiCl.

proven by ^{1}H NMR (^3J coupling CH_2SiMe_2H) and ^{29}Si NMR (comparison of chemical shifts) spectroscopy. The two isomeric (2-silyloxy)allylsilanes were prepared by silylation of the dianion of 1,1-diphenylacetone with one equivalent each of Me_3SiCl and Me_2HSiCl.[5d] Formation of **2** can be explained by 1,3 O → C migration of the trimethylsilyl group of carbanion **A** to give the enolate **B** (see Scheme 1), followed by reaction of the latter with Me_2HSiCl. The unusual 1,3 O → C migration can be explained by the greater stability of the enolate anion compared to the initially formed allyl anion.[7] For electroneutral substrates, the opposite mode of silyl migration (1,3 C → O), the Brook rearrangement, is generally observed: this reaction allows the transformation of α-silyl ketones into silyl enol ethers. The formation of silyl enol ether **3** suggests that, for a significant amount of the starting material, nucleophilic cleavage of the Me_3Si–O bond must have occurred.

Trimethylsilyl enol ethers are readily transformed into lithium enolates by organolithium compounds.[8a] It is known from the protective-group chemistry of alcohols that silyl ethers that contain the bulky *tert*-butyldimethylsilyl (TBDMS) or triisopropylsilyl (TIPS) group are more stable towards nucleophilic cleavage than silyl ethers with a trimethylsilyl (TMS) group.[8b] Therefore, silyl enol ethers that contain a sterically hindered silyl group were expected to be significantly more stable against cleavage of the oxygen–silicon bond than the respective trimethylsilyl enol ethers. Interestingly, reaction of *tert*-butyldimethylsilyl enol ether **5a** with one equivalent of LDA, stirring for 6 h, and subsequent addition of Me_3SiCl gave completely different results from those obtained for trimethylsilyl enol ether **1**: starting with **5a**, a 2:1 mixture of starting material **5a** and bissilylated allene **6a** was obtained in 90% combined yield. Based on this experiment we decided to use an excess of LDA. Much to our satisfaction, addition of **5a** to a solution of 3.3 equivalents of LDA in THF, stirring for 6 h, and subsequent addition of Me_3SiCl (3.5 equiv) afforded the bissilylated allene **6a** in 84% yield with very good regioselectivity (Scheme 2, Table 1). When reaction times of less than 6 h were employed, mixtures of allene **6a** and silyl enol ether **5a** were obtained (Table 1).



Scheme 2. Lithiation of sterically hindered silyl enol ethers **5a** and **5b**. a) 1) 1.1 equiv KH, THF, 0 °C; 2) 1.5 equiv $R^2R^1_2SiCl$, 0 °C; b) 1) 3.3 equiv LDA, THF, 0 °C; 2) 3.5 equiv Me_3SiCl.

Table 1. Optimization of the synthesis of allene **6a**.

Entry	Starting material	Base	Equiv	*t* [min][a]	Conversion [%][b]	Yield of **6a** [%][c]
1	**1**	LDA	1.1	360	100	0
2	**5a**	LDA	1.1	360	33	14
3	**5a**	LDA	3.3	360	100	84
4	**5a**	*n*BuLi	3.3	360	90	70
5	**5a**	LDA	3.3	15	32	22
6	**5a**	LDA	3.3	45	73	57
7	**5a**	LDA	3.3	90	88	68
8	**5a**	LDA	3.3	300	96	73
9	**5b**	LDA	3.3	360	100	82

[a] Deprotonation at 20 °C. [b] According to ^{1}H NMR spectrum of the crude product. [c] Yield of isolated product.

The use of LDA proved superior to the use of *n*BuLi which resulted in the formation of a 10:1 mixture of **6a** and **5a** (reaction time: 6 h). The starting material was not completely transformed into allene **6a**, presumably the result of an attack by *n*BuLi on the solvent THF.[9] It is noteworthy that, despite the nucleophilicity of *n*BuLi, no cleavage of the oxygen–silicon bond and formation of the enolate of 1,1-diphenylacetone was observed.[8a] Reaction of this enolate with Me_3SiCl would have resulted in the formation of silyl enol ether **1** which could not be detected in the product mixture (Scheme 3).

Formation of **6a** can be explained by the following mechanism: in a slow step, the allyl system of **5a** is lithiated

Abstract in German: *Die unseres Wissens ersten Eliminierungsreaktionen von Silylenolethern ermöglichen eine direkte Umwandlung leicht zugänglicher Silylenolether in Allene. Dabei werden die Substrate zunächst mit 3 bis 4 Äquivalenten Diisopropylamid (LDA) umgesetzt, wobei dilithiierte Allene gebildet werden. Diese Reaktion verläuft vermutlich über allylische Lithiierung der Silylenolether, Eliminierung von Lithiumsilanolat und anschließende Lithiierung des gebildeten Allen-Intermediats. Die Deprotonierung von Silyliminoethern, die bequem ausgehend von Amiden hergestellt werden können, liefert lithiierte Ketenimine. Die hergestellten lithiierten Allene wurden mit einer Reihe unterschiedlicher Elektrophile (Chlorsilane, Trimethylchlorstannan, Dimethylsulfat und Ethanol) umgesetzt. Eine Eliminierung von Lithiumsilanolat und die Bildung von Allenen wurde ausschließlich für Silylenolether beobachtet, die sterisch gehinderte Silylgruppen ($SiMe_2tBu$ oder $Si(iPr)_3$) tragen, nicht dagegen für Trimethylsilylenolether. Die Umsetzung von 1,1-Dilithio-3,3-diphenylallen mit Ketonen ermöglicht eine einfache und effiziente Darstellung von 1,1-Di(hydroxymethyl)allenen, die bei Behandlung mit p-Toluolsulfonsäure eine neuartige Domino Nazarov–Friedel–Crafts Reaktion eingehen.*

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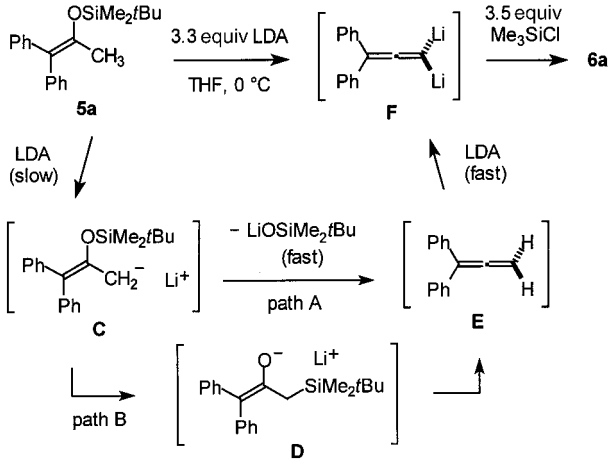
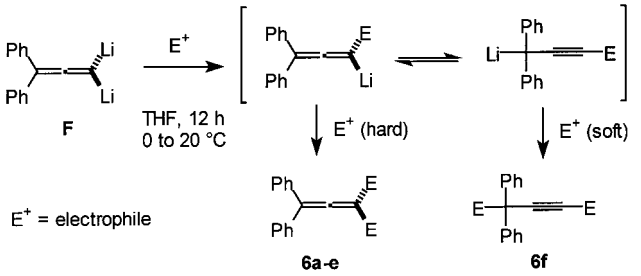


Scheme 3. Mechanism for the formation of allene **6a**.

to give the allylic carbanion **C**.[10] Fast elimination of $LiOSiMe_2tBu$ subsequently leads to the allenic intermediate **E**. The elimination step could proceed either directly (path A) or by a domino 1,3 O → C silyl migration/Peterson reaction (via enolate **D**, path B).[11] The elimination of lithium silanolate was proven by isolation of $MePh_2SiOSiMe_2tBu$ after quenching with $MePh_2SiCl$ (vide infra). Because of the enhanced acidity of the allene protons (relative to olefins),[12] intermediate **E** is rapidly deprotonated to give the 1,1-bislithiated allene **F**. Addition of Me_3SiCl finally gives the bissilylated allene **6a**. The 1,1-bislithiated allene **F** was previously generated by double lithiation of 1,1-diphenylcyclopropene.[13]

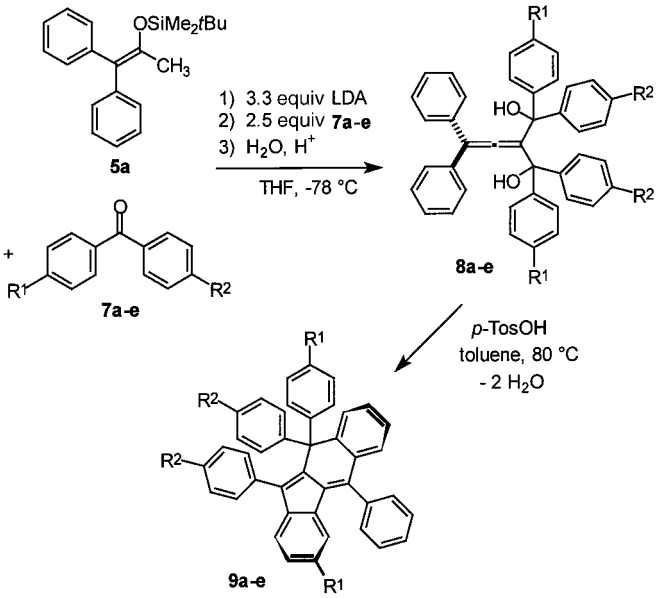
Preparative scope of the allene synthesis: To study the preparative scope of the new reaction, the starting materials were systematically varied. Reaction of **5a** with 3.3 equivalents of LDA and subsequent addition of Me_2HSiCl or $MePh_2SiCl$ afforded the 1,1-diphenyl-3,3-bis(silyl)allenes **6b** and **6c** in 82 and 61 % yields, respectively, and with very good regioselectivities (Table 2). Addition of Me_3SnCl afforded the interesting bisstannylated allene **6d** with very good regioselectivity. Interception of dianion **F** with ethanol gave 1,1-diphenylallene (**6e**).[14] Reaction of $Ph_2C{=}C{=}CLi_2$ with dimethyl sulfate gave the alkyne **6f**[15a] (68 %) rather than 1,1-dimethyl-3,3-diphenylallene.[15b] The regioselectivities can be explained as follows (Scheme 4): reaction of dianion **F** with one equivalent of the electrophile results in the formation of a monolithium species. Following the hard/soft acid/base (HSAB) principle, the monoanion reacts with hard electrophiles (Me_3SiCl, Me_3SnCl, H^+) at the (hard) unsubstituted



Scheme 4. Interception of 1,1-dilithio-3,3-diphenylallene with hard and soft electrophiles.

carbon atom. In contrast, soft electrophiles (dimethyl sulfate) prefer to attack the (soft) phenyl-substituted carbon atom.[16]

The reaction of allene dianion **F** with ketones was studied next. Much to our satisfaction, the addition of a solution of aryl ketones **7a–e** (two equivalents) in THF to a solution of dianion **F** in THF regioselectively afforded the novel, sterically encumbered di(hydroxymethyl)allenes **8a–e** in good yields (Scheme 5, Table 3).[5b, 17] Treatment of allenes **8a–e** with *p*-toluenesulfonic acid in toluene resulted in the elimination of two equivalents of water and selective formation of the orange-colored 5,10,10,11-tetraaryl-10*H*-benzo[*b*]fluorenes **9a–e** in very good yields. In the case of allene **8b**, which contains two asymmetric carbon atoms, the cyclization proceeds regioselectively via the *p*-methoxyphenyl group rather than via the phenyl group to give **9b** in good yield.



Scheme 5. Synthesis of di(hydroxymethyl)allenes **8** and of 10*H*-benzo[*b*]-fluorenes **9**.

Table 2. Reaction of 1,1-dilithio-3,3-diphenylallene with electrophiles.

6	Electrophile	Product	Yield [%][a]
a	Me_3SiCl	$Ph_2C{=}C{=}C(SiMe_3)_2$	84
b	Me_2HSiCl,	$Ph_2C{=}C{=}C(SiMe_2H)_2$	82
c	$MePh_2SiCl$	$Ph_2C{=}C{=}C(SiPh_2Me)_2$	61
d	Me_3SnCl	$Ph_2C{=}C{=}C(SnMe_3)_2$	60
e	EtOH	$Ph_2C{=}C{=}CH_2$	36
f	$(MeO)_2SO_2$	$Ph_2(Me)C\text{-}C{\equiv}CMe$	68

[a] Yield of isolated product.

Table 3. Synthesis of di(hydroxymethyl)allenes **8** and of 10*H*-benzo[b]-fluorenes **9**.

8, 9	R^1	R^2	Yield (**8**) [%][a]	Yield (**9**) [%][a]
a	H	H	80	85
b	MeO	H	62	73
c	MeO	MeO	75	76
d	Me	Me	76	83
e	Cl	Cl	71	86

[a] Yield of isolated product.

Pentafulvenes related to **9** have been used as intermediates in the synthesis of fullerene fragments.[18]

The structure of 10*H*-benzo[*b*]fluorene **9a** was independently proven by X-ray crystallography (Figure 1). The benzofulvene unit (C1 – C9) is twisted out of the plane of C11-C12-C13 (by 24.4°) which results in a curved structure of the molecule. Therefore, 10*H*-benzo[*b*]fluorenes **9a – e** are chiral. This was independently demonstrated by separation of the two atropic enantiomers of **8a** by HPLC on a chiral stationary phase (see the Experimental Section for details). According to the bond lengths, C7 – C10 and C8 – C9 are true double bonds whereas C6 – C9 and C7 – C8 represent single bonds.

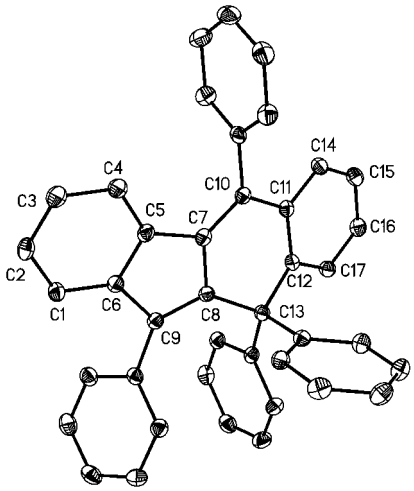
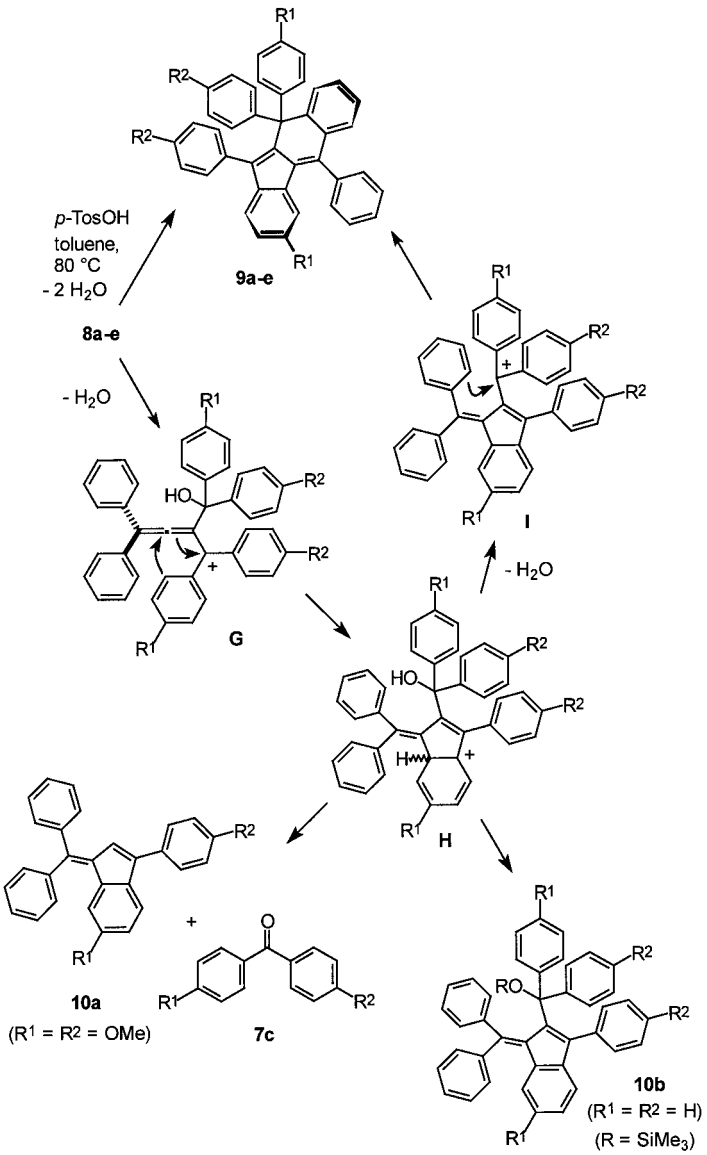


Figure 1. ORTEP plot of **9a** with the atom numbering scheme. The thermal ellipsoids with 50% probability are shown for the non-hydrogen atoms. Selected bond lengths [Å] and angles [°]: C1 – C6 138.2(3), C2 – C3 138.1(4), C4 – C5 138.9(3), C5 – C7 146.8(3), C7 – C10 135.6(3), C8 – C9 136.6(3), C9 – C18 148.5(3), C11 – C12 140.4(3), C12 – C13 154.2(3), C13 – C30 156.7(3), C15 – C16 137.7(4), C1 – C2 138.5(4), C3 – C4 139.1(3), C5 – C6 140.0(3), C6 – C9 148.0(3), C7 – C8 146.9(3), C8 – C13 152.5(3), C10 – C11 147.2(3), C11 – C14 140.3(3), C12 – C17 139.3(3); C6-C1-C2 119.2(2), C2-C3-C4 120.9(3), C4-C5-C6 120.0(2), C1-C6-C9 130.4(2), C10-C7-C8 122.2(2), C6-C9-C18 119.7(2), C10-C7-C5 130.9(2), C7-C8-C13 118.9(2), C17-C12-C11 118.7(2).

The formation of 10*H*-benzo[*b*]fluorenes **9** can be explained by what we believe to be the first domino Nazarov – Friedel – Crafts reaction: carbocation **G** is initially generated by the elimination of water (Scheme 6). The central allene carbon atom is attacked by the *ortho* carbon atom of one of the aryl groups to give the five-membered ring in intermediate **H**. Aromatization and elimination of water subsequently leads to formation of the cationic intermediate **I**. The *ortho* carbon of the allene-derived phenyl group is attacked by the carbocation adjacent to the ketone-derived aryl groups. Aromatization finally leads to the products **9a – e**. This mechanism is supported by the following observation: starting with the *p*-methoxyphenyl-substituted allene **8c**, the benzofulvene **10a** is obtained as a minor product in 10% yield. Formation of **10a** can be explained by the formation of the benzofulvene moiety and subsequent elimination of di(*p*-methoxyphenyl)ketone or, alternatively, by initial elimination of the ketone, formation of a cumulene (vide infra), and subsequent isomerization of the latter. During the formation



Scheme 6. Mechanism for the formation of 10*H*-benzo[*b*]fluorenes **9**.

of 10*H*-benzo[b]fluorene **9a**, the benzofulvene **10b** was obtained as a side-product in low yield. For practical reasons, the product was isolated and crystallized as a trimethylsilyl ether. The structure of **10b** was independently proven by X-ray crystallography (Figure 2). This result further supports the mechanism suggested for the formation of 10*H*-benzo[*b*]-fluorenes **9**.

It is noteworthy that in the domino reaction that leads to **9a – e**, the allenic phenyl group became *sterically* accessible for the cationic π cyclization only after the previous cyclization that involved the rigid allene moiety had occurred. The domino reaction thus represents a combination of cyclizations as observed for *mono*(hydroxymethyl)allenes[19a] and for aryl-substituted di(hydroxymethyl)*alkenes* $Ar_2C{=}C[C(OH)Ar_2]_2$. The latter have been used as precursors for the generation of (hexaaryltrimethylene)methane dications.[19b] Domino reactions[20] of alkynes have been used for the efficient synthesis of carbocycles and polycyclic aromatic hydrocarbons (PAHs).[21] Hydroxymethylalkynes have been converted into the more

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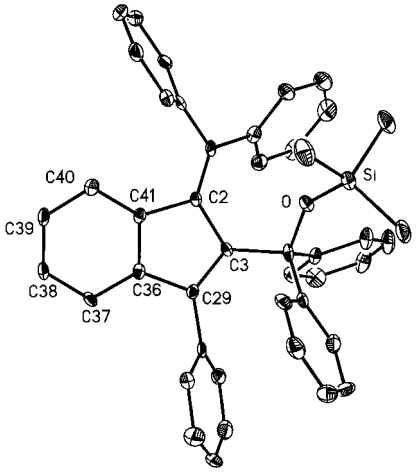


Figure 2. ORTEP plot of **10b** with the atom numbering scheme. The thermal ellipsoids with 50% probability are shown for the non-hydrogen atoms. Selected bond lengths [Å] and angles [°]: Si–O 1.639(5), O–C4 1.440(7), C2–C41 1.480(8), C2–C3 1.482(9), C3–C29 1.386(8), C29–C36 1.458(9), C36–C41 1.399(9), C36–C37 1.412(8), C37–C38 1.395(9), C38–C39 1.346(9), C39–C40 1.404(9), C40–C41 1.390(9); C41-C2-C3 106.8(5), C29-C3-C2 108.3(5), C41-C36-C37 121.3(6), C41-C36-C29 110.6(5), C37-C36-C29 128.2(6), C38-C39-C40 122.3(6).

labile allenes and cumulenes which were used in situ for the preparation of [4]radialenes, macrocycles and 1,2-dihydrocyclobutaarenes.[21b] However, only a few domino reactions that use allenes as starting materials have been reported so far.[22](Figure 3)

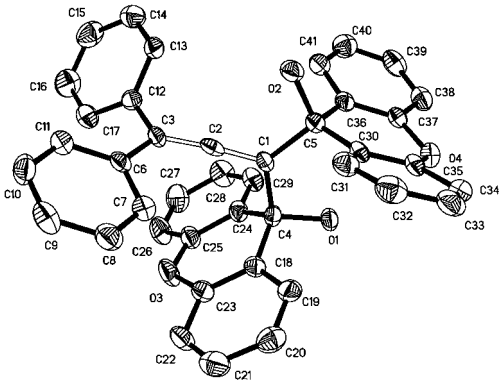
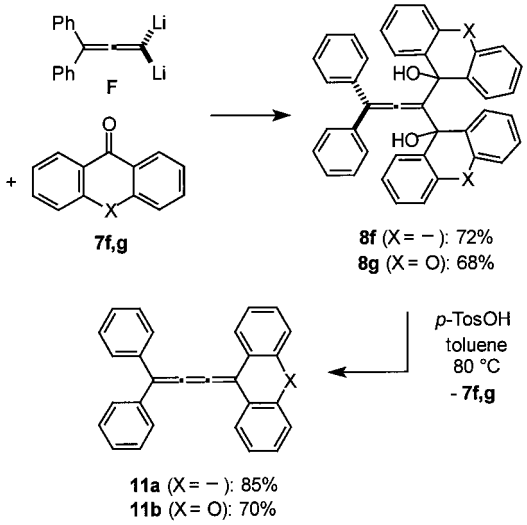


Figure 3. ORTEP plot of **8g** with the atom numbering scheme. The thermal ellipsoids with 50% probability are shown for the non-hydrogen atoms. Selected bond lengths [Å] and angles [°]: C1–C5 154.3(5), C3–C12 147.8(5), C1–C2 131.3(6), C1–C4 155.3(6), C2–C3 131.6(6); C2-C1-C5 119.6(3), C1-C2-C3 173.6(4), C2-C3-C12 117.6(3), O2-C5-C36 104.4(3), O1-C4-C1 107.1(3).

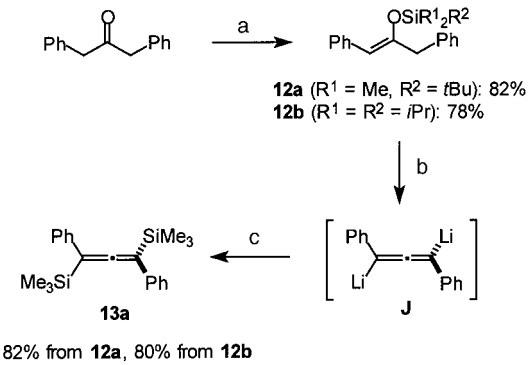
The reaction of dilithioallene **F** with two equivalents of fluorenone and xanthone gave the colorless allenes **8f** and **8g** in 72 and 68% yields, respectively (Scheme 7). As minor products, the yellow cumulenes **11a** and **11b** were isolated in 10 and 14% yields, respectively. The structure of allene **8g** was independently proven by X-ray crystallography (Figure 3). The two xanthone moieties have different orientations relative to the allene unit because of steric reasons. Each xanthone moiety is slightly twisted out of plane. The allene unit is slightly bent (by 7°).



Scheme 7. Synthesis and elimination reactions of allenes **8f** and **8g**.

Treatment of the allenes **8f** and **8g** with *p*-toluenesulfonic acid resulted in the elimination of fluorenone or xanthone and formation of the cumulenes **11a** and **11b** in 85 and 70% yields, respectively, rather than in cyclization (Scheme 7). Previously, formation of cumulenes has only been observed for α-unsubstituted (hydroxymethyl)allenes.[23] The striking difference between the reactions of allenes **8a–e** and **8f–g** with *p*-toluenesulfonic acid can be explained by the fact that cyclization would lead to a strained unsaturated 5,5,6-ring system.[24] In addition, the antiaromatic character of the 9-fluorenyl cation in the ground state and the rigid character of the ketone-derived subunits of **8f** and **8g** are presumed to direct the course of the reaction.[25]

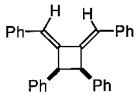
Variation of the silyl enol ether in our new allene synthesis was studied next. Silyl enol ether **12a** was prepared from 1,3-diphenylacetone in good yield (Scheme 8). Addition of **12a** to



Scheme 8. Lithiation of silyl enol ethers **12a** and **12b**. a) 1) 1.2 equiv LDA, THF, 0 °C; 2) 1.5 equiv tBuMe$_2$SiCl, 0 °C; b) 1) 3.3 equiv LDA, THF, 0 °C; 2) 3.5 equiv Me$_3$SiCl.

a solution of 3.3 equivalents of LDA in THF and addition of Me$_3$SiCl after stirring for 6 h afforded 1,3-diphenyl-1,3-bis(trimethylsilyl)allene (**13a**) in 82% yield via the 1,3-dilithioallene intermediate **J**.[26] Starting with triisopropylsilyl enol ether **12b**, allene **13a** was formed in 80% yield. Interception of dianion **J** with Me$_3$SnCl afforded the bisstannylated allene **13b** (Table 4). Reaction of **J** with ethanol

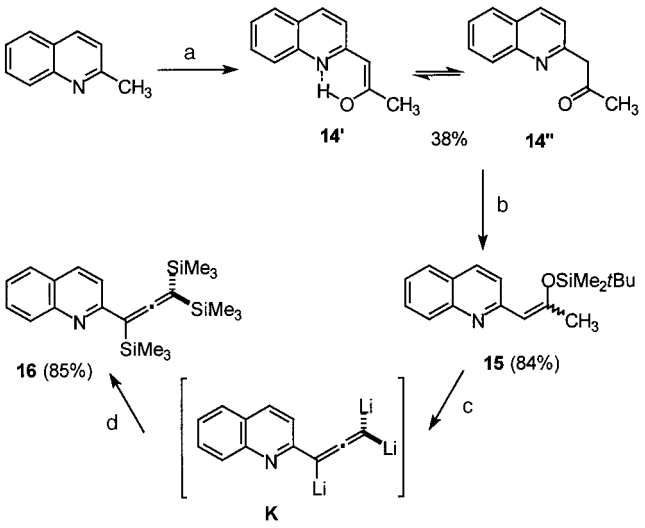
Table 4. Reaction of 1,3-dilithio-1,3-diphenylallene with electrophiles.

13	Electrophile	Product	Yield [%][a]
a	Me_3SiCl	$Ph(Me_3Si)C{=}C{=}C(SiMe_3)Ph$	82
b	Me_3SnCl	$Ph(Me_3Sn)C{=}C{=}C(SnMe_3)Ph$	53
c	EtOH		51
d	$(MeO)_2SO_2$	$Ph(Me)_2C\text{-}C{\equiv}CPh$,	65[b]
e		$Ph(Me)C{=}C{=}C(Me)Ph$	

[a] Yield of isolated product. [b] Combined yield of a separable 2:1 mixture of **13d** and **13e**.

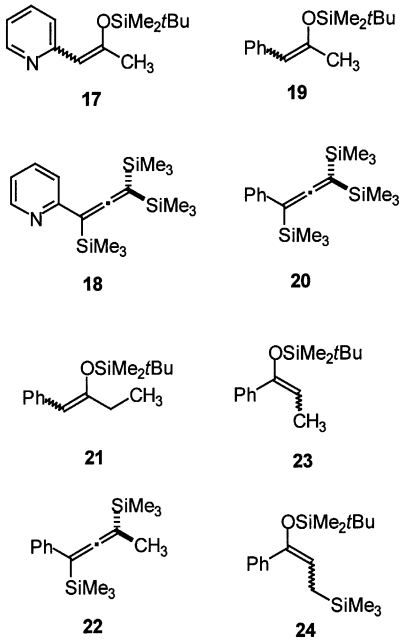
afforded the cyclobutane derivative **13c** which was formed by the dimerization of 1,3-diphenylallene.[27] Treatment of 1,3-dilithioallene **J** with dimethyl sulfate afforded a separable 2:1 mixture of alkyne **13d** and the isomeric allene **13e**.[28] The regioselectivities observed can again be explained based on the HSAB concept.

The applicability of our new allene synthesis to silyl enol ethers that contain only one aryl group was studied next (Scheme 9). 2-Quinolylacetone (**14**)[29] was prepared by condensation of the carbanion of 2-methylquinoline with ethyl acetate. This compound mainly resides in the enolic form **14′** (^{1}H NMR spectroscopy). Ketone **14** was transformed into silyl enol ether **15** in 84% yield. Treatment of **15** with 3.3 equivalents of LDA, stirring for 6 h, and subsequent addition of Me_3SiCl resulted in the formation of a complex mixture. In contrast, addition of **15** to a solution of 4.4 equivalents of LDA in THF, stirring for 6 h, and subsequent addition of Me_3SiCl cleanly afforded the trisilylated allene **16** in 85% yield via the trilithiated allene **K**.



Scheme 9. Lithiation of silyl enol ether **15**. a) 1) 1.2 equiv LDA, THF, 0 °C, 2 h; 2) 1.5 equiv EtOAc, 0 °C → 20 °C, 24 H; 38% (**14′**:**14″** = 4:1); b) 1) 1.1 equiv KH, THF, 1 h; 2) 1.5 equiv *t*BuMe$_2$SiCl, 0 °C → 20 °C, 48 H; 84%; c) 4.4 equiv LDA, THF, 0 °C → 20 °C, 6 h; d) 4.5 equiv Me_3SiCl, 0 °C → 20 °C, 12 H; 85%.

Treatment of the pyridyl-substituted silyl enol ether **17** (prepared from 2-pyridylacetone) afforded allene **18** in low yield. Reaction of the phenylacetone-derived silyl enol ether **19** afforded allene **20** (as indicated by MS and IR spectra of the crude product).[30] Unfortunately, this product could not be isolated in a pure form. Silyl enol ether **21** was prepared from 1-phenyl-2-butanone in good yield. Treatment of **21** with 3.3 equivalents of LDA and subsequent addition of Me_3SiCl afforded allene **22**. Starting with the propiophenone-derived silyl enol ether **23**, a complex mixture was obtained. The IR spectrum of the crude product showed a strong allene vibration band. However, only the C-silylated silyl enol ether **24** could be isolated from the mixture (52%).



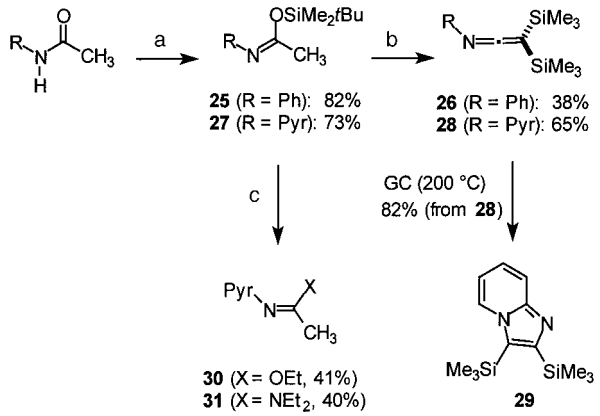
A brief discussion of the spectroscopic properties of selected examples of the new silyl- and stannyl-substituted allenes is appropriate (Table 5). The central carbon atom is more deshielded in silylated allenes than in stannylated allenes. The chemical shifts of the respective carbons do not depend on the substitution mode (1,1 versus 1,3-substitution). In contrast, the $SiPh_2Me$ moiety (**6c**) effects a shift to lower field. The relative order of vibration bands (IR) is as follows: **13b** ($\tilde{\nu}$ = 1879 cm^{-1}) < **6d** < **16** < **13a** < **6c** < **6a** < **6b** < 1,1-dimethyl-3,3-diphenylallene ($\tilde{\nu}$ = 1960 cm^{-1}).

Table 5. Selected spectral features of silyl- and stannyl-substituted allenes.

Allene	IR [cm^{-1}]	^{1}H NMR [δ]	^{13}C NMR [δ]
6a	1899	0.17	208.89
6b	1912	0.24	210.45
6c	1895	0.56	215.80
6d	1882	0.24	201.35
13a	1891	0.21	209.22
13b	1879	0.32	200.50
16	1887	0.19, 0.31	208.98

The new elimination reaction proved applicable to silyl imino ethers which were readily prepared from the corresponding amides (Scheme 10). Treatment of the acetanilide-derived silyl imino ether **25** with 3.3 equivalents of LDA,

0947-6539/01/0703-0578 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 3



Scheme 10. Lithiation of silyl imino ethers **25** and **27**. a) a) 1.1 equiv LDA, THF, 0 °C ; b) 1.5 equiv *t*BuMe$_2$SiCl, −78 °C; b) 1) 3.3 equiv LDA, THF, 0 °C; 2) 3.5 equiv Me$_3$SiCl; c) 1) 3.3 equiv LDA, THF, 0 °C; 2) 3.5 equiv EtOH (for **30**), 3.5 equiv HNEt$_2$ (for **31**); pyr = 2-pyridyl.

stirring for 6 h, and subsequent addition of Me$_3$SiCl afforded the silylated ketenimine **26** via the dilithiated ketenimine PhNC=C=CLi$_2$.[31] Reaction of pyridyl-substituted silyl imino ether **27** (prepared from (2-Pyr)NH(CO)CH$_3$ in 73% yield) with 3.0 equivalents of LDA, stirring for 6 h, and subsequent addition of Me$_3$SiCl afforded ketenimine **28** via the dilithiated ketenimine PyrNC=C=CLi$_2$. Under the conditions of preparative gas chromatography, ketenimine **28** underwent an interesting rearrangement reaction to give the imidazo[1,2-a]pyridine **29**. In the course of this cyclization, a 1,2-migration of a Me$_3$Si group occurred. Interception of dianion PyrNC=C=CLi$_2$ with ethanol afforded the imino ether **30** and treatment with diethylamine afforded the amidine **31**. These reactions proceeded by protonation of PyrNC=C=CLi$_2$ to give the ketenimine PyrN=C=CH$_2$. The central carbon atom of the latter is subsequently attacked by ethanol and diethylamine to give the final products **30** and **31**, respectively.

Conclusion

We have developed what we believe to be the first direct transformation of silyl enol ethers and silyl imino ethers into *lithiated* allenes and ketenimines, respectively. An important parameter for the success of this reaction is the steric demand of the silyl group. Allene formation was observed with the SiMe$_2$*t*Bu and the Si(*i*Pr)$_3$ groups, but not with the SiMe$_3$ group. On the one hand, our methodology allows the use of readily available silyl enol ethers as starting materials which opens a new synthetic pathway; on the other hand, the transformations are currently limited to the use of aryl-substituted substrates. In the Skattebøl dibromocarbene method, both aliphatic and aromatic alkenes can be used; however, the starting materials are not always readily available. In contrast to the Skattebøl method and to the formation of allenes from enol phosphates, our reactions allow a direct synthesis of *functionalized* allenes, since lithiated allenes are formed as intermediates which can be trapped with electrophiles. In fact, this methodology appears to be most convenient at present for preparation of the polylithiated allenes Ph$_2$C=C=CLi$_2$, Ph(Li)C=C=C(Li)Ph, and Ar(Li)C=C=CLi$_2$ which have recently been applied to organic synthesis.[32] Known procedures for the formation of *polylithiated* allenes have to rely on less readily available starting materials. In addition, our transformations are easy to carry out. For the sake of convenience of isolation and characterization, we have chosen for the most part to convert the polylithiated intermediates to organosilicon products. Also, silyl-substituted allenes have demonstrated utility in organic synthesis,[33] as have stannyl-substituted allenes.[34]

Our current work is directed towards extension of the preparative scope of the reaction and towards the application of our methodology in organic synthesis.

Experimental Section

General comments: All reactions were carried out under an inert atmosphere and solvents were dried by standard methods. Chlorosilanes were purchased from Hüls Inc. and distilled from magnesium chips before use. *n*-Butyllithium was used as obtained from Aldrich (1.6 M solution in hexane). Potassium hydride was purified by washing with a solution of lithium aluminum hydride in THF. Analytical gas chromatography (GC) analyses were performed on a Hewlett–Packard 5890A gas chromatograph equipped with a 6 foot, 0.25 in column packed with 10% SE-30 silicon rubber gum on Chromosorb P. Preparative GC was performed on a Gow-Mac Instrument Gas Chromatograph Series 350 with a thermal conductivity cell. The following temperatures were used for all separations: injector port 220 °C, column 200 °C, detector 240 °C. The identity of the products isolated by preparative GC and those contained in the crude reaction mixture was checked by comparison of the respective ^{1}H NMR data and retention times (analytical GC).

^{1}H NMR spectra were recorded at 200, 250, or 300 MHz and the shifts are reported in ppm relative to tetramethylsilane. ^{13}C NMR spectra were obtained at 75, 62.5, or 50 MHz and carbons were quoted as: CH$_3$, CH$_2$, CH, and C for primary, secondary, tertiary, and quaternary carbon atoms, respectively. The ^{29}Si NMR spectra were recorded at 59.59 MHz in CDCl$_3$ with tetramethylsilane as the external standard. Mass spectra were obtained with the electron impact method (70 eV) or the chemical ionization technique (H$_2$O or NH$_3$). Preparative-scale chromatography was carried out on J. T. Baker silica gel (60–200 mesh) or aluminum oxide (active neutral, activity 1, 70–230 mesh). Melting points were measured on a Büchi apparatus and are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev (Denmark) or by the Microanalytical Laboratory of the University of Göttingen (Germany).

Preparation of 2-quinolylacetone (14): This ketone was prepared according to a literature procedure.[29] ^{1}H NMR (CDCl$_3$, 200 MHz) data of **14** have, to our knowledge, not been previously reported: δ = 2.14 (s, CH$_3$, **14′**), 2.75 (s, CH$_3$, **14″**), 4.12 (s, CH$_2$, **14″**), 5.33 (s, =CH-, **14′**), 6.6–8.2 (m, Ar), 11.69 (br, OH, **14′**); equilibrium of enol and ketone tautomers **14′** and **14″** (**14′**:**14″** = 4:1).

General procedure for the preparation of silyl enol ethers (1), (5a), (15), and (17): To a suspension of potassium hydride (1.1 g, 27.5 mmol) in THF (50 mL) was added a solution of the ketone (25 mmol) in THF (10 mL) at 0 °C. The color of the solution became orange-red and the evolution of hydrogen was observed. After stirring at 20 °C for 2 h, a solution of *t*BuMe$_2$SiCl (5.6 g, 1.5 equiv) in THF (10 mL) was added and precipitation of LiCl was observed. The suspension was stirred for 48 h at 20 °C. The solvent was removed in vacuo and the residue was extracted with hexane (3 × 80 mL). The extracts were filtered through Celite and the solvent was removed in vacuo. The product was isolated by vacuum distillation.

Trimethyl[(1-methyl-2,2-diphenylethenyl)oxy]silane (1): Starting with 1,1-diphenylacetone (5.24 g, 25 mmol), **1** was isolated as a colorless oil (6.55 g, 88%). The spectroscopic data of **1** were identical to that reported in the literature.[6]

***tert*-Butyldimethyl[(1-methyl-2,2-diphenylethenyl)oxy]silane (5a)**: Prepared from 1,1-diphenylacetone (15.72 g, 75 mmol). Pale yellow oil (19.95 g, 82%); b.p. 106–108 °C/0.03 mbar; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = -0.05$ (s, 6H; Me_2Si), 0.79 (s, 9H; *t*Bu), 1.93 (s, 3H; CH_3), 7.10–7.35 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -4.19$ (CH_3, Me_2Si), 18.19 (C, *C*Me$_3$), 21.60 (CH_3), 25.64 (CH_3, C*Me*$_3$), 123.03 (C, *C*Ph$_2$), 125.69, 126.06, 127.54, 127.97, 130.56, 130.57 (CH, Ph), 141.12, 142.40 (C, Ph), 146.22 (C, *C*OSi); ^{29}Si NMR ($CDCl_3$, 300 MHz): $\delta_{Si} = -18.87$. IR ($CHCl_3$): $\tilde{\nu} = 3075$ (m), 3015 (m), 2965 (s), 2910 (m), 1615 (s), 1490 (s), 1440 (s), 1400 (m), 1270 (s), 1230 (s), 1190 (s), 1105 (s) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{28}OSi$: C 77.72, H 8.70; found: C 77.68, H 8.95.

***tert*-Butyldimethyl[(1-methyl-2-(2′-quinolyl)ethenyl)oxy]silane (15)**: Prepared from 2-quinolylacetone (**14**, 3.83 g, 20.7 mmol). Orange oil (5.2 g, 84%; *E*:*Z* = 5:1 or 1:5); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.20$ (s, 6H; Me_2Si), 0.96 (s, 9H; *t*Bu), 2.10 (s, 3H; CH_3), 5.88 (s, 1H; =CH-), 7.43 (t, 1H; Ar), 7.72 (d, 1H; Ar), 7.63 (t, 1H; Ar), 7.96, 8.10, 8.15 (d, 2H; Ar); elemental analysis calcd (%) for $C_{18}H_{25}NOSi$: C 72.19, H 8.41; found: C 71.94, H 8.52.

***tert*-Butyldimethyl[(1-methyl-2-(2′-pyridyl)ethenyl)oxy]silane (17)**: Prepared from 2-pyridylacetone (1.62 g, 12 mmol). Yellow oil (2.3 g, 78%; *E*:*Z* = 1.2:1 or 1:1.2); ^{1}H NMR ($CDCl_3$, 80 MHz): $\delta = 0.18$, 0.23 (s, 6H; Me_2Si), 0.95, 0.98 (s, 9H; *t*Bu), 2.02, 2.28 (s, 3H; CH_3), 7.10–7.80 (m, 3H; Pyr), 8.55 (m, 1H; Pyr); MS (20 °C): *m*/*z*: 250 [M^++1].

General procedure for the preparation of silyl enol ethers (12a), (12b), (19), (21), and (23): To a solution of LDA (27.5 mmol) in THF (50 mL) [prepared by the addition of *n*BuLi (18.9 mL) to a solution of diisopropylamine (4.1 mL) in THF], was added a solution of the ketone (25 mmol) in THF (10 mL) at 0 °C. The solution turned red. After the mixture had been stirred for 2 h at 20 °C, a solution of *t*BuMe$_2$SiCl (5.6 g, 1.5 equiv) in THF (10 mL) was added and precipitation of LiCl was observed. After the mixture had been stirred for 48 h, the products were isolated according to the procedure for the preparation of **1**.

***tert*-Butyldimethyl[(1-phenylmethyl-2-phenylethenyl)oxy]silane (12a)**: Prepared from 1,3-diphenylacetone (5.25 g, 25 mmol). Pale yellow solid (6.64 g, 82%; one isomer, *E* or *Z*); m.p. 44–46 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.05$ (s, 6H; Me_2Si), 0.88 (s, 9H; *t*Bu), 3.52 (s, 2H; CH_2), 5.31 (s, 1H; =CH-), 7.10–7.40 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -3.51$ (Me_2Si), 18.31 (C, *C*Me$_3$), 25.85 (CH_3, C*Me*$_3$), 43.83 (CH_2), 110.18 (=CH–), 125.51, 126.36, 127.77, 128.33, 128.43, 129.16 (CH, Ph), 136.52, 138.13 (C, Ph), 151.19 (C, COSi); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = 19.22$; IR ($CHCl_3$): $\tilde{\nu} = 1254$ (Me_3Si) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{28}OSi$: C 77.72, H 8.70; found: C 77.38, H 8.82.

Triisopropyl[(1-phenylmethyl-2-phenylethenyl)oxy]silane (12b): Prepared from 1,3-diphenylacetone (5.00 g, 23.8 mmol); **12b** was isolated by kugelrohr distillation as a viscous, colorless oil (6.80 g, 78%; one isomer, *E* or *Z*); b.p. 150°/0.05 mbar; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.04$ (d, J = 7 Hz, 18H; Me), 1.07 (sept, J = 7 Hz, 3H; C*H*Me$_2$), 3.58 (s, 2H; CH_2), 5.12 (s, 1H; =CH-), 7.05–7.50 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.63 (*C*HMe$_2$), 17.88 (Me), 43.85 (CH_2), 109.85 (=CH-), 125.37, 126.36, 127.65, 128.21, 128.31, 129.23 (CH, Ph), 136.58, 137.85 (C, Ph), 152.27 (C, COSi); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = 13.71$; IR ($CHCl_3$): $\tilde{\nu} = 1277$ (Me_2CHSi) cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{34}OSi$: C 78.63, H 9.35; found: C 78.34, H 9.16.

***tert*-Butyldimethyl[(1-ethyl-2-phenylethenyl)oxy]silane (21)**: Prepared from 1-phenyl-2-butanone (2.8 mL, 19.57 mmol). Isolated by chromatography (activated Al_2O_3, hexane) as a light yellow, viscous oil (3.60 g, 70%; *E*:*Z* = 1:1); b.p. 129–133 °C/0.1 mbar; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.15, 0.31 (s, 6H; Me_2Si), 1.00, 1.05 (s, 9H; *t*Bu), 1.20, 1.23 (t, J = 9 Hz, 3H; CH_2CH_3), 2.30, 2.37 (q, J = 9 Hz, 2H; CH_2CH_3), 5.20, 5.84 (s, 1H; =CH-), 7.05–7.65 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -4.38$, -3.56 (Me_2Si), 11.88, 12.15 (CH_2CH_3), 18.18, 18.38 (C, *C*Me$_3$), 25.48, 25.65 (CH_2CH_3), 25.74, 25.92 (CH_3, C*Me*$_3$), 106.51, 108.64 (=CH-), 125.24, 125.34, 127.80, 128.13, 128.38, 128.47 (CH, Ph), 136.89, 137.57 (C, Ph), 155.77, 156.50 (C, COSi); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = 17.95$; IR ($CHCl_3$): $\tilde{\nu} = 1255$ (Me_2Si) cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{26}OSi$: C 73.22, H 9.99; found: C 73.88, H 9.85.

***tert*-Butyldimethyl[(1-methyl-2-phenylethenyl)oxy]silane (19)**: Prepared from phenylacetone (2.0 g, 15.0 mmol). Colorless oil (3.20 g, 86%; *E*:*Z* = 3:1 or 1:3); ^{1}H NMR ($CDCl_3$, 80 MHz, the first values of each pair of signals refer to those of the major component): $\delta = 0.16$, 0.23 (s, 6H; Me_2Si), 0.96, 1.00 (s, 9H; *t*Bu), 2.00, 2.02 (q, J = 9 Hz, 3H; CH_3), 5.42, 5.87 (s, 1H; =CH-), 7.10–7.60 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta_C = -3.36$, -4.34 (Me_2Si), 18.34, 18.09 (C, *C*Me$_3$), 24.19, 19.55 (CH_3), 25.89, 25.59 (CH_3, C*Me*$_3$), 108.16, 110.32 (=CH-), 125.15, 125.82, 126.17, 126.69, 128.04, 128.33 (CH, Ph), 136.89, 137.60 (C, Ph), 149.41, 151.43 (C, *C*OSi).

***tert*-Butyldimethyl[(1-phenyl-1-propenyl)oxy]silane (23)**: Prepared from propiophenone (2.0 g, 15.0 mmol). Colorless oil (2.68 g, 72%); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = -0.02$ (s, 6H; Me_2Si), 1.00 (s, 9H; *t*Bu), 1.75 (d, J = 10 Hz, 3H; =CH*C*H$_3$), 5.20 (q, J = 10 Hz, 1H; =CH-), 7.20–7.50 (m, 5H; Ph).

General procedure for the transformation of silyl enol ethers into allenes: All reactions were carried out on a 4–10 mmol scale. To a solution of LDA (19.8 mmol, 3.3 molar equiv) in THF (50 mL) [prepared by addition of *n*BuLi (13.6 mL) to a solution of diisopropylamine (3.0 mL) in THF], was added a solution of the silyl enol ether in THF (10 mL) at 0 °C. The ice bath was removed and the color of the solution turned deep red. A solution of the electrophile (3.5 equiv) in THF (10 mL) was added at 0 °C after stirring for 6 h. Precipitation of LiCl was observed. The suspension was stirred for 12 h at 20 °C. The solvent was removed and the residue was dried in vacuo and extracted with hexane (3 × 50 mL). The extracts were filtered through Celite, the solvent was removed in vacuo, and the product was isolated and purified as indicated.

1,1-Bis(trimethylsilyl)-3,3-diphenylallene (6a): Prepared from **5a** (1.94 g, 6 mmol) and Me_3SiCl (2.7 mL, 3.5 equiv). Isolated by chromatography (activated Al_2O_3, hexane) as a colorless viscous oil which crystallized at 0 °C (1.70 g, 84%); m.p. 58–60 °C. The ^{1}H NMR, ^{13}C NMR and IR data are identical to those reported in the literature.[13] Elemental analysis calcd (%) for $C_{21}H_{28}Si_2$: C 74.93, H 8.38; found: C 75.09, H 8.51.

1,1-Bis(dimethylsilyl)-3,3-diphenylallene (6b): Prepared from **5a** (1.94 g, 6 mmol) and Me_2HSiCl (2.3 mL, 3.5 equiv). Isolated by chromatography (activated Al_2O_3, hexane) as a colorless viscous oil (1.52 g, 82%); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.24$ (d, J = 3.5 Hz, 12H; Me_2Si), 4.26 (d, J = 3.5 Hz, 2H; SiH), 7.28 (m, 10H; Ph); ^{13}C NMR{^{1}H} ($CDCl_3$, 75 MHz): $\delta_C = -3.02$ (q, J = 120.0 Hz, Me_2Si), 88.18 (s, CSi_2), 97.67 (s, CPh_2), 126.01, 127.73, 128.44 (d, J = 160.2 Hz, Ph), 137.08 (s, Ph), 210.45 (s, C=*C*=C); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = -16.08$; IR (KBr): $\tilde{\nu} = 2125$ (SiH), 1912 (C=C=C), 1253 (MeSi) cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{24}Si_2$: C 73.98, H 7.84; found: C 74.48; H 8.15.

1,1-Bis(methyldiphenylsilyl)-3,3-diphenylallene (6c) and *tert*-Butyldimethylmethyldiphenylsiloxane: Prepared from **5a** (2.38 g, 7.3 mmol) and $Ph_2MeSiCl$ (4.88 g, 3.5 equiv). Isolated by kugelrohr distillation (air bath 190 °C, 0.05 mbar) as a colorless solid (2.62 g, 61%); m.p. 73–75 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.56$ (s, 6H; MeSi), 7.10–7.50 (m, 30H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -2.20$ (MeSi), 87.90 (CSi_2), 98.80 (CPh_2), 125.99, 127.62, 127.77, 128.08, 129.30, 134.93 (CH, Ph), 135.76, 136.85 (C, Ph), 215.80 (C, C=*C*=C); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = -12.69$; IR (KBr): $\tilde{\nu} = 1895$ (m, C=C=C), 1253 (s) cm^{-1}; elemental analysis calcd (%) for $C_{41}H_{36}Si_2$: C 84.19, H 6.20; found: C 83.83, H 6.28. Vacuum distillation afforded *tert*-butyldimethylmethyldiphenylsiloxane as a colorless liquid (1.47 g, 61%); b.p. 97–100 °C (0.05 mbar); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.03$ (s, 6H; Me_2Si), 0.62 (s, 3H; MeSi), 0.88(s, 9H; *t*Bu), 7.20 (m, 10H; Ph); elemental analysis calcd (%) for $C_{19}H_{28}OSi_2$: C 69.45, H 8.59; found: C 69.03, H 8.78.

1,1-Bis(trimethylstannyl)-3,3-diphenylallene (6d): Prepared from **5a** (2.38 g, 7.3 mmol) and Me_3SnCl (5.1 g, 3.5 equiv). Yellow **6d** was crystallized from hexane (2.29 g, 60%); m.p. 70–72 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.24$ (s, 18H; Me_3Sn), 7.20–7.30 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -7.39$ (Me_3Sn), 81.93 (CSn_2), 91.02 (CPh_2), 124.84, 127.49, 128.28 (CH, Ph), 139.16 (C, Ph), 201.35 (C, C=*C*=C); ^{119}Sn NMR ($CDCl_3$): $\delta_{Sn} = 1.20$; IR ($CHCl_3$): 1882 (C=C=C) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{28}Sn_2$: C 48.71, H 5.45; found: C 48.93, H 5.59.

1,1-Diphenylallene (6e): Prepared from **5a** (1.94 g, 6 mmol) and ethanol (6 equiv). Isolated by rapid chromatography (activated Al_2O_3, hexane) as a light yellow oil (415 mg, 36%).[14] The ^{13}C NMR data of **6e** have not been previously reported. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 5.25$ (s, 2H; $=CH_2$), 7.25–7.35 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = 78.05$ ($=CH_2$), 109.08 ($=CPh_2$), 127.10, 128.05, 128.13 (CH, Ph), 136.09 (C, Ph), 209.60 (C, C=*C*=C); IR (KBr): $\tilde{\nu} = 3057$ (s), 3028 (m), 1934 (m, C=C=C), 1598 (s), 1491 (s), 1452 (s), 1030 (m) cm^{-1}; MS (20 °C): *m*/*z*: 192 [M^+].

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4,4-Diphenyl-prop-2-yne (6f): Prepared from **5a** (1.94 g, 6 mmol) and dimethyl sulfate (2.0 mL, 3.5 equiv). Isolated by vacuum distillation as a colorless oil (898 mg, 68%); b.p. 132–136 °C/2 mbar). The spectroscopic data are identical to those reported in the literature;[15b] elemental analysis calcd (%) for $C_{17}H_{16}$: C 92.68, H 7.32; found: C 92.62, H 7.31.

1,3-Bis(trimethylsilyl)-1,3-diphenylallene (13a): Prepared from **12a** (1.94 g, 6 mmol) and Me_3SiCl (2.7 mL, 3.5 equiv). Isolated by chromatography (activated Al_2O_3, hexane) as a light yellow oil (1.65 g, 82%). When prepared from **12b** (2.20 g, 6 mmol), 1.57 g (80%) of **13a** was isolated. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.21$ (s, 18H; Me_3Si), 7.05–7.30 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = 0.17$ (Me_3Si), 94.99 (=*C*PhSi), 125.78, 127.38, 128.44 (CH, Ph), 136.97 (C, Ph), 209.22 (C, C=*C*=C); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = -18.88$; IR ($CHCl_3$): $\tilde{\nu} = 1891$ (C=C=C), 1250 (Me_3Si) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{28}Si_2$: C 74.93, H 8.38; found: C 75.11, H 8.67.

1,3-Bis(trimethylstannyl)-1,3-diphenylallene (13b): Prepared from **7a** (2.34 g, 7.3 mmol) and Me_3SnCl (5.1 g, 3.5 equiv). Crystallized from hexane (2.00 g, 53%); m.p. 58–60 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.32$ (s, 18H; Me_3Sn), 7.10–7.30 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -7.80$ (Me_3Sn), 89.98 (=*C*PhSn), 125.61, 127.76, 128.64 (CH, Ph), 138.61 (C, Ph), 200.50 (C, C=*C*=C); ^{119}Sn NMR ($CDCl_3$): $\delta_{Sn} = -10.51$; IR ($CHCl_3$): 1879 (C=C=C) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{28}Sn_2$: C 48.71, H 5.45; found: C 48.58, H 5.29.

1,3-Dimethyl-1,3-diphenylallene (13e) and 3-methyl-1,3-diphenylbut-1-yne (13d): The reaction of **12a** (1.84 g, 5.65 mmol) and dimethyl sulfate (1.90 mL, 3.5 equiv) gave a 1:2 mixture of **13e** and **13d** (816 mg, 65%). The mixture was separated by preparative GC.

13d: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.68$ (s, 6H; CH_3), 7.20–7.65 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = 31.70$ (*C*H$_3$), 36.39 (C≡C-*C*PhMe$_2$), 82.06 C≡*C*-CPhMe$_2$, 96.49 (-C≡*C*-Ph), 123.82, 125.59, 126.40, 127.68, 128.18, 128.28 (CH, Ph), 131.60 (C, -C≡C-*Ph*), 146.95 (C, Ph); IR ($CHCl_3$): $\tilde{\nu} = 3058$ (w), 3030 (m), 2974 (s), 2360 (w), 1598 (m), 1491 (s), 1444 (s), 1360 (m), 1293 (m), 1101 (m) cm^{-1}; MS (70 eV): 220 [M^+], 205 [M^+ – Me], 190 [M^+ – 2Me]; elemental analysis calcd (%) for $C_{17}H_{16}$: C 92.68, H 7.32; found: C 92.62, H 7.31.

***cis*-1,2-Diphenyl-*anti*-3,4-dibenzylidenecyclobutane (13c)**: Prepared from **12a** (2.31 g, 7.15 mmol) and ethanol (excess). A crude product was obtained which was dissolved in THF and refluxed for 2 h. Subsequently, the solvent was removed in vacuo and yellow **13c** was recrystallized from ether (700 mg, 51%). The ^{1}H NMR and IR data and the melting point of **13c** were identical to those reported in the literature,[27] m.p. 194–196 °C. To our knowledge, ^{13}C NMR data of **13c** have not been previously reported; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 5.05$ (s, 2H; -CHPh), 6.89 (s, 10H), 6.90–7.25 (m, 12H; Ph, =CHPh); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = 54.58$ (-*C*HPh-), 119.88 (=*C*HPh); 125.83, 126.73, 127.44, 128.07, 128.65, 128.80 (CH, Ph), 135.91, 136.74 (C, Ph), 142.47 (*C*=CHPh); IR (KBr): $\tilde{\nu} = 3065$ (m), 3020 (m), 1605 (m), 1495 (s), 1460 (m), 905 (s), 735 (s) cm^{-1}; MS (20 °C): *m*/*z*: 384 [M^+], 307 [M^+ – Ph], 192 [0.5 M^+].

1,3-Bis(trimethylsilyl)-1-phenyl-3-methylallene (22): Prepared from **21** (2.06 g, 7.86 mmol) and Me_3SiCl (3.5 mL, 3.5 equiv). Isolated by preparative GC as a light yellow oil (410 mg, 19%, GC); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.13$ (s, 9H; Me_3Si), 0.22 (s, 9H; Me_3Si), 1.75 (s, 3H; CH_3), 7.05–7.30 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -1.62$, –0.04 (Me_3Si), 14.33 (CH_3), 85.38 (=*C*(CH_3)Si), 91.78 (=*C*(Ph)Si), 125.31, 127.35, 128.35 (CH, Ph), 138.57 (C, Ph), 207.34 (C, C=*C*=C); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = -4.74$, –2.94. IR ($CHCl_3$): $\tilde{\nu} = 1904$ (C=C=C), 1249 (Me_3Si) cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{26}Si_2$: C 70.00, H 9.55; found: C 70.04, H 9.83.

Lithiation of silyl enol ether (1): To a solution of LDA (6.6 mmol, 1.1 equiv) in THF (30 mL) [prepared by the addition of *n*BuLi (4.5 mL) to a solution of diisopropylamine (1.0 mL) in THF], was added one equivalent of silyl enol ether **1** dissolved in THF (10 mL) at 0 °C. The ice bath was removed and the solution was stirred at 20 °C for 4 h. Dimethylchlorosilane (0.79 mL, 1.2 equiv) was added at 0 °C and precipitation of LiCl was observed. Nonaqueous work-up afforded a 1:1 mixture of **2** and **3** in 76% combined yield. Pure samples of **2** and **3** were isolated by preparative GC.

2: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.03$ (s, 9H; Me_3Si), 0.07 (d, $J = 2.5$ Hz, 6H; Me_2SiO), 1.78 (s, 2H; CH_2Si), 4.52 (sept, $J = 2.5$ Hz, 1H; SiH), 7.25 (m, 10H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -0.10$, –0.08, 25.1, 120.8, 125.2, 125.8, 126.4, 127.2, 129.7, 130.4, 141.2, 142.9, 149.5; ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = 4.20$ (CSi), 4.75 (OSi); elemental analysis calcd (%) for $C_{20}H_{28}OSi_2$: C 70.53, H 8.29; found: C 70.97, H 8.18.

Preparation of di(hydroxymethyl)allenes (8): A solution of silyl enol ether **5a** (950 mg, 2.95 mmol) in THF (10 mL) was added to a solution of LDA in THF [prepared by the addition of *n*BuLi (1.6 M solution in hexane)] to a solution of diisopropylamine (3.3 equiv) in THF (30 mL) at 0 °C. The mixture was stirred at 20 °C for 6 h during which time the color of the solution became deep red. A solution of benzophenone (1.34 g, 7.38 mmol) in THF (10 mL) was added at –78 °C by syringe. The temperature was allowed to rise to 20 °C within 12 h to give a deep blue solution. The mixture was poured into water (50 mL) and then extracted with diethyl ether (4 × 60 mL). The combined yellow organic layers were dried ($MgSO_4$), filtered, and the solvent of the filtrate was removed in vacuo. Purification by column chromatography (silica gel, diethyl ether:petroleum ether = 1:5 → 1:1) afforded the allene **8a** (1.31 g, 80%) as a colorless solid. M.p. 110 °C (decomp).

8a: ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 3.82$ (s, 2H; OH), 6.32 (m, 4H; Ph), 7.10–7.40 (m, 26H; Ph); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta_c = 82.90$ (C, *C*OH), 114.85, 116.11 (C, *C*=C=*C*), 126.79, 127.91, 128.04 (CH, Ph), 127.18, 127.29, 127.83 (CH, Ph), 136.56, 146.56 (C, Ph), 205.26 (C, C=*C*=C); IR (KBr): $\tilde{\nu} = 3385$ (w), 3057 (w), 1949 (m, C=C=C), 1598 (w), 1493 (m), 1447 (m), 1348 (w), 1177 (w), 1031 (m), 698 (s) cm^{-1}; MS (CI, H_2O): 539 [M^++1 – H_2O), 521 [M^++1 – 2H_2O); MS (EI): *m*/*z* (%): 356 (100) [Ph_2C=C=C=CPh_2]; elemental analysis calcd (%) for $C_{41}H_{32}O_2$: C 88.46, H 5.79; found: C 88.23, H 5.75.

8b: Yield: 62%; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 3.78$ (s, 6H; OCH_3), 5.80 (s, 2H; OH), 6.38 (m, 4H; Ar), 6.70–6.90 (m, 4H; Ar), 7.10–7.50 (m, 20H; Ar); ^{13}C NMR ([D$_8$]THF, 75 MHz): $\delta_c = 69.82$, 86.11, 116.05, 116.78, 129.94, 130.67, 130.96, 131.15, 131.22, 131.31, 131.76, 132.07, 143.69, 151.77, 162.39, 162.48, 208.68; IR (KBr): $\tilde{\nu} = 1950$ (m, C=C=C), 1594 (w), 1490 (m), 1448 (m), 1346 (w), 1175 (w), 1028 (m) cm^{-1}; MS (CI, H_2O, Na^+): 639 [(*M*+Na)$^+$]. MS (EI): 598 [M^+ – H_2O], 580 [M^+ – 2H_2O].

8c: Yield: 75%; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.80$ (s, 12H; OCH_3), 5.72 (s, 2H; OH), 6.50 (m, 4H; Ar), 6.80 (d, $J = 10$ Hz, 8H; Ar), 7.25 (m, 6H; Ar), 7.30 (d, $J = 10$ Hz, 8H; Ar); ^{13}C NMR ([D$_6$]acetone, 75 MHz): $\delta_c = 55.47$ (OCH_3), 83.15 (C, *C*OH), 114.75, 118.90 (C, *C*=C=*C*), 113.37, 127.96, 128.66, 128.85, 129.19 (CH, Ph), 137.84, 140.99, 159.48 (C, Ph), 206.11 (C, C=*C*=C); IR (KBr): $\tilde{\nu} = 1954$ (m, C=C=C) cm^{-1}; MS (CI, H_2O, Na^+): 699 [(*M*+Na)$^+$]; elemental analysis calcd (%) for $C_{45}H_{40}O_6$: C 79.86, H 5.96; found: C 79.97, H 6.09.

8d: Yield: 76%; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.40$ (s, 12H; CH_3), 3.98 (s, 2H; OH), 6.42 (m, 4H; Ar), 7.10–7.40 (m, 22H; Ar); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta_c = 20.97$ (CH_3), 82.65 (C, *C*OH), 114.45, 116.31 (C, *C*=C=*C*), 126.64, 127.12, 127.75, 128.11, 128.42 (CH, Ar), 136.60, 136.83, 144.00 (C, Ph), 205.07 (C, C=*C*=C). IR (KBr): $\tilde{\nu} = 1948$ (m, C=C=C) cm^{-1}; MS (CI, H_2O, Na^+): 635 [(*M*+Na)$^+$]; MS (EI): *m*/*z* (%): 384 (100) [Ph_2C=C=C=CTol_2]; elemental analysis calcd (%) for $C_{45}H_{40}O_2$: C 88.20, H 6.58; found: C 88.06, H 6.49.

8e: Yield: 71%; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 4.21$ (s, 2H; OH), 6.44 (m, 4H; Ar), 7.20–7.45 (m, 22H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta_c = 82.33$ (C, *C*OH), 112.25, 115.72 (C, *C*=C=*C*), 127.87, 128.18, 128.27, 128.34, 128.56 (CH, Ar), 133.59, 135.79, 144.69 (C, Ph), 205.10 (C, C=*C*=C); IR (KBr): $\tilde{\nu} = 1950$ (m, C=C=C) cm^{-1}; MS (CI, NH_3): 712 [M^++1 + 17], 695 [M^++1]; MS (EI): 676 [M^+ – 18], 424 (100) [Ph_2C=C=C=C($C_6H_4Cl)_2$]; elemental analysis calcd (%) for $C_{41}H_{28}O_2Cl_4$: C 70.91, H 4.06; found: C 70.60, H 3.86.

8f: Yield: 72%; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 3.78$ (br, 2H; OH), 6.70–7.40 (m, 26H; Ph); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta_c = 83.40$ (C, *C*OH), 114.89, 115.60 (C, *C*=C=*C*), 119.51, 124.82, 127.01, 127.69, 127.81, 128.00, 128.57 (CH, Ar), 135.84, 139.37, 148.77 (C, Ph), 202.84 (C, C=*C*=C); IR (KBr): $\tilde{\nu} = 1952$ (m, C=C=C) cm^{-1}; MS (CI, H_2O, Na^+): 575 [(*M*+Na)$^+$]; elemental analysis calcd (%) for $C_{41}H_{28}O_2$: C 91.76, H 5.26; found: C 91.52, H 5.20.

8g: Yield: 68%; ^{1}H NMR ([D$_8$]THF, 200 MHz): $\delta = 5.58$ (s, 2H; OH), 6.70 (m, 10H; Ar), 7.00–7.40 (m, 16H; Ar); ^{13}C NMR ([D$_8$]THF, 50 MHz): $\delta_c = 69.63$ (C, *C*OH), 115.51 (C, *C*=C=C), 116.28, 122.80 (CH), 125.53 (C, *C*=C=C), 127.49 (CH), 127.84 (C), 128.62, 129.18, 129.68 (CH), 138.08, 150.69 (C, Ph), 205.93 (C, C=*C*=C); IR ($CHCl_3$): $\tilde{\nu} = 1955$ (m, C=C=C) cm^{-1}; MS (CI, H_2O): *m*/*z*: 586 [M^++1], 584 [M^+ – 1], 568 [M^++1 – H_2O]; MS (EI): 566.5 (1) [M^+ – H_2O], 370 (100)

[$Ph_2C{=}C{=}C{=}C(C_{12}H_8O)$]; elemental analysis calcd (%) for $C_{41}H_{28}O_4$: C 84.23; H 4.83; found: C 84.46, H 4.60.

Preparation of 5,10,10,11-tetraphenyl-10*H*-benzo[*b*]fluorenes (9): Allene **8a** (200 mg, 0.36 mmol) and *para*-toluenesulfonic acid (60 mg) were heated in toluene (30 mL) at 80 °C for 2 h. The color of the solution changed from light yellow to deep orange. The crude mixture was purified by column chromatography (silica gel, diethyl ether:petroleum ether 1:5 → 1:1) to give **9a** (159 mg, 85 %) as orange crystals. M.p. 176 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 6.20$ (d, $J = 7$ Hz, 1H; Ar), 6.56 (m, 2H; Ar), 6.71 (d, $J = 7$ Hz, 1H; Ar), 6.11 (dd, $J = 7$ Hz, $J = 1.5$ Hz, 1H; Ar), 6.41 (m, 2H; Ar), 6.58 (m, 3H; Ar), 6.85 – 7.25 (m, 18H; Ar); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta_c = 57.42$ (C, *C*Ph$_2$), 119.89, 123.25, 124.70, 126.05, 126.23, 127.33, 127.34, 127.81, 127.99, 128.08, 128.20, 128.77, 128.99, 129.28, 130.14, 130.15, 130.37 (CH, Ar), 133.57, 133.81, 134.32, 135.51, 137.78, 139.80, 140.13, 142.24, 145.54, 145.82, 147.23 (C, Ar); IR (KBr): $\tilde{\nu} = 3056$ (m), 3024 (m), 2924 (m), 1600 (m), 1492 (m), 1448 (m), 1368 (w), 1076 (w), 1032 (w), 760 (s), 744 (s), 724 (s), 700 (s) cm^{-1}; MS (FAB): *m*/*z*: 521 (100) [M^++1]; elemental analysis calcd (%) for $C_{41}H_{28}$: C 94.58, H 5.42; found: C 94.27, H 5.50. During the formation of **9a**, benzofulvene **10b** was isolated as a sideproduct in low yield: ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 6.85 - 7.65$ (m, Ar).

Conditions for the separation of the enantiomers of (9a): Stationary phase: tris(phenylcarbamoyl)cellulose/SiO_2; eluent: EtOH; UV detection: $\lambda =$ 320 nm; polarimetric detection: $\lambda = 436$ nm; $c = 1$ mg mL^{-1} (injection of 50 µL); $p = 63$ bar; $T = 25$ °C; flow: 0.5 mL min^{-1}; $t_1 = 9$ min; $k_{1'} = 0.44$. These results were independently confirmed by the use of different conditions: stationary phase: triacetylcellulose/SiO_2; eluent: MeOH; UV detection: $\lambda = 278$ nm; polarimetric detection: $\lambda = 405$ nm; $c = 1$ mg mL^{-1} (injection of 150 µL); $p = 68$ bar; $T = 25$ °C; flow: 1.0 mL min^{-1}; $t_1 =$ 12.6 min; $k_{1'} = 0.60$.

9b: Yield: 73 %; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.76$, 3.78 (2 × s, 2 × 3H; OCH_3), 5.75 (d, 2H; Ar), 6.30 (s, 1H; Ar), 6.40 – 6.70 (m, 6H; Ar), 6.80 – 7.20 (m, 17H; Ar), 7.40 – 7.70 (m, 6H; Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_c = 55.15$, 55.31 (OCH_3), 56.84 (C, *C*Ph$_2$), 112.64, 113.22, 121.71, 125.65, 125.83, 126.10, 126.94, 127.24, 127.56, 127.76, 127.93, 128.61, 129.04, 129.11, 129.36, 130.13, 130.32, 131.19 (CH), 131.81, 132.92, 133.69, 134.75, 135.29, 135.93, 137.93, 138.05, 138.95, 142.29, 144.14, 147.43, 155.00, 157.61 (C); MS (EI): *m*/*z*: 580 [M^+], 374 [88]; elemental analysis calcd (%) for $C_{43}H_{32}O_2$: C 88.94, H 5.55; found: C 88.68, H 5.44.

9c: Yield: 76 %; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.25$ (s, 3H; OCH_3), 3.36 (s, 2 × 3H; OCH_3), 3.37 (s, 3H; OCH_3), 6.19 (m, 1H; Ar), 6.50 – 7.10 (m, 11H; Ar), 7.15 – 7.50 (m, 12H; Ar); ^{13}C NMR (C_6D_6, 75 MHz): $\delta_c = 54.73$, 54.79 (OCH_3), 57.15 (C, *C*Ph$_2$), 110.65, 113.18, 113.34, 113.37, 113.67, 120.93, 126.46, 128.07 (CH), 128.12, 128.73 (C), 129.28, 129.63, 130.29, 130.56, 131.71, 132.40 (CH), 134.59, 135.70, 136.25, 138.43, 138.60, 139.32, 139.40, 139.63, 143.05, 148.24, 158.44, 158.62 (C); MS (EI): *m*/*z* (%): 640 (100) [M^+], 533 (42); elemental analysis calcd (%) for $C_{45}H_{36}O_4$: C 84.35, H 5.66; found: C 84.46, H 5.56.

During the formation of **9c**, benzofulvene **10a** was isolated as a side product in 10 % yield; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 3.49$ (s, 3H; OCH_3), 3.90 (s, 3H; OCH_3), 6.21 (d, $J = 2$ Hz, 1H; Ar), 6.60 (s, 1H; Ar), 6.75 (dd, $J = 2$ Hz, $J = 7$ Hz, 1H; Ar), 6.96 (m, 2H; Ar), 7.35 – 7.65 (m, 13H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta_c = 55.06$, 55.33 (OCH_3), 109.94, 112.72, 113.97, 120.43, 124.84, 127.87, 127.96, 128.34 (CH), 128.49 (C), 128.66, 128.73, 130.22, 131.42 (CH), 136.04, 138.11, 139.04, 141.65, 142.30, 143.89, 145.30, 157.67, 159.32 (C); MS (EI): 416 (100) [M^+]; MS (CI, NH_3): *m*/*z*: 417 [M^++1]; elemental analysis calcd (%) for $C_{30}H_{24}O_2$: C 86.51, H 5.81; found: C 86.35, H 5.62.

9d: Yield: 83 %; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.20$ (s, 3H; CH_3), 2.30 (s, 3 × 3H; CH_3), 6.02 (s, 1H; Ar), 6.55 (d, 2H; Ar), 6.70 – 7.70 (m, 21H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta_c = 20.87$, 21.13, 21.52 (CH_3), 56.92 (C, *C*Ph$_2$), 119.56, 124.28, 126.04, 127.58, 127.71, 127.82, 127.89, 128.19, 128.44, 128.51, 128.85, 128.99, 129.21, 129.39, 130.05, 130.12, 130.46, 131.52, 132.73, 133.94, 133.97, 134.06, 134.66, 135.21, 135.33, 137.99, 139.11, 139.70, 142.28, 143.02, 143.21, 147.40; MS (EI): *m*/*z* (%): 576 (36) [M^+], 384 (100); elemental analysis calcd (%) for $C_{45}H_{36}$: C 93.71, H 6.29; found: C 93.58, H 6.18.

9e: Yield: 86 %; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 6.20$ (s, 1H; Ar), 6.58 (d, $J = 1.5$ Hz, 2H; Ar), 7.10 – 7.70 (m, 21H; Ar); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta_c = 56.87$ (C, *C*Ph$_2$), 120.68, 123.86, 125.38, 127.07, 127.46, 127.84, 127.93, 128.13, 128.31, 128.72, 128.76, 128.81, 128.87, 128.92, 129.03, 129.11, 129.32, 129.81, 129.85, 130.46, 131.23, 131.33, 131.70, 132.74, 132.86, 133.37, 133.64, 134.94, 136.72, 140.24, 141.03, 141.78, 142.96, 143.64, 146.27; MS (CI, NH_3): *m*/*z*: 659 [M^++1].

11a: Yield: 85 %; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 7.20 - 7.80$ (m, 18H; Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_c = 120.13$, 123.39, 127.15 (CH), 127.46 (C), 128.29, 128.61 (CH), 128.75 (C), 128.88, 129.64 (CH), 138.48, 139.00, 139.73, 146.66, 151.93 (C); MS (EI): *m*/*z* (%): 354 (100) [M^+]; elemental analysis calcd (%) for $C_{28}H_{18}$: C 94.88, H 5.12; found: C 94.56, H 4.94.

11b: Yield: 70 %; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 7.10 - 7.20$, 7.25 – 7.55, 7.65 (m, 18H; Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, APT): $\delta_c = 110.49$ (C), 116.85 (CH), 118.89 (C), 121.74 (C), 123.98, 127.48, 127.70, 128.50, 129.23, 129.67 (CH), 137.20, 139.24, 150.90, 151.22 (C); MS (EI): *m*/*z* (%): 370 (100) [M^+]; elemental analysis calcd (%) for $C_{28}H_{18}O$: C 90.78, H 4.90; found: C 90.48, H 4.72.

General procedure for the generation of trisilylated allenes from silyl enol ethers: All reactions were carried out on a 4 – 10 mmol scale. To a solution of LDA (26.4 mmol, 4.4 equiv) in THF (50 mL) [prepared by the addition of *n*BuLi (18.1 mL) to a solution of diisopropylamine (4.0 mL) in THF (50 mL)], was added a solution of the silyl enol ether (1 equiv) in THF (10 mL) at 0 °C. The ice bath was removed and the solution was stirred at 20 °C for 6 h. A solution of Me_3SiCl (4.5 equiv) in THF (10 mL) was added at 0 °C. The reaction was worked-up according to the procedure given for the preparation of allene **6a**.

Tris(trimethylsilyl)-(2′-quinolyl)allene (16): Prepared from **15** (1.80 g, 6 mmol) and Me_3SiCl (3.5 mL, 4.5 equiv). Isolated by chromatography (activated Al_2O_3, hexane) as a yellow oil (1.95 g, 85 %); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.19$ (s, 18H; Me_3Si), 0.31 (s, 9H; Me_3Si), 7.35 (t, 1H; Ar); 7.42 (d, 1H; Ar), 7.57 (t, 1H; Ar), 7.68 (d, 1H; Ar), 7.87, 7.88 (d, 2H; Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = 0.04$, 0.48 (Me_3Si), 83.98, 85.94 (C, =*C*Si, =*C*Si$_2$), 119.61, 124.72, 125.77, 127.21, 128.77, 128.86, 135.01, 148.28 (CH, C, Ar), 208.98 (C, C=*C*=C); ^{29}Si NMR: ($CDCl_3$): $\delta_{Si} = -5.07$, −2.76; IR ($CHCl_3$): $\tilde{\nu} = 1887$ (C=C=C), 1249 (Me_3Si) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{33}NSi_3$: C 65.73, H 8.67; found: C 66.20, H 8.61.

Tris(trimethylsilyl)-(2′-pyridyl)allene (18): Prepared from **17** (750 mg, 3 mmol) and Me_3SiCl (1.75 mL, 4.5 equiv). Isolated by preparative GC as a yellow oil (18 %, GC); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.13$ (s, 18H; Me_3Si), 0.20 (s, 9H; Me_3Si), 6.90, 7.37, 7.48, 7.47 (m, 4H; Pyr); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_c = 0.01$, 0.40 (Me_3Si), 84.40, 84.72 (C, =*C*Si, =*C*Si$_2$), 118.73, 120.68, 135.39, 148.73 (CH, Pyr), 159.73 (C, Pyr), 208.98 (C, C=*C*=C); IR ($CHCl_3$): $\tilde{\nu} = 1888$ (s, C=C=C), 1252 (s, Me_3Si) cm^{-1}; MS (20 °C): *m*/*z*: 333 [M^+].

Tris(trimethylsilyl)phenylallene (20): Prepared from **19** (753 mg, 3 mmol) and Me_3SiCl (1.75 mL, 4.5 equiv). A complex reaction mixture was obtained. An nonpolar fraction (280 mg) was obtained by chromatography (silica gel, hexane). The ^{1}H NMR, MS, and IR data indicated the presence of **20** by comparison with the data reported for this compound in the literature.[30] IR ($CHCl_3$): 1880 (s, C=C=C), 1248 (s, Me_3Si) cm^{-1}; MS (20 °C): *m*/*z*: 332 [M^+].

Lithiation of silyl enol ether (23): Prepared from **23** (753 mg, 3 mmol) and Me_3SiCl (1.75 mL, 4.5 equiv). A complex reaction mixture was obtained. Presence of an allene product was detected by IR. GC-MS indicated formation of **24** as the main product which was isolated by preparative GC (52 %); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.07$ (s, 6H; Me_2Si), 0.09 (s, 9H; Me_3Si), 0.86 (s, 9H; *t*Bu), 1.52 (d, $J = 10$ Hz, 2H; CH_2), 5.2 (t, $J = 10$ Hz, 1H; =CH-), 7.10 – 7.40 (m, 4H; Ph).

General procedure for the preparation of silyl imino ethers (25), (27), and (32): To a solution of LDA (27.5 mmol) in THF (50 mL) [prepared by addition of *n*BuLi (18.9 mL) to a solution of diisopropylamine (4.1 mL) in THF], was added a solution of the amide (25 mmol) in THF (10 mL) at 0 °C. The color of the solution became yellow. After the mixture had been stirred at 20 °C for 2 h, a solution of *t*BuMe_2SiCl (5.6 g, 1.5 equiv) in THF (10 mL) was added and the precipitation of LiCl was observed. The suspension was stirred for 48 h at 20 °C. The solvent was removed and the residue was dried in vacuo and extracted with hexane (3 × 80 mL). The extracts were filtered through Celite and the solvent was removed in vacuo.

***tert*-Butyldimethyl[(1-phenylimino)ethyloxy]silane (25)**: Prepared from acetanilide (4.42 g, 32.8 mmol). Yellow oil (6.7 g, 82 %) which was purified for elemental analysis by preparative GC. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.31$ (s, 6H; Me_2Si), 0.95 (s, 9H; *t*Bu), 1.79 (s, 3H; CH_3), 7.00 – 7.30 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_C = -4.55$ (CH_3, Me_2Si), 17.13

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(CH_3), 17.81 (C, CMe_3), 25.87 (CMe_3), 120.85, 122.58, 128.78 (CH, Ph), 149.17 (C, Ph), 160.15 (C, COSi); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = 21.73$; IR ($CHCl_3$): $\tilde{\nu} = 1290$ (Me_2Si) cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{23}ONSi$: C 67.42, H 9.30; found: C 67.07, H 9.40.

***tert*-Butyldimethyl[(1-(2′-pyridyl)imino)ethyloxy]silane (27)**: Prepared from 2-pyridylacetamide (4.85 g, 35.6 mmol). Isolated by kugelrohr distillation (air bath 90 °C, 0.05 mbar) as a colorless, analytically pure oil (6.5 g, 73 %). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.34$ (s, 6H; Me_2Si), 0.95 (s, 9H; *t*Bu), 1.88 (s, 3H; CH_3), 6.70, 6.92, 7.57, 8.34 (m, 4H; Pyr); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta_C = -4.70$ (CH_3, Me_2Si), 17.66 (CH_3), 18.12 (C, CMe_3), 25.66 (CMe_3), 116.64, 118.22, 137.39, 148.55 (CH, Pyr), 160.97, 162.55 (C, COSi, Pyr); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = 23.04$; IR ($CHCl_3$): $\tilde{\nu} = 1254$ (Me_2Si) cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{22}N_2OSi$: C 62.26, H 8.83; found: C 62.53, H 9.22.

General procedure for the lithiation of silyl imino ethers: All reactions were carried out on a 4–10 mmol scale. To a suspension of LDA (18 mmol, 3.0 equiv) in THF (50 mL) [prepared by the addition of *n*BuLi (12.4 mL) to a solution of diisopropylamine (2.7 mL) in THF], was added a solution of the silyl enol ether (1 equiv) in THF (10 mL) at 0 °C. The ice bath was removed and the solution was stirred at 20 °C for 6 h. A solution of the electrophile (3.5 equiv) in THF (10 mL) was added at 0 °C and precipitation of LiCl was observed. The suspension was stirred for 12 h at 20 °C. The solvent was removed in vacuo and the residue was dried in vacuo and extracted with hexane (3 × 50 mL). The extracts were filtered through Celite and the solvent was removed in vacuo.

***N*-Phenyl-bis(trimethylsilyl)-1-aza-1,2-propadiene (26)**: Prepared from **25** (1.88 g, 7.54 mmol). Isolated from 1.5 g of crude product as a colorless oil by preparative GC (38 %, GC). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.05$ (s, 18H; Me_3Si), 6.85–7.25 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_c = 1.08$ (CH_3, Me_3Si), 119.35 (C, $=C(SiMe_3)_2$), 91.78 (C, $=CPhSi$), 122.91, 125.47, 129.72 (CH, Ph), 142.34 (C, Ph), 172.82 (C, N=C=C); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = -0.45$; IR ($CHCl_3$): $\tilde{\nu} = 2146$ (N=C=C), 1250 (Me_3Si) cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{23}NSi_2$: C 64.30, H 8.87; found: C 64.40, H 9.16.

***N*-(2′-Pyridyl)-bis(trimethylsilyl)-1-aza-1,2-propadiene (28)**: Prepared from **27** (2.12 g, 8.48 mmol) to give 1.45 g of crude **28** (≈85 % purity, ≈65 % yield); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.06$ (s, 18H; Me_3Si); 6.70–8.34 (4H; Pyr); IR ($CHCl_3$): $\tilde{\nu} = 2145$ (N=C=C), 1250 (Me_3Si) cm^{-1}.

2,3-Bis(trimethylsilyl)imidazo[1,2-a]pyridine (29): A sample of crude **28** was subjected to preparative GC to give **29** as an orange oil (82 %, GC). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.40$, 0.45 (s, 18H; Me_3Si), 6.68 (t, H6), 7.08 (t, H7), 7.69 (d, H8); 8.25 (d, H5); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_c = 0.78$, 1.02 (CH_3, Me_3Si), 111.80, 118.11, 124.11, 126.69, 128.68, 149.03 (C, CH, Ar), 155.81 (C=N); ^{29}Si NMR ($CDCl_3$): $\delta_{Si} = -11.91$, -7.32; IR ($CHCl_3$): $\tilde{\nu} = 3073$ (m), 2954 (s), 2896 (s), 1629 (m), 1526 (m), 1496 (s), 1446 (m), 1345 (s), 1329 (s), 1253 (s), 1177 (m), 1040 (m) cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{22}Si_2$: C 59.49, H 8.45; found: C 59.59, H 8.55.

2-Ethoxy-1-(2′-pyridyl)-1-azaprop-1-ene (30): Prepared from **27** (2.10 g, 8.48 mmol). Isolated by chromatography (activated Al_2O_3, hexane:diethyl ether = 3:1) as an orange oil (570 mg, 41 %). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.30$ (t, $J = 7$ Hz, 3H; CH_2CH_3), 1.85 (s, 3H; CH_3), 4.23 (q, $J = 7$ Hz, 2H; CH_2CH_3), 6.72 (d, $J = 7$ Hz, 1H; Pyr), 6.93 (t, $J = 7$ Hz, 1H; Pyr), 7.56 (t, $J = 7$ Hz, 1H; Pyr), 8.33 (d, $J = 7$ Hz, 1H; Pyr); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_c = 14.11$ (CH_2CH_3), 16.94 (CH_3), 61.93 (CH_2CH_3), 116.43, 118.40, 137.67, 148.74 (CH, Pyr), 161.39, 163.31 (C, Pyr, N=COEt); IR ($CHCl_3$): $\tilde{\nu} = 2980$ (m), 1669 (m), 1590 (s), 1559 (m), 1488 (s), 1429 (m), 1374 (s), 1289 (s), 1255 (s), 1145 (m), 1095 (m) cm^{-1}.

[(1-(2′-Pyridyl)imino)ethyl]diethylamine (31): Prepared from **27** (2.10 g, 8.48 mmol). Isolated by chromatography (activated Al_2O_3, hexane:diethyl ether 3:1) as an orange oil (648 mg, 40 %). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.15$ (t, $J = 7$ Hz, 6H; CH_2CH_3), 1.93 (s, 3H; CH_3), 3.45 (q, $J = 7$ Hz, 4H; CH_2CH_3), 6.67 (d, $J = 7$ Hz, 1H; Pyr), 6.78 (t, $J = 7$ Hz, 1H; Pyr), 7.48 (t, $J = 7$ Hz, 1H; Pyr), 8.28 (d, $J = 7$ Hz, 1H; Pyr) ; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta_c = 13.33$ (CH_2CH_3), 15.22 (CH_3), 41.98 (CH_2CH_3), 116.21, 117.50, 136.99, 148.23 (CH, Pyr), 156.83, 163.75 (C, Pyr, N=COEt) ; IR ($CHCl_3$): $\tilde{\nu} = 2971$ (m), 2931 (m), 1604 (m), 1582 (s), 1549 (m), 1453 (s), 1415 (s), 1360 (s), 1266 (s), 1204 (m), 1143 (m), 1040 (m) cm^{-1} ; MS (20 °C): m/z: 191 [M^+], 162 [$M^+ - Et$], 119 [$M^+ - NEt_2$].

Crystal structure analyses:[35] The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated $Mo_{K\alpha}$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[36] The structures were solved by direct methods (SHELXS)[37] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97)[38]. The hydrogen atoms of the structures were included at the calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[38] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal data for 8g: $C_{41}H_{28}O_4$, $M_r = 584.63$ g mol^{-1}, colorless prism, 1.00 × 0.90 × 0.20 mm^3, monoclinic, space group $P2_1/n$, $a = 13.154(17)$, $b = 15.14(3)$, $c = 14.52(2)$ Å, $\beta = 91.90(10)°$, $V = 5527(1)$ Å^3 , $T = 200(2)$ K, $Z = 4$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.343$ g cm^{-3}, $F(000) = 1224$, absorption coefficient = 0.086 mm^{-1}, 3778 reflections in $-14 \le h \le 14$, $0 \le k \le 16$, $-10 \le l \le 15$, measured in the range $3.52 \le \theta \le 22.51°$, 3766 [$R$(int) = 0.1196] independent reflections, data/restraints/parameters = 3751/0/406, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0598$, $wR2 = 0.1268$, R indices (all data): $R1 = 0.0979$, $wR2 = 0.1653$, GOF = 1.080, largest difference peak and hole: 0.219 and -0.260 e Å^{-3}.

Crystal data for 9a: $C_{41}H_{28}$, $M_r = 520.63$ g mol^{-1}, colorless prism, 0.40 × 0.38 × 0.20 mm^3, monoclinic, space group $C2/c$, $a = 22.292(4)$, $b = 14.475(2)$, $c = 19.982(3)$ Å, $\beta = 120.99(1)°$, $V = 5527(1)$ Å^3 , $T = 183(2)$ K, $Z = 8$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.251$ g cm^{-3}, $\mu = Mo_{K\alpha} = 3.62$ cm^{-1}, $F(000) = 2192$, absorption coefficient = 0.071 mm^{-1}, 5346 reflections in $-23 \le h \le 26$, $-18 \le k \le 0$, $-24 \le l \le 0$, measured in the range $2.23 \le \theta \le 26.31°$, 5191 [$R$(int) = 0.0243] independent reflections, data/restraints/parameters = 3863/0/371, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0472$, $wR2 = 0.1033$, R indices (all data): $R1 = 0.1637$, $wR2 = 0.1405$, GOF = 0.954, extinction coefficient: 0.0010(2), largest difference peak and hole: 0.207 and -0.193 e Å^{-3}.

Crystal data for 10b: Empirical formula: $C_{44}H_{38}OSi$, $M_r = 610.83$ g mol^{-1}, colorless prism, 0.40 × 0.38 × 0.36 mm^3, monoclinic, space group $P2(1)/c$, $a = 19.594(4)$, $b = 13.658(3)$, $c = 12.189(2)$ Å, $\beta = 91.51(3)°$, $V = 3260.8(11)$ Å^3, $T = 183(2)$ K, $Z = 4$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.244$ g cm^{-3}, $\mu = Mo_{K\alpha} = 3.62$ cm^{-1}, $F(000) = 1296$, absorption coefficient = 0.107 mm^{-1}, 602 reflections in $-23 \le h \le 23$, $-16 \le k \le 0$, $-14 \le l \le 0$, measured in the range $2.98 \le \theta \le 25.00°$, 5732 [$R$(int) = 0.025] independent reflections, data/restraints/parameters = 5671/0/415, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0847$, $wR2 = 0.1854$, R indices (all data): $R1 = 0.2456$, $wR2 = 0$. 0.3672, GOF = 1.431, extinction coefficient: 0.0010(2), largest difference peak and hole: 0.594 and -0.439 e Å^{-3}.

Acknowledgements

P.L. thanks Prof. Dr. A. de Meijere for his support and Prof. A. Mannschreck for his help with the separation of the enantiomers of **9a**. Financial support from the Fonds der Chemischen Industrie (Liebig scholarship and funds for P.L.) and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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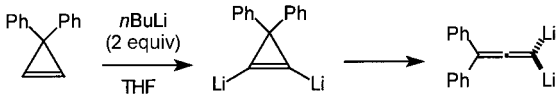

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Received: June 19, 2000 [F2550]