Articles

Novel and Convenient Synthesis of Aroyl-, Heteroaroyl-, Alkenoyl-, and Alkynoylsilanes

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A new and convenient two-step route to aryl-, heteroaryl-, alkenyl-, and alkynylacylsilanes is described. The corresponding aldehyde−benzotriazole−ethanol condensation products are treated with butyllithium and then reacted with trialkylsilyl chlorides to yield the substituted intermediates. Subsequent *in-situ* mild hydrolysis affords the title compounds in good to excellent yields.

Introduction

Acylsilanes show unusual spectroscopic features and unique reactivity, for example, as aldehyde equivalents in diastereoselective nucleophilic addition reactions[1,2] and stereoselective Wittig reactions.[3] The increasing interest is evidenced by several reviews.[4−7] Despite a large number of previous investigations, the development of novel efficient synthetic methodologies is still a challenge. Among the known methods,[5−8] the "dithiane route" developed by Corey[9] and Brook[10] in the 1960s remains one of the most general means of access to alkanoyl- ($R'COSiR_3$) and aroylsilanes ($ArCOSiR_3$) and is frequently applied for the synthesis of new acylsilanes. The major drawback of this synthesis lies in the final hydrolysis step; the ease of the hydrolysis depends significantly on the nature of the substituents R, R′, and Ar. Normally, a heavy-metal salt ($HgCl_2$ or HgO), which can form a complex with the thiol, is used; this route is also unfavorable for the synthesis of α,β-unsaturated acylsilanes. Anodic oxidation[11] was reported as an alternative to mercury-mediated deprotection. In another approach for the preparation of acylsilanes, Mandai *et al.*[12] reported the alkylation of methoxy(phenylthio)trialkylsilylmethane and subsequent oxidation with $NaIO_4$; however, this acyl anion synthon method is not applicable for the synthesis of aroyl-, heteroaroyl-, alkenoyl- and alkynoylsilanes.

Recent work in our group has demonstrated the significance of benzotriazole acyl anion methodologies for the synthesis of a variety of alkenyl,[13,14] alkynyl,[15] aryl, and heteroaryl ketone derivatives.[16] Our approaches in this previous work consisted of three-step sequences: *i.e.*, (i) condensation of an aldehyde with benzotriazole, ethanol, and ethyl orthoformate or, alternatively, direct reactions of the corresponding acetals with benzotriazole to form the acyl anion equivalents, (ii) treatment of these intermediates with butyllithium followed by reaction with an electrophile, and (iii) subsequent hydrolysis under mild conditions to produce the ketones. In these operations, steps ii and iii can be conveniently combined into one-pot operations without isolation of the intermediates. A variety of electrophiles were employed including alkyl halides, aldehydes, ketones, imines, esters, *etc.*, and this led to a wide variety of α-functionalized ketones. Work in our group has also demonstrated the convenient formation and trapping of various substituted formylsilanes by using (benzotriazol-1-yl)(carbazol-1-yl)methane as a formyl anion equivalent.[17] α-Silylalkylated heterocycles and *N*,*N*-dialkylanilines were readily prepared by lithiations of *N*-(benzotriazol-1-ylmethyl)carbazole and -indole and 4-(benzotriazol-1-ylmethyl)-*N*,*N*-dimethylaniline followed by reaction with trialkylsilyl chlorides and subsequent displacement of the benzotriazolyl group.[18] We now report our successful extension of this benzotriazole acyl synthon methodology to reactions with trialkylsilyl chlorides and demonstrate that this provides a facile method for the preparation of various aroyl-, heteroaroyl- α,β-unsaturated alkenoyl-, and alkynoylsilanes.

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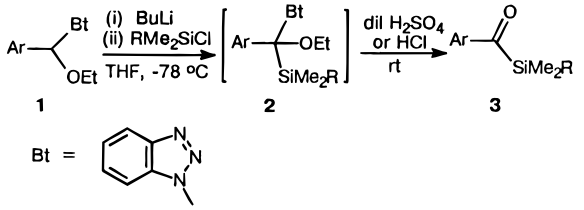
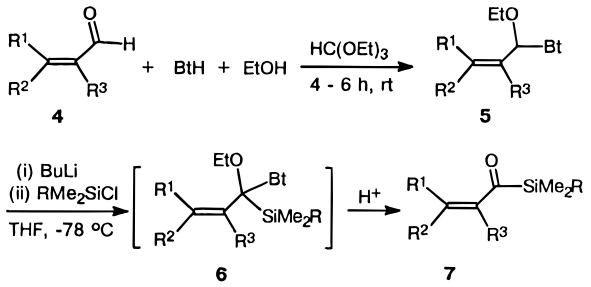
Table 1. Preparative Data of Aryl- and Heteroarylacylsilanes 3a−n

final compd	Ar (starting material)	R	yield (%)	molecular formula	CHN analysis (calcd/found) C	H
3a	Ph (**1a**)	Me	80	$C_{10}H_{14}OSi$	67.36/67.31	7.91/7.98
3b	Ph (**1a**)	*n*-C_8H_{17}	90	$C_{17}H_{28}OSi$	73.85/73.69	10.21/10.36
3c	2-MeO-C_6H_4 (**1b**)	Me	82	$C_{11}H_{16}O_2Si$	63.42/63.28	7.74/7.88
3d	2-MeO-C_6H_4 (**1b**)	*n*-C_8H_{17}	84	$C_{18}H_{30}O_2Si$	70.53/70.71	9.86/10.15
3e	2-Cl-C_6H_4 (**1c**)	Me	97	$C_{10}H_{13}OSiCl$	56.46/56.36	6.16/6.13
3f	2-Cl-C_6H_4 (**1c**)	*n*-C_8H_{17}	96	$C_{17}H_{27}OSiCl$	65.67/65.59	8.75/8.79
3g	4-Me-C_6H_4 (**1d**)	Me	81	$C_{11}H_{16}OSi$	68.69/68.82	8.38/8.44
3h	4-Me-C_6H_4 (**1d**)	*n*-C_8H_{17}	81	$C_{18}H_{30}OSi$	74.42/74.24	10.41/10.53
3i	1-naphthalyl (**1e**)	Me	86	$C_{14}H_{16}OSi$	73.63/73.94	7.06/7.13
3j	1-naphthalyl (**1e**)	*n*-C_8H_{17}	86	$C_{21}H_{30}OSi$	77.24/77.38	9.26/9.38
3k	2-furyl (**1f**)	Me	75	$C_8H_{12}O_2Si$	57.10/57.14	7.19/6.90
3l	2-furyl (**1f**)	*n*-C_8H_{17}	89	$C_{15}H_{26}O_2Si$	67.62/67.43	9.84/10.08
3m	2-thiophenyl (**1g**)	Me	76	$C_8H_{12}OSSi$	52.13/51.91	6.56/6.50
3n	2-thiophenyl (**1g**)	*n*-C_8H_{17}	57	$C_{15}H_{26}OSSi$	63.77/63.44	9.28/9.35

Scheme 1



Scheme 2



4,5,6 **a** R^1 = R^2 = Me, R^3 = H; **b** R^1 = H, R^2 = Ph, R^3 = Me

7 **a** R^1 = R^2 = Me, R^3 = H, R = *n*-C_8H_{17}; **b** R^1 = H, R^2 = Ph, R^3 = Me, R = Me

Results and Discussion

The α-(benzotriazol-1-yl)arylmethyl ethyl ethers **1** were prepared according to the previously described procedure[16] by reacting the aldehyde, benzotriazole, ethanol, and triethyl orthoformate in THF. The aldehydes used included 4-methyl, 2-chloro-, and 2-methoxybenzaldehydes, 1-naphthalenecarboxaldehyde, 2-furaldehyde, and 2-thiophenecarboxaldehyde. Treatment of compounds **1** with butyllithium at −78 °C for 1−5 min followed by addition of a trialkylsilyl chloride gave intermediates **2**, which were then hydrolyzed in dilute HCl or H_2SO_4 at room temperature for 2−10 h to afford the expected aryl and heteroaryl acylsilanes in 57−97% yields (Scheme 1, Table 1). The trialkylsilyl chlorides used in the present cases [Me_3SiCl and (*n*-C_8H_{17})Me_2SiCl] reacted satisfactorily with all the tertiary anions at −78 °C to room temperature to give the desired products.

Benzotriazole derivatives **5a,b** were also prepared by reactions of the corresponding aldehydes **4a,b** with benzotriazole and ethanol using a procedure similar to that described[16] for the aryl derivatives **1**. When **5a** was treated with BuLi and then with dimethyloctylsilyl chloride followed by hydrolysis, α,β-unsaturated acylsilane **7a** was obtained in 80% yield without detection of any γ-silylated products. In the case of **5b**, reaction with trimethylsilyl chloride gave the desired product **7b** in 71% yield. Previous work in our group[14] demonstrated that successive treatment of *N*-(α-ethoxyallyl)-benzotriazole (**5**: $R^1 = R^2 = R^3 = H$; obtained by direct reaction of benzotriazole with acrolein diethyl acetal in performance fluid)[19] with BuLi and trimethylsilyl chloride results in formation of the α- and γ-substituted products in a ratio of *ca.* 3:1.[14] The exclusive formation of the α-product in the present cases can be attributed to steric hindrance at the γ-position and the relatively strong nucleophilicity of the α-position. However, when a more sterically hindered dimethyloctylsilyl chloride was used in the reaction with **5b**, only traces of the desired product (<2%) together with 11% γ-silylated product were generated: this reaction produces mainly benzotriazole ring-opened products. Due to the bulky group, the electrophile can attack neither the α-position nor the γ-position, and the α-anion formed after lithiation finally undergoes benzotriazole ring-opening. Generally, the benzotriazole ring is stable, but we have observed ring scission in several previous cases.[20−22]

We previously reported[15] the preparation of 1-(trimethylsilyl)-2-nonyn-1-one, an acetylenic acylsilane, by the benzotriazole acyl anion equivalent methods. We have now further investigated this preparative route. Using a procedure similar to **5** → **6** → **7**, **8** was easily prepared in 51% yield (see Scheme 3). However, when octyldimethylsilyl chloride [(*n*-C_8H_{17})Me_2SiCl] was used as an electrophile, a mixture of three products **(12, 13, 14)** was obtained after hydrolysis (Scheme 3). Perhaps deprotonation of **9** generates an equilibrium between the two lithium species **10** and **11**. In the less sterically hindered case of trimethylsilyl chloride, intermediate **10/11** yields exclusively the acetylenic acylsilane **8**. However, the steric effect in octyldimethylsilyl chloride causes a partial reaction to produce γ-silylated allene derivative **13** along with the desired product **12**. Partial hydrolysis of **13** led to the β-silylated α,β-unsaturated

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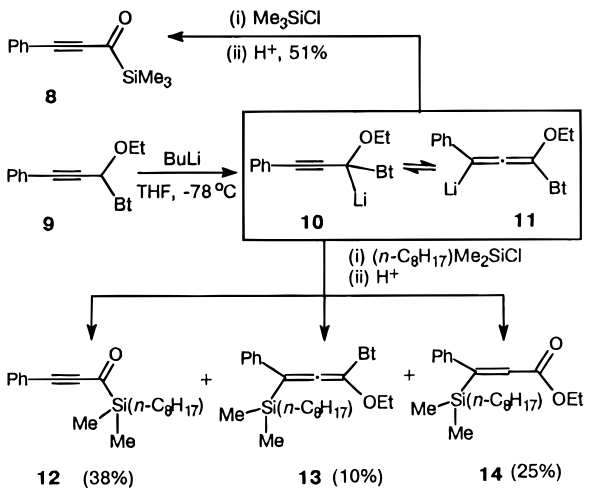
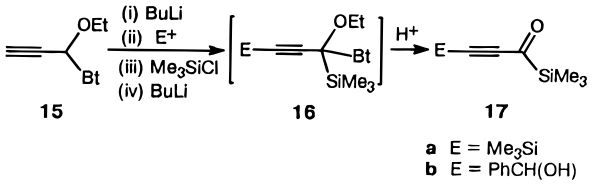
Scheme 3



Scheme 4



ester **14**. An equilibrium between species of types **10** and **11** has been postulated by previous workers.[23,24]

A more general access to alkynoylsilanes is available *via* elaboration of **15**. Since an active hydrogen is present in the acetylenic group, **15** can be doubly lithiated to give the substituted alkynoylsilanes. Thus, successive treatment of **15** with 1 equiv of BuLi in THF followed by quenching with trimethylsilyl chloride or benzaldehyde, then with trimethylsilyl chloride, and lastly with another equivalent of butyllithium gave the regiospecifically doubly substituted intermediates **16a,b** which were then hydrolyzed to yield acylsilanes **17a,b**. It is notable that a "reverse process" in steps 3 and 4 was used, *i.e.*, the addition of trimethylsilyl chloride prior to the BuLi. This is critical for a successful reaction; complicated mixtures were otherwise obtained. The starting materials **9** and **15** were prepared by direct reaction of the corresponding acetals with benzotriazole in refluxing benzene or toluene according to our previously described method.[14]

All the acylsilanes presently obtained are yellow oils. Their structures were confirmed by ^{1}H and ^{13}C NMR and elemental analyses. The known compounds have been compared with data reported in the literature. The ^{13}C NMR shows the carbonyl carbon resonance in the range of 220.9−243.7 ppm, which is typical for acylsilanes.

Previous preparations of aroylsilanes of type **3** have employed the "dithiane route",[9−11] the reductive silylation of alkyl benzoates with chlorotrimethylsilane/magnesium/hexamethylphosphoric triamide,[25] and the reaction of aroyl chlorides with trimethylsilyl cuprate generated from (trimethylsilyl)lithium and CuCN.[26] The (π-allyl-PdCl)$_2$-catalyzed reactions of aroyl chlorides with hexamethyldisilane have been used for the synthesis of aroyltrimethylsilanes[27] and heteroaroylsilanes.[28] The present routes compare favorably in terms of convenience and versatility.

As described earlier, the Corey and Brook strategy[9,10] cannot be used for the synthesis of alkenoylsilanes of type **7** since they polymerize under strong hydrolytic conditions.[6] The present mild hydrolysis makes our acyl anion synthon method applicable. Metalations of allenyl ethers and subsequent reaction with chlorotrimethylsilane followed by hydrolysis have been a most efficient approach for the preparation of alkenoylsilanes,[29−31] but the preparation of multisubstituted alkenoylsilanes of type **7a,b** by this process requires multistep manipulations.

Alkynoylsilanes of type **8** were previously prepared from expensive (trimethylsilyl)methanol in 24−60% yields by oxidation of intermediate (α-hydroxyalkyl)silanes.[32] Reich's method[30,31] for the preparation of alkenoylsilanes has also been used in the synthesis of alkynoylsilanes; however, this requires a multistep manipulation of allenyl ethers including triple lithiations *via* selenium intermediates. Interestingly, Kruithof *et al.*[24] reported a masked acyl anion synthon approach for the synthesis of alkynoylsilanes; reaction of (trimethylsilyl)propynal with 1,3-propanediol gave 2-[(trimethylsilyl)ethynyl]-1,3-dioxane. Subsequent treatment with BuLi followed by reaction with chlorotrimethylsilane yielded a mixture of propargylic and allenylic products in a ratio that is solvent-dependent (60:40 in THF; 35:65 in diethyl ether). This 1,3-dioxane approach is restricted to only 2-[(trimethylsilyl)ethynyl]-1,3-dioxane, and reported attempts to place substituents other than trimethylsilyl on the triple bond were unsuccessful.[24]

In conclusion, a novel and convenient two-step route to aroyl-, heteroaroyl-, alkenoyl-, and alkynoylsilanes was developed from readily available starting materials, utilizing simple operations and giving high yields.

Experimental Section

General Comments. Melting points were determined on a hot-stage apparatus without correction. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Gemini-300 spectrometer in $CDCl_3$ with TMS or $CDCl_3$, respectively, as the internal reference. Elemental analyses were performed using a Carlo Erba 1106 elemental analyzer. High-resolution mass spectra were measured on an AEI-30 mass spectrometer. Column chromatography was carried out on MCB silica gel (230−400 mesh). Tetrahydrofuran (THF) was freshly distilled from sodium−benzophenone. Lithiation reactions were carried out under the protection of dry nitrogen.

α-(Benzotriazol-1-yl)-substituted ethyl ethers **1a**−**g**, **9**, and **15** were prepared according to the literature.[16]

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General Procedure for the Preparation of α-(Benzotriazol-1-yl)-Substituted Ethyl Ethers (5a,b). A mixture of the appropriate aldehyde **4a,b** (20 mmol), benzotriazole (25 mmol), absolute ethanol (40 mmol), triethyl orthoformate (60 mmol), and a catalytic amount of sulfuric acid (6 drops) was stirred in THF (30 mL) at 20 °C for 5−6 h. Diethyl ether (200 mL) was then added, and the solution was washed with saturated Na_2CO_3 solution (2 × 100 mL) and water (100 mL). Evaporation of the solvents gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate 30:1).

1-(Benzotriazol-1-yl)-1-ethoxy-3-methyl-2-butene (5a). Obtained as an colorless oil: yield 51%; ^{1}H NMR δ 1.12 (t, 3 H, J = 7.1 Hz), 1.72 (s, 3 H), 1.73 (s, 3 H), 3.21−3.29 (m, 1 H), 3.53−3.58 (m, 1 H), 5.80−5.86 (m, 1 H), 6.74 (d, 1 H, J = 7.2 Hz), 7.35 (t, 1 H, J = 7.2 Hz), 7.45 (t, 1 H, J = 7.2 Hz), 7.76 (d, 1 H, J = 8.4 Hz), 8.04 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 14.6, 18.4, 25.5, 64.0, 87.0, 111.3, 119.9, 120.3, 124.0, 127.2, 131.0, 140.4, 146.7; HRMS calcd for $C_{13}H_{17}N_3O$ M + 1/z 232.1450, found M + 1/z 232.1443.

***trans*-2-[(Benzotriazol-1-yl)ethoxymethyl]-2-methylphenylethene (5b).** Obtained as white crystals: yield 71%; mp 100−102 °C; ^{1}H NMR δ 1.22 (t, 3 H, J = 7.1 Hz), 1.73 (s, 3 H), 3.42−3.50 (m, 1 H), 3.65−3.76 (m, 1 H), 6.57 (s, 1 H), 7.16 (s, 1 H), 7.21−7.46 (m, 7 H), 7.70 (d, 1 H, J = 8.0 Hz), 8.10 (d, 1 H, J = 7.2 Hz); ^{13}C NMR δ 14.4, 14.5, 64.7, 91.7, 111.4, 119.8, 124.0, 127.0, 127.3, 128.1, 128.9, 131.3, 131.7, 136.3, 146.7. Anal. Calcd for $C_{18}H_{19}N_3O$: C, 73.70; H, 6.53; N, 14.32. Found: C, 73.50; H, 6.46; N, 14.31.

General Procedure for the Lithiation of 1a−g, 5a,b, and 9. Preparation of Acylsilanes 3a−n, 7a,b, 8, and 12, and Byproducts 13 and 14. To a solution of benzotriazole adducts **1a−g** or **9** (5 mmol) in THF (70 mL) was added *n*-butyllithium (2 M in cyclohexane, 2.5 mL, 5 mmol) at −78 °C. The solution was stirred at this temperature for 2−5 min and then the appropriate trialkylsilyl chloride (6 mmol) was added (for **5a,b** the trialkylsilyl chloride was added prior to *n*-butyllithium). The solution was kept at this temperature for 1 h and at 20 °C for a further 1 h. After addition of water (30 mL) and dilute acid (4 mL of concentrated HCl or H_2SO_4 in 10 mL of water), the solution was stirred at room temperature for 10 h, extracted with diethyl ether (150 mL), washed with saturated Na_2CO_3 solution (2 × 100 mL) and water (100 mL), and dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel (hexane/ethyl acetate 30:1). The yields and elemental analysis data for **3a−n** are given in Table 1.

Benzoyltrimethylsilane (3a): ^{1}H NMR δ 0.37 (s, 9 H), 7.46−7.52 (m, 3 H), 7.82−7.85 (m, 2 H); ^{13}C NMR δ −1.5, 127.4, 128.6, 132.6, 141.2, 235.5.

Benzoyldimethyloctylsilane (3b): ^{1}H NMR δ 0.38 (s, 6 H), 0.86−0.93 (m, 5 H), 1.25−1.33 (m, 12 H), 7.45−7.54 (m, 3 H), 7.83−7.86 (m, 2 H);^{13}C NMR δ −3.0, 14.0, 15.1, 22.6, 23.6, 29.1, 31.8, 33.3, 127.3, 128.6, 132.5, 141.6, 235.7.

(2-Methoxybenzoyl)trimethylsilane (3c): ^{1}H NMR δ 0.24 (s, 9 H), 3.88 (s, 3 H), 6.92−7.01 (m, 2 H), 7.40−7.44 (m, 2 H); ^{13}C NMR δ −2.5, 54.4, 110.6, 120.8, 126.7, 132.8, 133.3, 158.7, 237.4.

(2-Methoxybenzoyl)dimethyloctylsilane (3d): ^{1}H NMR δ 0.22 (s, 6 H), 0.79−0.90 (m, 5 H), 1.22−1.40 (m, 12 H), 3.89 (s, 3 H), 6.92−6.99 (m, 2 H), 7.37−7.44 (m, 2 H); ^{13}C NMR δ −4.1, 14.0, 14.1, 22.6, 23.7, 29.1, 31.8, 33.4, 54.5, 110.5, 120.9, 126.6, 133.1, 133.3, 158.6, 237.8.

(2-Chlorobenzoyl)trimethylsilane (3e): ^{1}H NMR δ 0.30 (s, 9 H), 7.15−7.19 (m, 1 H), 7.30−7.36 (m, 3 H); ^{13}C NMR δ −2.4, 126.6, 127.0, 129.7, 129.9, 131.0, 143.8, 241.9.

(2-Chlorobenzoyl)dimethyloctylsilane (3f): ^{1}H NMR δ 0.27 (s, 6 H), 0.78−0.88 (m, 5 H), 1.24−1.27 (m, 12 H), 7.12−7.15 (m, 1 H), 7.27−7.35 (m, 3 H); ^{13}C NMR δ −4.0, 14.0, 14.1, 22.5, 23.4, 29.0, 31.7, 33.2, 126.5, 126.9, 129.7, 130.8, 144.1, 241.7.

(4-Methylbenzoyl)trimethylsilane (3g): ^{1}H NMR δ 0.37 (s, 9 H), 2.40 (s, 3 H), 7.27 (d, 2 H, J = 8.1 Hz), 7.76 (d, 2 H, J = 8.1 Hz); ^{13}C NMR δ −1.4, 21.5, 127.6, 129.2, 139.1, 143.3, 234.6.

(4-Methylbenzoyl)dimethyloctylsilane (3h): ^{1}H NMR δ 0.36 (s, 6 H), 0.85−0.90 (m, 5 H), 1.24−1.32 (m, 12 H), 2.40 (s, 3 H), 7.27 (d, 2 H, J = 8.1 Hz), 7.75 (d, 2 H, J = 8.1 Hz); ^{13}C NMR δ −3.0, 14.0, 15.2, 21.5, 22.6, 23.6, 29.1, 31.8, 33.3, 127.5, 129.2, 139.4, 143.2, 243.7.

(1-Naphthoyl)trimethylsilane (3i): ^{1}H NMR δ 0.37 (s, 9 H), 7.49−7.56 (m, 3 H), 7.77 (d, 1 H, J = 7.2 Hz), 7.83 (d, 1 H, J = 8.0 Hz), 7.91 (d, 1 H, J = 8.2 Hz), 8.57 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ −1.6, 124.2, 125.6, 126.3, 127.8, 128.1, 128.6, 129.1, 132.0, 134.0, 139.5, 241.7.

(1-Naphthoyl)dimethyloctylsilane (3j): ^{1}H NMR δ 0.36 (s, 6 H), 0.84−0.90 (m, 5 H), 1.21−1.36 (m, 12 H), 7.47−7.57 (m, 3 H), 7.76 (d, 1 H, J = 7.1 Hz), 7.82 (d, 1 H, J = 7.6 Hz), 7.90 (d, 1 H, J = 8.2 Hz), 8.59 (d, 1 H, J = 8.1 Hz); ^{13}C NMR δ −3.1, 14.0, 14.9, 22.5, 23.6, 29.1, 31.8, 33.2, 124.2, 125.6, 126.3, 127.8, 128.1, 128.6, 128.9, 131.9, 134.0, 139.9, 241.8.

(2-Furoyl)trimethylsilane (3k): ^{1}H NMR δ 0.36 (s, 9 H), 6.55 (dd, 1 H, J = 3.6, 1.8 Hz), 7.09 (dd, 1 H, J = 3.6, 1.0 Hz), 7.62 (dd, 1 H, J = 1.7, 1.0 Hz); ^{13}C NMR δ −2.6, 111.8, 114.7, 145.7, 157.9, 220.9.

(2-Furoyl)dimethyloctylsilane (3l): ^{1}H NMR δ 0.35 (s, 6 H), 0.84−0.91 (m, 5 H), 1.26−1.33 (m, 12 H), 6.55 (dd, 1 H, J = 3.6, 1.5 Hz), 7.09 (dd, 1 H, J = 3.6, 0.9 Hz), 7.61 (dd, 1 H, J = 1.5, 0.9 Hz); ^{13}C NMR δ −4.1, 14.0, 14.1, 22.6, 23.5, 29.1, 31.8, 33.3, 111.9, 114.6, 145.8, 158.3, 221.4.

(2-Thenoyl)trimethylsilane (3m): ^{1}H NMR δ 0.39 (s, 9 H), 7.17 (dd, 1 H, J = 4.9, 3.8 Hz), 7.64 (dd, 1 H, J = 5.0, 1.0 Hz), 7.78 (dd, 1 H, J = 3.8, 0.9 Hz); ^{13}C NMR δ −1.8, 128.0, 132.6, 132.9, 150.5, 224.5.

(2-Thenoyl)dimethyloctylsilane (3n): ^{1}H NMR δ 0.36 (s, 6 H), 0.84−0.88 (m, 5 H), 1.23−1.40 (m, 12 H), 7.15 (dd, 1 H, J = 5.0, 3.8 Hz), 7.62 (dd, 1 H, J = 5.0, 1.1 Hz), 7.74 (dd, 1 H, J = 3.8, 1.1 Hz); ^{13}C NMR δ −3.3, 14.0, 14.7, 22.6, 23.5, 29.1, 31.8, 33.3, 128.0, 132.4, 132.8, 150.9, 224.7.

(3-Methyl-2-butenoyl)dimethyloctylsilane (7a): obtained as a yellow oil, yield 80%; ^{1}H NMR δ 0.19 (s, 6 H), 0.72−0.75 (m, 2 H), 0.90 (t, 3 H, J = 6.6 Hz), 1.28−1.32 (m, 12 H), 1.90 (s, 3 H), 2.11 (s, 3 H), 6.57 (s, 1 H); ^{13}C NMR δ −4.8, 13.6, 14.1, 21.0, 22.6, 23.6, 27.5, 29.2, 29.3, 31.9, 33.4, 127.4, 149.7, 237.9. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88. Found: C, 70.47; H, 11.94.

(α-Methyl-*trans*-cinnamoyl)trimethylsilane (7b): obtained as a yellow oil, yield 71%; ^{1}H NMR δ 0.38 (s, 9 H), 2.00 (s, 3 H), 7.38−7.50 (m, 6 H); ^{13}C NMR δ −0.7, 11.3, 128.5, 128.7, 129.7, 135.9, 143.1, 144.5, 236.3. Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.29; H, 8.42.

(1-Trimethylsilyl)-3-phenylpropyn-1-one (8): obtained as a yellow oil, yield 51%; ^{1}H NMR δ 0.33 (s, 9 H), 7.38−7.45 (m, 3 H), 7.54−7.58 (m, 2 H); ^{13}C NMR δ −3.6, 90.5, 100.2, 120.4, 128.5, 130.6, 132.7, 225.7. Anal. Calcd for $C_{12}H_{14}OSi$: C, 71.24; H, 6.97. Found: C, 71.38; H, 7.16.

1-(Dimethyloctylsilyl)-3-phenylpropyn-1-one (12): obtained as a yellow oil, yield 38%; ^{1}H NMR δ 0.31 (s, 6 H), 0.81−0.88 (m, 5 H), 1.25−1.41 (m, 12 H), 7.36−7.55 (m, 3 H), 7.55−7.58 (m, 2 H); ^{13}C NMR δ −5.1, 13.2, 14.0, 22.6, 23.4, 29.1, 31.8, 33.3, 90.9, 100.0, 120.6, 128.6, 130.6, 132.8, 225.9. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.63; H, 9.56.

1-(Dimethyloctylsilyl)-1-phenyl-3-(benzotriazol-1-yl)-3-ethoxyallene (13): obtained as a yellow oil, yield 10%; ^{1}H NMR δ 0.33 (s, 6 H), 0.80−0.91 (m, 5 H), 1.10−1.40 (m, 12 H), 1.48 (t, 3 H, J = 7.1 Hz), 4.00 (q, 2 H, J = 7.1 Hz), 7.32−7.54 (m, 7 H), 7.68 (d, 1 H, J = 8.1 Hz), 8.10 (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ −2.2, −2.0, 14.1, 14.7, 15.8, 22.6, 23.7, 29.1, 29.2, 31.8, 33.3, 65.4, 111.3, 119.9, 124.1, 126.4, 127.8, 127.9, 128.0, 128.7, 131.2, 132.5, 137.3, 146.0, 195.7. Anal. Calcd for $C_{27}H_{37}N_3OSi$: C, 72.44; H, 8.33; N, 9.39. Found: C, 72.73; H, 8.46; N, 9.09.

Ethyl 3-(Dimethyloctylsilyl)-3-phenylacrylate (14): obtained as a pale yellow oil, yield 25%; ^{1}H NMR δ 0.13 (s, 6 H), 0.75−0.80 (m, 2 H), 0.88 (t, 3 H, J = 6.8 Hz), 1.23−1.33 (m, 15 H), 4.22 (q, 2 H, J = 7.1 Hz), 6.34 (s, 1 H), 7.03 (d, 2 H, J = 7.8 Hz), 7.21−7.31 (m, 3 H); ^{13}C NMR δ −1.6, 14.1, 14.3, 15.7, 22.7, 24.0, 29.2, 31.9, 33.5, 60.3, 126.2, 126.4, 127.9, 133.2, 145.5, 165.3, 166.7. Anal. Calcd for $C_{21}H_{34}O_2Si$: C, 72.78; H, 9.89. Found: C, 72.59; H, 10.06.

General Procedure for the Lithiation of 1-(Benzotriazolyl)propargyl Ethyl Ether (15). Preparation of 17a,b. To a solution of 1-(benzotriazolyl)propargyl ethyl ether (**15**) (1.02 g, 5 mmol) in THF (70 mL) was added *n*-butyllithium (2 M in cyclohexane, 2.5 mL, 5 mmol) at −78 °C. The solution was stirred at this temperature for 5 min and then the appropriate electrophile (trialkylsilyl chloride for **17a** and benzaldehyde for **17b**) (5 mmol) was added. The solution was kept at this temperature for 5 min for **17b**; in the case of **17a**, the solution was warmed to room temperature for 5 min and then cooled to −78 °C. After addition of trimethylsilyl chloride (5 mmol), the second equivalent of butyllithium (5 mmol) was added, and the resulting solution was kept at this temperature for 5 min. Water (30 mL) and dilute acid (4 mL of concentrated HCl or H_2SO_4 in 10 mL of water) were added, and the solution was stirred at room temperature for 10 h, extracted with diethyl ether (150 mL), washed with saturated Na_2CO_3 solution (2 × 100 mL) and water (100 mL), and dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel (for **17a**, hexane/ethyl acetate 100:1; for **17b**, hexane/ethyl acetate 20:1).

1,3-Bis-(trimethylsilyl)propyn-1-one (17a): obtained as a yellow oil, yield 46%; ^{1}H NMR δ 0.26 (s, 18 H); ^{13}C NMR δ −3.8, −0.8, 104.7, 107.2, 226.9. Anal. Calcd for $C_9H_{18}OSi_2$: C, 54.48; H, 9.14. Found: C, 54.25; H, 8.93.

4-Hydroxy-4-phenyl-1-(trimethylsilyl)butyn-1-one (17b): obtained as a yellow oil, yield 70%; ^{1}H NMR δ 0.25 (s, 9 H), 3.46 (br s, 1 H), 5.66 (s, 1 H), 7.32−7.40 (m, 3 H), 7.49−7.52 (m, 2 H); ^{13}C NMR δ −3.8, 64.4, 87.4, 100.2, 126.5, 128.7, 139.1, 226.3; HRMS calcd for $C_{13}H_{16}O_2Si$ M + 1/z 233.0997, found M + 1/z 233.0985.

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